A Facile Synthesis of 6,12-Disubstituted 5,7-Dihydroindolo[2,3-*b*]carbazoles from the Reaction of 1*H*-Indole and Aldehydes Catalyzed by Molecular Iodine

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Received 24 September 2007

Abstract: The reaction of 1*H*-indole and various aldehydes in the presence of molecular iodine as a catalyst in refluxing acetonitrile affords 6,12-disubstituted 5,7-dihydroindolo[2,3-*b*]carbazoles in good to excellent yields.

Key words: indolo[2,3-*b*]carbazole, indole, aldehyde, molecular iodine, antitumor

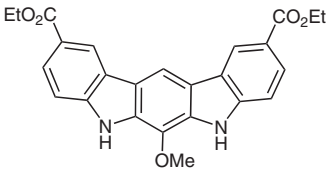


Figure 1 Diethyl 6-methoxy-5,7-dihydroindolo[2,3-*b*]carbazole-2,10-dicarboxylate

Since the first isolation[1] of an indolocarbazole (ICZ) alkaloid in 1977, the importance of this family of natural products has been recognized by chemists, biologists, physicians, and pharmaceutical companies.[2] Compounds with this ring system possess significant biological activity. Therefore, considerable efforts have been made to prepare and synthetically alter these molecules to find useful compounds.[3] As a result of these efforts a number of ICZ analogues have been obtained with diverse biological activity, some of which are currently potential drugs[4] and others are being tested in clinical trials to evaluate their future use against cancer and other diseases.[2,5]

Indolo[2,3-*b*]carbazole is one of the five possible isomeric indolocarbazoles that possesses anti-tumor, anticancer activity (Figure 1).[6] Interestingly, a literature survey reveals only a few reports on the synthesis of indolo[2,3-*b*]carbazoles. Von Dobeneck and Maas reported the first synthesis of indolo[2,3-*b*]carbazole from an acid-catalyzed reaction of 1*H*-indole and formaldehyde,[7] which was later contradicted by other reports.[3c,8] Bearse et al. reported the synthesis of indolo[2,3-*b*]carbazole from catalytic cyclodehydrogenation of *N*,*N*-diphenyl-*m*-phenylenediamine in 1961.[8] The reactions were carried out in the vapor phase at very high temperature (500 °C) and the products were obtained in less than 5% yield. In the same year, as an extension of the work of Von Dobeneck, Venkiteswaran and co-workers reported the synthesis of indolo[2,3-*b*]carbazoles using acetone with indoles in presence of maleic acid or ethanolic hydrochloric acid.[9] However, this reaction has a number of disadvantages, e.g. long reaction times, drastic conditions, a tedious workup procedure, poor yields of the desired products, and, particularly, the lack of generality. Since then only two reports[10] have been made in literature for the synthesis of indolo[2,3-*b*]carbazoles, but these also have a number of drawbacks and limitations in terms of their reaction conditions, yield, and generality.

The use of molecular iodine in organic synthesis has been known for a long time and, in recent years, it has received considerable attention as an inexpensive, nontoxic, readily available, and mild Lewis acid catalyst for various organic reactions under convenient conditions affording the desired products in excellent yields.[11] Moreover, it has high solubility in organic solvents and is easily removed from the reaction mixture.

As a part of our continued[12] work on indoles and the synthesis of diverse heterocyclic compounds of biological significance, we reporting here a very simple, highly efficient, and cost-effective procedure for the synthesis of 6,12-disubstituted 5,7-dihydroindolo[2,3-*b*]carbazoles from the reaction of indoles with aldehydes using molecular iodine (I_2) as the catalyst.

The reaction of indoles and aldehydes is very complicated and depends on the reaction conditions and the catalyst used. In the reaction of indoles and aldehydes it was observed that the use of protic acids like hydrochloric acid or sulfuric acid gave indolo[3,2-*b*]carbazoles via isomerization of an intermediate formed during the reaction.[13] The mechanism proposed for such reaction shows the involvement of acid proton (H^+) in the reaction. On the other hand, the use of a catalyst like phosphoryl chloride gives a mixture of both the indolo[2,3-*b*]- and indolo[3,2-*b*]carbazoles via a different mechanism.[10a] In a recent study it was reported that the reaction of two equivalents of 1*H*-indole and one equivalent of an aldehyde in presence of iodine at room temperature in a very short time affords bis(indol-3-yl)methanes.[11a] On the other hand when the same reaction is allowed to continue for an extended period (14 h) at room temperature the bis(indol-3-yl)methane isomerized to an (indol-2-yl)(indol-3-yl)methane.[14] By observing various mechanisms, we planned to study the reaction using equimolar amounts of 1*H*-indole and an aldehyde under thermal conditions without giving time for

SYNTHESIS 2008, No. 2, pp 0286–0292
Advanced online publication: 18.12.2008
DOI: 10.1055/s-2008-1000849; Art ID: P11307SS

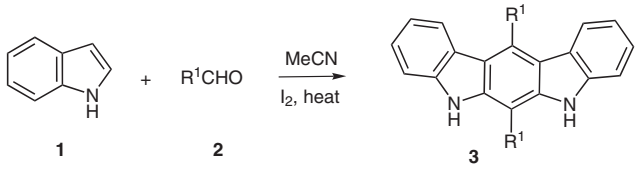
isomerization of the bis(indol-3-yl)methane formed during the reaction and allowing a second aldehyde molecule to become involved in the reaction to afford indolo[2,3-*b*]carbazoles.

In our reaction strategy, utilizing equimolar amounts of 1*H*-indole (**1**) and benzaldehyde (**2a**) in the presence of a catalytic amount of molecular iodine (2 mol%) in refluxing acetonitrile afforded 6,12-diphenyl-5,7-dihydroindolo[2,3-*b*]carbazole (**3a**) in excellent yield. The product was isolated simply by filtration and was then recrystallized from a mixture of *N*,*N*-dimethylformamide and chloroform. The structure of the compound was determined from spectroscopic data and elemental analysis. The generality of the reaction was established by utilizing 1*H*-indole (**1**) with various aromatic or aliphatic aldehydes **2b**–**l** (Scheme 1) The products **3b**–**l** were obtained in good to excellent yields in short reaction times (4–45 min, Table 1).

