An Improved Synthesis of Carbazoles *via* Domino Reaction of *N*-Protected-2-methylindoles with DMF-DMA/DMA-DMA

Radhakrishnan Sureshbabu and Arasambattu K. Mohanakrishnan*

Department of Organic Chemistry, University of Madras, Guindy Campus,
Chennai 600 025, Tamil Nadu, India
*E-mail: mohanakrishnan@unom.ac.in

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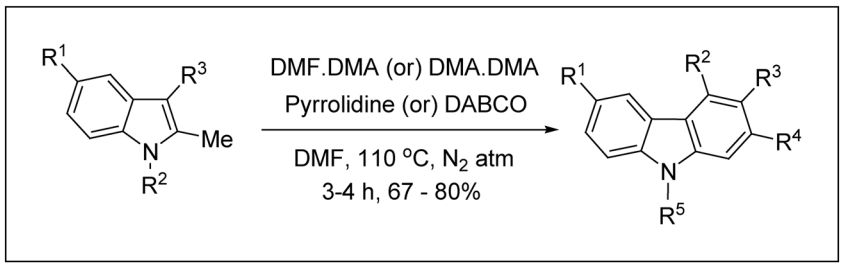

An efficient synthesis of carbazole analogs has been achieved *via* interaction of *N*-protected-2-methylindoles with *N,N*-dimethylformamide dimethylacetal as well as *N,N*-dimethylacetamide dimethylacetal in the presence of pyrrolidine or 1,4-diazabicyclo(2.2.2)octane (DABCO).

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INTRODUCTION

Development of new methods for the synthesis of carbazole and its derivatives is of current interest because increasing number of carbazole alkaloids have displayed varied biological activities [1–3]. Recently, the synthesis of benz-annulated carbazoles received considerable attention due to their antitumor [4] and anti-inflammatory activities [5]. The carbazole derivatives are also widely useful owing to their photorefractive, photoconductive, hole-transporting, and light-emitting properties [6]. The dihydroindolo carbazole derivatives could be used as active materials for organic light-emitting diodes [7], organic field-effect transistors [8], organic thin-film transistors [9], and photovoltaic cells [10]. Over the years, the thermal electrocyclization methodology has been widely used for the synthesis of carbazole-based natural products [11]. Recently, Konakahara and coworkers [12] described a Me_3SiCl-mediated three-component coupling reaction of a functionalized enamine, *N,N*-dimethylformamide diethylacetal, and an internal alkyne having an electron withdrawing group to afford pyridine derivatives. Tois *et al*. [13] reported a rapid two-step synthesis of 4(1*H*)quinolones *via* interaction of *o*-nitroacetophenone with *N,N*-dimethylformamide•dimethylacetal (DMF-DMA) followed by reductive cyclization. Hua *et al*. [14] synthesized disubstituted dihydronaphthalenes with high yields by the cycloaddition of vinylarenes with electron-deficient alkynes in the presence of DMF-DMA.

RESULTS AND DISCUSSION

In continuation of our interest on annulated carbazole analogs [15], we have reported [16] the synthesis of substituted carbazoles **2** in moderate yields *via* interaction of 1-phenylsulfonyl-2/(3)-methyl-3/(2)-vinylindoles **1** with DMF-DMA/*N,N*-dimethylacetamide dimethylacetal (DMA-DMA) (Scheme 1).

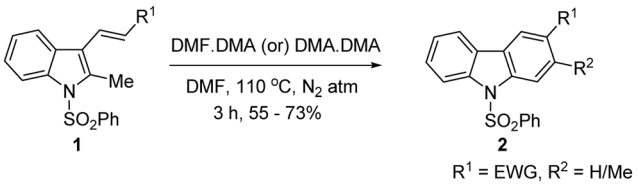
Even though this methodology was found to be facile with a variety of 2-methyl-3-vinylindoles **1**, carbazoles **2** could be obtained only in moderate yields. Hence, to increase the yields of the substituted carbazoles, different reaction parameters including solvent and reaction temperature were varied. But these variations were found to be of no use. Finally, the use of pyrrolidine was proved pivotal for the formation of desired products in good yields. Thus, the reaction of 2-methylindoles **1a–d** with 2 equiv of DMF-DMA or DMA-DMA in the presence of pyrrolidine afforded substituted carbazoles in 67–80% yields (Scheme 2).

It has been proved that the use of highly reactive pyrrolidine acetal or *in situ* generation of the same *via* addition of pyrrolidine with DMF-DMA has significantly enhanced the rate of enamine formation [17]. Hence, we reasoned that the better yield of **2a–d/3a–c** obtained in the presence of pyrrolidine might be due to the enhanced rate of formation of the required enamine (Scheme 3).

