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APPENDIX

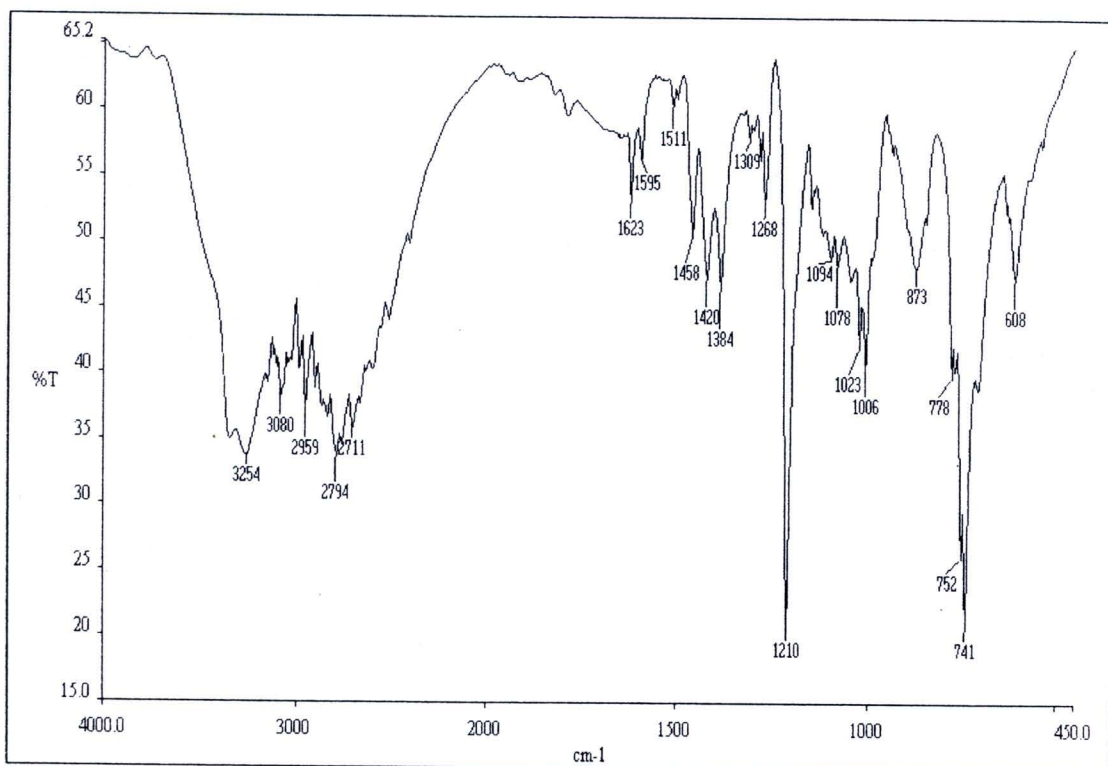


Figure 1 IR spectrum of 1*H*-benzo[*d*][1,2,3]triazole (**1a**)

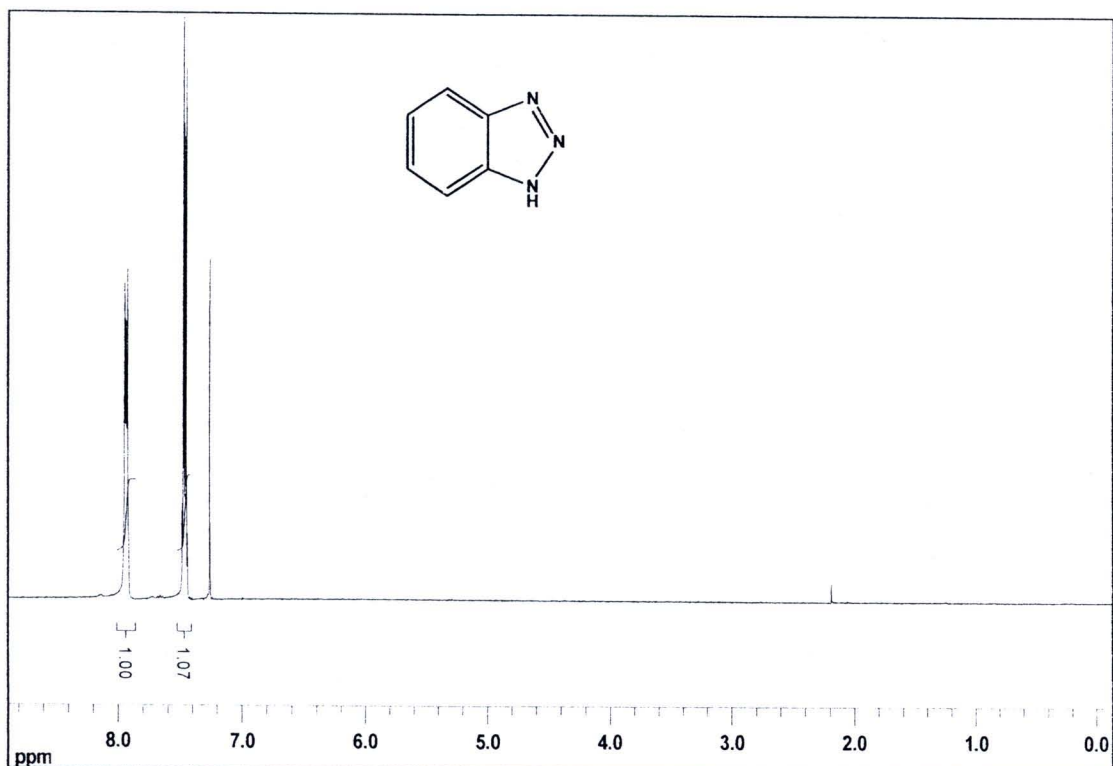


Figure 2 ¹H NMR spectrum of 1*H*-benzo[*d*][1,2,3]triazole (**1a**)

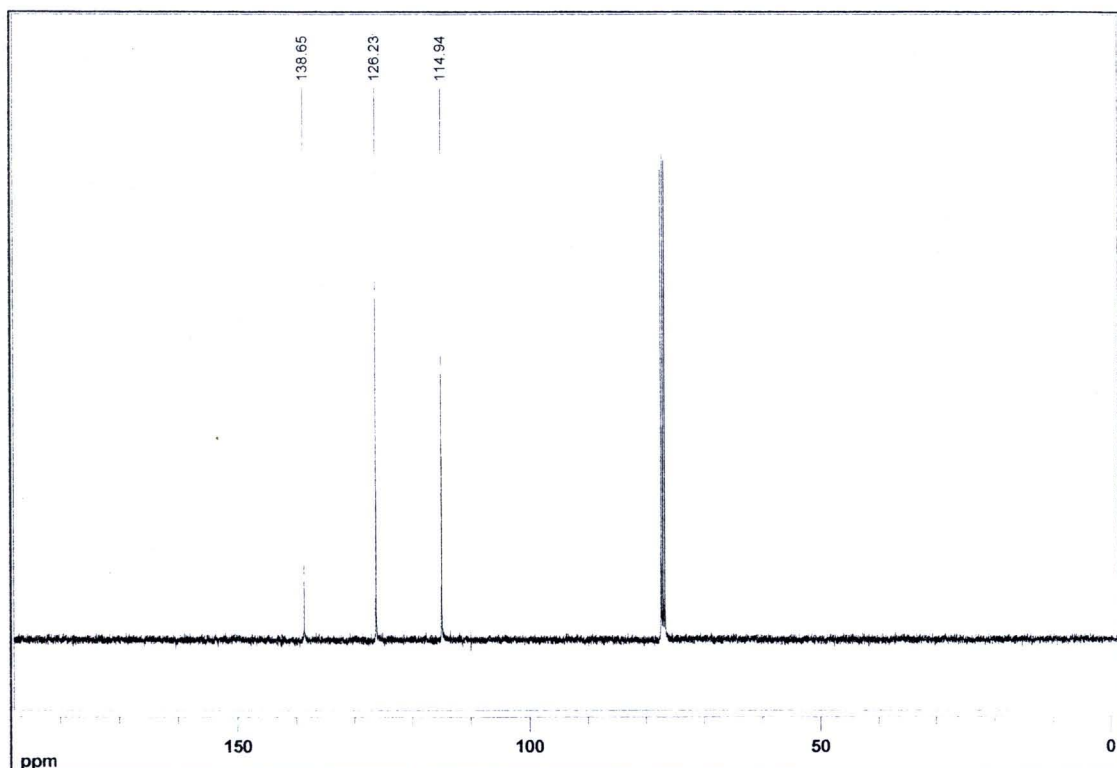


Figure 3 ^{13}C NMR spectrum of 1H-benzo[d][1,2,3]triazole (**1a**)

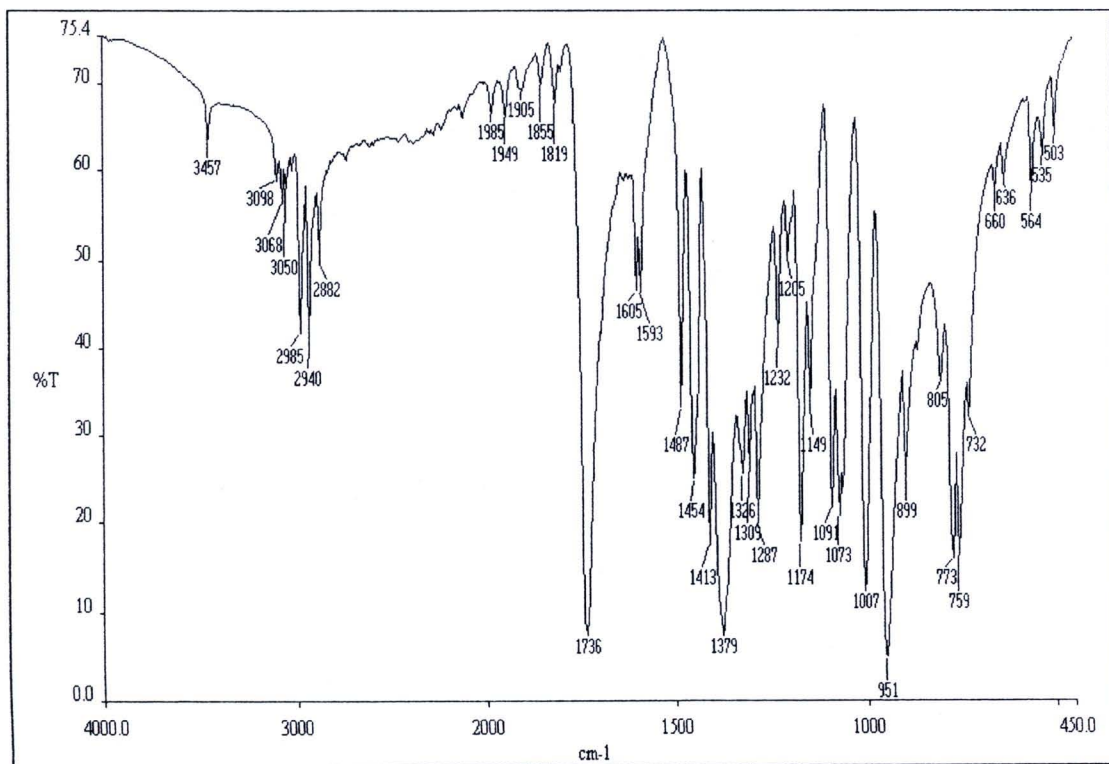


Figure 4 IR spectrum of 1-(1H-benzo[d][1,2,3]triazol-1-yl)propan-1-one (**2a**)

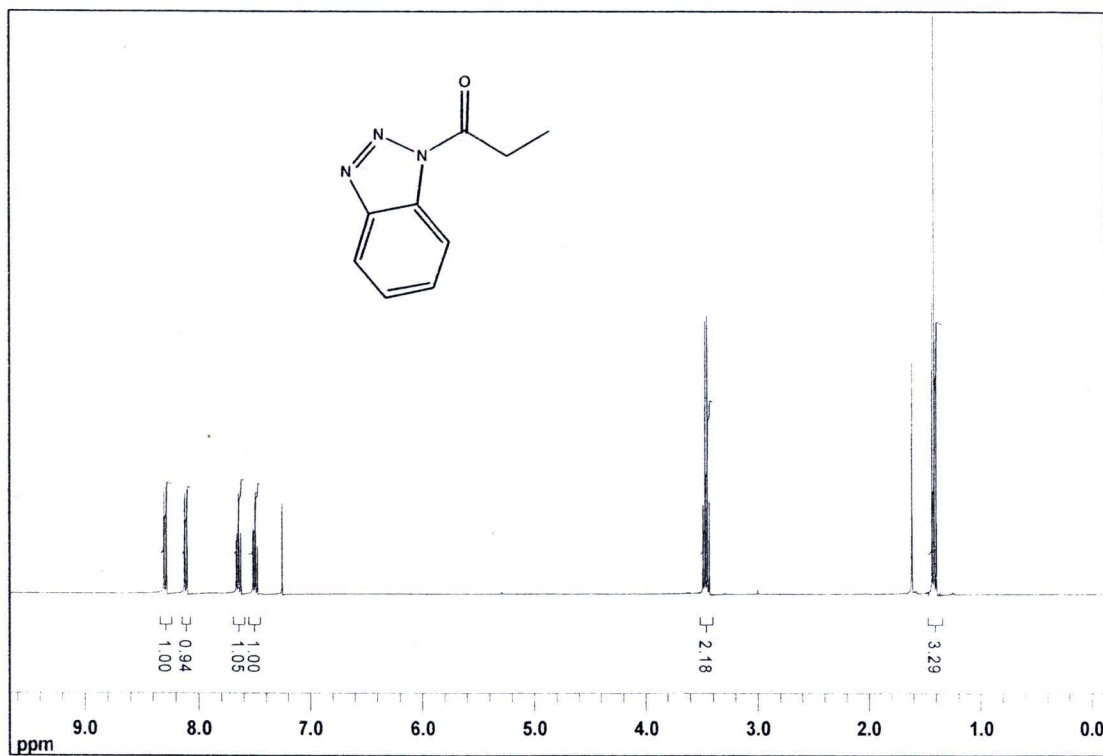


Figure 5 ^1H NMR spectrum of 1-(1H-benzo[d][1,2,3]triazol-1-yl)propan-1-one (2a)

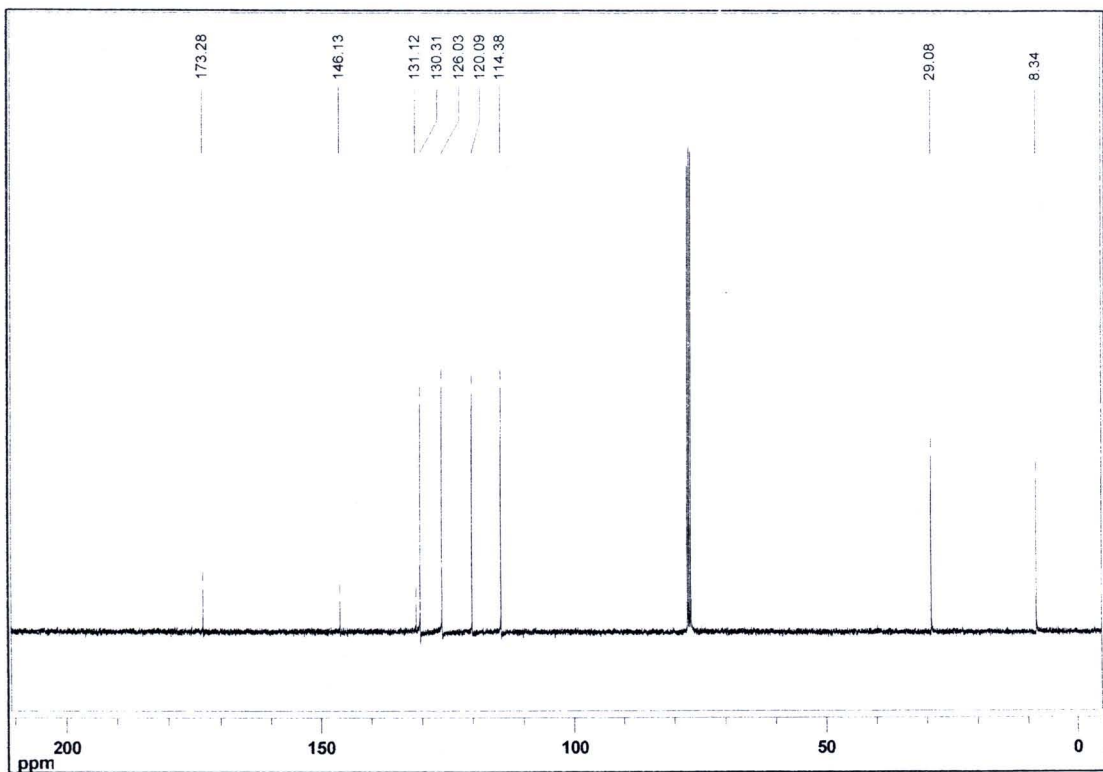


Figure 6 ^{13}C NMR spectrum of 1-(1H-benzo[d][1,2,3]triazol-1-yl)propan-1-one (2a)

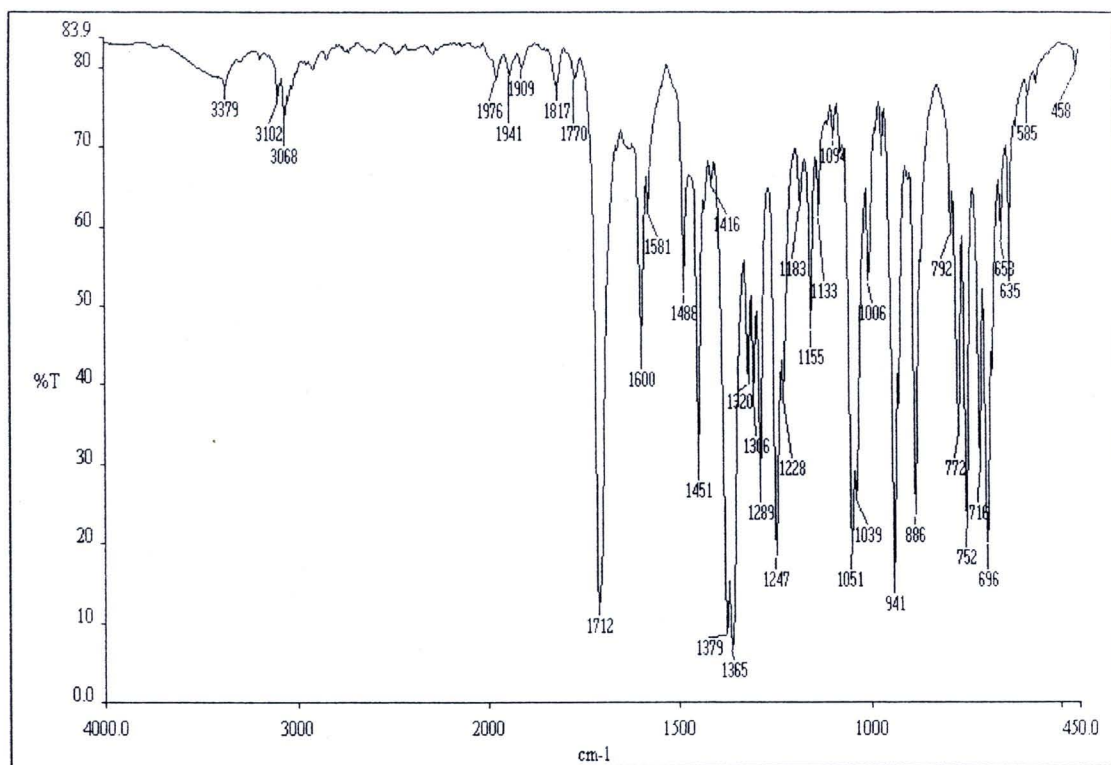


Figure 7 IR spectrum of (1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methanone (2b)

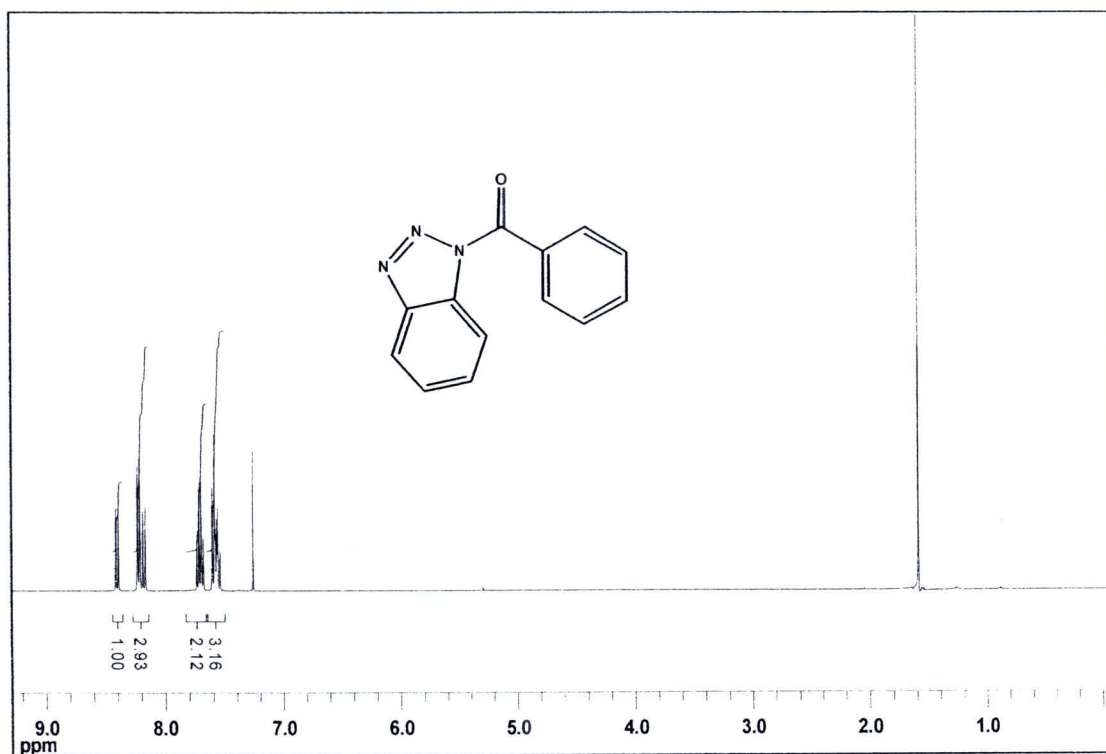


Figure 8 ^1H NMR spectrum of (1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methanone (2b)

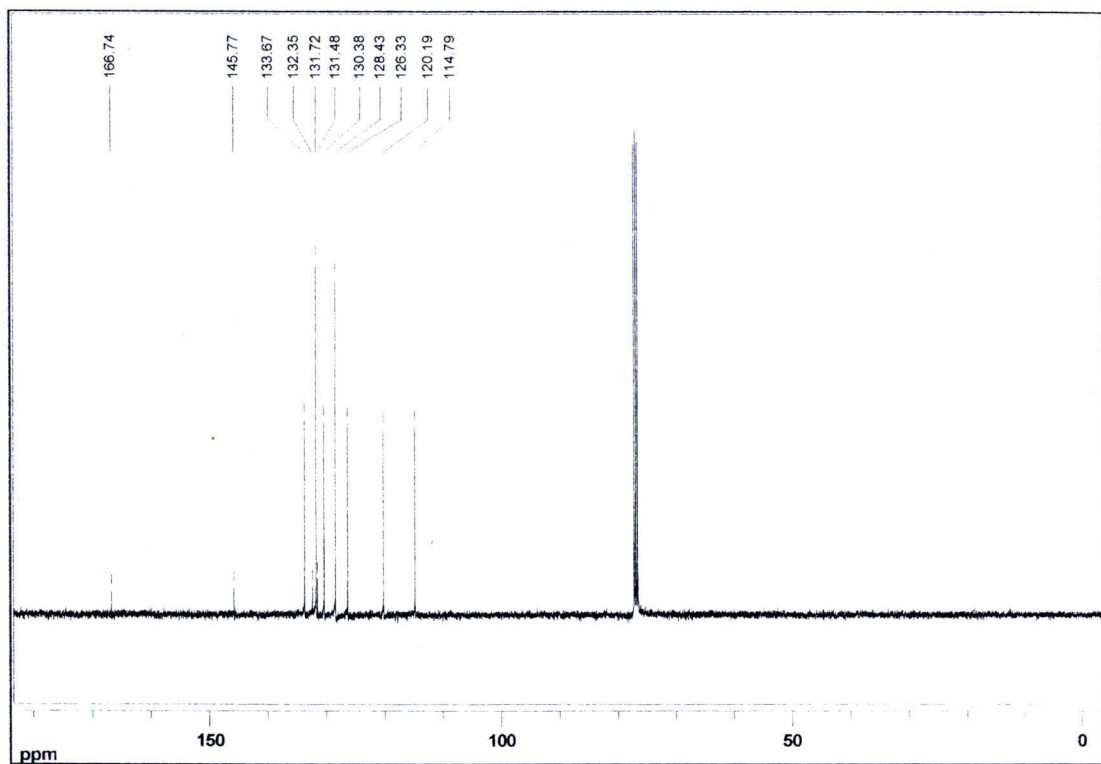


Figure 9 ^{13}C NMR spectrum of (1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methanone (2b)

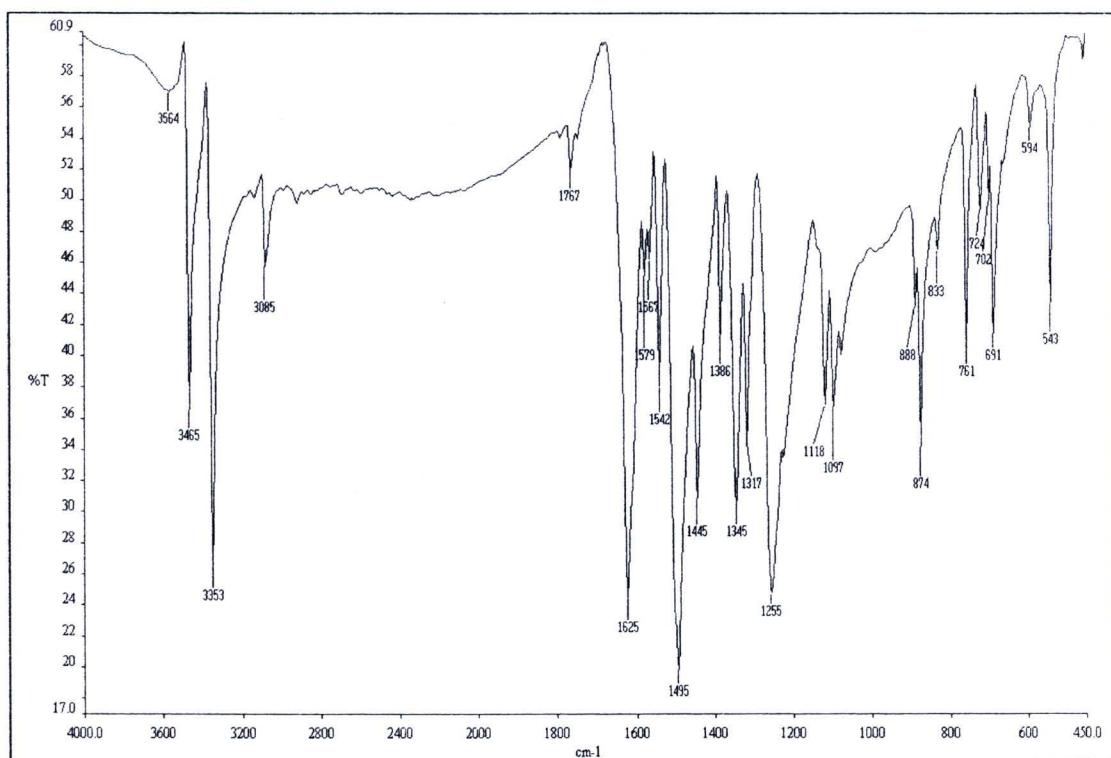


Figure 10 IR spectrum of 2,4-dibromo-6-nitroaniline (9)

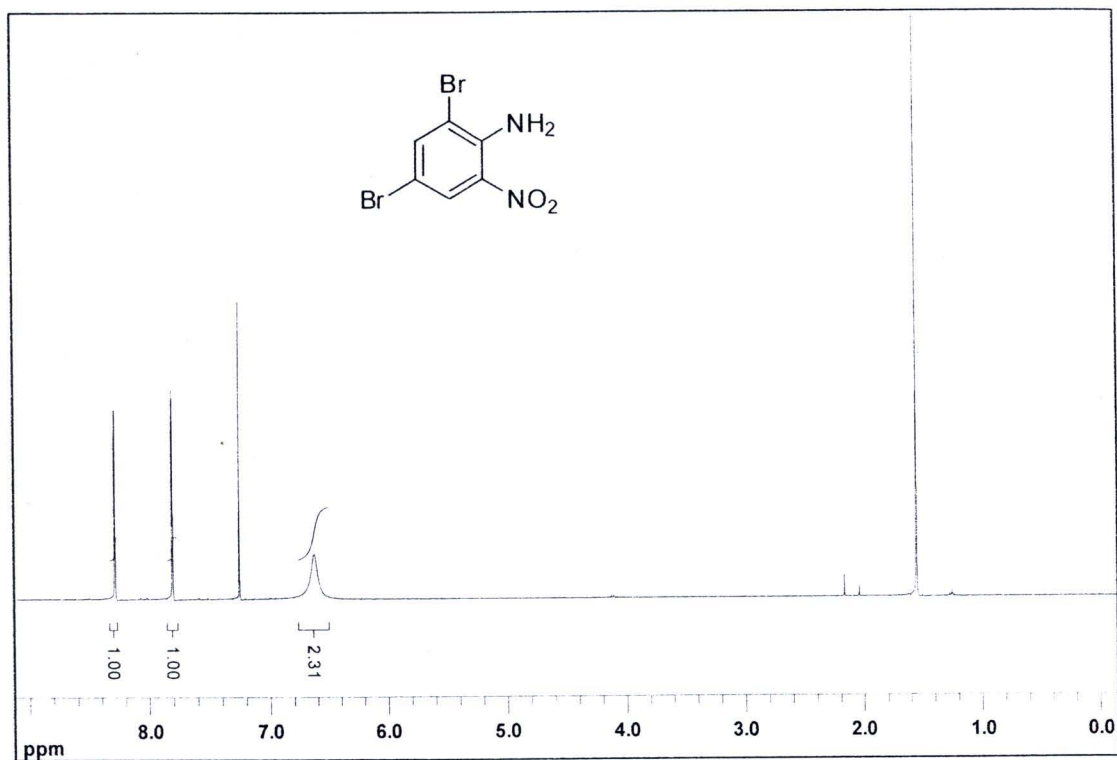


Figure 11 ^1H NMR spectrum of 2,4-dibromo-6-nitroaniline (9)

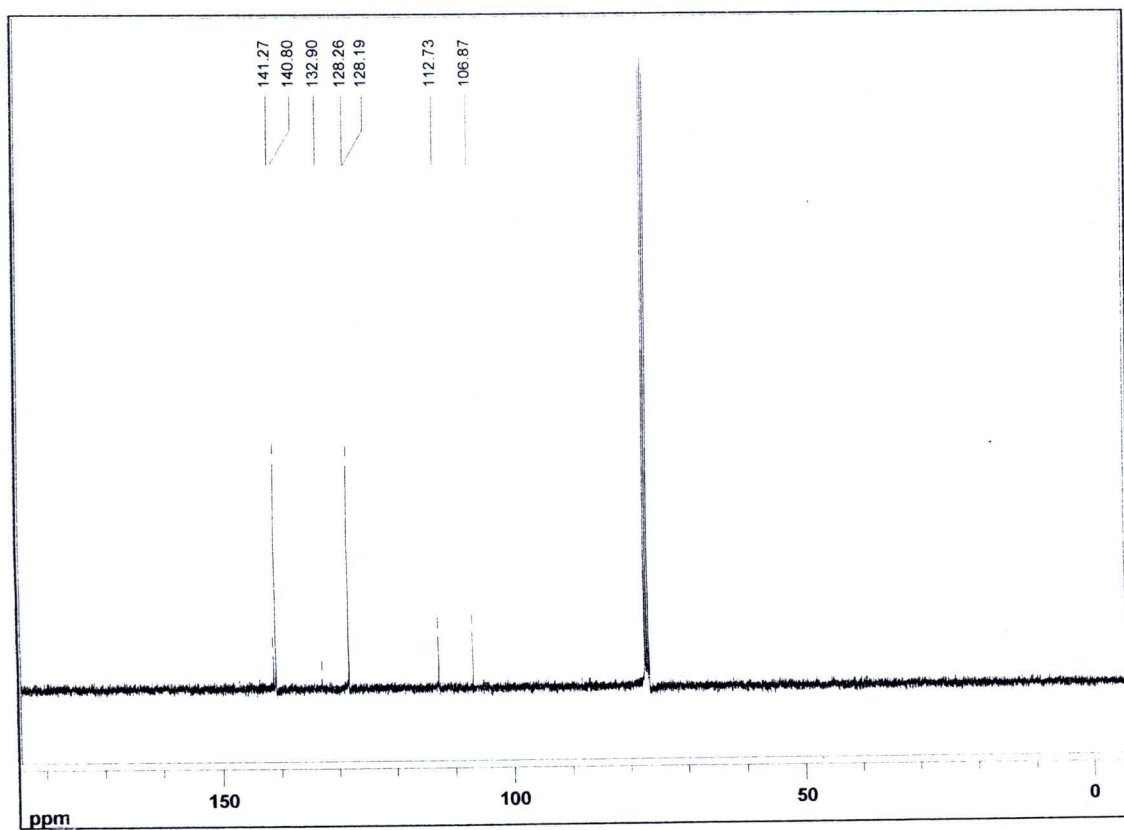


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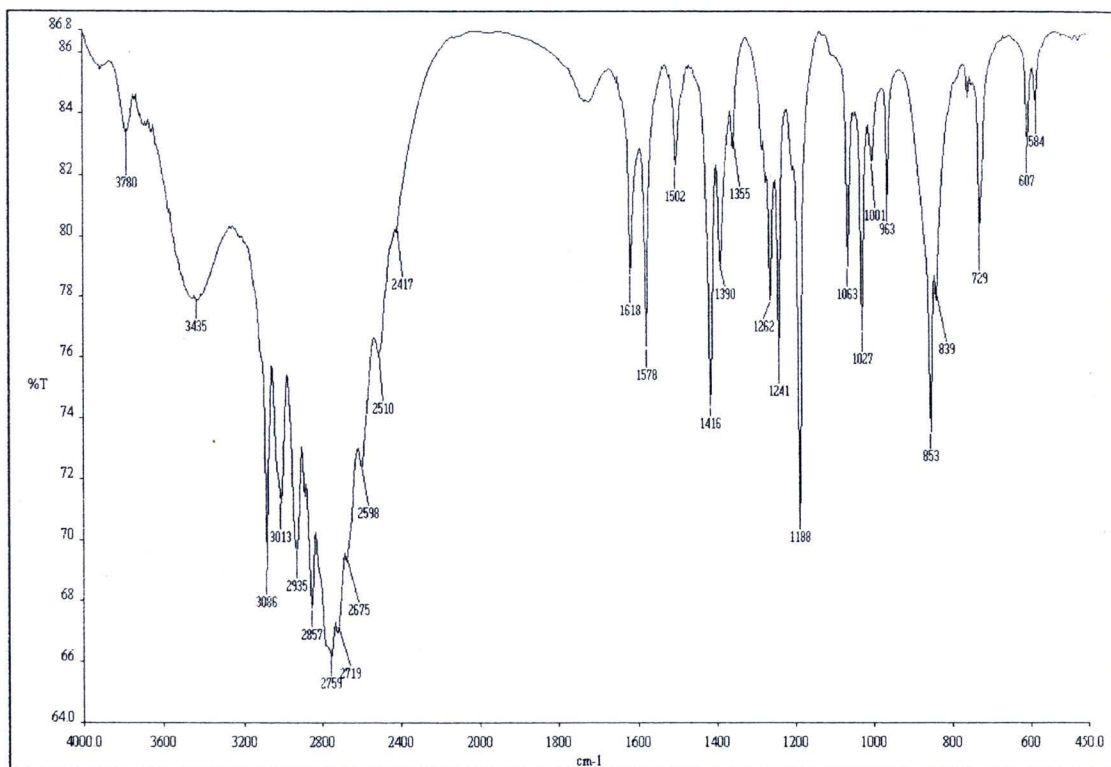


Figure 13 IR spectrum of 4,6-dibromo-1H-benzo[d][1,2,3]triazole (11a)

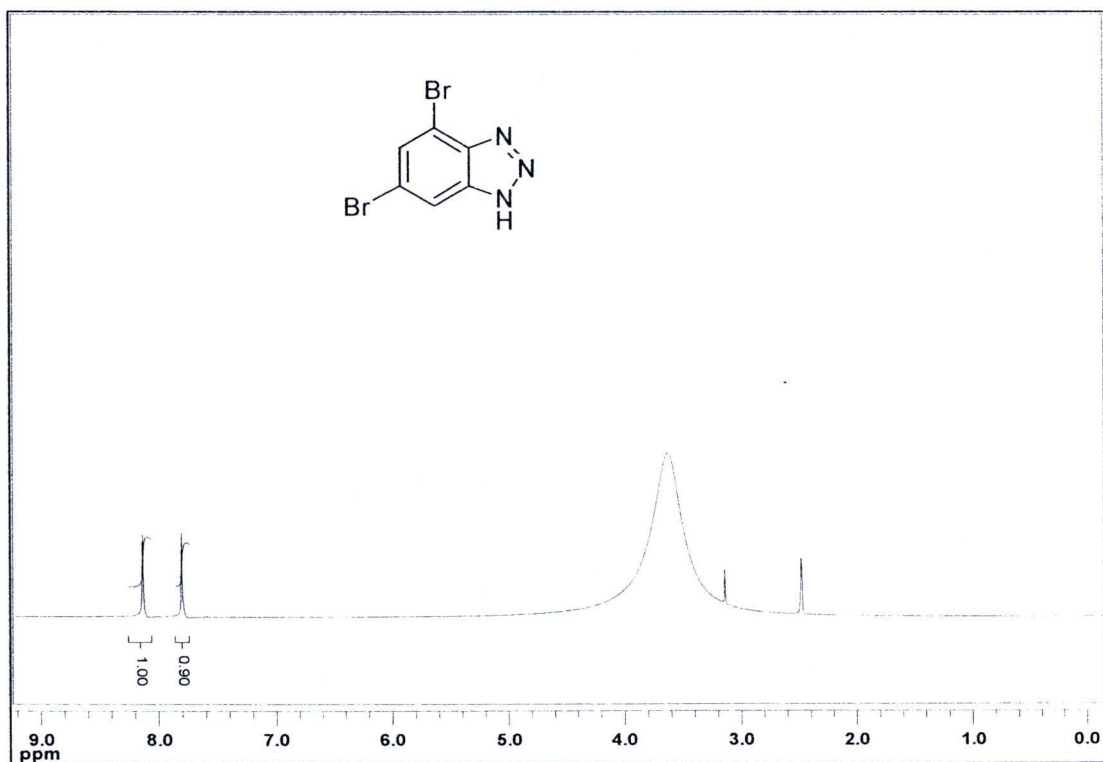


Figure 14 ¹H NMR spectrum of 4,6-dibromo-1H-benzo[d][1,2,3]triazole (11a)

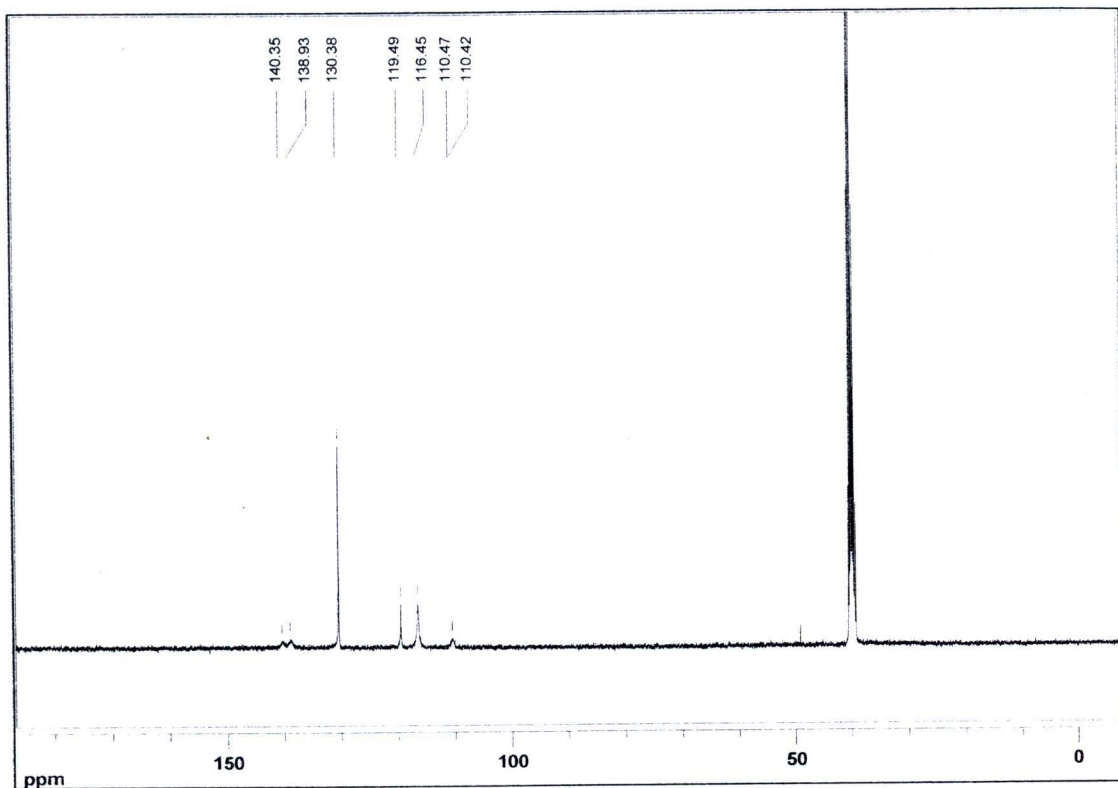


Figure 15 ¹³C NMR spectrum of 4,6-dibromo-1H-benzo[d][1,2,3]triazole (11a)

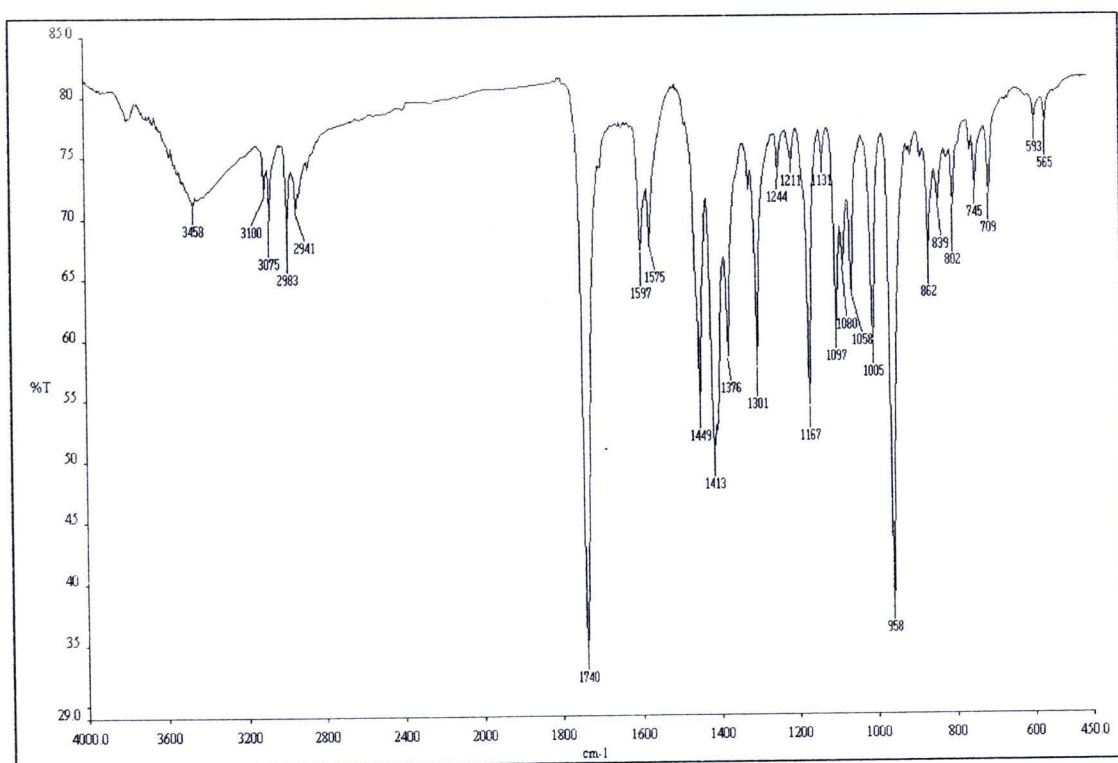


Figure 16 IR spectrum of 5,7-dibromo-1H-benzo[d][1,2,3]triazol-1-yl(phenyl)methanone (12a)

