Trichloroisocyanuric Acid-Catalyzed Reaction of Indoles: An Expeditious Synthesis of Bis-Indolyl, Tris-Indolyl, Di(bis-Indolyl), Tri(bis-Indolyl), and Tetra(bis-Indolyl)methane under Solid-State Conditions

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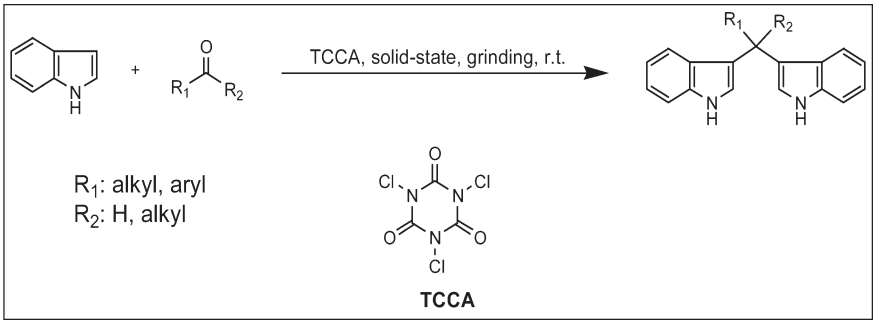

Trichloroisocyanuric acid is found to be an efficient catalyst for the electrophilic substitution reaction of indole with aldehydes/ketones to afford the corresponding bis-indolyl, tris-indolyl, di(bis-indolyl), tri(bis-indolyl), and tetra(bis-indolyl)methanes under solid-state conditions by pulverization-activation method at room temperature with excellent yields. The remarkable features of this new procedure are high conversions, shorter reaction times, cleaner reaction profiles, and simple experimental and work-up procedures.

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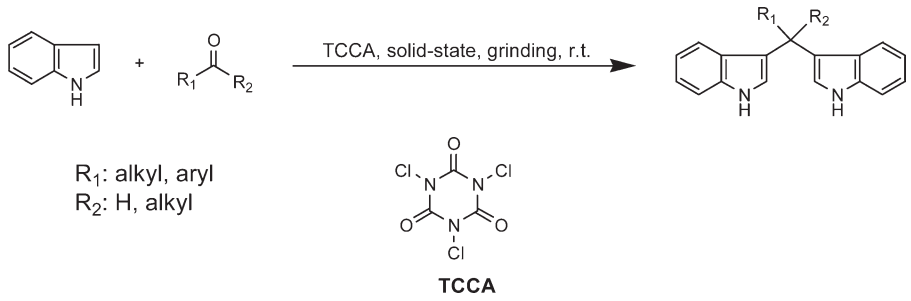
INTRODUCTION

The development of bis(indolyl)alkane synthesis has been of considerable interest in organic synthesis because of their wide occurrence in various natural products possessing biological activity and usefulness for drug design [1]. Bis(indolyl)methanes are found in cruciferous plants and are known to promote beneficial estrogen metabolism [2] and induce apoptosis in human cancer cell. Thus, the development of facile and environmentally friendly synthetic methods for the preparation of these compounds constitutes an active area of investigation in pharmaceutical and organic synthesis [3–5].

Synthetically the reaction of 1H-indole with aldehydes or ketones produces azafulvenium salts that react further with a second 1H-indole molecule to form bis(indol-3-yl)methanes [6]. In recent years, synthesis of this class of molecules under mild conditions have been reported, with promoters, such as montmorillonite clay K-10 [7], trichloro-1,3,5-triazine [8], $AlPW_{12}O_{40}$ [9], sodium dodecyl sulfate [10], $ZrCl_4$ [11], H_2NSO_3H [12], I_2 [13], zeolites [14], bentonite [15], $In(OTf)_3$/ionic liquid [16], $CuBr_2$ [17], $Dy(OTf)_3$/ionic liquid [18], $HClO_4$-SiO_2 [19], $InCl_3$ [20], MW/Lewis acids ($FeCl_3$, $BiCl_3$, $InCl_3$, $ZnCl_2$, $CoCl_2$) [21], $NaHSO_4$ and Amberlyst-15 [22], sulfated zirconia [23], $ZrOCl_2/SiO_2$ [24], silica sulfuric acid [25], TiO_2 [26], $(NH_4)_2HPO_4$ [27], acidic ionic liquid [28], $NaBF_4$ [29], metal hydrogen sulfates [30], tetrabutylammonium tribromide [31], superacid SO_4^{2-}/TiO_2 [32], $NaHSO_4$/ionic liquid [33], NBS [34], Ph_3CCl [35], $H_3PW_{12}O_{40}$ [36], $LiClO_4$ [37], Zr(DS)4 [38], and $Bi(NO_3)_3.5H_2O$ [39]. However, most of the existing methods involve toxic metal ions and solvent, high cost and cumbersome work-up procedures. Consequently, new procedures that address these drawbacks are desirable. Although TCCA has been produced on large scale for use in household and industry since the 1950s, it has never had a real breakthrough in organic chemistry laboratories. It also has not found its way into textbooks in

