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A Study of the Solvolysis Reactions of Tetrahydrofurfuryl Tosylate

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A Study of The Solvolysis Reactions of Tetrahydrofurfuryl Tosylate

Rebecca Centko

**Advisor: Dr. Ram S. Mohan
Chemistry Research Honors Thesis
Illinois Wesleyan University
April 25, 2000**

Approval Page

A Study of The Solvolysis Reactions
of Tetrahydrofurfuryl Tosylate

By
Rebecca Centko

A PAPER SUBMITTED AS PART OF THE REQUIREMENT
FOR RESEARCH HONORS IN CHEMISTRY

Approved:

Ram S. Mohan April 26, 2000

Ram S. Mohan, Ph. D., Research Advisor

Illinois Wesleyan University, 1999-2000

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Abstract

The solvolysis of epoxycarbonyl substrates **1** has been the subject of several mechanistic studies. In spite of these investigations, it has not been established whether these solvolysis reactions proceed with anchimeric assistance from the epoxide oxygen and involve an oxabicyclobutonium ion intermediate or whether unassisted solvolysis occurs. Conflicting data in the literature suggest that the ability of the epoxide oxygen to provide anchimeric assistance is dependant upon structural and electronic features of the epoxycarbonyl substrate in question. The aim of this project was to study the nucleophilic substitution reactions of tetrahydrofurfuryl and tetrahydropyranyl sulfonates **2a** and **2b** as well as cyclopentylmethyl and cyclohexylmethyl sulfonates **3a** and **3b**, respectively, to probe the effect of a neighboring oxygen on solvolyses rates and product distribution. The rates of solvolyses of cyclopentylmethyl tosylate and tetrahydrofuranomethyl tosylate have been compared to determine if the oxygen lends anchimeric assistance to the leaving group in the solvolyses reactions of the latter. This research has led to an increased understanding of the role of the ether oxygen in reaction of tetrahydrofurfuryl tosylate.

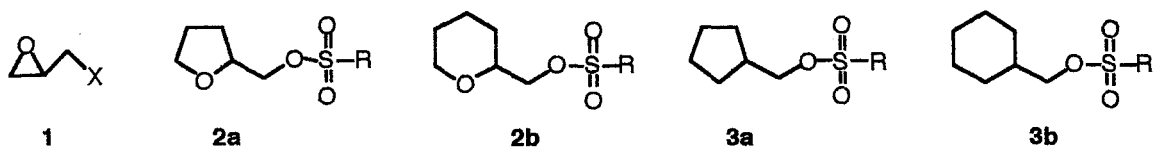


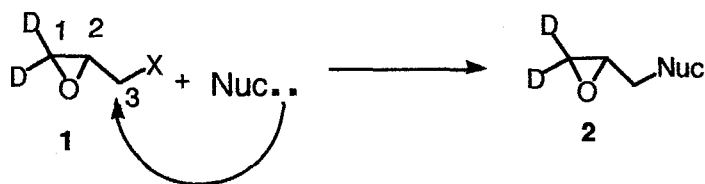
Table of Contents

I.	Introduction.....	1
II.	Specific Aims.....	10
III.	Results and Discussion.....	11
	A. Synthesis.....	11
	B. Acetolysis.....	11
	C. ^1H NMR Analysis.....	18
	D. Solvolysis in aqueous acetone.....	22
	E. Conclusions.....	22
IV.	Experimental Section.....	24
V.	^1H NMR Studies.....	34
VI.	References.....	39
VII.	Appendix. Spectral Data.....	40

I. Introduction

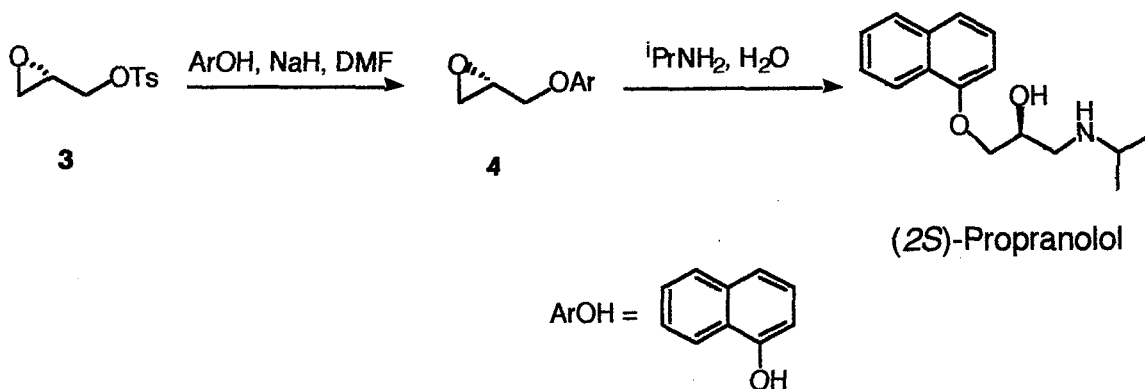
Epoxycarbinyll substrates **1** are useful chiral synthons^{1,2} and their solvolyses has been studied extensively. These substrates present two sites of reactivity toward nucleophiles, at carbon-1 and carbon-3.

Scheme 1



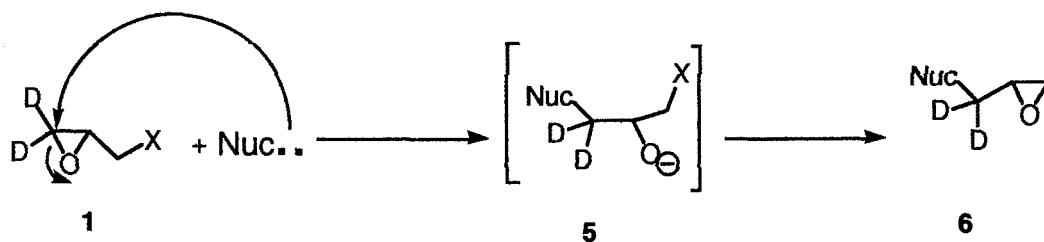
Regioselective ring opening of these epoxycarbinyll substrates has assumed importance because of the applications of these reactions to the synthesis of chiral β -adrenergic blocking agents and β -hydroxybutyric acids.^{3,4} The synthesis of (2*S*)-propranolol, a β -adrenergic blocking agent used to control high blood pressure, involved an epoxycarbinyll compound **3** as the key intermediate (Scheme 2)³.

Scheme 2

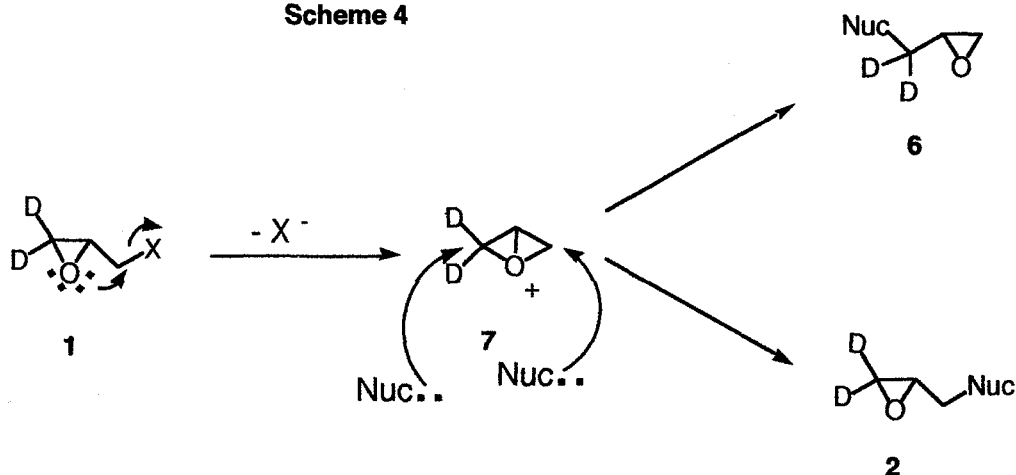


Solvolyses reactions of substrate **1** can occur through direct displacement of the leaving group by nucleophilic attack as shown in Scheme 1 or by nucleophilic attack at the terminal epoxide carbon followed by ring opening and concomitant departure of the leaving group (Payne rearrangement^{5,6}) as shown in Scheme 3. A third possibility is the involvement of an oxabicyclobutonium ion as shown in Scheme 4. The oxygen can assist the departure of the leaving group through the formation of the ion **7**. The nucleophile can then attack at either of the secondary carbons of ion **7** to give products **2** or **6**.

Scheme 3



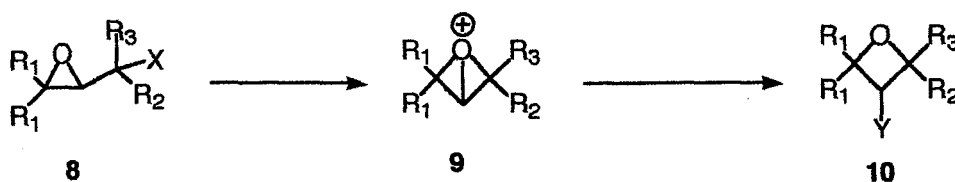
Scheme 4



Previous studies of epoxycarbinyll compounds have not unequivocally established whether their solvolyses reactions proceed with anchimeric assistance from the epoxide oxygen and involve an oxabicyclobutonium ion intermediate or if they proceed without involvement of the neighboring oxygen. There are conflicting data in the literature, which suggest that the ability of the epoxide oxygen to provide anchimeric assistance is dependent on structural and electronic features of the epoxycarbinyll substrate.

Richey and co-workers studied the solvolysis of esters of 2,3-epoxy-1-propanols **8a-c**⁷ in 80 % aqueous acetone (Scheme 5).

Scheme 5

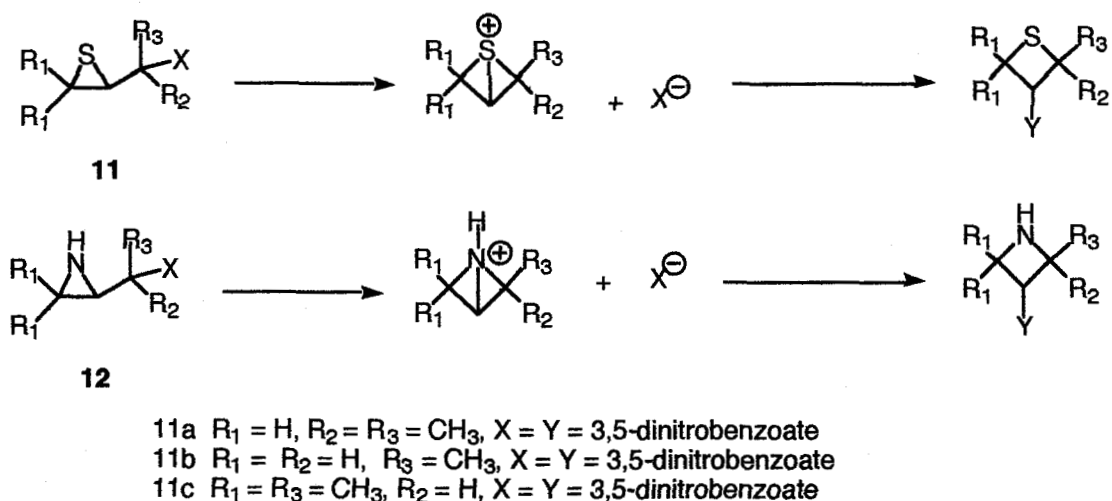


8a -10a $R_1 = \text{H}, R_2 = R_3 = \text{CH}_3, X = Y = 3,5\text{-dinitrobenzoate}$
8b -10b $R_1 = R_2 = \text{H}, R_3 = \text{CH}_3, X = Y = 3,5\text{-dinitrobenzoate}$
8c -10c $R_1 = R_3 = \text{CH}_3, R_2 = \text{H}, X = Y = 3,5\text{-dinitrobenzoate}$

Rearrangement of the secondary (**8b, 8c**) and tertiary (**8a**) substrates at 100 °C followed first order kinetics ($k = 8 \times 10^{-6}$ and $\sim 9 \times 10^{-6} \text{ sec}^{-1}$). These rate constants are of the same order of magnitude as the rate of solvolysis of *t*-butyl-3,5- dinitrobenzoate ($17 \times 10^{-6} \text{ sec}^{-1}$) under similar conditions. If these reactions involved the intermediacy of a free carbocation (S_N1 pathway), one would expect the tertiary substrate to undergo solvolyses at a rate much faster than the secondary substrate. The similar rate constants of secondary

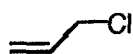
and tertiary substrates was taken as evidence that the solvolysis of the secondary substrate must be accelerated, possibly by the involvement of an oxabicyclobutonium ion intermediate. Results from solvolysis of thiirane **11**⁸ and aziridine **12**⁹ analogs of **8a-c** show rates which seem to be accelerated by the three-membered heterocyclic rings compared to the cyclopropane ring. This evidence supports the formation of ions similar to the oxabicyclobutonium ion (Scheme 6).

Scheme 6



Work by Morita and co-workers¹⁰ also supports the formation of an oxabicyclobutonium ion intermediate. It was determined that relative rates of acetolysis of allyl chloride **13**, cyclopropylcarbinyl chloride **14**, 3-chloropropylene oxide **15**, and 3-chloropropylene sulfide **16** were 1, 30, 100, and 3000, respectively. The high relative rate of solvolysis of **15** compared to solvolysis of **14** was attributed to participation by the

neighboring oxygen. The increased relative rate of the sulfur compound could also be attributed to an ion similar to the oxabicyclobutonium ion. These studies were complicated because under acidic conditions the epoxide ring of 3-acetoxypropylene oxide, an expected product of acetolysis of **15**, forms a hydroxyester.



13
Rel Rate = 1



14
Rel Rate = 30



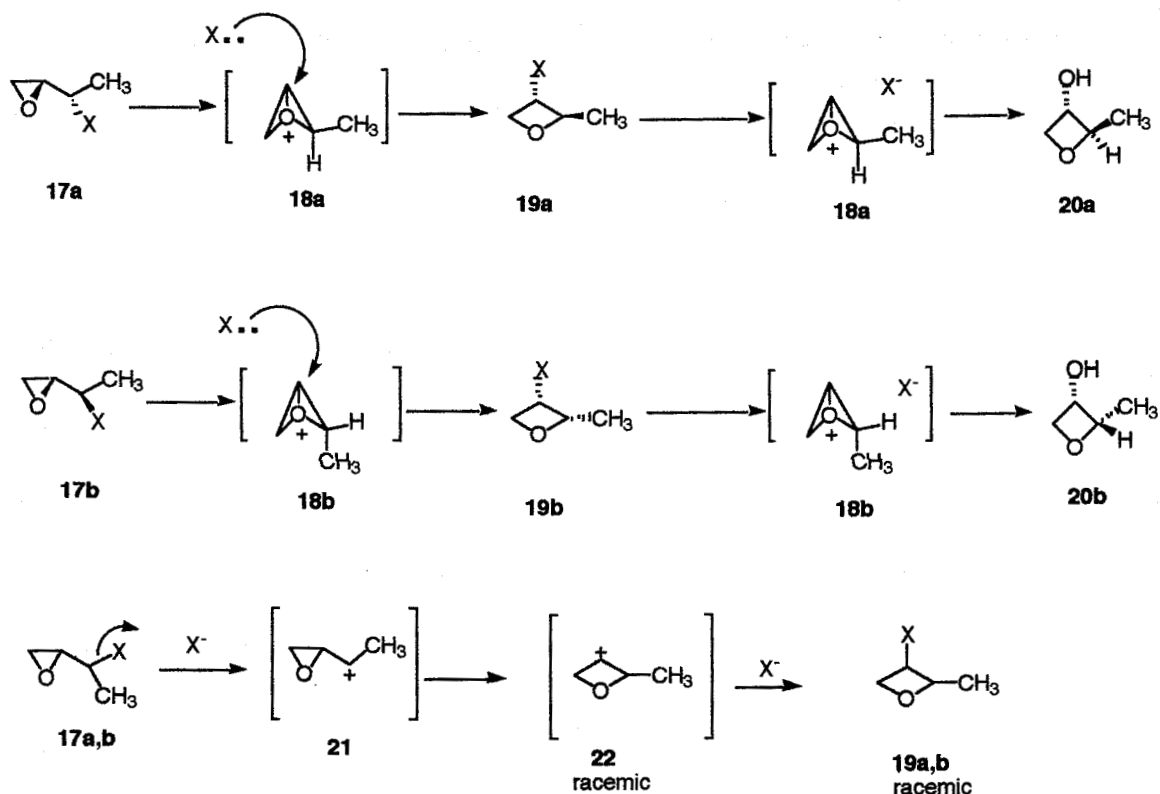
15
Rel Rate = 100



16
Rel Rate = 3000

Swindell and co-workers¹¹ provided additional evidence for the formation of an oxabicyclobutonium ion in the solvolysis of *erythro* and *threo*-3,4-epoxybut-2-yl-3,5-dinitrobenzoates **17a,b** (Scheme 7, next page). Solvolysis (80 % aqueous acetone) of these epoxy dinitrobenzoates led to the stereospecific formation of the corresponding oxetane **19a,b** and oxetanol **20a,b**. It was shown that **19a,b** were generated faster than **20a,b** were. It was also determined that when the oxetanes **19a,b** were subjected to the same reaction conditions, oxetanols **20a,b** were formed. This observation led to the proposal of the oxabicyclobutonium ion intermediates **18a,b**. A direct nucleophilic attack by solvent was ruled out since this would lead to inversion of configuration at the ionizing carbon.

Scheme 7

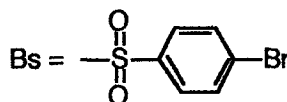
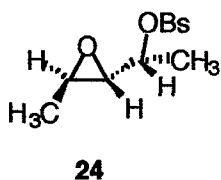


X = 3,5-dinitrobenzoate

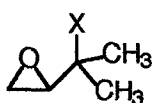
Molecular mechanics calculations suggested that ions **21** and **22** were not likely intermediates. The oxetane ion **22** was ruled out as an intermediate because its formation is energetically less favorable than that of **18a,b** and **21**. Ab initio molecular orbital theory calculations at the MP2 / 6-31 G* level showed that ion **22** is more than 20 kcal / mol less stable than ions **18a,b** and **21**, which were also considered as intermediates. The increased stability of **18a,b** were attributed to the fact that they can adopt a puckered conformation while **22** is planar. Furthermore, the epoxycarbinyl cation **21** was ruled out because of the formation of stereospecific products.

While there is evidence supporting the existence of the oxabicyclobutonium ion

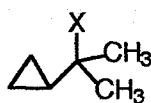
intermediates, Whalen and co-workers¹² give evidence refuting its existence. Whalen et. al. carried out the solvolysis of secondary epoxycarbinyll *p*-bromobenzenesulfonate ester **24** in 80 % ethanol-water mixtures. The alcohols resulting from the solvolysis showed inversion of configuration at the ionizing carbon. This result ruled out an oxabicyclobutonium ion intermediate as well as an epoxycarbinyll cation intermediate. The observed results seemed to support an S_N2-type displacement by the solvent or a tight ion pair mechanism, which would both be consistent with the observed inversion of configuration. Whalen also determined that the relative rates of solvolyses in ethanol/water mixtures of this epoxycarbinyll ester was 106 times less than the corresponding cyclopropylcarbinyll system. This suggested that the epoxide oxygen had a destabilizing effect on the transition state and that the oxabicyclobutonium ion was not an intermediate.



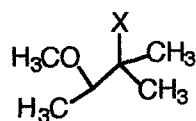
Peters¹³ studied the solvolysis of 2-oxiryl-2-propyl *p*-nitrobenzoate **25** and 2-cyclopropyl-2-propyl *p*-nitrobenzoate **26** in 80 % acetone/ water mixture and determined that the epoxide group enhanced the rate ten fold over the acyclic analog **27**, but the cyclopropyl group increased the rate by a factor of 10⁵ over the epoxide analog.



25
Rel. Rate = 1



26
Rel. Rate = 10^5



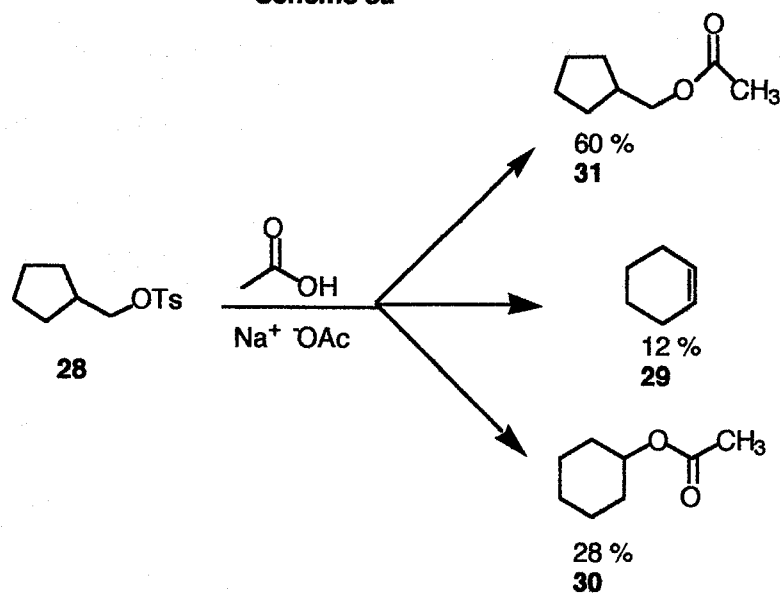
27
Rel. Rate = 0.1

X = *p*-nitrobenzoate

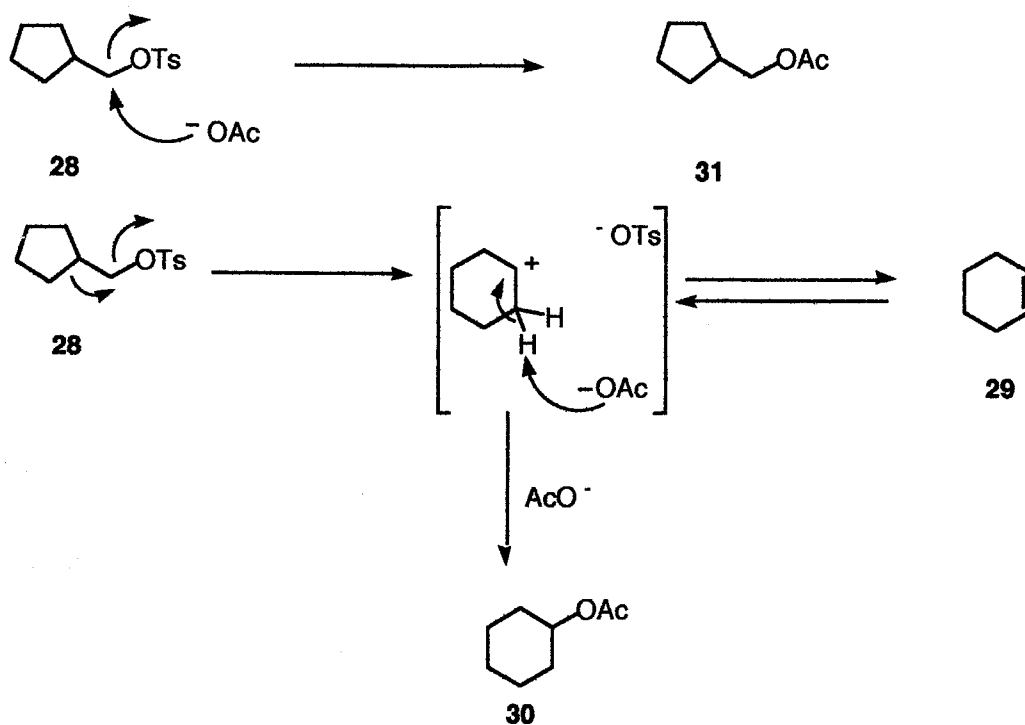
The increased rate in the oxirane **25** was attributed to the release of strain energy of the three membered ring upon solvolyses. The electron withdrawing effect of the oxygen also plays a role in the reduced rate of solvolysis of **25** compared to **26**. The slower rate of solvolysis of the oxirane is evidence that the oxygen does not render anchimeric assistance. The increased rate of **26** was attributed to ability of the cyclopropyl group to stabilize a positive charge adjacent to it.

Solvolysis of cyclopentylmethyl tosylate **28** (Scheme 8a,b, next page) has been reported¹⁴. It was found that acetolysis of **28** leads to 60 % of the acetate **31**, which resulted from direct displacement of the leaving group, 28 % of the ring expanded acetate **30**, and 12 % of the ring expanded alkene **29**. The rate of acetolysis was determined to be $2.54 \pm 0.10 \times 10^5 \text{ sec}^{-1}$ at 100 °C.

