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# Synthesis of substituted carbazoles via electrocyclization of in situ generated enamines from 1-phenylsulfonyl-2/(3)-methyl-3/(2)-vinylindoles and DMF·DMA/DMA·DMA

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ABSTRACT

Interaction of 2/(3)-methyl-3/(2)-vinylindoles and DMF·DMA/DMA·DMA at 110 °C led to the in situ generation of enamines, which on concurrent electrocyclization followed by subsequent aromatization afforded substituted carbazoles.



## 1. Introduction

Ever since the first isolation of the carbazole alkaloid, murrayanine[1] organic chemists have been interested in the synthesis of carbazole alkaloids due to their promising biological activities. In particular, biomimetic oxidation products of 3-methylcarbazole are isolated in plenty and their syntheses have been widely reported.[2] Recently Knölker and Reddy extensively reviewed the synthesis of biologically important carbazole alkaloids.[3]

Thermal electrocyclization methodology has been widely used for the synthesis of carbazole based natural products.[4] Mohanakrishnan and Srinivasan outlined a versatile synthesis of quino[4,3-*b*]carbazoles involving electrocyclization of stable *N*-phenylsulfonyl-2,3-divinylindoles as key step.[5] Very recently synthesis of several multi functional carbazoles is reported[6] involving either cycloaddition or base mediated cyclization reactions.

## 2. Results and discussion

In continuation of our interest on annulated carbazole analogues,[7] we planned to utilize DMF·DMA (*N*,*N*-dimethylformamide dimethyl acetal) as a one carbon electrophilic synthon. Accordingly, a survey of literature revealed that the interaction of arene/heteroarene containing acidic methyl function with DMF·DMA (*N*,*N*-dimethylformamide dimethyl acetal) at 100–120 °C led to the formation of corresponding enamines. These enamines on oxidative hydrolysis using $NaIO_4$ led to the formation of benzaldehydes, pyridinealdehydes, naphthaldehydes and quinolinaldehydes.[8–10] The enamine intermediate prepared from substituted 2-nitrotoluenes on reductive cyclization furnished variety of inaccessible 4-, 5-, and 7-substituted indoles.[11] Similarly, the enamines generated using DMF·DMA has also been utilized for the synthesis of azaindoles,[12] pyrroles[13] and quinolones.[14]

Kim and co-workers[15] accomplished the formylation/acetylation of acetylenic systems via interaction with DMF·DMA/DMA·DMA (*N*,*N*-dimethylformamide dimethyl acetal/*N*,*N*-dimethylacetamide dimethyl acetal) at 80 °C. Very recently, Sasada and co-workers reported[16] the synthesis of tetra substituted pyridines involving trimethylsilyl chloride-promoted three component coupling reaction of functionalized enamine, DMF·DEA (*N*,*N*-dimethylformamide diethyl acetal) and DMAD. Thus, in all these cases DMF·DMA/DMF·DEA has been used as potential one carbon synthon. In further continuation of preliminary report on the synthesis of *N*-protected carbazoles involving electrocyclization of in situ generated enamines,[17] we report herein our detailed study on the synthesis of carbazoles using 1-phenylsulfonyl-2/(3)-methyl-3/(2)-vinylindoles with DMF·DMA/DMA·DMA.

As per Coe's protocol,[8–10] we presumed that the condensation of vinyl ester **1a** with DMF·DMA followed by oxidative hydrolysis might lead to the aldehyde **2**. However, when **1a** was treated with 5 equiv of DMF·DMA at 110 °C for 4 h followed by oxidative

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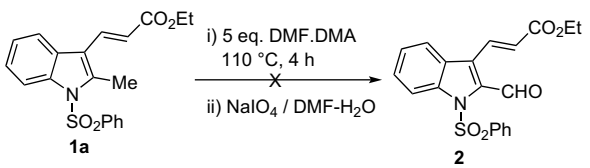
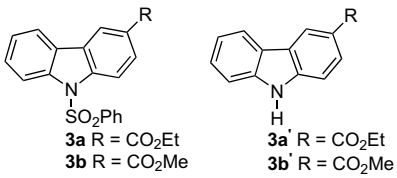
hydrolysis using $NaIO_4$ in DMF–$H_2O$, the expected aldehyde **2** was not obtained (Scheme 1).



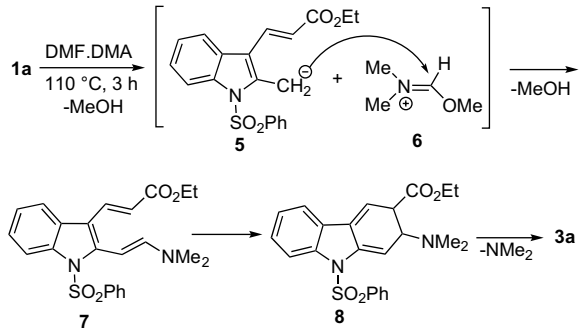

**Scheme 1.**

When **1a** was treated with DMF·DMA and the resulting crude product was carefully analyzed using mass spectrometry, the presence of $M^+$ ions at $m/z$ 379, 365, 239 and 225, corresponding to carbazoles **3a**,**b** and **3a**′,**b**′ were observed (Scheme 2).




**Scheme 2.**

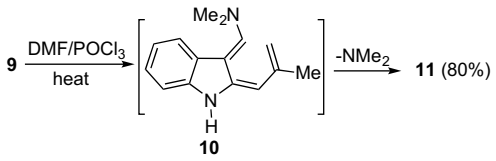
The mechanism of formation of carbazole **3a** can be understood through the electrocyclization of an intermediate enamine **7** followed by aromatization of dihydrocarbazole **8** via elimination of dimethylamine (Scheme 3). The formation of the remaining carbazoles **3b**, **3a**′ and **3b**′ must involve the secondary reaction of **3a** with methoxide ion. This was further confirmed by prolonging the reaction period or by using excess of DMF·DMA, wherein carbazoles **3a**′ and **3b** were isolated as major products. When the reaction was performed using 2 equiv of DMF·DMA for 3 h at 110 °C, the carbazole **3a** was obtained as sole product in 73% yield.




**Scheme 3.** Mechanistic rational for the formation of **3a**.

The formation of carbazole **3a** also supported our earlier observation[5] that N-protection is essential for smooth electrocyclization of 2,3-divinylindole systems. Thus, the presence of the electron withdrawing phenylsulphonyl unit on the indole nitrogen provides typical triene character to the 2,3-divinylindole system and there by electrocyclization is facilitated.

It should be noted that Bergman and Pelcman have reported the formation of 2-methylcarbazole in excellent yield during Vilsmeier formylation of 2-(2-methylprop-1-enyl)-1H-indole **9** at elevated temperature. Indeed, the formation of 2-methylcarbazole **11** was realized through enamine intermediate **10** (Scheme 4). However, the preparations of 1-substituted-2-methylcarbazole analogues under identical conditions were found to proceed only in very low yields.[18]




**Scheme 4.**

The enamine-based electrocyclization methodology was then tested with a variety of 2-methyl-3-vinylindoles and 3-methyl-2-vinylindoles **1a**–**m** via interaction with acetals DMF·DMA/DMA·DMA to afford the respective carbazoles in 0–73% yields. The exact conditions employed and the resulting carbazoles obtained are presented in Table 1. Comparatively, the reaction of 2-methyl-3-vinylesters **1a**–**c**[5] with DMF·DMA/DMA·DMA afforded the corresponding carbazoles **3a**–**c**/**4a**–**c** in better yields (entries 1–3). The presence of 5-methoxy group in the case of 2-methyl-3-vinylindole **1c** didn't have much influence on the yield of the carbazole **3c**. Always, the interaction of 3-vinylindoles **1a**–**c** with DMF·DMA provided better yields carbazoles **3a**–**c** than the corresponding carbazoles **4a**–**c** obtained using DMA·DMA (entries 1–3). As a representative case, structure of carbazole **3a** was confirmed[19] by a single crystal X-ray analysis.

The expected enamine formation and its subsequent annulation was failed with 3-methyl-2-vinylindole **1d**[5] even under forcing conditions (140 °C for 4 h), only the starting material was recovered in quantitative yield (entry 4). Obviously, the observed failure to form required enamine might be due to the relatively enhanced nucleophilicity of the indole-3-position. Gratifyingly, when the annulation of 3-carbomethoxymethyl-2-vinylindole **1e**[20] was performed with DMF·DMA, the respective carbazole **3e** could be isolated in 65% yield. Hence, it may be concluded that the failure to form enamine in the case of **1d** can be attributed to the relatively less acidic nature of 3-methyl group. The annulation of the isomeric 2-carbomethoxymethyl-3-vinylindole **1f**[20] with DMF·DMA afforded the expected carbazole **3f** in 65% yield (entry 6). Possibly, the formation of the enamine in the case of **1f** may be facilitated by the electron withdrawing ester group. However, the isolation of carbazole **3f** in 65% yield confirms that the subsequent electrocyclization of the resulting enamine may be somewhat unfavourable. Further, the interaction of 2-carbomethoxymethyl-3-vinylindole **1f** with DMA·DMA failed to produce expected carbazole **4f**, which confirms that the carbanion stabilized by the ester group has not reacted with iminium ion $CH_3C(OMe)=^+NMe_2$ derived from DMA·DMA to form the required enamine. Obviously, for the same reason, the interaction of 3-vinylindole-2-methylphosphonate ester **1g**[5] with DMF·DMA also failed to generate the required enamine and hence carbazole **3g** could not be prepared (entry 7). Interaction of 3-vinylindole-2-sulfinylmethylindole **1h**[21] with DMF·DMA led to the formation of ether **3h** via the cleavage of the *N*-phenylsulfonyl group followed by nucleophilic displacement of sulfoxide unit. The observed cleavage of *N*-phenylsulfonyl unit can be visualized only through the nucleophilic attack of the methoxy ion followed by subsequent elimination of methyl benzenesulfonate.

