Selective Synthesis of Some 4,5-Dihydro-2*H*-benzo[*g*]indazoles and 8,9-Dihydro-2*H*-benzo[*e*]indazoles Via the Vilsmeier-Haack Reaction Under Thermal and Microwave Assisted Conditions

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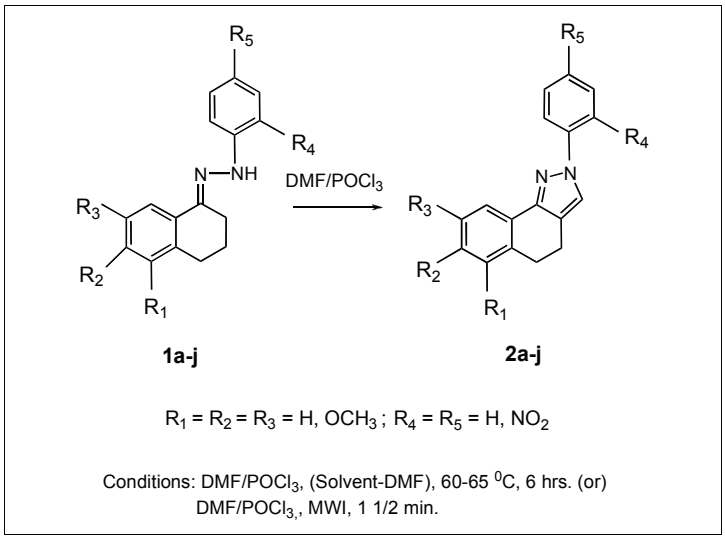

A selective and easy method is described for the synthesis of 4,5-dihydro-2*H*-benzo[*g*]indazoles and 8,9-dihydro-2*H*-benzo[*e*]indazoles by the Vilsmeier-Haack reaction of various tetralone phenylhydrazones under thermal and microwave irradiation conditions.

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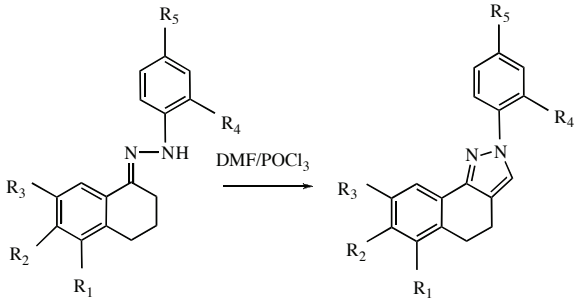
Several indazoles are reliable pharmacophores and proved to possess significant levels of activity as HIV protease inhibitors, serotonin 5-HT1α, 5-HT2, 5-HT3 receptor antagonists, acetyl cholinesterase inhibitors and aldol reductase inhibitors [1]. In particular, examples of differently substituted dihydrobenzo[*g*]indazoles showing antimicrobial, antiallergic and non-estrogenic contraceptive activities have been cited in the literature. More recently also tyrosine kinase inhibitors, dopamine receptor ligands, anti-inflammatory and analgesic compounds have been reported quite extensively in the patent literature [2]. The benzoindazoles have attracted considerable attention in recent years due to the discovery of their potential usage as anticryptosporidial [3], selective cyclooxygenase-2 inhibitor [4], human dopamine D4 receptor [5], antiproliferative [6], and fungal enzyme inhibitor [7]. bis-Benzo[*g*]indazole derivatives were found to possess antiproliferative activity. Many synthetic methods for the synthesis of 4,5-dihydro-2*H*-benzo[*g*]indazoles require several steps with low yield with formation of other isomers. For example, the 4,5-dihydro-2*H*-benzo[*g*]-indazole derivatives were prepared along with 4,5-dihydro-1*H*-benzo[*g*]indazole derivatives in 35% yield from 2,4-diketoester [6] and in 19% yield from dithioketeneacetal [8]. Hence a selective and general procedure for the formation of substituted 4,5-dihydro-2*H*-benzo[*g*]indazoles from easily accessible starting materials is desirable.

