SYNTHESIS OF VARIOUS IODYL COMPOUNDS OF IODOARENES AND TETRAZOLES USING OXONE® AS AN OXIDANT

by

Ram Chandra Dhakal

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Thesis Committee:

Dr. Scott T. Handy, Major Professor

Dr. Dwight J. Patterson

Dr. Paul C. Kline

This thesis is dedicated to my wife and my parents for their endless love, support, and encouragement.

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ABSTRACT

Iodyls are interesting compounds. To date, much of this interest has been focused on the application of iodyls as unique oxidants in organic synthesis. In this work, we are interested in their application as energetic materials.

When Oxone® was used as an oxidant in the preparation of iodyl compounds, more than 99% pure product based on NMR analysis was obtained without extra purification of the products. This method is also able to recover the unreacted starting material by washing the precipitate of iodyl compound with appropriate organic solvents.

Eleven iodyl compounds with good yields have been synthesized using Oxone®. After successfully establishing the reactions, the scales of some starting materials were increased up to 10 mmol. After increasing the reaction scales, the yields of the products did not decrease, indicating that this method is readily scalable. Due to the presence of two iodyl groups on the benzene ring, 1,4-diiodylbenzene was not soluble in DMSO. The melting points of the iodyl compounds are the decomposition points. *p*-Diiodylbenzene decomposed vigorously compared to the iodyl compounds having only one iodyl group, such as iodylbenzene, 2-iodylnitrobenzene, 3-iodylbenzonitrile, and 4-iodylbenzonitrile. From this observation, when the iodyl group on the benzene ring is more than one, the explosive character of the compounds increases. Iodyl compounds of the tetrazole derivatives, such as 5-(3-iodylphenyl)-1*H*-tetrazole and 5-(4-iodylphenyl)-1*H*-tetrazole, also decomposed vigorously at the corresponding decomposition points.

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LIST OF ABBREVIATIONS

Ac = acetate

AcOH = acetic acid

$(Ac)_2O$ = acetic anhydride

ACS = American Chemical Society

Ar = aryl

br = broad

Bu (*n*-Bu) = butyl

t-Bu = *tert*-butyl

^{13}C NMR = carbon 13 NMR

$CDCl_3$ = chloroform-d

d = doublet

Dec = decomposition

D.P. or dec. point = decomposition point

DI = Deionized Water

DMF = dimethylformamide

DMP = Dess-Martin periodinane

DMSO = dimethyl sulfoxide

ESI-MS = electrospray ionization mass spectroscopy

Et = ethyl

etc. = et cetera

EtoAc = ethyl acetate

FT-IR = Fourier transform infrared spectroscopy

^1H NMR = Proton NMR

g = gram

GC = gas chromatography

GC-MS = gas chromatography mass spectrometry

h = hour (s)

hrs = hours

n-Hep = heptyl

n-Hex = hexyl

Hz = Hertz

IBX = 2-iodobenzoic acid

IR = infrared

IUPAC = International Union of Pure and Applied Chemistry

KJ = kilojoules

LC-MS = liquid chromatography mass spectrometry

lit = literature

m = multiplet

Me = methyl

mg = milligram

min = minute

MHz = megahertz

mL = milliliter

µl = microliter

mmol = millimole

mol-equiv = mole equivalent

mp = melting point

MS = Mass Spectroscopy

N.R. = No Reaction

NMR = nuclear magnetic resonance

Ph = phenyl

ppm = parts per million

i-Pr = isopropyl

n-Pr = normal propyl

PTP = protein tyrosine phosphates

q = quartet

rt = room temperature

s = singlet

t = triplet

TBAB = tetra-*n*-butylammonium bromide

temp. = temperature

Tf = triflate

TFA = trifluoroacetate

THF = tetrahydrofuran

TLC = thin layer chromatography

TsOH = *p*-toluenesulfonic acid or tosylic acid

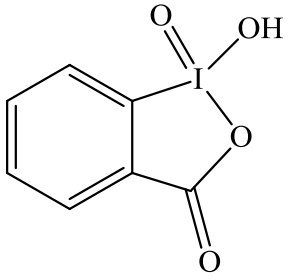
TMS = trimethylsilyl

$VO(acac)_2$ = vanadyl acetylacetonate

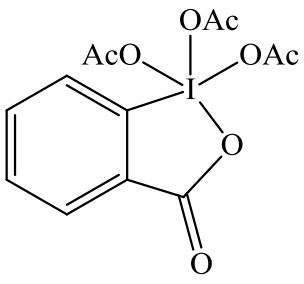
CHAPTER I

INTRODUCTION

Aromatic iodides, ArI, are usually more reactive than the corresponding bromides and chlorides. They are broadly applied in chemical laboratories, chemical industries, and medicines. They are also used to synthesize a huge variety of stable, aromatic polyvalent iodine compounds, which have found wide application as versatile and environmentally friendly oxidizing agents in modern organic synthesis.[1-4] Particularly useful oxidizers, such as the pentavalent iodine compounds, namely, 1-hydroxy-(1*H*)-benzo-1,2-iodoxol-3-one-1-oxide (2-iodoxybenzoic acid, IBX, **1**) and its acetylation product, (Dess-Martin periodinane, DMP, **2**), are now widely applied for the synthesis of various organic compounds as mild and very selective reagents for the oxidation of alcohols to carbonyl compounds as well as for a variety of other synthetically applicable and effective oxidative transformations.[5-7] The various catalytic uses of polyvalent iodine derivatives have also recently become known.



1 (IBX)

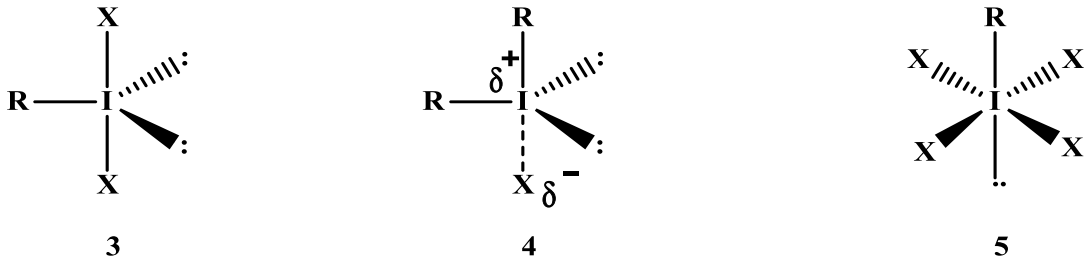


2 (DMP)

Over the past two decades, many reviews on specific classes of hypervalent organoiodine compounds and their synthetic applications have been published.[1-46] Most remarkable is the monograph by Varvoglis[2] on the application of polyvalent iodine compounds in organic synthesis as well as the volume of "Topics in Current Chemistry"[36] on polyvalent iodine chemistry.

According to IUPAC recommendations, all known organic hypervalent iodine derivatives belong to two common structural types (Figure 1):[1, 3-4, 8, 37, 45]

1. Iodine (III) compounds **3** and **4**, also named λ^3 –iodanes.
2. Iodine (V) compounds **5**, or λ^5 –iodanes.



R = carbon ligand; X = halogen, oxygen or nitrogen ligand

Figure 1: Structural types of polyvalent iodine species.

Due to the presence of a total 10 electrons of the iodine atom in λ^3 –iodanes (**3**, **4**), its overall geometry is a distorted trigonal bipyramid. The two heteroatom ligands X occur in the apical positions. Both electron pairs and the least electronegative carbon ligand R occur in the equatorial positions. In this polyvalent model, the bonding in RIX_2 applies the non-hybridized 5p orbital of iodine in the linear X-I-X bond. Because of higher polarization of this linear three-center, four-electron (3c – 4e) bond, which is longer and weaker than the usual covalent bond, this bond is termed "hypervalent or polyvalent" and

this bond in λ^3 –iodanes is responsible for their electrophilic reactivity.[45] Therefore, it shows good elimination and oxidation rates and finds application in organic synthesis.[8, 32] In the case of organic λ^5-iodane **5**, it has a distorted octahedral structure. The organic group R and the electron pair lie in the apical positions and the four heteroatom ligands X lie in basal positions. The apical group R is linked to iodine by a normal covalent bond using a 5sp-hybridized orbital and two orthogonal hypervalent three-center, four-electron (3c – 4e) bonds bind all the ligands X.[1]

Using different computational methods, the structures and reactivities of a number of specific classes of polyvalent iodine compounds were explored theoretically.[47-59] Several X-ray crystal structures and numerous important spectroscopic (NMR, LC-MS, ESI-MS, and ESI-MS/MS) structural studies have been reported for all main classes of organic hypervalent iodine compounds.[45, 56-60]

All polyvalent iodine reagents are solids-amorphous or crystalline-colorless and odorless. They are insensitive to atmospheric oxygen and moisture but they are sensitive to light. They are fairly stable at room temperature and they should be stored in dark places to protect from light.

Being less developed in contrast with trivalent iodine reagents, the chemistry of iodine (V) compounds (λ^5 –iodanes) has also taken significant attention in current years. This is because 2-iodoxybenzoic acid (IBX), and Dess-Martin periodinane (DMP) are mild and selective oxidizers for alcohols and amines, for conversions of carbonyl compounds to their respective α,β-unsaturated derivatives, and for effecting a number of other unique and useful synthetic transformations.[41]

Non-cyclic Iodyl Compounds or Iodylarenes ($ArIO_2$)

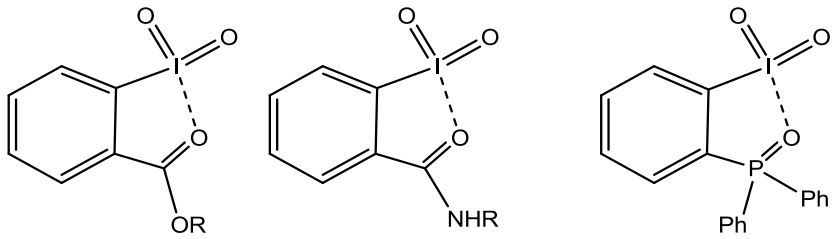
The noncyclic iodyl compounds are also known as iodoxy compounds. The aliphatic iodyl compounds, RIO_2, have found very limited practical application because of their low stability. Iodylalkanes can exist only at very low temperatures. Clark and coworkers reported the matrix isolation of unstable aliphatic iodyl derivatives in an argon matrix at14 - 16K.[41, 61-63]

There are numerous iodylarenes ($ArIO_2$) reported in the literature. They have a polymeric structure, which makes them insoluble in the majority of organic solvents, with the exception of DMSO. Infinite polymeric chains with strong I•••O secondary intermolecular interactions has been observed by X-ray crystal structural analysis of $PhIO_2$.[64-66] They are fairly stable thermally, but their melting points are, actually, their decomposition points, accompanied by explosion. They are explosive under excessive heating (more than 200^0C). A violent decomposition of $PhIO_2$ (dry sample) has been induced by scraping with a spatula. Therefore, they should be handled with appropriate precautions.[2]

Pseudocyclic Iodyl Compounds

The aryliodyl derivatives having a suitable substituent in the *ortho*-position to the iodyl group (IO_2) are called pseudocyclic iodyl compounds. The solubility of pseudocyclic iodyl compounds is much better than non-cyclic iodylarene derivatives because the iodyl group forms a strong intramolecular secondary bonding between the polyvalent iodine center and the oxygen atom of the *ortho*-substituent (Figure 2). Due to

this strong intramolecular secondary bonding, the polymeric nature of iodyl groups with *ortho*-substituent is partially disrupted.[65-67]



IBX-ester IBX-amide *Ortho*-Phosphoryl aryliodyl derivative

Figure 2: Formation of a strong intramolecular secondary bonding between the polyvalent iodine center and the oxygen atom in the *ortho*-substituent.

IBX or 2-iodoxybenzoic acid is one of the most important pentavalent pseudocyclic iodyl compounds **1**. The IUPAC name of this compound is 1-hydroxy-1-oxo-1*H*-1λ^5-benzo[*d*][1,2]iodoxol-3-one. In the solid state, it has a complex polymeric structure due to the formation of strong intermolecular secondary I•••O contacts and hydrogen bonding. Due to this nature, it is insoluble in most of the organic solvents except DMSO. It is a potentially dangerous compound because it explodes at about 233 ^{0}C.[68] It is used in the organic synthesis as an oxidizing agent.

Stevenson reported that the powder form of IBX is more reactive in the reaction with acetic anhydride than the macrocrystalline form. Therefore, it is more applicable for the preparation of DMP.[69] If the macrocrystalline IBX is treated with aqueous sodium hydroxide and then HCl, it gives the more reactive powder form (Figure 3).

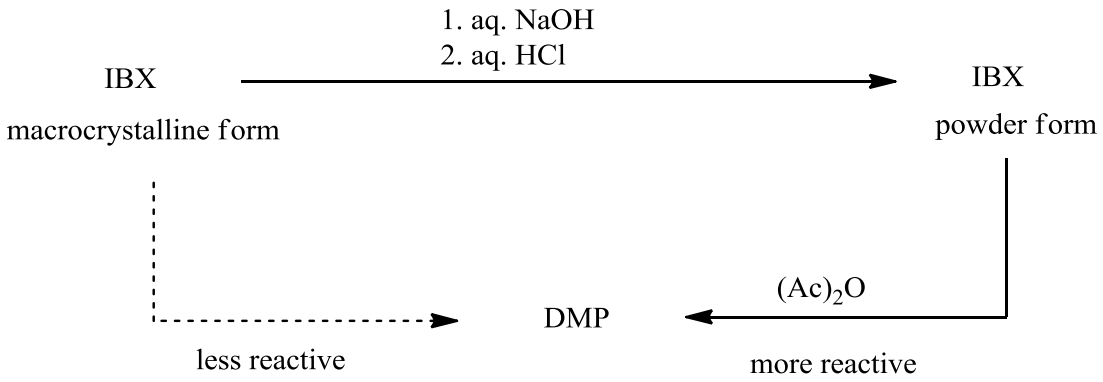
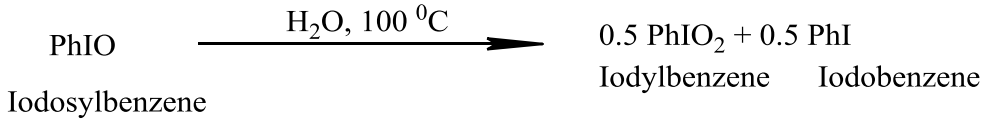


Figure 3: Comparison between macrocrystalline and powder forms of IBX to form DMP.

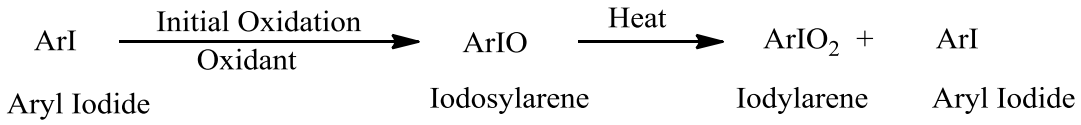
Preparation of Iodylarenes

Various methods for the preparation of iodylarenes have been reported. Willgerodt explored the first method for the preparation of iodylbenzene, $PhIO_2$, from the disproportionation of iodosylbenzene under steam distillation 100 years ago (Scheme 1).[70]



Scheme 1

The initial oxidation of iodoarenes, ArI, leads to iodosylarenes, ArIO, which then slowly disproportionate to ArI and $ArIO_2$ upon mild heating (Scheme 2).[71-73]



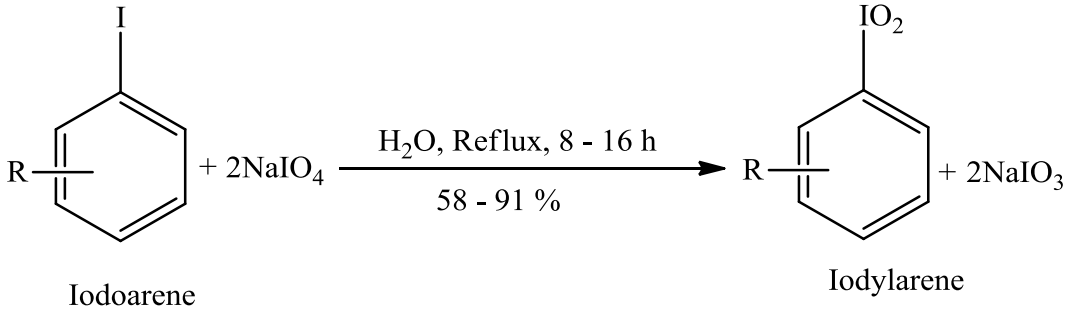
Scheme 2

Different oxidizing agents, such as sodium hypochlorite (NaClO),[71, 74] potassium bromate ($KBrO_3$),[75] dimethyldioxirane,[76] and Oxone®,[68, 77] have been used for the synthesis of various iodylarenes. Some of the results of these oxidizing agents are summarized in the following table (Table 1).

Table 1: Preparation of different iodylarenes by using various oxidizing agents.

Reactants	**Conditions**	**Yields (%)**
C_6H_5I	Oxone®, H_2SO_4, 0 °C, 4 h	72
C_6H_5I	$KBrO_3$, H_2SO_4, heating, 2 h	45
3-$NO_2C_6H_4I$	$KBrO_3$, H_2SO_4, heating, 2 h	46
4-BrC_6H_4I	$KBrO_3$, AcOH/H_2SO_4, heating, < 1 h	98
2-$CH_3O_3SC_6H_4I$	Dimethyldioxirane, CH_2Cl_2, 0 ^{0}C to rt, 8 h	89
2-*i*$PrO_2CC_6H_4I$	5% aq. NaOCl, dry ice, rt, 12 h	89
2-$Ph_2(O)PC_6H_4I$	5% aq. NaOCl, TBAB, H_2O/CH_2Cl_2, rt, 12 h	71

A few years ago, Skulski and coworkers explored a new method for the synthesis of different iodylarenes from corresponding iodoarenes employing a boiling aqueous solution of sodium periodate ($NaIO_4$) as an oxidant (Scheme 3, Table 2).[72]

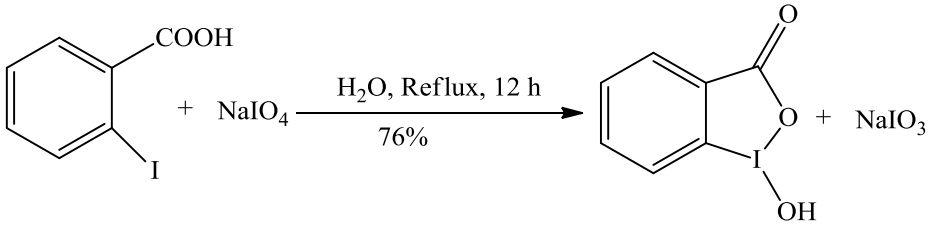


Scheme 3

Table 2: Preparative details and melting points of various iodylarenes (R-ArIO_2) from Scheme 3.[72]

S.N.	R	Time (h)	Crude Yield (%)	Melting Point or Dec. Point (^{0}C)
1.	H	8	86	235
2.	4-OMe	8	85	224
3.	2-Me	8	61	209
4.	3-Me	8	77	219
5.	4-Me	8	80	226
6.	4-F	12	91	262
7.	3-Cl	12	75	232
8.	4-Cl	12	80	248
9.	4-Br	16	73	241
10.	3-NO_2	8	85	233
11.	4-NO_2	16	58	230
12.	2-COOH	12	76	260
13.	3-COOH	12	89	250
14.	2-COONa	12	71	233
15.	4-COONa	16	88	240

In the case of 2-iodobenzoic acid, it was oxidized with boiling aq. $NaIO_4$ solution to give 2-iodosylbenzoic acid (1-hydroxy-1,2-benziodoxol-3(1*H*)-one) (Scheme 4).[72]

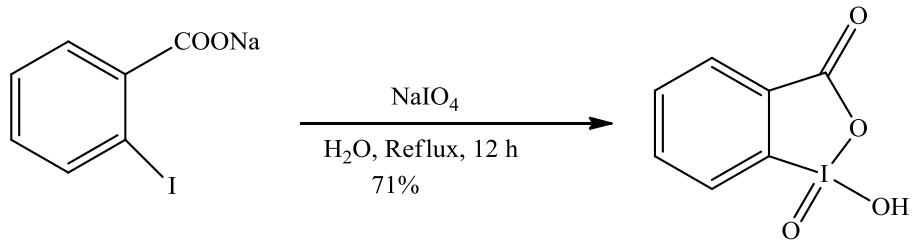


2-Iodobenzoic acid

1-Hydroxy-1,2-benziodoxol-3(1*H*)-one

Scheme 4

On the other hand, when the sodium salt of 2-iodobenzoic acid was treated with boiling aq. $NaIO_4$ solution, 2-iodylbenzoic acid (1-hydroxy-1,2-benziodoxol-3(1*H*)-one-1-oxide) was isolated (Scheme 5).[72]

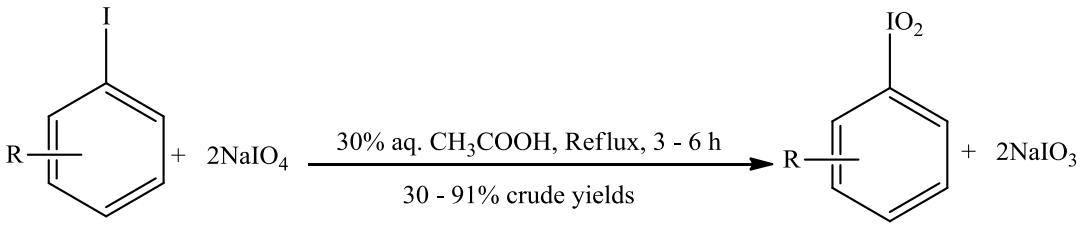


2-Iodo sodium benzoate

1-Hydroxy-1,2-benziodoxol-3(1*H*)-one-1-oxide (IBX)

Scheme 5

Skulski and coworkers also reported a new improved method for the preparation of iodylarenes from the oxidation of various iodoarenes using sodium periodate ($NaIO_4$) and boiling 30 % aqueous acetic acid (Scheme 6).[73] This protocol allows shortening the time of reaction from 8 -16 hours to 3 - 6 h with good yields (Table 3).[73]



Iodoarene

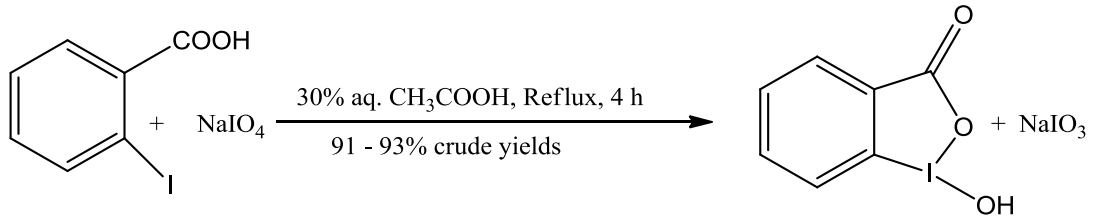
Iodylarene

Scheme 6

Table 3: Preparative details and melting points of various iodylarenes (R-ArIO_2) from Scheme 6.[73]

S.N.	R	Time (h)	Crude Yield (%)	Melting Point or Dec. Point (^{0}C)
1.	H	4	76	235
		6	84	
2.	2-Me	4	70	206-207
3.	3-Me	3(+1)	75	218
4.	4-Me	3(+1)	84	227
5.	2-Cl	5(+1)	40	205-206
6.	3-Cl	3(+1)	75	231
7.	4-Cl	3(+1)	87	240
8.	4-Br	3(+1.5)	81	236
9.	2-NO_2	3(+1)	54	212
10.	3-NO_2	3(+1.5)	84	215
11.	4-NO_2	3(+1)	58	214
12.	3-F	4	91	226-227
13.	4-F	2(+1)	87	245
14.	2,4-$(CH_3)_2$	4	54	194
15.	2,4-Cl_2	3(+1)	30	223

In the case of 2-iodobenzoic acid, it was refluxed with sodium periodate in 30% (v:v) aq. acetic acid to give the colorless, 2-iodosylbenzoic acid (Scheme 7).[73]

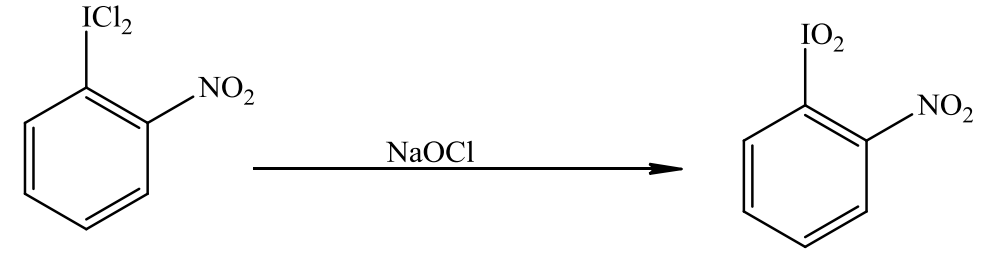


2-Iodobenzoic acid

1-hydroxy-1,2-benziodoxol-3(1*H*)-one

Scheme 7

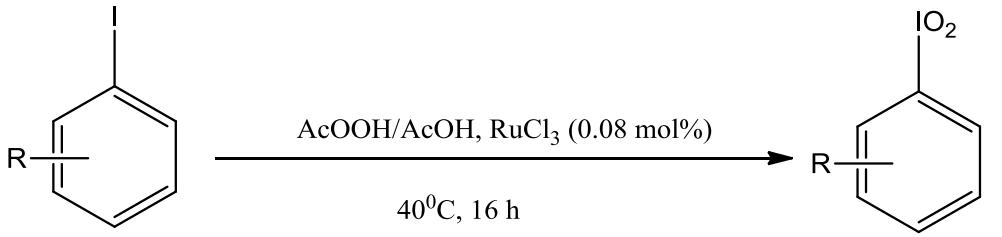
A few years ago, Nikiforov and coworkers reported a new method for the synthesis of *o*-iodylnitrobenzene from *o*-nitroiodobenzene dichloride in the presence of sodium hypochlorite (NaOCl) (Scheme 8).[78]



o-Nitroiodobenzene dichloride *o*-Iodylnitrobenzene

Scheme 8

Recently, Zhdankin *et al.* reported a new technique for the synthesis of various iodylarenes from the catalytic oxidation of corresponding iodoarenes using ruthenium trichloride ($RuCl_3$) in the presence of peracetic acid (AcOOH) (Scheme 9).[79]

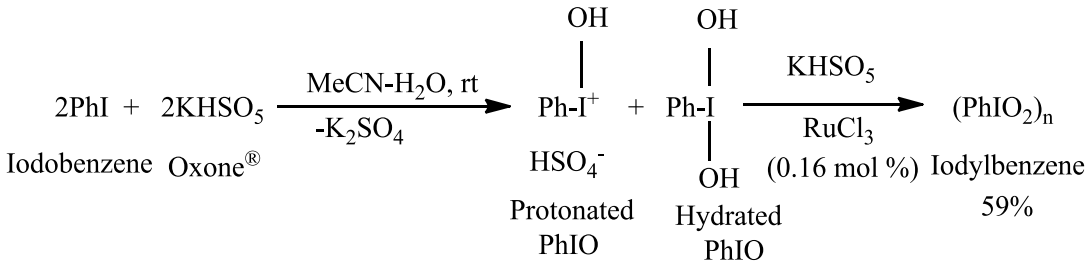


Iodoarene Iodylarenes

R = **H** (89%), **4-CH_3** (94%), **2-CH_3** (64%), **2,4,6-CH_3** (0%), **2-OCH_3** (23%), **2-$CH(CH_3)_2$** (36%), **2-Cl** (89%), **3-Cl** (91%), **4-Cl** (90 %), **4-Br** (96 %), **4-F** (87%), **4-CF_3** (83%), **3,5-CF_3** (91%), **2-COOH** (85 %) 1-hydroxy-(1H)-benzo-1,2-iodoxol-3-one)

Scheme 9

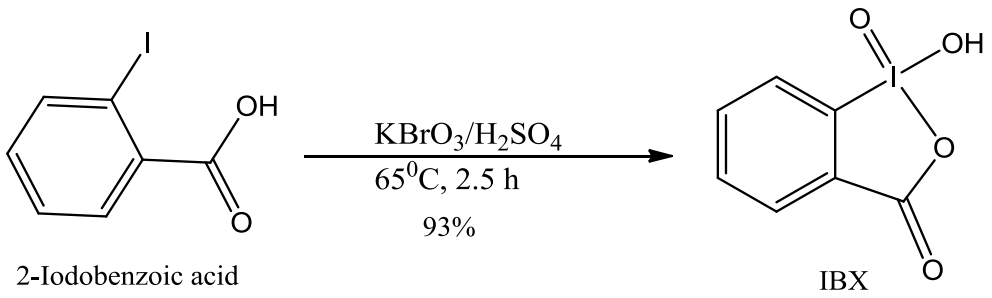
Very recently, Zhdankin *et al.* reported a new method for the preparation of iodylbenzene using Oxone® as an oxidizing agent, as well as aqueous ruthenium chloride as a catalyst, in the presence of acetonitrile and water with 1:1 ratio.[80] In this technique, the reaction starts with the initial oxidation of iodoarenes to the iodine (III) species (protonated PhIO and hydrated PhIO) by Oxone® at room temperature which is further converted to iodylbenzene in 59% yield via a ruthenium catalyzed oxidation with Oxone® (Scheme 10).



Scheme 10

Preparation of IBX (Five-membered Iodine (V) Heterocycles: Benzoidoxole Diodes)

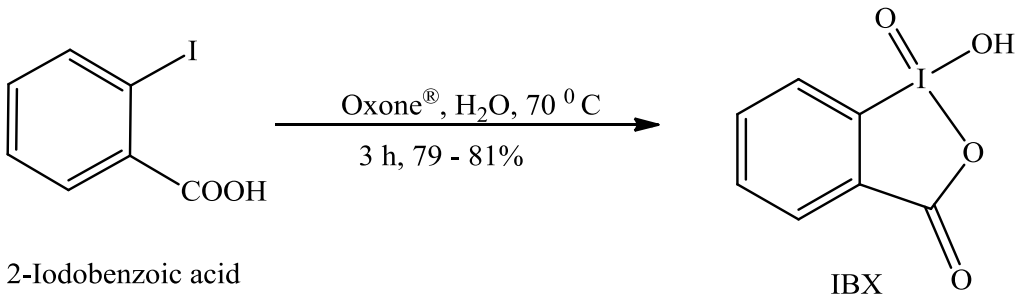
Boeckman *et al.* reported an improved procedure for the preparation of IBX from 2-iodobenzoic acid using potassium bromate and sulfuric acid at 65 ^{0}C (Scheme 11).[81-82] But this method is less green because the $KBrO_3$ is classified as a carcinogen, and the liberation of bromine vapor from the reaction mixture causes personal and environmental hazards.



Scheme 11

Oxone® is a water soluble inorganic triple salt of two moles of potassium peroxymonosulfate ($2KHSO_5$), one mole of potassium bisulfate ($KHSO_4$), and one mole of potassium sulfate (K_2SO_4). The general composition of Oxone® is written as $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. The active component of this salt is potassium peroxymonosulfate ($KHSO_5$). Oxone® has been used as an oxidizing agent in disinfection of swimming pools, chemical disinfectant, and degradation of organic contaminants.[83, 84] It only produces innocuous by-products, such as sodium or potassium sulfates.[84] According to the previous report, Oxone® has been used as a green and mild oxidizing agent for the synthesis of various hypervalent compounds.[68, 77, 80]

One of the best new methods for the preparation of IBX involves the oxidation of 2-iodobenzoic acid with Oxone® in the presence of water at 70 ^{0}C, which was reported by Santagostino and coworkers (Scheme 12).[68] This method is greener than previous techniques because Oxone® does not have any health and environmental hazards.



