Chapter one
Introduction

1.1 Naturally occurring Quinones:

Naturally occurring quinones have captured human attention for thousands of years. Initially by reason of their bright colors with possible uses as dyes and as drugs. Pigments of various colors, now characterized as quinones have been isolated from high and lower plants, fungi, as well from animals, crude preparations of plants. Presently known to contain quinones as active ingredients were prescribed more than 400 years ago as purgatives or drugs.

Throughout history, several other medicinal benefits have been adding on to the list associated with the use of naturally occurring quinones.

The discoveries of antibiotic and antitumor properties assigned to several naturally occurring quinones have raised interest among scientist for use as pharmaceuticals. Some natural quinones, such as the kinamycins A, B, C and D1a–d and streptonigrin (STN) are only week antibiotic antitumor agents but have attracted attention because of novel structural features which suggest unusual biosynthetic processes and possibly novel mechanisms of bioactivity.

Recently, during the screening of natural products for inhibition against the HIV virus, STN has demonstrated one more interesting fact by testing positive as an inhibitor toward the reverse transcriptase (RT) of HIV-1. This revelation, along with other observations of simpler quinones demonstrating anti-RT
activity, implies that quinones analogs might also offer promising results in the against AIDS.

1.1.2 Chemistry of Quinones:

Quinones are cyclic unsaturated diketones in double bonds and the keto groups are conjugated, thus, they are not aromatic compounds, but they readily prepared from and readily converted into aromatic compounds.

The term quinones refers generally to a 1,4- diketone formally derived from dihydro aromatic compounds in which the two carbonyl groups are connected by a system of conjugated double bonds. Two quinones of benzene are possible: $O$-benzoquinone and $P$-benzoquinone:

![O-benzoquinone](image.png)

$O$-benzoquinone

![P-benzoquinone](image.png)

$P$-benzoquinone

No $m$-quinone is known presumably because it impossible to arrange two carbonyl oxygen atoms in the ring in the $m$-position and still maintain a valency of four for carbon. In polynuclear quinones the carbonyl groups may be present in different rings.

The chemistry of quinones is similar to that of open chain $\alpha,\beta$-unsaturated ketones. They are however more reactive than the later
and can undergo a wide range of 1,4-reductive additions of the Micheal type. Thus quinones are electrophilic Micheal acceptors stabilized by conjugation.

![1,4-naphthoquinone]  
![9,10-Anthraquinone]

The term quinones is also used more generally for a large class of compounds formally derived from aromatic quinones through replacement of some hydrogen atoms by other atoms or radicals such as chloranil, lawsone, DDQ and etc.

![chloranil]  
![lawsone]  
![DDQ]
1.1.2.1 Chemical synthesis and preparation of Quinones:

Since the mid 19\textsuperscript{th} century, chemists have been studying the chemical properties of various quinones. The first synthesized and most common quinone is \textit{P}-benzoquinone, it was discovered in the late 1830’s in Liebig’s laboratory as the result of the oxidation of quinic acid with manganese dioxide and sulphuric acid. The reaction involves a dehydration, decarboxylation and oxidation.

\[
\begin{align*}
\text{CO}_2\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{OH} & \quad \text{OH} \\
\text{MnO}_2, \text{H}_2\text{SO}_4 & \\
\rightarrow & \\
\text{quinone}
\end{align*}
\]

In general, \textit{P}-quinones (\textit{P}-benzoquinones) can be obtained by the oxidation of hydroquinones or quinol with acid ferric chloride, lead tetra-acetate, manganese dioxide, acid dichromate or sodium chlorate in dilute acid in the presence of \textit{V}_2\text{O}_5 catalyst.
Oxidation of \textit{p}-aminophenol with potassium bromate and sulfuric acid also gives quinone.

