Studies on Lewis-acid mediated domino reaction of N-protected bromomethylindoles with arenes/heteroarenes

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A systematic study on Lewis-acid mediated domino reaction of N-protected 2/3-bromomethylindoles with various types of arenes and heteroarenes is reported.

Keywords: Arylation, domino reaction, carbazoles, electrocyclization, annulation

Domino reaction is one of the most powerful synthetic routes for the synthesis of various types of heterocycles\(^1\)\(^2\) as well as carbocycles\(^3\). The synthesis of several highly complex heterocyclic systems and natural products has been realized via Lewis acid-mediated domino reactions\(^4\)\(^6\). Recently, a plethora of aromatic and hetero-aromatic annulation reactions have been reported\(^7\). Dehaen and co-workers reported a general method for the synthesis of indolo[b]-carbazoles\(^8\) involving iodine-mediated domino reaction of indole with aryl aldehydes. Fillion and co-workers reported\(^9\) the preparation of tetrahydrobenzo-[b]fluoren-11-one involving the domino reaction initiated via Lewis acid catalyzed 1,5-hydrogen shift at room temperature.

Over the years, N-protected bromomethylindoles have been widely utilized for the synthesis of substituted indole derivatives\(^10\). One-pot synthesis of substituted carbazoles has been achieved involving Michael addition\(^11\) and electrocyclization\(^12\) methodologies. Several transition-metal mediated protocols have been described for carbazoles\(^13\)\(^15\). In continuation of the recent reports on synthesis of annulated carbazoles\(^16\)\(^17\), herein are reported the systematic study on arylation as well as annulation of N-protected bromomethylindoles with different types of arenes as well as heteroarenes.

Results and Discussion

Recently this group reported\(^16\), a facile ZnBr\(_2\) mediated arylation of 1-phenylsulfonyl-2-bromomethylindole 1 and 1-phenylsulfonyl-3-bromomethyl-indole 2 with arenes/heteroarenes which led to the formation of the carbazoles 3. The formation of the carbazoles involves an arylation reaction followed by a facile 1,5-hydrogen shift to form a triene, which, upon electrocyclization followed by aromatization via elimination of diethyl malonate, afforded annulated carbazoles (Scheme I).

The present research work is undertaken to understand the reaction pathway and if possible also to enhance the yield of annulated carbazoles 3. Towards the realization of these objectives, the reaction of bromo compound 1 with naphthalene in the presence of 0.2 equiv. of ZnBr\(_2\) and anhydrous K\(_2\)CO\(_3\) at RT followed by thermolysis at 80°C furnished the arylated product 4a in 68% yield. Similarly, the reaction of bromo compound 1 with bithiophene in the presence of 0.2 equiv. of ZnBr\(_2\) and
anhydrous K$_2$CO$_3$ at RT gave 4b in 81% yield (Scheme II).

It should be noted that the reaction of bromo compound 1 with bithiophene using 0.2 equiv. of ZnBr$_2$ in the absence of K$_2$CO$_3$ at RT followed by thermolysis afforded annulated heterocycle\(^\text{16}\). Hence, the reactions performed herein clearly confirm that hydrogen bromide generated during the arylation reaction plays a crucial role in the formation of carbazole.

The domino reaction of bromo compound 1 with naphthalene using 2 equiv. of ZnBr$_2$ in the presence of anhydrous K$_2$CO$_3$ at RT followed by subsequent thermolysis at 80°C for 1 hr gave naphtho[\(b\)]carbazole 5a in 50% yield. However, the domino reaction of bromo compound 1 with bithiophene in the presence of 2 equiv. of ZnBr$_2$ and anhydrous K$_2$CO$_3$ at RT furnished thieno[\(2,3-b\)]carbazole 5b in 58% yield (Scheme III). It should be noted that in the absence of K$_2$CO$_3$ these reactions resulted in poor yield of 5a and 5b (Ref 16). This clearly confirms that sufficient concentration of Lewis-acid/hydrogen bromide is essential for triggering subsequent triene formation, which eventually leads to the carbazole 5a/5b.

The arylation of isomeric bromo compound 2 with \(p\)-xylene/anisole in the presence of 0.2 equiv. of ZnBr$_2$ and anhydrous K$_2$CO$_3$ at reflux gave 6a/6b in 74 and 71% yields, respectively. As expected, the annulation of compound 6a/6b using ZnBr$_2$ in 1,2-DCE at reflux furnished carbazoles 7a and 7b in 67% and 62% yields, respectively (Scheme IV).

As a representative case, the Lewis acid mediated domino reaction of bromomethylindole 2 with bithiophene was carried out using 0.2 equiv. of different Lewis acids (Scheme IV) and the results obtained are presented in Table I. It is clear that among the various Lewis acids employed, a maximum of 62% yield for annulated product 7c can be obtained using 0.2 equiv. of InBr$_3$. Among the divalent zinc salts, triflate was found to be better (entries 4, 5 and 6). However, the annulation was found to be unsuccessful with Yb(OTf)$_3$ as well as Gd(OTf)$_3$ (entries 9 and 10).

Having established the facile domino reaction of the bromo compounds 1 and 2 containing malonylidene unit, the preparation of bromo compound containing other vinylidene units were planned to test their efficacy in annulation reactions.
As expected, Knoevenagel condensation of aldehyde 8 with N,N-dimethylbarbituric acid, followed by allylic bromination produced bromo compound 10 in 69% overall yield. Similar condensation of the aldehyde 8 with malononitrile/meldrum acid produced vinyl compounds 11 and 13, respectively. However, attempted allylic bromination of 11 and 13 were unsuccessful due to their poor solubility in CCl₄ (Scheme V).

The domino reaction of dimethyl barbiturate bromo compound 10 was successfully carried out with arenes and heteroarenes to afford respective carbazoles 5a-g in moderate yields (Scheme VI).

Full details on reaction conditions, and the yields of annulated carbazoles obtained are described in Table II. The yields of the carbazoles 5a-g were relatively lower in comparison with those obtained from bromo compound 1.

Comparatively less electron withdrawing nature of dimethylbarbiturate unit of 10 was expected to make it relatively more reactive to produce the respective arylated compounds. However, the less annulation yields obtained with this bromo compound indicates that the dimethylbarbiturate unit may be less suitable for subsequent steps namely triene formation, electrocyclization or elimination.
As a representative case, the structure of the benzo[b]carbazole 5f (Figure 1) was confirmed by a single crystal X-ray diffraction analysis. The domino reaction of bromo compound 10 with benzofuran using 0.2 equiv. of ZnBr$_2$ gave carbazole 5g in 55% yield. The spectral data of compound 5g was identical in all aspects with the annulated heterocycle prepared using bromo compound 1.

However, contrary to the earlier report, an isomeric structure for 5g (Figure 2) was confirmed by a single crystal X-ray diffraction analysis. Obviously, the Friedel-Crafts indolylmethylation of benzo[b]furan takes place at the 2-position to afford the benzofuro[2,3-b]carbazole 5g. Thereafter, the bromo compound 1 was transformed into acetate 15 via interaction with potassium acetate in dry DMF at RT. The annulation of indolylmethylacetate 15 with arene/heteroarene in the presence of anhydrous FeCl$_3$ afforded corresponding annulated heterocycles 5e-j in 40-55% of yield (Scheme VII).

