# MIT Organic Chemistry 5.13
## Drill Problems – Organic Structure Elucidation & Review

*BDC*

While moving equipment and chemicals into his new lab space, Professor Meyer has discovered a collection of old chemicals left by former grad students. Unfortunately, the labels on the containers yield only the dates of preparation, and no identifying information. A quick IR analysis allows him to make reasonably accurate guesses as to the compounds' functional groups, and he cleverly leaves it to the students in his undergraduate laboratory course to determine exact identities. Each student is given a container of an unknown chemical with instructions to react the chemical with known substances in order to analyze the products and thus identify the compounds. Please help these beleaguered students accomplish their assigned tasks! *(Please note that all Figures referred to in the text are in the back of the drill problem set.)*

1. Nick is given a small vial of Compound A along with its IR spectrum **(Fig.1)**, and is instructed to perform two experiments. For the first, he dissolves anhydrous zinc chloride in concentrated hydrochloric acid, then adds half of his unknown sample. Nothing seems to happen upon stirring at room temperature, but after stirring on heat for about 10 minutes, a cloudy layer begins to form that is distinct in appearance and odor from the starting material. Nick extracts this layer into dichloromethane, and performs an IR **(Fig.2)** and EA on the material thus isolated. EA (found): C: 61.35%; H: 5.79%. For the second experiment, Nick dissolves the remainder of his sample in pyridine, and then adds acetyl chloride dropwise to this solution. The reaction becomes quite exothermic, as the glass vessel becomes uncomfortably hot to the touch. After workup, Nick isolates a colorless liquid with a sweet, spicy/fruity odor. He also gathers IR **(Fig.3)** and MS **(Fig.4)** data for the product.
   - **a.** What functional group(s) is/are indicated most clearly by the original sample IR? Does it tell any additional info about the structure?
   - **b.** What is the class of reactions to which Nick's first experiment belongs? What does the compound's reactivity tell you about its structure?

c. Explain the IR spectrum of the product of experiment 1. Can the elemental analysis data tell you all the information you need to determine a formula at this point?

d. What functional group(s) is/are present in the product of experiment 2? What functional group(s) is/are absent?

e. From the information gathered to this point as well as the newly gathered information (i.e., data from experiment 2), deduce reasonable structures for the two experimental products and, most importantly, the unknown compound A.

f. Had Nick neglected to add pyridine to the reaction mixture in experiment 2, his desired product would have been contaminated by a nonnegligible amount of the product from experiment 1! Explain the important role of pyridine to the successful execution of this synthesis.

2. Angela receives a vial of Compound B along with its infrared spectrum (**Fig. 5**), and notices that it is a liquid with a sweet, pleasant odor. Her first task is to prepare a weakly acidic solution of 2,4-dinitrophenylhydrazine, and when she adds her unknown sample to this solution, a bright golden precipitate forms. She isolates this solid by filtration, recrystallizes it twice for purity, and finally collects an IR spectrum (**Fig. 6**). Angela's second experiment is quite a bit more complicated; she first adds methyl bromide to an mixture of anhydrous ethyl ether and polished magnesium turnings. When the reaction has ceased, she adds to the reaction vessel the remainder of her unknown compound, again resulting in an exothermic reaction. Aqueous workup and subsequent isolation of the product yields a high-boiling liquid with a faintly floral odor, which she analyzes by IR (**Fig. 7**) and elemental analysis. EA (found): C: 79.96%; H: 9.39%.

   a. Based on the IR spectrum of the original unknown compound, what can be concluded about the functional group(s) and structure with a fair degree of certainty?

   b. Based on the answer to the previous question, use the information gathered in the second experiment to propose a reasonable structure for Compound B. Don't forget to determine IHD!

   c. Now that you know the likely structure of the compound, write an equation and mechanism for the reaction performed in the first experiment. Justify the product's structure using the gathered IR data, and explain why a weakly acidic medium is necessary for this type of reaction.

   d. Finally, do the same as in part **c** with the reaction performed in Angela's second experiment (i.e., write equation & mechanism, use given data to justify product's structure). What is the name of this type of reaction? And why does this reaction absolutely require anhydrous conditions?

3. Sachiko is given a vial containing Compound C, a musty-smelling, clumpy purple solid. She is also given the compound's IR spectrum (**Fig. 8**). Since she is a transfer student who has completed her organic labs at another school, Professor Meyer trusts her to be independent and assigns her only the task of hydrolysis, without specifying exact conditions (chemistry is, after all, an experimental science). Using her previous training, she sets up a reflux under strongly basic conditions (heat, KOH, several hours' reflux), but when she performs an acidic workup, she finds that no organic layer separates from the aqueous mixture! So she sets up strongly acidic conditions (heat, sulfuric acid, several hours' reflux) instead and repeats her hydrolysis procedure, but once again, when she performs a basic workup, no product separates from the alkaline aqueous mixture! In frustration, she asks Professor Meyer for advice, and he in turn suggests less vigorous conditions for her reaction. To her delight, when she refluxes the last portion of the compound for 15 minutes in phosphoric acid, a solid product precipitates upon basic workup, which she then isolates and analyzes by IR (**Fig. 9**) and MS (**Fig.10**).
   a. Using your knowledge of functional group interconversions by hydrolysis as well as the spectral data given in the problem, suggest a reasonable molecular formula and structure for Compound C.
   b. Write a complete mechanism for the successfully executed hydrolysis. In examining the structure of the unknown compound, is it accurate to say that the first two hydrolysis attempts failed? Why or why not? Explain Sachiko's observations in light of your own chemical knowledge (writing equations would probably help here).
4. Kevin is given a small vial containing Compound D, a slightly viscous, bright yellow liquid, as well as its corresponding IR spectrum (**Fig. 11**) and mass spectrum (**Fig. 12**). As he discovers much too late, it tends to go right through gloves and stain his fingers an interesting yellow color that will amuse his friends for weeks. He also is given only one experiment: to add the compound to a solution of aniline in dichloromethane, isolate the product, and identify both the starting material and the product. As soon as he adds his compound to the aniline solution, the color of the compound pervades the entire mixture, and when he isolates the product from the reaction, it is a vivid "day-glo" orange mass of

needle-like crystals! He promptly collects IR (**Fig. 13**) and mass spectra (**Fig. 14**) and prepares to write his report. When he returns to clean his glassware the next day, he discovers that the inner rim of the glass reaction vessel he was using has been etched away to a small, yet noticeable, degree. Thankfully, he did perform the reaction under a fume hood…

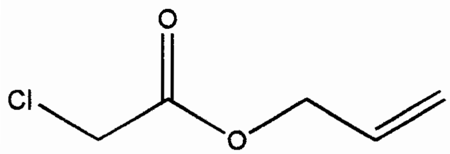
**a.** Using the IR spectrum and the mass spectral information, suggest a reasonable structure for Compound D. Be careful! Don't neglect all the information that you can extract from a single mass spectrum!

**b.** Likewise, once you have deduced the structure of the unknown compound, you should recall how such a compound could participate in the reaction described above. Using the spectral information provided, propose a reasonable structure for the product, and make sure that you can explain the course of the reaction (writing the mechanism might suffice if it is briefly annotated). How could you explain the partial destruction (etching away) of the rim of the glass reaction vessel?

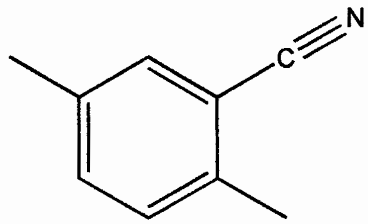
**c.** Compound D is a very important compound in the history of biochemistry, and was actually instrumental in determining the amino acid sequence of insulin, which work led to the Nobel prize in chemistry in 1958! The compound is added to a polypeptide in a slightly basic aqueous solution (usually containing bicarbonate ions), and after a complete hydrolysis of the polypeptide, this reagent facilitates identification of the N-terminal amino acid residue. Recall the general structure of the α-amino acids found in peptides, and explain with a mechanistic diagram how this reagent came to be so useful.

5. For the final two questions, you will be provided with a number of spectra and chemical structures. Your task is to match the appropriate structures (given on the following two pages) with the given spectra. But be careful! On both questions there are more structures given than will be used! For question 5, you will be given paired IR and $^{13}C$ NMR spectra. (See **Figs. 15 – 22**)
6. For the structures in question 6, you will be given paired IR and MS data. (See **Figs. 23 – 30**)

