CHAPTER 1
Chapter 1: synthesis of benzo[g]-2H-indazoles

1.1 General information about Indazole

Indazole is a ten- \( \pi \) electron aromatic heterocyclic system. Like the pyrazole molecule indazole resembles both pyridine and pyrole and its reactivity this dual behavior \(^1\). There is three tautomeric forms for indazole, the 1\( H \)-, 2\( H \)- and 3\( H \)- form.

![Tautomers of indazole](image)

**Tautomers of indazole**

Tautomeric equilibrium between 1\( H \)- and 2\( H \)-indazole has been calculated by thermochemical and photo physical techniques \(^2,3\), the results shows 1\( H \) tautomer more stable than 2\( H \) tautomer, for example 1-methyl-1\( H \)-indazole 3.2 kcal more stable than 2-methyl-2\( H \)-indazole. However 3\( H \)-indazole not calculated by this way because only few example of 3\( H \) tautomer are known, which carry alkyl or aryl groups on the five member ring \(^4\).

Dipole moment of 2\( H \) tautomer is more than 1\( H \) tautomer, for example the experimental dipole moment of 1-methyl-1\( H \)-indazole is 1.50D, but this value for 2-methyl-2\( H \)-indazole is 3.4D \(^5,6\).

2\( H \) tautomer compare 1\( H \) tautomer is much stronger base, for example Pk\(_b\) for 1-methyl-1\( H \)-indazole is 0.42 but Pk\(_b\) for 2-methyl-2\( H \)-indazole is 2.02 \(^7,8,9\).

For distinguish 1\( H \) tautomer and 2\( H \) tautomer \(^1\)\( H \), \(^{13}\)C, \(^{14}\)N and \(^{15}\)N NMR is used \(^10,11,12,13\). The chemical shift of methyl protons 1-methyl and 2-methyl-indazole differ only by 0.1-0.2ppm \(^14,15\), fortunately 13C NMR spectra very helpful in the structural
elucidation isomeric indazoles, and the chemical shift of the signal of the C3 atom is especially suitable. This amount for 1H tautomer is 132-133ppm and for 2H tautomer is 123-124ppm\textsuperscript{12,13}.

### 1.2 Biological importance of Indazole

In fact compounds containing the indazole skeleton are known to show a variety of biological activities. Indazole compounds as the molecular shape and electrostatic distribution play a crucial role in enzyme and receptor recognition and contribute extensively to binding affinity. Literatures have been showed three type indazoles such as 1H-indazole, 2H-indazole and benzo[g]indazole, as biological activity. Some of products containing 1H-indazole moiety are listed in Table 1 and some of products containing 2H-indazole moiety are listed in Table 2.

#### 1.2.1 1H-indazole

**Table 1: Examples for biological activity of 1H-indazoles**

<table>
<thead>
<tr>
<th>Activity</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ABT-102</strong> 1 is a C (4)-substituted indazolamine has been identified as potent vanilloid receptor (V R 1) antagonist and is a chronic pain\textsuperscript{16}</td>
<td><img src="image" alt="ABT-102" /></td>
</tr>
<tr>
<td><strong>N-(1-propylpiperidin-3-yl)-1H-indazol-5-amine</strong> was tested in Rho-kinase inhibitors\textsuperscript{17}</td>
<td><img src="image" alt="N-(1-propylpiperidin-3-yl)-1H-indazol-5-amine" /></td>
</tr>
<tr>
<td>Chemical Structure</td>
<td>Description</td>
</tr>
<tr>
<td>-------------------</td>
<td>-------------</td>
</tr>
<tr>
<td><img src="image" alt="N-(quinuclidin-3-yl)-1H-indazole-5-carboxamide" /></td>
<td><strong>N-(quinuclidin-3-yl)-1H-indazole-5-carboxamide</strong> is A7 nicotinic acetylcholine receptor.¹⁸</td>
</tr>
<tr>
<td><img src="image" alt="1-((1H-indazol-5-yl)methyl)-4,7-dibenzyl-3-ethyl-5,6-dihydroxy-1,3-diazepan-2-one" /></td>
<td><strong>1-((1H-indazol-5-yl)methyl)-4,7-dibenzyl-3-ethyl-5,6-dihydroxy-1,3-diazepan-2-one</strong> is anti-HIV protease inhibitor.¹⁹</td>
</tr>
<tr>
<td><img src="image" alt="Granistron" /></td>
<td><strong>Granistron</strong> has been used clinically to prevent nausea and emesis induced by cancer chemotherapeutic agents.²⁰</td>
</tr>
<tr>
<td><img src="image" alt="YC-1" /></td>
<td><strong>YC-1</strong> has been reported as activator of the physiological receptor for nitric oxide sGC, and inhibition of endothelial cell function.²¹</td>
</tr>
<tr>
<td><img src="image" alt="1-(2,4-dichlorobenzyl)-1H-indazole-3-carboxylic acid" /></td>
<td><strong>1-(2,4-dichlorobenzyl)-1H-indazole-3-carboxylic acid</strong> is a compromises non-hormonal and non-steroidal, antispermagenic agents and found interest in male contraception.²²</td>
</tr>
<tr>
<td><img src="image" alt="1-(1-methyl-1H-indazol-4-yloxy)-3-aminopropan-2-ol" /></td>
<td><strong>1-(1-methyl-1H-indazol-4-yloxy)-3-aminopropan-2-ol</strong> exhibit antiarrhythmic, and analgesic activities.²³</td>
</tr>
</tbody>
</table>
1-(2-aminopropyl)-1H-indazol-5-ol was identified as a peripherally acting potent 5-HT₂ receptor agonist.\(^{24}\)

### 1.2.2 2H-indazoles and benzo[g]indazoles

Compared with 1H-indazole, 2H-indazole and benzo[g]indazole have been much less studied. Only a few compounds were investigated for biological activity, which listed in **Table 2**.

**Table 2:** Examples for biological activity of 2H-indazoles

<table>
<thead>
<tr>
<th>Activity</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-chloro-2-(4-hydroxy phenyl)-2H-indazol-5-ol exhibit ligand for the estrogen receptor β.(^{25})</td>
<td><img src="image1" alt="3-chloro-2-(4-hydroxyphenyl)-2H-indazol-5-ol" /></td>
</tr>
<tr>
<td>4,5,6,7-tetrahydro-3-phenyl-2-(pyridin-2-yl)-2H-indazole was identified as an anti-inflammatory.(^{26})</td>
<td><img src="image2" alt="4,5,6,7-tetrahydro-3-phenyl-2-(pyridin-2-yl)-2H-indazole" /></td>
</tr>
<tr>
<td>2-methyl-2H-benzo[g]indazole-3-carboxylic acid exhibit antiproliferative.(^{27})</td>
<td><img src="image3" alt="2-methyl-2H-benzo[g]indazole-3-carboxylic acid" /></td>
</tr>
<tr>
<td>PHA-408 has been reported as anti-inflammatory.(^{28})</td>
<td><img src="image4" alt="PHA-408" /></td>
</tr>
</tbody>
</table>
7-chloro-1-(4-chlorophenyl)-4,5-dihydro-N-(piperidin-1-yl)-1H-benzo[g]indazole-3-carboxamide showed high CB receptor affinities\(^{29}\).

The 4,5-dihydro-1-methyl-3-(4-phenethylpiperazin-1-yl)-1H-benzo[g]indazole reported as high Dopamine D\(_4\) receptor affinity\(^{30}\).

### 1.3 Known methods for synthesis of 2H-indazoles and benzo[g]indazoles

#### 1.3.1 Synthesis of 2H-indazoles: The chemistry of 2H-indazoles has not been explored as well as the chemistry of 1H-indazoles. However, the discovery that N-2 substituted 2H-indazole compounds may exhibit biological activities has generated recent interest in their simple and efficient preparation.

**Method-1**

A synthesis of 2-aryl-2H-indazoles via a palladium-mediated intramolecular amination reaction of N-aryl-N-(obromobenzyl)-hydrazines has been reported by Song and Yee\(^{31}\). The best conditions to effect the transformation are heating in toluene at 90°C for 15h in the presence of Pd(OAc)\(_2\) (5 mol%), dppf (7.5 mol%), and t-BuONa (15 0 mol%). Yields were comprised in the 50 to 60% range. The catalytic system is equally effective for electron-rich and electron-deficient substituents on both phenyl rings. In a mechanistic point of view the formation of the sp\(^2\) C-N bond is
followed by the spontaneous oxidation of the dihydroindazole intermediates to give the 2-aryl-2H-indazole products.

\[
\begin{align*}
R_1 & = H, \text{OMe, F} \\
R_2 & = \text{Me, Cl, CN}
\end{align*}
\]

**Method-2**

Starting from Baylis-Hillman adducts of cyclohexenone, a two-step procedure for the formation of N-Ph-2H-indazoles featuring DDQ oxidation of pyrazoles intermediates has been reported\(^\text{32}\). Moderate overall yields were obtained (35%).

\[
\begin{align*}
\text{PhNHNH}_2\text{HCl} & \quad \text{CICH}_2\text{CH}_2\text{Cl} \\
\text{reflux} & \quad \text{DDQ(2equiv)} \\
\text{Ph-H, reflux} & \quad \text{R=Ph, 4-Me-Ph, 4-OMe-Ph, 2-OMe-Ph, C}_5\text{H}_1
\end{align*}
\]

**Method-3**

Akazome et al.\(^\text{33}\) reported the palladium-catalyzed intramolecular reductive N-heterocyclization of (2-nitrobenzylidene) amines to give the corresponding 2H-indazole products in 48-75% isolated yields. Reactions were conducted in a stainless reactor at 100°C for 16h under 20 kg cm\(^{-2}\) of initial CO pressure and in the presence of a PdCl\(_2\)(PPh\(_3\))\(_2\) (5 mol%) - SnCl\(_2\) (50 mol%) system.

