



CHAPTER III

EXPERIMENTAL

3.1 Apparatus and Instruments

PARR Stirred Pressure Reactor, model 4550

Eyela Aspirator SB-55

Aldrich Kugelrohr Apparatus, model 213-196-2

High Vacuum Pump : Edwards, model E2M2 20035

Digital Melting Point Apparatus : Electrothermal

Gas Chromatograph : Shimadzu, model GC-RIA

Infrared Spectrophotometer : Perkin Elmer, model
780 with grating infrared
spectrophotometer

Fourier-Transform NMR Spectrometer : Jeol, model
JNX-FX 90 Q

3.2 Reagents and Their Purifications

(1) Tin powder : a commercial reagent grade tin powder was added to about twice its weight of 10% aqueous sodium hydroxide solution and shaken vigorously for 10 minutes. This treatment removed the oxide film on the surface of the powder and stearic acid, which

sometimes was added for the pulverization. The powder was then washed with water until the washing had shown no alkalinity to litmus and rinsed with ethanol, dried at 100 °c and pulverized in a mortar and kept in a desiccator.

(2) Zinc powder : a reagent grade zinc powder was washed twice with 10% aqueous hydrochloric acid solution until the powder became grey and then washed with ethanol until the washings had shown no acidity to litmus, dried at 100 °c and kept in desiccator.

(3) Tetrabutylammonium iodide : reagent grade, Fluka, Switzerland.

(4) Tributylamine : reagent grade, Fluka, Switzerland.

(5) Alkyl halides : n-butyl chloride, benzyl chloride, allyl chloride and allyl bromide (reagent grade) were dried in anhydrous calcium chloride and distilled before use.

(6) Organotin compounds : tetrabutyltin, tributyltin chloride, dibutyltin dichloride, dimethyltin dichloride and tetraoctyltin, reagent grade, E.Merck, Germany; used without further purification.

(7) Solvents : hexane, mesitylene, n-butanol, toluene and acetone, dried with anhydrous calcium chloride, distilled at its boiling temperature and kept in closed containers. Absolute ethanol dried with molecular sieve (4A). And distilled water.

(8) Magnesium turnings : reagent grade, Fluka, Switzerland.

(9) Anhydrous ethyl ether : removed trace of water by refluxing with sodium metal and distilled before use.

(10) Anhydrous tetrahydrofuran : treated in the same manner as ether.

(11) Anhydrous toluene : treated in the same manner as ether.

(12) Stannic chloride anhydrous : reagent grade, Fluka, Switzerland.

(13) Iodine crystals

(14) Magnesium sulfate anhydrous

(15) Ammonium chloride : 10% aqueous solution and saturated aqueous solution.

(16) Pyridine : refluxed with sodium hydroxide and distilled before use.

(17) 1,10-Phenanthroline : E. Merck, Germany.

(18) Sodium diethyldithiocarbamate (Na dtc) : recrystallized from ethanol and dried.

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3.3 Preparation, Purification and Identification of Organotin Compounds

3.3.1 Direct syntheses of organotin compounds

3.3.1.1 Direct synthesis of tetrabutyltin

(1) Direct synthesis of tetrabutyltin from tin powder and butyl chloride at atmospheric pressure. (23)-(24)

A mixture of tetrabutylammonium iodide(24.7 g, 0.067 mole), zinc dust(26.1 g, 0.400 mole) and tin powder(23.7 g, 0.200 mole) was added to a 500 mL round-bottomed flask fitted with a reflux condenser, a stirrer and a dropping funnel containing butyl chloride(37.0 g, 0.400 mole). The air inside the flask was removed by passing in dry nitrogen, and the contents of the flask were heated to 160 °c with stirring. When the mixture became dark grey, mobile liquid, the butyl chloride from the funnel was added dropwise. The mixture was then heated with continued stirring for a further 3 hours after the butyl chloride was completely added. Then it was allowed to cool slightly when the isolation procedure began by adding hexane(100 mL) slowly to the mixture and refluxing at its boiling point for 30 minutes. The flask was then cooled down and the hexane layer was removed by decantation. The residue was

washed with further small portions of hexane and the washings was combined with the extract. Hexane was distilled off to give the organotin product 14 g, a yield of 40.3 % based on butyl chloride.

Paper chromatography (Whatman filter paper No.1, butanol: ethanol = 3 : 1, saturated with water)(51). Irradiated with ultraviolet radiations and sprayed with catechol violet(0.1% in 95% ethanol) gave a blue spot at $R_f = 9.8$ indicating a tetrabutyltin compound.

Gas chromatography (using FFAP column : column temperature 180 °c, injection temperature 200 °c, nitrogen carrier gas flow rate 55 mL/min. and using FID detector) showed that the tetrabutyltin obtained is more than 98.5% purity and tributyltin chloride constituted less than 1.5%(retention time : tetrabutyltin 2.9 min., tributyltin chloride 7.3 min., dibutyltin dichloride 12.7 min.)

(2) Direct synthesis of tetrabutyltin from tin metal and butyl chloride in a pressure reactor.

A mixture of tetrabutylammonium iodide (24.7 g, 0.067 mole), zinc dust (26.1 g, 0.400 mole), tin powder (23.7 g, 0.200 mole) and n-butyl chloride (74 g, 0.800 mole) was added to the reactor. Nitrogen gas was passed through the reactor tank through a gas-inlet-

outlet valve for 15 minute to replace the air inside and then the valve was closed, the temperature was raised to 160 °c with continual stirring at 500 rpm and the temperature was maintained at 160 °c for 5 hours. The mixture was allowed to cool to room temperature and hexane (100 mL) was added to the reaction mixture and refluxed at its boiling point for 45 minutes. The cooled reaction mixture was decanted and the residue was extracted with hexane (50 mL). Hexane was distilled off to leave the crude product 19 g., a yield of 54% based on butyl chloride.

Paper chromatography : Sprayed with catechol violet solution gave blue spot and a reddish orange spot at $R_f = 0.95, 0.97$ indicating a mixture of di- and tributyltin chloride.

Gas chromatography showed that a mixture of di-, tri- and tetrabutyltin was obtained and the yields of dibutyltin dichloride, tributyltin chloride and tetrabutyltin were 87.9%, 9.15% and 2.92% respectively.

(3) Direct synthesis of tetrabutyltin from tin metal and butylchloride in a pressure reactor (using solvent : mesitylene)

A mixture of tributylamine (12.42 g, 0.067 mole), zinc dust (26.1 g, 0.400 mole), tin powder (23.7 g, 0.200 mole) and n-butyl chloride (74 g, 0.800 mole)

was suspended in mesitylene (300 mL) in the reactor with continual stirring. The temperature of the mixture was raised to 160-165 °c and maintained for 5 hours. After the reaction mixture was allowed to cool to room temperature. The cooled reaction mixture was decanted. Mesitylene was distilled off to leave the crude product 8.5 g, a yield of 25.5% based on butyl chloride.

Paper chromatography showed a long streak at Rf 0.95-0.97 with blue and reddish orange colour indicating a mixture of di-, tributyltin chloride.

Gas chromatography showed that tetrabutyltin, tributyltin chloride and dibutyltin dichloride were obtained in 37.85%, 60.5%, 1.58% yield respectively.

3.3.1.2 Direct syntheses of tribenzyltin chloride and dibenzyltin dichloride

(1) Direct synthesis of tribenzyltin chloride from tin metal and benzyl chloride

(a) Water as solvent

To a suspension of tin powder (17.8 g, 0.15 mole) in boiling water (150 mL) kept in an oil bath at 100 °c with efficient stirring, benzyl chloride (19.2 g, 0.15 mole) was added in 2 minutes. Refluxing and stirring were continued for 1.5 hours, and after cooling, solid mass containing the product and unreacted

tin powder was filtered off and dried in air. The solid was extracted with acetone for 3 hours in Soxhlet apparatus. Unreacted metallic tin (5.5 g, 0.046 mole) was recovered. Evaporation of the acetone solution under reduced pressure gave pale yellow powder which on recrystallization from ethyl alcohol gave 17.1 g of tribenzyltin chloride as colourless needles, a yield of 80% based on benzyl chloride, m.p. 143-144 °c.

Elemental analysis : $C_{21}H_{21}SnCl$ requires %C 58.99 %H 4.95 %Sn 27.76 ; found %C 59.06 %H 5.01 %Sn 27.22

IR (KBr) : ν (cm^{-1}) 3030, 3060, 3083(aromatic C-H), 2930 (aliphatic C-H), 1667-2000 (monosubstituted aromatic), 1455, 1495, 1600 (C-C in ring) , see Fig.1

1H NMR ($CDCl_3$), δ (ppm) 2.653 (s, CH_2-Sn), 6.810-7.386 (m, Ph)

^{13}C NMR ($CDCl_3$), δ (ppm) 25.57 (CH_2-Sn), 125.034, 128.014, 128.935, 138.199 (Ph), see Fig.2

(b) n-Butanol as solvent

A suspension of tin powder (17.8g, 0.15 mole) in n-butanol (150 ml) was treated at 110 °c with benzyl chloride (19.2 g, 0.15 mole) for 3 hours and the reaction mixture was evaporated to almost dryness. The residue was extracted with acetone and the acetone solution was poured with stirring into 700 mL of aqueous 3 N hydrochloric acid. The white precipitate thus formed was filtered off and washed with water. After

drying, recrystallized from ethyl alcohol gave colourless needles of tribenzyltin chloride 15.8 g, a yield of 75% based on benzyl chloride, m.p. 142-144 °c. The product was identical to that previously characterized in section (a)

(2) Direct synthesis of dibenzyltin dichloride from tin metal and benzyl chloride in toluene.

Water (2-3 drops) was added to tin powder (17.8 g, 0.15 mole) and kneaded together. The mixture was then suspended in toluene (100 mL) and stirred vigorously and heated to 110 °c. At this point, benzyl chloride (19.2 g, 0.15 mole) was added dropwise within 3 minutes and stirring and refluxing was continued for an additional 3 hours. After cooling, the slurry was filtered and the residue was extracted with acetone. The acetone solution was evaporated under diminished pressure to leave a pale yellow solid. When the toluene solution was evaporated, an additional yellow solid was obtained. These solids were combined and recrystallized from ethyl alcohol to give white, silky crystals 19.6 g., a yield of 70% based on benzyl chloride, m.p. 161-163 °c.

Elemental analysis : $C_{13}H_{14}SnCl_2$ requires %Sn 31.92; found %Sn 30.00

3.3.2 Syntheses of organotin compounds by Grignard method

3.3.2.1 Synthesis of tetrabutyltin by Grignard method

(1) Process for the synthesis of tetrabutyltin by Grignard method

n-butylmagnesium chloride was prepared from magnesium turnings (12 g, 0.49 mole) and n-butyl chloride (44 g, 0.475 mole) in ether (300 mL) contained in 100 mL flask fitted with a double surface condensor, stirrer, dropping funnel and inlet and outlet tubes for dry nitrogen. After the reaction had been initiated by adding a small quantities of iodine, the butyl chloride was added dropwise. When the addition was completed, refluxing was continued for an additional 1 hour. Then the reaction mixture was cooled to 0 °c., and anhydrous stannic chloride (26 g, 0.1 mole) was added dropwise. When the addition was completed, refluxing was continued for 3 hours. After cooling, the product began to separate. The excess Grignard reagent was decomposed by adding 10% aqueous ammonium chloride solution (100 mL) and stirring the cooled solution for one half hour. The ether layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed by distillation and the residue was distilled at reduced

pressure to give pure tetrabutyltin 26.4 g, 76% yield based on stannic chloride, b.p. 128-130 °c /3 mm. Hg

Elemental analysis : $C_{16}H_{36}Sn$ requires %C 55.35 %H 10.45 %Sn 34.24; found %C 54.72 %H 10.96 %Sn 34.10

IR (neat) : ν (cm^{-1}), 2850, 2875, 2925, 2960 (aliphatic C-H), see Fig.3

1H NMR ($CDCl_3$), δ (ppm) 0.888 (approximately triplet, $J = 6.1$ Hz, CH_3), 1.177-1.547 (m, CH_2 -)

^{13}C NMR ($CDCl_3$), δ (ppm) 8.884 (CH_2-Sn , $J(^{119}Sn-^{13}C) = 156.3$ Hz), 13.706, 27.466, 29.416(CH_2 -), see Fig.4

(2) Modified process for the synthesis of tetrabutyltin by Grignard method

The procedure for the synthesis of n-butyilmagnesium chloride by Grignard method(1) was followed but after the Grignard reagent was obtained, ether was distilled off from the reaction mixture using Dean-Stark apparatus, toluene (300 mL) was added and then stannic chloride (26 g) was added dropwise with continuous stirring. The reaction mixture was refluxed at 110 °c for additional one hour. The excess Grignard reagent was decomposed by the addition of small amount of saturated ammonium chloride solution. The toluene layer was separated and evaporated at diminished pressure to yield the crude product which was distilled at reduced pressure giving tetrabutyltin 30.6 g, 88%

yield based on stannic chloride. The product was identical to that previously characterized in section (1)

3.3.2.2 Synthesis of tetraallyltin by Grignard method

Allyl chloride (57.5 g, 0.75 mole) was added dropwise to magnesium turnings (20 g, 0.82 mole) in ether (400 mL) with efficient stirring and refluxing, using the same equipment as described in section (1). White solid mass formed and increased as the reaction proceeded. Refluxing was continued for additional 1 hour after the addition. After cooling, 10% aqueous ammonium chloride solution was added dropwise to the cooled reaction mixture (-10°C) with stirring. The ether layer was separated and dried over anhydrous magnesium sulfate. After evaporation of ether to reduce the original volume by half, 100 mL of 5% potassium fluoride solution was added to remove any triallyltin chloride by precipitation as triallyltin fluoride. The ether layer was again separated, dried and evaporated, the residue was distilled under reduced pressure to give pure tetraallyltin 9.4 g, 55% yield based on stannic chloride, b.p. $84-88^{\circ}\text{C}/2\text{ mm.Hg}$.

