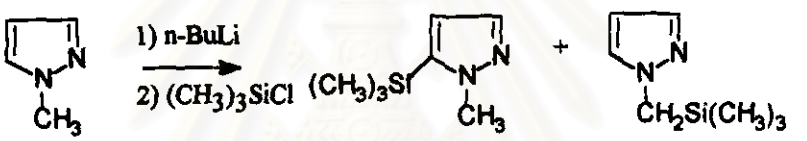
CHAPTER III

RESULTS AND DISCUSSIONS

3.1 Syntheses of photochemical reactants

3.1.1 Synthesis of 5-(trimethylsilyl)-1-methylpyrazole

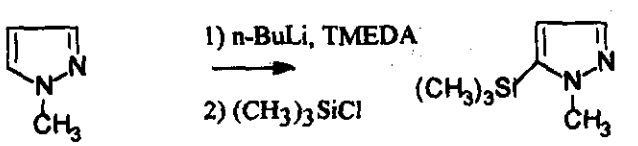
The synthesis of 5-(trimethylsilyl)-1-methylpyrazole was reported earlier by Butler and Alexander [7].



[1] [33] [34]

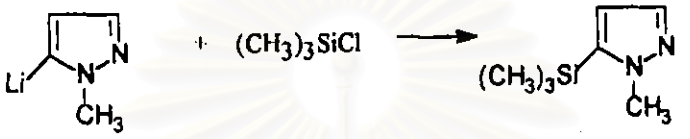
However, the competitive reaction at the N-methyl group could lead to the formation of a mixture of **[33]** and **[34]**.

Effenberger and Krebs [8] prepared 5-(trimethylsilyl)-1-methylpyrazole **[33]** from 1-methylpyrazole **[1]** via lithiation by n-butyllithium in the presence of TMEDA and subsequent silylation with chlorotrimethylsilane. They had avoided the competitive reaction by adding a complexing agent *N,N,N',N'*-tetramethyl-1,2-ethanediamine to the reaction.



[1] [33]

Pyrazole, [33] was therefore synthesized following the method of Effenberger and Krebs. The lithio derivative of [1] was obtained by rem deprotonation at position 5 of the pyrazole ring. And then the lithio derivative was quenched by adding chlorotrimethylsilane, led to the formation of [33] that was suitable for photochemical investigation.



[35] [33]

The ^{1}H-NMR spectrum of the purified product (Figure 1) revealed signals for 3-H and 4-H of the pyrazole ring at δ 7.44 (d, J = 2 Hz) and 6.33 (d, J = 2 Hz). It also exhibited a three-proton singlet at δ 3.94 for the methyl group on nitrogen. In addition, the spectrum showed a nine-proton singlet at δ 0.31 for the three equivalent methyl substituents of the trimethylsilyl group on the C-5 ring position. This data is thus consistent with the structure of 5-(trimethylsilyl)-1-methylpyrazole.

The proton decoupled ^{13}C-NMR spectrum (Figure 2) exhibited signals at δ 138.1, 114.4 and 146 ppm for C-3,C-4 and C-5 of the pyrazole ring, respectively. The two singlets at δ 39.5 and -1.10 ppm correspond to N-methyl substituent and trimethylsilyl group substituted on C-5, respectively.

The mass spectrum (Figure 3) revealed a parent peak at m/z 154 consistent with the substitution of a hydrogen at position 5 of pyrazole ring with a trimethylsilyl group. The base peak at m/e 139 indicated the loss of -CH_3 from trimethylsilyl group to give the stable tertiary silicon cation.

Consequently, these spectroscopy confirmed the resulting compound synthesized to be 5-(trimethylsilyl)-1-methylpyrazole.

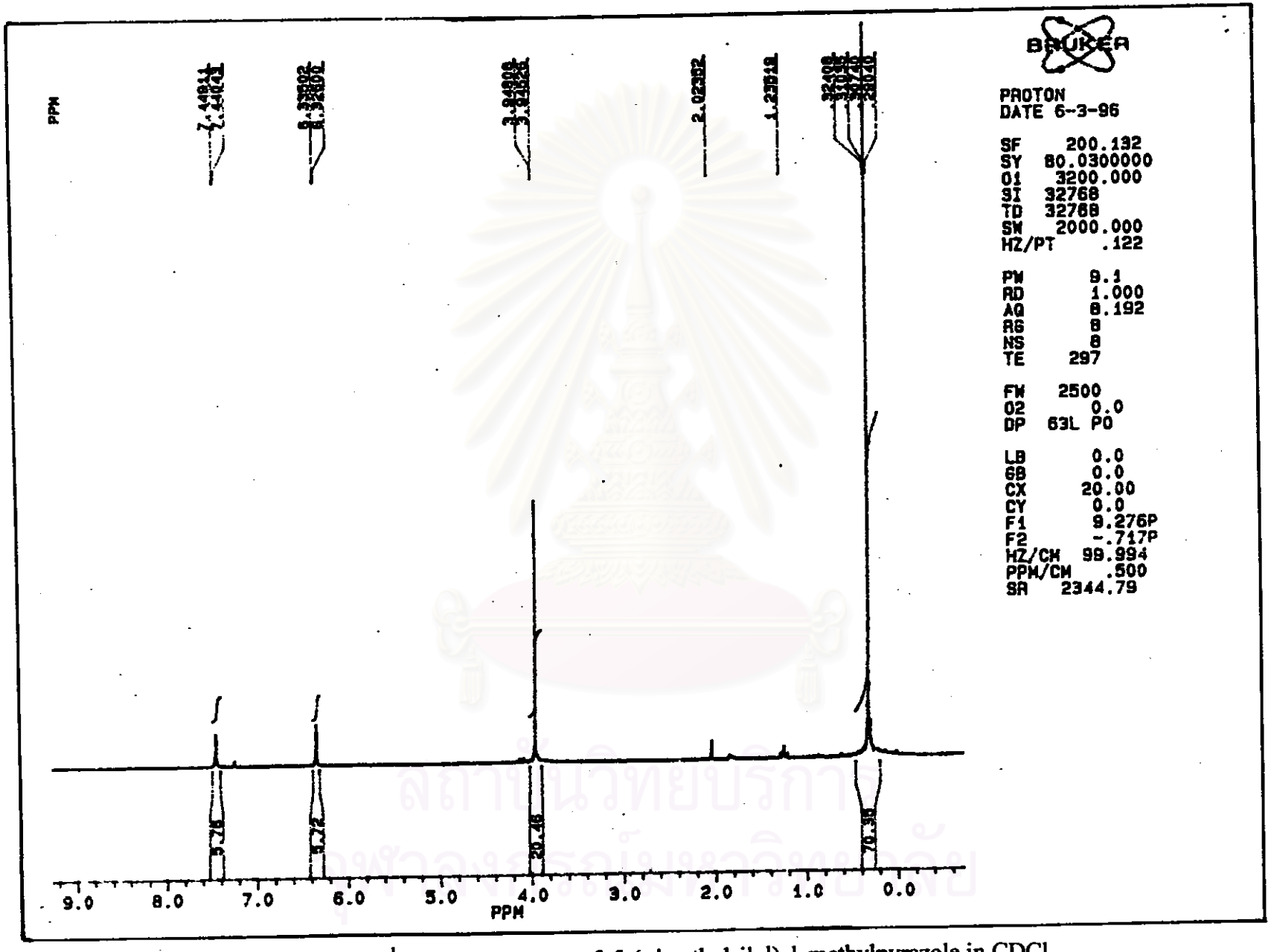


Figure 1 The ^{1}H-NMR spectrum of 5-(trimethylsilyl)-1-methylpyrazole in $CDCl_3$

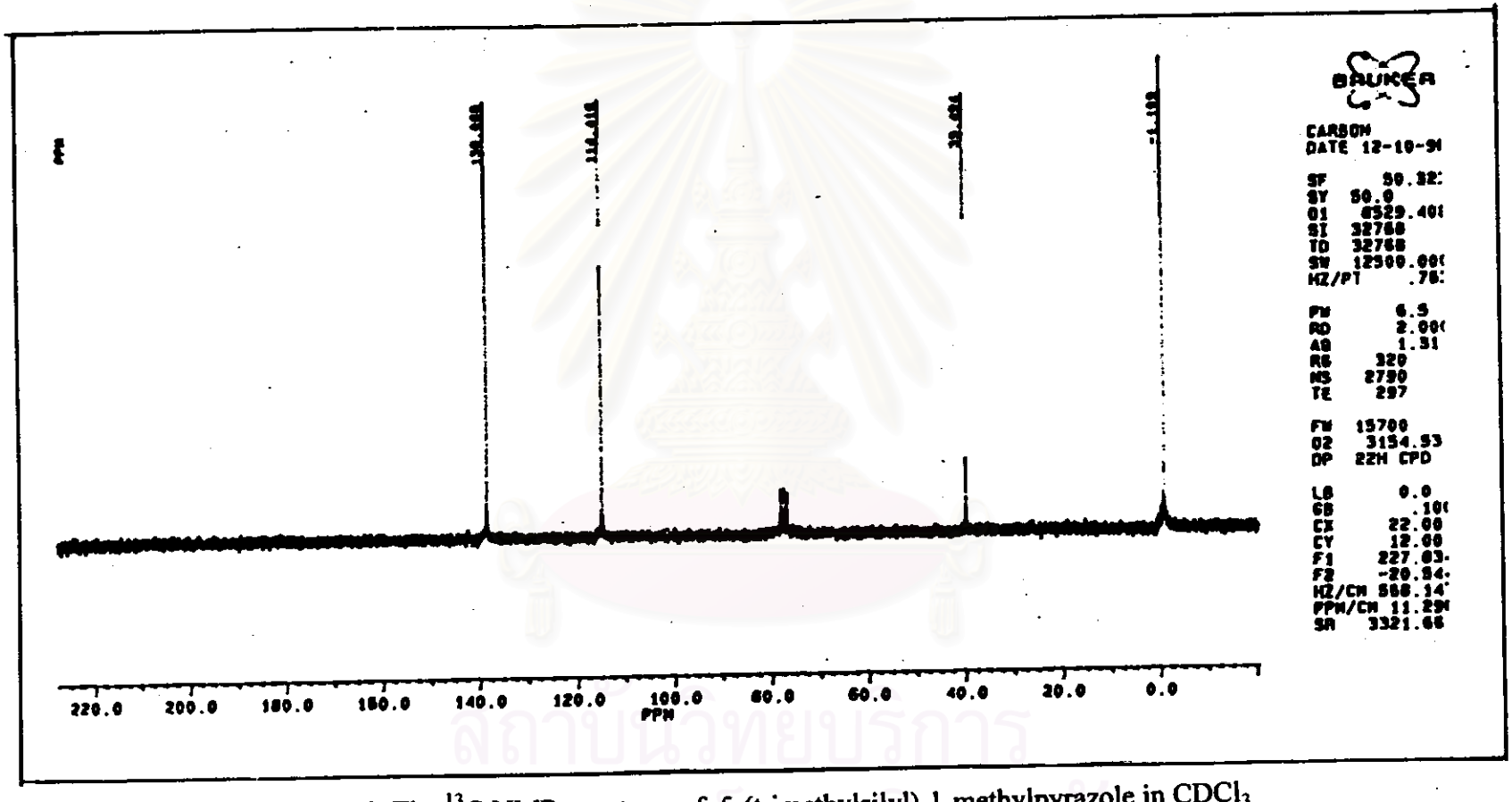


Figure 2 The ^{13}C-NMR spectrum of 5-(trimethylsilyl)-1-methylpyrazole in $CDCl_3$

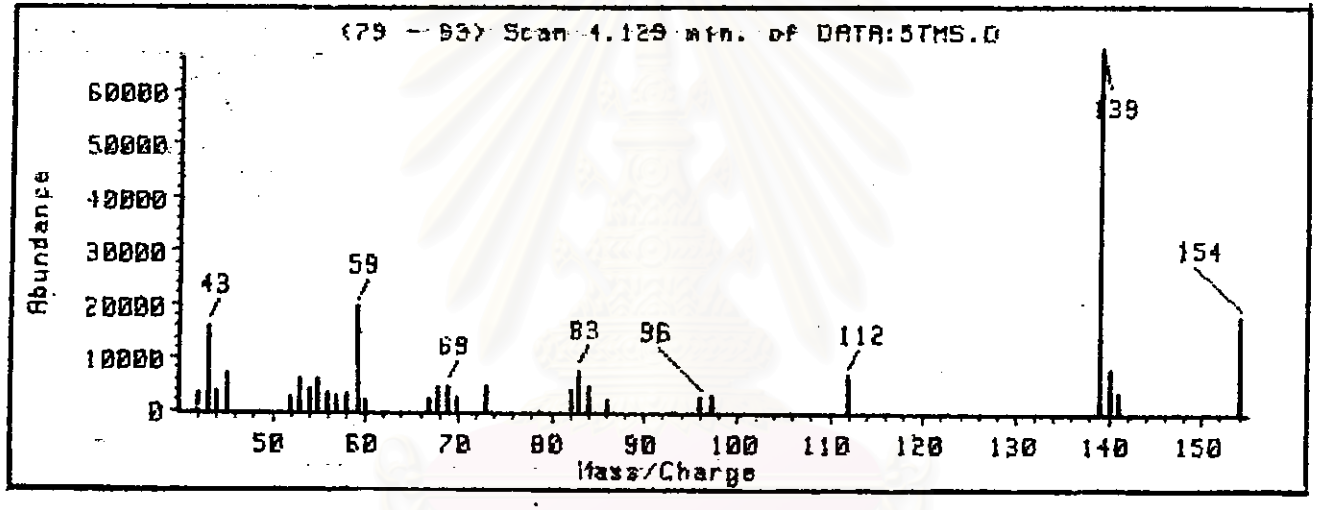
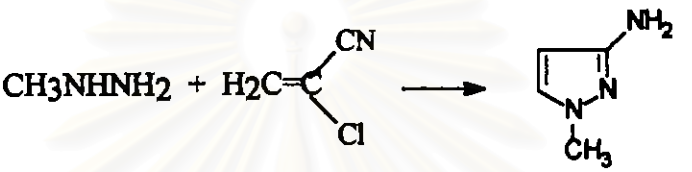


Figure 3 The mass spectrum of 5-(trimethylsilyl)-1-methylpyrazole

3.1.2 Synthesis of 3-amino-1-methylpyrazole

The synthesis of 3-amino-1-methylpyrazole [38] was by the method of Ege and Arnold [9]. It was understood that the nucleophilic attack of methyl hydrazine [36] on 2-chloroacrylonitrile [37] and subsequent ring closure, could easily occurred to yield [38]. The product was isolated and purified as a colorless liquid.



[36] [37] [38]

This product was characterized using ^{1}H-NMR, ^{13}C-NMR and MS data. ^{1}H-NMR spectrum (Figure 4) showed two 1-H doublets at δ 5.47(J= 4Hz) and 6.99 (J= 4Hz) consistent with protons at the C-5 and C-4 ring positions.The amino substitution at C-3 ring position led to the absence of the C-3 proton signal at δ ~ 7.49. It also exhibited the intense signal δ 3.61 which was belong to N-methyl substituent and amino group substituted on C-3 ring position. It is due to the integration indicated 5 protons on this signal.

The ^{13}C-NMR spectrum of the product shown in (Figure 5) exhibited signals at δ 154.1, 130.6, 91.9, and 37.7 for C-5, C-3, C-4 pyrazole ring carbons and N-methyl substituent, respectively.

The mass spectrum (Figure 6) showed a parent peak at m/z 97 as expected for 3-aminosubstituted-1-methylpyrazole.

Consequently, these spectroscopy confirmed the resulting compound synthesized to be 3-amino-1-methylpyrazole.

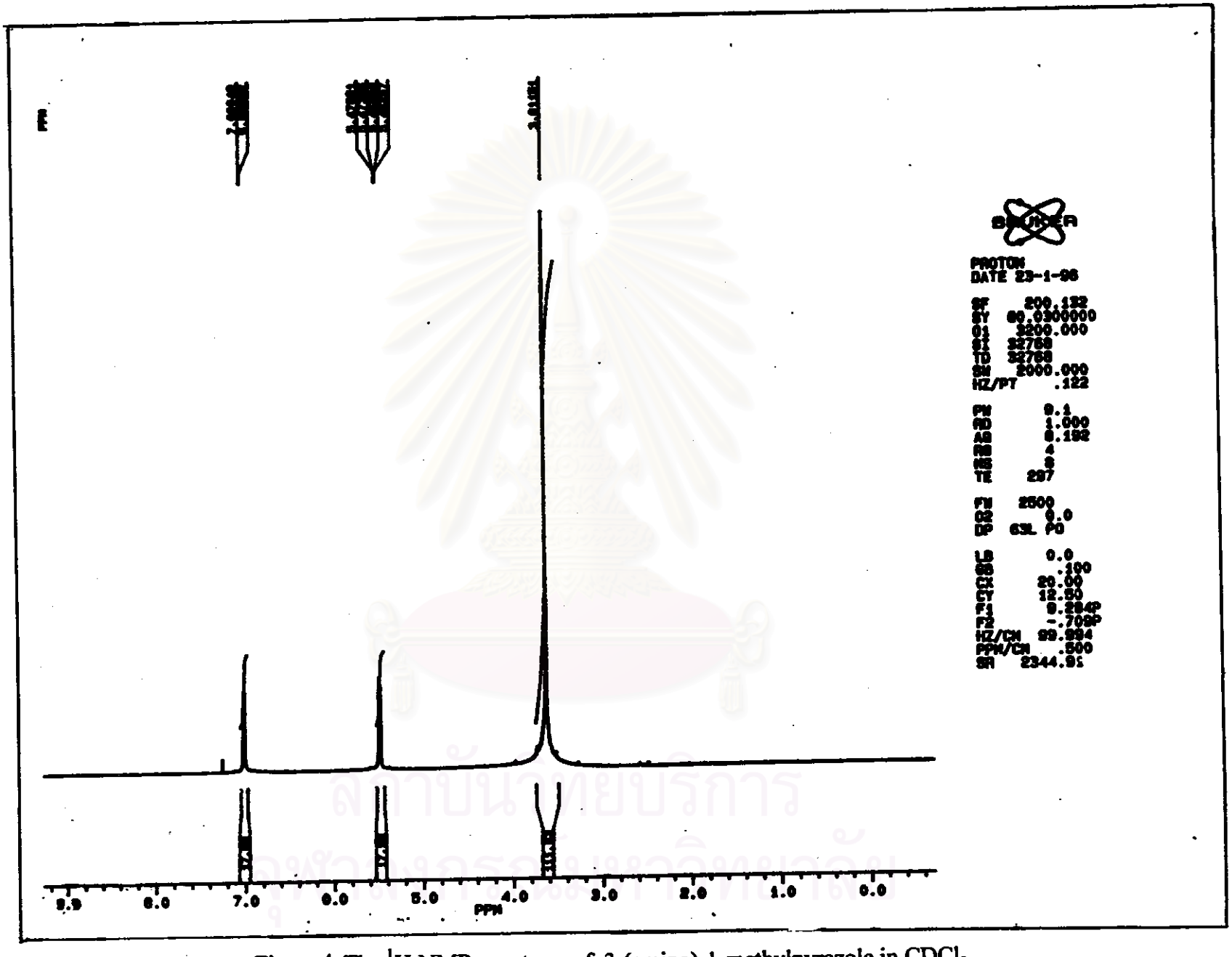


Figure 4 The ^{1}H-NMR spectrum of 3-(amino)-1-methylpyrazole in $CDCl_3$

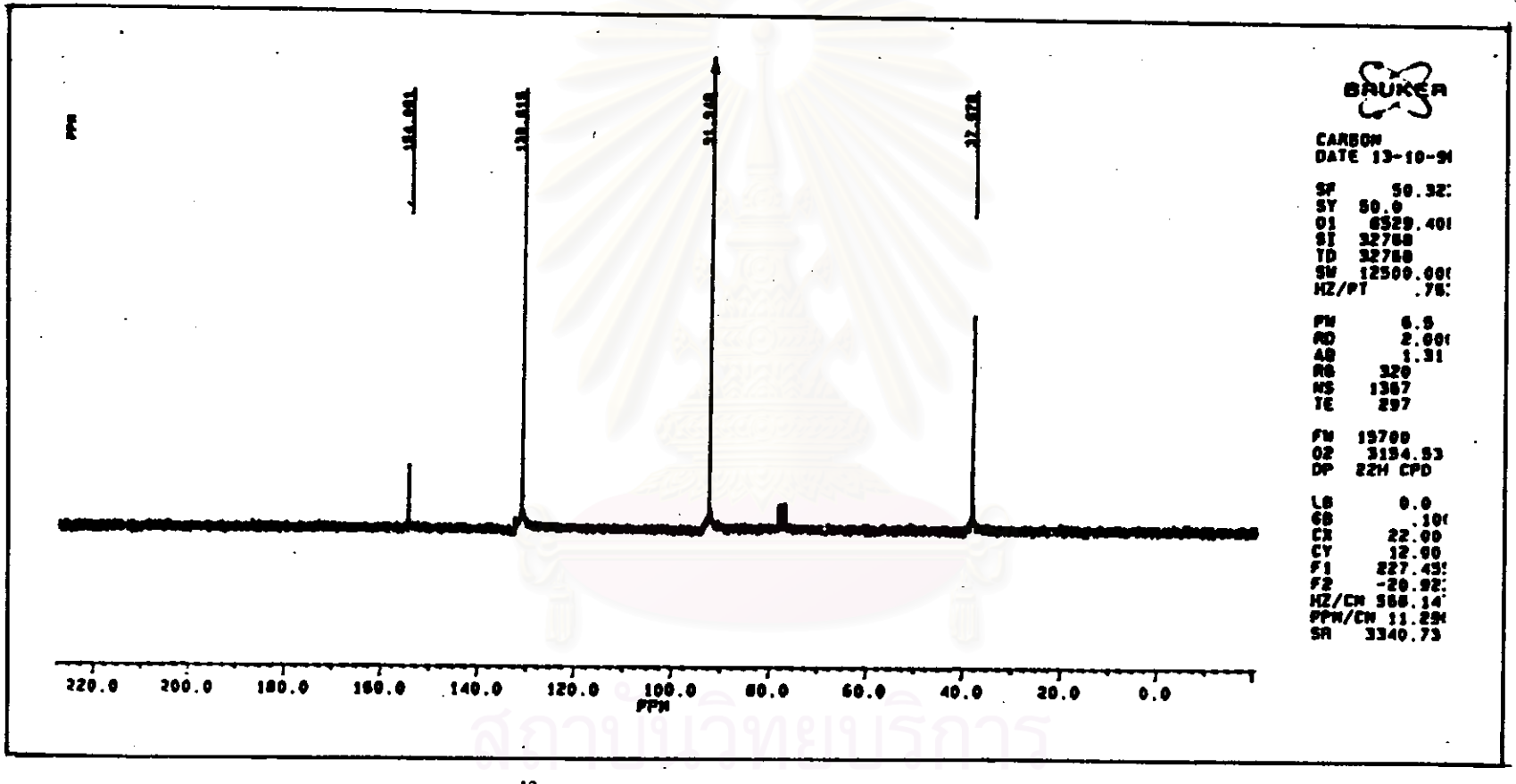


Figure 5 The ^{13}C-NMR spectrum of 3-(amino)-1-methylpyrazole in $CDCl_3$

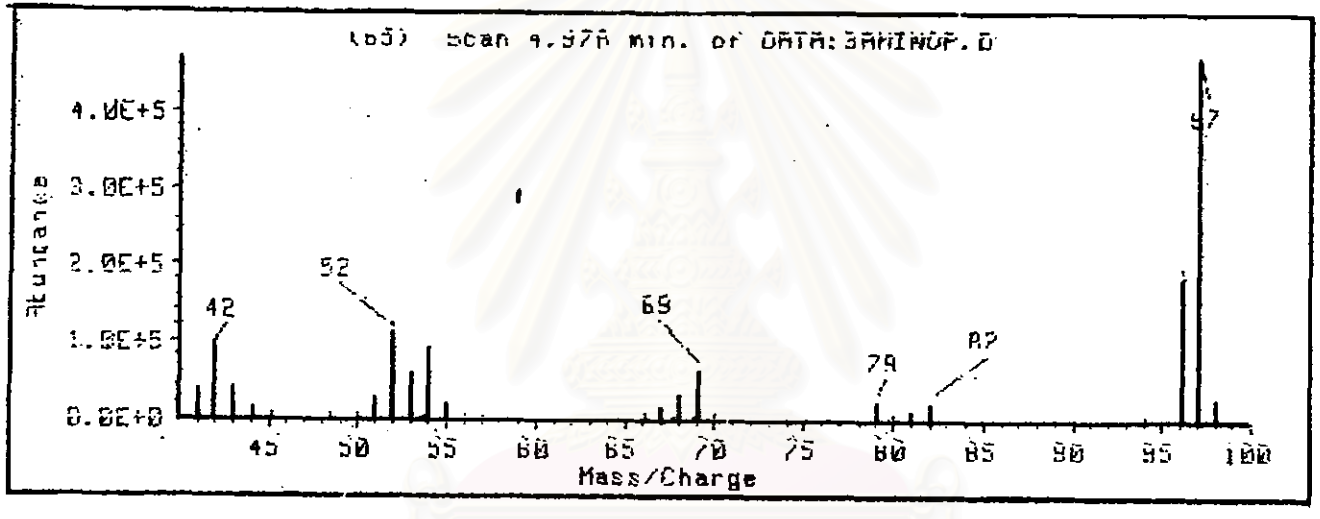
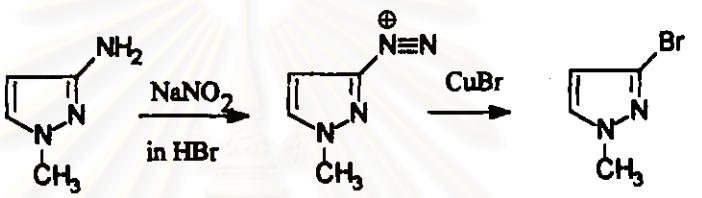


Figure 6 The mass spectrum of 3-(amino)-1-methylpyrazole

3.1.3 Synthesis of 3-bromo-1-methylpyrazole

Fabra and co-workers [10] reported that 3-fluoro-1-methylpyrazole could be synthesized by diazotization of 3-amino-1-methylpyrazole in tetrafluoroboric acid. In this study, 3-bromo-1-methylpyrazole was prepared by a modification of their method. 3-Amino-1-methylpyrazolewas diazotized in aqueous HBr and treated with copper (I) bromide in Sandmeyer reaction.



[38] [39] [40]

^{1}H-NMR spectrum of 3-bromo-1-methylpyrazole shown in Figure 7 exhibited two 1H doublets at δ 7.23(J= 2Hz) and 6.22(J= 2Hz) for the protons at C-5 and C-4 ring position, respectively and 3H singlet at δ 3.85 for *N*-methyl substituent. Its mass spectrum shown in (Figure 8) exhibited a parent peak at m/z 161.9 and 159.9 in a ratio of relative abundance 1:1 that indicate the isotope ratio of ^{81}Br to ^{79}Br in the nature.

3.1.4 Synthesis of 3-(trimethylsilyl)-1-methylpyrazole

Pavlik and Kurzweil [11] observed that under strictly controlled experimental conditions, metallation of **[40]** with t-butyllithium can be restricted to the C-3 position for lithium-bromine exchange. Then the reaction could be quenched by addition of an electrophile leading to the formation of the expected 3-substituted 1-methylpyrazole.

