SYNTHESIS AND CHARACTERIZATION OF 2-(SUBSTITUTED ARYL)-3, 3a-DIHYDRO-8H-PYRAZOLO [5,1-a] ISOINDOL-8-ONES VIA CHALCONE BASED N-FORMYL-PYRAZOLINES

A DISSERTATION

Submitted in partial fulfillment of the requirements for the award of the degree of

MASTER OF TECHNOLOGY

in

ADVANCED CHEMICAL ANALYSIS

By

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JUNE, 2011

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CERTIFICATE

This is to certify that the thesis entitled "***Synthesis and characterization of 2-(substituted aryl)-3,3a-dihydro-8H-pyrazolo [5,1-a]isoindol-8-ones via chalcone based N-formyl-pyrazolines***" submitted by Dharm Dev, who has registered as M.Tech student in Advanced Chemical Analysis in chemistry department, Indian Institute of Technology Roorkee since July 2009. This work is done by him under my supervision and neither this thesis nor any part of it has been submitted for any degree / diploma or any other academic award any where before.

Date: 27/6/2011

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CANDIDATE'S DECLARATION

I hereby certify that the progress report presented in the dissertation in the entitled ***"Synthesis and characterization of 2-(substituted aryl)-3,3a-dihydro-8H-pyrazolo [5,1-a]isoindol-8-ones via chalcone based N-formyl-pyrazolines"*** for the award of the degree of Master of Technology submitted to the Indian institute of Technology Roorkee is an authentic record of my won work carried out by me during the period from July 2010 to June 2011 under the supervision of Dr. Naseem Ahmed, Assistant Professor, Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institute.

Place: Roorkee **(DHARM DEV)**

Date: 27-6-2011

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

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Abstract

N-formyl-pyrazoline is the central intermediate in the biogenesis of naturally occurring pyrazoloisoindole derivatives and a useful material in the laboratory synthesis. These derivatives (N-formyl-pyrazoline and pyrazoloisoindoles) were displayed many interesting biological properties, such as hypoglycemic, antimicrobial, amoebicidal, antibacterial, antipyretic, and analgesic activities. An alternate synthetic approach of 2-(substituted aryl)-3,3a-dihydro-8H-pyrazolo [5,l-a] isoindol-8-ones via chalcone based N-formyl-pyrazolines is described. N-formyl-pyrazolines (**1b-15b**) were prepared in excellent yield (81-96%) by the reaction of chalcones (**1a-15a**) with hydrazine hydrate in presence of formic acid, which undergoes intramolecular Friedal-Craft acylation in the presence of trifluoroacetic acid (TFA) as a catalyst to afford functionalized 2-(substituted phenyl)-3,3a-dihydro-8H-pyrazolo[5,1-a]isoindol-8-one (**3c-15c**) in good to excellent yield (74-94%) at refluxed in acetonitrile. Our synthetic route avoids expensive reagents and significantly improved the yield.

Acknowledgement

As I reflect upon the years gone by, I deeply feel the need to acknowledge my gratitude to many wonderful people who have helped me reach this day.

In the first place, I would like to express my deep and sincere gratitude to my supervisors, Dr. Naseem Ahmed for their supervision, advice and guidance from the very early stage of this research as well as giving me extraordinary experiences throughout the work. Above all and the most needed, they provided me unflinching encouragement and support in various ways. Their scientific intuitions have made them as a constant oasis of ideas and passions in science, which inspired and enriched my growth as a student, a researcher and to become a scientist. I am indebted to them for their valuable guidance.

I would like to express my heartiest thankful to Dr. V.K.Gupta, Professor and Head, Department of Chemistry, Indian Institute of Technology, Roorkee for extending various facilities during the course of this work.

I am especially indebted Dr. R. K. Dutta (Coordinator of M.Tech Programme), Assistant Professor, all the faculty members and staff of Department of Chemistry, IIT Roorkee, for their support during the entire period of M.Tech programme.

I wish to express my thanks to my lab mats B. Venkata Babu , Naveen kumar, Praveen, Sunita Dey, friends, the staff of Institute Instrumentation Centre, Central Library and Computer Centre, who are the part to the completion of my work.

Where would I be without my family? In my family special thank to my BADE PAPA Mr. Man Raj and BADI MAMMA Mrs. Prabha Baudh support throughout my life; this work is simply impossible without them. I am indebted to my father, Mr. Radhe Shyam, for his care and love. I cannot ask for more from my mother, Mrs. Chanarama Devi, as she is simply perfect. I have no suitable word that can fully describe them everlasting love to me and I remember, most of all for her delicious dishes.

Last but not least, thanks to God for granting me the faith and will to obtain this academic achievement that has culminated in this thesis.

Place: Roorkee

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CHAPTER 1

INTRODUCTION

1.1 Introduction:

The plant chemistry is a wide and distinct field, which concerned with enormous variety of organic substances accumulated by plants, for example alkaloids, amino acids, pyrazoloisoindole, pyrazoline, etc. In literature, derivatives of nitrogenated heterocyclic aromatics of five members have been described with the inhibition of prostaglandin biosynthesis. Some of these azole derivatives are pyrrols[1–3], imidazoles[4], pyrazoles[5,6] and pyrazolines, which are pyrazole derivatives[7,8]. It has been suggested that biological evaluation of new bioactive molecules containing pyrazol nucleus is important for the creation of promising new analgesic agents[9–10]. Some pyrazoline-derived compounds including dipyrone (metamizol) have been shown to possess analgesic activities mediated by peripheral mechanisms such as inhibitions of cyclooxygenase enzyme activity, arachidonic acid cascade and prostaglandin biosynthesis[1–8]. However, some other pyrazoline-derived compounds have been reported as centrally acting analgesic agents[9–11]. Decrease of on/off cell firing in the periaqueductal gray[10], activation of endogen opioid mechanisms[9] and spinal noradrenergic and serotonergic systems[11] are some of the suggested mechanisms about this centrally mediated analgesia.

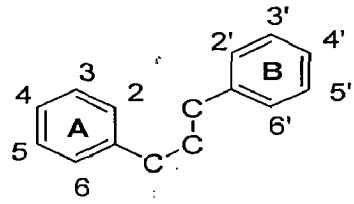
Pyrazoloisoindolone derivatives (Figure 2) are known for their plant growth regulating properties[12]. These structures can be regarded as aza-pyrroloindolones or aza-analogues of tripentones which possess anti-cancer properties and which are widely studied in laboratorys[13]. Pyrazoloisoindole, Pyrazoline and its derivatives have attracted considerable attention due to the wide variety of biological activities (Figure 3). They exhibit hypoglycemic, antimicrobial, amoebicidal, antibacterial, antipyretic, and analgesic activities[14]. Specifically, 5-hydroxy-4,5-dihydro-1*H*-pyrazoles are known to possess anti-inflammatory and analgesic activity[15]. Pyrazoles exhibit analgesic[16], antimicrobial[17], anti-inflammatory[18], antihypertensive[19] and hypoglycemicactivities[20]. Also as potential antiprotozoal, cytotoxic agents[21], and CB_1 cannabinoid receptor antagonists as appetite supp``ressants for the treatment of obesity[22]. Even today,the pyrazole core concontinues to emerge as a central candidate for pharmaceutical and agricultural applications[23]. The pyrazoline function is quite stable, and has inspired chemists to

utilize this stable fragment in bioactive moieties to synthesize new compounds possessing biological activities[24]. Pyrazoloisoindole and pyrazoline derivatives synthesized based on moiety of chalcone.

Chalcones are well known natural compounds and in synthetic chemistry a well known intermediates for synthesizing various heterocyclic compounds bearing the 1, 3- diphenylprop-2-en-1-one framework that have displayed a wide biological activities such as antimicrobial, anti-inflammatory, analgesic, antiplatelet, antiulcerative, antimalarial, anticancer, antiviral, antileishmanial , antioxidant , antitubercular, antihyperglycemic, immunomodulatory inhibition of chemical mediators, release inhibition of leukotriene B_4, inhibition of tyrosinase and inhabition of aldose reductase activities[25-29].

The majority of the naturally occurring chalcones contain either hydroxyl (OH) or methoxy (OCH_3) substituents on the two aromatic rings[30]. However, the number of different chalcones that are theoretically possible in nature is extremely high since each of the groups can be substituted by one or more sugars, which in turn can be acylated with different phenolic of aliphatic moieties. Synthetic and naturally occurring hydroxychalcones and methoxychalcones are of particular interest as they display a wide range of biological properties and exert diverse pharmacological activities. In fact, because of their chemical structures, these compounds can promote both antioxidant and pro-oxidant effects and, as a consequence, have been shown to be effective chemopreventive agents as well as to exert bactericidal, antifungal, anticarcinogenic, and anti-inflammatory actions[31,32]. The mechanism(s) responsible for this pleiotropism remain to be fully understood, but it is becoming evident that more than one specific cellular target is implicated in the pharmacological actions mediated by chalcones. For instance, the anti-inflammatory properties of 4-dimethylamino-3′,4′-dimethoxychalcone and 2′,5′-dihydroxy-4-chloro-dihydrochalcone in murine macrophages were initially reported to involve a direct scavenging effect on superoxide anion production and inhibition of inducible nitric oxide synthase (iNOS) expression[33,34].

Many studies of chalcone related to cancer have demonstrated. The presence of a reactive α,β-unsaturated keto function in the chalcone is found to be responsible for their microbial activity. The chalcone are acyclic polyphenolic compounds possessing 15carbon atoms(Figure 1) ; two benzene rings joined by a linear three carbon chain[35]. They constitute one of the most characteristic classes of compounds in higher plants.



The skeleton above, can be represented as the

$C_6 - C_3 - C_6$ system.

Figure1:

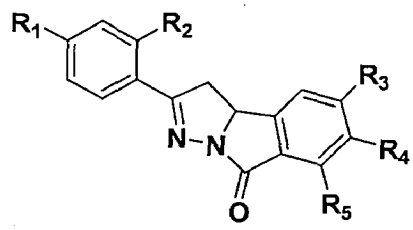
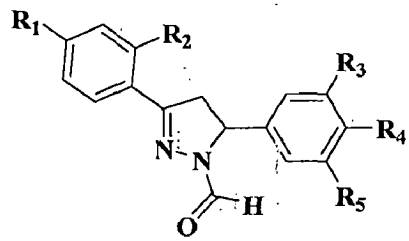


Figure 2: General Structure of Pyrazoloisoindole

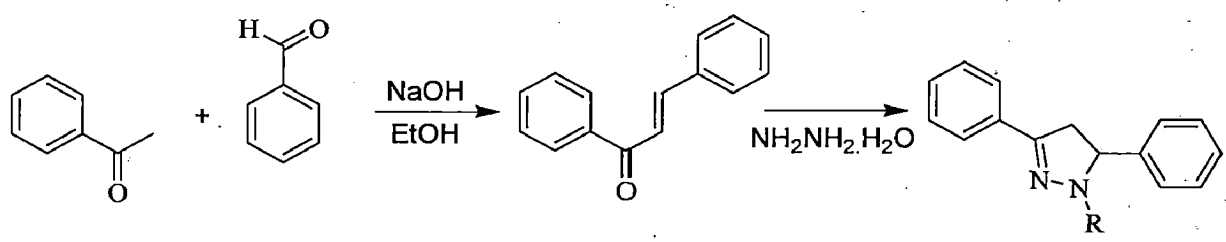


R_1 = H, OH, Br, Cl; R_2 = H, OH; R_3 = H, OCH_3;
R_4 = H, CH_3, OCH_3, OH, Cl, Br, NO_2;
R_5 = H, OCH_3, NO_2.

Figure 3: General Structure of Pyrazoline

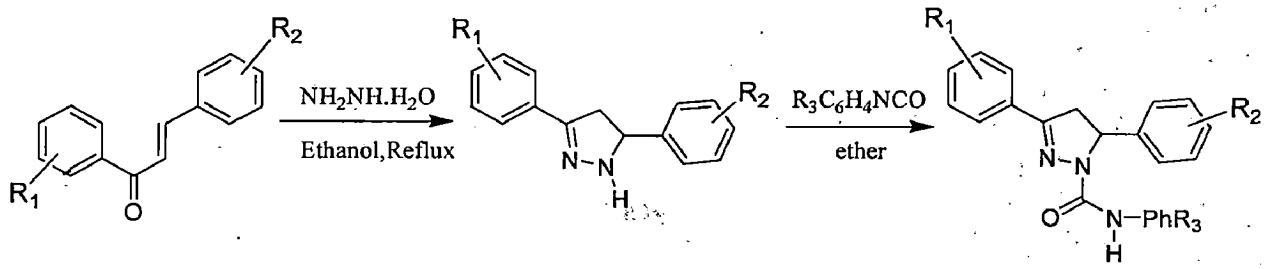
1.2 Literature survey:

Chalcone was synthesized using Claisen-Schmidt reaction. In chalcone, more important moiety is α,β unsaturated ketone, which has more important for biological activity. The α,β-unsaturated ketones can play the role of versatile precursors in the syntheses of the corresponding pyrazoline derivatives[36-41]. Pyrazoline are very important intermediate in organic chemistry and can serve as versatile precursor in synthesis of many natural products and drug moieties. Some reagent including, hydrazine hydrate, phenylhydrazine, and methyl hydrazine, have used in cyclization of chalcone to form pyrazoline[42].



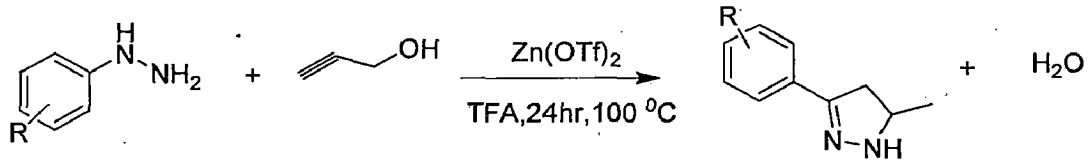
Route: 1 (R=-H, Ph, CH_3)

Rolf van Hes, Kobus Wellinga, and Arnold C. Grosscurt was Synthesis and Insecticidal Properties of 3,5-Diphenyl-1-phenylcarbamoyl-2-pyrazolines. They are Synthesis these product by chalcone derivatives[43].



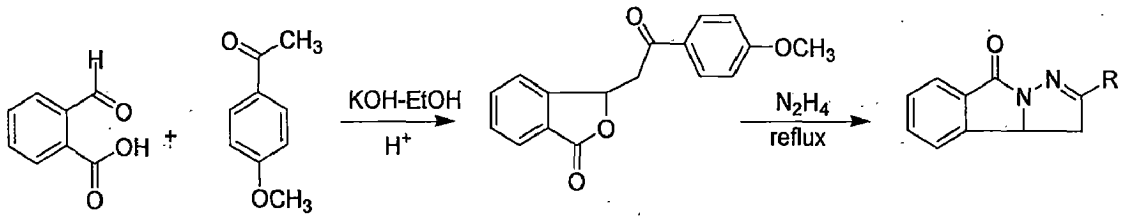
Route: 2 (R_1= -Cl, $-C_2H_5$, $-N(CH_3)_2$; R_2= H, -Cl, CH_2; R_3=-Cl, -Br, CF_3).

Karolin Alex, Annegret Tillack, Nicolle Schwarz, and Matthias Beller have been developed a method for novel regioselective synthesis of aryl-substituted pyrazolines. Substituted phenylhydrazines react with 3-butynol in the presence of a catalytic amount of zinc triflate to give pyrazoline derivatives. The resulting products are easily oxidized in a one-pot procedure to the corresponding pyrazoles[44].



Route: 3(R = Cl, Br, CH_3).

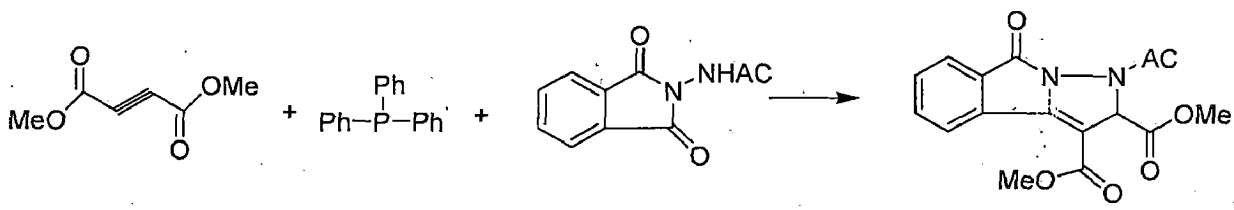
Alexander L. Johnson and Philip B. Sweetser have described the synthesis of 2-(4-methoxyphenyl)-8H-pyrazolo[5,1-u]isoindol-8-one from its 3,3a-dihydro derivative, which was prepared from phthalaldehydic acid, 4-methoxyacetophenone, and hydrazine[45]. The reverse cyclisation of 2-[3(5)-arylpyrazol-3(5)-yl] benzoic acid proceeded with thionyl dichloride, phosphoric trichloride or acetic anhydride[46].



R = 4-$CH_3OC_6H_4$; 4-$C_2H_5OC_6H_4$; 2,4-$(CH_3)_2C_6H_3$; 2,4,6-$(CH_3)_3C_6H_2$; 3-$CH_3C_6H_4$; 4-$CF_3C_6H_4$; 3-BrC_6H_4; 3,4 -$Cl_2C_6H_3$; 4-FC_6H_4; $(CH_3)_3C$.

Route: 4

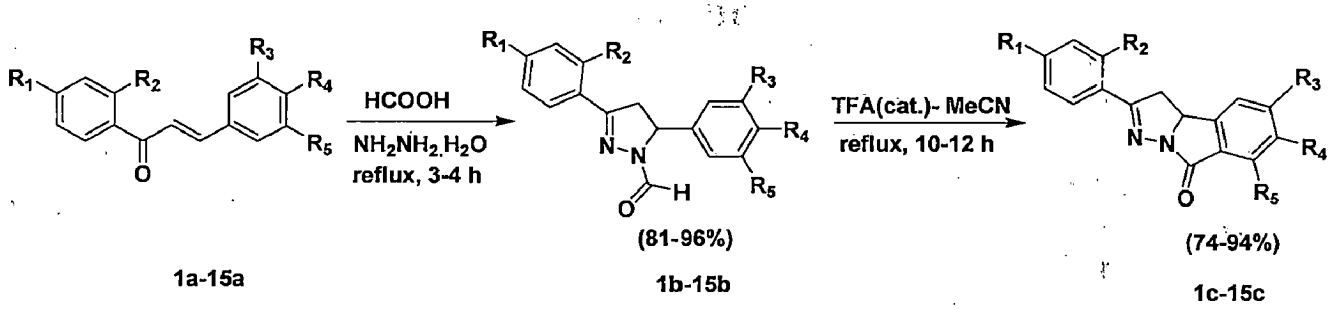
Islami, Mohammad Reza and Abedini-Torghabeh was synthesized fused pyrazole systems as biological important molecules. An efficient two-step protocol has been developed to maked molecules of this family via the reaction between di-Methylacetylenedicarboxylate, triphenylphosphine and N-aminophthalimide in the presence of benzoic acid or N-aminophthalimide derives. This reaction occurred easily at ambient temperature to give stable phosphorus ylides, which upon heating undergoes an intramolecular Wittig reaction to afford the pyrazolo[5,1-a]isoindole derives[47].



Route: 5

Aim and scope of the present work

Chalcone is a very special α,β-unsaturated ketone system. The α,β-unsaturated ketones play the important role of versatile precursors in the synthesis of the many natural product and biological active compounds. Chalcone are convenient and versatile materials for the synthesis of pyrazolines. Some reagent including, hydrazine hydrate, phenylhydrazine, and methyl hydrazine, have used in cyclization of chalcone to form pyrazoline. The present study deals with the synthesis of N-formylpyrazoline as a new representative of this compound class by reaction of an α,β-unsaturated ketone with hydrazine hydrate and formic acid and report an alternate method for the preparation of functionalized 2-(substituted aryl)-3,3a-dihydro-8H-pyrazolo[5,1-a]iso-indol-8-one (**1c-15c**) via chalcone based N-formyl-pyrazolines using trifluoroacetic acid as catalyst at refluxed in acetonitrile (Scheme 1).



1a-15a

1b-15b

1c-15c

R_1 = H, OH, Br,Cl , R_2 = H, OH , R_3 = H, OCH_3 ,
R_4 = H, CH_3 ,OCH_3 , OH , Cl, Br. NO_2 , R_5 = H, OCH_3 , NO_2.

Scheme 1

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Chapter - 2

Synthesis and Characterization

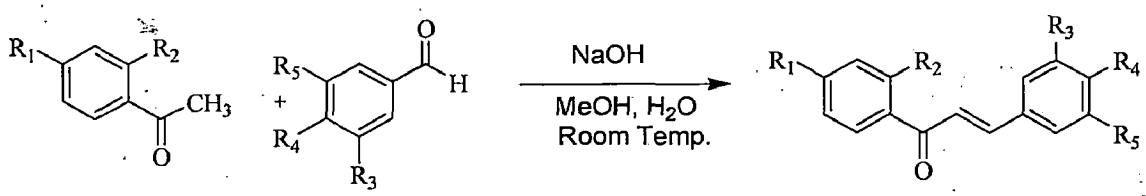
2A: SYNTHESIS OF CHALCONE DERIVATIVES

2A. 1 Instruments and Chemicals used

Flash chromatography was performed on silica gel (Rankem laboratory, 60-120 mesh). TLC was performed on aluminum-backed silica plates (contain -13% $CaSO_4$ ½ H_2O, SILICA Gel /UV_{254}), which were developed by using UV fluorescence. Melting points were determined on kofler apparatus melting point apparatus and are uncorrected. Elemental analysis was performed on a Vario EL CHNS analyzer. Infrared spectra were recorded on a Nexus Thermo Nicolet FT-IR spectrometer using KBr pellets .^{1}H NMR spectra were recorded at 500 MHz on Brucker ultra shield AC 300 and DPX 300 instruments, respectively; ^{13}C NMR spectra at 125.5 MHz's chemical shifts are given in parts per million (ppm) referenced to TMS. High resolution mass spectra (m/z) were recorded on a Perkin Elamer GC-MS spectrometer. All commercially available chemicals were used with further purification. Anhydrous solvents were distilled from appropriate drying agents prior to use.

2A. 2 General procedure for the synthesis of Chalcones

Different Acetophenone (1 mmol) and different aromatic aldehyde (1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a yellow/white cloudy solution. The reaction mixture was stirred for 2-5 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or MeOH/CH_2Cl_2) to give the product or silica gel column chromatography is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product.



R_1=H, OH, Br,Cl; R_2= H, OH; R_3 = H, OCH_3
R_4 =H, CH_3 ,OCH_3 , OH , Cl, Br. NO_2.
R_5 = H, OCH_3 , NO_2.

Scheme 2

2A.3 Synthesis of chalcone(1a)

Acetophenone (0.116 mL, 1 mmol) and benzaldehyde (0.101 ml, 1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a white solution. The reaction mixture was stirred for 2 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or $MeOH/CH_2Cl_2$) to give the product or silica gel column chromatography is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product. Yield=92%, m.p. = 71-73^{0}C. ^{1}HNMR ($CDCl_3$, 500MHz) δ ppm: 8.05-8.03 (m, Ar-H, 2H), 7.83 (d, *J*=11.5Hz, =CH-Ar, 1H), 7.69-7.63 (m, Ar-H, 2H), 7.62-7.57 (m, Ar-H, 1H), 7.55-.51 (m, Ar-H, 3H), 7.47-7.43 (m, Ar-H, 3H); IR ν_{max} (KBr, cm^{-1}): CO $\nu_{stretch}$ 1640, N-$H_{bending}$ 1534, 1203, 1157.47 1085.32, 997.17, 820.12, 760.04 , 679.28.

2A.4 Synthesis of (E)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one(2a)

Acetophenone (0.116 mL, 1 mmol) and p-chlorobenzaldehyde (140.5 mg, 1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a white solution. The reaction mixture was stirred for 4 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or $MeOH/CH_2Cl_2$) to give the product or silica gel column chromatography

is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product. Yield=93%, m.p. =111-112^{0}C. ^{1}HNMR ($CDCl_3$, 500MHz) δ ppm: 8.06-8.04 (m, Ar-H, 2H), 7.96 (d, *J*=15.5Hz, =CH-Ar, 1H), 7.83-7.64 (m, Ar-H, 2H), 7.63 (d, *J*=12.0Hz, O=C-CH=, 1H), 7.61-7.54 (m, Ar-H, 2H), 7.46-7.40 (m, Ar-H, 3H); IR ν_{max} (KBr, cm^{-1}): CO $\nu_{stretch}$ 1644, N-$H_{bending}$ 1523, 1206, 1157, 1075, 997, 820, 760 , 679.

2A. 5 Synthesis of (E)-1, 3-bis(4-chlorophenyl)prop-2-en-1-one(3a)

4-chloroacetophenone (0.1295 mL, 1 mmol) and 4-chlorobenzaldehyde (140.5 mg, 1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a yellowish solution. The reaction mixture was stirred for 6 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or MeOH/CH_2Cl_2) to give the product or silica gel column chromatography is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product. Yield= 91%, m.p. = 78-81^{0}C. ^{1}HNMR ($CDCl_3$, 500MHz) δ ppm: 8.03-7.93 (m, , Ar-H, 2H), 7.80 (d, *J*=12.5Hz,=CH-Ar, 1H), 7.77-7.58 (m, Ar-H, 2H), 7.52-7.50 (m, Ar-H, 2H), 7.46 (d,*J* = 13.0Hz, 1H), 7.44-7.41 (m, Ar-H, 2H); IR ν_{max} (KBr, cm^{-1}): CO $\nu_{stretch}$ 1647, N-$H_{bending}$ 1533, 1206, 1157, 1076, 987, 824, 764 , 679.

3A. 6 Synthesis of (E)-3-(4-bromophenyl)-1-phenylprop-2-en-1-one(4a)

Acetophenone (0.1205 mL, 1 mmol) and 4-bromobenzaldehyde (185.03 mg, 1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a yellow solution. The reaction mixture was stirred for 3 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or MeOH/CH_2Cl_2) to give the product or silica gel column chromatography is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product. Yield = 93%, m.p. = 74-79^{0}C ^{1}HNMR ($CDCl_3$, 500MHz) δ ppm: 8.02-8.00 (m, Ar-H, 2H), 7.68 (d, *J*=6.5Hz, =CH-Ar, 1H), 7.62-7.55 (m, 3H), 7.53 (d, *J*=12.0Hz, CO-CH=, 1H), 7.51-7.41 (m, Ar-

H, 2H), 7.40-7.28 (m, Ar-H, 2H); IR ν_{max} (KBr, cm^{-1}): CO $\nu_{stretch}$ 1640, N-$H_{bending}$ 1534, 1200, 1158, 1076, 987, 824, 764 , 679, 643, 512.

3A.7 Synthesis of (E)-1-(4-bromophenyl)-3-phenylprop-2-en-1-one(5a)

4-Bromoacetophenone (199.00 mg, 1 mmol) and benzaldehyde (0.101 mL, 1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a yellow solution. The reaction mixture was stirred for 5 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or MeOH/CH_2Cl_2) to give the product or silica gel column chromatography is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product. Yield = 92%, m.p. = 111-113^{0}C. ^{1}HNMR ($CDCl_3$, 500MHz) δ ppm: 7.63 (d, J=8.5Hz, Ar-H, 1H), 7.72 (d, *J*=11.0Hz, =CH-Ar, 1H), 7.35-7.31(m, Ar-H, 1H), 7.28 (d, *J*=11.5Hz, -CO-CH=, 1H), 7.18-7.16 (m, Ar-H, 2H), 7.12-7.09 (m, Ar-H, 1H), 7.04-7.01 (m, Ar-H, 1H), 6.93 (d, J= 11.0Hz, CO-CH=, ,1H), 6.89-6.88 (m, Ar-H, 2H), IR ν_{max} (KBr, cm^{-1}): CO $\nu_{stretch}$ 1647, N-$H_{bending}$ 1533, 1206, 1157, 1076, 987, 824, 764 , 679, 511, 502.

3A.8 Synthesis of (E)-1,3-bis(4-bromophenyl)prop-2-en-1-one(6a)

4-Bromoacetophenone (199.00 mg, 1 mmol) and 4-bromobenzaldehyde (0.196 mg, 1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a yellow solution. The reaction mixture was stirred for 6 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or MeOH/CH_2Cl_2) to give the product or silica gel column chromatography is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product.(Yellow solid). Yield = 94%, m.p. = 125-127 ^{0}C. ^{1}HNMR ($CDCl_3$, 500MHz) δ ppm: 8.07-8.06 (m, Ar-H, 2H), 7.75 (d, *J*=15.5Hz, =CH-Ar, 1H), 7.59-7.57 (m, Ar-H, 2H), 7.53-7.49 (m, Ar-H, 3H), 7.22-7.20 (m, Ar-H, 2H); IR ν_{max} (KBr, cm^{-1}): CO $\nu_{stretch}$ 1643.59, N-$H_{bending}$ 1533.98, 1209.26, 1157.47 1085.32, 997.17, 820.12, 760.04 , 679.28.

3A.9 Synthesis of (E)-1-(4-bromophenyl)-3-p-tolylprop-2-en-1-one(7a)

4-Bromoacetophenone (199.00 mg, 1 mmol) and 4-methylbenzaldehyde (0.118 mL, 1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a yellow solution. The reaction mixture was stirred for 4 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or MeOH/CH_2Cl_2) to give the product or silica gel column chromatography is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product (yellow solid). Yield = 92%, m.p. = 118-120 ^{0}C. ^{1}HNMR ($CDCl_3$, 500MHz) δ ppm: 7.89-7.87 (m, Ar-H, 3H), 7.79 (d, *J*=8.0Hz, =CH-Ar, 1H), 7.64-7.63 (m, Ar-H, 3H), 7.45 (d, *J*= 15.5Hz, CO-CH=, 1H), 7.24-7.22 (m, Ar-H, 2H), 2.39(s, 3H). IR ν_{max} (KBr, cm^{-1}): CO $\nu_{stretch}$ 1657, N-$H_{bending}$ 1536, 1205, 1156, 1076, 987, 814, 765 , 679, 511, 506.

3A.10 Synthesis of (E)-1-(4-bromophenyl)-3-(3, 4-dimethoxy- phenyl)prop-2-en-1-one(8a)

4-Bromoacetophenone (199.00 mg, 1 mmol) and 3,4-methoxybenzaldehyde (166.15 mg, 1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a yellow cloudy solution. The reaction mixture was stirred for 2 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or MeOH/CH_2Cl_2) to give the product or silica gel column chromatography is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product (white Solid). Yield= 94%. m.p. = 97-100^{0}C ^{1}HNMR ($CDCl_3$, 500MHz) δ ppm: 7.89-7.87 (m, Ar-H, 2H), 7.81-7.75 (m, Ar-H, 1H), 7.65-7.59 (m, Ar-H, 2H), 7.34 (d, *J*= 15.5Hz, =CH-Ar, 1H), 7.27-7.22 (m, Ar-H, 2H), 6.92 (d, *J*= 8.5Hz, CO-CH=, 1H), 3.92 (s, 6H); IR ν_{max} (KBr, cm^{-1}): CO $\nu_{stretch}$ 1650, N-$H_{bending}$ 1535, 1206, 1156, 1076, 987, 824, 764 , 679, 514, 502.

3A.11 Synthesis of (E)-1-(4-bromophenyl)-3-(3,4,5-trimethoxyphenyl) prop-2-en-1-one(9a)

4-Bromoacetophenone (199.00 mg, 1 mmol) and 3,4,5-methoxybenzaldehyde (196.20 mg, 1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a white cloudy solution. The reaction mixture was stirred for 3 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or MeOH/CH_2Cl_2) to give the product or silica gel column chromatography is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product. (White crystalline solid) Yield= 93%. m.p. = 119-121 ^{0}C. ^{1}HNMR ($CDCl_3$, 500MHz) δ ppm: 7.89-7.86 (m, Ar-H, 2H), 7.74 (d, *J*=15.5Hz, =CH-Ar, 1H), 7.73-7.63 (m, Ar-H, 2H), 7.36 (d, *J*=12.5Hz, OC-CH=, 1H), 6.86-6.85 (m, Ar-H, 2H), 3.99 (s, 9H); IR ν_{max} (KBr, cm^{-1}): CO $\nu_{stretch}$ 1650, N-$H_{bending}$ 1535, 1206, 1156, 1076, 987, 824, 764 , 679, 514, 502.

3A.12 Synthesis of (E)-1-phenyl-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (10a)

Acetophenone (0.116 mL, 1 mmol) and 3,4,5-trimethoxybenzaldehyde (196.20 mg, 1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a white cloudy solution. The reaction mixture was stirred for 3 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or MeOH/CH_2Cl_2) to give the product or silica gel column chromatography is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product. Yield= 95%. m.p. = 90-95^{0}C. ^{1}HNMR ($CDCl_3$, 500MHZ) δ ppm: 8.04 (dd, *J*=3Hz, 1Hz, Ar-H, 2H), 7.82 (d, *J*=15.5, =CH-Ar, 1H), 7.59-7.55 (m, Ar-H, 2H), 7.53 (d, *J*=15Hz, -CO-CH= 1H), 7.51-7.48 (m, Ar-H, 3H), 7.22 (d, *J*=8Hz, Ar-H, 2H), 3.83 (s, 9H); IR ν_{max} (KBr, cm^{-1}): CO $\nu_{stretch}$ 1647, N-$H_{bending}$ 1537, 1200, 1156, 1076, 987, 824, 764 , 679, 514, 502.

3A.13 Synthesis of (E)-3-(4-chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one(11a)

2-hydroxyacetophenone (0.120 mL, 1 mmol) and 4-Chlorobenzaldehyde (140.5 mg, 1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a white cloudy solution. The reaction mixture was stirred for 3 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or MeOH/CH_2Cl_2) to give the product or silica gel column chromatography is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product. (White crystalline solid) Yield= 96%. m.p. = 98-100 ^{0}C ^{1}HNMR ($CDCl_3$, 500MHz) δ ppm: 8.01-7.99 (m, Ar-H, 2H), 7.73 (d, *J*=16Hz, =CH-Ar, 1H), 7.59-7.55 (m, Ar-H, 1H), 7.55 (d, *J*=11.0Hz, -CO-CH=, 1H), 7.52-7.45 (m, Ar-H, 5H); IR ν_{max} (KBr, cm^{-1}): CO $\nu_{stretch}$ 1656, N-H$_{bending}$ 1535, 1200, 1146, 1075, 987, 827, 765 , 679, 514, 508.

3A.14 Synthesis of (E)-1-(4-hydroxyphenyl)-3-phenylprop-2-en-1-one(12a)

4-hydroxyacetophenone (0.120 mL, 1 mmol) and benzaldehyde (0.101 mL, 1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a white cloudy solution. The reaction mixture was stirred for 5 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or MeOH/CH_2Cl_2) to give the product or silica gel column chromatography is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product. (white solid) Yield 94%, m.p. = 131-132 ^{0}C. ^{1}HNMR ($CDCl_3$, 500MHz δ ppm: 8.46 (dd, *J*=2Hz, 1.5Hz, Ar-H, 1H), 8.22 (dd, *J*=1.0Hz, 1.0Hz, Ar-H, 1H), 8.03 (d, *J*=7Hz, Ar-H, 2H), 7.92 (d, *J*= 8Hz, 1H), 7.80 (d, *J*= 16Hz, =CH-Ar, 1H), 7.65 (d, *J*=15.5Hz, -CO-CH=, 1H), 7.60-7.57 (m, Ar-H, 2H), 7.51 (dd, *J*=7.5Hz, 1.5Hz, Ar-H, 2H); IR ν_{max} (KBr, cm^{-1}): CO $\nu_{stretch}$ 1640.59, N-H$_{bending}$ 1533.98, 1209.26, 1157.47 1085.32, 997.17, 820.12, 760.04 , 679.28.

3A.15 Synthesis of (E)-3-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one(13a)

Acetophenone (0.116 mL, 1 mmol) and 4-hydroxybenzaldehyde (122.0 mg, 1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a white solution. The reaction mixture was stirred for 5 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or $MeOH/CH_2Cl_2$) to give the product or silica gel column chromatography is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product. (white solid) Yield 94%, m.p. = 128-130 ^{0}C. ^{1}HNMR ($CDCl_3$, 500MHz δ ppm: 8.03-8.01 (m, Ar-H, 2H), 7.78 (d, *J*=15.0Hz, O=C-CH=, 1H), 7.60-7.58 (m, Ar-H, 1H), 7.53-7.47 (m, 3H), 7.31-7.28 (m, ArH, 1H), 7.23 (d, *J*=15.5Hz, Ar-H, 1H), 7.51-7.14 (m, Ar-H, 1H), 6.92 (m, Ar-H, 1H); IR ν_{max} (KBr, cm^{-1}): CO $\nu_{stretch}$ 1640.59, N-$H_{bending}$ 1533.98, 1209.26, 1157.47 1085.32, 997.17, 820.12, 760.04 , 679.28.

3A.16 Synthesis of (E)-1-(2-hydroxyphenyl)-3-(4-nitrophenyl)prop-2-en-1-one (14a)

2-hydroxyacetophenone (0.12 mL, 1 mmol) and 4-nitrobenzaldehyde (151.0 mg, 1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a white solution. The reaction mixture was stirred for 5 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or $MeOH/CH_2Cl_2$) to give the product or silica gel column chromatography is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product. (white solid) Yield 94%, m.p. = 120-122 ^{0}C. ^{1}HNMR ($CDCl_3$, 500MHz δ ppm: 8.00-7.98 (m, Ar-H, 2H), 7.86 (d, *J*=15.5Hz, O=C-CH=, 1H), 7.68-7.66 (m, Ar-H, 2H), 7.51-7.48 (m, 2H), 7.38-7.35 (m, ArH, 1H), 7.23 (d, *J*=15.5Hz, =C-H, 1H), 7.51-7.14 (m, Ar-H, 1H); IR ν_{max} (KBr, cm^{-1}): CO $\nu_{stretch}$ 1640.59, N-$H_{bending}$ 1533.98, 1209.26, 1157.47 1085.32, 997.17, 820.12, 760.04 , 679.28.

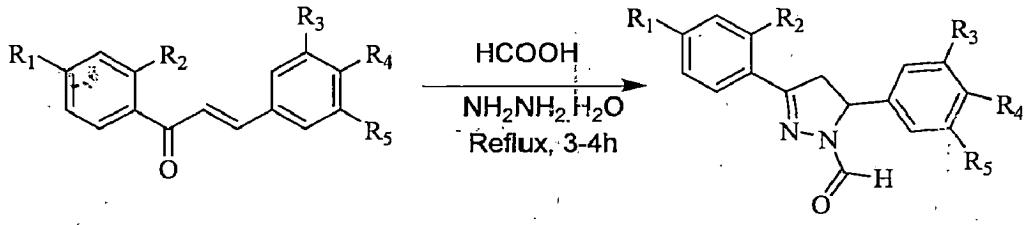
3A.17 Synthesis of (E)-1-(4-chlorophenyl)-3-(3-nitrophenyl)prop-2-en-1-one (15a)

4-chloroacetophenone (0.1295 mL, 1 mmol) and 3-nitrobenzaldehyde (151.5 mg, 1 mmol) were dissolving in methanol (10 mL) with stirring at room temperature. Aqueous NaOH (0.080 g, 2 mmol) was added in portion, which gave a yellow solution. The reaction mixture was stirred for 4 hours at the same temperature. The solution was directly poured into crushed ice and 1N HCl (10 mL) was added to neutralize the solution. The resulting solution was precipitated on neutralization, filtered, and washed with water (2 × 20 mL). The precipitate was crystallized from solvent (EtOH or MeOH/CH_2Cl_2) to give the product or silica gel column chromatography is used in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent to purify the product. Yield= 91%, m.p. = 78-81^{0}C. ^{1}HNMR ($CDCl_3$, 500MHz) δ ppm: 8.49-8.43 (m, Ar-H, 1H), 8.25 (d, *J*=12.5Hz,=CH-Ar, 1H), 8.05-8.03 (m, Ar-H, 2H), 7.91 (d, *J*=15.5Hz, O=C-CH=,1H), 7.87 (d,*J* = 13.0Hz, Ar-H, 1H), 7.67-7.63 (m, Ar-H, 2H), 7.56 (m, Ar-H, 2H); IR ν_{max} (KBr, cm^{-1}): CO $\nu_{stretch}$ 1650, N-$H_{bending}$ 1535, 1206, 1156, 1076, 987, 824, 764 , 679, 514, 502.

2B. SYNTHESIS OF N-FORMYLPYRAZOLINE

2B.1 General procedure for the synthesis of N-formylpyrazoline

Chalcones (1.00 mmol), hydrazine hydrate (5.00 mmol) and formic acid (5 mL) was heated at reflux for 3-4h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to obtain the N-formyl-pyrazolines in 81-96% yields.



R_1=H, OH, Br,Cl; R_2= H, OH; R_3 = H, OCH_3
R_4 =H, CH_3 ,OCH_3 , OH , Cl, Br. NO_2.
R_5 = H, OCH_3 , NO_2.

Scheme 3

2B.2 Synthesis of 3,5-diphenyl-4,5-dihydropyrazole-1-carbaldehyde(1b)

Chalcones (104 mg, 0.50 mmol), hydrazine hydrate (0.121 mL, 2.50 mmol) and formic acid (2.50 mL, 64.50) was heated at reflux for 3h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to gave 96% Yield; White powder m.p: 140-142^{0}C; ^{1}H NMR ($CDCl_3$, 500Mz) δ (ppm): 8.97 (s, 1H), 7.75-7.73 (m, 2H), 7.45-7.42 (m, 3H), 7.36-7.28 (m, 5H), 5.54(dd, *J*= 4.5, 12.0Hz, 1H), 3.82 (dd, *J*= 12.0, 16.0Hz, 1H), 3.22 (dd, *J*= 4.5, 16.0Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ(ppm): 159.92, 155.59, 140.40, 130.70, 130.49, 128.86(2C), 128.65(2C), 127.82, 126.51(2C), 125.47(2C), 58.84, 42.45; IR ν_{max} (KBr, cm^{-1}):1656, 1605, 1424, 1383, 1329, 1262, 1142, 904, 764, 696, 536; GCMS (m/z) = 250 [M^+, $C_{16}H_{14}N_2O$],222, 221, 145(100%), 119, 114, 77, 65, 51.

2B.3 Synthesis of 5-(4-chlorophenyl)-3-phenyl-4,5-dihydropyrazole-1-carb - aldehyde(2b)

(E)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (121.0 mg, 0.50 mmol), hydrazine hydrate (0.121 mL, 2.50 mmol) and formic acid (2.50 mL, 64.50 mmol) was heated at reflux for 3.30h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to gave 95% yields; White solid m.p: 102-104 ^{0}C; ^{1}H NMR ($CDCl_3$, 500Mz) δ(ppm): 8.98 (s, 1H), 7.74 (d, *J* = 6.0Hz, 2H), 7.46-7.43 (m, 3H), 7.32-7.30 (m, 2H), 7.21 (d, *J* = 7.0Hz, 2H), 5.50 (dd, *J* = 4.5, 11.5Hz, 1H), 3.82 (dd, *J* = 11.5, 17.5Hz, 1H), 3.21 (dd, *J* = 4.5, 16.9Hz, 1H); ^{13}C NMR ($CDCl_3$, 125MHz) δ ppm:160.22, 152.59, 135.46, 131.74, 130.00, 128.82 (2C),128.47 (2C), 127.37, 125.68 (2C), 125.60 (2C), 59.28, 40.09; IR ν_{max} (KBr, cm^{-1}):1664, 1604, 1494, 1421, 1326, 1241, 1089, 1026, 823, 755; GCMS (m/z) = 284 [M^+, $C_{16}H_{13}ClN_2O$], 286, 285, 255, 249, 207, 178, 97, 65, 51.

2B.4 Synthesis of 3,5-bis(4-chlorophenyl)-4,5-dihydropyrazole-1-carbaldehy - de(3b)

(E)-1,3-bis(4-chlorophenyl)prop-2-en-1-one (138.0 mg, 0.50 mmol), hydrazine hydrate (0.121 mL, 2.50 mmol) and formic acid (2.50 mL, 64.50 mmol) was heated at reflux for 3h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to gave 95% yields; White solid; m.p: 145-146^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ(ppm): 8.93 (s, 1H), 7.68-7.65(m, 2H), 7.42-7.40 (m, 2H), 7.33-7.30(m, 2H), 7.19-7.17 (m, 2H), 5.50(dd, *J* = 5.0, 12.0, 1H), 3.80 (dd, *J* = 11.5, 17.5Hz, 1H), 3.16 (dd, *J* = 5.5, 16.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm: 160.19, 153.89, 132.94, 131.04, 131.02, 130.12, 128.17 (2C), 125.97 (2C), 124.36 (2C), 123.95 (2C), 59.00, 40.80; IR ν_{max} (KBr, cm^{-1}): 1676, 1616, 1480, 1426, 1314, 1251, 1229, 1086, 1013, 980, 826, 765, 645; GCMS (m/z) = 318 [M^+, $C_{19}H_{18}Cl_2N_2O$], 320, 318, 291,191,179,153,138(100%), 222, 209, 206, 194, 153, 145, 77, 69, 51.

2B. 5 Synthesis of 5-(4-bromophenyl)-3-phenyl-4,5-dihydropyrazole-1-carb - aldehyde(4b)

(E)-3-(4-bromophenyl)-1-phenylprop-2-en-1-one (142.92 mg, 0.50 mmol), hydrazine hydrate (0.121 mL, 2.50 mmol) and formic acid (2.50 mL, 64.50 mmol) was heated at reflux for 3h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to gave 94% yields; White solid; m.p: 104-106 ^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ(ppm): 8.95 (s, 1H), 7.77-7.71 (m, 2H), 7.54-7.29 (m, 5H), 7.18-7.12 (m, 2H), 5.50 (dd, J = 5.0, 12.5Hz, 1H), 3.82 (dd, J = 11.9, 18.0Hz, 1H), 3.20 (dd, J = 5.0, 16Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δppm: 160.09, 155.66, 139.63, 132.21, 130.84, 130.70 (2C), 128.91 (2C), 127.54 (2C), 126.72 (2C), 124.98, 60.53, 42.45. IR v_{max} (KBr, cm^{-1}): 1669, 1598, 1423, 1322, 1134, 1071, 1017, 831, 756, 690, 536, 442. GCMS (m/z) = 328 [M^+, $C_{16}H_{13}BrN_2O$], 330, 329, 327, 299, 250, 222, 153, 145, 145, 77, 51.

2B.6 Synthesis of 3-(4-bromophenyl)-5-phenyl-4,5-dihydropyrazole-1-carb - aldehyde(5b)

(E)-1-(4-bromophenyl)-3-phenylprop-2-en-1-one (142.92 mg, 0.50 mmol), hydrazine hydrate (0.121 mL, 2.50 mmol) and formic acid (2.50 mL, 64.50 mmol) was heated at reflux for 3h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to gave 93% yields; White solid; m.p: 145-147 ^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ(ppm): 8.95 (s, 1H), 7.59-7.50 (m, 4H), 7.45-7.35 (m, 1H), 7.29-7.23(m, 4H), 5.54 (dd, J = 5.0, 17.0Hz, 1H), 3.78 (dd, J = 12.0, 13.0Hz, 1H), 3.20 (dd, J = 5.0, 17.5Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ(ppm): 159.93, 155.71, 139.59, 132.15, 130.61, 130.42 (2C), 128.88 (2C), 127.45 (2C), 126. 27 (2C), 124.98, 60.48, 42.30; IR v_{max} (KBr, cm^{-1}): 1668, 1598, 1413, 1322, 1134,1071, 1017, 831, 756, 690, 536, 442; GCMS (m/z) = 328 [M^+, $C_{16}H_{13}BrN_2O$], 330, 329, 327, 299, 250, 222, 153, 145, 145, 77, 51.

2B.7 Synthesis of 3,5-bis(4-bromophenyl)-4,5-dihydropyrazole-1-carbaldehyde (6b)

(E)-1,3-bis(4-bromophenyl)prop-2-en-1-one (142.92 mg, 0.50 mmol), hydrazine hydrate (0.121 mL, 2.50 mmol) and formic acid (2.50 mL, 64.50 mmol) was heated at reflux for 3h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to gave 92% yields; White solid; m.p: 138-140 ^{0}C; ^{1}H NMR ($CDCl_3$, 500Mz) δ(ppm): 8.93 (s, 1H), 7.86-7.84(m, 2H), 7.58-7.54 (m, 2H), 7.45-7.36 (m, 2H), 7.28-7.19 (m, 2H), 5.53 (dd, J = 5.0, 12.0Hz,1H), 3.79 (dd, J = 12.5, 17.0Hz, 1H), 3.19 (dd, J = 5.0, 16.0Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm: 160.21, 151.89, 131.94, 131.54, 131.22, 130.16, 128.22 (2C), 127.67 (2C), 125.97 (2C), 124.36 (2C), 60.00, 40.80; IR ν_{max} (KBr, cm^{-1}): 1649, 1611, 1511, 1430, 1362, 1324, 1225, 1129, 1076,1017, 823, 735, 536; GCMS (m/z) = 405 [M^+, $C_{16}H_{12}Br_2N_2O$],408, 407, 376, 328, 248, 221, 207, 154, 91, 77, 51.

2B.8 Synthesis of 3-(4-bromophenyl)-5-p-tolyl-4,5-dihydropyrazole-1-carbaldehyde(7b)

(E)-1-(4-bromophenyl)-3-p-tolylprop-2-en-1-one (150.0 mg, 0.50 mmol), hydrazine hydrate (0.121 mL, 2.50 mmol) and formic acid (2.50 mL, 64.50 mmol) was heated at reflux for 3.10h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to gave 91% yields; White solid; m.p: 180-182 ^{0}C; ^{1}H NMR ($CDCl_3$, 500Mz) δ (ppm): 8.93 (s, 1H), 7.71-7.65 (m, 4H), 7.22-7.13 (m, 4H), 5.49 (dd, J = 5.0, 11.0Hz, 1H), 3.76 (dd, J = 12.0, 17.5Hz, 1H), 3.18 (dd, J = 5.0, 16.5Hz, 1H), 2.18 (s, 3H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm: 160.08, 154.67, 137.89, 137.54, 132.08, 130.75, 129.95 (2C), 128.12 (2C), 125.61(2C), 125.0 (2C), 59.06, 42.51, 21.14; IR ν_{max} (KBr, cm^{-1}): 1650, 1596, 1507, 1423, 1317, 1246, 1122, 1059, 1005, 819, 748, 553, 408; GCMS (m/z) = 342 [M^+, $C_{17}H_{15}BrN_2O$], 344, 343, 342, 327, 313, 249, 243, 221, 145, 104, 77, 51, 15.

2B.9 Synthesis of 3(4-bromophenyl)-5-(3,4-dimethoxyphenyl)-4,5-dihydro-pyrazole-1-carbaldehyde(8b)

(E)-1-(4-bromophenyl)-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (173.0 mg, 0.50 mmol), hydrazine hydrate (0.121 mL, 2.50 mmol) and formic acid (2.50 mL, 64.50 mmol) was heated at reflux for 3h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to gave 93% yields; White solid; m.p: 118-120 ^{0}C; ^{1}H NMR ($CDCl_3$, 500Mz) δ(ppm): 8.95 (s, 1H), 7.70-7.65 (m, 4H), 6.68-6.62 (m, 3H), 5.49 (dd, J = 4.5, 11.9Hz, 1H), 3.82 (s, 6H), 3.74 (dd, J = 11.0,18.0Hz, 1H), 3.18 (dd, J = 5.0, 17.0Hz, 1H); ^{13}C NMR ($CDCl_3$, 125MHz) δ ppm: 160.26, 154.97, 153.67, 137.55, 136.34, 130.80, 128.90 (2C), 126.73 (2C), 125.34, 124.01, 123.30, 123.10, 112.29, 60.90, 59.37, 40.90; IR ν_{max} (KBr, cm^{-1}): 2942, 1659, 1590, 1514, 1421, 1311, 1248, 1165, 1069, 1020, 822, 755, 632, 586, 528; GCMS (m/z) = 388 [M^+, $C_{18}H_{17}BrN_2O_3$], 390, 389, 388, 359, 357, 327, 309, 249, 221, 154, 119, 91, 77, 65, 51, 31.

2B. 10 Synthesis of 3-(4-bromophenyl)-5-(3,4,5-trimethoxyphenyl)-4,5-dihydro -pyrazole-1-carbaldehyde(9b)

(E)-1-(4-bromophenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (188.0 mg, 0.50 mmol), hydrazine hydrate (0.121 mL, 2.50 mmol) and formic acid (2.50 mL, 64.50 mmol) was heated at reflux for 3.15h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to gave 93% yields; White solid; m.p: 175-177 ^{0}C; ^{1}H NMR ($CDCl_3$, 500Mz) δ(ppm): 8.98 (s, 1H), 7.81-7.65 (m, 4H), 6.46 (s, 2H), 5.47 (dd, J = 5.0, 13.0Hz, 1H), 3.80 (s, 9H), 3.60 (dd, J = 12.0, 17.0Hz, 1H), 3.16 (dd, J = 5.0, 16.5Hz, 1H); ^{13}C NMR ($CDCl_3$, 125MHz) δ ppm: 160.09, 155.79 153.52, 137.42, 136.28, 130.74 (2C), 128.88 (2C), 126.65 (2C), 125.04, 103.19 (2C), 60.81, 59.31, 56.21 (2C), 42.82; IR ν_{max} (KBr, cm^{-1}): 2929, 1665, 1595, 1503, 1422, 1327, 1241, 1124, 1022, 835, 752, 648, 542; GCMS (m/z) = 418 [M^+, $C_{19}H_{19}BrN_2O_4$], 420, 419, 418, 390, 389, 388, 359, 357, 327, 309, 249, 221, 154, 119, 91, 77, 65, 51, 31.

2B.11 Synthesis of 3-phenyl-5-(3,4,5-trimethoxyphenyl)-4,5dihydropyrazole-1-carbaldehyde(10b)

(E)-1-phenyl-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (149.0 mg, 0.50 mmol), hydrazine hydrate (0.121 mL, 2.50 mmol) and formic acid (2.50 mL, 64.50 mmol) was heated at reflux for 3h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to gave 94% yields; White solid; m.p: 145-146 ^{0}C; ^{1}H NMR ($CDCl_3$, 500Mz) δ (ppm): 9.00 (s, 1H), 7.73 (dd, J = 1.5, 6.5Hz, 2H), 7.48-7.42 (m, 3H), 6.46 (s, 2H), 5.47 (dd, J = 5.0, 12.0Hz, 1H), 3.83 (s, 9H), 3.80 (dd, J = 5.0, 16.0Hz, 1H), 3.23 (dd, J = 5.0, 16.5Hz, 1H). ^{13}C-NMR ($CDCl_3$, 125MHz) δ (ppm): 160.26, 155.97, 153.77, 137.55, 136.34, 130.80 (2C), 128.90 (2C), 126.73 (2C), 125.12, 102.29 (2C), 60.9, 59.27, 56.15 (2C), 42.90; IR v_{max} (KBr, cm^{-1}): 1667, 1593, 1508, 1459, 1419, 1325, 1243, 1226, 1011, 827, 759, 693,644. GCMS (m/z) = 340 [$M^{+\cdot}$, $C_{19}H_{20}N_2O_4$], 340, 339, 311, 237, 222, 209, 206, 194, 19, 153, 145, 77(100%), 76,65, 61.

2B.12 Synthesis of 5-(4-chlorophenyl)-3-(2-hydroxyphenyl)-4,5-dihydro -pyrazole-1-carbaldehyde(11b)

(E)-3-(4-chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one (129.0 mg, 0.50 mmol), hyd -razine hydrate (0.121 mL, 2.50 mmol) and formic acid (2.50 mL, 64.50 mmol) was heated at reflux for 4h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to gave 87% yields; Yellow solid; m.p: 185-187 ^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ(ppm): 8.90 (s, 1H), 7.44-7.32 (m, 4H), 7.22-7.20 (m, 3H), 6.92 (m, 1H), 5.48 (dd, J = 5.0, 12.0Hz, 1H), 3.90 (dd, J = 11.5, 17.0Hz, 1H), 3.33 (dd, J = 5.0, 17.5Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm:. 160.45, 153.05, 151.56, 140.85, 132.55, 132.34, 131.44, 128.95 (2C), 127.29 (2C), 127.19, 125.23, 112.26, 59.14, 41.96; IRv_{max} (KBr, cm^{-1}): 3423, 1670, 1610, 1490, 1428, 1324, 1251, 1219, 1086, 1013, 990, 825, 765, 640, 557; GCMS (m/z) = 300 [$M^{+\cdot}$, $C_{16}H_{13}ClN_2O_2$], 302, 301, 300, 283, 265, 271, 249,221, 173, 97,77,51.