2-Iodobenzoic acid

Scheme 12

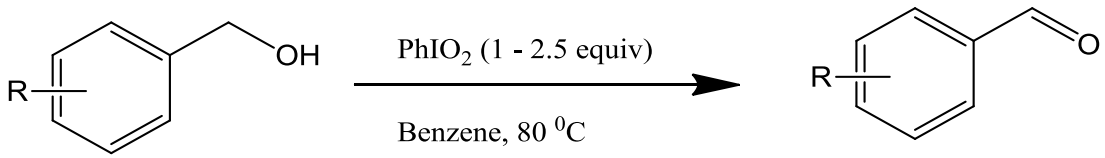
Application of Iodylarenes, $ArIO_2$

A. Oxidizing and Dehydrogenating Agents

Iodylarenes have found some practical applications as oxidizing agents. Although several noncyclic iodylarenes have been reported in the literature, iodylbenzene $PhIO_2$ is the most established reagent.[71]

1. Oxidation of Alcohols Using Iodylbenzene ($PhIO_2$) (Without Catalyst)

Barton and co-workers developed the oxidation of benzyl alcohol in the presence of iodylbenzene ($PhIO_2$) to give the corresponding aldehydes in good yields (Scheme 13a & 13b).[85] $PhIO_2$ is also a good oxidizing agent for the conversion of glycols to the corresponding carbonyl derivatives (Scheme 13).[85]

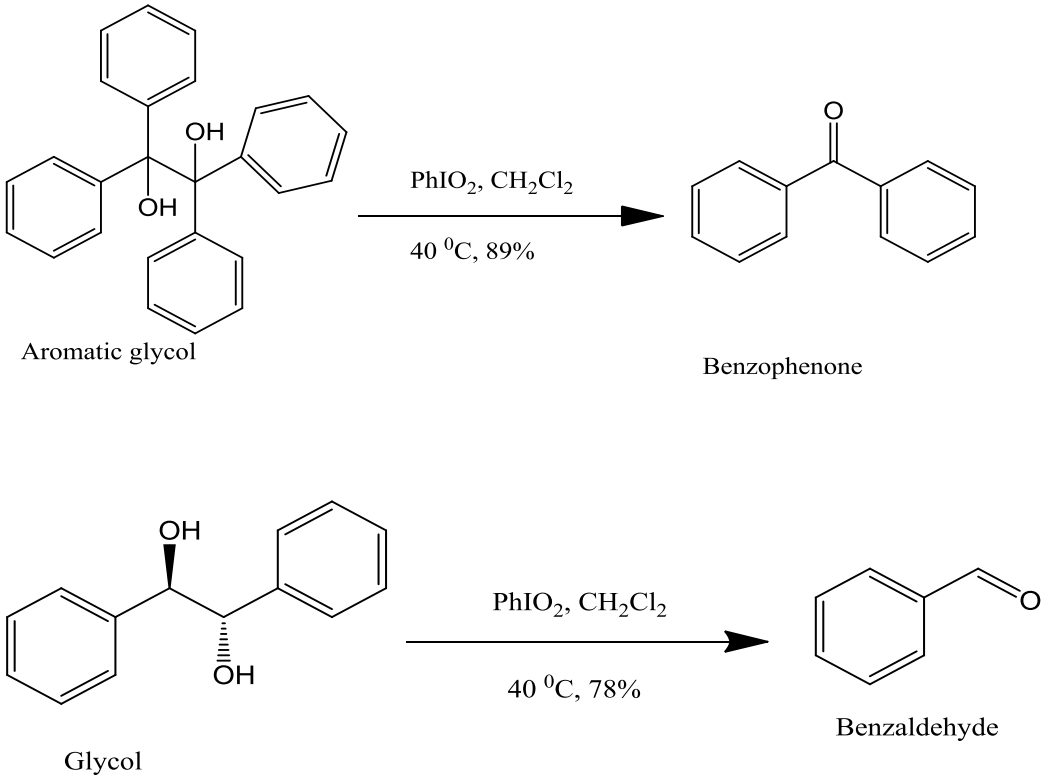


Alcohol

R = H, 4-NO_2, 4-*t*-Bu

Aldehyde

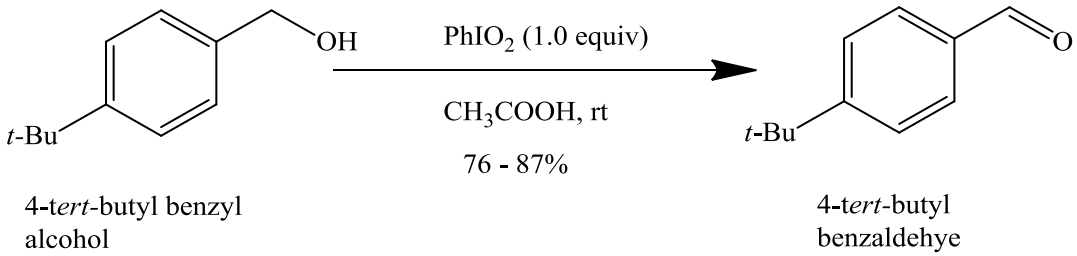
Scheme 13a



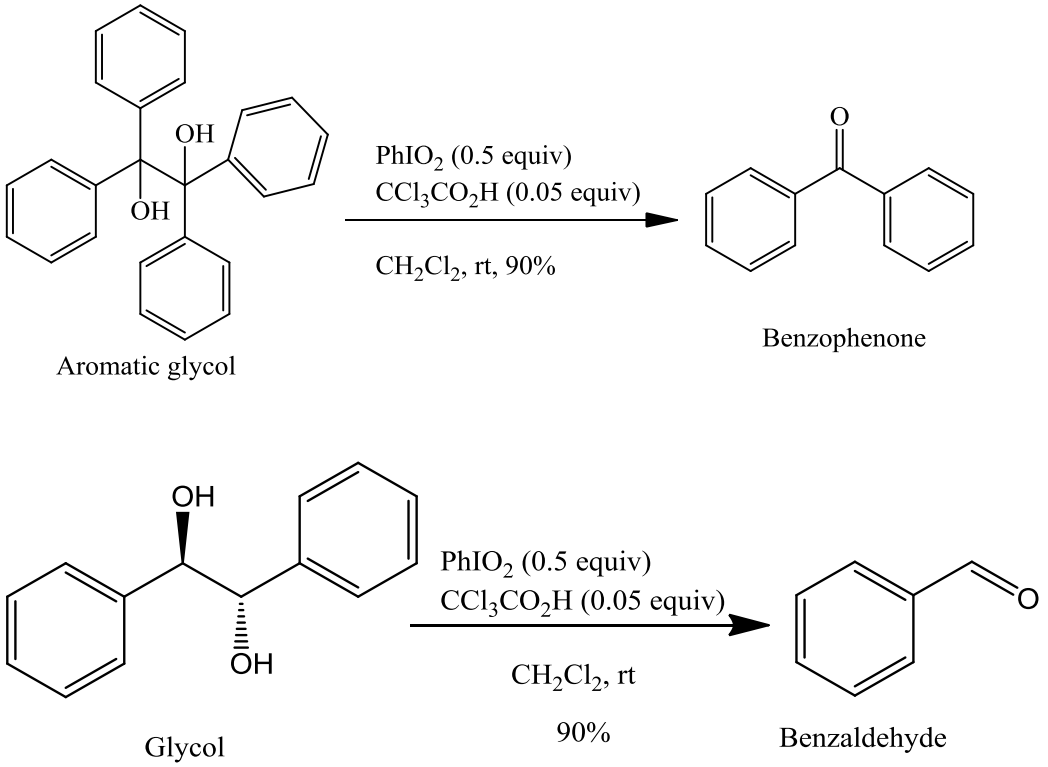
Scheme 13b

2. Catalytic Oxidation of Alcohols Using Iodylbenzene ($PhIO_2$)

The benzylic alcohols, or glycols, are also oxidized using iodylbenzene in the presence of carboxylic acids as catalysts (Scheme 14a & 14b).[85-87]

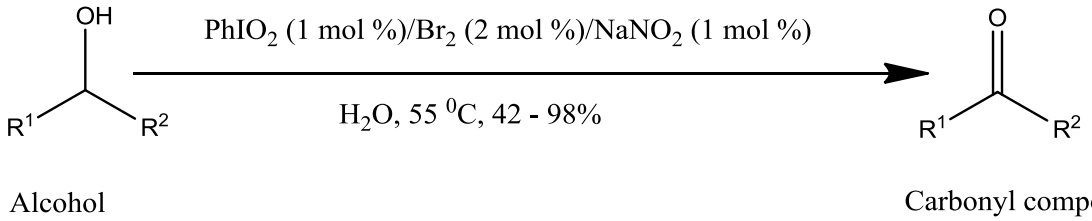


Scheme 14a



Scheme 14b

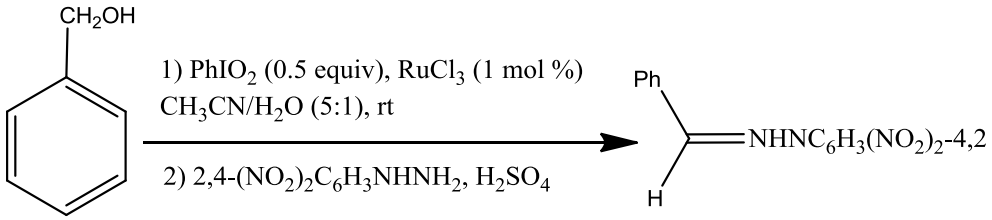
Recently, an effective catalytic system for the selective aerobic oxidation of alcohols in water has been developed. In this method, alcohol is treated with $PhIO_2$, bromine, and sodium nitrite in the presence of water at 55 ^{0}C to form a carbonyl compound (Scheme 15).[86]



Alcohol Carbonyl compound

Scheme 15

The oxidation of benzylic alcohol is also possible using iodylbenzene in the presence of ruthenium chloride as a catalyst. In this reaction, the benzylic alcohol is first treated with $PhIO_2$ in the presence of $RuCl_3$ and then with 2,4-dinitrophenylhydrazine to give 2,4-dinitrophenylhydrazone derivatives in high yield (Scheme 16).[87]



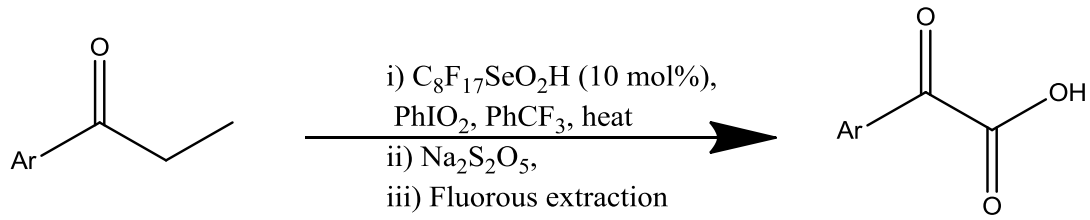
Benzyl alcohol

2,4-dinitrophenylhydrazone derivatives of benzaldehyde
92%

Scheme 16

3. Oxidation of Aryl Alkyl Ketone Using Iodylbenzene

Aryl alkyl ketone is oxidized with iodoxybenzene as an oxidant in the presence of perfluoro-octylseleninic acid used as a catalyst to obtain the corresponding ketoacids (Scheme 17).[88] In this reaction, the oxidation occurs adjacent to the carbonyl group that gives ketoacid.



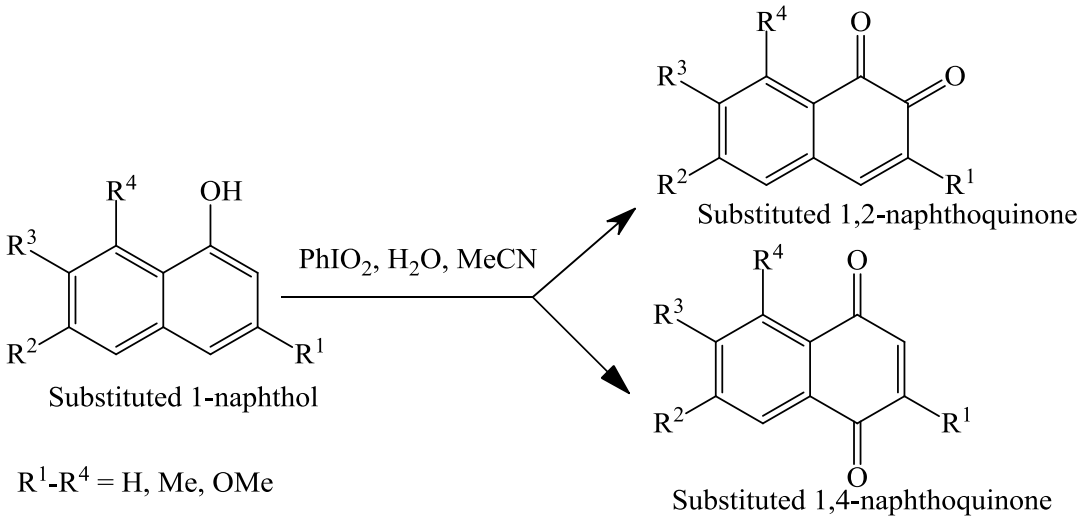
Aryl Alkyl Ketone

Ketoacid
70 - 90%

Scheme 17

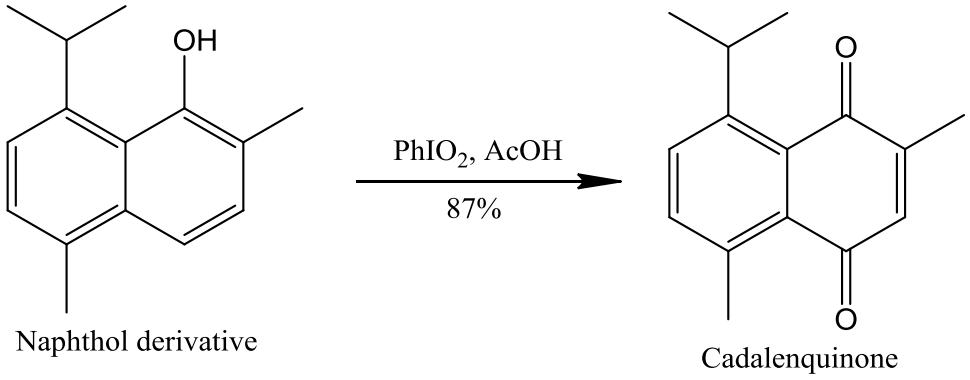
4. Oxidation of Activated Aromatic Rings Using $PhIO_2$

When activated aromatic rings are oxidized with iodylbenzene in an aqueous acetonitrile or acetic acid media, quinones are obtained (Scheme 18).[41]



Scheme 18

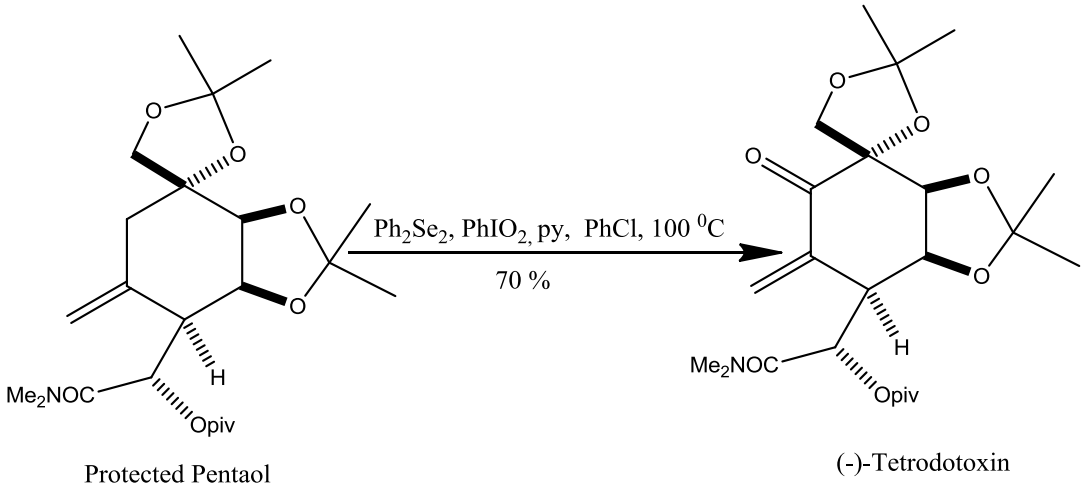
Cadalenquinone was synthesized from activated naphthol by using the above protocol (Scheme 19).[41]



Scheme 19

5. Stereoselective Synthesis of (-)-Tetrodotoxin by the Oxidation of the Protected Pentaol Using $PhIO_2$

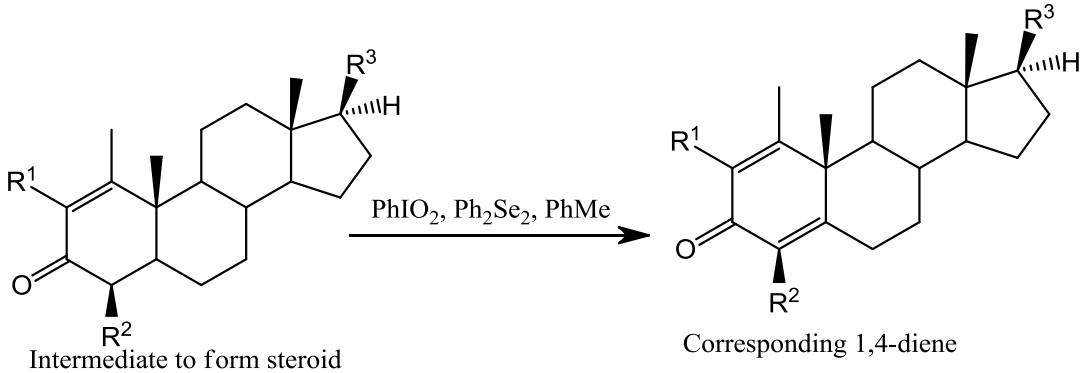
Du Bois and coworkers reported a stereoselective synthesis of (-)-tetrodotoxin by the oxidation of the protected pentaol with $PhIO_2/Py_2Se_2$ (Scheme 20).[89]



Scheme 20

6. Dehydrogenation in the Regioselective Synthesis of Polymethylated Steroids

Kuenzer *et al.* reported a dehydrogenation protocol in the regioselective synthesis of ring A of polymethylated steroids. When an intermediate is dehydrogenated using $PhIO_2/Ph_2Se_2/PhMe$, a corresponding 1,4-diene is formed. They are the key precursors to the synthesis of target steroids (Scheme 21).[90]



Intermediate to form steroid

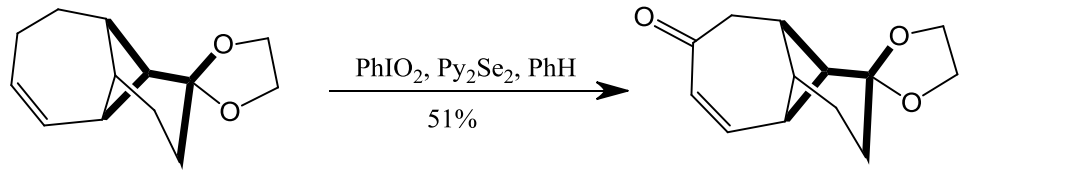
Corresponding 1,4-diene

R^1 = H, R^2 = Me, R^3 = OTBDMS; R^1 = Me, R^2 = H, Me, R^3 = OAc

Scheme 21

7. Oxidation of Ketone Protected Spiro-Compound Using $PhIO_2$

In the synthesis of tricyclo[5.4.0.$0^{2,8}$]undeca-3,5,9-triene, the ketone protected spiro-compound is oxidized using 2-pyridyldiselenide, iodylbenzene and toluene (Scheme 22).[91] The product thus obtained is an unsaturated ketone. In this compound, there are two mutually perpendicular π-systems.



Ketone Protected Spiro-Compound

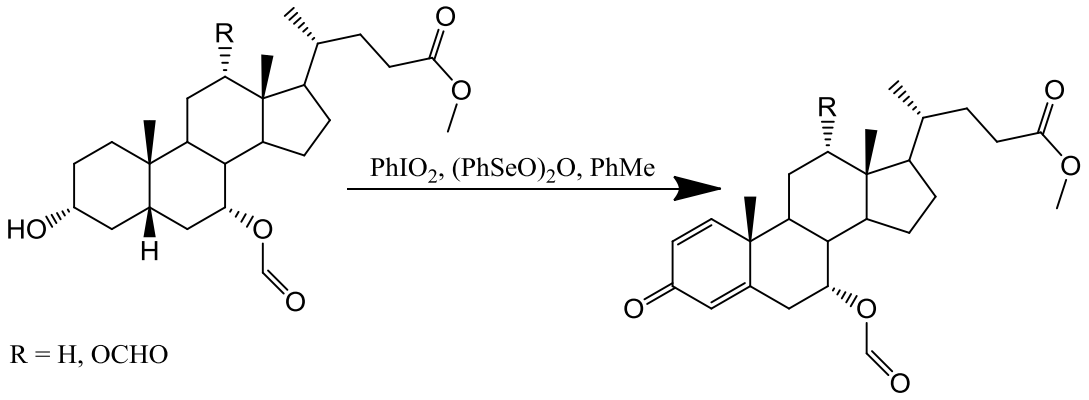
Unsaturated Ketone of Spiro-Compound

Scheme 22

8. Oxidation-dehydrogenation of 3α-hydroxy-5β-bile Acid Formyl Ester Using $PhIO_2$

Iida *et al.* reported a new method for the synthesis of allochenodeoxycholic and allocholic acids from the corresponding cholic acid using iodylbenzene.[92] When 3α-

hydroxy-5β-bile acid formyl ester is treated with $PhIO_2/(PhSeO)_2$ in the presence of toluene, oxodiene is formed (Scheme 23). This is the oxidation-dehydrogenation reaction.



R = H, OCHO

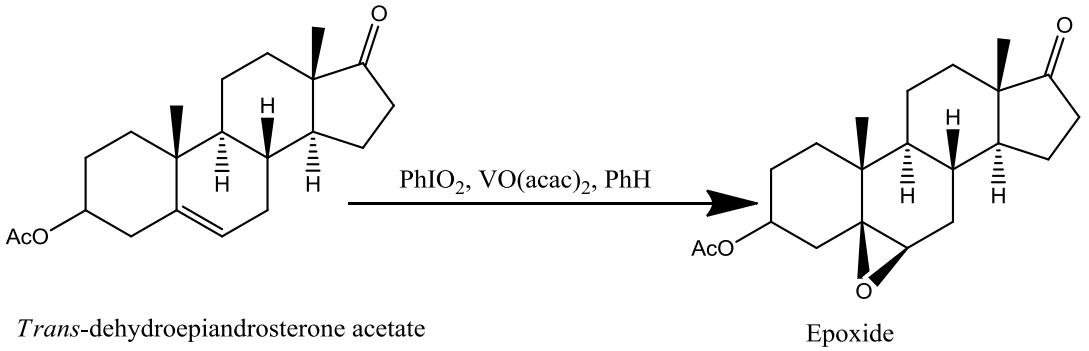
3α-hydroxy-5β-bile acid formyl ester

Oxodiene

Scheme 23

9. Epoxidation of Δ5-Steroids Using $PhIO_2$

Barret *et al.* reported that *trans*-dehydroepiandrosterone acetate is oxidized with iodylbenzene in the presence of vanadyl bis(acetylacetonate) [$VO(acac)_2$] and toluene to give corresponding epoxide (Scheme 24).[41]



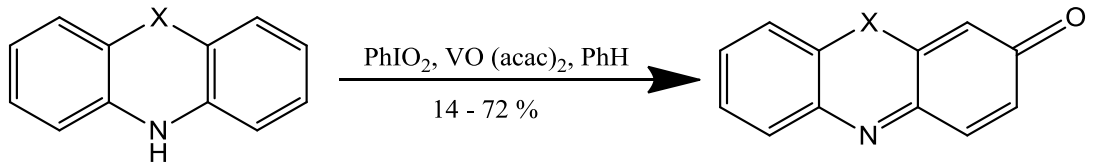
Trans-dehydroepiandrosterone acetate

Epoxide

Scheme 24

10. Oxidation of Tricyclic Scaffold Using $PhIO_2$

Barret *et al.* again reported a new route for the synthesis of quinine imines.[93] When the tricyclic scaffold is oxidized with $PhIO_2$ in the presence of $VO(acac)_2$, quinine imines are obtained in 14 - 72% yield (Scheme 25).



X = S, O, CH_2CH_2

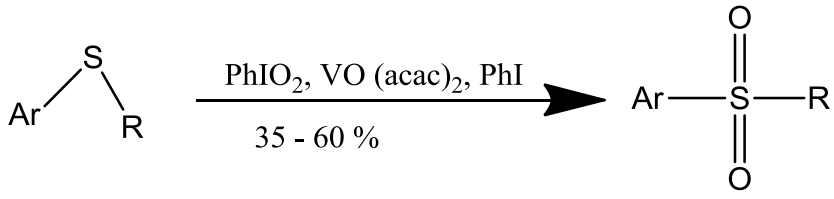
Tricyclic scaffold

Quinine imines

Scheme 25

11. Oxidation of Aryl Alkyl Sulfides Using $PhIO_2$

According to Barret *et al.* aryl alkyl sulfides are oxidized with $PhIO_2$ in the presence of $VO(acac)_2$ to give sulfones in 35 - 60% (Scheme 26).[94]



Aryl alkyl sulfide

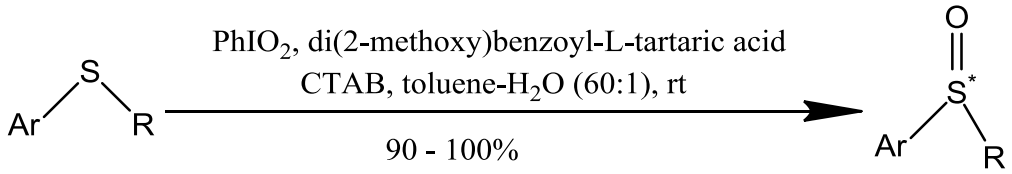
Sulfone

Ar = Ph, 4-FC_6H_4
R = Me, $MeO(CO)CH_2$, $Ph(CO)CH_2$, CH_2CN, $PhCH_2$

Scheme 26

Kita and co-workers reported a catalytic asymmetric oxidation of aryl alkyl sulfides using iodylbenzene in the presence of chiral tartaric acid derivatives.[32] Under these

conditions, sulfides are oxidized to sulfoxides in high yield with moderate to good enantioselectivity (Scheme 27).



Aryl alkyl sulfide

Sulfoixde

up to 72% ee

R = Me or Et

Ar = 4-$MeOC_6H_5$, 4-MeC_6H_5, 4-$NO_2C_6H_5$, 4-CNC_6H_5, 4-BrC_6H_5, 3-$NO_2C_6H_5$, 2-naphthyl, etc.

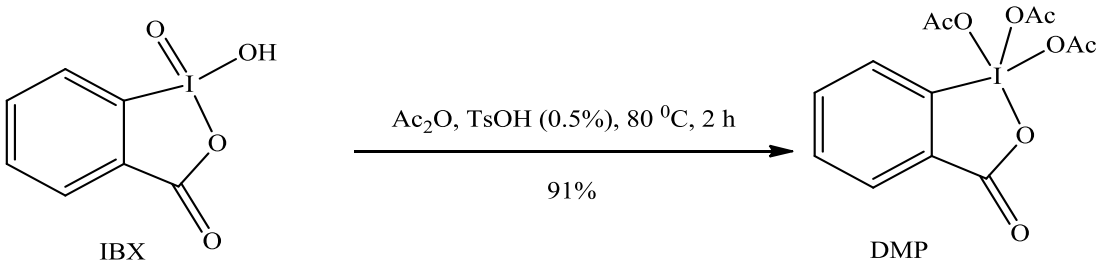
Scheme 27

B. Biological Application of Iodylarenes[95]

Protein tyrosine phosphates (PTP) inhibition activities of different iodylarenes, such as 1-iodoxy-4-nitrobenzene, DMP, 4-iodoxybenzoic acid, 3-iodoxybenzoic acid, 4-iodoxyimidazole, 1-iodoxy-3-nitrobenzene, IBX, 1,4-diiodoxybenzene, 4-iodoxytoluene, and iodoxybenzene, have been reported. The activities of iodylarenes are more effective than vanadates. The vanadium compounds are used as antidiabetic agents due to their PTP inhibition ability. Due to the high toxicity of vanadium compounds, the syntheses of different iodylarenes are very important for the design of antidiabetic drugs.

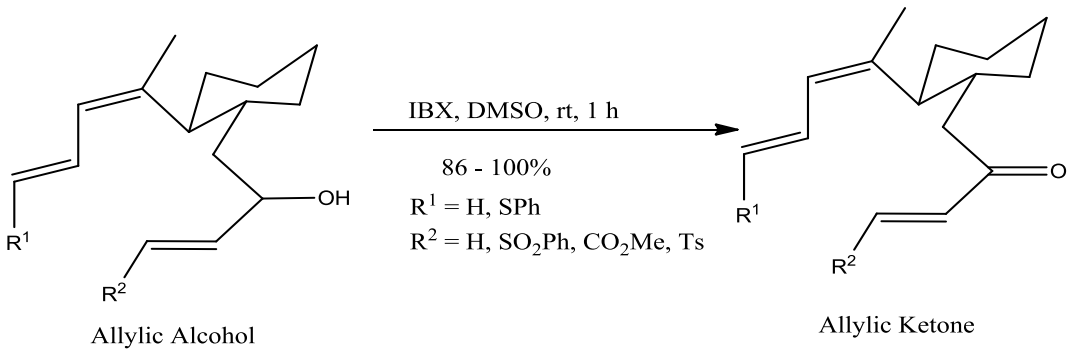
C. Application of IBX

IBX is used as a starting material for the preparation of Dess-Martin periodinane (DMP) (Scheme 28). In this reaction, acetic anhydride is applied as a reagent in the presence of *p*-toluenesulfonic acid (TsOH) at 70 ^{0}C.[96]



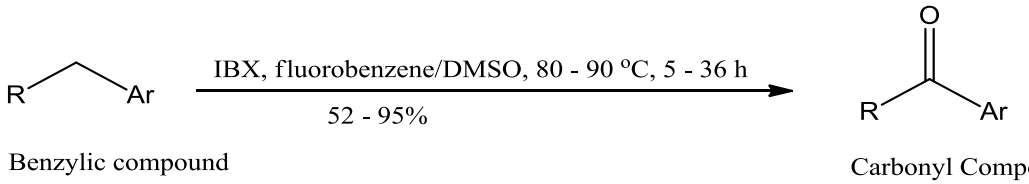
Scheme: 28

IBX is used as a mild and selective oxidizing agent for the oxidation of various alcohols to carbonyl compounds.[41] For an example, the following allylic alcohol is selectively oxidized by IBX to ketone in high yield (Scheme 29).



