Aromatization and Halogenation of 3,3a,4,5-Tetrahydro-3-aryl-2-phenyl-2*H*-benzo[g]indazole Using I_2/DMSO, $CuCl_2$/DMSO, and *N*-Bromosuccinimide

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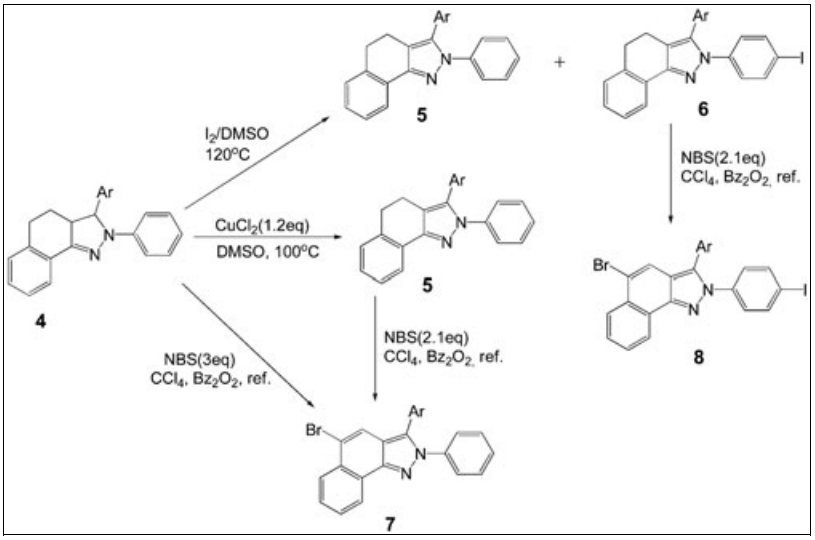

The treatment of 3,3a,4,5-tetrahydro-3-aryl-2-phenyl-2*H*-benzo[g]indazoles **4** with I_2/DMSO led to the oxidation of the five-member rings (**5**) as well as the iodination of *N*-phenyl moieties along with oxidation of the five-member rings (**6**). However, the reactions of **4** with $CuCl_2$/DMSO gave only compounds **5**. The reaction of *N*-bromosuccinimide (NBS) with compounds **4** resulted in fully aromatization along with bromination at C-5 of the indazole rings (**7**). The indazole six-member rings in compounds **5** and **6** also underwent aromatization along with bromination by using NBS (**7** and **8**).

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INTRODUCTION

Indazole derivatives, which are bioisosteres of indoles, are an important class of compound in the medicinal arena [1]. They have been reported to possess a variety of biological activities including high binding affinity for estrogen receptor [2], inhibition of protein kinase C-β [3], 5-HT_2 and 5-HT_3 receptor antagonisms [4], HIV protease inhibition [5], and antitumor activity [6]. Lonidamine, a derivative of indazole-3-carboxylic acid, is an anticancer drug for the treatment of lung, breast, prostate, and brain cancers [7]. The homologues of 2*H*-indazole, namely benzo[g]-2*H*-indazole, are a potential pharmacophore studied as an estrogen receptor β ligand [8], antiproliferative agent [9] and exhibit good affinity to the imidazoline I_2 receptor with low affinity to the α_2-andrenoceptor [10]. However, compared to 1*H*-indazoles, benzo[g]-2*H*-indazoles have been much less studied, partly due to the difficulty in their preparation. Most of the existing methods contain synthesis of 3,4-dihydrobenzo[g]-1*H*-indazole. For the construction of these compounds, usually α-tetralon is used, such as the reaction of lithium enolate of α-tetralon with isonipecotic acid and subsequent condensation with hydrazine [11], condensation of hydrazone of α-tetralon with substituted aromatic ester in the presence of LDA [12], Claisen condensation of diethyloxalate with α-tetralon, followed by reaction with hydrazine hydrochloride [13] or methylhydrazine [10], and condensation of α-tetralon with aldehydes followed by reaction with *p*-cyanophenylhydrazine [14]. On the other hand, oxidation of hydrogenated indazole derivatives has been less encountered in literature and mostly requires drastic reaction conditions and expensive reagents with long reaction times and low yields. Examples are the reaction of tetrahydro-3-aryl-1*H*-indazole with 10% Pd/C in trans-decaline at reflux for 24 h [15], dehydrogenation of tetrahydro-2,3-diaryl-2*H*-indazole by DDQ

(2,3-dichloro-5,6-dicyano-1,4-benzoquinone) in benzene at reflux for 24 h [16], and oxidation of five-member ring in hexahydro-2,3-diaryl-2*H*-indazole by DDQ in dioxane at reflux with 32% yield [17]. To the best of our knowledge, there is no report about dehydrogenation of dihydro-2*H*-indazoles. Herein, we disclose our preliminary results using different oxidizing agents for the oxidation of tetrahydrobenzo[g]-2*H*-indazoles to the corresponding benzo[g]-2*H*-indazoles. We have recently reported the use of I_2/DMSO as an efficient catalytic system for the oxidation of pyrazoline to pyrazole [18] and dehydrogenation of flavanones [19]. In continuation of our research programmed on applications of such a system, it was found that the products of the condensation reaction of α-tetralon with substituted aromatic aldehydes followed by cyclization with phenyl hydrazine may undergo oxidative dehydrogenation by I_2/DMSO system to construct the corresponding benzo[g]-2*H*-indazoles. Furthermore, $CuCl_2$/DMSO and *N*-bromosuccinimide (NBS) were investigated for their oxidation behavior toward the substrates.

RESULTS AND DISCUSSION

Preparation of 3,3a,4,5-tetrahydro-3-aryl-2-phenyl-2*H*-benzo[g]indazole. The precursor chalcones **3a–e** were prepared from the reaction of α-tetralon **1** with substituted aromatic aldehydes **2** in methanolic KOH solution (Scheme 1). The formation of **3a–e** was confirmed on the basis of their infrared (IR) and ^{1}H-NMR data. The chalcones were then reacted with phenyl hydrazine in refluxing methanol for 4–6 h to form stable 2*H*-benzo[g] indazoles **4a–e** in 78–86% yield (Scheme 1). This reaction probably takes place through mediation of an appropriate hydrazone, which immediately cyclizes to 2*H*-benzo[g] indazole ring system. Compounds **4a–e** show in their IR spectra absorbances for C=N at ν = 1603–1609 cm^{-1}. 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, at the δ = 1.93, 2.27, and 3.24 ppm (for **4b**), each integrating for one proton.