Vilsmeier-Haack reaction is primarily concerned with the facile synthesis of aldehydes [9]. The halo-methyleneiminium salts [10] generated under Vilsmeier-Haack reaction are capable of producing iminium species from numerous aromatic compounds [11], alkene derivatives [12], carbonyl compounds [13] and in addition, oxygen and nitrogen nucleophiles [14]. The presence of proton source facilitates cyclisation to produce wide variety of carbocyclic as well as heterocyclic compounds. Earlier reports from our laboratory have described

the synthesis of pyran, quinoline, pyrrole, pyridine, quinazolinone, oxazole, imidazole and pyrazole derivatives [15] using Vilsmeier reagent. The Vilsmeier reagent has been extensively utilized to generate a variety of precursors for the synthesis of condensed heterocycles, and a large number of fluorescent compounds viz, indazole, coumarin and quinoline derivatives for dyeing polyester and polyamide [16]. The Vilsmeier-Haack cyclisation of iminium species provides access to a large number of heterocyclic systems [17]. Hydrazones and semicarbazones cyclise under Vilsmeier –Haack reaction condition to give pyrazole aldehydes. Though a wide variety of hydrazones of aromatic ketones like acetophenones and aliphatic ketones [18,19,20] were studied under Vilsmeier-Haack condition, the cylization potential of hydrazones of cyclic keto compounds remains unexplored which prompted us to carry out the cyclization of various tetralone hydrazones and semicarbazones under Vilsmeier-Haack reaction conditions.

Scheme 1



1a-j **2a-j**

$R_1 = R_2 = R_3 = H, OCH_3$; $R_4 = R_5 = H, NO_2$

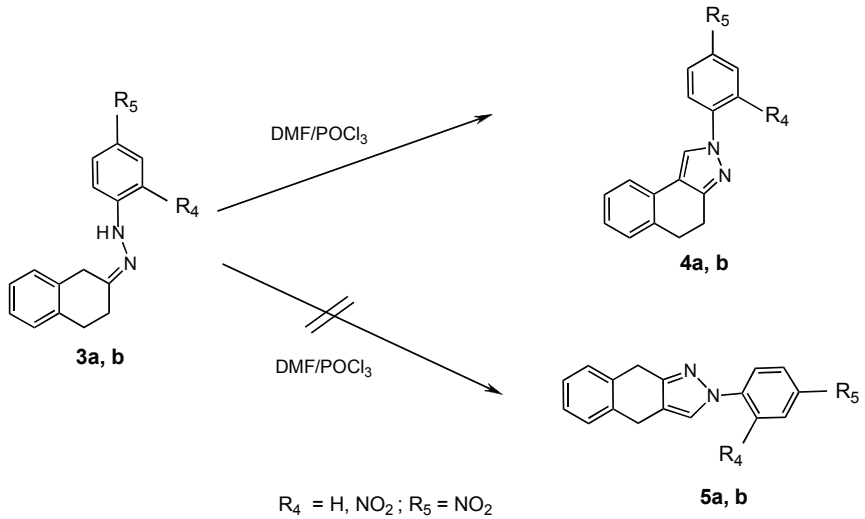
Conditions: DMF/$POCl_3$, (Solvent-DMF), 60-65 0C, 6 hrs. (or) DMF/$POCl_3$,, MWI, 1 1/2 min.

Accordingly the reaction of 1-tetralone phenylhydrazones (**1a-j**) with 6 equivalents of Vilsmeier-Haack reagent yielded 4,5-dihydro-2*H*-benzo[*g*]-indazoles (**2a-j**).

In case of compounds containing active methylene group, (for example hydrazones of β-ketoesters) the cyclisation occurs at active methylene carbon atom under Vilsmeier-Haack reaction condition [20]. Similarly when 2-tetralone phenylhydrazones (**3a,b**) were subjected to Vilsmeier-Haack reaction condition, only 8,9-dihydro-2*H*-benzo[*e*]indazoles (**4a,b**) were obtained and there was no formation of 2-phenyl-4,9-dihydro-2*H*-benzo[*f*]indazole (**5a,b**). Of the two possible attacks of Vilsmeier-Haack reagent on the substrate, only one isomer is obtained.