\[
\begin{align*}
PdCl_2(PPh_3)_2 & \quad \text{(5mol%)} \\
\text{SnCl}_2 & \quad \text{(50mol%)} \\
\text{CO(20Kg Cm}^{-2}) & \quad \text{THF, 100°C, 16h} \\
R & = \text{Pr}^\text{t}, 2,5\text{-dimethyl-Ph}
\end{align*}
\]
Method-4

A series of 3-cyano-2H-indazole N1-oxides has been synthesized in order to evaluate the trypanocidal and leishmanocidal activities of each derivative. Following the route shown in, o-nitrobenzaldehyde was first transformed, via a Schiff base, to an aminonitrile derivative which was next cyclized to a 3-cyano-2H-indazole N1-oxide by treatment with a base (Et3N or NaHCO3).

\[
\begin{align*}
\text{CHO} & \xrightarrow{\text{RNH}_2\text{-KCN, AcOH, r.t.}} \left[ \begin{array}{c}
\text{CN} \\
\text{NHR} \\
\text{NO}_2 \\
\end{array} \right] \\
& \xrightarrow{\text{Base}} \left[ \begin{array}{c}
\text{CN} \\
\text{N-R} \\
\end{array} \right]
\end{align*}
\]

R=4-Iodophenyl
Yield: 64%

Method-5

A rapid and efficient synthesis of 2H-indazoles have been reported, which starting from arynes and easily obtained sydnones by a sequence involving [3+2] dipolar cycloaddition/decarboxylation.

\[
\begin{align*}
\text{R}_1 & = \text{Me, OMe} \\
\text{R}_2 & = \text{2-tuphene, 2-pyridine, isopropyl} \\
\text{R}_3 & = \text{Ph, 4-Cl-Ph}
\end{align*}
\]

1.3.2 Synthesis of benzo[g]indazoles: Preparation of 3, 4-dihydro benzo[g]indazole and benzo[g]indazole has been less reported. For the construction of these compounds usually α-tetralon was used.
Method-6

A synthesis of 3-(4-Piperidinyl)-4, 5-dihydro-1H-benzo[g]indazole via condensation two equivalents of the lithium enolat of α-tetralon with protected isonipecotic acid, as the imidazolide, gave the diketopiperidine after N-deprotection. Alkylation of diketone and subsequent condensation with hydrazine afforded the dihydrobenzo[g]indazoles 37.

Reagent and condition: a) N,N-carbonyldiimidazole, solvent, rt; b) α-tetralon, LDA, THF, -78°C c) HCl, EtOAc, rt, 48%; d) RBr, iPr2Net, DMF, rt -70°C 47%; e) N2H4·H2O, MeOH, rt, 55%

Method-7

Addition of one equivalent of the α-tetralon to diethyloxalate in ethanol at room temperature in the presence of two equivalent of base, afforded the Claisen condensation product. Subsequent reaction of one equivalent of this mixture with 1.15 equiv of the appropriate hydrazine hydrochloride at reflux in ethanol afforded dihydrobenzo[g]indazoles 38.
Method-8

Condensation of dilithiated \( \alpha \)-tetralon carboalkoxyhydrazones with a variety of aromatic esters followed by acid cyclization of C-acylated was reported \(^{39} \) to give substituted dihydrobenzo[g]indazoles.

\[
\begin{align*}
\text{H}_2\text{NNHCO}_2\text{R}_1 & \xrightarrow{\text{LDA, 0}\degree\text{C}} \text{N}^{+}\text{COOR}_1 \quad \text{N}_2, \text{THF} \quad \text{N}^{-}\text{COOR}_1 \\
\text{R}_1 & = \text{Me}, \text{Et} \\
\text{H}_2\text{O}, \text{reflux} & \quad \text{C-Acylated} \\
\text{R}_2 & = \text{4-OMeC}_6\text{H}_4, \text{3,5-}(\text{OMe})_2\text{C}_6\text{H}_3, \\
& \text{3,4,5-}(\text{OMe})_3\text{C}_6\text{H}_2
\end{align*}
\]

Method-9

Dehydrogenation of 4,5-dihydro-\( 1H \)-benzo[g]indazole by heating in Decalin at reflux (200 \degree\text{C}) for 12 hours with palladium affords \( 1H \)-benzo[g]indazole in 60\% yield \(^{40} \).

\[
\begin{align*}
P\text{d/C} \\
\text{Decalin} & \quad 200 \degree\text{C}, 12 \text{h} \quad 60\% \\
\text{Pd/C} \quad \text{Decalin} & \quad 200 \degree\text{C}, 12 \text{h} \quad 60\% \\
\end{align*}
\]

Method-10

For aromatization of tetrahydro-\( 2H \)-benzo[g]indazole \( \text{Me}_3\text{SiN}_3 \) in presence of [bis (trifluoroacetoxy)iodo] benzene was used \(^{41} \).
1.4 Present work

According to activity of benzo[g]indazoles in pharmaceutical, we describe new method for synthesis of benzo[g]-2H-indazoles. In this method I₂/DMSO, CuCl₂/DMSO and NBS was used for dehydrogenation of tetrahydro benzo[g]-2H-indazole toward the synthesis of benzo[g]-2H-indazoles. Tetrahydro benzo[g]-2H-indazole can be easily prepared from condensation reaction of α-tetralon with substituted aromatic aldehydes followed by cyclization with phenyl hydrazine. The methods for synthesis of benzo[g]indazole, which were described in literature 37-41, require drastic reaction conditions, expensive reagents with long reaction times and low yields, but we synthesized the dihydro benzo[g]-2H-indazole and benzo[g]-2H-indazole in excellent yield, low cost reagents, easy to handle and with less reaction time.
1.4.1 Result and Discussion

The precursor 2-arylidene-3,4-dihydronaphthalen-1(2H)-one 3a-e were prepared from the reaction of α-tetralon 1 with substituted aromatic aldehydes 2 in methanolic KOH solution. The formation of 3a-e was confirmed on the basis of their IR and $^1$H NMR data. The IR spectra show characteristic absorptions for conjugated carbonyl groups at $\nu = 1661-1689$ cm$^{-1}$. The $^1$H NMR spectrum of 3d displays two triplet at $\delta = 2.97$, and 3.17 ppm and a singlet at $\delta = 6.68$ ppm indicating the protons on C-4, C-3 and C-2' respectively (Scheme 1, Table 3).

![Scheme 1: synthesis of 2-arylidene-3,4-dihydronaphthalen-1(2H)-one (3a-e)](image)

Table 3: Physico-chemical data of 3a-e

<table>
<thead>
<tr>
<th>entry</th>
<th>R$_1$</th>
<th>R$_2$</th>
<th>R$_3$</th>
<th>m.p °C</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>152</td>
<td>89</td>
</tr>
<tr>
<td>3b</td>
<td>H</td>
<td>OMe</td>
<td>H</td>
<td>106</td>
<td>91</td>
</tr>
<tr>
<td>3c</td>
<td>H</td>
<td>OMe</td>
<td>OMe</td>
<td>102</td>
<td>87</td>
</tr>
<tr>
<td>3d</td>
<td>OMe</td>
<td>OMe</td>
<td>OMe</td>
<td>138</td>
<td>86</td>
</tr>
<tr>
<td>3e</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>124</td>
<td>90</td>
</tr>
</tbody>
</table>

The chalcones 3a-e were then reacted with phenyl hydrazine in refluxing methanol for 4-6 h to form tetrahydro-2H-benzo[g]indazoles 4a-e in 78-86% yield (Scheme 2, Table 4). This reaction probably takes place through mediation of an appropriate hydrazone, which immediately cyclizes to tetrahydro-2H-benzo[g]indazole ring
Compounds 4a-e show in their IR spectra absorbances for C=N at $\nu = 1605$ cm$^{-1}$ (4c) and absence of stretching for carbonyl group, while in the $^1$H NMR spectra of these compounds generally exhibit an AMX pattern for the presence of two diastereotopic protons at C-4 and one single proton at the C-3a positions. These protons appear as two multiplets and a triplet of doublet, respectively, in the $\delta = 1.93$, 2.27 and 3.24 ppm (4b), each integrating for one proton, in other words compound 4A was not generated.

**Scheme 2:** Synthesis of 3, 3a, 4, 5-tetrahydro-3-aryl-2-phenyl-2H-benzo[g] indazole

<table>
<thead>
<tr>
<th>entry</th>
<th>R$_1$</th>
<th>R$_2$</th>
<th>R$_3$</th>
<th>m.p $^\circ$C</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>169</td>
<td>78</td>
</tr>
<tr>
<td>4b</td>
<td>H</td>
<td>OMe</td>
<td>H</td>
<td>158</td>
<td>79</td>
</tr>
<tr>
<td>4c</td>
<td>H</td>
<td>OMe</td>
<td>OMe</td>
<td>174</td>
<td>83</td>
</tr>
<tr>
<td>4d</td>
<td>OMe</td>
<td>OMe</td>
<td>OMe</td>
<td>182</td>
<td>86</td>
</tr>
<tr>
<td>4e</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>146</td>
<td>80</td>
</tr>
</tbody>
</table>
Oxidation of 3,3a,4,5-tetrahydro-3-aryl-2-phenyl-2H-benzo[g]indazole 4 by using \( \text{I}_2\)-DMSO

Initially, we attempted the oxidation of 3,3a,4,5-tetrahydro-2,3-diphenyl-2H-benzo[g]indazole 4a using iodine (10%) in DMSO at 60 °C as per our laboratory work for the pyrazole synthesis \(^{42}\). After 10 h, TLC confirmed the absence of the reactant and two new spots were developed. Spectral data such as \(^1\)H NMR, \(^{13}\)C NMR and GC-Mass spectra indicated the formation of two products, 5a and 6a, in a ratio of 92:8. The \(^1\)H NMR spectra of the two products showed the absences of hydrogens on C\(_3\) and C\(_{3a}\) when compared to the spectrum of the reactant 4a. The \(^1\)H NMR of 6a showed two doublets at \(\delta=7.12\) ppm, 2H and 7.67 ppm, 2H, with the same coupling constant (8.7 Hz). Furthermore, its \(^{13}\)C NMR spectrum revealed a distinct absorbance at \(\delta=91.4\) ppm and its MS spectrum showed 127 mass units greater than that of 5a.