\[
\text{Hydroquinone} \xrightarrow{\text{NaClO}_3 / \text{H}_2\text{SO}_4} \text{\textit{p}-benzoquinone}
\]

\[
\text{\textit{p}-aminophenol} \xrightarrow{\text{NaBrO}_3 / \text{H}_2\text{SO}_4} \text{\textit{p}-benzoquinone}
\]
In laboratory it is prepared by the oxidation of aniline with either acid dichromate or manganese dioxide and acid.

\[
\text{aniline} \quad \xymatrix@R-1pc{\ar@<1ex>[rr]^+ & & \text{p -benzoquinone} \\
+ 2\text{MnO}_2 + 3\text{H}_2\text{SO}_4 & \ar@<1ex>[rr]^+ & & + 2\text{MnSO}_4 + 2\text{H}_2\text{O} + \text{NH}_4\text{HSO}_4}
\]

Oxidation of \(P\)-phenylenediamine with potassium dichromate and sulphuric acid yield \(P\)-benzoquinone.

\[
\text{p -aminoaniline} \quad \xymatrix@R-1pc{\ar@<1ex>[rr]^+ & & \text{p -benzoquinone} \\
\xymatrix@C-1pc{\ar@<1ex>[rr]^{\text{K}_2\text{Cr}_2\text{O}_7} & & \text{[O]}}
\]
O-Benzquinones (O-quinone) C₆H₄O₂ it is generally unstable and difficult to isolate. It is obtained by oxidation of catechol with manganese dioxide and acid or with silver oxide in dry ethereal solution in the presence of anhydrous sodium sulphate.

\[
\text{catechol} \xrightarrow{\text{MnO₄} / \text{H₂SO₄ or Ag₂O} / \text{Ether}} \text{O-benzoquinone}
\]

1.1.2.2 Reactions of quinones:
There are several reactions of quinones have been known which are:

1. Addition of halogens
   It adds halogen like bromine to form initially dibromo and then tetra bromo-derivatives

   \[
   \begin{align*}
   \text{p-benzoquinone} \quad & \xrightarrow{\text{Br}_2} \quad \text{Quinone dibromide} \quad & \xrightarrow{\text{Br}_2} \quad \text{tetra bromo quinone}
   \end{align*}
   \]

   It reacts with halogen acid to form haloquinols.
   The reaction probably involves a 1,4-addition followed by enolization.
Addition excess of HCl and then oxidation gives tetra chlorobenzoquinones, also known as chloranil. It is used as fungicide.

3. Reaction with NH$_2$OH.

The reaction yield $P$-benzoquinone monoxime and dioxime.

The oximes are tautomeric with $P$-nitrosophenols.

4- Reaction with hydrogen cyanide HCN, Dicyanoquinol is formed.
5- Thiele acetylation.

It reacts with acetic anhydride in presence of sulphuric acid to give hydroxyquinol triacetate.

\[
\text{\( p \)-benzoquinone} \quad \xrightarrow{\text{(CH}_3\text{CO}_2\text{)}} \quad \text{hydroxyquinol triacetate}
\]

6- \( p \)-Benzoquinone acts as adienophile in Diels-Alder reaction.

\[
\text{Butadiene} \quad \text{\( p \)-benzoquinone} \quad \xrightarrow{\text{benzene}} \quad \text{tetrahydro-1,4-naphthaquinone}
\]

7- The reaction of \( p \)-quinone with hydrogen sulfide H2S or sulphurous acid or sodium hydrosulfide. It yields quinol, it is thus, used as oxidizing agent.

\[
\text{\( p \)-quinone} \quad \xrightarrow{\text{H}_2\text{SO}_4} \quad \text{quinol}
\]
8- Oxidization of \( P \)-Benzoquinone by silver oxide to maleic acid

\[
\begin{align*}
\text{O} & \text{O} \\
\text{p-benzoquinone} & \xrightarrow{\text{Ag}_2\text{O}} \text{CH–COOH} & \text{CH–COOH} & \xrightarrow{\Delta} \text{maleic acid} & \xrightarrow{\Delta} \text{maleic anhydride}
\end{align*}
\]

1.1.3 Physical properties and spectral data of quinones.

A characteristic property of quinones is their colour. The \( P \)-compounds being yellow and the \( O \)-compounds being “usually” red. Their m.p is 116\(^\circ\)C behaving prismastic crystals. They possess a pleasant smell and sublimes on heating, it is steam-volatile and turns brown on exposure to light for \( P \)-benzoquinone, it gives transient blue color with FeCl\(_3\).

