Synthesis of terminal acetylenes, alkynyl aldehydes and acids from aryl halides

M. Phil Thesis

SUBMITTED IN PARTIAL FULFILMENT OF THE
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M.PHIL IN CHEMISTRY

SUBMITTED BY
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Department of Chemistry

The Thesis titled "Synthesis of terminal acetylenes, alkynyl aldehydes and acids from aryl halides"

SUBMITTED BY

Mst. Laila Arifun Nahar

has been accepted as satisfactory in partial fulfilment of the requirements for the degree of Master of Philosophy (M. Phil) in Chemistry and certify that the student has demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on August 31, 2009.

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Mst. Laila Arifun Nahar

Author

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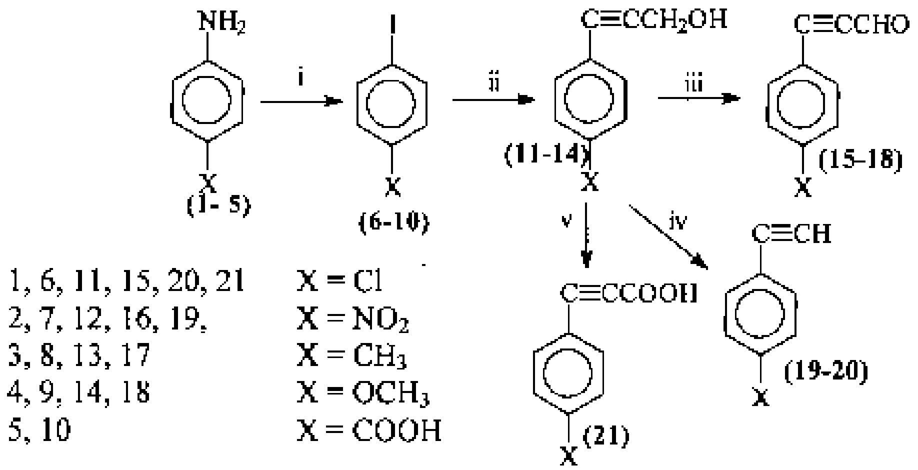
Abstract

Thesis title: Synthesis of terminal acetylenes, alkynyl aldehydes and acids from aryl halides.

There are few basic type reactions that generate a new carbon-carbon bond, although this is one of the most critical operation in the synthesis of organic molecules. Acetylenes and alkynes derivatives are versatile compounds in the synthetic chemistry and hence various methods for their synthesis has been explored. In view of the extensive natural occurrence and biological importance of unsaturated alcohol a general method for the synthesis of substituted propargyl-alcohol through palladium-catalyzed reaction using aryl halide and propargyl alcohol is reported.



1, 6, 11, 15, 20, 21 X = Cl
2, 7, 12, 16, 19, X = NO_2
3, 8, 13, 17 X = CH_3
4, 9, 14, 18 X = OCH_3
5, 10 X = COOH

i) $NaNO_2$, H_2SO_4, KI, 0-5 °C, 30min.
ii) $(PPh_3)_2PdCl_2$, $CHCl_3$, Et_3N, CuI, $HC{\equiv}CCH_2OH$, 40 °C, 2hr
iii) Jones reagents (5.6 g $K_2Cr_2O_7$ in 5-6 ml H_2SO_4 conc. & 30 ml H_2O), CH_2Cl_2, 40 °C, 1 hr.
iv) KOH powder, MnO_2 powder, C_6H_6, r.t, 1hr.
v) Jones reagents (5.6 g $K_2Cr_2O_7$ in 5 - 6 ml H_2SO_4 conc. & 30 ml H_2O). $CHCl_3$, 80 °C, 6 hr.

The coupling reaction was carried out by stirring a mixture of aryliodide **6-10** and propargyl alcohol in presence of bis (triphenyl phosphine) palladium(II) chloride as a catalyst, copper iodide as a co-catalyst and triethylamine as a base in chloroform at 40 ° C. The condensed product was purified by column chromatography to afford 3-aryl unsaturated alcohol (**11-14**). The alcohol was subjected to oxidation with Jones reagent to yield unsaturated terminal aldehyde (**15-18**) at mild condition. Then the alcohol was subjected to oxidation-decarbonylation to yield unsaturated terminal acetylenes (**19-20**) by using manganese dioxide in presence of alkali. Finally, synthesis of ethynyl carboxylic acids (**21**) by oxidation of 3-aryl propargyl alcohols using Jones reagents at vigorous conditions. The synthesized compounds were characterized based on analytical data obtained from IR, UV, ^1H NMR, ^{13}C NMR and melting point.

Summary

Investigation incorporated in this dissertation entitled " Synthesis of terminal acetylenes, aldehydes & acids from aryl halides have been presented in two chapters. Introduction, background and the important synthetic methods are present in chapter 1. Chapter 2 deals with the detailed methodologies, experimental procedures for the synthesis of substituted unsaturated alcohols, aldehydes, acetylenes, acids, results and discussion of the synthesis. It also deals with the oxidation of the synthesized unsaturated alcohols.

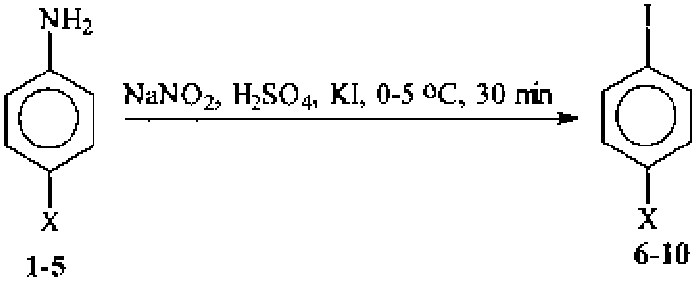
Chapter 1:

It represents the importance and synthesis of unsaturated alcohols, acetylenes, aldehydes and acids. These are synthetic organic compounds that are of increasing interest in synthetic and pharmaceutical chemistry. Various methods are described for the synthesis of unsaturated alcohols, aldehydes, acetylenes and acids here.

Chapter 2 :

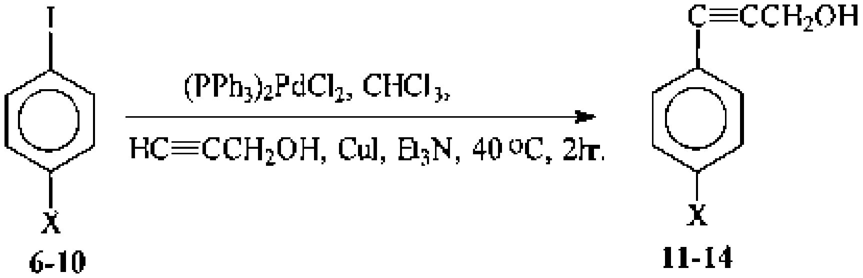
A facile method for the regioselective synthesis of unsaturated aryl alcohol **11 - 14** is reported . The aryliodides **6 - 10** were synthesized by usual procedure as shown in the scheme-1. The coupling reaction between aryliodide and propargyl alcohol was carried out through palladium catalyzed reaction. The palladium catatyzed reaction was usually performed by stirring the mixture of aryliodide **6 – 10** (500 mg) and propargyl alcohol (1.3 eq.) in presence of bis (triphenyl phosphine) palladium (II) chloride (3 mol%) Et_3N (2-equiv), copper iodide (8 mol%) in chloroform at 40 °C for 2 hrs under nitrogen

atmosphere as shown in the scheme – 2. After usual workup and purification by column chromatography aryl unsaturated alcohol **11 - 14** were obtained in good yield.



1, 6	X = Cl
2, 7	X= NO_2
3, 8	X= CH_3
4, 9	X= OCH_3
5, 10	X= COOH

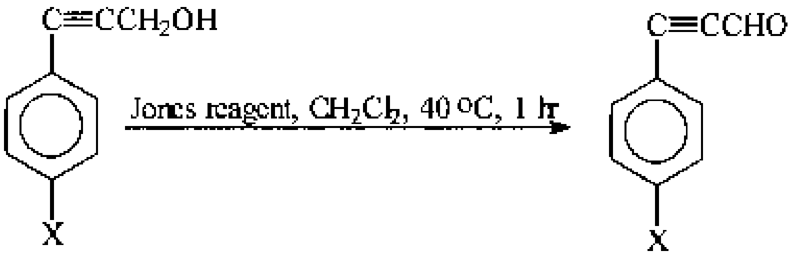
Scheme-1



6, 11	X = Cl
7, 12	X= NO_2
8, 13	X = CH_3
9, 14	X= OCH_3
10	X= COOH

Scheme-2

It also deals with the preparation of substituted unsaturated aldehydes **15 - 18** through oxidation reaction which was carried out by refluxing the mixture of 3-aryl propargyl alcohol and Jones reagent (i.e. 5.6 g $K_2Cr_2O_7$ in 5 - 6 ml H_2SO_4 conc. & 30 ml H_2O) in chloroform at 40 °C for 1hr as shown in the scheme - 3. After usual workup and purification 3-aryl-propargynal **15 - 18** were obtained.

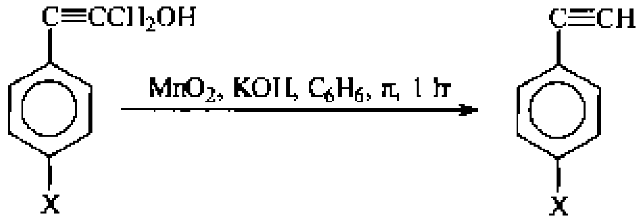


11-14 **15-18**

11, 15 X=Cl
12, 16 X=NO_2
13, 17 X=CH_3
14, 18 X=OCH_3

Scheme-3

It also deals with the preparation of substituted unsaturated acetylenes **19 - 20** through oxidation decarbonylation reaction which was carried out by refluxing the mixture of 3 - aryl propargyl alcohol in presence of potassium hydroxide powder (5 equiv.), manganesedioxide (10 equiv.) in dichloromethane at room temperature for 1 hr under nitrogen atmosphere as shown in the scheme - 4. After usual workup and purification by column chromatography aryl unsaturated acetylene **19 - 20** were obtained in good yield.

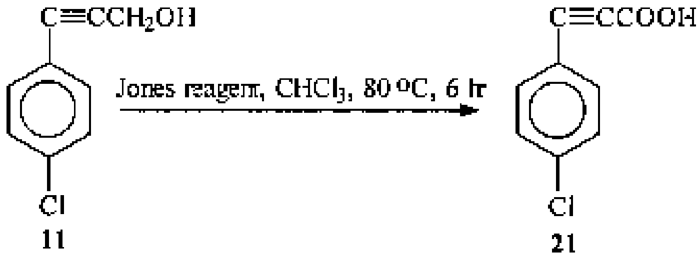


11-12 **19-20**

11, 19 X= Cl
12, 20 X= NO_2

Scheme-4

It also deals with the preparation of substituted unsaturated carboxylic acid **21** through oxidation of our synthesized 3 - aryl propargyl alcohol **11.** The oxidation reaction was carried out by refluxing the mixture of 3 - aryl propargyl alcohol and Jones reagents (5.6 g $K_2Cr_2O_7$ in 5 - 6 ml H_2SO_4 conc. in 30 ml H_2O) in $CHCl_3$ at 80 ° C for 6 hr as shown in the scheme - 5. After usual workup and purification 3 - aryl propargyl acids **21** was obtained.



11, 21 X = Cl

Scheme-5

Chapter- I

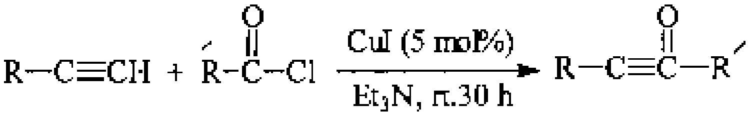
INTRODUCTION

1.1. Background of the present work.

1.1.1. Introduction:

There are relatively few basic type reactions that generate a new carbon-carbon bond, although this is one of the most critical operations in the synthesis of organic molecules. Acetylene and alkyl derivatives are versatile compounds in the synthetic organic chemistry and hence various methods for their synthesis have been explored. A conventional method for the preparation of aryl acetylene derivatives is the coupling reaction of aryl-halides with copper (I) acetylides, known as Castro reaction[1]. The cross coupling of organotin reagents with variety of organic electrophiles, catalyzed by palladium, provides a novel method for generating a carbon-carbon bond[2] known as Stille coupling.The palladium-catalyzed coupling of haloarenes and haloalkenes with alkenes known as the Heck reaction is well established[3]. The Sonogashira coupling reaction of terminal alkynes with synthesis provides an efficient route to arylalkynes[4]. Numerous applications to natural product synthesis have been reported, including the construction of complex enediyne antibiotics[5]. The synthesis of methyl enyonates and enyones is of interest as the alkyl enynones moiety has been found in naturally occurring compounds and they are usefull synthetic intermediates[6]. Jeffery has established palladium catalyzed vinylation of vinylic halides[7] and vinylation of acetylenic iodides under solid-liquid phase - transfer conditions[8]. Only a few examples of the synthesis of unsaturated alcohols, aldehydes, acetylene and acids from organic halides and alkylic substrates have been reported in the literature.

Conjugated acetylenic ketones have evoked considerable interest because of their utility as synthetic intermediates[9-10]. Also, many of them are of biological interest[11-12]. Because of their importance, a number of methods have been developed for the synthesis of conjugated acetylenic ketones[13]. Recent trends have been the synthesis of α, β-acetylenic ketones by pd - catalysis from 1 - alkynes and acyl chlorides[14] or from 1-alkynes and aryl or vinyl halides in the presence of carbon monoxide[15]. The acylation of alkynyl zincs[16] and alkynyl stannanes[17] with acyl chlorides in the presence of pd catalysts leading to α, β - acetylenic ketones has also been reported. This communication describes a very facile method for the synthesis of acetylenic ketones by the reaction of 1-alkynes with acyl halides in the presence of catalytic amounts of copper (I) salts only as shown in the scheme-1.



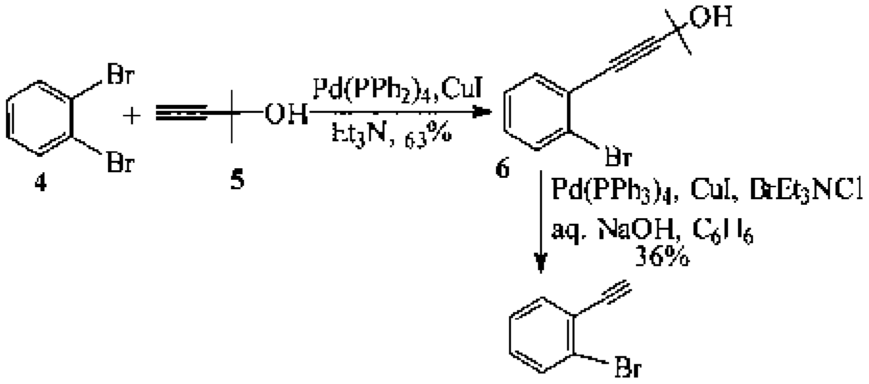
$$\underset{\mathbf{1}}{R-C\equiv CH} + \underset{\mathbf{2}}{R'-\overset{O}{\overset{\|}{C}}-Cl} \xrightarrow[Et_3N,\ rt.30\ h]{CuI\ (5\ mol\%)} \underset{\mathbf{3}}{R-C\equiv C-\overset{O}{\overset{\|}{C}}-R'}$$

Scheme-1

Among the various methods available for the synthesis of terminal acetylenes[18], the most convenient ones are based on the cross coupling reactions of organic halides with trimethylsilylacetylene[19], copper (I) tetrahydropyranyloxyprop-1-ynide[20], or copper (I) benzoylacetylide[21] and subsequent removal of the protecting groups. Ethynylarenes not containing electron - withdrawing substituents can be obtained by palladium - catalysed cross - coupling of ethynylzinc chloride with aryl halides[22]. Stephens - Castro coupling of copper (I) arylacetylenes with iodoarenes[23] or iodoalkenes[24] is a useful reaction for the synthesis of acetylenes in laboratories, its scope being sometimes limited by the violent reaction conditions and by the difficulties in preparations of cuprous acetylides. Cassar[25] and Heck[26] reported independently the same substitution reaction catalyzed by similar catalysts. A convenient synthesis of terminal acetylenes by oxidation - decarboxylation of 3-aryl-propargyl -alcohols[27] using manganese dioxide in the presence of alkali under mild condition was peported[27]. The simplicity of the procedures and the mildness of the reaction conditions suggest that the reaction will be highly useful for the preparation of internal acetylenes from acetylene gas and terminal acetylenes in laboratories. The C-H bond in acetylene itself and mono - substituted acetylenes, RC=CH are very much more acedic than that in an alkane or an alkene, e. g acetylene has pK 25 and forms the acetylide ion when treated with amide ion in liquid NH_3, where as methane (pK 45) is unreactive. Aryl alkynes represent a number of natural products such as freelingyne[28] and Junipal[29].

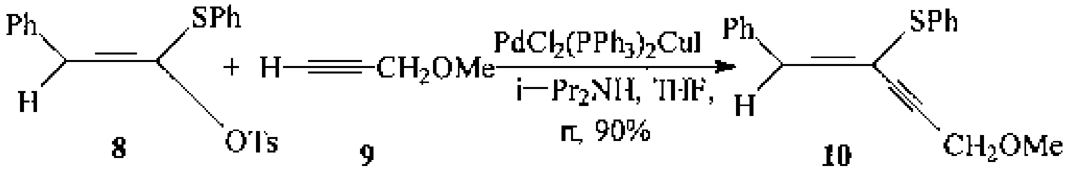
1.1.2. Important synthesis.

Another protected acetylenes are propargyl alcohol and 2-methyl-3 butyn-2-ol. After coupling with halides, deprotection by alkaline hydrolysis gives 1-alkynes. Monocoupling of *o* - dibromo-benzene with **5** afforded the protected alkyne **6**. Treatment of **6** with Pd(0)-CuI catalyst NaOH and quaternary ammonium chloride generates the deprotected 1 alkyne[30] 7 as shown in the scheme - 2.



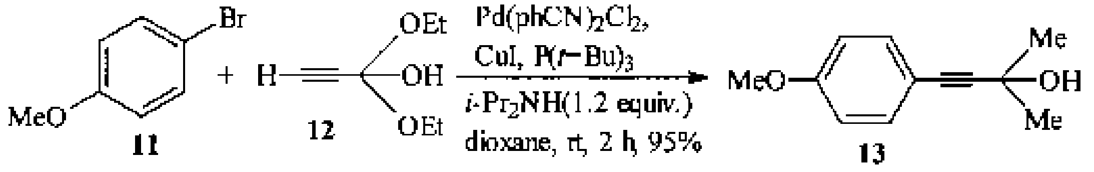
Scheme-2

Coupling of the vinyl tosylate **8** with an 1-alkyne afforded the enyne **10**. Only the use of $PdCl_2(PPh_3)_2$, CuI and *i*-Pr_2NH gave satisfactory result[31] is shown in scheme - 3



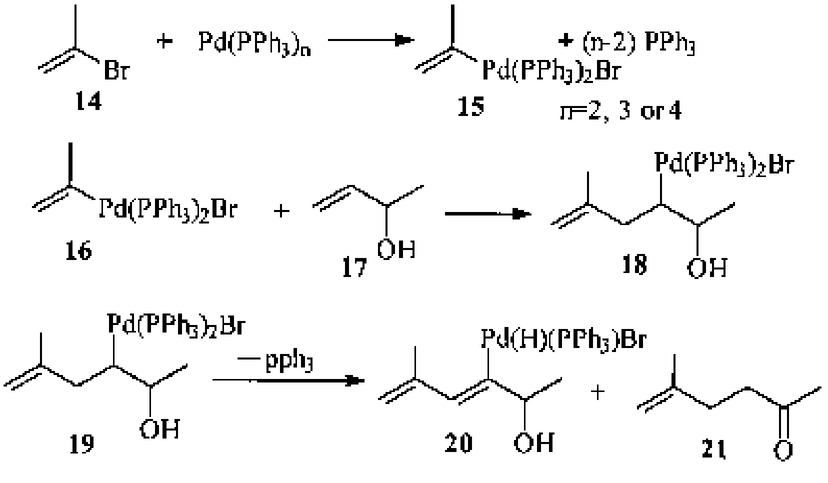
Scheme-3

Thorand and Krause[32] Claimed that THF is a very good solvent, but Ho *et al.*[33] reported that THF is a poor solvent in their reaction. One drawback of the Sonogashira reaction is the use of a large excess of amines almost as a solvent. Buchwald and Fu *et al.* reported that coupling of inactivated 4 - bromoanisole **11** could be carried out at room temperature by using $Pd(PhCN)_2Cl_2$ as a catalyst. *p* - (*t* - Bu)$_3$ as a ligand and only 1.2 equivalent of di – isopropyl - amine. Poor results were obtained when PPh_3, PCy_3, P(*o*-Tol)$_3$ and DPPF are used instead of *p* - (*t* - Bu)$_3$ under similar conditions[34] are shown in scheme-4



Scheme-4

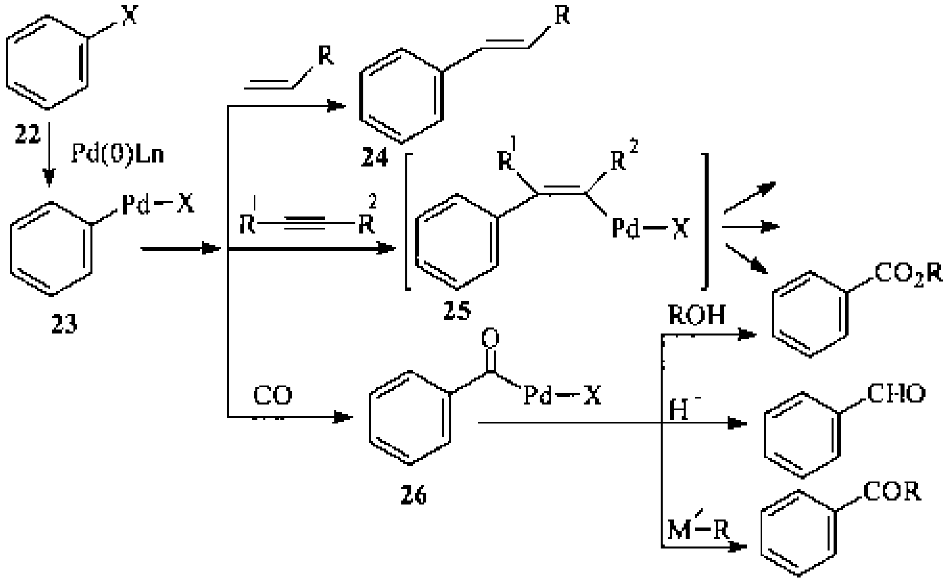
Another variation of the coupling reaction occurred when vinylic halides were reacted with allylic alcohols[35]. The elimination of the hydridopalladium group from the initial adduct often occurred with loss of a hydrogen from the carbon bearing the hydroxyl group. When this occurred, 4 - enones or 4 - enals are produced as shown in the scheme-5.



Scheme-5

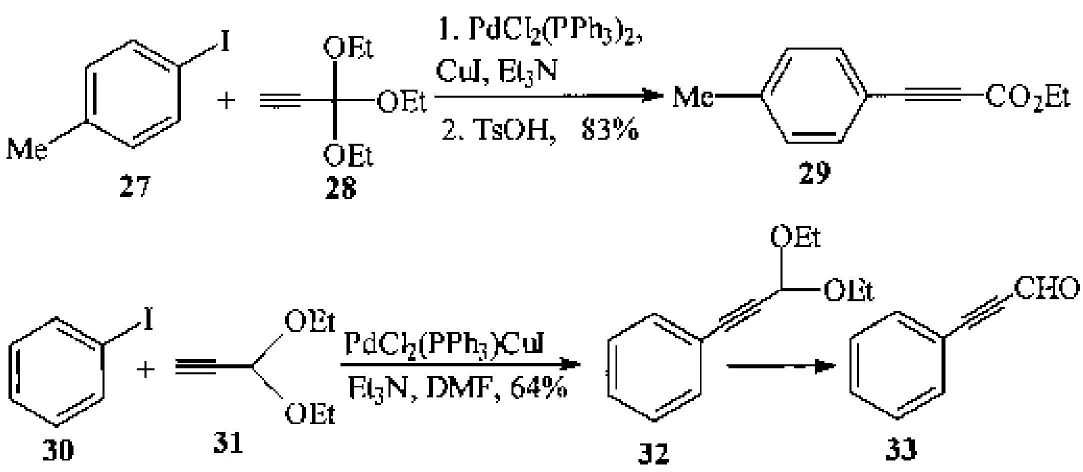
The phenyl palladium halides **23** are living species and undergo several further transformations before termination. Insertion of unsaturated bonds in one of them as summarized in scheme-6.

Alkene insertion was followed by β-H elimination to yield arylalkenes **24**. Alkyne insertion gave rise to the alkenylpalladiums **25**. This species **25** undergo further reaction before termination. The acyl-palladium **26** was formed by CO insertion, from which esters, aldehydes and ketones are produced.



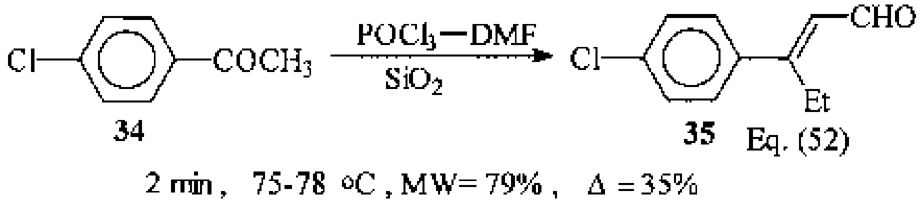
Scheme-6: Insertion to phenyl palladium intermediates.

Alkynes with EWGs such as propiolate are poor substrates for the coupling with halides. Therefore, instead of inactive propiolate triethyl *ortho* propiolate **28** was used for the coupling with aryl halides to prepare the aryl propiolate **29**. The coupling product **32** obtained from 3,3-diethoxy -1-propyne **31** and halides was found to be a precursor of the aryl alkynal[36] **33** as shown in the scheme-7.



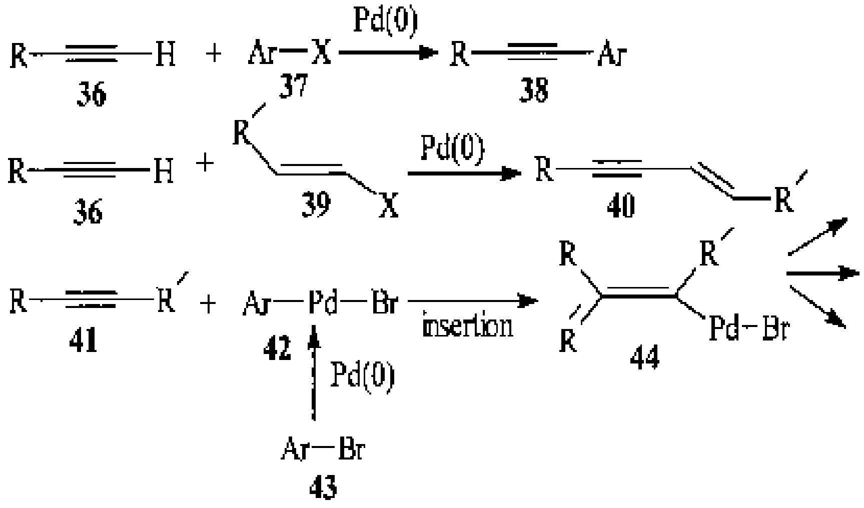
Scheme-7

Formylation using Vilsmeier reagent[37]. Substituted acetophenones were irradiated in a domestic microwave oven with $POCl_3$ – DMF / SiO_2 to give β-chlorovinylaldehydes in 2 min with yields of 75 - 88 %. Under the same conditions, conventional heating lead to only 30 - 40 % (Eq. 52) as shown in the scheme - 8.



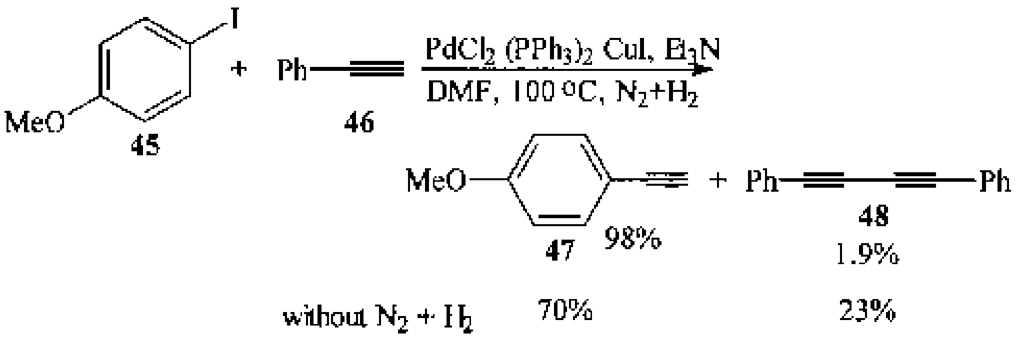
Scheme-8

Pd catalysed coupling reactions of terminal and internal alkynes **36** and **41** with halides are surveyed in this section. Reactions of alkynes with aryl and alkenyl halides were classified in two types. The first one was the preparation of arylalkynes **38** and alkenyl alkynes (1,3-enynes) **40** by the reaction of terminal alkynes **36** with aryl and alkenyl halides in the presence of Pd(0) and CuI as catalysts. The second one was insertion of internal alkynes **41** to aryl and alkenyl palladium bonds formed by oxidative addition of halides, generating alkeynyl palladiums **44**, which are living species and undergo further transformations before termination. Terminal alkynes also undergo the insertion in the absence of CuI catalyst as shown in the scheme-9.



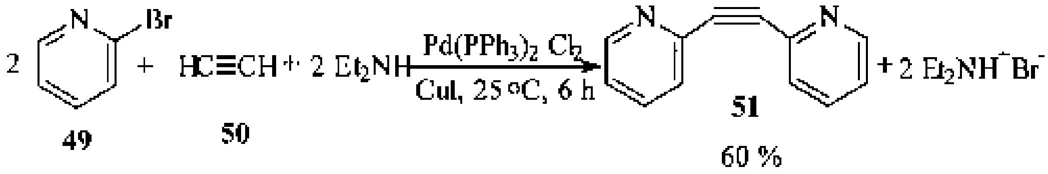
Scheme-9

Various results are obtained in Sonogashira coupling depending on the substrates used and the reaction conditions. Homocoupling and decomposition of alkynes are serious compititive reactions, and poor results are obtained sometimes due to these side reactions in the Sonogashira reaction particularly when less reactive electron-rich aryl halides are used. It is well known that CuI catalyzes oxidative homocoupling of 1-alkynes in O_2 atmosphere (Glaser reaction). Also Pd (II) promotes the homocoupling. Therefore the reaction should be carried out with strict exclusion of O_2. Homocoupling in the Sonogashira reaction[38] can be decreased by slow addition of alkynes in THF and use of phase transfer agent (n-Bu_4NI) in H_2O – tolune[39]. Ho *et al.* reported that the bromocoupling of phenyl acetylene with 4-iodoanisole **45** can be reduced drastically by carrying out the reaction in an atmosphere of H_2 diluted with N_2 or argon[40] as shown in scheme - 10.



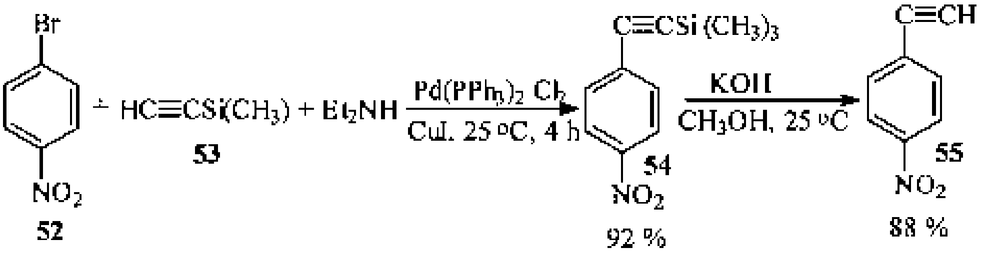
Scheme-10

The use of acetylene it self in the reaction leads to the formation of disubstituted acetylenes as major products[41] as shown in scheme - 11.



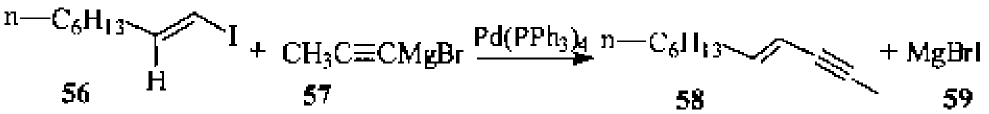
Scheme-11

Mono substituted products obtained in two steps in good yield, however, employing trimethylsilylacetylene with the organic halide and then removing the silyl group[42,43] as shown in the scheme - 12.



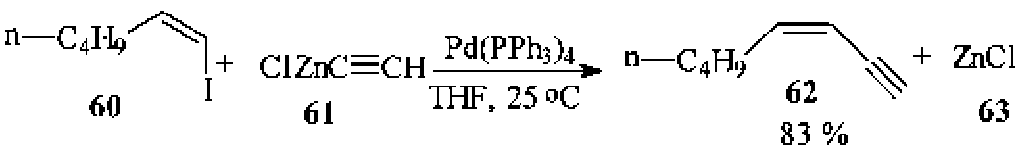
Scheme-12

Alkynyl Grignard reagent[44] react stereospecifically with alkenyl iodides in the presence of a catalytic amount of $Pd(PPh_3)_4$ as shown in the scheme - 13.



Scheme-13

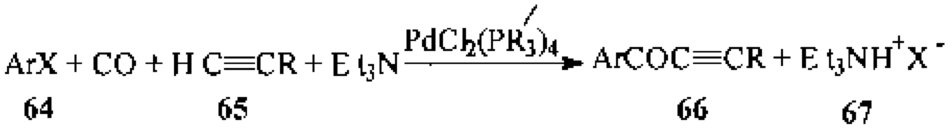
Alkynylzinc chlorides react similarly with alkenyl iodides or bromides with a $pd(pph_3)_4$ catalyst[45] as shown in the scheme - 14.



Scheme-14

Formation of Aroylacetylenes:

The acetylene anion apparently is another example of a nucleophile that can attack intermediate benzoylpalladium complexes under catalytic carbonylation conditions. The reaction forms aroylacetylenes in fair-to-good yields[46]. Some examples are appear in table 1.



$$\underset{64}{ArX} + CO + \underset{65}{HC{\equiv}CR} + Et_3N \xrightarrow{PdCl_2(PR_3)_4} \underset{66}{ArCOC{\equiv}CR} + \underset{67}{Et_3NH^+X^-}$$

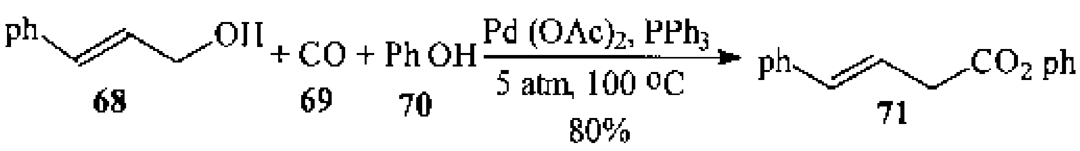
Scheme-15

Table 1: Formation of aroylacetylenes from aryl-halides.

Halide 64	Acetylene 65	Catalyst	Conditions	Product 66	Yield %
C_6H_5I	HC≡CPh	$PdCl_2(PPh_3)_2$	120°C, 1 h, 20 atm	PhCOC≡CPh PhC≡CPh	48 43
C_6H_5I	HC≡CPh	$PdCl_2(DPPF)^b$	120 °C, 4h, 20atm	PhCOC≡CPh PhC≡CPh	86 0.8
C_6H_5I	HC≡CPh	$PdCl_2(DPPF)^b$	80°C, 26h, 1atm	PhCOC≡CPh PhC≡CPh	93 3
$4\text{-}CH_3OC_6H_4I$	HC≡CPh	$4\text{-}CH_3C_6H_4PdI(Asph_3)_2$	120 °C, 4h, 20 atm	$4\text{-}CH_3OC_6H_4COC{\equiv}CPh$ $4\text{-}CH_3OC_6H_4C{\equiv}CPh$	77 5
$4\text{-}O_2NC_6H_4I$	HC≡Cph	$PdCl_2(DPPF)^b$	100°C, 1.5h, 20atm	$4\text{-}O_2NC_6H_4COC{\equiv}CPh$	58

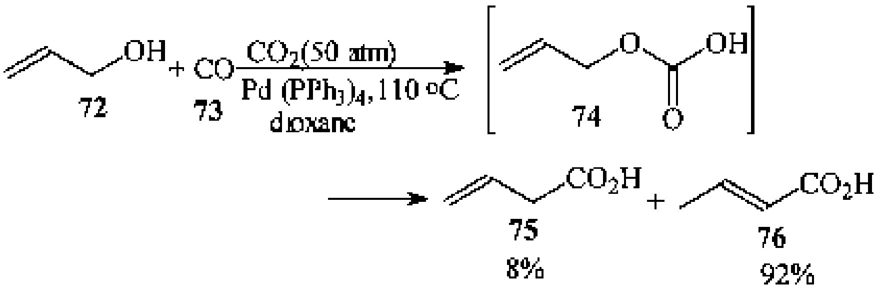
[b] DPPF = 1,1'-Bis(diphenyl phosphine) ferrocene.

Less reactive allylic alcohols are carbonylated under harsh conditions. However, carbonylation of allylic alcohols proceed smoothly in the presence of phenol as a nucleophile. Phenyl 4 – phenyl - 3-butenoate 71 was obtained in 80% yield from Cinanyl alcohol[47] under 5 atm of CO at 100 °C as shown in the scheme-16.



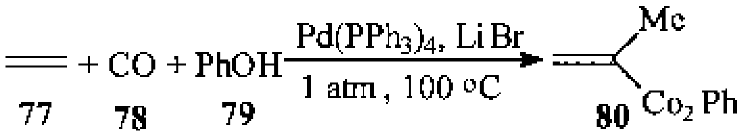
Scheme-16

Allyl alcohol was carbonylated under high presser of CO_2 (50 atm) and CO (50 atm) in dioxane to provide 2 - butenoic acid as the main product and 3 - butenoic acid as the minor product at 110 °C. Presumably monoallyl carbonate 74 was generated from allyl alcohol and CO_2, and carbonylated to give 3 - butenoic acid, which isomerized to 2 - butenoic acid[48] as shown in the scheme - 17.



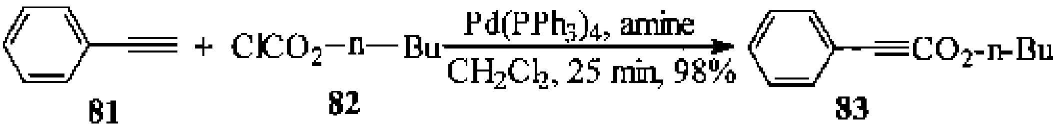
Scheme-17

Few studies on Pd - catalyzed carbonylation of alkenes had been reported Grigg carried out the carbonylation of alkene in the presence of phenol under 1 atm at 100 ° C and obtained phenyl methacrylate **80** by the attack of the central carbon[49] as shown in the scheme - 18.



Scheme-18

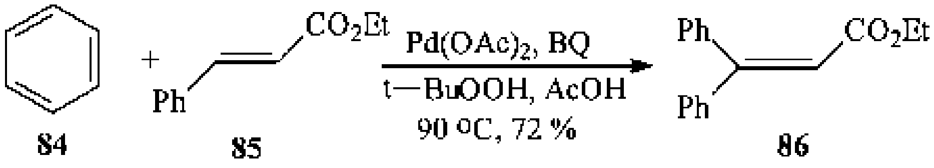
Henkelmann and Co - workers found that chloroformates are good coupling partners of 1-alkynes and the reaction offers a useful synthetic method for aryl – propionates[50]. Reaction of *n* - butyl chloroformate with phenylacetylene in the presence of 1,2,2,6,6 - pentamethylpiperidine as a hindered base and a small amount of N,N - dimethyl aminopyridine afforded *n* - butyl phenyl propiolate **83** in 98% yield with in 25 min in refluxing dichloromethane as shown in the scheme – 19.



Amine = 1,2,2,6,6- pentamethyl piperidine, dimethylaminopyridine

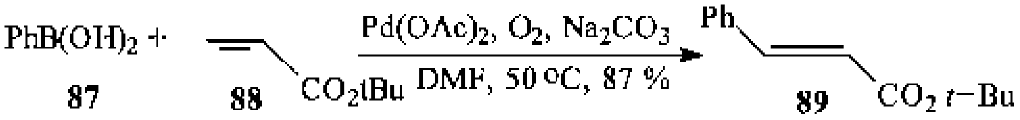
Scheme-19

Efficient catalytic reaction of Cinnamate **85** with benzene to afford **86** was carried out using BQ and *t*-butyl hydroperoxide as oxidant in AcOH[51]. The coupling proceed smoothly in the presence of catalytic amounts of $Pd(OAc)_2$ and molybdovanado-phosphoric acid (HPMoV) under oxygen (1 atm) in AcOH[52] as shown in the scheme - 20.



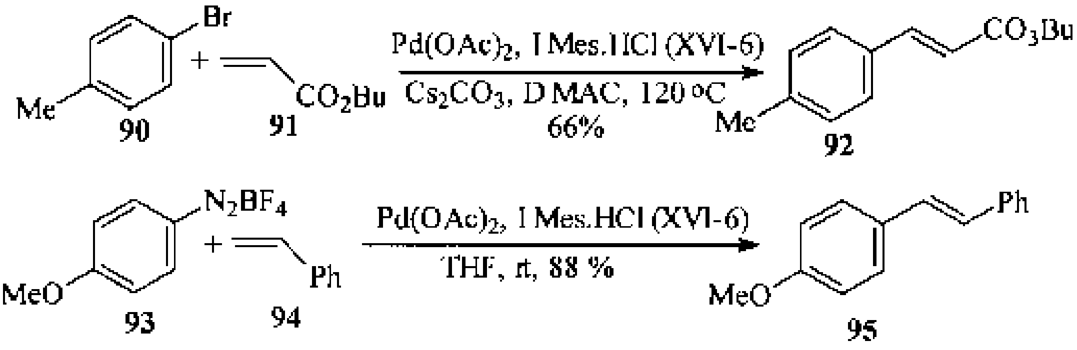
Scheme-20

Reaction of acrylate with phenylboronic acid in the presence of $Pd(OAc)_2$ under O_2 afforded cinamate **89** in 87 % yield[53,54] as shown in the scheme - 21.



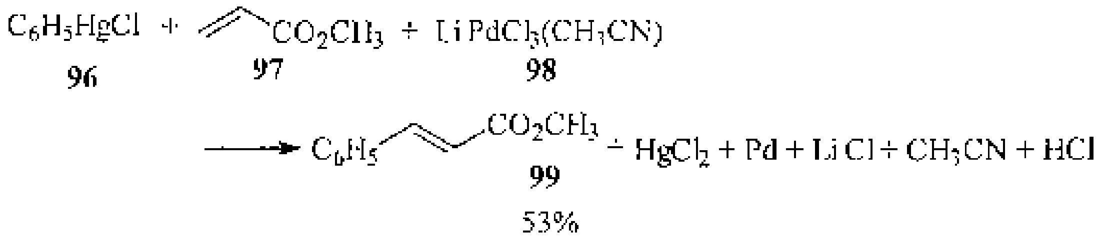
Scheme-21

In addition electron – rich and bulky heterocyclic carbenes are attracting attention as effective phosphine mimics[55]. Using carbene ligand XVI - 6, HR of aryl bromides[56] proceeds at 120 °C and that of diazonium salts at room temperature[57] as shown in the scheme 22.



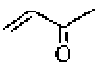
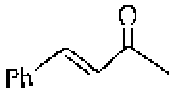
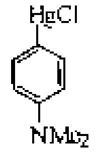
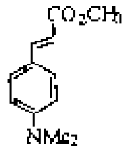
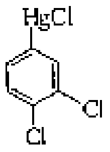
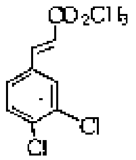
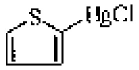
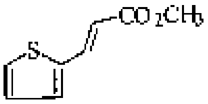
Scheme-22

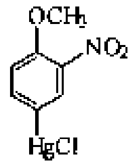
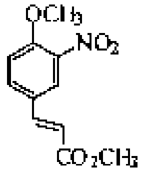
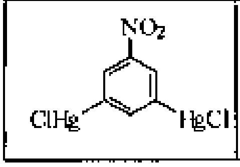
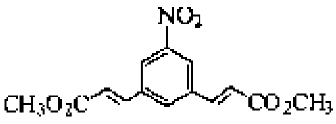
Various arylmetal derivatives undergo metathesis reactions with Pd(II) salt to form arylpalladium salts, and in the presence of alkenes these procedure arylated alkenes. The metal aryls that have been employed include aryl derivatives of Mercury[58], Tin[58], Lead[58] Silicon[59,60] and magnesium[61] The reactions of mercurials are shown in the scheme - 23. Some examples of the reaction appear in table -2.



Scheme-23

Table 2. Arylation of alkenes Stoichmetric in palladium (II)] with organomercury compounds.

Mercurial 996	Alkene 97	Pd compd. 98	Solvent	Product 99	Yield %
Ph_2Hg	$CH_2=CH_2$	$LipdCl_3$	CH_3CN	$PhCH=CH_2$	63
Ph_2Hg	$CH_2=CHCHO$	$LipdCl_3$	CH_3CN		60
Ph_2Hg		$LipdCl_3$	CH_3CN		64
		Li_2pdCl_4	CH_3OH		22
		Li_2pdCl_4	CH_3OH		45
		Li_2pdCl_4	CH_3OH		36

Mercurial **996**	Alkene **97**	Pd compd. **98**	Solvent	Product **99**	Yield %
		Li_2PdCl_4	CH_3OH		40
		Li_2PdCl_4	CH_3OH		45

Terminal acetylenes may be carbonylated either to acetylene carbonylic acids and derivatives[62] or to acrylic acid derivatives[63]. Acetylenecarbonylate esters are obtained with $PdCl_2$ as catalyst and cupric chloride as reoxidant in the presence of sodium acetate as shown in the scheme - 24. Other examples are appear in table 3.

$$\underset{\mathbf{100}}{PhC{\equiv}CH} + \underset{\mathbf{101}}{CO} + \underset{\mathbf{102}}{CH_3OH} + \underset{\mathbf{103}}{CuCl_2} + \underset{\mathbf{104}}{NaOAc} \xrightarrow[\text{1 atm, } 25\ {}^{o}C,\ 2hr]{PdCl_2} \underset{\mathbf{105}}{PhC{\equiv}CCO_2CH_3} + CuCl + NaCl + HOAc$$

Scheme-24

Table – 3: Alkoxy carbonylation of terminal acetylenes

Acetylene **100**	Alcohol **102**	Product **105**	Yield
$PhC{\equiv}CH$	$(CH_3)_2CHOH$	$PhC{\equiv}CCO_2CH(CH_3)_2$	67 %
$H_{11}C_5C{\equiv}CH$	CH_3OH	$H_{11}C_5C{\equiv}CCO_2CH_3$	74 %
$H_{11}C_5C{\equiv}CH$	$(CH_3)_2CHOH$	$H_{11}C_5C{\equiv}CCO_2CH(CH_3)_2$	59 %
$PhOCH_2C{\equiv}CH$	CH_3OH	$PhOCH_2C{\equiv}CCO_2CH_3$	60 %

The carbonylation of terminal acetylenes with dichloro bis - (triarylphosphine) palladium – stannous chloride catalysts in alcohol solution produces α - β-unsaturated ester[63] as shown in the scheme - 25.

$$\underset{\mathbf{106}}{RC\equiv CH} + CO + \underset{\mathbf{107}}{R'OH} \xrightarrow[\text{MIBK, 240 atm, 22 °C, 30-40 hr}]{PdCl_2(PAr_3)_2,SnCl_2} \underset{\mathbf{108}}{RCH{=}CHCO_2R}$$

MIBK= methyl isobutyl ketone

Scheme-25

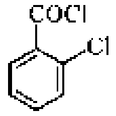
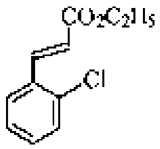
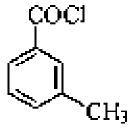
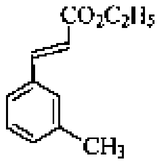
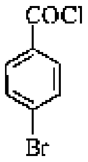
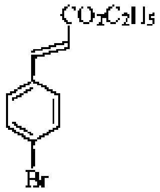
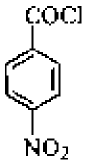
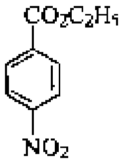
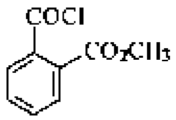
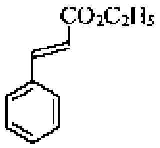
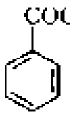
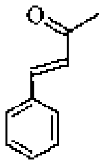
Decarbonylation of aromatic acid chlorides occurs very efficiently under mild conditions in the presence of a tertiary amine and activated alkenes, in which case arylated alkenes are formed in moderate to high yields[64]. The aroyl bromides and iodides offer no advantages over the chloride as shown in the scheme - 26. Some examples are appear in table 4.

$$\underset{\mathbf{109}}{C_6H_5COCl} + \underset{\mathbf{110}}{CH_2{=}CHCO_2C_2H_5} + \underset{\mathbf{111}}{C_6H_5CH_2N(CH_3)_2} \xrightarrow[\text{Pd(OAc)}_2\text{, toluene}]{100\ °C,\ 2\ h}$$

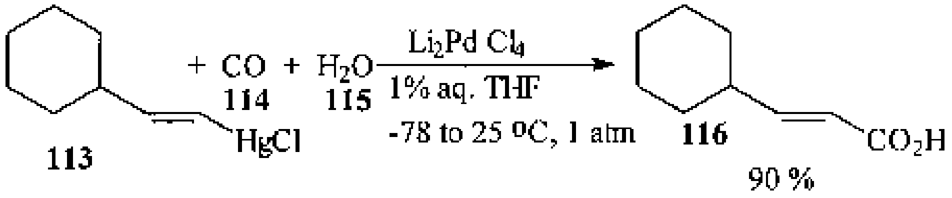
$$\underset{\mathbf{112}}{C_6H_5CH{=}CHCO_2C_2H_5} + C_6H_5CH_2N(CH_3)_2H^+Cl^- + CO$$

Scheme-26

Table-5: Arylation of activated Alkenes with Aroyl Chlorides.