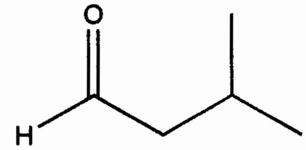
# Structures for Question 5



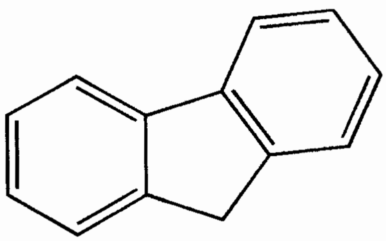

**Compound 5A**



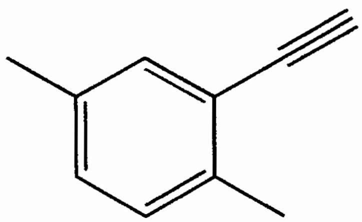

**Compound 5B**



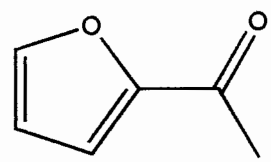

**Compound 5C**



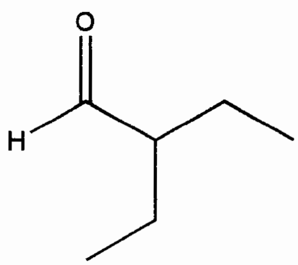
**Compound 5D**



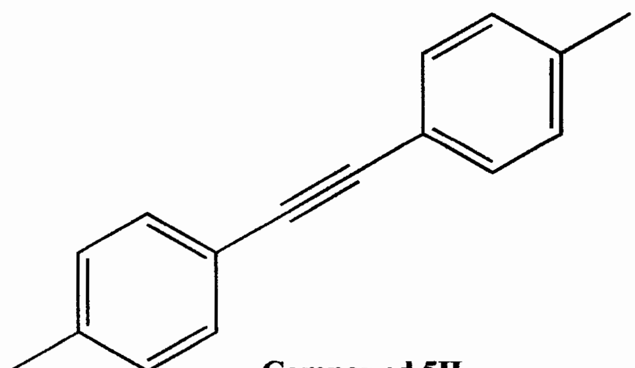
**Compound 5E**




**Compound 5F**

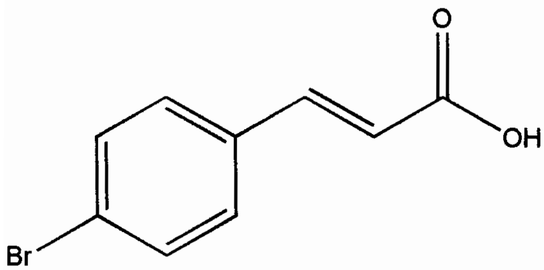



**Compound 5G**

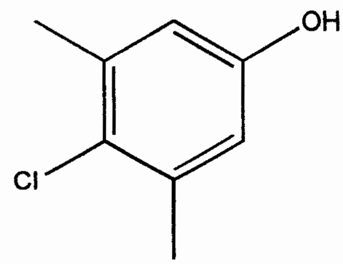


**Compound 5H**

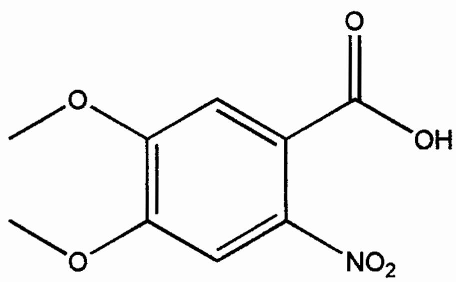
# Structures for Question 6



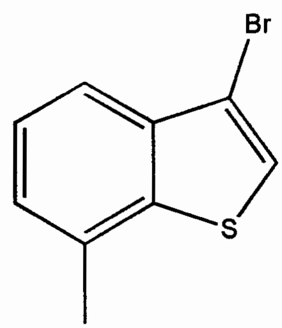

**Compound 6A**



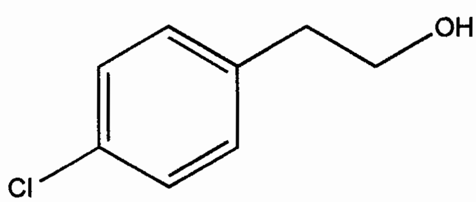

**Compound 6B**



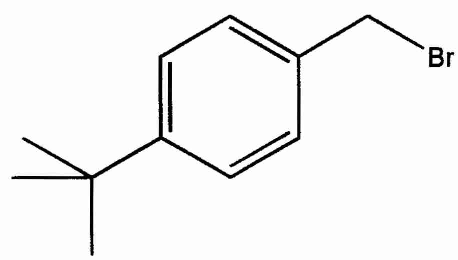

**Compound 6C**



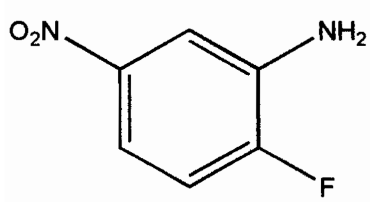

**Compound 6D**



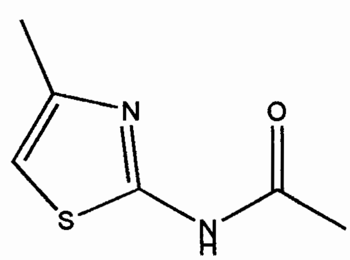

**Compound 6E**




**Compound 6F**

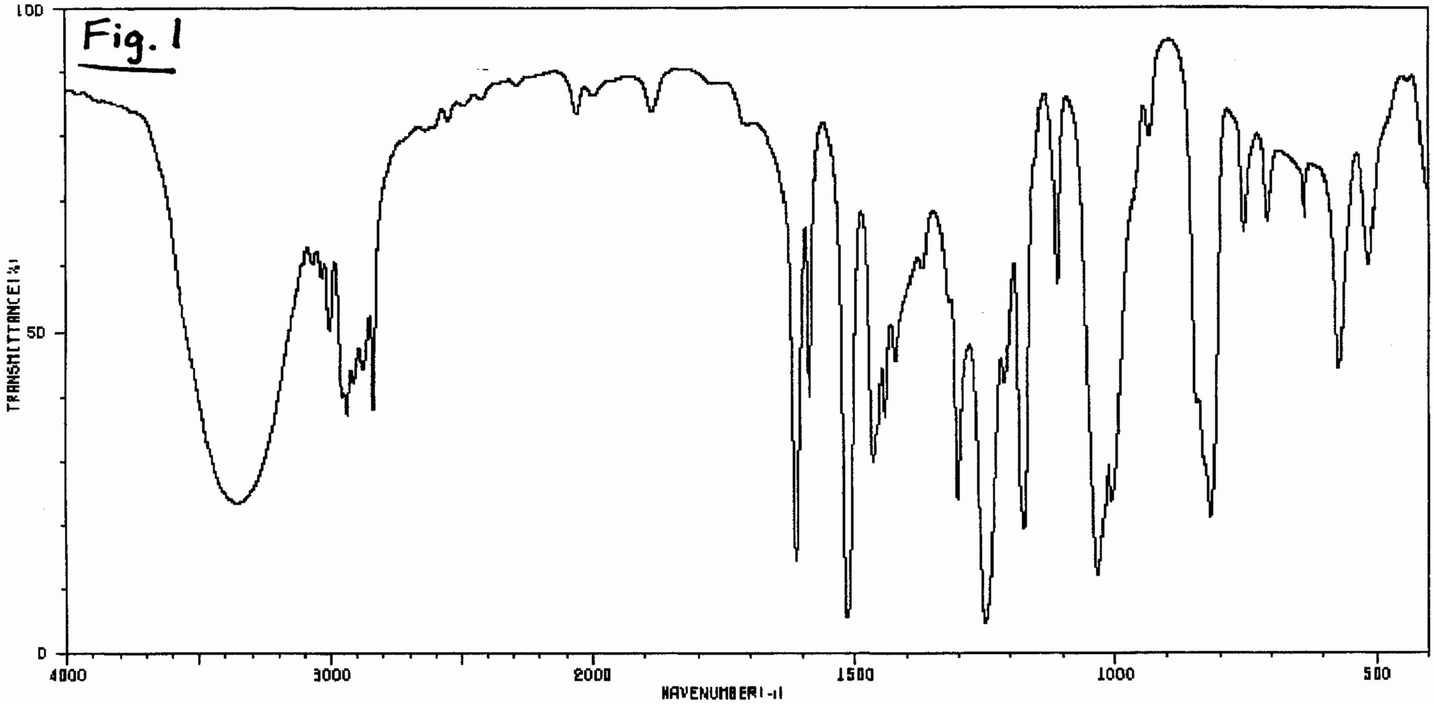



**Compound 6G**




**Compound 6H**

Fig. 1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2000
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1000
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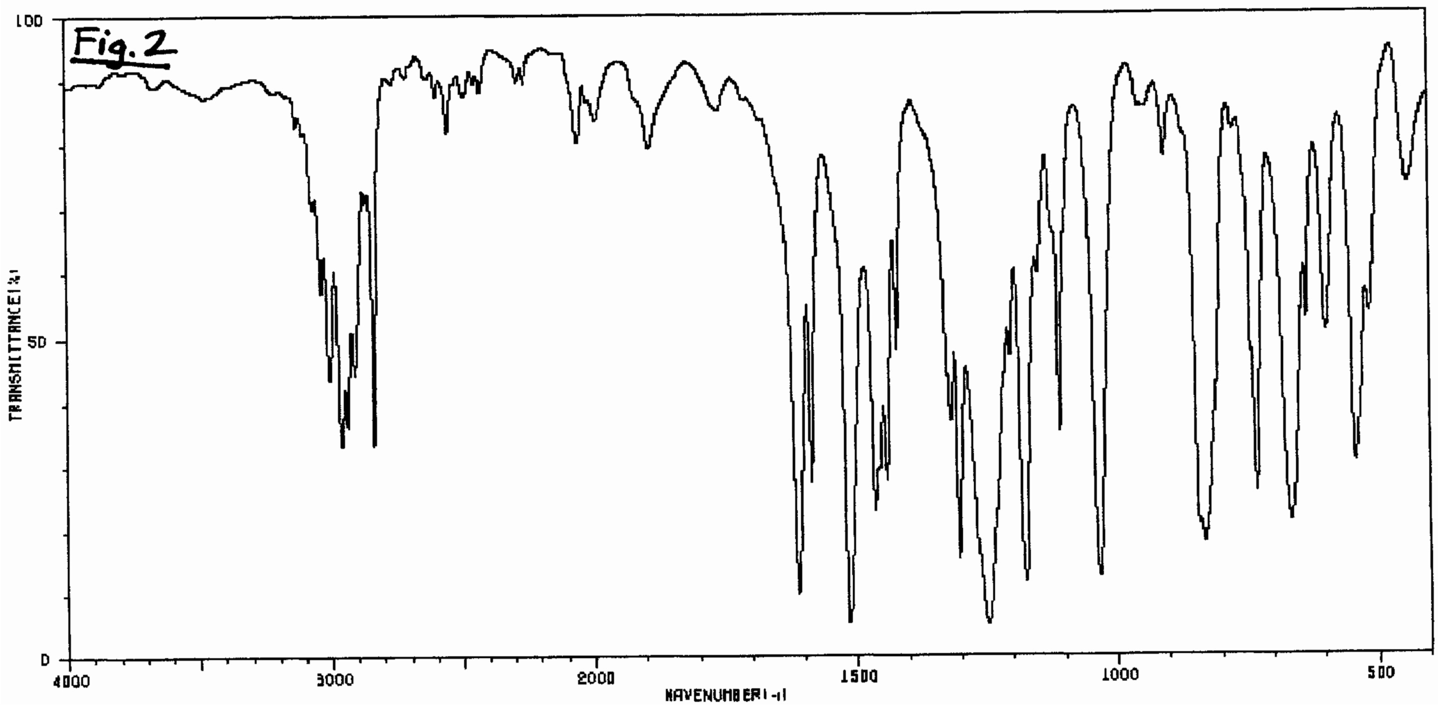
WAVENUMBER(-1)

Fig. 2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TRANSMITTANCE(%)
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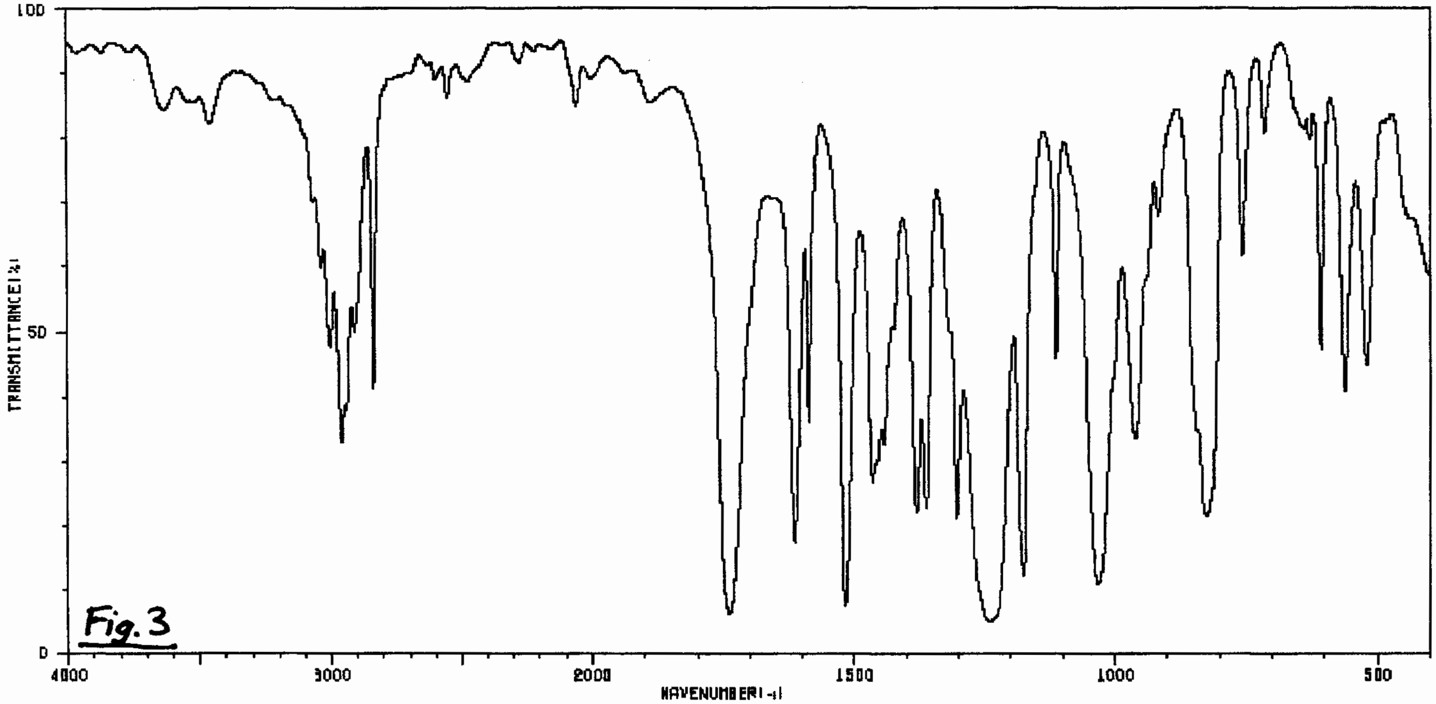


Fig. 3

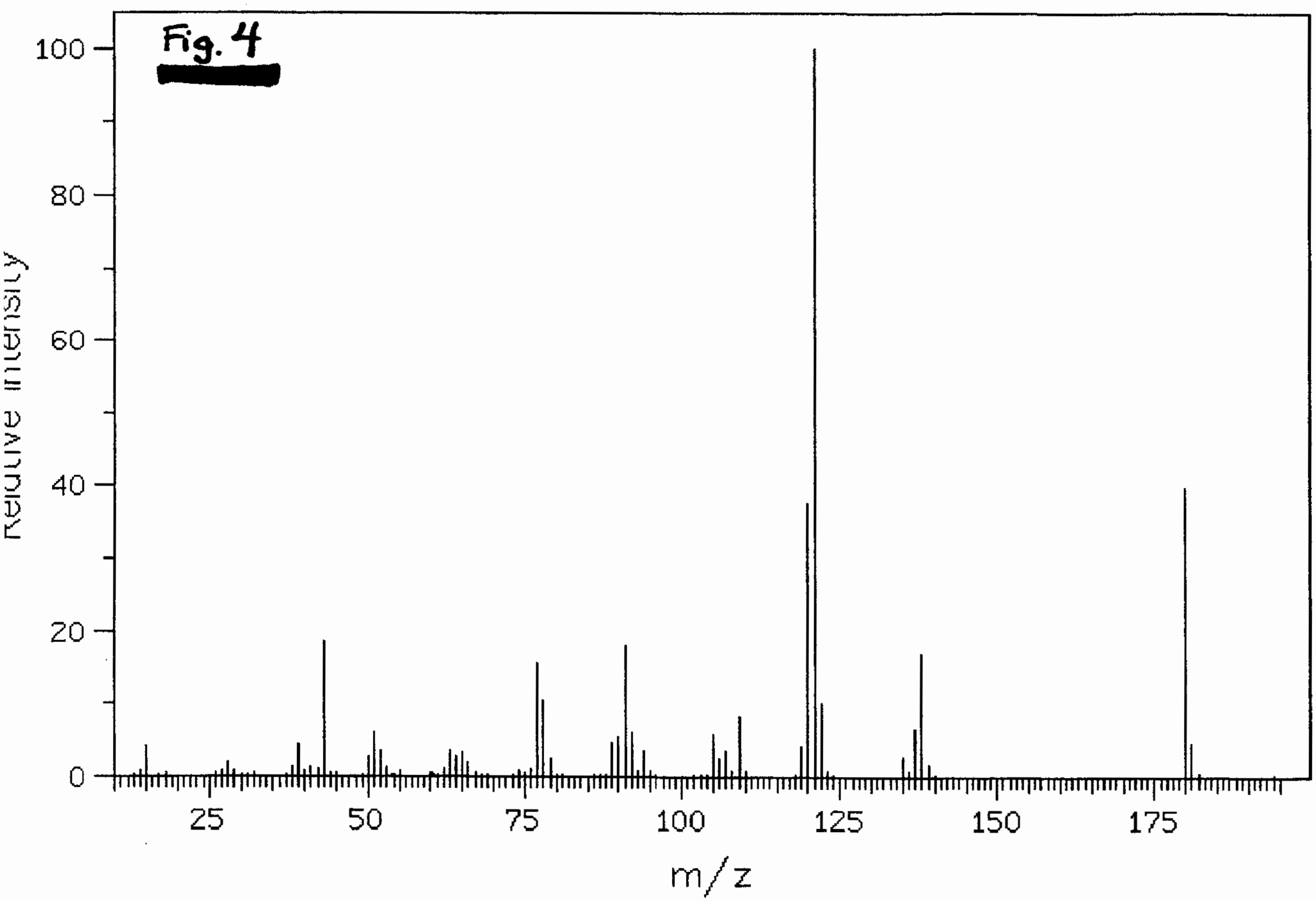


Fig. 4

| m/z | Rel. Intensity |
|---|---|
| 15.0 | 4 |
| 28.0 | 1 |
| 38.0 | 1 |
| 39.0 | 4 |
| 41.0 | 1 |
| 42.0 | 1 |
| 43.0 | 18 |
| 50.0 | 2 |
| 51.0 | 6 |
| 52.0 | 3 |
| 53.0 | 1 |
| 62.0 | 1 |
| 63.0 | 3 |
| 64.0 | 2 |
| 65.0 | 3 |
| 66.0 | 1 |
| 76.0 | 1 |
| 77.0 | 15 |
| 78.0 | 10 |
| 79.0 | 2 |
| 89.0 | 4 |
| 90.0 | 5 |
| 91.0 | 18 |
| 92.0 | 5 |
| 94.0 | 3 |
| 105.0 | 5 |
| 106.0 | 2 |
| 107.0 | 3 |
| 109.0 | 8 |
| 119.0 | 4 |
| 120.0 | 37 |
| 121.0 | 100 |
| 122.0 | 10 |
| 135.0 | 2 |
| 137.0 | 6 |
| 138.0 | 16 |
| 139.0 | 1 |
| 180.0 | 39 |
| 181.0 | 4 |