We were surprised to discover that the N-phenyl ring in compound 6a was iodinated at para position \(^{43}\). The reaction was then studied with different amounts of iodine and at different temperatures. As shown in Table 5, the reaction time and the products ratio depended on the catalyst amount and the applied temperature. Thus, while the conversation of 4a to the products at room temperature did not occur (Table 5, entry 1 & 9), the best yield of 5a was obtained by using 10% iodine in DMSO at 120 °C for 3h (Table 5, entry 4).
**Table 5**: Effects of the amount of the catalyst iodine and temperature on the conversion of 4a to 5a and 6a

![Reaction scheme]

<table>
<thead>
<tr>
<th>entry</th>
<th>%I₂</th>
<th>Temp °C</th>
<th>Time</th>
<th>5a:6a a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10%</td>
<td>rt b</td>
<td>15h</td>
<td>- c</td>
</tr>
<tr>
<td>2</td>
<td>10%</td>
<td>60</td>
<td>10h</td>
<td>92:8</td>
</tr>
<tr>
<td>3</td>
<td>10%</td>
<td>90</td>
<td>6h</td>
<td>94:6</td>
</tr>
<tr>
<td>4</td>
<td>10%</td>
<td>120</td>
<td>3h</td>
<td>95:5</td>
</tr>
<tr>
<td>5</td>
<td>20%</td>
<td>120</td>
<td>2.5h</td>
<td>85:15</td>
</tr>
<tr>
<td>6</td>
<td>40%</td>
<td>120</td>
<td>2h</td>
<td>65:35</td>
</tr>
<tr>
<td>7</td>
<td>60%</td>
<td>120</td>
<td>100min</td>
<td>50:50</td>
</tr>
<tr>
<td>8</td>
<td>1eq</td>
<td>120</td>
<td>70min</td>
<td>30:70</td>
</tr>
<tr>
<td>9</td>
<td>1.3eq</td>
<td>rt b</td>
<td>10h</td>
<td>- c</td>
</tr>
<tr>
<td>10</td>
<td>1.3eq</td>
<td>60</td>
<td>3h</td>
<td>25:75</td>
</tr>
<tr>
<td>11</td>
<td>1.3eq</td>
<td>90</td>
<td>80min</td>
<td>10:90</td>
</tr>
<tr>
<td>12</td>
<td>1.3eq</td>
<td>120</td>
<td>30min</td>
<td>5:95</td>
</tr>
</tbody>
</table>

a The ratio of compounds 5a and 6a were confirmed based on 1H NMR spectroscopy and GC.
b Room temperature
c No reaction

The optimal conditions for the preparation of 6a were found to be using 1.3 equivalents iodine in DMSO at 120 °C for 30 minute (Table 5, entry 12). The products were easily purified by recrystallization from ethanol (the yields were 73% and 86% for 5a and 6a respectively). Encouraged by these results, various 3,3a,4,5-tetrahydro-3-aryl-2-phenyl-2H-benzo[g]indazoles 4 were converted to the corresponding 4,5-dihydro-2,3-diaryl-2H-benzo[g]indazoles 5 and 4,5-dihydro-2-(4-iodophenyl)-3aryl-2H-benzo[g]indazoles 6 (Scheme 3, Table 6). On the other hand,
under the same conditions as for the conversions of 4 to 6, compounds 5 did not undergo iodination at the \textit{para} position of the N-phenyl rings (Scheme 3). Apparently, due to the aromatization of the five member rings, the nitrogen (N2) lone pair electrons are not available for the N-bound phenyl rings.

\begin{table}[h]
\centering
\begin{tabular}{ccccc}
\hline
entry & \( R_1 \) & \( R_2 \) & \( R_3 \) & m.p \( ^\circ \text{C} \) & Yield% \\
\hline
5a & H & H & H & 148 & 73 \\
5b & H & OMe & H & 126 & 71 \\
5c & H & OMe & OMe & 118 & 72 \\
5d & OMe & OMe & OMe & 153 & 75 \\
5e & H & Cl & H & 135 & 72 \\
6a & H & H & H & 120 & 88 \\
\hline
\end{tabular}
\caption{Physico-chemical data of 5 & 6}
\end{table}

\textbf{Scheme 3:} synthesis of 4, 5-dihydro-2, 3-diaryl-2H-benzo[g]indazole 5 and 4, 5-dihydro-2-(4-iodophenyl)-3aryl-2H-benzo[g]indazole 6
<table>
<thead>
<tr>
<th>6b</th>
<th>H</th>
<th>OMe</th>
<th>H</th>
<th>130</th>
<th>86</th>
</tr>
</thead>
<tbody>
<tr>
<td>6c</td>
<td>H</td>
<td>OMe</td>
<td>OMe</td>
<td>165</td>
<td>90</td>
</tr>
<tr>
<td>6d</td>
<td>OMe</td>
<td>OMe</td>
<td>OMe</td>
<td>173</td>
<td>91</td>
</tr>
<tr>
<td>6e</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>160</td>
<td>90</td>
</tr>
</tbody>
</table>

Therefore, we obtained compound 5 by using I₂ (10%)-DMSO in good yields (71-75%) as compare to oxidation of five member ring in hexahydro-2,3-diaryl-2H-indazole by DDQ 44 with 32% yield. However oxidation of six member ring did not obtained on increasing the molar ratio of reagent up to six molar for 48 h at 120 °C. Hence, in order to fully aromatization of compound 4 we select CuCl₂-DMSO as oxidizing reagent.

**Oxidation of 3,3a,4,5-tetrahydro-3-aryl-2-phenyl-2H-benzo[g]indazole 4 by using CuCl₂-DMSO**

Copper (II) chloride has low cost, readily available and easy to work-up due to its solubility in water. Literature survey revealed that CuCl₂-TBHP (tert-butyl hydroperoxide) applied for oxidation of alcohols 45,46 to aldehydes or ketones and oxidation of alkynes 47 to α,β-acetylenic ketones. CuCl₂-O₂ was used for oxidative cleavage of carbon-carbon double bond of enol ethers to corresponding ketones 48. Anhydrous copper chloride in pyridine was applied for dehydrogenation of indolines to indoles 49 and CuCl₂-DMSO (dimethylsulfoxide) showed oxidative amidation activity towards terminal alkynes 50. On account on these results, we used copper chloride in dimethylsulfoxide for the oxidation of tetrahydro-2H-benzo[g]indazole 4. Compound 4a was chosen as a model substrate to optimize the reaction conditions such as the amount of CuCl₂, the reaction temperature and the reaction time. At room temperature, treatment of 4a with 10% or 1.3 equivalent copper chloride in DMSO.
resulted in a very poor conversion, yielding only 5-8% of 5a (Table 7, entry 1 & 8).

Table 7 shows that the rate and yield of the reaction were improved with increasing the amount of CuCl\(_2\) and the reaction temperature. The best results were obtained with the use of 2 equivalent of copper chloride at 100 °C, in which the reaction was accomplished within 25 min and with an excellent yield (94%). The authenticity of the product was confirmed by its spectral data. Encouraged by these result we turned our attention to the other substituted of 4 (Scheme 4).

Table 7: Effect of the catalyst CuCl\(_2\) and temperature on the synthesis of 4, 5-dihydro-2, 3-diphenyl-2H-benzo[g]indazole 5a

<table>
<thead>
<tr>
<th>entry</th>
<th>%CuCl(_2)</th>
<th>Temp °C</th>
<th>Time</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10%</td>
<td>r.t.</td>
<td>25h</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>10%</td>
<td>60</td>
<td>15h</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>20%</td>
<td>60</td>
<td>11h</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>20%</td>
<td>100</td>
<td>7h</td>
<td>55</td>
</tr>
<tr>
<td>5</td>
<td>40%</td>
<td>60</td>
<td>5.5h</td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td>60%</td>
<td>100</td>
<td>3h</td>
<td>75</td>
</tr>
<tr>
<td>7</td>
<td>1eq</td>
<td>100</td>
<td>1.5h</td>
<td>85</td>
</tr>
<tr>
<td>8</td>
<td>1.3eq</td>
<td>r.t.</td>
<td>21h</td>
<td>8</td>
</tr>
<tr>
<td>9</td>
<td>1.5eq</td>
<td>60</td>
<td>70min</td>
<td>88</td>
</tr>
<tr>
<td>10</td>
<td>2eq</td>
<td>100</td>
<td>25min</td>
<td>94</td>
</tr>
</tbody>
</table>
It is noteworthy that the products 5a-e did not undergo dehydrogenation oxidation at their C₄-C₅ bonds 7, even on increasing the molar ratio of the oxidant up to six molar and increasing the reaction temperatures up to 160 °C for 48 hr. (Scheme 4).

\[
\begin{array}{c}
\text{R₁} \quad \text{R₂} \quad \text{R₃} \quad \text{N-Ph} \\
\text{CuCl₂(2eq)/DMSO} \\
100 °C, 25min \\
\text{4} \\
\end{array}
\]

\[
\begin{array}{c}
\text{R₁} \quad \text{R₂} \quad \text{R₃} \quad \text{N-Ph} \\
\text{CuCl₂(6eq)/DMSO} \\
160 °C \\
\text{7} \\
\end{array}
\]

4 and 5
a: R₁=R₂=R₃ = H
b: R₁=R₂= H, R₃ = OMe
c: R₁ = H, R₂ = R₃ = OMe
d: R₁=R₂ =R₃ = OMe
e: R₁=R₂= H, R₃ = Cl

**Scheme 4:** synthesis of 4, 5-dihydro-2, 3-diaryl-2H-benzo [g] indazole 5a-e

We studied two methods for preparation of compounds 5a-e (10% I₂ or 2 equiv CuCl₂ in DMSO as solvent), however, copper chloride as compared to molecular iodine gave better yields and exclusively one compound (Table 8).