\( P \)-Benzoquinone exhibits the reaction of \( \alpha,\beta \)-unsaturated ketones rather than those of aromatic compounds. The spectral data of quinone shows the absorption of radiation in the IR region of carbonyl groups ((C=O)) str., their stretching between 1690 – 1660 cm\(^{-1}\) which is similar to that of \( \alpha,\beta \)-unsaturated ketones. \( O \)-Benzoquinone exists in two forms, on as unstable green needles and the other, stable light-red crystalline plates, it is odourless, not steam-volatile, and is reduced to catechol by sulphurous acid, it is strong oxidizing
agent. Many benzoquinone compounds occur naturally and are the cause of colour in pigments in which they are found.

The yellow colour of $P$-benzoquinone is due to the presence of quinonoid structure. This structure is also known as crossed conjugated system, it contains three or more double bonds which are not arranged in a continuous chain.

The resonance energy is 5 kcal.
1.1.4 Biological Activities of P-Quinones:

Natural and synthetic quinoid compounds are well known substances which possess a variety of biological properties such as antibacterial, antifungal, antiprotozoal, inhibiting of HIV-1 reverse transcriptase, and antitumor activity. Some of these pharmacological effects have been attributed to the formation of DNA-damaging anion-redical intermediates formed by bio-reduction of the quinone nucleus. Biological redox activity is recognized as playing a key role in a number of processes, including the triggering of cellular events that can be exploited for therapeutic uses.

Streptonigrin (STN) which was known to be an antitumor antibiotic was first shown to possess against RT by chirigosetal who studied RT form AMV later, Hafurietal, demonstrated that inhibition of AMV RT was the result of redox reaction of the quinone portion of STN and that other much simpler synthetic P-quinones could inhibit AMV RT. The term quinone was used to refer to what was believed to be a common binding site on AMV RT which accommodated the quinone containing RT inhibitors, later a comparative study of the effectiveness of such quinone against mammalian DNA polymerases (α and β), HIV RT and AMV RT was reported from that study several naphthoquinones were
identified as structures with significant affinity for the HIV-1 RT relative to mammalian DNA polymerase.
1.1.4 Aims of Project

1,4-naphthoquinone derivatives become the subject of intense research because of their interesting pharmacological (Biological activities), for example, antitumor, antifungal, antibacterial and antiviral activities.

This project is specially aimed to:

I. Synthesis of some 1,4–naphthoquinone derivatives, exactly (2-{5-[(2-phenylhydrazinylindene)methyl]furan–2-yl} naphthalene-1,4-dione and 2-{4-[(2-phenyl hydrazinylidene) methyl] phenyl} naphthalene -1,4– dione, Through designing the suitable retrosynthetic analysis which leads to more than one possible route towards synthesis of intermediates and target molecules, suggesting the required mechanisms of the reactions, monitoring the progress of each reaction by the Thin layer chromatography; using aluminium-backed sheets precoatd with Silica gel and accomplishing column chromatography for purification the products using silica gel.