2B.13 Synthesis of 3-(4-hydroxyphenyl)-5-phenyl-4,5-dihydro- pyrazole-1-carbaldehyde(12b)

(E)-1-(4-hydroxyphenyl)-3-phenylprop-2-en-1-one (112.0 mg, 0.50 mmol), hydrazine hydrate (0.121 mL, 2.50 mmol) and formic acid (2.50 mL, 64.50 mmol) was heated at reflux for 3.50h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to gave 85% yields; White solid; m.p: 128-130 ^{0}C; ^{1}H NMR ($CDCl_3$, 500Mz) δ (ppm): 9.00 (s, 1H), 7.73-7.71 (m, 2H), 7.46-7.42 (m, 3H), 7.29-7.23 (m, 1H), 7.17-7.00 (m, 1H), 6.70-6.68(m, 2H), 5.49 (dd, J = 4.5, 12.0Hz, 1H),3.79 (dd, J = 12.0, 17.0Hz, 1H), 3.23 (dd, J = 4.0, 16.0Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm: 160.45, 154.21, 151.12, 131.54, 131.56, 130.15, 128.12 (2C), 127.32 (2C), 125.40 (2C), 123.50 (2C), 59.56, 40.14; IR ν_{max} (KBr, cm^{-1}): 3443, 1660, 1596, 1490, 1428, 1324, 1251, 1219, 1086, 1013, 990, 825, 765, 640, 557; GCMS(m/z) = 266 [M^+, $C_{16}H_{14}N_2O_2$], 268, 267, 266, 249, 221, 173, 97, 51.

2B.14 Synthesis of 5-(3-hydroxyphenyl)-3-phenyl-4,5-dihydro- pyrazole-1-carbaldehyde(13b)

(E)-3-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one (112.0 mg, 0.50 mmol), hydrazine hydrate (0.121 mL, 2.50 mmol) and formic acid (2.50 mL, 64.50 mmol) was heated at reflux for 4h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to gave 83% yields; White solid; m.p: 176-178 ^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ(ppm): 9.00 (s, 1H), 7.77-7.72 (m, 2H), 7.48-7.41 (m, 3H), 7.29-7.23 (m, 1H), 7.17(m, 1H), 6.70-6.68 (m, 2H), 5.49 (dd, J = 4.5, 11.5Hz, 1H), 3.79 (dd, J = 12.0, 17.2Hz,1H), 3.23 (dd, J = 4.5, 16.5Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ (ppm): 159.45, 152.65, 151.10, 132.34, 130.56, 130.15, 127.82 (2C), 127.32 (2C), 124.40 (2C), 122.50 (2C), 59.36, 40.84; IR ν_{max} (KBr, cm^{-1}): 3443, 1660, 1596, 1490, 1428, 1324, 1251, 1219, 1086, 1013, 990, 825, 765, 640, 557; GCMS(m/z) = 266 [M^+, $C_{16}H_{14}N_2O_2$]; 268, 267, 266, 249, 221, 173, 97, 51.

2B.15 Synthesis of 3-(2-hydroxyphenyl)-5-(4-nitrophenyl)-4,5-dihydro -pyrazole-1-carb -aldehyde(14b)

(E)-1-(2-hydroxyphenyl)-3-(4-nitrophenyl)prop-2-en-1-one (134.5 mg, 0.50 mmol), hydrazine hydrate (0.121 mL, 2.50 mmol) and formic acid (2.50 mL, 64.50 mmol) was heated at reflux for 4h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to gave 85% yields; White solid; m.p: 178-180 ^{0}C; ^{1}H NMR ($CDCl_3$, 500Mz) δ (ppm): 8.95 (s, 1H), 7.76-7.67 (m, 2H),7.41-7.35 (m, 3H), 7.34-7.25 (m, 3H), 5.53 (dd, *J* = 5.0, 11.0Hz, 1H), 3.75 (dd, J = 12.0, 17.0Hz, 1H), 3.20 (dd, *J* = 4.5, 16.0Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm: 160.32, 153.23, 151.23, 140.79, 133.51, 132.29, 131.16, 128.58 (2C), 128.10 (2C), 127.15, 125.52, 113.46, 59.14, 41.96; IR ν_{max} (KBr, cm^{-1}): 3440, 1667, 1588, 1490, 1428, 1324, 1251, 1219, 1086, 1013, 990, 835, 746, 640, 557; GCMS (m/z) = 311 [M^+; $C_{16}H_{13}N_3O_4$]; 313, 312, 311, 265, 249, 221, 219, 144, 97,77, 51,45.

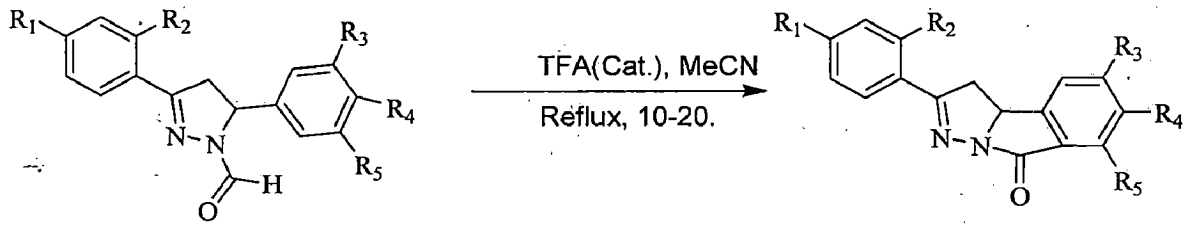
2B.16 Synthesis of 3-(4-chlorophenyl)-5-(3-nitrophenyl)-4,5-dihydro pyrazole-1-carbaldehyde(15b)

(E)-1-(4-chlorophenyl)-3-(3-nitrophenyl)prop-2-en-1-one (143.5 mg, 0.50 mmol), hydrazine hydrate (0.121 mL, 2.50 mmol) and formic acid (2.50 mL, 64.50 mmol) was heated at reflux for 4h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice. The precipitate was separated by filtration, washed with water under reduced pressure, and recrystallized from methanol to gave 81% yields; White solid; m.p: 139-141 ^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ(ppm): 8.96 (s, 1H), 8.21-8.18 (m, 2H), 7.67-7.58 (m, 3H), 7.35-7.22 (m, 3H), 5.65 (dd, *J* = 5.0, 11.5Hz,1H), 3.89 (dd, *J* = 12.0, 16.0Hz, 1H), 3.21 (dd, *J* = 5.0, 16Hz,1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δppm: 160.41, 140.10, 139.35, 132.34, 131.46, 130.14, 128.92 (2C), 127.32 (2C), 125.17, 124.19, 123.82, 116.40, 59.36, 41.14; IR ν_{max}(KBr, cm^{-1}): 1636, 1594, 1528, 1420, 1351, 1092, 823, 760, 686, 477; GCMS(m/z) = 329 [M^+, $C_{16}H_{12}ClN_3O_3$], 331, 330, 329, 294, 249, 221, 144, 97, 77, 51, 29.

2C SYNTHESIS OF PYRAZOLOISOINDOLE

2C.1 General procedure for the synthesis of pyrazoloisoindole

A well stirred and refluxed solution of N-formyl-pyrazoline (1.0 mmol) in acetonitrile (10 mL) was added 6-8 drops of TFA and the reaction was continued for 10-20 h. After TLC monitoring, the reaction mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent.



R_1=H, OH, Br,Cl; R_2= H, OH; R_3 = H, OCH_3
R_4 =H, CH_3 ,OCH_3 , OH , Cl, Br. NO_2
R_5 =H, OCH_3 , NO_2.

Scheme 4

2C.2 Synthesis of 2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one(1c)

A well stirred and refluxed solution of 3,5-diphenyl-4,5-dihydropyrazole-1-carbaldehyde (100 mg, 0.40 mmol) in acetonitrile (4 mL) was added 3-5 drops of TFA and the reaction was continued for 10 h. After TLC monitoring, the reaction mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent we got 94% yields; White crystaline solid; m.p: 108-110^{0}C; ^{1}H NMR ($CDCl_3$, 500Mz) δ(ppm): 7.72-7.70 (m, 2H), 7.41-7.36 (m, 3H), 7.29-

7.22 (m, 2H), 7.18-7.16 (m, 2H), 5.54 (dd, J = 4.5, 11.5Hz, 1H), 3.73 (dd, J = 11.5, 17.5Hz, 1H), 3.19 (dd, J = 4.5, 17.5Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm: 156.87, 138.47, 131.02 130.32, 129.03, 128.15 (2C), 127.85 (2C), 127.37 , 126.19 (2C), 124.55 (2C), 60.33, 40.76; IR ν_{max} (KBr, cm^{-1}): 1692, 1471, 1401, 1233, 1183, 1028, 943, 823, 750. GCMS(m/z) = 248 [M^+, $C_{16}H_{12}N_2O$], 241, 221, 215, 206, 205, 204, 178, 165, 146, 132, 115, 104, 103, 102; HR-MS (m/z) for $C_{16}H_{12}N_2O$ calcd. 248.0950; found: 248.0946.

2C.3 Synthesis of 6-chloro-2-phenyl-3,3a-dihydropyrazolo[5,1-a] isoindol-8-one(2c)

A well stirred and refluxed solution of 5-(4-chlorophenyl)-3-phenyl-4,5-dihydropyrazole-1-carbaldehyde (113.6 mg, 0.40 mmol) in acetonitrile (4 mL) was added 3-5 drops of TFA and the reaction was continued for 12 h. After TLC monitoring, the reaction mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent we got 90% yields; White solid; m.p: 145-147 ^{0}C; ^{1}H NMR ($CDCl_3$, 500Mz) δ(ppm): 7.71 (d, J = 8.0Hz, 2H), 7.42-7.38 (m, 3H), 7.24 (d, J = 6.5Hz, 1H), 7.12 (d, J = 6.5Hz, 2H), 5.50 (dd, J = 4.5, 11.5Hz, 1H), 3.73 (dd, J = 11.5, 17.5, 1H), 3.16 (dd, J = 4.5, 17.0Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm:156.21, 136.47, 132.74, 129.90, 128.47, 127.82 (2C), 127.37 (2C), 125.68 (2C), 125.60 (2C), 123.54, 59.28, 40.09; IR ν_{max} (KBr, cm^{-1}): 2924, 1703, 1560, 1469, 1403, 1275, 1221, 1196, 1170, 1144, 1084, 1009, 947, 843, 760, 698; GCMS(m/z) = 282 [M^+, $C_{16}H_{11}ClN_2O$], 284, 283, 282, 271, 206, 191,104, 102; HR-MS (m/z) for $C_{16}H_{11}ClN_2O$ calcd. 282.0560; found: 282.0546.

2C.4 Synthesis of 6-chloro-2-(4-chlorophenyl)-3,3a-dihydropyrazolo [5,1-a]isoindol-8-one(3c)

A well stirred and refluxed solution of 3,5-bis(4-chlorophenyl)-4,5-dihydropyrazole-1-carbaldehyde (127.2 mg, 0.40 mmol) in acetonitrile (4 mL) was added 3-5 drops of TFA and the reaction was continued for 13 h. After TLC monitoring, the reaction mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane

and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent we got 93% yields; White solid; m.p: 146-148^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ(ppm):7.72-7.69 (m, 2H), 7.43-7.41 (m, 2H), 7.33-7.30 (m, 2H), 7.18-7.16 (m, 1H), 5.52 (dd, *J* = 5.0, 11.5Hz, 1H), 3.78 (dd, *J* = 11.5, 17.5Hz, 1H), 3.20 (dd, *J* = 5.0, 17.0Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm: 156.45, 135.42, 132.74, 129.00, 127.82 (2C), 127.47 (2C), 125.68, 125.60, 124.63, 123.93, 122.14, 118.02, 60.18, 41.09; IR ν_{max} (KBr, cm^{-1}): 1706, 1567, 1464, 1410, 1270, 1221, 1196, 1160, 1154, 1084, 1014, 943, 863, 763, 686; GCMS (m/z) = 316[$M^{+\cdot}$, $C_{16}H_{10}Cl_2N_2O$]; 318, 317, 316, 281, 247, 171, 104, 102; HR-MS (m/z) for $C_{16}H_{10}Cl_2N_2O$ calcd. 316.0170; found: 316.0181.

2C.5 Synthesis of 6-bromo-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one(4c)

A well stirred and refluxed solution of 5-(4-bromophenyl)-3-phenyl-4,5-dihydropyrazole-1-carbaldehyde (131.2 mg, 0.40 mmol) in acetonitrile (4 mL) was added 3-5 drops of TFA and the reaction was continued for 14 h. After TLC monitoring, the reaction mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent we got 89% yields; Light pink solid; m.p: 162-164 ^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ (ppm):7.76-7.69 (m, 2H), 7.55-7.45 (m, 2H), 7.45-7.28 (m, 2H), 7.10-7.04 (m, 2H), 5.49 (dd, *J* = 5.0, 11.5Hz, 1H), 3.72 (dd, *J* = 5.0, 17.5Hz, 1H), 3.15 (dd, *J* = 4.5, 16.5Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm: 156.32, 137.53, 130.60, 130.33, 128.31, 127.64 (2C), 127.04 (2C), 125.17, 124.28, 123.95, 122.54, 116.20, 59.89, 40.09, IR ν_{max} (KBr, cm^{-1}): 1691, 1463, 1401, 1282, 1199,1159, 1070, 1010, 943, 826, 732, 657, 543. GCMS (m/z) =326 [$M^{+\cdot}$, $C_{16}H_{11}BrN_2O$]; 328, 327, 326, 247, 249, 171, 102; HR-MS (m/z) for $C_{16}H_{11}BrN_2O$ calcd. 326.0055; found: 326.0145.

2C.6 Synthesis of 2-(4-bromophenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one(5c)

A well stirred and refluxed solution of 3-(4-bromophenyl)-5-phenyl-4,5-dihydropyrazole-1-carbaldehyde (131.2 mg, 0.40 mmol) in acetonitrile (4 mL) was added 3-5 drops of TFA and the reaction was continued for 12 h. After TLC monitoring, the reaction mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent we got 90% yields; White solid; m.p: 146-148 ^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ(ppm): 7.76-7.69 (m, 2H), 7.56-7.49 (m, 3H), 7.43-7.40 (m, 3H), 5.65 (dd, J = 4.5, 11.5Hz, 1H), 3.76 (dd, J = 12.0, 17.5Hz, 1H), 3.23 (dd J = 4.5, 17.5Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm: 156.89, 137.28, 130.10, 130.01, 128.47, 127.45 (2C), 127.34 (2C), 125.32, 124.16, 123.41, 122.51, 117.18, 60.52, 41.05; IR ν_{max} (KBr, cm^{-1}):1697, 1586, 1468, 1391, 1215, 1178, 1071, 1013, 943, 832, 752 , 698, 658, 538. GCMS (m/z) =326 [M^+ $C_{16}H_{11}BrN_2O$]; 328, 327, 326, 247, 249, 171, 102; HR-MS (m/z) for $C_{16}H_{11}BrN_2O$ calcd. 326.0055; found: 326.0154.

2C.7 Synthesis of 6-bromo-2-(4-bromophenyl)-3,3a-dihydropyrazolo[5,1-a] isoindol-8-one(6c)

A well stirred and refluxed solution of 3,5-bis(4-bromophenyl)-4,5-dihydropyrazole-1-carbaldehyde (161.97 mg, 0.40 mmol) in acetonitrile (4 mL) was added 3-5 drops of TFA and the reaction was continued for 11 h. After TLC monitoring, the reaction mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent we got 89% yields; White solid; m.p: 138-140 ^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ (ppm): 7.79 (dd, J = 5.5, 8.0Hz, 2H), 7.48 (d, J = 8.0Hz, 2H), 7.15-7.11 (m, 3H), 5.55(dd, J = 4.5, 11.5Hz, 1H), 3.80 (dd, J = 11.5, 17.0Hz, 1H), 3.20 (dd J = 4.5, 16Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm: 156.20, 136.98, 133.25, 129.15, 128.51 (2C), 126.92 (2C), 125.59, 125.40, 124.57, 124.00, 122.03, 119.10,

59.23, 40.10; IR ν_{max} (KBr, cm^{-1}): 1702, 1598, 1452, 1403, 1341, 1219, 1161, 1017, 951, 839, 735, 594, 545; GCMS (m/z) = 404 [M^+, $C_{16}H_{10}Br_2N_2O$]; 407, 405, 403, 324, 247, 171, 104, 102. HR-MS(m/z) for $C_{16}H_{11}BrN_2O$ calcd. 403.9160; found: 403.9154.

2C.8 Synthesis of 2-(4-bromophenyl)-6-methyl-3,3a-dihydro pyrazolo[5,1a] isoindol-8-one(7c)

A well stirred and refluxed solution of 3-(4-bromophenyl)-5-p-tolyl-4,5-dihydropyrazole-1-carbaldehyde (136.81 mg, 0.40 mmol) in acetonitrile (4 mL) was added 3-5 drops of TFA and the reaction was continued for 14 h. After TLC monitoring, the reaction mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent we got 89% yields; Yellow solid; m.p: 165-167 ^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ (ppm): 7.72-7.65 (m, 2H), 7.63-7.58 (m, 2H), 7.19-7.10 (m, 3H), 5.58 (dd, J = 4.5, 11.0Hz, 1H), 3.72 (dd, J = 11.5, 16.5Hz, 1H), 3.18 (dd =4.5, 16.0Hz, 1H), 2.34 (s, 3H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm: 156.30, 136.21, 130.60, 130.33, 128.22, 127.59 (2C), 127.04 (2C), 126.23, 125.35, 124.28, 124.20, 123.77, 59.89, 40.09, 28.12; IR ν_{max} (KBr, cm^{-1}): 1698, 1596, 1507, 1413, 1318, 1256, 1112, 1049, 1005, 819, 748, 543, 40; GCMS (m/z) =340 [M^+, $C_{17}H_{13}BrN_2O$]; 342, 341, 340, 324, 247, 171, 102; HR-MS (m/z) for $C_{17}H_{13}BrN_2O$ calcd. 340.2110; found: 340.2117.

2C. 9 Synthesis of 2-(4-bromophenyl)-6,7-dimethoxy-3,3a-dihydro pyrazolo - [5,1-a]isoindol-8-one(8c)

A well stirred and refluxed solution of 3-(4-bromophenyl)-5-(3,4-dimethoxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde (155.21 mg, 0.40 mmol) in acetonitrile (4 mL) was added 3-5 drops of TFA and the reaction was continued for 13 h. After TLC monitoring, the reaction mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent we got 88% yields; Yellow solid; m.p: 142-144 ^{0}C; ^{1}H NMR ($CDCl_3$, 500Mz) δ (ppm): 7.57 (d, J = 8.5Hz,

2H), 7.51 (d, J = 8.5Hz, 2H), 6.75 (m, 2H), 5.49 (dd, J = 4.5, 11.0Hz, 1H), 3.76 (m, 6H), 3.67 (dd, J = 4.5, 16.5Hz, 1H), 3.16 (dd, J = 4.5, 16Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm:156.32, 147.87, 147.53, 130.60 (2C), 130.33, 127.64, 127.06 (2C), 124.28, 116.20, 115.77, 113.59, 110.02, 59.69, 54.36 (2C), 40.09; IR ν_{max} (KBr, cm^{-1}): 1695, 1598, 1519, 1461, 1409, 1253, 1221,1193, 1157, 1024, 810, 727. GCMS (m/z) = 386 [M^+, $C_{18}H_{15}BrN_2O_3$]; 386, 387, 386, 307, 277, 247, 171, 102; HR-MS (m/z) for $C_{18}H_{15}BrN_2O_3$ calcd. 386.0266; found: 386.0255.

2C.10 Synthesis of 2-(4-bromophenyl)-5,6,7-trimethoxy-3,3a-dihydropyrazolo[5,1-a] isoindol-8-one(9c)

A well stirred and refluxed solution of 3-(4-bromophenyl)-5-(3,4,5-trimethoxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde (167.22 mg, 0.40 mmol) in acetonitrile (4 mL) was added 3-5 drops of TFA and the reaction was continued for 14 h. After TLC monitoring, the reaction mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent we got 87% yields; Yellowish solid; m.p: 188-190 ^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ (ppm): 7.65 (dd, J = 1.5, 6.5Hz, 2H), 7.59-7.57 (m, 2H), 6.40 (s, 1H), 5.56 (dd, J = 4.5, 11.5Hz, 1H), 3.80 (s, 9H), 3.79 (dd, J = 11.5, 18.0Hz, 1H), 3.23 (dd, J = 4.5, 18.0Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm: 158.00, 147.79, 137.94, 135.04, 132.22, 129.12, 128.67 (2C), 127.52 (2C), 125.97, 117.36, 116.17, 115.23, 60.79, 57.80, 56.14 (2C), 41.80; IR ν_{max} (KBr, cm^{-1}): 1695, 1592, 1503, 1464, 1418, 1337, 1224, 1164,1126, 1067, 1001, 837, 701,636, 536; GCMS (m/z) = 416 [M^+, $C_{19}H_{17}BrN_2O_4$]; 418, 417, 416, 385, 355, 337, 324, 247, 171; HR-MS (m/z) for $C_{19}H_{17}BrN_2O_4$ calcd. 416.0372; found: 416.0364.

2C.11 Synthesis of 5,6,7-trimethoxy-2-phenyl-3,3a-dihydro pyrazolo[5,1-a] isoindol-8-one(10c)

A well stirred and refluxed solution of 3-phenyl-5-(3,4,5-trimethoxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde (136.14 mg, 0.40 mmol) in acetonitrile (4 mL) was added 3-5 drops of TFA and the reaction was continued for 13 h. After TLC monitoring, the reaction

mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent we got 90% yields; White solid; m.p: 175-178 ^{0}C; ^{1}H NMR ($CDCl_3$, 500Mz) δ(ppm):7.80 (d, *J* = 6.5Hz, 2H), 7.47 (dd, *J* = 7.0, 12.5Hz, 3H), 6.42 (d, *J* = 3.0, 1H), 5.57 (dd, *J* = 4.5, 11.5Hz, 1H), 3.82-3.79 (3s, 9H), 3.49 (dd, *J* = 11.5, 16.5Hz, 1H), 3.27 (dd, *J* = 4.5, 16.0Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm:158.45, 146.85, 132.55, 131.54, 131.44, 128.95 (2C), 127.29 (2C), 126.52, 125.42, 118.64, 117.48, 116.71, 61.64, 60.59, 56.45 (2C), 41.96; IR ν_{max} (KBr, cm^{-1}): 1702, 1594, 1510, 1462, 1421, 1342, 1163, 1130, 1002, 893, 831, 771, 631, 537 631, 537. GCMS (m/z) = 338 [M^+; $C_{19}H_{18}N_2O_4$],340, 339, 311, 236(100%), 222, 209, 206, 194, 153, 145, 77, 69, 51; HR-MS (m/z) for $C_{19}H_{18}N_2O_4$ calcd. 338.1267; found 338.1271.

2C.12 Synthesis of 6-chloro-2-(2-hydroxyphenyl)-3,3a-dihydropyrazolo[5,1-a] isoindol-8-one(11c)

A well stirred and refluxed solution of 5-(4-chlorophenyl)-3-(2-hydroxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde (120.02 mg, 0.40 mmol) in acetonitrile (4 mL) was added 3-5 drops of TFA and the reaction was continued for 16 h. After TLC monitoring, the reaction mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent we got 78% yields; Yellow solid; m.p: 157-159 ^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ(ppm): 7.34-7.33 (m, 2H), 7.24-7.18 (m, 3H), 7.10-6.97 (m, 1H), 6.97-6.94 (m, 1H), 5.57 (dd, *J* = 4.5, 11.5Hz, 1H), 3.94 (dd, J = 12.0, 17.5Hz, 1H), 3.38 (dd *J* = 4.0, 17.0Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm: 156.85, 141.12, 132.34, 130.46, 130.25, 127.92 (2C), 126.89 (2C), 125.42, 124.37, 123.19, 120.54, 119.48, 60.36, 40.80; IR ν_{max} (KBr, cm^{-1}): 3431, 1694, 1606, 1470, 1407, 1304, 1225, 1073, 1013, 910, 814, 764, 503; GCMS(m/z) = 298 [M^+, $C_{16}H_{11}ClN_2O_2$]; 300, 299, 298, 281, 263, 247, 171, 77; HR-MS (m/z) for $C_{16}H_{11}ClN_2O_2$ calcd. 298.0509; found: 298.0510.

2C.13 Synthesis of 2-(4-hydroxyphenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one(12c)

A well stirred and refluxed solution of 3-(4-hydroxyphenyl)-5-phenyl-4,5-dihydropyrazole-1-carbaldehyde (106.44 mg, 0.40 mmol) in acetonitrile (4 mL) was added 3-5 drops of TFA and the reaction was continued for 17 h. After TLC monitoring, the reaction mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent we got 76% yields; White solid; m.p: 126-128 ^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ(ppm):7.60-7.59 (m, 2H), 7.29-7.27 (m, 2H), 7.22 (d, J = 7.5Hz, 1H), 7.18-7.16 (m, 2H), 6.80-6.78 (m, 1H), 5.52 (br, D_2-Exchangeble, 1H), 5.52 (dd, J = 4.5, 11.5Hz, 1H), 3.26 (dd, J = 11.5, 17.5Hz, 1H), 3.15(dd, J = 4.5, 17.0Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm:156.38, 141.13, 131.39, 130.49, 130.22, 128.88 (2C), 127.27 (2C), 125.31, 123.09, 117.32, 115.49, 112.90, 60.63, 40.12; IR ν_{max} (KBr, cm^{-1}): 3349, 1669, 1600, 1490, 1451, 1358, 1271, 1222, 1169, 1038, 939, 841, 773, 615, 541, 470. GCMS (m/z) = 264 [M^+, $C_{16}H_{12}N_2O_2$]; 266, 265, 264, 247, 171, 102, 77, 55; HR-MS (m/z) for $C_{16}H_{12}N_2O_2$ calcd. 264.0899; found: 264.0889.

2C.14 Synthesis of 7-hydroxy-2-phenyl-3,3a-dihydropyrazolo[5,1-a] isoindol-8-one(14c)

A well stirred and refluxed solution of 5-(4-hydroxyphenyl)-3-phenyl-4,5-dihydropyrazole-1-carbaldehyde (106.44 mg, 0.40 mmol) in acetonitrile (4 mL) was added 3-5 drops of TFA and the reaction was continued for 18 h. After TLC monitoring, the reaction mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent we got 75% yields; White solid; m.p: 148-150 ^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ (ppm): 7.78-7.72 (m, 2H), 7.50-7.42 (m, 3H), 6.77-6.67 (m, 3H), 5.55 (br, D_2-Exchangeble, 1H), 5.53 (dd, J = 4.5, 12.0Hz, 1H), 3.78 (dd, J = 11.5, 17.5Hz, 1H), 3.26 (dd, J = 4.5, 17.0Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm:

156.40, 141.10, 131.44, 130.56, 130.15, 128.92 (2C), 127.32 (2C), 125.34, 123.14, 117.40, 115.54, 112.70, 61.36, 41.84; IR ν_{max} (KBr, cm^{-1}): 3457, 1679, 1604, 1588, 1402, 1353, 1217, 1158, 760, 695. GCMS (m/z)= 264 [M^+, $C_{16}H_{12}N_2O_2$]; 266, 265, 264, 247, 171, 102, 77, 55; HR-MS (m/z) for $C_{16}H_{12}N_2O_2$ calcd. 264.0899; found: 264.0898.

2C.15 Synthesis of 2-(2-hydroxyphenyl)-6-nitro-3,3a-dihydro- pyrazolo[5,1-a]isoindol-8-one(14c)

A well stirred and refluxed solution of 3-(2-hydroxyphenyl)-5-(4-nitrophenyl)-4,5-dihydropyrazole-1-carbaldehyde (124.43 mg, 0.40 mmol) in acetonitrile (4 mL) was added 3-5 drops of TFA and the reaction was continued for 18 h. After TLC monitoring, the reaction mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent we got 74% yields; White solid; m.p: 156-158 ^0C; ^1H NMR ($CDCl_3$, 500Mz) δ (ppm): 7.64 (dd, J = 1.5, 7.0Hz, 2H), 7.62-7.33 (m, 2H), 7.29-7.27 (m, 1H), 7.22 (m, 2H), 5.55 (dd, J = 4.5, 11.5Hz, 1H), 3.70 (dd, J = 11.5, 17.5Hz, 1H), 3.15 (dd J = 4.5, 17.5Hz, 1H); ^{13}CNMR ($CDCl_3$, 125MHz) δ ppm:156.45, 143.85, 137.55, 132.34, 131.44, 128.95, 127.29 (2C), 126.82, 125.23, 123.85, 122.17, 121.35, 119.06, 60.82, 41.96; IR ν_{max} (KBr, cm^{-1}): 3443, 1696, 1584, 1480, 1418, 1334, 1246, 1215, 1086, 1014, 986, 845, 746, 641, 558; GCMS(m/z) = 309 [M^+,$C_{16}H_{11}N_3O_2$]; 311, 310, 309, 292, 247, 171, 102, 77, 55; HR-MS (m/z) for $C_{16}H_{11}N_3O_2$ calcd. 309.0750; found: 309.0744.

2C.16 Synthesis of 2-(4-chlorophenyl)-7-nitro-3,3a-dihydropyrazolo [5,1-a] isoindol-8-one(15c)

A well stirred and refluxed solution of 3-(4-chlorophenyl)-5-(3-nitrophenyl)-4,5-dihydropyrazole-1-carbaldehyde (131.62 mg, 0.40 mmol) in acetonitrile (4 mL) was added 3-5 drops of TFA and the reaction was continued for 20 h. After TLC monitoring, the reaction mixture was cooled, evaporated the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with 10% aq.Na_2CO_3. After extraction, the organic layer was dried on anhyd. Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel

column chromatography in a mixture of hexane and ethyl acetate (9:1 v/v) as eluent we got 75% yields; White solid; m.p: 180-182 ^{0}C; ^{1}HNMR ($CDCl_3$, 500Mz) δ (ppm): 8.21-8.19 (m, 1H), 7.73 (d, *J* = 8.5Hz, 2H), 7.58-7.55 (m, 2H), 7.46 (d, *J* = 9.0Hz, 2H), 5.58 (dd, *J* = 5.0, 12.0Hz, 1H), 3.92 (dd, J = 11.5, 17.5, 1H), 3.23 (dd, *J* = 4.5, 17.5Hz, 1H); ^{13}C-NMR ($CDCl_3$, 125MHz) δ ppm: 156.40, 141.10, 142.35, 132.44, 130.56, 130.15, 128.92, 127.32 (2C), 126.52 (2C), 125.11, 124.30, 117.40, 60.36, 40.14; IR ν_{max} (KBr,cm^{-1}): 1701, 1594, 1538, 1425, 1355, 1087, 833, 766, 714, 676, 524 467, GCMS(m/z) =327 [$M^{+\cdot}$, $C_{16}H_{10}ClN_3O_3$]; 329, 328, 327, 292, 291, 171, 77, 55; HR-MS (m/z) for $C_{16}H_{10}ClN_3O_3$ calcd. 327.0411; found: 327.0412.

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Chapter - 3

Results and Discussion

RESULTS AND DISCUSSION

2.1 Synthesis and Characterization of synthesis and characterization of 2-(substituted aryl)-3,3a-dihydro-8h-pyrazolo [5,1-a]isoindol-8-ones derivatives

Using Claisen-Schmidt reaction condition, acetophenone and benzaldehyde gave α, β-unsaturated ketone (chalcone) using 10-60 wt% of alkaline hydroxide as a catalyst over a period of 2-6 hrs at room temperature. The product obtained was in 90% yields. The yield decrease or increase depends upon electron withdraw or electron donating group attached on the different positions of aryl. Followed by cyclization of chalcone derivaties, the reaction was carried out with hydrazine hydrate in formic acid, which gave derivatives of N-formyl-pyrazoline in good yield. Using Lewis acid (trifouroacetic acid) again cyclization of N-formyl-pyrazoline in acetonitrile, which gave pyrazoloisoindole. Along with chalcone, N-formylpyrazoline and final product (pyrazoloisoindole) was characterized on the basis of their spectroscopic data. All product were assigned on the basis of their ^{1}H NMR (500MHz), ^{13}C NMR (125MHz), IR and GC-MS spectra analysis.

3.2 Characterization of Compound 1: {1 2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one (3a)}

Characterization of (E)-chalcone(1a)

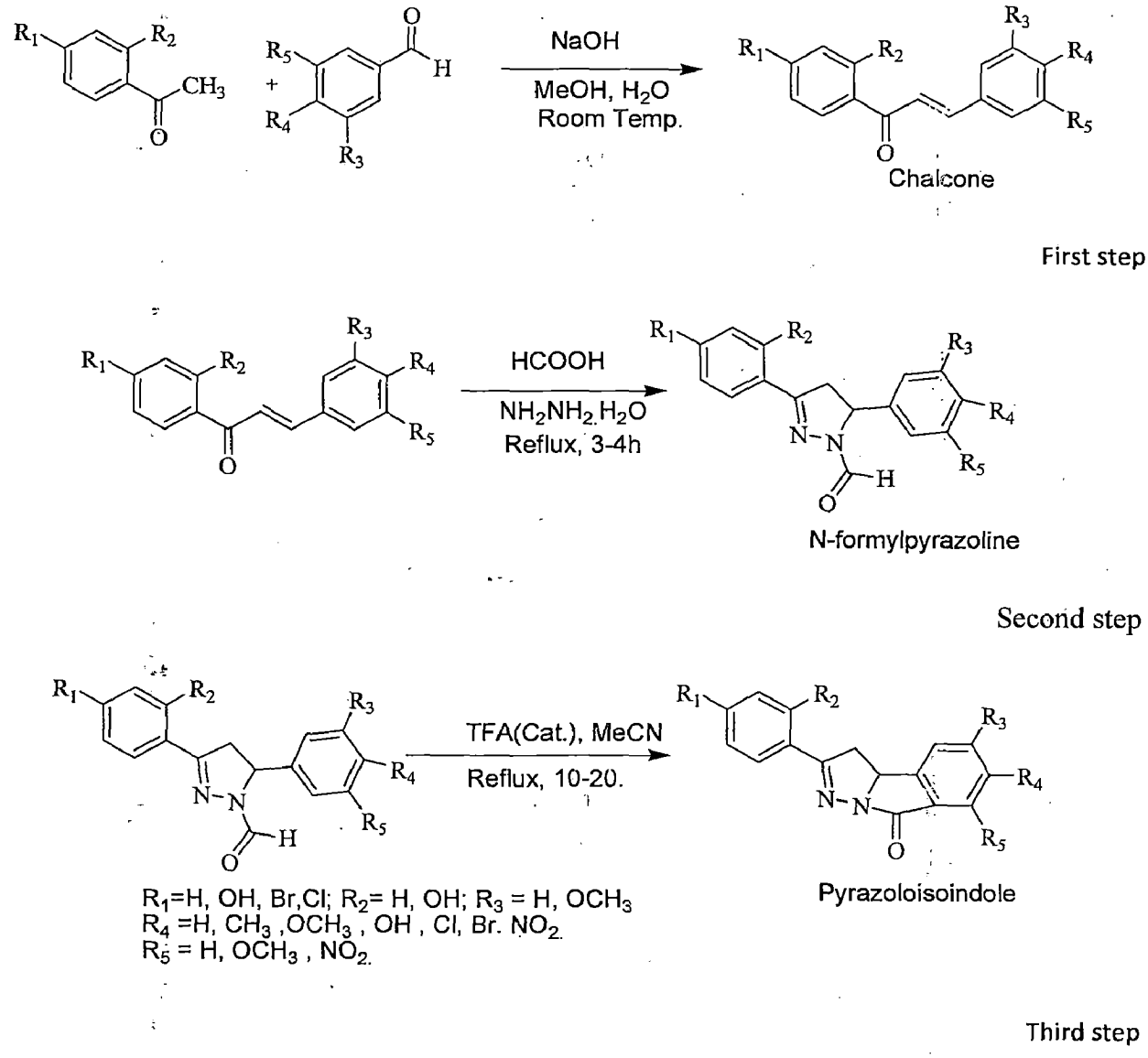
In ^{1}HNMR 7.82 (d, J=15.5Hz, =CH-Ar, 1H), 7.59 (d, J=10.5Hz, CO-CH=, 1H) indicated trans (J_{Ha-Hb} = 12-16Hz) protons and ten aromatic protons were present from 8.08 – 7.30 ppm; IR ν_{max} (KBr, cm^{-1}): vibration frequency for the carbonyl group at 1640-1660 $cm^{-1}$and, peak at 1500-1400 cm^{-1} indicate the presence of aromatic bonds. On the basis of these spectral data of product was characterized as (E)-chalcone.

Characterization of 3,5-diphenyl-4,5-dihydropyrazole-1-carbaldehyde(1b)

The product was characterization for the molecular formula $C_{16}H_{14}N_2O$, melting point 140-142^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.21–3.25, 3.79–3.85 and 5.53–5.50 with J_{AB} = 17.5 Hz, J_{AX} = 4.5 Hz, and J_{BX} = 12.0 Hz, respectively, formyl proton as a singlet at 8.90 ppm, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 42.37, a methine carbon at 58.36, C=N carbon at 148.6, and aldehyde carbon at 160.14 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1656, C=N at 1602 and C-N at 1142. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (1b). The molecular ion peak at 250 [M^+, $C_{16}H_{14}N_2O$], 222, 221, 145(100%), 119, 114, 77, 65, 51. On the basis of these spectral data of product was characterized as 3,5-diphenyl-4,5-dihydropyrazole-1-carbaldehyde.

Characterization of 2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one(1c)

The product was characterization for the molecular formula $C_{16}H_{12}N_2O$, melting point 108-110^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.19, 3.37 and 5.54 with J_{AB} = 17.5 Hz, J_{AX} = 4.5 Hz, and J_{BX} = 11.5 Hz, respectively, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 40.76, a methine carbon at 60.33, C=N carbon at 138.47, and ketonic carbon at 156.87 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1692, C=N at 1401 and C-N at 1183. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (1c). The molecular ion peak at 248 [M^+, $C_{16}H_{12}N_2O$], 241, 221, 215, 206, 205, 204, 178, 165, 146, 132, 115, 104, 103, 102. On the basis of these spectral data of product was characterized as 2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one.



Scheme 4

3.3 Characterization of Compound 2: {5-(4-chlorophenyl)-3-phenyl-4,5-di -hydropyrazole -1-carbaldehyde (2b)}

Characterization of (E)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one(2a)

In ^{1}HNMR 7.96 (d, J=15.5Hz, =CH-Ar, 1H), 7.63 (d, J=10.5Hz, CO-CH=, 1H) indicated trans (J_{Ha-Hb} = 12-16Hz) protons and nine aromatic protons were present from 8.06 – 7.40 ppm. IR ν_{max} (KBr, cm^{-1}): vibration frequency for the carbonyl group at 1642 cm^{-1} and, peak at 1500-

1400 cm^{-1} indicate the presence of aromatic bonds. On the basis of these spectral data of product was characterized as (E)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one.

Characterization of 5-(4-chlorophenyl)-3-phenyl-4,5-dihydropyrazole-1-carbaldehyde(2b)

The product was characterization for the molecular formula $C_{16}H_{13}ClN_2O$, melting point 102-104 ^0C. In ^1H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.21, 3.82 and 5.50 with J_{AB} = 16.9 Hz, J_{AX} = 4.5 Hz, and J_{BX} = 11.5 Hz, respectively, formyl proton as a singlet at 8.98 ppm; ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 40.09, a methine carbon at 59.28, C=N carbon at 152.59, and aldehyde carbon at 160.22 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1664, C=N at 1604 and C-N at 1241. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (2b). The molecular ion peak at 284 [M^+, $C_{16}H_{13}ClN_2O$], 286, 285, 255, 249, 207, 178, 97, 65, 51. On the basis of these spectral data of product was characterized as 5-(4-chlorophenyl)-3-phenyl-4,5-dihydropyrazole-1-carbaldehyde.

Characterization of 6-chloro-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one(2c)

The product was characterization for the molecular formula $C_{16}H_{11}ClN_2O$, melting point 145-147 ^0C. In ^1H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.16, 3.73 and 5.50 with J_{AB} = 17.0 Hz, J_{AX} = 4.5 Hz, and J_{BX} = 11.5 Hz, respectively, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 40.09, a methine carbon at 59.28, C=N carbon at 136.47, and ketonic carbon at 156.21 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1703, C=N at 1403 and C-N at 1196. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (2c). The molecular ion peak at 282 [M^+, $C_{16}H_{11}ClN_2O$], 284, 283, 282, 271, 206, 191,104, 102. On the basis of these spectral data of product was characterized as 6-chloro-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one.

3.4 Characterization of Compound 3: {6-chloro-2-(4-chlorophenyl)-3,3a-dihydro pyrazolo [5,1-a] isoindol-8-one (3c)}

Characterization of (E)-1, 3-bis(4-chlorophenyl)prop-2-en-1-one (3a)

In ^{1}HNMR 7.80 (d, J=15.5Hz, =CH-Ar, 1H), 7.46 (d, J=10.5Hz, CO-CH=, 1H) indicated trans (J_{Ha-Hb} = 12-16Hz) protons and eight aromatic protons were present from 8.03 – 7.41 ppm. IR ν_{max} (KBr, cm^{-1}): vibration frequency for the carbonyl group at 1655 $cm^{-1}$and, peak at 1500-600 cm^{-1} indicate the presence of aromatic bonds. On the basis of these spectral data of product was characterized as (E)-1, 3-bis(4-chlorophenyl)prop-2-en-1-one.

Characterization of 3,5-bis(4-chlorophenyl)-4,5-dihydropyrazole-1-carbaldehyde(3b)

The product was characterization for the molecular formula $C_{19}H_{18}Cl_2N_2O$, melting point 145-146^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.16, 3.80 and 5.50 with J_{AB} = 16.9 Hz, J_{AX} = 4.5 Hz, and J_{BX} = 11.5 Hz, respectively, formyl proton as a singlet at 8.93 ppm, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 40.80, a methine carbon at 59.00, C=N carbon at 153.89, and aldehyde carbon at 160.19 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1676, C=N at 1480 and C-N at 1229. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (3c). The molecular ion peak at 318 [M^+,$C_{19}H_{18}Cl_2N_2O$], 320, 318, 291,191,179,153,138(100%), 222, 209, 206, 194, 153, 145, 77, 69, 51. On the basis of these spectral data of product was characterized as 3,5-bis(4-chlorophenyl)-4,5-dihydropyrazole-1-carbaldehyde.

Characterization of 6-chloro-2-(4-chlorophenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one (3c)

The product was characterization for the molecular formula $C_{16}H_{10}Cl_2N_2O$, melting point 146-148^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.20, 3.78 and 5.52 with J_{AB} = 17.0 Hz, J_{AX} = 5.0Hz, and J_{BX} = 11.5 Hz, respectively, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 41.09, a methine carbon at 60.18, C=N carbon at 135.42, and ketonic carbon at 156.45 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1706,

C=N at 1410 and C-N at 1196. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (3c). The molecular ion peak at 316[$M^{+\cdot}$, $C_{16}H_{10}Cl_2N_2O$]; 318, 317, 316, 281, 247, 171, 104, 102. On the basis of these spectral data of product was characterized as 6-chloro-2-(4-chlorophenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one.

3.5 Characterization of Compound 4: {6-bromo-2-phenyl-3,3a-dihydro -pyrazolo[5,1-a]isoindol-8-one (4c)}

Characterization of (E)-3-(4-bromophenyl)-1-phenylprop-2-en-1-one(4a)

In ^{1}HNMR 7.68 (d, J=15.5Hz, =CH-Ar, 1H), 7.53 (d, J=10.5Hz, CO-CH=, 1H) indicated trans (J_{Ha-Hb} = 12-16Hz) protons and nine aromatic protons were present from 8.02 – 7.28 ppm. IR ν_{max} (KBr, cm^{-1}): vibration frequency for the carbonyl group at 1640 $cm^{-1}$and, peak at 1500-600 cm^{-1} indicate the presence of aromatic bonds. On the basis of these spectral data of product was characterized as (E)-3-(4-bromophenyl)-1-phenylprop-2-en-1-one.

Characterization of 5-(4-bromophenyl)-3-phenyl-4,5-dihydropyrazole-1-carbaldehyde(4b)

The product was characterization for the molecular formula $C_{16}H_{13}BrN_2O$, melting point 104-106 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.20, 3.82 and 5.50 with J_{AB} = 18.0 Hz, J_{AX} = 5.0 Hz, and J_{BX} = 12.5 Hz, respectively, formyl proton as a singlet at 8.95 ppm, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 42.45, a methine carbon at 60.53, C=N carbon at 155.66, and aldehyde carbon at 160.09 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1669, C=N at 1423 and C-N at 1134. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (4b). The molecular ion peak at 328 [$M^{+\cdot}$, $C_{16}H_{13}BrN_2O$], 330, 329, 327, 299, 250, 222, 153, 145, 145, 77, 51. On the basis of these spectral data of product was characterized as 5-(4-bromophenyl)-3-phenyl-4,5-dihydropyrazole-1-carbaldehyde .

Characterization of 6-bromo-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one(4c)

The product was characterization for the molecular formula $C_{16}H_{11}BrN_2O$, melting point 162-164 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.15, 3.72 and 5.49 with J_{AB} = 17.5 Hz, J_{AX} = 5.0Hz, and J_{BX} = 11.5 Hz, respectively, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 41.09, a methine carbon at 59.89, C=N carbon at 137.53, and ketonic carbon at 156.32 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1691, C=N at 1401 and C-N at 1199. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (4c). The molecular ion peak at 326 [M^+, $C_{16}H_{11}BrN_2O$]; 328, 327, 326, 247, 249, 171, 102. On the basis of these spectral data of product was characterized as 6-bromo-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one.

3.6 Characterization of Compound 5: {2-(4-bromophenyl)-3,3a-dihydro -pyrazolo[5,1-a]isoindol-8-one (5c)}

Characterization of (E)-1-(4-bromophenyl)-3-phenylprop-2-en-1-one(5a)

In ^{1}HNMR 7.72 (d, J=15.5Hz, =CH-Ar, 1H), 7.28 (d, J=10.5Hz, CO-CH=, 1H) indicated trans (J_{Ha-Hb} = 12-16Hz) protons and nine aromatic protons were present from 8.02 – 7.28 ppm. IR ν_{max} (KBr, cm^{-1}): vibration frequency for the carbonyl group at 1651 cm^{-1}and, peak at 1500-600 cm^{-1} indicate the presence of aromatic bonds. On the basis of these spectral data of product was characterized as (E)-1-(4-bromophenyl)-3-phenylprop-2-en-1-one.

Characterization of 3-(4-bromophenyl)-5-phenyl-4,5-dihydropyrazole-1-carbaldehyde (5b)

The product was characterization for the molecular formula $C_{16}H_{13}BrN_2O$, melting point 145-147 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.20, 3.82 and 5.50 with J_{AB} = 17.5 Hz, J_{AX} = 5.0 Hz, and J_{BX} = 12.0 Hz, respectively, formyl proton as a singlet at 8.95 ppm, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 42.30, a methine carbon at 60.48, C=N carbon at 155.71, and aldehyde carbon at 159.93 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1668, C=N at 1413 and C-N at 1134. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (5b).

The molecular ion peak at 328 [M^+, $C_{16}H_{13}BrN_2O$], 330, 329, 327, 299, 250, 222, 153, 145, 145, 77, 51. On the basis of these spectral data of product was characterized as 3-(4-bromophenyl)-5-phenyl-4,5-dihydropyrazole-1-carbaldehyde.

Characterization of 2-(4-bromophenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one(5c)

The product was characterization for the molecular formula $C_{16}H_{11}BrN_2O$, melting point 146-148 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.23, 3.76 and 5.65 with J_{AB} = 17.5 Hz, J_{AX} = 5.5Hz, and J_{BX} = 11.5 Hz, respectively, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 41.05, a methine carbon at 60.52, C=N carbon at 137.28, and ketonic carbon at 156.89 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1697, C=N at 1391 and C-N at 1178. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (5c). The molecular ion peak at 326 [M^+ $C_{16}H_{11}BrN_2O$]; 328, 327, 326, 247, 249, 171, 102. On the basis of these spectral data of product was characterized 2-(4-bromophenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one.

3.7 Characterization of Compound 6: {6-bromo-2-(4-bromophenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one (6c)}

Characterization of (E)-1,3-bis(4-bromophenyl)prop-2-en-1-one (6a)

In ^{1}HNMR 7.75 (d, J=15.5Hz, =CH-Ar, 1H), 7.22 (d, J=10.5Hz, CO-CH=, 1H) indicated trans (J_{Ha-Hb} = 12-16Hz) protons and eight aromatic protons were present from 8.07 – 7.20 ppm. IR ν_{max} (KBr, cm^{-1}): vibration frequency for the carbonyl group at 1660 cm^{-1} and, peak at 1500-600 cm^{-1} indicate the presence of aromatic bonds. On the basis of these spectral data of product was characterized as (E)-1,3-bis(4-bromophenyl)prop-2-en-1-one.

Characterization of 3,5-bis(4-bromophenyl)-4,5-dihydropyrazole-1-carbaldehyde(6b)

The product was characterization for the molecular formula $C_{16}H_{12}Br_2N_2O$, melting point 138-140 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.19, 3.79 and 5.53 with J_{AB} = 17.5 Hz, J_{AX} = 5.0 Hz, and J_{BX} = 12.0 Hz, respectively, formyl proton as a singlet at 8.93 ppm, ^{13}CNMR

spectrum δ (ppm), revealed the presence of a methylene carbon at 40.80, a methine carbon at 60.00, C=N carbon at 151.89, and aldehyde carbon at 160.21 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1649, C=N at 1430 and C-N at 1129. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (6b). The molecular ion peak at 405 [M^+, $C_{16}H_{12}Br_2N_2O$],408, 407, 376, 328, 248, 221, 207, 154, 91, 77, 51. On the basis of these spectral data of product was characterized as 3,5-bis (4-bromophenyl)-4,5-dihydropyrazole-1-carbaldehyde.

Characterization of 6-bromo-2-(4-bromophenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one (6c)

The product was characterization for the molecular formula $C_{16}H_{11}BrN_2O$, melting point 138-140 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.20, 3.80 and 5.55 with J_{AB} = 17.5 Hz, J_{AX} = 4.5Hz, and J_{BX} = 11.5 Hz, respectively, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 40.10, a methine carbon at 59.23, C=N carbon at 137.28, and ketonic carbon at 156.20 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1702, C=N at 1403 and C-N at 1219. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (6c). The molecular ion peak at 404 [M^+, $C_{16}H_{10}Br_2N_2O$]; 407, 405, 403, 324, 247, 171, 104, 102. On the basis of these spectral data of product was characterized 6-bromo-2-(4-bromophenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one.

3.8 Characterization of Compound 7 :{2-(4-bromophenyl)-6-methyl-3,3a-dihydro –pyrazolo[5,1a]isoindol-8-one (7c)}

Characterization of (E)-1-(4-bromophenyl)-3-p-tolylprop-2-en-1-one(7a)

In ^{1}HNMR 7.89 (d, J=15.5Hz, =CH-Ar, 1H), 7.45 (d, J=10.5Hz, CO-CH=, 1H) indicated trans (J_{Ha-Hb} = 12-16Hz) protons, eight aromatic protons were present from 7.89 – 7.22 ppm and three methyl protons were present on 2.39 ppm. IR ν_{max} (KBr, cm^{-1}): vibration frequency for the carbonyl group at 1656 $cm^{-1}$and, peak at 1500-600 cm^{-1} indicate the presence of aromatic bonds. On the basis of these spectral data of product was characterized as (E)-1-(4-bromophenyl)-3-p-tolylprop-2-en-1-one.

Characterization of 3-(4-bromophenyl)-5-p-tolyl-4,5-dihydropyrazole-1-carbaldehyde(7b)

The product was characterization for the molecular formula $C_{17}H_{15}BrN_2O$, melting point 180-182 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.18, 3.76 and 5.49 with J_{AB} = 17.5 Hz, J_{AX} = 5.0 Hz, and J_{BX} = 12.0 Hz, respectively, formyl proton as a singlet at 8.93 ppm, methyl proton as a singlet at 2.18 ppm, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methyl carbon 21.14, methylene carbon at 42.51, a methine carbon at 59.06, C=N carbon at 154.67, and aldehyde carbon at 160.08 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1650, C=N at 1423 and C-N at 1122. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (7b). The molecular ion peak at 342 [M^+, $C_{17}H_{15}BrN_2O$], 344, 343, 342, 327, 313, 249, 243, 221, 145, 104, 77, 51, 15. On the basis of these spectral data of product was characterized as 3-(4-bromophenyl)-5-p-tolyl-4,5-dihydropyrazole-1-carbaldehyde.

Characterization of 2-(4-bromophenyl)-6-methyl-3,3a-dihydropyrazolo[5,1a]isoindol-8-one (7c)

The product was characterization for the molecular formula $C_{17}H_{13}BrN_2O$, melting point 165-167 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.20, 3.80 and 5.55 with J_{AB} = 17.5 Hz, J_{AX} = 4.5Hz, and J_{BX} = 11.5 Hz, respectively, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 40.10, a methine carbon at 59.23, C=N carbon at 137.28, and ketonic carbon at 156.20 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1702, C=N at 1413 and C-N at 1112. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (7c). The molecular ion peak at 340 [M^+, $C_{17}H_{13}BrN_2O$]; 342, 341, 340, 324, 247, 171, 102. On the basis of these spectral data of product was characterized 2-(4-bromophenyl)-6-methyl-3,3a-dihydropyrazolo[5,1a]isoindol-8-one.

3.9 Characterization of Compound 8 :{ 2-(4-bromophenyl)-6,7-dimethoxy-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one (8c)}

Characterization of (E)-1-(4-bromophenyl)-3-(3,4-dimethoxy- phenyl)prop-2-en-1-one (8a)

In ^{1}HNMR 7.34 (d, J=15.5Hz, =CH-Ar, 1H), 6.92 (d, J=8.5Hz, CO-CH=, 1H) indicated trans (J_{Ha-Hb} = 12-16Hz) protons, eight aromatic protons were present from 7.89 – 7.22 ppm and six methoxy protons were present 3.92 ppm. IR ν_{max} (KBr, cm^{-1}): vibration frequency for the carbonyl group at 1659 $cm^{-1}$and, peak at 1500-600 cm^{-1} indicate the presence of aromatic bonds. On the basis of these spectral data of product was characterized as (E)-1-(4-bromophenyl)-3-(3,4-dimethoxy- phenyl)prop-2-en-1-one.

Characterization of 3(4-bromophenyl)-5-(3,4-dimethoxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde(8b)

The product was characterization for the molecular formula $C_{18}H_{17}BrN_2O_3$, melting point 118-120 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.18, 3.74 and 5.49 with J_{AB} = 17.0 Hz, J_{AX} = 5.0 Hz, and J_{BX} = 11.0 Hz, respectively, formyl proton as a singlet at 8.95 ppm, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 40.90, a methine carbon at 59.37, C=N carbon at 153.67, and aldehyde carbon at 160.26 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1659, C=N at 1421 and C-N at 1165. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (8c). The molecular ion peak at 388 [M^+, $C_{18}H_{17}BrN_2O_3$], 390, 389, 388, 359, 357, 327, 309, 249, 221, 154, 119, 91, 77, 65, 51, 31. On the basis of these spectral data of product was characterized as 3(4-bromophenyl)-5-(3,4-dimethoxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde.

Characterization of 2-(4-bromophenyl)-6,7-dimethoxy-3,3a-dihydropyrazolo[5,1-a]isoindol -8-one (8c)

The product was characterization for the molecular formula $C_{18}H_{15}BrN_2O_3$, melting point 142-144 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.67, 3.76 and 5.75 with J_{AB} = 16.5 Hz, J_{AX} = 4.5Hz, and J_{BX} = 11.0 Hz, respectively, methoxy hydrogen at 3.76 ppm, ^{13}CNMR spectrum δ

(ppm), revealed the presence of a methoxy carbon at 54.36, methylene carbon at 40.10, a methine carbon at 59.23, C=N carbon at 147.53, and ketonic carbon at 156.32 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1695, C=N at 1409 and C-N at 1193. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (8c). The molecular ion peak at 386 [$M^{+\cdot}$, $C_{18}H_{15}BrN_2O_3$]; 386, 387, 386, 307, 277, 247, 171, 102. On the basis of these spectral data of product was characterized 2-(4-bromophenyl)-6,7-dimethoxy-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one.