The annulation of 3-vinylindole **1i** with DMF·DMA furnished expected carbazole **3i** in 62% yield (entry 9). However, the reaction of **1i** with DMA·DMA led to the isolation of tri-ester **4i** in 60% yield (entry 10). The formation of **4i** can be realized only through the Michael addition of **1i** with iminium-carbanion **12** to form the intermediate **13**. The latter on subsequent hydrolysis may lead to the tri-ester **4i** (Scheme 5).

The structure of **4i** was confirmed by a single crystal X-ray analysis[22] (Fig. 1).

**Table 1**
Synthesis of substituted carbazoles from 2-/(3)-methyl-3/(2)-vinylindoles and DMF·DMA/DMA·DMA

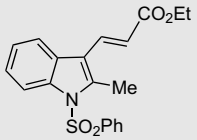
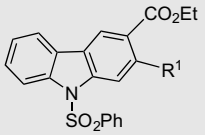
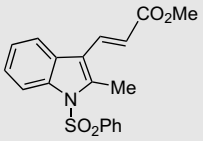
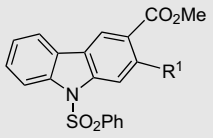
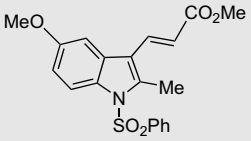
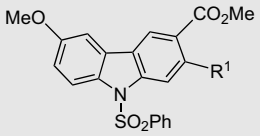
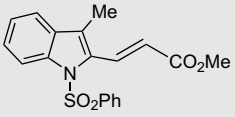
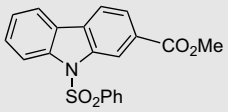
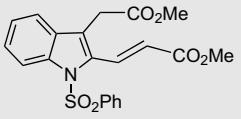
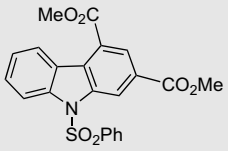
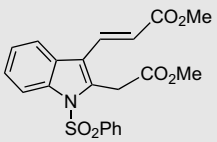
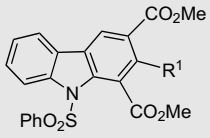
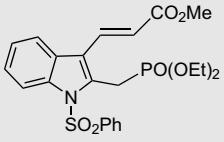
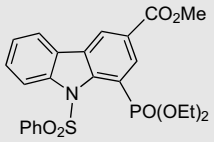
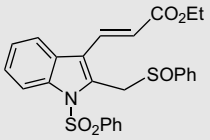
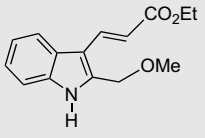
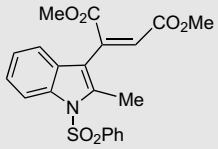
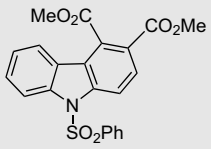
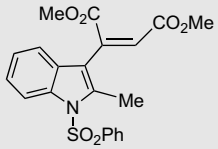
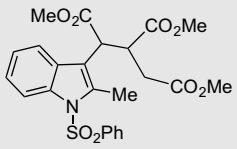
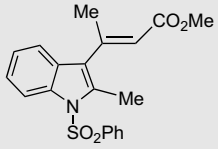
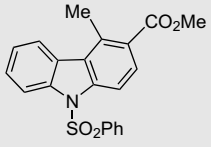
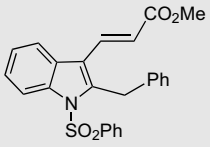
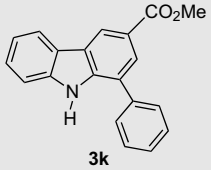
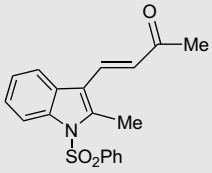
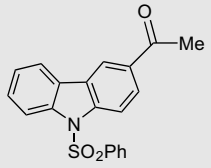
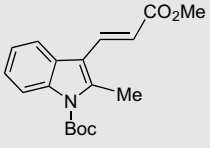
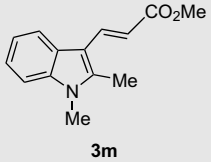
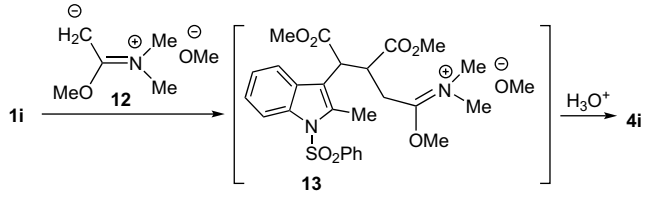
| Entry | Vinylindoles | Acetal & condition | Carbazole | Yield[a] (%) mp |
|---|---|---|---|---|
| 1 |  **1a** | DMF·DMA, 110 °C, 3 h<br>DMA·DMA, 110 °C, 3 h |  **3a** $R^1$ = H<br>**4a** $R^1$ = Me | 73 (180 °C)<br>67 (174 °C) |
| 2 |  **1b** | DMF·DMA, 110 °C, 3 h<br>DMA·DMA, 110 °C, 3 h |  **3b** $R^1$ = H<br>**4b** $R^1$ = Me | 70 (188 °C)<br>68 (171 °C) |
| 3 |  **1c** | DMF·DMA, 110 °C, 3 h<br>DMA·DMA, 110 °C, 3 h |  **3c** $R^1$ = H<br>**4c** $R^1$ = Me | 68 (183 °C)<br>55 (175 °C) |
| 4 |  **1d** | DMF·DMA, 140 °C, 5 h |  **3d** | 0 |
| 5 |  **1e** | DMF·DMA, 110 °C, 3 h |  **3e** | 65 (210 °C) |
| 6 |  **1f** | DMF·DMA, 110 °C, 3 h<br>DMA·DMA, 110 °C, 5 h |  **3f** $R^1$ = H<br>**4f** $R^1$ = Me | 65 (102 °C)<br>0 |
| 7 |  **1g** | DMF·DMA, 110 °C, 4 h |  **3g** | 0 |
| 8 |  **1h** | DMF·DMA, 110 °C, 3 h |  **3h** | 56 (116 °C) |

**Table 1** (*continued*)

| Entry | Vinylindoles | Acetal & condition | Carbazole | Yield[a] (%) mp |
|---|---|---|---|---|
| 9 |  **1i** | DMF·DMA, 110 °C, 3 h |  **3i** | 62 (128 °C) |
| 10 |  **1i** | DMA·DMA, 110 °C, 4 h |  **4i** | 60 (122 °C) |
| 11 |  **1j** | DMF·DMA, 140 °C, 5 h |  **3j** | 0 |
| 12 |  **1k** | DMF·DMA, 110 °C, 3 h |  **3k** | 66 (142 °C) |
| 13 |  **1l** | DMF·DMA, 110 °C, 1 h |  **3l** | 56 (192 °C) |
| 14 |  **1m** | DMF·DMA, 110 °C, 3 h |  **3m** | 65 (130 °C) |

[a] Isolated yield after column chromatography.



**Scheme 5.** Mechanistic rational for the formation of **4i**.

Surprisingly, the reaction of 3-vinylindole **1j** with DMF·DMA at 140 °C for 5 h didn't give the expected carbazole **3j**, only the starting material was recovered unchanged (entry 11). Upon interaction of 3-vinyl-2-benzylindole **1k** with DMF·DMA, furnished the corresponding 1-phenylcarbazole **3k** in 66% yield with cleavage of *N*-phenylsulfonyl group (entry 12). When, 2-methylindole **1l**[5] tethered with sensitive ketone-methyl function was reacted with DMF·DMA at 110 °C for 1 h, the expected carbazole **3l** could be obtained in 56% yield (entry 13). Finally, the

