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Synthesis of Cyclo[*b*]fused Carbazoles via $SnCl_4$-Mediated Domino Reaction of 2-Indolylmethylpivalates with Arenes and Heteroarenes

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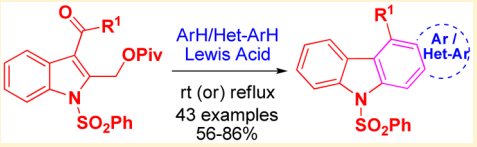
Supporting Information

ABSTRACT: A straightforward synthesis of aryl and heteroaryl-annulated cyclo[*b*]carbazoles has been developed via $SnCl_4$-mediated one-pot arylation, cyclization and aromatization reaction sequence from 3-acetyl/aroyl-2-pivaloyloxymethylindoles. The starting material is easily accessible from commercially available 2-methylindole via Friedel–Crafts acylation, bromination and pivaloylation. Remarkably, electron withdrawing/donating aroyl units including heterocyclic systems are well tolerated in the present domino reaction protocol. Furthermore, this methodology could be extended to the synthesis of dibenzofurocarbazole via bis-annulation of 2,5-bis(2-pivaloyloxymethyl)pyrrole.



Over the years, the structural features and potential biological properties of the carbazole alkaloids stimulated research in this area.[1] Isolation and synthesis of biologically active carbazole alkaloids have been reviewed in detail by Knölker[2a−f] and Mal.[2g] Aryl- and heteroaryl fused carbazoles are often explored because of their pharmacological activities and applications in material sciences.[3] The benzo[*b*]carbazole derivatives showed remarkable cytostatic activity against leukemia type L 1210 cell culture.[4] Recently, a variety of benzo- and naphtho-carbazole analogs were investigated as potential anticancer agents.[5] Furthermore, because of promising optical and chemical properties of annulated benzocarbazoles, they have been exploited as functional building blocks in the construction of optoelectronic devices.[6]

In the past few decades, several methods were developed for the synthesis of the parent system of benzo[*b*]carbazole. Kano et al.[7] reported the first synthesis of benzo[*b*]carbazole involving pyrolysis of *N*-free indole. Later, the synthesis of benzo[*b*]carbazole was achieved via benzannulation of indoles,[8] Fischer indolization of phenylhydrazones,[9] Nenitzescu indolization of *p*-benzoquinone aminomethylene indanone,[10] and Diels–Alder reaction of pyranoindolones,[11] furanoindoles[12] and 2,4-dihydropyrroloindole[13] with aryne.

Several strategies have been reported for the syntheses of aryl and heteroaryl-annulated carbazoles (Figure 1) through intramolecular dehydro-Diels–Alder reactions of *N*-(*o*-ethynyl)aryl ynamides,[14] Pd-catalyzed domino reaction of 2-alkynylbenzaldehydes with indoles,[15] reaction between 2-ethynyl-*N*-triphenylphosphoranylidene anilines and diazoketones via ketenimine intermediates,[16] CuI_2-catalyzed Friedel–Crafts alkylation of 2-(2-(alkynyl)benzylidene)malonates with indoles followed by electrophilic cyclization and aromatization,[17] iron-catalyzed domino isomerization/cyclodehydration sequences from substituted 2-[(indoline-3-ylidene)(methyl)]-benzaldehydes,[18] Brønsted acid-catalyzed reactions of indoles with *o*-[α-(hydroxy)benzyl]benzaldehyde acetals,[19] and iron-catalyzed 5-*exo*-*dig* cyclization and a subsequent electrocyclization.[20]

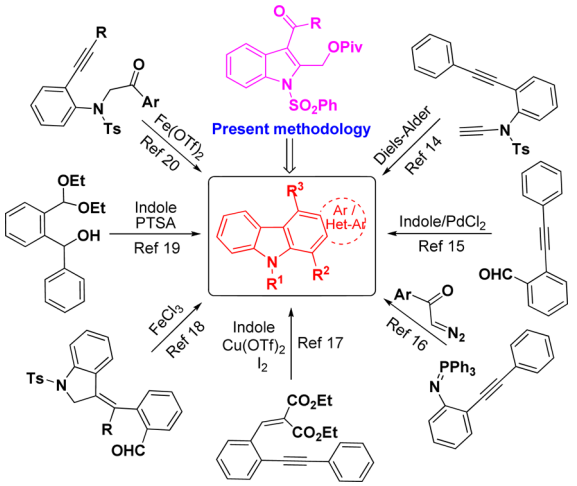


Figure 1. Syntheses of cyclo[*b*]fused carbazoles.

However, most of these protocols have disadvantages such as harsh reaction conditions and restricted substitution in both aryl and heteroaryl system. Therefore, the development of a facile approach for benzo[*b*]carbazoles from a readily available starting material and cost-effective method is highly desirable. Our strategy is to utilize easily accessible 1-phenylsulfonyl-2-bromomethylindole and arenes as well as heteoarenes as synthetic equivalents for the construction of the annulated carbazoles. In our earlier reports, the 2/3-bromomethylindoles which have adjacent carbonyl groups masked either as diethyl malonylidene[21] or diacetoxymethine[22] were explored for annulation strategy. However, moderate reactivity of the malonylidene tethered bromomethylindole and the less stable nature of the acetoxymethine unit limited the substrate scope of these methodologies. To overcome these short comings, we

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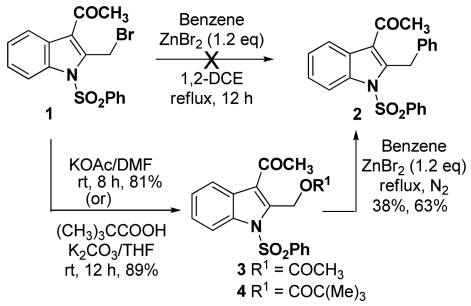
report herein, an annulation protocol by employing 2-pivaloyloxymethylindole that contain an unmasked carbonyl group at 3-position as a bidentate synthon for the construction of diversely substituted carbazole derivatives.

To date, several methods have been developed for the arylation of bromomethyl compounds.[23] However, no literature reports are available for the arylation of bromomethyl compounds that contain electron withdrawing ketone functionality at the adjacent position. On the basis of our earlier reports on $ZnBr_2$-mediated domino reactions,[21] the initial phenylation of 2-bromomethylindole **1**[24] using 20 mol % $ZnBr_2$ was unsuccessful even at refluxing condition (Scheme 1). In

Scheme 1. Reactivity of 2-Bromomethylindole 1, 2-Acetoxymethylindole 3, and 2-Pivaloyloxymethylindole 4



addition, increasing the $ZnBr_2$ equivalents was also of no use and only led to the recovery of the starting material. Even though the bromo compound **1** underwent $ZnBr_2$-mediated Arbuzov reaction,[25] it has failed to undergo the acetamidation reaction.[26] Obviously, the reactivity of the bromo compound is sufficient only for phosphorus nucleophile and not for carbon and nitrogen nucleophiles. To enhance the possibility of arylation, bromo compound **1** was converted into acetate **3** and pivalate **4**.

As expected, the phenylation of acetoxymethylindole **3** with benzene at reflux afforded the benzylindole **2**, but only in 38% yield. Under identical conditions, the reaction of 2-pivaloyloxymethylindole **4** with benzene led to the formation of **2** in 63% yield. The formation of phenylation product **2** from acetate **3** and pivalate **4** confirmed the coordination of $ZnBr_2$ on to benzyloxy carbonyl units.

Next, arylation of pivaloyloxymethylindole **4** with various arenes was investigated. To our surprise, the reaction of pivalate **4** with *m*-xylene using 1.2 equiv of $ZnBr_2$ in 1,2-DCE at reflux for 9 h provided the arylation and annulation products **5a** and **6a** in 46% and 12% yields, respectively (Scheme 2). The reaction of pivalate **4** with naphthalene also produced both the naphthylated indole **5b** and annulated carbazole **6b**.

To enhance the feasibility of annulation products, the reaction of **4** with naphthalene was tested using different Lewis acids (Table 1).

The reaction of pivaloyloxymethylindole **4** with naphthalene using 1.2 equiv of $ZnBr_2$ or $AlCl_3$ afforded carbazole **6b** in poor yields (entries 1 and 2) along with major portion of naphthylated compound **5b**. Obviously, the $ZnBr_2/AlCl_3$ is not favoring the intramolecular cyclization of **5b** to form the carbazole **6b**. Under identical conditions, the reaction of pivaloyloxymethylindole **4** with naphthalene in the presence of 1.2 equiv $CuBr_2/Zn(OTf)_2$ failed to produce even the arylated compound **5b** (entries 3 and 4). However, the reaction of pivalate **4** with naphthalene using 1.2 equiv $FeCl_3$, $SnCl_4$ and

Scheme 2. Arylation vs Annulation of 2-Pivaloyloxymethylindole 4

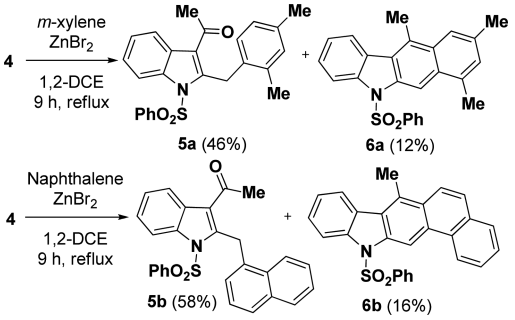


Table 1. Effect of Lewis Acids (LA) on Annulation of 2-Pivaloyloxymethylindole 4 with Naphthalene

entry	LA[a]	time (h)	yield (%)[b]
1	$ZnBr_2$	12	16[c]
2	$AlCl_3$	12	>10[c]
3	$CuBr_2$	12	nr
4	$Zn(OTf)_2$	12	nr
5	$FeCl_3$	6	54
6	**$SnCl_4$**	**6**	**68**
7	$BF_3{\cdot}OEt_2$	8	63
8	$InCl_3$	6	72
9	$InBr_3$	6	70
10	$Cu(OTf)_2$	12	73

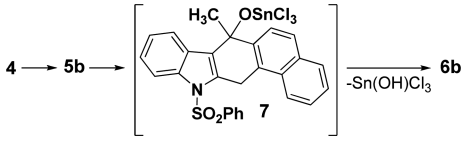
[a]Annulation of 2-pivaloyloxymethylindole **4** (1 equiv) with naphthalene (1.1 equiv) using Lewis acid (1.2 equiv) in 1,2-DCE at reflux. [b]Isolated yield of **6b** by column chromatography. [c]A major portion of naphthylated compound **5b** was also formed.

$BF_3{\cdot}OEt_2$ in 1,2-DCE under reflux furnished carbazole **6b** in 54%, 68% and 63% yields, respectively (entries 5−7). In the presence of expensive Lewis acids such as $InCl_3$, $InBr_3$ and $Cu(OTf)_2$, the domino reaction of pivaloyloxymethylindole **4** proceeded in better yields than the other Lewis acids (entries 8−10). The above-mentioned results indicated that the stronger Lewis acids are favoring both naphthylation as well as cyclization (entries 5−10). Since, the reaction requires a minimum of 1.2 equiv of Lewis acid, the further annulations of pivaloyloxymethylindole **4** with arenes were performed with $SnCl_4$, which is less expensive.

The requirement of 1.2 equiv of $SnCl_4$ for annulation could be explained through the formation of intermediate **7** followed by its aromatization via elimination of $Sn(OH)Cl_3$[27] (Scheme 3).

To extend the scope of this reaction protocol, the domino reaction of pivaloyloxymethylindole **4** was performed with arenes and heteroarenes using $SnCl_4$ as the mediator. First, the reaction of pivalate **4** with *m*-xylene was performed under standard reaction condition, which led to the isolation of benzocarbazole **6a** in 61% yield. The reaction of pivalate **4** with

Scheme 3. Proposed Mechanism for $SnCl_4$-Mediated Annulation of 4



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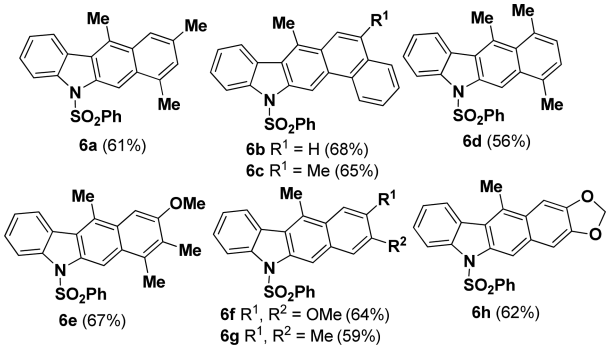
naphthalene and 1-methylnaphthalene also produced the naphtho[*b*]carbazoles **6b** and **6c** in 68% and 65% yields, respectively. The domino reaction of **4** with *p*-xylene, 2,3-dimethylanisole, 1,2-dimethoxybenzene, *o*-xylene and 1,3 benzenedioxole using 1.2 equiv of $SnCl_4$ afforded annulated carbazoles **6d−h** in 56−67% yields (Scheme 4). Obviously, the

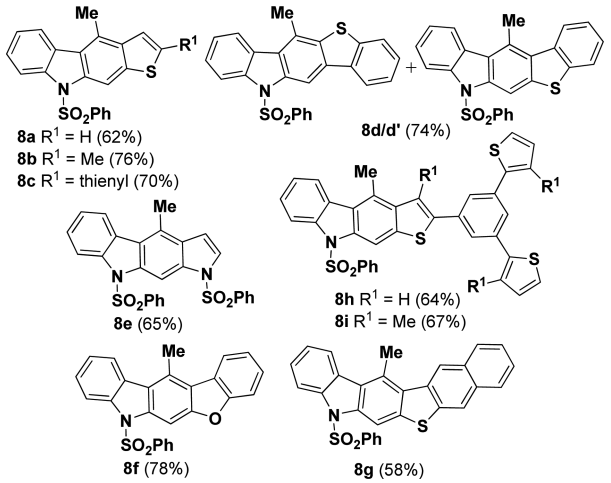
Scheme 4. Structures of Annulated Carbazoles 6a−h Synthesized Using $SnCl_4$



domino reaction of the pivalate **4** with benzene stops at the arylation stage, whereas in the case of substituted benzenes, the further reaction of the arylated compounds facilitated by the electron releasing substitutents led to the formation of carbazoles **6a−h**.

Next, the domino reaction of pivalate **4** with thiophene using 1.2 equiv of $SnCl_4$ in 1,2-DCE afforded thieno[*b*]carbazole **8a** in 62% yield (Scheme 5). To our delight, the annulation of pivalate **4** with 2-methylthiophene and bithiophene also afforded the heteroannulated carbazoles **8b** and **8c** in 76% and 70% yields, respectively.

Scheme 5. Synthesis of Heteroannulated Carbazoles 8a−i



Ambiguously, the domino reaction of the pivalate **4** with thianaphthene using $SnCl_4$ at room temperature for 3 h gave an inseparable mixture of the isomeric carbazoles **8d** and **8d′** (1:0.4 ratio based on ^{1}H NMR spectrum) in 74% yield. The structures of benzo[*b*]thieno carbazoles **8d** and **8d′** could be assigned based on our earlier reports.[22] Under identical conditions, the domino reaction of the pivalate **4** with *N*-sulfonyl pyrrole/benzo[*b*]furan led to the formation of respective heterocycles **8e** and **8f**. Furthermore, the domino reaction of pivalate **4** with naphtho[*b*]thiophene[28] afforded heterocycle **8g**. To our delight, the reaction of pivalate **4** with 1,3,5-trithienyl benzene/1,3,5-tris(3-methylthienyl)benzene[22] also produced the corresponding complex heterocycles **8h** and **8i** in 64% and 67% yields (Scheme 5).

Next, to generalize the scope of the reaction, synthesis of cyclo[*b*]carbazoles containing an aryl unit at the C-4 position was investigated. An aroylation of 2-methylindole[29] produced the corresponding aroylindole **9a−d**, which upon bromination followed by the pivalic acid displacement gave the corresponding pivaloyloxyindoles **11a−d**. The annulation reaction of these pivalates **11a−d** with arenes as well as heteroarenes furnished the carbazoles **12a−d**, **13a−d**, **14a−d**, **15a−d** and **16a−d** (Scheme 6).