A list of various types of 2-methylindoles **1a–d** used, reaction conditions, the respective carbazoles **2a–d/3a–c**, and the yields obtained are summarized in Table 1.

Always enhanced yields of carbazoles were obtained when the domino reaction of 2-methylindole was performed in the presence of pyrrolidine. The reaction of 2-methyl-3-vinylester indoles **1a–b** with DMF-DMA/DMA-DMA afforded the corresponding carbazoles **2a** and **2b/3a** and **3b** in better yields (entry 1 and 2), and

Scheme 1. Annulation of 2-methylindole **1** with DMF-DMA/DMA-DMA.

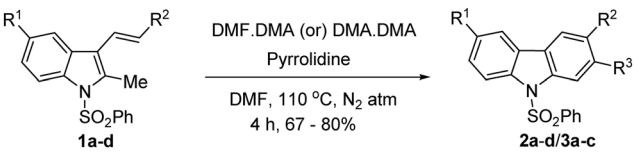


also enhanced yield of the carbazole **2c/3c** was obtained with the 5-methoxyindole **1c** (entry 3). Always, the interaction of 2-methyl-3-vinylindoles **1a–c** with DMF-DMA gave carbazoles **2a–c** in better yields than the corresponding carbazoles **3a–c** obtained using DMA-DMA. Similarly, the reaction of 2-methylindole having vinyl ketone functionality at the indol 3-position **1d** with DMF-DMA furnished the respective carbazole **2d** in 67% yield (entry 4).

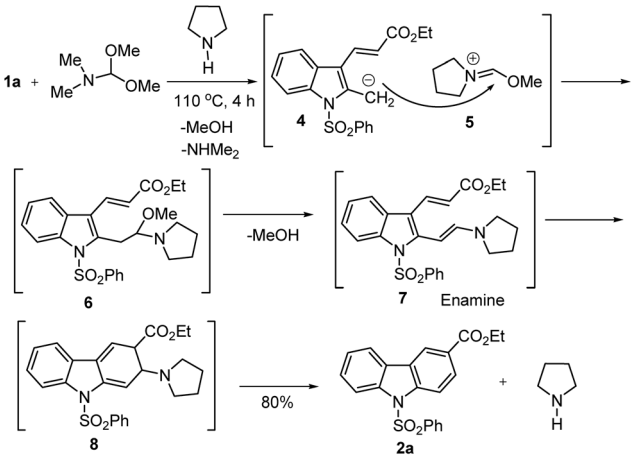
As a representative case, the domino reaction of 2-methyl-3-vinylindole **1b** with DMF-DMA in the presence of 0.2 equiv of DABCO afforded *N*-phenylsulfonyl cleaved carbazole **9a** in 62% yield. Gratifyingly, when the interaction of **1b** was performed with DMF-DMA in the presence of 1 equiv of DABCO gave *N*-methylated carbazole **9b** in 63% yield. However, the interaction of **1b** with DMA-DMA in the presence of 1 equiv of DABCO led to the isolation of *N*-methylated-2-methyl-3-vinyl indole **10** (Scheme 4).

The annulation of 1-phenylsulfonyl-2-methyl-3-acetyl indole **1e** with DMF-DMA at 110°C for 4 h led to the isolation of *N*-phenylsulfonyl-4-hydroxycarbazole-3-carboxaldehyde **11** in 65% yield. In our earlier report [16b], we wrongly assigned the structure as *N*-phenylsulfonyl-4-hydroxycarbazole-1-carboxaldehyde **12**. The structure of *N*-phenylsulfonyl-4-hydroxycarbazole-3-carboxaldehyde **11** was confirmed by matching its melting point and spectral data with an authentic sample prepared using Michael addition methodology [18]. The annulation of **1e** with DMF-DMA in the presence of pyrrolidine has slightly increased the yield of the carbazole **11**. The interaction of **1e** with DMF-DMA in presence of DABCO led to the isolation of 4-hydroxycarbazole-3-carboxaldehyde **13** in 68% yield. The initial reaction of **1e** with DMF-DMA may lead to the formation of bis-enamine **14**. Electrocyclization of enamine **14** followed by the elimination of dimethyl amine and subsequent work up led to the formation of compound **11** (Scheme 5).

Scheme 2. Tandem reaction of 2-methylindoles **1a–d** with DMF-DMA/DMA-DMA in the presence of pyrrolidine.