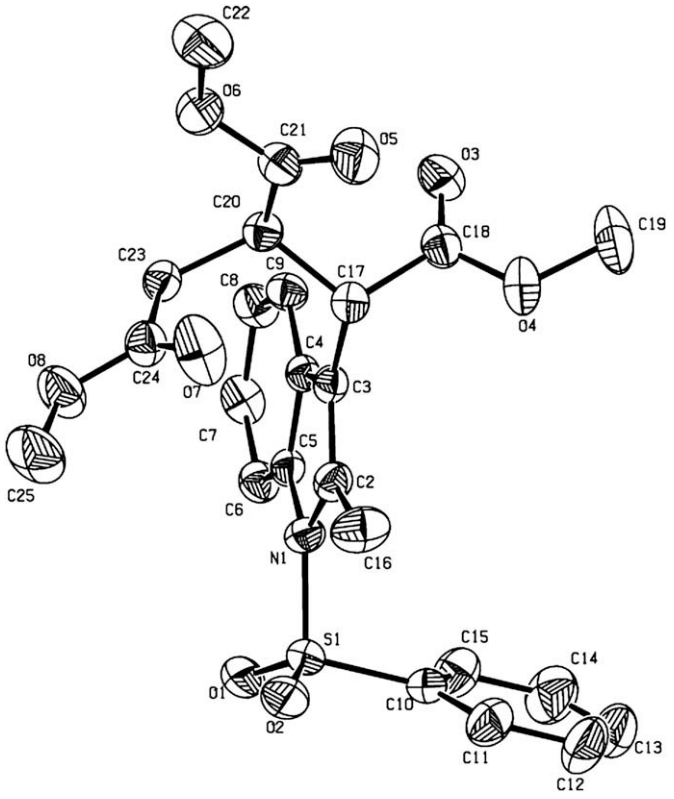
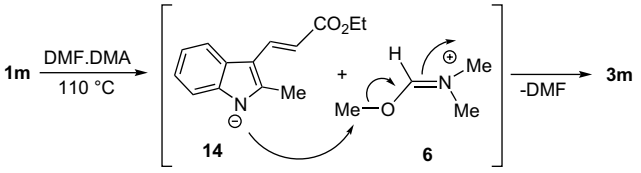



**Figure 1.** ORTEP diagram of tri-ester **4**.

attempted annulation of 1-*tert*-butoxycarbonyl-3-vinyl-2-methylindole **1m** led to the isolation of 1,2-dimethyl-3-vinylindole **3m** in 65% yield (entry 14). The formation of **3m** can be visualized through thermal cleavage of the *N*-Boc unit followed by its subsequent N-methylation of carbanion **14** with iminium ion **6** (Scheme 6).

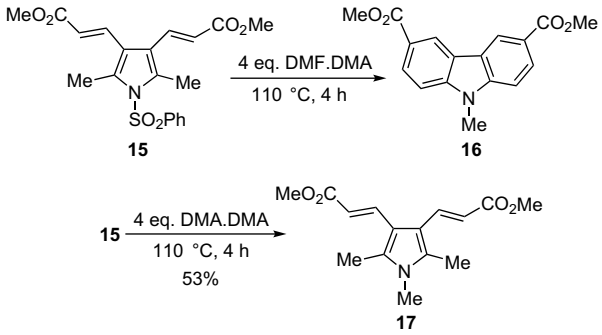



**Scheme 6.** Mechanistic rational for the formation of **3m**.

A survey of literature revealed that interaction of sulfonamide with DMF·DMA at 70–80 °C led to the formation of the corresponding methylated product.[23]

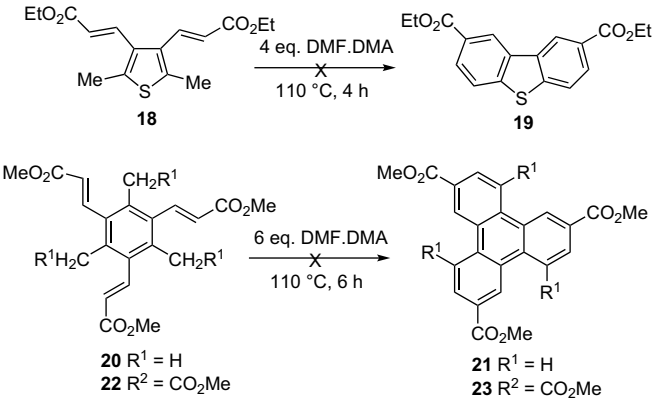
As expected, the bis-annulation of 3,4-divinyl-2,5-dimethylpyrrole **15** with 4 equiv of DMF·DMA at 110 °C for 4 h followed by usual workup and crystallization from methanol furnished *N*-methylcarbazole **16** in 55% yield. Presumably, dimethyl 1-phenylsulfonylcarbazole-3,6-dicarboxylate underwent facile cleavage of the phenylsulfonyl group followed by methylation to afford **16** (Scheme 7). However, the attempted bis-annulation of **15** with DMA·DMA furnished only *N*-methyl pyrrole **17** in 53% yield.

A bis-annulation of thiophenyl methyl compound **18** was found to be unsuccessful possibly due to the less acidic character of thiophenyl methyl protons. Similarly, attempted tris-annulation of mesitylenes **20**/**22** with 6 equiv of DMF·DMA also failed to produce the expected products **21**/**23**. While in the case of compound **20**,



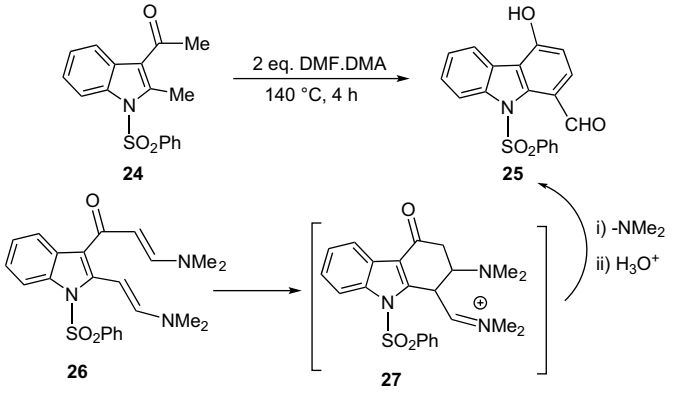

**Scheme 7.**

starting material was recovered and for **22**, complex mixture was obtained (Scheme 8).




**Scheme 8.**

Finally, the annulation of 1-phenylsulfonyl-2-methyl-3-acetylindole **24** with DMF·DMA at 140 °C for 4 h followed by column chromatographic purification led to the isolation of *N*-phenylsulfonyl-4-hydroxy-carbazole-1-carboxaldehyde **25** in 65% yield (Scheme 9). The initial reaction of **24** with DMF·DMA may lead to the formation of bis-enamine **26**. Intramolecular Michael addition of **26** followed by elimination of dimethylamine and subsequent workup may furnish **23**.

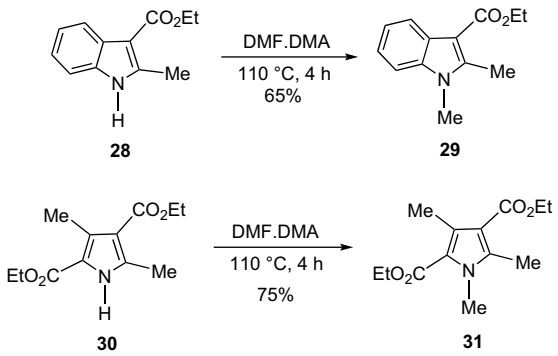



**Scheme 9.**

It is worthwhile to mention that an attempted annulation of 2-methylacetophenone with DMF·DMA at 120 °C for 12 h failed to

produce the expected enamine, only the starting material was recovered unchanged.

During the above-mentioned annulation reactions, in some of the cases N-methylation was observed as a prominent side reaction. Hence, it was decided to explore methylation character of DMF·DMA. Accordingly, when ethyl 2-methylindole-3-carboxylate **28** was treated with DMF·DMA at 110 °C, *N*-methylindole **29** could be isolated in 65% yield (Scheme 10).




**Scheme 10.**

Under identical conditions, 2,3-dimethylindole failed to produce the corresponding *N*-methylindole. However, pyrrole **30** on heating with DMF·DMA at 110 °C furnished expected product **31** in 75% yield. Obviously, the observed N-methylation of indole/pyrrole is taking place only when it possesses an electron withdrawing unit. Attempted one-pot desulfonylation followed by N-methylation of 1-phenylsulfonylindole[24] with excess of DMF·DMA even at 140 °C failed to produce the expected *N*-methylindole, only the starting material was recovered unchanged. Now, it is clear that cleavage of *N*-phenylsulfonyl unit is taking place only in the case compounds containing electron withdrawing groups. However, the precise mechanism for the selective cleavage of *N*-phenylsulfonyl group and subsequent N-methylation using DMF·DMA is not clear.

## 3. Conclusions

In conclusion, we have developed a convenient one-carbon annulation protocol for the synthesis of functionalized carbazoles involving electrocyclization of in situ generated enamine through the interaction of 1-phenylsulfonyl-2/(3)-methyl-3/(2)-vinylindoles with DMF·DMA or DMA·DMA at a moderate temperature. While, the bis-annulation could be performed with *N*-phenylsulfonyl-3,4-divinylpyrrole, the same could not be performed with the corresponding thienyl system. Similarly, attempted tris-annulation with mesitylenes was also found to be unsuccessful. Finally, a facile N-methylation of indole/pyrrole containing electron withdrawing ester function could be performed in good yields. Further research work to utilize the N-methylation character of DMF·DMA is in progress.