Scheme 1



organic chemistry and even books on heterocyclic chemistry fail to mention this very useful reagent. Also there is a nice article review by Tilstam [40] that they have shown that trichloroisocyanuric acid (TCCA) is a safe and efficient reagent, useful for chlorination and oxidation reactions.

RESULTS AND DISCUSSION

In continuation of our interest in the application of N-halo reagents in organic synthesis [41–44], we report the use of TCCA as an catalyst in the electrophilic substitutions of indole with a variety of aldehydes and ketones under solid-state conditions to afford bis(indolyl)methanes by pulverization-activation method at room temperature with excellent yields (Scheme 1).

As TCCA contain chlorine atoms, which are attached to nitrogen atoms, it is also possible that it release Cl^+ *in situ*, which can act as Lewis acid to activate the carbonyl oxygen to form the bis-indole derivatives.

First, we examined the TCCA in the model reaction of indole with benzaldehyde in different reaction media to investigate the best conditions. The results are summarized in the Table 1 and show that under solvent-free conditions TCCA (0.1 mmol) led to the best result (Table 1, Entry 8). However, the solvent-free (grinding at solid-state condition) was found to be best for the catalytic reaction at room temperature in terms of yield, reaction time, and product isolation.

These results promoted us to investigate the scope and the generality of this new protocol for various aldehydes and ketones under optimized conditions. As shown in Table 2, a series of aromatic, aliphatic and heterocyclic aldehydes underwent electrophilic substitution reaction with indole smoothly to afford a wide range of substituted bis(indolyl)methanes in good to excellent yields. The electron deficiency and nature of the substituents on the aromatic ring effect the conversion rate; aromatic aldehydes having electron-withdrawing groups on the aromatic ring (Table 2, entries 10, 11) react slower than electron-donating groups (Table 2, entries 4, 8, 9, 12). Furthermore, unsaturated aldehydes, such as cinnamaldehyde, give the corresponding bis(indolyl)methanes without polymerization or halogenation under the above reaction conditions. Ketones required longer reaction times, which is most probably because of the electron-donating and steric effects of the methyl group.

This reaction was further explored for the synthesis of tri-indolylmethane (**3**), (**4**) by the condensation of indol-3-carbaldehyde (**1**) or isatin (**2**) with two equivalents of indole under similar conditions with our method in good yields (Scheme 2).

Selective condensation of a dialdehyde, that is, terephthaldialdehyde to the corresponding bis-indolyl methane was achieved by controlling the molar ratio of indole (Scheme 3). The results showed that addition of 2 equivalents of indole to terephthaldialdehyde, gives (**5**) in good yield (Scheme 3). Treatment of 4 equivalents of indole with terephthaldialdehyde gives the corresponding di(bis-indolyl methanes), (**6**) in excellent yield at room temperature under same conditions [38].

This reaction was further explored for the synthesis of tri(bis-indolyl)methane (**8**) and tetra(bis-indolyl)methanes (**10**) as new triarylmethanes, by the condensation of aldehyde (**7**) with 6 equivalents indole and aldehydes (**9**) with 8 equivalents indole under similar condition (solid-state, grinding) in high yields (Schemes 4 and 5).

