

CHAPTER III

EXPERIMENTAL

Instruments.

1. Infrared Spectrophotometers : Perkin-Elmer FT-IR 1760 X (The Scientific and Technological Research Equipment Center, Chulalongkorn University).
2. Nuclear Magnetic Resonance Spectrometers : Jeol JNM-A500 (500 MHz) (The Scientific and Technological Research Equipment Center, Chulalongkorn University).
3. Mass Spectrometer : Varian Saturn 4D (The Scientific and Technological Research Equipment Center, Chulalongkorn University).
4. Melting Point Apparatus : Buchi capillary melting point apparatus (Department of Pharmaceutical Chemistry, Faculty of Pharmaceutical Sciences, Chulalongkorn University).

Chemicals.

Diethyl malonate (Fluka Chemika)
Diethyl propylmalonate (Aldrich Chemicals Co.)
n-Propyl bromide (Fluka Chemika)
3-Chloro-2-methyl-1-propene (Aldrich Chemicals Co.)
Allyl bromide (Fluka Chemika)
Sodium (Laboratory Grade)
Lithium chloride (Laboratory Grade)
Dimethyl sulfoxide (Aldrich Chemicals Co.)
Potassium hydroxide (Merck)
Thionyl Chloride (Laboratory Grade)
Urea (Merck)
Hydrochloric acid (Merck)
All solvent used were either B.P. or laboratory grade.

Chemical Preparations.

1. Synthesis of N-(2-propyl-4-pentenoyl) urea (CU-763-11-01).

1.1. Diethyl propylmalonate.

Prepare a solution of sodium ethoxide from 6.9 g. (0.3 mole) of clean sodium and 100 ml. of absolute ethanol in a 250 ml. flask. Attached the flask to a condenser and arranged for reflux. When the sodium ethoxide solution, which was vigorously stirred, had cooled to

about 50 °C, add 48.0 g. (45.5 ml., 0.3 mole) of diethyl malonate slowly through the condenser, to the resulting clear solution introduced gradually (90 minutes) 37.0 g. (27.3 ml., 0.3 mole) of *n*-propyl bromide through the condenser. Reaction occurred almost immediately and much heat was evolved. Refluxed the reaction mixture on a water bath until it was neutral to moist litmus (about 6 hours). Removed as much of the ethanol as possible by distillation under reduced pressure (rotary evaporator) on a water bath. Cooled the contents of flask to room temperature, added 100 ml. of water and extracted with 3 x 50 ml. of hexane. Combined hexane layer was washed with water, dried over anhydrous sodium sulfate, and evaporated. The oily liquid was separated by distillation. A low boiling point fraction, past over first, followed by diethyl propylmalonate. The yield, b.p. 218-225 °C, mainly 219.5-221.5 °C, was 42.6 g. (70.3 %).

IR:	2964,2938,2876	cm ⁻¹	(ν C-H)
(Neat)	1736,1732	cm ⁻¹	(ν C=O)
	1466,1448	cm ⁻¹	(δ C-H)
	1178	cm ⁻¹	(ν C(=O)-O)
	1032	cm ⁻¹	(ν C(=O)-O-C-C)
	898	cm ⁻¹	(ν out-of-plane C-H (alkene))

(Figure 10.)

¹ H-NMR:	0.94	ppm	(3H, t, J=7.3 Hz, CH ₃ -CH ₂ -CH ₂ -)
(CDCl ₃)	1.27	ppm	(6H, t, J=7.3 Hz, CH ₃ -CH ₂ -O-)
	1.36	ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)

1.88	ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
3.33	ppm	(1H, t, J-7.6 Hz, -CH-)
4.20	ppm	(4H, m, CH ₃ -CH ₂ -CH ₂ -)

(Figure 11-13)

1.2. Diethyl (2-methyl-2-propenyl)propylmalonate.

Prepare a solution of sodium ethoxide from 3.45 g. (0.15 mole) of clean sodium and 45 ml. of absolute ethanol in a 250 ml. flask. Attached the flask to a condenser arranged for reflux. When the sodium ethoxide solution, which was vigorously stirred, had cooled to about 50 °C, add 30.3 g. (30.7 ml., 0.15 mole) of diethyl propylmalonate slowly through the condenser, to the resulting clear solution introduced gradually (90 minutes) 13.6 g. (14.8 ml., 0.15mole) of 3-chloro-2-methyl-1-propene through the condenser . Reaction occurred almost immediately and much heat was evolved. Refluxed the reaction mixture on a water bath about 12 hours. Removed as much of the ethanol as possible by distillation under reduced pressure (rotary evaporator) on a water bath. Cooled the contents of flask to room temperature, added 70 ml. of water and extracted with 3 x 30 ml. of hexane. Combined hexane layer was washed with water, dried over anhydrous sodium sulfate, and evaporated. The oily liquid was purified by the column chromatography using silica gel as stationary phase and hexane:ethylacetate (40:1) as mobile phase. The yield of the product was 32.8 g. (85.4%).

IR	:	3076	cm ⁻¹	(ν C=C-H)
(Neat)		2964,2938,2874	cm ⁻¹	(ν C-H)
		1736,1732,	cm ⁻¹	(ν C=O ester)
		1646,	cm ⁻¹	(ν C=C)
		1466,1446	cm ⁻¹	(δ C-H)
		1028	cm ⁻¹	(ν C(=O)-O-C-C)
		898	cm ⁻¹	(δ out-of-plane C-H(alkene))

(Figure 14)

¹ H-NMR:	0.91	ppm	(3H, t, J=7.3 Hz, CH ₃ -CH ₂ -CH ₂ -)
(CDCl ₃)	1.18-1.27	ppm	(5H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.25	ppm	(3H, t, J=7.3 Hz, CH ₃ -CH ₂ -O-)
	1.66	ppm	(3H, s, CH ₃ -C(CH ₃)-)
	1.84-1.89	ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
	2.70	ppm	(1H, s, -CH-)
	4.17	ppm	(2H, 2q, J=7.2 Hz, CH ₃ -CH ₂ -O-)
	4.72	ppm	(1H, s, CH ₂ =C(CH ₃)-)
	4.85	ppm	(1H, s, CH ₂ =C(CH ₃)-)

(Figure 15-17)

1.3. Ethyl 4-methyl-2-propyl-4-pentenoate.

Diethyl (2-methyl-2-propenyl)propylmalonate (7.7 g., 0.03 mole), dimethyl sulfoxide (DMSO) (50 ml.), water (1.0 g., 0.06 mole), and lithium chloride (2.5 g., 0.06 mole) were placed in a 100 ml. round-bottom flask equipped with a magnetic stirrer and fitted with a

condenser. The mixture was heated at refluxing for 36 hours. At this point, a brown color had developed and suspended solid (lithium carbonate, Li_2CO_3) was evident. The mixture is then distilled up to 185°C . The distillate was poured into 200 ml. of ice water and the aqueous layer was saturated with sodium chloride. The ester was extracted with 4 x 30 ml. of hexane, and the hexane extract was washed with water, dried over anhydrous sodium sulfate and concentrated to yield 5.0 g. (91.0 %) of ester which pure enough to continue the following reaction. The ester product can be further purified by column chromatography using silica gel as stationary phase and hexane:ethylacetate (40:1) as a mobile phase.

IR	:	3076	cm^{-1}	(ν C=C-H)
(Neat)		2960,2936,2874	cm^{-1}	(ν C-H)
		1732	cm^{-1}	(ν C=O)
		1652	cm^{-1}	(ν C=C)
		1466,1446	cm^{-1}	(δ C-H)
		1160	cm^{-1}	(ν C(=O)-O)
		1032	cm^{-1}	(ν C(=O)-O-C-C)
		892	cm^{-1}	(δ out-of-plane C-H (alkene))

(Figure 18)

$^1\text{H-NMR}$:	0.90	ppm	(3H, t, $J=7.3$ Hz, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$)
(CDCl_3)	1.22-1.35	ppm	(2H, complex, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$)
	1.24	ppm	(3H, t, $J=7.3$ Hz, $\text{CH}_3\text{-CH}_2\text{-O-}$)
	1.40-1.45	ppm	(1H, m, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$)

1.56-1.63	ppm	(1H, m, CH ₃ -CH ₂ -CH ₂ -)
1.72	ppm	(3H, s, CH ₂ =C(CH ₃)-)
2.10-2.15	ppm	(1H, m, CH ₂ =C(CH ₃)-CH ₂ -)
2.32-2.37	ppm	(1H, m, CH ₂ =C(CH ₃)-CH ₂ -)
2.53-2.60	ppm	(1H, m, -CH-)
4.09-4.14	ppm	(2H, q, J=7.3 Hz, CH ₃ -CH ₂ -O-)
4.70	ppm	(1H, m, CH ₂ =C(CH ₃)-)
4.74	ppm	(1H, m, CH ₃ -CH ₂ -CH ₂ -)

(Figure 19-21)

1.4. 4-Methyl-2-propyl-4-pentenoic acid.

1.68 g. (0.03 mole) of potassium hydroxide was dissolved in 4 ml. of water in a 100 litre round-bottom flask. 2.55 g. (0.15 mole) of Ethyl 4-methyl-2-propyl-4-pentenoate was added into these flask with stirring. Then, 20 ml. of 95 % ethanol was added to produce a homogeneous solution. A reflux condenser was Attached to the flask and the mixture was refluxed for 2 hours; hydrolysis was then completed. Ethanol was distilled off as much as possible by a rotary evaporator. The residue was added 30 ml. of water and washed with 30 ml of hexane to remove unreacted ester. After that, the aqueous phase was acidified by addition of 20% hydrochloric acid and then extracted with 3 x 30 ml. of hexane. The hexane extract was washed with water, dried over anhydrous sodium sulfate and evaporated. The yield was 2.25 g.(96.2 %).

IR :	3000-2500	cm ⁻¹	(ν O-H)
(Neat)	3078	cm ⁻¹	(ν C=C-H)
	2960,2936,2874	cm ⁻¹	(ν C-H)
	1710	cm ⁻¹	(ν C=O acid)
	1652	cm ⁻¹	(ν C=C)
	1450	cm ⁻¹	(δ C-H)
	1422	cm ⁻¹	(δ O-H)
	1288	cm ⁻¹	(ν C-O)
	942	cm ⁻¹	(δ out-of-plane O-H)
	894	cm ⁻¹	(δ out-of-plane C-H (alkene))

(Figure 22)

¹ H-NMR:	0.92	ppm	(3H, t, J=7.3 Hz, CH ₃ -CH ₂ -CH ₂ -)
(CDCl ₃)	1.30-1.65	ppm	(4H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.73	ppm	(3H, s, CH ₂ =C(CH ₃)-)
	2.13-2.18	ppm	(1H, m, CH ₂ =C(CH ₃)-CH ₂ -)
	2.35-2.40	ppm	(1H, m, CH ₂ =C(CH ₃)-CH ₂ -)
	2.56-2.62	ppm	(1H, m, -CH-)
	4.70	ppm	(1H, s, CH ₂ =C(CH ₃)-)
	4.74	ppm	(1H, s, CH ₂ =C(CH ₃)-)
	11.1	ppm	(1H, s, broad, -COOH)

(Figure 23-25)

1.5. N-(4-Methyl-2-propyl-4-pentenoyl) urea.

1.43 g. (0.88 ml., 0.012 mole) of redistilled thionyl chloride was placed in the 50 ml. round-bottom flask and 1.56 g. (0.01 mole) of 4-methyl-2-propyl-4-pentenoic acid was added slowly with stirring. There was a slight evolution of heat, sulfur dioxide was evolved and the liquid darkened considerably. When all the acid had been added, the mixture was heated in the hot water bath (temperature 40-50 °C) for 3 hours. The apparatus for distillation was arranged and the excess of thionyl chloride was removed in vacuo to yield the crude acyl chloride, which was not further purified. The acid chloride was then added dropwisely into a mixture of urea (1.8 g., 0.03 mole) and potassium carbonate (1.38 g., 0.01 mole) in dry benzene. The mixture was refluxed for 8 hours. Benzene was distilled off by a rotary 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 combined ethylacetate extract was washed with water to remove the residual potassium carbonate and dried over anhydrous sodium sulfate. Later, the solvent was evaporated in vacuo to yield crude product as oily liquid which was purified by the column chromatography using silica gel as stationary phase and 2% methanol in chloroform as mobile phase. After evaporated, the white solid was precipitated. The yield was 1.02 g. (51.5 %) of the product, melting point 130.0-131.0°C.

IR	3398	cm^{-1}	(ν_{asym} N-H, primary amide)
(KBr)	334	cm^{-1}	(ν N-H, imide)
(Pellet)	3246	cm^{-1}	(ν_{sym} N-H, primary amide)
	3088	cm^{-1}	(ν C=C-H)
	2960,2932,2878	cm^{-1}	(ν C-H)
	1716	cm^{-1}	(ν C=O, imide)
	1678	cm^{-1}	(ν C=O, primary amide)
	1624	cm^{-1}	(ν C=C)
	1410	cm^{-1}	(δ C-N)

(Figure 26)

$^1\text{H-NMR}$:	0.92	ppm	(3H, t, $J=7.3$ Hz, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$)
(CDCl_3)	1.30-1.50	ppm	(4H, m, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$)
	1.73	ppm	(3H, s, $\text{CH}_2\text{=C(CH}_3\text{)-}$)
	2.12-2.16	ppm	(1H, m, $\text{CH}_2\text{=C(CH}_3\text{)-CH}_2\text{-}$)
	2.33-2.40	ppm	(1H, m, $\text{CH}_2\text{=C(CH}_3\text{)-CH}_2\text{-}$)
	2.49-2.54	ppm	(1H, m, -CH-)
	4.72	ppm	(1H, s, $\text{CH}_2\text{=C(CH}_3\text{)-CH}_2\text{-}$)
	4.78	ppm	(1H, s, $\text{CH}_2\text{=C(CH}_3\text{)-CH}_2\text{-}$)
	5.16	ppm	(1H, s, broad, -CO-NH_2)
	8.35	ppm	(1H, s, broad, -CO-NH_2)
	9.32	ppm	(1H, s, broad, -CO-NH-CO-)

(Figure 27-29)

$^{13}\text{C-NMR}$: see Figure 30.

(CDCl_3)

EIMS : 199(M+1⁺,15%), 198(M⁺,16%), 183(1%), 181(2%),
 (m/e) 169(7%), 156 (27%), 139(22%),138(95%), 111(26%),
 110(16%), 69(100%), 44(79%)
 (Figure 31)

2. Synthesis of N-(2-propyl-4-pentenoyl) urea (CU763-11-02).

2.1. Diethyl allyl(propyl)malonate.

Prepare a solution of sodium ethoxide from 3.45 g. (0.15 mole) of clean sodium and 45 ml. of absolute ethanol in a 250 ml. flask. Attached the flask to a condenser arranged for reflux. When the sodium ethoxide solution, which was vigorously stirred, had cooled to about 50 °C, add 30.3 g. (30.7 ml., 0.15 mole) of diethyl propylmalonate slowly through the condenser, to the resulting clear solution introduced gradually (90 minutes) 18.2 g. (12.7 ml., 0.15 mole) of 1-bromopropene (allyl bromide) through the condenser . Reaction occurred almost immediately and much heat was evolved. Refluxed the reaction mixture on a water bath about 12 hours. Removed as much of the ethanol as possible by distillation under reduced pressure (rotary evaporator) on a water bath. Cooled the contents of flask to room temperature, added 100 ml. of water and extracted with 3 x 30 ml. of hexane. Combined hexane layer was washed with water, dried over anhydrous sodium sulfate, and evaporated. The oily liquid was purified by the column chromatography using silica gel as stationary phase and hexane:ethylacetate (40:1) as mobile phase. The yield of the product was 31.8 g. (82.8 %).

IR	:	3080	cm ⁻¹	(v C=C-H)
(Neat)		964,2938,2876	cm ⁻¹	(v C-H)
		1736,1732	cm ⁻¹	(v C=O ester)
		1642	cm ⁻¹	(v C=C)
		1466,1446	cm ⁻¹	(δ C-H)
		1196	cm ⁻¹	(v C(=O)-O)
		1040	cm ⁻¹	(v C(=O)-O-C-C)
		918	cm ⁻¹	(δ out-of-plane C-H (alkene))

(Figure 32)

¹ H-NMR:	0.92	ppm	(3H, t, J=7.3 Hz, CH ₃ -CH ₂ -CH ₂ -)
(CDCl ₃)	1.17-1.26	ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.25	ppm	(6H, t, J=7.3 Hz, CH ₃ -CH ₂ -O-)
	1.82-1.87	ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
	2.63-2.66	ppm	(2H, ddt, J=7.3, 1.2, CH ₂ =CH-CH ₂ -)
	4.15-4.20	ppm	(4H, q, J=7.2 Hz, CH ₃ -CH ₂ -O-)
	5.05-5.12	ppm	(2H, m, CH ₂ =CH-)
	5.61-5.70	ppm	(1H, m, CH ₂ =CH-CH ₂ -)

(Figure 33-35)

2.2. Ethyl 2-propyl-4-pentenoate.

Diethyl allyl(propyl)malonate (7.3 g., 0.03 mole), DMSO 50 ml.), water (1.0 g., 0.06 mole), and lithium chloride (2.5 g., 2.06 mole) were placed in a 100 ml. round-bottom flask equipped with a magnetic stirrer and fitted with a condenser. The mixture was heated at

refluxing for 36 hours. At this point, a brown color had developed and suspended solid (lithium carbonate, Li_2CO_3) was evident. The mixture is then distilled up to 185°C . The distillate was poured into 200 ml. of ice water and the aqueous layer was saturated with sodium chloride. The ester was extracted with 4 x 30 ml. of hexane, and the yellow hexane extract was washed with water, dried over anhydrous sodium sulfate and concentrated to yield 4.6 g. (90.2 %) of ester which pure enough to continue the following reaction. The ester product can be further purified by column chromatography using silica gel as stationary phase and hexane:ethylacetate (40:1) as a mobile phase.

IR	:	3080	cm^{-1}	(ν C=C-H)
(Neat)		960,2936,2874	cm^{-1}	(ν C-H)
		1732	cm^{-1}	(ν C=O)
		1642	cm^{-1}	(ν C=C)
		1466,1444	cm^{-1}	(δ C-H)
		1178	cm^{-1}	(ν C(=O)-O)
		1032	cm^{-1}	(ν C(=O)-O-C-C)
		916	cm^{-1}	(δ out-of-plane C-H (alkene))

(Figure 36)

$^1\text{H-NMR}$:	0.90	ppm	(3H, t, $J=7.3$ Hz, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$)
(CDCl_3)	1.25	ppm	(3H, t, $J=7.3$ Hz, $\text{CH}_3\text{-CH}_2\text{-O-}$)
	1.18-1.35	ppm	(2H, m, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$)
	1.41-1.49	ppm	(1H, m, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$)

1.57-1.65	ppm	(1H, m, CH ₃ -CH ₂ -CH ₂ -)
2.19-2.25	ppm	(1H, m, -CH-)
2.32-2.39	ppm	(1H, m, CH ₂ =CH-CH ₂ -)
2.40-2.46	ppm	(1H, m, CH ₂ =CH-CH ₂ -)
4.11-4.16	ppm	(2H, q, J=7.3 Hz, CH ₃ -CH ₂ -O-)
4.98-5.08	ppm	(2H, m, CH ₂ =CH-CH ₂ -)
5.70-5.79	ppm	(1H, m, CH ₂ =CH-CH ₂ -)

(Figure 37-39)

2.3. 2-Propyl-4-pentenoic acid.

1.68 g.(0.03 mole) of potassium hydroxide was dissolved in 4 ml. of water in a 100 litre round-bottom flask. 2.55 g. (0.015 mole) of ethyl 2-propyl-4-pentenoate was added into these flask with stirring. Then, 20 ml. of 95 % ethanol was added to produce a homogeneous solution. A reflux condenser was Attached to the flask and the mixture was refluxed for 2 hours; hydrolysis was then completed. Ethanol was distilled off as much as possible by a rotary evaporator. The residue was added 30 ml. of water and washed with 30 ml. of hexane to remove unreacted ester. After that, the aqueous phase was acidified by addition of 20% hydrochloric acid and then extracted with 3 x 30 ml. of hexane. The hexane extract was washed with water, dried over anhydrous sodium sulfate and evaporated. The yield was 2.10 g.(98.6 %).

IR	:	3300-2500	cm ⁻¹	(ν O-H)
(Neat)		3080	cm ⁻¹	(ν C=C-H)
		2960,2934,2874	cm ⁻¹	(ν C-H)
		1708	cm ⁻¹	(ν C=O acid)
		1642	cm ⁻¹	(ν C=C)
		1444	cm ⁻¹	(δ C-H)
		1420	cm ⁻¹	(δ O-H)
		1280	cm ⁻¹	(δ C-O)
		938	cm ⁻¹	(δ out-of plane O-H)
		918	cm ⁻¹	(δ out-of-plane C-H (alkene))

(Figure 40)

¹ H-NMR:	0.92	ppm	(3H, t, J=7.3 Hz, CH ₃ -CH ₂ -CH ₂ -)
(CDCl ₃)	1.30-1.43	ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.45-1.53	ppm	(1H, s, CH ₃ -CH ₂ -CH ₂ -)
	1.59-1.67	ppm	(1H, s, CH ₃ -CH ₂ -CH ₂ -)
	2.22-2.29	ppm	(1H, m, CH ₂ =CH ₂ -CH ₂ -)
	2.36-2.42	ppm	(1H, m, CH ₂ =CH ₂ -CH ₂ -)
	2.43-2.50	ppm	(1H, m, -CH-)
	5.02-5.05	ppm	(1H, dt, J=10.1, 0.9 Hz, CH ₂ =CH-CH ₂ -)
	5.06-5.11	ppm	(1H, t, J=11.09, 1.8 Hz, CH ₂ =CH-CH ₂ -)
	5.72-5.82	ppm	(1H, m, CH ₂ =CH-CH ₂ -)
	10.92	ppm	(1H, s, broad, -COOH)

(Figure 41-43)

2.4. N-(2-Propyl-4-pentenoyl) urea.

1.43 g. (0.88 ml., 0.012 mole) of redistilled thionyl chloride was placed in the 50 ml. round-bottom flask and 1.56 g. (0.01 mole) of 2-propyl-4-pentenoic acid was added slowly with stirring. There was a slight evolution of heat, sulfur dioxide was evolved and the liquid darkened considerably. When all the acid had been added, the mixture was heated in the hot water bath (temperature 40-50 °C) for 3 hours. The apparatus for distillation was arranged and the excess of thionyl chloride was removed in vacuo to yield the crude acyl chloride, which was not further purified. The acid chloride was then added dropwisely into a mixture of urea (1.8 g., 0.03 mole) and potassium carbonate (1.38 g., 0.01 mole) in dry benzene. The mixture was refluxed for 8 hours. Benzene was distilled off by a rotary evaporator until the residue became pasty. The mixture was added 50 ml. of water and extracted with three 30 ml. portions of ethylacetate. The combined ethylacetate extract was washed with water to remove the residual potassium carbonate and dried over anhydrous sodium sulfate. Later, the solvent was evaporated in vacuo to yield crude product as oily liquid which was purified by the column chromatography using silica gel as stationary phase and 2% methanol in chloroform as mobile phase. After evaporated, the white solid precipitated. The yield was 1.02 g. (55.4 %) of the product, melting point 166.0-167.0°C.

IR	:	3394	cm ⁻¹	(ν_{asym} N-H, primary amide)
(Kbr)		3330	cm ⁻¹	(ν N-H, imide)
(Pellet)		3240	cm ⁻¹	(ν sym N-H, primary amide)
		3084	cm ⁻¹	(ν C=C-H)
		2962,2934,2874	cm ⁻¹	(ν C-H)
		1702	cm ⁻¹	(ν C=O, imide)
		1688	cm ⁻¹	(ν C=O, primary amide)
		1592	cm ⁻¹	(δ N-H)
		1390	cm ⁻¹	(δ C-N)

(Figure 44)

¹ H-NMR:	0.92	ppm	(3H, t, J=7.3 Hz, CH ₃ -CH ₂ -CH ₂ -)
(CDCl ₃)	1.27-1.38	ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.146-1.51	ppm	(1H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.60-1.68	ppm	(1H, m, CH ₃ -CH ₂ -CH ₂ -)
	2.20-2.28	ppm	(1H, m, CH ₂ =CH-CH ₂ -)
	2.33-2.41	ppm	(2H, m, CH ₂ =CH-CH ₂ -, -CH-)
	5.02-5.11	ppm	(2H, complex, CH ₂ =CH-CH ₂ -)
	5.45	ppm	(1H, s, broad, -CO-NH ₂ -)
	5.69-5.78	ppm	(1H, m, CH ₂ =CH-CH ₂ -)
	8.34	ppm	(1H, s, broad, -CO-NH ₂)
	9.17	ppm	(1H, s, broad, -CO-NH-CO-)

(Figure 45-47)

¹³C-NMR : see Figure 48.

(CDCl₃)

EIMS : 185(M+1⁺,11%), 184(M⁺,4%), 167 (1%), 155(17%),
 (m/e) 142(57%), 125(6%), 124 (22%), 97(8%),
 96(9%), 44(100%)

(Figure 49)

3. Synthesis of N-(4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenoyl) urea (CU-763-11-03).

3.1. Diethyl di-(2-methyl-2-propenyl)malonate.

Prepare a solution of sodium ethoxide from 6.9 g. (0.3 mole) of clean sodium and 90 ml. of absolute ethanol in a 250 ml. flask. Attached the flask to a condenser arranged for reflux. When the sodium ethoxide solution, which was vigorously stirred, had cooled to about 50 °C, add 24.0 g. (22.8 ml., 0.15 mole) of diethyl malonate slowly through the condenser, to the resulting clear solution introduced gradually (90 minutes) 27.2 g. (29.8 ml., 0.3 mole) of 3-chloro-2-methyl-1-propene through the condenser . Reaction occurred almost immediately and much heat was evolved. Refluxed the reaction mixture on a water bath about 6 hours. If the reactant remained, an alkyl halide will be added. Removed as much of the ethanol as possible by distillation under reduced pressure (rotary evaporator) on a water bath. Cooled the contents of flask to room temperature, added 100 ml. of water and extracted with 3 x 30 ml. of hexane. Combined hexane layer was washed with water, dried over anhydrous sodium sulfate, and evaporated. The oily liquid was purified by the column chromatography using silica gel as stationary phase and

hexane:ethylacetate (40:1) as mobile phase. The yield of the product was 33.8 g. (84.1 %).

IR	:	3070	cm ⁻¹	(ν C=C-H)
(Neat)		2982,2936,2874	cm ⁻¹	(ν C-H)
		1736,1732	cm ⁻¹	(ν C=O ester)
		1644	cm ⁻¹	(ν C=C)
		1446	cm ⁻¹	(δ CH)
		1182	cm ⁻¹	(ν C(=O)-O)
		1036	cm ⁻¹	(ν C(=O)-O-C-C)
		896	cm ⁻¹	(δ out-of-plane C-H(alkene))
		(Figure 50)		

¹ H-NMR:	1.25	ppm	(6H, t, J=7.3 Hz, CH ₃ -CH ₂ -O-)
(CDCl ₃)	1.69	ppm	(6H, t, J=7.3 Hz, CH ₂ =C(CH ₃)-)
	2.74	ppm	(4H, d, J=0.7 Hz, CH ₂ =C(CH ₃)-CH ₂ -)
	4.14-4.19	ppm	(2H, q, J=7.2 Hz, CH ₃ -CH ₂ -O-)
	4.74,4.85	ppm	(4H, 2s, CH ₂ =C(CH ₃)-CH ₂ -)
	(Figure 51-52)		

3.2. Ethyl 4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenoate.

Diethyl di-(2-methyl-2-propenyl)malonate (8.0 g., 0.03 mole), DMSO (50 ml.), water (1.0 g., 0.06 mole), and lithium chloride (2.5 g., 0.06 mole) were placed in a 100 ml. round-bottom flask equipped with a magnetic stirrer and fitted with a condenser. The mixture was

heated at refluxing for 36 hours. At this point, a brown color had developed and suspended solid (lithium carbonate, Li_2CO_3) was evident. The mixture is then distilled up to 185°C . The distillate was poured into 200 ml. of ice water and the aqueous layer was saturated with Sodium chloride. The ester was extracted with 4 x 30 ml. of hexane, and the hexane extract was washed with dried over anhydrous sodium sulfate and concentrated to yield 5.5 g. (93.2 %) of ester which pure enough to continue the following reaction. The ester product can be further purified by column chromatography using silica gel as stationary phase and hexane:ethylacetate (40:1) as a mobile phase.

IR	:	3078	cm^{-1}	(v C=C-H)
(Neat)		2972,2936,2856	cm^{-1}	(v C-H)
		1732	cm^{-1}	(v C=O)
		1650	cm^{-1}	(v C=C)
		1446	cm^{-1}	(δ C-H)
		1174	cm^{-1}	(v C(=O)-O)
		1032	cm^{-1}	(v C(=O)-O-C-C)
		894	cm^{-1}	(δ out-of-plane (-H (alkene)))

(Figure 53)

$^1\text{H-NMR}$:	1.23	ppm	(3H, t, $J=7.3$ Hz, $\text{CH}_3\text{-CH}_2\text{-O-}$)
(CDCl_3)	1.73	ppm	(6H, s, $\text{CH}_2=\text{C}(\text{CH}_3)\text{-}$)
	2.12-2.17	ppm	(2H, 2d, $J=5.8,5.8$ Hz, $\text{CH}_2=\text{C}(\text{CH}_3)\text{-CH}_2$)
	2.30-2.37	ppm	(2H, 2d, $J=9.2,9.2$ Hz, $\text{CH}_2=\text{C}(\text{CH}_3)\text{-CH}_2$)

2.74-2.81 ppm (1H, m, -CH-)
 4.08-4.13 ppm (2H, q, J=7.3 Hz, CH₃-CH₂-O-)
 4.73,4.76 ppm (4H, 2s, CH₂=C(CH₃)-)

(Figure 54-56)

3.3. 4-Methyl-2-(2'-methyl-2'-propenyl)-4-pentenoic acid.

1.68 g. (0.03 mole) of potassium hydroxide was dissolved in 4 ml. of water in a 100 ml. round-bottom flask 2.94 g.(0.015 mole) of ethyl 4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenoate was added into these flask with stirring. Then, 20 ml. of 95 % ethanol was added to produce a homogeneous solution. A reflux condenser was Attached to the flask and the mixture was refluxed for 2 hours; hydrolysis was then completed. Ethanol was distilled off as much as possible by a rotary evaporator. The residue was added 30 ml. of water and washed with 30 ml. of hexane to remove unreacted ester. After that, the aqueous phase was acidified by addition of 20% hydrochloric acid and then extracted with 3 x 30 ml. of hexane. The hexane extract was washed with water, dried over anhydrous sodium sulfate and evaporated. The yield was 2.40 g. (95.2 %).

IR : 3300-2500 cm⁻¹ (v O-H)
 (Neat) 3076 cm⁻¹ (v C=C-H)
 2970,2936 cm⁻¹ (v C-H)
 1712 cm⁻¹ (v C=O acid)
 1652 cm⁻¹ (v C=C)

1444	cm ⁻¹	(δ C-H)
1290	cm ⁻¹	(ν C-O)
938	cm ⁻¹	(δ out-of-plane O-H)
894	cm ⁻¹	(δ out of plane C-H (alkene))

(Figure 57)

¹ H-NMR:	1.74	ppm	(6H, s, CH ₂ =C(CH ₃)-)
(CDCl ₃)	2.14-2.20	ppm	(2H, 2d, J=6.1,5.8 Hz, CH ₂ =C(CH ₃)-CH ₂)
	2.33-2.38	ppm	(2H, 2d, J=9.2,8.9 Hz, CH ₂ =C(CH ₃)-CH ₂)
	2.76-2.82	ppm	(1H, m, -CH-)
	4.75,4.79	ppm	(4H, 2s, CH ₂ =C(CH ₃)-)

(Figure 58-59)

3.4. N-(4-Methyl-2-(2'-methyl-2'-propenyl)-4-pentenoyl) urea.

1.43 g. (0.88 ml., 0.012 mole) of redistilled thionyl chloride was placed in the 50 ml. round-bottom flask and 1.68 g.(0.01 mole) of 4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenoic acid was added slowly with stirring. There was a slight evolution of heat, sulfur dioxide was evolved and the liquid darkened considerably. When all the acid had been added, the mixture was heated in the hot water bath (temperature 40-50°C) for 3 hours. The apparatus for distillation was arranged and the excess of thionyl chloride was removed in vacuo to yield the crude acyl chloride, which was not further purified. The acid chloride was then added dropwisely into a mixture of urea (1.8 g., 0.03 mole) and potassium carbonate (1.38 g., 0.01 mole) in dry benzene. The mixture was refluxed

for 8 hours. Benzene was distilled off by a rotary evaporator until the residue became pasty. The mixture was added 50 ml. of water and extracted with three 30 ml. portions of ethylacetate. The combined ethylacetate extract was washed with water to remove the residual potassium carbonate and dried over anhydrous sodium sulfate. Later, the solvent was evaporated in vacuo to yield crude oily product. Purification was achieved by column chromatographic method using silica gel as stationary phase and 2% methanol in chloroform as a mobile phase. After evaporated, the white solid was precipitated. The yield was 0.99g. (47.1 %) of product, melting point 94.0-95.0 °C.

IR	:	3396	cm ⁻¹	(ν_{asym} N-H, primary amide)
(KBr)		3336	cm ⁻¹	(ν N-H, imide)
(Pellet)		3250	cm ⁻¹	(ν_{sym} N-H, primary amide)
		3084,2976	cm ⁻¹	(ν C=C-H)
		2938	cm ⁻¹	(ν C-H)
		1708	cm ⁻¹	(ν C=O, imide)
		1678	cm ⁻¹	(ν C=O, primary amide)
		1620	cm ⁻¹	(ν C=C)
		1400	cm ⁻¹	(δ C-N)

(Figure 60)

¹ H-NMR:	1.74	ppm	(6H, s, CH ₂ =C(CH ₃)-)
(CDCl ₃)	2.14-2.19	ppm	(2H, 2d, J=5.5,5.8 Hz, CH ₂ =C(CH ₃)-CH ₂)
	2.34-2.40	ppm	(2H, 2d, J=8.9,9.2Hz, CH ₂ =C(CH ₃)-CH ₂)
	2.65-2.72	ppm	(1H, m, -CH-)

4.74	ppm	(2H, dd, J=0.92 Hz, $CH_2=C(CH_3)-$)
4.82	ppm	(2H, t, J=1.53 Hz, $CH_2=C(CH_3)-$)
5.27	ppm	(1H, s, broad, $-CO-NH_2$)
8.27	ppm	(1H, s, broad, $-CO-NH_2$)
8.93	ppm	(1H, s, broad, $-CO-NH-CO-$)

(Figure 61-62)

^{13}C -NMR : see Figure 63.