Oxidation of 3,3a,4,5-tetrahydro-3-aryl-2-phenyl-2*H*-benzo[g]indazole 4 by using I_2-DMSO. Initially, we attempted the oxidation of 3,3a,4,5-tetrahydro-2,3-diphenyl-2*H*-benzo[g] indazole **4a** using iodine (10%) in DMSO at 60°C as per our known procedures for the pyrazole synthesis [18]. After 10 h, thin layer chromatography (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 absence of hydrogens on C_3 and C_{3a} when compared with the spectrum of the reactant **4a**. Surprisingly, the spectral analysis of **6a** revealed that its *N*-phenyl ring was iodinated at the *para* position. The ^{1}H-NMR of **6a** showed two doublets at δ = 7.12 ppm (2H) and 7.67 ppm (2H), with the same coupling constant (8.7 Hz). Furthermore, its ^{13}C-NMR spectrum exhibited a distinct absorbance at δ = 91.4 ppm, and its MS spectrum showed 126 mass units greater than that of **5a**. The reaction was then carried out using different amounts of iodine and at different temperatures. As shown in Table 1, the reaction time and the products ratio were found to be dependent on the quantity of the catalyst and the reaction temperature. Thus, while the conversion of **4a** to the products at room temperature did not occur (entries 1 and 9), the best yield of **5a** was obtained by using 10% iodine in DMSO at 120°C for 3 h (entry 4). The optimal conditions for the preparation of **6a** were found to be using 1.3 equiv iodine in DMSO at 120°C for 30 min (entry 12). The products were easily purified by recrystallization from ethanol (the yields were 73 and 86% for **5a** and **6a**, respectively). To generalize the synthetic procedure, various 3,3a,4,5-tetrahydro-3-aryl-2-phenyl-2*H*-benzo[g]indazoles **4** were converted to the corresponding 4,5-dihydro-2,3-diaryl-2*H*-benzo[g]indazoles **5** and 4,5-dihydro-2-(4-iodophenyl)-

Scheme 1. Synthesis of 3,3a,4,5-tetrahydro-3-aryl-2-phenyl-2*H*-benzo[g]indazoles.

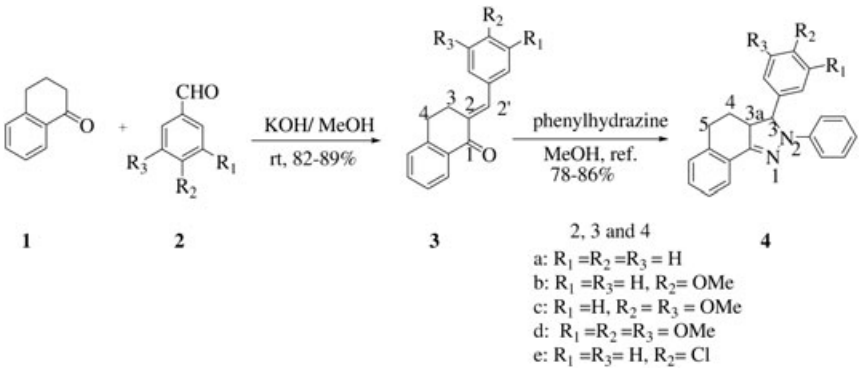
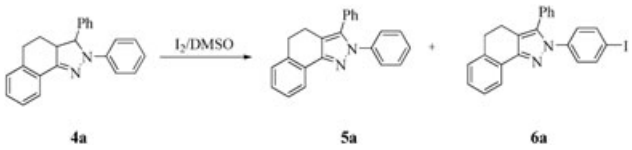


Table 1

Effects of the amount of the iodine catalyst and temperature on the conversion of **4a** to **5a** and **6a**.



4a **5a** **6a**

Entry	I_2 (%)	Temp (°C)	Time	5a:6a[a]
1	10%	rt[b]	15 h	–[c]
2	10%	60	10 h	92:08
3	10%	90	6 h	94:06
4	10%	120	3 h	95:05
5	20%	120	2.5 h	85:15
6	40%	120	2 h	65:35
7	60%	120	100 min	50:50
8	1eq	120	70 min	30:70
9	1.3eq	rt[b]	10 h	–[c]
10	1.3eq	60	3 h	25:75
11	1.3eq	90	80 min	10:90
12	1.3eq	120	30 min	5:95

[a]The ratio of compounds **5a** and **6a** were obtained based on ^{1}H-NMR spectroscopy and GC.
[b]Room temperature.
[c]No reaction.

3aryl-2*H*-benzo[g]indazoles **6** (Scheme 2). Furthermore, it was realized that under the same conditions as for the conversion of **4–6**, compound **5** did not undergo iodination at the *N*-phenyl rings (Scheme 2). Apparently, due to the aromatization of the five-member rings, the nitrogen (N_2) lone pair electrons are not available for the *N*-bound phenyl rings. It is noteworthy that in none of the dehydrogenation–oxidation cases of the six-member ring was observed, even on increasing the molar ratio of the reagent up to six molar and conducting the reaction for 48 h at 120°C.

Oxidation of 3,3a,4,5-tetrahydro-3-aryl-2-phenyl-2*H*-benzo [g]indazole 4 by using $CuCl_2$-DMSO. Copper (II) chloride has low cost, readily available, and easy to work-up due to its solubility in water. Literature survey revealed that $CuCl_2$-TBHP (*tert*-butyl hydroperoxide) applied for the oxidation of alcohols [20,21] to aldehydes or ketones and oxidation of alkynes [22] to α,β-acetylenic ketones. $CuCl_2$–O_2 was used for oxidative cleavage of carbon–carbon double bond of enol ethers to corresponding ketones [23]. Anhydrous copper chloride in pyridine was applied for dehydrogenation of indolines to indoles [24], and $CuCl_2$-DMSO showed oxidative amidation activity toward terminal alkynes [25]. On account of these reports, we used copper chloride in dimethylsulfoxide for the oxidation of tetrahydro-2*H*-benzo[g]indazoles **4**. Compound **4a** was chosen as a model substrate to optimize the reaction conditions such as the amount of $CuCl_2$, the reaction temperature, and the reaction time. As shown in Table 2, while at room temperature the treatment of **4a** with 10% or 1.3 equiv copper chloride in DMSO resulted in very low yields of **5a** (entries 1 and8), the rate and the yield of the reaction were improved with increasing the reaction temperature and the amount of $CuCl_2$. The best result was obtained with the use of 2 equiv of copper chloride at 100°C, in which the reaction was accomplished within 25 min and with an excellent yield (94%). To assess the generality of the procedure, a variety of substituted **4** were converted to the corresponding compound **5** by the action of $CuCl_2$-DMSO system (Scheme 2). Similar to what was observed in the reaction with I_2/DMSO, the product **5** did not undergo dehydrogenation–oxidation at their C_4—C_5 bonds, even on increasing the molar ratio of the oxidant up to six molar and increasing the reaction temperature and time up to 160°C for 48 h. Therefore, we have developed two methods for the preparation of compounds **5** (10% I_2 or 2 equiv $CuCl_2$ in DMSO); however, copper chloride when compared with molecular iodine gave better yields and exclusively one product (Table 3).