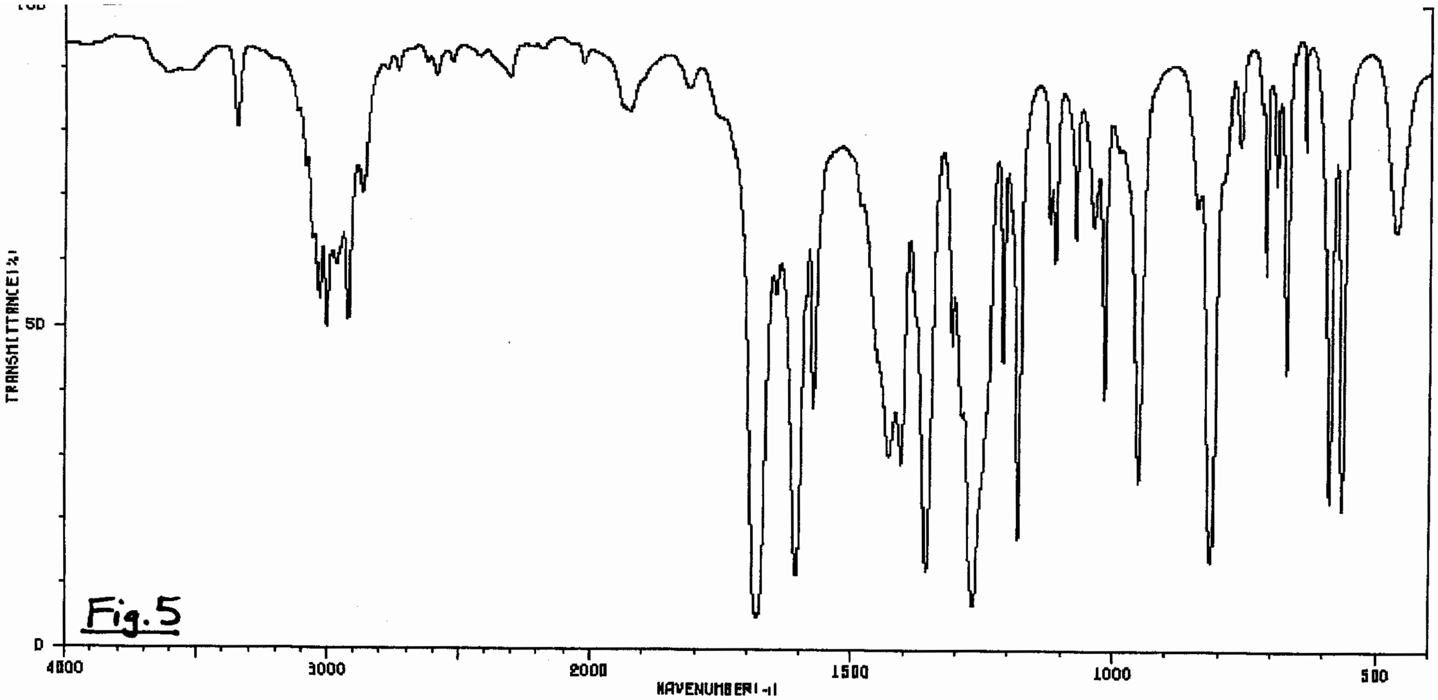

Fig. 5

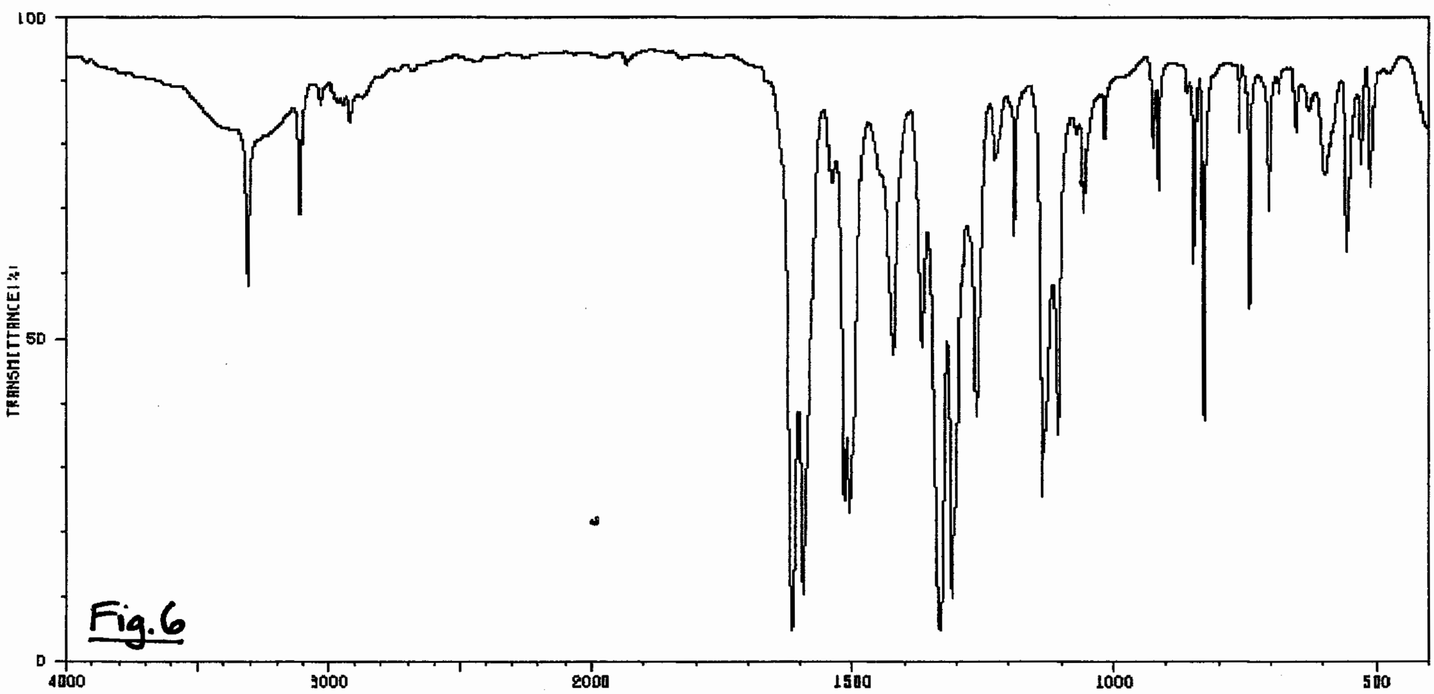

Fig. 6

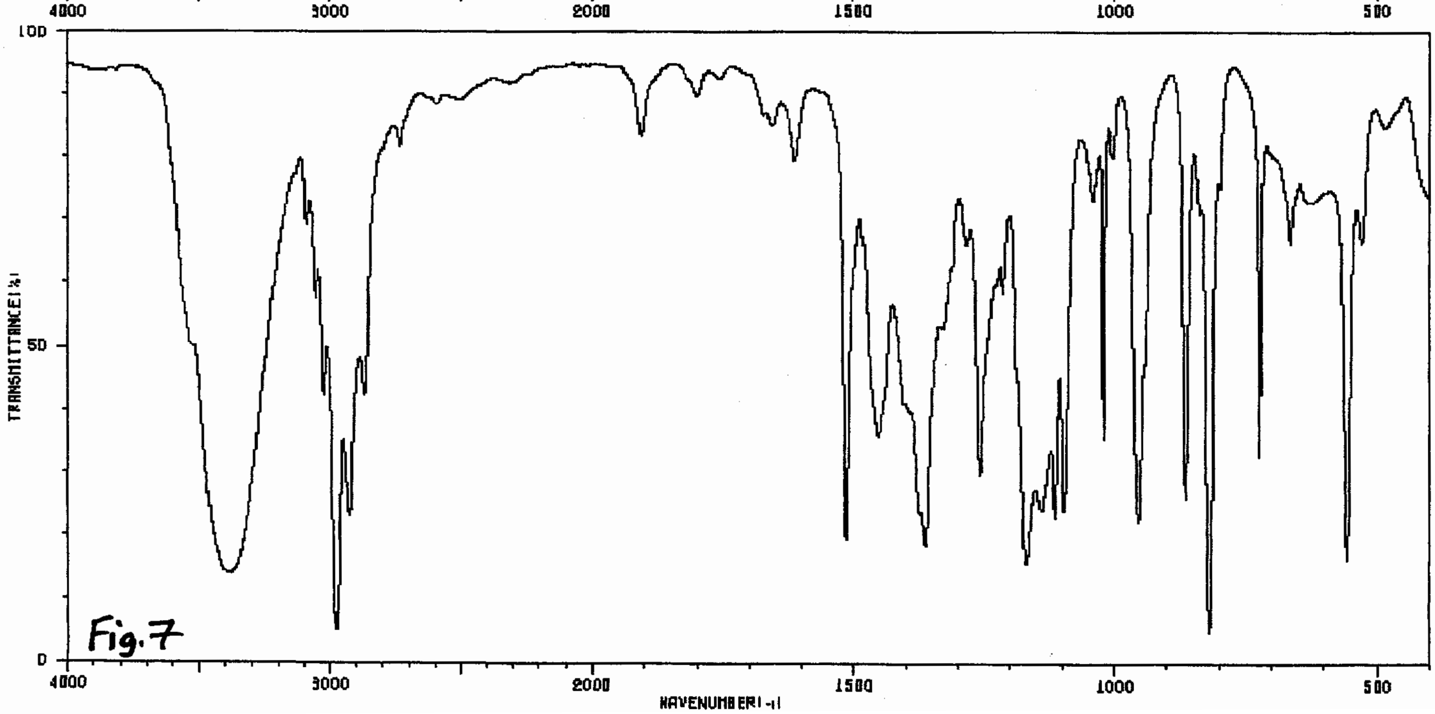

Fig. 7

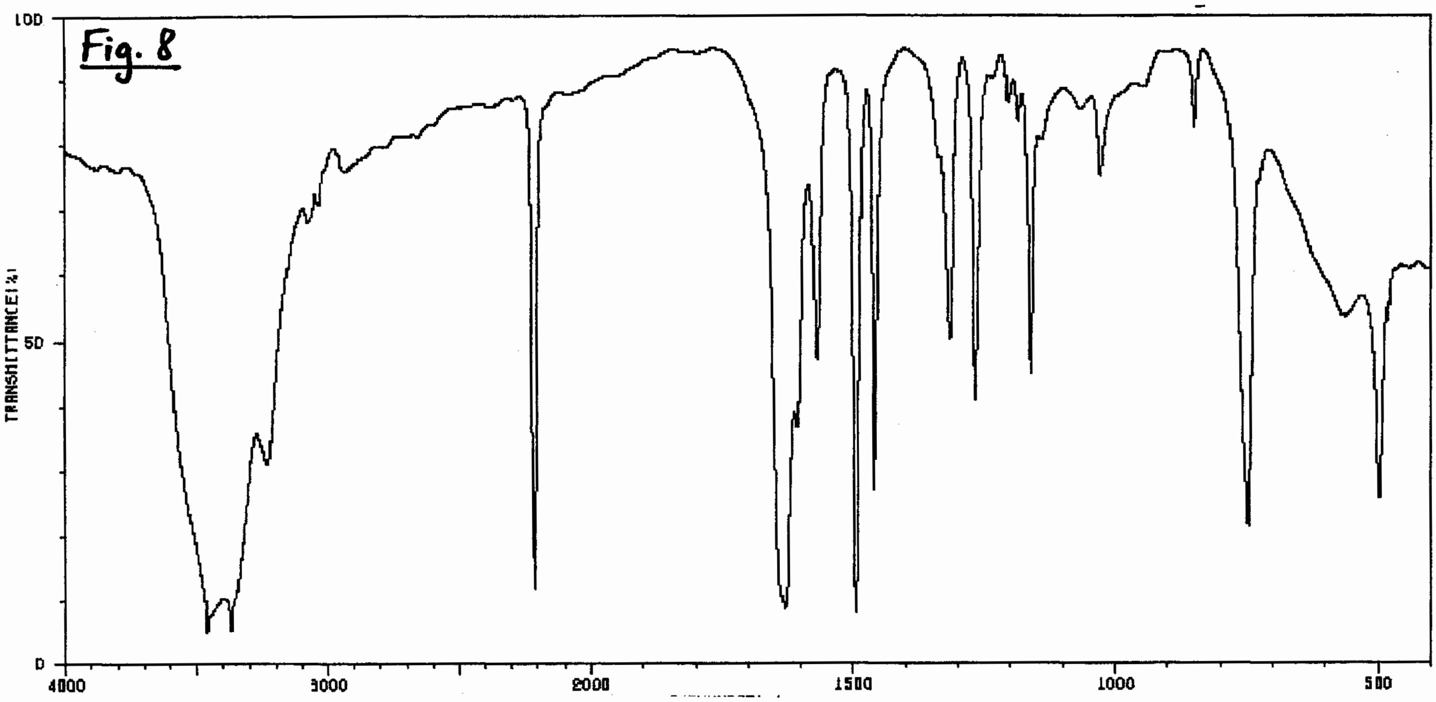
Fig. 8
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1500
1000
500

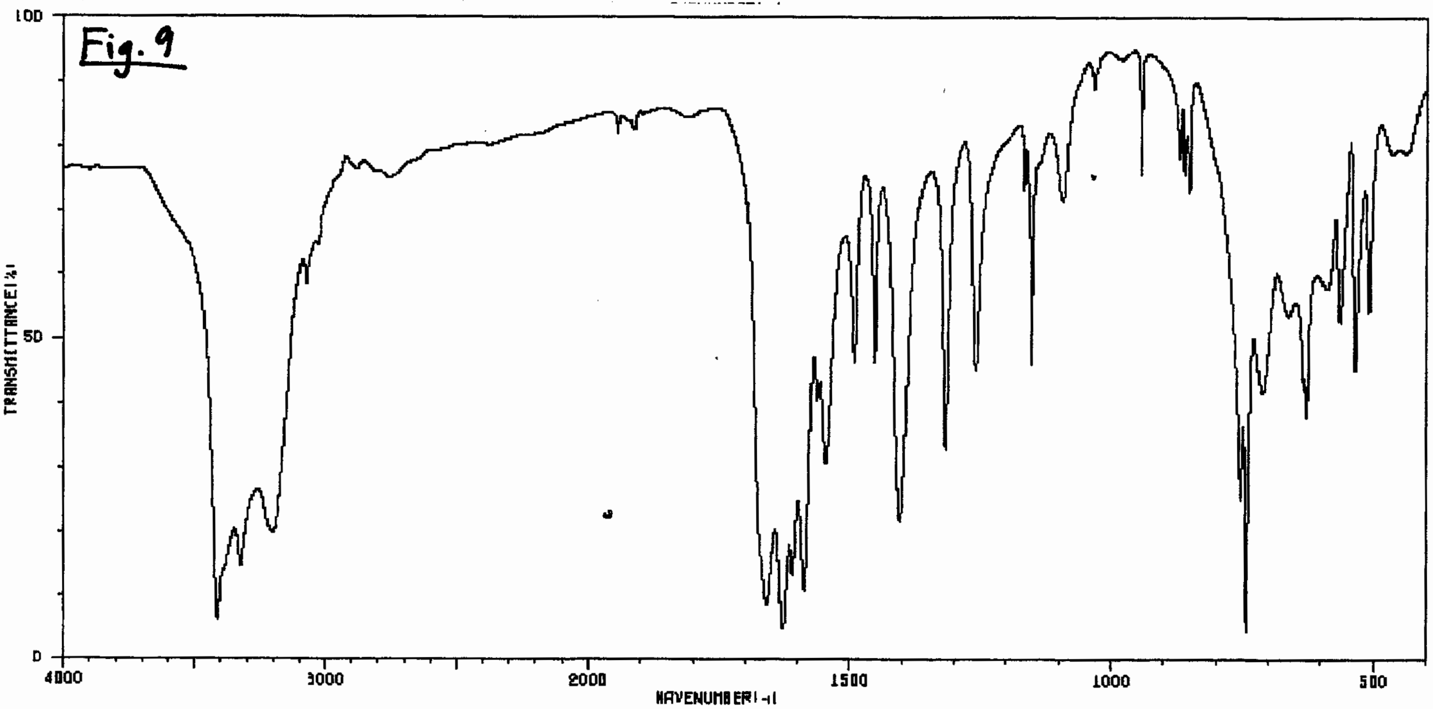
Fig. 9
TRANSMITTANCE(%)
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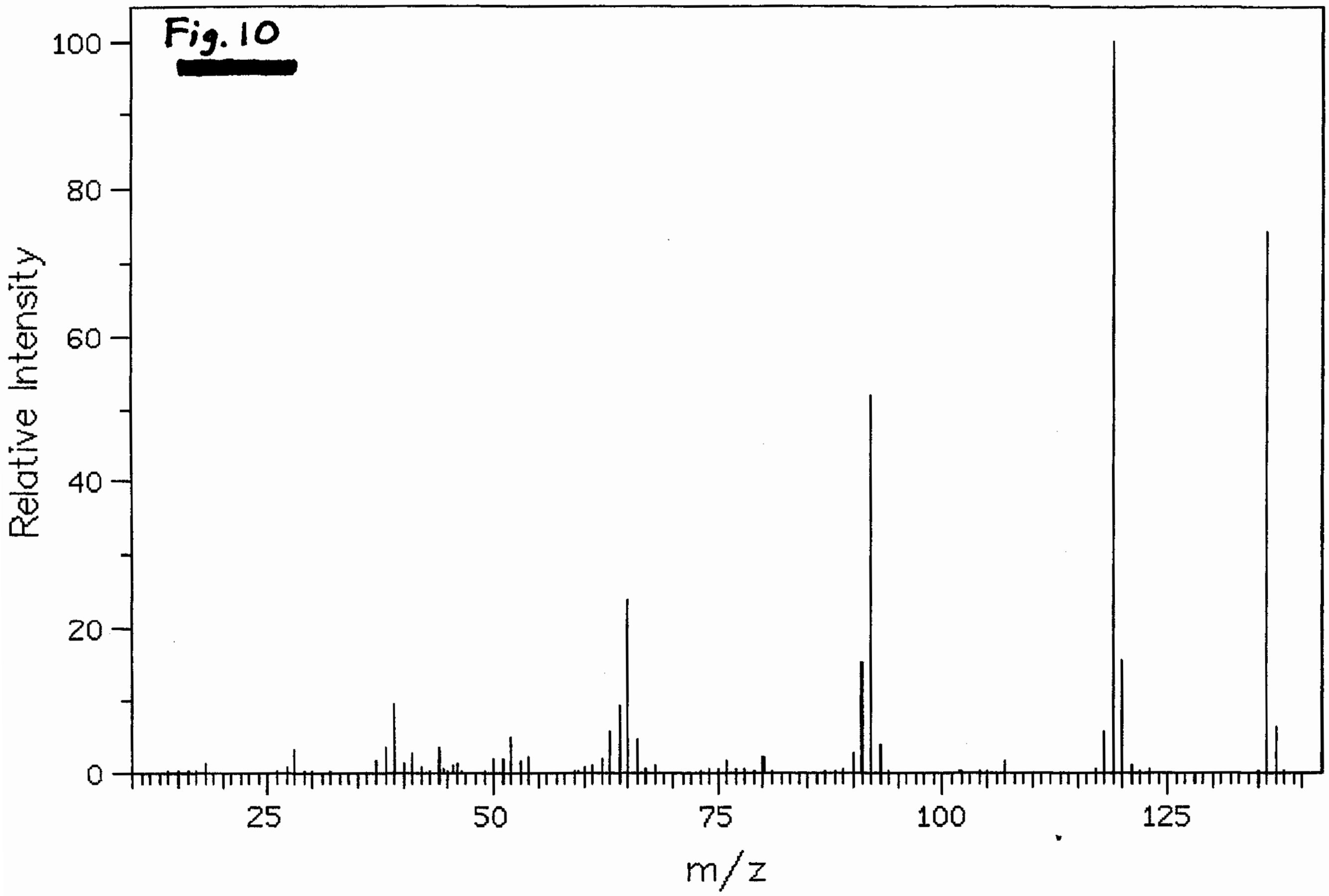
0
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)