Scheme 8a



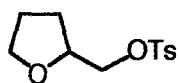
Scheme 8b



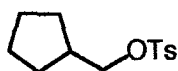
II. Specific Aims

If neighboring group participation can occur in three-membered epoxide rings, there is a possibility that there could be a similar effect in five-membered furan rings and six-membered pyran rings.

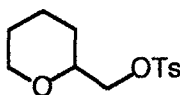
The aim of this project is to study the solvolyses reactions of five and six membered sulfonates, tetrahydrofurfuryl tosylate **32**, cyclopentylmethyl tosylate **28**, tetrahydropyranomethyl tosylate **33**, and cyclohexylmethyl tosylate **34** to determine if an intermediate similar to the oxabicyclobutonium ion is formed during solvolyses, and how the oxygen affects the rate of solvolysis of **32** and **33** relative to the rates of solvolyses of **28** and **34**, respectively.



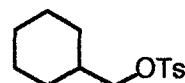
32



28



33



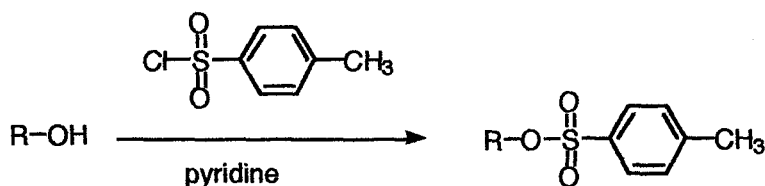
34

Rate and product analysis of solvolyses reactions of tetrahydrofurfuryl tosylate and cyclopentylmethyl tosylate, as well as from the six-membered tosylates, could provide further insight into the mechanism of the reaction, which would present evidence for or against oxygen participation in solvolysis reactions.

III. Results and Discussion

A. Synthesis

Tetrahydrofurfuryl tosylate, cyclopentylmethyl tosylate, tetrahydropyran-2-methyl tosylate, cyclohexylmethyl tosylate, tetrahydrofurano-3-methyl tosylate, and cyclohexyl tosylate were synthesized in 55 %, 83 %, 57 %, 61 %, 78 %, 83 % yield, respectively, from the corresponding alcohols using 1.1 – 1.3 eq of *p*-toluenesulfonyl chloride in pyridine (Scheme 10). The yields were not optimized as enough tosylate was obtained from the unoptimized reactions for use in solvolyses reactions. The synthesis of cyclopentylmethyl acetate was carried out by the reaction of cyclopentylmethanol in acetic anhydride with a catalytic amount of zinc chloride.¹⁵



B. Acetolysis

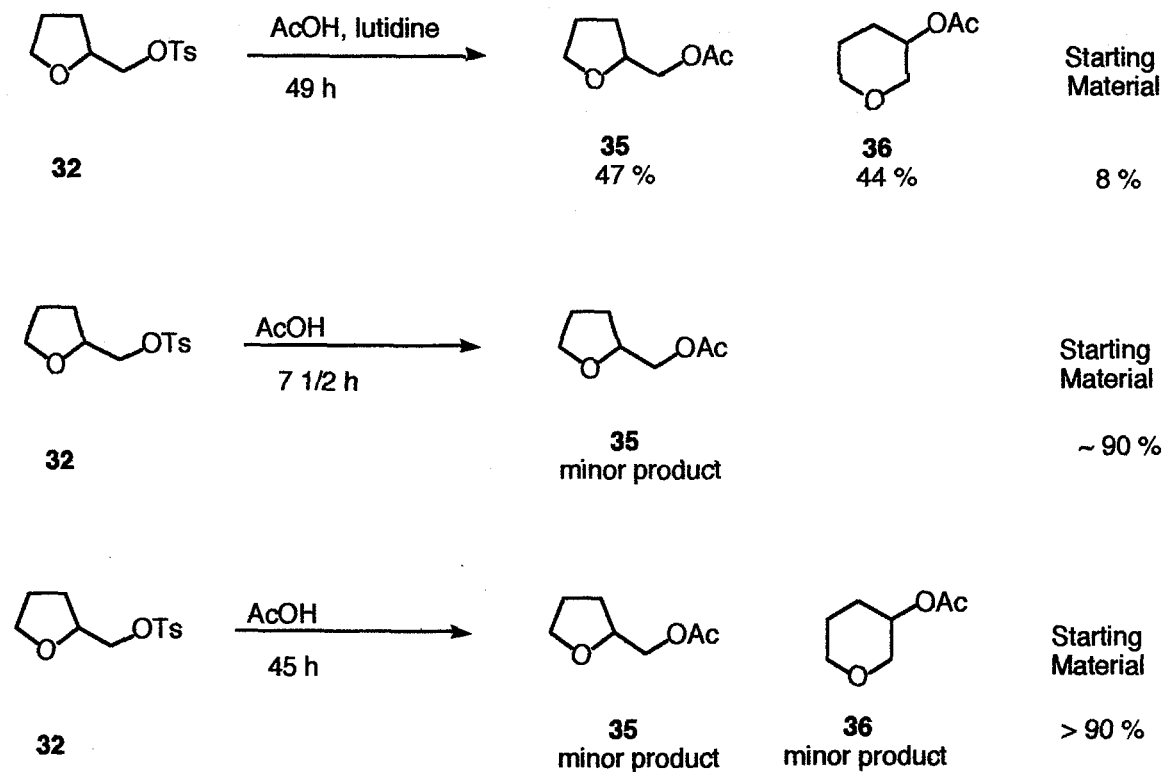
Acetolysis of tetrahydrofurfuryl tosylate, cyclopentylmethyl tosylate, and tetrahydrofurano-3-methyl tosylate was carried out. The reaction progress was followed by TLC (30 % EtOAc / 70 % Hexanes) and spots were visualized by UV and PMA spray. Workup was completed by adding saturated aqueous NaCl solution followed by extraction with ether. The ether layer was washed with sodium bicarbonate until the

aqueous layer was basic. The organic layer was dried and the solvent was removed on a rotary evaporator.

¹H NMR analysis of the crude reaction mixture showed that acetolysis of tetrahydrofurfuryl tosylate for 49 h in the presence of lutidine gave approximately 47 % tetrahydrofurfuryl acetate **35**, 44 % tetrahydropyran-3-acetate **36**, and 8 % unreacted tetrahydrofurfuryl tosylate (Scheme 9, next page). Acetolysis of tetrahydrofurfuryl tosylate for 7.5 h showed that mainly the starting material was recovered, but some tetrahydrofurfuryl acetate was formed. An estimate of the ratio of product : starting material could not be made based on the ¹H NMR because shifts of the acetate peak from the product overlapped with shifts from the ether ring protons of the starting material.

When the acetolysis of tetrahydrofurfuryl tosylate was carried out for 45 h, it was found by ¹H NMR that the starting material was disappearing and the amount of products were increasing over time. But after 45 h, over 90 % of starting material was still present. Two minor peaks at δ 2.04 and 2.06 were assigned to the CH₃ of the acetyl group in the two different acetate products (tetrahydrofurfuryl acetate, and tetrahydropyran-3-acetate), but an estimate of relative amounts could not be made because shifts of the acetate peak from the product overlapped with shifts from the ether ring protons of the starting material.

Scheme 9

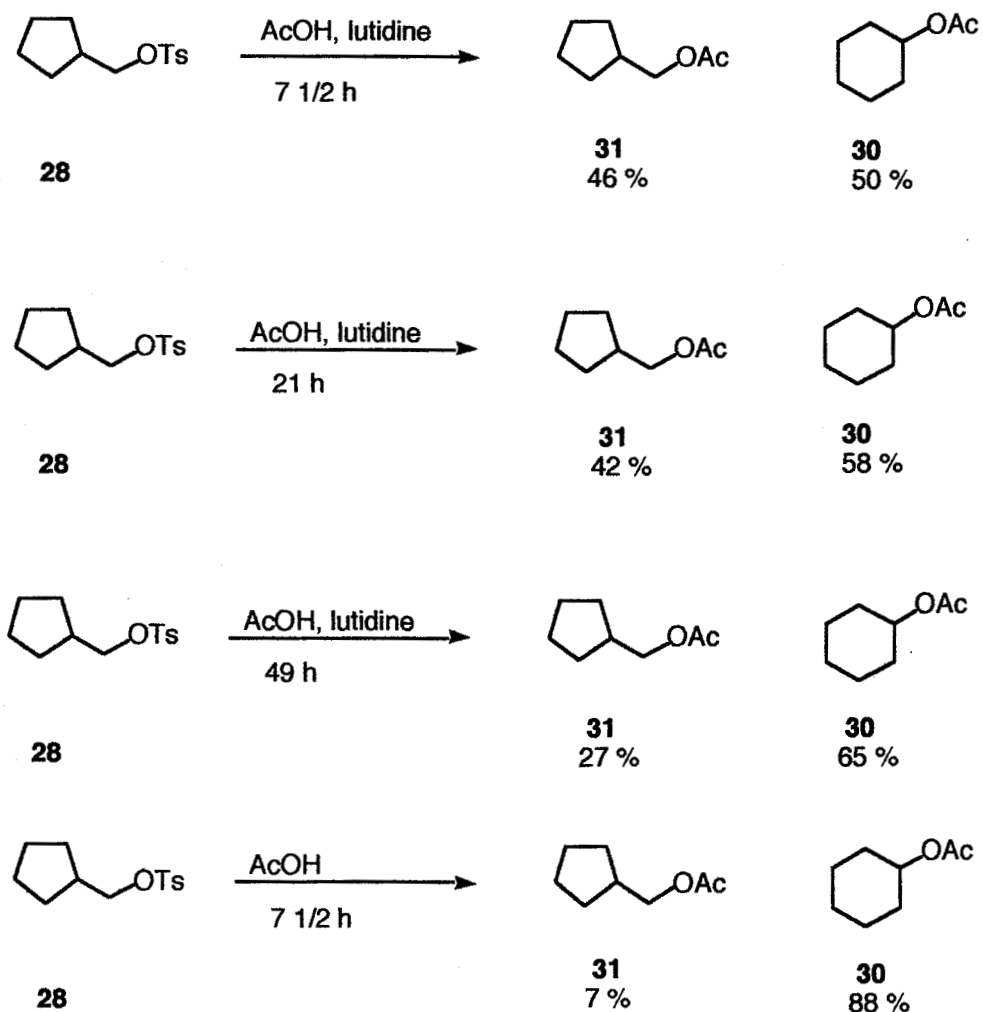


The product mixture obtained from acetolysis of cyclopentylmethyl tosylate in the presence of lutidine for 7.5 h was found to contain approximately 50 % cyclohexyl acetate and 46 % cyclopentylmethyl acetate (Scheme 10, next page). After 21 h, the material recovered was 58 % cyclohexyl acetate and 42 % cyclopentylmethyl acetate, and after 49 h, material recovered was approximately 65 % cyclohexyl acetate and 27 % cyclopentylmethyl acetate. It appears that the cyclopentylmethyl acetate undergoes further rearrangement under the reaction conditions to form cyclohexyl acetate. To test this hypothesis, cyclopentylmethyl acetate was synthesized from the corresponding

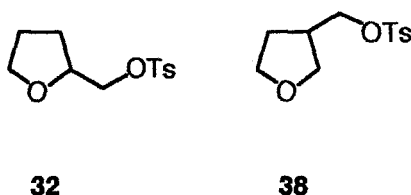
alcohol. The control experiment in which this acetate will be subjected to the above solvolysis conditions has not yet been carried out.

Product obtained from acetolysis of cyclopentylmethyl tosylate (in the absence of lutidine) for 7.5 h was found to contain approximately 88 % cyclohexyl acetate, and 7 % cyclopentylmethyl acetate.

Scheme 10



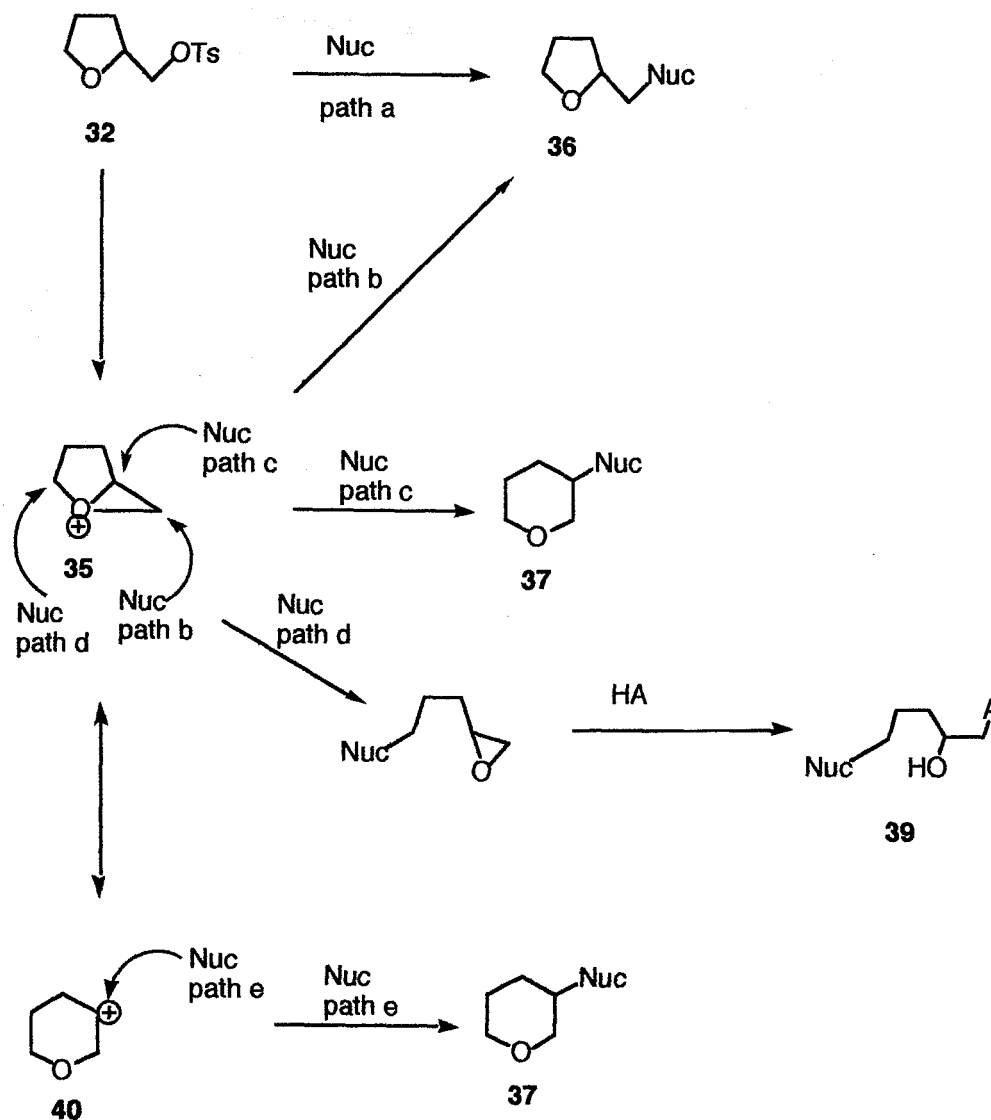
The results of the acetolysis of cyclopentylmethyl tosylate were compared to literature results ¹⁴. No cyclohexene could be seen in the ¹H NMR spectra though its formation is reported in the literature. It is likely that it was lost in the workup because of its high volatility. It was decided to monitor product formation by direct ¹H NMR analysis of the reaction mixture.



The acetolysis of tetrahydrofurano-3-methyl tosylate **38** was also studied. Analysis of product by ¹H NMR after 45 h showed that it consisted of 75 % starting material and 25 % tetrahydrofurano-3-methyl acetate. In contrast, the acetolysis of tetrahydrofurfuryl tosylate **32** was much slower. After 45 h, ¹H NMR analysis of mixture showed that 90 % of starting material was still present.

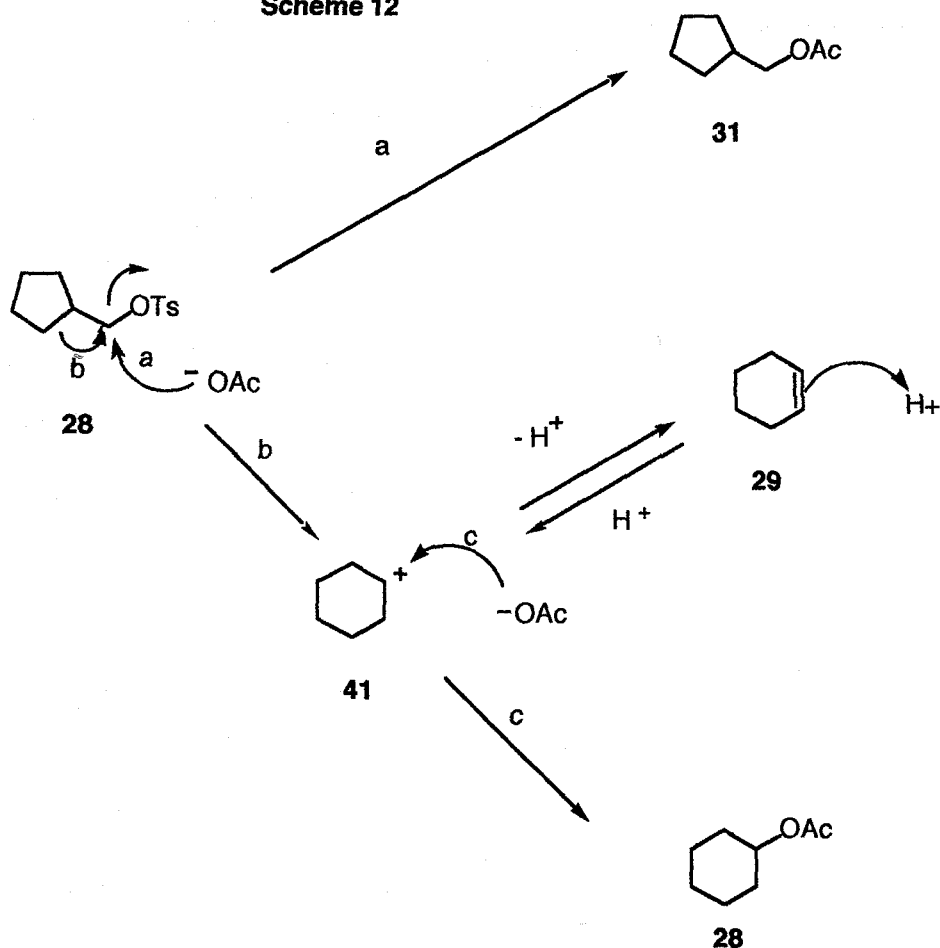
The possible pathways by which tetrahydrofurfuryl tosylate **32** can undergo solvolysis are shown in Scheme 11 (next page). Direct nucleophilic attack on the tetrahydrofurfuryl tosylate **32** would lead to product **36**, or the reaction could proceed via an intermediate **35**. This oxabicyclo[3.1.0]hexonium ion could lead to three products, **36**, **37**, or **39** depending on which carbon is attacked by the nucleophile. Ion **35** could also be in resonance with ion **40**. Attack on this resonance form would lead to product **37**.

Scheme 11



The possible pathways by which cyclopentylmethyl tosylate **28** can undergo solvolysis are shown in Scheme 12 (next page). Direct nucleophilic attack on the cyclopentylmethyl tosylate **28** would lead to product **31**. Anchimeric assistance by a C-C bond would lead to **41**, which can undergo elimination to give **29** or react with the nucleophile to give **28**.

Scheme 12



In the solvolysis of tetrahydrofurfuryl tosylate, **36** and **37** are formed, but **39** is not. In the solvolysis of cyclopentylmethyl tosylate, **31** and **28** are formed, but **29** is not. It can be seen from the results that the solvolysis is considerably faster in the presence of lutidine. Presumably, lutidine reacts with acetic acid to generate the acetate ion. The latter is a much better nucleophile than acetic acid and would be expected to increase the rate of the bimolecular reaction leading to formation of **31** (Scheme 12).

C. ^1H NMR Studies

Acetolysis of tetrahydrofurfuryl tosylate and cyclopentylmethyl tosylate were carried out in deuterated acetic acid in order to analyze aliquots by ^1H NMR, thus eliminating the need to work up the reaction. This would allow the direct observation by ^1H NMR of any volatile products formed in the reaction. The acetolysis of tetrahydrofurfuryl tosylate was followed by ^1H NMR. After ca. 23 h, the starting material was still present and no new peaks could be seen. N,N-dimethyl formamide (DMF) was used as an internal standard. A comparison of the ratios of CH_3 of tosylate : CH_3 of DMF showed that there was no significant decrease in amount of starting material over the ca. 23 h.

The acetolysis of tetrahydrofurfuryl tosylate in the presence of deuterated sodium acetate showed that over the 26 h that the reaction was followed, new peaks were formed at δ 7.74 (d), 7.24 (d), 5.95 (s), 4.79 (m), 3.01 (d), and 2.35 (s). The peak at δ 4.79 was assigned to the CH proton the tetrahydropyran-3-acetate. The other peaks did not match any of the predicted products. DMF was used as an internal standard. A comparison of the ratios of CH_3 of tosylate : CH_3 of DMF showed that the starting material did not decrease significantly over time.

The acetolysis of cyclopentylmethyl tosylate (without sodium acetate) showed that during the 4 h and 30 min the reaction was followed, products formed were cyclohexyl acetate (δ 4.7, m, 1 H), cyclohexene (δ 5.6, s, 2 H), and tosic acid (δ 2.3, s, 3 H) (Figure 1). Ratios of starting material (δ 2.41, s, 3 H) : DMF (δ 3.0, d, 6 H) were computed (Table 1).

Table 1	
Time (min)	Starting Material : DMF
0	2.3 : 1
20	2.2 : 1
90	2.0 : 1
155	1.8 : 1
210	1.6 : 1
270	1.4 : 1

The amount of starting material decreases over the progress of the reaction, while the tosic acid generated increases. Cyclohexene (δ 5.65, s) and cyclohexyl acetate (δ 4.75, m, -CHOAc) were detected as products. The formation of cyclopentylmethyl acetate could not be detected because the acetate methyl peak would be expected to be deuterated.

The acetolysis of cyclopentylmethyl tosylate in the presence of deuterated sodium acetate showed that over the course of ca. 3 h the following products formed: cyclohexyl acetate (δ 4.75, m, 1 H), cyclohexene (δ 5.65, s, 2 H), and *p*-tosic acid (δ 2.3, s, 3 H) (Figure 2). An estimate of the extent of disappearance of starting material was obtained by comparing integrals of peaks from starting material (CH_3 of tosylate) to those from an internal standard (DMF) (Table 2).

Table 2	
Time (min)	Starting Material : DMF
0	0.89 : 1
20	1.0 : 1
75	0.52 : 1
120	0.4 : 1
195	0.24 : 1

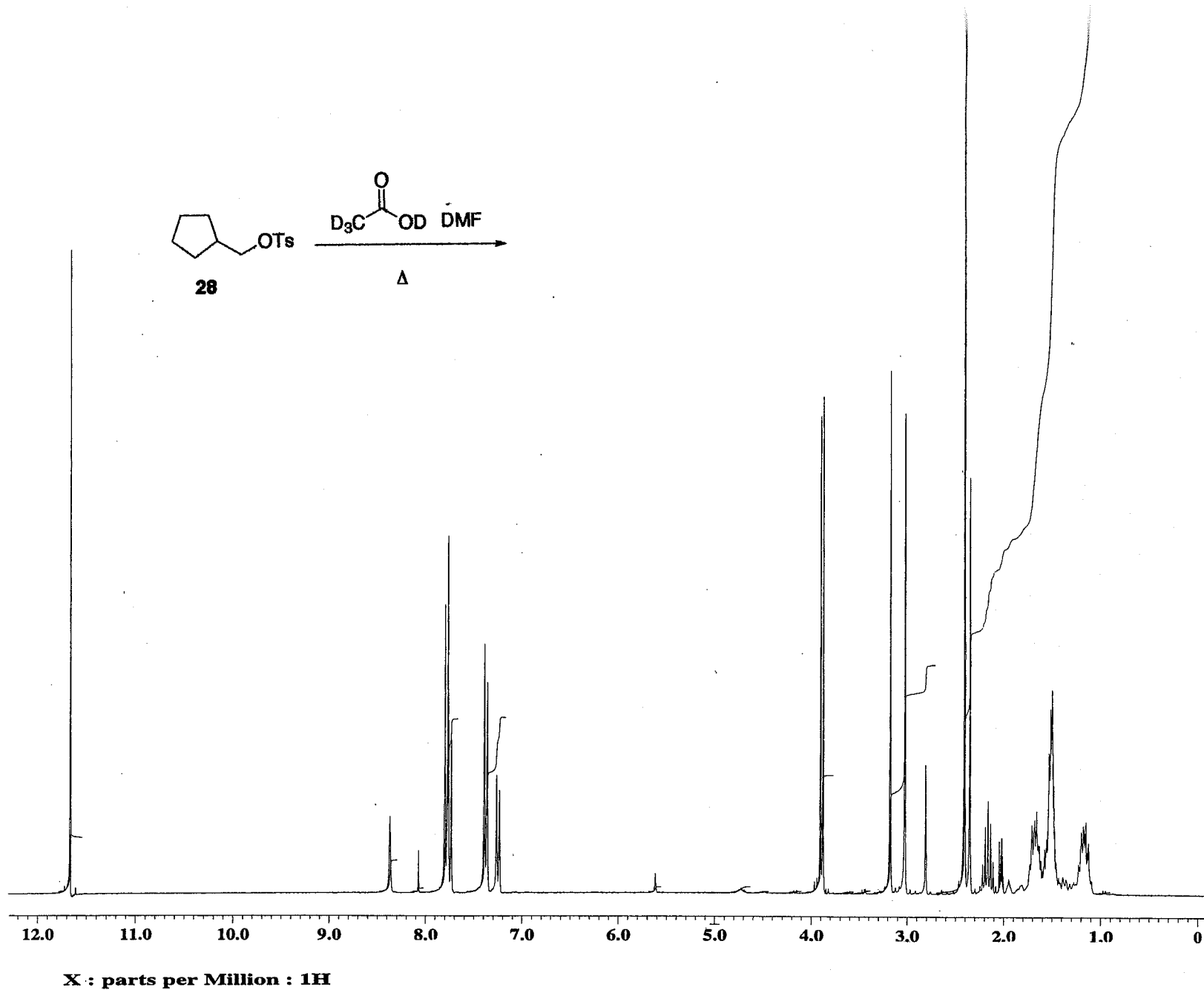


Figure 1. 270 MHz 1H spectrum of deuterated acetolysis of cyclopentylmethyl tosylate at time = 155 min.