The choice of FeCl$_3$ as a Lewis acid for the domino reaction of 15 is based on the literature reports wherein a facile arylation of benzylic acetates was performed in excellent yields. Full details on reaction conditions, and the yields of annulated carbazoles obtained are described in Table III. Similar to the case of diethylmalonate tethered bromo compound 1, annulation was found to be successful with indolylmethylacetate 15. However, the yields of the carbazoles 5e-j obtained were relatively less compared with the bromo compound 1.

To further understand the influence of electronic effect on the annihilation reaction, the domino reaction

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**Table III — Annulation of 15 with arenes/heteroarenes**

<table>
<thead>
<tr>
<th>Entry</th>
<th>ArH</th>
<th>FeCl$_3$ &amp; Condition</th>
<th>Product</th>
<th>Yield (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>2 equiv., reflux, 4 hr</td>
<td>5e</td>
<td>50 (55)$^b$</td>
</tr>
<tr>
<td>2</td>
<td>OMe</td>
<td>2 equiv., reflux, 5 hr</td>
<td>5f</td>
<td>50/57$^b$</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.2 equiv., RT, 2 hr</td>
<td>5g</td>
<td>55/60$^b$</td>
</tr>
<tr>
<td>4</td>
<td>Me</td>
<td>0.2 equiv., RT, 2 hr</td>
<td>5h</td>
<td>52 (55)$^b$</td>
</tr>
<tr>
<td>5</td>
<td>Me</td>
<td>2 equiv., reflux, 2 hr</td>
<td>5i</td>
<td>55 (56)$^b$</td>
</tr>
<tr>
<td>6</td>
<td>Me</td>
<td>0.2 equiv., RT, 2 hr</td>
<td>5j</td>
<td>40 (40)$^b$</td>
</tr>
</tbody>
</table>

$^a$ Isolated yield after column chromatography

$^b$ Yield obtained from the bromo compound 1.
of bromo compound 16 containing t-butoxycarbonyl unit at the indole nitrogen was planned. Similar to the case of 1-phenylsulfonyl bromo compound 1, the interaction of bromo compound 16 with veratrole or naphthalene/1-methylnaphthalene using ZnBr₂ in the presence of K₂CO₃ in 1,2-DCE at RT afforded the respective arylated compounds 17a-c (Scheme VIII).

Subsequently, the attempted annulation of bromo compound 16 with naphthalene using 0.2 equiv. of ZnBr₂ at RT for 8 hr gave aldehyde 18a in 53% yield (Scheme IX).

The mechanism of formation of the aldehyde 18a can be visualized as mentioned in Scheme X. The arylated intermediate 17b may undergo a facile cleavage of the tertiary butoxy carbonyl (Boc) group with in situ generated hydrobromic acid to give N-free indole 19, which on ZnBr₂-mediated 1,5-hydrogen shift leads to the formation of ene-imine 20. The ene-imine intermediate 20 during aqueous work up via addition of water followed by elimination of diethyl malonate furnished the aldehyde 18a.

The interaction of bromo compound 16 with electron-rich arenes in the presence of 0.2 equiv. of anhydrous ZnBr₂ in 1,2-DCE at RT gave respective arylated indole-3-aldehydes 18b-e in 54-64% yields. Similar to the earlier observation 16, the interaction of bromo compound 16 with ZnBr₂ in the absence of arene gave lactone 22 in 62% yield (Scheme XI).

The formation of an aldehyde 18c via interaction of bromo compound 16 with m-xylene was found to be general with other Lewis-acids as well. The nature of Lewis-acid employed, and the yields of the aldehyde 18c isolated are outlined in Table IV. With the exception of Sc(OTf)₃ and Yb(OTf)₃, in all other cases the aldehyde 18c was isolated in reasonable yields.

Surprisingly, the interaction of the bromo compound 16 with 1,2-dimethoxybenzene led to the formation of annulated carbazole 23a in 62% yield. Gratifyingly, the interaction of bromo compound 16 with heteroarenes also led to the formation of...
respective annulated carbazoles 23b-f (Scheme XII). This clearly indicates that in the case of 1,2-dimethoxybenzene or heteroaarenes, the electron density of veratryl/heteroaryl unit induces the formation of carbazoles.

The arylated intermediate 24 upon intramolecular cyclization may lead to the formation of cyclized product 26. The latter upon elimination of diethyl malonate followed by cleavage of Boc unit might have furnished carbazole 23a-f (Scheme XIII).

Full details on nature of heteroarenes, reaction conditions employed, and the yields of annulated carbazoles 23b-f obtained are described in Table V.

The annulation of bromo compound 16 with benzofuran in the presence of 0.2 equiv. of ZnBr₂ afforded carbazole 23b in 59% yield (entry 1). Similarly, the domino reaction of bromo compound 16 with heteroaarenes such as 1-hexylindole, 2-methylthiophene, bithiophene, terthiophene, using 0.2 equiv. of ZnBr₂ at RT led to the formation of carbazoles 23c-f in 55-66% yield (entries 2, 3, and 4).

As a representative case, the structure of the benzofuro[2,3-b]carbazole 23b (Figure 3) was...
confirmed by a single crystal X-ray diffraction analysis.

**Experimental Section**

All reactions were carried out in oven-dried apparatus using dry solvent under anhydrous condition, unless otherwise noted. Analytical thin layer chromatography (TLC) was performed on silica gel and components were visualized by observation under iodine vapour or UV-light. Flash chromatography was performed using silica gel (230-400 mesh). All the melting points are uncorrected. IR spectra were recorded on a Shimadzu FT-IR 8300 instrument. NMR spectra (Bruker 300 MHz) were determined in CDCl₃ solution containing TMS as an internal standard unless otherwise stated. Organic extracts were dried over anhydrous Na₂SO₄. The following abbreviations explain the multiplicity s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (J) were reported in Hertz (Hz). Carbon types were determined from ¹³C NMR and DEPT experiments. 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.

**Diethyl-2-((2-(naphthalene-1-yl)methyl)-1-(phenylsulfonyl)-1H-indol-3-yl)methylene)malonate, 4a**

To a solution of bromo compound 1 (0.31 g, 0.59 mmol) in dry DCE (10 mL), anhydrous ZnBr₂ (0.03 g, 0.13 mmol), K₂CO₃ (0.16 g, 1.15 mmol) and naphthalene (0.09 g, 0.70 mmol) were added. It was then stirred at RT for 3 hr and then refluxed for 1 hr under N₂ atmosphere. The solvent was removed and the residue was quenched with ice-water (20 mL) containing 1 mL of conc. HCl, extracted with chloroform (2 × 10 mL) and dried (anhyd. Na₂SO₄). Removal of solvent followed by flash column chromatographic purification (n-hexane/ethyl acetate 98:2) led to the isolation of arylated product 4a (0.23 g, 68%) as a colourless solid; m.p. 124-26°C; IR (KBr): 1728, 1713, 1624, 1376, 1177 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 8.31 (d, J = 8.4 Hz, 1 H), 8.08 (d, J = 8.1 Hz, 1 H), 7.87 (d, J = 7.5 Hz, 1 H), 7.66 (d, J = 8.1 Hz, 1 H), 7.57-7.35 (m, 8 H), 7.28 (t, J = 7.5 Hz, 1 H), 7.18 (t, J = 7.8 Hz, 2 H), 7.06 (t, J = 7.8 Hz, 1 H), 6.74 (d, J = 6.9 Hz, 1 H), 4.97 (s, 2 H), 4.18 (q, J = 7.2 Hz, 2 H), 3.87 (q, J = 6.9 Hz, 2 H), 2.73 (t, J = 7.2 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃): δ 164.7, 163.5, 138.0, 137.7, 136.1, 133.2, 132.6, 131.2, 129.0, 128.5, 128.2, 127.1, 126.8, 126.0, 125.9, 125.3, 125.1, 124.9, 124.6, 123.4, 122.7, 119.1, 117.8, 114.4, 61.1, 60.7, 29.0, 13.5, 12.8; MS (EI): m/z (%) 567 (M⁺, 76%). Anal. Calcd for C₃₉H₂₃NO₃S (567.17): C, 69.82; H, 5.15; N, 2.47; S, 5.65. Found: C, 69.65; H, 5.01; N, 2.67; S, 5.93%.