In the study it was observed that substituents in the aromatic ring of the aldehyde have a tremendous effect on the reaction process. Electron-withdrawing groups in the aromatic ring of the aldehyde retarded the reaction while electron-donating groups accelerated the reaction; we could not prepare the indolo[2,3-*b*]carbazoles of 4-nitrobenzaldehyde. 4-(Benzoyloxy)- (**2j**) and 4-chlorobenzaldehyde (**2d**) gave the desired compounds **3j** and **3d**, respectively, but in comparatively long reaction times. In the case of aliphatic aldehydes, the yields were low. Heterocyclic aldehydes (e.g., 1*H*-pyrrole-2-carbaldehydes, furfuraldehyde) were not found to react with 1*H*-indole (**1**) in the presence of iodine to give the desired indolo[2,3-*b*]carbazoles. The reaction stopped at the bis(indol-3-yl)methane stage. Interestingly, the use of 1*H*-indole-3-carbaldehyde as an aldehyde gave tris(indol-3-yl)methane (TIM) in excellent yield (>98%). The reaction of 1*H*-indole-3-carbaldehyde with 1*H*-indole (**1**) leading to the formation of tris(indol-3-yl)methane has been reported by several authors[15] using some unfamiliar catalysts. Therefore, iodine is potentially a much better alternative for this reaction. Under identical conditions, bulky aldehydes such as 2-chloroquinoline-3-carbaldehyde gave simply the bis(indol-3-yl)methane products.

1-Methyl-1*H*-indole did not react under these reaction conditions even on refluxing for more than one hour. It was also noticed that the yield of the products decreased with increasing load of the catalyst.

A reasonable mechanism for the formation of compounds **3** is outlined in Scheme 2. The reaction occurs via initial formation of bis(indol-3-yl)methane **4**, which reacts with the second aldehyde molecule in the presence of iodine and eliminates a molecule of water to give the intermediate **5**, which is not isolable and is subsequently oxidized to the fully aromatized 6,12-disubstituted 5,7-dihydroindolo[2,3-*b*]carbazole **3**. The molecule of iodine first catalyzed the reaction for the formation of bis(indol-3-yl)methane **4** and then enhances the electrophilic charac-

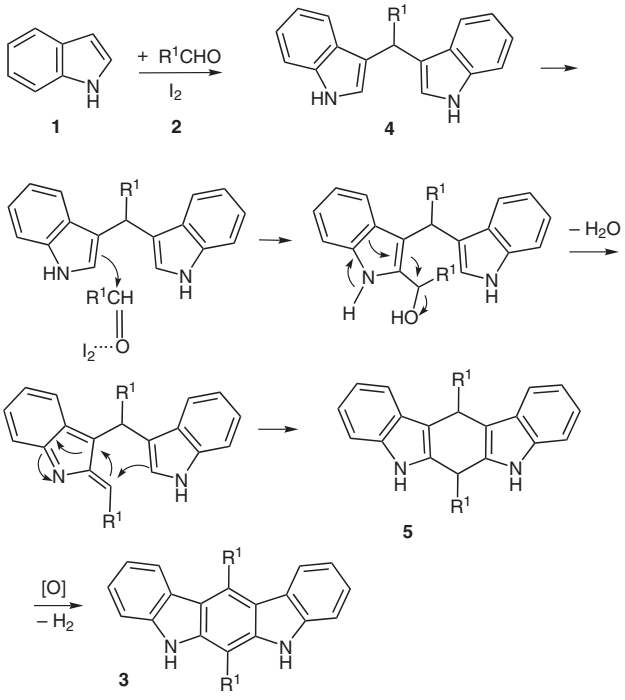


Scheme 1

Table 1 6,12-Disubstituted 5,7-Dihydroindolo[2,3-*b*]carbazoles **3** from 1*H*-Indole (**1**) and Aldehydes **2**

Entry	Product[a]	R^1	Time (min)	Yield[b] (%)	Mp (°C)
1	**3a**	Ph	5	75	395–396
2	**3b**	4-MeC_6H_4	4	80	>400
3	**3c**	4-$MeOC_6H_4$	4	79	377
4	**3d**	4-ClC_6H_4	25	50	355–357
5	**3e**	2-ClC_6H_4	25	46	348–351
6	**3f**	4-HOC_6H4	5	70	398–399
7	**3g**	2-HOC_6H4	7	77	384–386
8	**3h**	3-MeO-4-HOC_6H_3	7	75	381 (dec)
9	**3i**	3,4,5-$(MeO)_3C_6H_2$	4	85	>400
10	**3j**	4-$BzOC_6H_4$	18	72	351 (dec)
11	**3k**	Me	35	25	282–283
12	**3l**	Et	45	20	311–312

[a] All the reactions were performed on a 2 mmol scale using I_2 (2 mol%).
[b] Isolated yield.



Scheme 2

ter of the second aldehyde molecule by a loose coordination with oxygen, to react and give the product.

As proposed in the mechanism the NH proton is required for the formation of the desired product. It is supported by the non-formation of indolo[2,3-*b*]carbazoles from the reaction of 1-methyl-1*H*-indole and arylaldehydes.

The failure to synthesize indolo[2,3-*b*]carbazole by utilizing heterocyclic aldehydes might be due to conjugation of the lone pair on the heteroatom with the exocyclic double bond of the intermediate formed during the process, which makes the exocyclic β-carbon less electrophilic for further attack by the α-position of second indole moiety (Figure 2).

