Microwave-Assisted Cadogan Reaction for the Synthesis of 2-Aryl-2*H*-indazoles, 2-Aryl-1*H*-benzimidazoles, 2-Carbonylindoles, Carbazole, and Phenazine

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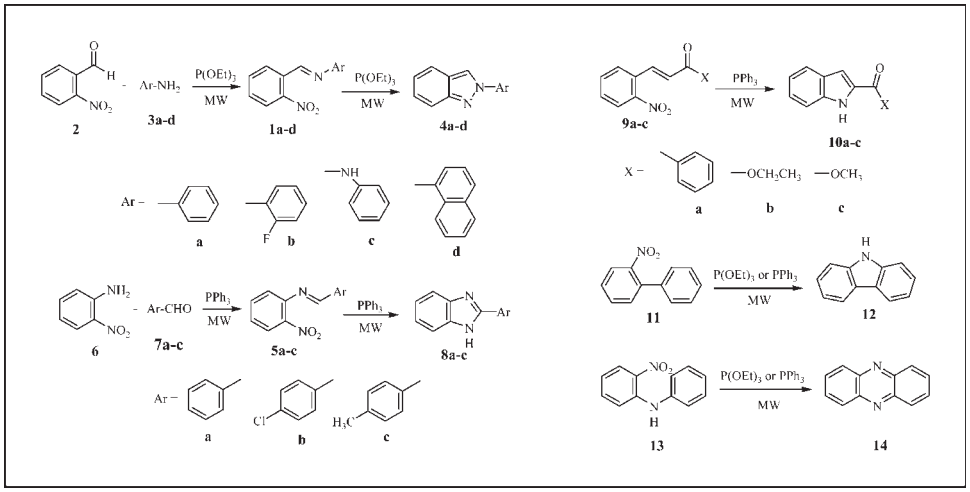

The Cadogan reaction, a widely accepted route for the synthesis of nitrogen containing heterocycles, is modified by using microwave radiation as the source of heat instead of the conventional heating by reflux in a nitrogen atmosphere for several hours. Appropriate starting materials were mixed with triethyl phosphite or triphenylphosphine and irradiated with microwaves for several minutes at a specific power to give the desired products. The indazoles were prepared by irradiating *N*-(2-nitrobenzylidene) anilines with triethyl phosphite at 200 W for 12–14 min to give 85–92% product yields. Irradiation of the mixture of *N*-benzylidene-2-nitroanilines and triphenylphosphine at 200 W for 3–5 min yielded 93–96% of the benzimidazoles. The carbonylindoles were obtained in 61–68% yields by irradiating 2-nitrochalcone or alkyl 2-nitrocinnamates and triphenylphosphine with microwaves at 80–200 W for 8–11 min. The mixture of 2-nitrobiphenyl and triphenylphosphine yielded 96% of carbazole when irradiated with microwaves at 200 W for 2 min while 75% of phenazine was obtained by irradiating the mixture of 2-nitrodiphenylamine and triphenylphosphine with microwaves at 200 W for 3.5 min. These results show that microwave-assisted Cadogan reactions gave better product yields at shorter reaction times.

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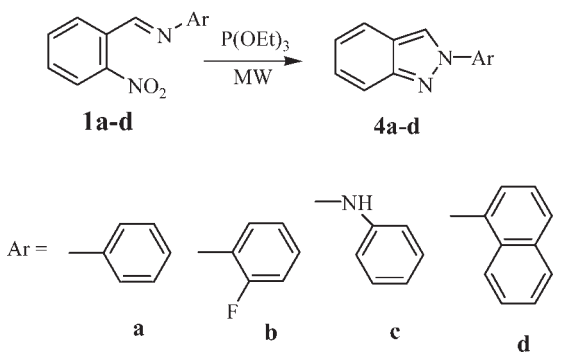
INTRODUCTION

The search for better methods for the syntheses of *N*-containing heterocyclic compounds has never ended as evidenced by the increasing number of articles devoted to this topic. This has led some researchers to look into the possibility of improving the reaction by heating the reaction mixture with microwave radiation instead of the usual conventional heating procedure. The microwave ovens have been with us for some time now but it was not until 1986 when researchers started to utilize the microwave oven for chemical syntheses [1]. Since then, many researchers have been using the technique for organic syntheses, thus contributing to the enormous volume of literatures we now see in print. Microwave-assisted heating under controlled conditions is a valuable technology for chemical syntheses as it can increase the rate of reaction, improve the product yield, and reduce the formation of side products [2].

Several methods for the syntheses of indazoles, indoles and benzimidazoles have been modified by carrying out the reactions under microwave irradiation [3].

Scheme 1



Dubey and Moorthy did a comparative study on conventional and microwave assisted synthesis of benzimidazoles and their derivatives and concluded that the microwave assisted reactions have reduced the reaction times by 96–98% and increased the yields by about 10 to 50% [3(d)]. Yu *et al*. and Navarrete-Vazquez *et al*. have developed a simple and rapid synthesis of substituted benzimidazoles under solvent-free condition using readily available reagents and the microwave oven [3(l,m)]. Sridar as well as Abramovitch and Bulman have reported that rate enhancement in the Fischer indole synthesis was observed when assisted by microwave radiations, that the reaction goes to completion in a short time furnishing good yields [3(n,o)]. Furthermore, Varma described the microwave-enhanced solvent-free synthetic approach to a variety of heterocyclic compounds and observed that the method was simple, easy to manipulate, uses minimal amounts of solvents, and give good product yields [3(p)]. Thus, the prospect of using microwave radiation for organic synthesis seems to be limitless, offering routes of shorter reaction times, minimal side products, and better product yields. It is this idea that led our laboratory to venture into microwave-assisted organic synthesis.

The reduction or deoxygenation of aromatic nitro-compounds by triethyl phosphite and related reagents is referred to as the Cadogan reaction [4]. The reaction is carried out at high temperature under nitrogen atmosphere for several hours. This reaction has been widely investigated as a synthetic route for *N*-containing heterocycles [5] and since the discovery of the reaction in 1962 [4], the reduction of aromatic nitro-compounds by triethyl phosphite and related reagents has been exploited as a route to a wide variety of nitrogen

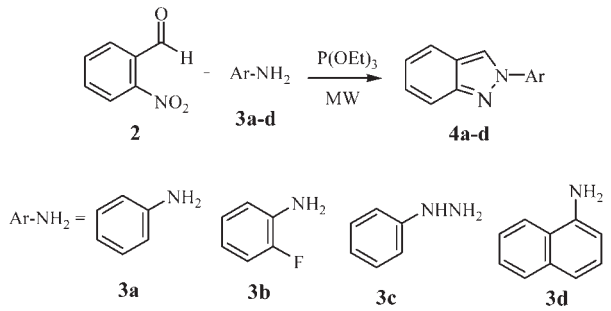
Table 1

Microwave-assisted Cadogan reaction for the synthesis of 2-aryl-2*H*-indazoles.