As expected, the reaction of pivalates **11a−d** with 1-methylnaphthalene in the presence of $SnCl_4$ in 1,2-DCE at reflux led to the isolation of respective naphtho[*b*]carbazoles **12a−d** in 61−73% yields. Electron releasing-aroyl units containing pivalates **11a**/**11b** required longer reaction time for annulation than electron deficient-aroyl units based counter parts **11c**/**11d**. Likewise, the domino reaction of pivalates **11a−d** with veratrole produced the corresponding benzo[*b*]-carbazoles **13a−d** in 58%, 64%, 72% and 70% yields. Similarly, the reaction of pivalates **11a−d** with the heteroarenes such as 2-methylthiophene, 1,3,5-trithienyl benzene and benzo[*b*]furan afforded heteroannulated carbazoles **14a−d**, **15a−d** and **16a−d** in good yields (Scheme 6). Invariably, the electron withdrawing aroyl units containing pivalates **11c**/**11d** produced better yields of annulated carbazoles than the electron releasing aroyl units tethered pivalates **11a**/**11b**.

Next, the domino reaction of 3-thienoyl 2-pivaloyloxymethylindole **17** with representative arenes and heteroarenes afforded the respective 4-thienyl cyclo[*b*]fused carbazoles **18a−e** in 57−69% yields (Scheme 7).

The domino reaction of pivaloyloxymethylindoles **11a−d**/**17** confirmed that the formation of the annulated carbazoles is more facile and also produced better yields with electron withdrawing 4-nitrobenzoyl/4-chlorobenzoyl unit rather than the donating systems such as veratroyl and 2-thienoyl.

The structure of the representative heteroannulated carbazoles **14c** and **16c** were unambiguously confirmed by single crystal X-ray diffraction analyses (see SI).[30]

Finally, bis-annulation of the 2,5-bis(pivaloyloxmethyl)-dibenzoyl pyrrole **19**[31] with benzo[*b*]furan afforded the dibenzofuro carbazole **20** as a colorless solid in 71% yield (Scheme 8). The structure of the carbazole **20** was confirmed through a single crystal X-ray diffraction analysis (see SI).[32]

In summary, we have developed an efficient and straightforward protocol for the synthesis of aryl- and heteroaryl-annulated cyclo[*b*]carbazoles via one-pot arylation of 1-phenylsulfonyl-2-pivaloyloxymethylindole followed by cyclization and aromatization. A wide range of the annulated carbazoles containing an easily removable phenylsulfonyl group was prepared to generalize the scope of the reaction. The influence of the electronic effect on annulations was investigated by incorporating the electron donating/withdrawing aroyl units. Finally, the symmetrical dibenzofuro[*b*]-carbazole was synthesized through bis-annulation of 1-phenylsulfonyl-2,5-bis(pivaloyloxymethyl)pyrrole. The structures of the representative heteroannulated carbazoles were confirmed through single crystal X-ray analyses. Since our methodology relies on benzylic bromination for accessing the required

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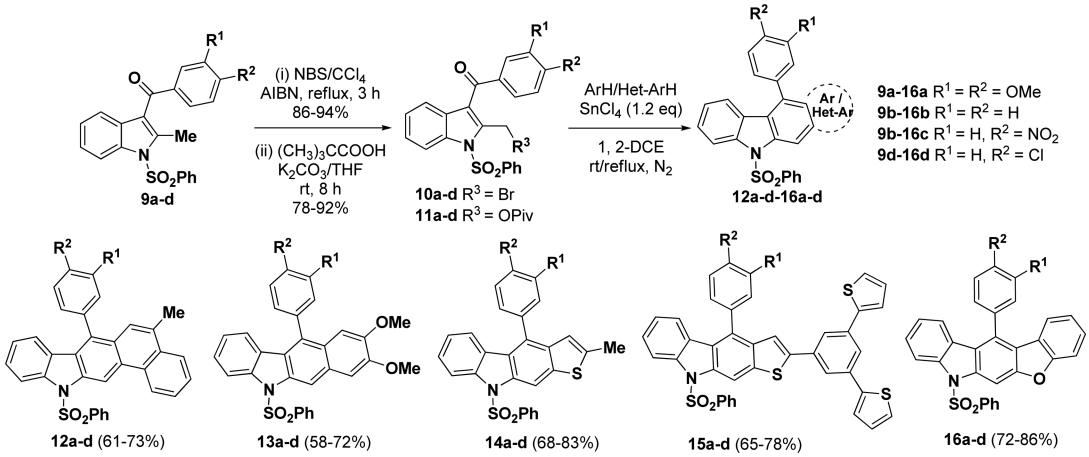
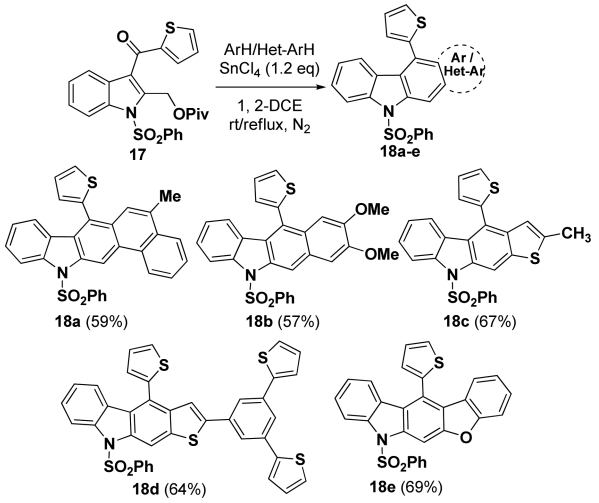
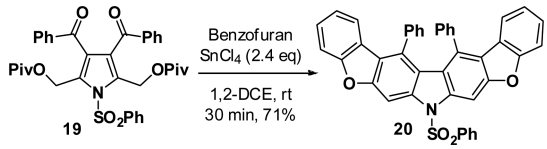
Scheme 6. Preparation of 4-Aryl Annulated/Heteroannulated Carbazoles 12a−d to 16a−d



Scheme 7. Synthesis of 4-(Thienyl) Annulated/ Heteroannulated Carbazoles 18a−e



Scheme 8. Synthesis of Symmetric Heteroannulated Carbazole



pivalates, the presence of electron withdrawing 1-phenylsulfonyl group on indole nitrogen is indispensable.

EXPERIMENTAL SECTION

General Remarks. Melting points were uncorrected. Solvents were dried by standard procedures. All the experiments carried out under the nitrogen atmosphere unless otherwise stated. The Lewis acids were used in the form of anhydrous condition under nitrogen atmosphere. The progression of all the reaction was monitored by TLC using hexane/ethyl acetate mixtures as eluent. Column chromatography was carried out on Silica gel (230−400 mesh, Merck) by using increasing polarity. Infrared spectra were recorded neat and reported in cm^{-1}. ^1H, ^{13}C and DEPT-135 spectra were recorded in $CDCl_3$ and DMSO-d_6 using TMS as an internal standard on a 300 MHz spectrometer at room temperature. Chemical shift values were quoted in parts per million (ppm) and coupling constants (J) were quoted in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on EI and ESI mass spectrometers.

*(3-Acetyl-1-(phenylsulfonyl)-1H-indol-2-yl)methyl acetate (**3**).* A suspension of 2-bromomethylindole **1** (1.0 g, 2.55 mmol) and potassium acetate (0.5 g, 5.10 mmol) in DMF (10 mL) was stirred at room temperature for 8 h. After completion of the reaction (TLC), it was poured over crushed ice (100 g) containing Conc. HCl (5 mL). The precipitate obtained was filtered, washed with water (200 mL) and dried ($CaCl_2$). The crystallization of crude product from MeOH (5 mL) afforded indolylmethyl acetate **3** as a colorless solid (0.766 g, 81%); mp 114−116 °C. IR (neat) 1743 (ester), 1673 (CO), 1380 and 1180 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, J = 8.1 Hz, 1H), 7.94−7.90 (m, 3H), 7.61 (t, J = 7.5 Hz, 1H), 7.51−7.36 (m, 4H), 5.75 (s, 2H), 2.70 (s, 3H), 2.02 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.9, 170.0, 138.8, 136.9, 136.2, 134.4, 129.4, 126.7, 126.3, 126.2, 124.8, 124.7, 121.5, 114.8, 56.4, 31.8, 20.7 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.4, 129.4, 126.8, 126.3, 124.7, 121.5, 114.8, 56.4, 31.9, 20.7 ppm. Elemental Analysis Calcd for $C_{19}H_{17}NO_5S$: C, 61.44; H, 4.61; N, 3.77; S, 8.63. Found: C, 61.26; H, 4.46; N, 3.53; S, 8.39.

*(3-Acetyl-1-(phenylsulfonyl)-1H-indol-2-yl)methyl pivalate (**4**).* To a solution of 2-bromomethylindole **1** (5.0 g, 12.75 mmol) in dry THF (120 mL), potassium carbonate (5.28 g, 38.26 mmol) and pivalic acid (2.60 g, 25.51 mmol) were added. The reaction mixture was allowed to stir at room temperature for 12 h. After completion of the reaction (TLC), the solvent was removed under reduced pressure. Then, the residue was diluted with DCM (100 mL), washed with water (3 × 50 mL) and dried (Na_2SO_4). Removal of solvent followed by trituration of the crude product with MeOH (15 mL) furnished pivalate **4** as a colorless solid (4.68 g, 89%); mp 122−124 °C. IR (neat) 1730, (ester) 1676 (CO), 1382 and 1180 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, J = 7.8 Hz, 1H), 7.96−7.94 (m, 1H), 7.88 (d, J = 7.8 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.49−7.34 (m, 4H), 5.68 (s, 2H), 2.67 (s, 3H), 1.22 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.5, 177.6, 138.4, 137.6, 136.1, 134.5, 129.5, 126.6, 126.4, 126.2, 124.8, 124.7, 121.7, 114.8, 56.5, 38.9, 31.7, 27.2 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.5, 129.5, 126.6, 126.2, 124.8, 121.7, 114.8, 56.5, 31.7, 27.2 ppm. Elemental Analysis Calcd for $C_{22}H_{23}NO_5S$: C, 63.90; H, 5.61; N, 3.39; S, 7.75, found C, 63.74; H, 5.44; N, 3.27; S, 7.59.

*1-Phenylsulfonyl 2-benzyl-3-acetylindole (**2**) from 2-Acetoxymethylindole.* A mixture of 2-acetoxymethylindole **3** (0.2 g, 0.54 mmol) and $ZnBr_2$ (0.145 g, 0.65 mmol) in dry benzene (10 mL) was refluxed under nitrogen atmosphere for 24 h. Then, it was poured over ice water (100 mL) containing Conc. HCl (3 mL), the organic layer was separated and the aqueous layer was extracted with DCM (2 × 20 mL). The combined extract was washed with water (2 × 15 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (Silica gel, EtOAc-hexane 1:9) led to the isolation of 2-benzylindole **2** as a colorless solid (0.079 g, 38%); mp 164−166 °C. IR (neat) 1670 (CO) 1380 and 1182 (SO_2) cm^{-1}. ^1H NMR (300

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MHz, $CDCl_3$) δ 8.26−8.23 (m, 1H), 7.97−7.94 (m, 1H), 7.43−7.40 (m, 3H), 7.38−7.35 (m, 2H), 7.24−7.16 (m, 5H), 7.12−7.10 (m, 2H), 4.92 (s, 2H), 2.63 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.9, 144.1, 138.4, 137.6, 136.1, 134.0, 129.2, 128.5 (2C), 127.0, 126.6, 126.4, 125.1, 124.5, 122.2, 121.1, 115.0, 32.0, 31.9 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.0, 129.2 128.5 (2C), 126.7, 126.4, 125.2, 124.5, 121.1, 115.0, 32.1, 31.9 ppm. HRMS (ESI-TOF, DCM) m/z Calcd for $C_{23}H_{19}NO_3S$ + H^+ $[M + H]^+$: 390.1164, found 390.1153.

*Preparation of 2-Benzylindole (**2**) from 2-Pivaloyloxymethylindole.* To a solution of indol-2-ylmethyl pivalate **4** (0.2 g, 0.48 mmol) in dry benzene (10 mL), $ZnBr_2$ (0.131 g, 0.58 mmol) was added and it was refluxed for 8 h under nitrogen atmosphere. Then, the usual work up adopting the above-mentioned procedure followed by column chromatographic purification (Silica gel, EtOAc-hexane 1:9) furnished the 2-benzylindole **2** as a colorless solid (0.118 g, 63%).

*Annulation of Pivalate **4** with m-Xylene.* A mixture of pivalate **4** (0.2 g, 0.48 mmol), $ZnBr_2$ (0.131 g, 0.58 mmol) and *m*-xylene (0.15 g, 1.45 mmol) in dry DCE (10 mL) was refluxed under nitrogen atmosphere for 9 h. Then, the usual workup followed by column chromatographic purification (Silica gel, EtOAc-hexane 1:9) afforded carbazole **6a**. Further elution of the column afforded arylated product **5a**.

*1-(2-(2,4-Dimethylbenzyl)-1-(phenylsulfonyl)-1H-indol-3-yl)-ethanone (**5a**).* Colorless solid (0.093 g, 46%); mp 160−162 °C. IR (neat) 1666 (CO), 1380 and 1176 (SO_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26−8.23 (m, 1H), 7.98−7.95 (m, 1H), 7.43−7.40 (m, 2H), 7.37−7.31 (m, 3H), 7.18−7.13 (m, 2H), 6.95 (s, 1H), 6.49 (d, J = 7.8 Hz, 1H), 6.20 (d, J = 7.8 Hz, 1H), 4.68 (s, 2H), 2.49 (s, 3H), 2.36 (s, 3H), 2.17 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.7, 144.1, 138.4, 136.2, 135.7, 135.6, 133.8, 132.8, 130.9, 129.0, 127.0, 126.7, 126.6, 125.1, 124.5, 122.5, 121.2, 114.8, 31.6, 29.2, 20.8, 19.7 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.8, 131.0, 129.1, 126.7, 126.6, 125.1, 124.5, 121.3, 114.8, 31.7, 29.2, 20.9, 19.8 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{25}H_{23}NO_3S$ $[M^+]$: 417.1399, found 417.1397.

*7,9,11-Trimethyl-5-(phenylsulfonyl)-5H-benzo[b]carbazole (**6a**).* Colorless solid (0.023 g, 12%); mp >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.37 (d, J = 8.1 Hz, 1H), 8.16 (d, J = 7.8 Hz, 1H), 7.81 (s, 1H), 7.71 (d, J = 7.5 Hz, 2H), 7.45 (t, J = 7.35 Hz, 1H), 7.36−7.29 (m, 2H), 7.20−7.17 (m, 3H), 3.00 (s, 3H), 2.77 (s, 3H), 2.48 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.3, 137.6, 136.4, 134.7, 134.0, 133.6, 130.4, 130.3, 129.0, 128.9, 127.7, 127.4, 126.5, 124.4, 124.1, 123.7, 121.1, 115.3, 106.8, 22.0, 20.2, 15.7 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.7, 129.0, 128.9, 127.4, 126.5, 124.1, 123.7, 121.1, 115.3, 106.8, 22.1, 20.2, 15.7 ppm. HRMS (ESI-TOF, MeOH) m/z Calcd for $C_{25}H_{21}NO_2S$ + H^+ $[M + H]^+$ 400.1371, found 400.1362.

*Annulation of Pivalate **4** with Naphthalene.* A mixture of 2-indolylmethyl pivalate **4** (0.2 g, 0.48 mmol), $ZnBr_2$ (0.131 g, 0.58 mmol) and naphthalene (0.068 g, 0.53 mmol) in dry DCE (10 mL) was refluxed under nitrogen atmosphere for 9 h. Then, the usual work up adopting the above-mentioned procedure followed by column chromatographic purification (Silica gel, EtOAc-hexane 1:9) gave carbazole **6b**. Further elution of the column afforded arylated product **5b**.