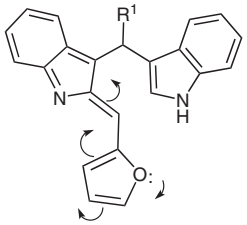
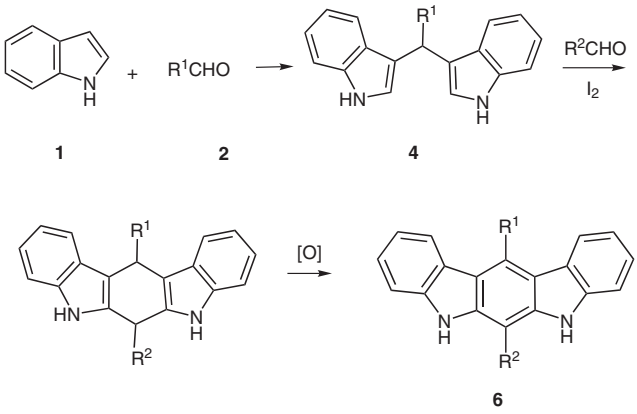


Figure 2

The mechanism and the formation of the product were established by performing the reaction in two steps (Scheme 3). First we synthesized bis(indol-3-yl)methanes **4** from **1** and **2** using iodine as a catalyst by following the existing method.[11a] The bis(indol-3-yl)methanes **4** so obtained were reacted with an equimolar amount of an aldehyde ($R^1 = R^2$) in refluxing acetonitrile, using iodine as the catalyst. The products isolated from the reaction in each case were characterized and found to be identical in all respects with the compounds **3** obtained in the one-pot process (Scheme 1). Then, we synthesized various unsymmetrical 6,12-disubstituted 5,7-dihydroindolo[2,3-*b*]carbazoles **6a**–**h** following the same procedure but using a different aldehyde ($R^1 \neq R^2$) in the second step (Table 2, Scheme 3). The structures of the compounds were confirmed by spectroscopic data and elemental analysis. The appearance of a sharp singlet in the ^{1}H NMR spectra and in the IR for the two symmetrical NH protons of the indolo[2,3-*b*]carbazoles ruled out the formation of indolo[3,2-*b*]carbazoles and further evidenced their structures. It has already been mentioned that under identical reaction conditions bulky aldehydes, e.g. 2-chloroquinoline-3-carbaldehyde, give simply the bis(indol-3-yl)methane products. But when the bis(indol-3-yl)methanes so obtained were reacted with simple aromatic aldehydes, e.g. benzaldehyde, under similar conditions, the desired 6,12-disubstituted 5,7-dihydroindolo[2,3-*b*]carbazole, for example **6g**, were obtained in good yield (Table 2). In the study we found that the use of aromatic aldehydes containing strongly electron-withdrawing groups in the aromatic ring does not result in the formation of the desired product; the reaction stops at the bis(indol-3-yl)methane stage. We failed in our attempt to react such bis(indol-3-yl)methane compounds with another aldehyde possessing an electron-donating substituent in the aromatic ring, to get the unsymmetrical indolo[2,3-*b*]carbazoles. We also failed in the reverse process, i.e. by using an electron-donating group in aromatic ring of the aldehyde for the synthesis of the bis(indol-3-yl)methane and an electron-withdrawing group in the aromatic ring of the aldehyde in the next step.



Scheme 3

In order to explore the synthetic utility of the process further, we attempted the reaction of acetone with 1*H*-indole (**1**) in the presence of iodine. Unfortunately we could not determine the structure of the product, which has a molecular weight of 386.2.

In summary, we have reported a very simple, mild, and highly efficient method for the synthesis of 6,12-disubstituted 5,7-dihydroindolo[2,3-*b*]carbazoles **3a**–**l** from the reaction of 1*H*-indole (**1**) and aldehyde in the presence of molecular iodine as the catalyst. The formation of the product is explained by a suitable mechanism. The mechanism was established by performing the reaction in two steps. By exploring the two-step reaction sequence, a number of unsymmetrical indolo[2,3-*b*]carbazoles **6a**–**h** were synthesized. This very simple, mild, and cost-effective procedure for the synthesis of various symmetrical and unsymmetrical 6,12-disubstituted 5,7-dihydroindolo[2,3-*b*]carbazoles is a valuable addition to the chemistry of indolocarbazoles.

All reagents and solvents were of reagent grade. All chemicals, including solvents, were used without drying. Indole, aldehydes, and I_2 were purchased from Aldrich Chemical Co. and other commercially available reagents were used without further purification. IR spectra were recorded on Perkin Elmer system-2000 FTIR spectrometer; ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-DPX 300 MHz and 75 MHz FT NMR in DMSO-d_6 using TMS as an internal standard. MS spectra were recorded in Bruker Daltonics ESQUIRE 3000 LC ESI ion trap mass spectrometer. Elemental analyses were performed on Perkin Elmer-2400 spectrometer. Analytical TLC was performed using E. Merck aluminum-backed silica gel plates coated with a 0.2 mm thickness of silica gel; petroleum ether = PE. Melting points (uncorrected) were determined on a Buchi B-540 apparatus. All products were characterized by spectroscopic data and elemental analysis.

Table 2 Unsymmetrical 6,12-Disubstituted 5,7-Dihydroindolo[2,3-*b*]carbazoles **6** from Bis(indol-3-yl)methanes **4** and Aldehydes **2**

Product[a]	R^1	R^2	Time (min)	Yield[b] (%)	Mp (°C)
6a	Ph	4-MeC_6H_4	5	75	391–393
6b	4-MeC_6H_4	Ph	4	80	385–386
6c	4-MeC_6H_4	4-$MeOC_6H_4$	4	79	377–379
6d	4-$MeOC_6H_4$	4-MeC_6H_4	5	72	355–356
6e	4-$MeOC_6H_4$	Ph	5	74	348–351
6f	Ph	4-$MeOC_6H_4$	5	69	381–382
6g[c]	2-chloroquinolin-3-yl	Ph	8	55	375–378
6h	Me	Ph	30	40	331–332

[a] All the reactions were performed on a 1-mmol scale using I_2 (2 mol%).
[b] Isolated yield.
[c] The aldehyde has been prepared by a reported method.[12h]

6,12-Diaryl-5,7-dihydroindolo[2,3-*b*]carbazoles 3a–l; General Procedure

In a simple experimental procedure, equimolar amounts of indole **1** (2 mmol) and aldehyde **2** (2 mmol) were added to a round-bottomed flask containing MeCN (5 mL). I_2 (2 mol%) was added to the mixture and it was refluxed for 4–25 min (Table 1). The solid compound obtained was filtered, dried, and recrystallized (DMF–$CHCl_3$). There was no need to remove I_2 with $Na_2S_2O_3$.