($CDCl_3$)

EIMS : 210(M^+ ,3%), 193(7%), 151(7%), 150(53%)

(m/e) 123(13%), 122 (12%), 44(100%)

(Figure 64)

4. Synthesis of N-(2-allyl-4-pentenoyl) urea (CU-763-11-04).

4.1. Diethyl diallylmalonate.

Prepare a solution of sodium ethoxide from 6.9 g. (0.3mole) of clean sodium and 90 ml. of absolute ethanol in a 250 ml. flask. Attached the flask to a condenser arranged for reflux. When the sodium ethoxide solution, which was vigorously stirred, had cooled to about 50 °C, add 24.0 g. (22.8 ml., 0.15 mole) of diethyl malonate slowly through the condenser, to the resulting suspension introduced gradually (90 minutes) 24.0 g. (22.8 ml., 0.15 mole) of 1-bromopropene (allyl bromide) through the condenser . Reaction occurred almost immediately and much

heat was evolved. Refluxed the reaction mixture on a water bath about 15 hours. If the reactant remains, an alkyl halide will be added. Removed as much of the ethanol as possible by distillation under reduced pressure (rotary evaporator) on a water bath. Cooled the contents of flask to room temperature, added 100 ml. of water and extracted with 3 x 30 ml. of hexane. Combined hexane layer was washed with water, dried over anhydrous sodium sulfate, and evaporated. The oily liquid was purified by the column chromatography using silica gel as stationary phase and hexane:ethylacetate (40:1) as mobile phase. The yield of the product was 28.4 g. (78.9 %).

IR	:	3080	cm ⁻¹	(ν C=C-H)
(Neat)		2982,2936,2874	cm ⁻¹	(ν C-H)
		1736,1732	cm ⁻¹	(ν C=O ester)
		1642	cm ⁻¹	(ν C=C)
		1466,1444	cm ⁻¹	(δ C-H)
		1196	cm ⁻¹	(ν C(=O)-O)
		1036	cm ⁻¹	(ν C(=O)-O-C-C)
		920	cm ⁻¹	(δ out-of plane C-H (alkene))

(Figure 65)

¹ H-NMR:	1.25	ppm	(6H, t, J=7.3 Hz, CH ₃ -CH ₂ -O-)
(CDCl ₃)	2.63-2.66	ppm	(4H, ddt, J=7.3, 1.2 Hz, CH ₂ =CH-CH ₂ -)
	4.16-4.21	ppm	(4H, q, J=7.2 Hz, CH ₃ -CH ₂ -O-)
	5.08-5.14	ppm	(4H, m, CH ₂ =CH-)
	5.60-5.71	ppm	(2H, m, CH ₂ =CH-CH ₂)

(Figure 66-68)

4.2. Ethyl 2-allyl-4-pentenoate.

Diethyl diallylmalonate (7.2 g., 0.03 mole), DMSO (50 ml.), water (1.0 g., 0.06 mole), and lithium chloride (2.5 g., 0.06 mole) were placed in a 100 ml. round-bottom flask equipped with a magnetic stirrer and fitted with a condenser. The mixture was heated at refluxing for 36 hours. At this point, a brown color had developed and suspended solid (lithium carbonate, Li_2CO_3) was evident. The mixture is then distilled up to 185 °C. The distillate was poured into 200 ml. of ice water and the aqueous layer was saturated with Sodium chloride. The ester was extracted with 4 x 30 ml. of hexane, and the hexane extract was washed with water, dried over anhydrous sodium sulfate and concentrated to yield 4.48 g. (88.9 %) of ester which pure enough to continue the following reaction. The ester product can be further purified by column chromatography using silica gel as stationary phase and hexane:ethylacetate (40:1) as a mobile phase.

IR	:	3080	cm^{-1}	(ν C=C-H)
(Neat)		2982,2936,2874	cm^{-1}	(ν C-H)
		1734	cm^{-1}	(ν C-O)
		1642	cm^{-1}	(ν C=C)
		466,444	cm^{-1}	(δ C-H)
		1196	cm^{-1}	(ν C(=O)-O)

1036	cm ⁻¹	(ν C(=O)-O-C-C)
920	cm ⁻¹	(δ out-of plane C-H (alkene))

(Figure 69)

¹ H-NMR:	1.24	ppm	(3H, t, J=7.3 Hz, CH ₃ -CH ₂ -O-)
(CDCl ₃)	2.22-2.29	ppm	(2H, m, CH ₂ =CH-CH ₂ -)
	2.33-2.41	ppm	(2H, m, CH ₂ =CH-CH ₂ -)
	2.48-2.54	ppm	(1H, m, -CH-)
	4.11-4.16	ppm	(2H, q, J=7.3 Hz, CH ₃ -CH ₂ -O-)
	5.01-5.09	ppm	(4H, complex, CH ₂ =CH-CH ₂ -)
	5.70-5.79	ppm	(2H, m, CH ₂ =CH-CH ₂ -)

(Figure 70-72)

4.3. 2-Allyl-4-pentenoic acid.

1.68 g.(0.03 mole) of potassium hydroxide was dissolved in 4 ml. of water in a 100 ml. round-bottom flask. 2.52 g.(0.015 mole) of ethyl 2-allyl-4-pentenoate was added into these flask with stirring. Then, 20 ml. of 95 % ethanol was added to produce a homogeneous solution. A reflux condenser was Attached to the flask and the mixture was refluxed for 2 hours; hydrolysis was then completed. Ethanol was distilled off as much as possible by a rotary evaporator. After that, the mixture was acidified by addition of 20% hydrochloric acid . The aqueous phase was then extracted with 3 x 30 ml. of hexane. The hexane extract was washed with water, dried over anhydrous sodium sulfate and evaporated. The yield was 1.98 g. (94.2 %).

IR	3200-2500	cm ⁻¹	(ν O-H)
(Neat)	3080	cm ⁻¹	(ν C=C-H)
	3006,2980,2924	cm ⁻¹	(ν C-H)
	1712	cm ⁻¹	(ν C=O acid)
	1644	cm ⁻¹	(ν C=C)
	1444	cm ⁻¹	(δ C-H)
	1418	cm ⁻¹	(δ C-H)
	1282	cm ⁻¹	(δ C-O)
	894	cm ⁻¹	(δ out-of-plane C-H (alkane))

(Figure 73)

¹ H-NMR:	2.26-2.33	ppm	(2H, m, CH ₂ =CH-CH ₂ -)
(CDCl ₃)	2.36-2.44	ppm	(2H, m, CH ₂ =CH-CH ₂ -)
	2.52-2.59	ppm	(1H, m, -CH-)
	5.05-5.12	ppm	(4H, complex, CH ₂ =CH-)
	5.73-5.82	ppm	(2H, complex, CH ₂ =CH-CH ₂ -)

(Figure 74-75)

4.4. N-(2-Allyl-4-pentenoyl) urea.

1.43 g. (0.88 ml., 0.012 mole) of redistilled thionyl chloride was placed in the 50 ml. round-bottom flask and 1.56 g. (0.01 mole) of 2-allyl-4-pentenoic acid was added slowly with stirring. There was a slight evolution of heat, sulfur dioxide was evolved and the liquid darkened considerably. When all the acid had been added, the mixture was heated

in the hot water bath (temperature 40-50°C) for 3 hours. The apparatus for distillation was arranged and the excess of thionyl chloride was removed in vacuo to yield the crude acyl chloride, which was not further purified. The acid chloride was then added dropwisely into a mixture of urea (1.8 g., 0.03 mole) and potassium carbonate (1.38 g., 0.01 mole) in dry benzene. The mixture was refluxed for 8 hours. Benzene was distilled off by a rotary evaporator until the residue became pasty. The mixture was added 50 ml. of water and extracted with three 30 ml. portions of ethylacetate. The combined ethylacetate extract was washed with water to remove the residual potassium carbonate and dried over anhydrous sodium sulfate. Later, the solvent was evaporated in vacuo to yield crude oily product which was purified by column chromatography using silica gel as stationary phase and 2% methanol in chloroform as a mobile phase. After evaporated, the white solid was precipitated. The yield was 0.85 g. (46.7%) of product, melting point 155.0-156.0 °C.

IR	:	3378	cm ⁻¹	(ν_{asym} N-H, primary amide)
(KBr)		3330	cm ⁻¹	(ν N-H, imide)
(Pellet)		3218	cm ⁻¹	(ν_{sym} N-H, primary amide)
		3078	cm ⁻¹	(ν C=C-H)
		3004,2980,2924	cm ⁻¹	(ν C-H)
		1702	cm ⁻¹	(ν C=O, imide)
		1687	cm ⁻¹	(ν C=O, primary amide)
		1640	cm ⁻¹	(ν C=C)
		1592	cm ⁻¹	(δ N-H)
		1400	cm ⁻¹	(δ C-N)

(Figure 76)

$^1\text{H-NMR}$:	2.24-2.34	ppm	(2H, m, $\text{CH}_2=\text{CH}-\text{CH}_2-$)
(CDCl_3)	2.36-2.46	ppm	(3H, complex, $\text{CH}_2=\text{CH}-\text{CH}_2$, $-\text{CH}-$)
	5.06-5.12	ppm	(4H, complex, $\text{CH}_2=\text{CH}-$)
	5.38	ppm	(1H, broad, s, $-\text{CO}-\text{NH}_2$)
	5.70-5.79	ppm	(2H, m, $\text{CH}_2=\text{CH}-\text{CH}_2$)
	8.27	ppm	(1H, s, broad, $-\text{CO}-\text{NH}_2$)
	8.92	ppm	(1H, s, broad, $-\text{CO}-\text{NH}-\text{CO}-$)

(Figure 77-79)

$^{13}\text{C-NMR}$: see Figure 80.

(CDCl_3)

EIMS : 183($\text{M}+1^+$, 9%), 182(M^+ , 1%), 165(2%), 123(4%),
(m/e) 122(24%), 95(16%), 94(10%), 44(100%)

(Figure 81)

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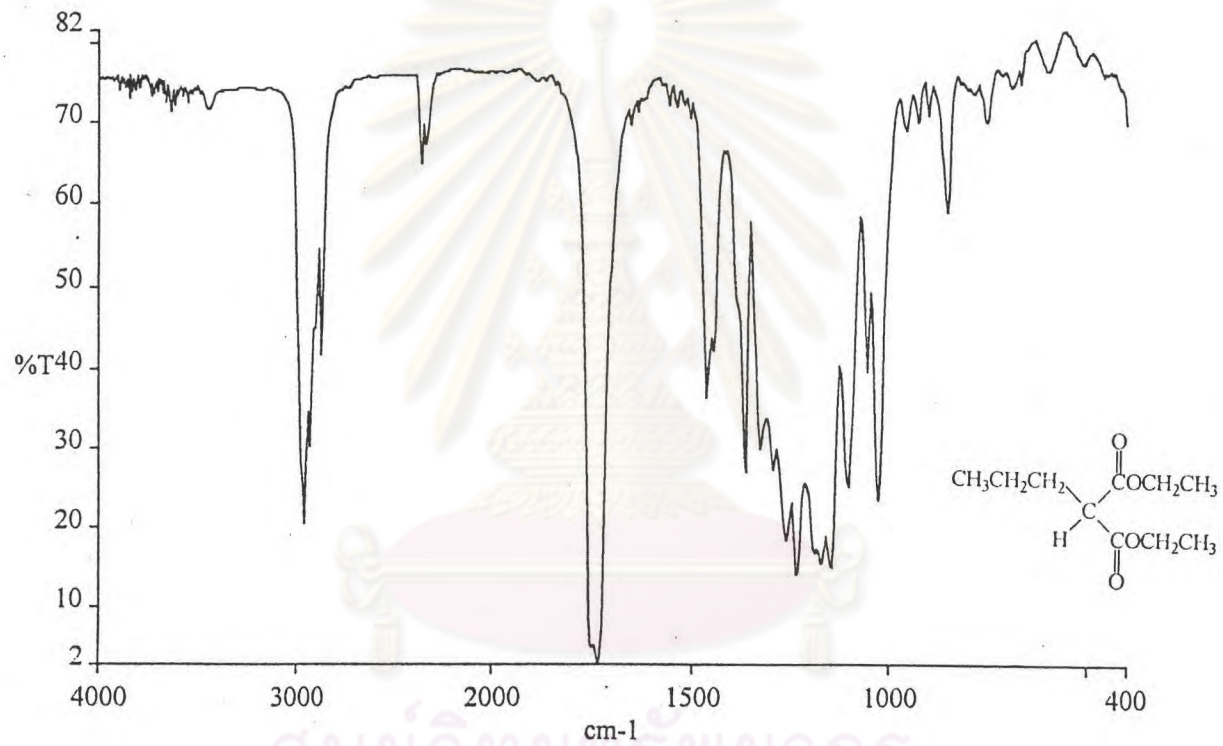


Figure 10. The IR spectrum (Neat) of diethyl propylmalonate.

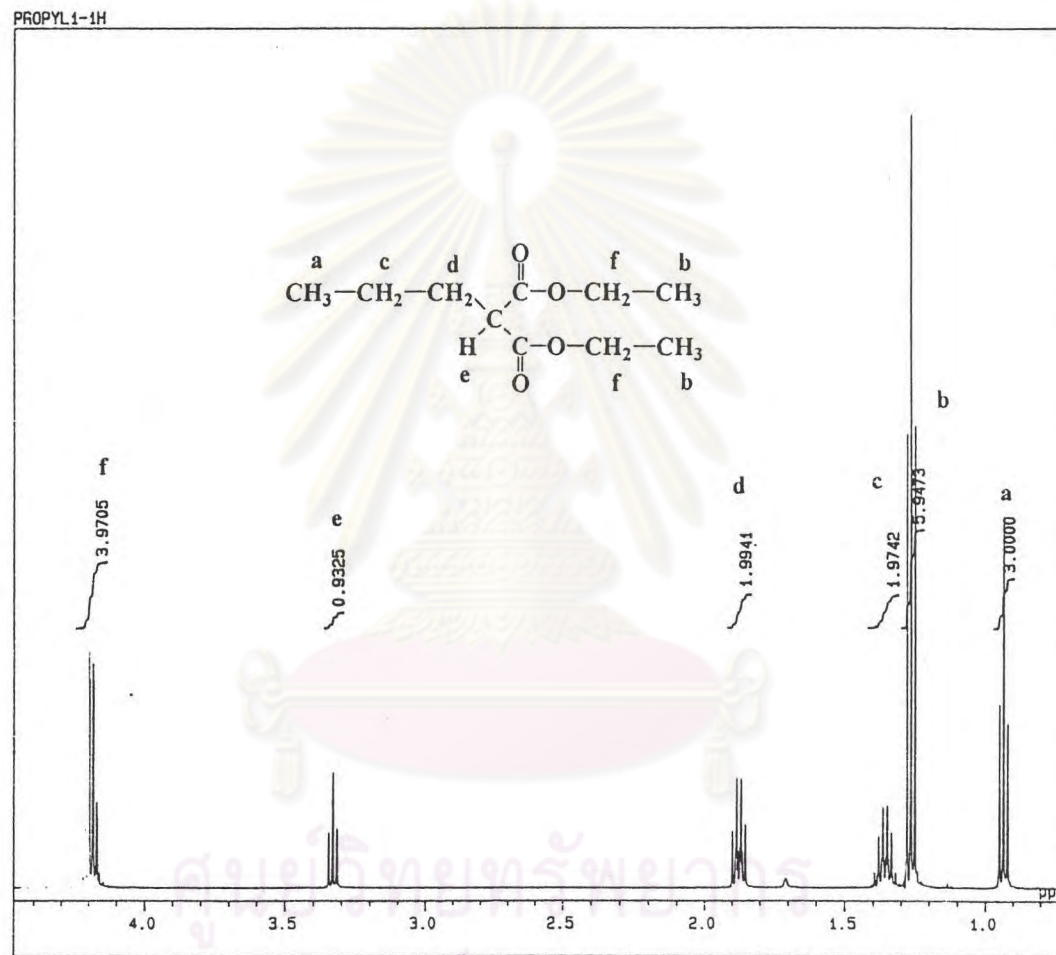


Figure 11. The 500 MHz ^1H -NMR spectrum of diethyl propylmalonate in CDCl_3 .

PROPYL1-1H

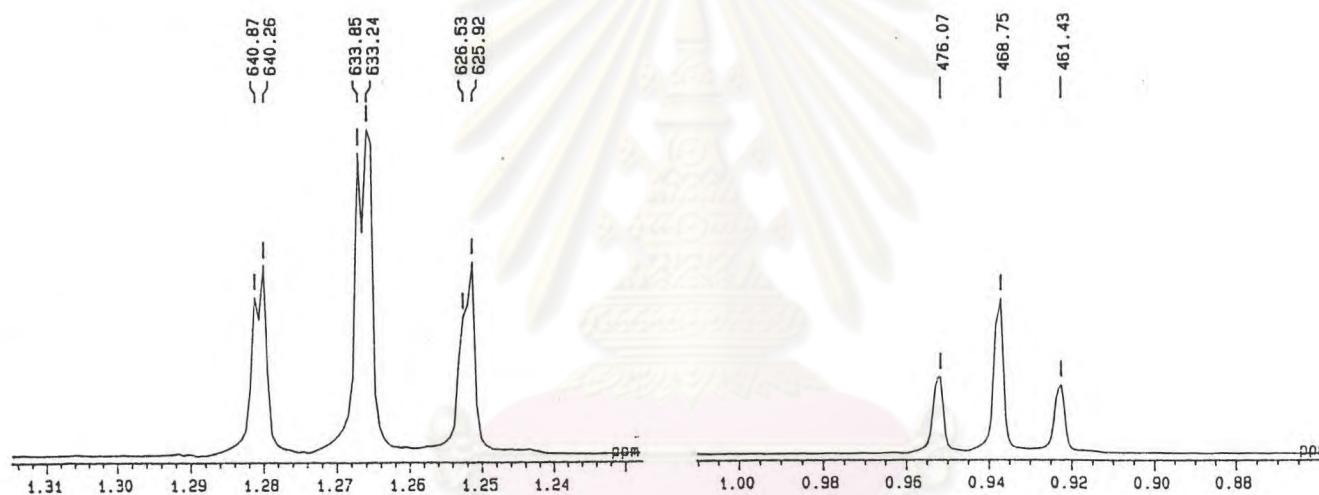


Figure 12. The 500 MHz ¹H-NMR spectrum of diethyl propylmalonate in CDCl₃ (Enlarged scale : 0.90-1.30 ppm).

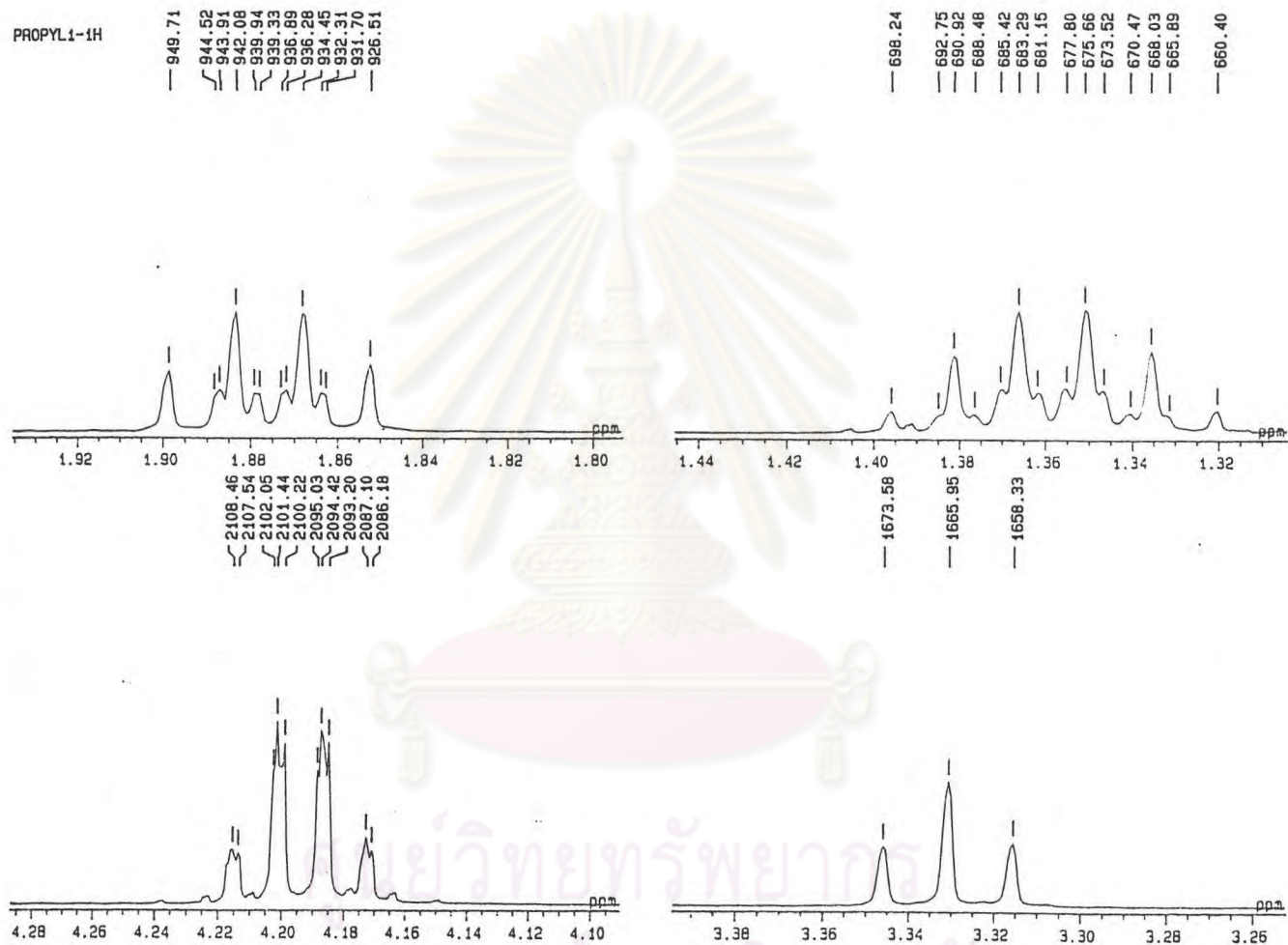


Figure 13. The 500 MHz ^1H -NMR spectrum of diethyl propylmalonate in CDCl_3 (Enlarged scale : 1.31-4.28 ppm).

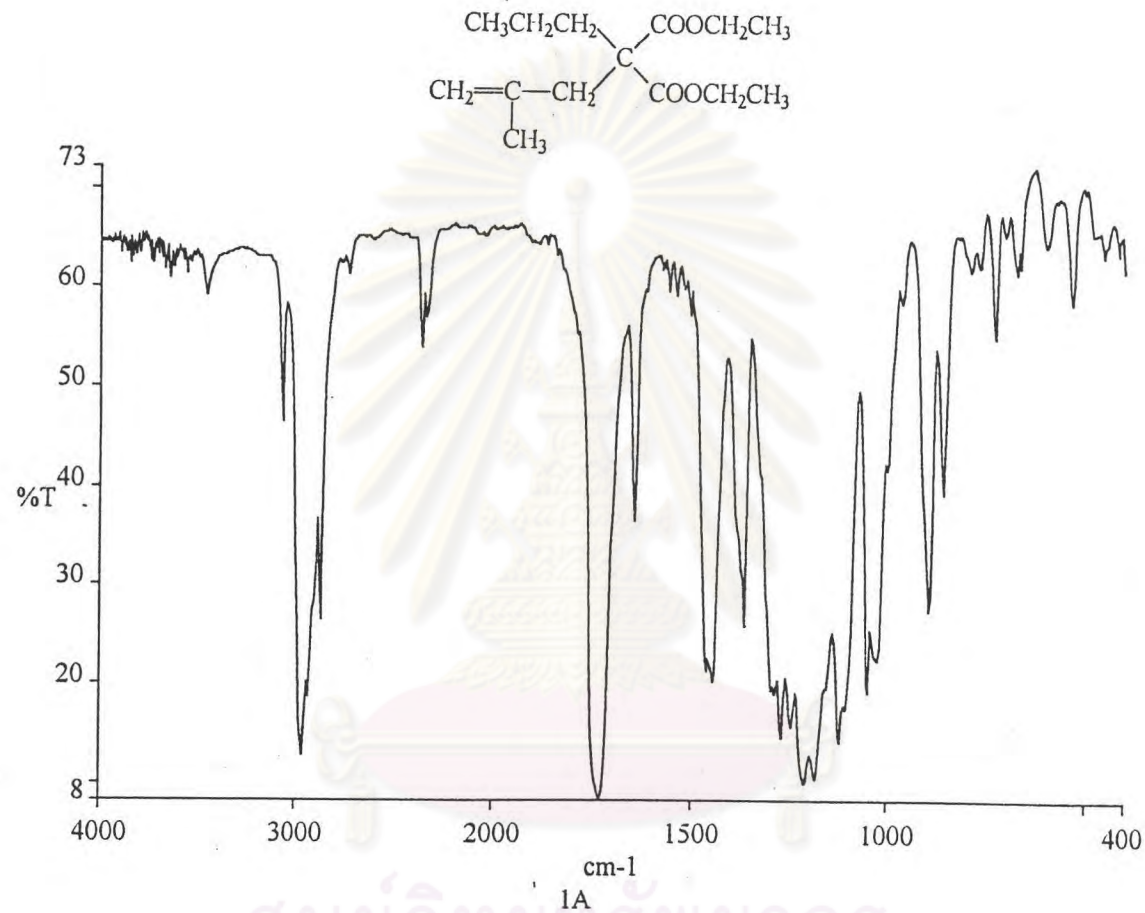


Figure 14. The IR spectrum (Neat) of diethyl (2-methyl-2-propenyl)propyl malonate.

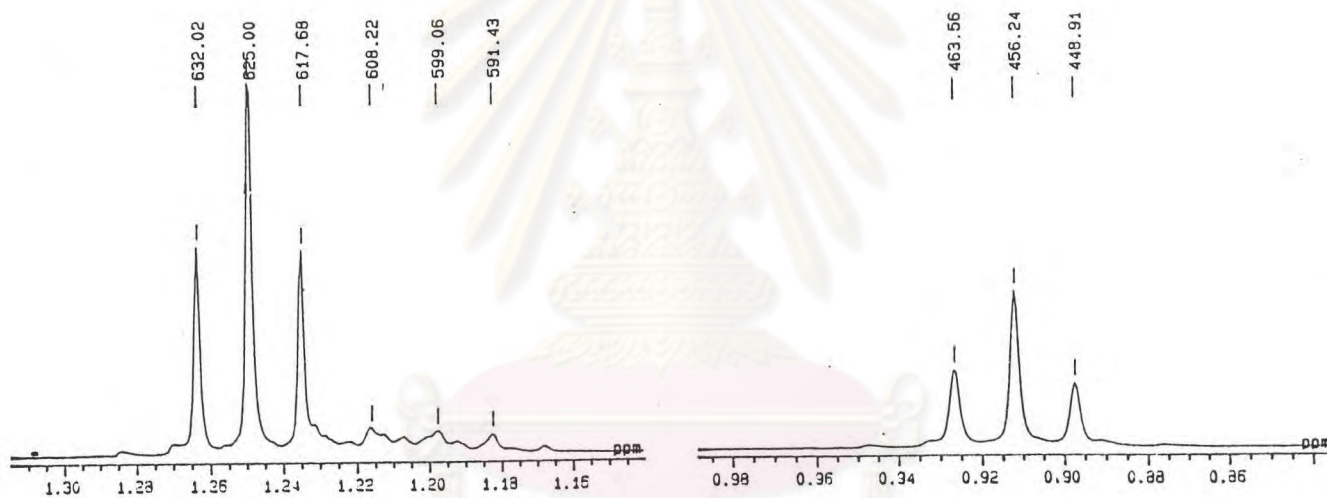


Figure 16. The 500 MHz $^1\text{H-NMR}$ spectrum of diethyl (2-methyl-2-propenyl)propylmalonate in CDCl_3 (Enlarged scale : 0.86-1.30 ppm).

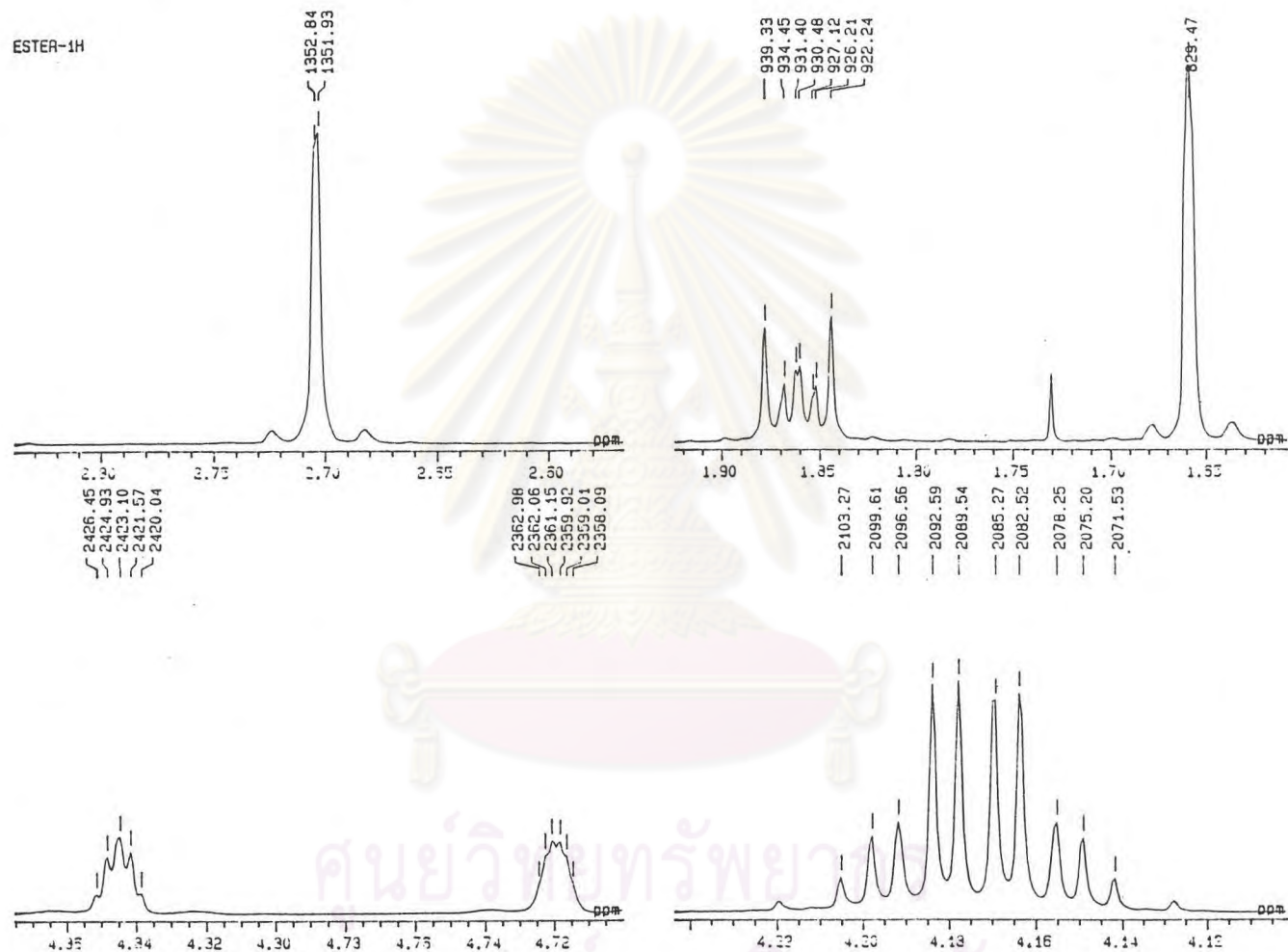


Figure 17. The 500 MHz ^1H -NMR spectrum of diethyl (2-methyl-2-propenyl)propylmalonate in CDCl_3 (Enlarged scale : 1.62-4.85 ppm).

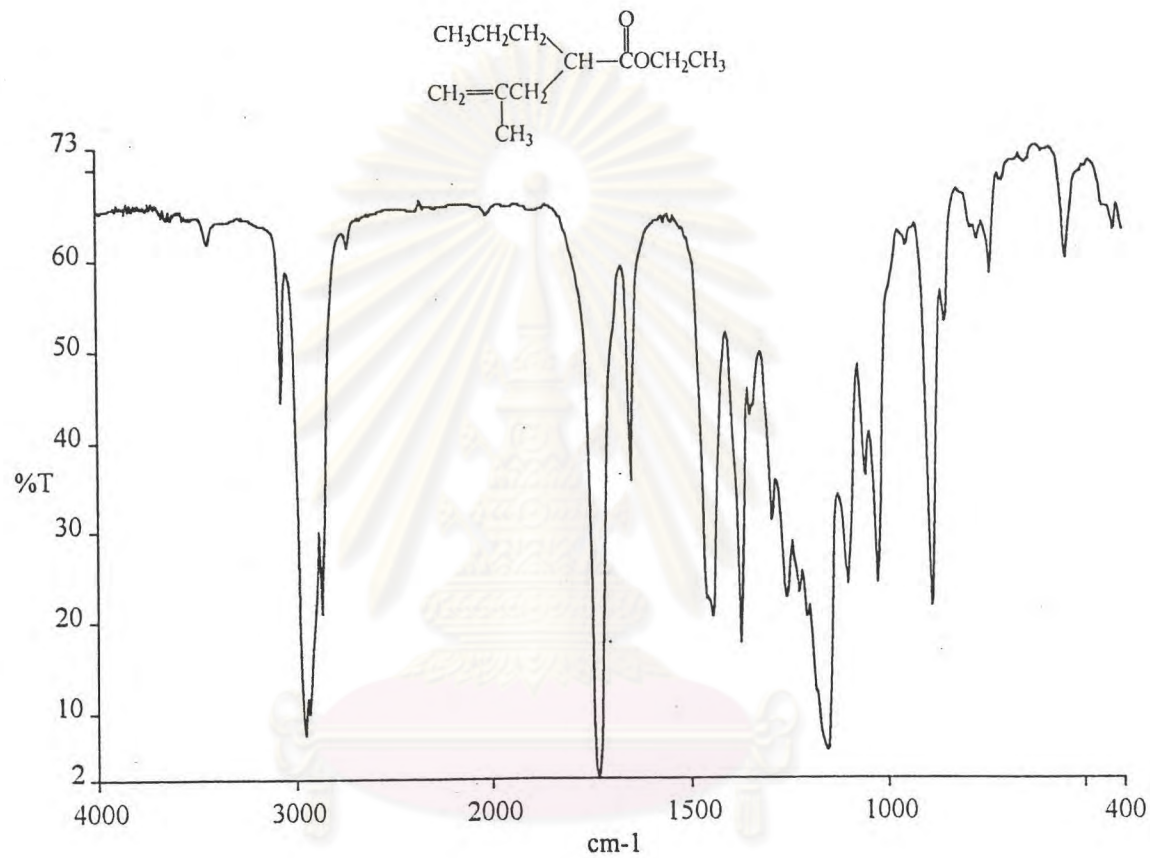


Figure 18. The IR spectrum (Neat) of ethyl 4-methyl-2-propyl-4-pentenoate.