Aroyl chloride **109**	Alkene **110**	Product **112**	Yield %
	$H_2C{=}CHCO_2C_2H_5$		74
	$H_2C{=}CHCO_2C_2H_5$		72
	$H_2C{=}CHCO_2C_2H_5$		79
	$H_2C{=}CHCO_2C_2H_5$		55
	$H_2C{=}CHCO_2C_2H_5$		57
	$H_2C{=}CHCOCH_3$		48

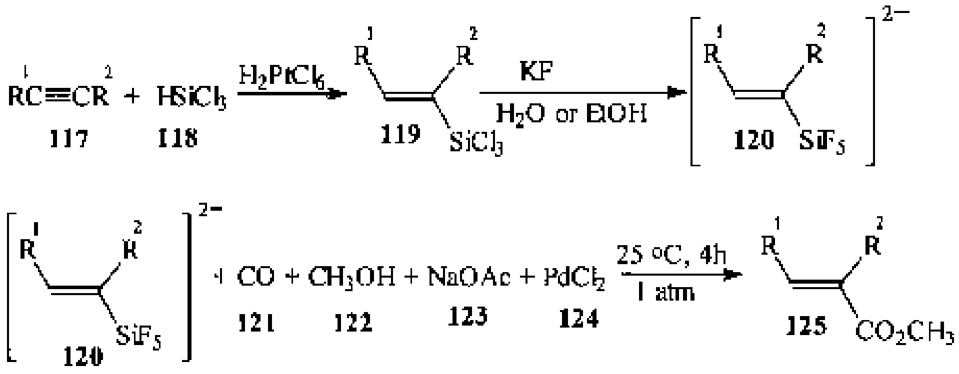
vinylmercurials readily react at atmospheric pressure with carbon monoxide, lithium chloride and $PdCl_2$ in aqueous THF solvent at $< -20\ ^{o}C$ to give high yields of α, β - unsaturated acids[65] as shown in the scheme-27.



Scheme-27

The yields of acid were quite sensitive to the concentration of water in the THF. Similarly, esters can be made in generally better yields using an alcohol instead of aqueous THF as solvent. Both reactions can be made catalytic in Palladium if cupric chloride is added, although rather large amounts of catalyst (10 %) were used in two of the three examples given. while these reactions proceed in high yields, the difficulty of obtaining and working with vinylic mercurials makes the method appear generally less attractive than other methods available for the synthesis of unsaturated acid derivatives.

A similar method for synthesizing α, β - unsaturated esters involves the carbonylation of vinylic pentafluorosilicates in methanol solution[66] as shown in the scheme - 28. Some examples are appear in table 5.



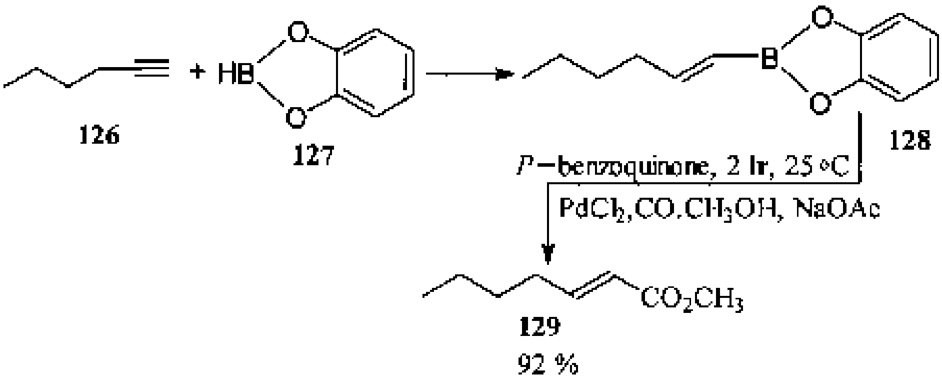
Scheme-28

Since some vinylic silanes are available by direct hydrosilation of alkynes, the reaction may be a convenient method to use although it is stoichiometric in $PdCl_2$. The carbonylation reaction is highly stereospecific; however, the hydrosilation may not be, so an initial purification may be necessary.

Table-6: Formation of α, β - unsaturated esters from alkenyl pentafluorosilicates.

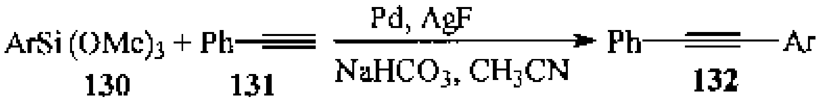
Silicates **120**	Products **125**	Yield %
(E)-$(CH_3)_3CCH{=}CHSiF_5^{2-}$	(E)-$(CH_3)_3CCH{=}CHCO_2CH_3$	90
(E)-$PhCH{=}CHSiF_5^{2-}$	(E)-$PhCH{=}CHCO_2CH_3$	76
(E)-$CH_3OCH_2CH{=}CHSiF_5^{2-}$	(E)-$CH_3OCH_2CH{=}CHCO_2CH_3$	61
(E)-$CH_3O_2C(CH_2)_8CH{=}CHSiF_5^{2-}$	(E)-$CH_3O_2C(CH_2)_8CH{=}CHCO_2CH_3$	72

A third related method employes 1 – alkenyl - boranes and carbonylates them in methanol solution to form stereospecifically α, β - unsaturated esters in good yield[67]. Some 1 - alkenyl boranes can be prepared conveniently by the hydroboration of alkynes with catechol borane or similar boranes. The reaction is made catalytic in Pd by use of *p* - benzoquinone as reoxidant as shown in the scheme - 29.



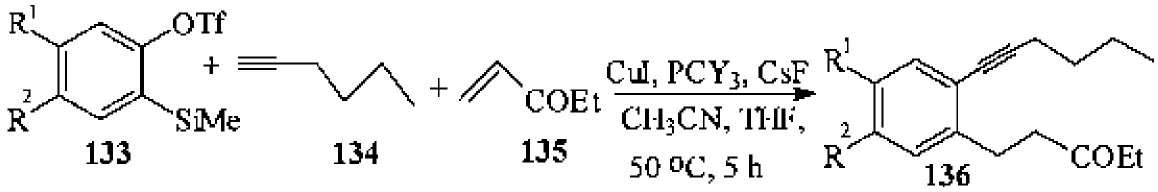
Scheme-29

A palladium - catalyzed cross-coupling reaction of aryl trimethoxysilanes with terminal alkynes was developed by Cheng.J. *et al.*[68] as shown in the scheme- 30


$$\mathrm{ArSi(OMe)_3} + \mathrm{Ph{-}C{\equiv}CH} \xrightarrow[\mathrm{NaHCO_3,\ CH_3CN}]{\mathrm{Pd,\ AgF}} \mathrm{Ph{-}C{\equiv}C{-}Ar}$$

Scheme-30

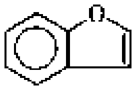
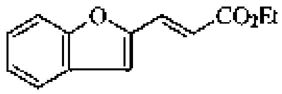
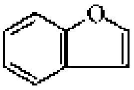
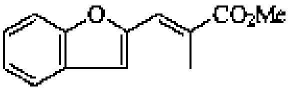
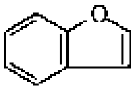
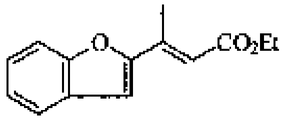
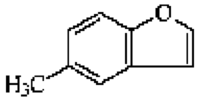
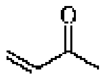
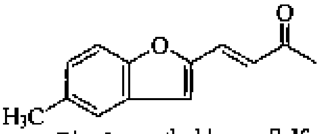
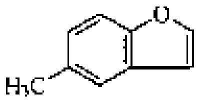
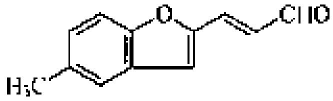
The three component coupling of benzynes with terminal alkynes and activated alkenes in the presence of CuI, PCy_3 and CsF in a 1:1 mixture of CH_3CN and THF at 50 °C for 5 h gave 1-alkyl-2-alkynylbenzenes in good to moderate yields was reported by Chien-Hong Cheng *et al.*[69] as shown in the scheme - 31.



Scheme-31

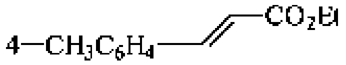
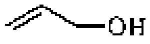
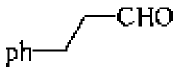
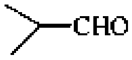
Benzo [b] furans undego palladation and addition to various olefins in reasonable yields forming 2 - substituted benzofuran **139** products along with minor amounts of the bifurans[70] as shown in the table-6.

Table 6 : Coupling of benzo [b] furans **137** with olefins **138**

Benzo[b]furan **137**	Olefin **138**	Product **139**	Yield %
			70
			53
			60
		 Bi−5−methyl benzo[b]furan	67
		 Bi−5−methyl benzo[b]furan	55

Coupling of aryldiazonium salts and alkenes with Pd(dba)$_2$ as catalyst[71] are shown in the table-7.

Table-7: Coupling of aryldiazonium salts and alkenes with Pd(dba)$_2$ as catalyst

Diazonium salt **140**	Alkene **141**	Product **142**	Yield
$4Cl_3C_6H_4N_2^+BF_4^-$			94%
$PhN_2^+Cl^-$		 	36%, 5%

Chapter- II

SECTION - I

1.2 **Present work**: Synthesis of terminal acetylenes, alkynyl aldehydes and acids from aryl halides.

1.2.1 Rationale:-

There are relatively few basic type reactions that generate a new carbon - carbon bond, although this is one of the most critical operations in the synthesis of organic molecules. Acetylene and alkyl derivatives are versatile compounds in the synthetic organic chemistry and hence various methods for their synthesis have been explored. A conventional method for the preparation of aryl acetylene derivatives is the coupling reaction of aryl - halides with copper(I) acetylides, known as Castro reaction[1]. The cross coupling of organotin reagents with variety of organic electrophiles, catalyzed by palladium, provides a novel method for generating a carbon - carbon bond[2] known as Stille coupling.

The palladium - catalyzed coupling of haloarenes and haloalkenes with alkenes known as the Heck reaction is well established[3].

The Sonogashira coupling reaction of terminal alkynes with synthesis provides an efficient route to arylalkynes[4]. Numerous applications to natural product synthesis have been reported, including the construction of complex enediyne antibiotics[5]. The synthesis of methyl enyonates and enyones is of interest as the alkyl enynones moiety has been found in naturally occurring compounds and they are useful synthetic intermediates[6]. Jeffery has established palladium catalyzed vinylation of vinylic halides[7] and vinylation of acetylenic iodides under solid - liquid phase - transfer conditions[8]. Only a few examples of the synthesis of unsaturated alcohols, aldehydes, acetylene and acids from organic halides and alkylic substrates have been reported in the literature.

Palladium catalyzed reactions[72] have been extensively utilized for carboannulation[73]and heteroannulation processes[73]. In recent years our research group has developed methods for the synthesis of benzo - fused heterocyclic compounds, isoindolinones, e.g. benzo [b] Furans[75] , isoquinolinone[76] and indole derivatives[77] by palladium - catalyzed reactions with terminal alkynes and alkenes.

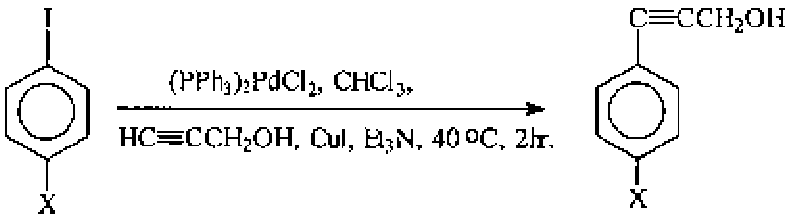
In view of the extensive natural occurrence and biological importance of unsaturated terminal alcohol, aldehydes, acetylenes and acids and lack of convenient palladium - catalysed procedures for their synthesis, we were interested in developing a general and facile method for the synthesis of unsaturated terminal alcohol, aldehydes, acetylenes and acids.

In continuation of our studies on the synthesis of various heterocyclic structures through palladium - catalyzed reactions using terminal alkynes, we became interested in the palladium - catalyzed coupling reaction between aryliodide and propargyl alcohol to afford unsaturated 3 - aryl propargyl alcohols, later which were oxidized to aldehyde, acetylenes and acids.

1.2.2. Results and Discussion:-

A facile method for the synthesis of 3-aryl propargyl alcohol **11-14** through palladium catalyzed coupling reaction of aryl iodide **6-10** with propargyl alcohol as shown in the scheme 1 is reported and the results are demonstrated in the table **1**.

The reactions were usually carried out by stirring the mixture of aryliodide **6-10 (500mg)** and propargyl alcohol (1.3 equ.) in $CHCl_3$ (10ml) in the presence of bis (triphenyl phosphine) palladium (II) chloride (0.063 m.mol, 3mol%), copper iodide (0.17 m.mol, 8mol%) and triethylamine (2 equ.) for 2 hr at 40 °C under nitrogen atmosphere. After usual work up and purification on column chromatography over silica gel 3-aryl propargyl alcohols **11-14** (scheme – 1) were obtained in good yields.



6-10

11-14

6, 11	X = Cl
7, 12	X= NO_2
8, 13	X = CH_3
9, 14	X= OCH_3
10	X= COOH

Scheme-1

Table 1: Synthesis of 3 - aryl propargyl alcohols **11 - 14**

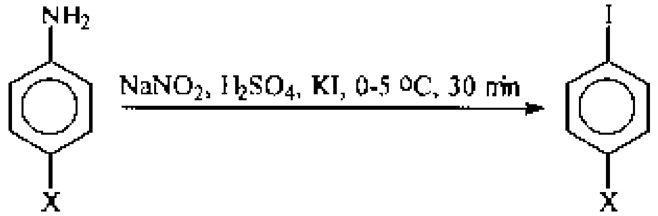
Aryl iodide **6-10**	propergyl alcohols	Solvent	Product **11-14**	Yield%
p-Cl-C_6H_4I **6**	$HC\equiv C\text{-}CH_2OH$	$CHCl_3$	*p*-$ClC_6H_4C\equiv CCH_2OH$ **11**	89
p-$NO_2C_6H_4I$ **7**	$HC\equiv C\text{-}CH_2OH$	C_6H_6	*P*-$NO_2C_6H_4C\equiv CCH_2OH$ **12**	86
p-$CH_3C_6H_4I$ **8**	$HC\equiv C\text{-}CH_2OH$	$CHCl_3$	*P*-$CH_3C_6H_4C\equiv CCH_2OH$ **13**	92
p-$CH_3OC_6H_4I$ **9**	$HC\equiv C\text{-}CH_2OH$	$CHCl_3$	*P*-$CH_3OC_6H_4C\equiv CCH_2OH$ **14**	87
p-$COOHC_6H_4I$ **10**	$HC\equiv C\text{-}CH_2OH$	$CHCl_3$	Nil.	

1.2.3 Starting Materials:

a. Synthesis and characterization of aryl iodide **6-10.**

Aryl iodide have been used as starting materials, because of their easy availability from primary arylamine. Diazotization of primary arylamine followed by Sandmeyer iodination with potassium iodide afforded aryl iodide **6-10** (scheme - 2).

The results are demonstrated in table - **2.**



1-5 **6-10**

1, 2 X = Cl
2, 7 X= NO_2
3, 8 X= CH_3
4, 9 X= OCH_3
5, 10 X= COOH

Scheme-2

Table 2: Preparation of substituted iodobenzene **6-10**.

SI.NO.	Arylamine **1-5**	Aryliodide **6-10**	Yield%
1	*p*-$ClC_6H_4NH_2$ **1**	*p*-ClC_6H_4I **6**	62
2	*p*-$NO_2C_6H_4NH_2$ **2**	*p*-$NO_2C_6H_4I$ **7**	94
3	*p*-$CH_3C_6H_4NH_2$ **3**	*p*-$CH_3C_6H_4I$ **8**	88
4	*p*-$CH_3OC_6H_4NH_2$ **4**	*p*-$CH_3OC_6H_4I$ **9**	84
5	*p*-$COOHC_6H_4NH_2$ **5**	*p*-$COOHC_6H_4I$ **10**	76

The starting materials aryliodides **6 - 10** were characterized by their melting points which are compatible with the literature[78] value. The IR spectra of the aryl iodide showed the absence of NH_2 stretching vibration peak(P. 54 - 59). The presence of iodide in all the aryliodide was confirmed by Lassaigne test.

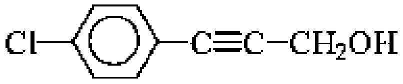
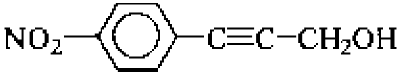
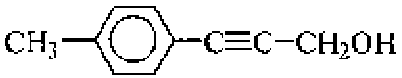
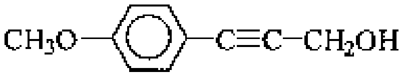
<u>b. Synthesis and characterization of 3-aryl propargyl alcohol **11-14**:</u>

The coupling reaction of aryliodide with alkyl substrates in the presence of $(PPh_3)_2PdCl_2$, CuI and Et_3N in $CHCl_3$ afforded 3-aryl propargyl alcohol (table – 1, scheme – 1). All the alcohols were well characterized by their satisfactory spectroscopic (IR, UV, ^{1}H NMR & ^{13}C NMR) and analytical data (P. 60 - 85).

The formation of the condensed products (substituted alcohol) was established on the basis of the following observations. Comparison of some spectral data of 3-aryl propargyl alcohol is shown in table - **3**.

The infrared spectra of 3-aryl propargyl alcohol **11 - 14** showed the following position of stretching absorption bands of the different functional groups.

Table-3: Comparison of some spectral data of 3-aryl-propargyl alcohol **11-14**.

Sl. NO.	Compound	^{1}H NMR(δ) J=Hz	^{13}C NMR(δ)	IR (cm^{-1})	UV (n m)	m.p (°c)	Yield (%)
1	 **11**	7.26 (d, 2H, J=8.4Hz, Ar-CH) 7.33 (d, 2H, J=8.4Hz, Ar-CH), 4.46 (s, 2H, CH_2), 1.9 (s, 1H, OH)	51.56(C≡CCH_2), 84.60 & 88.16(ArC≡C), 121.01 & 134.58(Ar-C), 128.67 & 132.90(Ar-CH). DEPT-132.93, 128.7, 51.59.	750.3 (C-Cl) 2235 (C≡C) 3282.6 (OH)	285.8 278.4 259.8 250 234.2	78-79	89
2	 **12**	7.56 (d, 2H, J=8.7Hz, Ar-CH) 8.16(d, 2H, J=8.7Hz, Ar-CH), 4.53 (s, 2H, CH_2), 1.86 (s, 1H, OH)	51.50 (C≡CCH_2), 83.82 & 92.52 (ArC≡C), 129.45 & 147.27 (Ar-C), 123.5 & 132.41 (Ar-CH), DEPT-132.42, 123.59, 51.50	1344.3 (NO_2) 2200 (C≡C) 3310 (OH) 1517.9	297.6 238.8 254.6	87-88	86
3	 **13**	7.10 (d, 2H, J=7.5Hz, Ar-CH) 7.31 (d, 2H, J=7.8Hz, Ar-CH), 4.47 (s, 2H, CH_2), 2.33 (s, 3H, Ar-CH_3). 1.95(s, 1H, OH)	21.45 (Ar-CH_3), 51.63 (C≡CCH_2), 85.79 & 86.57 (ArC≡C), 119.47 & 138.60 (Ar-C), 129.05 & 131.58 (Ar-CH). DEPT-131.41, 129.20, 51.46, 21.28	2250 (C≡C) 3419.6 (OH) 2919 (CH_3)	359 247 232.6 223	Semi-solid	92
4	 **14**	6.82 (d, 2H, J=8.7Hz, Ar-CH) 7.35 (d, 2H, J=8.7Hz, Ar-CH) 4.46 (s, 2H, CH_2), 3.82 (s, 3H, OCH_3), 1.9(s, 1H, OH)	51.65 (C≡CCH_2) 55.26 (Ar- OCH_3) 85.60 & 85.90 (ArC≡C), 114.63 & 159.72 (Ar-C), 113.93 & 133.16 (Ar-CH). DEPT-113.93, 133.16, 55.26, 51.65	2230 (C≡C) 3310 (OH) 2934 (OCH_3)	257.2 229.2	Semi-solid	87

Functional groups	**Stretching position (Cm^{-1})**
C-**H** Stretching (Aromatic)	3000 - 3100
C≡C Stretching (Disubstituted)	2200 - 2250
O-**H** Stretching	3282 - 3419

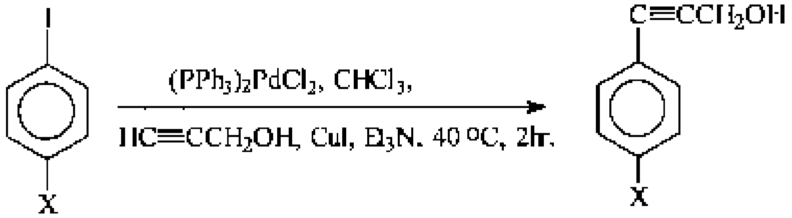
Ultraviolet-visible spectra of the synthesized alcohols **11-14** showed the approximate absoption position of carbon - carbon multiple bonded systems at 220 - 297nm which indicates the presence of unsaturation in the compound. The ^{1}H NMR spectra of 3 - aryl propargyl alcohol **11 - 14** exibited the following characteristics chemical shift of disubstituted alkynic proton indicate the structure of the compound.

Proton	Chemical shift(δ)
Ar-C**H**	6.82 - 7.56 (d, 2H, J = 7.5-8.7 Hz), 7.33 - 8.16 (d, 2H, J = 7.8-8.7 Hz),
$Ar\text{-}C\equiv C\mathbf{CH_2}$	4.46 - 4.53 (s, 2H)
O-H	1.86 - 1.95 (s, 1H)

The ^{13}C NMR spectra of 3-aryl propargyl alcohol **11-14** showed the following characteristic chemical shift which are compatible with structure of the compound.

Carbon	Chemical shift position (δ)
$-C\equiv CCH_2$	51.50 - 51.65
Ar-**C≡C**	83.82 - 85.79 & 85.90 - 92.52
Ar-**C**	114.63 - 129.45 & 134.58 - 159.72
Ar-CH	113.93 - 129.45 & 131.58 - 133.16

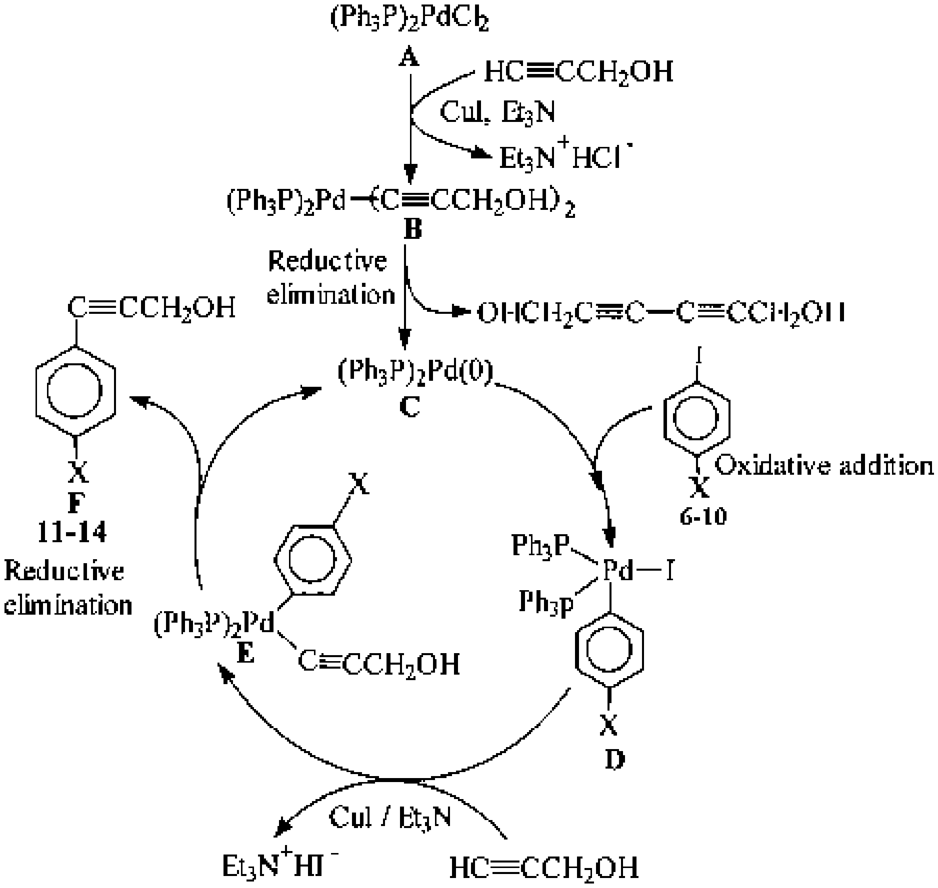
1.2.4. Mechanism of palladium-catalyzed reactions of aryliodide with terminal alkynes.



6-10

11-14

6, 11	X = Cl
7, 12	X= NO_2
8, 13	X = CH_3
9, 14	X= OCH_3
10	X= COOH



Scheme-3

It can be perceived that the reactions proceed according to scheme - 3 although the detailed mechanism of the reaction is yet to be clarified. It was observed that the presence of Palladium - Catalyzed and base were very essential for the success of heteroannulation reactions. The key steps of the possible mechanism were based on the following observations.

A coordinating unsaturated 14 - electron palladium (0) species is normally generated in situ from bis - (triphenyl phosphine) palladium(II) chloride in the presence of base (Et_3N) and alkynes[79].

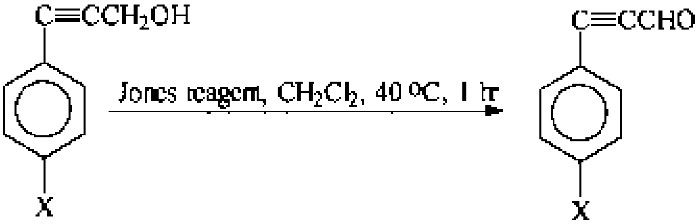
In the first step of the catalytic cycle step aryliodide are assumed to be oxidatively added to bis - (triphenyl phosphine) palladium(0), generating a σ – aryl palladium (II) complex. The reaction should lead to the thermodynamically stable arylpalladium (II) complex in several steps.

In the next step, at first CuI activates propergylalcohol molecule by forming the copper acetylides which undergo transmetallation with aryl palladium halides to form the alkynyl palladium species (step-E). This insertion is known as carbopalladation of alkynes.

Then reductive elimination to give 3-aryl propargyl alcohol (step-F) is the final step.
The catalyst is generated after reductive elimination of HI in presence of the base. The regenerated Pd(0) usually participate in the reaction as a catalyst.

1.2.5. Preparation & Characterization of 3 - aryl propargyl aldehyde 15 - 18:-

3 - aryl - propargyl alcohol **11-14** were oxidized by using Jones reagent i.e 5.6 g $K_2Cr_2O_7$ mixed with 5 - 6 ml conc. H_2SO_4 and 30 ml H_2O in CH_2Cl_2 solvents at 40 °C under reflux for 1 hr. After usual workup 3-aryl propargyl aldehyde **15-18** were obtained.



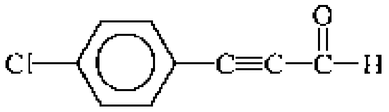
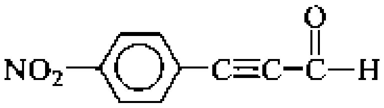
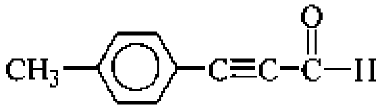
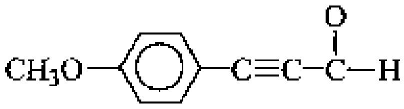
11-14 **15-18**

Scheme-4

From all the alcohols quantitative yield of aldehyde were obtained. The characterization of the aldehydes were done by spectral data UV, IR, ^1H NMR and ^{13}C NMR (P. 86 - 107). The comparison of some spectral data of substituted aldehyde is shown in the table -5.

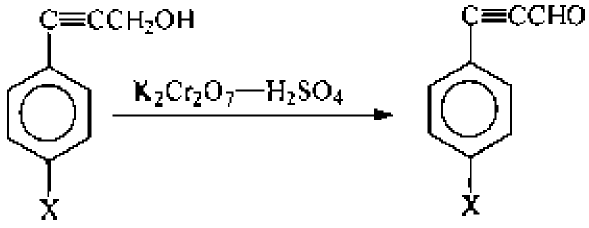
In infrared spectra carbonyl stretching frequency (1625 -1654) cm^{-1}, C≡C stretching absorption at (2191 - 2200) cm^{-1}, aldehydic C-H at (2854 - 2964) cm^{-1} were obtained. Ultraviolet - visible spectra of the synthesized aldehyde **15-18** showed the approximate absoption position of aldehyde (-CHO) at 242 – 249 nm which indicates the presence of unsaturation in the compound. The ^1H NMR spectra of the aldehydes showed the chemical shift position at δ (9.4 - 9.89) for –CHO proton. The ^{13}C NMR spectra of the aldehydes exhibited the chemical shift position at (176.03-176.76) for –CHO, at (89.02 - 90.63) & (90.76 - 93.58) for -C≡C- and indicates the structure of the desired compound.

Table-4: Comparison of some spectral data of substituted aldehydes **15-18**.

Sl. No.	Compound	^{1}H NMR(δ) J=Hz	^{13}C NMR(δ)	IR (cm^{-1})	UV (n m)	m.p (^{o}c)	Yied (%)
1	 **15**	7.38 (d, 2H, J=8.3Hz, Ar-CH), 7.52 (d, 2H, J=8.4Hz, Ar-CH), 9.4 (s, 1H, CHO),	89.02 & 93.579 (ArC≡C), 129.27 & 134.45 (Ar-CH), 117.94 & 137.84 (ArC), 176.49 (CHO) DEPT-76.49,134.45,129.27	1652.9 (CO) 2191 (C≡C) 2854.5 (C-H, Aaldehydic)	248.6	93	65
2	 **16**	7.75 (d, 2H, J=8.7Hz, Ar-CH) 8.25 (d, 2H, J=8.7Hz, Ar-CH), 9.45 (s, 1H, CHO)	90.63 & 90.76 (ArC≡C), 123.86 & 133.87 (Ar-CH), 126.01 & 148.87(ArC), 176.03(CHO) DEPT-176.03, 133.87, 123.86.	1654.8 (CO) 2194.8 (C≡C) 2964.4 (C-H, Aaldehydic	242.20	110	60
3	 **17**	7.20 (d, 2H, J=8.18 Hz, Ar-C), 7.48(d, 2H,J=8.05Hz, Ar-C), 9.40(s, 1H, -CHO) 2.3 (s. 3H, Ar-CH$_3$)	129.56 & 133.35 (Ar-CH), 21.80 (Ar-CH$_3$), 176.76 (CHO) DEPT-176.03, 133.87, 129.5, 21.79.	1625 (CO) 2200 (C≡C) 2920 (C-H, Aaldehydic)	249.40	Semi-solid	82
4	 **18**	6.91 (d, 2H, J=8.78 Hz , Ar-CH) 7.55 (d, 2H, J=8.78Hz, ArC), 9.89 (s, 2H, CHO), 3.85 (s, 3H, Ar-OCH$_3$)				Semi-solid	48

1.2.6. Mechanism of 3 - aryl propargyl aldehyde 15:-

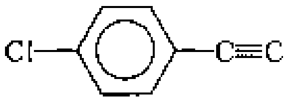
The probable mechanism for acid- catalysed oxidation is illustrated below with 3 - phenyl propargyl aldehyde 15.

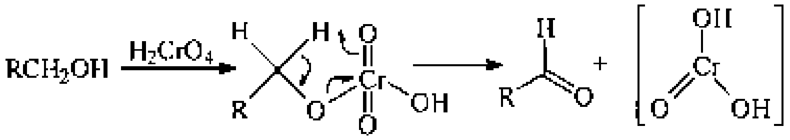


11 15

Reaction occurs through the chromate ester, via a cyclic transition state:

Here, R =



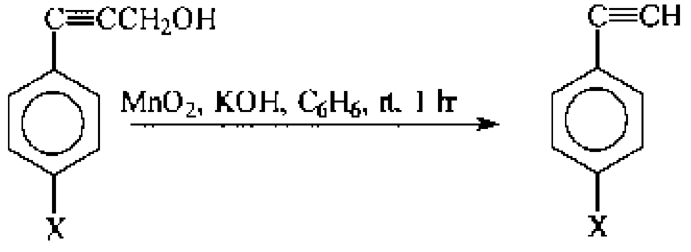


The chromium (iv) then disproportionates to give chromium(iii) and chromium (vi).

Scheme-5

1.2.7. Preparation & Characterization of terminal acetylenes of aryl 19-20:-

Terminal acetylenes of aryl **19-20** were obtained by oxidation - decarbonylation of 3 - aryl propargyl alcohols **11-12** using manganese dioxide in the presence of alkali in C_6H_6 solvent[27] at room temperature for 1 hr.



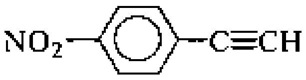
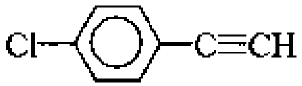
11-12 19-20

Scheme-6

From all the alcohols quantitative yield of acetylenes were obtained. The charectarization of the terminal acetylenes were done by spectral data IR, UV, ^1H NMR & ^{13}C NMR (P. 108 – 116). The comparision of some spectral data of substituted acetylene is shown in the table-**6**.

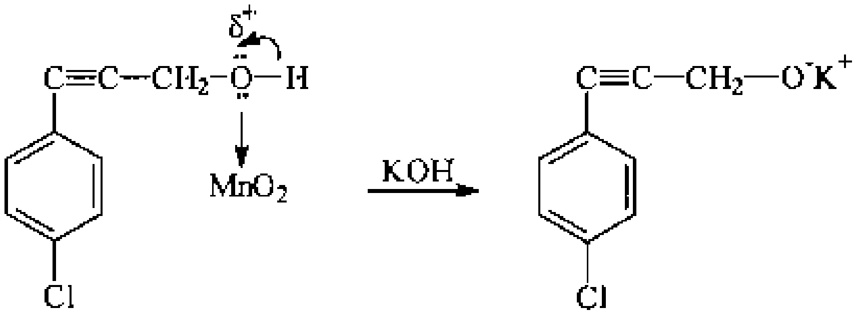
In infrared spectra alkynyl ≡C-H stretching at (3110 - 3251) cm^{-1} and C≡C stretching absorption at (2100 – 2150) were obtained. Ultraviolet - visible spectra of the synthesized acetylenes **19-20** showed the approximate absoption position of carbon - carbon multiple bonded systems at 238 – 289 nm which indicates the presence of unsaturation in the compound. The ^1H NMR spectra of the alkyne proton showed the chemical shift position at δ (3.09 - 3.34) for -C≡CH proton. The ^{13}C NMR spectra of the terminal acetylenes exhibited the chemical shift position at 81.63 & 82.30 for -C≡CH and indicates the structure of the desired compound.

Table-5: Comparison of some spectral data of substituted acetylenes **19-20.**

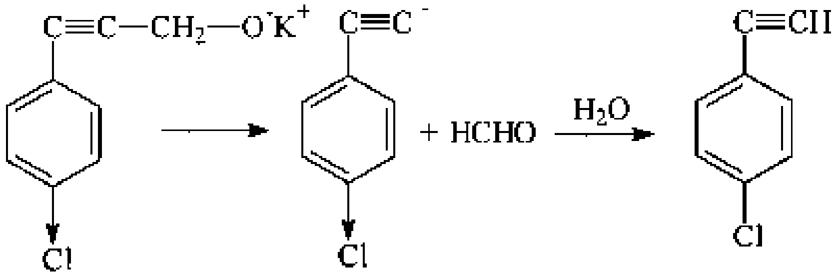
Sl. No.	Compound	^{1}H NMR(δ) J=Hz	^{13}C NMR(δ)	IR (cm^{-1})	UV (n m)	m.p (°c)	Yied (%)
1	 **19**	7.62 (d, 2H, J=8.75Hz, Ar-CH), 8.18 (d, 2H, J=8.76Hz, Ar-CH), 3.34 (s, 1H, Ar-C≡CH)	81.63 & 82.30 (ArC≡C) 123.56 & 132.97(ArCH) 128.93 & 147.57(Ar-C) DEPT-133, 123.48, 82.12.	1342.4 (NO$_2$) 2100 (C≡C) 3251.8 (≡C-H)	289.4 238	150	35
2	 **20**	7.29(d, 2H, J=8.3Hz, Ar-CH) 7.43(d, 2H, J=8.2Hz, Ar-CH), 3.09(s, 1H, Ar-C≡CH)		819.7 (C-Cl) 2150 (C≡C) 3110 (≡C-H)		48	62

1.2.8. Mechanism terminal acetylenes of aryl 19:-

Step-1: Attacks MnO_2 to the lone pair alcoholic group. As a result alcoholic group become more acedic.

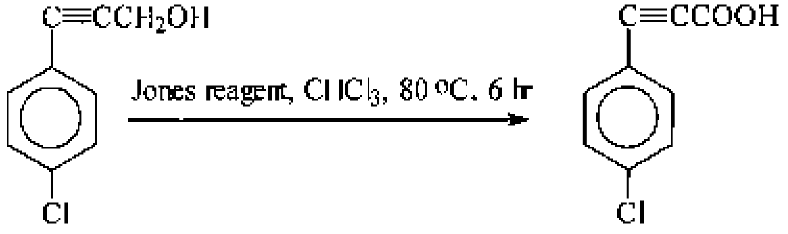


Step-2: Produced formaldehyde and anionic system from ionic species. Then desired compound was formed.



1.2.9. Preparation & Charecterization of terminal acids 21:-

3 – aryl propargyl acids were obtained by using Jones reagents i.e. 5.6 g $K_2Cr_2O_7$ mixed with 5-6 ml conc. H_2SO_4 and 30 ml H_2O in $CHCl_3$ solvents at 80 °C under reflux for 6 hr.



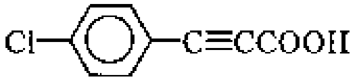
11 **21**

Scheme-7

From all the alcohols quantitative yield of acids were obtained. The characterization of the terminal acids were done by spectral data IR, UV, ^{1}H NMR & ^{13}C NMR (P. 117 – 122). The comparison of some spectral data of substituted acids are shown in the table 7.

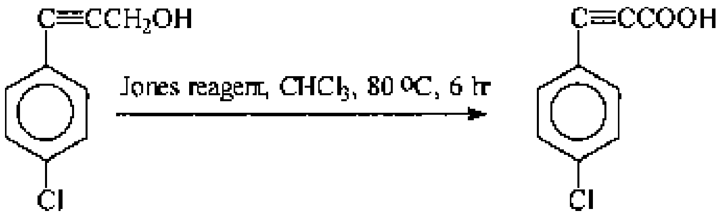
In infrared spectra carbonyl stretching 1681 cm^{-1} and C≡C stretching absorption at 2100 were obtained. Ultraviolet - visible spectra of the synthesized acid **21** showed the approximate absoption position of carbon - carbon multiple bonded systems at 245-283 nm which indicates the presence of unsaturation in the compound. The ^{1}H NMR spectra of the acids showed the chemical shift position at δ 9.75 for –COOH proton. The ^{13}C NMR spectra of the acids exhibited the chemical shift position at 169.5 for –COOH, at 128.64 and 128.52 for -C≡C- and indicates the structure of desired compound.

Table-6: Comparison of some spectral data of substituted acetylenes **21.**

Sl. No.	Compound	^{1}H NMR(δ) J=Hz	^{13}C NMR(δ)	IR (cm^{-1})	UV (n m)	m.p (°c)	Yied (%)
1	 **21**	7.43 (d, 2H, J=7.6Hz, Ar-CH), 8.01 (d, 2H, J=7.6Hz, Ar-CH), 9.75 (s, 1H, ArC≡CCOOH)	169.50 (-COOH), 132.11 & 128.80 (ArCH), 132.20 & 131.52(Ar-C), 128.64 & 128.52 (ArC≡C)	1681.8 (C= O) 2100 (C≡C)	283.2 245.6	160	48

1.2.12. Mechanism of terminal acids 21:-

The probable mechanism for acid - catalysed oxidation is illustrated below with 3 - phenyl propargyl alcohol 11.

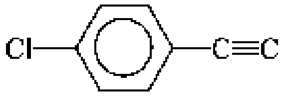


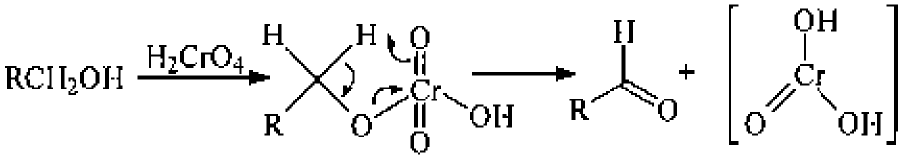
11 → 21

Firstly the alcohol was converted to aldehyde at normal condition (r.t) with Jones reagents and then converted to acids at vigorous condition (80 °C temp. & 6 hr) as illustrated.

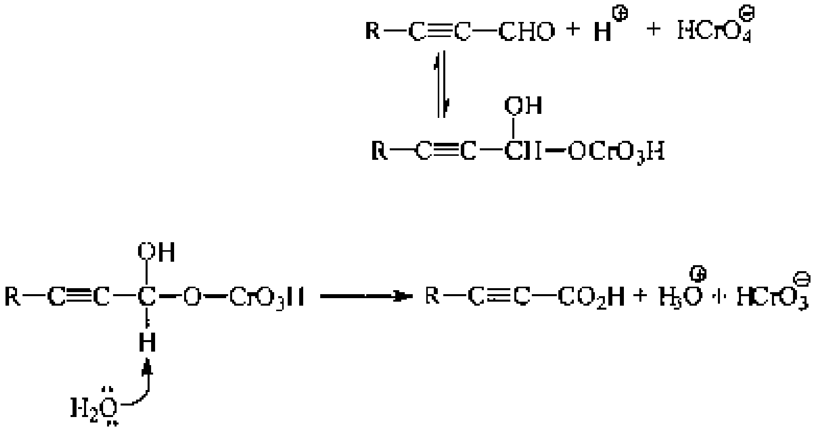
Reaction occurs through the chromate ester, via a cyclic transition state:

Here, R =





The chromium (iv) then disproportionates to give chromium(iii) and chromium (vi).



Scheme-8

Conclusion

We have described a convenient and facile method for the preparation of 3-aryl propargyl alcohol from the reaction of aryliodide with propargyl alcohol by a $(Ph_3P)_2$ Pd(II) Cl_2, CuI, Et_3N system.

Later 3-aryl propargyl alcohol was oxidized to produce 3-aryl propargyl aldehyde by using Jones reagents.

Then terminal acetylenes were prepared by oxidation decarbonylation of 3-aryl propargyl alcohol by using manganese dioxide in presence of alkali in C_6H_6 solvent at room temperature for 1 hr.

Then 3-aryl propargyl acid was obtained from 3-aryl propargyl alcohol by using Jones reagents.

The most important features of the synthesis are that readily available starting materials are used under relatively mild reaction conditions. Also, no toxic and hazardous compounds are produced in this procedure.

By using this methodology researchers will be able to synthesize different unsaturated alcohol, aldehydes, terminal alkyne and unsaturated carboxylic acids which might have versatile synthetic importance.

Chapter- II

SECTION - II

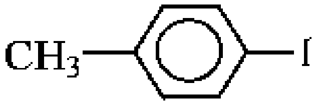
Experimental

1.3.1. Preparation of substituted iodobenzene (6-10)

a. Preparation of *p*-Iodotoluene 8:-

p-Toluidine (5g, 0.047 mol) was dissolved in distilled water (60 ml) containing conc. H_2SO_4 (7 ml) in a large round bottom flask. The mixture was cooled at 0 - 5 °C with vigorous stirring by immersion in a freezing mixture of ice and salt. The resulting mixture was diazotized by gradual addition of a cold solution of sodium nitrite (3.17g, 0.045 mol, 1 eq.) in water (10 ml) with stirring, maintaining the temperature of the solution at 0 - 5 °C. Then a solution of potassium iodide (9.16g, 0.055 mol, 1.2 eq.) in water (10 ml) was added to the resultant clear solution gradually with stirring. Then the mixture was allowed to stand for 1 hr. at the laboratory temperature and heated to boiling on a water bath until evolution of nitrogen ceases for minimum 30 minutes. Then the solution mixture was cooled, a dark colored oil was settled to the bottom and soon solidified.

The residue obtained by filtration was washed with distilled cooled water. Then the residue obtained was dissolved with Chloroform. The organic layer was washed with saturated $NaHCO_3$ and then sodium thiosulfate solution with the help of separator funnel. Finally, the organic layer was washed with distilled water and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The compound were obtained as a crude gum which were then purified by column chromatography on silica gel with chloroform : hexane (1: 3) to give yellowish crystal (8.82g, 86%) m.p. 35-36 ° C .



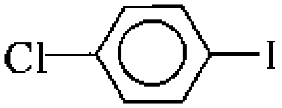
8

The characteristics data of this compound are as follows-

IR (KBr): υ_{max} 2964, 1585, 1485, 1286, 1245, 1174, 1028, 999 and 823 cm^{-1} .