Scheme 29

IBX is also an efficient and selective reagent for the oxidation of benzylic positions without overoxidation (Scheme 30).[97]



Ar = Ph, 4-*t*-BuC_6H_4, 2-MeC_6H_4, 3-IC_6H_4, 4-BrC_6H_4,3,4-$(MeO)_2C_6H_3$, 2-PhC_6H_4, 4-(4-pyridyl)C_6H_4, etc.
R = H, C_3H_7, etc.

Scheme 30

Current Project

Due to the limited solubilities of iodylarenes, there has not been much research on them reported. Although iodylbenzene and IBX are used as mild and highly selective reagents for the oxidation of alcohols to carbonyl compounds, as well as for a variety of other synthetically useful oxidative transformations, the effective synthesis and broad applications of other iodylarenes are still required.

According to many review papers,[1-46] the melting points of various iodoxyarenes are generally explosive.[68, 98] Due to this nature, these compounds may be potentially energetic. They may have great potential scopes as propellants, explosives, and pyrotechnics. There are many organic compounds such as nitro compounds, and azides, which are usually employed as explosives, propellants, and pyrotechnics, but nitro aromatic compounds are acutely toxic and mutagenic, azides are also toxic and less stable compounds, and some other others compounds are synthetically tough due to the ring strain.[99] Iodylarenes are highly stable, readily accessible synthetically, environmentally less hazardous, and inexpensive. That is why, the iodyl ($-IO_2$) group may be an important class of highly energetic materials and there is a need for more thorough research.[100]

This project is mainly focused on the synthesis of novel iodylarenes as well as the new techniques to synthesize the various iodoxyarenes. We use Oxone® and potassium periodate (KIO_4) as oxidizing agents for the preparation of different iodyl compounds. Both are commercially available materials, but we generally focus on Oxone® because it is highly soluble in water as well as it is more stable than KIO_4.

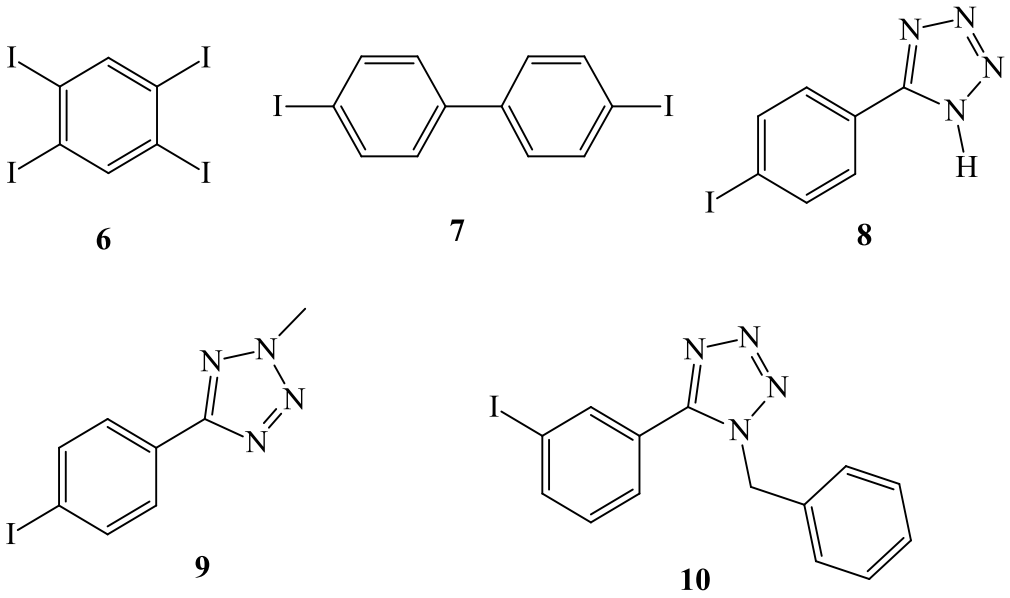
CHAPTER II

EXPERIMENTAL

General Methods

All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL AS 500 MHz NMR or a 300 MHz NMR using $CDCl_3$ and DMSO – d_6 as solvents. All chemical shifts are reported in ppm. All IR spectra were collected on a Varian 7000 FT-IR. The melting points were recorded on Fisher-Johns Melting Point Apparatus. The mixtures of two insoluble liquid solutions were separated by separatory funnel. All commercial reagents were ACS reagent grade and used without further purification. All other reagents and solvents were of commercial quality from freshly opened containers. The solvents were evaporated using a Buchi rotary evaporator under reduced pressure. Thin-layer chromatography was performed using silica pre-coated TLC plates. Flash column chromatography was performed using 230 – 400 mesh silica gel.

Some of the starting materials, such as 1,2,4,5-tetraiodobenzene[101, 102] **6**, 4,4'-diiodobiphenyl[103] **7**, 5-(4-iodophenyl)-1*H*-tetrazole[104] **8**, 5-(4-iodophenyl)-2-methyl-2*H*-tetrazole[104] **9**, and 5-(3-iodophenyl)-1-(phenyl methyl)-1*H*-tetrazole[105] **10**, were prepared in our laboratory by the reported methods. Although the compounds **6**, **7**, **8**, and **9** are commercially available, they were synthesized in our lab to minimize the cost of our project.



A. Synthesis of Iodylarenes from Iodoarenes

1. 3-iodylbenzonitrile

Method I:

Potassium periodate (KIO_4) (2.2 mmol, 0.506 g, 10% excess) was stirred with 3 mL boiling 30% (v/v) aq. acetic acid in a 50 mL round bottom flask and 3-iodobenzonitrile (1.0 mmol, 0.2290 g) was added into the mixture with stirring. Two drops of toluene were also added into the flask to prevent the accumulation of the reaction mixture in the reflux condenser. The reaction mixture was stirred vigorously and refluxed at 118 ^{0}C. After 3 hours, boiling water (3 mL) was added into the flask with stirring and heating to reflux was continued for one additional hour. At this point, ice water (40 mL) was poured into the flask and the temperature was reduced to room temperature. Then the mixture was filtered to separate the white precipitate. The white solid residue was first washed with cold DI water (3 × 10 mL) to remove the water soluble impurities and then by

acetone (3 × 10 mL) to remove the unreacted starting material and toluene. The white solid of 3-iodylbenzonitrile was air-dried in the dark to afford 170 mg (65%). Then the crude product was further recrystallized from boiling water to obtain the pure product (138 mg, 53%) for the analytical tests.

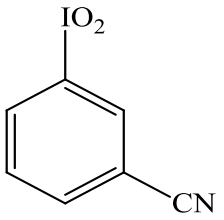
Method II:

Potassium periodate (KIO_4) (2.2 mmol, 0.506 g, 10% excess) was stirred at reflux with 3 mL DI water in a 50 mL round bottom flask and 3-iodobenzonitrile (1.0 mmol, 0.2290 g) was added into the mixture with stirring. Two drops of toluene were also added into the flask to prevent the accumulation of the reaction mixture in the reflux condenser. The reaction mixture was stirred vigorously and refluxed at 100 ^{0}C. After 7 hours, ice water (40 mL) was poured into the flask and the temperature was cooled to room temperature. Then the mixture was filtered to separate the white precipitate. The white solid residue was first washed by cold DI water (3 × 10 mL) to remove the water soluble impurities and then by acetone (3 × 10 mL) to remove the unreacted starting material and toluene. The white solid of 3-iodylbenzonitrile was air-dried in the dark to afford 183 mg (70%). Then the crude product was further recrystallized from boiling water to obtain pure product (157 mg, 60%) for the analytical tests.

Method III:

A mixture of 3-iodobenzonitrile (1.0 mmol, 0.2290 g), Oxone® (0.54 mmol, 0.33 g), and DI water (4 mL) was stirred vigorously in a 50 mL closed round bottom flask at room temperature. After vigorous stirring for 30 minutes, the second portion of Oxone® (0.52 mmol, 0.32 g) was added into the mixture. After vigorous stirring for another 30

minutes, the last portion of Oxone® (0.18 mmol, 0.11 g) was added into the mixture. Then the reaction mixture was heated with vigorous stirring at about 90 ^{0}C. After 2 hours, the flask was cooled by the addition of ice water (40 mL) and filtered to separate the white precipitate. The white solid residue was first washed with cold DI water (3 × 10 mL) to remove the water soluble impurities and then with acetone (3 × 10 mL) to remove the unreacted 3-iodobenzonitrile. Then the white solid of 3-iodylbenzonitrile was air-dried in the dark to afford 229 mg (88%), dec. point 192 – 199 ^{0}C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.32 – 8.30 (m, 2H), 8.05 (d, J = 7.45 Hz, 1H), 7.82 (t, J = 7.16 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 153.1, 135.7, 132.3, 131.3, 131.0, 119.1, 112.45. IR (neat) 3074, 2238 (-C≡N), 1552, 1467, 1407, 1159, 1084, 1060, 995, 790, 762, 741, 709 (-IO_2), 669 cm^{-1}.



3-iodylbenzonitrile

2. 4-iodylbenzonitrile[105]

Method I:

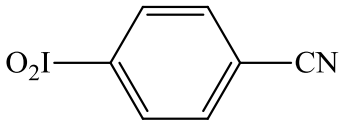
Potassium periodate (KIO_4) (2.2 mmol, 0.506 g, 10% excess) was stirred at reflux with 3 mL boiling DI water in a 50 mL round bottom flask and 4-iodobenzonitrile (1.0 mmol, 0.2290 g) was added into the mixture with stirring. Two drops of toluene were also added into the flask to prevent the accumulation of the reaction mixture in the reflux

condenser. The reaction mixture was stirred vigorously and heated at 100 ^{0}C. After 7 hours, ice water (40 mL) was poured into the flask and the temperature was reduced to room temperature. Then the mixture was filtered to separate the white precipitate. The white solid residue was first washed by cold DI water (3 × 10 mL) to remove the water soluble impurities and then by acetone (3 × 10 mL) to remove the unreacted starting material and toluene. The white solid of 4-iodylbenzonitrile was air-dried in the dark to afford 99 mg (38 %). Then the crude product was further recrystallized from boiling water to obtain pure product (78 mg, 30%) for the analytical tests.

Method II:

A mixture of 4-iodobenzonitrile (1.0 mmol, 0.2290 g), Oxone® (0.54 mmol, 0.33 g), and DI water (4 mL) was stirred vigorously in a 50 mL closed round bottom flask at room temperature. After vigorous stirring for 30 minutes, the second portion of Oxone® (0.52 mmol, 0.32 g) was added into the mixture. After vigorous stirring for another 30 minutes, the last portion of Oxone® (0.18 mmol, 0.11 g) was added into the mixture. Then the reaction mixture was heated with vigorous stirring at about 90 ^{0}C. After 2 hours, the flask was cooled by the addition of ice water (40 mL) and filtered to separate the white precipitate. The white solid residue was first washed with cold DI water (3 × 10 mL) to remove the water soluble impurities and then with acetone (3 × 10 mL) to remove the unreacted 4-iodobenzonitrile. Then the white solid of 4-iodylbenzonitrile was air-dried in the dark to afford 240 mg (92%), dec. point 190 – 198 ^{0}C (lit.[105] mp 174 ^{0}C). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.03 (d, J = 8.59 Hz, 2H), 7.65 (d, J = 8.59 Hz, 2H). ^{13}C

NMR (125 MHz, DMSO-d_6): δ 157.1, 133.6, 128.5, 119.1, 114.5. IR (neat) 3083, 2238 (-C≡N), 1618, 1610, 1480, 1391, 1046, 1012, 835, 823, 794, 766, 713 (-IO_2) cm^{-1}.



4-iodylbenzonitrile

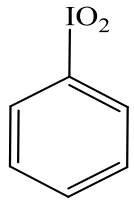
3. 1,4-diiodylbenzene[95]

A mixture of 1,4-diiodobenzene (1.0 mmol, 0.3299 g), Oxone® (1.08 mmol, 0.66 g), and DI water (7 mL) was stirred vigorously in a 50 mL closed round bottom flask at room temperature. After stirring for 30 minutes, the second portion of Oxone® (1.04 mmol, 0.64 g) was added into the mixture. After vigorous stirring for another 30 minutes, the last portion of Oxone® (0.36 mmol, 0.22 g) was added into the mixture. Then the reaction mixture was heated with vigorous stirring at about 90 ^{0}C. After 3 hours, the flask was cooled by the addition of ice water (40 mL) and filtered to separate the white precipitate. The white solid residue was first washed with cold DI water (3 × 15 mL) to remove the water soluble impurities and then with acetone (3 × 15 mL) to remove the unreacted 1,4-diiodobenzene. Then the white solid of 1,4-diiodylbenzene was air-dried in the dark to afford 275 mg (70%), dec. point 215 – 223 ^{0}C. IR (neat) 3026, 1380, 1282, 994, 798, 773, 758, 700 (-IO_2) cm^{-1}.

1,4-diiodylbenzene

4. Iodylbenzene[72, 73]

A mixture of iodobenzene (1.0 mmol, 0.2040 g), Oxone® (0.54 mmol, 0.33 g), and DI water (4 mL) was stirred vigorously in a 50 mL closed round bottom flask at room temperature. After stirring for 30 minutes, the second portion of Oxone® (0.52 mmol, 0.32 g) was added into the mixture. After vigorous stirring for another 30 minutes, the last portion of Oxone® (0.18 mmol, 0.11 g) was added into the mixture. Then the reaction mixture was heated with vigorous stirring at about 90 ^{0}C. After 3 hours, the flask was cooled by the addition of ice water (35 mL) and filtered to separate the white precipitate. The white solid residue was first washed with cold DI water (3 × 10 mL) to remove the water soluble impurities and then with acetone (3 × 10 mL) to remove the unreacted iodobenzene. Then the white solid of iodylbenzene was air-dried in the dark to afford 155 mg (66%), dec. point 230 – 237 ^{0}C (lit. [72, 73] mp 235 – 236 ^{0}C). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.01 – 7.99 (m, 2H), 7.64 – 7.57(m, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 151.8, 132.4, 130.0, 127.5. IR (neat) 3052, 1470, 1441, 1043, 919, 770, 756, 729, 712 (-IO_2), 678 cm^{-1}.

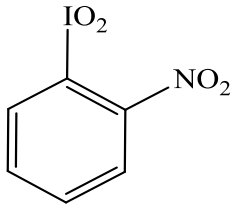


Iodylbenzene

5. 2-iodylnitrobenzene[73]

A mixture of 2-iodonitrobenzene (1.0 mmol, 0.2490 g), Oxone® (0.54 mmol, 0.33 g), and DI water (4 mL) was stirred vigorously in a 50 mL closed round bottom flask at

room temperature. After stirring for 30 minutes, the second portion of Oxone® (0.52 mmol, 0.32 g) was added into the mixture. After vigorous stirring for another 30 minutes, the last portion of Oxone® (0.18 mmol, 0.11 g) was added into the mixture. Then the reaction mixture was heated with vigorous stirring at about 90 ^{0}C. After 5 hours, the flask was cooled by the addition of ice water (40 mL) and filtered to separate the white precipitate. The yellow solid residue was first washed with cold DI water (3 × 10 mL) to remove the water soluble impurities and then with acetone (3 × 10 mL) to remove the unreacted 2-iodonitrobenzene. Then the yellow solid of 2-iodylnitrobenzene was air-dried in the dark to afford 239 mg (85%), dec. point 207 – 214 ^{0}C (lit. [73] mp 212 ^{0}C). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.42 – 8.41 (m, 1H), 8.34 – 8.33 (m, 1H), 8.25 – 8.22 (m, 1H), 7.95 – 7.92 (m, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 145.0, 144.7, 137.6, 133.9, 126.0, 125.8. IR (neat) 3045, 1587, 1524 (-NO_2), 1450, 1335, 1308, 1105, 857, 793, 770, 756, 736, 699 (-IO_2) cm^{-1}.



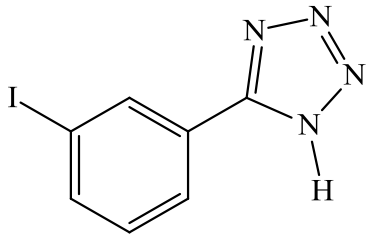
2-iodylnitrobenzene

B. Synthesis of Tetrazoles

1. **5-(3-iodophenyl)-1*H*-tetrazole**[105]

A mixture of 3-iodobenzonitrile (2.3 mmol, 516 mg), sodium azide (2.5 mmol, 163 mg), and ammonium chloride (2.5 mmol, 133 mg) in DMF was stirred for 22 hours at

100^0 C. Then, 1N aq. hydrochloric acid (50 mL) was added into the reaction mixture to obtain white solid precipitate. The white solid material was collected by the filtration. Then the white residue was first washed with 1N aq. HCl (2 × 10 mL) and then with cold DI water (3 × 10 mL). Finally, the white solid was dried under high vacuum to afford 563 mg (92%) of 5-(3-iodophenyl)-1*H*-tetrazole, mp 138 - 143 ^{0}C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.41 (t, J = 1.72 Hz, 1H), 8.10 – 8.08 (m, 1H), 8.00 – 7.98 (m, 1H), 7.44 (t, J = 7.45 Hz,1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ140.7, 136.0, 132.4, 127.2, 96.5. IR (neat) 3442, 3322, 3219, 3035, 1602, 1552, 1469, 1407, 1353, 1298, 1243, 1128, 1087, 1061, 999, 891, 795, 729, 678 cm^{-1}.

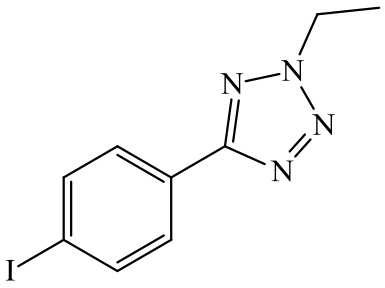


5-(3-iodophenyl)-1*H*-tetrazole

2. 5-(4-iodophenyl)-2-ethyl-2*H*-tetrazole

A mixture of 5-(4-iodophenyl)-1*H*-tetrazole (1.0 mmol, 272 mg) and tetrabutylammonium bromide ($Bu_4N^+Br^-$) (2.0 mmol, 645 mg) was treated with ethyl iodide (2.0 mmol, 312 mg) in 1N aq. NaOH solution (6 mL) and CH_2Cl_2 (6 mL); and the mixture was stirred vigorously for 26 h at room temperature. The lower organic layer was separated and washed with 1N aq. NaOH solution (2 × 10 mL), aq. NH_4Cl solution (2 × 10 mL), and brine (2 × 10 mL). The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvent was evaporated by rotavapor. The crude product was

further purified by flash chromatography using 230 – 400 mesh silica gel and 5% EtOAc in hexane as eluent to afford 189 mg (63%) of the desired product as a white crystalline solid, mp 45 – 52 ^{0}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.59 Hz, 2H), 7.83 (d, *J* = 8.59 Hz, 2H), 4.70 (q, *J* = 7.45 Hz, 2H), 1.69 (t, *J* = 7.45 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.0, 138.7, 129.0, 127.6, 97.1, 49.1, 15.2. IR (neat) 3200, 3044, 2924, 2853, 1599, 1444, 1412, 1353, 1266, 1186, 1131, 1057, 1000, 828, 752, 665 cm^{-1}.

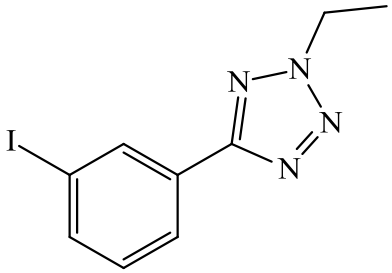


5-(4-iodophenyl)-2-ethyl-2*H*-tetrazole

3. 5-(3-iodophenyl)-2-ethyl-2*H*-tetrazole

A mixture of 5-(3-iodophenyl)-1*H*-tetrazole (1.8 mmol, 500 mg) and tetrabutylammonium bromide (3.66 mmol, 1.18 g) was treated with ethyl iodide (3.6 mmol, 562 g) in 1N aq. NaOH solution (10 mL) and CH_2Cl_2 (10 mL); and the mixture was stirred vigorously for 26 h at room temperature. The lower organic layer was separated and washed with 1N aq. NaOH solution (2 × 15 mL), aq. NH_4Cl solution (2 × 15 mL), and brine (2 × 15 mL). The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvent was evaporated by rotavapor. The crude product was further purified by flash chromatography using 230 – 400 mesh silica gel and 5% EtOAc in hexane as eluent to afford 324 mg (60%) of the desired product as a white crystalline

solid, mp 40 – 45 ^{0}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (t, *J* = 2.0 Hz, 1H), 8.12 – 8.11 (m, 1H), 7.80 – 7.79 (m, 1H), 7.22 (t, *J* = 8.02 Hz, 1H), 4.70 (q, *J* = 7.45 Hz, 2H), 1.69 (t, *J* = 7.45 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0, 139.5, 135.9, 130.9, 129.8, 126.2, 94.8, 48.9, 15.0. IR (neat) 3250, 3035, 2924, 2853, 1564, 1513, 1435, 1405, 1357, 1307, 1190, 1043, 974, 885, 740, 673 cm^{-1}.

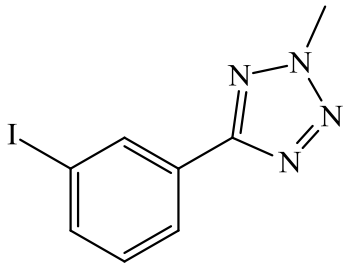


5-(3-iodophenyl)-2-ethyl-2*H*-tetrazole

4. 5-(3-iodophenyl)-2-methyl-2*H*-tetrazole

A mixture of 5-(3-iodophenyl)-1*H*-tetrazole (1.8 mmol, 500 mg) and tetrabutylammonium bromide (3.66 mmol, 1.18 g) was treated with methyl iodide (3.6 mmol, 511mg) in 1N aq. NaOH solution (10 mL) and CH_2Cl_2 (10 mL); and the mixture was stirred vigorously for 26 h at room temperature. The lower organic layer was separated and washed with 1N aq. NaOH solution (2 × 15 mL), aq. NH_4Cl solution (2 × 15 mL), and brine (2 × 15 mL). The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvent was evaporated by rotavapor. The crude product was purified by flash chromatography using 230 – 400 mesh silica gel, and 5% EtOAc in hexane as eluent to afford 283 mg (55%) of the desired product as a white crystalline solid, mp 80 – 85 ^{0}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (t, *J* = 1.72 Hz, 1H), 8.11 –

8.10 (m, 1H), 7.80 – 7.79 (m, 1H), 7.21 (t, J = 8.02, 1H), 4.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2, 139.6, 135.9, 130.9, 129.6, 126.2, 94.8, 39.9. IR (neat) 3250, 3035, 2924, 2853, 1564, 1517, 1442, 1418, 1347, 1196, 1046, 993, 886, 796, 749, 683 cm^{-1}.



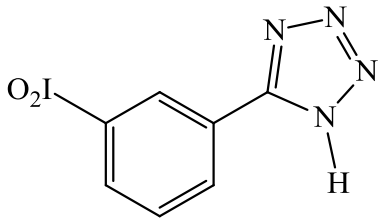
5-(3-iodophenyl)-2-methyl-2*H*-tetrazole

C. Synthesis of Iodyl Compounds from the Tetrazoles of Iodoarenes

1. 5-(3-iodylphenyl)-1*H*-tetrazole

A mixture of 5-(3-iodophenyl)-1*H*-tetrazole (1 mmol, 0.2720 g), Oxone® (0.54 mmol, 0.33 g), and DI water (4 mL) was stirred vigorously in a 50 mL closed round bottom flask at room temperature. After vigorous stirring for 30 minutes, the second portion of Oxone® (0.52 mmol, 0.32 g) was added into the mixture. After vigorous stirring for 50 minutes, the last portion of Oxone® (0.18 mmol, 0.11 g) was added into the mixture. Then the reaction mixture was heated with vigorous stirring at about 90 ^{0}C. After 2 hours and 30 minutes, the flask was cooled by the addition of ice water (40 mL) and filtered to separate the white precipitate. The white solid residue was first washed with cold DI water (3 × 10 mL) to remove the water soluble impurities and then with acetone (3 × 10 mL) to remove the unreacted 5-(3-iodophenyl)-1*H*-tetrazole. Then the white solid of 5-(3-iodylphenyl)-1*H*-tetrazole was air-dried in the dark to afford 292 mg (96%), dec. point

179 – 185 ^{0}C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.69 (s, 1H), 8.20 (t, J = 7.16 Hz, 2H), 7.83 (t, J = 8.02 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 157, 153.5, 131.0, 130.7, 130.6, 126.2, 126.1. IR (neat) 3470, 3345, 3234, 3045, 1607, 1568, 1416, 1130, 1095, 1002, 785, 739, 702 (-IO_2), 667 cm^{-1}.

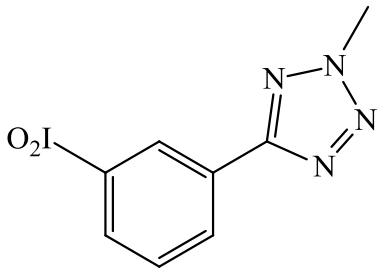


5-(3-iodylphenyl)-1*H*-tetrazole

2. 5-(3-iodylphenyl)-2-methyl-2*H*-tetrazole

A mixture of 5-(3-iodophenyl)-2-methyl-2*H*-tetrazole (1 mmol, 0.2860 g), Oxone® (0.54 mmol, 0.33 g), and DI water (4 mL) was stirred vigorously in a 50 mL closed round bottom flask at room temperature. After vigorous stirring for 30 minutes, the second portion of Oxone® (0.52 mmol, 0.32 g) was added into the mixture. After vigorous stirring for 50 minutes, the last portion of Oxone® (0.18 mmol, 0.11 g) was added into the mixture. Then the reaction mixture was heated with vigorous stirring at about 90 ^{0}C. After 2 hours and 30 minutes, the flask was cooled by the addition of ice water (40 mL) and filtered to separate the white precipitate. The white solid residue was first washed with cold DI water (3 × 10 mL) to remove the water soluble impurities and then with acetone (3 × 10 mL) to remove the unreacted 5-(3-iodophenyl)-2-methyl-2*H*-tetrazole. Then the white solid of 5-(3-iodylphenyl)-2-methyl-2*H*-tetrazole was air-dried in the dark to afford 270 mg (85%), dec. point 238 – 242 ^{0}C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.74

(s, 1H), 8.23 (d, J = 7.45 Hz, 1H), 8.15 (d, J = 8.02 Hz, 1H), 7.80 (t, J = 7.45 Hz,1H), 4.52 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.4, 153.2, 130.7, 129.7, 129.6, 128.2, 125.4. IR (neat) 3218, 3045, 2930, 1517, 1424, 1348, 1043, 892, 799, 769, 749, 711(-IO_2) cm^{-1}.

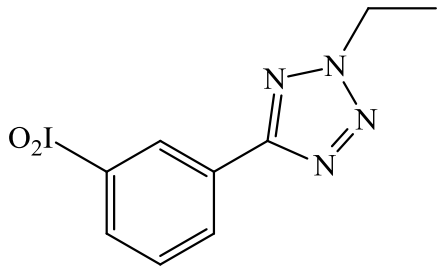


5-(3-iodylphenyl)-2-methyl-2*H*-tetrazole

3. 5-(3-iodylphenyl)-2-ethyl-2*H*-tetrazole

A mixture of 5-(3-iodophenyl)-2-ethyl-2*H*-tetrazole (1 mmol, 0.30 g), Oxone® (0.54 mmol, 0.33 g), and DI water (4 mL) was stirred vigorously in a 50 mL closed round bottom flask at room temperature. After vigorous stirring for 30 minutes, the second portion of Oxone® (0.52 mmol, 0.32 g) was added into the mixture. After vigorous stirring for 50 minutes, the last portion of Oxone® (0.18 mmol, 0.11 g) was added into the mixture. Then the reaction mixture was heated with vigorous stirring at about 90 ^{0}C. After 2 hours and 30 minutes, the flask was cooled by the addition of ice water (40 mL) and filtered to separate the white precipitate. The white solid residue was first washed with cold DI water (3 × 10 mL) to remove the water soluble impurities and then with acetone (3 × 10 mL) to remove the unreacted 5-(3-iodophenyl)-2-ethyl-2*H*-tetrazole. Then the white solid of 5-(3-iodylphenyl)-2-ethyl-2*H*-tetrazole was air-dried in the dark to afford 299 mg (90%), dec. point 220 - 228 ^{0}C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.73

(s, 1H), 8.24 (d, *J* = 7.45 Hz, 1H), 8.14 (d, *J* = 7.45 Hz, 1H), 7.79 (t, *J* = 7.45 Hz,1H), 4.83 (q, *J* = 7.45 Hz, 2H), 1.63 (t, *J* = 7.45 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.4, 153.1, 130.7, 129.7, 129.6, 128.3, 125.5, 49.2, 15.2. IR (neat) 3219, 3035, 2930, 2853, 1517, 1433, 1357, 1191, 1072, 1043, 974, 890, 780, 751, 716(-IO_2), 672 cm^{-1}.

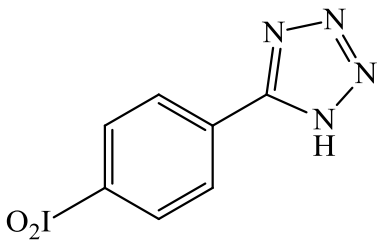


5-(3-iodylphenyl)-2-ethyl-2*H*-tetrazole

4. 5-(4-iodylphenyl)-1*H*-tetrazole

A mixture of 5-(4-iodophenyl)-1*H*-tetrazole (1 mmol, 0.2720 g), Oxone® (0.54 mmol, 0.33 g), and DI water (4 mL) was stirred vigorously in a 50 mL closed round bottom flask at room temperature. After vigorous stirring for 30 minutes, the second portion of Oxone® (0.52 mmol, 0.32 g) was added into the mixture. After vigorous stirring for 50 minutes, the last portion of Oxone® (0.18 mmol, 0.11 g) was added into the mixture. Then the reaction mixture was heated with vigorous stirring at about 90 ^{0}C. After 2 hours and 30 minutes, the flask was cooled by the addition ice water (40 mL) and filtered to separate the white precipitate. The white solid residue was first washed with cold DI water (3 × 10 mL) to remove the water soluble impurities and then with acetone (3 × 10 mL) to remove the unreacted 5-(4-iodophenyl)-1*H*-tetrazole. Then the white solid of 5-(4-iodylphenyl)-1*H*-tetrazole was air-dried in the dark to afford 259 mg (85%), dec. point 209 – 215 ^{0}C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.04 (d, *J* = 8.02 Hz, 2H), 7.86 (d, *J* =

8.02 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 139.3, 134.7, 129.7, 99.5 . IR (neat) 3080, 1602, 1548, 1364, 1279, 987, 831, 775, 728, 715 (-IO_2), 666 cm^{-1}.