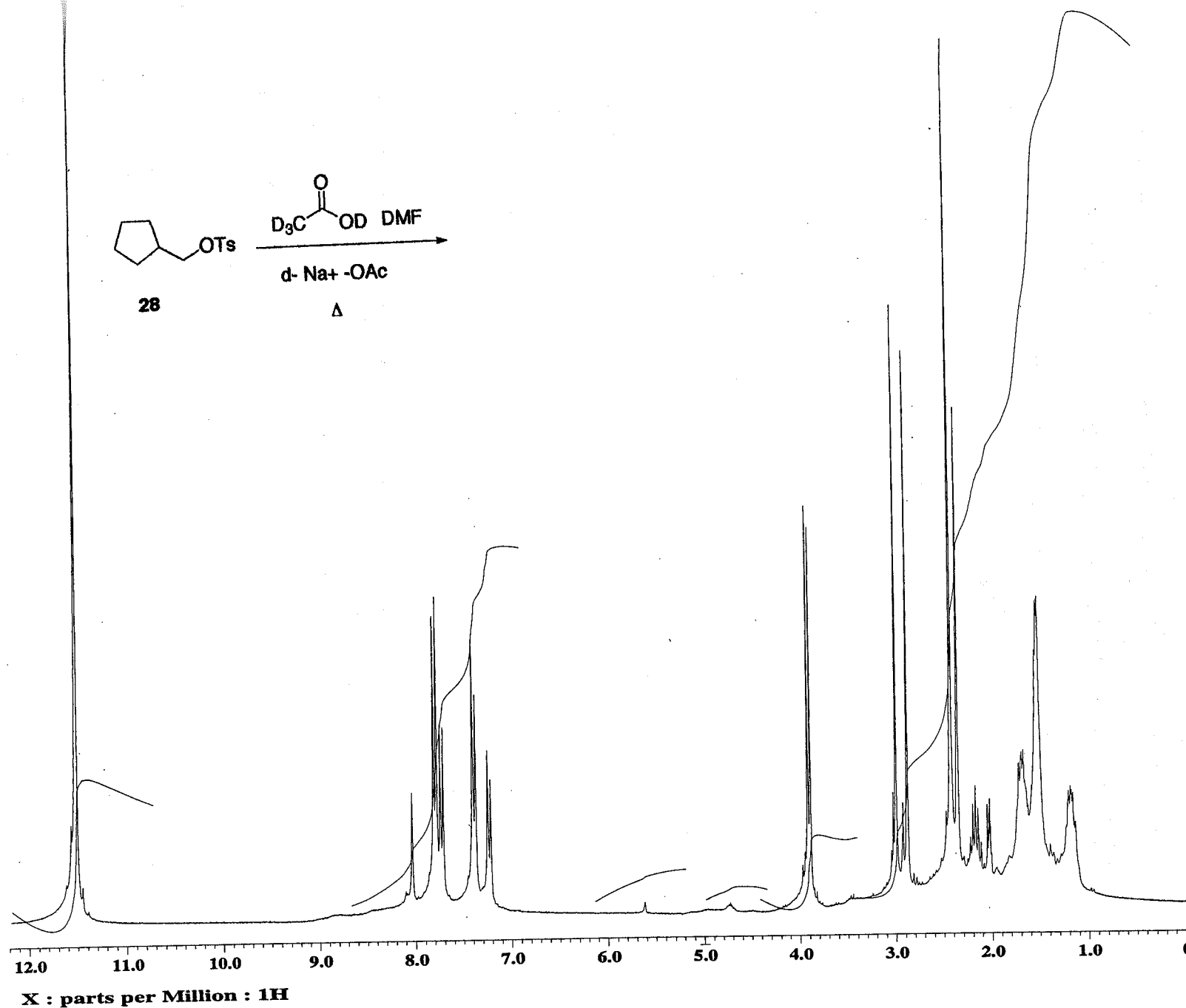


Figure 2. 270 MHz ^1H spectrum of deuterated acetolysis of cyclopentylmethyl tosylate in the presence of deuterated sodium acetate at time = 155 min.

The amount of starting material decreases over the progress of the reaction, while the tosic acid generated increases. Cyclohexene and cyclohexyl acetate were detected as products. The formation of cyclopentylmethyl acetate could not be followed because the acetate methyl peak would be expected to be deuterated. The observed ratios suggest that the acetolysis of cyclopentylmethyl tosylate is faster in the presence of sodium acetate, which suggests that the sodium acetate is acting as a nucleophile.

D. Solvolysis in aqueous acetone

Solvolysis of both tetrahydrofurfuryl tosylate and cyclopentylmethyl tosylate were also carried out in 80 % aqueous acetone. The reaction progress was followed by TLC (30 % EtOAc / 70 % Hexanes). Acetone was removed on a rotary evaporator, and then saturated aqueous NaCl solution was added. The mixture was extracted into ether, dried (Na_2SO_4), and solvent was removed on a rotary evaporator.

The hydrolysis of cyclopentylmethyl tosylate in the presence of lutidine for 48 h gave cyclopentylmethanol as the major product. In comparison, the solvolysis of tetrahydrofurfuryl tosylate in the presence of lutidine for 24 hr only gave unreacted starting material.

E. Conclusions

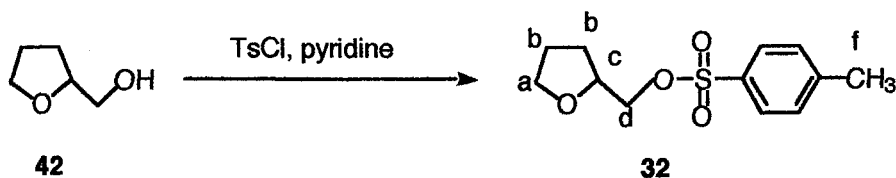
Based on these comparisons, it is apparent that solvolyses reactions of tetrahydrofurfuryl tosylate are slower than those of cyclopentylmethyl tosylate. The slower rate is attributed to the destabilization of the transition state by the oxygen. The

oxygen exerts an inductive effect which would destabilize any developing positive charge at the transition state. Thus the reaction must proceed via a pathway in which bond breaking (C-OTs) exceeds bond formation (C-Nuc). This is further supported by the acetolysis of tetrahydrofurfuryl-3-methyl tosylate, which is faster than the acetolysis of tetrahydrofurfuryl tosylate. In tetrahydrofurfuryl-3-methyl tosylate, the magnitude of the inductive effect is less than in tetrahydrofurfuryl tosylate because the oxygen is one carbon farther removed from the ionizing carbon.

A mixture of products is obtained from the acetolysis of tetrahydrofurfuryl tosylate. This suggests that nucleophilic displacement is not the only pathway leading to products. Rather, it suggests that the oxygen is involved in the departure of the leaving group through an oxabicyclohexonium ion. This, however, is not the major pathway for these solvolyses reactions since the rate is not increased compared to the cyclopentyl analogs. It is proposed that there is a competition between an S_N2 pathway and oxygen assisted pathways.

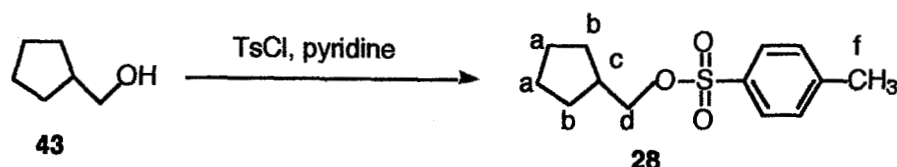
IV. Experimental Section

General Aspects. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a JEOL Eclipse NMR spectrometer at 270 and 67.5 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent peak ($\delta 7.24$ for ^1H NMR and $\delta 77.0$ for ^{13}C NMR) and coupling constants are reported in Hz. All chemicals used were reagent grade and were used as obtained. Deuterated acetic acid was 99.9 atom % D and deuterated sodium acetate was 99+ atom % D. All solvolysis reactions were followed by TLC (30 % EtOAc / 70 % Hexanes) and spots were visualized by UV and PMA spray.

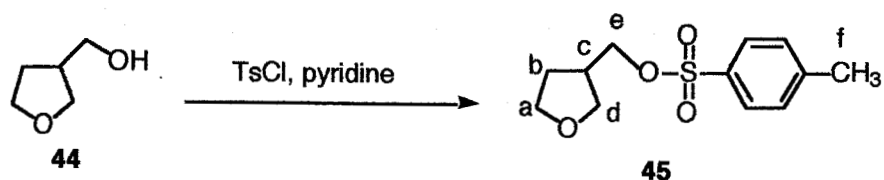


Tetrahydrofurfuryl tosylate (rsc1119). A solution of tetrahydrofurfuryl alcohol (9.97 g, 0.979 mol, 1 eq) in pyridine (100 ml) was stirred under nitrogen as *p*-toluenesulfonyl chloride (20.6 g, 0.1077 mol, 1.1 eq) was added slowly. The mixture was swirled by hand until the *p*-toluenesulfonyl chloride dissolved. The resulting solution was stirred for 24 h. The mixture was then poured over ice (40 g) and was extracted with ether (3 x 70 ml). The ether layer was washed with 2 M H_2SO_4 (5 x 20 ml), H_2O (3 x 40 ml), and 10 % NaHCO_3 (3 x 40 ml). The organic layer was dried (Na_2SO_4) and solvent was removed on a rotary evaporator to give 11.52 g of a colorless oil. The crude product (6.01 g) was

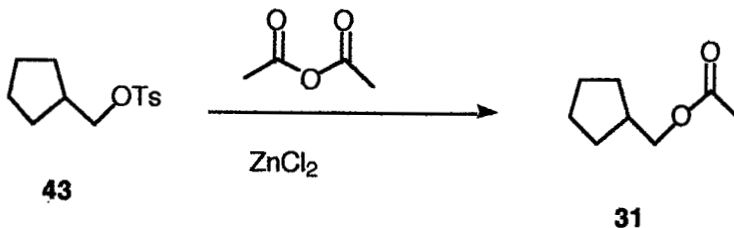
purified by flash chromatography on silica gel (200 g) using 30 % EtOAc / 70 % Hexanes as the eluent to yield 5.29 g of a colorless oil (88 %). ^1H NMR (rsc1119) : δ 1.57 (m, 1 H, CH₂b), 1.80 (m, 2 H, CH₂b), 1.84 (m, 1 H, CHb), 2.36 (s, 3H, CH₃f), 3.68 (m, 2 H, CH₂a), 3.91 (d, 2 H, CH₂d, J = 4.185 Hz), 3.98 (m, 1 H, CHc), 7.29 (d, 2 H, 2 CHring, J = 8.42 Hz), 7.73 (d, 2 H, 2 CHring, J = 8.15 Hz) ^{13}C NMR (rsc1119c13) : δ 21.66 (CH₃f), 25.61 (CH₂b), 27.81 (CH₂b), 68.60 (CH₂a), 71.65 (CHc), 75.93 (CH₂d), 127.94 (CH), 129.91 (CH), 132.90 (CH), 144.93 (CH).



Cyclopentylmethyl tosylate ¹⁴ (rsc1139). A solution of cyclopentylmethanol (1.0183 g, 9.98 mmol, 1 eq) in pyridine (20 ml) was stirred under nitrogen as *p*-toluenesulfonyl chloride (2.1147 g, 10.98 mmol, 1.1 eq) was added slowly. The resulting solution was stirred for 40 h. The mixture was then poured over ice (20 g) and was extracted with ether (3 x 25 ml). The ether layer was washed with 2 M H₂SO₄ (3 x 20 ml), H₂O (3 x 20 ml), and 10 % NaHCO₃ (3 x 20 ml). The organic layer was dried (Na₂SO₄) and solvent was removed on a rotary evaporator to give 1.3856 g (54 %) of a very light brown oil. ^1H NMR (rsc1139b): δ 1.15 (m, 2 H, CH₂b), 1.47 (m, 4 H, CH₂a), 1.67 (m, 2 H, CH₂b), 2.18 (m, 1 H, CHc, J =7.18, 7.43, 7.67 Hz), 2.40 (s, 3 H, CH₃f), 3.86 (d, 2 H, CH₂d, J = 7.16 Hz), 7.32 (d, 2 H, CHring, J = 7.42 Hz), 7.74 (d, 2 H, CHring, J = 7.42 Hz) ^{13}C NMR (rsc1149c13): 21.68 (CH₃f), 25.29 (CH₂a), 29.02 (CH₂b), 38.63 (CHc), 74.36 (CH₂d), 127.89 (CH), 129.89 (CH), 133.20 (CH), 144.73 (CH).

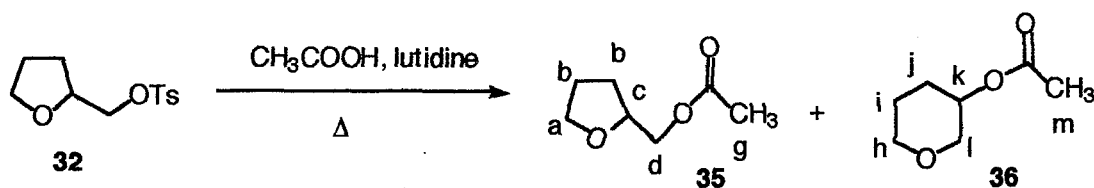


Tetrahydrofuran-3-methyl tosylate (rsc2027). A solution of tetrahydro-3-furano methanol (2.9720 g, 29.4 mmol, 1 eq) in pyridine (20 ml) was stirred under nitrogen as *p*-toluenesulfonyl chloride (6.7820 g, 35.3 mmol, 1.2 eq) was added slowly. The resulting mixture was stirred for 49 h. The mixture was then poured over ice (20 g) and was extracted with ether (3 x 25 ml). The ether layer was washed with 2 M H_2SO_4 (3 x 20 ml), H_2O (3 x 20 ml), and 10 % NaHCO_3 (3 x 20 ml). The organic layer was dried (Na_2SO_4) and solvent was removed on a rotary evaporator to give 5.8251 g (78 %) of a colorless oil. ^1H NMR (rsc2027): δ 1.47 (m, CH_2b), 1.90 (m, CH_2b), 2.36 (s, CH_3f), 2.47 (m, CH_2c), 3.40 (m, CHe), 3.63 (m, CH_3a), 3.87 (m, CH_2d), 7.29 (d, CHring , $J=7.91$ Hz), 7.71 (d, CHring , $J=8.40$ Hz) ^{13}C NMR (rsc2027c133): 21.66 (CH_3f), 28.45 (CH_2b), 38.35 (CH_2c), 67.58 (CHe), 69.97 (CH_2a), 71.61 (CH_2d), 127.87 (CH), 130.02 (CH), 132.78 (CH), 145.07 (CH).



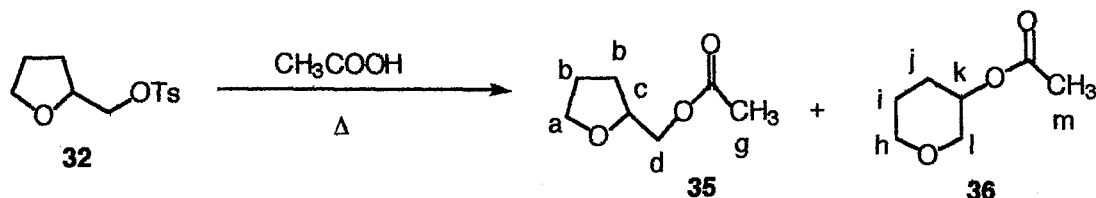
Cyclopentylmethyl acetate (rsc2013). A solution of cyclopentyl methanol (101.7 mg, 0.998 mmol, 1 eq), acetic anhydride (0.1 ml, 1.10 mmol, 1.1 eq), and zinc chloride (10

mg, 0.73 mmol) was stirred under nitrogen and heated in an oil bath (70 – 80 °C). After 2 h, solution was cooled. The solution was diluted with ether (20 ml) and washed with NaHCO₃ (3 x 10 ml) and NaCl (3 x 10 ml) and dried (Na₂SO₄). Solvent was removed on a rotary evaporator to give 0.0896 g of light brown oil (63 %). ¹H NMR: δ 1.20 (m, 2 H, CH₂b), 1.56 (m, 4 H, CH₂a and a'), 1.70 (m, 2 H, CH₂b'), 2.00 (s, 3 H, CH₃h), 2.15 (m, 1 H, CHc), 3.94 (d, 2 H, CH₂ d) ¹³C NMR: 21.04 (CH₃h), 25.31 (CH₂a), 29.38 (CH b), 38.52 (CH₂c), 68.54 (CH₂d), 171.37 (CH g).



Acetolysis (with lutidine) of tetrahydrofurfuryl tosylate (rsc1153). A solution of tetrahydrofurfuryl tosylate (0.2057 g, 0.803 mmol, 1 eq), and 2,6-lutidine (0.1184 g, 1.04 mmol, 1.3 eq), in glacial acetic acid (5 ml) was refluxed under nitrogen and the reaction was followed by TLC (30% EtOAc / 70% Hexanes). After 49 h, the solution was cooled. Enough saturated aqueous NaCl (10 ml) was added to form a precipitate, and then just enough water was added to re-dissolve the precipitate. The resulting mixture was extracted with ether (4 x 20 ml). The ether layer was washed with NaHCO₃ (7 x 20 ml) until basic. The organic layer was dried (Na₂SO₄) and solvent was removed on a rotary evaporator to yield 0.054 g of a brown oil (46 % based on tetrahydrofurfuryl acetate). ¹H NMR analysis showed that material recovered was approximately 47 % tetrahydrofurfuryl acetate, 44 % tetrahydropyran-3-acetate, and 8 % unreacted tetrahydrofurfuryl tosylate ¹H NMR: δ 1.57 (m, ring), 1.68 (m, ring'), 2.02 (s, CH₃m),

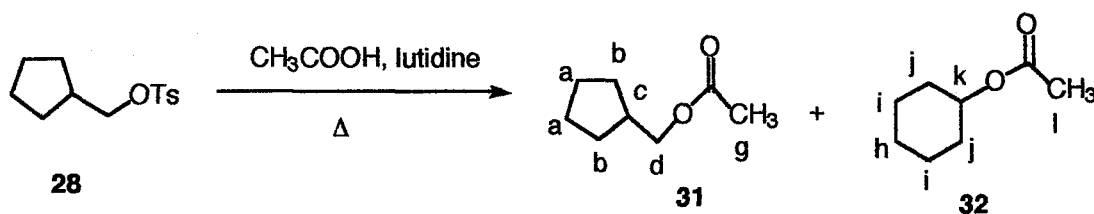
2.05 (s, CH₃g), 3.65 (m, ring), 3.72 (m, ring), 4.05 (m, ring), 4.12 (m, ring), 4.78 (m, CHk), 7.33 (d, tosylate ring, $J = 8.15$ Hz), 7.79 (d, tosylate ring, $J = 8.40$ Hz). An unidentifiable peak at δ 1.40 was also seen.



Acetolysis of tetrahydrofurfuryl tosylate (rsc1121, rsc1123). A solution of tetrahydrofurfuryl tosylate (0.1030 g, 0.390 mmol) in acetic acid (4 ml) was refluxed under nitrogen. The reaction was followed by TLC. After 24 h, a 2 ml aliquot was diluted with H₂O (5 ml) and extracted with ether (4 x 10 ml). The ether layer was washed with 10 % NaHCO₃ (8 x 5 ml). The organic layer was dried (Na₂SO₄) and solvent was removed on a rotary evaporator to give 0.027 g of a black-brown oil (rsc1121). After 45 h, the remaining reaction solution (2 ml) was worked up by above procedure to give 0.021 g of a black-brown oil (rsc1123). ¹H NMR analysis showed that amount of starting material was decreasing over time and products were increasing over time. However, even after 45 hours, approximately 70 % of the starting material was still present. An estimate of product distribution could not be made because shifts of the acetate peak from the products (tetrahydrofurfuryl acetate and tetrahydropyran-3-methyl acetate) overlapped with shifts from the ring of the starting material. ¹H NMR (rsc1121): δ 1.66 (m, ring), 1.85 (m, ring), 2.04 (s, CH₃m), 2.06 (s, CH₃g), 2.43 (s, CH₃f), 3.72 (m, ring), 3.99 (m, ring), 4.05 (m, ring), 4.78 (m, CHk), 7.34 (d, tosylate ring, $J = 8.42$ Hz), 7.80 (d,

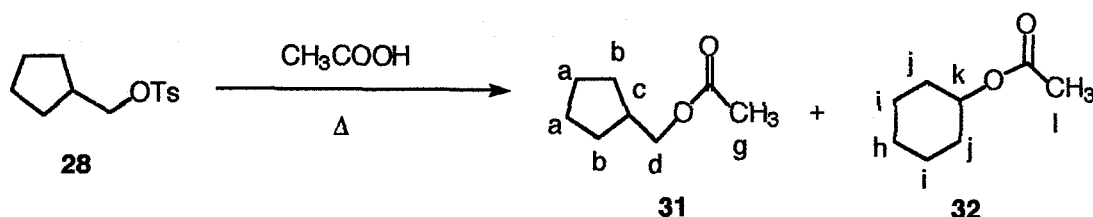
tosylate ring, $J = 8.42$ Hz). An unidentifiable peak at δ 1.40 could also be seen. **¹H NMR (rsc1123):** 1.66 (m, ring), 1.85 (m, ring), 2.03 (s, CH₃m), 2.06 (s, CH₃g), 2.43 (s, CH₃f), 3.76 (m, ring), 3.99 (m, ring), 4.06 (m, ring), 4.80 (m, CHk), 5.29 (CH₂Cl₂), 7.34 (d, tosylate ring, $J = 7.91$ Hz), 7.80 (d, tosylate ring, $J = 8.15$ Hz). An unidentifiable peak at δ 1.41 was also seen.

Acetolysis of tetrahydrofurfuryl tosylate (rsc2011). A solution of tetrahydrofurfuryl tosylate (1.0050 g, 3.90 mmol) in acetic acid (10 ml) was refluxed under nitrogen. After 7.5 h, the solution was cooled and saturated NaCl (10 ml) was added. Enough water was added to re-dissolve the precipitate. The mixture was extracted with ether (5 x 20 ml). The ether layer was washed with 10 % NaHCO₃ (9 x 20 ml) until basic. The organic layer was dried (Na₂SO₄) and the solvent was removed on a rotary evaporator to give 0.64 g of an oil. **¹H NMR analysis** showed that > 90 % of starting material was still present. A small amount of tetrahydrofurfuryl acetate was also present but no tetrahydropyran 3-acetate could be detected. **¹H NMR (rsc20112):** δ 1.60 (m, ring), 1.83 (m, ring), 1.99 (s, CH₃m), 2.02 (s, CH₃g), 2.39 (s, CH₃f), 3.71 (m, ring), 3.94 (m, ring), 4.01 (m, ring), 5.25 (CH₂Cl₂), 7.31 (d, tosylate ring, $J = 8.15$ Hz), 7.75 (d, tosylate ring, $J = 8.15$ Hz).