Elemental analysis : $\text{C}_{12}\text{H}_{20}\text{Sn}$ requires %Sn 41.98; found %Sn 40.85

IR (neat) : ν (cm^{-1}), 3080 (olefinic C-H), 2905, 2962 (aliphatic C-H), 1625 (olefinic C = C), 894, 930 ($\text{CH}_2=\text{CH-R}$), see Fig.5

^1H NMR (CDCl_3), δ (ppm) 1.91 (d, $J = 8.3$ Hz, $\text{CH}_2\text{-Sn}$, $J(^{119}\text{Sn}-^1\text{H} = 31.5$ Hz), 5.686-6.174 (m, $J = 8.6$ Hz), 4.670-4.958 (m, $\text{CH}_2\text{-}$)

^{13}C NMR (CDCl_3), δ (ppm) 16.198 ($-\text{CH}_2\text{-Sn}$, $J(^{119}\text{Sn}-^{13}\text{C} = 125.7)$), 111.115 ($\text{H}_2\text{C-}$), 136.52 ($-\text{CH-R}$), see Fig.6

3.3.2.3 Synthesis of diallyldibutyltin by Grignard method

Allyl chloride (36.7 g, 0.48 mole) was added dropwise to magnesium turnings (13.5 g, 0.555 mole) in ether (300 mL) with stirring. After allylmagnesium chloride was obtained in ether, dibutyltin dichloride (54.2 g, 0.178 mole) dissolved in ether (100 mL) was added. Refluxed for 3 hours and after isolation of the crude product according to the procedure described above, it was distilled under reduced pressure to yield 55 g of diallyldibutyltin, a yield of 88% based on dibutyltin dichloride.

Attempted to improve the yield of the product by using allyl bromide was unsuccessful. Since allylmagnesium bromide was a liquid and it was easier to stir than allylmagnesium chloride which formed as a solid mass. But when allyl bromide was used, the yield

of the product was only 52.7% based on dibutyltin dichloride. The product has a boiling point of 114-115 °C/ 2 mm.Hg.

Elemental analysis : $C_{14}H_{28}Sn$ requires %Sn 37.67; found %Sn 37.06

IR (neat) : ν (cm^{-1}), 3080 (olefinic C-H), 2850, 2925, 2962 (aliphatic C-H), 1625 (olefinic C = C), 894, 930 (out of plane H deformation), see Fig.7

1H NMR ($CDCl_3$), δ (ppm) 5.789-6.182 (m, =CH-, J = 7.3 Hz), 4.604-4.882 (m, CH_2 =), 1.818 (d, J = 8.5 Hz, CH_2 -Sn), 1.212-1.531 (unresolved multiplet, CH_2 in butyl), 0.959 (approximately triplet, CH_3)

^{13}C NMR ($CDCl_3$), δ (ppm) 137.494 (=CH-R), 109.920 (H_2C =), 16.360 (CH_2 -Sn), 29.037, 27.249, 13.651, 9.534 (C in butyl), see Fig.8

3.3.2.4 Synthesis of dibenzyl dibutyltin by Grignard method

Benzyl chloride (38 g, 0.30 mole) was added dropwise to magnesium turnings (8.5 g, 0.35 mole) in ether (300 mL) with stirring. After the Grignard reaction was completed, the ether was distilled off and replaced with the same volume of toluene. Dibutyltin dichloride (30g, 0.099 mole) in toluene was added to the reaction mixture and refluxed at 110 °C for 1 hour. The toluene layer was separated and the solvent

was distilled off at diminished pressure to leave a crude product which was distilled at reduced pressure to yield 37g of dibenzyl dibutyltin, 90.2% yield based on dibutyltin dichloride, b.p. 164-166 °C/ 6 mm.Hg.

Elemental analysis : $C_{22}H_{38}Sn$ requires %C 68.64 %H 7.77 %Sn 28.8; found %C 72.08 %H 7.90 %Sn 26.18

IR (neat) : $\nu(\text{cm}^{-1})$ 3030, 3060, 3085 (aromatic C-H), 2850, 2920, 2950 (aliphatic C-H), 1667-2000 (monosubstituted aromatic), 1455, 1495, 1600 (C-C in ring), see Fig.9

^1H NMR (CDCl_3), δ (ppm) 6.874-7.337 (m, Ph), 2.912 (s, $\text{CH}_2\text{-Ph}$), 0.825-1.50 (m, CH_2)

^{13}C NMR (CDCl_3), δ (ppm) 123.138, 125.901, 127.147, 127.64, 128.339, 128.447 (Ph), 37.922 ($\text{CH}_2\text{-Sn}$), 9.859, 13.597, 27.249, 28.766 (CH_2 in butyl), see Fig.10

3.3.2.5 Synthesis of tribenzyl-n-butyltin by Grignard method

Butyl chloride (9.3 g, 0.10 mole) was added dropwise to magnesium turnings (3.24 g, 0.13 mole) in tetrahydrofuran (150 mL). When the Grignard reaction was completed, a solution of tributyltin chloride (25 g, 0.0585 mole) in tetrahydrofuran (100 mL) was added. After the addition had completed, refluxing was continued for 1 hour. When the reaction was completed, tetrahydrofuran was distilled off and the same volume of

toluene was replaced and refluxing was continued for 1 hour. The excess Grignard reagent was decomposed by the addition of a small amount of saturated ammonium chloride solution with stirring. The toluene layer was separated and distilled off at diminished pressure. The residue was distilled under reduced pressure to give 25 g of tribenzyl-n-butylin, a yield of 95% based on tribenzyltin chloride, b.p. 200-203 °C/ 3 mm.Hg.

Elemental analysis : $C_{25}H_{30}Sn$ requires %C 66.85 %H 6.73 %Sn 26.42; found %C 62.70 %H 6.72 %Sn 25.80

IR (neat) : $\nu(\text{cm}^{-1})$ 3030, 3060, 3085 (aromatic C-H), 2850, 2920, 2950 (aliphatic C-H), 1700-2000 (monosubstituted aromatic), 1455, 1495, 1600 (C-C in ring), see Fig.11

3.3.3 Syntheses of the coordination complexes of organotin compounds with some ligands

3.3.3.1 Organotin compounds and N-donor ligands

(1) Dimethyltin dichloride and pyridine

Dimethyltin dichloride (0.5 g, 2.2×10^{-3} mole) was dissolved in dry toluene (30 mL) and pyridine (0.39g, 4.96×10^{-3} mole) was added dropwise with stirring

while a white precipitate formed. Stirring was continued for 0.5 hour. Then the solid residue was filtered off. The product (0.79 g) after washing with ethanol and drying melted at 161 °c , a yield of 95% based on dimethyltin dichloride.

Elemental analysis : $C_{12}H_{10}N_2Cl_2Sn$ requires %C 38.14 %H 4.27 %N 7.41 %Sn 31.41; found %C 37.59 %H 4.28 %N 7.48 %Sn 31.07

IR (neat) : $\nu(\text{cm}^{-1})$ 3010, 3085 (aromatic C-H), 2925 (aliphatic C-H), 1430-1600 (C-C, C-N in ring), see Fig.12

^1H NMR (CDCl_3): δ (ppm) 1.321 (s, $\text{CH}_3\text{-Sn}$, $J(^{119}\text{Sn}-\text{H})=45.4$ Hz), 7.402- 7.55 (m, meta H),

^{113}C NMR (CDCl_3): δ (ppm) 124.709, 138.144, 148.329 , see Fig.13

(2) Dibutyltin dichloride and 1,10-phenanthroline

Dibutyltin dichloride (0.5 g, 1.65×10^{-3} mole) was dissolved in dry ether (30 mL) and a solution of 1,10-phenanthroline (0.36 g, 1.82×10^{-3} mole) in dry ether (20 mL) was added dropwise with stirring for 0.5 hours. A white precipitate was formed. The product was filtered off to yield 0.8 g of white powder. After recrystallization from ethanol, white prism crystals was obtained (0.72 g), m.p. 200 °c, a yield of 90% based on dibutyltin dichloride.

Elemental analysis: $C_{20}H_{27}Cl_2N_2Sn$ requires %C 49.62 %H 5.41 %N 5.78 %Sn 24.52; found %C 49.45 %H 5.49 %N 5.61 %Sn 24.24

IR(KBr): ν (cm^{-1}) 3030,3085(aromatic C-H), 2850,2920,2950 (aliphatic C-H), 1430-1600(C-C,C-N in ring), see Fig.14

1H NMR ($CDCl_3$): δ (ppm) 0.585 (approximately triplet, CH_2-Sn), 0.90-1.73 (m, CH_2), 7.968-8.18(m, aromatic H) 9.797(dd, $J=4.7$ Hz, aromatic H)

^{13}C ($CDCl_3$): δ (ppm) 13.435, 25.841, 28.224, 42.472 (butyl C), 125.197, 127.743,129.910,139.770,149.088(C in ring), see Fig.15

3.3.3.2 Organotin compound and S-donor ligand

(1) Triallyltin chloride and sodium diethyldithiocarbamate (Na dtc) (novel compound)

Anhydrous stannic chloride (17 g, 0.06 mole) in dry toluene (50 mL) was added dropwise to a cooled solution of tetraallyltin (5.21 g,0.02 mole) in dry toluene (150 mL) while dry nitrogen gas was passed through the solution with thoroughly stirring. When the addition was completed, the stirring was continued at room temperature ($>25^\circ C$) for 1 hour. A solution of sodium diethyldithiocarbamate (18.2 g, 0.08 mole) in absolute ethanol (100 mL) was added dropwise with

stirring. The solution became cloudy. The stirring was continued for 1 hour after the addition had completed. The suspension was filtered off and the filtrate was evaporated under diminished pressure to leave a crude product which was purified by adding dry hexane and sodium chloride thus formed was filtered off. The filtrate was again evaporated to leave viscous, yellow liquid (27.3 g), a yield of 87.3% based on stannic chloride.

Elemental analysis : $C_{14}H_{25}NS_2Sn$ requires %Sn 30.36; found %Sn 32.03

IR (neat) : $\nu(\text{cm}^{-1})$ 3080 (olefinic C-H), 2962 (aliphatic C-H), 1625 (C=C), 1510 (C-N), 990 (C-S), see Fig.16

^1H NMR (CDCl_3), δ (ppm) 1.291 (t, $J = 7.0$ Hz, CH_3), 2.833 (s, $\text{CH}_2\text{-Sn}$), 3.798 (m, CH_2), 5.1 ($\text{CH}_2\text{=C-}$), 6.09 (m, -CH-R)

^{13}C NMR (CDCl_3), δ (ppm) 12.080, 40.739, 49.298, 114.524, 134.406, 198.87, see Fig.17

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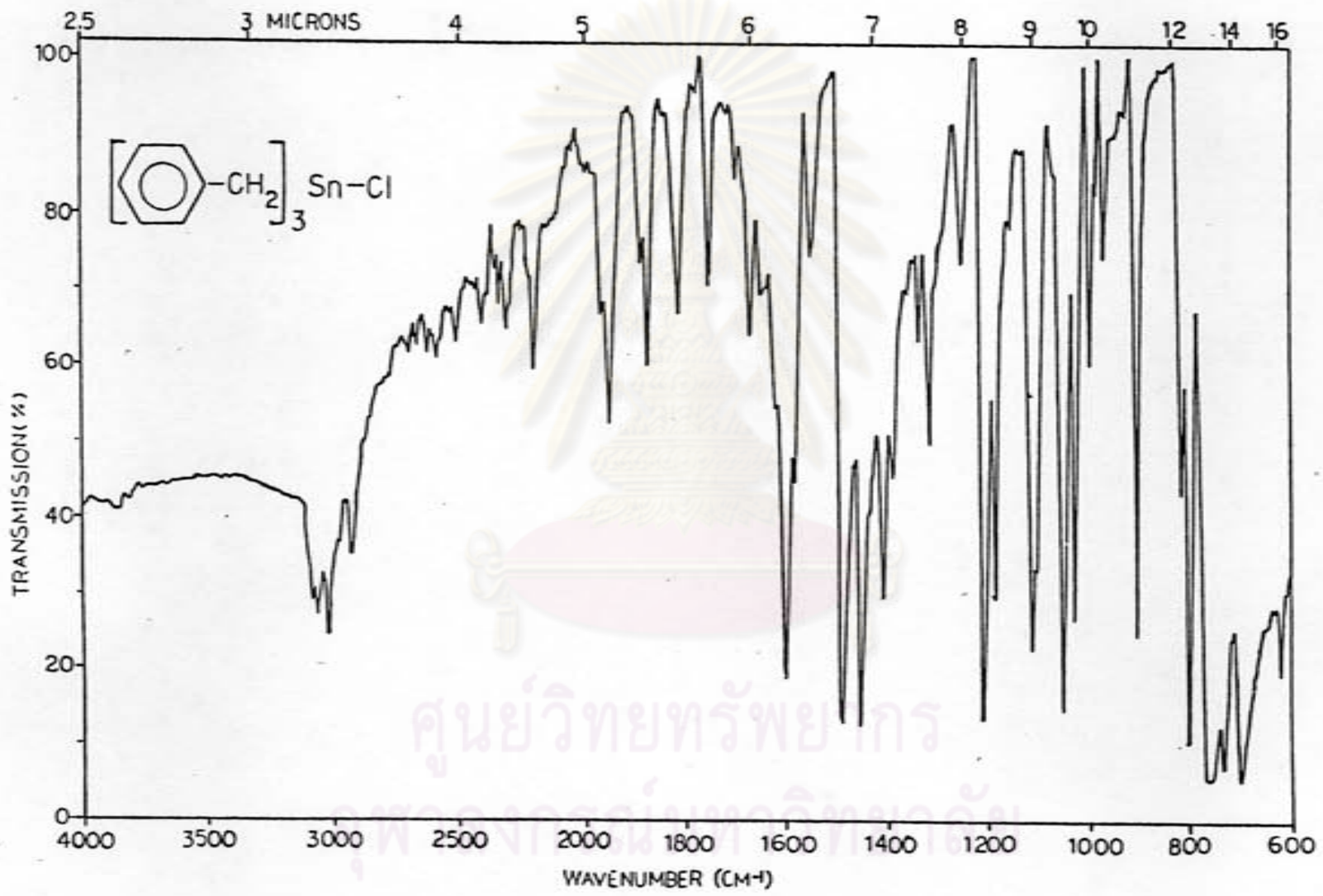