Entry	Starting material[a,b]	$P(OEt)_3$ (mmol)	Power (W)	Time (minutes)	Power (W)	Time (minutes)	Product	Yield[c] (%)
1	**1a**	4.0	600	4	–	–	**4a**	33
2	**1a**	4.0, 4.0[d]	600	4, 4	–	–	**4a**	67
3	**1a**	4.0	200	14	–	–	**4a**	77
4	**1a**	8.0	200	14	–	–	**4a**	76
5	**1a**	4.0, 4.0[e]	200	14, 14	–	–	**4a**	86
6	**1a**	4.0, 4.0, 4.0[f]	200	14, 14, 14	–	–	**4a**	89
7	**1b**	4.0	200	13	–	–	**4b**	92
8	**1c**	4.0	200	12	–	–	**4c**	85
9	**1d**	4.0	200	14	–	–	**4d**	89
10[g]	**2** + **3a**	4.0	200	9	–	–	**4a**	17
11[g]	**2** + **3b**	4.0	200	10	–	–	**4b**	16
12[g]	**2** + **3c**	4.0	200	12	–	–	**4c**	47
13[g]	**2** + **3d**	4.0	200	12	–	–	**4d**	32
14[h]	**2** + **3a**	4.0	80	2	200	8	**4a**	45
15[h]	**2** + **3b**	4.0	80	2	200	12	**4b**	38
16[h]	**2** + **3c**	4.0	80	1	200	12	**4c**	63
17[h]	**2** + **3d**	4.0	80	2	200	11	**4d**	55

[a] Starting material: 1.0 mmol.
[b] Reaction vessel: test tube.
[c] Isolated yield.
[d] The starting material was added with 4.0 mmol $P(OEt)_3$ and irradiated for 4 min followed by the addition of another 4 mmol $P(OEt)_3$ and irradiated for 4 min more.
[e] The starting material was added with 4.0 mmol $P(OEt)_3$ and irradiated for 14 min followed by the addition of another 4 mmol $P(OEt)_3$ and irradiated for 14 min more.
[f] Same as [e], after which another 4 mmol of $P(OEt)_3$ was added and the mixture irradiated for 14 min more.
[g] One-pot-one-step reaction.
[h] One-pot-two-steps reaction.

Scheme 2



containing heterocyclic compounds, including carbazoles [4,6], indoles [4,7], indazoles [6], and other related compounds [5(b),6,8].

Because of the versatility of Cadogan reaction, a number of researchers have tried to modify the method to shorten the reaction time and improve the yield by using microwave radiations as the source of heat and were successful [9].

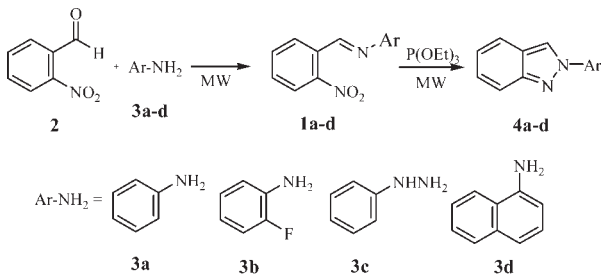
In this article, we report the microwave-assisted Cadogan reaction for the synthesis of indazoles, benzimidazoles, indoles, carbazole and phenazine.

RESULTS AND DISCUSSION

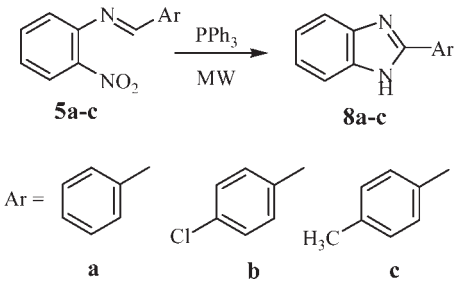
The starting materials used were either synthesized according to literature or purchased from the manufacturer and used as received. The Cadogan reaction was done by irradiating the starting materials with microwaves from a domestic microwave oven. For the synthesis of indazoles, the imines **1a–d** were mixed with triethyl phosphite and irradiated with microwaves to give the corresponding indazoles **4a–d** (Scheme 1). The results are tabulated in Table 1. Initially, 1.0 mmol of *N*-(2-nitrobenzylidene)aniline **1a** was added with 4.0 mmol triethyl phosphite in a Pyrex test tube and irradiated for 4 min at 600 W. The reaction afforded 2-phenyl-2*H*-indazole **4a** in 33% yield (Table 1, Entry 1). The procedure was repeated but this time after 4 min of irradiation, another 4.0 mmol of triethyl phosphite was added and the mixture irradiated for 4 min more. This resulted to an increase in the yield (67%) of 2-phenyl-2*H*-indazole **4a** (Table 1, Entry 2). However, the reaction mixture showed signs of decomposition, so the reaction was further investigated by using lower power rating. A mixture of 1.0 mmol of *N*-(2-nitrobenzylidene)aniline **1a** and 4.0 mmol of triethyl phosphite was irradiated for 14 min at 200 W. The reaction afforded 2-phenyl-2*H*-indazole **4a** in 77% yield (Table 1, Entry 3). Increasing the amount of triethyl phosphite to 8.0 mmol and irradiating the mixture for 14 minutes at 200 W did not give any significant change in the yield (76%, Table 1, Entry 4). The procedure was repeated using 4.0 mmol of triethyl phosphite. After irradiation for 14 min, the mixture was added with another 4.0 mmol of triethyl phosphite and irradiated for another 14 min at 200 W. The reaction afforded 2-phenyl-2*H*-indazole **4a** in 86% yield (Table 1, Entry 5). A third addition of 4.0 mmol of triethyl phosphite and 14 min more of irradiation gave only a slight increase in the yield of 2-phenyl-2*H*-indazole **4a** (89%, Table 1, Entry 6). These results show that irradiation of the mixture of *N*-(2-nitrobenzylidene)aniline **1a** and triethyl phosphite at 200 W gave better results than irradiation of the mixture at 600 W, and a second addition of the triethyl phosphite can increase the yield further. This method gave a better yield of 2-phenyl-2*H*-indazole **4a** (89%) compared to that reported by Song and Yee in the palladium-catalyzed intramolecular amination of *N*-phenyl-*N*-(*o*-bromobenzyl)hydrazine which yielded only 58% of 2-phenyl-2*H*-indazole **4a** after 15 h [10]. On the other hand, Varughese *et al*. reported a 60–65% yields of 2-phenyl-2*H*-indazole **4a** by the microwave-assisted Cadogan reaction of 2-nitrobenzaldehyde and aniline [9(b)] while the classical Cadogan method yielded 60% of 2-phenyl-2*H*-indazole **4a** after 6 h [6,11].