Oxidation of 3,3a,4,5-tetrahydro-3-aryl-2-phenyl-2*H*-benzo[g] indazole 4 by using *N*-bromosuccinimide. *N*-bromosuccinimide (NBS) is a known reagent for the oxidation of primary and secondary alcohols [26,27], 1,4-dihydropyridine [28], cyclohexa-1,4-dien-3-carboxylates [29], *N*-substituted indoles to isatins [30], pyrazolines to pyrazoles [31], 1,2,3,4-tetrahydroquinuline to 4-bromoquinuline [32], 2,3-dihydrobenzofuran to 3-bromobenzofuran [33], and 2, 3-dihydroinden-1-one to 3-bromo-1*H*-inden-1-one [34]. In addition, NBS is a preferred reagent for allylic [35] and benzylic [36,37] bromination. Herein, we describe a new approach for the oxidation of 3,3a,4,5-tetrahydro-3-aryl-2-phenyl-2*H*-benzo[g]indazoles **4** to the corresponding 2*H*-benzo[g]indazole derivatives using commercially available NBS. As a model reaction, we selected compound **4e** to react with 1 equiv of NBS in CCl_4 and in the presence of a catalytic amount of benzoylperoxide. After overnight refluxing, TLC showed that the reaction was not 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 **7e** (Scheme 2). The ^{1}H-NMR spectrum of **7e**, when compared with that of the reactant, showed the absence of the aliphatic hydrogens and also the singlet peak at δ = 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 **7a–e** with high yields (Scheme 2).

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) was studied. In these cases also, the six-member rings of the reactants underwent aromatization and also

Scheme 2. Aromatization of 3,3a,4,5-tetrahydro-3-aryl-2-phenyl-2*H*-benzo[g]indazoles **4** by using I_2/DMSO, $CuCl_2$/DMSO, and NBS.

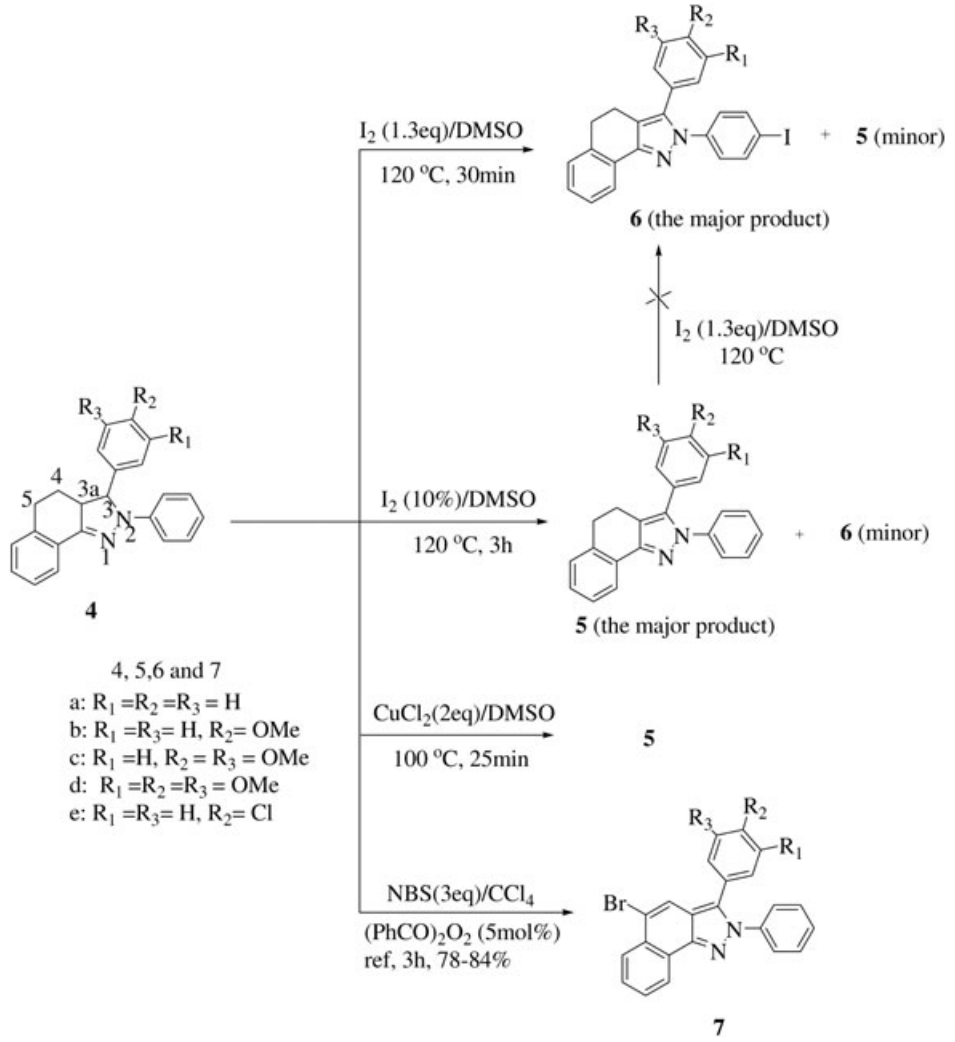


Table 2

Effects of the $CuCl_2$ catalyst and temperature on the synthesis of **5a**.