3.10 Characterization of Compound 9 :{ 2-(4-bromophenyl)-5,6,7-trimethoxy-3,3a-dihydropyrazolo[5,1-a]iso indol-8-one (9c)}

Characterization of (E)-1-(4-bromophenyl)-3-(3,4,5-trimethoxyphenyl) prop-2-en-1-one(9a)

In ^{1}HNMR 7.74 (d, J=15.5Hz, =CH-Ar, 1H), 6.92 (d, J=8.5Hz, CO-CH=, 1H) indicated trans (J_{Ha-Hb} = 12-16Hz) protons, seven aromatic protons were present from 7.89 – 6.85 ppm and nine methoxy protons were present 3.99 ppm. IR ν_{max} (KBr, cm^{-1}): vibration frequency for the carbonyl group at 1661 $cm^{-1}$and, peak at 1500-600 cm^{-1} indicate the presence of aromatic bonds. On the basis of these spectral data of product was characterized as (E)-1-(4-bromophenyl)-3-(3,4,5-trimethoxyphenyl) prop-2-en-1-one.

Characterization of 3-(4-bromophenyl)-5-(3,4,5-trimethoxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde(9b)

The product was characterization for the molecular formula $C_{19}H_{19}BrN_2O_4$, melting point 175-177 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.16, 3.60 and 5.47 with J_{AB} = 17.0 Hz, J_{AX} = 5.0 Hz, and J_{BX} = 12.0 Hz, respectively, formyl proton as a singlet at 8.95 ppm, methoxy carbon signal at 3.80, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methoxy carbon at 56.21, methylene carbon at 40.90, a methine carbon at 60.81, C=N carbon at 153.52, and aldehyde carbon at 160.26 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1659, C=N at 1421 and C-N at 1165. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (9b). The molecular ion peak at 418 [$M^{+\cdot}$, $C_{19}H_{19}BrN_2O_4$], 420, 419, 418, 390, 389, 388, 359, 357, 327, 309, 249, 221, 154, 119, 91, 77, 65,

51, 31. On the basis of these spectral data of product was characterized as 3-(4-bromophenyl)-5-(3,4,5-trimethoxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde.

Characterization of 2-(4-bromophenyl)-5,6,7-trimethoxy-3,3a-dihydropyrazolo[5,1-a]iso indol-8-one(9c)

The product was characterization for the molecular formula $C_{19}H_{17}BrN_2O_4$; melting point 188-190 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.79, 3.80 and 5.56 with J_{AB} = 18.0 Hz, J_{AX} = 4.5Hz, and J_{BX} = 11.5 Hz, respectively, methoxy hydrogen at 3.80 ppm, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methoxy carbon at 56.14, methylene carbon at 41.80, a methine carbon at 60.79, C=N carbon at 147.53, and ketonic carbon at 158.0 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1695, C=N at 1418 and C-N at 1164. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (9c). The molecular ion peak at 416 [M^+, $C_{19}H_{17}BrN_2O_4$]; 418, 417, 416, 385, 355, 337, 324, 247, 171. On the basis of these spectral data of product was characterized 2-(4-bromophenyl)-5,6,7-trimethoxy-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one.

3.11 Characterization of Compound 10 :{ 5,6,7-trimethoxy-2-phenyl-3,3a-dihydro -pyrazolo[5,1-a]isoindol-8-one (10c)}

Characterization of (E)-1-phenyl-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one(10a)

In ^{1}HNMR 7.82 (d, J=15.5Hz, =CH-Ar, 1H), 7.53 (d, J=8.5Hz, CO-CH=, 1H) indicated trans (J_{Ha-Hb} = 12-16Hz) protons, seven aromatic protons were present from 8.04 – 7.22 ppm and nine methoxy protons were present 3.83 ppm. IR ν_{max} (KBr, cm^{-1}): vibration frequency for the carbonyl group at 1641 cm^{-1}and, peak at 1500-600 cm^{-1} indicate the presence of aromatic bonds. On the basis of these spectral data of product was characterized as (E)-1-phenyl-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one.

Characterization of 3-phenyl-5-(3,4,5-trimethoxyphenyl)-4,5dihydropyrazole-1-carb -aldehyde(10b)

The product was characterization for the molecular formula $C_{19}H_{20}N_2O_4$, melting point 145-146 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.23, 3.80 and 5.47 with J_{AB} = 17.0 Hz, J_{AX} = 5.0 Hz, and J_{BX} = 12.0 Hz, respectively, formyl proton as a singlet at 9.00 ppm, methoxy carbon signal at 3.83, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methoxy carbon at 56.15, methylene carbon at 40.90, a methine carbon at 60.90, C=N carbon at 153.77, and aldehyde carbon at 160.26 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1667, C=N at 1419 and C-N at 1226. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (10c). The molecular ion peak at 340 [M^+, $C_{19}H_{20}N_2O_4$], 340, 339, 311, 237, 222, 209, 206, 194, 19, 153, 145, 77(100%), 76,65, 61. On the basis of these spectral data of product was characterized as 3-phenyl-5-(3,4,5-trimethoxyphenyl)-4,5dihydropyrazole-1-carbaldehyde.

Characterization of 5,6,7-trimethoxy-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one (10c)

The product was characterization for the molecular formula $C_{19}H_{18}N_2O_4$, melting point 175-178 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.27, 3.49 and 5.57 with J_{AB} = 16.5 Hz, J_{AX} = 4.5Hz, and J_{BX} = 12.0 Hz, respectively, methoxy hydrogen at 3.80 ppm, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methoxy carbon at 56.14, methylene carbon at 41.96, a methine carbon at 60.59, C=N carbon at 147.53, and ketonic carbon at 158.45 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1702, C=N at 1421 and C-N at 1130. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (10c). The molecular ion peak at 338 [M^+, $C_{19}H_{18}N_2O_4$],340, 339, 311, 236(100%), 222, 209, 206, 194, 153, 145, 77, 69, 51. On the basis of these spectral data of product was characterized 5,6,7-trimethoxy-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one.

3.12 Characterization of Compound 11 :{ 6-chloro-2-(2-hydroxyphenyl)-3,3a-di -hydropyrazolo[5,1-a]isoindol-8-one (11c)}

Characterization of (E)-3-(4-chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one(11a)

In ^{1}HNMR 7:73 (d, J=16.0Hz, =CH-Ar, 1H), 7.55 (d, J=11.0Hz, CO-CH=, 1H) indicated trans (J_{Ha-Hb} = 12-16Hz) protons and eight aromatic protons were present from 8.01 – 7.45 ppm. IR ν_{max} (KBr, cm^{-1}): vibration frequency for the carbonyl group at 1645 $cm^{-1}$and, peak at 1500-600 cm^{-1} indicate the presence of aromatic bonds. On the basis of these spectral data of product was characterized as (E)-3-(4-chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one.

Characterization of 5-(4-chlorophenyl)-3-(2-hydroxyphenyl)-4,5-dihydropyrazole-1-carb -aldehyde(11b)

The product was characterization for the molecular formula $C_{16}H_{13}ClN_2O_2$, melting point 185-187 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.33, 3.90 and 5.45 with J_{AB} = 17.0 Hz, J_{AX} = 5.0 Hz, and J_{BX} = 11.5 Hz, respectively, formyl proton as a singlet at 8.90 ppm, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 41.96, a methine carbon at 60.90, C=N carbon at 153.05, and aldehyde carbon at 160.45 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1670, C=N at 1428 and C-N at 1219. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (11b). The molecular ion peak at 300 [M^+, $C_{16}H_{13}ClN_2O_2$], 302, 301, 300, 283, 265, 271, 249, 221, 173, 97, 77, 51. On the basis of these spectral data of product was characterized as 5-(4-chlorophenyl)-3-(2-hydroxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde.

Characterization of 6-chloro-2-(2-hydroxyphenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one(11c)

The product was characterization for the molecular formula $C_{16}H_{11}ClN_2O_2$, melting point 157-159 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.38, 3.94 and 5.57 with J_{AB} = 17.0 Hz, J_{AX} = 4.0Hz, and J_{BX} = 12.0 Hz, respectively, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 40.80;, a methine carbon at 60.36, C=N carbon at 141.12, and ketonic

carbon at 156.85 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1694, C=N at 1407 and C-N at 1225. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (11c). The molecular ion peak at 298 [$M^{+\cdot}$, $C_{16}H_{11}ClN_2O_2$]; 300, 299, 298, 281, 263, 247, 171, 77. On the basis of these spectral data of product was characterized 6-chloro-2-(2-hydroxyphenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one.

3.13 Characterization of Compound 12 :{ 2-(4-hydroxyphenyl)-3,3a-dihydro -pyrazolo[5,1-a]isoindol-8-one(12c)}

Characterization of (E)-3-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one(12a)

In ^{1}HNMR 7.80 (d, J=15.5Hz, =CH-Ar, 1H), 7.65 (d, J=16.0Hz, CO-CH=, 1H) indicated trans (J_{Ha-Hb} = 12-16Hz) protons and nine aromatic protons were present from 8.46 – 7.51 ppm. IR ν_{max} (KBr, cm^{-1}): vibration frequency for the carbonyl group at 1651 $cm^{-1}$and, peak at 1500-600 cm^{-1} indicate the presence of aromatic bonds. On the basis of these spectral data of product was characterized as (E)-3-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one.

Characterization of 3-(4-hydroxyphenyl)-5-phenyl-4,5-dihydropyrazole-1-carbaldehyde (12b)

The product was characterization for the molecular formula $C_{16}H_{14}N_2O_2$; melting point 128-130 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.23, 3.79 and 5.49 with J_{AB} = 17.0 Hz, J_{AX} = 4.5 Hz, and J_{BX} = 12.0 Hz, respectively, formyl proton as a singlet at 9.00 ppm, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 40.14, a methine carbon at 59.56, C=N carbon at 151.12, and aldehyde carbon at 160.45 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1660, C=N at 1428 and C-N at 1219. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (12b). The molecular ion peak at 266 [$M^{+\cdot}$, $C_{16}H_{14}N_2O_2$], 268, 267, 266, 249, 221, 173, 97, 51. On the basis of these spectral data of product was characterized as 3-(4-hydroxyphenyl)-5-phenyl-4,5-dihydropyrazole-1-carbaldehyde.

Characterization of 2-(4-hydroxyphenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one(12c)

The product was characterization for the molecular formula $C_{16}H_{12}N_2O_2$; melting point 126-128 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.15, 3.26 and 5.52 with J_{AB} = 17.5 Hz, J_{AX} = 4.5Hz, and J_{BX} = 11.5 Hz, respectively, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 40.12;, a methine carbon at 60.63, C=N carbon at 141.13, and ketonic carbon at 156.38 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1669, C=N at 1451 and C-N at 1222. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (12c). The molecular ion peak at 264 [M^+, $C_{16}H_{12}N_2O_2$]; 266, 265, 264, 247, 171, 102, 77, 55. On the basis of these spectral data of product was characterized 2-(4-hydroxyphenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one.

3.14 Characterization of Compound 13 :{7-hydroxy-2-phenyl-3,3a-dihydro -pyrazolo[5,1-a]isoindol-8-one(13c)}

Characterization of (E)-3-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one(13a)

In ^{1}HNMR 7.84 (d, J=15.5Hz, =CH-Ar, 1H), 7.45 (d, J=12.0Hz, CO-CH=, 1H) indicated trans (J_{Ha-Hb} = 12-16Hz) protons and nine aromatic protons were present from 8.03 – 6.92 ppm. IR ν_{max} (KBr, cm^{-1}): vibration frequency for the carbonyl group at 1661 cm^{-1}and, peak at 1500-600 cm^{-1} indicate the presence of aromatic bonds. On the basis of these spectral data of product was characterized as (E)-3-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one.

Characterization of 5-(3-hydroxyphenyl)-3-phenyl-4,5-dihydropyrazole-1-carbaldehyde (13b)

The product was characterization for the molecular formula $C_{16}H_{14}N_2O_2$; melting point 176-178 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.23, 3.79 and 5.49 with J_{AB} = 17.2 Hz, J_{AX} = 4.5 Hz, and J_{BX} = 12.0 Hz, respectively, formyl proton as a singlet at 9.00 ppm, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 40.84, a methine carbon at 59.36, C=N carbon at 152.65, and aldehyde carbon at 159.45 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1660, C=N at 1428 and C-N at 1219. GC-MS for

EIMS fragmentations followed the established pattern, where further confirmed the product (13b). The molecular ion peak at 266 [$M^{+\cdot}$, $C_{16}H_{14}N_2O_2$]; 268, 267, 266, 249, 221, 173, 97, 51. On the basis of these spectral data of product was characterized as 5-(3-hydroxyphenyl)-3-phenyl-4,5-dihydropyrazole-1-carbaldehyde.

Characterization of 7-hydroxy-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one(13c)

The product was characterization for the molecular formula $C_{16}H_{12}N_2O_2$, melting point 148-150 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.26, 3.78 and 5.53 with J_{AB} = 17.5 Hz, J_{AX} = 4.5Hz, and J_{BX} = 11.5 Hz, respectively,^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 41.84, a methine carbon at 61.36, C=N carbon at 141.10, and ketonic carbon at 156.40 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1679, C=N at 1402 and C-N at 1217. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (13c). The molecular ion peak at 264 [$M^{+\cdot}$, $C_{16}H_{12}N_2O_2$]; 266, 265, 264, 247, 171, 102, 77, 55. On the basis of these spectral data of product was characterized 7-hydroxy-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one.

3.15 Characterization of Compound 14 :{ 2-(2-hydroxyphenyl)-6-nitro-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one(14c)}

Characterization of (E)-1-(2-hydroxyphenyl)-3-(4-nitrophenyl)prop-2-en-1-one(14a)

In ^{1}HNMR 7.86 (d, J=15.5Hz, =CH-Ar, 1H), 7.23 (d, J=12.0Hz, CO-CH=, 1H) indicated trans (J_{Ha-Hb} = 12-16Hz) protons and eight aromatic protons were present from 8.00 – 7.14 ppm. IR ν_{max} (KBr, cm^{-1}): vibration frequency for the carbonyl group at 1651 cm^{-1}and, peak at 1500-600 cm^{-1} indicate the presence of aromatic bonds. On the basis of these spectral data of product was characterized as (E)-1-(2-hydroxyphenyl)-3-(4-nitrophenyl)prop-2-en-1-one.

Characterization of 3-(2-hydroxyphenyl)-5-(4-nitrophenyl)-4,5-dihydropyrazole-1-carb – aldehyde(14b)

The product was characterization for the molecular formula $C_{16}H_{13}N_3O_4$; melting point 178-180 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.20, 3.75 and 5.53 with J_{AB} = 17.0 Hz, J_{AX} = 4.5 Hz, and J_{BX} = 12.0 Hz, respectively, formyl proton as a singlet at 9.00 ppm, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 41.96, a methine carbon at 59.14, C=N carbon at 151.23, and aldehyde carbon at 160.32 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1667, C=N at 1428 and C-N at 1219. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (14b). The molecular ion peak at 311 [M^+, $C_{16}H_{13}N_3O_4$]; 313, 312, 311, 265, 249, 221, 219, 144, 97,77, 51,45. On the basis of these spectral data of product was characterized as 3-(2-hydroxyphenyl)-5-(4-nitrophenyl)-4,5-dihydropyrazole-1-carbaldehyde.

Characterization of 2-(2-hydroxyphenyl)-6-nitro-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one (14c)

The product was characterization for the molecular formula $C_{16}H_{11}N_3O_2$; melting point 156-158 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.15, 3.70 and 5.55 with J_{AB} = 17.5 Hz, J_{AX} = 4.5Hz, and J_{BX} = 11.5 Hz, respectively, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 41.96, a methine carbon at 60.82, C=N carbon at 143.85, and ketonic carbon at 156.45 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1696, C=N at 1418 and C-N at 1215. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (14c). The molecular ion peak at 309 [M^+,$C_{16}H_{11}N_3O_2$]; 311, 310, 309, 292, 247, 171, 102, 77, 55. On the basis of these spectral data of product was characterized 2-(2-hydroxyphenyl)-6-nitro-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one.

3.16 Characterization of Compound 15 :{ 2-(4-chlorophenyl)-7-nitro-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one(15c)}

Characterization of (E)-1-(4-chlorophenyl)-3-(3-nitrophenyl)prop-2-en-1-one(15a)

In ^{1}HNMR 8.25 (d, J=15.5Hz, =CH-Ar, 1H), 7.91 (d, J=12.0Hz, CO-CH=, 1H) indicated trans (J_{Ha-Hb} = 12-16Hz) protons and eight aromatic protons were present from 8.49 – 7.56 ppm. IR ν_{max} (KBr, cm^{-1}): vibration frequency for the carbonyl group at 1641 cm^{-1} and, peak at 1500-600 cm^{-1} indicate the presence of aromatic bonds. On the basis of these spectral data of product was characterized as (E)-1-(4-chlorophenyl)-3-(3-nitrophenyl)prop-2-en-1-one.

Characterization of 3-(4-chlorophenyl)-5-(3-nitrophenyl)-4,5-dihydropyrazole-1-carb - aldehyde(15b)

The product was characterization for the molecular formula $C_{16}H_{12}ClN_3O_3$, melting point 139-141 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.21, 3.89 and 5.65 with J_{AB} = 16.0 Hz, J_{AX} = 5.0 Hz, and J_{BX} = 11.0 Hz, respectively, formyl proton as a singlet at 8.96 ppm, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 41.14, a methine carbon at 59.36, C=N carbon at 140.10, and aldehyde carbon at 160.41 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1636, C=N at 1420 and C-N at 1219. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (15b). The molecular ion peak at 329 [M^+, $C_{16}H_{12}ClN_3O_3$], 331, 330, 329, 294, 249, 221, 144, 97, 77, 51, 29. On the basis of these spectral data of product was characterized as 3-(4-chlorophenyl)-5-(3-nitrophenyl)-4,5-dihydropyrazole-1-carbaldehyde.

Characterization of 2-(4-chlorophenyl)-7-nitro-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one (15c)

The product was characterization for the molecular formula $C_{16}H_{10}ClN_3O_3$, melting point 180-182 ^{0}C. In ^{1}H NMR gave characteristic peak in δ (ppm), an ABX- type pattern was observed where H_A, H_B and H_X appear as double doublets at 3.23, 3.92 and 5.58 with J_{AB} = 17.5 Hz, J_{AX} = 4.5 Hz, and J_{BX} = 11.5 Hz, respectively, ^{13}CNMR spectrum δ (ppm), revealed the presence of a methylene carbon at 40.14, a methine carbon at 60.36, C=N carbon at 142.35, and ketonic carbon

at 156.40 ppm. The FT-IR spectrum in ν_{max} (KBr, cm^{-1}) gave a strong band for C=O at 1701, C=N at 1425 and C-N at 1215. GC-MS for EIMS fragmentations followed the established pattern, where further confirmed the product (15c). The molecular ion peak at 327 [$M^{+\cdot}$, $C_{16}H_{10}ClN_3O_3$]; 329, 328, 327, 292, 291, 171, 77, 55. On the basis of these spectral data of product was characterized 2-(4-chlorophenyl)-7-nitro-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one.

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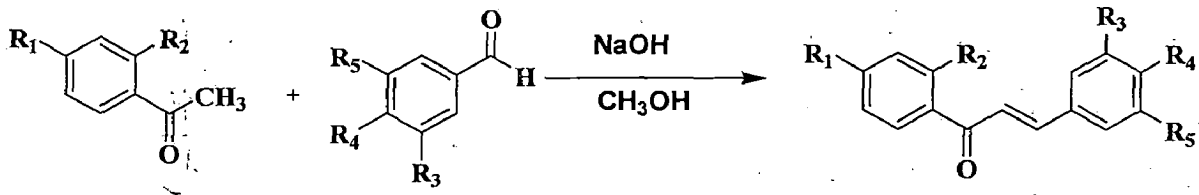
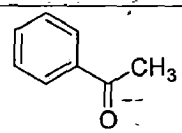
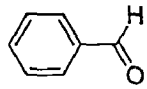
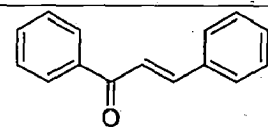
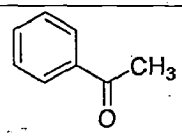
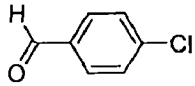
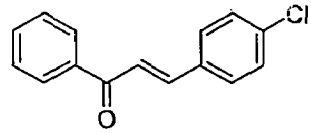
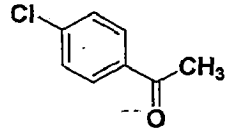
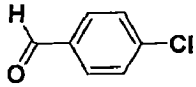
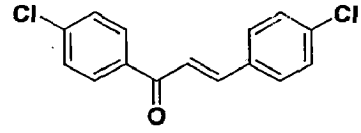
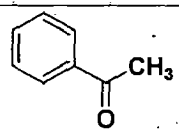
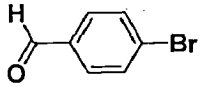
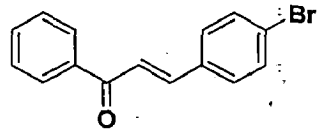
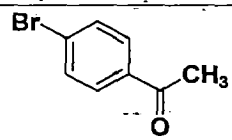
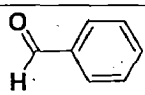
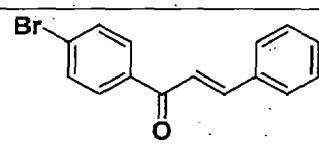
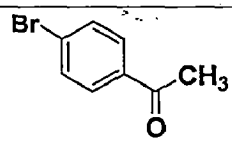
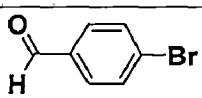
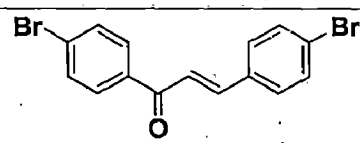
Table 1 Construction of chalcones by a variety of acetophenones and a variety of aromatic aldehydes.



(1a - 15a)

R_1 = H, OH, Br,Cl; R_2= H, OH; R_3 = H, OCH_3
R_4 = H, CH_3 ,OCH_3 , OH , Cl, Br, NO_2.
R_5 = H, OCH_3 , NO_2.

S.No	Acetophenone	Aldehyde	Reaction time(h)	Chalcone	Product (Yield %)
1.			10		1a (92)
2.			15		2a (93)
3.			14		3a (91)
4.			16		4a (93)
5.			15		5a (92)
6.			14		6a (94)

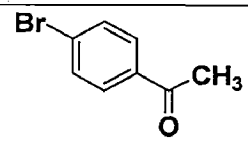
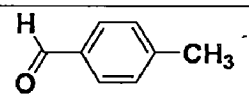
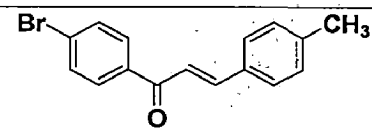
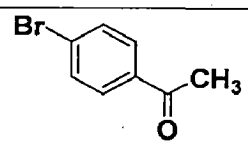
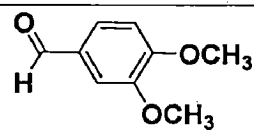
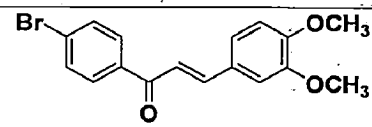
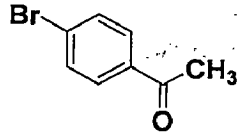
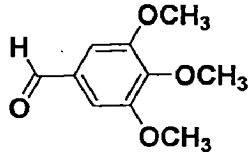
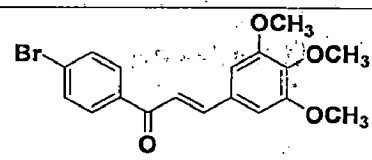
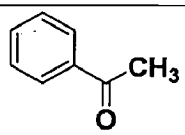
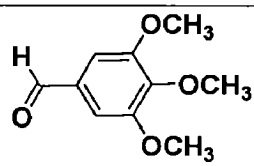
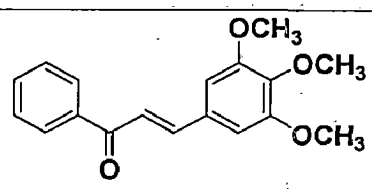
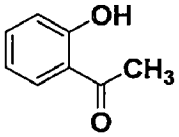
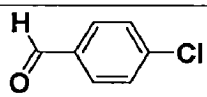
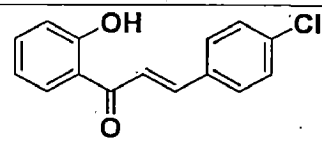
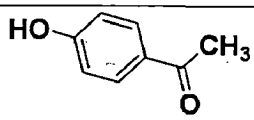
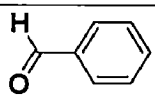
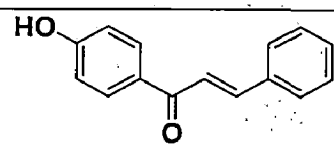
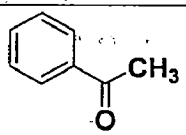
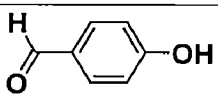
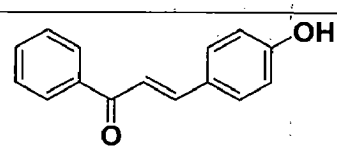
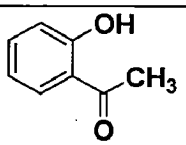
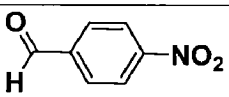
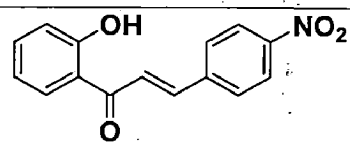
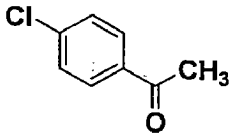
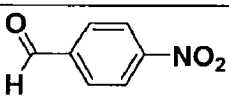
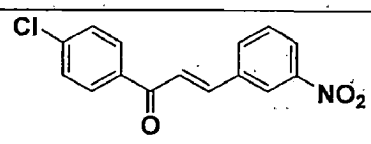
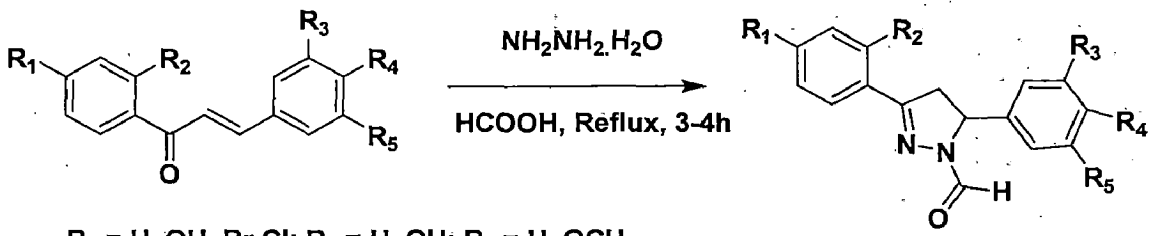
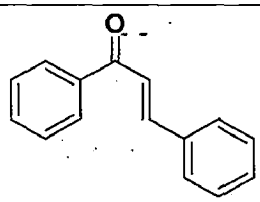
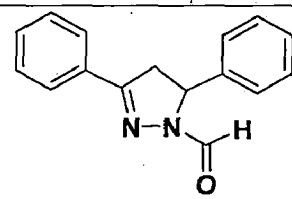
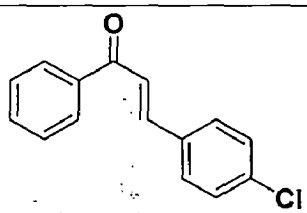
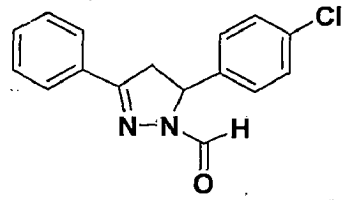
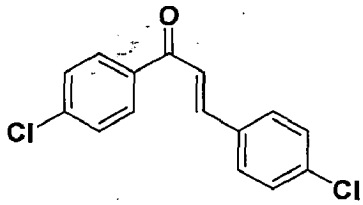
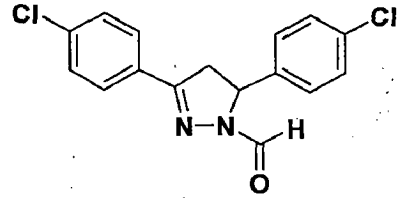
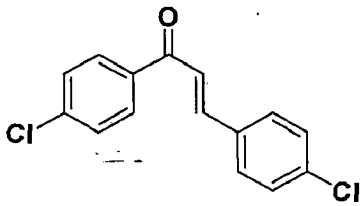
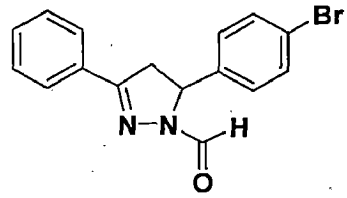
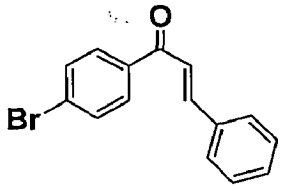
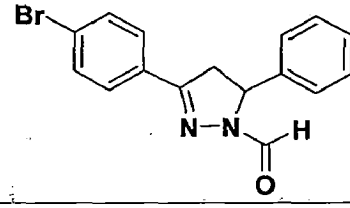
7.			16		7a (92)
8.			8		8a (94)
9.			7		9a (96)
10.			6		10a (93)
11.			8		11a (95)
12.			5		12a (94)
13.			11		13a (96)
14.			12		14a (98)
15.			10		15a (94)

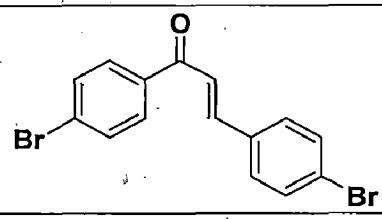
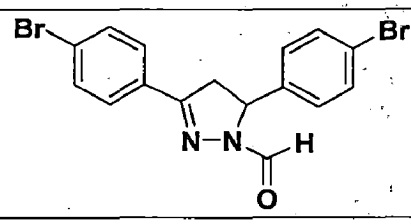
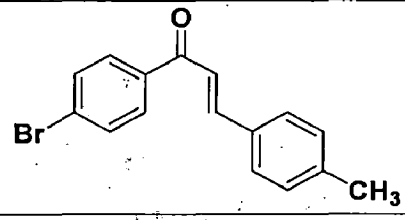
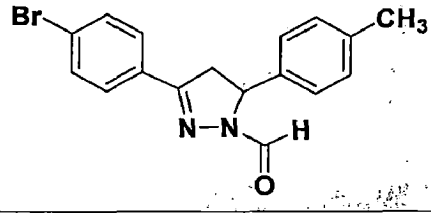
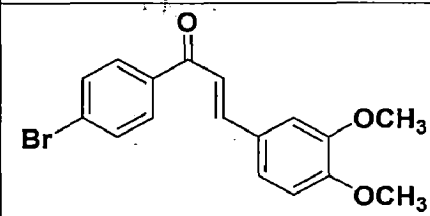
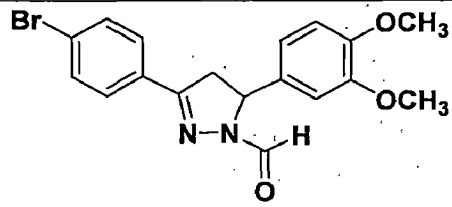
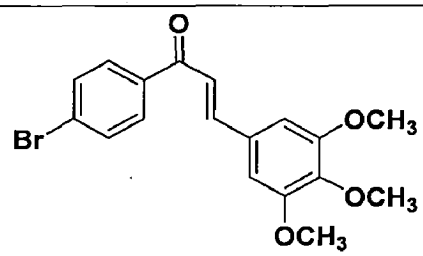
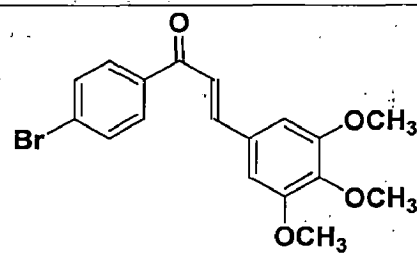
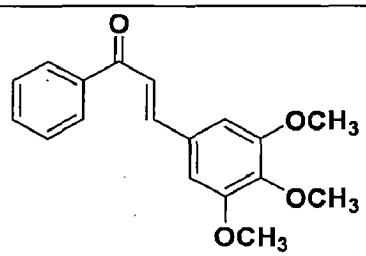
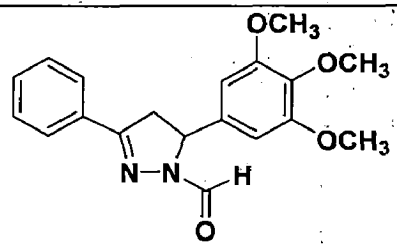
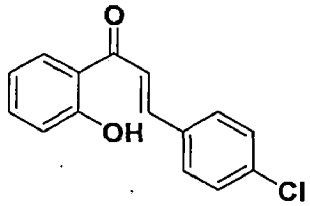
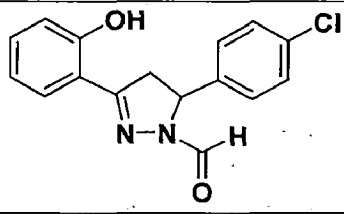
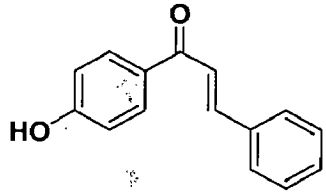
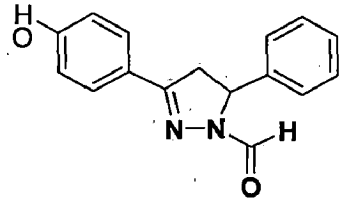
Table 2 Formation of N-formylpyrazoline from chalcone



R_1 = H, OH, Br,Cl; R_2 = H, OH; R_3 = H, OCH_3
R_4 = H, CH_3 ,OCH_3 , OH , Cl, Br. NO_2.
R_5 = H, OCH_3 , NO_2.

1b - 15b

S.No.	Chalcone	Reaction time(hs)	N-formylpyrazoline	Product (Yield%)
1.		3		1b (96)
2.		3.30		2b (95)
3.		3		3b (95)
4.		3		4b (94)
5.		3.20		5b (93)

6.		3		6b (92)
7.		3.10		7b (91)
8.		3		8b (93)
9.		3.15		9b (93)
10.		3		10b (94)
11.		4		11b (87)
12.		3.50		12b (85)

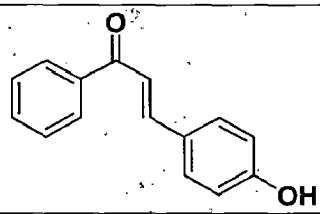
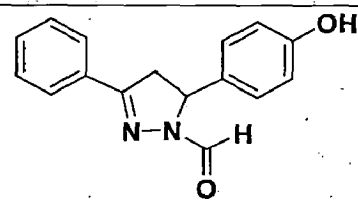
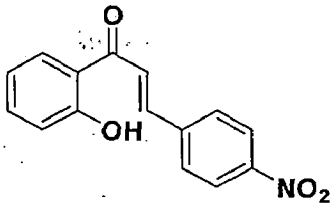
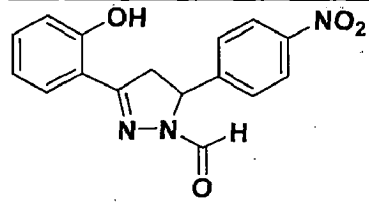
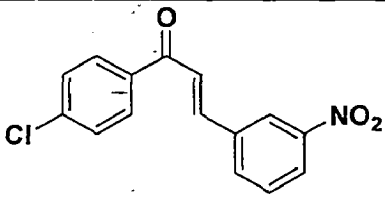
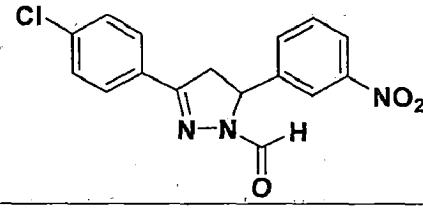
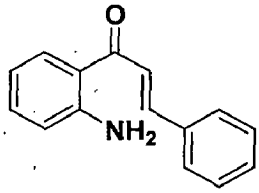
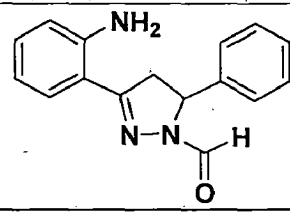
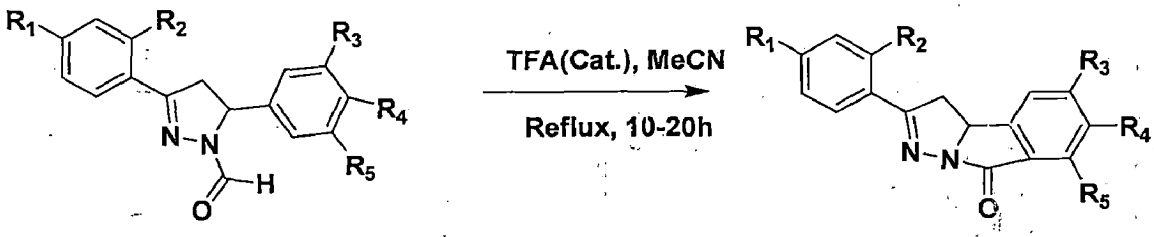
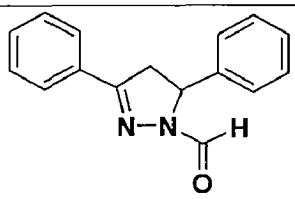
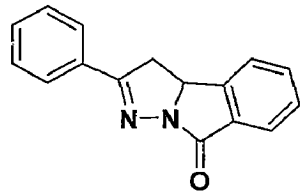
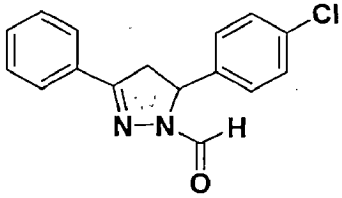
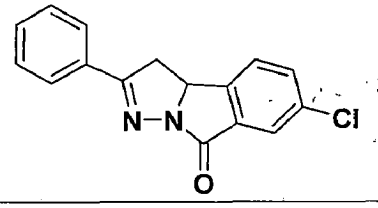
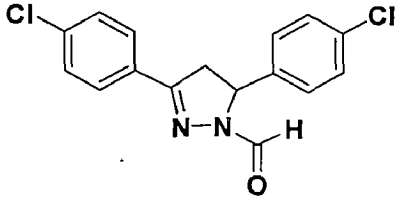
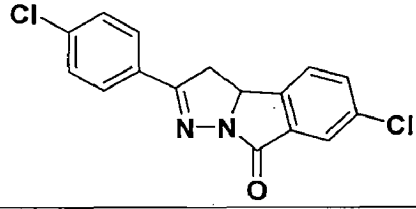
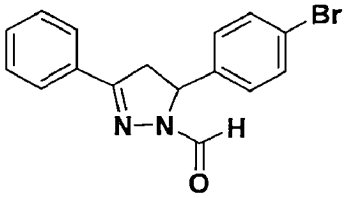
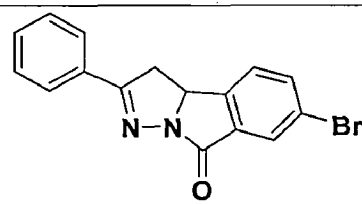
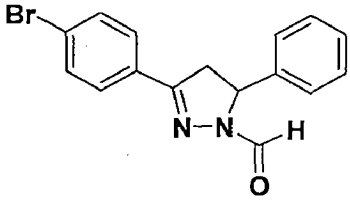
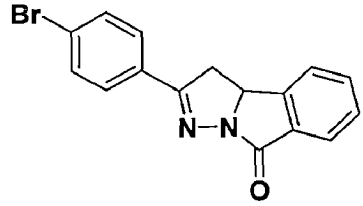
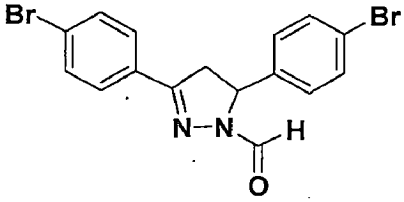
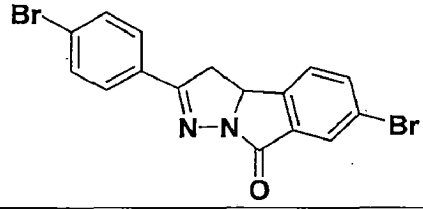
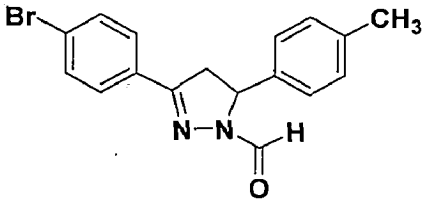
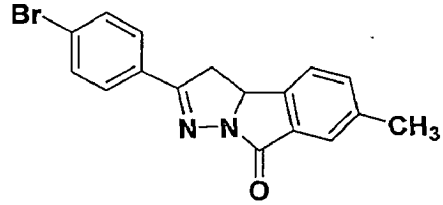
13.		4		13b (83)
14.		4		14b (85)
15.		4		15b (81)
16		-		0

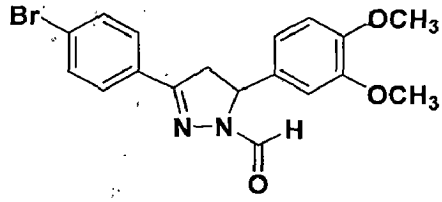
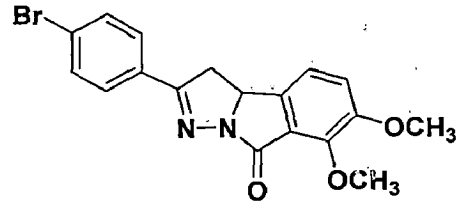
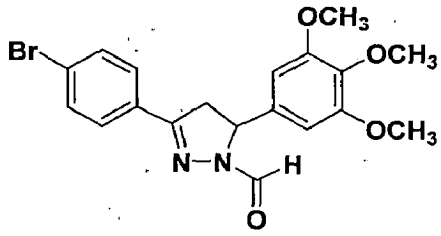
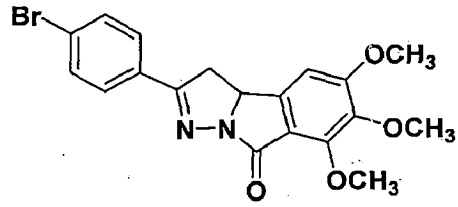
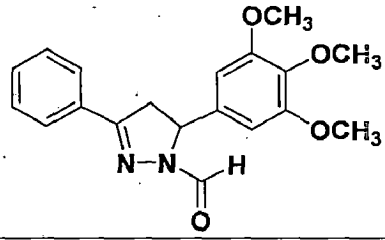
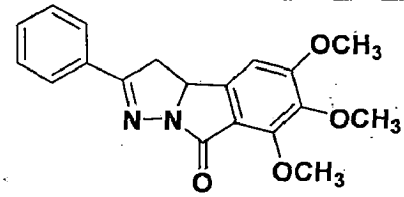
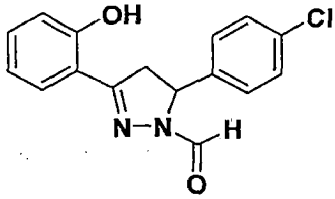
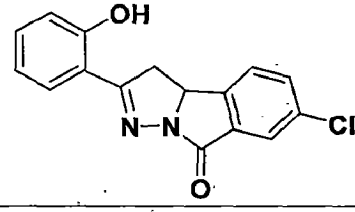
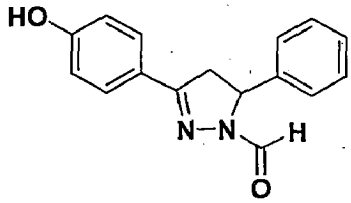
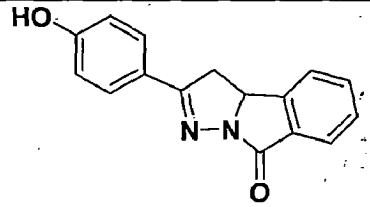
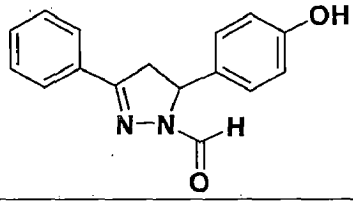
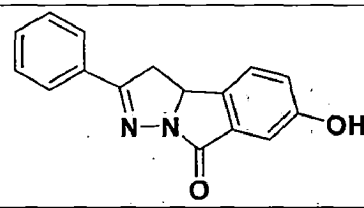
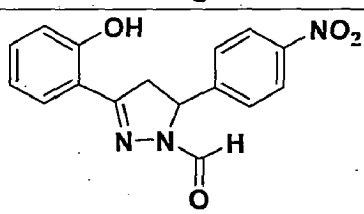
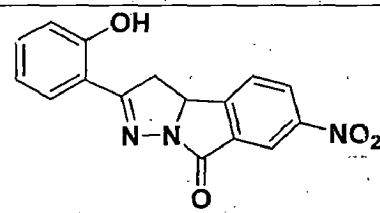
Table 3 Formation of Pyrazoloisoindole from N-formylpyrazoline

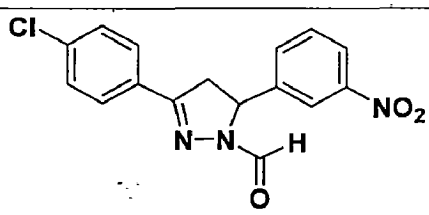
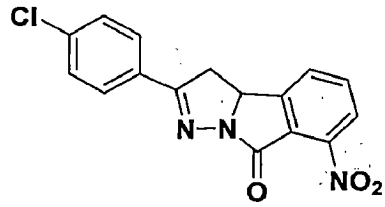


(1c -15c)

R_1 = H, OH, Br,Cl; R_2 = H, OH; R_3 = H, OCH_3
R_4 = H, CH_3 ,OCH_3 , OH , Cl, Br. NO_2.
R_5 = H, OCH_3 , NO_2.

S.No.	N-formylpyrazoline	Reaction time	Pyrazoloisoindone	Product (Yield%)
1.		10		1c (94)
2.		12		2c (90)
3.		13		3c (93)
4.		14		4c (89)
5.		12		5c (90)
6.		11		6c (89)
7.		14		7c (89)

8.		13		8c (88)
9.		14		9c (87)
10.		13		10c (90)
11.		16		11c (78)
12.		17		12c (76)
13.		18		13c (75)
14.		18		14c (74)

15.		20		15c (74)

Chapter - 4

Conclusion

Conclusion

An alternate synthetic approach of 2-(substituted aryl)-3,3a-dihydro-8H-pyrazolo [5,1-a] isoindol-8-ones via chalcone based N-formyl-pyrazolines is described. N-formyl-pyrazolines(**1b-15b**) were prepared in excellent yield (81-96%) by the reaction of chalcones (**1a-15a**) with hydrazine hydrate in presence of formic acid, which undergoes intramolecular Friedal-Craft acylation in the presence of trifluoroacetic acid(TFA) as a catalyst to afford functionalized 2-(substituted phenyl)-3,3a-dihydro-8H-pyrazolo[5,1-a]isoindol-8-one (**3c-15c**) in good to excellent yield (74-94%) at refluxed in acetonitrile. Our synthetic route avoids expensive reagents and significantly improved the yield.