For the other three imines, **1b-d**, the reaction was carried out at 200W and various reaction times. When 1.0 mmol of *N*-(2-nitrobenzylidene)-2-fluoroaniline **1b** and 4.0 mmol triethyl phosphite were mixed and irradiated for 13 min at 200 W, 92% of 2-(2-fluorophenyl)-2*H*-indazole **4b** was obtained (Table 1, Entry 7). Irradiation of 1-(2-nitrobenzylidene)-2-phenylhydrazine **1c** at 200 W for 12 min gave 85% of 2-phenylamino-2*H*-indazole **4c** (Table 1, Entry 8). Dyablo *et al*. obtained 16% of 2-phenylamino-2*H*-indazole **4c** by mixing the corresponding amine with cupric acetate, phenylboric acid and triethylamine and stirring the mixture at 20°C for 17 h [12]. Irradiation of *N*-(2-nitrobenzylidene)-1-naphthylamine **1d** at 200 W for 14 min gave 89% of 2-(1-naphthyl)-2*H*-indazole **4d** (Table 1, Entry 9). The classical Cadogan reaction produced 51% of 2-α-naphthylamine after 6 h [6]. Sequential addition of triethyl phosphite

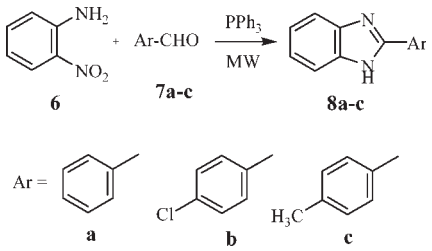
Scheme 3



Scheme 4



Scheme 5



was no longer done because yields of the products were already good.

In the interest of saving time, a one-pot-one-step and one-pot-two-steps reaction procedures for the synthesis of indazoles were developed. For the one-pot-one-step procedure, 2-nitrobenzaldehyde **2** and aryl amines **3a-d** were mixed together in a test tube and added with triethyl phosphite. This mixture was then irradiated at 200 W for several minutes (Scheme 2). The results in Table 1 show that the procedure gave a fair yield of 2-phenylamino-2*H*-indazole **4c** when the mixture was irradiated for 12 min at 200 W (47%, Table 1, Entry 12). For the one-pot-two-steps procedure, 2-nitrobenzaldehyde **2** and aryl amines **3a–d** were mixed in a test tube and irradiated at 80 W for 1–2 min. After this, triethyl phosphite was added and the mixture irradiated again at 200 W for several minutes (Scheme 3). The results show that this method gave higher yields compared to the one-pot-one-step procedure (Table 1, Entries 14–17). However, the synthesis of indazoles from the starting imines is a better method as it gave better yield. These imply that the formation of the imine is an important step in the synthesis of indazoles.

For the synthesis of benzimidazoles, the imines **5a–c** were added with triethyl phosphite and irradiated with microwaves for several minutes at a specific power. However, the reactions gave poor product yields. Triethyl phosphite was replaced with triphenylphosphine as this reagent can also deoxygenate aromatic nitro-compounds and is easily handled, inexpensive and a stable solid (Scheme 4) [6,13]. One millimole of *N*-benzylidene-2-nitroaniline **5a** was mixed with 4.0 mmol of triphenylphosphine and irradiated with microwaves for 5 min at 200 W. The reaction gave 96% of 2-phenyl-1*H*-benzimidazole **8a** (Table 2, Entry 1). 2-(4-Chlorophenyl)-1*H*-benzimidazole **8b** and 2-(4-methylphenyl)-1*H*-benzimidazole **8c** were also synthesized from the corresponding imines, *N*-(4-chlorobenzylidene)-2-nitroaniline **5b** and *N*-(4-methylbenzylidene)-2-nitroaniline **5c**, respectively, by irradiating the mixture with microwaves for 3 min at 200 W. The reactions gave 94% of 2-(4-chlorophenyl)-1*H*-benzimidazole **8b** and 93% of 2-(4-methylphenyl)-1*H*-benzimidazole **8c** (Table 2, Entries 2, 3). The group of Sharghi reported the synthesis of benzimidazoles by the reaction of phenylenediamine and benzaldehyde in the presence of phorphyrinatoiron(III) complex as catalyst. They were able to synthesize 2-phenyl-1*H*-benzimidazole **8a** at 97% by carrying out the reaction for 30 min, 2-(4-chlorophenyl)-1*H*-benzimidazole **8b** at 94% by carrying out the reaction for 55 min and 2-(4-methylphenyl)-1*H*-benzimidazole **8c** at 95% by carrying out the reaction for 55 min [14]. The results of the two methods are comparable but the microwave-assisted Cadogan reaction does not require a metal-complex catalyst and was complete in 3 to 5 min only. Other researchers also reported the synthesis of 2-

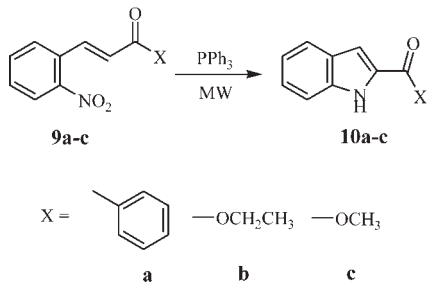
Table 2

Microwave-assisted Cadogan reaction for the synthesis of 2-aryl-1*H*-benzimidazoles.

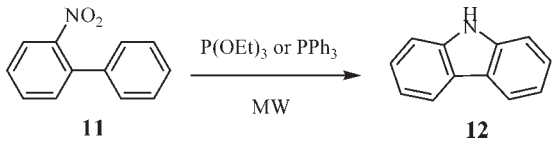
Entry	Starting material[a,b]	PPh_3 (mmol)	Power (W)	Time (minutes)	Product	Yield[c] (%)
1	**5a**	4.0	200	5	**8a**	96
2	**5b**	4.0	200	3	**8b**	94
3	**5c**	4.0	200	3	**8c**	93
4[d]	**6** + **7a**	4.0	200	4	**8a**	82
5[d]	**6** + **7b**	4.0	200	2.5	**8b**	78
6[d]	**6** + **7c**	4.0	200	4	**8c**	81

[a] Starting material: 1.0 mmol.
[b] Reaction vessel: test tube.
[c] Isolated yield.
[d] One-pot-one-step reaction.

Scheme 6



Scheme 7



phenylbenzimidazole by other methods but the yields were relatively low and reaction times longer [15].

The one-pot-one-step synthesis of the benzimidazoles (Scheme 5) gave relatively lower yields compared to the synthesis from the corresponding imines (Table 2, Entries 4, 5, 6). However, the one-pot-one-step synthesis is a simple and convenient procedure.