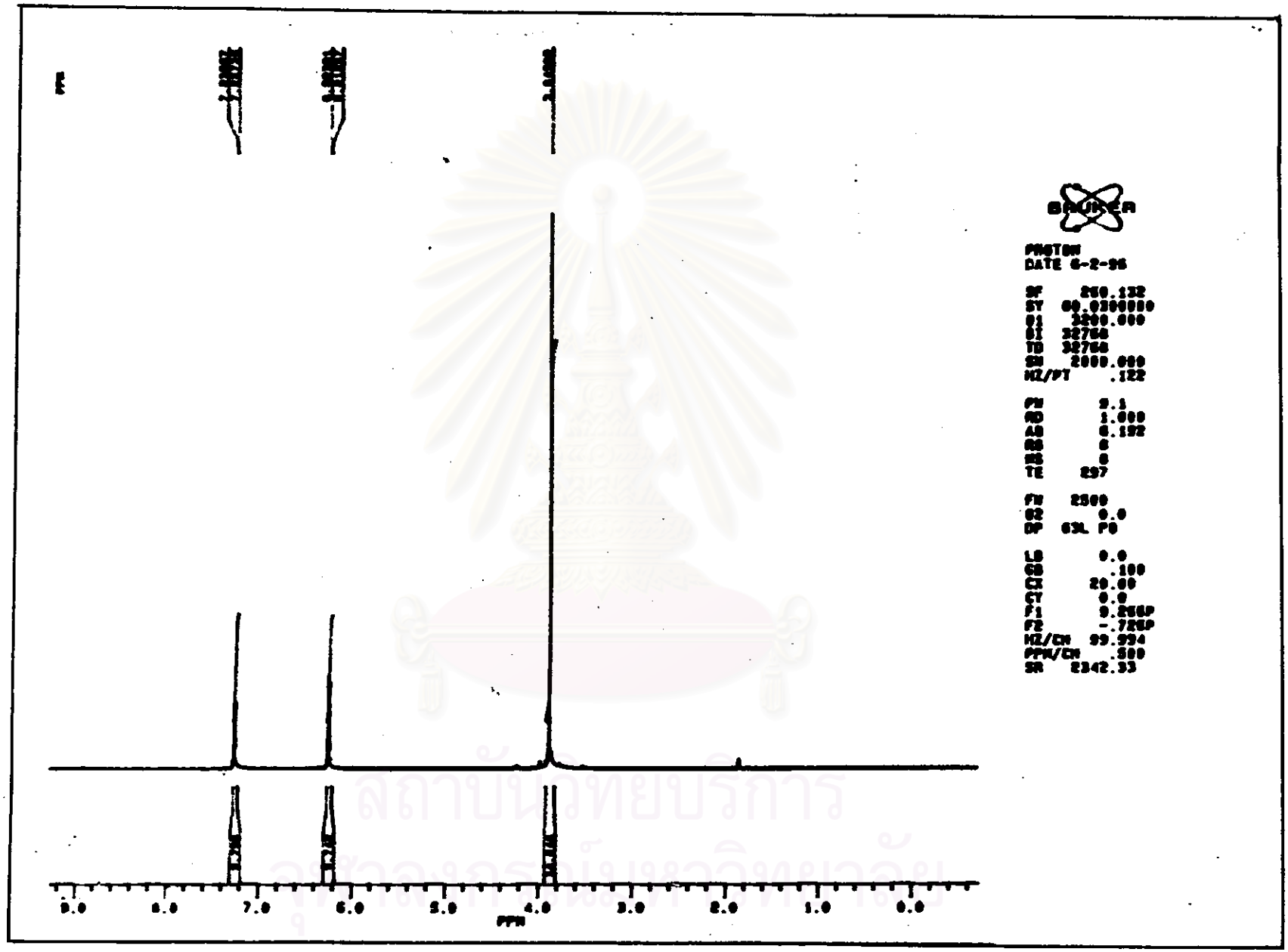


Figure 7 The ^{1}H-NMR spectrum of 3-(bromo)-1-methylpyrazole in $CDCl_3$

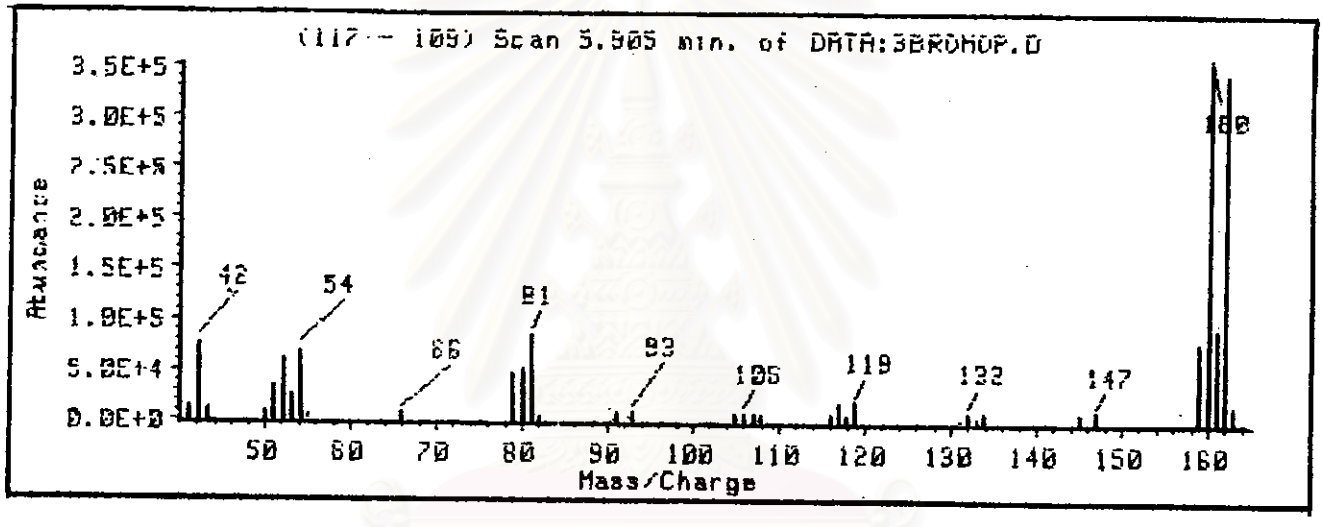
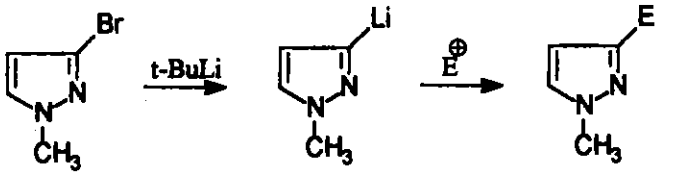
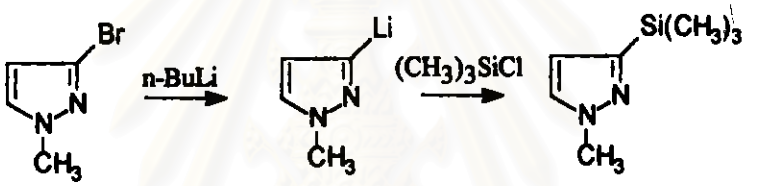


Figure 8 The mass spectrum of 3-(bromo)-1-methylpyrazole



[40] [41] [42]

For the synthesis of 3-(trimethylsilyl)-1-methylpyrazole, chlorotrimethylsilane was used as an electrophilic reagent. The experiment was carried out by using t-butyllithium but the yield of 3-(trimethylsilyl)-1-methylpyrazole was relatively low. So n-butyllithium was used instead to provide 3-(trimethylsilyl)-1-methylpyrazole in a higher yield.



[40] [41] [43]

The product **[43]** was purified by column chromatography and characterized by ^{1}H- NMR, ^{13}C-NMR and MS data.

^{1}H-NMR of **[9]** (Figure 9) showed the absence of the signal at $\delta \sim 7.49$ ppm due to the C-3 proton of 1-methylpyrazole which indicated the substitution by the trimethylsilyl group. The signal of C-4 proton was observed as a doublet at δ 6.35 ppm ($J_{H5,H4} = 2$ Hz), as required for a 3-substituted 1-methylpyrazole.

The mass spectrum of **[43]** (Figure 10) exhibited a parent peak at m/z 154 consistent with substitution of bromine by a trimethylsilyl group. These spectral data confirmed that the C-3 bromine in **[40]** has been replaced by trimethylsilyl group in **[43]**.

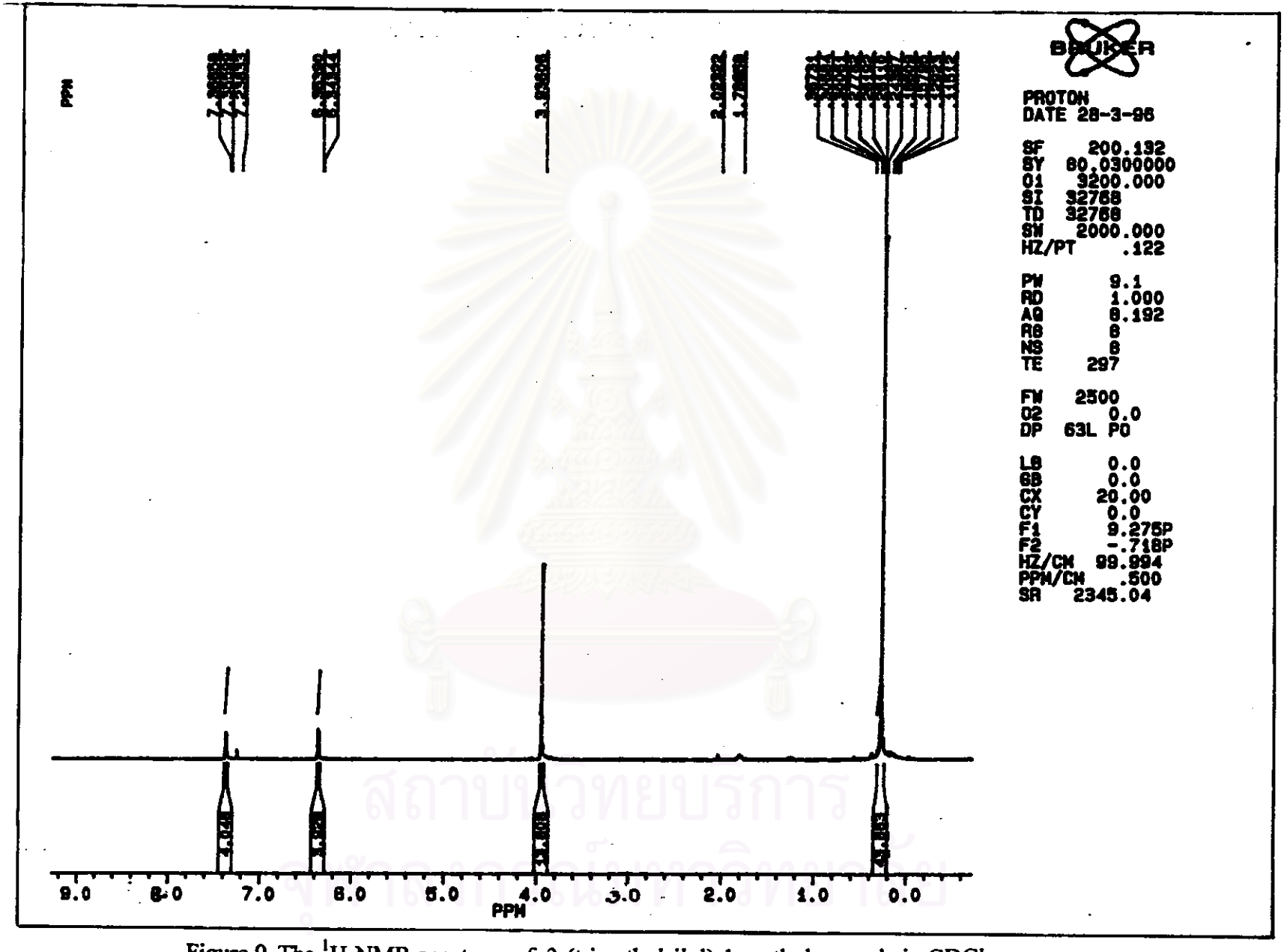


Figure 9 The ^{1}H-NMR spectrum of 3-(trimethylsilyl)-1-methylpyrazole in $CDCl_3$

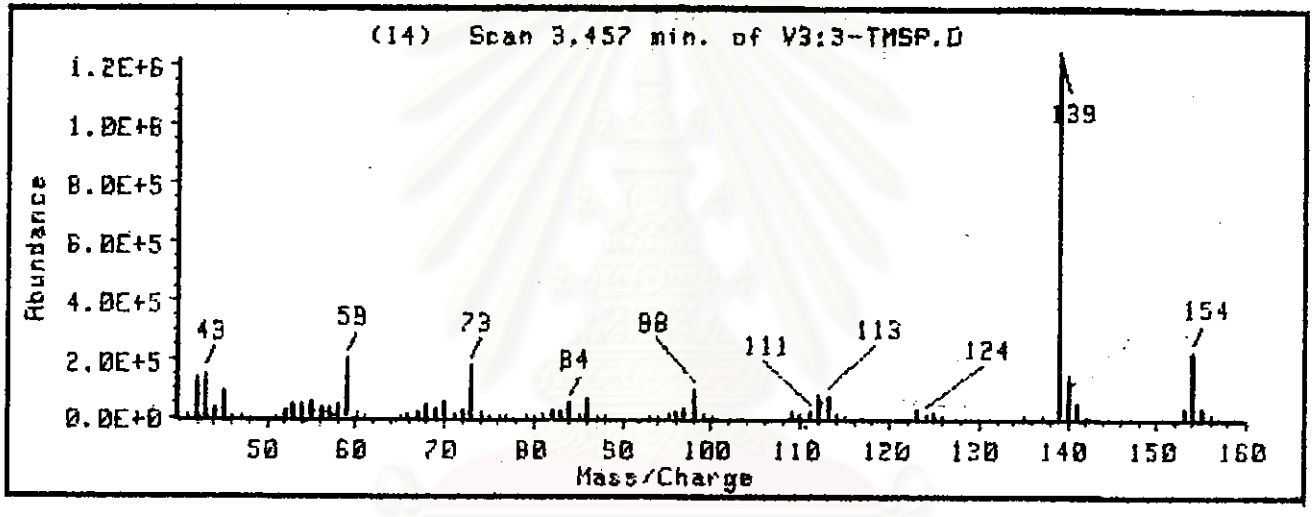


Figure 10 The mass spectrum of 3-(trimethylsilyl)-1-methylpyrazole

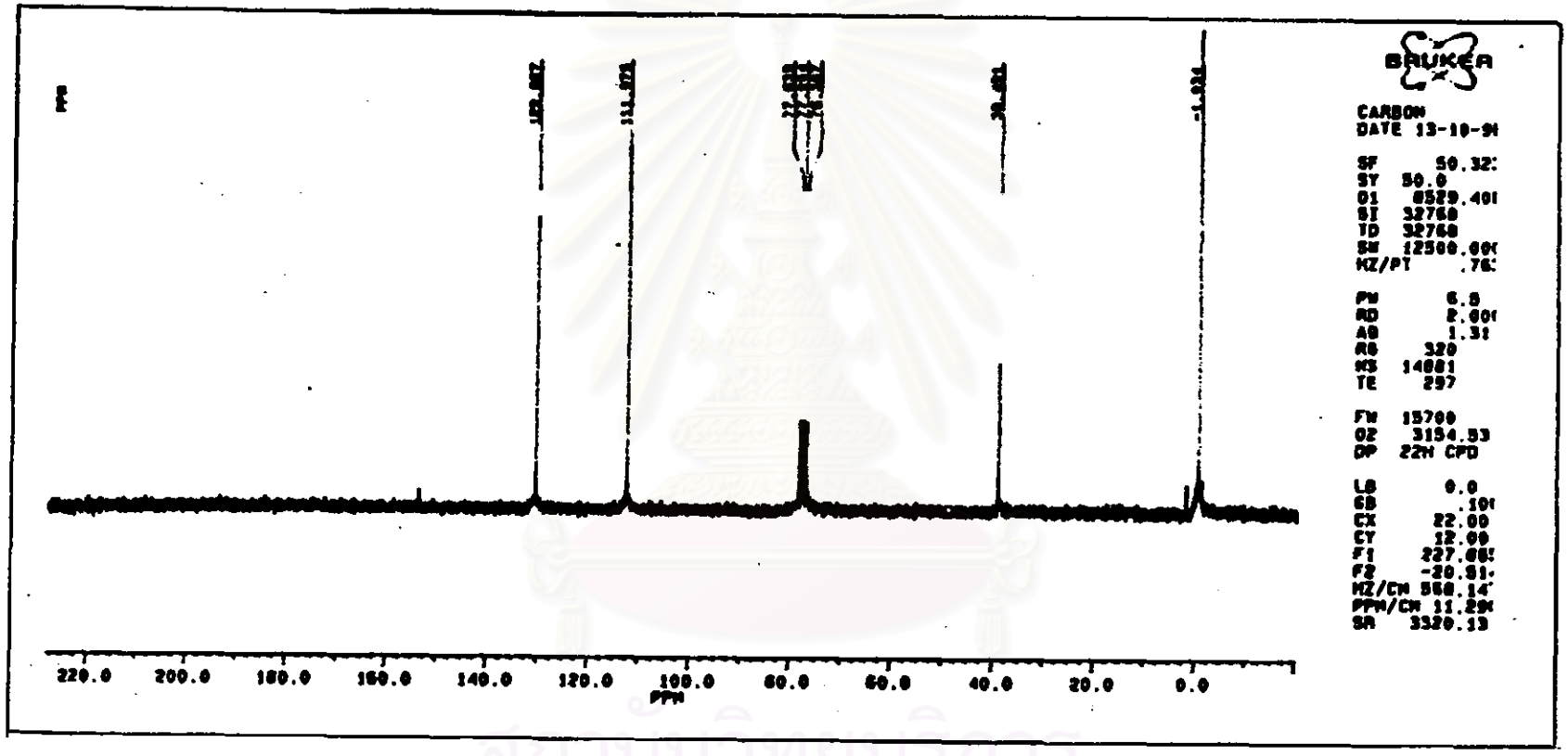


Figure 11 The ^{13}C-NMR spectrum of 3-(trimethylsilyl)-1-methylpyrazole in $CDCl_3$

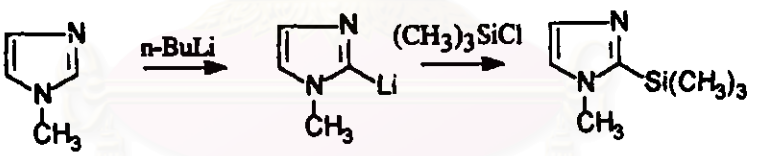
The ^{13}C-NMR spectrum (Figure 11) exhibited signals at δ 154, 129.9, 111.9, 38.5, and -1.9 ppm for C-5, C-3, C-4 pyrazole ring carbons, N-methyl substituent and three equivalent methyl protons of trimethylsilyl group respectively. The data is consistent with substitution of a C-3 hydrogen with trimethylsilyl group.

Consequently, these spectroscopy confirmed the resulting compound synthesized to be 3-(trimethylsilyl)-1-methylpyrazole.

3.2 Syntheses of expected photochemical products

3.2.1 Synthesis of 2-(trimethylsilyl)-1-methylimidazole

The synthesis of 2-(trimethylsilyl)-1-methylimidazole **[45]** followed the method of Jutzi and Sakriβ [12] by reacting lithio derivative of 1-methylimidazole **[2]** with chlorotrimethylsilane under high temperature.



[2] [44] [45]

It was filtered by using a double ended filter and the solvent was distilled off under reduced pressure. Jutzi and Sakriβ had reported that **[45]** is very sensitive to moisture, which causes its conversion to 1-methylimidazole by loss of the trimethylsilyl group. For this reason, the crude product was not purified but examined directly by ^{1}H-NMR and MS.

The ^{1}H-NMR spectrum (Figure 12) of the product exhibited a 3-H singlet at δ 3.77 for the *N*-methyl substituent. It also showed the absence of the signal at δ ~ 7.40 ppm according to C-2 proton which indicated the substitution of trimethylsilyl group.

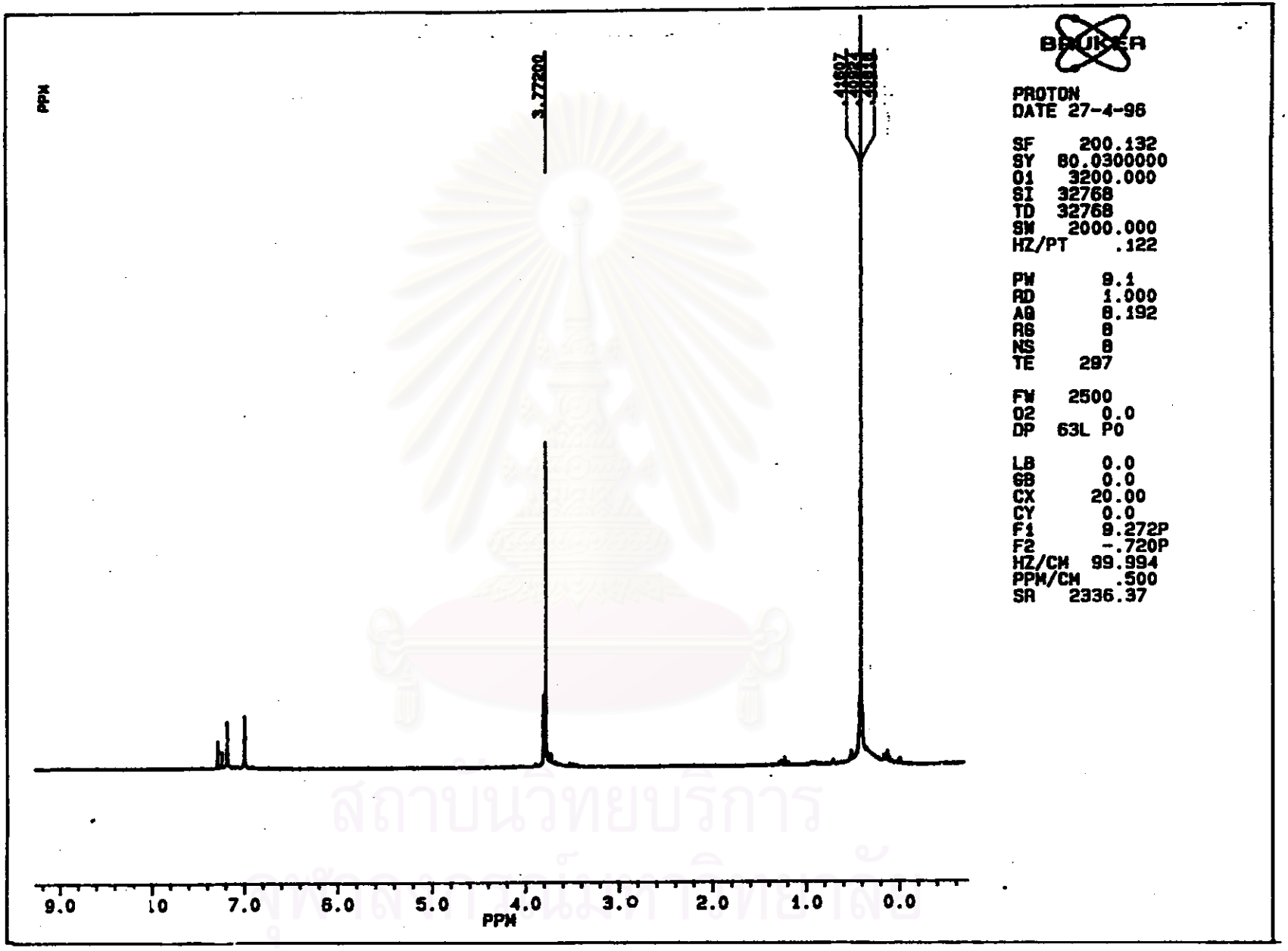


Figure 12 The ^{1}H-NMR spectrum of 2-(trimethylsilyl)-1-methylimidazole in $CDCl_3$

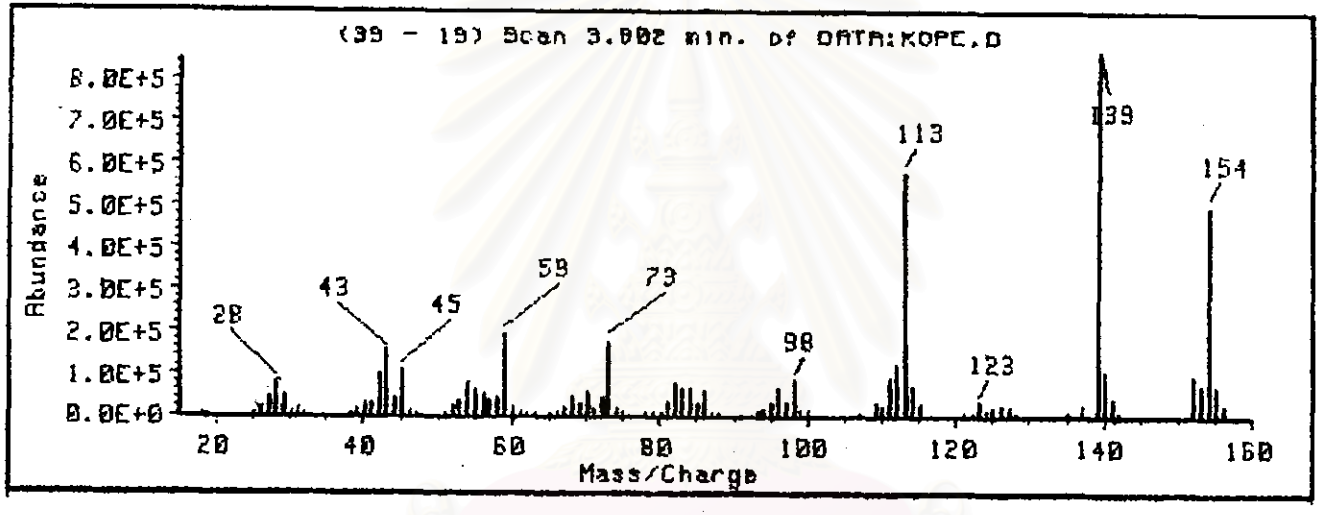


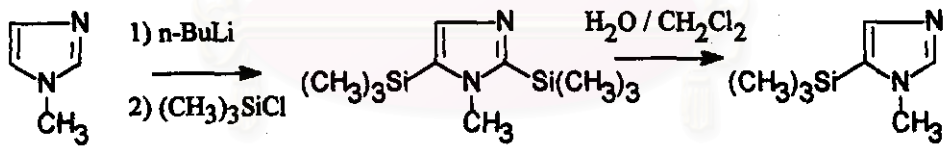
Figure 13 The mass spectrum of 2-(trimethylsilyl)-1-methylimidazole

The mass spectrum shown in Figure 13 exhibited a parent peak at m/z 154 consistent with the trimethylsilyl substitution on 1-methylimidazole ring.

All spectroscopic data confirmed the synthesized product to be 2-(trimethylsilyl)-1-methylimidazole.

3.2.2 Synthesis of 5-(trimethylsilyl)-1-methylimidazole

5-(Trimethylsilyl)-1-methylimidazole was synthesized by the method of Effenberger and co-workers [13]. The reaction was performed by reacting the lithio derivative of 1-methylimidazole [2] with chlorotrimethylsilane under high temperature in 1:2:2 mol ratio of [2] to n-BuLi and chlorotrimethylsilane to provide 2,5-(ditrimethylsilyl)-1-methylimidazole [46]. The trimethylsilyl group on C-2 was then removed by hydrolysis in the mixture of water and dichloromethane and purified by vacuum distillation. 5-(Trimethylsilyl)-1-methylimidazole was characterized by ^{1}H-NMR, ^{13}C-NMR and MS.



[2] [46] [47]

^{1}H-NMR spectrum (Figure 14) indicated two singlets at δ 7.54 and 7.10 for protons on C-2 and C-4 respectively. The absence of the signal of a proton on C-5 at δ ~ 6.79 confirmed the substitution of trimethylsilyl group.

In addition, ^{13}C-NMR spectrum (Figure 15) showed signals at δ ~ −1.2 ppm consistent with the substitution of trimethylsilyl group on C-5.