Scheme 3. Mechanistic rationale for the formation of **2a.**



Surprisingly, the reaction of **1e** with DMA-DMA at 110°C gave 4-amino carbazole **16** in 52% yield. The mechanism of formation of amino carbazole **16** can be visualized through intramolecular Michael addition of carbanion **17** followed by the addition of dimethylamide and subsequent elimination of water molecule (Scheme 6).

The domino reaction of 2-methyl-3-vinylnitro indole **1f** [19] with DMF-DMA at 110°C for 4 h yielded 3-nitro-2-indolylcarbazole **19** in 48% yield. The formation of **19** can be realized through the Diels–Alder reaction of quino-dimethane intermediate **20** with **1f** to afford intermediate **21**. The latter on elimination of nitromethane may lead to carbazole **19** (Scheme 7).

The annulation of malonylidene tethered 2-methylindole **1g** [11c] with DMF-DMA led to the isolation of carbazole **2a** in 70% yield. The initial reaction of **1g** with DMF-DMA led to the formation of enamine **22**, which on electrocyclization followed by elimination of ethyl dimethylcarbamate gave the carbazole **2a** (Scheme 8).

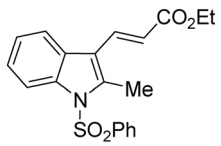
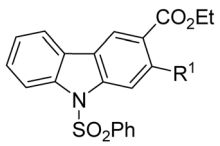
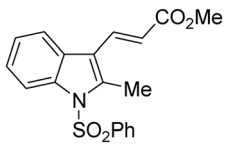
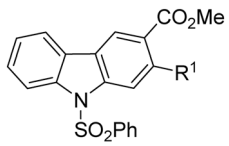
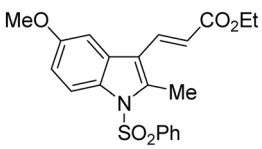
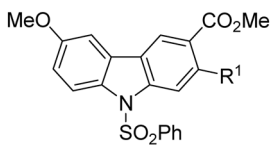
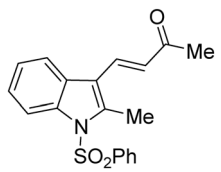
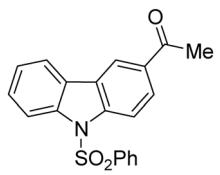
Finally, the reaction of 3-carbethoxy 2-methylindole **1h** with DMF-DMA/DMA-DMA afforded indolylmethyl aldehyde **24**/*N*-methylated indole **25** in 75 and 59% yields, respectively, whereas 2-methyl-3-benzoylindole **1i** on reaction with DMF-DMA gave an inseparable mixture of indolylmethyl aldehyde **26** and enamino indole **27** (Scheme 9).

CONCLUSIONS

In conclusion, we have achieved an improved synthesis of substituted carbazoles *via* interaction of 2-methylindoles **1a–e** with DMF-DMA/DMA-DMA in the

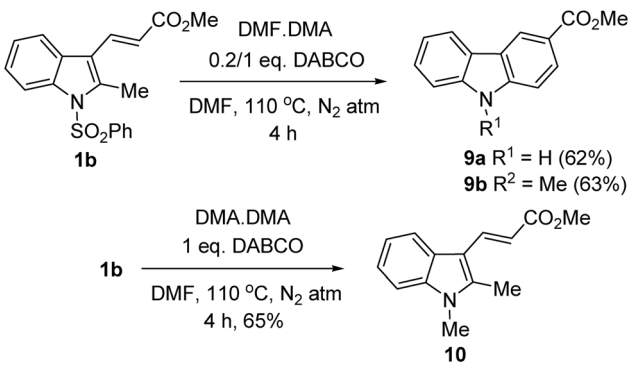
Table 1

Synthesis of substituted carbazoles **2a–d/3a–c**.

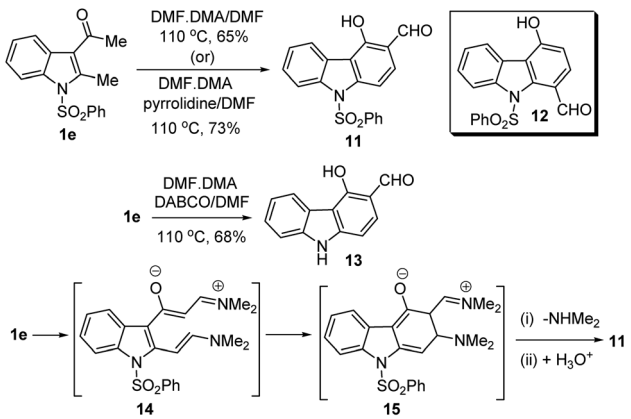
Entry	Vinylindoles	Condition	Carbazole	Yield (%)[a]
1	 **1a**	Pyrrolidine, DMF-DMA Pyrrolidine, DMA-DMA	 **2a** R^1 = H **3a** R^1 = Me	80 75
2	 **1b**	Pyrrolidine, DMF-DMA Pyrrolidine, DMA-DMA	 **2b** R^1 = H **3b** R^1 = Me	78 77
3	 **1c**	Pyrrolidine, DMF-DMA Pyrrolidine, DMA-DMA	 **2c** R^1 = H **3c** R^1 = Me	74 69
4	 **1d**	Pyrrolidine, DMF-DMA	 **2d**	67