**12-(Phenylsulfonyl)-12H-naphtho[1,2-b]carbazole, 5a**

To a solution of bromo compound 1 (0.31 g, 0.59 mmol) in dry DCE (10 mL), anhydrous ZnBr₂ (0.27 g, 1.19 mmol), K₂CO₃ (0.16 g, 1.15 mmol) and naphthalene (0.09 g, 0.70 mmol) were added. It was then stirred at RT for 3 hr and then refluxed for 1 hr under N₂ atmosphere. The solvent was removed and the residue was quenched with ice-water (20 mL) containing 1 mL of conc. HCl, extracted with chloroform (2 × 10 mL) and dried (anhyd. Na₂SO₄). Removal of solvent followed by flash column chromatographic purification (n-hexane/ethyl acetate 99:1) led to the isolation of naphtho[1,2-b]carbazole 5a (0.12 g, 50%) as a colourless solid; m.p. 210-211°C (Lit.¹⁶ 212°C).

**9-(Phenylsulfonyl)-2-(thiophen-2-yl)-9H-thieno[2,3-b]carbazole, 5b**

The domino reaction of bromo arylation of bromo compound 1 (0.31 g, 0.59 mmol) with bithiophene (0.12 g, 0.72 mmol) in the presence of anhydrous ZnBr₂ (0.03 g, 0.13 mmol) and K₂CO₃ (0.16 g, 1.15 mmol) in dry DCE (10 mL) following the same procedure as that of 4a afforded the compound 4b (0.29 g, 81%) as a pale yellow liquid; IR (KBr): 1730, 1712, 1624, 1376, 1260, 1238, 1177 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 8.13 (d, J = 8.4 Hz, 1 H), 7.84 (s, 1 H), 7.46 (d, J = 7.8 Hz, 2 H), 7.35-7.08 (m, 8 H), 6.95-6.87 (m, 1 H), 6.78 (d, J = 3.3 Hz, 1 H), 4.59 (s, 2 H), 4.25 (q, J = 6.9 Hz, 2 H), 3.81 (q, J = 7.2 Hz, 2 H), 1.25 (t, J = 7.2 Hz, 3 H), 0.59 (t, J = 7.2 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃): δ 165.3, 164.0, 139.4, 138.4, 138.1, 137.3, 136.5, 136.3, 133.8, 130.1, 129.0, 127.8, 127.5, 126.8, 126.4, 125.4, 124.2, 124.1, 123.5, 123.4, 119.9, 117.5, 115.0, 61.9, 61.3, 27.4, 14.2, 13.2; MS (EI): m/z (%) 605 (M⁺, 46%). Anal. Calcd for C₃₈H₂₃NO₃S (605.74): C, 61.47; H, 4.49; N, 2.31; S, 15.88. Found: C, 61.69; H, 4.29; N, 2.48; S, 15.69%.
**Diethyl-2-((3-(2,5-dimethylbenzyl)-1-(phenylsulfonyl)-1H-indol-2-yl) methylene) malonate, 6a** The arylation of bromo compound 2 (0.3 g, 0.57 mmol) with p-xylene (0.08 mL, 0.65 mmol) and K$_2$CO$_3$ (0.16 g, 1.16 mmol) in the presence of ZnBr$_2$ (0.03 g, 0.13 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of 4a afforded the compound 6a (0.23 g, 74%) as a colourless solid; m.p. 126°C. IR (KBr): 1730, 1714, 1624, 1372, 1173 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$): δ 8.13 (s, 1 H), 8.08 (d, J = 8.4 Hz, 1 H), 7.97 (d, J = 7.2 Hz, 2 H), 7.54-7.26 (m, 4 H), 7.08-6.86 (m, 4 H), 6.38 (s, 1 H), 4.34 (q, J = 7.2 Hz, 2 H), 3.85 (s, 2 H), 3.69 (q, J = 7.2 Hz, 2 H), 2.21 (s, 3 H), 2.07 (s, 3 H), 1.36 (t, J = 7.2 Hz, 3 H), 0.99 (t, J = 7.2 Hz, 3 H); $^{13}$C NMR (75.4 MHz, CDCl$_3$): δ 164.7, 163.3, 139.7, 131.7, 135.8, 135.1, 134.8, 133.8, 133.0, 131.0, 130.6, 129.9, 129.1, 128.9, 127.9, 127.0, 126.2, 125.2, 123.9, 121.1, 114.7, 61.9, 61.3, 28.8, 21.0, 19.2, 14.1, 13.8; MS (EI): m/z (%) 545 (M$^+$, 87%). Anal. Calcd for C$_3$H$_5$NO$_3$S (545.65): C, 68.24; H, 5.73; N, 2.57; S, 5.88. Found: C, 68.48; H, 5.61; N, 2.80; S, 5.66%.

**Diethyl-2-((3-(4-methoxybenzyl)-1-(phenylsulfonyl)-1H-indol-2-yl)methylene)malonate, 6b** The arylation of bromo compound 2 (0.3 g, 0.57 mmol) with anisole (0.07 mL, 0.68 mmol) and K$_2$CO$_3$ (0.16 g, 1.16 mmol) in the presence of ZnBr$_2$ (0.03 g, 0.13 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of 4a afforded the compound 6b (0.22 g, 71%) as a colourless solid; m.p. 142°C; IR (KBr): 1729, 1716, 1622, 1376, 1177 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$): δ 8.16 (s, 1 H), 8.07 (d, J = 8.4 Hz, 1 H), 7.95 (d, J = 8.4 Hz, 2 H), 7.52-7.39 (m, 3 H), 7.30-7.26 (m, 1 H), 7.09-0.76 (m, 2 H), 6.88 (d, J = 8.7 Hz, 2 H), 6.73 (d, J = 6.6 Hz, 2 H), 4.36 (q, J = 6.9 Hz, 2 H), 3.88 (q, J = 8.7 Hz, 4 H), 3.73 (s, 3 H), 3.17 (t, J = 7.2 Hz, 3 H), 0.98 (t, J = 7.2 Hz, 3 H); MS (EI): m/z (%) 547 (M$^+$, 39%). Anal. Calcd for C$_{30}$H$_{32}$NO$_7$S (547.62): C, 65.80; H, 5.34; N, 2.56; S, 5.86. Found: C, 65.62; H, 5.15; N, 2.56; S, 5.86%.