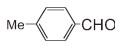
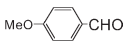
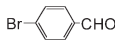
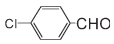
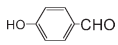
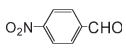
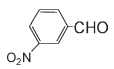
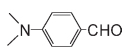
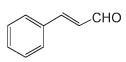
Table 1

Screening of the reaction conditions for the synthesis of bis(indolyl)methane by reaction of benzaldehyde and indole.

Entry	Condition	Time	Yield (%)
1	MeCN/no reagent	12 h	0
2	MeCN/(0.1 mmol) TCCA	1 h	95
3	CH_2Cl_2/(0.1 mmol) TCCA	2 h	85
4	$CHCl_3$/(0.1 mmol) TCCA	2 h	80
5	EtOH/(0.1 mmol) TCCA	1.5 h	90
6	MeCN/(0.2 mmol) TCCA	1 h	95
7	Solvent-free/(0.05 mmol) TCCA/grinding	5 min	90
8	Solvent-free/(0.1 mmol) TCCA/grinding	1 min	98
9	Solvent-free/(0.2 mmol) TCCA/grinding	1 min	98

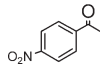
Table 2

Synthesis of bis(indolyl)methanes by the reaction of indole with aldehydes and ketones under solid-state conditions.

Entry	Carbonyl compound	Time (min)	Yield (%)[a]	m.p. (°C)	m.p. (°C) [Lit.]
1		1	98	124–125	124–125 [45]
2		1.5	95	94–95	93–94 [10]
3		1	98	134–136	133–135 [39]
4		1.2	96	190–192	192–193 [45]
5		3	90	110–112	112–113 [38]
6		2	96	76–78	78–80 [45]
7		1	98	70–72	70–71 [10]
8		2	85	>300	>300 [10]
9		3	90	123–125	123–125 [46]
10		5	80	218–220	217–220 [10]
11		4.5	85	258–260	260–261 [47]
12		3	80	224–226	225–226 [39]
13		3	85	98–100	98–99 [10]
14		2.5	80	151–154	150–153 [10]
15		5	75	121–123	122–124 [38]

(*Continued*)

Table 2
(*Continued*)

Entry	Carbonyl compound	Time (min)	Yield (%)[a]	m.p. (°C)	m.p. (°C) [Lit.]
16		4	85	165–167	166–168[38]
17		5	80	190–192	190–191 [38]
18		5	75	115–116	114–116 [39]

[a] Products were characterized from their physical properties, comparison with authentic samples and by spectroscopic methods.

3-Substituted indole was examined for this reaction under the above reaction conditions with aldehydes (Scheme 6). As the more active site (C-3) in indole was blocked in this case electrophilic substitution took place at C-2 in indole giving the corresponding bis(indolyl)-methane in high yield under solid-state conditions.

The chemo selectivity of the present method is also demonstrated by competitive reactions of indol with arylaldehydes in the presence of aliphatic ones and ketones. For example, when a 1:1 mixture of benzaldehyde and propionaldehyde was allowed to react with 2 equivalents of indole in the presence of TCCA under grinding conditions, it was found that the arylaldehydes was chemo selectively converted to the corresponding bis(indolyl)methane but the aliphatic ones was converted slightly. Also, in an equimolar mixture arylaldehyde and ketone, only arylaldehyde was converted to the corresponding bis(indolyl)methane, whereas ketone remained (Scheme 7). The reaction was clean and the products were obtained in high yields without the formation of any side products, such as N-alkylated products.

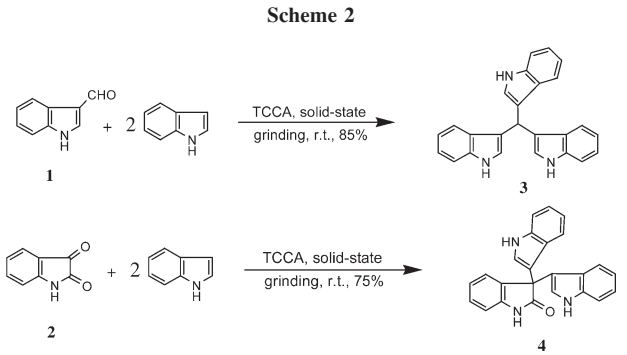
CONCLUSIONS

In conclusion, we have introduced TCCA as a catalytic reagent for the efficient preparation of bis-indolyl, tris-indolyl, di(bis-indolyl), tri(bis-indolyl), and tetra(bis-indolyl)methanes from indole with various aldehydes and ketones under solid-state conditions by pulverization-activation method at room temperature with excellent yields. This method is applicable to a wide range of aldehydes, including aromatic, aliphatic, α,β-unsaturated, heterocyclic substrates, and ketones. In addition, efficiency, mild reaction conditions, easy work up, simplicity and chemoselectivity of this protocol provide a fast, green, and low cost procedure for the synthesis of these compounds.