[a]Isolated yield after column chromatography.

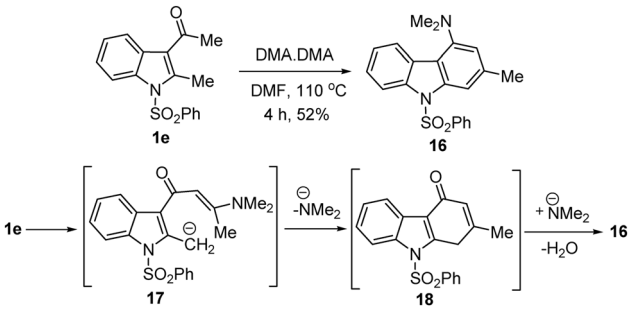
Scheme 4. Tandem reaction of 2-methylindole **1b** with DMF-DMA/DMA-DMA in the presence of DABCO.



Scheme 5. Tandem reaction of 2-methyl-3-acetylindole **1e** with DMF-DMA.



Scheme 6. Tandem reaction of 2-methyl-3-acetylindole **1e** with DMA-DMA.



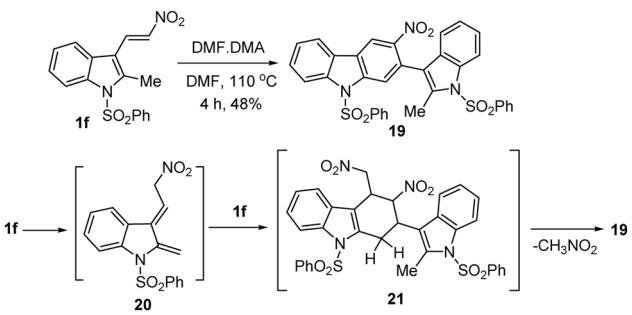
presence of pyrrolidine. As a representative case, the tandem reaction of 2-methylindole **1b** with varying amount of DABCO led to the isolation of *N*-free as well as *N*-methyl carbazoles. Further, the tandem reaction of 2-methylindoles **1e–i** with DMF-DMA/DMA-DMA was also performed. The mechanistic pathways for the formation of carbazole derivatives are also proposed.

EXPERIMENTAL

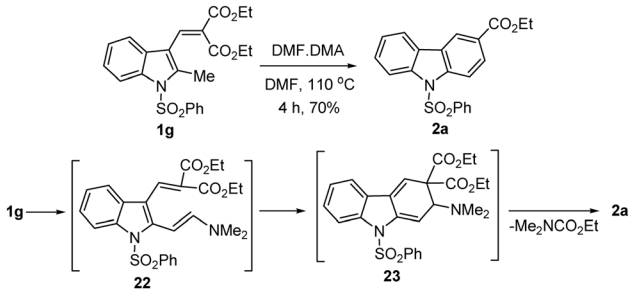
All melting points were uncorrected. Reagents were purchased from commercial sources and used as received without purification. Solvents were dried by standard procedures. Column chromatography was carried on silica gel (grade 60, mesh size 230–400, Merck). IR spectra were recorded on a SHIMADZU FT-IR 8300 instrument. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard on a Bruker-300 spectrometer. Chemical shift values were quoted in ppm, and coupling constants were quoted in Hz. Chemical shift multiplicities were reported as s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Mass spectra were recorded on a JEOL DX 303 HF spectrometer. Elemental analyses were carried out on Perkin-Elmer series II 2400 (IIT Madras) equipment. The required 2-methyl-3-vinylester indoles **1a–d** are prepared from the corresponding 2-methylindole-3-carboxaldehyde following the published procedure [20].