SUPPORTING INFORMATION

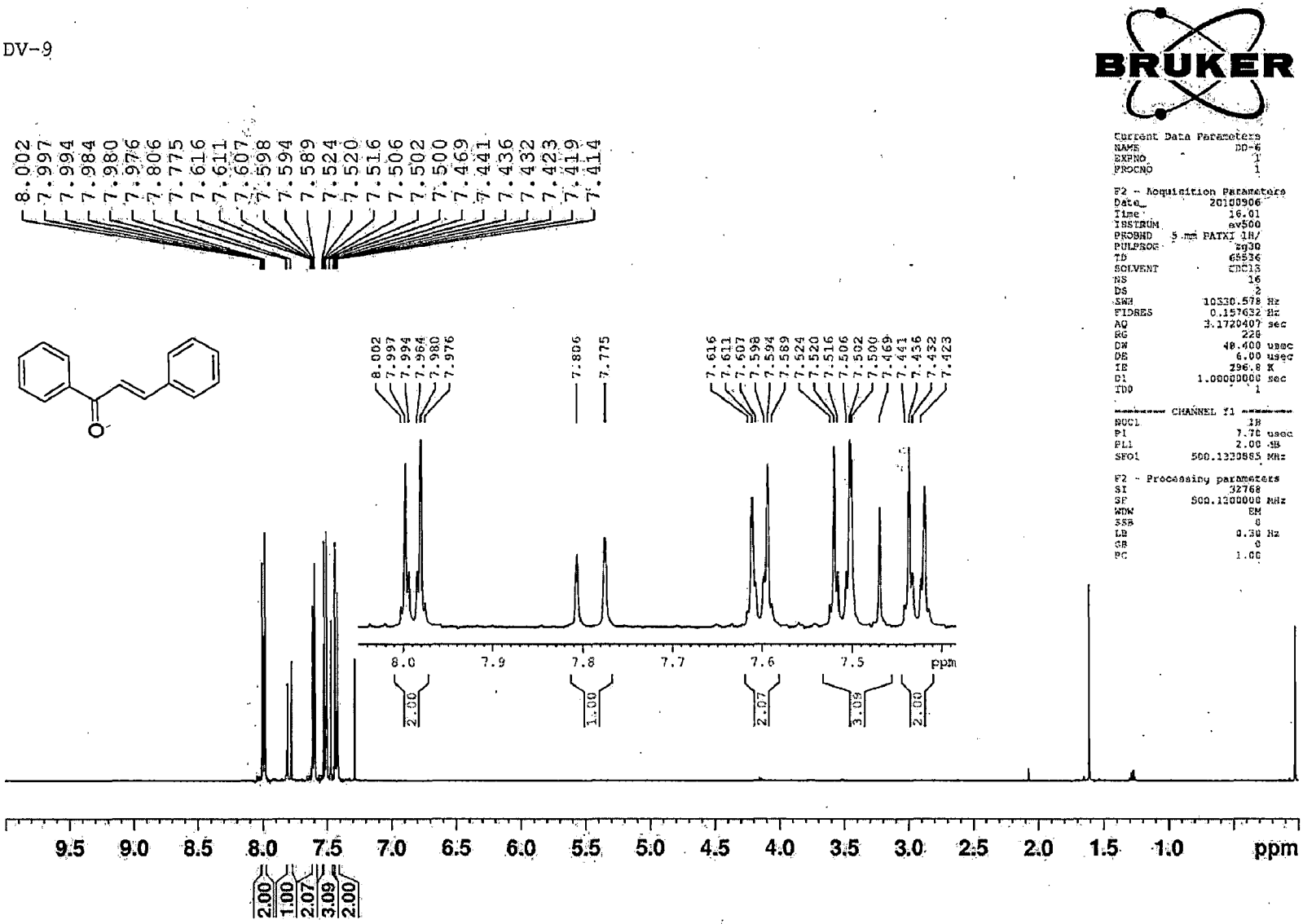


Figure 1a ^{1}H NMR spectra of chalcone

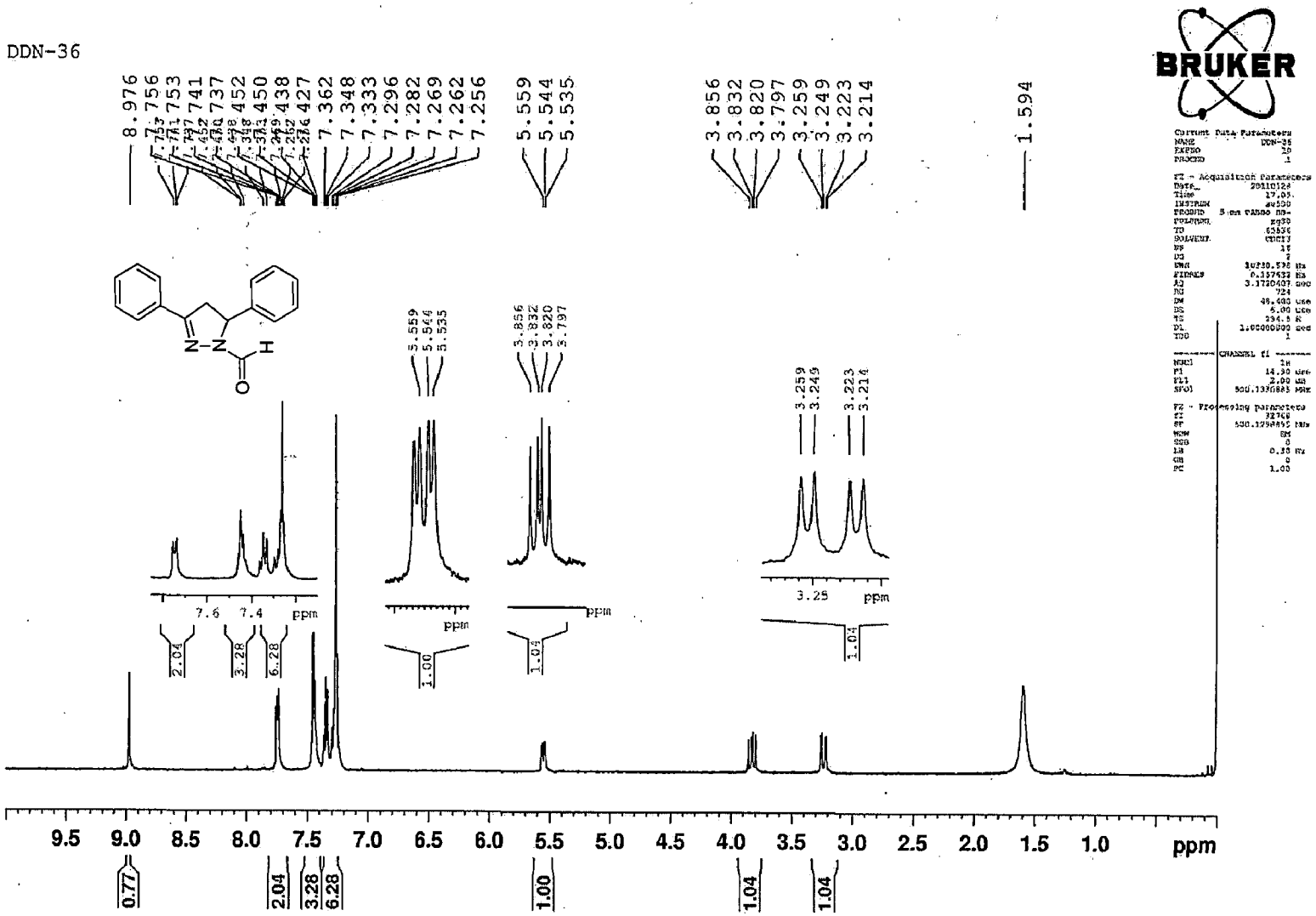


Figure 1b ^{1}H NMR spectra of 3,5-diphenyl-4,5-dihydropyrazole-1-carbaldehyde

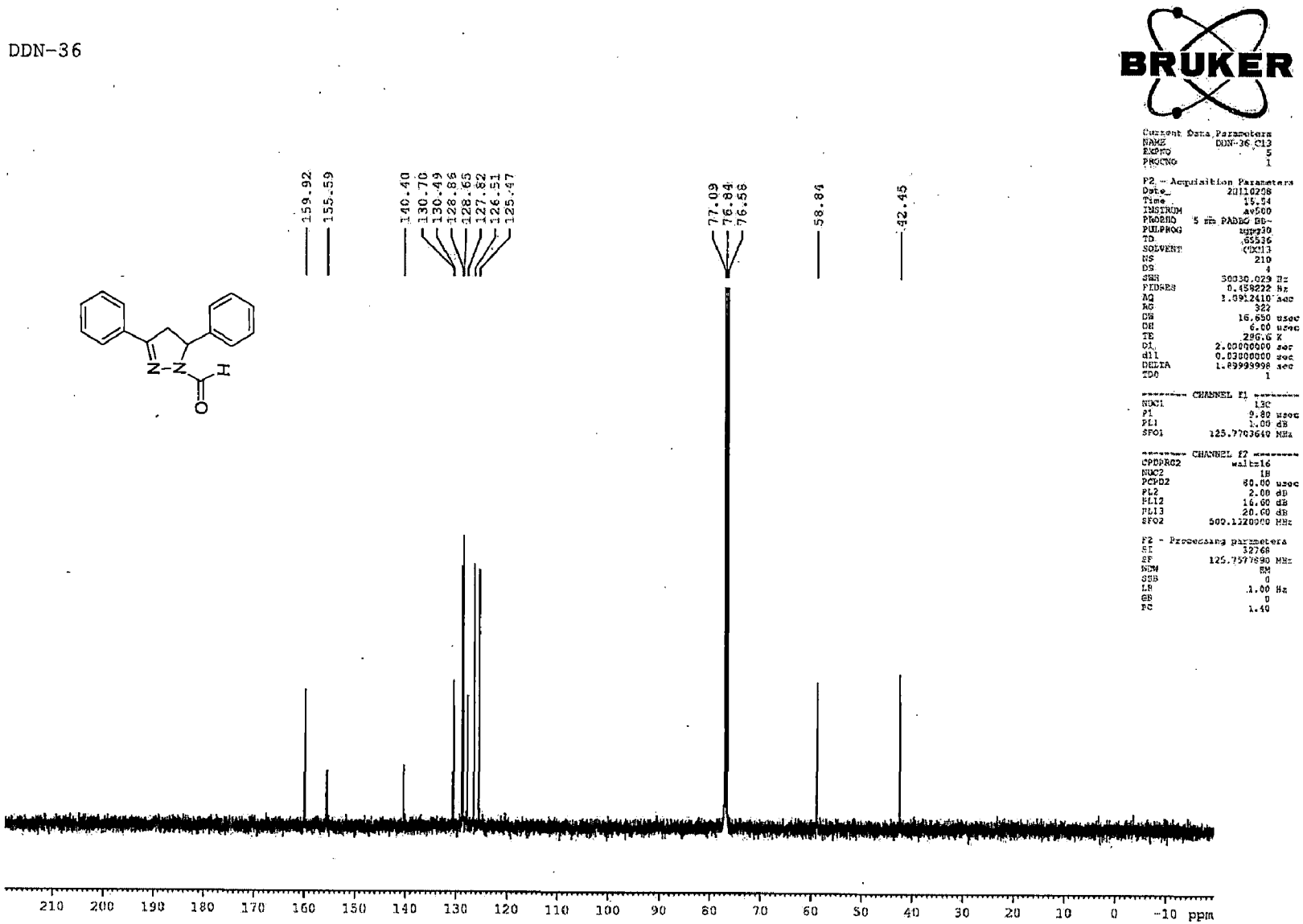


Figure 1b ^{13}C NMR spectra of 3,5-diphenyl-4,5-dihydropyrazole-1-carbaldehyde

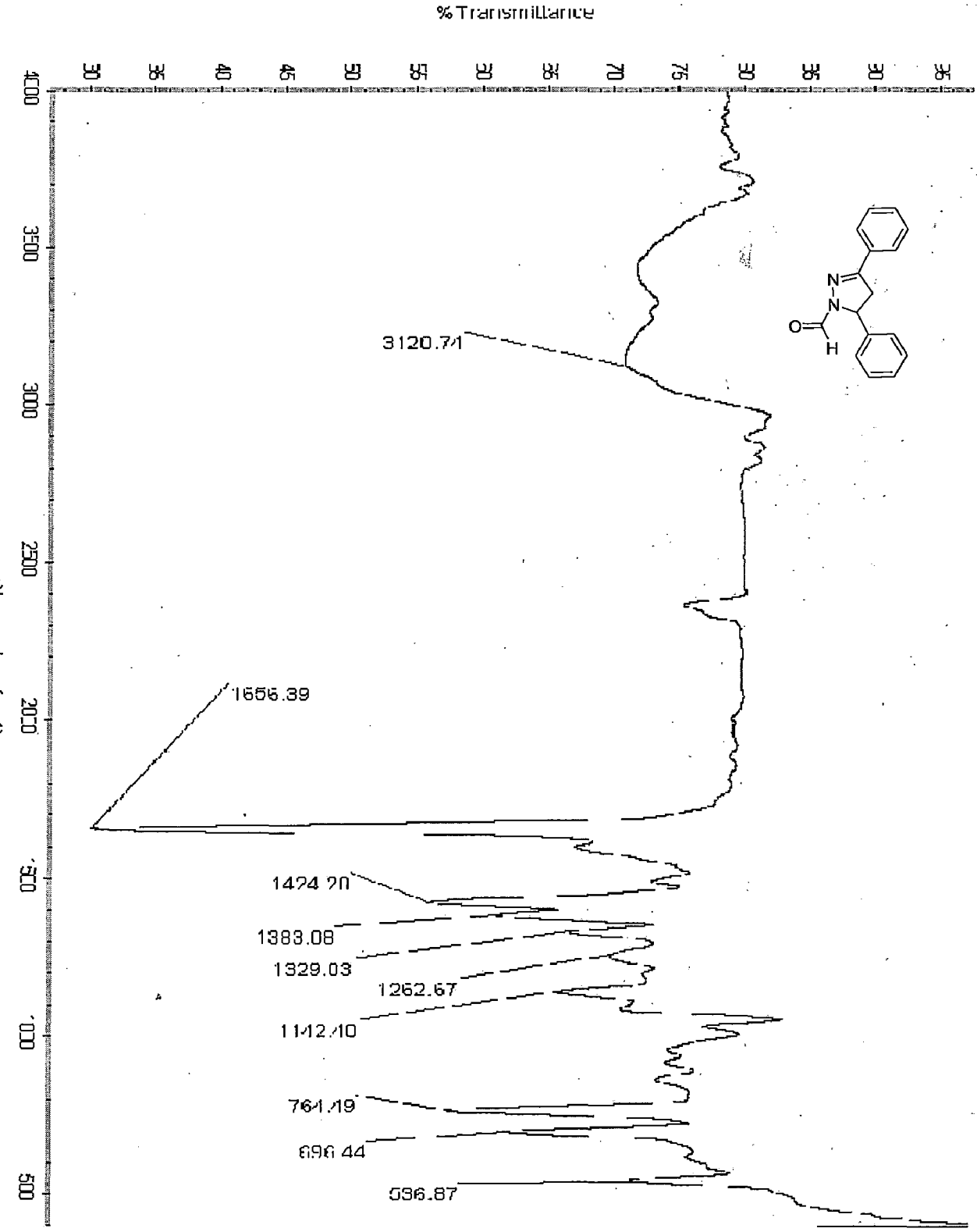


Figure 1b IR spectra of 3,5-diphenyl-4,5-dihydropyrazole-1-carbaldehyde

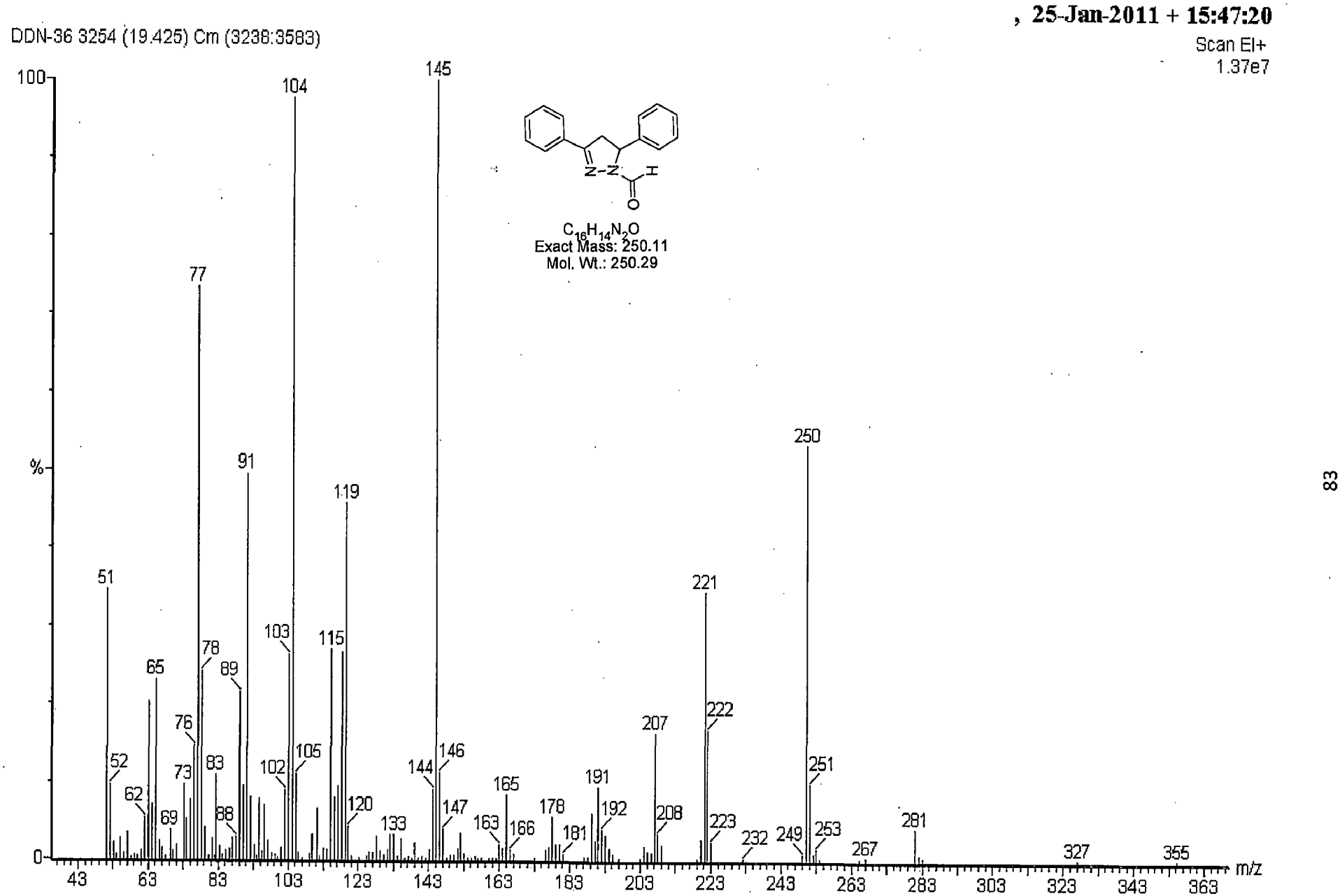


Figure 1b GC-MS spectra of 3,5-diphenyl-4,5-dihydropyrazole-1-carbaldehyde

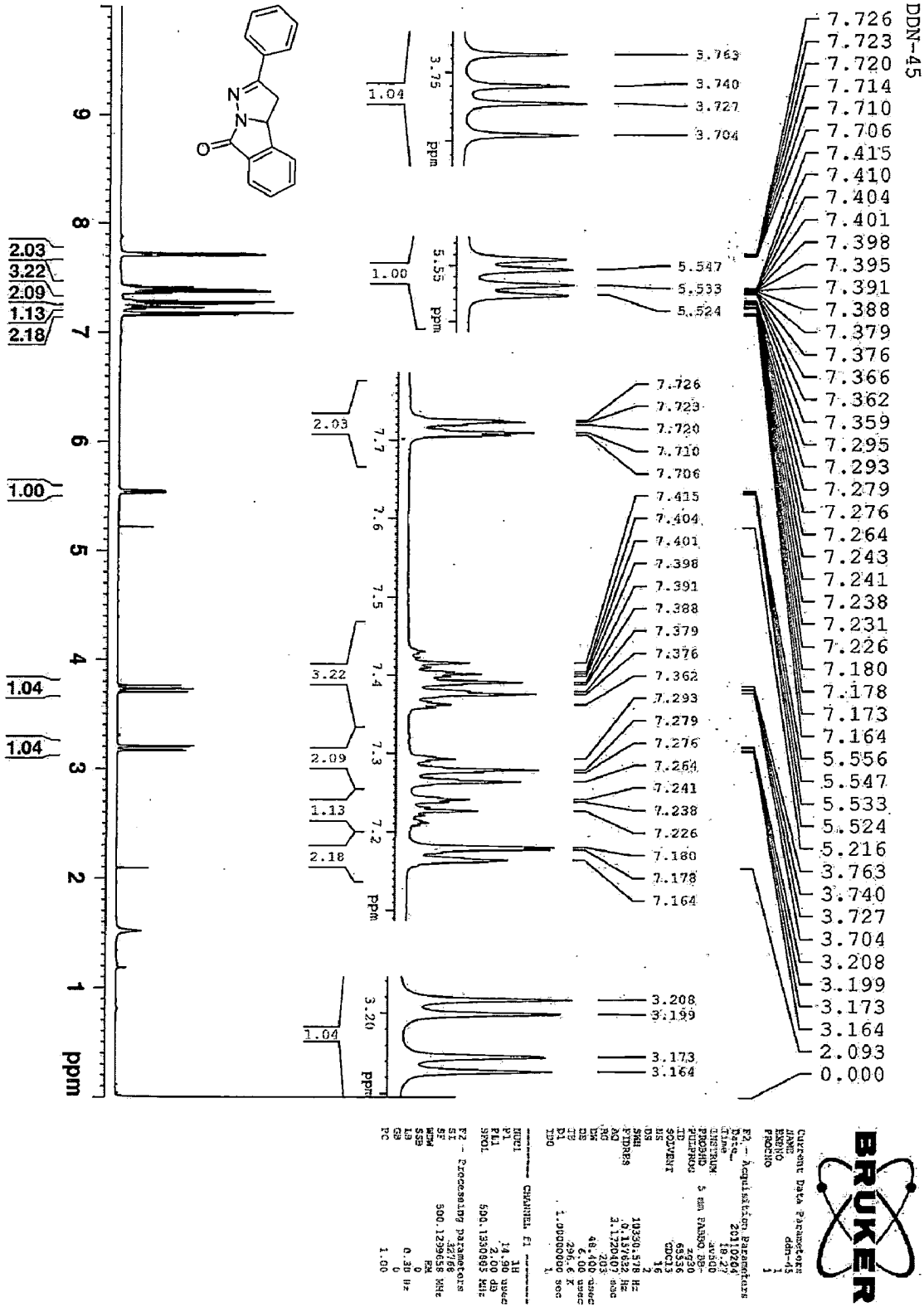


Figure 1c ^{1}H NMR spectra of 2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

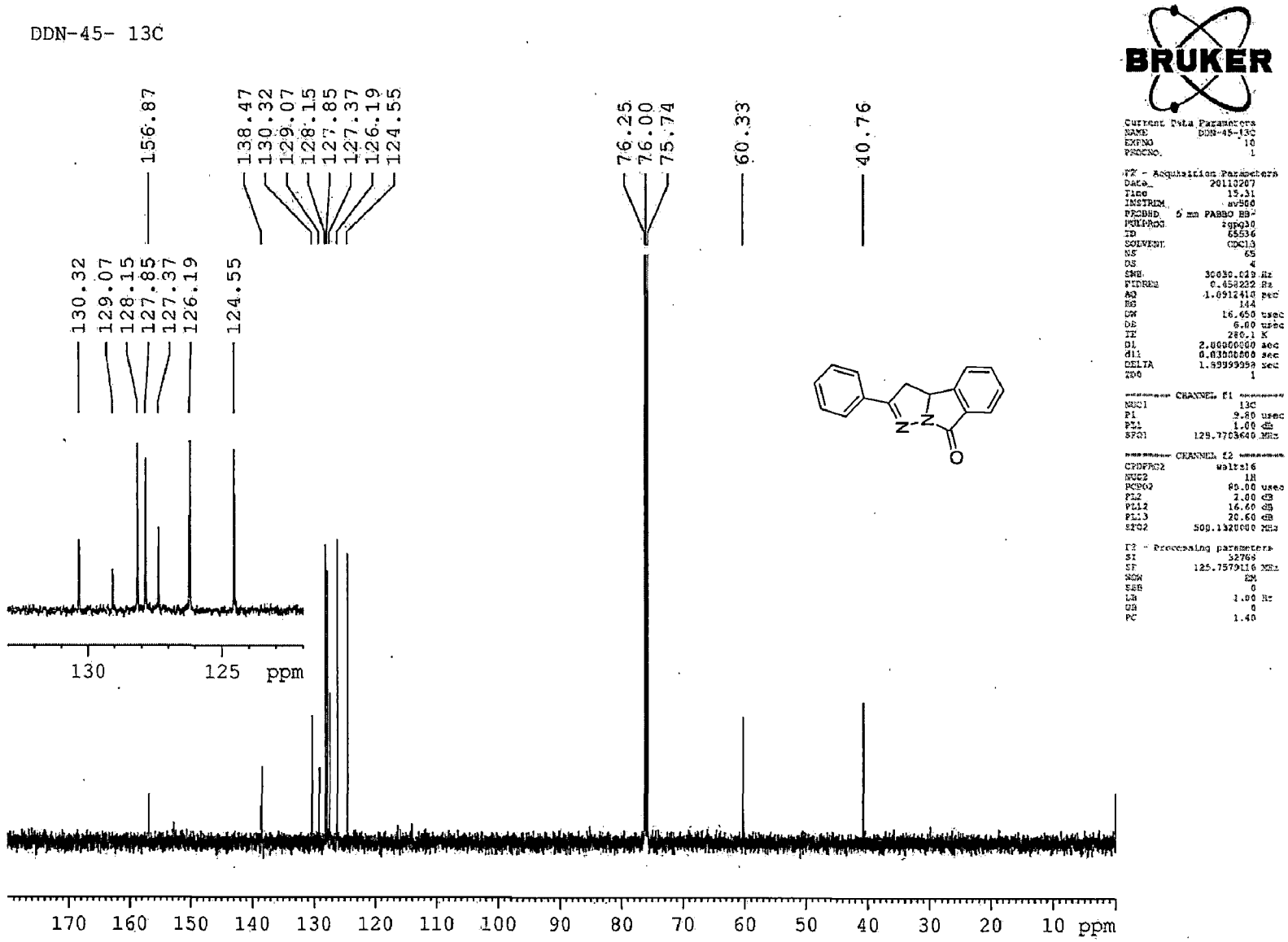


Figure 1c ^{13}C NMR spectra of 2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

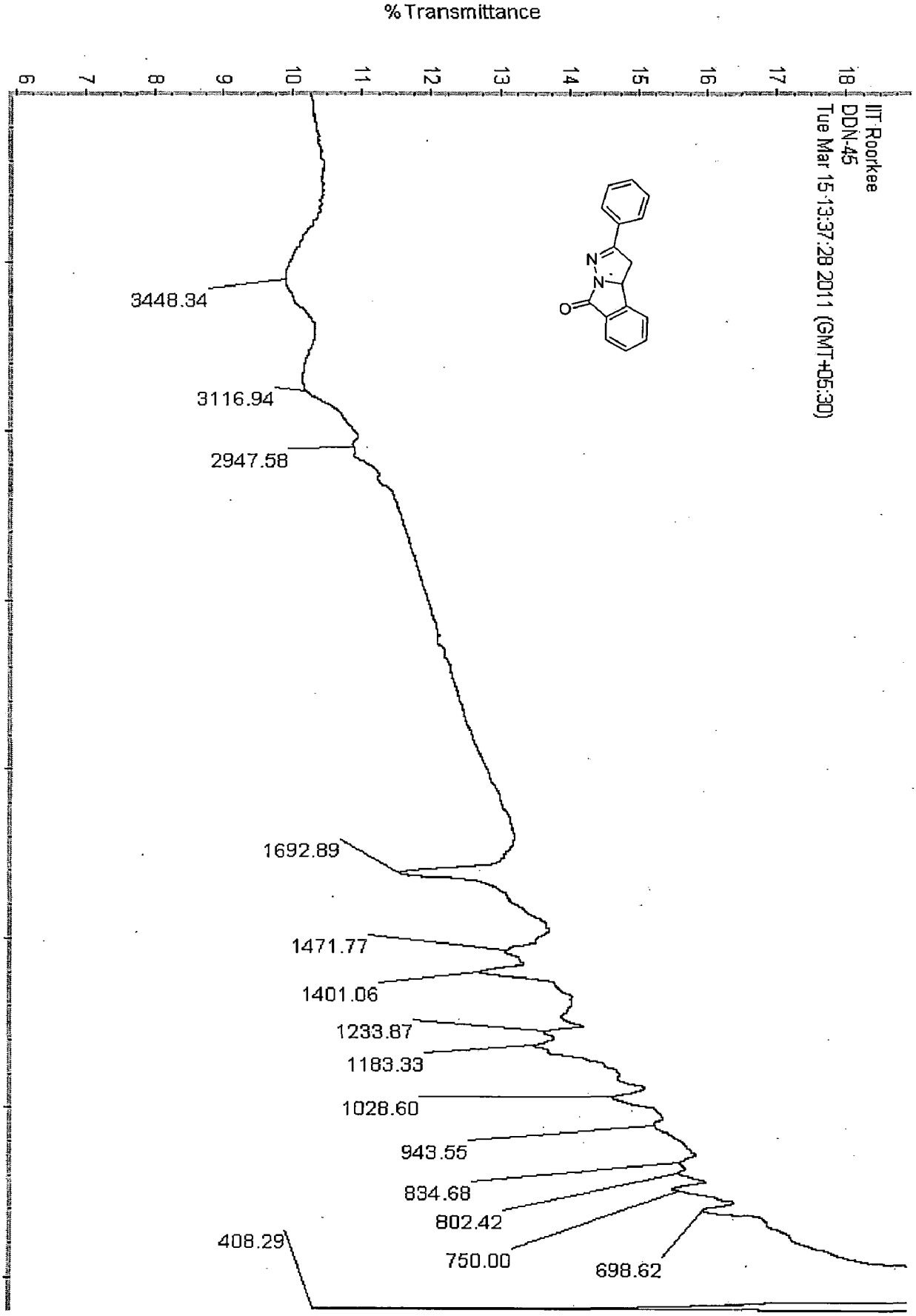


Figure 1c IR spectra of 2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

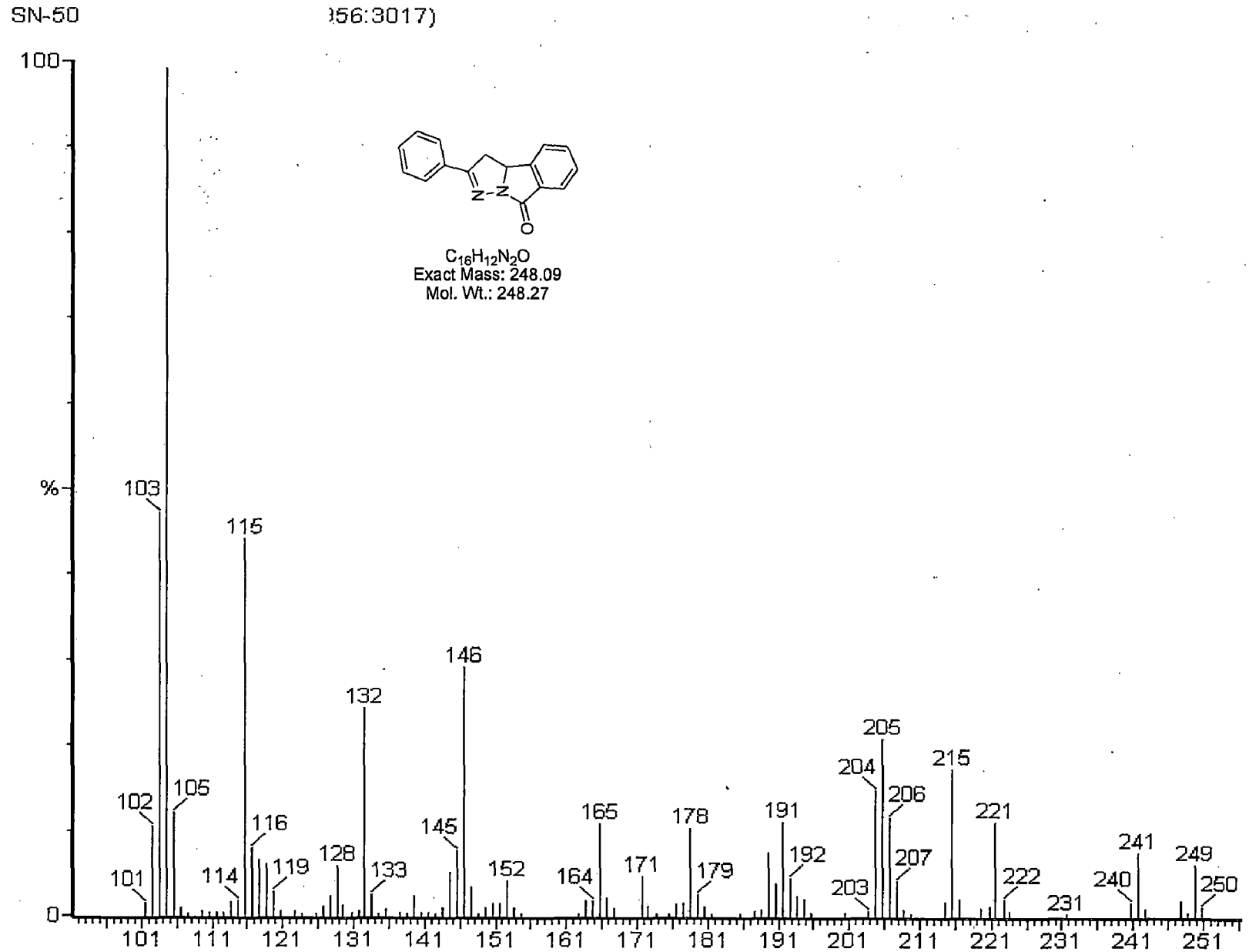


Figure 1c GC-MS spectra of 2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

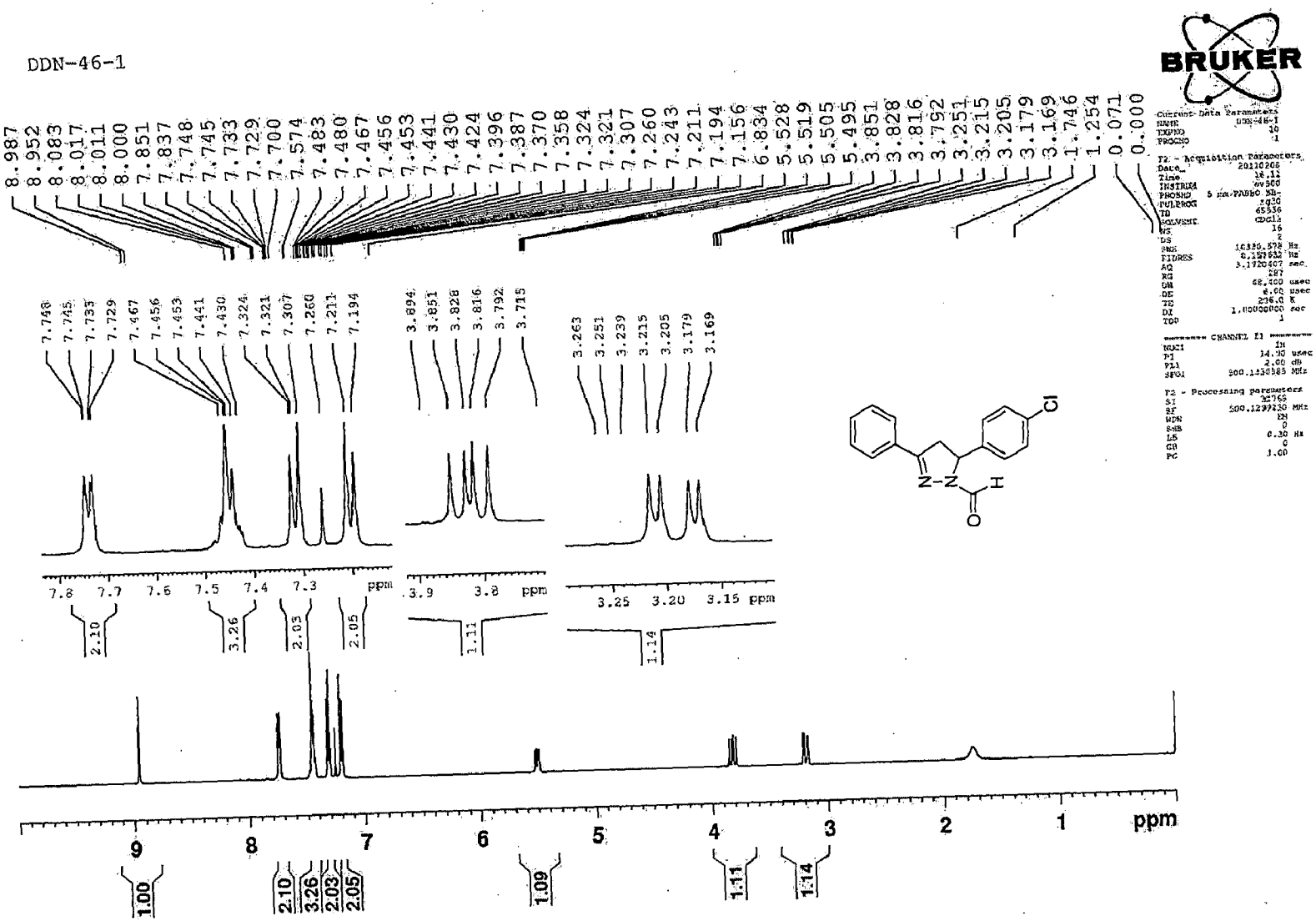


Figure 2b ^{1}H NMR spectra of 5-(4-chlorophenyl)-3-phenyl-4,5-dihydropyrazole-1-carbaldehyde

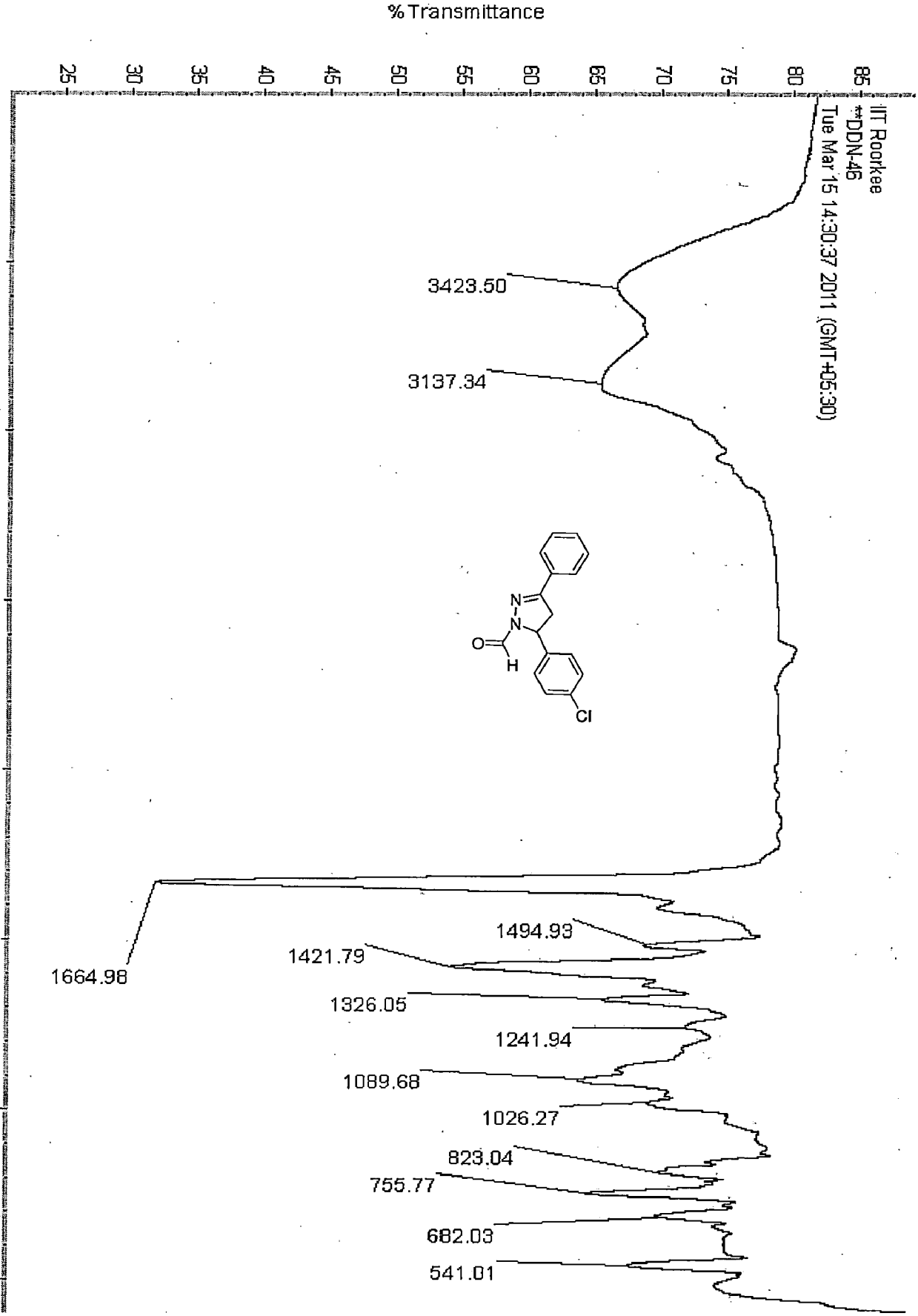


Figure 2b IR spectra of 5-(4-chlorophenyl)-3-phenyl-4,5-dihydropyrazole-1-carbaldehyde

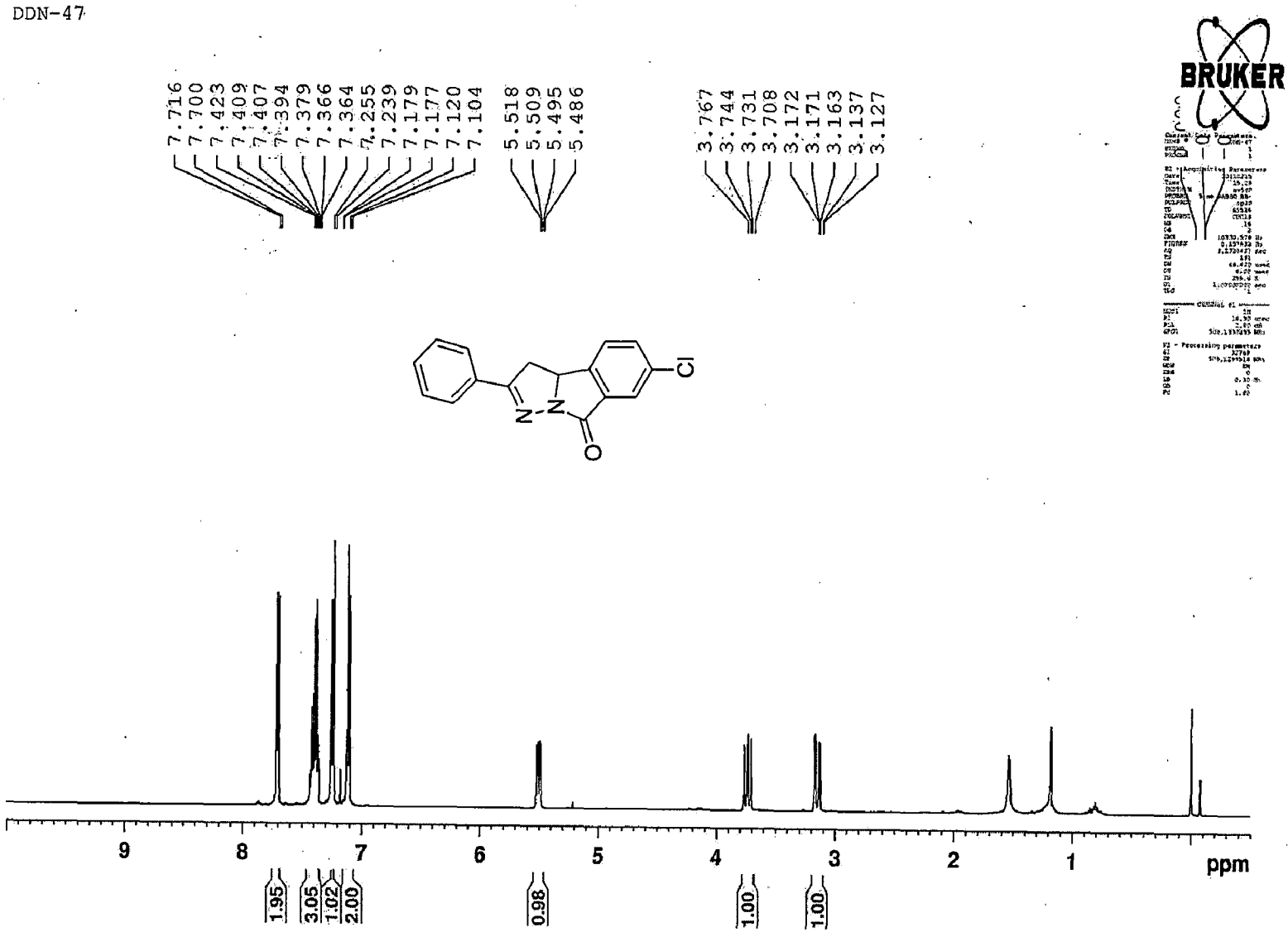
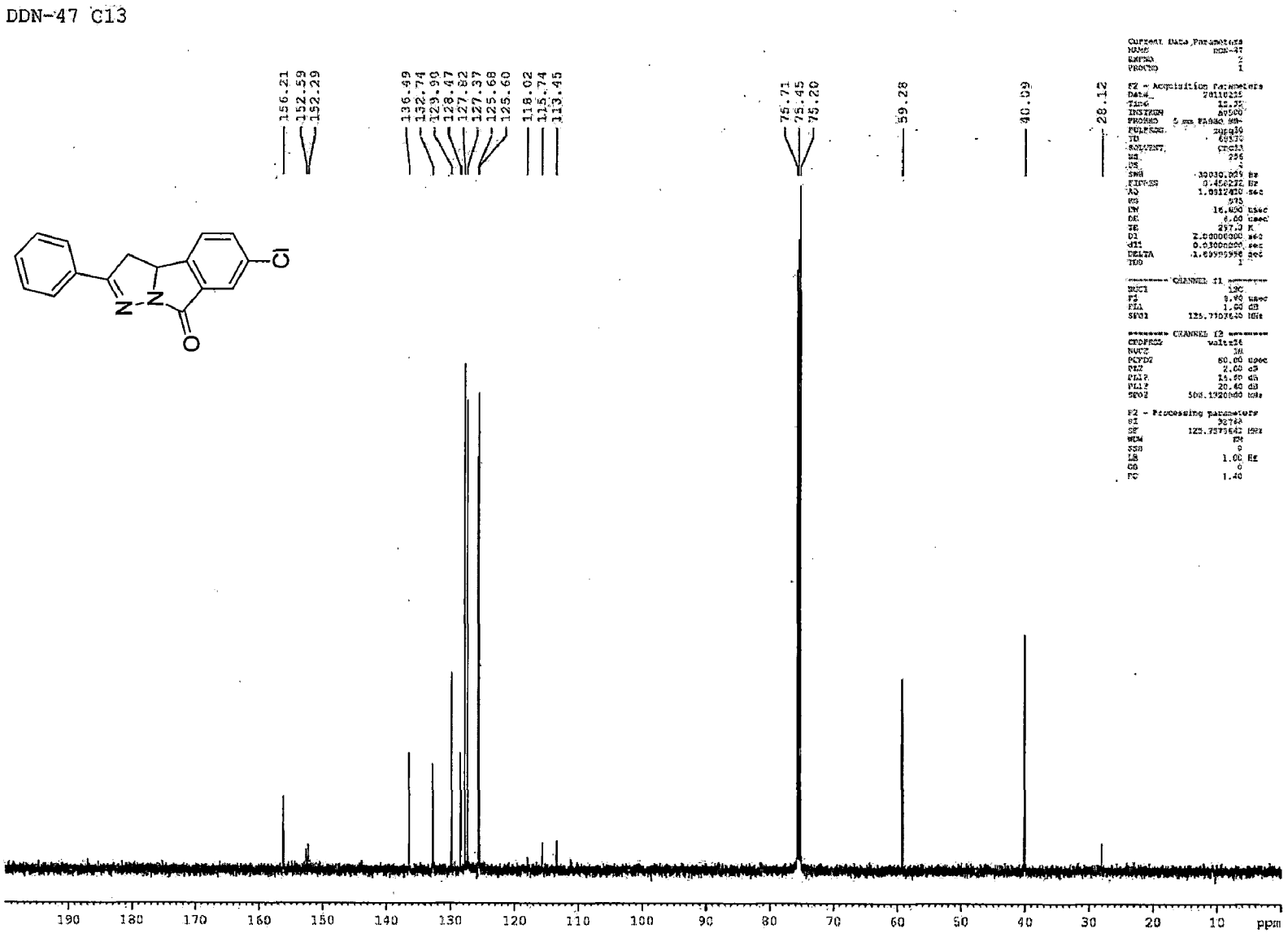


Figure 2c ^{1}H NMR spectra of 6-chloro-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one



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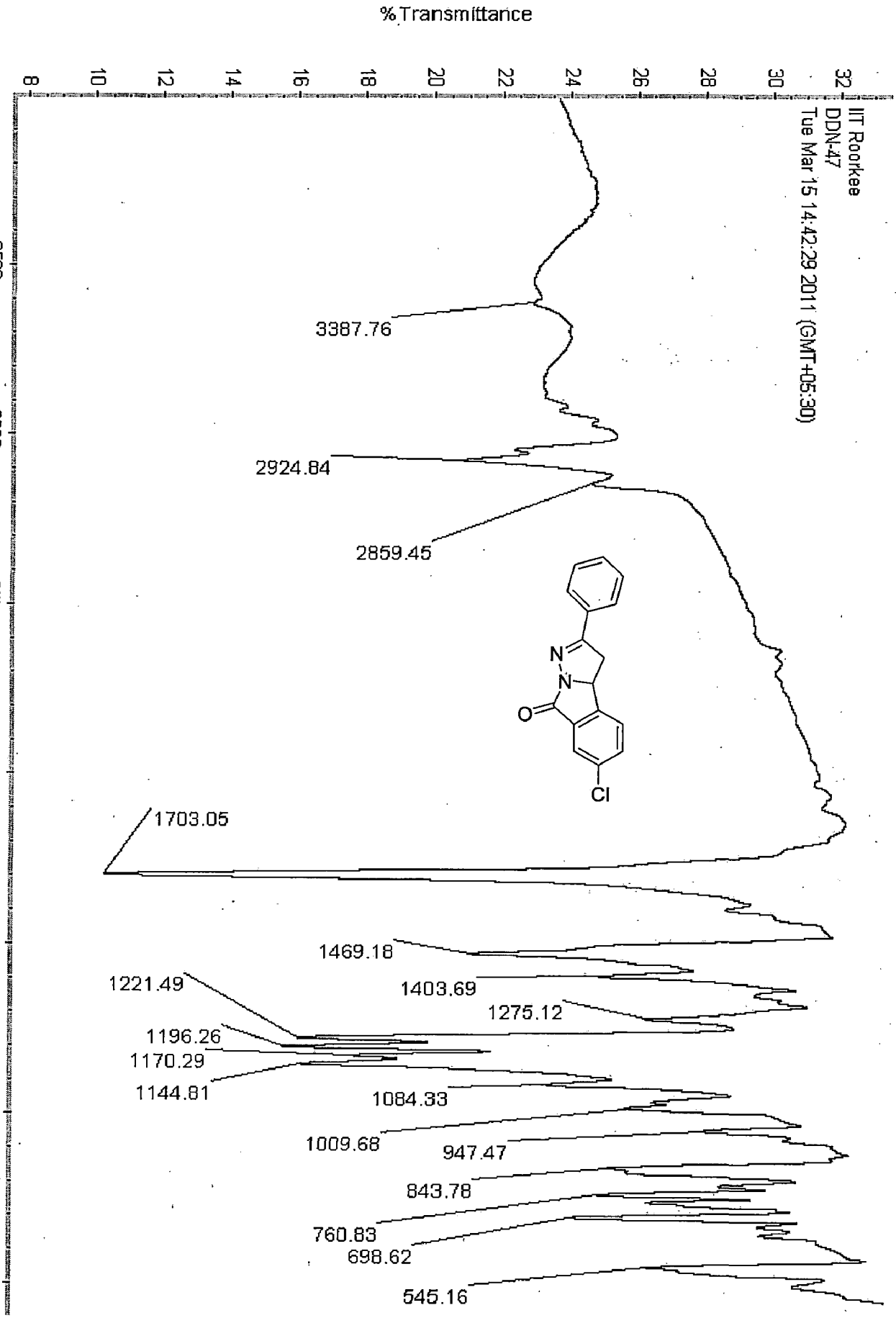
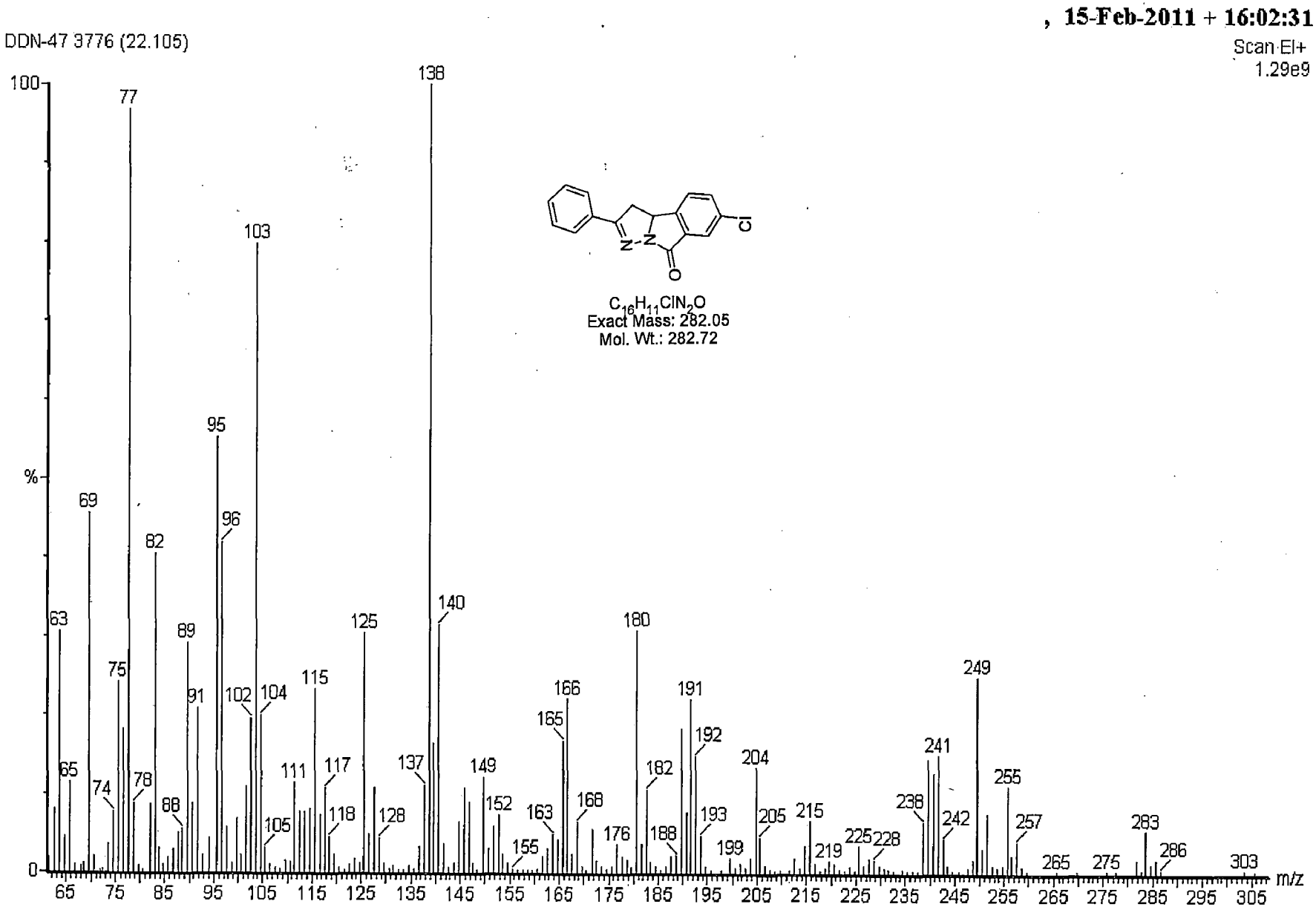


Figure 2c IR spectra of 6-chloro-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one



93

Figure 2c GC-MS spectra of 6-chloro-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

DDN-52

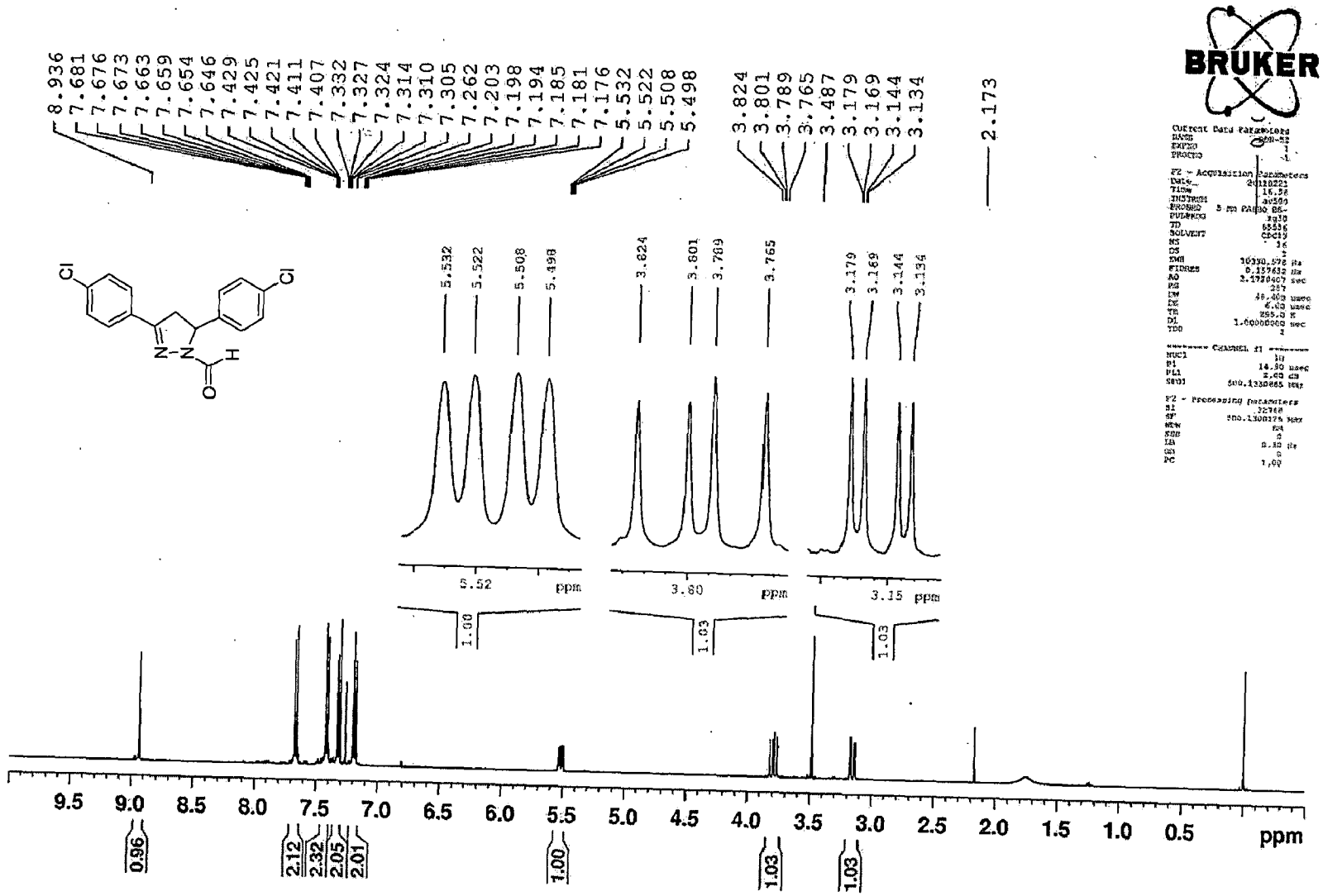


Figure 3b ^{1}H NMR spectra of 3,5-bis(4-chlorophenyl)-4,5-dihydropyrazole-1-carbaldehyde

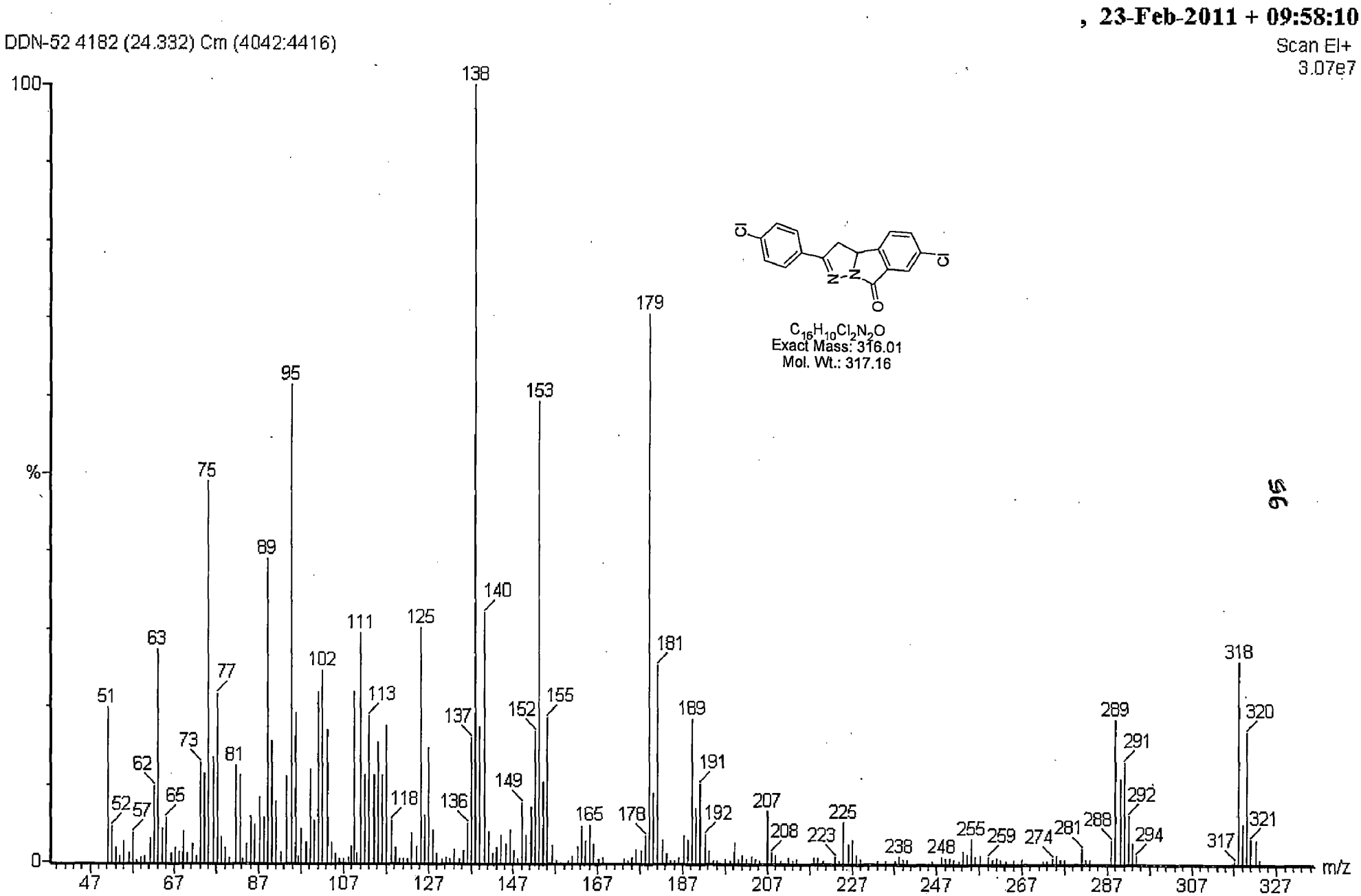


Figure 3b GC-MS spectra of 3,5-bis(4-chlorophenyl)-4,5-dihydropyrazole-1-carbaldehyde

