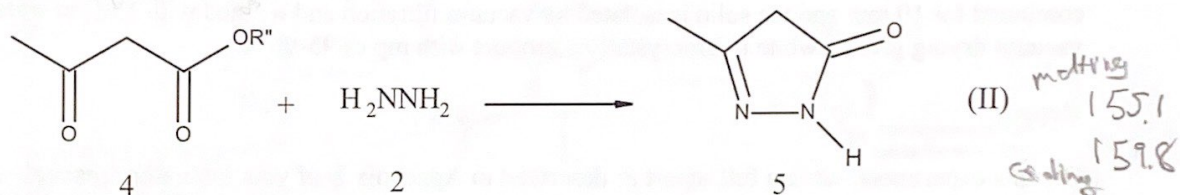
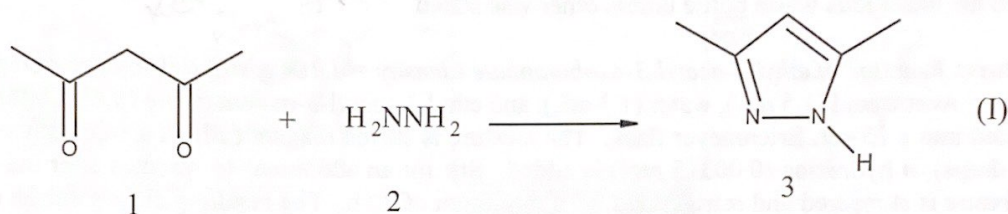


① 0.205 molting
10
② 152.3

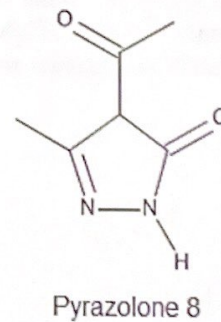
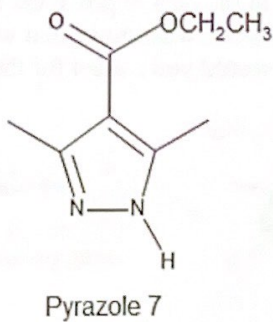
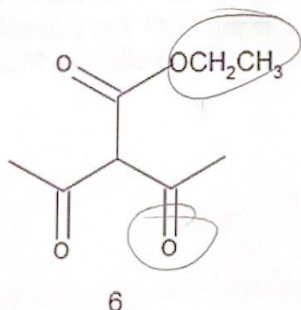
PATHWAY DETERMINATION
Experiment 2

Introduction

β -Dicarbonyl compounds react with hydrazine (2) to give products with a 5-membered ring containing two nitrogens. For example, β -diketones (1) react with hydrazine (2) to yield pyrazoles (3) via nucleophilic addition, followed by loss of water, at both keto groups (equation I) and β -ketoesters (4) react with hydrazine (2) to yield pyrazolones (5) via nucleophilic substitution at the ester group (equation II)



This chemistry is the basis of a puzzle-solving experiment. Does ethyl 2-acetyl-3-oxobutanoate (ethyl diacetoacetate) (6) react with hydrazine (2) like a β -diketone to give pyrazole (7) or like a β -ketoester to give pyrazolone (8). To solve the puzzle, 6 is to be reacted with hydrazine (2) to see if pyrazole (7) or pyrazolone (8) forms. The analysis of the products by ^1H NMR (proton nuclear magnetic resonance), IR (infrared spectroscopy), and GC/MS (gas chromatography coupled with mass spectroscopy) will be used to establish the structures as pyrazole (7) or pyrazolone (8).



NOTE: DO NOT SCALE UP THIS REACTION. PERFORM THE REACTION ON THE SCALE INDICATED IN THE PROCEDURE!!

CAUTION: Hydrazine is highly toxic, and a cancer suspect agent. Hydrazine should be used in the hood; eye and hand protection should be worn. Hydrazine is not to be stored in the laboratory. Therefore, when you require hydrazine you must request it from the instructor and return it immediately after use.