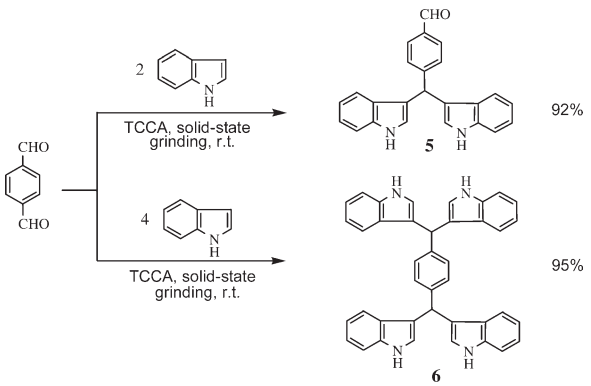
EXPERIMENTAL

Synthesis of bis(indolyl)methanes in solid-state grinding catalyzed by TCCA. A mixture of indole (2.0 mmol), aldehyde or ketone (1.0 mmol), and TCCA (0.1 mmol) were

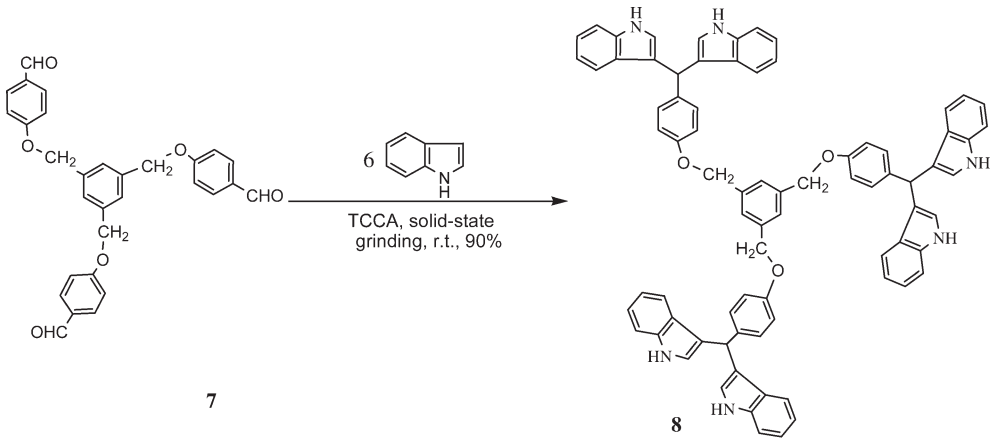
Scheme 2



Scheme 3



Scheme 4



added to a mortar and the mixture was pulverized with a pestle. A spontaneous reaction took place [1–5 min, Table 2, monitored by TLC (4:1, hexane/ acetone)]. After completion of the reaction, CH_2Cl_2 (10 mL) was added, and insoluble reagents were removed by filtration. The filtrate was evaporated under reduced pressure and the resulting crude material was purified by recrystallization from ethanol-water to afford pure products.

3,3′-Bisindolyl-phenylmethane (Table 2, entry 1) Pink solid, m.p.: 124–125°C; IR (KBr): 3402, 3050, 2986, 1615, 1600, 1455, 1112 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ_H (ppm) 5.88 (s, 1H), 6.68 (s, 2H), 7.13–7.45 (m, ArH, 13H), 7.95 (br s, NH, 2H); ^{13}C NMR ($CDCl_3$): δ_c (ppm) 31.6, 110.9, 111.9, 118.4, 119.5, 1121.2, 124.0, 126.3, 127.1, 128.5, 128.6, 137.0, 145.2; MS: *m*/*z* 322.