A representative procedure for the domino reaction of 2-methylindoles 1a–d with DMF-DMA/DMA-DMA in the presence of pyrrolidine. To a stirred solution of 2-methyl-3-vinylindoles **1a–d** (1.35 mmol) in dry DMF (1.5 mL), DMF-DMA/DMA-DMA (2.71 mmol) and pyrrolidine (0.5 mL) were

Scheme 7. Tandem reaction of 2-methyl-3-vinylnitro indole **1f** with DMF-DMA.



Scheme 8. Tandem reaction of 2-methylindole **1g** with DMF-DMA.



added. The reaction mixture was heated at 110°C for 4 h under nitrogen atmosphere. It was poured in to crushed ice (50 g) containing few drops of concentrated HCl and extracted with $CHCl_3$ (2 × 20 mL). The combined extracts were washed with water (10 mL), brine (10 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (20% EA/hexane) afforded carbazoles **2a–d**.

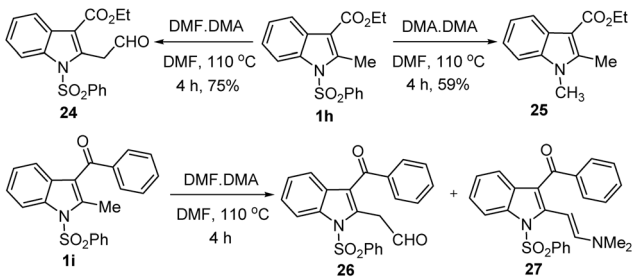
Ethyl 9-(phenylsulfonyl)-9H-carbazole-3-carboxylate (2a). This compound was obtained as colorless solid (0.41 g, 80%), mp: 178–180°C (Lit. [16] 180°C); IR (KBr): 1709 (—CO_2Et), 1369 and 1176 (—SO_2Ph) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.53 (s, 1 H), 8.31–8.25 (m, 2 H), 8.11 (dd, *J* = 1.5 Hz, *J* = 1.5 Hz, 1 H), 7.90 (d, *J* = 7.5 Hz, 1 H), 7.75 (d, *J* = 8.1 Hz, 2 H), 7.49–7.24 (m, 5 H), 4.35 (q, *J* = 7.1 Hz, 2 H), 1.36 (t, *J* = 7.2 Hz, 3 H).

Ethyl 2-methyl-9-(phenylsulfonyl)-9H-carbazole-3-carboxylate (3a). This compound was obtained as colorless solid (0.40 g, 75%), mp: 174–176°C (Lit. [16] 174°C); IR (KBr): 1712 (—CO_2Et), 1360 and 1174 (—SO_2Ph) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.47 (s, 1 H), 8.29 (d, *J* = 8.1 Hz, 1 H), 8.20 (s, 1 H), 7.91 (d, *J* = 7.5 Hz, 1 H), 7.82 (d, *J* = 7.5 Hz, 2 H), 7.51–7.44 (m, 2 H), 7.39–7.31 (m, 3 H), 4.40 (q, *J* = 7.1 Hz, 2 H), 2.80 (s, 3 H), 1.43 (t, *J* = 7.05 Hz, 3 H).

Methyl 9-(phenylsulfonyl)-9H-carbazole-3-carboxylate (2b). This compound was obtained as colorless solid (0.40 g, 78%), mp: 188–190°C (Lit. [16] 188°C); IR (KBr): 1710 (—CO_2Me), 1354 and 1170 (—SO_2Ph) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.61 (d, *J* = 1.5 Hz, 1 H), 8.39–8.32 (m, 2 H), 8.18 (dd, *J* = 1.5 Hz, *J* = 1.5 Hz, 1 H), 7.97 (d, *J* = 7.5 Hz, 1 H), 7.84 (d, *J* = 7.8 Hz, 2 H), 7.54–7.32 (m, 5 H), 3.97 (s, 3 H).

Methyl 2-methyl-9-(phenylsulfonyl)-9H-carbazole-3-carboxylate (3b). This compound was obtained as colorless solid (0.41 g, 77%), mp: 170–172°C (Lit. [16] 171°C); IR (KBr): 1720 (—CO_2Me), 1369 and 1172 (—SO_2Ph) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.51 (s, 1 H), 8.31 (d, *J* = 8.1 Hz, 1 H),

Scheme 9. Tandem reaction of 2-methylindole **1h** and **1i** with DMF-DMA/DMA-DMA.



8.23 (s, 1 H), 7.94–7.84 (m, 3 H), 7.50–7.28 (m, 5 H), 3.96 (s, 3 H), 2.83 (s, 3 H).