The carbonylindoles were synthesized using 2-nitrochalcone **9a** and alkyl 2-nitrocinnamates **9b-c**. The reaction with triethyl phosphite gave low product yields so triphenylphosphine was used instead (Scheme 6). The reaction of 2-nitrochalcone **9a** with triphenylphosphine at 200 W and 8 min gave 68% of 2-benzoylindole **10a** (Table 3, Entry 1). Mahboobi *et al*. obtained 73% 2-benzoylindole **10a** from a reaction which required heating the reagents under reflux for 12 h [16]. On the other hand, the reaction with ethyl 2-nitrocinnamate **9b** yielded 64% of 2-ethoxycarbonylindole **10b** while reaction with methyl 2-nitrocinnamate **9c** yielded 61% of 2-methoxycarbonylindole **10c**, with the reactions being carried out at 80 W for 10 min and 11 min, respectively (Table 3, Entries 2, 3). At higher power, decomposition products are formed. Csomos *et al*. obtained 83% of 2-ethoxycarbonylindole **10b** by reacting indole-2-carboxylic acid, thionyl chloride and dry ethanol, and carrying out the reaction at different temperatures, requiring a total of 4.5 h for the reaction to complete [17]. Cadogan *et al*. reacted *o*-nitrocinnamic acid with triethyl phosphite for 24 h to give 7.5% of 2-ethoxycarbonylindole **10b** [6]. Sechi *et al*., on the other hand, heated azidocinnamates in xylene under reflux for 15 min to yield 67% of 2-methoxycarbonylindole **10c** [18].

Deoxygenation of 2-nitrobiphenyl **11** to give carbazole **12** was done with triethyl phosphite and triphenylphosphine (Scheme 7). The results show that 64% of carbazole **12** was obtained when 2-nitrobiphenyl **11** and triethyl phosphite were irradiated with microwaves for 7.5 min at 600 W while 96% of carbazole **12** was obtained when triphenylphosphine was used instead and irradiating the mixture for 2 min at 200 W (Table 4, Entries 2, 3). With the classical Cadogan reaction, 82.5% of carbazole **12** was obtained by refluxing 2-nitrobiphenyl **11** and triethyl phosphite, under nitrogen atmosphere, for 9 hours, and 43% of carbazole **12** was obtained when triphenylphosphine was used and the mixture placed in a sealed tube and heated at 130°C for 9 h [6]. On the other hand, Freeman *et al*. obtained 91% of carbazole **12** by refluxing 2-nitrobiphenyl **11** in triphenylphosphine for 21 h [13(a)]. When 2-nitrodiphenylamine **13** was mixed with triethyl phosphite and irradiated with microwaves for 5 min at 600 W, 43% of phenazine **14** was obtained (Table 4, Entry 4) (Scheme 8). When triphenylphosphine was used and the mixture irradiated at 200 W for 3.5 min, 75% of phenazine **14** was obtained (Table 4, Entry 5).

The results in this article indicate that the use of microwave radiation greatly enhances the yield of the products and reduces the reaction time from hours to minutes. When decomposition is observed, triphenylphosphine is a better alternative because the reaction can be carried out at lower power and still gives good yields. The procedure can be used to synthesize a variety of *N*-containing heterocyclic compounds once the appropriate starting materials have been prepared.

Table 3

Microwave-assisted Cadogan reaction for the synthesis of 2-carbonylindoles from chalcone and alkyl 2-nitrocinnamates.

Entry	Starting material[a]	PPh_3 (mmol)	Power (W)	Time (minutes)	Product	Yield[b] (%)
1[c]	**9a**	4.0	200	8	**10a**	68
2[d]	**9b**	3.0	80	10	**10b**	64
3[d]	**9c**	3.0	80	11	**10c**	61

[a] Starting material: 1.0 mmol.
[b] Isolated yield.
[c] reaction vessel: test tube.
[d] reaction vessel: 50-mL round bottom flask.

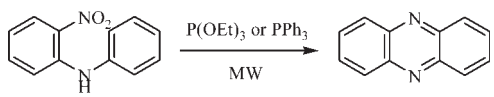
Table 4

Microwave-assisted Cadogan reaction for the synthesis of carbazole and phenazine.

Entry	Starting material	$(POEt)_3$ (mmol)	PPh_3 (mmol)	Power (W)	Time (minutes)	Product	Yield[a] (%)
1[b]	**11**[c]	4.0	–	600	15	**12**	63
2[d]	**11**[e]	3.0	–	600	7.5	**12**	64
3[d]	**11**[c]	–	3.0	200	2	**12**	96
4[d]	**13**[e]	2.0	–	600	5	**14**	43
5[d]	**13**[c]	–	3.0	200	3.5	**14**	75

[a] Isolated yield.
[b] Reaction vessel: 50-mL Erlenmeyer flask.
[c] Starting material: 1.0 mmol.
[d] Reaction vessel: test tube.
[e] Starting material: 0.5 mmol.

Scheme 8



13 **14**

EXPERIMENTAL

The microwave oven used for the reactions was Model YD-17 (W), Yoshii Electric Co., Ltd. The reaction vessel was either a Pyrex test tube (15 mm i.d. × 19 mm o.d. × 129 mm h.) placed in a 50-mL Erlenmeyer flask for support, a 50-mL round bottom flask placed in a beaker for support, or a 50-mL Erlenmeyer flask. The melting points are uncorrected. Column chromatography was performed on silica gel (Wakogel C-200). Unless otherwise stated, anhydrous sodium sulfate was used as the drying agent. The IR spectra were measured on a Hitachi Model 270-30 IR spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were measured at 500 MHz and 125 MHz, respectively, on a Varian Unity plus-500W NMR spectrometer, using tetramethylsilane as the internal standard. The starting materials were synthesized according to literature while those which were available commercially were used as received.

***N*-(2-nitrobenzylidene)aniline (1a).** Compounds **1a–d** were prepared according to the procedure in literature [9(b)]. *o*-Nitrobenzaldehyde (3.022 g, 20 mmol) and aniline (2.235 g, 24 mmol) were placed into a 100 mL round bottom flask. The mixture was heated in a water bath at 70°C for 15 min with continuous stirring. The resulting product was separated from the mixture and recrystallized from ethanol to give yellow plates of *N*-(2-nitrobenzylidene)aniline **1a** (4.203 g, 93%), mp 63–64°C (ref. [9(b)] mp 64–65°C); IR (KBr): 1518 cm^{-1} and 1346 cm^{-1} (NO_2); ^{1}H NMR ($CDCl_3$): δ 7.26–7.31 (m, 3H, 3 Ar-H), 7.43 (dd, J = 7.5 Hz and 7.5 Hz, 2H, 2 Ar-H), 7.63 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.75 (dd, J = 7.5Hz and 7.5Hz, 1H, Ar-H), 8.08 (d, J = 7.5Hz, 1H, Ar-H), 8.32 (d, J = 7.5Hz, 1H, Ar-H), 8.95 (s, 1H, N=CH); ^{13}C NMR ($CDCl_3$): δ 121.2 (d), 124.5 (d), 126.9 (d), 129.2 (d), 129.7 (s), 131.1 (d), 131.2 (d), 133.5 (d), 149.3 (s), 151.0 (s), 155.8 (d).