## 4. Experimental

### 4.1. General

All melting points are uncorrected. Solvents were purified using standard procedure. Reactions were done under atmosphere of dry nitrogen with magnetic stirring. All chemicals were used as received. Analytical thin layer chromatography (TLC) was performed on silica and components were visualized by observation under iodine or UV-light. Column chromatography was performed using silica gel (60–120 mesh). IR spectra were recorded on a SHIMADZU FT-IR 8300 instrument. $^1$H and $^{13}$C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on a JEOL 400 and Bruker-300 spectrometers. Elemental analyses were performed on a Perkin–Elmer series II 2400 (IIT Madras) elemental analyzer. The Mass spectra were recorded on a JEOL DX 303 HF mass spectrometer.

#### *4.1.1. (E)-Methyl 3-(3-(2-methoxy-2-oxoethyl)-1-(phenylsulfonyl)-1H-indol-2-yl)acrylate (**1e**)*

A two necked flask containing (*E*)-methyl 3-(3-(bromomethyl)-1-(phenylsulfonyl)-1*H*-indol-2-yl)acrylate[5] (1 g, 2.31 mmol), $Pd(PPh_3)_2Cl_2$ (162 mg, 0.23 mmol) and $K_2CO_3$ (320 mg, 2.31 mmol) was evacuated. To this, dry THF (35 mL) and MeOH (10 mL) were added via syringe. The reaction mixture was then purged with dry carbon monoxide gas for 5 min and stirred under a carbon monoxide atmosphere at room temperature for 10 h. The reaction mixture was then diluted with water (50 mL) and extracted with ethyl acetate (2×20 mL). The combined extracts were washed with $H_2O$ (10 mL) and dried ($Na_2SO_4$). Removal of solvent followed by column chromatographic purification (20% EA/Hexane) afforded **1e** (0.20 g, 42%) as a yellow solid; mp 150 °C. [Found: C, 61.28; H, 4.36; N, 3.69; S, 7.50. $C_{21}H_{19}NO_6S$ requires: C, 61.01; H, 4.63; N, 3.39; S, 7.76%.] $R_f$ (20% EA/Hexane) 0.42; $\nu_{max}$ (KBr) 1726, 1716, 1362, 1158 cm$^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.24 (2H, d, *J* 7.5 Hz, ArH), 7.70 (2H, d, *J* 7.5 Hz, ArH), 7.52–7.28 (6H, m, ArH), 6.16 (1H, d, *J* 16.2 Hz, Vinylic CH), 4.14 (2H, s, $CH_2$), 3.72 (3H, s, $CH_3$), 3.65 (3H, S, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 169.3, 167.9, 138.3, 136.3, 134.8, 134.5, 129.7, 127.1, 126.3, 125.7, 124.4, 121.1, 120.7, 118.7, 114.3, 52.7, 51.4, 32.2; *m*/*z* (EI) 413 (32, M$^+$).

#### *4.1.2. (E)-Methyl 3-(2-(2-methoxy-2-oxoethyl)-1-(phenylsulfinyl)-1H-indol-3-yl)acrylate (**1f**)*

Following the above mentioned procedure, diester **1f** (0.43 g, 45%) was obtained using (*E*)-methyl 3-(2-(bromomethyl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)acrylate[5] (1 g, 2.31 mmol), $Pd(PPh_3)_2Cl_2$ (162 mg, 0.23 mmol), $K_2CO_3$ (320 mg, 2.31 mmol) in dry THF (35 mL) and methanol (10 mL) as a colourless solid; mp 124 °C. [Found: C, 61.29; H, 4.38; N, 3.70; S, 7.51. $C_{21}H_{19}NO_6S$ requires: C, 61.01; H, 4.63; N, 3.39; S, 7.76%.] $R_f$ (20% EA/Hexane) 0.42; $\nu_{max}$ (KBr) 1724, 1712, 1372, 1164 cm$^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 7.98 (1H, d, *J* 8.4 Hz, ArH), 7.79 (2H, d, *J* 7.5 Hz, ArH), 7.73–7.68 (2H, m, ArH), 7.49 (1H, t, *J* 7.2 Hz, ArH), 7.38 (2H, t, *J* 7.8 Hz, ArH), 7.26 (2H, t, *J* 3.9 Hz, ArH), 6.67 (1H, d, *J* 15.9 Hz, Vinylic CH), 4.19 (2H, s, $CH_2$), 3.76 (3H, s, $CH_3$), 3.67 (3H,s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 169.5, 167.4, 138.7, 136.4, 134.8, 134.2, 129.4, 127.1, 126.8, 125.5, 124.4, 120.3, 120.1, 118.5, 114.6, 52.5, 51.8, 32.4; *m*/*z* (EI) 413 (34, M$^+$).

#### *4.1.3. Dimethyl 2-(2-methyl-1-(phenylsulfonyl)-1H-indol-3-yl)maleate (**1i**)*

To a solution of 2-methylindole (2 g, 15.2 mmol) in dry diethylether (10 mL), oxalyl chloride (3. 9 g, 30.53 mmol) was slowly added at 0 °C and allowed to stir for 1 h. To the reaction mixture, dry methanol (10 mL) was then added slowly and stirred for another 1 h. The resulting reaction mixture was poured over crushed ice (200 g) and solid formed was filtered and dried ($CaCl_2$) to give methyl 2-(2-methyl-1*H*-indol-3-yl)-2-oxoacetate (2.65 g, 80%), which was used as such for *N*-protection; mp 156 °C; *m*/*z* (EI) 217 (93, M$^+$).

To a solution of methyl 2-(2-methyl-1*H*-indol-3-yl)-2-oxoacetate (2 g, 9.21 mmol) in dry DCM (25 mL), $Et_3N$ (1.86 g, 18.4 mmol), DMAP (100 mg, 0.92 mmol) were added and stirred at room temperature for 15 min. To this, benzenesulfonylchloride (2.1 g, 11.9 mmol) in dry DCM (10 mL) was added and stirred for additional 6 h. It was then poured into 2% aq HCl (10 mL) and extracted with DCM (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 (10% EA/hexane) afforded methyl 2-(2-methyl-1-(phenylsulfonyl)-1*H*-indol-3-yl)-2-oxoacetate (2.13 g, 65%) as light brown solid; mp 86 °C. [Found: C, 60.80; H, 3.95; N, 4.19; S, 8.71. $C_{18}H_{15}NO_5S$ requires: C, 60.49; H, 4.23; N, 3.92; S, 8.97%.] $R_f$ (20% EA/Hexane) 0.51; $\nu_{max}$ (KBr) 1720, 1676, 1354, 1170 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.25 (1H, d, *J* 8.0 Hz, ArH), 7.89–7.85 (3H, m, ArH), 7.62–7.59 (1H, t, *J* 7.0 Hz, ArH), 7.49 (2H, t, *J* 7.2 Hz, ArH), 7.38–7.31 (2H, m, ArH), 3.53 (3H, s, $CH_3$), 2.64 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 183.5, 164.7, 146.4, 138.5, 136.0, 134.7, 129.8, 126.7, 126.5, 125.6, 125.0, 120.6, 115.8, 114.4, 62.6, 14.2, 14.0; *m*/*z* (EI) 357 (46, $M^+$).

A solution of methyl 2-(2-methyl-1-(phenylsulfonyl)-1*H*-indol-3-yl)-2-oxoacetate (2 g, 5.6 mmol) and (carbomethoxymethylene) triphenylphosphorane (2.2 g, 6.7 mmol) in dry benzene (60 mL) was refluxed under $N_2$ for 12 h. Removal of solvent followed by column chromatographic separation (5% EA/hexane) afforded compound **1i** (1.62 g, 70%) as a thick yellow liquid. [Found: C, 61.30; H, 4.33; N, 3.68; S, 7.52. $C_{21}H_{19}NO_6S$ requires: C, 61.01; H, 4.63; N, 3.39; S, 7.76%.] $R_f$ (20% EA/Hexane) 0.50; $\nu_{max}$ (KBr) 1695, 1689, 1370, 1168 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.05 (1H, d, *J* 7.8 Hz, ArH), 7.68–7.65 (2H, m, ArH), 7.42 (1H, t, *J* 7.3 Hz, ArH), 7.32 (2H, t, *J* 7.5 Hz, ArH), 7.19–7.12 (2H, m, ArH), 7.10–7.02 (2H, m, ArH), 3.63 (3H, s, $CH_3$), 3.33 (3H, s, $CH_3$), 2.36 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 166.1, 164.6, 139.2, 136.3, 136.1, 135.7, 133.6, 132.1, 129.3, 129.2, 126.3, 124.2, 123.7, 118.8, 115.2, 114.5, 52.9, 51.7, 14.0; *m*/*z* (EI) 413 (75, $M^+$).