FIGURE 1 : IR Spectrum of tribenzyltin chloride

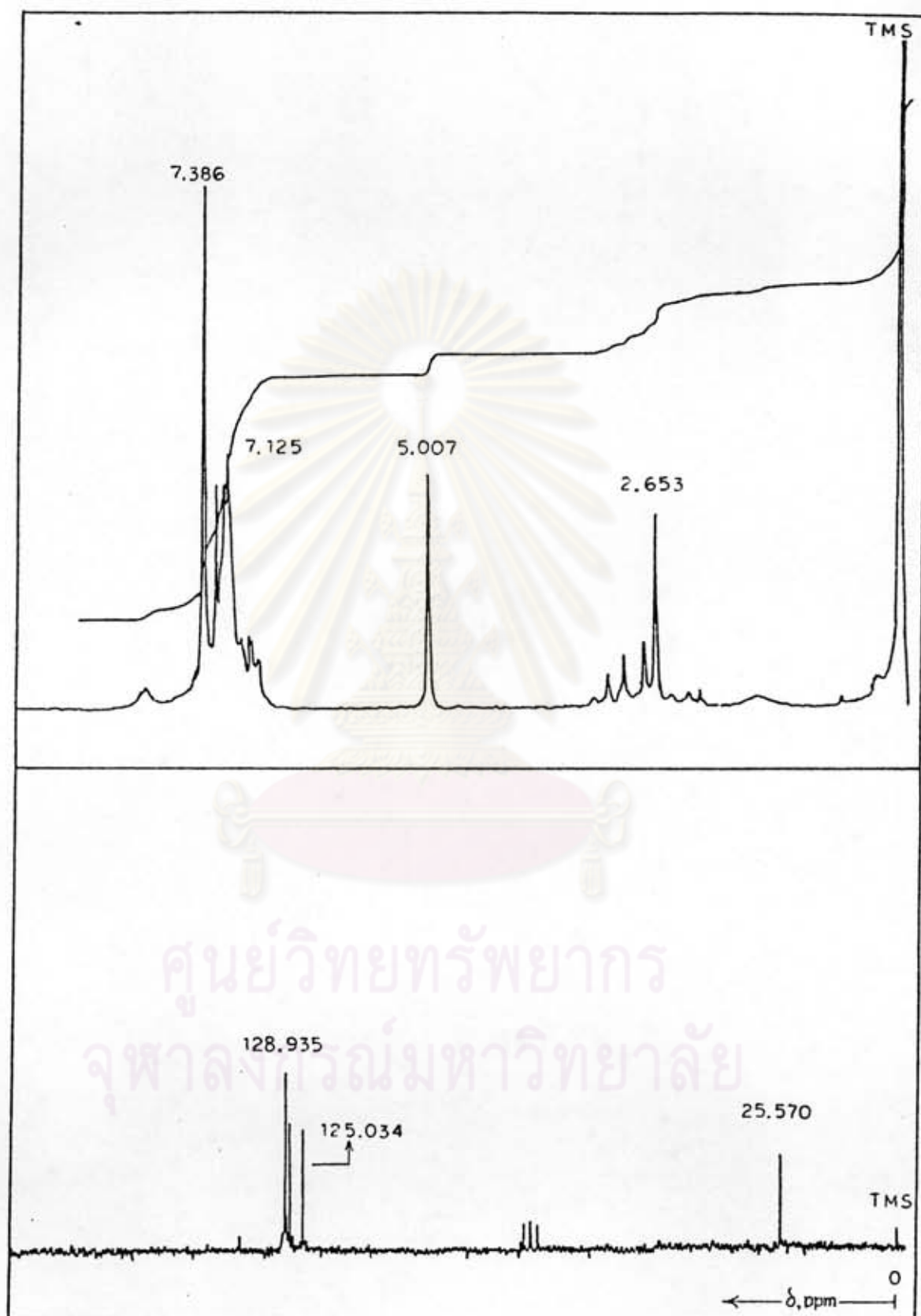


FIGURE 2 : ^1H and ^{13}C NMR Spectra of tribenzyltin chloride

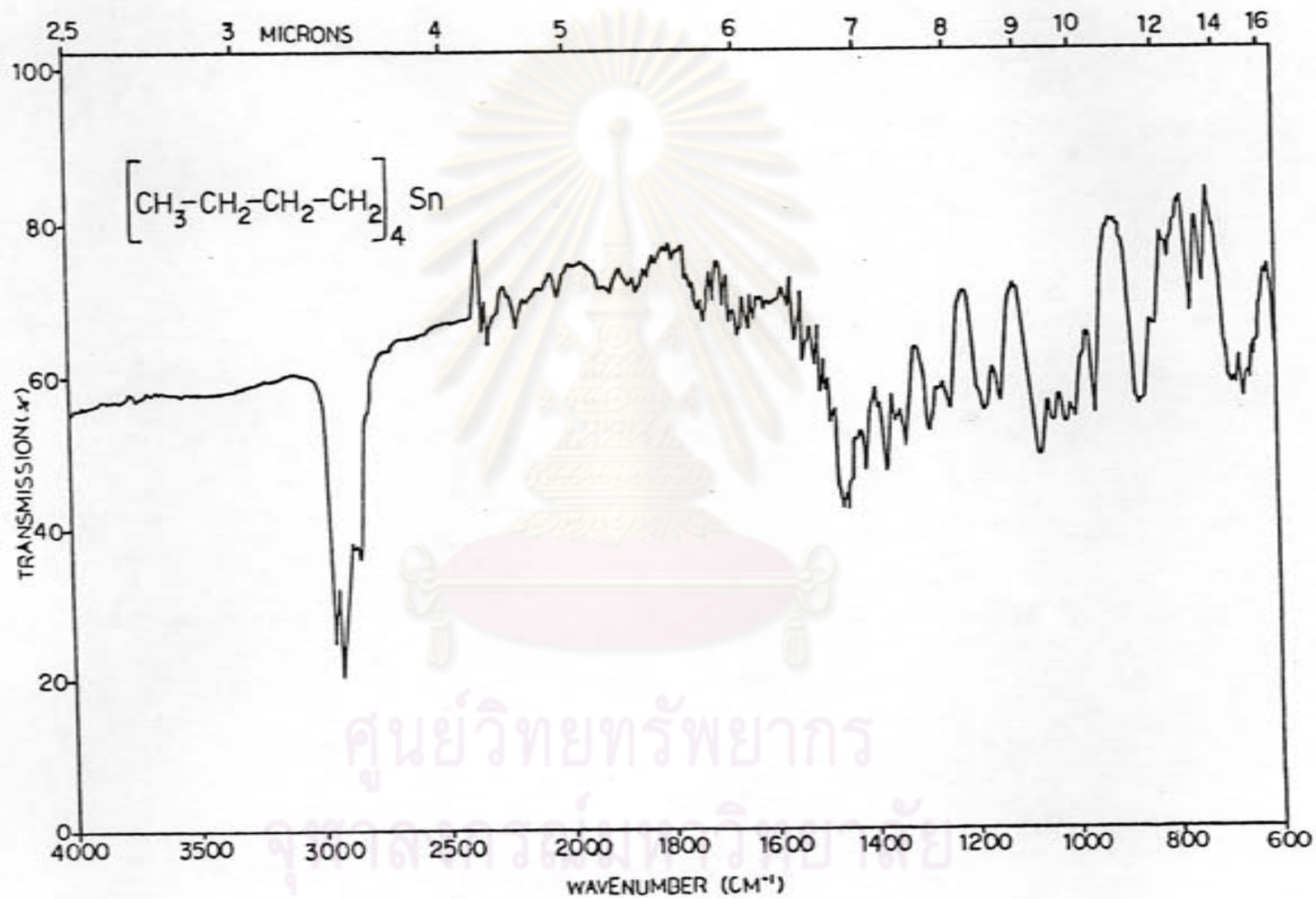


FIGURE 3 : IR Spectrum of tetrabutyltin

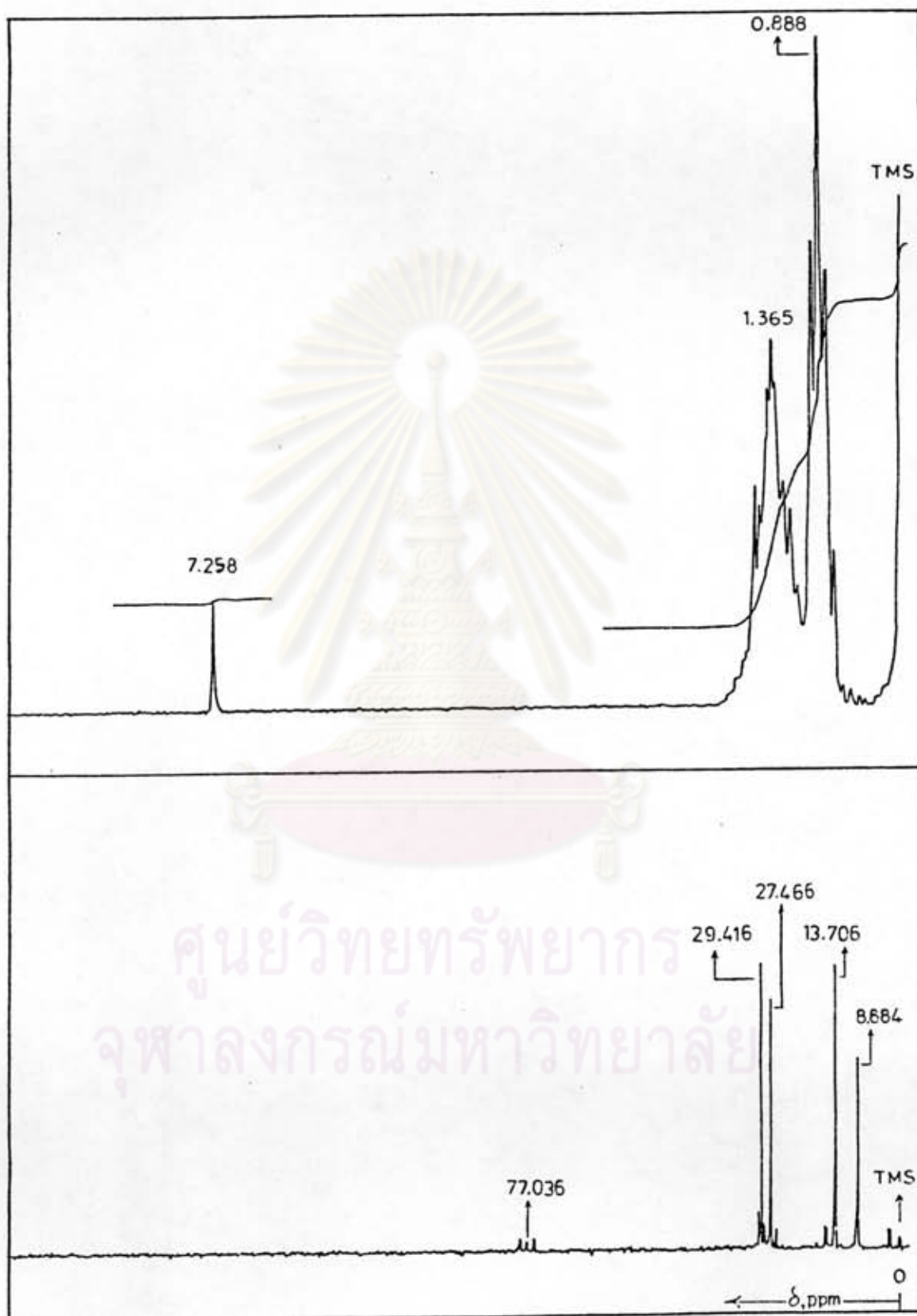


FIGURE 4 : ^1H and ^{13}C NMR Spectra of tetrabutyltin

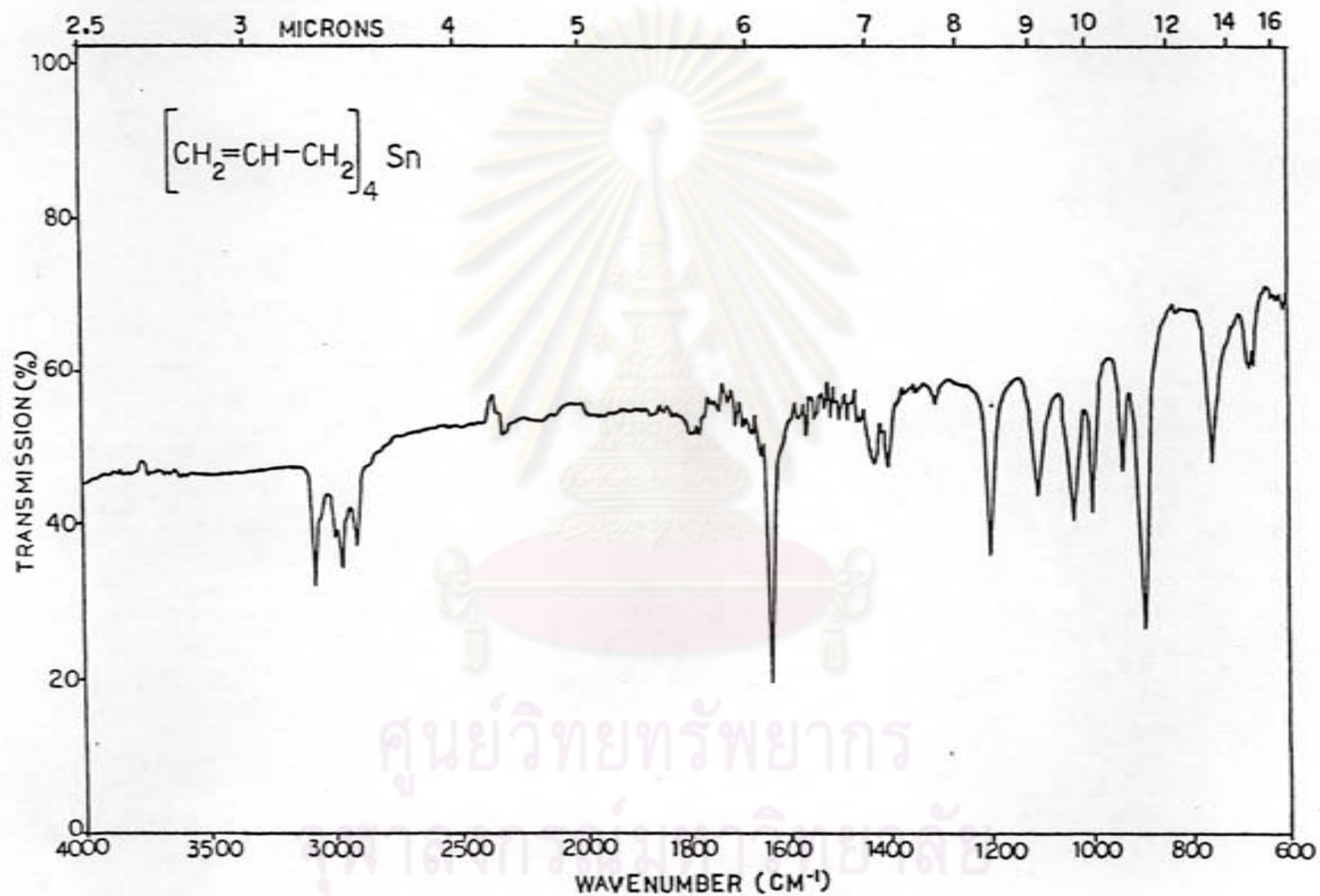


FIGURE 5 : IR Spectrum of tetraallyltin

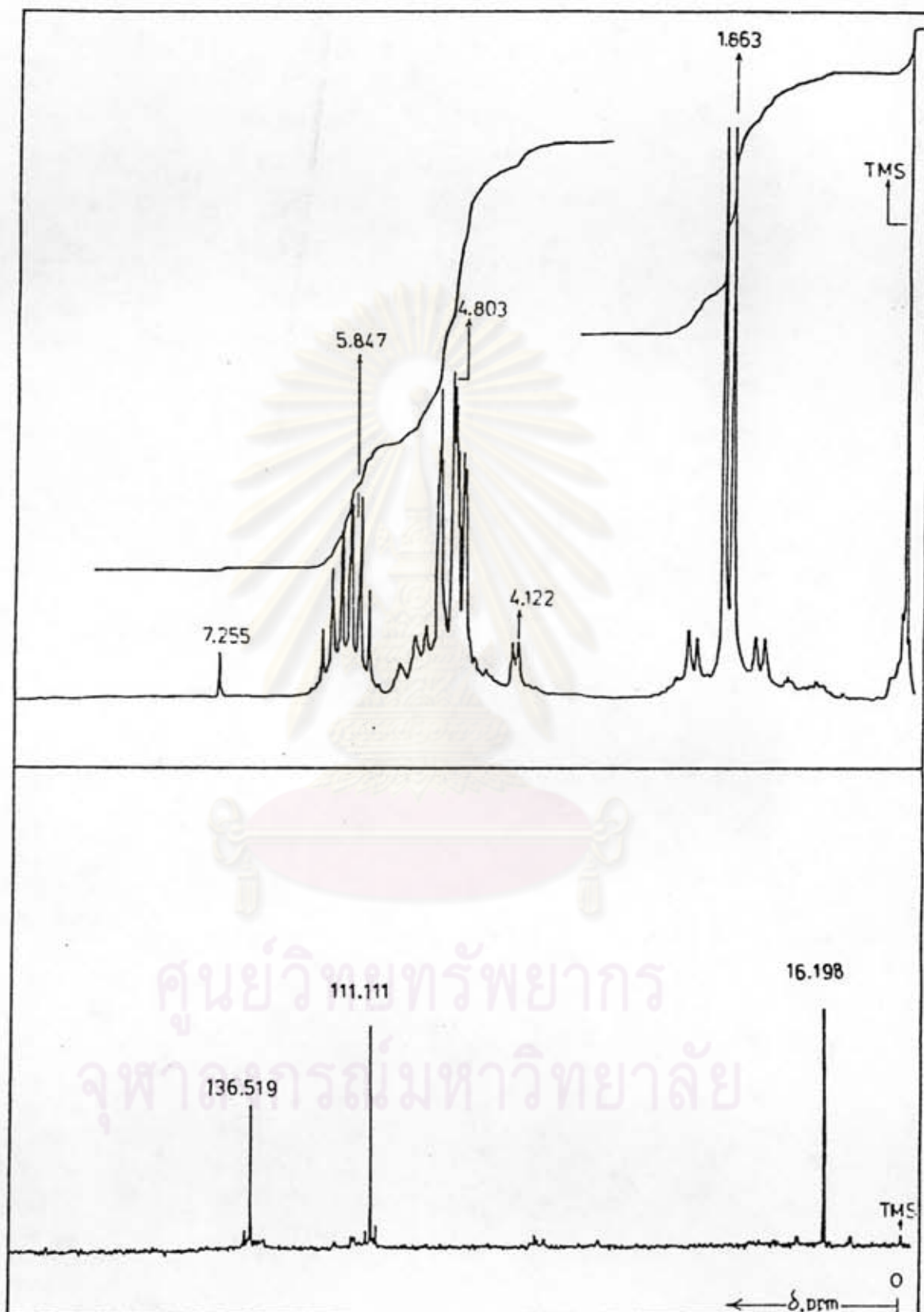


FIGURE 6 : ^1H and ^{13}C NMR Spectra of tetraallyltin

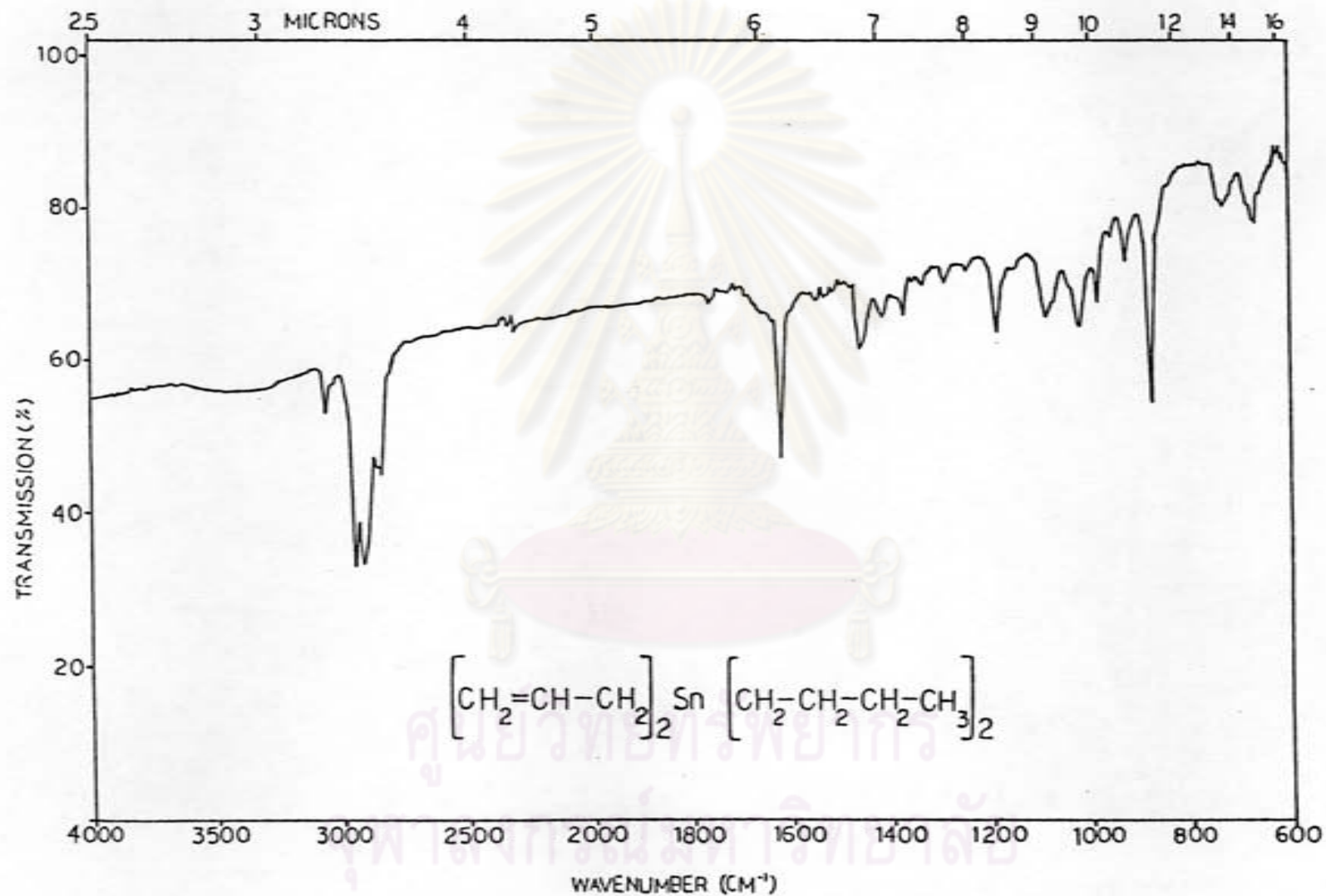


FIGURE 7 : IR Spectrum of diallyldibutyltin

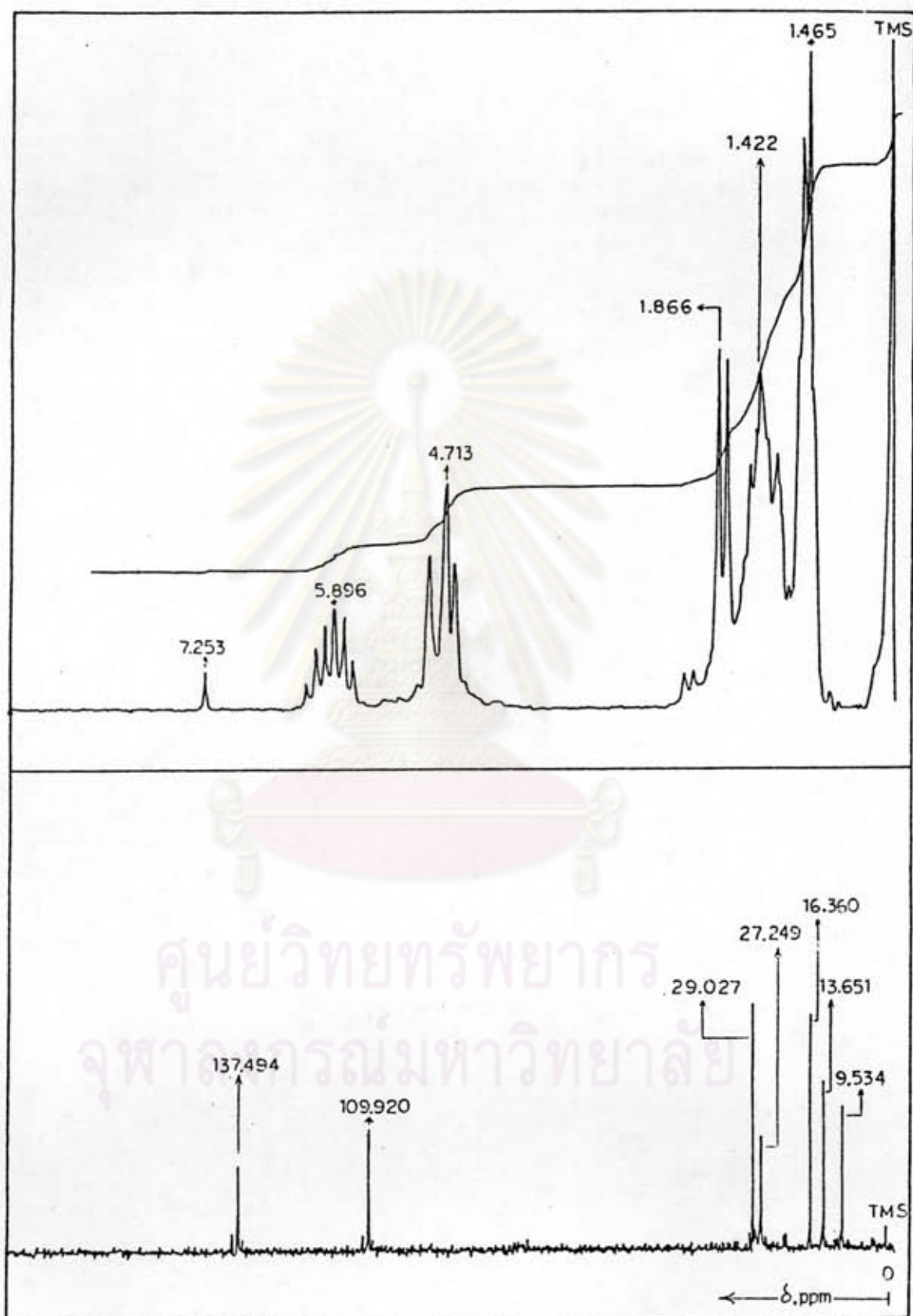


FIGURE 8 : ^1H and ^{13}C NMR Spectra of diallyl-dibutyltin

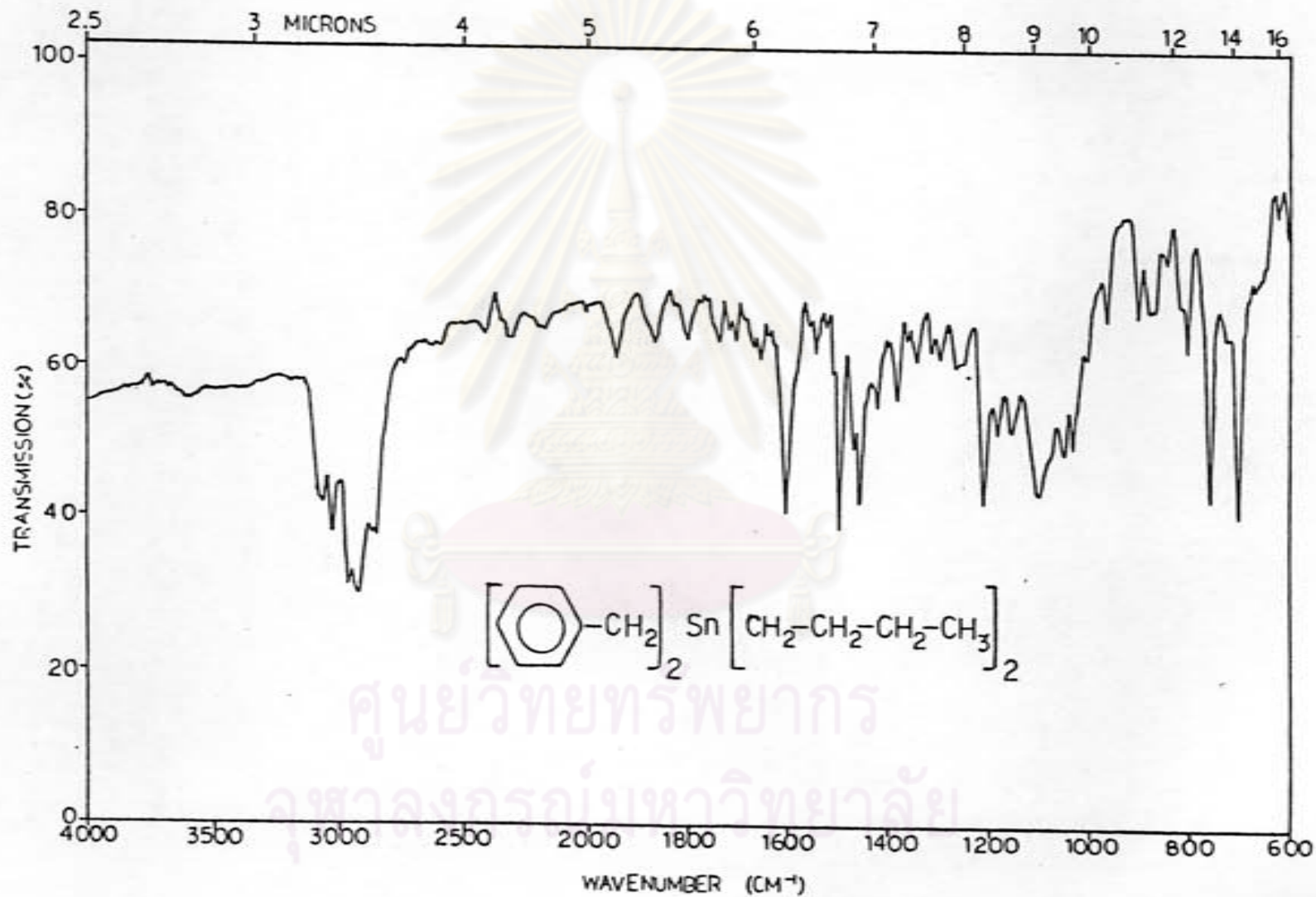