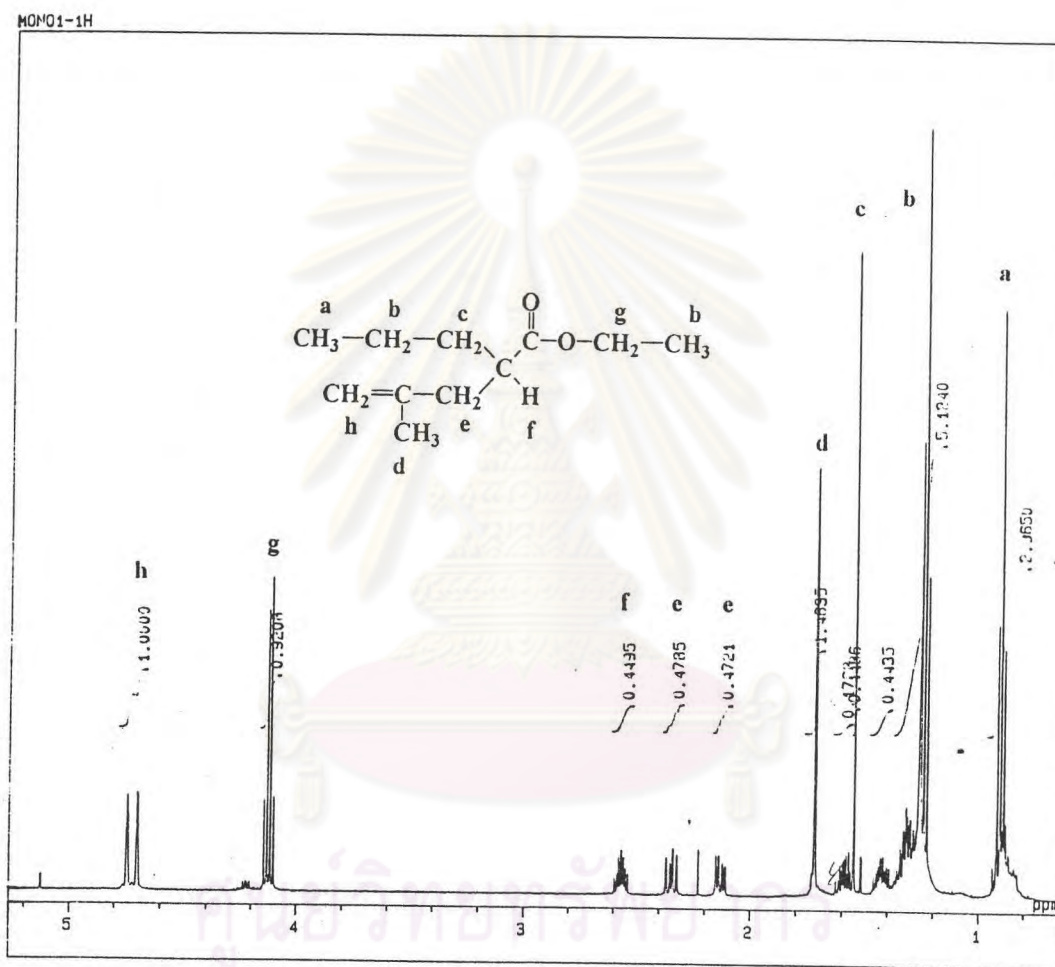


Figure 19. The 500 MHz ^1H -NMR spectrum of ethyl 4-methyl-2-propyl-4-pentenoate in CDCl_3 .

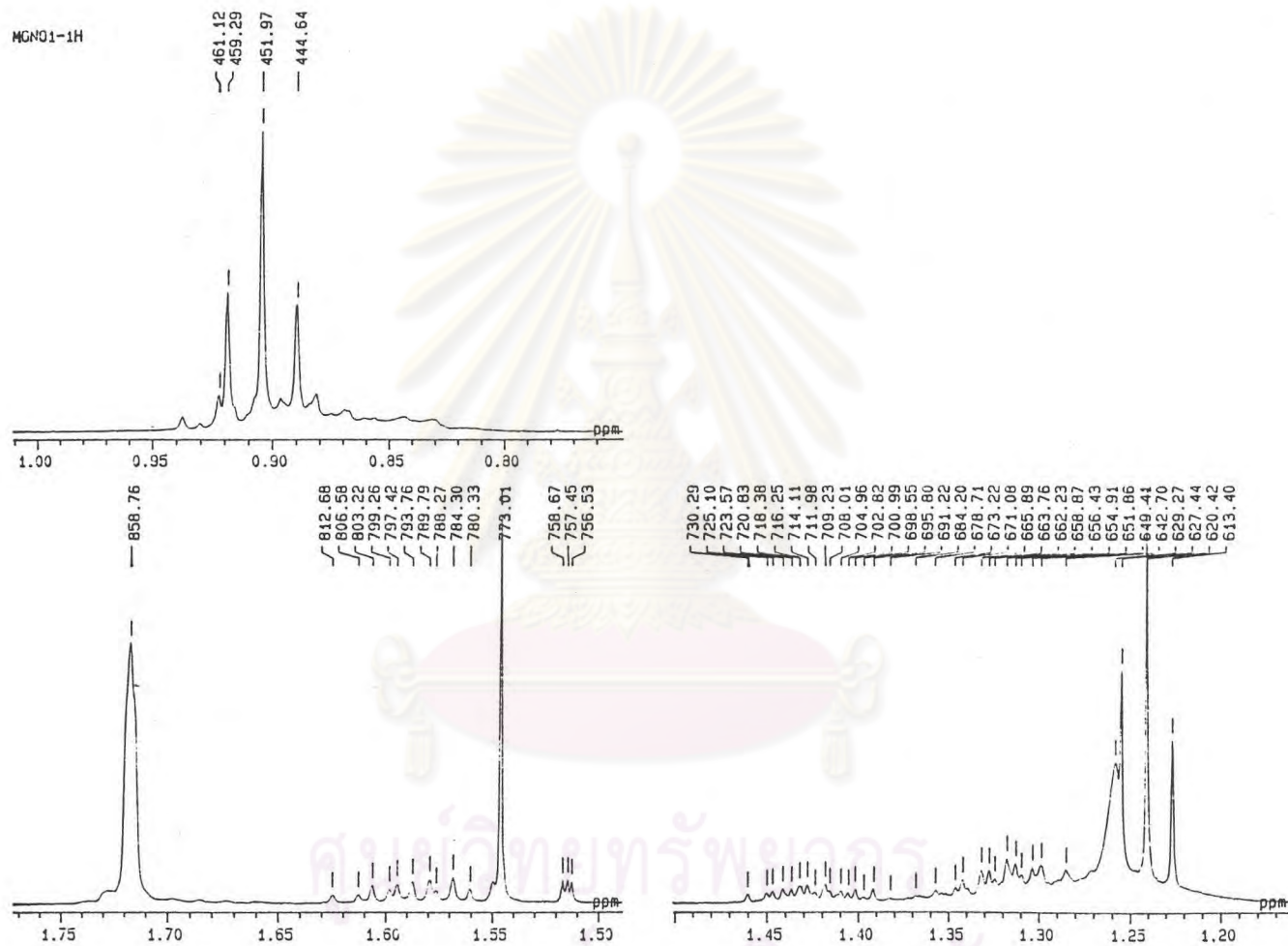


Figure 20. The 500 MHz ^1H -NMR spectrum of ethyl 4-methyl-2-propyl-4-pentenoate in CDCl_3 (Enlarged scale : 0.80-1.75 ppm).

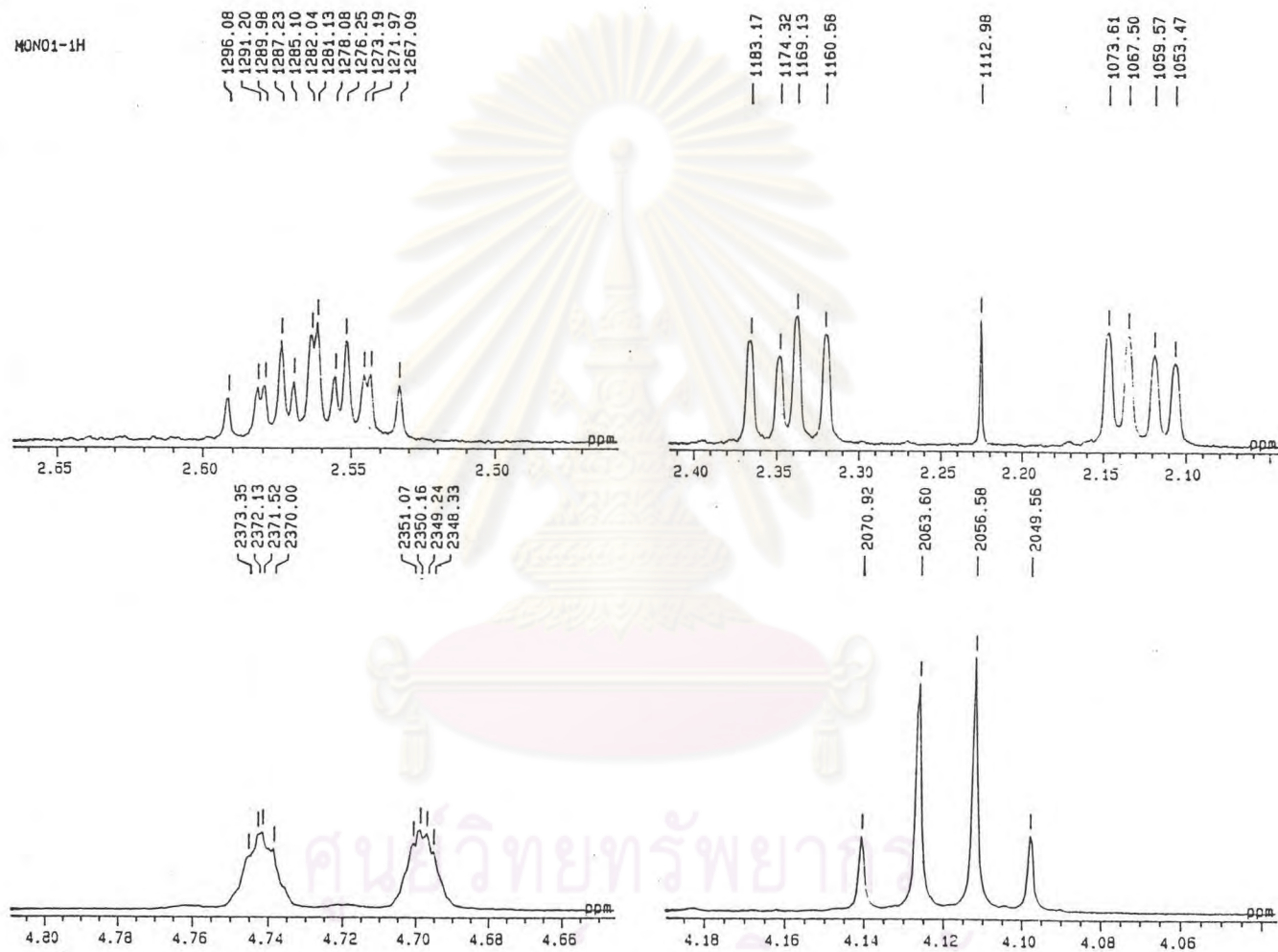


Figure 21. The 500 MHz ^1H -NMR spectrum of ethyl 4-methyl-2-propyl-4-pentenoate in CDCl_3 (Enlarged scale : 2.10-4.80 ppm).

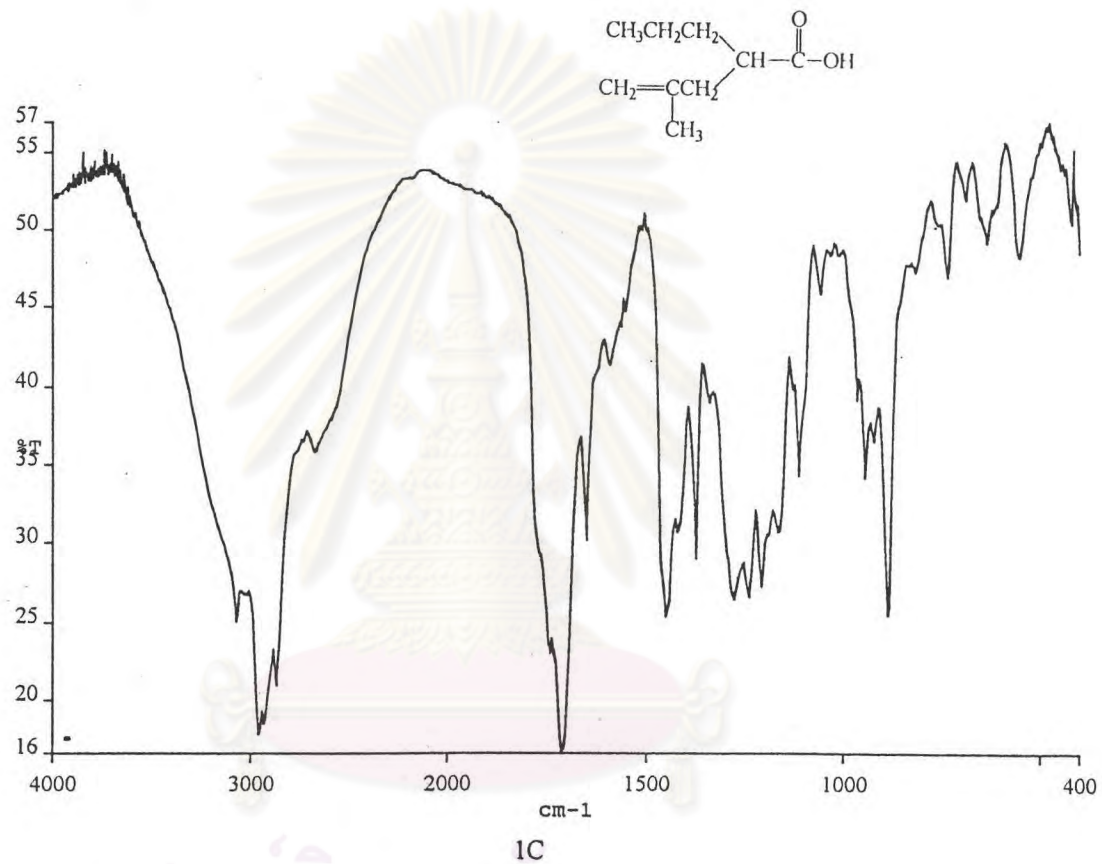


Figure 22. The IR spectrum (Neat) of 4-methyl-2-propyl-4-pentenoic acid.

จุฬาลงกรณ์มหาวิทยาลัย

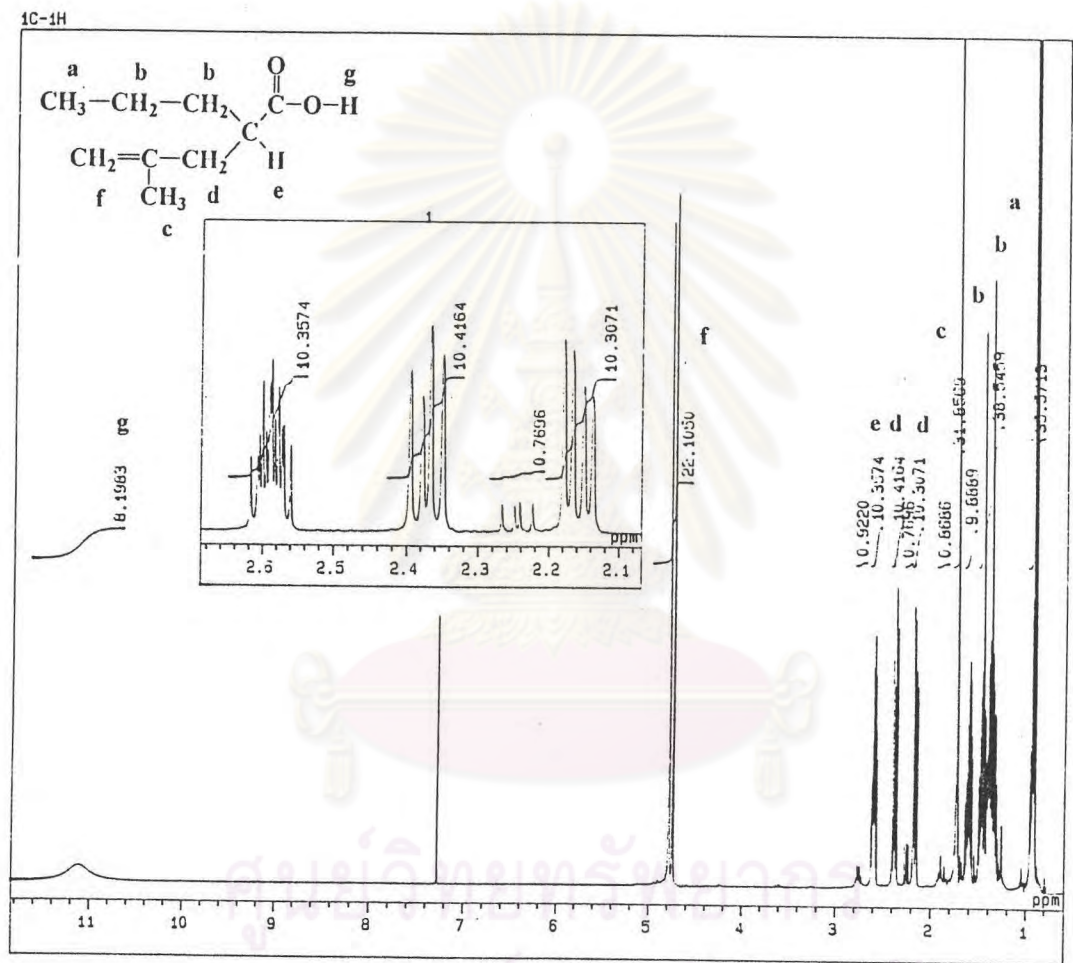


Figure 23. The 500 MHz ¹H-NMR spectrum of 4-methyl-2-propyl-4-pentenoic acid in CDCl₃.

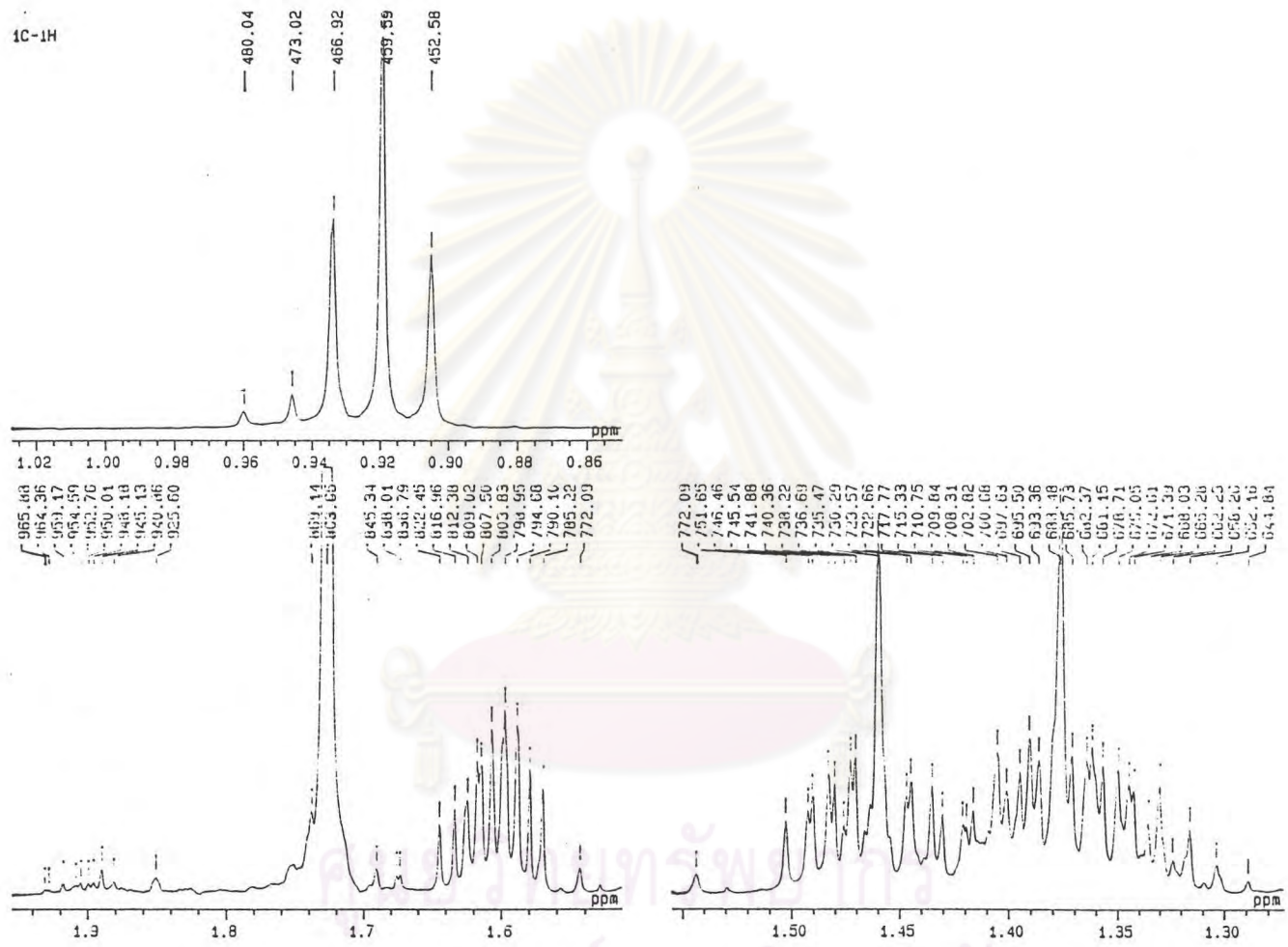


Figure 24. The 500 MHz $^1\text{H-NMR}$ spectrum of 4-methyl-2-propyl-4-pentenoic acid in CDCl_3 (Enlarged scale : 0.86-1.93 ppm).

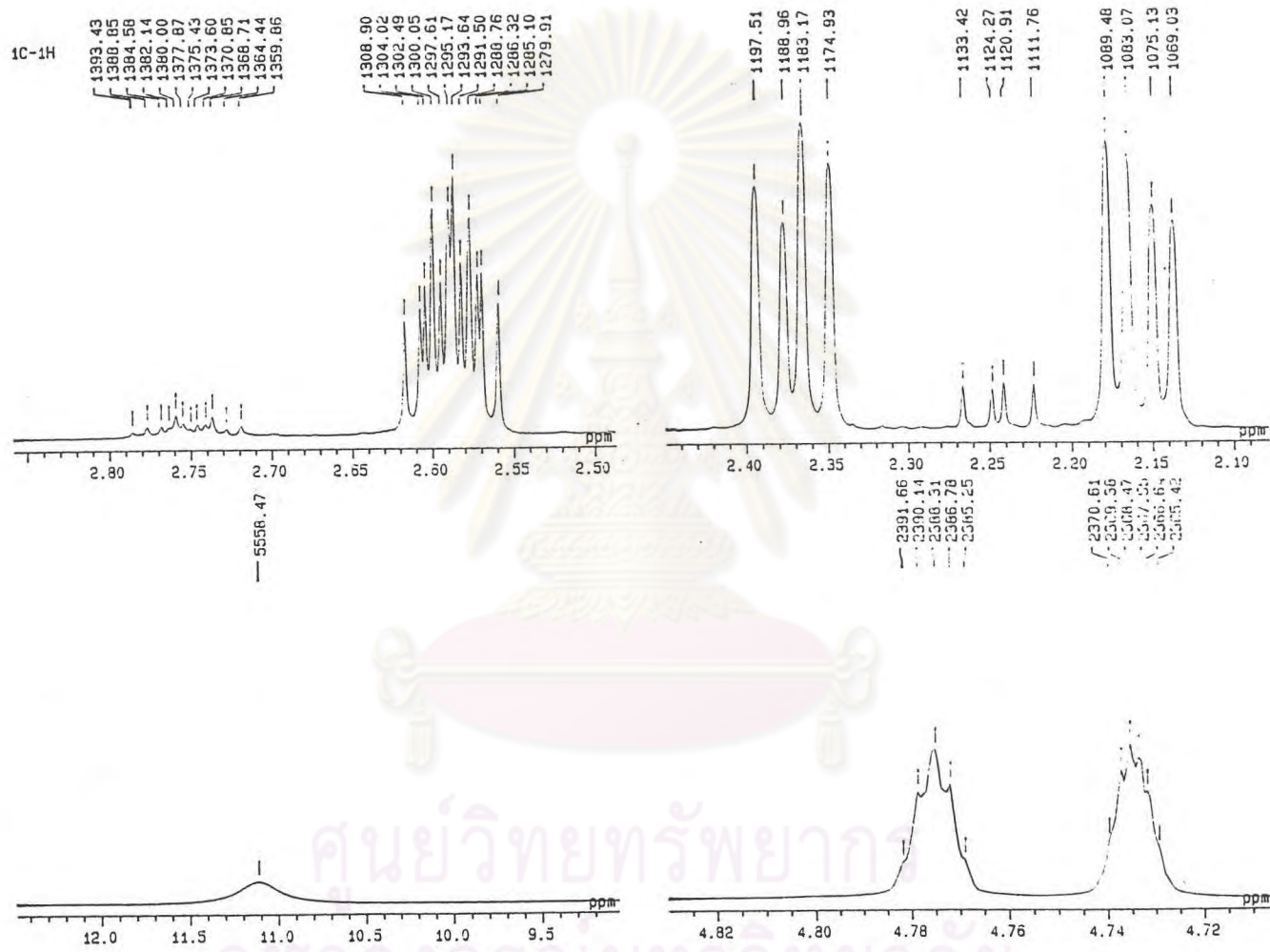


Figure 25. The 500 MHz ¹H-NMR spectrum of 4-methyl-2-propyl-4-pentenoic acid in CDCl₃ (Enlarged scale : 2.10-12.0 ppm).

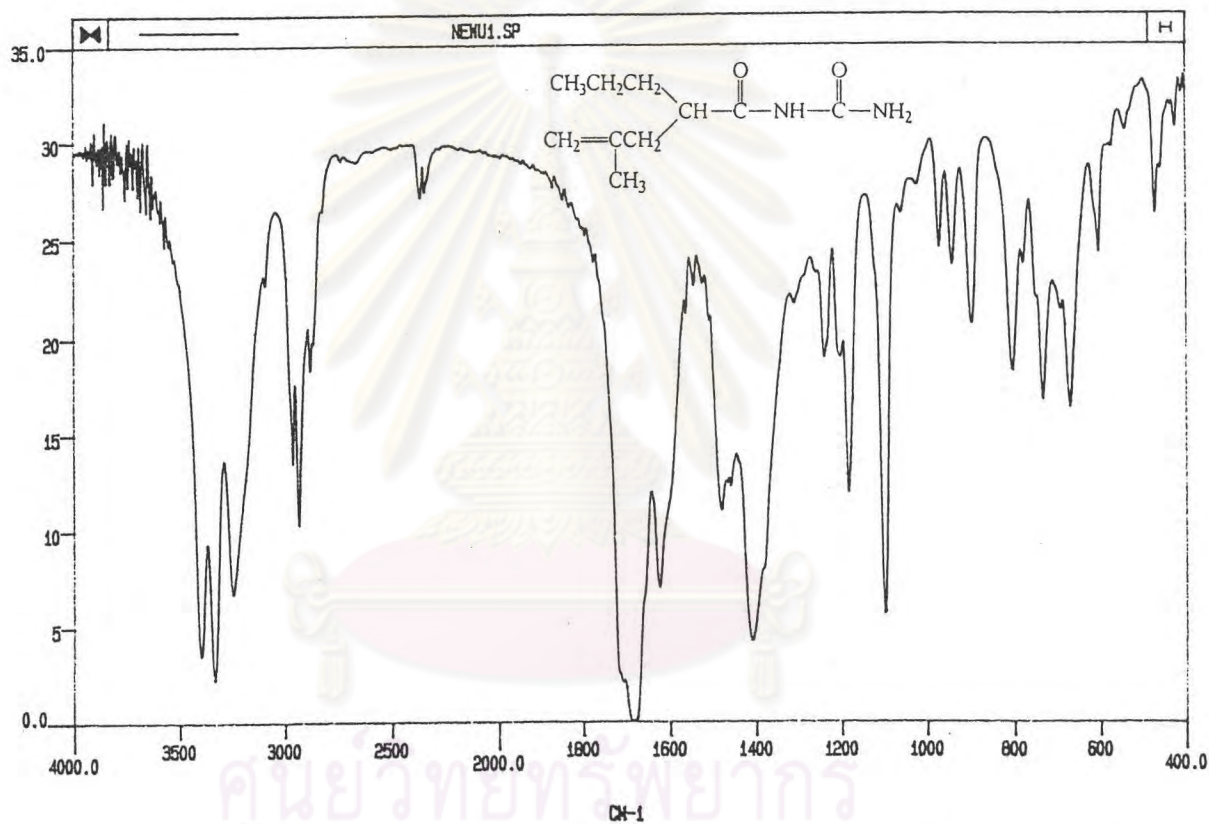


Figure 26. The IR spectrum (Neat) of N-(4-methyl-2-propyl-4-pentenyl) urea.

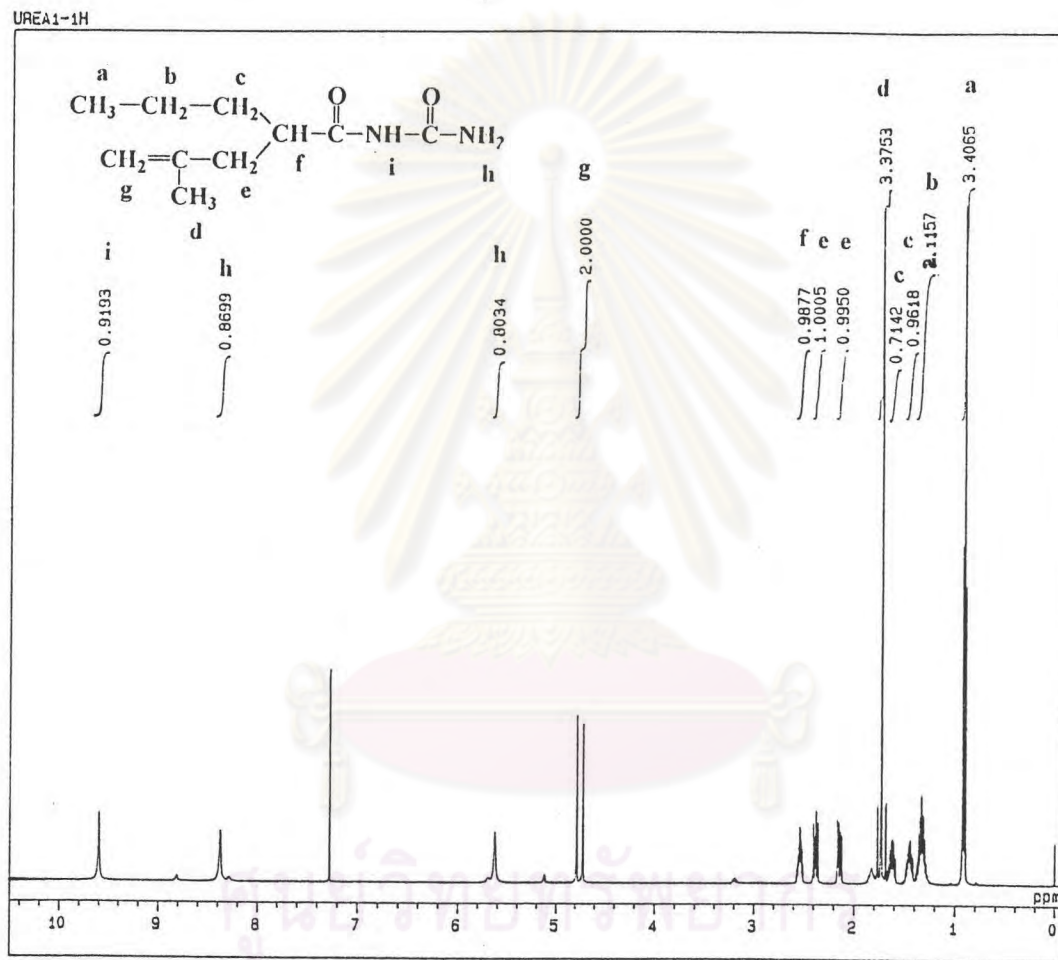


Figure 27. The 500 MHz ^1H -NMR spectrum of N-(4-methyl-2-propyl-4-pentenyl) urea in CDCl_3 .