Wear safety glasses during the entire laboratory period and use gloves when handling any chemicals. All chemicals, reactions and procedures should be used or performed in the hood. All organic wastes should be put in the hazardous waste bottle unless otherwise stated.

Procedure: Reaction of ethyl 2-acetyl-3-oxobutanoate (density = 1.104 g/mL) (ethyl diacetoacetate) with hydrazine: Acetic acid (1.5 mL), water (1.3 mL), and ethyl 2-acetyl-3-oxobutanoate (0.48g, 0.00279 mol) are placed into a 25-mL Erlenmeyer flask. The mixture is stirred magnetically in an ice bath while 0.10 mL (2 drops) of hydrazine (0.00315 mol) is added. Stir for an additional 15 minutes after the addition. The mixture is stoppered and refrigerated for a minimum of 20 h. The resulting clear solution is poured into 3.0 mL of 15 M ammonia, which was being stirred in an ice bath. White solid forms. Stirring is continued for 10 min and the solid is isolated by vacuum filtration and washed with 1mL of water. Air or vacuum drying gives a white microcrystalline product with mp of 95-96 °C.

Report

For this experiment, write a full report as described in Appendix B of your laboratory manual. Attention to detail is essential. Consider and elaborate on all relevant aspects of the seven required sections to be included in the report. Mechanisms of the reactions being explored should be included as well as assignment of all distinguishing spectroscopic features.

Organic Chemistry 242L Pre Lab / Pathway Determination

- Using line-bond structures, draw a complete and concise reaction scheme. Include **only the essential reagents**. Under each structure write the molecular formula and molecular weight.
- Calculate the theoretical yield for the reaction and show all calculations.
- Briefly state the objective of the experiment and how the outcome of the experiment will be determined. What should you see in the data to prove the identity of the product? For example, how many ^{13}C and ^1H NMR absorptions and what molecular weight should be observed in the MS. What functional groups and frequencies would you expect for the IR?