**Table 8:** comparison yield of 4, 5-dihydro-2, 3-diaryl-2H-benzo [g] indazole 5a-e by I₂(10%) and CuCl₂(2 eq) in dimethylsulfoxide as solvent

<table>
<thead>
<tr>
<th>Entry</th>
<th>I₂(10%)</th>
<th>CuCl₂(2 eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>73</td>
<td>94</td>
</tr>
<tr>
<td>5b</td>
<td>71</td>
<td>90</td>
</tr>
<tr>
<td>5c</td>
<td>75</td>
<td>93</td>
</tr>
<tr>
<td>5d</td>
<td>75</td>
<td>94</td>
</tr>
<tr>
<td>5d</td>
<td>72</td>
<td>91</td>
</tr>
</tbody>
</table>
Oxidation of 3, 3a, 4, 5-tetrahydro-3-aryl-2-phenyl-2H-benzo[g]indazole 4 by using N-bromosuccinimide

N-bromosuccinimide (NBS) is a known reagent for the oxidation of primary and secondary alcohols \(^{51,52}\), 1,4-dihydropyridine \(^{53}\), cyclohexa-1,4-dien-3-carboxylates \(^{54}\), \(N\)-substituted of indoles to isatins \(^{55}\), pyrazolines to pyrazoles \(^{56}\), 1,2,3,4-tetrahydroquinuline to 4-bromoquinuline \(^{57}\), 2,3-dihydrobenzofuran to 3-bromobenzofuran \(^{58}\) and 2,3-dihydroinden-1-one to 3-bromo-1H-inden-1-one \(^{59}\). In addition, NBS is a preferred reagent for allylic \(^{60}\) and benzylic \(^{61,62}\) bromination.

Herein, we describe a new approach for the oxidation of 3,3a,4,5-tetrahydro-3-aryl-2-phenyl-2H-benzo[g]indazoles 4 to the corresponding 2H-benzo[g]indazole derivatives using commercially available \(N\)-bromosuccinimide. As a model reaction, we selected compound 4e to react with one equivalent of NBS in CCl\(_4\) and in the presence of a catalytic amount of benzoylperoxide. After overnight refluxing, TLC showed that the reaction wasn't completed. So we increased the molar ratio of NBS, slowly and at different times till 3 equiv whereupon TLC confirmed the absence of reactant 4e. Spectroscopic analysis of the product indicated that the reaction led to dehydrogenation in both five and six member rings of the indazole system, and also bromination to form compound 8e (Scheme 5). The \(^1\)H NMR spectrum of 8e, when compared to that of the reactant showed the absence of the aliphatic hydrogens and also the singlet peak at \(\delta = 7.84\) ppm (1H) in the spectrum of 4e. Furthermore, the mass spectrum of 7e showed a peak at \(m/z = M^+ - 79\). Under the same reaction conditions, the other derivatives of 4 were also converted to the corresponding 5-bromo-2,3-diaryl-2H-benzo[g] indazoles 8a-e with high yields (Scheme 5).
In an extension of this procedure, the oxidation of the six member rings of compounds 5a-e and 6a-e by NBS (2.1 equiv) were studied. In these cases also the six member rings of the reactants underwent aromatization and also bromination at C₅, with high yields (Scheme 6, Table 9). The structures of the products were determined by spectroscopic methods. Among all, the structure of compound 9b was further confirmed by X-ray crystallographic analysis. The molecular structure of 9b is depicted in Figure 1 and the selected interatomic distances and angles are listed in Table 10. The benzo[g]indazole moiety is essentially planar and makes dihedral angles of 27.1(3) ° with the N-bound aromatic ring, and 57.6(2) ° with the C-bound aromatic ring. An interesting future of the structure is a Br...Br interaction between the adjacent molecules, related by the symmetry of -x+1,-y+3,-z+1 (Table 10), with the interatomic distance of 3.2538(18) Å, which is significantly shorter than the sum of the Van der Waals radii of the relevant atoms (3.70 Å).
Scheme 6

Table 9: Physico-chemical data of 8 and 9

<table>
<thead>
<tr>
<th>entry</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>R₄</th>
<th>m.p. °C</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>194</td>
<td>91</td>
</tr>
<tr>
<td>8b</td>
<td>H</td>
<td>OMe</td>
<td>H</td>
<td>H</td>
<td>182</td>
<td>89</td>
</tr>
<tr>
<td>8c</td>
<td>H</td>
<td>OMe</td>
<td>OMe</td>
<td>H</td>
<td>161</td>
<td>88</td>
</tr>
<tr>
<td>8d</td>
<td>OMe</td>
<td>OMe</td>
<td>OMe</td>
<td>H</td>
<td>174</td>
<td>92</td>
</tr>
<tr>
<td>8e</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>H</td>
<td>168</td>
<td>93</td>
</tr>
<tr>
<td>9a</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>I</td>
<td>180</td>
<td>89</td>
</tr>
<tr>
<td>9b</td>
<td>H</td>
<td>OMe</td>
<td>H</td>
<td>I</td>
<td>208</td>
<td>92</td>
</tr>
<tr>
<td>9c</td>
<td>H</td>
<td>OMe</td>
<td>OMe</td>
<td>I</td>
<td>170</td>
<td>87</td>
</tr>
<tr>
<td>9d</td>
<td>OMe</td>
<td>OMe</td>
<td>OMe</td>
<td>I</td>
<td>192</td>
<td>88</td>
</tr>
<tr>
<td>9e</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>I</td>
<td>210</td>
<td>91</td>
</tr>
</tbody>
</table>
**Figure 1:** X-Ray crystal structure of 9b

**Table 10:** Selected geometric parameters for 9b

<table>
<thead>
<tr>
<th>Interatomic distances (Å)</th>
<th>Bond angles(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I(1)-C(22)</td>
<td>C(11)-N(1)-C(19)</td>
</tr>
<tr>
<td>Br(1)-C(8)</td>
<td>N(1)-C(11)-C(12)</td>
</tr>
<tr>
<td>Br(1)-Br(1)#1</td>
<td></td>
</tr>
<tr>
<td>N(1)-N(2)</td>
<td></td>
</tr>
<tr>
<td>N(1)-C(19)</td>
<td></td>
</tr>
<tr>
<td>C(8)-C(9)</td>
<td></td>
</tr>
<tr>
<td>C(11)-C(12)</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: #1 - x+1,-y+3,-z+1
1.4.2 Summary

We described the action of I$_2$/DMSO, CuCl$_2$/DMSO and NBS on 3,3a,4,5-tetrahydro-3-aryl-2-phenyl-2H-benzo[g]indazoles 4a-e towards oxidation and halogenation. The five member rings of compounds 4a-e were aromatized by using I$_2$ (10%) and CuCl$_2$ (2 eq) in dimethylsulfoxide as solvent, whereas by using 1.3 eq I$_2$, aromatization along with iodination at the para position of N-phenyl moiety occurred. While within these procedures the six member rings of the reactants remained intact, aromatization of five and six member rings and also bromination at C$_5$ of compounds 4a-e took place by NBS.

Crystallography

Diffraction data were measured with a Bruker SMART Apex II CCD area-detector diffractometer (graphite-monochromated Mo-K$\alpha$ radiation, $\lambda$ = 0.71073 Å). The orientation matrix, unit-cell refinement, and data reduction were all handled by the Apex2 software (SAINT integration, SADABS absorption correction). The structure was solved using direct method in the program SHELXS-97 and was refined by the full matrix least-squares method on $F^2$ with SHELXL-97. All the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were placed at calculated positions and refined isotropically. Drawing of the molecule was produced with XSEED. Crystal data and refinement are summarized in Tables 11. CCDC 819875 contains the supplementary crystallographic data for the crystal. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).
**Table 11:** Crystal data and structure refinement for 9b

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{24}$ H$</em>{16}$ Br I N$_2$O</td>
</tr>
<tr>
<td>Formula weight</td>
<td>555.20</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Crystal system, Space group</td>
<td>Triclinic, P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>9.4851(3)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>10.5697(3)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>11.9829(3)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>114.723(2)</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>91.544(2)</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>111.295(2)</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>993.76(5)</td>
</tr>
<tr>
<td>Z, Density (calculated) (g cm$^{-3}$)</td>
<td>2, 1.855</td>
</tr>
<tr>
<td>Absorption coefficient (mm$^{-1}$)</td>
<td>3.640</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>540</td>
</tr>
<tr>
<td>Crystal size (mm$^3$)</td>
<td>0.15 x 0.11 x 0.02</td>
</tr>
<tr>
<td>$\theta$ range for data collection (°)</td>
<td>2.23 to 25.24</td>
</tr>
<tr>
<td>Index ranges</td>
<td>[-11&lt;=h&lt;=11, -12&lt;=k&lt;=12, -14&lt;=l&lt;=14]</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>7616 / 3578 [R(int) = 0.0659]</td>
</tr>
<tr>
<td>Completeness</td>
<td>To $\theta$ = 25.00° : 99.2 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9308 and 0.6112</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3578 / 0 / 263</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>0.958</td>
</tr>
<tr>
<td>Final $R$ indices [$I&gt;2\sigma$ (I)]</td>
<td>$R_I = 0.0560$, $wR_2 = 0.1233$</td>
</tr>
<tr>
<td>$R$ indices (all data)</td>
<td>$R_f = 0.1033$, $wR_2 = 0.1401$</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e.Å$^{-3}$)</td>
<td>1.107 and -0.737</td>
</tr>
</tbody>
</table>
1.4.3 Experimental Section

General procedure for synthesis of 2-arylidene-3,4-dihyronaphthalen-1(2H)-one (3a-e). To a mixture of α-tetralone (3.5 mmol) and appropriate benzaldehyde (3.5 mmol) in 50 ml methanol, KOH (4 mmol) was added. The reaction mixture was stirred at room temperature until formation of a precipitate. The solid obtained was isolated by filtration, washed and recrystalized by methanol.