***N*-(2-nitrobenzylidene)-2-fluoroaniline (1b).** *o*-Nitrobenzaldehyde (3.022 g, 20 mmol) and 2-fluoroaniline (2.667 g, 24 mmol) were placed into a 100-mL round bottom flask. The mixture was heated in a water bath at 70°C for 15 min with continuous stirring. The resulting product was separated from the mixture and recrystallized from ethanol to give yellow needles of *N*-(2-nitrobenzylidene)-2-fluoroaniline **1b** (4.099 g, 84%), mp 76–78°C (ref. [19] mp 72–73°C); IR (KBr): 1520 cm^{-1} and 1348 cm^{-1} (NO_2); ^{1}H NMR ($CDCl_3$): δ 7.15–7.26 (m, 4H, 4 Ar-H), 7.65 (dd, J = 8.0 Hz and 8.0 Hz, 1H, Ar-H), 7.76 (dd, J = 8.0 Hz and 8.0 Hz, 1H, Ar-H), 8.10 (d, J = 8.0 Hz, 1H, Ar-H), 8.35 (d, J = 8.0 Hz, 1H, Ar-H), 9.02 (s, 1H, N=CH); ^{13}C NMR ($CDCl_3$): δ 116.3 (d), 121.8 (s), 124.5 (d), 124.6 (d), 127.7 (d), 129.9 (d), 130.9 (s), 131.5 (d), 133.7(d), 139.4 (d), 149.2 (s), 155.4 (s), 158.2 (d).

1-(2-nitrobenzylidene)-2-phenylhydrazine (1c) [20]. *o*-Nitrobenzaldehyde (3.022 g, 20 mmol) and phenylhydrazine (2.595 g, 24 mmol) were placed into a 100-mL round bottom flask. The mixture was heated in a water bath at 70°C for 5 min with continuous stirring. The product was separated from the mixture and recrystallized from ethanol to give red crystals of 1-(2-nitrobenzylidene)-2-phenylhydrazine **1c** (4.627 g, 96%), mp 118–119°C (ref. [20] mp 117°C); IR (KBr): 3292 cm^{-1} (NH), 1532 cm^{-1}, and 1334 cm^{-1} (NO_2); ^{1}H NMR ($CDCl_3$): δ 6.93 (t, J = 8.0 Hz, 1H, Ar-H), 7.14 (d, J = 8.0 Hz, 2H, 2 Ar-H), 7.31 (dd, J = 8.0 Hz and 8.0 Hz, 2H, 2 Ar-H), 7.40 (dd, J = 8.0 Hz and 8.0 Hz, 1H, Ar-H), 7.61 (dd, J = 8.0 Hz and 8.0 Hz, 1H, Ar-H), 7.99 (d, J = 8.0 Hz, 1H, Ar-H), 8.06 (br s, 1H, Ph-NH), 8.27 (d, J = 8.0 Hz, 1H, Ar-H), 8.32 (s, 1H, N=CH); ^{13}C NMR ($CDCl_3$): δ 113.1 (d), 121.0 (d), 124.8 (d), 127.7 (s), 128.1 (d), 129.4 (d), 130.4 (d), 131.6 (d), 133.1 (d), 143.8 (s), 146.9 (s).

***N*-(2-nitrobenzylidene)-1-naphthylamine (1d) [21].** *o*-Nitrobenzaldehyde (3.022 g, 20 mmol) and 1-naphthylamine (3.437 g, 24 mmol) were placed into a 100-mL round bottom flask. The mixture was heated in a water bath at 70°C for 15 min with continuous stirring. The product was separated from the mixture and recrystallized from ethanol to give yellow plates of *N*-(2-nitrobenzylidene)-1-naphthylamine **1d** (6.536 g, 95%), mp 110–111°C; IR (KBr): 1514 cm^{-1} and 1336 cm^{-1} (NO_2); ^{1}H NMR ($CDCl_3$): δ 7.17 (d, J = 8.0 Hz, 1H, Ar-H), 7.50 (dd, J = 8.0 Hz and 8.0 Hz, 1H, Ar-H), 7.52–7.55 (m, 2H, 2 Ar-H), 7.66 (dd, J = 8.0 Hz and 8.0 Hz, 1H, Ar-H), 7.81 (d, J = 8.0 Hz, 2H, 2 Ar-H), 7.87–7.88 (m, 1H, Ar-H), 8.10 (d, J = 8.0 Hz, 1H, Ar-H), 8.34-8.36 (m, 1H, Ar-H), 8.50 (d, J = 8.0 Hz, 1H, Ar-H), 9.04 (s, 1H, N=CH); ^{13}C NMR ($CDCl_3$): δ 113.2 (d), 123.6 (s), 124.5 (s), 126.0 (d), 126.0 (d), 126.5 (d), 126.8 (d), 127.7 (d), 128.8 (d), 130.0 (s), 131.1 (d), 131.2 (d), 133.5 (d), 133.9 (d), 148.2 (s), 155.7 (s), 155.8 (d).

***N*-benzylidene-2-nitroaniline (5a).** Imine compounds **5a-c** were prepared according to literature [22]. *o*-Nitroaniline (2.486g, 18 mmol), benzaldehyde (1.592 g, 15 mmol), sulfuric acid (5 drops), and molecular sieves (15 g) were added to benzene (30 mL) in a 100-mL round bottom flask. The mixture was heated under reflux for 8.5 h using Soxhlet extractor packed with molecular sieves. The resulting mixture was extracted with benzene, filtered to remove the molecular sieves, and the solvent evaporated under reduced pressure. The extract was then chromatographed on a silica gel column and eluted with hexane:EtOAc (85:15, 2% triethylamine) to give *N*-benzylidene-2-nitroaniline **5a** (2.787g, 82%). The structure of *N*-benzylidene-2-nitroaniline **5a** was determined by comparison of mp and ^{1}H NMR spectrum with those of literature [22]. Recrystallization from hexane gave yellow crystals, mp 70–71°C (ref. [22] mp 71–72°C); IR (KBr): 1594 cm^{-1} and 1334 cm^{-1} (NO_2); ^{1}H NMR ($CDCl_3$): δ 7.06 (d, J = 7.5 Hz, 1H, Ar-H), 7.30 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.47–7.55 (m, 3H, 3 Ar-H), 7.59 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.91 (d, J = 7.5 Hz, 2H, 2 Ar-H), 7.96 (d, J = 7.5 Hz, 1H, Ar-H), 8.41 (s, 1H, CH=N); ^{13}C NMR ($CDCl_3$): δ 121.0 (d), 124.6 (d), 125.3 (d), 128.8 (d), 129.2 (d), 132.1 (d), 133.8 (d), 135.4 (s), 142.9 (s), 146.8 (s), 161.8 (d).