^{1}H NMR (400 MHz, $CDCl_3$): 7.53 (d, 2H, J = 3.0 Hz, Ar-H). 6.56 (d, 2H, J = 3.0Hz, Ar-H), δ 2.36 (s, 3H, Ar-CH_3).

b. Preparation of *p*-iodochlorobenzene **6:**



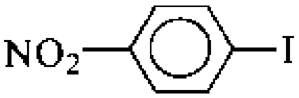
6

This compound **6** was synthesized from *p*-chloro aniline by following the procedure described above. It was crystaline white coloured compound (mp. 53-54 °C). The characteristics data of this compound are as follows-

IR (KBr): υ_{max} 3100-3080, 1548.7, 1257.7, 1217.0, 1006.8, 977.8, 727 cm^{-1} .

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.52 (d, 2H, J = 8.4Hz, Ar-H), 7.38 (d, 2H, J = 8.3Hz, Ar-H)

c. Preparation of *p*-iodo nitrobenzene 7:



7

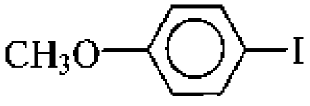
This compound 7 was synthesized from *p*- nitro aniline by following the procedure described above. It was crystaline light yellow coloured compound (mp. 173-175 °C). The characteristics data of this compound are as follows-

IR (KBr): υ_{max} 3100-3080, 1508, 1340, 1307, 850, 837 cm^{-1} .

UV (EtOH) : λ_{max} 252.0 nm.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.25(d, 2H, J = 8.7Hz, Ar-H), 7.75(d, 2H,J = 8.7Hz, Ar-H)

d. Preparation of *p*-iodoanisol **9:**



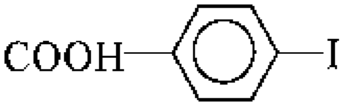
9

This compound **9** was synthesized from *p*- anisidine by following the procedure described above. It was crystaline light yellow coloured compound (mp. 48 - 50 °C). The characteristics data of this compound are as follows-

IR (KBr): υ_{max} 3100-2900, 1548.7,1257, 1217, 1006.8, 977.8 and 727cm^{-1} .

^{1}**H NMR** (400 MHz, CDCl$_3$): δ 7.56 (d, 2H, J=8.77Hz, Ar-H), 6.10 (d, 2H, J=8.78Hz, Ar-H), 3.77 (s, 3H, Ar-OCH$_3$)

e. Preparation of *p*-iodobenzoic acid **10:**



10

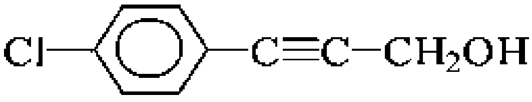
This compound **10** was synthesized from p- iodobenzoic acid by following the procedure described above. It was crystaline light yellow coloured compound (mp. 272 - 273 °C). The characteristics data of this compound are as follows-

IR (KBr): υ_{max} 3100-2900, 1750,1251, 1217, 1006, 977 and 727cm^{-1} .

1.3.2. General procedure for the synthesis of unsaturated alcohols 11-14.

a. Synthesis of 3-(*p*-chlorophenyl)-prop-2-yn-1-ol **11**:-

Into a round bottom flask equipped with a reflux condenser carrying a calcium chloride guard tube on the top, bis-triphenyl phosphine palladium(II) chloride (44 mg, 0.063 m.mol, 3 mol %) and copper iodide (32mg, 0.17 m.mol, 8 mol %) were added to a solution of propargyl alcohol (153 mg, 2.74 m.mol, 1.3eq.), triethylamine (0.42g, 4.19 m.mol, 2 eq.) and *p*-chloro- iodobenzene (500mg, 2.096 m.mol) in chloroform (10 ml). The mixture was stirred at 40 ℃ for 2 hours with reflux. After 2 hr the mixture was diluted with chloroform. Then the organic layer was washed with distilled water by separator funnel and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The compound was obtained as a crude solid which is then purified by column chromatography on silica gel with chloroform : hexane (1:2) to give colorless crystal of 11 (0.322 g, 92%), m.p. 78-79 ° C.



11

The characteristics data of this compound are as follows-

IR (KBr): υ_{max} 3282.6, 2854.5, 2235, 750.3 cm^{-1} .

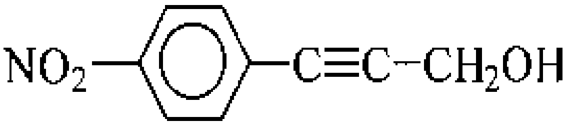
UV ($CHCl_3$) : λ_{max} 285.8, 278.4, 259.8, 250, 234.2 nm.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, 2H, J=8.4Hz, Ar-CH), 7.26 (d, 2H, J=8.4Hz, Ar-CH), 4.46 (s, 2H. CH_2), 1.9 (s, 1H, OH)

^{13}C NMR (100 MHz, $CDCl_3$): δ 128.67 & 132.90(Ar-CH), 121.01 & 134.58(ArC=), 84.60 & 88.16(ArC≡C), 51.56(C≡CCH_2),

DEPT- 132.93, 128.7, 51.5

b.Synthesis of 3 - (*p* - nitrophenyl) - prop - 2-yn - 1 - ol **12**:-



12

This compound **11** was synthesized from *p*-iodo nitro benzene by coupling reaction of (triphenylphosphine) palladium (II) chloride, triethylamine and propargyl alcohol in chloroform by the following procedure described above. It was crystaline light yellow coloured compound (mp. 87 – 88 ° C). The characteristics data of this compound are as follows-

IR (KBr): υ_{max} 3310, 2200,1517,1344.3 cm^{-1} .

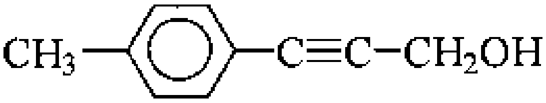
UV ($CHCl_3$) : λ_{max} 297.6, 254.6, 238.8 nm.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.16(d, 2H,J=8.7Hz, ArCH), 7.56 (d, 2H, J=8.7Hz, Ar-CH), 4.53(s, 2H, CH_2). 1.86(s, 1H, OH)

^{13}**C NMR** (100 MHz, $CDCl_3$): δ 129.45 & 147.27 (Ar-**C**), 123.5 & 132.41 (Ar-**CH**), 83.82 & 92.52(Ar**C≡C**), 51.50(C≡CCH_2).

DEPT-132.42, 123.59, 51.50

c.Synthesis of 3 - (*p* - methylphenyl) - prop - 2-yn - 1 - ol **13**:-



13

This compound **13** was synthesized from *p* - iodo toluene by following the procedure described above. It was semi - solid light yellow coloured compound. The characteristics data of this compound are as follows-

IR (KBr): υ_{max} 3419.6, 2919, 2250, 850, 670 cm^{-1} .

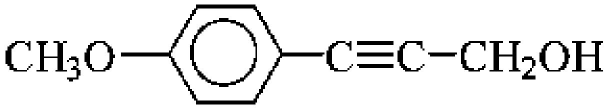
UV ($CHCl_3$) : λ_{max} 359, 247, 232.6, 223 nm.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, 2H, J=7.8Hz, Ar-CH), 7.10 (d, 2H, J=7.5Hz, Ar-CH), 4.47 (s, 2H, CH_2), 2.33 (s, 3H, Ar-CH_3), 1.95 (s, 1H, OH)

^{13}C NMR (100 MHz, $CDCl_3$): δ 129.05 & 131.58(Ar-CH), 119.47 & 138.60 (Ar-**C**), 85.79 & 86.57 (Ar**C≡C**), 51.63 (C≡CCH_2), 21.45 (ArCH_3)

DEPT-131.41, 129.20, 51.46, 21.28

d. Synthesis of 3 - (*p* - methoxiphenyl) - prop - 2-yn - 1 - ol **14**:-



14

This compound **14** was synthesized from *p*-iodoanisol by following the procedure described above. It was semi - solid light yellow coloured compound. The characteristics data of this compound are as follows-

IR (KBr): υ_{max} 3310, 2934.4, 2230, cm^{-1} .

UV ($CHCl_3$) **:** λ_{max} 257.2, 229.2 nm.

^{1}H NMR (400 MHz, $CDCl_3$)**:** δ 7.35 (d, 2H, J=8.7Hz, 6.82 (d, 2H, J=8.7Hz, Ar-CH), Ar-CH), 4.46 (s, 2H, CH_2), 3.82(s, 2H, OCH_3), 1.9(s, 1H, OH)

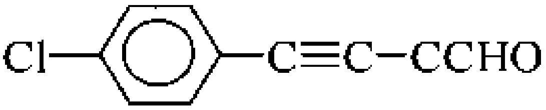
^{13}C NMR (100 MHz, $CDCl_3$): δ 114.63 & 159.72 (Ar-C), 113.93 & 133.16 (Ar-CH), 85.60 & 85.90 (ArC≡C), 55.26 (Ar- OCH_3), 51.65 (C≡CCH_2).

DEPT-113.93, 133.16, 55.26, 51.65

1.3.3. General procedure for the synthesis of unsaturated aldehyde 15-18.

a. Synthesis of 3-(*p*-chlorophenyl)-prop-2-yn-1-al **15**:-

Into a round bottom flask equipped with a reflux condenser carrying a calcium chloride guard tube on the top, 3-(*p*-chlorophenyl) prop -2-yn-1-ol (100 ml, 0.60 m. mol) was taken in dichloromethene (10 ml). The mixture was stirred at 40 °C with reflux. Then the Jones reagents (i.e. 5.6 g $K_2Cr_2O_7$, 5-6 ml of conc. H_2SO_4 in 30 ml H_2O mixture) was added to the solution gradually. The mixture was stirred at 40 °C for 1 hour with reflux. After 1hr the mixture was diluted with chloroform. Then the organic layer was washed with distilled water by separator funnel and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The compound was obtained as a crude solid which was then purified by column chromatography on silica gel with chloroform : hexane (1: 3) to give colorless crystal of **15** (70 mg, 65%) m.p. 93° C.



15

The characteristics data of this compound are as follows-

IR(KBr): υ_{max} 2854.5, 2191, 1652.9, 825.5, 760 cm^{-1} .

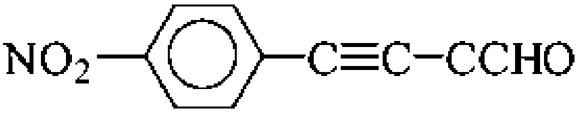
UV ($CHCl_3$) : λ_{max} 248.6, 234.8 nm.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, 2H, J=8.4Hz, Ar-CH), 7.38 (d, 2H, J=8.3Hz, Ar-CH), 9.4(s, 1H, CHO)

^{13}C NMR (100MHz,$CDCl_3$): 176.49(CHO), 129.27 & 134.45 (Ar-CH), 117.94 & 137.84 (Ar-C), δ 89.02 & 93.579 (ArC≡C)

DEPT-176.49, 134.45, 129.27

b. Synthesis of 3-(*p*-nitrophenyl)-prop-2-yn-1-al **16**:-



16

This compound **16** was synthesized from 3-(*p*-nitrophenyl)-prop-2-yn -1-ol) by oxidation reaction of Jones reagent (i.e. 5.6 g $K_2Cr_2O_7$, 5-6 ml of conc. H_2SO_4 in 30 ml H_2O mixture) and 3-(*p*-nitrophenyl)-prop-2-yn-1-ol in dichloromethene by the following procedure described above. It was crystaline light yellow coloured compound (m.p. 110 ° C). The characteristics data of this compound are as follows-

IR (KBr): υ_{max} 2964.4, 2194.8, 1654.8, 1344.3 cm^{-1} .

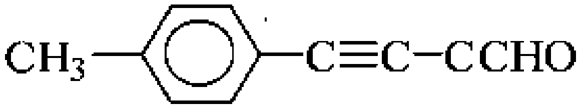
UV ($CHCl_3$) **:** λ_{max} 293.80, 242.20, 234.10, 231.80, 223.20 nm.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, 2H, J=8.7Hz, Ar-CH), 7.75 (d, 2H, J=8.7Hz, Ar-CH), 9.45(s, 1H, CHO)

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.03 (CHO), 126.01 & 148.87 (Ar-C), 123.86 & 133.87(Ar-**CH**), 90.63 & 90.76(Ar**C**≡**C**)

DEPT-176.03, 133.87, 123.86.

c. Synthesis of 3-(*p*-methylphenyl)-prop-2-yn-1-al **17**:-



17

This compound **17** was synthesized from 3-(*p*-methylphenyl)-prop-2-yn-1-ol by following the procedure described above. It was semi-solid light yellow coloured compound. The characteristics data of this compound are as follows-

IR (KBr): υ_{max} 2920, 2200, 1625, 800 cm^{-1} .

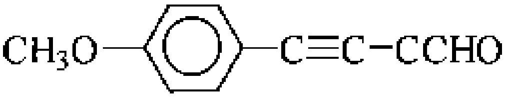
UV (CHCl$_3$) **:** λ_{max} 249.40 nm.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.49 (d, 2H, J=8.05Hz, Ar-C), 7.20 (d, 2H, J=8.18Hz, Ar-CH), 9.40 (s, 1H, -CHO), 2.3 (s, 3H, Ar-CH$_3$)

^{13}C NMR (100 MHz, CDCl$_3$): δ 176.76 (CHO), 129.56 & 133.35 (Ar-CH), 118.12 & 136.94 (Ar-C), 89.01 & 92.03 (ArC≡**C**), 21.80 (Ar-CH$_3$)

DEPT-176.03, 133.87, 129.5, 21.79.

d. Synthesis of 3-(*p*-methoxyphenyl)-prop-2-yn-1-al **18**:-



18

This compound **18** was synthesized from 3-(*p*-methoxyphenyl)-prop-2-yn-1-ol by following the procedure described above. It was solid light yellow coloured compound. The characteristics data of this compound are as follows-

IR (KBr): υ_{max} 2930, 2210, 1610cm^{-1} .

UV ($CHCl_3$) : λ_{max} 249.40 nm.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.89(s, 2H, CHO), 7.56 (d, 2H, J=8.78Hz, Ar-C), 6.91 (d, 2H, J=8.78Hz, Ar-CH), 3.85(s, 3H, Ar-OCH_3)

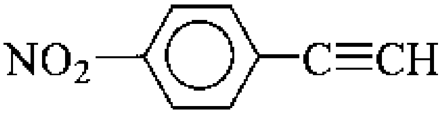
1.3.4. Preparation of active MnO_2:

Into a large (2 liter) round bottom flask with three necked equipped with a reflux condenser carrying a calcium chloride guard tube on the top, a solution of $MnSO_4.H_2O$ (139 g in 250 ml H_2O) and 40 % NaOH were added simultaneously to a hot solution of $KMnO_4$ (160g in 1liter H_2O) over a period of 1 hour. The boiling mixture was stirred for an additional hour and it was then allowed to stand overnight. Then the ppt. was collected with the help of filter paper on buchner funnel and washed with distilled water until the p^H of the wetted sample reaches 8. The ppt. was transferred into a beaker and boiled with water for five minutes with occasional stirring, then filtered. The most active MnO_2 was obtained when the washing with distilled water was done for several times. The ppt. was dried at 110 ° C for overnight and powdered before use.

1.3.5. General procedure for the synthesis of unsaturated acetylene19-20.

a. Synthesis of *p*-nitrophenyl-acetylene **19**:-

Into a round bottom flask equipped with a calcium chloride guard tube on the top, 3 - (*p* - nitrophenyl)-prop-2-yn-1-ol (200 mg, 1.13 m.mol) was taken in benzene (10ml) and potassium hydroxide powder (0.317g, 5.6m.mol, 5eq) and manganese dioxide (0.98 g, 11m.mol, 10eq) were added. Then the mixture was stirred at room temperature for 1 hour. The solution was filtered with the help of filter paper and the residue was extracted with ether (3*50 ml). Then the organic layer was washed with distilled water by separator funnel and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The compound was obtained as a crude solid which was then purified by column chromatography on alumina with hexane : chloroform (3:1) to give pale yellow crystal of **19** (110 mg, 64%) m.p. 149-150 ° C.



19

The characteristics data of this compound are as follows-

IR(KBr): υ_{max} 3251.8, 2100, 1342.4 cm^{-1} .

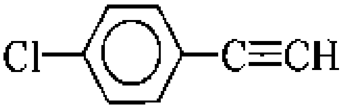
UV ($CHCl_3$) : λ_{max} 289.4, 238, 221.8, 218 nm.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, 2H, J=8.76Hz ,Ar-CH), 7.62 (d, 2H, J=8.75Hz, Ar-CH), 3.34(s, 1H, Ar-C≡**CH**)

^{13}C NMR (100 MHz, $CDCl_3$): δ 128.93 & 147.57 (Ar-C), 123.56 & 132.97(Ar-CH), 81.63 & 82.30 (ArC≡C),

DEPT-133, 123.48, 82.12

b. Synthesis of *p*-chlorophenyl-acetylene **20**:-



20

This compound **20** was synthesized from 3-(*p*-chlorophenyl)-prop-2-yn-1-ol) by oxidation decarbonylation reaction of potassium hydroxide powder and manganese dioxide with 3-(*p*-chlorophenyl)-prop-2-yn-1-ol in chloroform by the following procedure described above. It was crystallized white coloured compound (m.p. 48 °C). The characteristics data of this compound are as follows-

IR (KBr): υ_{max} 3110, 2150, 819.7 cm^{-1} .

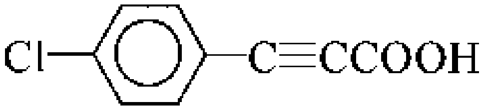
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, 2H, J=8.2Hz, Ar-CH), 7.30 (d, 2H, J=8.3Hz, Ar-CH), 3.09 (s, 1H, Ar-C≡CH),

1.3.6. General procedure for the synthesis of unsaturated carboxylic acids 21.

a. Synthesis of 3-(*p*-chlorophenyl)-prop-2-yn-1-oic acid **21**:-

Into a round bottom flask equipped with a reflux condenser carrying a calcium chloride guard tube on the top, 3-(*p*-chlorophenyl)-Prop-2-yn-1ol (200 mg,1.2 m.mol) was taken in chloroform (10 ml). The mixture was stirred at 80 °C with reflux. Then the Jones reagents (i.e 5.6 g $K_2Cr_2O_7$, 5-6 ml H_2SO_4 and 30 ml distilled water mixture) was added to the solution gradually. Then the mixture was stirred at 80 °C for 6 hours.

After 6 hours the mixture was diluted with $CHCl_3$. Then the organic layer was washed with distilled water with the help of separator funnel and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The compound was obtained as a crude solid which was then purified by column chromatography on silica gel with chloroform to give colorless crystal of **21** (105 mg, 48 %) m.p. 160 ° C .



21

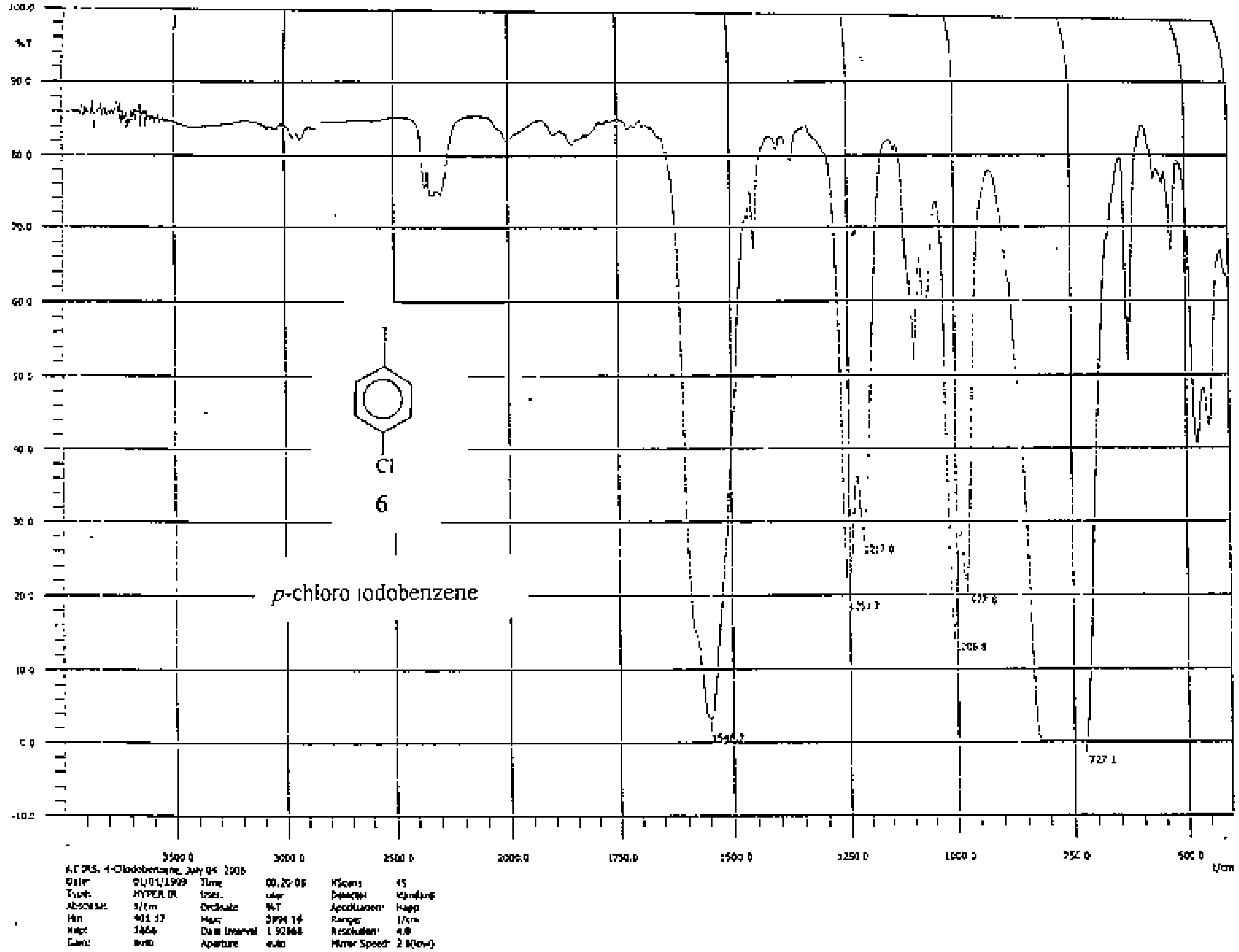
The characteristics data of this compound are as follows-

IR(KBr): υ_{max} 3500-2500, 3064, 2100, 1681, 1425.3, 1296.1, 852.5, 759.9 cm^{-1} .

UV ($CHCl_3$) : λ_{max} 283.2, 245.6, 222.4, 218.2 nm.

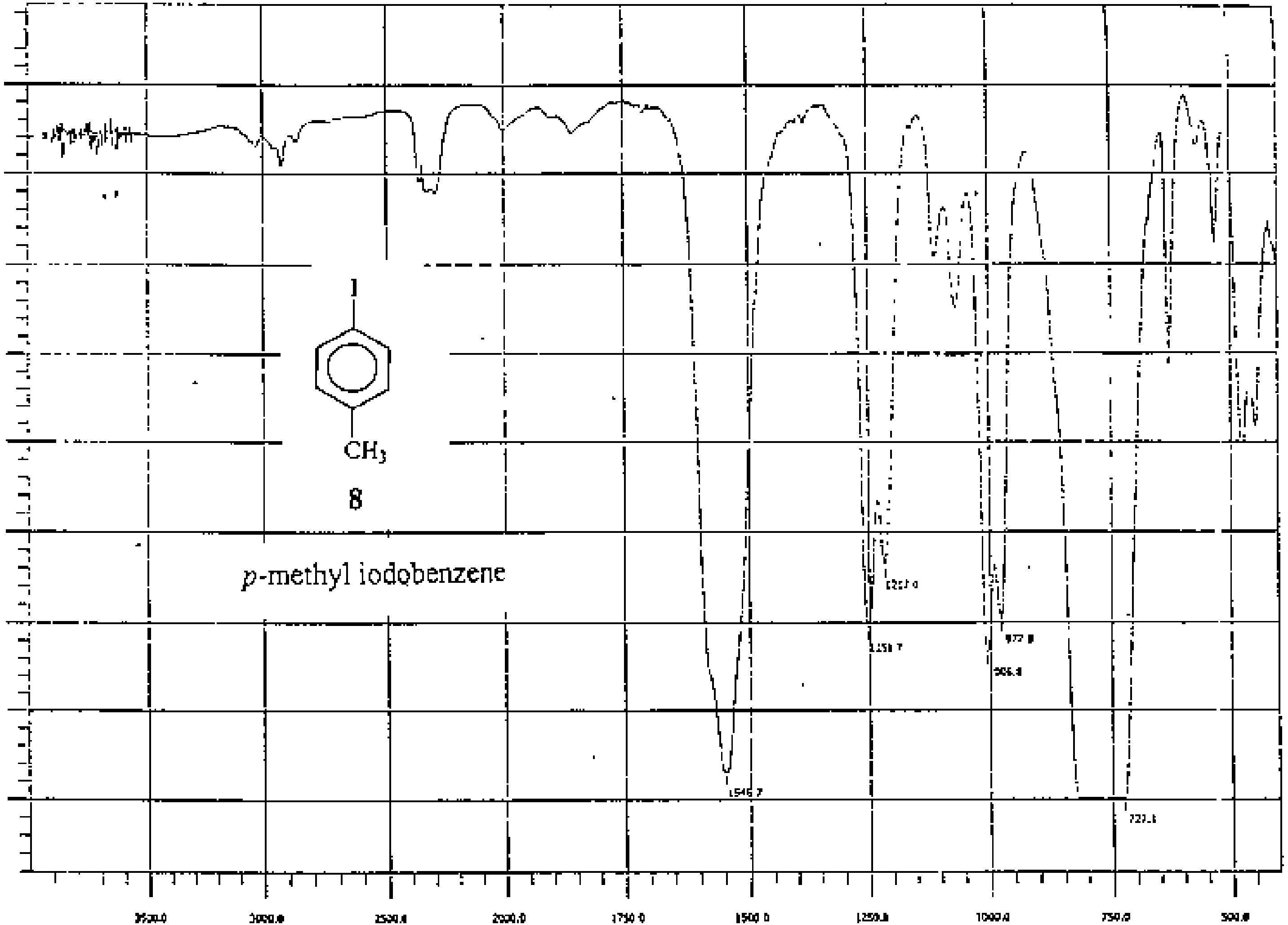
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, 2H, J=7.6Hz, Ar-CH), 8.02 (d, 2H, J=7.6Hz, Ar-CH), 9.75 (S, 1H, Ar-C=COOH)

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.50 (-COOH),132.11 & 128.80 (Ar-CH), 132.20 & 131.52 (Ar-C), 128.64 & 128.52 (Ar-C≡C)



6

p-chloro iodobenzene

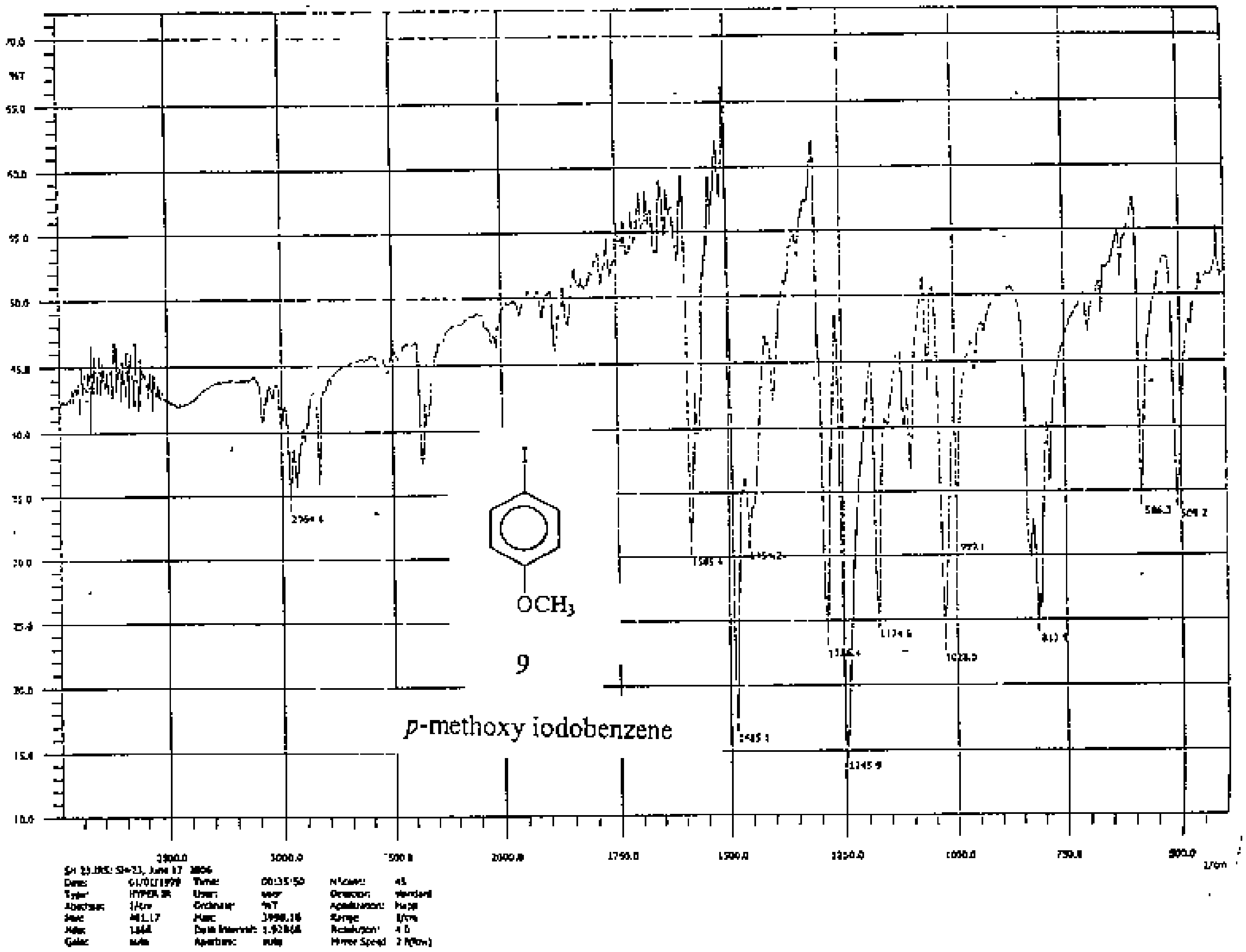


8

p-methyl iodobenzene

S. 4-Iodotoluene, July 04 2006

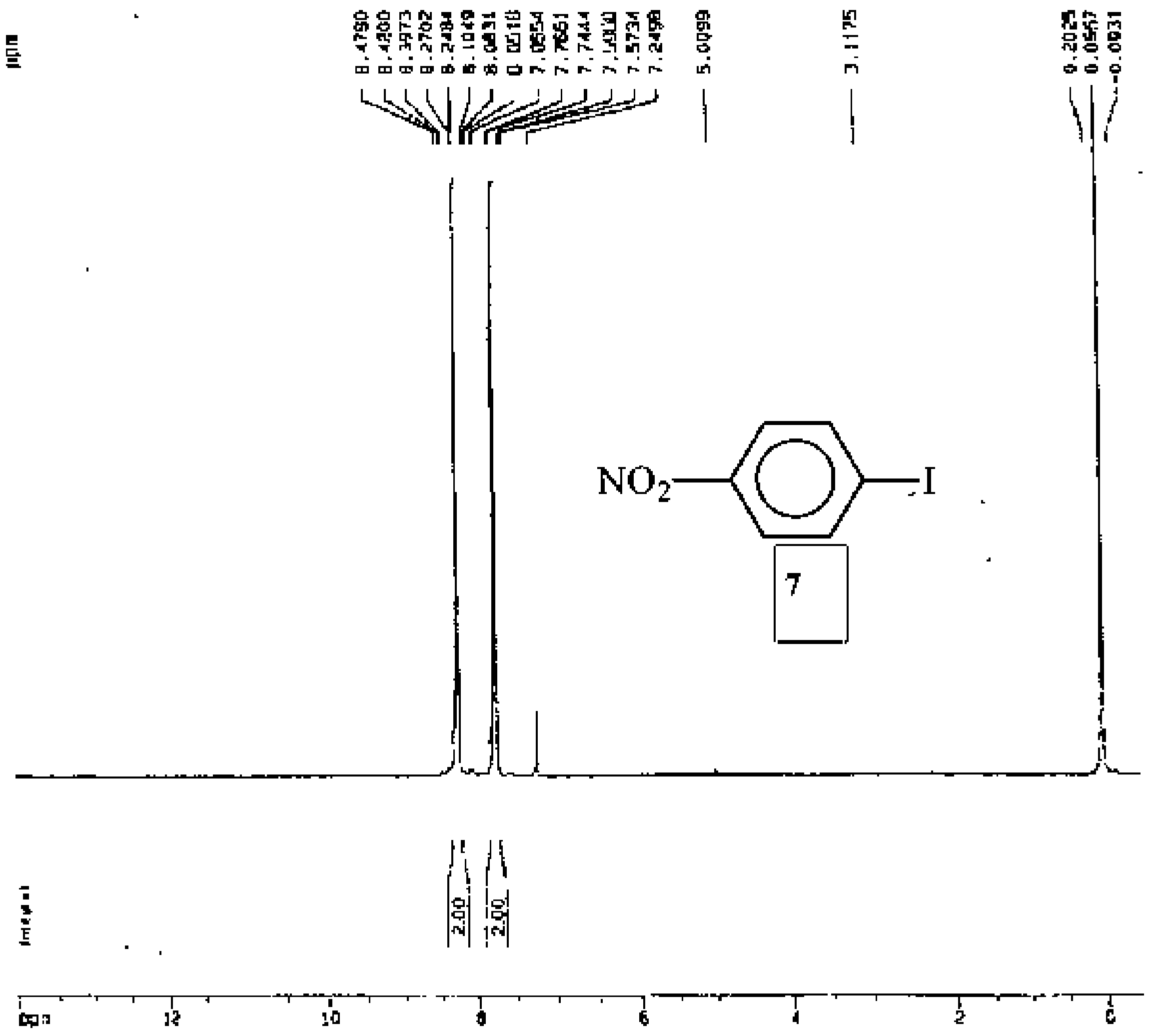
Date:	01/01/1999	Time:	00:59:05	nScans:	45
Type:	HYPER IR	User:	user	Detector:	standard
Abscissa:	1/cm	Ordinate:	%T	Apodization:	Happ
Min:	401.17	Max:	3998.16	Range:	1/cm
Npts:	1466	Data Interval:	1.92848	Resolution:	4.0
Class:	auto	Aperture:	auto	Mirror Speed:	2.8(mm)



9

p-methoxy iodobenzene

Analytical, BCSIR, 1H Spectrum, LK-4 in CDCl3, Laila, BUET



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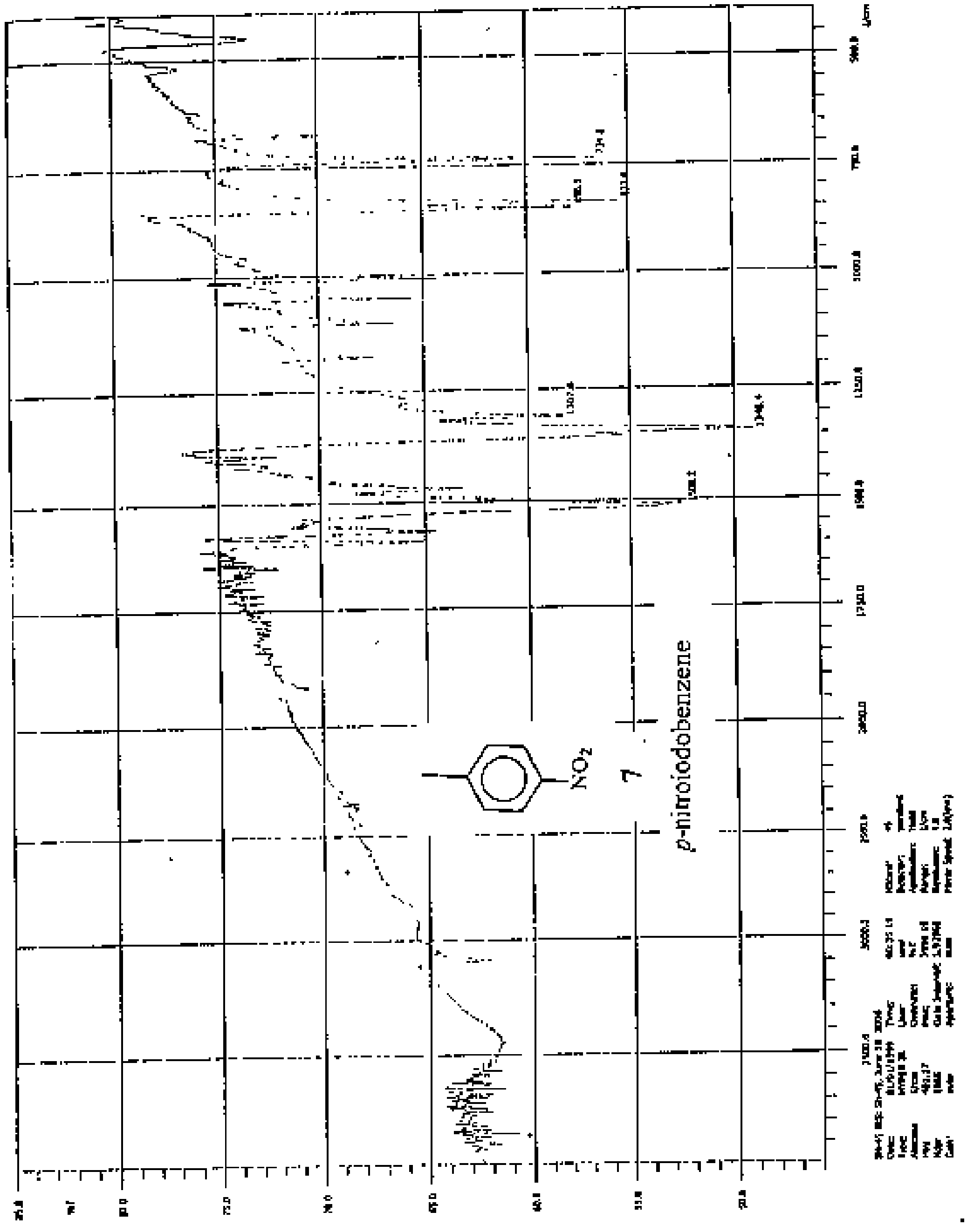
EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
Date_        20070531
Time            11 15
INSTRUM         dpx400
PROBHD   5 mm Multinuc
PULPROG          zg30
TD              32768
SOLVENT         CDCl3
NS                 66
DS                  2
SWH          6410.256 Hz
FIDRES       0.195625 Hz
AQ          2.5559540 sec
RG              322.5
DW             78.000 usec
DE               6.00 usec
TE              310.0 K
D1         1.00000000 sec

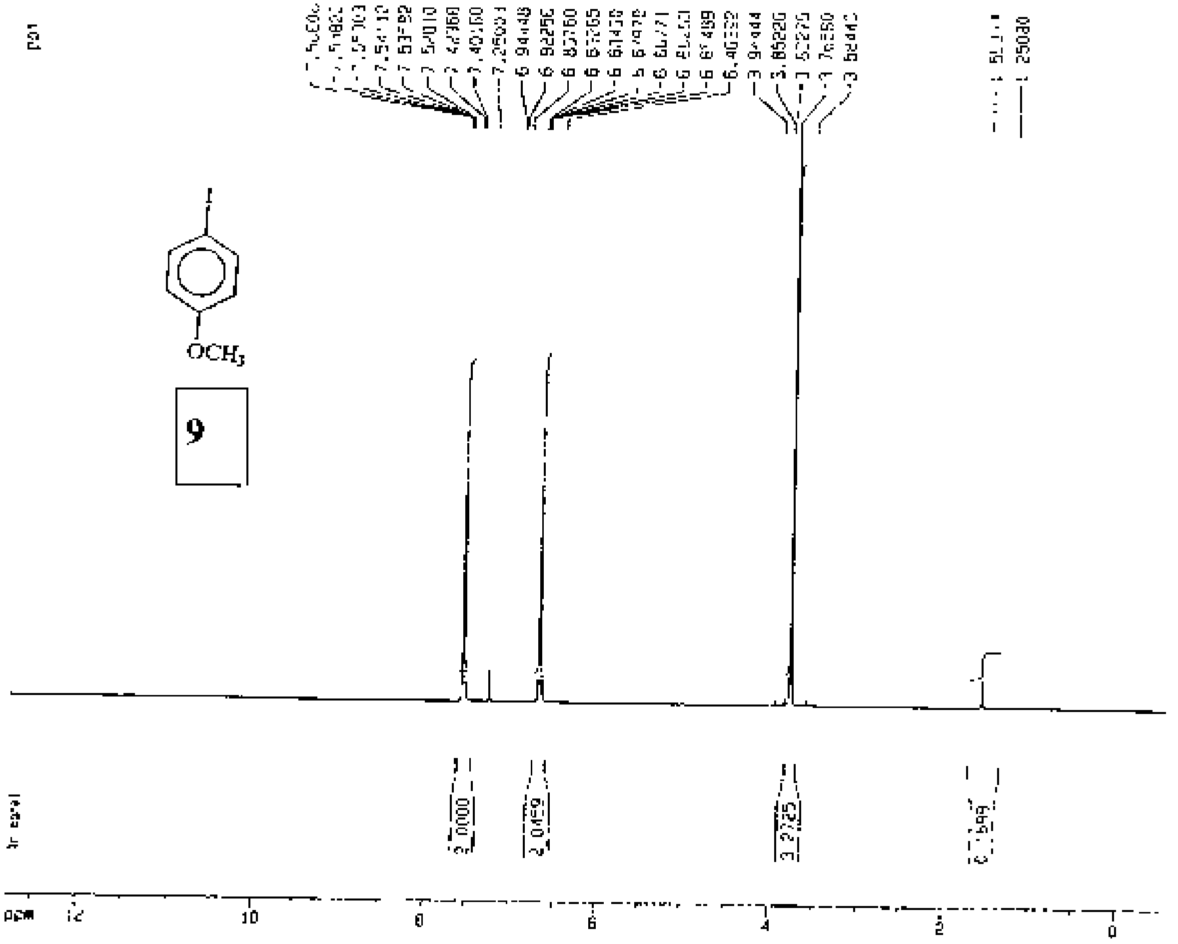
============ CHANNEL f1 ========
NUC1               1H
P1               8.30 usec
PL1             -6.00 dB
SFO1      400.1428010 MHz

F2 - Processing parameters
SI              32768
SF        400.1400123 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.40

1D NMR plot parameters
CX              20.00 cm
F1P            14.015 ppm
F1            5607.64 Hz
F2P            -0.417 ppm
F2            -166.80 Hz
PPMCM         0.72153 ppm/cm
HZCM        288.73203 Hz/cm
```


NO2
7
p-nitroiodobenzene
1348.4
1307.6
1/cm
500.0
750.0
1000.0
1250.0
1500.0
1750.0
2000.0
2500.0
3000.0
3500.0
85.0
80.0
75.0
70.0
65.0
60.0
55.0
50.0

Analytical BCSIR, 1H Spectrum-Sm-23 in CDCl3



9

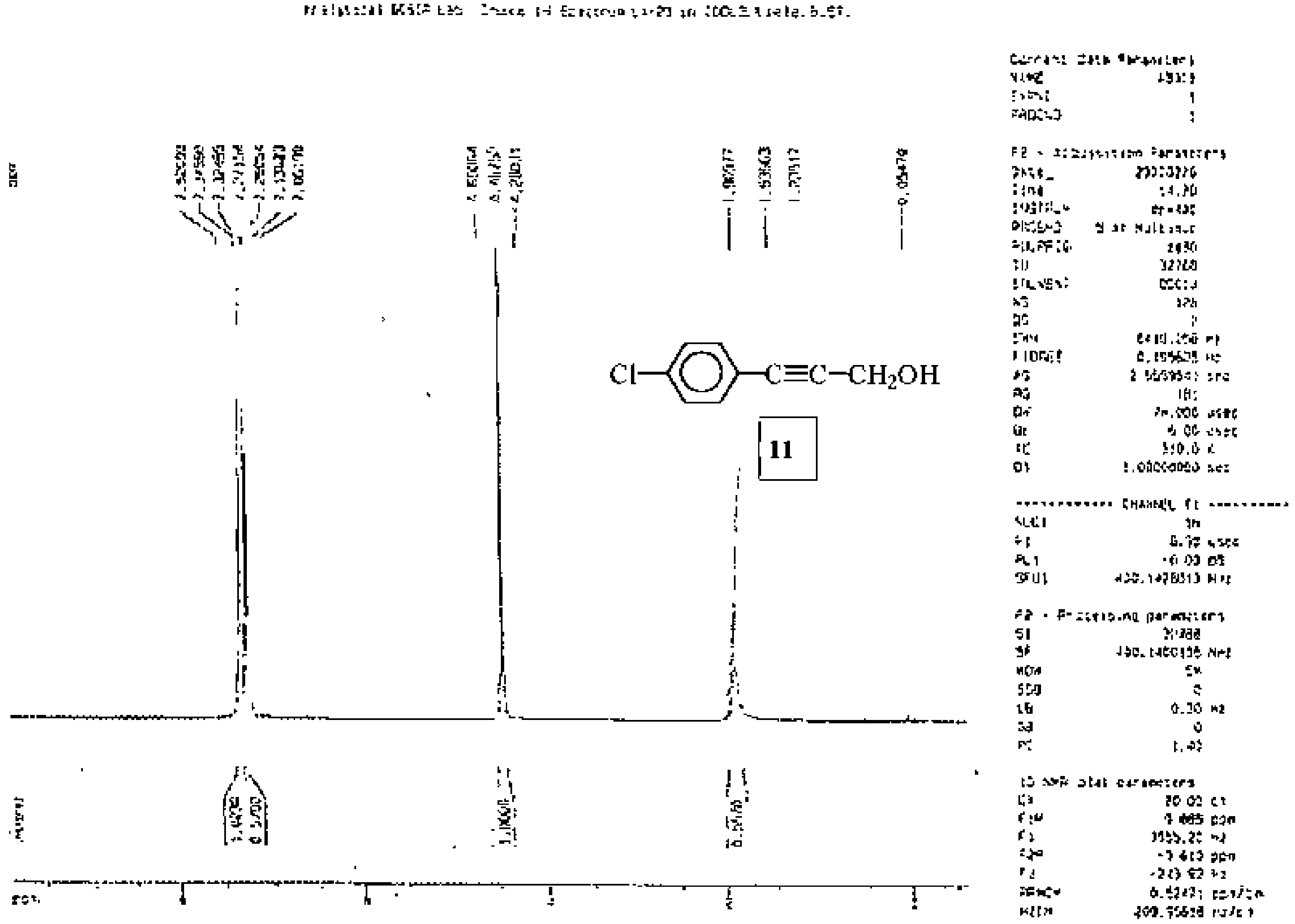
```
Current Data Parameters
NAME             #2477
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20050323
Time             11.05
INSTRUM         dpx400
PROBHD   5 mm Multinuc
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  74
DS                   2
SWH          6410.256 Hz
FIDRES       0.195625 Hz
AQ          2.5559540 sec
RG                 256
DW              78.000 usec
DE                6.00 usec
TE               310.0 K
D1         1.00000000 sec

