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Nano Copper-Cobalt Ferrite Catalyzed One-Pot Green Combination of β , γ -Unsaturated Ketones by Ultrasonication Method

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Abstract— Nano Copper-Cobalt ferrite materials have been used as magnetically separable and reusable heterogeneous catalysts for the synthesis of β , γ - unsaturated ketones over the allylation of acid chlorides with allyl bromides is presented. Ultrasonication method used to the reaction between substituted acid chlorides with allyl halides is carried out in attendance of Nano Copper-Cobalt ferrites at room temperature by using Tetrahydrofuran (THF) as a Solvent. The present method is environmentally benign and gives very good yields. The catalyst is separated from the reaction medium using a strong magnet and reused several intervals without the loss of much catalytic activity. The mechanism of the reaction and characterization of the products are presented.

Keywords: Nano Copper-Cobalt ferrites $\text{Cu}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 1, 0.75, 0.5, 0.25$ and 0), β , γ -unsaturated ketones, heterogeneous catalyst, Ultrasonication

1. INTRODUCTION

β , γ -unsaturated ketones are the most broadly explored photochemical frameworks because of the rich photochemistry displayed by ketones and olefins. It is seen that the consolidation of both the gatherings into a similar particle would prompt an assortment of captivating responses [1]. The factors which influence the competition between them is not yet completely understood. The synthesis of these moieties is always encouraging for the chemists due to their extensive use in organic synthesis.

The prototropic rearrangement [2-3] has been happened to highly producing conjugated α , β -unsaturated ketones from β , γ -unsaturated ketones. It obscures the synthesis of this class of compounds. Manufactured natural scientific expert-created various strategies to get ready β , γ -unsaturated ketones, yet a considerable lot of these methodologies give isomeric blends

of α , β and β , γ unsaturated ketones [4-6]. Poor regioselectivity [7-8] of different methods using transition metals such as rhodium and nickel have been reported. A stimulating aspect of the Friedel-Crafts acylation of olefins is the frequent and sometimes exclusive formation of β , γ -unsaturated ketonic products [9-13]. It is often found that the accompanying and generally more stable. α , β -unsaturated ketones are produced by the isomerization of the initially formed unconjugated isomer. This union is entangled by an inclination towards prototropic adjustments creating conjugated α , β -unsaturated ketones [14-15]. One of the ongoing critical achievements in organo-magnesium science is the improvement of a non-ordinary way to deal with without halide organomagnesium reagents dependent on the immediate metalation of conjugated dienes with enacted magnesium [16-20] i.e. organometallics of silicon [21-23], copper [24], rhodium [25], manganese [26],

titanium [27], mercury [28] and tin [29]. It is observed that these reactions have some limitations and their own merits at the same time not being very simple and straight forward. Lanthanum metal i.e Ytterbium [30] also used to prepare β,γ -unsaturated ketones by coupling allylic bromides with α -oxonitriles, but these method gives low yield, tedious, and forms isomeric products. Allyl ketones have also been prepared via Hiyama-Nozaki reaction followed by a chromium-mediated [31] Oppenauer Oxidation resulting in a mixture of products. They produced very low yields and the methods are not very simple and straight forward.

In the synthesis of natural products [28] and many heterocyclic compounds the β,γ -unsaturated ketones are used as a hypothetical unit. The synthesized heterocyclic compounds used as drugs in pharmaceuticals. Even though there are a few advantages of metal impetuses, yet the primary disadvantage is the recuperating of the impetus from the response blend that is the reason it forestalls their utilization in the industry. The most focal points of heterogeneous catalysis is a simple partition and reusing of the impetus. Recent research methods reveal that magnetic Nano-sized metals and metal oxides are efficient catalysts because of their large surface area to volume ratio of the metal oxide [3] and they can be simply separated [32-34]. The metals like zinc [35], indium [36], cadmium [37], bis(cyclooctadiene) Nickel(0) [7], BuSnCl_2 +Additive [38] are a portion of the progress metal powders detailed before, which are utilized as impetuses to orchestrate these β,γ -unsaturated ketones. Copper ferrite which is a reusable impetus [39] is additionally utilized to combine β,γ -unsaturated ketones at room temperature, and steady blending for about 2.0 to 3.5 hours, yet the procedure of response utilized for time taking and tedious.

During the time spent improvement of new impetuses, upgrading the response yields and diminishing the response times for the responses, another strategy was created in which a progression of reusable Nano Copper-Cobalt ferrite impetuses was utilized for the allylation of substituted acid chlorides by utilizing Tetrahydrofuran as a dissolvable at room temperature by ultrasonication technique, which gives significant returns at shorter response times (0.5-1.5 hours) and without the development of isomeric items. The whole manufactured plan is available in Scheme 1&2.

2. Experimental

2.1. Chemicals and Apparatus

Different concentrations of Synthesized Nano Copper-Cobalt Ferrites were Characterized by XRD spectra which gives information about average crystalline size was recorded on PANalytical-Xpertpro diffractometer. The instrument used for Scanning Electron Microscope (SEM) is JEOL-JSM 6610 LV and finds out the Morphology of the structure. The particle size was showing by HR-TEM images was recorded on JEOL/JEM 2100. Bruker Alpha 6.1 was used for the FT-IR Analysis. Nova 2000 series, UK was used for BET surface area analysis. Digital Melting point by synchronic was used for Melting point analysis. DMSO- d_6 Bruker Avance 300-MHz Spectrophotometer was used for ^1H NMR analysis. The internal standard of ^1H NMR is Tetramethylsilane (TMS). ESI source of Perkin-Elmer PE SCIEX-API 2000 was used for MASS spectra Analysis. Reactions were conducted in SS basket containing REVOTEK™ Ultrasonic cleaner with 50Watts power and the progress the reaction was monitored by thin-layer chromatography which contains aluminum-backed plates coated with Merck

Kieselgel160 F254 silica gel, visualizing the spots under Ultraviolet light.

2.2. Preparation of the Nano Copper-Cobalt Ferrite Catalysts

In this method Ferric Citrate, Nitrates of Copper, Cobalt, and Citric acid (SD Fine Chem. Limited 99% pure AR grade) having molar ratio 1:3 were dissolved in deionized water. Citric acid acts as a chelating agent and helps in the homogenous distribution of metal ions. Copper-Cobalt Ferrites with formula $Cu_xCo_{1-x}Fe_2O_4$ ($x = 1, 0.75, 0.5, 0.25$ and 0) have been chosen for the study and was synthesized by a chemical sol-gel co-precipitation method. Aqueous solutions of 3 moles of citric acid mixed with different stoichiometric amounts of 1 molar copper nitrate, cobalt nitrate, and ferric citrate. The P^H of the entire solution was maintained with 7 by adding an Ammonia solution and the reaction was completed by adding ethylene glycol. Heat the solution slowly and evaporate to dryness up to 9 to 11 hours. Finally, the solution was turned in to puffy and dry gel undergoes a self-ignition reaction to form a very fine powder. Residual carbon was removed under calcination by Muffle Furnace up to $600^\circ C$ for 2 hours. That is known as a synthesized catalyst and cool the furnace. The samples were characterized by XRD, FT-IR, SEM, and TEM.

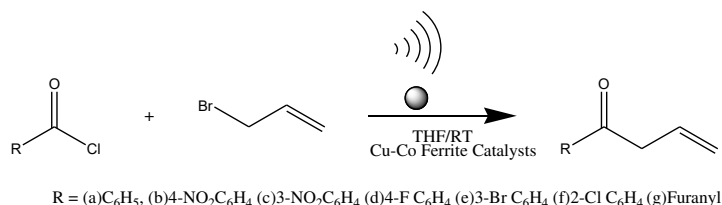
2.3. General procedure for one-pot synthesis of β,γ -unsaturated ketones

In a 25 mL beaker, a mixture of allyl bromide (1 mmol) and cinnamyl chloride (1 mmol) in THF (5ml) with stirring and 0.1 mol % (250 mg) of copper-cobalt ferrite ($Cu_{0.5}Co_{0.5}Fe_2O_4$) was taken. To that Acyl chloride (1 mmol) in THF (10 ml) was added, then the beaker containing the reaction mixture was placed in an ultrasonication tray and the contents are sonicated at room temperature for 0.5-1.5

hours (as shown in [Table 1](#)). The progress of the reaction was monitored by TLC using the Mobile phase in the ratio 2:1 (hexane, ethyl acetate). After finishing the response as showed by TLC, the impetus was expelled by utilizing an amazing magnet at the base of the measuring utensil and the substance was moved into another compartment. The impetus washed with 5 mL of THF to flush the impetus for the items. The dissolvable was expelled under decreased tension and the items recrystallized with ethanol to get the last results of β,γ -unsaturated ketones.

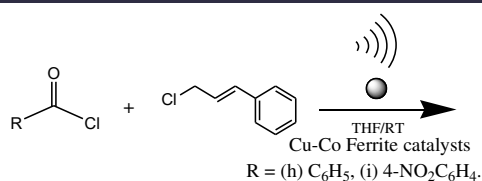
In the wake of getting items the impetus was dried, isolated, and washed with diethyl ether, ethyl acetic acid derivation, and liquor, further dried and exposed to microwave illumination to enact the impetus and the recouped impetus is reused for hardly any more cycles. It is additionally seen that there was no draining of impetus in the item.

Model reaction:



Scheme 1. One-pot production of β,γ -unsaturated ketones

The outcomes with allyl bromide have been reached out with cinnamyl chloride. The engineered course is introduced in "Scheme 2". The response was completed under streamlined conditions. The outcomes are recorded in "Table 1".



