

# Novel synthesis of 6,12-dihydroindolo[3,2-*b*]carbazoles catalysed by *p*-toluenesulfonic acid

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An efficient and straightforward procedure for the synthesis of 6,12-dihydroindolo[3,2-*b*]carbazoles has been achieved through the one-pot reaction of indole with aromatic aldehydes in the presence of *p*-toluenesulfonic acid (*p*TSA) as the catalyst.

**Keywords:** 6,12-dihydroindolo[3,2-*b*]carbazole, one-step reaction, *p*-toluenesulfonic acid, aromatic aldehyde, indole

Several methods for the synthesis of 6,12-dihydroindolo[3,2-*b*]carbazoles have been reported including (1) cyclodimerisation of 3-(1-phenylvinyl)indole catalysed by hydrochloric acid,<sup>1</sup> (2) dimerisation of indole and benzaldehyde under strongly acidic conditions,<sup>2</sup> (3) reaction of 2-hydroxybenzylideneaniline with indole,<sup>3</sup> (4) Lewis acid catalysed dimerisation of 1-(1-benzotriazol-1-yl-alkyl)indoles,<sup>4,5</sup> (5) reaction of 4,6-dimethoxyindole with aryl aldehydes and phosphoryl chloride,<sup>6</sup> (6) acid-catalysed dimerisation of 2-(3'-hydroxy-3'-methyl-E-but-1'-enyl)indole,<sup>7</sup> (7) reaction of 2,3'-bis(indolyl)methanes with aromatic aldehydes under acidic conditions,<sup>8</sup> and (8) dimeric condensation of 2-(1-hydroxyethyl)-1-methylindole.<sup>9</sup>

However, these methodologies suffered from one or more disadvantages such as inaccessibility of the starting materials, prolonged reaction time, use of toxic organic solvents, requirement for excess reagents or catalyst, special apparatus, harsh reaction conditions and a poor yield of the desired product and selectivity. Thus, there is a need for the development of an alternative route to construct dihydroindolo[3,2-*b*]carbazole derivatives.

We now report an efficient and convenient method for the synthesis of 6,12-dihydroindolo[3,2-*b*]carbazoles involving one-step condensation of indole and aromatic aldehydes in the presence of *p*-toluenesulfonic acid (*p*TSA) as the catalyst.

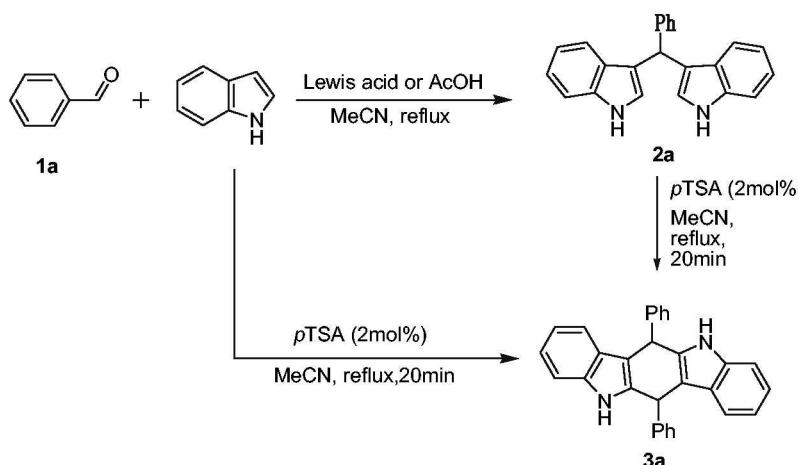
In an initial study to examine the catalytic activity of different catalysts, we examined the model reaction of benzaldehyde with indole (Scheme 1, Table 1) in acetonitrile (5 mL) for 20 minutes under reflux conditions in the presence of different catalyst (0.02 equiv) including  $\text{AlCl}_3$ ,  $\text{ZnCl}_2$ ,