6,12-Diphenyl-5,7-dihydroindolo[2,3-*b*]carbazole (3a)

White cotton-like solid; yield: 306 mg (75%); mp 395–396 °C; R_f = 0.82 (7% EtOAc–PE).

IR (KBr): 3395 (NH stretch), 3062 (w), 3019 (w), 1492 (w), 1456 (s), 745 (s), 698 cm^{-1} (m).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.72–6.77 (t, *J* = 7.41 Hz, 2 H), 6.87–6.92 (t, *J* = 7.32 Hz, 2 H), 6.98–7.0 (d, *J* = 7.71 Hz, 4 H), 7.05–7.08 (d, *J* = 7.83 Hz, 2 H), 7.14–7.19 (t, *J* = 7.14 Hz, 6 H), 7.54 (s, 2 H), 9.71 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 140.10, 139.42, 136.22, 134.0, 133.66, 133.37, 132.29, 132.18, 129.60, 129.20, 128.09, 126.5, 123.92, 123.06, 121.65, 120.0, 118.76, 112.42.

MS: *m*/*z* = 409.5 $[M + H]^+$.

Anal. Calcd for $C_{30}H_{20}N_2$; C, 88.21; H, 4.93; N, 6.86. Found: C, 88.26; H, 4.88; N, 6.89.

6,12-Bis(4-methylphenyl)-5,7-dihydroindolo[2,3-*b*]carbazole (3b)

Shiny white solid; yield: 348 mg (80%); mp >400 °C; R_f = 0.81 (7% EtOAc–PE).

IR (KBr): 3395 (NH stretch), 3061 (w), 3019 (w), 2930 (w), 2855 (w), 1492 (w), 1456 (s), 745 (s), 698 cm^{-1} (m).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.29 (s, 3 H), 2.31 (s, 3 H), 6.85–6.90 (t, *J* = 7.61 Hz, 2 H), 6.99–7.04 (t, *J* = 7.25 Hz, 2 H), 7.07–7.10 (d, *J* = 7.68 Hz, 4 H), 7.16–7.18 (d, *J* = 7.79 Hz, 2 H), 7.24–7.26 (d, *J* = 7.56 Hz, 5 H), 7.44 (s, 1 H), 9.93 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 141.28, 139.02, 136.29, 134.07, 133.66, 133.23, 132.22, 132.05, 129.63, 129.06, 128.12, 126.15, 123.91, 123.06, 121.68, 120.0, 118.76, 112.06, 20.91, 20.74.

MS: *m*/*z* = 435.3 $[M - H]^+$.

Anal. Calcd for $C_{32}H_{24}N_2$; C, 88.04; H, 5.54; N, 6.42. Found: C, 88.09; H, 5.55; N, 6.46.

6,12-Bis(4-methoxyphenyl)-5,7-dihydroindolo[2,3-*b*]carbazole (3c)

Whitish powder; yield: 370 mg (79%); mp 377 °C; R_f = 0.80 (7% EtOAc–PE).

IR (KBr): 3392 (NH stretch), 3061 (w), 3031 (w), 2965 (w), 2837 (w), 1492 (w), 1456 (s), 1248 (m), 745 (s), 698 cm^{-1} (m).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.40 (s, 3 H), 3.42 (s, 3 H), 6.75–6.79 (t, *J* = 7.41 Hz, 2 H), 6.91–6.93 (t, *J* = 7.34 Hz, 2 H), 7.1–7.13 (d, *J* = 7.79 Hz, 4 H), 7.14–7.16 (d, *J* = 7.81 Hz, 2 H), 7.21–7.24 (t, *J* = 7.56 Hz, 5 H), 7.81 (s, 1 H), 9.98 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 159.13, 158.68, 141.10, 139.32, 136.55, 136.16, 134.27, 134.18, 133.10, 132.26, 129.33, 128.05, 122.21, 122.0, 121.68, 120.22, 118.78, 109.11, 55.20, 55.06.

MS: *m*/*z* = 469.5 $[M + H]^+$.

Anal. Calcd for $C_{32}H_{24}N_2O_2$; C, 82.03; H, 5.16; N, 5.98. Found: C, 82.07; H, 5.10; N, 5.93.

6,12-Bis(4-chlorophenyl)-5,7-dihydroindolo[2,3-*b*]carbazole (3d)

Light yellowish powder; yield: 238 mg (50%); mp 355–357 °C; R_f = 0.81 (7% EtOAc–PE).

IR (KBr): 3385 (NH stretch), 3051 (w), 3032 (w), 1493 (w), 1456 (s), 741 (s), 701 cm^{-1} (m).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.76–6.80 (t, *J* = 7.47 Hz, 2 H), 6.86–6.89 (t, *J* = 7.43 Hz, 2 H), 7.0–7.03 (d, *J* = 7.75 Hz, 4 H), 7.07–7.10 (d, *J* = 7.76 Hz, 2 H), 7.19–7.22 (t, *J* = 7.55 Hz, 5 H), 7.71–7.73 (d, *J* = 3.07 Hz, 1 H), 9.98 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 139.29, 139.16, 137.20, 136.14, 135.21, 134.09, 133.23, 131.26, 131.01, 130.31, 129.07, 128.26, 128.14, 127.46, 123.44, 121.78, 118.77, 111.98.

MS: *m*/*z* (%) = 477.2 ($[M + H]^+$, 2 ^{35}Cl, 100) 479.2 ($[M + H]^+$, ^{35}Cl, ^{37}Cl, 62), 481.2 ($[M + H]^+$, 2 ^{37}Cl, 10).

Anal. Calcd for $C_{30}H_{18}Cl_2N_2$; C, 75.48; H, 3.80; N, 5.87. Found: C, 75.52; H, 3.86; N, 5.81.