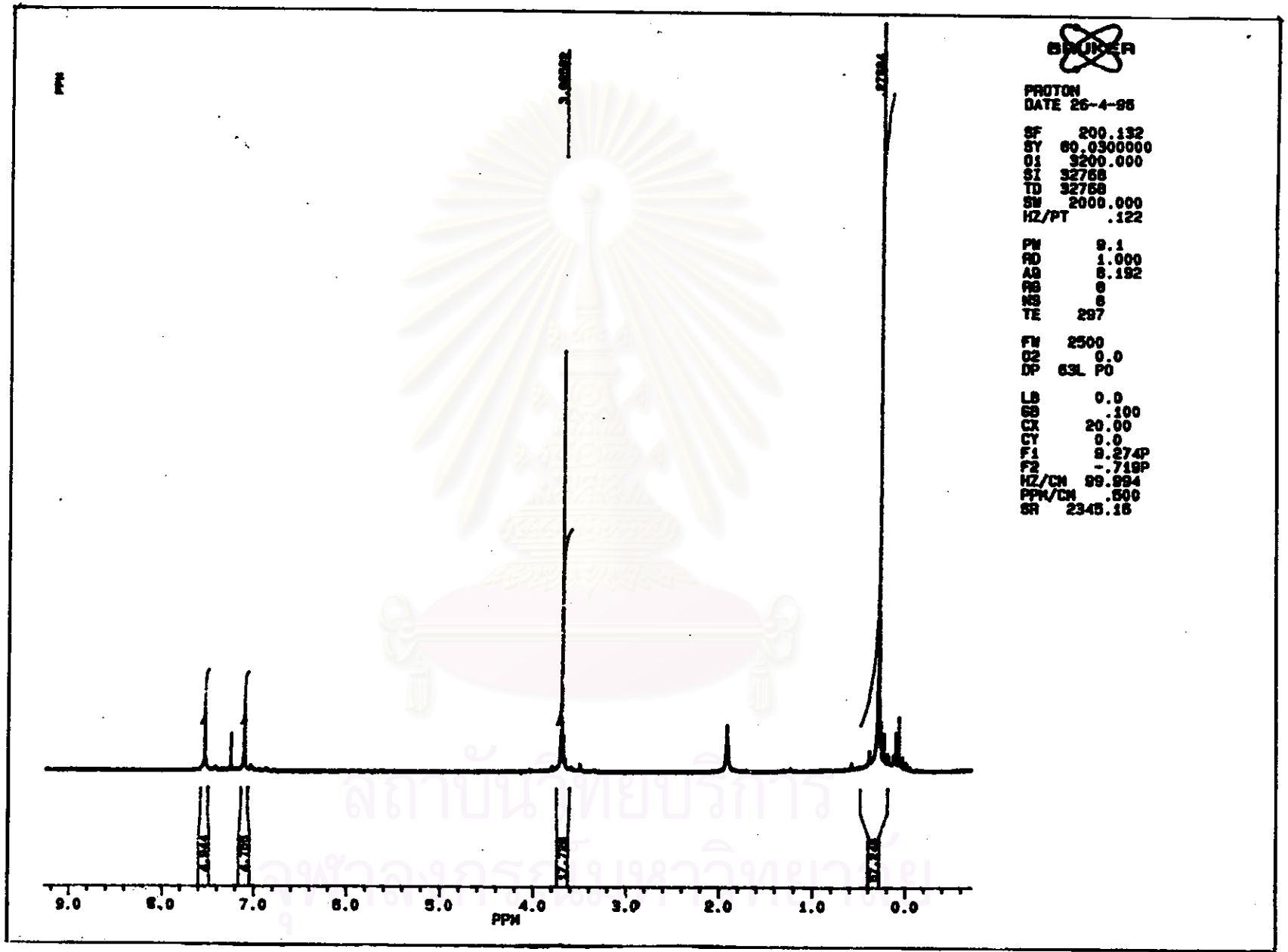


Figure 14 The ^{1}H-NMR spectrum of 5-(trimethylsilyl)-1-methylimidazole in $CDCl_3$

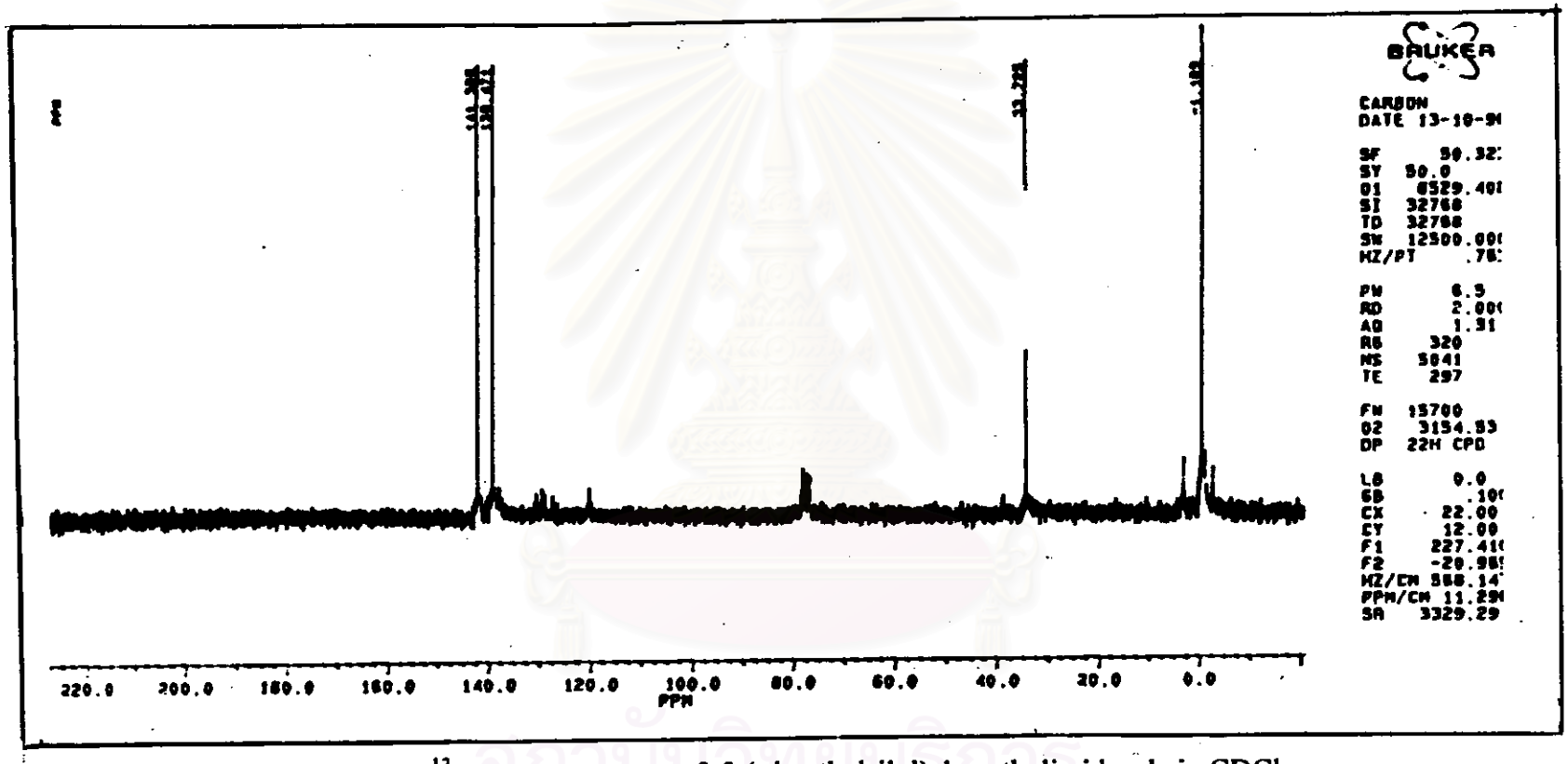


Figure 15 The ^{13}C-NMR spectrum of 5-(trimethylsilyl)-1-methylimidazole in $CDCl_3$

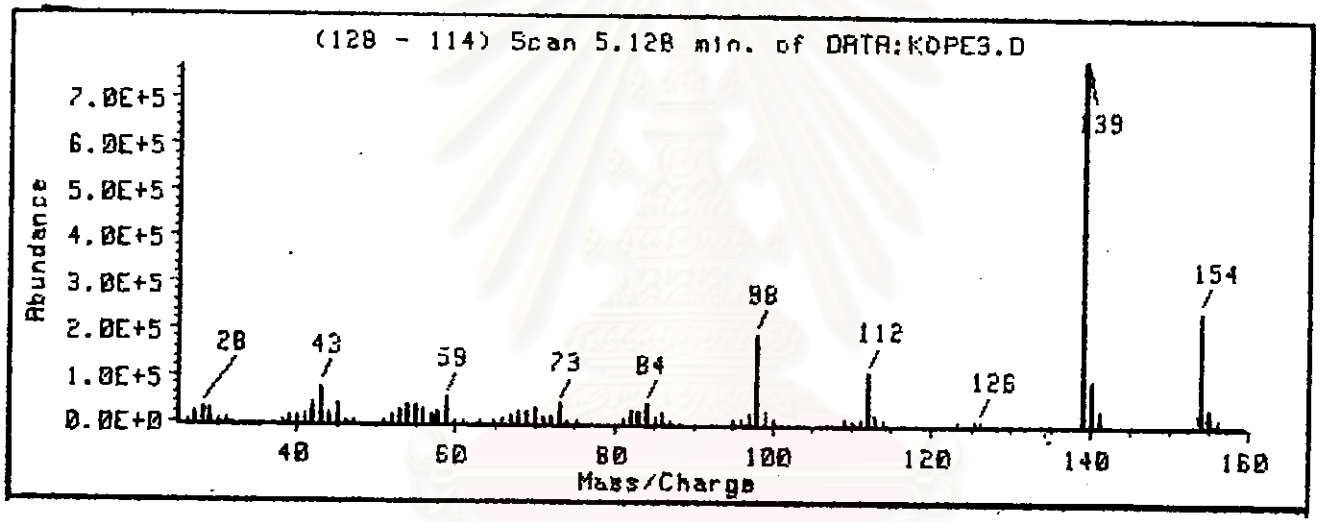
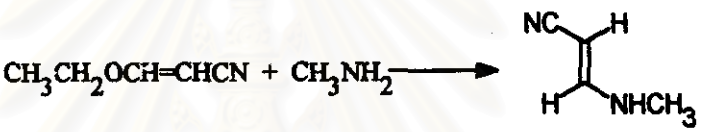


Figure 16 The mass spectrum of 5-(trimethylsilyl)-1-methylimidazole

Mass spectrum (Figure 16) showed a parent peak at m/z 154 consistent with the expected 5-(trimethylsilyl)-1-methylimidazole.

3.2.3 Synthesis of 3-(*N*-methylamino)-propenenitrile (2-cis and 2-trans)

The synthesis of 3-(*N*-methylamino)propenenitrile **[50]** was straight forward following Peeter and co-workers [14] method. It was obtained by the reaction of 3-ethoxyacrylonitrile with methylamine at room temperature. However, both cis and trans isomers were formed.



[48] **[49]** **[50]**

^{1}H-NMR spectrum (Figure 17) showed the two doublet signals at δ 2.67 and 2.96 (J = 5 Hz) for *N*-methyl groups of trans and cis isomers respectively. It also showed a broad peak centered at δ 4.88 for *N*-hydrogen.

The proton decoupled ^{13}C-NMR spectrum (Figure 18) exhibited signals at δ 152.1, 122.5, 59.9, and 29.3 ppm for C-2, C-1 (cyano group), C-3 (adjacent to nitrogen) and N-methyl group respectively. From the ^{1}H-NMR and ^{13}C-NMR, it can be concluded for 3-(*N*-methylamino)propenenitrile.

The mass spectrum (Figure 19) showed a parent peak at m/z 82 consistent with the expected 3-(*N*-methylamino)propenenitrile.

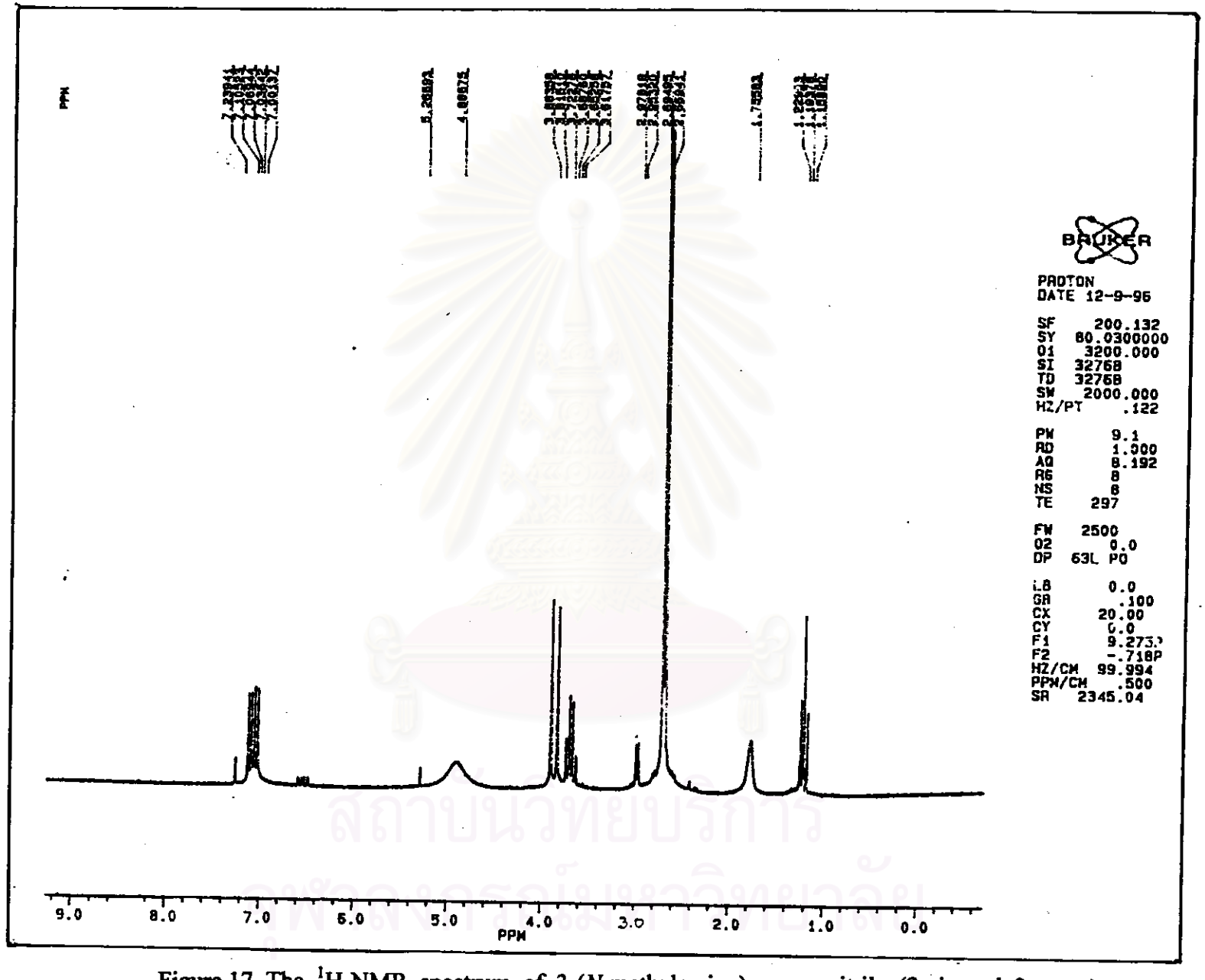


Figure 17 The ^{1}H-NMR spectrum of 3-(*N*-methylamino)propenenitrile (2-cis and 2- trans) in $CDCl_3$

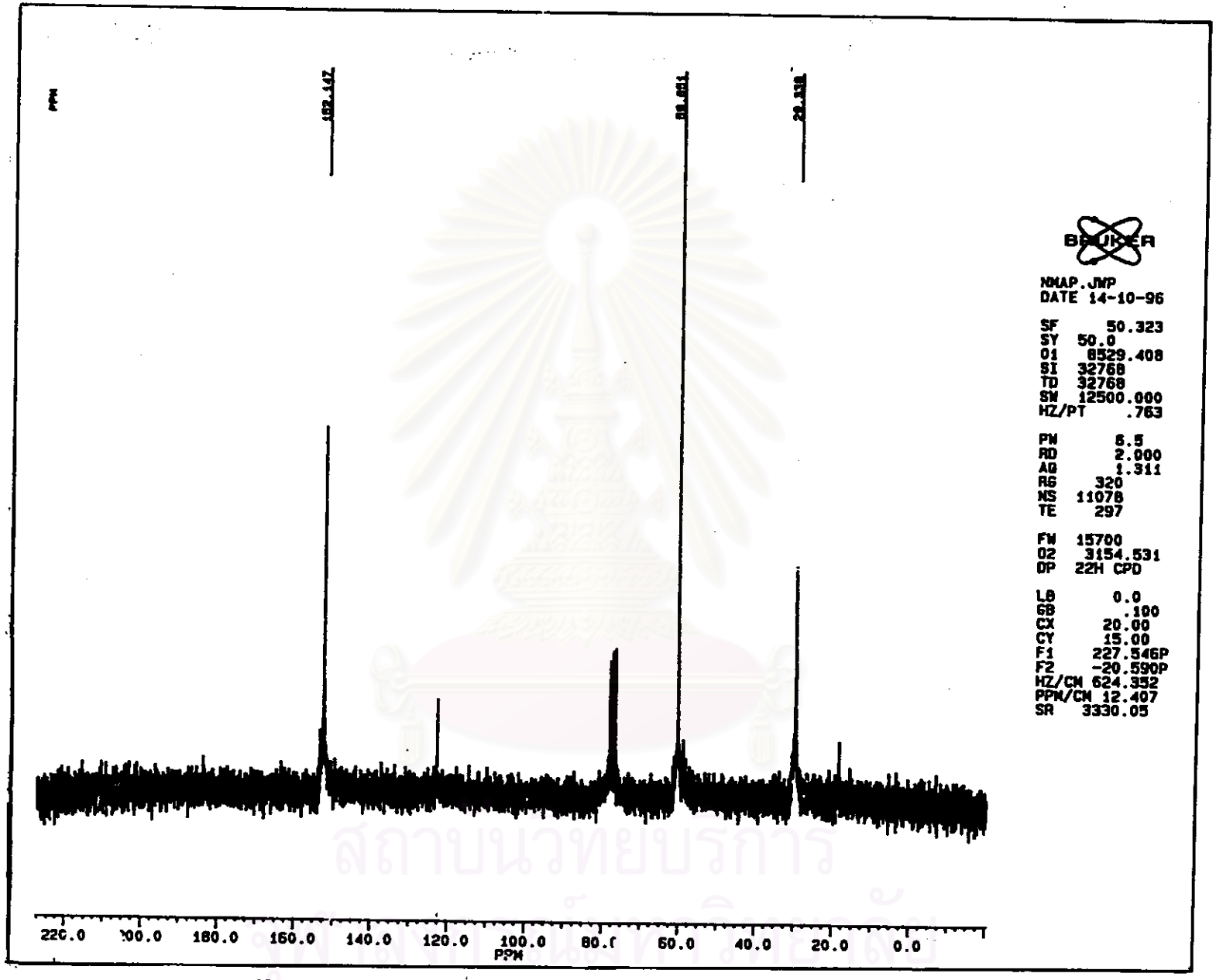


Figure 18 The ^{13}C-NMR spectrum of 3-(*N*-methylamino)propenenitrile(2-cis and 2- trans)

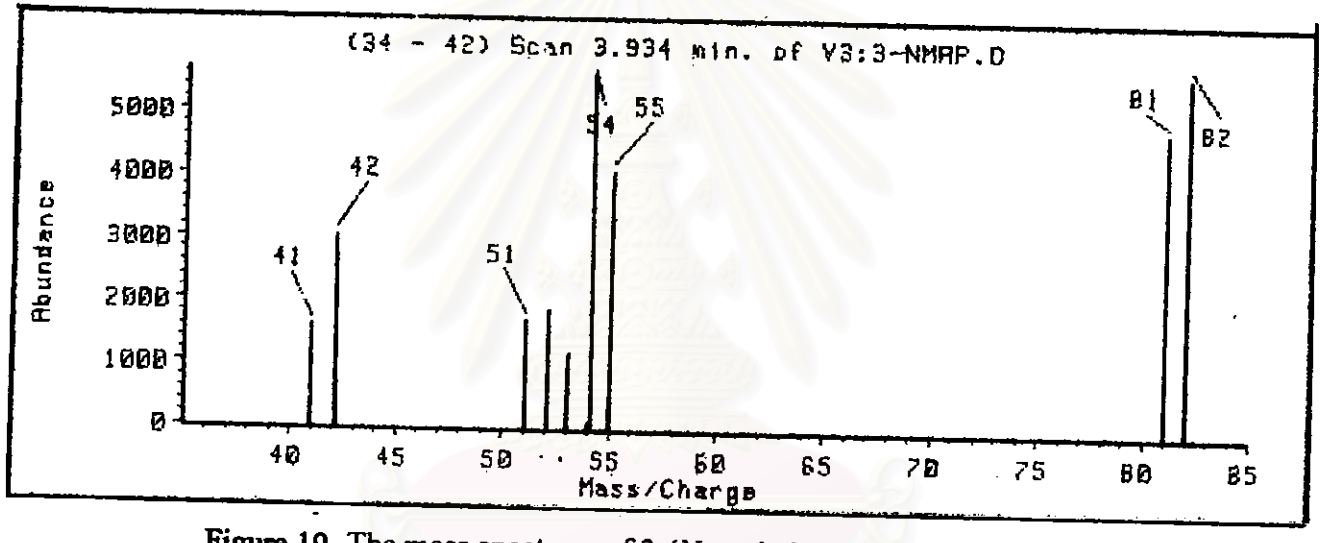


Figure 19 The mass spectrum of 3-(*N*-methylamino)propenenitrile

3.3 Attempt to synthesize 4-(trimethylsilyl)-1-methylpyrazole

3.3.1 Synthesis of 4-bromo-1-methylpyrazole

4-Bromo-1-methylpyrazole was prepared by the method of Effenberger and Habich [15].

[1] [51]

^{1}H-NMR spectrum shown in Figure 20 exhibited two singlets at δ 7.41 and 7.36 ppm for the protons at C-3 and C-5 ring positions respectively and 3H singlet at δ 3.87 ppm for N-methyl substituent.

The mass spectrum of **[51]** (Figure 21) exhibited a parent peak at m/e 161.7 and 159.8 in a ratio of relative abundance 1:1 that indicated the isotope ratio of ^{81}Br to ^{79}Br in the nature.

Consequently, these spectroscopy confirmed the resulting compound synthesized to be 4-bromo-1-methylpyrazole.

3.3.2 Synthesis of 4-(trimethylsilyl)-1-methylpyrazole

Effenberger and Habich [15] prepared 4-(trimethylsilyl)-1-methylpyrazole from 4-bromo-1-methylpyrazole **[51]** by an "in situ Grignard synthesis".

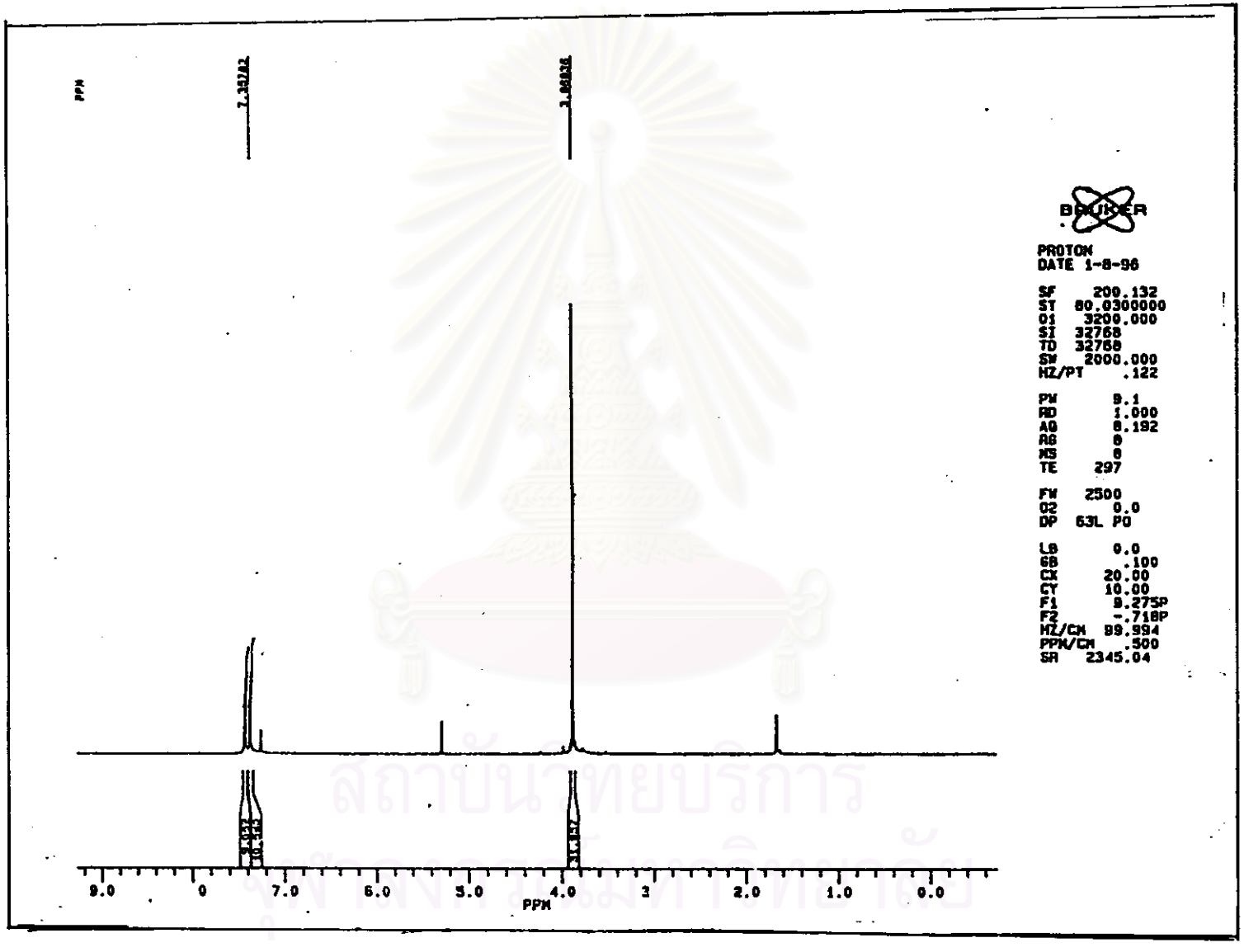


Figure 20 The ^{1}H-NMR spectrum of 4-bromo-1-methylpyrazole in $CDCl_3$

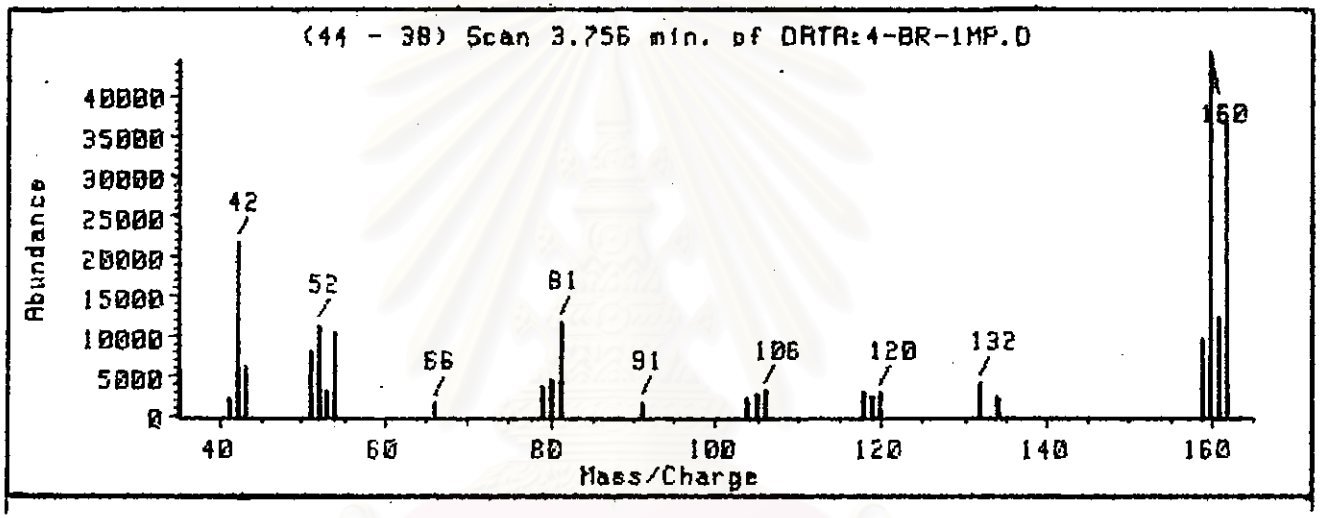
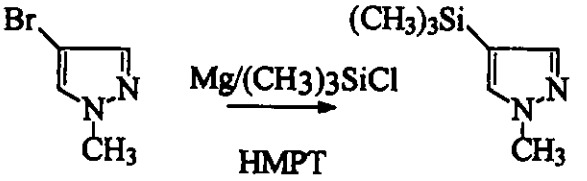


Figure 21 The mass spectrum of 4-bromo-1-methylpyrazole

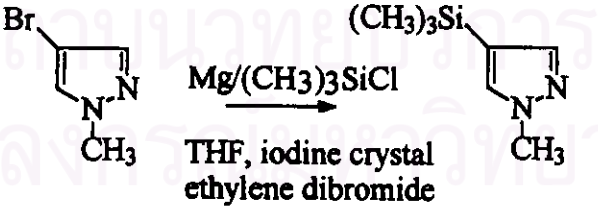


[51] [52]

The first attempt to synthesize [52] was performed by "in situ Grignard synthesis" following their work. The crude product mixture was examined by ^{1}H-NMR to show the spectrum of [51]. It indicated that the reaction did not take place. [51] might not have been converted into the Grignard reagent. Although the reaction was carried out several times, no reaction took place.

In 1968, Brooklyn and Finar [16] were able to synthesize 4-acetyl-1-phenylpyrazole from acetyl chloride and 1-phenyl-4-pyrazolyl magnesium bromide, which was prepared from 4-bromo-1-phenylpyrazole and magnesium using ethylene dibromide as an entrainer [17,18]. So the modification of their methods was used.