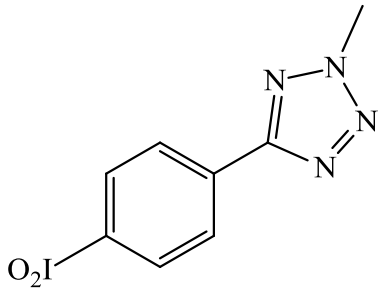


5-(4-iodylphenyl)-1*H*-tetrazole

5. 5-(4-iodylphenyl)-2-methyl-2*H*-tetrazole

A mixture of 5-(4-iodophenyl)-2-methyl-2*H*-tetrazole (1 mmol, 0.2865 g), Oxone® (0.54 mmol, .33 g), and DI water (4 mL) was stirred vigorously in a 50 mL closed round bottom flask at room temperature. After vigorous stirring for 30 minutes, the second portion of Oxone® (0.52 mmol, 0.32 g) was added into the mixture. After vigorous stirring for 50 minutes, the last portion of Oxone® (0.18 mmol, 0.11 g) was added into the mixture. Then the reaction mixture was heated with vigorous stirring at about 90 ^{0}C. After 2 hours and 30 minutes, the flask was cooled by the addition of ice water (40 mL) and filtered to separate the white precipitate. The white solid residue was first washed with cold DI water (3 × 10 mL) to remove the water soluble impurities and then with acetone (3 × 10 mL) to remove the unreacted 5-(4-iodophenyl)-2-methyl-2*H*-tetrazole. Then the white solid of 5-(4-iodylphenyl)-2-methyl-2*H*-tetrazole was air-dried in the dark to afford 205 mg (65%), dec. point 240 – 248 ^{0}C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.28 (d, J = 8.02 Hz, 2H), 8.18 (d, J = 8.59 Hz, 2H), 4.50 (s, 3H). ^{13}C NMR (125 MHz,

DMSO-d_6): δ 164.5, 139.1, 129.0, 127.3, 98.3. IR (neat) 3060, 2935, 1696, 1514, 1447, 1409, 1284, 1131, 1045, 999, 742, 752, 764, 699 (-IO_2) cm^{-1}.

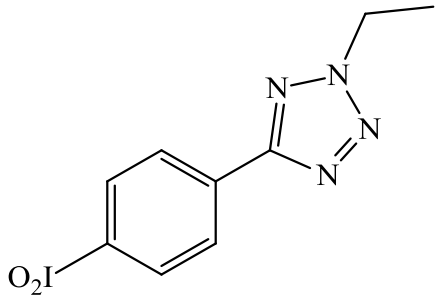


5-(4-iodylphenyl)-2-methyl-2*H*-tetrazole

6. 5-(4-iodylphenyl)-2-ethyl-2*H*-tetrazole

A mixture of 5-(4-iodophenyl)-2-ethyl-2*H*-tetrazole (1 mmol, 0.30 g), Oxone® (0.54 mmol, 0.33 g), and DI water (4 mL) was stirred vigorously in a 50 mL closed round bottom flask at room temperature. After vigorous stirring for 30 minutes, the second portion of Oxone® (0.52 mmol, 0.32 g) was added into the mixture. After vigorous stirring for 50 minutes, the last portion of Oxone® (0.18 mmol, 0.11 g) was added into the mixture. Then the reaction mixture was heated with vigorous stirring at about 90 ^{0}C. After 2 hours and 30 minutes, the flask was cooled by the addition ice water (40 mL) and filtered to separate the white precipitate. The white solid residue was first washed with cold DI water (3 × 10 mL) to remove the water soluble impurities and then with acetone (3 × 10 mL) to remove the unreacted 5-(4-iodophenyl)-2-ethyl-2*H*-tetrazole. Then the white solid of 5-(4-iodylphenyl)-2-ethyl-2*H*-tetrazole was air-dried in the dark to afford 299 mg (77%), dec. point 235 – 242 ^{0}C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.29 (d, J = 8.59 Hz, 2H), 8.18 (d, J = 8.59 Hz, 2H), 4.82 (q, J = 7.45 Hz, 2H), 1.63 (t, J = 7.45 Hz,

3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.3, 139.1, 129.1, 127.7, 98.3, 49.2, 15.3 IR (neat) 3265, 3060, 2987, 1596, 1513, 1444, 1411, 1275, 1188, 1042, 975, 828, 761, 698 (-IO_2) cm^{-1}.



5-(4-iodylphenyl)-2-ethyl-2*H*-tetrazole

Laboratory Precautions

Iodyl compound is not itself a toxic substance[95], but dry iodylarene is a generally hazardous compound because scraping with a spatula can induce a violent decomposition.[72] Therefore, they were handled with appropriate precautions. The decomposition point of these compounds is explosive. That is why, the melting point apparatus was placed in the hood and the decomposition point was observed by keeping the door of the hood closed.

CHAPTER III

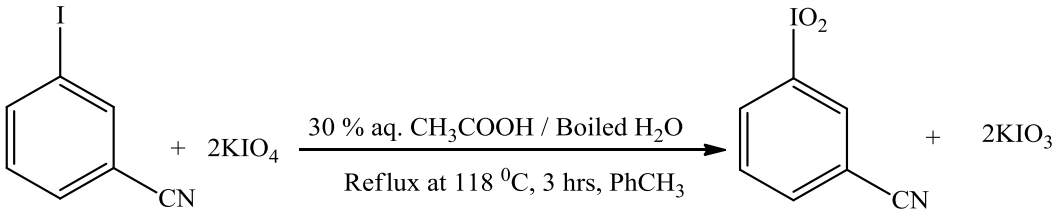
RESULTS AND DISCUSSION

Iodylarenes are hypervalent iodine compounds. They are generally synthesized by oxidizing the corresponding iodo compounds. They are broadly employed as oxidizing agents in organic chemistry.[41] Although there are many different iodylarenes, iodylbenzene and IBX are the most common selective reagents for the oxidation of various organic compounds.[41] Because of the strong intermolecular secondary bonding generating a three-dimensional polymeric structure of the iodyl group, they are almost insoluble in the all organic solvents except DMSO.[64-65] The melting point of these compounds is explosive.[72-73] Some explosions of iodyl compounds have been reported in the literature,[68, 98] but these compounds have not been studied systematically as energetic compounds.[100] Green synthesis of reported or novel iodyl compounds could be of practical interest in their systematic study as energetic compounds.

Optimization of the Oxidants for the Synthesis of Iodylarenes

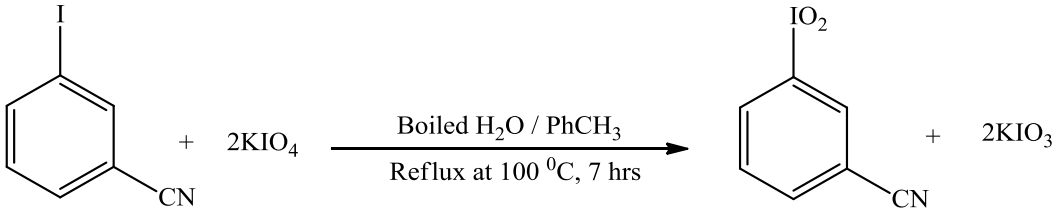
Previously, sodium periodate ($NaIO_4$) was used as an oxidant in the preparation of various iodylarenes. According to the literature, sodium periodate was used with two different solvent systems. First, iodoarenes were refluxed with $NaIO_4$ in the presence of water[72] and second, iodoarenes were refluxed with $NaIO_4$ in the presence of 30% (v/v) aq. acetic acid.[73] Previously, Oxone® was also used as an oxidant for the preparation of different iodylbenzenes.[68,77,87,100]

We used these three methods for the optimization of the oxidant for the iodyl synthesis. One mmol of 3-iodobenzonitrile was refluxed under stirring with 2.2 mmols (10% excess) of potassium periodate (KIO_4) in the presence of 30% (v/v) aq. acetic acid and boiling water for 4 hours to give a 65% yield of 3-iodylbenzonitrile (Scheme 31).



Scheme 31

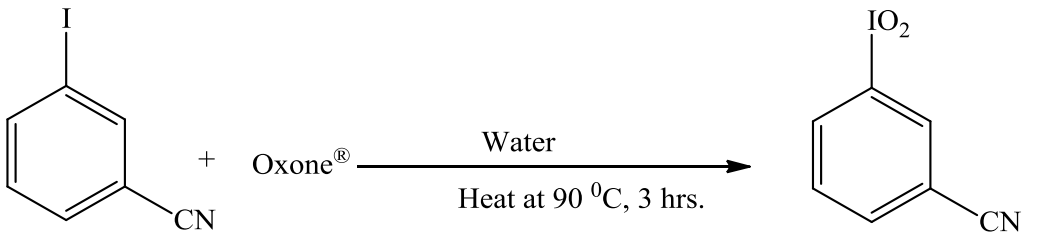
When water was used as a solvent instead of 30% aq. acetic acid, a 70% yield of 3-iodylbenzonitrile was obtained in 7 hours, which is longer than the above method (Scheme 32).



Scheme 32

Moreover, one mmol of 3-iodobenzonitrile was heated under stirring with 1.24 mmols of Oxone® in the presence of water for 3 hours at about 90 ^{0}C to give only a 50%

yield of 3-iodylbenzonitrile (Scheme 33). Here, water was used as a solvent. To increase the yield of the product, Oxone® was taken in three different parts with the starting material. First, one mmole of 3-iodobenzonitrile was stirred vigorously with 0.54 mmol (0.33 g) of Oxone® at room temperature. After stirring for 30 minutes, the second portion of 0.52 mmol (0.32 g) of Oxone® was added into the mixture with continuous stirring. After stirring for another 30 minutes, the final portion of 0.18 mmol (0.11 g) of Oxone® was added and the reaction mixture was heated with vigorous stirring at about 90 ^{0}C for two hours. After cooling by the addition of ice water, an 88% yield of 3-iodylbenzonitrile was separated by the filtration.



3-iodobenzonitrile

3-iodylbenzonitrile

88 %

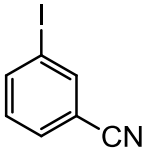
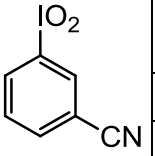
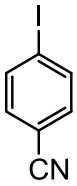
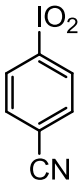
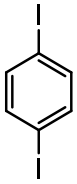
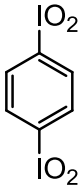
Scheme 33

In the case of 4-iodobenzonitrile, it gave only 61% yield of 4-iodlybenzonitrile with 1.24 mmol of Oxone®. When the Oxone® was added in three different parts, the yield was increased to 92%. Likewise, 1,4-diiodobenzene gave only 40% yield of 1,4-diiodylbenzene with 2.48 mmole of Oxone®. When the Oxone® was taken in three different parts for four hrs, the yield was increased to 70%. Due to the presence of two

iodine atoms on the benzene ring of 1,4-diiodylbenzene, the amount of Oxone® was doubled compared to iodoarenes containing a single iodine atom.

The overall results of the optimization of the oxidants for the synthesis of iodylarenes are summarized in the Table 4.

Table 4: Results of the optimization of the oxidants for the synthesis of iodylarenes.

Entry	Starting material	Oxidant	Time (h)	Temperature (^{0}C)	Product	Yield (%)
1.		KIO_4 / 30% AcOH/H_2O	3	118[a]		65
		KIO_4 / H_2O	7	100[a]		70
		Oxone®	3	90[b]		88
2.		KIO_4 / 30% aq. AcOH/H_2O	3	118[a]		-
		KIO_4 / H_2O	7	100[a]		38
		Oxone®	3	90[b]		92
3.		KIO_4 / 30% AcOH/H_2O	4	118[a]		-
		KIO_4 / H_2O	10	100[a]		-
		Oxone®	4	100[b]		70

[a] Reflux temperature.

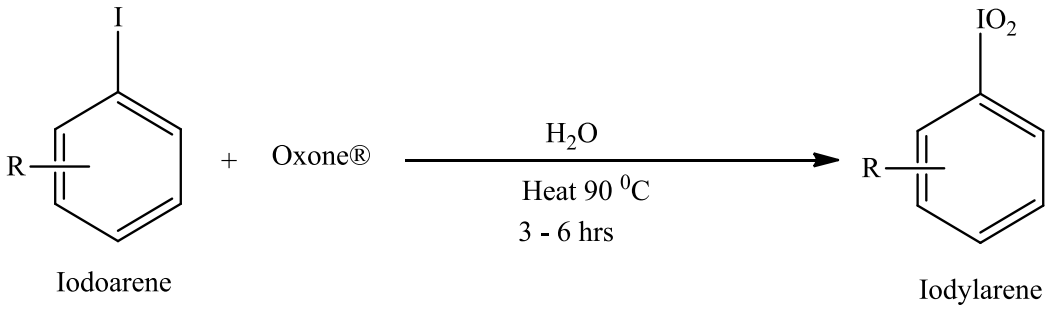
[b] Heating temperature.

From the results of the optimization of the oxidants, Oxone® gave higher yields of the corresponding iodylarenes than potassium periodate. In the case of 1,4-diiodobenzene, it did not react with KIO_4 to give the corresponding iodyl compound. Due to low solubility of potassium periodate, it was also very difficult to purify the corresponding products.

When Oxone® was used as an oxidant, more than 99% pure product was obtained without extra purification of the products because the Oxone® is highly soluble in water. Oxone® is an inexpensive, highly stable, readily available, and environmentally friendly oxidizing agent. Therefore, Oxone® was selected as the best and greenest oxidant for the iodyl synthesis and it was used for the preparation of various iodylarenes.

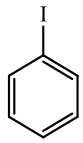
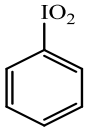
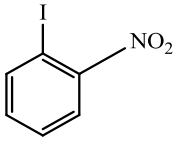
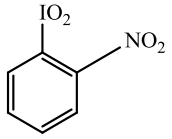
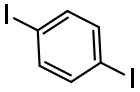
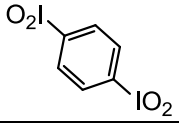
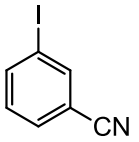
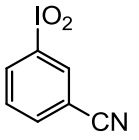
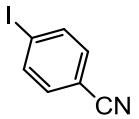
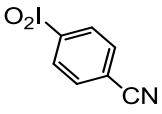
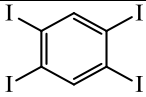
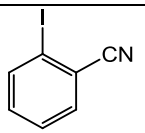
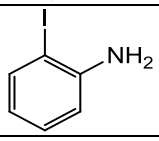
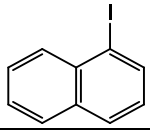
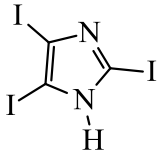
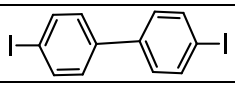
Synthesis of Iodylarenes Using Optimized Oxidant Oxone®

After the results of the optimization of the oxidant, Oxone® was employed to synthesize the different iodylarenes from iodobenzene, 2-iodonitrobenzene, 1,2,4,5-tetraiodobenzene, 2-iodobenzonitrile, 2-iodoaniline,1-iodonaphthalene, 2,4,5-triiodoimidazole, and 4,4'-diiodobiphenyl which are summarized in the Table 5 (Scheme 34). The reactions of 1,2,4,5-tetraiodobenzene, *o*-iodobenzonitrile, 2-iodoaniline, *α*-iodonaphthalene, 2,4,5-triiodoimidazole, and 4,4'-diiodobiphenyl (Table 5, entry 6, 7, 8, 9, and 10) did not afford the corresponding iodyl compounds.



Scheme 34

Table 5: Synthesis of iodylarenes.[a]

Entry	Starting Material	Time (h)	Product	Yield (%)	D.P.[b] (^{0}C)
1.		4		66	230 - 237
2.		6		85	207 - 214
3.		4		70	215 - 223
4.		3		88	192 - 199
5.		3		92	190 -198
6.		4	-	-	-
7.		3	-	-	-
8.		3	-	-	-
9.		3	-	-	-
10.		3	-	-	-
11.		3	-	-	-

[a] Reaction temperature was about 90 ^{0}C.

[b] D.P. is decomposition point where the compound exploded.

After adding the final portion of Oxone®, the reactions (Table 5, entry 1, 3, and 6) were heated with vigorous stirring at about 90 ^{0}C for 3 hours, but the reaction (Table 5, entry 2) was heated with vigorous stirring at about 90 ^{0}C for 5 hours.

p-Diiodylbenzene decomposed more vigorously than the iodyl compounds having only one iodyl group such as, iodylbenzene, 2-iodylnitrobenzene, 3-iodylbenzonitrile, and 4-iodylbenzonitrile. From this simple observation, when the iodyl group on the benzene ring is more than one, the explosive character of the compounds increases. Therefore, further research and quantitative analysis of this character are still required.

The iodyl compounds are only soluble in DMSO. When the number of iodyl groups on the benzene ring increases, the solubility of the corresponding iodyl compounds decreases. Iodylbenzene was soluble in DMSO, but 1,4-diiodylbenzene was virtually insoluble in this solvent. Due to the presence of more iodyl groups (IO_2) on the benzene ring, the infinite polymeric chains of iodyl groups[64-65] are even stronger than in the case of the iodyl compounds having only one iodyl group. As a result, the solubility of these iodyl compounds even in DMSO solvent decreased. Due to this nature, NMR data were not obtained for 1,4-diiodylbenzene.

After successfully establishing the two iodyl groups on a benzene ring, such as 1,4-diiodylbenzene; we also tried to introduce more than two iodyl groups on the benzene ring. Therefore; 1,2,4,5-tetraiodobenzene was attempted to synthesize by the reported method.[101] According to the reported method, 30 mL of concentrated sulfuric acid was cooled to less than 0 ^{0}C and 10 mmol (2.25 g) of *N*-iodosuccinimide was added into the cold acid. Then the mixture was stirred over the ice bath to make the solution

homogeneous. After 30 minutes, 10 mmol (2.04 g, 1.1 mL) iodobenzene was slowly introduced into the homogeneous solution to obtain the dark brown solution. After stirring the reaction mixture over ice bath for 30 minutes, it was poured into 100 mL ice water and then 3 grams of sodium sulfite was added into the mixture. The mixture was filtered, washed by water, and dried to afford 1.5 grams white substance. After that, it gave the two major peaks at δ 7.21 and δ 7. 18 including some small peaks of ^{1}H NMR in chloroform-*d*. When the white substance was further oxidized with Oxone®, a white solid of iodyl substance was obtained (610 mg) which was even insoluble in DMSO solvent. Therefore, the NMR spectra of this substance were not obtained. This substance decomposed vigorously at about 195 – 202 ^{0}C, and it gave the strong IR peak of iodyl group (-IO_2) at 698 cm^{-1}.

After this result, we again tried to reproduce this substance following the same process, but the starting materials, such as iodobenzene and *N*-iodosuccinimide, were taken in 4.4 mmol. Finally, one gram of reddish brown substance was obtained. It gave only one major peak at δ 7.4 including some very small peaks of ^{1}H NMR in chloroform-*d*. It also gave δ 139. 8 and δ 93.9 peaks of ^{13}C NMR. When this substance (300 mg) was further oxidized with Oxone®, a white solid of iodyl substance was obtained (240 mg). It was insoluble in DMSO, so NMR spectra were not obtained. All the IR peaks as well as melting point of this iodyl compound corresponds with 1,4-iodylbenzene compound.

After all these results; 1,2,4,5-tetraiodobenzene was synthesized by another reported method.[102] In this method, periodic acid (1.0 g, 4.4 mmol) was dissolved in concentrated sulfuric acid (20 mL) and iodine (3.339 gram, 13 mmol) was added into the mixture.

Then the mixture was stirred in an ice bath. After 30 minutes, benzene (0.7 mL, 8 mmol) was slowly added into the mixture with stirring. Then the reaction was stirred overnight at room temperature. The reaction mixture was filtered and washed first with water (3 × 40) and then with methanol (3 × 20). Afterward, the residue was dried to afford 3 g (64%) of crude product of 1,2,4,5-tetraiodobenzene. Then, further oxidation with Oxone® was attempted, but all the starting material was recovered which was confirmed by the melting point, ^{1}H NMR, and IR.

Preparation of Tetrazoles

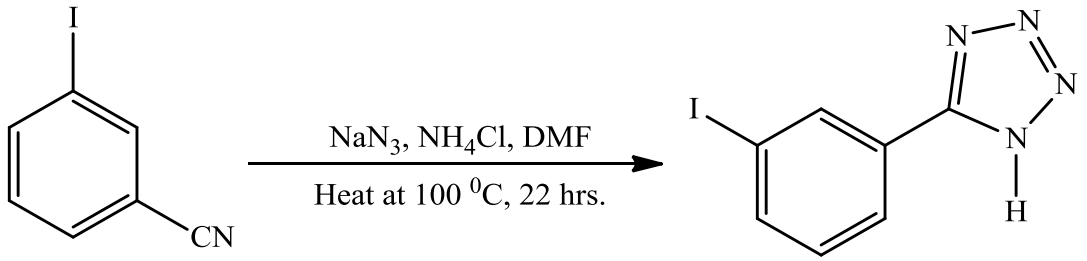
Nitrogenous compounds are generally explosive because nitrogen atom does not bind strongly to other atoms. When these compounds are heated, they release the nitrogen gases. Molecule of nitrogen gas is composed of two nitrogen atoms. These two nitrogen atoms in nitrogen molecule are bonded together by means of three bonds. These bonds are very strong. Therefore, during the formation of this bond, it liberates 950 KJ energy.[99, 106] When the compounds having nitrogen atoms explode, they liberate huge amount of nitrogen gas.[99, 106] The formation of nitrogen gas is exothermic which produces lots of energy.[99, 106] Therefore, a variety of stabilities and detonation properties can be produced using nitrogen rich materials.[107]

Because of the aromatic ring system in the tetrazoles, they have good thermal stability.[108] Due to this outstanding property of combining a high nitrogen content, they are highly endothermic compounds.[108] Although they are stable compounds, the tetrazoles having iodyl group could be of practical interest to observe the explosive

characters. Therefore, the syntheses of the iodyl compounds of the tetrazoles are very important.

Before starting to prepare the iodylarenes of the tetrazoles, unreported or commercially unavailable tetrazoles of iodoarenes and their derivatives as the starting materials for the iodyl synthesis were isolated by the different methods.

5-(3-iodophenyl)-1*H*-tetrazole is a reported compound, but not commercially available. 3-benzonitrile as a starting material was heated with sodium azide (NaN_3) and ammonium chloride in the presence of DMF for 22 hours at 100 ^{0}C to give 92% yield of 5-(3-iodophenyl)-1*H*-tetrazole (Scheme 34). This method was previously reported for the preparation of 5-(4-iodophenyl)-1*H*-tetrazole.[105] This compound showed only five peaks of the ^{13}C NMR spectra and the missing two peaks may be overlapped with other peaks or with solvent peaks.



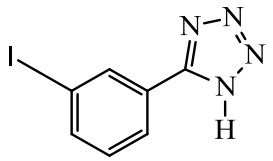
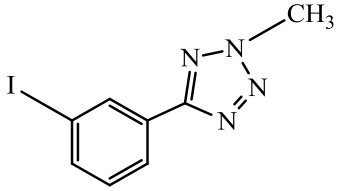
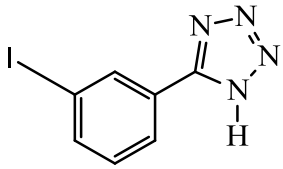
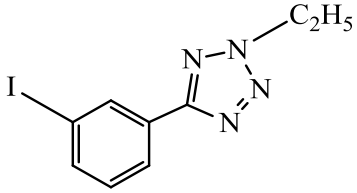
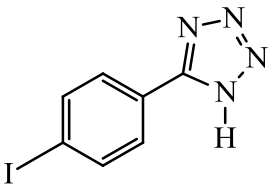
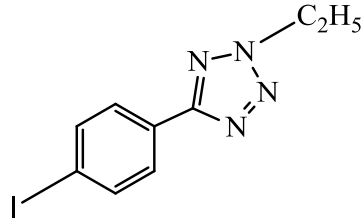
3-iodobenzonitrile

5-(3-iodophenyl)-1*H*-tetrazole
92 %

Scheme 34

Unreported methylated and ethylated derivatives of 1*H*-tetrazoles of iodoarenes were also synthesized by the reported methods,[105] which are summarized in the Table 6.

Table 6: Preparation of methylated and ethylated derivatives of 1*H*-tetrazoles of iodoarenes.[a]

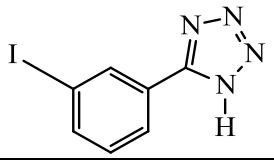
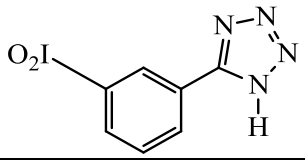
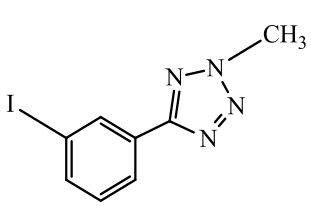
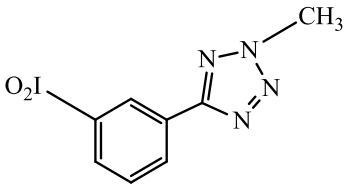
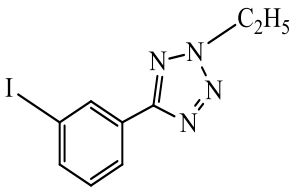
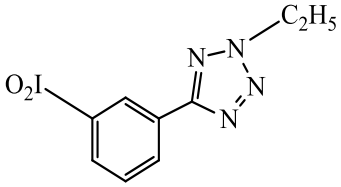
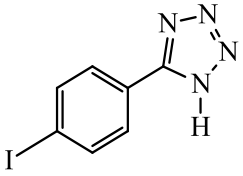
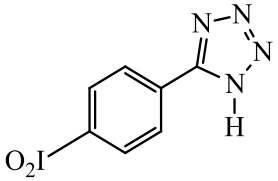
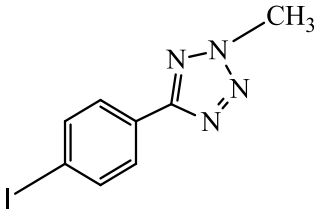
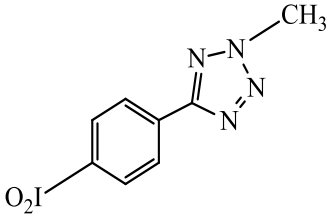
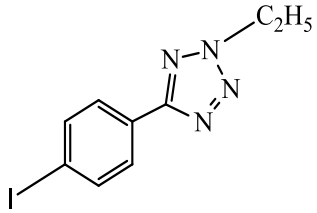
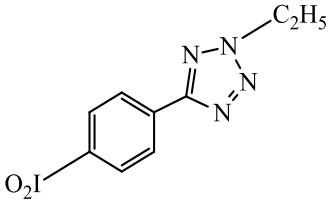
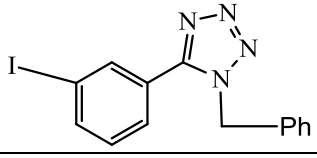
Entry	Starting Material	Reagent	Product	Yield (%)
1.		CH_3I		50
2.		C_2H_5I		60
3.		C_2H_5I		55

[a] Reactions were performed in the presence of $Bu_4N^+Br^-$, 1N aq. NaOH, and CH_2Cl_2.

Preparation of Iodyl Compounds of Various Tetrazoles

The optimized oxidant Oxone® was used to synthesize the iodyl compounds of the tetrazoles. One mmol of the tetrazoles of iodoarenes was stirred vigorously with 0.54 mmol of Oxone® in the presence of water at about 90 ^{0}C. After 30 minutes, the second portion of 0.52 mmol of Oxone® was added into the mixture with continuous stirring. After 50 minutes, the third portion of 0.18 mmol of Oxone® was added and the reaction mixture was stirred vigorously at about 90 ^{0}C for 2 hours 30 minutes to get the products of the corresponding iodyl compounds of the tetrazoles. The overall results of the reactions are summarized in the Table 7.

Table 7: Preparation of iodyl compound of the tetrazoles.

Entry	Starting Material	Product	Yield (%)	D.P.[a] (^{0}C)
1.			96	179-185
2.			85	238-242
3.			90	220-228
4.			85	209-215
5.			65	240-248
6.			77	235-242
7.		N.R.	-	-

[a] D.P. is decomposition point. At this temperature, compound exploded.

Among these iodyl compounds of the tetrazoles, the products (Table 7, entries 1, 3, and 4) exploded vigorously at the corresponding decomposition points. The product (Table 7, entry 1) was more soluble in DMSO than the other iodyl compounds of the tetrazoles. When the compound (Table 7, entry 7) was tried to form the corresponding iodyl compound, all the starting materials were recovered. The compounds (Table 7, entries 1, 2, and 3) gave all the peaks of ^{13}C NMR whereas the compounds (Table 7, entries 4, 5, and 6) did not give good peaks of ^{13}C NMR with DMSO-d_6 solvent due to low solubility. Due to the impure starting material (Table 7, entry 4) of iodo compounds, the product of iodyl compound (Table 7, entry 4) was not further purified. Therefore, the some peaks of impurities were also observed in ^{1}H NMR.

Characterization of Iodyl Compounds

Due to low solubility of these compounds, it was very difficult to take the NMR spectra particularly ^{13}C NMR. The iodyl compounds, such as iodylbenzene, 2-iodylnitrobenzene, 3-iodylbenzonitrile, and 4-iodylbenzonitrile, were soluble in DMSO, so the NMR spectra of these compounds were easily taken. However, 1,4-diiodylbenzene was not soluble in DMSO, so the NMR spectra were not obtained. The compound 5-(3-iodylphenyl)-2-methyl-2*H*-tetrazole showed only seven peaks of the ^{13}C NMR. One peak of methyl group may be overlapped with the peak of DMSO-d_6 solvent. Similarly, one peak of methyl group of 5-(4-iodylphenyl)-2-methyl-2*H*-tetrazole may be also overlapped with the peak of DMSO-d_6 solvent. Even after scans 1600, some of the peaks of ^{13}C NMR spectra of iodyl compounds especially *para*-substituted compounds, were not observed clearly.

Solid substances were used to take the IR spectra of each iodyl compound. The IR peaks of the iodyl group (-IO_2) of these compounds were observed from 716 to 698 cm^{-1}.

The melting points of these compounds are the decomposition points. They exploded at the corresponding decomposition points of these compounds. The decomposition points were observed from 179 to 248 ^{0}C.

All these iodyl compounds were characterized based on the above information, starting materials, and previous reported[72, 73, 87] information.

Reproducibility Character of the Iodyl Compounds

At the beginning, all the reactions were performed on one mmol scale. After successfully establishing the reactions, the scales of some starting materials, such as 3-iodobenzonitrile, 4-iodobenzonitrile, 1,4-diiodobenzene, 2-iodonitrobenzene, 5-(3-iodophenyl)-1*H*-tetrazole, and 5-(4-iodophenyl)-1*H*-tetrazole, were increased up to 10 mmol. After increasing the reaction scales, the yield of the products were not decreased. Therefore, this method can be also employed to produce iodyl compounds in industrial scale.

CHAPTER IV

CONCLUSIONS

Although there are various oxidants reported for the preparation of iodyl compounds, Oxone® is the best oxidizing agent. When Oxone® was used as an oxidant, more than 99% pure product based on NMR analysis was obtained without extra purification of the products because Oxone® is highly soluble in water. It is an inexpensive, highly stable, readily available, and environmentally friendly oxidizing agent compared to the other oxidizing agent, such as potassium or sodium periodate ($NaIO_4$ or KIO_4). That is why, Oxone® has been selected as the best and green oxidant for the iodyl synthesis.