UREA1-1H

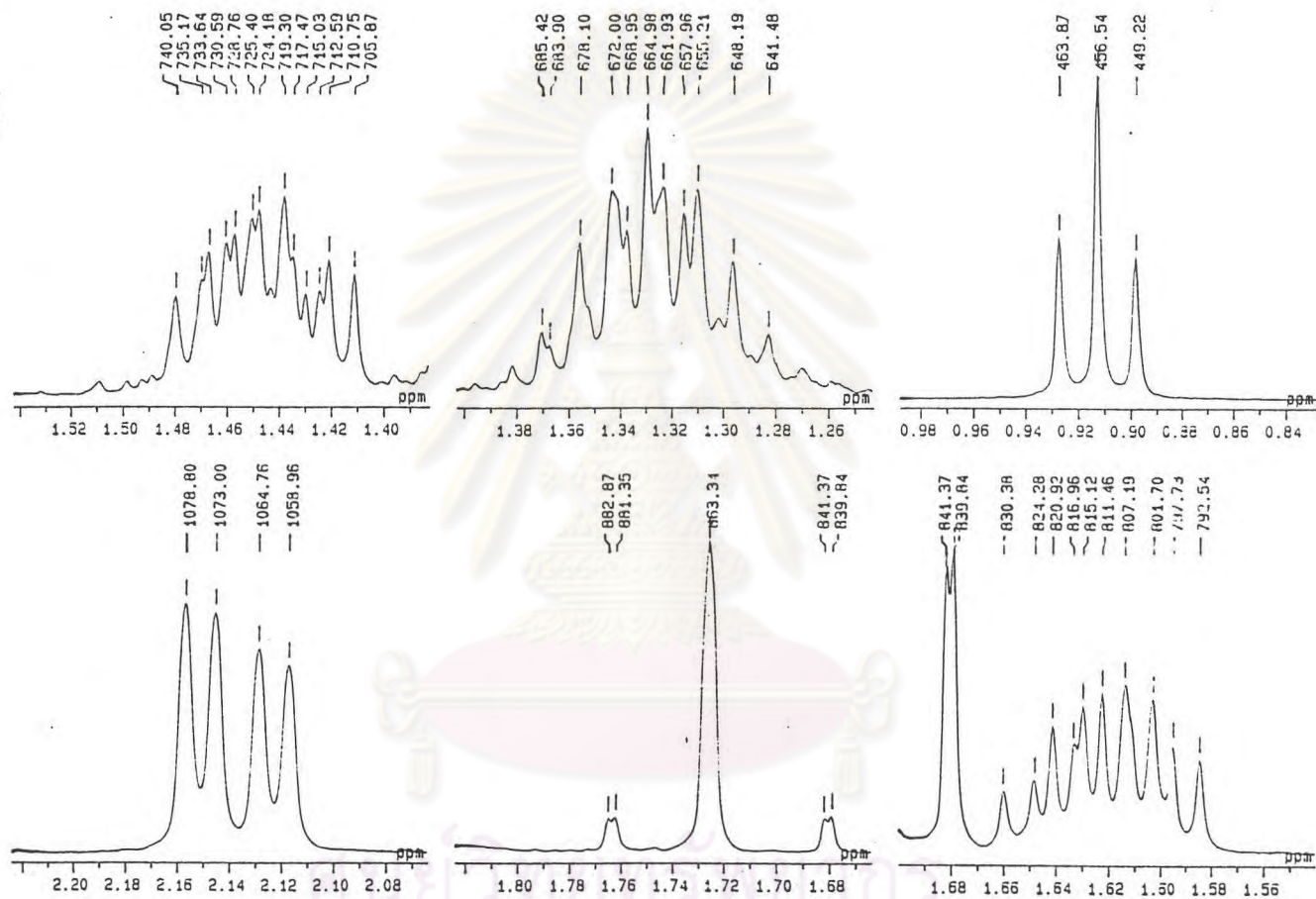


Figure 28. The 500 MHz ¹H-NMR spectrum of N-(4-methyl-2-propyl-4-pentenyl) urea in CDCl₃ (Enlarged scale : 0.84-2.20 ppm).

UREA1-1H

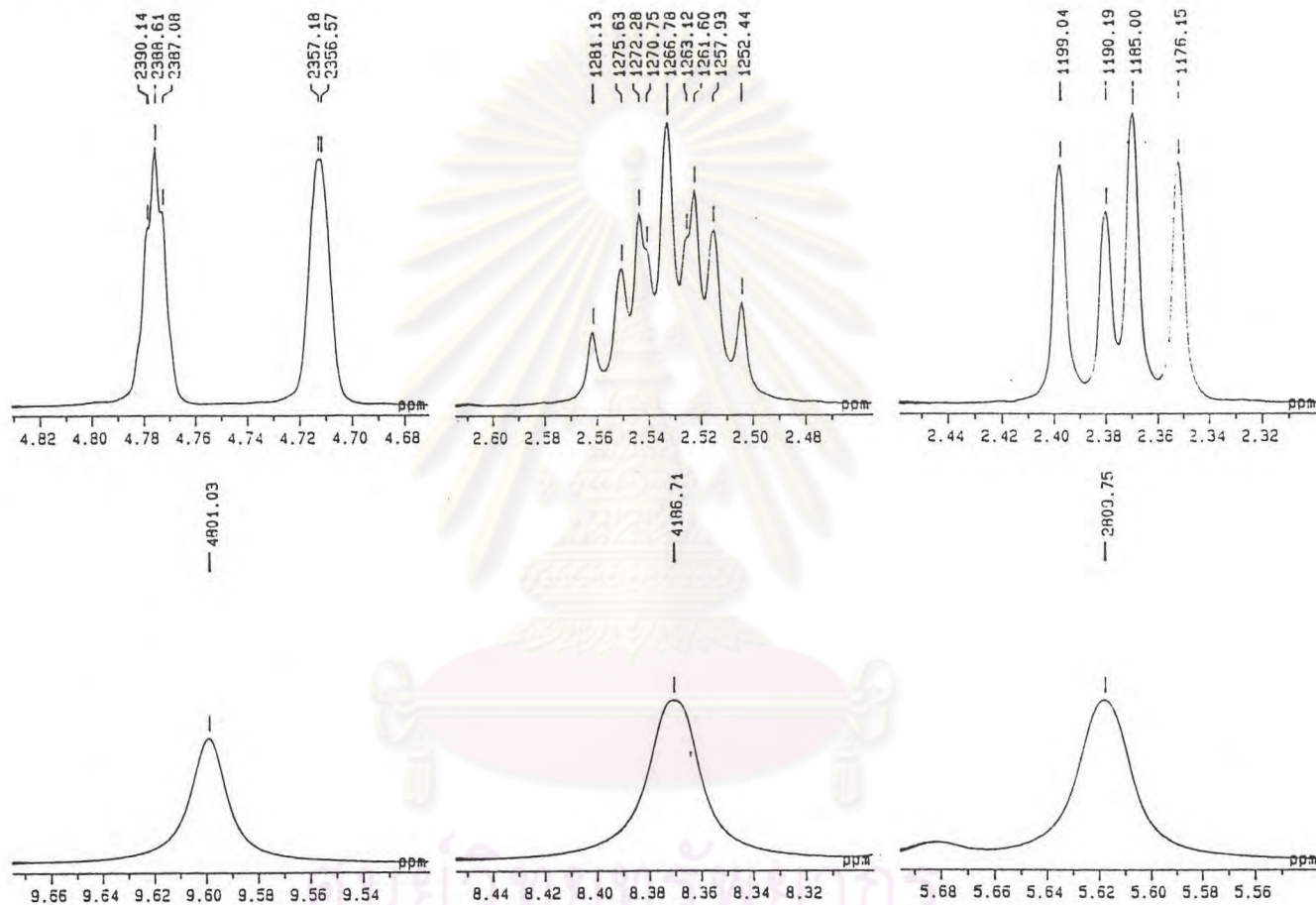


Figure 29. The 500 MHz ^1H -NMR spectrum of N-(4-methyl-2-propyl-4-pentenyl) urea in CDCl_3 (Enlarged scale : 2.32-9.66 ppm).

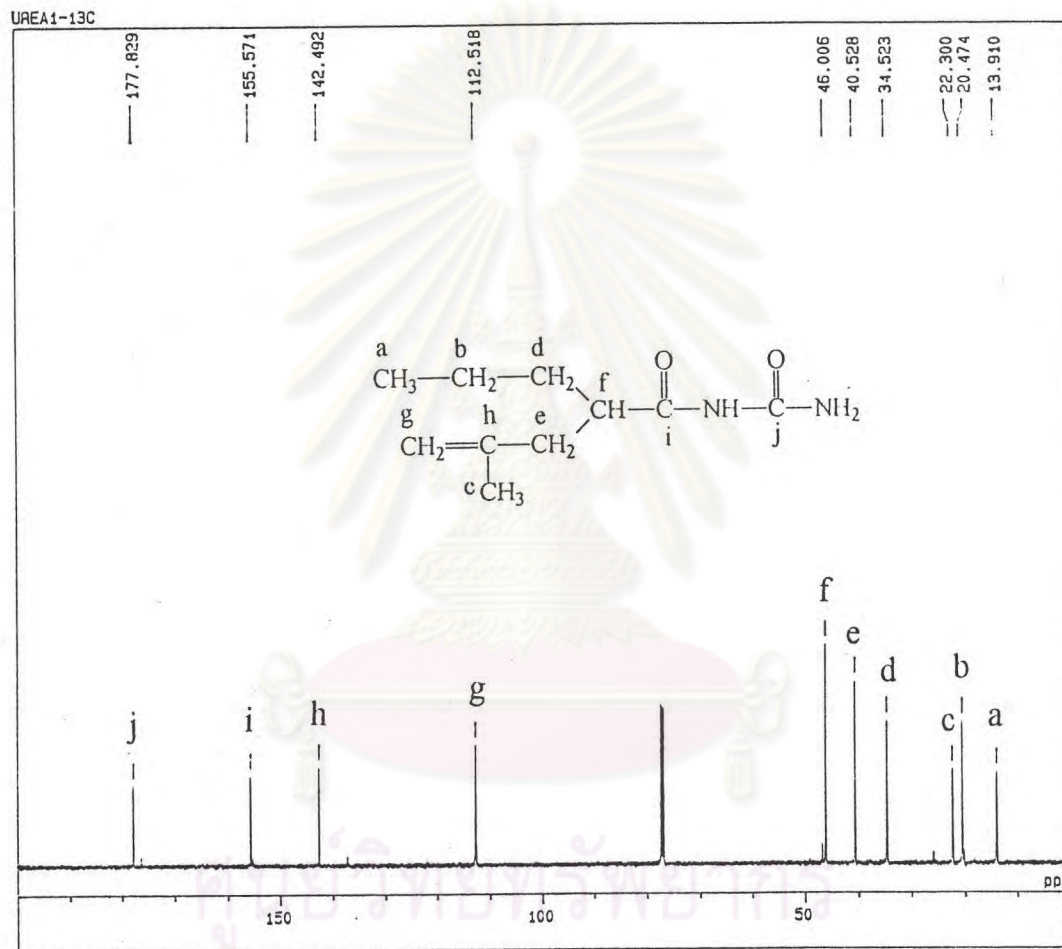


Figure 30. The 500 MHz ¹³C-NMR spectrum of N-(4-methyl-2-propyl-4-pentenoyl) urea in CDCl₃.

Background Subtract C:\SATURN\DATA\NEWU1-5 Date: 03/15/96 12:37:02
 Comment: DB5-MS 30X.25MM 22/2/39
 Average of: 713 to 717 Minus: 589 to 973 100% = 27673
 100%

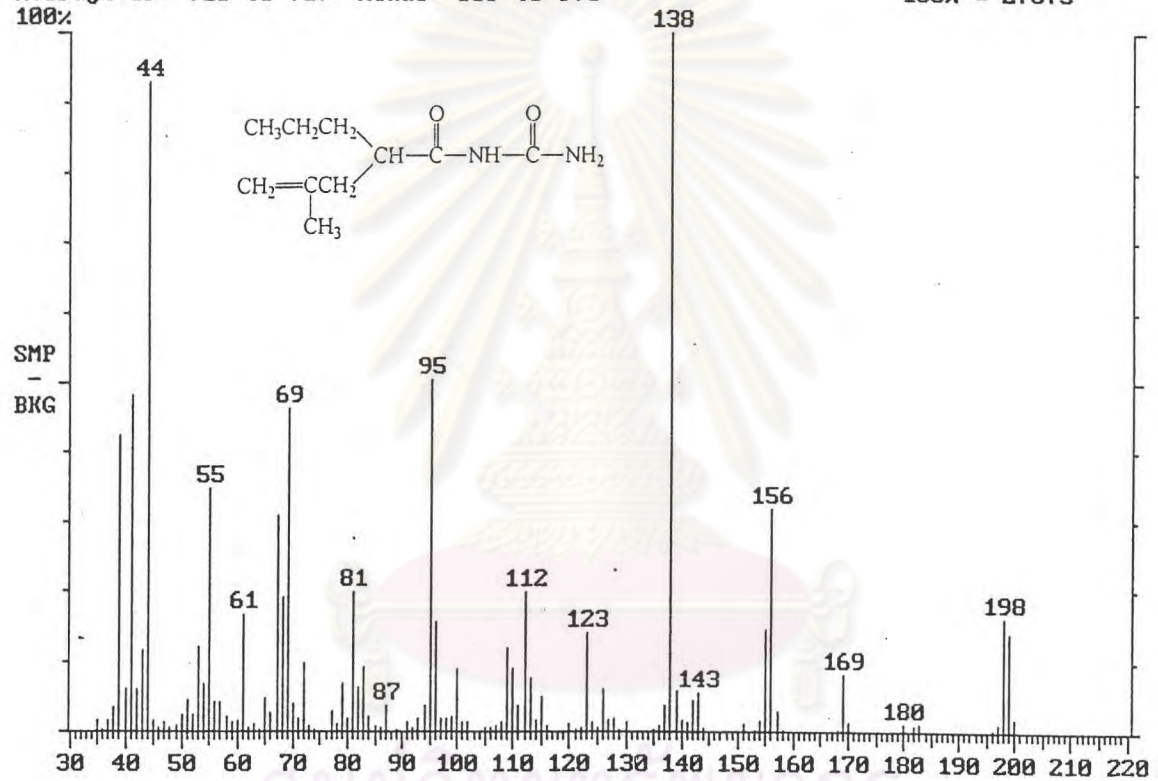


Figure 31. The EIMS spectrum of N-(4-methyl-2-propyl-4-pentenyl) urea.

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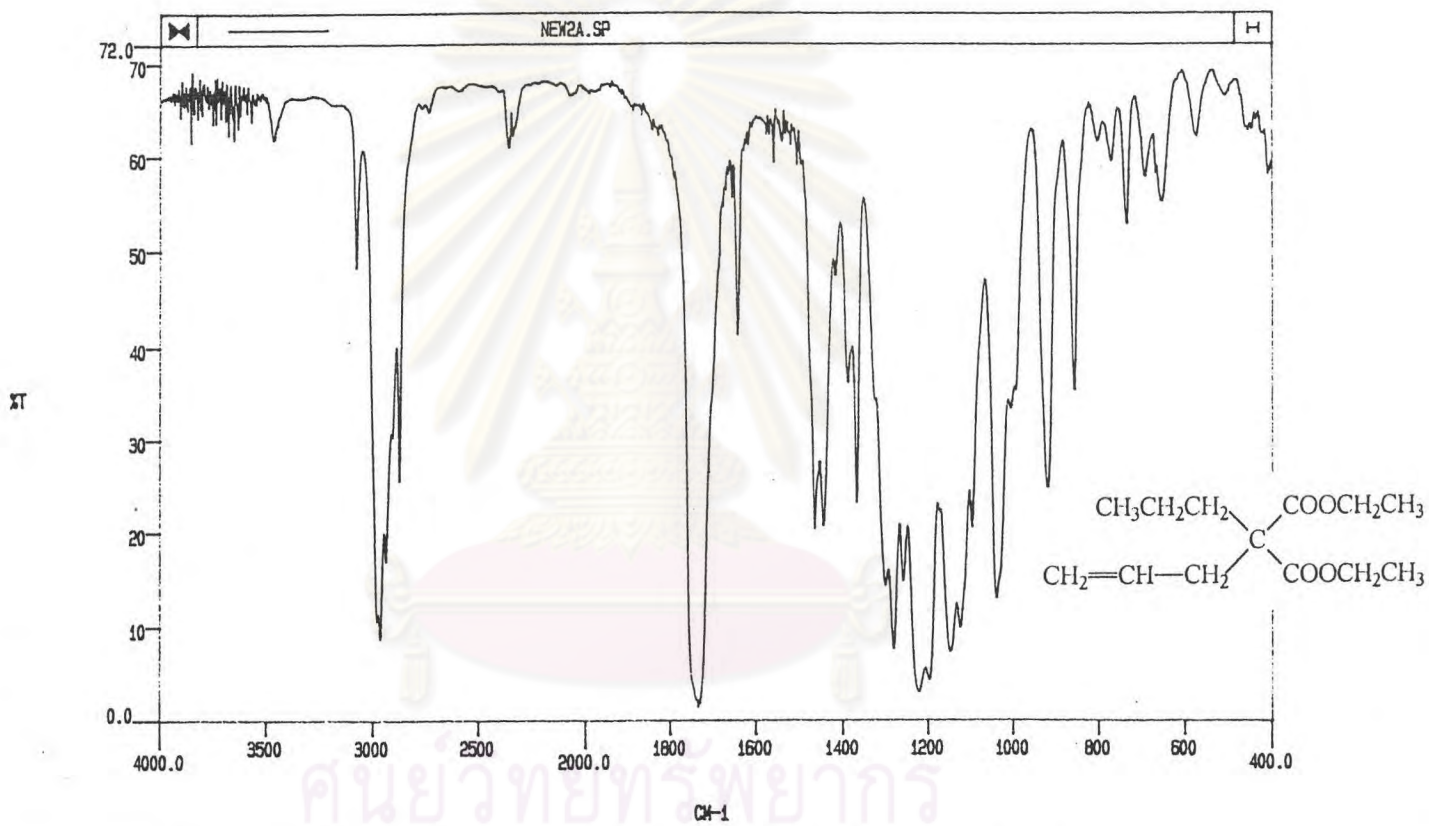


Figure 32. The IR spectrum (Neat) of diethyl allyl(propyl)malonate.

2A 1H

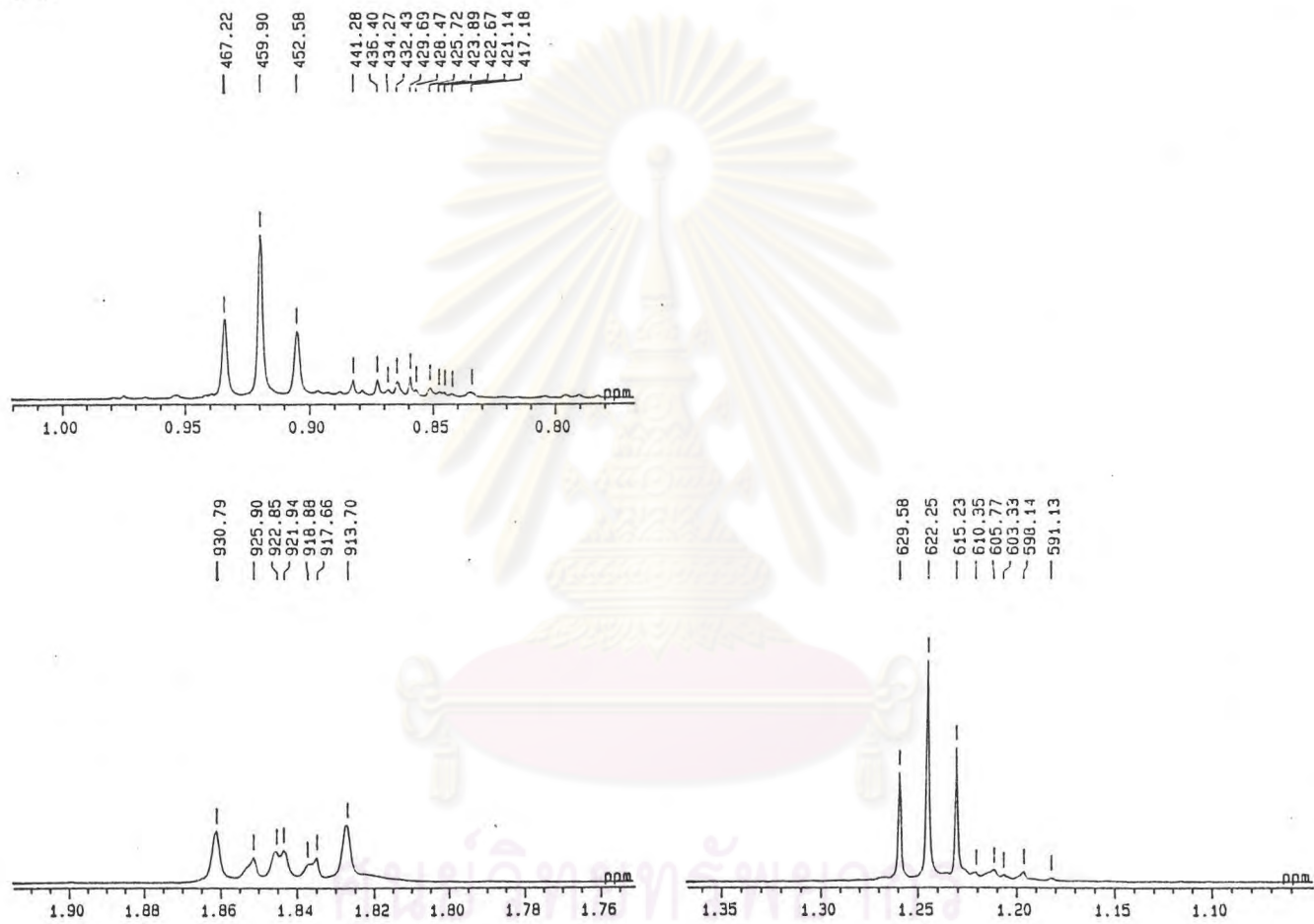


Figure 34. The 500 MHz ^1H -NMR spectrum of diethyl allyl(propyl) malonate in CDCl_3 (Enlarged scale : 0.80-1.90 ppm).

2A 1H

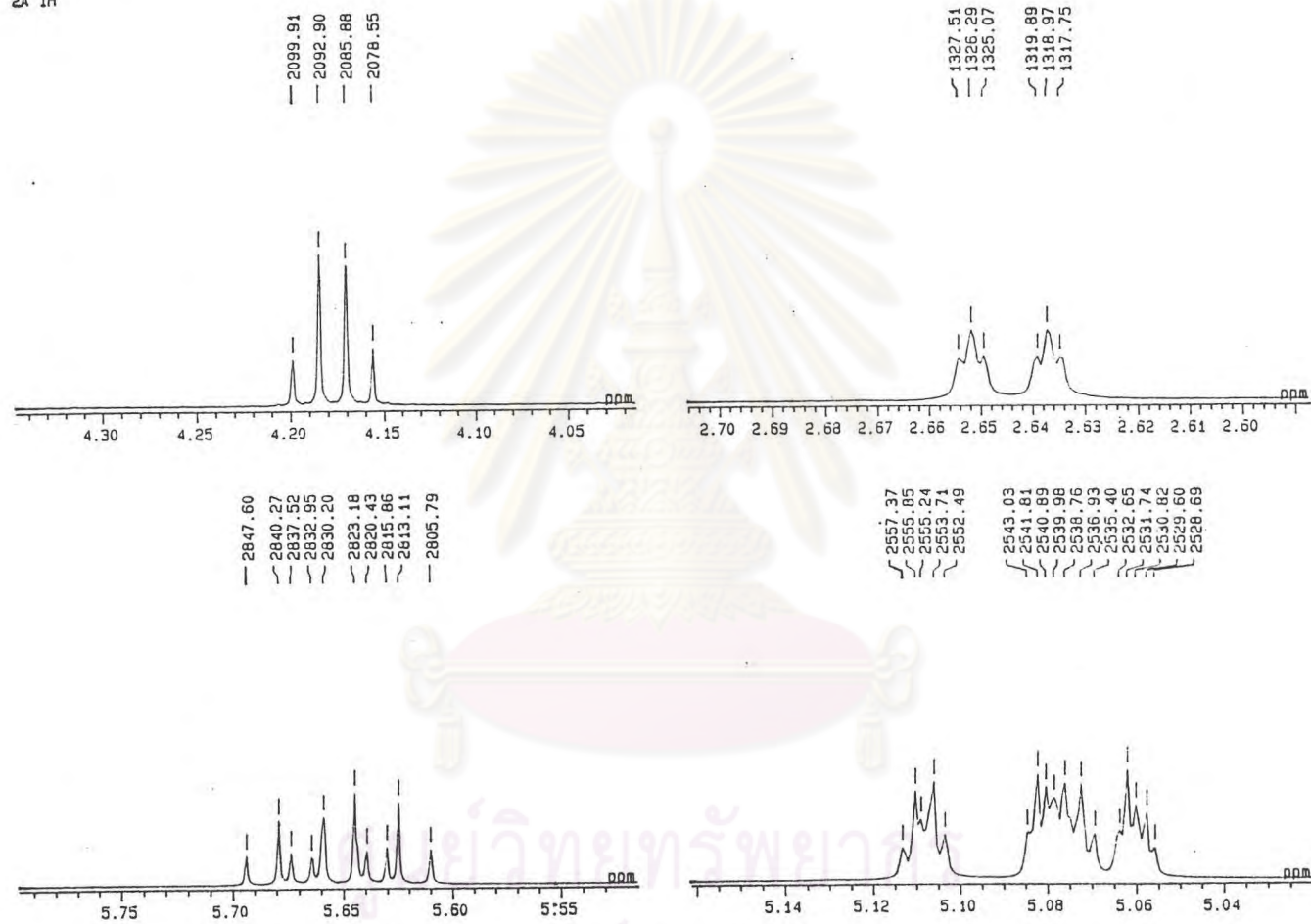


Figure 35. The 500 MHz ^1H -NMR spectrum of diethyl allyl(propyl) malonate in CDCl_3 (Enlarged scale : 2.60-5.75 ppm).

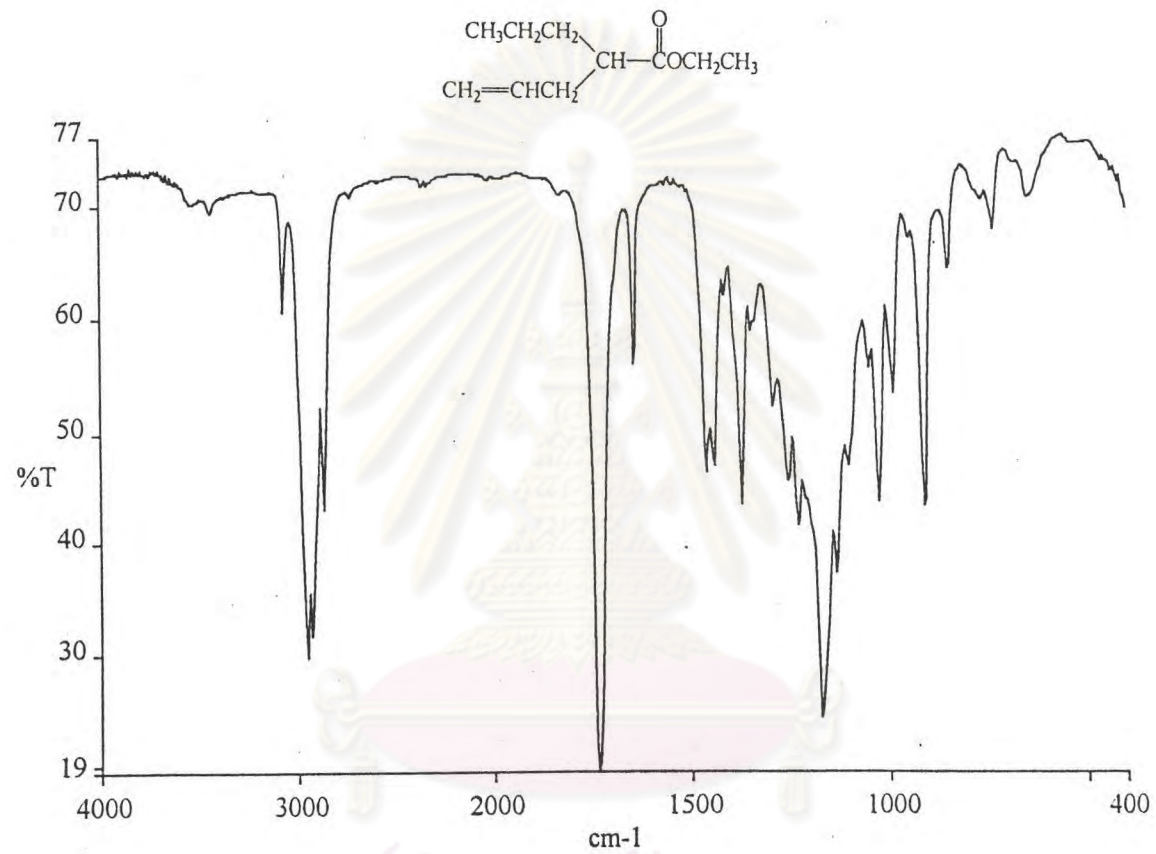


Figure 36. The IR spectrum (Neat) of ethyl 2-propyl-4-pentenoate.

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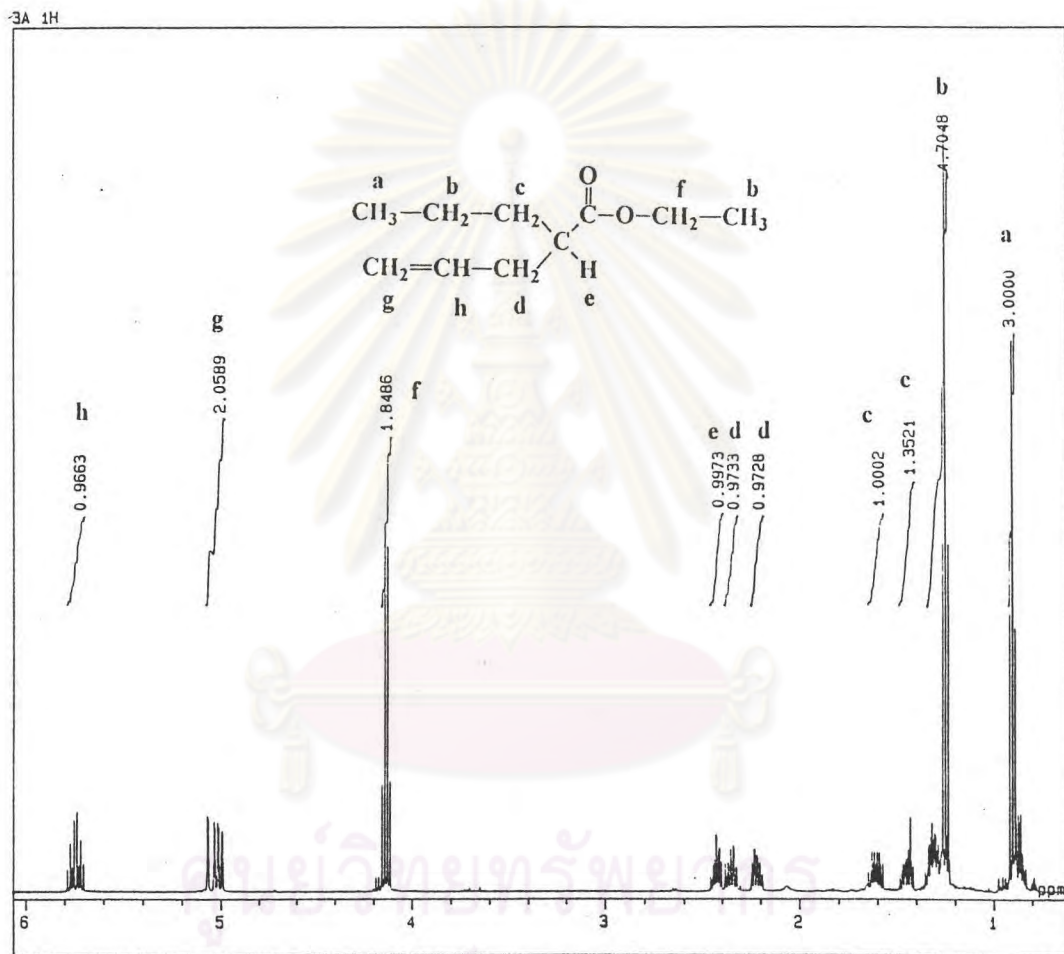


Figure 37. The 500 MHz ^1H -NMR spectrum of ethyl 2-propyl-4-pentenoate in CDCl_3 .

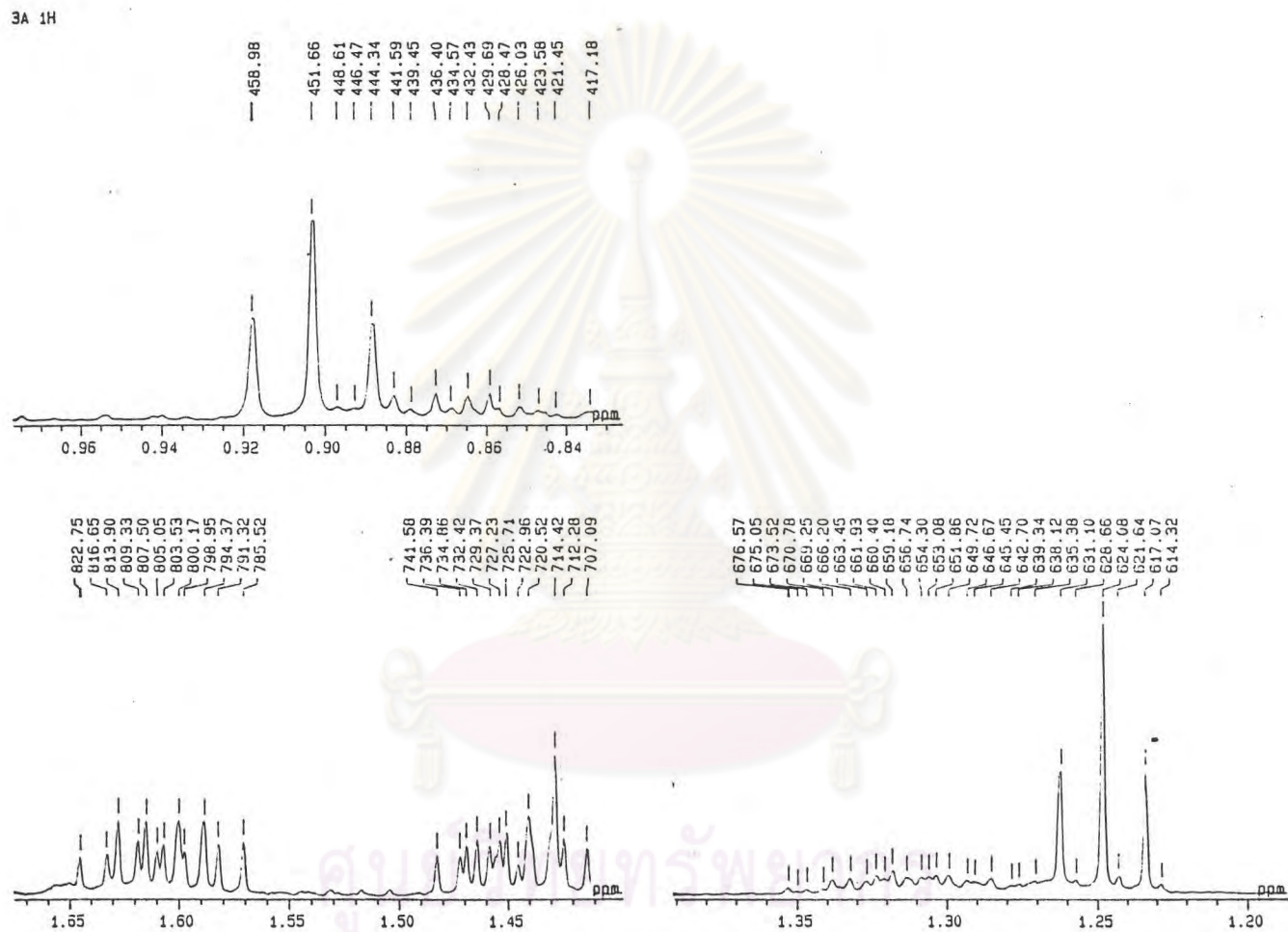


Figure 38. The 500 MHz ^1H -NMR spectrum of ethyl 2-propyl-4-pentenoate in CDCl_3 (Enlarged scale : 0.84-1.65 ppm).