A new attempt began by changing the solvent to anhydrous THF. Anhydrous THF was used as solvent with ethylene dibromide as an entrainer and a crystal of iodine to achieve the magnesium.



[51] [52]

Flash column chromatography and vacuum distillation of [52] resulted in 24% yield. The purity was less than 80%, so it was not suitable for photochemical investigation.

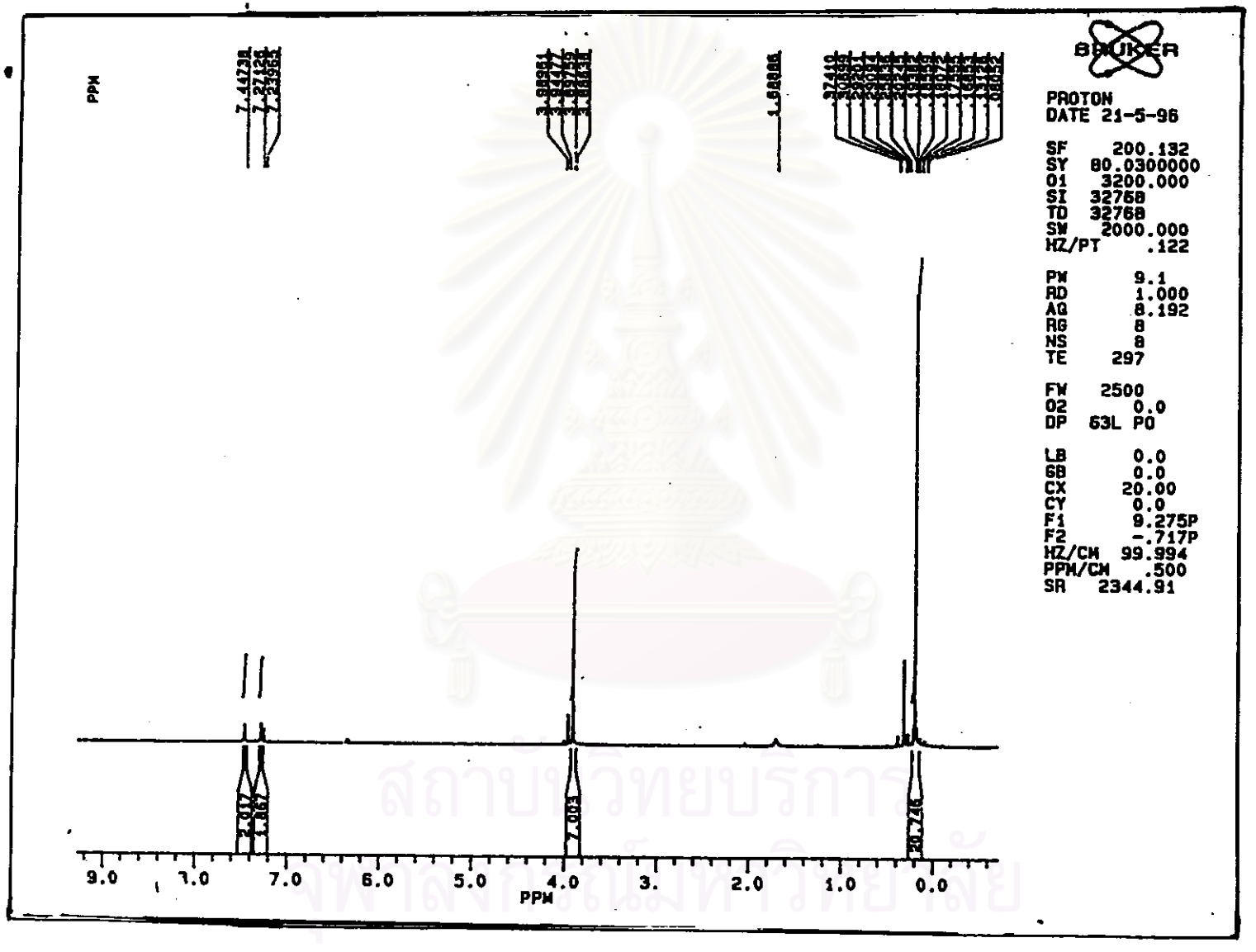


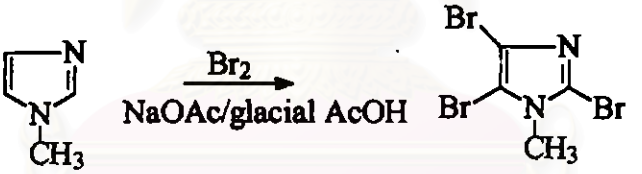
Figure 22 The ^{1}H-NMR spectrum of 4-(trimethylsilyl)-1-methylpyrazole in $CDCl_3$

^{1}H-NMR spectrum of **[52]** (not pure) shown in Figure 22 indicated two 1H singlets at δ 7.45 and 7.27 ppm for the proton at C-3 and C-5 ring position respectively and 3H singlet at δ 3.89 for N-methyl substituent. In addition, the spectrum showed a nine-proton singlet at δ 0.17 ppm for the three equivalent methyl protons substituents of trimethylsilyl group on the C-4 ring position. This data is consistent with a structure of **[52]**.

3.4 Attempt to synthesize 4-(trimethylsilyl)-1-methylimidazole

3.4.1 Synthesis of 1-methyl-2,4,5-tribromoimidazole

The synthesis of 1-methyl-2,4,5-tribromoimidazole **[53]** was followed the Rapoport and co-workers method [19] by the reaction of 1-methylimidazole with bromine in the presence of sodium acetate in glacial acetic acid.



[2] **[53]**

1-Methyl-2,4,5-tribromoimidazole **[53]** was isolated and recrystallized as a white solid. 32% yield of **[53]** was obtained.

^{1}H-NMR of **[53]** (Figure 23) showed only one signal at δ 3.62 ppm due to N-methyl substituent. They showed the absence of signal at δ 7.49, 6.22, and 7.35 ppm due to the C-3, C-4 and C-5 protons which indicated the replacement of bromine at all three positions.

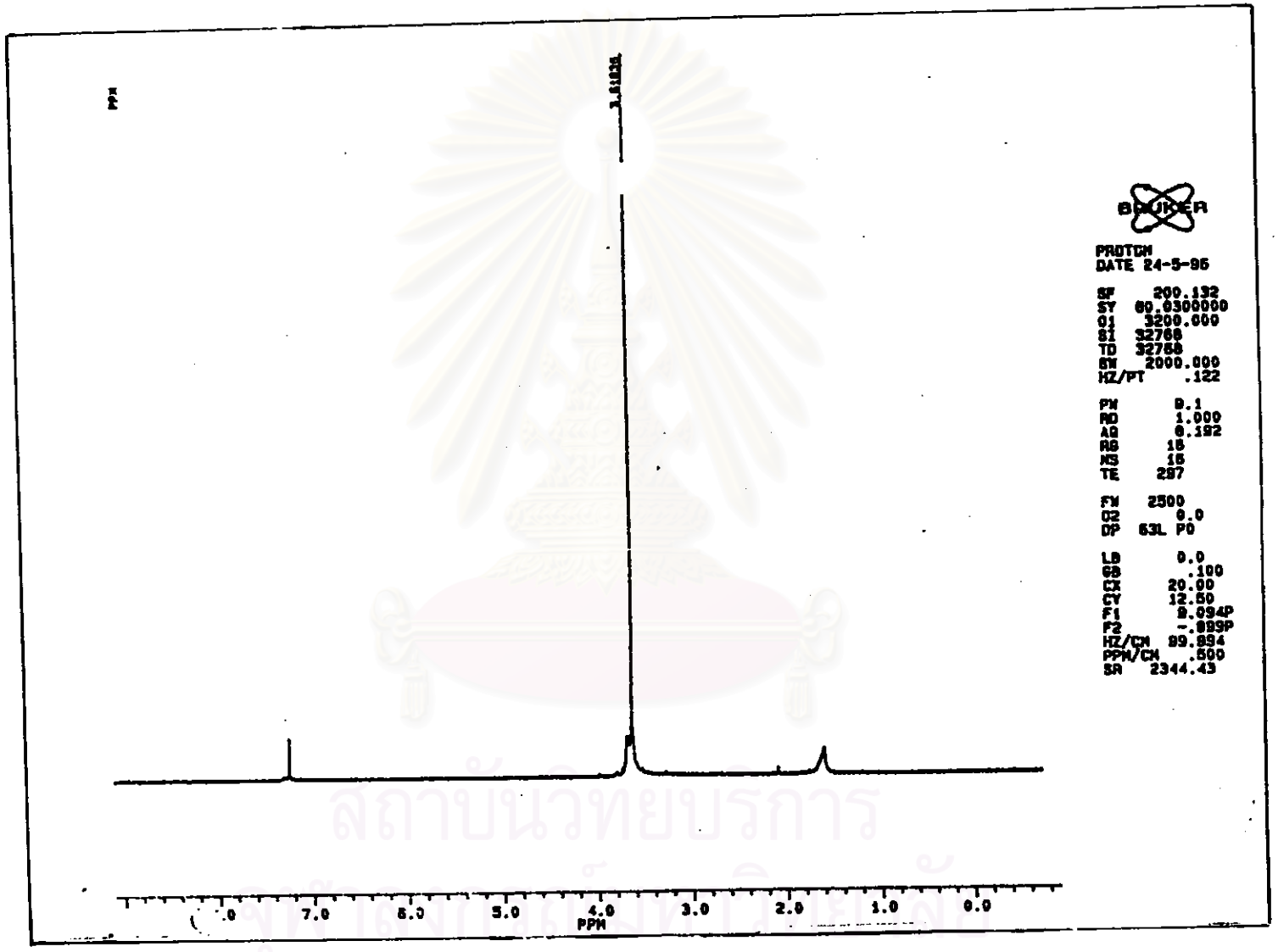
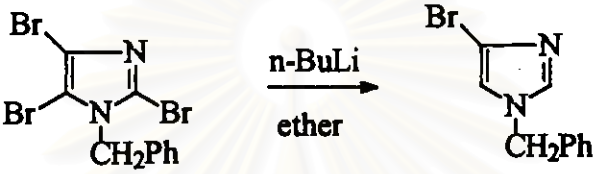


Figure 23 The ^{1}H-NMR spectrum of 1-methyl-2,4,5-tribromoimidazole in $CDCl_3$

3.4.2 Synthesis of 4-bromo-1-methylimidazole

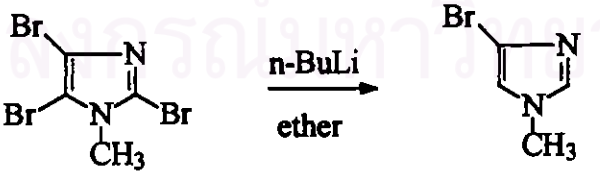
Iddon and Khan [20] prepared 1-benzyl-4-bromoimidazole [55] by metal-halogen exchange reaction of 1-benzyl-2,4,5-tribromoimidazole [54]. Treatment of [54] with 2 mol equiv. butyllithium (in ether or THF at -78 °C) followed by addition of water gave [55] in 71% yield.



[54] [55]

They reported that 1-protected-2,4,5-tribromoimidazoles do not react regioselectively with 1 mol equiv. of butyllithium (in ether or THF at -78 °C). Both 2 and 5-bromine atoms undergo exchange under these conditions. The difficulty in exchanging the 4-bromine atom for lithium in this system is probably due to destablization of any carbanionic character at C-4 both by the adjacent N-3 lone pair as well as by the carbanionic character at C-5.

A modification of their method was used for the synthesis of 4-bromo-1-methylimidazole.



[53] [56]

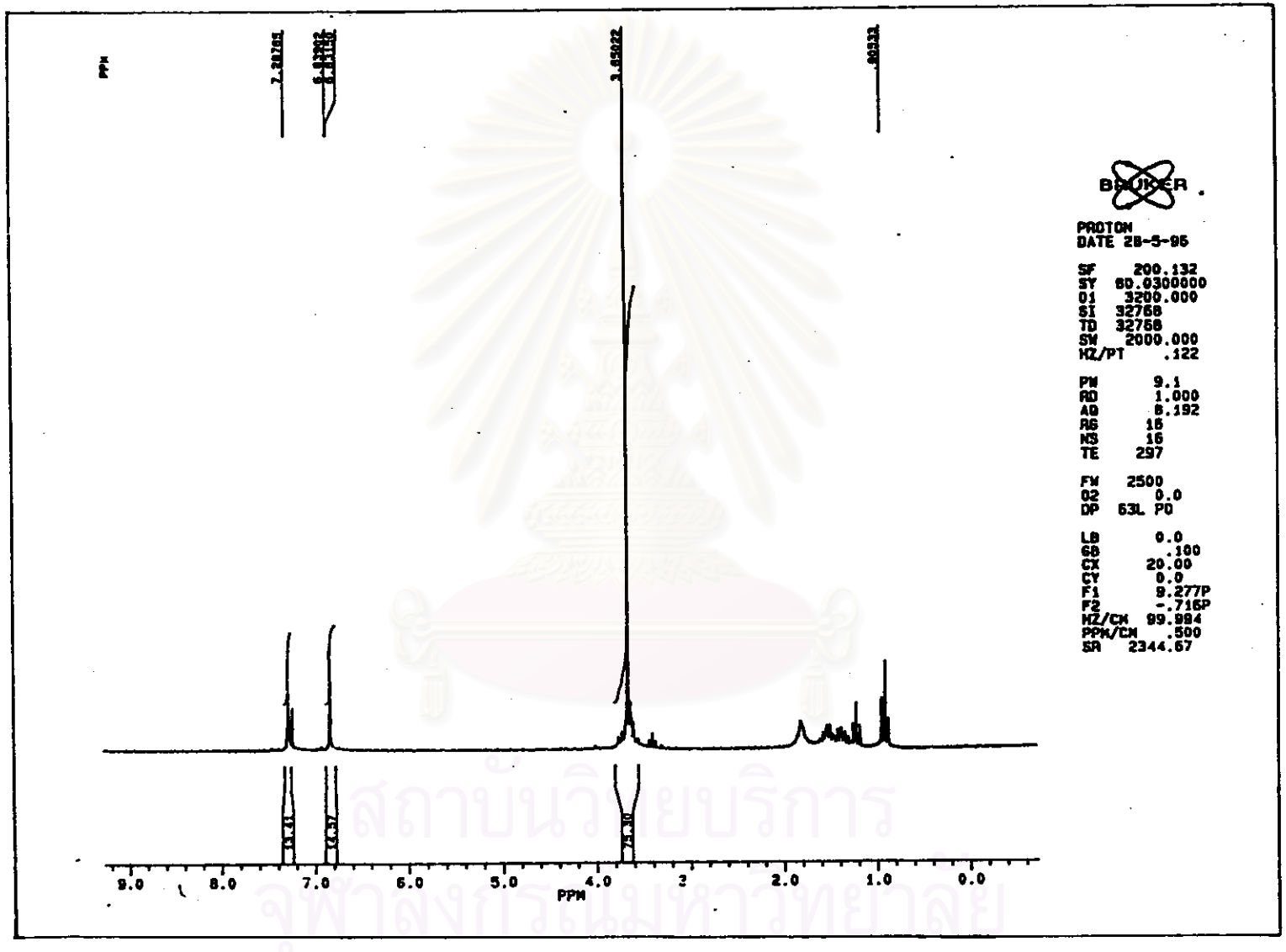


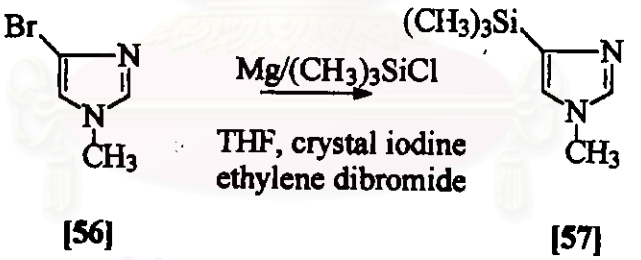
Figure 24 The ^{1}H-NMR spectrum of 4-bromo-1-methylimidazole in $CDCl_3$

This was performed by the reaction of 1-methyl-2,4,5-tribromoimidazole [53] with 2 mol equiv. of n-butyllithium followed by addition of water to give 4-bromo-1-methylimidazole as a colorless liquid.

^{1}H-NMR spectrum shown in Figure 24 exhibited two 1H singlets at δ 7.29 and 6.38 ppm for the protons at C-3 and C-5 ring position respectively and 3H singlet at δ 3.65 ppm for N-methyl substituent. This data is consistent with the structure of [56].

3.4.3 Synthesis of 4-(trimethylsilyl)-1-methylimidazole

Effenberger and co-workers [13] prepared [57] via "in situ Grignard synthesis" of 4-chloro-1-methylimidazole. This reaction was used to performed in the synthesis of 4-(trimethysilyl)-1-methylpyrazole (chapter 3.3.2) via 4-bromo-1-methypyrazole. A modification of their method was used for the synthesis of [57].



[56] [57]

The tiny crystal of iodine was added to make magnesium more reactive and ethylene dibromide was used as an entrainer. The solution mixture was worked-up to give a yellow liquid.

^{1}H-NMR spectrum of resulting liquid showed spectrum of [56] indicating that no reaction took place. Although the reaction was performed several times, [57] still was not formed. This experiment indicated that the "in situ Grignard synthesis" was not suitable for the synthesis of [57] from [56].

3.5 Photoreaction of 5-(trimethylsilyl)-1-methylpyrazole

According to the prediction by permutation analysis, 5-(trimethylsilyl)-1-methylpyrazole [33] should transpose to mainly three photoproducts, 5-(trimethylsilyl)-1-methylimidazole, 2-(trimethylsilyl)-1-methylimidazole, and 4-(trimethylsilyl)-1-methylimidazole that are predicted by P_4, P_6, and P_7 permutation pattern respectively. In order to find out whether the products from the photoreaction of 5-(trimethylsilyl)-1-methylpyrazole will follow the prediction, the photoreaction of 5-(trimethylsilyl)-1-methylpyrazole [33] was carried out.

3.5.1 Irradiation of 5-(trimethylsilyl)-1-methylpyrazole

UV absorption of 5-(trimethylsilyl)-1-methylpyrazole [33] in acetonitrile, as shown in Figure 25, indicated the maximum absorption at 220 nm due to a $\pi \rightarrow \pi^*$ transition.

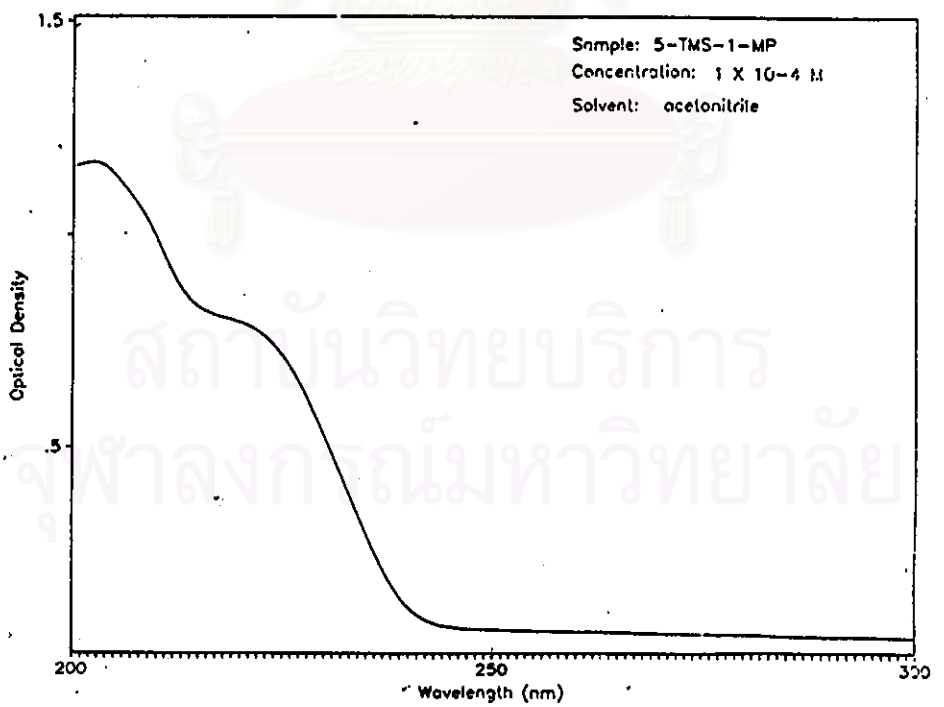


Figure 25 UV absorption spectrum of [33]

Direct irradiation of 2 x 10^{-2} M solution of pyrazole [33] in acetonitrile with high pressure Hanovia lamp was investigated and analyzed by UV spectroscopy. The reaction mixture was monitored at time 30, 60, and 90 mins. The UV absorption spectra from photolysate of [33] after 1:200 dilution in acetonitrile (Figure 26) showed the formation of a species that absorbed light at a longer wavelength, λ_{max} 268. The optical density at λ_{max} 268 nm increased with irradiation time which was 0.80 within 90 min of irradiation. In contrast the absorption peak at λ_{max} 220 nm decreased at time intervals. This indicated that the photoreactant was consumed to form the new photoproducts which absorbs light at 268 nm.

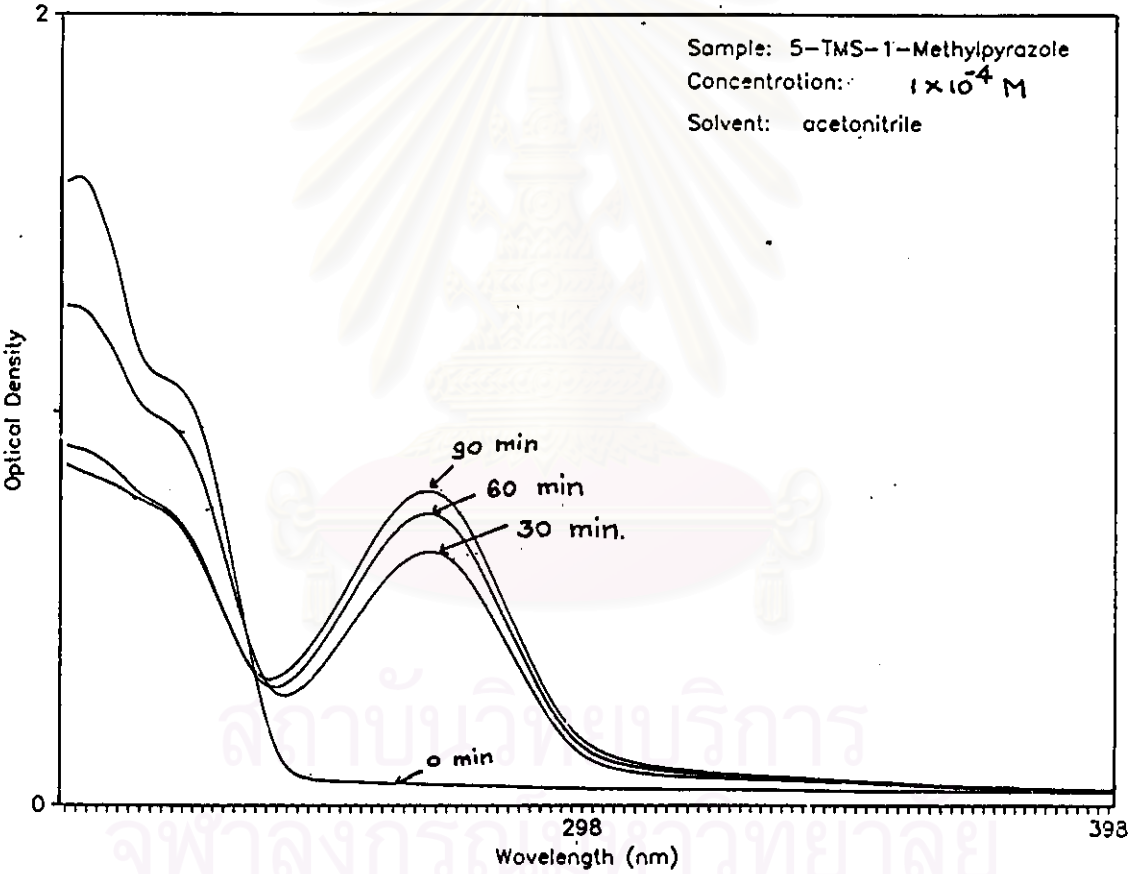


Figure 26 UV absorption spectra at time intervals photolysis of [33]

3.5.2 Investigation of the photoreaction by Gas Chromatography

To monitor the photoreaction of 5-(trimethylsilyl)-1-methylpyrazole, 1 μL of the reaction solution was taken at the irradiation times 30, 60, and 90 mins for analysis using gas chromatography, GC1 (PE-8500 FID instrument equipped with a

30m x 0.25mm i.d. fused column coated with 0.25μ Supelwax 10 bonded phase) as shown in Figures 27-30.

Figure 27 GC trace of [33] before irradiation

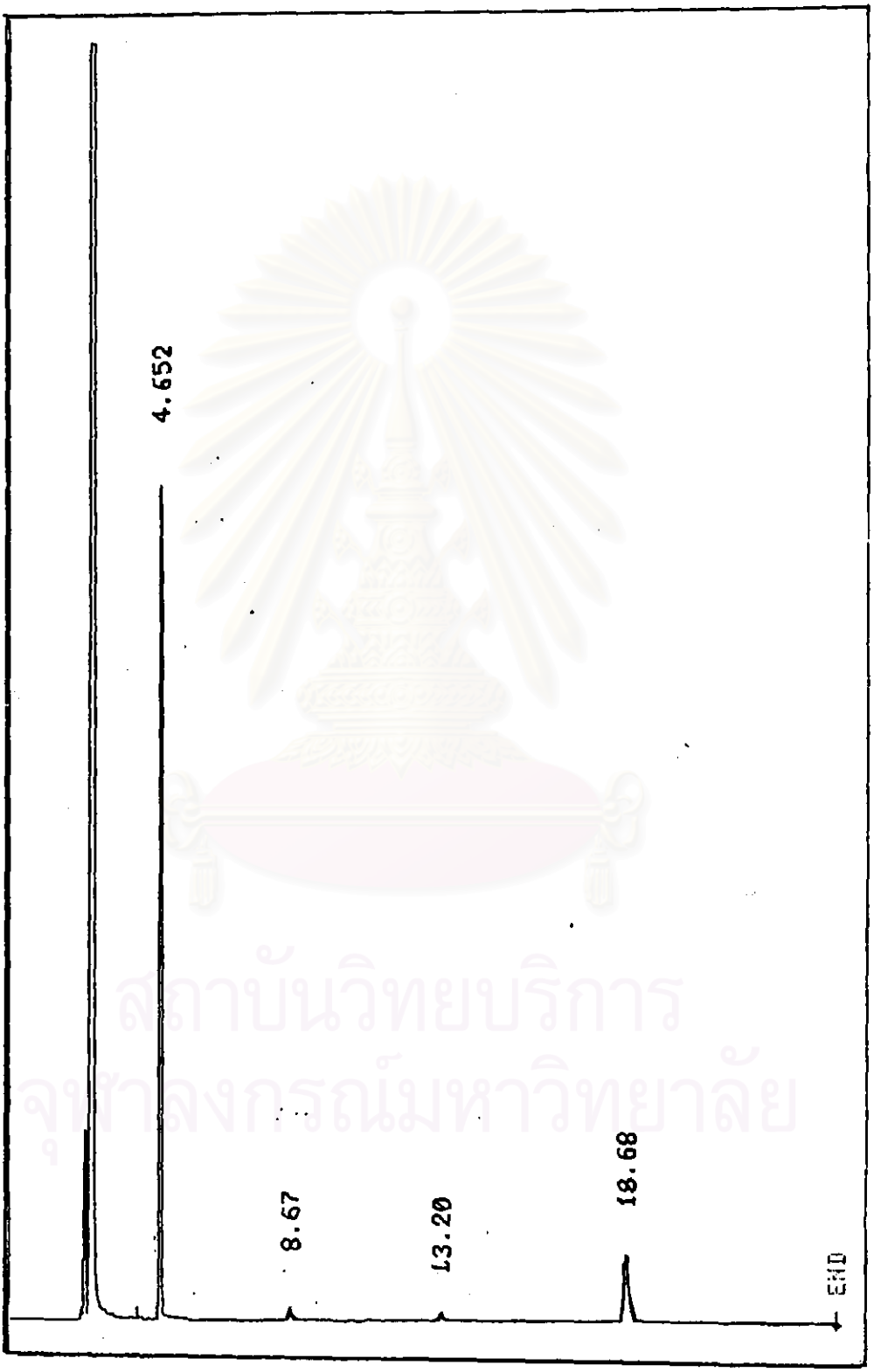


Figure 28 GC trace of [33] after 30 min of irradiation

Figure 29 GC trace of [33] after 60 min of irradiation

Figure 30 GC trace of [33] after 90 min of irradiation

These are the gas chromatographs of the solution of **[33]** before and after 30, 60, and 90 mins of irradiation, respectively. All of them showed the peak of photoreactant at retention time 4.68 min and three additional peaks at retention time 8.72, 13.30, and 18.78 mins. As the reaction proceeded, the photoreactant decreased while the photoproducts increased as indicated by the relative peak heights in these gas chromatographs. It is possible that three additional peaks are three expected products i.e., 2-,4-, and 5-(trimethysilyl)-1-methylimidazoles as predicted by the permutation pathway.