**7,10-Dimethyl-5-(phenylsulfonyl)-5H benzo[b]carbazole, 7a** To a solution of compound 6a (0.3 g, 0.55 mmol) in dry 1,2-DCE (10 mL), ZnBr$_2$ (0.02 g, 0.09 mmol) was added. It was then refluxed for 1 hr under N$_2$ atmosphere. The solvent was removed and the residue was quenched with ice-water (50 mL) containing 1 mL of conc. HCl. Removal of solvent followed by flash column chromatographic purification (n-hexane/ethyle acetate 99:1) led to the isolation of carbazole 7a (0.14 g, 67%) as a colourless solid; m.p. 180°C (Lit.$^{16}$ 182°C).

**8-Methoxy-5-(phenylsulfonyl)-5H-benzo[b]carbazole, 7b** The domino reaction of bromo compound 6b (0.3 g, 0.54 mmol) using ZnBr$_2$ (0.02 g, 0.09 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of 7a afforded the compound 7b (0.13 g, 62%) as a colourless solid; m.p. 215-16°C (Lit.$^{16}$ 214°C).

**General procedure for domino reaction of bromo compound 2 with bithiophene**

To a solution of bromo compound 2 (0.38 mmol) in dry 1,2-DCE (8 mL), bithiophene (0.48 mmol) and Lewis-acid (0.09 mmol) were added. It was then stirred at RT for specified time period (Table I) under N$_2$ atmosphere. The solvent was removed and the residue was quenched with ice-water (50 mL) containing 1 mL of conc. HCl. It was then extracted with chloroform (2 × 10 mL) and dried (anhyd. Na$_2$SO$_4$). Removal of solvent followed by column chromatography purification (n-hexane/ethyle acetate 99:1) led to the isolation of thieno[3,2-b]carbazole 7c as a pale yellow solid; m.p. 227°C (Lit.$^{16}$ 228°C).

**1-Phenylsulfonyl-1,3-dimethyl-5-((2-methyl-1H-indol-3-yl)methylene)pyrimidine-2,4,6(1H,3H,5H)-trione, 9** To a solution of aldehyde 8 (5 g, 16.72 mmol) in dry benzene (120 mL), N,N-dimethylbarbituric acid (2.87 g, 18.38 mmol), piperidine (6 drops) and acetic acid (3 drops) were added and refluxed in Dean-Stark apparatus for 15 hr. Removal of solvent followed by crystallisation from methanol afforded the compound 9 (5.8 g, 79%) as a pale yellow solid; m.p. 284°C (Lit.$^{16}$ 284°C).
the compound 10 (1.04 g, 88%) as a pale yellow solid; m.p. 200-02°C; IR (KBr): 1678, 1378, 1178 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)); \(\delta\) 8.55 (s, 1 H), 8.03 (d, \(J = 8.4\) Hz, 1 H), 7.91 (d, \(J = 7.8\) Hz, 2 H), 7.53-7.48 (m, 1 H), 7.42-7.37 (m, 2 H), 7.33-7.27 (m, 1 H), 7.22-7.17 (m, 2 H), 5.02 (s, 2 H), 3.37 (s, 3 H); 13\(^C\) NMR (75.4 MHz, CDCl\(_3\)); \(\delta\) 161.5, 159.3, 151.1, 146.8, 138.9, 138.1, 136.4, 134.4, 129.5, 127.1, 126.9, 125.1, 124.3, 121.4, 119.5, 119.1, 115.1, 32.1, 29.0, 28.5.

**General procedure for ZnBr\(_2\)-mediated domino reaction of bromo compound 10 with heteroarene**

To a solution of bromo compound 10 (0.96 mmol) in dry DCE (15 mL), anhydrous ZnBr\(_2\) (0.18 mmol) and heteroarene (1.14 mmol) were added. It was then stirred at RT for the specified time period (Table II) under N\(_2\) atmosphere. The solvent was removed and the residue was quenched with ice-water (50 mL) containing 1 mL of conc.HCl, extracted with chloroform (2x10 mL) and dried (anhyd. Na\(_2\)SO\(_4\)). Removal of solvent followed by flash column chromatographic purification (n-hexane/ethyl acetate) led to the isolation of carbazole analogs 5a, 5c, 5e and 5f.

**1-Phenylsulfonyl-2-(2-methyl-1H-indol-3-yl)methylene)malononitrile**, 11 To a solution of aldehyde 8 (5 g, 16.72 mmol) in dry benzene (120 mL), malononitrile (1.21 g, 18.31 mmol), piperidine (6 drops) and acetic acid (3 drops) were added and refluxed in a Dean-Stark apparatus for 18 hr. Removal of solvent followed by crystallisation from methanol afforded the compound 11 (4.7 g, 81%) as a pale yellow solid; m.p 192-94°C; IR (KBr): 1678, 1378, 1178 cm\(^{-1}\); 13\(^C\) NMR (75.4 MHz, CDCl\(_3\)); \(\delta\) 160.8, 127.1, 126.9, 125.1, 124.3, 121.4, 119.5, 119.1, 115.1, 32.1, 29.0, 28.5.

**General procedure for ZnBr\(_2\)-mediated domino reaction of bromo compound 10 with arene**

To a solution of bromo compound 10 (0.96 mmol) in dry DCE (15 mL), anhydrous ZnBr\(_2\) (0.18 mmol) and arene (1.14 mmol) were added. It was then refluxed for the specified time period (Table II) under N\(_2\) atmosphere. The solvent was removed and the residue was quenched with ice-water (50 mL) containing 1 mL of conc.HCl, extracted with chloroform (2x10 mL) and dried (anhyd. Na\(_2\)SO\(_4\)). Removal of solvent followed by flash column chromatographic purification (n-hexane/ethyl acetate) led to the isolation of carbazole analogs 5a, 5c, 5e and 5f.

**To a solution of arene**

To a solution of arene (1.14 mmol) in dry DCE (15 mL), following the general procedure for arene and subsequent flash column chromatographic purification (n-hexane/ethyl acetate 99:1) led to the isolation of carbazole analogs 5b, 5d, and 5g.

**12-(Phenylsulfonyl)-12H-naphtho[1,2-b]carbazole, 5a** The domino reaction of bromo compound 10 (0.50 g, 0.96 mmol) with naphthalene (0.15 g, 1.17 mmol) using anhydrous ZnBr\(_2\) (0.44 g, 1.95 mmol) in dry DCE (15 mL), following the general procedure for arene and subsequent flash column chromatographic purification (n-hexane/ethyl acetate 99:1) led to the isolation of naphtho[1,2-b]carbazole 5a (0.15 g, 38%) as a colourless solid; m.p. 210°C (Lit.\(^{16}\) 212°C).

**9-(Phenylsulfonyl)-2-(thiophen-2-yl)-9H-thieno[2,3-b]carbazole, 5b** The domino reaction of bromo compound 10 (0.50 g, 0.96 mmol) with thiophene (0.19 g, 1.14 mmol) anhydrous ZnBr\(_2\) (0.04 g, 0.18 mmol) in dry DCE (15 mL), following the general procedure for heteroarene and subsequent flash column chromatographic purification (n-hexane/ethyl acetate 99:1) led to the isolation of thiieno[2,3-b]carbazole 5b (0.19 g, 44%) as a pale yellow solid; m.p. 186-87°C (Lit.\(^{16}\) 188°C).