The reaction of 1-tetralonesemicarbazones (**6a,b**) with Vilsmeier-Haack reagent (6 eq.) yielded 4,5-dihydro-2*H*-benzo[*g*]indazole (**7a,b**) in very low yields along with the formation of β-chloroaldehyde (**8a,b**) [22,23] of the corresponding tetralone. Moreover no cyclised products could be

Scheme 2

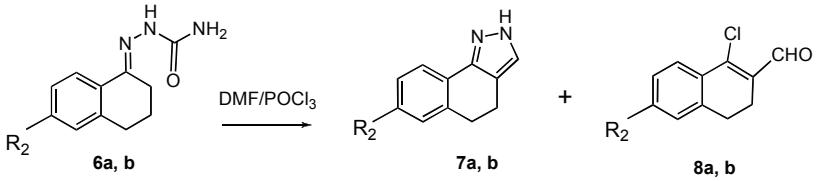


3a, b **4a, b** **5a, b**

R_4 = H, NO_2 ; R_5 = NO_2

Conditions: DMF/$POCl_3$, (Solvent-DMF), 60-65 °C, 6 hrs. (or) DMF/$POCl_3$,, MWI, 1 1/2 min.

Scheme 3



R_2 = H, OCH_3

Conditions: DMF/$POCl_3$, (Solvent-DMF), 60-65 ^{0}C, 6 hrs.

obtained from cyclohexanone semicarbazones due to steric configuration that does not favour cyclisation [21].

The reaction products are summarised in Table 1.

The prepared indazoles were found to exhibit fluorescence. The fluorescence emission spectra of 2-(4-nitrophenyl)-4,5-dihydro-2*H*-benzo[*g*]indazole is given below as representative.

Table 1

Synthesis of various 4,5-dihydro-2*H*-benzo[*g*]indazoles and 8,9-dihydro-2*H*-benzo[*e*]indazoles by the Vilsmeier-Haack reaction under thermal and microwave assisted condition.

Entry	R_1	R_2	R_3	R_4	R_5	Product [a]	Yield [b] %	
							Method A	Method B
1	H	H	H	H	NO_2	**2a**	71	79
2	OCH_3	H	H	H	NO_2	**2b**	72	81
3	H	OCH_3	H	H	NO_2	**2c**	74	83
4	H	H	OCH_3	H	NO_2	**2d**	74	82
5	H	H	H	NO_2	NO_2	**2e**	64	71
6	OCH_3	H	H	NO_2	NO_2	**2f**	71	80
7	H	OCH_3	H	NO_2	NO_2	**2g**	67	77
8	H	H	OCH_3	NO_2	NO_2	**2h**	72	81
9	H	H	H	H	H	**2i**	74	85
10	H	OCH_3	H	H	H	**2j**	77	87
11	H	H	H	H	NO_2	**4a**	70	79
12	H	H	H	NO_2	NO_2	**4b**	67	76
13	H	H	H	-	-	**7a**	15	-
14	H	OCH_3	H	-	-	**7b**	16	-
15	H	H	H	-	-	**8a**	78	-
16	H	OCH_3	H	-	-	**8b**	74	-

[a] All the products were characterized by IR, NMR and Mass spectrum; [b] The yield is based on isolation by column chromatography for products obtained by conventional heating (Method A) and microwave irradiation condition (Method B).

A selective, convenient and easy method for the preparation of various benzo[*g*]indazoles and benzo-[*e*]indazoles by microwave irradiation under solvent free condition is described and a comparison is made between the conventional method and microwave assisted solvent free method. The solvent free method affords easy methodology as well as reduced reaction time along with only slightly higher yield (11-15%).

The reaction of phenyl hydrazones of 2-tetralones afforded benzo[*e*]indazole as the exclusive single product. This may be due to the stabilization of the benzylic position by the benzene ring. These compounds not only possess proven biological activity but also the dyeing property. This encouraged us to synthesize them in this new methodology.