Fig. 10




| m/z | Rel. Intensity |
|---|---|
| 28.0 | 3 |
| 37.0 | 1 |
| 38.0 | 3 |
| 39.0 | 9 |
| 40.0 | 1 |
| 41.0 | 2 |
| 44.0 | 3 |
| 45.5 | 1 |
| 46.0 | 1 |
| 50.0 | 1 |
| 51.0 | 1 |
| 52.0 | 5 |
| 53.0 | 1 |
| 54.0 | 2 |
| 61.0 | 1 |
| 62.0 | 1 |
| 63.0 | 5 |
| 64.0 | 9 |
| 65.0 | 23 |
| 66.0 | 4 |
| 68.0 | 1 |
| 76.0 | 1 |
| 80.0 | 2 |
| 90.0 | 2 |
| 91.0 | 15 |
| 92.0 | 51 |
| 93.0 | 3 |
| 107.0 | 1 |
| 118.0 | 5 |
| 119.0 | 100 |
| 120.0 | 15 |
| 121.0 | 1 |
| 136.0 | 74 |
| 137.0 | 6 |

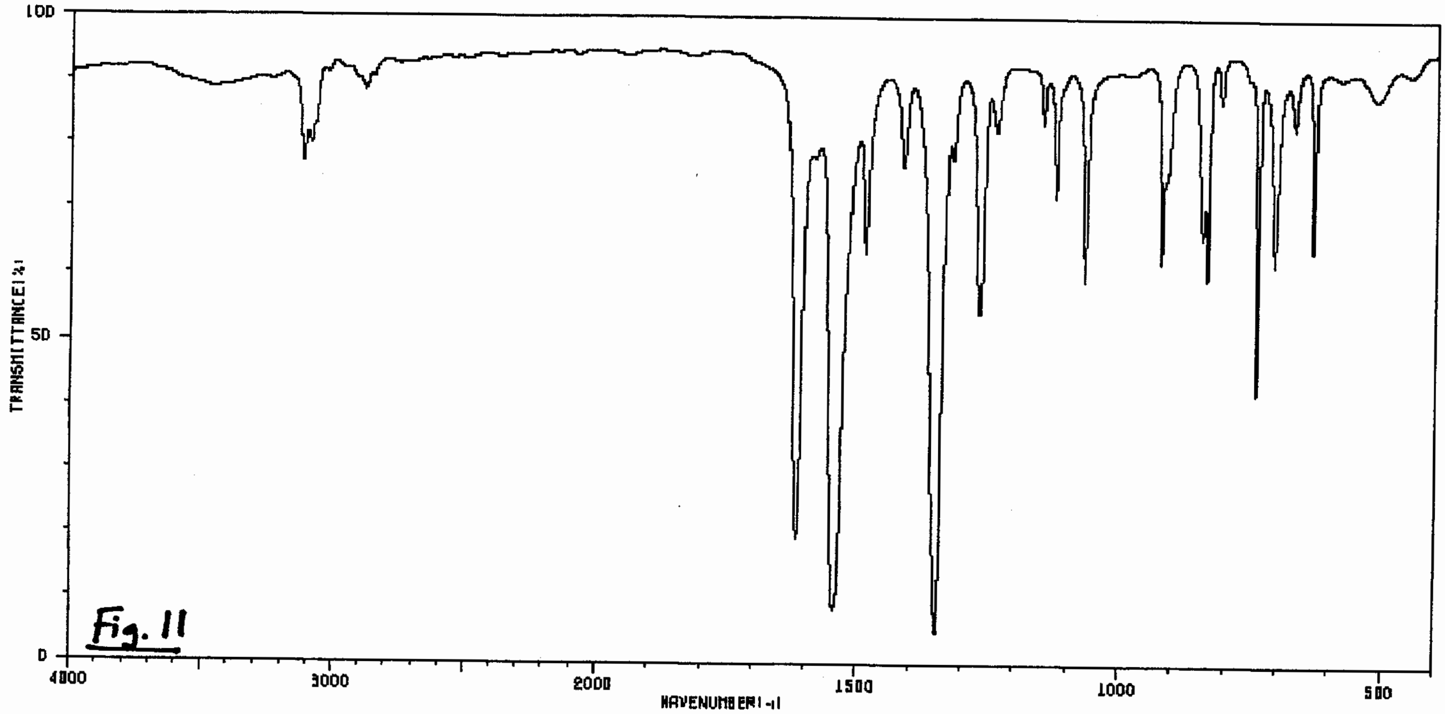



Fig. 11

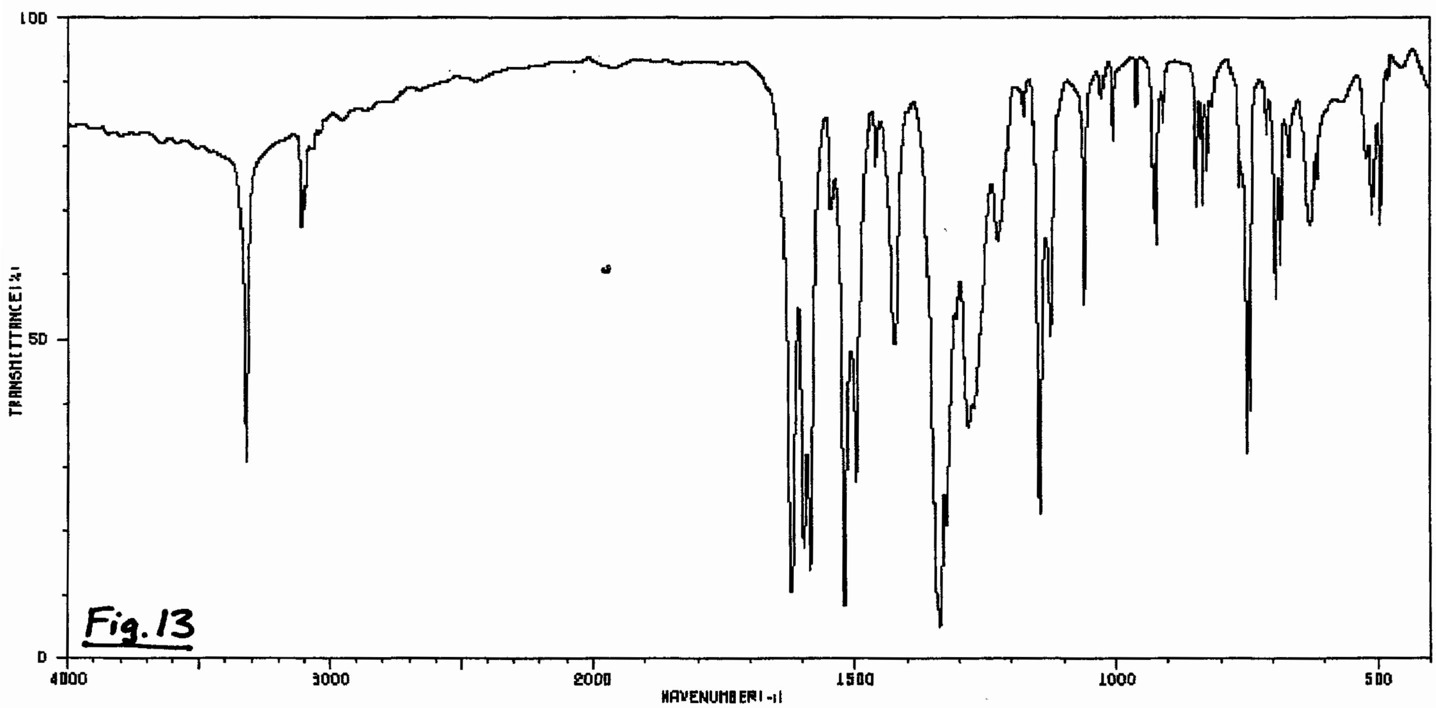
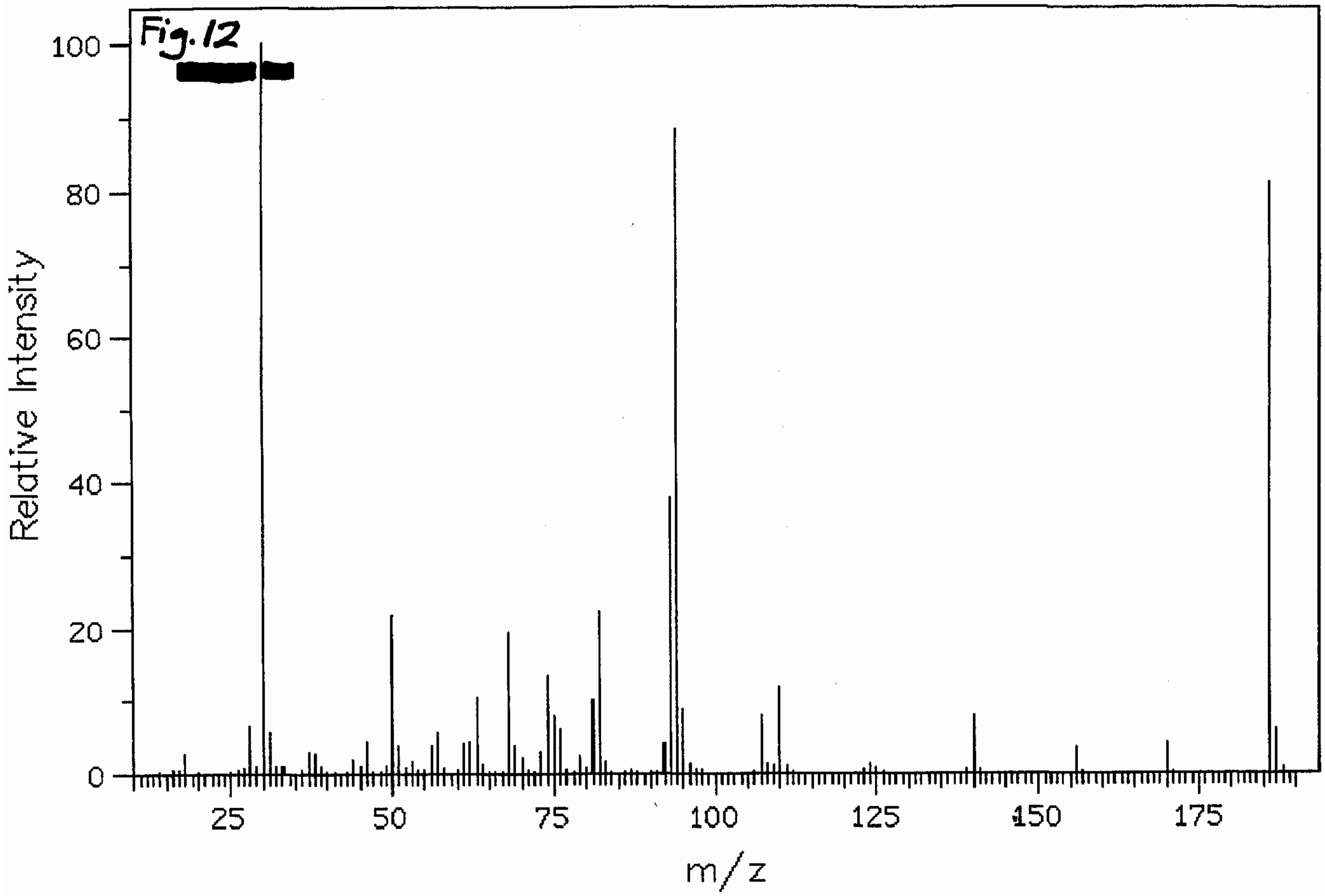