3A 1H

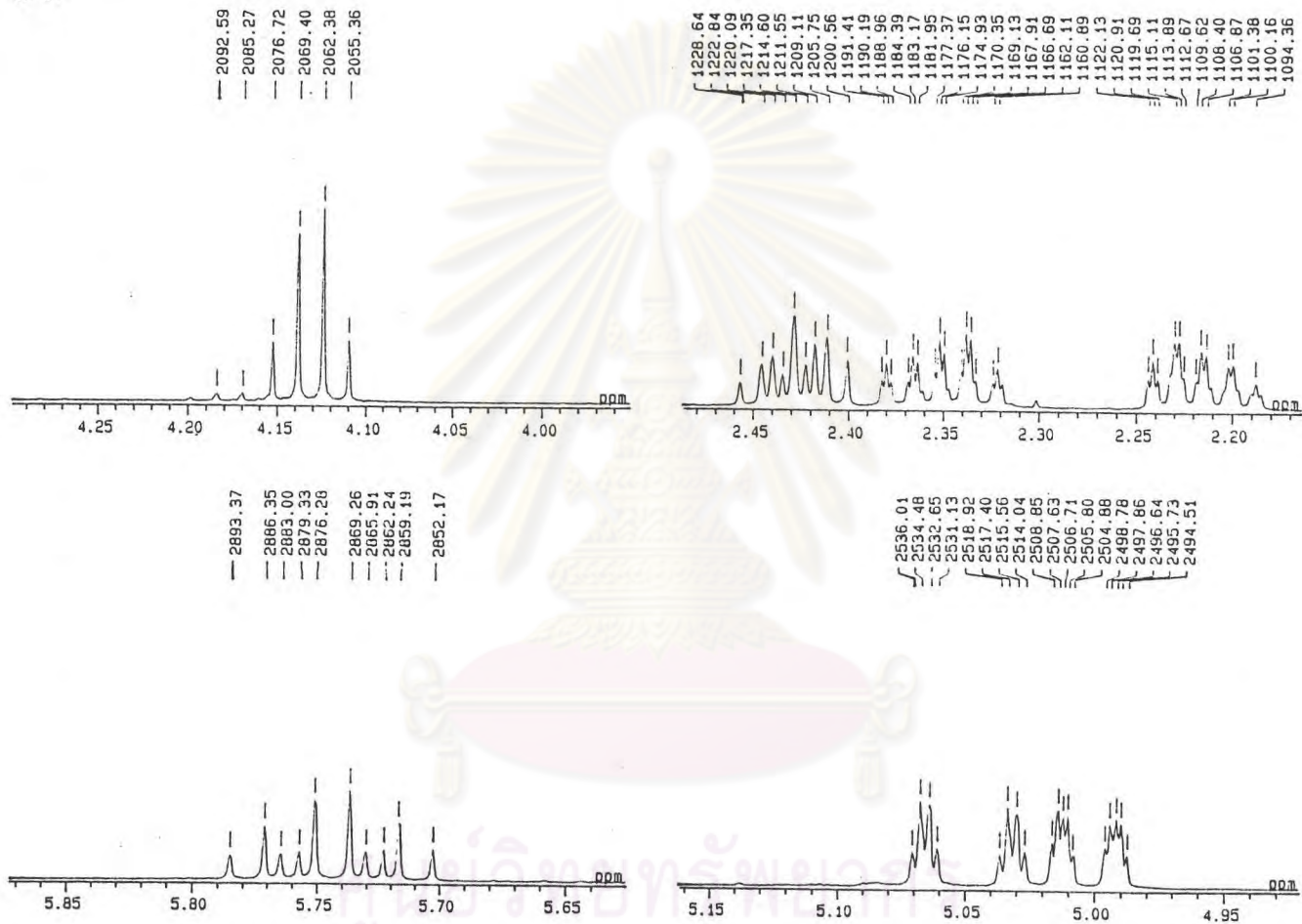


Figure 39. The 500 MHz ^1H -NMR spectrum of ethyl 2-propyl-4-pentenoate in CDCl_3 (Enlarged scale : 2.17-5.85 ppm).

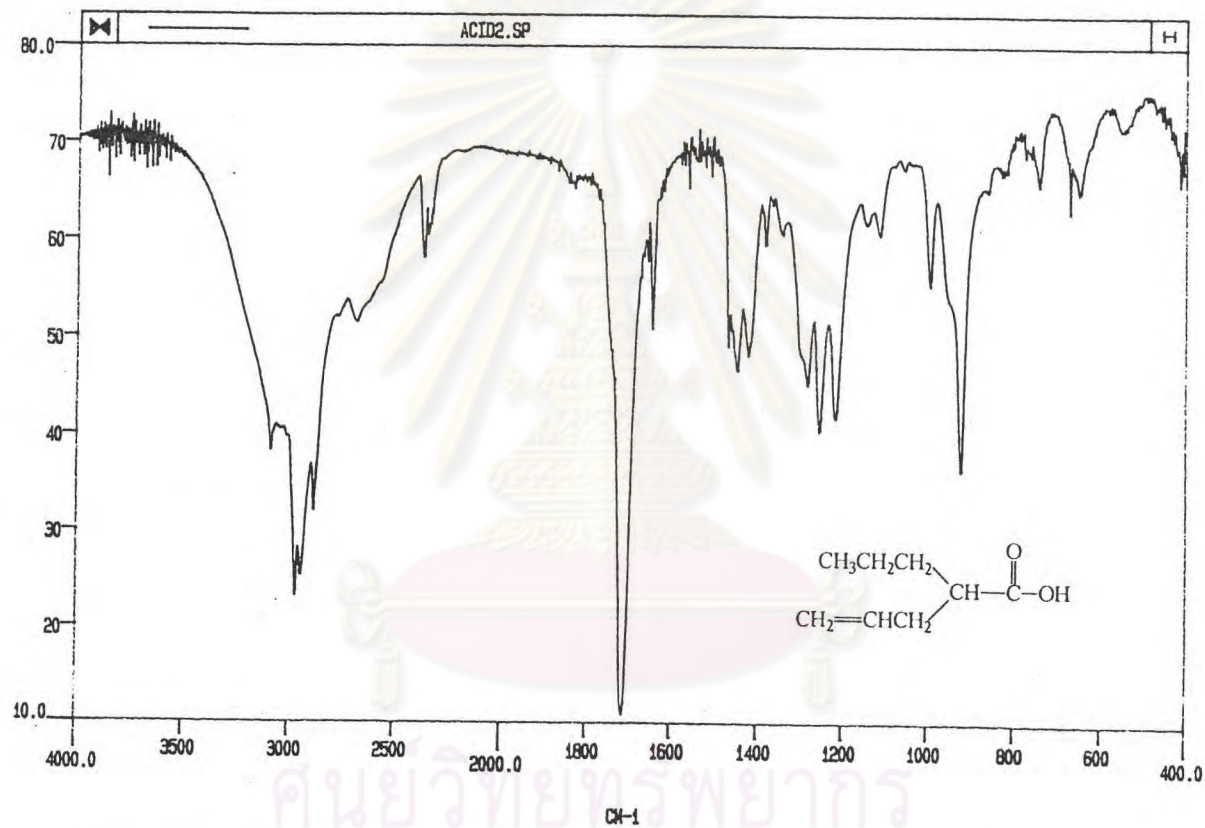


Figure 40. The IR spectrum (Neat) of 2-propyl-4-pentenoic acid.

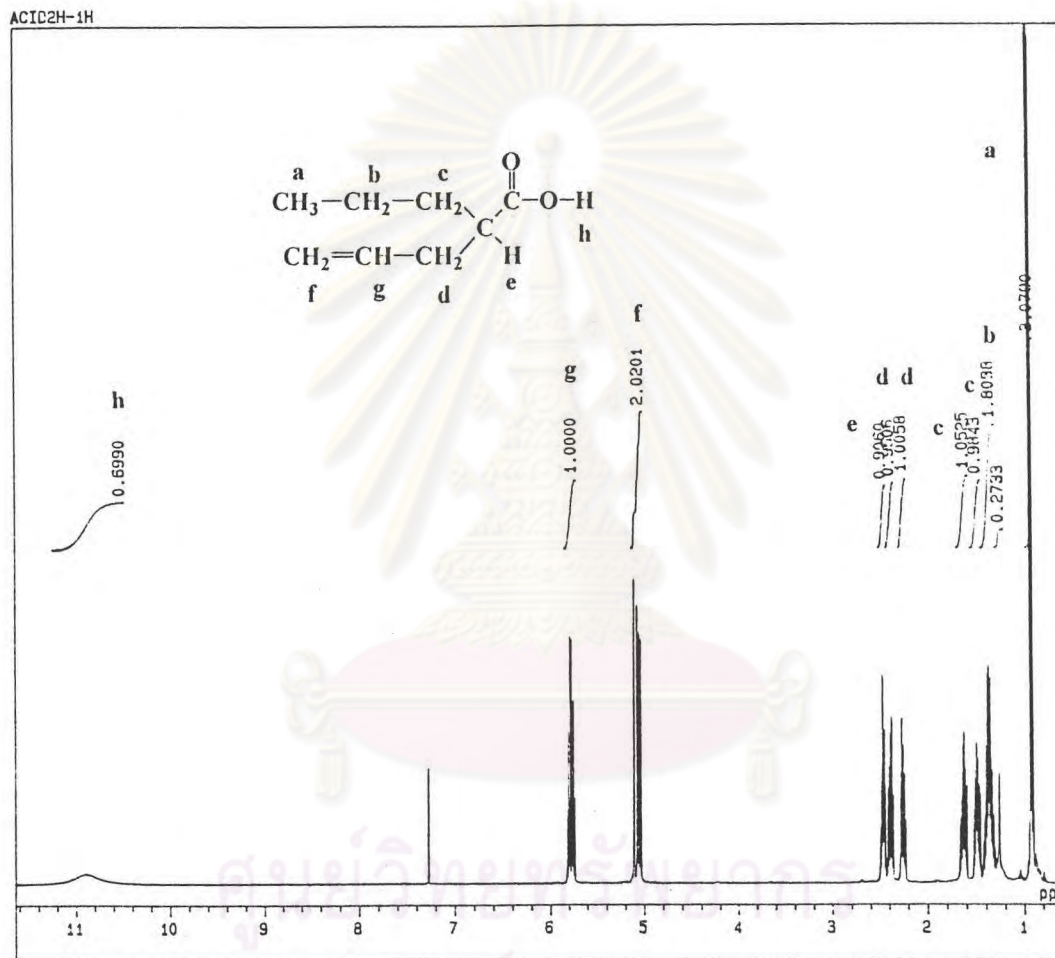


Figure 41. The 500 MHz ^1H -NMR spectrum of 2-propyl-4-pentenoic acid in CDCl_3 .

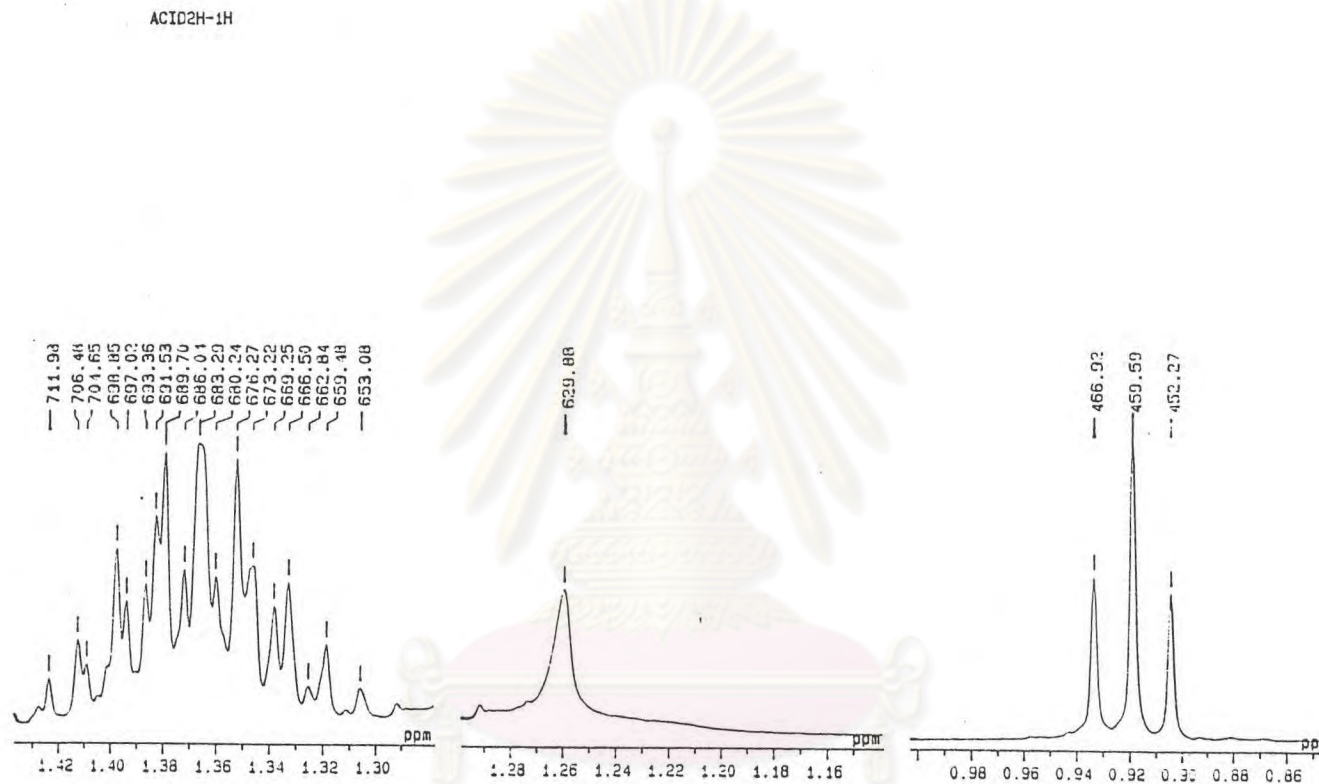


Figure 42. The 500 MHz $^1\text{H-NMR}$ spectrum of 2-propyl-4-pentenoic acid in CDCl_3 (Enlarged scale : 0.86-1.42 ppm).

ACID2H-1H

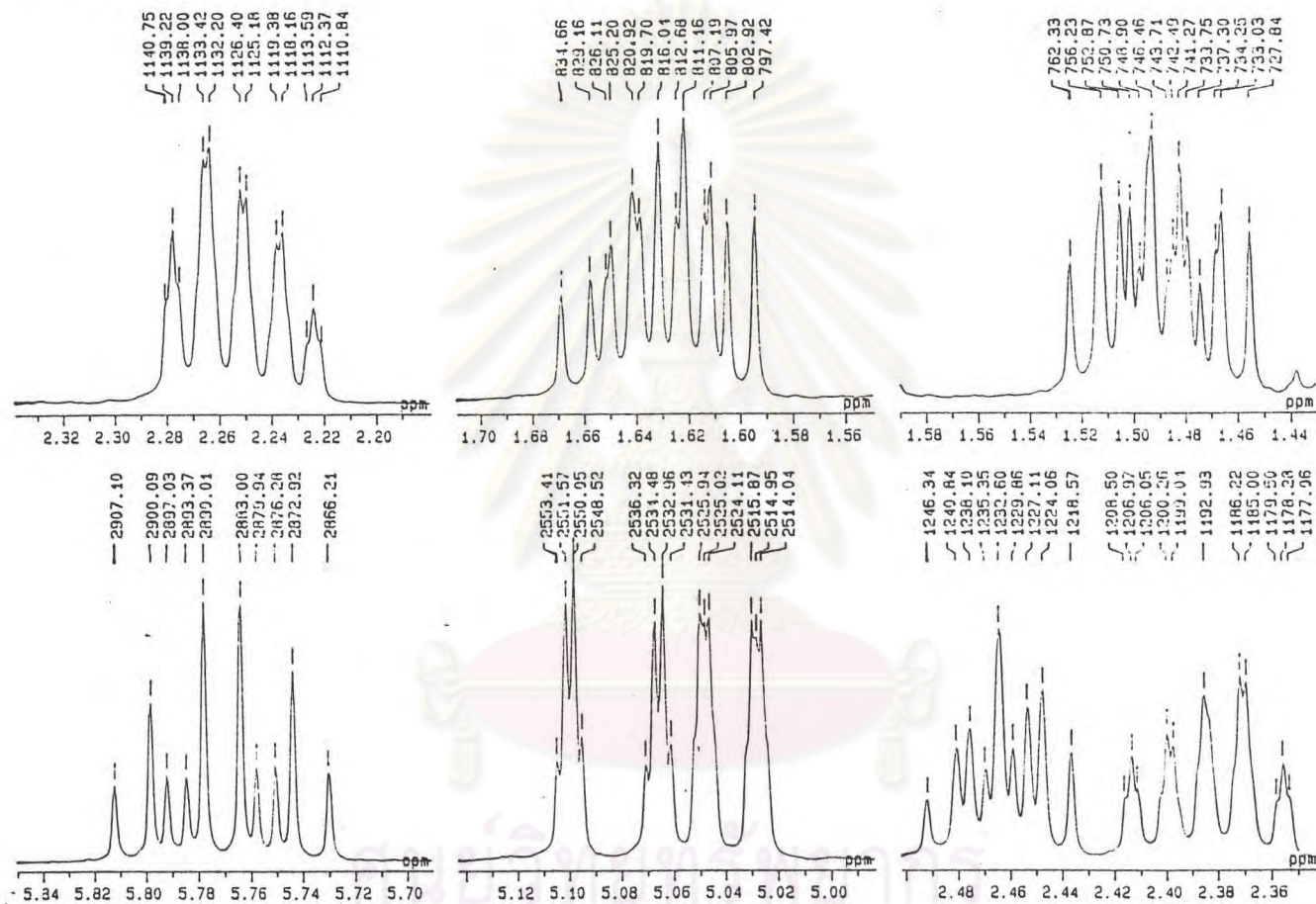


Figure 43. The 500 MHz ^1H -NMR spectrum of ethyl 2-propyl-4-pentenoic acid in CDCl_3 (Enlarged scale : 1.44-5.84 ppm).

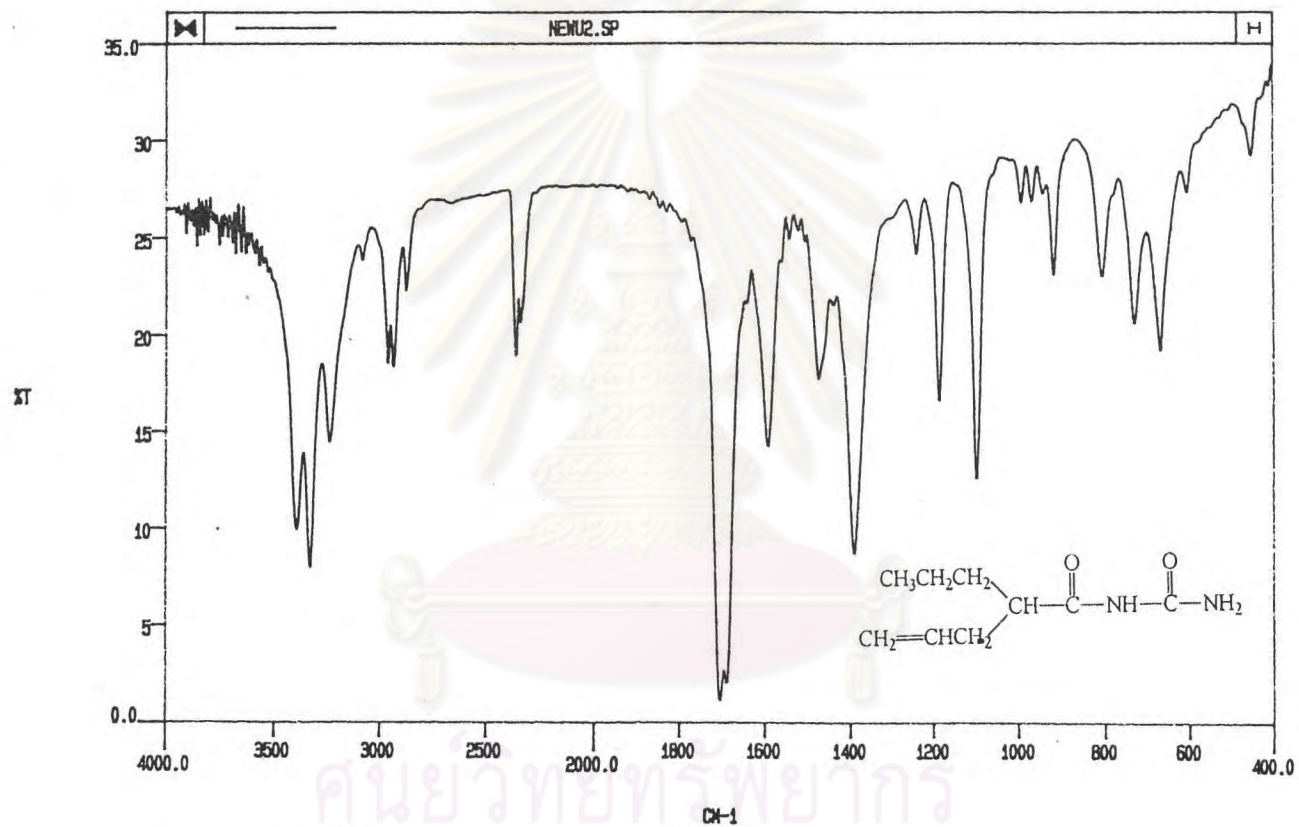


Figure 44. The IR spectrum (Neat) of N-(2-propyl-4-pentenyl) urea.

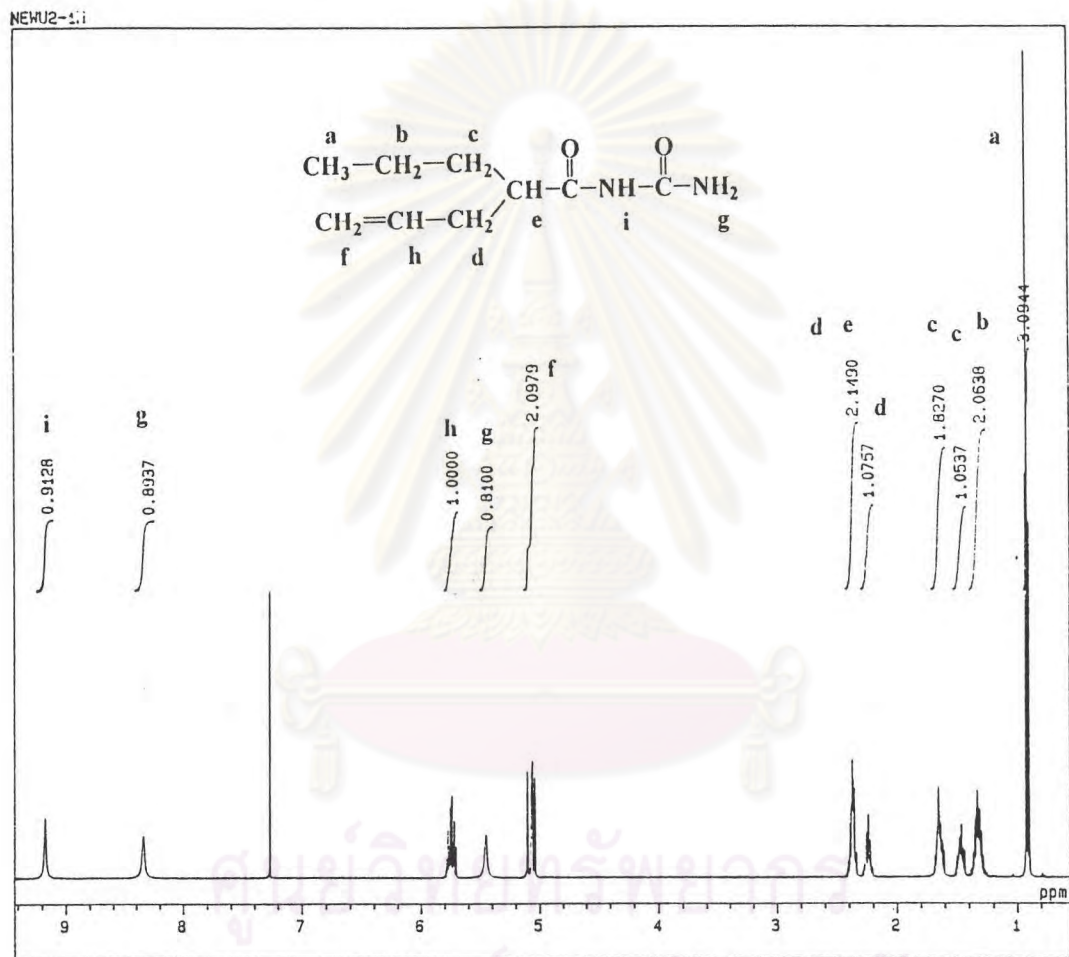


Figure 45. The 500 MHz ^1H -NMR spectrum of N-(2-propyl-4-pentenoyl) urea in CDCl_3 .

NEU2-1H

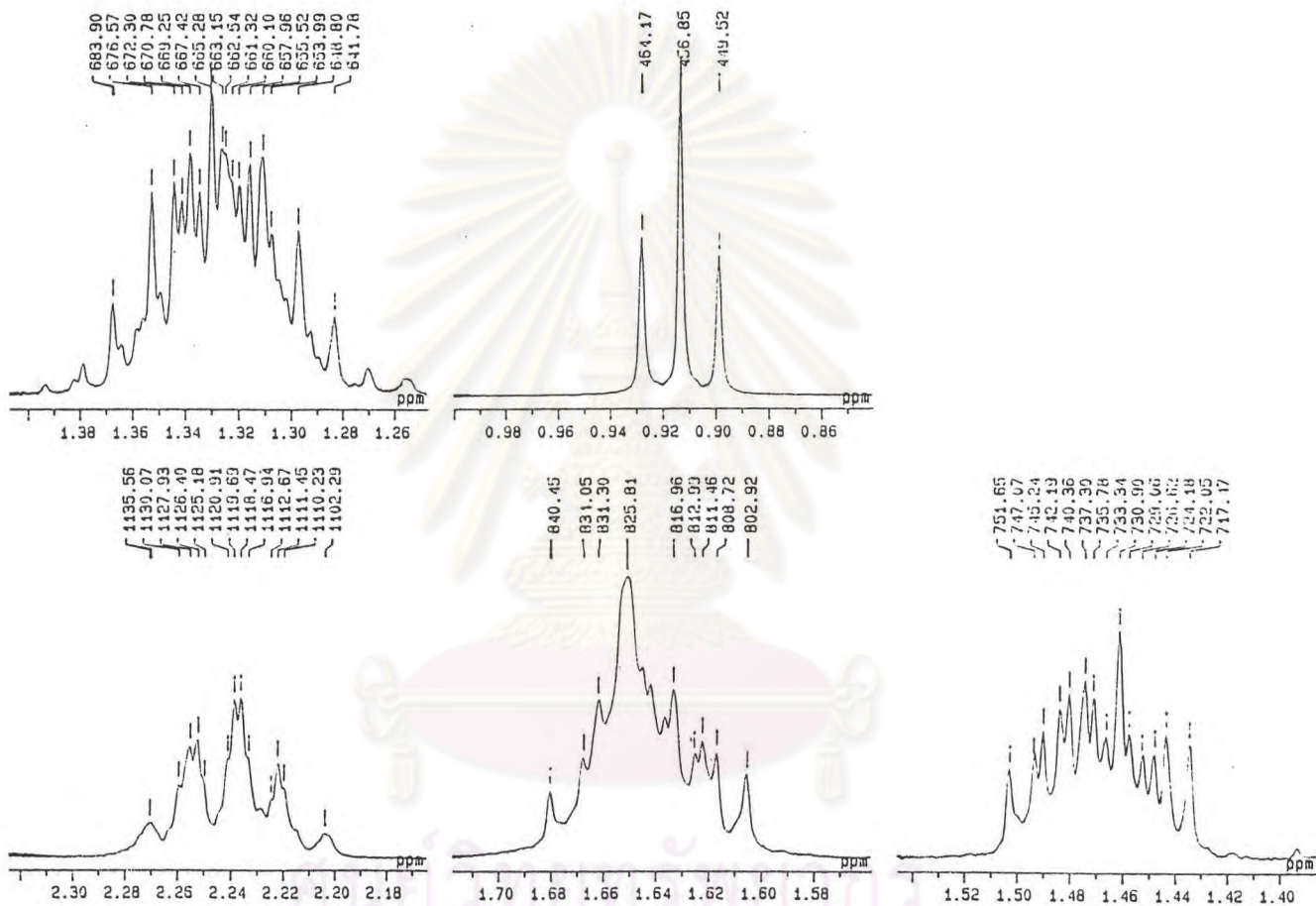


Figure 46. The 500 MHz $^1\text{H-NMR}$ spectrum of N -(2-propyl-4-pentenyl) urea in CDCl_3 (Enlarged scale : 0.86-2.30 ppm).

NEHU2-1H .

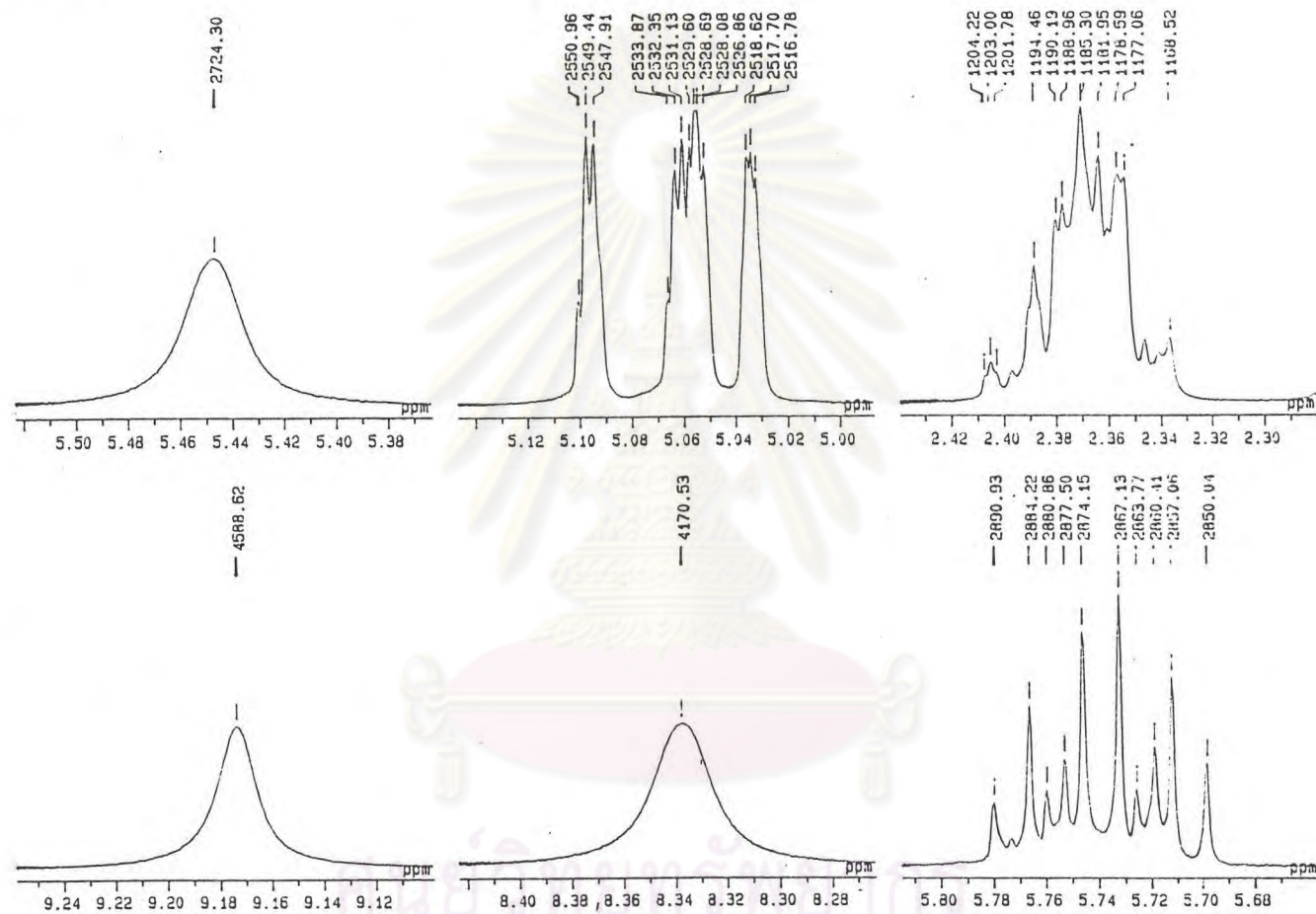


Figure 47. The 500 MHz ¹H-NMR spectrum of N-(2-propyl-4-pentenyl) urea in CDCl₃ (Enlarged scale : 2.30-9.24 ppm).