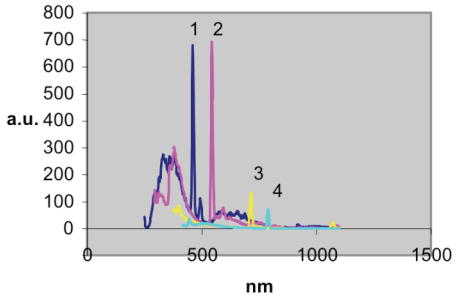


Figure 1. Fluorescence emission spectra of 2-(4-nitrophenyl)-4,5-dihydro-2*H*-benzo[*g*]indazole at 1) 230 nm, 2) 273 nm, 3) 358 nm and 4) 396 nm.

The spectral properties of the prepared indazoles were studied qualitatively using UV-Visible absorption as well

as fluorescent emission techniques. The results were summarized in Table 2.

Table 2

UV-Visible absorption and fluorescence emission spectral data of various 4,5-dihydro-2*H*-benzo[*g*]indazoles and 8,9-dihydro-2*H*-benzo[*e*]indazoles.

Entry	UV-Visible absorption λ max	fluorescence emission λ max
2a	345	421
2b	343	418
2c	345	426
2d	360	423
2e	345	445
2f	345	372
2g	380	492
2h	372	457
2i	302	346
2j	302	355
4a	344	423
4b	345	447

EXPERIMENTAL

Melting points were determined in capillary tubes and are uncorrected. Analytical TLC was performed on pre-coated plastic sheets of silica gel G/UV-254 of 0.2 mm thickness (Machery-Nagel, Germany). IR spectra were taken as KBr pellets on a Perkin Elmer RXI FT-IR spectrometer. ^{1}H NMR (500 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ solutions with TMS as internal standard. Column chromatography was performed on silica gel (60 – 120 mesh, SRL, India). The *p*-nitrophenylhydrazones, 2,4-dinitrophenyl-hydrazones, phenylhydrazones and semicarbazones of various tetralones (**1a-j, 3a,b and 5a,b**) were prepared by standard procedure. The Vilsmeier-Haack reagent is prepared by dropwise addition of one equivalent of $POCl_3$ to one equivalent of DMF in ice cold condition with stirring and the resulting semi-solid is refrigerated. The microwave reactions were carried out in a domestic microwave oven. A BPL microwave cooking system, Model BMO-7000T, manufactured by BPL-SANYO Utilities and Appliances Ltd., Bangalore, India was used in the present studies. The overall dimensions of the domestic oven are 525(W) x 419 (D) x 281 (H) mm with a chamber of 350 (W) x 370 (D) x 208 (H) mm. The microwave frequency is 50 Hz and the oven capacity is 26 liters. The absorbance and fluorescence spectra were measured on a CARY 50 CONC. UV-Visible and fluorescence spectrophotometer using methanol as solvent.

General Procedure for the Synthesis of 2-(4-Nitrophenyl)-4,5-dihydro-2*H*-benzo[*g*]indazole (**2a**) Under Conventional Conditions.

Method A.

The 3,4-dihydronaphthalen-1(2*H*)-one (4-nitrophenyl)hydrazone (1.4 mmol) **1a** was dissolved in DMF (10 mL) in a RB flask fitted with calcium chloride guard tube through a pressure equalizer and cooled to 0° C. $POCl_3$ (6 equivalents, 11.5 mmol) was added dropwise with stirring over a period of 20–30 minutes. The reaction mixture was stirred for 1 hr. at room temperature and then stirred at 60-65 °C for 6 hr. After completion of the reaction (monitored by TLC), the reaction mixture was cooled and neutralized by pouring into crushed ice. The precipitate was collected by filtration and purified by column chromatography using silica gel (60–120 mesh), eluting with petroleum ether:ethyl acetate (75:25), to afford 2-(4-nitrophenyl)-4,5-dihydro-2*H*-benzo[*g*]indazole **2a** as a yellowish solid. The same procedure was followed to prepare other compounds in the series.

Synthesis of 2-(4-Nitrophenyl)-4,5-dihydro-2*H*-benzo[*g*]indazole (**2a**) Under Solvent Free Microwave Irradiation.

Method B.