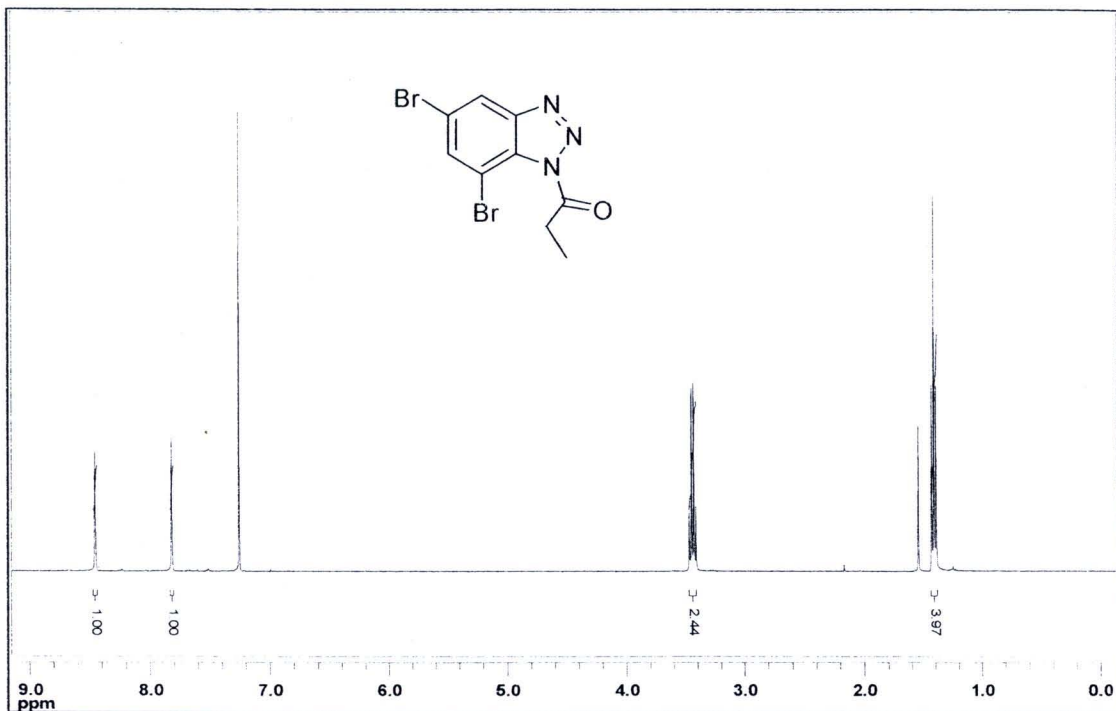


Figure 17 ^1H NMR spectrum of 5,7-dibromo-1H-benzo[d][1,2,3]triazol-1-yl-(phenyl)methanone (**12a**)

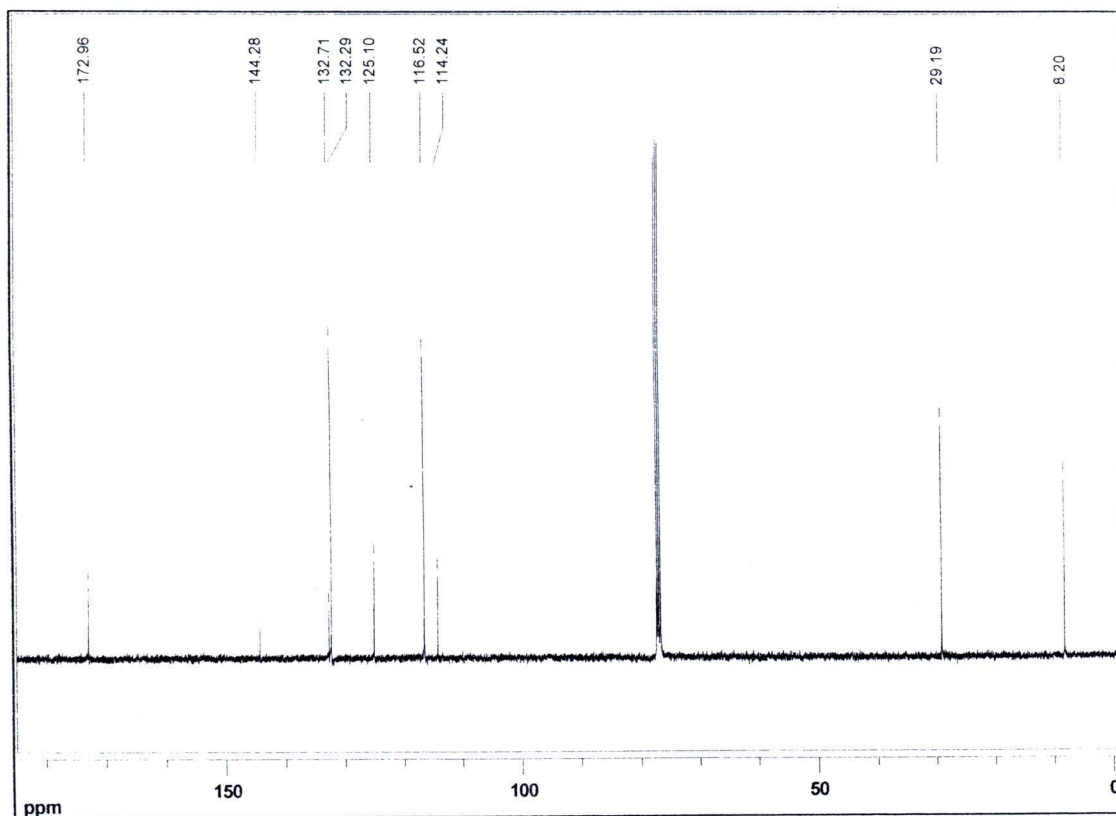


Figure 18 ^{13}C NMR spectrum of 5,7-dibromo-1H-benzo[d][1,2,3]triazol-1-yl-(phenyl)methanone (**12a**)

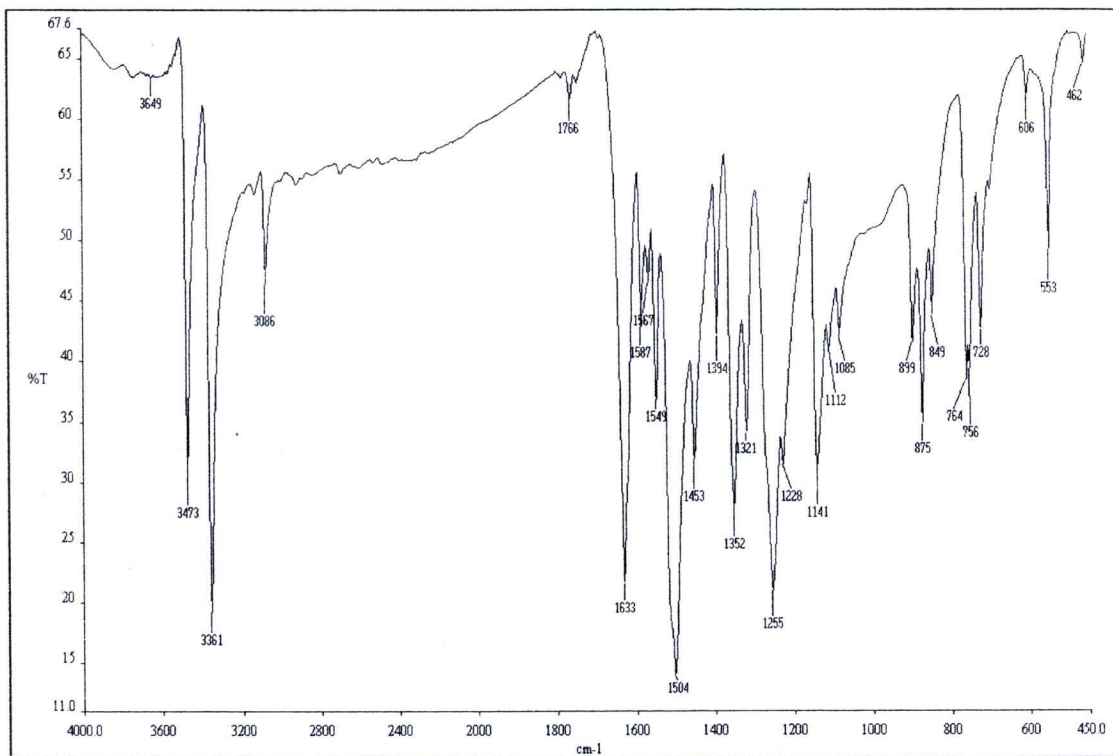


Figure 19 IR spectrum of 2,4-dichloro-6-nitroaniline (**9b**)

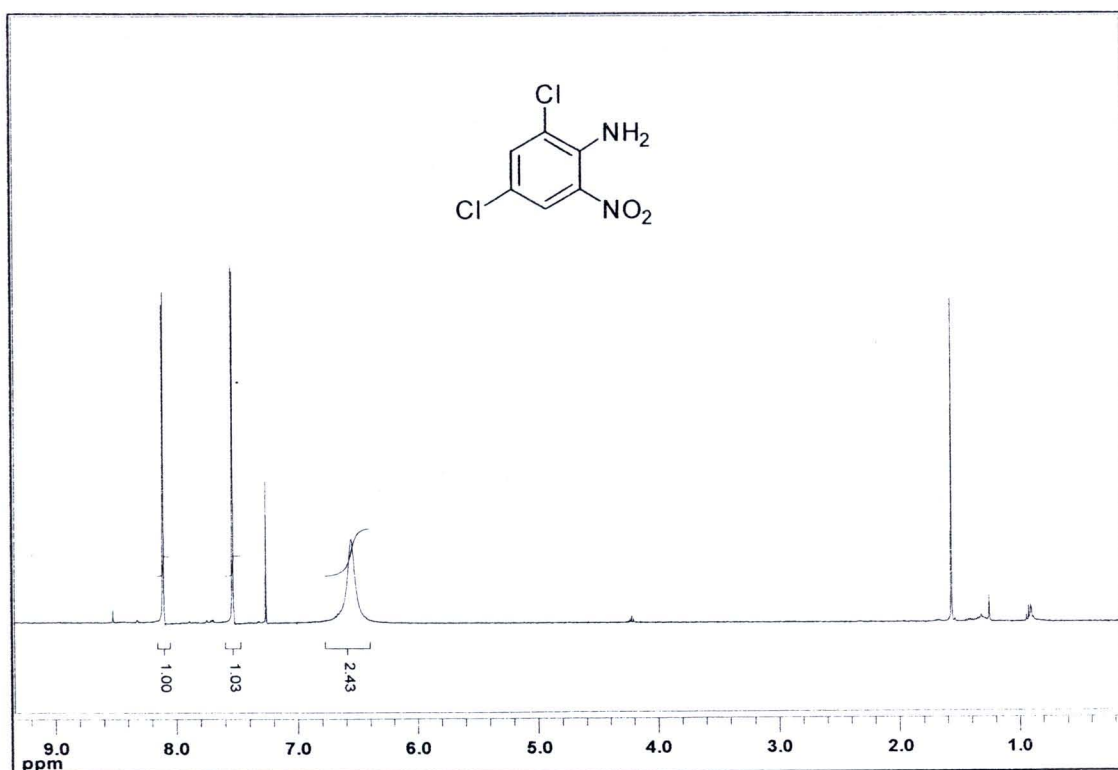


Figure 20 ¹H NMR spectrum of 2,4-dichloro-6-nitroaniline (**9b**)

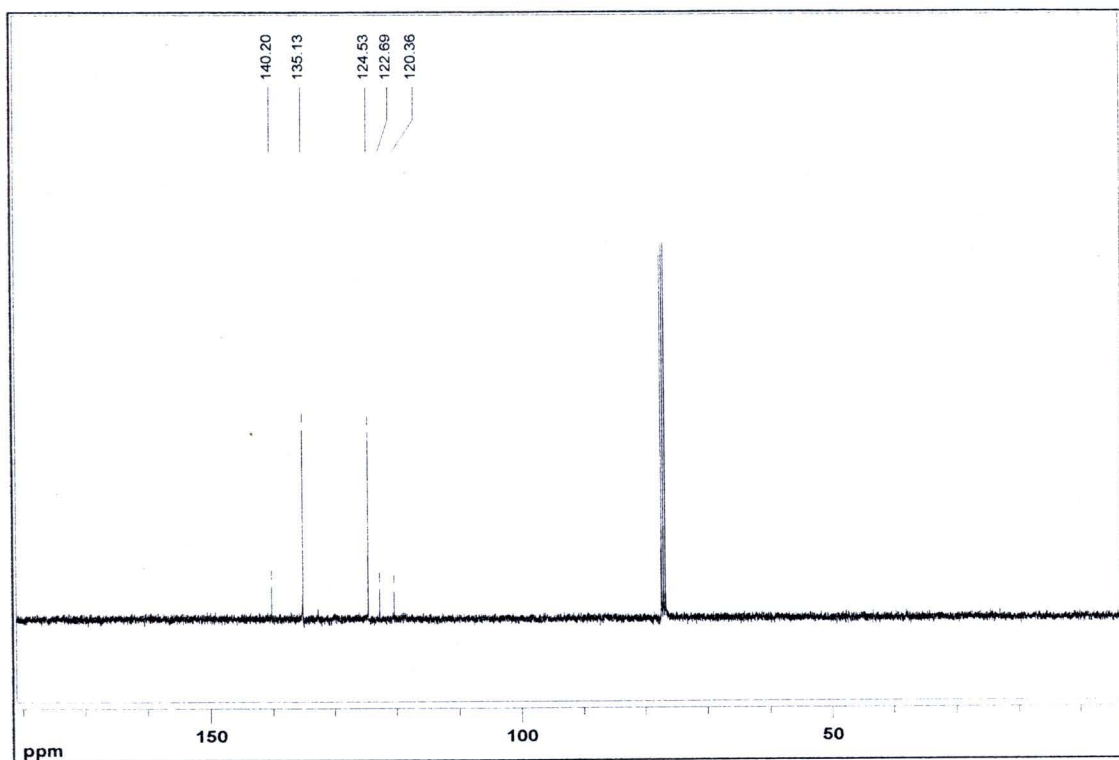


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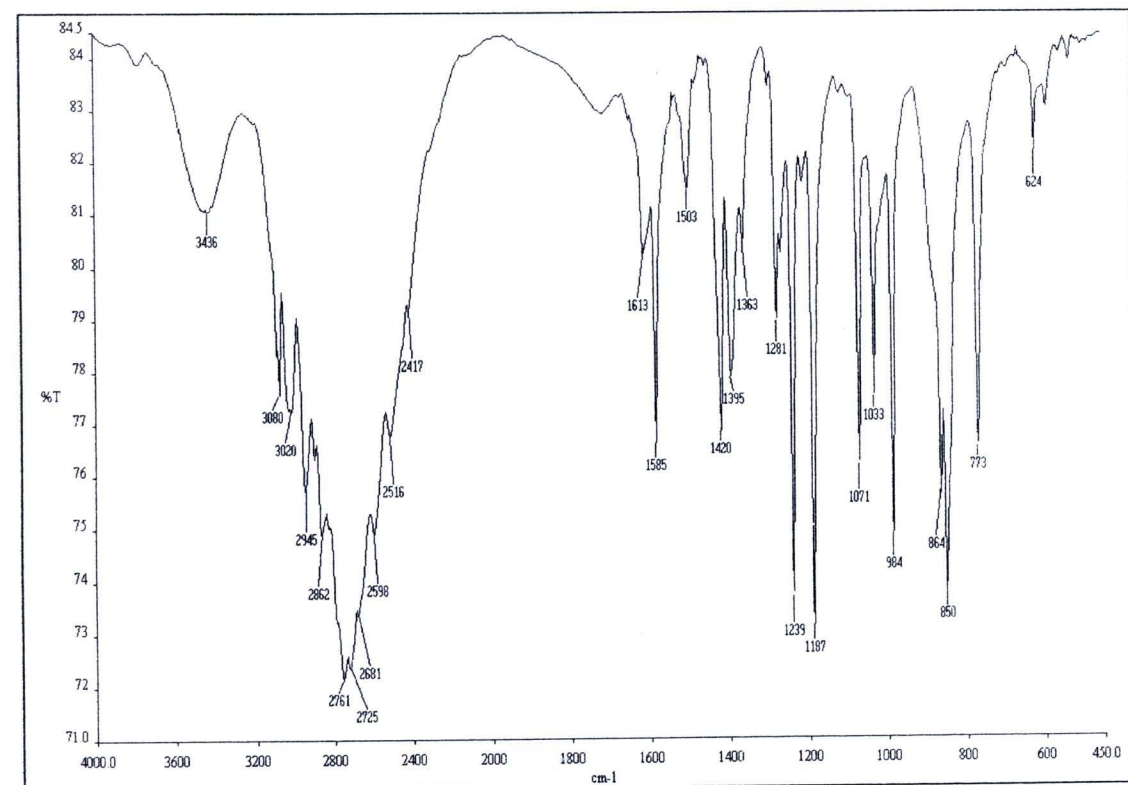


Figure 22 IR spectrum of 4,6-dichloro-1H-benzo[d][1,2,3]triazole (11b)

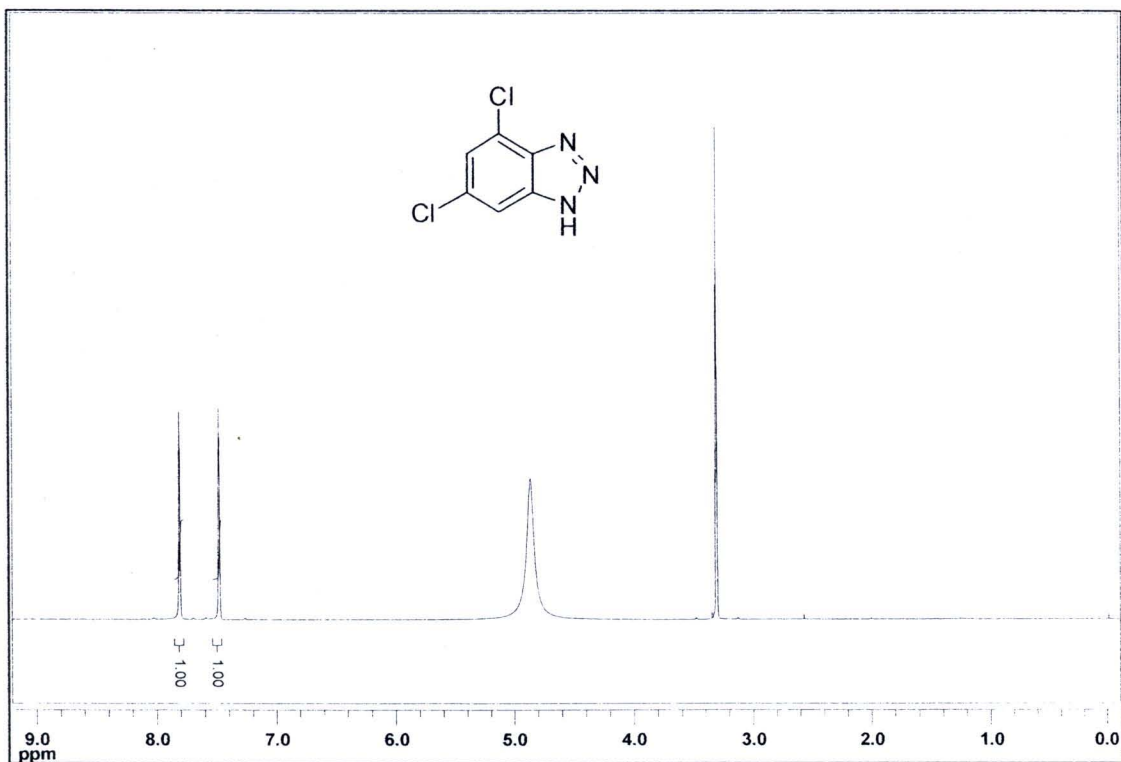


Figure 23 ^1H NMR spectrum of 4,6-dichloro-1H-benzo[*d*][1,2,3]triazole (11b)

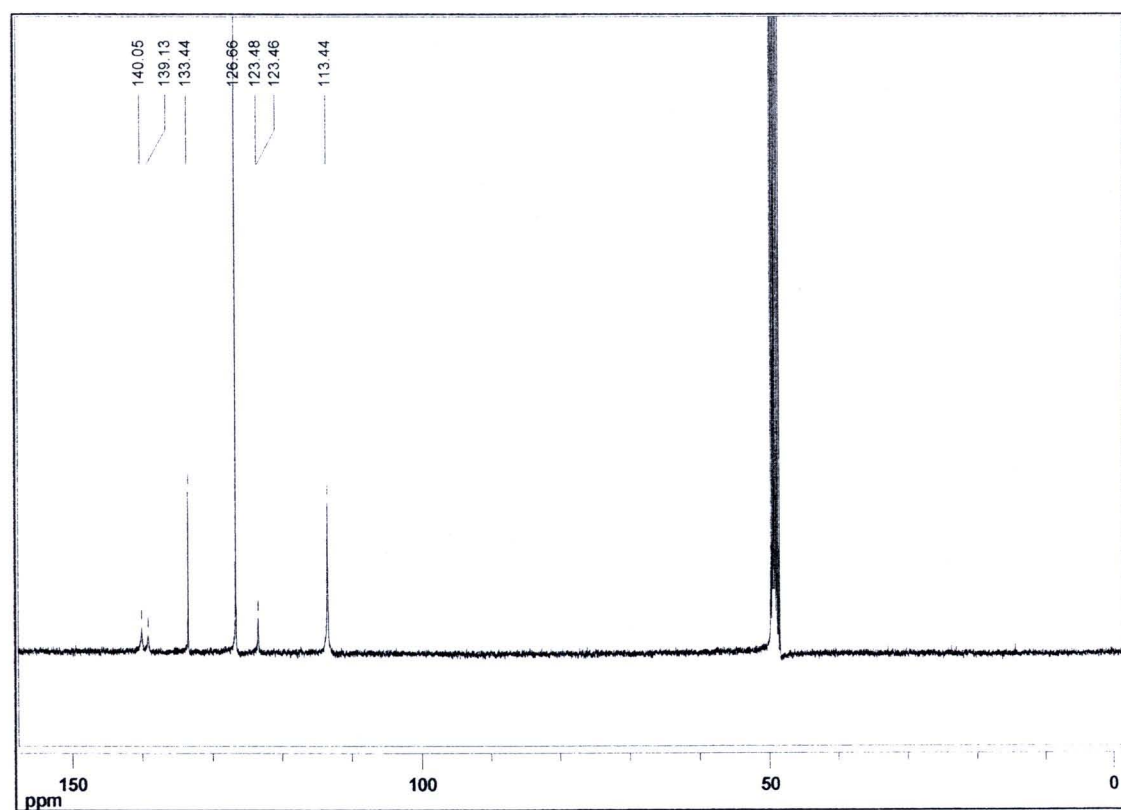


Figure 24 ^{13}C NMR spectrum of 4,6-dichloro-1H-benzo[*d*][1,2,3]triazole (11b)

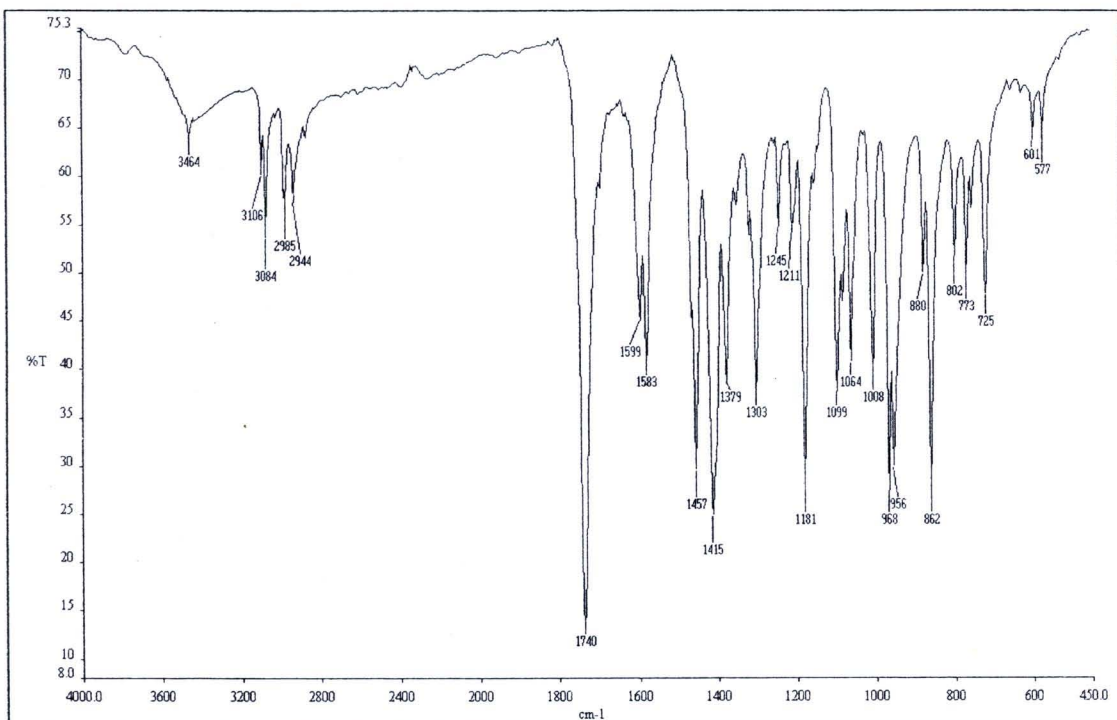


Figure 25 IR spectrum of 5,7-dibromo-1H-benzo[d][1,2,3]triazol-1-yl(phenyl) methanone (**12b**)

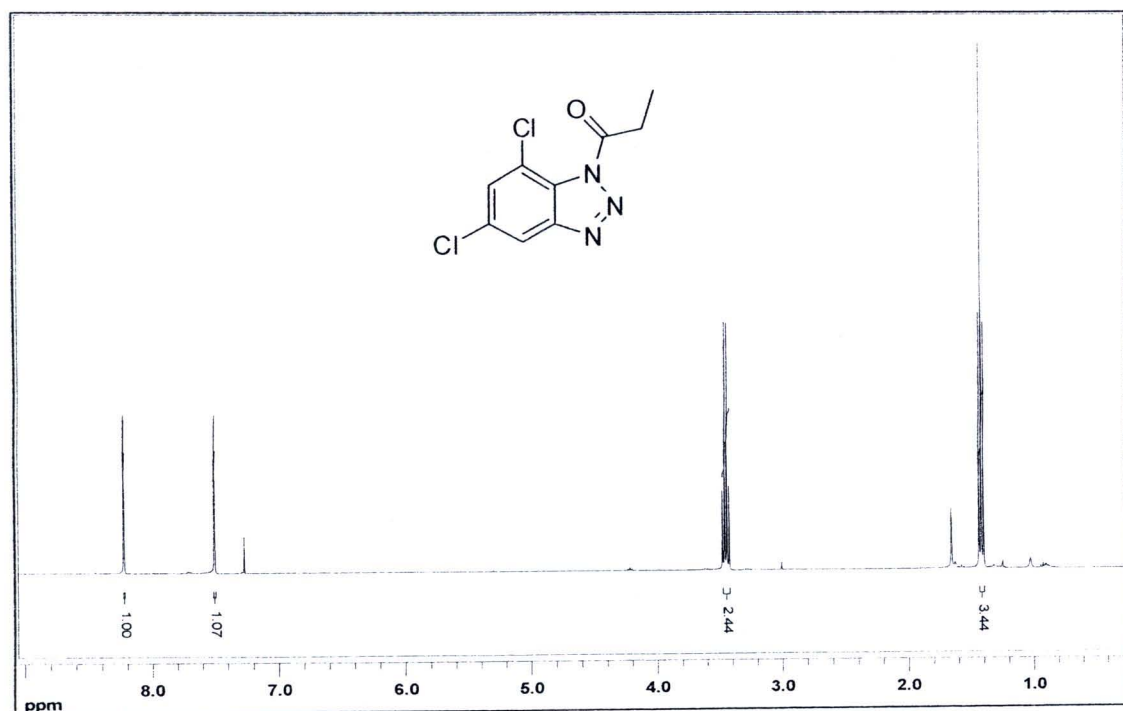


Figure 26 ¹H NMR spectrum of 5,7-dibromo-1H-benzo[d][1,2,3]triazol-1-yl(phenyl) methanone (**12b**)

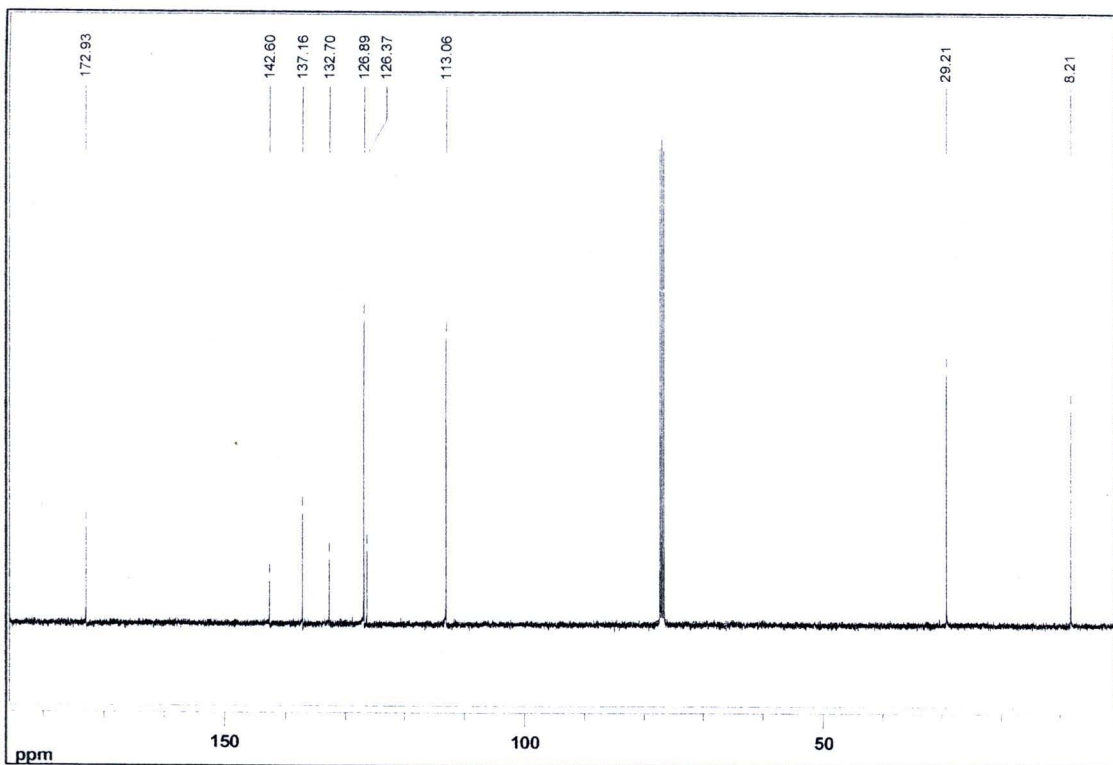


Figure 27 ^{13}C NMR spectrum of 5,7-dibromo-1*H*-benzo[*d*][1,2,3]triazol-1-yl(phenyl)methanone (**12b**)

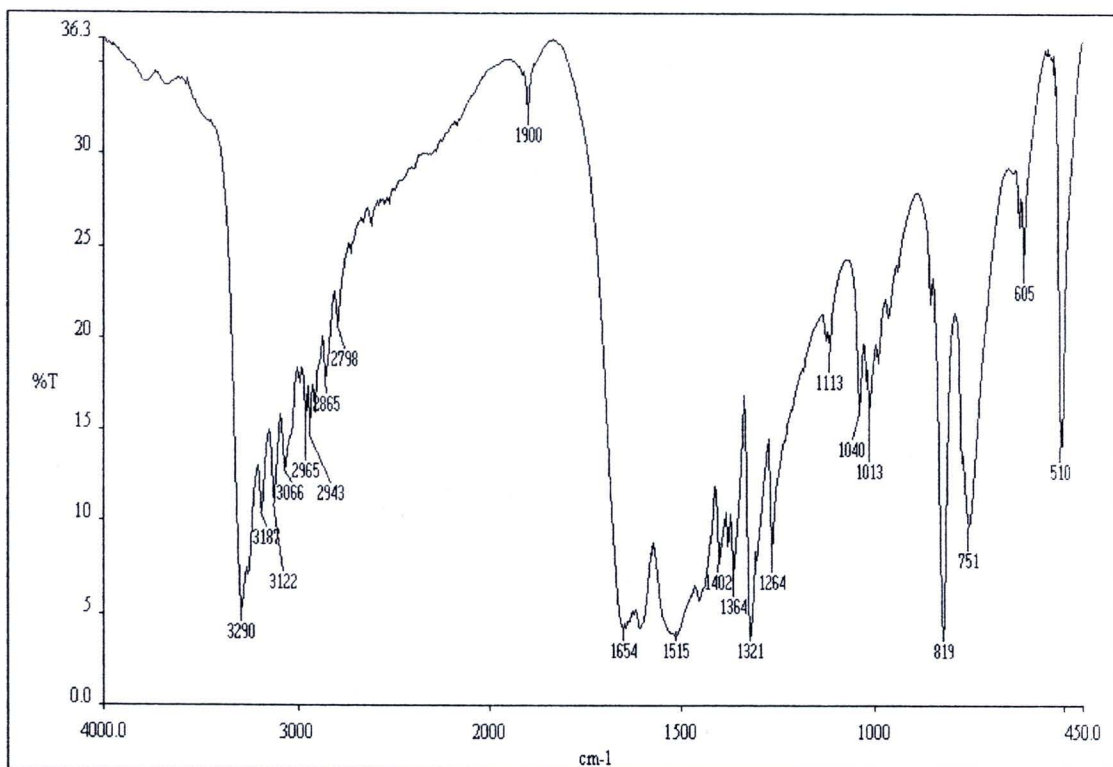


Figure 28 IR spectrum of *N*-*p*-tolylacetamide (**13**)

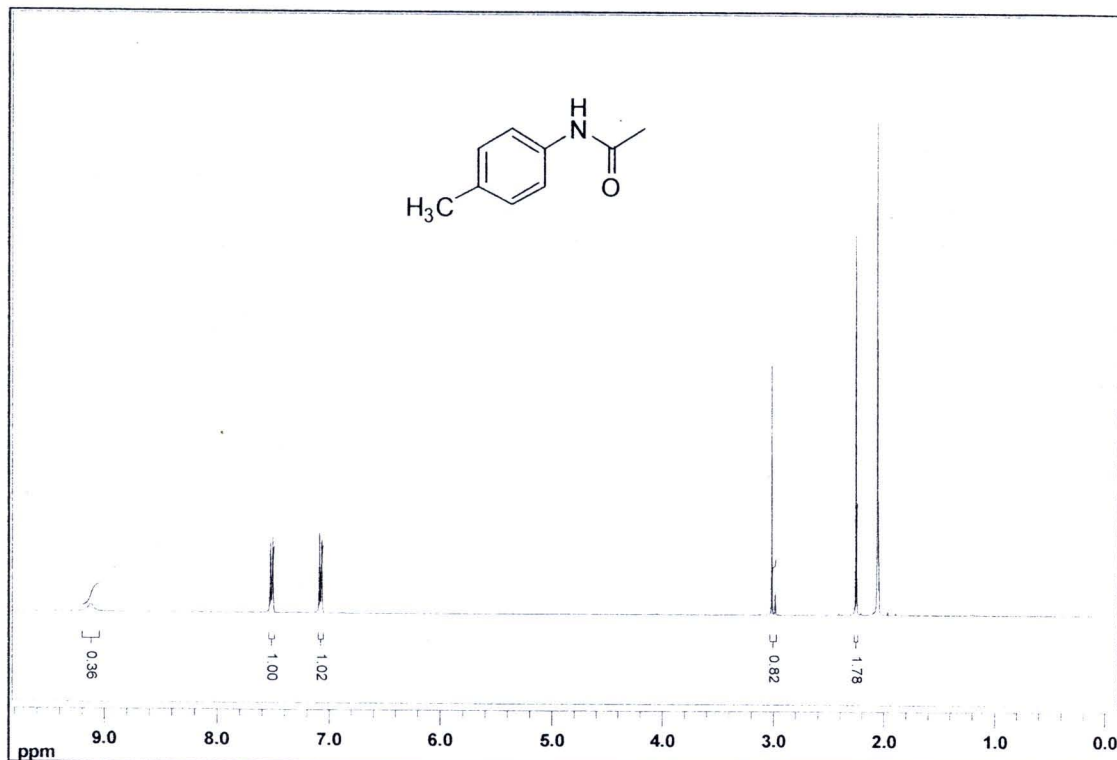


Figure 29 ^1H NMR spectrum of *N-p*-tolylacetamide (13)

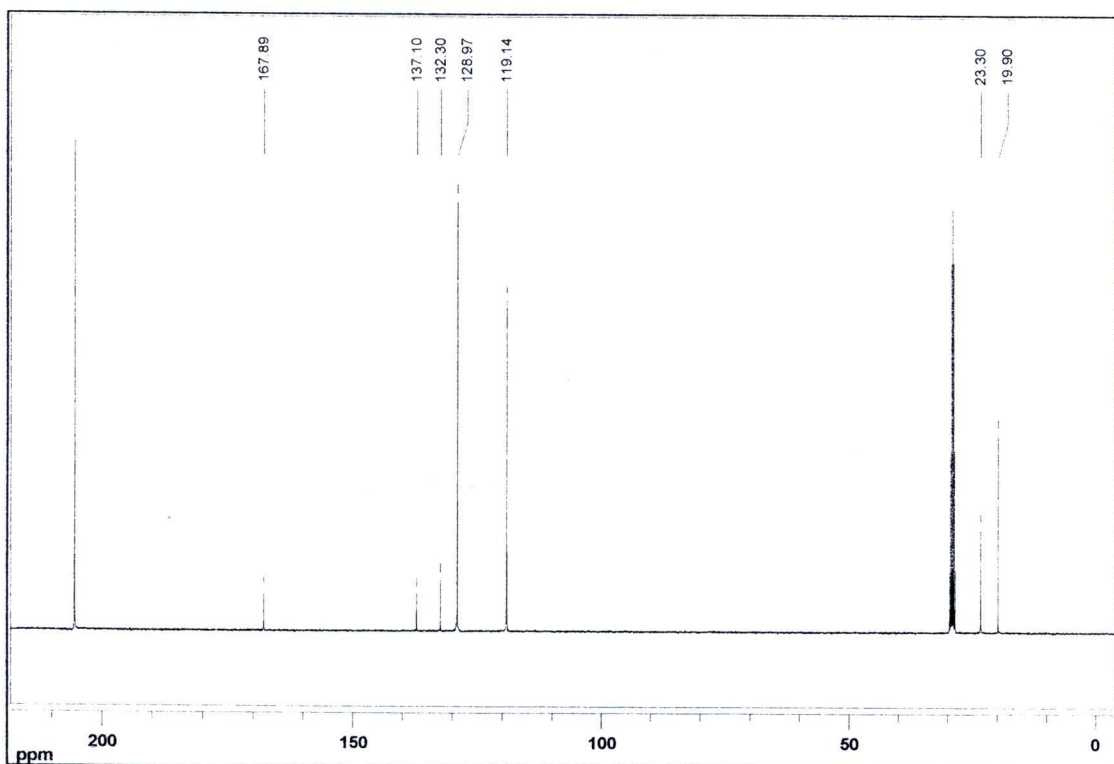


Figure 30 ^{13}C NMR spectrum of *N-p*-tolylacetamide (13)

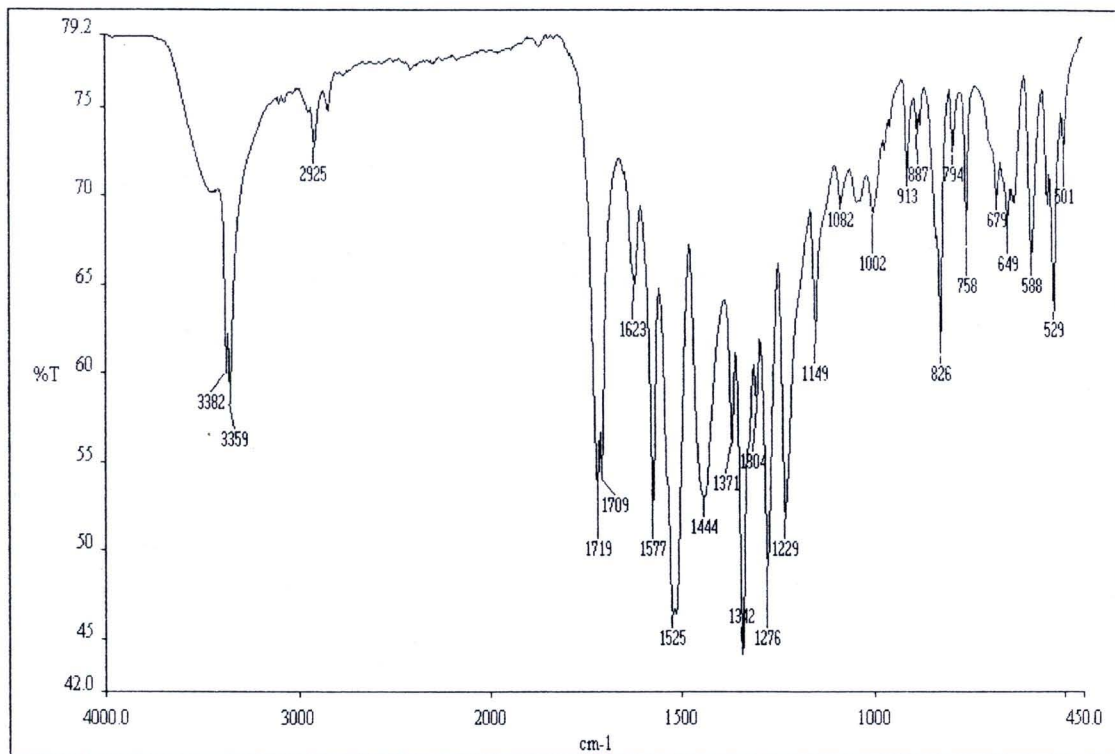


Figure 31 IR spectrum of *N*-(4-methyl-2-nitrophenyl)acetamide (**14**)

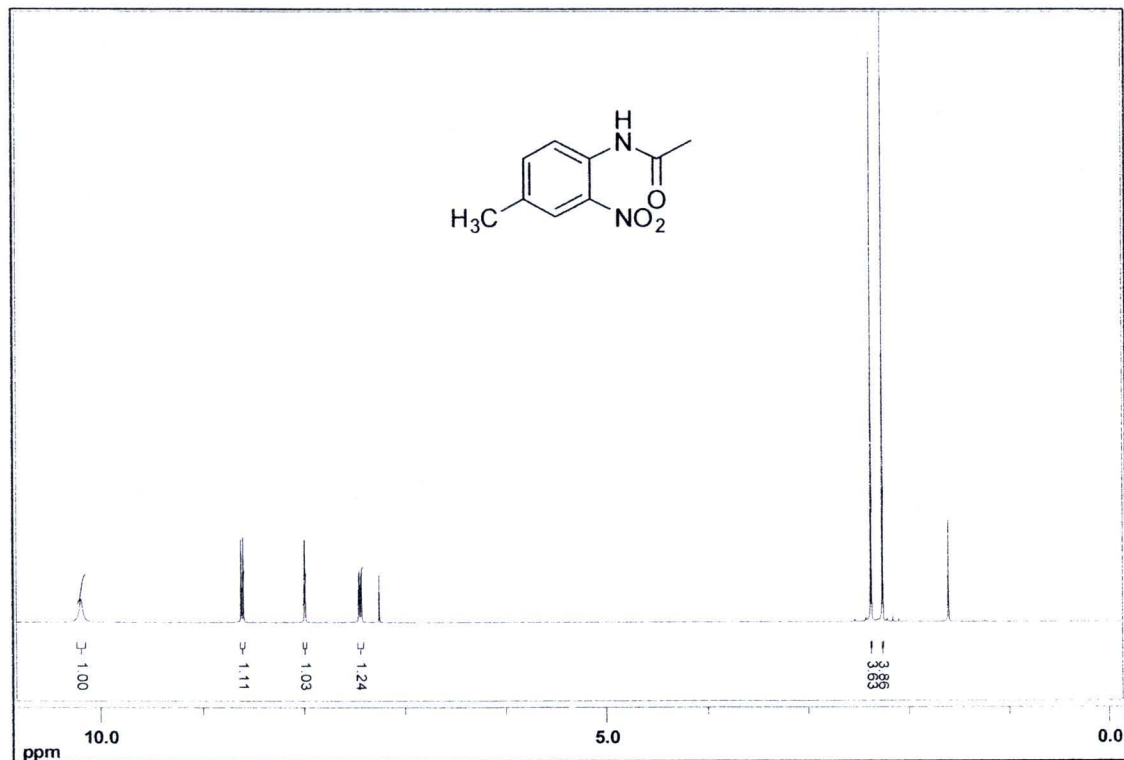


Figure 32 ^1H NMR spectrum of *N*-(4-methyl-2-nitrophenyl)acetamide (**14**)

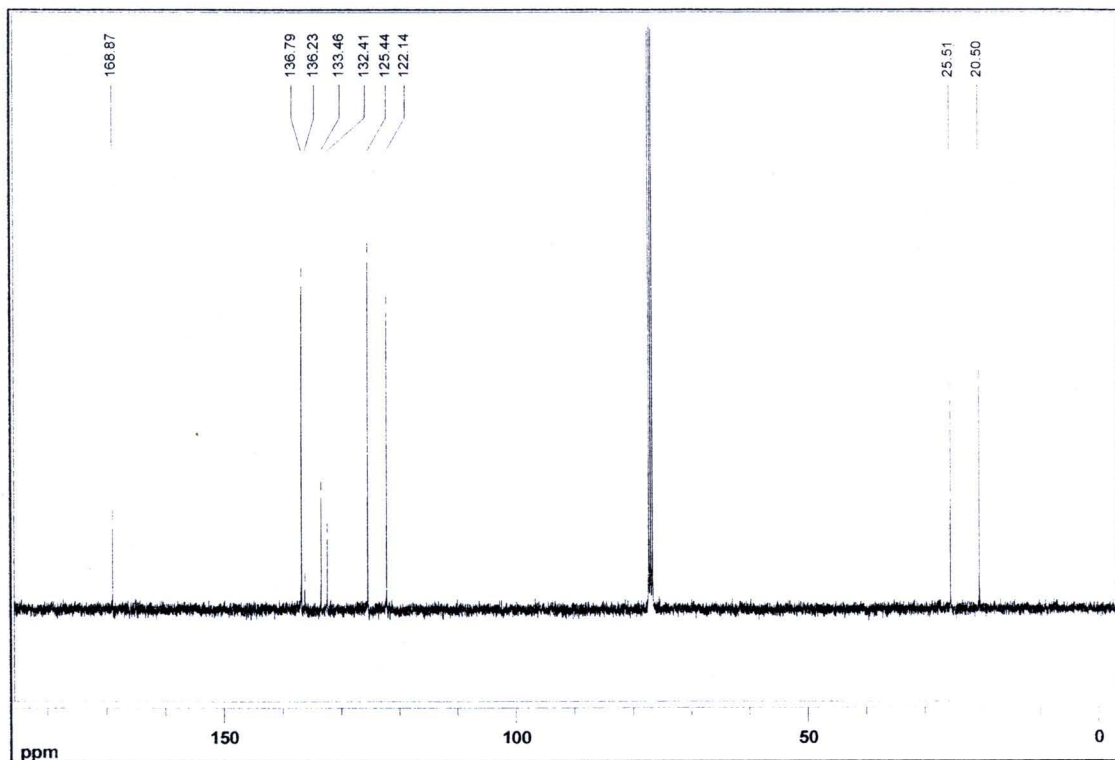


Figure 33 ^{13}C NMR spectrum of *N*-(4-methyl-2-nitrophenyl)acetamide (**14**)