Scheme 2. The readiness of β,γ -unsaturated ketones by cinnamyl chloride

2.4. Spectral Data

(BGUK-1): 1-phenyl but-3-ene 1-one

Colourless solid, Yield 94%.; FTIR: ν_{\max} (KBr): 1693(C=O), 1602(C=C), 3062(Ar-C-H), 1517, 1500, 1408(Aromatic C=C bend), 721, 678 cm^{-1} ; ¹HNMR (400MHz, CDCl₃/TMS): δ (ppm)= 7.0-8.0 (m, ArH), 5.9 (m, 1H), 5.2(dd, 2H), 3.5(d, 2H); LCMS: m/z: 146 (M⁺): Elemental analysis of C₁₀H₁₀O [Found: C= 82.05%; H=6.59%; O= 10.87%]. C₁₀H₁₀O required [C= 82.16%; H=6.89%; O=10.94%]

(BGUK-2): 1-(4-nitrophenyl) but-3-en-1-one

Yellow colour solid, Yield 89%: FTIR: ν_{\max} (KBr): 1692(C=O), 1606(C=C), 3062(Ar-C-H), 1542, 1350(Ar-N=O), 1494, 1426(Aliphatic C-H bend), 822 cm^{-1} (Out of plane aromatic CH bend); ¹HNMR(400MHz, CDCl₃/TMS): δ (ppm)= 7.2-8.0(m, ArH), 5.8(m, 1H), 5.2(dd, 2H), 3.0(d, 2H), LCMS: m/z: 191 (M⁺): Elemental analysis of C₁₀H₉NO₃ [Found: C= 62.72%; H=4.69%; N=7.28%; O= 25.07%]. C₁₀H₉NO₃ required [C= 62.82%; H=4.74%; N=7.33%; O=25.11%]

(BGUK-3): 1-(3-nitrophenyl) but-3-en-1-one

Yellow colour solid, Yield 87%: FTIR: ν_{\max} (KBr): 1705 (C=O), 1619 (C=C), 3094 (Ar-C-H), 1531, 1352 (Ar-N=O), 1483, 1446(aliphatic CH bend), 823, 720 cm^{-1} ; ¹HNMR (400MHz, CDCl₃/TMS): δ (ppm)= 7.6-8.9(m, ArH), 5.22-5.28(dd, 2H), 3.4(d, 2H), 5.9(m, 1H): LCMS: m/z: 191 (M⁺):

Elemental analysis of C₁₀H₉NO₃ [Found: C= 62.72%; H=4.69%; N=7.28%; O= 25.07%]. C₁₀H₉NO₃ required [C= 62.82%; H=4.74%; N=7.33%; O=25.11%]

(BGUK-4): 1-(4-fluorophenyl) but-3-en-1-one

Colourless solid, Yield 85%: FTIR: ν_{\max} (KBr): 1683(C=O), 1604(C=C), 3082(Ar-C-H), 1509, 1482, 1430(Aliphatic CH bend), 1314(Ar-C-F), 854 cm^{-1} ; ¹HNMR (400MHz, CDCl₃/TMS): δ (ppm)= 7.2-8.2(m, ArH), 5.2-5.4(dd, 2H); 3.2(d, 2H), 5.9(m, 1H); LCMS: m/z: 164 (M⁺): Elemental analysis of C₁₀H₉FO [Found: C= 73.07%; H=5.49%; F=11.45%; O= 9.63%]. C₁₀H₉FO required [C= 73.16%; H=5.53%; F=11.57%; O=9.75%]

(BGUK-5): 1-(3-bromophenyl) but-3-en-1-one

colourless solid, Yield 84%: FTIR: ν_{\max} (KBr): 1685 (C=O), 1637 (C=C), 3069 (Ar-C-H), 1507, 1498, 1436(Aliphatic CH bend), 815, 748, 648(Ar-C-Br) cm^{-1} ; ¹HNMR (400MHz, CDCl₃/TMS): δ (ppm)= 7.5-8.3(m, ArH), 4.5-4.6(dd, 2H), 3.2 (d, 2H), 5.6(m, 1H); LCMS: m/z: 223.6 (M⁺): Elemental analysis of C₁₀H₉BrO [Found: C= 53.29%; H=3.98%; Br =35.49%; O= 7.04%]. C₁₀H₉BrO required [C= 53.36%; H=4.03%; Br =35.50%; O=7.11%]

(BGUK-6): 1-(2-chlorophenyl) but-3-en-1-one

Colourless solid, Yield 83%: FTIR: ν_{\max} (KBr): 1686(C=O), 1636(C=C), 2960(aliphatic C-H), 1507, 1497, 1437(Aliphatic CH bend), 792(Ar-C-Cl), 744 cm^{-1} ; ¹HNMR (400MHz, CDCl₃/TMS): δ (ppm)=7.2-8.0 (m, ArH), 5.3(m, 1H), 4.5 (dd, 2H), 3.5(d, 2H); LCMS: (m/z) 180.5 (M⁺): Elemental analysis of C₁₀H₉OCl [Found C= 66.39%; H=4.89%; Cl=19.58%; O= 8.75%]. C₁₀H₉OCl required [C= 66.49%; H=5.02%; Cl=19.63%; O=8.86%]

(BGUK-7): 1-(Furan-2-yl) But-3-ene-1-one

Colourless solid, Yield 78%: FTIR: ν_{\max} (KBr): 1718(C=O), 1637(C=C), 3142(Ar-C-H), 1508, 1475, 1424(Aliphatic CH bend), 1299 (Ar-C-O), 1183(Ar-C-O), 668 cm^{-1} ; $^1\text{H NMR}$ (400MHz, CDCl_3/TMS): $\delta(\text{ppm}) = 6.5-7.7$ (m, ArH), 5.9(m, 1H), 5.3(dd, 2H), 3.2 (d, 2H); LCMS: (m/z) 136 (M^+): Elemental analysis of $\text{C}_8\text{H}_8\text{O}_2$ [Found C = 70.49%; H = 5.89%; O = 23.44%]. $\text{C}_8\text{H}_8\text{O}_2$ required [C = 70.57%; H = 5.92%; O = 23.50%]

(BGUK-8): (E)-1,4-diphenylbut-3-en-1-one

Colourless solid, Yield 85%: FTIR: ν_{\max} (KBr): 1687(C=O), 1621(C=C), 3069(Ar-C-H), 1510, 1493, 1417(Aliphatic CH bend), 707, 665 cm^{-1} ; $^1\text{H NMR}$ (400MHz, CDCl_3/TMS): $\delta(\text{ppm}) = 7.0-8.0$ (m, ArH), 6.2(d, 1H), 6.0(t, 1H), 3.2(d, 2H); LCMS: (m/z) 222 (M^+): Elemental analysis of $\text{C}_{16}\text{H}_{14}\text{O}$ [Found C = 86.34%; H = 6.29%; O = 7.11%]. $\text{C}_{16}\text{H}_{14}\text{O}$ required [C = 86.45%; H = 6.35%; O = 7.20%]



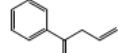


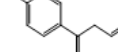


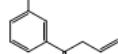


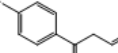


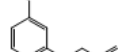


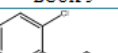


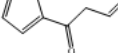

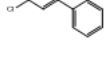
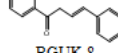

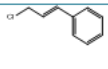
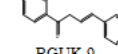
(BGUK-9): (E)-1-(4-nitrophenyl)-4-phenylbut-3-en-1-one

Yellow colour solid, Yield 80%: FTIR: ν_{\max} (KBr): 1695(C=O), 1605(C=C), 3061(Ar-C-H), 1541, 1350(Ar-NO₂), 1494, 1429(Aliphatic CH bend), 822, 716, 698 cm^{-1} ; $^1\text{H NMR}$ (400MHz, CDCl_3/TMS): $\delta(\text{ppm}) = 7.2-8.8$ (m, ArH), 6.4(d, 1H), 5.2(t, 1H), 3.1(d, 2H); LCMS: (m/z) 267 (M^+): Elemental analysis of $\text{C}_{16}\text{H}_{13}\text{NO}_3$ [Found C = 71.79%; H = 4.89%; N = 5.12%; O = 17.92%]. $\text{C}_{16}\text{H}_{13}\text{NO}_3$ required [C = 71.90%; H = 4.90%; N = 5.24%; O = 17.96%]

3. Results and Discussion

3.1. Optimization of reaction conditions on synthesis of β,γ -unsaturated ketone derivatives

Table 1. Reactants, conditions, and structures of β,γ -unsaturated ketones

S.N	Acid Chloride	Allyl Bromide	β,γ -unsaturated ketones	Time (min)	Yield (%)
1			 BGUK-1	30	95
2			 BGUK-2	60	89
3			 BGUK-3	70	87
4			 BGUK-4	60	85
5			 BGUK-5	55	84
6			 BGUK-6	60	83
7			 BGUK-7	75	78
8			 BGUK-8	80	85
9			 BGUK-9	90	80

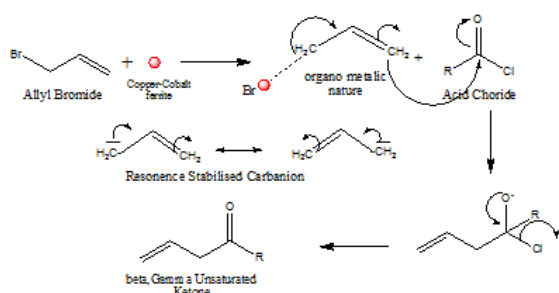
The reaction products substituted β,γ -unsaturated ketones were characterized by IR-peaks at around 1695 cm^{-1} indicating Ketone C=O functional group, 1620 cm^{-1} indicating C=C functional groups present in the compound.

The $^1\text{H NMR}$ spectra of the chemical shift at δ 4.5-6.0 (dd, 2H) as a doublet of doublet, peak at δ 3.0-3.5 (d, 2H) confirm the presence of double bond, and a multiplet at δ 7-8.8 confirms the presence of aromatic protons.

The mass spectrum provides the molecular weight of the molecule along with the M+1

peak, and the fragments give the information about the daughter ions.

3.3. Catalytic study



The mechanism (“Scheme 3”) shows that the Nano copper-cobalt ferrite is helped to create organometallic reagent with allyl halides, that reagent acts as a nucleophile attack on the carbonyl carbon of substituted acid chlorides. In this reaction a resonance stabilized allyl carbanion is observed, and finally gets β,γ -unsaturated ketones by nano ferrites. All the acylation responses continue with allylic revision [26,27, 40-41], so the double bond was expelled from the conjugation. The development of stable allyl ketone was affirmed by FT-IR, MASS, and ^1H NMR ghastrly examinations. In which ^1H NMR spectra shows the compound move at δ 4.5-6.0 demonstrates doublet of doublet affirms the nearness of arrangement of stable olefinic security. This demonstrates allylation happens at carbonyl carbon with no prototropic modification.