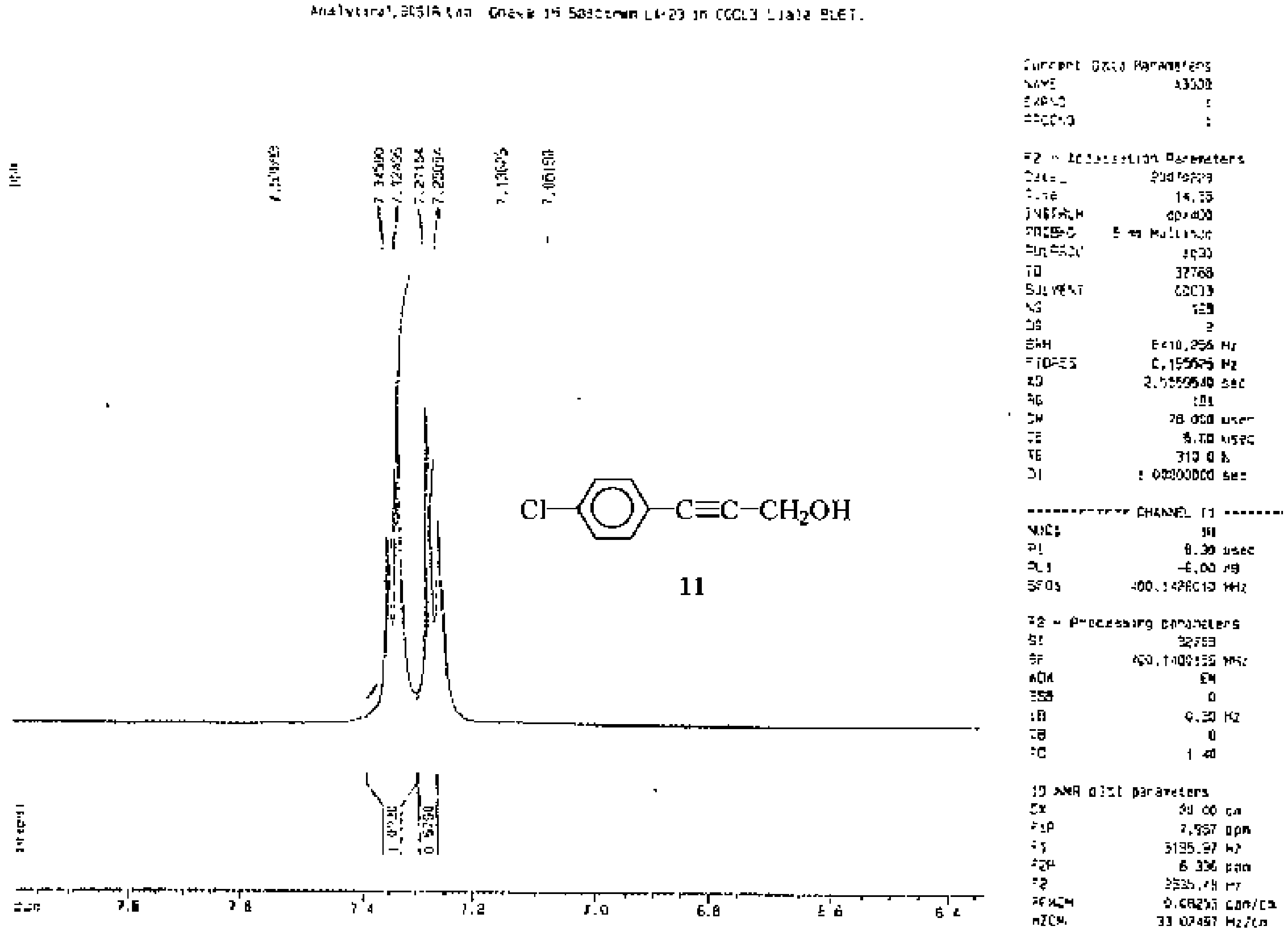
============ CHANNEL f1 ========
NUC1                1H
P1                8.30 usec
PL1              -6.00 dB
SFO1       400.1428010 MHz

F2 - Processing parameters
SI               32768
SF         400.1400130 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.40

1D NMR plot parameters
CX               20.00 cm
F1P             12.781 ppm
F1             5114.03 Hz
F2P             -0.553 ppm
F2             -221.09 Hz
PPMCM          0.66666 ppm/cm
HZCM         266.75592 Hz/cm
```



11



11

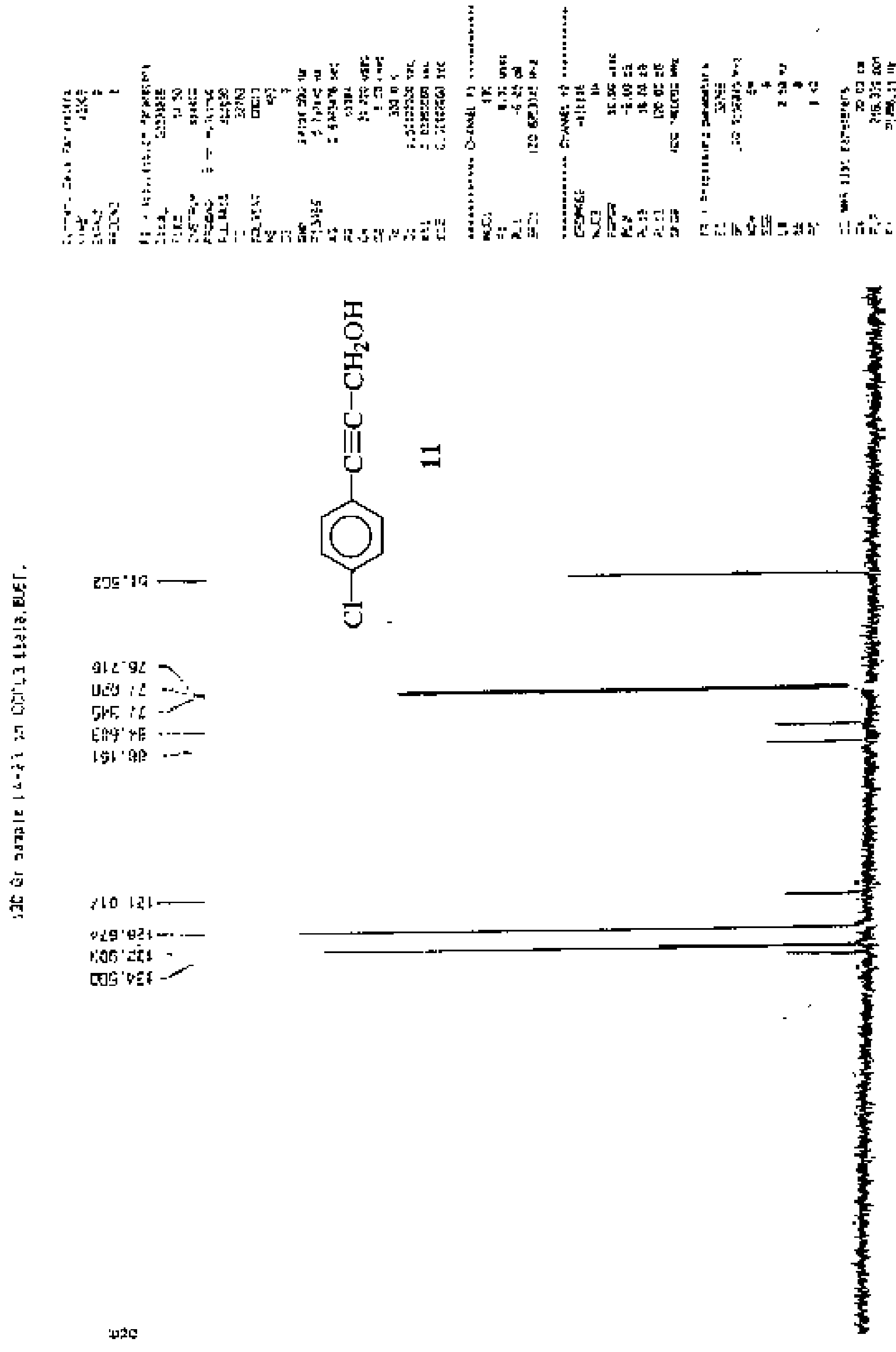
```
Current Data Parameters
NAME            A3500
EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
Date_        20010529
Time            14.35
INSTRUM        dpx400
PROBHD   5 mm Multinuc
PULPROG          zg30
TD              32768
SOLVENT         CDCl3
NS                128
DS                  2
SWH          6410.256 Hz
FIDRES       0.195625 Hz
AQ          2.5559540 sec
RG                101
DW             78.000 usec
DE               6.00 usec
TE              310.0 K
D1         1.00000000 sec

============ CHANNEL f1 ========
NUC1               1H
P1               8.30 usec
PL1             -6.00 dB
SFO1      400.1428013 MHz

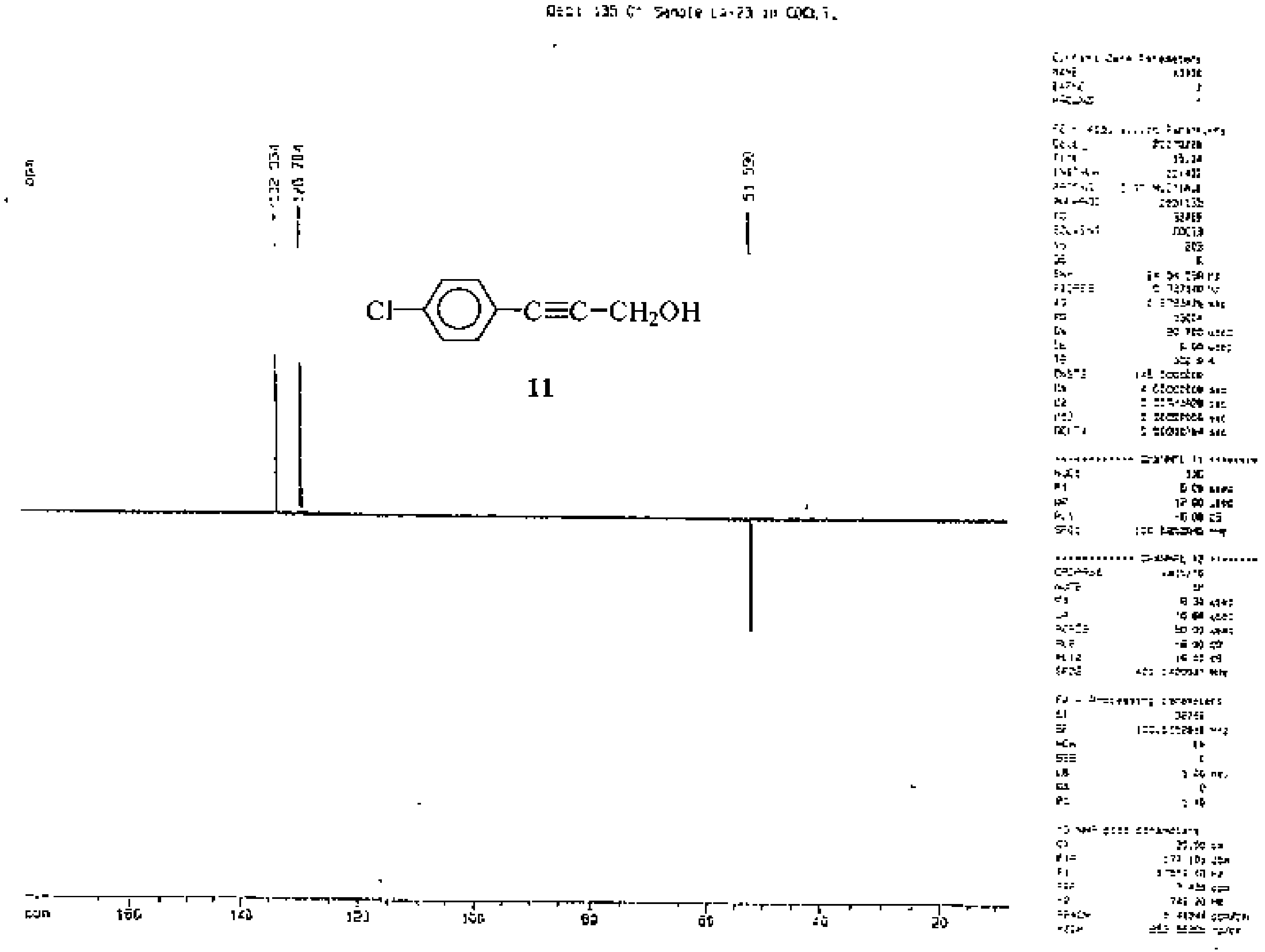
F2 - Processing parameters
SI              32768
SF        400.1400155 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.40

1D NMR plot parameters
CX              20.00 cm
F1P             7.957 ppm
F1            3185.97 Hz
F2P             6.336 ppm
F2            2535.74 Hz
PPMCM         0.08253 ppm/cm
HZCM         33.02457 Hz/cm
```

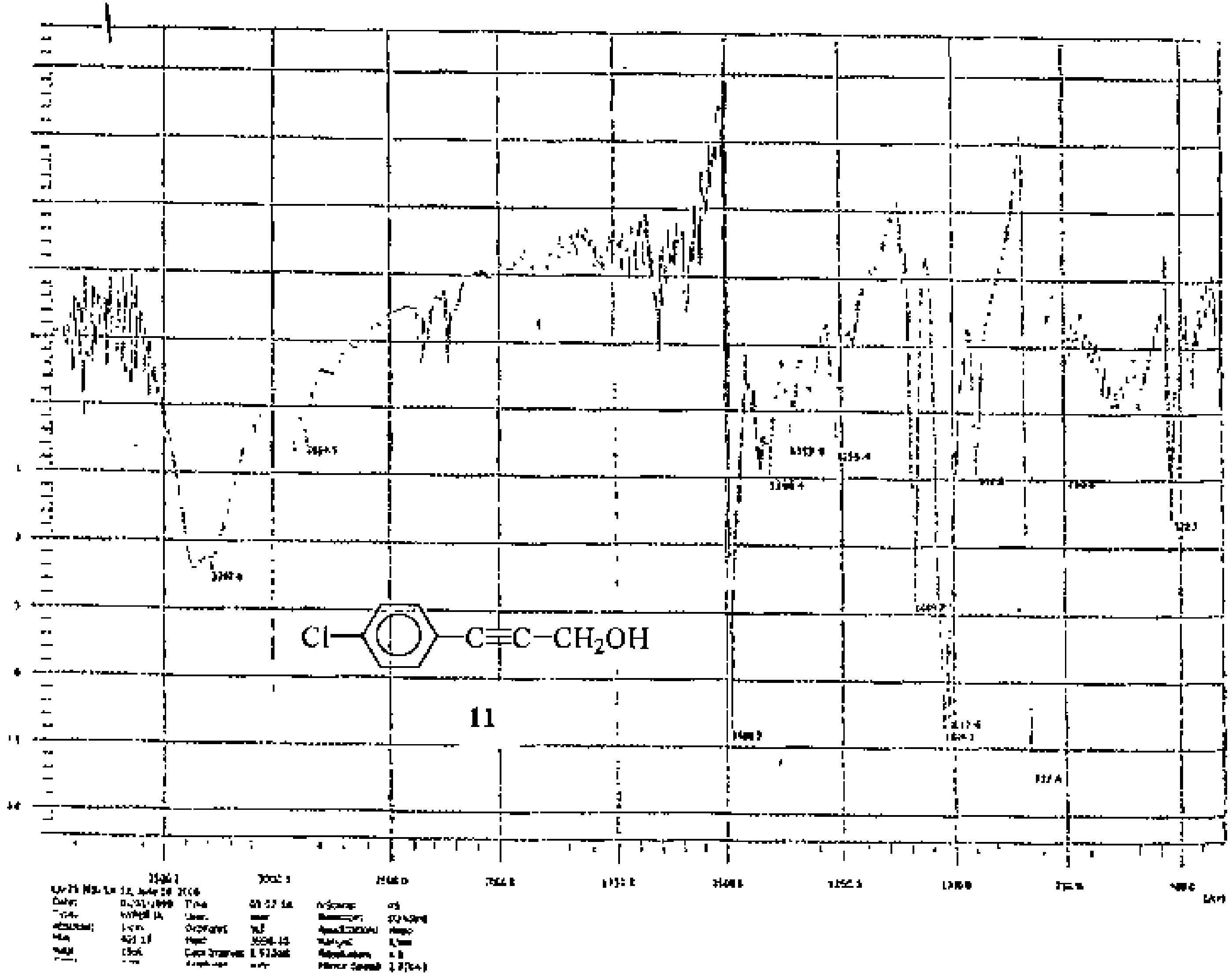

51.502
76.716
77.030
77.345
84.603
88.161
121.017
128.674
132.901
134.500
Cl
C≡C−CH$_2$OH
0
25
50
75
100
125
150
175
200
ppm

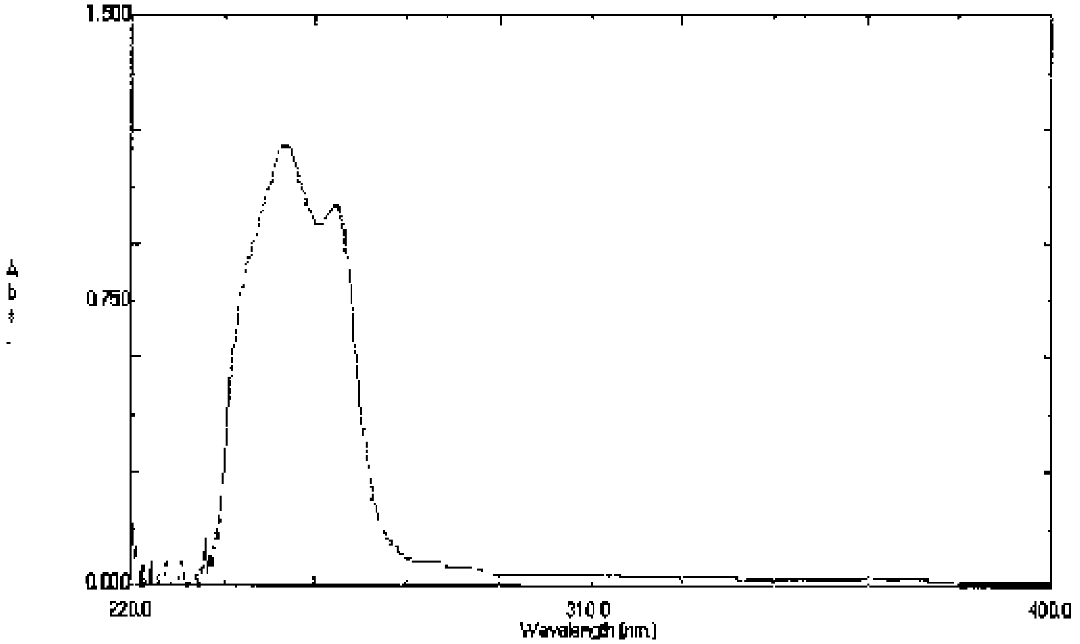
11

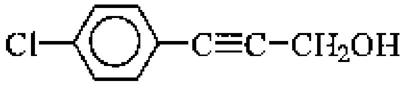
107329


Dept 135 C* Sample LA-23 in CDCl3
ppm
132.934
128.704
51.590
Cl—C6H4—C≡C—CH2OH
11
ppm
160
140
120
100
80
60
40
20

11


Cl–C₆H₄–C≡C–CH₂OH
11





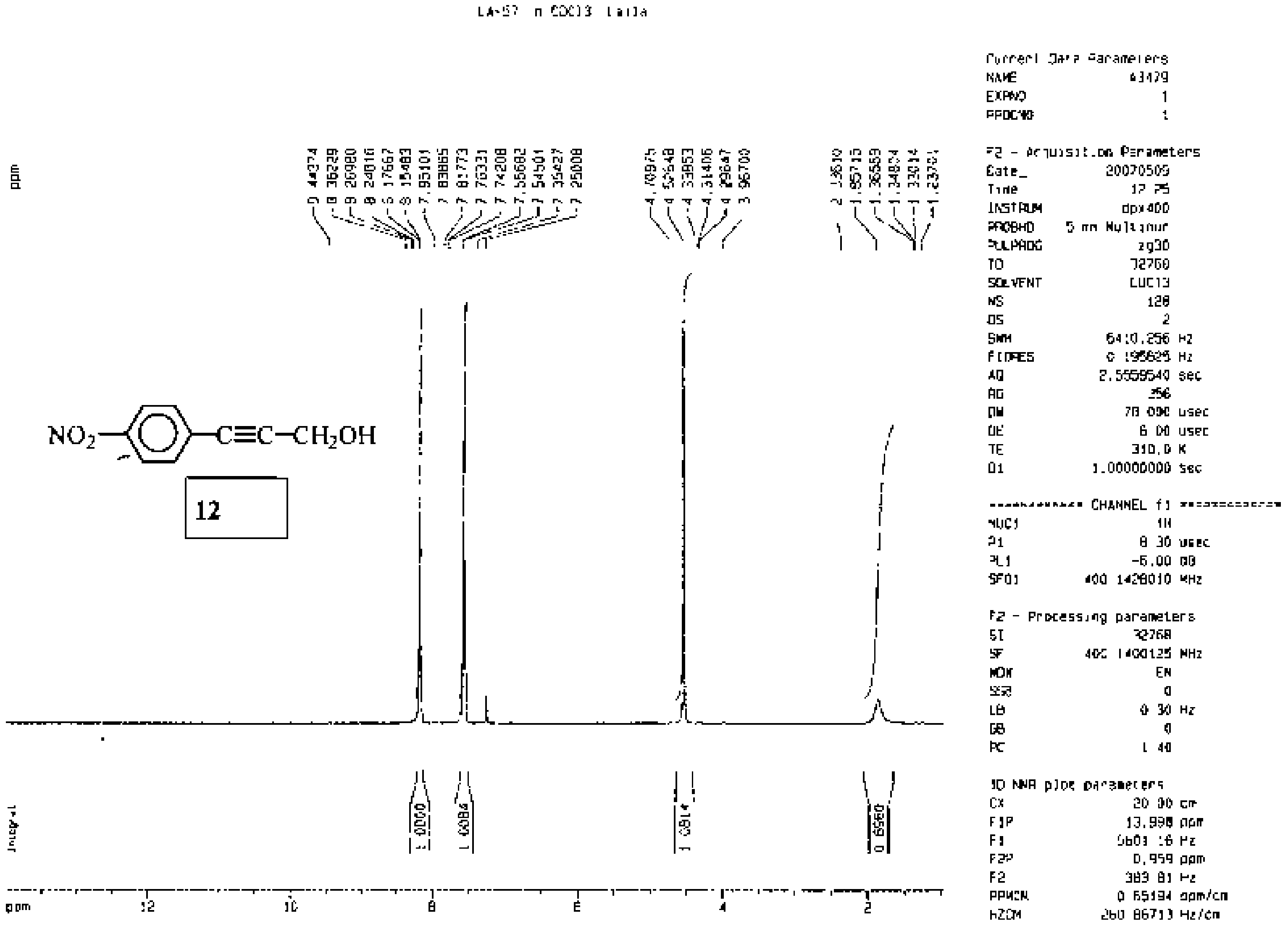
11

File Name: **LA23**

Created: 14:10 10/03/07
Data: Original

Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

No.	Wavelength (nm.)	Abs.
1	307.60	0.0261
2	285.80	0.0465
3	278.40	0.0682
4	259.80	0.9990
5	250.00	1.1609
6	234.20	0.1266



12

```
Current Data Parameters
NAME              43479
EXPNO                 1
PROCNO                1

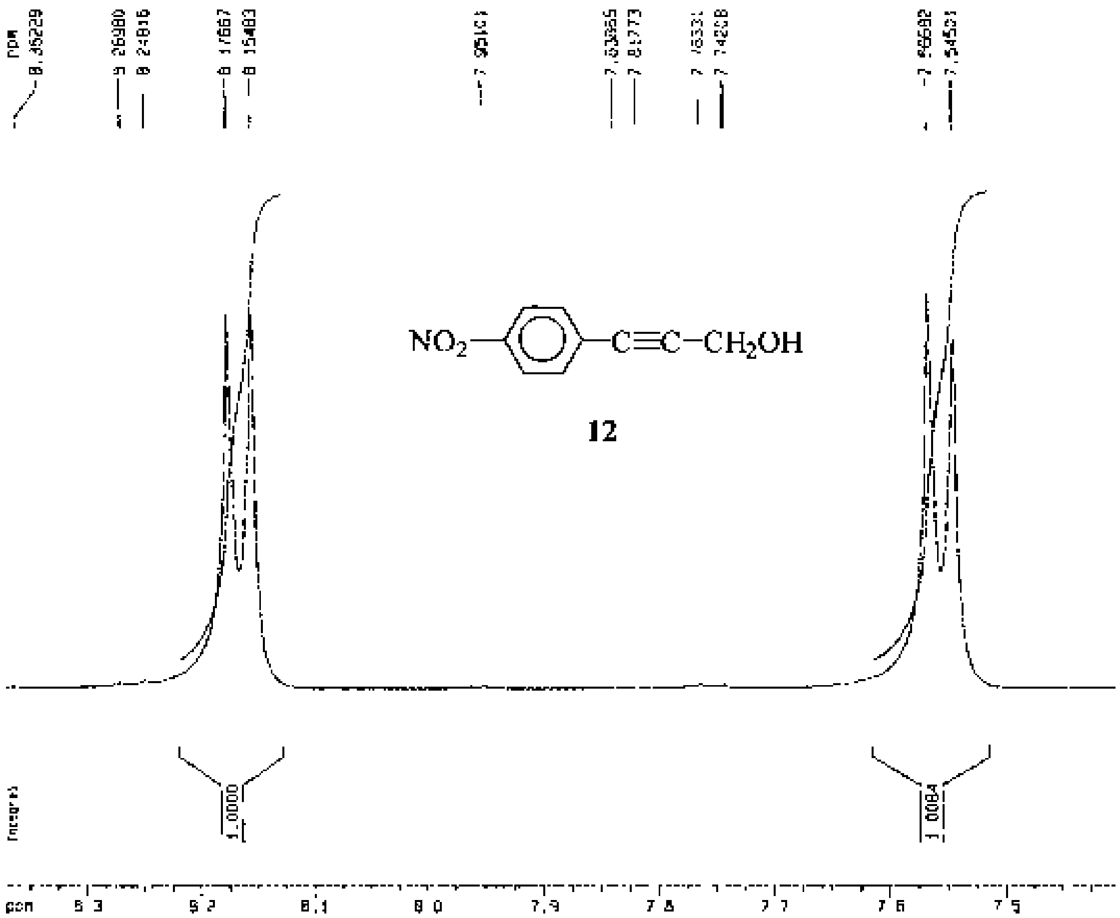
F2 - Acquisition Parameters
Date_          20070509
Time              17 75
INSTRUM          dpx400
PROBHD     5 mm Multinur
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                  128
DS                    2
SWH            6410.256 Hz
FIDRES         0 195625 Hz
AQ            2.5559540 sec
RG                  256
DW               78 000 usec
DE                 6 00 usec
TE                310,0 K
D1           1.00000000 sec

============ CHANNEL f1 ============
NUC1                 1H
P1                 8 30 usec
PL1               -6.00 dB
SFO1       400 1428010 MHz

F2 - Processing parameters
SI                32768
SF         400 1400125 MHz
WDW                  EM
SSB                   0
LB                 0 30 Hz
GB                    0
PC                 1 40

1D NMR plot parameters
CX                20 00 cm
F1P              13,998 ppm
F1              5603 16 Hz
F2P               0,959 ppm
F2               383 81 Hz
PPMCM           0 65194 ppm/cm
HZCM          260 86713 Hz/cm
```

LA-57 in CDCl3 Lara



12

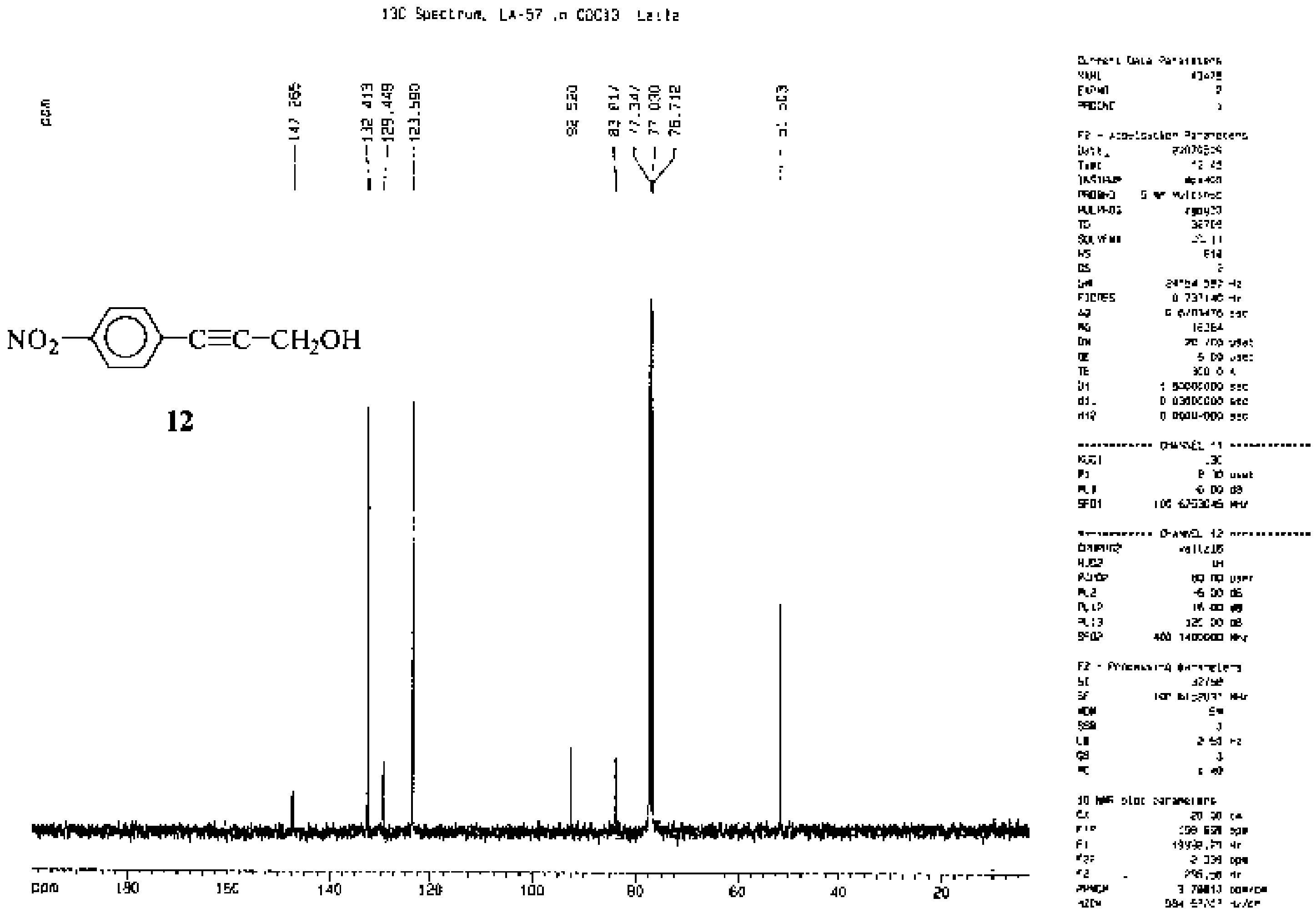
```
Current Data Parameters
NAME             A3479
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20070509
Time             12 25
INSTRUM         dpx400
PROBHD   5 mm Multinuc
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                 128
DS                   2
SWH           6410 256 Hz
FIDRES        0 195625 Hz
AQ           2.5559540 sec
RG                 256
DW              78 000 usec
DE                6.00 usec
TE               300 0 K
D1          1.00000000 sec

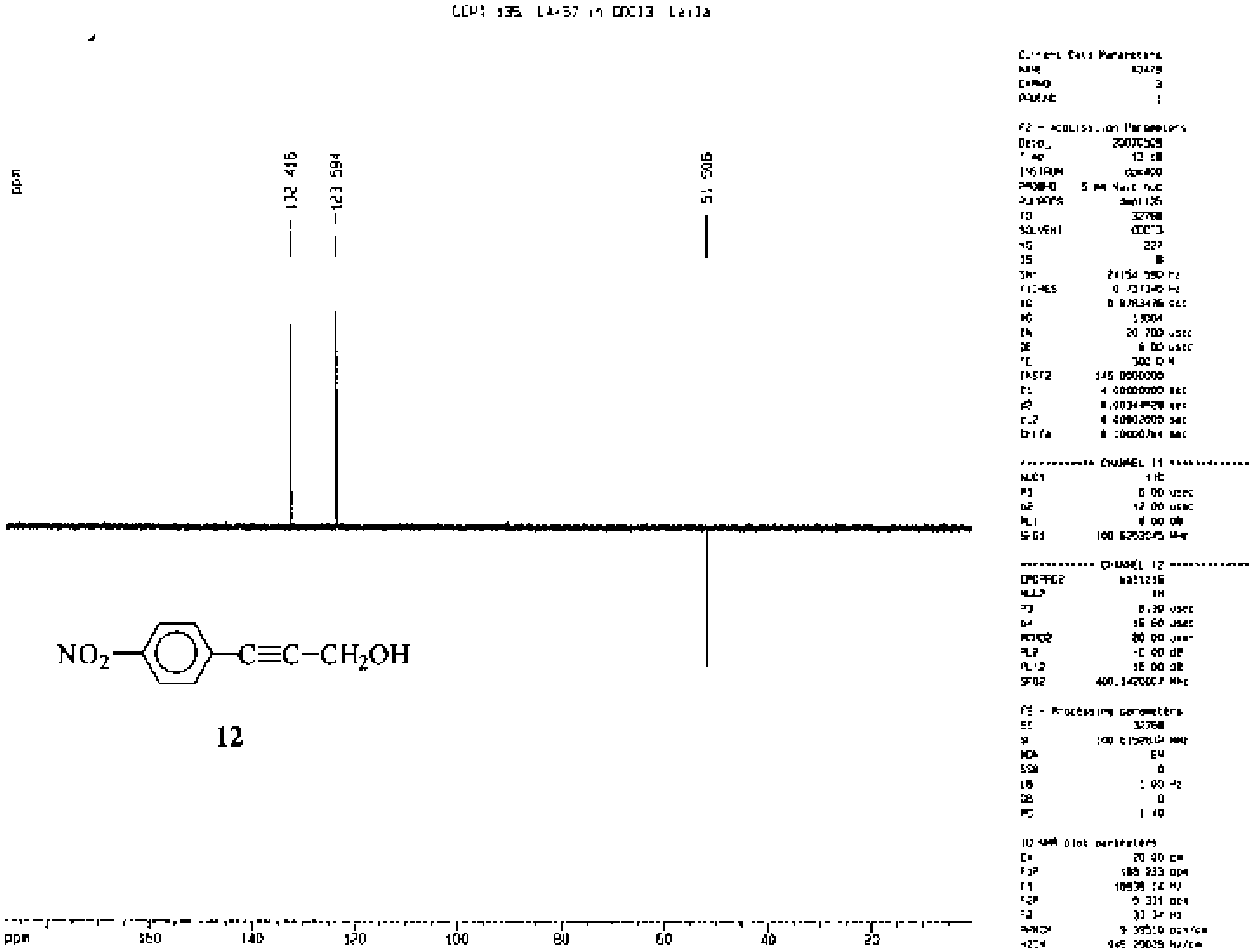
============ CHANNEL f1 ============
NUC1                1H
P1                8 30 usec
PL1              -6.00 dB
SFO1       400 1428013 MHz

F2 - Processing parameters
SI               32768
SF         400.1400125 MHz
WDW                 EM
SSB                  0
LB                0 30 Hz
GB                   0
PC                1 40

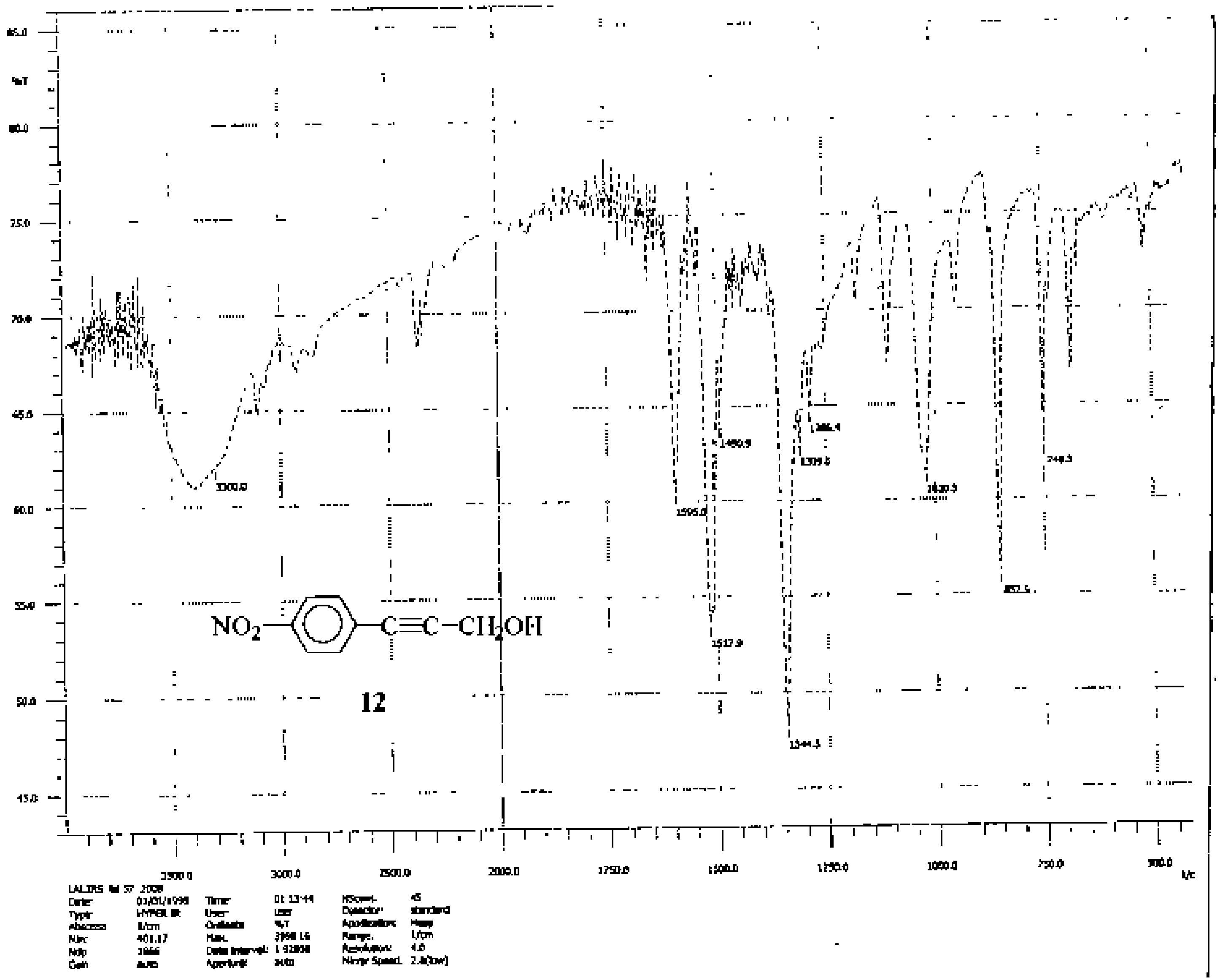
1D NMR plot parameters
CX               20 00 cm
F1P              8.372 ppm
F1             3350 05 Hz
F2P              7 404 ppm
F2             2962 55 Hz
PPMCM          0 04842 ppm/cm
HZCM          19.37496 Hz/cm
```


13C Spectrum, LA-57 in CDCl3 Leila
ppm
147.265
132.413
129.449
123.590
92.520
83.617
77.347
77.030
76.712
51.563
200
180
160
140
120
100
80
60
40
20
ppm
NO2
C≡C−CH2OH

12

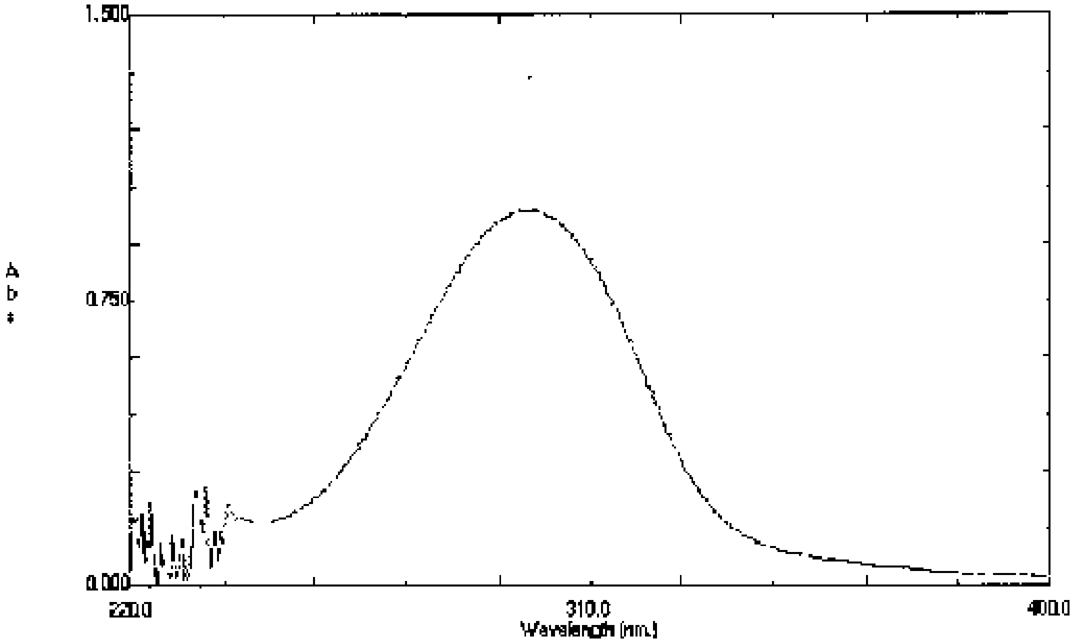

DEPT 135 LA-57 in CDCl3 Leila
132.416
123.594
51.506
ppm
NO2
C≡C−CH2OH
Current Data Parameters
F2 - Acquisition Parameters
INSTRUM spect
SOLVENT CDCl3
CHANNEL f1
NUC1 13C
SFO1 100.6253045 MHz
CHANNEL f2
SFO2 400.1420007 MHz
F2 - Processing parameters
1D NMR plot parameters
ppm 160 140 120 100 80 60 40 20

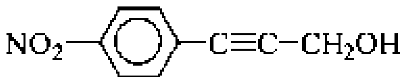
12



12

LALIRS Vol 57 2058
Date: 01/01/1998 Time: 01 13:44 #Scan: 45
Type: HYPER IR User: User Detector: standard
Abscissa: 1/cm Ordinate: %T Apodization: Happ
Min: 401.17 Max: 3958.16 Range: 1/cm
Ndp: 1866 Data Interval: 1.92808 Resolution: 4.0
Gain: auto Aperture: auto Mirror Speed: 2.8(low)





12

File Name: LA57

Created: 14:05 10/03/07
Data: Original

Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

No.	Wavelength (nm.)	Abs.
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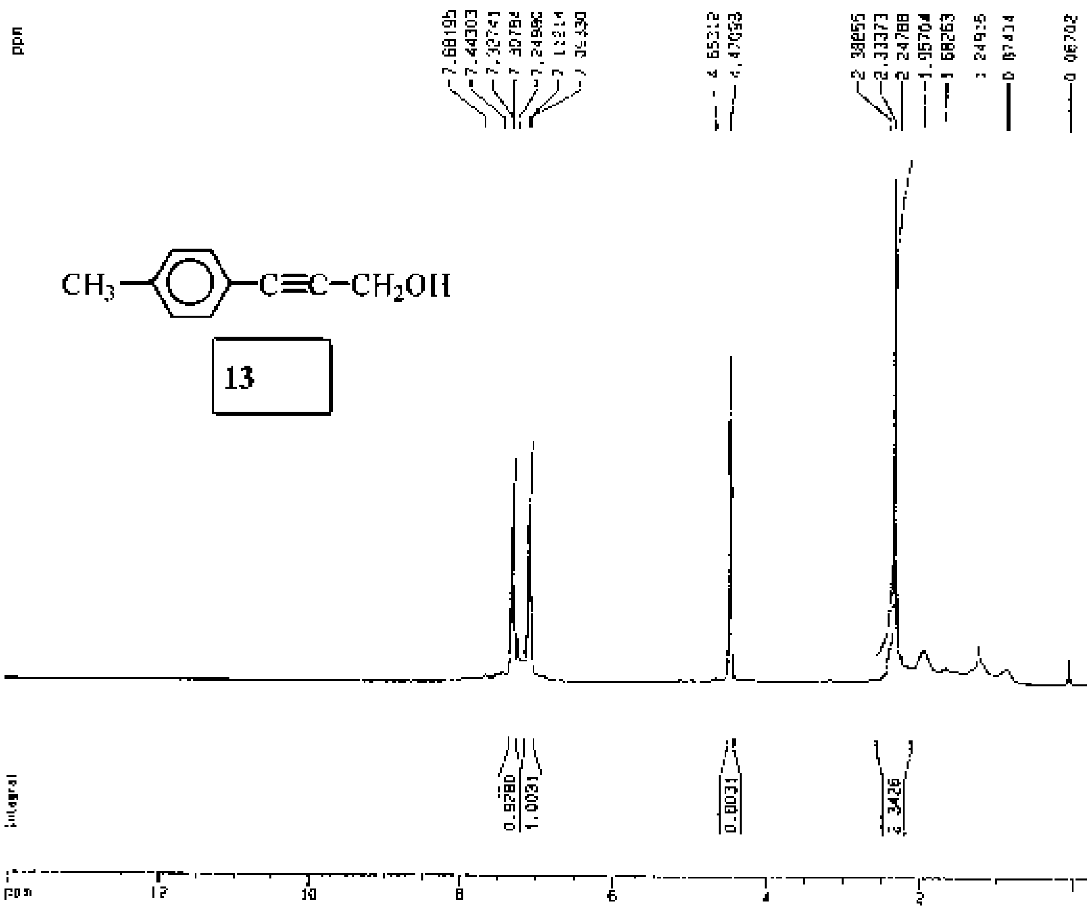
2	238.80	0.2137
3	234.60	0.2585

Analytical BCSIR, 1H Spectrum LA-42 in CDCl3 Laila, BUET



13

```
Current Data Parameters
NAME               A3222
EXPNO                  1
PROCNO                 1

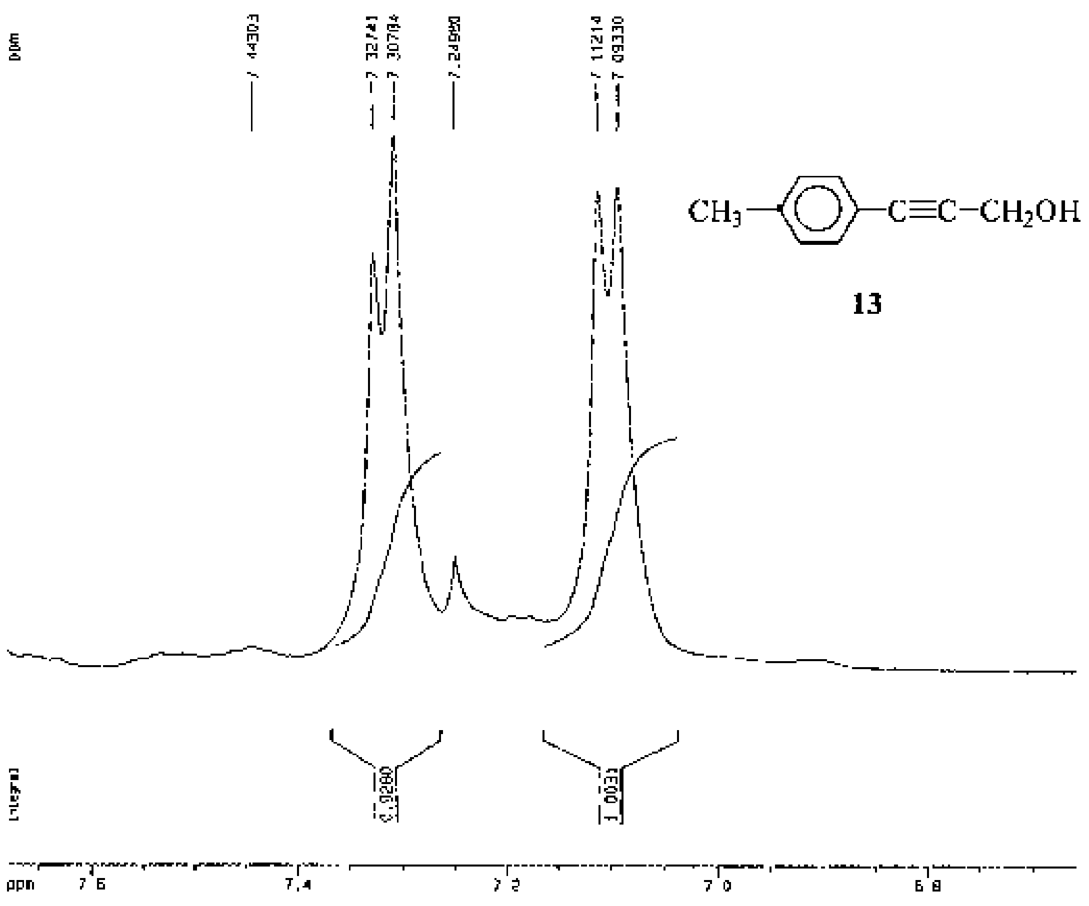
F2 - Acquisition Parameters
Date_           20070121
Time                8 49
INSTRUM           dpx400
PROBHD     5 mm Multinuc
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                   128
DS                     2
SWH             6410 256 Hz
FIDRES          0.195625 Hz
AQ             2 5559540 sec
RG                  90.5
DW                78 000 usec
DE                  5.00 usec
TE                 310 0 K
D1            1 00000000 sec