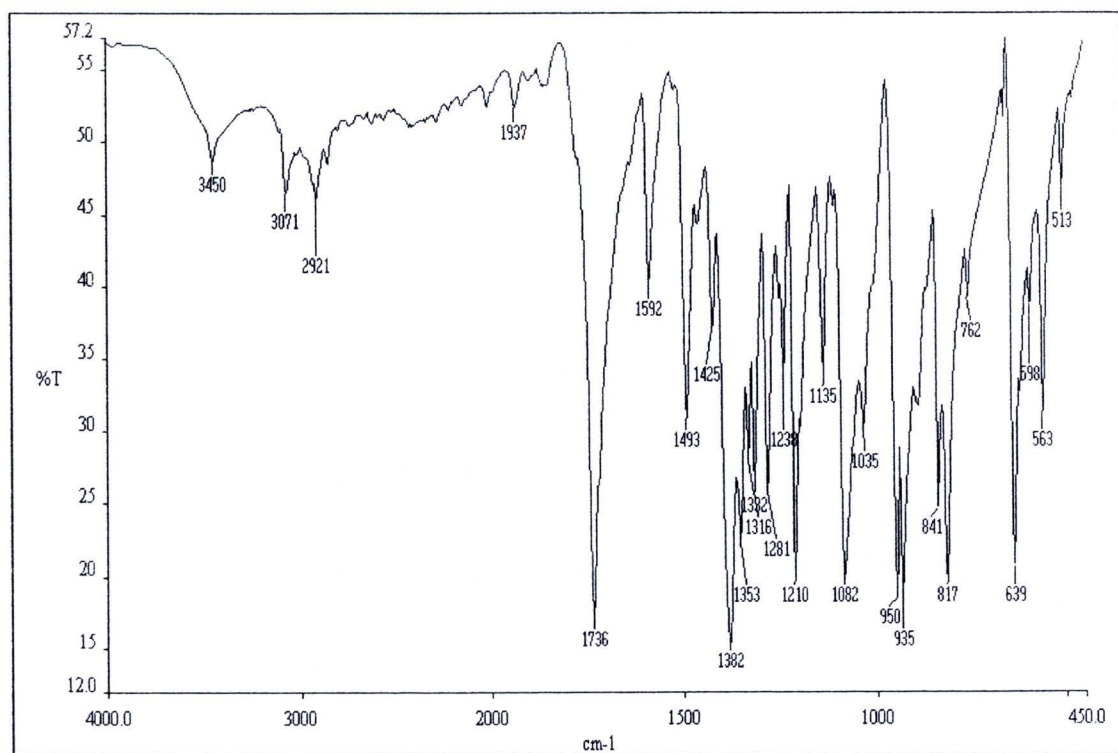


Figure 34 IR spectrum of 1-(5-methyl-1*H*-benzo[*d*][1,2,3]triazol-1-yl)ethanone (**16**)

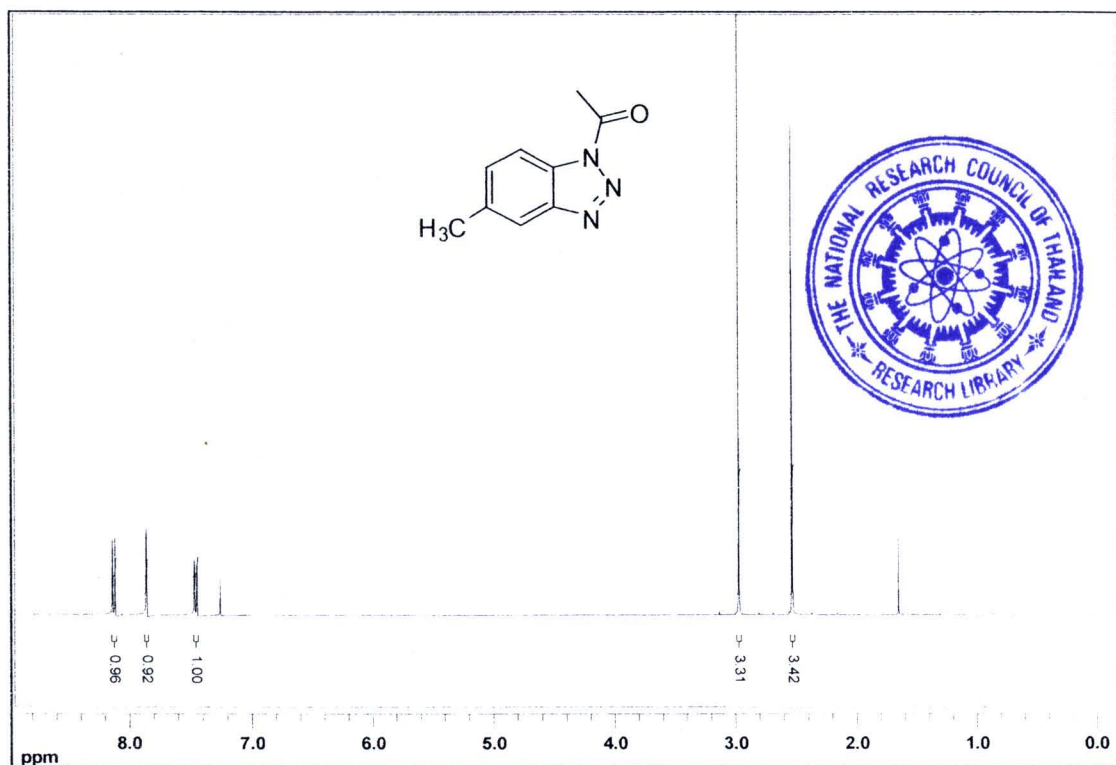


Figure 35 ¹H NMR spectrum of 1-(5-methyl-1H-benzo[d][1,2,3]triazol-1-yl)ethanone (16)

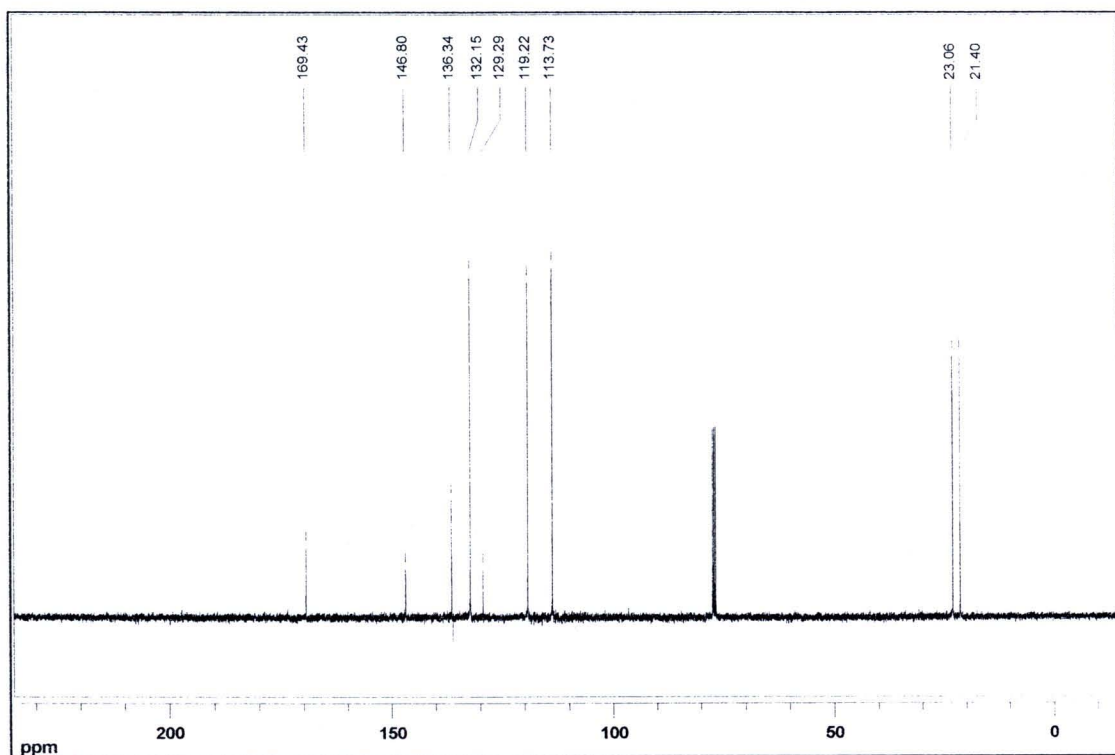


Figure 36 ¹³C NMR spectrum of 1-(5-methyl-1H-benzo[d][1,2,3]triazol-1-yl)ethanone (16)

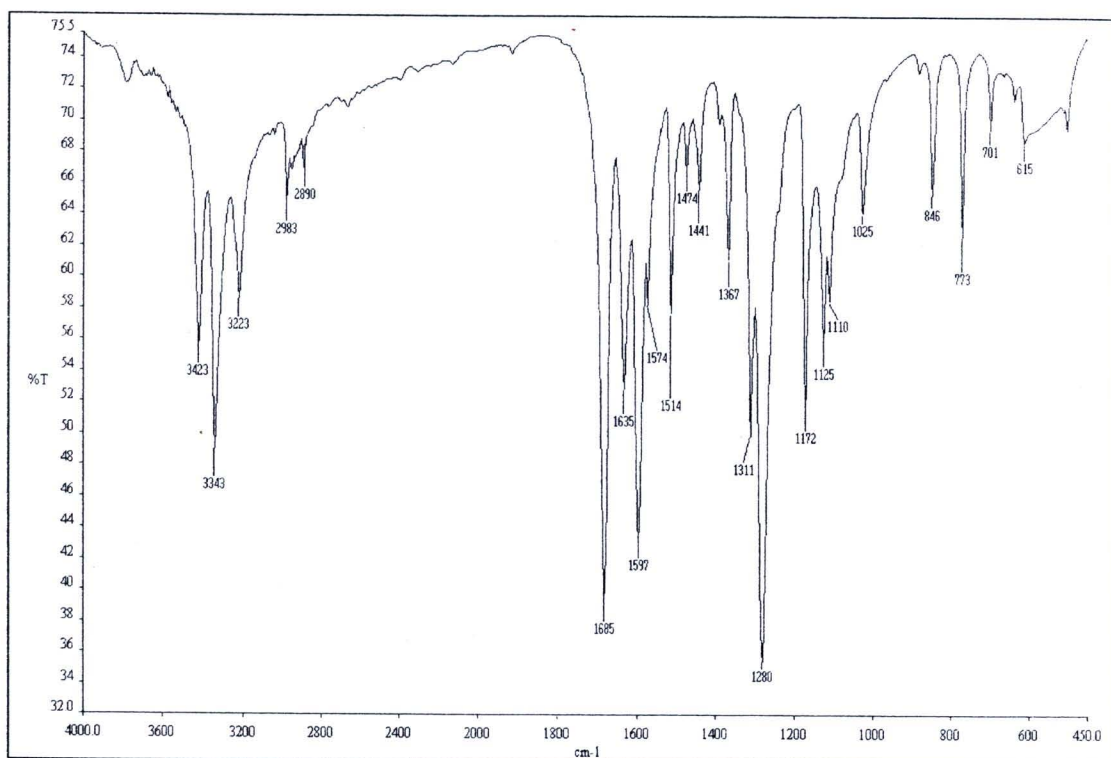


Figure 37 IR spectrum of ethyl-4-aminobenzoate (**18**)

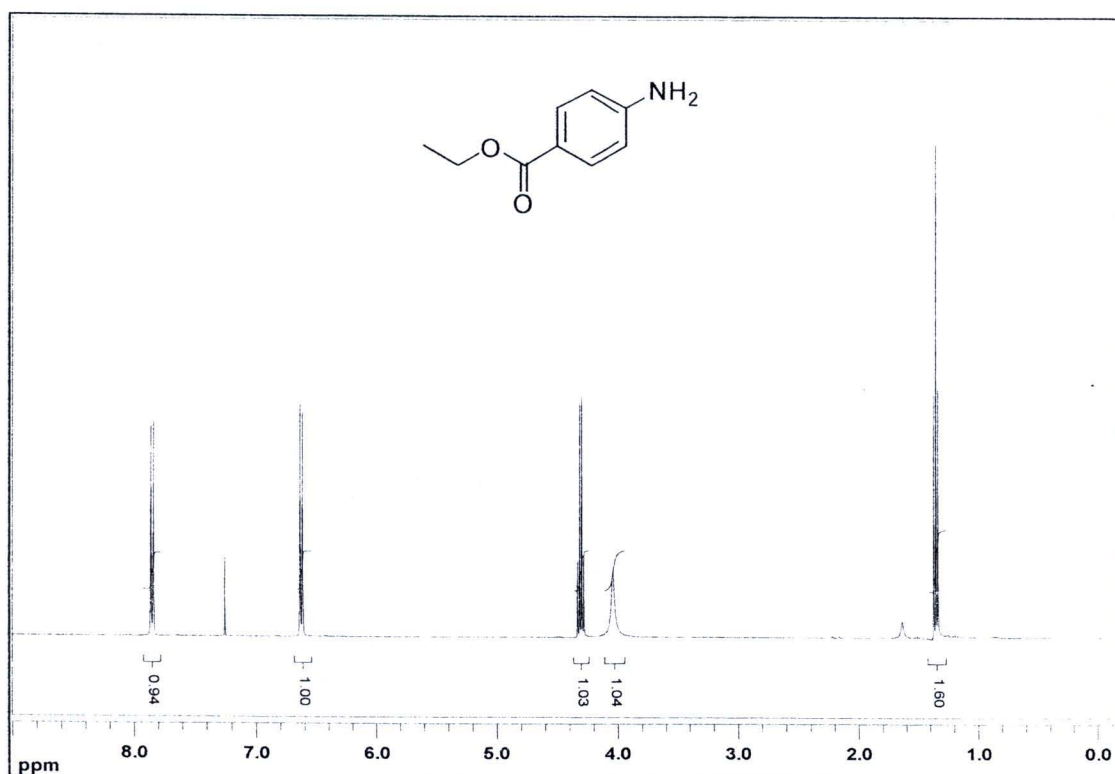


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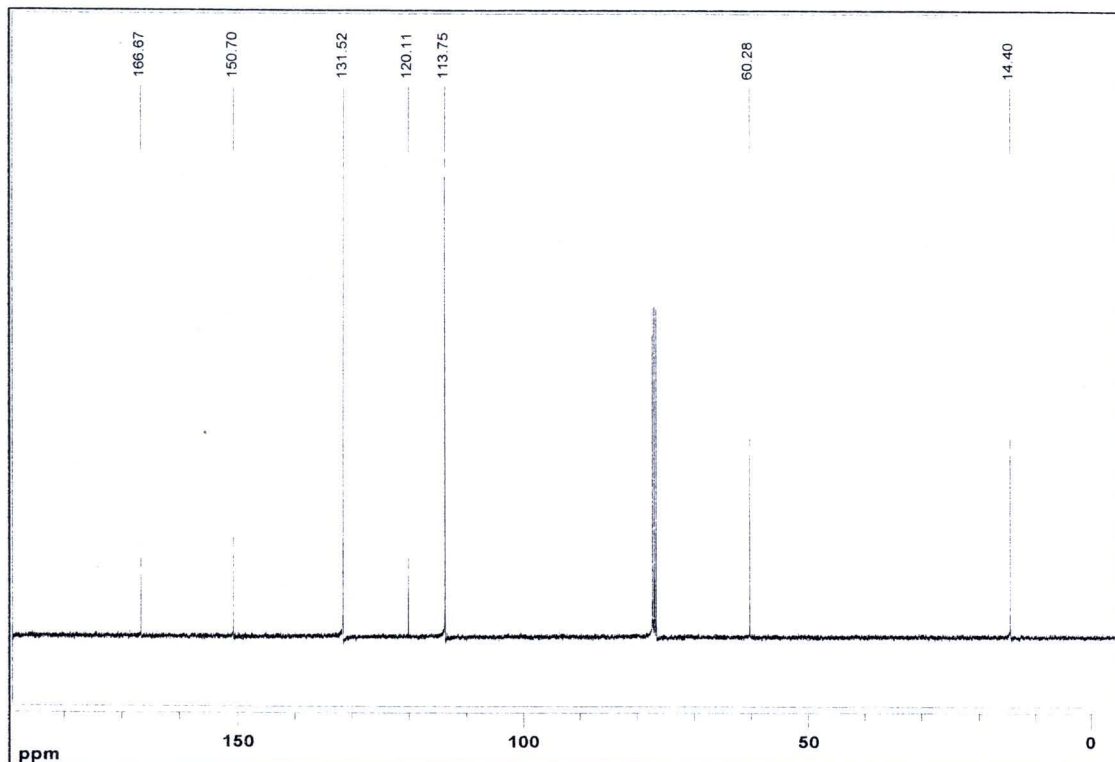


Figure 39 ^{13}C NMR spectrum of ethyl-4-aminobenzoate (18)

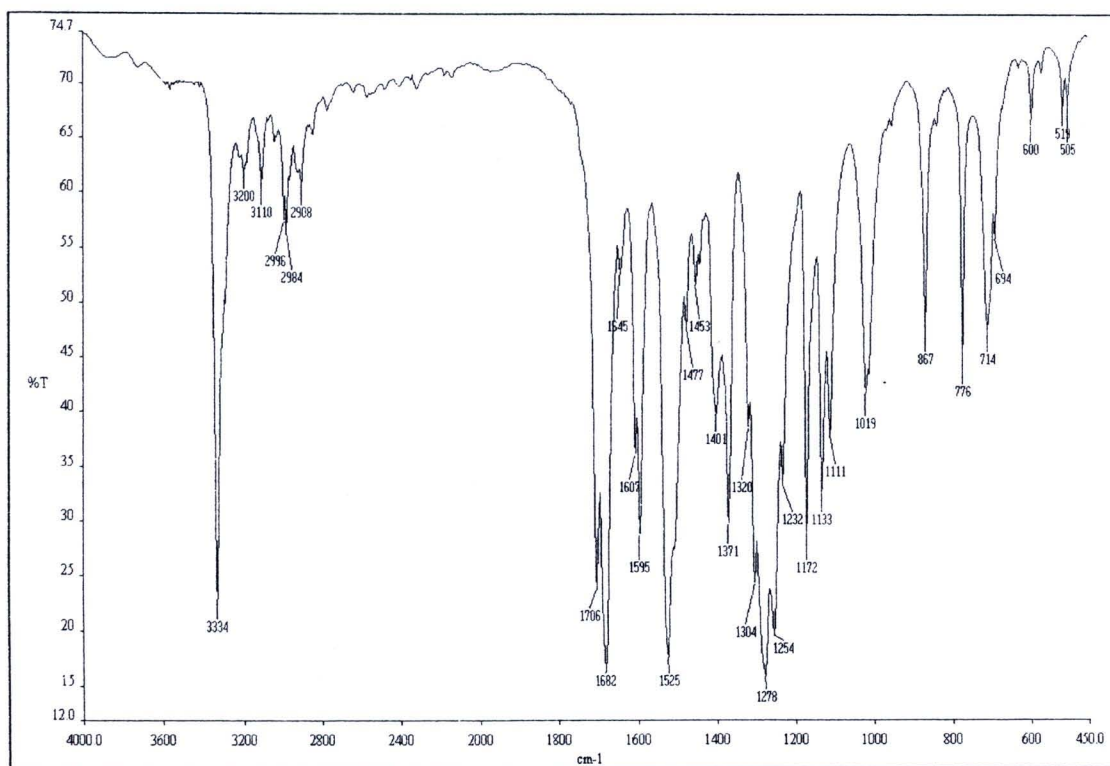


Figure 40 IR spectrum of ethyl-4-acetamidobenzoate (19a)

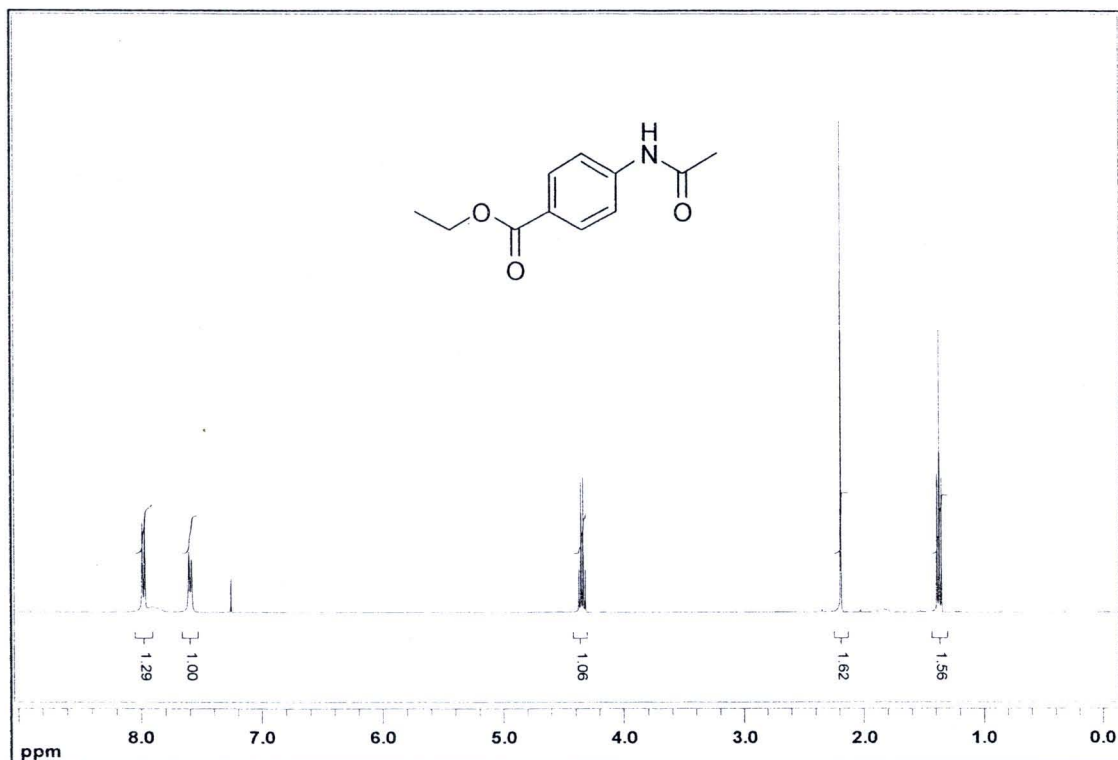


Figure 41 ^1H NMR spectrum of ethyl-4-acetamidobenzoate (19a)

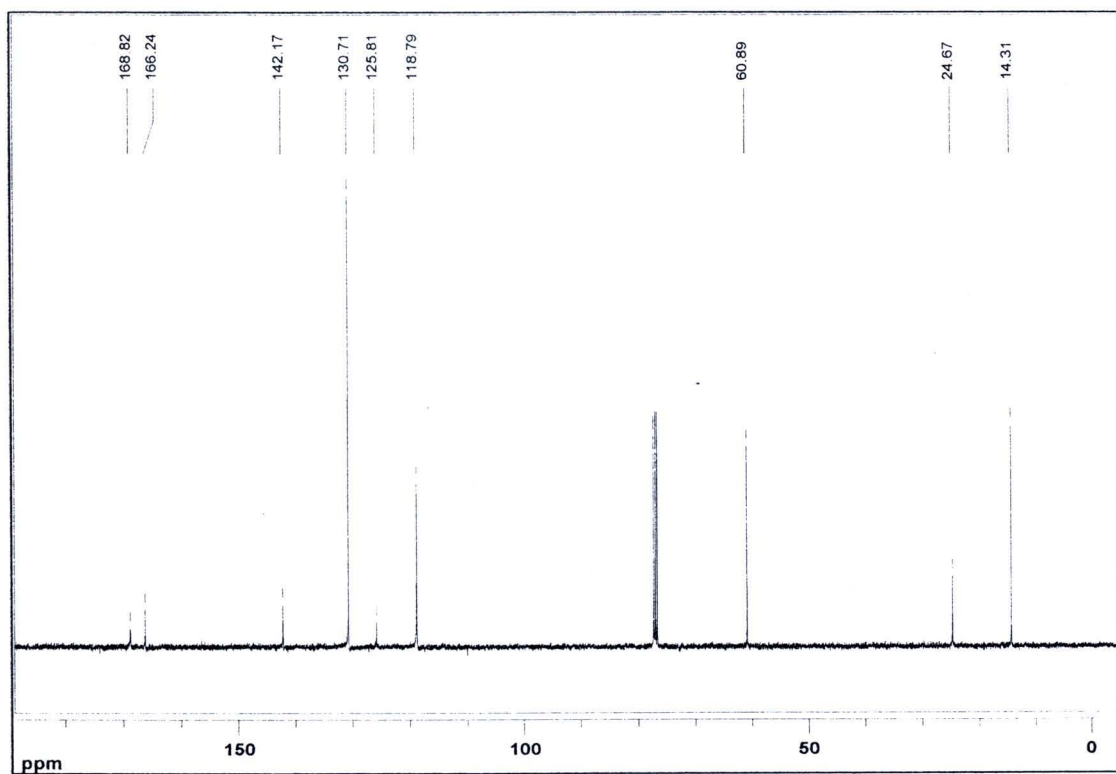


Figure 42 ^{13}C NMR spectrum of ethyl-4-acetamidobenzoate (19a)

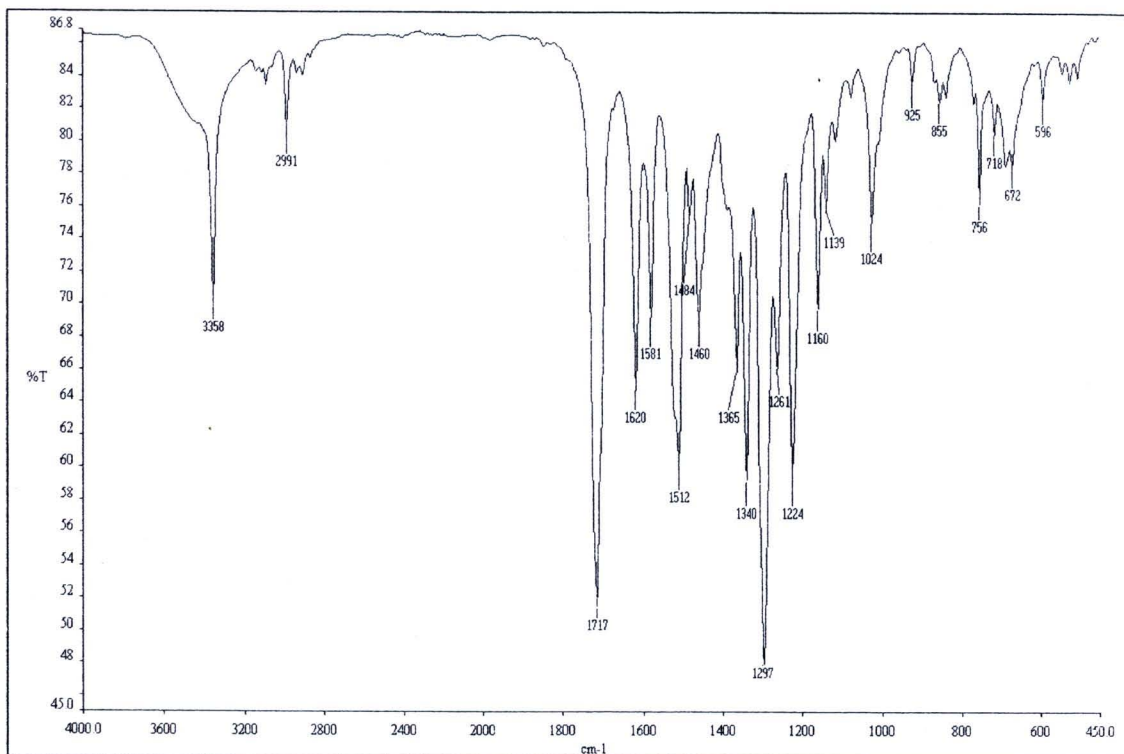


Figure 43 IR spectrum of ethyl-4-acetamido-3-nitrobenzoate (**20a**)

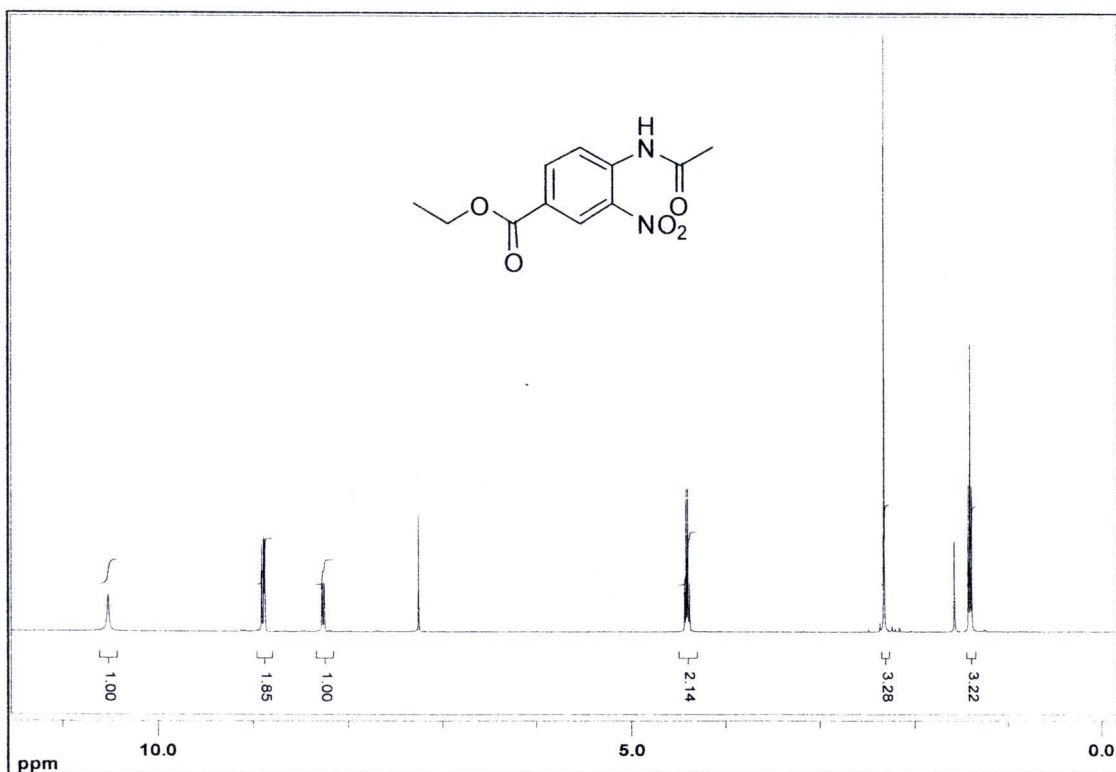
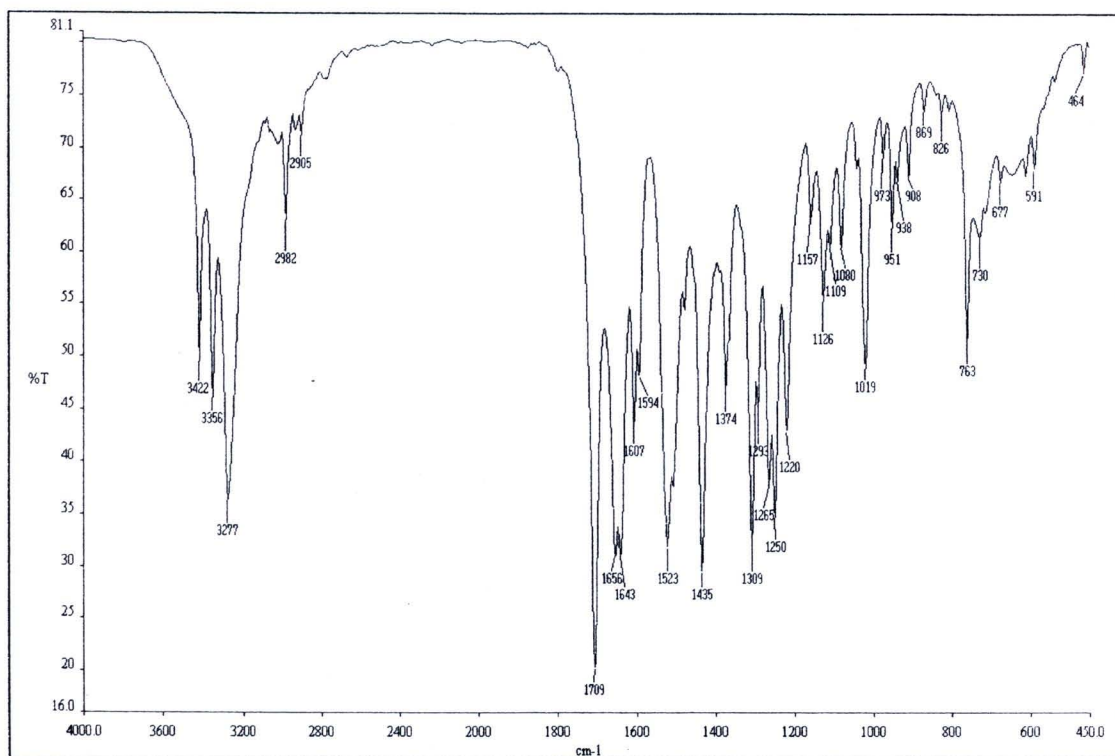
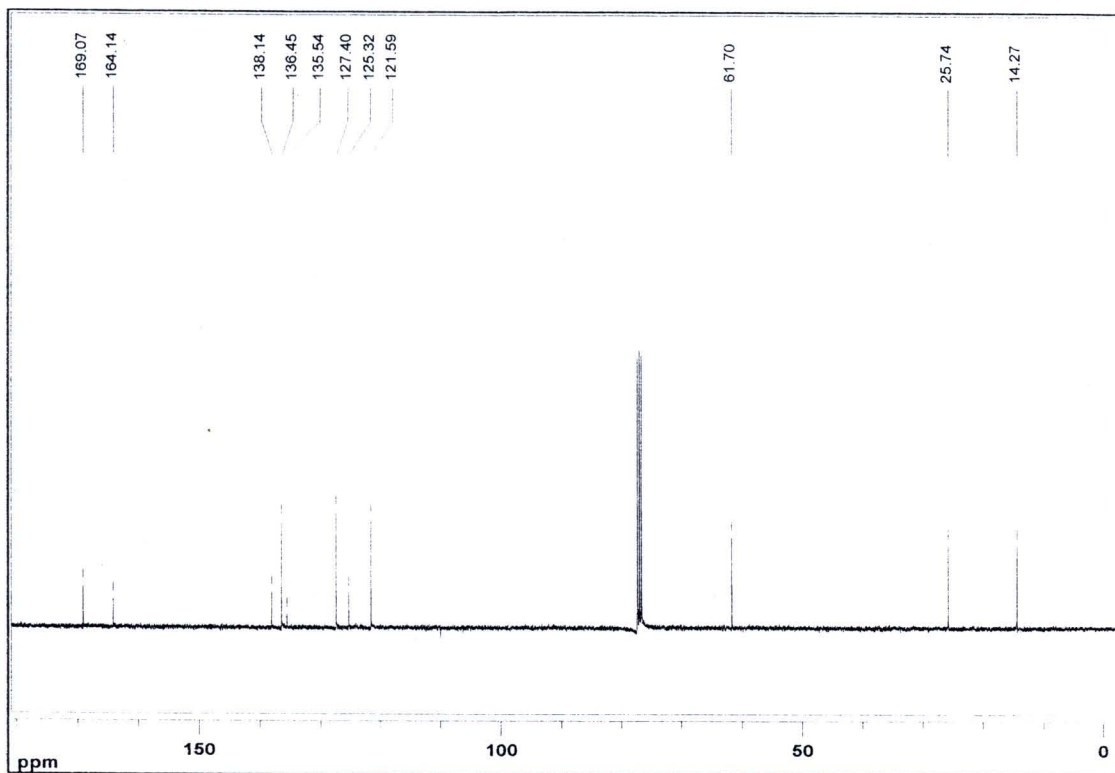


Figure 44 ^1H NMR spectrum of ethyl 4-acetamido-3-nitrobenzoate (**20a**)



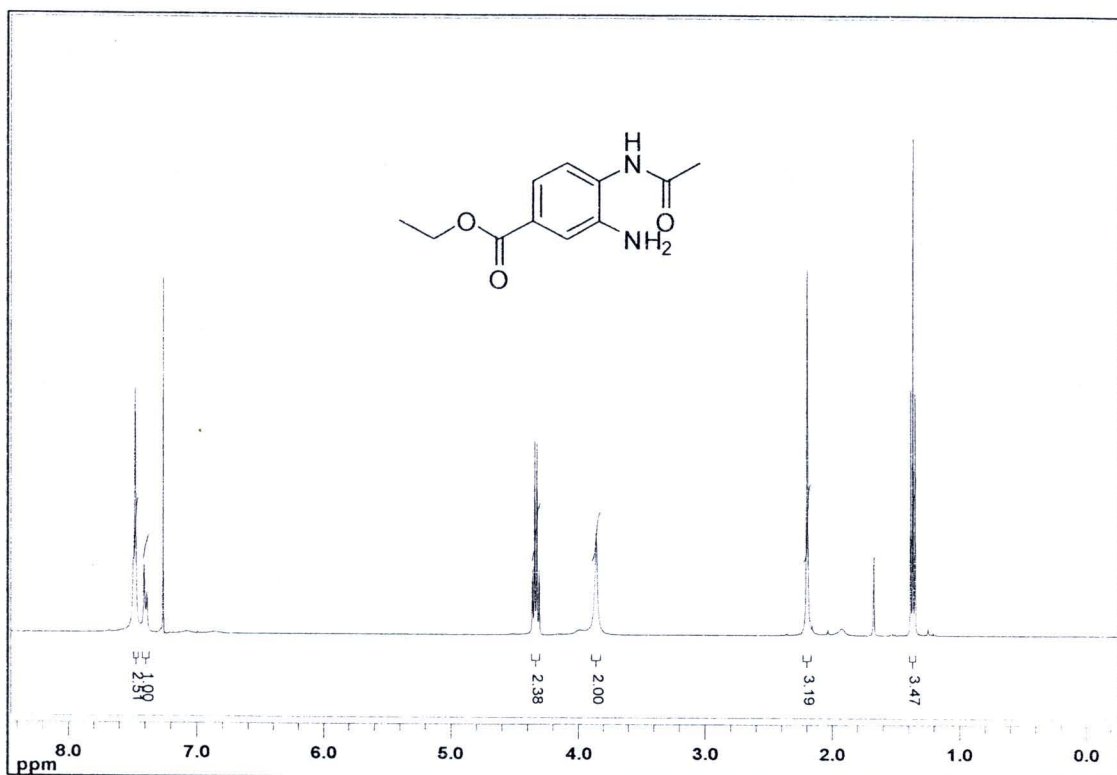


Figure 47 ^1H NMR spectrum of ethyl-4-acetamido-3-aminobenzoate (21a)

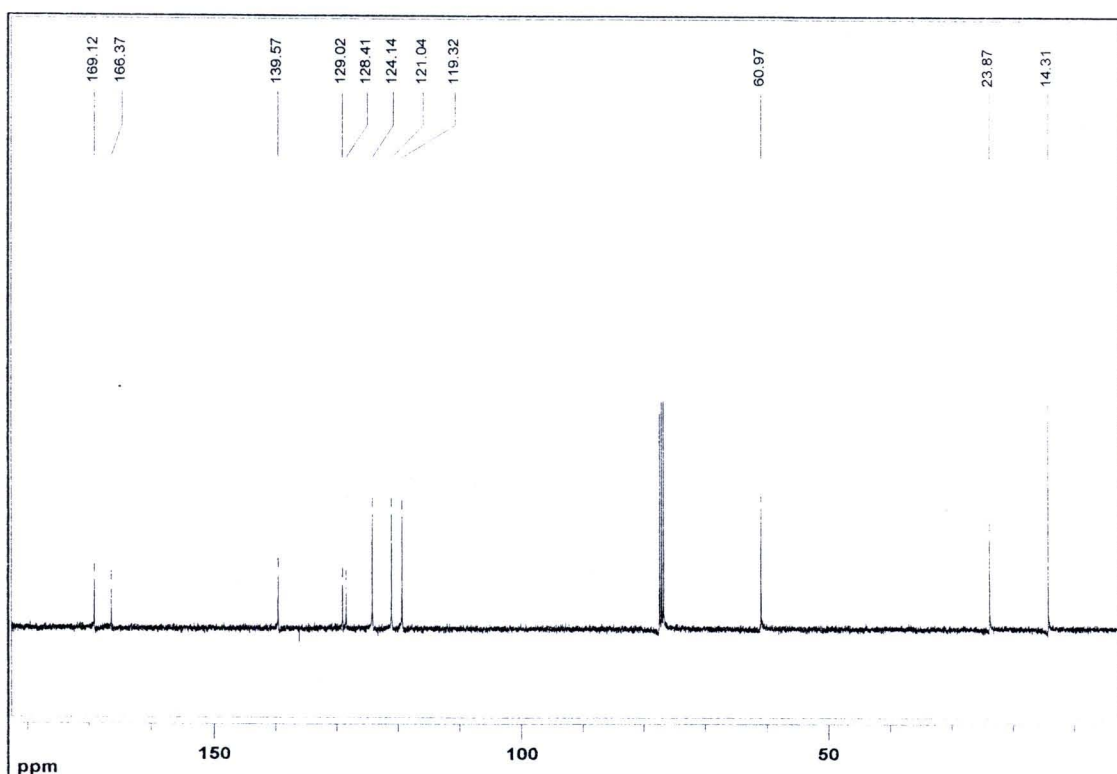


Figure 48 ^{13}C NMR spectrum of ethyl-4-acetamido-3-aminobenzoate (21a)

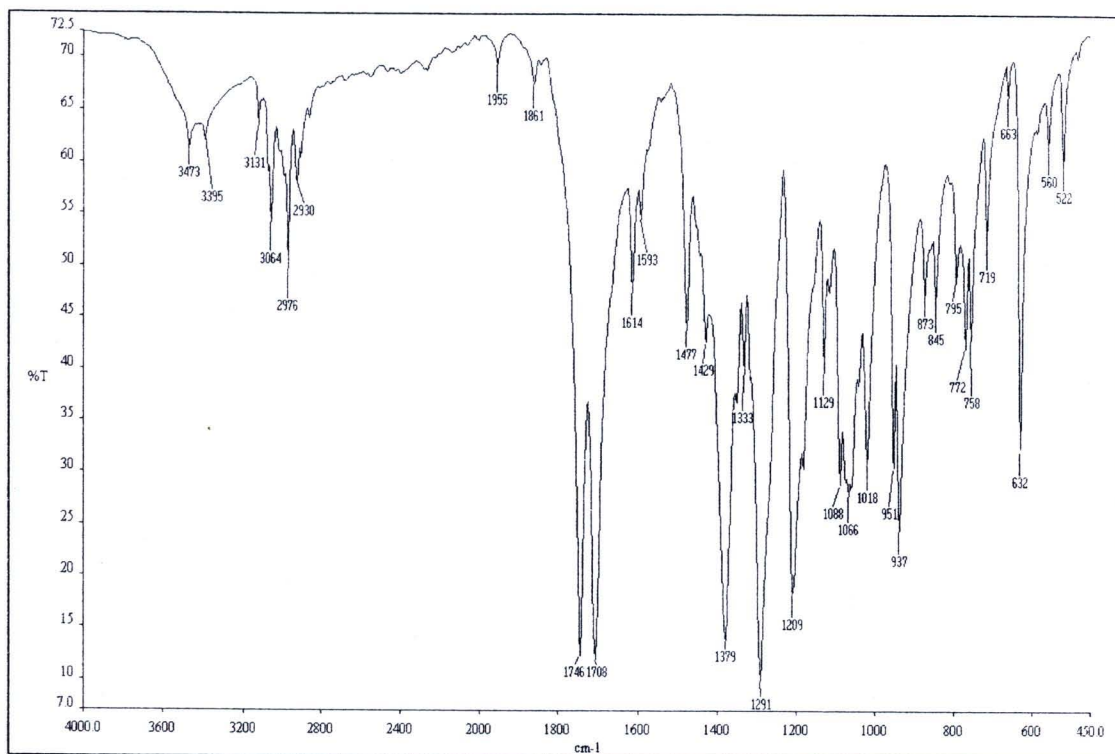


Figure 49 IR spectrum of ethyl-1-acetyl-1H-benzo[d][1,2,3]triazole-5-carboxylate (22a)