6,12-Bis(2-chlorophenyl)-5,7-dihydroindolo[2,3-*b*]carbazole (3e)
Yellowish fibrous solid; yield: 219.5 mg (46%); mp 348–351 °C; R_f = 0.80 (7% EtOAc–PE).

IR (KBr): 3385 (NH stretch), 3051 (w), 3032 (w), 1493 (w), 1456 (s), 743 (s), 700 cm^{-1} (m).

^1H NMR (300 MHz, DMSO-d_6): δ = 6.78–6.84 (t, *J* = 7.49 Hz, 2 H), 6.86–6.90 (t, *J* = 7.46 Hz, 2 H), 7.0–7.03 (d, *J* = 7.74 Hz, 4 H), 7.07–7.09 (d, *J* = 7.76 Hz, 2 H), 7.21–7.25 (t, *J* = 7.58 Hz, 5 H), 7.71–7.74 (d, *J* = 3.01 Hz, 1 H), 10.0 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 139.31, 138.98, 138.75, 137.54, 135.28, 136.24, 134.19, 134.07, 133.23, 131.22, 131.11, 130.31, 129.07, 128.66, 128.16, 127.43, 125.96, 123.44, 121.70, 119.70, 118.77, 111.99.

MS: *m*/*z* (%) = 477.5 ($[M + H]^+$, 2 ^{35}Cl, 100), 479.5 ($[M + H]^+$, ^{35}Cl, ^{37}Cl, 64), 481.5 ($[M + H]^+$, 2 ^{37}Cl, 10).

Anal. Calcd for $C_{30}H_{18}Cl_2N_2$; C, 75.48; H, 3.80; N, 5.87. Found: C, 75.56; H, 3.86; N, 5.92.

6,12-Bis(4-hydroxyphenyl)-5,7-dihydroindolo[2,3-*b*]carbazole (3f)
White shiny solid; yield: 308 mg (70%); mp 398–399 °C; R_f = 0.56 (7% EtOAc–PE). Due to the lower solubility of **3f**, its ^{13}C NMR spectrum could not be recorded.

IR (KBr): 3397 (br), 3051 (w), 2922 (w), 1491 (w), 1456 (s), 1216 (m), 741 (s), 698 cm^{-1} (m).

^1H NMR (300 MHz, DMSO-d_6): δ = 5.68 (s, 1 H, OH), 5.70 (s, 1 H, OH), 6.72–6.75 (t, *J* = 7.44 Hz, 2 H), 6.84–6.87 (t, *J* = 7.43 Hz, 2 H), 7.02–7.04 (d, *J* = 7.73 Hz, 4 H), 7.07–7.09 (d, *J* = 7.72 Hz, 2 H), 7.21–7.24 (t, *J* = 7.58 Hz, 5 H), 7.71–7.72 (d, *J* = 3.02 Hz, 1 H), 9.98 (s, 2 H, NH).

MS: *m*/*z* = 441.4 $[M + H]^+$.

Anal. Calcd for $C_{30}H_{20}N_2O_2$; C, 81.80; H, 4.58; N, 6.36. Found: C, 81.84; H, 4.49; N, 6.31.

6,12-Bis(2-hydroxyphenyl)-5,7-dihydroindolo[2,3-*b*]carbazole (3g)
Light yellow solid; yield: 339 mg (77%); mp 384–386 °C; R_f = 0.59 (7% EtOAc–PE).

IR (KBr): 3397 (br), 2922 (w), 1592 (s), 1456 (m), 1216 (m), 771 (s), 668 cm^{-1} (w).

^1H NMR (300 MHz, DMSO-d_6): δ = 6.03 (s, 1 H, OH), 6.06 (s, 1 H, OH), 6.72–6.76 (t, *J* = 7.47 Hz, 2 H), 6.84–6.87 (t, *J* = 7.43 Hz, 2 H), 7.02–7.04 (d, *J* = 7.74 Hz, 4 H), 7.08–7.10 (d, *J* = 7.77 Hz, 2 H), 7.21–7.24 (t, *J* = 7.58 Hz, 5 H), 7.72 (s, 1 H), 10.02 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 158.0, 157.86, 141.11, 139.40, 138.36, 137.42, 136.15, 134.09, 133.28, 131.64, 131.10, 130.47, 128.66, 128.20, 127.44, 125.99, 123.44, 121.70, 119.73, 118.77, 111.98.

MS: *m*/*z* = 441.3 $[M + H]^+$.

Anal. Calcd for $C_{30}H_{20}N_2O_2$; C, 81.80; H, 4.58; N, 6.36. Found: C, 81.87; H, 4.52; N, 6.41.

6,12-Bis(4-hydroxy-3-methoxyphenyl)-5,7-dihydroindolo[2,3-*b*]carbazole (3h)
Bright yellow crystals; yield: 375 mg (75%); mp 381 °C (dec); R_f = 0.78 (7% EtOAc–PE).

IR (KBr): 3395 (br), 3061 (w), 3031 (w), 2965 (w), 1492 (w), 1456 (s), 1248 (m), 1234 (m), 745 (s), 698 cm^{-1} (m).

^1H NMR (300 MHz, DMSO-d_6): δ = 3.40 (s, 3 H), 3.42 (s, 3 H), 5.43 (s, 1 H, OH), 5.44 (s, 1 H, OH), 6.75–6.78 (t, *J* = 7.40 Hz, 2 H), 6.92–6.94 (t, *J* = 7.38 Hz, 2 H), 7.14–7.16 (d, *J* = 7.14 Hz, 3 H), 7.14–7.16 (d, *J* = 7.20 Hz, 2 H), 7.21–7.24 (t, *J* = 7.56 Hz, 4 H), 7.83 (s, 1 H), 9.96 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 158.26, 158.09, 156.41, 156.10, 142.54, 140.41, 138.01, 135.14, 133.18, 132.41, 131.39, 131.06, 130.42, 128.42, 128.09, 122.21, 122.06, 121.49, 120.22, 118.76, 109.11, 55.36, 55.11.

MS: *m*/*z* = 501.5 $[M + H]^+$.

Anal. Calcd for $C_{32}H_{24}N_2O_4$; C, 76.79; H, 4.83; N, 5.60. Found: C, 76.74; H, 4.85; N, 5.65.