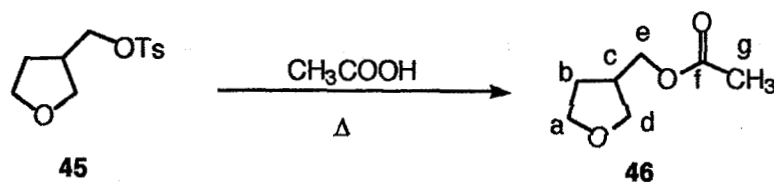


Acetolysis (with lutidine) of cyclopentylmethyl tosylate (rsc2001). A solution of cyclopentylmethyl tosylate (1.0108 g, 3.93 mmol, 1 eq) and lutidine (0.5510 g, 5.109 mmol, 1.3 eq) in acetic acid (10 ml) was refluxed under nitrogen. The reaction was followed by TLC (30 % EtOAc/ 70 % Hexanes). After 7 1/2 h, the solution was cooled, and saturated NaCl (10 ml) was added. Enough water was added to re-dissolve the precipitate. The solution was extracted with ether (5 x 20 ml). The ether layer was washed with 10 % NaHCO₃ (9 x 20 ml) until basic. The organic layer was dried (Na₂SO₄) and solvent was removed on a rotary evaporator to give 0.13 g of a light brown oil (23 %). ¹H NMR analysis showed approximately 4 % of starting material, 50 % cyclohexyl acetate and 46 % cyclopentylmethyl acetate were present. ¹H NMR (rsc20012): δ 1.24 (m, ring), 1.50 (m, ring), 1.65 (m, ring), 1.93 (s, CH₃l), 1.95 (s, CH₃g), 2.10 (m, CHc), 3.81 (d, CH₂d of tosylate, *J* = 6.91 Hz), 3.87 (d, CH₂d, *J* = 7.18 Hz), 4.64 (m, CHk), 7.27 (d, tosylate ring, *J* = 7.43 Hz), 7.71 (d, tosylate ring, *J* = 8.42 Hz).

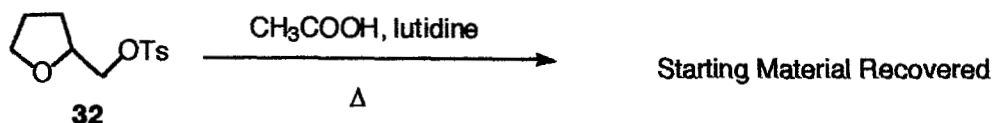
Acetolysis (with lutidine) of cyclopentylmethyl tosylate (rsc1155). The above reaction was carried out for 49 h and worked up in a similar manner. ¹H NMR analysis showed that the product consisted of approximately 8 % cyclopentylmethyl tosylate (starting material), 65 % cyclohexyl acetate, and 27 % cyclopentylmethyl acetate. ¹H NMR: δ 1.23 (m, ring), 1.36 (m, ring), 1.55 (m, ring), 1.72 (m, ring), 1.82 (m, ring), 2.01 (s, CH₃l), 2.03 (s, CH₃d), 2.17 (m, CHc), 3.89 (d, CH₂d of tosylate, *J* = 6.67 Hz), 3.95 (d, CH₂d, *J* = 7.16 Hz), 4.72 (m, CHk), 7.34 (d, tosylate ring, *J* = 8.42 Hz), 7.79 (d, tosylate ring, *J* = 8.18 Hz). An unidentifiable peak at δ 1.41 was also seen.



Acetolysis of cyclopentylmethyl tosylate (rsc2007). A solution of cyclopentylmethyl tosylate (4.0102 g, 15.73 mmol, 1 eq) in acetic acid (20 ml) was refluxed under nitrogen. The reaction was followed by TLC (10 % EtOAc/ 90 % Hexanes). After 8 h, the solution was cooled and saturated with NaCl (20 ml), and enough water was added to re-dissolve the precipitate. Solution was extracted with ether (4 x 25 ml). The ether layer was washed with 10 % NaHCO₃ (10 x 25 ml) until basic. The organic layer was dried (Na₂SO₄) and solvent was removed on a rotary evaporator to yield 0.90 g of a light brown oil (40 %). ¹H NMR analysis showed that the product was approximately 3 % starting material, 92 % cyclohexyl acetate, and 6 % cyclopentylmethyl acetate. ¹H NMR (rsc2007): δ 1.31 (m, ring), 1.47 (m, ring), 1.66 (m, ring), 1.77 (m, ring), 1.94 (s, CH₃l), 1.96 (s, CH₃g), 2.37 (s, CH₃f of tosylate), 3.82 (d, CH₂d of tosylate, *J* = 7.16 Hz), 3.88 (d, CH₂d, *J* = 7.16 Hz), 4.65 (m, CHk), 5.23 (CH₂Cl₂), 7.27 (d, tosylate ring, *J* = 7.69 Hz), 7.73 (d, tosylate ring, *J* = 8.40 Hz). ¹³C NMR: δ 21.40 (CH₃l), 23.82 (CH₂b), 25.39 (CH₂h), 31.65 (CH₂j), 72.63 (CHk), 170.51 (C=O).

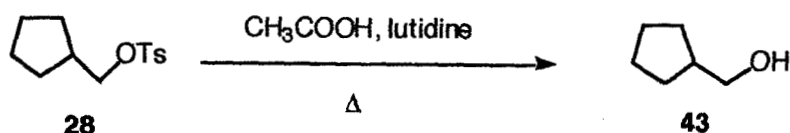


Acetolysis of tetrahydrofurfuryl-3-methyl tosylate (rsc2043). A solution of tetrahydrofuran-3-methyl tosylate (0.3220 g, 1.26 mmol) in acetic acid (5 ml) was refluxed under nitrogen and the reaction was followed by TLC. After 45 h, solution was cooled, saturated NaCl (5 ml) was added, and extracted with ether (3 x 25 ml). The ether layer was washed with 10 % NaHCO₃ (3 x 25 ml). The organic layer was dried (Na₂SO₄) and solvent was removed on a rotary evaporator to give 0.2265 g of a light brown oil. ¹H NMR analysis showed that it consisted of 75 % starting material and 25 % tetrahydrofurano-3-methyl acetate. ¹H NMR: δ 1.53 (m, CH₂b), 2.01 (m, CH₂b), 2.42 (s, CH₃f), 2.56 (m, CH₂c), 3.47 (m, CH_e), 3.73 (m, CH₃a), 3.92 (m, CH₂d), 7.34 (d, CH_{ring}, J = 7.91 Hz), 7.77 (d, CH_{ring}, J = 8.15 Hz)



Solvolysis (with lutidine) of tetrahydrofurfuryl tosylate in aqueous acetone (rsc1125). A solution of tetrahydrofurfuryl tosylate (0.1086 g, 0.390 mmol), and 2,6-lutidine (2 drops) in aqueous acetone (water : acetone, 20 : 80, 5 ml) was refluxed under nitrogen. The reaction was followed by TLC (30% EtOAc / 70% Hexanes). After 24 h,

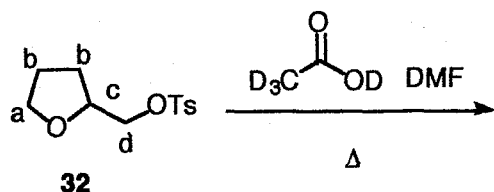
the acetone was removed on a rotary evaporator. Saturated aqueous NaCl (5 ml) was added to the residue. This was extracted with ether (3 x 20 ml), dried (Na_2SO_4) and the solvent was removed on a rotary evaporator to give 0.072 g of an oil. $^1\text{H NMR}$ (rsc1129): δ 1.63 (m, ring), 1.85 (m, ring), 1.94 (m, ring), 2.43 (s, CH_3 of tosylate), 2.96 (s, possibly alcohol of tetrahydrofurfuryl alcohol), 3.75 (d, tosylate ring), 3.98 (m, ring of tosylate), 4.07 (m, ring of tosylate), 7.34 (d, tosylate ring, $J = 8.4$ Hz), 7.80 (d, tosylate ring, $J = 8.40$ Hz).



Solvolysis (with lutidine) of cyclopentylmethyl tosylate in aqueous acetone (rsc1143).

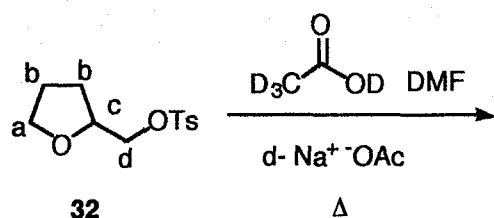
A solution of cyclopentylmethyl tosylate (0.1052 g, 0.393 mmol, 1 eq), 2,6-lutidine (0.0606 g, 0.472 mmol, 1.2 eq), in 43 % aqueous acetone (7 ml) was refluxed under nitrogen. The reaction was followed by TLC (30 % EtOAc, 70 % Hexanes). After 48 h, the solution was cooled and the acetone was removed on a rotary evaporator. The remaining residue was saturated with sat. NaCl (10 ml). This was extracted with ether (3 x 20 ml), dried (Na_2SO_4) and solvent was removed on a rotary evaporator to give 0.086 g of an oil. $^1\text{H NMR}$ analysis showed that starting material was still present.

V. ^1H NMR Studies



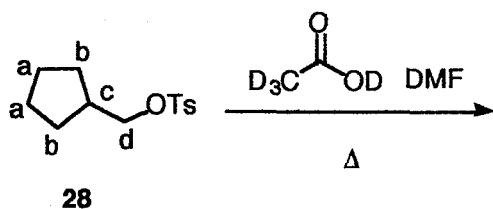
Acetolysis of tetrahydrofurfuryl tosylate (rsc2021). A solution of tetrahydrofurfuryl tosylate (0.250 g, 0.976 mmol) and N,N-dimethylformamide (34 mg, 0.466 mmol) in deuterated acetic acid (7 ml) was refluxed under nitrogen. Aliquots were taken at 0, 20, 90, 150, 220, 275, 545, 1400 min time intervals and analyzed directly by ^1H NMR spectroscopy. The disappearance of product was estimated by comparing the integral of CH_3 of DMF (δ 2.99, 6H) to CH_3 of tetrahydrofurfuryl tosylate (δ 2.42, 3 H) (Table 3). The amount of the expected product, tetrahydrofurfuryl acetate, could not be determined because the acetate peak was deuterated and the CH_2d peak shift overlapped with the protons in the starting material. No other peaks formed during the reaction.

Table 3	
Time (min)	Starting Material : DMF
0	2.26 : 1
20	2.0 : 1
90 (1h,30min)	2.3 : 1
150 (2h,30min)	2.0 : 1
220 (3h,40min)	2.3 : 1
275 (4h,35min)	2.0 : 1
545 (9h,5min)	2.0 : 1
1400 (23h,20min)	2.1 : 1



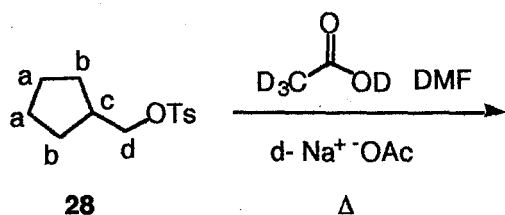
Acetolysis (with sodium acetate) of tetrahydrofurfuryl tosylate (rsc2031). A solution of tetrahydrofurfuryl tosylate (0.2559 g, 0.976 mmol, 1 eq) deuterated sodium acetate (0.1048 g, 1.27 mmol, 1.3 eq) and dimethylformamide (30.7 mg, 0.421 mmol) in deuterated acetic acid (10 ml) was refluxed under nitrogen. Aliquots were taken at 0, 205, 375, 1320, and 1585 min time intervals and analyzed by directly ^1H NMR spectroscopy. By 3100 min, the reaction had run dry, so no more samples were taken. The extent of disappearance of product was estimated by comparing the integral of CH_3 of DMF (δ 2.99, 6 H) to CH_3 of tetrahydrofurfuryl tosylate (δ 2.42, 3 H) (Table 4). Other minor peaks formed during reaction are δ 7.74 (d), 7.24 (d), 5.95 (s), 4.79 (m), 3.01 (d), and 2.35 (s). These peaks did not match any of the predicted products. There is some discrepancy in these results, so this experiment needs to be repeated.

Table 4	
Time (min)	Starting Material : DMF
0	2.5 : 1
205 (3h,25min)	3.1 : 1
375 (6h,15min)	3.9 : 1
1320 (22h)	2.7 : 1
1585 (26h,15min)	2.6 : 1



Acetolysis of cyclopentylmethyl tosylate (rsc2017). A solution of cyclopentylmethyl tosylate (0.2495 g, 0.97 mmol, 1 eq) and dimethylformamide (32.5 mg, 0.445 mmol) in deuterated acetic acid (5 ml) was refluxed under nitrogen. Aliquots were taken at 0, 20, 90, 155, 210, and 270 min time intervals and analyzed directly by ^1H NMR spectroscopy. By 330 min, the reaction had run dry, so no more samples were taken. The extent of disappearance of product was estimated by comparing the integral of the CH_3 of DMF (δ 2.99, 6H) to the CH_3 of cyclopentylmethyl tosylate (δ 3.8, 2 H) (Table 5). The amount of the expected product, cyclopentylmethyl acetate, could not be determined because the acetate peak was deuterated and the CH_2d peak shift overlapped with the protons in the starting material. Other products formed during reaction are cyclohexyl acetate (δ 4.7, d, 1 H), cyclohexene (δ 5.6, s, 2 H), and tosic acid (δ 2.3, s, 3 H).

Table 5			
Time (min)	DMF	Starting Mat.	Cyclohexyl acetate
0	1	2.3	0
20	1	2.2	0
90 (1h,30min)	1	2	0
155 (2h,35min)	1	1.8	0.17
210 (3h,30min)	1	1.6	0.25
270 (4h,30min)	1	1.4	0.22



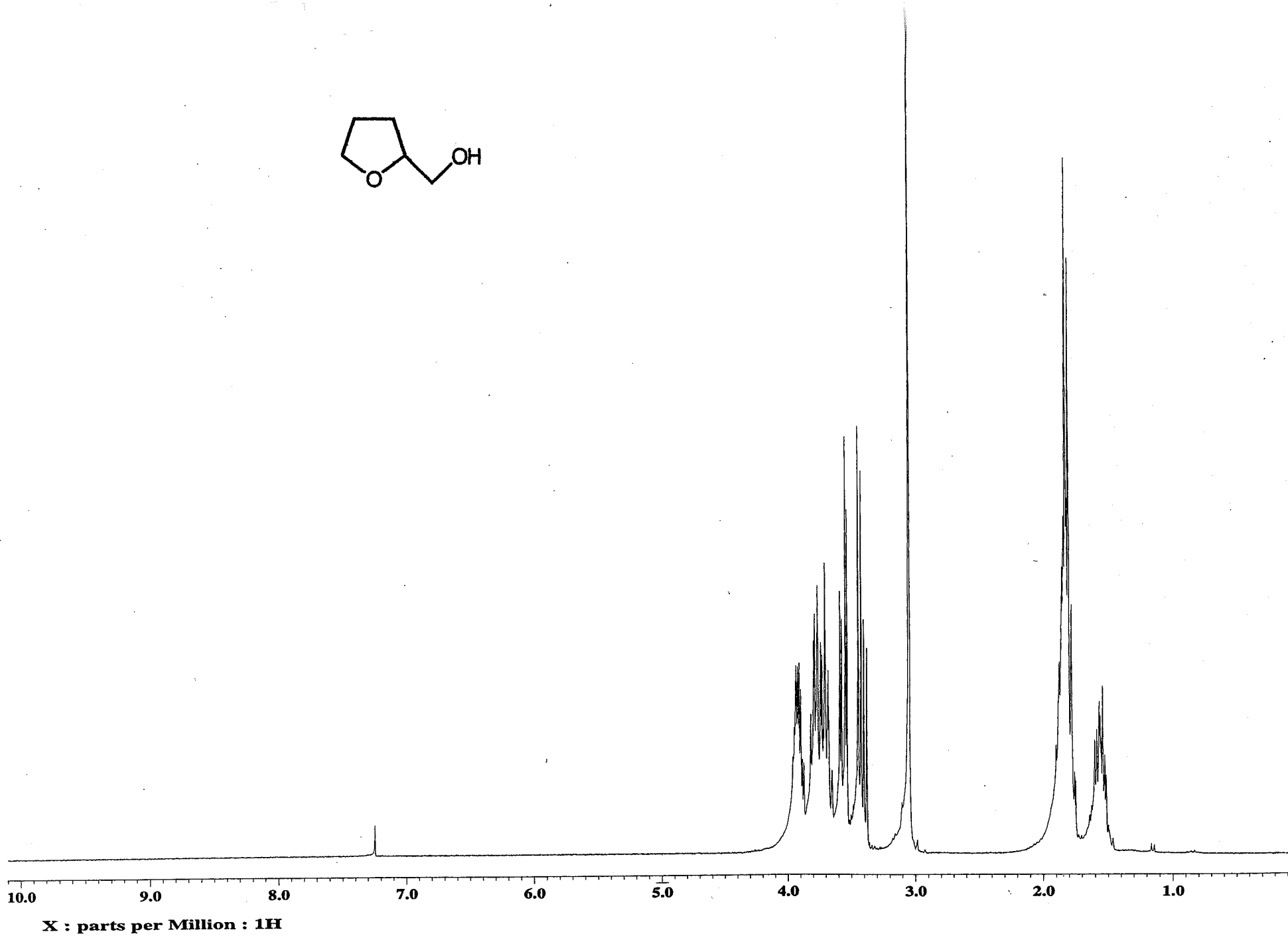
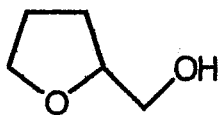
Acetolysis (with sodium acetate) of cyclopentylmethyl tosylate (rsc2025). A solution of cyclopentylmethyl tosylate (0.2605 g, 0.97 mmol) deuterated sodium acetate (0.0837 g, .97 mmol) and dimethylformamide (29.5 mg, 0.404 mmol) in deuterated acetic acid (6 ml) was refluxed under nitrogen. Aliquots were taken at 0, 20, 75, 120, and 195 min time intervals and analyzed directly by ^1H NMR spectroscopy. By 315 min, the reaction had run dry, so no more samples could be taken. The extent of disappearance of product was estimated by comparing the integral of the CH_3 of DMF (δ 2.99, 6H) to the CH_3 of cyclopentylmethyl tosylate (δ 3.8, 2 H) (Table 6). Other products formed during reaction are cyclohexyl acetate (δ 4.7, d, 1 H), cyclohexene (δ 5.6, s, 2 H), and tosic acid (δ 2.3, s, 3 H).

Table 6			
Time (min)	DMF	Starting Mat.	Cyclohexyl acetate
0	1	0.89	0
20	1	1	0
75 (1h,15 min)	1	0.52	0.02
120 (2h)	1	0.4	0.06
195 (3h,15min)	1	0.24	0.13

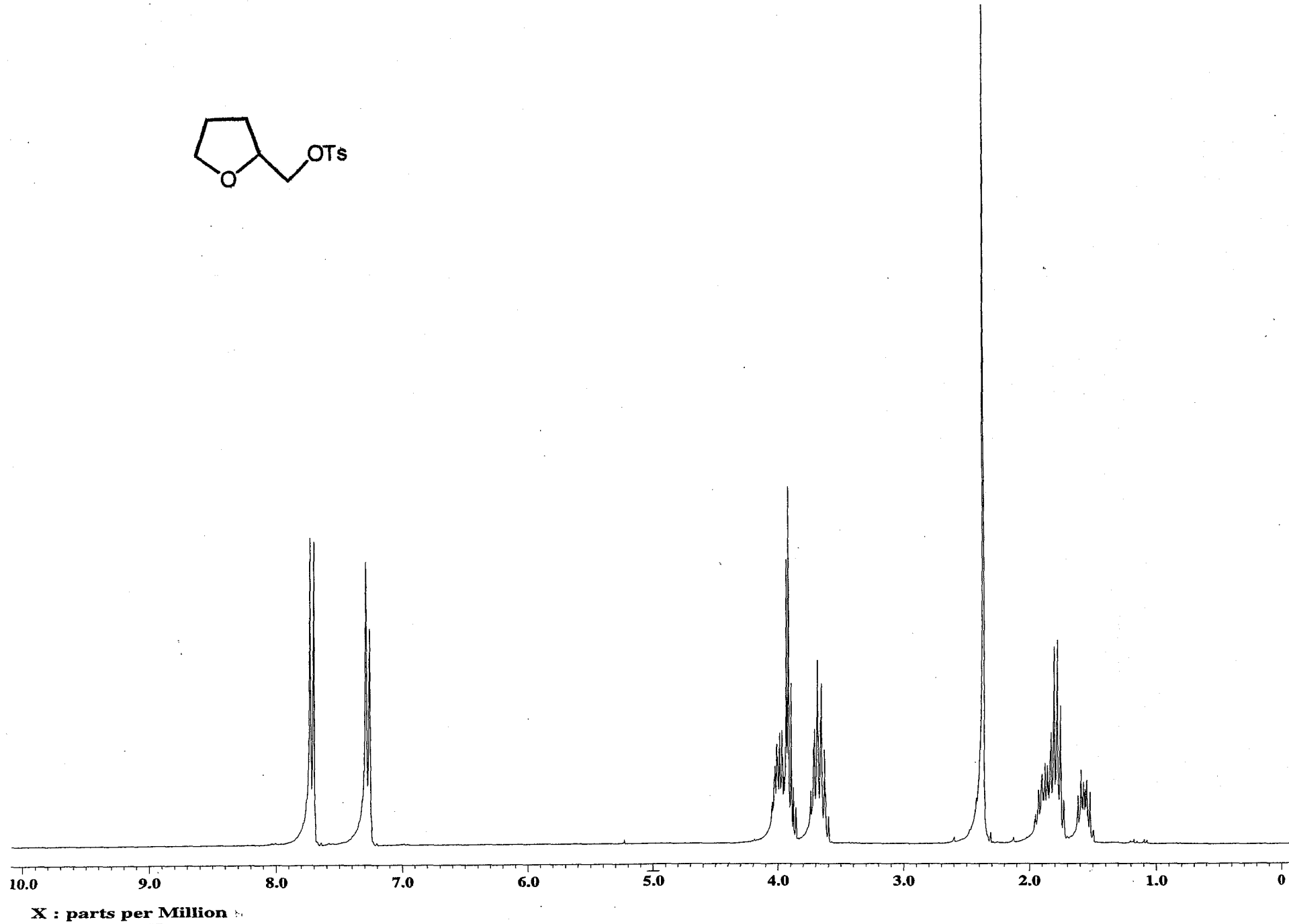
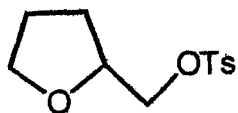
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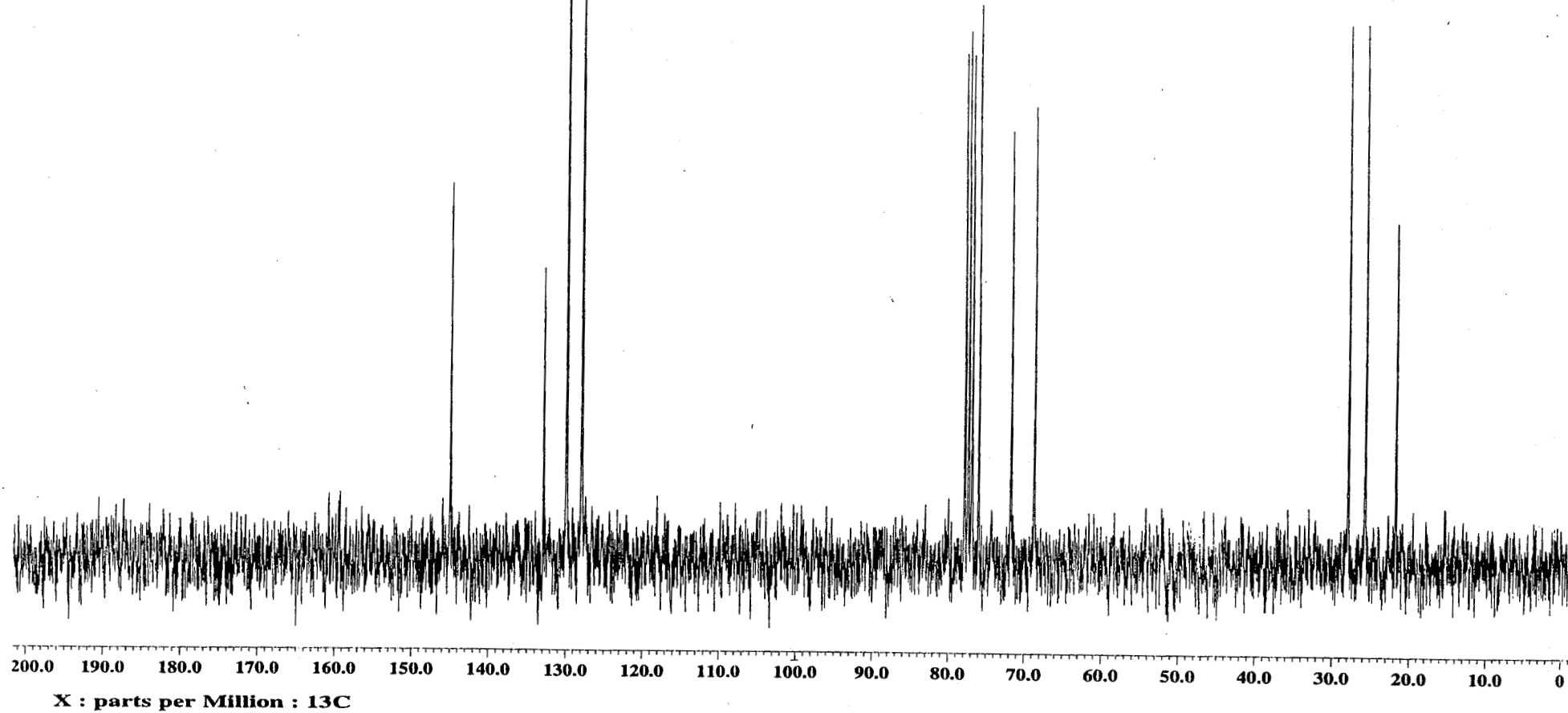
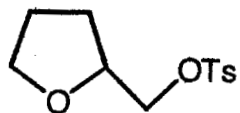
VII. Appendix. Spectral Data