4a **5a**

Entry	$CuCl_2$ (%)	Temp (°C)	Time	Yield (%)
1	10%	r.t.	25 h	5
2	10%	60	15 h	35
3	20%	60	11 h	40
4	20%	100	7 h	55
5	40%	60	5.5 h	75
6	60%	100	3 h	75
7	1eq	100	1.5 h	85
8	1.3eq	r.t.	21 h	8
9	1.5eq	60	70 min	88
10	2eq	100	25 min	94

Table 3

Comparison of yields of **5a–e** obtained by I_2(10%) and $CuCl_2$(2 equiv) in dimethylsulfoxide solvent.

	Yield (%)	
Entry	I_2(10%)	$CuCl_2$(2 equiv)
5a	73	94
5b	71	90
5c	75	93
5d	75	94
5d	72	91

bromination at C_5, with high yields (Scheme 3). The structures of the products were determined by spectroscopic methods. Among all, the structure of compound **8b** was further confirmed by X-ray crystallographic analysis. The molecular structure of **8b** is depicted in Figure 1, and the selected interatomic distances and angles are listed in Table 4. The benzo

Scheme 3. Synthesis of 5-bromo-2,3-diaryl-2*H*-benzo[g]indazoles.

[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 $-x + 1$, $-y + 3$, $-z + 1$, 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).

CONCLUSION

We described the action of I_2/DMSO, $CuCl_2$/DMSO, and NBS on 3,3a,4,5-tetrahydro-3-aryl-2-phenyl-2*H*-benzo[g] indazoles **4a–e** toward oxidation and halogenation. The five-member rings of compounds **4a–e** were aromatized by using I_2 (10%) and $CuCl_2$ (2 equiv) in dimethylsulfoxide as solvent, whereas by using 1.3 equiv I_2, aromatization along with iodination at the *para* position of *N*-phenyl moiety occurred. Although 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.

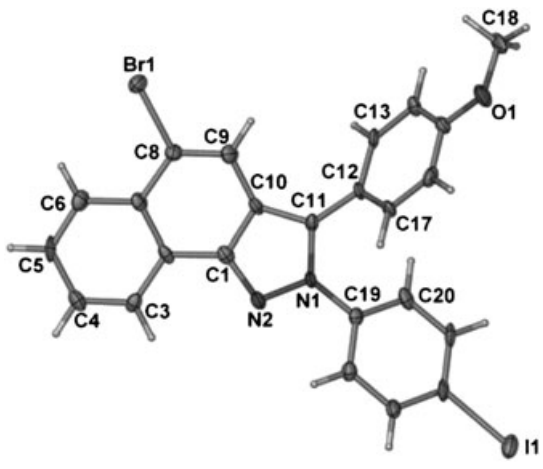


Figure 1. 5-Bromo-2-(4-iodophenyl)-3-(4-methoxyphenyl)-2H-benzo[g] indazole (**8b**).

Table 4

Selected geometric parameters for **8b**.

Interatomic distances (Å)	
I(1)–C(22)	2.111(8)
Br(1)–C(8)	1.895(8)
Br(1)–Br(1)#1	3.2538(18)
N(1)–N(2)	1.372(9)
N(1)–C(19)	1.420(10)
C(8)–C(9)	1.345(11)
C(11)–C(12)	1.466(11)
Bond angles (°)	
C(11)–N(1)–C(19)	128.1(7)
N(1)–C(11)–C(12)	126.4(7)

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

EXPERIMENTAL

^{1}H-NMR and ^{13}C-NMR spectra were recorded on 300 and 75 MHz, respectively, and chemical shift values were recorded in δ units (ppm) relative to Me_4Si as internal standard. Melting points were determined by using a Buchi melting point apparatus. IR spectra were recorded using KBr pellets on a Perkin-Elmer 240C analyzer. Mass spectra were recorded in an AE-IMS-30 spectrometer. TLC was performed on silica gel 60 PF254 plates or aluminum oxide plates from Merck. Elemental analyses were performed on a Thermo Flash EA 1112 analyzer.

General procedure for synthesis of 2-arylidene-3,4-dihydronaphthalen-1(2*H*)-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 the formation of a precipitate. The solid obtained was isolated by filtration, washed, and recrystallized by methanol.

2-Benzylidene-3,4-dihydronaphthalen-1(2*H*)-one (3a). Yield: 78%; mp: 98°C; IR (KBr) ν = 1661, 1598 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.96 (t, 2H, *J* = 6 Hz), 3.15 (t, 2H, *J* = 6 Hz), 7.25–7.28 (m, 2H), 7.34–7.43 (m, 6H), 7.89 (s, 1H), and 8.15 (d, 1H, *J* = 7.2 Hz); ^{13}C-NMR ($CDCl_3$) 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, and 187.7; ms: *m/z* 234(M^+). Anal. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.17; H, 5.98.

2-(4-Methoxybenzylidene)-3,4-dihydronaphthalen-1(2*H*)-one (3b). Yield: 78%; mp: 90°C; IR (KBr) ν = 1670, 1601 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.95 (t, 2H, *J* = 6.6 Hz), 3.15 (t, 2H, *J* = 6.6 Hz), 3.85 (s, 3H), 6.95 (d, 2H, *J* = 9 Hz), 7.34–7.51 (m, 5H), 7.85 (s, 1H), and 8.12 (d, 1H, *J* = 6.3 Hz); ^{13}C-NMR ($CDCl_3$) 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, and 187.8; ms: *m/z* 264(M^+). Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.82; H, 6.07.

2-(3,4-Dimethoxybenzylidene)-3,4-dihydronaphthalen-1(2*H*)-one (3c). Yield: 78%; mp: 95°C; IR (KBr) ν = 1670, 1595 cm^{-1};

^{1}H-NMR ($CDCl_3$) δ: 2.98 (t, 2H, *J* = 6 Hz), 3.17 (t, 2H, *J* = 6 Hz), 3.87 (s, 3H), 3.89 (s, 3H), 6.73 (s, 1H), 7.12 (d, 1H, *J* = 7.8 Hz), 7.22–7.51 (m, 4H), 7.82 (s, 1H), and 8.10 (d, 1H, *J* = 6.9 Hz); ^{13}C-NMR ($CDCl_3$) 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, and 188.3; ms: *m/z* 294(M^+).