============ CHANNEL f1 ============
NUC1                  1H
P1                  8.30 usec
PL1                -6.00 dB
SFO1         400.1428010 MHz

F2 - Processing parameters
SI                 32768
SF           400.1400126 MHz
WDW                   EM
SSB                    0
LB                  0 30 Hz
GB                     0
PC                  1 40

1D NMR plot parameters
CX                 20 00 cm
F1P               14 049 ppm
F1               5621.56 Hz
F2P               -0 180 ppm
F2                -71.94 Hz
PPMCM            0 71144 ppm/cm
HZCM           284 67490 Hz/cm
```

Analytical 90STA 1H Spectrum, 14-42 in CDCl3, Layla, BUET



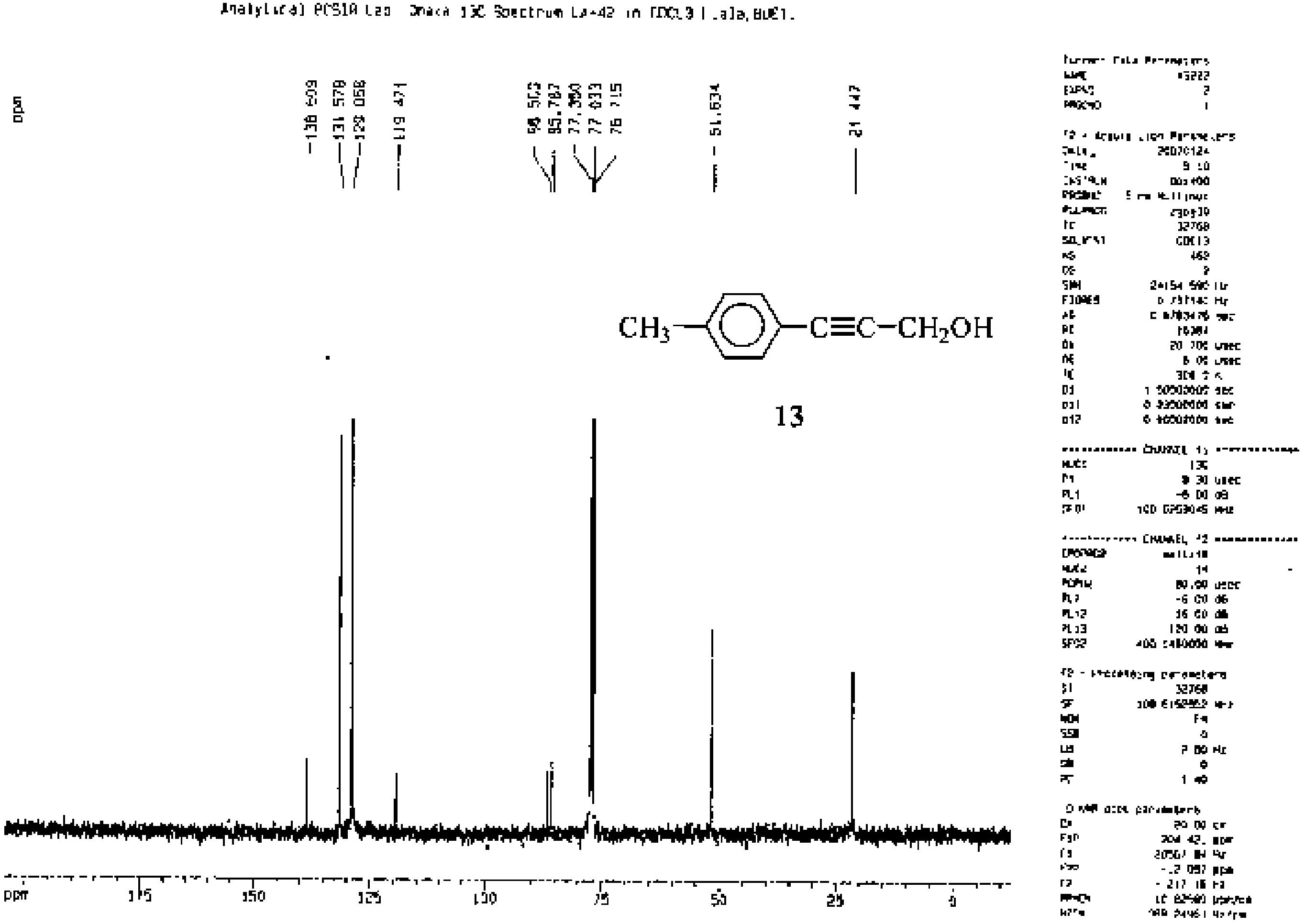
```
Current Data Parameters
NAME              A3722
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20070121
Time               3 49
INSTRUM          dpx400
PROBHD     5 mm Multinuc
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                  128
DS                    2
SWH            6410 256 Hz
FIDRES         0 195625 Hz
AQ            2.5559540 sec
RG                 90.5
DW               78 000 usec
DE                 6 00 usec
TE                300 0 K
D1           1 00000000 sec

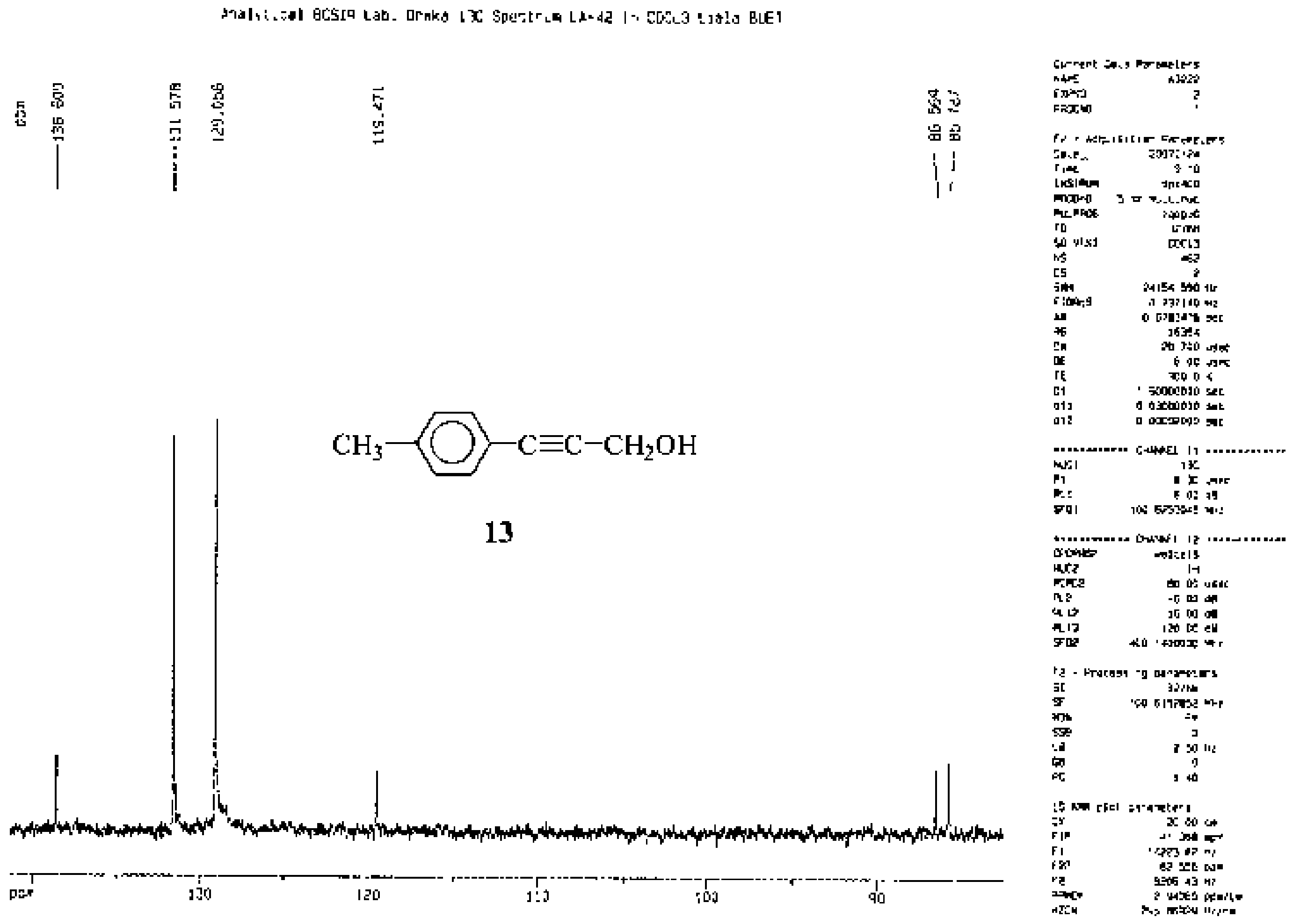
============ CHANNEL f1 ============
NUC1                 1H
P1                 8 30 usec
PL1               -6 00 dB
SFO1        400.1428010 MHz

F2 - Processing parameters
SI                32768
SF          400.1400126 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1 40

1D NMR plot parameters
CX                20 00 cm
F1P               7 681 ppm
F1              3073 64 Hz
F2P               6 659 ppm
F2              2664 48 Hz
PPMCM           0 05113 ppm/cm
HZCM           20 45772 Hz/cm
```

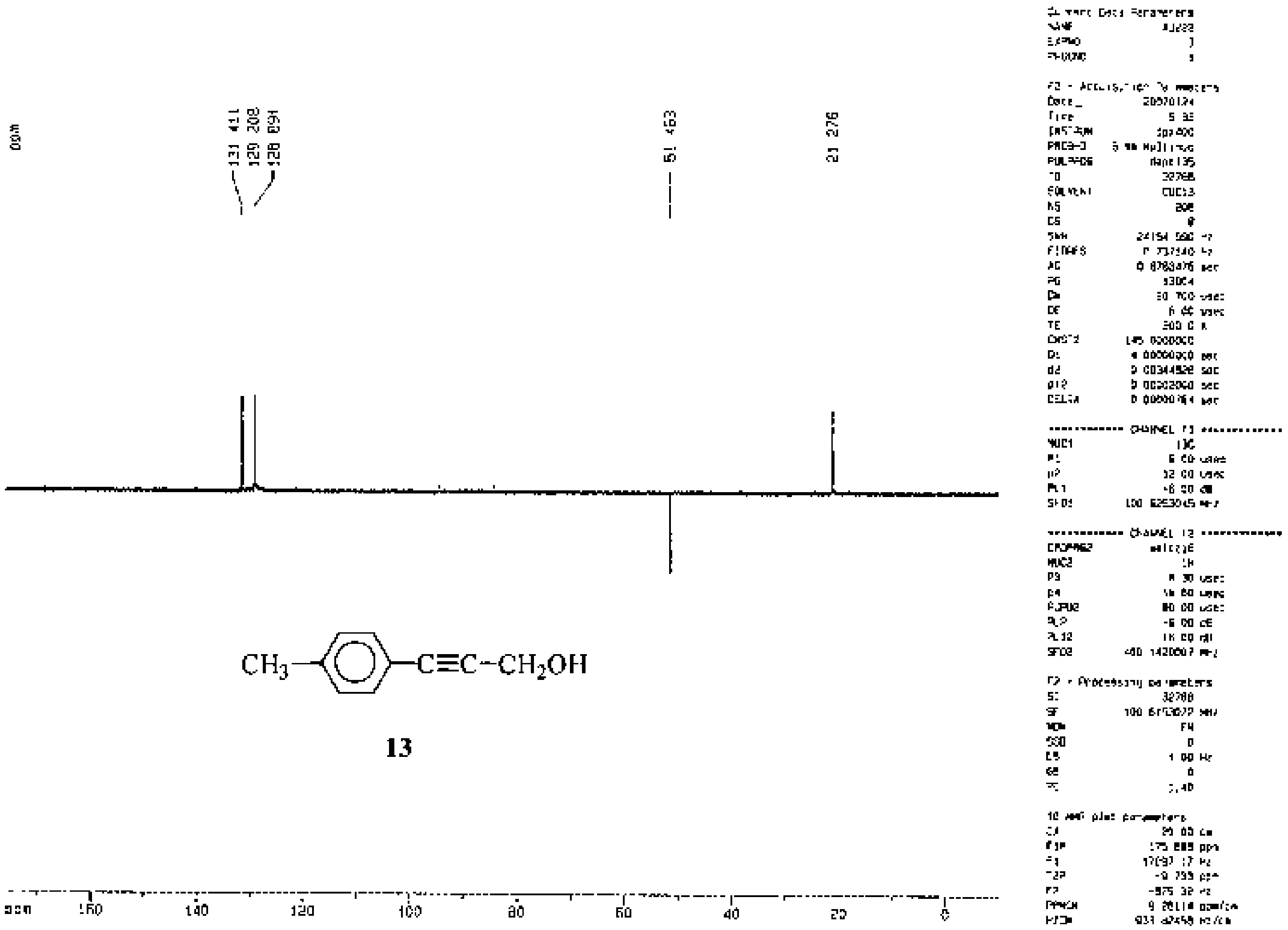

Analytical PCSIR Lab Dhaka 13C Spectrum La-42 in CDCl3 | Lala, BUET.
ppm
138.609
131.578
129.058
119.471
98.503
85.787
77.350
77.033
76.715
51.634
21.447
CH_3
$C{\equiv}C{-}CH_2OH$
ppm
175
150
125
100
75
50
25
0
Current Data Parameters
NAME #3222
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070124
Time 9.10
INSTRUM DDs400
PROBHD 5 mm Multinuc
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 462
DS 2
SWH 24154.590 Hz
FIDRES 0.737140 Hz
AQ 0.6783476 sec
RG 16384
DW 20.700 usec
DE 6.00 usec
TE 300.2 K
D1 1.50000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 9.30 usec
PL1 -6.00 dB
SFO1 100.6253045 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 16.00 dB
PL13 120.00 dB
SFO2 400.1480000 MHz
F2 - Processing parameters
SI 32768
SF 100.6152952 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 204.421 ppm
F1 20567.84 Hz
F2P -2.097 ppm
F2 -217.16 Hz
PPMCM 10.32560 ppm/cm
HZCM 1038.24461 Hz/cm

13

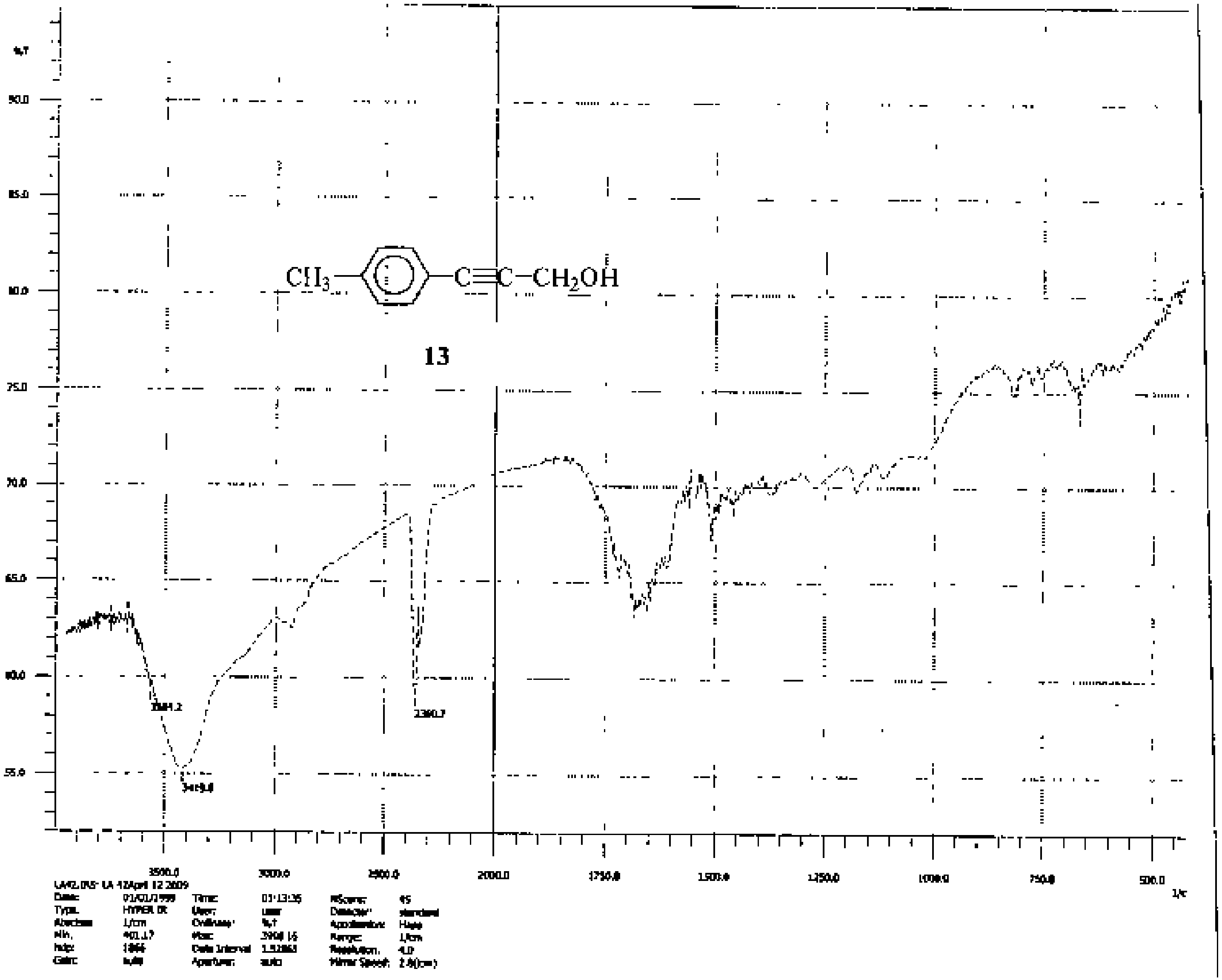

Analytical BCSIR Lab. Dhaka 13C Spectrum LA-42 in CDCL3 Lipid BUET
ppm
136.809
131.578
129.066
119.471
86.564
85.727
$CH_3-C_6H_4-C{\equiv}C-CH_2OH$
ppm
130
120
110
100
90
Current Data Parameters
NAME A3929
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071124
Time 9.10
INSTRUM spect
PULPROG zgpg30
TD 65536
SOLVENT CDCL3
NS 462
DS 2
SWH 24154.590 Hz
AQ 0.6782976 sec
DE 6.00 usec
TE 300.0 K
D1 1.50000000 sec
======== CHANNEL f1 ========
NUC1 13C
SFO1 100.6253945 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
SFO2 400.1420000 MHz
F2 - Processing parameters
SI 32768
SF 100.6127852 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F2 9206.43 Hz

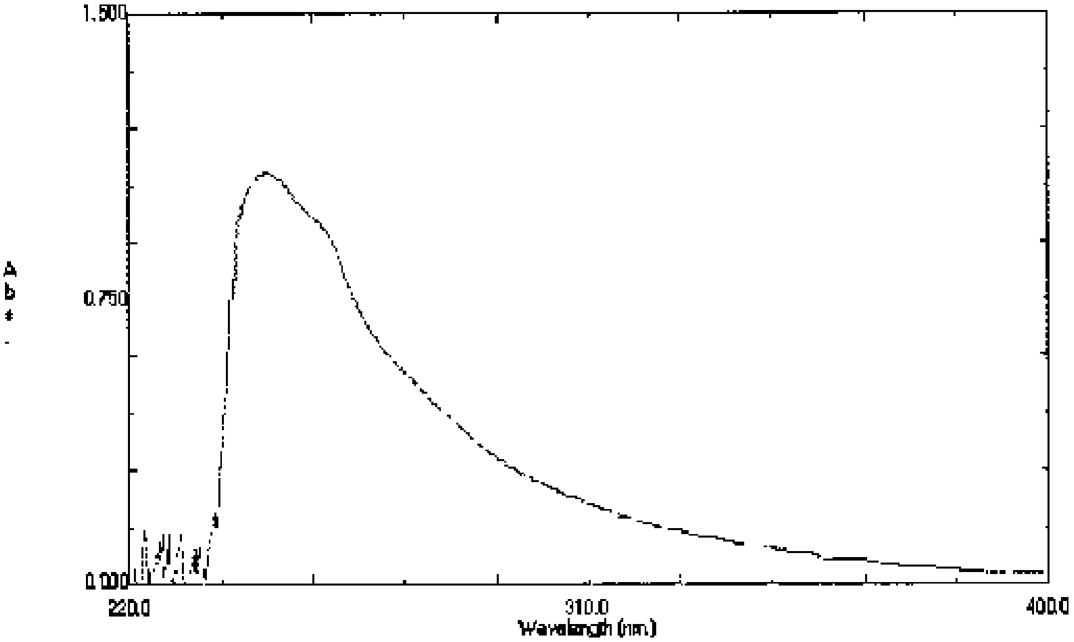
13

Dept.135 of Sample LA-42 in CDCl3

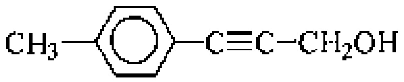


13





File Name: LA42



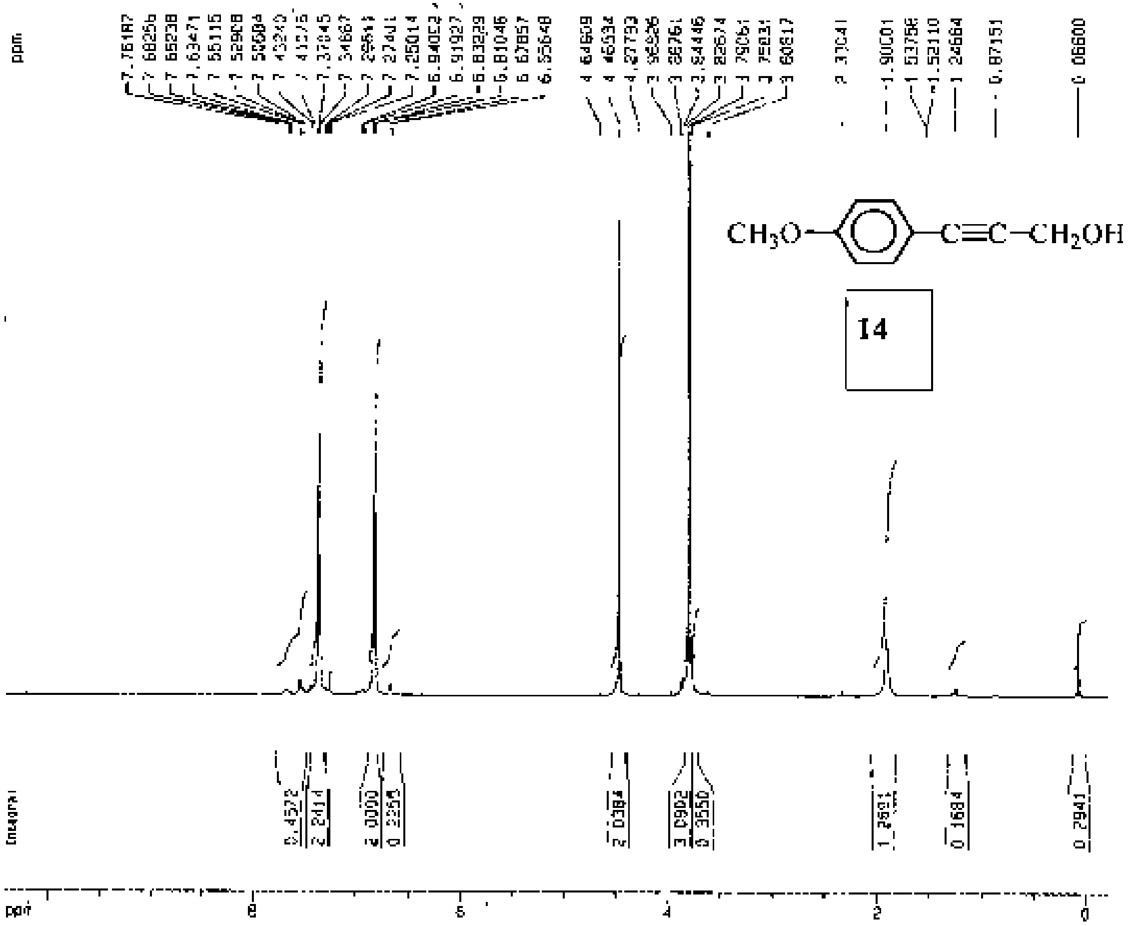
13

Created: 14:23 10/03/07
Data: Original

Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

No.	Wavelength (nm.)	Abs.
1	359.00	0.0685
2	247.00	1.0806
3	232.60	0.0958
4	223.00	0.1448

Analytical BCSIR Lab Dhaka 1H Spectrum I4-30 in CDCl3 Lipla BUET



I4

```
Current Data Parameters
NAME                  43557
EXPNO                     1
PROCNO                    1

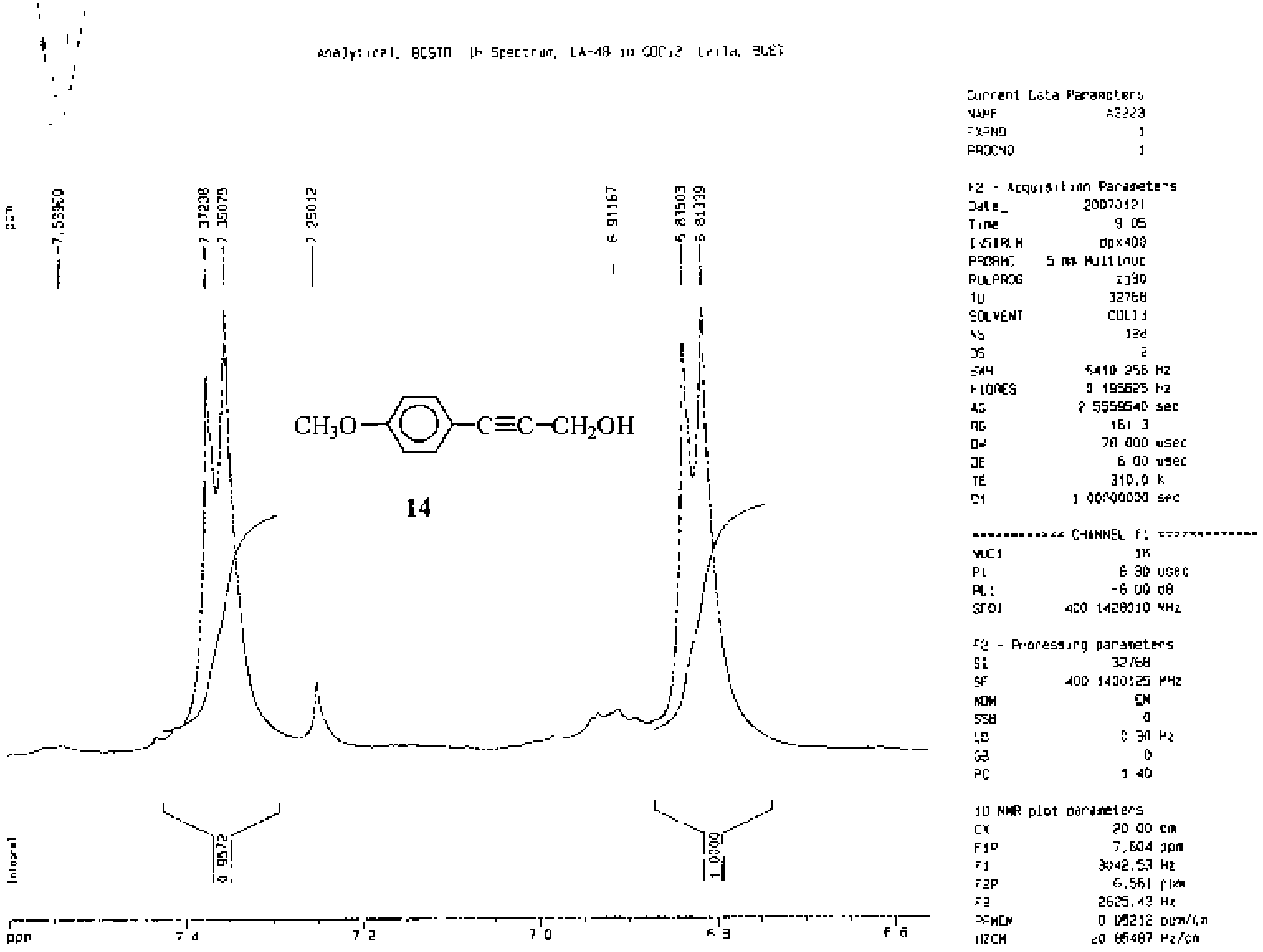
F2 - Acquisition Parameters
Date_              20061226
Time                  14 76
INSTRUM              dpx400
PROBHD     5 mm Multinuc
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                      128
DS                        2
SWH               6410 256 Hz
FIDRES            0 195625 Hz
AQ               2 5559540 sec
RG                    203 2
DW                 78 000 usec
DE                   6 00 usec
TE                  310.0 K
D1            . 00000000 sec

============ CHANNEL f1 ============
NUC1                     1H
P1                   6 30 usec
PL1                 -6 00 dB
SFO1          400.1428010 MHz

F2 - Processing parameters
SI                    32768
SF            400.1400124 MHz
WDW                      EM
SSB                       0
LB                     0 30 Hz
GB                        0
PC                     1 40

1D NMR plot parameters
CX                    20 00 cm
F1P                 10 416 ppm
F1                 4157 95 Hz
F2P                 -0 213 ppm
F2                  -55 27 Hz
PPMCM              0 53147 ppm/cm
HZCM             212 66093 Hz/cm
```

Analytical, BCSTD 1H Spectrum, LA-48 in CDCl3 Leila, BLEI



14

```
Current Data Parameters
NAME             A2223
EXPNO                1
PROCNO               1

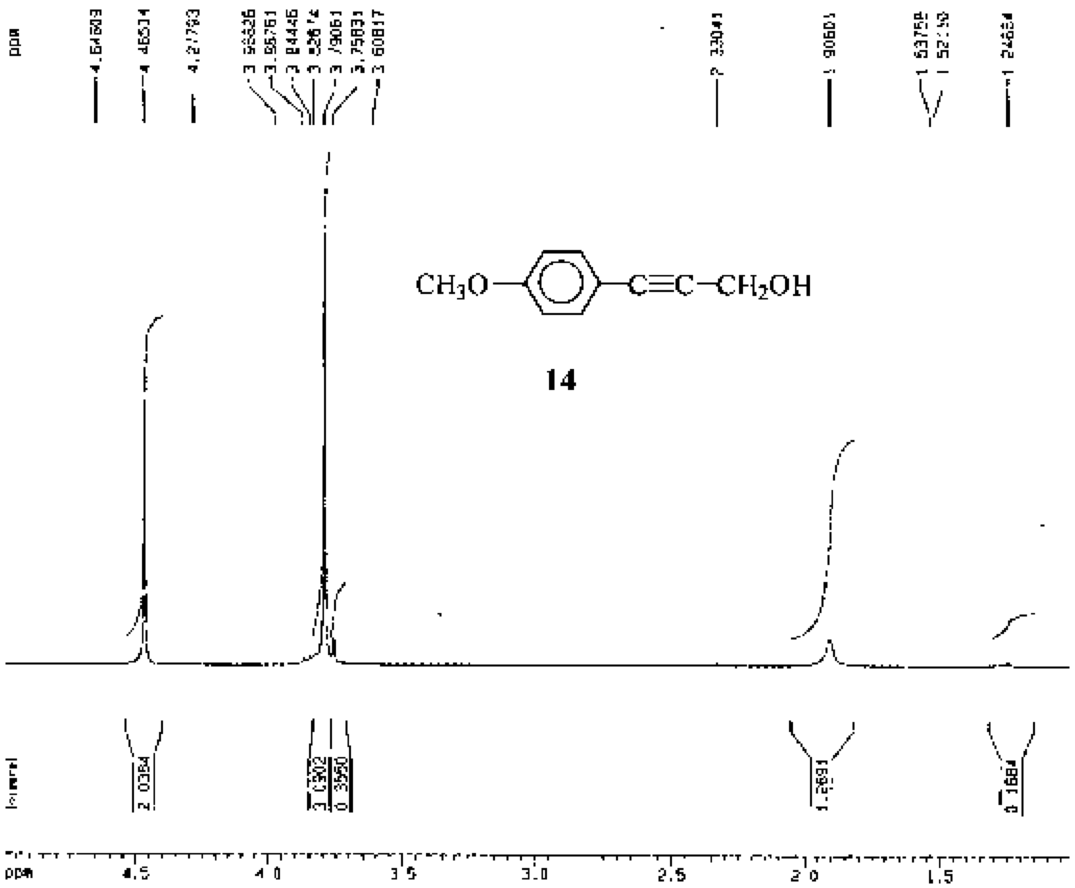
F2 - Acquisition Parameters
Date_          20070121
Time               9.05
INSTRUM          dpx400
PROBHD    5 mm Multinuc
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                  128
DS                    2
SWH         5410.256 Hz
FIDRES      0.165625 Hz
AQ        3.0277540 sec
RG                161.3
DW           78.000 usec
DE             6.00 usec
TE              310.0 K
D1       1.00000000 sec

============ CHANNEL f1 ============
NUC1                 1H
P1             6.30 usec
PL1            -6.00 dB
SFO1       400.1428010 MHz

F2 - Processing parameters
SI                32768
SF         400.1400125 MHz
WDW                  EM
SSB                   0
LB              0.30 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX             20.00 cm
F1P           7.604 ppm
F1           3042.53 Hz
F2P           6.561 ppm
F2           2625.43 Hz
PPMCM       0.05212 ppm/cm
HZCM       20.85487 Hz/cm
```

Analytical,BCSIR lab Dhaka 1H Spectrum La-30 in CDCL3,Liala,BUET



14

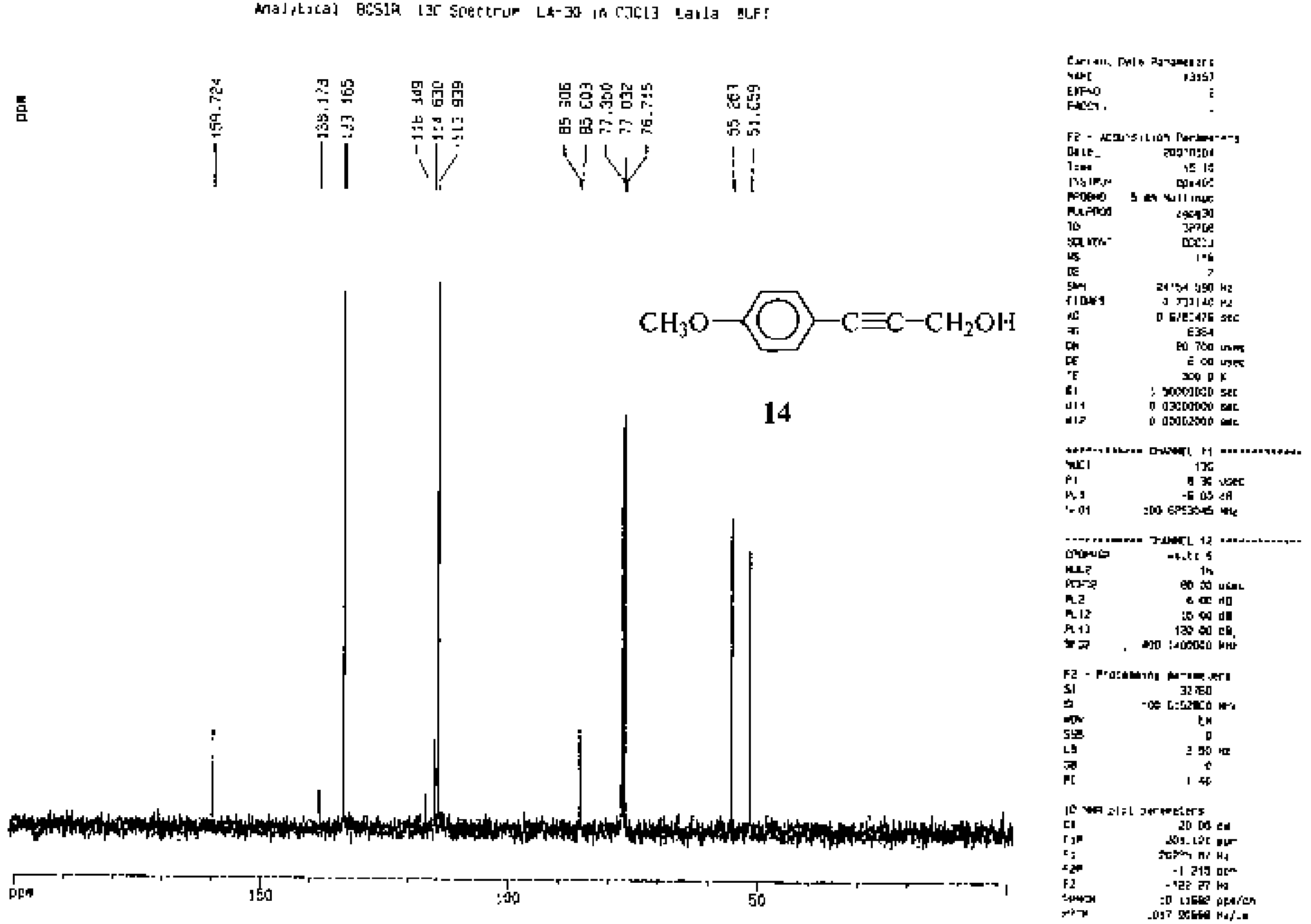
```
Current Data Parameters
NAME              AJ157
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20061226
Time              14 26
INSTRUM          dpx400
PROBHD     5 mm Multinu
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                  128
DS                    2
SWH          6410 256 Hz
FIDRES       0 195625 Hz
AQ          2 5559540 sec
RG                203 2
DW             78 000 usec
DE               6 00 usec
TE              310 0 K
D1         1 00000000 sec

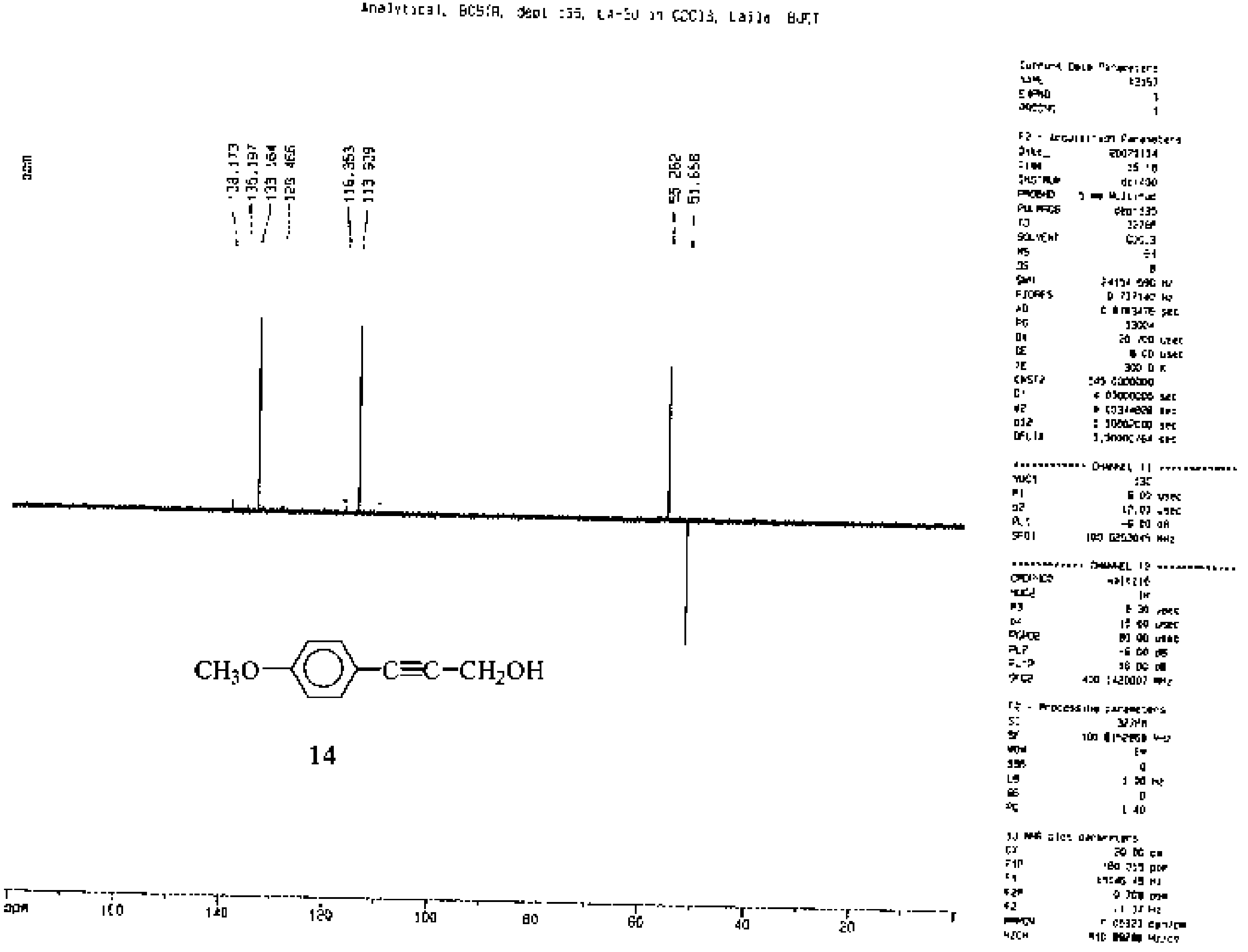
============ CHANNEL f1 ============
NUC1                 1H
P1               8 30 usec
PL1             -6 00 dB
SFO1      400 1428010 MHz

F2 - Processing parameters
SI                32768
SF         400.1400124 MHz
WDW                  EM
SSB                   0
LB               0 30 Hz
GB                    0
PC                 1 40