In order to prove this, three authentic compounds, 2-(trimethylsilyl)-1-methylimidazole, 4-(trimethylsilyl)-1-methylimidazole, and 5-(trimethylsilyl)-1-methylimidazole were synthesized and their GC retention times were determined. 2-(trimethylsilyl)-1-methylimidazole **[45]** and 5-(trimethylsilyl)-1-methylimidazole **[47]** were completely synthesized and their GC retention times were determined using the same conditions with photolysate. GC retention time of **[45]** and **[47]** were at 7.76 and 18.70 mins respectively.

Unfortunately, the synthesis of 4-(trimethylsilyl)-1-methylimidazole was unsuccessful. Thus its GC retention time could not be determined.

The products of photoreaction were identified by their gas chromatographic retention times. The first interesting peak was at the retention time 18.78 min. Its retention time was very close to the retention time of authentic 5-(trimethylsilyl)-1-methylimidazole. In order to confirm its identity, authentic 5-(trimethylsilyl)-1-methylimidazole was spiked into the solution of photolysate. GC trace showed no separation between the authentic 5-(trimethylsilyl)-1-methylimidazole and peak at the longest retention time (Figure 31). So it clearly indicated that the GC peak at the longest retention time is 5-(trimethylsilyl)-1-methylimidazole.

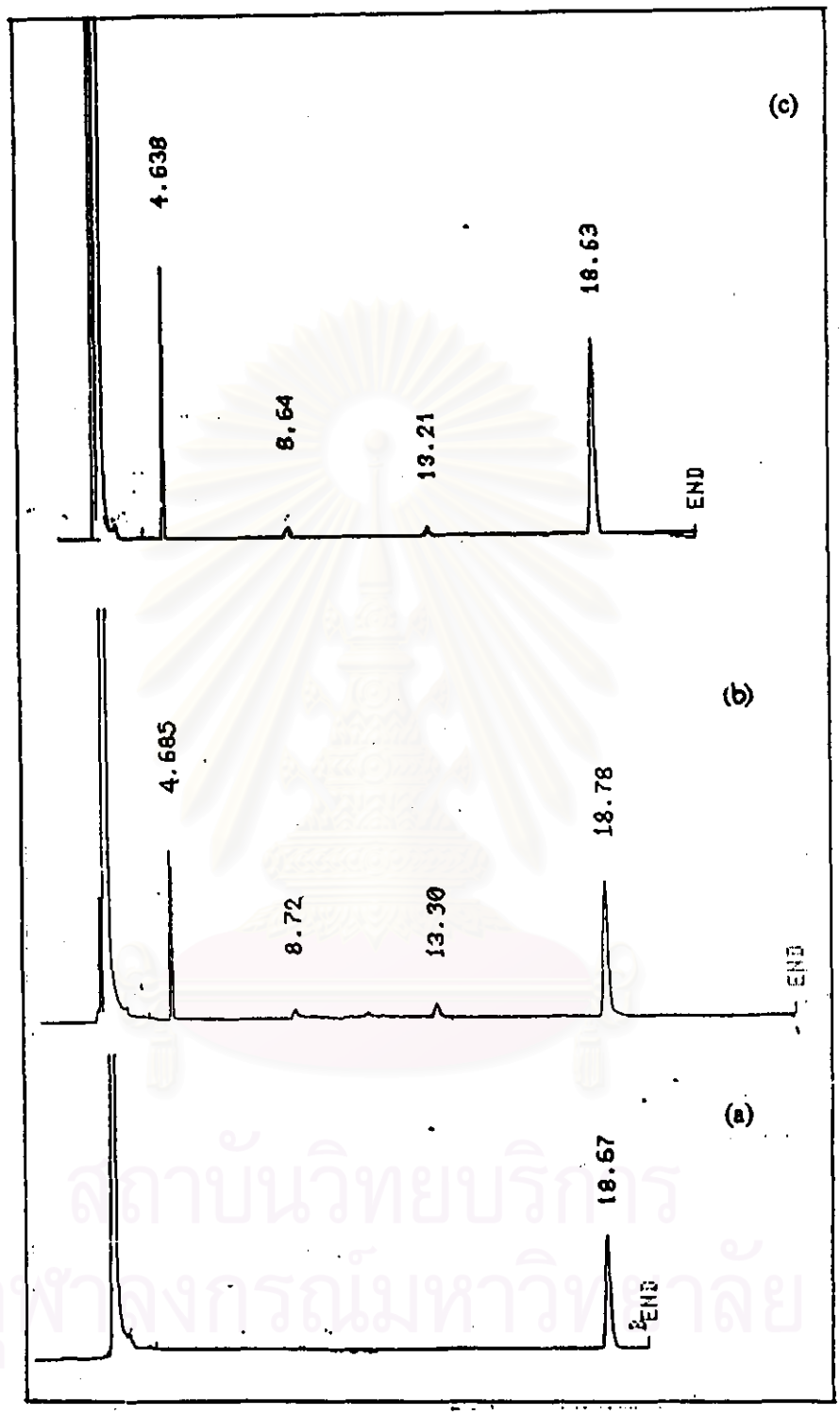


Figure 31 GC trace of (a) authentic 5-(trimethylsilyl)-1-methylimidazole [47], (b) [33] after 90 min of irradiation, and (c) (b) spiked with authentic 5-(trimethylsilyl)-1-methylimidazole

The second product expected to occur was 2-(trimethylsilyl)-1-methylimidazole which had a GC retention time at 7.76 min. Surprisingly the GC trace of photolysate shows no peak at that retention time indicating that 2-(trimethylsilyl)-1-methylimidazole was not one of these products.

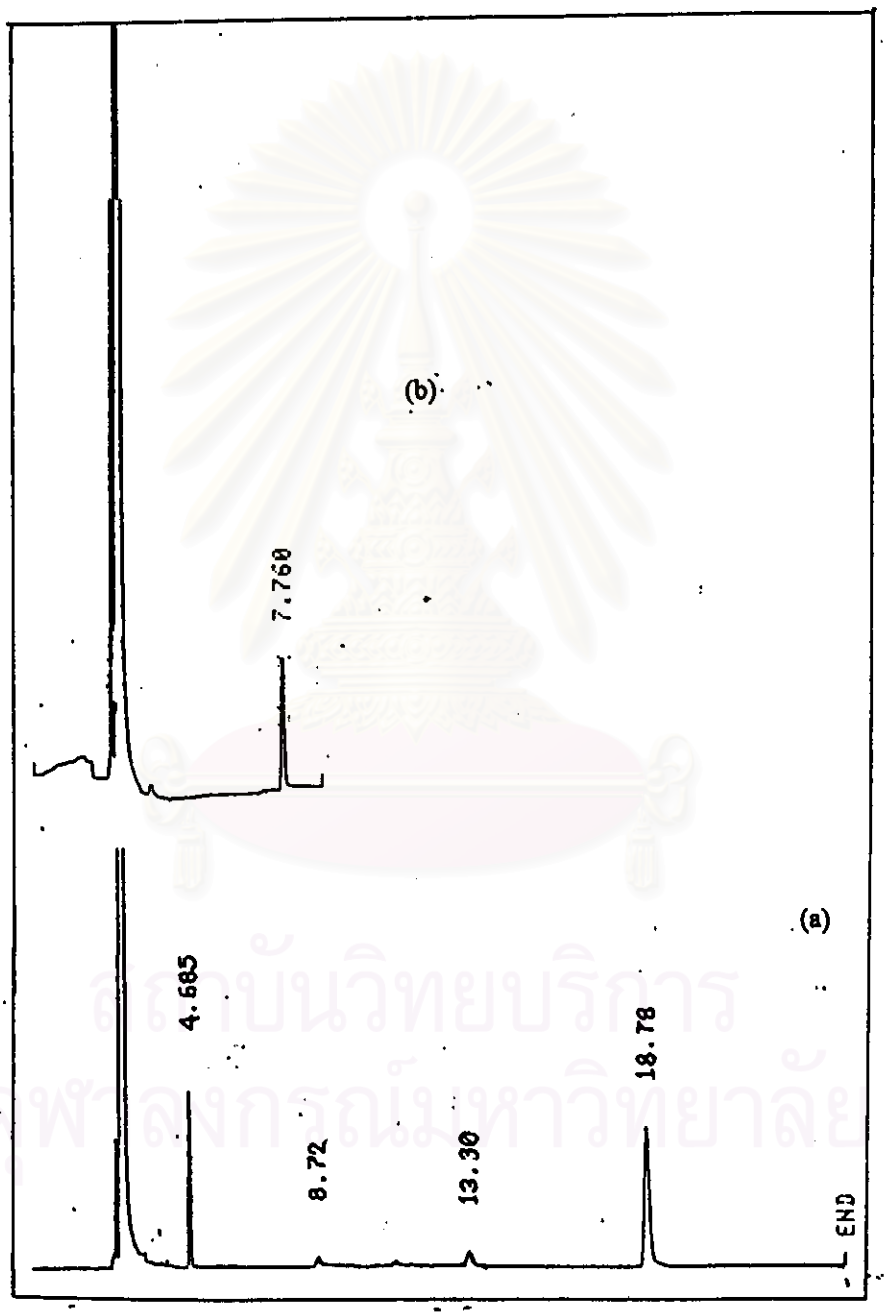
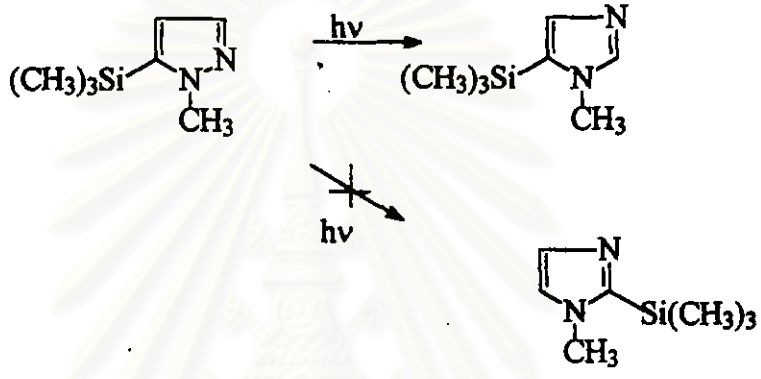


Figure 32 GC trace of (a) [33] after 90 min of irradiation and (b) authentic 2-(trimethylsilyl)-1-methylimidazole

The one of these two unidentified peaks was possible to be another expected 4-(trimethylsilyl)-1-methylimidazole. Comparison between GC retention time of authentic sample and photoproduct could not be done since 4-(trimethylsilyl)-1-methylimidazole could not be synthesized.

GC analysis indicated the photoproduct as following.



3.5.3 Investigation of the photoreaction by GC-MS

To clear the ambiguity, the photolysate was analyzed by the GC-MS and the mass spectra of the photoproducts were compared with the mass spectra of the authentic compounds synthesized. Figure 33 are the gas chromatographs of the photolysate of **[33]** after 90 min of irradiation. It showed the peak of photoreactant at retention time 4.52 min. Surprisingly, there were five peaks of photoproducts formed at retention time 4.11, 8.49, 11.51, 14.06, and 16.79 mins.

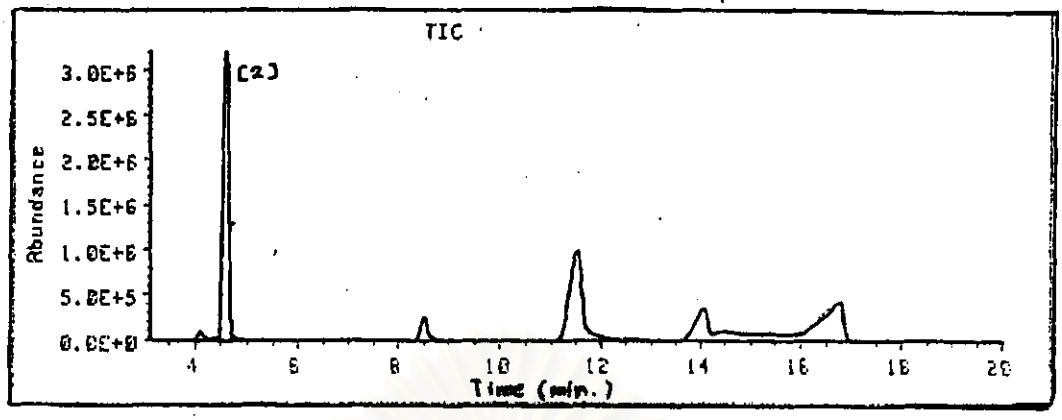


Figure 33 GC trace of **[33]** after 90 min of irradiation (from GC-MS)

However the peaks at retention time 4.11, 8.49, and 11.51 probably are the same compounds as detected by GC (see Figures 28-30). But two peaks at 14.06 and 16.79 were the additional peaks different from the previous chromatogram. Since different type of column packing material and the instrument condition, these two new peaks appear while they could not be observed before.

The first interesting peak was at retention time 11.51 min. Its mass spectrum indicated that the molecular mass equals to 154. And the comparison between mass spectrum of authentic 5-(trimethylsilyl)-1-methylimidazole and mass spectrum of product at this retention time (Figures 34a and b) showed the same fragmentation patterns. This result also confirmed the result from GC that one product formed from the photoreacion was 5-(trimethylsilyl)-1-methylimidazole.

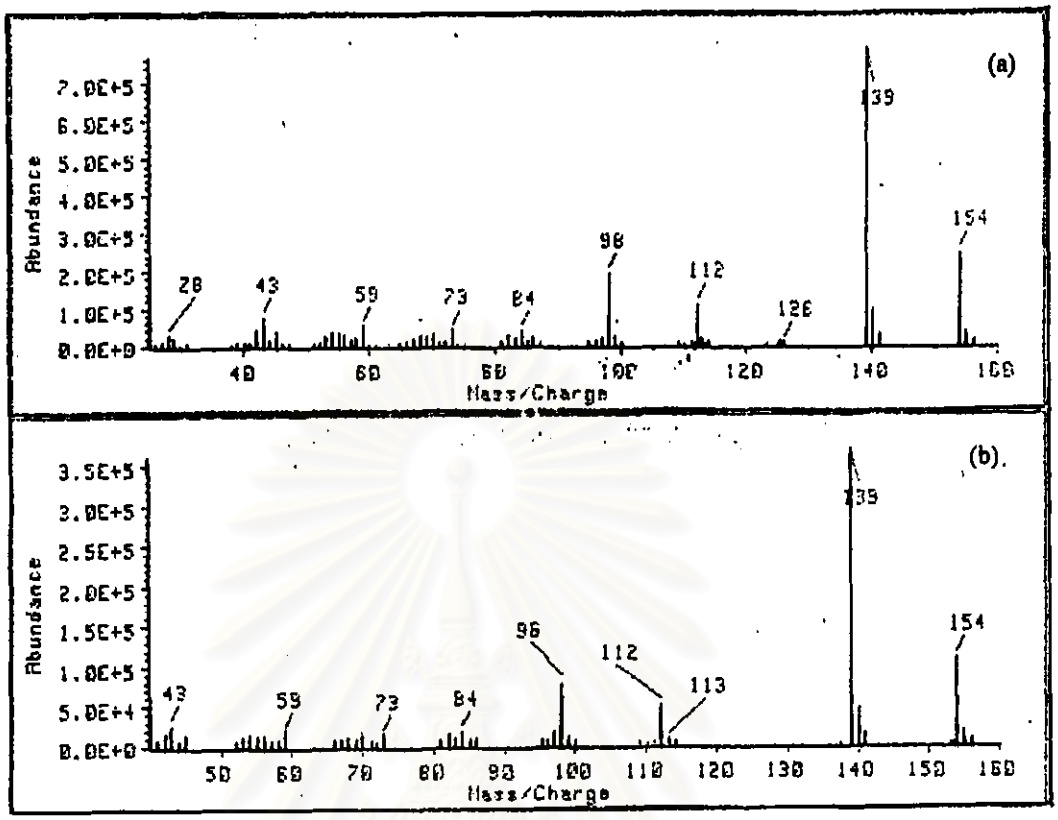


Figure 34 The mass spectra of (a) 5-(trimethylsilyl)-1-methylimidazole synthesized and (b) photoproduct at retention time 11.51 min

The peak at retention time 4.11 min was the ambiguous one. It has the molecular mass 82. From the line of syntheses of any expected photoproducts, they all were started from available 1-methylimidazole which has the molecular mass 82 and it is consistent with the molecular mass of product at retention time 4.11 min. So they probably were the same compound. The comparison between the mass spectrum of authentic 1-methylimidazole and the mass spectrum of product at retention time 4.11 min was shown in Figure 35.

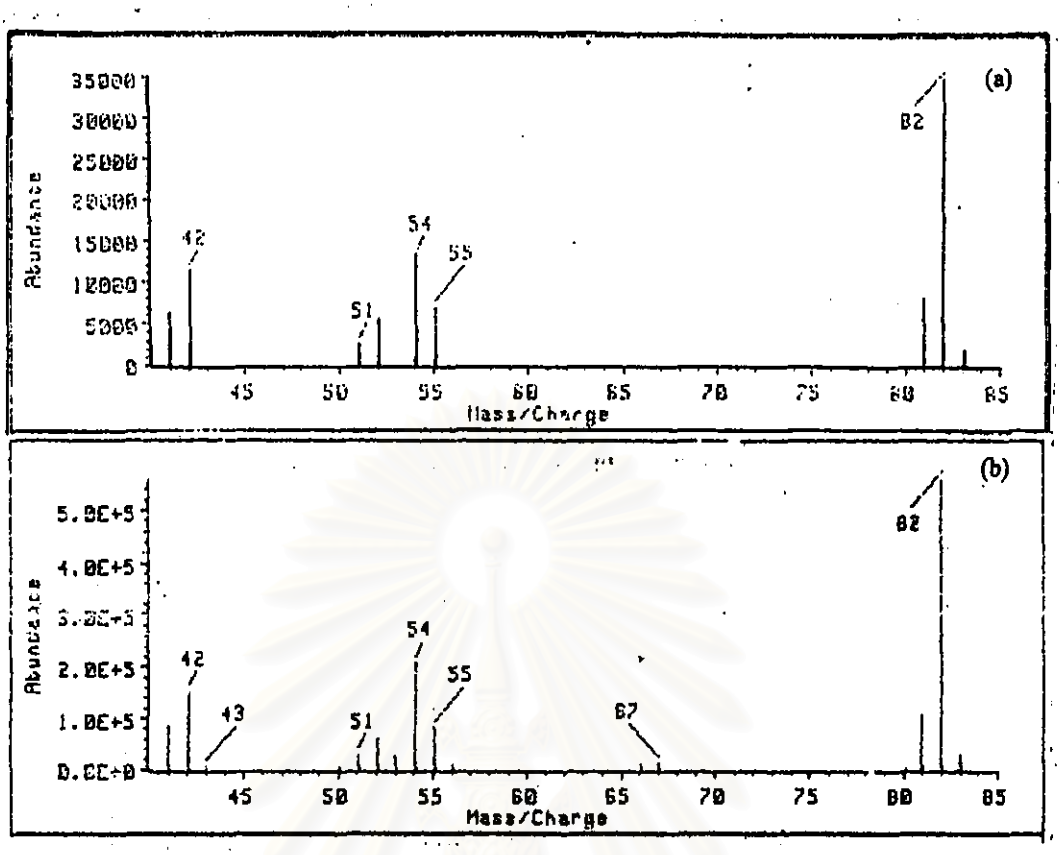


Figure 35 The mass spectra of (a) authentic 1-methylimidazole and (b) photoproduct at retention time 4.11 min

They showed the same fragmentation pattern. The fragmentation at m/z 55 was according to the fragment of 1-methylimidazole losing HC≡N group. Consequently the product at retention time 4.11 min was identified as 1-methylimidazole that was the same compound analyzed by GC at retention time 8.72 min. (see Figures 28-30) Since the authentic 1-methylimidazole was spiked into the photolysate and analyzed by GC. It showed no separation between peak at retention time 8.72 min and authentic 1-methylimidazole.

For the peak at retention time 8.49 min, it showed the molecular mass at 154 (Figure 36) which was in line with molecular mass of 2-, 4-, and 5-(trimethylsilyl)-1-methylimidazoles, three expected photoproducts of this series. 5-(Trimethylsilyl)-1-methylimidazole was already identified to be the one of photopoducts which was at retention time 11.51 min and 2-(trimethylsilyl)-1-methylimidazole was not one of these products. Since the fragmentation pattern of product at retention time 8.49 min

is similar to fragmentation pattern of 5-(trimethylsilyl)-1-methylimidazole, it must be the compound that is an isomer of 5-(trimethylsilyl)-1-methylimidazole. Thus 4-(trimethylsilyl)-1-methylimidazole must be that compound.

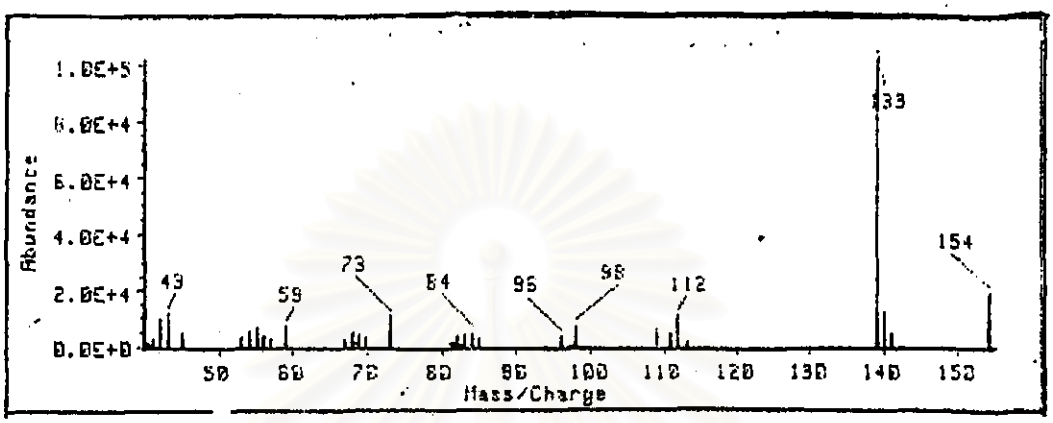
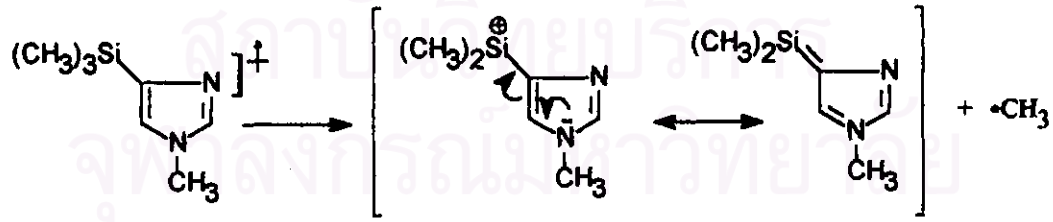


Figure 36 The mass spectrum of the photoproduct at retention time 8.486 min

Its mass spectrum showed the highest relative abundance at m/z 139 that caused from losing one methyl group of trimethylsilyl substituent to form the stable tertiary silicon cation as shown in scheme 3.

Scheme 3 Fragmentation of 4-(trimethylsilyl)-1-methylimidazole by losing one methyl group



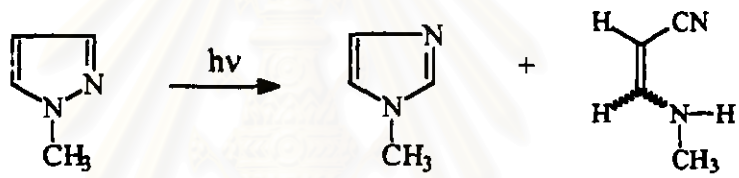
m/z = 139

The peak at retention time 8.48 min was identified as 4-(trimethylsilyl)-1-methylimidazole that was the same compound as shown in GC at retention time 13.30 min. (see Figure 28-30) Unfortunately, attempt to synthesize 4-(trimethylsilyl)-

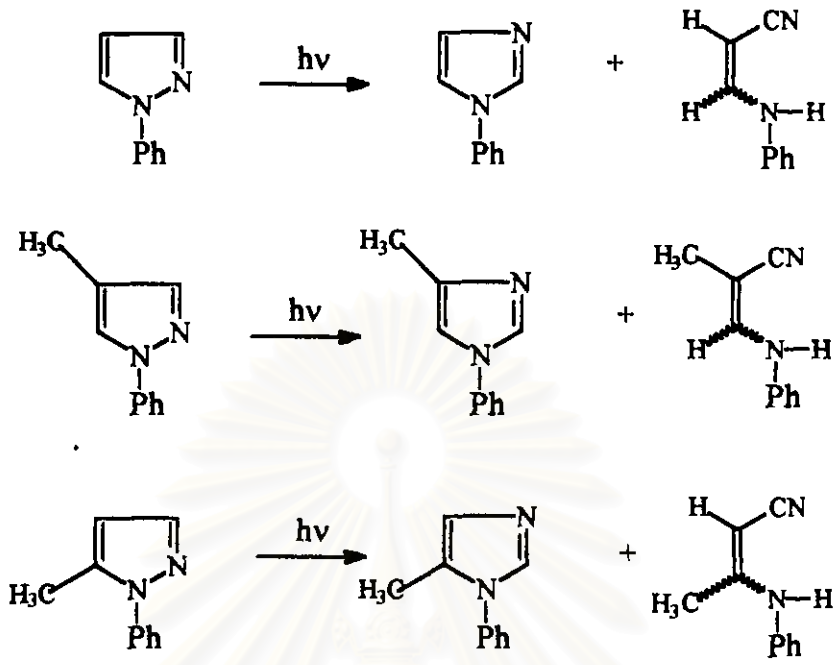
1-methylimidazole was unsuccessful, thus it could not be confirmed by the comparison of GC retention time.

The mass spectra of products at the retention time 14.06 and 16.79 mins (Figures 37 a and b) showed parent peaks at m/z 154. Since their fragmentation patterns look similar, they must be the geometrical isomers.

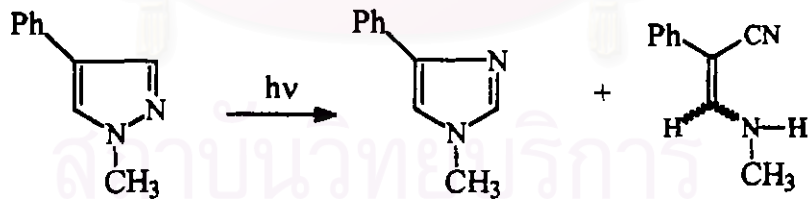
In 1991, Pavlik and Kurzweil [3] reported that 1-methylpyrazole underwent not only photoisomerization to 1-methylimidazole but also photocleavage to 3-(*N*-methylamino)propenenitrile.



In 1993, Pavlik and co-workers [21] reported the photoisomerization of 1-phenylpyrazole, 4-methyl-1-phenylpyrazole, and 5-methyl-1-phenylpyrazole to give the phototransposition products as well as photocleavage products.



And in 1995, Pavlik and Kebede [22] also reported that 1-methyl-4-phenylpyrazole underwent not only phototransposition to 1-methyl-4-phenylimidazole but also photocleavage to 3-(*N*-methylamino)-2-phenylpropenenitrile.



According to their works, it is possible that 5-(trimethylsilyl)-1-methylpyrazole, a trimethylsilyl-substituted-1-methylpyrazole, would undergo not only photoisomerization to three substituted-1-methylimidazoles but also photocleavage to the other product. Imitating their work, 5-(trimethylsilyl)-1-methylpyrazole would undergo photocleavage to 3-(trimethylsilyl)-3-(*N*-methylamino)propenenitrile which would be the same product at retention time 14.06 and 16.79 mins. The products at retention time 14.06 and 16.79

mins would be cis/trans isomers of 3-(trimethylsilyl)-3-(*N*-methylamino) propenenitrile.