*1-(2-(Naphthalen-1-ylmethyl)-1-(phenylsulfonyl)-1H-indol-3-yl)-ethanone (**5b**).* Colorless solid (0.123 g, 58%); mp 176−178 °C. IR (neat) 1670 (CO), 1380 and 1182 (SO_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41−8.38 (m, 1H), 8.19 (d, J = 8.4 Hz, 1H), 8.12−8.09 (m, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.66−7.62 (m, 2H), 7.58−7.53 (m, 1H), 7.48−7.36 (m, 5H), 7.14 (t, J = 8 Hz, 2H), 7.00 (t, J = 7.7 Hz, 1H), 6.49 (d, J = 7.2 Hz, 1H), 5.33 (s, 2H), 2.53 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.6, 143.4, 138.4, 136.5, 134.0, 133.7, 133.6, 131.6, 129.0, 128.8, 127.1, 127.0, 126.6, 126.4, 125.9, 125.3, 124.6, 124.3, 123.1, 122.8, 121.4, 114.9, 31.6, 29.2 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.0, 129.0, 128.8, 127.0, 126.6, 126.4, 125.9, 125.4, 124.7, 124.3, 123.1, 121.4, 114.9, 31.7, 29.2 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{27}H_{21}NO_3S$ $[M^+]$ 439.1242, found 439.1240.

*7-Methyl-12-(phenylsulfonyl)-12H-naphtho[1,2-b]carbazole (**6b**).* Colorless solid (0.033 g, 16%); mp 238−240 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.92 (d, J = 8.1 Hz, 1H), 8.46 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 9.3 Hz, 1H), 7.90 (d, J = 7.5 Hz, 1H), 7.82 (d, J = 7.8 Hz, 2H), 7.76−7.73 (m, 2H), 7.67−7.62 (m, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.44−7.34 (m, 2H), 7.25−7.20 (m, 2H), 3.10 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 137.7, 137.5, 133.8, 131.7, 130.8, 130.0, 129.9, 129.0, 128.4, 127.9, 127.5, 127.4, 126.9, 126.8, 126.5, 126.0, 124.7, 124.2, 123.5, 123.4, 122.4, 115.3, 106.1, 15.9 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.8, 129.0, 128.4, 127.4, 126.9, 126.8, 126.5, 126.0, 124.2, 123.5 (2C), 122.4, 115.3, 106.1, 15.9 ppm. HRMS (ESI-TOF, MeOH) m/z Calcd for $C_{27}H_{19}NO_2S$ + Na^+ $[M + Na]^+$ 444.1034, found 444.1032.

General Procedure for the Synthesis of Annulated Carbazoles (6a−h). A solution of 2-indolylmethyl pivalate **4** (0.2 g, 0.48 mmol), $SnCl_4$ (0.151 g, 0.58 mmol) and arene (0.53 mmol) in dry DCE (10 mL) was refluxed under nitrogen atmosphere until the reaction was completed (TLC). Then, the reaction mixture was poured into ice water (30 mL) containing Conc. HCl (3 mL), the organic layer was separated and the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layer was washed with water (2 × 20 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (Silica gel, EtOAc-hexane 1:9) furnished annulated benzo[*b*]carbazoles **6a−h**.

*7,9,11-Trimethyl-5-(phenylsulfonyl)-5H-benzo[b]carbazole **6a**.* The reaction of pivalate **4** (0.2 g, 0.48 mmol) with *m*-xylene (0.151 g, 1.45 mmol) using $SnCl_4$ (0.151 g, 0.58 mmol) in dry DCE (10 mL) at reflux for 6 h under nitrogen atmosphere followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 1:9) afforded carbazole **6a** as a colorless solid (0.118 g, 61%).

*7-Methyl-12-(phenylsulfonyl)-12H-naphtho[1,2-b]carbazole (**6b**).* The annulation of pivalate **4** (0.2 g, 0.48 mmol) with naphthalene (0.068 g, 0.53 mmol) in the presence of $SnCl_4$ (0.151 g, 0.58 mmol) in dry DCE (10 mL) at reflux for 6 h followed by usual work up and column chromatographic purification (Silica gel, EtOAc-hexane 1:9) furnished carbazole **6b** as a colorless solid (0.134 g, 68%).

*5,7-Dimethyl-12-(phenylsulfonyl)-12H-naphtho[1,2-b]carbazole (**6c**).* The reaction of pivalate **4** (0.2 g, 0.48 mmol) with 1-methylnaphthalene (0.076 g, 0.53 mmol) using $SnCl_4$ (0.151 g, 0.58 mmol) in dry DCE (10 mL) at reflux for 6 h followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 1:9) gave naphthocarbazole **6c** as a colorless solid (0.137 g, 65%); mp 254−256 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.95 (d, J = 8.1 Hz, 1H), 8.45 (d, J = 7.8 Hz, 1H), 8.20 (d, J = 7.5 Hz, 1H), 8.06 (d, J = 7.5 Hz, 1H), 7.92 (s, 1H), 7.80 (d, J = 7.8 Hz, 2H), 7.75−7.66 (m, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.42−7.33 (m, 2H), 7.25−7.19 (m, 2H), 3.06 (s, 3H), 2.76 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 137.7, 137.0, 133.7, 131.8, 131.5, 130.9, 129.4, 129.0, 127.8, 127.6, 127.2, 126.9, 126.5, 124.7, 124.6, 124.1, 123.8, 123.4, 122.2, 115.4, 106.0, 20.6, 15.8 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.7, 129.0, 127.2, 126.9, 126.5, 124.6, 124.2, 123.8, 123.5, 122.2, 115.4, 106.0, 20.6, 15.8 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{28}H_{21}NO_2S$ $[M^+]$ 435.1293, found 435.1290.

*7,10,11-Trimethyl-5-(phenylsulfonyl)-5H-benzo[b]carbazole (**6d**).* To solution of pivalate **4** (0.2 g, 0.48 mmol) in dry DCE (10 mL), $SnCl_4$ (0.151 g, 0.58 mmol) and *p*-xylene (0.154 g, 1.45 mmol) were added and refluxed for 6 h. The usual workup followed by the column chromatographic purification (Silica gel, EtOAc-hexane 1:9) afforded benzocarbazole **6d** as a colorless solid (0.108 g, 56%); mp 174−176 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.68 (s, 1H), 8.37 (d, J = 8.7 Hz, 1H), 8.28 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.67−7.60 (m, 1H), 7.58−7.42 (m, 4H), 7.36−7.31 (m, 1H), 7.25−7.23 (m, 1H), 3.18 (s, 3H), 2.89 (s, 3H), 2.76 (s, 3H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6) δ 139.3, 136.2, 135.5, 134.6, 133.2, 132.8, 132.0, 131.9, 131.0, 129.6, 128.6, 127.9, 126.6, 126.5, 126.1, 125.1, 124.5, 124.3, 114.5, 106.3, 25.8, 21.2, 20.1 ppm. Dept-135 (75 MHz, DMSO-d_6) δ 134.7, 129.7, 128.7, 128.0, 126.5, 126.2, 124.6, 124.3 114.6, 106.4, 25.9, 21.3, 20.1 ppm. Elemental Analysis Calcd for $C_{25}H_{21}NO_2S$: C, 75.16; H, 5.30; N, 3.51; S, 8.03. Found: C, 75.02; H, 5.18; N, 3.39; S, 8.14.

*9-Methoxy-7,8,11-trimethyl-5-(phenylsulfonyl)-5H-benzo[b]-carbazole (**6e**).* The annulation of pivalate **4** (0.2 g, 0.48 mmol) with 2,3-dimethylanisole (0.072 g, 0.53 mmol) using $SnCl_4$ (0.151 g, 0.58 mmol) adopting the above-mentioned procedure followed by column

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chromatographic purification (Silica gel, EtOAc-hexane 1:9) afforded carbazole **6e** as a colorless solid (0.139 g, 67%); mp 272−274 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.46 (d, J = 8.1 Hz, 1H), 8.19 (d, J = 7.8 Hz, 1H), 7.83−7.78 (m, 3H), 7.52 (t, J = 7.7 Hz, 1H), 7.42−7.35 (m, 2H), 7.26−7.12 (m, 2H), 4.02 (s, 3H), 3.02 (s, 3H), 2.50 (s, 3H), 2.44 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8, 140.3, 137.7, 136.6, 135.3, 133.6, 129.6, 128.9, 128.7, 127.7, 127.3, 126.6, 126.3, 126.0, 124.2, 124.0, 123.6, 119.5, 115.2, 104.6, 61.4, 21.2, 15.5, 12.6 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.6, 128.9, 127.4, 126.6, 124.1, 123.6, 119.5, 115.3, 104.6, 61.4, 21.2, 15.5, 12.6 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{26}H_{23}NO_3S$ [M^+] 429.1399, found 429.1390.

*8,9-Dimethoxy-11-methyl-5-(phenylsulfonyl)-5H-benzo[b]-carbazole (**6f**).* The domino reaction of pivalate **4** (0.2 g, 0.48 mmol) with veratrole (0.073 g, 0.53 mmol) in the presence of $SnCl_4$ (0.151 g, 0.58 mmol) adopting the above-mentioned procedure followed by the column chromatographic purification (Silica gel, EtOAc-hexane 1:9) gave carbazole **6f** as a colorless solid (0.134 g, 64%); mp 256−258 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 7.5 Hz, 1H), 7.79 (d, J = 7.8 Hz, 2H), 7.48 (t, J = 7.7 Hz, 1H), 7.39−7.35 (m, 3H), 7.32 (s, 1H), 7.28−7.23 (m, 2H), 4.08 (s, 3H), 4.06 (s, 3H) 2.99 (s, 3H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6) δ 149.7, 149.0, 138.7, 136.5, 135.1, 134.6, 129.6, 128.8, 127.8, 127.3, 127.0, 126.2, 125.3, 124.5, 123.5, 122.0, 114.5, 108.5, 107.5, 102.9, 55.5 (2C), 15.5 ppm. Dept-135 (75 MHz, DMSO-d_6) δ 134.5, 129.5, 127.2, 126.1, 124.4, 123.4, 114.4, 108.4, 107.4, 102.8, 55.5, 55.4, 15.4 ppm. HRMS (ESI-ion trap, MeOH) m/z Calcd for $C_{25}H_{21}NO_4S$ + Na^+ [M + Na]$^+$ 454.1089, found 454.1084.

*8,9,11-Trimethyl-5-(phenylsulfonyl)-5H-benzo[b]carbazole (**6g**).* The annulation of pivalate **4** (0.2 g, 0.48 mmol) with *o*-xylene (0.056 g, 0.53 mmol) using $SnCl_4$ (0.151 g, 0.58 mmol) adopting the above-mentioned procedure followed by column chromatographic purification (Silica gel, EtOAc-hexane 1:9) gave carbazole **6g** as a colorless solid (0.114 g, 59%); mp >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$-DMSO-d_6 (4:1)) δ 8.44 (s, 1H), 8.26 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 7.5 Hz, 1H), 7.86 (s, 1H), 7.70−7.67 (m, 3H), 7.41 (t, J = 7.05 Hz, 1H), 7.32−7.28 (m, 2H), 7.16 (t, J = 7.5 Hz, 2H), 2.94 (s, 3H), 2.40 (s, 3H), 2.39 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$-DMSO-d_6 (4:1)) δ 139.9, 137.4, 136.4, 135.6, 134.7, 133.7, 131.7, 128.9, 128.8, 128.4, 128.3, 127.8, 127.2, 126.4, 124.1, 123.9, 123.5, 123.3, 115.1, 109.4, 20.6, 20.0, 15.3 ppm. Dept-135 (75 MHz, $CDCl_3$-DMSO-d_6 (4:1)) δ 133.7, 128.9, 128.4, 127.2, 126.4, 124.1, 123.5, 123.3, 115.0, 109.3, 20.6, 20.0, 15.3 ppm. Elemental Analysis Calcd for $C_{25}H_{21}NO_2S$: C, 75.16; H, 5.30; N, 3.51; S, 8.03. Found: C, 75.24; H, 5.12; N, 3.37; S, 7.88.

*7-Methyl-12-(phenylsulfonyl)-12H-naphtho[1,2-b]carbazole (**6h**).* The annulation of pivalate **4** (0.2 g, 0.48 mmol) with 1,3-benzodioxole (0.065 g, 0.53 mmol) using $SnCl_4$ (0.151 g, 0.58 mmol) adopting the above-mentioned procedure followed by column chromatographic purification (Silica gel, EtOAc-hexane 1:9) afforded carbazole **6h** as a colorless solid (0.124 g, 62%); mp 232−234 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.39 (d, J = 7.8 Hz, 1H), 8.16 (d, J = 7.5 Hz, 1H), 7.78 (d, J = 7.2 Hz, 2H), 7.51−7.46 (m, 3H), 7.40−7.35 (m, 2H), 7.30−7.26 (m, 2H), 6.07 (s, 2H, CH_2), 2.96 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6, 139.7, 137.7, 136.3, 133.7, 130.3, 128.9, 128.1, 127.7, 127.1, 127.0, 126.6, 124.1, 123.4, 123.3, 115.2, 109.9, 104.6, 101.3 (CH_2), 100.1, 15.9 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.7, 128.9, 127.1, 126.5, 124.1, 123.3, 115.2, 109.9, 104.6, 101.3 (CH_2), 100.1, 15.9 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{24}H_{17}NO_4S$ [M^+] 415.0878, found 415.0875.

General Procedure for the Preparation of Heteroannulated Carbazoles (8a−i). A solution of 2-indolylmethyl pivalate **4** (0.48 mmol), heteroarene (0.53 mmol) and $SnCl_4$ (0.58 mmol) in dry DCE (10 mL) was stirred at room temperature under nitrogen atmosphere. After the completion of the reaction (TLC), it was then poured into ice water (30 mL) containing Conc. HCl (3 mL). The organic layer was separated and the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layer was washed with water (2 × 20 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (Silica gel, EtOAc-hexane) afforded heteroannulated carbazoles **8a−i**.

*4-Methyl-9-(phenylsulfonyl)-9H-thieno[2,3-b]carbazole (**8a**).* The reaction of pivalate **4** (0.2 g, 0.48 mmol) with thiophene (0.081 g, 0.96 mmol) using $SnCl_4$ (0.151 g, 0.58 mmol) adopting the above-mentioned procedure followed by column chromatographic purification (Silica gel, EtOAc-hexane 1:9) gave thienocarbazole **8a** as a colorless solid (0.113 g, 62%); mp 224−226 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.32 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 7.5 Hz, 1H), 7.71 (d, J = 7.5 Hz, 2H), 7,45−7.41 (m, 2H), 7.38−7.36 (m, 1H), 7.31 (d, J = 7.2 Hz, 2H), 7.21−7.17 (m, 2H), 2.91 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 139.2, 137.8, 136.7 (2C), 133.7, 129.0, 127.5, 127.3, 126.8, 126.5, 125.5, 124.0, 122.9, 122,7, 121.7, 115.2, 106.1, 17.4 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.7, 129.0, 126.8, 126.5, 125.5, 124.0, 122.7, 121.7, 115.2, 106.1, 17.4 ppm. HRMS (ESI-ion trap, MeOH) m/z Calcd for $C_{21}H_{15}NO_2S_2$ + Na^+ [M + Na]$^+$ 400.0442, found 400.0437.

*2,4-Dimethyl-9-(phenylsulfonyl)-9H-thieno[2,3-b]carbazole (**8b**).* The annulation of pivalate **4** (0.2 g, 0.48 mmol) with 2-methylthiophene (0.052 g, 0.53 mmol) in the presence of $SnCl_4$ (0.151 g, 0.58 mmol) adopting the above-mentioned procedure followed by column chromatographic purification (Silica gel, EtOAc-hexane 1:9) furnished thieno[*b*]carbazole **8b** as a colorless solid (0.144 g, 76%); mp 248−250 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.30 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 7.8 Hz, 2H), 7.38 (t, J = 7.8 Hz, 1H), 7.29 (q, J = 8.2 Hz, 2H), 7.20−7.15 (m, 2H), 7.05 (s, 1H), 2.81 (s, 3H), 2.53 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 139.3, 139.0, 137.7, 137.3, 136.0, 133.6, 128.9, 127.7, 126.5 (2C), 126.2, 123.9, 122.6, 119.3, 115.1, 105.8, 17.3, 16.4 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 132.7, 127.9, 125.5 (2C), 122.9, 121.6, 118.3, 114.1, 104.7, 16.3, 15.4 ppm. HRMS (ESI-ion trap, MeOH) m/z Calcd for $C_{22}H_{17}NO_2S_2$ + Na^+ [M + Na]$^+$ 414.0598, found 414.0587.