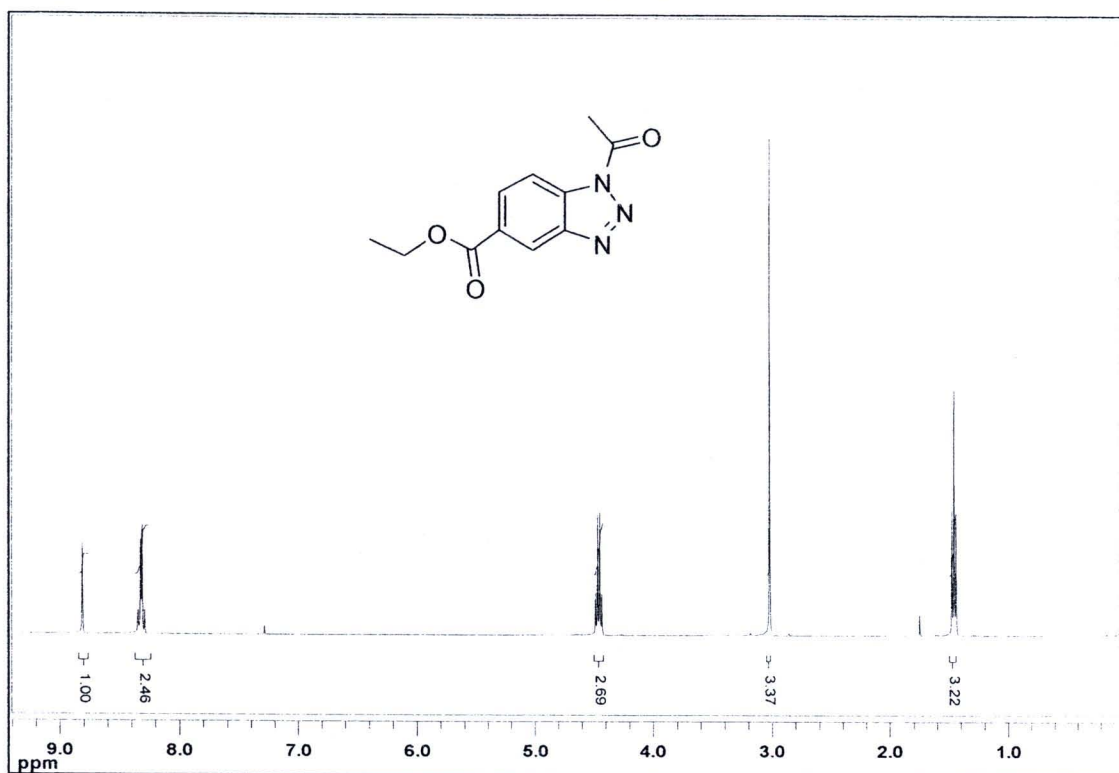
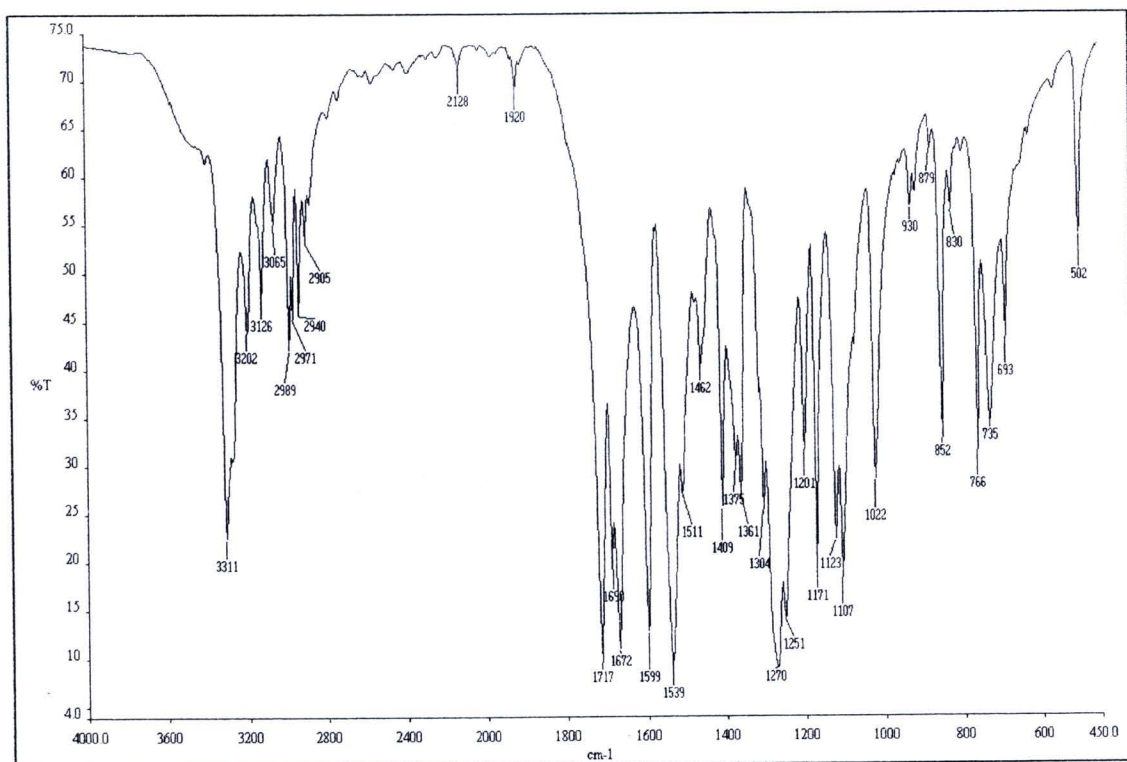
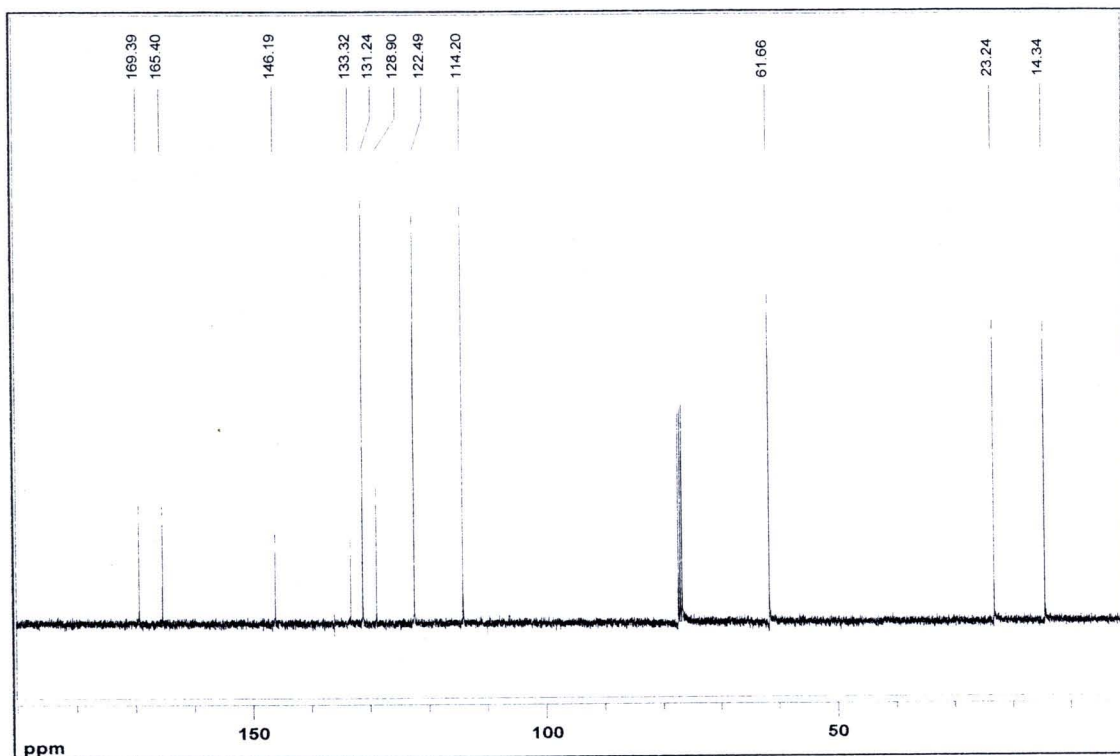


Figure 50 ¹H NMR spectrum of ethyl-1-acetyl-1H-benzo[d][1,2,3]triazole-5-carboxylate (22a)



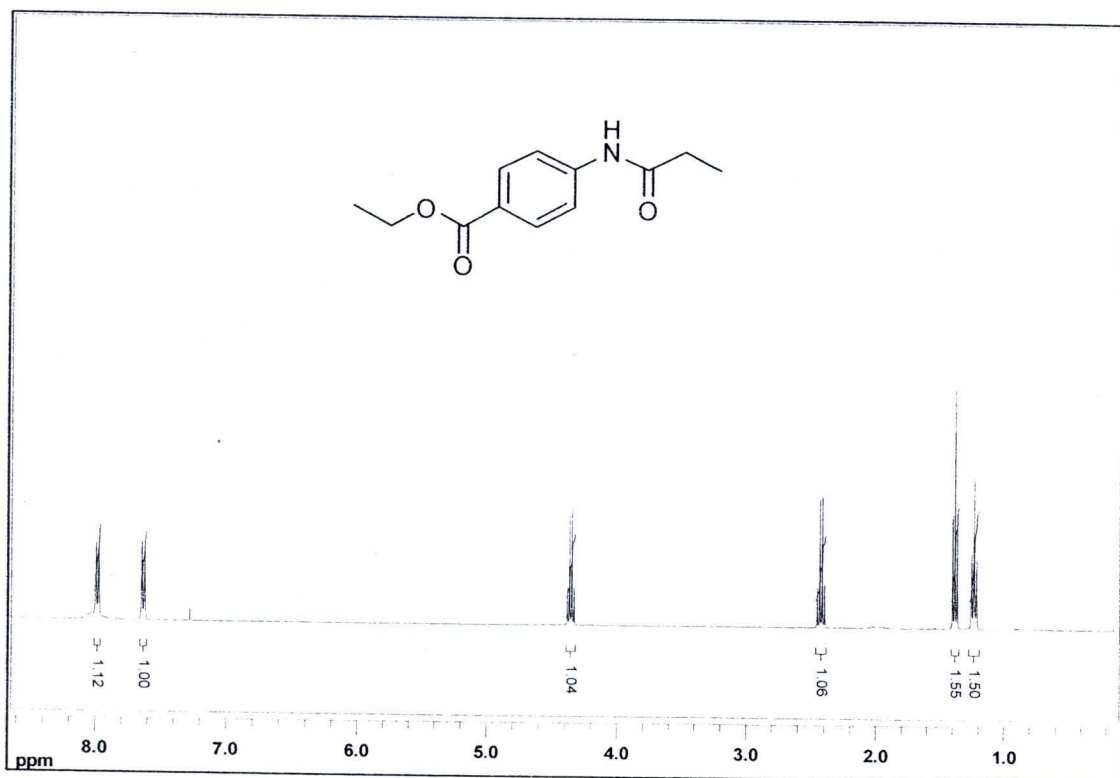


Figure 53 ¹H NMR spectrum of ethyl-4-propionamidobenzoate (19b)

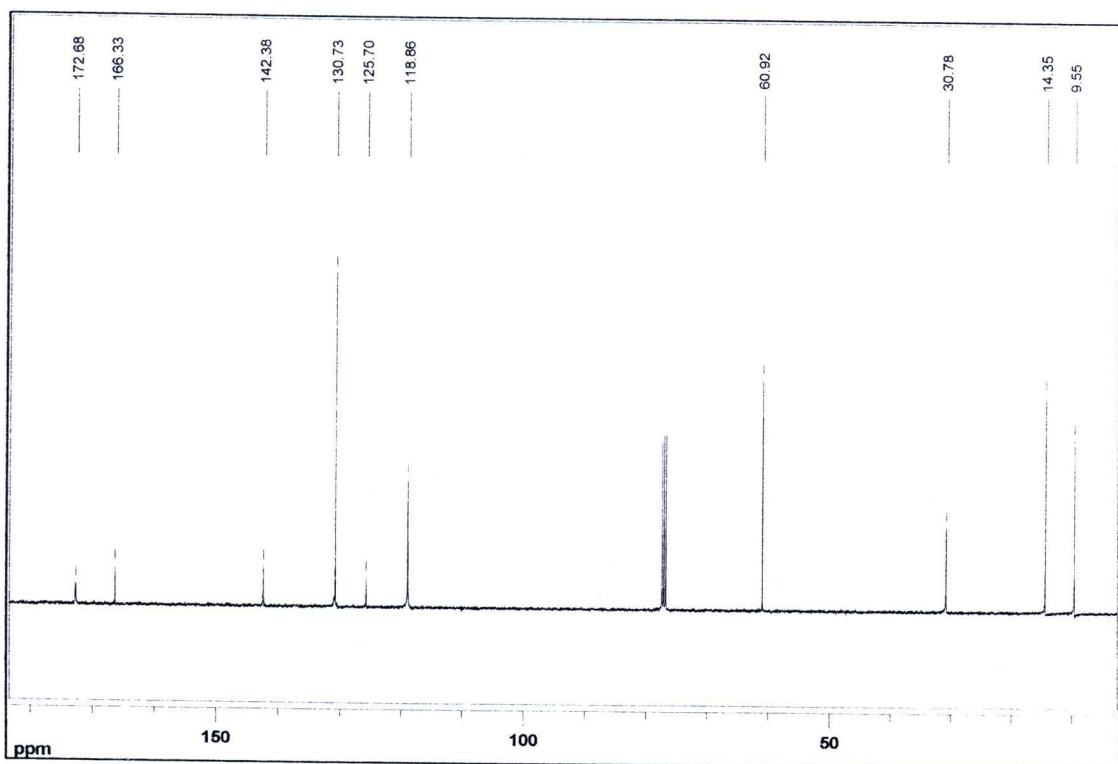


Figure 54 ¹³C NMR spectrum of ethyl-4-propionamidobenzoate (19b)

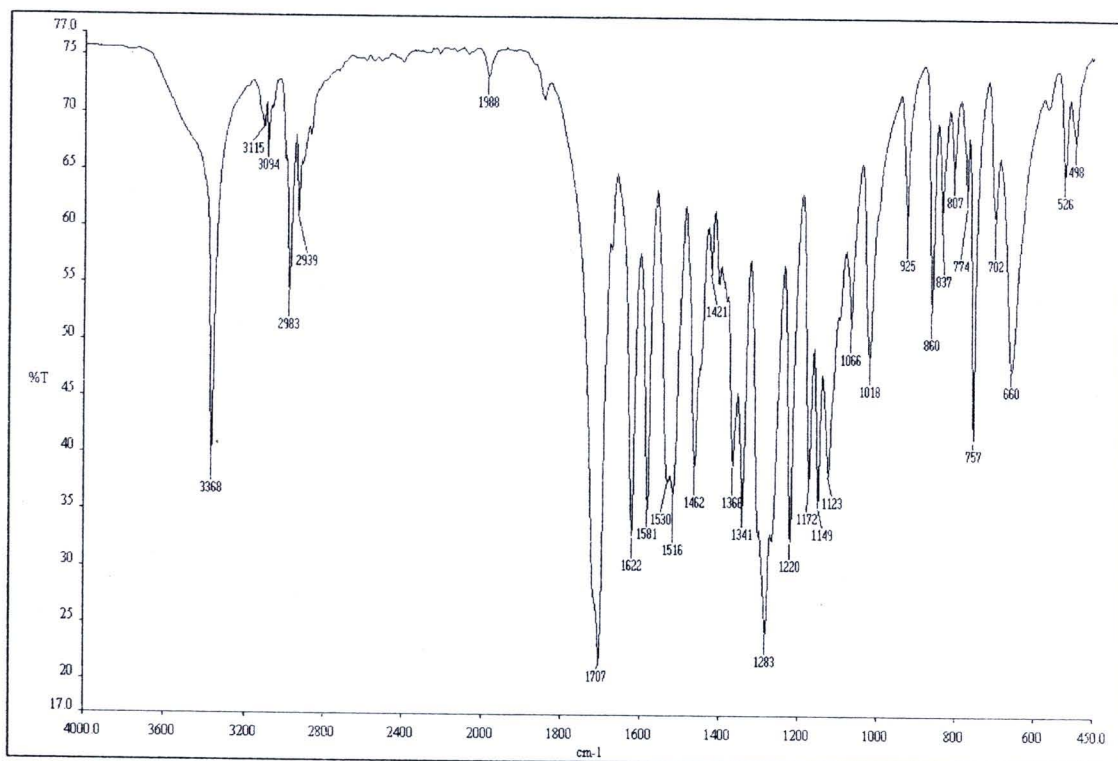


Figure 55 IR spectrum of ethyl-3-nitro-4-propionamidobenzoate (**20b**)

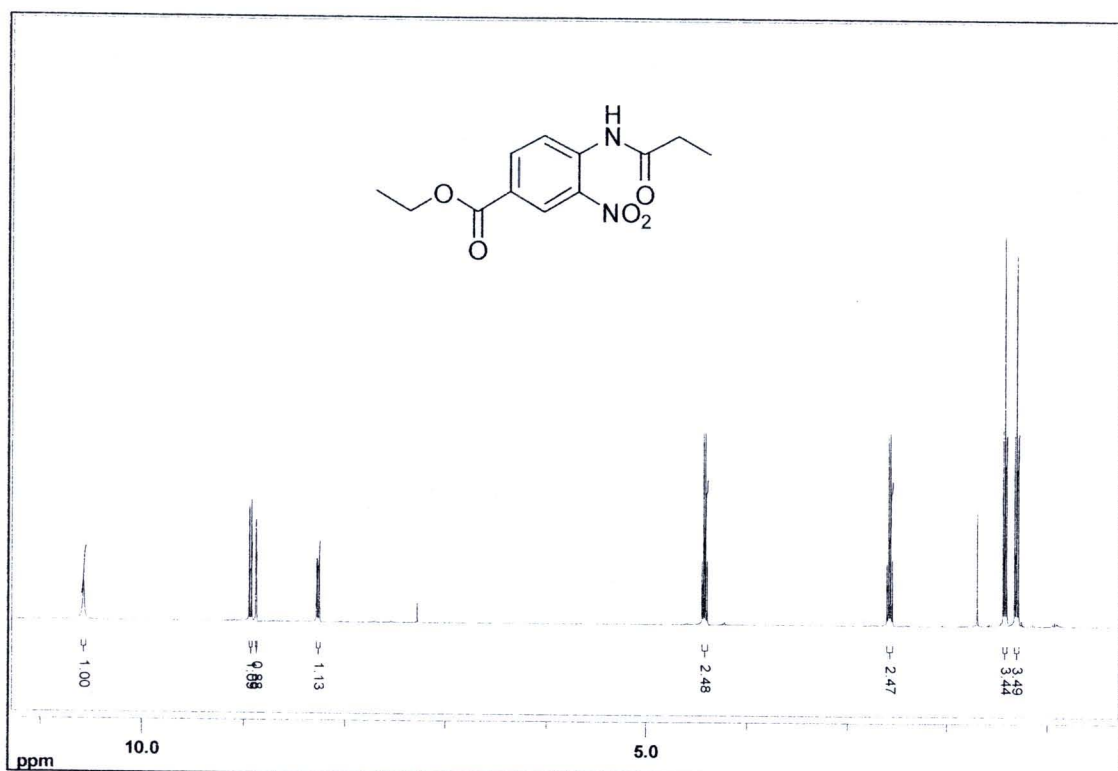


Figure 56 ¹H NMR spectrum of ethyl-3-nitro-4-propionamidobenzoate (**20b**)

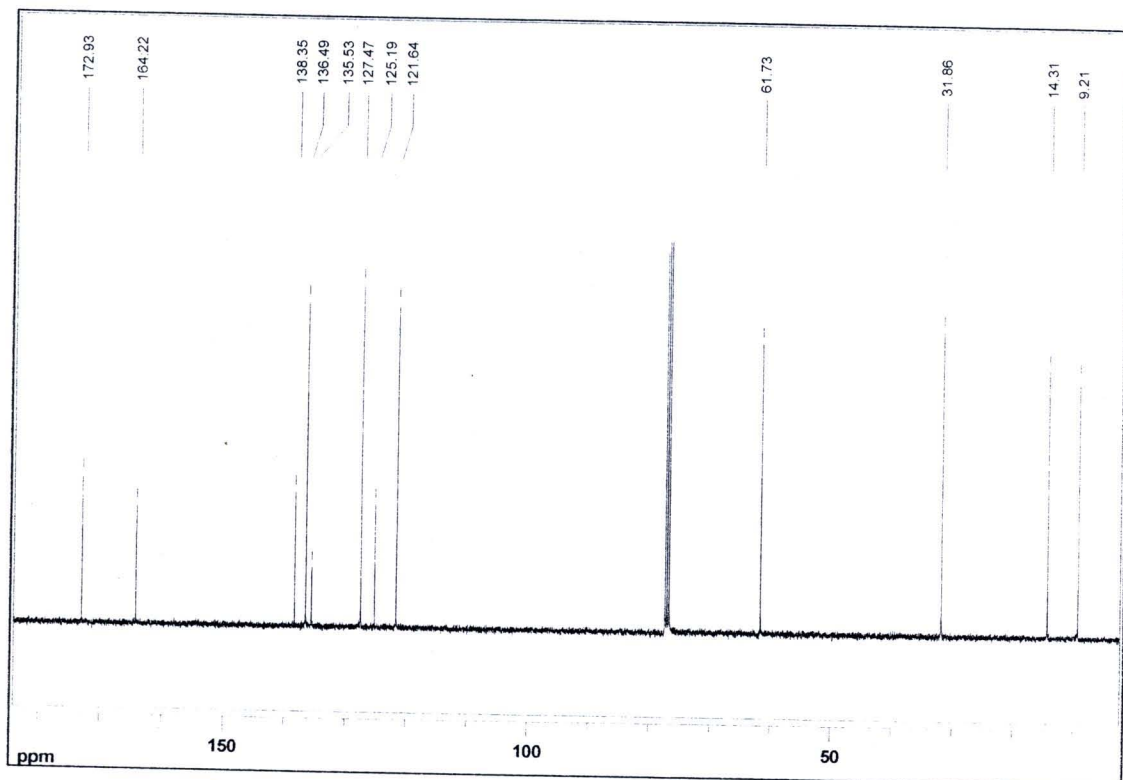


Figure 57 ^{13}C NMR spectrum of ethyl-3-nitro-4-propionamidobenzoate (20b)

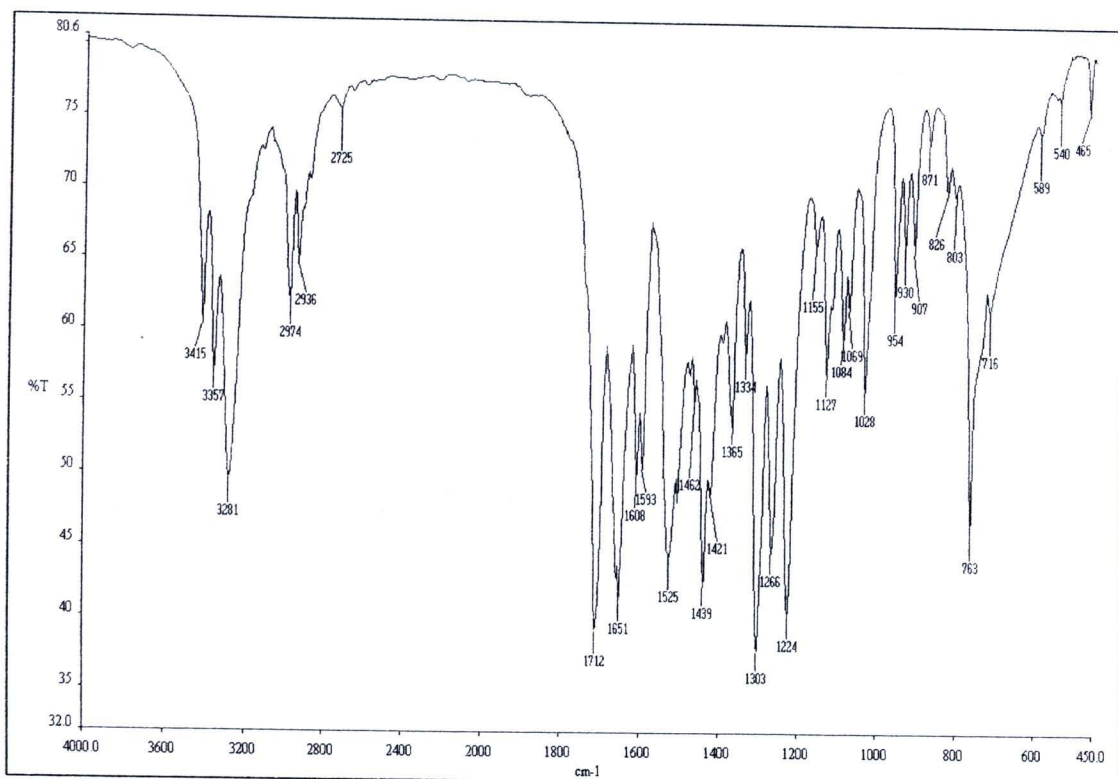


Figure 58 IR spectrum of ethyl-3-amino-4-propionamidobenzoate (21b)

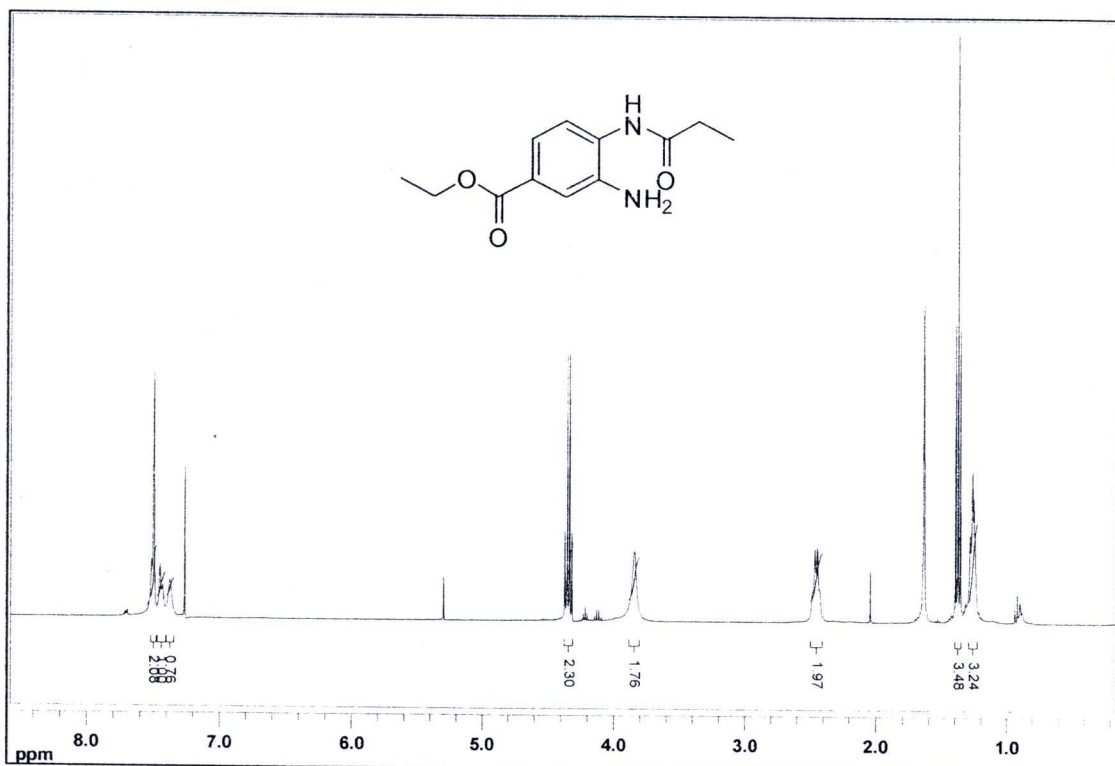


Figure 59 ¹H NMR spectrum of ethyl-3-amino-4-propionamidobenzoate (21b)

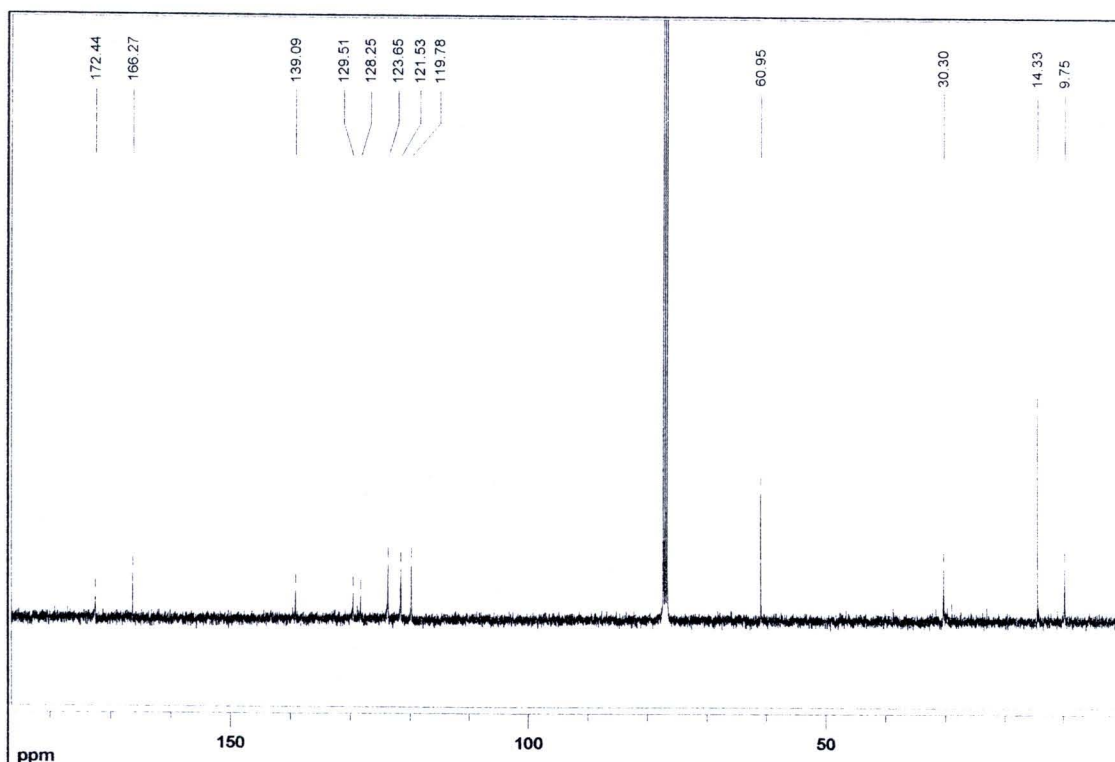


Figure 60 ¹³C NMR spectrum of ethyl-3-amino-4-propionamidobenzoate (21b)

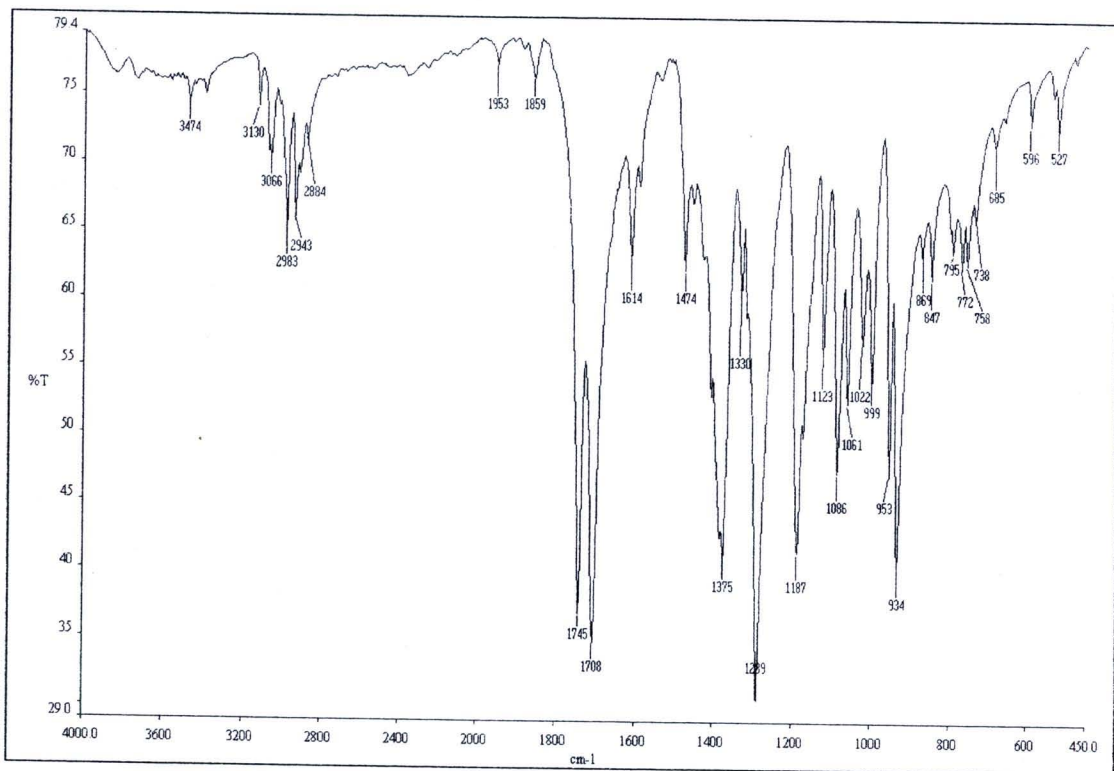


Figure 61 IR spectrum of ethyl-1-propionyl-1H-benzo[d][1,2,3]triazole-5-carboxylate (22b)

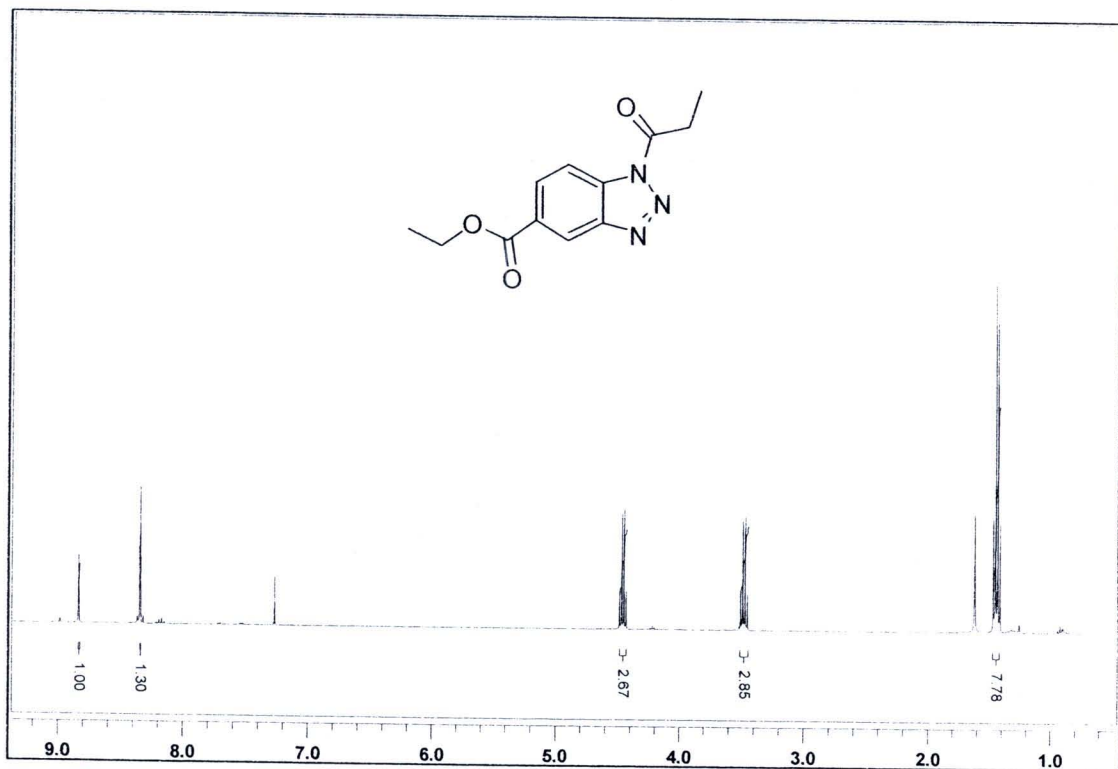


Figure 62 ¹H NMR spectrum of ethyl-1-propionyl-1H-benzo[d][1,2,3]triazole-5-carboxylate (22b)

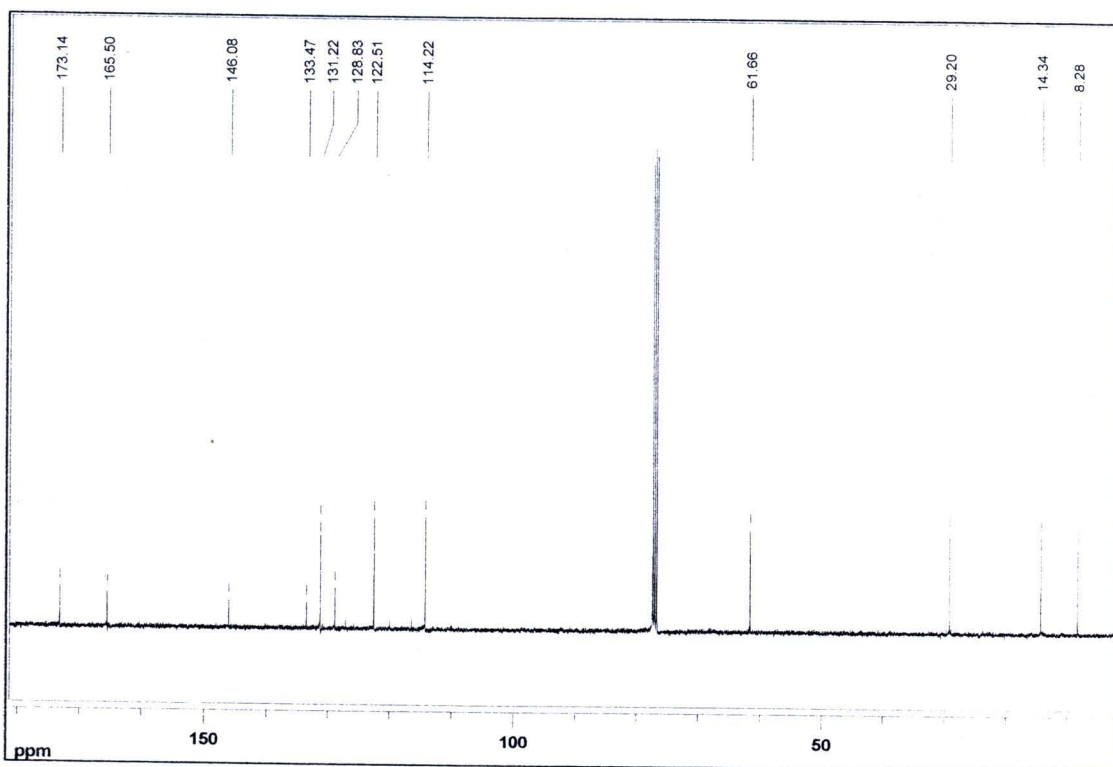


Figure 63 ^{13}C NMR spectrum of ethyl-1-propionyl-1H-benzo[d][1,2,3]triazole-5-carboxylate (**22b**)

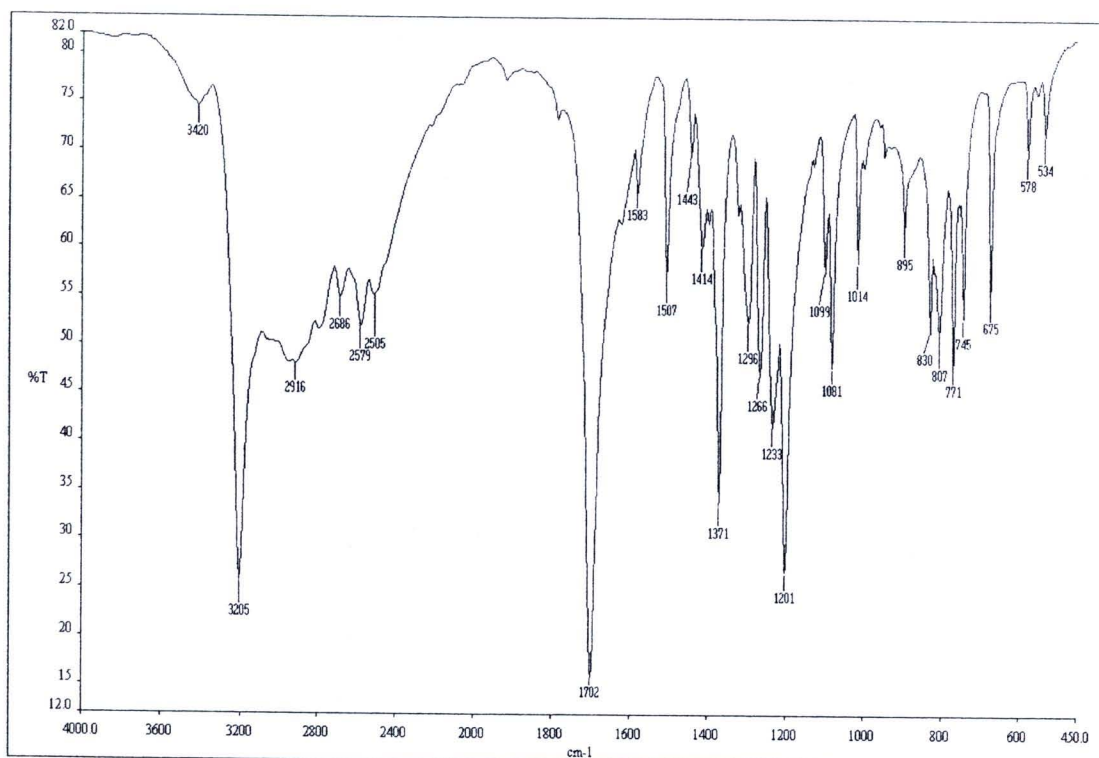


Figure 64 IR spectrum of 1H-benzo[d][1,2,3]triazole-5-carboxylic acid (**23**)

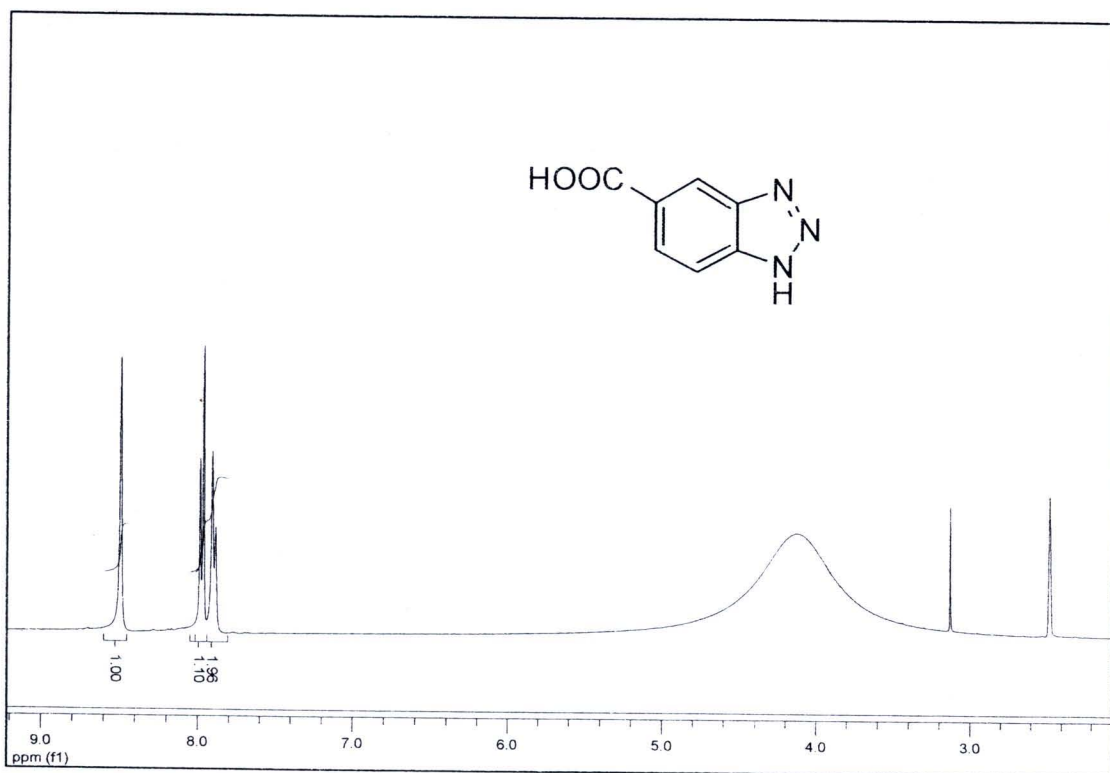


Figure 65 ^1H NMR spectrum of 1H-benzo[*d*][1,2,3]triazole-5-carboxylic acid (23)