Another advantage of this method is the ability to recover the unreacted starting material by washing the precipitate of iodyl compound with appropriate organic solvents.

Eleven iodyl compounds with good yields have been synthesized using Oxone®. After successfully establishing the reactions, the scales of some starting materials were increased up to 10 mmol. After increasing the reaction scales, the yields of the products did not decrease indicating that this method is readily scalable.

All the compounds have been characterized by IR, ^{1}H NMR, ^{13}C NMR, and previous reported information. Due to low solubility of these compounds, it was very difficult to take the NMR spectra especially ^{13}C NMR. The iodyl compounds, such as iodylbenzene, 2-iodylnitrobenzene, 3-iodylbenzonitrile, and 4-iodylbenzonitrile, were

soluble in DMSO, so the NMR spectra of these compounds were easily obtained. Due to the presence of two iodyl groups on the benzene ring, 1,4-diiodylbenzene was not soluble in DMSO, so the NMR spectra were not obtained. Even after scans 1600, some of the peaks of ^{13}C NMR spectra of some iodyl compounds of tetrazoles particularly *para*-substituted compounds, were not observed clearly.

The IR peaks of the iodyl group ($-IO_2$) of these compounds were observed from 716 to 698 cm^{-1}. The melting points of these compounds are the decomposition points. They exploded at the corresponding decomposition points. The decomposition points were observed from 179 to 248 ^0C.

p-Diiodylbenzene decomposed more vigorously than the iodyl compounds having only one iodyl group, such as iodylbenzene, 2-iodylnitrobenzene, 3-iodylbenzonitrile, and 4-iodylbenzonitrile. From this simple observation, when there are more iodyl groups on benzene ring than one, the explosive character of the compounds increases. Iodyl compounds of the tetrazole derivatives, such as 5-(3-iodylphenyl)-1*H*-tetrazole and 5-(4-iodylphenyl)-1*H*-tetrazole, also decomposed vigorously at the corresponding decomposition points. Therefore, further research of this character by the quantitative analysis is still required.

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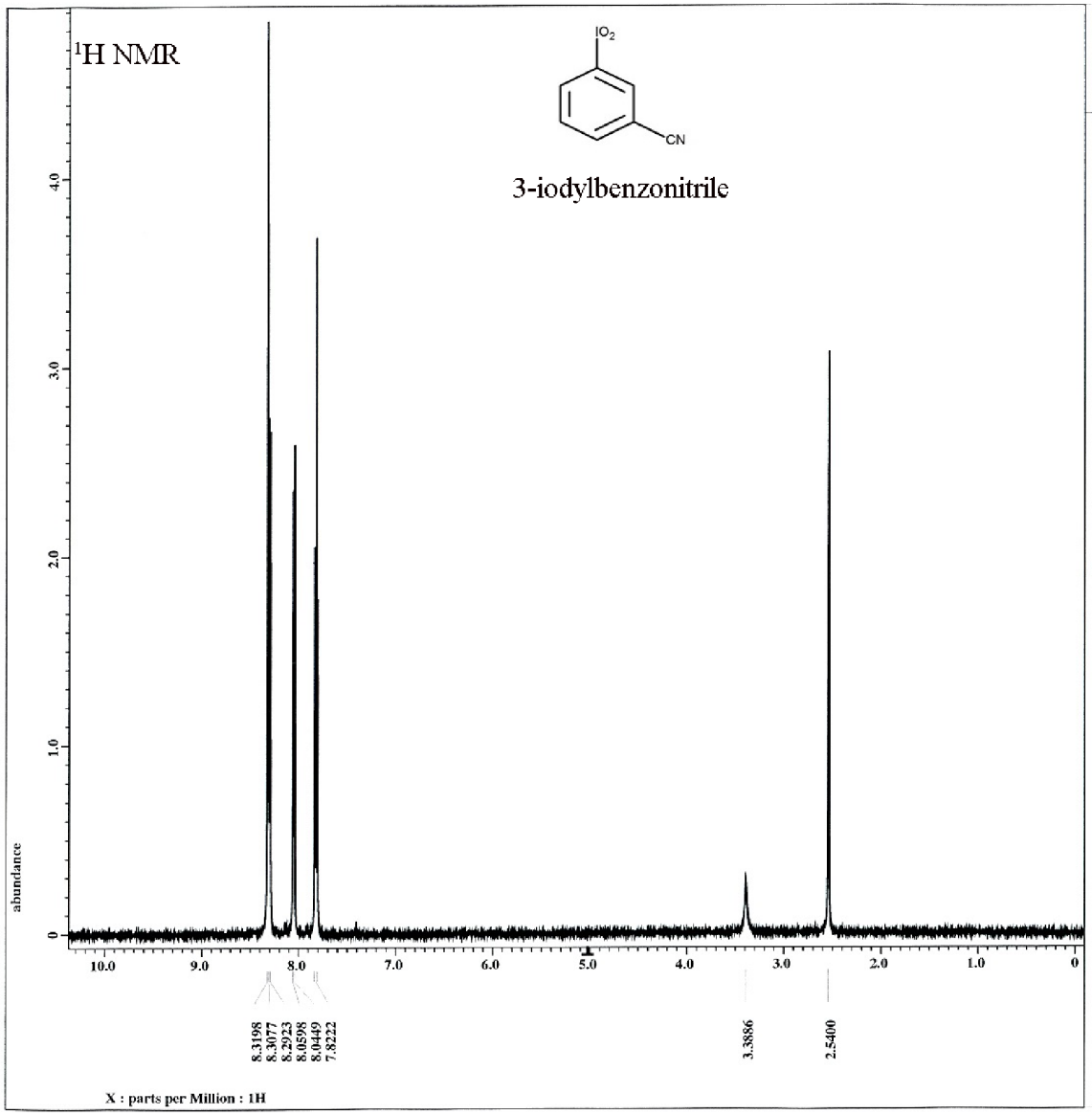
APPENDIX



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X_points          = 16384
X_prescans        = 1
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
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Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
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Mod_return        = 1
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Total_scans       = 16

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X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 3[dB]
X_pulse           = 6.901[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 58
Relaxation_delay  = 4[s]
Repetition_time   = 5.74587904[s]
Temp_get          = 21.1[dC]
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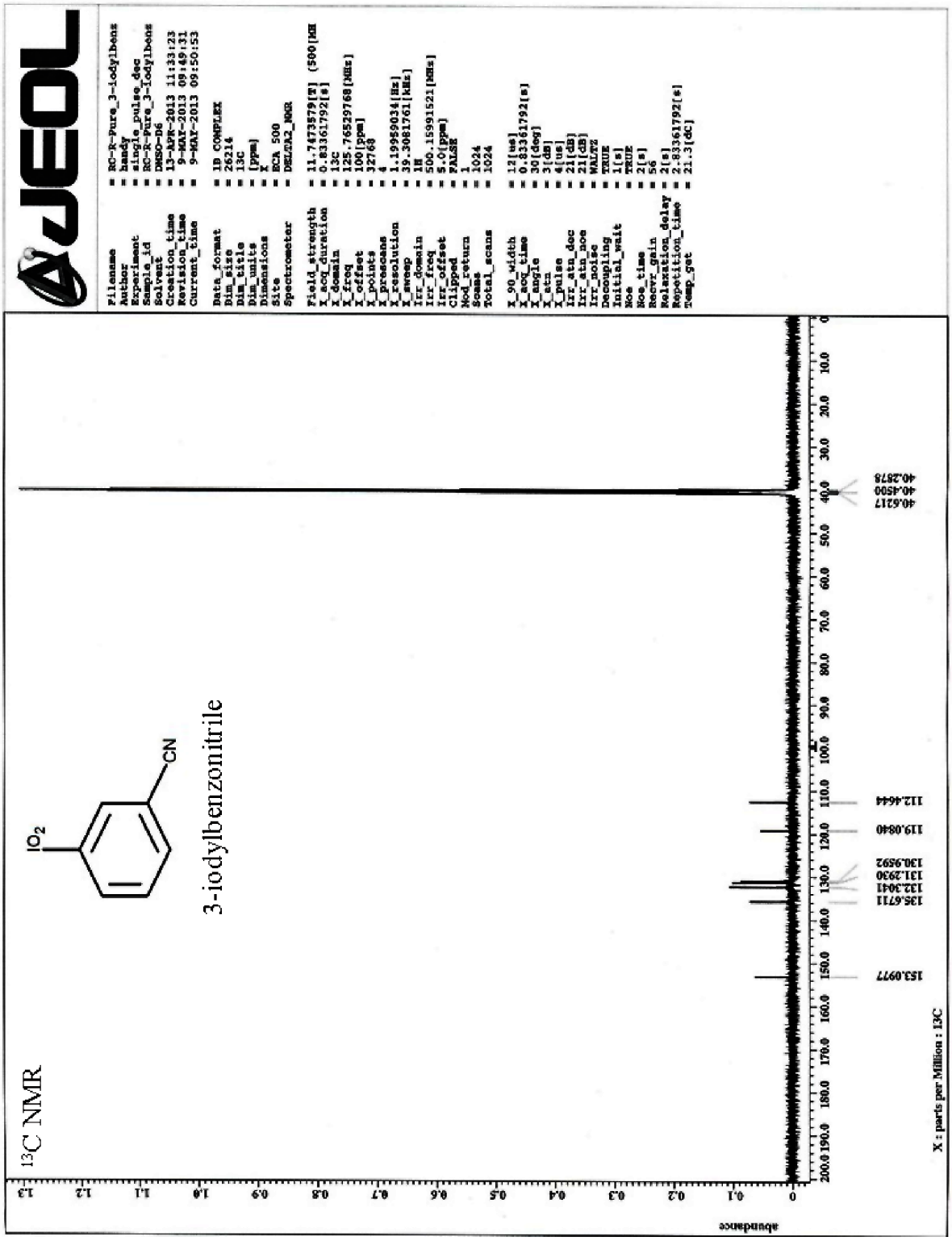
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X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
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Clipped = FALSE
Mod_return = 1
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Total_scans = 1024
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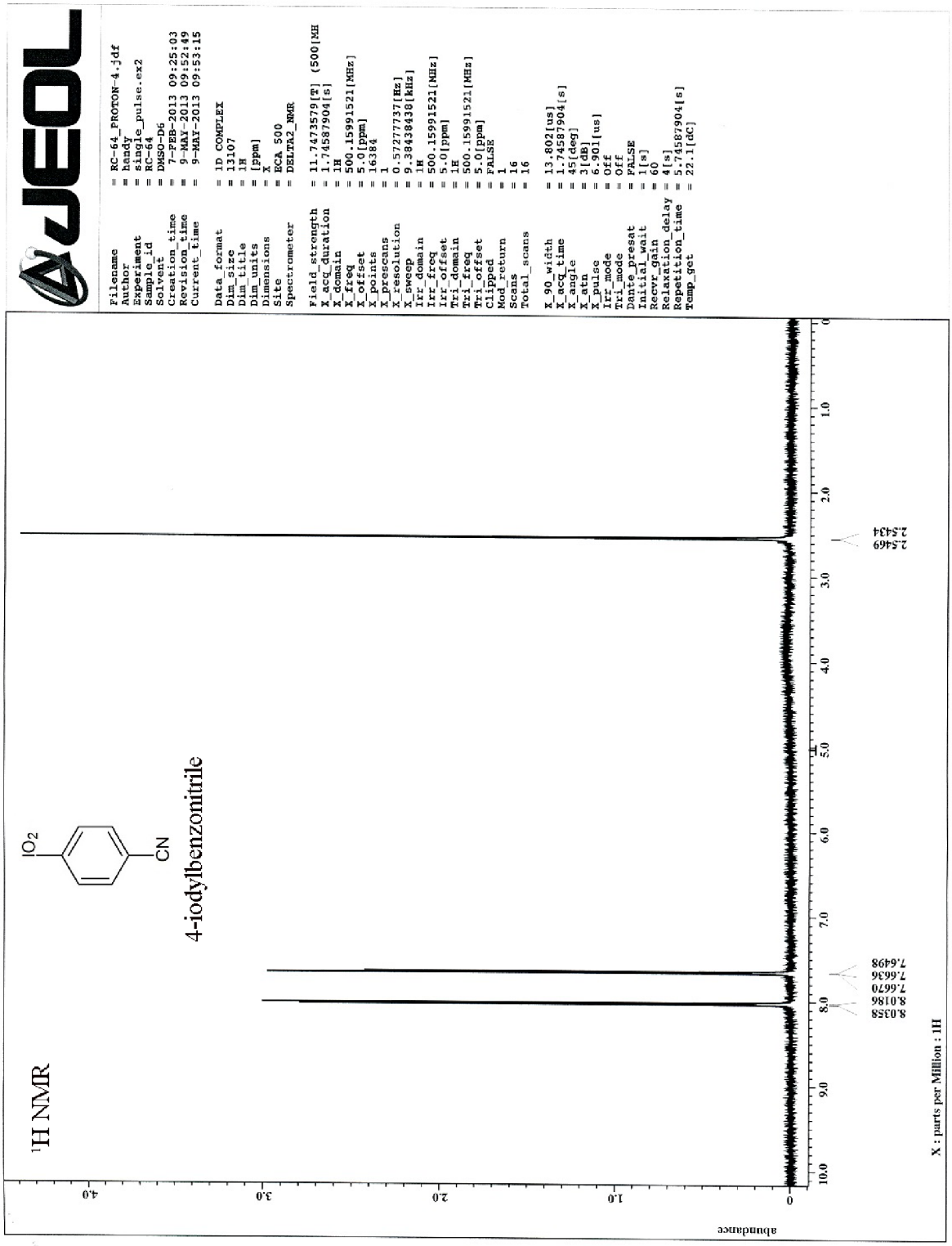
X_angle = 30[deg]
X_atn = 3[dB]
X_pulse = 4[us]
Irr_atn_dec = 21[dB]
Irr_atn_noe = 21[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 56
Relaxation_delay = 2[s]
Repetition_time = 2.83361792[s]
Temp_get = 21.3[dC]
13C NMR
3-iodylbenzonitrile
I
O2
CN
abundance
X : parts per Million : 13C
153.0977
135.6711
132.3041
131.2930
130.9592
119.0840
112.4644
40.6217
40.4500
40.2878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Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
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Mod_return = 1
Scans = 16
Total_scans = 16
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X_acq_time = 1.74587904[s]
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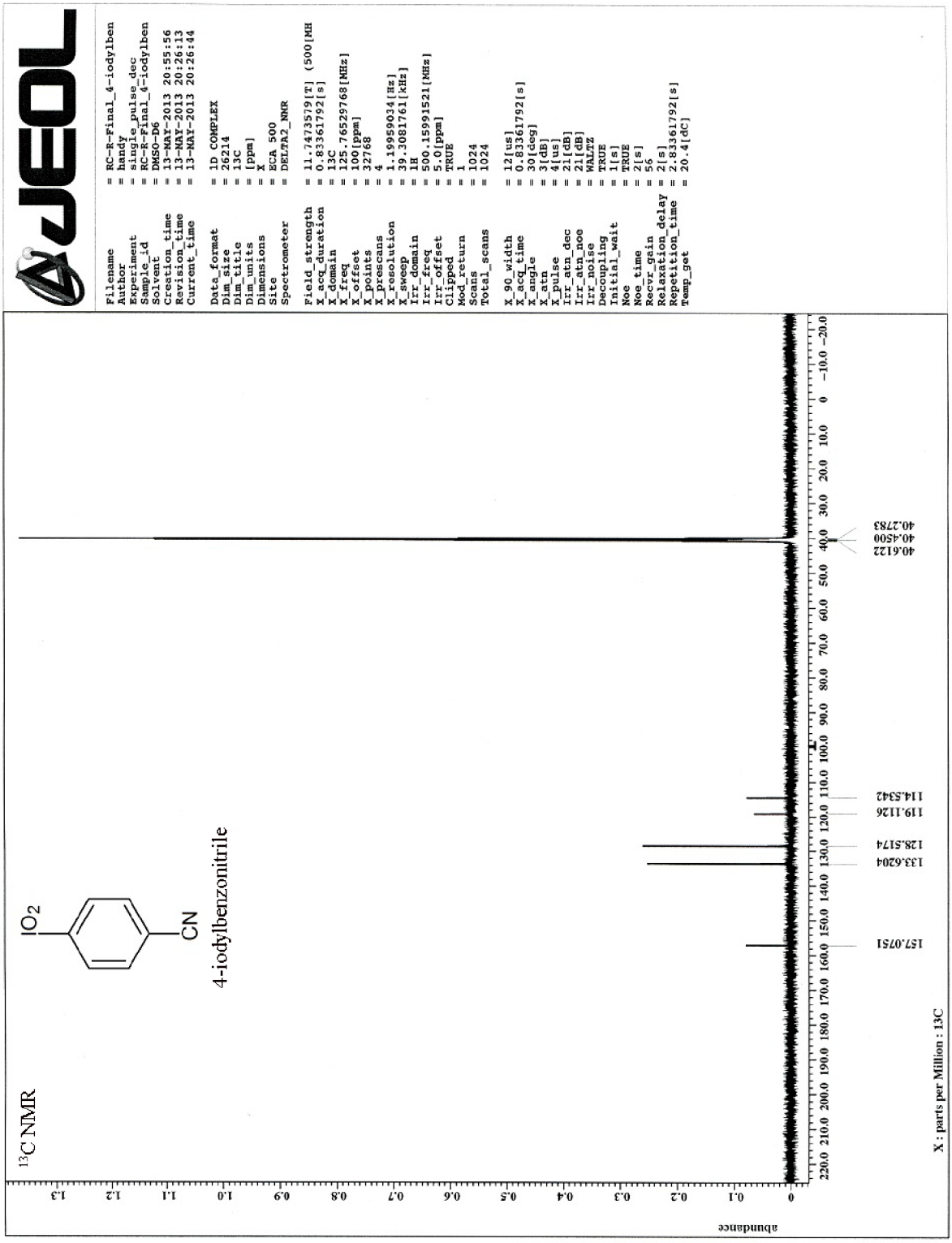
1H NMR
4-iodylbenzonitrile
IO2
CN
abundance
X : parts per Million : 1H
8.0358
8.0186
7.6670
7.6636
7.6498
2.5469
2.5434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Irr_atn_noe = 21[dB]
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Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recv_gain = 56
Relaxation_delay = 2[s]
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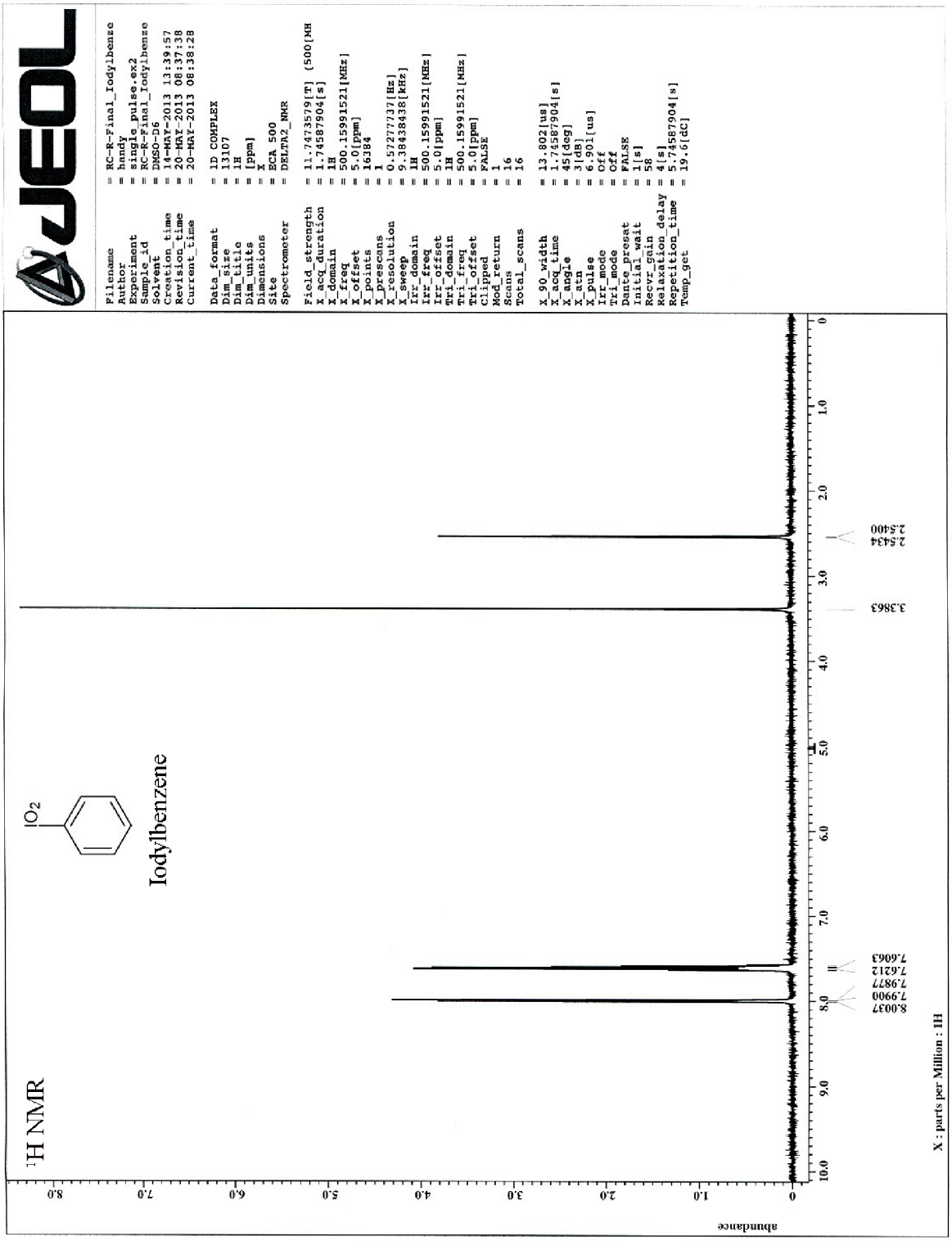
13C NMR
IO2
CN
4-iodylbenzonitrile
abundance
157.0751
133.6204
128.5174
119.1126
114.5342
40.6122
40.4500
40.2783
X : parts per Million : 13C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Tri_domain = 1H
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Mod_return = 1
Scans = 16
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Irr_mode = Off
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Dante_presat = FALSE
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Recvr_gain = 58
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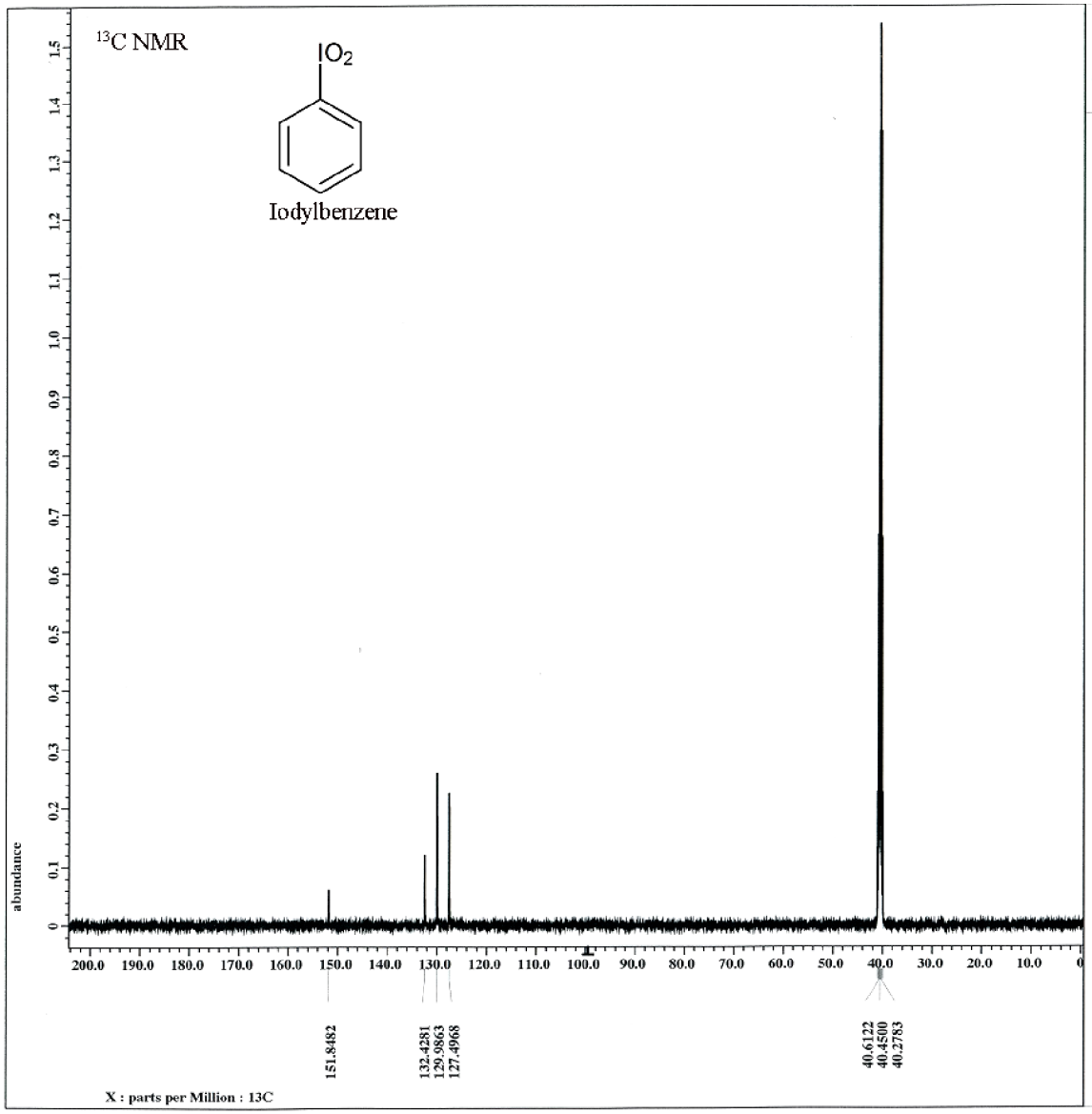
1H NMR
IO2
Iodylbenzene
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3.3863
2.5434
2.5400
8.0037
7.9900
7.9877
7.6212
7.6063
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H



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X_offset	= 100[ppm]
X_points	= 32768
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X_resolution	= 1.19959034[Hz]
X_sweep	= 39.3081761[kHz]
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Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
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Irr_atn_noe	= 21[dB]
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Initial_wait	= 1[s]
Noe	= TRUE
Noe_time	= 2[s]
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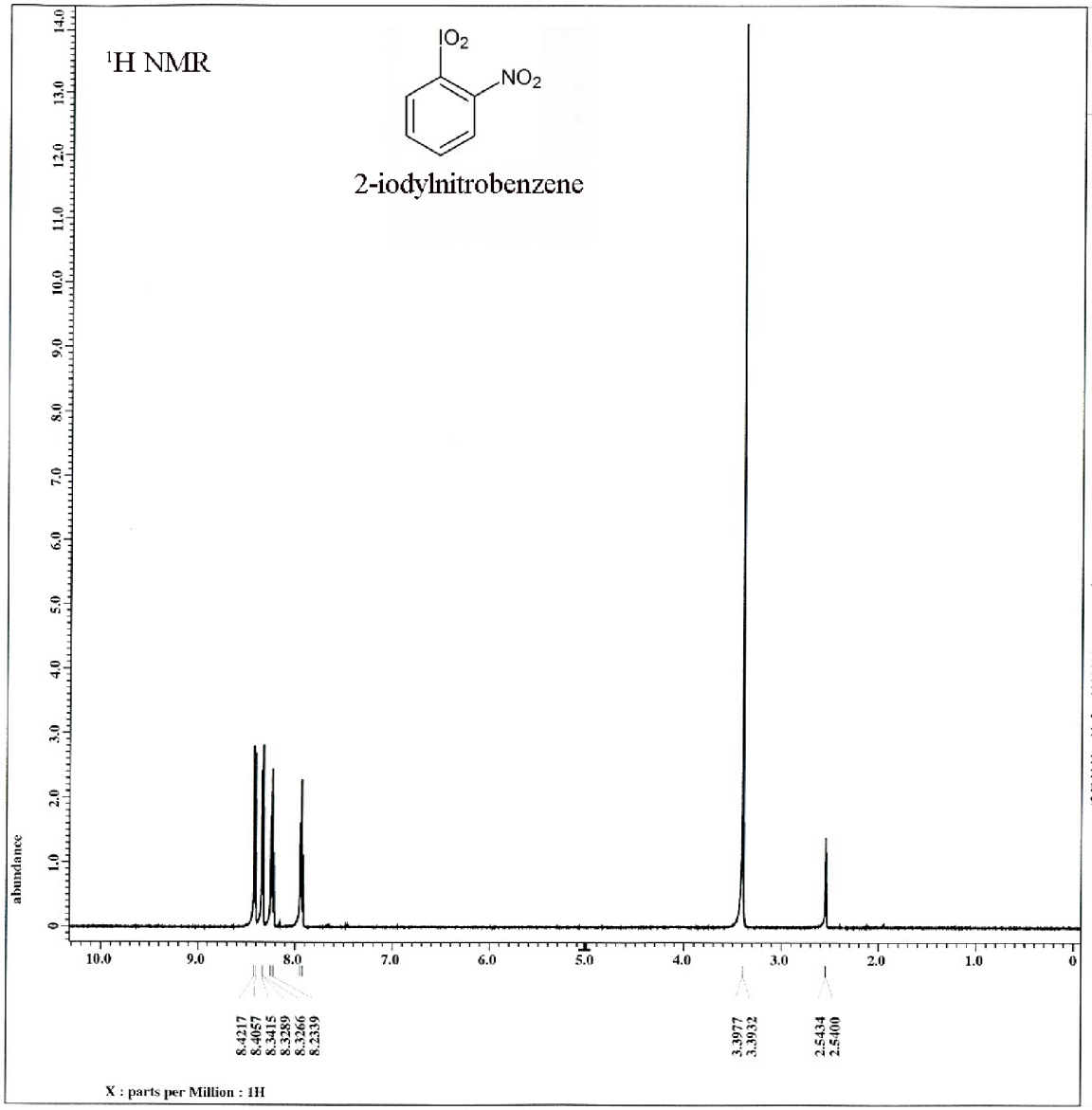