FIGURE 9 : IR Spectrum of dibenzyl dibutyltin

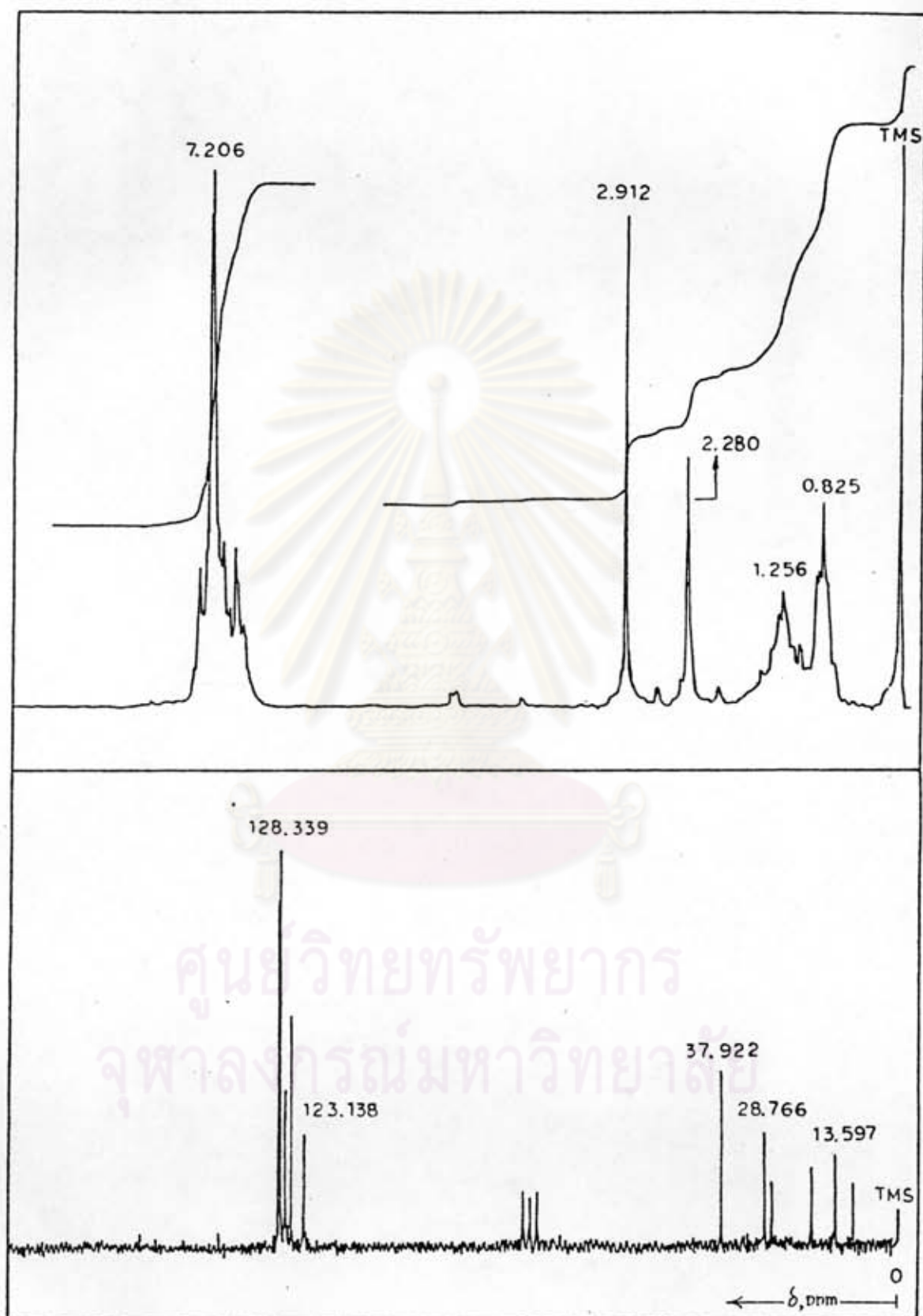


FIGURE 10 : ^1H and ^{13}C NMR Spectra of dibenzyl-dibutyltin

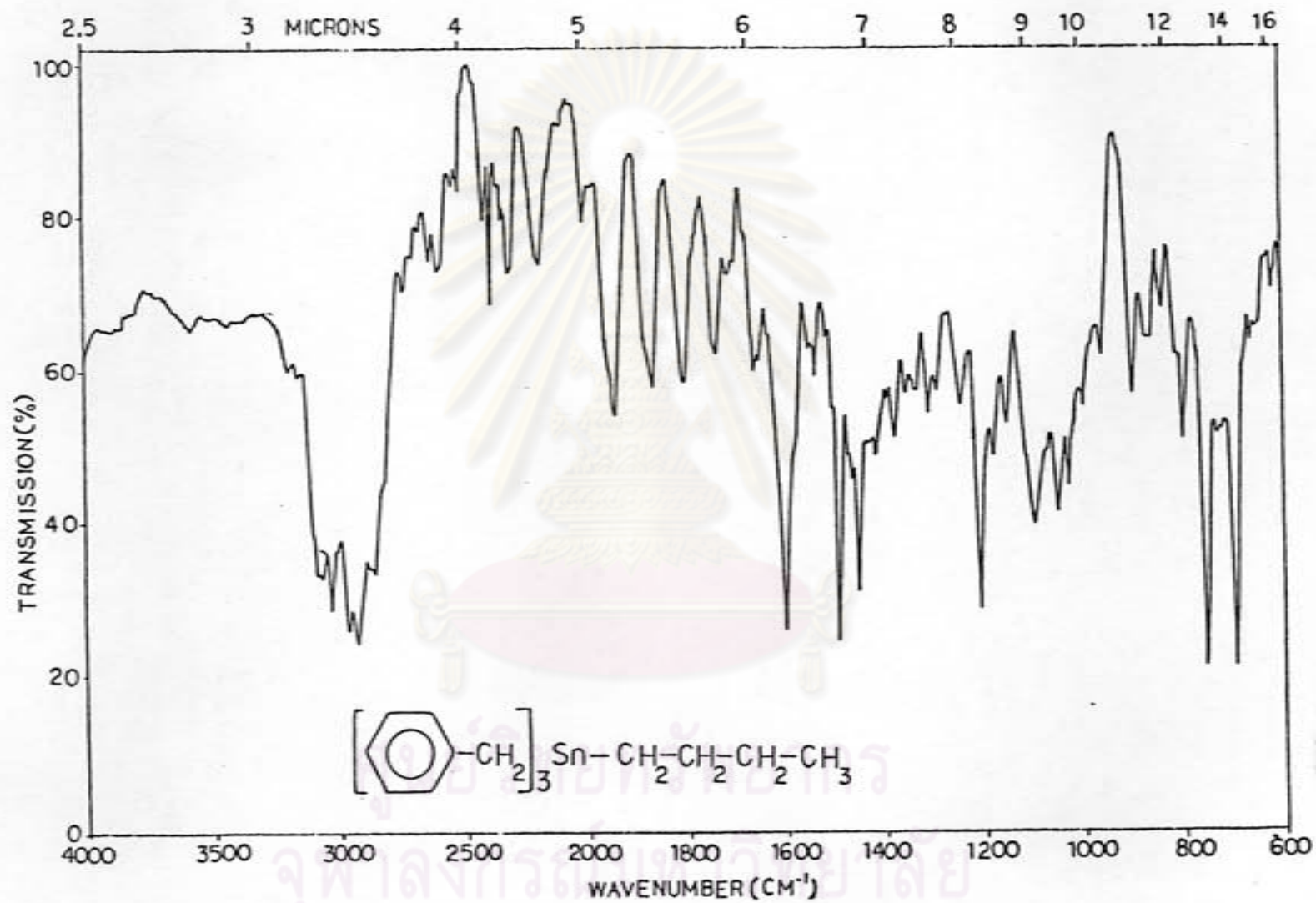


FIGURE 11 : IR Spectrum of tribenzyl-n-butyltin

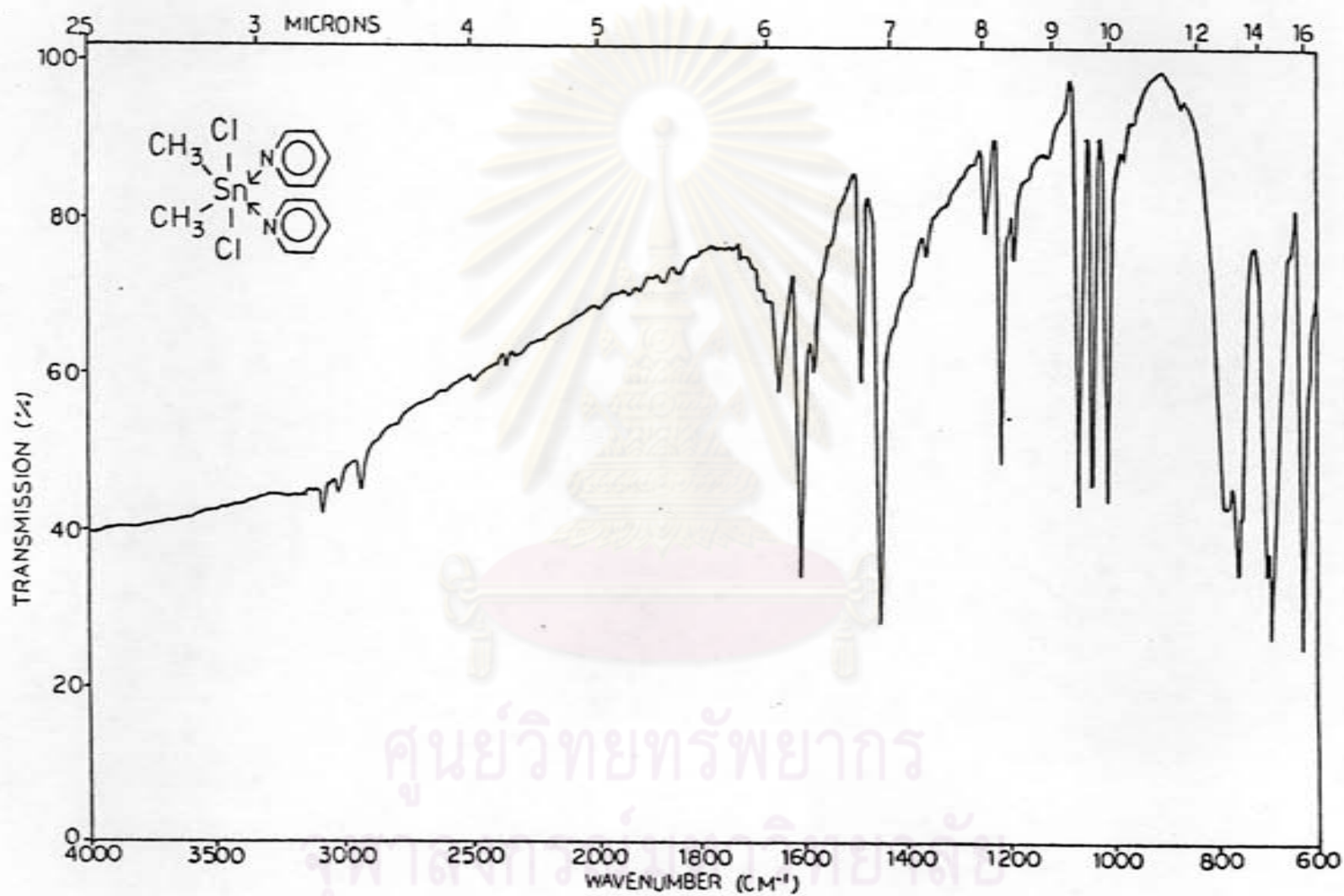


FIGURE 12 : IR Spectrum of dimethyltin dichloride.2 pyridine

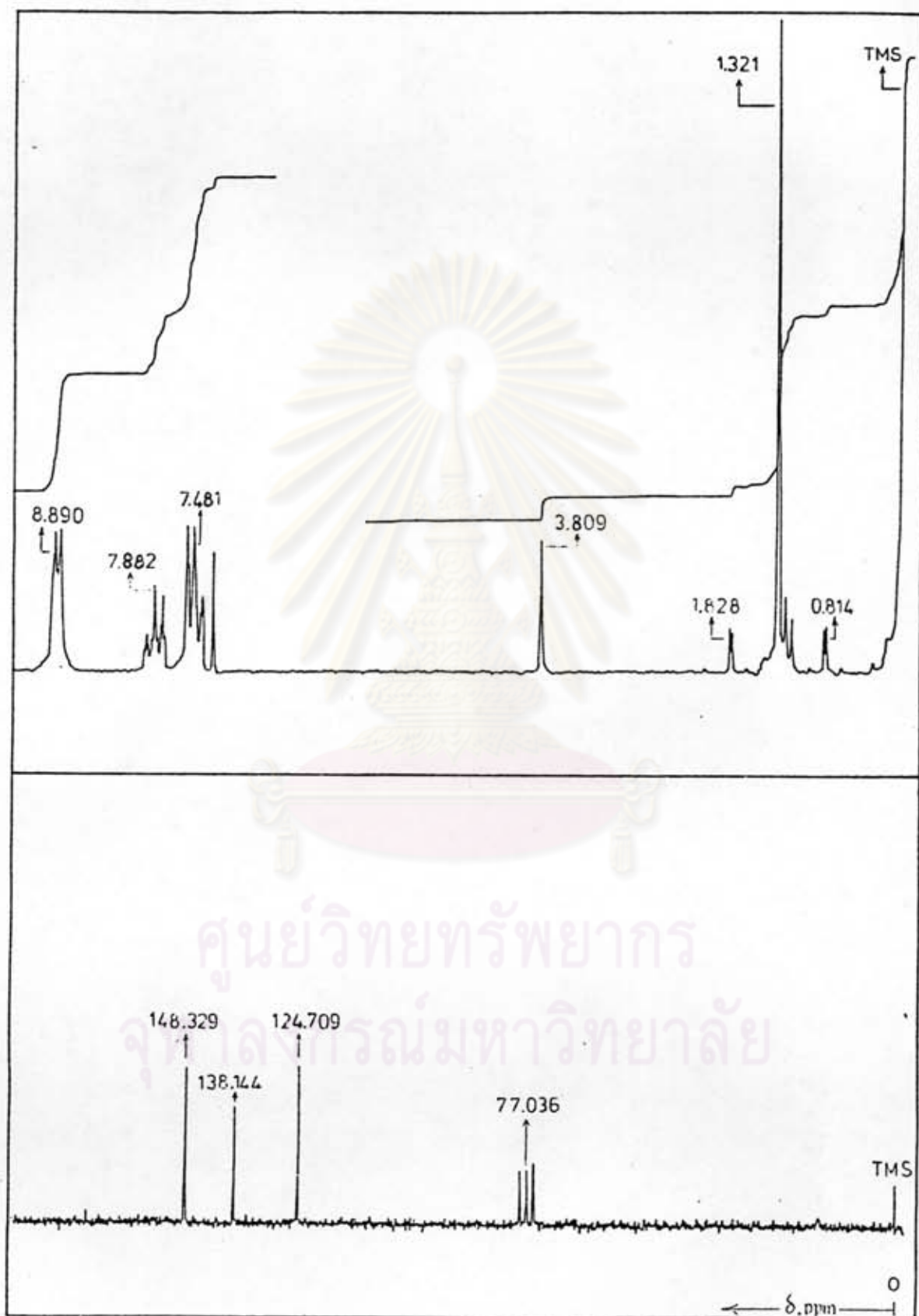


FIGURE 13 : ^1H and ^{13}C NMR Spectra of dimethyltin dichloride.2 pyridine

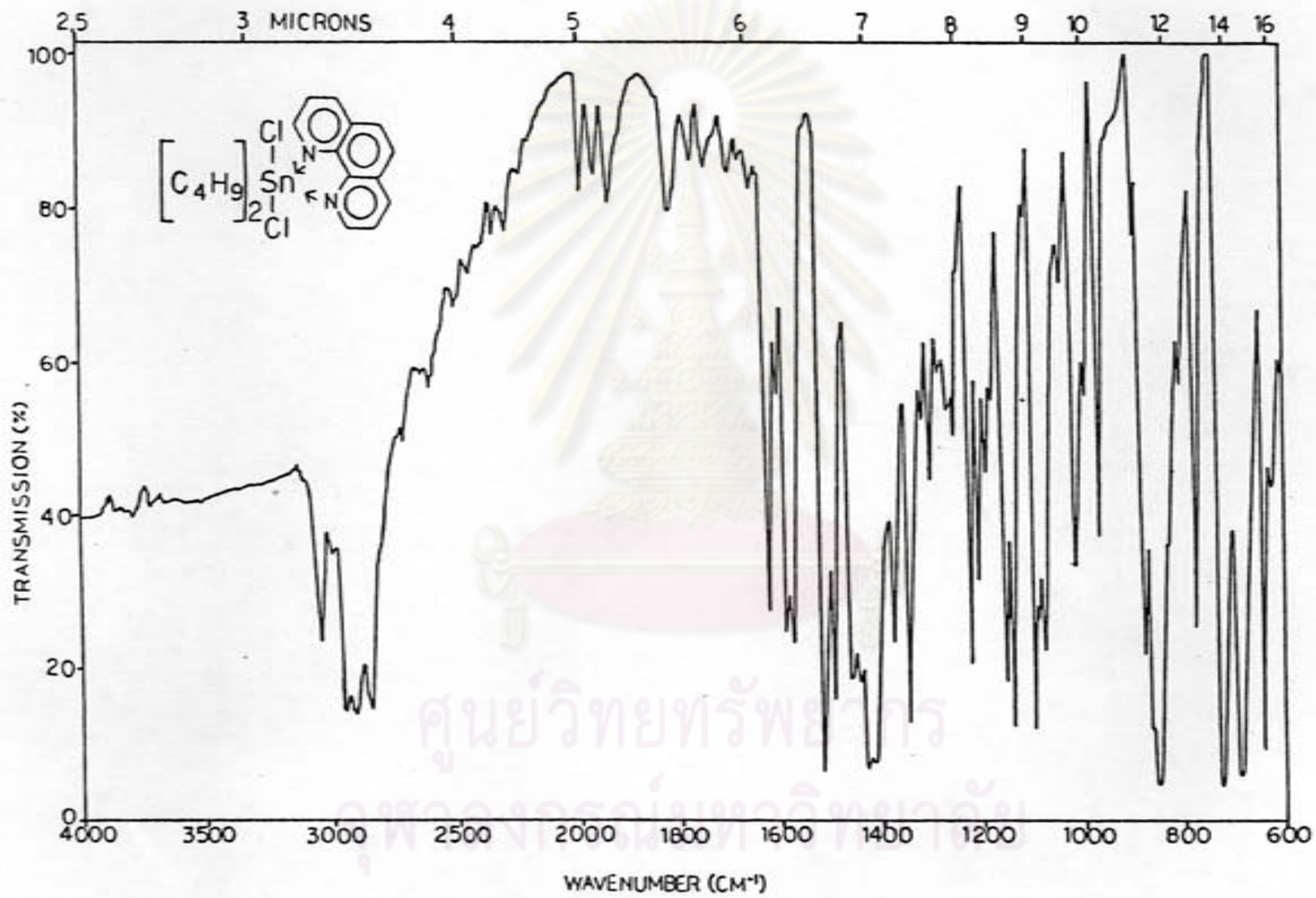


FIGURE 14 : IR Spectrum of dibutyltin dichloride.1,10- phenanthroline

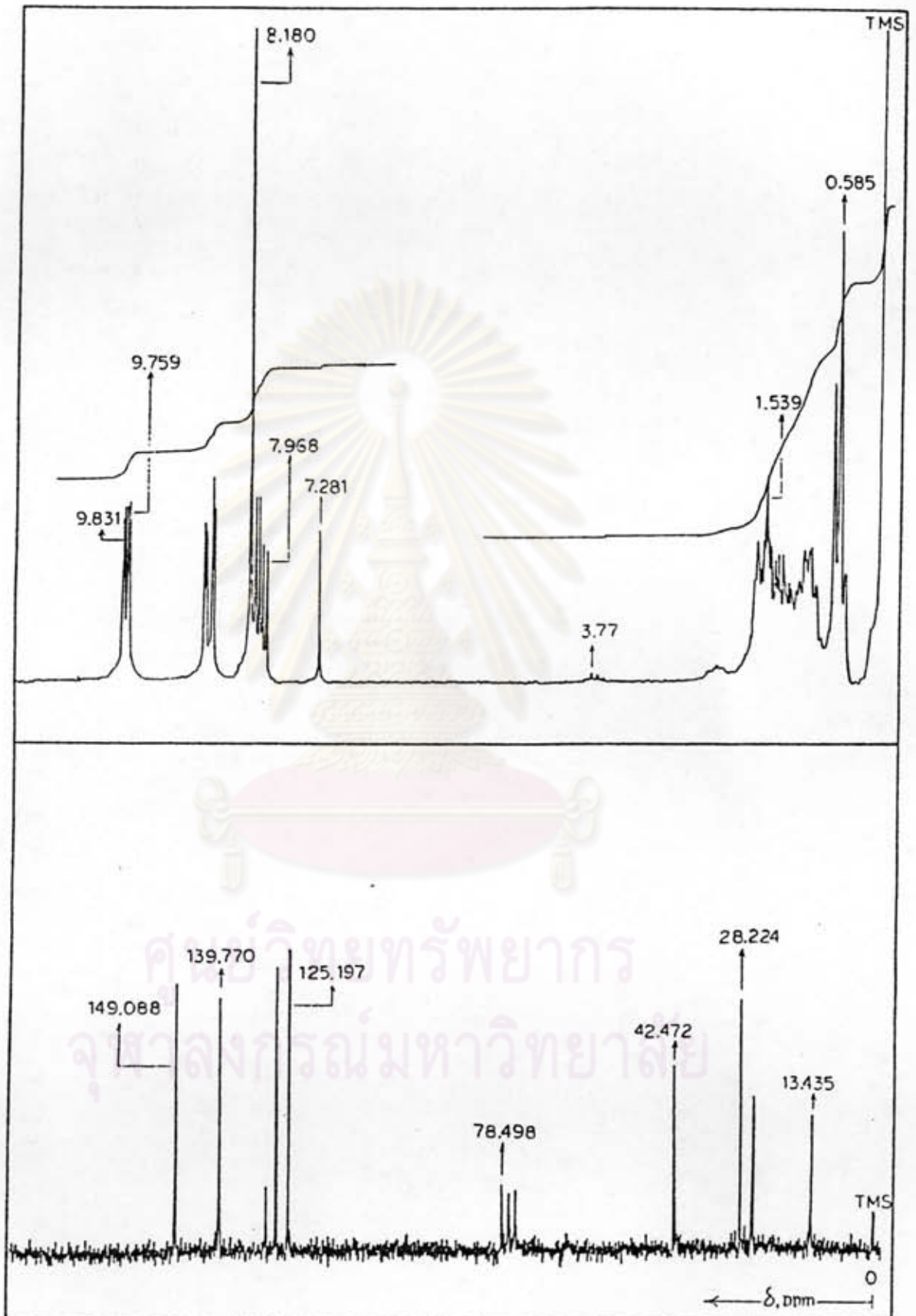


FIGURE 15 : ^1H and ^{13}C NMR of dibutyltin dichloride.

1, 10-phenanthroline

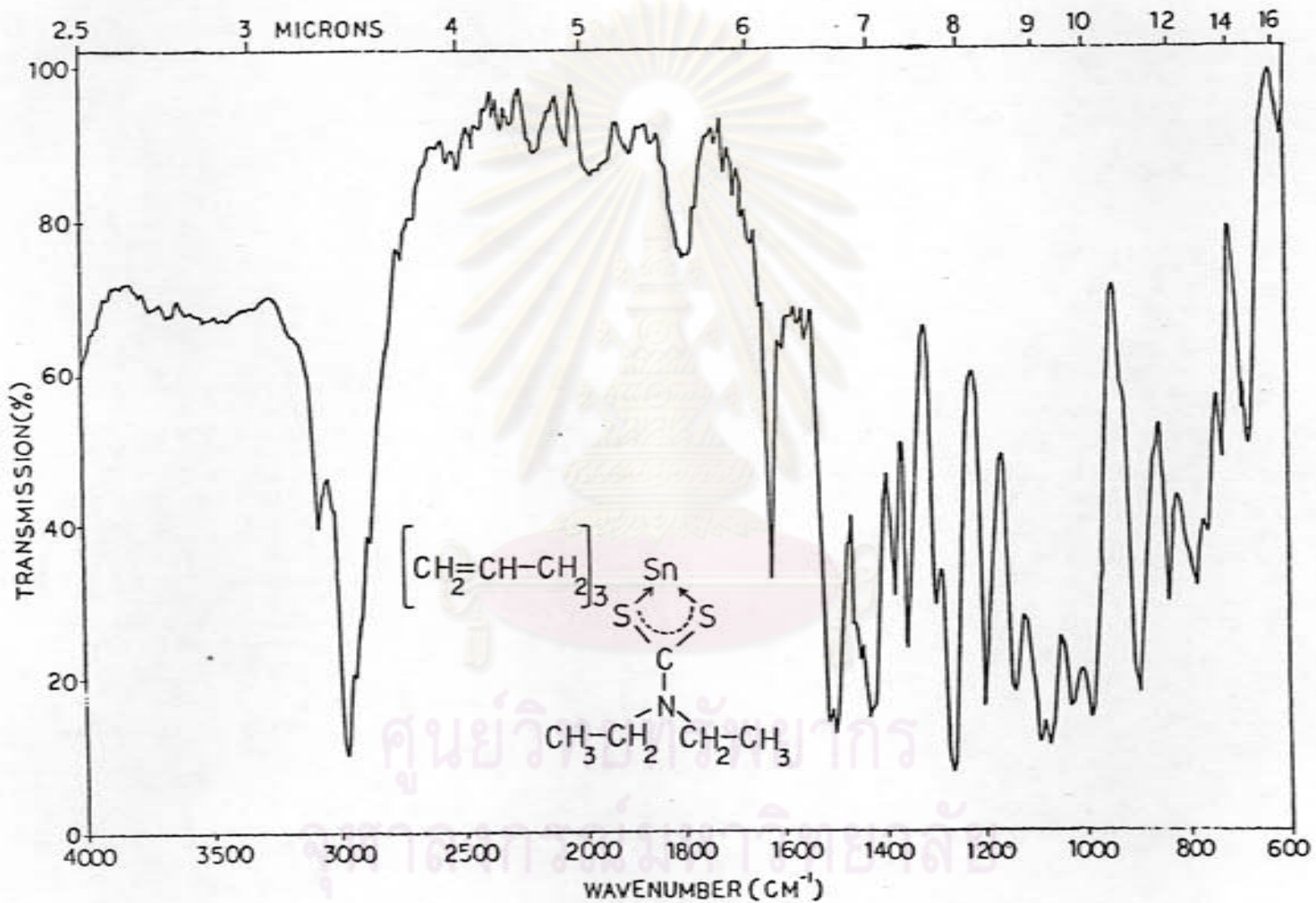