***N*-(4-chlorobenzylidene)-2-nitroaniline (5b).** *o*-Nitroaniline (2.486 g, 18 mmol), *p*-chlorobenzaldehyde (2.109 g, 15 mmol), sulfuric acid (5 drops), and molecular sieves (10 g) were added to benzene (30 mL) in a 100-mL round bottom flask. The mixture was heated under reflux for 10 h using Soxhlet extractor packed with molecular sieves. The resulting mixture was extracted with benzene, filtered to remove the molecular sieves, and the solvent was evaporated under reduced pressure. The extract was then chromatographed on a silica gel column and eluted with hexane:EtOAc (85:15, 2% triethylamine) to give *N*-(4-chlorobenzylidene)-2-nitroaniline **5b** (2.226 g, 57%). Recrystallization from hexane gave yellow crystals, mp 78–79°C (ref. [23] mp 79–80°C); IR (KBr): 1586 cm^{-1} and 1348 cm^{-1} (NO_2); ^{1}H NMR ($CDCl_3$): δ 7.05 (d, J = 7.5 Hz, 1H, Ar-H), 7.32 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.47 (d, J = 7.5 Hz, 2H, 2 Ar-H), 7.60 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.85 (d, J = 7.5 Hz, 2H, 2 Ar-H), 7.97 (d, J = 7.5 Hz, 1H, Ar-H), 8.37 (s, 1H, CH=N); ^{13}C NMR ($CDCl_3$): δ 120.9 (d), 124.6 (d), 125.5 (d), 129.2 (d), 130.4 (d), 133.9 (d), 133.9 (s), 138.3 (s), 142.9 (s), 146.5 (s), 160.4 (d).

***N*-(4-methylbenzylidene)-2-nitroaniline (5c).** *o*-Nitroaniline (2.486 g, 18 mmol), *p*-methylbenzaldehyde (1.802 g, 15 mmol), sulfuric acid (5 drops), and molecular sieves (7.5 g) were added to benzene (30 mL) in a 100-mL round bottom flask. The mixture was heated under reflux for 9 h using Soxhlet extractor packed with molecular sieves. The resulting mixture was extracted with benzene, filtered to remove the molecular sieves, and the solvent evaporated under reduced pressure. The extract was then chromatographed on a silica gel column and eluted with hexane:EtOAc (85:15, 2% triethylamine) to give *N*-(4-methylbenzylidene)-2-nitroaniline **5c** (1.783 g, 49%). Recrystallization from hexane gave yellow crystals, mp 71–72°C (ref. [23] mp 72–74°C); IR (KBr): 1592 cm^{-1} and 1348 cm^{-1} (NO_2); ^{1}H NMR ($CDCl_3$): δ 2.43 (s, 3H, CH_3), 7.05 (d, J = 7.5 Hz, 1H, Ar-H), 7.27–7.30 (m, 3H, 3 Ar-H), 7.58 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.80 (d, J = 7.5 Hz, 2H, 2 Ar-H), 7.95 (d, J = 7.5 Hz, 1H, Ar-H), 8.36 (s, 1H, CH=N); ^{13}C NMR ($CDCl_3$): δ 21.6 (q), 121.1 (d), 124.5 (d), 125.0 (d), 129.2 (d), 132.1 (d), 133.8 (s), 135.4 (d), 142.9 (s), 142.9 (s), 146.8 (s), 161.8 (d).

Ethyl 2-nitrocinnamate (9b). 2-Nitrobenzaldehyde (1.09 g, 7 mmol), triphenylphosphine (2.56 g, 9.8 mmol), ethyl bromoacetate (1.87 g, 11.2 mmol) and saturated aqueous solution of $NaHCO_3$ (15 mL) were placed in an Erlenmeyer flask and stirred for 1.5 hours at 20°C. The resulting mixture was extracted with benzene, dried over anhydrous sodium sulfate, and the solvent evaporated under reduced pressure. The extract was chromatographed on a silica gel column and eluted with hexane:EtOAc (3:1) to give ethyl 2-nitrocinnamate **9b** (1.09 g, 68%) as colorless liquid. The structure of ethyl2-nitrocinnamate **9b** was determined by comparison of IR, ^{1}H NMR and ^{13}C NMR spectra with those of literature [24]. IR (neat): 1700 cm^{-1} (CO_2), 1510 cm^{-1}, and 1272 cm^{-1} (NO_2); ^{1}H NMR ($CDCl_3$): δ 1.36 (t, J = 7.5 Hz, 3H, CH_3); 4.30 (q, J = 7.5 Hz, 2H, CH_2), 6.37 (d, J = 17 Hz, 1H, C=CH), 7.55 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.64–7.65 (m, 2H, 2 Ar-H), 8.04 (d, J = 7.5 Hz, 1H, Ar-H), 8.11 (d, J = 17 Hz, 1H, Ph-CH=C); ^{13}C NMR ($CDCl_3$): δ 14.7 (q), 60.9 (t), 123.9 (d), 125.5 (d), 129.8 (d), 130.9 (s), 132.8 (d), 134.1 (d), 139.1 (d), 140.4 (s), 165.7 (s).

Methyl 2-nitrocinnamate (9c). 2-Nitrobenzaldehyde (1.09 g, 7 mmol), triphenylphosphine (2.56 g, 9.8 mmol), methyl bromoacetate (1.71 g, 11.2 mmol) and saturated aqueous solution of $NaHCO_3$ (15 mL) were placed in an Erlenmeyer and stirred for 1.5 h at 20°C. The resulting mixture was extracted with benzene, dried over anhydrous sodium sulfate, and the solvent evaporated under reduced pressure. The extract was chromatographed on a silica gel column and eluted with hexane:EtOAc (3:1) to give methyl 2-nitrocinnamate **9c** (0.98 g, 66%). The structure of methyl 2-nitrocinnamate **9c** was determined by comparison of mp, ^{1}H NMR and ^{13}C NMR spectra with those of literature [25]. Recrystallization from hexane gave colorless plates, mp 70–73°C (ref. [25(a)] mp 71–73°C); IR (KBr): 1712 cm^{-1} (CO_2), 1504 cm^{-1}, and 1332 cm^{-1} (NO_2); ^{1}H NMR ($CDCl_3$): δ 3.84 (s, 3H, CH_3), 6.37 (d, J = 17 Hz, 1H, C=CH), 7.56 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.64–7.66 (m, 2H, 2 Ar-H), 8.05 (d, J = 7.5 Hz, 1H, Ar-H), 8.12 (d, J = 17 Hz, 1H, Ph-CH=C); ^{13}C NMR ($CDCl_3$): δ 52.5 (q), 123.5 (d), 125.5 (d), 129.7 (d), 131.0 (s), 132.9 (d), 134.2 (d), 139.4 (d), 140.7 (s), 166.2 (s).