3.4. Comparison of the present catalyst with other catalysts which are reported earlier

Table 2. Comparative study of reaction times of allylation of acid chlorides with Cu-Co Ferrites and other catalysts

S.No	Catalyst	Method	Temp ($^{\circ}$ C).	Time (hours)	Reference
1	Bis (cyclooctadiene) Nickel(0)	Conventional	RT	15.0	40
2	Zn	Conventional	RT	3.0	37
3	Cd	Conventional	RT	3.0	39
4	In	Conventional	RT	3.0	38
5	BuSnCl ₂ + Additive	Conventional	RT	2.0	41
6	CuFe ₂ O ₄	Conventional	RT	2.0	42
7	Cu _{0.5} Co _{0.5} Fe ₂ O ₄	Conventional	RT	1.0	-
8	Cu _{0.5} Co _{0.5} Fe ₂ O ₄	Ultrasonication	RT	0.5	-

3.5. Effect of cobalt substitution on the preparation of β,γ -unsaturated ketones

Table 3. Impact of metal proportion in the impetus complex on the readiness of β,γ -unsaturated ketones

S.N	Catalyst	Conventional vs. Ultrasonication	Time (min)	Yield (%)
1	CuFe ₂ O ₄	Conventional	120	80
		Ultrasonication	90	80
2	Cu _{0.75} Co _{0.25} Fe ₂ O ₄	Conventional	70	80
		Ultrasonication	40	90
3	Cu _{0.5} Co _{0.5} Fe ₂ O ₄	Conventional	60	80
		Ultrasonication	30	95
4	Cu _{0.25} Co _{0.75} Fe ₂ O ₄	Conventional	60	85
		Ultrasonication	30	95
5	CoFe ₂ O ₄	Conventional	60	85
		Ultrasonication	30	95

According to “Table 2” and “Table 3” shows that cobalt substituted copper ferrites have to show better yields under ultrasonication for the synthesis of β,γ -unsaturated ketones. When these reactions have been compared with copper ferrite at room temperature [42] the time of reaction was 120 minutes. Whereas in this case, a combined effect of both the catalyst and the

ultrasonication drastically reduced the time of the reaction, which is an important contribution from this study.

Different solvents like tetrahydrofuran, diethyl ether, dichloromethane, and acetonitrile were screened for this response. It is discovered the response was productive in tetrahydrofuran contrasted with different solvents utilized. The results are listed in "Table 4".

3.6. Effect of solvent on the preparation of β,γ -unsaturated ketones

Table 4. Comparative study in different solvent systems of Allylated Acid Chlorides

S.no	Catalyst	solvent	Time (hours)	Yield (%)
1	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	THF	0.5	95
2	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	$(\text{C}_2\text{H}_5)_2\text{O}$	2	80
3	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	Dichloromethane	5	64
4	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	MeCN	10	Trace

3.7. Recycling of the Catalyst

Catalyst is removed from the reaction mixture by using a strong magnet at the bottom of the flask after which the solid was separated by removing the solution by dropper. The separated catalyst washed with ethyl alcohol and acetone after that the catalyst was activated by putting it into a microwave oven up to a few minutes. That activated catalyst was reused for the next run. The same procedure was used to follow the recovery of the catalyst and recycling up to five times without loss of catalytic activity. Therefore, the complete separation of the catalyst which increases the purity and yield of the product.

4. Conclusion

It is concluded that an efficient method has been developed for the synthesis of β, γ -

unsaturated ketones using Nano Copper-Cobalt Ferrites under ultrasonication. The most advantages of this method for getting high percentages of yield, magnetically easy separation and reusability of the catalyst, and less reaction time.

Acknowledgments

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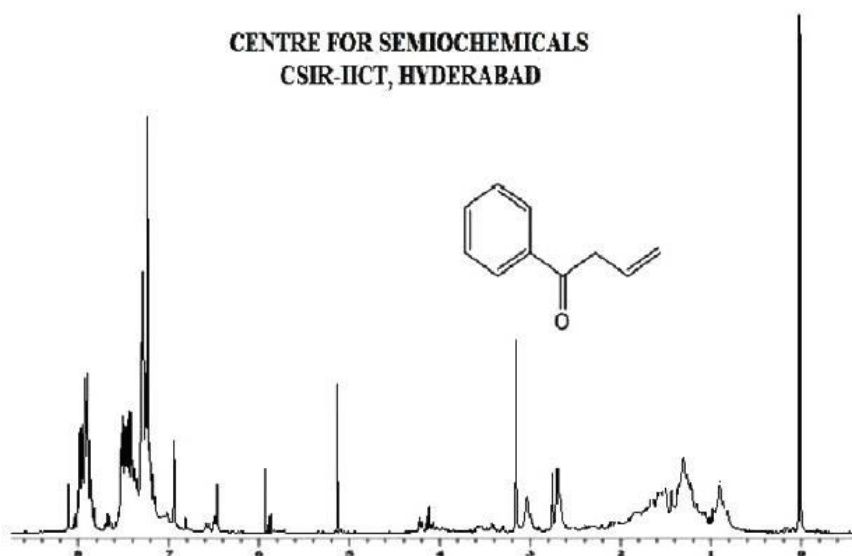