The 3,4-dihydronaphthalen-1(2*H*)-one (4-nitrophenyl)hydrazone (1.4 mmol) **1a** is taken in a flat bottomed flask fitted with a calcium chloride guard tube. The Vilsmeier reagent (6 equivalents) is added and then irradiated with microwaves for 1 ½ min. with 50% power with a pulse rate of 5 sec. After completion of the reaction (monitored by TLC), the reaction mixture was poured into crushed ice and the purification procedure of Method A was followed to afford **2a** as a yellowish solid. The same procedure was adhered to prepare other compounds in the series.

2-(4-Nitrophenyl)-4,5-dihydro-2*H*-benzo[*g*]indazole (**2a**).

This compound was obtained as yellow colour solid, mp 178 °C; IR (KBr): 3126, 2927, 2839, 2440, 1596, 1510, 1373, 1111, 1049, 945, 746, 685, 555 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ **=** 2.86 (t, 2H, *J*= 7.45 Hz), 2.98 (t, 2H, *J*= 7.45Hz), 7.25-7.34 (m, 3H), 7.79 (s, 1H), 7.87 (d, 2H, *J*= 9.2 Hz), 7.97-7.98 (m, 1H), 8.30 (d, 2H, *J*= 9.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.32, 29.33, 117.87, 120.92, 123.06, 123.53, 125.50, 127.19, 128.64, 128.68, 128.70, 128.71, 137.39, 144.80, 151.69; MS: *m/z* 291 (M^+).

Anal. Calcd. for $C_{17}H_{13}N_3O_2$: C, 70.09; H, 4.50; N, 14.42. Found: C, 70.10; H, 4.49; N, 14.41.

6-Methoxy-2-(4-nitrophenyl)-4,5-dihydro-2*H*-benzo[*g*]indazole (**2b**).

This compound was obtained as yellow colour solid, mp 186 °C; IR (KBr): 3431, 3125, 2934, 2838, 2440, 1566, 1511, 1448, 1370, 1178, 1103, 1029, 948, 748, 683, 545 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.83 (t, 2H, *J*= 7.45 Hz), 3.00 (t, 2H, *J*= 7.45 Hz), 3.87 (s, 1H), 6.88-6.87 (d, 1H, *J*= 7.45 Hz), 7.29 (t, 1H, *J*= 7.45 Hz), 7.62-7.63 (d, 1H, *J*=7.45 Hz), 7.79 (s, 1H), 7.87-7.88 (d, 2H, *J*= 7.45 Hz), 8.30-8.32 (d, 2H, *J*= 7.45Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.69, 21.15, 55.64, 110.61, 115.52, 117.87, 120.87, 123.43, 125.52, 125.75, 127.89, 129.67, 144.76, 144.80, 151.73, 156.95; MS: *m/z* 321 (M^+).

Anal. Calcd. for $C_{18}H_{15}N_3O_3$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.30; H, 4.72; N, 13.09.

7-Methoxy-2-(4-nitrophenyl)-4,5-dihydro-2*H*-benzo[*g*]indazole (**2c**).

This compound was obtained as yellow colour solid, mp 206 °C; IR (KBr): 3432, 3134, 2930, 2830, 1571, 1506, 1461, 1370, 1178, 1111, 1040, 940, 746, 674, 604, 500 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.84 (t, 2H, *J*= 7.45, Hz), 2.95 (t, 2H, *J*= 7.45 Hz), 3.84 (s, 3H), 6.81 (d, 1H, *J*= 2.3 Hz), 6.86 (dd, 1H, *J*= 8.6 Hz), 7.77 (s, 1H), 7.85 (d, 2H, *J*= 8.6 Hz), 7.89 (d, 1H, *J*= 8.6 Hz), 8.29 (d, 2H, *J*= 8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ =

19.40, 29.70, 55.42, 112.60, 114.15, 117.66, 120.31, 121.59, 123.40, 124.48, 125.53, 139.28, 144.58, 144.84, 151.74, 160.09; MS: *m/z* 321 (M^+).

Anal. Calcd. For $C_{18}H_{15}N_3O_3$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.27; H, 4.72; N, 13.07.

8-Methoxy-2-(4-nitrophenyl)-4,5-dihydro-2*H*-benzo[*g*]indazole (**2d**).