II. Identification of the synthesized compounds with spectroscopy analysis methods.
Chapter Two
Experimental

2.1 Materials:

2.1.1 Chemicals:

- 1,4-naphthoquinone (Alpha chemika-India)
- Benzaldehyde (Alpha chemika-India)
- Furfuraldehyde (Alpha chemika-India)
- Phenylhydrazine (Alpha chemika-India)
- Silica gel 60-120 Mesh (Loba chemica – India)

2.1.2 Reagents:

- Glacial acetic acid (Alpha chemika-India)
- Sodium carbonate (Alpha chemika-India)
- Sodiumhydrogencarbonate (Alpha chemika-India)

2.1.3 Solvents:

- Acetone (Alpha chemik-India)
- Dichloromethane (Alpha chemika-India)
- Ethylacetate (Alpha chemika-India)
- Ethanol (Alpha chemika-India)
- Hexane (Alpha chemika – India)
2.2. Instrumentations:

Infrared and General Equipments:

- IR spectra were recorded in KBr on Perkin Elmer Spectrum – Bx series FT – IR Spectrometer. Name of Instrument (FT – IR Spectrometer), Make: SHIMADZU. Model No (FT–IR – 8400) Made in Japan.

- Magnetic stirrer with hot plat model L.M.S 100 volts, 220 volts 50/60 Hz. Serial No. 0401401, melting point apparatus (smplo , bibly stuart scientific, Uk ).

- All of the glasses were used of pyrex type.
2.3 Methods:

2.3.1 Preparation of 1–(Furan–2–ylmethylidene)–2–phenyl hydrazine

2.00 ml of Phenylhydrazine and 2.00 ml of Furfuraldehyde were placed in small round bottomed flask, 15 ml of Ethanol was added. The flask was covered well, the mixture was slightly heated through water bath with continuous shaking for 25 minutes, after that the contents of flask were cooled in ice bath till separation of crystals were occurred, then the crystals were filtered in which represent the product of the reaction, the precipitation was dried, weighed in which 0.67 g (670 mg) were obtained as slight buffer to brown solid.

2.3.2 Synthesis of 2–{(5–[(2–phenylhydrazinylidene)methyl]furan–2–yl}naphthalene-1,4-dione

A suspension of hydrazone 1–(Furan–2–yl methylidene)–2–phenyl hydrazine about 0.093 g (93 mg, 0.5 mmol) and (150 mg, 0.9 mmol) of 1,4-naphthoquinone were placed in around bottomed flask, 15 ml of glacial acetic acid was added to the contents of flask, the mixture was vigorously stirred for 12 h at room temperature. The reaction mixture was poured into water (100 ml), neutralized by sodium carbonate and extracted with dichloromethane (2×30 ml). The organic extract was dried, the solvent was evaporated under reduced pressure and residue was submitted to successive purification by column chromatography (4: 1 hexane /ethyl acetate). (0.0975 gm, 57% was obtained).
2.3.3 Preparation of 1–(Benzyldene )–2–phenyl hydrazine

2.00ml of Phenylhydrazine and 2.00ml benzaldehyde were placed in small round bottomed flask, 15.00ml of ethanol were added, the mixture was heated a little by water bath with well continuous shaking for 20 minutes contents were cooled in ice bath till separation of crystals was occurred, the crystals were dried, washed and 1.19g (1190mg) was obtained, as slightly yellow solid crystals.

2.3.4 Synthesis of 2–{4–[(2–phenylhydrazinyliden)methyl]phenyl}naphthalene-1,4-dione

98 mg (0.5mmol) of a suspension of 1–(Benzyldene )–2–phenyl hydrazine and 150mg (0.9mmol ) of 1.4-naphthquinone were placed in round bottomed flask,15 ml of glacial acetic acid was added to the contents of flask,The mixture was vigorously stirred for 12 h at room temperature . The reaction mixture was poured into 100 ml water then the solution was neutralized with sodium hydrogen carbonate and extracted with dichloromethane (2x30 ml). The organic extract was dried and the solvent was evaporated under reduced pressure, and (0.0968 gm, 55% was obtained).
2.4. The schemes:

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<tr>
<th>Scheme (1)</th>
<th>Synthesis of 1–(furan -2-yl methylidene) -2-phenyl hydrazine</th>
<th>Page No.</th>
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<th>Synthesis of 2 – {5-[2-phenyl hydrazinylidene) methyl] furan-2-yl} naphthalene -1,4 – dione</th>
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Chapter Three
Results and Discussion

3.1 Results and Discussion

The retrosynthesis analysis for intermediates and desired products has been designed to predict the suitable reaction mechanisms. The completeness of reactions were achieved by carried out the thin layer chromatography analysis. The presence of desired functional groups in required compounds were obtained through the IR data analysis which were proved that the synthesized products were the targeted compounds.