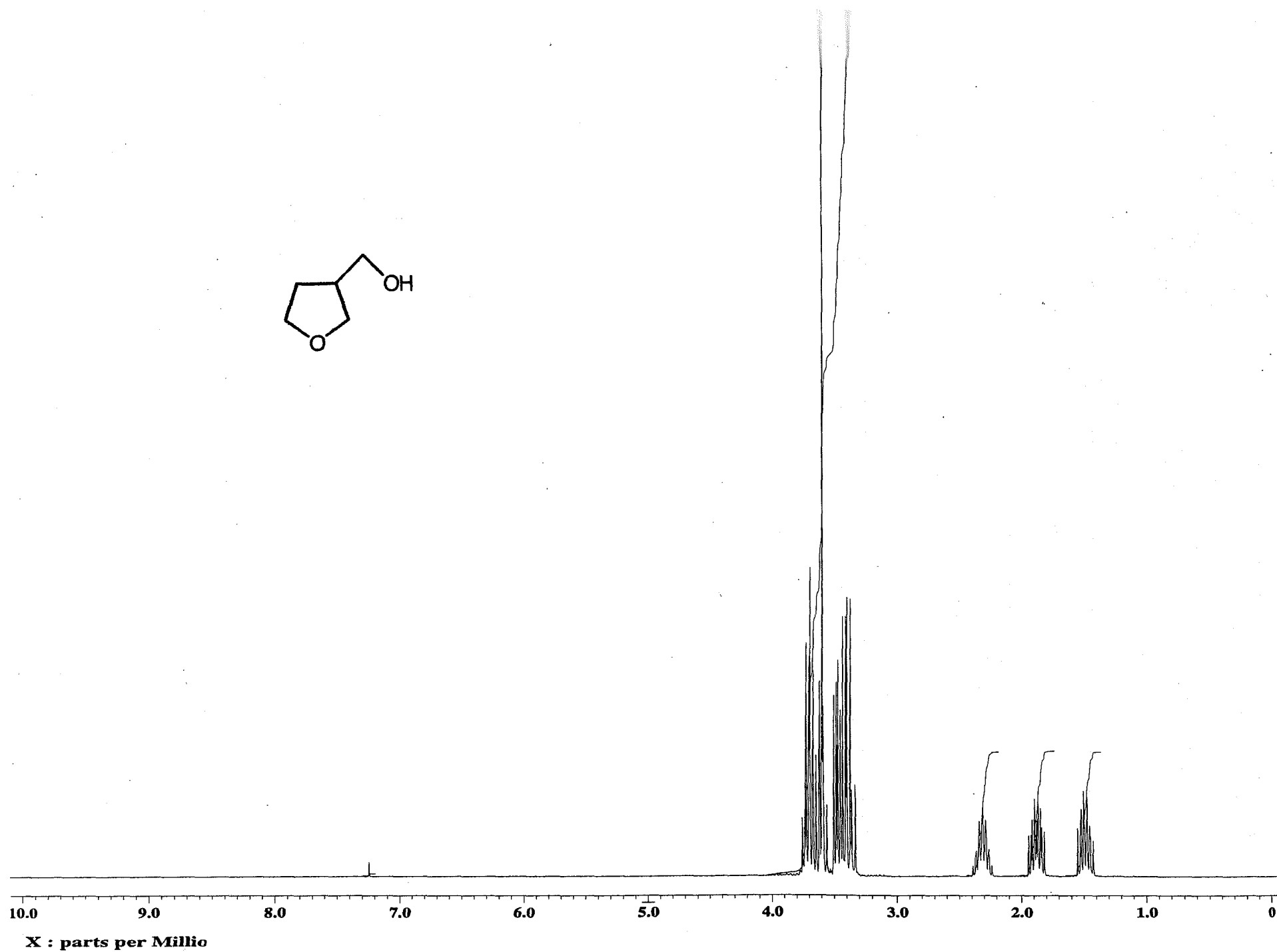
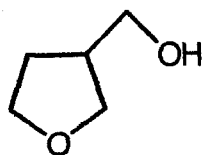
Spectrum 1. 270 MHz ^1H spectrum of tetrahydrofurfuryl alcohol.



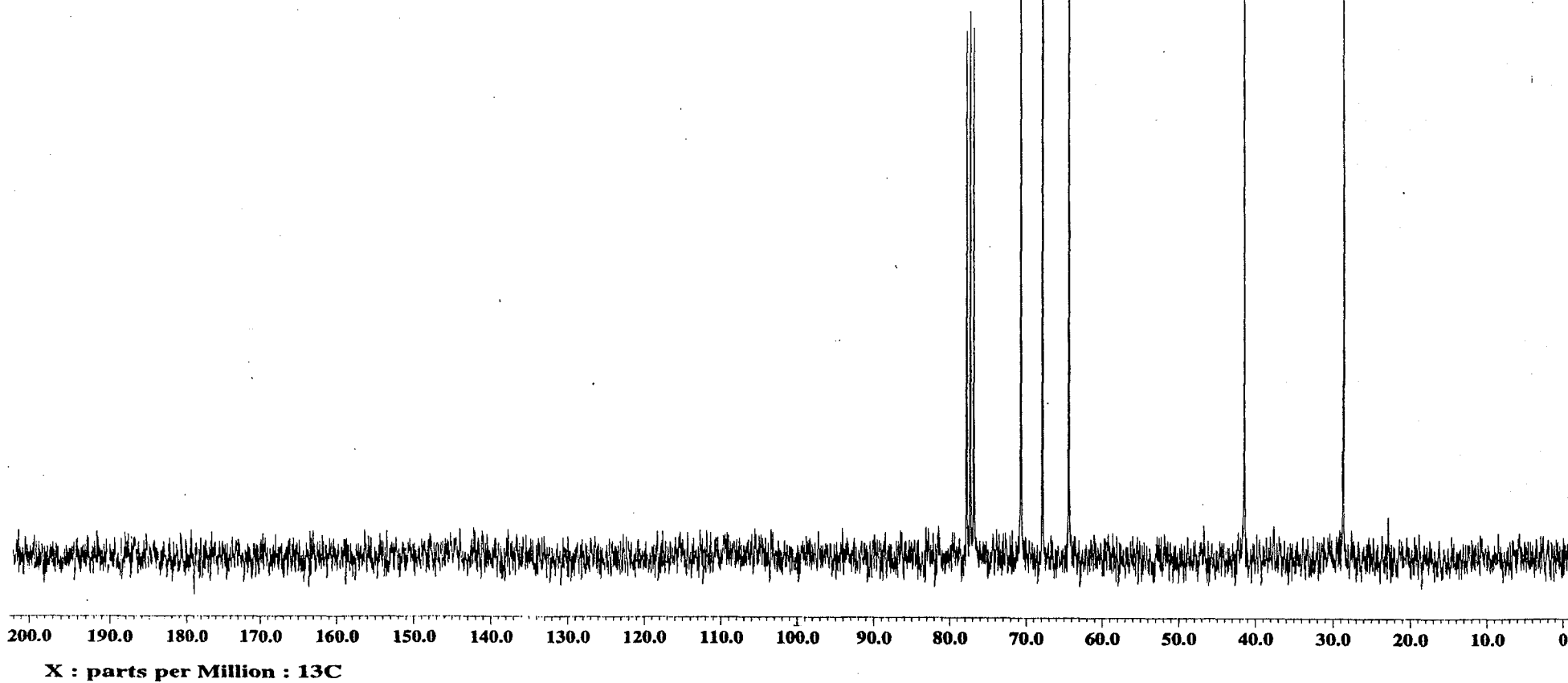
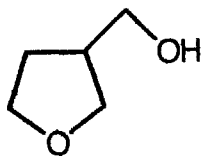
Spectrum 2. 270 MHz ^1H spectrum of tetrahydrofurfuryl tosylate.



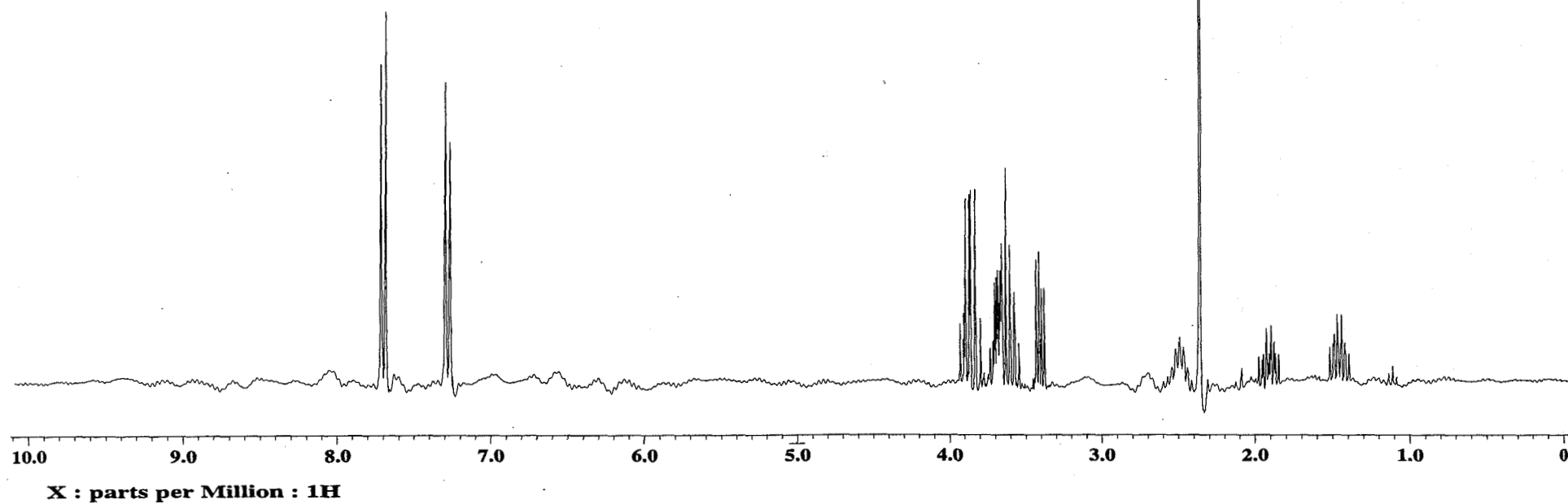
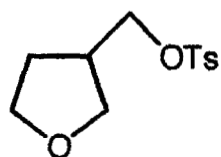
Spectrum 3. 67.5 MHz ^{13}C spectrum of tetrahydrofurfuryl tosylate.



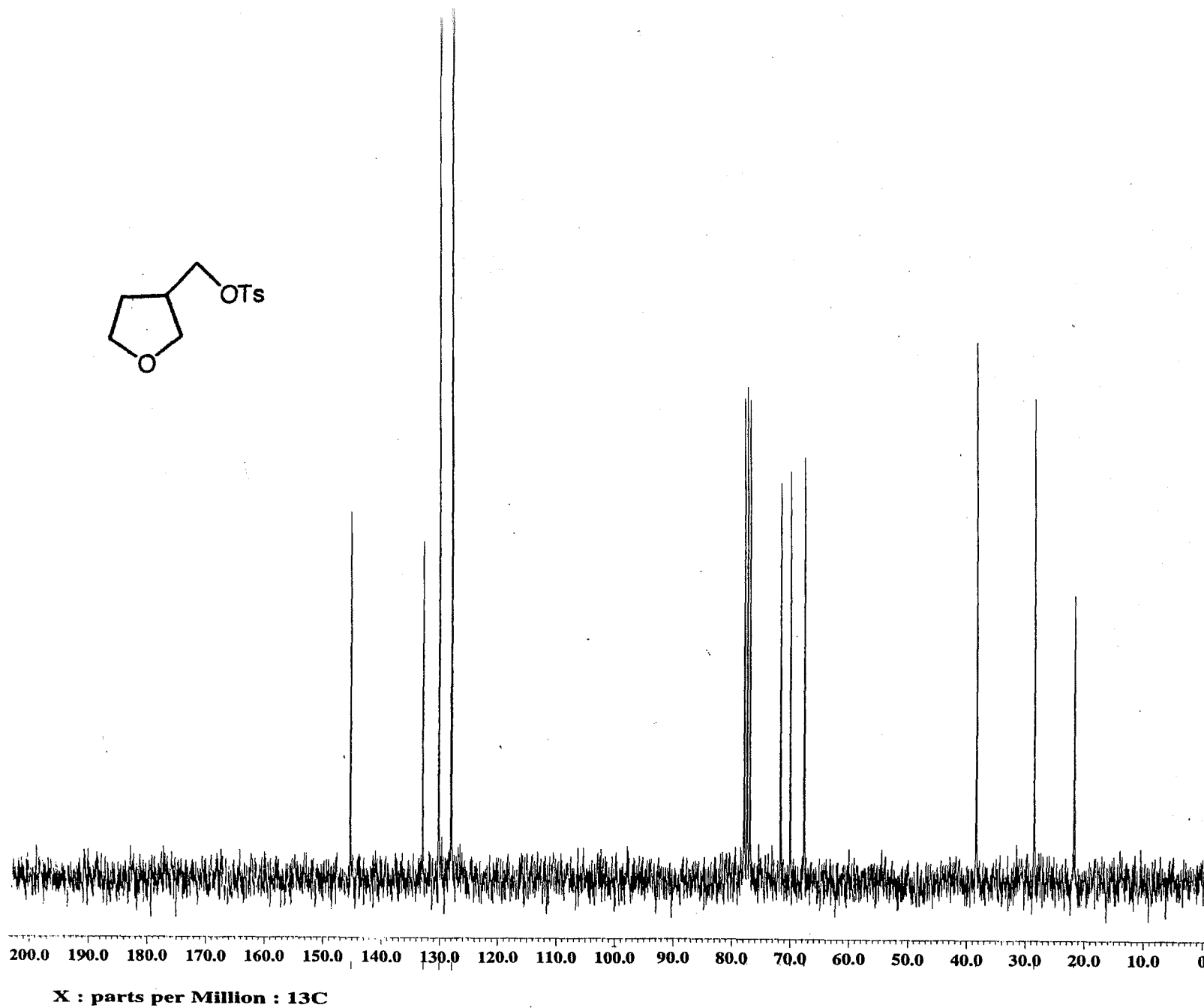
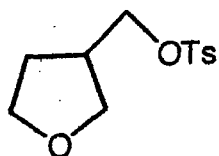
Spectrum 4. 270 MHz ^1H spectrum of tetrahydrofurfuryl-3-methanol.



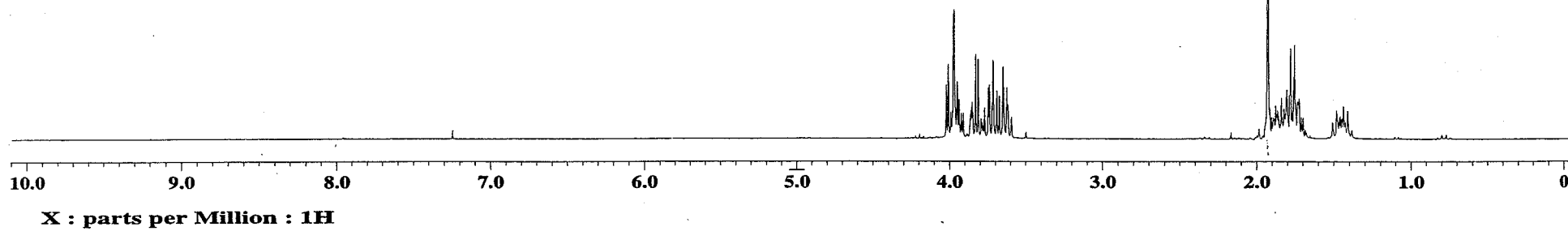
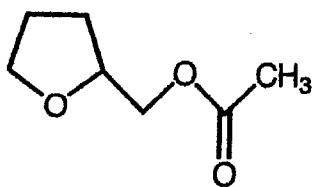
Spectrum 5. 67.5 MHz ^{13}C spectrum of tetrahydrofurfuryl-3-methanol.



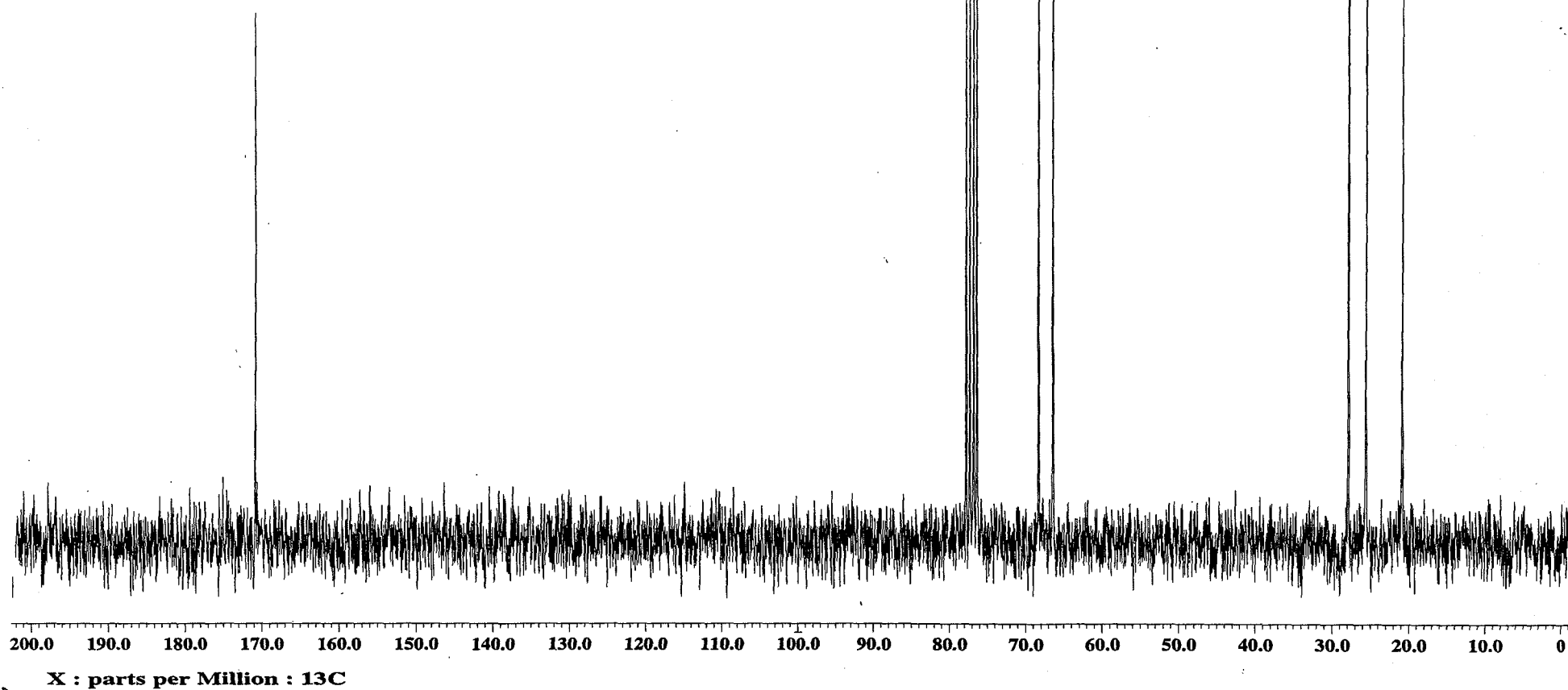
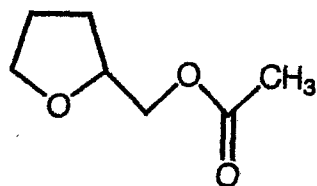
Spectrum 6. 270 MHz ^1H spectrum of tetrahydrofurfuryl-3-methyl tosylate.



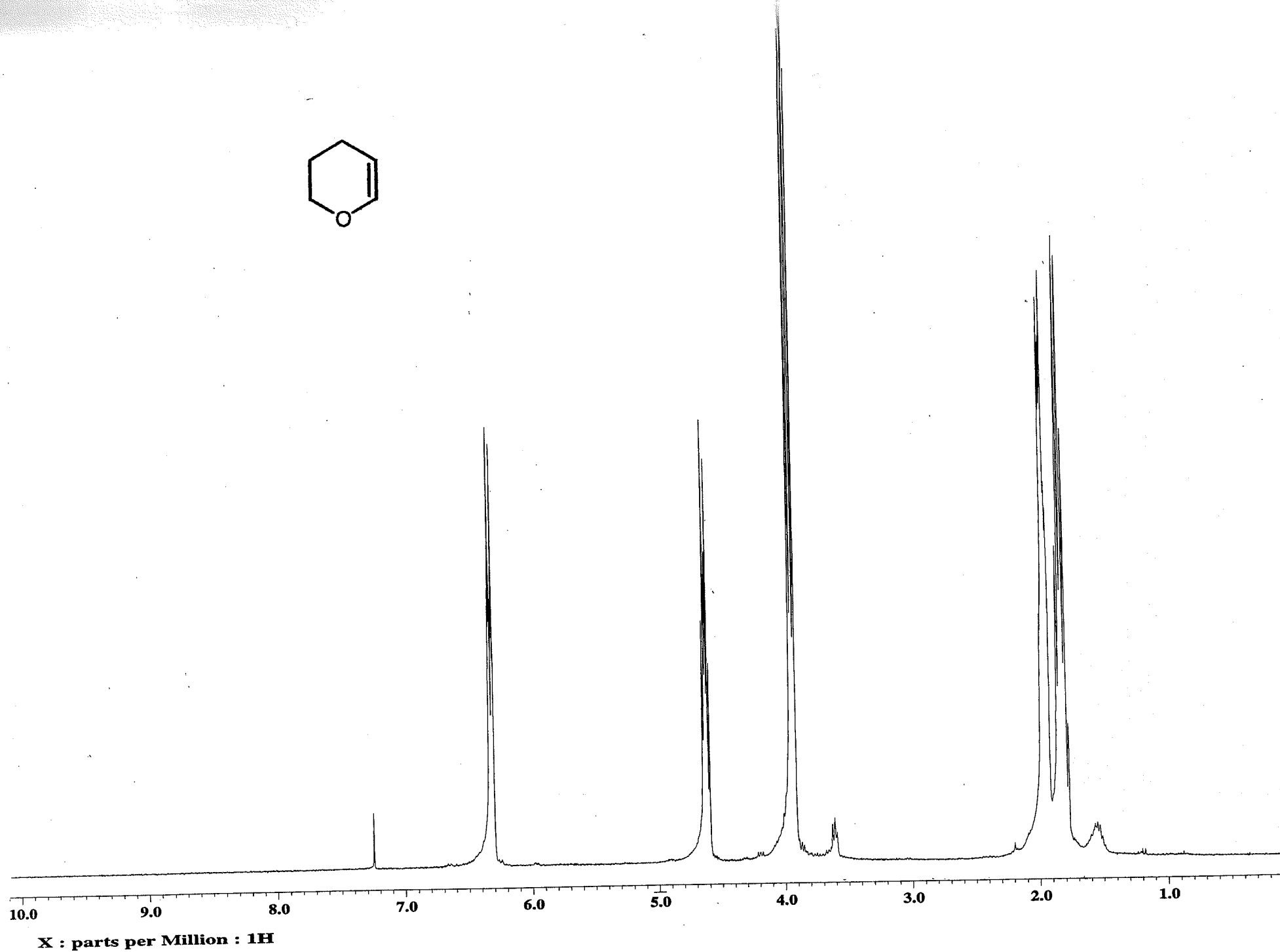
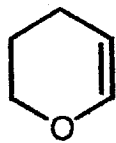
Spectrum 7. 67.5 MHz ¹³C spectrum of tetrahydrofurfuryl-3-methyl tosylate.