Fig. 13

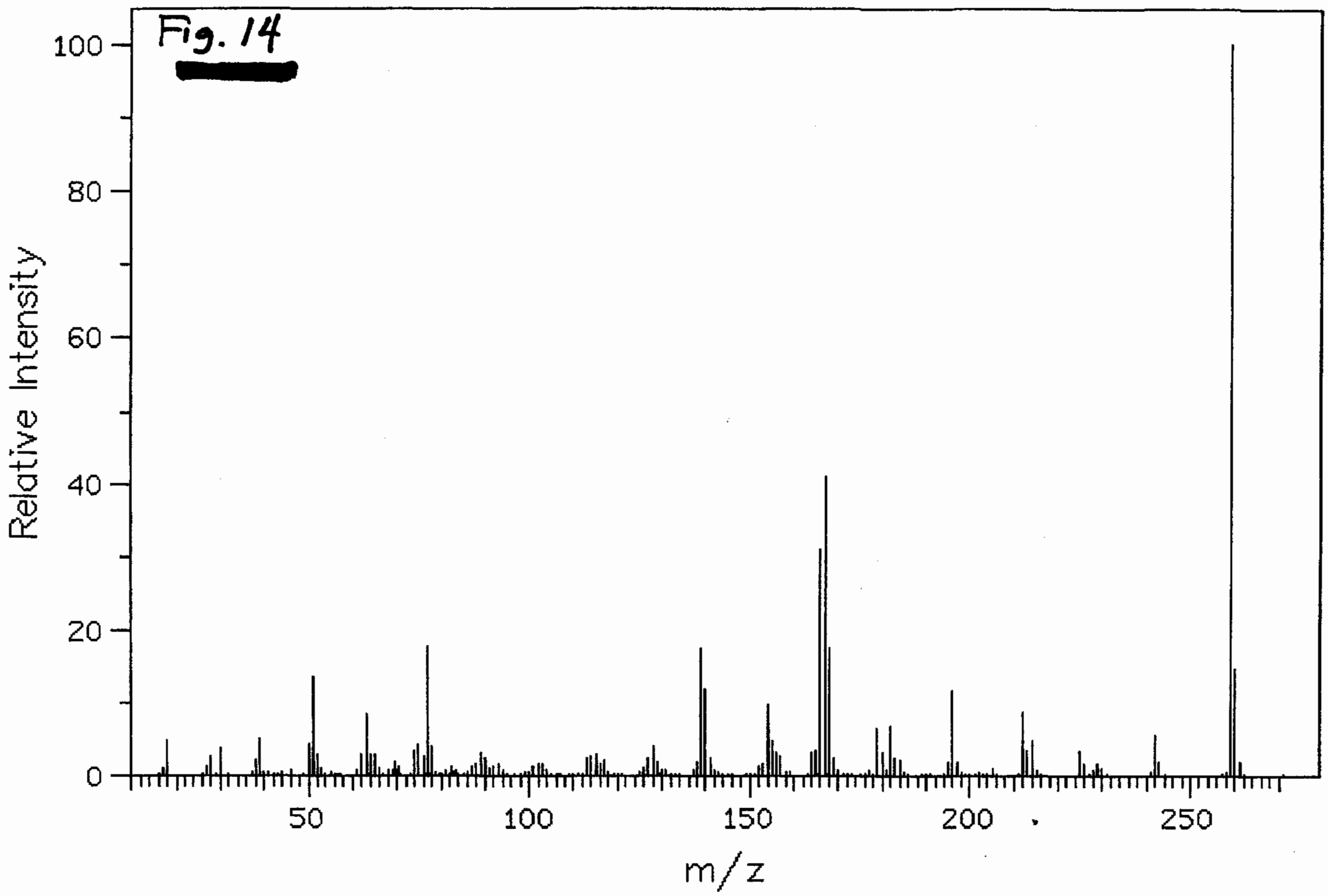
(Fig. 12 on next page)




| m/z | Rel. Intensity |
|---|---|
| 28.0 | 6 |
| 29.0 | 1 |
| 30.0 | 100 |
| 31.0 | 5 |
| 32.0 | 1 |
| 33.0 | 1 |
| 37.0 | 2 |
| 38.0 | 2 |
| 39.0 | 1 |
| 44.0 | 2 |
| 45.0 | 1 |
| 46.0 | 4 |
| 49.0 | 1 |
| 50.0 | 21 |
| 51.0 | 3 |
| 53.0 | 1 |
| 56.0 | 3 |
| 57.0 | 5 |
| 61.0 | 4 |
| 62.0 | 4 |
| 63.0 | 10 |
| 64.0 | 1 |
| 68.0 | 19 |
| 69.0 | 3 |
| 70.0 | 2 |

| m/z | Rel. Intensity |
|---|---|
| 73.0 | 2 |
| 74.0 | 13 |
| 75.0 | 8 |
| 76.0 | 5 |
| 79.0 | 2 |
| 81.0 | 10 |
| 82.0 | 22 |
| 83.0 | 1 |
| 92.0 | 4 |
| 93.0 | 38 |
| 94.0 | 88 |
| 95.0 | 8 |
| 96.0 | 1 |
| 107.0 | 7 |
| 108.0 | 1 |
| 109.0 | 1 |
| 110.0 | 11 |
| 111.0 | 1 |
| 124.0 | 1 |
| 140.0 | 7 |
| 156.0 | 3 |
| 170.0 | 4 |
| 186.0 | 81 |
| 187.0 | 6 |

Fig. 14




| m/z | Rel. Intensity |
|---|---|
| 30.0 | 3 |
| 38.0 | 2 |
| 39.0 | 5 |
| 50.0 | 4 |
| 51.0 | 13 |
| 52.0 | 3 |
| 53.0 | 1 |
| 62.0 | 3 |
| 63.0 | 8 |
| 64.0 | 3 |
| 65.0 | 3 |
| 66.0 | 1 |
| 69.5 | 1 |
| 70.5 | 1 |
| 74.0 | 3 |
| 75.0 | 4 |
| 76.0 | 2 |
| 77.0 | 17 |
| 78.0 | 4 |
| 82.5 | 1 |
| 114.0 | 2 |
| 115.0 | 3 |
| 116.0 | 1 |
| 117.0 | 2 |
| 126.0 | 1 |
| 127.0 | 2 |
| 128.0 | 4 |
| 129.0 | 1 |
| 138.0 | 1 |
| 139.0 | 17 |
| 140.0 | 12 |
| 141.0 | 2 |
| 152.0 | 1 |

| m/z | Rel. Intensity |
|---|---|
| 154.0 | 9 |
| 155.0 | 5 |
| 156.0 | 3 |
| 157.0 | 2 |
| 164.0 | 3 |
| 165.0 | 3 |
| 166.0 | 31 |
| 167.0 | 41 |
| 168.0 | 17 |
| 169.0 | 2 |
| 179.0 | 6 |
| 180.0 | 3 |
| 182.0 | 6 |
| 183.0 | 2 |
| 184.0 | 2 |
| 195.0 | 1 |
| 196.0 | 11 |
| 197.0 | 1 |
| 205.0 | 1 |
| 212.0 | 8 |
| 213.0 | 3 |
| 214.0 | 5 |
| 225.0 | 3 |
| 226.0 | 1 |
| 229.0 | 1 |
| 230.0 | 1 |
| 242.0 | 5 |
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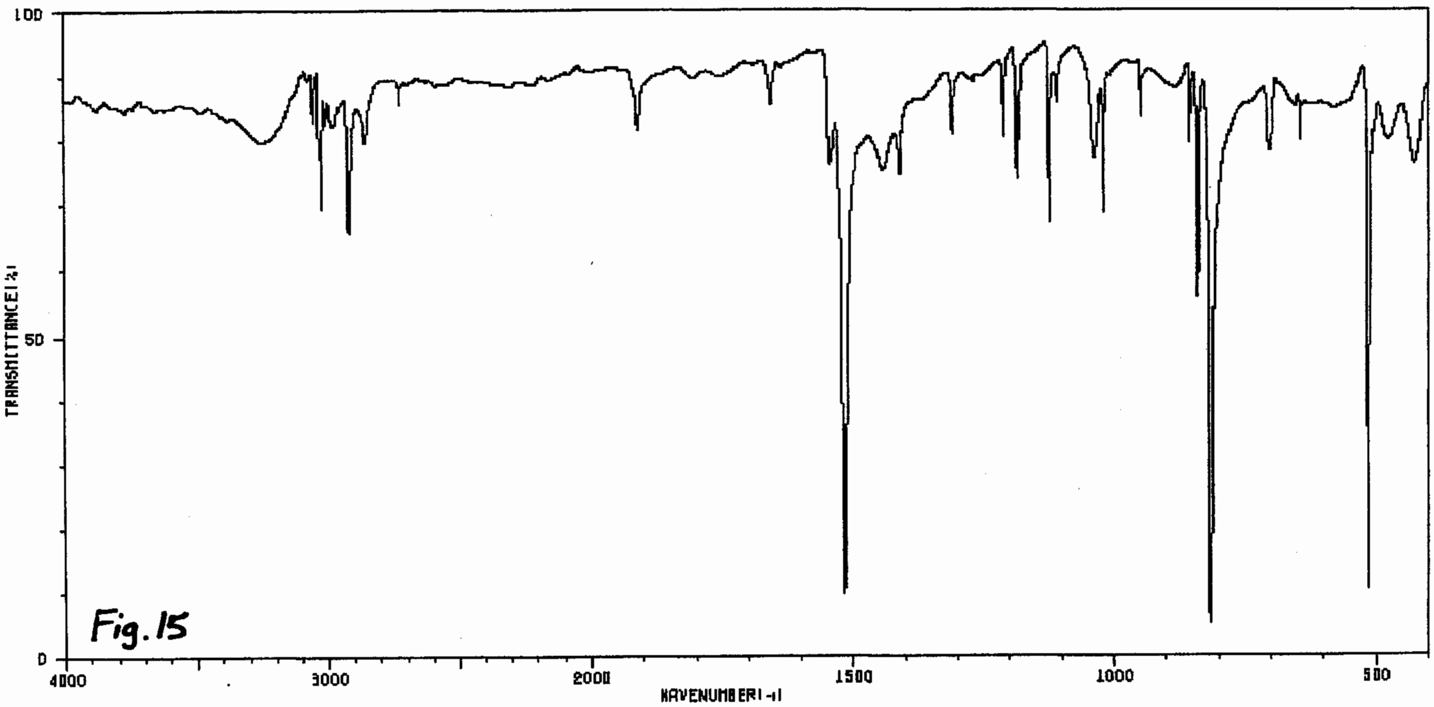
| 259.0 | 100 |
| 260.0 | 14 |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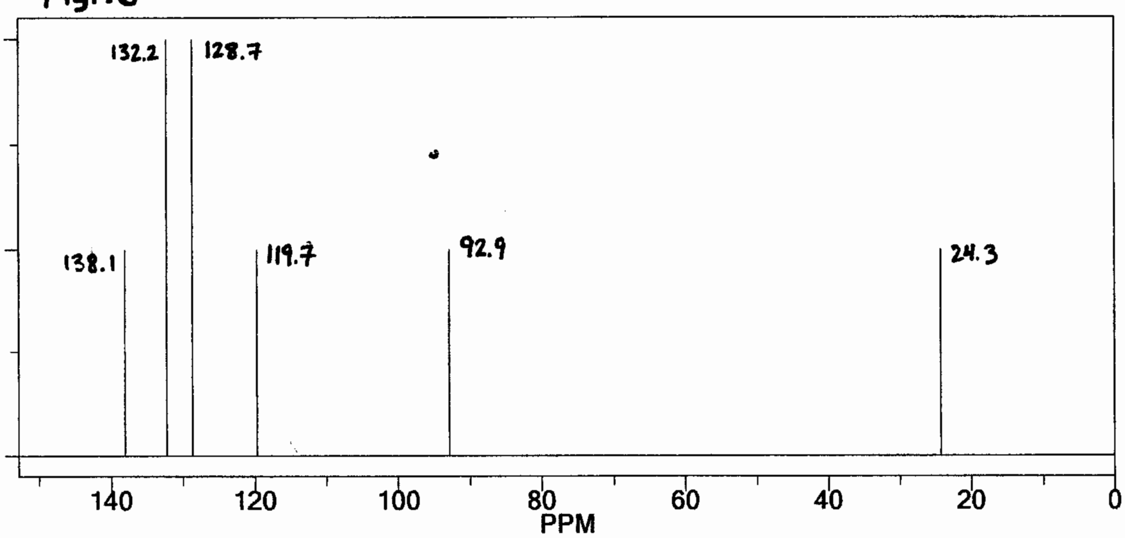
50
0
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)

Fig. 15

Fig. 16


132.2
128.7
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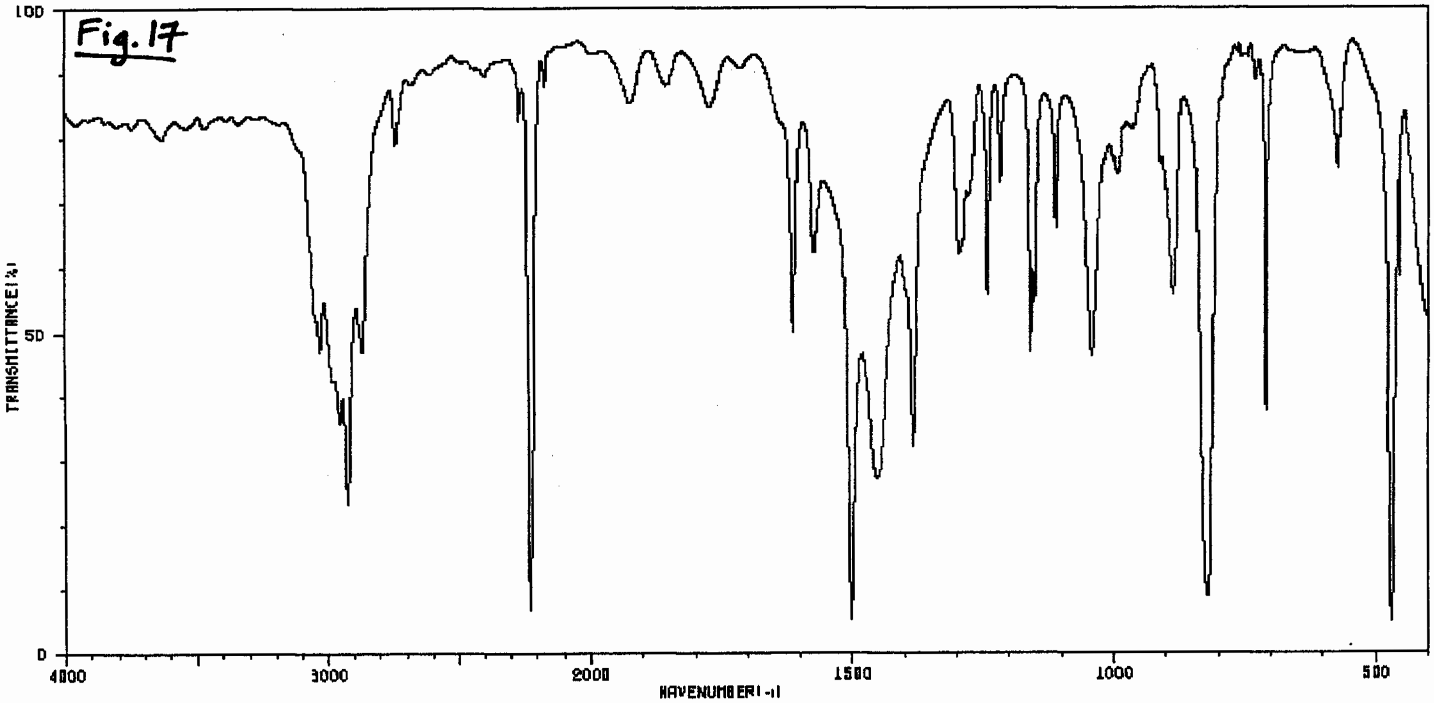
119.7
92.9
24.3
140
120
100
80
60
40
20
0
PPM