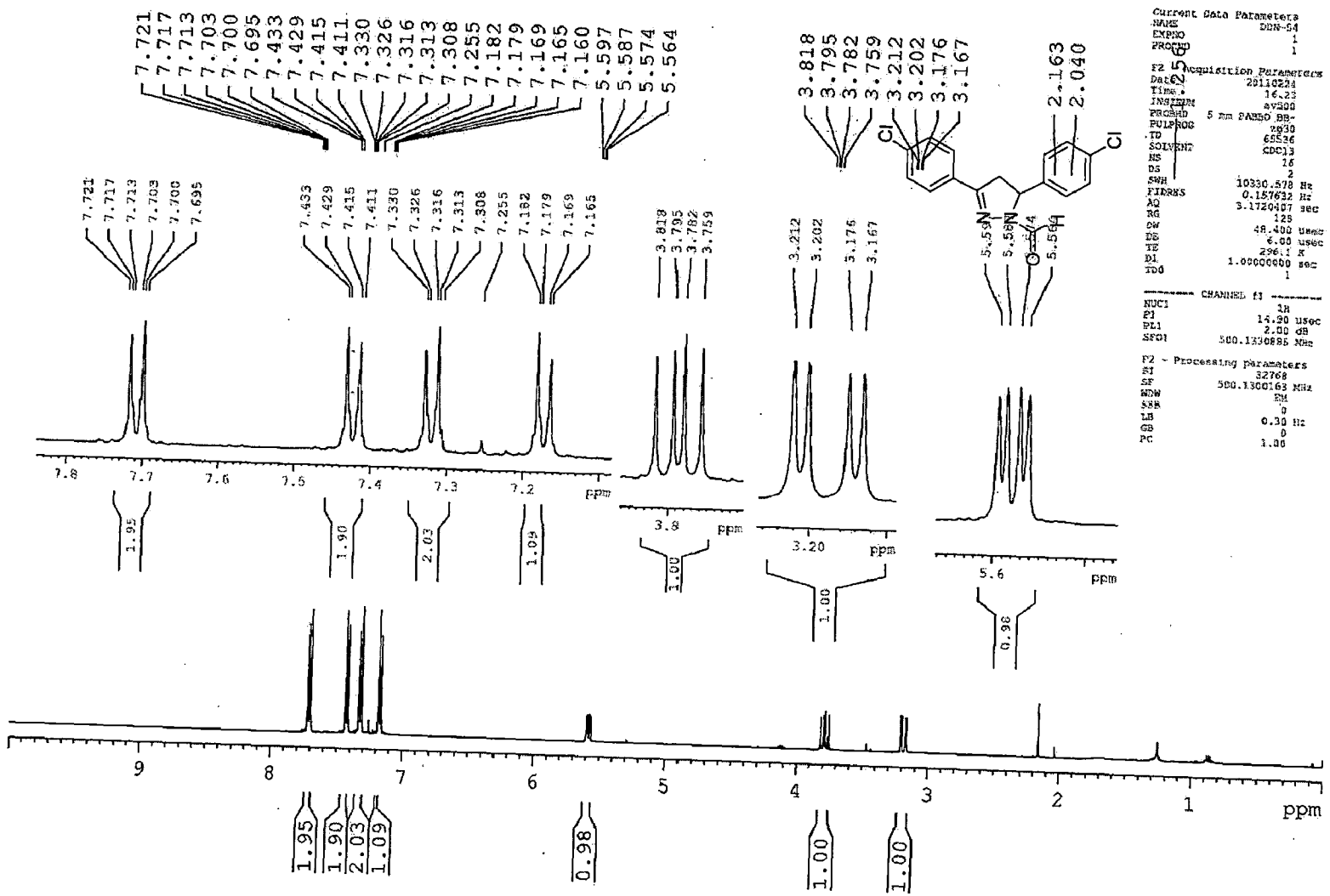


Figure 3c ^{1}H NMR spectra of 6-chloro-2-(4-chlorophenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

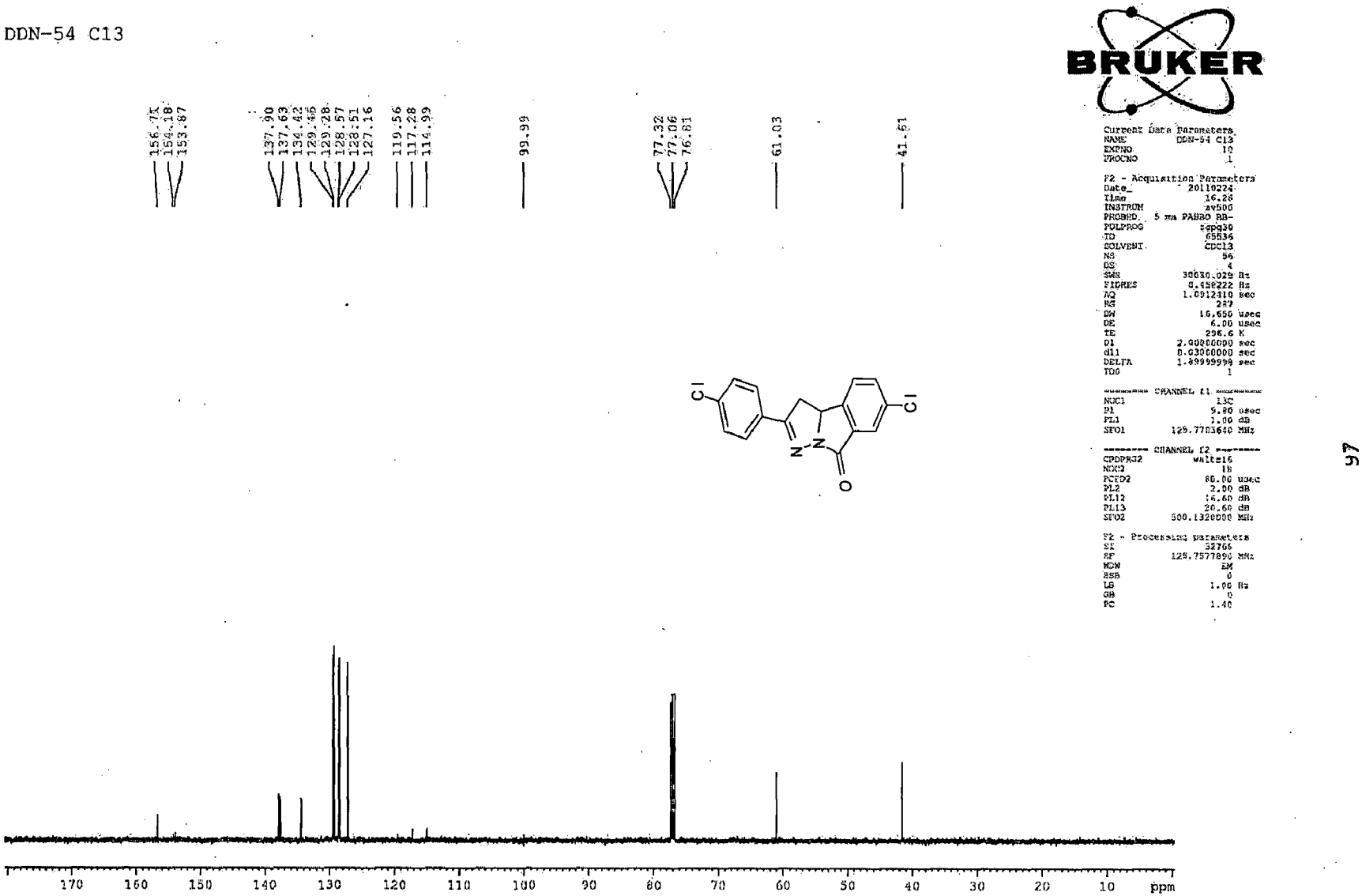


Figure 3c ^{13}C NMR spectra of 6-chloro-2-(4-chlorophenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

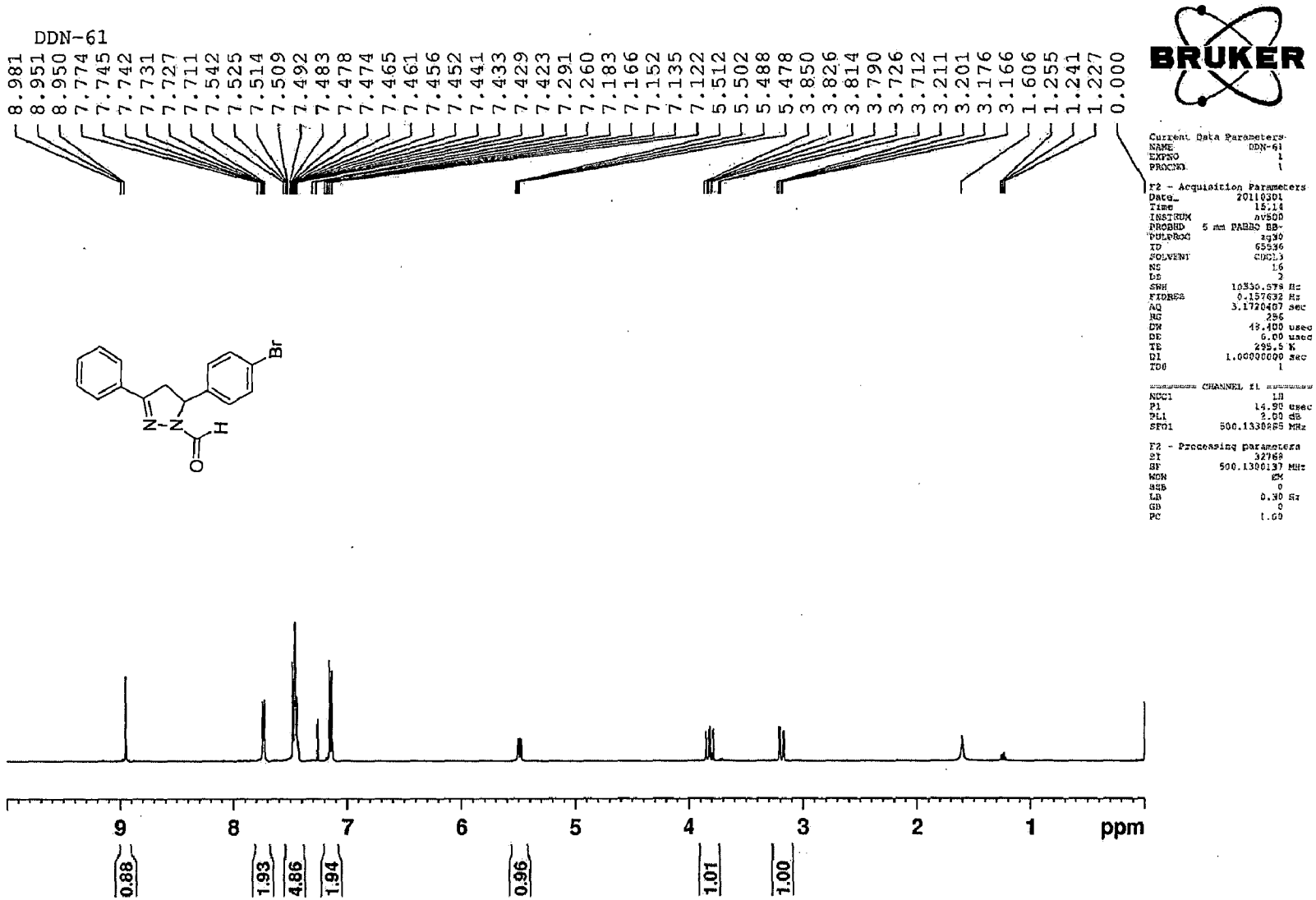


Figure 4b ^{1}H NMR spectra of 5-(4-bromophenyl)-3-phenyl-4,5-dihydropyrazole-1-carbaldehyde

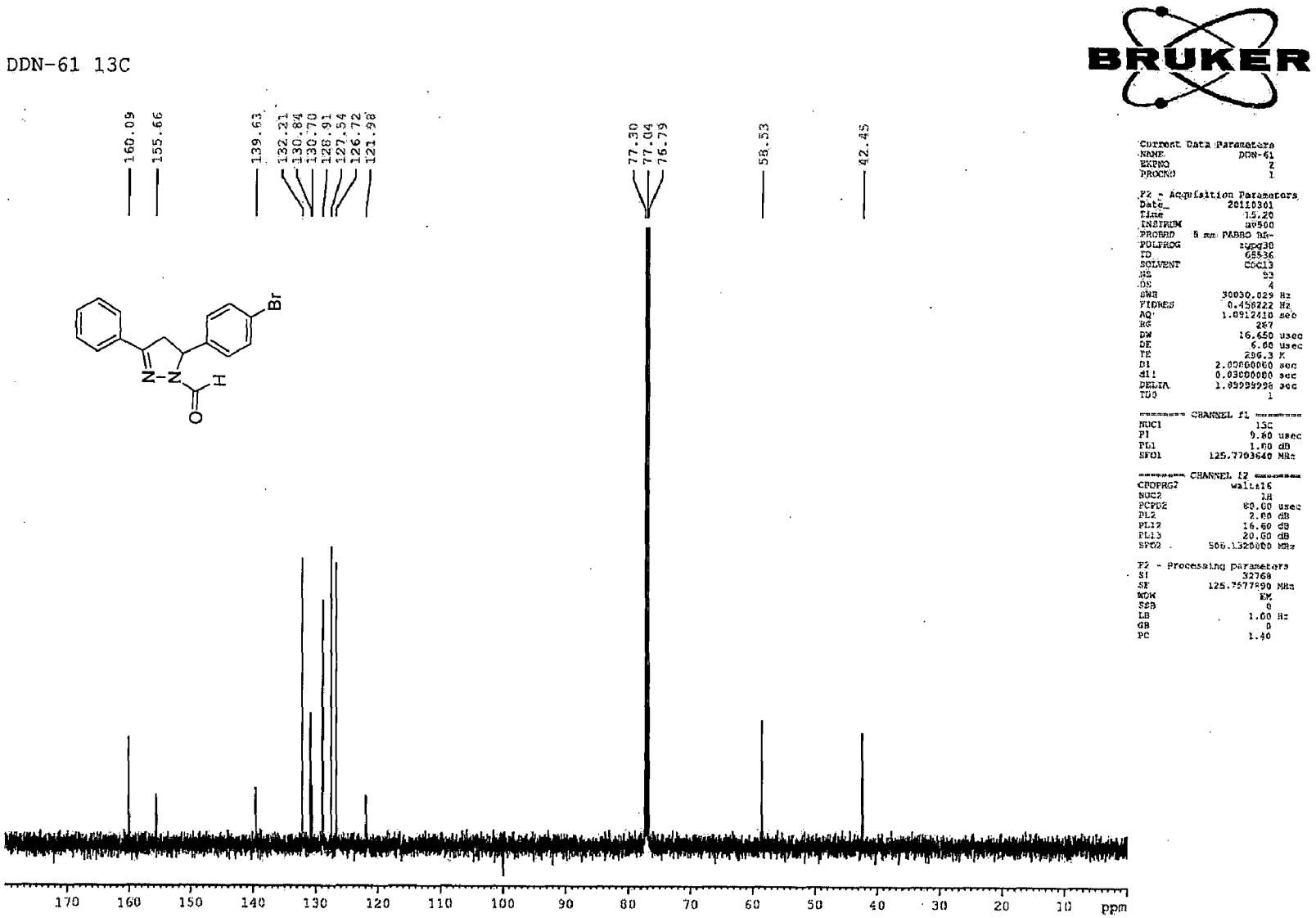


Figure 4b ^{13}C NMR spectra of 5-(4-bromophenyl)-3-phenyl-4,5-dihydropyrazole-1-carbaldehyde

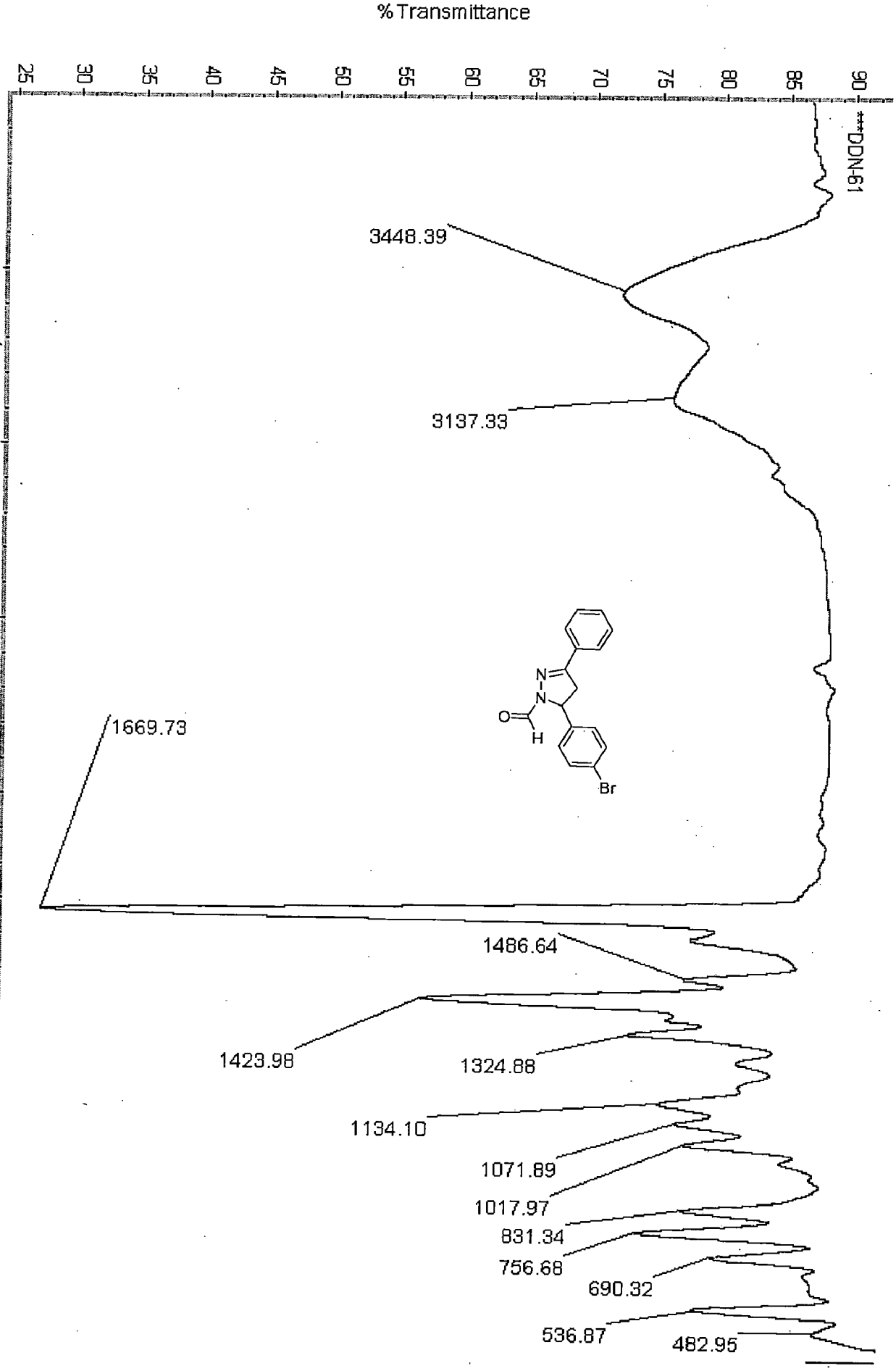


Figure 4b IR spectra of 5-(4-bromophenyl)-3-phenyl-4,5-dihydropyrazole-1-carbaldehyde

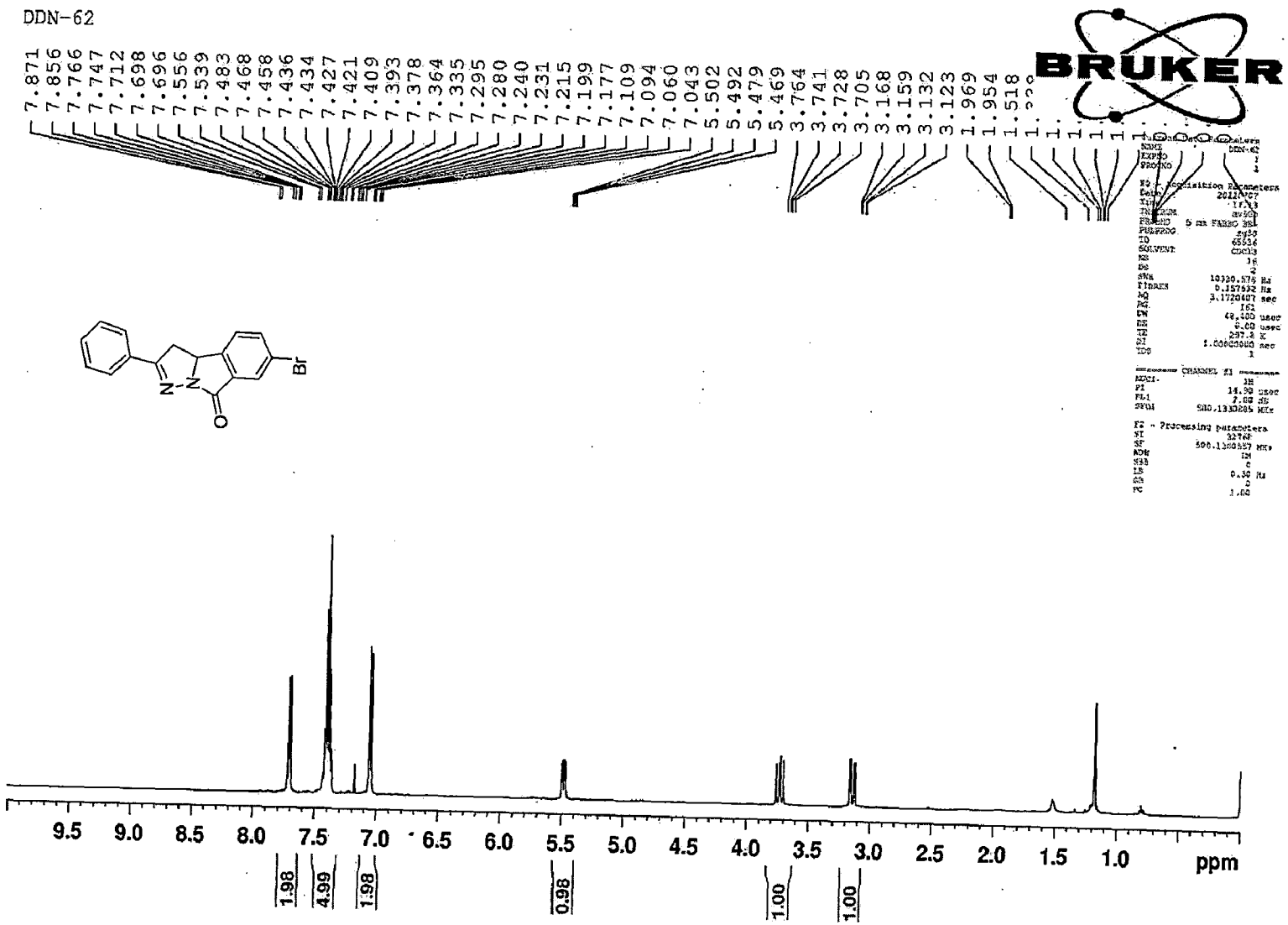


Figure 4c ^{1}H NMR spectra of 6-bromo-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

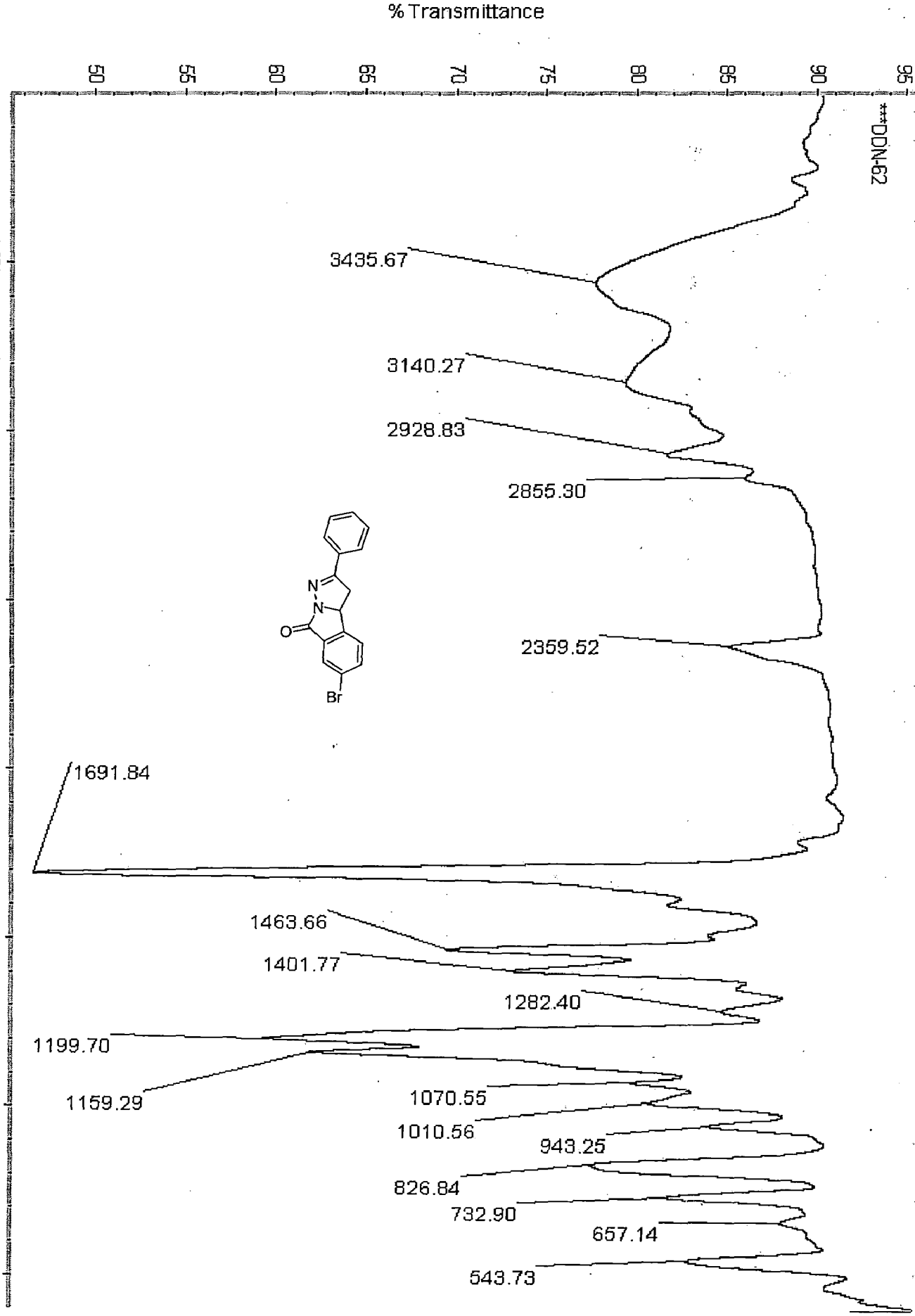


Figure 4c IR spectra of 6-bromo-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

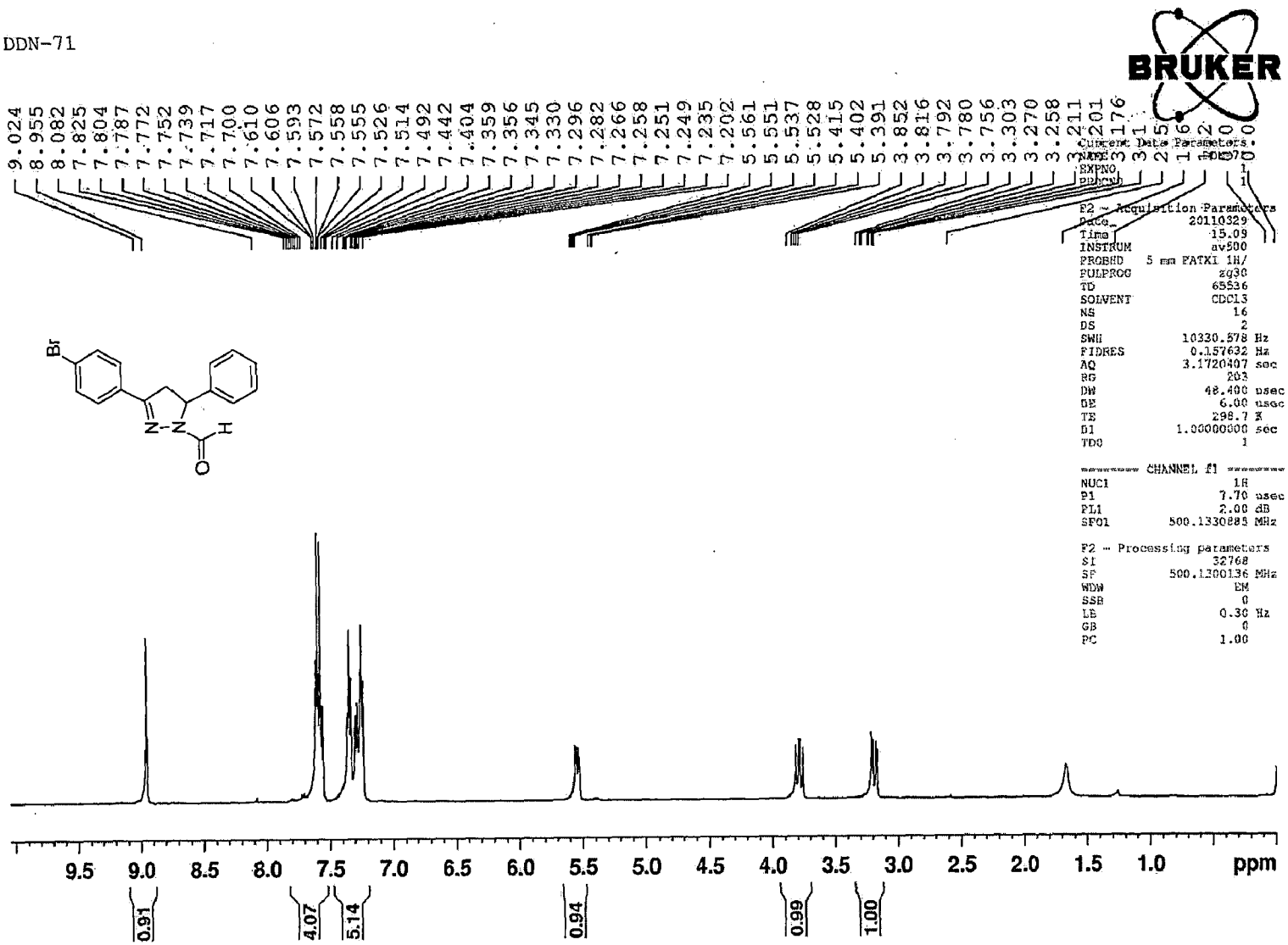


Figure 5b ^{1}H NMR spectra of 3-(4-bromophenyl)-5-phenyl-4,5-dihydropyrazole-1-carbaldehyde

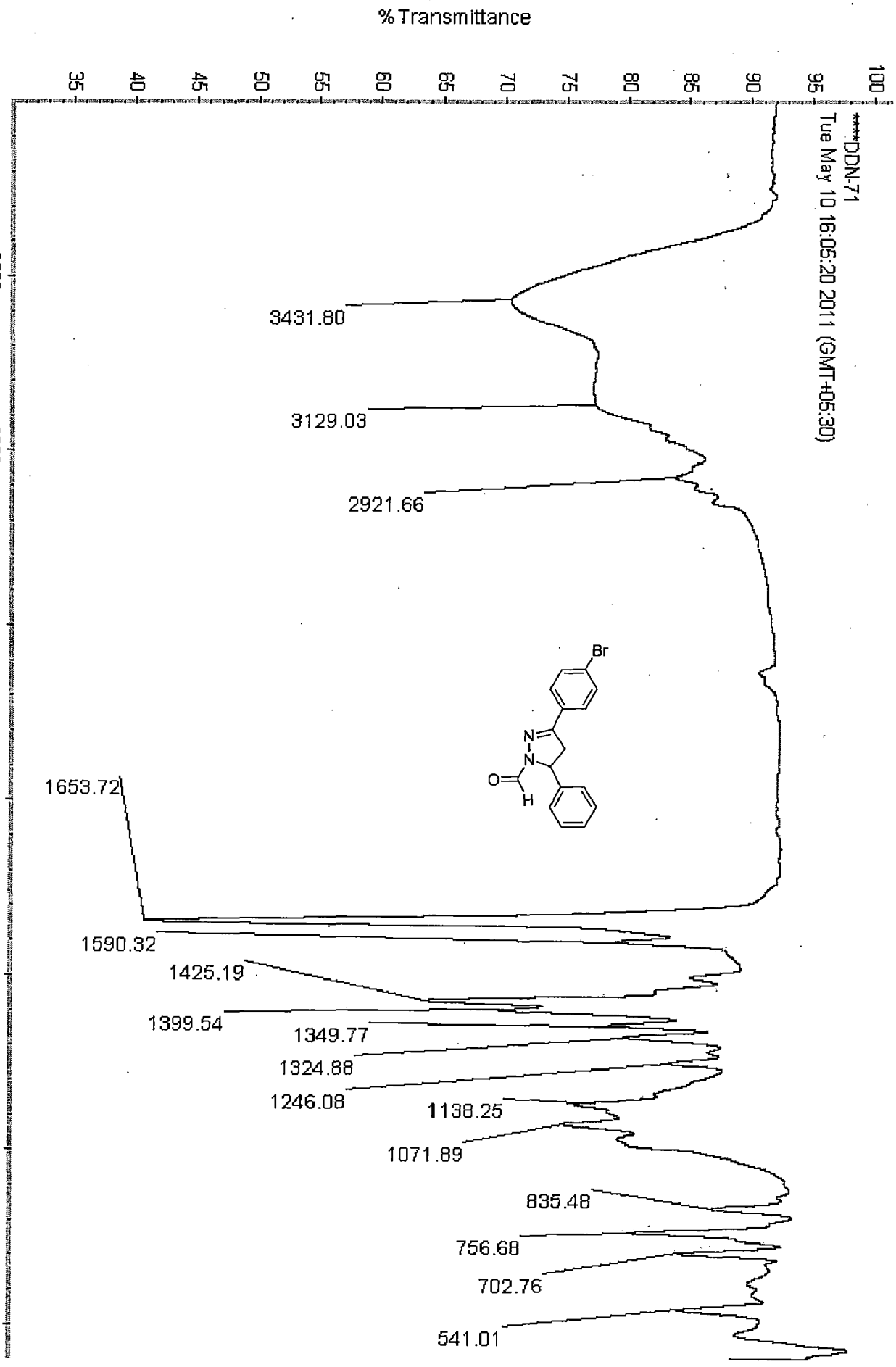


Figure 5b IR spectra of 3-(4-bromophenyl)-5-phenyl-4,5-dihydropyrazole-1-carbaldehyde

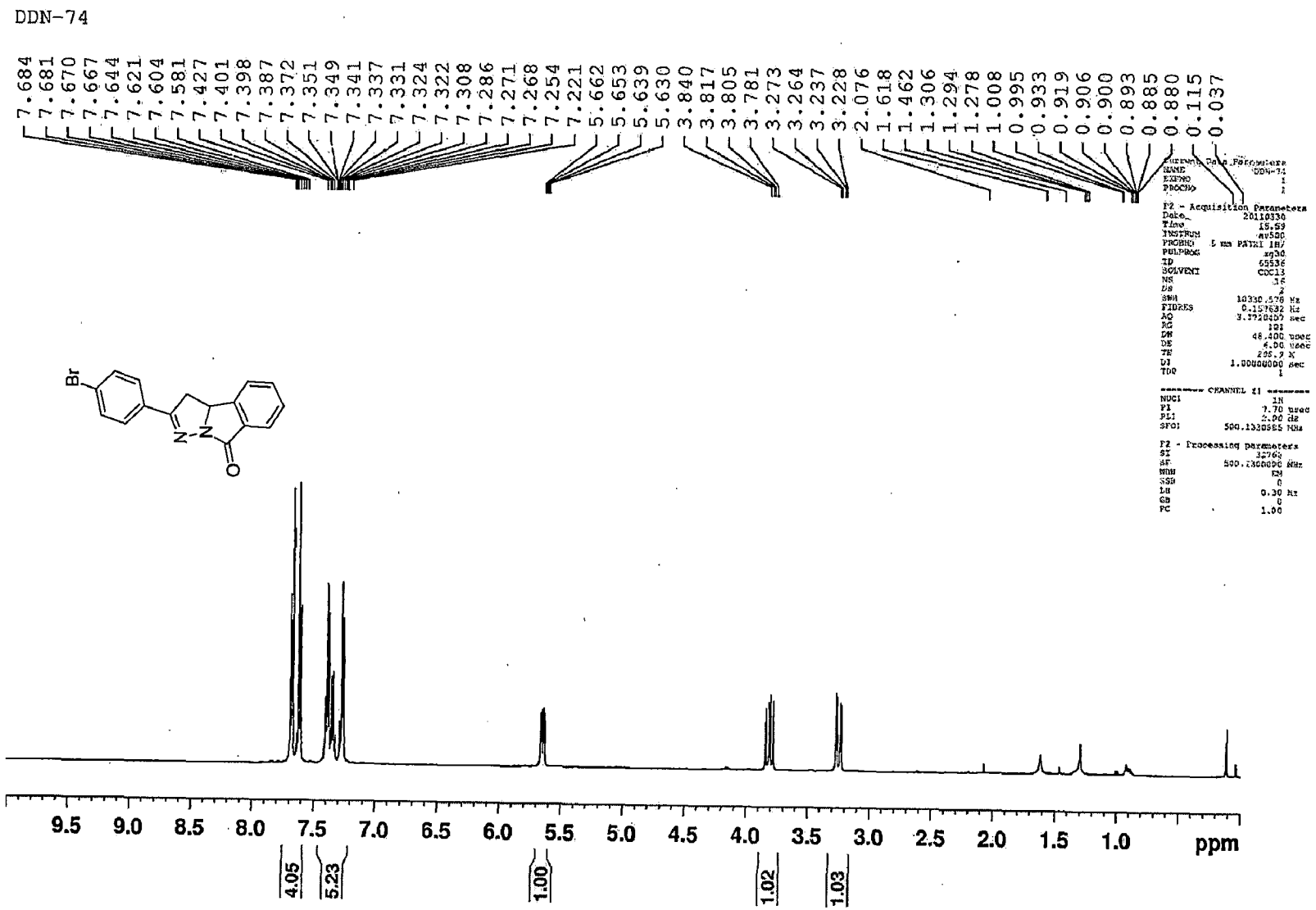


Figure 5c ^{1}H NMR spectra of 2-(4-bromophenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

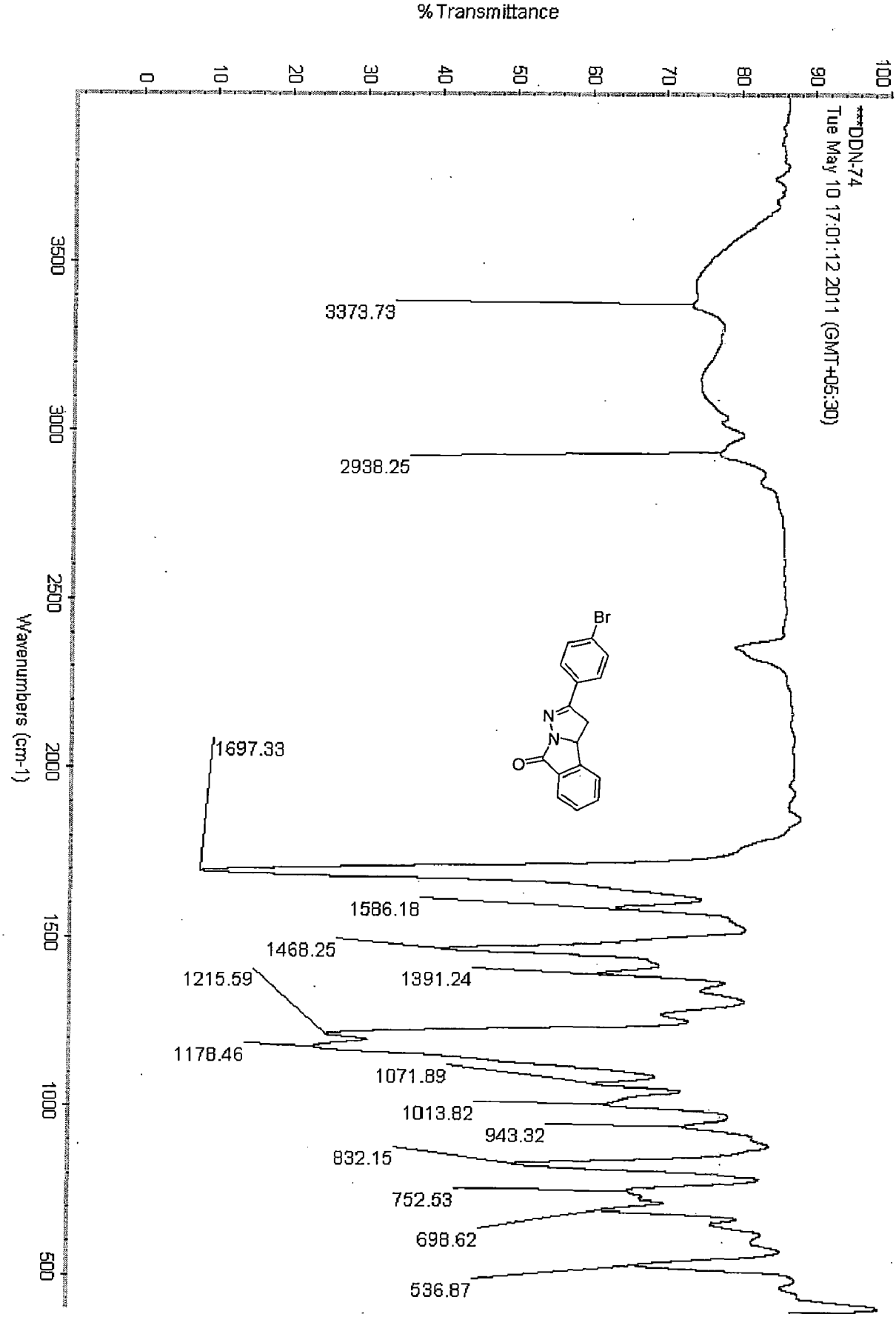


Figure 5c IR spectra of 2-(4-bromophenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

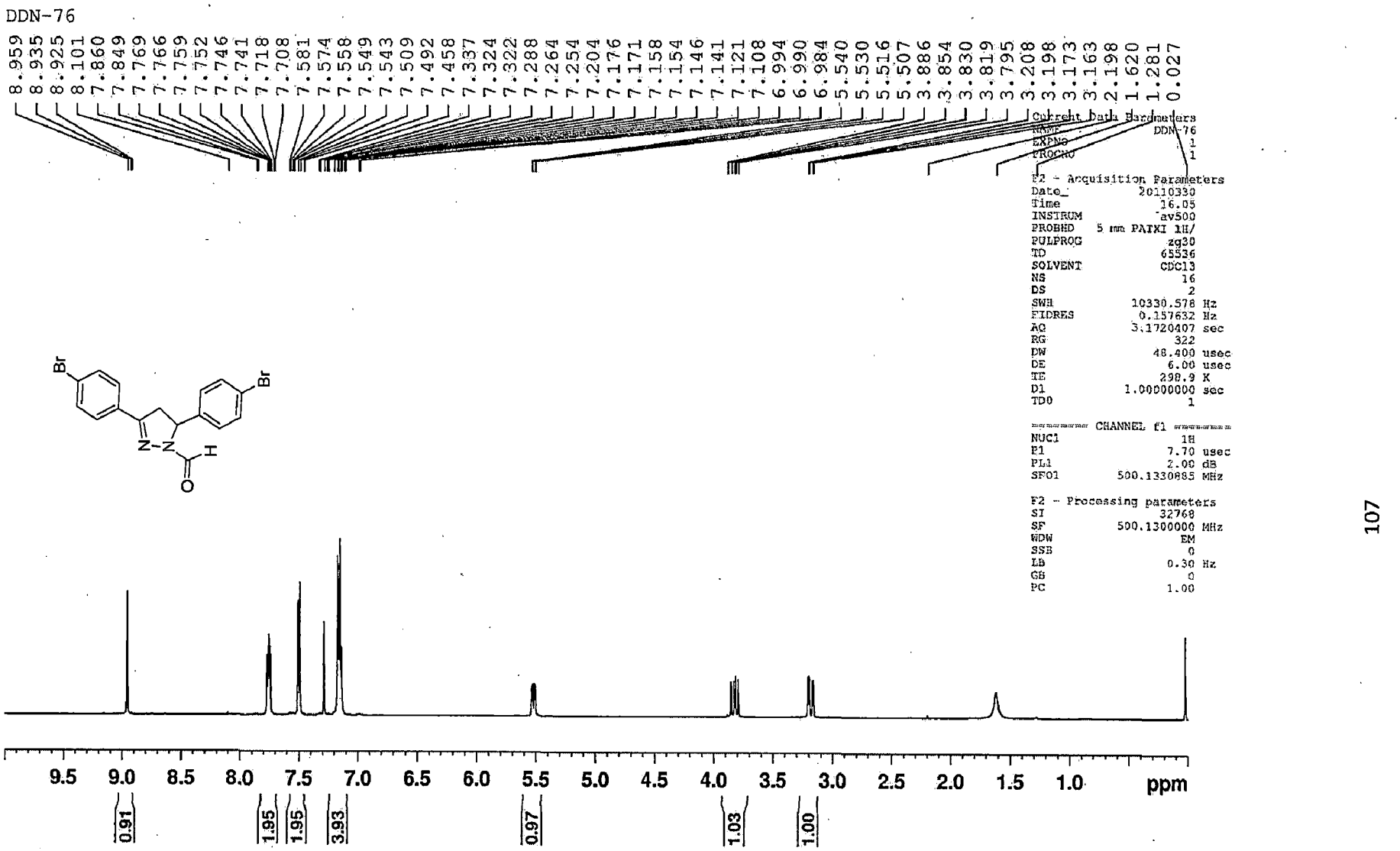


Figure 6b ^{1}H NMR spectra of 3,5-bis(4-bromophenyl)-4,5-dihydropyrazole-1-carbaldehyde

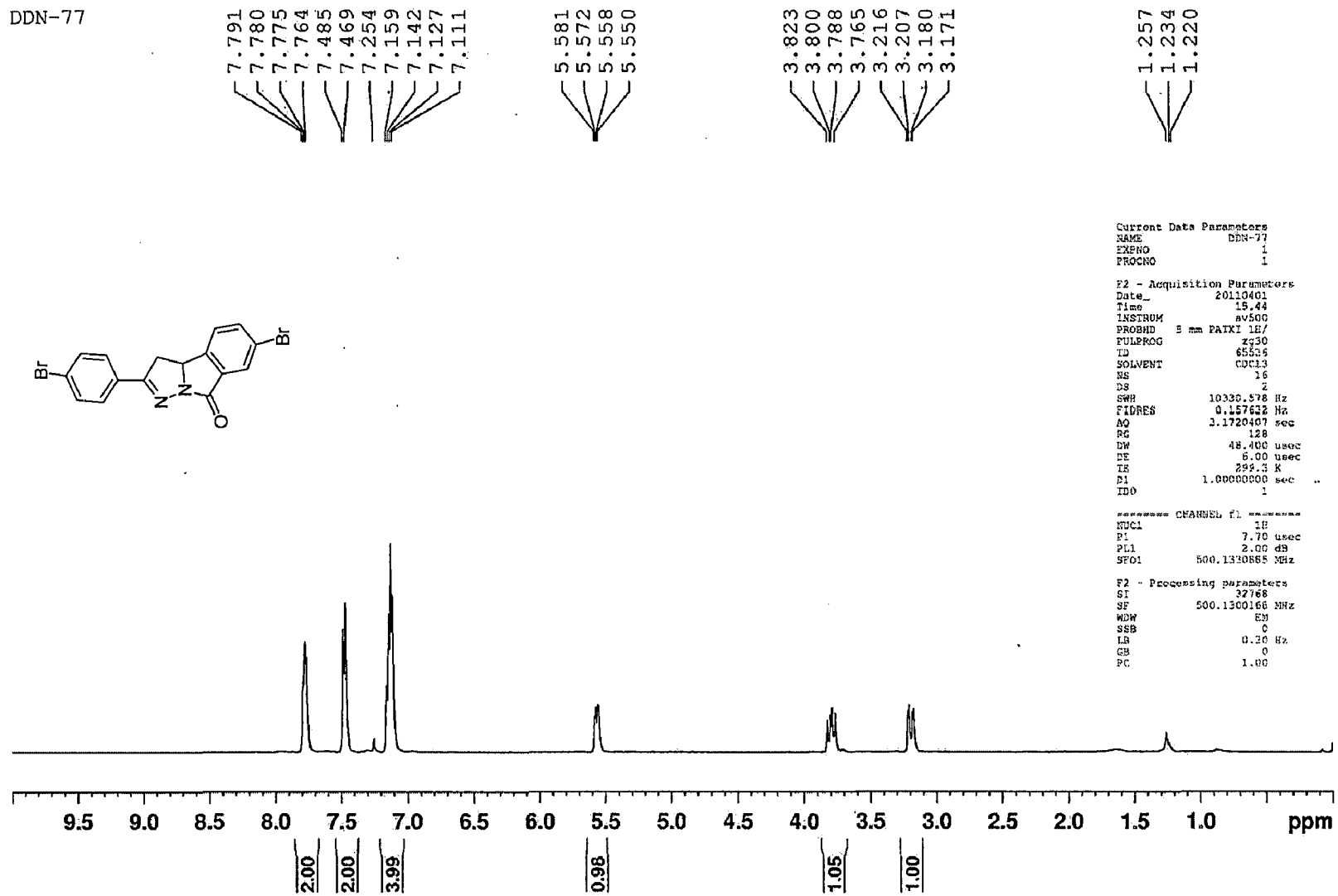


Figure 6c ^{1}H NMR spectra of 6-bromo-2-(4-bromophenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

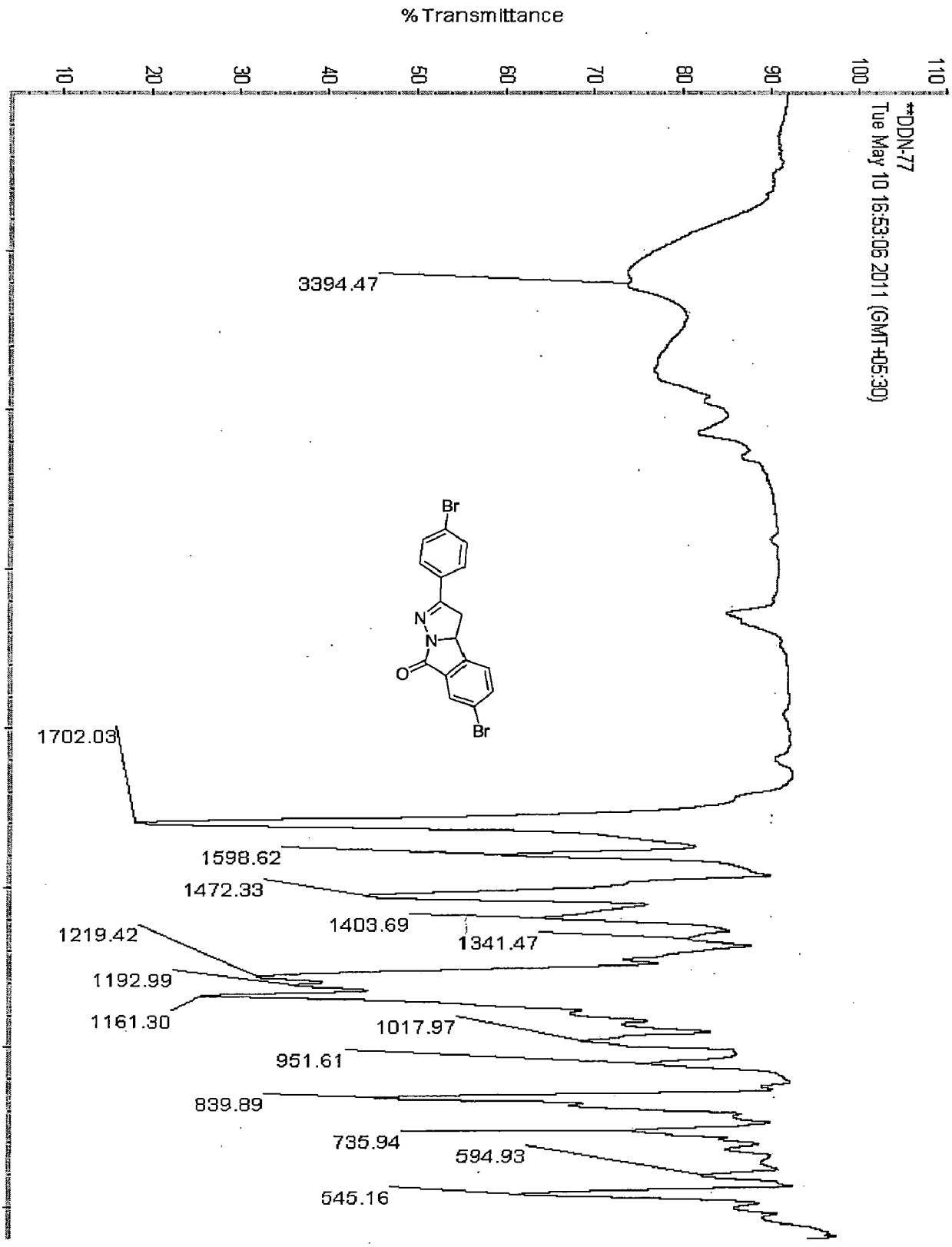


Figure 6c IR spectra of 6-bromo-2-(4-bromophenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

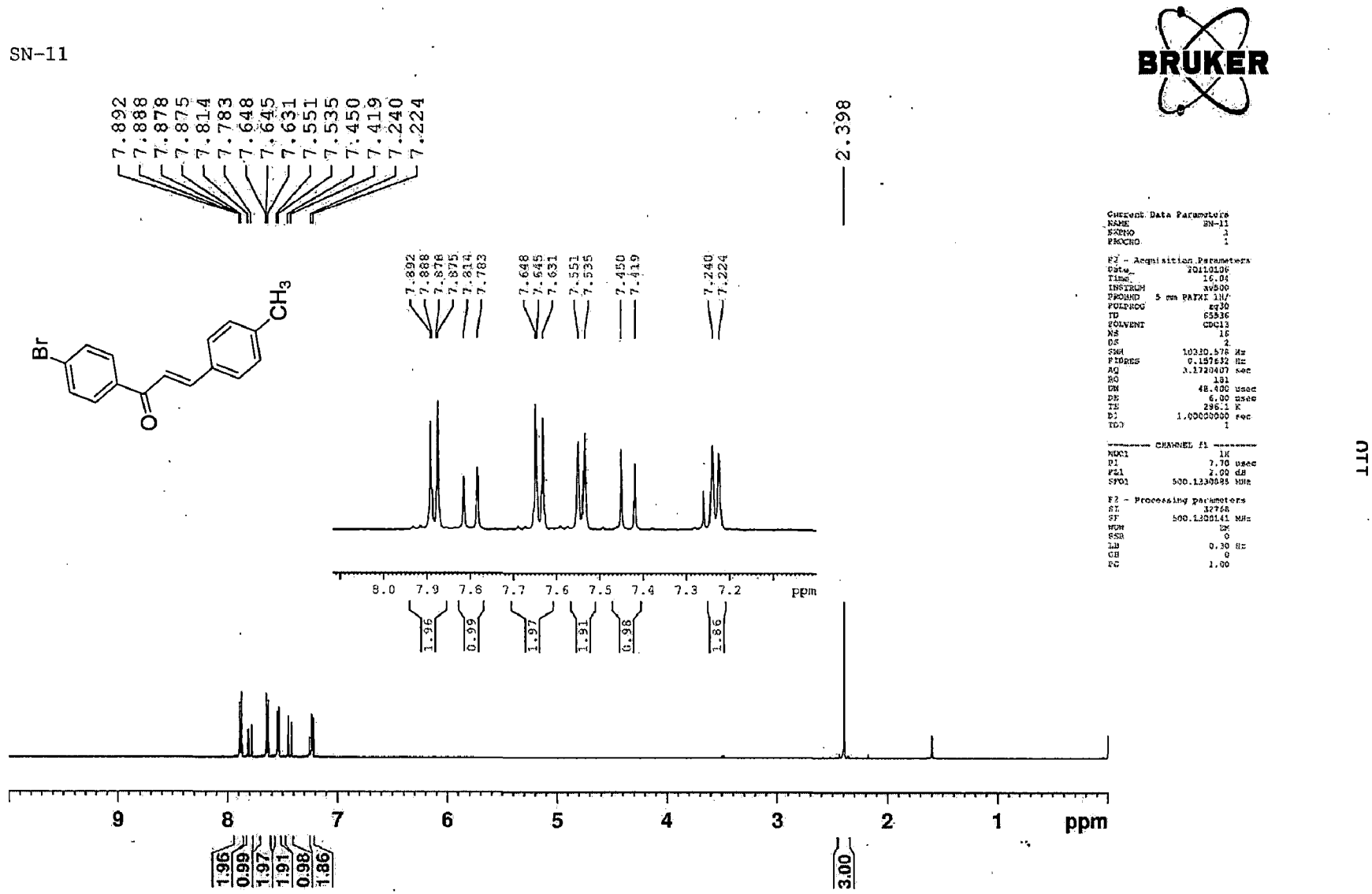


Figure 7a ^{1}H NMR spectra of (E)-1-(4-bromophenyl)-3-p-tolylprop-2-en-1-one

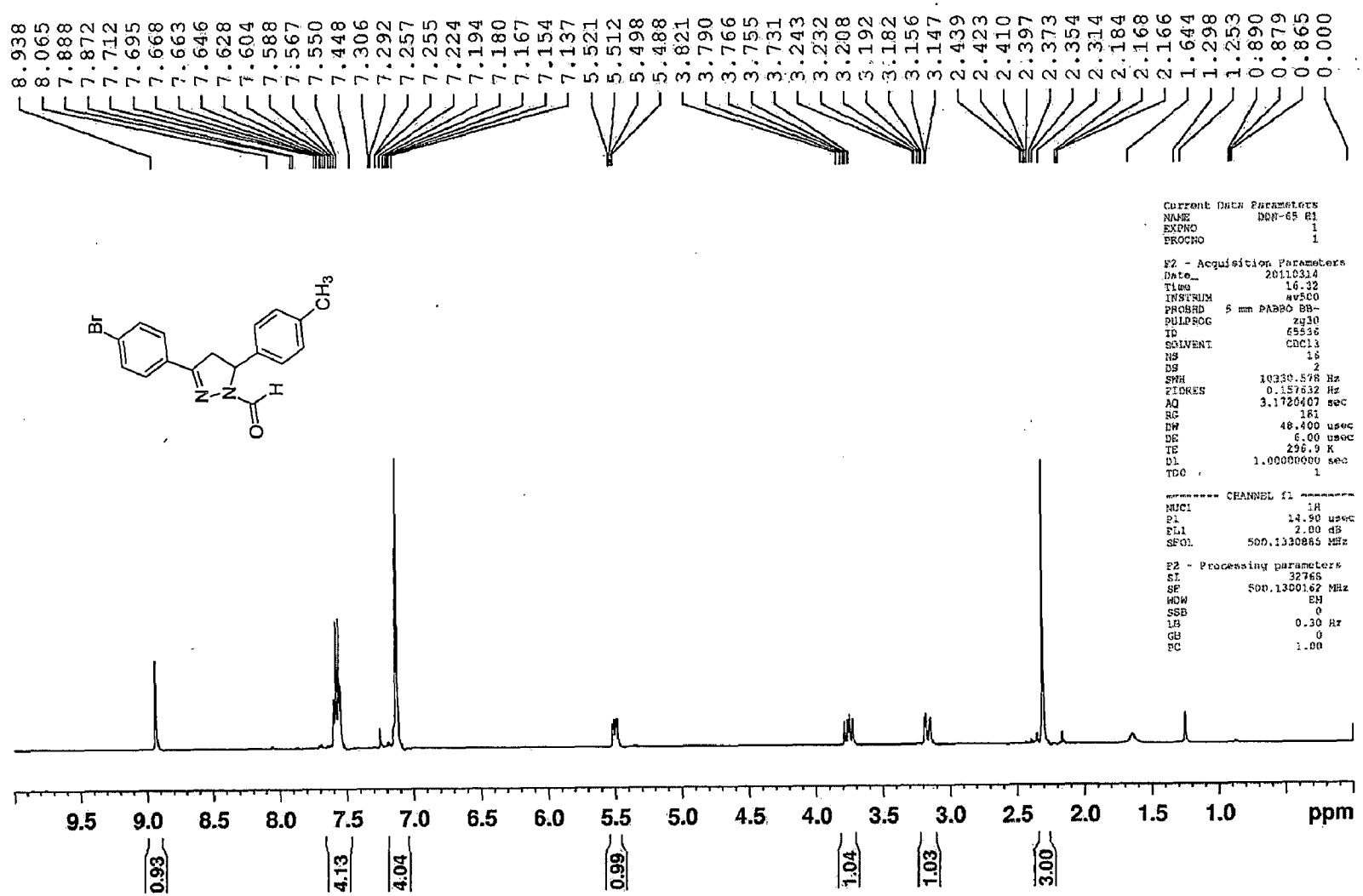


Figure 7b ^{1}H NMR spectra of 3-(4-bromophenyl)-5-p-tolyl-4,5-dihydropyrazole-1-carbaldehyde