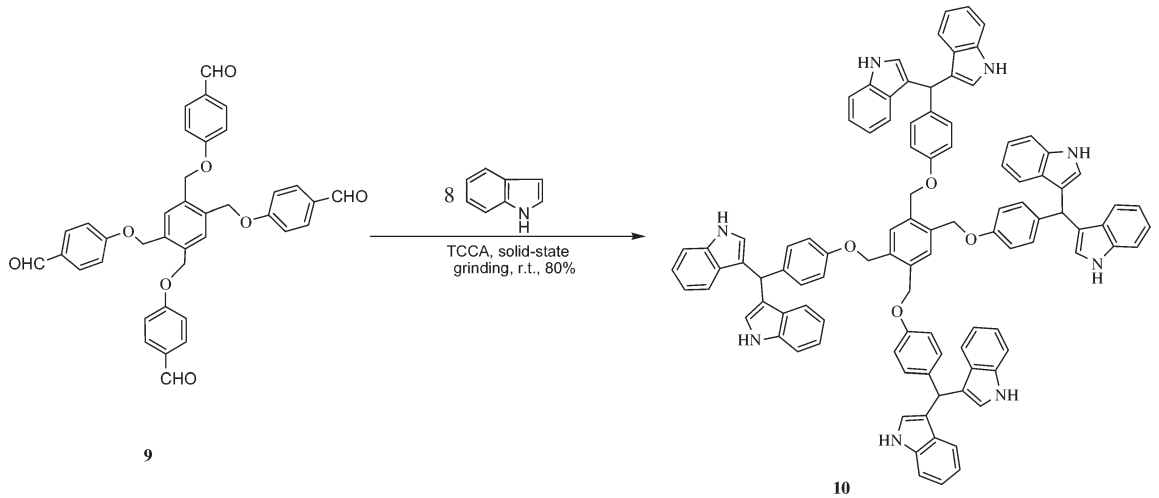
3,3′-Bisindolyl-4-methylphenylmethane (Table 2, entry 2) Pinkish solid, m.p.: 94–95°C; IR (KBr): 3452, 3112, 3045, 2950, 1604, 1523, 1210, 1052, 765 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ_H (ppm) 2.38 (s, 3H), 5.85 (s, 1H), 6.70–7.55 (m, ArH, 14H), 7.85 (br s, NH, 2H); MS: *m*/*z* 336; *Anal*. Calcd. for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.45; H, 5.88; N, 8.14.

3,3′-Bisindolyl-2-methoxylphenylmethane (Table 2, entry 3) Red solid, m.p.: 134–136°C; IR (KBr): 3408, 3056, 2932, 1597, 1486, 1450, 1335, 1102, 745 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ_H (ppm) 3.82 (s, 3H), 6.32 (s, 1H), 6.61 (s, 2H), 6.81–7.40 (m, ArH, 12H), 7.80 (br s, NH, 2H); ^{13}C NMR ($CDCl_3$): δ_c (ppm) 32.3, 56.0, 110.0, 110.8, 111.1, 119.2, 119.8, 120.2, 120.6, 121.9, 123.7, 127.2, 129.9, 132.5, 136.9, 157.1; *Anal*. Calcd. for $C_{24}H_{20}N_2O$: C, 81.79; H, 5.72; N, 7.95. Found: C, 81.24; H, 5.45; N, 7.86.

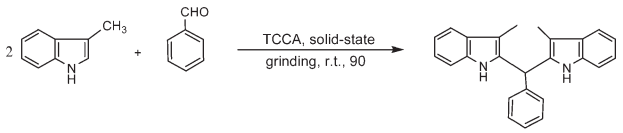
3,3′-Bisindolyl-4-methoxyphenylmethane (Table 2, entry 4) Pinkish solid, m.p. 190–192°C; ^1H NMR (90 MHz, $CDCl_3$): δ_H (ppm) 3.84 (s, 3H), 5.90 (s, 1H), 6.64–7.65 (m, ArH, 14H), 7.80 (br s, NH, 2H); ^{13}C NMR (ppm): 39.7, 55.6, 111.5, 114.0, 119.6, 120.4, 120.4, 122.3, 123.9, 127.5, 130.0, 136.7, 137.1, 158.3.