FIGURE 16 : IR Spectrum of triallyltin diethyldithio carbamate

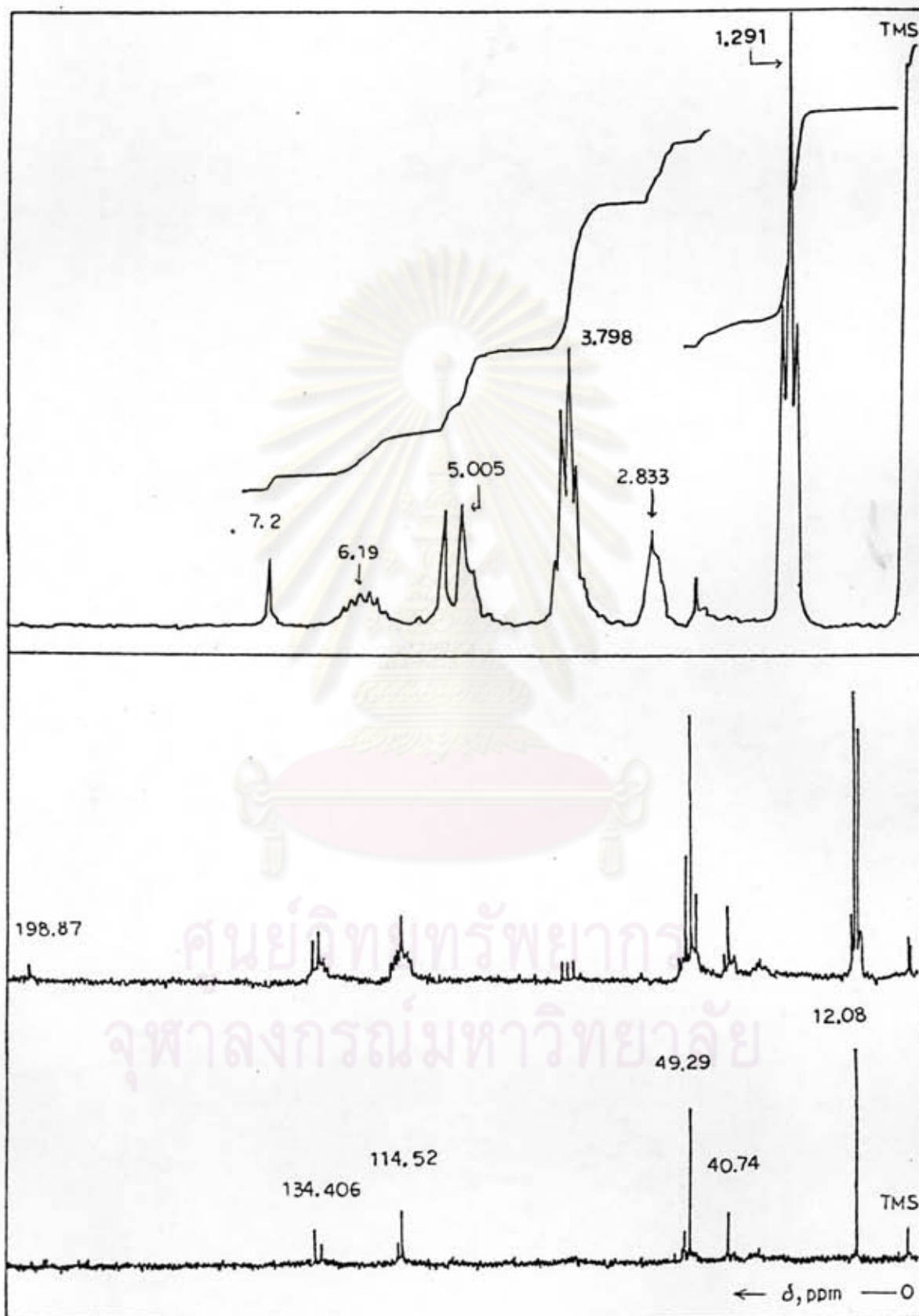


FIGURE 17 : ^1H and ^{13}C NMR of triallyltin diethyl-dithiocarbamate

3.4 The Solubility and Stability of Organotin Products

The organotin compounds which are used for gasoline blendings should achieve the gasoline solubility and stability. The properties of organotin products were summarized in the table below.

Table 1 : The solubility and stability of organotin products

Compounds	State/(b.p.) or m.p.	Solubility and Stability
Tetrabutyltin	liquid/(128-130 °C, 3 mm.Hg)	soluble in hexane, gasoline; stable
Tetraallyltin	liquid/(84-88 °C, 2 mm.Hg)	soluble in hexane, gasoline; unstable in gasoline
Tribenzyltin chloride	solid/142-144 °C	soluble in toluene, less soluble in hexane; stable