#### 4.1.4. (E)-Methyl 3-(2-methyl-1-(phenylsulfonyl)-1H-indol-3-yl)but-2-enoate (**1j**)

To a solution of 2-methylindole (1 g, 7.6 mmol) in dry 1,2-dichloroethane (30 mL), methyl 3-oxobutanoate (1.06 g, 9.1 mmol) and $FeCl_3$ (0.25 g, 1.5 mmol) were added. The reaction mixture was stirred at room temperature for 3 h. After the completion of the reaction (monitored by TLC), DCE was evaporated under vacuo, 20 mL of $H_2O$ was added and extracted with ethyl acetate (2×20 mL). The combined extracts were washed with water (10 mL), brine (10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave crude indole, which was dissolved in benzene (30 mL). To this solution, benzenesulfonylchloride (1.6 g, 9.1 mmol), tetra butyl ammoniumhydrogensulfate (0.2 g) and 50% NaOH solution (10 mL) were added and stirred for 3 h at room temperature. Benzene layer was separated and dried ($Na_2SO_4$). Evaporation of the solvent gave crude compound, which was recrystallized from methanol to give pure **1j** [2 g, 71% (two steps)] as dull white solid; mp 104 °C. [Found: C, 65.31; H, 4.91; N, 4.09; S, 8.44. $C_{20}H_{19}NO_4S$ requires: C, 65.02; H, 5.18; N, 3.79; S, 8.68%.] $R_f$ (20% EA/Hexane) 0.60; $\nu_{max}$ (KBr) 1698, 1362, 1168 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.22 (1H, d, *J* 8.1 Hz, ArH), 7.79 (2H, d, *J* 7.5 Hz, ArH), 7.55 (1H, d, *J* 7.2 Hz, ArH), 7.46–7.38 (3H, m, ArH), 7.35–7.23 (2H, m, ArH), 5.82 (1H, s, CH), 3.75 (3H, s, $CH_2$), 2.57 (3H, s, $CH_3$), 2.48 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 166.7, 149.7, 139.1, 136.2, 133.8, 132.8, 129.3, 128.5, 126.3, 124.7, 124.5, 123.7, 121.1, 119.2, 114.6, 51.1, 20.3, 13.6; *m*/*z* (EI) 369 (65, $M^+$).

#### 4.1.5. (E)-Methyl 3-(2-benzyl-1-(phenylsulfonyl)-1H-indol-3-yl)acrylate (**1k**)

To a suspension of (*E*)-methyl 3-(2-(bromomethyl)-1-phenylsulfonyl-1*H*-indol-3-yl)acrylate (1 g, 2.3 mmol) in dry benzene (30 mL), anhydrous $ZnBr_2$ (0.62 g, 2.8 mmol) was added and the reaction mixture was refluxed under $N_2$ atmosphere for 12 h. The solvent was removed and then reaction mixture was quenched with ice water (100 mL) containing 2 mL of concd HCl, extracted with chloroform (3×10 mL) and dried ($Na_2SO_4$). Removal of solvent followed by flash column chromatographic purification (4% EA/Hexane) afforded 2-benzylindole **1k** (0.4 g, 40%) as a colourless solid; mp 152 °C. [Found: C, 69.31; H, 5.21; N, 2.94; S, 7.61. $C_{25}H_{21}NO_4S$ requires: C, 69.59; H, 4.91; N, 3.25; S, 7.43%.] $R_f$ (20% EA/Hexane) 0.68; $\nu_{max}$ (KBr) 1705, 1369, 1165 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.23 (1H, d, *J* 7.5 Hz, ArH), 7.89 (1H, d, *J* 16.5 Hz, Vinylic CH), 7.85 (1H, d, *J* 8.4 Hz, ArH), 7.43–7.36 (5H, m, ArH), 7.22–7.19 (5H, m, ArH), 7.11–7.02 (2H, m, ArH), 6.59 (1H, d, *J* 16.2 Hz, Vinylic CH), 4.67 (2H, s, $CH_2$), 3.78 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 167.6, 141.2, 138.3, 137.5, 136.7, 135.6, 133.7, 129.0, 128.6, 128.4, 127.2, 126.6, 126.5, 125.2, 124.3, 120.1, 119.2, 117.6, 115.1, 51.7, 29.7; *m*/*z* (EI) 431 (54, $M^+$).

#### 4.1.6. tert-Butyl 3-((E)-2-(methoxycarbonyl)vinyl)-2-methyl-1H-indole-1-carboxylate (**1m**)

To a solution of 2-methyl-1*H*-indole-3-carboxaldehyde (2 g, 12.5 mmol) in dry DCM, $Et_3N$ (2.54 g, 25.1 mmol), DMAP (0.15 g, 1.2 mmol) and $(Boc)_2O$ (3.5 g, 16.3 mmol) were added at 0 °C. After 4 h, the reaction mixture was poured in to 2% aq HCl (10 mL) solution and extracted with DCM (2×20 mL). The combined extracts were washed with water (10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent followed by crystallization from methanol afforded 2-methyl-1*tert*-butoxycarbonylindole-3-carboxaldehyde as a colourless solid. It was then dissolved in dry toluene (70 mL). To this (carbomethoxymethylene)triphenylphosphorane (5.0 g, 15.1 mmol) was added and refluxed under $N_2$ for 12 h. Removal of solvent followed by column chromatographic separation (5% EA/hexane) afforded compound **1m** [2.1 g, 53% (two steps)] as a white solid; mp 58 °C. [Found: C, 68.28; H, 7.02; N, 4.13. $C_{18}H_{21}NO_4$ requires: C, 68.55; H, 6.71; N, 4.44%.] $R_f$ (20% EA/Hexane) 0.59; $\nu_{max}$ (KBr) 1747, 1692 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.14–8.11 (1H, m, ArH), 7.93 (1H, d, *J* 15.9 Hz, Vinylic CH), 7.80–7.77 (1H, m, ArH), 7.29–7.26 (2H, m, ArH), 6.52 (1H, d, *J* 16.2 Hz, Vinylic CH), 3.82 (3H, s, $CH_3$), 2.69 (3H, s, $CH_3$), 1.69 (9H, s, Boc $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 168.2, 150.1, 140.9, 136.6, 136.2, 127.0, 124.2, 123.5, 119.4, 116.6, 115.5, 114.5, 84.7, 51.5, 28.2, 14.3; *m*/*z* (EI) 315 (48, $M^+$).

#### 4.1.7. Ethyl 9-(phenylsulfonyl)-9H-carbazole-3-carboxylate (**3a**)

To a stirred solution of vinyl ester **1a** (0.5 g, 1.35 mmol) in dry DMF (1.5 mL), DMF·DMA (322 mg, 2.71 mmol) was added. The reaction mixture was heated at 110 °C under $N_2$ for 3 h. It was then poured into 2% aq HCl (15 mL) 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 carbazole **3a** [0.38 g, 73%] as a colourless solid; mp 180 °C. [Found: C, 66.52; H, 4.59; N, 3.74; S, 8.31. $C_{21}H_{17}NO_4S$ requires: C, 66.47; H, 4.52; N, 3.69; S, 8.45%.] $R_f$ (20% EA/Hexane) 0.52; $\nu_{max}$ (KBr) 1709, 1369, 1176 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.61 (1H, s, ArH), 8.39–8.33 (1H, m, ArH), 8.21–8.18 (2H, m, ArH), 7.98 (1H, d, *J* 7.32 Hz, ArH), 7.83 (2H, d, *J* 7.32 Hz, ArH), 7.55–7.36 (5H, m, ArH), 4.43 (2H, q, *J* 7.32 Hz, $CH_2$), 1.43 (3H, t, *J* 7.08 Hz, $CH_3$); $\delta_C$ (100.6 MHz, $CDCl_3$) 166.4, 141.0, 138.8, 137.7, 134.0, 129.1, 128.7, 128.0, 126.4, 126.3, 125.8, 124.3, 121.9, 120.4, 115.1, 114.6, 61.1, 14.4; *m*/*z* (EI) 379 (100, $M^+$), 239 (68%), 194 (42%), 165 (72%).

#### 4.1.8. Ethyl 2-methyl-9-(phenylsulfonyl)-9H-carbazole-3-carboxylate (**4a**)

Following the procedure similar to that of **3a**, carbazole **4a** (0.35 g, 67%) was obtained using vinyl ester compound **1a** (0.5 g, 1.35 mmol), DMA·DMA (360 mg, 2.7 mmol) and dry DMF (1.5 mL) as a colourless solid; mp 174 °C. [Found: C, 67.28; H, 5.02; N, 3.83; S, 8.42. $C_{22}H_{19}NO_4S$ requires: C, 67.16; H, 4.87; N, 3.56; S, 8.15%.] $R_f$ (20% EA/Hexane) 0.56; $\nu_{max}$ (KBr) 1712, 1360, 1174 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.48 (1H, s, ArH), 8.29 (2H, d, *J* 8.32 Hz, ArH), 8.20 (1H, s, ArH), 7.92 (1H, d, *J* 7.84 Hz, ArH), 7.82 (2H, d, *J* 7.32 Hz, ArH), 7.49–7.45 (2H, m, ArH), 7.39–7.32 (2H, m, ArH), 4.40 (2H, q, *J* 6.84 Hz, $CH_2$), 2.83 (3H, s, $CH_3$), 1.43 (3H, t, *J* 7.08 Hz, $CH_3$); $\delta_C$ (100.6 MHz, $CDCl_3$) 167.4, 140.4, 139.9, 138.6, 137.8, 134.0, 129.1, 127.5, 126.4, 126.1, 125.9, 124.2, 124.1, 122.8, 120.0, 117.2, 115.0, 60.9, 22.9, 14.4; *m*/*z* (EI) 393 (100, $M^+$), 349 (17%), 209 (73%), 181 (37%).