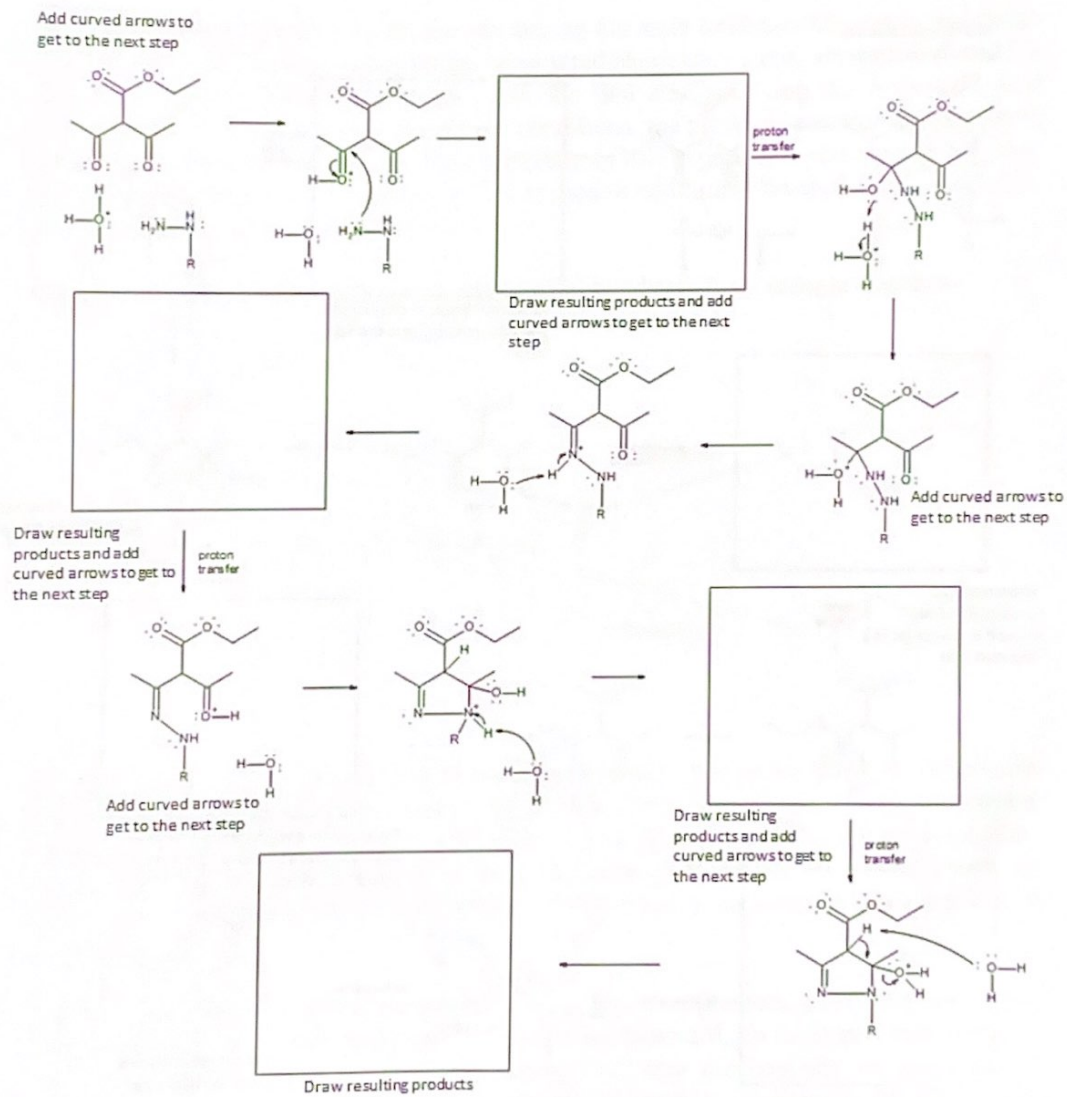
mass spectrum

IR

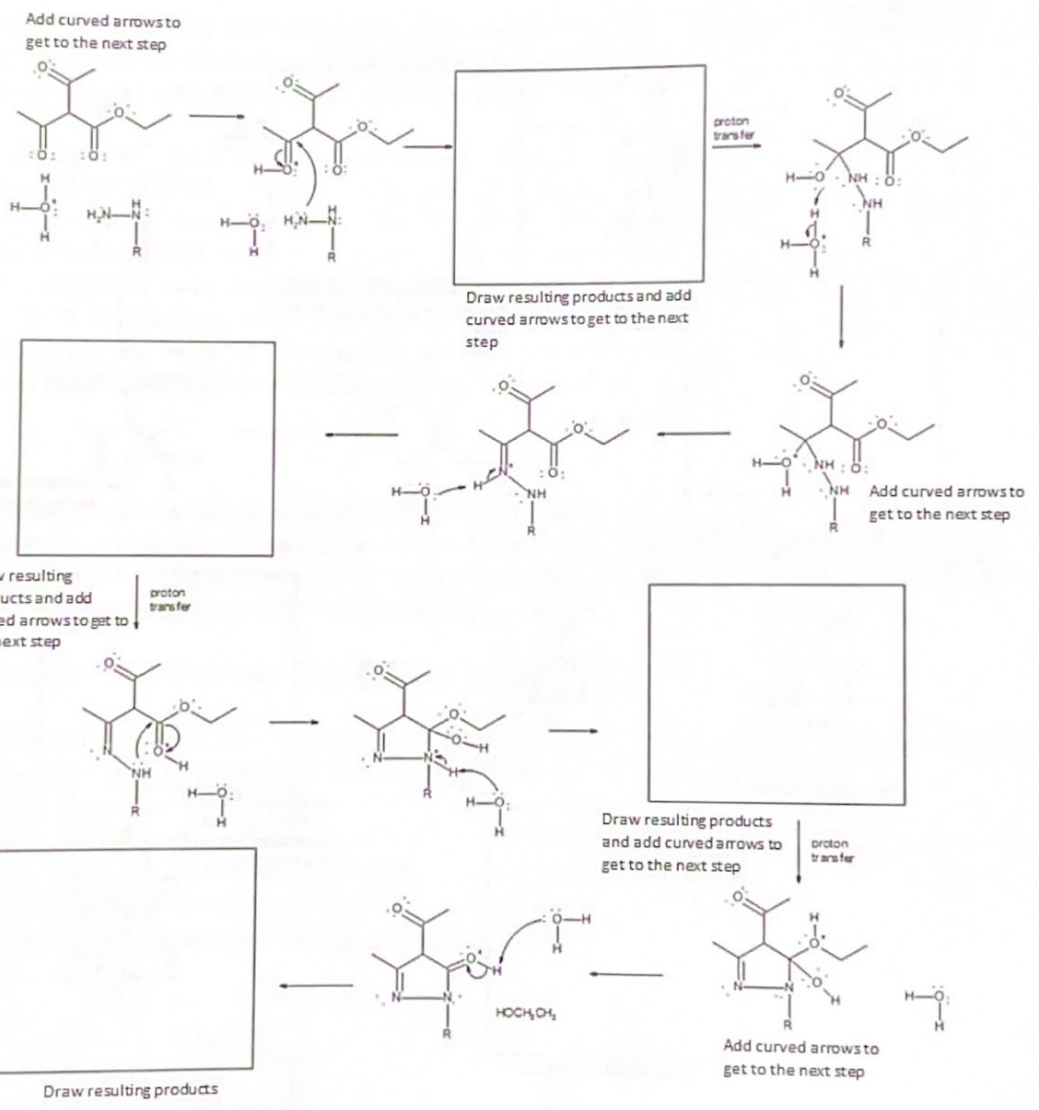
^1H -NMR