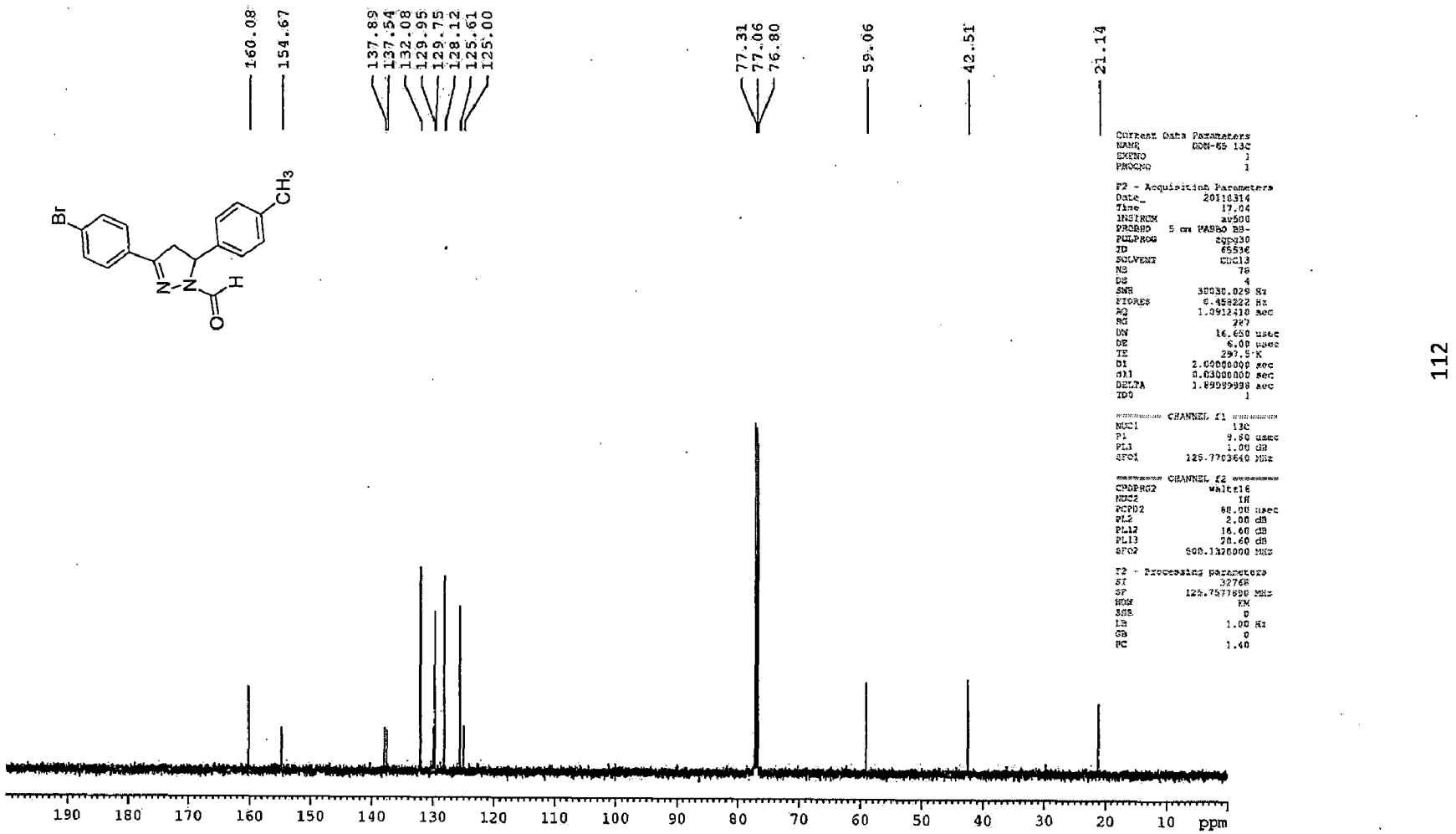


Figure 7b ^{13}C NMR spectra of 3-(4-bromophenyl)-5-p-tolyl-4,5-dihydropyrazole-1-carbaldehyde

DDN-72-1F

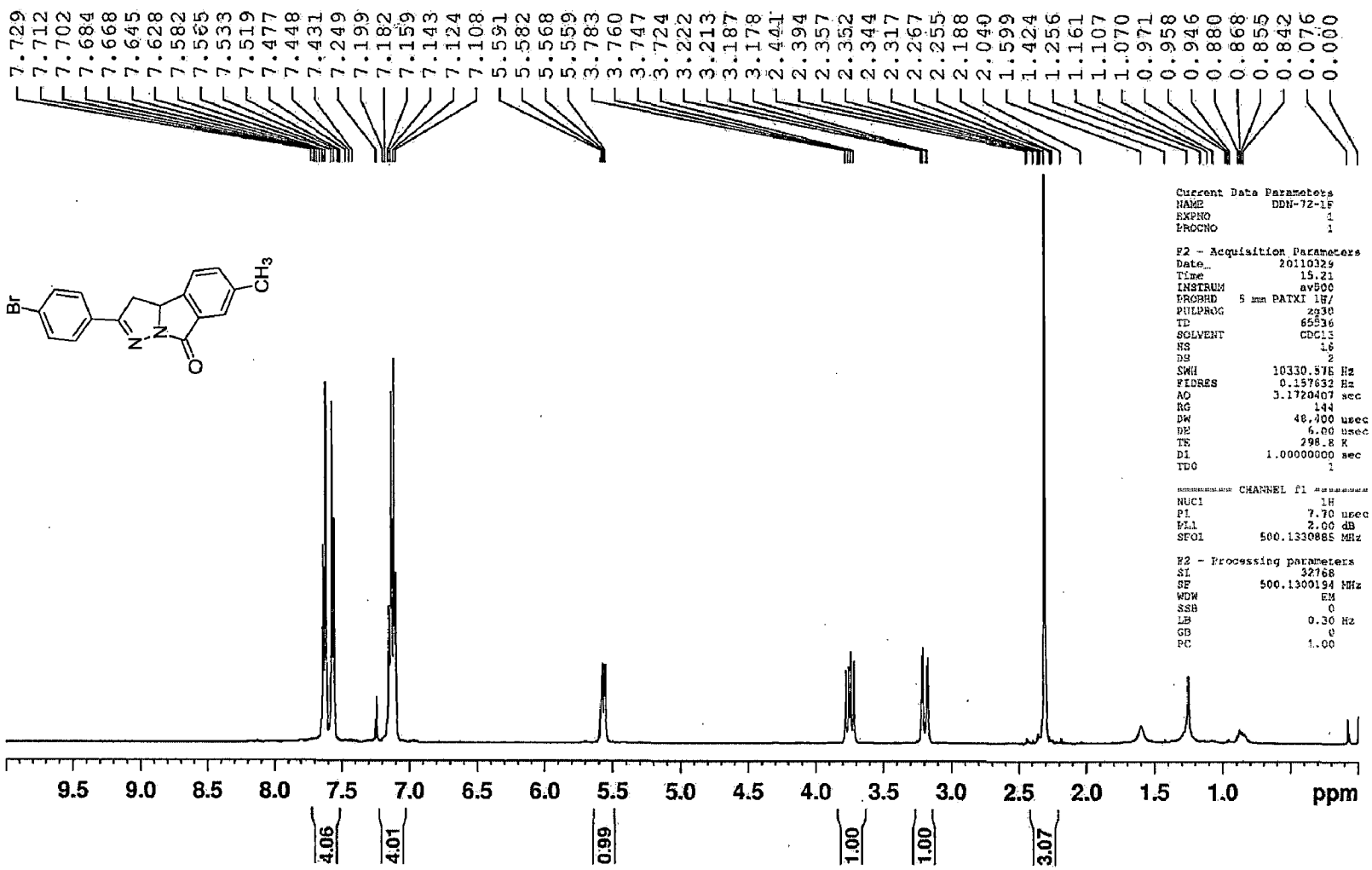


Figure 7c ^{1}H NMR spectra of 2-(4-bromophenyl)-6-methyl-3,3a-dihydropyrazolo[5,1a]isoindol-8-one

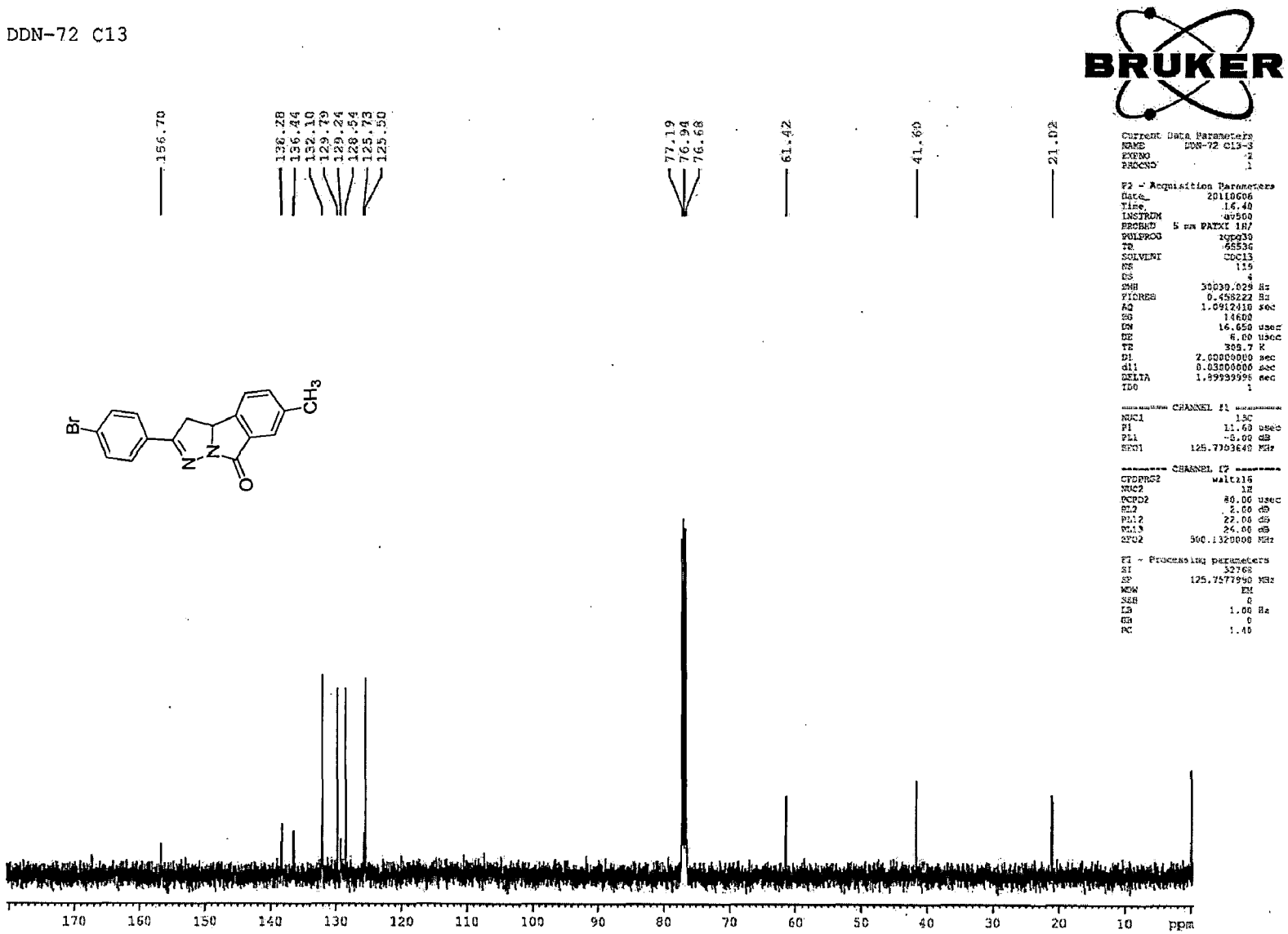


Figure 7c ^{13}C NMR spectra of 2-(4-bromophenyl)-6-methyl-3,3a-dihydropyrazolo[5,1a]isoindol-8-one

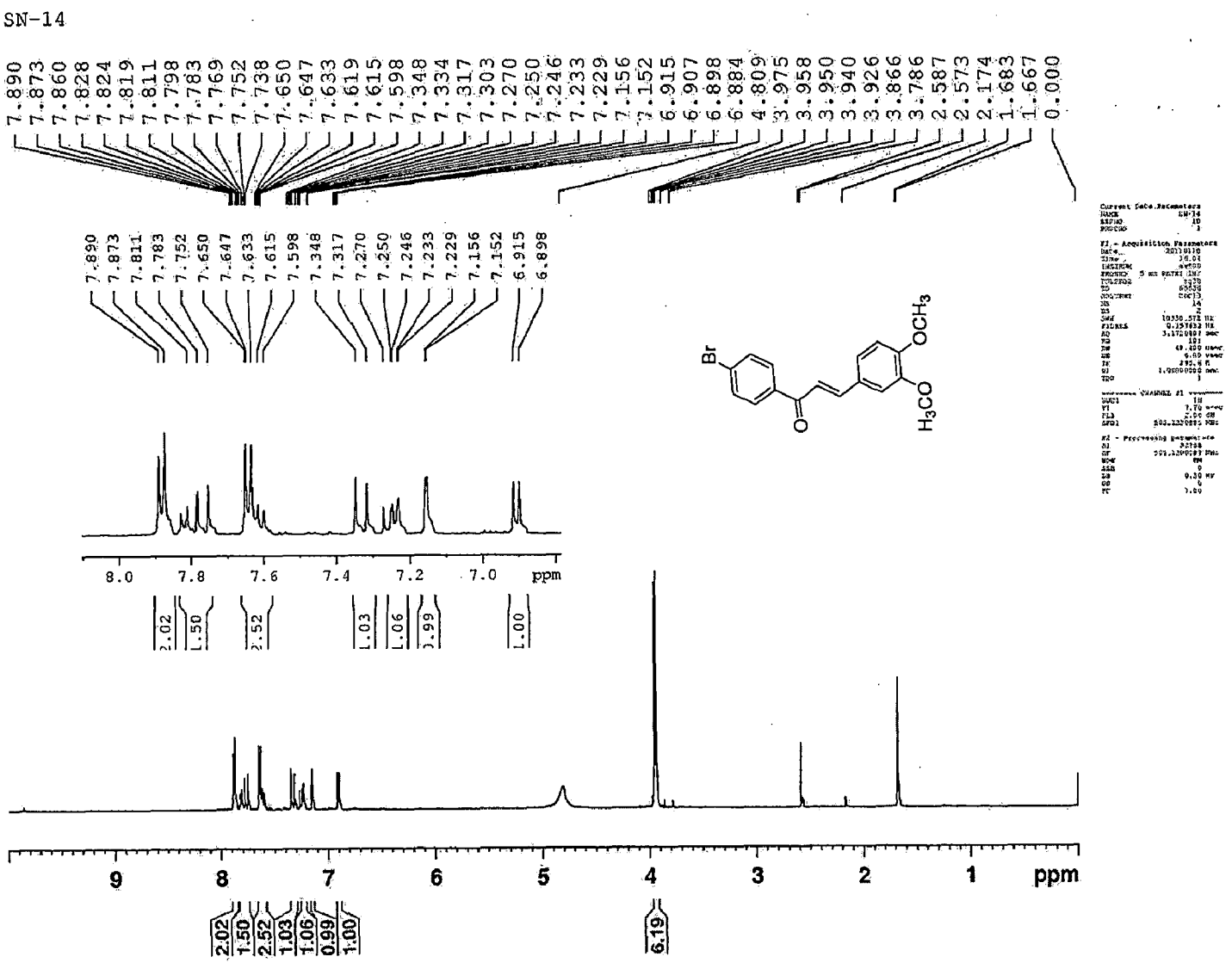


Figure 8a ^{1}H NMR spectra of (E)-1-(4-bromophenyl)-3-(3,4-dimethoxyphenyl)prop-2-en-1-one

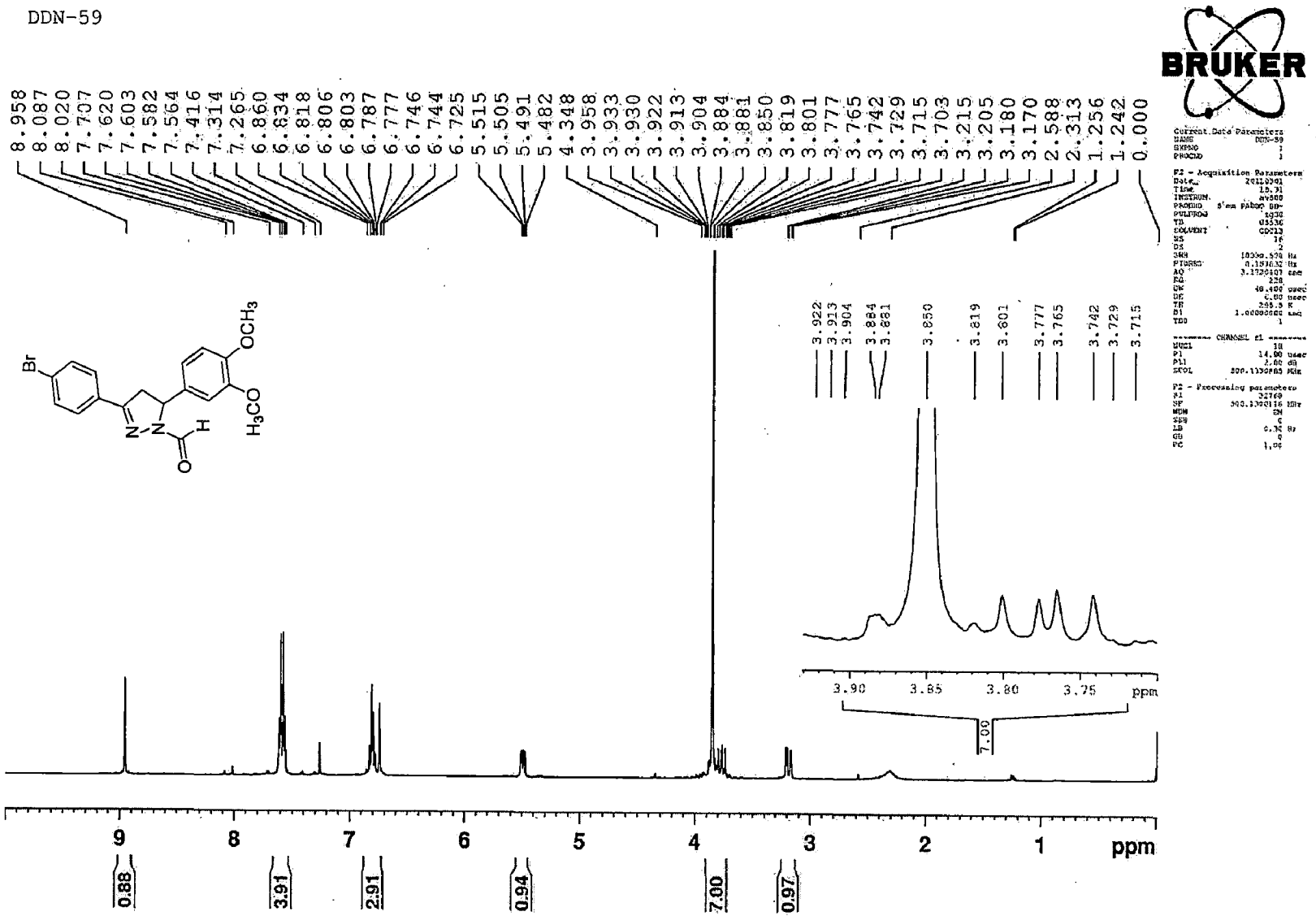


Figure 8b ^{1}H NMR spectra of 3(4-bromophenyl)-5-(3,4-dimethoxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde

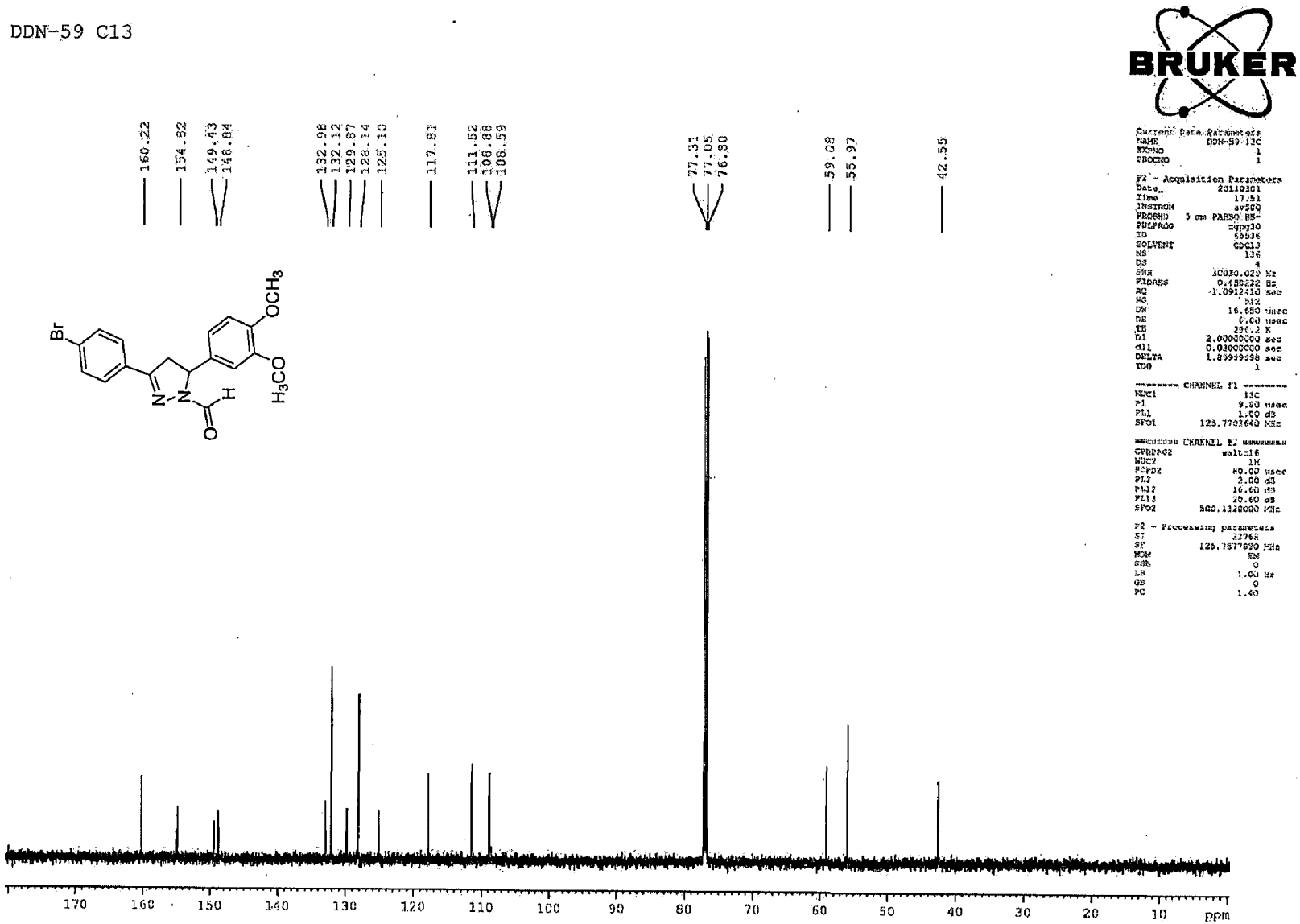


Figure 8b ^{13}C NMR spectra of 3(4-bromophenyl)-5-(3,4-dimethoxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde

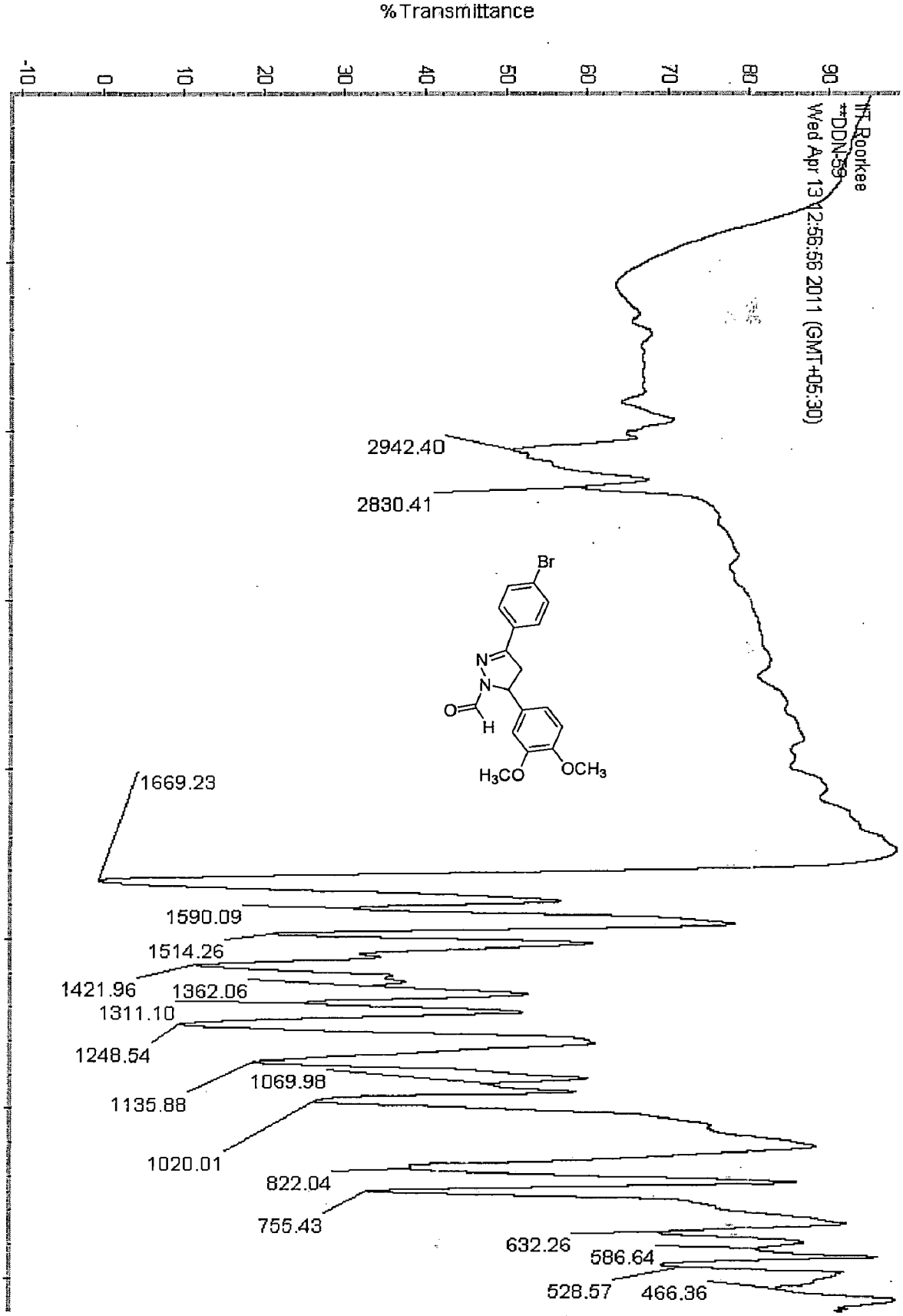


Figure 8b IR spectra of 3(4-bromophenyl)-5-(3,4-dimethoxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde

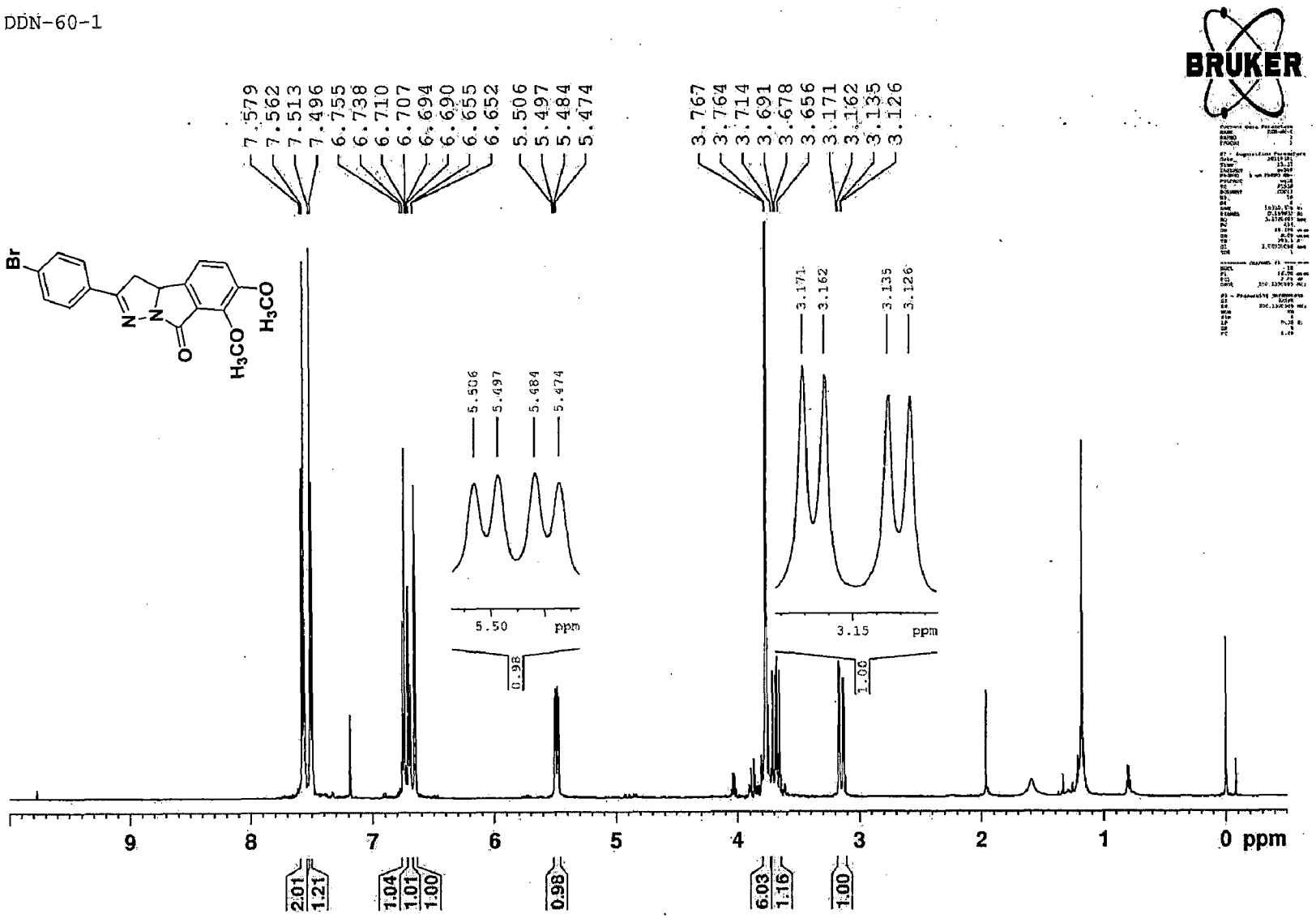


Figure 8c ^{1}H NMR spectra of 2-(4-bromophenyl)-6,7-dimethoxy-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

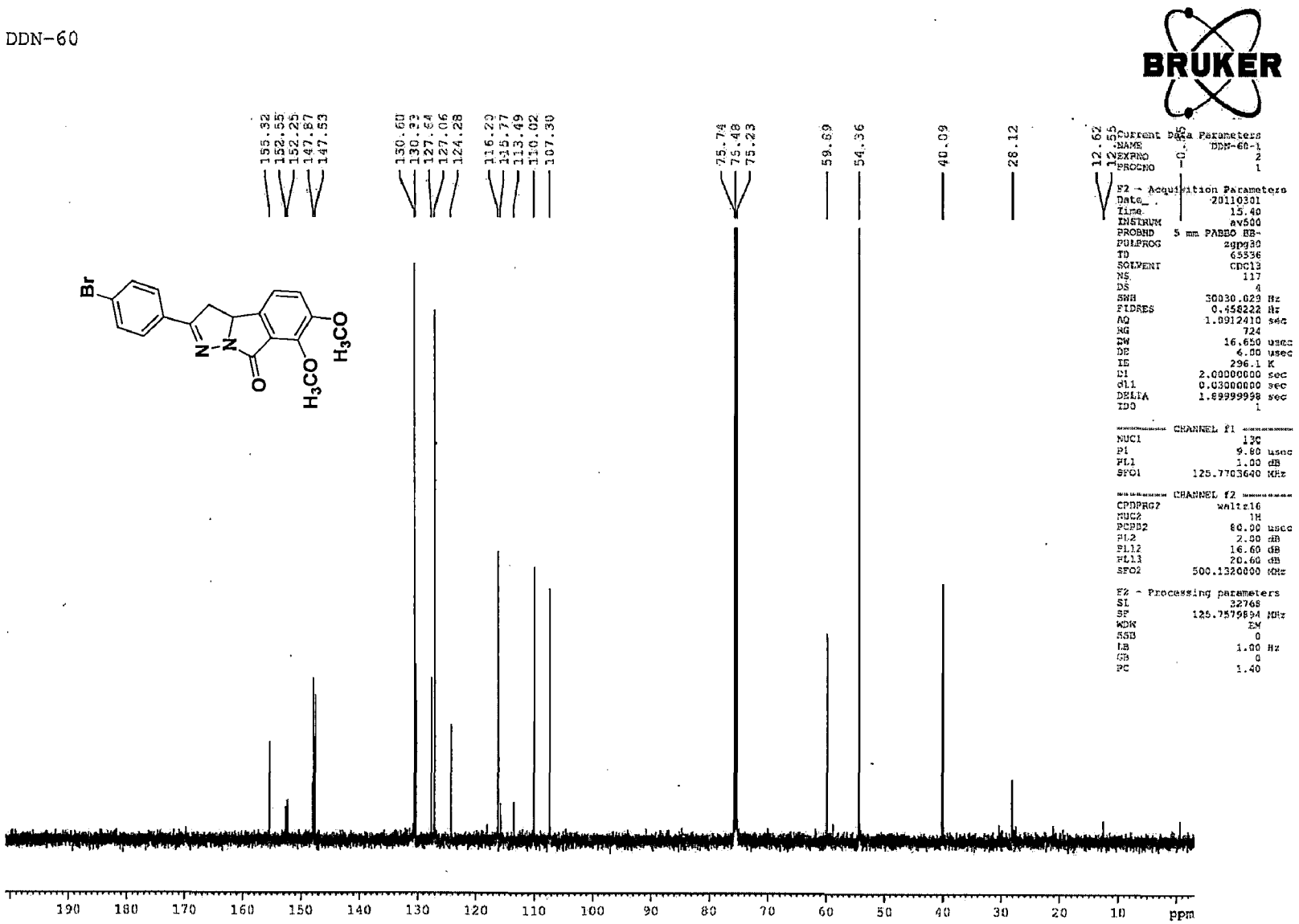


Figure 8c ^{13}C NMR spectra of 2-(4-bromophenyl)-6,7-dimethoxy-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

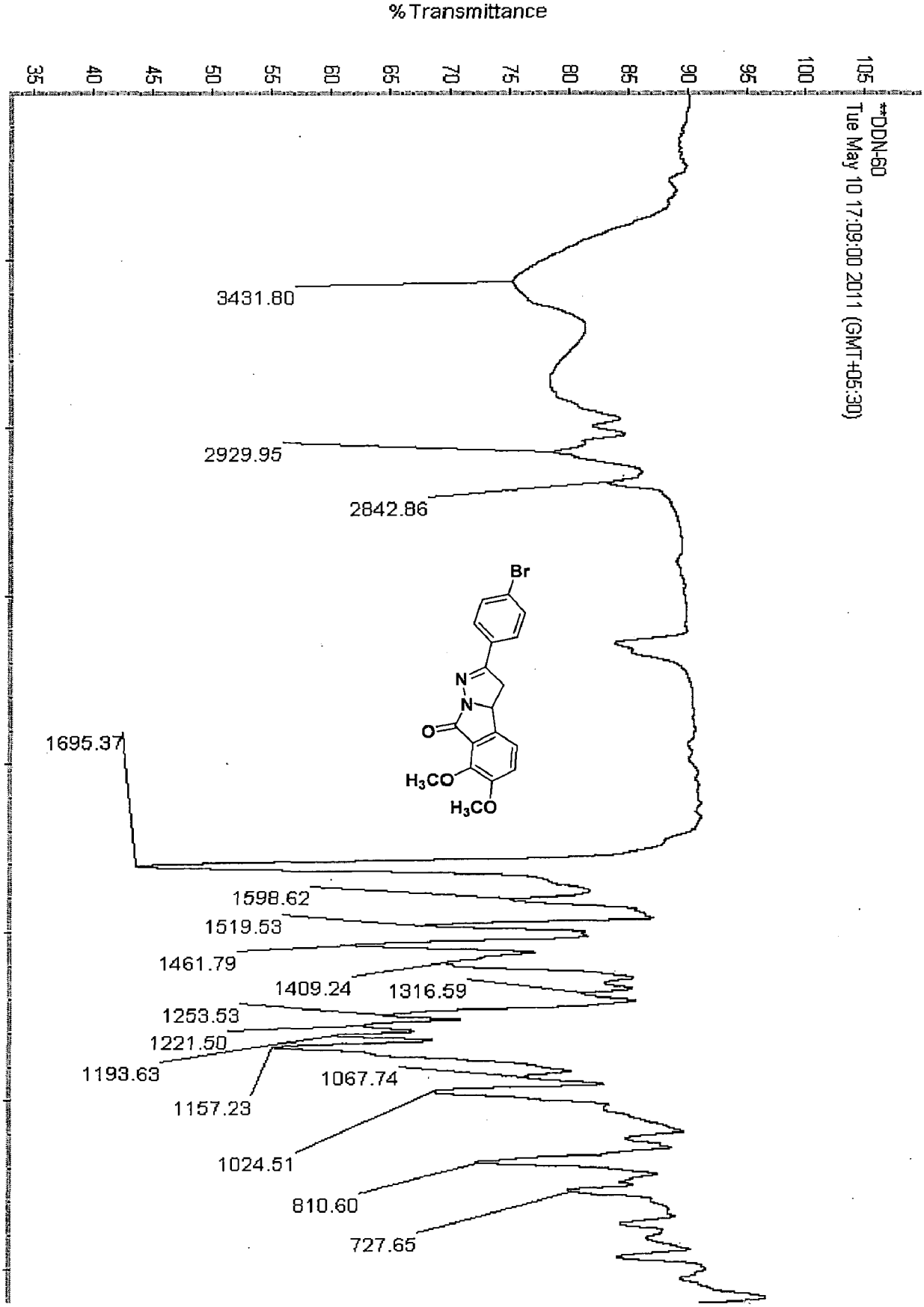


Figure 8c IR spectra of 2-(4-bromophenyl)-6,7-dimethoxy-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

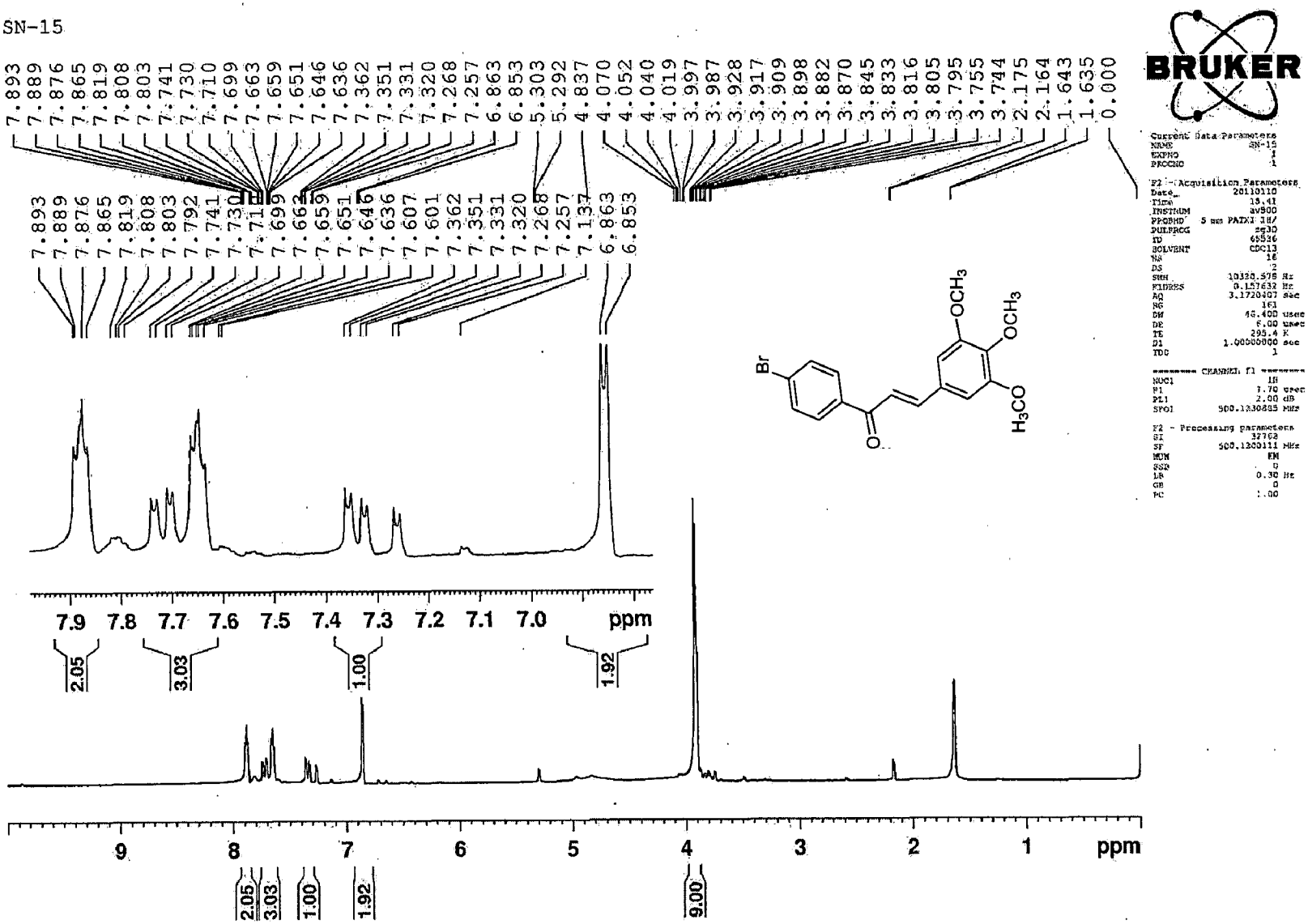


Figure 9a ^{1}H NMR spectra of (E)-1-(4-bromophenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one

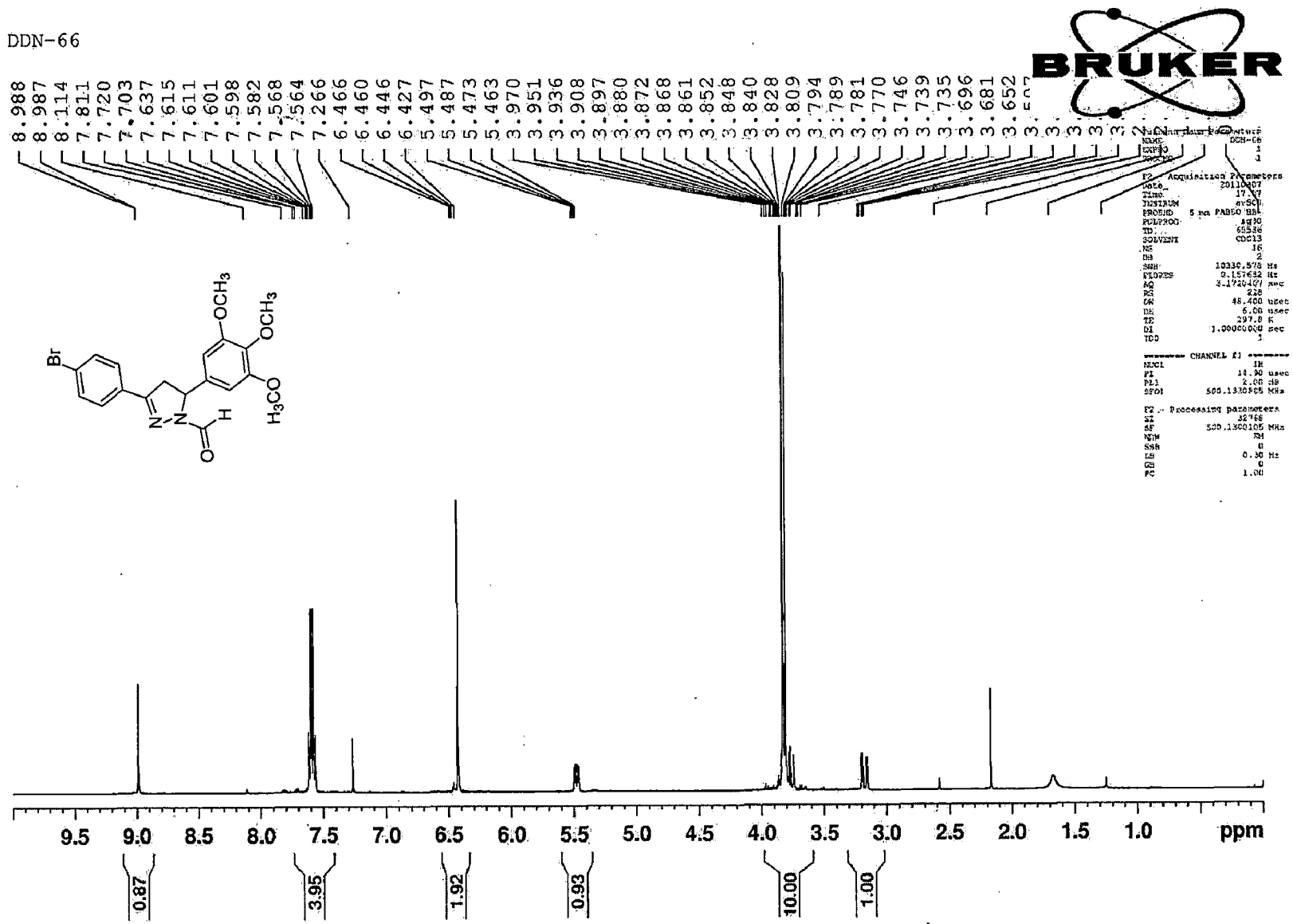


Figure 9b ^{1}H NMR spectra of 3-(4-bromophenyl)-5-(3,4,5-trimethoxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde

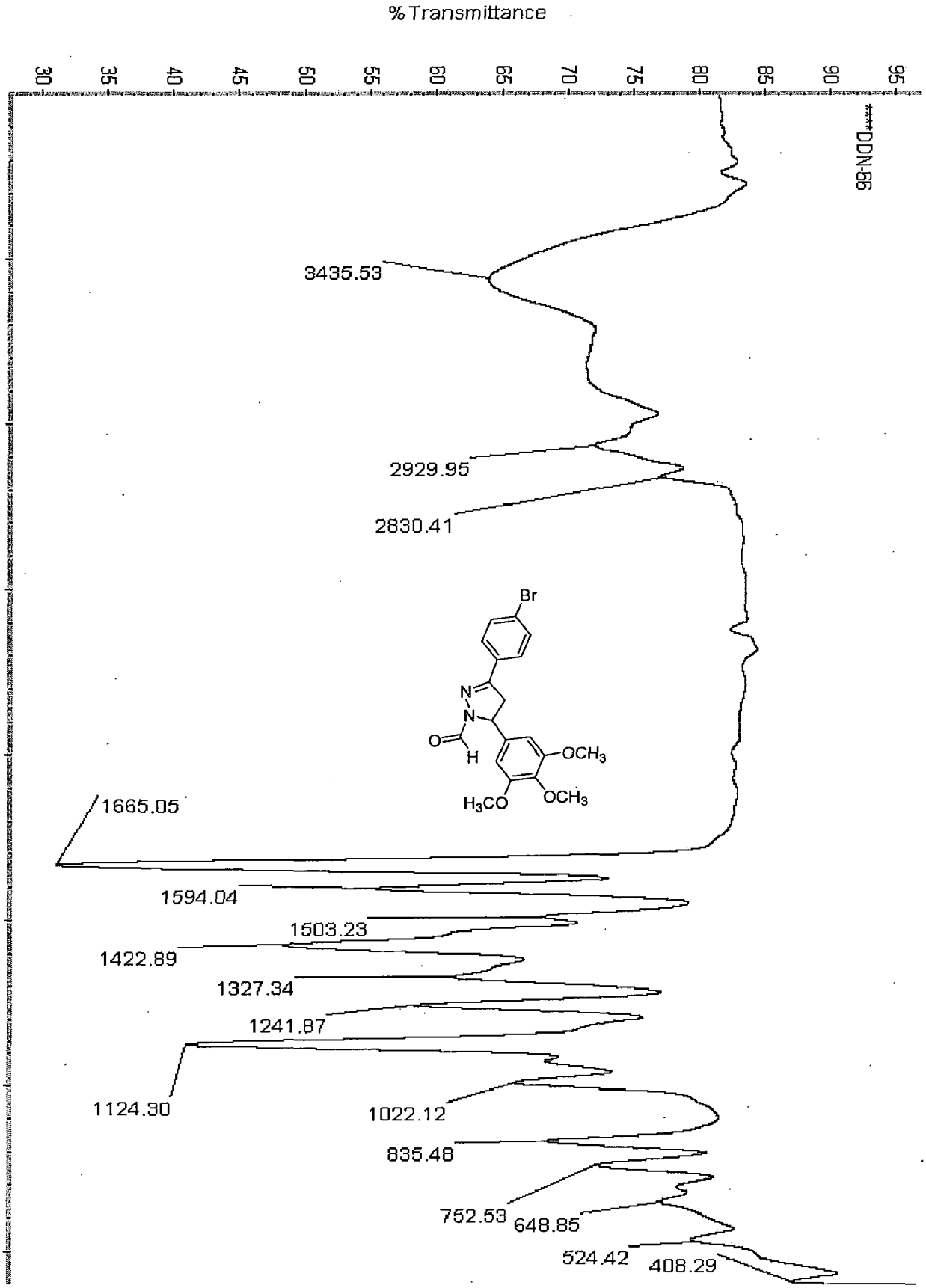


Figure 9b IR spectra of 3-(4-bromophenyl)-5-(3,4,5-trimethoxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde

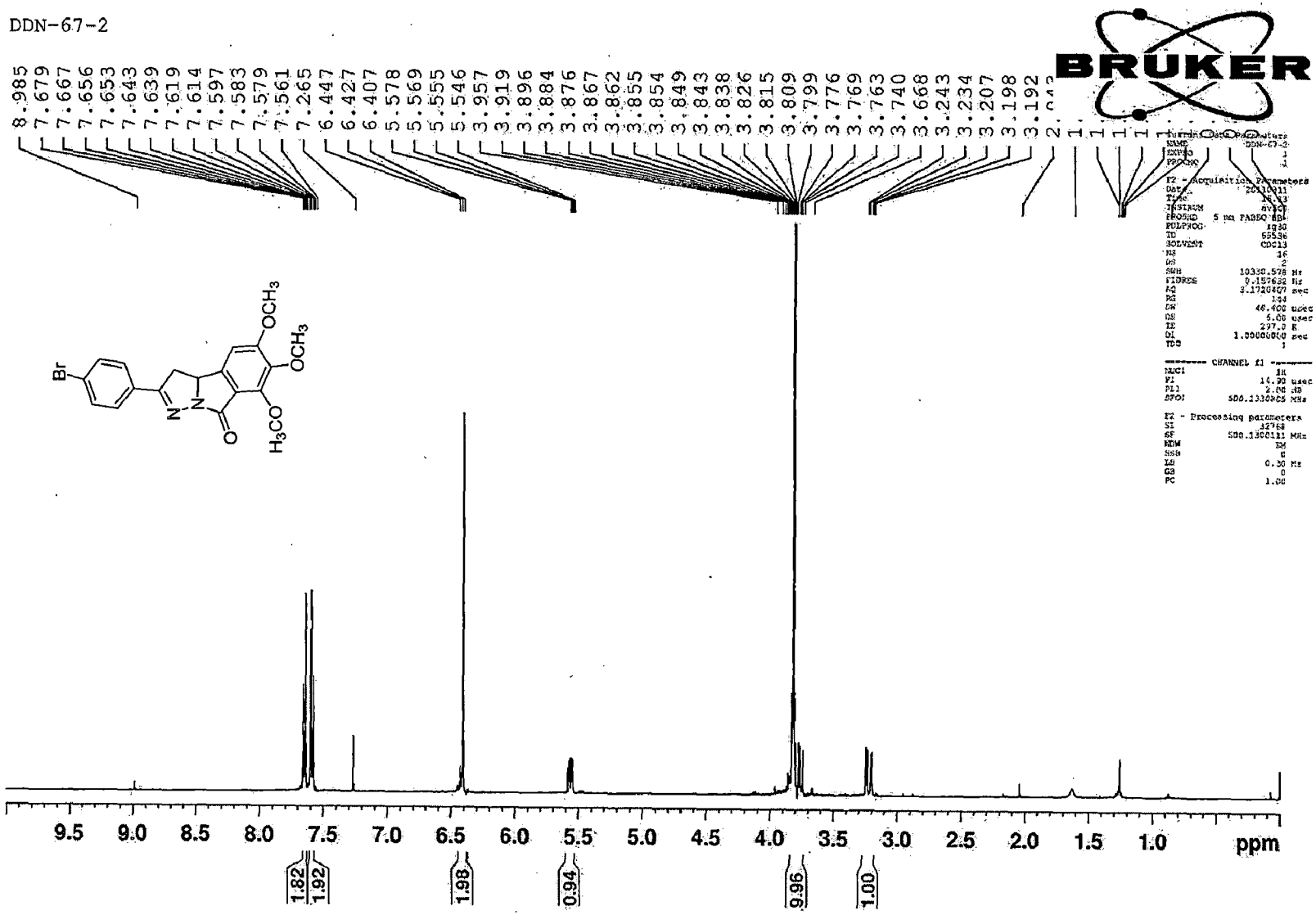


Figure 9c ^{1}H NMR spectra of 2-(4-bromophenyl)-5,6,7-trimethoxy-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