2-(3,4,5-Trimethoxybenzylidene)-3,4-dihydronaphthalen-1(2*H*)-one (3d). Yield: 78%; mp: 117°C; IR (KBr) ν = 1667 and 1599 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.97 (t, 2H, *J* = 6 Hz), 3.17 (t, 2H, *J* = 6 Hz), 3.89 (s, 6H), 3.90 (s, 3H), 6.68 (s, 2H), 7.26 (d, 1H, *J* = 7.2 Hz), 7.37 (t, 1H, *J* = 7.2 Hz), 7.50 (t, 1H, *J* = 7.2 Hz), 7.81 (s, 1H), and 8.12 (d, 1H, *J* = 7.2 Hz); ^{13}C-NMR ($CDCl_3$) 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, and 188.6; ms: *m/z* 324(M^+).

2-(4-Chlorobenzylidene)-3,4-dihydronaphthalen-1(2*H*)-one (3e). Yield: 78%; mp: 79°C; IR (KBr) ν = 1673, 1595 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.95 (t, 2H, *J* = 6.3 Hz), 3.09 (t, 2H, *J* = 6.3 Hz), 7.25 (d, 2H, *J* = 7.2 Hz), 7.27–7.41 (m, 4H), 7.50 (t, 1H, *J* = 7.2 Hz), 7.80 (s, 1H), and 8.12 (d, 1H, *J* = 7.2 Hz); ^{13}C-NMR ($CDCl_3$) 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, and 187.1; ms: *m/z* 268 (M^+).

General procedure for preparation of 3,3a,4,5-tetrahydro-2,3-diphenyl-2*H*-benzo[g]indazole (4a-e). To solution of 2-arylidene-3,4-dihydronaphthalen-1(2H)-one **3a–e** (0.03 mol) in 25 mL methanol, phenylhydrazin (3.24 g, 0.03 mol) was added. The resulting mixture was refluxed for 5–7 h (monitored by TLC). The mixture of reaction was cooled at room temperature, and 3,3a,4,5-tetrahydro-3aryl-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-2*H*-benzo[g]indazole (4a). Yield: 78%; mp: 169°C; IR (KBr) ν = 3027, 2932, 1603, 1583, and 1486 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 1.95 (m, 1H), 2.31 (m, 1H), 2.90 (m, 2H), 3.28 (td, 1H, J_1 = 24.9 Hz, J_2 = 4.8 Hz), 4.63 (d, 1H, *J* = 12.3 Hz), 6.81 (t, 1H, *J* = 7.2 Hz), 7.06–7.19 (m, 5H), 7.22–7.29 (m, 2H), 7.31–7.48 (m, 5H), and 8.06–8.07 (m, 1H); ^{13}C-NMR ($CDCl_3$) 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, and 153.6; ms: *m/z* 324(M^+), 280, 247, 196, 146, and 77. Anal. Calcd. for $C_{23}H_{20}N_2$: 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-2*H*-benzo[g]indazole (4b). Yield: 77%; mp: 158°C; IR (KBr) ν = 3055, 2929, 1603, 1610, 1584, 1510, and 1486 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 1.93 (m, 1H), 2.27 (m, 1H), 2.90 (m, 2H), 3.24 (td, 1H, J_1 = 24.9 Hz, J_2 = 4.5 Hz), 3.81 (s, 3H), 4.58 (d, 1H, *J* = 12 Hz), 6.81 (t, 1H, *J* = 7.5 Hz), 6.93 (d, 2H, *J* = 8.7 Hz), 7.07–7.22 (m, 5H), 7.23–7.25 (m, 2H), 7.38 (d, 2H, *J* = 8.4 Hz), and 8.05 (m, 1H); ^{13}C-NMR ($CDCl_3$) 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, and 159.1; ms: *m/z* 354(M^+), 339, 323, 247, 218, 207, 188, 91, 77, and 51. Anal. Calcd. for $C_{24}H_{22}N_2O$: 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). Yield: 86%; mp: 174°C; IR (KBr) ν = 3045, 2938, 1605, 1581, 1504, and 1488 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 1.97 (m, 1H), 2.30 (m, 1H), 2.93 (dd, 2H, J_1 = 10.35 Hz, J_2 = 3.3 Hz), 3.27 (td, 1H, J_1 = 24.9 Hz, J_2 = 5.4 Hz), 3.85 (s, 3H), 3.90 (s, 3H), 4.55 (d, 1H, *J* = 12.3 Hz), 6.83 (t, 1H, *J* = 7.2 Hz), 6.89 (d, 1H, *J* = 8.7 Hz), 6.98–7.01 (m, 2H), 7.09–7.20 (m, 5H), 7.24–7.27 (m, 2H), and 8.05–8.08 (m, 1H); ^{13}C-NMR ($CDCl_3$) 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, and 154.5; ms: *m/z* 384(M^+), 369, 247, 199, 56, and 44. Anal. Calcd. for $C_{25}H_{24}N_2O_2$: 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-2*H*-benzo[g]indazole (4d). Yield: 84%; mp: 182°C; IR (KBr) ν = 3056, 2931, 1609, 1588, and 1491 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 1.96 (m, 1H), 2.30 (m, 1H), 2.94 (m, 2H), 3.28 (td, 1H, J_1 = 24.75, J_2 = 4.8 Hz), 3.85 (s, 6H), 3.86 (s, 3H), 4.51 (d, 1H, *J* = 11.7 Hz), 6.68 (s, 2H), 6.85 (t, 1H, *J* = 7.2 Hz), 7.10–7.28 (m, 7H), and 8.06 (dd, 1H, J_1 = 6 Hz, J_2 = 3.6 Hz); ^{13}C-NMR ($CDCl_3$) 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, and 153.9; ms: *m/z* 414(M^+), 399, 381, and 247. Anal. Calcd. for $C_{26}H_{26}N_2O_3$: C, 75.34; H, 6.32; N, 6.76. Found: C, 75.35; H, 6.33; N, 6.77.

3-(4-Chlorophenyl)-3,3a,4,5-tetrahydro-2-phenyl-2*H*-benzo[g]indazole (4e). Yield: 80%; mp: 146°C; IR (KBr) ν = 3030, 2951, 1604, 1591, and 1485 cm^{-1}; ^{1}H-NMR ($CDCl_3$) 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), and 8.03–8.06 (m, 1H); ^{13}C-NMR ($CDCl_3$) 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, and 153.2; ms: *m/z* 358(M^+), 323, and 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-2*H*-benzo[g]indazole (5a–e). *Method a*: To solution of **4** (0.024 mol) in 15 mL dimethylsulfoxide, iodine (0.0024 mmol) was added. The resulting mixture was heated at 120°C for 3 h. 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** (0.024 mol) 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-2*H*-benzo[g]indazole (5a). mp: 148°C; IR (KBr) ν = 3051, 2928, 1594, 1494, 1436, 1366, 1032, and 969 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.85 (t, 2H, *J* = 6.6 Hz), 2.99 (t, *J* = 6.9 Hz), 7.18–7.35 (m, 13H), and 8.07 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ: 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, and 153.4; ms: *m/z* 322(M^+), 280, 245, 230, 218, 204, 189, 180, 153, and 77. Anal. Calcd. for $C_{23}H_{18}N_2$: C, 85.68; H, 5.63; N, 8.69. Found: C, 85.65; H, 5.63; N, 8.68.