2-benzylidene-3,4-dihyronaphthalen-1(2H)-one (3a)

Yield: 78%; mp: 98°C; IR (KBr) ν= 1661, 1598 cm⁻¹; ¹H NMR (CDCl₃) δ: 2.96(t, 2H, J = 6Hz) 3.15(t, 2H, J = 6Hz) 7.25-7.28(m, 2H) 7.34-7.43(m, 6H) 7.89(s, 1H) 8.15(d, 1H, J=7.2Hz); ¹³C NMR (CDCl₃) δ: 27.5, 28.9, 125.1, 127.8, 129.1, 129.2, 129.4, 129.7, 133.6, 133.7, 134.1, 135.3, 139.5, 143.8, 187.7; ms: m/z 234(M⁺). Anal. Calcd. for C₁₇H₁₄O: C, 87.15; H, 6.02. Found: C, 87.17; H, 5.98.

2-(4-methoxybenzylidene)-3,4-dihyronaphthalen-1(2H)-one (3b)

Yield: 78%; mp: 90°C; IR (KBr) ν= 1670, 1601 cm⁻¹; ¹H NMR (CDCl₃) δ: 2.95(t, 2H, J=6.6Hz) 3..15(t, 2H, J=6.6Hz) 3.85(s, 3H) 6.95(d, 2H, J= 9Hz) 7.34-7.51(m, 5H) 7.85(s, 1H) 8.12(d, 1H, J = 6.3Hz); ¹³C NMR (CDCl₃) δ: 28.1, 28.7, 59.3, 112.2, 125.7, 125.8, 126.1, 127.5, 128.8, 131.8, 134.3, 134.7, 134.9, 144.1, 158.5, 187.8; ms: m/z 264(M⁺). Anal. Calcd. for C₁₈H₁₆O₂: C, 81.79; H, 6.10. Found: C, 81.82; H, 6.07.

2-(3,4-dimethoxybenzylidene)-3,4-dihyronaphthalen-1(2H)-one (3c)
Yield: 78%; mp: 95 °C; IR (KBr) ν = 1670, 1595 cm⁻¹; ¹H NMR (CDCl₃) δ: 2.98(t, 2H, J=6Hz) 3.17(t, 2H, J=6Hz) 3.87(s, 3H) 3.89(s, 3H) 6.73(s, 1H) 7.12(d, 1H, J= 7.8Hz) 7.22-7.51(m, 4H) 7.82(s, 1H) 8.10(d, 1H, J= 6.9Hz); ¹³C NMR (CDCl₃) δ: 27.5, 28.7, 58.4, 59.0, 109.6, 113.2, 117.7, 128.6, 128.7, 128.9, 129.7, 131.2, 131.8, 133.0, 133.2, 142.8, 151.4, 152.7, 188.3; ms: m/z 294(M⁺).

2-(3,4,5-trimethoxybenzylidene)-3,4-dihyronaphthalen-1(2H)-one (3d)

Yield: 78%; mp: 117 °C; IR (KBr) ν = 1667, 1599 cm⁻¹; ¹H NMR (CDCl₃) δ: 2.97(t, 2H, J=6Hz) 3.17(t, 2H, J=6Hz) 3.89(s, 6H) 3.90(s, 3H) 6.68(s, 2H) 7.26(d, 1H, J=7.2Hz) 7.37(t, 1H, J=7.2Hz) 7.50(t, 1H, J=7.2Hz) 7.81(s, 1H) 8.12(d, 1H, J=7.2Hz); ¹³C NMR (CDCl₃) δ: 27.8, 29.1, 59.3, 60.3, 101.3, 124.3, 125.1, 125.8, 127.1, 130.3, 130.5, 133.9, 134.3, 139.4, 143.4, 155.9, 188.6; ms: m/z 324(M⁺).

2-(4-chlorobenzylidene)-3,4-dihyronaphthalen-1(2H)-one (3e)

Yield: 78%; mp: 79 °C; IR (KBr) ν = 1673, 1595 cm⁻¹; ¹H NMR (CDCl₃) δ: 2.95(t, 2H, J=6.3Hz) 3.09(t, 2H, J=6.3Hz) 7.25(d, 2H, J= 7.2Hz) 7.27-7.41(m, 4H) 7.50(t, 1H, J= 7.2Hz) 7.80(s, 1H) 8.12(d, 1H, J= 7.2Hz); ¹³C NMR (CDCl₃) δ: 27.3, 28.8, 125.1, 126.8, 126.9, 128.3, 129.7, 130.1, 130.5, 132.4, 132.6, 133.1, 135.1, 143.3, 187.1; ms: m/z 268 (M⁺).
General procedure for preparation of 3,3a,4,5-tetrahydro-2,3-diphenyl-2H-benzo[g]indazole (4a-e). To solution of 2-arylidene-3,4-dihydronaphthalen-1(2H)-one 3a-e (0.03mol) in 25ml methanol, phenylhydrazin (3.24gr, 0.03mol) was added. The resulting mixture was refluxed for 5-7h (monitored by TLC). The mixture of reaction was cooled at room temperature, and 3, 3a, 4, 5-tetrahydro-3-aryl-2-phenyl-2H-benzo[g]indazole 4 was precipitated. The mixture was filtered and recrystallized by methanol.

3,3a,4,5-tetrahydro-2,3-diphenyl-2H-benzo[g]indazole (4a)

![Chemical Structure](image)

Yield: 78%; mp: 169 °C; IR (KBr) ν= 3027, 2932, 1603, 1583, 1486 cm⁻¹; ¹H NMR (CDCl₃) δ: 1.95(m, 1H) 2.31(m, 1H) 2.90(m, 2H) 3.28(td, 1H, J₁=24.9Hz, J₂=4.8Hz) 4.63(d, 1H, J=12.3Hz) 6.81(t, 1H, J=7.2Hz) 7.06-7.19(m, 5H), 7.22-7.29(m, 2H) 7.31-7.48(m, 5H) 8.06-8.07(m, 1H); ¹³C NMR (CDCl₃) δ: 26.3, 30.0, 54.8, 57.2, 112.8, 116.7, 125.2, 125.6, 128.7, 128.9, 128.9, 129.3, 130.1, 131.1, 132.8, 141.4, 143.5, 145.3, 153.6; ms: m/z 324(M⁺), 280, 247, 196, 146, 77. Anal. Calcd. for C₂₃H₂₀N₂: C, 85.15; H, 6.21; N, 8.63. Found: C, 85.11; H, 6.19; N, 8.65.

3,3a,4,5-tetrahydro-3-((4-methoxyphenyl)-2-phenyl-2H-benzo[g]indazole (4b)

![Chemical Structure](image)

Yield: 77%; mp: 158 °C; IR (KBr) ν= 3055, 2929, 1603, 1610, 1584, 1510, 1486 cm⁻¹; ¹H NMR (CDCl₃) δ: 1.93(m, 1H) 2.27(m, 1H) 2.90(m, 2H) 3.24(td, 1H, J₁=24.9Hz, J₂=4.5Hz) 3.81(s, 3H) 4.58(d, 1H, J=12Hz) 6.81(t, 1H, J=7.5Hz) 6.93(d, 2H, J=8.7Hz) 7.07-7.22(m, 5H) 7.23-7.25(m, 2H) 7.38(d, 2H, J=8.4Hz) 8.05(m, 1H); ¹³C NMR (CDCl₃) δ: 27.0, 30.1, 55.1, 55.9, 56.4, 113.1,
116.8, 118.3, 125.4, 128.5, 129.5, 129.7, 129.8, 130.3, 132.3, 132.6, 141.2, 144.9, 154.3, 159.1; ms: m/z 354(M⁺), 339, 323, 247, 218, 207, 188, 91, 77, 51.

**Anal. Calcd.** for C₂₄H₂₂N₂O: C, 81.33; H, 6.26; N, 7.90. **Found:** C, 81.34; H, 6.26; N, 7.88.

**3,3a,4,5-tetrahydro-3-(3,4-dimethoxyphenyl)-2-phenyl-2H-benzo[g]indazole (4c)**

![Chemical structure of 4c]

**Yield:** 86%; **mp:** 174 °C; **IR (KBr)** ν = 3045, 2938, 1605, 1581, 1504, 1488 cm⁻¹; ¹H NMR (CDCl₃) δ: 1.97(m, 1H) 2.30(m, 1H) 2.93(dd, 2H, J₁=10.35Hz, J₂=3.3Hz) 3.27(td, 1H, J₁=24.9Hz, J₂=5.4Hz) 3.85(s, 3H) 3.90(s, 3H) 4.55(d, 1H, J₁=12.3Hz) 6.83(t, 1H, J=7.2Hz) 6.89(d, 1H, J=8.7Hz) 6.98-7.01(m, 2H) 7.09-7.20(m, 5H) 7.24-7.27(m, 2H) 8.05-8.08(m, 1H) ; ¹³C NMR (CDCl₃) δ: 25.7, 28.9, 55.4, 55.8, 55.9, 57.1, 112.4, 115.5, 116.1, 116.3, 122.7, 127.3, 128.6, 129.0, 129.3, 129.9, 132.1, 134.8, 141.3, 144.1, 149.2, 151.6, 154.5; ms: m/z 384(M⁺), 369, 247, 199, 56, 44. **Anal. Calcd.** for C₂₅H₂₄N₂O₂: C, 78.10; H, 6.29; N, 7.29. **Found:** C, 78.08; H, 6.28; N, 7.28.

**3,3a,4,5-tetrahydro-3-(3,4,5-trimethoxyphenyl)-2-phenyl-2H-benzo[g]indazole (4d)**

![Chemical structure of 4d]

**Yield:** 84%; **mp:** 182 °C; **IR (KBr)** ν = 3056, 2931, 1609, 1588, 1491 cm⁻¹; ¹H NMR (CDCl₃) δ: 1.96(m, 1H) 2.30(m, 1H) 2.94(m, 2H) 3.28(td, 1H, J₁=24.75, J₂=4.8Hz) 3.85(s, 6H) 3.86(s, 3H) 4.51(d, 1H, J=11.7Hz) 6.68(s, 2H) 6.85(t, 1H, J=7.2Hz) 7.10-7.28(m, 7H) 8.06(dd, 1H, J₁=6Hz, J₂=3.6Hz) ; ¹³C NMR (CDCl₃) δ: 27.4, 31.0, 55.8, 56.0, 56.1, 56.2, 109.3, 112.3, 117.0, 127.1, 128.8, 129.1, 129.2, 129.8, 129.9, 138.2, 138.4, 141.3, 144.8, 149.1, 153.9; ms: m/z
414(M⁺), 399, 381, 247. **Anal. Calcd.** for C_{26}H_{26}N_{2}O_{3}: C, 75.34; H, 6.32; N, 6.76.