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Irr_freq          = 500.15991521[MHz]
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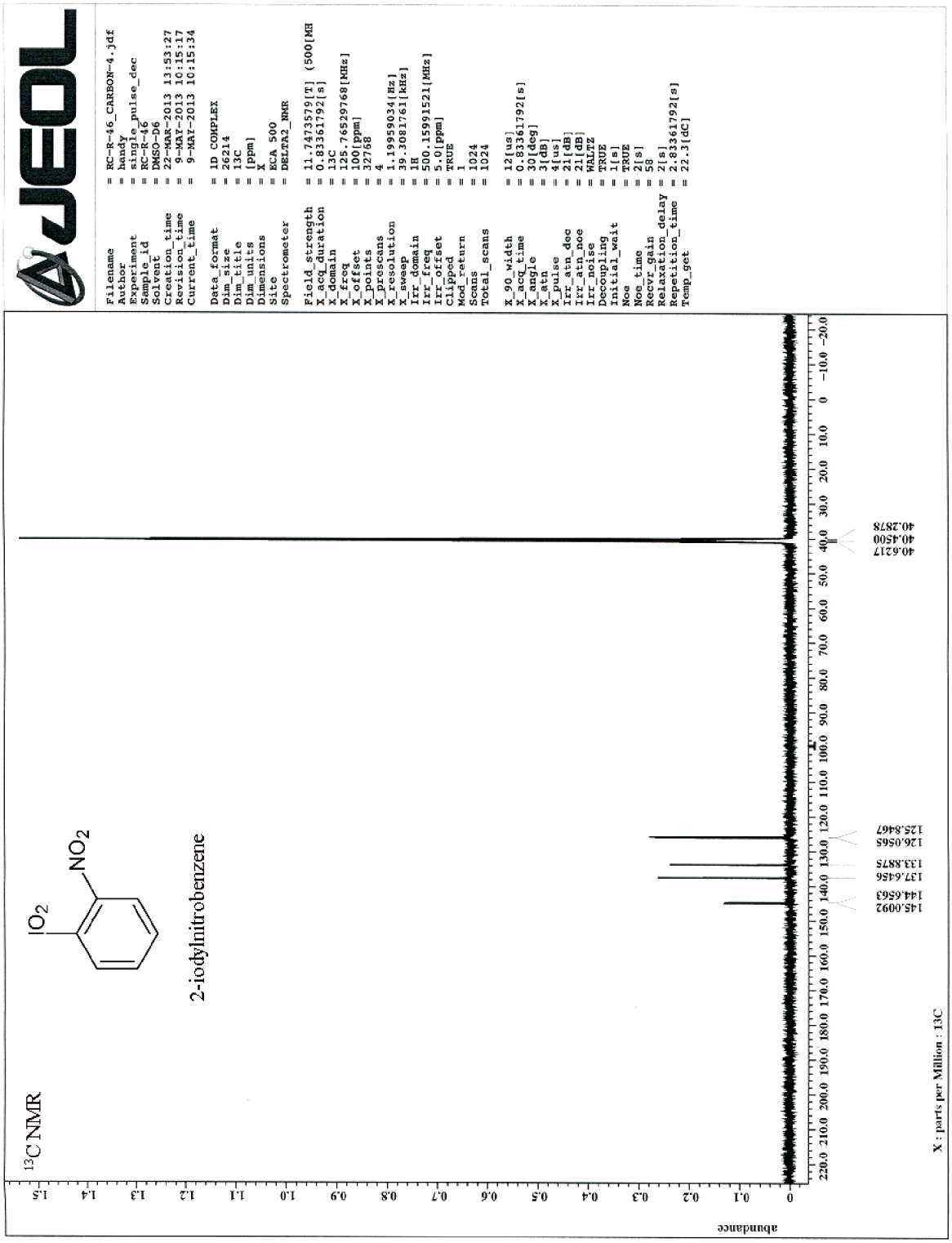
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X_pulse = 4[us]
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Irr_atn_noe = 21[dB]
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Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 58
Relaxation_delay = 2[s]
Repetition_time = 2.83361792[s]
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2-iodylnitrobenzene
IO_2
NO_2
abundance
145.0092
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137.6456
133.8875
126.0565
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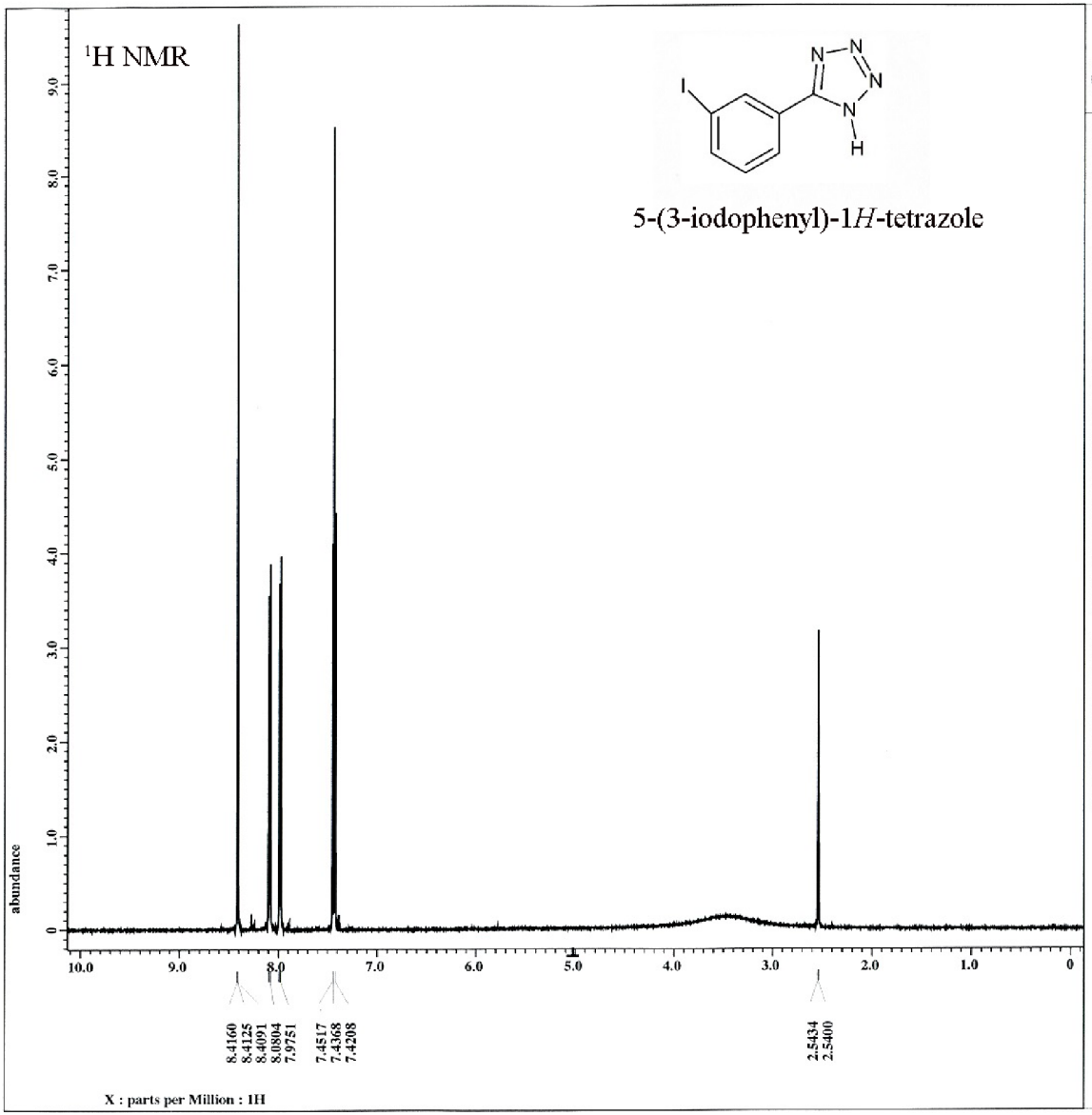
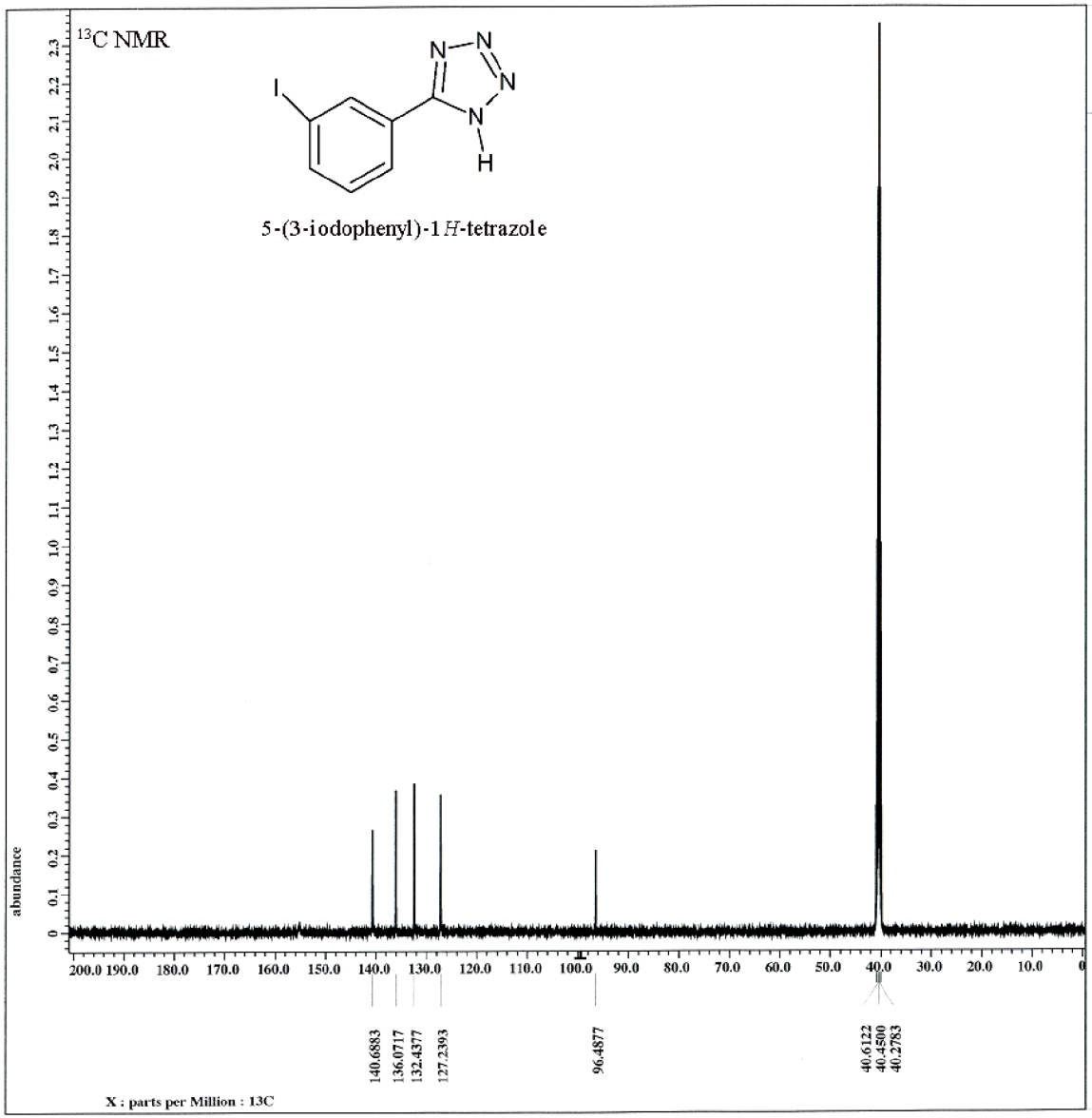
40.4500
40.2878
X : parts per Million : 13C

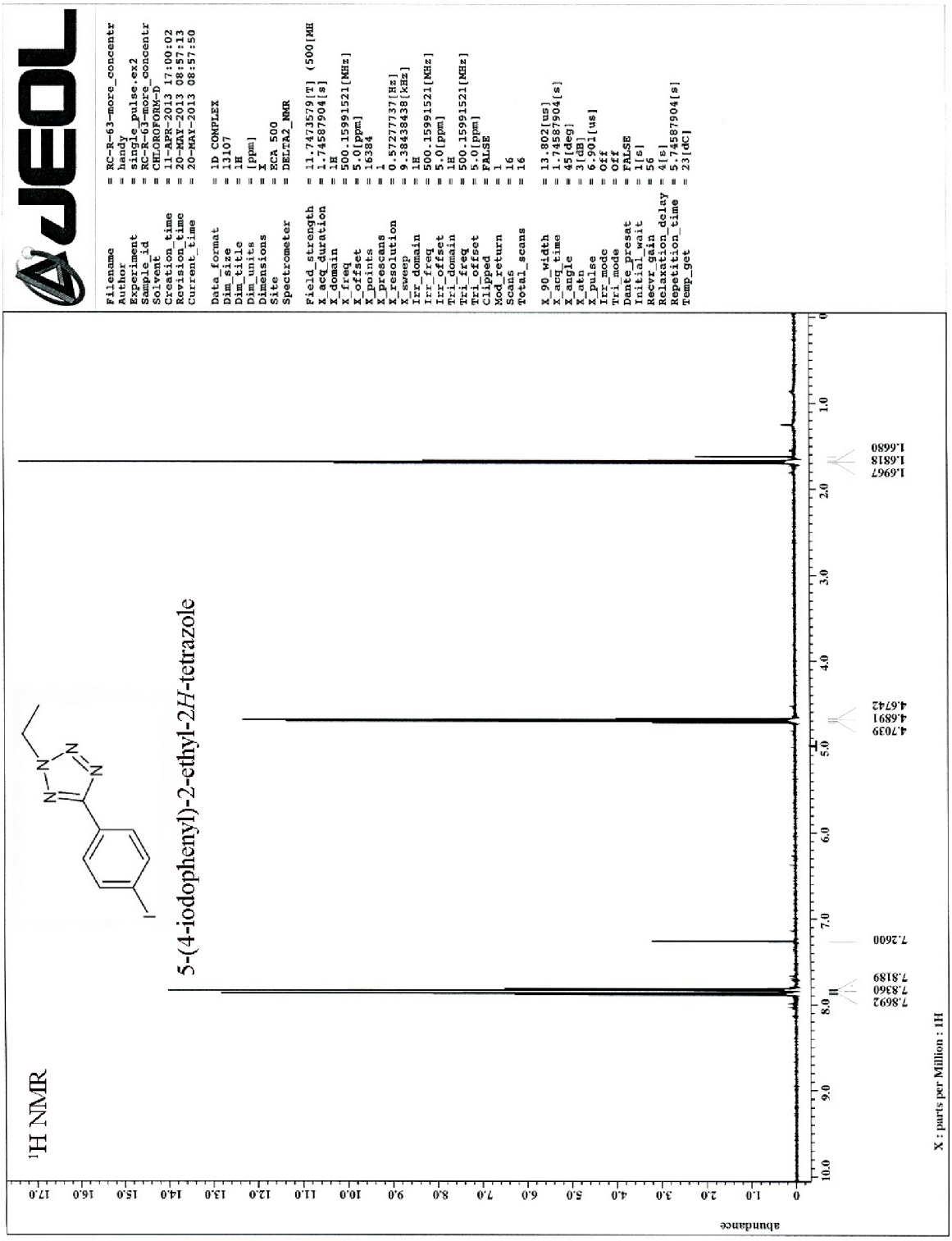


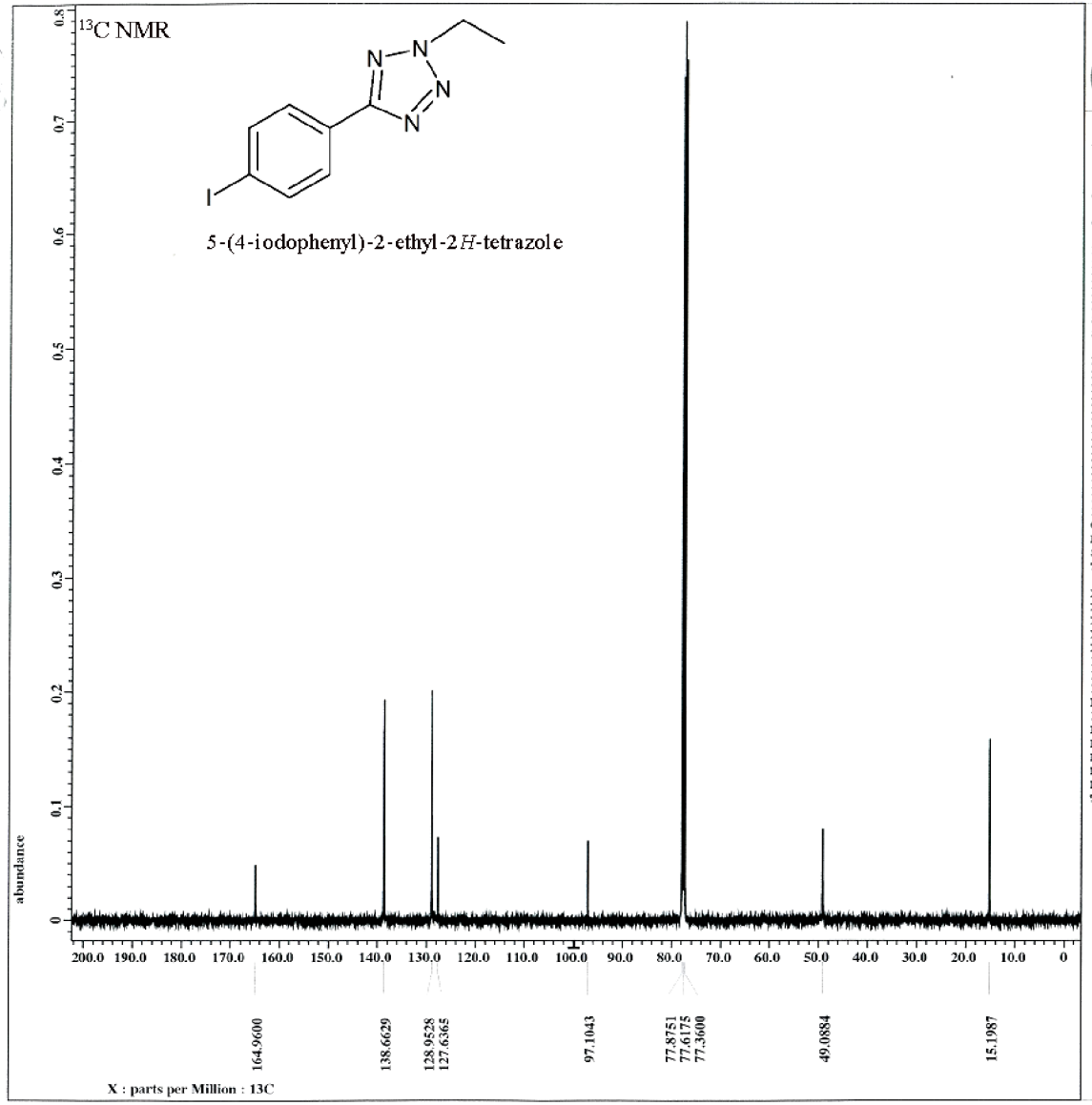

```
Filename          = RC-R-76-4_PROTON-4.jd
Author            = handy
Experiment        = single_pulse.ex2
Sample_id         = RC-R-76-4
Solvent           = DMSO-D6
Creation_time     = 23-APR-2013 20:18:54
Revision_time     = 20-MAY-2013 09:00:39
Current_time      = 20-MAY-2013 09:00:55

Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 13.802[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 3[dB]
X_pulse           = 6.901[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 54
Relaxation_delay  = 4[s]
Repetition_time   = 5.74587904[s]
Temp_get          = 21.1[dC]
```



JEOL

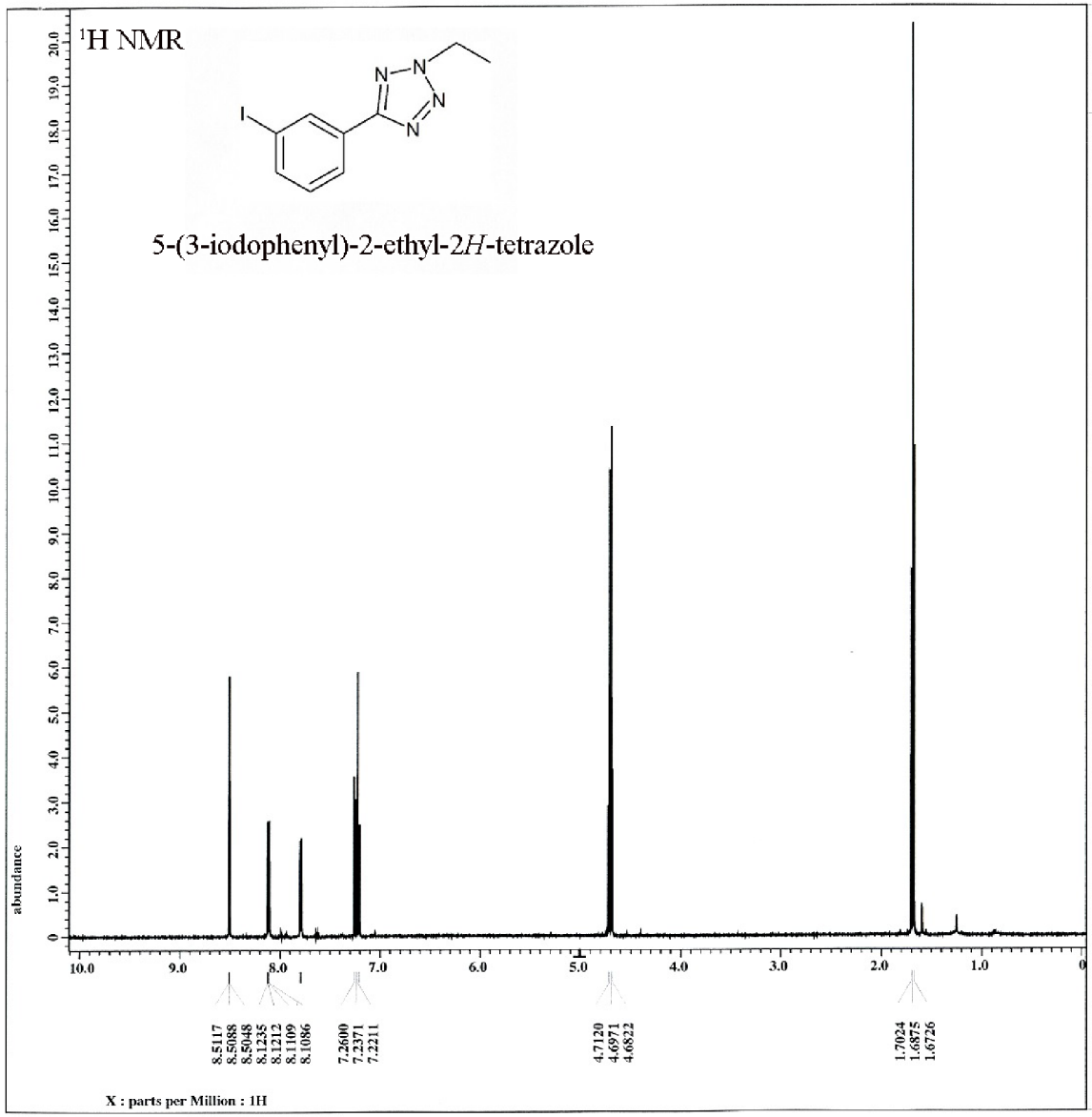
```
Filename          = RC-R-76-4_CARBON-4.jd
Author            = handy
Experiment        = single_pulse_dec
Sample_id         = RC-R-76-4
Solvent           = DMSO-D6
Creation_time     = 23-APR-2013 21:07:48
Revision_time     = 23-MAY-2013 12:39:09
Current_time      = 23-MAY-2013 12:39:55

Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 1024
Total_scans       = 1024

X_90_width        = 12[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 3[dB]
X_pulse           = 4[us]
Irr_atn_dec       = 21[dB]
Irr_atn_noe       = 21[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 60
Relaxation_delay  = 2[s]
Repetition_time   = 2.83361792[s]
Temp_get          = 21.5[dC]
```


JEOL
Filename = RC-R-63-more_concentr
Author = handy
Experiment = single_pulse.ex2
Sample_id = RC-R-63-more_concentr
Solvent = CHLOROFORM-D
Creation_time = 11-APR-2013 17:00:02
Revision_time = 20-MAY-2013 08:57:13
Current_time = 20-MAY-2013 08:57:50
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = RCA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.74735579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 13.802[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 3[dB]
X_pulse = 6.901[us]
Irr_mode = Off
Tri_mode = Off
Date_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 56
Relaxation_delay = 4[s]
Repetition_time = 5.74587904[s]
Temp_get = 23[dC]
1H NMR
5-(4-iodophenyl)-2-ethyl-2H-tetrazole
I
N
N
N
N
abundance
X : parts per Million : 1H
7.8692
7.8360
7.8189
7.2600
4.7039
4.6891
4.6742
1.6967
1.6818
1.6680

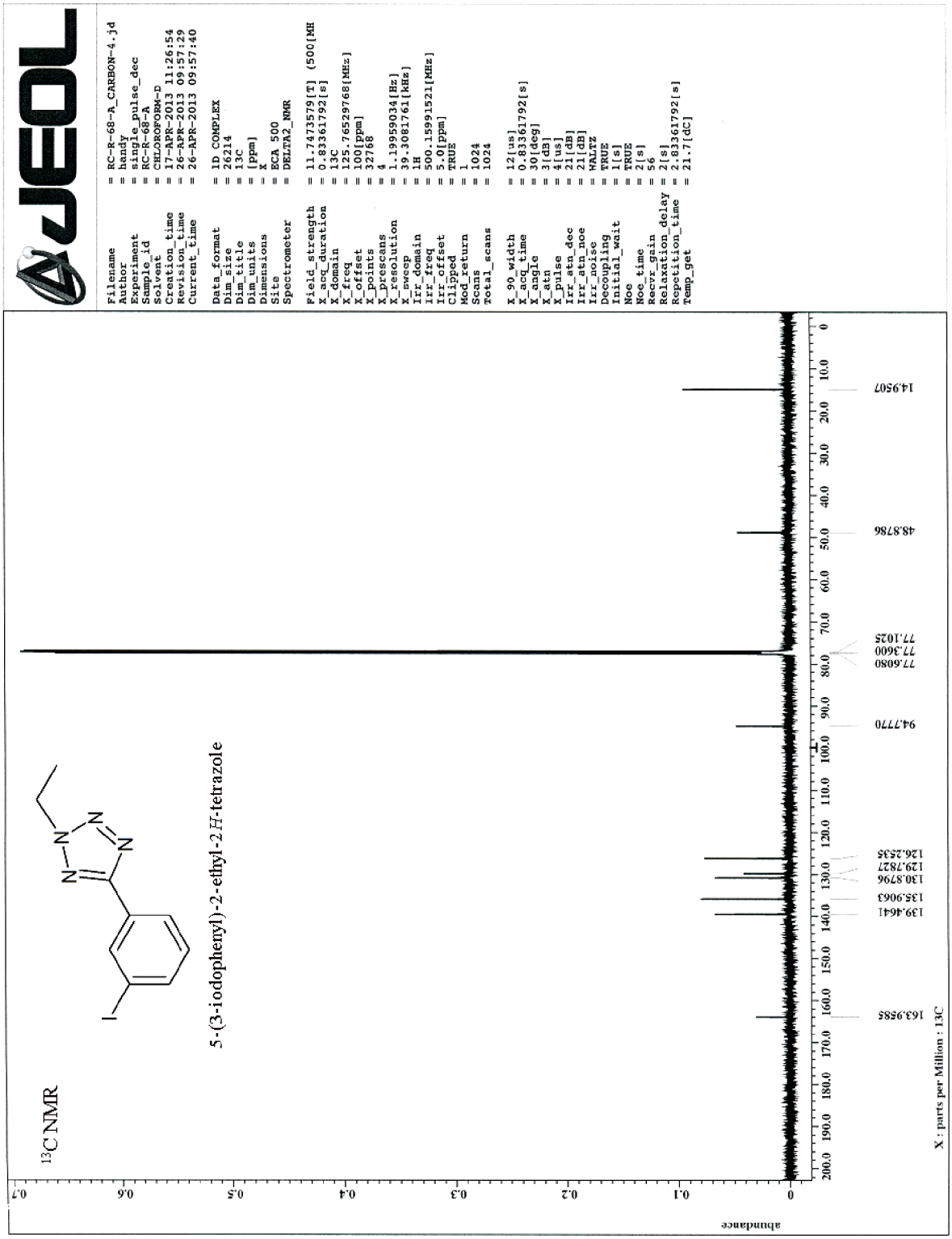


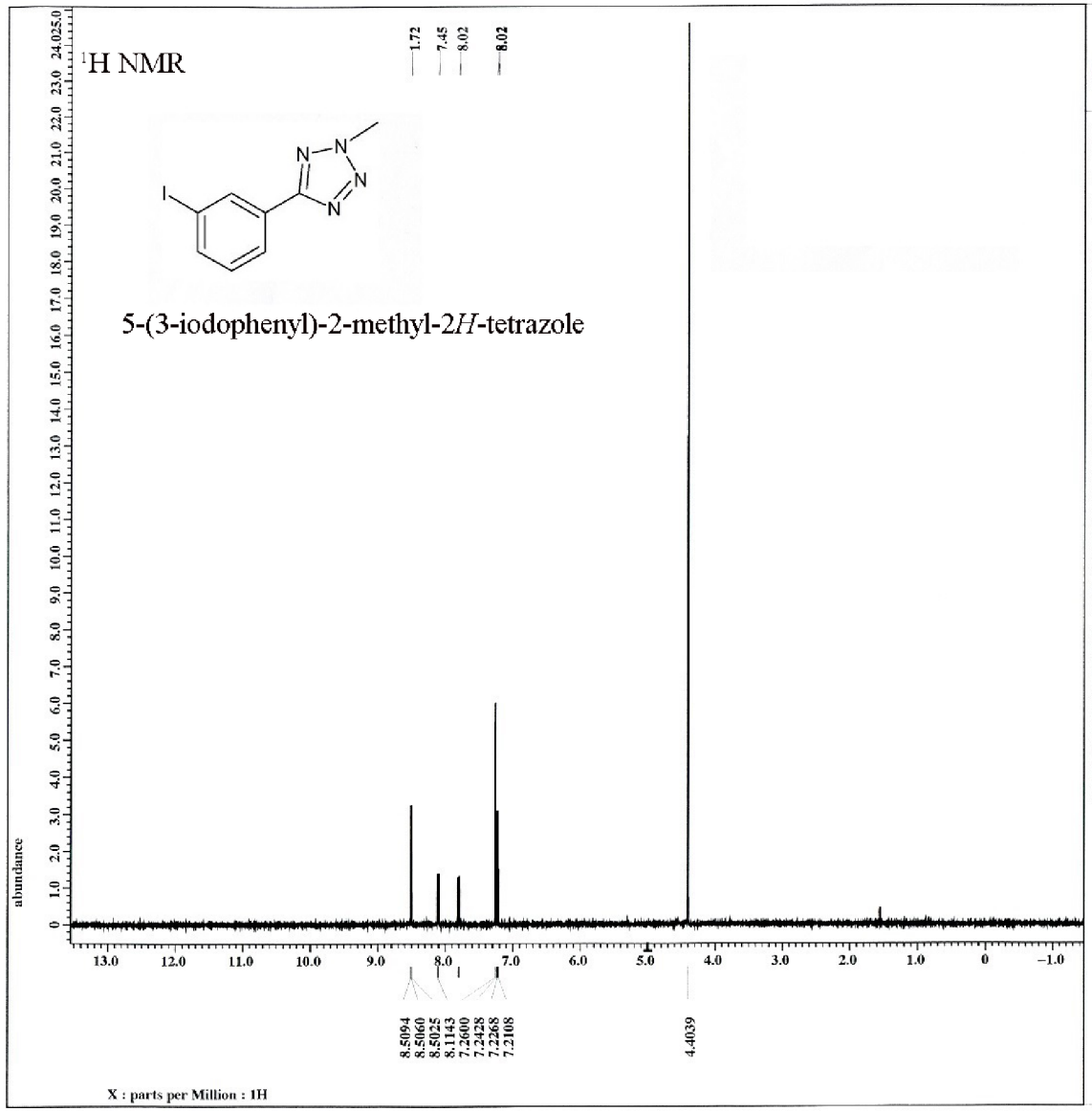
JEOL

```
Filename          = RC-R-63-more_concentr
Author            = handy
Experiment        = single_pulse_dec
Sample_id         = RC-R-63-more_concentr
Solvent           = CHLOROFORM-D
Creation_time     = 11-APR-2013 17:49:02
Revision_time     = 25-APR-2013 20:07:39
Current_time      = 25-APR-2013 20:08:56

Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 1024
Total_scans       = 1024

X_90_width        = 12[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 3[dB]
X_pulse           = 4[us]
Irr_atn_dec       = 21[dB]
Irr_atn_noe       = 21[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 2.83361792[s]
Temp_get          = 23.2[dC]
```