$\text{Yb}(\text{OTf})_3$ ,  $\text{Cu}(\text{OTf})_2$ ,  $\text{CaCl}_2$ ,  $\text{BF}_3\text{TfONH}_2\text{Ph}$ ,  $\text{NaHSO}_4$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{HCl}$  and *p*TSA. In the course of the study it was found that only  $\text{HCl}$  and *p*TSA gave the desired product in 60% and 86% yield respectively. Most Lewis acids or  $\text{CH}_3\text{COOH}$  only afforded the 3,3'-bis(indolyl)methanes **2a** (Scheme 1, Table 1) in moderate to good yield. Compound **2a** could be easily converted to **3a** when treated with *p*TSA (Scheme 1). The solvent effect was also examined by the model reaction of benzaldehyde (2 mmol) and indole (1 mmol) in the presence of *p*TSA (0.02 mmol) under reflux (Table 2). Although the reaction proceeded in other organic solvents such as alcohol and chloroform, the yield of the desired 6,12-dihydroindolo[3,2-*b*]carbazole was lower than in  $\text{CH}_3\text{CN}$ . Hence *p*TSA was chosen as the optimal

**Table 1** Reaction of benzaldehyde (1 mmol) and indole (1 mmol) in the presence of various catalysts (0.02 mmol) in acetonitrile

Entry	Catalyst	Time/min	Yield/% <sup>a</sup> of <b>3a</b>
1	<i>p</i> TSA	20	86
2	$\text{HCl}$	20	60
3	$\text{CH}_3\text{COOH}$	60	0
4	$\text{AlCl}_3$	60	0
5	$\text{ZnCl}_2$	60	0
6	$\text{Yb}(\text{OTf})_3$	60	0
7	$\text{Cu}(\text{OTf})_2$	60	0
8	$\text{CaCl}_2$	60	0
9	$\text{BF}_3$	60	0
10	$\text{TfONH}_2\text{Ph}$	60	0
11	$\text{NaHSO}_4$	60	0

<sup>a</sup>Isolated yield based on aldehydes.



**Scheme 1**

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**Table 2** Reaction of benzaldehyde (1 mmol) and indole (1 mmol) in the presence of *p*TSA (0.02 mmol) in different refluxing solvents

Entry	Solvent	Time/min	Yield/% <sup>a</sup>
1	CH <sub>3</sub> CN	20	86
2	CH <sub>3</sub> NO <sub>2</sub>	20	80
3	CH <sub>3</sub> CH <sub>2</sub> OH	60	77
4	CH <sub>3</sub> OH	60	60
5	CICH <sub>2</sub> CH <sub>2</sub> Cl	60	50
6	CHCl <sub>3</sub>	60	35

<sup>a</sup>Isolated yield based on aldehydes.

catalyst and  $\text{CH}_3\text{CN}$  was used as the best solvent for the purpose of this reaction.

In our reaction strategy, indole and aromatic aldehydes with a catalytic amount of *p*TSA in refluxing acetonitrile for 10–90 minutes afforded dihydroindolo[3,2-*b*]carbazoles **3** in good yields (Scheme 2). Thus in a simple experimental procedure when indole and the aromatic aldehyde **1a** were heated in the presence of a catalytic amount of *p*TSA (2 mol%), in refluxing acetonitrile for 20 minutes dihydroindolo[3,2-*b*]carbazole **3a** was obtained in 86% yield (Table 3). The product was isolated simply by filtration and purified by washing with solvent. The structure of the compound was determined from spectroscopic data. Our observations are recorded in Table 3. No dehydrogenated product was detected by <sup>1</sup>H NMR spectroscopy. These dihydro compounds seemed to be stable in air at room temperature for months without dehydrogenation.

It was found that all substituted benzaldehydes with an electron-donating group reacted with indole completely and afforded the corresponding products **3** in high yields. In contrast, aldehydes with an electron-withdrawing group were less active and the reaction proceeded relatively slowly and the yield was lower. Thus the common aromatic aldehydes were acceptable substrates in the protocol. Aliphatic aldehydes and some aromatic aldehydes having strong electron-withdrawing substituents such as 4-fluorobenzaldehyde, and picinaldehyde when treated under these reaction conditions

**Table 3** Synthesis of 6,12-dihydroindolo[3,2-*b*]carbazoles from indole (1 mmol) and aromatic aldehydes (1 mmol) catalysed by *p*TSA<sup>a</sup>