6,12-Bis(3,4,5-trimethoxyphenyl)-5,7-dihydroindolo[2,3-*b*]carbazole (3i)
Off white solid; yield: 500 mg (85%); mp >400 °C; R_f = 0.74 (7% EtOAc–PE).

IR (KBr): 3392 (NH stretch), 3061 (w), 2945 (w), 1492 (w), 1456 (s), 1248 (m), 745 (s), 698 cm^{-1} (m).

^1H NMR (300 MHz, DMSO-d_6): δ = 3.76–3.79 (m, 18 H), 6.85–6.88 (t, *J* = 7.47 Hz, 2 H), 7.02–7.06 (t, *J* = 7.48 Hz, 2 H), 7.14–7.16 (d, *J* = 7.28 Hz, 3 H), 7.24–7.27 (t, *J* = 7.47 Hz, 4 H), 7.87 (s, 1 H), 10.06 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 158.80, 158.61, 158.33, 158.08, 139.13, 136.14, 134.23, 133.32, 132.39, 132.05, 130.88, 128.91, 128.50, 121.96, 121.49, 120.22, 118.70, 109.11, 55.61, 55.34, 55.21, 55.04.

MS: *m*/*z* = 587.5 $[M - H]^+$.

Anal. Calcd for $C_{36}H_{32}N_2O_6$; C, 73.45; H, 5.48; N, 4.76. Found: C, 73.51; H, 5.42; N, 4.79.

6,12-Bis[4-(benzoyloxy)phenyl]-5,7-dihydroindolo[2,3-*b*]carbazole (3j)
Orange crystals; yield: 466 mg (72%); mp 351 °C (dec); R_f = 0.72 (7% EtOAc–PE).

IR (KBr): 3394 (NH stretch), 3058 (w), 1737 (s), 1492 (w), 1456 (s), 1271 (m), 745 (s), 702 cm^{-1} (m).

^1H NMR (300 MHz, DMSO-d_6): δ = 6.81–6.84 (t, *J* = 7.43 Hz, 3 H), 7.06–7.09 (t, *J* = 7.43 Hz, 4 H), 7.18–7.23 (m, 9 H), 7.29–7.32 (t, *J* = 7.41 Hz, 3 H), 7.92–7.98 (m, 7 H), 10.09 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 166.04, 165.89, 152.91, 152.72, 141.21, 140.80, 138.31, 136.25, 136.12, 134.29, 133.56, 133.41, 131.23, 131.02, 129.73, 129.59, 128.52, 128.33, 124.29, 124.08, 122.33, 120.26, 118.85, 116.42, 111.13, 110.56, 109.83.

MS: *m*/*z* = 649.8 $[M + H]^+$.

Anal. Calcd for $C_{44}H_{28}N_2O_4$; C, 81.47; H, 4.35; N, 4.32. Found: C, 81.52; H, 4.28; N, 4.37.

6,12-Dialkyl-5,7-dihydroindolo[2,3-*b*]carbazoles 3k,l; General Procedure
In a simple experimental procedure, equimolar amounts of indole **1** (2 mmol) and aliphatic aldehyde **2** (2 mmol) were added to a round-bottomed flask containing MeCN (5 mL). I_2 (2 mol%) was added to the mixture and it was refluxed for 35–45 min (Table 1). The solvent was removed under reduced pressure and the desired compound was isolated from the residue by column chromatography [silica gel, 100–200 mesh, 10% EtOAc–PE (bp 60–80 °C)].

6,12-Dimethyl-5,7-dihydroindolo[2,3-*b*]carbazole (3k)
Light yellow solid; yield: 71 mg (25%); mp 282–283 °C; R_f = 0.83 (7% EtOAc–PE).

IR (KBr): 3396 (NH stretch), 3055 (w), 2933 (w), 1455 (s), 748 cm^{-1} (w).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.29 (s, 3 H), 2.31 (s, 3 H), 6.94–6.99 (d, *J* = 7.68 Hz, 2 H), 7.12–7.17 (dd, *J* = 7.51, 7.55 Hz, 2 H), 7.29–7.34 (m, 2 H), 7.41–7.44 (d, *J* = 7.18 Hz, 2 H) 10.10 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 138.18, 135.04, 133.29, 129.74, 129.23, 122.71, 118.0, 114.21, 112.20, 112.0, 20.38, 20.21.

MS: *m*/*z* = 285.5 [M + H]$^+$.

Anal. Calcd for $C_{20}H_{16}N_2$; C, 84.48; H, 5.67; N, 9.85. Found: C, 84.42; H, 5.59; N, 9.93.

6,12-Diethyl-5,7-dihydroindolo[2,3-*b*]carbzole, (3l)
Orange solid; yield: 62 mg (20%); mp 311–312 °C; R_f = 0.81 (7% EtOAc–PE).

IR (KBr): 3393 (NH stretch), 3061 (w), 2933 (w), 1455 (s), 748 cm^{-1} (w).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.63–1.67 (m, 6 H), 2.33 (q, *J* = 6.61 Hz, 2 H), 2.34 (q, *J* = 6.64 Hz, 2 H), 6.98–7.03 (d, *J* = 7.40 Hz, 2 H), 7.16–7.19 (t, *J* = 6.98 Hz, 2 H), 7.32–7.36 (m, 2 H), 7.43–7.49 (t, *J* = 7.73 Hz, 2 H), 9.99 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 144.47, 144.28, 136.25, 133.12, 130.11, 122.64, 118.10, 115.16, 111.46, 111.10, 29.19, 29.01, 15.47, 15.28.

MS: *m*/*z* = 313.6 [M + H]$^+$.

Anal. Calcd for $C_{22}H_{20}N_2$; C, 84.58; H, 6.45; N, 8.09. Found: C, 84.63; H, 6.48; N, 8.03.

Unsymmetrical Indolo[2,3-*b*]carbazoles 6a–h; General Procedure
In a simple experimental procedure, equimolar amounts of bis(indol-3-yl)methane **4**[11a] (1 mmol) and aldehyde (1 mmol) were added to a round-bottomed flask containing MeCN (5 mL). I_2 (2 mol%) was added to the mixture and it was refluxed for 5–30 min (Table 2). The solid compound obtained was filtered, dried and recrystallized (DMF–$CHCl_3$).