**Found:** C, 75.35; H, 6.33; N, 6.77.

3-(4-chlorophenyl)-3a,4,5-tetrahydro-2-phenyl-2H-benzo[g]indazole (4e)

![Chemical Structure](image)

**Yield:** 80%; **mp:** 146 °C; **IR (KBr)** ν = 3030, 2951, 1604, 1591, 1485 cm⁻¹; **¹H NMR (CDCl₃) δ:** 1.96(m, 1H) 2.29(m, 1H) 2.92(dd, 2H, \(J_1=8.7\)Hz, \(J_2=2.7\)Hz) 3.22(td, 1H, \(J_1=24.9\)Hz, \(J_2=4.8\)Hz) 4.60(d, 1H, \(J=11.7\)Hz) 6.83(t, 1H, \(J=7.2\)Hz) 7.04(d, 2H, \(J=7.5\)Hz) 7.15-7.20(m, 3H) 7.23-7.27(m, 2H) 7.35-7.42(m, 4H) 8.03-8.06(m, 1H); **¹³C NMR (CDCl₃) δ:** 26.0, 28.9, 54.9, 55.3, 112.5, 117.3, 125.8, 128.0, 128.7, 128.8, 129.2, 129.9, 130.0, 131.3, 131.9, 140.1, 140.3, 144.8, 153.2; **ms:** m/z 358(M⁺), 323, 247. **Anal. Calcd.** for C_{23}H_{19}ClN_{2}: C, 76.98; H, 5.34; N, 7.81. **Found:** C, 77.01; H, 5.35; N, 7.78.

**General procedure for preparation of 4,5-dihydro-2,3-diaryl-2H-benzo [g] indazole (5a-e).** **Method a:** To solution of 4 (0.024mol) in 15 ml dimethylsulfoxide, iodine (0.0024 mmol) was added. The resulting mixture was heated at 120 °C for three hours. After completion, the mixture of reaction was cooled at room temperature. The reaction mixture was diluted with water and the untreated iodine was removed by washing with a saturated solution of sodium thiosulfate. The product was isolated by filtration and recrystallized by ethanol. **Method b:** To solution of 4 (0.024mol) in 20 ml dimethylsulfoxide, 2 equiv copper chloride was added. The resulting mixture was heated at 100 °C for 25 min. After completion, the mixture of reaction was cooled at room temperature. Then the mixture was poured in crushed ice. The precipitate compound was filtered, and recrystallized by ethanol.
4,5-dihydro-2,3-diphenyl-2H-benzo[g]indazole (5a)

\[
\text{mp: 148 °C; IR (KBr) v= 3051, 2928, 1594, 1494, 1436, 1366, 1032, 969 cm}^{-1}; \quad ^1\text{H NMR (CDCl}_3\text{) }\delta: 2.85(t, 2H, J=6.6Hz) \quad 2.99(t, J=6.9Hz) \quad 7.18-7.35(m, 13H) \quad 8.07(m, 1H) \quad ; \quad ^{13}\text{C NMR (CDCl}_3\text{) }\delta: 17.4, 31.1, 118.4, 122.3, 126.1, 127.3, 127.4, 127.6, 127.7, 128.6, 129.6, 130.1, 131.3, 131.5, 134.5, 135.5, 141.2, 152.8, 153.4; \quad \text{ms: m/z } 322(M^+) \quad 280, 245, 230, 218, 204, 189, 180, 153, 77. \quad \text{Anal. Calcd. for C}_{23}\text{H}_{18}\text{N}_{2}: C, 85.68; H, 5.63; N, 8.69. \quad \text{Found: C, 85.65; H, 5.63; N, 8.68.}
\]

4,5-dihydro-3-(4-methoxyphenyl)-2-phenyl-2H-benzo[g]indazole (5b)

\[
\text{mp: 126 °C; IR (KBr) v= 3043, 2939, 1583, 1479, 1375 cm}^{-1}; \quad ^1\text{H NMR (CDCl}_3\text{) }\delta: 2.82(t, 2H, J=7.18Hz) \quad 2.98(t, 2H, J=7.2Hz) \quad 3.82(s, 3H) \quad 6.87(d, 2H, J=8.4Hz) \quad 7.12(d, 2H, J=9Hz) \quad 7.26-7.34(m, 8H) \quad 8.00(d, 1H, J=6.6Hz) \quad ; \quad ^{13}\text{C NMR (CDCl}_3\text{) }\delta: 17.1, 30.9, 56.7, 117.5, 118.5, 119.5, 126.6, 126.8, 126.9, 127.3, 127.4, 128.5, 130.1, 131.2, 131.4, 138.2, 140.0, 152.7, 152.9, 158.9; \quad \text{ms: m/z } 352(M^+) \quad 335, 307, 275, 261, 248, 218, 202, 168, 153, 115, 77. \quad \text{Anal. Calcd. for C}_{24}\text{H}_{20}\text{N}_{2}O: C, 81.79; H, 5.72; N, 7.95. \quad \text{Found: C, 81.77; H, 5.73; N, 7.99.}
\]

4,5-dihydro-3-(3,4-dimethoxyphenyl)-2-phenyl-2H-benzo[g]indazole (5c)

\[
\text{mp: 118 °C; IR (KBr) v= 3051, 2944, 1601, 1493, 1377 cm}^{-1}; \quad ^1\text{H NMR (CDCl}_3\text{) }\delta: 2.83(t, 2H, 6.8Hz) \quad 2.96(t, 2H, 6.8Hz) \quad 3.77(s, 3H) \quad 3.89(s,,
3H), 6.59(s, 1H) 6.83(d, 1H, J=8.4Hz) 6.89(d, 1H, J=8.4Hz) 7.25-7.36(m, 8H) 8.01(d, 1H, J=6.9Hz) ; $^{13}$C NMR (CDCl$_3$) $\delta$: 17.1, 30.6, 55.8, 56.1, 111.8, 116.8, 118.6, 121.3, 122.3, 125.1, 126.6, 128.2, 128.4, 128.5, 130.1, 131.7, 131.8, 138.5, 142.2, 147.3, 149.1, 151.3, 153.2; $\text{ms: m/z}$ 382(M$^+$), 367, 352, 335, 321, 305, 278, 218, 204, 191, 168, 153, 115, 77. Anal. Calcd. for C$_{25}$H$_{22}$N$_2$O$_2$: C, 78.51; H, 5.80; N, 7.32. Found: C, 78.49; H, 5.78; N, 7.35.

4,5-dihydro-3-(3,4,5-trimethoxyphenyl)-2-phenyl-2H-benzo[g]indazole (5d)

mp: 153 °C; IR (KBr) $\nu$ = 3052, 2948, 1596, 1489, 1376 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$: 2.90(t, 2H, J=6.6Hz) 2.99(t, 2H, J=6.3Hz) 3.67(s, 6H) 3.87(s, 3H) 6.38(s, 2H) 7.26-7.38(m, 8H) 8.02(d, 1H, J=6.6Hz) ; $^{13}$C NMR (CDCl$_3$) $\delta$: 16.9, 29.8, 55.3, 56.1, 109.4, 117.1, 119.1, 127.2, 128.1, 128.3, 128.5, 128.6, 130.0, 130.6, 130.8, 138.4, 139.3, 141.9, 150.1, 152.0, 152.4; $\text{ms: m/z}$ 412(M$^+$), 397, 381, 368, 351, 335, 307, 248, 199, 145, 77, 56. Anal. Calcd. for C$_{26}$H$_{24}$N$_2$O$_3$: C, 75.71; H, 5.86; N, 6.79. Found: C, 75.74; H, 5.88; N, 7.81.

3-(4-chlorophenyl)-4,5-dihydro-2-phenyl-2H-benzo[g]indazole (5e)

mp: 135 °C; IR (KBr) $\nu$ = 3058, 2944, 1595, 1474, 1433, 1363, 1162, 1040, 927, 838 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$: 2.82(t, 2H, J=7.2Hz) 2.99(t, 2H, J=7.5Hz) 7.12(d, 2H, J=8.1Hz) 7.26-7.35(m, 10H) 7.01(d, 1H, J=7.2Hz) ; $^{13}$C NMR (CDCl$_3$) $\delta$: 16.9, 30.4, 118.3, 119.8, 125.9, 127.4, 128.3, 128.9, 129.1, 129.4, 129.5, 130.3, 130.4, 132.3, 135.5, 140.1, 141.2, 152.8, 153.7; $\text{ms: m/z}$ 356(M$^+$), 215, 201,
161, 115, 102, 77, 63, 41. **Anal. Calcd.** for C\(_{23}\)H\(_{17}\)ClN\(_2\): C, 77.41; H, 4.80; N, 7.85.

**Found:** C, 77.40; H, 4.81; N, 7.85.

**General procedure for preparation of 4, 5-dihydro-2-(4-iodophenyl)-3aryl-2H-benzo[g]indazole (6a-e):** To solution of 4 (0.024mol) in 15 ml dimethylsulfoxide, 1.3 equivalents iodine was added. The resulting mixture was heated at 120 °C for 30 min. After completion, the mixture of reaction was cooled at room temperature. The reaction mixture was diluted with water and the untreated iodine was removed by washing with a saturated solution of sodium thiosulfate. The product was isolated by filtration and recrystallized by ethanol.