Entry	R	Time/min	Prduct	Yield/% <sup>b</sup>
1	C <sub>6</sub> H <sub>5</sub>	20	3a	86
2	2-HO-C <sub>6</sub> H <sub>4</sub>	10	3b	90
3	4-HO-C <sub>6</sub> H <sub>4</sub>	15	3c	90
4	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	15	3d	92
5	2,4-(CH <sub>3</sub> O) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	15	3e	94
6	4-HO-3-CH <sub>3</sub> O-C <sub>6</sub> H <sub>3</sub>	15	3f	92
7	3,4-CH <sub>3</sub> -C <sub>6</sub> H <sub>3</sub>	15	3g	88
8	3-Cl-C <sub>6</sub> H <sub>4</sub>	50	3h	65
9	4-Cl-C <sub>6</sub> H <sub>4</sub>	50	3i	75
10	3-Br-C <sub>6</sub> H <sub>4</sub>	90	3j	60
11	4-Br-C <sub>6</sub> H <sub>4</sub>	90	3k	72
12	3-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	60	3l	75
13		15	3m	92

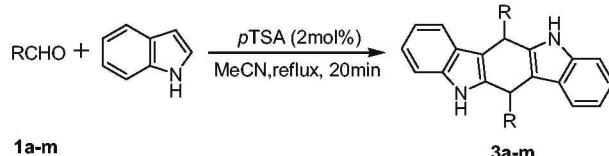
<sup>a</sup>All reactions were performed on a 1 mmol scale using 2 mol% of *p*TSA.

<sup>b</sup>Isolated yield based on aldehydes.

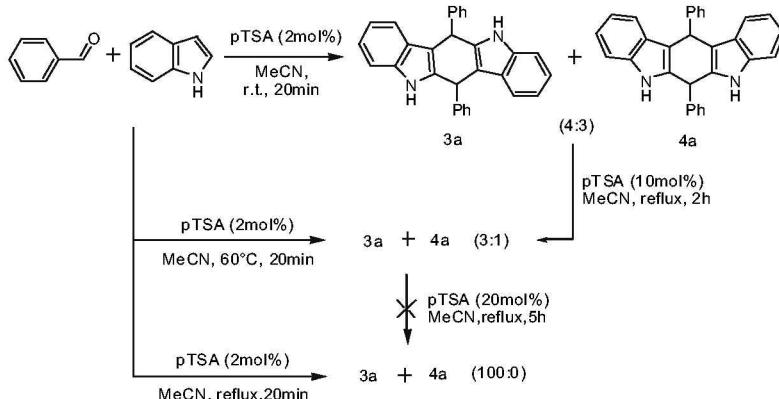
even for 5 h only gave the 3, 3'-bis(indolyl)methane derivatives **2**, which were rather stable and did not form the dihydroindolo[3, 2-b]carbazoles. It should be pointed out that steric effects were not observed, hindered benzaldehydes such as 2, 4-dimethoxybenzaldehyde and 2-hydroxybenzaldehyde reacted with indole faster and in higher yields than benzaldehyde under the present reaction condition.

Although the yield of products in the reaction were not very high in some cases, there was a selective formation of the dihydroindolo[3,2-*b*]carbazole. In many reported methods, both the indolo[3,2-*b*]carbazoles and indolo[2,3-*b*]carbazoles were formed which were difficult to separate due to their insolubility. In the present case, there was no formation of the dihydroindolo[2,3-*b*]carbazole isomer in refluxing acetonitrile.

Interestingly (Scheme 3), the reaction at room temperature gave dihydroindolo[3,2-*b*]carbazoles **3a** and dihydroindolo[2,3-*b*]carbazoles **4a** in fair yields (**3a/4a** = 4:3).



**Scheme 2**



**Scheme 3**

as observed in the <sup>1</sup>H NMR and MS. The ratio of **3a** and **4a** varied depending on the reaction temperature and at 60 °C it was 3:1. The dihydroindolo[2,3-*b*]carbazoles **4a** could partly be converted to dihydroindolo[3,2-*b*]carbazoles **3a** in refluxing acetonitrile in the presence of *p*TSa as catalyst until the ratio of **3a**/**4a** achieved 3:1. The reaction at 0 °C formed an insoluble and unknown complex. In the light of our experimental results, a plausible reaction mechanism is shown in Scheme 4.

In summary, we have reported a very simple, mild, and highly efficient method for the synthesis of dihydroindolo[3,2-*b*]carbazoles from indole and aromatic aldehydes in the presence of *p*TSa as catalyst. This very simple, mild, and effective method is a valuable addition to the chemistry of dihydroindolo[3,2-*b*]carbazoles.