3,3′-Bisindolyl-4-bromophenylmethane (Table 2, entry 5) Pink solid, m.p.: 110–112°C; IR (KBr): 3410, 3054, 1487, 1455, 1089 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ_H (ppm) 6.66

Scheme 5



Scheme 6



11

(s, 2H), 7.02–7.45 (m, ArH, 12H), 7.85 (br s, NH, 2H); MS: *m*/*z* 361.

3,3′-Bisindolyl-4-chlorophenylmethane (Table 2, entry 6) Pink solid, m.p.: 76–78°C; IR (KBr): 3409, 2958, 1456, 1488; ^{1}H NMR (300 MHz, acetone-d_6) δ(ppm): 5.90 (s, 1H), 6.82 (s, 2H), 6.89–7.39 (m, 12H), 9.99 (s, 2H, N—H); ^{13}C NMR (75 MHz, acetone-d_6) δ(ppm): 40.8, 112.1, 119.2, 120.1, 120.3, 121.9, 124.5, 128.1, 129.2, 138.0, 143.4.

3,3′-Bisindolyl-2-chlorophenylmethane (Table 2, entry 7) Pinkish solid, m.p.: 70–72; ^{1}H NMR ($CDCl_3$): 7.89 (br s, 2H), 7.07–7.51 (m, 12H), 6.53 (s, 2H), 6.36 (s, 1H); ^{13}C NMR ($CDCl_3$): (36.9, 110.1, 111.3, 119.3, 119.8, 122.0, 124.0, 126.7, 127.0, 128.3, 30.4, 130.7, 135.3, 136.7, 141.5.

3,3′-Bisindolyl-2-furylmethane (Table 2, entry 8) Pale red solid, m.p.: >300; ^{1}H NMR ($CDCl_3$): 7.74 (br s, 2H), 7.32–7.63 (m, 9H), 7.09 (s, 2H), 6.21–6.35 (m, 2H), 5.82 (s, 1H); ^{13}C NMR ($CDCl_3$): d 41.2, 102.1, 110.3, 111.8, 112.6, 119.4, 120.3, 121.5, 122.6, 131.0, 136.4, 141.2, 152.0.

3,3′-Bisindolyl-4-hydroxyphenylmethane (Table 2, entry 9) Pink solid, m.p.: 123–125°C; IR (KBr): 3420, 3239, 1455, 1511, 1616 cm^{-1}; ^{1}H NMR (DMSO): 7.58 (br s, 2H), 6.69–7.24 (m, 13H), 6.67 (s, 2H), 5.85 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ(ppm): 31.12, 111.89, 115.28, 118.58, 119.19, 119.71, 121.30, 123.89, 127.17, 129.66, 135.71, 136.93, 137.10, 155.79.

3,3′-Bisindolyl-4-nitrophenylmethane (Table 2, entry 10) Red solid, m.p.: 218–220; ^{1}H NMR ($CDCl_3$): 8.19 (d, 2H, *J* = 7.81), 7.76 (br s, 2H), 7.40–7.58 (m, 10H), 7.03 (s, 2H), 6.05 (s, 1H); ^{13}C NMR ($CDCl_3$): d 44.5, 110.0, 112.1, 119.6, 119.8, 120.9, 121.3, 121.9, 130.2, 133.8, 136.2, 143.1, 145.2.

3,3′-Bisindolyl-3-nitrophenylmethane (Table 2, entry 11) Pinkish solid, m.p.: 258–260; ^{1}H NMR ($CDCl_3$): 8.46 (br s, 2H), 7.02–7.87 (m, 12H), 6.61 (s, 2H), 5.34 (s, 1H); ^{13}C NMR ($CDCl_3$): d 34.9, 111.5, 111.6, 119.5, 120.7, 121.9, 122.2, 124.3, 126.8, 129.6, 131.2, 132.6, 134.2, 136.8, 149.7.

3,3′-Bisindolyl-4-(N,N-dimethyl)phenylmethane (Table 2, entry 12) Pinkish solid, m.p.: 224–226; ^{1}H NMR (90 MHz, $CDCl_3$): δ_H (ppm) 3.28 (s, 6H), 5.75 (s, 1H), 6.76–7.84 (m, ArH, 14H), 7.82 (br s, NH, 2H); MS: *m*/*z* 365.