6-(4-Methylphenyl)-12-phenyl-5,7-dihydroindolo[2,3-*b*]carbazole (6a)
White cotton-like solid; yield: 316 mg (75%); mp 391–393 °C; R_f = 0.82 (7% EtOAc–PE).

IR (KBr): 3395 (NH stretch), 3061 (w), 2930 (w), 2855 (w), 1492 (w), 1456 (s), 745 (s), 698 cm^{-1} (m).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.28 (s, 3 H), 6.80–6.85 (t, *J* = 7.38 Hz, 2 H), 6.94–7.0 (t, *J* = 7.23 Hz, 2 H), 7.06–7.08 (d, *J* = 7.62 Hz, 2 H), 7.13–7.18 (t, *J* = 7.38 Hz, 2 H), 7.22–7.29 (m, *J* = 7.35 Hz, 6 H), 7.35–7.37 (d, *J* = 7.53 Hz, 2 H), 7.68 (s, 1 H), 9.95 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 140.22, 138.88, 136.19, 134.57, 133.61, 132.23, 132.05, 129.27, 129.16, 128.52, 128.12, 126.15, 123.91, 123.09, 121.68, 120.0, 118.54, 111.06, 21.02.

MS: *m*/*z* = 423.3 [M + H]$^+$.

Anal. Calcd for $C_{31}H_{22}N_2$; C, 88.12; H, 5.25; N, 6.63. Found: C, 88.07; H, 5.19; N, 6.69.

12-(4-Methylphenyl)-6-phenyl-5,7-dihydroindolo[2,3-*b*]carbazole (6b)
White crystalline solid; yield: 337 mg (80%); mp 385–386 °C; R_f = 0.81 (7% EtOAc–PE).

IR (KBr): 3394 (NH stretch), 3061 (w), 2933 (w), 2855 (w), 1492 (w), 1456 (s), 745 (s), 698 cm^{-1} (m).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.28 (s, 3 H), 6.82–6.86 (t, *J* = 7.36 Hz, 2 H), 6.95–7.0 (t, *J* = 7.14 Hz, 2 H), 7.06–7.08 (d, *J* = 7.61 Hz, 2 H), 7.13–7.17 (t, *J* = 7.37 Hz, 2 H), 7.22–7.29 (m, *J* = 7.38 Hz, 6 H), 7.39–7.43 (d, *J* = 7.47 Hz, 2 H), 7.64 (s, 1 H), 9.98 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 141.30, 138.49, 136.17, 134.57, 133.63, 132.29, 132.05, 129.27, 129.14, 128.54, 128.11, 126.18, 123.98, 123.17, 121.68, 120.07, 118.79, 111.18, 21.31.

MS: *m*/*z* = 423.7 [M + H]$^+$.

Anal. Calcd for $C_{31}H_{22}N_2$; C, 88.12; H, 5.25; N, 6.63. Found: C, 88.18; H, 5.19; N, 6.58.

6-(4-Methoxyphenyl)-12-(4-methylphenyl)-5,7-dihydroindolo[2,3-*b*]carbazole (6c)
Pale yellow solid; yield: 357 mg (79%); mp 377–379 °C; R_f = 0.80 (7% EtOAc–PE).

IR (KBr): 3392 (NH stretch), 3061 (w), 2965 (w), 2849 (w), 1492 (w), 1456 (s), 1248 (m), 745 (s), 702 cm^{-1} (m).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.27 (s, 3 H), 3.41 (s, 3 H), 6.80–6.84 (t, *J* = 7.33 Hz, 2 H), 6.96–7.03 (t, *J* = 7.28 Hz, 2 H), 7.06–7.08 (d, *J* = 7.58 Hz, 2 H), 7.16–7.21 (t, *J* = 7.35 Hz, 2 H), 7.24–7.31 (m, *J* = 7.33 Hz, 5 H), 7.35–7.38 (d, *J* = 7.53 Hz, 2 H), 7.71 (s, 1 H), 10.10 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 159.18, 140.25, 136.79, 134.27, 133.93, 132.76, 132.36, 129.27, 129.18, 128.24, 128.12, 126.15, 123.87, 123.0 121.68, 120.12, 118.41, 111.09, 55.91, 20.82.

MS: *m*/*z* = 453.5 [M + H]$^+$.

Anal. Calcd for $C_{32}H_{24}N_2O$; C, 84.93; H, 5.35; N, 6.19. Found: C, 84.87; H, 5.40; N, 6.15.

12-(4-Methoxyphenyl)-6-(4-methylphenyl)-5,7-dihydroindolo[2,3-*b*]carbazole (6d)
Light yellow crystal; yield: 325 mg (72%); mp 355–356 °C; R_f = 0.82 (7% EtOAc–PE).

IR (KBr): 3392 (NH stretch), 3061 (w), 2922 (w), 2856 (w), 1492 (w), 1456 (s), 1248 (m), 745 (s), 702 cm^{-1} (m).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.28 (s, 3 H), 3.40 (s, 3 H), 6.80–6.84 (t, *J* = 7.34 Hz, 2 H), 6.94–7.01 (t, *J* = 7.24 Hz, 2 H), 7.06–7.09 (d, *J* = 7.62 Hz, 2 H), 7.14–7.19 (t, *J* = 7.34 Hz, 2 H), 7.22–7.30 (m, *J* = 7.32 Hz, 5 H), 7.35–7.37 (d, *J* = 7.53 Hz, 2 H), 7.71 (s, 1 H), 9.98 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 159.14, 140.10, 136.74, 134.27, 133.95, 132.71, 132.38, 129.21, 129.11, 128.26, 128.11, 126.14, 123.88, 123.0 121.63, 120.10, 118.74, 111.09, 55.71, 21.0.

MS: *m*/*z* = 453.3 [M + H]$^+$.