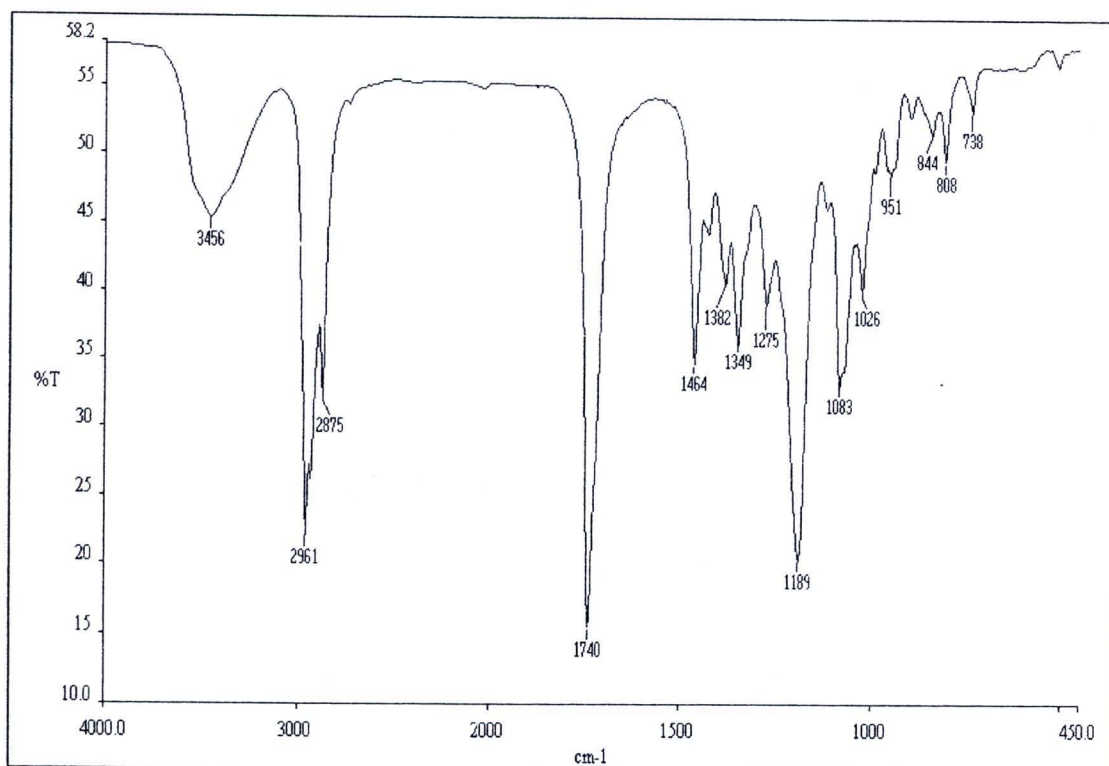


Figure 66 IR spectrum of butyl propionate (4c)

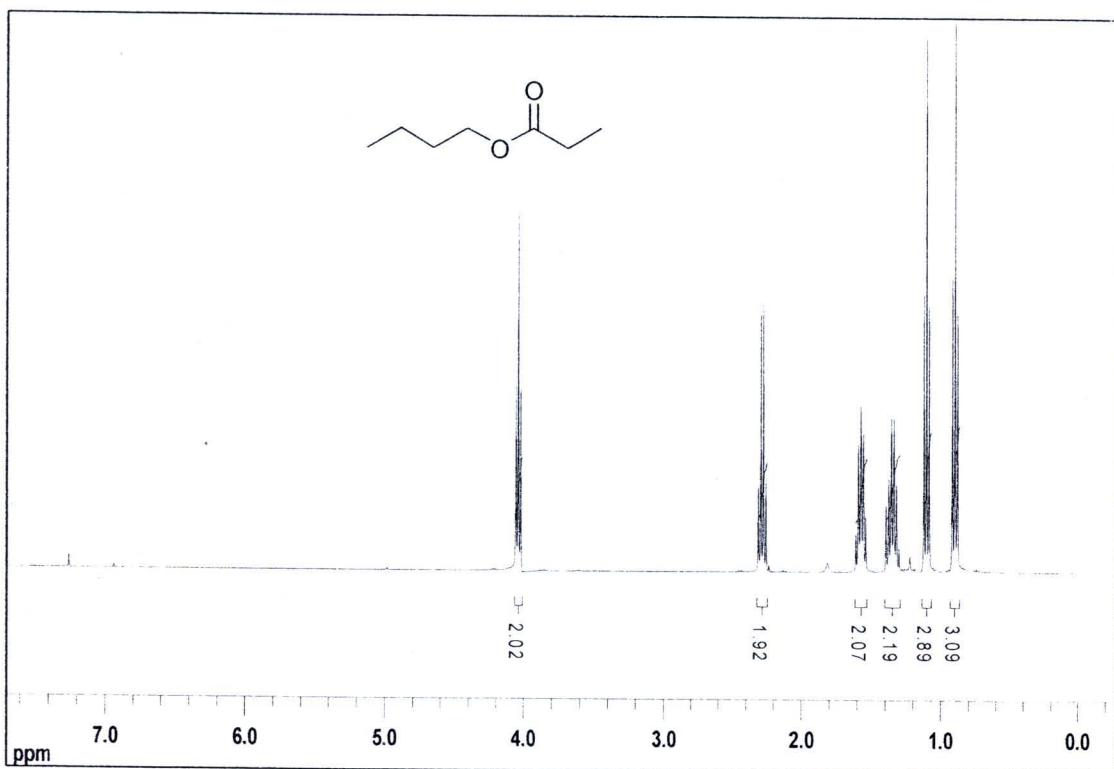


Figure 67 ^1H NMR spectrum of butyl propionate (4c)

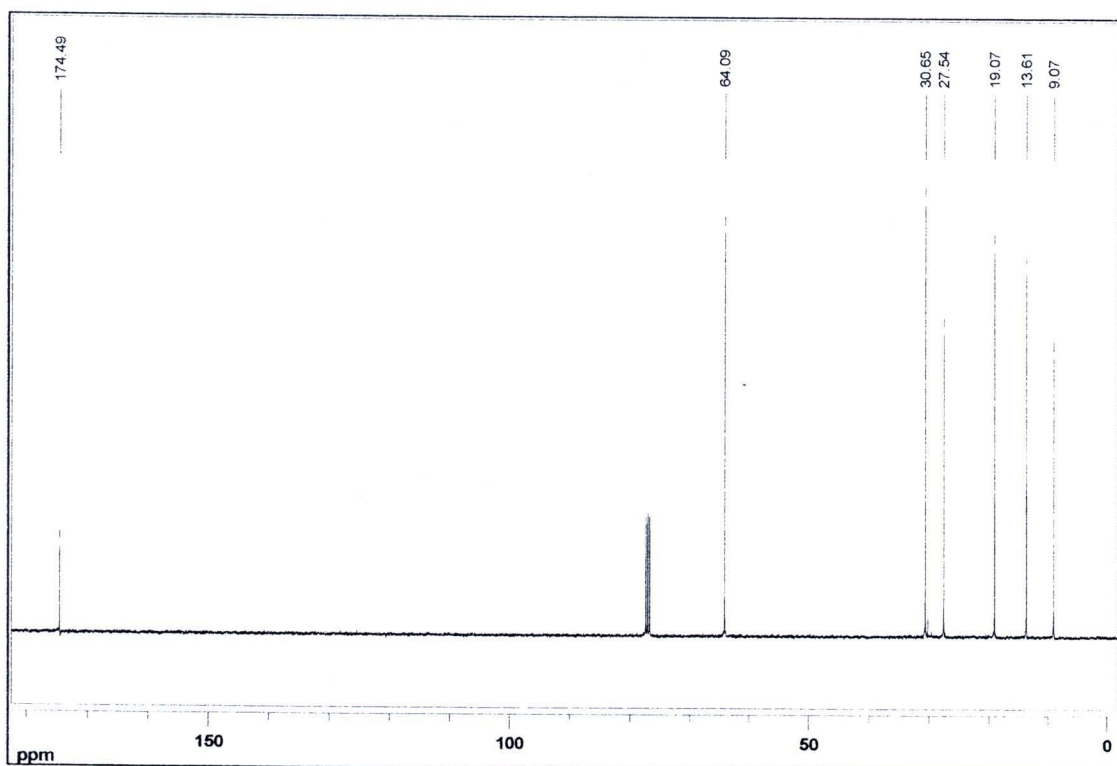


Figure 68 ^{13}C NMR spectrum of butyl propionate (4c)

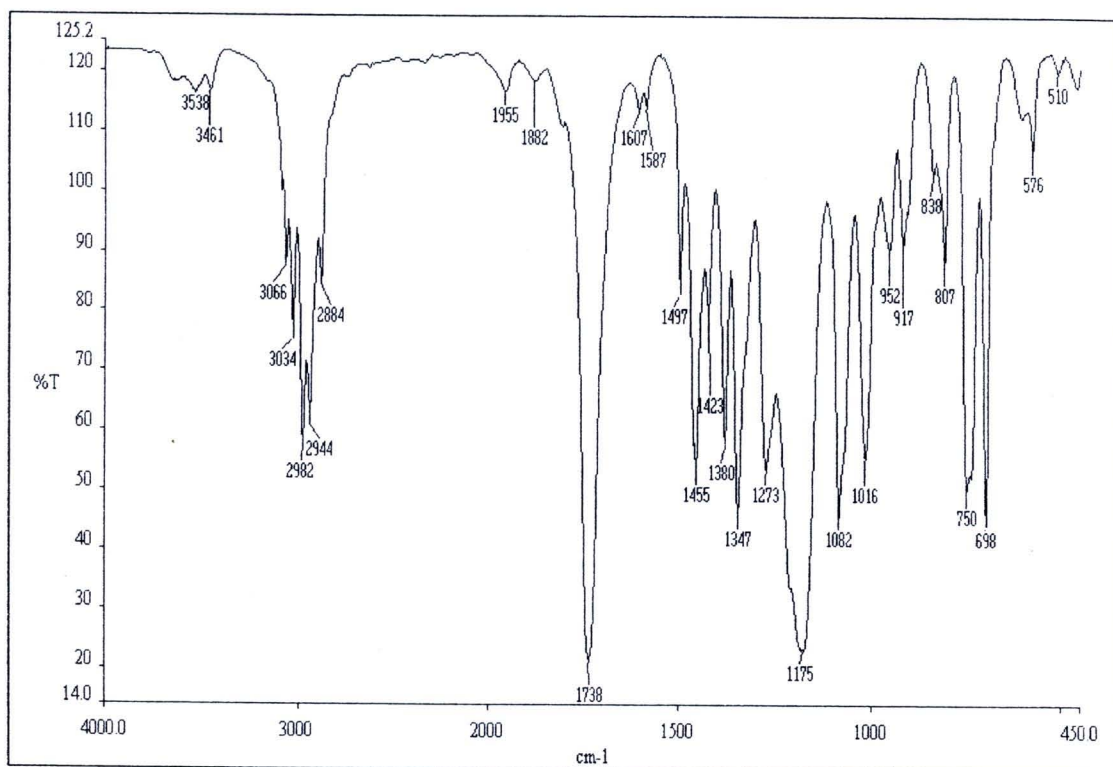


Figure 69 IR spectrum of benzyl propionate (**4d**)

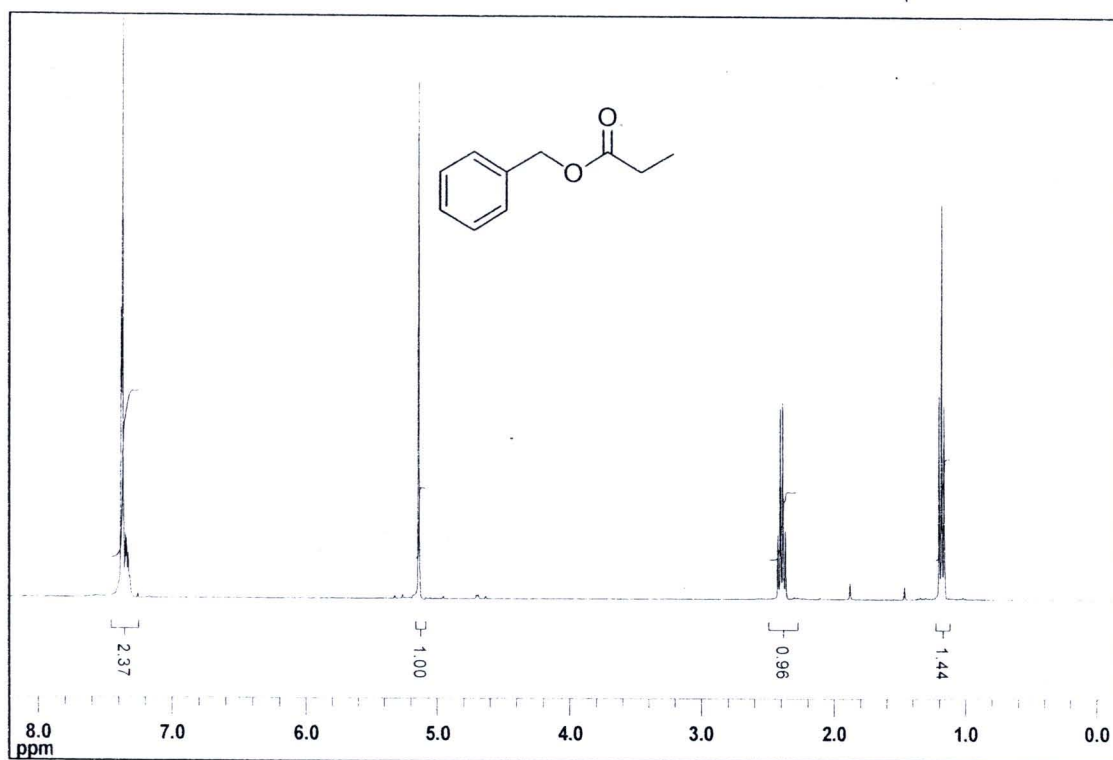


Figure 70 ^1H NMR spectrum of benzyl propionate (**4d**)

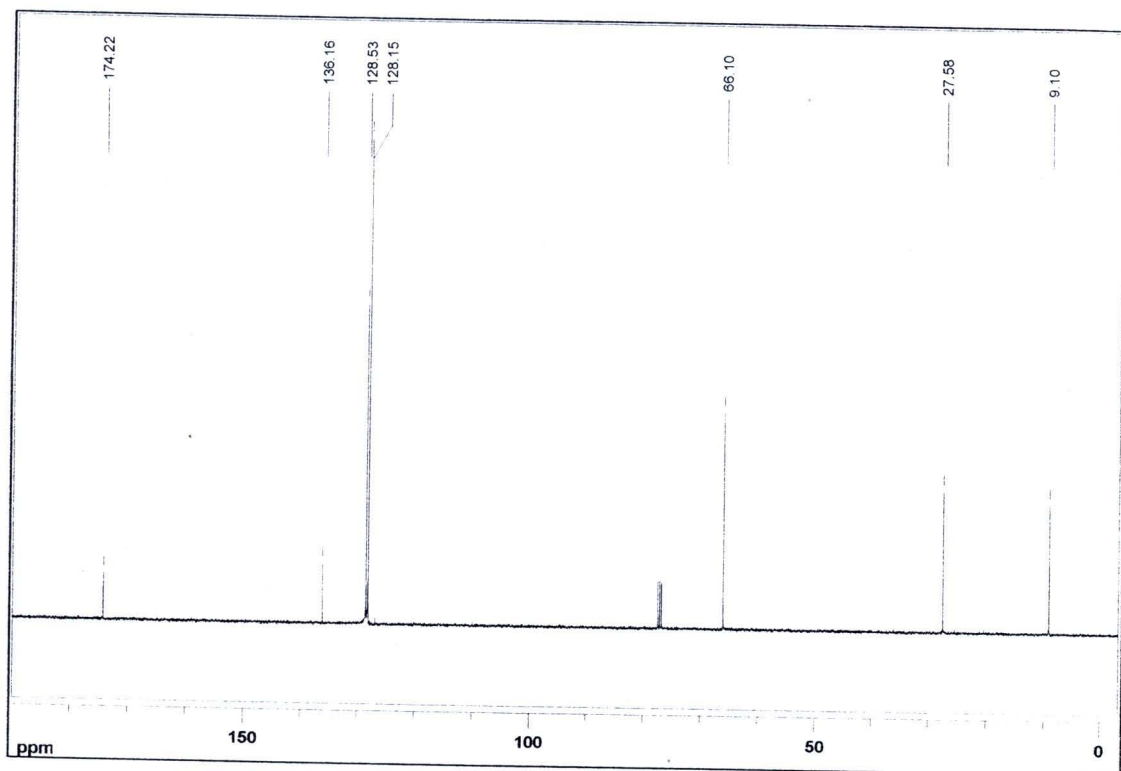


Figure 71 ^{13}C NMR spectrum of benzyl propionate (4d)

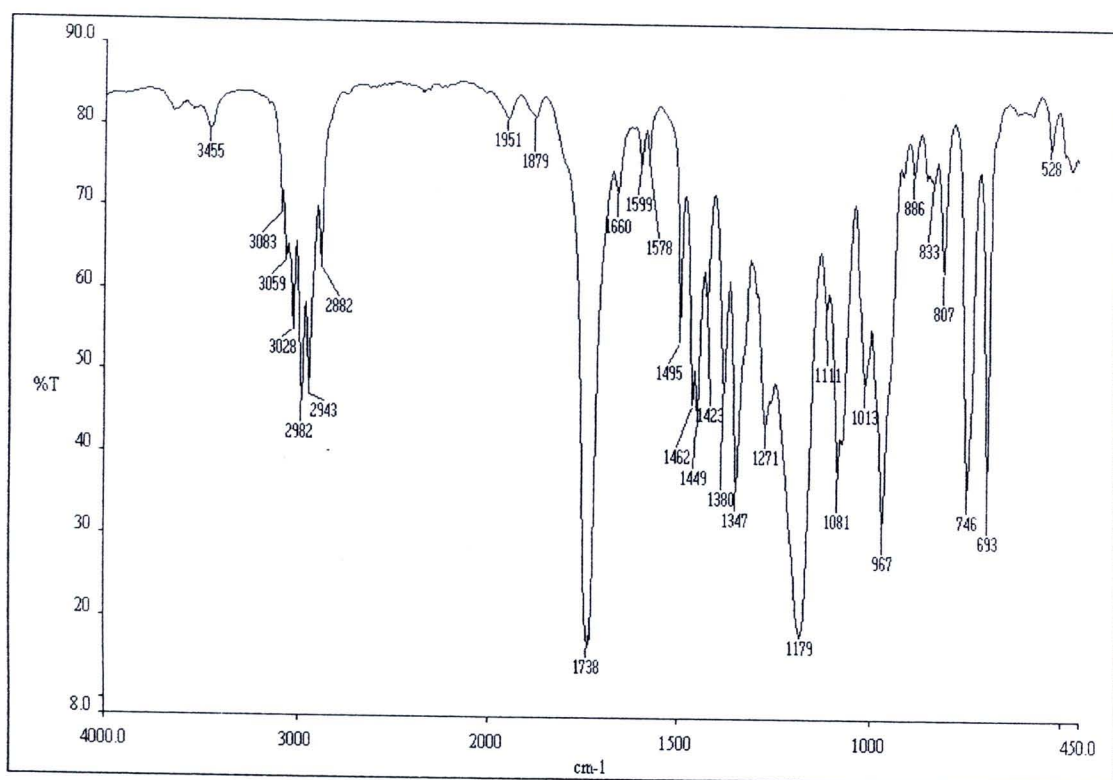


Figure 72 IR spectrum of cinnamyl propionate (4e)

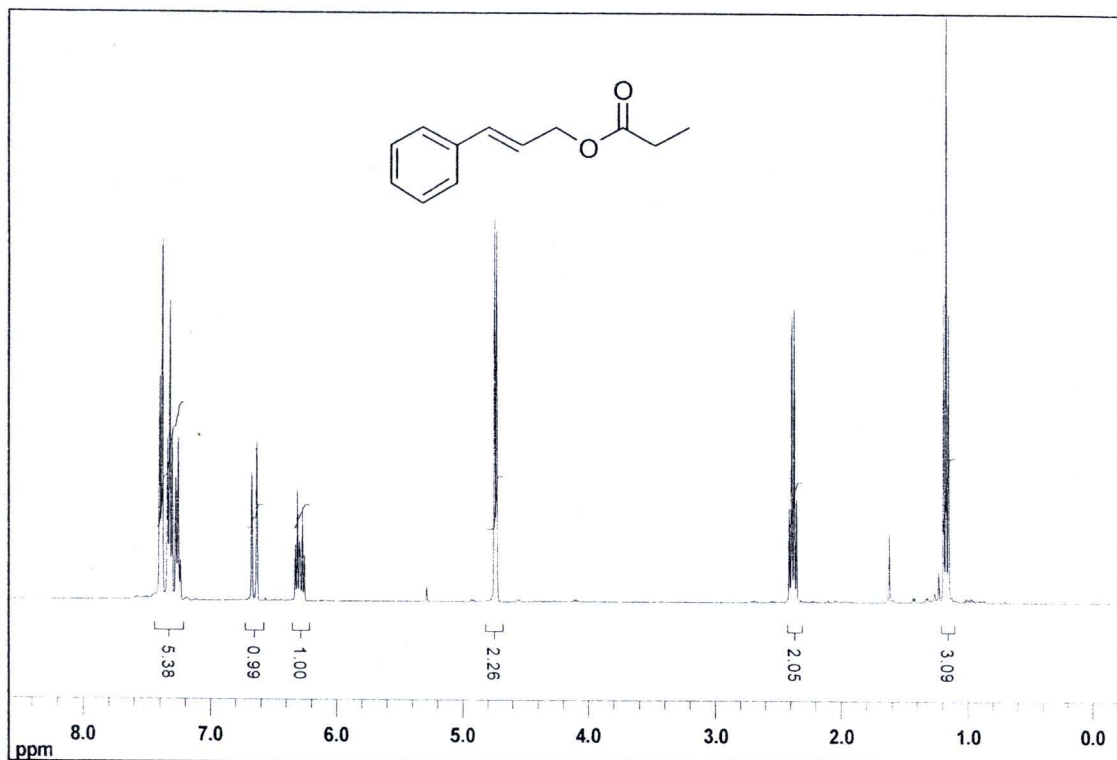


Figure 73 ^1H NMR spectrum of cinnamyl propionate (4e)

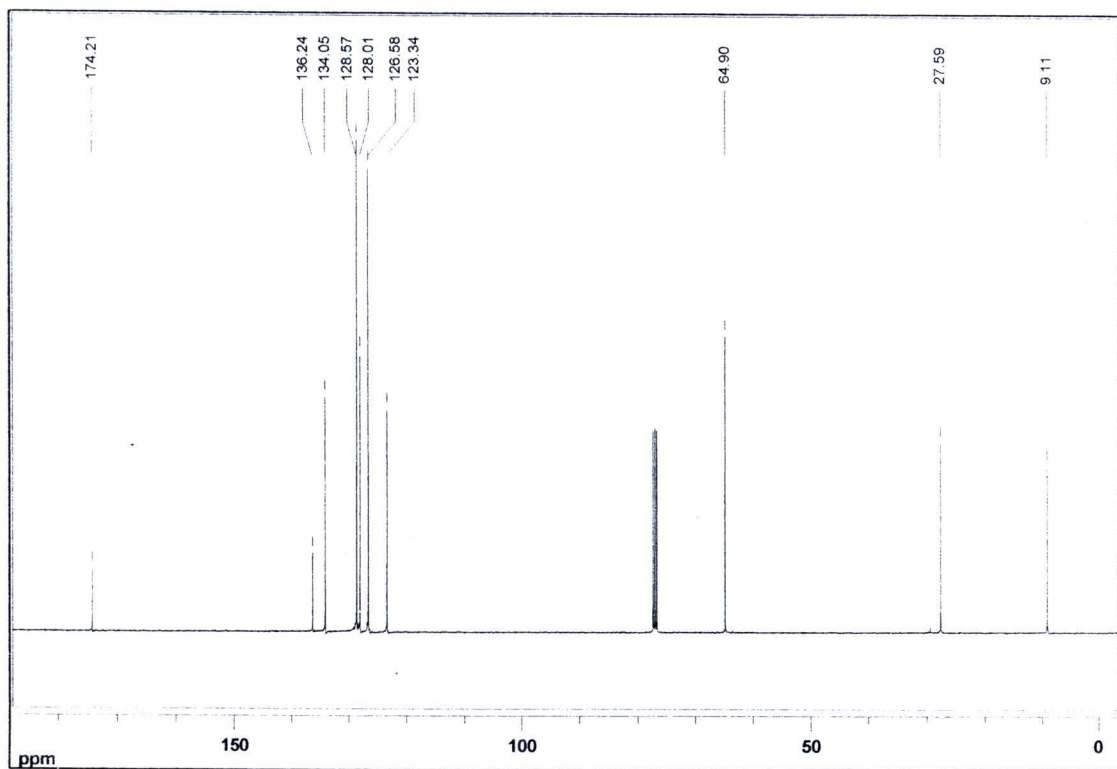


Figure 74 ^{13}C NMR spectrum of cinnamyl propionate (4e)

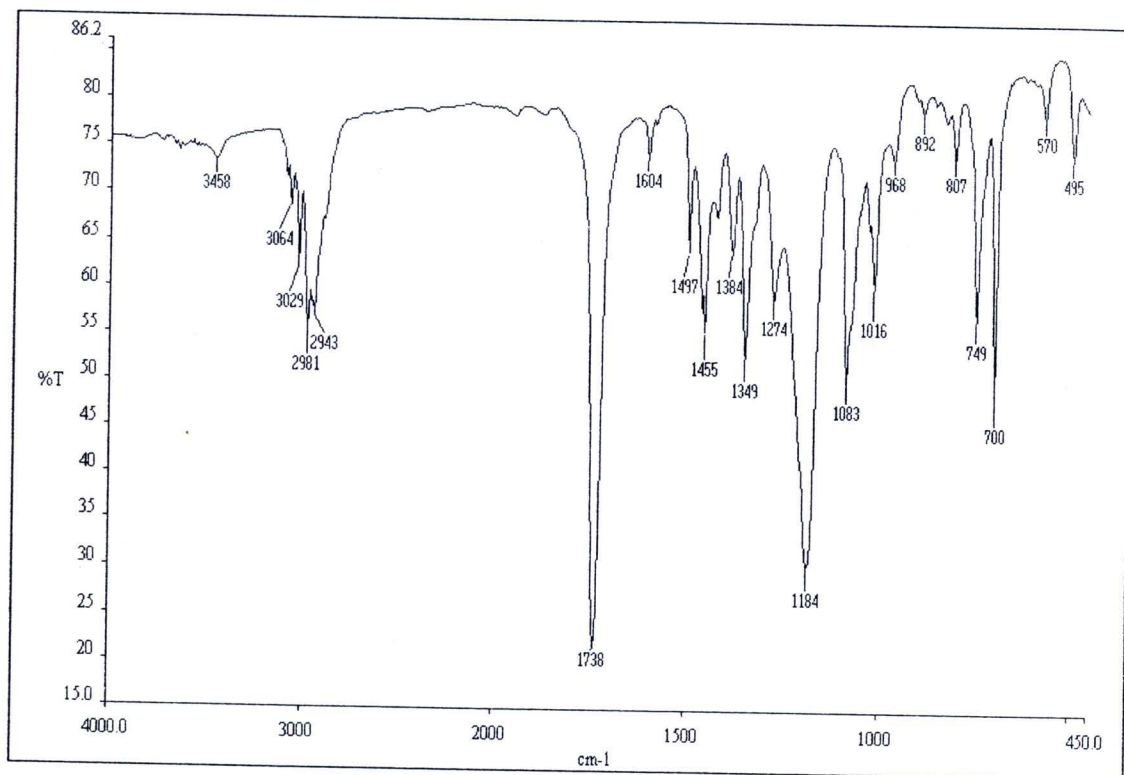


Figure 75 IR spectrum of phenethyl propionate (4f)

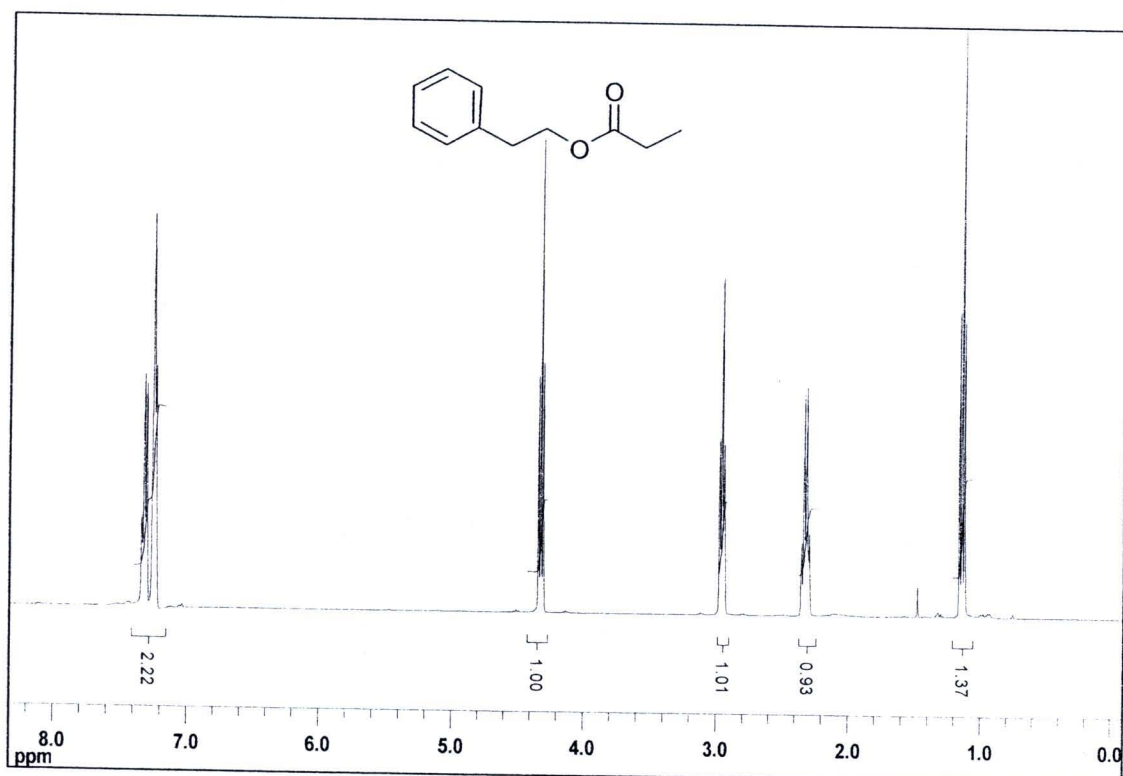


Figure 76 ^1H NMR spectrum of phenethyl propionate (4f)

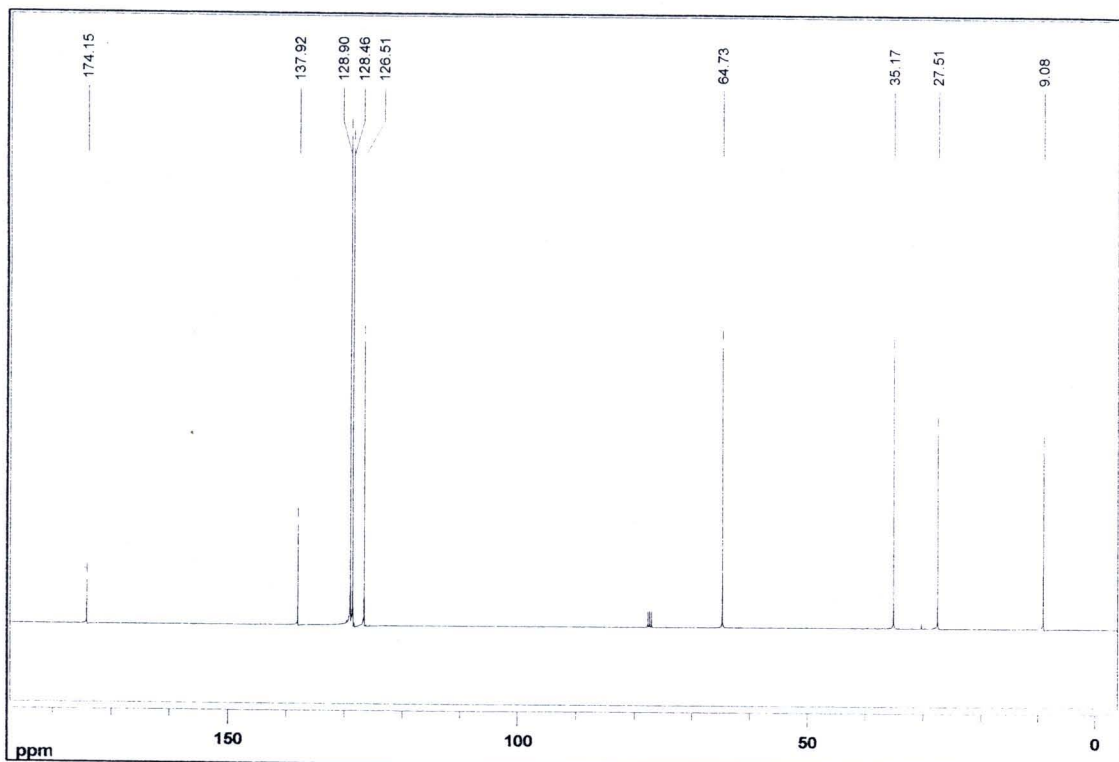


Figure 77 ^{13}C NMR spectrum of phenethyl propionate (4f)

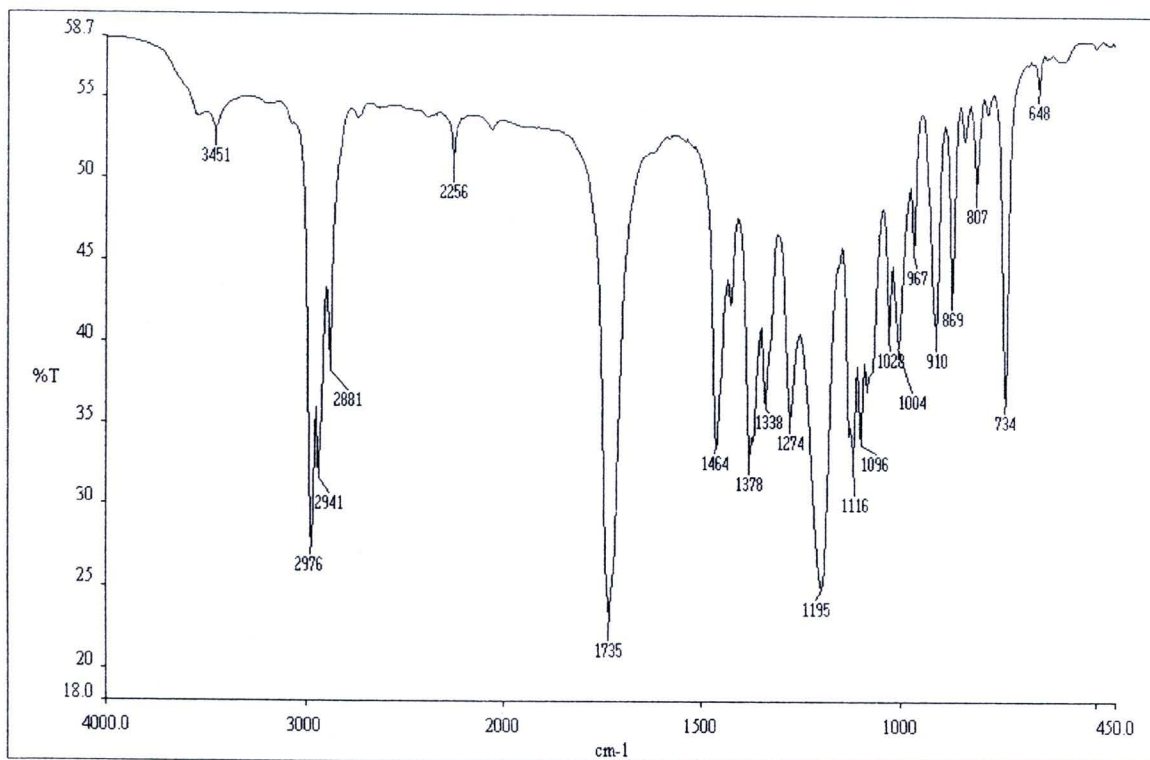


Figure 78 IR spectrum of sec-butyl propionate (4g)

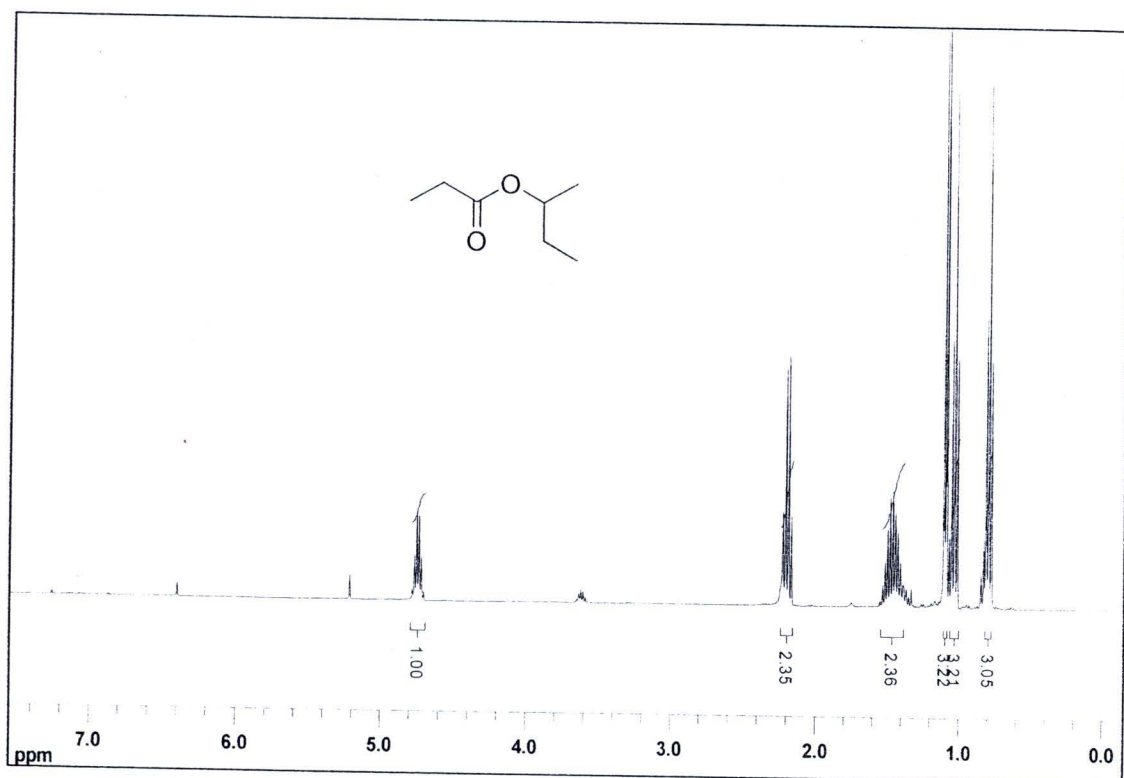


Figure 79 ^1H NMR spectrum of sec-butyl propionate (4g)

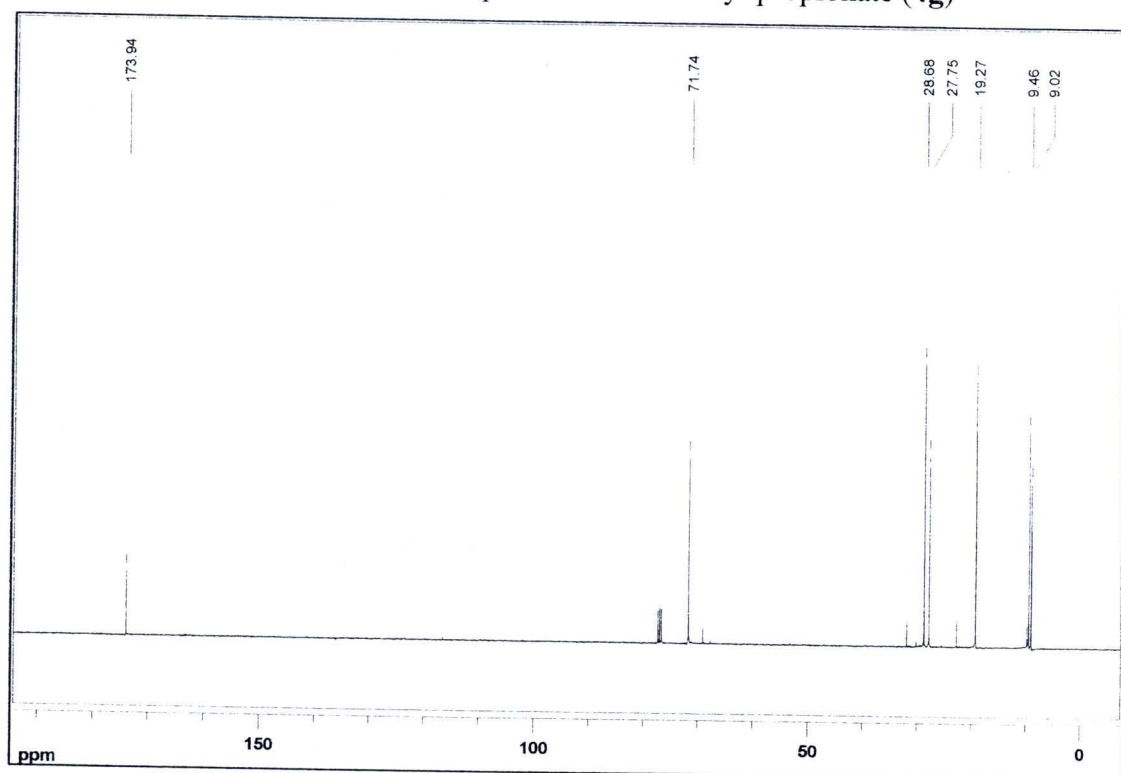


Figure 80 ^{13}C NMR spectrum of sec-butyl propionate (4g)

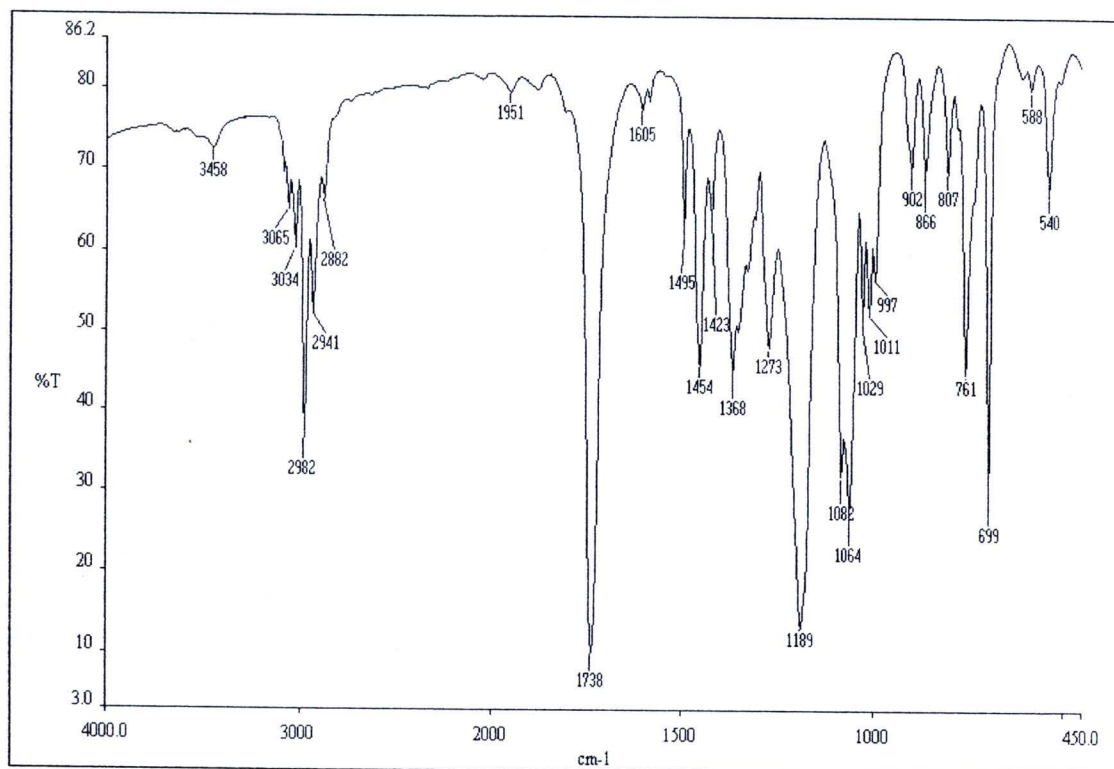


Figure 81 IR spectrum of 1-phenylethyl propionate (**4h**)

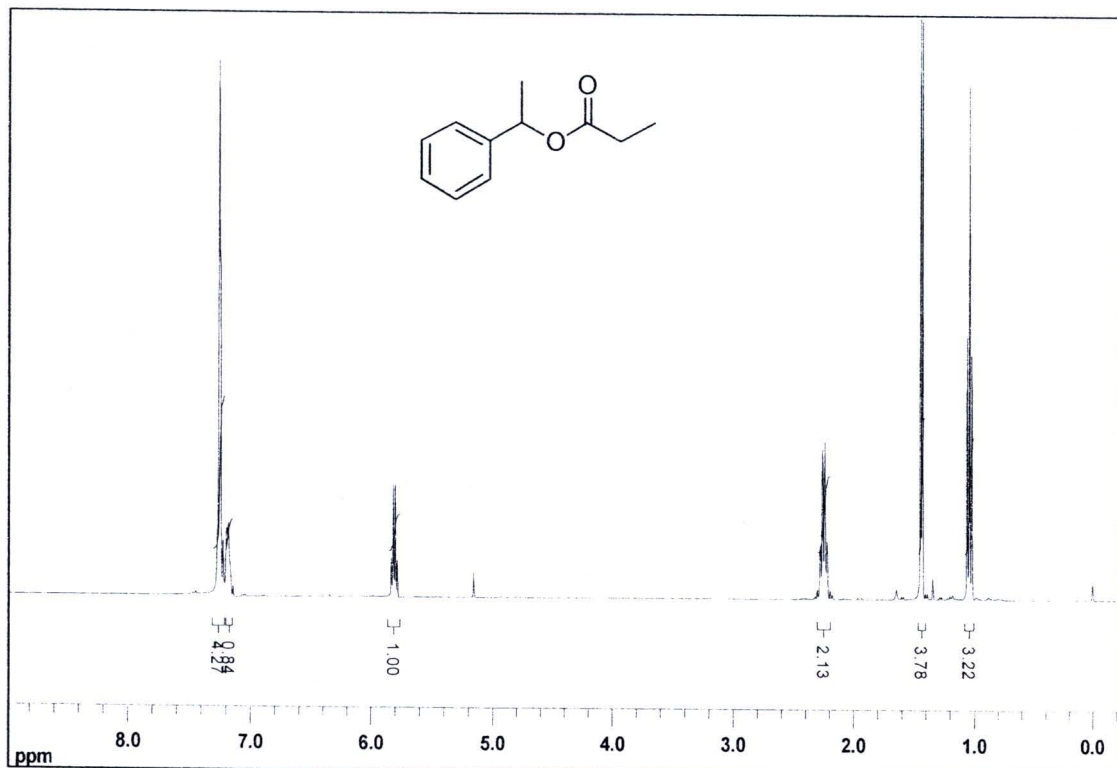


Figure 82 ¹H NMR spectrum of 1-phenylethyl propionate (**4h**)