Fig. 17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0
TRANSMITTANCE(%)
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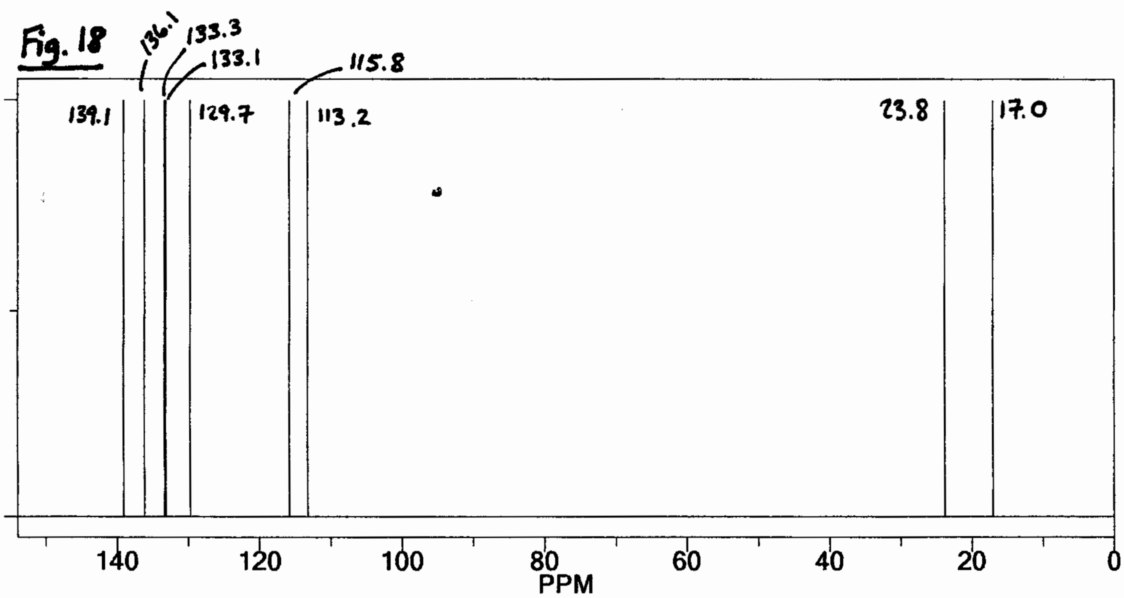
2000
1500
1000
500
WAVENUMBER(-1)

Fig. 18


136.1
133.3
133.1
115.8
139.1
129.7
113.2
23.8
17.0
140
120
100
80
60
40
20
0
PPM

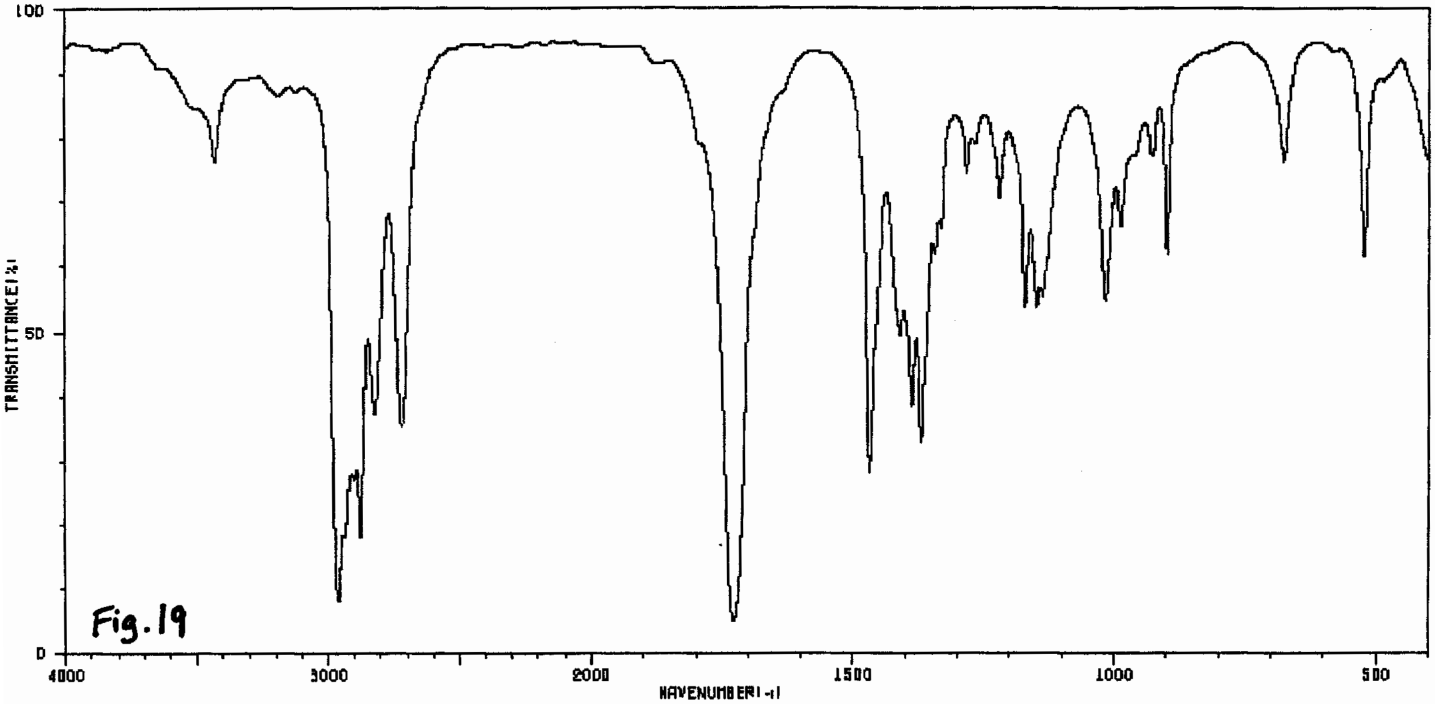
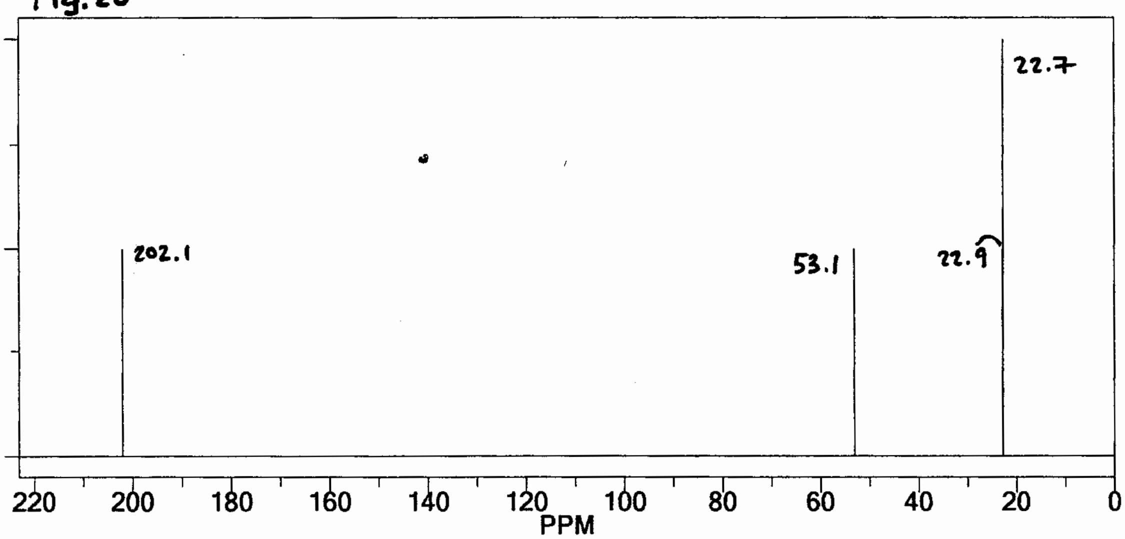

100
50
0
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)

Fig. 19

Fig. 20


202.1
53.1
22.9
22.7
220
200
180
160
140
120
100
80
60
40
20
0
PPM

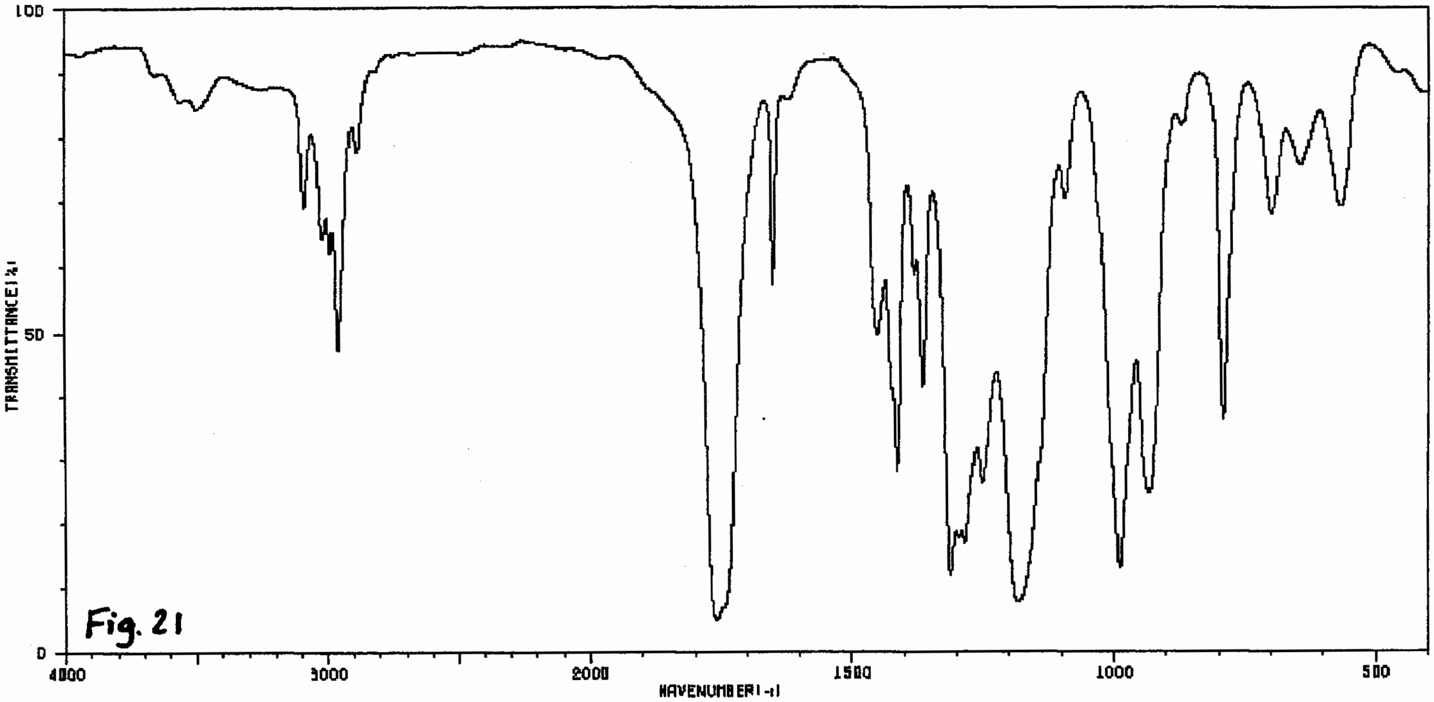
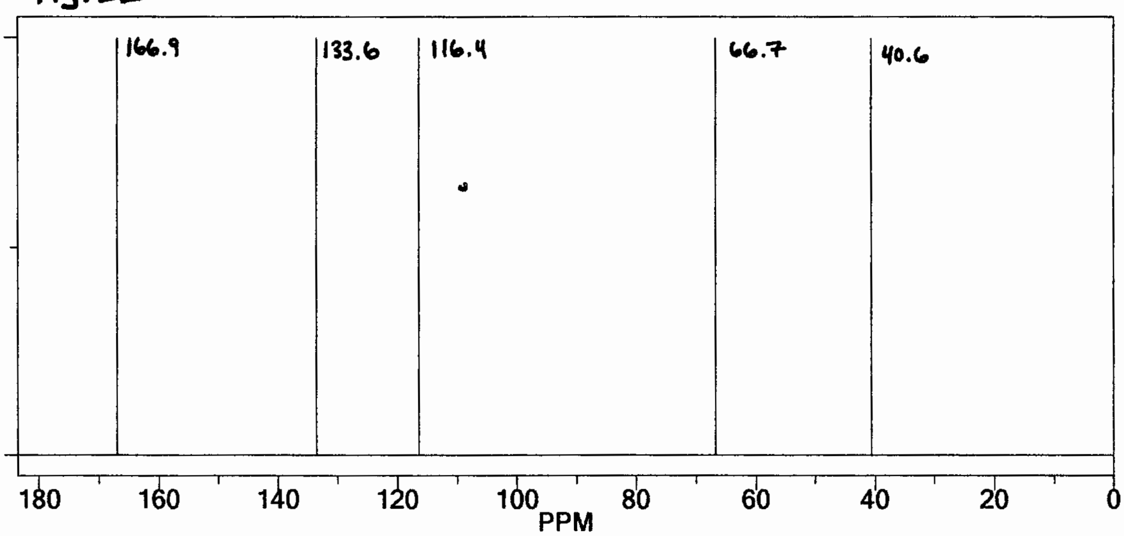
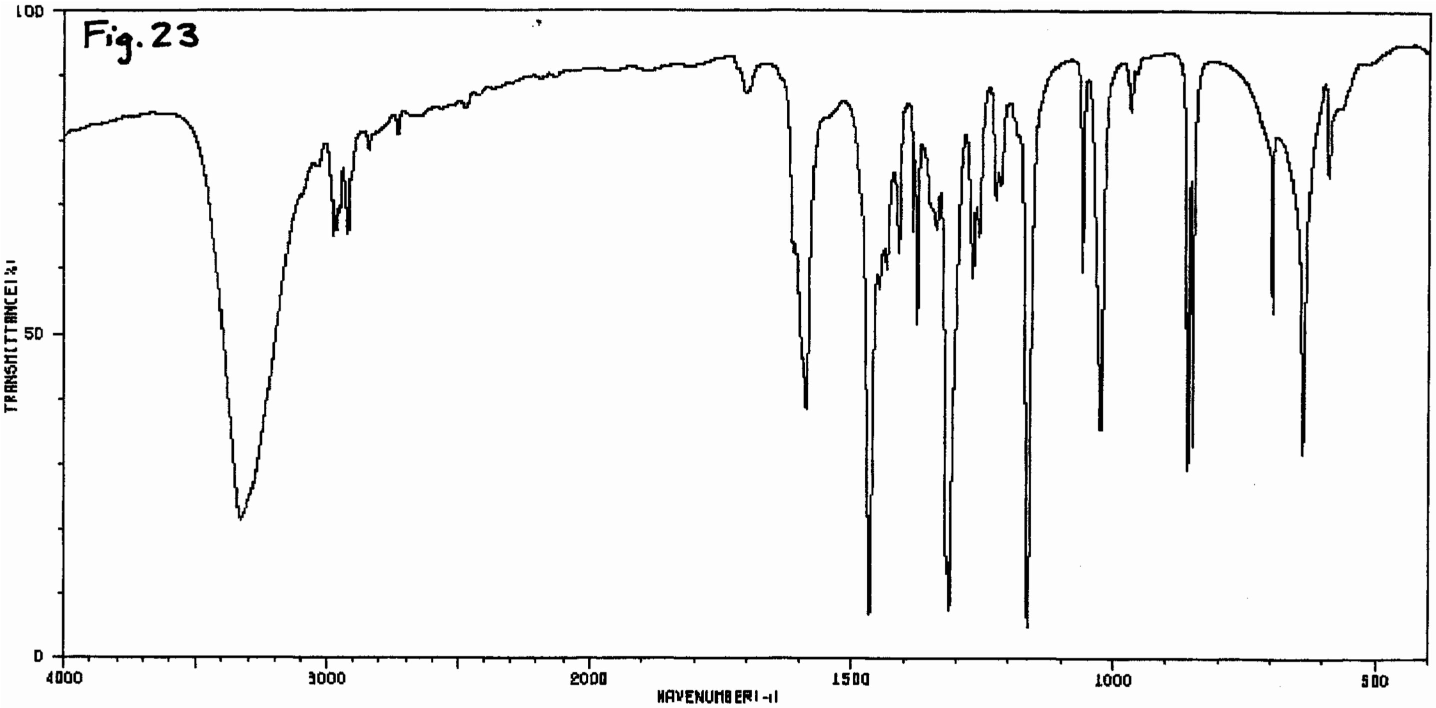
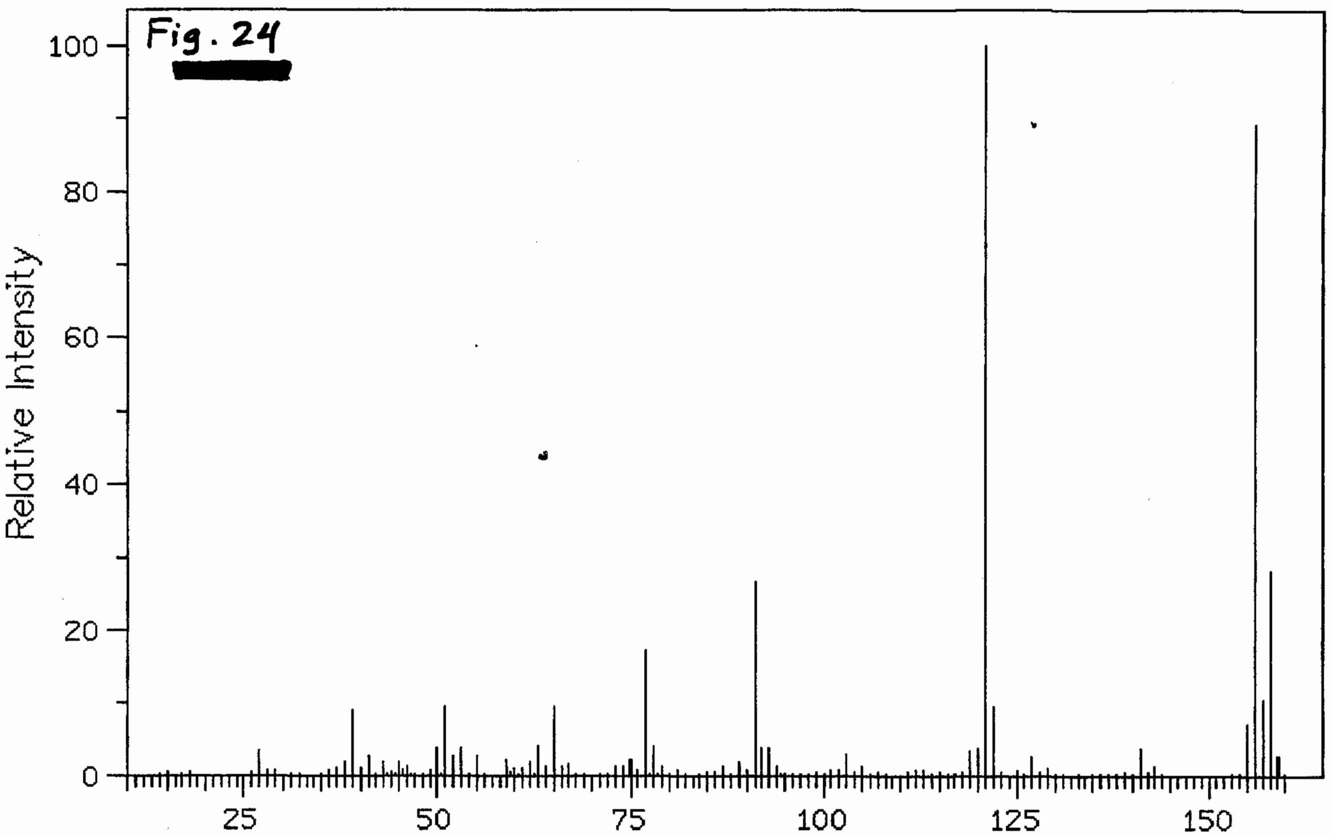