**8,9-Dihydro[1,4]dioxo-5-(phenylsulfonyl)-5H-benzo[b]carbazole, 5c** The domino reaction of bromo compound 10 (0.5 g, 0.96 mmol) with 1,4-benzodioxan (0.14 mL, 1.17 mmol) in the presence of anhydrous ZnBr\(_2\) (0.44 g, 1.95 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of 5a afforded the compound 5c (0.21 g, 52%) as a colourless solid; m.p. 252°C; \(^1\)H NMR (300 MHz, CDCl\(_3\)); \(\delta\) 8.52 (s, 1 H), 8.29 (d, \(J = 7.2\) Hz, 1 H), 8.07 (s, 1 H), 8.03 (d, \(J = 7.2\) Hz, 1 H), 7.89 (d, \(J = 7.5\) Hz, 1 H), 7.78 (d, \(J = 7.2\) Hz, 2 H), 7.53-7.25 (m, 2 H), 7.41-7.23 (m, 3 H), 2.67 (s, 3 H), 1.80 (s, 6 H); MS (EI); m/z (%) 425 (M\(^+\), 62%).
6.87. Found: C, 74.52; H, 5.47; N, 6.25; S, 6.60%.

C ole, compound carbazole, 5e following the same procedure as that of 1.95 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of 5e: 125.9, 124.0, 123.6, 122.9, 120.7, 119.8, 118.9, 115.7, 137.6, 133.6, 132.6, 128.9, 127.4, 127.2, 126.5, 126.3, 125.9, 124.0, 123.6, 122.9, 120.7, 119.8, 118.9, 115.7, 108.7, 106.9, 98.5, 43.3, 29.5, 28.6, 22.5, 14.0; MS (EI): m/z (%) 466 (M⁺, 56%). Anal. Calc'd for C29H26N2O5S (466.59): C, 74.65; H, 5.62; N, 6.00; S, 18.73; Found: C, 74.58; H, 5.41; N, 6.25; S, 6.60%.

1-Pentyl-7-(phenylsulfonyl)-indolo[3,2-b]carbazole, 5d The domino reaction of bromo compound 10 (0.5 g, 0.96 mmol) with 1-pentyllindole (0.22 g, 1.18 mmol) in the presence of ZnBr₂ (0.04 g, 0.18 mmol) in dry 1,2-DCE (8 mL) following the same procedure as that of 5b afforded the compound 5d (0.25 g, 55%) as a colourless solid; m.p. 207-08°C (Lit. 208°C).

7,9-Dimethoxy-5-(phenylsulfonyl)-5H-benzo[b]carbazole, 5e The domino reaction of bromo compound 10 (0.5 g, 0.96 mmol) with m-xylene (0.14 mL, 1.13 mmol) in the presence of anhydrous ZnBr₂ (0.44 g, 1.95 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of 5a afforded the compound 5e (0.19 g, 51%) as a colourless solid; m.p. 207-08°C (Lit. 10 208°C).

8,9-Dimethoxy-5-(phenylsulfonyl)-5H-benzo[b]carbazole, 5f The domino reaction of bromo compound 10 (0.5 g, 0.96 mmol) with veratrole (0.15 mL, 1.16 mmol) in the presence of ZnBr₂ (0.44 g, 1.95 mmol) in dry 1,2-DCE (12 mL) following the same procedure as that of 5a afforded the compound 5f (0.22 g, 55%) as a colourless solid; m.p. 207-08°C (Lit. 10 210°C).

7-(Phenylsulfonyl)-7H-benzofuro[2,3-b]carbazole, 5g The domino reaction of bromo compound 10 (0.5 g, 0.96 mmol) with benzo[b]furan (0.13 mL, 1.18 mmol) in the presence of ZnBr₂ (0.04 g, 0.18 mmol) in dry 1,2-DCE (8 mL) following the same procedure as that of 5b afforded the compound 5g (0.21 g, 55%) as a colourless solid; m.p. 191°C (Lit. 192-94°C).

Diethyl-2-[1-(2-acetoxyethyl)-1-(phenylsulfon-yl)-1H-indol-3-yl)methylene] malonate, 15 To a solution of bromo compound 1 (0.8 g, 1.53 mmol) in dry DMF (15 mL), anhydrous KOAc (0.3 g, 3.05 mmol) was added. The reaction mixture was stirred at RT for 8 hr. It was then quenched with ice-water (50 mL), extracted with chloroform (3 × 10 mL) and dried (anhyd. Na₂SO₄). Removal of solvent followed by flash column chromatographic purification (n-hexane/ethyl acetate 95:5) led to the isolation of product 15 (0.63 g, 82%) as a colourless liquid; IR (KBr): 1758, 1735, 1702, 1383, 1185 cm⁻¹; 1H NMR (300 MHz, CDCl₃): δ 8.04-7.85 (m, 4 H), 7.45-7.19 (m, 6 H), 5.02 (s, 2 H), 4.30 (q, J = 7.2 Hz, 2 H), 3.98 (q, J = 7.2 Hz, 2 H), 1.95 (s, 3 H), 1.31 (t, J =7.2 Hz, 3 H), 0.90 (t, J =7.2 Hz, 3 H); 13C NMR (75.4 MHz, CDCl₃): δ 170.6, 163.3, 162.6, 137.6, 136.3, 134.2, 133.9, 131.6, 130.9, 129.1, 128.9, 127.4, 126.4, 124.1, 120.6, 119.2, 114.2, 62.1, 61.5, 57.4, 20.7, 14.1, 13.7; MS (EI): m/z (%) 499 (M⁺, 65%).

General procedure for FeCl₃-mediated domino reaction of compound 15 with arenes

To a solution of compound 15 (1.00 mmol) in dry DCE (15 mL), anhydrous FeCl₃ (2.00 mmol) and arene (1.20 mmol) were added. It was then refluxed for the specified time period (Table III) under N₂ atmosphere. The solvent was removed and the residue was quenched with ice-water (50 mL) containing 1 mL of conc.HCl, extracted with chloroform (2 × 10 mL) and dried (anhyd. Na₂SO₄). Removal of solvent followed by flash column chromatography (n-hexane/ethyl acetate) led to the isolation of carbazole analogs 5e, 5f and 5i.

General procedure for FeCl₃-mediated domino reaction of compound 15 with heteroarenes

To a solution of compound 15 (1.00 mmol) in dry DCE (15 mL), anhydrous FeCl₃ (0.18 mmol) and heteroarenes (1.20 mmol) were added. It was then stirred at RT for the specified time period (Table III) under N₂ atmosphere. The solvent was removed and the residue was quenched with ice-water (50 mL) containing 1 mL of conc.HCl, extracted with chloroform (2 × 10 mL) and dried (anhyd. Na₂SO₄). Removal of solvent followed by flash column chromatography (n-hexane/ethyl acetate) led to the isolation of carbazole analogs 5g, 5h and 5j.

7,9-Dimethyl-5-(phenylsulfonyl)-5H-benzo[b]carbazole, 5e The domino reaction of compound 15 (0.5 g, 1.00 mmol) with m-xylene (0.15 mL, 1.22 mmol) using anhydrous FeCl₃ (0.32 g, 1.97 mmol) in dry DCE (15 mL), following the general procedure for arene and subsequent flash column chromatographic purification (n-hexane/ethyl acetate 99:1) led to the isolation of carbazole 5e (0.19 g, 50%) as a colourless solid; m.p. 206-07°C (Lit. 208°C).
8,9-Dimethoxy-5-(phenylsulfonyl)-5H-benzo[6]-carbazole, 5f The domino reaction of compound 15 (0.50 g, 1.00 mmol) with veratrole (0.16 mL, 1.23 mmol) in the presence of FeCl₃ (0.32 g, 1.97 mmol) in dry 1,2-DCE (12 mL) following the same procedure as that of 5e afforded the compound 5f (0.21 g, 50%) as a colourless solid; m.p. 208-09°C (Lit.¹⁶ 210°C).