Figure 1. ¹HNMR Spectrum of BGUK 1

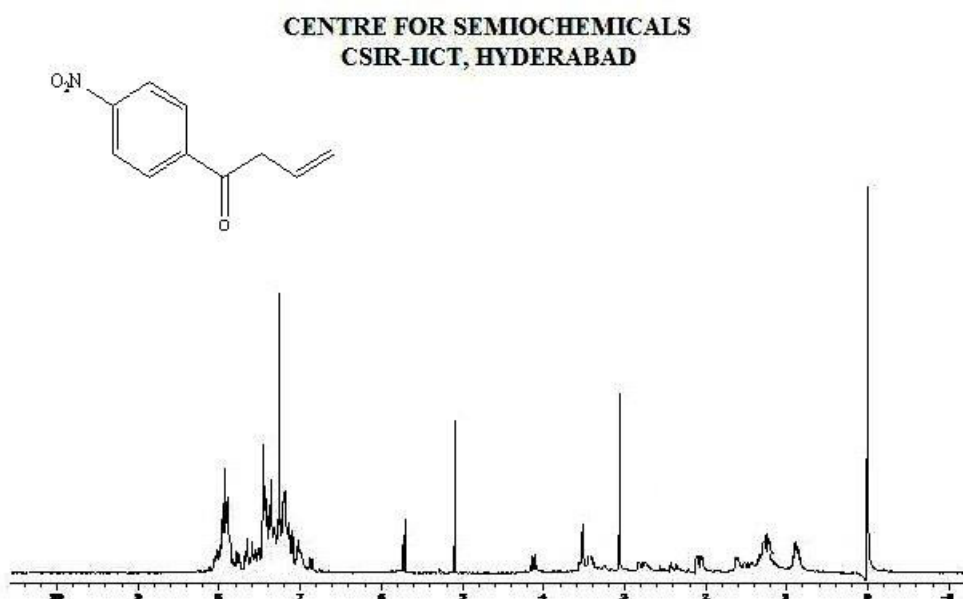


Figure 2. ¹HNMR Spectrum of BGUK 2

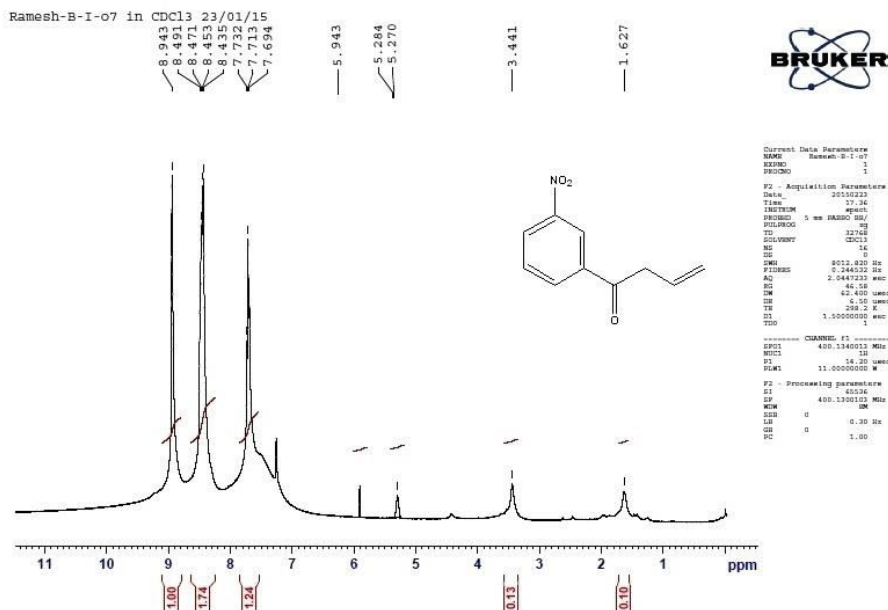


Figure 3. ¹HNMR Spectrum of BGUK 3

CENTRE FOR SEMIOCHEMICALS
CSIR-IICT, HYDERABAD

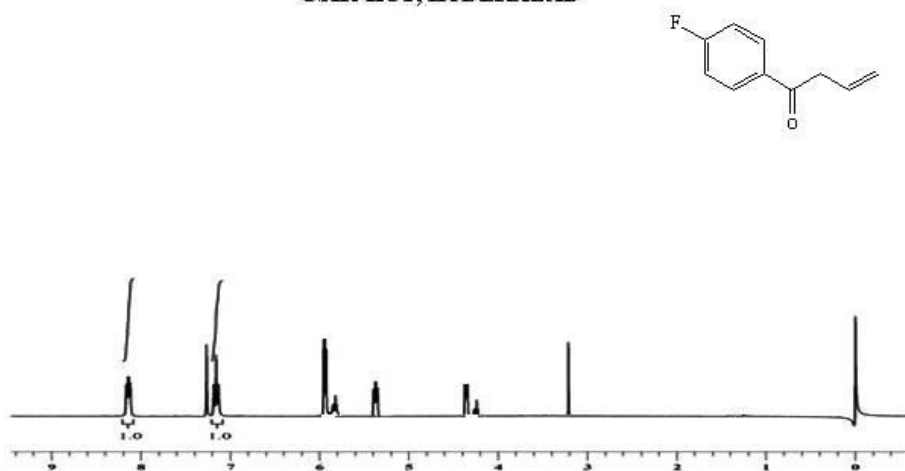


Figure 4. ¹HNMR Spectrum of BGUK 4

CENTRE FOR SEMIOCHEMICALS
CSIR-IICT, HYDERABAD

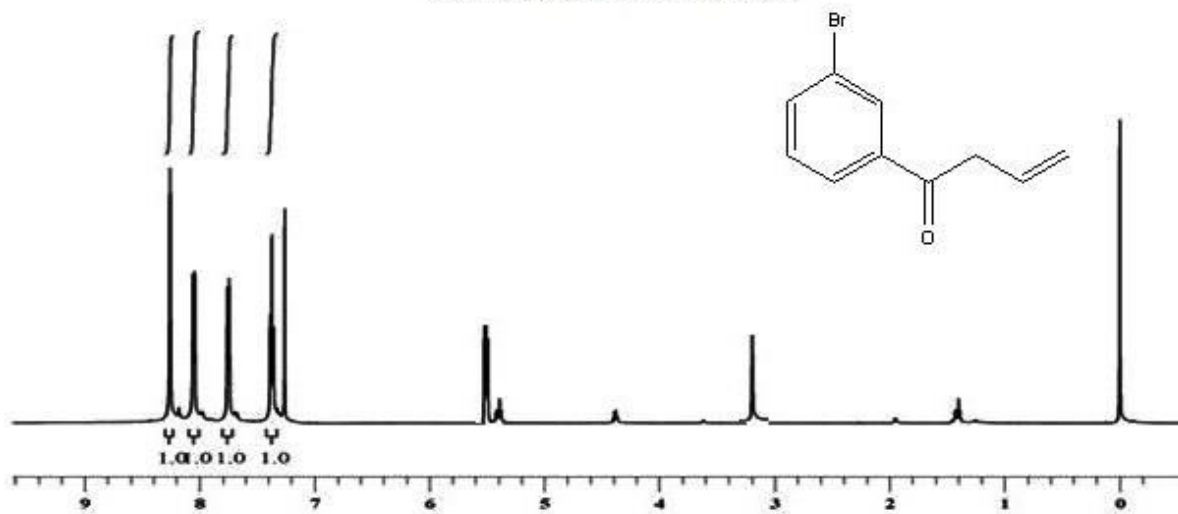


Figure 5. ¹H NMR Spectrum of BGUK 5

CENTRE FOR SEMIOCHEMICALS
CSIR-IICT, HYDERABAD