4,5-Dihydro-3-(4-methoxyphenyl)-2-phenyl-2H-benzo[g]indazole (5b). mp: 126°C; IR (KBr) ν = 3043, 2939, 1583, 1479, and 1375 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.82 (t, 2H, *J* = 7.18 Hz), 2.98 (t, 2H, *J* = 7.2 Hz), 3.82 (s, 3H), 6.87 (d, 2H, *J* = 8.4 Hz), 7.12 (d, 2H, *J* = 9 Hz), 7.26–7.34 (m, 8H), and 8.00 (d, 1H, *J* = 6.6 Hz);

^{13}C-NMR ($CDCl_3$) δ: 17.1, 30.9, 56.7, 117.5, 118.3, 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, and 158.9; ms: *m/z* 352 (M^+), 335, 307, 275, 261, 248, 218, 202, 168, 153, 115, and 77. Anal. Calcd. for $C_{24}H_{20}N_2O$: C, 81.79; H, 5.72; N, 7.95. Found: C, 81.77; H, 5.73; N, 7.99.

4,5-Dihydro-3-(3,4-dimethoxyphenyl)-2-phenyl-2*H*-benzo[g] indazole (5c). mp: 118°C; IR (KBr) ν = 3051, 2944, 1601, 1493, and 1377 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.83 (t, 2H, 6.8 Hz), 2.96 (t, 2H, 6.8 Hz), 3.77 (s, 3H), 3.89 (s, 3H), 6.59 (s, 1H), 6.83 (d, 1H, *J* = 8.4 Hz), 6.89 (d, 1H, *J* = 8.4 Hz), 7.25–7.36 (m, 8H), and 8.01 (d, 1H, *J* = 6.9 Hz); ^{13}C-NMR ($CDCl_3$) δ: 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, and 153.2; ms: *m/z* 382(M^+), 367, 352, 335, 321, 305, 278, 218, 204, 191, 168, 153, 115, and 77. Anal. Calcd. for $C_{25}H_{22}N_2O_2$: 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-2*H*-benzo[g] indazole (5d). mp: 153°C; IR (KBr) ν = 3052, 2948, 1596, 1489, and 1376 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.90 (t, 2H, *J* = 6.6 Hz), 2.99 (t, 2H, *J* = 6.3 Hz), 3.67 (s, 6H), 3.87 (s, 3H), 6.38 (s, 2H), 7.26–7.38 (m, 8H), and 8.02 (d, 1H, *J* = 6.6 Hz); ^{13}C-NMR ($CDCl_3$) δ: 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, and 152.4; ms: *m/z* 412(M^+), 397, 381, 368, 351, 335, 307, 248, 199, 145, 77, and 56. Anal. Calcd. for $C_{26}H_{24}N_2O_3$: 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-2*H*-benzo[g]indazole (5e). mp: 135°C; IR (KBr) ν = 3058, 2944, 1595, 1474, 1433, 1363, 1162, 1040, 927, and 838 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.82 (t, 2H, *J* = 7.2 Hz), 2.99 (t, 2H, *J* = 7.5 Hz), 7.12 (d, 2H, *J* = 8.1 Hz), 7.26–7.35 (m, 10H), and 7.01 (d, 1H, *J* = 7.2 Hz); ^{13}C-NMR ($CDCl_3$) δ: 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, and 153.7; ms: *m/z* 356(M^+), 215, 201, 161, 115, 102, 77, 63, and 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-2*H*-benzo[g]indazole (6a–e). To solution of **4** (0.024 mol) in 15 mL dimethylsulfoxide, 1.3 equiv 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-2*H*-benzo[g]indazole (6a). Yield: 88%; mp: 120°C; IR (KBr) ν = 3038, 3012, 2931, 1610, 1584, and 1485 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.79 (t, 2H, *J* = 6.9 Hz), 2.95 (t, 2H, *J* = 6.9 Hz), 7.06 (d, 2H, *J* = 8.4 Hz), 7.17–7.20 (m, 2H), 7.23–7.37 (m, 6H), 7.60 (d, 2H, *J* = 8.7 Hz), and 7.94 (d, 1H, *J* = 7.2 Hz); ^{13}C-NMR ($CDCl_3$) δ: 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, and 153.3; ms: *m/z* 448(M^+), 371, 320, 256, 228, 218, 160, 128, 89, and 44. Anal. Calcd. for $C_{23}H_{17}IN_2$: 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)-2*H*-benzo[g]indazole (6b). Yield: 86%; mp: 130°C; IR (KBr) ν = 3044, 2971, 1621, 1573, and 1495 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.81 (t, 2H, *J* = 7.5 Hz), 2.99 (t, 2H, *J* = 7.5 Hz), 3.85 (s, 3H), 6.92 (d, 2H, *J* = 8.7 Hz), 7.12 (m, 4H), 7.27–7.32 (m, 3H), 7.64 (d, 2H, *J* = 8.1 Hz), and 7.97 (d, 1H, *J* = 6.9 Hz); ^{13}C-NMR ($CDCl_3$) 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, and 160.1; ms: *m/z* 478 (M^+), 461, 433, 371, 350, 349, 292, 275, 217, 175, 153, and 76. Anal. Calcd. for $C_{24}H_{19}IN_2O$: 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)-2*H*-benzo[g]indazole (6c). Yield: 90%; mp: 165°C; IR (KBr) ν = 3065, 2998, 1619, 1580, 1514, 1474, 1239, 1142, 1022, 997, and 825 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.82 (t, 2H, *J* = 6.9 Hz), 3.01 (t, 2H, *J* = 6.6 Hz), 3.71 (s, 3H), 3.92 (s, 3H), 6.64 (s, 1H), 6.80 (d, 1H, *J* = 8.7 Hz), 6.88 (d, 1H, *J* = 8.4 Hz), 7.01 (d, 2H, *J* = 8.7 Hz), 7.12–7.35 (m, 3H), 7.64 (d, 2H, *J* = 8.4 Hz), and 7.97 (d, 1H, *J* = 7.5 Hz); ^{13}C-NMR ($CDCl_3$) 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, and 153.8; ms: *m/z* 508(M^+), 493, 463, 381, 338, 245, 193, 56, and 44. Anal. Calcd. for $C_{25}H_{21}IN_2O_2$: 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)-2*H*-benzo[g]indazole (6d). Yield: 91%; mp: 173°C; IR (KBr) ν = 3055, 2983, 1625, and 1591 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.85 (t, 2H, *J* = 7.5 Hz), 2.99 (t, 2H, *J* = 7.2 Hz), 3.71 (s, 6H), 3.89 (s, 3H), 6.38 (s, 2H), 7.12 (d, 2H, *J* = 9 Hz), 7.26–7.32 (m, 3H), 7.67 (d, 2H, *J* = 8.7 Hz), and 7.96 (d, 1H, *J* = 6.9 Hz); ^{13}C-NMR ($CDCl_3$) 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, and 153.1; ms: *m/z* 538 (M^+), 523, 480, 411, 396, 305, 279, 205, 190, 160, 133, 89, and 45. Anal. Calcd. for $C_{26}H_{23}IN_2O_3$: 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)-2*H*-benzo[g] indazole (6e). Yield: 90%; mp: 160°C; IR (KBr) ν = 3045, 2985, 1609, 1589, and 1482 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.79 (t, 2H, *J* = 6.6 Hz), 2.98 (t, 2H, *J* = 7.2 Hz), 7.07 (d, 2H, *J* = 8.7 Hz), 7.14 (d, 2H, *J* = 8.4 Hz), 7.27–7.30 (m, 3H), 7.36 (d, 2H, *J* = 8.7 Hz), 7.65 (d, 2H, *J* = 8.7 Hz), and 7.95 (d, 1H, *J* = 6.6 Hz); ^{13}C-NMR ($CDCl_3$) 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, and 149.4; ms: *m/z* 482(M^+), 354, 344, 279, 217, 203, 178, 160, 76 (100), and 50. Anal. Calcd. for $C_{23}H_{16}ClIN_2$: 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-2*H*-benzo[g]indazole (7a-e). To a solution of **4** (1.54 mmol) in CCl_4 (100 mL) were added NBS (0.81 g, 4.62 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 crud product was crystallized from methanol.