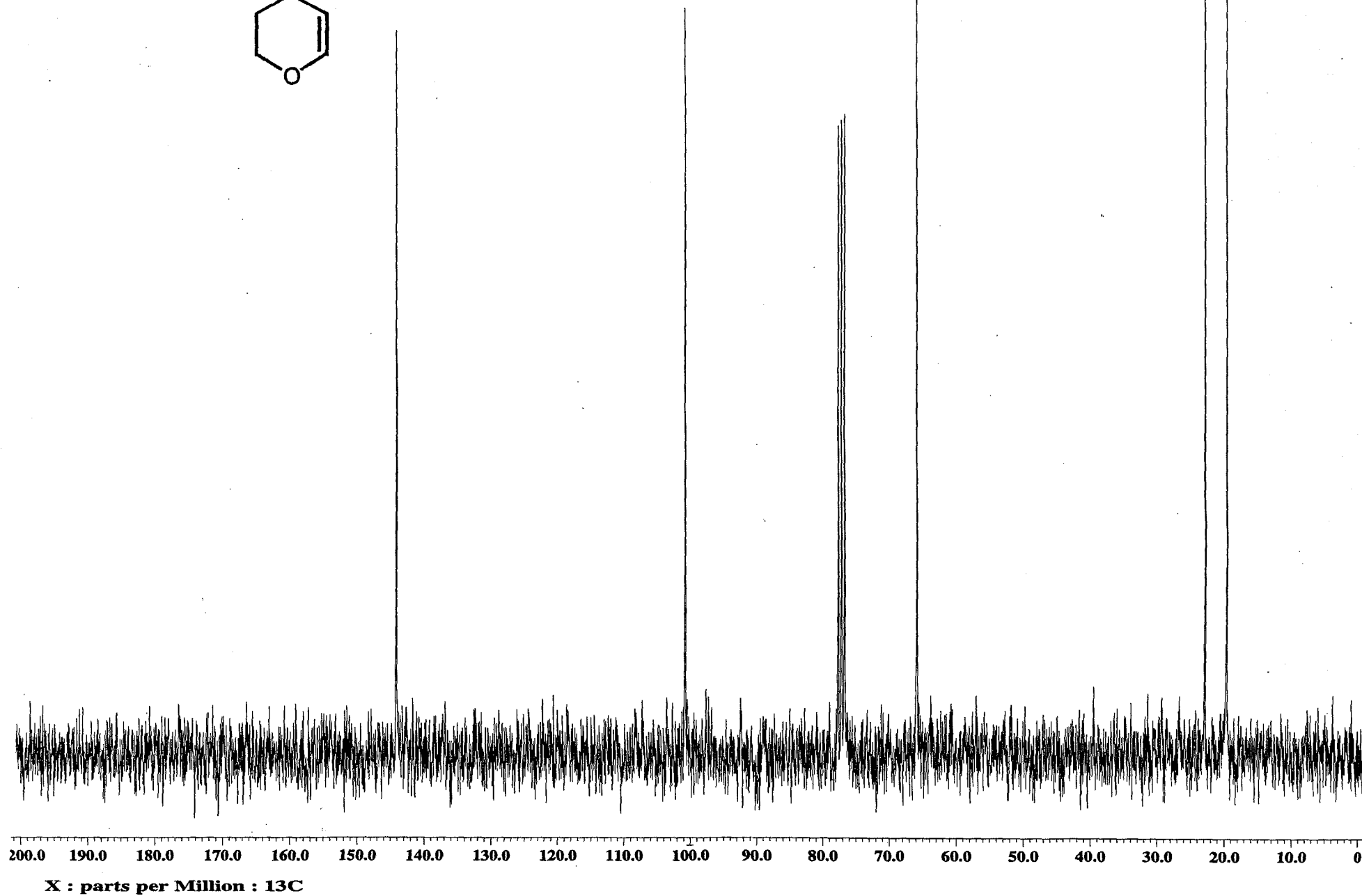
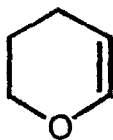
Spectrum 8. 270 MHz ^1H spectrum of tetrahydrofurfuryl acetate.



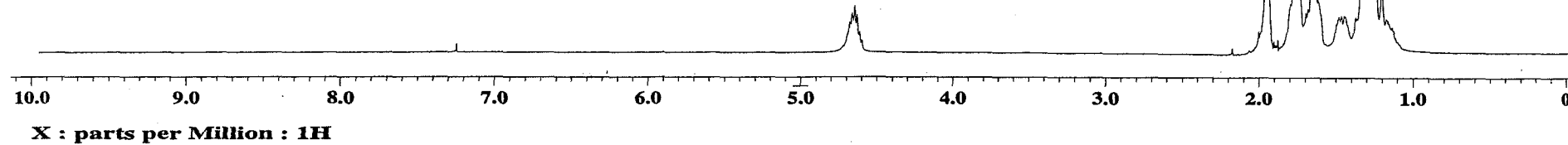
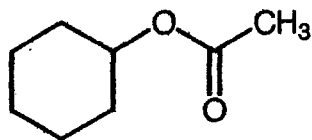
Spectrum 9. 67.5 MHz ¹³C spectrum of tetrahydrofurfuryl acetate.



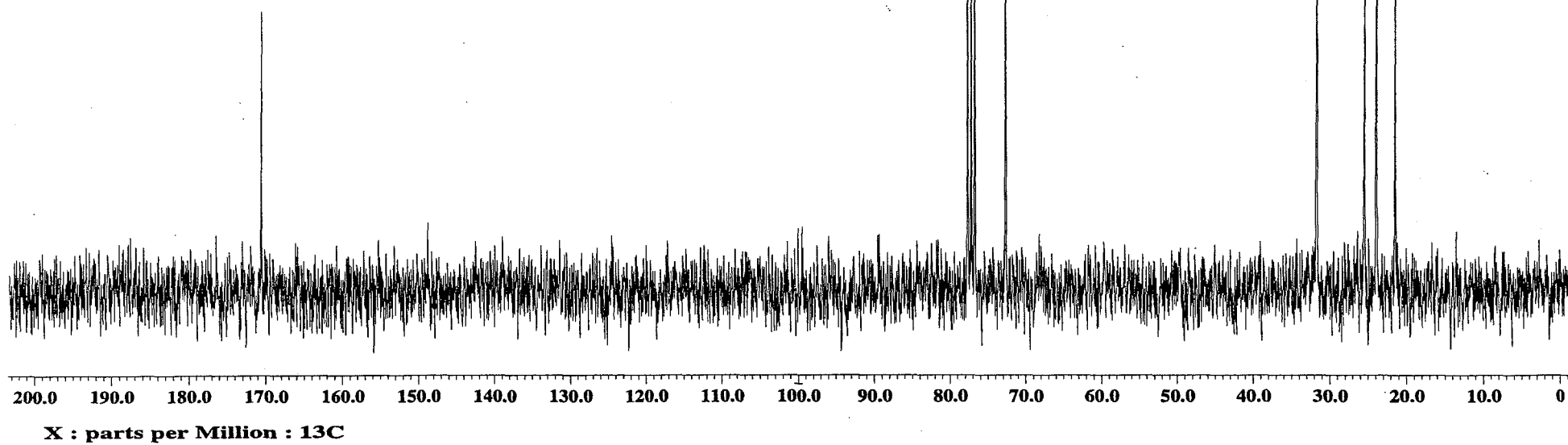
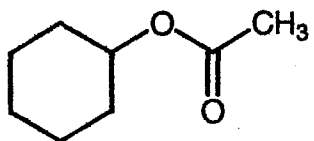
Spectrum 10. 270 MHz ^1H spectrum of dihydropyran.



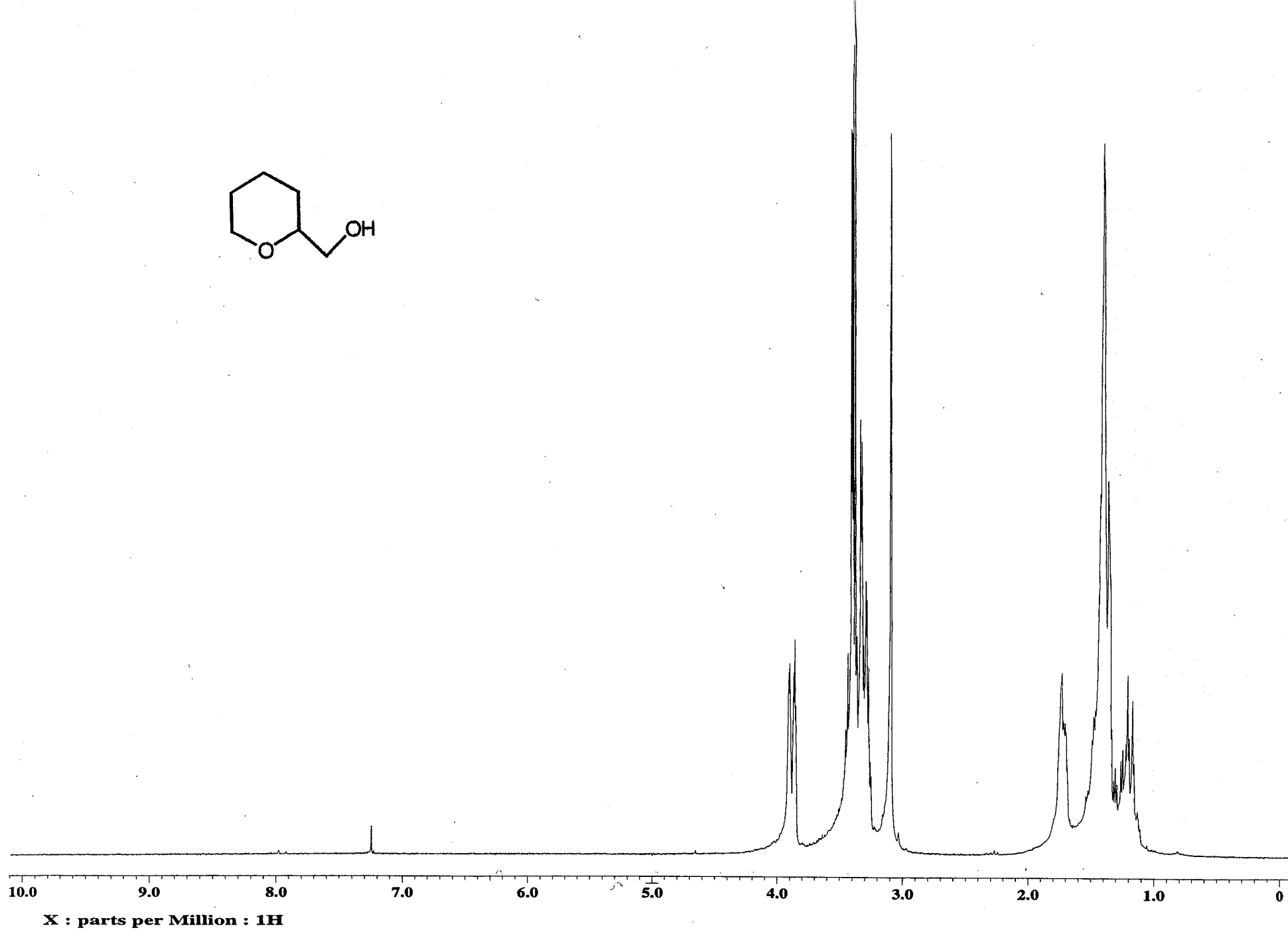
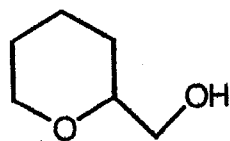
Spectrum 11. 67.5 MHz ^{13}C spectrum of dihydropyran.



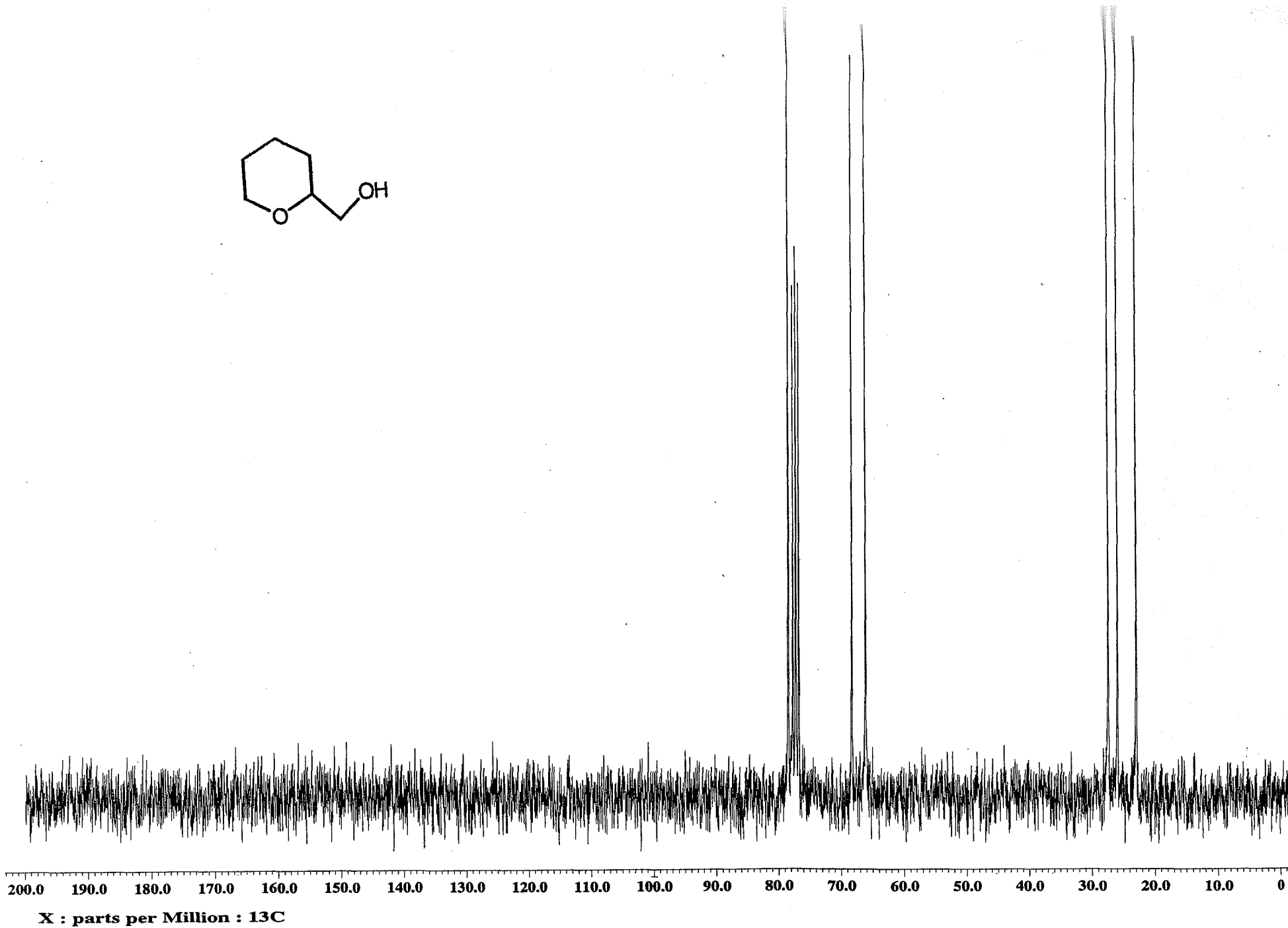
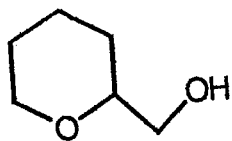
Spectrum 12. 270 MHz ^1H spectrum of cyclohexyl acetate.



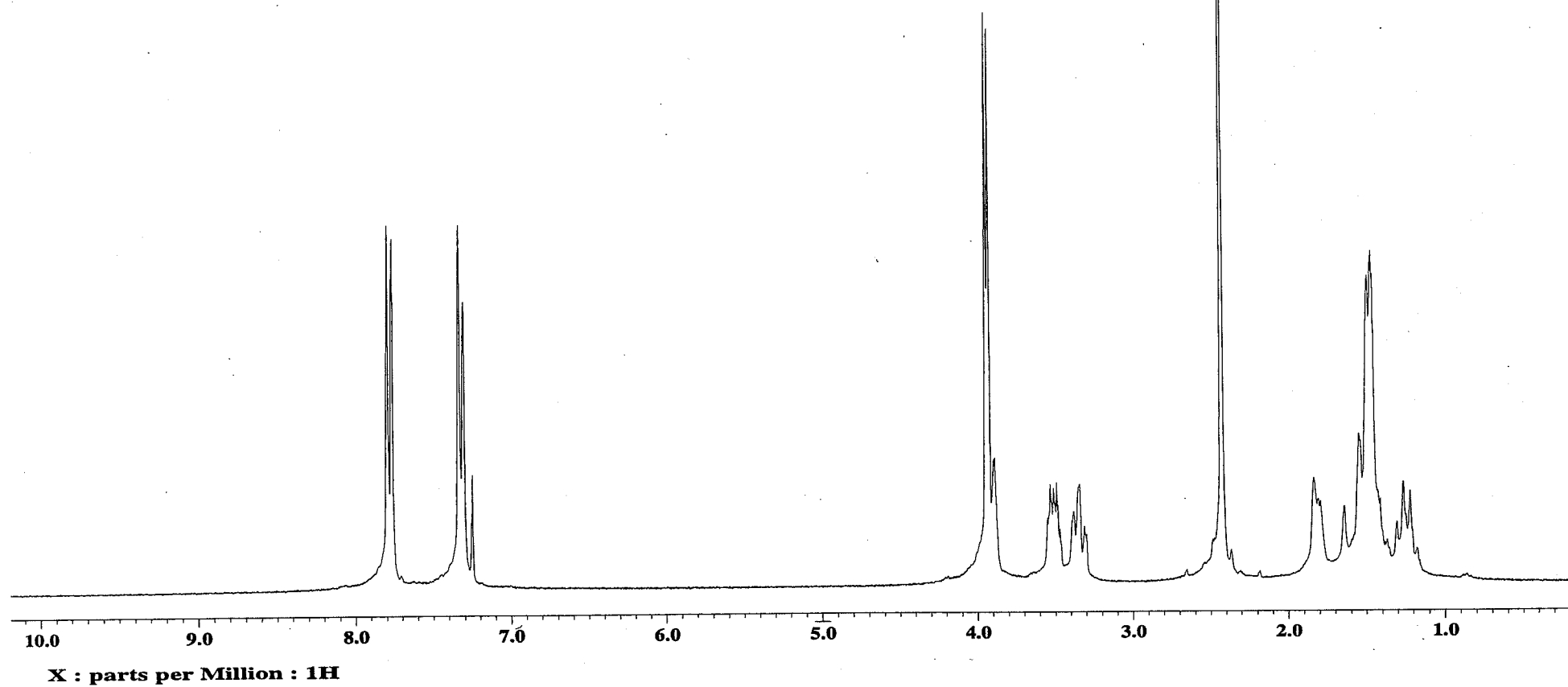
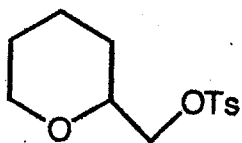
Spectrum 13. 67.5 MHz ^{13}C spectrum of cyclohexyl acetate.



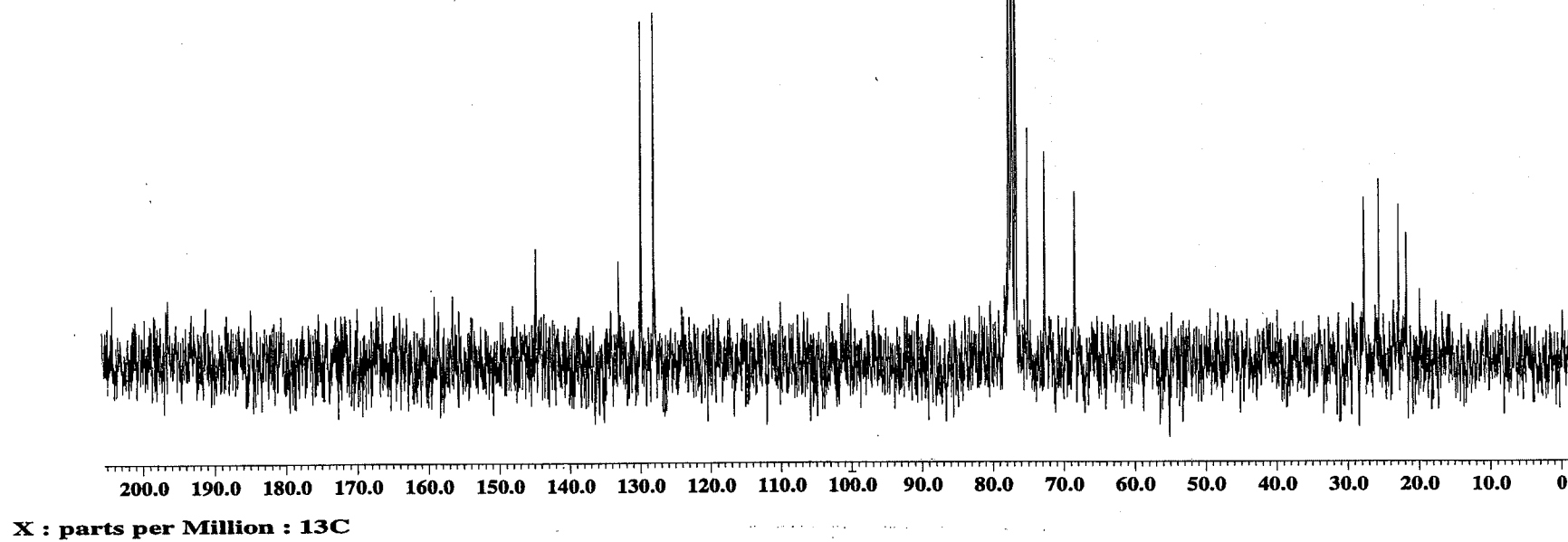
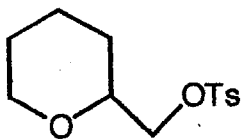
Spectrum 14. 270 MHz ^1H spectrum of tetrahydropyran methanol.