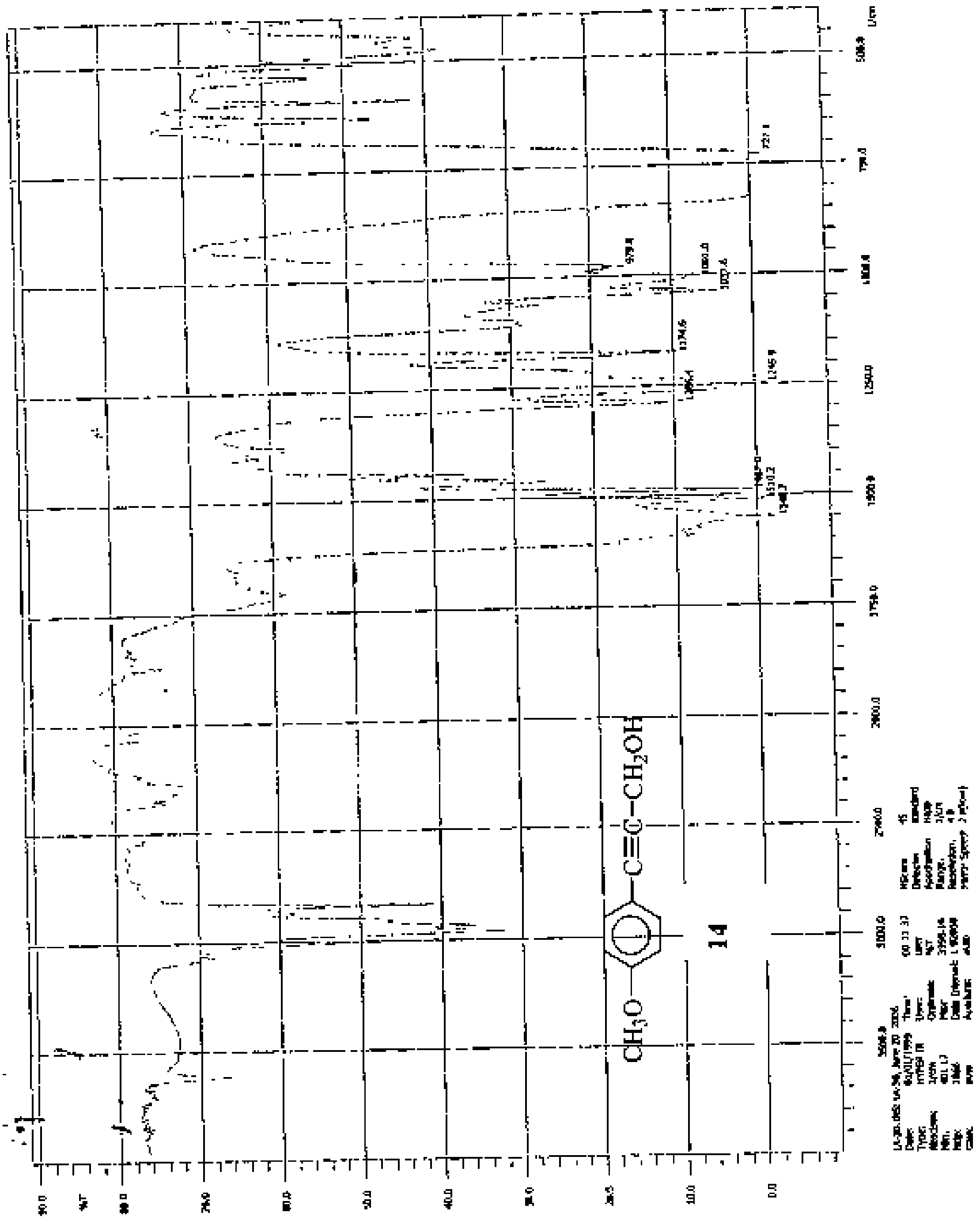
1D NMR plot parameters
CX               20 00 cm
F1P              4.992 ppm
F1             1997,39 Hz
F2P              1 021 ppm
F2              406 35 Hz
PPMCM          0 19856 ppm/cm
HZCM          79 45202 Hz/cm
```


Analytical BCSIR 13C Spectrum LA-30 in CDCl3 Laila BUET
ppm
159.724
135.173
133.165
116.149
114.630
113.939
85.306
85.603
77.350
77.032
76.715
55.263
51.659
CH3O—C6H4—C≡C—CH2OH
150
100
50
ppm
Current Data Parameters
NAME 13353
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070504
Time 15.16
INSTRUM dpx400
PROBHD 5 mm Multinuc
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 176
DS 2
SWH 24154.590 Hz
FIDRES 0.737140 Hz
AQ 0.6782476 sec
RG 6384
DW 20.700 usec
DE 6.00 usec
TE 300.0 K
D1 1.50000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.35 usec
PL1 -6.00 dB
SFO1 100.6253045 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 6.00 dB
PL12 18.90 dB
PL13 130.00 dB
SFO2 400.1400050 MHz
F2 - Processing parameters
SI 32768
SF 100.6152800 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 205.120 ppm
F2P -1.215 ppm
F2 -122.27 Hz
PPMCM 10.31682 ppm/cm
HZCM 1037.95660 Hz/cm

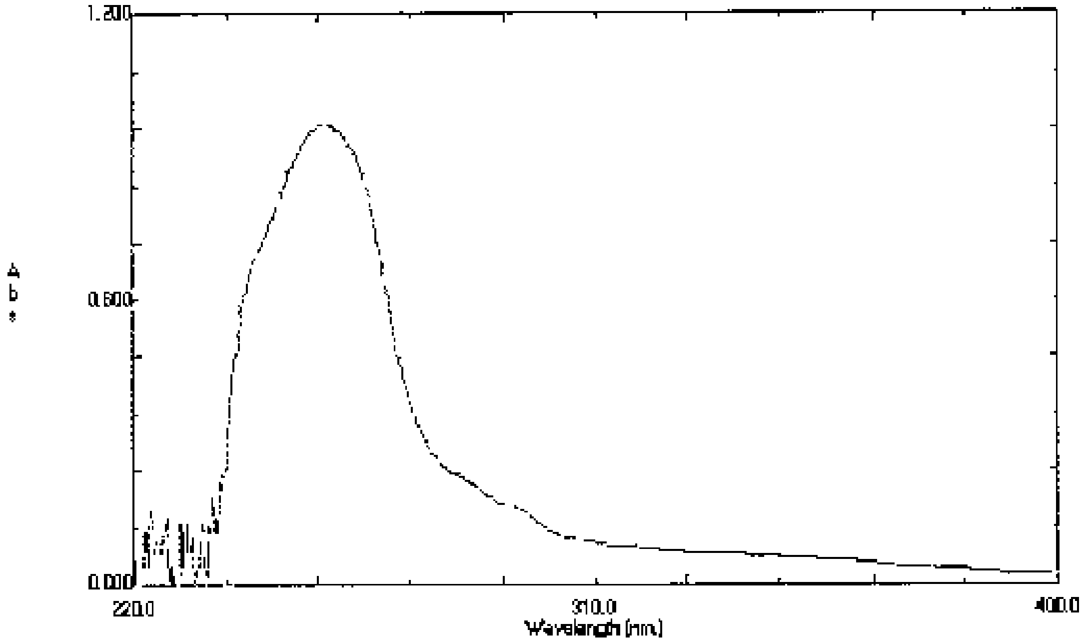
14

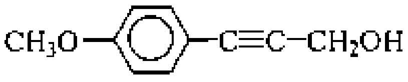

Analytical, BCSIR, dept 135, LA-50 in CDCl3, Laila BUET
ppm
138.173
135.197
133.164
129.466
116.353
113.939
55.262
51.658
CH_3O
$C{\equiv}C{-}CH_2OH$
ppm
160
140
120
100
80
60
40
20

14



CH₃O–C₆H₄–C≡C–CH₂OH
14
%T
90.0
80.0
70.0
60.0
50.0
40.0
30.0
10.0
0.0
1/cm
500.0
750.0
1000.0
1250.0
1500.0
1750.0
2000.0
3000.0
3500.0
1174.6
1510.2





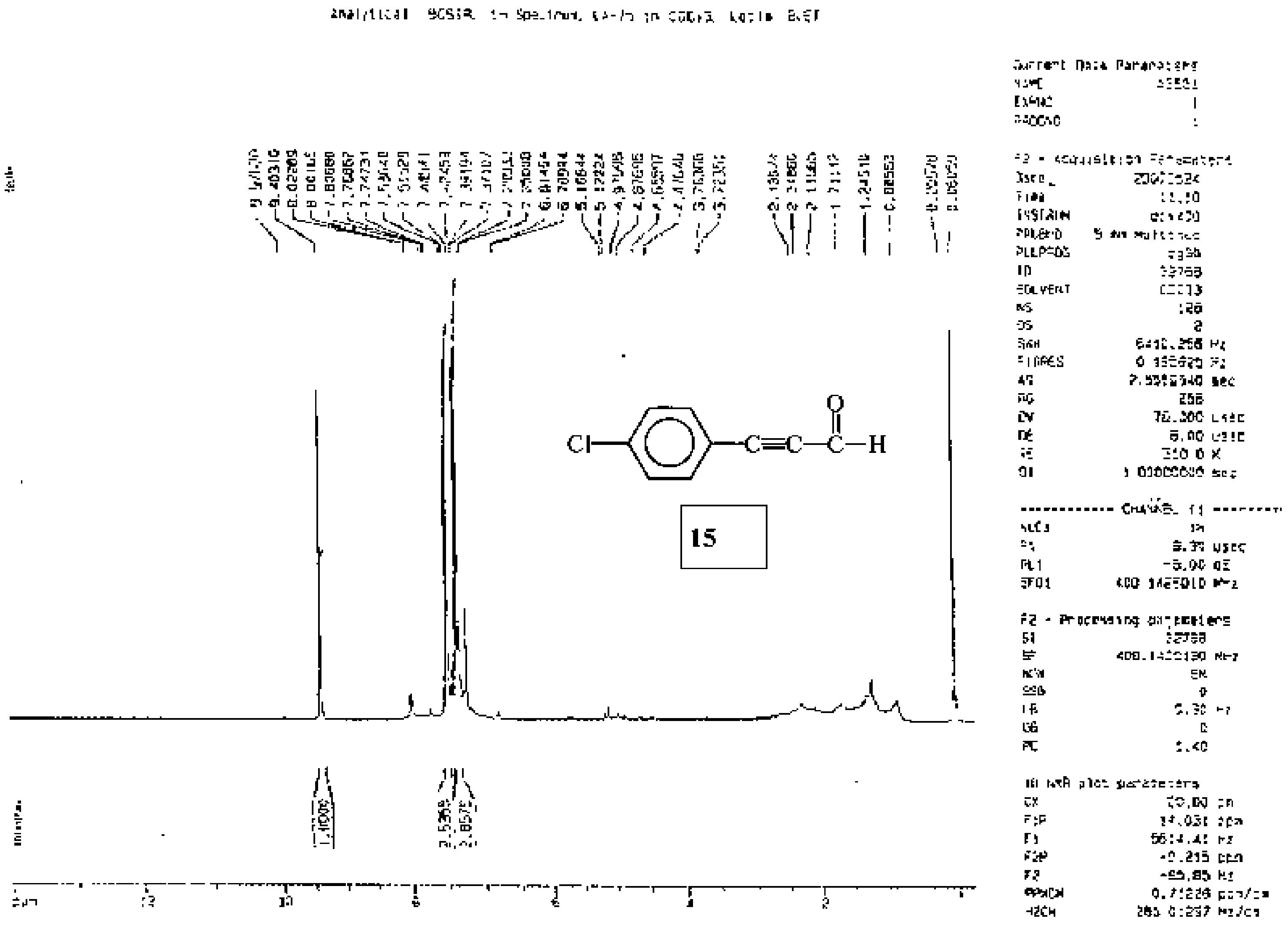
14

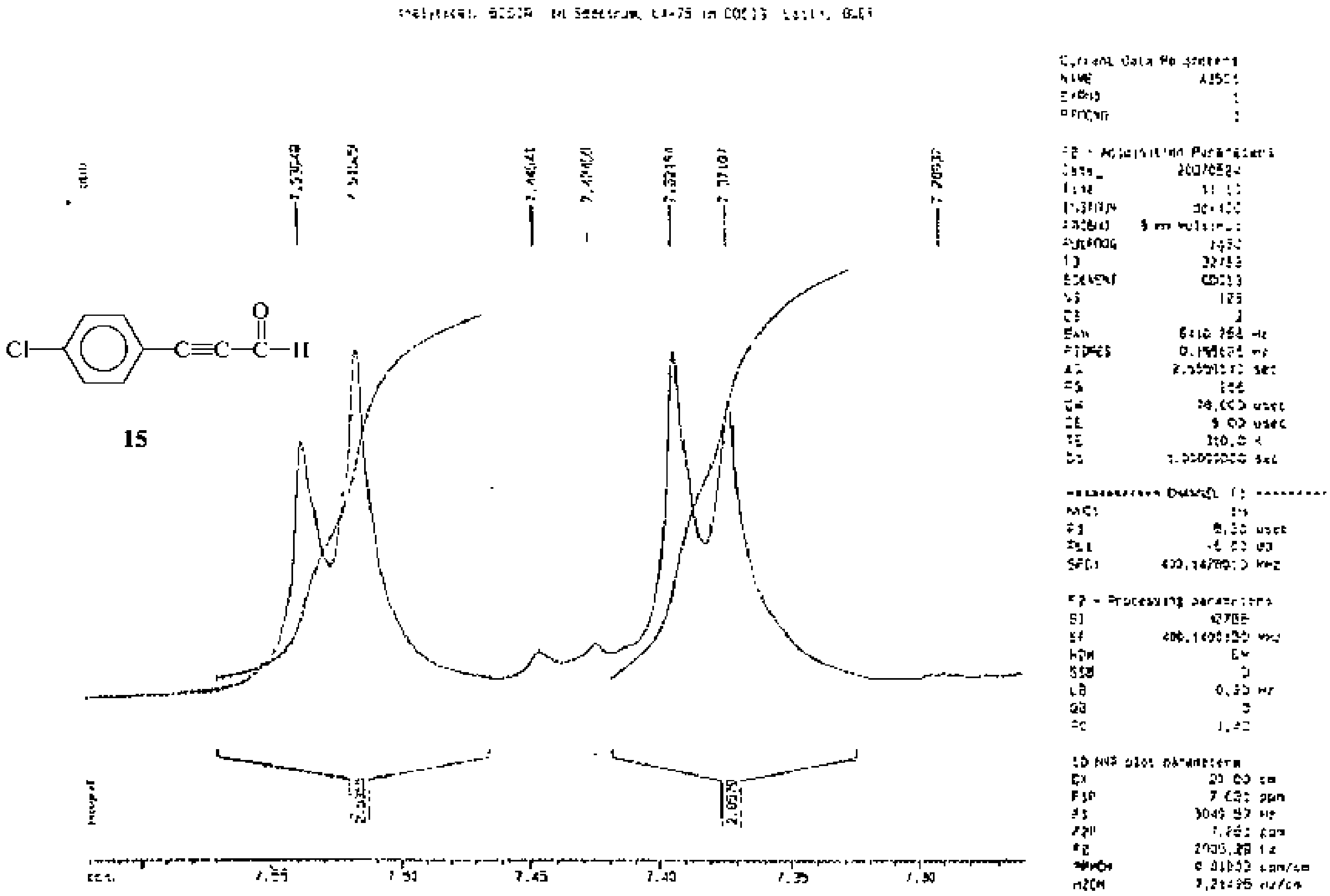
File Name: **LA30**

Created: 14:13 10/03/07
Data: Original

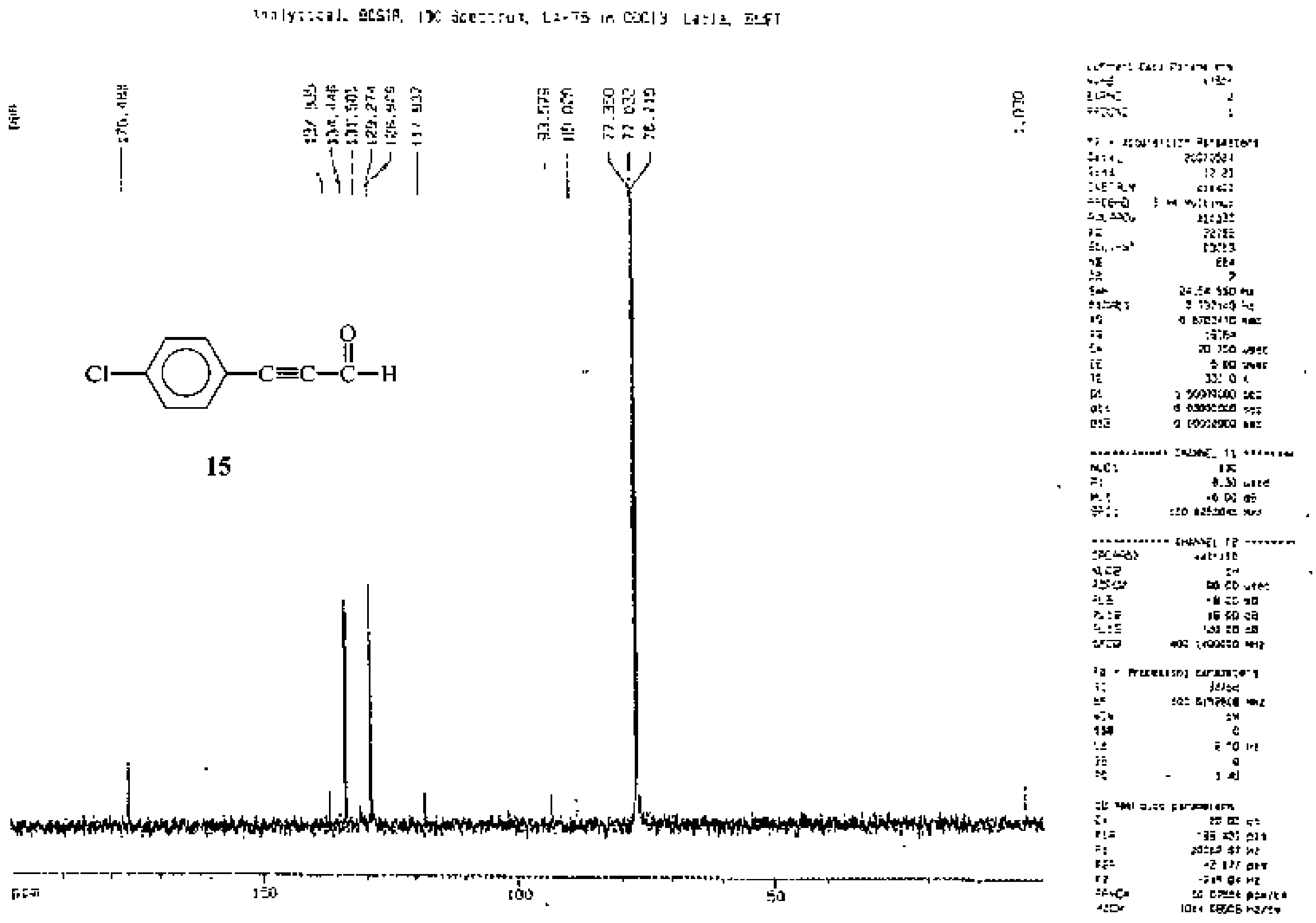
Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

No.	Wavelength (nm.)	Abs.
1	257.20	0.9662
2	229.20	0.1289

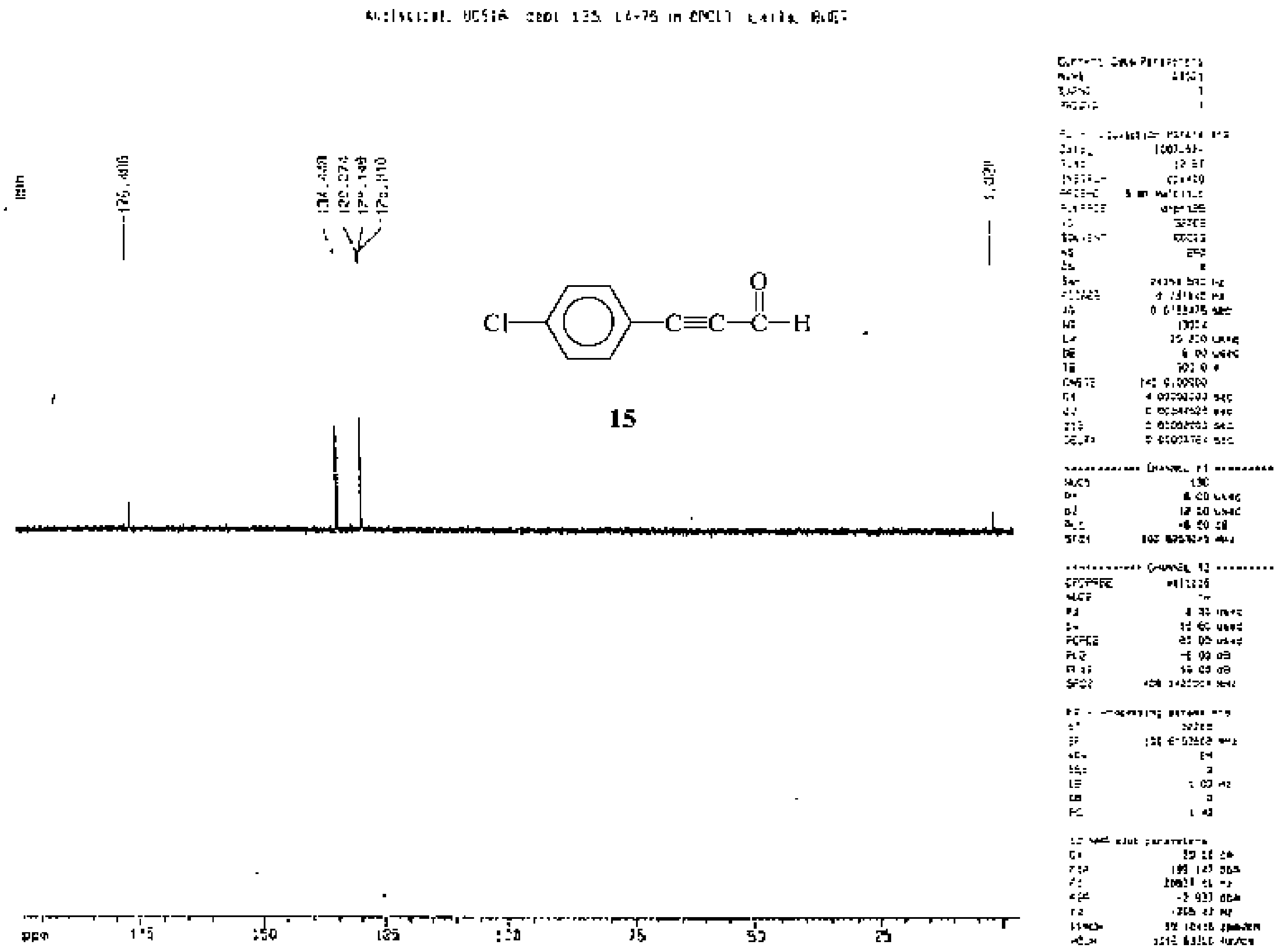

Analytical BCSIR 1H Spectrum in CDCl3
9.40310
8.02209
7.80680
7.76867
7.74731
7.42453
7.39194
6.81454
6.70984
5.16644
5.12224
3.76306
1.24518
0.88553
Cl
C≡C—C—H
O
15
1.1400
2.5368
2.8572
ppm
12
10
8
6
4
2
Current Data Parameters
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 128
DS 2
AQ 2.5559540 sec
RG 256
DW 78.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
PL1 -6.00 dB
SFO1 400.1425010 MHz
F2 - Processing parameters
SI 32768
SF 400.1400130 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1 5614.41 Hz
F2P -0.215 ppm
F2 -85.85 Hz
PPMCM 0.71226 ppm/cm



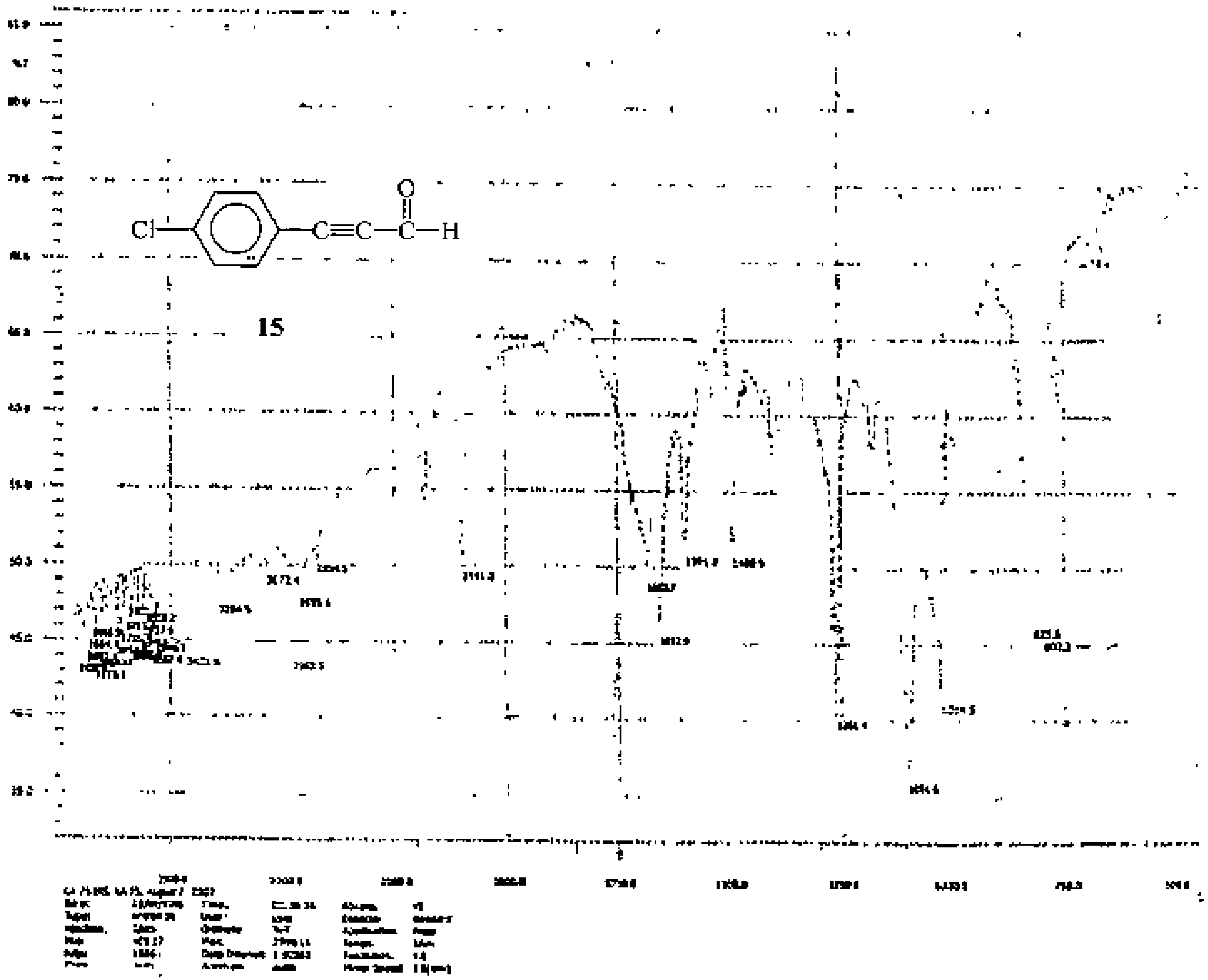
15


Analytical 90518, 13C Spectrum, LA-75 in CDCl3
176.488
137.905
134.446
131.501
129.274
126.925
117.937
93.575
89.029
77.350
77.032
76.715
1.070
Cl
C≡C—C—H
O
ppm
150
100
50

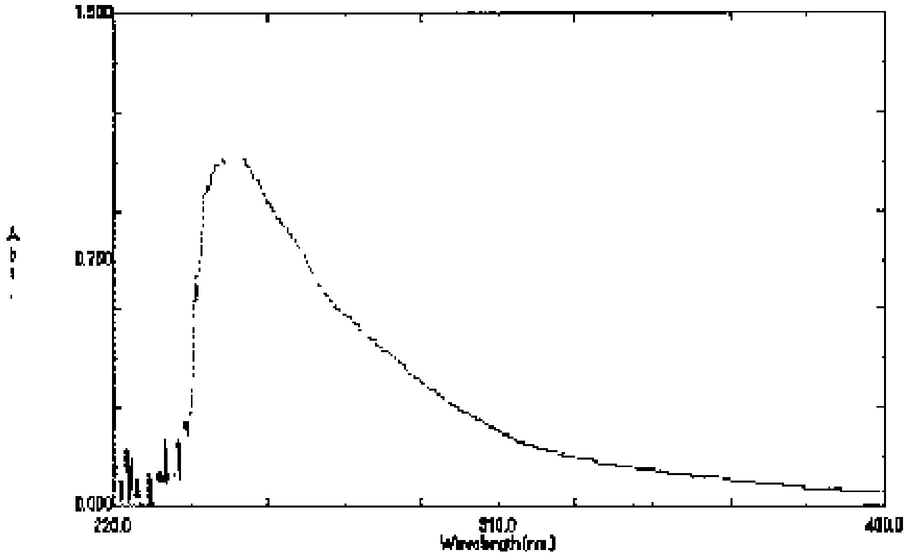
15

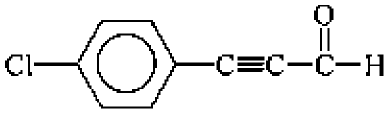


15



15





15

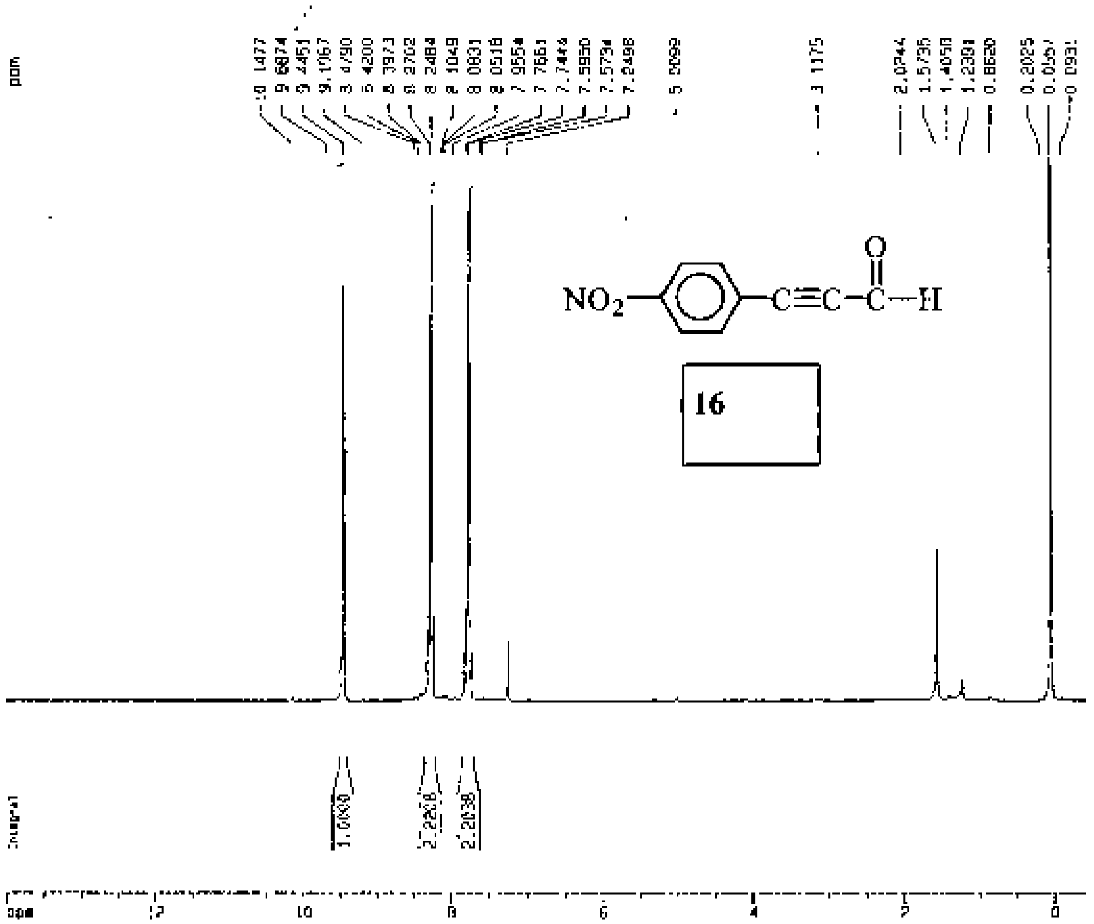
File Name: LA75

Created: 14:26 10/03/07
Data: Original

Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

No.	Wavelength (nm.)	Abs.
1	248.60	1.0590
2	234.80	0.2021

Analytical, BLSIA, 1H spectrum LX-77 in CDCl3, [illegible], BLEF



16

```
Current Data Parameters
NAME              A3511
EXPNO                 1
PROCNO                1

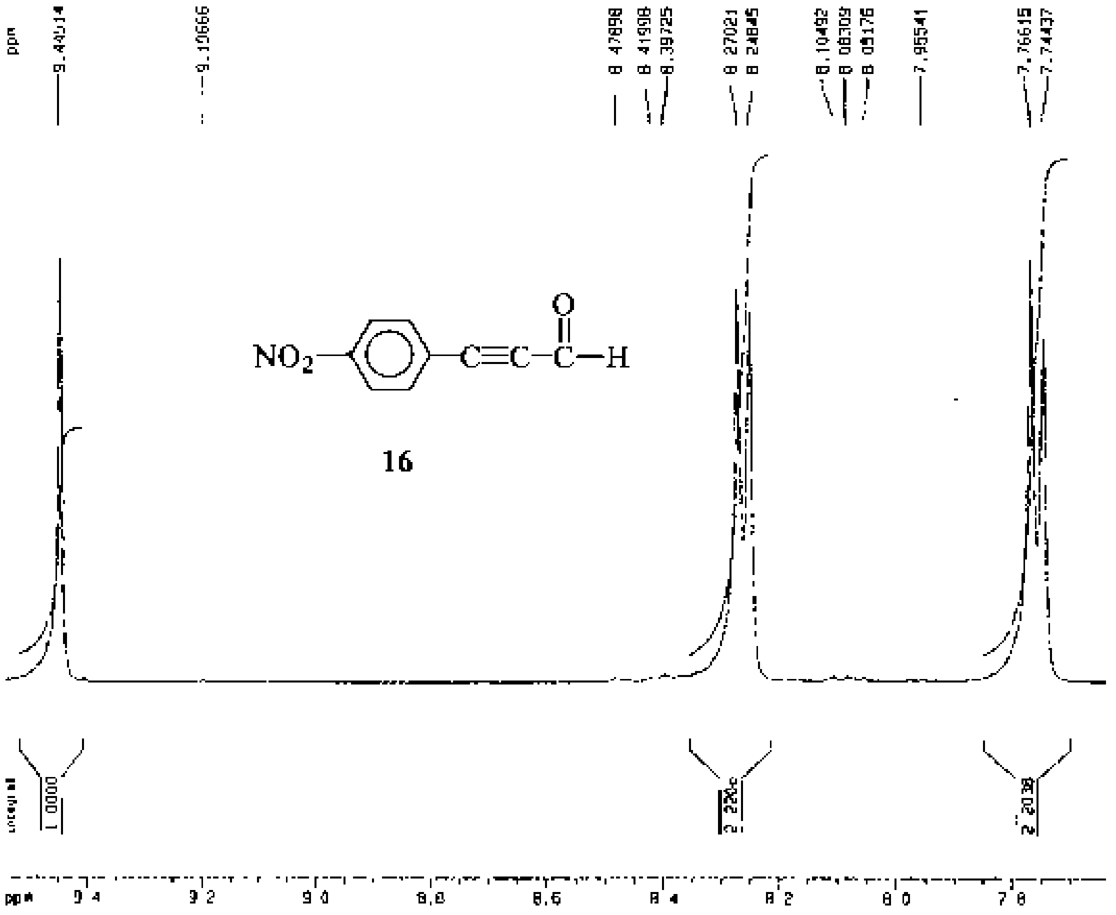
F2 - Acquisition Parameters
Date_          20070531
Time              11.18
INSTRUM          dpx400
PROBHD   5 mm Multinuc
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   86
DS                    2
SWH           6410.256 Hz
FIDRES        0.195625 Hz
AQ           2.5559540 sec
RG                322.5
DW               78.000 usec
DE                 6.00 usec
TE                310.0 K
D1          1.00000000 sec

============ CHANNEL f1 ============
NUC1                 1H
P1                 8.30 usec
PL1               -6.00 dB
SFO1        400.1428010 MHz

F2 - Processing parameters
SI                32768
SF          400.1400128 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P              14.015 ppm
F1              5607.84 Hz
F2P              -0.417 ppm
F2              -166.80 Hz
PPMCM           0.72158 ppm/cm
HZCM          288.73203 Hz/cm
```

Analytical, BCSIR, 1H Spectrum LA-77 in CDCl3 Laila, BUET


16

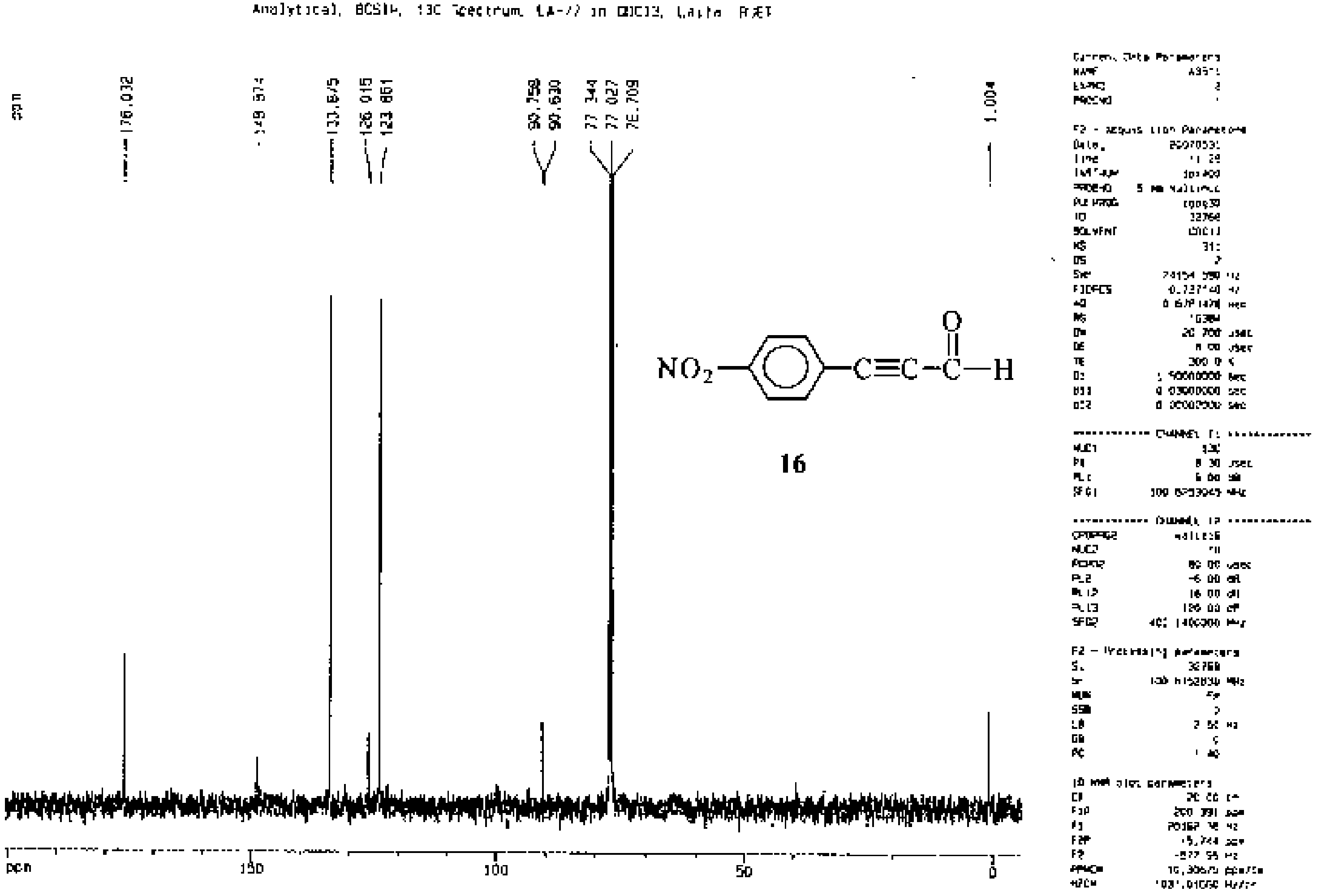
```
Current Data Parameters
NAME                43511
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070531
Time                11.18
INSTRUM            dpx400
PROBHD     5 mm Multinuc
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     86
DS                      2
SWH             6410.256 Hz
FIDRES          0.195625 Hz
AQ             2.5559540 sec
RG                  322.5
DW                 78.000 usec
DE                   6.00 usec
TE                  310.0 K
D1            1.00000000 sec

============ CHANNEL f1 =============
NUC1                   1H
P1                   8.30 usec
PL1                 -6.00 dB
SFO1          400.1428010 MHz

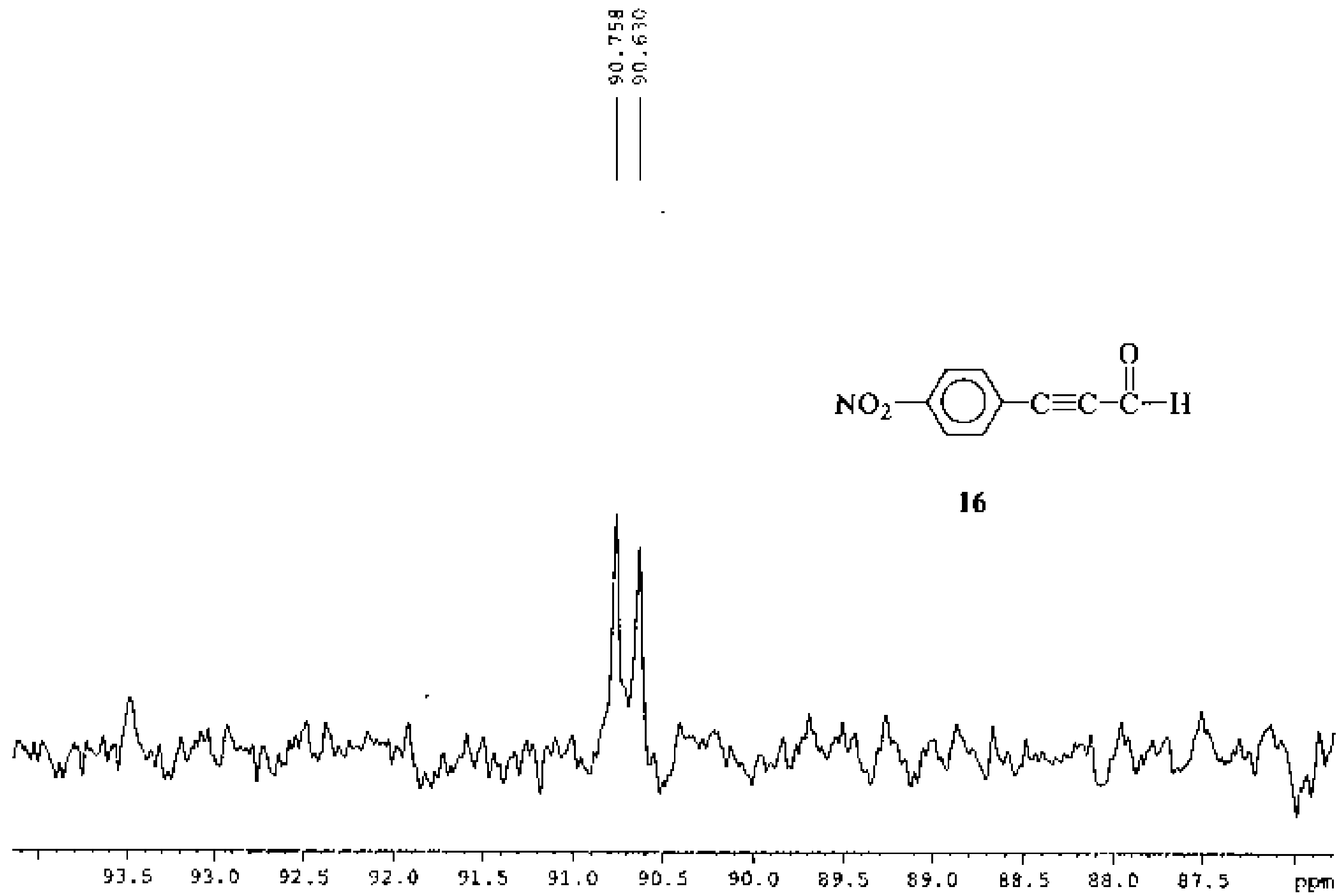
F2 - Processing parameters
SI                  32768
SF            400.1400128 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.40

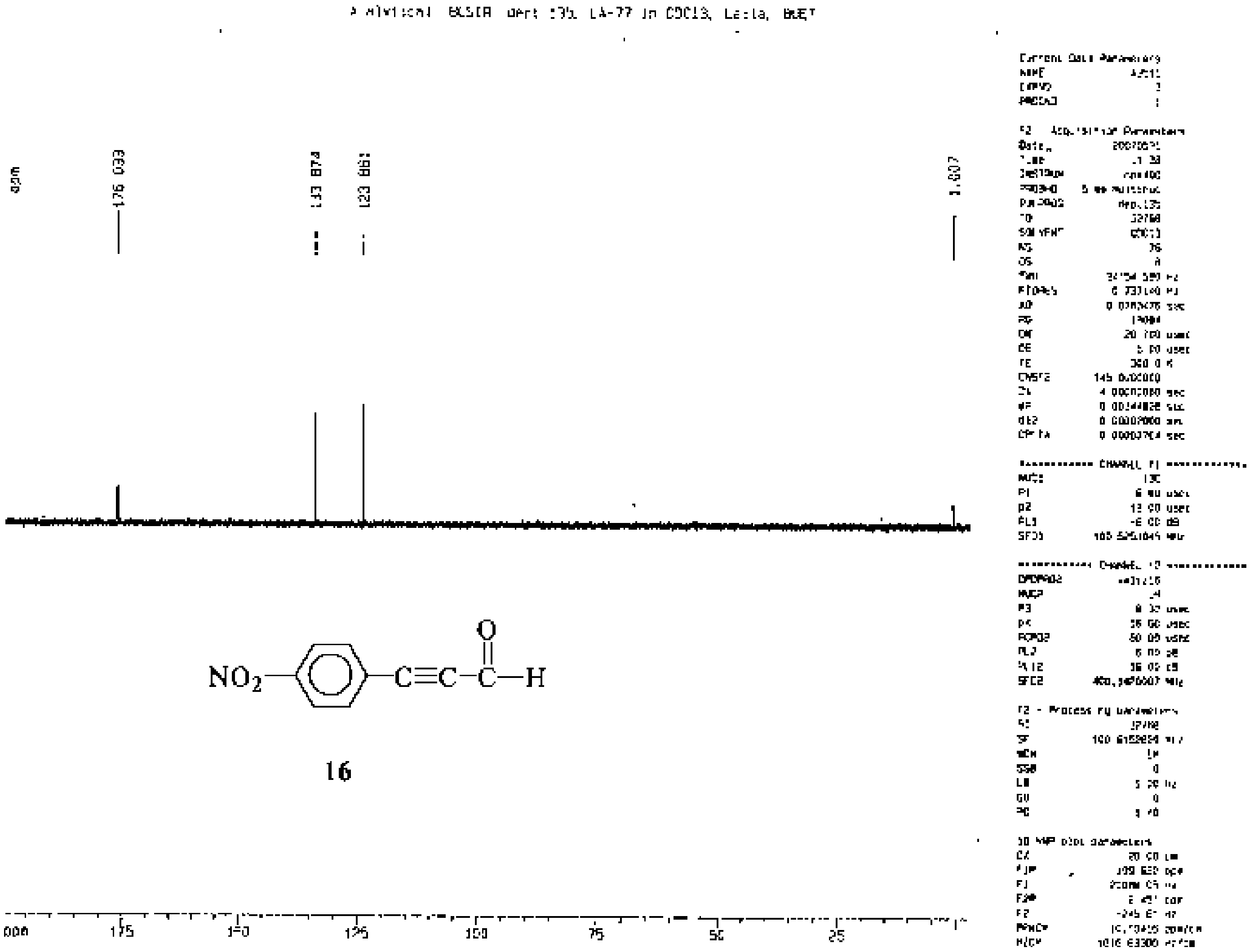
1D NMR plot parameters
CX                  20.00 cm
F1P                 9.545 ppm
F1                3819.50 Hz
F2P                 7.638 ppm
F2                3056.20 Hz
PPMCM             0.09538 ppm/cm
HZCM             38.16470 Hz/cm
```


Analytical, BCSIR, 13C Spectrum, LA-77 in CDCl3, Latia RAT
176.032
149.974
133.675
126.015
123.861
90.758
90.630
77.344
77.027
76.709
1.004
ppm
150
100
50
0
NO2
C≡C
C
O
H
Current Data Parameters
NAME A3571
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070531
Time 11.29
INSTRUM dpx400
PROBHD 5 mm Multinuc
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 312
DS 2
SWH 24154.590 Hz
FIDRES 0.737140 Hz
AQ 0.6783476 sec
RG 16384
DW 20.700 usec
DE 6.00 usec
TE 300.0 K
D1 1.50000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
============ CHANNEL f1 ============
NUC1 13C
P1 8.30 usec
PL1 6.00 dB
SFO1 100.6253043 MHz
============ CHANNEL f2 ============
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 16.00 dB
PL13 126.00 dB
SFO2 400.1400300 MHz
F2 - Processing parameters
SI 32768
SF 100.6152830 MHz
WDW EM
SSB 0
LB 2.50 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 200.391 ppm
F1 20162.38 Hz
F2P -5.744 ppm
F2 -577.95 Hz
PPMCM 10.30675 ppm/cm
HZCM 1037.01050 Hz/cm

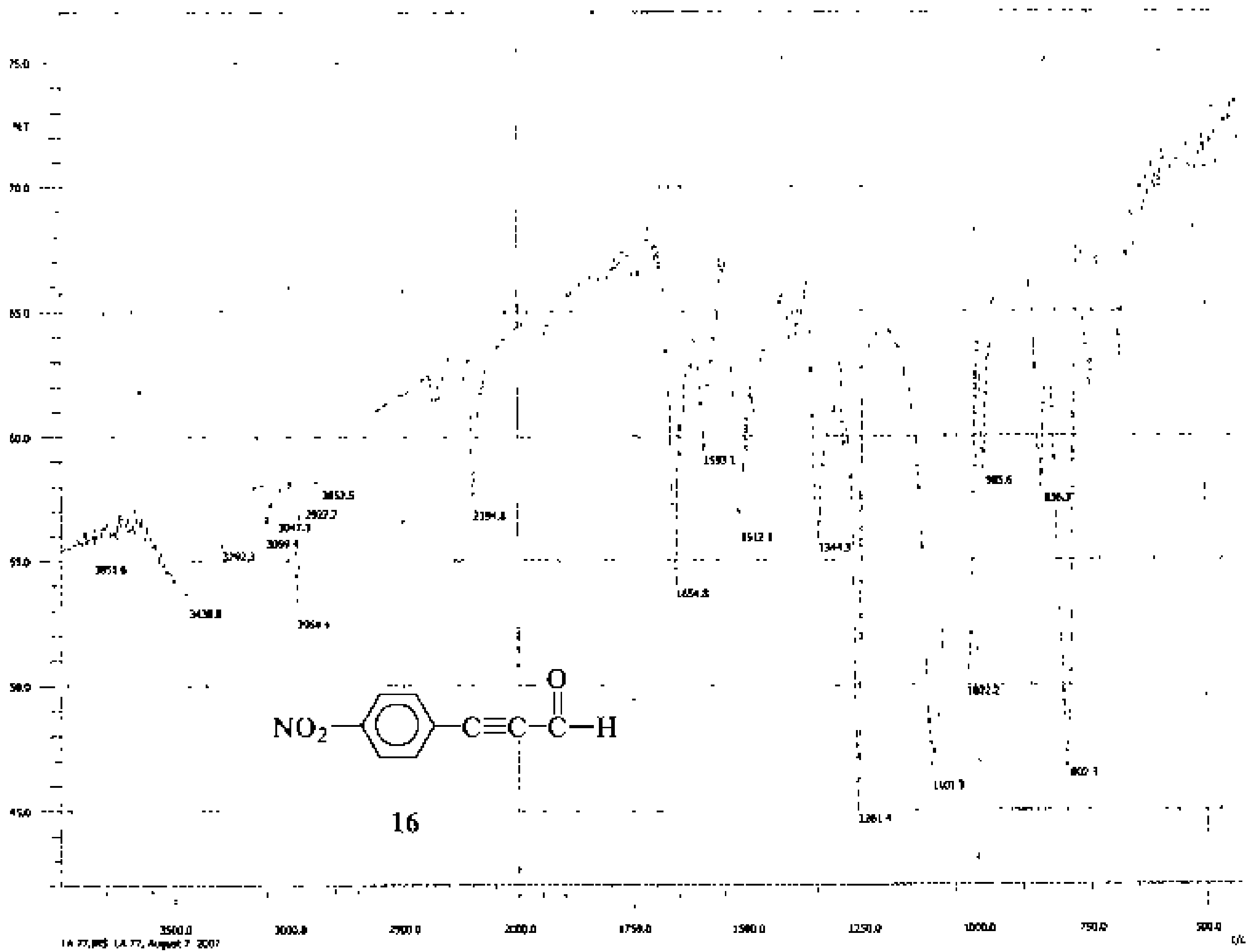
16

Analytical, BCSIR, 13C Spectrum, LA-77 in CDCl3, Laila, BUET



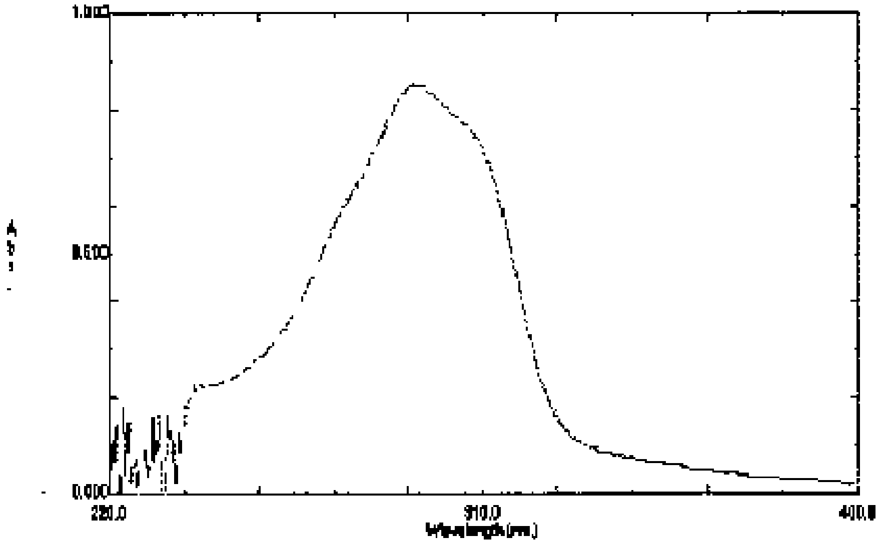

BCSIR dept 135 LA-77 in CDCl3, Laila, BUET
ppm
176 033
133 874
123 881
1.007
200
175
150
125
100
75
50
25
Current Data Parameters
NAME
EXPNO
PROCNO
F2 - Acquisition Parameters
Date_
Time
INSTRUM
PROBHD 5 mm Multinuc
PULPROG dept135
TD 32768
SOLVENT CDCl3
NS
DS
SWH
FIDRES
AQ
RG
DW 20 700 usec
DE 5 00 usec
TE 300 0 K
CNST2 145 0000000
D1 4 00000000 sec
d2
d12 0 00002000 sec
CHANNEL f1
NUC1 13C
P1 6 00 usec
p2 12 00 usec
PL1 -6 00 dB
SFO1 100 6251045 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
P3 8 30 usec
p4 16 60 usec
PCPD2 80 00 usec
PL2 0 00 dB
PL12 16 00 dB
SFO2 400 1420007 MHz
F2 - Processing parameters
SI 32768
SF 100 6152854 MHz
WDW EM
SSB 0
LB 5 00 Hz
GB 0
PC 1 40
1D NMR plot parameters
CX 20 00 cm
F1P 199 820 ppm
F1
F2P
F2
PPMCM
HZCM 1016 63300 Hz/cm
NO2
C≡C
C
H
O

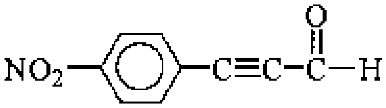
16



LA 77.IRS LA 77, August 7 2007

Date	01/01/1990	Time	01 06 14	NScans	45
Type	HYPER IR	User	user	Detector	standard
Abscissa	1/cm	Ordinate	%T	Apodization	Happ
Min	403.17	Max	3998.16	Range	1/cm
Points	1866	Data Interval	1.92868	Resolution	4.0
Gain	auto	Aperture	open	Mirror Speed	2.8(mm)





16

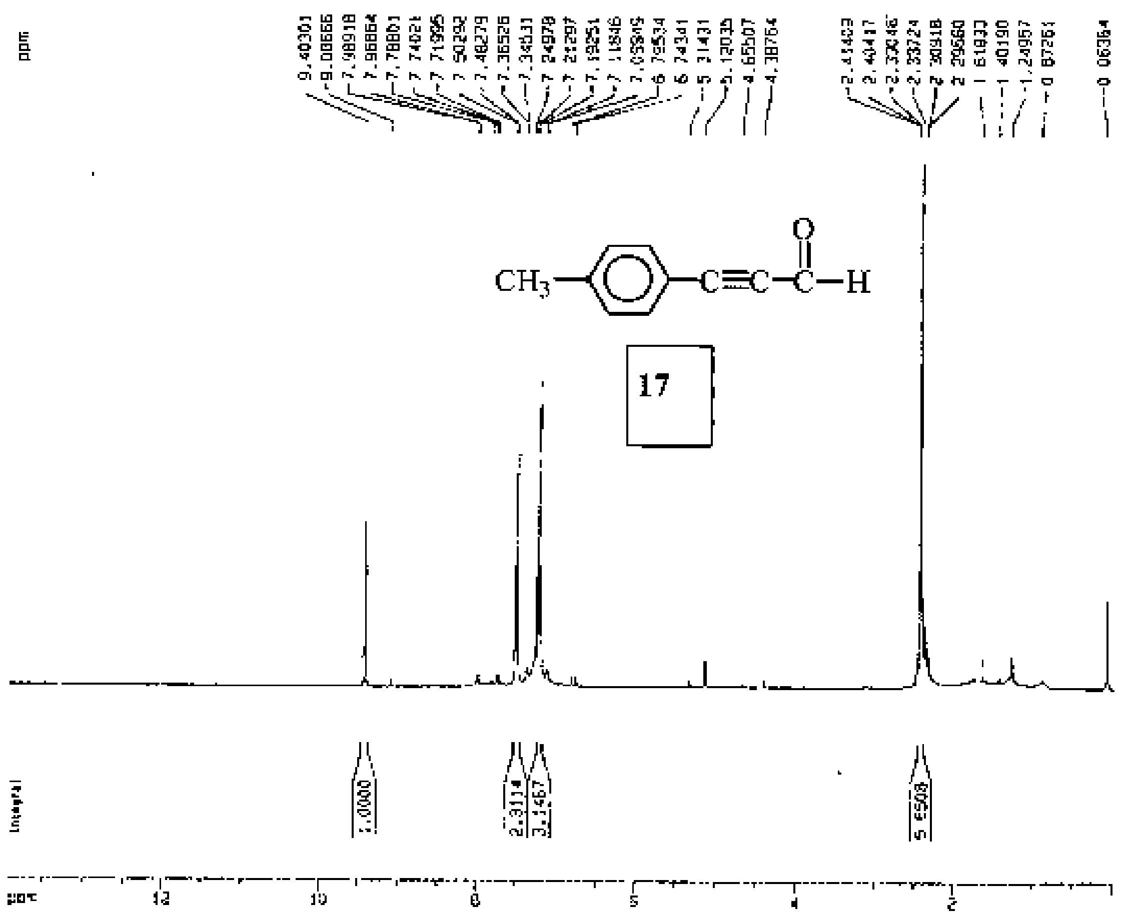
File Name: LA77

Created: 14:30 10/03/07
Data: Original

Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

No.	Wavelength (nm.)	Abs.
1	293.80	0.8519
2	242.20	0.2240
3	234.20	0.1581
4	231.80	0.1591
5	223.20	0.1757

Analytical BCSIR, NMR Spectrum EA-8C in CDCl3, sai.a, BUET



17