100
50
0
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)

Fig. 21

Fig. 22


166.9
133.6
116.4
66.7
40.6
180
160
140
120
100
80
60
40
20
0
PPM




| | | | | | |
|---|---|---|---|---|---|
| 27.0 | 3 | 63.0 | 4 | 103.0 | 3 |
| 37.0 | 1 | 64.0 | 1 | 105.0 | 1 |
| 38.0 | 1 | 65.0 | 9 | 119.0 | 3 |
| 39.0 | 9 | 66.0 | 1 | 120.0 | 3 |
| 40.0 | 1 | 67.0 | 1 | 121.0 | 100 |
| 41.0 | 2 | 73.0 | 1 | 122.0 | 9 |
| 43.0 | 1 | 74.0 | 1 | 127.0 | 2 |
| 45.0 | 1 | 75.0 | 2 | 129.0 | 1 |
| 46.0 | 1 | 77.0 | 17 | 141.0 | 3 |
| 50.0 | 3 | 78.0 | 4 | 143.0 | 1 |
| 51.0 | 9 | 79.0 | 1 | 155.0 | 7 |
| 52.0 | 2 | 87.0 | 1 | 156.0 | 89 |
| 53.0 | 3 | 89.0 | 1 | 157.0 | 10 |
| 55.0 | 2 | 91.0 | 26 | 158.0 | 28 |
| 59.0 | 2 | 92.0 | 3 | 159.0 | 2 |
| | | 93.0 | 3 | | |

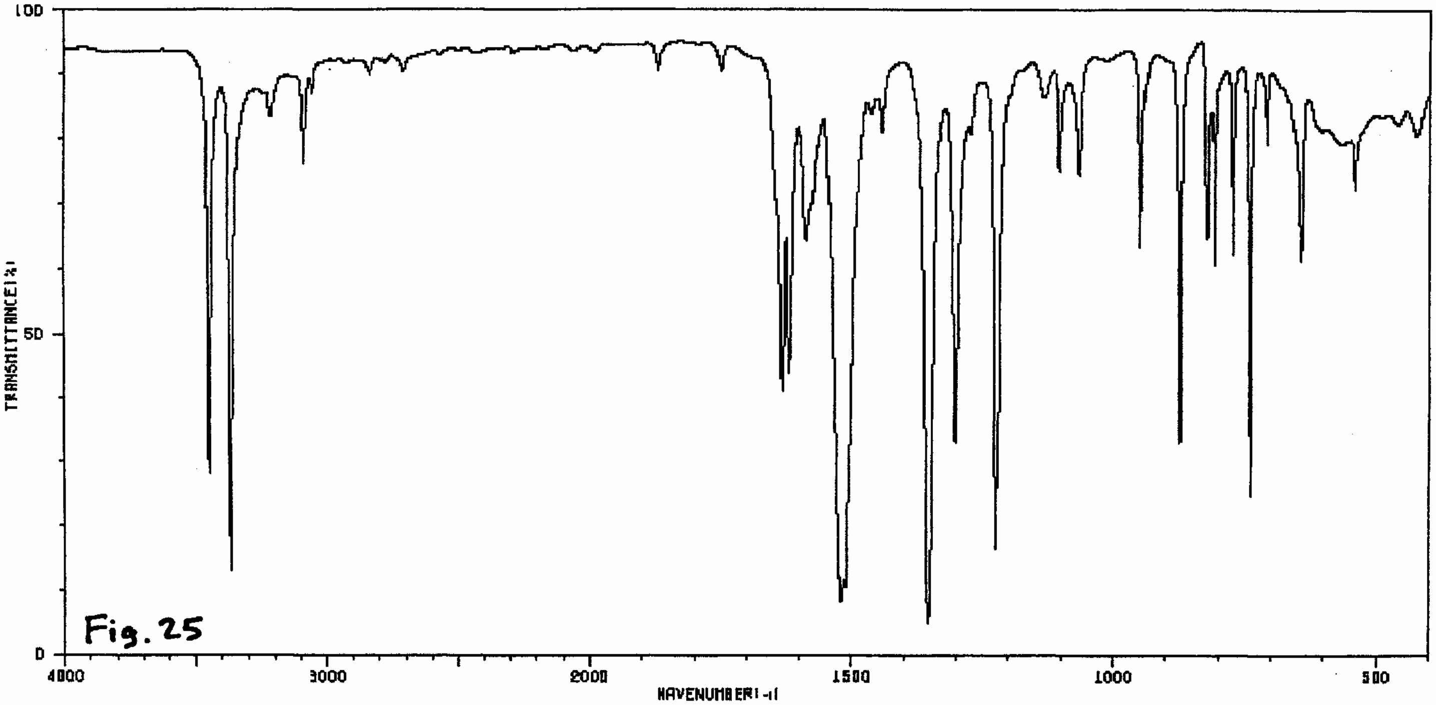


Fig. 25

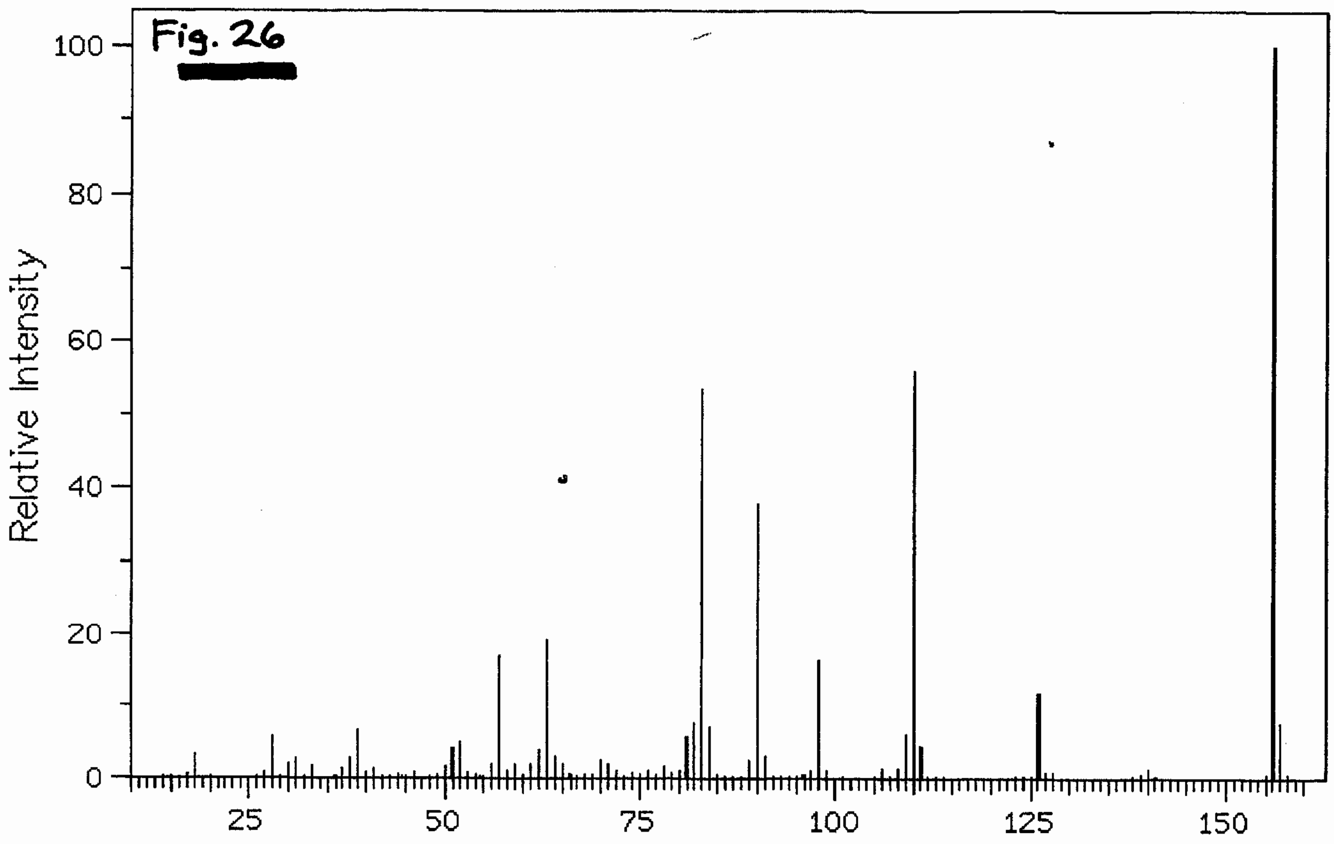


Fig. 26

| | | | | | |
|---|---|---|---|---|---|
| 18.0 | 3 | 61.0 | 2 | 98.0 | 16 |
| 28.0 | 5 | 62.0 | 3 | 99.0 | 1 |
| 30.0 | 1 | 63.0 | 19 | 106.0 | 1 |
| 31.0 | 2 | 64.0 | 2 | 108.0 | 1 |
| 33.0 | 1 | 65.0 | 2 | 109.0 | 6 |
| 37.0 | 1 | 70.0 | 2 | 110.0 | 56 |
| 38.0 | 2 | 81.0 | 5 | 111.0 | 4 |
| 39.0 | 6 | 82.0 | 7 | 126.0 | 11 |
| 41.0 | 1 | 83.0 | 53 | 155.0 | 0 |
| 50.0 | 1 | 84.0 | 7 | 156.0 | 100 |
| 51.0 | 4 | 89.0 | 2 | 157.0 | 7 |
| 52.0 | 4 | 90.0 | 37 | | |
| 56.0 | 1 | 91.0 | 2 | | |
| 57.0 | 16 | | | | |