Dibenzyltin dichloride	solid/161-163 °C	soluble in ether, less soluble in gasoline; stable
Diallyldibutyltin	liquid/(114-115 °C, 2 mm.Hg)	soluble in hexane, gasoline; moderately stable
Dibenzylidibutyltin	liquid/(164-166 °C, 6 mm.Hg)	soluble in hexane, toluene; stable
Tribenzylbutyltin	liquid/(200-203 °C, 3 mm.Hg)	soluble in hexane, gasoline; stable
Dimethyltin dichloride .2 pyridine	solid/161 °C	less soluble in toluene, gasoline
Dibutyltin dichloride .1,10-phenanthroline	solid/200 °C	less soluble in toluene, gasoline
Triallyltin .diethyldithiocarbamate	liquid/-	soluble in hexane, toluene; unstable in gasoline
Tetraoctyltin (E.Merck)	liquid	soluble in hexane; stable

3.5 Determination of Antiknock Property of the Organotin Compounds in Various Gasoline Bases.

The octane numbers of various gasoline bases blended with organotin compounds were presented in the tables below. The octane determination was made by Petroleum Authority of Thailand (PTT).

TABLE 2 Blends of tetraethyltin with unleaded gasoline base (see figure 18)

Unleaded Gasoline Base				
Blend composition	Gasoline 1 (aromatics 10.22% vol.)		Gasoline 2 (aromatics 41.44% vol.)	
	RON	MON	RON	MON
Base (clear)	78.0	-	-	90.0
Base + 0.72 gSn/L	80.5	-	-	91.4
Base + 1.44 gSn/L	81.3	-	-	92.0
Base + 2.16 gSn/L	81.7	-	-	92.1
Base + 2.88 gSn/L	81.7	-	-	92.3
Base + 3.60 gSn/L	83.5	-	-	92.4

The octane number of the blends increased as tin content increased. The octane number increased 2-3 units.