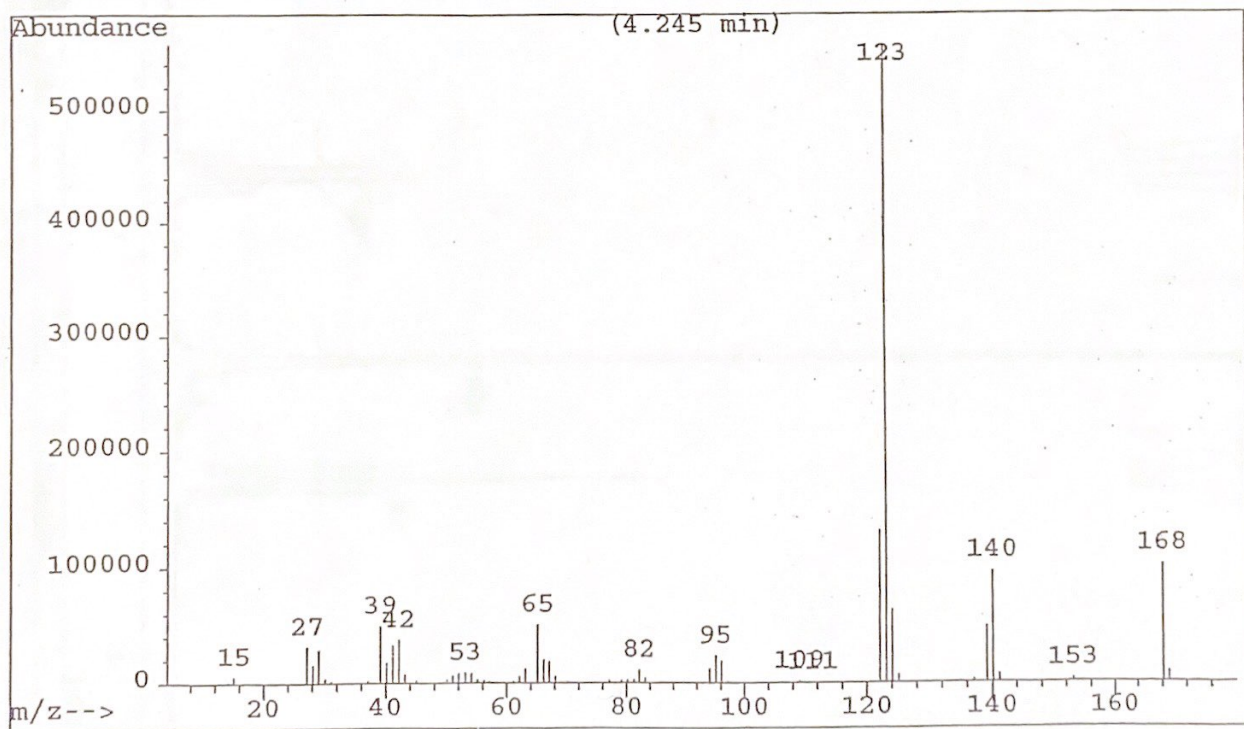
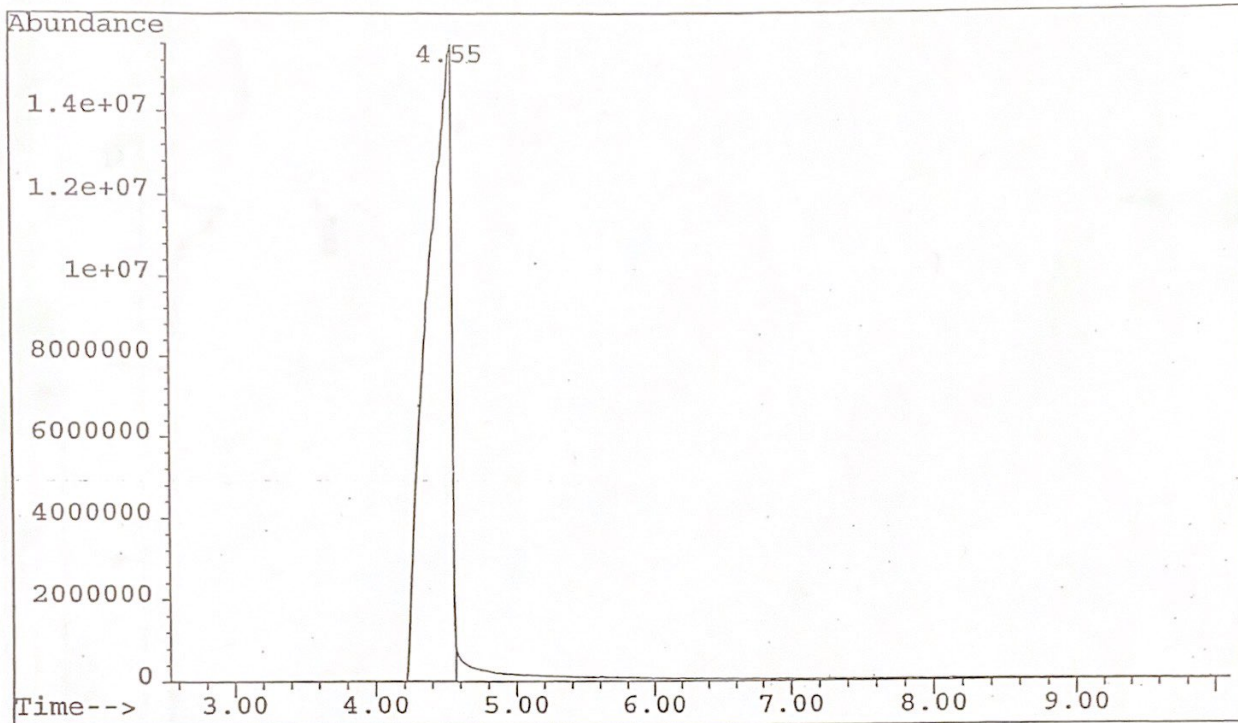
^{13}C -NMR

4. Draw the resulting structure in each of the boxes, add all missing curved arrows and formal charges, and label all unlabeled elementary steps to complete the mechanism shown below.