*4-Methyl-9-(phenylsulfonyl)-2-(thiophen-2-yl)-9H-thieno[2,3-b]-carbazole (**8c**).* The domino reaction of pivalate **4** (0.2 g, 0.48 mmol) with bithiophene (0.088 g, 0.53 mmol) using $SnCl_4$ (0.151 g, 0.58 mmol) adopting the above-mentioned procedure followed by column chromatographic purification (Silica gel, EtOAc-hexane 1:9) afforded carbazole **8c** as a colorless solid (0.156 g, 70%); mp 252−254 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.31 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 7.5 Hz, 1H), 7.72 (d, J = 7.8 Hz, 2H), 7.49 (s, 1H), 7.44−7.28 (m, 3H), 7.24−7.23 (m, 4H), 7.02−6.99 (m, 1H), 2.90 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 138.8, 137.7, 137.5, 137.3, 136.7, 136.3, 133.8, 129.0, 128.0, 127.4, 127.2, 126.8, 126.5, 125.4, 125.1, 124.1, 123.2, 122.7, 117.5, 115.2, 105.8, 17.4 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 132.8, 128.0, 127.0, 125.8, 125.5, 124.4, 124.1, 123.1, 121.7, 116.5, 114.2, 104.8, 16.4 ppm. HRMS (ESI-ion trap, MeOH) m/z Calcd for $C_{25}H_{17}NO_2S_3$ + Na^+ [M + Na]$^+$ 482.0319, found 482.0310.

*6-Methyl-11-(phenylsulfonyl)-benzo[b]thieno[2,3-b]carbazole and 11-Methyl-7-(phenylsulfonyl)-benzo[b]thieno[3,2-b]carbazole (**8d/8d′**).* The domino reaction of pivalate **4** (0.2 g, 0.48 mmol) with thianaphthene (0.071 g, 0.53 mmol) using $SnCl_4$ (0.151 g, 0.58 mmol) in DCE (10 mL) at room temperature for 3 h followed by column chromatographic purification (Silica gel, EtOAc-hexane 1:9) led to an inseparable mixture of carbazoles **8d** and **8d′**as a colorless solid (0.153 g, 74%); mp 244−246 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.02 (s), 8.74 (s), 8.44−8.40 (m), 8.35−8.32 (m), 8.21 (d, J = 7.8 Hz), 8.09 (d, J = 7.5 Hz), 7.89−7.85 (m), 7.81−7.78 (m), 7.54−7.44 (m), 7.40 (t, J = 7.5 Hz), 7.31−7.23 (m), 3.29 (s), 2.94 (s) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.8, 139.7, 139.4, 139.0, 137.7, 137.5, 137.2, 136.7, 136.3, 136.1, 134.6, 133.8 (2C), 131.2, 130.3, 129.1, 129.0, 127.4, 127.1, 127.0, 126.9, 126.7, 126.5 (2C), 125.8, 125.0, 124.6, 124.4, 124.3, 124.2, 124.1, 122.9, 122.7, 122.1, 115.3, 115.2, 106.2, 105.6, 19.2, 18.4 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.9, 133.8, 129.1, 129.0, 127.1, 127.0, 126.7, 126.5 (2C), 125.8, 125.0, 124.6, 124.3, 124.2, 124.1, 122.9, 122.7, 122.1, 115.3, 115.2, 106.2, 105.6, 19.2, 18.4 ppm. HRMS (ESI-ion trap, MeOH) m/z Calcd for $C_{25}H_{17}NO_2S_2$ + H^+ [M + H]$^+$ 428.0779, found 428.0785.

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*4-Methyl-1,9-bis(phenylsulfonyl)-1,9-dihydropyrrolo[2,3-b]-carbazole (**8e**).* The domino reaction of pivalate **4** (0.2 g, 0.48 mmol) with *N*-sulfonyl pyrrole (0.11 g, 0.53 mmol) using $SnCl_4$ (0.151 g, 0.58 mmol) adopting the procedure similar to that of **8a** followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) furnished pyrolocarbazole **8e** as a colorless solid (0.158 g, 65%); mp 258−260 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.34 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 7.5 Hz, 3H), 7.69 (d, J = 7.8 Hz, 2H), 7.60 (d, J = 8.4 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.43−7.38 (m, 3H), 7.35−7.26 (m, 2H), 7.21−7.16 (m, 2H), 6.75 (d, J = 8.4 Hz, 1H), 2.75 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 138.0, 137.7, 136.7, 133.9, 133.7, 129.4, 129.0, 128.2, 127.2, 126.6, 126.5, 126.4, 125.1, 124.0, 122.4, 121.5, 115.1, 107.1, 97.9, 16.6 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.9, 133.8, 129.4, 129.0, 127.2, 126.6, 126.5, 126.3, 124.0, 122.4, 115.1, 107.2, 97.9, 16.6 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{27}H_{20}N_2O_4S_2$ [M^+] 500.0864, found 500.0861.

*12-Methyl-7-(phenylsulfonyl)-7H-benzofuro[2,3-b]carbazole (**8f**).* The domino reaction of pivalate **4** (0.2 g, 0.48 mmol) with benzofuran (0.063 g, 0.53 mmol) using $SnCl_4$ (0.151 g, 0.58 mmol) in dry DCE (10 mL) at room temperature followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 1:9) gave benzofuro[2,3-*b*]carbazole **8f** as a colorless solid (0.155 g, 78%); mp 256−258 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.43 (d, J = 8.4 Hz, 1H), 8.17−8.14 (m, 2H), 7.83 (d, J = 7.5 Hz, 2H), 7.61 (d, J = 8.1 Hz, 1H), 7.49−7.37 (m, 5H), 7.32−7.26 (m, 2H), 3.19 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9, 155.7, 139.0, 138.2, 137.7, 133.8, 129.0, 128.2, 127.3, 126.5 (2C), 126.2, 124.1, 122.8, 122.3, 122.2, 121.2, 120.6, 115.1, 111.6, 96.3, 17.1 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.9, 129.1, 126.5 (2C), 126.2, 124.1, 122.8, 122.3, 122.2, 115.1, 111.6, 96.3, 17.1 ppm. HRMS (ESI-ion trap, MeOH) m/z Calcd for $C_{25}H_{17}NO_3S + Na^+$ [M + Na]$^+$ 434.0827, found 434.0822.

*8-Methyl-13-(phenylsulfonyl)-naphtho[b]thieno[2,3-b]carbazole (**8g**).* The domino reaction of pivalate **4** (0.2 g, 0.48 mmol) with naphtho[*b*]thiophene[28] (0.089 g, 0.53 mmol) using $SnCl_4$ (0.151 g, 0.58 mmol) in 1,2-DCE at room temperature for 7 h followed by column chromatographic purification (Silica gel, EtOAc-hexane 1:9) gave carbazole **8g** as a colorless solid (0.134 g, 58%); mp >300 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.16 (s, 2H), 8.58 (s, 1H), 8.39 (d, J = 8.4 Hz, 1H), 8.31−8.25 (m, 2H), 8.06−8.03 (m, 1H), 7.97 (d, J = 7.8 Hz, 2H), 7.68−7.58 (m, 4H), 7.54−7.46 (m, 3H), 2.96 (s, 3H) ppm. Due to the solubility problem of the carbazole **8g**, ^{13}C NMR could not be recorded. HRMS (EI, 70 eV) m/z Calcd for $C_{29}H_{19}NO_2S_2$ [M^+] 477.0857, found 477.0850.

*2-(3,5-Di(thiophen-2-yl)phenyl)-4-methyl-9-(phenylsulfonyl)-9H-thieno[2,3-b]carbazole (**8h**).* The domino reaction of pivalate **4** (0.2 g, 0.48 mmol) with 1,3,5-tri(thiophen-2-yl)benzene (0.172 g, 0.53 mmol) in the presence of $SnCl_4$ (0.151 g, 0.58 mmol) in 1,2-DCE at room temperature for 5 h followed by work up and column chromatographic purification (Silica gel, EtOAc-hexane 1:9) afforded carbazole **8h** as a colorless solid (0.191 g, 64%); mp 172−174 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.41 (d, J = 8.1 Hz, 1H), 8.14 (d, J = 7.5 Hz, 1H), 7.86 (s, 2H), 7.82 (d, J = 6.9 Hz, 4H), 7.52 (d, J = 7.8 Hz, 1H), 7.47−7.44 (m, 3H), 7.42−7.41 (m, 1H), 7.38 (d, J = 7.8 Hz, 2H), 7.33−7.28 (m, 2H), 7.17−7.14 (m, 2H), 3.06 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 142.3, 139.3, 139.2, 137.7, 137.5, 136.8, 135.9, 135.7, 133.8, 129.1, 128.2, 127.5 (2C), 126.9, 126.5, 125.6, 124.1 (2C), 123.5, 123.2, 123.1, 122.8, 118.1, 115.2, 106.0, 17.5 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.8, 129.1, 128.2, 126.9, 126.6, 125.6, 124.1 (2C), 123.5, 123.1, 122.8, 118.1, 115.2, 106.0, 17.5 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{35}H_{23}NO_2S_4$ [M^+] 617.0612, found 617.0610.

*2-(3,5-Bis(3-methylthiophen-2-yl)phenyl)-3,4-dimethyl-9-(phenylsulfonyl)-9H-thieno[2,3-b]carbazole (**8i**).* The domino reaction of pivalate **4** (0.2 g, 0.48 mmol) with 1,3,5-tris(3-methylthiophen-2-yl)benzene (0.195 g, 0.53 mmol) using $SnCl_4$ (0.151 g, 0.58 mmol) in 1,2-DCE at room temperature for 6 h followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 1:9) afforded carbazole **8i** as a colorless solid (0.214 g, 67%); mp 184−186 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.31 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 7.5 Hz, 2H), 7.51−7.49 (m, 3H), 7.38 (t, J = 7.7 Hz, 1H), 7.33−7.24 (m, 2H), 7.20−7.15 (m, 4H), 6.88−7.87 (m, 2H), 3.06 (s, 3H), 2.67 (s, 3H), 2.34 (s, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 139.2, 137.7, 137.6, 137.0, 136.6, 136.3, 135.5, 135.4, 133.9, 133.7, 131.3, 129.6, 129.3, 129.0, 128.9 (2C), 127.7, 126.7, 126.5, 124.1, 124.0, (2C), 123.2, 115.1, 106.0, 18.2, 17.6, 15.2 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.8, 131.3, 129.3, 129.0, 128.9, 126.7, 126.5, 124.0 (2C), 123.2, 115.2, 106.0, 18.2, 17.7, 15.2 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{38}H_{29}NO_2S_4$ [M^+] 659.1081, found 659.1080.

General Procedure for the Preparation of Benzoylindoles (9a−d). To a solution of aroyl chloride (11.07 mmol) in dry DCM (15 mL) at 0 °C, $SnCl_4$ (2.88 g, 11.07 mmol) was added dropwise for 5 min. To this, *N*-phenylsulfonyl-2-methylindole[29] (2 g, 7.38 mmol) in dry DCM (10 mL) was added (5 min) and allowed to stir at room temperature. After completion of the reaction (monitored by TLC), it was poured into ice−water (50 mL) containing Conc. HCl (10 mL). The organic layer was separated and the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layer was washed with water (3 × 25 mL) and dried (Na_2SO_4). The subsequent purification of crude product either by MeOH washing or column chromatographic purification (Silica gel, EtOAc-hexane) furnished benzoyl indoles **9a−d**.

*(3,4-Dimethoxyphenyl)(2-(2,4-dimethylbenzyl)-1-(phenylsulfonyl)-1H-indol-3-yl)methanone (**9a**).* The Friedel−Crafts benzoylation of *N*-phenylsulfonyl-2-methylindole[29] (2 g, 7.38 mmol) with veratroyl chloride (2.23 g, 11.07 mmol) in the presence of $SnCl_4$ (2.88 g, 11.07 mmol) in dry DCM (20 mL) adopting the above-mentioned procedure followed by trituration of the crude with MeOH (5 mL) gave veratroylindole **9a** as a colorless solid (2.79 g, 87%); mp 164−166 °C. IR (neat) 1641 (CO), 1378 and 1182 (SO_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 7.5 Hz, 2H), 7.61 (t, J = 7.35 Hz, 1H), 7.51−7.45 (m, 3H), 7.36−7.31 (m, 3H), 7.23−7.18 (m, 1H), 6.84 (d, J = 8.4 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H), 2.62 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4, 153.6, 149.0, 139.7, 138.8, 135.8, 134.1, 131.4, 129.5, 128.3, 126.5, 125.1, 124.7, 123.9, 120.6, 120.6, 114.2, 111.2, 110.0, 56.0, 55.9, 14.5 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.2, 128.6, 125.5, 124.2, 123.8, 123.0, 119.7, 113.3, 110.3, 109.1, 55.1, 55.0, 13.6 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{24}H_{21}NO_5S$ [M^+] 435.1140, found 435.1137.

*(2-Methyl-1-(phenylsulfonyl)-1H-indol-3-yl)(phenyl)methanone (**9b**).*[33] The Friedel−Crafts reaction of *N*-phenylsulfonyl-2-methylindole[29] (2 g, 7.38 mmol) with benzoyl chloride (1.56 g, 11.07 mmol) using $SnCl_4$ (2.88 g, 11.07 mmol) adopting the above-mentioned procedure followed by workup afforded benzoylindole **9b** as a colorless solid (2.54 g, 92%); mp 138−140 °C (Lit.[33] 130.5−132 °C). IR (neat) 1648 (CO), 1380 and 1184 (SO_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, J = 8.7 Hz, 1H), 7.87 (d, J = 7.8 Hz, 2H), 7.76 (d, J = 7.2 Hz, 2H), 7.62−7.56 (m, 2H), 7.50−7.41 (m, 4H), 7.35−7.25 (m, 2H), 7.21−7.16 (m, 1H), 2.62 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.0, 141.0, 139.0, 138.9, 136.0, 134.3, 133.2, 129.6 (2C), 128.6, 128.2, 126.6, 124.9, 124.1, 120.7, 120.5, 114.4, 14.6 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.3, 133.2, 129.6 (2C), 128.6, 126.6, 124.9, 124.1, 120.7, 114.3, 14.7 ppm.

*(2-Methyl-1-(phenylsulfonyl)-1H-indol-3-yl)(4-nitrophenyl)-methanone (**9c**).* The Friedel−Crafts benzoylation of *N*-phenylsulfonyl-2-methylindole[29] (2 g, 7.38 mmol) with 4-nitrobenzoyl chloride (2.06 g, 11.07) using $SnCl_4$ (2.88 g, 11.07 mmol) in dry DCM (30 mL) at room temperature for 48 h followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) furnished benzoylindole **9c** as a colorless solid (1.92 g, 62%); mp 162−164 °C. IR (neat) 1652 (CO), 1526 and 1346 (NO_2), 1381 and 1186 (SO_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, J = 8.4 Hz, 3H), 7.91 (d, J = 8.1 Hz, 4H), 7.65 (t, J = 7.35 Hz, 1H), 7.56−7.51 (m, 2H), 7.39−7.35 (m, 1H), 7.24−7.19 (m, 1H) 2.69 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.0, 150.2, 144.0, 142.7, 138.7, 135.9, 134.5, 130.4, 129.7, 127.4, 126.6, 125.2, 124.4, 123.9, 120.5, 119.3, 114.5, 14.6 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.6, 130.4, 129.7, 126.6, 125.2, 124.4, 123.9, 120.5, 114.5, 14.7 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{22}H_{16}N_2O_5S$ [M^+] 420.0780, found 420.0770.