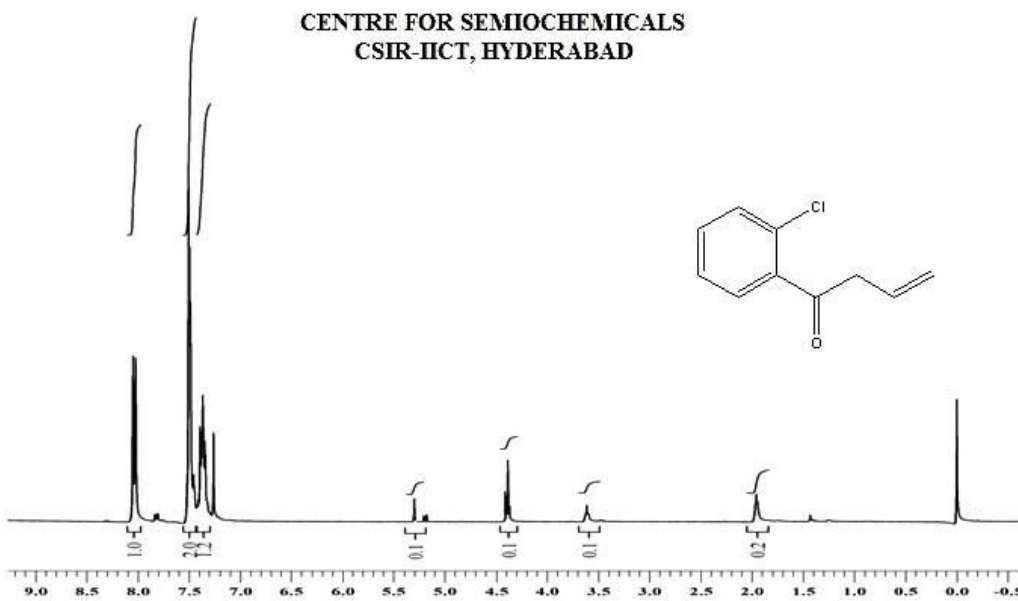


Figure 6. ¹H NMR Spectrum of BGUK 6

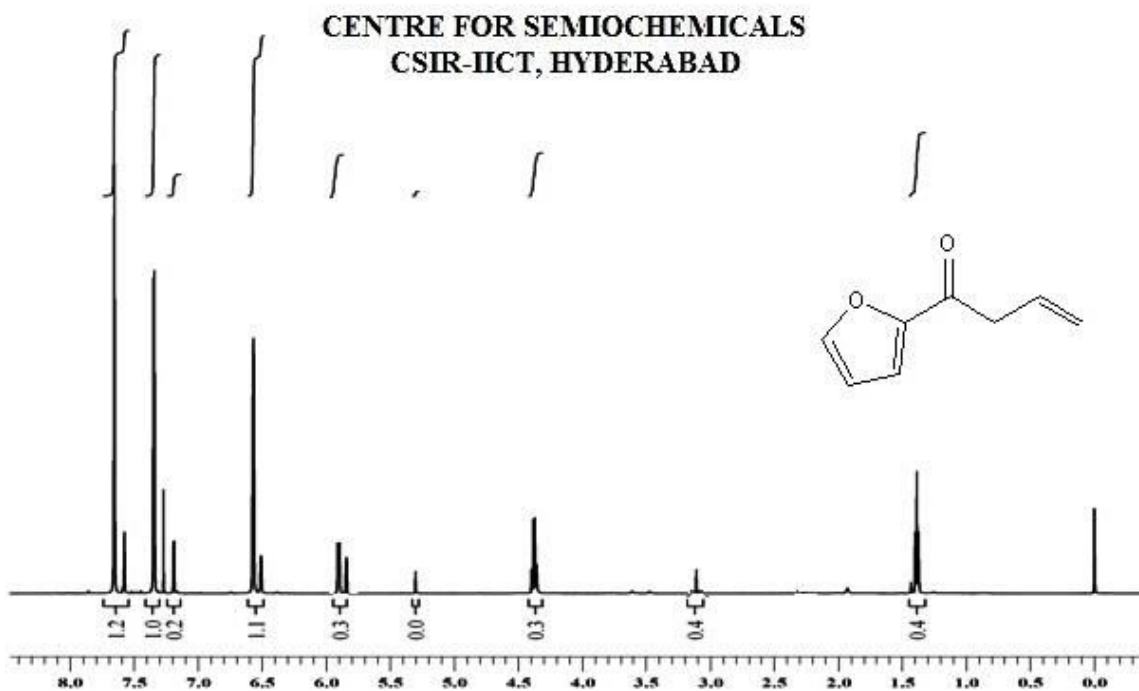


Figure 7. ¹H NMR Spectrum of BGUK 7

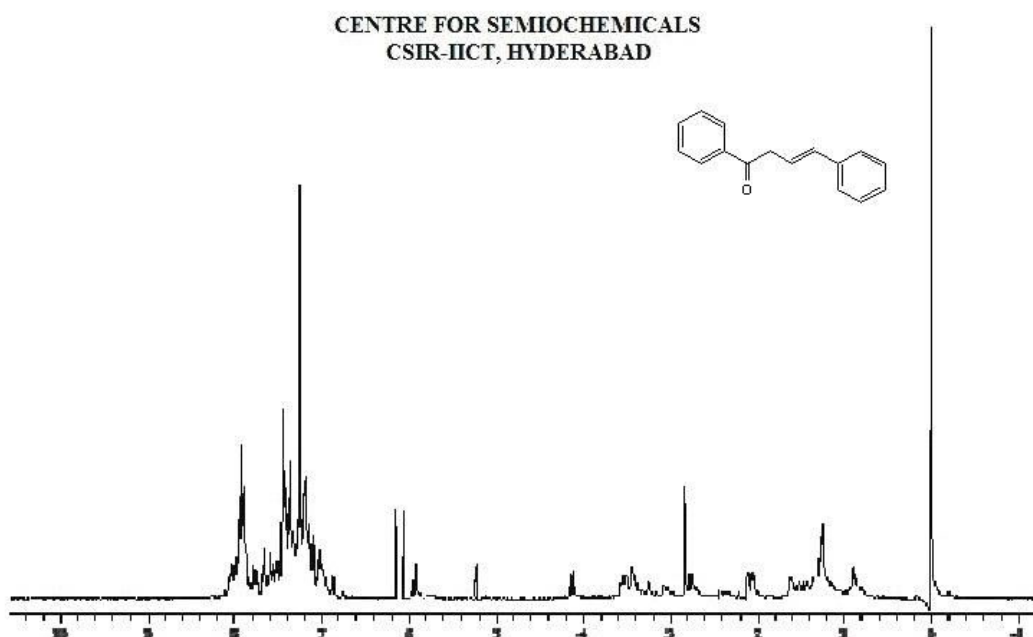


Figure 8. ¹H NMR Spectrum of BGUK 8

CENTRE FOR SEMIOCHEMICALS
CSIR-IICT, HYDERABAD

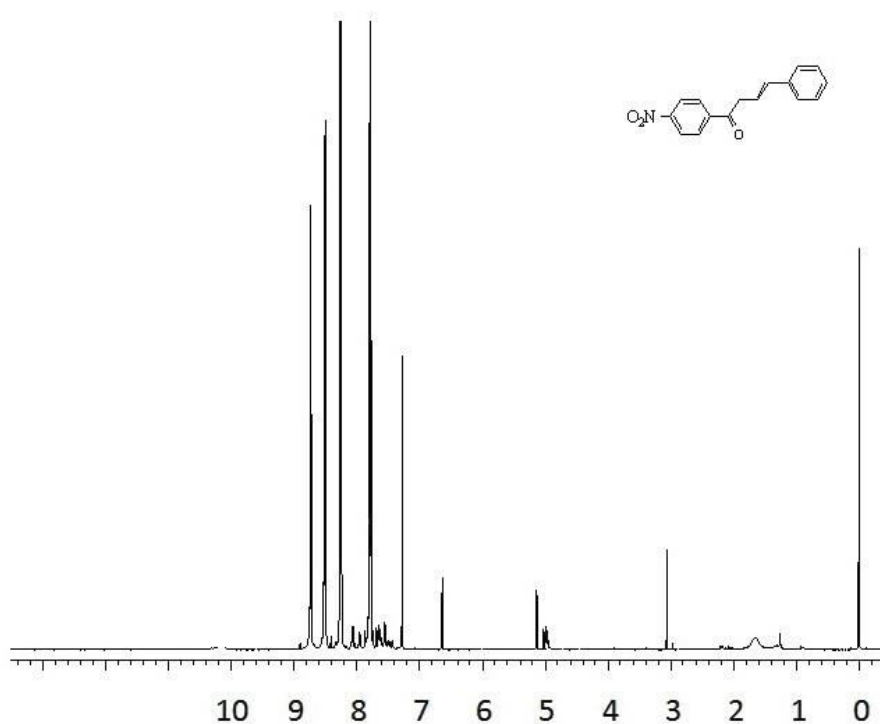


Figure 9. ¹H NMR Spectrum of BGUK 9

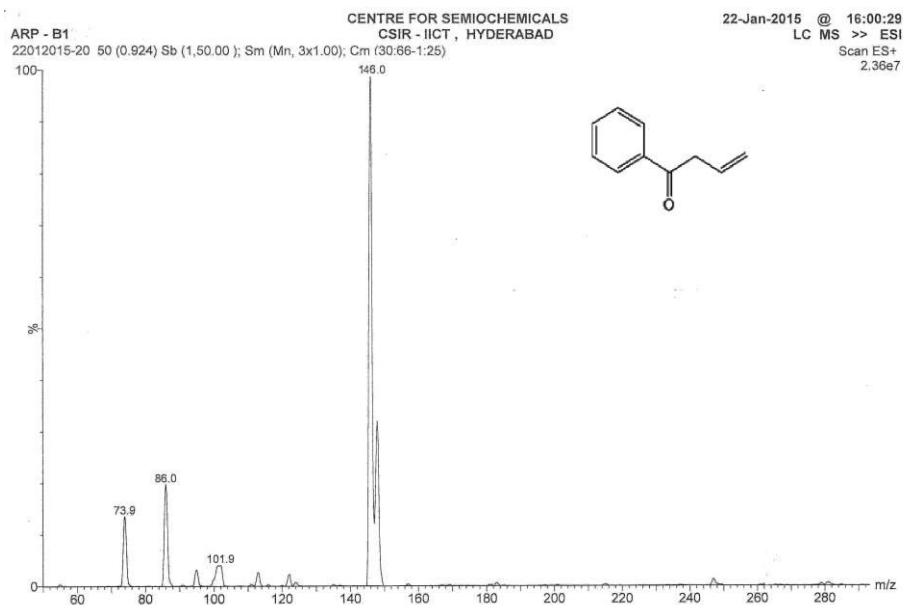


Figure 10. MASS Spectrum of BGUK 1

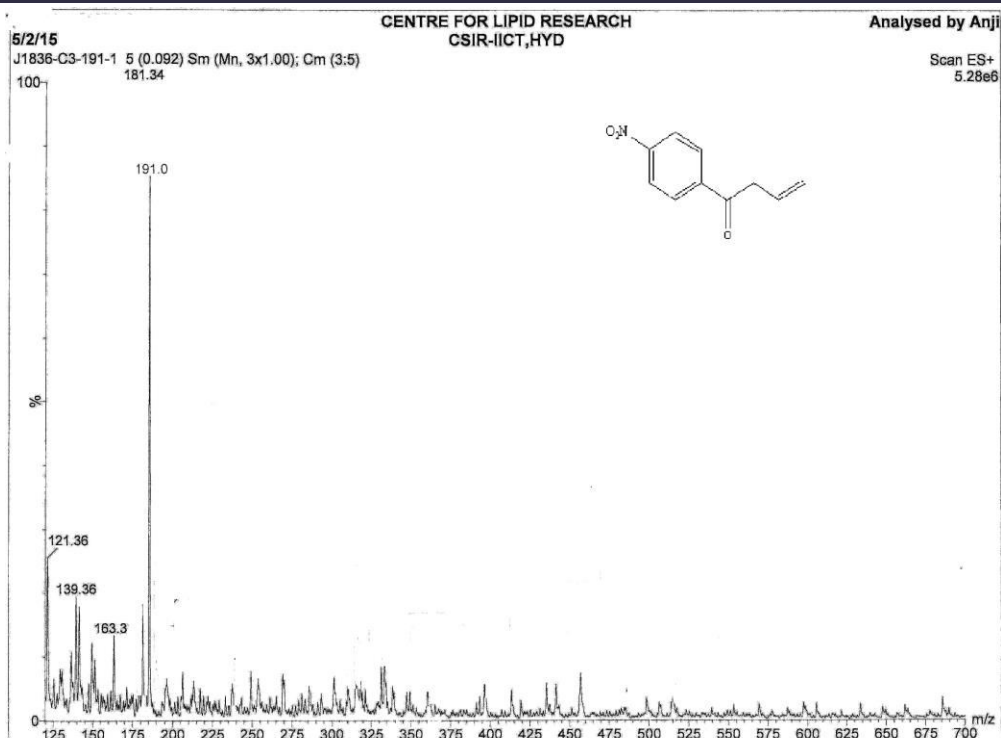