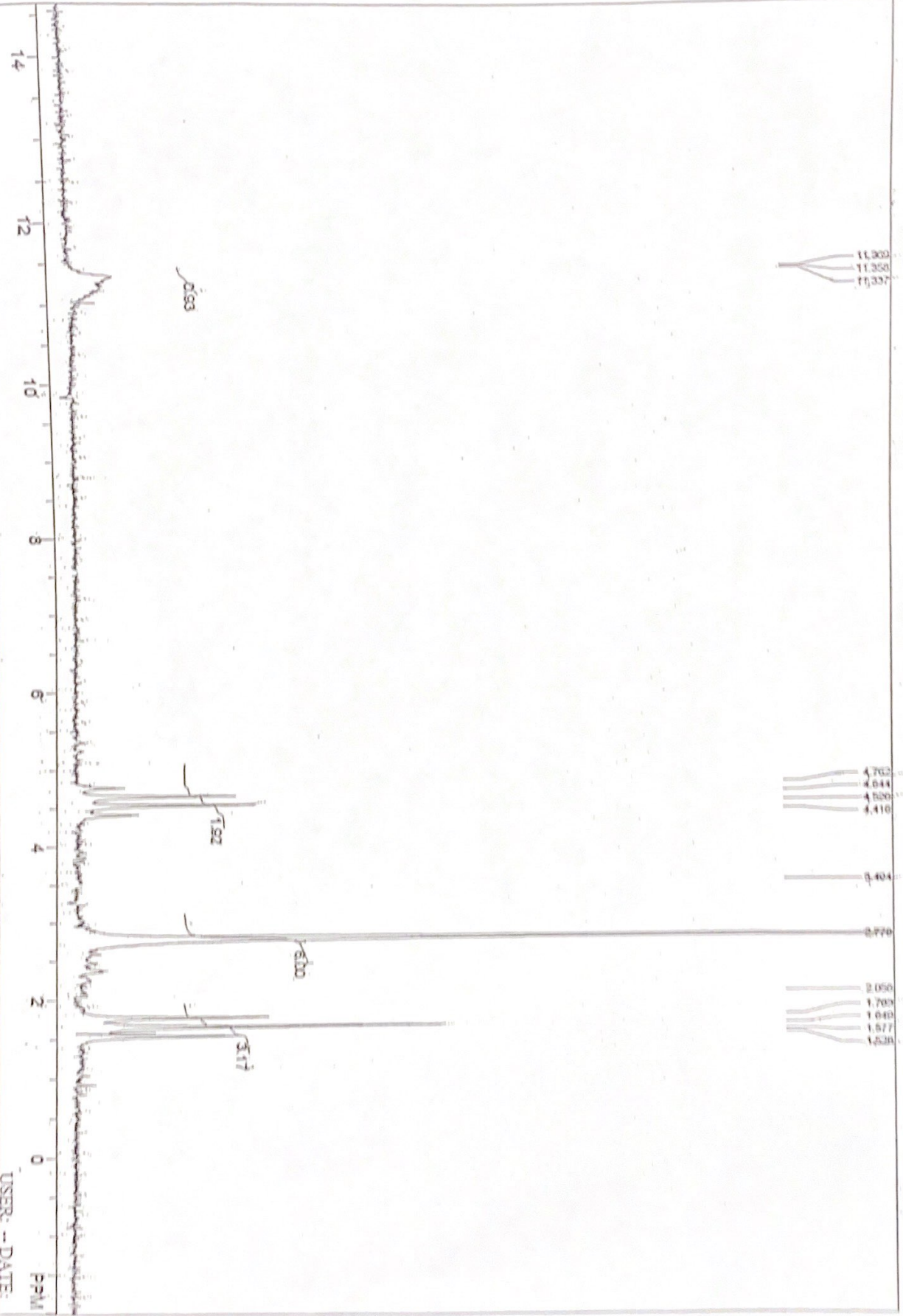


Note: question 4 continues on the following page.