*4.1.9. Methyl 9-(phenylsulfonyl)-9H-carbazole-3-carboxylate (**3b**)*

Yield: 0.36 g (70%); colourless solid; mp 188 °C. [Found: C, 65.53; H, 4.37; N, 3.64; S, 9.03. $C_{20}H_{15}NO_4S$ requires: C, 65.74; H, 4.14; N, 3.83; S, 8.78%.] $R_f$ (20% EA/Hexane) 0.53; $\nu_{max}$ (KBr) 1710, 1354, 1170 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.61 (1H, s, ArH), 8.40–8.33 (2H, m, ArH), 8.19 (1H, d, *J* 8.6 Hz, ArH), 7.96 (1H, d, *J* 7.8 Hz, ArH), 7.84 (2H, d, *J* 7.8 Hz, ArH), 7.53 (1H, t, *J* 7.6 Hz, ArH), 7.45 (1H, t, *J* 7.0 Hz, ArH), 7.41–7.32 (3H, m, ArH), 3.98 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 166.8, 141.1, 138.8, 137.7, 134.1, 129.2, 128.7, 128.0, 126.4, 126.3, 125.9, 125.7, 124.3, 122.0, 120.3, 115.0, 114.6, 52.2; *m*/*z* (EI) 365 (100, $M^+$), 224 (98%), 193 (82%), 165 (66%).

*4.1.10. Methyl 2-methyl-9-(phenylsulfonyl)-9H-carbazole-3-carboxylate (**4b**)*

Yield: 0.36 g (68%); colourless solid; mp 171 °C. [Found: C, 66.38; H, 4.72; N, 3.72; S, 8.57. $C_{21}H_{17}NO_4S$ requires: C, 66.47; H, 4.52; N, 3.69; S, 8.45%.] $R_f$ (20% EA/Hexane) 0.57; $\nu_{max}$ (KBr) 1720, 1369, 1172 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.51 (1H, s, ArH), 8.31 (1H, d, *J* 8.17 Hz, ArH), 8.23 (1H, s, ArH), 7.94–7.84 (3H, m, ArH), 7.50–7.28 (5H, m, ArH), 3.96 (3H, s, $CH_3$), 2.83 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 167.7, 140.4, 140.1, 138.5, 137.7, 135.2, 134.0, 129.1, 127.5, 126.4, 124.2, 124.0, 122.9, 120.0, 117.2, 115.0, 51.9, 19.7; *m*/*z* (EI) 379 (92, $M^+$), 238 (100%), 206 (34%).

*4.1.11. Methyl 6-methoxy-9-(phenylsulfonyl)-9H-carbazole-3-carboxylate (**3c**)*

Yield: 0.34 g (68%); mp 183 °C. [Found: C, 63.69; H, 4.39; N, 3.94. $C_{21}H_{17}NO_5S$ requires: C, 63.79; H, 4.33; N, 3.54%.] $R_f$ (20% EA/Hexane) 0.52; $\nu_{max}$ (KBr) 1698, 1354, 1168 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.52 (1H, s, ArH), 8.32 (1H, d, *J* 7.5 Hz, ArH), 8.19 (2H, t, *J* 8.2 Hz, ArH), 7.76 (2H, m, ArH), 7.44–7.30 (4H, m, ArH), 7.10 (1H, d, *J* 6.6 Hz, ArH), 3.95 (3H, s, $CH_3$), 3.88 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 166.8, 157.1, 141.7, 137.5, 134.0, 133.0, 129.1, 128.6, 126.9, 126.5, 126.4, 125.8, 121.9, 116.3, 116.1, 114.9, 103.2, 55.7, 52.2; *m*/*z* (EI) 396 (80, $M^+$), 254 (100%), 240 (46%).

*4.1.12. 6-Methoxy-2-methyl-9-(methyl phenylsulfonyl)-9H-carbazole-3-carboxylate (**4c**)*

Yield: 0.29 g (55%); colourless solid; mp 175 °C. [Found: C, 64.29; H, 4.95; N, 3.21; S, 8.09. $C_{22}H_{19}NO_5S$ requires: C, 64.53; H, 4.68; N, 3.42; S, 7.83%.] $R_f$ (20% EA/Hexane) 0.50; $\nu_{max}$ (KBr) 1702, 1363, 1166 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.35 (1H, s, ArH), 8.11–8.09 (2H, m, ArH), 7.75–7.68 (3H, m, ArH), 7.40–7.22 (3H, m, ArH), 6.98 (1H, d, *J* 6.9 Hz, ArH), 3.86 (3H, s, $CH_3$), 3.80 (3H, s, $CH_3$), 2.71 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 167.7, 157.1, 141.1, 137.6, 135.7, 134.0, 132.9, 129.1, 127.0, 126.3, 124.3, 122.9, 117.5, 116.1, 115.5, 112.9, 103.1, 55.7, 51.9, 13.2; *m*/*z* (EI) 409 (34, $M^+$), 269 (53%), 268 (100%), 239 (15%).

*4.1.13. Dimethyl 9-(phenylsulfonyl)-9H-carbazole-2,4-dicarboxylate (**3e**)*

Yield: 0.33 g (65%); pale yellow solid; mp 210 °C. [Found: C, 62.22; H, 4.33; N, 3.09; S, 7.78. $C_{22}H_{17}NO_6S$ requires: C, 62.40; H, 4.05; N, 3.31; S, 7.57%.] $R_f$ (20% EA/Hexane) 0.49; $\nu_{max}$ (KBr) 1719, 1712, 1384, 1195 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.25–8.21 (3H, m, ArH), 7.79 (1H, s, ArH), 7.70 (2H, d, *J* 7.5 Hz, ArH), 7.52–7.28 (5H, m, ArH), 3.73 (3H, s, $CH_3$), 3.80 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 167.9, 167.0, 141.5, 138.8, 137.7, 133.1, 129.6, 128.7, 127.7, 126.7, 126.2, 125.9, 125.7, 124.5, 122.3, 120.5, 116.6, 115.8, 52.8, 52.5; *m*/*z* (EI) 423 (72, $M^+$), 282 (100%), 251 (23%), 223 (11%).

*4.1.14. Dimethyl 9-(phenylsulfonyl)-9H-carbazole-1,3-dicarboxylate (**3f**)*

Yield: 0.43 g (65%); pale yellow solid; mp 102 °C. [Found: C, 62.13; H, 4.34; N, 3.08; S, 7.79. $C_{22}H_{17}NO_6S$ requires: C, 62.40; H, 4.05; N, 3.31; S, 7.57%.] $R_f$ (20% EA/Hexane) 0.49; $\nu_{max}$ (KBr) 1716, 1710, 1382, 1192 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.43–8.38 (2H, m, ArH), 8.31 (1H, s, ArH), 7.78 (1H, d, *J* 8.0 Hz, ArH), 7.55–7.34 (5H, m, ArH), 7.26 (2H, t, *J* 3.9 Hz, ArH), 3.93 (3H, s, $CH_3$), 3.80 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 168.1, 167.2, 141.3, 139.1, 137.9, 133.3, 129.8, 128.9, 127.9, 126.9, 126.4, 126.2, 125.9, 124.7, 122.5, 120.7, 116.8, 116.0, 53.0, 52.7; *m*/*z* (EI) 423 (4, $M^+$), 297 (100%), 283 (93%), 266 (53%).

*4.1.15. (E)-Ethyl 3-(2-(methoxymethyl)-1H-indol-3-yl)acrylate (**3h**)*

Yield: 0.13 g (56%); yellow solid; mp 116 °C. [Found: C, 69.23; H, 6.91; N, 5.13. $C_{15}H_{17}NO_3$ requires: C, 69.48; H, 6.61; N, 5.40%.] $R_f$ (20% EA/Hexane) 0.59; $\nu_{max}$ (KBr) 3314, 1708 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 10.35 (1H, s, NH), 8.30 (1H, d, *J* 15.9 Hz, Vinylic CH), 8.01 (1H, d, *J* 8.0 Hz, ArH), 7.95 (1H, d, *J* 7.2 Hz, ArH), 7.47 (2H, t, *J* 7.5 Hz, ArH), 6.63 (1H, d, *J* 15.9 Hz, Vinylic CH), 4.33 (2H, q, *J* 7.2 Hz, $CH_2$), 4.11 (3H, s, $OCH_3$), 3.05 (2H, s, $CH_2$), 1.37 (3H, t, *J* 7.05 Hz, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 167.2, 138.3, 136.1, 134.2, 126.7, 125.7, 123.9, 120.2, 119.1, 114.8, 106.2, 63.1, 57.9, 51.7, 13.2; *m*/*z* (EI) 259 (70, $M^+$).