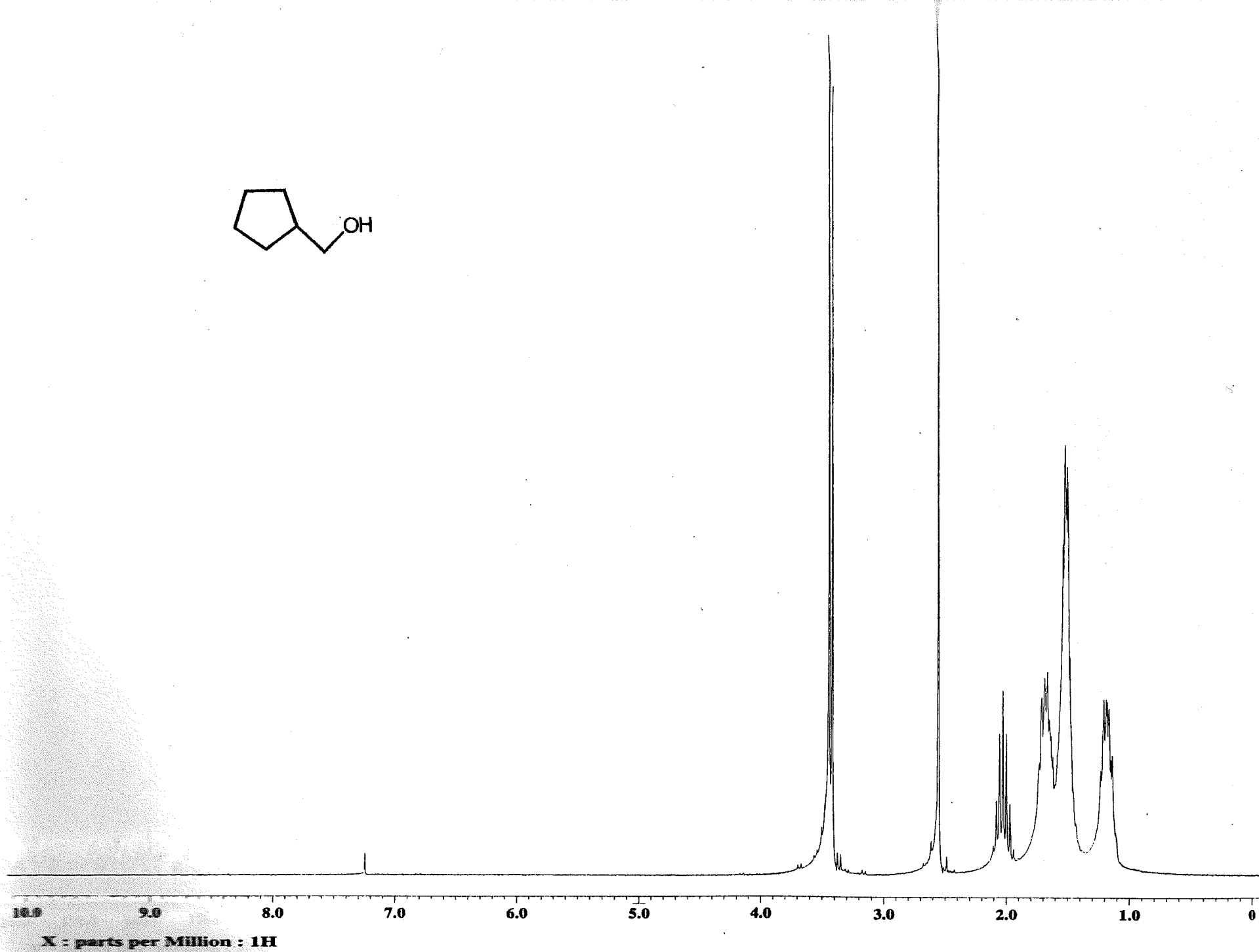
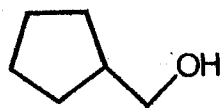
Spectrum 15. 67.5 MHz ^{13}C spectrum of tetrahydropyran methanol.



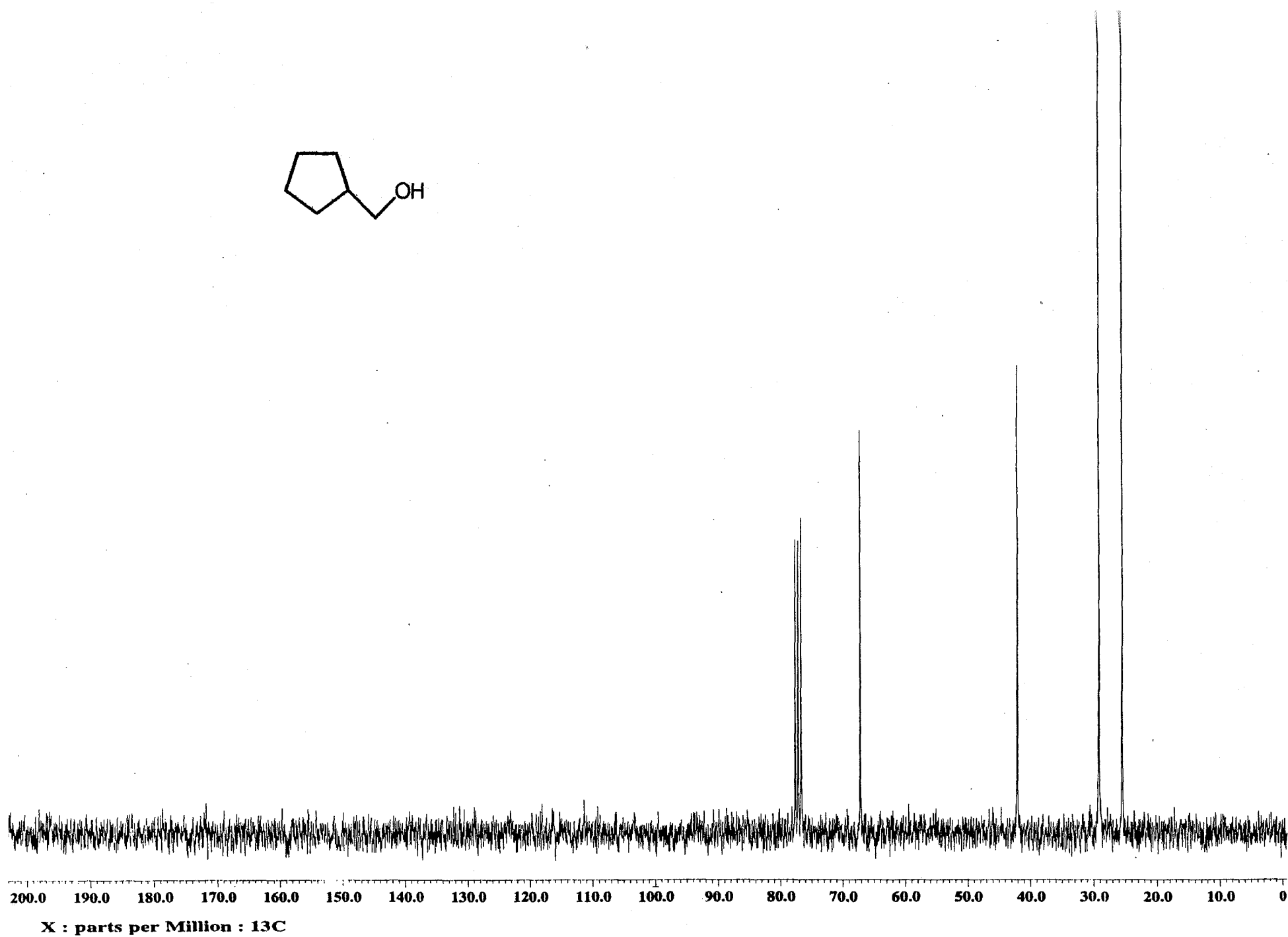
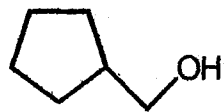
Spectrum 16. 270 MHz ^1H spectrum of tetrahydropyranmethyl tosylate.



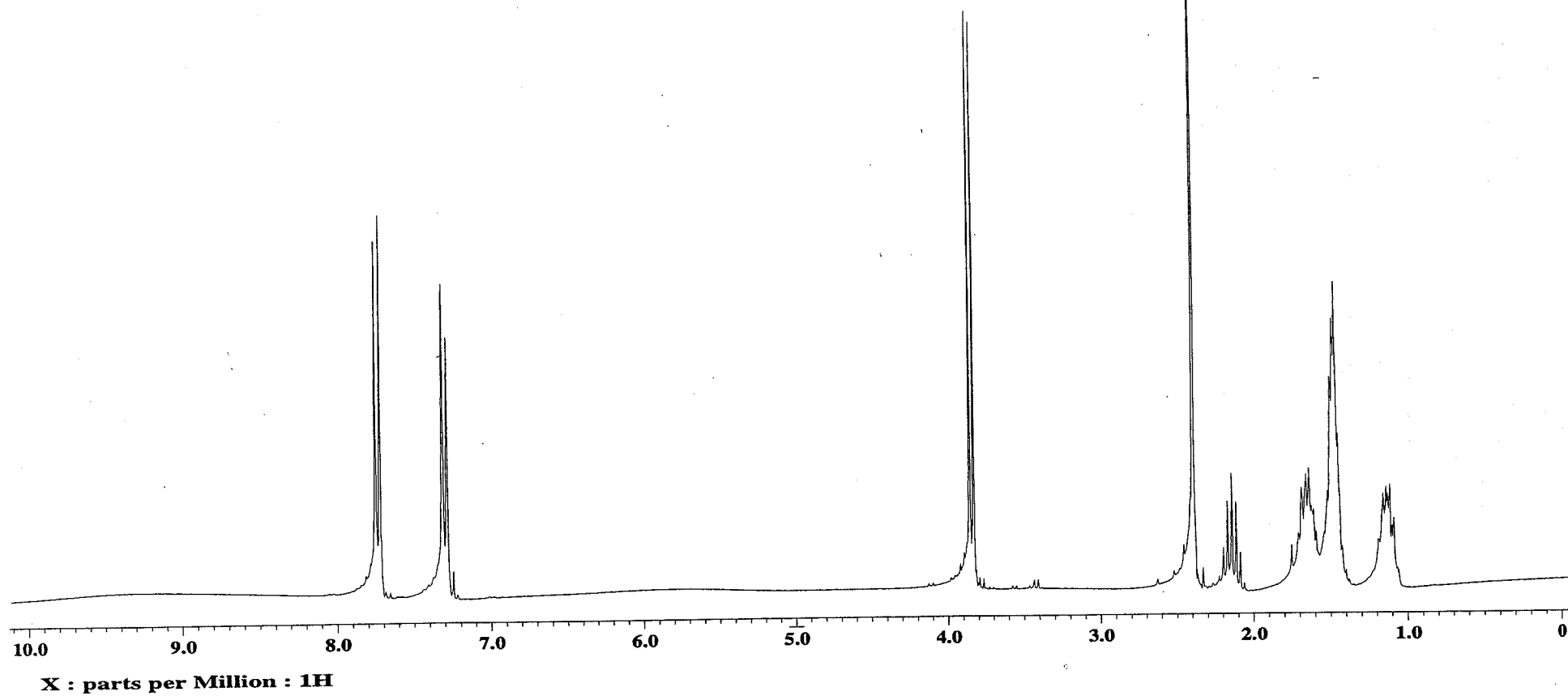
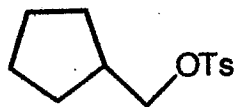
Spectrum 17. 67.5 MHz ^{13}C spectrum of tetrahydropyranmethyl tosylate.



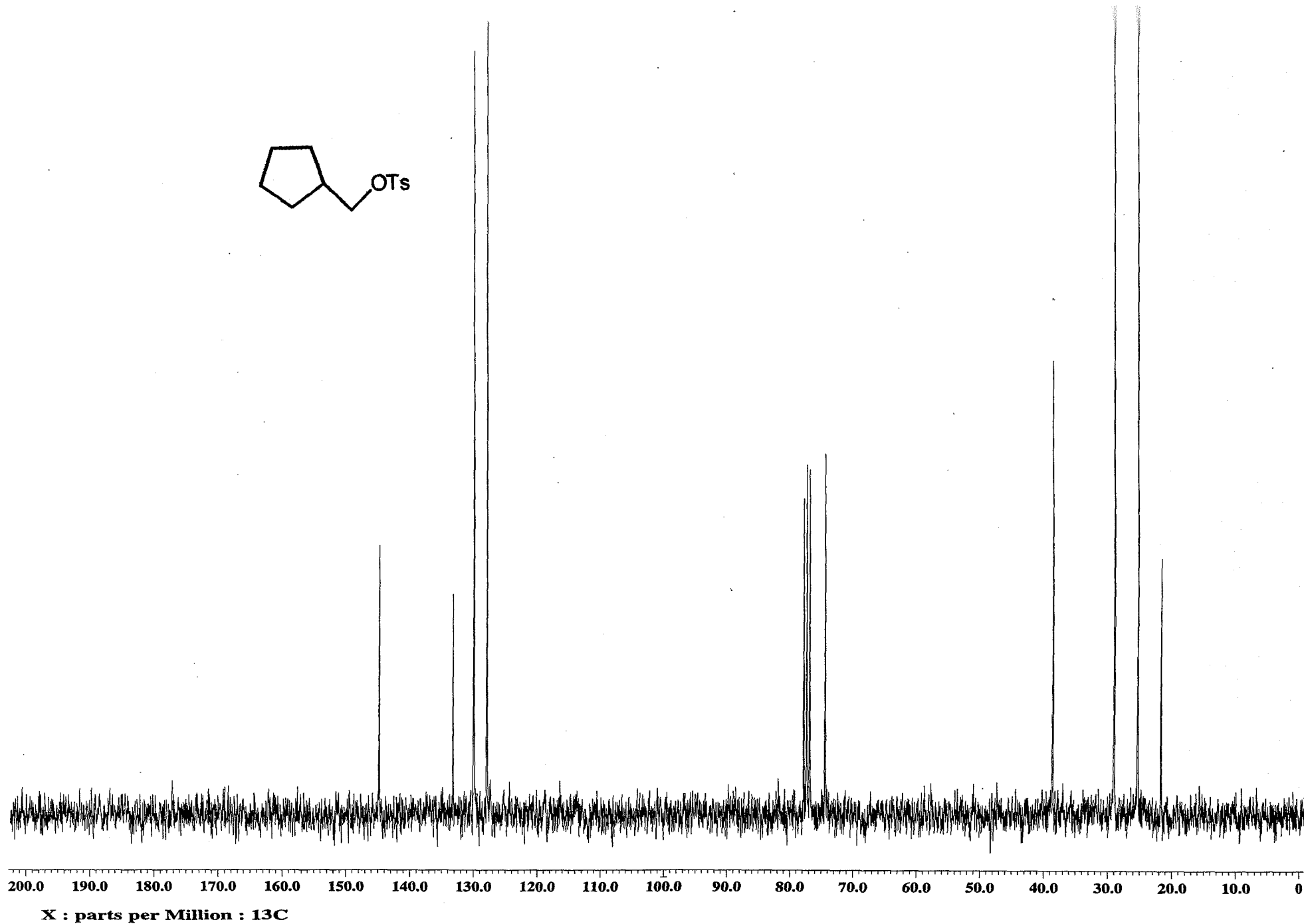
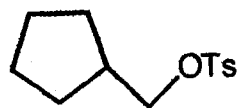
Spectrum 18. 270 MHz ^1H spectrum of cyclopentylmethanol.



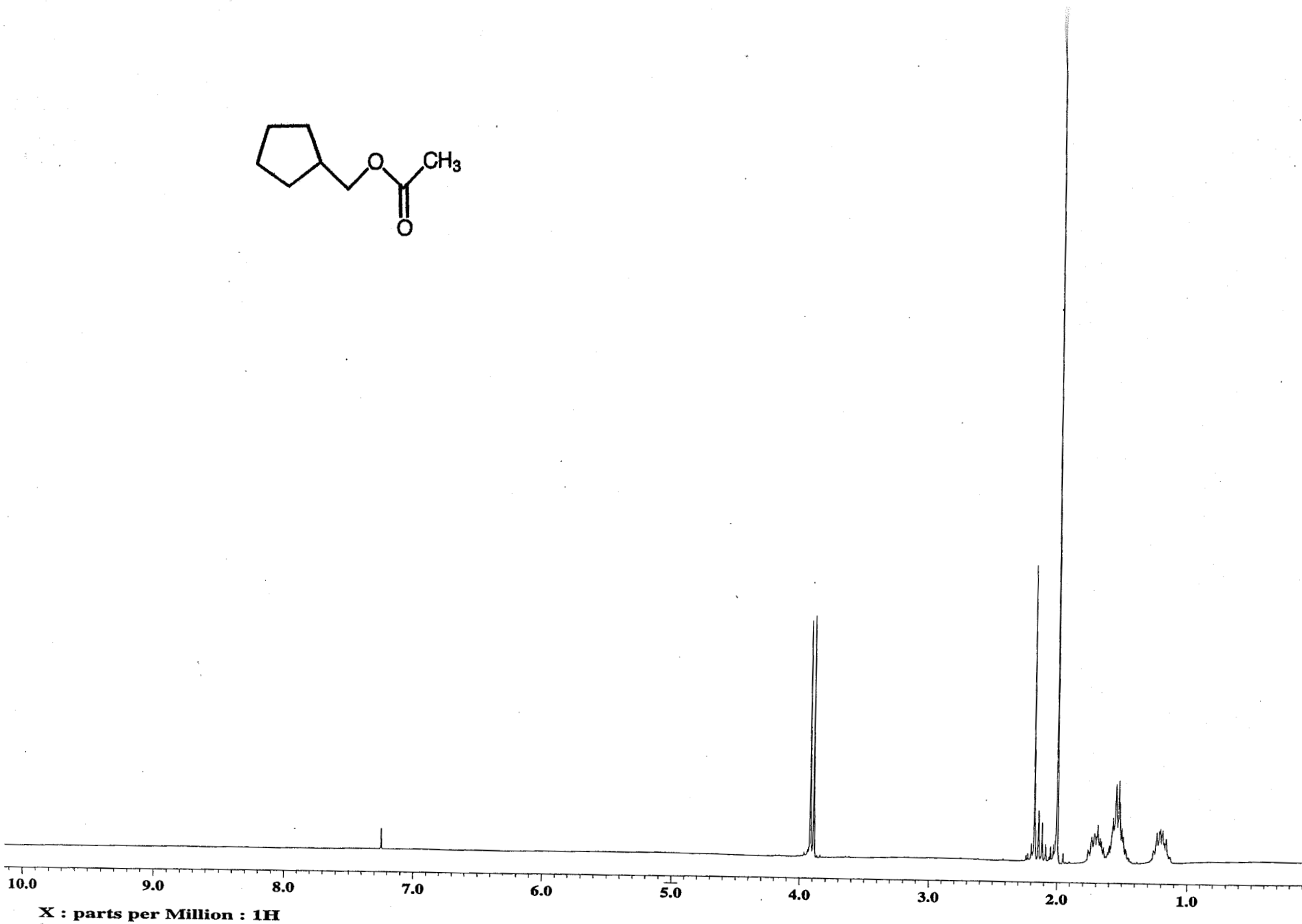
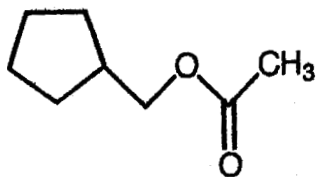
Spectrum 19. 67.5 MHz ^{13}C spectrum of cyclopentylmethanol.



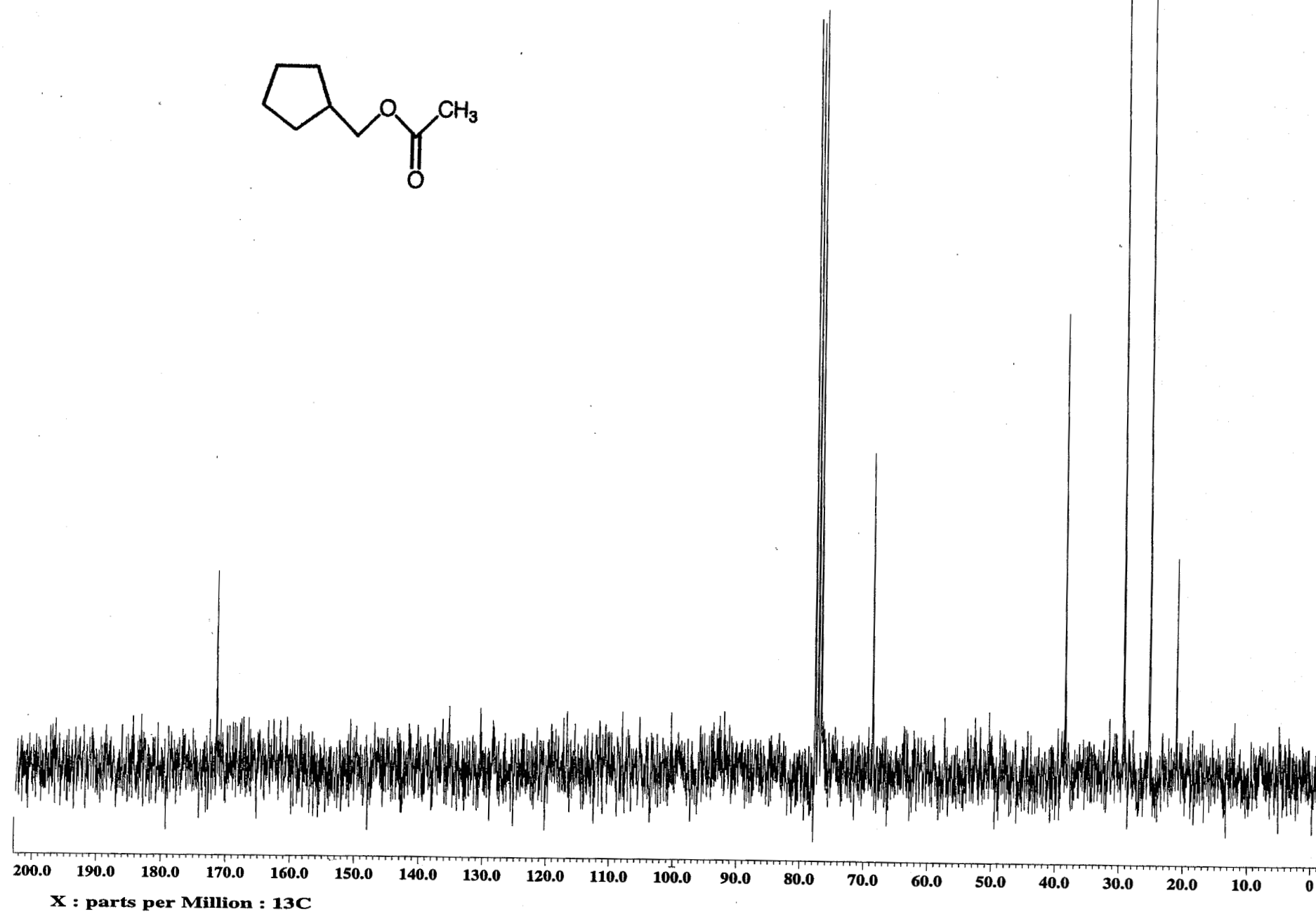
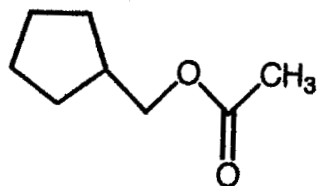
Spectrum 20. 270 MHz ^1H spectrum of cyclopentylmethyl tosylate.



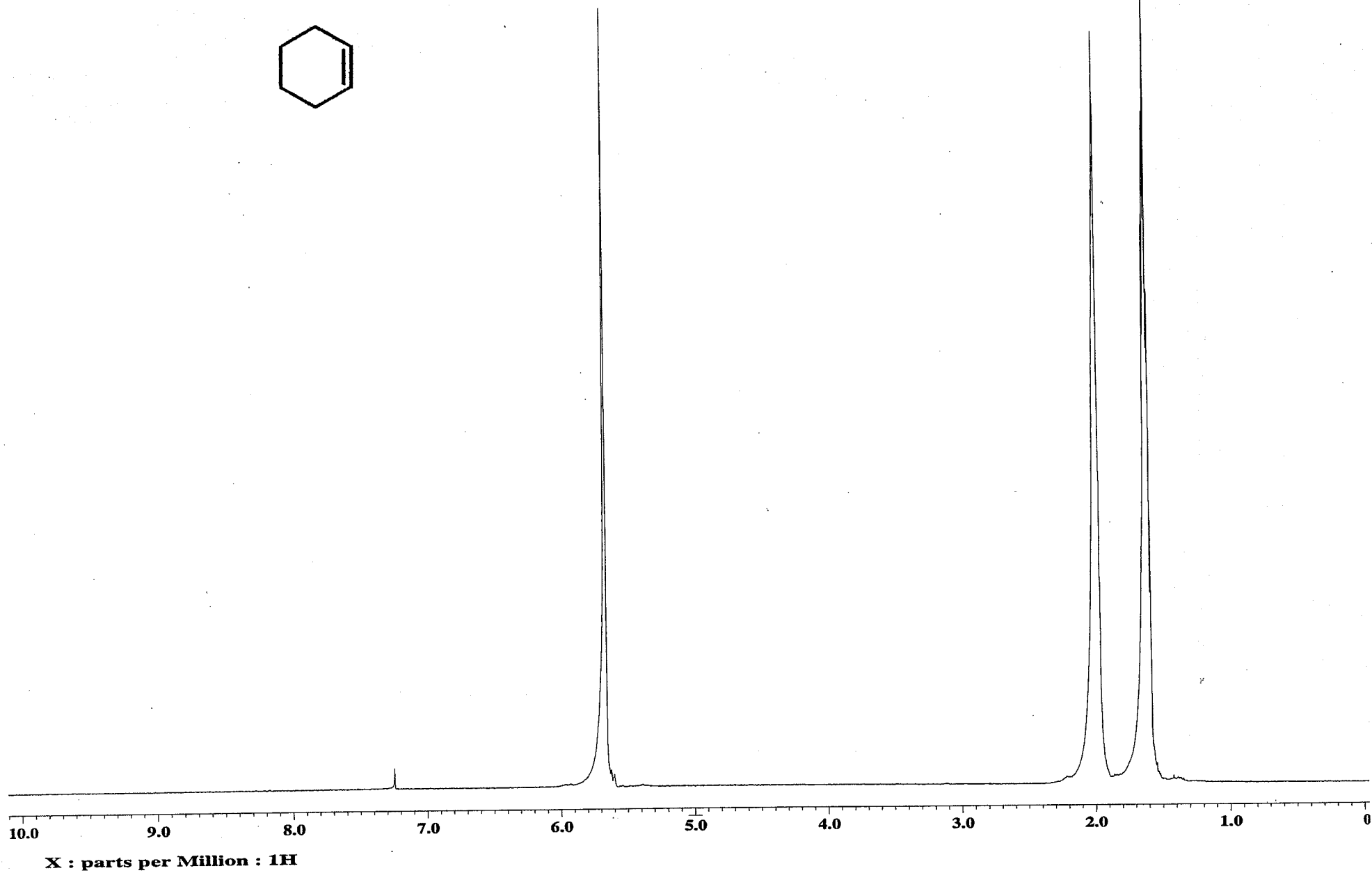
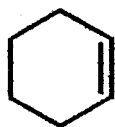
Spectrum 21. 67.5 MHz ^{13}C spectrum of cyclopentylmethyl tosylate.