3,3′-Bisindolyl-1-(2-phenylethylene)methane (Table 2, entry 13) Pinkish solid, m.p.: 98–100; ^{1}H NMR (90 MHz, $CDCl_3$): 5.92–6.07 (m, 2H), 5.76 (m, 1H), 6.71 (s, 2H), 6.89–7.68 (m, 15H), 8.02 (br s, 2H, NH); MS: *m*/*z* 348.

3,3′-Bisindolyl-[2]thienylmethane (Table 2, entry 14) Brown solid, m.p.: 151–154°C; IR (KBr): 3412, 1715, 1452, 1260, 1105 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$): δ_H (ppm) 6.18 (s, 1H), 6.87 (s, 2H), 6.92–7.48 (m, ArH, 11H), 7.98 (br s, NH, 2H); *Anal*. Calcd. for $C_{21}H_{16}N_2S$: C, 76.80; H, 4.91; N, 8.53. Found: C, 76.52; H, 5.10; N, 8.35.

3,3′-Bisindolyl-1-butylmethane (Table 2, entry 15) Pale red solid, m.p.: 121–123; ^{1}H NMR (90 MHz, $CDCl_3$): 0.80 (t, *J* = 6.7 Hz, 3H), 1.25–1.29 (m, 6H), 4.62 (t, *J* = 6.7 Hz, 1H), 6.80 (d, *J* = 2.5 Hz, 2H), 6.89–7.68 (m, 8H), 8.12 (br s, 2H, NH); MS: *m*/*z* 302.

3,3′-Bisindolyl-1-methyl-1-phenylmethane (Table 2, entry 16) Pinkish solid, m.p.: 165–167°C; ^{1}H NMR (90 MHz, $CDCl_3$): 2.40 (s, 3H), 6.67 (s, 2H), 6.95–7.43 (m, 13H), 7.91 (br s, 2H, NH); MS: *m*/*z* 336.

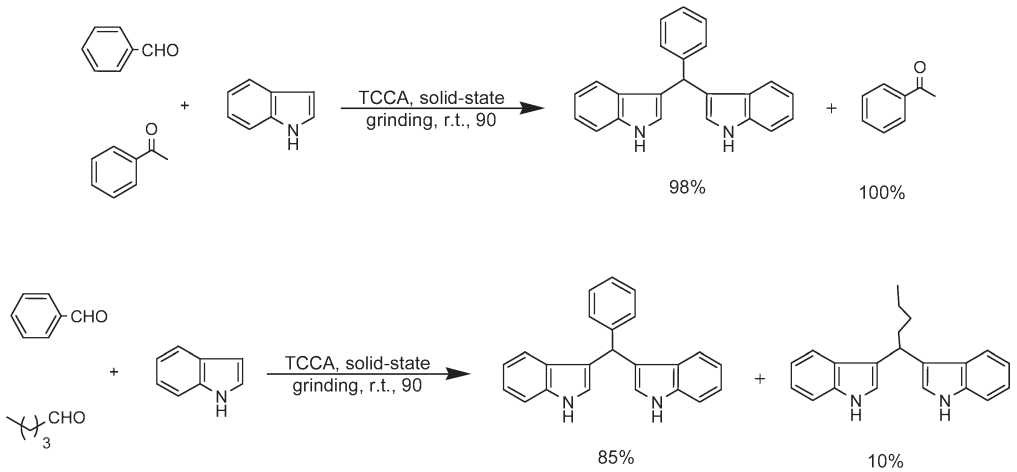
3,3′-Bisindolyl-1-methyl-1-(4-nitro)phenylmethane (Table 2, entry 17) Pink solid, m.p.: 190–192; ^{1}H NMR (90 MHz, $CDCl_3$): 2.46 (s, 3H), 6.78 (s, 2H), 6.79–7.68 (m, 12H), 7.98 (br s, 2H, NH); MS: *m*/*z* 381.

3,3′-Bisindolyl-[1,1]cyclohexane (Table 2, entry 18) Red solid, m.p.: 115–116°C; IR (KBr): 3478, 3020, 2935, 1603, 1522, 1421, 1335, 1216, 1099, 1017, 758, 699 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$): δ_H (ppm) 1.56 (m, 6H), 2.48 (m, 4H), 6.81 (s, 2H), 7.03–7.65 (m, 8H), 7.84 (br s, NH, 2H).