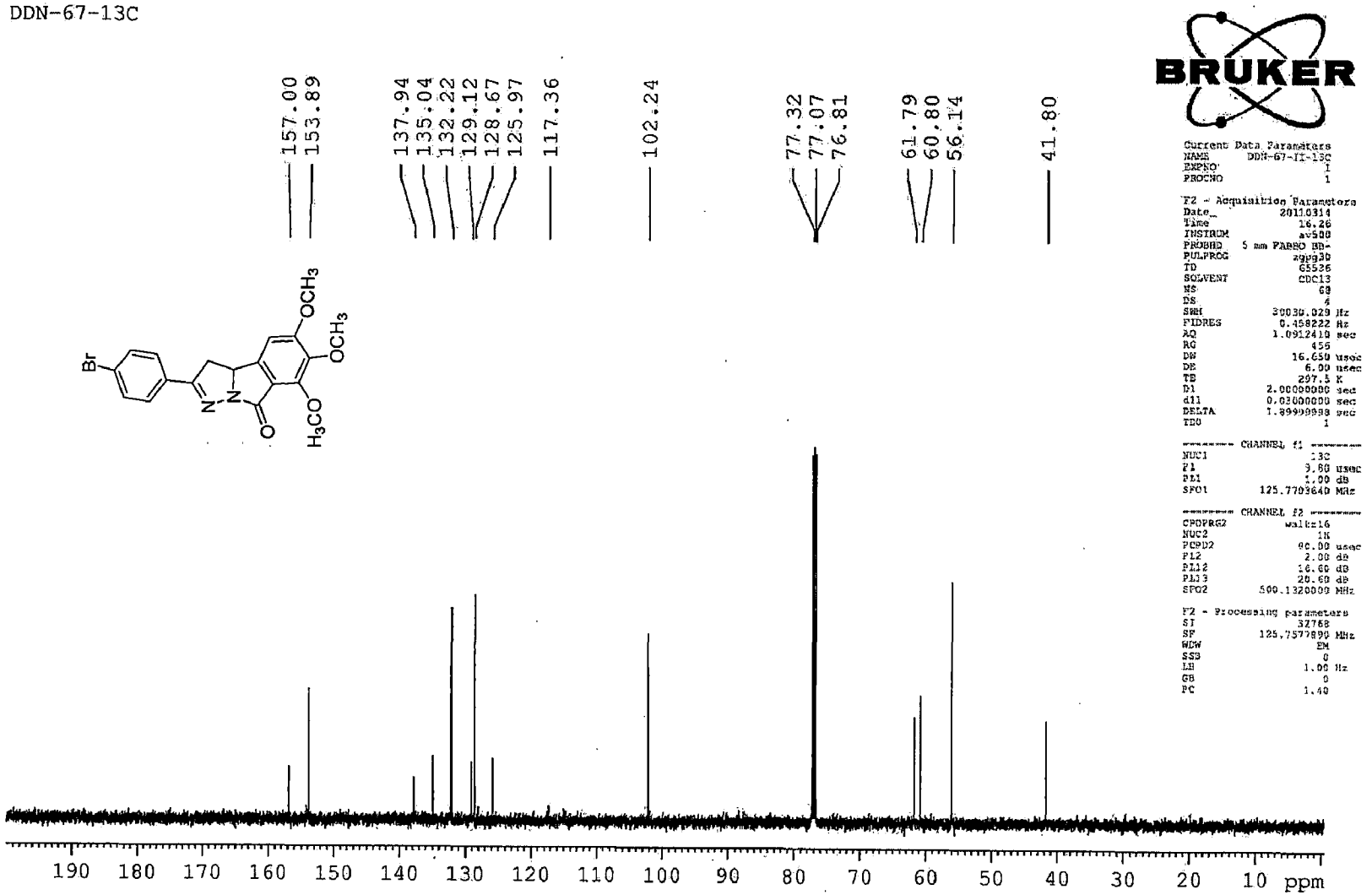


Figure 9c ^{13}C NMR spectra of 2-(4-bromophenyl)-5,6,7-trimethoxy-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

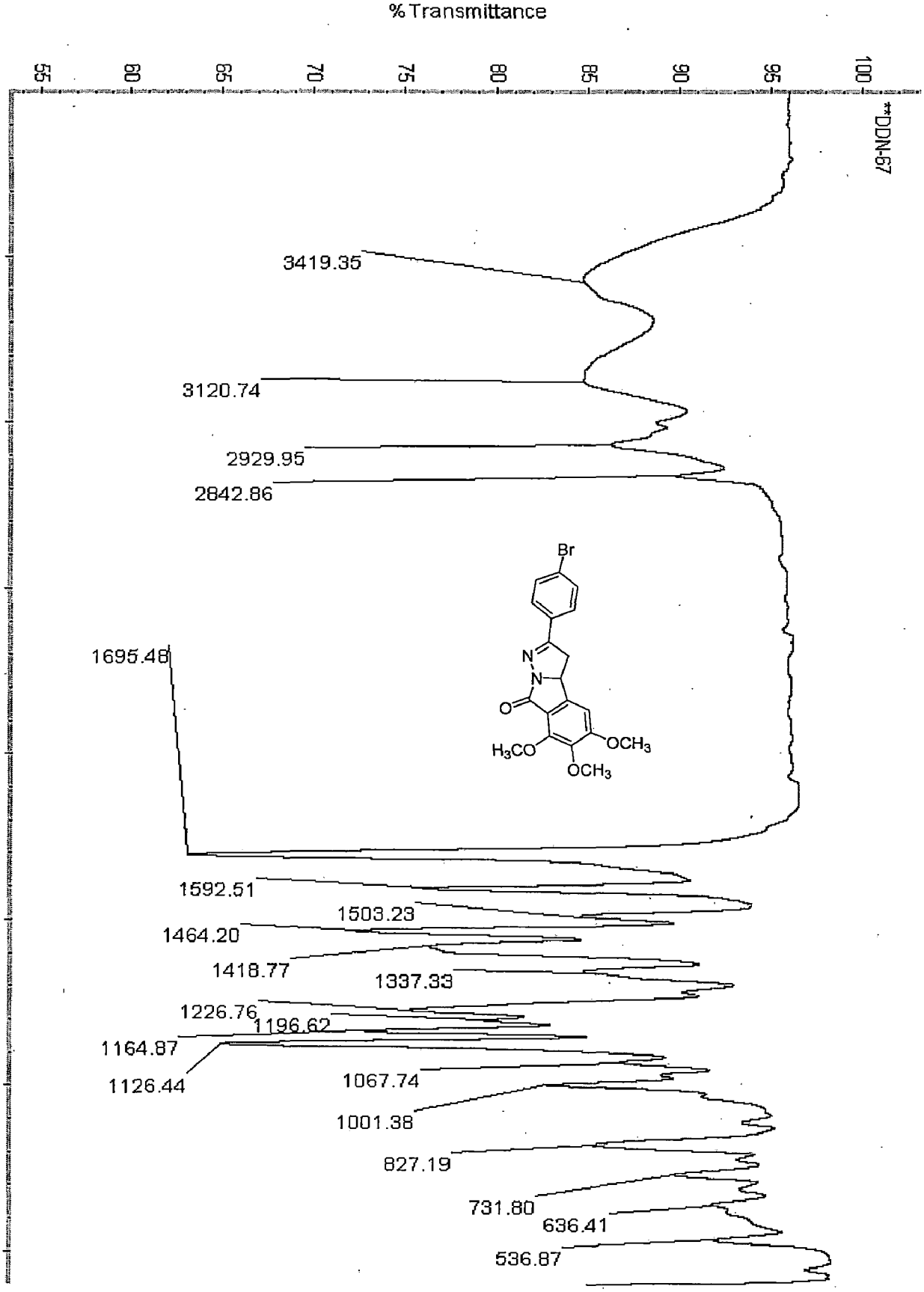


Figure 9c IR spectra of 2-(4-bromophenyl)-5,6,7-trimethoxy-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

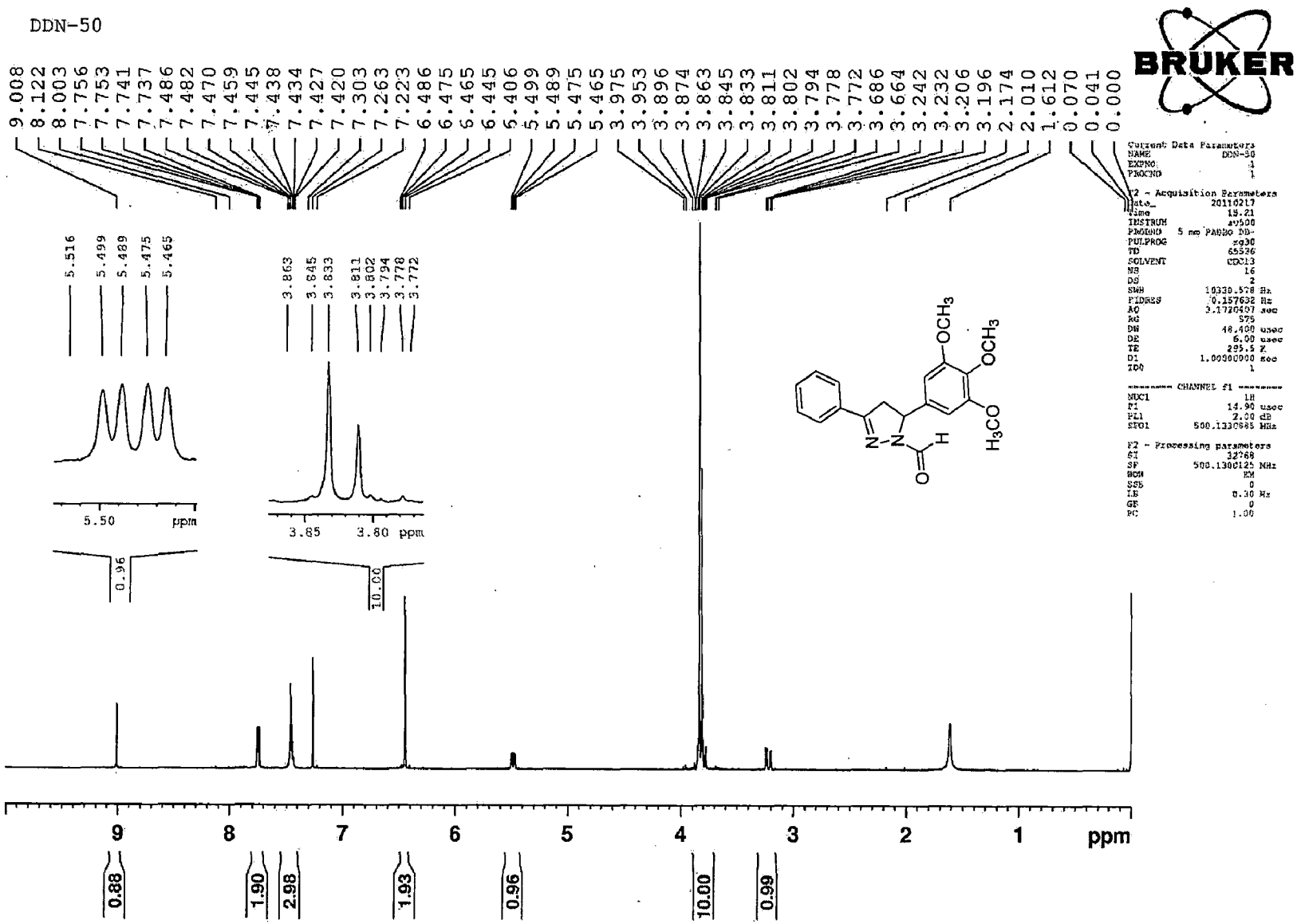


Figure 10 b ^{1}H NMR spectra of 3-phenyl-5-(3,4,5-trimethoxyphenyl)-4,5dihydropyrazole-1-carbaldehyde

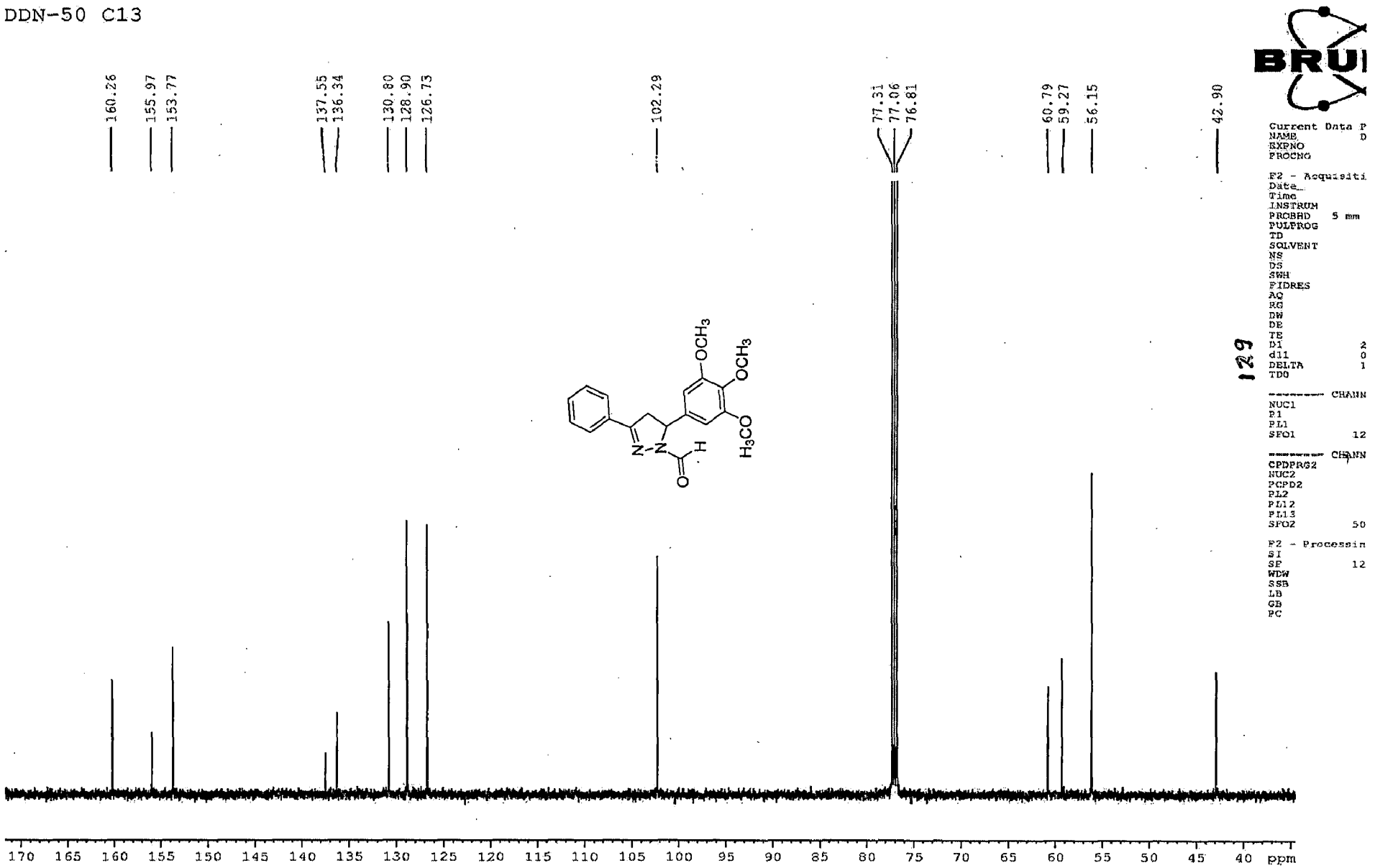


Figure 10b ^{13}C NMR spectra of 3-phenyl-5-(3,4,5-trimethoxyphenyl)-4,5dihydropyrazole-1-carbaldehyde

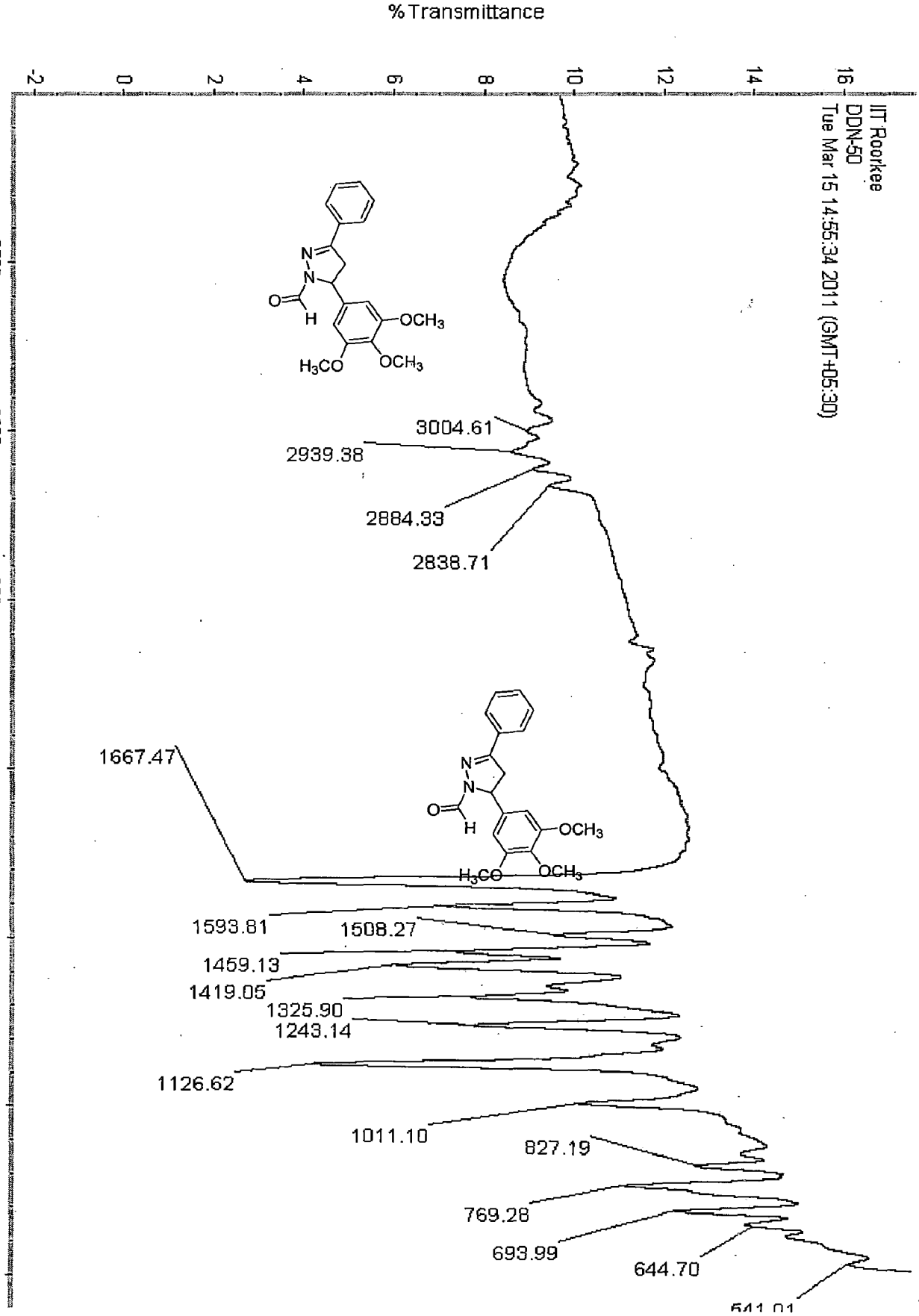


Figure 10b IR spectra of 3-phenyl-5-(3,4,5-trimethoxyphenyl)-4,5dihydropyrazole-1-carbaldehyde

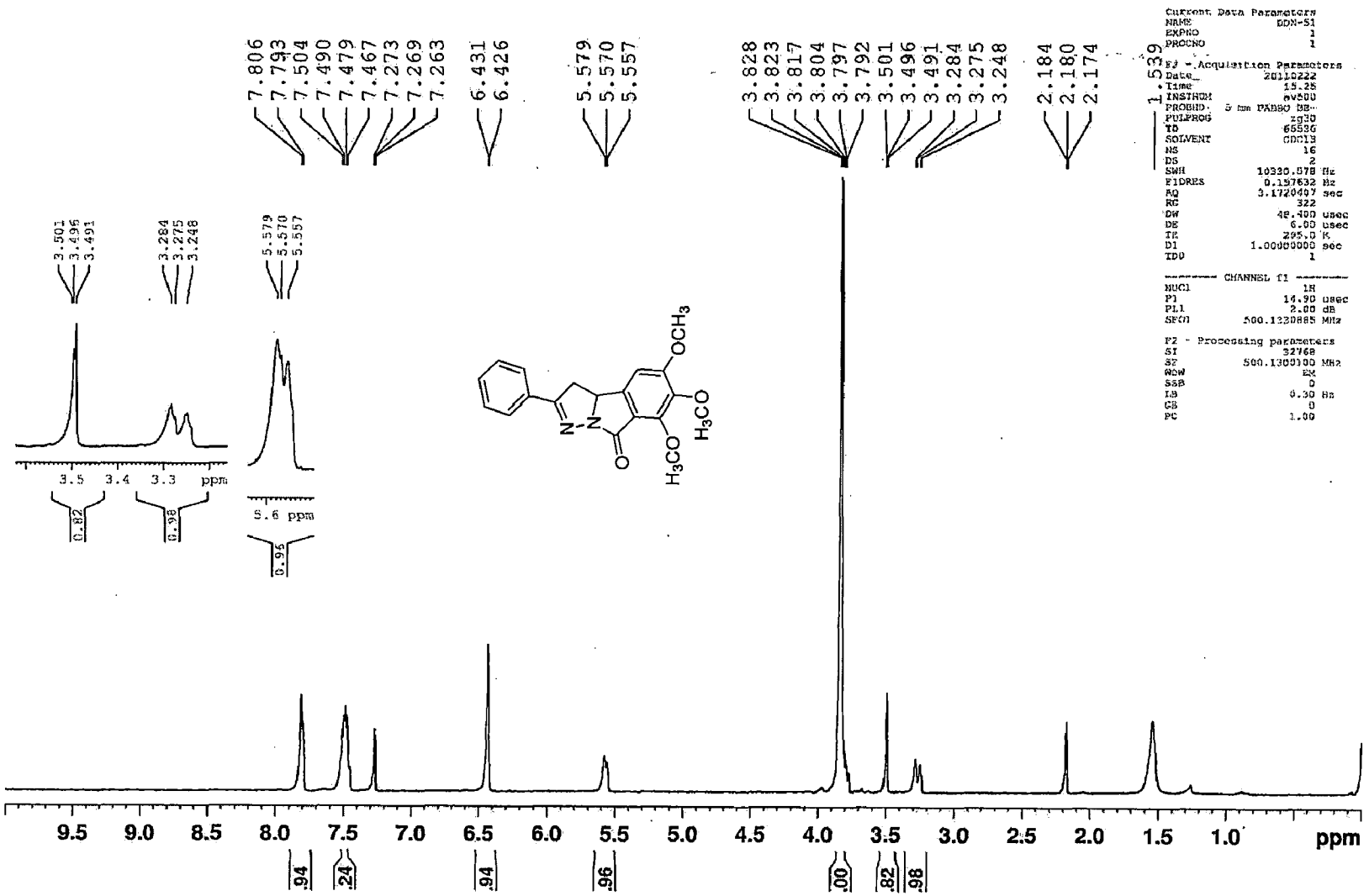


Figure 10c ^{1}H NMR spectra of 5,6,7-trimethoxy-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

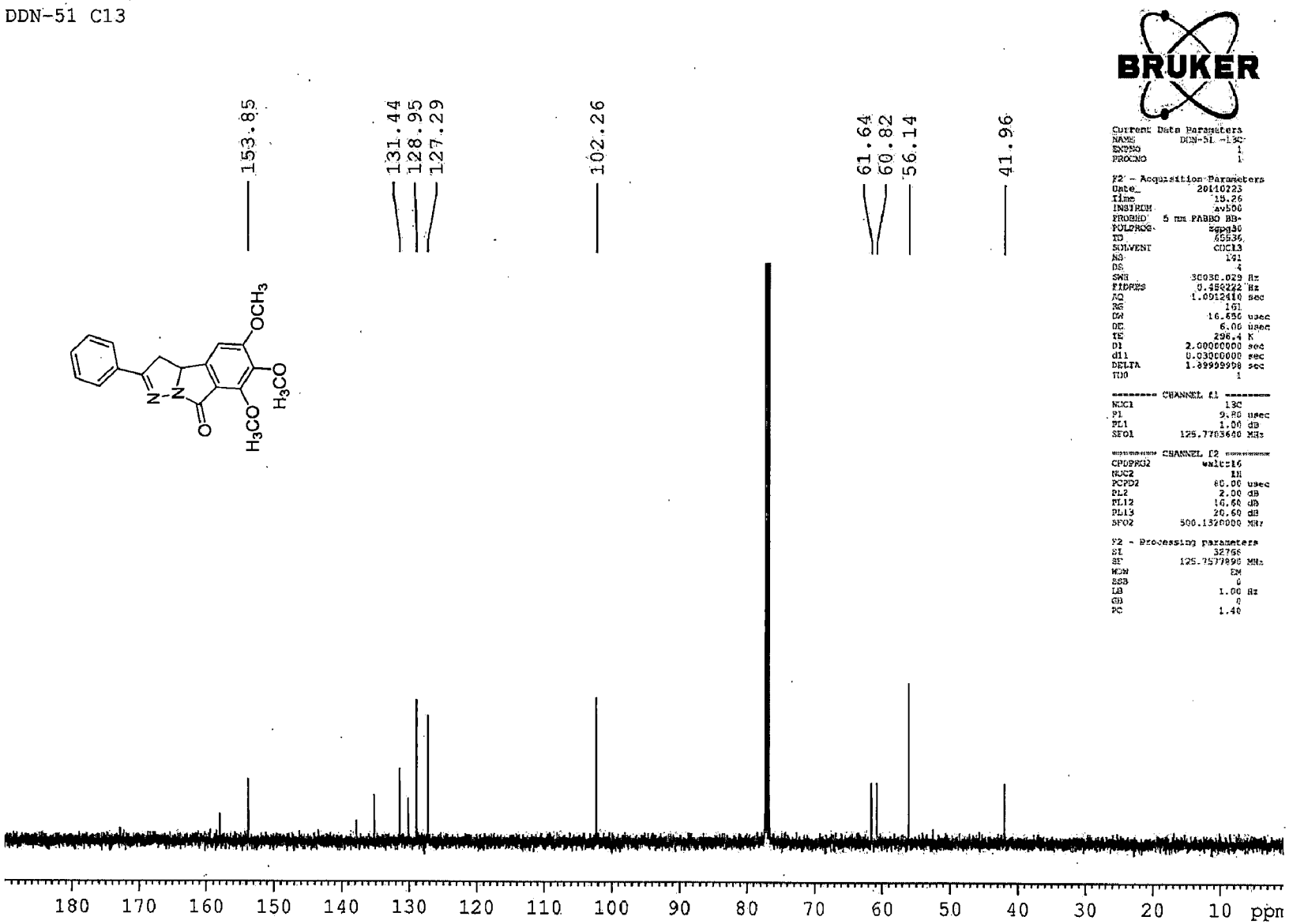


Figure 10c ^{13}C NMR spectra of 5,6,7-trimethoxy-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

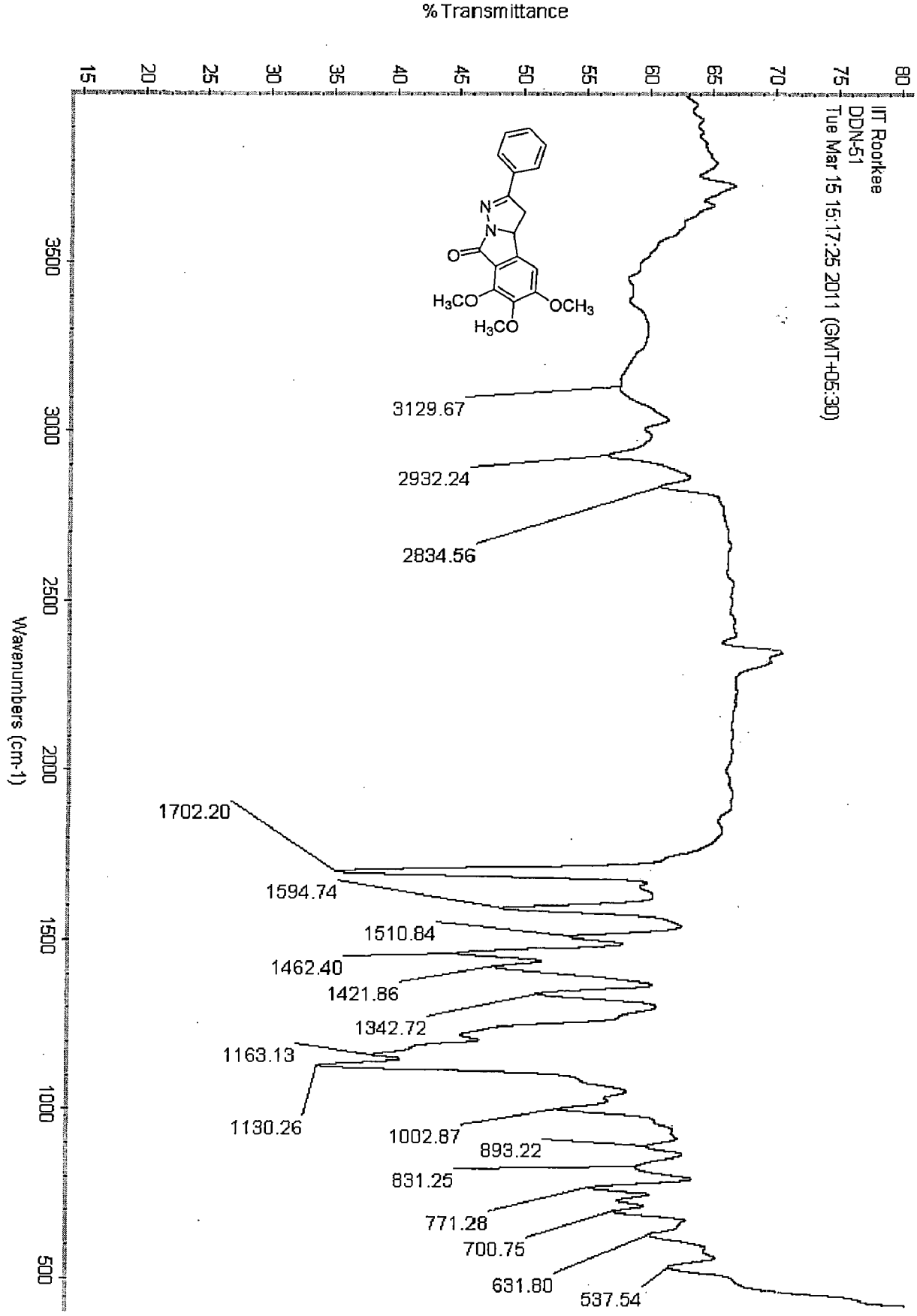


Figure 10c IR spectra of 5,6,7-trimethoxy-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

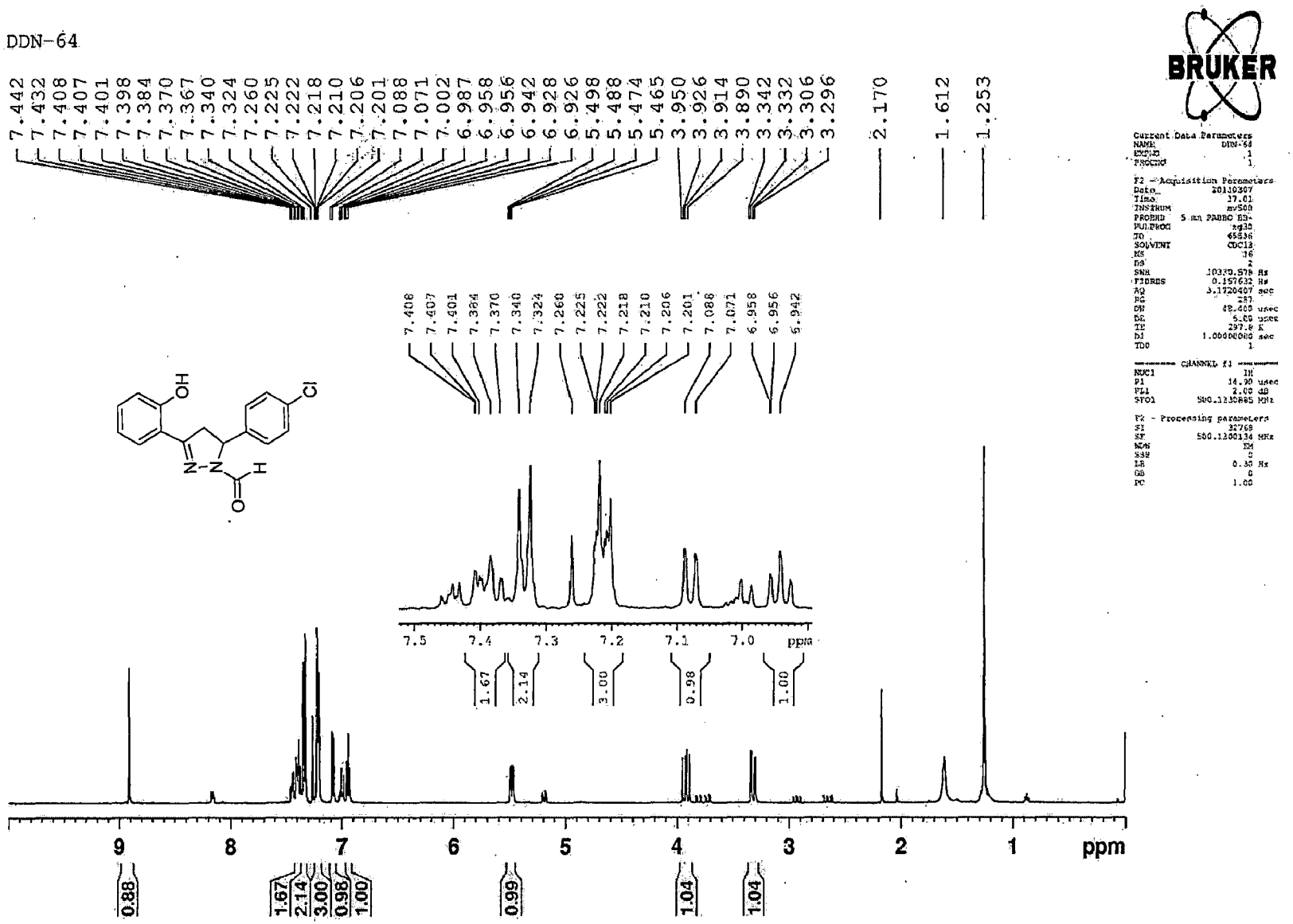


Figure 11b ^{1}H NMR spectra of 5-(4-chlorophenyl)-3-(2-hydroxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde

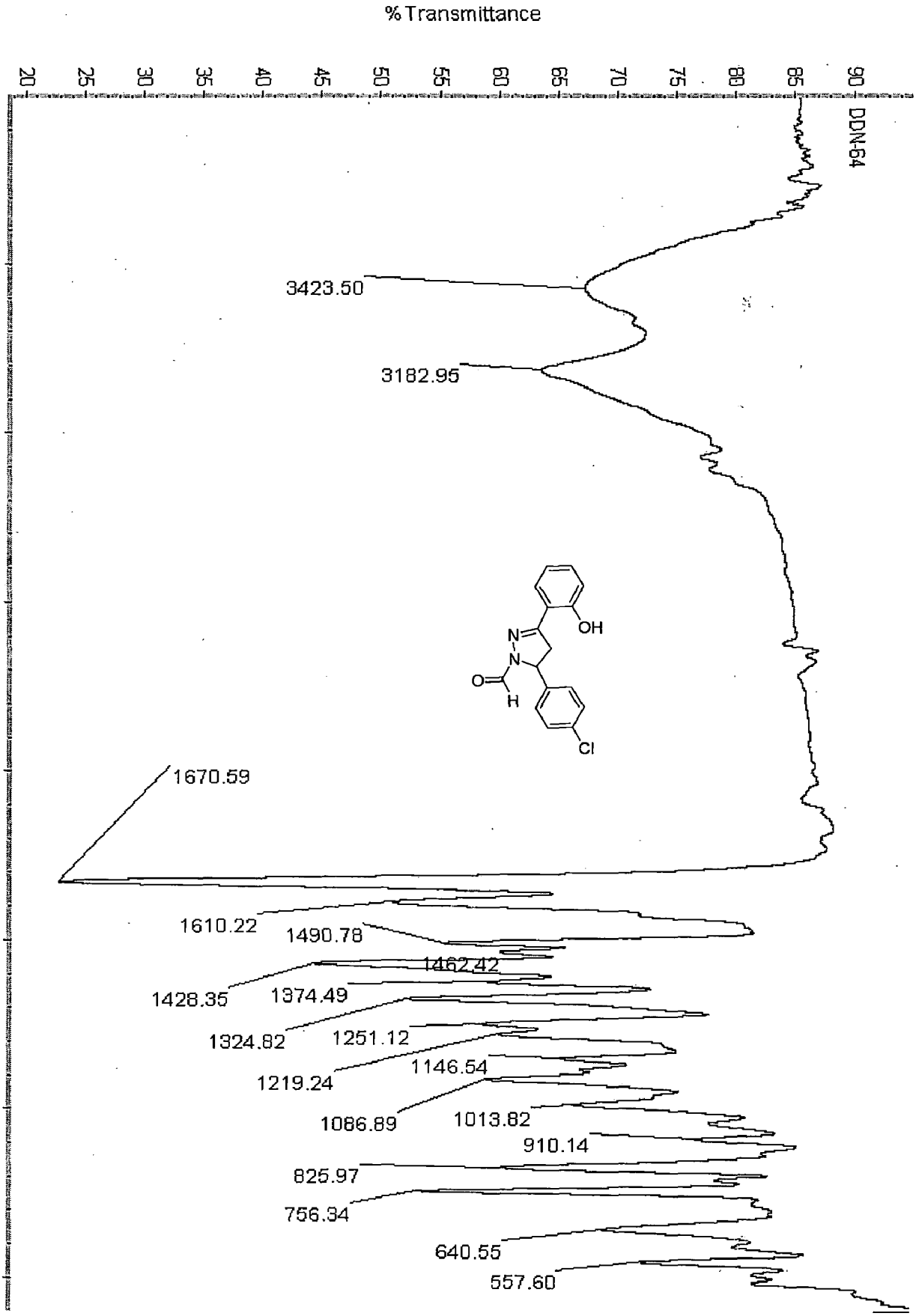


Figure 11b IR spectra of 5-(4-chlorophenyl)-3-(2-hydroxyphenyl)-4,5-dihydropyrazole-1-carbaldehyde

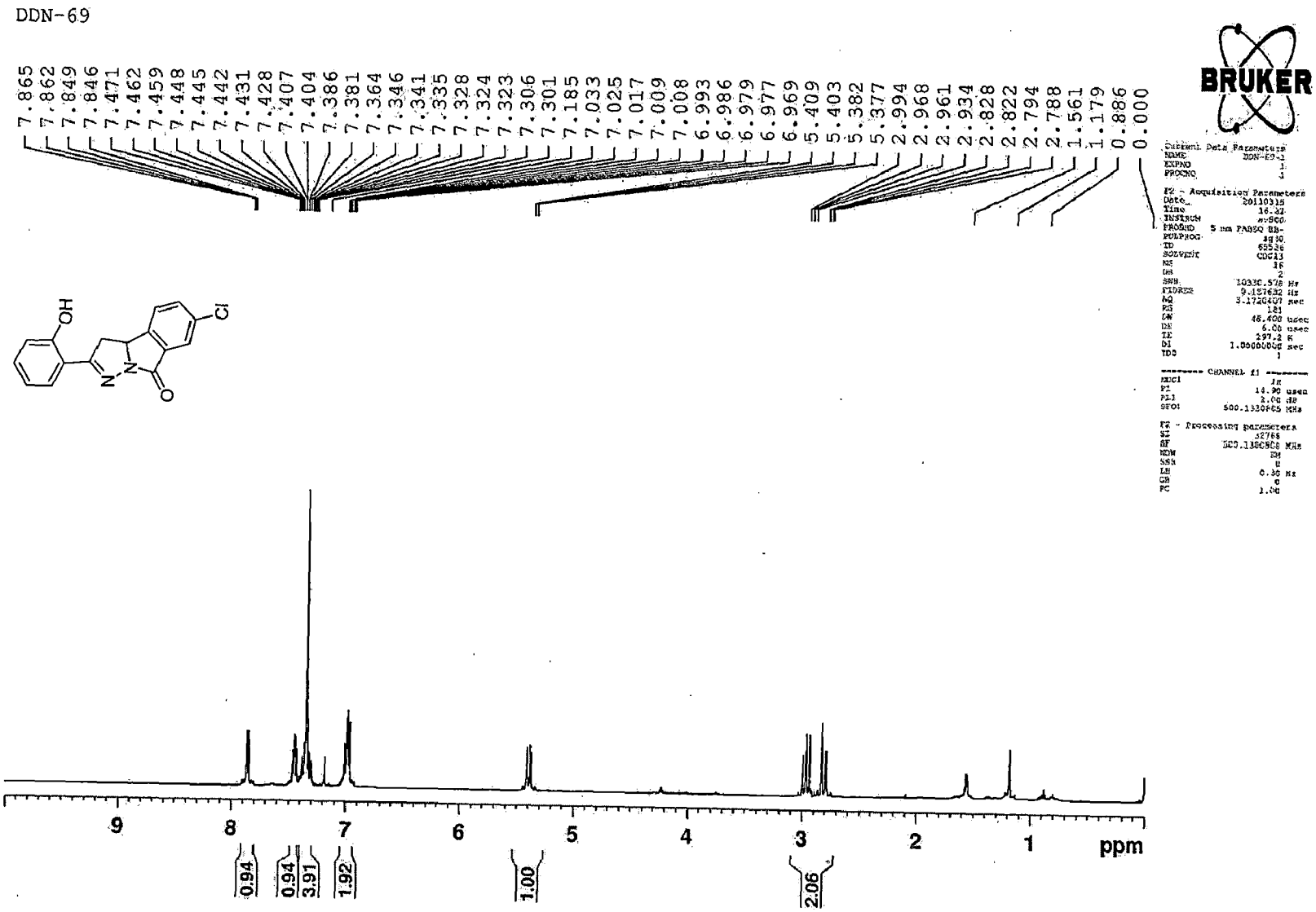


Figure 11c ^{1}H NMR spectra of 6-chloro-2-(2-hydroxyphenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

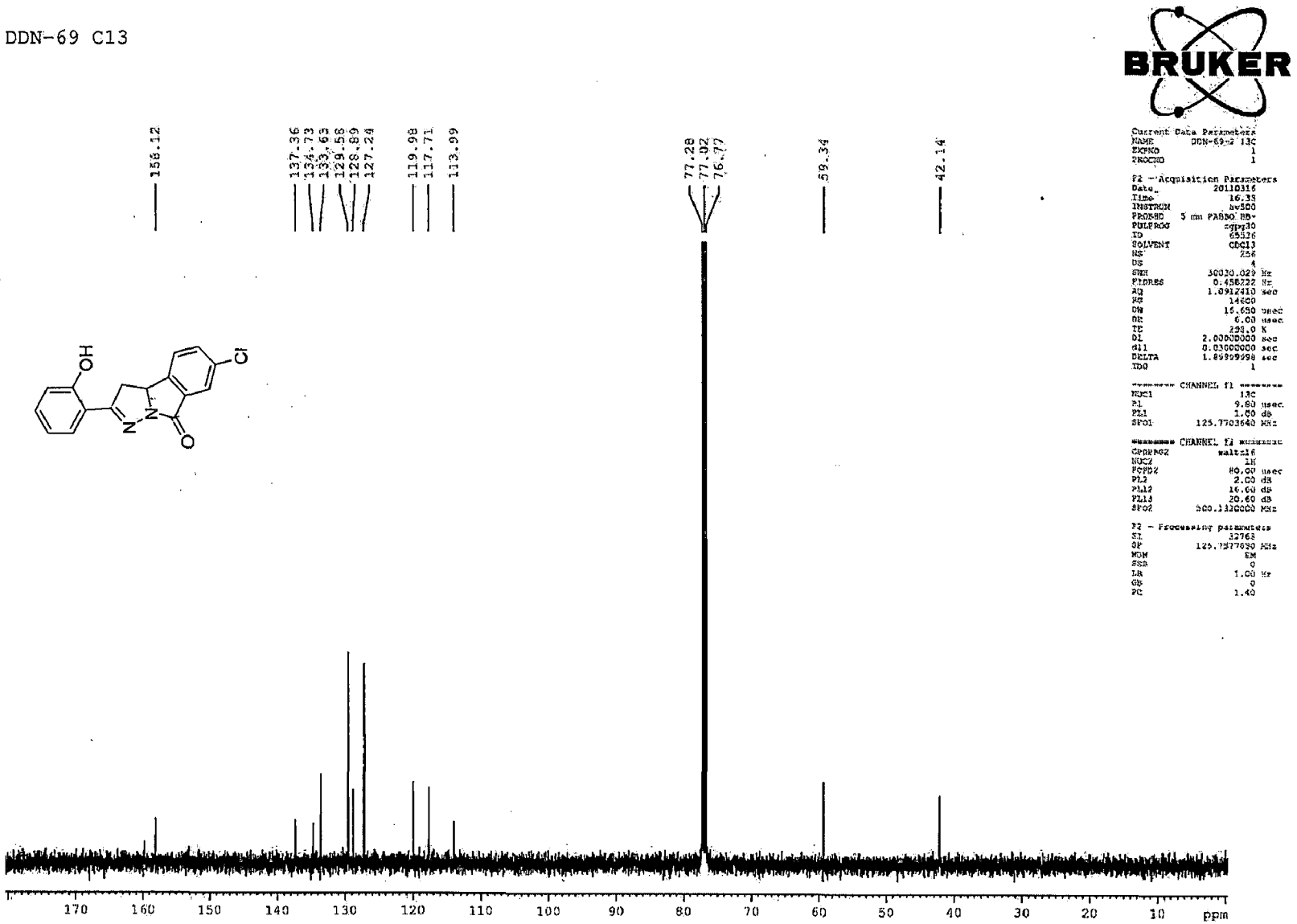


Figure 11c ^{13}C NMR spectra of 6-chloro-2-(2-hydroxyphenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

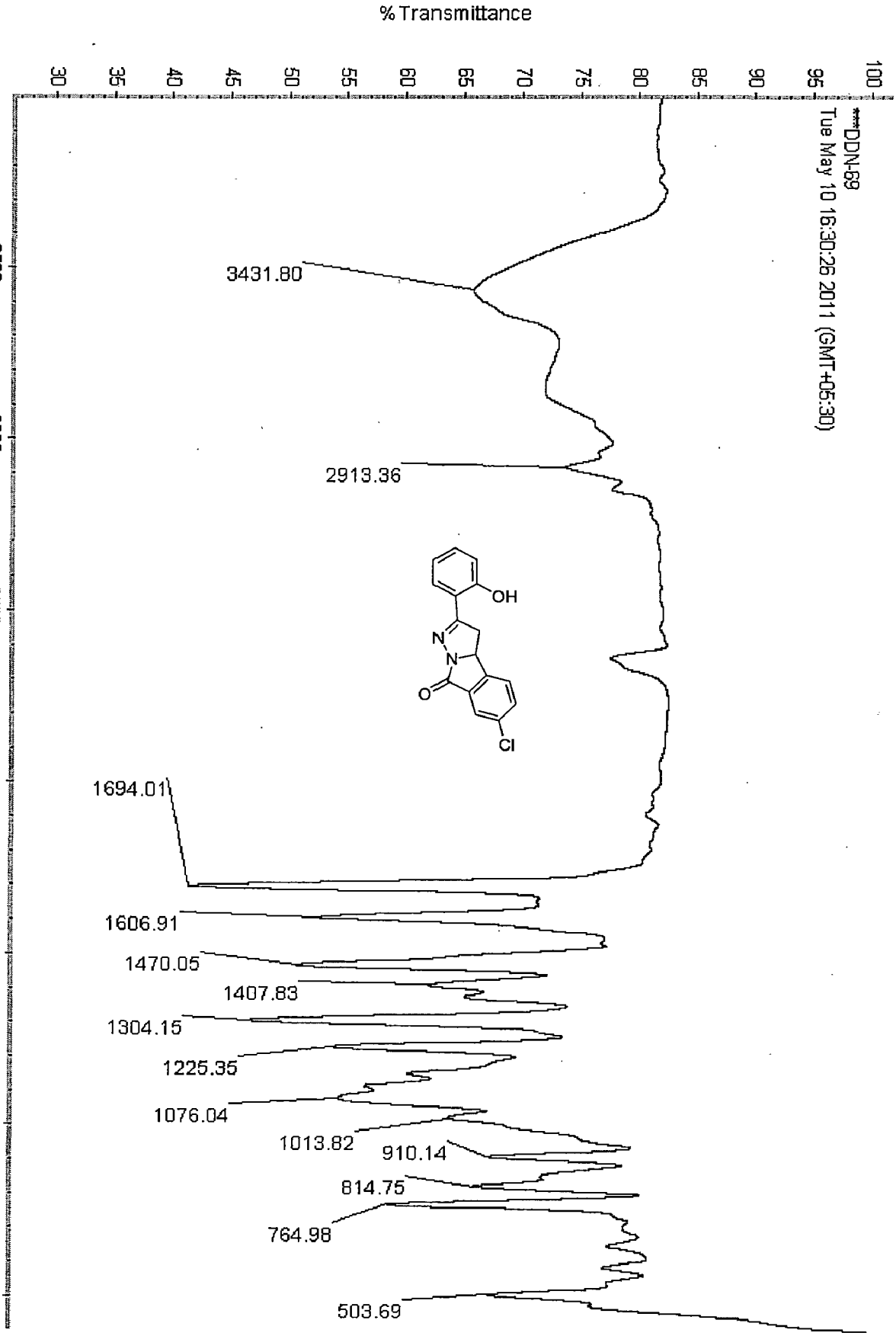


Figure 11c IR spectra of 6-chloro-2-(2-hydroxyphenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

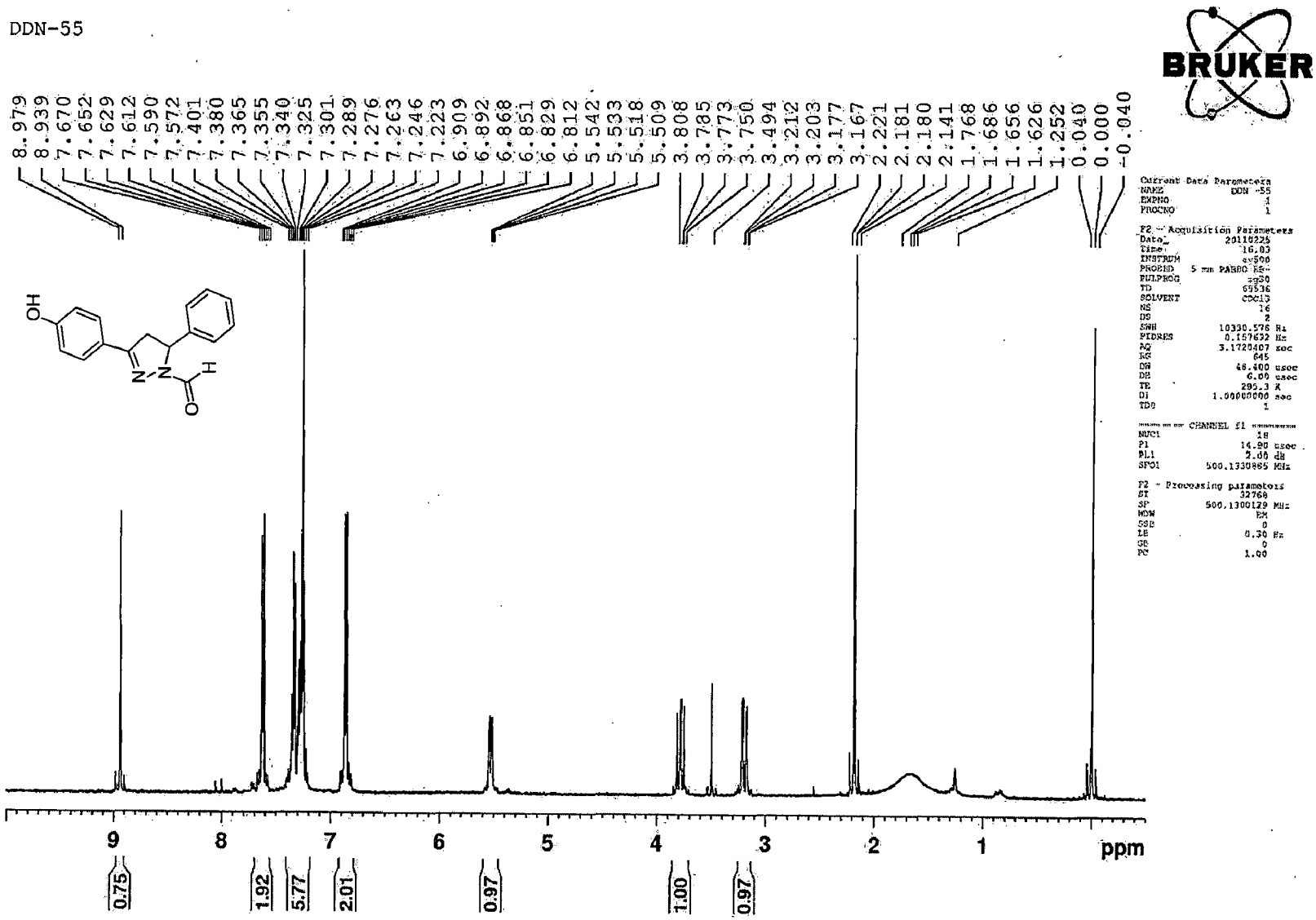


Figure 12b ^{1}H NMR spectra of 3-(4-hydroxyphenyl)-5-phenyl-4,5-dihydropyrazole-1-carbaldehyde