Figure 11. MASS Spectrum of BGUK 2

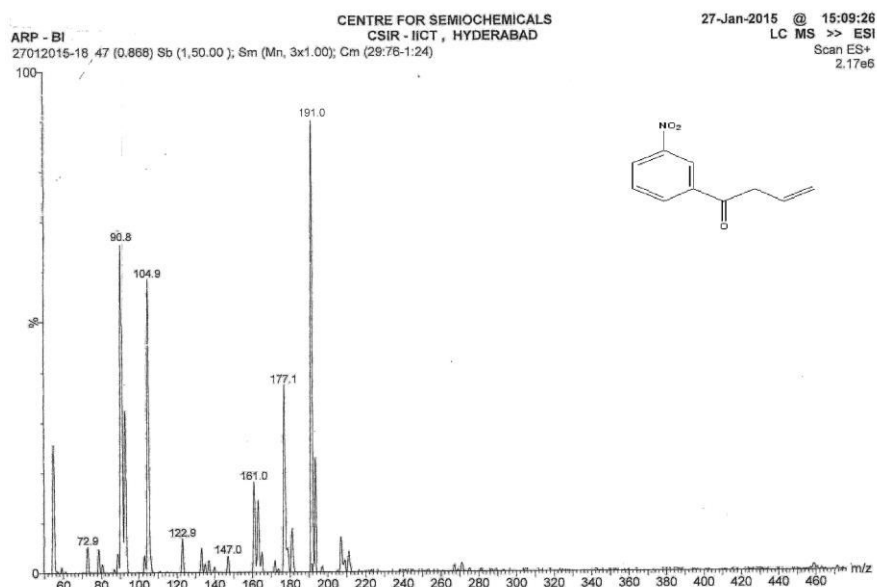


Figure 12. MASS Spectrum of BGUK 3

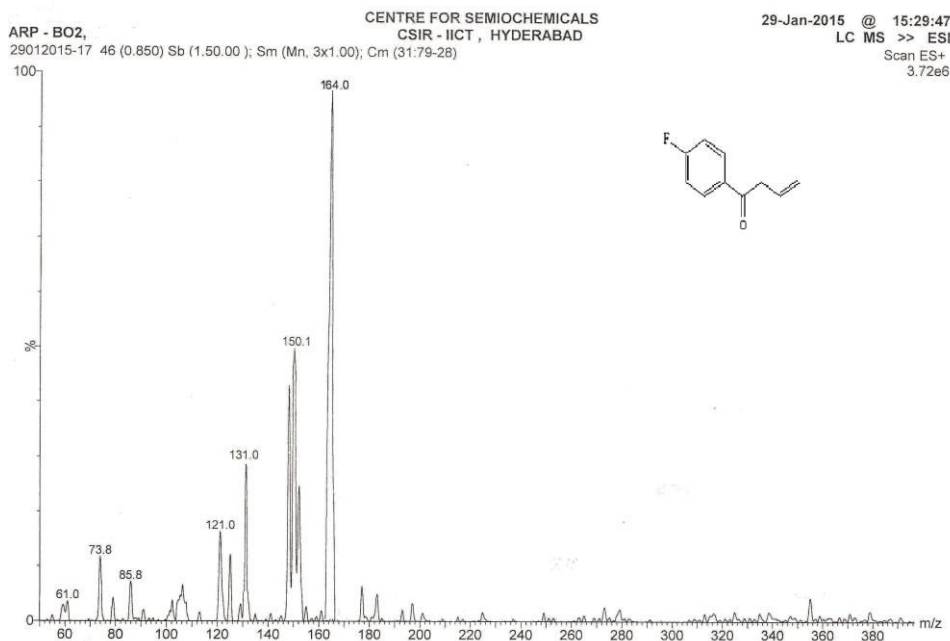


Figure 13. MASS Spectrum of BGUK 4

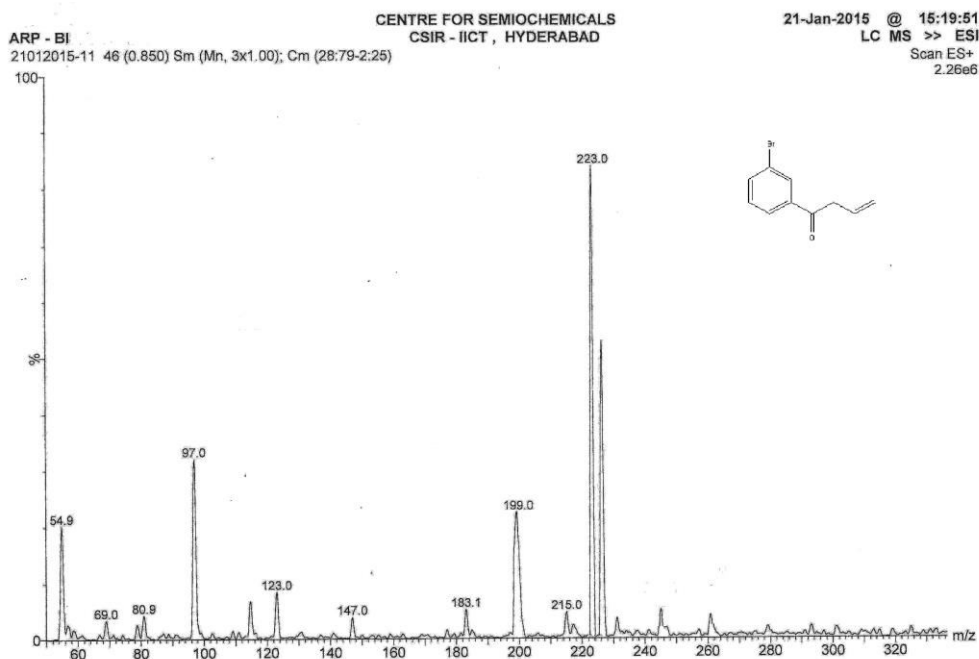


Figure 14. MASS Spectrum of BGUK 5

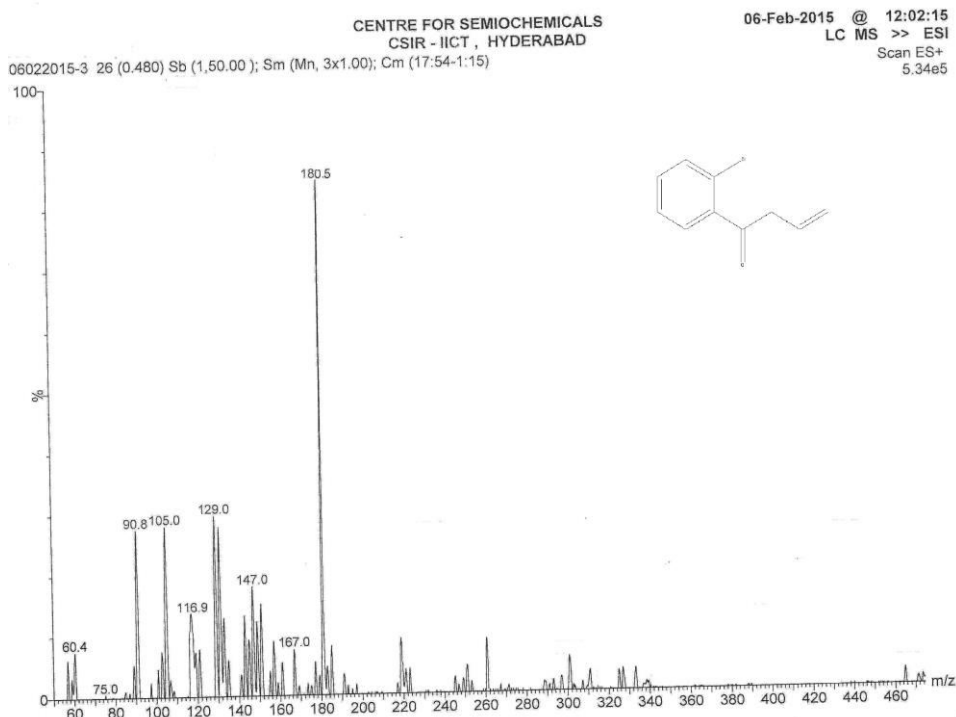


Figure 15. MASS Spectrum of BGUK 6

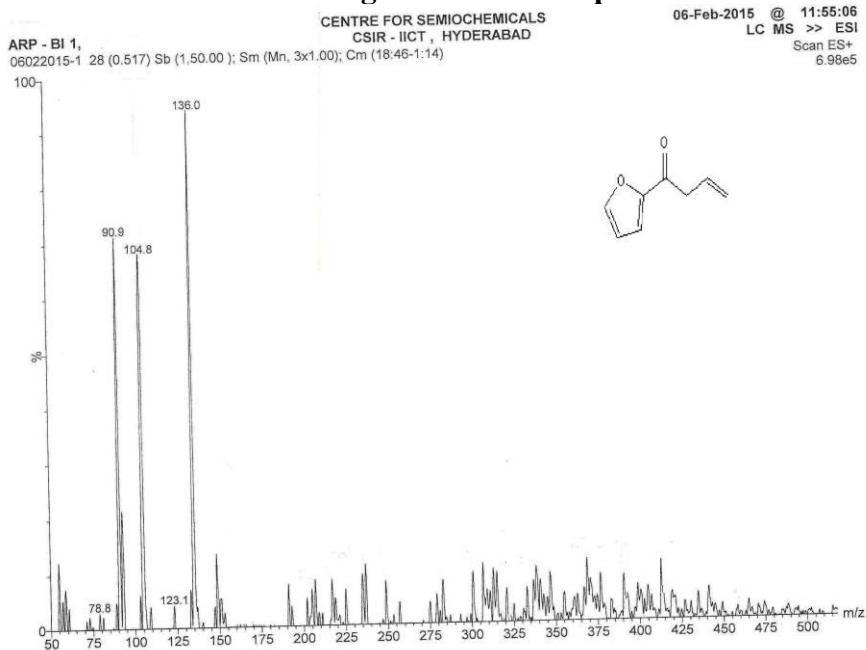
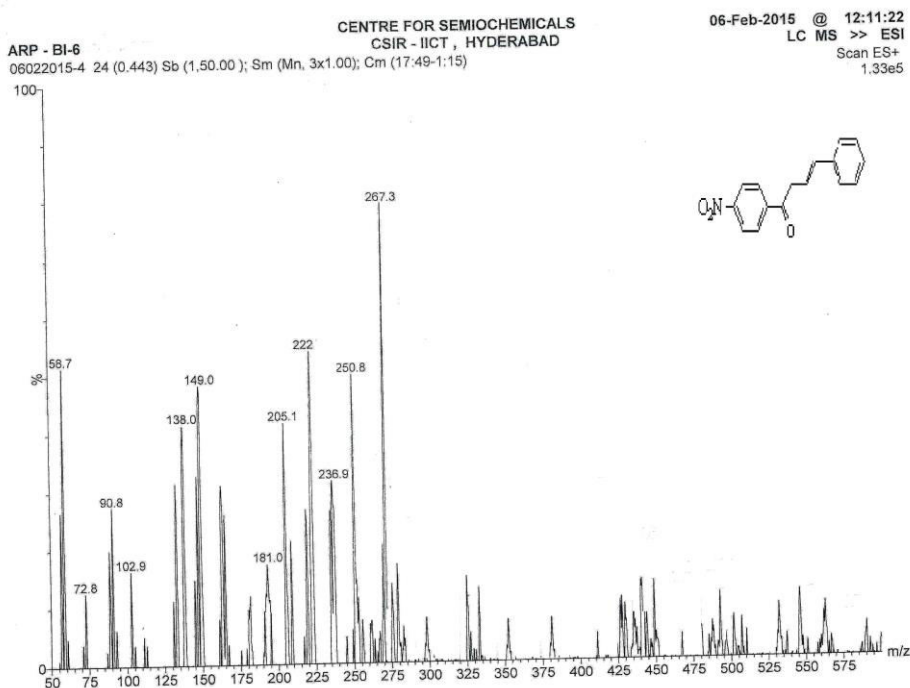
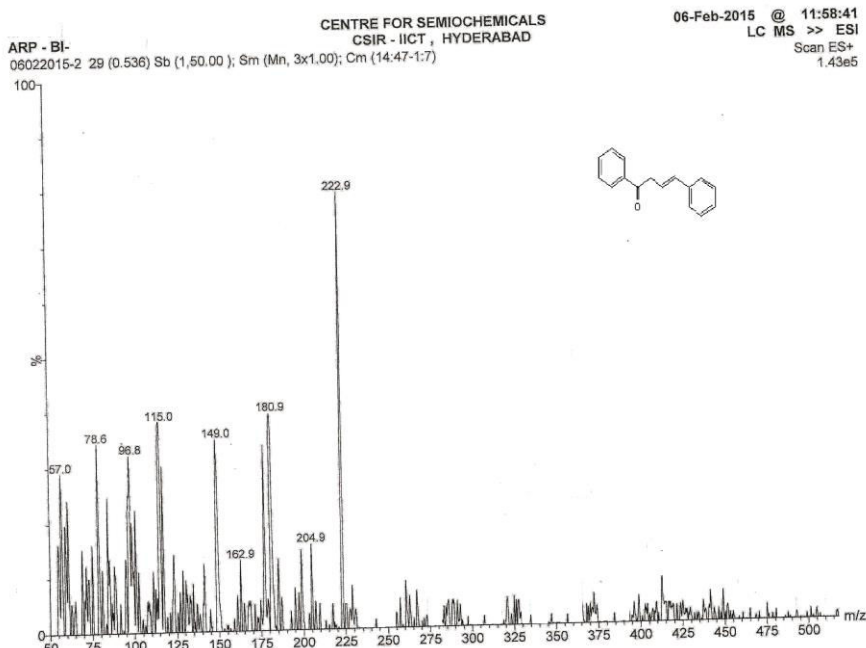