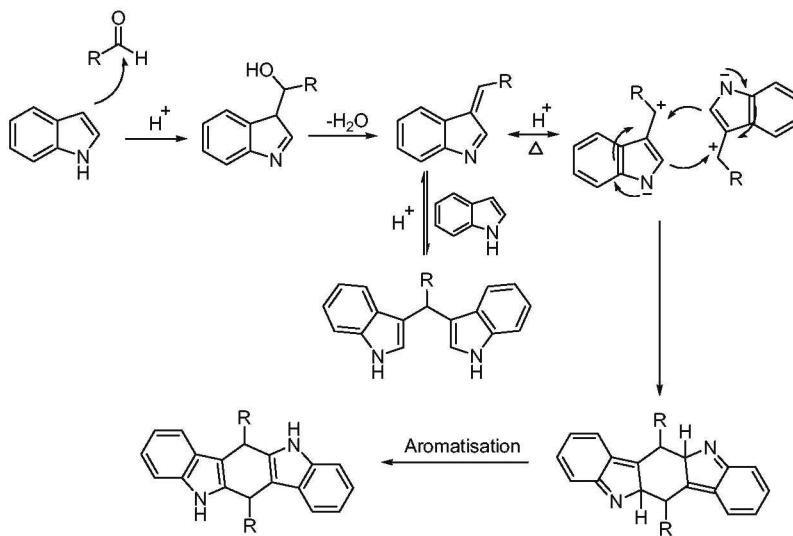
## Experimental

Melting points were measured on a Büchi B-540 apparatus and are uncorrected. IR spectra were recorded on a Nicolet Avatar-370 instrument. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian 400 MHz or Bruker Avance III (500 MHz) instrument in CDCl<sub>3</sub> or DMSO-d<sub>6</sub> as the solvent, and chemical shifts were expressed in parts per million (ppm) using TMS as an internal standard. Mass spectra were measured with a Trace Finnigan DSQ. High resolution mass spectral (HRMS) analyses were measured on an Agilent 6210 TOF LC/MS.

### Typical procedure

*p*-Toluene sulfonic acid (0.02 mmol) was added to a solution of indole (1.0 mmol) and the appropriate aldehyde (**1a**, 1.0 mmol) in CH<sub>3</sub>CN (5 mL), and the reaction mixture was refluxed for 20 min. The precipitate which formed was filtered off, washed with EtOH and carefully dried to constant weight to yield **3a** (0.176 g, 86%). The filtrate was concentrated, then purified by column chromatography and eluted with ethyl acetate-petroleum ether (1:4) to afford **2a** (0.008 g, 5%). The structure of the compound obtained was identified from spectroscopic data.

*3,3'-bis(indolyl)phenylmethane* (**2a**): Red solid. M.p. 125–126 °C (Lit.<sup>10</sup> M.p. 125–126 °C). IR (cm<sup>-1</sup>): 3408 (NH). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 5.89 (s, 1H, CH), 6.66 (d, 2H, *J* = 2.5 Hz), 7.00 (t, 2H, *J* = 8.0 Hz), 7.15–7.18 (m, 2H), 7.19–7.22 (m, 1H), 7.25–7.29 (m, 2H), 7.34–7.36 (m, 4H), 7.39 (d, 2H, *J* = 8.5 Hz), 7.90 (s, 2H, NH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 40.1, 111.0, 119.1, 119.6, 119.8, 121.8, 123.6, 126.1, 127.0, 128.2, 128.7, 136.6, 144.0. MS(ESI): *m/z* = 322.3 (M<sup>+</sup>).



Scheme 4

**6,12-bis(phenyl)-6,12-dihydroindolo[3,2-*b*]carbazole** (**3a**): White solid. M.p. 350–352 °C (Lit.<sup>2</sup> M.p. 353–355 °C). IR (cm<sup>-1</sup>): 3393 (NH). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ: 5.70 (s, 2H), 6.79 (d, 2H, *J* = 7.0 Hz), 6.93–6.95 (m, 2H), 7.08 (d, 2H, *J* = 7.5 Hz), 7.20 (d, 2H, *J* = 7.0 Hz), 7.24 (d, 2H, *J* = 8.5 Hz), 7.29 (d, 4H, *J* = 8.5 Hz), 10.70 (s, 2H, NH). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 109.8, 111.0, 118.1, 118.4, 120.5, 125.6, 126.3, 128.2, 128.4, 136.6, 137.1, 144.1. MS(ESI): *m/z* = 410.5 (M<sup>+</sup>).