3.1.1 Synthetic Designing and mechanisms of the reactions

3.1.1.1 Retrosynthesis analysis of 1–(Furan–2–yl methylidene)–2– phenyl hydrazine

1. Functional group interconversion (FGI) method
2. Disconnection method

\[
\text{Reaction Mechanism of } 1-\text{(Furan–2–ylmethylidene)–2–phenyl hydrazine}
\]

**Scheme(1)**

**Step (1):** protonation of furaldehyde.
Step (2): phenylhydrazine nucleophile attacks on carbonyl carbon

Step (3): Elimination of water molecule
3.1.1.3 Synthesis of 2−{5−[(2−phenylhydrazinylidene)methyl]furan−2−yl}naphthalene-1,4-dione

Scheme (2)

3.1.1.4 Retro Synthesis of 1−(Benzyldiene)−2−phenyl hydrazine

1. Functional group interconversion (FGI) method
2. Disconnection method

\[
\text{CH}_2\left\{\text{N}\text{-NH}\right\}\text{C} \xrightarrow{\text{FGL}} \text{CH}_2\text{C}^2\oplus + \text{N}\text{-NH}\text{C}^2\oplus
\]

\[
\text{synthon 1} \hspace{2cm} \text{synthon 2}
\]

3.1.1.5 Reaction Mechanism of 1–(Benzyldiene)–2–phenyl hydrazine

Scheme(3)

In the first step the carbonyl oxygen was protonated by acid, then in second step the carbonyl carbon was attacked by nucleophile to form carbon-nitrogen bond, and in third step the elimination of water molecule was occurred to form an imine.
3.1.1.6 Synthesis of 2–{4–[(2–phenylhydrazinyliden)methyl]phenyl}naphthalene-1,4-dione

Scheme (4)
3.1.2 - Thin layer chromatography (TLC):

Figure (1)

The results of TLC test for the products by solvent system (4:1, Hexane/Ethylacetate).

The right hand side spot is TLC result of 2-{5[(2phenylhydrazinylidene)methyl]furan–2–yl}-1,4-naphthoquinone in which its RF value found to be equal 0.66 and the left hand side spot for 2–{4-[(2–phenylhydrazinyliden)methyl]phenyl}–1,4-naphthoquinone, its RF value was found to be equal 0.64.
3.1.3 – Infrared data analysis

3.1.4 - IR spectrum data analysis of 1–(Furan–2–yl methyldene)–2–phenyl hydrazine

![1-(furan-2-ylmethyldene)-2-phenylhydrazine](image)

Log p = 3.03 +/- 0.57
Mpc⁰ = 96-100 c⁰

Table (1)

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<th>type of vibration and functional group</th>
<th>Frequency</th>
<th>intensity</th>
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<tr>
<td>N – H secondary amine (stretching)</td>
<td>3317.34 cm⁻¹</td>
<td>Strong</td>
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<tr>
<td>C = C Ring stretch absorption</td>
<td>1600.81 and 1483.16 cm⁻¹</td>
<td>strong</td>
</tr>
<tr>
<td>C = N stretch in an imine</td>
<td>1595.02 cm⁻¹</td>
<td>Strong</td>
</tr>
<tr>
<td>= C – H stretch sp² - C - H</td>
<td>3100 cm⁻¹</td>
<td>Medium</td>
</tr>
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</table>
3.1.5 IR spectrum data analysis of 1–(Benzylidene )–2–phenyl hydrazine

\[ \text{1-benzylidene-2-phenylhydrazine} \]

\[ \log p = 4.24 \pm 0.56 \]

\[ Mpc^0 = 124-128 \]