**4,5-dihydro-2-(4-iodophenyl)-3-phenyl-2H-benzo[g]indazole (6a)**

![Chemical structure](image)

**Yield:** 88%; **mp:** 120 °C; **IR (KBr)** \(\nu =\) 3038, 3012, 2931, 1610, 1584, 1485 cm\(^{-1}\); **\(^1\)H NMR (CDCl\(_3\))** \(\delta: \) 2.79(t, 2H, \(J=6.9Hz\)) 2.95(t, 2H, \(J=6.9Hz\)) 7.06(d, 2H, \(J=8.4Hz\)) 7.17-7.20(m, 2H) 7.23-7.37(m, 6H), 7.60(d, 2H, \(J=8.7Hz\)) 7.94(d, 1H, \(J=7.2Hz\)); **\(^{13}\)C NMR (CDCl\(_3\))** \(\delta: \) 17.3, 30.1, 92.8, 116.3, 123.1, 125.3, 127.9, 128.1, 128.3, 128.5, 128.8, 131.3, 131.4, 135.2, 135.4, 139.2, 141.2, 152.3, 153.3; **ms:** \(m/z\) 448(M\(^+\)), 371, 320, 256, 228, 218, 160, 128, 89, 44. **Anal. Calcd.** for C\(_{23}\)H\(_{17}\)ClN\(_2\): C, 61.62; H, 3.82; N, 6.25. **Found:** C, 61.61; H, 3.82; N, 6.24.

**4,5-dihydro-2-(4-iodophenyl)-3-(4-methoxyphenyl)-2H-benzo[g]indazole (6b)**
**Yield:** 86%; **mp:** 130 °C; **IR (KBr)** ν = 3044, 2971, 1621, 1573, 1495 cm⁻¹; **¹H NMR (CDCl₃) δ:** 2.81(t, 2H, J=7.5Hz) 2.99(t, 2H, J=7.5Hz) 3.85(s, 3H) 6.92(d, 2H, J=8.7Hz) 7.12(m, 4H) 7.64(d, 2H, J=8.1Hz) 7.97(d, 1H, J=6.9Hz); **¹³C NMR (CDCl₃) δ:** 17.6, 30.3, 53.2, 91.9, 116.7, 118.3, 122.5, 124.2, 127.3, 127.8, 127.9, 129.8, 136.8, 137.8, 138.3, 138.4, 139.3, 151.2, 154.1, 160.1; **ms:** m/z 478(M⁺), 461, 433, 371, 350, 292, 275, 217, 175, 153, 76.

**Anal. Calcd.** for C₂₄H₁₉IN₂O: C, 60.26; H, 4.00; N, 5.86. **Found:** C, 60.22; H, 3.98; N, 5.89.

4,5-dihydro-2-(4-iodophenyl)-3-(3,4-dimethoxyphenyl)-2H-benzo[g]indazole (6c)

**Yield:** 90%; **mp:** 165 °C; **IR (KBr)** ν = 3065, 2998, 1619, 1580, 1514, 1474, 1239, 1142, 1022, 997, 825 cm⁻¹; **¹H NMR (CDCl₃) δ:** 2.82(t, 2H, J=6.9Hz) 3.01(t, 2H, J= 6.6Hz), 3.71(s, 3H), 3.92(s, 3H) 6.64(s, 1H) 6.80(d, 1H, J=8.7Hz) 6.88(d, 1H, J=8.4Hz) 7.01(d, 2H, J=8.7Hz) 7.12-7.35(m, 3H) 7.64(d, 2H, J=8.4Hz) 7.97(d, 1H, J=7.5Hz); **¹³C NMR (CDCl₃) δ:** 17.1, 29.9, 50.9, 51.3, 92.9, 114.8, 116.4, 116.8, 122.1, 122.2, 127.5, 127.7, 127.8, 128.9, 131.2, 131.3, 137.5, 137.9, 139.3, 150.8, 152.1, 151.3, 153.8; **ms:** m/z 508(M⁺), 493, 463, 381, 338, 245, 193, 56, 44. **Anal. Calcd.** for C₂₅H₂₁IN₂O₂: C, 59.07; H, 4.16; N, 5.51. **Found:** C, 59.10; H, 4.14; N, 5.54.

4,5-dihydro-2-(4-iodophenyl)-3-(3,4,5-trimethoxyphenyl)-2H-benzo[g]indazole (6d)
Yield: 91%; mp: 173 °C; IR (KBr) ν = 3055, 2983, 1625, 1591 cm⁻¹; ¹H NMR (CDCl₃) δ: 2.85(t, 2H, J=7.5Hz) 2.99(t, 2H, J=7.2Hz) 3.71(s, 6H) 3.89(s, 3H) 6.38(s, 2H) 7.12(d, 2H, J=9Hz) 7.26-7.32(m, 3H) 7.67(d, 2H, J=8.7Hz) 7.96(d, 1H, J=6.9Hz); ¹³C NMR (CDCl₃) δ: 19.5, 29.5, 56.0, 60.9, 91.4, 106.5, 117.3, 122.6, 125.2, 126.5, 126.8, 127.9, 128.2, 129.2, 136.8, 137.7, 137.9, 138.3, 139.9, 149.2, 153.1; ms: m/z 538(M⁺), 523, 480, 411, 396, 305, 279, 205, 190, 160, 133, 89, 45. Anal. Calcd. for C₂₆H₂₃IN₂O₃: C, 58.00; H, 4.31; N, 5.20. Found: C, 57.97; H, 4.33; N, 5.23.

3-(4-chlorophenyl)-4,5-dihydro-2-(4-iodophenyl)-2H-benzo[g]indazole (6e)

Yield: 90%; mp: 160 °C; IR (KBr) ν = 3045, 2985, 1609, 1589, 1482 cm⁻¹; ¹H NMR (CDCl₃) δ: 2.79(t, 2H, J=6.6Hz) 2.98(t, 2H, J=7.2Hz) 7.07(d, 2H, J=8.7Hz) 7.14(d, 2H, J=8.4Hz) 7.27-7.30(m, 3H) 7.36(d, 2H, J=8.7Hz) 7.65(d, 2H, J=8.7Hz) 7.95(d, 1H, J=6.6Hz); ¹³C NMR (CDCl₃) δ: 19.3, 29.4, 91.8, 117.8, 122.6, 126.4, 126.9, 128.0, 128.3, 128.4, 128.9, 129.1, 130.5, 134.3, 136.8, 137.2, 137.9, 139.7, 149.4; ms: m/z 482(M⁺), 354, 344, 279, 217, 203, 178, 160, 76(100), 50. Anal. Calcd. for C₂₃H₁₆ClIN₂: C, 57.22; H, 3.34; N, 5.80. Found: C, 57.25; H, 3.32; N, 5.77.

General procedure for preparation 5-bromo-2,3-diaryl-2H-benzo[g]indazole (8a-e). To a solution of 4 (1.54mmol) in CCl₄ (100 mL) were added N-
bromosuccinimide (0.81g, 4.62mmol) and a catalytic amount of benzoyl peroxide, and the mixture was refluxed for 3 h. The mixture was cold-filtered and evaporated to dryness. The crude product was crystallized from methanol.

5-bromo-2, 3-diphenyl-2H-benzo[g]indazole (8a)

![Structure of 5-bromo-2, 3-diphenyl-2H-benzo[g]indazole (8a)](image)

**Yield:** 91%; **mp:** 194 °C; **IR (KBr)** ν = 3062, 1592, 1500, 1452, 1349, 1256, 1187, 1149, 1100, 1033, 920, 854 cm⁻¹; **¹H NMR (CDCl₃)** δ: 7.35-7.49(m, 10H) 7.65-7.68(m, 2H) 7.92(s, 1H) 8.28(m, 1H) 8.71(m, 1H) ; **¹³C NMR (CDCl₃)** δ: 113.9, 119.3, 122.8, 124.6, 124.9, 125.1, 126.5, 127.3, 127.6, 127.8, 128.1, 128.7, 129.1, 130.3, 130.5, 134.6, 141.2, 144.5, 145.1; **ms:** m/z 398(M⁺), 318, 298, 214, 159, 145, 77, 55. **Anal. Calcd.** for C₂₃H₁₅BrN₂: C, 69.19; H, 3.79; N, 7.02. **Found:** C, 69.22; H, 3.81; N, 7.04.

5-bromo-3-(4-methoxyphenyl)-2-phenyl-2H-benzo[g]indazole (8b)

![Structure of 5-bromo-3-(4-methoxyphenyl)-2-phenyl-2H-benzo[g]indazole (8b)](image)

**Yield:** 89%; **mp:** 182 °C; **IR (KBr)** ν = 3052, 2954, 1606, 1505, 1460, 1378, 1351, 1291, 1250, 1181, 1108, 1027, 969, 840, 767 cm⁻¹; **¹H NMR (CDCl₃)** δ: 3.85(s, 3H) 6.95(d, 2H, J=8.7Hz) 7.28(d, 2H, J=8.7Hz) 7.37-7.49(m, 5H) 7.63-7.69(m, 2H) 7.90(s, 1H) 8.27(m, 1H) 8.70(m, 1H) ; **¹³C NMR (CDCl₃)** δ: 55.2, 114.3, 118.0, 118.6, 121.4, 122.3, 122.7, 125.8, 126.1, 126.2, 127.5, 127.7, 128.0, 128.1, 128.9, 130.8, 135.9, 139.9, 145.9, 159.7; **ms:** m/z 428(M⁺), 397, 347, 321, 254, 158, 44. **Anal. Calcd.** for C₂₄H₁₇BrN₂O: C, 67.14; H, 3.99; N, 6.53. **Found:** C, 67.15; H, 3.99; N, 6.51.
5-bromo-3-(3,4-dimethoxyphenyl)-2-phenyl-2H-benzo[g]indazole (8c)

![Chemical structure of 5-bromo-3-(3,4-dimethoxyphenyl)-2-phenyl-2H-benzo[g]indazole (8c)]

**Yield:** 88%; **mp:** 161 °C; **IR (KBr) ν:** 3049, 2932, 1603, 1505, 1466, 1374, 1288, 1103 cm⁻¹; **¹H NMR (CDCl₃) δ:** 3.73(s, 3H) 3.85(s, 3H) 6.71(s, 1H) 6.77(d, 1H, J=8.1Hz) 6.81(d, 1H, J=8.1Hz) 7.22-7.33(m, 5H) 7.64(d, 2H, J=7.8Hz) 7.97(s, 1H) 8.18-8.21(m, 1H) 8.66-8.69(m, 1H) ; **¹³C NMR (CDCl₃) δ:** 55.3, 55.6, 112.8, 114.3, 116.2, 118.3, 119.4, 121.3, 122.9, 124.3, 124.8, 126.1, 126.2, 127.1, 128.2, 130.1, 131.2, 131.3, 138.6, 141.5, 147.2, 153.6, 154.3; **ms: m/z** 458(M⁺), 427, 377, 245, 159, 44. **Anal. Calcd.** for C$_{25}$H$_{19}$BrN$_2$O$_2$: C, 65.37; H, 4.17; N, 6.10. **Found:** C, 65.40; H, 4.15; N, 6.07.