This compound was obtained as yellow colour solid, mp 179 °C; IR (KBr): 3429, 3126, 2938, 2836, 2434, 1568, 1511, 1440, 1372, 1178, 1108, 1038, 945, 745, 686, 602 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.83 (t, 2H, *J*= 8 Hz), 2.91 (t, 2H, *J*= 8 Hz), 3.88 (s, 1H), 6.84 (dd, 1H, *J*= 8 Hz), 7.16 (d, 1H, *J*= 8 Hz), 7.51 (d, 1H, *J*= *8* Hz), 7.79 (s, 1H), 7.88 (d, 2H, *J*= 8 Hz), 8.30 (d, 2H, *J*= 8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.53, 28.48, 55.63, 107.20, 115.47, 117.91, 121.10, 123.62, 125.52, 129.53, 129.63, 129.66, 144.76, 144.80, 151.78, 158.87; MS: *m/z* 321 (M^+).

Anal. Calcd. for $C_{18}H_{15}N_3O_3$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.29; H, 4.70; N, 13.09.

2-(2,4-Dinitrophenyl)-4,5-dihydro-2*H*-benzo[*g*]indazole (**2e**).

This compound was obtained as yellow colour solid, mp 176 °C; IR (KBr): 3430, 2931, 1604, 1526, 1469, 1339, 1079, 949, 830, 740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.86 (t, 2H, *J*= 7.45 Hz), 2.98 (t, 2H, *J*= 7.45 Hz), 7.23-7.31 (m, 3H,), 7.54 (s, 1H), 7.84-7.85 (m, 1H), 7.86 (d, 1H, *J*=9.15 Hz), 8.46 (dd, 1H, *J*= 9.15 Hz), 8.63 (d, 1H, *J*= 2.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.28, 29.08, 121.33, 121.80, 123.47, 124.58, 125.56, 127.28, 127.41, 128.00, 128.62, 129.20, 137.46, 137.50, 142.25, 144.51, 152.98; MS: *m/z* 336 (M^+).

Anal. Calcd. for $C_{17}H_{12}N_4O_4$: C, 60.71; H, 3.60; N, 16.66. Found: C, 60.72; H, 3.61; N, 16.65.

2-(2,4-Dinitrophenyl)-6-methoxy-4,5-dihydro-2*H*-benzo[*g*]-indazole (**2f**).

This compound was obtained as yellow colour solid, mp 160 °C; IR (KBr): 3432, 2925, 2852, 2363, 1604, 1533, 1465, 1340, 1080, 948, 835, 735, 670 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.83 (t, 2H, *J*= 7.45 Hz), 2.98 (t, 2H, *J*= 7.45 Hz), 3.90 (s, 3H), 6.87 (d, 1H, *J*=7.45 Hz), 7.25 (t, 1H, *J*=7.45 Hz), 7.49 (d, 1H, *J*=7.45 Hz), 7.53 (s, 1H), 7.85 (d, 1H, *J*= 7.45 Hz), 8.45 (dd, 1H, *J*= 8.6 Hz), 8.63 (d, 1H, *J*= 2.25 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.63, 20.98, 55.65, 110.99, 115.86, 121.31, 121.76, 124.51, 125.43, 125.90, 127.38, 127.58, 128.95, 137.48, 142.20, 144.44, 152.99, 156.92; MS: *m/z* 366 (M^+).

Anal. Calcd. for $C_{18}H_{14}N_4O_5$: C, 59.02; H, 3.85; N, 15.29. Found: C, 59.00; H, 3.86; N, 15.30.

2-(2,4-Dinitrophenyl)-7-methoxy-4,5-dihydro-2*H*-benzo[*g*]-indazole (**2g**).