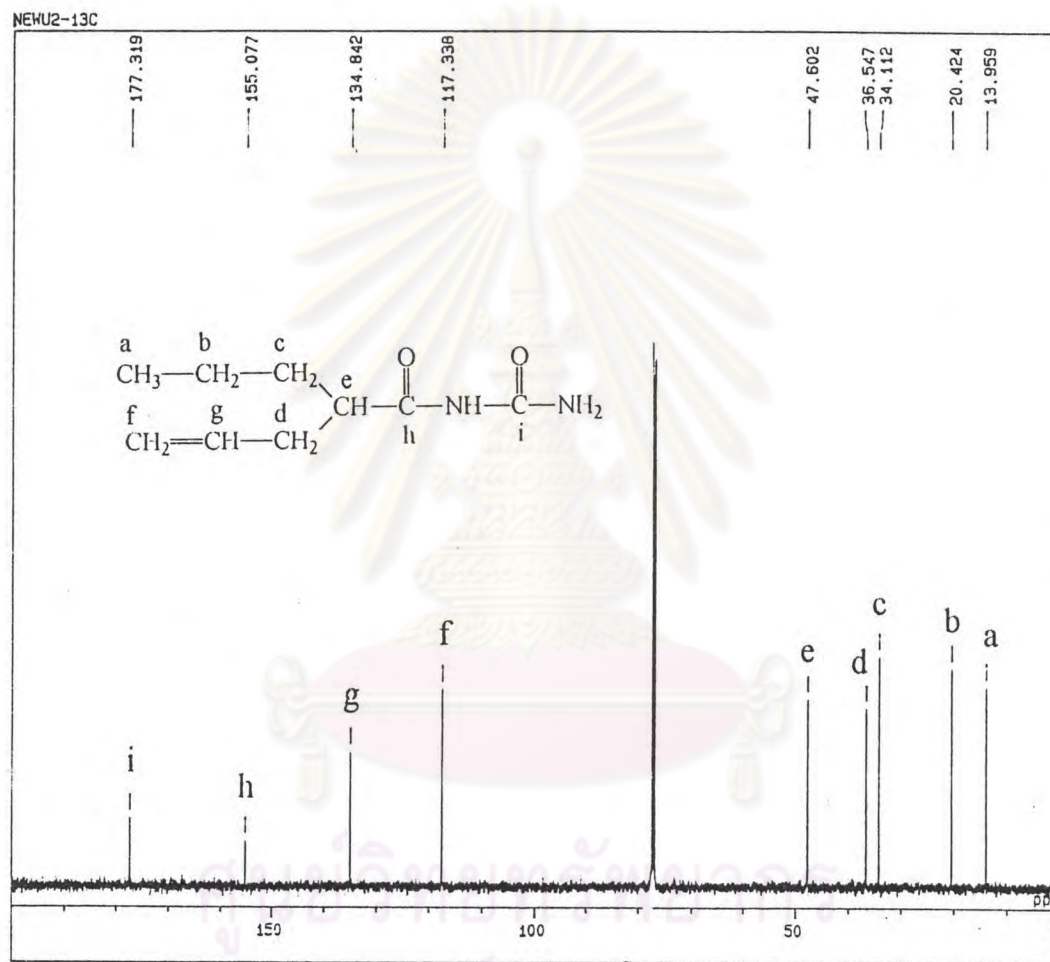


Figure 48. The 500 MHz ^{13}C -NMR spectrum of N-(2-propyl-4-pentenyl) urea in CDCl_3 .

Background Subtract C:\SATURN\DATA\UREA2-1 Date: 02/28/96 08:00:10
Comment: DB5-MS 30X.25MH 21/2/39
Average of: 656 to 667 Minus: 283 to 1115 100% = 26925

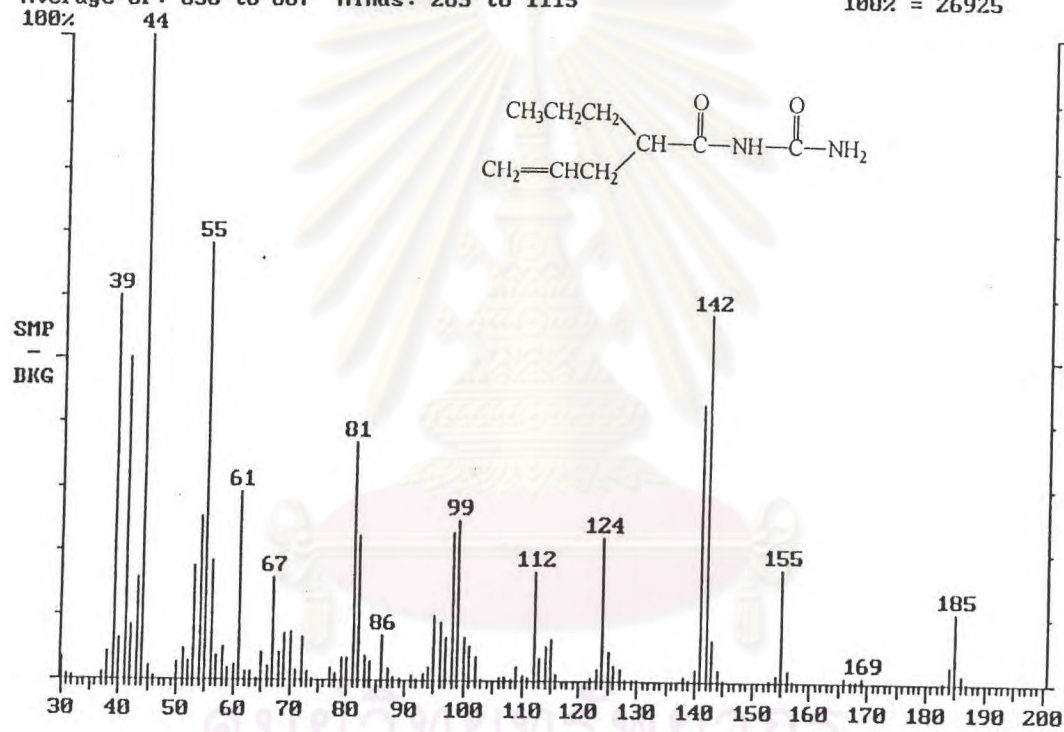
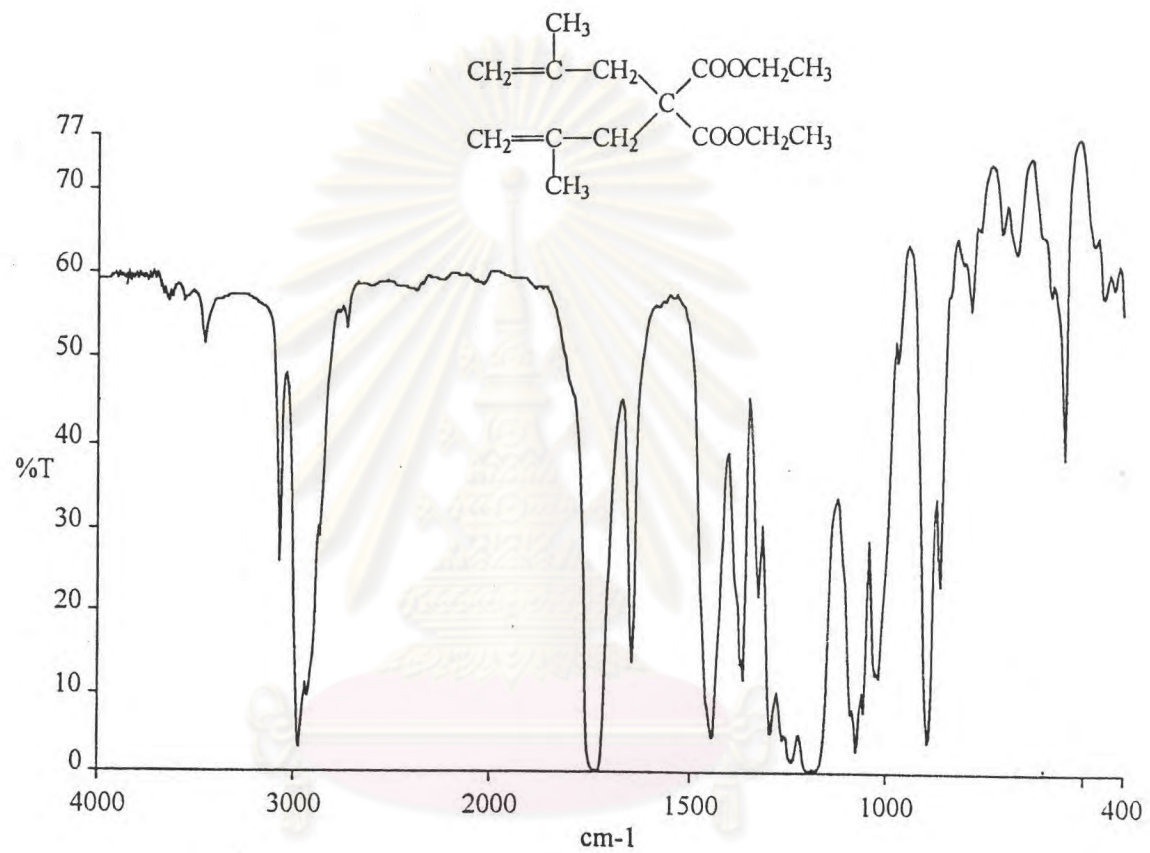


Figure 49. The EIMS spectrum of N-(2-propyl-4-pentenyl) urea.



4A
 Figure 50. The IR spectrum (Neat) of diethyl di-(2-methyl-2-propenyl) malonate.

4ANEW-1H

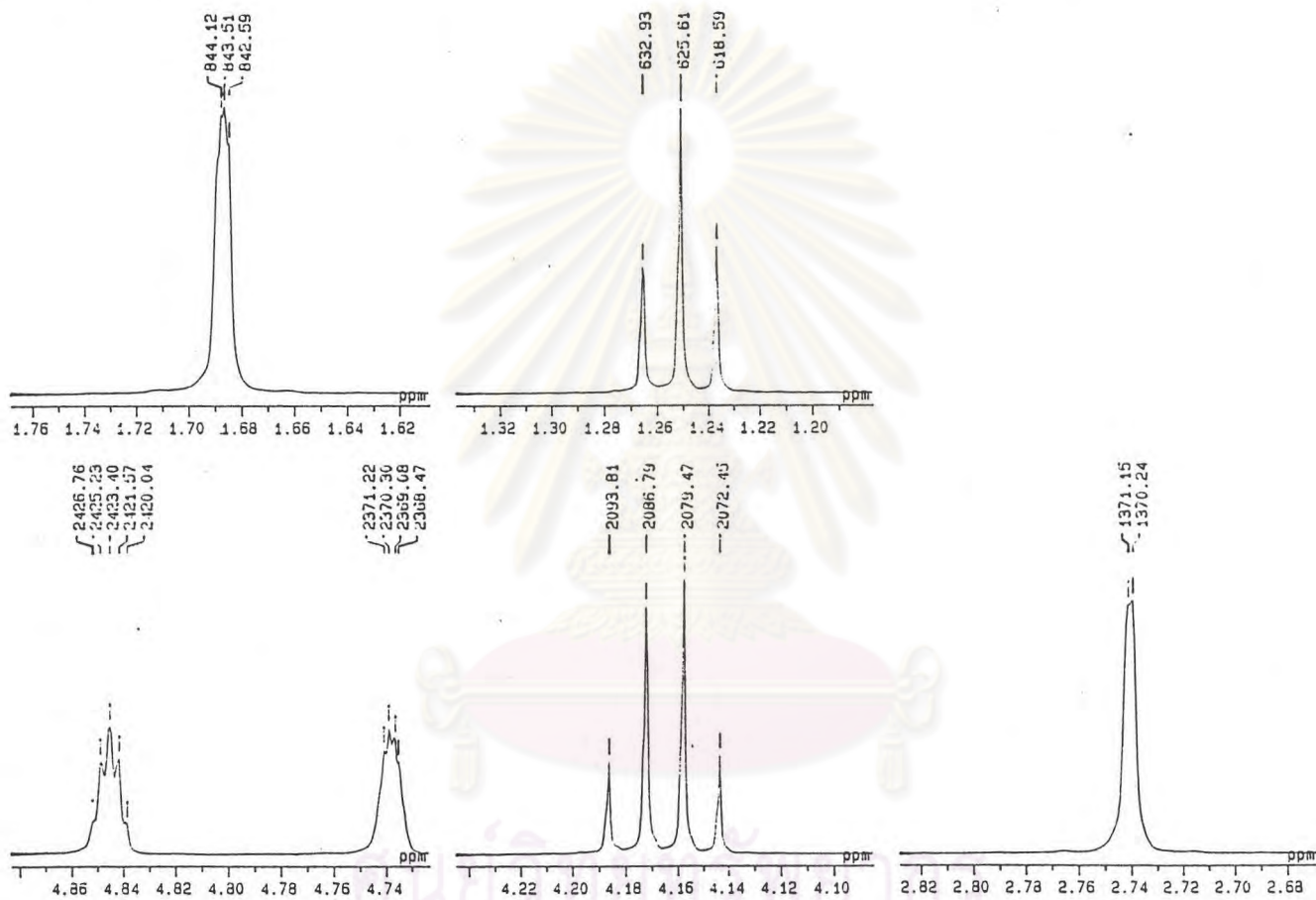


Figure 52. The 500 MHz ¹H-NMR spectrum diethyl di-(2-methyl-2-propenyl)malonate in CDCl₃ (Enlarged scale : 1.2-4.86 ppm).

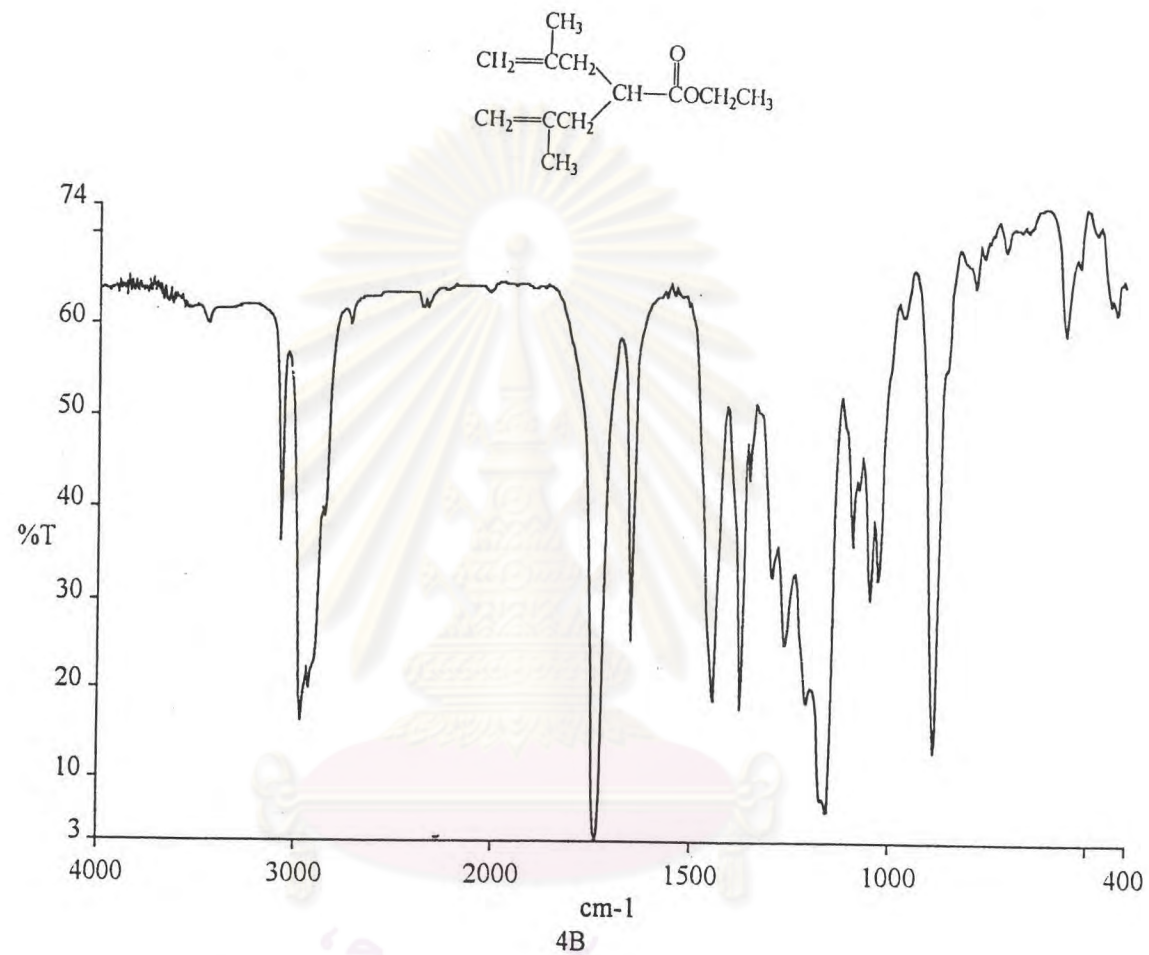


Figure 53. The IR spectrum (Neat) of ethyl 4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenoate.

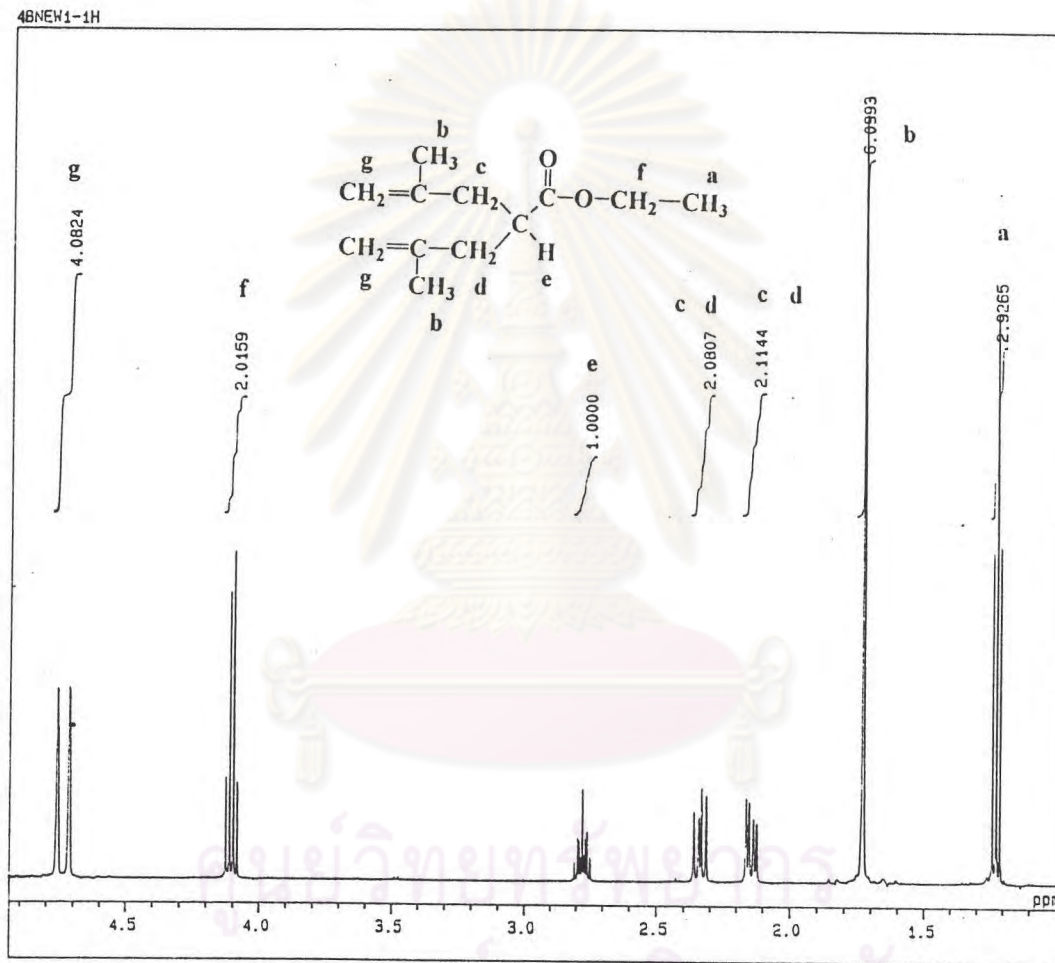


Figure 54. The 500 MHz ¹H-NMR spectrum of ethyl 4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenoate in CDCl₃.

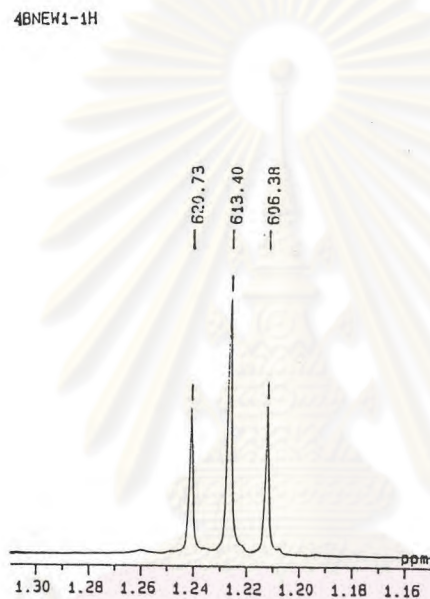


Figure 55. The 500 MHz ^1H -NMR spectrum of ethyl 4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenoate in CDCl_3 (Enlarged scale : 1.20-1.26 ppm).

4BNEH1-1H

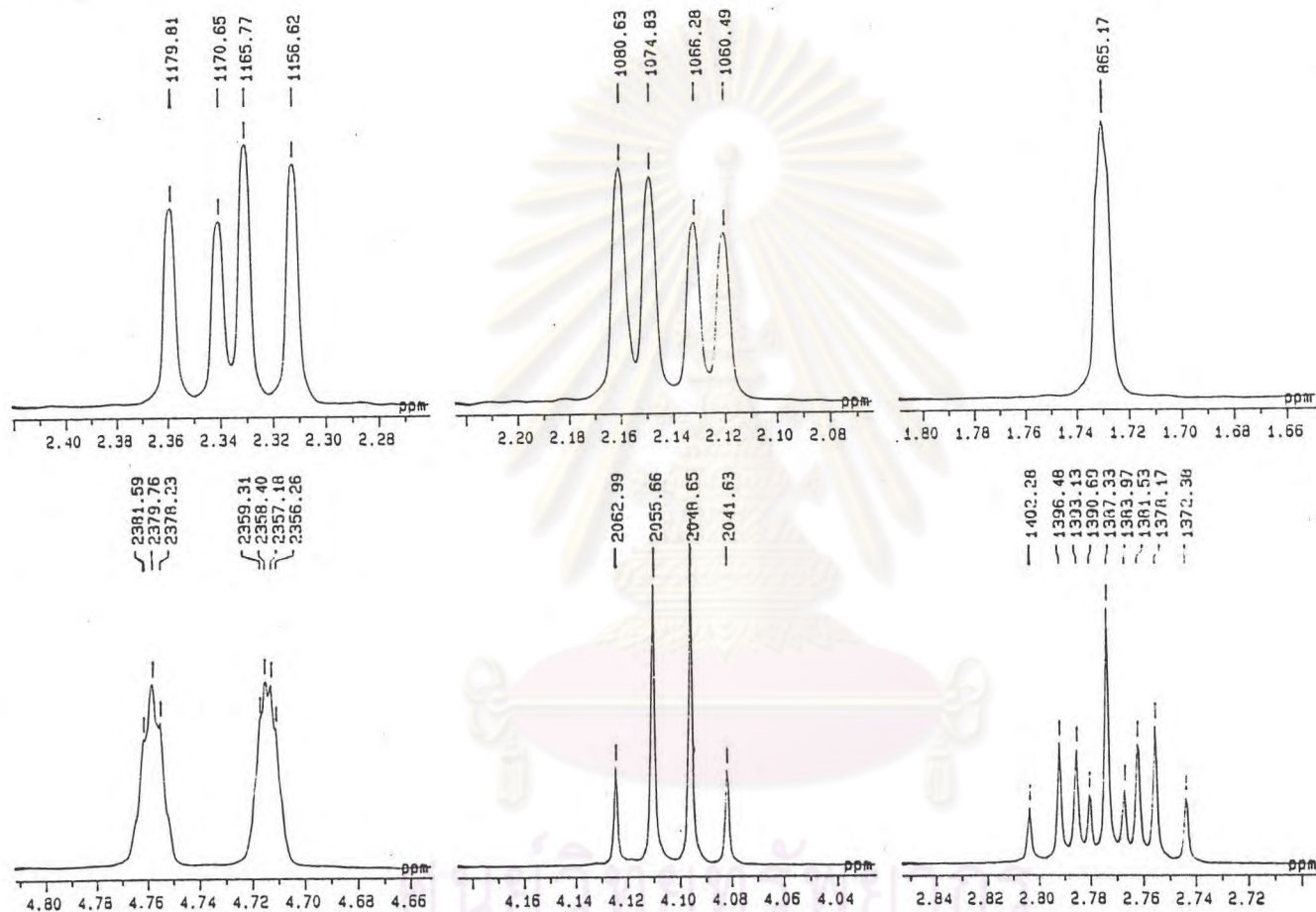


Figure 56. The 500 MHz ^1H -NMR spectrum of ethyl 4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenoate in CDCl_3 (Enlarged scale : 1.66-4.80 ppm).

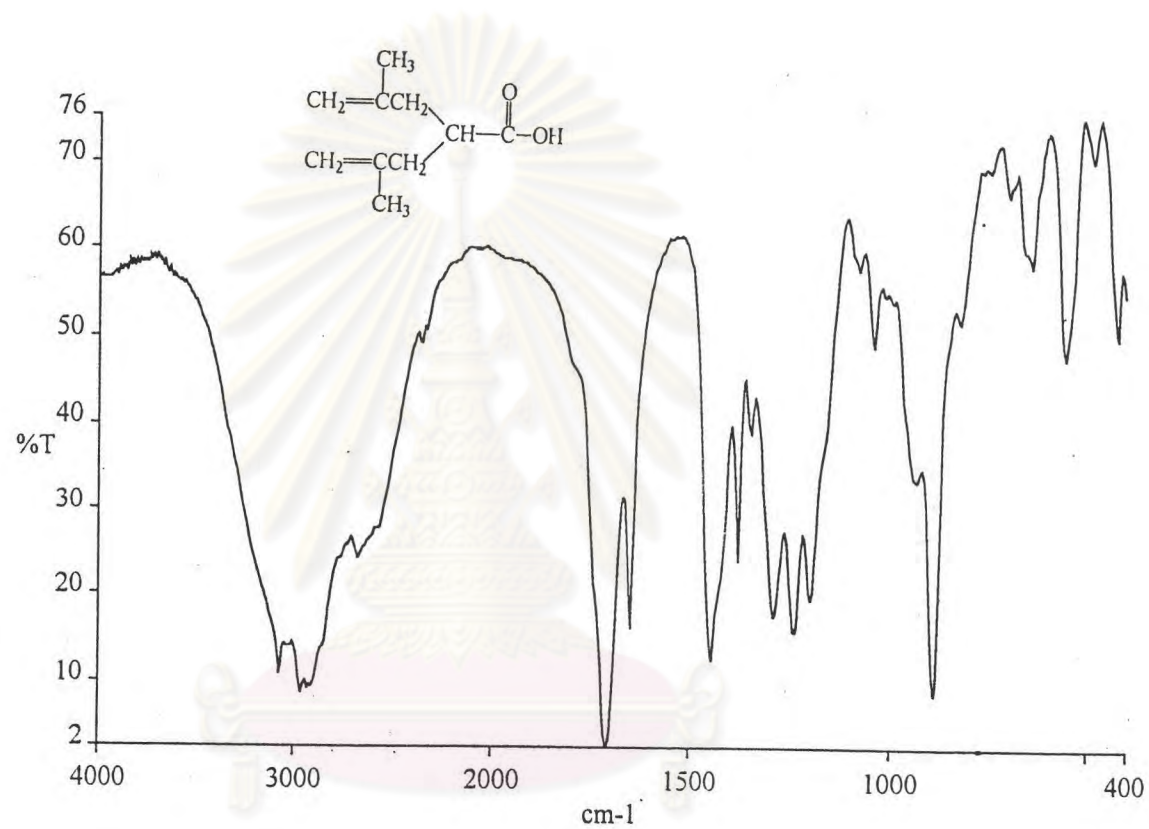


Figure 57. The IR spectrum (Neat) of 4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenoic acid.

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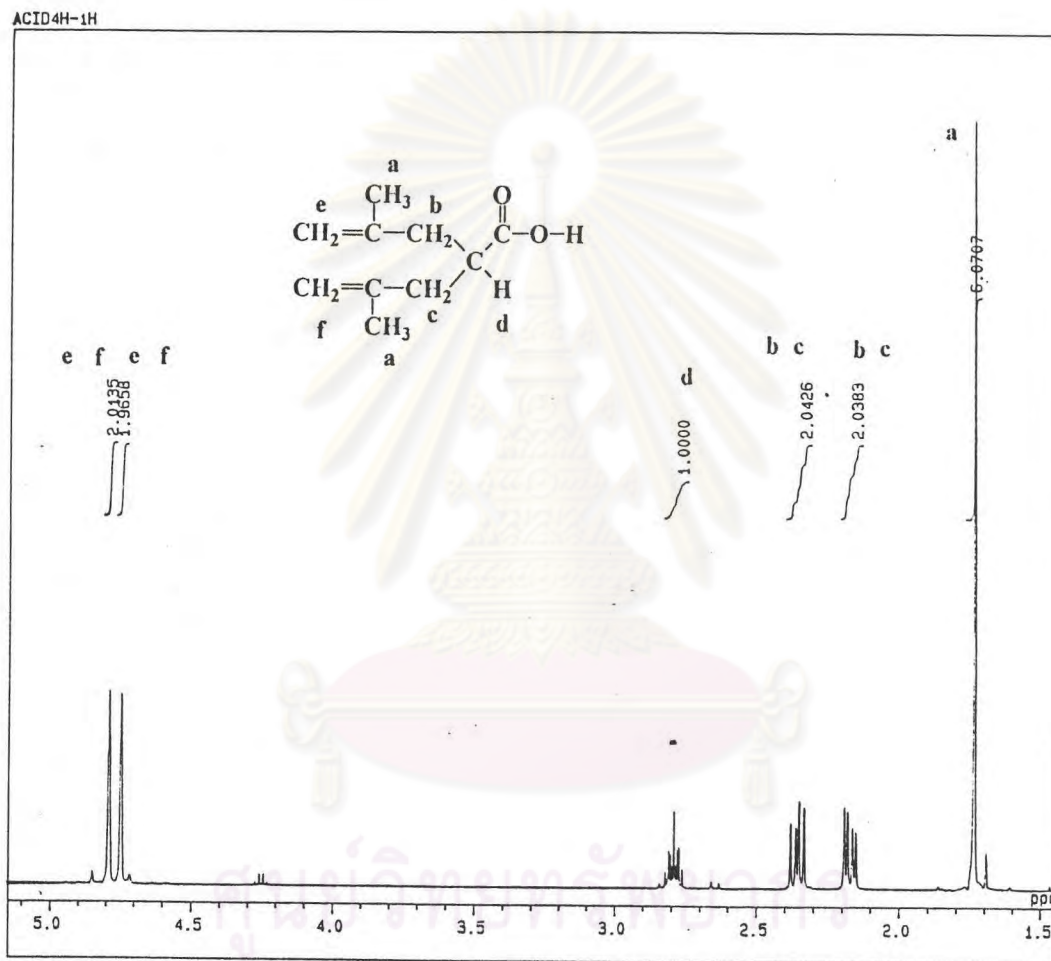


Figure 58. The 500 MHz ^1H -NMR spectrum of 4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenoic acid in CDCl_3 .

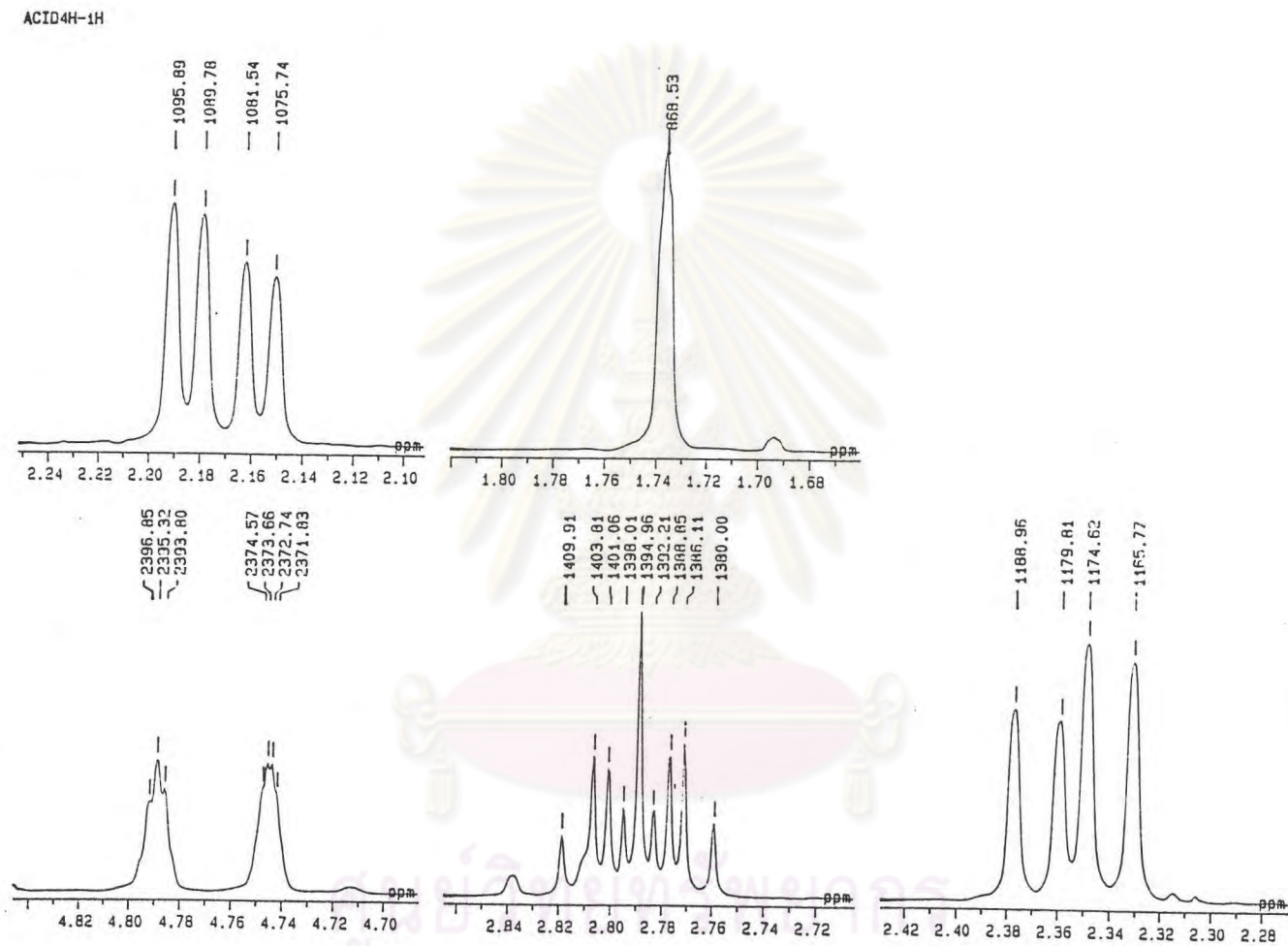


Figure 59. The 500 MHz $^1\text{H-NMR}$ spectrum of 4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenoic acid in CDCl_3 (Enlarged scale : 1.68-4.82 ppm).