```
Current Data Parameters
NAME              A3585
EXPNO                 1
PROCNO                1

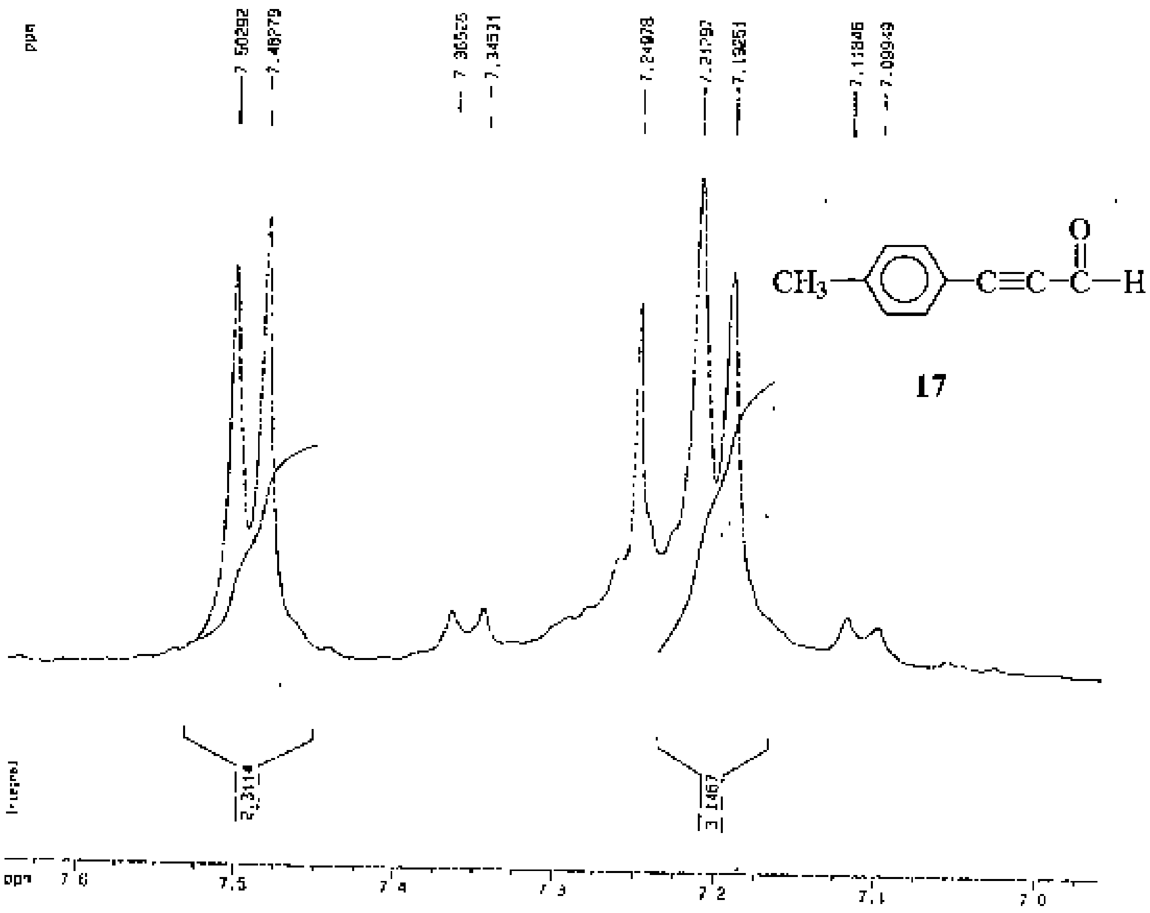
F2 - Acquisition Parameters
Date_          20070628
Time              13 13
INSTRUM          dpx400
PROBHD    5 mm Multinuc
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                  128
DS                    2
SWH            5747.126 Hz
FIDRES         0.175388 Hz
AQ            2 8508661 sec
RG                322.5
DW               87.000 usec
DE                 6 00 usec
TE                310.0 K
D1           1.00000000 sec

============ CHANNEL f1 =============
NUC1                 1H
P1                 8 30 usec
PL1               -6 00 dB
SFO1        400.1428614 MHz

F2 - Processing parameters
SI                32768
SF          400 1400123 MHz
WDW                  EM
SSB                   0
LB                 0 30 Hz
GB                    0
PC                 1 40

1D NMR plot parameters
CX                20 00 cm
F1P               13 923 ppm
F1              5571 10 Hz
F2P              -0.016 ppm
F2                -6 28 Hz
PPMCM           0.69693 ppm/cm
HZCM          278.06902 Hz/cm
```

Analysis: ... 9CSJR 1H Spectrum, LA-80 in CDCl3 Laila, BUET



17

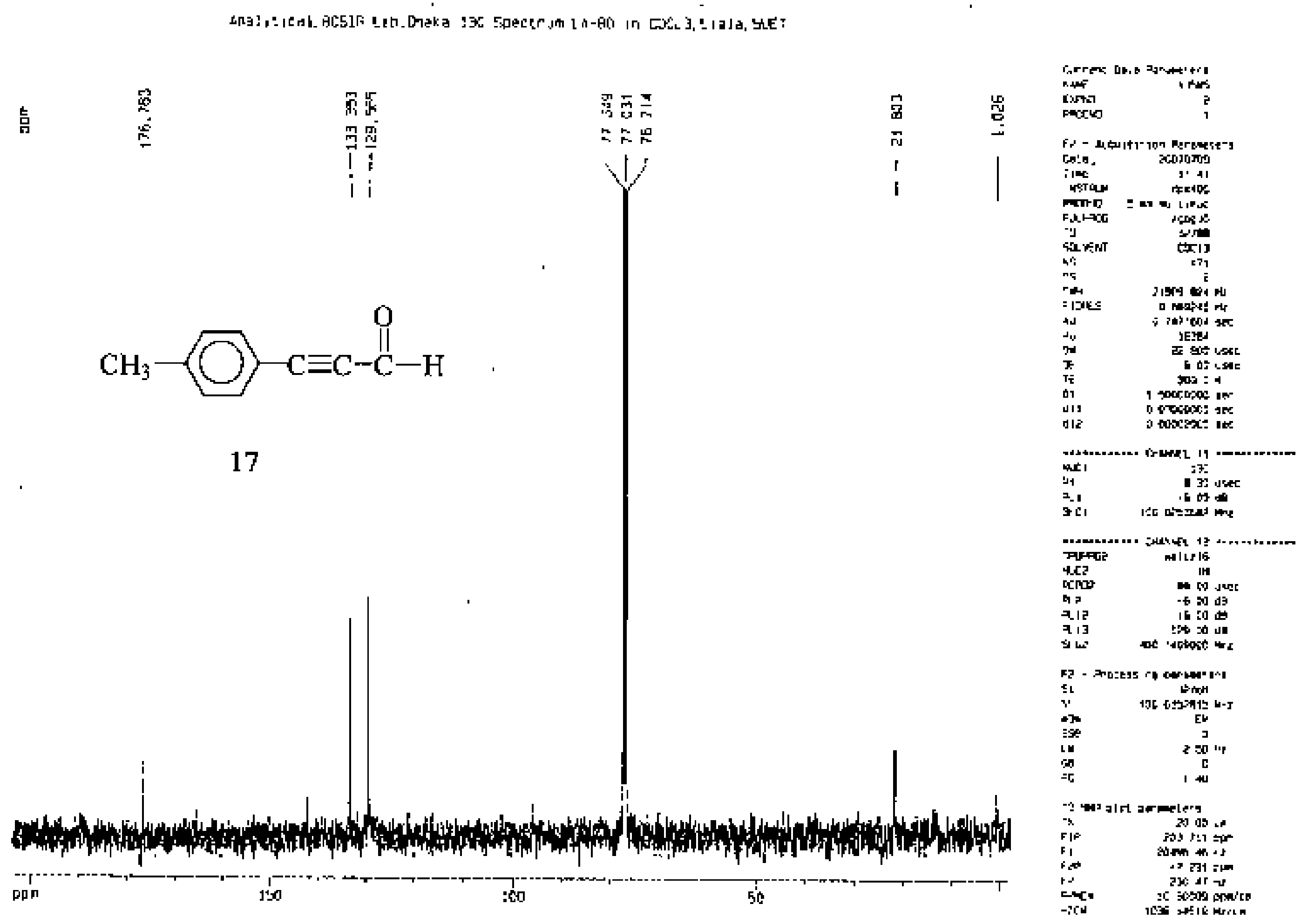
```
Current Data Parameters
NAME               A3585
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070529
Time               13 13
INSTRUM           spx400
PROBHD   5 mm Multinuc
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                   128
DS                     2
SWH          5747.126 Hz
FIDRES       0.175386 Hz
AQ          2.8508661 sec
RG                 322 5
DW            87 000 usec
DE             6 00 usec
TE               310 0 K
D1        1 00000000 sec

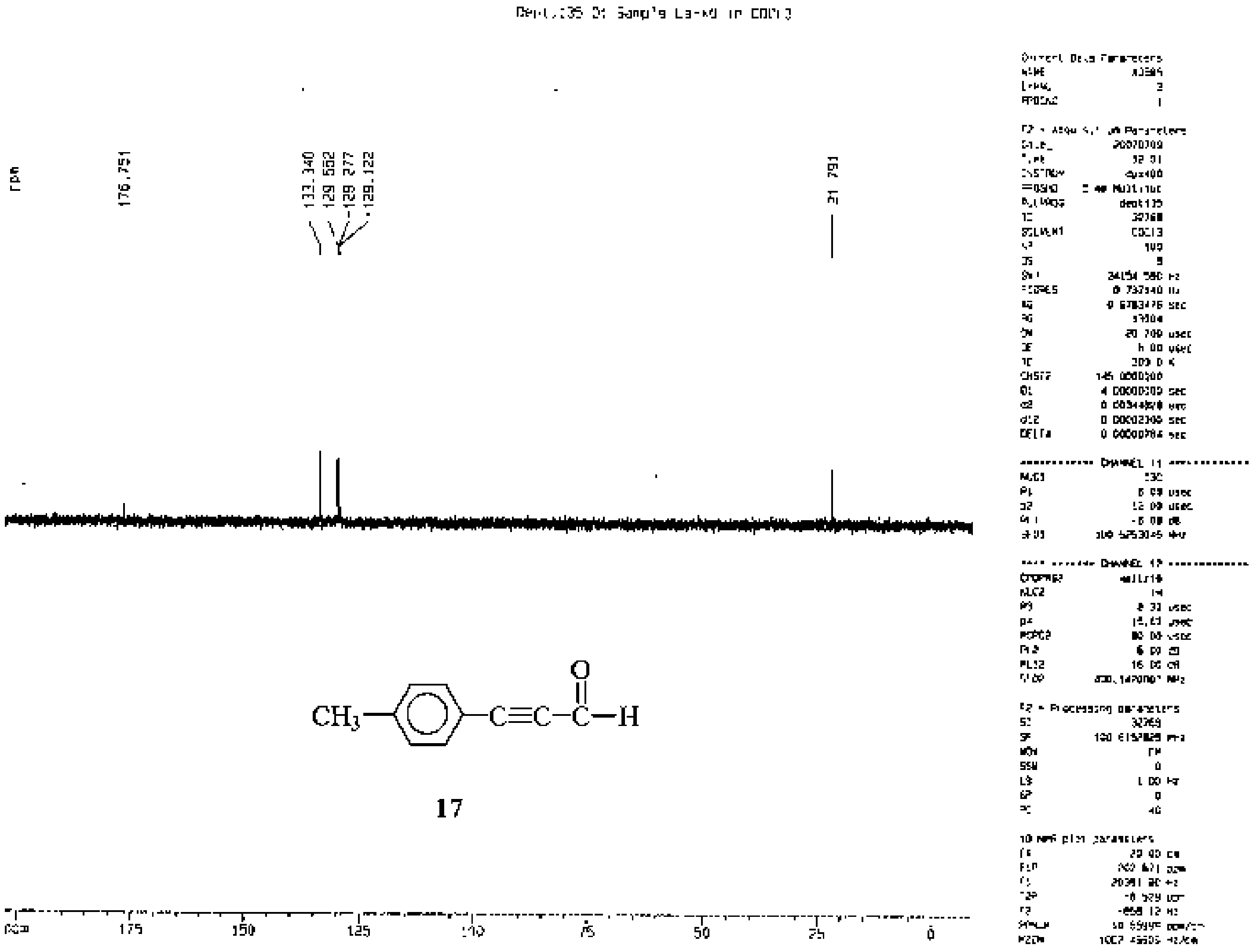
============ CHANNEL f1 ============
NUC1                  1H
P1             8.30 usec
PL1             -6 00 dB
SFO1     400 1428614 MHz

F2 - Processing parameters
SI                 32768
SF       400.1400123 MHz
WDW                   EM
SSB                    0
LB               0.30 Hz
GB                     0
PC                  1 40

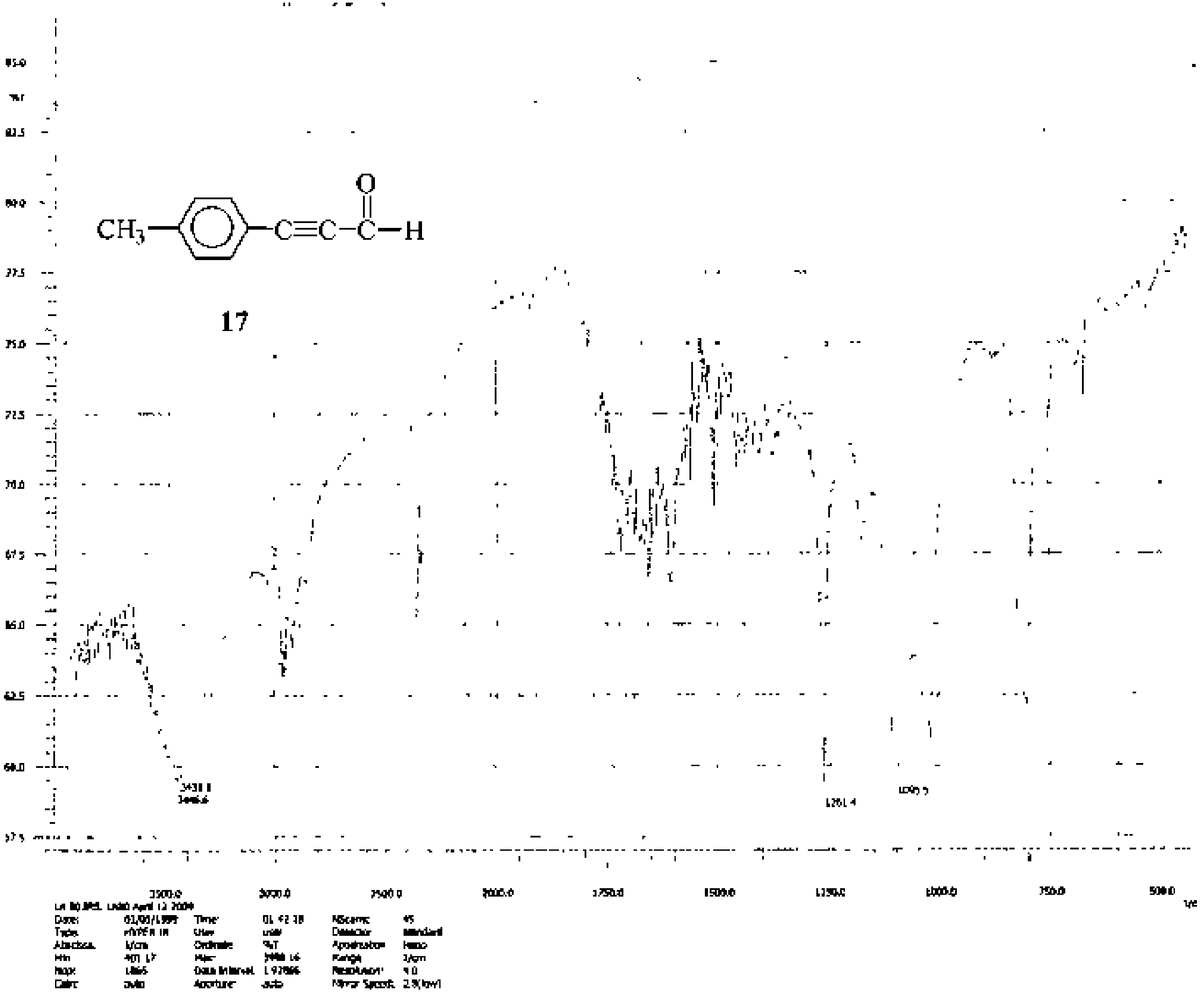
1D NMR plot parameters
CX              20 00 cm
F1P            7 642 ppm
F1           3058.39 Hz
F2P            6 559 ppm
F2            2784 54 Hz
PPMCM      0 03421 ppm/cm
HZCM      13 50700 Hz/cm
```

Analytical BCSIR Lab.Dhaka 13C Spectrum 1A-80 in CDCL3,Siala,SUET
176.763
133.353
129.565
77.349
77.031
76.714
21.803
1.026
CH3
C≡C–C–H
O
ppm
150
100
50

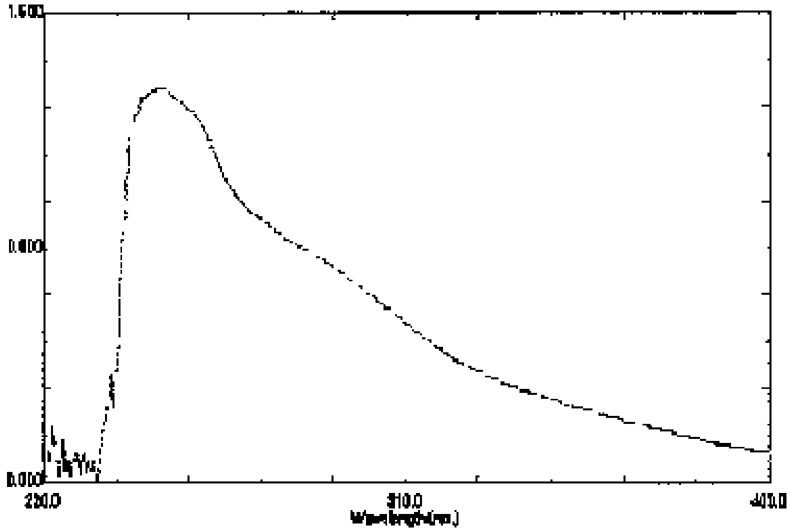
17

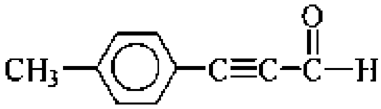

Dept.135 Of Sample La-kd in CDCl3
ppm
176.751
133.340
129.562
129.277
129.122
31.791
CH3
C≡C
O
H
175
150
125
100
75
50
25
0
ppm

17


17

CH3
C≡C
C
O
H
%T
85.0
82.5
80.0
77.5
75.0
72.5
70.0
67.5
65.0
62.5
60.0
57.5
3500.0
3000.0
2500.0
2000.0
1750.0
1500.0
1250.0
1000.0
750.0
500.0
1/cm
3431.8
3446.6
1261.4
1095.5
Date:
Type:
Abscissa:
Min:
Nopt:
Cabrt:
Time:
Ordinate: %T
Data Interval:
Aperture: auto
NScans:
Detector: Standard
Apodization:
Range:
Resolution:
Mirror Speed:





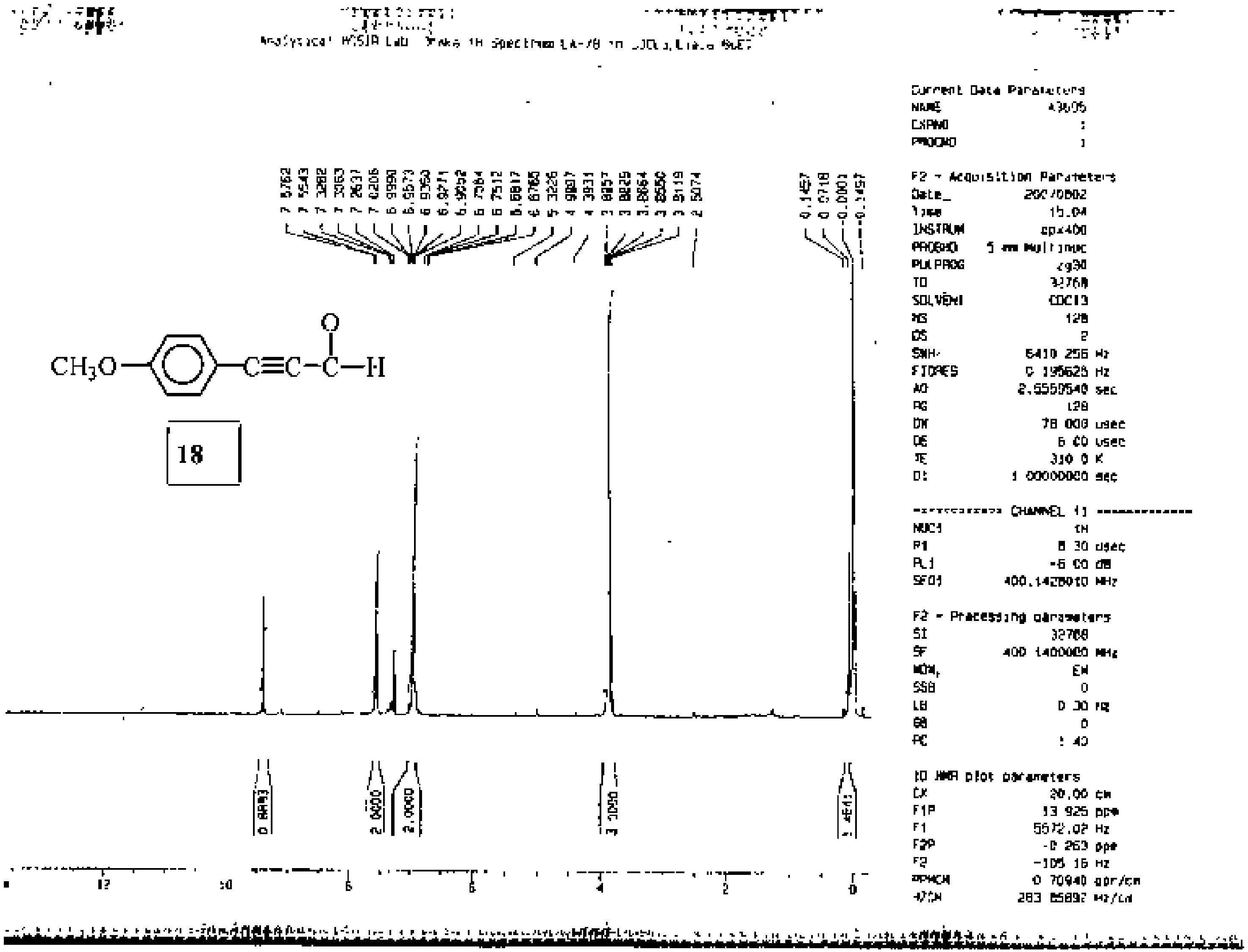
17

File Name: LA80

Created: 14:32 10/03/07
Data: Original

Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

No.	Wavelength (nm.)	Abs.
1	249.40	1.3438



18

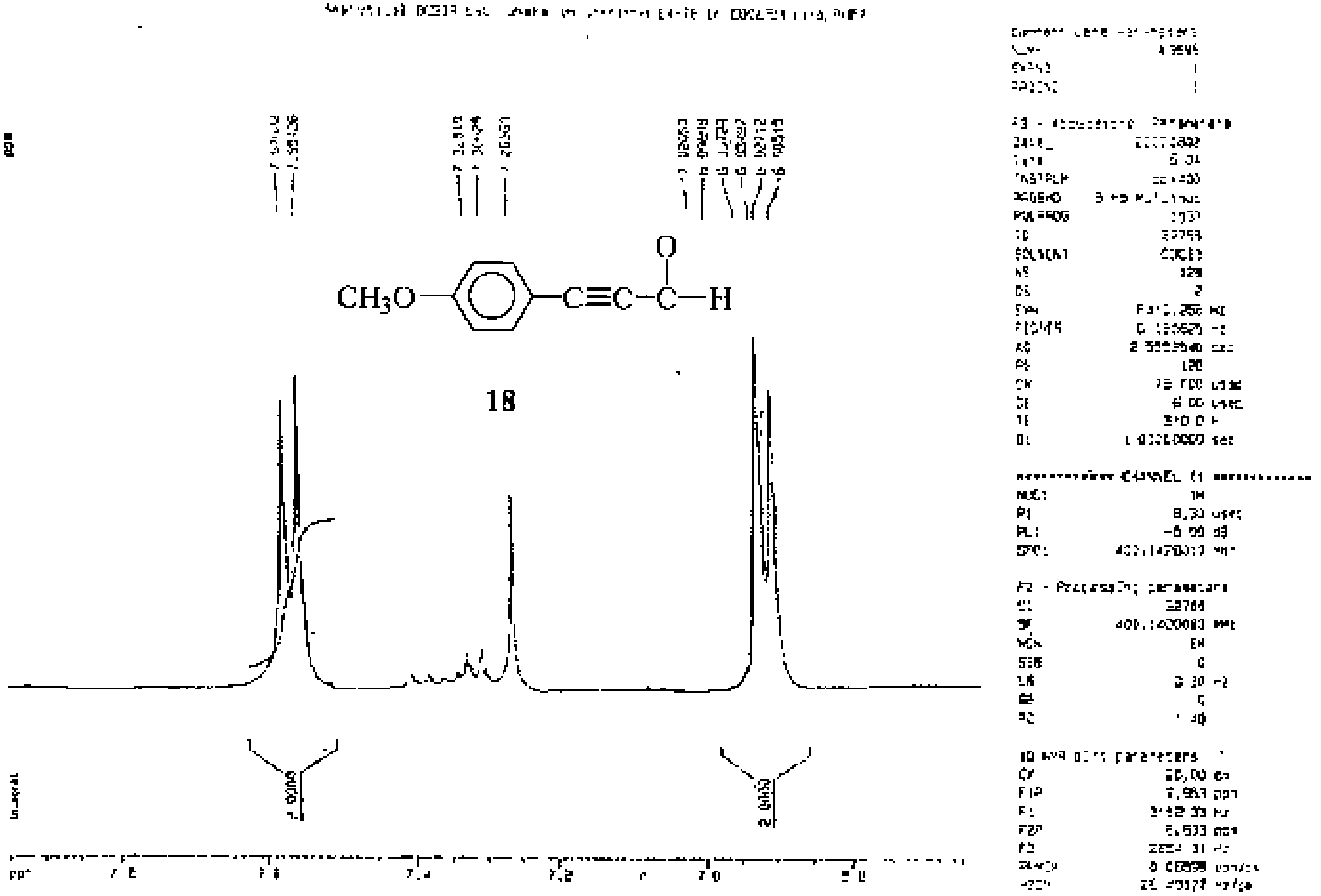
```
Current Data Parameters
NAME               43605
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070802
Time               15.04
INSTRUM           spx400
PROBHD     5 mm Multinuc
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                   128
DS                     2
SWH             6410 256 Hz
FIDRES          0 195625 Hz
AQ             2.5559540 sec
RG                   128
DW                78 000 usec
DE                 6 00 usec
TE                 310 0 K
D1            1 00000000 sec

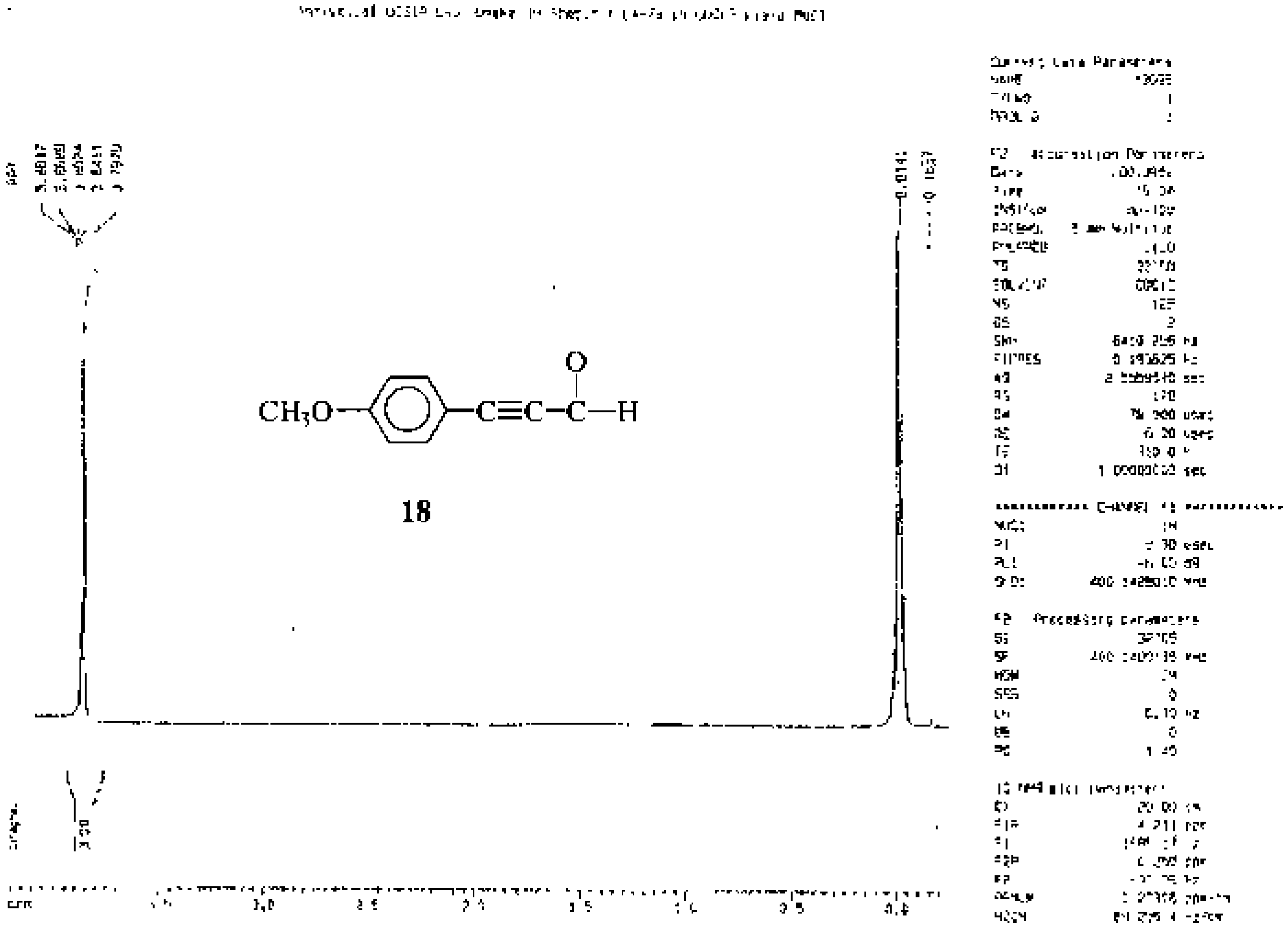
============ CHANNEL f1 ============
NUC1                  1H
P1                  8 30 usec
PL1                -6 00 dB
SFO1         400.1428010 MHz

F2 - Processing parameters
SI                 32768
SF           400 1400000 MHz
WDW                   EM
SSB                    0
LB                  0 30 Hz
GB                     0
PC                  1 40

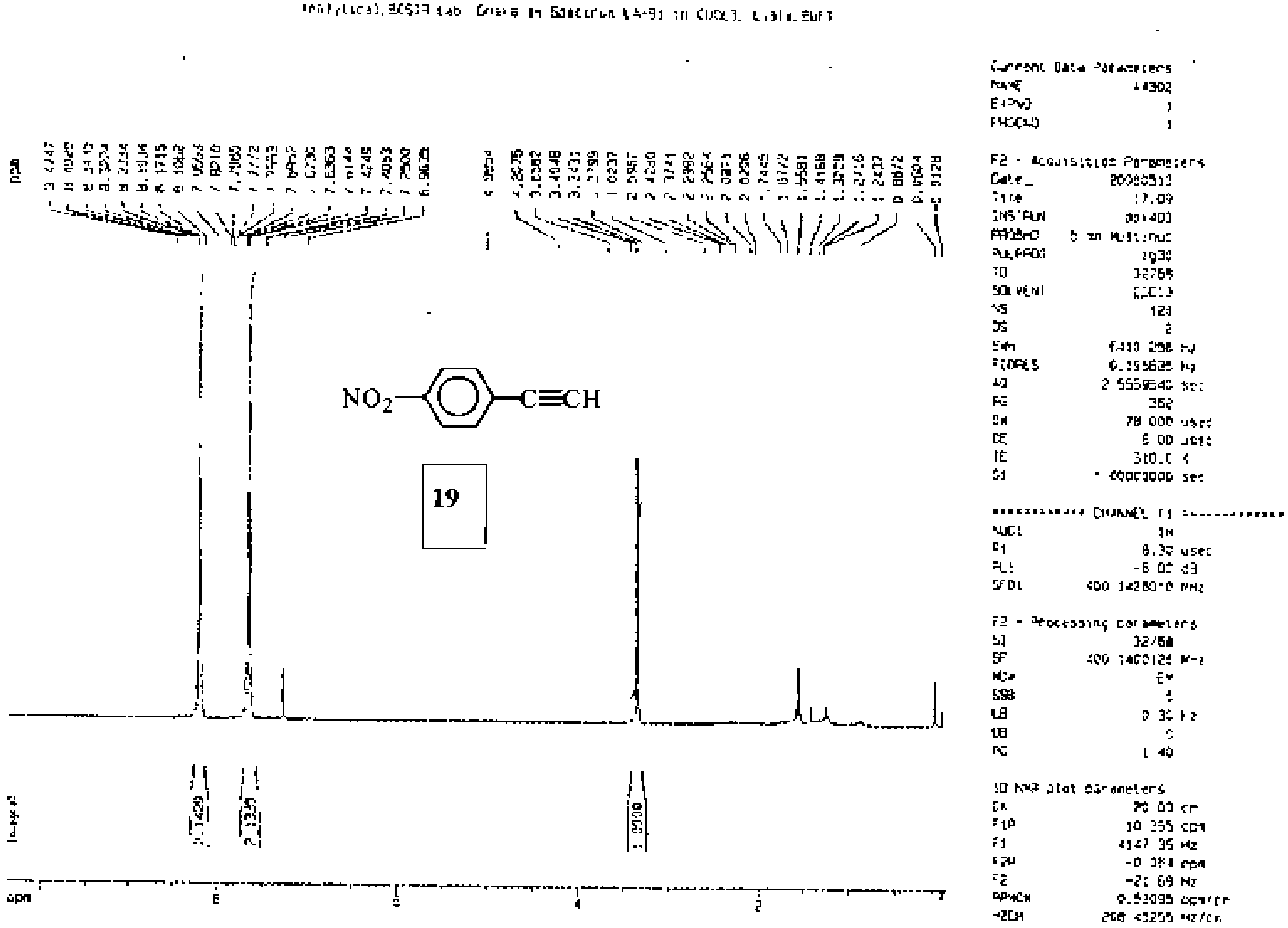
1D NMR plot parameters
CX                 20,00 cm
F1P               13 925 ppm
F1               5572.02 Hz
F2P               -0 263 ppm
F2               -105 16 Hz
PPMCM            0 70940 ppm/cm
HZCM           283 85892 Hz/cm
```


CH₃O
C≡C
O
H
F2 - Acquisition Parameters
SOLVENT CDCl3
NS 128
DS 2
CHANNEL f1
NUC1 1H
P1 8.30 usec
F2 - Processing parameters
SF 400.1420083 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F2P 6.533 ppm
ppm
7.8
7.6
7.4
7.2
7.0
6.8

18

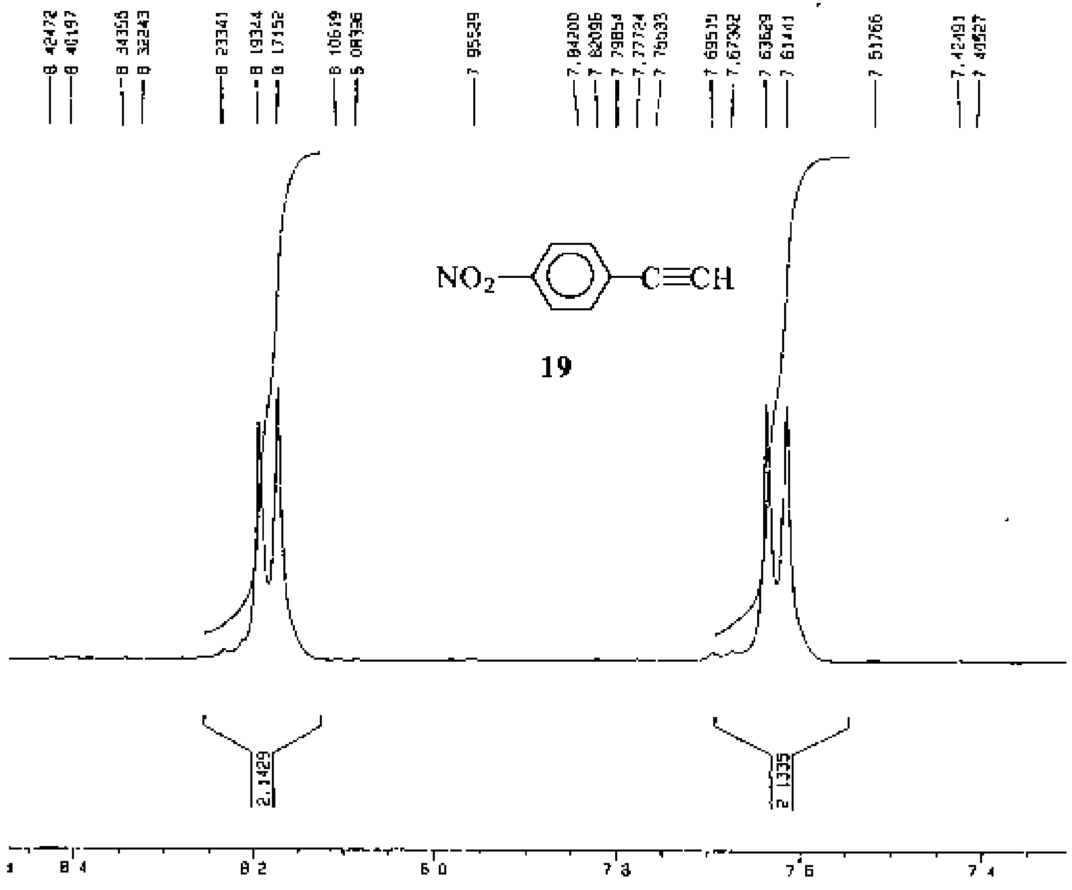


18


NO2
C≡CH
Current Data Parameters
NAME 44302
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080513
Time 17.09
INSTRUM dpx400
PROBHD 5 mm Multinuc
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 128
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 362
DW 78.000 usec
DE 6.00 usec
TE 310.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.32 usec
PL1 -6.00 dB
SFO1 400.1428010 MHz
F2 - Processing parameters
SI 32768
SF 400.1400124 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 10.355 ppm
F1 4147.35 Hz
F2P -0.054 ppm
F2 -21.69 Hz
PPMCM 0.53095 ppm/cm
HZCM 208.43255 Hz/cm
ppm
2.1420
2.1334
1.0000
Integral
ppm
8
6
4
2

19

Analytical BCSIR Lab Dhaka 1H Spectrum LA-91 in CDCL3, Lisla BUET



19

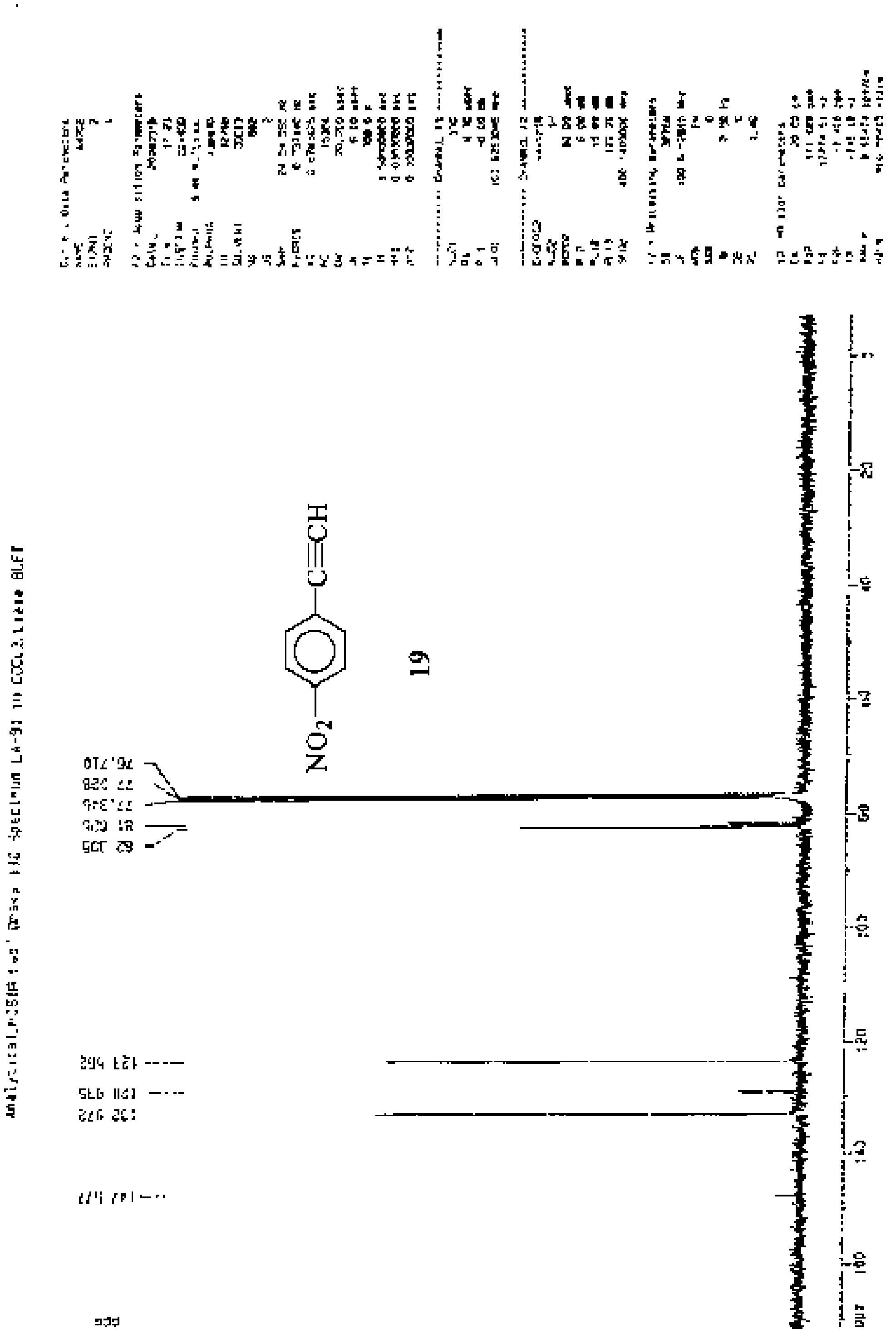
```
Current Data Parameters
NAME               44302
EXPNO .                1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080528
Time               17 09
INSTRUM           dpx400
PROBHD     5 mm Multinuc
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                   128
DS                     2
SWH            6410 256 Hz
FIDRES         0 195625 Hz
AQ            2 5559540 sec
RG                   362
DW              78 000 usec
DE                6.00 usec
TE                310.0 K
D1           1 00000000 sec