5-bromo-3-(3,4,5-trimethoxyphenyl)-2-phenyl-2H-benzo[g]indazole (8d)

![Chemical structure of 5-bromo-3-(3,4,5-trimethoxyphenyl)-2-phenyl-2H-benzo[g]indazole (8d)]

**Yield:** 92%; **mp:** 174 °C; **IR (KBr) ν:** 3056, 2945, 1614, 1519, 1445, 1379, 1110 cm⁻¹; **¹H NMR (CDCl₃) δ:** 3.56(s, 6H) 3.68(s, 3H) 6.41(s, 2H) 7.28-7.31(m, 5H) 7.61(d, 2H, J=7.8Hz) 7.91(s, 1H) 8.01-8.04(m, 1H) 8.52-8.53(m, 1H); **¹³C NMR (CDCl₃) δ:** 55.6, 55.9, 104.3, 114.1, 122.1, 123.9, 124.7, 124.9, 125.2, 125.3, 125.4, 126.9, 127.2, 128.3, 131.3, 131.4, 133.0, 143.6, 146.2, 148.3, 153.4; **ms: m/z** 488(M⁺), 457, 407, 372, 345, 294, 201, 159, 44. **Anal. Calcd.** for C$_{26}$H$_{21}$BrN$_2$O$_3$: C, 63.81; H, 4.33; N, 5.72. **Found:** C, 63.80; H, 4.33; N, 5.69.

5-bromo-3-(4-chlorophenyl)-2-phenyl-2H-benzo[g]indazole (8e)
Yield: 93%; mp: 168 °C; IR (KBr) $v =$ 3057, 1593, 1501, 1457, 1350, 1256, 1182, 1095, 1021, 927, 868, 837 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$: 7.28-7.35 (m, 5H), 7.45 (d, 2H, $J$=8.7Hz) 7.55 (d, 2H, $J$=8.7Hz) 7.66-7.69(m, 2H) 7.84(s, 1H) 8.27-8.30(m, 1H) 8.65-8.69(m, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$: 114.3, 119.9, 122.9, 124.1, 125.7, 125.8, 127.2, 127.3, 127.9, 128.1, 128.8, 131.3, 131.4, 131.8, 131.9, 133.2, 141.3, 143.2, 144.3; ms: m/z 432 (M$^+$), 397, 353, 316, 289, 241,214, 199, 158, 144, 131, 75. Anal. Calcd. for C$_{23}$H$_{14}$BrClN$_2$: C, 63.69; H, 3.25; N, 6.46. Found: C, 63.67; H, 3.24; N, 6.44.

General procedure for preparation 5-bromo-2-(4-iodophenyl)-3-aryl-2H-benzo[g]indazole (9a-e). To a solution of 6 (0.54 mmol) in CCl$_4$ (100 mL) were added N-bromosuccinimide (0.19g, 1.08 mmol) and a catalytic amount of benzoyl peroxide, and the mixture was refluxed for 3 h. The mixture was cold-filtered and evaporated to dryness. The crude product was crystallized from methanol.

5-bromo-2-(4-iodophenyl)-3-phenyl-2H-benzo[g]indazole (9a)
127.6, 127.9, 128.1, 128.8, 129.6, 130.1, 130.2, 133.7, 135.0, 139.1, 141.6, 148.3; ms: m/z 524(M⁺), 444, 396, 317, 289, 256, 214, 199, 159, 144, 76, 44. Anal. Calcd. for C₂₃H₁₄BrIN₂: C, 52.60; H, 2.69; N, 5.33. Found: C, 52.58; H, 2.68; N, 5.33.

5-bromo-2-(4-iodophenyl)-3-(4-methoxyphenyl)-2H-benzo[g]indazole (9b)

Yield: 92%; mp: 208 °C; IR (KBr) ν = 3060, 2935, 1609, 1575, 1492, 1250, 1177, 1029, 966, 831, 763 cm⁻¹; ¹H NMR (CDCl₃) δ: 3.87(s, 3H) 6.98(d, 2H, J=9Hz) 7.22-7.30(m, 4H) 7.65-7.70(m, 2H) 7.73(d, 2H, J=9Hz) 7.86(s, 1H) 8.27(m, 1H) 8.67(m, 1H); ¹³C NMR (CDCl₃) δ: 55.3, 93.1, 114.5, 118.4, 118.9, 121.2, 122.2, 122.7, 126.1, 126.4, 127.3, 127.6, 127.9, 128.1, 130.8, 135.9, 138.1, 139.7, 146.2, 160.0; ms: m/z 554(M⁺), 539, 473, 426, 335, 267, 205, 183, 159, 44. Anal. Calcd. for C₂₄H₁₆BrIN₂O: C, 51.92; H, 2.90; N, 5.05. Found: C, 51.90; H, 2.89; N, 5.07.

5-bromo-2-(4-iodophenyl)-3-(3,4-dimethoxyphenyl)-2H-benzo[g]indazole (9c)

Yield: 87%; mp: 170 °C; IR (KBr) ν = 3058, 3002, 2959, 2930, 1607, 1583, 1510, 1253, 1238, 1144, 864, 824, 763 cm⁻¹; ¹H NMR (CDCl₃) δ: 3.74(s, 3H) 3.96(s, 3H) 6.75(s, 1H) 6.95-6.99(m, 2H) 7.25(d, 2H, J=8.7Hz) 7.66-7.69(m, 2H) 7.74(d, 2H, J=8.4Hz) 7.89(s, 1H) 8.28(m, 1H) 8.68(m, 1H); ¹³C NMR (CDCl₃) δ: 59.1, 59.3, 92.6, 113.1, 114.2, 119.3, 120.8, 122.1, 122.4, 125.1, 125.5,
126.3, 126.4, 126.8, 129.3, 130.1, 134.2, 138.3, 139.1, 142.2, 144.9, 156.3, 157.1; 
**ms:** m/z 584(M⁺), 569, 553, 505,456, 397, 326, 287, 201, 179, 158, 44.  
Anal. Calcd. for C₂₅H₁₈BrIN₂O₂: C, 51.31; H, 3.10; N, 4.79.  
**Found:** C, 51.29; H, 3.11; N, 4.82.

5-bromo-2-(4-iodophenyl)-3-(3,4,5-trimethoxyphenyl)-2H-benzo[g]indazole(9d)

![Chemical structure](image)

**Yield:** 88%; **mp:** 192 °C; **IR (KBr)** ν= 3043, 2938, 1610, 1590, 1485, 1168, 1041, 959 cm⁻¹; **¹H NMR (CDCl₃)** δ: 3.76(s, 6H) 3.98(s, 3H) 6.41(d, 2H) 7.19(d, 2H, J=9Hz) 7.61-7.65(m, 2H) 7.76(d, 2H, J=9Hz) 7.83(s, 1H) 8.19(m, 1H) 8.71(m, 1H) ; **¹³C NMR (CDCl₃)** δ: 55.9, 56.3, 92.0, 103.4, 114.1, 119.9, 121.8, 122.0, 126.1, 126.8, 126.9, 127.3, 127.4, 131.3, 133.9, 138.3, 138.8, 140.7, 145.1, 149.3, 154.7; **ms:** m/z 614(M⁺), 599, 583, 486, 533, 498, 449, 315, 301, 298, 204, 155, 43.  
Anal. Calcd. for C₂₆H₂₀BrIN₂O₃: C, 50.76; H, 3.28; N, 4.55.  
**Found:** C, 50.78; H, 3.29; N, 4.52.

5-bromo-3-(4-chlorophenyl)-2-(4-iodophenyl)-2H-benzo[g]indazole (9e)

![Chemical structure](image)

**Yield:** 91%; **mp:** 210 °C; **IR (KBr)** ν= 3068, 1615, 1595, 1465 cm⁻¹; **¹H NMR (CDCl₃)** δ: 7.13(d, 2H, J=8.4Hz), 7.29(d, 2H, J=7.8Hz 7.59-7.62(m, 2H) 7.66(d, 2H, J=7.8Hz) 7.69(d, 2H, J=8.4Hz) 7.87(s, 1H) 8.16(m, 1H) 8.68(m, 1H) ; **¹³C NMR (CDCl₃)** δ: 92.4, 114.4, 121.7, 121.8, 122.1, 123.2, 127.1, 127.3, 127.8, 128.6, 129.6, 130.0, 131.1, 133.9, 136.3, 139.3, 140.5, 142.8, 144.6; **ms:**
m/z 558(M⁺), 512, 478, 432, 341, 316, 214, 199, 158, 145, 105, 76. Anal. Calcd. for C₂₃H₁₃BrClIN₂: C, 49.36; H, 2.34; N, 5.01. Found: C, 49.34; H, 2.34; N, 5.03.
1.5 References


1.6 Spectral Data

4e) $^1$H NMR

4b) $^1$H NMR
6b) $^1\text{H}$ NMR

6b) GCMS
6e) $^{13}$C NMR

6e) GCMS
5e) GCMS

5b) $^{13}$C NMR
5d] $^1$H NMR

5a] $^{13}$C NMR
8a) $^1$H NMR

8b) $^{13}$C NMR
8b) $^1$H NMR

8e) $^1$H NMR
8e] GCMS

9b] $^1$H NMR
9b] \(^{13}\)C NMR

9e] GCMS