Methyl 6-methoxy-9-(phenylsulfonyl)-9H-carbazole-3-carboxylate (2c). This compound was obtained as colorless solid (0.38 g, 74%), mp: 182–184°C (Lit. [16] 183°C); IR (KBr): 1698 (—CO_2Me), 1354 and 1168 (—SO_2Ph) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.52 (s, 1 H), 8.32 (d, *J* = 7.5 Hz, 1 H), 8.19 (t, *J* = 8.2 Hz, 2 H), 7.76–7.72 (m, 2 H), 7.44–7.30 (m, 4 H), 7.10 (d, *J* = 6.6 Hz, 1 H), 3.95 (s, 3 H), 3.88 (s, 3 H).

Methyl 6-methoxy-2-methyl-9-(phenylsulfonyl)-9H-carbazole-3-carboxylate (3c). This compound was obtained as colorless solid (0.37 g, 69%), mp: 174–176°C (Lit. [16] 175°C); IR (KBr): 1702 (—CO_2Me), 1363 and 1166 (—SO_2Ph) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.35 (s, 1 H), 8.11–8.09 (m, 2 H), 7.75–7.68 (m, 3 H), 7.40–7.22 (m, 3 H), 6.98 (d, *J* = 6.9 Hz, 1 H), 3.86 (s, 3 H), 3.80 (s, 3 H), 2.71 (s, 3 H).

3-Acetyl 9-(phenylsulfonyl)-9H-carbazole (2d). This compound was obtained as colorless solid (0.34 g, 67%), mp: 192–194°C (Lit. [16] 192°C); IR (KBr): 1670 (—COMe), 1382 and 1172 (—SO_2Ph) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.59 (s, 1 H), 8.41–8.35 (m, 2 H), 8.11 (d, *J* = 8.7 Hz, 1 H), 7.99 (d, *J* = 8.1 Hz, 1 H), 7.84 (d, *J* = 7.2 Hz, 1 H), 7.55 (t, *J* = 7.3 Hz, 2 H), 7.49–7.42 (m, 2 H), 7.30 (t, *J* = 7.6 Hz, 2 H), 2.70 (s, 3 H).

A representative procedure for the domino reaction of 2-methylindole 1b with DMF-DMA/DMA-DMA in the presence of DABCO. To a stirred solution of 2-methyl-3-vinylindole **1b** (1.40 mmol) in dry DMF (1.5 mL), DMF-DMA/DMA-DMA (2.81 mmol) and DABCO (0.28 mmol; 1.40 mmol of DABCO was taken for **9b** and **10**) were added. The reaction mixture was heated at 110°C for 4 h under nitrogen atmosphere. It was poured in to crushed ice (50 g) containing few drops of concentrated HCl and extracted with $CHCl_3$ (2 × 20 mL). The combined extracts were washed with water (10 mL) and brine (10 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (20% EA/hexane) afforded **9a**, **9b**, and **10**.

Methyl 9H-carbazole-3-carboxylate (9a). This compound was obtained as brown solid (0.20 g, 62%), mp: 170–172°C; IR (KBr): 3226 (—NH), 1706 (—CO_2Me) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.74 (s, 1 H), 8.28 (s, 1 H), 8.08–8.04 (m, 2 H), 7.39–7.34 (m, 3 H), 7.26–7.21 (m, 1 H), 3.90 (s, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 167.8, 142.2, 139.9, 127.4, 126.5, 123.3, 123.1, 122.9, 121.4, 120.6, 120.3, 110.9, 110.1, 51.9. MS (EI) *m*/*z*: 225 [M^+]. Anal. calcd. for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.39; H, 5.11; N, 5.97.

Methyl 9-methyl-9H-carbazole-3-carboxylate (9b). This compound was obtained as colorless solid (0.21 g, 63%), mp: 124–126°C; IR (KBr): 1698 (—CO_2Me) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.63 (s, 1 H), 7.98 (q, *J* = 6.9 Hz, 2 H), 7.35 (t, *J* = 7.65 Hz, 1 H), 7.18–7.12 (m, 3 H), 3.84 (s, 3 H), 3.59 (s, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 167.9, 143.4, 141.5, 127.2, 126.3, 122.8, 122.7, 122.4, 120.6, 120.5, 119.8, 108.8, 107.9, 51.9, 29.1. MS (EI) *m*/*z*: 239 [M^+]. Anal. calcd. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.06; H, 5.68; N, 5.56.