TABLE 3 Blends of diallyldibutyltin with unleaded gasoline base (see figure 19)

Unleaded Gasoline Base				
Blend composition	Gasoline 1 (aromatics 10.22% vol.)		Gasoline 2 (aromatics 41.44% vol.)	
	RON	MON	RON	MON
Base (clear)	78.0	-	-	90.0
Base + 0.83 gSn/L	81.1	-	-	91.2
Base + 1.66 gSn/L	82.1	-	-	91.7
Base + 2.48 gSn/L	82.6	-	-	92.0
Base + 3.33 gSn/L	82.8	-	-	92.4
Base + 4.14 gSn/L	83.1	-	-	-

The octane number of the blends increased as tin content increased. The octane number increased 3-4 units.

TABLE 4 Blends of dibenzylidibutyltin with unleaded gasoline base

Unleaded Gasoline Base				
Blend composition	Gasoline 3 (aromatics 10.22% vol.)		Gasoline 4 (aromatics 41.44% vol.)	
	RON	MON	RON	MON
Base (clear)	80.1	-	-	90.0
Base + 0.6 gSn/L	81.6	-	-	91.0
Base + 1.2 gSn/L	82.0	-	-	91.1
Base + 1.8 gSn/L	82.0	-	-	91.1
Base + 2.4 gSn/L	82.0	-	-	91.1
Base + 3.0 gSn/L	82.6	-	-	91.1

The octane number of the blends increased as tin content increased. The octane number increased 1 -2 units.

TABLE 5 Blends of tetraoctyltin with unleaded gasoline base

Unleaded Gasoline Base				
Blend composition	Gasoline 3 (aromatics 10.22% vol.)		Gasoline 4 (aromatics 41.44% vol.)	
	RON	MON	RON	MON
Base (clear)	80.1	-	-	90.0
Base + 0.4 gSn/L	81.6	-	-	90.8
Base + 0.8 gSn/L	81.8	-	-	91.0
Base + 1.2 gSn/L	82.1	-	-	91.1
Base + 1.6 gSn/L	82.0	-	-	91.1
Base + 2.0 gSn/L	82.2	-	-	91.2

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 The octane number of the blends increased as tin content increased. The octane number increased 1-2 units.

TABLE 6 Blends of tribenzyltin chloride, dimethyltin dichloride.2 pyridine and dibutyltin dichloride.0-phenanthroline with unleaded gasoline base

Unleaded Gasoline Base				
Blend composition	Gasoline 3 (aromatics 10.22% vol.)		Gasoline 4 (aromatics 41.44% vol.)	
	RON	MON	RON	MON
Base (clear)	80.1	-	-	90.0
Base + 0.25 gSn/L from Bz SnCl	82.0	-	-	90.3
Base + 0.25 gSn/L from Me SnCl .2Py	82.0	-	-	91.5
Base + 0.25 gSn/L from Bu SnCl.phen	82.0	-	-	91.3

The blends of tribenzyltin chloride and the organotin - complexes with gasoline were not suitable for practical uses since the compounds were only sparingly soluble in gasoline; therefore, they must be dissolved in toluene (5% wt/vol) and 25 ml portions of the solutions were blended with gasoline in order to determine their octane number. In this case, the increment of octane number may be due to toluene.

TABLE 7 Blends of tribenzyl-n-butyltin with unleaded gasoline

Unleaded Gasoline Base
 Gasoline 5 - Light naphtha 70% + Reformate 30%
 Gasoline 6 - Light naphtha 20% + Reformate 80%

Blend composition	Gasoline 5		Gasoline 6	
	RON	MON	RON	MON
Base (clear)	70.6	-	-	86.1
Base + 0.62 gSn/L	70.9	-	-	86.2
Base + 1.24 gSn/L	70.9	-	-	86.2
Base + 2.17 gSn/L	70.9	-	-	86.2

The octane number of the blends did not increase significantly with addition of tin compound.

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TABLE 8 Blends of tetraethyltin with leaded gasoline base

Blend composition	Leaded Gasoline Base			
	Gasoline 5		Gasoline 6	
	RON	MON	RON	MON
Base (clear)	70.6	-	-	86.1
Base + 0.25 gPb/L	80.0	-	-	92.6
Base + 0.35 gPb/L	81.4	-	-	93.1
Base + 0.44 gPb/L	82.0	-	-	93.2
Base + 1.07 gSn + 0.25 gPb/L	77.4	-	-	89.3
Base + 2.14 gSn + 0.25 gPb/L	77.7	-	-	89.7
Base + 1.07 gSn + 0.35 gPb/L	78.0	-	-	90.1

The octane number of the leaded gasoline decreased by 3 units, with the presence of tin compound.

TABLE 9 Blends of tribenzyl-n-butyltin with leaded gasoline base
 Lead Gasoline Base
 Base : The same as used with tetrabutyltin

Blend composition	Gasoline 5		Gasoline 6	
	RON	MON	RON	MON
Base + 1.24 gSn + 0.25 gPb/L	76.5	-	-	89.6
Base + 2.17 gSn + 0.25 gPb/L	76.0	-	-	89.2
Base + 1.24 gSn + 0.35 gPb/L	77.7	-	-	89.8

The octane number of the leaded gasoline decreased by 3 units, with the presence of tin compound.

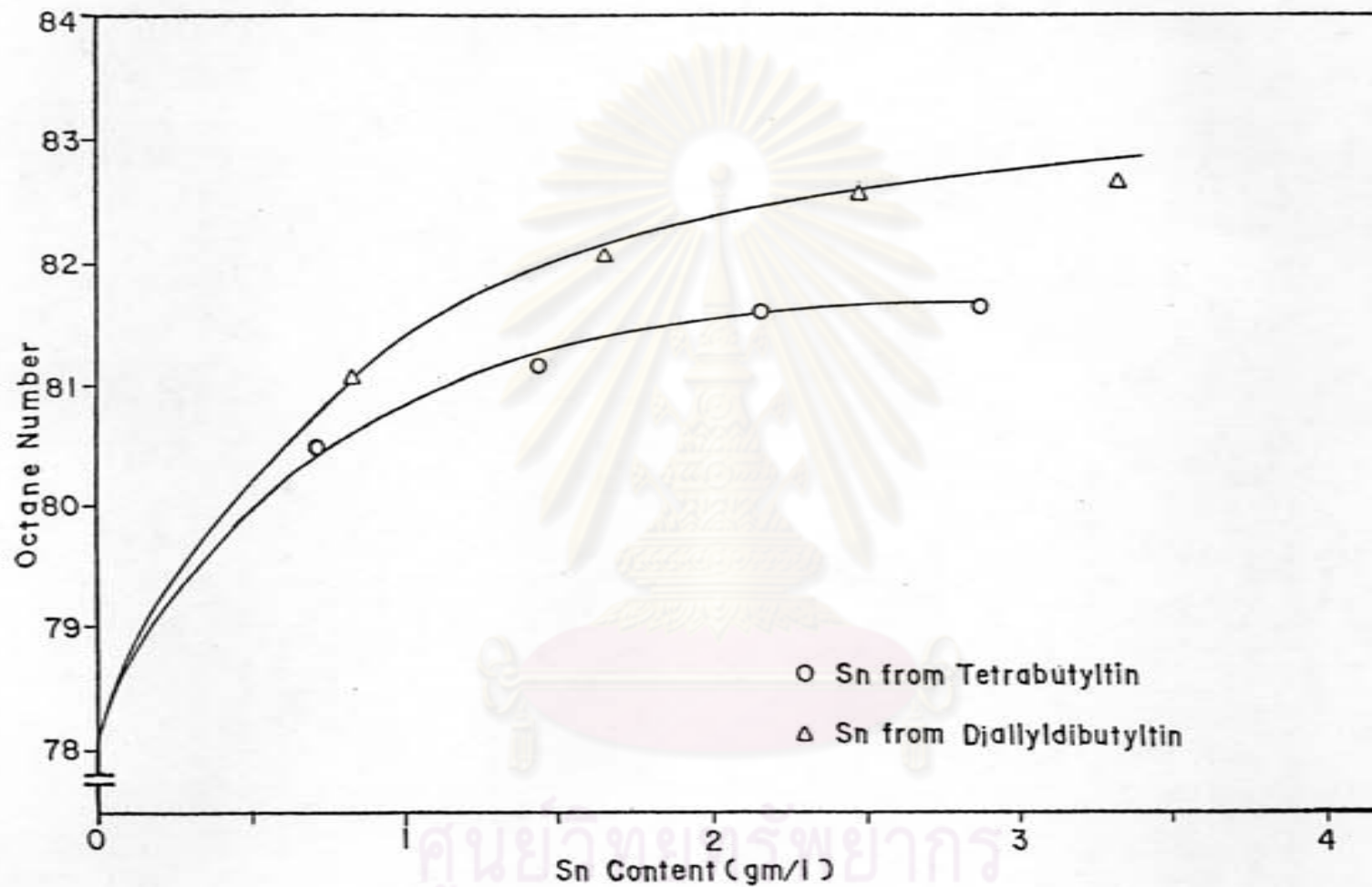


FIGURE 18 : Blends of tetrabutyltin and diallyldibutyltin with low octane unleaded gasoline base

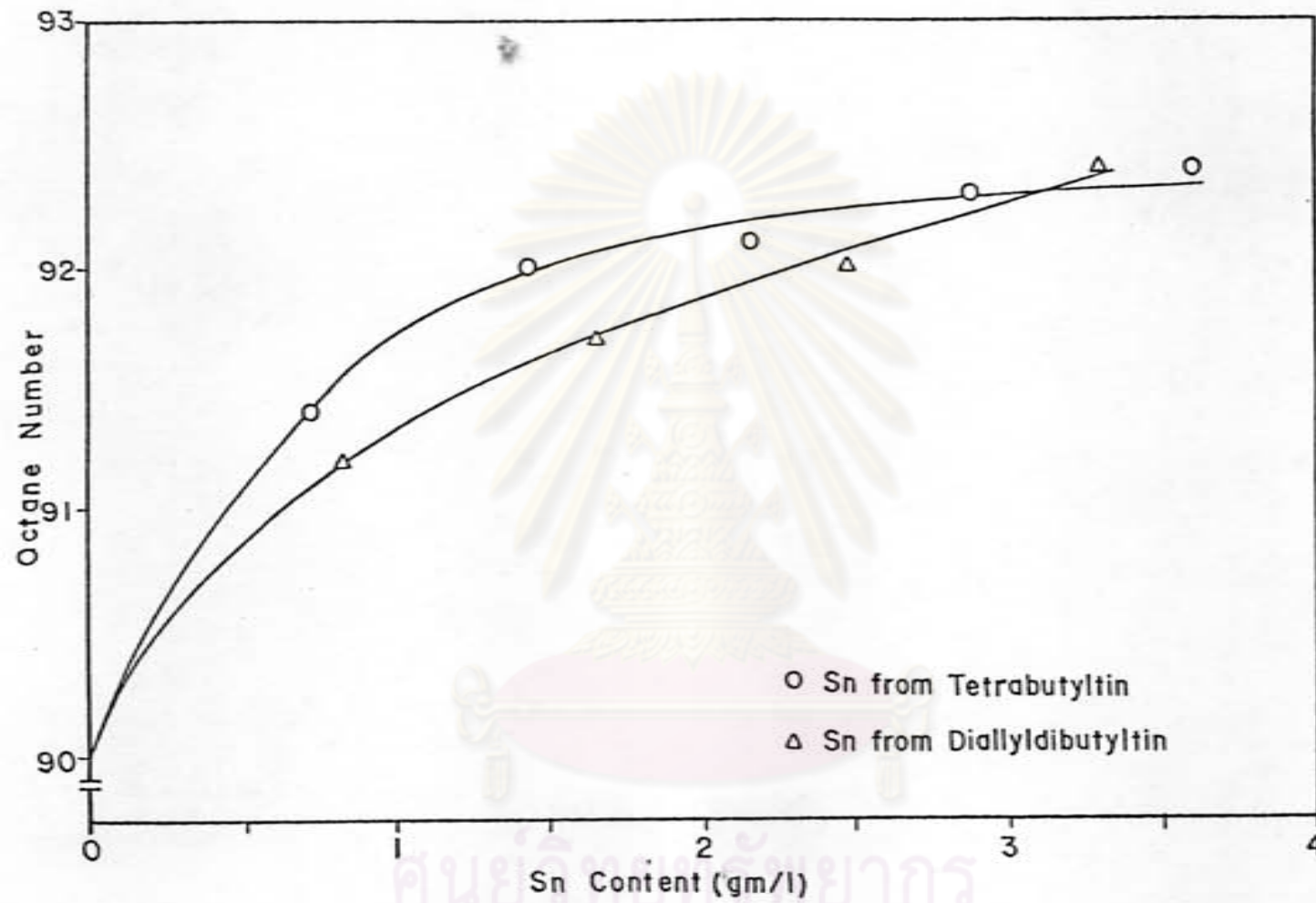


FIGURE 19 : Blends of tetrabutyltin and diallyldibutyltin with high octane unleaded gasoline base