Analytical data for compound tri-indolylmethane (3). Pale yellow solid, m.p.: 255–257°C (Lit. 256—258°C [48]); ^{1}H NMR (90 MHz, DMSO-d_6): δ_H (ppm) 9.67 (br s, 2H), 6.24 (s, 3H), 6.27–6.87 (m, 12H), 5.47 (s, 1H); IR (KBr): 3403, 3043, 2918 cm^{-1}; MS: *m*/*z* 361.

Analytical data for compound (4). White solid, m.p.: >300°C (Lit. >300°C [49]); ^{1}H NMR (90 MHz, DMSO-d_6): δ_H (ppm) 9.98 (br s, 2H), 9.81 (br s, 1H), 6.45 (m, 2H), 6.52–

Scheme 7



6.93 (m, 12H); ^{13}C NMR (90 MHz, DMSO-d_6): δ_c (ppm) 200.8, 160.5, 137.4, 136.8, 125.5, 124.4, 123.9, 121.0, 120.5, 118.3, 117.7, 117.0, 113.9, 111.7, 111.5; MS: *m*/*z* 364.

Analytical data for compound (6). Pink solid, m.p.: 194–195°C; FTIR (KBr): 3405, 3049, 1622, 1455, 1216 cm^{-1}; ^{1}H NMR (90 MHz, DMSO-d_6): δ_H (ppm) 5.75 (s, CH, 1H), 6.29 (s, 4H), 7.05–7.40 (m, CH aromatic, 20H), 7.31 (br s, NH, 4H); ^{13}C NMR (90 MHz, DMSO-d_6): δ_c (ppm) 142.5, 136.7, 128.1, 126.8, 123.6, 120.9, 119.2, 118.4, 118.3, 111.5, 29.1; MS: *m*/*z* 566.200.

Analytical data for compound (8). Light red solid, m.p.: 208–210°C; IR (KBr): 3421, 2950, 2900, 1635, 1506, 1457, 1377, 1216, 1173, 1082, 742 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 5.01 (s, CH_2 benzylic, 6H), 5.72 (s, CH, 3H), 6.74–7.50 (m, CH aromatic, 46H), 10.71 (s, NH, 6H); ^{13}C NMR (300 MHz, DMSO-d_6): δ_c (ppm) 40.08, 69.48, 111.85, 114.67, 115.24, 118.54, 118.82, 119.58, 121.25, 123.87, 127.05, 129.66, 137.03, 137.73, 138.15, 156.91; *Anal*. Calcd. for $C_{78}H_{60}N_6O_3$: C, 82.95; H, 5.35; N, 7.44. Found: C, 82.52; H, 5.21; N, 7.36.

Analytical data for compound (10). Red solid, m.p.: 250–251°C d; IR (KBr): 3417, 2926, 2854, 1609, 1506, 1456, 1413, 1338, 1218, 1172, 1127, 1012, 743 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 5.08 (s, CH_2 benzylic, 8H), 5.76 (s, CH, 4H), 6.82–7.65 (m, CH aromatic, 60H), 10.70 (s, NH, 8H); ^{13}C NMR (300 MHz, DMSO-d_6): δ_c (ppm) 41.05, 70.40, 111.45, 114.52, 115.12, 117.85, 118.85, 119.26, 120.85, 122.82, 126.65, 129.26, 136.76, 137.43, 138.63, 157.43; *Anal*. Calcd. for $C_{102}H_{78}N_8O_4$: C, 82.79; H, 5.31; N, 7.57. Found: C, 82.12; H, 5.20; N, 7.35.

2,2′-Bisindolyl-phenylmethane (11). ^{1}H NMR (90 MHz, DMSO-d_6): δ_H (ppm) 7.94 (br s, 2H), 7.22–7.66 (m, 13H), 6.04 (s, 1H), 2.23 (s, 6H); *Anal*. Calcd. for $C_{25}H_{22}N_2$: C, 85.68; H, 6.33; N, 7.99. Found: C, 85.43; H, 5.95; N, 7.68; MS: *m*/*z* 350.

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