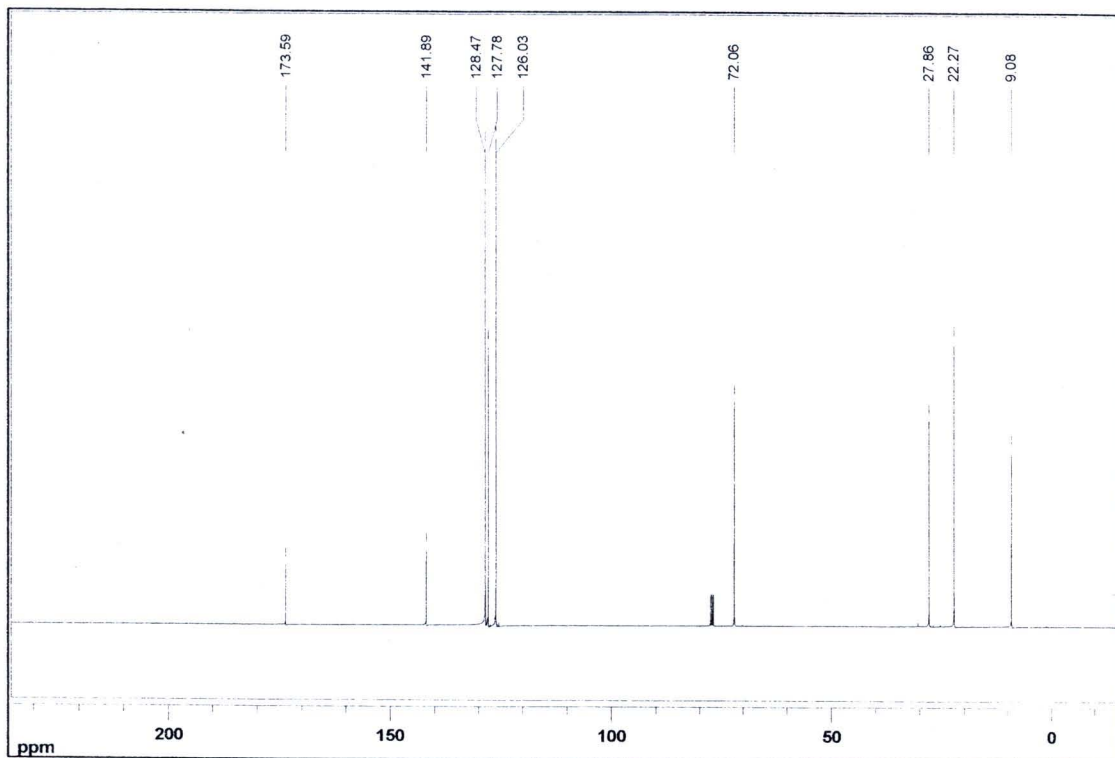


Figure 83 ^{13}C NMR spectrum of 1-phenylethyl propionate (4h)

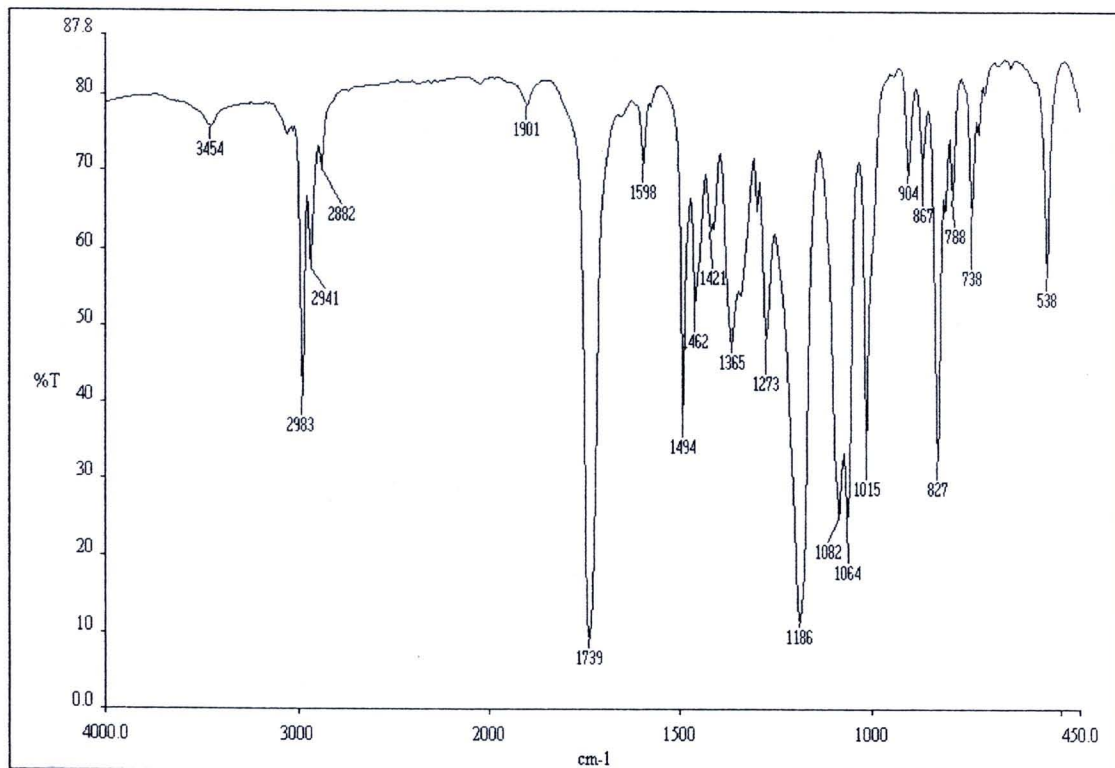


Figure 84 IR spectrum of 1-(4-chlorophenyl)ethyl propionate (4i)

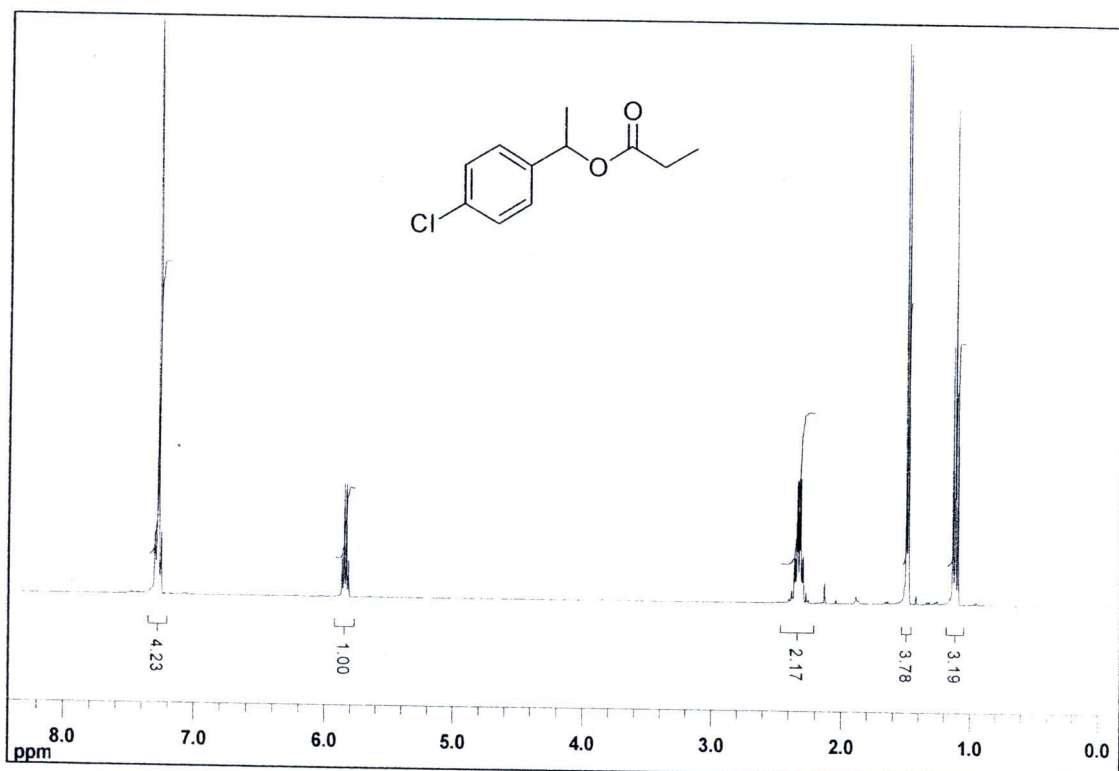


Figure 85 ^1H NMR spectrum of 1-(4-chlorophenyl)ethyl propionate (4i)

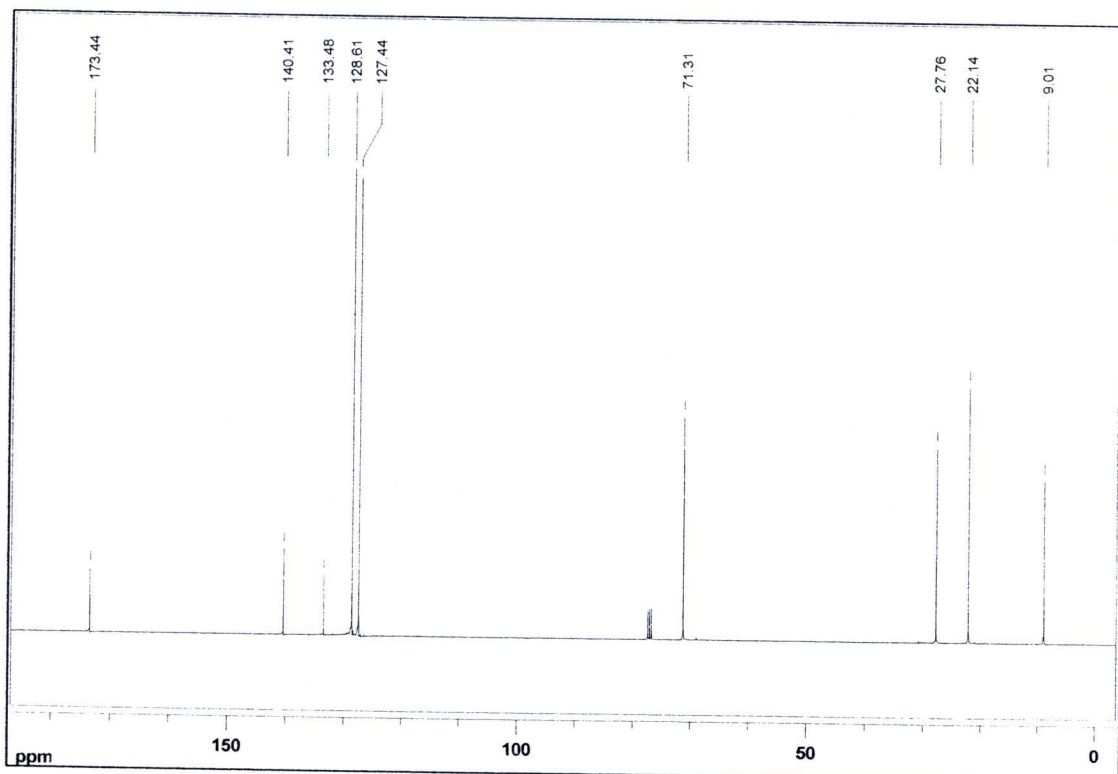


Figure 86 ^{13}C NMR spectrum of 1-(4-chlorophenyl)ethyl propionate (4i)

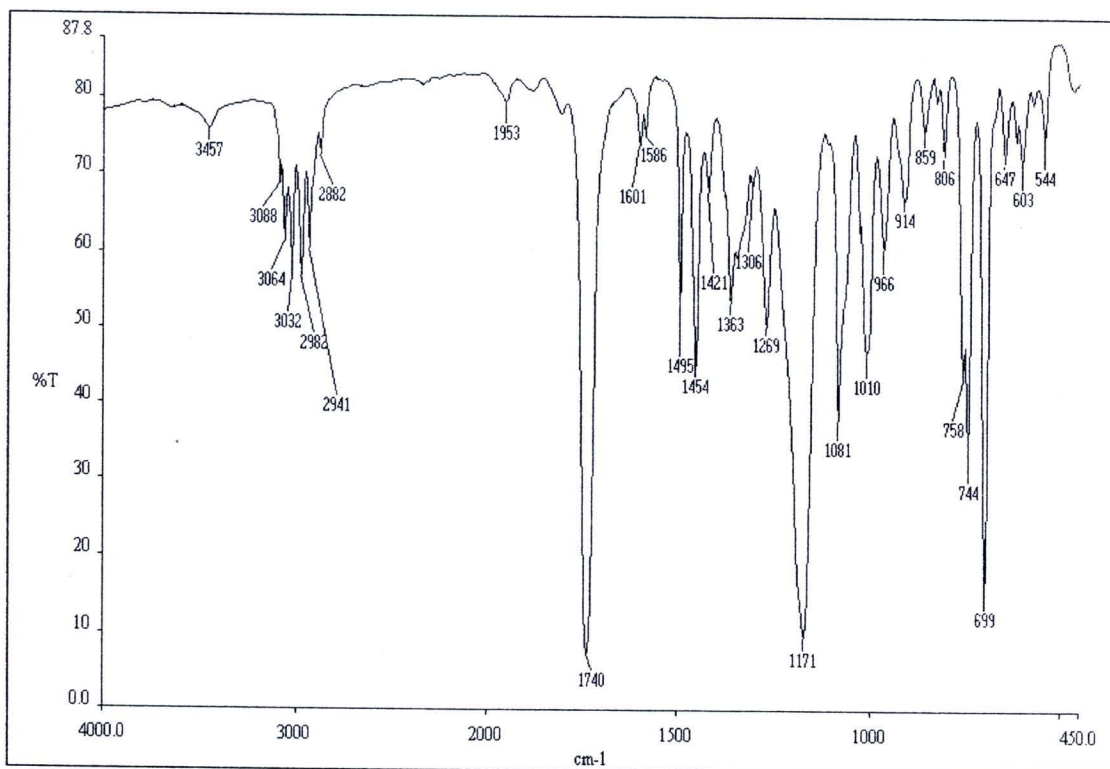


Figure 87 IR spectrum of benzhydryl propionate (**4j**)

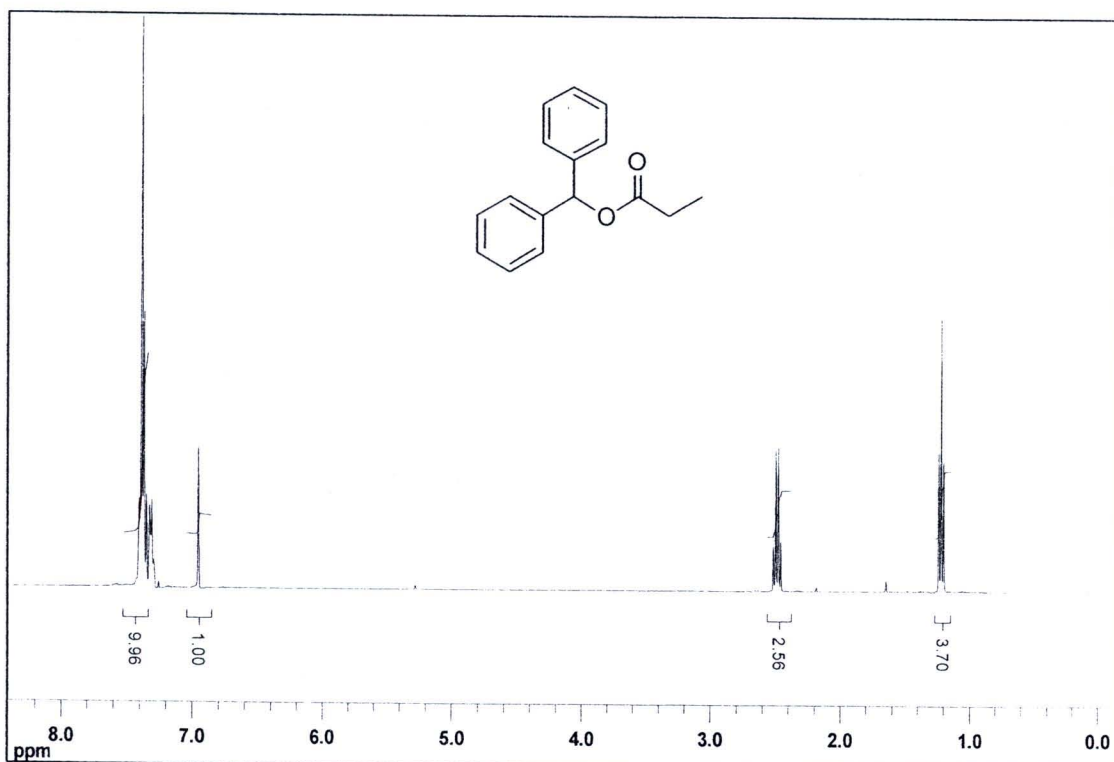


Figure 88 ¹H NMR spectrum of benzhydryl propionate (**4j**)

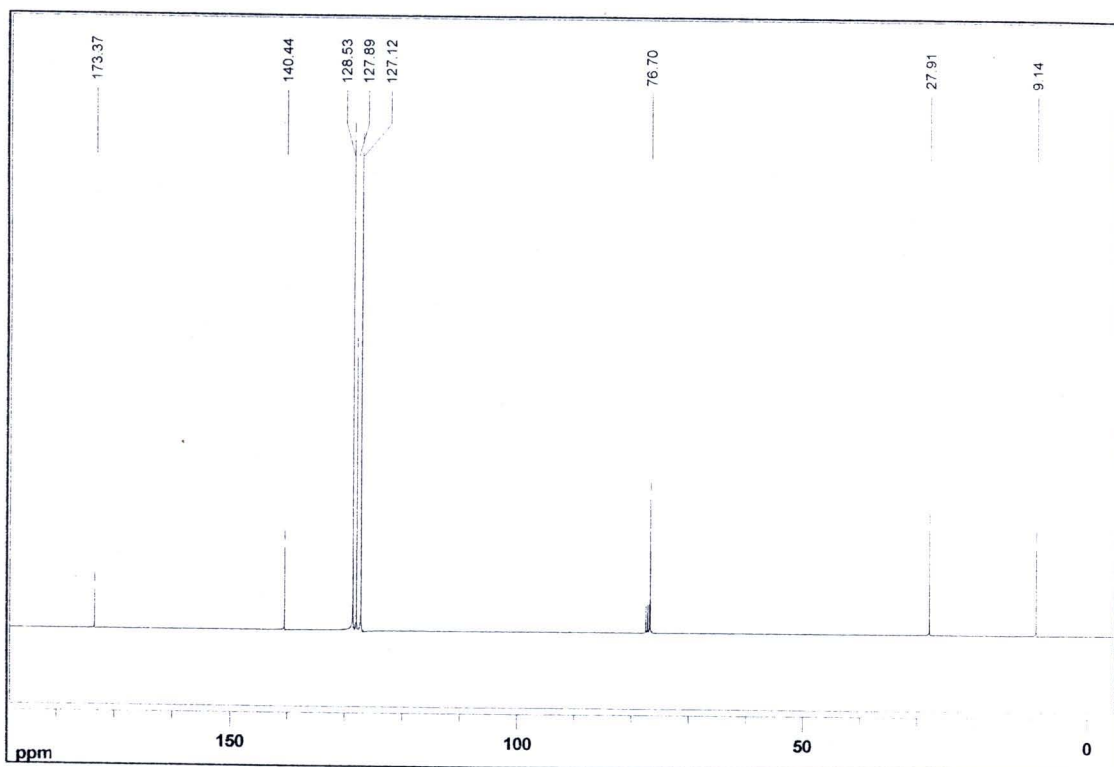


Figure 89 ^{13}C NMR spectrum of benzhydryl propionate (4j)

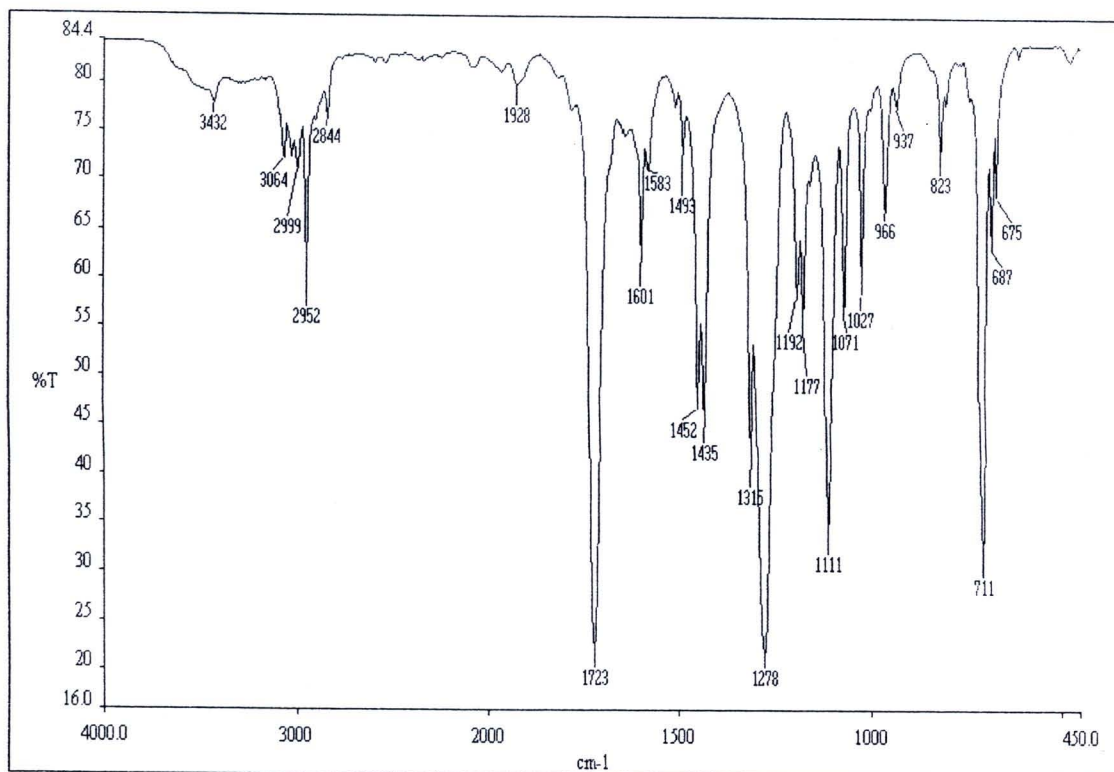


Figure 90 IR spectrum of methyl benzoate (5a)

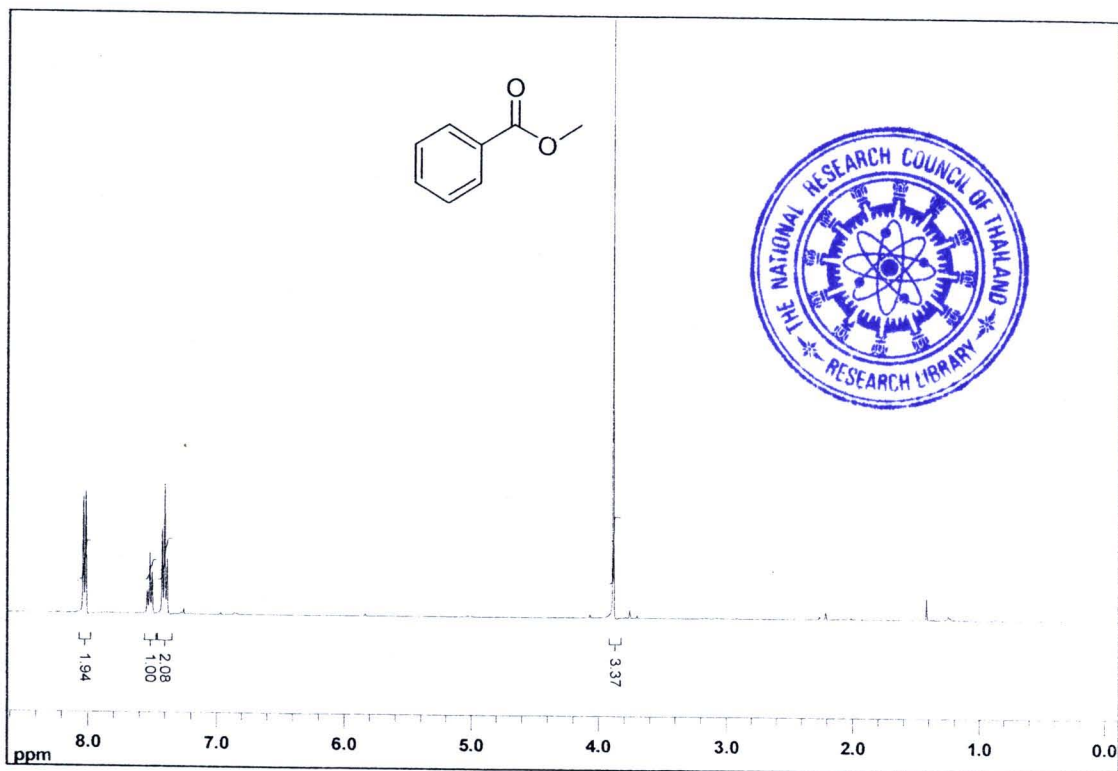


Figure 91 ^1H NMR spectrum of methyl benzoate (5a)

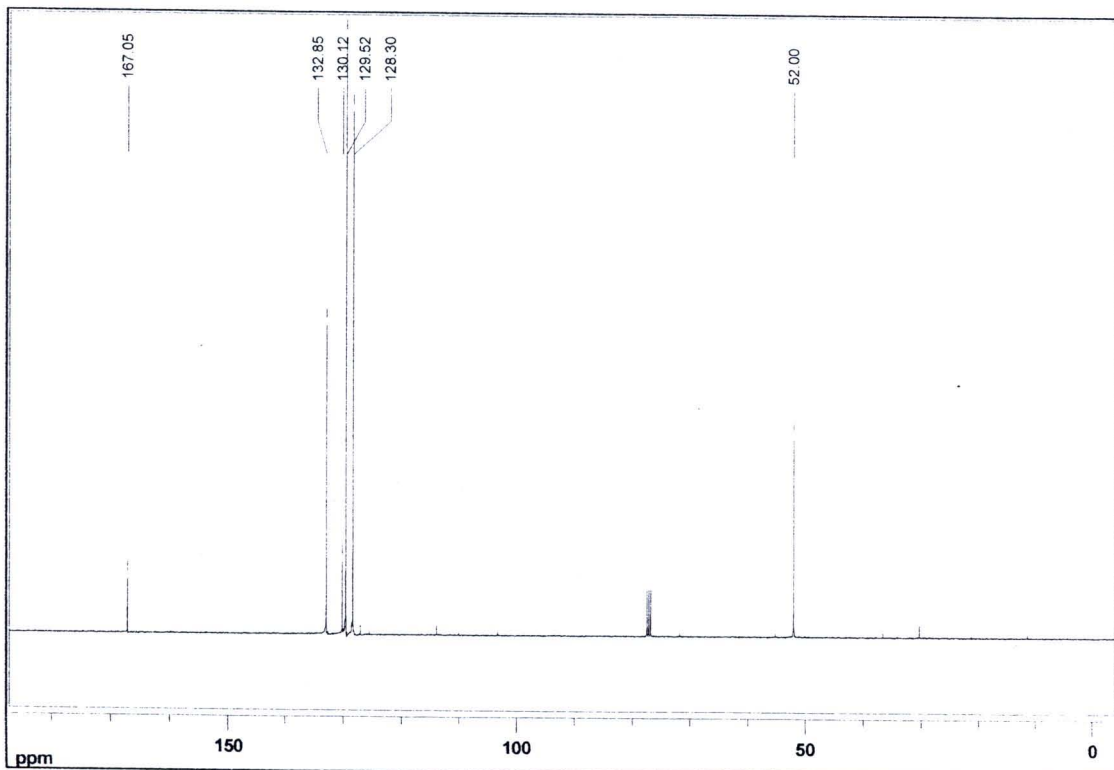


Figure 92 ^{13}C NMR spectrum of methyl benzoate (5a)

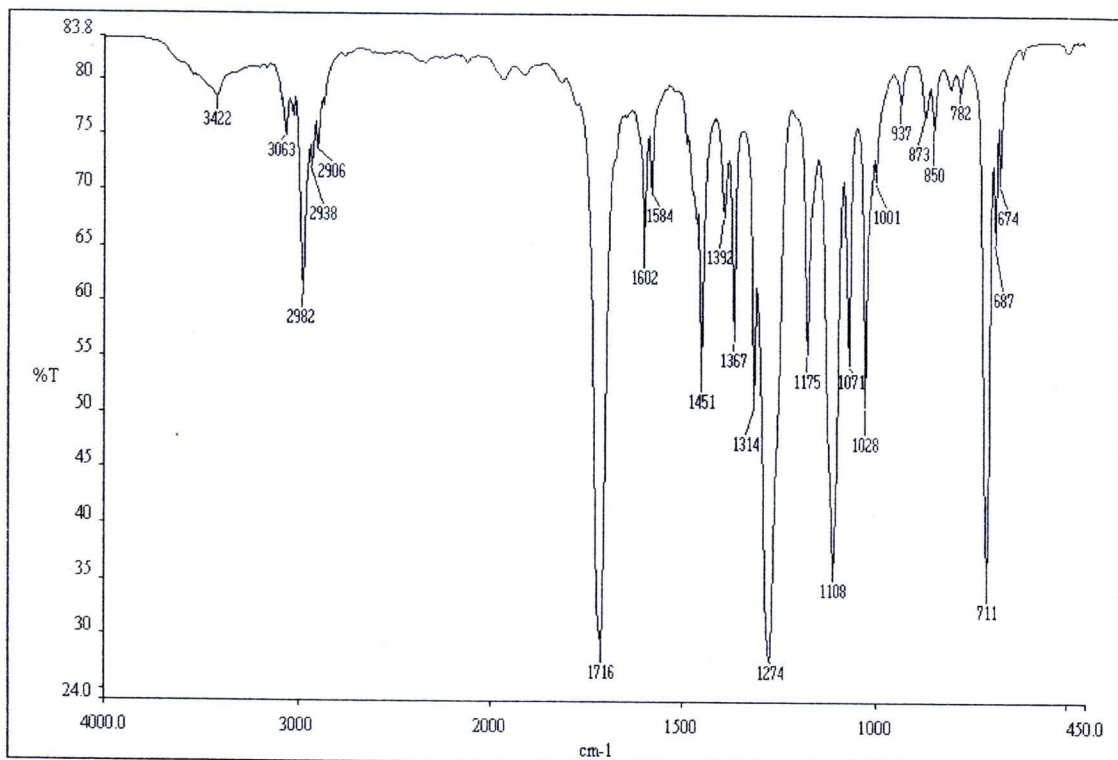


Figure 93 IR spectrum of ethyl benzoate (5b)

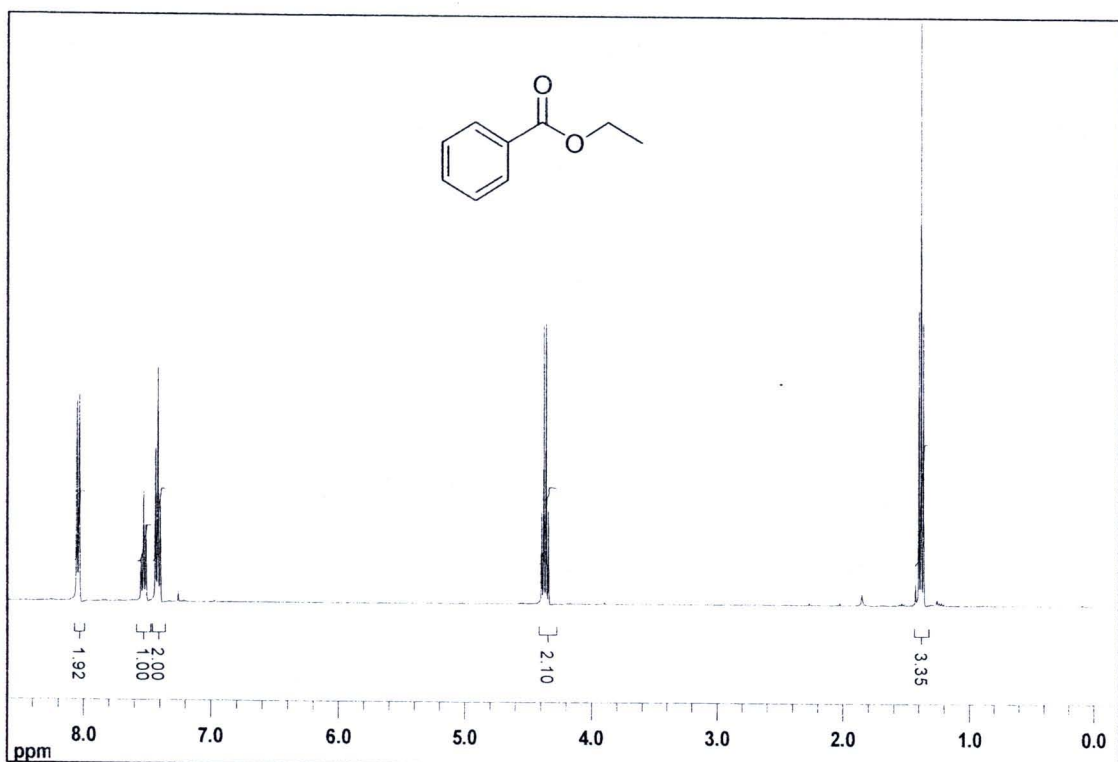


Figure 94 ¹H NMR ethyl benzoate (5b)

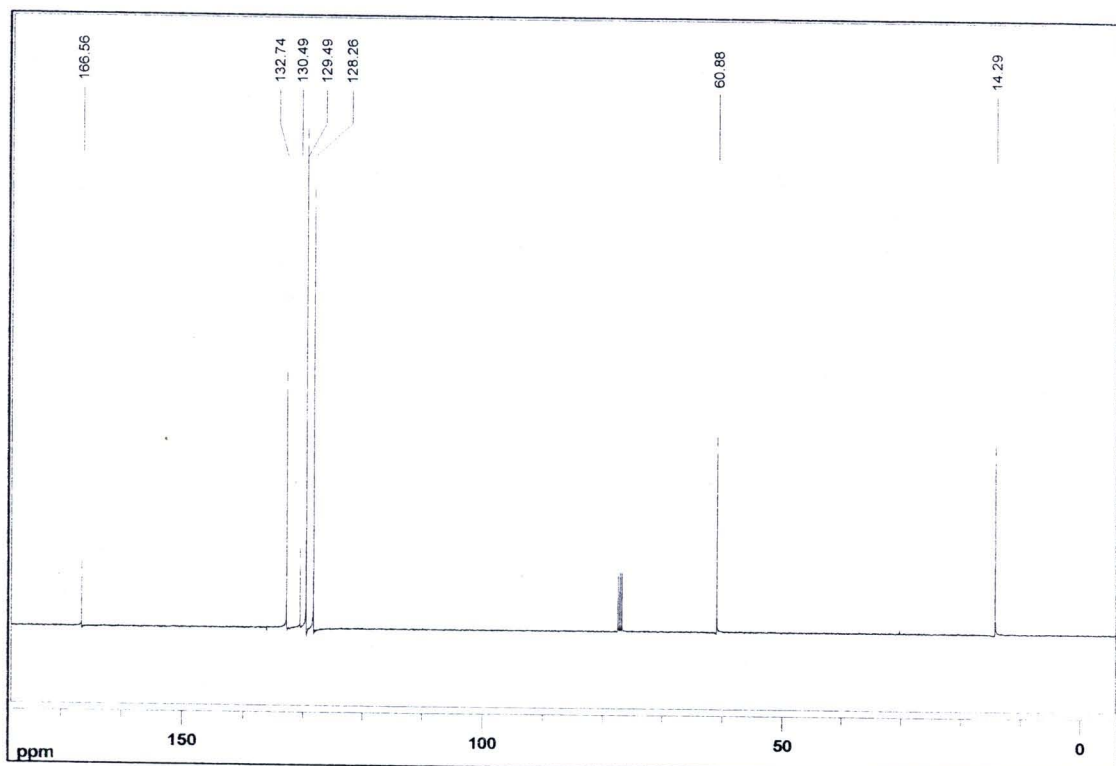


Figure 95 ^{13}C NMR spectrum of ethyl benzoate (5b)

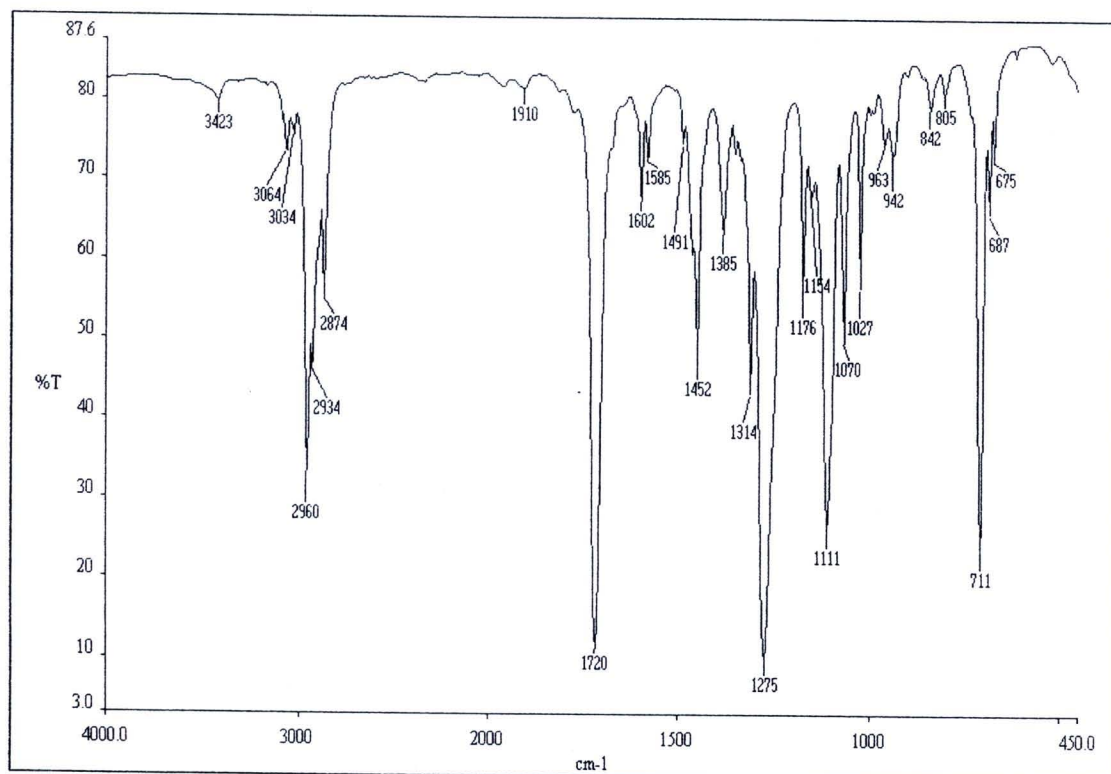


Figure 96 IR spectrum of butyl benzoate (5c)

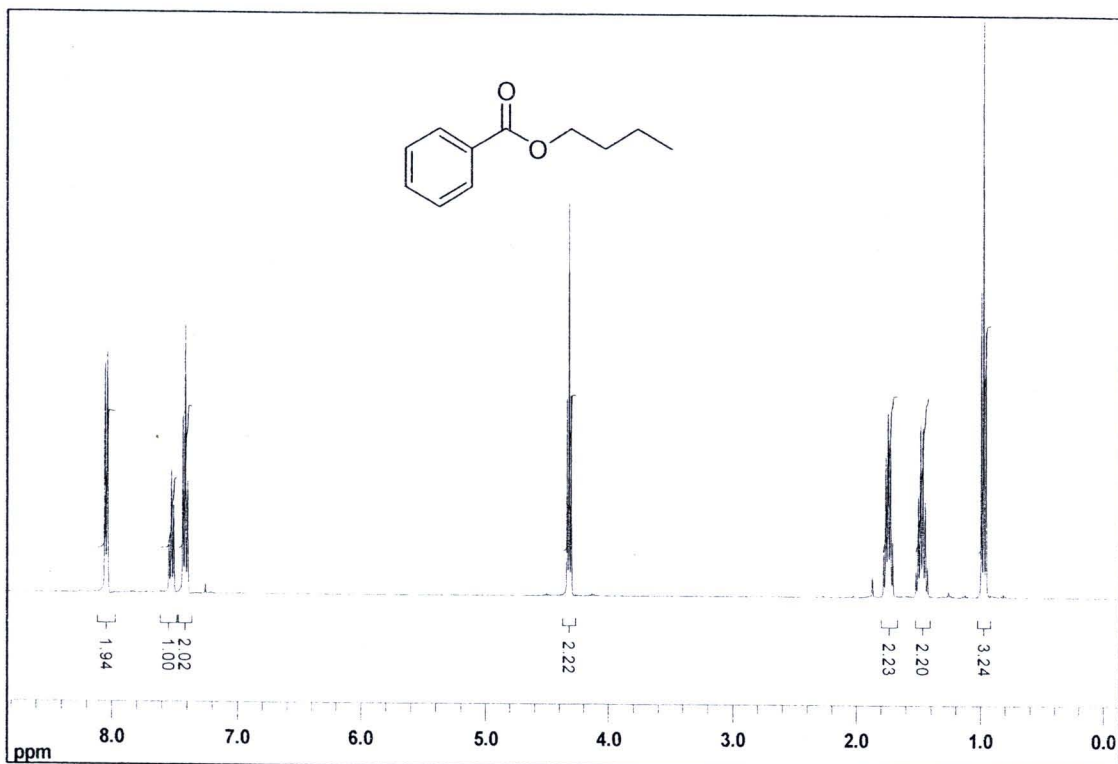


Figure 97 ^1H NMR spectrum of butyl benzoate (5c)

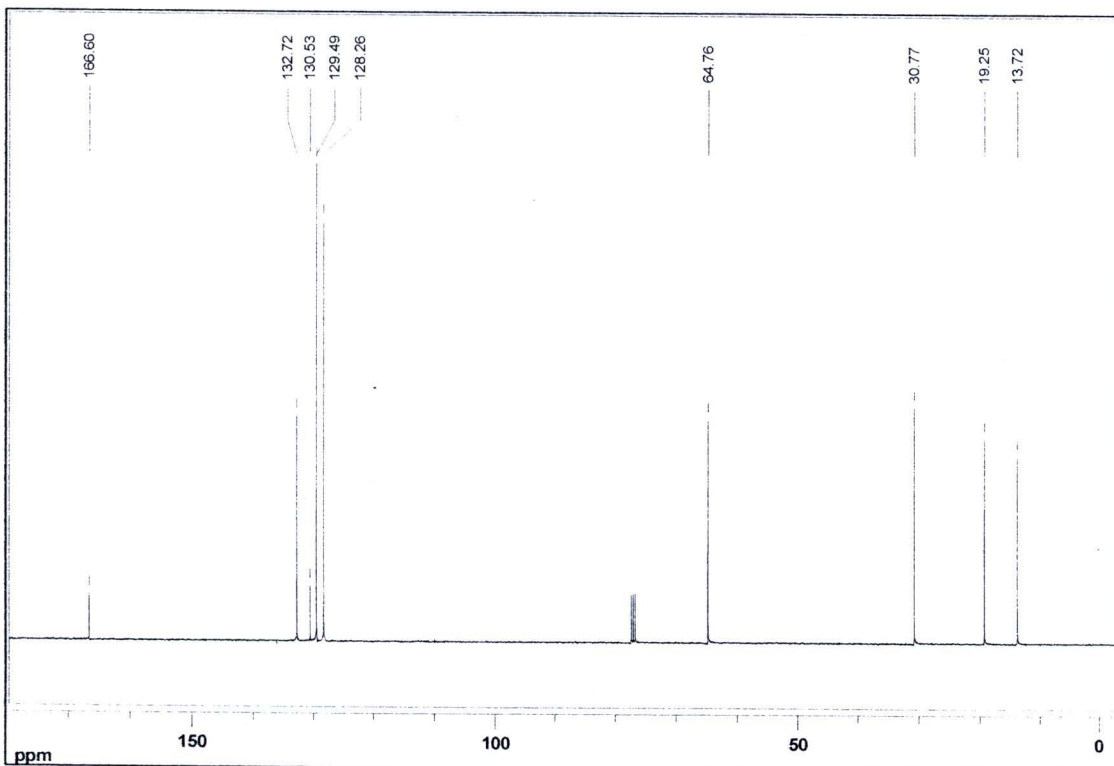


Figure 98 ^{13}C NMR spectrum of butyl benzoate (5c)