Figure 16. MASS Spectrum of BGUK 7



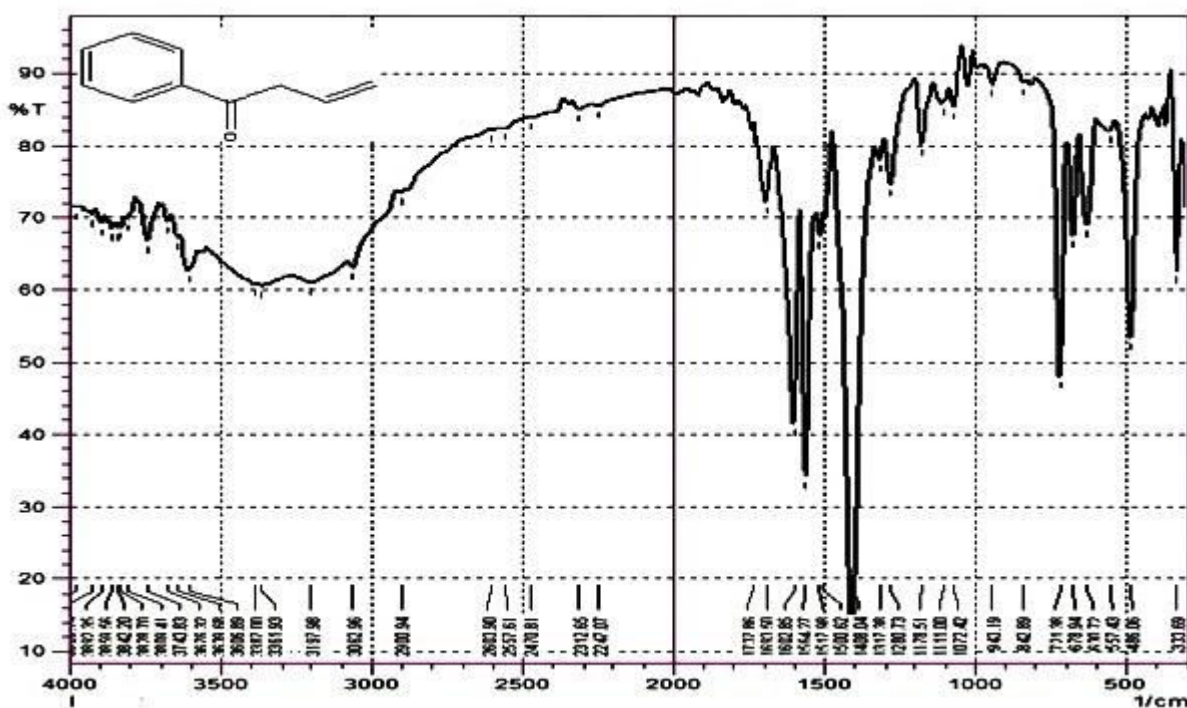


Figure 19. FT-IR Spectrum of BGUK 1

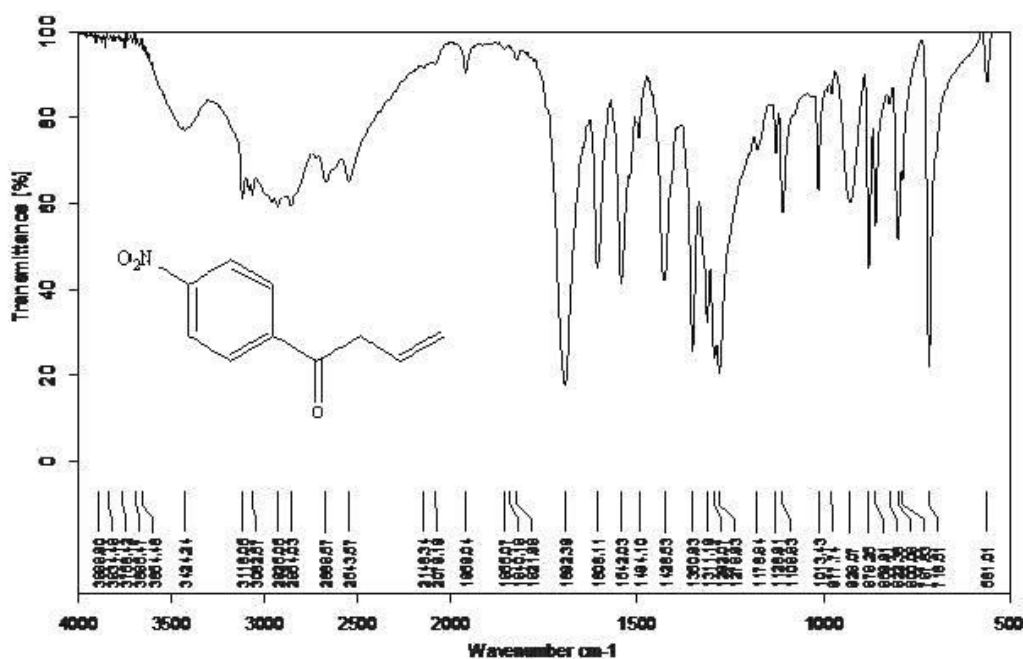


Figure 20. FT-IR Spectrum of BGUK 2

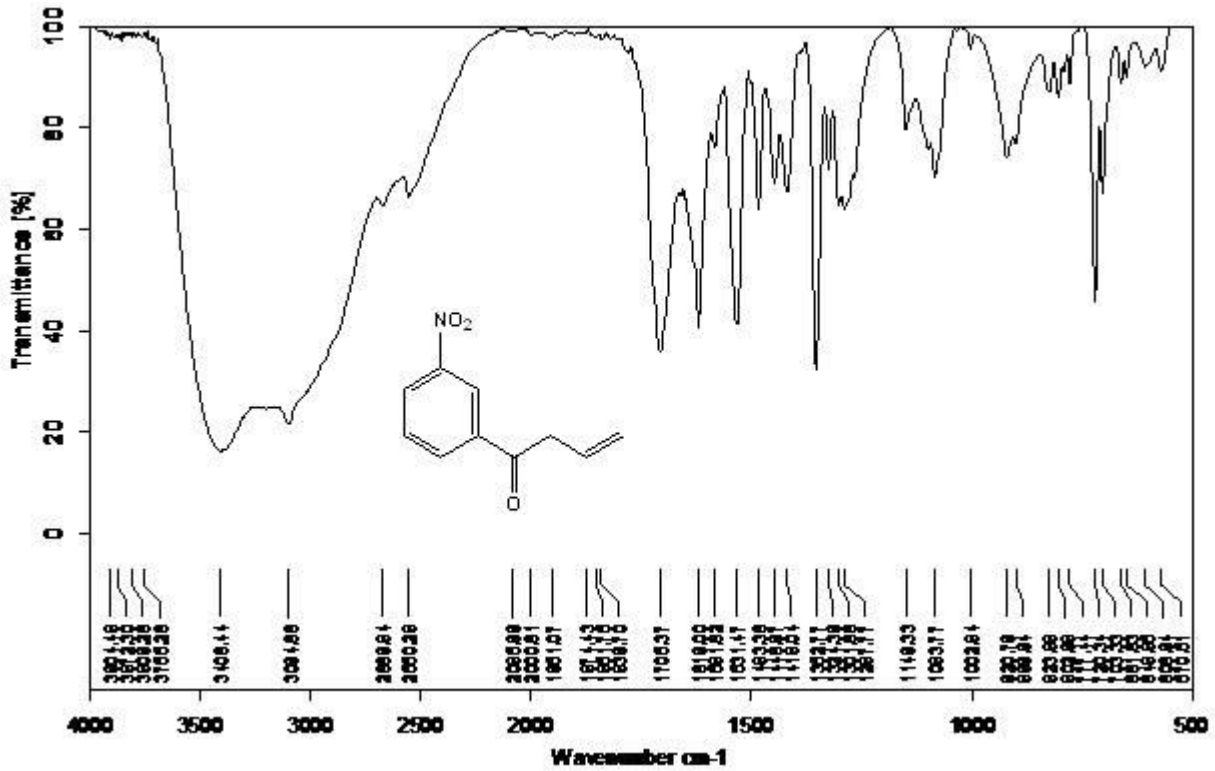


Figure 21. FT-IR Spectrum of BGUK 3

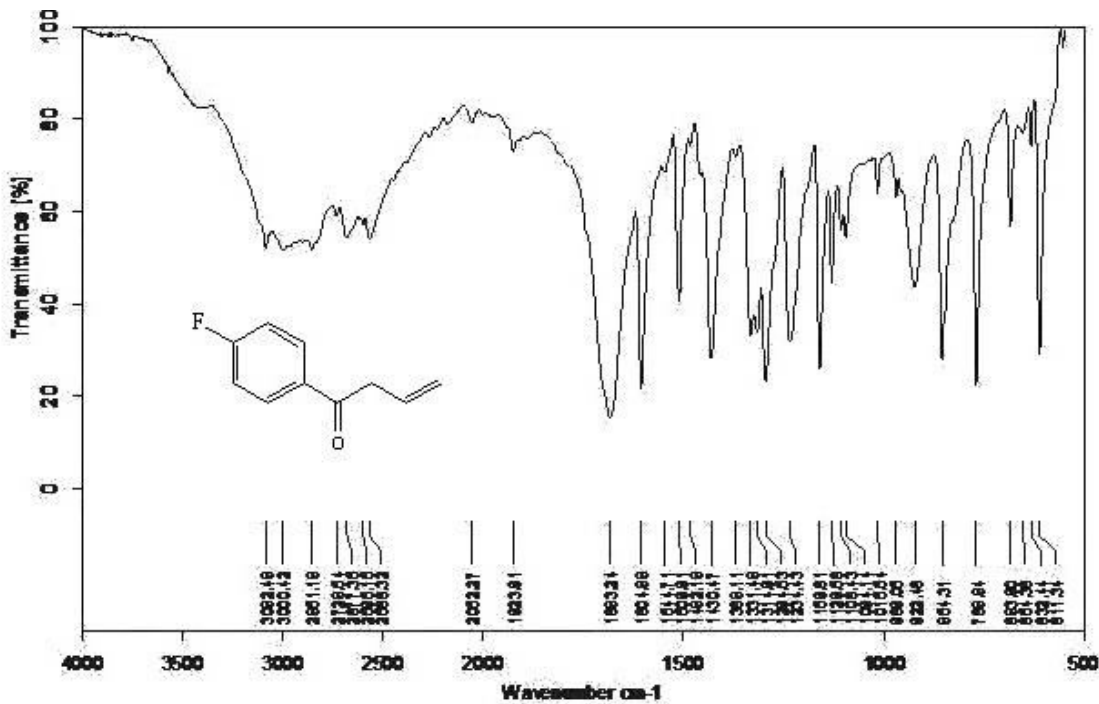


Figure 22. FT-IR Spectrum of BGUK 4