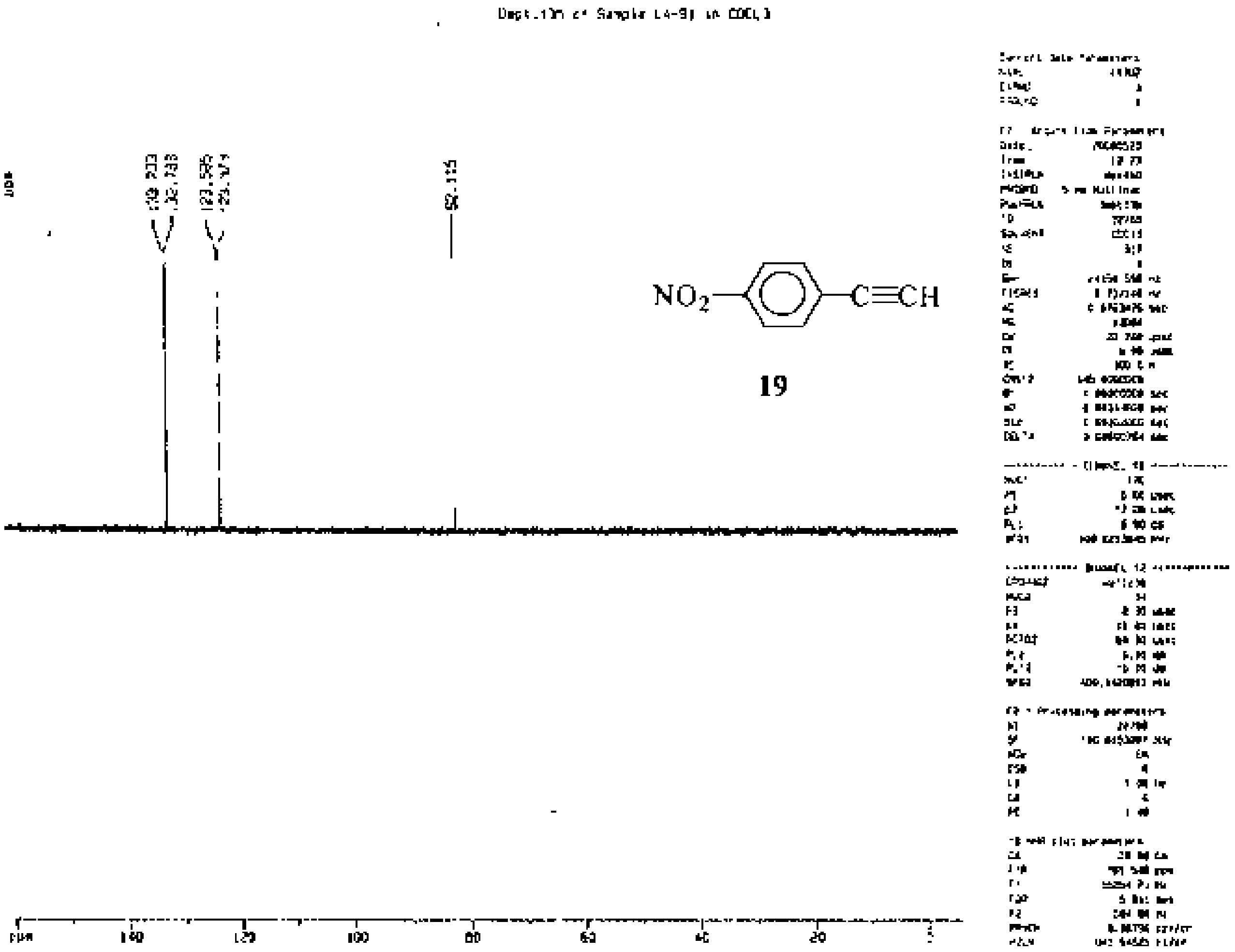
============= CHANNEL f1 =======
NUC1                  1H
P1                8 30 usec
PL1              -6.00 dB
SFO1        400 1428010 MHz

F2 - Processing parameters
SI                 32768
SF           400.1400126 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.40

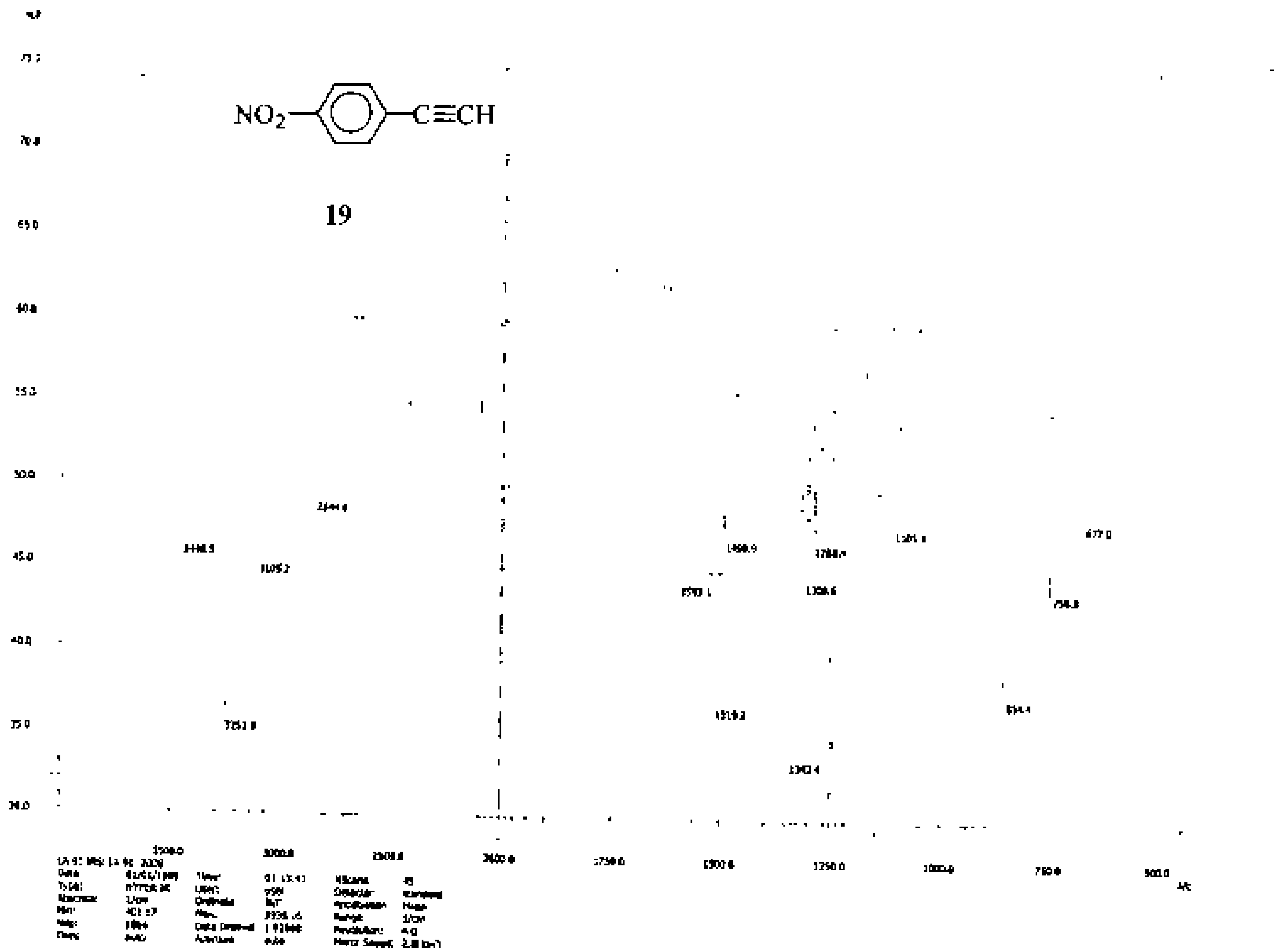
1D NMR plot parameters
CX                 20 00 cm
F1P                8 497 ppm
F1              3400 00 Hz
F2P                7 307 ppm
F2              2924 02 Hz
PPMCM            0.05948 ppm/cm
HZCM            23 79930 Hz/cm
```


62.305
61.620
77.346
77.028
76.710
123.562
130.935
132.972
147.477
ppm
200 180 160 140 120 100 80 60 40 20 0 ppm

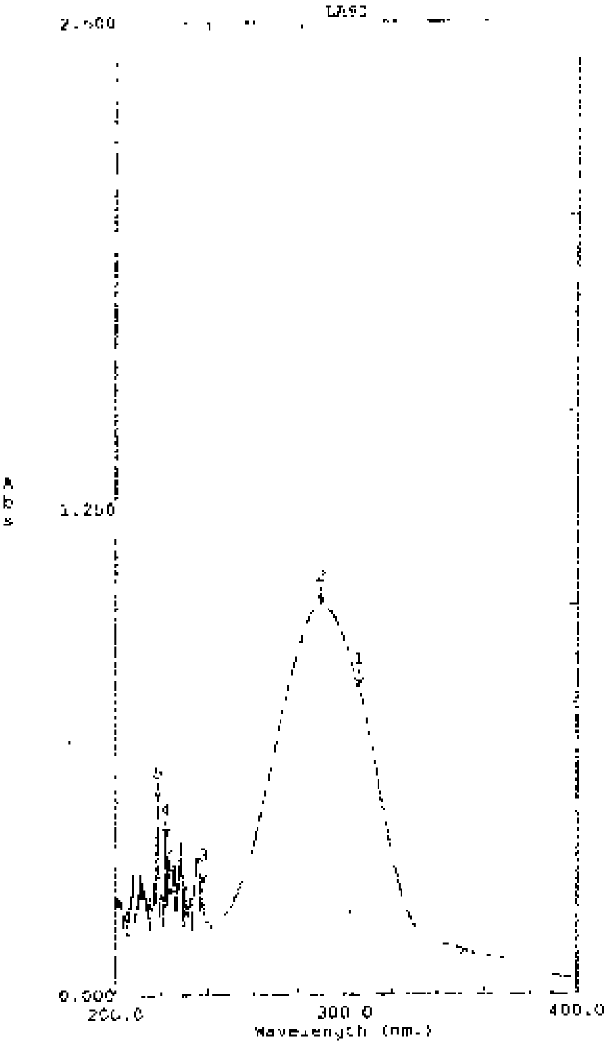
19

Dept.13C of Sample LX-81 in CDCl3
ppm
133.233
132.733
123.585
123.474
82.115
NO2
C≡CH
140
120
100
80
60
40
20
ppm

19

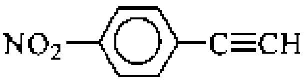

NO$_2$
C≡CH
70.0
65.0
60.0
55.0
50.0
45.0
40.0
35.0
30.0
3500.0
3000.0
2500.0
2000.0
1750.0
1500.0
1250.0
1000.0
750.0
500.0

19



Peak Pick

No.	Wavelength (nm.)	Abs.
1	306.20	0.7435
2	289.40	1.0048
3	230.00	0.2900
4	221.80	0.4076
5	210.20	0.5642



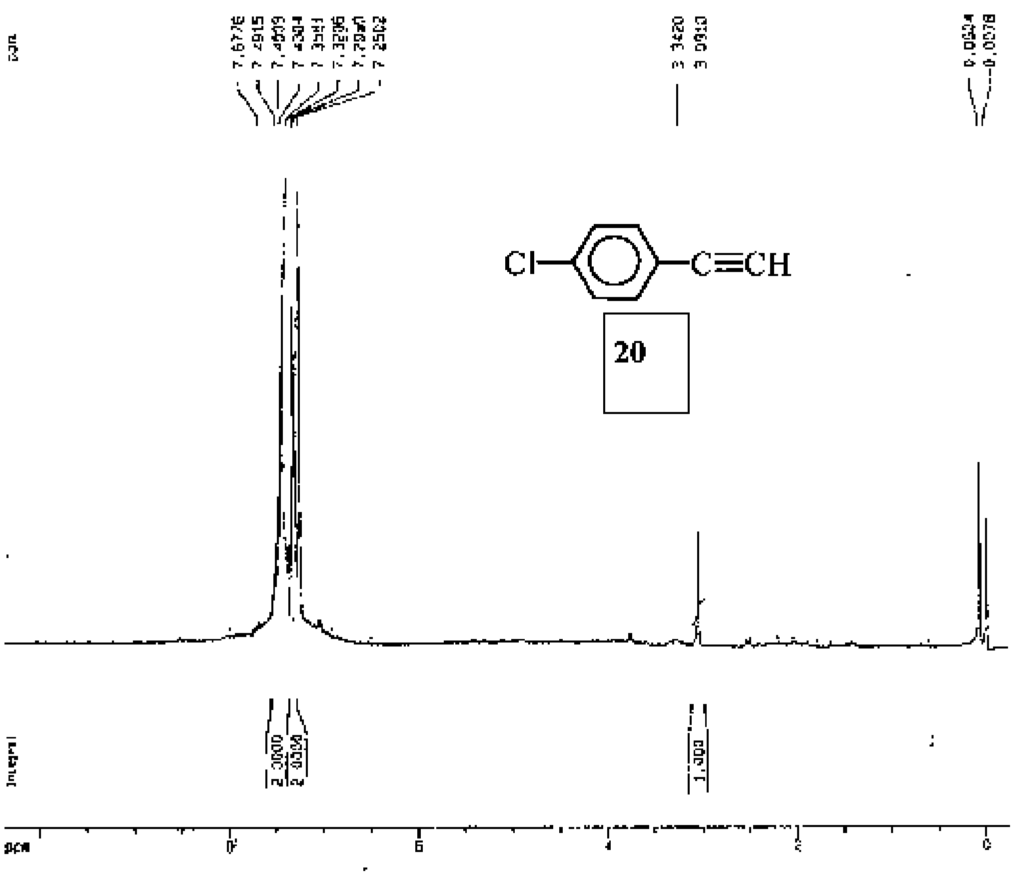
19

File Name   LA91

Created: 15:45   09/14/08
Data: Original

Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

Analytical,BCSIR Lab Dhaka 1H Spectrum LA-92 in CDCl3,Liala,BUET



Current Data Parameters

NAME	A4313
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20080528
Time	17.08
INSTRUM	dpx400
PROBHD	5 mm Multinuc
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	128
DS	2
SWH	6410.256 Hz
FIDRES	0.195625 Hz
AQ	2.5559540 sec
RG	645.1
DW	78.000 usec
DE	6.00 usec
TE	310.0 K
D1	1.00000000 sec

============ CHANNEL f1 ============

NUC1	1H
P1	11.30 usec
PL1	-6.00 dB
SFO1	400.1428010 MHz

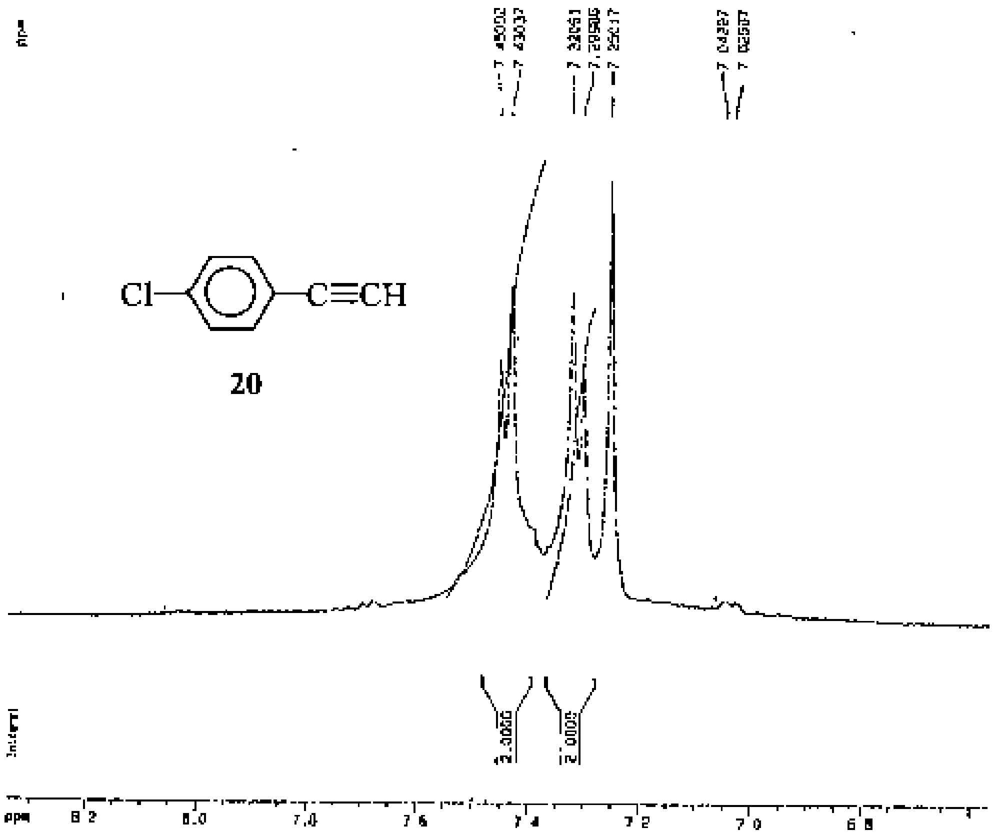
F2 - Processing parameters

SI	32768
SF	400.1400125 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	10.382 ppm
F1	4154.97 Hz
F2P	-0.241 ppm
F2	-96.43 Hz
PPMCM	0.53116 ppm/cm
HZCM	212.53984 Hz/cm

Analytical BCSIR Lab Dhaka 1H Spectrum (A-92 in CDCL3, Liala, BUET)



Cl—C6H4—C≡CH

20

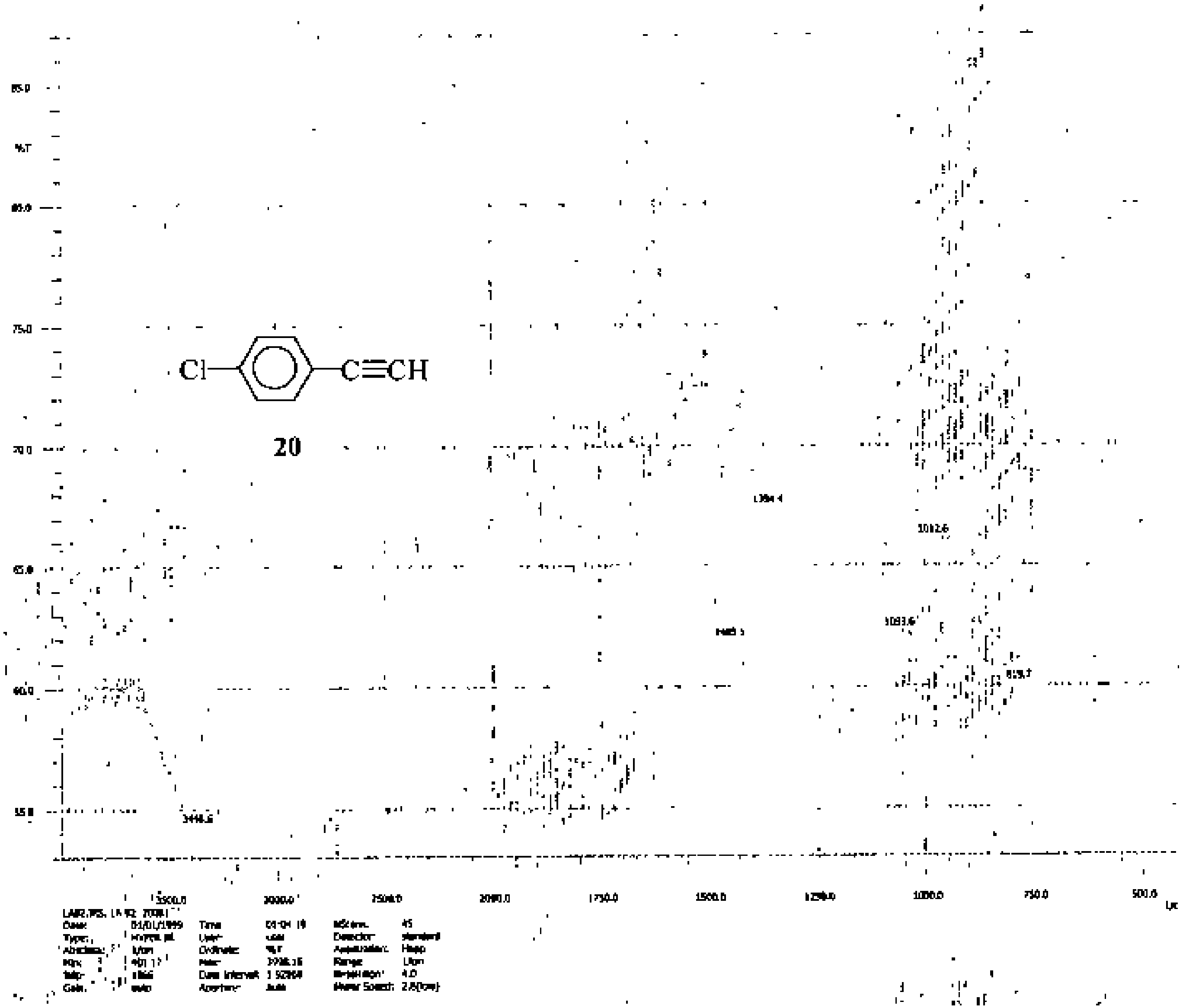
```
Current Data Parameters
NAME              A4313
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20080528
Time              17.06
INSTRUM          drx400
PROBHD   5 mm Multinuc
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                  128
DS                    2
SWH           6410.256 Hz
FIDRES        0.195625 Hz
AQ           2.5559540 sec
RG                645.1
DW               78.000 usec
DE                 6.00 usec
TE                310.0 K
D1           5.00000000 sec

============ CHANNEL f1 ============
NUC1                 1H
P1                 8.30 usec
PL1               -5.00 dB
SFO1       400.1428010 MHz

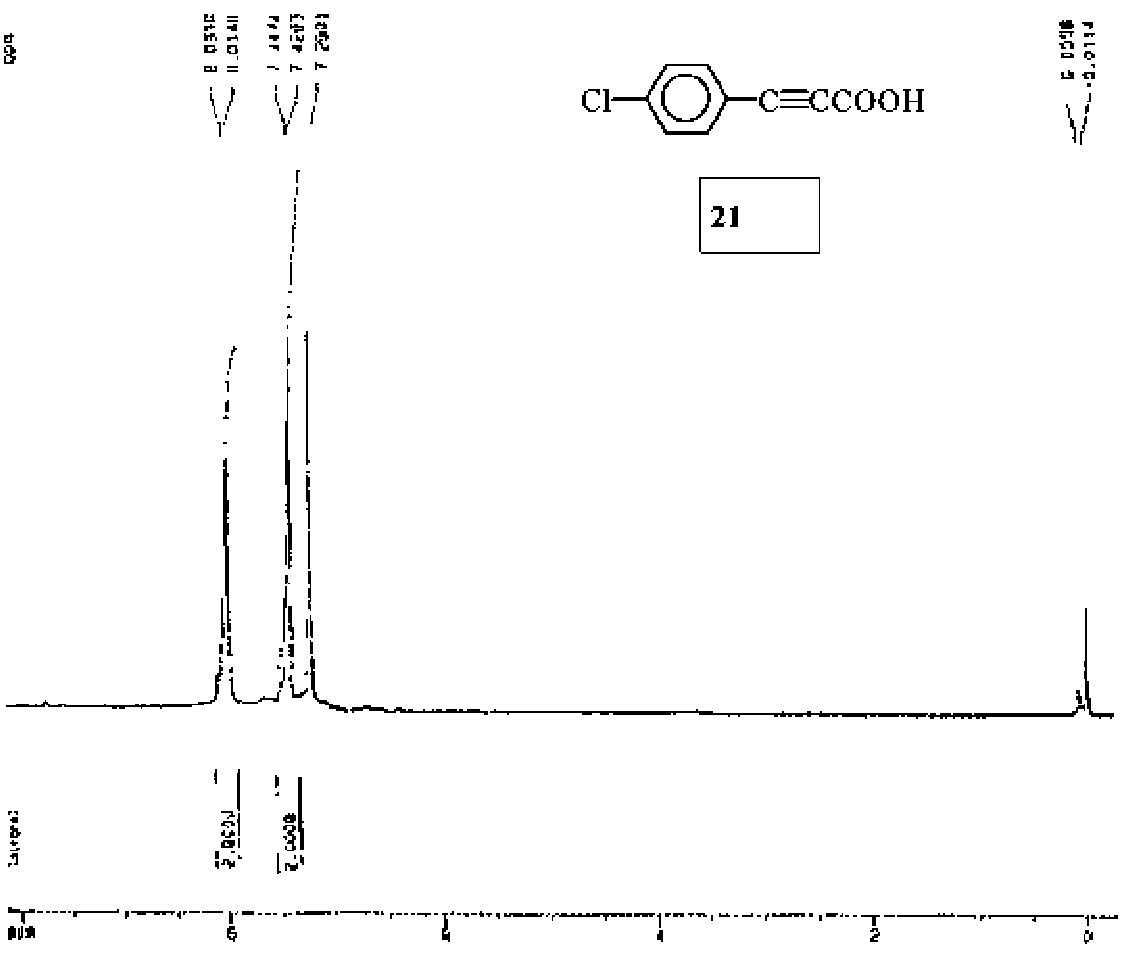
F2 - Processing parameters
SI                32768
SF          400.1400125 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P               8.342 ppm
F1              3338.10 Hz
F2P               6.564 ppm
F2              2626.36 Hz
PPMCM           0.08894 ppm/cm
HZCM           35.50595 Hz/cm
```


85.0
%T
80.0
75.0
70.0
65.0
60.0
55.0
3446.6
1384.4
1485.5
1093.6
1012.6
829.7
3500.0
3000.0
2500.0
2000.0
1750.0
1500.0
1250.0
1000.0
750.0
500.0
1/cm
Date: 01/01/1999
Time
User
Ordinate: %T
Abscissa: 1/cm
Data interval
Aperture: Auto
Gain: auto
No.Scans: 45
Detector: standard
Apodization: Happ
Range
Resolution: 4.0
Mirror Speed: 2.8(low)
Cl
C≡CH

20

Analytical, BCSIR Lab, Dhaka 1H Spectrum (1-5) in CDCl3 [illegible]



```
Current Data Parameters
NAME              14535
EXPNO                 1
PROCNO                1

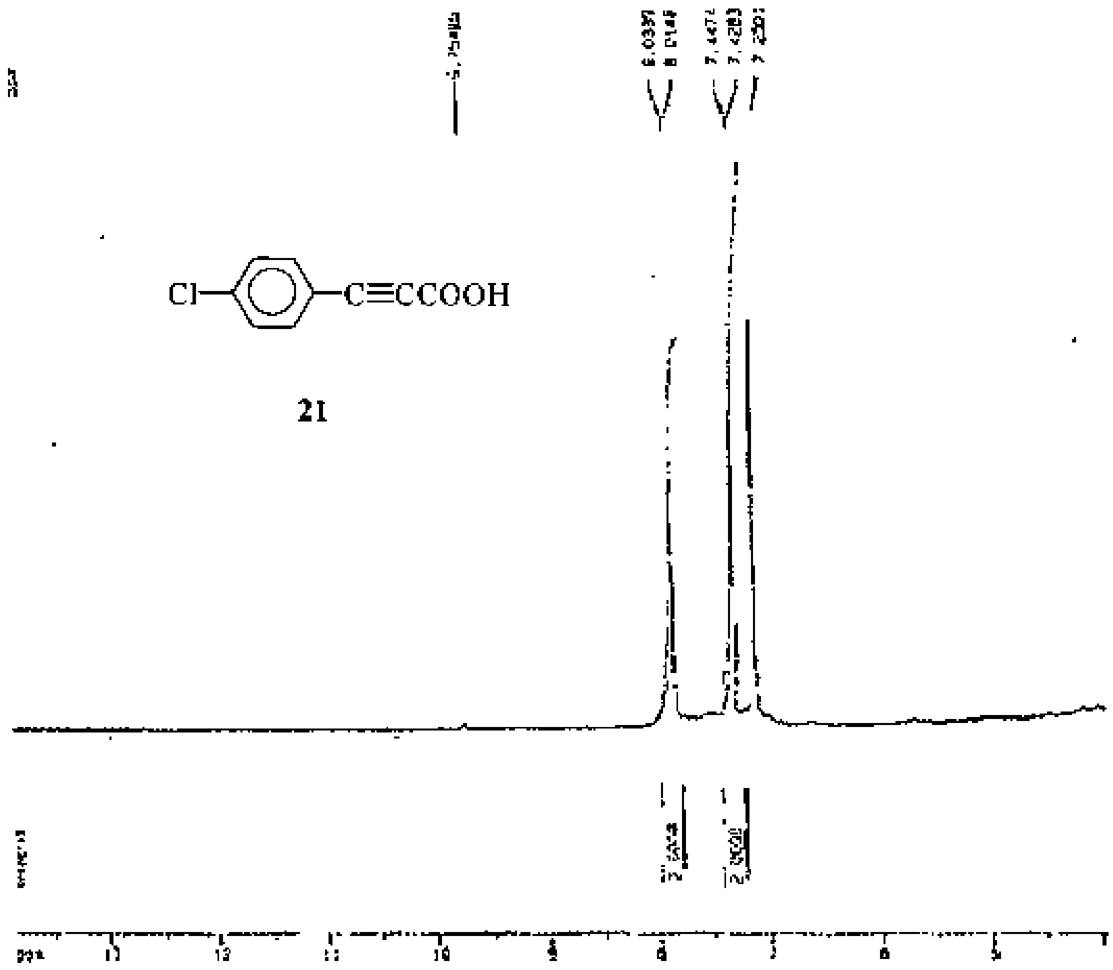
F2 - Acquisition Parameters
Date_          20080522
Time              15 25
INSTRUM           spect
PROBHD   5 mm Multinuc
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                  125
DS                    2
SWH           6410.256 Hz
FIDRES         0.195625 Hz
AQ            2.5559540 sec
RG                  362
DW               78.000 usec
DE                 6.00 usec
TE                310.0 K
D1          1.00000000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 8.30 usec
PL1               -6.00 dB
SFO1        400.1428010 MHz

F2 - Processing parameters
SI                32768
SF          400.1400231 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P              10.145 ppm
F1              4059.35 Hz
F2P              -0.257 ppm
F2              -102.85 Hz
PPMCM           0.52010 ppm/cm
HZCM          208.11135 Hz/cm
```

Analytical BCSIR Lab. Dhaka 1H Spectrum (4-9) in CDCl3 [illegible]



21

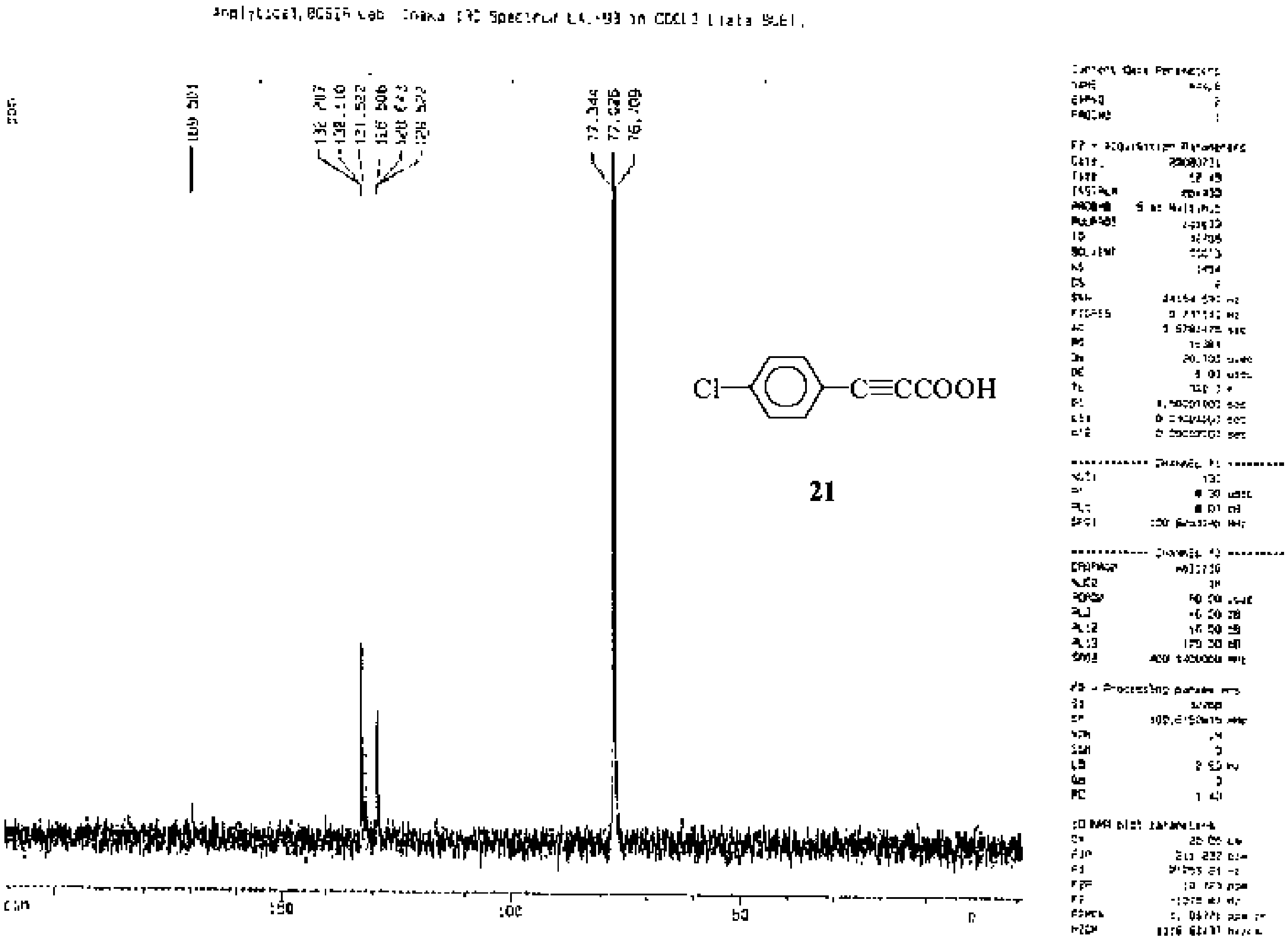
Current Data Parameters
NAME [illegible]
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ [illegible]
Time 15.23
INSTRUM dpx400
PROBHD 5 mm Multinuc
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 128
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 182
DW 78.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

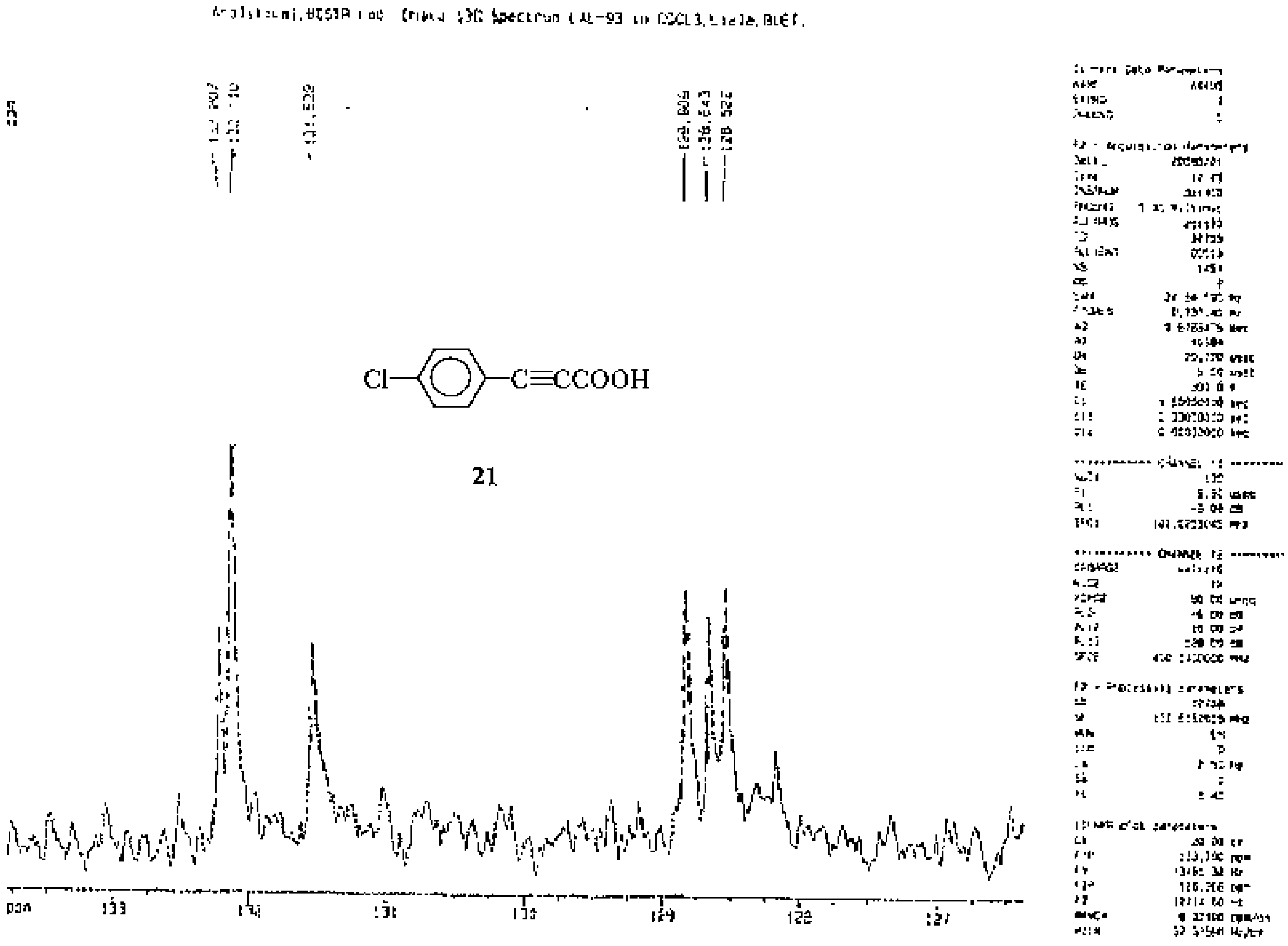
============ CHANNEL f1 ============
NUC1 1H
P1 8.70 usec
PL1 -6.00 dB
SFO1 400.1420010 MHz

F2 - Processing parameters
SI 32768
SF 400.1400121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

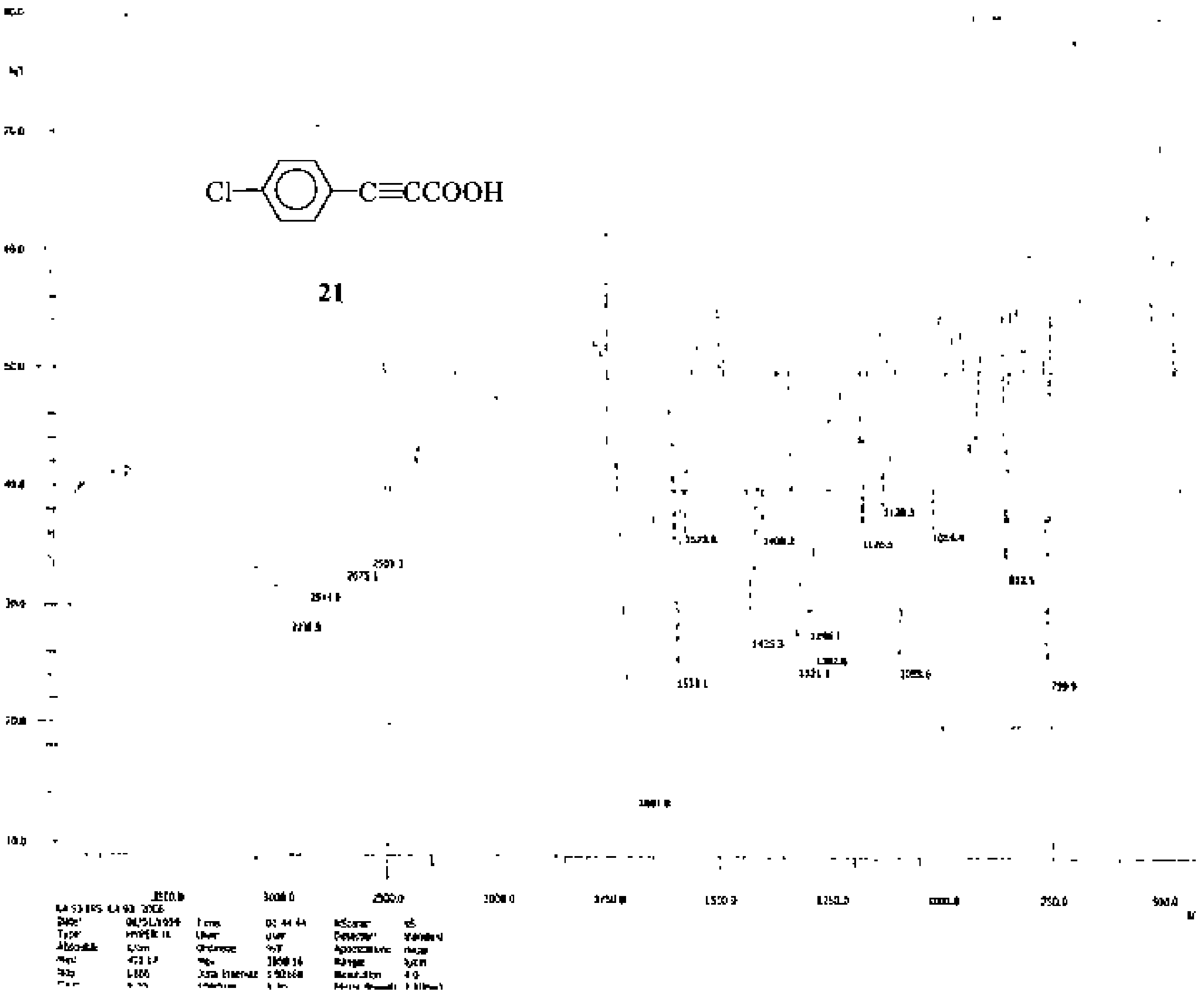
1D NMR plot parameters
CX 20.00 cm
F1P 13.473 ppm
F1 5391.26 Hz
F2P 3.966 ppm
F2 1586.67 Hz
PPMCM 0.47542 ppm/cm
HZCM 190.21427 Hz/cm

Analytical, BCSIR Lab. Dhaka 13C Spectrum in CDCl3
ppm
159.501
132.207
130.110
131.522
126.906
128.643
128.522
77.344
77.026
76.709
Cl—C6H4—C≡CCOOH
200
150
100
50
0

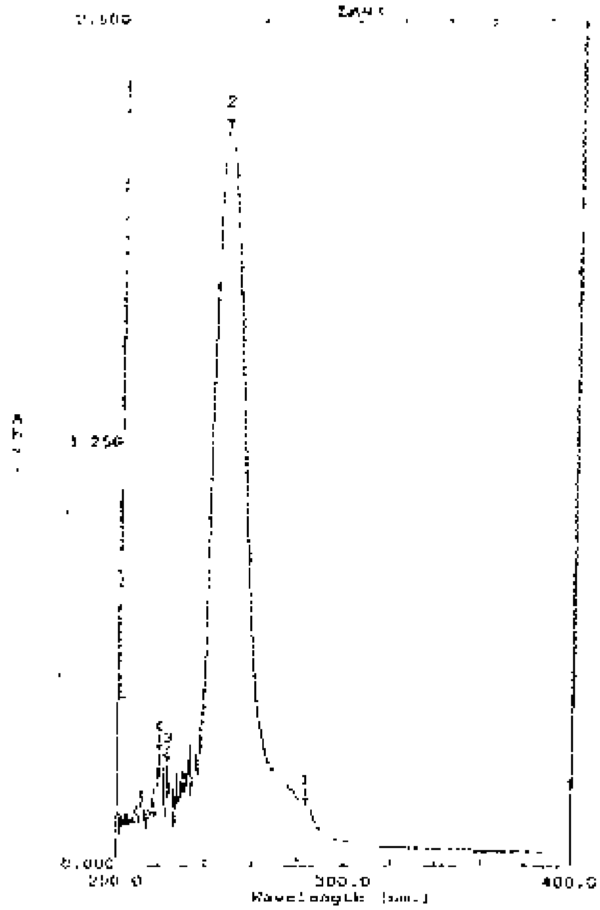
21



21

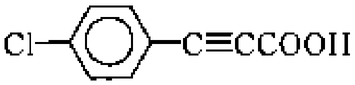

Cl
C≡CCOOH
80.0
%T
70.0
60.0
50.0
40.0
30.0
20.0
10.0
4000.0
3000.0
2500.0
2000.0
1750.0
1500.0
1250.0
1000.0
750.0
500.0
2590.1
2675.1
2544.8
2218.6
1681.8
1571.8
1511.1
1408.2
1425.3
1296.1
1282.8
1321.1
1128.5
1176.5
1085.6
1024.4
832.5
759.9

21



Peak Pick

No.	Wavelength (nm.)	Abs
1	283.96	0.1812
2	245.60	2.2940
3	222.40	[illegible]
4	217.20	[illegible]



21

File Name: LA93

Created: 15:54 09/14/00
Data: Original

Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

References

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