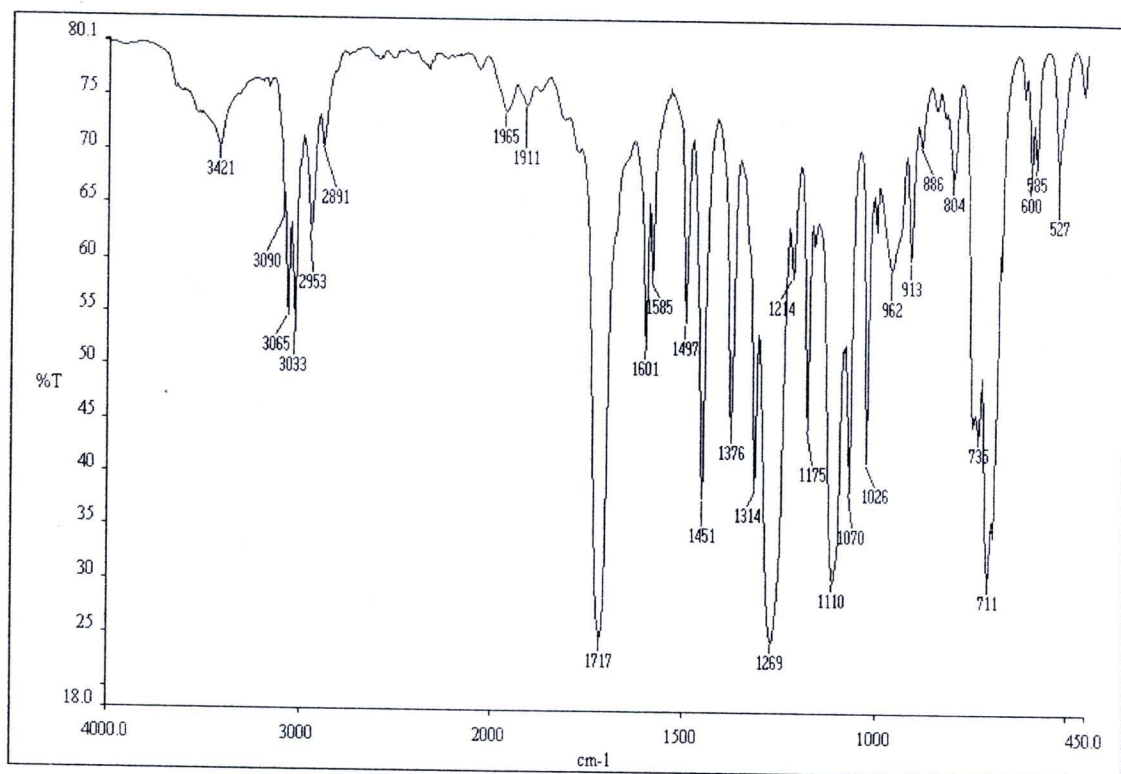


Figure 99 IR spectrum of benzyl benzoate (5d)

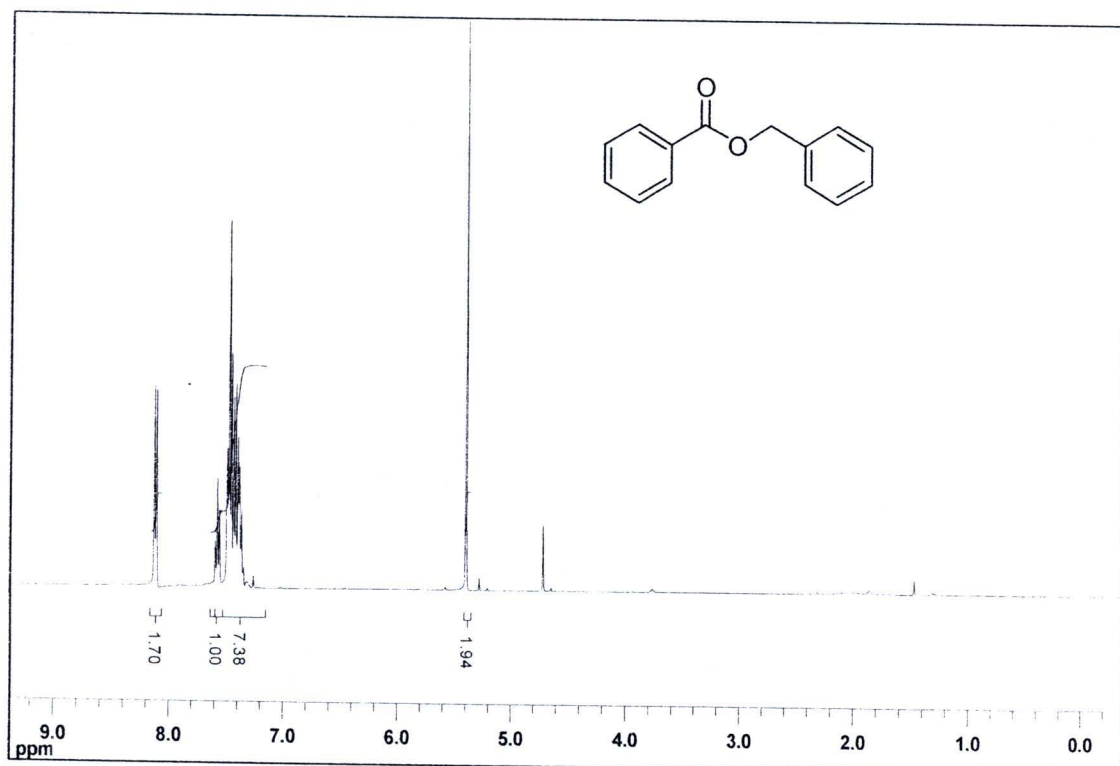


Figure 100 ¹H NMR spectrum of benzyl benzoate (5d)

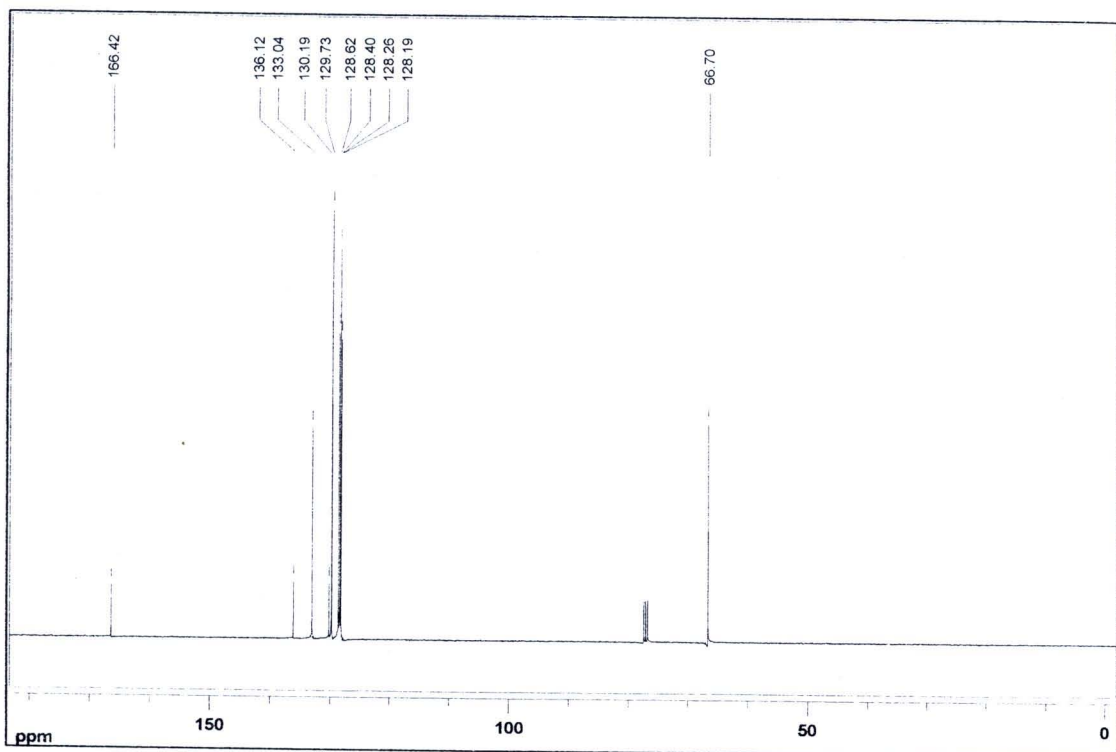


Figure 101 ^{13}C NMR spectrum of benzyl benzoate (5d)

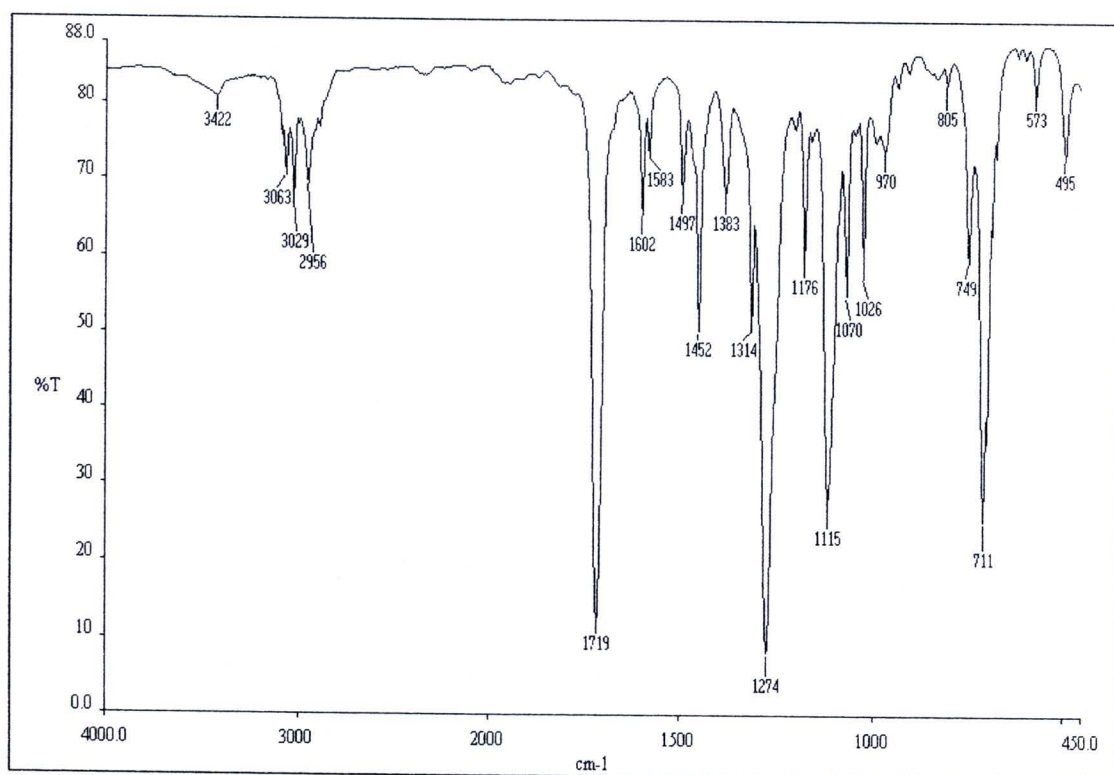


Figure 102 IR spectrum of phenethyl benzoate (5e)

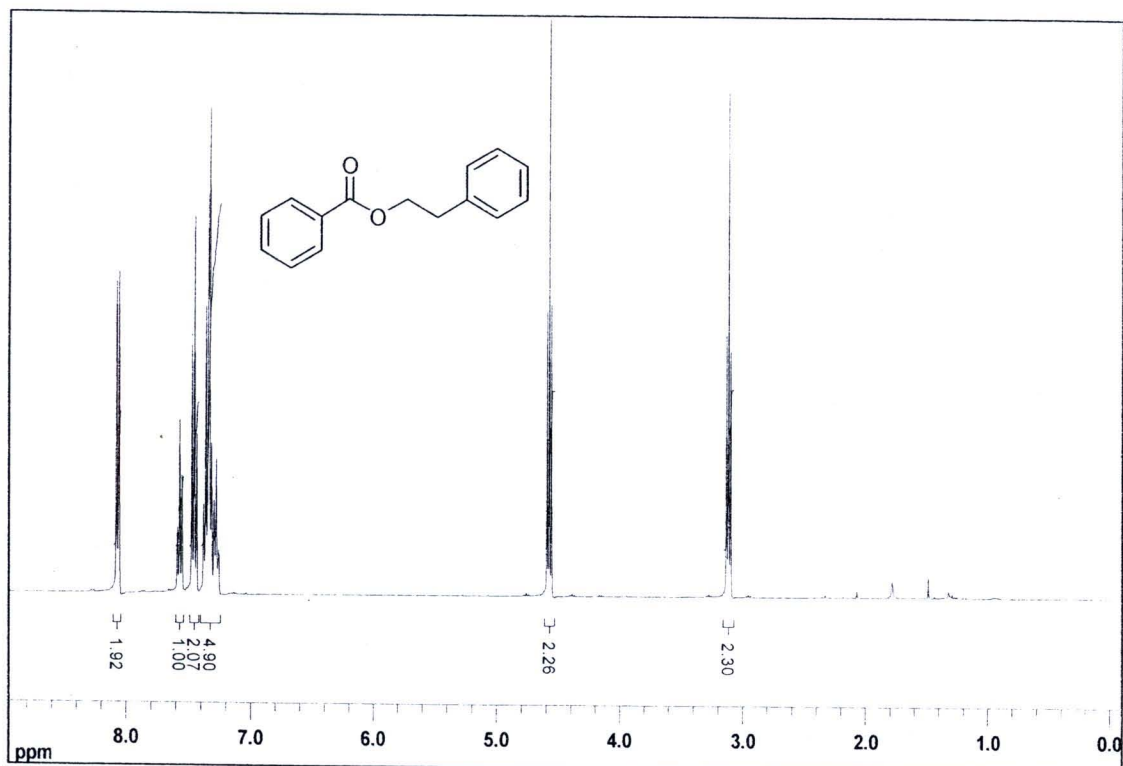


Figure 103 ¹H NMR spectrum of phenethyl benzoate (5e)

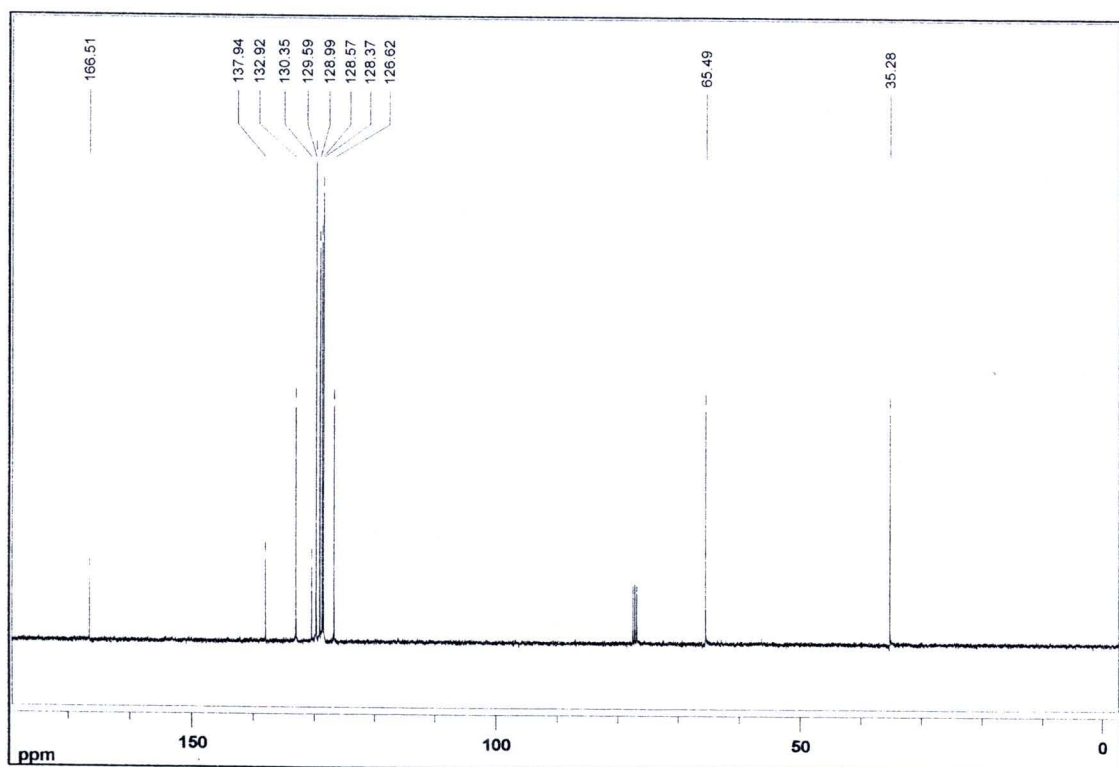


Figure 104 ¹³C NMR spectrum of phenethyl benzoate (5e)

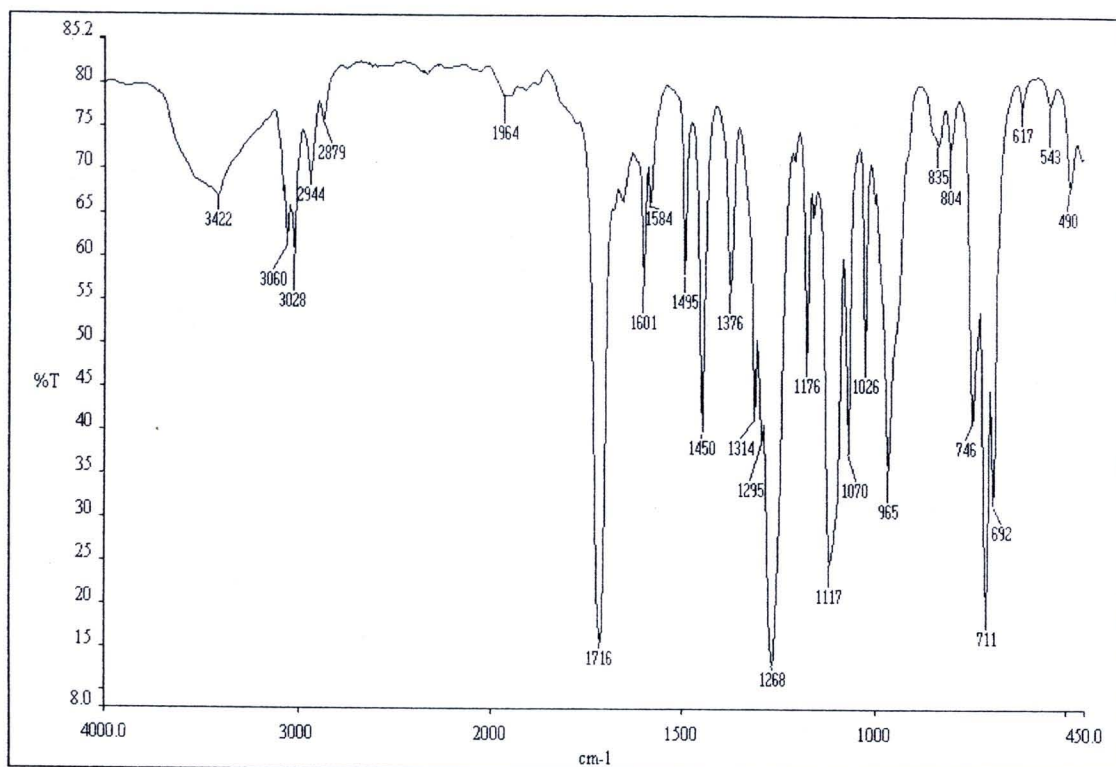


Figure 105 IR spectrum of cinnamyl benzoate (**5f**)

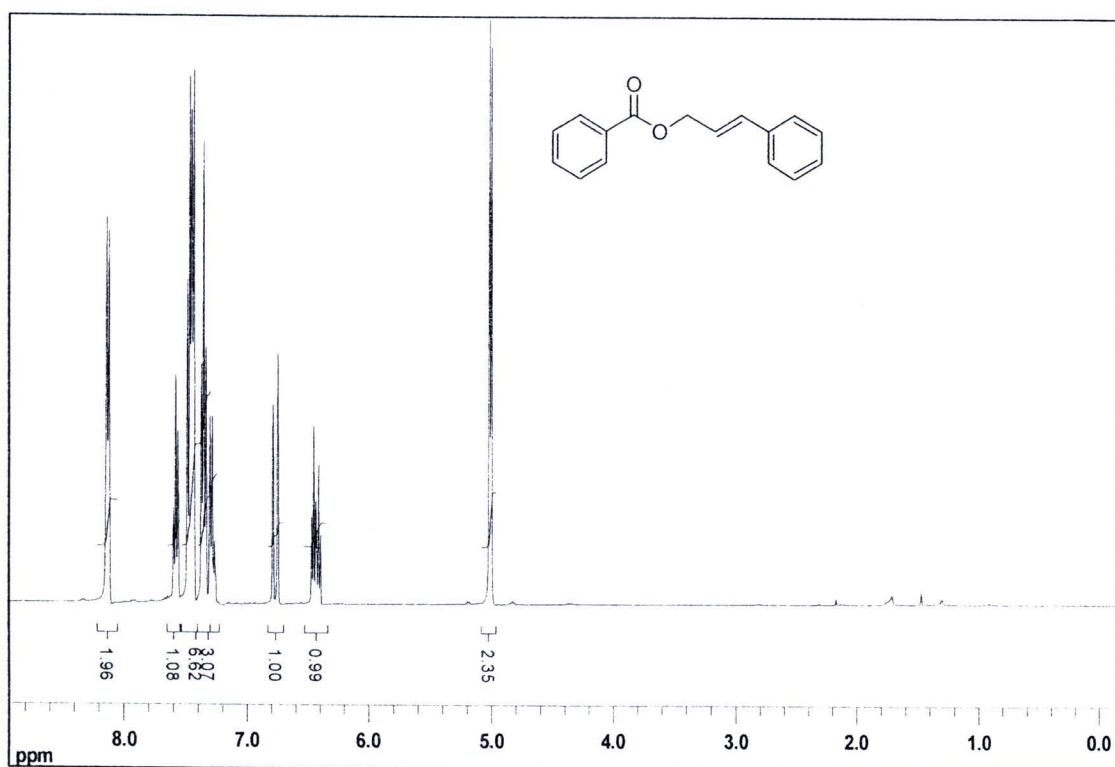


Figure 106 ¹H NMR spectrum of cinnamyl benzoate (**5f**)

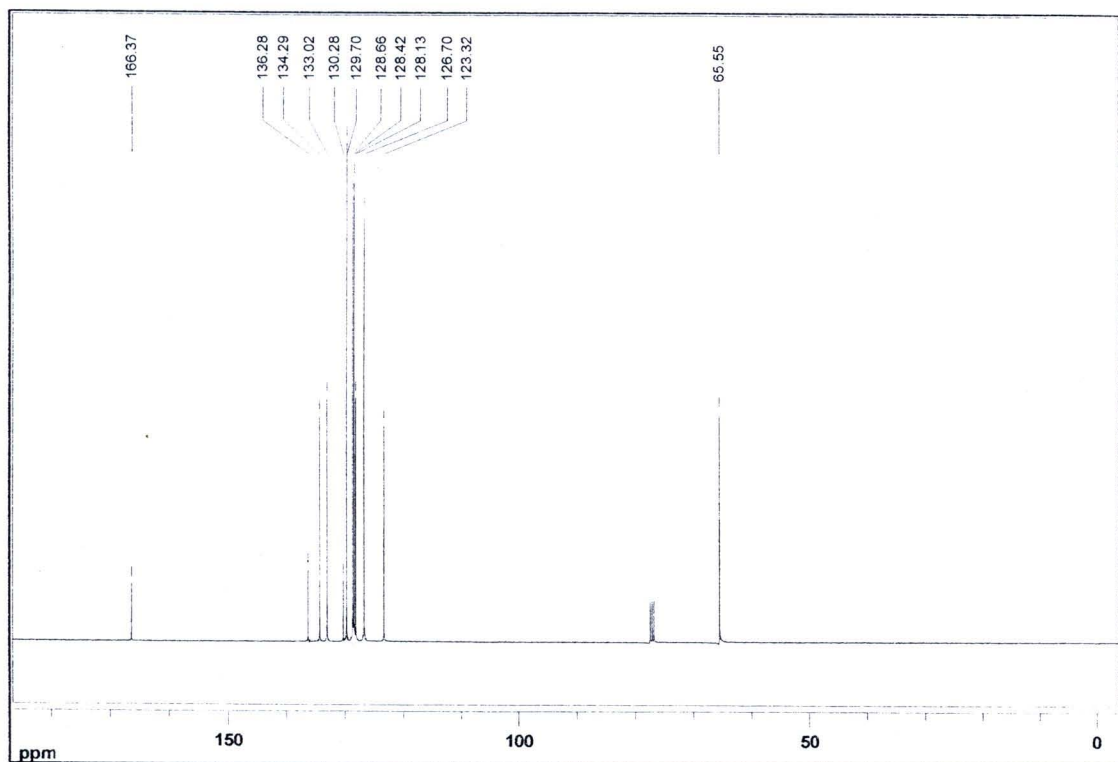


Figure 107 ^{13}C NMR spectrum of cinnamyl benzoate (5f)

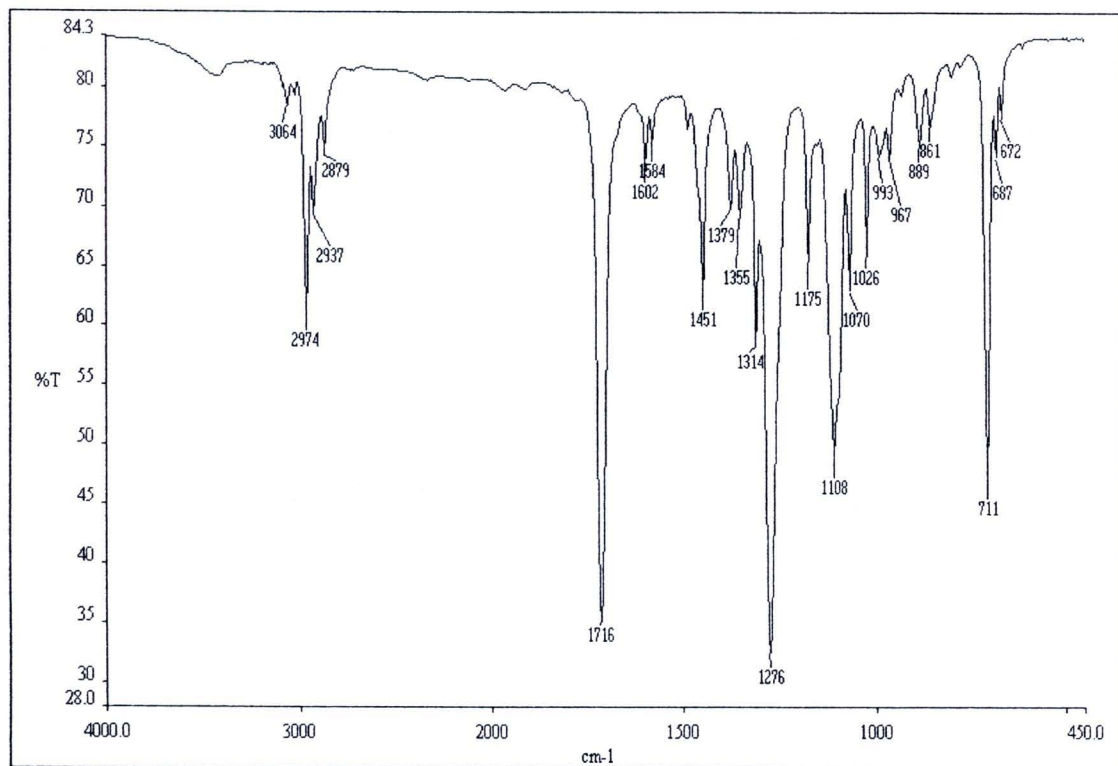


Figure 108 IR spectrum of sec-butyl benzoate (5g)

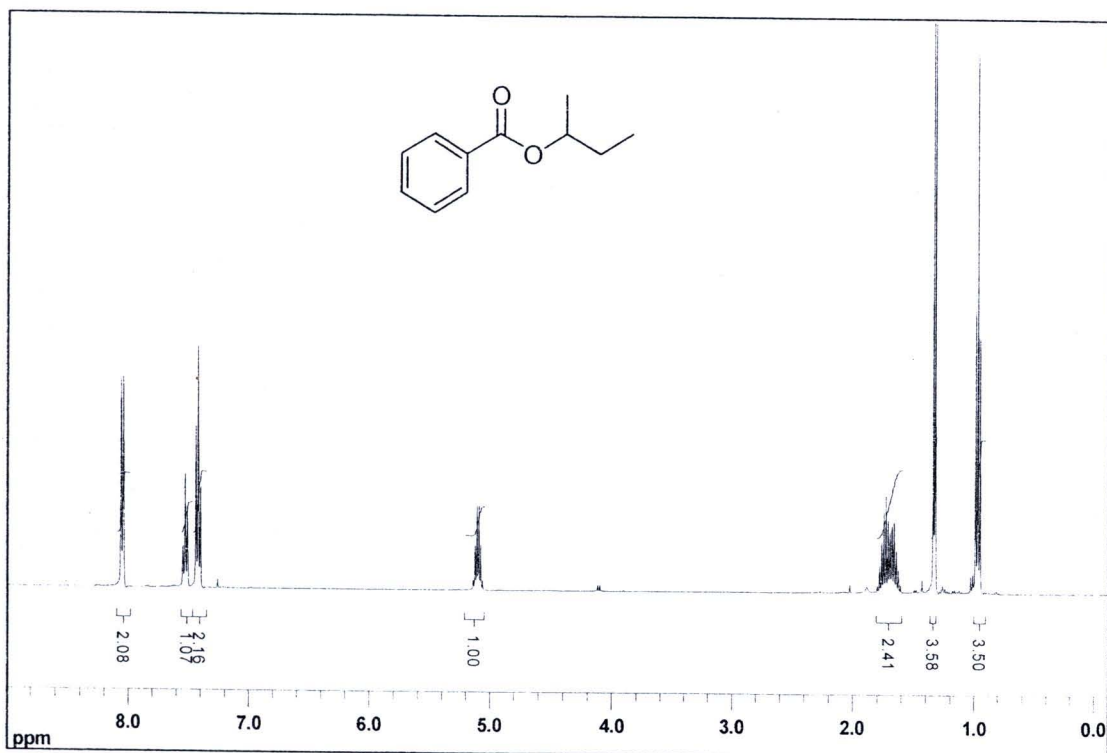


Figure 109 ^1H NMR spectrum of sec-butyl benzoate (5g)

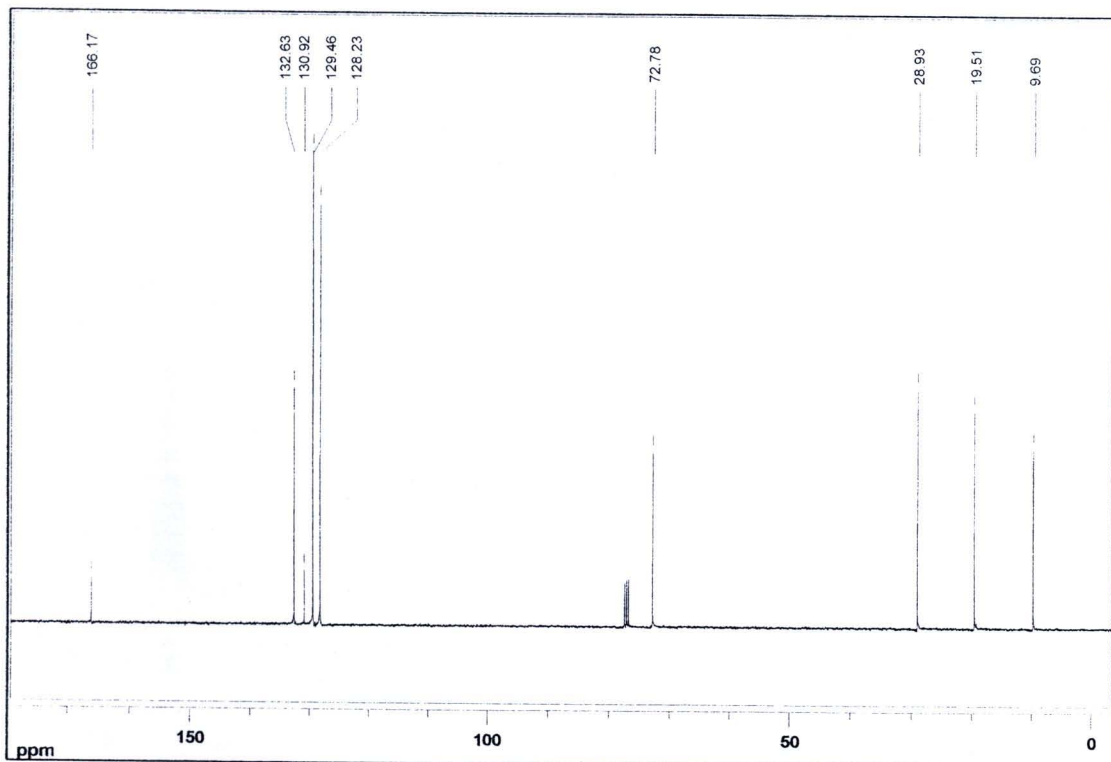


Figure 110 ^{13}C NMR spectrum of sec-butyl benzoate (5g)

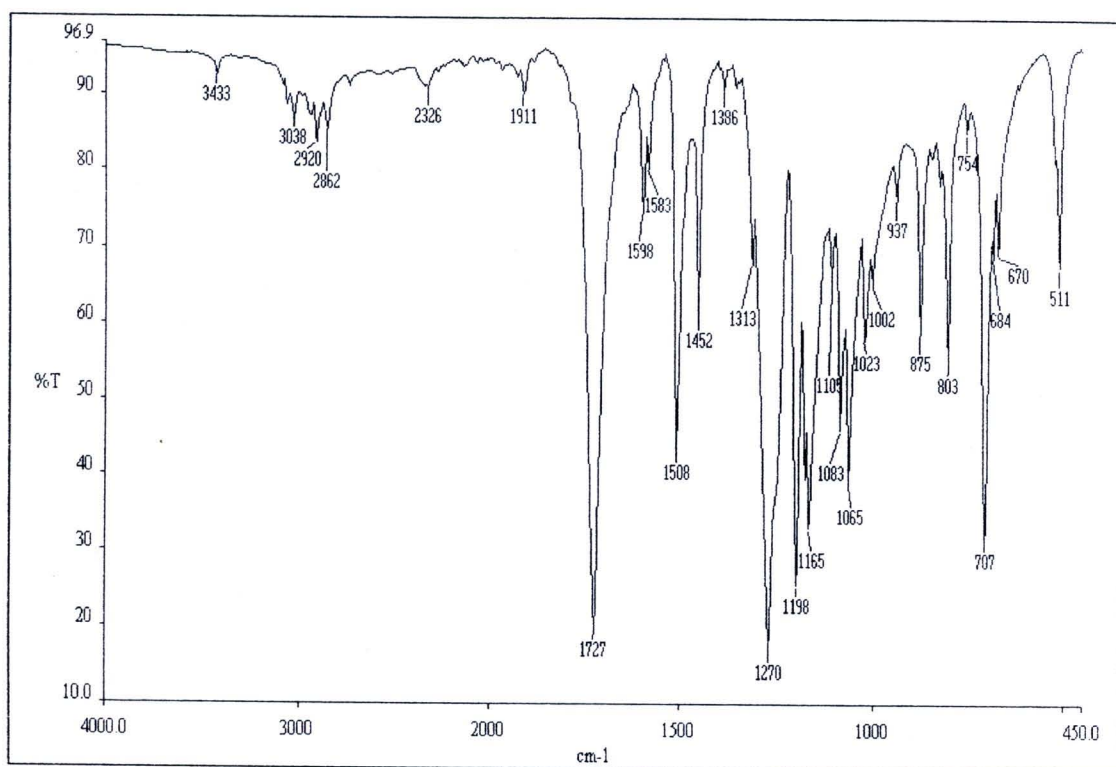


Figure 111 IR spectrum of 1-phenylethyl benzoate (**5h**)

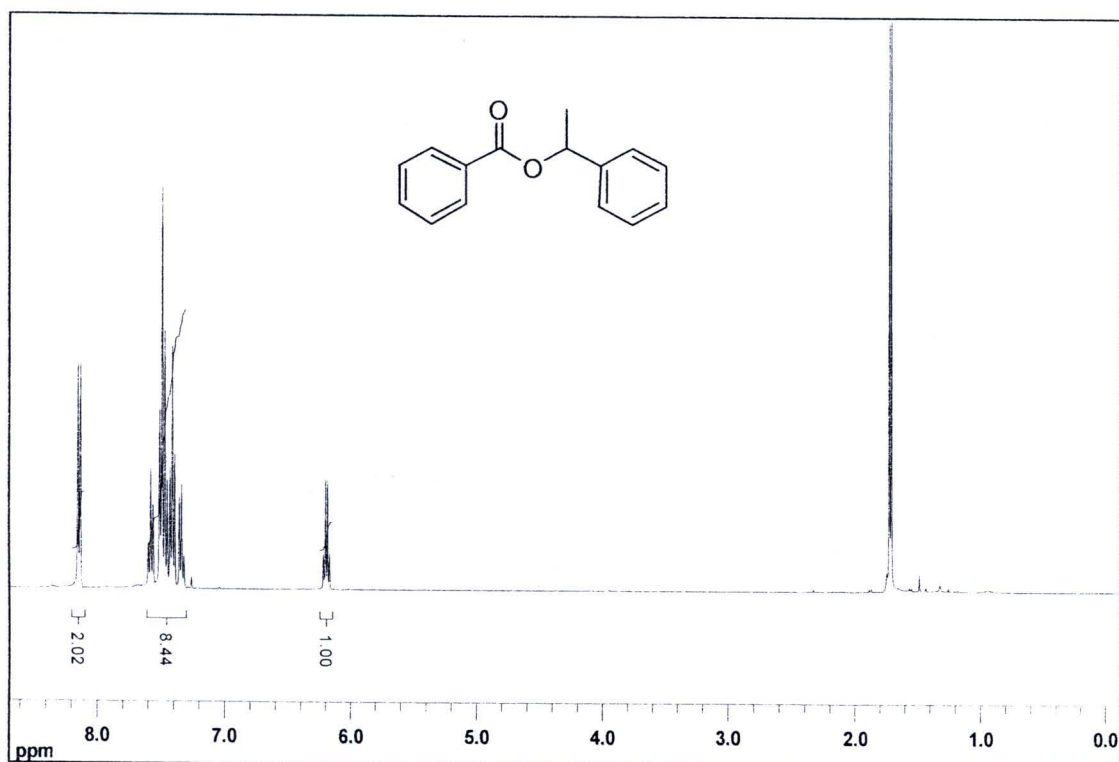


Figure 112 ^1H NMR spectrum of 1-phenylethyl benzoate (**5h**)

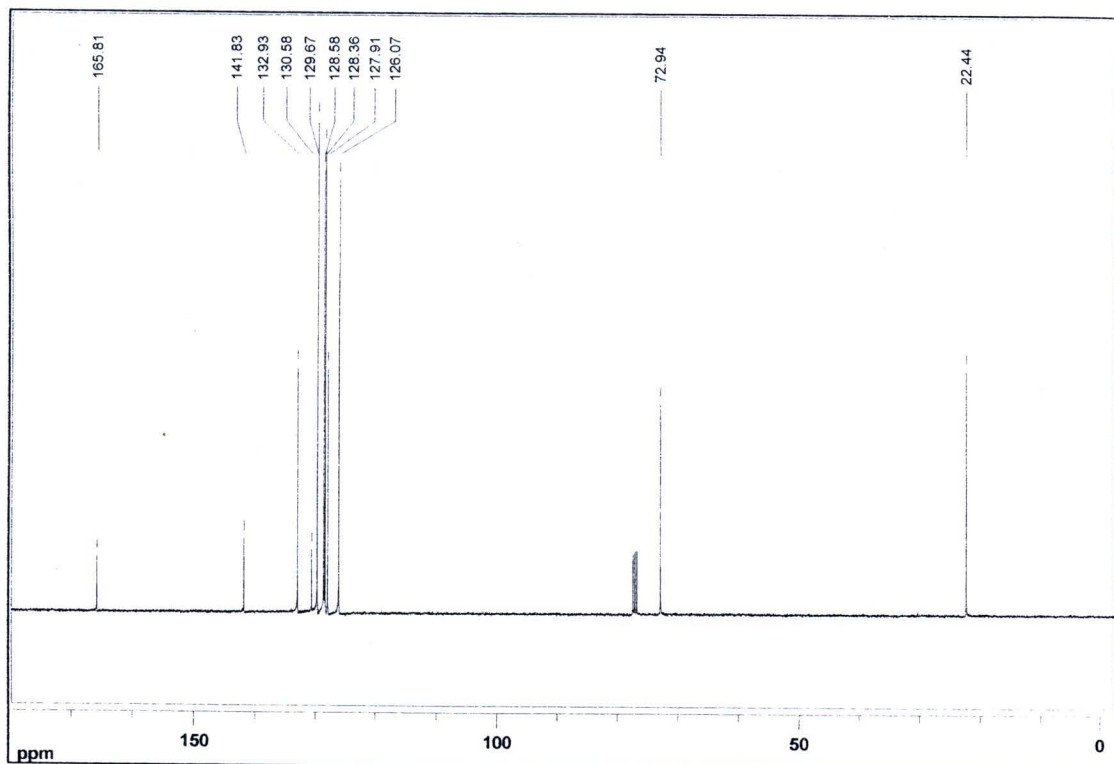


Figure 113 ^{13}C NMR spectrum of 1-phenylethyl benzoate (5h)

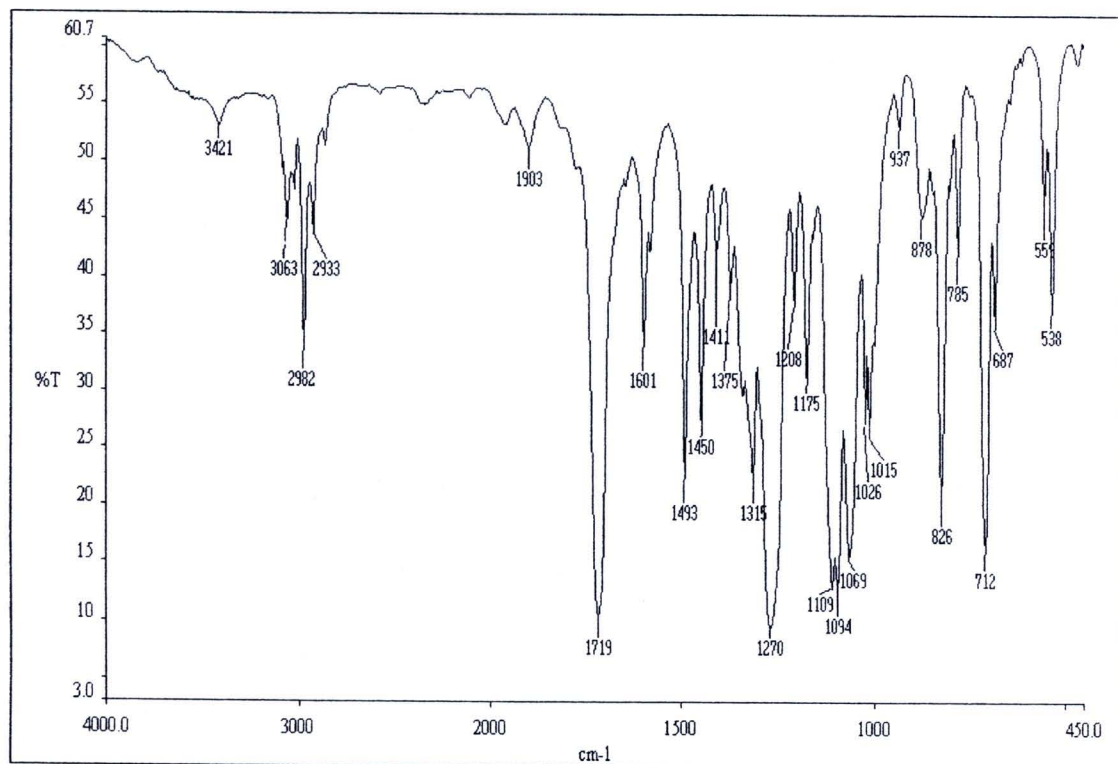


Figure 114 IR spectrum of 1-(4-chlorophenyl)ethyl benzoate (5i)

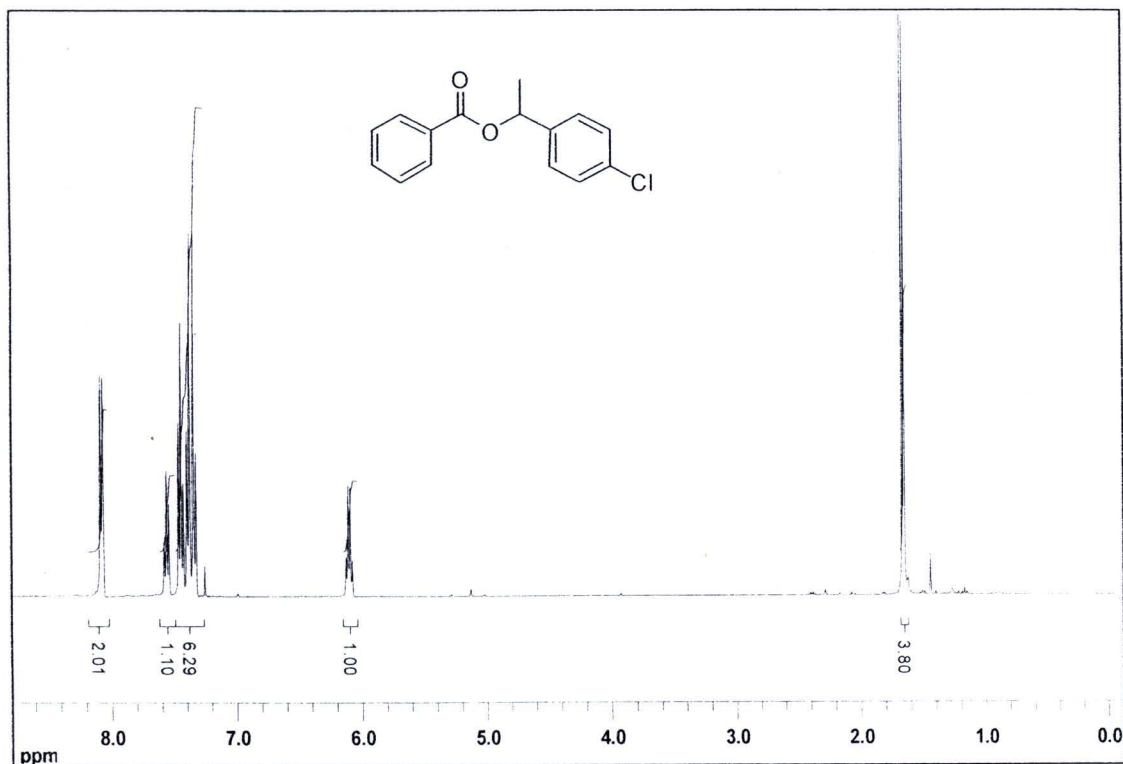


Figure 115 ^1H NMR spectrum of 1-(4-chlorophenyl)ethyl benzoate (5i)