Anal. Calcd for $C_{32}H_{24}N_2O$; C, 84.93; H, 5.35; N, 6.19. Found: C, 84.98; H, 5.39; N, 6.22.

12-(4-Methoxyphenyl)-6-phenyl-5,7-dihydroindolo[2,3-*b*]carbazole (6e)
Off-white solid; yield: 324 mg (74%); mp 348–351 °C; R_f = 0.82 (7% EtOAc–PE).

IR (KBr): 3392 (NH stretch), 3055 (w), 2933 (w), 2855 (w), 1492 (w), 1456 (s), 1247 (m), 745 (s), 698 cm^{-1} (m).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.41 (s, 3 H), 6.83–6.87 (t, *J* = 7.36 Hz, 2 H), 6.98–7.03 (t, *J* = 7.29 Hz, 2 H), 7.10–7.12 (d, *J* = 7.46 Hz, 2 H), 7.16–7.20 (t, *J* = 7.33 Hz, 2 H), 7.24–7.32 (m, *J* = 7.43 Hz, 6 H), 7.36–7.38 (d, *J* = 7.50 Hz, 2 H), 7.70 (s, 1 H), 9.97 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 158.98, 138.69, 136.98, 134.27, 133.63, 132.25, 132.05, 129.21, 129.12, 128.25, 128.09, 126.14, 123.91, 123.08 121.64, 120.06, 118.79, 111.06, 55.70.

MS: *m*/*z* = 439.6 [M + H]$^+$.

Anal. Calcd for $C_{31}H_{22}N_2O$; C, 84.91; H, 5.06; N, 6.39. Found: C, 84.86; H, 5.09; N, 6.33.

6-(4-Methoxyphenyl)-12-phenyl-5,7-dihydroindolo[2,3-*b*]carbazole (6f)

Off-white solid; yield: 302 mg (69%); mp 381–382 °C; R_f = 0.78 (7% EtOAc–PE).

IR (KBr): 3392 (NH stretch), 3055 (w), 2933 (w), 2855 (w), 1492 (w), 1456 (s), 1244 (m), 745 (s), 698 cm^{-1} (m).

^1H NMR (300 MHz, DMSO-d_6): δ = 3.40 (s, 3 H), 6.83–6.87 (t, *J* = 7.36 Hz, 2 H), 6.95–7.0 (t, *J* = 7.32 Hz, 2 H), 7.11–7.14 (d, *J* = 7.48 Hz, 2 H), 7.16–7.20 (t, *J* = 7.33 Hz, 2 H), 7.28–7.35 (m, *J* = 7.45 Hz, 6 H), 7.39–7.41 (d, *J* = 7.48 Hz, 2 H), 7.71 (s, 1 H), 9.97 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 159.10, 138.71, 136.96, 134.29, 133.63, 132.28, 132.05, 129.20, 129.12, 128.29, 128.05, 126.12, 123.90, 123.10, 121.71, 120.09, 118.79, 111.0, 55.90.

MS: *m*/*z* = 439.4 $[M + H]^+$.

Anal. Calcd for $C_{31}H_{22}N_2O$; C, 84.91; H, 5.06; N, 6.39. Found: C, 84.90; H, 5.02; N, 6.44.

12-(2-Chloroquinolin-3-yl)-6-phenyl-5,7-dihydroindolo[2,3-*b*]carbazole (6g)

Bright orange crystals; yield: 271 mg (55%); mp 375–378 °C; R_f = 0.65 (7% EtOAc–PE).

IR (KBr): 3417 (NH stretch), 2919 (w), 1631 (s), 1483 (w), 1455 (m), 772 (s), 741 cm^{-1} (m).

^1H NMR (300 MHz, DMSO-d_6): δ = 6.86–6.91 (t, *J* = 7.47 Hz, 2 H), 7.04–7.09 (t, *J* = 7.41 Hz, 2 H), 7.29–7.38 (m, *J* = 8.1 Hz, 4 H), 7.46–7.49 (d, *J* = 7.47 Hz, 4 H), 7.61–7.68 (m, *J* = 7.71 Hz, 3 H), 7.74 (s, 1 H), 7.91–7.94 (d, 2 H), 10.45 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 149.54, 144.21, 139.41, 138.23, 138.02, 136.37, 136.13, 134.91, 134.65, 134.21, 133.45, 132.92, 131.49, 129.61, 128.42, 127.31, 127.08, 122.54, 120.87, 118.56, 118.12, 111.91, 111.63.

MS: *m*/*z* (%) = 493.9 ($[M + H]^+$, ^{35}Cl, 100), 495.9 ($[M + H]^+$, ^{37}Cl, 31).

Anal. Calcd for $C_{33}H_{20}ClN_3$; C, 80.24; H, 4.08; N, 8.51. Found: C, 80.32; H, 4.04; N, 8.56.

12-Methyl-6-phenyl-5,7-dihydroindolo[2,3-*b*]carbazole (6h)

White crystalline solid; yield: 138 mg (40%); mp 331–332 °C; R_f = 0.83 (7% EtOAc–PE).

IR (KBr): 3405 (NH stretch), 2931 (w), 1471 (w), 1454 (m), 741 cm^{-1} (m).

^1H NMR (300 MHz, DMSO-d_6): δ = 2.29 (s, 3 H), 6.98–7.02 (d, *J* = 7.17 Hz, 2 H), 7.07–7.11 (d, *J* = 7.71 Hz, 2 H), 7.19–7.26 (m, 4 H), 7.31–7.36 (m, 3 H), 7.51–7.54 (d, *J* = 7.15 Hz, 2 H), 10.12 (s, 2 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 140.27, 138.07, 136.41, 133.24, 129.71, 128.23, 127.49, 126.54, 123.91, 118.11, 114.24, 114.10, 111.54, 109.21, 20.09.

MS: *m*/*z* = 347.4 $[M + H]^+$.

Anal. Calcd for $C_{25}H_{18}N_2$; C, 86.68; H, 5.24; N, 8.09. Found: C, 86.76; H, 5.29; N, 8.15.

Acknowledgement

M.L.D. thanks CSIR (India) for the award of a Senior Research Fellowship.

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