This compound was obtained as yellow colour solid, mp 116 °C; IR (KBr): 3405, 2927, 2846, 2365, 1598, 1530, 1465, 1337, 1079, 938, 827, 735, 674 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.84 (t, 2H, *J*= 7.45 Hz), 2.95 (t, 2H, *J*= 7.45 Hz), 3.83 (s, 3H), 6.79 (d, 1H, *J*= 2.3 Hz), 6.83 (dd, 1H, *J*= 8.6 Hz), 7.51 (s, 1H), 7.77 (d, 1H, *J*=8.6 Hz), 7.86 (d, 1H, *J*=8.6 Hz), 8.44 (dd, 1H, *J*= 8.6 Hz), 8.62 (d, 1H, *J*= 2.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.34, 29.44, 55.42, 112.73, 114.06, 121.13, 121.35, 123.97, 124.31, 124.98, 125.36, 127.37, 137.50, 139.36, 141.99, 144.22, 152.99, 160.44; MS: *m/z* 366 (M^+).

Anal. Calcd. for $C_{18}H_{14}N_4O_5$: C, 59.02; H, 3.85; N, 15.29. Found: C, 59.04; H, 3.86; N, 15.28.

2-(2,4-Dinitrophenyl)-8-methoxy-4,5-dihydro-2H-benzo[g]-indazole (**2h**).

This compound was obtained as yellow colour solid, mp 134 °C; IR (KBr): 3368, 2931, 2856, 2370, 1603, 1533, 1462, 1338, 1075, 945, 832, 739, 671 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.83 (t, 2H, *J*= 8.05 Hz), 2.91 (t, 2H, *J*= 8.05 Hz), 3.85 (s, 3H), 6.84 (dd, 1H, *J*= 8.6 Hz), 7.16 (d, 1H, *J*= 8.6 Hz), 7.38 (d, 1H, *J*= 2.85 Hz), 7.5 (s, 1H), 7.89 (d, 1H, *J*= 8.6 Hz), 8.47 (dd, 1H, *J*= 8.6 Hz), 8.65 (d, 1H, *J*= 2.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.48, 28.26, 55.58, 107.57, 115.87, 121.34, 121.97, 124.90, 125.73, 127.44, 128.84, 129.64, 129.75, 137.57, 142.27, 144.58, 153.05, 158.85; MS: *m/z* 366 (M^+).

Anal. Calcd. for $C_{18}H_{14}N_4O_5$: C, 59.02; H, 3.85; N, 15.29. Found: C, 59.01; H, 3.84; N, 15.30.

2-Phenyl-4,5-dihydro-2*H*-benzo[*g*]indazole (**2i**).

This compound was obtained as yellow colour solid, mp 94 °C; IR (KBr): 3111, 3051, 2927, 2831, 1594, 1500, 1468, 1374, 1199, 1049, 954, 745, 684 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.85 (t, 2H, *J*= 6.9 Hz), 2.98 (t, 2H, *J*= 6.9 Hz), 7.25-7.31 (m, 4H), 7.46 (t, 2H, *J*= 7.45 Hz), 7.70 (s, 1H), 7.73 (d, 2H, *J*= 7.45 Hz), 7.99 (d, 1H, *J*= 7.45 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.41, 29.65, 118.92, 122.70, 123.55, 125.96, 127.02, 127.86, 128.47, 129.48, 129.64, 137.01, 140.59, 149.93; MS: *m/z* 246 (M^+).

Anal. Calcd. for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.89; H, 5.74; N, 11.37.

8-Methoxy-2-phenyl-4,5-dihydro-2*H*-benzo[*g*]indazole (**2j**).

This compound was obtained as yellow colour solid, mp 113 °C; IR (KBr): 3430, 3125, 3000, 2934, 2833, 1594, 1508, 1368, 1276, 1122, 1036, 941, 741, 681 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.85 (t, 2H, *J*=6.85 Hz), 2.98 (t, 2H, *J*= 6.85 Hz), 3.84 (s, 3H), 6.80 (d, 1H, *J*=2.3 Hz), 6.84 (dd, 1H, *J*= 8.55), 7.23 (t, 1H, *J*= 8.55 Hz), 7.43 (t, 2H, *J*= 8.55 Hz), 7.68 (s, 1H), 7.72 (d, 2H, *J*= 8.55 Hz), 7.91 (d, 1H, *J*= 8.55 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.45, 30.01, 55.38, 112.24, 114.12, 118.18, 118.80, 122.57, 123.47, 124.01, 125.77, 129.46, 138.83, 140.59, 149.92, 159.43; MS: *m/z* 276 (M^+).