7-(Phenylsulfonyl)-7H-benzofuro[2,3-b]carbazole, 5g The domino reaction of compound 15 (0.5 g, 1.00 mmol) with benzo[b]furan (0.13 mL, 1.18 mmol) using anhydrous FeCl₃ (0.03 g, 0.18 mmol) in dry DCE (15 mL), following the general procedure for heteroarene and subsequent flash column chromatographic (n-hexane) purification led to the isolation of carbazole 5g (0.22 g, 55%) as a colourless solid; m.p. 191°C (Lit.¹⁵ 192-94°C).

1-Hexyl-7-(phenylsulfonyl)-indolo[3,2-b]carbazole, 5h The domino reaction of compound 15 (0.5 g, 1.00 mmol) with 1-hexylindole (0.24 g, 1.19 mmol) in the presence of FeCl₃ (0.03 g, 0.18 mmol) in dry 1,2-DCE (8 mL) following the same procedure as that of 5g afforded the compound 5h (0.25 g, 52%) as a colourless solid; m.p. 164-65°C (Lit.¹⁶ 166°C).

12-(Phenylsulfonyl)-5-methyl-12f-naphtho[1,2-b]carbazole, 5i The domino reaction of compound 15 (0.5 g, 1.00 mmol) with 1-methylnaphthalene (0.17 g, 1.19 mmol) in the presence of FeCl₃ (0.32 g, 1.97 mmol) in dry 1,2-DCE (12 mL) following the same procedure as that of 5e afforded the compound 5i (0.23 g, 55%) as a colourless solid; m.p. 205-06°C (Lit.¹⁶ 206°C).

2-(2,2-Bithiophen-5-yl)-(9-(phenylsulfonyl)-9H-thieno[2,3-b]carbazole, 5j The domino reaction of compound 15 (0.50 g, 1.00 mmol) with tert-thiophene (0.29 g, 1.17 mmol) in the presence of FeCl₃ (0.03 g, 0.18 mmol) in dry 1,2-DCE (12 mL) following the same procedure as that of 5g afforded the compound 5j (0.21 g, 40%) as a pale yellow solid; m.p. 244-46°C (Lit.¹⁶ 244°C).

tert-Butyl-3-(2,2-di(ethoxycarbonyl)vinyl)-2-(3,4-dimethoxybenzyl)-1H-indole-1-carboxylate, 17a To a solution of bromo compound 16 (0.5 g, 1.04 mmol) in dry DCE (15 mL), veratrole (0.17 g, 1.23 mmol), K₂CO₃ (0.28 g, 2.02 mmol) and ZnBr₂ (0.05 g, 0.22 mmol) were added. It was then stirred at RT for 5 hr under N₂ atmosphere. The solvent was removed and the residue was quenched with ice-water (50 mL) containing 1 mL of conc.HCl, extracted with chloroform (2 × 10 mL) and dried (anhyd. Na₂SO₄). Removal of solvent followed by flash column chromatography (n-hexane/ethyl acetate 98:2) led to the isolation of compound 17a (0.41 g, 73%) as a colourless solid; m.p. 120°C; IR (KBr): 1733, 1717, 1625 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆): δ 8.02 (d, J = 7.8 Hz, 1 H), 7.90 (s, 1 H), 7.34-7.23 (m, 3 H), 6.80 (d, J = 8.1 Hz, 1 H), 6.73 (s, 1 H), 6.44 (d, J = 7.5 Hz, 1 H), 4.40 (q, J = 6.9 Hz, 2 H), 3.95 (q, J = 7.2 Hz, 2 H), 3.67 (s, 3 H), 3.66 (s, 3 H), 1.46 (s, 9 H), 1.25 (t, J = 6.9 Hz, 3 H), 0.92 (t, J = 6.9 Hz, 3 H); ¹³C NMR (75.4 MHz, DMSO-d₆): δ 165.1, 163.8, 149.1, 148.7, 147.4, 140.0, 136.6, 135.5, 130.6, 127.8, 126.2, 124.6, 123.0, 119.4, 118.8, 115.1, 114.8, 112.1, 111.8, 85.0, 61.3, 61.0, 55.5, 55.3, 31.8, 27.2, 13.9, 13.3; MS (EI): m/z (%) 537 (M⁺, 76%). Anal. Calcd for C₃₅H₅₅NO₃ (537.60): C, 76.02; H, 6.56; N, 2.61. Found: C, 76.20; H, 6.76; N, 2.47%.

tert-Butyl-3-(2,2-di(ethoxycarbonyl)vinyl)-2-(naphthalene-1-yl)methyl)-1H-indole-1-carboxylate, 17b The arylation of bromo compound 16 (0.5 g, 1.04 mmol) with naphthalene (0.16 g, 1.24 mmol) and K₂CO₃ (0.28 g, 2.02 mmol) in the presence of ZnBr₂ (0.05 g, 0.22 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of 17a afforded the compound 17b (0.36 g, 65%) as a colourless solid; m.p. 137°C; IR (KBr): 1730, 1716, 1626 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 8.24 (d, J = 8.1 Hz, 1 H), 8.11 (d, J = 8.1 Hz, 1 H), 7.88 (d, J = 8.1 Hz, 1 H), 7.87 (s, 1 H), 7.71 (d, J = 8.4 Hz, 1H), 7.62-7.50 (m, 3 H), 7.37-7.24 (m, 3 H), 6.75 (d, J = 6.9 Hz, 1 H), 4.89 (s, 2 H), 4.24 (q, J = 7.2 Hz, 2 H), 3.95 (q, J = 7.2 Hz, 2 H), 1.27 (t, J = 7.2 Hz, 3 H), 1.13 (s, 9 H), 0.96 (t, J = 7.2 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃): δ 165.8, 164.3, 149.8, 138.0, 137.2, 136.7, 134.8, 133.6, 131.7, 128.8, 127.2, 127.0, 126.2, 125.8, 125.6, 124.7, 124.1, 123.2, 123.1, 119.3, 116.6, 115.7, 84.6, 61.5, 61.3, 30.9, 27.5, 14.1, 13.6. MS (EI): m/z (%) 527 (M⁺, 52%). Anal. Calcd for C₃₅H₃₃NO₅ (527.23): C, 72.85; H, 6.30; N, 2.65. Found: C, 72.70; H, 6.49; N, 2.90%.