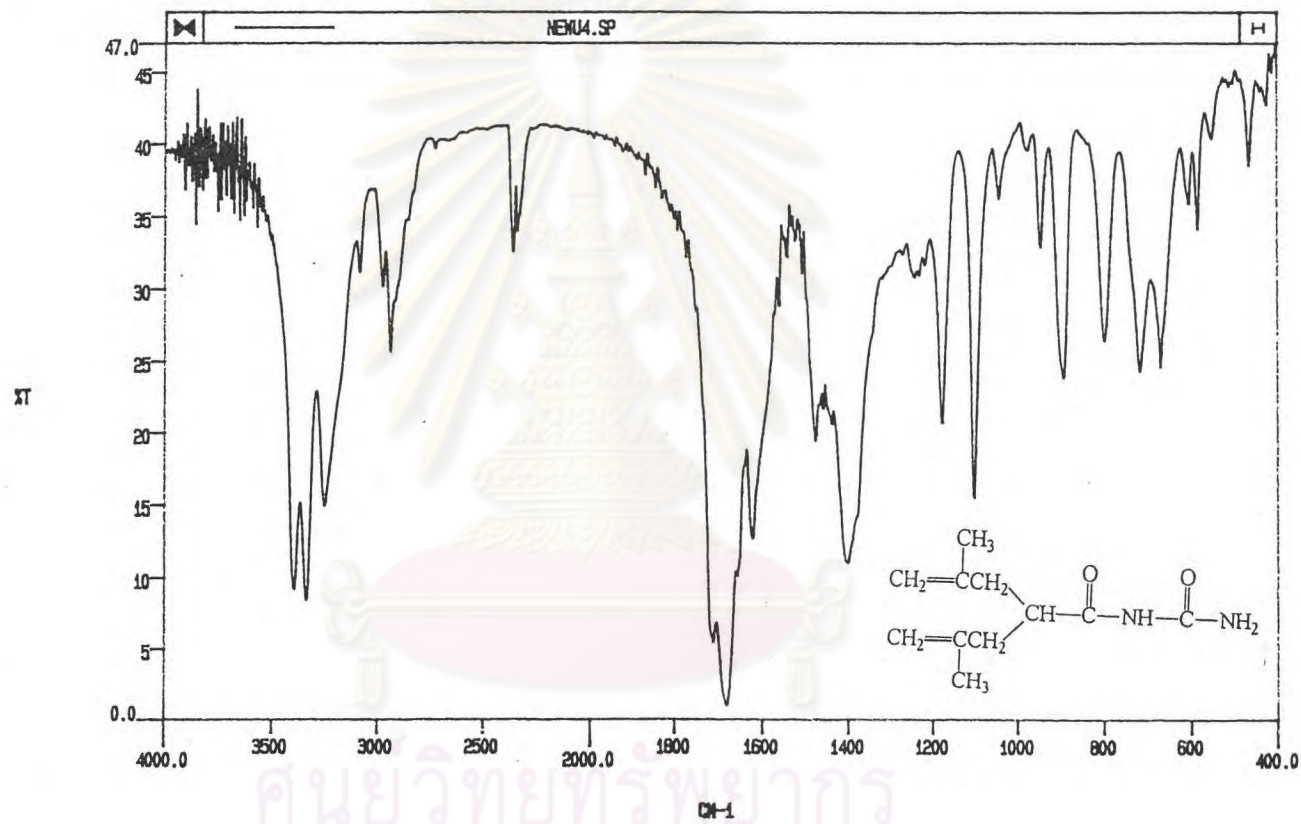


Figure 60. The IR spectrum (Neat) of N-(4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenyl) urea.

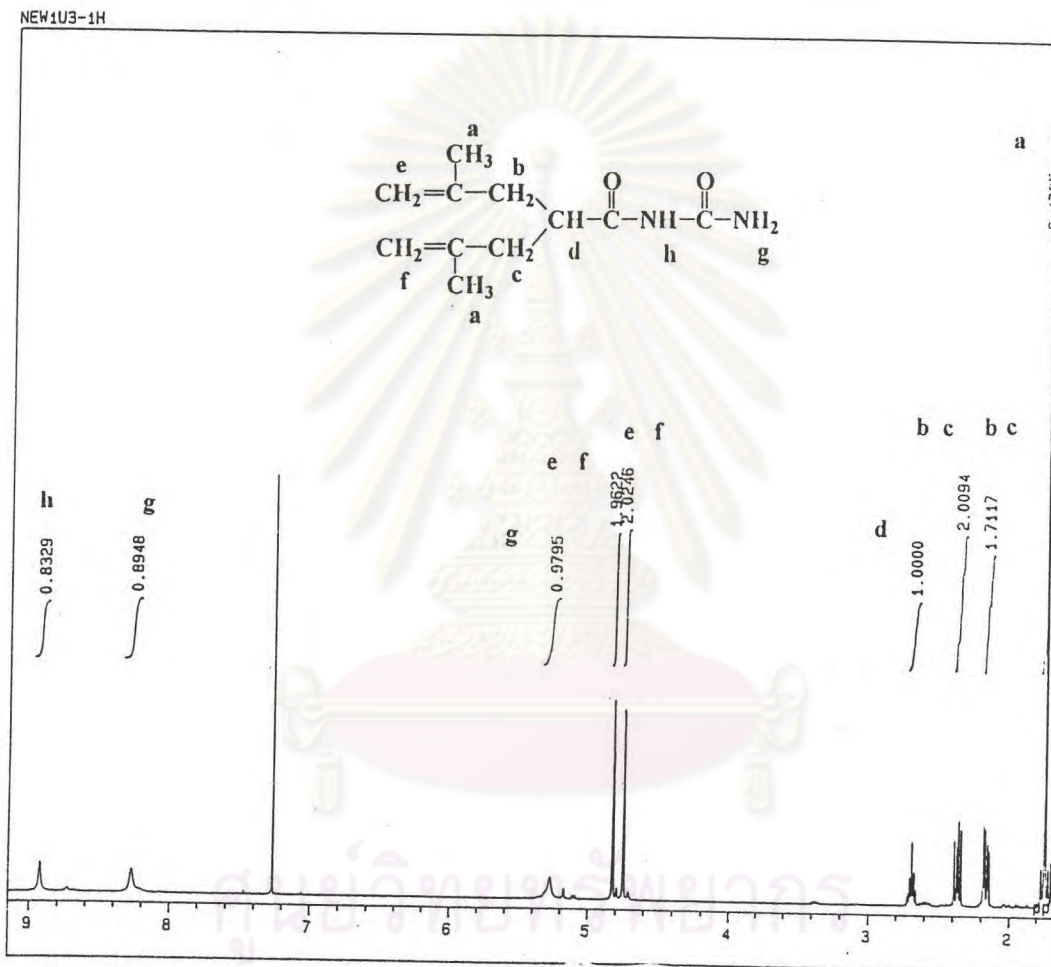


Figure 61. The 500 MHz ¹H-NMR spectrum N-(4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenoyl) urea.

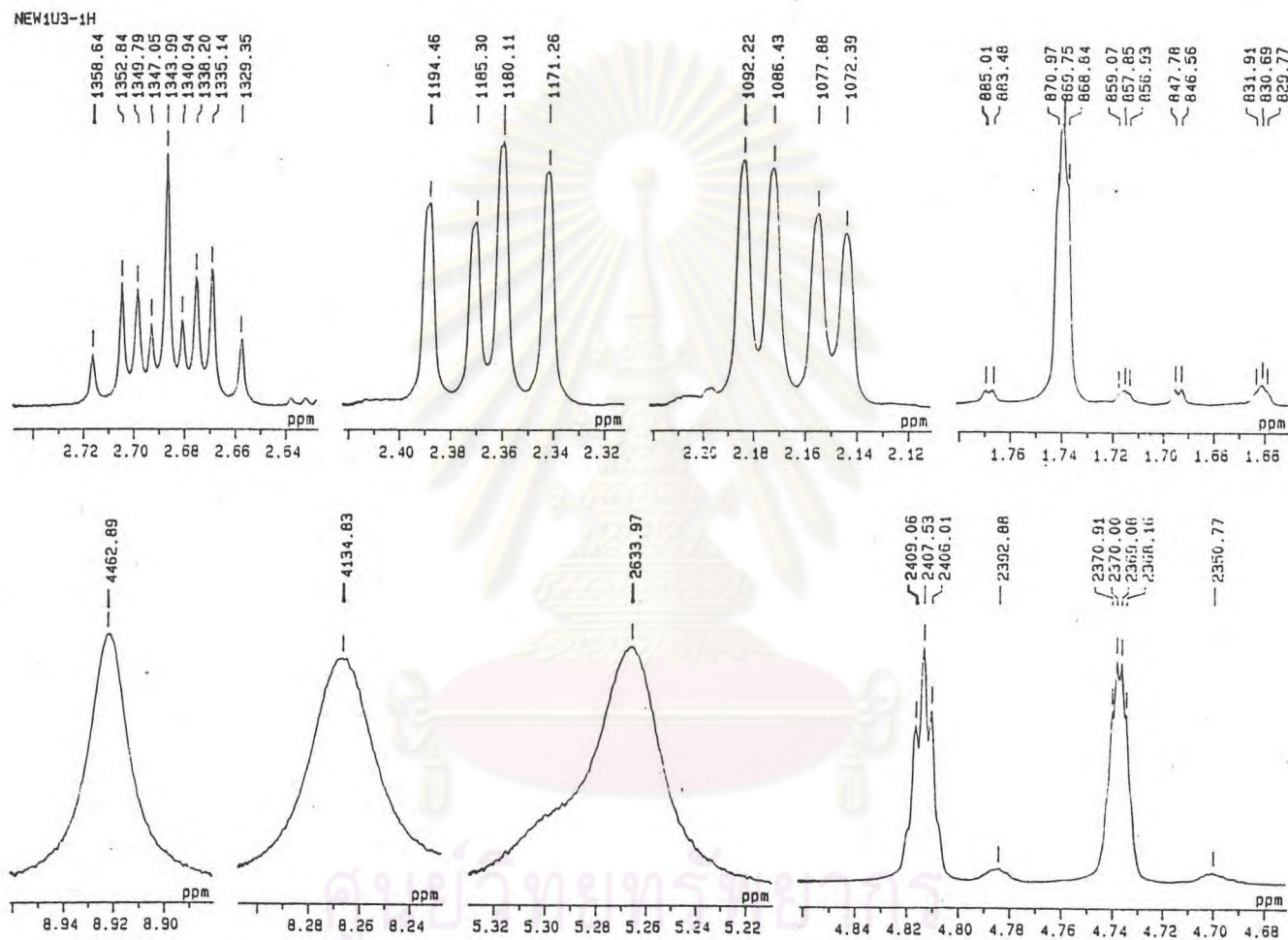


Figure 62. The 500 MHz $^1\text{H-NMR}$ spectrum N-(4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenoyl) urea in CDCl_3 (Enlarged scale : 1.66-8.96 ppm).

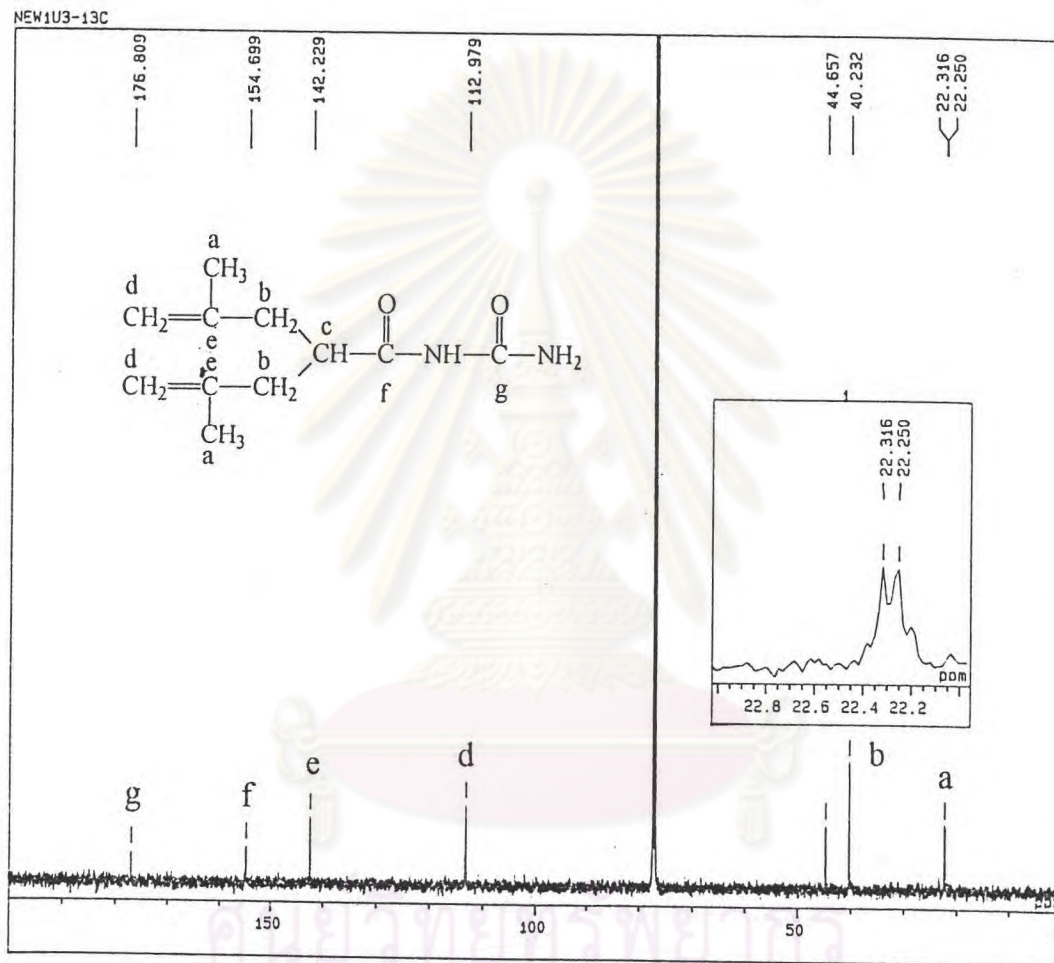


Figure 63. The 500 MHz ^{13}C -NMR spectrum of N-(4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenoyl) urea in CDCl_3 .

Background Subtract C:\SATURN\DATA\NEW1U3-3 Date: 03/15/96 10:40:57
 Comment: DB5-MS 30X.25MM 22/2/39
 Average of: 1275 to 1303 Minus: 1047 to 1816 100% = 2659
 100%

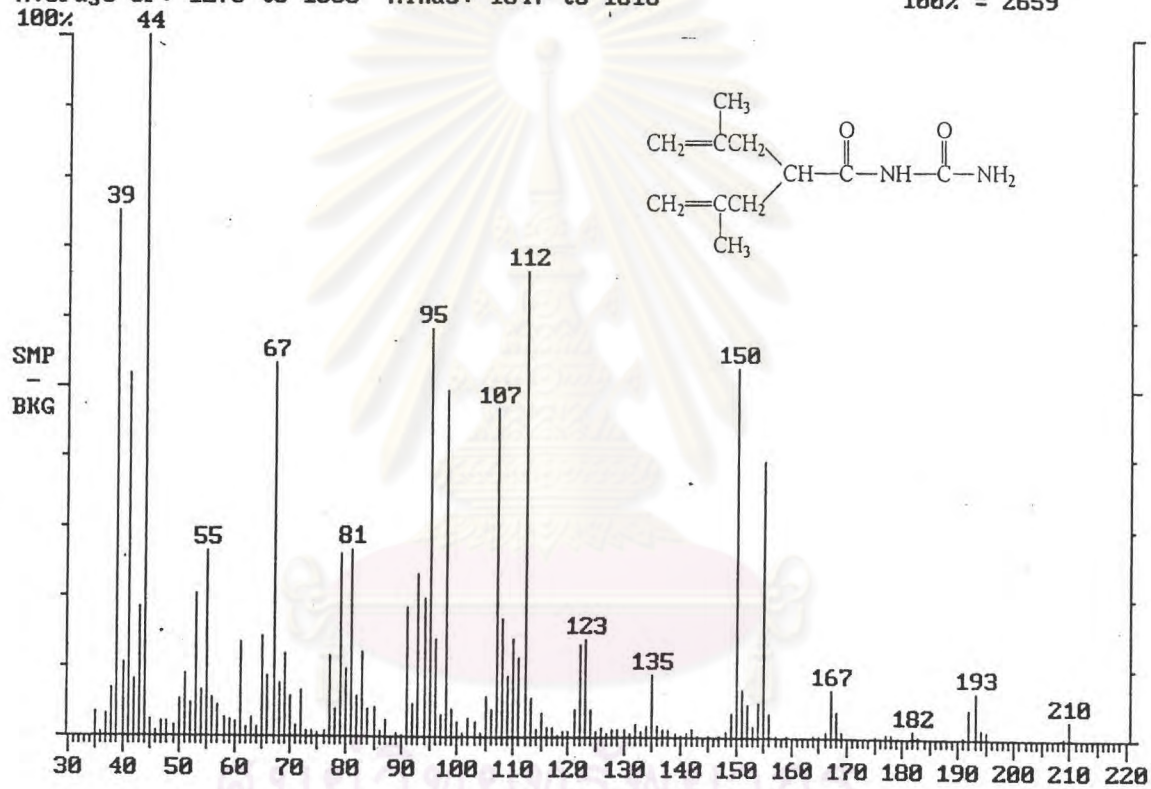


Figure 64. The EIMS spectrum of N-(4-methyl-2-(2'-methyl-2'-propenyl)-4-pentenyl) urea.

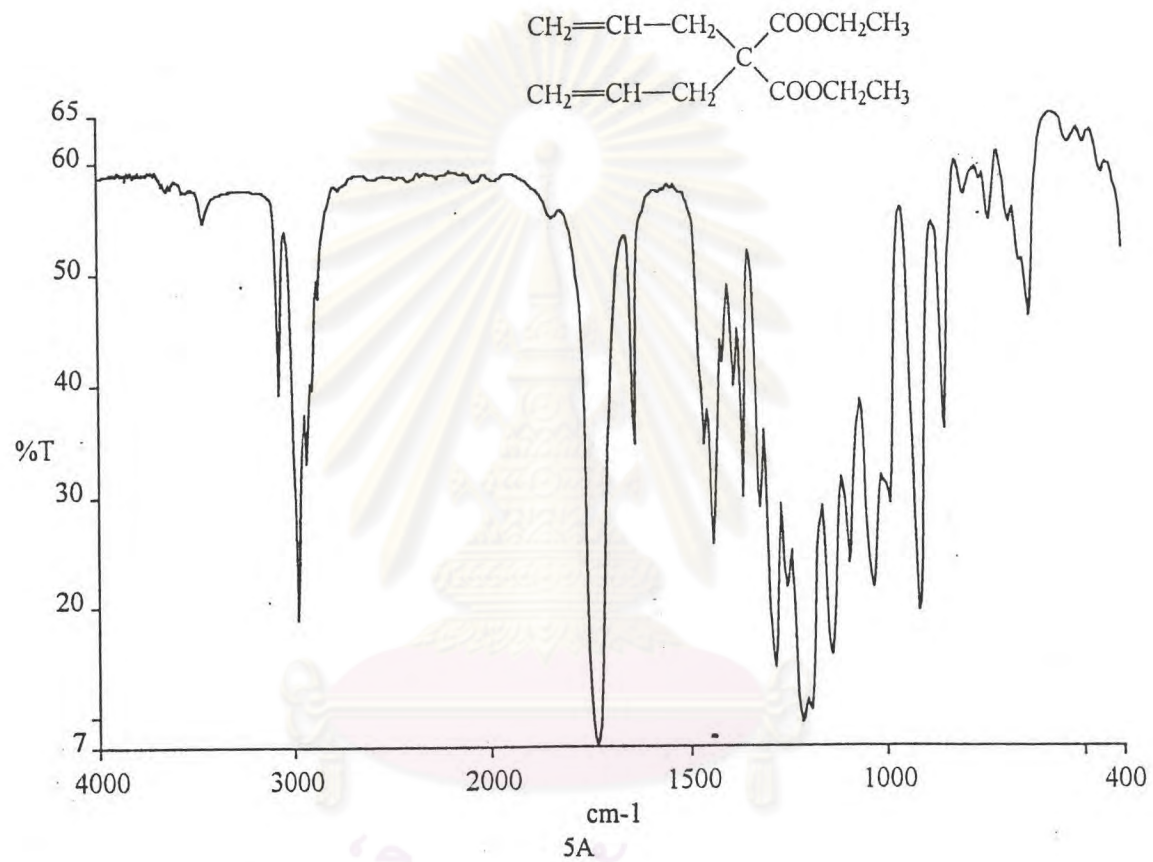


Figure 65. The IR spectrum (Neat) of diethyl diallylmalonate.

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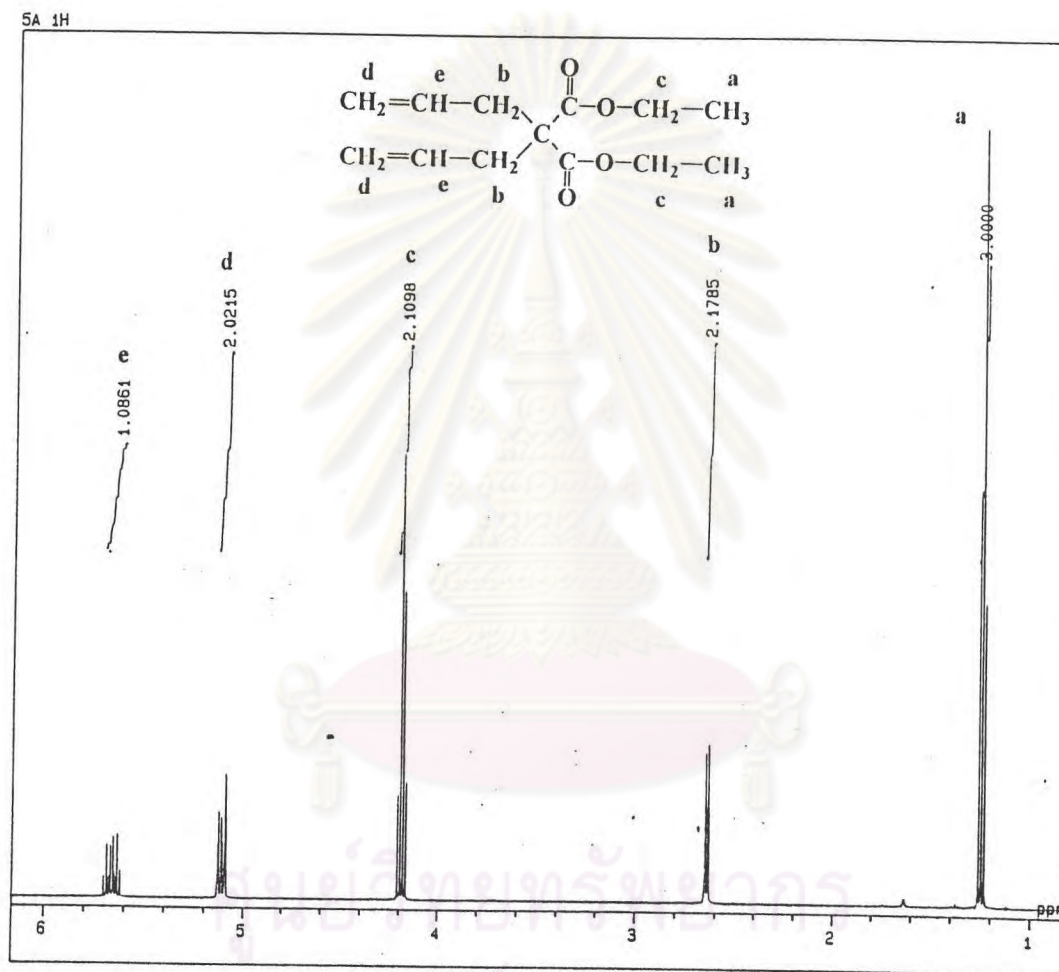


Figure 66. The 500 MHz ^1H -NMR spectrum of diethyl diallylmalonate in CDCl_3 .

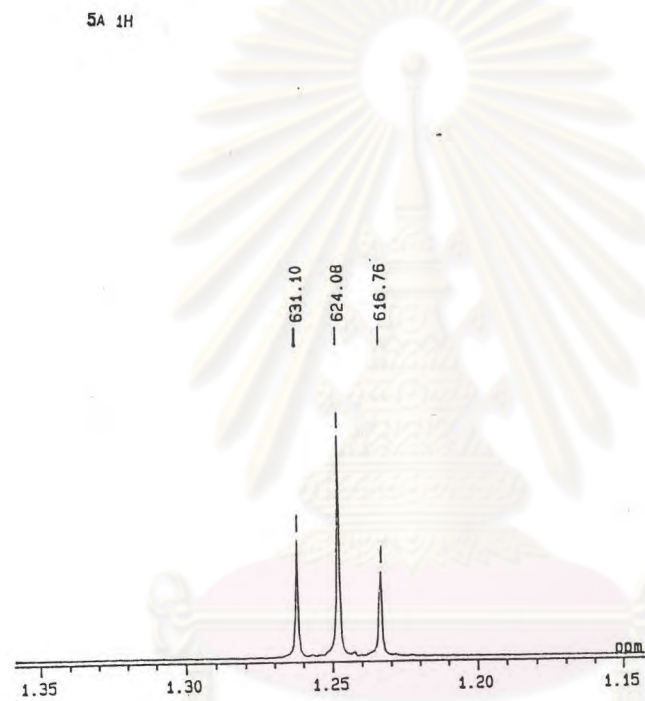


Figure 67. The 500 MHz ^1H -NMR spectrum of diethyl diallylmalonate in CDCl_3 (Enlarged scale : 1.20-1.30 ppm).

5A 1H

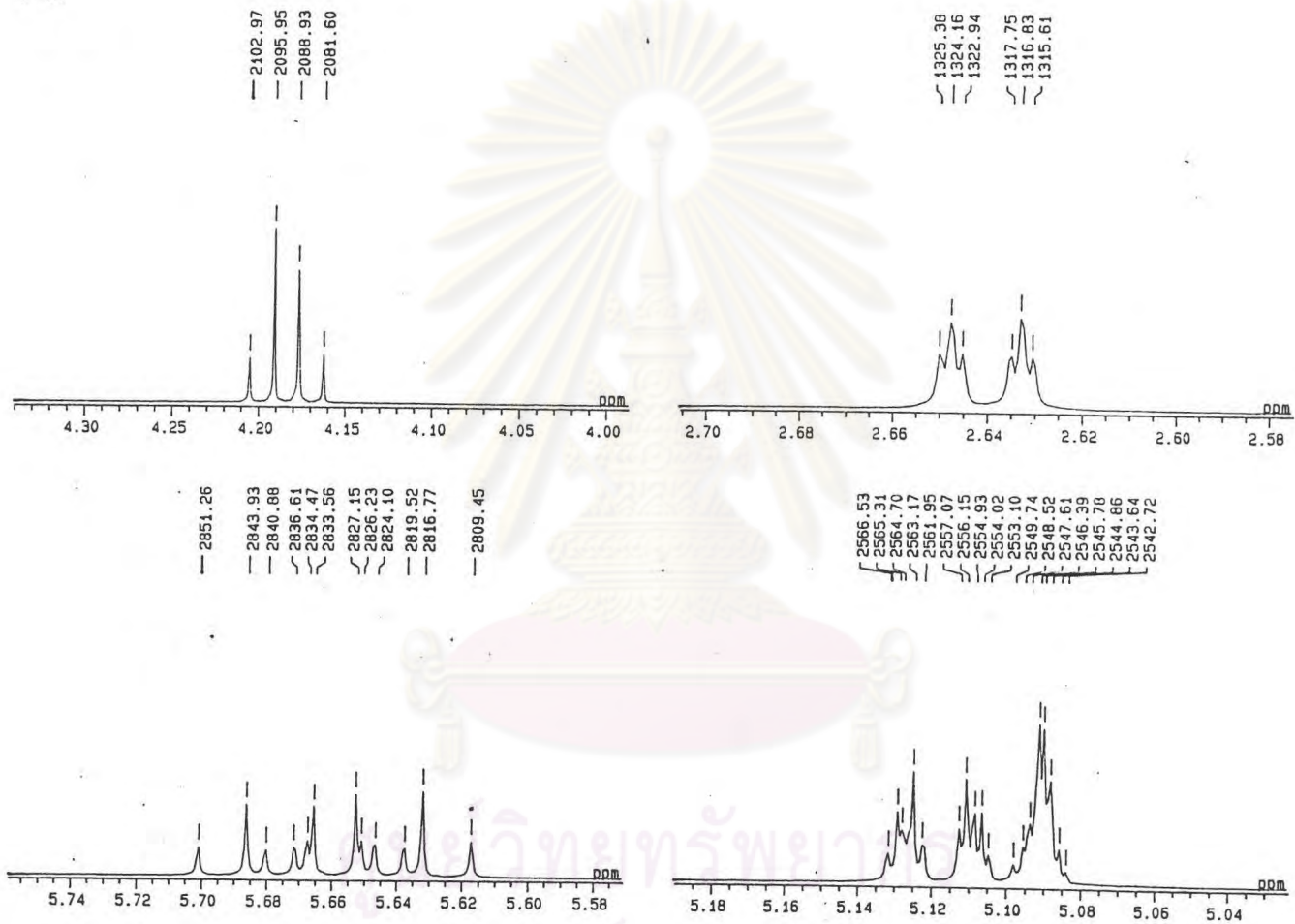


Figure 68. The 500 MHz ^1H -NMR spectrum of diethyl diallylmalonate in CDCl_3 (Enlarged scale : 2.58-5.74 ppm).

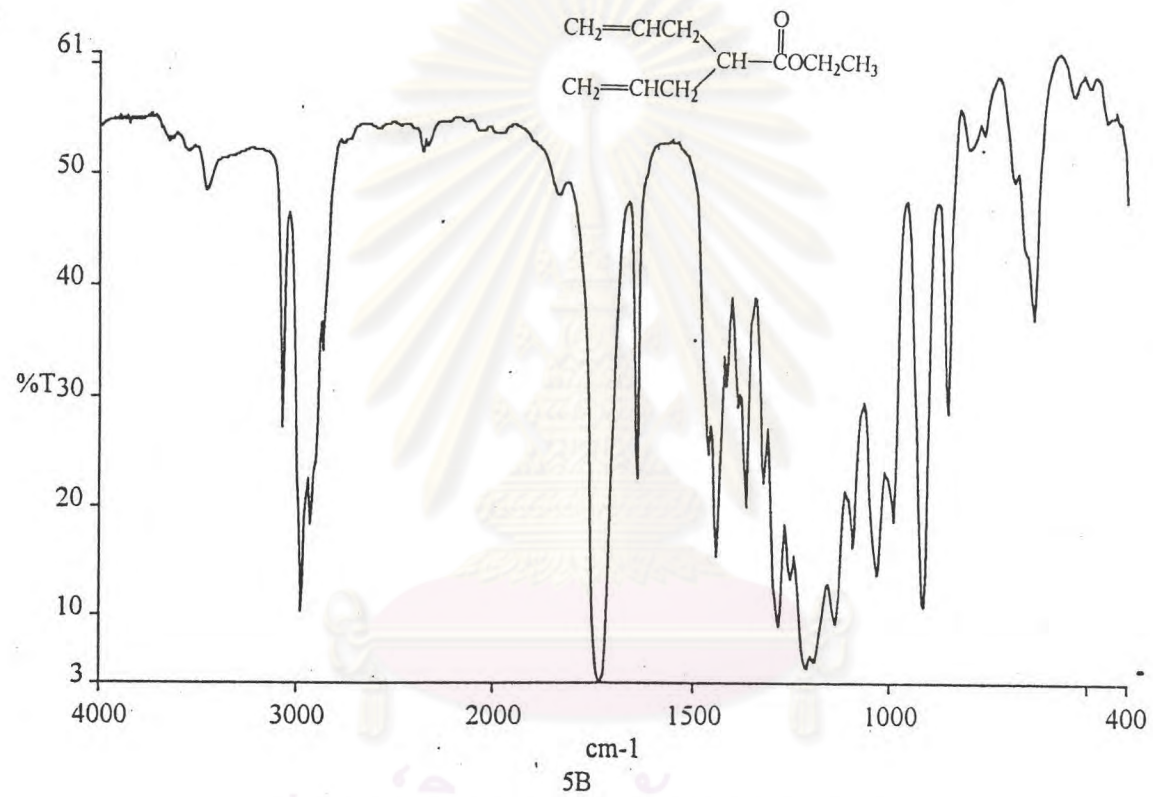


Figure 69. The IR spectrum (Neat) of ethyl 2-allyl-4-pentenoate.