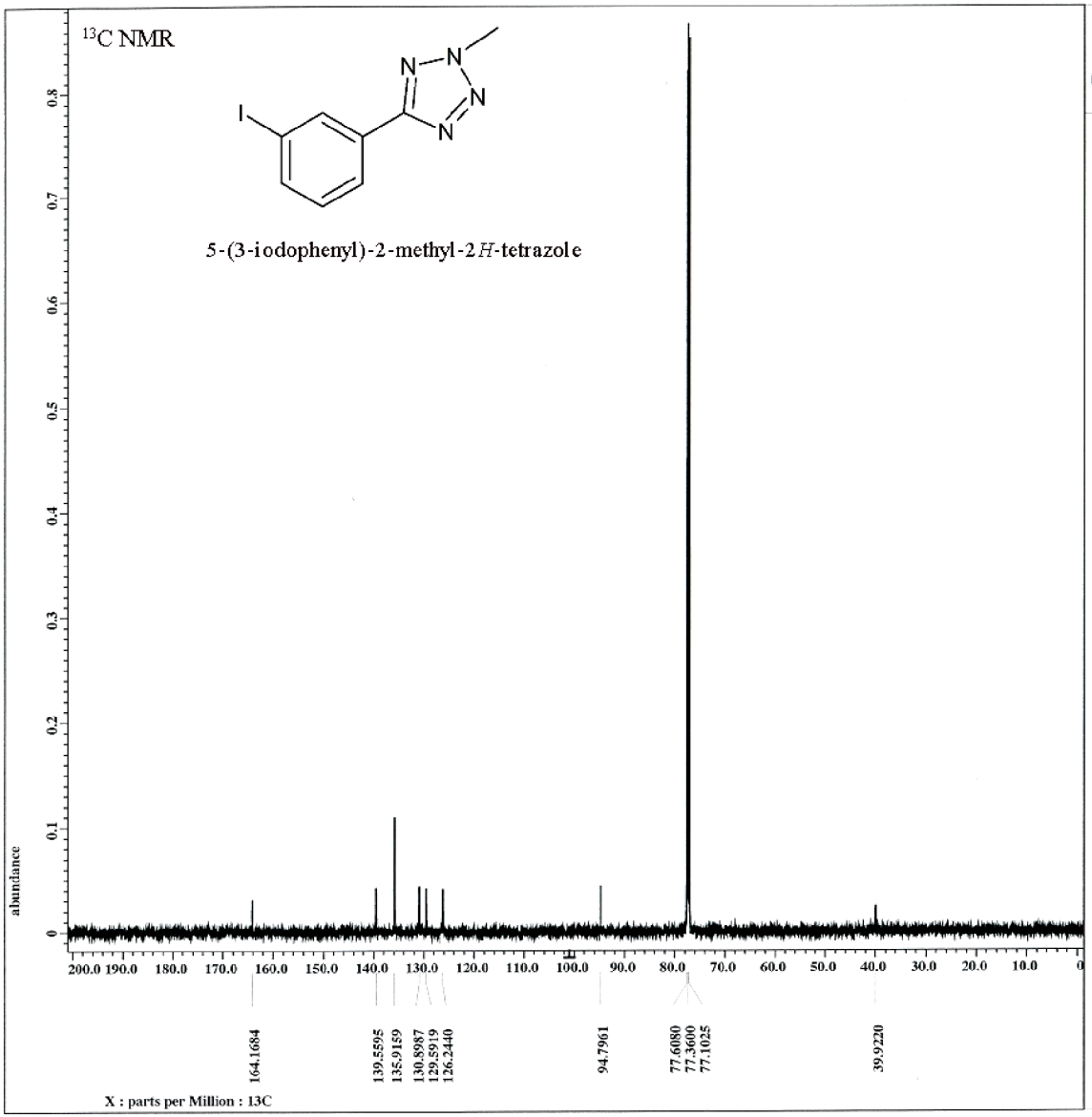

```
Filename          = RC-R-68-1_PROTON-4.jd
Author            = handy
Experiment        = single_pulse.ex2
Sample_id         = RC-R-68-1
Solvent           = CHLOROFORM-D
Creation_time     = 17-APR-2013 11:30:43
Revision_time     = 20-MAY-2013 08:53:46
Current_time      = 20-MAY-2013 08:54:57

Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 13.802[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 3[dB]
X_pulse           = 6.901[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 58
Relaxation_delay  = 4[s]
Repetition_time   = 5.74587904[s]
Temp_get          = 21.6[dC]
```


JEOL
Filename = RC-R-68-A_CARBON-4.jd
Author = handy
Experiment = single_pulse_dec
Sample_id = RC-R-68-A
Solvent = CHLOROFORM-D
Creation_time = 17-APR-2013 11:26:54
Revision_time = 26-APR-2013 09:57:29
Current_time = 26-APR-2013 09:57:40
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.74735791[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 1024
Total_scans = 1024
X_90_width = 12[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 3[dB]
X_pulse = 4[us]
Irr_atn_dec = 21[dB]
Irr_atn_noe = 21[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 56
Relaxation_delay = 2[s]
Repetition_time = 2.83361792[s]
Temp_get = 21.7[dC]
^{13}C NMR
5-(3-iodophenyl)-2-ethyl-2H-tetrazole
I
N
N
N
N
Abundance
X : parts per Million : 13C
163.9585
139.4641
135.9063
130.8796
129.7827
126.2535
94.7770
77.6080
77.3600
77.1025
48.8786
14.9507



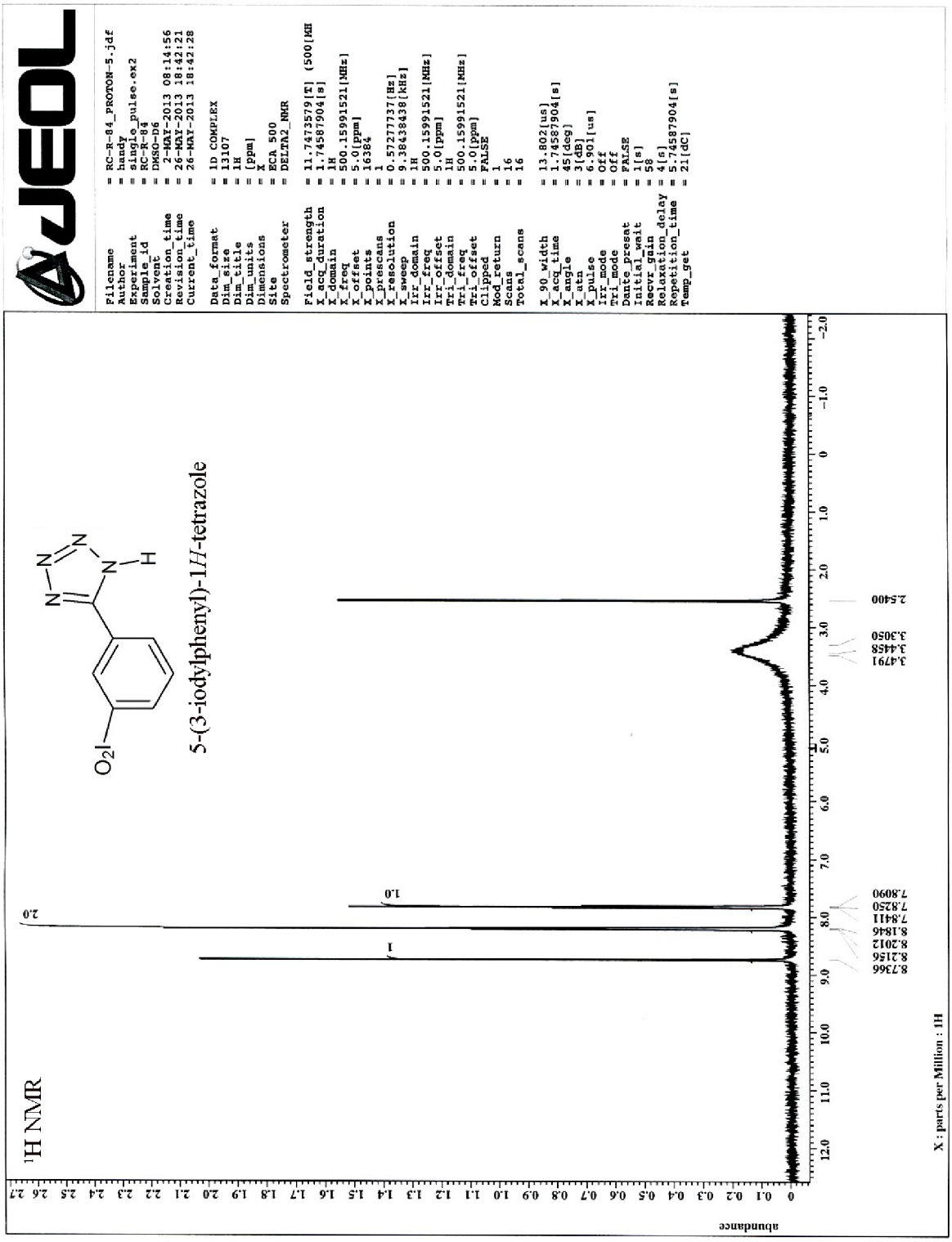
JEOL

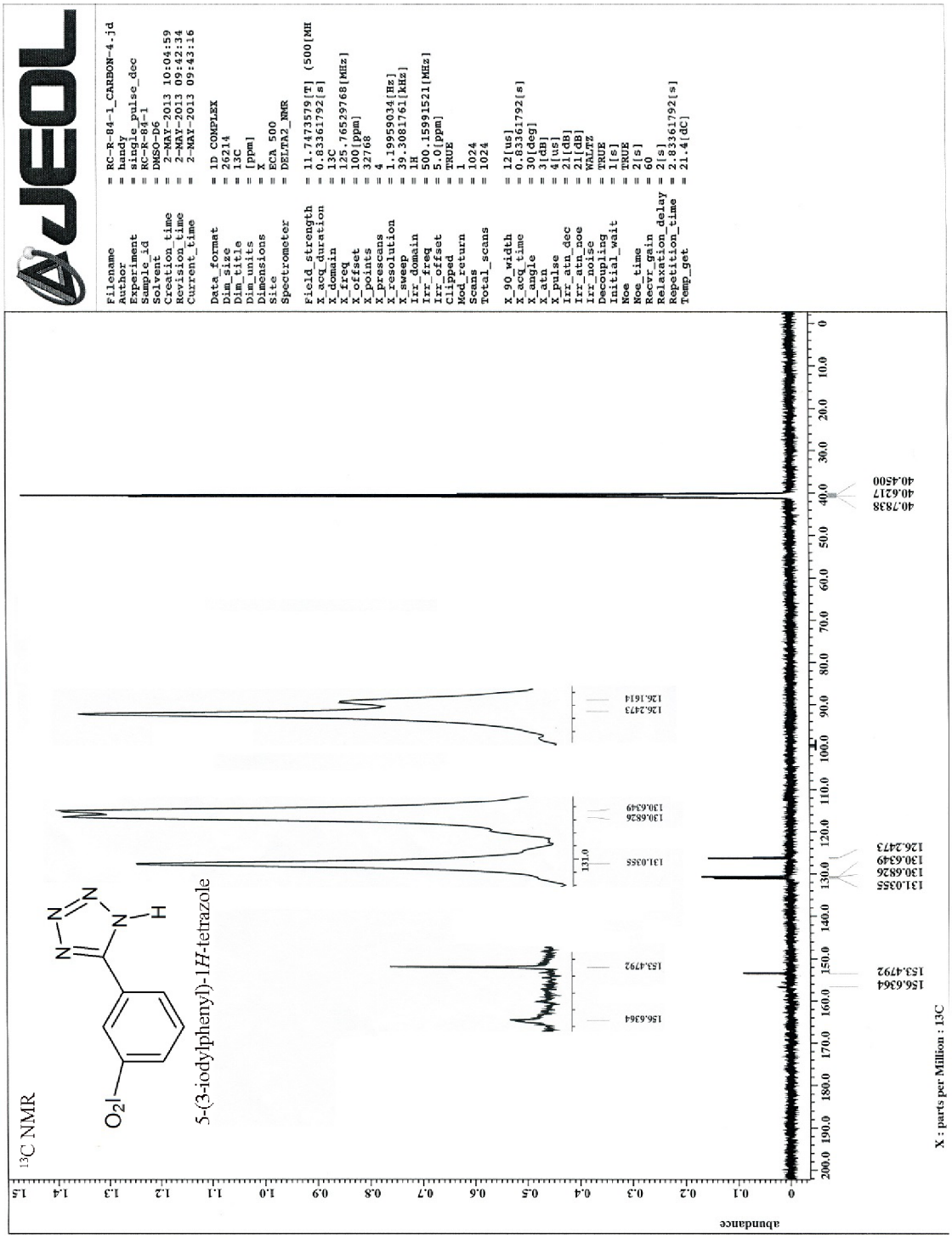
Filename	= RC-R-67-(_PROTON-7.jd
Author	= handy
Experiment	= single_pulse.ex2
Sample_id	= RC-R-67-6
Solvent	= CHLOROFORM-D
Creation_time	= 18-APR-2013 13:52:51
Revision_time	= 26-APR-2013 09:50:18
Current_time	= 26-APR-2013 09:51:03
Data_format	= 1D COMPLEX
Dim_size	= 13107
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= DELTA2_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 1.74587904[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5.0[ppm]
X_points	= 16384
X_prescans	= 1
X_resolution	= 0.57277737[Hz]
X_sweep	= 9.38438438[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Tri_domain	= 1H
Tri_freq	= 500.15991521[MHz]
Tri_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 16
Total_scans	= 16
X_90_width	= 13.802[us]
X_acq_time	= 1.74587904[s]
X_angle	= 45[deg]
X_atn	= 3[dB]
X_pulse	= 6.901[us]
Irr_mode	= Off
Tri_mode	= Off
Dante_presat	= FALSE
Initial_wait	= 1[s]
Recvr_gain	= 62
Relaxation_delay	= 4[s]
Repetition_time	= 5.74587904[s]
Temp_get	= 21.5[dC]

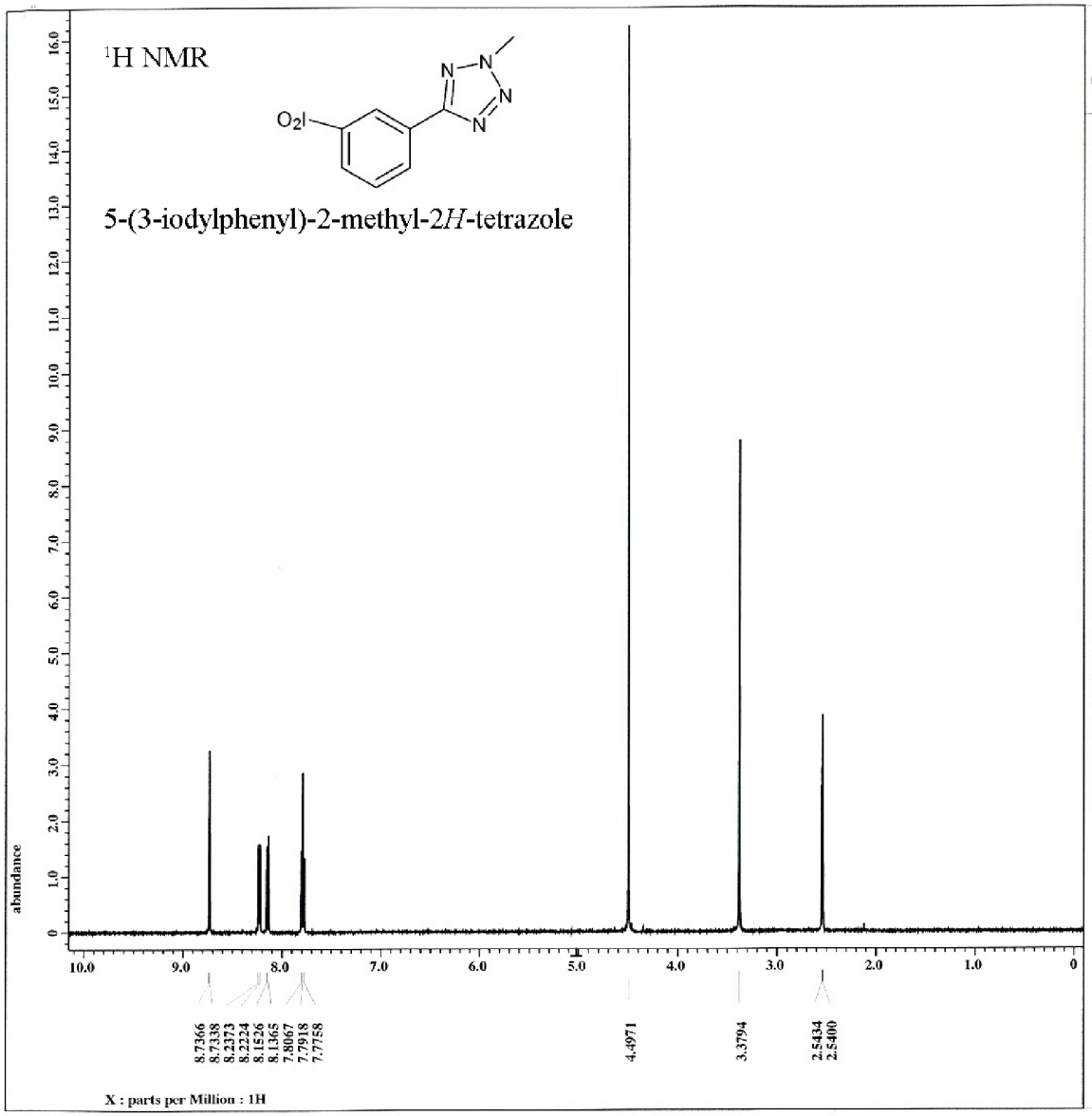


JEOL

```
Filename          = RC-R-67_CARBON-5.jdf
Author            = handy
Experiment        = single_pulse_dec
Sample_id         = RC-R-67
Solvent           = CHLOROFORM-D
Creation_time     = 16-APR-2013 19:48:18
Revision_time     = 26-APR-2013 09:53:37
Current_time      = 26-APR-2013 09:53:52

Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 1024
Total_scans       = 1024

X_90_width        = 12[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 3[dB]
X_pulse           = 4[us]
Irr_atn_dec       = 21[dB]
Irr_atn_noe       = 21[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 2.83361792[s]
Temp_get          = 22[dC]
```

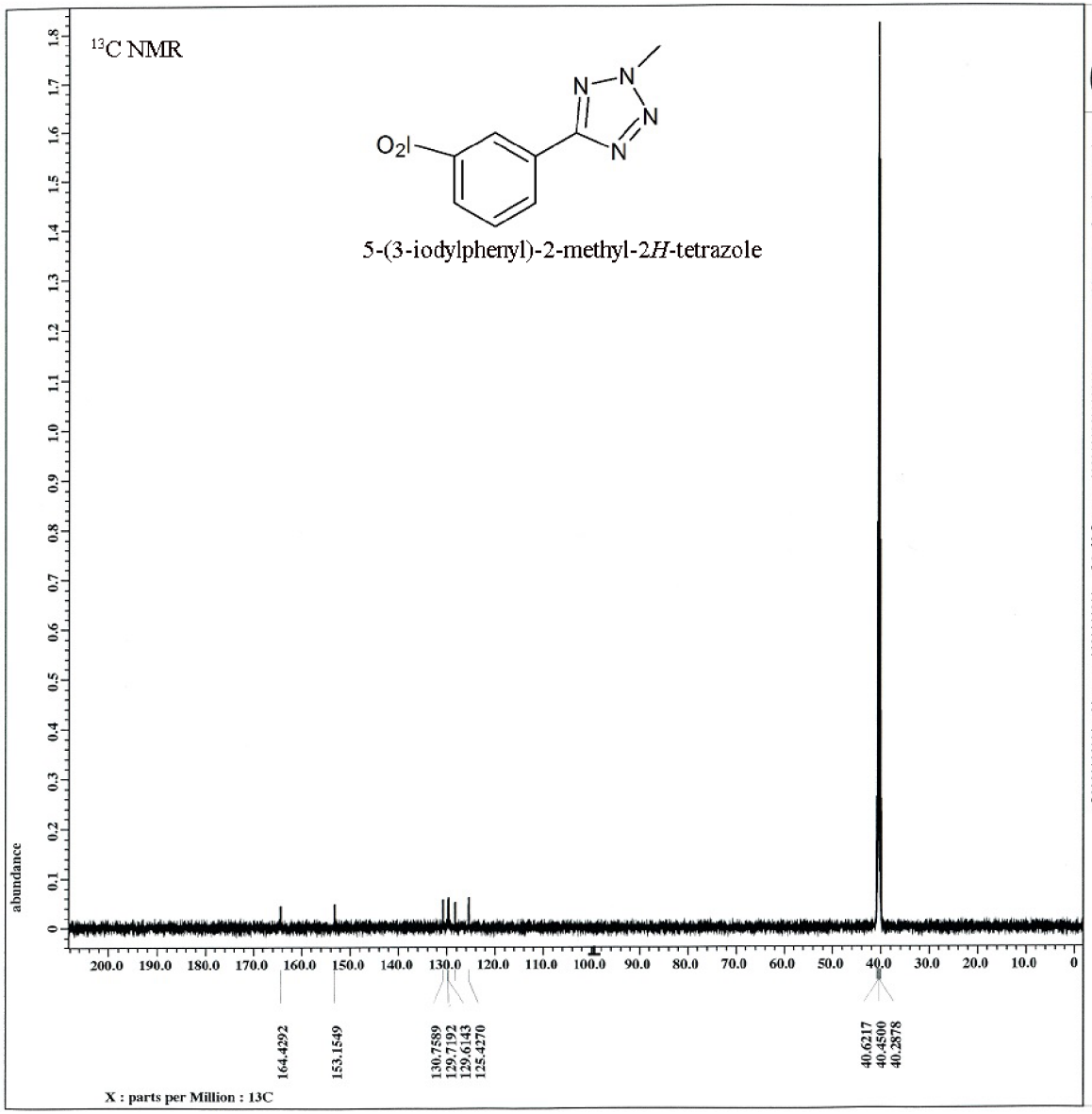

JEOL
Filename = RC-R-84_PROTON-5.jdf
Author = handy
Experiment = single_pulse.ex2
Sample_id = RC-R-84
Solvent = DMSO-D6
Creation_time = 2-MAY-2013 08:14:56
Revision_time = 26-MAY-2013 18:42:21
Current_time = 26-MAY-2013 18:42:28
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 13.802[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 3[dB]
X_pulse = 6.901[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 58
Relaxation_delay = 4[s]
Repetition_time = 5.74587904[s]
Temp_get = 21[dC]
1H NMR
5-(3-iodylphenyl)-1H-tetrazole
O2I
H
N
2.0
1.0
1
2.5400
3.4791
3.4458
3.3050
8.7366
8.2156
8.2012
8.1846
7.8411
7.8250
7.8090
abundance
X : parts per Million : 1H


JEOL
Filename = RC-R-84-1_CARBON-4.jid
Author = handy
Experiment = single_pulse_dec
Sample_id = RC-R-84-1
Solvent = DMSO-D6
Creation_time = 2-MAY-2013 10:04:59
Revision_time = 2-MAY-2013 09:42:34
Current_time = 2-MAY-2013 09:43:16
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.765297681MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.30811761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 1024
Total_scans = 1024
X_90_width = 12[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 3[dB]
X_pulse = 4[us]
Irr_atn_dec = 21[dB]
Irr_atn_noe = 21[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 2.83361792[s]
Temp_get = 21.4[dC]
13C NMR
5-(3-iodylphenyl)-1H-tetrazole
O2I
abundance
X : parts per Million : 13C
156.6364
153.4792
131.0355
130.6826
130.6349
126.2473
40.7838
40.6217
40.4500



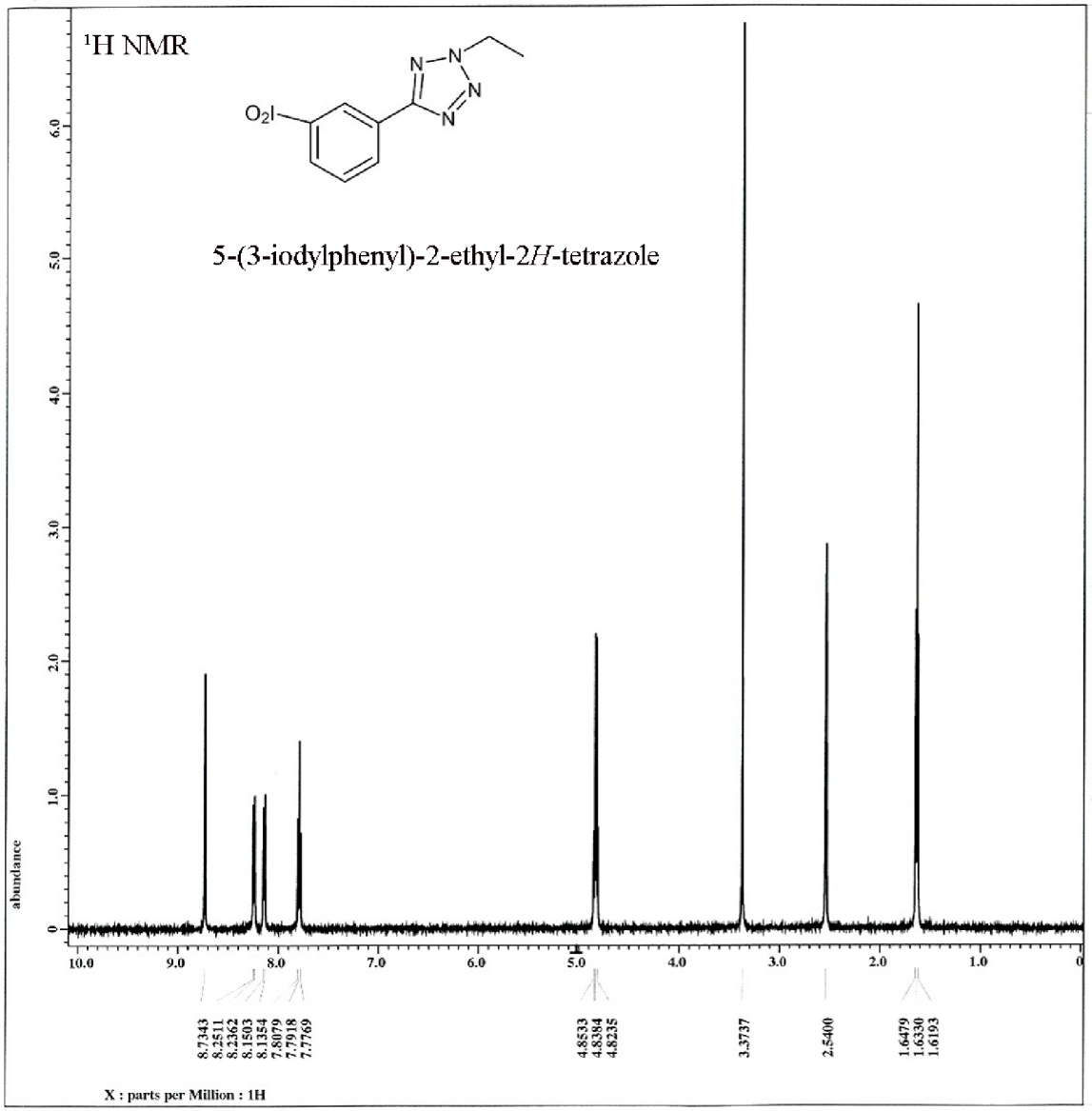
JEOL

```
Filename          = RC-R-70-2_PROTON-4.jd
Author            = handy
Experiment        = single_pulse.ex2
Sample_id         = RC-R-70-2
Solvent           = DMSO-D6
Creation_time     = 18-APR-2013 07:49:32
Revision_time     = 20-MAY-2013 08:49:51
Current_time      = 20-MAY-2013 08:50:03

Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 13.802[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 3[dB]
X_pulse           = 6.901[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 58
Relaxation_delay  = 4[s]
Repetition_time   = 5.74587904[s]
Temp_get          = 21.3[dC]
```



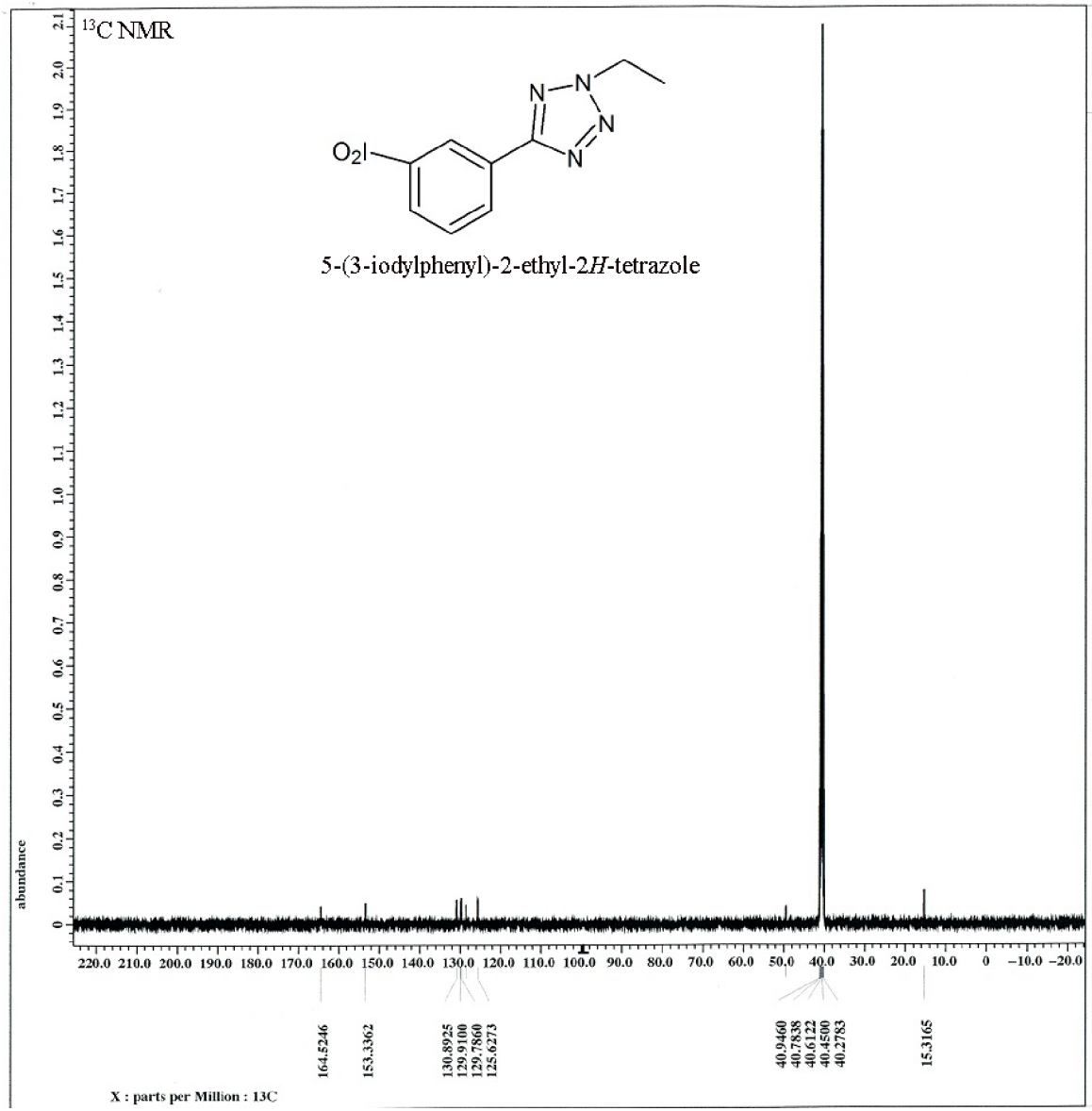
JEOL

```
Filename          = RC-R-70-2_CARBON-4.jd
Author            = handy
Experiment        = single_pulse_dec
Sample_id         = RC-R-70-2
Solvent           = DMSO-D6
Creation_time     = 18-APR-2013 08:38:32
Revision_time     = 20-MAY-2013 19:32:34
Current_time      = 20-MAY-2013 19:32:48

Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 1024
Total_scans       = 1024

X_90_width        = 12[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 3[dB]
X_pulse           = 4[us]
Irr_atn_dec       = 21[dB]
Irr_atn_noe       = 21[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 2.83361792[s]
Temp_get          = 21.6[dC]
```