**6,12-bis(2-hydroxyphenyl)-6,12-dihydroindolo[3,2-*b*]carbazole** (**3b**): White solid. M.p. 349–351 °C (Lit.<sup>3</sup> M.p. >300 °C). IR (cm<sup>-1</sup>): 3542 (ArOH), 3395 (NH). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 6.10 (s, 2H, CH), 6.51–6.59 (m, 4H), 6.79 (t, 2H, *J* = 7.6 Hz), 6.91–6.99 (m, 6H), 7.24 (t, 4H, *J* = 8.4 Hz), 9.89 (s, 2H, OH), 10.43 (s, 2H, NH). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 110.8, 111.0, 115.3, 117.9, 118.3, 119.1, 120.2, 125.7, 126.9, 129.4, 130.2, 136.8, 136.9, 155.4. MS(ESI): *m/z* = 442.4 (M<sup>+</sup>).

**6,12-bis(4-hydroxylphenyl)-6,12-dihydroindolo[3,2-*b*]carbazole** (**3c**): Pink solid. M.p. 334–335 °C. IR (cm<sup>-1</sup>): 3474 (ArOH), 3413 (NH). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 5.53 (s, 2H, CH), 6.65 (d, 4H, *J* = 8.4 Hz), 6.78 (t, 2H, *J* = 7.6 Hz), 6.93 (t, 2H, *J* = 7.4 Hz), 7.08 (t, 6H, *J* = 8.4 Hz), 7.23 (d, 2H, *J* = 8.4 Hz), 9.18 (s, 2H, OH), 10.56 (s, 2H, NH). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 110.0, 110.9, 115.0, 118.0, 118.5, 120.3, 125.8, 129.3, 134.4, 137.0, 155.8. HRMS(ESI): Calcd for C<sub>30</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub> 442.1681 (M<sup>+</sup>). Found 442.1687.

**6,12-bis(4-methoxylphenyl)-6,12-dihydroindolo[3,2-*b*]carbazole** (**3d**): Light yellow solid. M.p. 343–345 °C. IR (cm<sup>-1</sup>): 3413 (NH), 1247 (ArOCH<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 3.70 (s, 6H, OCH<sub>3</sub>), 5.61 (s, 2H, CH), 6.78 (t, 2H, *J* = 7.6 Hz), 6.83 (dd, 4H, *J*<sub>1</sub> = 2.0, *J*<sub>2</sub> = 6.8 Hz), 6.94 (td, 2H, *J*<sub>1</sub> = 1.2, *J*<sub>2</sub> = 7.6 Hz), 7.07 (d, 2H, *J* = 7.6 Hz), 7.22 (dd, 6H, *J*<sub>1</sub> = 2.0, *J*<sub>2</sub> = 6.8 Hz), 10.67 (s, 2H, NH). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 54.92, 109.9, 111.0, 113.6, 114.6, 118.0, 118.4, 120.4, 125.7, 129.3, 136.1, 136.9, 137.0, 155.8. HRMS(ESI): Calcd for C<sub>32</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub> 470.1994 (M<sup>+</sup>). Found 470.1999.

**6,12-bis(2,4-dimethoxyphenyl)-6,12-dihydroindolo[3,2-*b*]carbazole** (**3e**): Pink solid. M.p. 326–328 °C. IR (cm<sup>-1</sup>): 3386 (NH), 1206 (ArOCH<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 3.69 (s, 6H, OCH<sub>3</sub>), 4.08 (s, 6H, OCH<sub>3</sub>), 6.03 (s, 2H, CH), 6.27 (dd, 2H, *J*<sub>1</sub> = 2.4, *J*<sub>2</sub> = 8.4 Hz), 6.53 (s, 2H), 6.72 (d, 2H, *J* = 2.4 Hz), 6.79 (t, 2H, *J* = 7.6 Hz), 6.93 (t, 2H, *J* = 7.6 Hz), 7.05 (t, 2H, *J* = 7.6 Hz), 7.23 (d, 2H, *J* = 8.0 Hz), 10.36 (s, 2H, NH). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 55.0, 55.9, 98.2, 105.3, 110.5, 111.0, 118.1, 120.3, 124.2, 125.7, 129.8, 136.9, 137.1, 157.4, 158.8. HRMS(ESI): Calcd for C<sub>34</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub> 530.2206 (M<sup>+</sup>). Found 530.2217.