5-Bromo-2, 3-diphenyl-2*H*-benzo[g]indazole (7a). Yield: 91%; mp: 194°C; IR (KBr) ν = 3062, 1592, 1500, 1452, 1349, 1256, 1187, 1149, 1100, 1033, 920, and 854 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.35–7.49 (m, 10H), 7.65–7.68 (m, 2H), 7.92 (s, 1H), 8.28 (m, 1H), and 8.71 (m, 1H); ^{13}C-NMR ($CDCl_3$) 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, and 145.1; ms: *m/z* 398 (M^+), 318, 298, 214, 159, 145, 77, and 55. Anal. Calcd. for $C_{23}H_{15}BrN_2$: 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-2*H*-benzo[g]indazole (7b). Yield: 89%; mp: 182°C; IR (KBr) ν = 3052, 2954, 1606,

1505, 1460, 1378, 1351, 1291, 1250, 1181, 1108, 1027, 969, 840, and 767 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 3.85 (s, 3H), 6.95 (d, 2H, *J* = 8.7 Hz), 7.28 (d, 2H, *J* = 8.7 Hz), 7.37–7.49 (m, 5H), 7.63–7.69 (m, 2H), 7.90 (s, 1H), 8.27,(m, 1H), and 8.70 (m, 1H); ^{13}C-NMR ($CDCl_3$) 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, and 159.7; ms: *m/z* 428 (M^+), 397, 347, 321, 254, 158, and 44. Anal. Calcd. for $C_{24}H_{17}BrN_2O$: 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-2*H*-benzo[g] indazole (7c). Yield: 88%; mp: 161°C; IR (KBr) ν = 3049, 2932, 1603, 1505, 1466, 1374, 1288, and 1103 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 3.73 (s, 3H), 3.85 (s, 3H), 6.71 (s, 1H), 6.77 (d, 1H, *J* = 8.1 Hz), 6.81 (d, 1H, *J* = 8.1 Hz), 7.22–7.33 (m, 5H), 7.64 (d, 2H, *J* = 7.8 Hz), 7.97 (s, 1H), 8.18–8.21 (m, 1H), and 8.66–8.69 (m, 1H); ^{13}C-NMR ($CDCl_3$) 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, and 154.3; ms: *m/z* 458(M^+), 427, 377, 245, 159, and 44. Anal. Calcd. for $C_{25}H_{19}BrN_2O_2$: 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-2*H*-benzo[g] indazole (7d). Yield: 92%; mp: 174°C; IR (KBr) ν = 3056, 2945, 1614, 1519, 1445, 1379, and 1110 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 3.56 (s, 6H), 3.68 (s, 3H), 6.41 (s, 2H), 7.28–7.31 (m, 5H), 7.61 (d, 2H, *J* = 7.8 Hz), 7.91 (s, 1H), 8.01–8.04 (m, 1H), and 8.52–8.53 (m, 1H); ^{13}C-NMR ($CDCl_3$) 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, and 153.4; ms: *m/z* 488(M^+), 457, 407, 372, 345, 294, 201, 159, and 44. Anal. Calcd. for $C_{26}H_{21}BrN_2O_3$: 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-2*H*-benzo[g]indazole (7e). Yield: 93%; mp: 168°C; IR (KBr) ν = 3057, 1593, 1501, 1457, 1350, 1256, 1182, 1095, 1021, 927, 868, and 837 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.28–7.35 (m, 5H), 7.45 (d, 2H, *J* = 8.7 Hz), 7.55 (d, 2H, *J* = 8.7 Hz), 7.66–7.69 (m, 2H), 7.84 (s, 1H), 8.27–8.30 (m, 1H), and 8.65–8.69 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ: 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, and 144.3; ms: *m/z* 432 (M^+), 397, 353, 316, 289, 241,214, 199, 158, 144, 131, and 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-2*H*-benzo[g]indazole (8a-e). To a solution of **6** (0.54 mmol) in CCl_4 (100 mL) were added NBS (0.19 g, 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 crud product was crystallized from methanol.