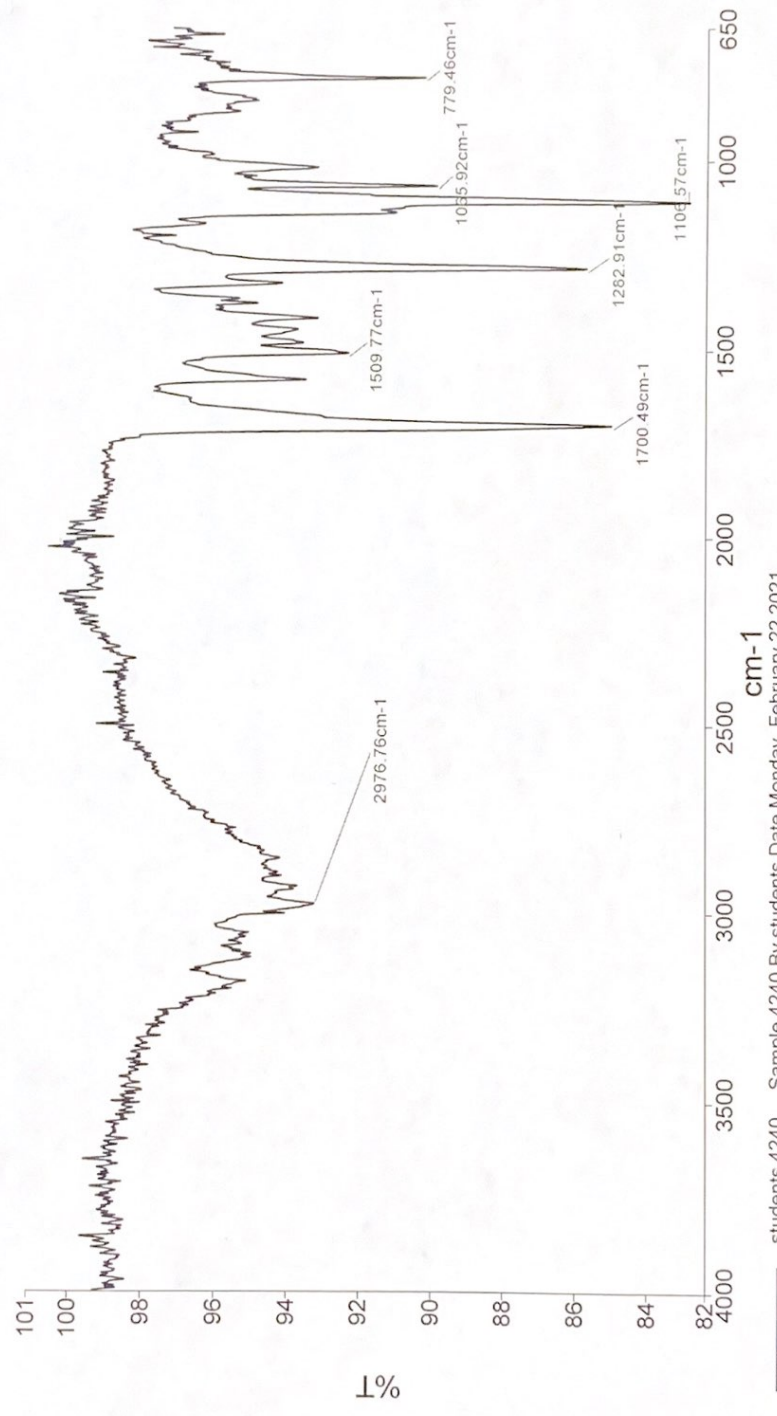




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