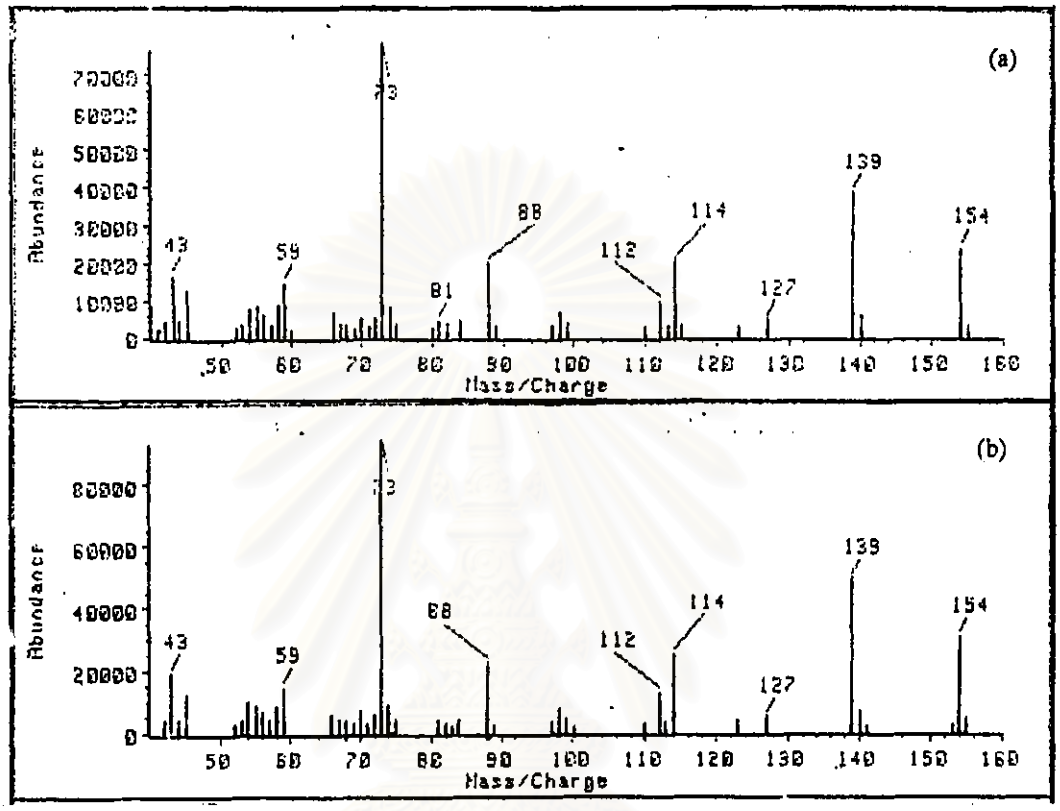
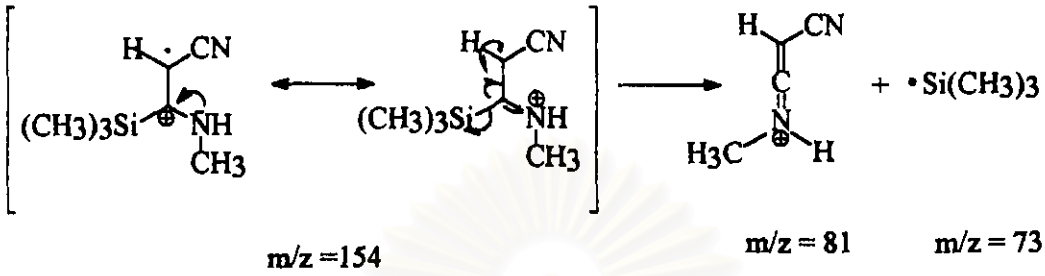


Figure 37 The mass spectra of the photoproducts at retention time (a) 14.06 min and (b) 16.79 min

The proposed fragmentations of 3-(trimethylsilyl)-3-(*N*-methylamino) propenenitrile were shown in scheme 4.

Scheme 4 proposed fragmentations of 3-(trimethylsilyl)-3-(*N*- methylamino) propenenitrile



The highest relative abundance (m/z 73) is the fragmentation of trimethylsilyl group which is lost easier than substituent on imidazole ring. Thus these two isomers should be formed by photocleavage of 5-(trimethylsilyl)-1-methylpyrazole.

3.5.4 Confirmation of photocleavage product by Infrared Spectroscopy

According to the structure of 3-(trimethylsilyl)-3-(*N*-methylamino) propenenitrile, cyano group is the dominate part in this compound. Normally, -CN would be detected by Infrared Spectroscopy to show symmetric stretching at 2200 cm^{-1}. This assumption was confirmed by the IR spectrum of photolysate (Figure 38). It showed sharp absorption at 2183 cm^{-1} according to the symmetric stretching of cyano group of the 3-(trimethylsilyl)-3-(*N*-methylamino) propenenitrile.

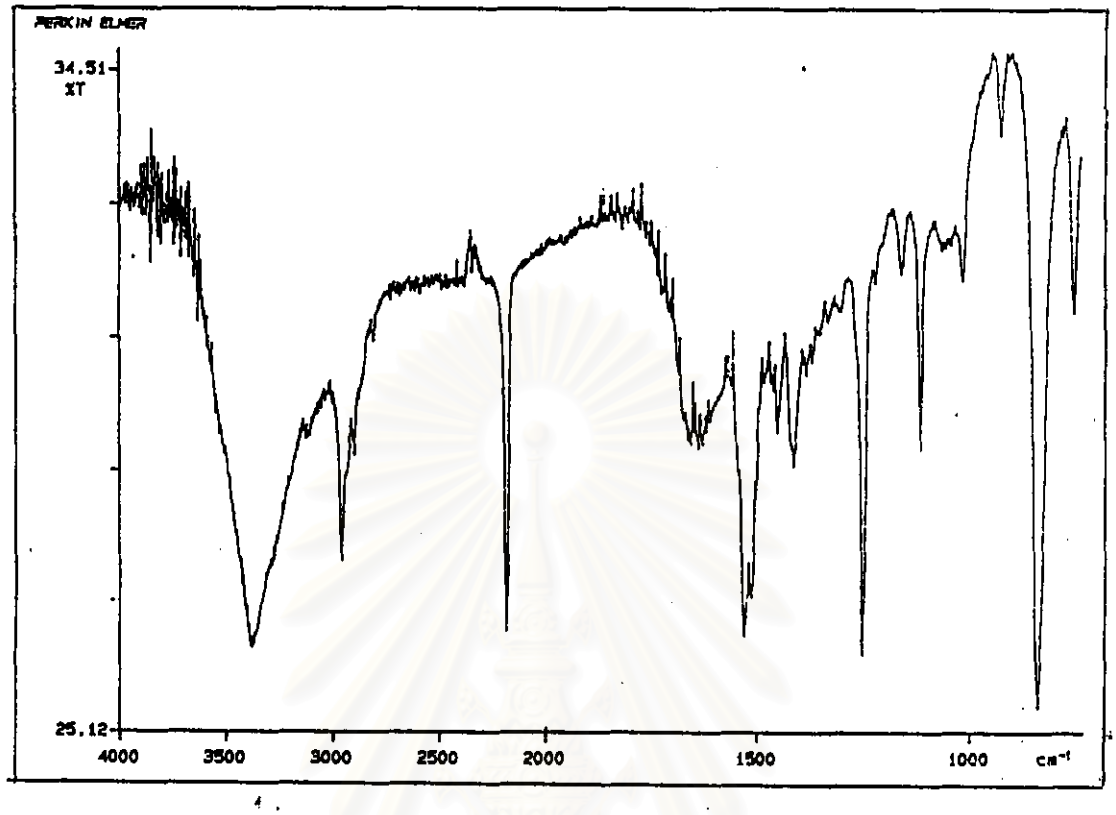
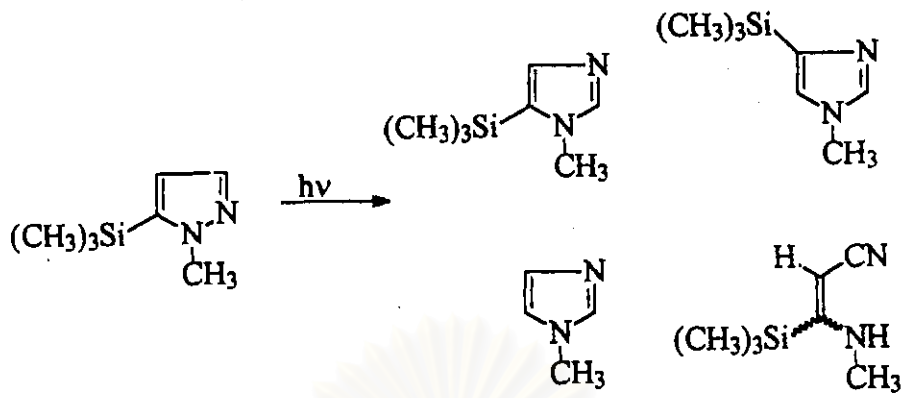


Figure 38 The IR spectrum of [33] after 90 min of irradiation

The products at retention time 14.06 and 16.79 were identified as cis/trans isomers of 3-(trimethylsilyl)-3-(*N*-methylamino)propenenitrile. Unfortunately both cis and trans 3-(trimethylsilyl)-3-(*N*-methylamino)propenenitrile have not been synthesized in this work. These two peaks could not be identified which peak belongs to cis or trans isomer.

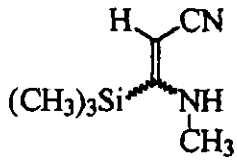
The results from GC-MS and IR identified peak at retention time 4.11, 8.49, 11.51, 14.06, and 16.79 mins as 1-methylimidazole, 4-(trimethylsilyl)-1-methylimidazole, 5-(trimethylsilyl)-1-methylimidazole, and cis/trans 3-(trimethylsilyl)-3-(*N*-methylamino)propenenitrile, respectively.



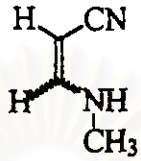
3.5.5 ^{1}H-NMR spectrum of the photolysate of 5-(trimethylsilyl)-1-methylpyrazole

The products mixture from 60 min-irradiation of 5-(trimethylsilyl)-1-methylpyrazole was analyzed by ^{1}H-NMR (Figures 39-40). ^{1}H-NMR spectrum of products mixture was compared with the spectra of the authentic compounds synthesized in this work. The chemical shifts at δ 0.31, 3.94, 7.44, and 6.33 are due to trimethylsilyl protons, N-methyl protons, a proton on C-3, and a proton on C-4, respectively of photoreactant, 5-(trimethylsilyl)-1-methylpyrazole. The photoproduct, 5-(trimethylsilyl)-1-methylimidazole showed at δ 0.28, 3.68, 7.10, and 7.54 which are consistent with trimethylsilyl protons, N-methyl protons, a proton on C-4, and a proton on C-2, respectively.

3-(Trimethylsilyl)-3-(*N*-methylamino)propenenitrile was also confirmed by ^{1}H-NMR signals. Comparison between the chemical shifts of authentic 3-(trimethylsilyl)-3-(*N*-methylamino)propenenitrile and products mixture could not be done since it has not been synthesized before. However, 3-(*N*-methylamino)propenenitrile was synthesized in this work and its structure is different from the structure of 3-(trimethylsilyl)-3-(*N*-methylamino)propenenitrile just only trimethylsilyl substitution on C-3 as shown below.



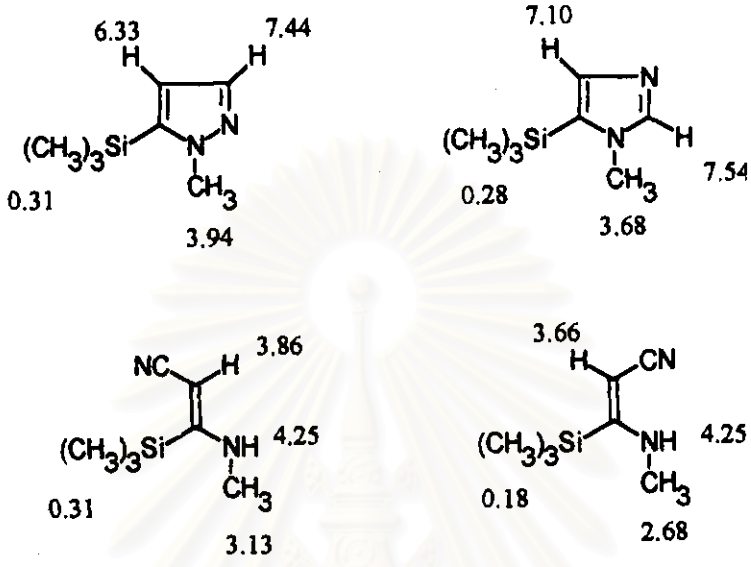
3-(trimethylsilyl)-3-(*N*-methylamino)propenenitrile



3-(*N*-methylamino)propenenitrile

So they would show the similar chemical shifts. The signals at δ 6.55-7.05 due to the protons on C-3 of cis/trans isomers on 3-(*N*-methylamino)propenenitrile were not seen because of the trimethylsilyl substitution on that position. The chemical shifts at 3.66, 0.18, 2.68, and 4.25 are consistent with the signals of a proton on C-2, trimethylsilyl protons, N-methyl protons, and a proton on nitrogen, respectively of trans isomer of 3-(trimethylsilyl)-3-(*N*-methylamino)propenenitrile. cis isomer of 3-(trimethylsilyl)-3-(*N*-methylamino)propenenitrile also showed at δ 3.86, 0.31, 3.13, and 4.25 which are consistent with the signals of a proton on C-2, trimethylsilyl protons, N-methyl protons, and a proton on nitrogen, respectively. The ratio of trans/cis equals to 2.4:1. The assignment of the chemical shifts for the protons of components in the photolysate **[33]** after 60 min of irradiation were shown in scheme 5.

Scheme 5 Assignment of the chemical shifts for the protons of components in the photolysate [2] after 60 min of irradiation



The signal of photoproduct, 1-methylimidazole must be seen at δ 7.40, 7.05, 6.87, and 3.68 due to the signals of a proton on C-2, a proton on C-4, a proton on C-5, and N-methyl protons, respectively. And the signals of 4-(trimethylsilyl)-1-methylimidazole [13] must be seen at δ 7.60, 7.03 due to protons on C-2 and C-5 respectively. Unfortunately, their signals could not be detected since their yield are very low when compare with 5-(trimethylsilyl)-1-methylimidazole and 3-(trimethylsilyl)-3-(*N*-methylamino)propenenitrile.

According to the prediction about three photoproducts of the photoreaction of 5-(trimethylsilyl)-1-methylimidazole, there are two of them, 5-(trimethylsilyl)-1-methylimidazole and 4-(trimethylsilyl)-1-methylimidazole, are exactly the same as the prediction while 2-(trimethylsilyl)-1-methylimidazole is out of the prediction. The photoproduct, 1-methylimidazole was observed instead.

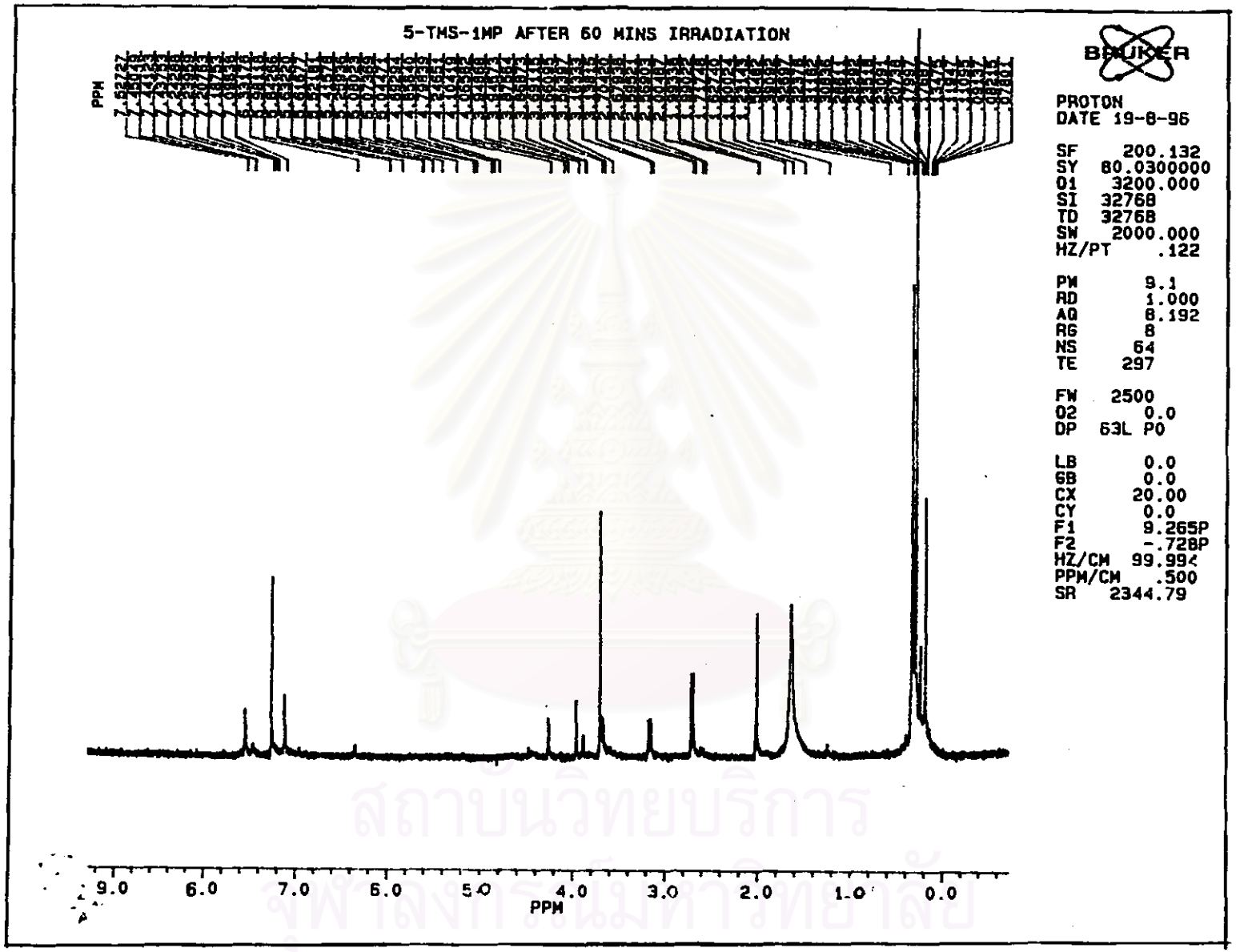


Figure 39 The ^{1}H-NMR spectrum of [33] after 60 min of irradiation

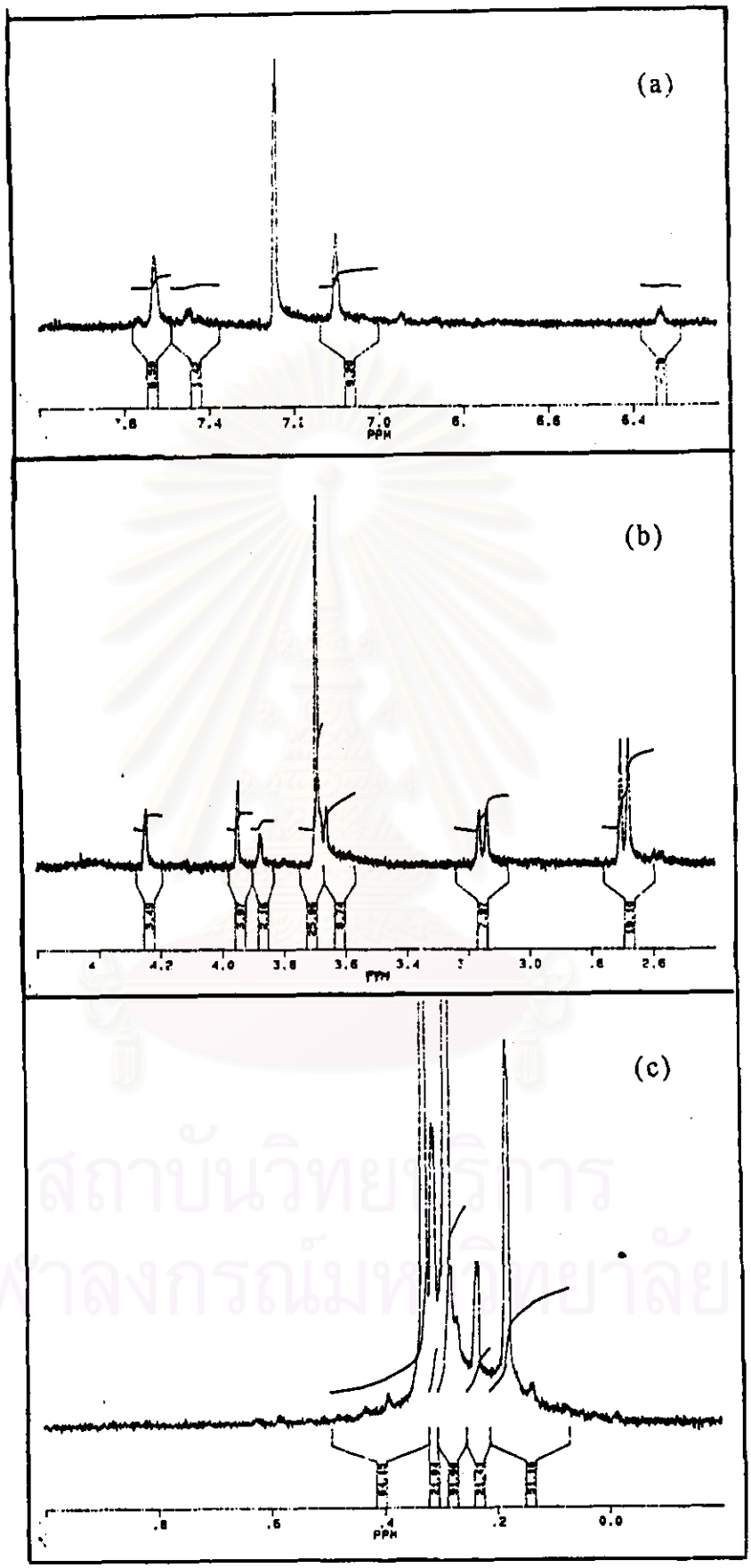


Figure 40 The expansion of ^{1}H-NMR spectra of [33] after 60 min of irradiation (a) 6.2-7.6 ppm, (b) 2.6-4.4 ppm, and (c) 0.0-0.6 ppm

3.6 Photoreaction of 3-(trimethylsilyl)-1-methylpyrazole

According to the prediction by permutation pathway, 3-(trimethylsily)-1-methylpyrazole **[43]** should transpose to two products, 2-(trimethylsilyl)-1-methylimidazole by P_4 & P_7 permutation pathway and 4-(trimethylsilyl)-1-methylimidazole by P_6 permutation pathway. In order to find out whether the products from the photoreaction of 3-(trimethylsily)-1-methylpyrazole will follow the permutation pettern analysis, the photoreaction of 3-(trimethylsily)-1-methylpyrazole was carried out.

3.6.1 Irradiation of 3-(trimethylsily)-1-methylpyrazole

UV absorption spectrum of 3-(trimethylsilyl)-1-methylpyrazole **[43]** in acetonitrile, as shown in Figure 41, displayed the maximum absorption at 220 nm according to a $\pi \rightarrow \pi^*$ transition.

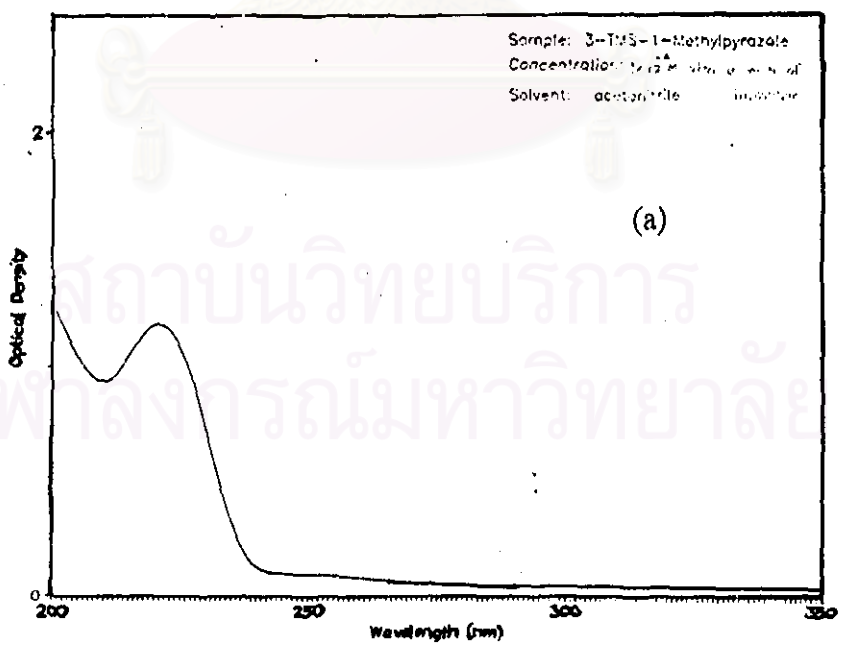


Figure 41 The UV absorption spectrum of **[43]**

The solution of **[43]**, 2.00 x 10^{-2} M in acetonitrile (3 mL) was then irradiated with the Hanovia lamp under nitrogen. The reaction was monitored by UV spectroscopy. The UV absorption spectra from photolysate of **[43]** after 1:200 dilution in acetonitrile (Figure 42) showed the formation of a species that absorbs light at longer wavelength, λ_{max} 251 nm. The optical density at λ_{max} 251 nm increased with irradiation time which was 2.00 within 80 min of irradiation in concomitant with the decrement of the optical density at λ_{max} 220 nm of photoreactant.