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*(4-Chlorophenyl)(2-methyl-1-(phenylsulfonyl)-1H-indol-3-yl)-methanone (**9d**).* The Friedel−Crafts benzoylation of *N*-phenylsulfonyl-2-methylindole[29] (2 g, 7.38 mmol) with 4-chlorobenzoyl chloride (1.94 g, 11.07 mmol) using $SnCl_4$ (2.88 g, 11.07 mmol) in dry DCM (30 mL) at room temperature for 24 h followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) gave 4-chlorobenzoylindole **9d** as a colorless solid (2.30 g, 76%); mp 92−94 °C. IR (neat) 1650 (CO), 1380 and 1186 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 7.5 Hz, 2H), 7.73 (t, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.36 (t, J = 7.7 Hz, 1H), 7.29−7.19 (m, 2H), 2.66 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.6, 141.3, 139.6, 138.8, 137.2, 135.9, 134.4, 131.0, 129.6, 129.0, 127.9, 126.6, 125.0, 124.2, 120.6, 120.0, 114.4, 14.6 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.4, 131.0, 129.6, 129.0, 126.6, 125.0, 124.2, 120.6, 114.4, 14.6 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{22}H_{16}ClNO_3S$ [M^+] 409.0539, found 409.0535.

General Procedure for the Preparation of 2-Bromomethylindoles (10a−d). To a solution of *N*-phenylsulfonyl-2-methylindole **9a−d** (1 equiv) and AIBN (0.05 g) in dry CCl_4 (30 mL) freshly recrystallized NBS (1.2 equiv) was added. The reaction mixture was refluxed and cooled to room temperature. The floated succinimide was filtered off and washed with carbon tetrachloride (10 mL). The combined filtrate was concentrated in vacuo to afford bromo compounds **10a−d**.

*(2-(Bromomethyl)-1-(phenylsulfonyl)-1H-indol-3-yl)(3,4-dimethoxyphenyl)methanone (**10a**).* The benzylic bromination of 2-methylindole **9a** (1.5 g, 3.45) using NBS (0.74 g, 4.14 mmol) and AIBN (0.05 g) adopting the above-mentioned procedure followed by workup and removal of solvent furnished bromo compound **10a** as a brown solid (1.61 g, 91%); mp 158−160 °C. IR (neat) 1646 (CO), 1378 and 1176 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, J = 8.7 Hz, 1H), 8.02 (d, J = 7.8 Hz, 2H), 7.64−7.59 (m, 1H), 7.53−7.48 (m, 3H), 7.40−7.30 (m, 2H), 7.24−7.19 (m, 2H), 6.83 (d, J = 8.4 Hz, 1H), 5.16 (s, 2H), 3.95 (s, 3H), 3.91 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 154.1, 149.2, 138.4, 138.2, 136.0, 134.4, 130.9, 129.4, 127.8, 127.1, 126.3, 125.7, 124.3, 123.7, 121.6, 114.8, 111.1, 110.1, 56.2, 56.1, 21.7 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.5, 129.4, 127.1, 126.3, 125.7, 124.3, 121.6, 114.8, 111.1, 110.0, 56.2, 56.1, 21.8 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{24}H_{20}BrNO_5S$ [M^+] 513.0246, found 513.0244.

*(2-(Bromomethyl)-1-(phenylsulfonyl)-1H-indol-3-yl)(phenyl)-methanone (**10b**).*[33] The benzylic bromination of 2-methylindole **9b** (1.5 g, 4.00 mmol) using NBS (0.85 g, 4.8 mmol) and AIBN (0.05 g) adopting the above-mentioned procedure gave bromo compound **10b** as a brown solid (1.71 g, 94%); mp 146−148 °C (Lit.[33] 156−158 °C). IR (neat) 1652 (CO), 1378 and 1186 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, J = 8.7 Hz, 1H), 8.03 (d, J = 7.5 Hz, 2H), 7.78−7.76 (m, 2H), 7.61 (t, J = 7.7 Hz, 2H), 7.52−7.42 (m, 4H), 7.39−7.33 (m, 1H), 7.18−7.08 (m, 2H), 5.21 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.2, 139.3, 138.3, 138.2, 135.9, 134.5, 133.6, 129.6, 129.4, 128.6, 127.4, 127.1, 126.2, 124.3, 123.0, 121.5, 114.7, 21.4 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.6, 133.7, 129.7, 129.5, 128.7, 127.2, 126.3, 124.4, 121.6, 114.8, 21.5 ppm.

*(2-(Bromomethyl)-1-(phenylsulfonyl)-1H-indol-3-yl)(4-nitrophenyl)methanone (**10c**).* The benzylic bromination of 2-methylindole **9c** (1.5 g, 3.57 mmol) using NBS (0.76 g, 4.29 mmol) in and AIBN (0.05 g) adopting the above-mentioned procedure gave bromo compound **10c** as a colorless solid (1.53 g, 86%); mp 66−68 °C. IR (neat) 1660 (CO), 1526 and 1348 (NO_2) 1379 and 1186 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, J = 8.1 Hz, 2H), 8.08 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.1 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.60−7.55 (m, 1H), 7.45 (t, J = 7.35 Hz, 2H), 7.30 (t, J = 7.8 Hz, 1H), 7.11−7.06 (m, 1H), 6.88 (d, J = 8.1 Hz, 1H), 5.17 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 150.5, 143.2, 140.9, 138.1, 135.9, 134.8, 130.5, 129.6, 127.3, 126.7, 126.6, 124.7, 124.0, 123.9, 121.2, 115.0, 21.0 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.8, 130.5, 129.6, 127.3, 126.6, 124.7, 123.9, 121.2, 115.0, 21.0 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{22}H_{15}BrN_2O_5S$ [M^+] 497.9885, found 497.9881.

*(2-(Bromomethyl)-1-(phenylsulfonyl)-1H-indol-3-yl)(4-chlorophenyl)methanone (**10d**).* The benzylic bromination of 2-methylindole **9d** (1.5 g, 7.32 mmol) using NBS (0.78 g, 4.39 mmol) and AIBN (0.05 g) following the above-mentioned procedure furnished bromo compound **10d** as a colorless solid (1.65 g, 92%); mp 132−134 °C. IR (neat) 1652 (CO) 1378 and 1186 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, J = 8.4 Hz, 1H), 8.09−8.05 (m, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.66−7.60 (m, 1H), 7.54−7.49 (m, 2H), 7.45−7.36 (m, 3H), 7.18 (t, J = 8 Hz, 1H), 7.11−7.09 (m, 1H), 5.24 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9, 140.2, 139.6, 138.3, 136.5, 135.9, 134.6, 131.1, 129.5, 129.1, 127.2, 126.4, 124.5, 122.4, 121.4, 114.9, 21.3 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.6, 131.1, 129.5, 129.1, 127.2, 126.4, 124.5, 121.4, 114.8, 21.3 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{22}H_{15}BrClNO_3S$ [M^+] 486.9645, found 486.9640.

General Procedure for the Preparation of Pivaloyloxyindoles (11a−d). To a stirred solution of 2-bromomethylindoles **10a−d** (1 equiv) in dry THF (30 mL), potassium carbonate (3 equiv) and pivalic acid (2 equiv) were added. The reaction mixture was allowed to stir at room temperature until the reaction was completed (TLC). Then, the usual work up adopting the above-mentioned procedure **4** furnished pivalates **11a−d**.

*(3-(3,4-Dimethoxybenzoyl)-1-(phenylsulfonyl)-1H-indol-2-yl)-methyl pivalate (**11a**).* The pivaloylation of 2-bromomethylindole **10a** (1.5 g, 2.92 mmol) using pivalic acid (0.60 g, 5.84 mmol) and potassium carbonate (1.21 g, 8.75 mmol) adopting the above-mentioned procedure followed by workup and trituration of crude product with MeOH (5 mL) gave pivalate **11a** as a colorless solid (1.40 g, 90%); mp 148−150 °C. IR (neat) 1728 (ester), 1646 (CO), 1380 and 1178 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 7.8 Hz, 2H), 7.53−7.46 (m, 2H), 7.42−7.36 (m, 2H), 7.33−7.28 (m, 2H), 7.26−7.23 (m, 1H), 7.19−7.13 (m, 1H), 6.73 (d, J = 8.4 Hz, 1H), 5.33 (s, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 1.08 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.5, 177.5, 154.1, 149.3, 138.6, 136.1, 135.2, 134.3, 131.1, 129.5, 127.9, 126.6, 126.2, 125.8, 124.7, 124.3, 121.4, 114.7, 110.1, 109.9, 57.0, 56.1 (2C), 38.8, 27.1 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.3, 129.5, 126.6, 126.2, 125.8, 124.3, 121.4, 114.7, 110.9, 109.9, 57.0, 56.1 (2C), 27.1 ppm. Elemental Analysis Calcd for $C_{29}H_{29}NO_7S$; C, 65.03; H, 5.46; N, 2.62; S, 5.99, found C, 64.86; H, 5.28; N, 2.48; S, 5.76.

*(3-Benzoyl-1-(phenylsulfonyl)-1H-indol-2-yl)methyl pivalate (**11b**).* The pivaloylation of 2-bromomethylindole **10b** (1.5 g, 3.30 mmol) using pivalic acid (0.67 g, 6.61 mmol) and potassium carbonate (1.36 g, 9.91 mmol) adopting the above-mentioned procedure followed by workup and trituration of crude product with MeOH (5 mL) afforded pivalate **11b** as a colorless solid (1.44 g, 92%); mp 134−136 °C. IR (neat) 1730 (ester), 1654 (CO), 1380 and 1184 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 7.8 Hz, 2H), 7.82 (d, J = 7.8 Hz, 2H), 7.63−7.56 (m, 2H), 7.49−7.42 (m, 4H), 7.38 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.4 Hz, 1H), 5.40 (s, 2H), 1.15 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 177.4, 138.6, 138.3, 136.2, 136.1, 134.3, 133.7, 129.7, 129.5, 128.6, 127.7, 126.6, 126.3, 124.4, 124.3, 121.4, 114.7, 56.8, 38.8, 27.1 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.4, 133.7, 129.7, 129.6, 128.7, 126.7, 126.3, 124.4, 121.5, 114.7, 56.8, 27.1 ppm. Elemental Analysis Calcd for $C_{27}H_{25}NO_5S$; C, 68.19; H, 5.30; N, 2.95; S, 6.74, found C, 68.02; H, 5.39; N, 2.72; S, 6.57.

*(3-(4-Nitrobenzoyl)-1-(phenylsulfonyl)-1H-indol-2-yl)methyl pivalate (**11c**).* The pivaloylation of 2-bromomethylindole **10c** (1.5 g, 3.01 mmol) using pivalic acid (0.61 g, 6.01 mmol) and potassium carbonate (1.24 g, 9.02 mmol) adopting the above-mentioned procedure followed by column chromatographic purification (Silica gel, EtOAc-hexane 2:8) afforded pivaloyloxyindole **11c** as a brown solid (1.22 g, 78%); mp 118−120 °C. IR (neat) 1730 (ester), 1662 (CO), 1528 and 1348 (NO_2), 1382 and 1185 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, J = 8.7 Hz, 2H), 8.12 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.7 Hz, 2H), 7.85 (d, J = 7.8 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45−7.40 (m, 2H), 7.37−7.32 (m, 1H), 7.19−7.16 (m, 2H), 5.37 (s, 2H), 1.07 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.3, 177.5, 150.5, 143.1, 138.4, 137.5, 136.1, 134.6, 130.6, 129.7, 127.0, 126.7, 126.6, 124.7, 123.8, 123.0, 121.2, 114.9, 56.4, 38.8, 27.1 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.6, 130.6, 129.7, 126.8, 126.6, 124.7,

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123.8, 121.2, 114.9, 56.4, 27.1 ppm. Elemental Analysis Calcd for $C_{27}H_{24}N_2O_7S$: C, 62.30; H, 4.65; N, 5.38; S, 6.16. Found: C, 62.14; H, 4.42; N, 5.24; S, 6.04.

*(3-(4-Chlorobenzoyl)-1-(phenylsulfonyl)-1H-indol-2-yl)methyl pivalate (**11d**).* The pivaloylation of 2-bromomethylindole **10d** (1.5 g, 3.07 mmol) using pivalic acid (0.63 g, 6.13 mmol) and potassium carbonate (1.27 g, 9.20 mmol) adopting the above-mentioned procedure by work up and trituration of crude product with MeOH (5 mL) afforded pivalate **11d** as a colorless solid (1.29 g, 83%); mp 138−140 °C. IR (neat) 1730 (ester), 1654 (CO), 1380 and 1184 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 7.5 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.51−7.38 (m, 5H), 7.33 (d, J = 7.8 Hz, 1H), 7.26−7.21 (m, 1H), 5.41 (s, 2H), 1.16 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8, 177.5, 140.2, 138.5, 136.5, 136.3, 136.1, 134.4, 131.1, 129.6, 129.0, 127.4, 126.7, 126.4, 124.5, 123.8, 121.3, 114.8, 56.7, 38.8, 27.1 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.5, 131.2, 129.6, 129.0, 126.7, 126.4, 124.5, 121.3, 114.8, 56.7, 27.1 ppm. Elemental Analysis Calcd for $C_{27}H_{24}ClNO_5S$: C, 63.59; H, 4.74; Cl, 6.95; N, 2.75; S, 6.29. Found: C, 63.34; H, 4.62; N, 2.58; S, 6.17.

General Procedure for Synthesis of 4-Arylbenzo[*b*]-carbazoles (12a−d to 13a−d). A solution of pivalates **11a−d** (1 equiv) in dry DCE (10 mL), $SnCl_4$ (1.2 equiv) and arene (1.1 equiv) were added and refluxed under nitrogen atmosphere (~4 h). After the completion of the reaction, it was poured into ice water (30 mL) containing Conc. HCl (3 mL). The organic layer was separated and the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layer was washed with water (2 × 20 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (Silica gel, EtOAc-hexane) furnished annulated carbazoles **12a−d** to **13a−d**.

*7-(3,4-Dimethoxyphenyl)-5-methyl-12-(phenylsulfonyl)-12H-naphtho[1,2-b]carbazole (**12a**).* The domino reaction of pivalate **11a** (0.2 g, 0.37 mmol) with 1-methylnaphthalene (0.058 g, 0.41 mmol) using $SnCl_4$ (0.116 g, 0.45) adopting the above-mentioned procedure followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 3:7) furnished naphtho[*b*]carbazole **12a** as a colorless solid (0.127 g, 61%); mp 230−232 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 9.76 (s, 1H), 9.02 (d, J = 7.8 Hz, 1H), 8.38 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 7.8 Hz, 2H), 7.84−7.74 (m, 2H), 7.46−7.41 (m, 3H), 7.337.30 (m, 2H), 7.13−7.01 (m, 2H), 6.95−6.90 (m, 2H), 6.74 (d, J = 7.5 Hz, 1H), 4.06 (s, 3H), 3.83 (s, 3H), 2.64 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.6, 148.8, 139.8, 137.9, 136.9, 133.7, 133.6, 131.9, 131.7, 130.7, 130.6, 129.4, 129.1, 128.2, 127.6, 127.1, 126.6 (2C), 124.7, 124.6, 124.0, 123.9, 123.7, 122.9, 122.2, 114.9, 113.0, 111.8, 107.3, 56.0, 20.3 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 132.8, 128.1, 126.6, 126.1, 125.6 (2C), 123.7, 123.0, 122.9, 122.7, 121.9, 121.2, 113.9, 112.0, 110.7, 106.3, 55.0, 19.3 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{35}H_{27}NO_4S$ [M^+] 557.1661, found 557.1660.

*5-Methyl-7-phenyl-12-(phenylsulfonyl)-12H-naphtho[1,2-b]-carbazole (**12b**).* The domino reaction of pivalate **11b** (0.2 g, 0.42 mmol) with 1-methylnaphthalene (0.066 g, 0.46 mmol) using $SnCl_4$ (0.131 g, 0.50 mmol) adopting the procedure as mentioned above followed by work up and column chromatographic purification (Silica gel, EtOAc-hexane 1:9) afforded cabazole **12b** as a colorless solid (0.138 g, 66%); mp 256−258 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 9.76 (s, 1H), 9.02 (d, J = 8.1 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 7.7 Hz, 1H), 7.80−7.67 (m, 2H), 7.60−7.58 (m, 3H), 7.42−7.36 (m, 4H), 7.34 (s, 1H), 7.27 (d, J = 7.8 Hz, 2H), 7.29−7.23 (m, 2H), 7.02 (t, J = 7.5 Hz, 1H), 6.56 (d, J = 7.2 Hz, 1H), 2.59 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 138.4, 137.8, 136.9, 133.8, 131.9, 131.8, 130.6, 130.0, 129.4, 129.2, 129.1, 128.2, 127.9, 127.6, 127.1, 126.7, 126.6, 124.8, 124.5, 124.0, 123.9, 123.8, 122.8, 115.1, 107.5, 20.3 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.8, 130.0, 129.2, 129.1, 128.2, 127.6, 127.1, 126.7, 126.6, 124.8, 124.0, 123.9, 123.8, 122.8, 115.1, 107.5, 20.3 ppm. HRMS (ESI-ion trap, MeOH) m/z Calcd for $C_{33}H_{23}NO_2S + Na^+$ [M + Na]$^+$ 520.1347, found 520.1339.