**6,12-bis(4-hydroxyl-3-methoxyphenyl)-6,12-dihydroindolo[3,2-*b*]carbazole** (**3f**): Light yellow solid. M.p. 368–370 °C. IR (cm<sup>-1</sup>): 3506 (ArOH), 3357 (NH), 1227 (ArOCH<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 3.72 (s, 6H, OCH<sub>3</sub>), 5.55 (s, 2H, CH), 6.58 (dd, 2H, *J*<sub>1</sub> = 2.0, *J*<sub>2</sub> = 8.0 Hz), 6.64 (d, 2H, *J* = 8.0 Hz), 6.79 (t, 2H, *J* = 7.6 Hz), 6.92–6.98 (m, 4H), 7.09 (d, 2H, *J* = 8.0 Hz), 7.24 (d, 2H, *J* = 8.0 Hz), 8.72 (s, 2H, OH), 10.54 (s, 2H, NH). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ:

δ: 55.7, 109.8, 110.9, 113.0, 115.4, 118.0, 118.7, 120.3, 120.6, 125.9, 135.0, 137.0, 137.2, 145.0, 147.2. HRMS(EI): Calcd for  $C_{32}H_{26}N_2O_4$  502.1893 ( $M^+$ ). Found 502.1909.

**6,12-bis(3,4-dimethylphenyl)-6,12-dihydroindolo[3,2-b]carbazole (3g):** Pale yellow solid. M.p. >400°C. IR (cm<sup>-1</sup>): 3406 (NH). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 2.13 (s, 6H, CH<sub>3</sub>), 2.15 (s, 6H, CH<sub>3</sub>), 5.59 (s, 2H, CH), 6.78 (t, 2H,  $J$  = 7.4 Hz), 6.93 (t, 2H,  $J$  = 7.6 Hz), 7.02–7.08 (m, 8H), 7.22 (d, 2H,  $J$  = 8.0 Hz), 10.57 (s, 2H, NH). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 18.9, 19.5, 109.8, 111.0, 118.0, 118.5, 120.4, 125.8, 125.9, 129.4, 134.0, 135.8, 136.8, 137.0, 141.5. HRMS(EI): Calcd for  $C_{34}H_{30}N_2$  466.2409 ( $M^+$ ). Found 466.2415.

**6,12-bis(3-chlorophenyl)-6,12-dihydroindolo[3,2-b]carbazole (3h):** White solid. M.p. 291–293°C. IR (cm<sup>-1</sup>): 3417 (NH). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 5.67 (s, 2H, CH), 6.86 (t, 2H,  $J$  = 7.6 Hz), 7.02 (t, 2H,  $J$  = 7.6 Hz), 7.13 (d, 2H,  $J$  = 7.6 Hz), 7.29–7.33 (m, 4H), 7.39 (t, 2H,  $J$  = 7.8 Hz), 7.45–7.47 (m, 4H), 11.00 (s, 2H, NH). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 108.8, 111.3, 118.3, 118.6, 121.0, 125.4, 126.6, 127.1, 128.1, 130.3, 133.1, 136.2, 137.1, 146.1. HRMS(EI): Calcd for  $C_{30}H_{20}N_2Cl_2$  478.1004 ( $M^+$ ). Found 478.1001.

**6,12-bis(4-chlorophenyl)-6,12-dihydroindolo[3,2-b]carbazole (3i):** Light yellow solid. M.p. >400°C. IR (cm<sup>-1</sup>): 3385 (NH). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 5.23 (s, 2H, CH), 6.82 (td, 2H,  $J_1$  = 0.8,  $J_2$  = 7.6 Hz), 6.97 (td, 2H,  $J_1$  = 1.2,  $J_2$  = 8.4 Hz), 7.08 (d, 2H,  $J$  = 7.6 Hz), 7.24 (d, 2H,  $J$  = 7.6 Hz), 7.34 (s, 8H), 10.75 (s, 2H, NH). HRMS(EI): Calcd for  $C_{30}H_{20}N_2Cl_2$  478.1004 ( $M^+$ ). Found 478.1003.