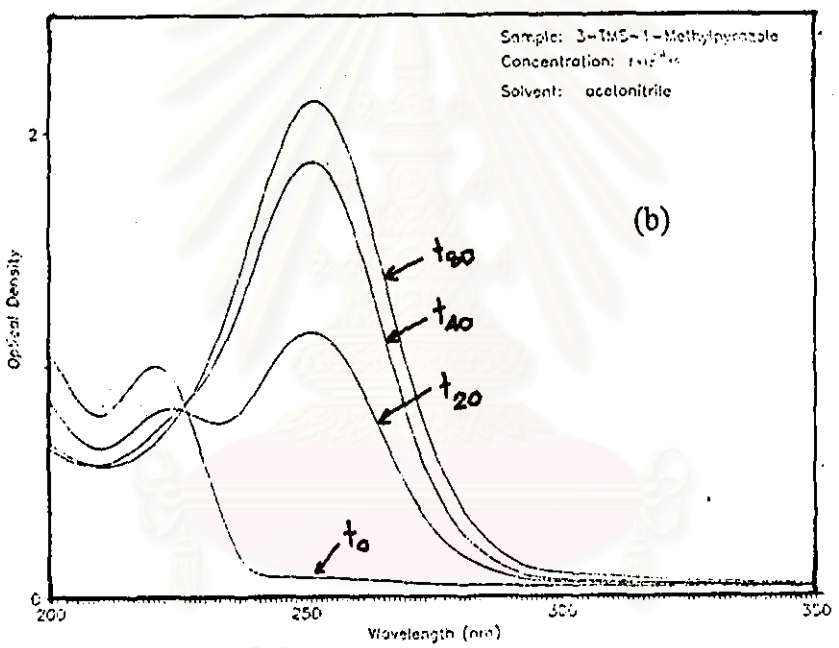


Figure 42 The UV absorption spectra of **[43]** at various irradiation times

3.6.2 Investigation of the photoreaction by gas chromatography

To monitor the photoreaction of 3-(trimethylsilyl)-1-methylpyrazole, 1μL of the reaction solution was taken at time 20, 40, and 80 mins for analysis using gas chromatography, GC1 (PE-8500 30m x 0.25 i.d. fused silica column coated with 0.25 μ supelwax 10 bonded phase). Figures 43-46 are the gas chromatographs of the solution of **[43]** before and after 20, 40, and 80 mins of irradiation, respectively. All of them showed the peak of photoreactant at retention time 4.1 min and two

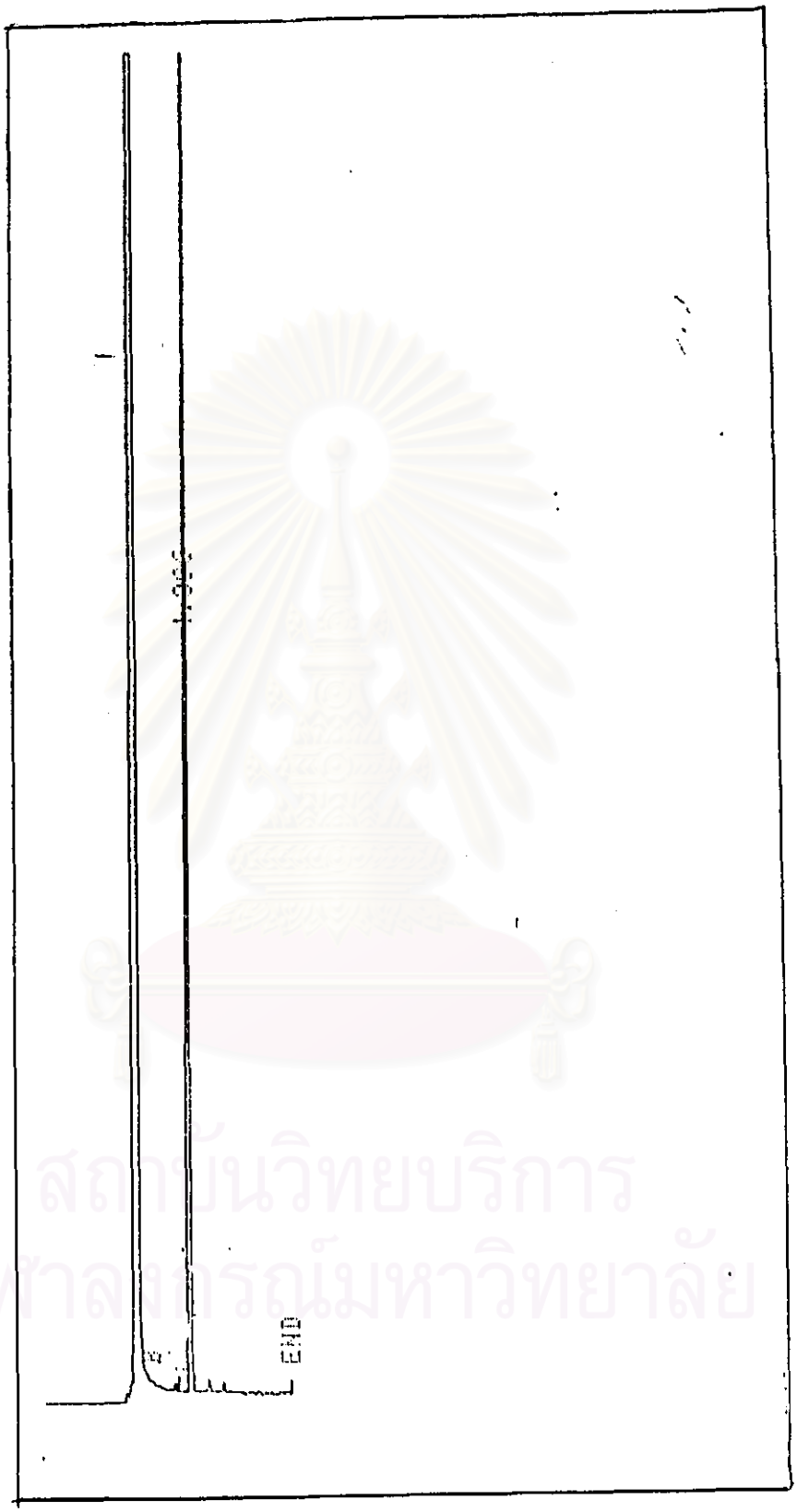


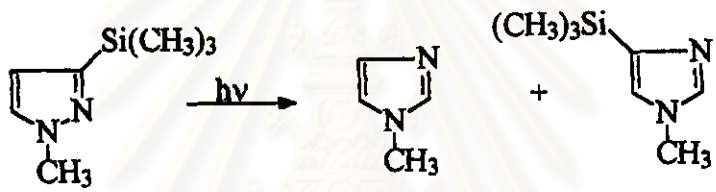
Figure 43 GC trace of [43] before irradiation

Figure 44 GC trace of [43] after 20 min of irradiation

Figure 45 GC trace of [43] after 40 min of irradiation

Figure 46 GC trace of [43] after 80 min of irradiation

additional peaks at retention time 8.7 and 13.2 mins, which were assumed to be due to the photoproducts. As the reaction proceeded, the photoreactant decreased while the photoproducts increased as indicated by the relative peak heights in these gas chromatographs. It shall be pointed out that the retention time of photoproducts appeared to be nearly the same as the ones of 1-methylimidazole and 4-(trimethylsilyl)-1-methylimidazole that were clearly identified before in the photoreaction of 5-(trimethylsilyl)-1-methylpyrazole. (see section 3.5.1) So two products formed in this reaction were expected to be 1-methylimidazole and 4-(trimethylsilyl)-1-methylimidazole.



3.6.3 Re-investigation of the photoreaction by another gas chromatography (Perkin Elmer)

As the previous observation, 5-(trimethylsilyl)-1-methylpyrazole underwent phototransposition as well as photocleavage to products. It is possible that 3-(trimethylsilyl)-1-methylpyrazole can undergo photocleavage as well. The type of column packing material and conditions of GC1 (PE-8500) might not be suitable to detect the photocleavage product. Therefore the photoreaction was re-investigated by another gas chromatographic instrument, GC2 (Perkin Elmer 15m x 0.53 mm methyl 50% phenyl silicone phase capillary column). GC trace showed three peaks at retention time 2.0, 3.08, and 6.18 mins. GC trace from GC2 (Figure 47) looks like GC trace from GC1.

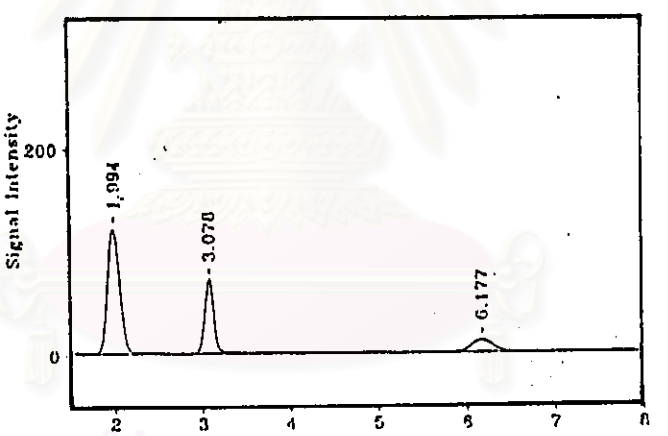


Figure 47 GC trace of [43] after 40 min of irradiation

The peak at retention time 2.0 min is due to the photoreactant [43]. It was interesting to find out whether two peaks at retention time 3.08 and 6.18 mins were the same compounds, 1-methylimidazole and 4-(trimethylsilyl)-1-methylimidazole, which were detected by GC1. The first interesting compound was 1-methylimidazole [2]. The spiking technique was used. The authentic [2] was spiked to the photolysate of 40 min of irradiation, and its GC trace (Figure 48) showed the peak area increment at retention time 2.0 min. The result indicated that 1-methylimidazole [2] showed the signal at the same retention

time with the photoreactant. This result also indicated that GC2 was not suitable for separation between [2] and [43], but GC1 could separate [43] and [2] into two retention times, 4.12 and 8.62 mins, respectivley. (see Figures 44-46). One product at retention time 2.0 min formed from this reaction was already identified by GC retention time as 1-methylimidazole.

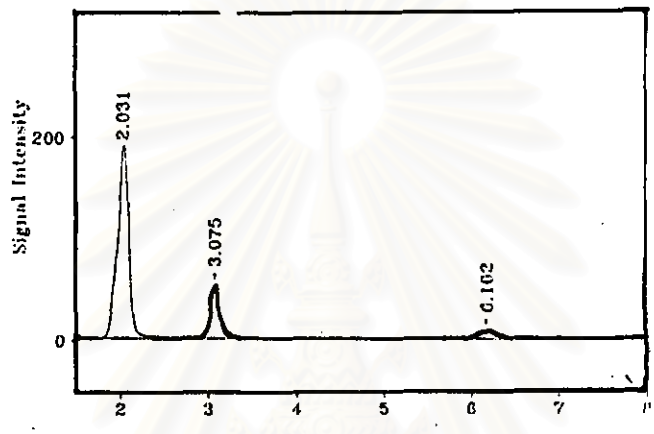
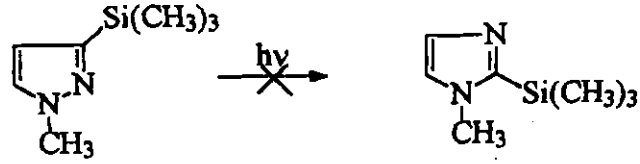


Figure 48 GC trace of [43] after 40 min of irradiation spiked with 1-methylimidazole

GC2 showed three peaks of products that one of them, 1-methylimidazole showed signal at the same retention time with photoreactant while GC1 showed only two peaks of product. Peak at retention time 3.08 min (GC2) seem to be the peak that could not be detected by GC1. And it must be the one that made a huge absorption in UV absorption spectrum of photolysate. 2-(Trimethylsilyl)-1-methylimidazole was the curious one. Then 2-(trimethylsilyl)-1-methylimidazole [45] was spiked into the photolysate. The retention time of [45] was 4.9 min which did not match any retention times of products as shown in Figure 49. The result indicated that 2-(trimethylsilyl)-1-methylimidazole was not formed from the photoreaction of [43].



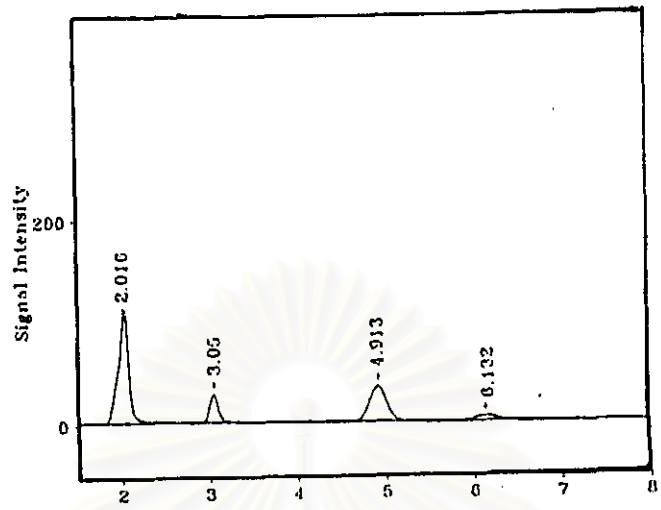


Figure 49 GC trace of [43] after 40 min of irradiation spiked with 2-(trimethylsilyl)-1-methylimidazole

The next interesting compound was 4-(trimethylsilyl)-1-methylimidazole Unfortunately, it could not be identified by GC retention time due to its unsuccessful synthesis. It must be one of two remaining peaks of products at retention times 3.08 and 6.18 mins.

3.6.4 Identification of photocleavage product and confirmation of phototransposition products of 3-(trimethylsilyl)-1-methylpyrazole by GC-MS

To identify the photocleavage product and confirm the phototransposition products, the photolysate at 80-min irradiation was analyzed by GC-MS (Hewlett Packard HP 5890A GC coupled HP 5970B mass spectrometer on 30m x 0.25 mm Supelcowax ™ 10 column). Figure 50 showed the GC trace of the photolysate at the retention time 4.09, 5.07, and 8.46 mins. It showed the similar pattern as by using GC2.

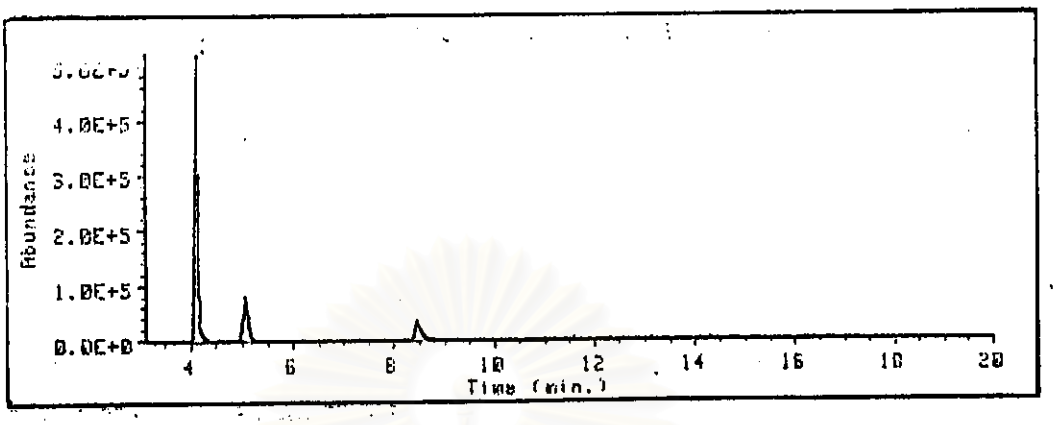


Figure 50 The GC trace of **[43]** after 80 min of irradiation (from GC-MS)

GC-MS also could not separate photoreactant **[43]** from 1-methylimidazole **[2]**. They showed at the same retention time, 4.09 min. According to the mass spectrum of 3-(trimethylsilyl)-1-methylpyrazole (see Figure 10), the relative abundance ratio of m/z 154 to 82 is about 5. But it is about 2 in the mass spectrum of the mixture of 3-(trimethylsilyl)-1-methylpyrazole and 1-methylimidazole. (Figure 5) That means the parent peak of 1-methylimidazole, which is 82, enhances the relative abundance at m/z 82. Thus their mass spectra combined each other to indicate the parent peak of compound bearing higher molecular mass, **[43]**.

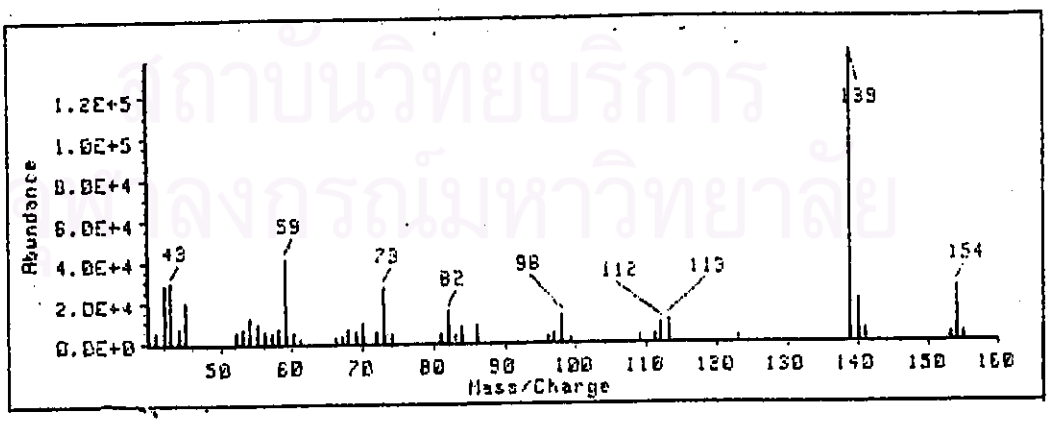
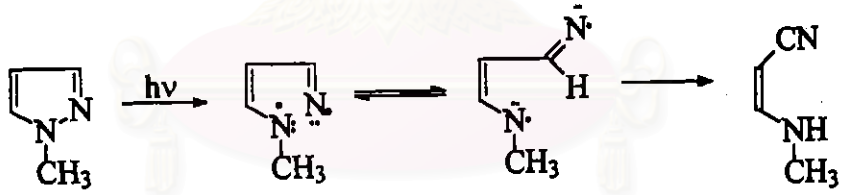


Figure 51 The mass spectrum of the mixture of 3-(trimethylsilyl)-1-methylpyrazole and 1-methylimidazole

For the peak at retention time 5.07 min, its mass spectrum (Figure 52b) showed molecular mass at 82. Even though the molecular mass of 1-methylimidazole is also 82 but it already performed at the same retention time of the photoreactant which was at 4.08 min. Therefore the product at retention time 5.07 min could not be 1-methylimidazole. As the previous observation, the photoreaction of 5-(trimethylsilyl)-1-methylpyrazole underwent photocleavage to the enaminonitrile isomer. Thus, 3-(trimethylsilyl)-1-methylpyrazole may undergo photocleavage in the same way to give the enaminonitrile isomer bearing molecular mass 154. Surprisingly, the molecular mass is not consistent with the molecular mass of photoproduct, trimethylsilyl-substituted-3-(*N*-methylamino)propenenitrile.

In 1982, Barltrop, Day, and Wakamasu [3] have reported that pyrazoles with hydrogen at position 3 not only undergo phototransposition but also photo-ring cleavage to enaminonitriles. In the presence of a hydrogen at C-3 of the 1-methylpyrazole ring, H-atom transfer from C-3 to N-1 would yield the enaminonitrile.



In the case of 3-(*N*-methylamino)propenenitrile, it has no H on C-3 to undergo photo-ring cleavage. However, it may undergo photocleavage by losing trimethylsilyl group to give the unsubstituted-3-(*N*-methylamino)propenenitrile bearing the molecular mass 82. Consequently, 3-(*N*-methylamino)propenenitrile was synthesized to confirm the assumption. By comparing the mass spectra patterns of authentic **[16]** and the photoproduct appearing at retention time 5.07 min, they showed the same fragmentation pattern as shown in Figures 52 a and b.

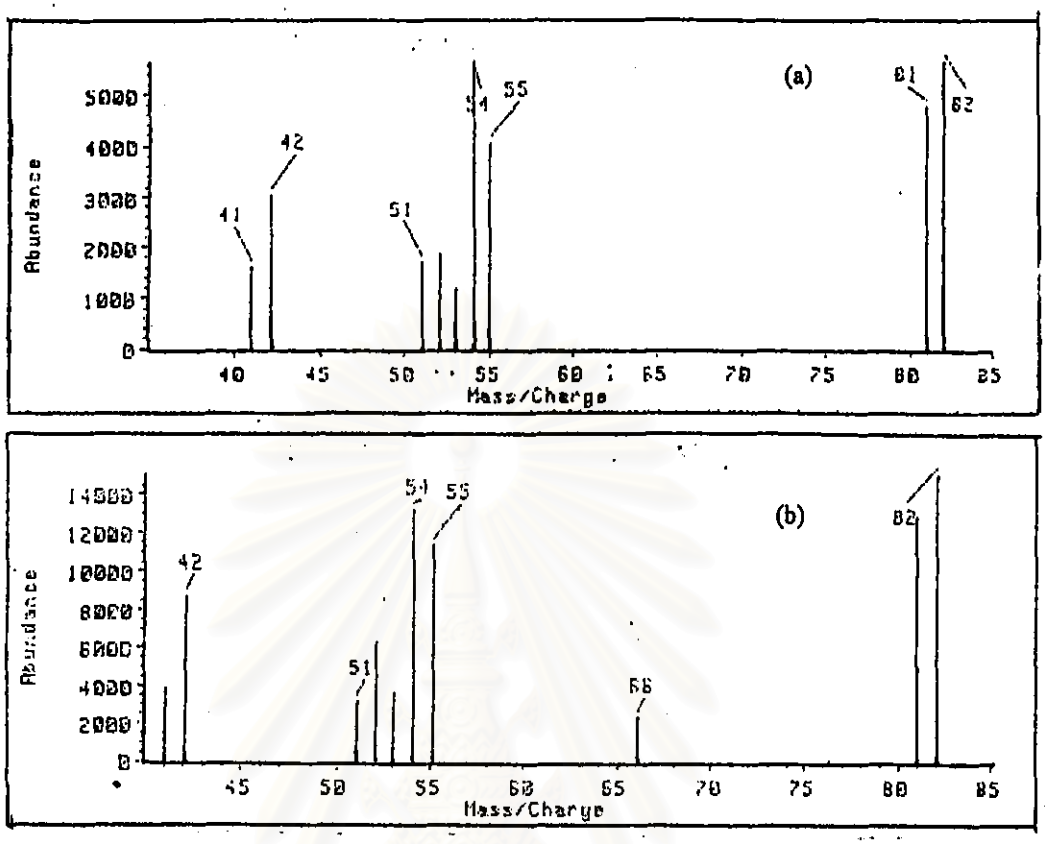


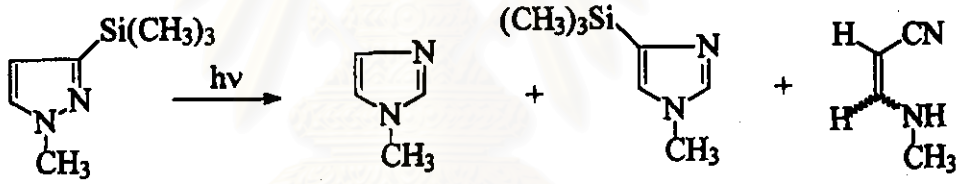
Figure 52 The mass spectra of (a) 3-(*N*-methylamino)propenenitrile synthesized and (b) photoproduct at retention time 5.07 min

Besides, 3-(*N*-methylamino)propenenitrile was spiked to 40-min irradiation of photolysate and analyzed by GC2. Figure 53a showed the peak of 3-(*N*-methylamino)propenenitrile at retention time 3.08 min. Figure 53b showed GC trace of [9] after 40 min of irradiation. And GC trace of photolysate spiked with 3-(*N*-methylamino)propenenitrile was shown in Figure 53c. It showed a single peak at retention time 3.08 min. It indicated no separation between peak of 3-(*N*-methylamino)propenenitrile and peak of photoreactant at retention time 3.08 min. These two results, mass spectra and GC spiking, indicated that 3-(*N*-methylamino)propenenitrile was formed indeed in this reaction.

Two peaks of photoproducts, at retention time 2.0 and 3.08 mins were already identified. The remaining peak was at retention time 8.46 min. Its mass spectrum was shown in Figure 54. Its molecular mass equals to 154 which was in line with

molecular mass of 2- and 4-(trimethylsilyl)-1-methylimidazole, two expected products of this photoreaction. 2-(Trimethylsilyl)-1-methylimidazole was already identified not to be the photoproduct of this photoreaction. Compared with the fragmentation pattern of 4-(trimethylsilyl)-1-methylimidazole, the product of the photoreaction of 5-(trimethylsilyl)-1-methylpyrazole (see Figure 36), the product at retention time 8.46 showed the same fragmentation pattern. So it was identified as 4-(trimethylsilyl)-1-methylimidazole. However, it could not be confirmed by the comparison of GC retention time.

The GC-MS indicated the photoproducts of 3-(trimethylsilyl)-1-methylpyrazole as 1-methylimidazole, 4-(trimethylsilyl)-1-methylimidazole, and 3-(*N*-methylamino)propenenitrile.



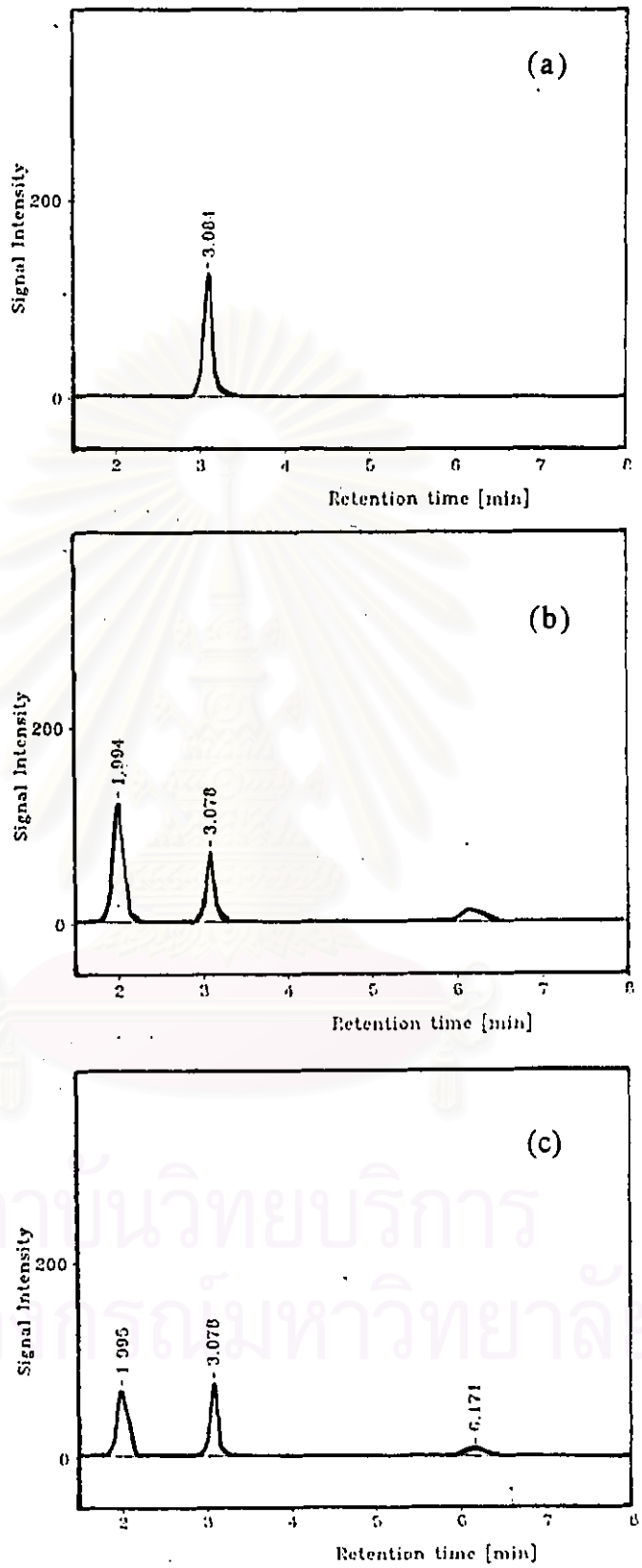


Figure 53 GC trace of (a) authentic 3-(*N*-methylamino)propenenitrile, (b) **[43]** after 40 min of irradiation, and (c) photolysate spiked with 3-(*N*-methylamino)propenenitrile

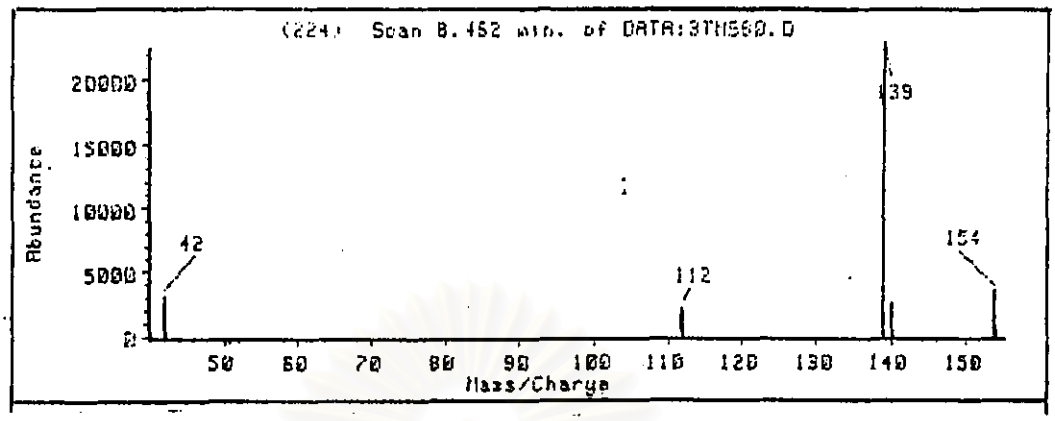


Figure 54 The mass spectrum of the photoproduct at retention time 8.46 min

3.6.5 ^{1}H-NMR spectrum of the photolysate of 3-(trimethylsilyl)-1-methylpyrazole

The photolysate of 80 min-irradiation of 3-(trimethylsilyl)-1-mehylpyrazole was analyzed by ^{1}H-NMR (Figure 55) and the enlargement of four important ranges were displayed in Figure 56. ^{1}H-NMR spectrum of products mixture was compared with the spectra of the authentic compounds synthesized in this work. The chemical shifts at δ 0.265, 3.94, 6.35, and 7.36 are due to trimethylsilyl protons, N-methyl protons, a proton on C-4, and a proton on C-5 respectively of photoreactant, 3-(trimethylsilyl)-1-mehylpyrazole.

The signals of photoproducts, 4-(trimethysilyl)-1-methylimidazole, 1-methylimidazole, and 3-(*N*-methylamino)propenenitrile could be clearly seen. 4-(Trimethylsilyl)-1-methylimidazole showed at δ 0.229, 3.93, 7.57, and 6.95 which are due to the signals of trimethylsilyl protons, N-methyl protons, a proton on C-2, and a proton on C-5 repectively.