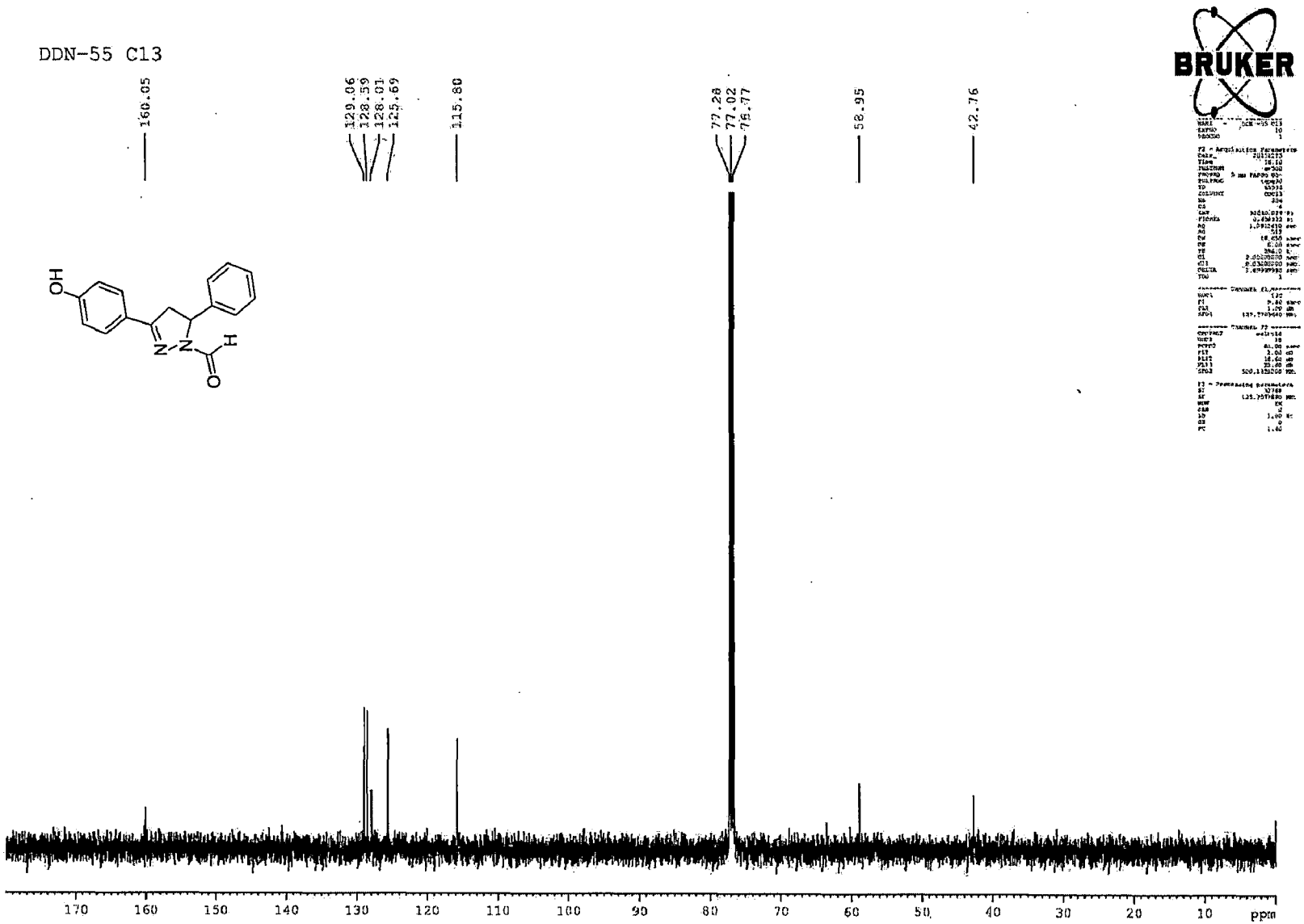


Figure 12b ^{3}C NMR spectra of 3-(4-hydroxyphenyl)-5-phenyl-4,5-dihydropyrazole-1-carbaldehyde

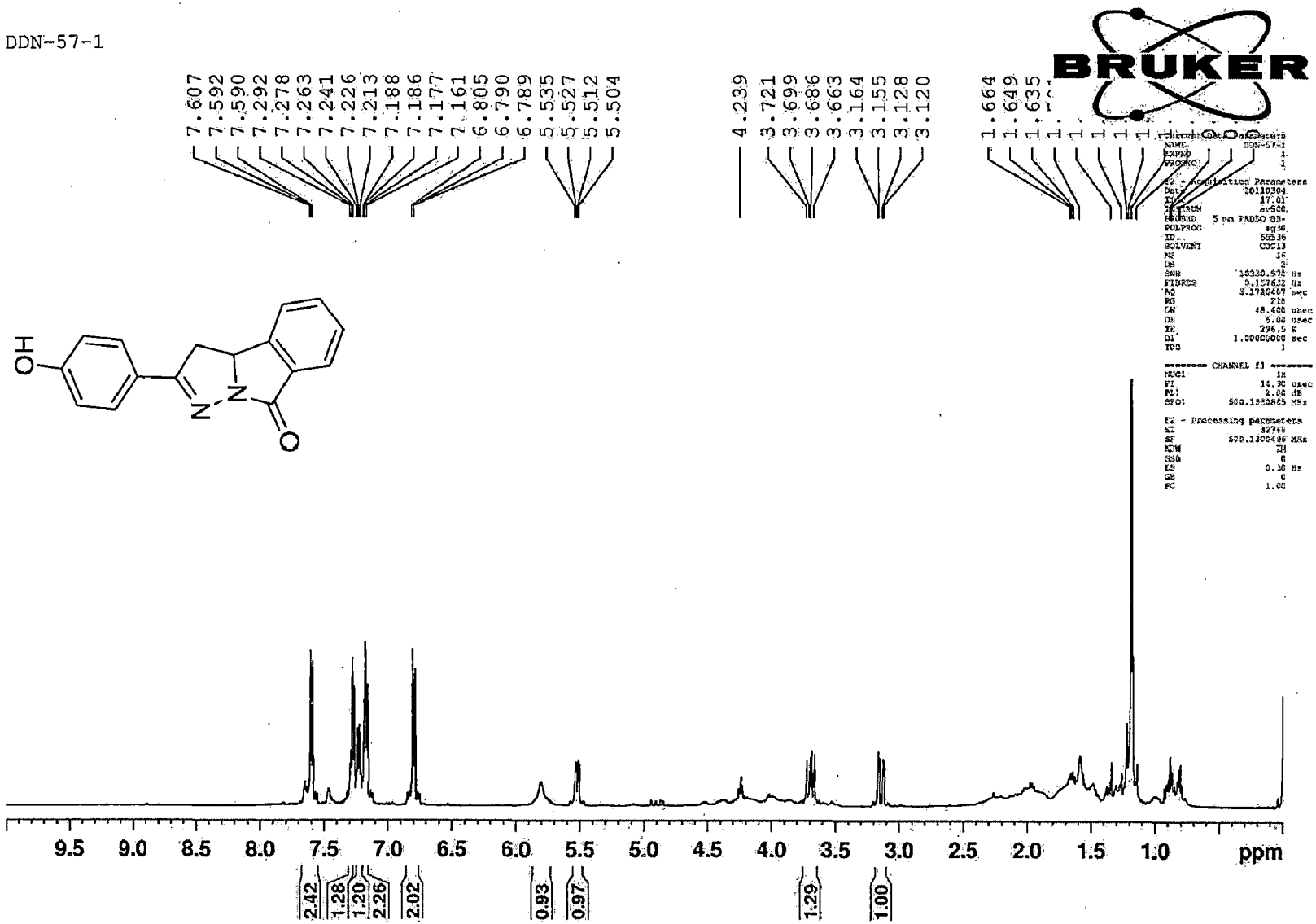


Figure 12c ^{1}H NMR spectra of 2-(4-hydroxyphenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

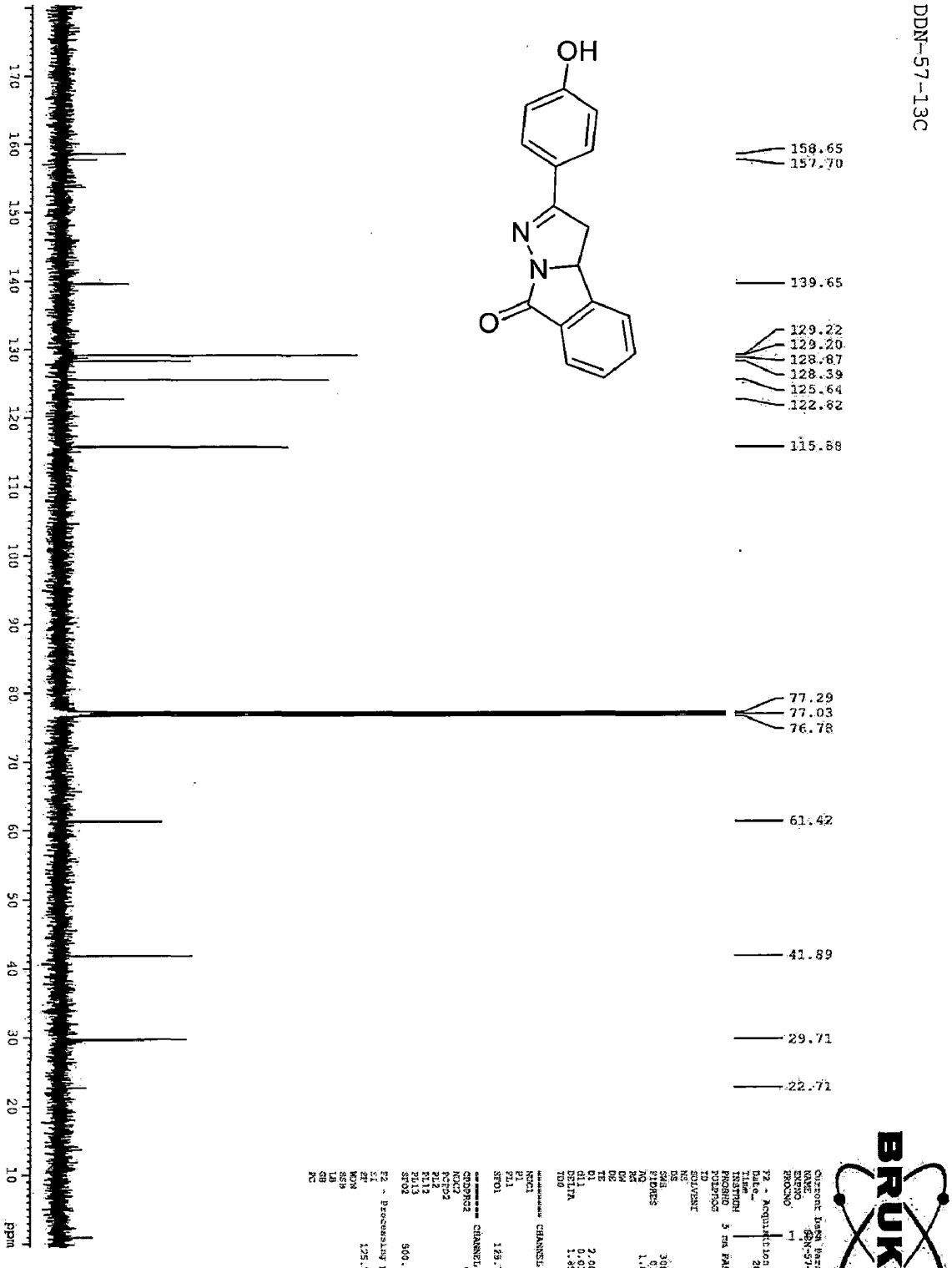


Figure 12c ^{13}C NMR spectra of 2-(4-hydroxyphenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

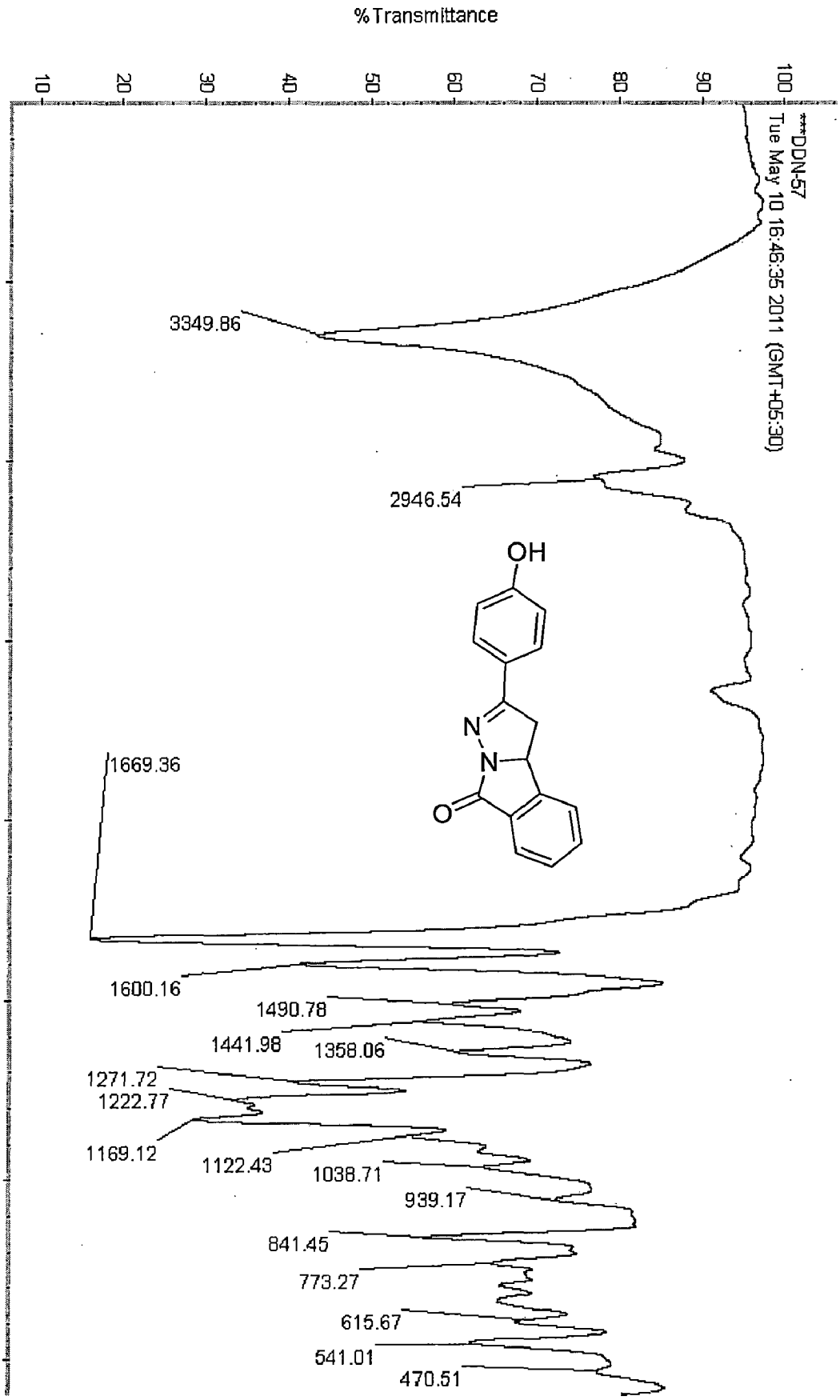


Figure 12c IR spectra of 2-(4-hydroxyphenyl)-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

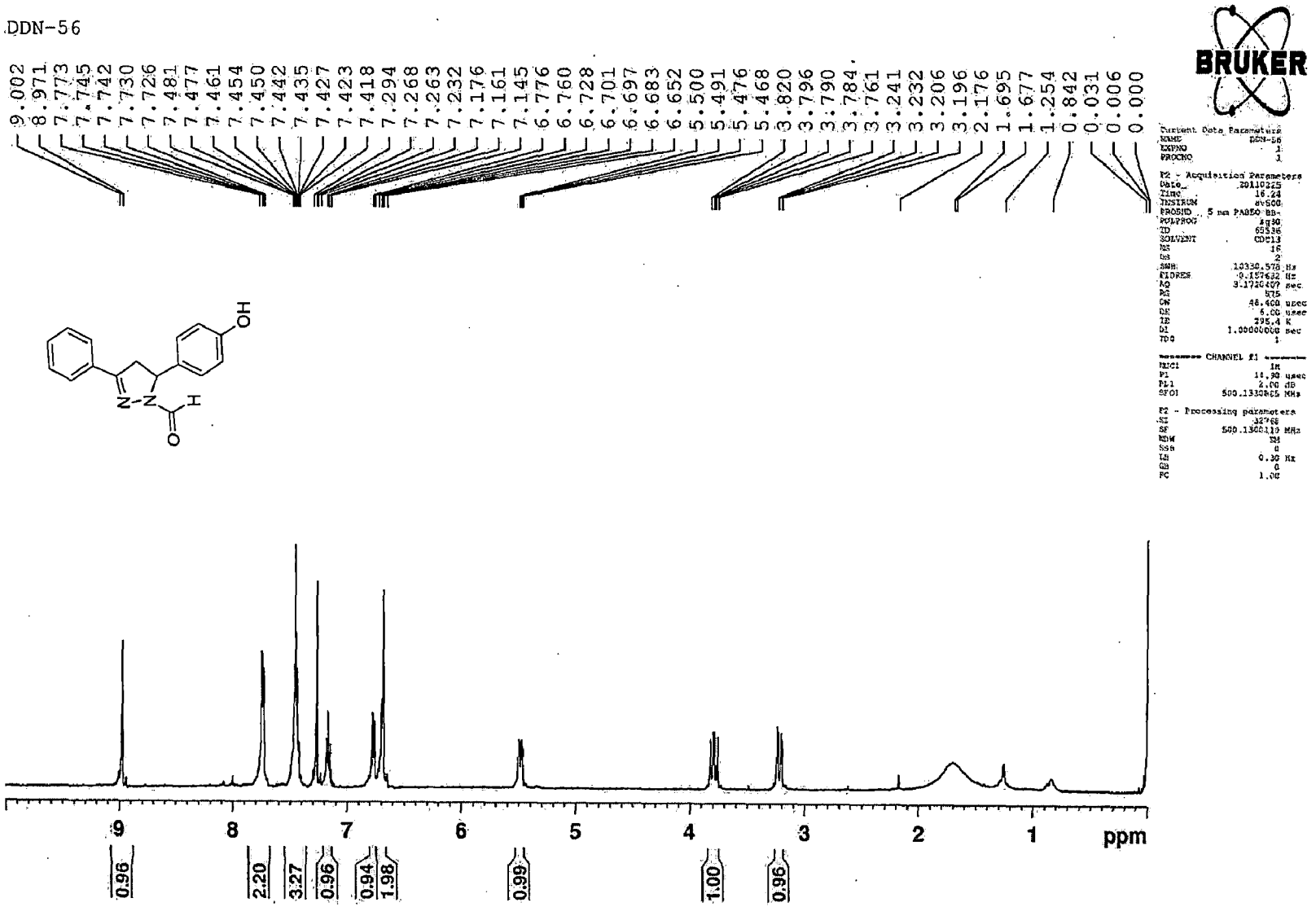


Figure 13b ^{1}H NMR spectra of 5-(3-hydroxyphenyl)-3-phenyl-4,5-dihydropyrazole-1-carbaldehyde

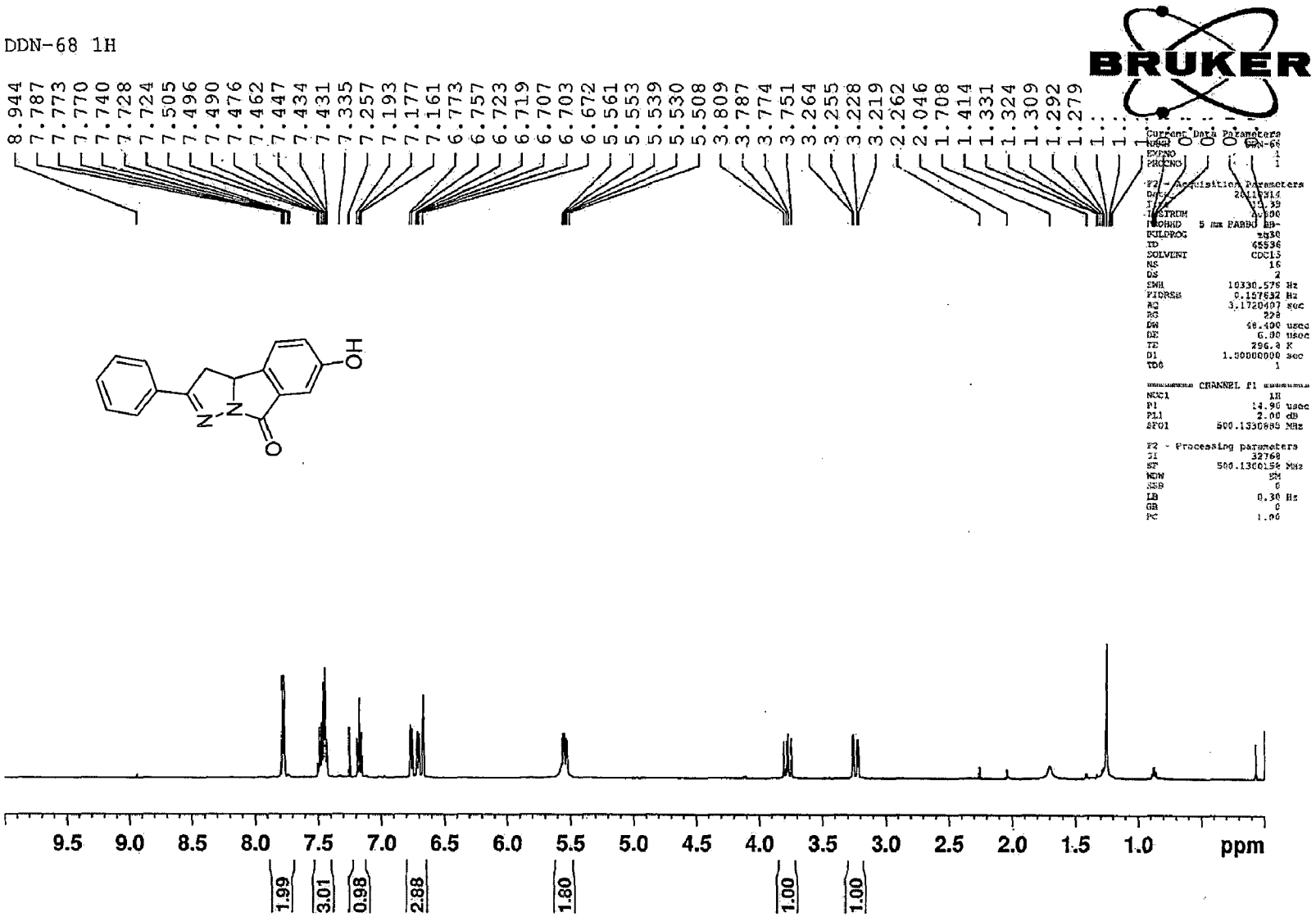


Figure 13c ^{1}H NMR spectra of 7-hydroxy-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

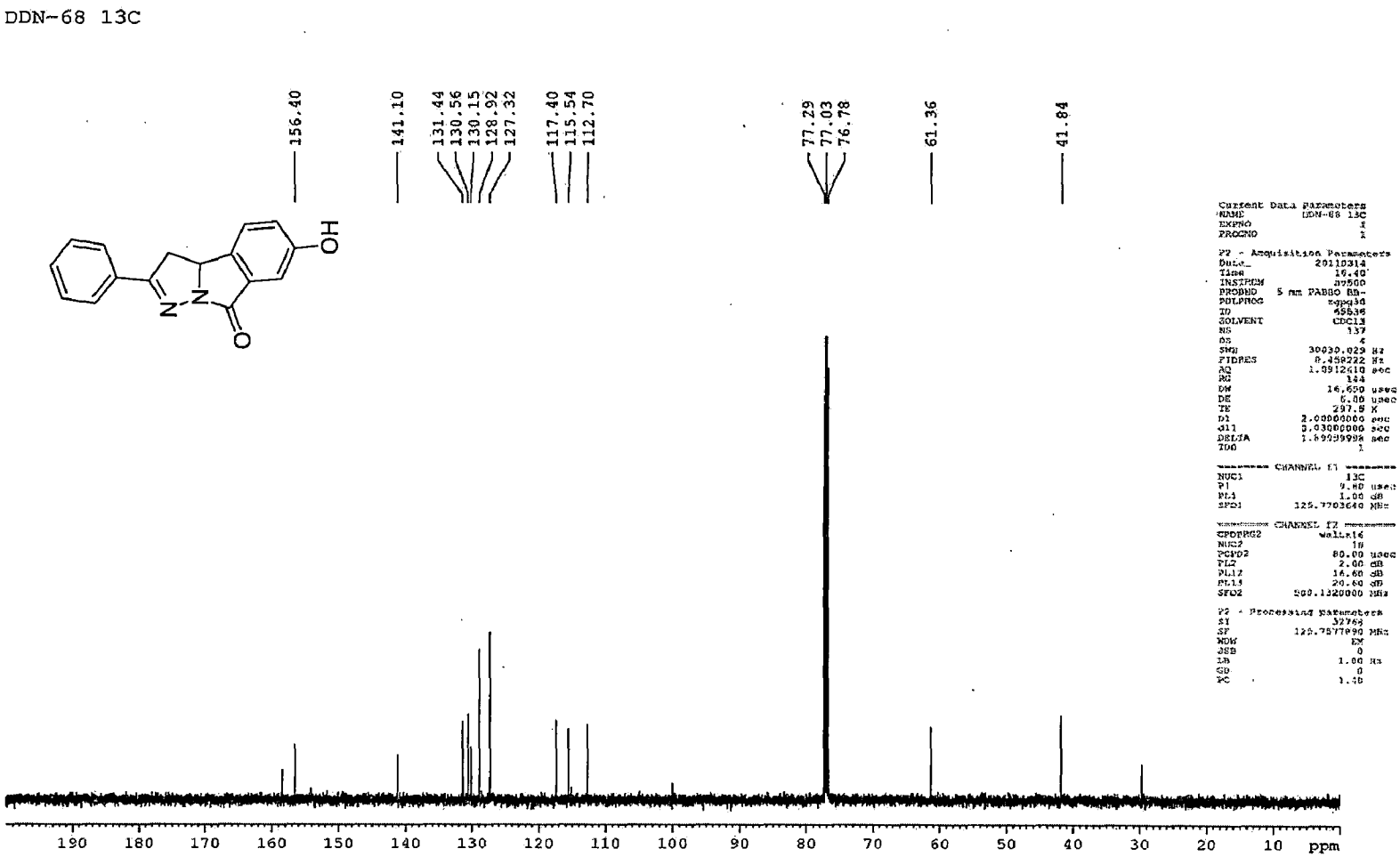


Figure 13c ^{13}CNMR spectra of 7-hydroxy-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

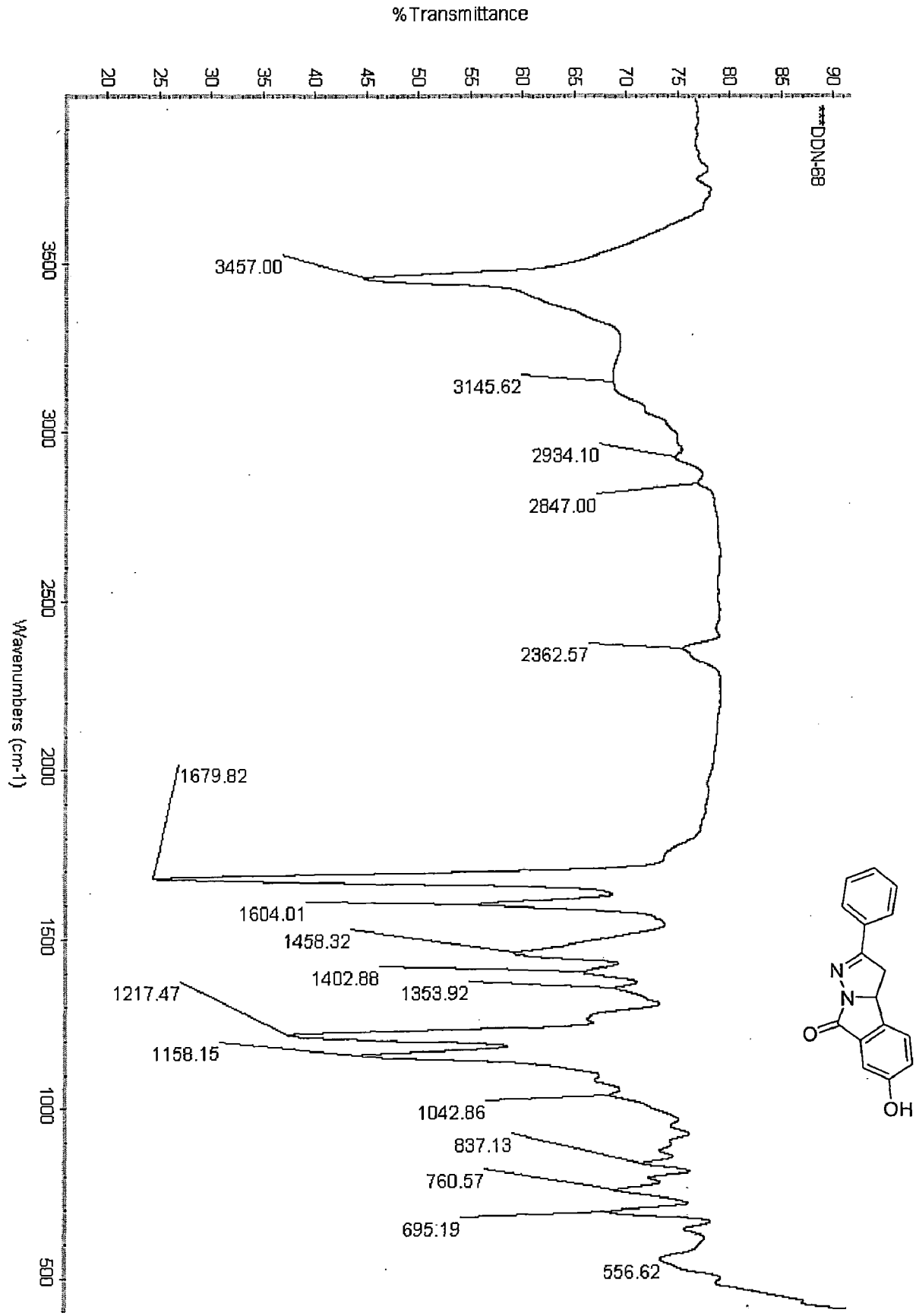


Figure 13c IR spectra of 7-hydroxy-2-phenyl-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

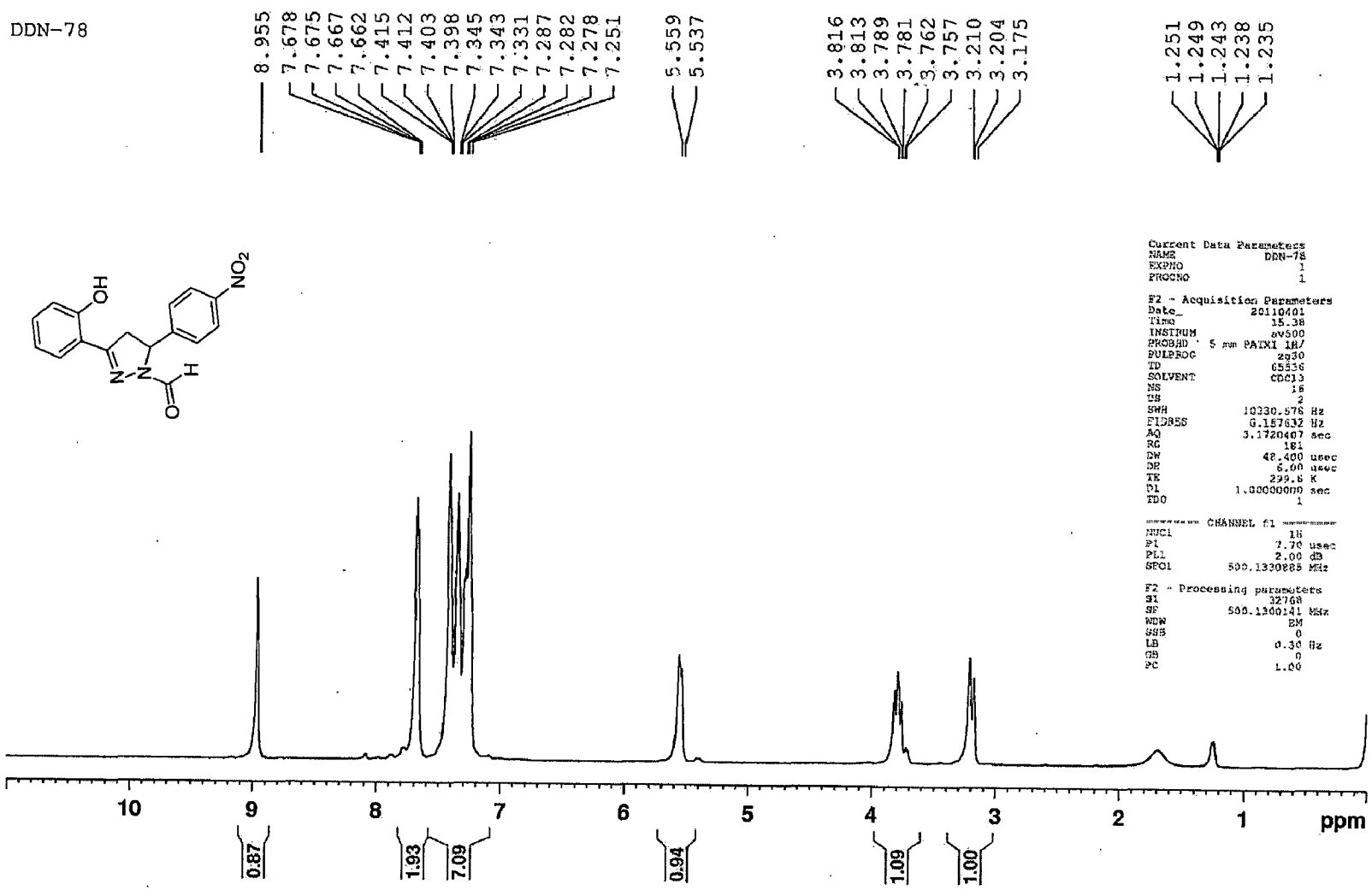


Figure 14b ^{1}H NMR spectra of 3-(2-hydroxyphenyl)-5-(4-nitrophenyl)-4,5-dihydropyrazole-1-carbaldehyde

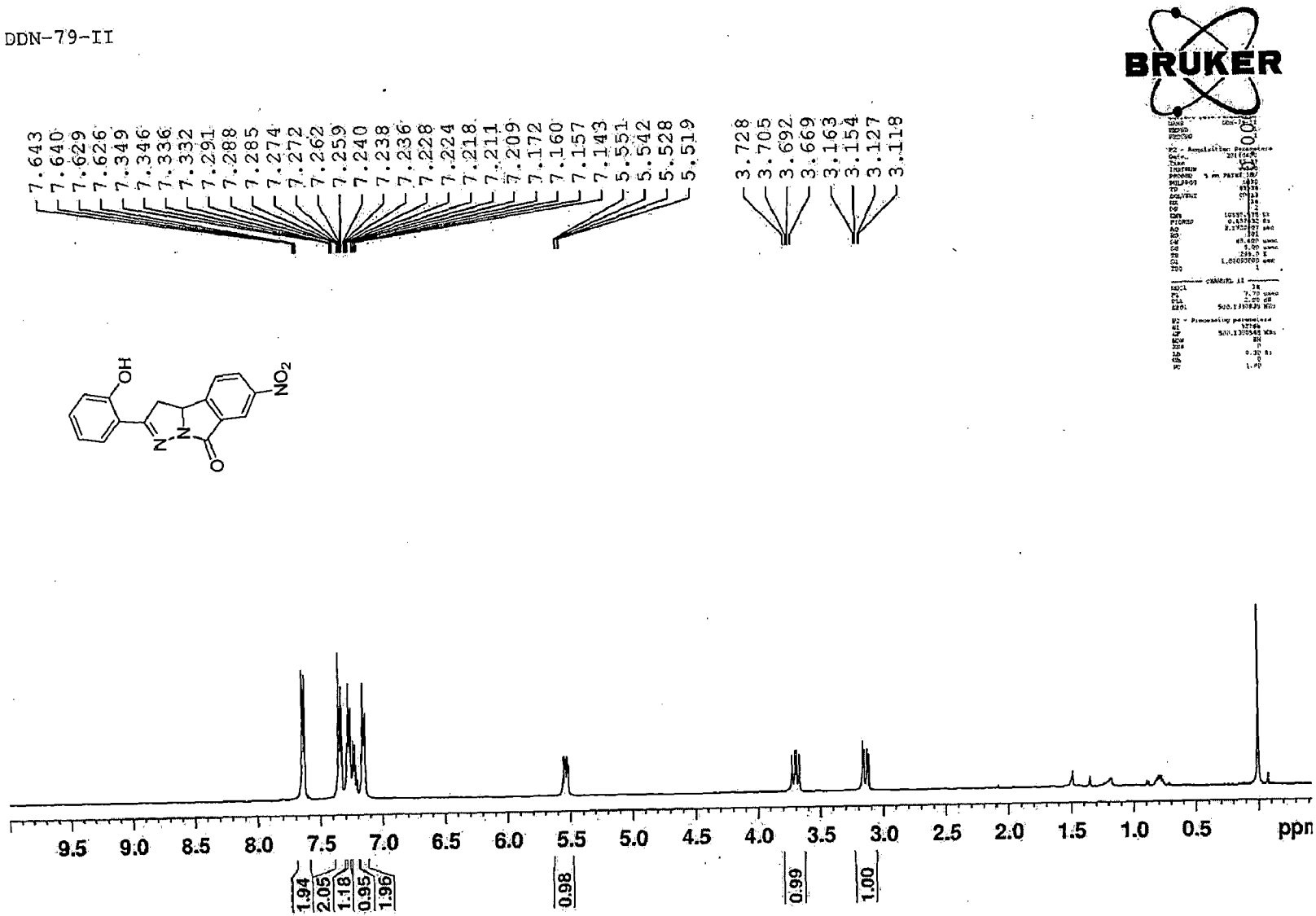


Figure 14c ^{1}H NMR spectra of 2-(2-hydroxyphenyl)-6-nitro-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

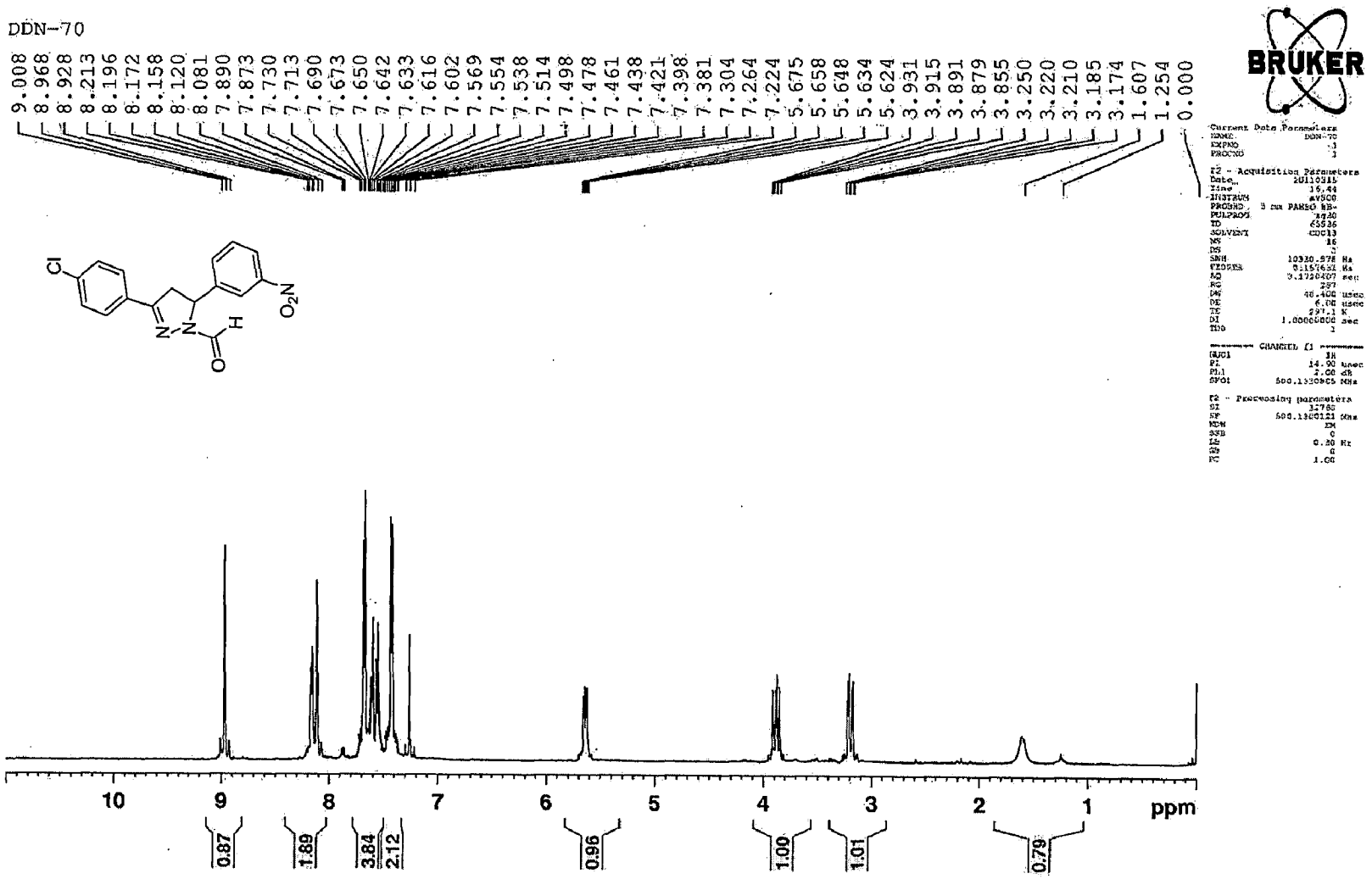


Figure 15b ^{1}H NMR spectra of 3-(4-chlorophenyl)-5-(3-nitrophenyl)-4,5-dihydropyrazole-1-carbaldehyde

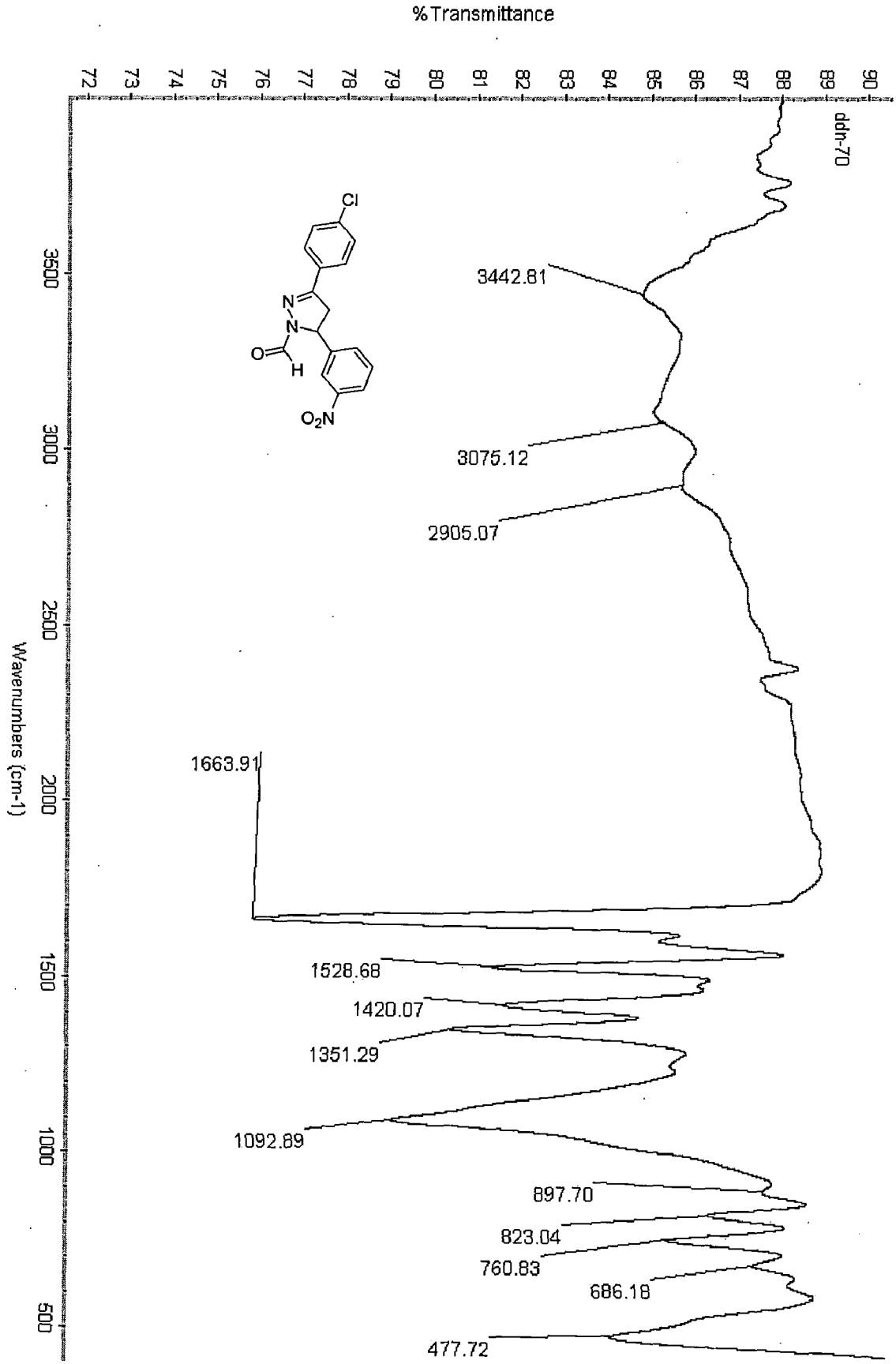


Figure 15b IR spectra of 3-(4-chlorophenyl)-5-(3-nitrophenyl)-4,5-dihydropyrazole-1-carbaldehyde

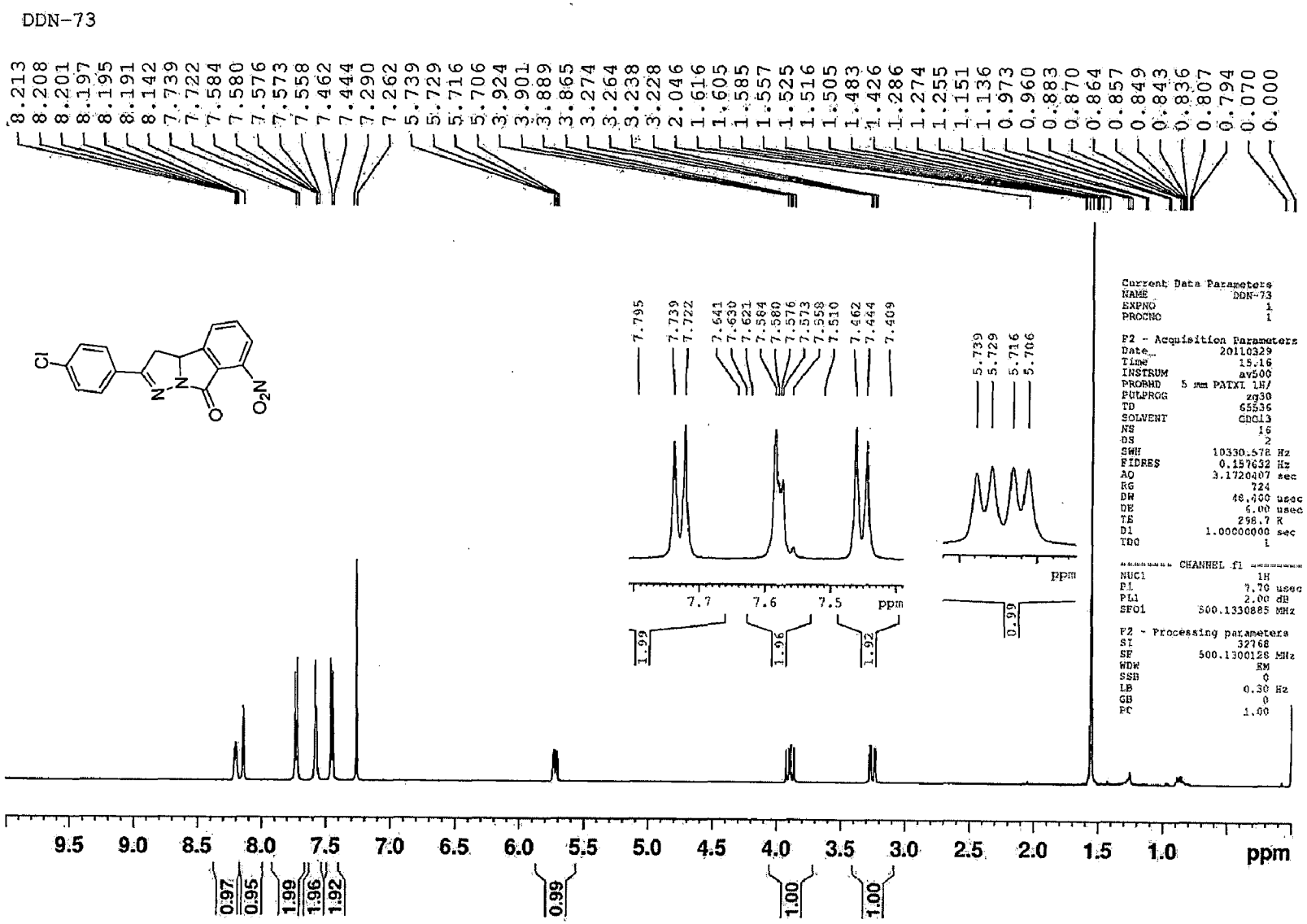


Figure 15c ^{1}H NMR spectra of 2-(4-chlorophenyl)-7-nitro-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

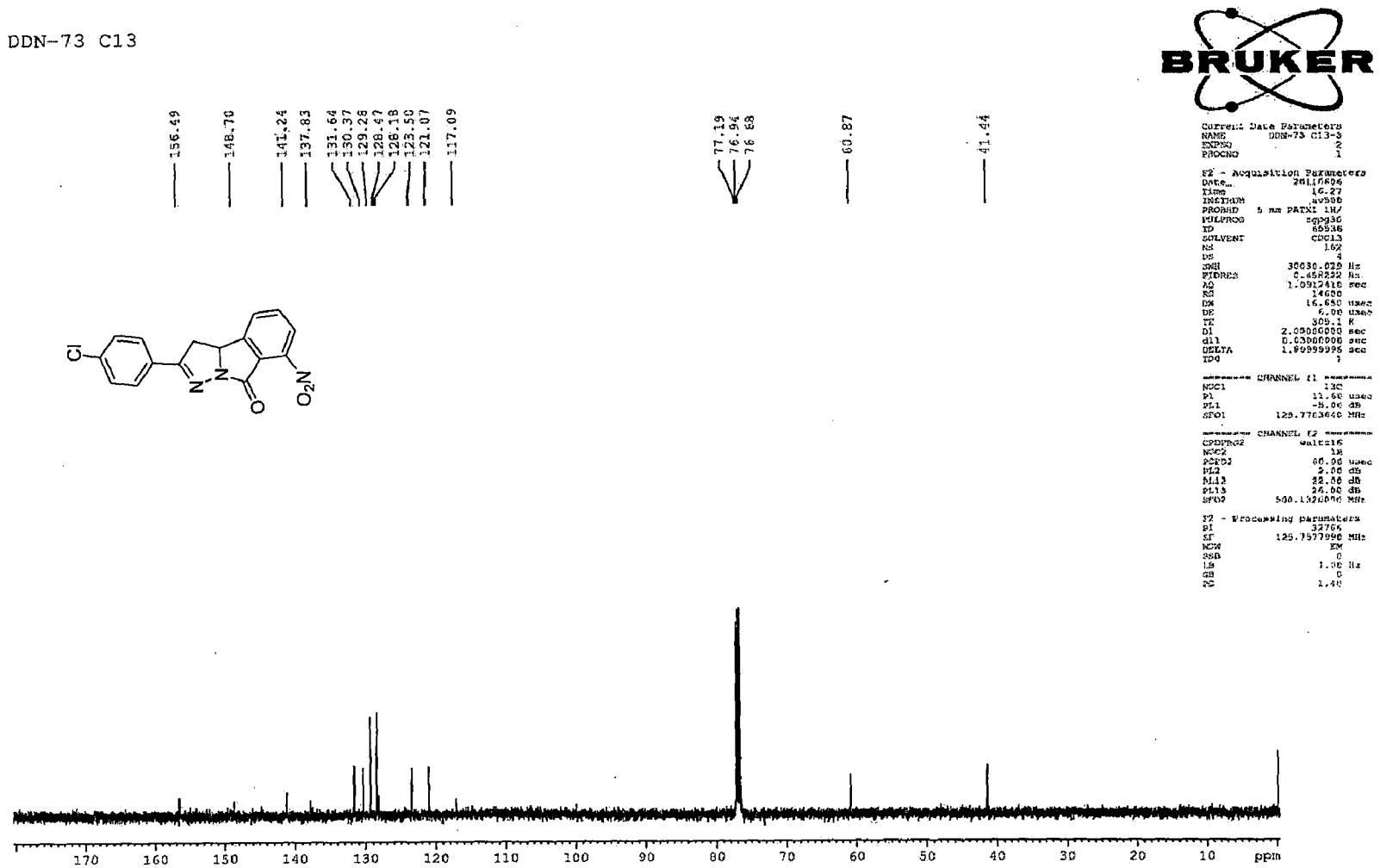


Figure 15c ^{13}CNMR spectra of 2-(4-chlorophenyl)-7-nitro-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one

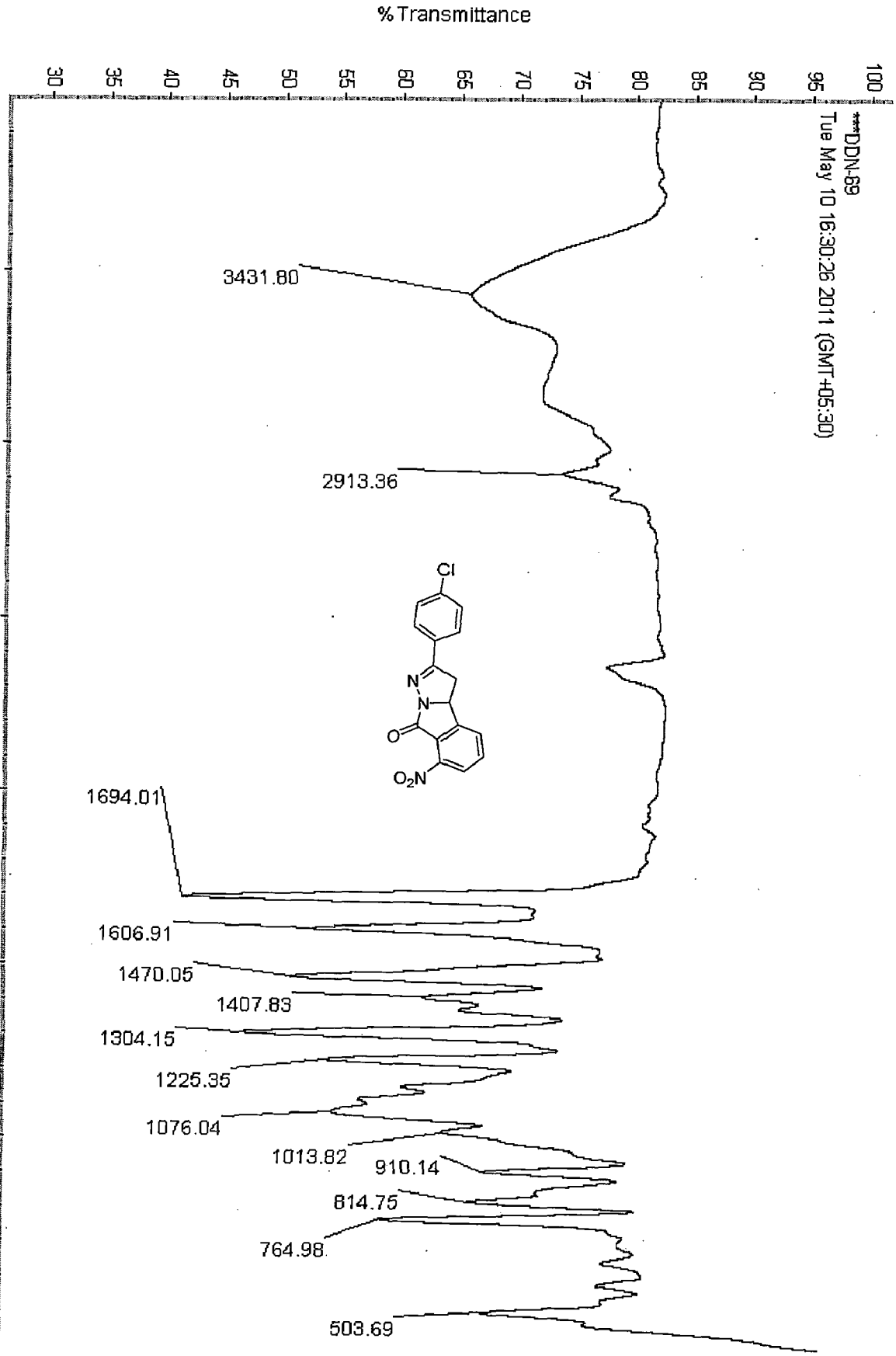


Figure 15c IR spectra of 2-(4-chlorophenyl)-7-nitro-3,3a-dihydropyrazolo[5,1-a]isoindol-8-one