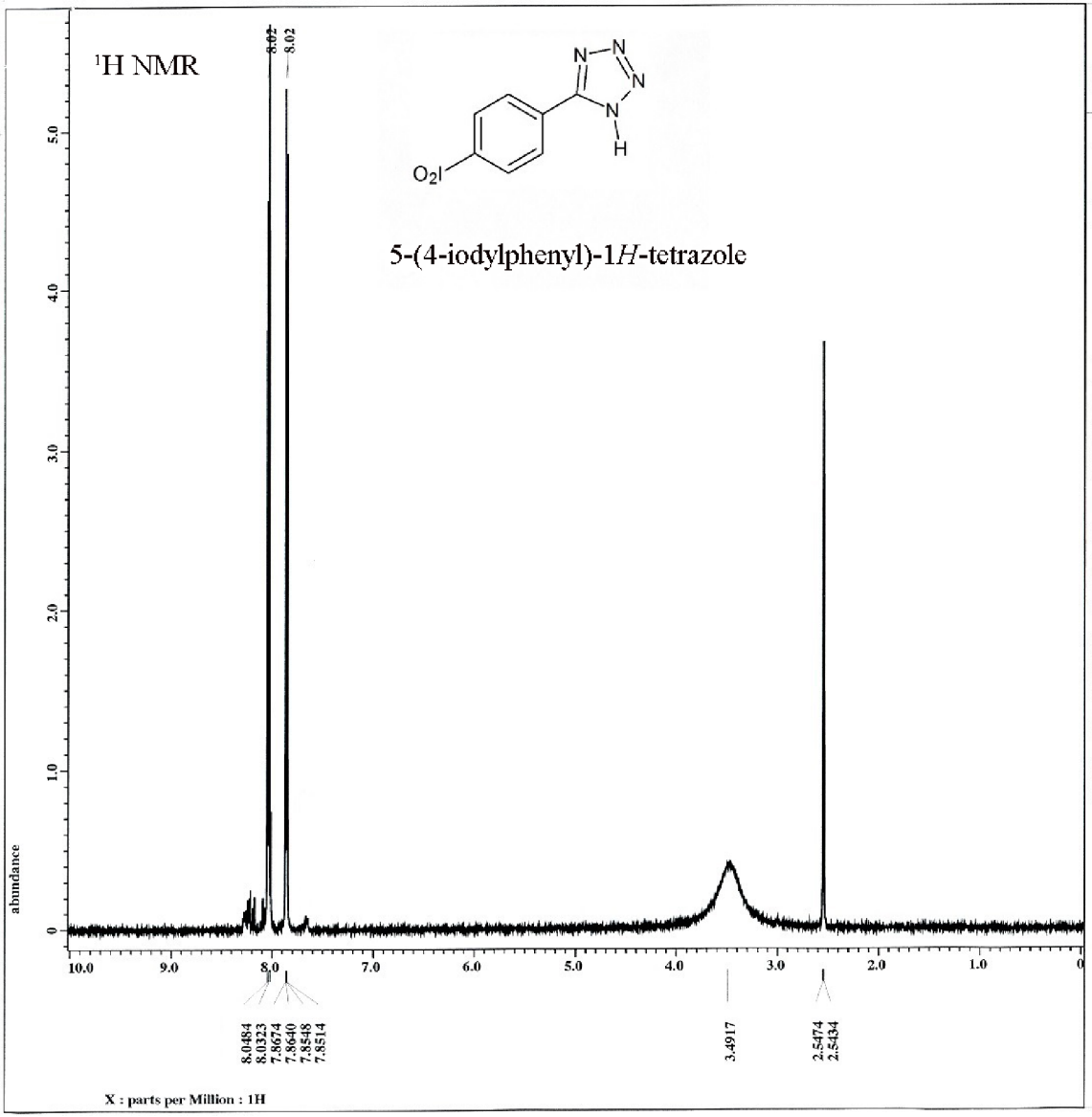
JEOL

Filename	= RC-R-71_PROTON-4.jdf
Author	= handy
Experiment	= single_pulse.ex2
Sample_id	= RC-R-71
Solvent	= DMSO-D6
Creation_time	= 17-APR-2013 20:59:06
Revision_time	= 20-MAY-2013 08:43:00
Current_time	= 20-MAY-2013 08:44:05
Data_format	= 1D COMPLEX
Dim_size	= 13107
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= DELTA2_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 1.74587904[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5.0[ppm]
X_points	= 16384
X_prescans	= 1
X_resolution	= 0.57277737[Hz]
X_sweep	= 9.38438438[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Tri_domain	= 1H
Tri_freq	= 500.15991521[MHz]
Tri_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 16
Total_scans	= 16
X_90_width	= 13.802[us]
X_acq_time	= 1.74587904[s]
X_angle	= 45[deg]
X_atn	= 3[dB]
X_pulse	= 6.901[us]
Irr_mode	= Off
Tri_mode	= Off
Dante_presat	= FALSE
Initial_wait	= 1[s]
Recvr_gain	= 58
Relaxation_delay	= 4[s]
Repetition_time	= 5.74587904[s]
Temp_get	= 21.5[dC]



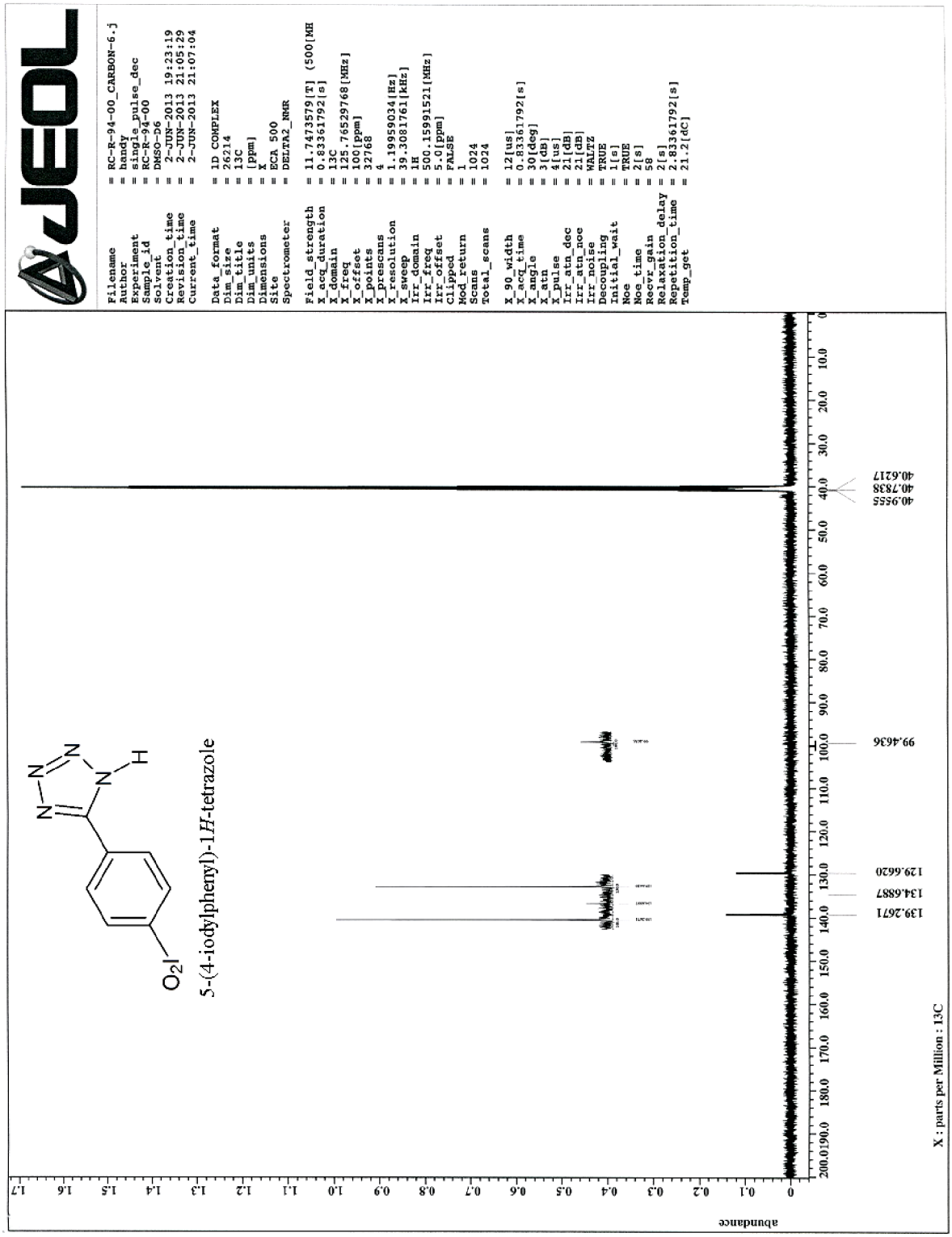
JEOL

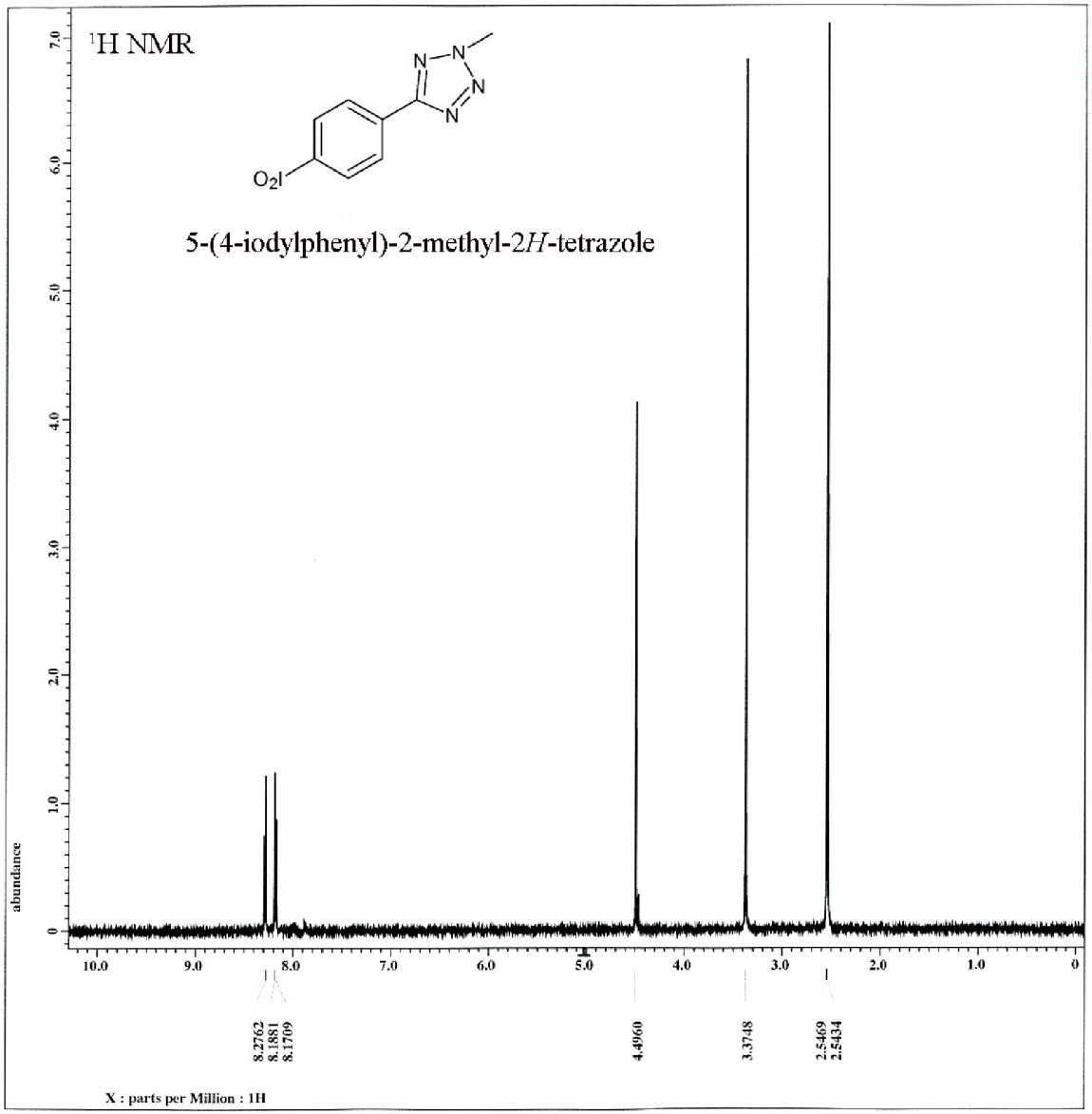
Filename	= RC-R-71_CARBON-4.jdf
Author	= handy
Experiment	= single_pulse_dec
Sample_id	= RC-R-71
Solvent	= DMSO-D6
Creation_time	= 17-APR-2013 21:47:59
Revision_time	= 25-APR-2013 20:21:21
Current_time	= 25-APR-2013 20:21:38
Data_format	= 1D COMPLEX
Dim_size	= 26214
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= DELTA2_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.83361792[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 32768
X_prescans	= 4
X_resolution	= 1.19959034[Hz]
X_sweep	= 39.3081761[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Clipped	= TRUE
Mod_return	= 1
Scans	= 1024
Total_scans	= 1024
X_90_width	= 12[us]
X_acq_time	= 0.83361792[s]
X_angle	= 30[deg]
X_atn	= 3[dB]
X_pulse	= 4[us]
Irr_atn_dec	= 21[dB]
Irr_atn_noe	= 21[dB]
Irr_noise	= WALTZ
Decoupling	= TRUE
Initial_wait	= 1[s]
Noe	= TRUE
Noe_time	= 2[s]
Recvr_gain	= 60
Relaxation_delay	= 2[s]
Repetition_time	= 2.83361792[s]
Temp_get	= 21.4[dC]



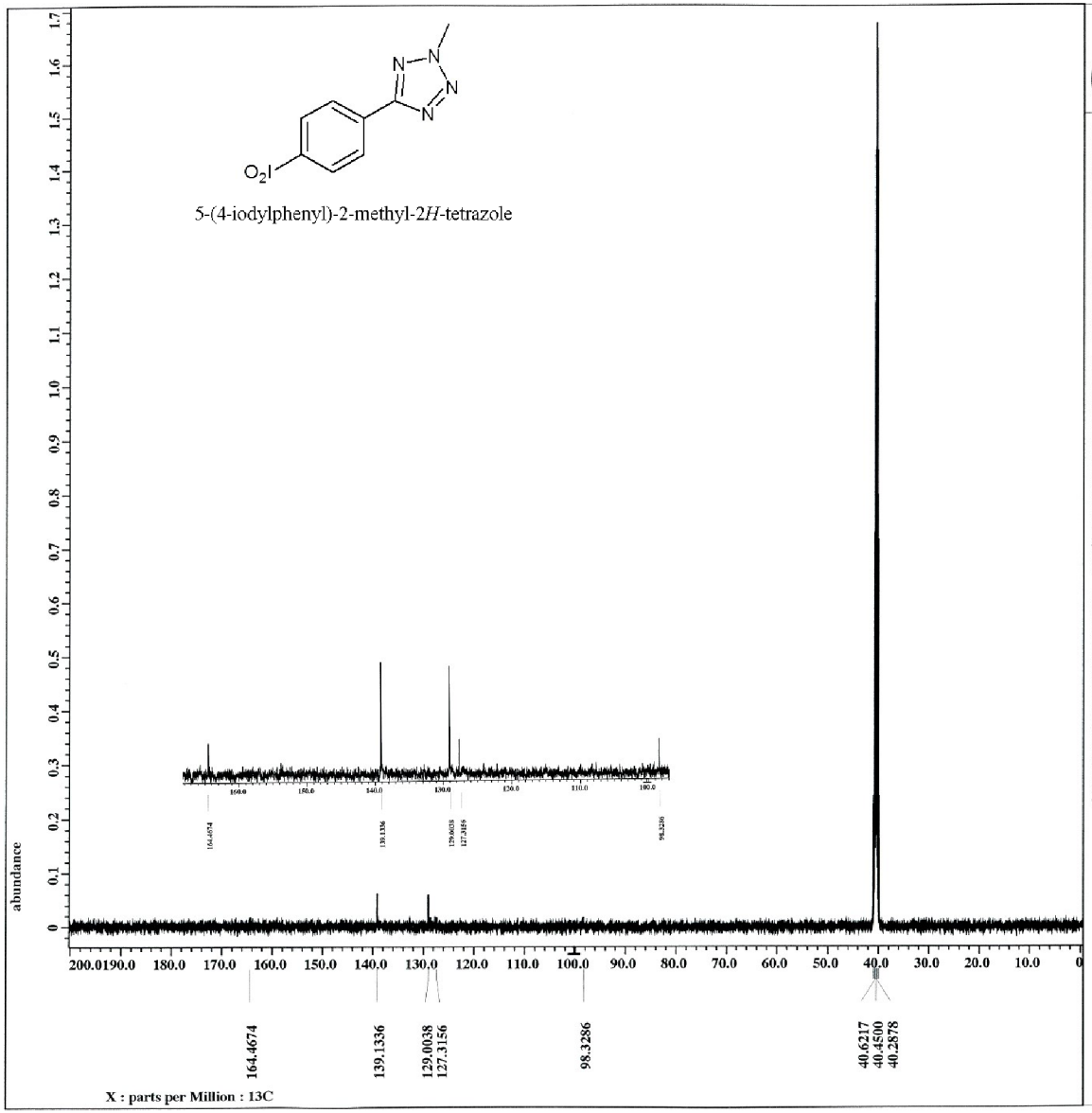
JEOL

```
Filename          = RC-R-[illegible]-3.jdf
Author            = hanky
Experiment        = single_pulse.ex2
Sample_id         = RC-[illegible]
Solvent           = DMSO-D6
Creation_time     = 17-MAY-2013 14:15:22
Revision_time     = 17-MAY-2013 13:52:04
Current_time      = 17-MAY-2013 13:52:22

Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 13.802[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 3[dB]
X_pulse           = 6.901[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 58
Relaxation_delay  = 4[s]
Repetition_time   = 5.74587904[s]
Temp_get          = 18.9[dC]
```


JEOL
Filename = RC-R-94-00_CARBON-6.j
Author = handy
Experiment = single_pulse_dec
Sample_id = RC-R-94-00
Solvent = DMSO-D6
Creation_time = 2-JUN-2013 19:23:19
Revision_time = 2-JUN-2013 21:05:29
Current_time = 2-JUN-2013 21:07:04
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 1024
Total_scans = 1024
X_90_width = 12[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 3[dB]
X_pulse = 4[us]
Irr_atn_dec = 21[dB]
Irr_atn_noe = 21[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 58
Relaxation_delay = 2[s]
Repetition_time = 2.83361792[s]
Temp_get = 21.2[dC]
5-(4-iodylphenyl)-1H-tetrazole
O2I
H
N
N
N
N
abundance
X : parts per Million : 13C
139.2671
134.6887
129.6620
99.4636
40.9555
40.7838
40.6217

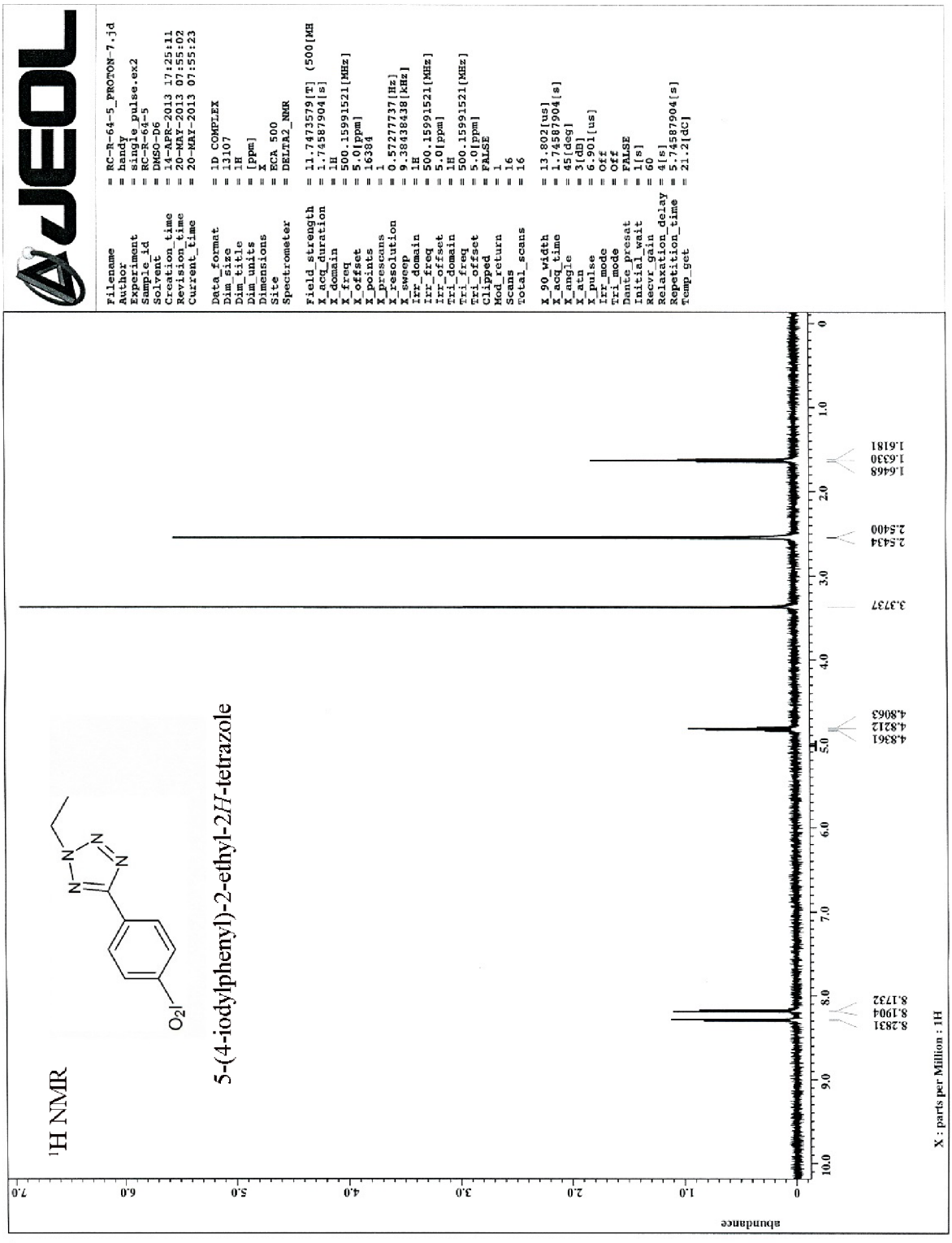


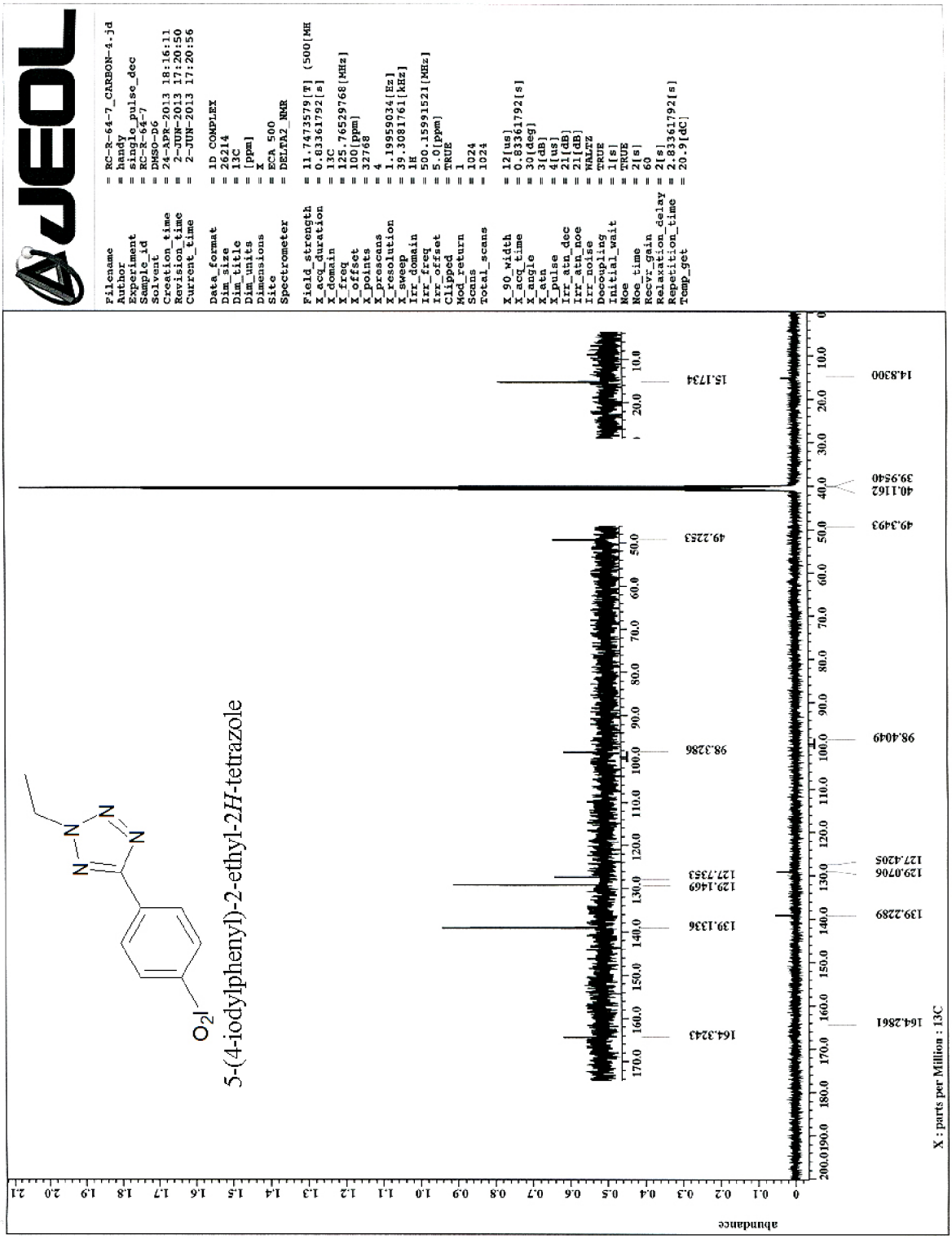

```
Filename          = RC-R-59-2_PROTON-4.jd
Author            = handy
Experiment        = single_pulse.ex2
Sample_id         = RC-R-59-2
Solvent           = DMSO-D6
Creation_time     = 14-APR-2013 18:44:40
Revision_time     =  9-MAY-2013 10:25:30
Current_time      =  9-MAY-2013 10:26:05

Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 13.802[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 3[dB]
X_pulse           = 6.901[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 62
Relaxation_delay  = 4[s]
Repetition_time   = 5.74587904[s]
Temp_get          = 21.1[dC]
```



JEOL

```
Filename          = RC-R-59-8_CARBON-10.j
Author            = handy
Experiment        = single_pulse_dec
Sample_id         = RC-R-59-8
Solvent           = DMSO-D6
Creation_time     = 24-APR-2013 17:14:50
Revision_time     =  4-JUN-2013 08:17:44
Current_time      =  4-JUN-2013 08:17:54

Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 1024
Total_scans       = 1024

X_90_width        = 12[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 3[dB]
X_pulse           = 4[us]
Irr_atn_dec       = 21[dB]
Irr_atn_noe       = 21[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 2.83361792[s]
Temp_get          = 20.9[dC]
```


JEOL
Filename = RC-R-64-5_PROTON-7.jd
Author = handy
Experiment = single_pulse.ex2
Sample_id = RC-R-64-5
Solvent = DMSO-D6
Creation_time = 14-APR-2013 17:25:11
Revision_time = 20-MAY-2013 07:55:02
Current_time = 20-MAY-2013 07:55:23
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.74735791[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 13.802[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 3[dB]
X_pulse = 6.901[us]
Irr_mode = Off
Tri_mode = Off
Decpl_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 60
Relaxation_delay = 4[s]
Repetition_time = 5.74587904[s]
Temp_get = 21.2[dC]
1H NMR
5-(4-iodylphenyl)-2-ethyl-2H-tetrazole
O2
abundance
X : parts per Million : 1H
8.2831
8.1904
8.1732
4.8361
4.8212
4.8063
3.3737
2.5434
2.5400
1.6468
1.6330
1.6181


JEOL
Filename = RC-R-64-7_CARBON-4.jd
Author = handy
Experiment = single_pulse_dec
Sample_id = RC-R-64-7
Solvent = DMSO-D6
Creation_time = 24-APR-2013 18:16:11
Revision_time = 2-JUN-2013 17:20:50
Current_time = 2-JUN-2013 17:20:56
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 1024
Total_scans = 1024
X_90_width = 12[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 3[dB]
X_pulse = 4[us]
Irr_atn_dec = 21[dB]
Irr_atn_noe = 21[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 2.83361792[s]
Temp_get = 20.9[dC]
5-(4-iodylphenyl)-2-ethyl-2H-tetrazole
O2I
N
N
N
N
15.1734
14.8300
40.1162
39.9540
49.3493
49.2253
98.4049
98.3286
139.2289
139.1336
129.0706
129.1469
127.4205
127.7353
164.2861
164.3243
abundance
X : parts per Million : 13C