tert-Butyl-3-(2,2-di(ethoxycarbonyl)vinyl)-2-(1-methylnaphthalene-4-yl)methyl)-1H-indole-1-carboxylate, 17c The arylation of bromo compound 16 (0.5 g, 1.04 mmol) with 1-methylnaphthalene (0.16 g, 1.12 mmol) and K₂CO₃ (0.28 g, 2.02 mmol) in the presence of ZnBr₂ (0.05 g, 0.22 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of 17a afforded the compound 17c (0.38 g, 68%) as a colourless solid; m.p. 142°C; IR (KBr): 1732, 1715, 1627 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 8.25-8.05 (m, 3 H), 7.86 (s, 1 H), 7.58-6.63 (m, 7 H), 4.86 (s, 2 H), 4.23 (q, J = 7.2 Hz, 2 H), 3.96 (q, J = 7.1 Hz, 2 H), 2.65 (s, 3 H), 1.26 (t, J = 6.9 Hz, 3 H), 1.14(s, 9
H), 0.95 (t, J = 6.9 Hz, 3 H); $^{13}$C NMR (75.4 MHz, CDCl$_3$): δ 165.8, 164.4, 149.8, 138.3, 137.4, 136.6, 133.0, 132.8, 132.7, 131.7, 128.6, 127.2, 126.3, 125.8, 125.6, 124.9, 124.6, 123.8, 123.6, 123.2, 119.3, 116.5, 115.7, 84.6, 61.5, 61.3, 30.9, 27.5, 19.4, 14.1, 13.6; MS (EI): m/z (%) 541 (M$^+$, 80%). Anal. Calcd for C$_{33}$H$_{32}$NO$_5$ (541.63): C, 73.18; H, 6.51; N, 2.59. Found: C, 73.42; H, 6.38; N, 2.78%.

General procedure for ZnBr$_2$-mediated domino reaction of bromo compound 16 with arene

To a solution of bromo compound 16 (0.14 mmol) in dry DCE (15 mL), anhydrous ZnBr$_2$ (0.22 mmol) and arene (1.24 mmol) were added. The mixture was stirred at RT for 6-8 hr under N$_2$ atmosphere. The solvent was removed and the residue was quenched with ice-water (50 mL) containing 1 mL ofconc. HCl. The solution was extracted with chloroform (2 × 10 mL) and dried (anhyd. Na$_2$SO$_4$). Removal of solvent followed by flash column chromatographic purification (n-hexane/ethyl acetate) led to the isolation of 18a.

- 2-(2,4-Dimethylbenzyl-1H-indole-3-carbaldehyde, 18a: The reaction of bromo compound 16 (0.23 g, 0.48 mmol) with m-xylene (0.12 mL, 0.96 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of 18a afforded the compound 18b.

2-(2,4-Dimethylbenzyl-1H-indole-3-carbaldeyde, 18c: The reaction of bromo compound 16 (0.02 g, 0.10 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of 18a afforded the compound 18c.

2-(2,4-Dimethylbenzyl-1H-indole-3-carbaldehyde, 18d: The reaction of bromo compound 16 (0.5 g, 1.04 mmol) with 1,4-dimethoxybenzene (0.17 g, 1.23 mmol) in the presence of ZnBr$_2$ (0.05 g, 0.22 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of 18a afforded the compound 18d.

2-(2,4-Dimethylbenzyl-1H-indole-3-carbaldehyde, 18e: The reaction of bromo compound 16 (0.5 g, 1.04 mmol) with mesitylene (0.17 g, 1.23 mmol) in the presence of ZnBr$_2$ (0.05 g, 0.22 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of 18a afforded the compound 18f.
(s, 1 H), 10.07 (s, 1 H), 8.05 (s, 1 H), 7.36 (s, 1 H), 7.13-6.90 (m, 4 H), 4.48 (s, 2 H), 2.24 (s, 3 H), 2.19 (s, 6 H); $^1$C NMR (75.4 MHz, DMSO-$d_6$): $\delta$ 184.4, 149.8, 136.8, 135.8, 135.6, 130.5, 129.0, 125.6, 122.5, 121.9, 119.9, 113.4, 111.9, 26.4, 20.5, 19.8; MS (EI): $m/z$ (%) 277 (M$^+$, 325). Anal. Calcd for C$_9$H$_9$NO (277.36): C, 82.28; H, 6.90; N, 5.05. Found: C, 82.39; H, 6.73; N, 5.25%.

(Z)-10-tert-Butyl-4-ethyl-3-oxo-1H-oxepino[3,4-b]indole-4,10(3H)-dicarboxylic acid, 22 To a solution of bromo compound 16 (0.5 g, 1.04 mmol) in dry 1,2-DCE (15 mL), anhydrous ZnBr$_2$ (0.05 g, 0.22 mmol) was added. It was then stirred at RT for 8 hr under N$_2$ atmosphere. The solvent was removed and the residue was quenched with ice-water (50 mL) containing 1 mL of conc.HCl, extracted with chloroform (2 x 10 mL) and dried (anhyd. Na$_2$SO$_4$). Removal of solvent followed by flash column chromatographic purification (n-hexane/ethyl acetate 90:10) led to the isolation of lactone 22 (0.24 g, 62%) as a colourless solid; m.p. 154°C; IR (KBr): 1746, 1744, 1711 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.36 (s, 1 H), 8.16 (d, $J = 8.4$ Hz, 1 H), 7.73 (d, $J = 7.5$ Hz, 1 H), 7.47-7.26 (m, 2 H), 5.68 (s, 2 H), 4.40 (q, $J = 6.9$ Hz, 2 H), 1.73 (s, 9 H), 1.40 (t, $J = 7.2$ Hz, 3 H); $^1$C NMR (75.4 MHz, CDCl$_3$): $\delta$ 165.4, 164.8, 149.4, 138.9, 136.5, 126.4, 126.2, 125.3, 124.4, 119.8, 118.7, 116.3, 86.6, 62.0, 60.2, 28.1, 14.2. MS (EI): $m/z$ (%) 371 (M$^+$, 69%). Anal. Calcd for C$_9$H$_9$NO (371.38): C, 64.68; H, 5.70; N, 3.77. Found: C, 64.85; H, 5.54; N, 3.92%.

8,9-Dimethoxy-5H-benzo[b]carbazole, 23a To a solution of bromo compound 16 (0.5 g, 1.04 mmol) in dry 1,2-DCE (15 mL), anhydrous ZnBr$_2$ (0.05 g, 0.22 mmol) and veratrole (0.17 g, 1.23 mmol) were added. It was then stirred at RT for 7 hr under N$_2$ atmosphere. The solvent was removed and the residue was quenched with ice-water (50 mL) containing 1 mL of conc.HCl, extracted with chloroform (2 x 10 mL) and dried (anhyd. Na$_2$SO$_4$). Removal of solvent followed by flash column chromatographic purification (n-hexane/ethyl acetate 70:30) led to the isolation of carbazole 23a (0.18 g, 63%) as a colourless solid; m.p. 198°C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 11.16 (s, 1 H), 8.83 (s, 1 H), 8.20 (d, $J = 7.8$ Hz, 1 H), 8.15 (d, $J = 7.2$ Hz, 1 H), 7.69 (s, 1 H), 7.65 (d, $J = 7.8$ Hz, 1 H), 7.53 (d, $J = 7.1$ Hz, 1 H), 7.46-7.35 (m, 3 H), 7.21 (t, $J = 7.2$ Hz, 1 H); $^1$C NMR (75.4 MHz, DMSO-$d_6$): $\delta$ 155.7, 155.1, 140.5, 140.2, 125.9, 125.3, 124.5, 122.8, 122.4, 120.1, 119.9, 119.8, 118.8, 116.5, 111.8, 111.0, 92.9; MS (EI): $m/z$ (%) 257 (M$^+$, 49%). Anal. Calcd for C$_{24}$H$_{15}$NO (275.29): C, 84.03; H, 4.31; N, 5.44. Found: C, 84.25; H, 4.46; N, 5.60%.