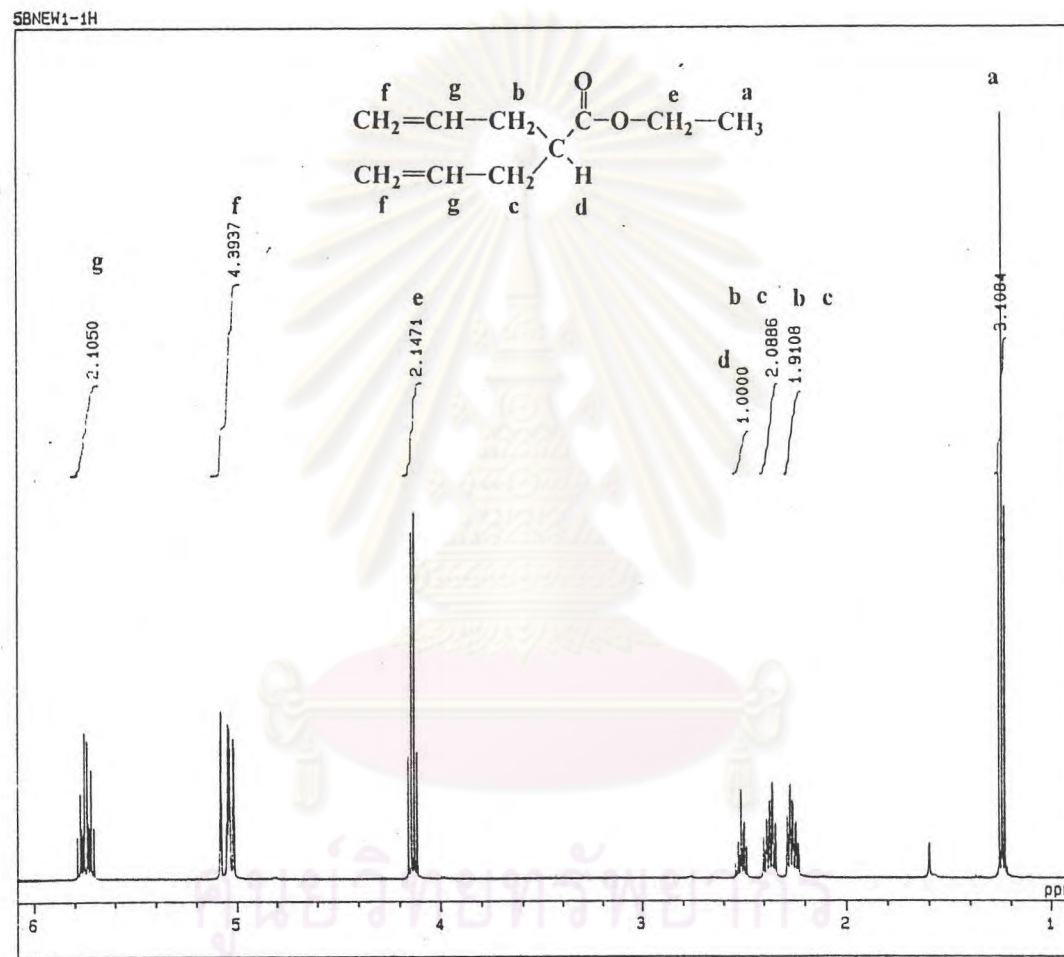


Figure 70. The 500 MHz ^1H -NMR spectrum of ethyl 2-allyl-4-pentenoate in CDCl_3 .

5BNEW1-1H

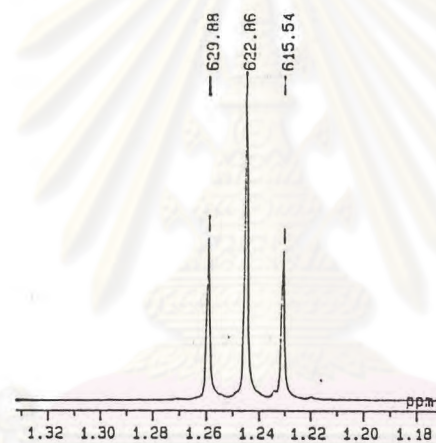


Figure 71. The 500 MHz ¹H-NMR spectrum of ethyl 2-allyl-4-pentenoate in CDCl₃ (Enlarged scale : 1.22-1.28 ppm).

จุฬาลงกรณ์มหาวิทยาลัย

5BNEW1-1H

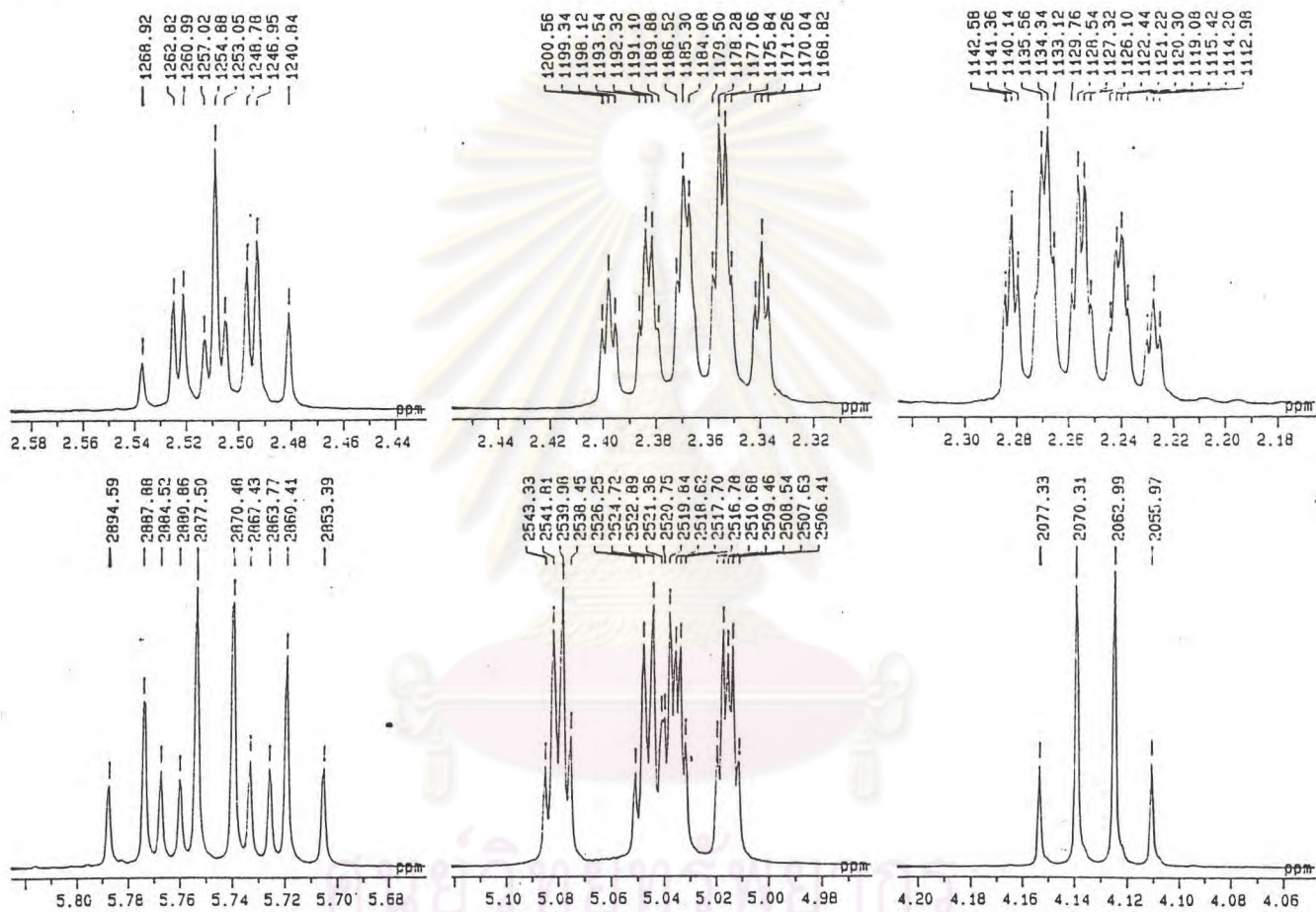


Figure 72. The 500 MHz $^1\text{H-NMR}$ spectrum of ethyl 2-allyl-4-pentenoate in CDCl_3 (Enlarged scale : 2.18-5.80 ppm).

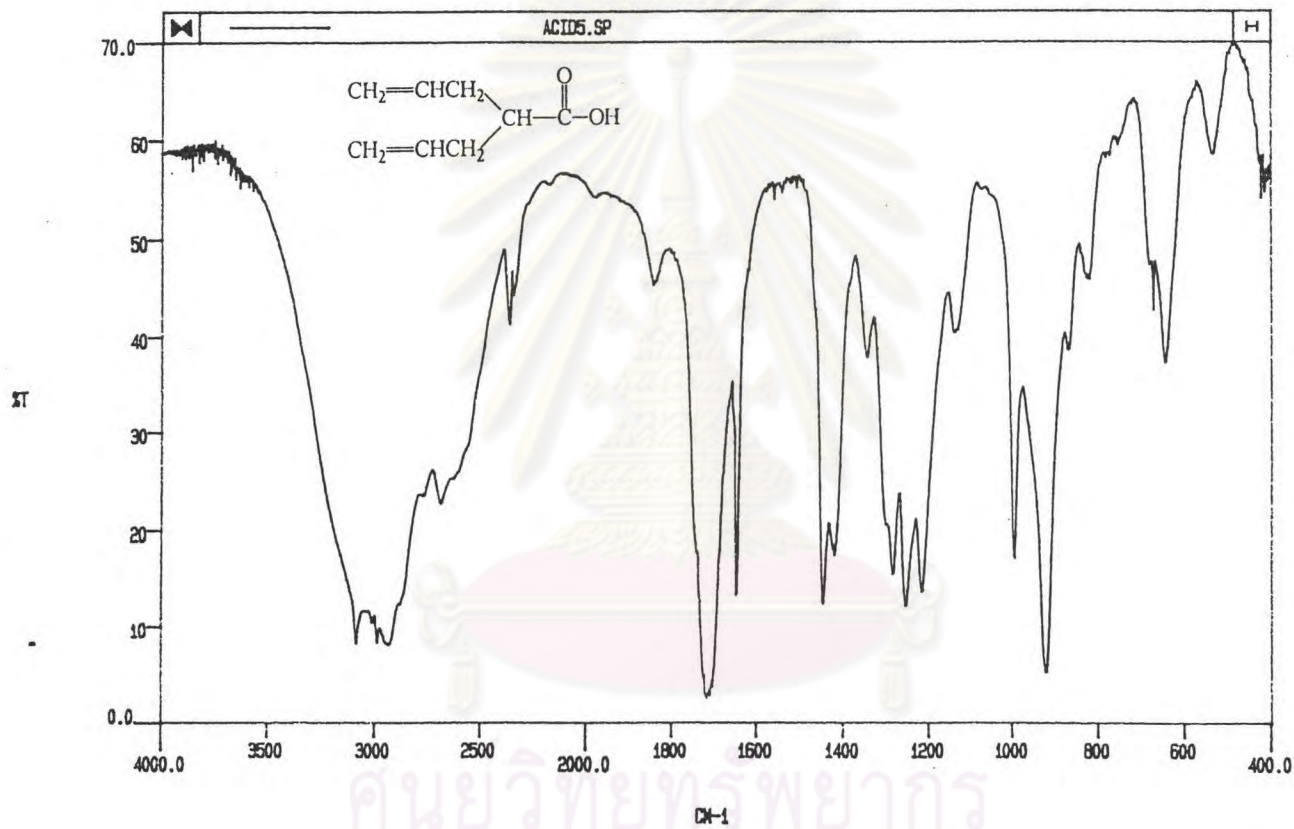


Figure 73. The IR spectrum (Neat) of 2-allyl-4-pentenoic acid.

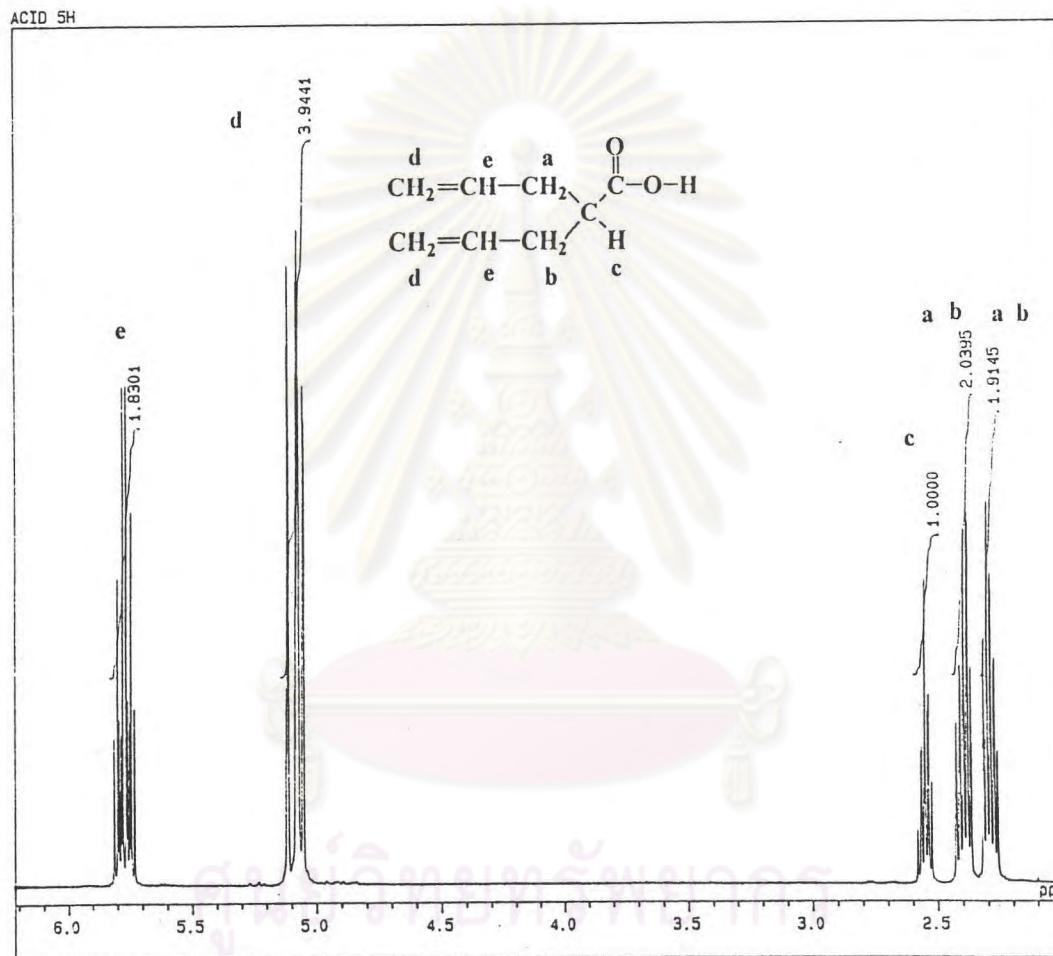


Figure 74. The 500 MHz ^1H -NMR spectrum of 2-allyl-4-pentenoic acid in CDCl_3 .

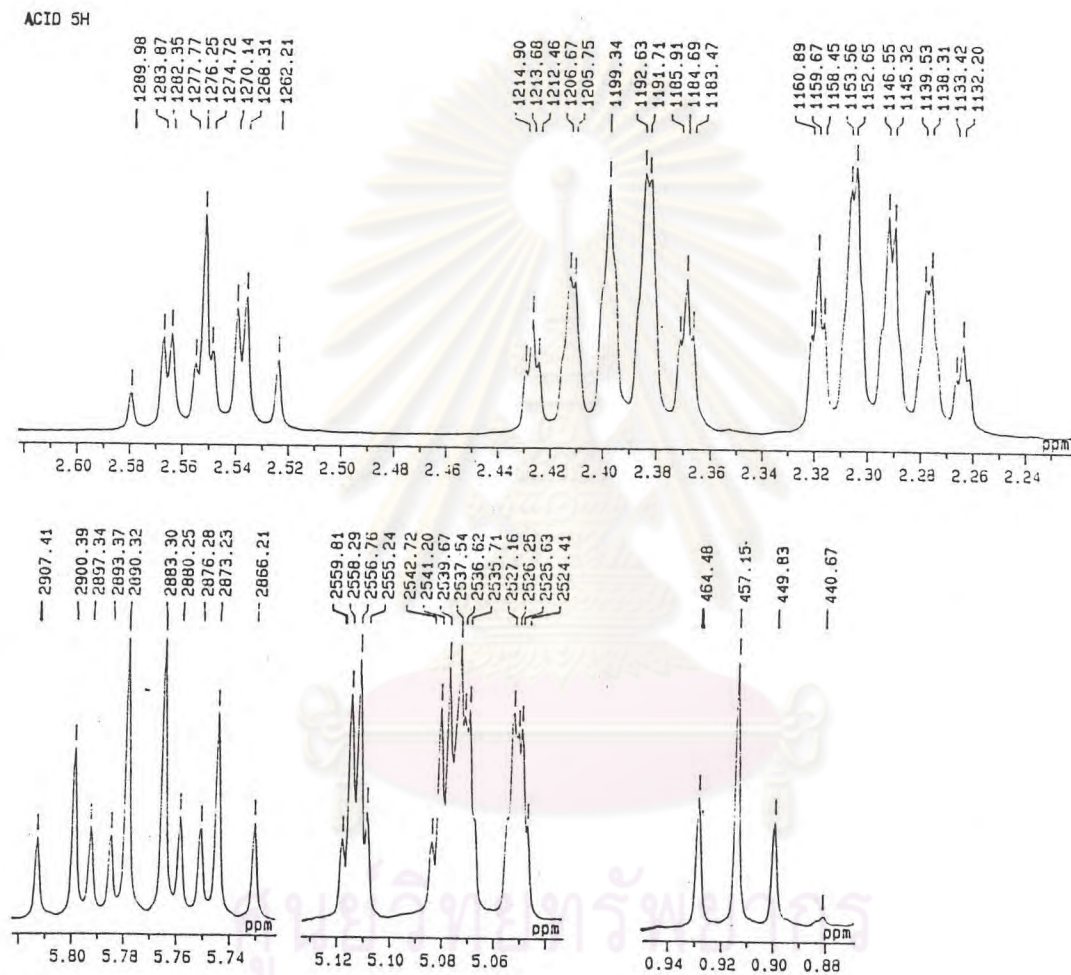


Figure 75. The 500 MHz ¹H-NMR spectrum of 2-allyl-4-pentenoic acid in CDCl₃ (Enlarged scale : 2.24-5.82 ppm).

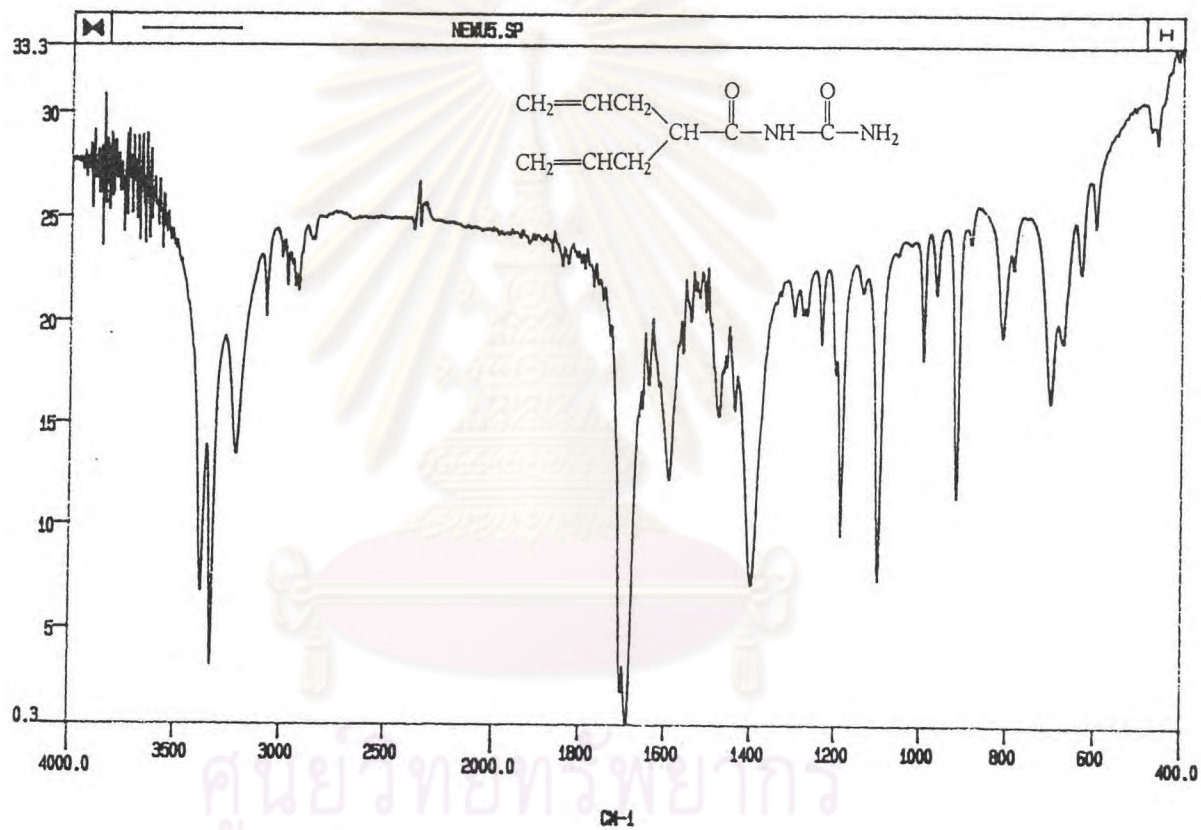


Figure 76. The IR spectrum (KBr) of N-(2-allyl-4-pentenoyl) urea.

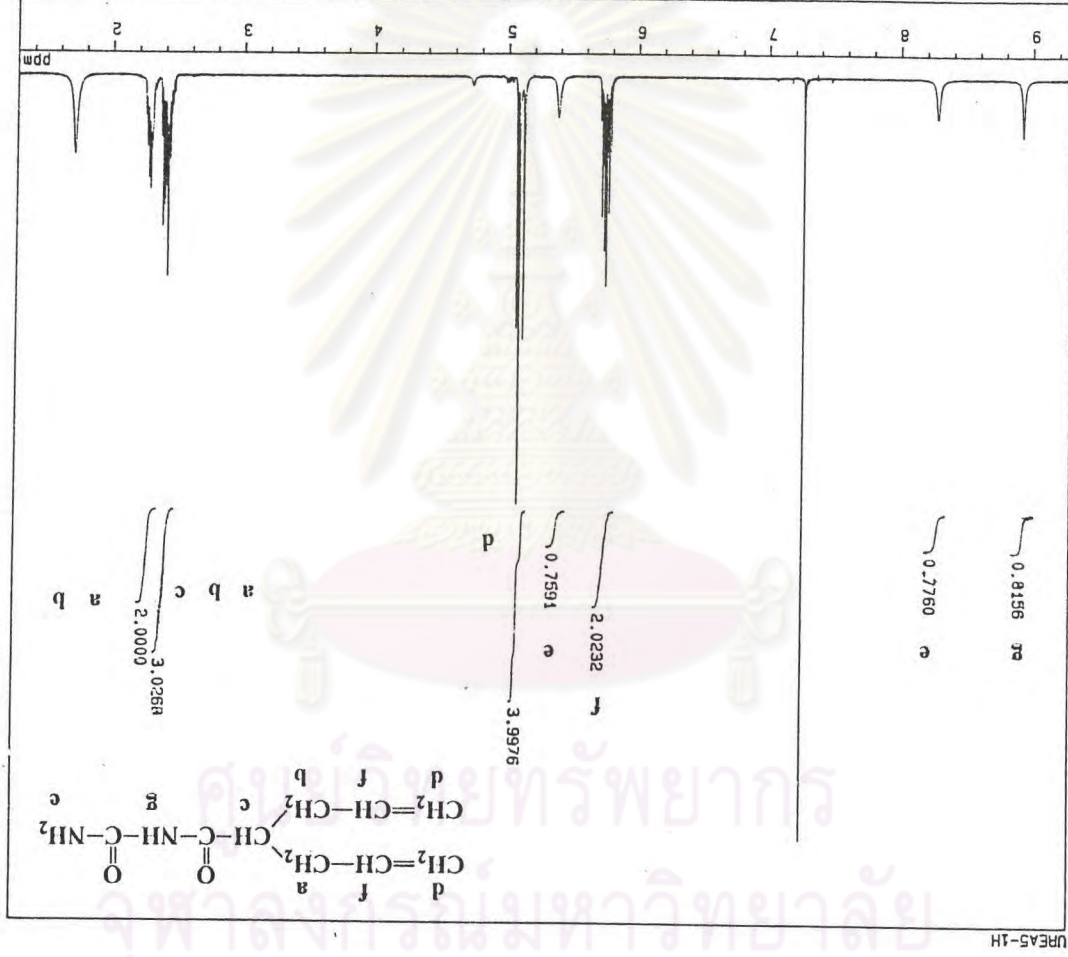
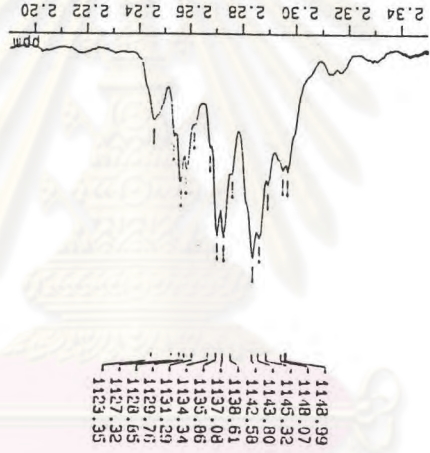


Figure 78. The 500 MHz $^1\text{H-NMR}$ spectrum of $\text{N}-(2\text{-allyl-4-pentenyl})$ urea in CDCl_3 (Enlarged scale : 2.20-2.34 ppm).



UREAS-1H

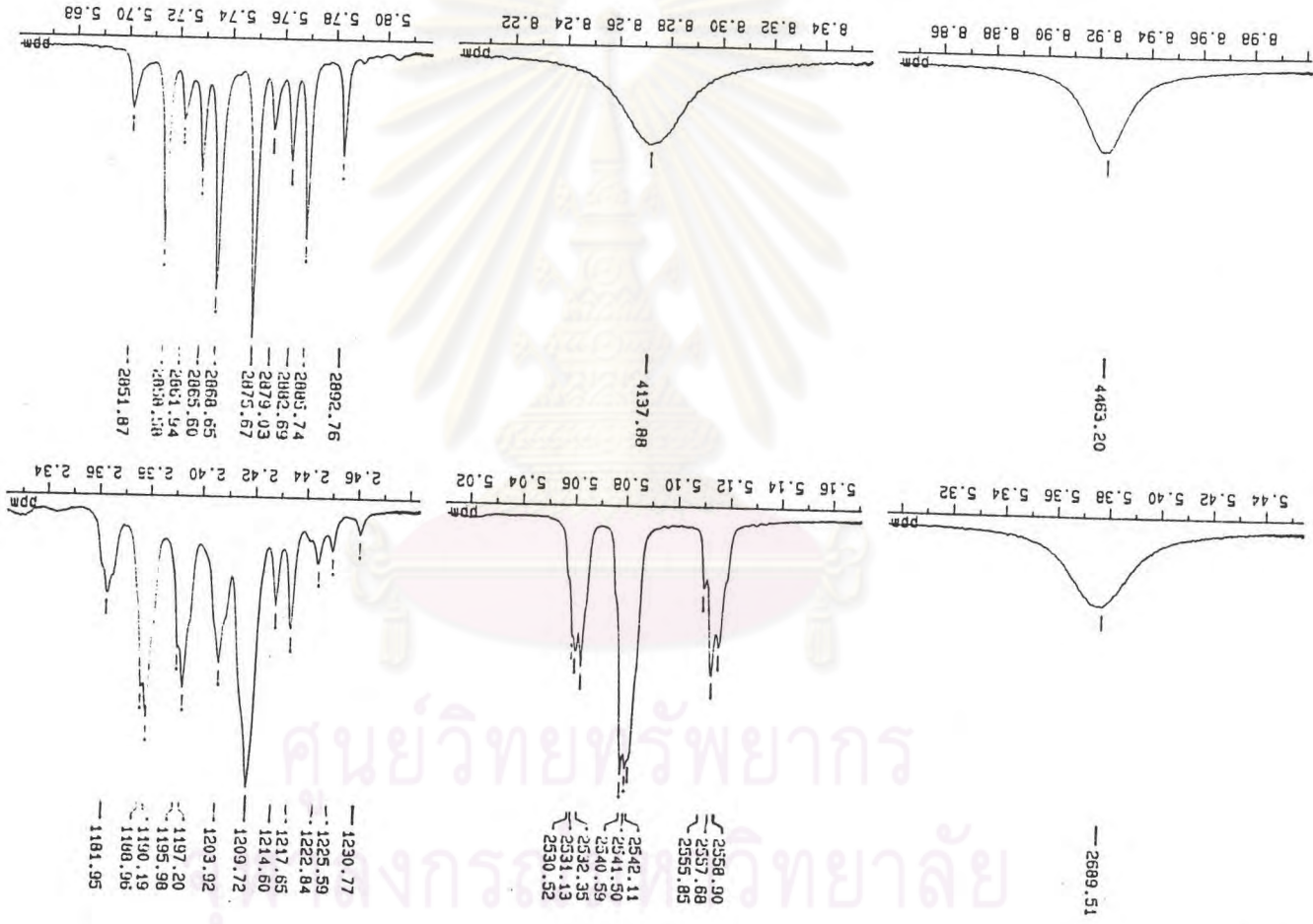


Figure 79. The 500 MHz ¹H-NMR spectrum of N-(4-allyl-4-pentenoyl)urea in CDCl₃ (Enlarged scale : 2.34-8.98 ppm).

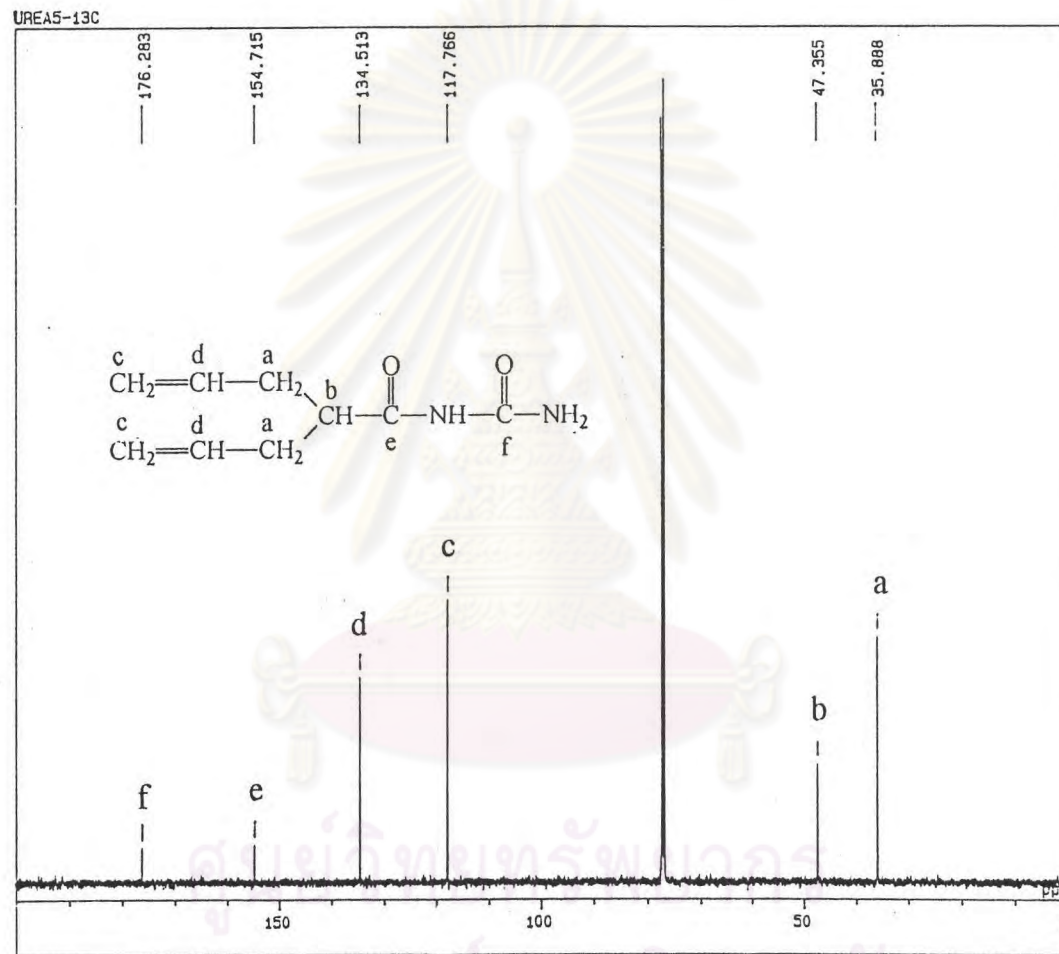


Figure 80. The 500 MHz ^{13}C -NMR spectrum of N-(2-allyl-4-pentenyl) urea in CDCl_3 .

Background Subtract C:\SATURN\DATA\UREA5-3 Date: 03/07/96 14:27:12
 Comment: DD5-MS 30X.25MM 21/2/39
 Average of: 642 to 651 Minus: 523 to 843 100% = 22294

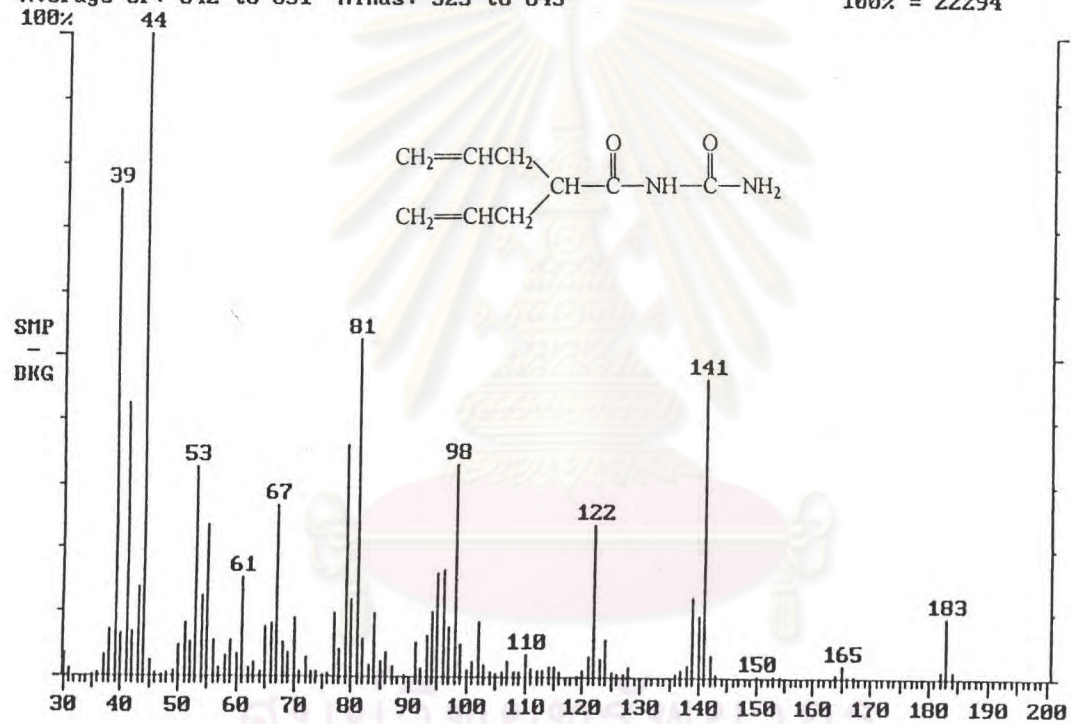


Figure 81. The EIMS spectrum of N-(2-allyl-4-pentenyl) urea.