General procedure of the microwave-assisted Cadogan reaction for the synthesis of indazoles, benzimidazoles, indoles, carbazole, and phenazine. Microwave-assisted Cadogan reaction for the synthesis of the various *N*-containing heterocyclic compounds was performed using the appropriate starting materials. Thus, for indazoles, the following starting materials were used: *N*-(2-nitrobenzylidene)aniline, *N*-(2-nitrobenzylidene)-2-fluoroaniline, 1-(2-nitrobenzylidene)-2-phenylhydrazine and *N*-(2-nitrobenzylidene)-1-naphthylamine; for benzimidazoles: *N*-benzylidene-2-nitroaniline, *N*-(4-chlorobenzylidene)-2-nitroaniline and *N*-(4-methylbenzylidene)-2-nitroaniline; for indoles: chalcone, ethyl 2-nitrocinnamate and methyl 2-nitrocinnamate; for carbazole: 2-nitrobiphenyl; and for phenazine: 2-nitrodiphenylamine. One millimole of the starting material was placed in the reaction vessel and added with 4 mmol of triethyl phosphite or triphenylphosphine. The reaction vessel containing the mixture was plugged with quartz

wool and then placed inside the cavity of the microwave oven (Model YD-17 (W), Yoshii Electric Co., Ltd.). The mixture was irradiated at various power ratings and different reaction times to get the best result. The resulting mixture was then extracted with acetone, filtered, and the solvent evaporated under reduced pressure. The extract was chromatographed on a silica gel column and eluted with benzene, benzene:EtOAc, hexane:EtOAc, or hexane:acetone to yield the different products.

In the one-pot-one-step procedure, 2-nitrobenzaldehyde and aryl amine or 2-nitroaniline and aryl aldehyde were mixed with triethyl phosphite or triphenylphosphine in the reaction vessel and irradiated with microwaves at different power ratings and reaction times to get the best results. In the one-pot-two-steps procedure, 2-nitrobenzaldehyde and aryl amine were placed in the reaction vessel and irradiated with microwaves at certain power rating and reaction time, after which, triethyl phosphite was added and the mixture irradiated again. The products were isolated in the same manner as described above.

2-Phenyl-2H-indazole (4a) [6]. Compound **4a** was obtained as white plates from hexane, mp 80–82°C (ref. [26] mp 80–82°C); ^{1}H NMR ($CDCl_3$): δ 7.12 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.32 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.40 (t, J = 7.5 Hz, 1H, Ar-H), 7.53, (dd, J = 7.5 Hz and 7.5 Hz, 2H, 2 Ar-H), 7.71 (d, J = 7.5 Hz, 1H, Ar-H), 7.80 (d, J = 7.5 Hz, 1H, Ar-H), 7.91 (d, J = 7.5 Hz, 2H, 2 Ar-H), 8.41 (s, 1H, N═CH═C); ^{13}C NMR ($CDCl_3$): δ 117.9 (d), 120.4 (d), 120.4 (d), 121.0 (d), 122.1 (d), 122.7 (s), 126.8 (d), 127.9 (d), 129.5 (d), 140.5 (s), 149.8 (s).

2-(2-Fluorophenyl)-2H-indazole (4b) [27]. Compound **4b** was obtained as yellow liquid, IR (neat): 1222 cm^{-1} (Ar-F); ^{1}H NMR ($CDCl_3$): δ 7.12 (dd, J = 8.0 Hz and 8.0 Hz, 1H, Ar-H), 7.28–7.40 (m, 4H, 4 Ar-H), 7.73 (d, J = 8.0 Hz, 1H, Ar-H), 7.79 (d, J = 8.0 Hz, 1H, Ar-H), 8.09 (dd, J = 8.0 Hz and 8.0 Hz, 1H, Ar-H), 8.51 (s, 1H, N═CH═C); ^{13}C NMR ($CDCl_3$): δ 116.9 (d), 117.7 (d), 120.5 (d), 122.4 (d), 122.5 (s), 124.5 (d), 124.6 (d), 125.0 (d), 125.8 (d), 127.1 (d), 129.0 (s), 149.1 (s), 154.1 (s).

2-Phenylamino-2H-indazole (4c). Compound **4c** was obtained as white needles from benzene-hexane, mp 138–139°C (ref. [12] mp 140–142°C); IR (KBr): 3168 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$): δ 6.54 (d, J = 7.5 Hz, 2H, 2 Ar-H), 6.97 (t, J = 7.5 Hz, 1H, Ar-H), 7.15 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.21 (dd, J = 7.5 Hz and 7.5 Hz, 2H, 2 Ar-H), 7.34 (dd. J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.65 (br s, 1H, NH), 7.70 (d, J = 7.5 Hz, 2H, 2 Ar-H), 8.14 (s, 1H, N═CH═); ^{13}C NMR ($CDCl_3$): δ 114.1 (d), 117.6 (d), 120.4 (d), 122.3 (d), 122.5 (d), 124.1 (s), 126.7 (d), 128.3 (d), 129.2 (d), 146.8 (s), 147.3 (s).

2-(1-Naphthyl)-2H-indazole (4d) [6]. Compound **4d** was obtained as yellow liquid, ^{1}H NMR ($CDCl_3$):δ 7.18 (dd, J = 8.0 Hz and 8.0 Hz, 1H, Ar-H), 7.38 (dd, J = 8.0 Hz and 8.0 Hz, 1H, Ar-H), 7.48 (dd, J = 8.0 Hz and 8.0 Hz, 1H, Ar-H), 7.54 (dd, J = 8.0 Hz and 8.0 Hz, 1H, Ar-H), 7.56 (dd, J = 8.0 Hz and 8.0 Hz, 1H, Ar-H), 7.64 (d, J = 8.0 Hz, 1H, Ar-H), 7.74 (d, J = 8.0 Hz, 1H, Ar-H), 7.77 (d, J = 8.0 Hz, 1H, Ar-H), 7.86 (d, J = 8.0 Hz, 1H, Ar-H), 7.94 (d, J = 8.0 Hz, 1H, Ar-H), 7.98 (d, J = 8.0 Hz, 1H, Ar-H), 8.28 (s, 1H, N═CH═); ^{13}C NMR ($CDCl_3$): δ 117.8 (d), 120.2 (d), 121.9 (d), 122.2 (d), 122.9 (d), 123.7 (d), 124.8 (d), 125.3 (s), 126.5 (d), 126.6 (d), 127.4 (d), 127.9 (d), 128.8 (s), 129.5 (d), 134.0 (s), 137.5 (s), 149.5 (s).