1-Hexyl-7H-indolo[3,2-b]carbazole, 23b The domino reaction of bromo compound 16 (0.5 g, 1.04 mmol) with benzo[b]furan (0.13 mL, 1.27 mmol) in the presence of ZnBr$_2$ (0.05 g, 0.22 mmol) in dry 1,2-DCE (10 mL) following the general procedure as mentioned above afforded the carbazole 23b (0.16 g, 59%) as a colourless solid; m.p. 267°C; $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 11.46 (s, 1 H), 8.83 (s, 1 H), 8.20 (d, $J = 7.8$ Hz, 1 H), 8.15 (d, $J = 7.2$ Hz, 1 H), 7.69 (s, 1 H), 7.65 (d, $J = 7.8$ Hz, 1 H), 7.53 (d, $J = 7.1$ Hz, 1 H), 7.46-7.35 (m, 3 H), 7.21 (t, $J = 7.2$ Hz, 1 H); $^1$C NMR (75.4 MHz, DMSO-$d_6$): $\delta$ 155.7, 155.1, 140.5, 140.2, 125.9, 125.3, 124.5, 122.8, 122.4, 120.1, 119.9, 119.8, 118.8, 116.5, 111.8, 111.0, 92.9; MS (EI): $m/z$ (%) 304 (M$^+$, 34%). Anal. Calcd for C$_{25}$H$_{17}$NO (325). C, 84.67; H, 7.11; N, 8.23. Found: C, 84.52; H, 7.30; N, 8.13%.

2-Methyl-9H-thieno[2,3-b]carbazole, 23c The domino reaction of bromo compound 16 (0.5 g, 1.04 mmol) with 2-methylthiophene (0.12 mL, 1.22 mmol) in the presence of ZnBr$_2$ (0.05 g, 0.22 mmol) in dry
1,2-DCE (10 mL) following the same procedure as that of 23b afforded the compound 23d (0.15 g, 60%) as a pale yellow solid; m.p. >300°C; 1H NMR (300 MHz, DMSO-d6): δ 11.17 (s, 1 H), 8.40 (s, 1 H), 8.14 (d, J = 7.5 Hz, 1 H), 7.89 (s, 1 H), 7.47-7.38 (m, 2 H), 7.17-7.15 (m, 2 H), 2.56 (s, 3 H); 13C NMR (75.4 MHz, DMSO-d6): δ 140.6, 137.9, 136.4, 133.1, 125.6, 122.2, 121.6, 121.3, 119.9, 118.1, 113.1, 110.5, 102.8, 102.7, 15.8; MS (EI): m/z (%) 237 (M+, 67%). Anal. Calcd for C15H11NS (237.32): C, 75.91; H, 4.67; N, 5.90; S, 13.63%. Found: C, 75.82; H, 4.50; N, 5.73; S, 13.63%.

2-(Thiophen-2-yl)-9H-thieno[2,3-b]carbazole, 23e The domino reaction of bromo compound 16 (0.5 g, 1.04 mmol) with tertthiophene (0.20 g, 1.20 mmol) in the presence of ZnBr2 (0.05 g, 0.22 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of 23b afforded the compound 23e (0.21 g, 66%) as a pale yellow solid; m.p. >310°C; 1H NMR (300 MHz, DMSO-d6): δ 11.31 (s, 1 H), 8.50 (s, 1 H), 8.15 (d, J = 7.2 Hz, 1 H), 7.97 (s, 1 H), 7.66 (s, 1 H), 7.55-7.06 (m, 6 H); 13C NMR (75.4 MHz, DMSO-d6): δ 140.8, 138.9, 137.1, 136.9 133.1, 132.6, 128.3, 126.1, 126.9, 124.4, 122.5, 122.2, 120.3, 119.8, 118.6, 114.5, 110.8, 103.1; MS (EI): m/z (%) 305 (M+, 33%). Anal. Calcd for C19H15NS2 (305.42): C, 70.79; H, 3.63; N, 4.59; S, 21.00. Found: C, 70.58; H, 3.50; N, 4.72; S, 21.20%.

2-(5-(Thiophen-2-yl)thieno[2,3-b]carbazole, 23f The domino reaction of bromo compound 16 (0.5 g, 1.04 mmol) with tertthiophene (0.31 g, 1.25 mmol) in the presence of ZnBr2 (0.05 g, 0.22 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of 23b afforded the compound 23f (0.22 g, 55%) as a pale yellow solid; m.p. >340°C; 1H NMR (300 MHz, DMSO-d6): δ 11.30 (s, 1 H), 8.53 (s, 1 H), 8.17 (d, J = 7.2 Hz, 1 H), 7.97 (s, 1 H), 7.72 (s, 1 H), 7.55 (d, J = 4.5 Hz, 1 H), 7.48-7.32 (m, 5 H), 7.19-7.12 (m, 2 H); 13C NMR (75.4 MHz, DMSO-d6): δ 140.9, 139.0, 136.9, 135.9, 135.8, 135.7, 133.1, 132.0, 128.5, 126.2, 125.8, 125.6, 125.0, 124.4, 122.6, 122.2, 120.3, 120.2, 118.6, 114.6, 110.8, 103.1; MS (EI): m/z (%) 387 (M+, 73%). Anal. Calcd for C23H17NS3 (387.54): C, 68.18; H, 3.38; N, 3.61; S, 24.82. Found: C, 68.10; H, 3.56; N, 3.75; S, 24.90%.

Conclusions
In conclusion, a facile ZnBr2 mediated arylation of 1-phenylsulfonyl-2-bromomethylindole 1 or 1-phenylsulfonyl-3-bromomethylindole 2 containing electron deficient malonylidene unit with arenes as well as heteroarenes led to the formation of the respective arylated products, which underwent a facile 1,5-hydrogen shift to form triene. These triene upon electrolyzercillation followed by aromatization via elimination of diethyl malonate afforded respective aryl/heteroaryl annulated carbazoles. The domino reaction of 1-phenylsulfonyl-2-bromomethylindole 10 containing a dimethylbarbiturate unit was also carried out. However, the exchange of malonylidene unit into the dimethylbarbiturate did not have much influence on the annulation yields. Annulation of 1-phenylsulfonyl-(indol-2-yl)methyl acetate 15 with arene/heteroarene was achieved using anhydrous FeCl3 as catalyst. The preparation of 2-bromomethylindole 12/14 containing a malononitrile/meldrum acid unit was found to be unsuccessful. Attempts to carry out a similar type of domino reaction with 1-tert-butoxycarbonyl-2-bromomethylindole 16 with arenes in the presence of anhydrous ZnBr2 led to the formation of 2-arylsubstituted carbazoles. The domino arylation 23b-f can be isolated by performing the domino reaction of bromomethylindole 1, 2 and 16 with arenes using 0.2 equiv of ZnBr2 in the presence of K2CO3. Two distinct mechanistic pathways for the formation of carbazoles starting from 1-phenylsulfonyl bromomethylindoles and 1-tert-butoxycarbonyl bromomethylindole have been proposed. The structure of benzo[b]furan fused carbazoles was thoroughly confirmed by single crystal X-ray diffraction studies.

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References


19 Crystallographic data for 5g and 23b have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 772034 and CCDC 772035. Copies of the data may be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 (0)1223 33603 or email: deposit@ccdc.cam.ac.uk).