*5-Methyl-7-(4-nitrophenyl)-12-(phenylsulfonyl)-12H-naphtho-[1,2-b]carbazole (**12c**).* The domino reaction of pivalate **11c** (0.2 g, 0.38 mmol) with 1-methylnaphthalene (0.060 g, 0.42 mmol) using $SnCl_4$ (0.120 g, 0.46 mmol) adopting the above-mentioned procedure followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) gave carbazole **12c** as a pale yellow solid (0.145 g, 70%); mp 296−298 °C. IR (neat) 1520 and 1348 (NO_2), 1370 and 1174 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 9.84 (s, 1H), 9.05 (d, J = 8.1 Hz, 1H), 8.52 (d, J = 8.4 Hz, 2H), 8.43 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.92 (d, J = 7.8 Hz, 2H), 7.83 (t, J = 7.5 Hz, 1H), 7.78 (d, J = 7.2 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.50−7.46 (m, 2H), 7.36−7.31 (m, 2H), 7.16 (s, 1H), 7.09 (t, J = 7.5 Hz, 1H), 6.56 (d, J = 8.1 Hz, 1H), 2.64 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 145.8, 140.0, 137.7, 136.8, 134.0, 132.7, 131.8, 131.5, 130.8, 130.4, 129.5, 129.2, 128.1, 127.4, 127.2, 127.0, 126.6, 125.8, 124.9, 124.4, 124.1, 123.9, 123.8, 122.9, 122.2, 115.3, 108.4, 20.4 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.0, 131.5, 129.2, 128.1, 127.5, 127.0, 126.6, 124.9, 124.5, 124.1, 123.8, 122.9, 122.2, 115.3, 108.4, 20.4 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{33}H_{22}N_2O_4S$ [M^+] 542.1300, found 542.1298.

*7-(4-Chlorophenyl)-5-methyl-12-(phenylsulfonyl)-12H-naphtho-[1,2-b]carbazole (**12d**).* The domino reaction of pivalate **11d** (0.2 g, 0.39 mmol) with 1-methylnaphthalene (0.061 g, 0.43 mmol) using $SnCl_4$ (0.122 g, 0.47 mmol) adopting the above-mentioned procedure followed by work up and column chromatographic purification (Silica gel, EtOAc-hexane 1:9) furnished carbazole **12d** as a colorless solid (0.152 g, 73%); mp 228−230 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 9.78 (s, 1H), 9.02 (d, J = 8.1 Hz, 1H), 8.39 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 7.8 Hz, 2H), 7.81 (t, J = 7.5 Hz, 1H), 7.75−7.70 (m, 1H), 7.60 (d, J = 8.1 Hz, 2H), 7.47−7.42 (m, 2H), 7.34 (d, J = 8.1 Hz, 3H), 7.30−7.28 (m, 2H), 7.09 (t, J = 7.7 Hz, 1), 6.66 (d, J = 8.1 Hz, 1H), 2.63 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 137.8, 136.8, 134.2, 133.9, 132.2, 132.1, 131.9, 131.6, 130.5, 129.5, 129.4, 129.1, 127.8 (2C), 127.2, 126.8, 126.6, 126.3, 124.8, 124.3, 124.0, 123.8, 123.5, 122.6, 115.1, 107.8, 96.1, 20.3 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.9, 131.6, 129.5, 129.1, 127.8, 127.2, 126.8, 126.6, 124.8, 124.0, 123.8, 123.5, 122.6, 115.1, 107.8, 20.3 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{33}H_{22}ClNO_2S$ [M^+] 531.1060, found 531.1057.

*11-(3,4-Dimethoxyphenyl)-8,9-dimethoxy-5-(phenylsulfonyl)-5H-benzo[b]carbazole (**13a**).* The domino reaction of pivalate **11a** (0.2 g, 0.37 mmol) with veratrole (0.057 g, 0.41 mmol) using $SnCl_4$ (0.116 g, 0.45 mmol) in dry DCE (10 mL) at reflux for 12 h followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 3:7) afforded benzo[*b*]carbazole **13a** as a colorless solid (0.119 g, 58%); mp 244−246 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.31 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 7.5 Hz, 2H), 7.48−7.43 (m, 1H), 7.39−7.30 (m, 4H), 7.10−7.01 (m, 2H), 6.94−6.92 (m, 2H), 6.88 (s, 1H), 6.71 (d, J = 7.8 Hz, 1H), 4.09 (s, 3H) 4.04 (s, 3H), 3.82 (s, 3H) 3.78 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 149.6, 149.1, 148.8, 139.6, 138.0, 136.1, 133.7, 132.3, 130.6, 129.0 (2C), 127.3, 126.8, 126.6, 126.1, 123.8, 123.1, 122.7, 122.0, 114.8, 112.7, 111.7, 110.3, 106.6, 104.4, 56.0, 55.9, 55.8 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.7, 129.1, 127.3, 126.6, 123.8, 122.7, 122.0, 114.8, 112.7, 111.7, 110.3, 106.6, 104.4, 56.0, 55.9, 55.8 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{32}H_{27}NO_6S$ [M^+] 553.1559, found 553.1550.

*8,9-Dimethoxy-11-phenyl-5-(phenylsulfonyl)-5H-benzo[b]-carbazole (**13b**).* The domino reaction of pivalate **11b** (0.2 g, 0.42 mmol) with veratrole (0.064 g, 0.46 mmol) using $SnCl_4$ (0.131 g, 0.50 mmol) adopting the above-mentioned procedure followed by usual work up and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) furnished carbazole **13b** as a colorless solid (0.132 g, 64%); mp 276−278 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 7.5 Hz, 2H), 7.52−7.50 (m, 3H), 7.41−7.36 (m, 1H), 7.32−7.22 (m, 6H), 6.92 (t, J = 7.5 Hz, 1H), 6.76 (s, 1H), 6.47 (d, J = 7.8 Hz, 1H), 4.02 (s, 3H), 3.67 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 149.0, 139.6, 138.3, 137.9, 136.1, 133.7, 132.5, 129.8, 129.2, 129.0 (2C), 128.2, 127.2, 126.8, 126.6, 125.8, 123.7, 122.9, 122.5, 114.9, 110.4, 106.6, 104.4, 56.0, 55.6 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 132.7, 128.8, 128.2, 128.0, 127.2, 126.2, 125.6, 122.7, 121.5, 113.8, 109.4, 105.6, 103.4, 55.0, 54.6 ppm. HRMS

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(EI, 70 eV) m/z Calcd for $C_{30}H_{23}NO_4S$ $[M^+]$ 493.1348, found 493.1345.

*8,9-Dimethoxy-11-(4-nitrophenyl)-5-(phenylsulfonyl)-5H-benzo[b]carbazole (**13c**).* The domino reaction of pivalate **11c** (0.2 g, 0.38 mmol) with veratrole (0.058 g, 0.42 mmol) using $SnCl_4$ (0.120 g, 0.46 mmol) in dry DCE (10 mL) at reflux for 9 h followed by usual workup and column chromatographic purification (Silica gel, EtOAc-hexane 3:7) gave benzo[*b*]carbazole **13c** as a pale yellow solid (0.149 g, 72%); mp 290−292 °C. IR (neat) 1518 and 1348 (NO_2), 1366 and 1166 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.50 (d, J = 7.5 Hz, 2H), 8.35 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 7.5 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2H), 7.52−7.34 (m, 5H), 7.05 (t, J = 7.7 Hz, 1H), 6.65 (s, 1H), 6.52 (d, J = 8.1 Hz, 1H), 4.12 (s, 3H) 3.76 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1, 149.6, 148.0, 145.7, 139.7, 137.7, 136.0, 133.9, 131.3, 129.4, 129.1, 127.8, 126.6, 126.0, 125.0, 124.5, 123.9, 122.5, 122.0, 115.2, 111.4, 106.8, 103.4, 56.1, 55.7 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.9, 131.3, 129.1, 127.8, 126.6, 124.5, 123.9, 122.0, 115.1, 111.4, 106.8, 103.4, 56.1, 55.7 ppm. HRMS (ESI-TOF, MeOH) m/z Calcd for $C_{30}H_{22}N_2O_6S + H^+$ $[M + H]^+$ 539.1277, found 539.1255.

*11-(4-Chlorophenyl)-8,9-dimethoxy-5-(phenylsulfonyl)-5H-benzo[b]carbazole (**13d**).* The domino reaction of pivalate **11d** (0.2 g, 0.39 mmol) with veratrole (0.060 g, 0.43 mmol) using $SnCl_4$ (0.122 g, 0.47 mmol) adopting the above-mentioned procedure followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) gave carbazole **13d** as a colorless solid (0.145 g, 70%); mp 262−264 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.31 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 7.8 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.49−7.37 (m, 3H), 7.34−7.30 (m, 4H), 7.04 (t, J = 7.7 Hz, 1H), 6.76 (s, 1H), 6.62 (d, J = 7.8 Hz, 1H), 4.09 (s, 3H) 3.76 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 149.2, 139.7, 137.8, 136.8, 136.0, 134.2, 133.8, 131.4, 130.9, 129.6, 129.1, 129.0, 127.5, 126.6, 126.5, 125.7, 123.8, 122.8, 122.3, 115.0, 110.7, 106.7, 104.0, 56.0, 55.7 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.8, 131.4, 129.6, 129.1, 127.5, 126.6, 123.8, 122.3, 115.0, 110.7, 106.7, 103.9, 56.0, 55.7 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{30}H_{22}ClNO_4S$ $[M^+]$ 527.0958, found 527.0954.

General Procedure for the Synthesis of 4-Aryl Heteroannulated Carbazoles 14a−d to 16a−d. A solution of pivalates **11a−d** (1 equiv), $SnCl_4$ (1.2 equiv) and heteroarenes (1.1 equiv) in dry DCE (10 mL) was stirred at room temperature under nitrogen atmosphere. After the completion of the reaction (TLC), it was then poured into ice water (30 mL) containing Conc. HCl (3 mL). The organic layer was separated and the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic extract was washed with water (2 × 20 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (Silica gel, EtOAc-hexane) led to benzocarbazoles **14a−d** to **16a−d**.

*4-(3,4-Dimethoxyphenyl)-2-methyl-9-(phenylsulfonyl)-9H-thieno[2,3-b]carbazole (**14a**).* The domino reaction of pivalate **11a** (0.2 g, 0.37 mmol) with 2-methylthiophene (0.116 g, 0.45 mmol) using $SnCl_4$ (0.116 g, 0.45 mmol) in dry DCE (10 mL) at for 3 h adopting the above-mentioned procedure followed by work up and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) afforded thienocarbazole **14a** as a colorless solid (0.130 g, 68%); mp 212−214 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.32 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 7.8 Hz, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.40−7.30 (m, 3H), 7.07−7.03 (m, 2H), 6.96−6.92 (m, 3H), 6.73 (s, 1H), 4.01 (s, 3H), 3.82 (s, 3H), 2.54 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3, 148.8, 140.5, 139.2, 139.1, 137.9, 137.6, 135.9, 133.8, 130.9, 130.3, 129.1, 127.0, 126.7, 126.6, 123.6, 122.3 (2C), 121.7, 120.5, 114.9, 112.5, 111.5, 107.2, 56.0 (2C), 16.4 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.8, 129.1, 127.0, 126.6, 123.7, 122.3, 121.6, 120.5, 114.9, 112.5, 111.5, 107.2, 56.0 (2C), 16.4 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{29}H_{23}NO_4S_2$ $[M^+]$ 513.1068, found 513.1065.

*2-Methyl-4-phenyl-9-(phenylsulfonyl)-9H-thieno[2,3-b]carbazole (**14b**).* The domino reaction of pivalate **11b** (0.2 g, 0.42 mmol) with 2-methylthiophene (0.045 g, 0.46 mmol) using $SnCl_4$ (0.131 g, 0.50 mmol) adopting the above-mentioned procedure followed by usual work and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) gave heteroannulated carbazole **14b** as a colorless solid (0.145 g, 76%); mp 222−224 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.31 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.5 Hz, 2H), 7.55−7.53 (m, 3H), 7.49−7.30 (m, 6H), 7.01 (t, J = 7.5 Hz, 1H), 6.81 (d, J = 7.8 Hz, 1H), 6.67 (s, 1H), 2.53 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6, 139.2, 139.1, 138.5, 137.8, 137.3, 136.0, 133.8, 130.4, 129.5, 129.1, 128.9, 128.1, 126.9, 126.7, 126.6, 123.6, 122.1, 120.4, 115.0, 107.3, 16.3 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.8, 129.5, 129.1, 128.9, 128.1, 126.9, 126.6, 123.6, 122.1, 120.4, 115.0, 107.3, 16.3 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{27}H_{19}NO_2S_2$ $[M^+]$ 453.0857, found 453.0850.

*2-Methyl-4-(4-nitrophenyl)-9-(phenylsulfonyl)-9H-thieno[2,3-b]-carbazole (**14c**).* The domino reaction of pivalate **11c** (0.2 g, 0.38 mmol) with 2-methylthiophene (0.041 g, 0.42 mmol) using $SnCl_4$ (0.120 g, 0.46 mmol) adopting the above-mentioned procedure followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) furnished carbazole **14c** as a yellow solid (0.154 g, 81%); mp 258−260 °C. IR (neat) 1520 and 1346 (NO_2), 1376 and 1172 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.43 (d, J = 8.4 Hz, 2H), 8.35 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 7.8 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2H), 7.51−7.42 (m, 2H), 7.39−7.32 (m, 2H), 7.05 (t, J = 7.7 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 6.59 (s, 1H), 2.55 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.8, 145.5, 141.9, 139.5, 139.2, 137.7, 136.6, 135.9, 133.9, 130.9, 129.2, 127.5, 126.6, 125.8, 124.2, 123.8, 121.7, 119.5, 115.2, 108.3, 16.4 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.0, 130.9, 129.2, 127.5, 126.6, 124.3, 123.8, 121.7, 119.5, 115.2, 108.3, 16.4 ppm. HRMS (ESI-ion trap, MeOH) m/z Calcd for $C_{27}H_{18}N_2O_4S_2 + Na^+$ $[M + Na]^+$ 521.0606, found 521.0617.

*4-(4-Chlorophenyl)-2-methyl-9-(phenylsulfonyl)-9H-thieno[2,3-b]carbazole (**14d**).* The domino reaction of pivalate **11d** (0.2 g, 0.39 mmol) with 2-methylthiophene (0.042 g, 0.43 mmol) using $SnCl_4$ (0.122 g, 0.47 mmol) adopting the above-mentioned procedure followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) gave annulated carbazole **14d** as a colorless solid (0.159 g, 83%); mp 200−202 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 7.5 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.33−7.22 (m, 2H), 7.26−7.17 (m, 2H), 6.95 (t, J = 7.5 Hz, 1H), 6.78 (d, J = 8.1 Hz, 1H), 6.55 (s, 1H), 2.42 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.1, 139.3, 139.1, 137.7, 137.2, 136.9, 135.9, 134.2, 133.9, 131.0, 129.3, 129.1, 128.9, 127.2, 126.6, 126.4, 123.7, 122.1, 122.0, 120.1, 115.1, 107.7, 16.4 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.9, 131.0, 129.3, 129.1, 127.2, 126.6, 123.7, 122.0, 120.1, 115.1, 107.7, 16.4 ppm. HRMS (ESI-TOF, DCM) m/z Calcd for $C_{27}H_{18}ClNO_2S_2 + H^+$ $[M + H]^+$ 488.0546, found 488.0524.