**6,12-bis(3-bromophenyl)-6,12-dihydroindolo[3,2-b]carbazole (3j):** White solid. M.p. 275–277°C. IR (cm<sup>-1</sup>): 3415 (NH). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 5.66 (s, 2H, CH), 6.87 (t, 2H,  $J$  = 7.2 Hz), 7.02 (t, 2H,  $J$  = 7.6 Hz), 7.14 (d, 2H,  $J$  = 7.6 Hz), 7.30–7.35 (m, 4H), 7.45 (dt, 2H,  $J_1$  = 0.8,  $J_2$  = 7.2 Hz), 7.52 (d, 2H,  $J$  = 7.6 Hz), 7.57 (s, 2H), 11.00 (s, 2H, NH). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 108.9, 111.3, 118.3, 118.6, 121.0, 121.8, 125.4, 127.5, 129.5, 130.6, 130.9, 136.2, 137.1, 146.3. HRMS(EI): Calcd for  $C_{30}H_{20}N_2Br_2$  565.9993 ( $M^+$ ). Found 565.9972.

**6,12-bis(4-bromophenyl)-6,12-dihydroindolo[3,2-b]carbazole (3k):** Light yellow solid. M.p. 343–345°C. IR (cm<sup>-1</sup>): 3384 (NH). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 5.71 (s, 2H, CH), 6.82 (td, 2H,  $J_1$  = 1.2,  $J_2$  = 7.6 Hz), 6.97 (td, 2H,  $J_1$  = 1.2,  $J_2$  = 7.6 Hz), 7.09 (d, 2H,  $J$  = 8.0 Hz), 7.23–7.29 (m, 6H), 7.47 (dd, 4H,  $J_1$  = 2.0,  $J_2$  = 7.6 Hz), 10.77 (s, 2H, NH). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 109.5, 111.1, 118.4, 119.4, 120.8, 125.4, 130.7, 131.1, 132.3, 136.2, 137.1, 143.4. HRMS(EI): Calcd for  $C_{30}H_{20}N_2Br_2$  565.9993 ( $M^+$ ). Found 565.9950.

**6,12-bis(3-nitrophenyl)-6,12-dihydroindolo[3,2-b]carbazole (3l):** Yellow solid. M.p. >400°C. IR (cm<sup>-1</sup>): 3408 (NH). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 6.04 (s, 2H, CH), 6.83 (t, 2H,  $J$  = 7.8 Hz), 6.99 (t, 2H,  $J$  = 7.4 Hz), 7.10 (d, 2H,  $J$  = 8.4 Hz), 7.25 (d, 2H,  $J$  = 8.4 Hz), 7.58 (t, 2H,  $J$  = 8.0 Hz), 7.74 (d, 2H,  $J$  = 8.4 Hz), 8.10 (dd, 2H,  $J_1$  = 2.8,  $J_2$  = 8.4 Hz), 8.28 (s, 2H), 10.98 (s, 2H, NH). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 109.3, 111.30, 118.4, 118.7, 121.1, 121.8, 123.0, 125.2, 130.0, 135.3, 136.0, 137.2, 146.2, 147.8. HRMS(EI): Calcd for  $C_{30}H_{20}N_2O_4$  500.1485 ( $M^+$ ). Found 500.1509.

**6,12-di(benzo[d][1,3]dioxol-5-yl)-6,12-dihydroindolo[3,2-b]carbazole (3m):** White or pink solid. M.p. 351–352°C. IR (cm<sup>-1</sup>): 3417 (NH), 1245 (ArOCH<sub>2</sub>O). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 5.62 (s, 2H, CH), 5.93 (d, 4H, ArOCH<sub>2</sub>O,  $J$  = 6.8 Hz), 6.70 (s, 2H, 6.80–6.84 (m, 4H), 6.89 (dd, 2H,  $J_1$  = 2.0,  $J_2$  = 8.0 Hz), 6.96 (td, 2H,  $J_1$  = 1.2,  $J_2$  = 8.4 Hz), 7.11 (d, 2H,  $J$  = 8.0 Hz), 7.25 (d, 2H,  $J$  = 8.0 Hz), 10.66 (s, 2H, NH). HRMS(EI): Calcd for  $C_{32}H_{22}N_2O_4$  498.1580 ( $M^+$ ). Found 498.1597.

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