2-Phenyl-1H-benzimidazole (8a). The structure of 2-phenyl-1*H*-benzimidazole **8a** was determined by comparison of mp, IR, ^{1}H NMR and ^{13}C NMR spectra with those of literature [14]. Colorless crystals from hexane-EtOAc, mp (hexane: EtOAc) 289–290°C (ref. [14] mp 290–292°C); IR (KBr): 3436 cm^{-1} (NH); ^{1}H NMR ($(CD_3)_2CO$): δ 7.21 (dd, J = 7.5 Hz and 7.5 Hz, 2H, 2 Ar-H), 7.47–7.68 (m, 5H, 5 Ar-H), 8.24 (d, J = 7.5 Hz, 2H, 2 Ar-H), 11.97 (br s, 1H, NH); ^{13}C NMR (CD_3OD): δ 123.9 (d), 123.9 (d), 127.7 (d), 130.1 (d), 130.9 (d), 131.3 (s), 153.3 (s).

2-(4-Chlorophenyl)-1H-benzimidazole (8b). The structure of 2-(4-chlorophenyl)-1*H*-benzimidazole **8b** was determined by comparison of mp, IR and ^{1}H NMR spectra with those of literature [14]. Colorless crystals from acetone, mp 291–292°C (ref. [14] mp 292–293°C); IR (KBr): 3405 cm^{-1} (NH); ^{1}H NMR ($(CD_3)_2CO$): δ 7.22–7.24 (m, 2H, 2 Ar-H), 7.51–7.70 (m, 4H, 4 Ar-H), 8.23 (d, J = 7.5 Hz, 2H, 2 Ar-H), 11.98 (br s, 1H, NH). No data for ^{13}C NMR, not determined due to low solubility.

2-(4-Methylphenyl)-1H-benzimidazole (8c). The structure of 2-(4-methylphenyl)-1*H*-benzimidazole **8c** was determined by comparison of mp, IR and ^{1}H NMR spectra with those of literature [14]. Colorless crystals from acetone, mp (acetone) 270–271°C (ref. [14] mp 270–272°C); IR (KBr): 3476 cm^{-1} (NH); ^{1}H NMR ($(CD_3)_2CO$): δ 2.40 (s, 3H, CH_3), 7.17–7.21 (m, 2H, 2 Ar-H), 7.35 (d, J = 7.5 Hz, 2H, 2 Ar-H), 7.49–7.66 (m, 2H, 2 Ar-H), 8.11 (d, J = 7.5 Hz, 2H. 2 Ar-H), 11.82 (br s, 1H, NH). No data for ^{13}C NMR, not determined due to low solubility.

2-Benzoylindole (10a). The structure of 2-benzoylindole **10a** was determined by comparison of mp, IR and ^{1}H NMR spectra with those of literature [16]. Pale yellow needles from hexane, mp 147–148°C (ref. [16] mp 145–147°C); IR (KBr): 3300 cm^{-1} (NH), 1610 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$): δ 7.17 (s, 1H, indole CH), 7.17 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.38 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.48 (d, J = 7.5 Hz, 1H, Ar-H), 7.54 (dd, J = 7.5 Hz and 7.5 Hz, 2H, 2 Ar-H), 7.62 (t, J = 7.5 Hz, 1H, Ar-H), 7.72 (d, J = 7.5 Hz, 1H, ArH), 8.00 (d, J = 7.5 Hz, 2H, 2 Ar-H), 9.31 (br s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 112.3 (d), 113.0 (d), 120.9 (d), 123.1 (d), 126.5 (d), 127.6 (s), 128.4 (d), 129.3 (d), 132.3 (d), 134.3 (s), 137.7 (s), 138.0 (s), 187.3 (s).

2-Ethoxycarbonylindole (10b). The structure of 2-ethoxycarbonylindole **10b** was determined by comparison of mp, IR, ^{1}H NMR and ^{13}C NMR spectra with those of literature [17]. Colorless needles from hexane, mp 121–123°C (ref. [17] mp 124–125°C); IR (KBr): 3300 cm^{-1} (NH), 1680 cm^{-1} (CO_2); ^{1}H NMR ($CDCl_3$): δ 1.42 (t, J = 7.5 Hz, 3H, CH_3), 4.41 (q, J = 7.5 Hz, 2H, CH_2), 7.15 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.23 (s, 1H, indole CH), 7.32 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.42 (d, J = 7.5 Hz, 1 H, Ar-H), 7.69 (d, J = 7.5 Hz, 1H, Ar-H), 8.91 (br s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 14.4 (q), 61.0 (t), 108.6 (d), 111.9 (d), 120.7 (d), 122.5 (d), 125.3 (d), 127.4 (s), 127.4 (s), 136.9 (s), 162.2 (s).

2-Methoxycarbonylindole (10c). The structure of 2-methoxycarbonylindole **10c** was determined by comparison of mp, IR and ^{1}H NMR spectra with those of literature [18]. Colorless crystal from hexane, mp 144–147°C (ref. [18] mp 145–147°C); IR (KBr): 3308 cm^{-1} (NH), 1680 cm^{-1} (CO_2); ^{1}H

NMR ($CDCl_3$): δ 3.95 (s, 3H, CH_3), 7.16 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.23 (s, 1H, indole CH), 7.33 (dd, J = 7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.42 (d, J = 7.5 Hz, 1H, Ar-H), 7.69 (d, J = 7.5 Hz, 1H, Ar-H), 8.90 (br s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 51.0 (q), 108.8 (d), 111.9 (d), 120.8 (d), 122.6 (d), 125.4 (d), 127.0 (s), 127.4 (s), 137.0 (s), 162.6 (s).

Carbazole (12). The mp, IR, ^{1}H NMR and ^{13}C NMR spectra of the compound were identical with those of commercially available sample. Colorless plates from ethanol, mp 245-250°C (ref. [6] mp 246–248°C); IR (KBr): 3420 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$): δ 7.24 (dd, J = 7.5 Hz and 7.5 Hz, 2H, 2 Ar-H), 7.42 (dd, J = 7.5 Hz and 7.5 Hz, 2H, 2 Ar-H), 7.42 (d, J = 7.5 Hz, 2H, 2 Ar-H), 8.04 (br s, 1H, NH), 8.09 (d, J = 7.5 Hz, 2H, 2 Ar-H); ^{13}C NMR ($CDCl_3$): δ 110.5 (d), 119.4 (d), 120.3 (d), 123.3 (s), 125.8 (d), 139.4 (s).

Phenazine (14). The mp, IR, ^{1}H NMR and ^{13}C NMR spectra of the compound were identical with those of commercially available sample. Pale yellow needles from ethanol, mp 169–171°C; ^{1}H NMR ($CDCl_3$): δ 7.80 (ddd, J = 7.5 Hz, 7.5 Hz and 1.5 Hz, 4H, 4 Ar-H), 8.26 (dd, J = 7.5 Hz and 1.5 Hz, 4H, 4 Ar-H); ^{13}C NMR ($CDCl_3$): δ 129.6 (d), 130.3 (d), 143.3 (s).

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