Fig. 27

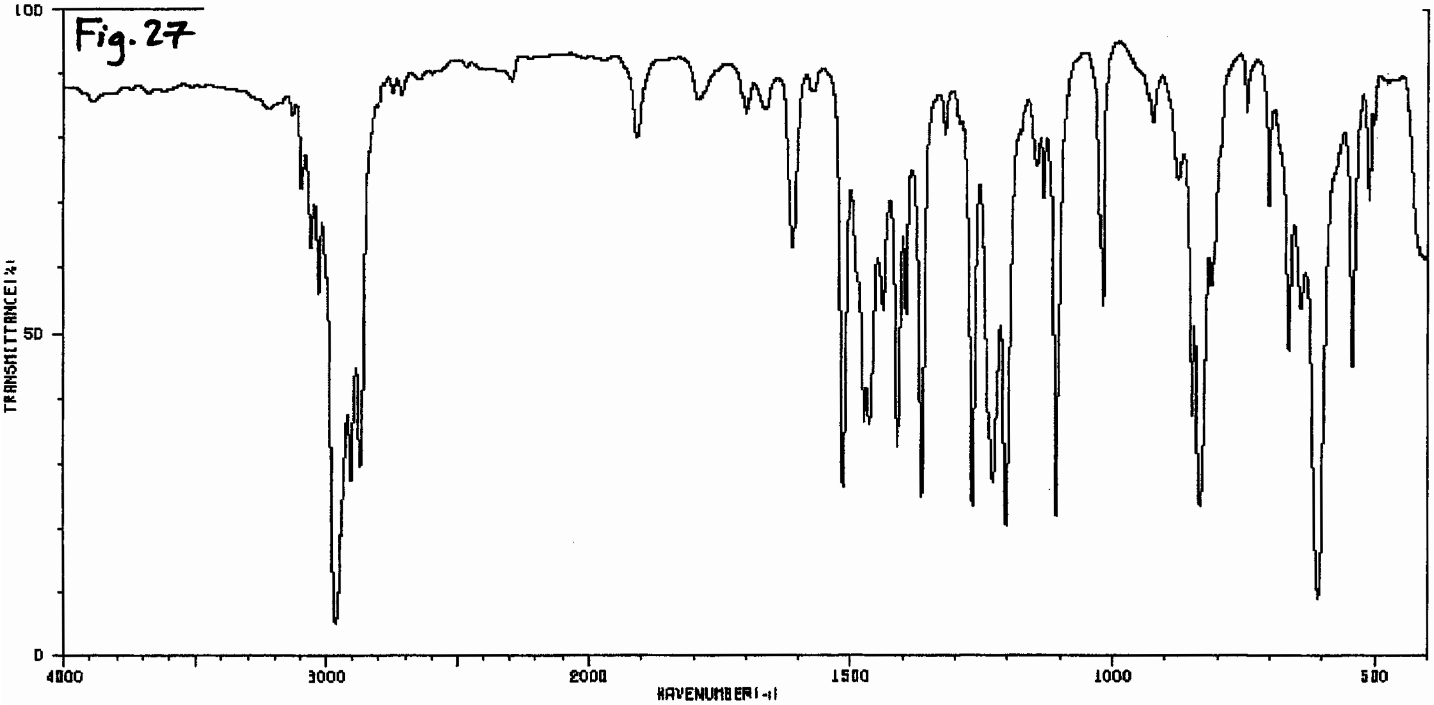
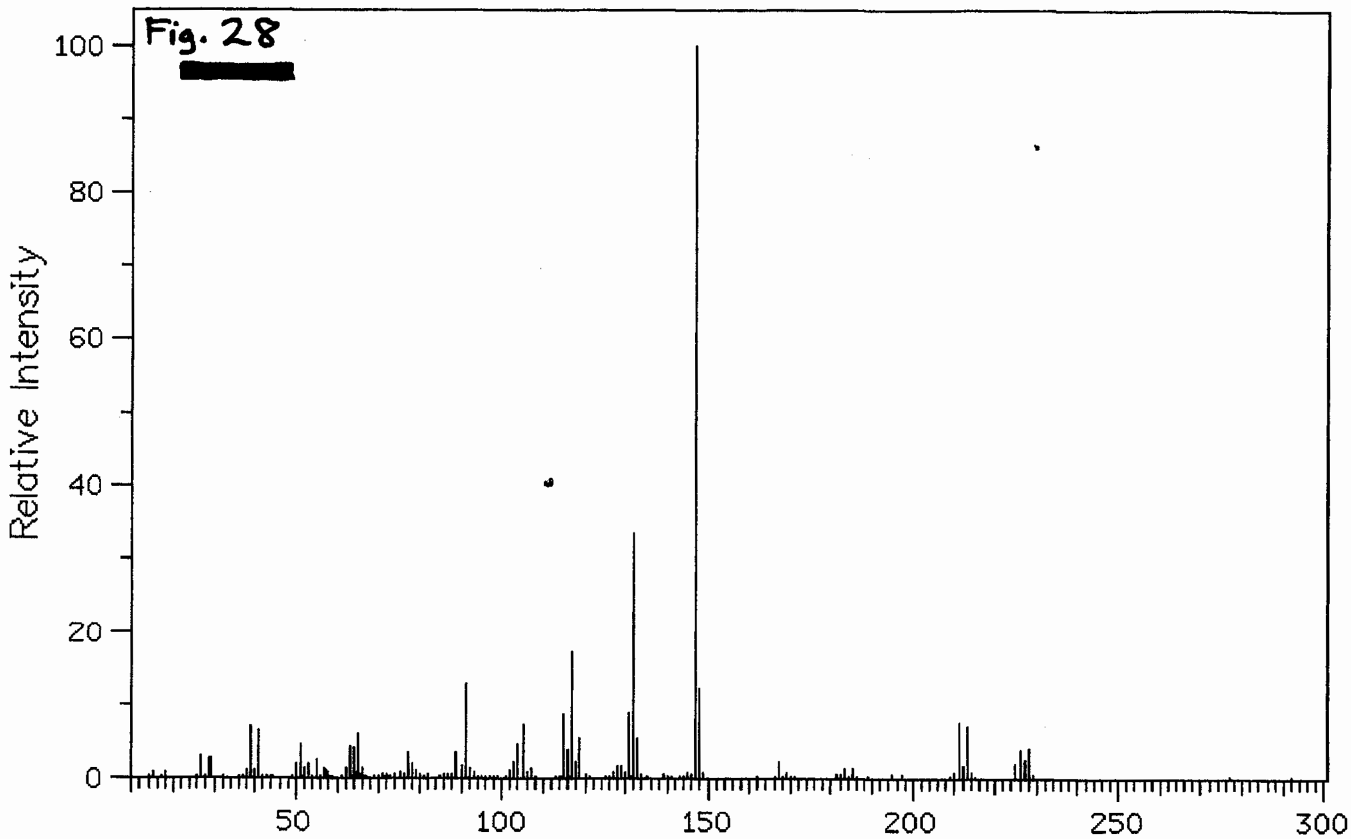



Fig. 28

[redacted]




m/z

| | | | | | |
|---|---|---|---|---|---|
| 39.0 | 7 | 78.0 | 2 | 131.0 | 9 |
| 40.0 | 1 | 79.0 | 1 | 132.0 | 33 |
| 41.0 | 6 | 89.0 | 3 | 146.0 | 0 |
| 50.0 | 1 | 90.0 | 1 | 147.0 | 100 |
| 51.0 | 4 | 91.0 | 12 | 148.0 | 12 |
| 52.0 | 1 | 92.0 | 1 | 167.0 | 2 |
| 53.0 | 1 | 102.0 | 1 | 183.0 | 1 |
| 55.0 | 2 | 103.0 | 2 | 185.0 | 1 |
| 57.0 | 1 | 104.0 | 4 | 211.0 | 7 |
| 57.5 | 1 | 105.0 | 7 | 212.0 | 1 |
| 62.0 | 1 | 107.0 | 1 | 213.0 | 7 |
| 63.0 | 4 | 115.0 | 8 | 225.0 | 2 |
| 64.0 | 4 | 116.0 | 3 | 226.0 | 3 |
| 65.0 | 6 | 117.0 | 17 | 227.0 | 2 |
| 66.0 | 1 | 118.0 | 2 | 228.0 | 4 |
| 77.0 | 3 | 119.0 | 5 | | |

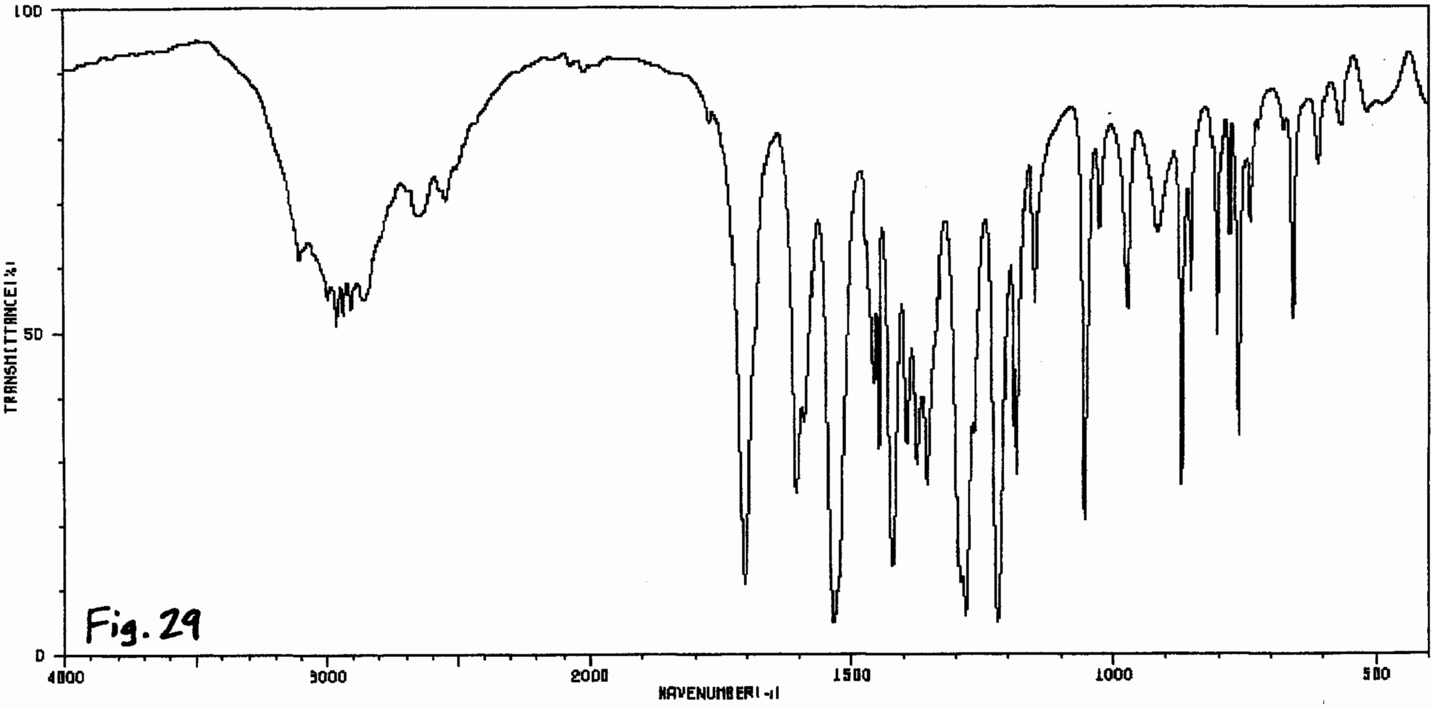


Fig. 29

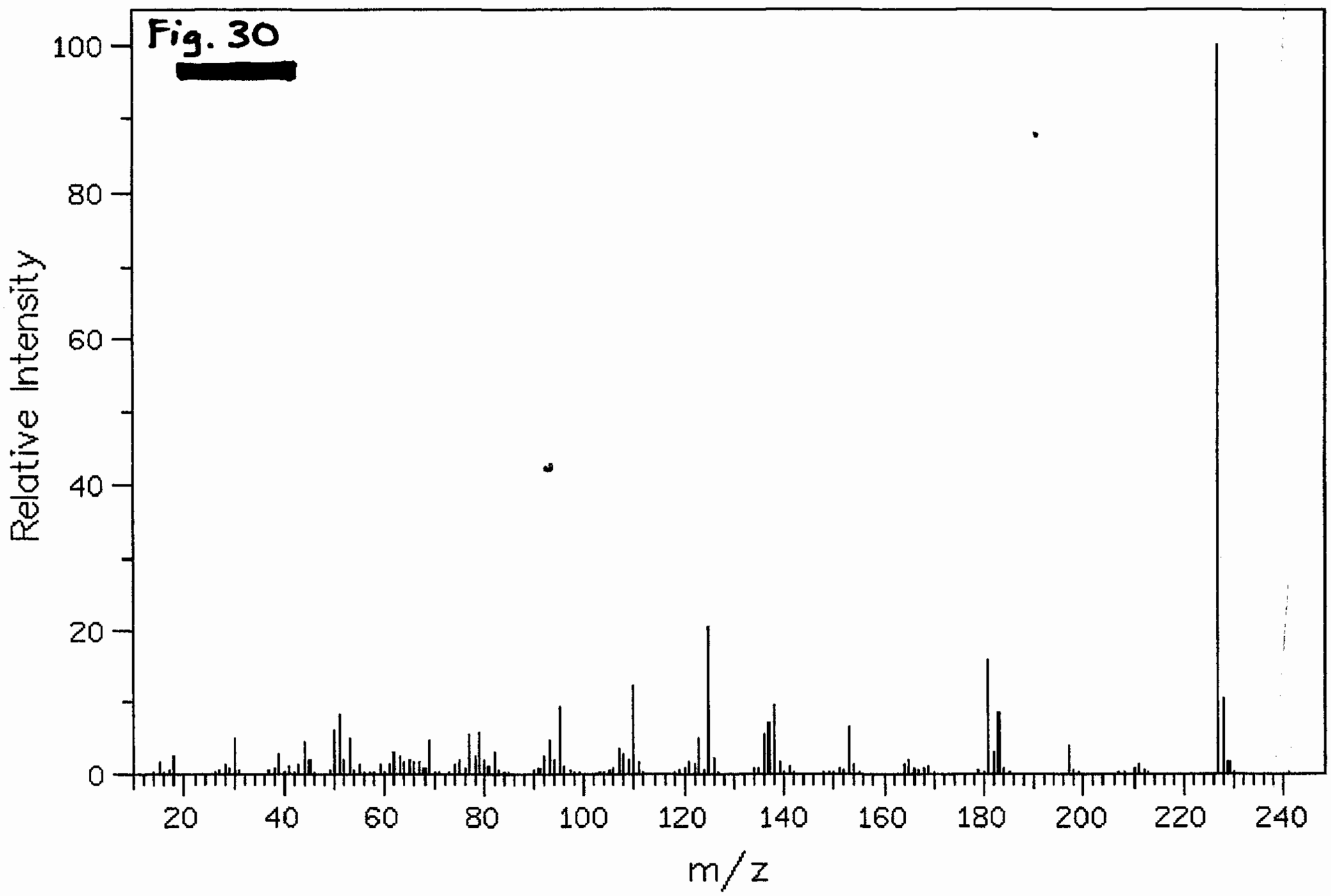


Fig. 30
[redacted]

(Fig. 30 continued on next page)

(Fig. 30, cont.)

| | |
|---|---|
| 15.0 | 1 |
| 18.0 | 2 |
| 28.0 | 1 |
| 30.0 | 5 |
| 39.0 | 2 |
| 41.0 | 1 |
| 43.0 | 1 |
| 44.0 | 4 |
| 45.0 | 1 |
| 50.0 | 6 |
| 51.0 | 8 |
| 52.0 | 1 |
| 53.0 | 4 |
| 55.0 | 1 |
| 59.0 | 1 |
| 61.0 | 1 |
| 62.0 | 3 |
| 63.0 | 2 |
| 64.0 | 1 |
| 65.0 | 1 |
| 66.0 | 1 |
| 67.0 | 1 |
| 69.0 | 4 |
| 74.0 | 1 |
| 75.0 | 1 |
| 77.0 | 5 |
| 78.0 | 2 |
| 79.0 | 5 |
| 80.0 | 1 |
| 81.0 | 1 |
| 82.0 | 3 |
| 92.0 | 2 |
| 93.0 | 4 |
| 94.0 | 1 |
| 95.0 | 9 |
| 107.0 | 3 |
| 108.0 | 2 |
| 109.0 | 1 |
| 110.0 | 12 |
| 111.0 | 1 |
| 121.0 | 1 |
| 122.0 | 1 |
| 123.0 | 5 |
| 125.0 | 20 |
| 126.0 | 2 |
| 136.0 | 5 |
| 137.0 | 7 |
| 138.0 | 9 |
| 139.0 | 1 |
| 141.0 | 1 |
| 153.0 | 6 |
| 154.0 | 1 |
| 164.0 | 1 |
| 165.0 | 1 |
| 169.0 | 1 |
| 181.0 | 15 |
| 182.0 | 3 |
| 183.0 | 8 |
| 197.0 | 3 |
| 213.0 | 0 |
| 227.0 | 100 |
| 228.0 | 10 |
| 229.0 | 1 |