*2-(3,5-Di(thiophen-2-yl)phenyl)-4-(3,4-dimethoxyphenyl)-9-(phenylsulfonyl)-9H-thieno[2,3-b]carbazole (**15a**).* The domino reaction of pivalate **11a** (0.2 g, 0.37 mmol) with 1,3,5-tri(thiophen-2-yl)benzene (0.133 g, 0.41 mmol) using $SnCl_4$ (0.116 g, 0.45 mmol) in dry DCE (10 mL) at room temperature for 6 h followed by usual workup and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) afforded heterocycle **15a** as a pale yellow solid (0.179 g, 65%); mp 140−142 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.35 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 7.8 Hz, 2H), 7.76 (s, 3H), 7.52−7.49 (m, 1H), 7.42−7.39 (m, 4H), 7.37−7.34 (m, 4H), 7.15−7.12 (m, 4H), 7.09−7.02 (m, 1H), 6.99−6.95 (m, 2H), 4.05 (s, 3H), 3.86 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 149.0, 143.3, 142.8, 139.2, 139.1, 137.8, 136.7, 135.8, 135.6, 133.9, 131.6, 130.5, 129.2, 128.2, 127.3, 126.7, 126.4, 125.6, 124.1, 123.8, 123.7, 123.2, 123.0, 122.5, 121.8, 119.2, 114.9, 112.5, 111.7, 107.3, 56.1, 56.0 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.9, 129.2, 128.2, 127.3, 126.7, 125.6, 124.1, 123.8, 123.6, 123.2, 122.5, 121.7, 119.2, 114.9, 112.5, 111.6, 107.3, 56.1, 56.0 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{42}H_{29}NO_4S_4$ $[M^+]$ 739.0979, found 739.0978.

*2-(3,5-Di(thiophen-2-yl)phenyl)-4-phenyl-9-(phenylsulfonyl)-9H-thieno[2,3-b]carbazole (**15b**).* The domino reaction of pivalate **11b** (0.2 g, 0.42 mmol) with 1,3,5-tri(thiophen-2-yl)benzene (0.15 g, 0.46 mmol) using $SnCl_4$ (0.131 g, 0.50 mmol) in dry DCE (10 mL) at room temperature for 6 h followed by work up and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) furnished annulated carbazole **15b** as a colorless solid (0.194 g, 68%); mp 174−

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176 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.27 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 7.5 Hz, 2H), 7.68−7.67 (m, 3H), 7.53−7.52 (m, 3H), 7.42−7.39 (m, 3H), 7.34−7.31 (m, 4H), 7.28 (d, J = 8.4 Hz, 3H), 7.23 (s, 1H), 7.07−7.04 (m, 2H), 6.97 (t, J = 7.5 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 142.9, 139.2, 139.1, 138.0, 137.8, 137.5, 136.7, 135.8, 135.6, 133.9, 131.8, 129.5, 129.2, 129.1, 128.4, 128.1, 127.2, 126.6, 126.4, 125.6, 124.1, 123.7, 123.3, 122.8, 122.3, 119.1, 115.0, 107.5 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 132.9, 128.5, 128.1 (2C), 127.4, 127.1, 126.2, 125.6, 124.5, 123.1, 122.7 (2C), 122.2, 121.3, 118.1, 113.9, 106.4 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{40}H_{25}NO_2S_4$ [M^+] 679.0768, found 679.0765.

*2-(3,5-Di(thiophen-2-yl)phenyl)-4-(4-nitrophenyl)-9-(phenylsulfonyl)-9H-thieno[2,3-b]carbazole (**15c**).* The annulation of pivalate **11c** (0.2 g, 0.38 mmol) with 1,3,5-tri(thiophen-2-yl)benzene (0.137 g, 0.42 mmol) using $SnCl_4$ (0.120 g, 0.46 mmol) adopting the procedure as mentioned above followed by usual workup and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) gave carbazole **15c** as a yellow solid (0.200 g, 72%); mp 180−182 °C. IR (neat) 1520 and 1346 (NO_2), 1372 and 1174 (SO_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.45 (d, J = 7.8 Hz, 2H), 8.27 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 7.5 Hz, 2H), 7.68−7.62 (m, 4H), 7.42−7.36 (m, 3H), 7.32−7.30 (m, 3H), 7.27−7.25 (m, 2H), 7.16 (s, 1H), 7.11 (s, 1H), 7.05−6.97 (m, 3H), 6.70 (d, J = 7.5 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1, 145.1, 144.1, 143.1, 139.32, 137.7, 136.7, 136.6, 135.9, 135.2, 134.1, 130.9, 129.3, 128.7, 128.2, 127.8, 126.6, 125.7, 125.6, 124.5, 124.1, 124.0, 123.9, 123.2, 122.4, 121.8, 117.9, 115.3, 108.4 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.1, 130.9, 129.3, 128.2, 127.8, 126.6, 125.7, 124.5, 124.2, 124.0, 123.9, 123.1, 121.9, 117.9, 115.2, 108.4 ppm. HRMS (ESI-ion trap, MeOH) m/z Calcd for $C_{40}H_{24}N_2O_4S_4 + Na^+$ [M + Na]$^+$ 747.0517, found 747.0517.

*4-(4-Chlorophenyl)-2-(3,5-di(thiophen-2-yl)phenyl)-9-(phenylsulfonyl)-9H-thieno[2,3-b]carbazole (**15d**).* The reaction of pivalate **11d** (0.2 g, 0.39 mmol) with 1,3,5-tri(thiophen-2-yl)benzene (0.140 g, 0.43 mmol) using $SnCl_4$ (0.122 g, 0.47 mmol) adopting the above-mentioned procedure followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) afforded thienocarbazole **15d** as a yellow solid (0.218 g, 78%); mp 120−124 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.27 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 7.8 Hz, 2H), 7.68−7.66 (m, 3H), 7.51 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 6.9 Hz, 1H), 7.37−7.31 (m, 6H), 7.28−7.26 (m, 3H), 7.18 (s, 1H), 7.06−7.03 (m, 2H), 7.00 (d, J = 7.5 Hz, 1H), 6.80 (d, J = 7.8 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 139.2, 139.2, 137.7, 137.4, 136.7, 136.5, 135.9, 135.4, 134.5, 134.0, 131.0, 130.2, 129.5, 129.2, 128.2, 127.5, 126.6, 126.1, 125.6, 124.1, 123.8, 123.8, 123.2, 122.7, 122.2, 118.6, 115.1, 107.8 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.0, 131.0, 129.5, 129.2, 128.2, 127.5, 126.6, 125.6, 124.1, 123.8, 123.8, 123.2, 122.2, 118.6, 115.1, 107.8 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{40}H_{24}ClNO_2S_4$ [M^+] 713.0378, found 713.0375.

*12-(3,4-Dimethoxyphenyl)-7-(phenylsulfonyl)-7H-benzofuro[2,3-b]carbazole (**16a**).* The annulation of pivalate **11a** (0.2 g, 0.37 mmol) with benzofuran (0.048 g, 0.41 mmol) using $SnCl_4$ (0.116 g, 0.45 mmol) adopting the above-mentioned procedure followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) furnished benzofurocarbazole **16a** as a colorless solid (0.143 g, 72%); mp 202−204 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.36 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 7.5 Hz, 2H), 7.58 (d, J = 8.4 Hz, 1H), 7.51−7.47 (m, 1H), 7.42−7.34 (m, 4H), 7.15−7.07 (m, 4H), 7.04−6.98 (m, 3H), 4.07 (s, 3H), 3.82 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 155.6, 149.7, 149.1, 139.0, 137.9 (2C), 133.9, 130.8, 129.7, 129.1, 126.8, 126.6, 126.5, 126.4, 124.0, 123.8, 122.6, 121.9, 121.1, 120.9, 120.6, 114.8, 111.9, 111.8, 111.4, 97.6, 56.0 (2C) ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.9, 129.2, 126.8, 126.7, 126.6, 123.8, 122.7, 122.0, 121.1, 114.8, 111.9, 111.8, 111.4, 97.7, 56.1, 56.0 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{32}H_{23}NO_5S$ [M^+] 533.1297, found 533.1290.

*12-Phenyl-7-(phenylsulfonyl)-7H-benzofuro[2,3-b]carbazole (**16b**).* The reaction of pivalate **11b** (0.2 g, 0.42 mmol) with benzofuran (0.054 g, 0.46 mmol) using $SnCl_4$ (0.131 g, 0.50 mmol) adopting the above-mentioned procedure followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) afforded annulated carbazole **16b** as a colorless solid (0.155 g, 78%); mp 218−220 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.36 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 7.5 Hz, 3H), 7.56 (d, J = 7.5 Hz, 3H), 7.50−7.45 (m, 3H), 7.37−7.32 (m, 4H), 7.06−7.02 (m, 2H), 6.85 (t, J = 7.05 Hz, 7H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 155.6, 139.1, 138.0, 137.8, 137.4, 134.0, 131.0, 129.5, 129.2, 129.0, 128.7, 126.8, 126.6 (2C), 126.4, 124.0, 123.8, 122.7, 121.9, 120.7, 120.4, 114.9, 111.4, 97.8 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.0, 129.5, 129.2, 128.9, 128.7, 126.8, 126.6 (2C), 123.8, 122.7, 121.9, 114.9, 111.4, 97.8 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{30}H_{19}NO_3S$ [M^+] 473.1086, found 473.1070.

*12-(4-Nitrophenyl)-7-(phenylsulfonyl)-7H-benzofuro[2,3-b]carbazole (**16c**).* The domino reaction of pivalate **11c** (0.2 g, 0.38 mmol) with benzofuran (0.050 g, 0.42 mmol) using $SnCl_4$ (0.120 g, 0.46 mmol) adopting the above-mentioned procedure followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) gave annulated carbazole **16c** as a colorless solid (0.159 g, 80%); mp >300 °C. IR (neat) 1520 and 1344 (NO_2), 1372 and 1186 (SO_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.53 (d, J = 8.1 Hz, 2H), 8.39 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 7.8 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 8.1 Hz, 1H), 7.51−7.48 (m, 1H), 7.45−7.35 (m, 4H), 7.09 (t, J = 7.35 Hz, 2H), 6.77 (t, J = 8.25 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 155.5, 148.3, 144.5, 139.1, 138.0, 137.7, 134.1, 130.5, 129.2, 127.9, 127.3, 127.0, 126.6, 125.6, 124.7, 123.9, 123.2, 122.9, 121.3, 120.1, 119.9, 115.1, 111.7, 98.7 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.1, 130.6, 129.3, 127.4, 127.1, 126.6, 124.8, 124.0, 122.9, 121.3, 115.1, 111.8, 98.7 ppm. HRMS (ESI-ion trap, MeOH) m/z Calcd for $C_{30}H_{18}N_2O_5S + Na^+$ [M + Na]$^+$ 541.0834, found 541.0845.

*12-(4-Chlorophenyl)-7-(phenylsulfonyl)-7H-benzofuro[2,3-b]carbazole (**16d**).* The reaction of pivalate **11d** (0.2 g, 0.39 mmol) with benzofuran (0.051 g, 0.43 mmol) using $SnCl_4$ (0.122 g, 0.47 mmol) adopting the above-mentioned procedure followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) furnished annulated carbazole **16d** as a colorless solid (0.171 g, 86%); mp 178−180 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.27 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 7.8 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.1 Hz, 1H), 7.40−7.34 (m, 3H), 7.30−7.22 (m, 4H), 6.99 (t, J = 7.7 Hz, 2H), 6.81−6.77 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 155.6, 139.1, 138.0, 137.7, 135.9, 134.8, 134.0, 130.6, 129.8, 129.4, 129.2, 127.0, 126.8, 126.6, 126.1, 123.9, 123.7, 122.8, 121.7 (2C), 120.6, 120.4, 115.0, 111.6, 98.1 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.1, 130.6, 129.8, 129.2, 127.0, 126.8, 126.6, 123.9, 122.8, 121.7 (2C), 115.0, 111.6, 98.1 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{30}H_{18}ClNO_3S$ [M^+] 507.0696, found 507.0693.

(2-Methyl-1-(phenylsulfonyl)-1H-indol-3-yl)(thiophen-2-yl)-methanone. To a solution of thiophene-2-carbonyl chloride (1.63 g, 11.07 mmol) and $SnCl_4$ (2.88 g, 11.07 mmol) in dry DCM (20 mL), 2-methylindole[29] (2 g, 7.38 mmol) in dry DCM (10 mL) was added (5 min) slowly at 0 °C. Then, it was stirred at room temperature for 30 min. After completion of the reaction (monitored by TLC), it was poured into ice−water (50 mL) containing Conc. HCl (10 mL). The organic layer was separated and the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layer was washed with water (3 × 25 mL) and dried (Na_2SO_4). Evaporation of the solvent followed by trituration of crude product with MeOH (5 mL) gave (2-methyl-1-(phenylsulfonyl)-1*H*-indol-3-yl) (thiophen-2-yl)methanone as a colorless solid (2.19 g, 78%); mp 106−108 °C. IR (neat) 1694 (CO), 1374 and 1192 (SO_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 7.5 Hz, 2H), 7.72 (d, J = 7.5 Hz, 1H), 7.60−7.46 (m, 5H), 7.34 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 8.1 Hz, 1H), 7.10−7.09 (m, 1H), 2.68 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 145.1, 139.6, 138.9, 135.9, 134.9, 134.3, 129.6, 128.2, 127.9, 126.5, 125.0, 124.1, 120.8, 120.4, 114.4, 14.6 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.9, 134.3, 129.6, 128.2, 126.6, 125.0, 124.1, 120.4, 114.4, 14.6 ppm.

(2-(Bromomethyl)-1-(phenylsulfonyl)-1H-indol-3-yl)(thiophen-2-yl)methanone. To a warmed solution of indole **17a** (1.5 g, 3.93

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mmol) and AIBN (0.05 g) in dry CCl_4 (30 mL), freshly crystallized NBS (0.84 g, 4.72 mmol) was added and refluxed for 3 h. After the consumption of NBS, the reaction was cooled to room temperature. The floated succinimide was filtered off and washed with CCl_4 (10 mL). The combined filtrate was concentrated in vacuo to afford (2-(bromomethyl)-1-(phenylsulfonyl)-1*H*-indol-3-yl) (thiophen-2-yl)-methanone as a colorless solid (1.56 g, 86%); mp 114−116 °C. IR (neat) 1630 (CO), 1380 and 1184 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 7.5 Hz, 2H), 7.77 (d, J = 7.5 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.50−7.47 (m, 3H), 7.44−7.36 (m, 2H), 7.24 (d, J = 8.4 Hz, 1H), 7.10 (t, J = 7.2 Hz, 1H), 5.18 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.5, 144.5, 138.3, 138.1, 136.1, 135.6, 134.5, 129.5, 128.3, 127.3, 127.1, 126.5, 124.4, 123.4, 121.4, 114.8, 21.5 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 135.6, 134.6, 129.5, 128.3, 127.1, 126.5, 124.4, 121.4, 114.8, 21.5 ppm.

*(1-(Phenylsulfonyl)-3-(thiophene-2-carbonyl)-1H-indol-2-yl)-methyl pivalate (**17**).* A mixture of (2-(bromomethyl)-1-(phenylsulfonyl)-1*H*-indol-3-yl) (thiophen-2-yl)methanone (1.5 g, 3.26 mmol), potassium carbonate (1.35 g, 9.78 mmol) and pivalic acid (0.67 g, 6.52 mmol) in dry THF (120 mL) was stirred at room temperature under nitrogen atmosphere for 12 h. After completion of the reaction (TLC), the solvent was removed under reduced pressure. Then, the residue was diluted with DCM (50 mL) and washed with water (3 × 20 mL) and dried (Na_2SO_4). Removal of solvent followed by trituration of the crude product with MeOH (5 mL) furnished pivalate **17** as a colorless solid (1.29 g, 82%); mp 126−128 °C. IR (neat) 1730 (ester), 1634 (CO), 1380 and 1181 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 7.8 Hz, 1H), 7.55−7.48 (m, 3H), 7.43−7.32 (m, 3H), 7.22 (d, J = 7.2 Hz, 1H), 7.03−7.00 (m, 1H), 5.35 (s, 2H), 1.11 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.5, 177.4, 144.9, 138.6, 136.2, 135.7, 135.4, 135.0, 134.4, 129.6, 128.2, 127.5, 126.6, 126.4, 124.5, 121.2, 114.7, 57.0, 38.8, 27.1 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 137.8, 135.4, 134.4, 129.6, 128.2, 126.6, 126.4, 124.5 121.2, 114.7, 57.0, 27.1 ppm. Elemental Analysis Calcd for $C_{25}H_{23}NO_5S_2$: C, 62.35; H, 4.81; N, 2.91; S, 13.32. Found: C, 62.14; H, 4.68; N, 2.78; S, 13.19.