5-Bromo-2-(4-iodophenyl)-3-phenyl-2*H*-benzo[g]indazole (8a). Yield: 89%; mp: 180°C; IR (KBr) ν = 3054, 1620, 1585, 1494, 1038, 832, 761, and 695 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.22 (d, 2H, *J* = 8.7 Hz), 7.35–7.38 (m, 2H), 7.44–7.48 (m, 3H), 7.66–7.70 (m, 2H), 7.72 (d, 2H, *J* = 8.7 Hz), 7.88 (s, 1H), 8.28 (m, 1H), and 8.68 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ: 92.9, 113.9, 119.9, 122.8, 123.1, 125.7, 127.6, 127.9, 128.1, 128.8, 129.6, 130.1, 130.2, 132.3, 133.7, 135.0, 139.1, 141.6, and 148.3; ms: *m/z* 524(M^+), 444, 396, 317, 289, 256, 214, 199, 159, 144, 76, and 44. Anal. Calcd. for $C_{23}H_{14}BrIN_2$: 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)-2*H*-benzo[g]indazole (8b). Yield: 92%; mp: 208°C; IR (KBr) ν = 3060, 2935, 1609, 1575, 1492, 1250, 1177, 1029, 966, 831, and 763 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 3.87 (s, 3H), 6.98 (d, 2H, *J* = 9 Hz), 7.22–7.30 (m, 4H), 7.65–7.70 (m, 2H), 7.73 (d, 2H, *J* = 9 Hz), 7.86 (s, 1H), 8.27 (m, 1H), and 8.67 (m, 1H); ^{13}C-NMR ($CDCl_3$) 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, and 44. Anal. Calcd. for $C_{24}H_{16}BrIN_2O$: 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)-2*H*-benzo[g]indazole (8c). Yield: 87%; mp: 170°C; IR (KBr) ν = 3058, 3002, 2959, 2930, 1607, 1583, 1510, 1253, 1238, 1144, 864, 824, and 763 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 3.74 (s, 3H), 3.96 (s, 3H), 6.75 (s, 1H), 6.95–6.99,(m, 2H), 7.25 (d, 2H, *J* = 8.7 Hz), 7.66–7.69 (m, 2H), 7.74 (d, 2H, *J* = 8.4 Hz), 7.89 (s, 1H) 8.28 (m, 1H), and 8.68 (m, 1H); ^{13}C-NMR ($CDCl_3$) 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, and 157.1; ms: *m/z* 584(M^+), 569, 553, 505,456, 397, 326, 287, 201, 179, 158, and 44. Anal. Calcd. for $C_{25}H_{18}BrIN2O_2$: 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)-2*H*-benzo[g]indazole(8d). Yield: 88%; mp: 192°C; IR (KBr) ν = 3043, 2938, 1610, 1590, 1485, 1168, 1041, and 959 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 3.76 (s, 6H), 3.98 (s, 3H), 6.41 (s, 2H), 7.19 (d, 2H, *J* = 9 Hz), 7.61–7.65 (m, 2H), 7.76 (d, 2H, *J* = 9 Hz), 7.83 (s, 1H), 8.19 (m, 1H), and 8.71(m, 1H); ^{13}C-NMR ($CDCl_3$) 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, and 154.7; ms: *m/z* 614(M^+), 599, 583, 486, 533, 498, 449, 315, 301, 298, 204, 155, and 43. Anal. Calcd. for $C_{26}H_{20}BrIN_2O_3$: 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)-2*H*-benzo[g] indazole (8e). Yield: 91%; mp: 210°C; IR (KBr) ν = 3068, 1615, 1595, and 1465 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.13 (d, 2H, *J* = 8.4 Hz), 7.29 (d, 2H, *J* = 7.8 Hz 7.59–7.62 (m, 2H), 7.66 (d, 2H, *J* = 7.8 Hz), 7.69 (d, 2H, *J* = 8.4 Hz), 7.87 (s, 1H), 8.16 (m, 1H), and 8.68 (m, 1H); ^{13}C-NMR ($CDCl_3$) 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, and 144.6; ms: *m/z* 558(M^+), 512, 478, 432, 341, 316, 214, 199, 158, 145, 105, and 76. Anal. Calcd. for $C_{23}H_{13}BrClIN_2$: C, 49.36; H, 2.34; N, 5.01. Found: C, 49.34; H, 2.34; N, 5.03.

Crystallography. Diffraction data were measured with a Bruker SMART Apex II CCD area-detector diffractometer (graphite-monochromated Mo-Kα radiation, γ = 0.71073 Å). The orientation matrix, unit-cell refinement, and data reduction were all handled by the Apex2 software (SAINT integration, SADABS absorption correction [38]). The structure was solved using direct method in the program SHELXS-97 and refined by the full matrix least-squares method on F2 with SHELXL-97 [39]. All the nonhydrogen 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 [40]. Crystal data and refinement are summarized in Table 5. 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

Table 5

Crystal data and structure refinement for **8b**.

Empirical formula	C_{24} H_{16} Br I N_2O
Formula weight	555.20
Temperature (K)	100(2) K
Crystal system, space group	Triclinic, P-1
Unit-cell dimensions	
a (Å)	9.4851(3)
b (Å)	10.5697(3)
c (Å)	11.9829(3)
α (°)	114.723(2)
β (°)	91.544(2)
γ (°)	111.295(2)
Volume (Å^3)	993.76(5)
Z, Density (calculated; g cm^{-3})	2, 1.855
Absorption coefficient (mm^{-1})	3.640
F(000)	540
Crystal size (mm^3)	0.15 × 0.11 × 0.02
θ range for data collection (°)	2.23–25.24
Index ranges	$-11<=h<=11$, $-12<=k<=12$, $-14<=l<=14$
Reflections collected/unique	7616/3578 [*R*(int) = 0.0659]
Completeness	To θ = 25.00: 99.2%
Max. and min. transmission	0.9308 and 0.6112
Data/restraints/parameters	3578/0/263
Goodness-of-fit on F^2	0.958
Final *R* indices [$I > 2\sigma$ (I)]	$R_1 = 0.0560$, $wR_2 = 0.1233$
R indices (all data)	$R_1 = 0.1033$, $wR_2 = 0.1401$
Largest diff. peak and hole (e Å^{-3})	1.107 and −0.737

Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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