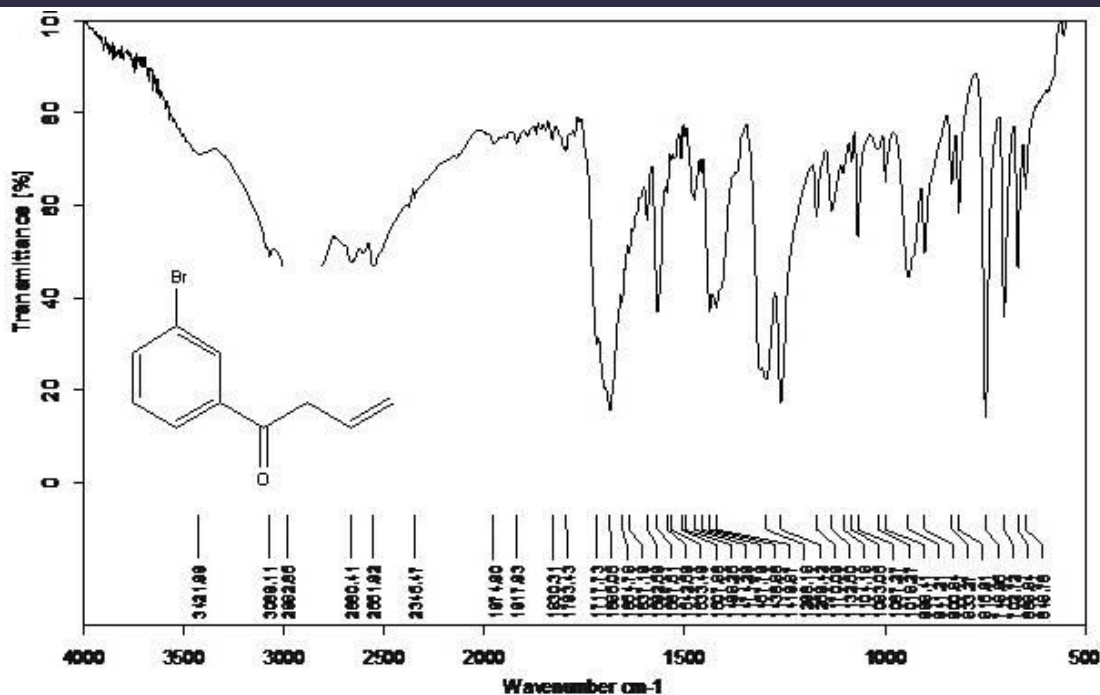


Figure 23. FT-IR Spectrum of BGUK 5

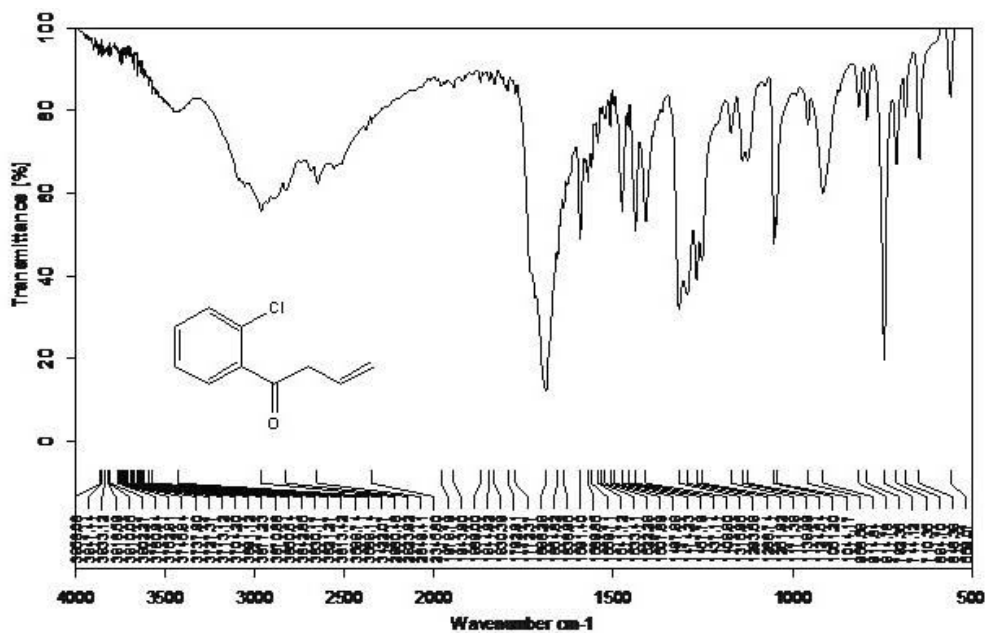


Figure 24. FT-IR Spectrum of BGUK 6

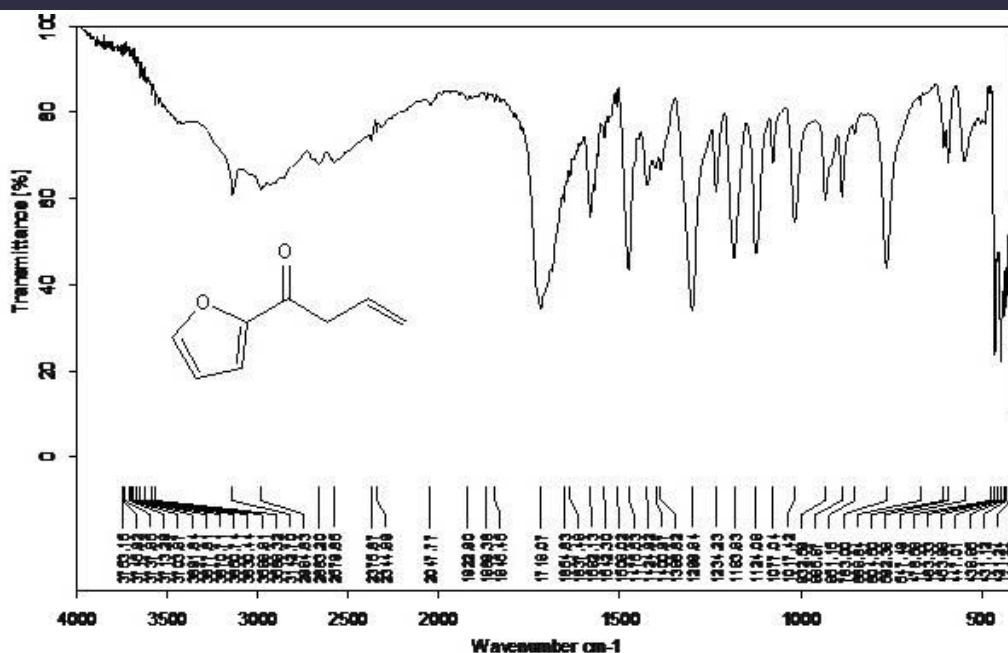


Figure 25. FT-IR Spectrum of BGUK 7

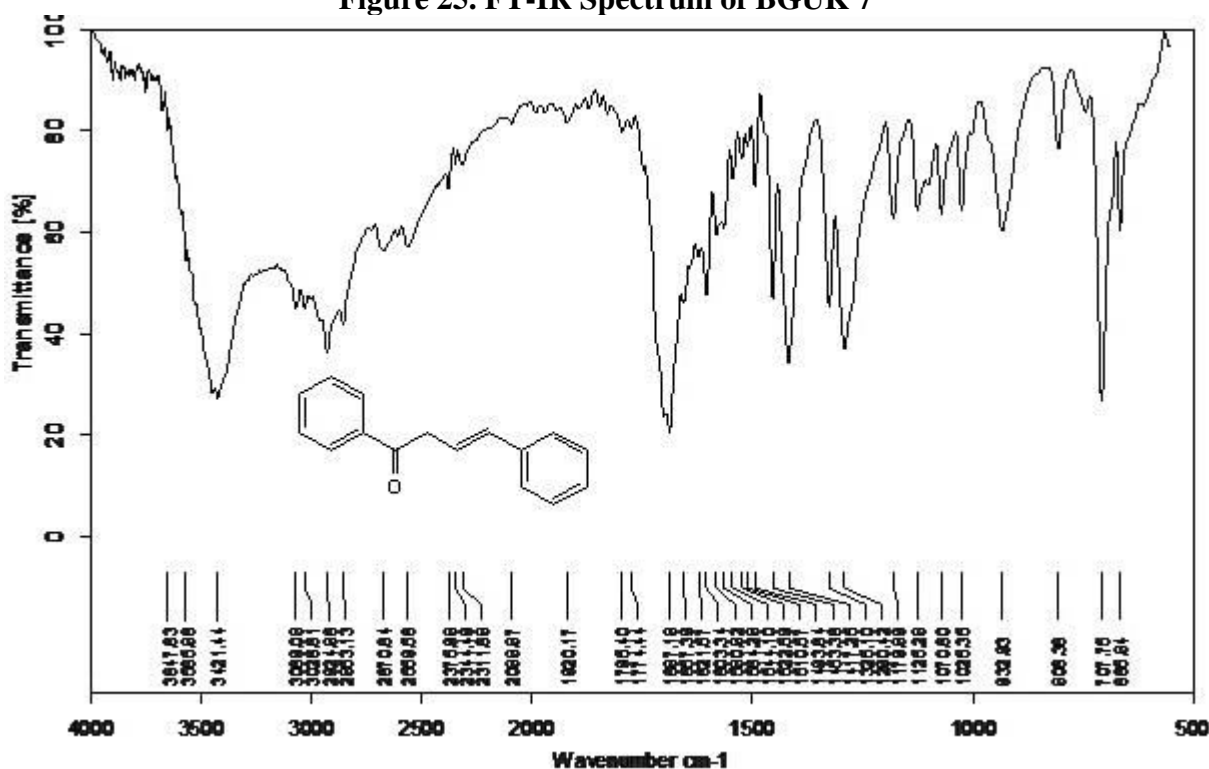


Figure 26. FT-IR Spectrum of BGUK 8

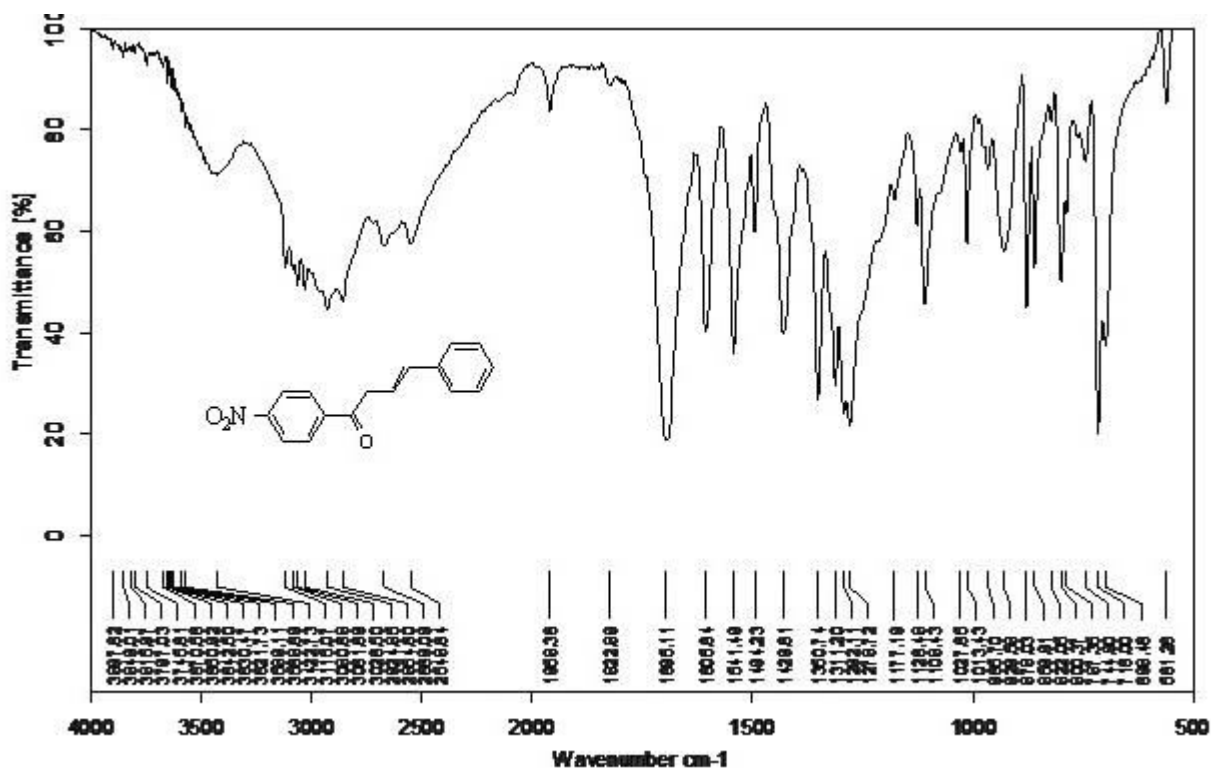


Figure 27. FT-IR Spectrum of BGUK 9