*4.1.16. Dimethyl 9-(phenylsulfonyl)-9H-carbazole-3,4-dicarboxylate (**3i**)*

Yield: 0.37 g (62%); brown solid; mp 128 °C. [Found: C, 62.66; H, 3.80; N, 3.58; S, 7.34. $C_{22}H_{17}NO_6S$ requires: C, 62.40; H, 4.05; N, 3.31; S, 7.57%.] $R_f$ (20% EA/Hexane) 0.49; $\nu_{max}$ (KBr) 1720, 1708, 1365, 1176 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.38–8.31 (2H, m, ArH), 8.17 (1H, d, *J* 7.5 Hz, ArH), 7.93 (1H, d, *J* 7.5 Hz, ArH), 7.82 (2H, d, *J* 7.5 Hz, ArH), 7.54–7.29 (5H, m, ArH), 3.95 (3H, s, $CH_3$), 3.79 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 167.7, 166.8, 141.1, 138.8, 137.7, 134.1, 129.2, 128.7, 128.0, 126.4, 126.3, 125.9, 125.7, 124.3, 122.0, 120.3, 115.0, 114.6, 52.2, 51.5; *m*/*z* (EI) 423 (15, $M^+$), 297 (100%), 266 (66%), 251 (26%).

*4.1.17. (2-Methyl-(1-phenylsulfonyl)-1H-indol-3-yl)-1,2,3-tricarbomethoxypropane (**4i**)*

Yield: 0.28 g (60%); colourless solid; mp 122 °C. [Found: C, 59.44; H, 4.91; N, 3.16; S, 6.32. $C_{24}H_{25}NO_8S$ requires: C, 59.13; H, 5.17; N, 2.87; S, 6.58%.] $R_f$ (20% EA/Hexane) 0.49; $\nu_{max}$ (KBr) 1724, 1712, 1695, 1354, 1160 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.19 (21H, d, *J* 8.1 Hz, ArH), 7.72 (2H, d, *J* 8.1 Hz, ArH), 7.55 (2H, t, *J* 8.7 Hz, ArH), 7.43 (2H, t, *J* 7.2 Hz, ArH), 7.31–7.20 (2H, m, ArH), 4.35 (1H, d, *J* 11.4 Hz, CH), 3.82 (1H, quint, *J* 5.47 Hz, CH), 3.74 (3H, s, $CH_3$), 3.59 (3H, s, $CH_3$), 3.38 (3H, s, $CH_3$), 2.56 (3H, s, $CH_3$), 2.46 (1H, dd, *J* 4.5, 4.5 Hz, $CH_2$), 2.05 (1H, dd, *J* 6, 6 Hz, $CH_2$); $\delta_C$ (75.6 MHz, $CDCl_3$) 173.5, 172.3, 171.0, 138.9, 136.5, 136.1, 133.7, 129.2, 128.2, 126.2, 124.5, 123.8, 119.4, 114.7, 114.3, 52.4, 52.3, 51.5, 42.5, 40.9, 33.4, 12.7; *m*/*z* (EI) 487 (56, $M^+$).

*4.1.18. Methyl 1-phenyl-9H-carbazole-3-carboxylate (**3k**)*

Yield: 0.18 g (66%); colourless solid; mp 142 °C. [Found: C, 79.41; H, 5.29; N, 4.36. $C_{20}H_{15}NO_2$ requires: C, 79.72; H, 5.02; N, 4.65%.] $R_f$ (20% EA/Hexane) 0.60; $\nu_{max}$ (KBr) 3321, 1710 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.78 (1H, s, ArH), 8.55 (1H, s, NH), 8.12 (2H, d, *J* 6 Hz, ArH), 7.66 (2H, d, *J* 7.8 Hz, ArH), 7.53 (2H, t, *J* 7.35 Hz, ArH), 7.45–7.42 (3H, m, ArH), 7.27 (1H, q, *J* 6.8 Hz, ArH), 3.96 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 167.9, 140.1, 139.9, 138.0, 129.3, 128.3, 127.9, 127.1, 126.6, 124.7, 123.6, 123.5, 121.9, 120.7, 120.4, 111.0, 52.0; *m*/*z* (EI) 301 (66, $M^+$).

*4.1.19. 3-Acetyl 9-(phenylsulfonyl)-9H-carbazole (**3l**)*

Yield: 0.29 g, (56%); orange solid; mp 192 °C. [Found: C, 68.45; H, 4.61; N, 3.72; S, 9.39. $C_{20}H_{15}NO_3S$ requires: C, 68.75; H, 4.33; N, 4.01; S, 9.18%.] $R_f$ (20% EA/Hexane) 0.52; $\nu_{max}$ (KBr) 1670, 1382, 1172 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.59 (1H, s, ArH), 8.41–8.35 (2H, m, ArH), 8.11 (1H, d, *J* 8.7 Hz, ArH), 7.99 (1H, d, *J* 8.1 Hz, ArH), 7.84 (1H, d, *J* 7.2 Hz, ArH), 7.55 (2H, t, *J* 7.3 Hz, ArH), 7.49–7.42 (2H, m, ArH), 7.3 (2H, t, *J* 7.6 Hz, ArH), 2.70 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$)

198.9, 141.2, 138.9, 137.5, 134.1, 129.2, 128.2, 127.8, 126.4, 124.4, 120.6, 120.3, 117.1, 115.1, 114.7, 106.2, 26.7; *m*/*z* (EI) 349 (82, $M^+$).

#### 4.1.20. (E)-Methyl 3-(1,2-dimethyl-1H-indol-3-yl)acrylate (**3m**)

Yield: 0.235 g (65%); dark brown solid; mp 130 °C. [Found: C, 73.63; H, 6.31; N, 6.39. $C_{14}H_{15}NO_2$ requires: C, 73.34; H, 6.59; N, 6.11%.] $R_f$ (20% EA/Hexane) 0.64; $\nu_{max}$ (KBr) 1705 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 7.92 (1H, d, *J* 15.9 Hz, Vinylic CH), 7.83 (1H, s, ArH), 7.20 (3H, s, ArH), 6.38 (1H, d, *J* 15.6 Hz, Vinylic CH), 3.79 (3H, s, $CH_3$), 3.51 (3H, s, $CH_3$), 2.38 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 169.1, 141.9, 137.9, 137.5, 125.6, 122.1, 121.3, 119.9, 110.8, 109.3, 108.8, 51.3, 29.7, 10.5; *m*/*z* (EI) 229 (100, $M^+$).

#### 4.1.21. (3E,4E)-Dimethyl 3,3′-(2,5-dimethyl-1-(phenylsulfonyl)-1H-pyrrole-3,4-diyl)diacrylate (**15**)

To a suspension of *t*-BuOK (5.9 g, 52.9 mmol) in dry THF (25 mL) and 18-crown-6 (0.7 g, 2.6 mmol), 2,5-dimethyl-1*H*-pyrrole-3,4-dicarbaldehyde[25] (4 g, 26.5 mmol) in dry THF (25 mL) was added slowly at room temperature and resulting reaction mixture was stirred for 15 min. To this, benzenesulfonylchloride (5.6 g, 31.7 mmol) in dry THF (15 mL) was added and stirred for another 4 h. It was then poured over ice water (200 mL) and extracted with $CHCl_3$ (2×30 mL). The combined organic extracts were washed with $H_2O$ (2×25 mL) and dried ($Na_2SO_4$). Removal of solvent gave crude 2,5-dimethyl-1-(phenylsulfinyl)-1*H*-pyrrole-3,4-dicarbaldehyde, which was dissolved in dry toluene (50 mL). To this, (carbomethoxymethylene)triphenyl phosphorane (18.5 g, 55.6 mmol) was added and refluxed under $N_2$ for 12 h. Removal of solvent followed by column chromatographic separation (10% EA/Hexane) afforded **15** [3.6 g, 34% (two steps)] as a white solid; mp 136 °C. [Found: C, 59.82; H, 4.96; N, 3.77; S, 7.73. $C_{20}H_{21}NO_6S$ requires: C, 59.54; H, 5.25; N, 3.47; S, 7.95%.] $R_f$ (20% EA/Hexane) 0.56; $\nu_{max}$ (KBr) 1708, 1373, 1176 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 7.73 (2H, d, *J* 7.5 Hz, ArH), 7.65 (2H, m, ArH), 7.55–7.53 (3H, m, ArH & Vinylic CH), 6.00 (2H, d, *J* 15.9 Hz, Vinylic CH), 3.78 (6H, s, $CH_3$), 2.49 (6H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 167.1, 139.4, 136.4, 134.1, 132.9, 129.7, 126.4, 120.8, 119.6, 51.6, 13.2; *m*/*z* (EI) 403 (58, $M^+$).

#### 4.1.22. 3,6-Dimethyl 9-(phenylsulfonyl)-9H-carbazole-3,6-dicarboxylate (**16**)

Following the procedure similar to that of **3a**, carbazole **16** (0.20 g, 55%) was obtained using divinyl ester compound **15** (0.5 g, 1.2 mmol), DMF·DMA (591 mg, 4.9 mmol) and dry DMF (1.5 mL) as a colourless solid; mp 192 °C. [Found: C, 68.97; H, 4.83; N, 4.99. $C_{17}H_{15}NO_4$ requires: C, 68.68; H, 5.09; N, 4.71%.] $R_f$ (20% EA/Hexane) 0.60; $\nu_{max}$ (KBr) 1669 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.78 (2H, s, ArH), 8.18 (2H, dd, *J* 1.2, 1.2 Hz, ArH), 7.36 (2H, d, *J* 8.7 Hz, ArH), 3.97 (6H, s, $CH_3$), 3.83 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 167.5, 144.1, 127.9, 122.8, 122.5, 121.8, 108.4, 52.0, 29.4; *m*/*z* (EI) 297 (100, $M^+$).