Table (2)

<table>
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<tr>
<td>N – H secondary amine (stretching)</td>
<td>3309.62 cm(^{-1})</td>
<td>Strong</td>
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<tr>
<td>C = C Ring stretch absorption</td>
<td>1600.81 and 1487.01 cm(^{-1})</td>
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<tr>
<td>C = N stretch in an imine</td>
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<td>Strong</td>
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<td>= C – H stretch ( sp^2 ) - C- H</td>
<td>3024.18 cm(^{-1})</td>
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3.1.6 IR spectrum data analysis of \( 2-\{5-[(2-\text{phenylhydrazinylidene})\text{methyl}]\text{furan-2-yl}\}\) naphthalene-1,4-dione

![Chemical structure](image)

Log \( p \) = 4.62 +/- 0.80

\( Mpc^0 = 165-170c^o \)

Table (3)

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<th>type of vibration and functional group</th>
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<td>C = O conjugation of carbonyl with ( \alpha, \beta ) C = C</td>
<td>1666.36 and 1739.67 ( cm^{-1} )</td>
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<tr>
<td>N – H secondary amine (stretching)</td>
<td>3419.56 ( cm^{-1} )</td>
<td>Medium</td>
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<tr>
<td>C = C Ring stretch absorption</td>
<td>1595.02 and 1496.66 ( cm^{-1} )</td>
<td>Medium</td>
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<tr>
<td>C = N stretch in an imine</td>
<td>1600.82 ( cm^{-1} )</td>
<td>Medium</td>
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<tr>
<td>= C – H stretch ( sp^2 ) - C - H</td>
<td>3060.82 ( cm^{-1} )</td>
<td>Strong</td>
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</table>
3.1.7 IR spectrum data analysis of 2-{4-[2-(phenylhydrazinyliden)methyl]phenyl}naphthalene-1,4-dione

\[
\text{Log } p = 6.01 +/- 0.75
\]

\[
Mpc^0 = 157-163 \text{ }^\circ C
\]

Table (4)

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<td>C = O conjugation of carbonyl with ( \alpha, \beta ) C = C</td>
<td>1664.54 and 1739.67 ( \text{cm}^{-1} )</td>
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<td>N – H secondary amine (stretching)</td>
<td>3274.9 ( \text{cm}^{-1} )</td>
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<td>C = C Ring stretch absorption</td>
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<td>C = N stretch in an imine</td>
<td>1600.82 ( \text{cm}^{-1} )</td>
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<tr>
<td>= C – H stretch ( sp^2 ) - C - H</td>
<td>2923.88 ( \text{cm}^{-1} )</td>
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3.2. Conclusion and Recommendations:

- In summary, the \( 2\{-[\text{phenylhydrazinylidene}]\text{methyl}\}\text{furan-2-yl}\}\text{naphthalene-1,4-dione} \) and \( 2\{-[\text{phenyl hydrazinylidene}]\text{methyl}\}\text{phenyl}\}\text{naphthalene-1,4-dione} \) were synthesized as 1,4-naphthoquinone derivatives and the functional groups of synthesized products were investigated by performing infrared spectra analysis.

- HPLC, GC–MS analysis and \(^{13}\text{C}-\text{NMR, }^{1}\text{H}-\text{NMR} \) spectrum analysis are recommended in order to complete the spectra data for synthesized compounds.

- The further studies on 1,4–naphthoquinone derivatives were suggested and the testing of the biological activities for synthesized compounds, in addition to study the structure–activity relationships were recommended.
Comment:
Benzaldehyde hydrazone

Central Laboratory, University of Khartoum Faculty of Science

Date: 17/3/2014
Chapter four

References

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