3-(*N*-methylamino)propenenitrile was also confirmed by ^{1}H-NMR signals. The chemical shifts at δ 3.66, 6.50, 2.98, and 4.70 are consistent with the signals of a proton on C-2, a proton on C-3, N-methyl protons, and a proton on nitrogen respectively of cis-isomer. Trans-isomer also showed at δ 3.87, 7.07, 2.70, and 4.70

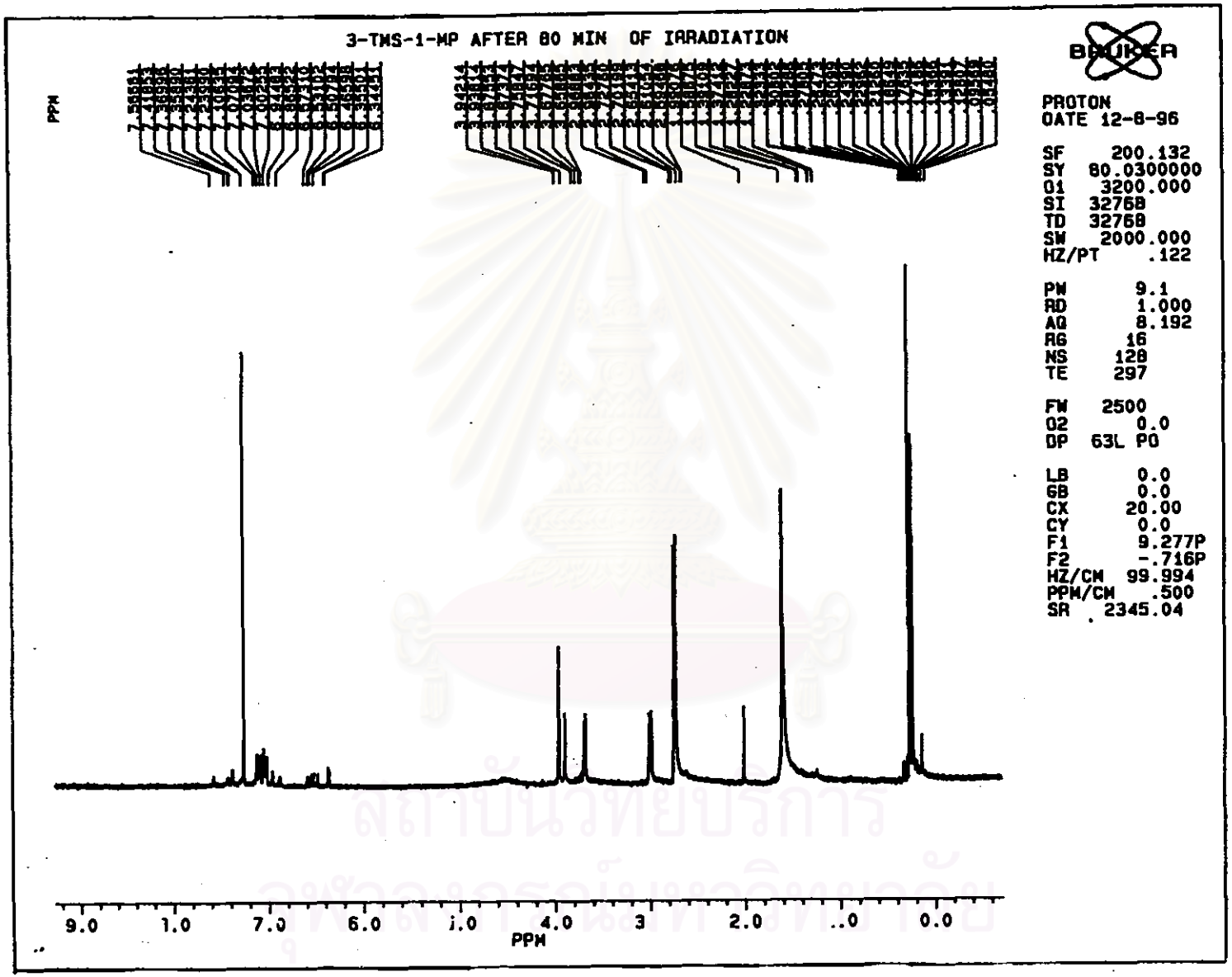


Figure 55 The ^{1}H-NMR spectrum of **[43]** after 80 min of irradiation

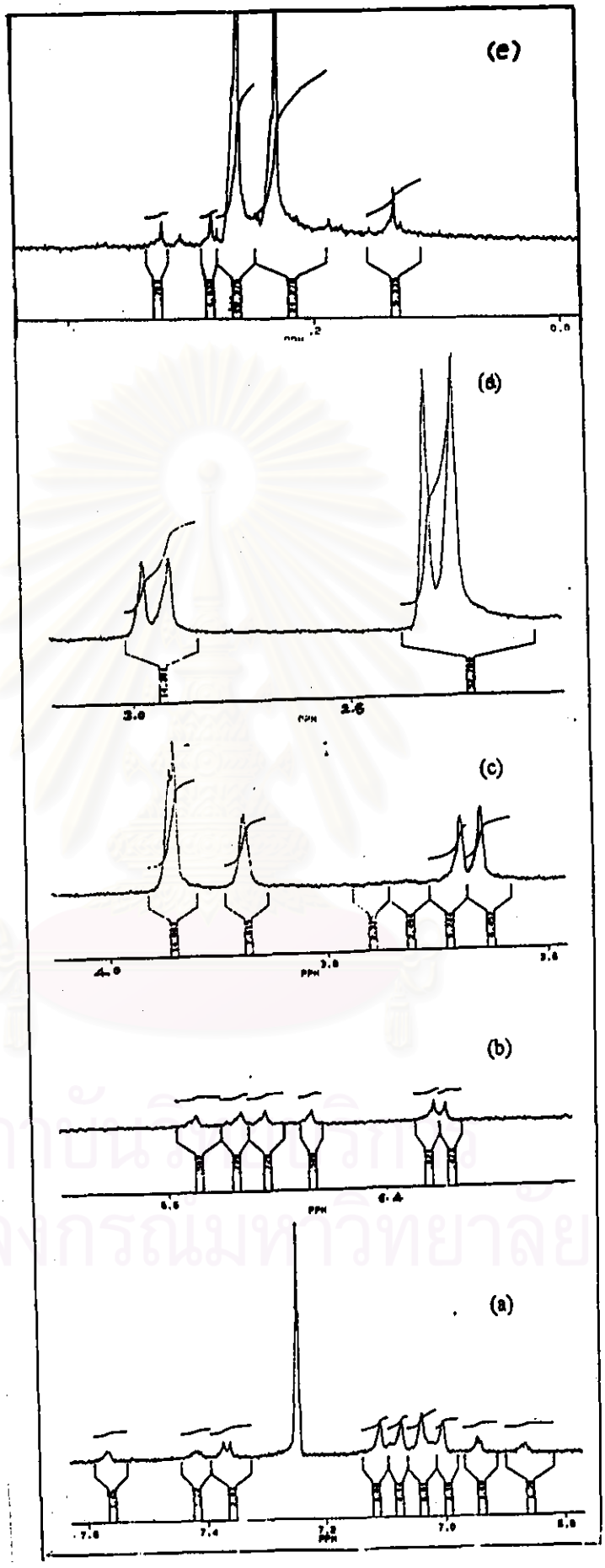
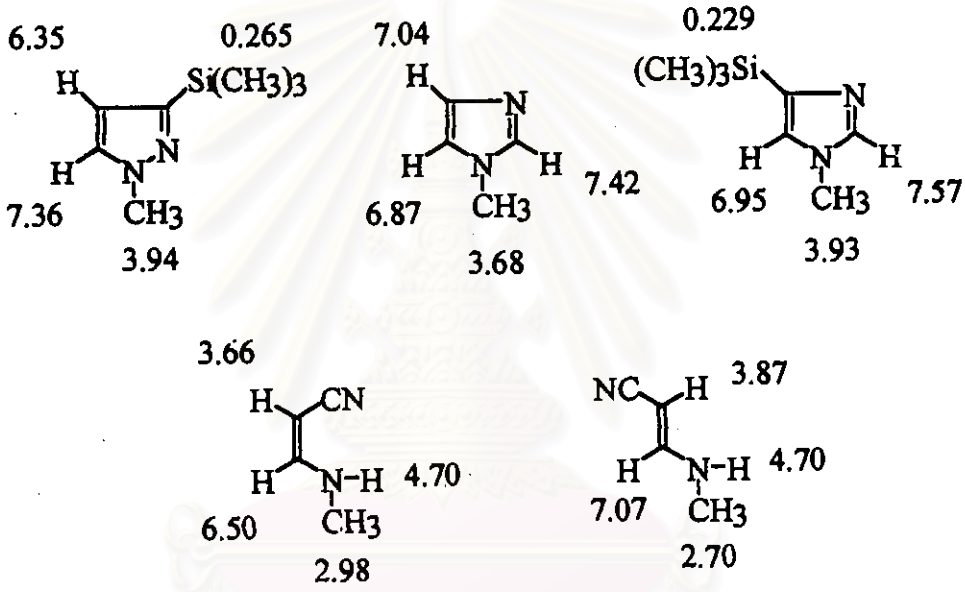


Figure 56 The expansion of ^{1}H-NMR spectra of [43] after 80 min of irradiation (a) 6.8-7.6 ppm, (b) 6.2-6.6 ppm, (c) 3.6-4.0 ppm, (d) 2.6-3.0 ppm, and (e) 0.0-0.4 ppm

which are consistent with the signals of a proton on C-2, a proton on C-3, N-methyl protons, and a proton on nitrogen respectively. The ratio of E/Z isomers equals to 4.07:1 The assignment of the chemical shifts for the protons of components in the photolysate **[43]** after 80 min of irradiation were shown in scheme 6.

Scheme 6 Assignment of the chemical shifts for the protons of components in the photolysate **[43]** after 80 min of irradiation



3.7 Irradiation of 2-(trimethylsilyl)-1-methylimidazole

According to the prediction by permutation pattern, 2-(trimethylsilyl)-1-methylimidazole should be formed from both phototransposition of 5-(trimethylsilyl)-1-methylpyrazole and 3-(trimethylsilyl)-1-methylpyrazole. However, 2-(trimethylsilyl)-1-methylimidazole was not observed in both photoreactions, 1-methylimidazole was observed instead.

In 1973, Jutzi and Sakriß [12] reported that 2-(trimethylsilyl)-1-methylimidazole is very sensitive to moisture to lose trimethylsilyl group from carbon

position 2 converting to 1-methylimidazole. Therefore 1-methylimdazole, the photoproduct, seems to be converted from 2-(trimethylsilyl)-1-methylimidazole by loss of trimethylsilyl group via the carrying out process. However, the photoreaction were carried out in very dry acetonitrile . Even though the conversion can take place by the way of analysis but it would not cause the total conversion. Thus, the conversion is probably caused by the other important factor. The assumption was that 2-(trimethylsilyl)-1-methylimidazole might be sensitive to light via irradiation process. Consequently, the photoreaction of 2-(trimethylsilyl)-1-methylimidazole was carried out and characterized by GC2. Figures 57a and b showed GC trace of 1-methylimidazole at the retention time 2.1 min and 2-(trimethylsilyl)-1-methylimidazole at 5 min. After 20 min of irradiation, the GC spectrum of 2-(trimethylsilyl)-1-methylimidazole disappeared while the peak area of 1-methylimidazole increased. It indicated that all 2-(trimethylsilyl)-1-methylimidazole converted to 1-methylimidazole via irradiation process since irradiation of 1-methylimidazole gave rise to 1-methylimidazole according to Beck and co-workers work [23]. It can be concluded that 3- and 5-(trimethylsilyl)-1-methylpyrazole undergo phototransposition to 2-(trimethylsilyl)-1-methylimidazole as the prediction but 2-(trimethylsilyl)-1-methylimidazole can undergo conversion to 1-methylimidazole by light afterwards.

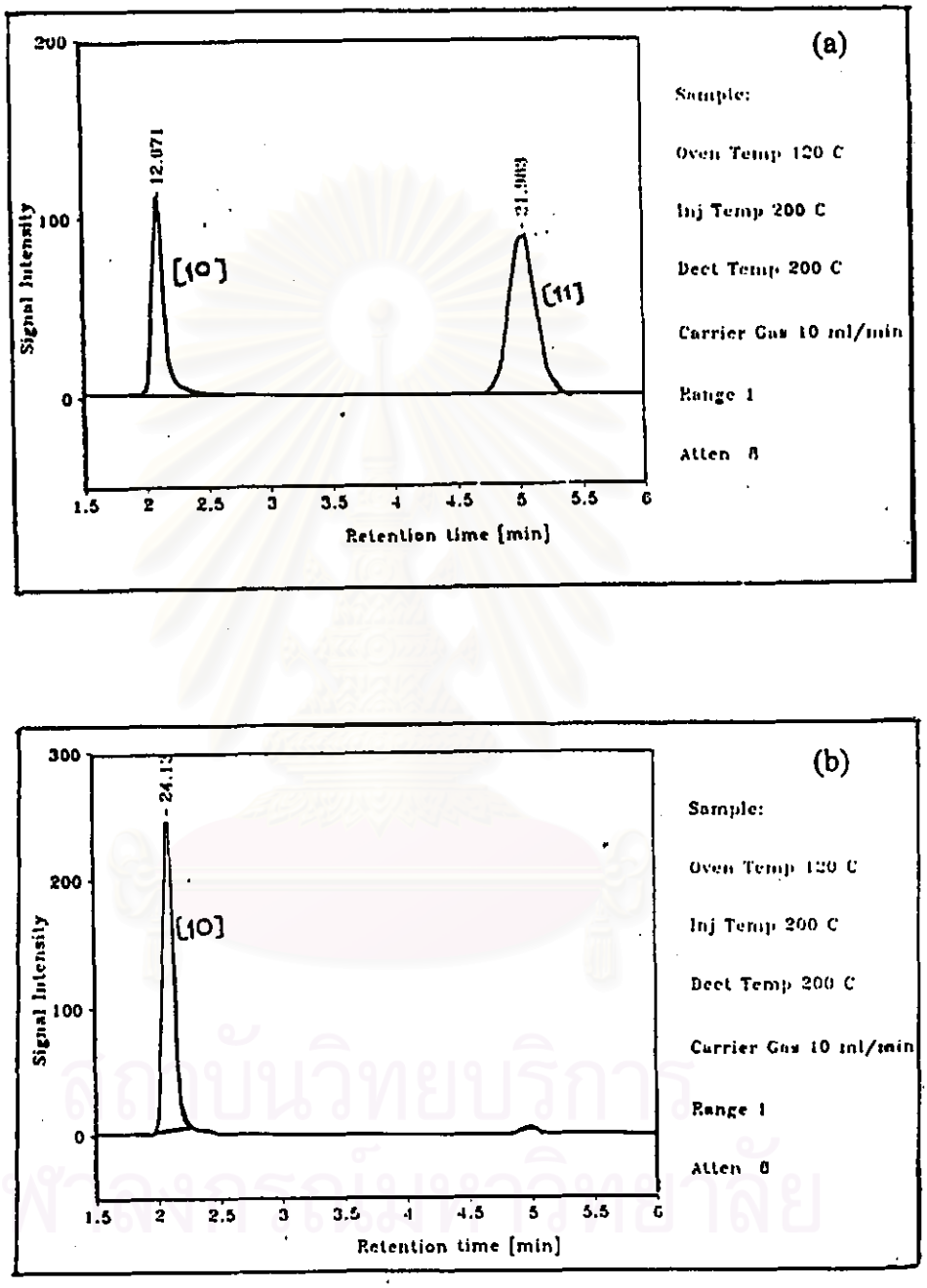


Figure 57 GC trace of the mixture of 1-methylimidazole **[2]** and 2-(trimethylsilyl)-1-methylimidazole **[45]** (a) before and (b) after 20 min of irradiation

3.8 The proposed mechanism for all photoproducts formed

3.8.1 The proposed mechanism for the formation of photoproducts of 5-(trimethylsilyl)-1-methylpyrazole

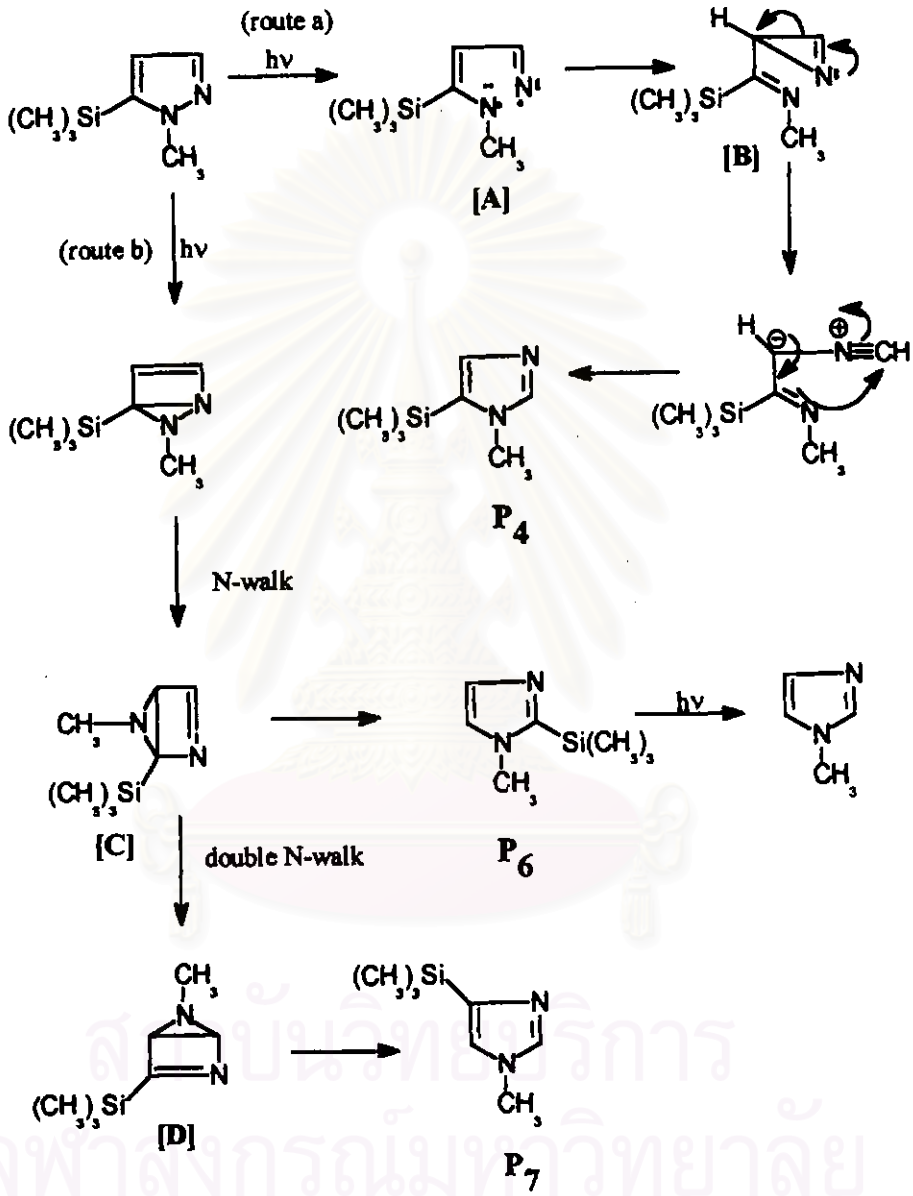
All photoproducts formed from the photoreaction of 5-(trimethylsilyl)-1-methylpyrazole are nearly consistent with the prediction by using permutation pattern.

Emulating the mechanistic interpretation of P_4, P_6, and P_7 processes of 1-methylpyrazole, the mechanism for all phototransposition products can be proposed as shown in scheme 7.

5-(Trimethylsilyl)-1-methylpyrazole undergoes ring contraction-ring expansion (route a) that involes N-N ring cleavage with the formation of a biradical [A]. The biradical [A] can undergo ring closure reaction with the formation of an arising [B] which further undergoes a ring expansion resulting in the formation of 5-(trimethylsilyl)-1-methylimidazole , P_4 product.

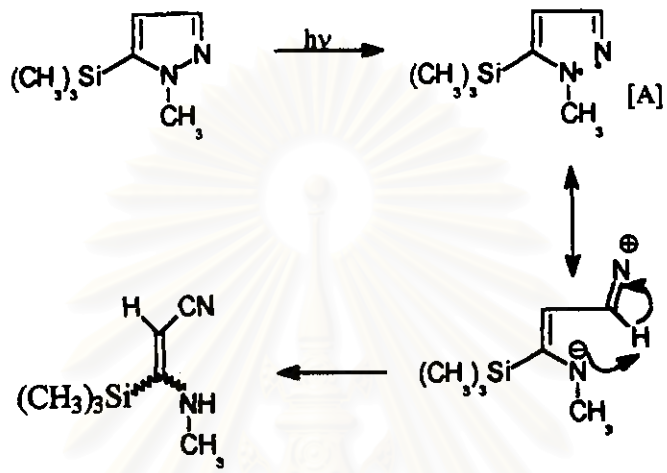
The second mechanism (route b), electrocyclic ring closure results in the formation of a bicyclic intermediate that can undergo 1,3 sigmatropic nitrogen shift (single N walk) to give [C]. Then [C] reaomatizes to give 2-(trimethylsilyl)-1-methylimidazole, P_4 product that is converted to 1-methylimidazole later. Furthermore [C] can again undergo a second 1,3-N shift (double nitrogen walk) to another bicyclic intermediate [D] that can rearomatize to form 4-(trimethylsilyl)-1-methylimidazole, P_7 product.

Scheme 7 The proposed mechanism for all phototransposition products of 5-(trimethylsilyl)-1-methylpyrazole



The proposed mechanism for the photocleavage product, 3-(trimethylsilyl)-3-(*N*-methylamino)propenenitrile is shown in scheme 8.

Scheme 8 The proposed mechanism for the photocleavage product of 5-(trimethylsilyl)-1-methylpyrazole



5-(Trimethylsilyl)-1-methylpyrazole undergoes N-N ring cleavage with the formation of a biradical [A] that can further undergo [1,4]-H shift with the formation of 3-(trimethylsilyl)-3-(*N*-methylamino)propenenitrile.

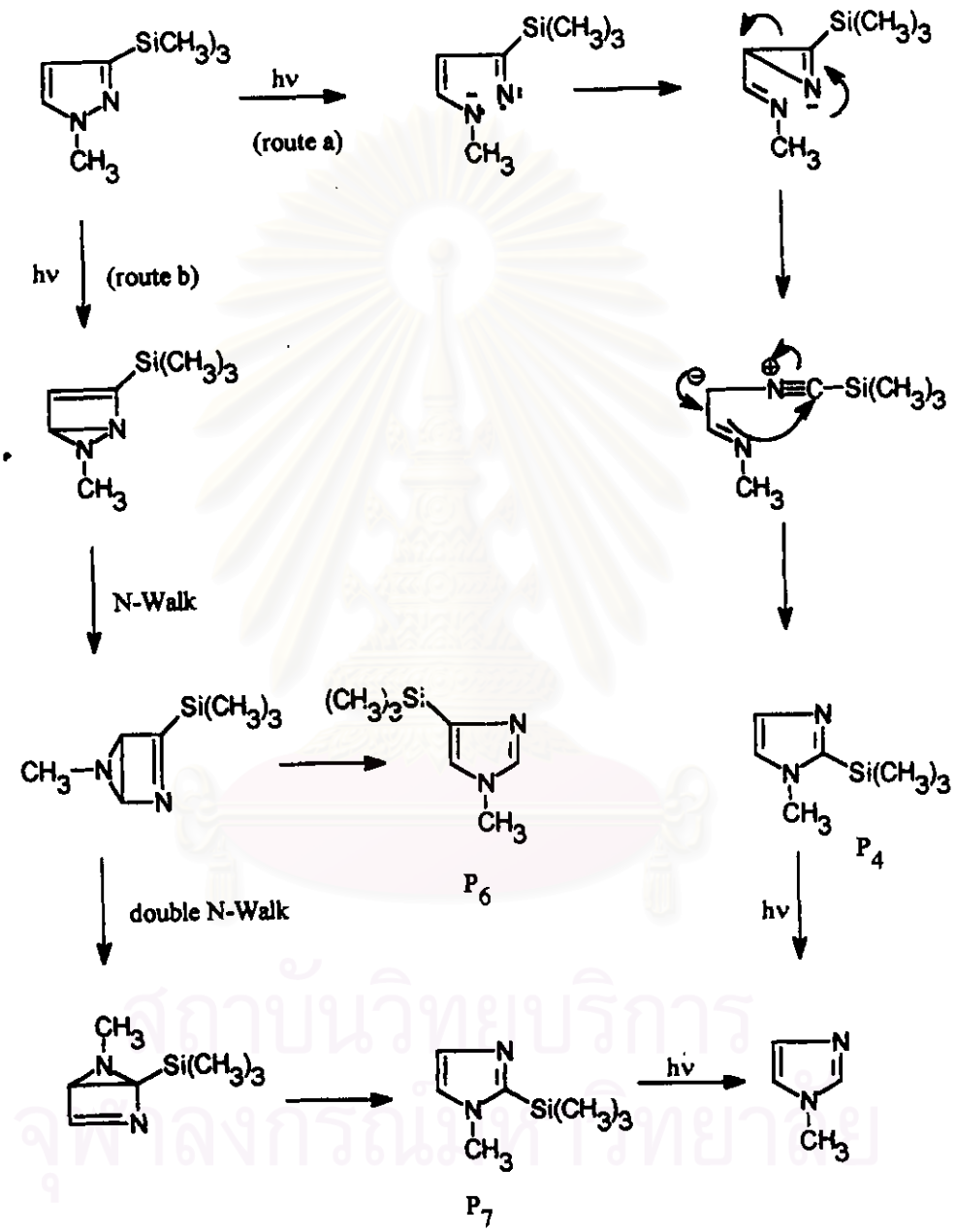
3.8.2 The proposed mechanism for the formation of photoproducts of 3-(trimethylsilyl)-1-methylpyrazole

All photoproducts formed from the photoreaction of 3-(trimethylsilyl)-1-methylpyrazole are nearly consistent with the prediction by using mechanistic interpretation of P_4, P_6, and P_7 processes of 1-methylpyrazole.

The proposed mechanism for two photoprotransposition products are shown in scheme 9.

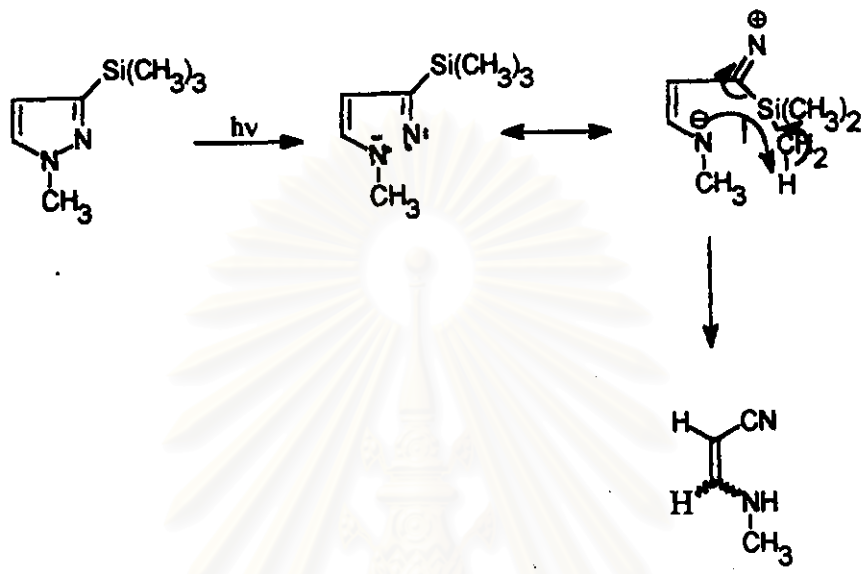
3-(Trimethylsilyl)-1-methylpyrazole undergoes ring contraction-ring expansion (route a) resulting in the formation of 2-(trimethylsilyl)-1-methylimidazole, P_4 product which is converted to 1-methylimidazole afterwards.

Scheme 9 The proposed mechanism for two phototransposition products of 3-(trimethylsilyl)-1-methylpyrazole



The proposed mechanism for the photocleavage product 3-(*N*-methylamino) propenenitrile must be different from the photocleavage of 5-(trimethylsilyl)-1-methylpyrazole (see scheme 8) because of lacking a proton on C-3. The mechanism can be proposed as in scheme 10.

Scheme 10 The proposed mechanism for the photocleavage product of 3-(trimethylsilyl)-1-methylpyrazole



[43] undergoes N-N ring cleavage with the formation of biradical and anion can abstract proton from trimethylsilyl group to give cis/trans isomers of 3-(*N*-methylamino)propenenitrile.

Ferris and Kuder reported the mechanism of photochemical conversion of enaminonitriles to imidazoles in 1970 [24]. It is possible that 3-(*N*-methylamino) propenenitrile can convert to 1-methylimidazole as well. The proposed mechanism imitating their work for such conversion is shown in scheme 11.

Scheme 11 The proposed mechanism for the conversion of 3-(*N*-methylamino) propenenitrile to 1-methylimidazole