#### 4.1.23. (3E,4E)-Dimethyl 3,4-(2,5-dimethyl-1-(methyl)-1H-pyrrole)diacrylate (**17**)

Following the procedure similar to that of **3a**, pyrrole **17** (0.18 g, 53%) was obtained using divinyl ester compound **15** (0.5 g, 1.2 mmol), DMA·DMA (660 mg, 4.9 mmol) and dry DMF (1.5 mL) as a colourless solid; mp 168 °C. [Found: C, 65.27; H, 6.65; N, 5.36. $C_{15}H_{19}NO_4$ requires: C, 64.97; H, 6.91; N, 5.05%.] $R_f$ (20% EA/Hexane) 0.42; $\nu_{max}$ (KBr) 1705 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 7.78 (2H, d, *J* 15.9 Hz, Vinylic CH), 5.96 (2H, d, *J* 15.9 Hz, Vinylic CH), 3.78 (6H, s, $CH_3$), 3.41 (3H, s, $CH_3$), 2.30 (6H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 168.2, 138.2, 131.5, 115.5, 115.1, 51.3, 30.7, 11.1; *m*/*z* (EI) 277 (100, $M^+$).

#### 4.1.24. (3E,4E)-Dimethyl 3,3′-(2,5-dimethylthiophene-3,4-diyl)diacrylate (**18**)

Using the procedure similar to that of **15**, thiophene divinyl ester **18** (1.04 g, 65%) was prepared using 2,5-dimethylthiophene-3,4-dicarbaldehyde[26] (1 g, 59.5 mmol) and (carbomethoxymethylene)triphenylphosphorane (4.77 g, 14.1 mmol) in dry toluene (30 mL) as a pale yellow solid; mp 102–104 °C; [Found: C, 60.28; H, 5.47; S, 11.71. $C_{16}H_{20}O_4S$ requires: C, 59.98; H, 5.75; S, 11.44%.] $R_f$ (20% EA/Hexane) 0.61; $\nu_{max}$ (KBr) 1707 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 7.64 (1H, d, *J* 16.1 Hz, Vinylic CH), 6.03 (1H, d, *J* 16.1 Hz, Vinylic CH), 4.26 (2H, q, *J* 7.3 Hz, $CH_2$), 2.46 (3H, s, $CH_3$), 1.34 (3H, t, *J* 7.0 Hz, $CH_3$); $\delta_C$ (100.6 MHz, $CDCl_3$) 166.9, 137.5, 137.2, 132.2, 121.2, 60.5, 14.4, 14.3; *m*/*z* (EI) 308 (43, $M^+$).

#### 4.1.25. (2E,4E,6E)-Trimethyl 3,3′,3″-(trimethylbenzene-1,3,5-triyl)triacrylate (**20**)

Using the procedure similar to that of **15**, benzene trivinylester **20** (3.31 g, 52%) was prepared using 2,4,6-trimethylbenzene-1,3,5-tricarbaldehyde[27] (3.5 g, 17.1 mmol) and (carbomethoxymethylene)triphenylphosphorane (20.6 g, 61.7 mmol) in dry THF (75 mL) as dull white solid; mp 118 °C. [Found: C, 67.99; H, 6.21. $C_{21}H_{24}O_6$ requires: C, 67.73; H, 6.50%.] $R_f$ (20% EA/Hexane) 0.52; $\nu_{max}$ (KBr) 1724 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 7.79 (1H, d, *J* 16.2 Hz, Vinylic CH), 5.96 (1H, d, *J* 16.2 Hz, Vinylic CH), 3.82 (3H, s, $CH_3$), 2.23 (3H, s, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 166.6, 144.1, 133.8, 133.7, 125.1, 51.7, 18.8; *m*/*z* (EI) 372 (53, $M^+$), 357 (60%), 340 (40%), 281 (66%).

#### 4.1.26. (2E,4E,6E)-Trimethyl (1,3,5-tris(methoxycarbonylmethyl)-benzene)triacrylate (**22**)

Following the procedure similar to that of **1e**, compound **22** (0.56 g, 63%) was obtained using (2*E*,4*E*,6*E*)-trimethyl (1,3,5-tris (bromomethyl)benzene)triacrylate (1 g, 1.6 mmol), Pd $(PPh_3)_2Cl_2$ (350 mg, 0.49 mmol) and $K_2CO_3$ (1.36 g, 9.8 mmol) in dry THF–MeOH (35–10 mL) under CO atmosphere as a yellow solid; mp 76 °C. [Found: C, 59.65; H, 5.27. $C_{27}H_{30}O_{12}$ requires: C, 59.34; H, 5.53%.] $R_f$ (20% EA/Hexane) 0.44; $\nu_{max}$ (KBr) 1726, 1715 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 7.70 (1H, d, *J* 16.5 Hz, Vinylic CH), 5.99 (1H, d, *J* 16.5 Hz, Vinylic CH), 3.80 (3H, s, $CH_3$), 3.66 (3H, s, $CH_3$), 3.62 (2H, s, $CH_2$); $\delta_C$ (75.6 MHz, $CDCl_3$) 171.1, 165.9, 142.3, 136.9, 130.4, 126.8, 52.2, 51.9, 37.3; *m*/*z* (EI) 546 (49, $M^+$).

#### 4.1.27. 9-Phenylsulfonyl-4-hydroxycarbazole-1-carboxaldehyde (**25**)

To a mixture of 2-methyl-3-acetylindole **24** (0.5 g, 1.6 mmol) and DMF·DMA (380 mg, 3.2 mmol), dry DMF (1.5 mL) was added and the reaction mixture was heated at 140 °C for 4 h under $N_2$ atmosphere. Usual workup followed by column chromatographic purification afforded title compound **25** (0.36 g, 65%) as a light brown solid; mp 190 °C. [Found: C, 65.25; H, 3.46; N, 4.30; S, 8.89. $C_{19}H_{13}NO_4S$ requires: C, 64.95; H, 3.73; N, 3.99; S, 9.13%.] $R_f$ (20% EA/Hexane) 0.61; $\nu_{max}$ (KBr) 3340, 1648, 1366, 1158 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 12.01 (1H, s, OH), 9.94 (1H, s, CHO), 8.30 (2H, t, *J* 7.3 Hz, ArH), 7.99 (1H, d, *J* 8.7 Hz, ArH), 7.86 (2H, d, *J* 7.8 Hz, ArH), 7.62 (1H, d, *J* 8.7 Hz, ArH), 7.53–7.35 (5H, m, ArH); $\delta_C$ (75.6 MHz, $CDCl_3$) 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; *m*/*z* (EI) 351 (100, $M^+$).

#### 4.1.28. Ethyl 1,2-dimethyl-1H-indole-3-carboxylate (**29**)

Following the procedure similar to that of **3a**, *N*-methylated product **29** (0.34 g, 65%) was obtained using ethyl 2-methyl-1*H*-indole-3-carboxylate **28** (0.5 g, 2.5 mmol) and DMF·DMA (588 mg, 4.9 mmol) as a colourless solid; mp 96 °C. [Found: C, 72.18; H, 6.69; N, 6.74. $C_{13}H_{15}NO_2$ requires: C, 71.87; H, 6.96; N, 6.45%.] $R_f$ (20% EA/Hexane) 0.80; $\nu_{max}$ (KBr) 1708 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 8.13–8.10 (1H, m, ArH), 7.28–7.20 (3H, m, ArH), 4.39 (2H, q, *J* 7 Hz, $CH_2$), 3.65 (3H, s, $CH_3$), 2.75 (3H, s, $CH_3$), 1.44 (3H, t, *J* 7.05 Hz, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 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; *m*/*z* (EI) 217 (87, $M^+$).

*4.1.29. Diethyl 1,3,5-trimethyl-1H-pyrrole-2,4-dicarboxylate (**31**)*

Following the procedure similar that of **3a**, *N*-methyl pyrrole **31** (0.40 g, 75%) was obtained using diethyl 3,5-dimethyl-1*H*-pyrrole-2,4-dicarboxylate **30** (0.5 g, 2.1 mmol) and DMF·DMA (498 mg, 4.2 mmol) as a colourless solid; mp 110 °C. [Found: C, 61.92; H, 7.26; N, 5.82. $C_{13}H_{19}NO_4$ requires: C, 61.64; H, 7.56; N, 5.53%.] $R_f$ (20% EA/Hexane) 0.81; $\nu_{max}$ (KBr) 1703, 1710 $cm^{-1}$; $\delta_H$ (300 MHz, $CDCl_3$) 4.30 (4H, quint, *J* 7.12 Hz, $CH_2$), 3.77 (3H, s, $CH_3$), 2.53 (3H, s, $CH_3$), 2.50 (3H, s, $CH_3$), 1.36 (6H, q, *J* 6.3 Hz, $CH_3$); $\delta_C$ (75.6 MHz, $CDCl_3$) 165.6, 162.2, 141.0, 131.0, 120.3, 112.5, 59.9, 59.5, 32.9, 14.3, 12.7, 11.9; *m*/*z* (EI) 253 (68, $M^+$).

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