Anal. Calcd. for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14. Found: C, 78.25; H, 5.83; N, 10.15.

2-(4-Nitrophenyl)-8,9-dihydro-2*H*-benzo[*e*]indazole (**4a**).

This compound was obtained as yellow colour solid, mp 182 °C; IR (KBr): 3125, 2924, 2837, 2438, 1594, 1508, 1467, 1371, 1108, 1047, 943, 744, 683, 554 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.99 (t, 2H, *J*= 7.45 Hz), 3.06 (t, 2H, *J*= 7.45 Hz), 7.18-7.28 (m, 3H), 7.45-7.47 (m, 1H), 7.86 (d, 2H, *J*= 9.15 Hz), 7.16 (s, 1H), 8.32 (d, 2H, *J*= 9.15 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.01, 29.51, 117.90, 120.81, 121.54, 123.73, 125.58, 127.20, 127.26, 128.74, 128.87, 135.21, 144.53, 144.92, 154.36; MS: *m/z* 291 (M^+).

Anal. Calcd. for $C_{17}H_{13}N_3O_2$: C, 70.09; H, 4.50; N, 14.42. Found: C, 70.07; H, 4.51; N, 14.43.

2-(2,4-Dinitrophenyl)-8,9-dihydro-2*H*-benzo[*e*]indazole (**4b**).

This compound was obtained as yellow colour solid, mp 192 °C; IR (KBr): 3431, 2932, 1605, 1528, 1471, 1341, 1081, 951, 831, 742 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.96 (t, 2H, *J*=

6.3 Hz), 3.05 (t, 2H, *J*= 6.3 Hz), 7.19-7.27 (m, 3H), 7.43-7.45 (m, 1H), 7.86 (d, 1H, *J*= 9.15 Hz), 7.90 (s, 1H), 8.48 (dd, 1H, *J*= 9.15 Hz), 8.66 (d, 1H, *J*= 9.15 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.93, 29.31, 121.38, 122.42, 122.94, 124.07, 124.90, 127.24, 127.52, 127.66, 128.16, 128.91, 135.34, 137.34, 142.37, 144.73, 155.70; MS: *m/z* 336 (M^+).

Anal. Calcd. for $C_{17}H_{12}N_4O_4$: C, 60.71; H, 3.60; N, 16.66. Found: C, 60.73; H, 3.59; N, 16.67.

4,5-Dihydro-2*H*-benzo[*g*]indazole (**7a**).

This compound was obtained as yellow colour solid, mp 78 °C; IR (KBr): 3353, 3156, 2934, 2323, 1681, 1469, 1433, 1316, 1085, 953, 770, 720 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.78 (2H, *J* = 6.85 Hz), 2.95 (2H, *J* = 6.85 Hz), 7.18-7.25 (m, 3H), 7.39 (s, 1H), 7.77 (d, 1H, *J* = 7.45 Hz), 8.76 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.29, 29.88, 116.16, 122.11, 126.94, 127.67, 128.17, 128.56, 129.03, 136.92, 146.05; MS: *m/z* 170 (M^+).

Anal. Calcd. for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N,16.46. Found: C, 77.60; H, 5.93; N, 16.45.

7-Methoxy-4,5-dihydro-2*H*-benzo[*g*]indazole (**7b**).

This compound was obtained as Viscous liquid; IR (KBr): 3345, 3155, 2936, 2335, 1614, 1487, 1279, 1215, 1034, 957, 856, 814 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.74 (t, 2H, *J* = 6.9 Hz), 2.85 (t, 2H, *J* = 6.9 Hz), 3.73 (s, 3H), 6.75 (dd, 1H, *J* = 8.6 Hz), 7.13 (d, 1H, *J* = 8.6 Hz), 7.34 (d, 1H, *J* = 2.3 Hz), 7.37, (s, 1H), 8.94, (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.51, 29.01, 55.38, 106.87, 113.92, 116.35, 127.89, 129.09, 129.44, 129.99, 146.48, 158.66; MS: *m/z* 200 (M^+).

Anal. Calcd. for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 71.97; H, 6.05; N, 13.98.

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