(E)-Methyl 3-(1,2-dimethyl-1H-indol-3-yl)acrylate (10). This compound was obtained as brown solid (0.21 g, 65%), mp: 130–132°C; IR (KBr): 1726 (—CO_2Me) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.89 (d, *J* = 15.9 Hz, 1 H), 7.80–7.77 (m, 1 H), 7.19–7.13 (m, 3 H), 6.33 (d, *J* = 15.6 Hz, 1 H), 3.73 (s, 3 H), 3.57 (s, 3 H), 2.42 (s, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 169.1, 141.8, 137.9, 137.5, 125.6, 122.1, 121.3, 120.0, 111.0, 109.3, 109.0, 51.2, 29.8, 10.6. MS (EI) *m*/*z*: 229 [M^+]. Anal. calcd. for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.09; H, 6.81; N, 5.88.

9-Phenylsulfonyl-4-hydroxycarbazole-3-carbaldehyde (11). This compound was obtained as pale brown solid (0.36 g, 65%), mp: 190–192°C; IR (KBr): 3340 (—OH), 1648 (—CHO), 1366 and 1158 (—SO_2Ph) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 12.01 (s, 1 H), 9.94 (s, 1 H), 8.30 (t, *J* = 7.3 Hz, 2 H), 7.99 (d, *J* = 8.7 Hz, 1 H), 7.86 (d, *J* = 7.8 Hz, 2 H), 7.62 (d, *J* = 8.7 Hz, 1 H), 7.53–7.35 (m, 5 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 195.8, 158.6, 143.9, 137.9, 137.8, 134.2, 132.3, 129.3, 127.2, 126.5, 124.8, 124.7, 123.4, 116.4, 114.6, 114.4, 106.9. MS (EI) *m*/*z*: 351 [M^+]. Anal. calcd. for $C_{19}H_{13}NO_4S$: C, 64.95; H, 3.73; N, 3.99. Found: C, 65.25; H, 3.46; N, 4.30.

4-Hydroxy-9H-carbazole-3-carbaldehyde (13). This compound was obtained as dark brown solid (0.23 g, 68%), mp: 114–116°C; IR (KBr): 3352 (—OH), 3268 (—NH), 1670 (—CHO) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 12.34 (s, 1 H), 9.80 (s, 1 H), 8.29 (d, *J* = 7.8 Hz, 1 H), 7.42 (d, *J* = 8.1 Hz, 1 H), 7.37 (d, *J* = 3.6 Hz, 2 H), 7.29–7.24 (m, 1 H), 7.18 (s, 1 H), 6.94 (d, *J* = 8.4 Hz, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 195.1, 147.2, 131.3, 129.0, 127.9, 126.5, 125.8, 123.2, 121.3, 114.5, 113.5, 110.0, 103.5. MS (EI) *m*/*z*: 211 [M^+]. Anal. calcd. for $C_{13}H_9NO_2$: C, 73.92; H, 4.29; N, 6.63. Found: C, 73.65; H, 4.51; N, 6.35.

A representative procedure for the domino reaction of 2-methylindoles 1e–i with DMF-DMA/DMA-DMA. To a stirred solution of 2-methylindoles **1e–i** (1.40 mmol) in dry DMF (1.5 mL), DMF-DMA/DMA-DMA (2.81 mmol) was added. The reaction mixture was heated at 110°C for 4 h under nitrogen atmosphere. It was poured in to crushed ice (50 g) containing few drops of concentrated HCl and extracted with $CHCl_3$ (2 × 20 mL). The combined extracts were washed with water (10 mL) and brine (10 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (20% EA/hexane) afforded **16**, **19**, **2a**, **24**, **25**, **26**, and **27**.

9-Phenylsulfonyl-N,N,2-trimethylcarbazol-4-amine (16). This compound was obtained as brown solid (0.30 g, 52%), mp: 192–194°C; IR (KBr): 1354 and 1162 (—SO_2Ph) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.29 (d, *J* = 7.5 Hz, 1 H), 7.81 (t, *J* = 7.95 Hz, 3 H), 7.55 (s, 1 H), 7.42 (t, *J* = 7.2 Hz, 1 H), 7.30 (d, *J* = 6.9 Hz, 4 H), 6.55 (s, 1 H), 3.07 (s, 6 H), 2.67 (s, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 150.3, 140.6, 138.1, 138.0, 133.5, 133.4, 128.9, 127.9, 126.4, 124.4, 123.8, 120.8, 114.9, 114.7, 111.7, 95.9, 40.9, 21.2. MS (EI) *m*/*z*: 364 [M^+]. Anal. calcd. for $C_{21}H_{20}N_2O_2S$: C, 69.20; H, 5.53; N, 7.69. Found: C, 68.91; H, 5.77; N, 7.51.