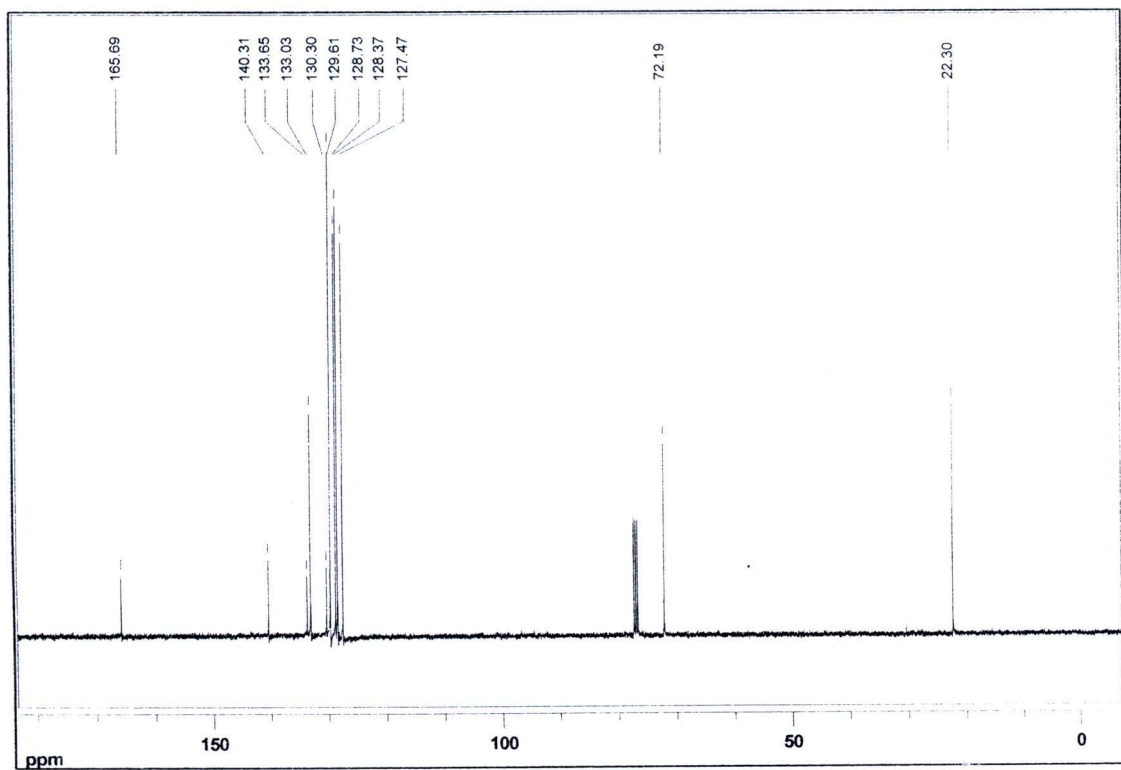


Figure 116 ^{13}C NMR spectrum of 1-(4-chlorophenyl)ethyl benzoate (5i)

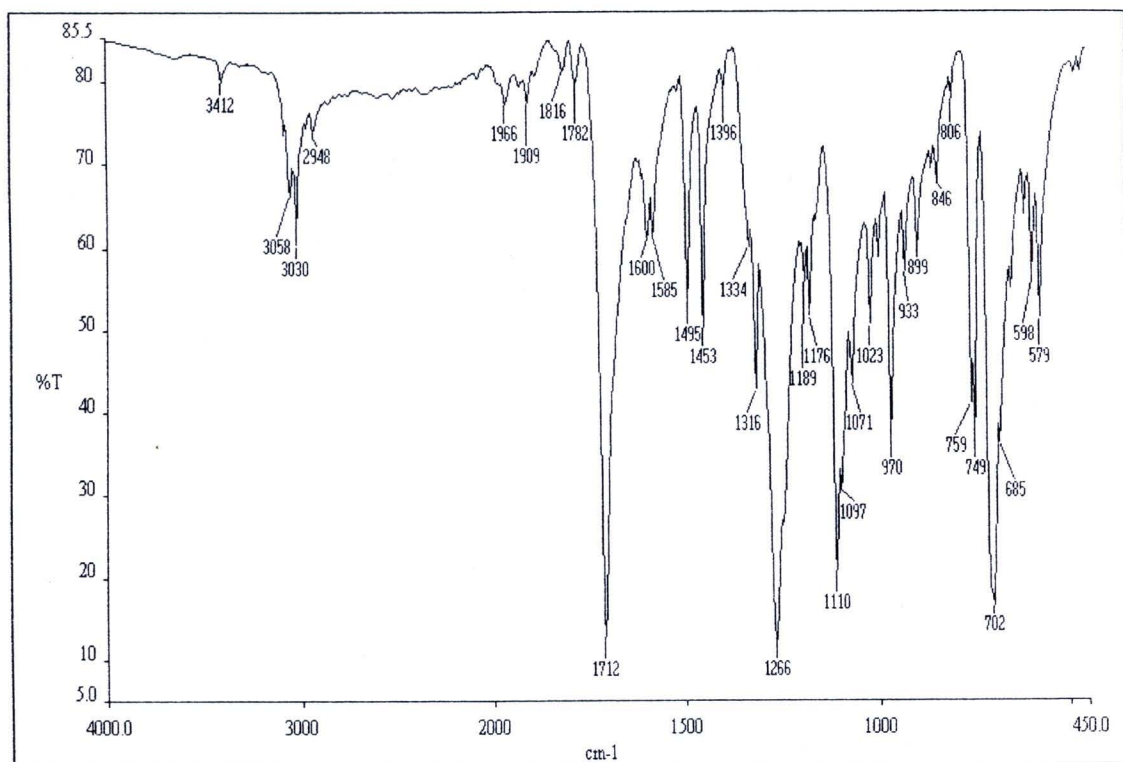


Figure 117 IR spectrum of benzhydryl benzoate (**5j**)

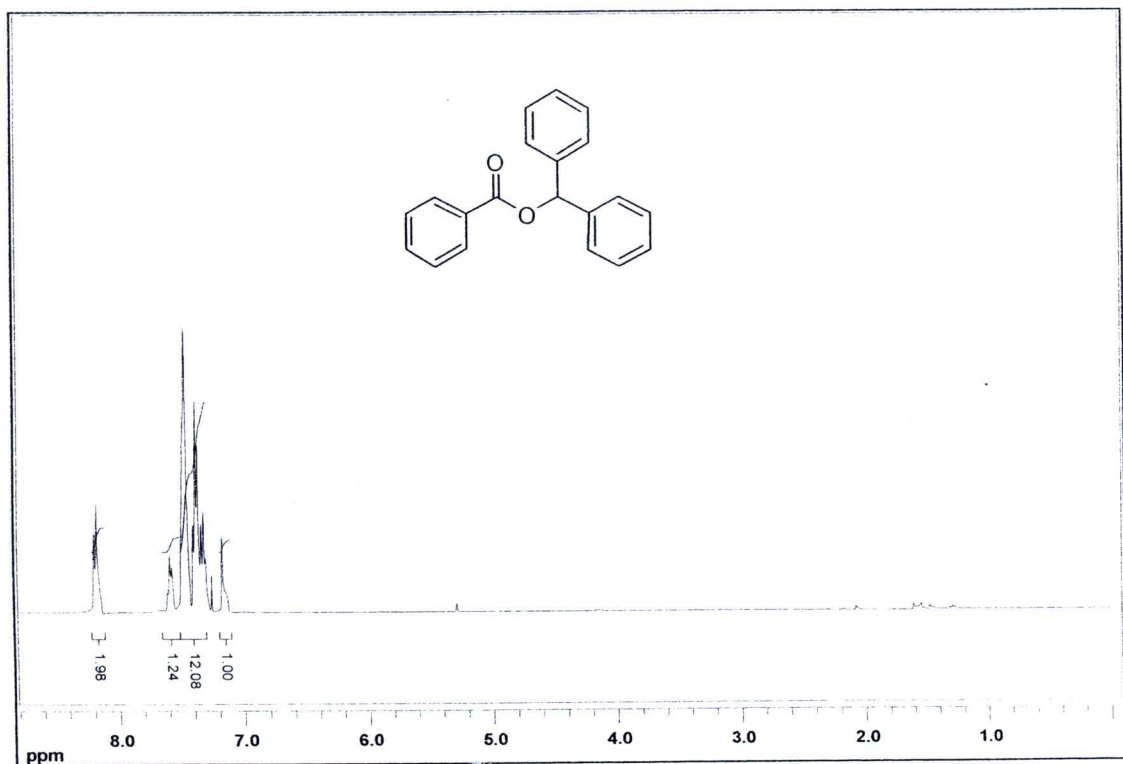


Figure 118 ^1H NMR spectrum of benzhydryl benzoate (**5j**)

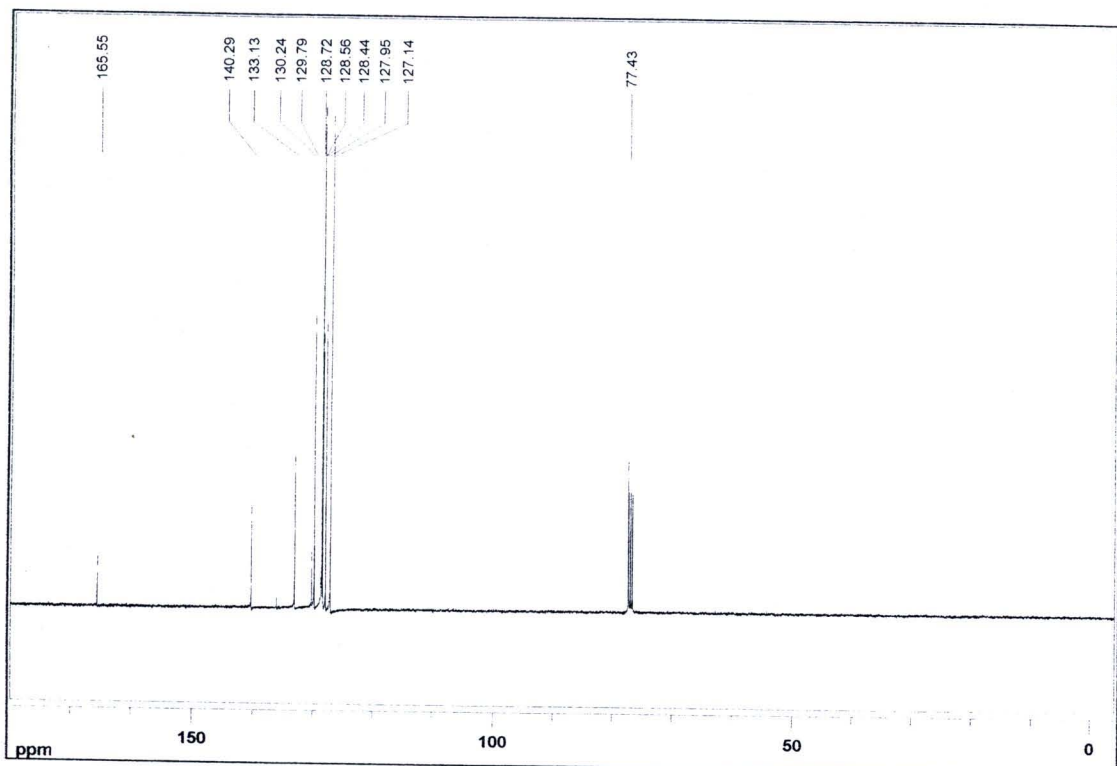


Figure 119 ^{13}C NMR spectrum of benzhydryl benzoate (5j)

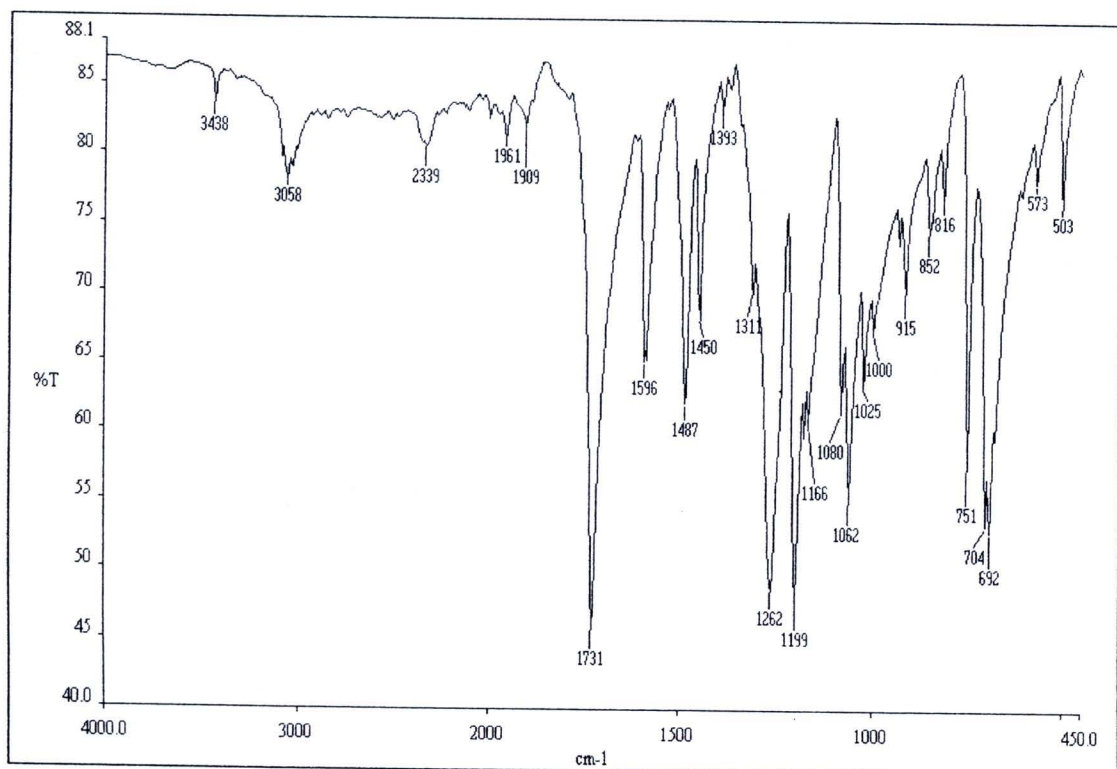


Figure 120 IR spectrum of phenyl benzoate (7a)

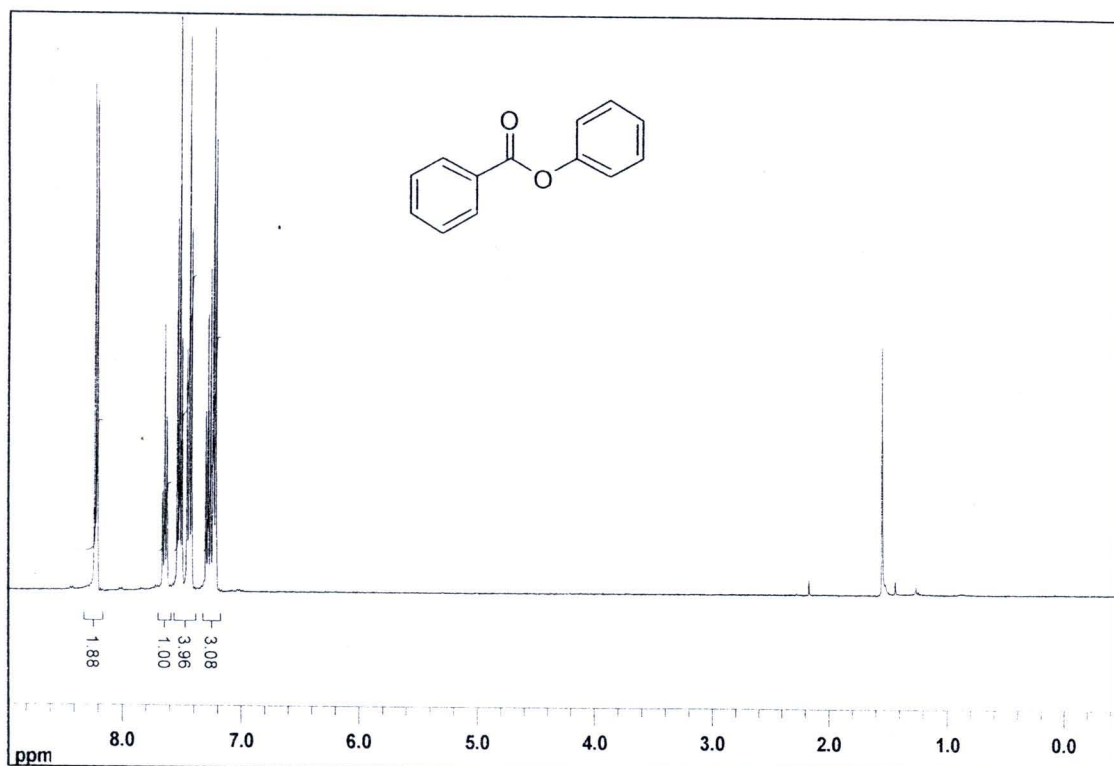


Figure 121 ^1H NMR spectrum of phenyl benzoate (7a)

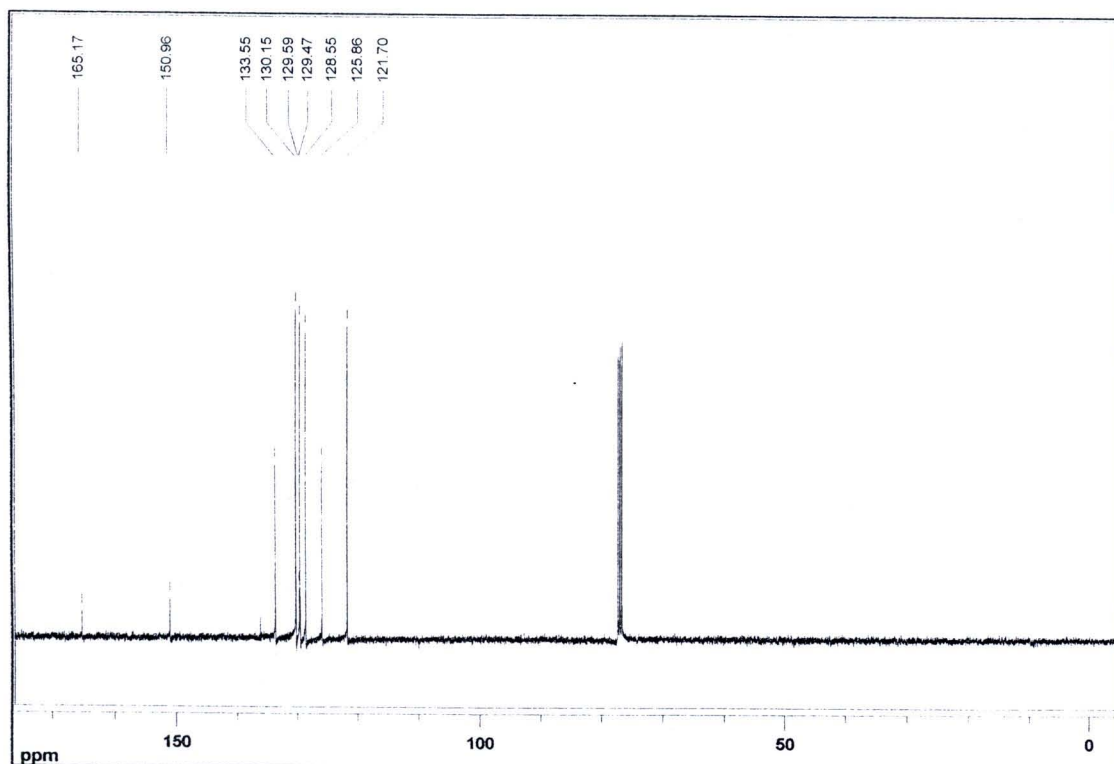


Figure 122 ^{13}C NMR spectrum of phenyl benzoate (7a)

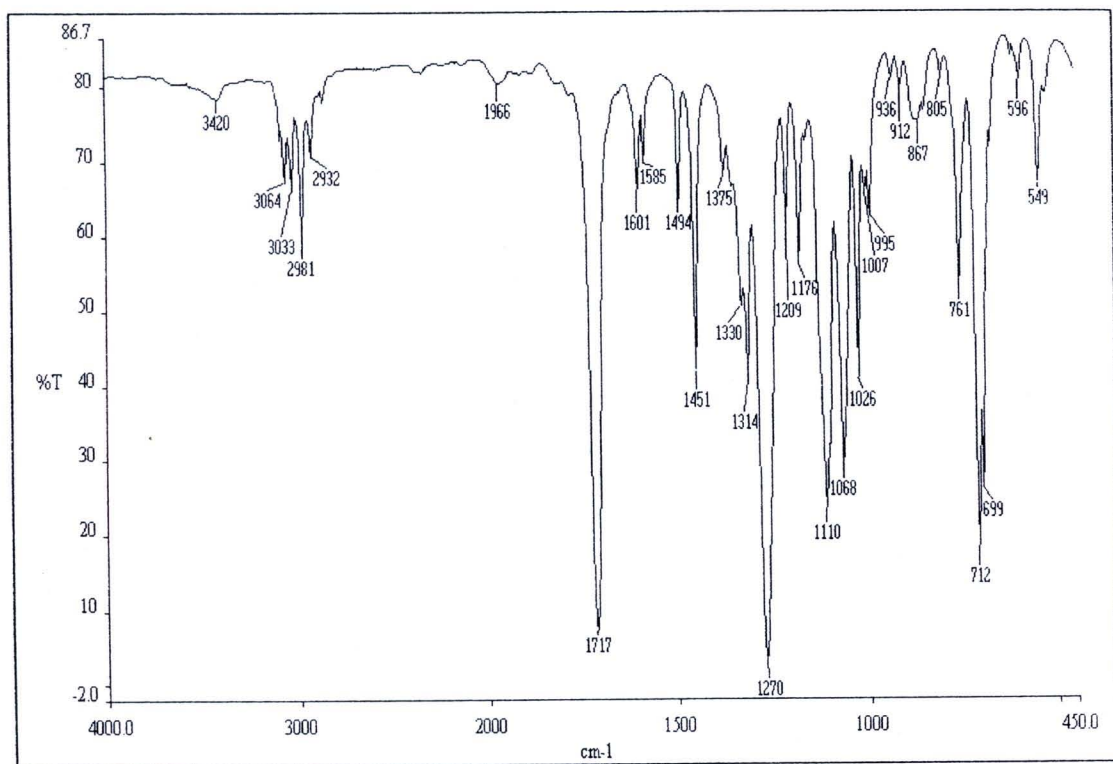


Figure 123 IR spectrum of *o*-tolyl benzoate (7b)

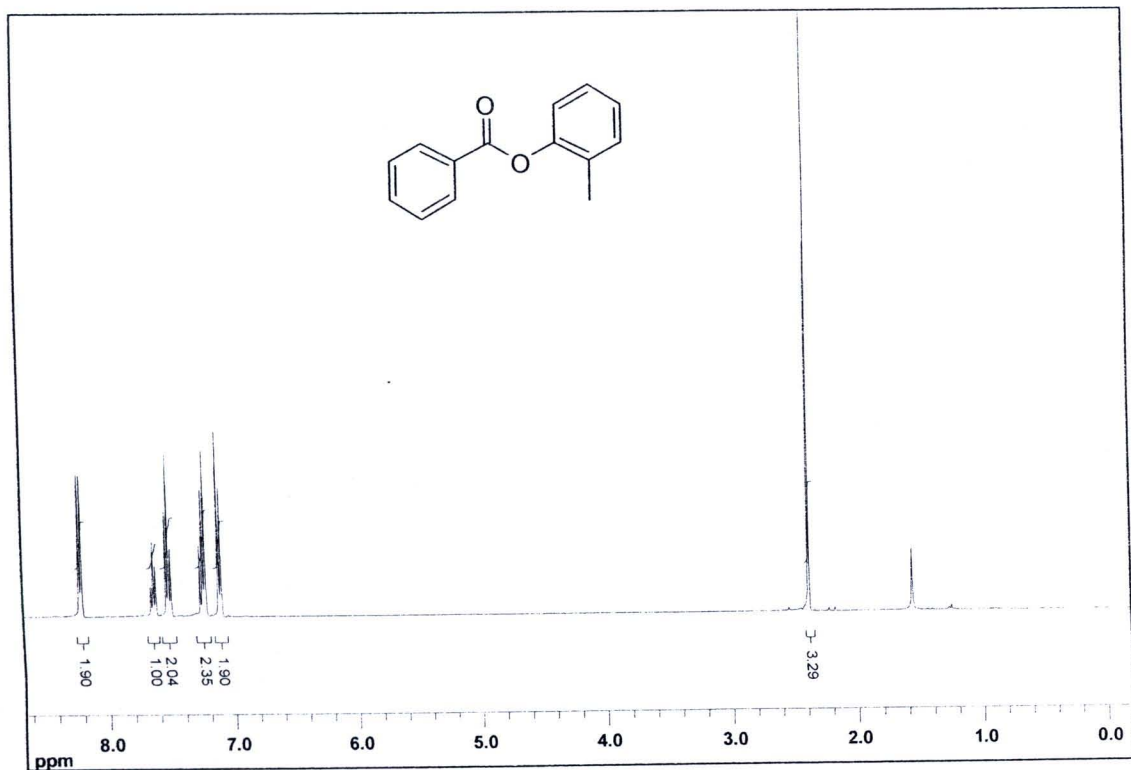


Figure 124 ¹H NMR spectrum of *o*-tolyl benzoate (7b)

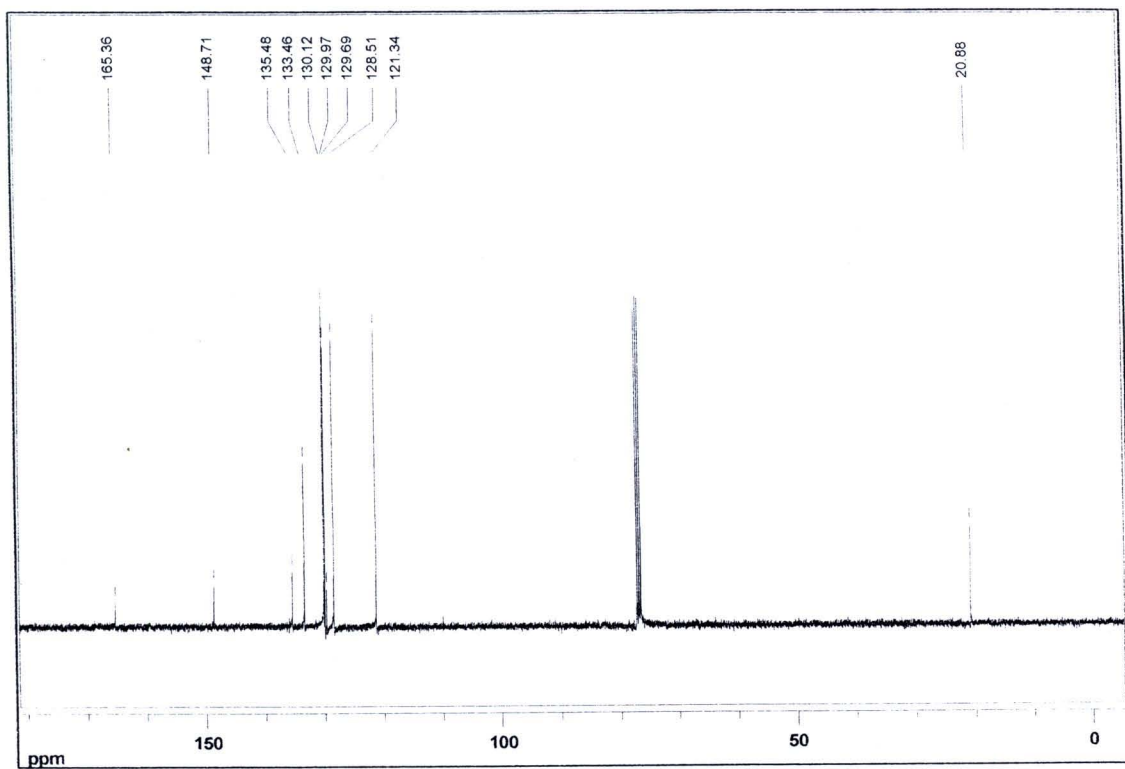


Figure 125 ^{13}C NMR spectrum of *o*-tolyl benzoate (7b)

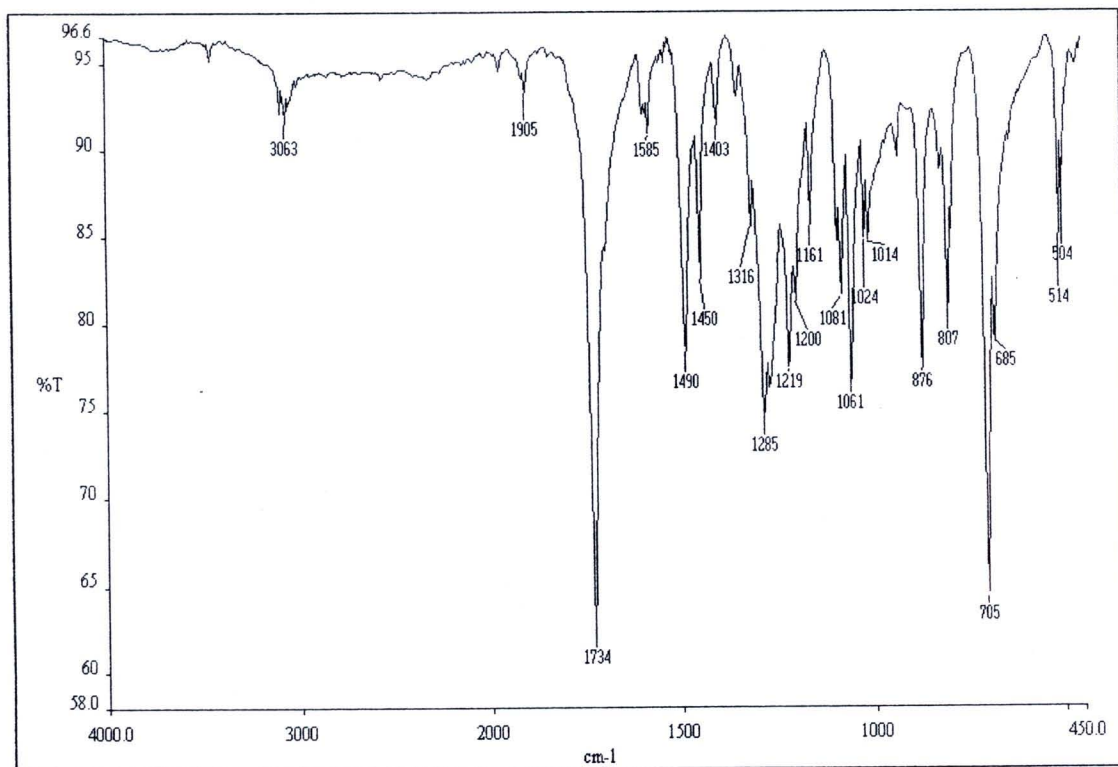


Figure 126 IR spectrum of 4-chlorophenyl benzoate (7c)

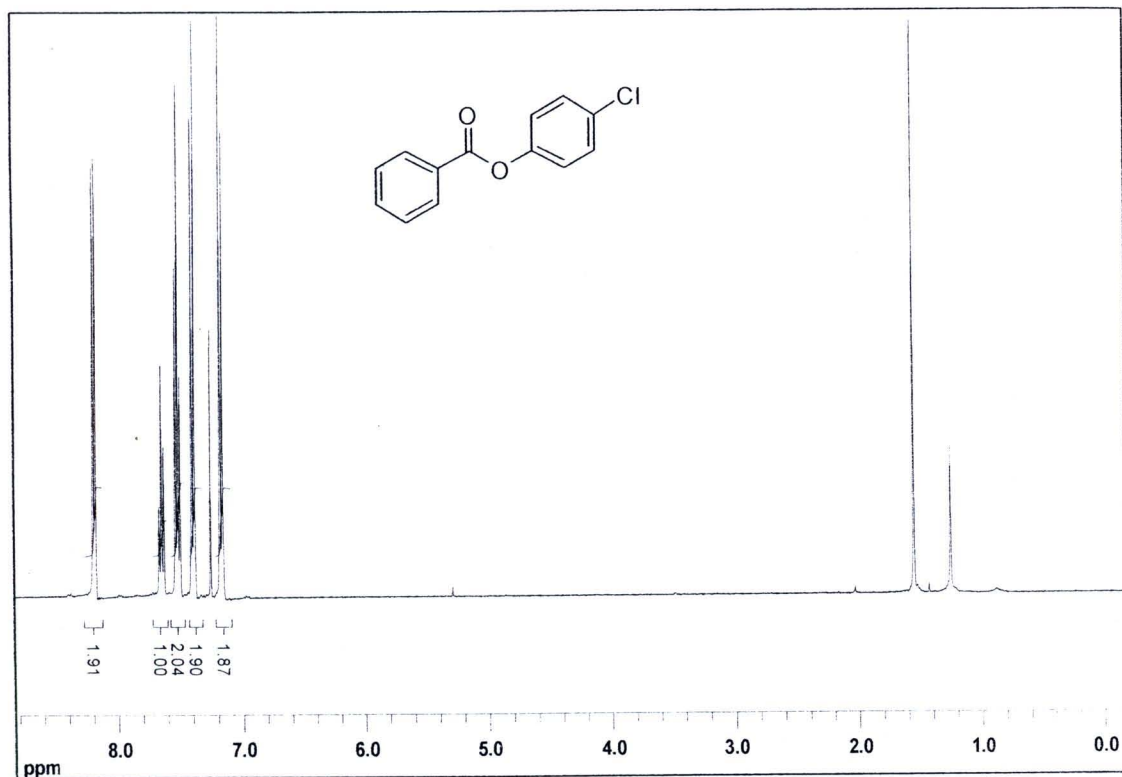


Figure 127 ¹H NMR spectrum of 4-chlorophenyl benzoate (7c)

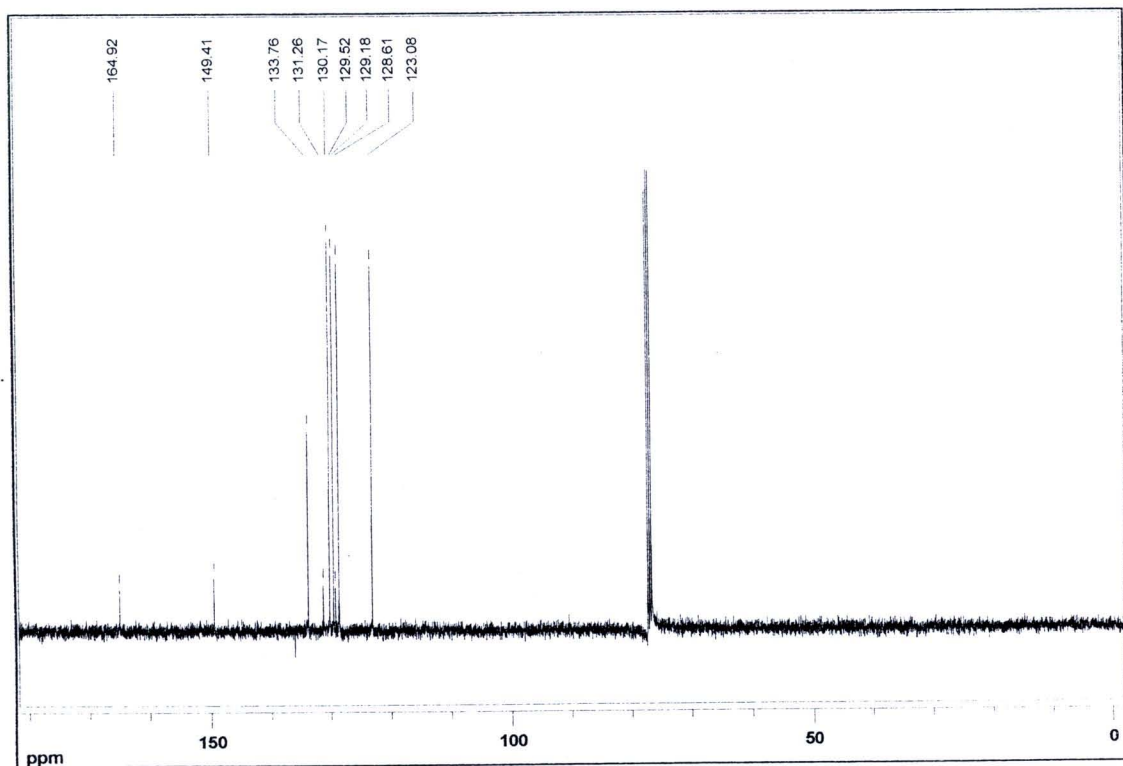


Figure 128 ¹³C NMR spectrum of 4-chlorophenyl benzoate (7a)

VITAE

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Convenient esterification of alcohols via acylbenzotriazoles : efficient and stable esterifying agents

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Abstract: Acylbenzotriazoles are known acylating agents for amines and carbonyl compounds due to the stability of the benzotriazolide anion which served as a good leaving group. However, the reagent failed to react with alcohols under previously known reaction conditions. This prompted us to the finding that esterification of alcohols with acylbenzotriazole could be realized only in the presence of K_2CO_3 in THF solution. Esterification of alcohols with acylbenzotriazoles gave the corresponding esters in good to excellent yields. The esterifying agents could easily be prepared in high yields from benzotriazole and the corresponding acid chlorides. Treatment of the crude esters from *N*-propionyl benzotriazole with methanol followed by extraction with 2 M Na_2CO_3 gave pure esters in good yields while those derived from *N*-benzoyl benzotriazole were isolated and purified by repeated extraction with 2 M Na_2CO_3 solution. This method thus served as an efficient and versatile alternative synthesis of ester under mild basic condition.

Introduction

Common route for ester synthesis is the treatment of carboxylic acid with alcohol in the presence of an acid catalyst such as concentrated sulfuric acid. However, the reaction takes a long period of time to reach its equilibrium and large excess of reagent is unavoidable in order to get high yield of ester. Although activated carboxylic acids such as acid chloride or acid anhydride give better results, they suffer from the problem of reagent handling and manipulating the reaction due to the highly reactive nature of the reagents. Exothermic reactions are always encountered and anhydrous conditions are required. In order to overcome these difficulties we have developed a much milder method for ester synthesis using *N*-acylbenzotriazoles as acylating agents which are stable solids that can easily be stored, handled and manipulated.

Materials and Methods

Preparation of Benzotriazole (1)

To a stirred cooled solution (15°C) of *o*-phenylenediamine (10.8 g, 0.1 mol) in glacial acetic acid (11.5 ml) was added a solution of sodium nitrite (7.5 g, 0.11 mol) in water (15 ml). Mild exothermic reaction commenced within a few minutes and rapidly

subsided while the deep red colour faded into pale brown. Stirring was continued for 15 minutes until the temp dropped to 35–40°C and the mixture was then chilled in an ice-water bath for 30 minutes. The pale brown precipitates were collected by vacuum filtration and washed with ice-cold water. Highly colored crude product was purified by repeated recrystallization from water using activated charcoal as a decolorizing agent. Benzotriazole (1) was obtained as fine white needles (7.97 g, 0.07 mol, 67%), mp. 95–97 °C. (lit. mp. 96–97 °C)

Preparation of *N*-propionyl benzotriazole (2)

To a stirred mixture of benzotriazole (1) (1.20 g, 0.01 mol) and anhydrous K_2CO_3 (2.76 g, 0.02 mol) in CH_2Cl_2 (30 ml) was slowly added propionyl chloride (1.05 ml, 0.012 mol). The mixture was stirred for 30 minutes and filtrated under reduced pressure through a celite pad. The filtrate was evaporated using a rotavaporator to dryness and the residue was purified by recrystallization from hexane to afford *N*-propionyl benzotriazole (2) as white crystals (1.65 g, 9.4 mmol, 94% yield).

Preparation of *N*-benzoyl benzotriazole (3)

To a stirred mixture of benzotriazole (1) (1.20 g, 0.01 mol) and anhydrous K_2CO_3 (2.76 g, 0.02 mol) in CH_2Cl_2 (30 ml) was slowly added benzoyl chloride (1.69 ml, 0.012 mol). The mixture was stirred for 30 minutes and filtrated under reduced pressure through a celite pad. The filtrate was evaporated using a rotavaporator to dryness and the residue was purified by recrystallization from hexane to afford *N*-benzoyl benzotriazole (3) as white crystals (2.29 g, 9.8 mmol, 98% yield).

General method for preparation of ester using *N*-propionylbenzotriazole (2)

A mixture of *N*-propionyl benzotriazole (2) (0.21 g, 1.2 mmol) and alcohol (1 mmol) and anhydrous K_2CO_3 (0.28 g, 2.0 mmol) in THF (5 ml) was refluxed for 30–60 minute. The mixture was cooled to room temperature and the solvent was evaporated under vacuum to dryness. The residue was added CH_2Cl_2 (2–3 ml) and methanol (2 ml) and further stirred for 5 minutes. The resulting mixture was added 2M Na_2CO_3 (2 ml) and stirring was continued for 30 minutes then extracted with CH_2Cl_2 (2x5 ml). Combine organic layer were dried and concentrated under reduced pressure to give pure ester (57–89%).

General method for preparation of ester using *N*-benzoyl benzotriazole (3)

A mixture of *N*-benzoyl benzotriazole (3) (0.28 g, 1.2 mmol) and alcohol (1 mmol) and anhydrous K_2CO_3 (0.28 g, 2.0 mmol) in THF (5 ml) was refluxed

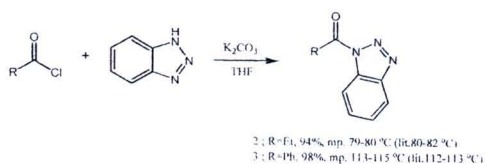
for 30-60 minute. The mixture was cooled to room temperature and the solvent was evaporated under vacuum to dryness. The residue was added CH_2Cl_2 (2-3 ml) and 2M Na_2CO_3 (2 ml) and stirring was continued for 30 minutes then extracted with CH_2Cl_2 (2x5 ml). Combine organic layer were dried and concentrated under reduced pressure to give pure ester (55-93%).

Results and Discussion

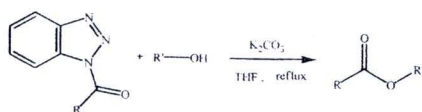
Benzotriazole was prepared from the reaction between *o*-phenylenediamine and sodium nitrite in acidic condition as shown below.



N-Acylbenzotriazoles were prepared from the reaction between acid chlorides and benzotriazole in basic condition with high yields as shown below.



N-Acylbenzotriazoles were allowed to react with 1° or 2° alcohols in THF in the presence of anhydrous K_2CO_3 at reflux to give the corresponding esters.



Crude esters derived from *N*-propionyl benzotriazole were easily purified by treatment with methanol followed by repeated extraction with 2M Na_2CO_3 while those derived *N*-benzoyl benzotriazole were isolated and purified by repeated extraction with 2M Na_2CO_3 . *N*-propionyl benzotriazoles and *N*-benzoyl benzotriazole both gave esters from 1° and 2° aliphatic alcohols in good to excellent yields. In addition, phenols could also be esterified with *N*-benzoyl benzotriazole in excellent yields.

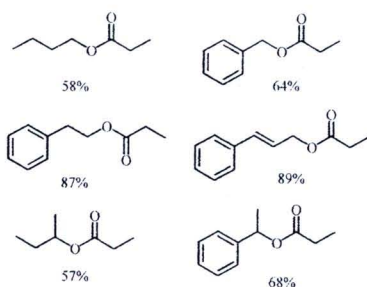


Figure 1. Esters from *N*- propionyl benzotriazole

In addition, *N*-benzoyl benzotriazoles with 1°, 2° and aromatic alcohols to give ester in good yields.

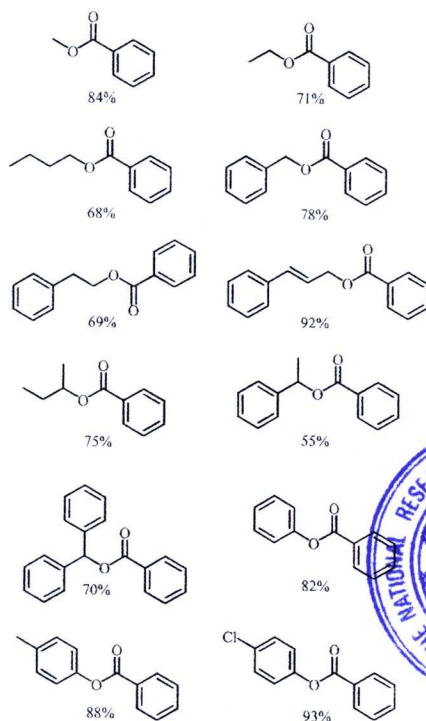


Figure 2. Esters from *N*- benzoyl benzotriazole

Conclusions

Benzotriazole was prepared in moderate yield. Purification was simply carried out by using water as a cheap and nontoxic solvent. Esters of 1° and 2° alcohols could be prepared using either *N*-propionyl benzotriazole or *N*-benzoyl benzotriazole in good to excellent yields. Product separation and purification could easily be achieved by basic extraction. An alternative mild and efficient method for ester preparation using *N*-acylbenzotriazoles as stable acylating solid reagents has been established.

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