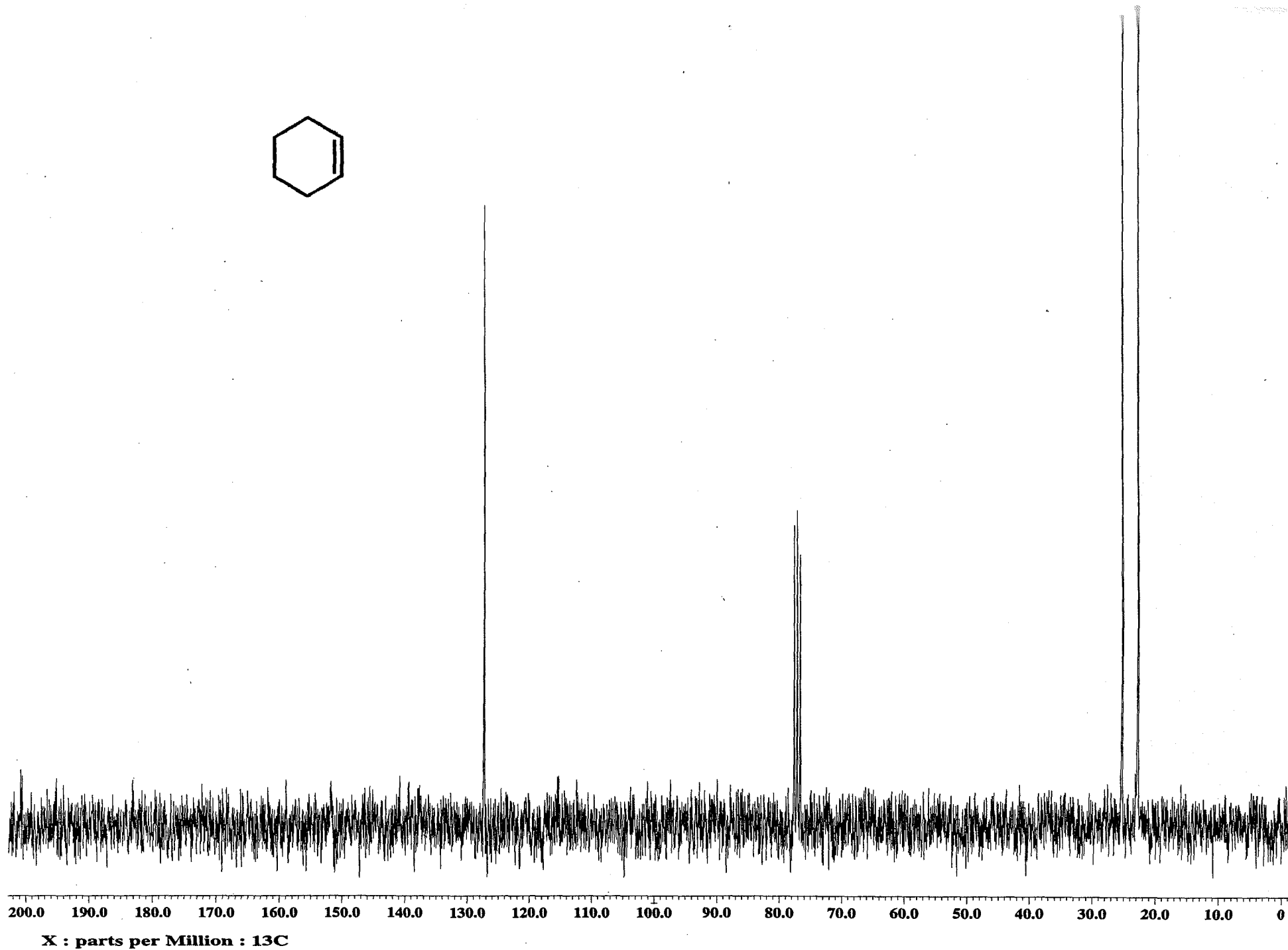
Spectrum 22. 270 MHz ^1H spectrum of cyclopentylmethyl acetate.



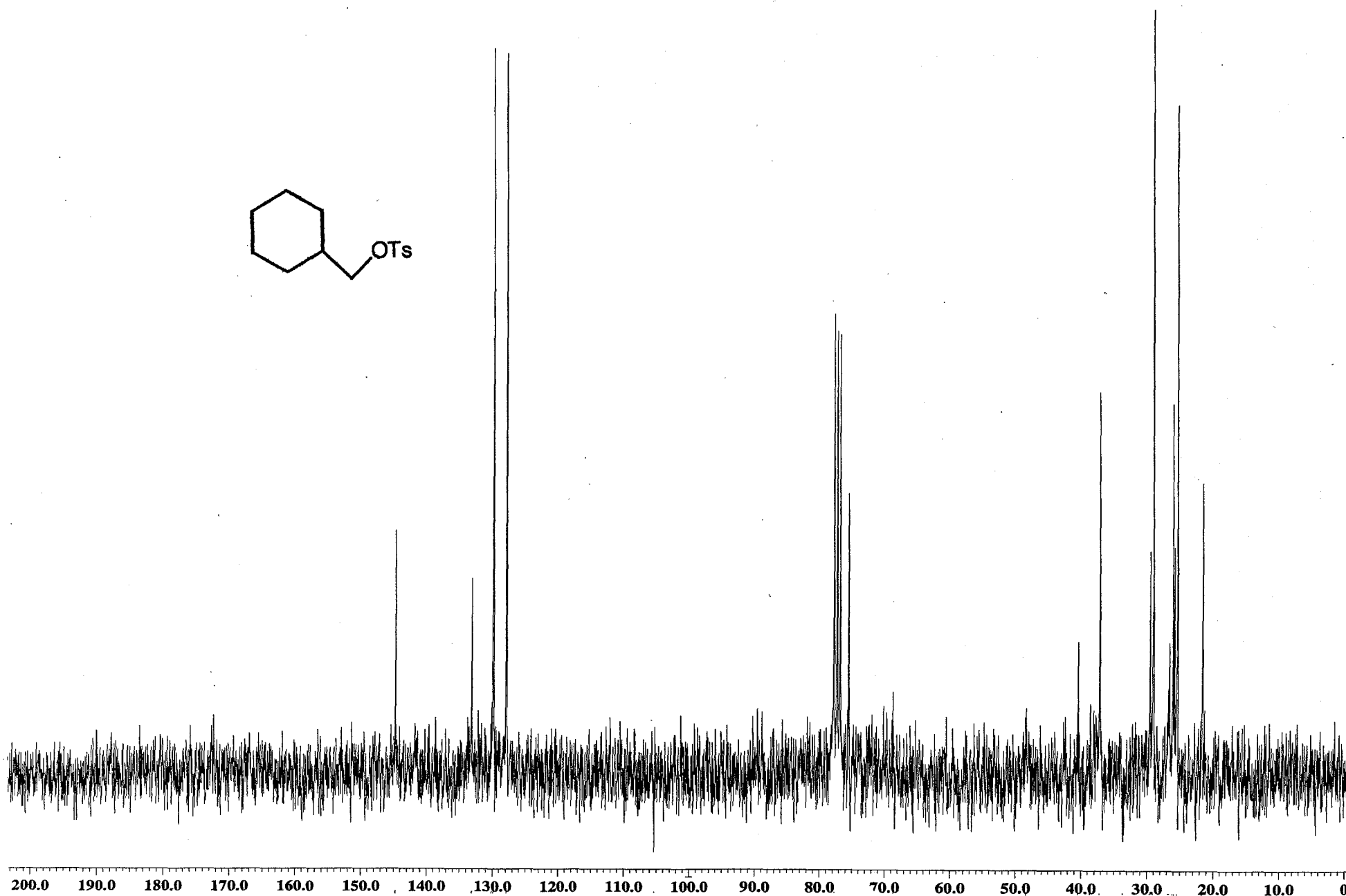
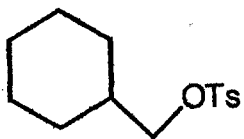
Spectrum 23. 67.5 MHz ^{13}C spectrum of cyclopentylmethyl acetate.



Spectrum 24. 270 MHz ^1H spectrum of cyclohexene.

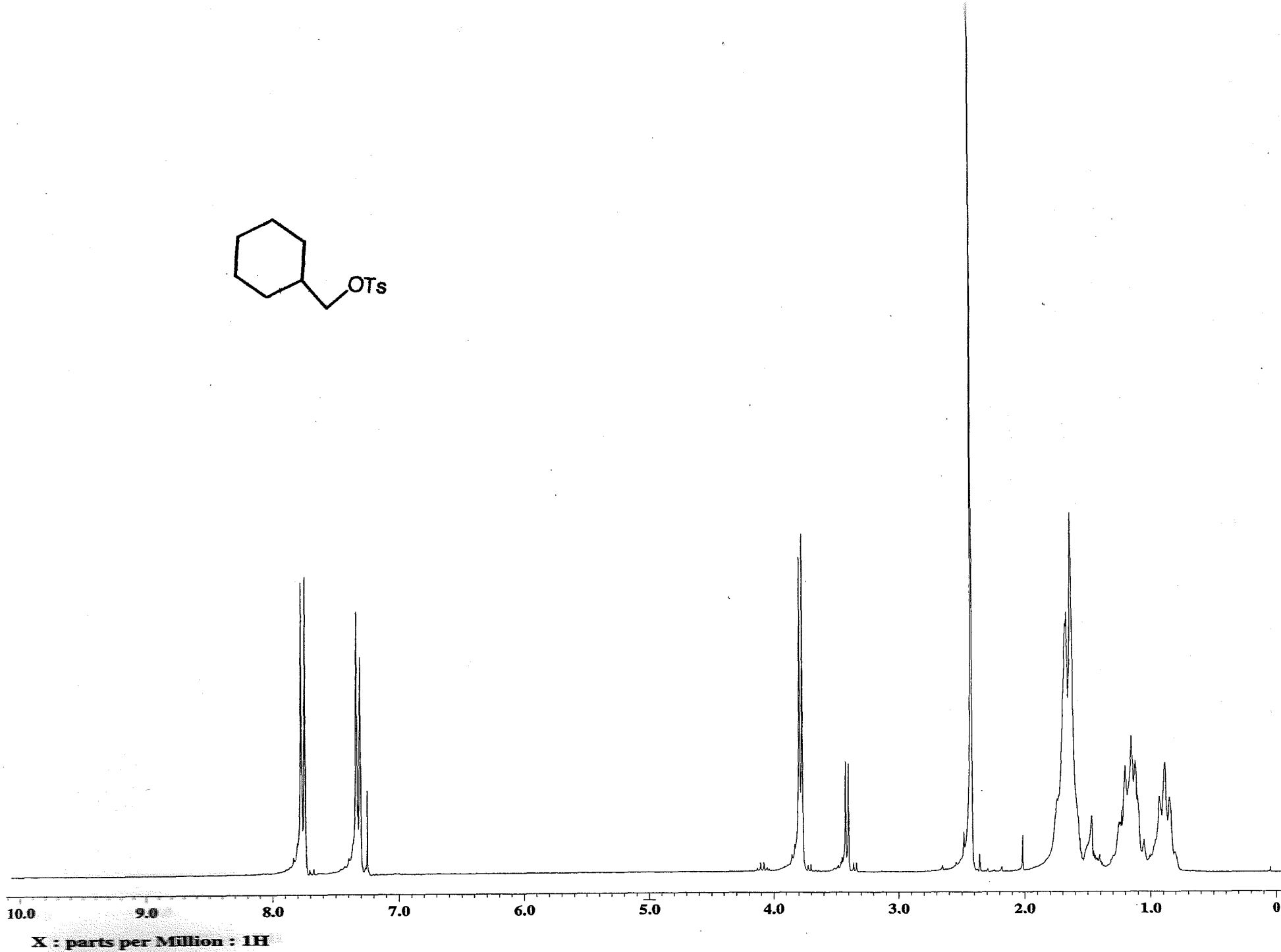
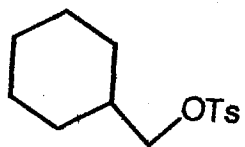


Spectrum 25. 67.5 MHz ^{13}C spectrum of cyclohexene.

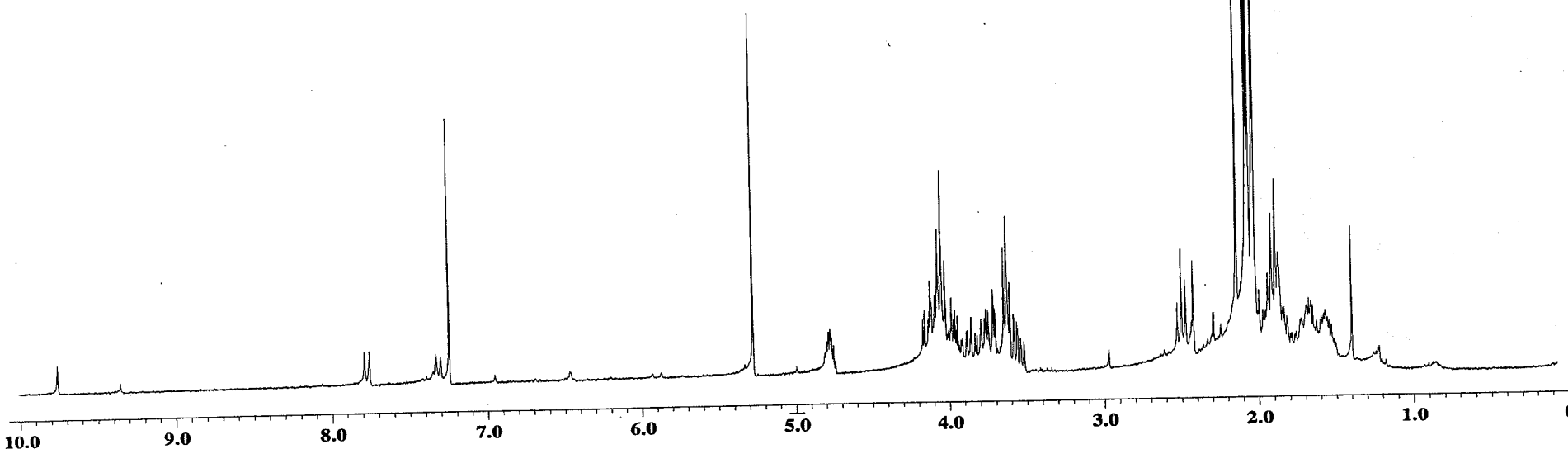


X : parts per Million : ^{13}C

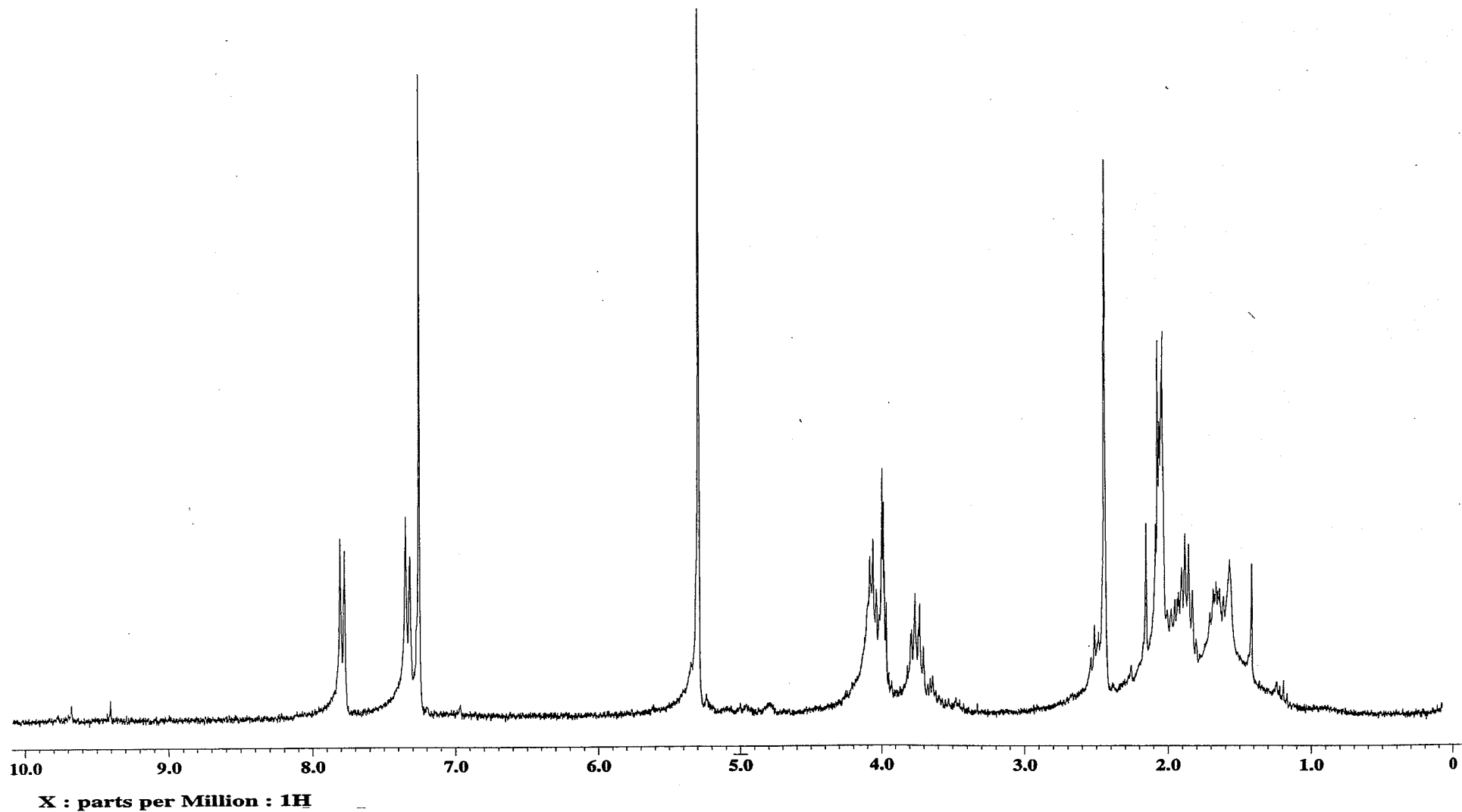
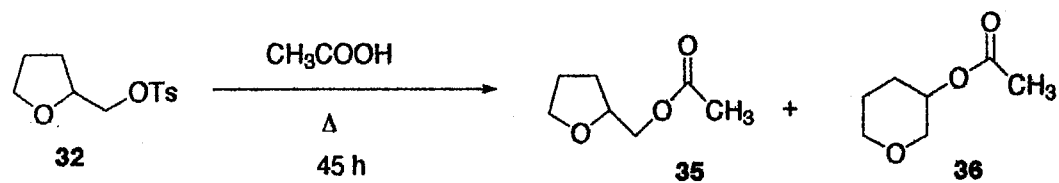
Spectrum 26. 67.5 MHz ^{13}C spectrum of cyclohexylmethyl tosylate.



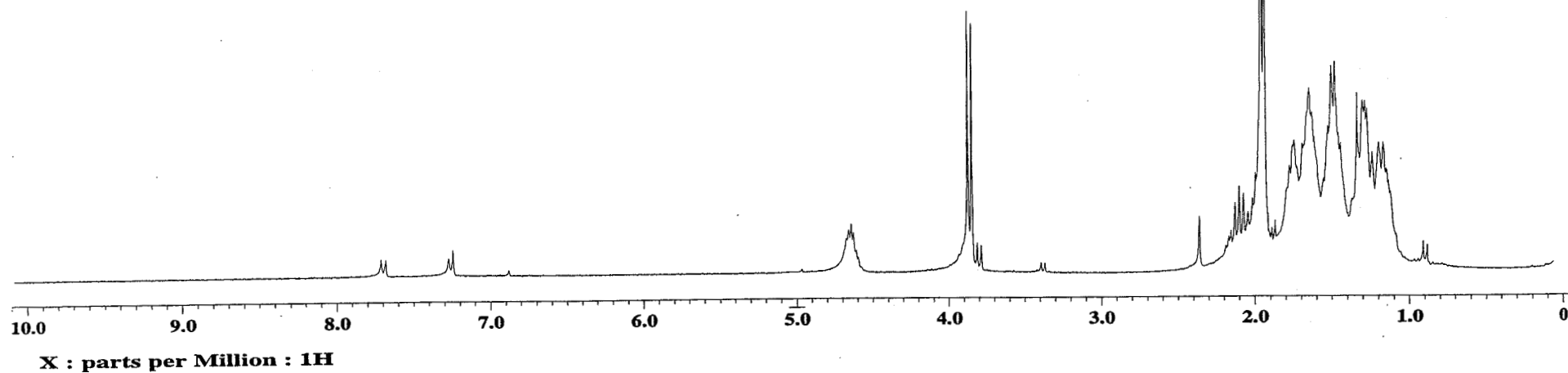
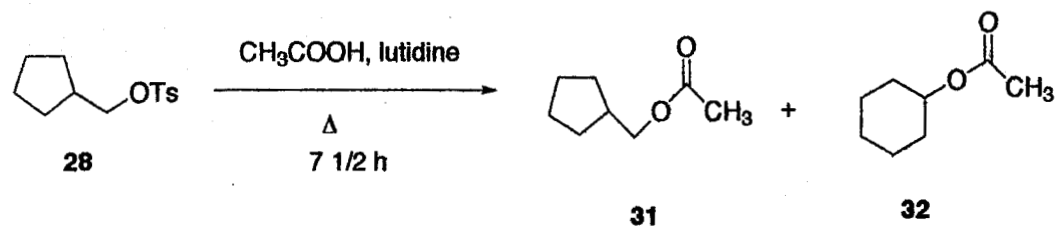
Spectrum 27. 270 MHz ^1H spectrum of cyclohexylmethyl tosylate.



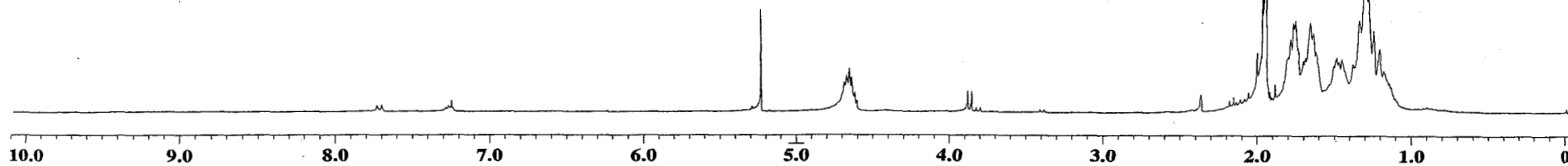
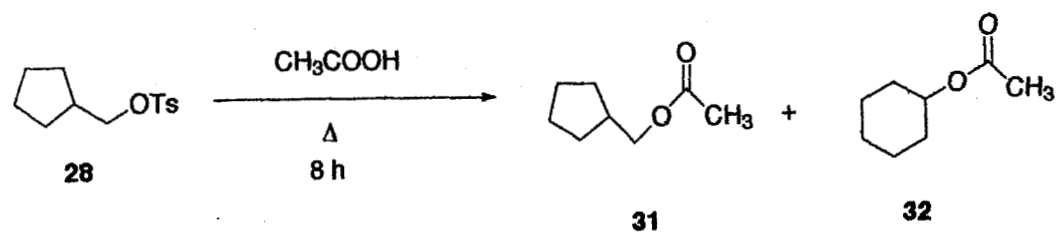
68



Spectrum 29. 270 MHz ^1H spectrum of products from acetolysis of tetrahydrofurfuryl tosylate after 45 h.



Spectrum 30. 270 MHz ^1H spectrum of products from acetolysis of cyclopentylmethyl tosylate in the presence of lutidine after 7 1/2 h.



X : parts per Million : ^1H

Spectrum 31. 270 MHz ^1H spectrum of products from acetolysis of cyclopentylmethyl
 tosylate after 8 h.