9-Phenylsulfonyl-2-(1-phenylsulfonyl-2-methyl-1H-indol-3-yl)-3-nitro-9H-carbazole (19). This compound was obtained as brown solid (0.22 g, 48%), mp: 232–234°C; IR (KBr): 1508 and 1325 (—NO_2), 1378 and 1180 (—SO_2Ph) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.64 (s, 1 H), 8.41 (d, *J* = 8.4 Hz, 1 H), 8.25 (t, *J* = 4.2 Hz, 2 H), 8.02 (d, *J* = 7.8 Hz, 1 H), 7.84–7.78 (m, 4 H), 7.68–7.31 (m, 9 H), 7.21 (d, *J* = 7.2 Hz, 1 H), 7.02 (d, *J* = 7.5 Hz, 1 H), 2.52 (s, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 139.8, 139.6, 139.1, 137.5, 136.3, 134.5, 133.8, 129.8, 129.4, 129.3, 126.8, 126.5, 126.2, 124.8, 124.7, 124.0, 120.7, 119.1, 118.7, 118.3, 117.2, 115.3, 114.9, 13.6. MS

(EI) *m/z*: 621 [M^+]. Anal. calcd. for $C_{33}H_{23}N_3O_6S_2$: C, 63.75; H, 3.73; N, 6.76. Found: C, 63.43; H, 4.01; N, 6.54.

Ethyl 2-(formylmethyl)-1-phenylsulfonyl-1H-indole-3-carboxylate (24). This compound was obtained as thick brown liquid (0.40 g, 75%), IR (KBr): 1715 (—CO_2Et), 1680 (—CHO), 1386 and 1178 (—SO_2Ph) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 9.75 (s, 1 H), 8.11–8.05 (m, 2 H), 7.85 (d, *J* = 7.5 Hz, 2 H), 7.57 (t, *J* = 7.35 Hz, 1 H), 7.46 (t, *J* = 7.65 Hz, 2 H), 7.35–7.34 (m, 2 H), 4.81 (s, 2 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 1.41 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.1, 164.4, 139.7, 134.5, 129.5, 129.4, 127.5, 126.8, 126.3, 125.5, 124.6, 122.2, 114.2, 60.8, 29.7, 14.3. MS (EI) *m/z*: 371 [M^+]. Anal. calcd. for $C_{19}H_{17}NO_5S$: C, 61.44; H, 4.61; N, 3.77. Found: C, 61.15; H, 4.84; N, 3.52.

Ethyl 1,2-dimethyl-1H-indol-3-carboxylate (25). This compound was obtained as colorless solid (0.19 g, 59%), mp: 96–98°C; IR (KBr): 1695 (—CO_2Et) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.14–8.10 (m, 1 H), 7.31–7.28 (m, 1 H), 7.24–7.21 (m, 2 H), 4.39 (q, *J* = 7.2 Hz, 2 H), 3.70 (s, 3 H), 2.77 (s, 3 H), 1.45 (t, *J* = 7.2 Hz, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 166.2, 145.2, 136.5, 126.5, 121.9, 121.6, 121.4, 109.0, 103.9, 59.3, 29.5, 14.6, 11.8. MS (EI) *m/z*: 217 [M^+]. Anal. calcd. for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.55; H, 7.21; N, 6.23.

2-(3-Benzoyl-1-phenylsulfonyl-1H-indol-2-yl)acetaldehyde (26) and (2-((dimethylamino)methyl)-1-phenylsulfonyl-1H-indol-3-yl)(phenyl)methanone (27). This compound was obtained as thick brown liquid, IR (KBr): 1685 (—CHO), 1660 and 1656 (—CO), 1372 and 1164 (—SO_2Ph) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 9.74 (s, 1 H), 8.24 (t, *J* = 4.65 Hz, 1 H), 8.06 (d, *J* = 8.4 Hz, 1 H), 7.90 (d, *J* = 7.5 Hz, 3 H), 7.77–7.69 (m, 4 H), 7.66–7.57 (m, 2 H), 7.52–7.41 (m, 8 H), 7.35–7.25 (m, 7 H), 7.17–7.10 (m, 2 H), 5.97 (d, *J* = 12.9 Hz, 1 H), 5.50 (d, *J* = 12.6 Hz, 1 H), 4.43 (s, 2 H), 2.51 (s, 6 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 195.8, 150.5, 147.5, 139.1, 138.7, 138.4, 138.2, 136.7, 136.2, 135.7, 134.5, 133.8, 133.3, 131.4, 130.3, 129.6, 129.5, 128.8, 128.6, 128.0, 126.9, 125.3, 124.6, 124.1, 124.0, 122.8, 121.2, 120.0, 114.7, 114.3, 85.5, 41.7, 40.2, 29.7.

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