*5-Methyl-12-(phenylsulfonyl)-7-(thiophen-2-yl)-12H-naphtho-[1,2-b]carbazole (**18a**).* A solution of pivalate **17** (0.2 g, 0.41 mmol), 1-methylnaphthalene (0.065 g, 0.46 mmol) and $SnCl_4$ (0.129 g, 0.50 mmol) in dry DCE (10 mL) was refluxed under nitrogen atmosphere for 12 h. After the completion of the reaction, it was then poured into ice water, the organic layer was separated and the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic extract was washed with water (2 × 20 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (Silica gel, EtOAc-hexane 1:9) furnished naphthocarbazole **18a** as a colorless solid (0.123 g, 59%); mp 228−230 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 9.81 (s, 1H), 9.03 (d, J = 8.4 Hz, 1H), 8.40 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.91 (d, J = 7.8 Hz, 2H), 7.84−7.80 (m, 1H), 7.77−7.72 (m, 1H), 7.67 (d, J = 7.7 Hz, 1H), 7.54 (s, 1H), 7.51−7.43 (m, 2H), 7.38−7.32 (m, 3H), 7.18−7.13 (m, 2H), 6.73 (d, J = 8.1 Hz, 1H), 2.99 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 138.5, 137.7, 136.6, 133.9, 132.4, 131.9, 130.4, 129.6, 129.1, 128.2, 127.9, 127.9, 127.2, 127.1, 126.7, 126.6, 126.3, 125.4, 124.8, 124.1, 123.7, 123.6, 122.8, 122.6, 115.0, 108.6, 20.4 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.9, 129.1, 128.2, 128.0, 127.9, 127.2, 127.1, 126.7, 126.6, 124.8, 124.1, 123.7, 123.6, 122.8, 115.0, 108.6, 20.4 ppm. HRMS (ESI-TOF, MeOH) m/z Calcd for $C_{31}H_{21}NO_2S_2 + H^+$ $[M + H]^+$ 504.1092, found 504.1082.

*8,9-Dimethoxy-5-(phenylsulfonyl)-11-(thiophen-2-yl)-5H-benzo-[b]carbazole (**18b**).* The domino reaction of pivalate **17** (0.2 g, 0.41 mmol) with veratrole (0.063 g, 0.46 mmol) using $SnCl_4$ (0.129 g, 0.50 mmol) in dry DCE (10 mL) at reflux for 9 h followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 2:8) gave benzocarbazole **18b** as a colorless solid (0.118 g, 57%); mp >300 °C. ^1H NMR (300 MHz, DMSO-d_6) δ 8.77 (s, 1H), 8.27 (d, J = 8.1 Hz, 1H), 7.96−7.94 (m, 3H), 7.75 (s, 1H), 7.65 (t, J = 7.2 Hz, 1H), 7.54−7.49 (m, 3H), 7.42−7.39 (m, 1H), 7.23−7.18 (m, 2H), 6.91 (s, 1H), 6.60 (d, J = 7.8 Hz, 1H), 3.99 (s, 3H), 3.67 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 149.4, 139.7, 138.4, 137.9, 135.9, 133.7, 129.1, 128.8, 128.0, 127.8, 127.6, 127.5, 127.1, 126.6, 126.5, 124.8, 124.1, 124.0, 122.6, 114.8, 111.6, 106.6, 104.2, 56.0, 55.7 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 132.8, 128.1, 127.0, 126.9, 126.6, 126.1, 125.6, 123.0, 121.6, 113.8, 110.6, 105.6, 103.2, 55.0, 54.7 ppm. HRMS (ESI-TOF, MeOH) m/z Calcd for $C_{28}H_{21}NO_4S_2 + H^+$ $[M + H]^+$ 500.0990, found 500.0976.

*2-Methyl-9-(phenylsulfonyl)-4-(thiophen-2-yl)-9H-thieno[2,3-b]-carbazole (**18c**).* The annulation of pivalate **17** (0.2 g, 0.41 mmol) with 2-methylthiophene (0.045 g, 0.46 mmol) using $SnCl_4$ (0.129 g, 0.50 mmol) in dry DCE (10 mL) at room temperature for 4 h followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 1:9) afforded thienocarbazole **18c** as a colorless solid (0.128 g, 67%); mp 238−240 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.24 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 7.8 Hz, 2H), 7.48 (d, J = 7.8 Hz, 1H), 7.40−7.30 (m, 2H), 7.26−7.17 (m, 3H), 7.04−6.90 (m, 2H), 6.85 (d, J = 7.8 Hz, 1H), 6.74 (s, 1H), 2.48 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 139.2, 139.0, 138.9, 138.6, 137.8, 135.7, 133.8, 129.1, 127.6, 127.3, 126.6 (2C), 126.3, 123.9, 123.8, 122.2, 120.4, 114.9, 108.4, 16.4 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 133.8, 129.1, 127.6 (2C), 127.3, 126.7, 126.6, 123.8, 122.2, 120.4, 114.9, 108.4, 16.4 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{25}H_{17}NO_2S_3$ $[M^+]$ 459.0421, found 459.0420.

*2-(3,5-Di(thiophen-2-yl)phenyl)-9-(phenylsulfonyl)-4-(thiophen-2-yl)-9H-thieno[2,3-b]carbazole (**18d**).* To a solution of pivalate **17** (0.2 g, 0.41 mmol) and 1,3,5-tri(thiophen-2-yl)benzene (0.148 g, 0.46 mmol) in dry DCE (10 mL), $SnCl_4$ (0.129 g, 0.50 mmol) was added and stirred at room temperature for 6 h. The usual workup followed by column chromatographic purification (Silica gel, EtOAc-hexane 1:9) gave annulated carbazole **18d** as a colorless solid (0.182 g, 64%); mp 188−190 °C. ^1H NMR (300 MHz, DMSO-d_6) δ 9.02 (s, 1H), 8.33 (d, J = 7.5 Hz, 1H), 8.04 (d, J = 7.5 Hz, 2H), 7.94 (d, J = 7.8 Hz, 1H), 7.86 (s, 1H), 7.80 (s, 2H), 7.72−7.71 (m, 2H), 7.68−7.61 (m, 4H), 7.58−7.55 (m, 3H), 7.42−7.40 (m, 1H), 7.35 (s, 1H), 7.23−7.19 (m, 3H), 6.83 (d, J = 8.1 Hz, 1H), ppm. ^{13}C NMR (75 MHz, DMSO-d_6) δ 142.9, 141.8, 138.4, 138.3, 136.7, 136.4, 135.5, 134.9 (2C), 129.8, 128.6, 128.3, 128.2, 128.1, 126.5, 126.5, 125.2 125.0, 124.1, 123.5, 123.4, 122.5, 122.1 121.8, 118.9, 114.5, 108.3 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 135.0, 129.8, 128.6, 128.3, 128.2, 128.1, 126.6, 126.5, 125.2, 124.1, 122.5, 122.1, 121.8, 118.9, 114.5, 108.3 ppm. HRMS (ESI-ion trap, MeOH) m/z Calcd for $C_{38}H_{23}NO_2S_5 + Na^+$ $[M + Na]^+$ 708.0230, found 708.0234.

*7-(Phenylsulfonyl)-12-(thiophen-2-yl)-7H-benzofuro[2,3-b]-carbazole (**18e**).* The domino reaction of pivalate **17** (0.2 g, 0.41 mmol) with benzofuran (0.054 g, 0.46 mmol) using $SnCl_4$ (0.129 g, 0.50 mmol) in dry DCE (10 mL) at room temperature for 3 h followed by workup and column chromatographic purification (Silica gel, EtOAc-hexane 1:9) afforded annulated benzocarbazole **18e** as a colorless solid (0.137 g, 69%); mp 188−190 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.27 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 7.5 Hz, 2H), 7.57 (d, J = 7.5 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.37−7.22 (m, 6H), 7.15−7.12 (m, 1H), 7.03 (t, J = 7.35 Hz, 2H), 6.92−6.87 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 155.3, 139.1, 137.8, 137.4, 134.0, 129.2, 128.1, 127.2 (2C), 126.9, 126.6, 126.1, 124.0, 123.7, 122.9, 122.8, 122.5, 122.3, 122.0, 121.9, 114.9, 111.5, 98.9 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.0, 129.2, 128.2, 127.3, 127.2, 126.9, 126.6, 124.0, 122.9, 122.0, 121.9, 114.9, 111.5, 98.9 ppm. HRMS (ESI-ion trap, MeOH) m/z Calcd for $C_{28}H_{17}NO_3S_2 + Na^+$ $[M + Na]^+$ 502.0548, found 502.0539.

(2,5-Dimethyl-1-(phenylsulfonyl)-1H-pyrrole-3,4-diyl)bis-(phenylmethanone). To a stirred solution of pyrrole dialdehyde[31] (1 g, 3.44 mmol) in dry THF (10 mL) at 0 °C, freshly prepared phenylmagnesium bromide (1.87 g, 10.30 mmol) in dry THF (20 mL) was added and it was allowed to stir at the same temperature for 30 min. After completion of the reaction (TLC), it was poured into ice water (30 mL) containing NH_4Cl (5 g). Then, it was extracted with DCM (2 × 30 mL) and dried (Na_2SO_4). The evaporation of the solvent followed by the trituration of the residue with 10% ethyl acetate in hexane (30 mL) afforded diol. To a suspension of crude diol (1.22 g, 2.71 mmol) in DCM (20 mL), MnO_2 (2.36 g, 27.14 mmol)

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was added and stirred at room temperature for 8 h. After completion of the reaction (TLC), it was passed through Celite bed. The subsequent evaporation of solvent followed by column chromatic purification (Silica gel, EtOAc-hexane 1:9) furnished dibenzoyl pyrrole as a brown solid (1.04 g, 68%); mp 138−140 °C. IR (neat) 1654 (CO), 1376 and 1188 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J = 7.8 Hz, 2H), 7.65 (t, J = 7.35 Hz, 1H), 7.57−7.52 (m, 2H), 7.29 (t, J = 7.2 Hz, 2H), 7.20 (d, J = 7.2 Hz, 4H), 7.12−7.07 (m, 4H), 2.50 (s, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.4, 139.1, 138.9, 135.4, 134.6, 132.6, 129.9, 128.7, 128.2, 126.9, 124.6, 13.7 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.7, 132.6, 129.9, 128.7, 128.2, 126.9, 13.7 ppm.

(2,5-Bis(bromomethyl)-1-(phenylsulfonyl)-1H-pyrrole-3,4-diyl)bis-(phenylmethanone). To a solution of 2,5-dimethyl-3,4-dibenzoylpyrrole **19a** (1 g, 2.25 mmol) in dry CCl_4 (20 mL), finely powdered NBS (0.96 g, 5.40 mmol) and AIBN (0.05 g) were added and refluxed for 2 h. After the consumption of the NBS, it was cooled to room temperature and floated succinimide was filtered off and washed with CCl_4 (10 mL). The combined filtrate was concentrated in vacuo to afford (2,5-bis(bromomethyl)-1-(phenylsulfonyl)-1*H*-pyrrole-3,4-diyl)bis(phenylmethanone) as a brown solid (1.177 g, 87%); mp 156−158 °C. IR (neat) 1660 (CO), 1382 and 1190 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J = 7.8 Hz, 2H), 7.70 (t, J = 7.35 Hz, 1H), 7.62−7.57 (m, 2H), 7.35−7.30 (m, 2H), 7.11−7.09 (m, 8H), 5.02 (s, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.3, 138.1, 135.9, 135.4, 133.1, 130.1, 128.5, 128.4, 128.0, 127.3, 20.7 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 135.5, 133.1, 130.1, 128.5, 128.4, 128.0, 20.7 ppm.

*(3,4-Dibenzoyl-1-(phenylsulfonyl)-1H-pyrrole-2,5-diyl)bis-(methylene)bis(2,2-dimethylpropanoate) (**19**).* To a solution of 2,5-bis(bromomethyl)-1-(phenylsulfonyl)-1*H*-pyrrole-3,4-diyl)bis-(phenylmethanone) (1 g, 1.66 mmol) in dry THF (20 mL), potassium carbonate (1.38 g, 9.98 mmol) and pivalic acid (0.679 g, 6.66 mmol) were added. The reaction mixture was allowed to stir at room temperature for 5 h. After completion of the reaction (TLC), the solvent was removed under reduced pressure. Then, the residue was diluted with DCM (30 mL) and washed with water (2 × 15 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (Silica gel, EtOAc-hexane 2:8) produced dipivalate **19** as a brown solid (0.90 g, 84%); mp 176−178 °C. IR (neat) 1731 (ester), 1663 (CO), 1384 and 1186 (SO_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 7.5 Hz, 2H), 7.66 (t, J = 7.05 Hz, 1H), 7.58−7.53 (m, 2H), 7.37−7.35 (m, 4H), 7.20−7.15 (m, 6H), 5.22 (s, 4H), 0.99 (s, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.1, 177.4, 139.0, 137.9, 134.9, 133.3, 132.8, 130.0, 128.9, 128.3, 126.8, 56.0, 38.7, 27.0 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.9, 133.3, 130.0, 129.0, 128.3, 126.9, 56.0, 27.0 ppm. Elemental Analysis Calcd for $C_{36}H_{37}NO_8S$: C, 67.17; H, 5.79; N, 2.18; S, 4.98. Found: C, 67.03; H, 5.53; N, 2.07; S, 4.72.

*14,15-Diphenyl-7-(phenylsulfonyl)-7H-dibenzofuro[2,3-b:3′,2′-h]-carbazole (**20**).* A solution of dipivalate **19** (0.2 g, 0.31 mmol), benzofuran (0.081 g, 0.68 mmol) and $SnCl_4$ (0.178 g, 0.68 mmol) in dry DCE (10 mL) was stirred at room temperature under nitrogen atmosphere for 30 min. After the completion of the reaction (TLC), it was then poured into ice water (30 mL) containing Conc. HCl (3 mL). The organic layer was separated and the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic extract was washed with water (2 × 20 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (Silica gel, EtOAc-hexane) furnished dibenzofuro[*b*]carbazole **20** as a colorless solid (0.141 g, 71%); mp 274−276 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.73 (s, 2H), 7.91 (d, J = 7.5 Hz, 2H), 7.53−7.49 (m, 3H), 7.37 (t, J = 7.8 Hz, 2H), 7.33−7.23 (m, 4H), 7.11 (t, J = 7.5 Hz, 4H), 6.92 (t, J = 7.5 Hz, 2H), 6.75 (d, J = 7.2 Hz, 4H), 6.38 (d, J = 7.8 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 155.0, 139.7, 139.4, 137.3, 134.1, 132.5, 129.1 (2C), 129.0, 126.9, 126.7, 126.6, 124.1, 122.3, 122.1, 121.7, 120.8, 111.2, 98.1 ppm. Dept-135 (75 MHz, $CDCl_3$) δ 134.1, 129.2, 129.1, 129.0, 126.9, 126.7, 126.6, 122.3, 122.1, 111.2, 98.1 ppm. HRMS (EI, 70 eV) m/z Calcd for $C_{42}H_{25}NO_4S$ [M^+]: 639.1504, found 639.1501.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01646.

Copies of ^1H and ^{13}C NMR spectra for **2**−**20**, DEPT-135 NMR spectra for **6h**, **8i**, **12a**−**d**, **13c**, **13d**, **14c**, **15c** and **20** (PDF)

X-ray crystallographic information for **14c** (CIF)

X-ray crystallographic information for **16c** (CIF)

X-ray crystallographic information for **20** (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Chakraborty, D. P. In *The Alkaloids*; Cordell, G. A., Ed.; Academic Press: New York, 1993; Vol. *44*, p 257. (b) Moody, C. J. *Synlett* **1994**, *1994*, 681. (c) Kawasaki, T.; Sakamoto, M. *J. Indian Chem. Soc.* **1994**, *71*, 443. (d) Knölker, H.-J. In *Advances in Nitrogen Heterocycles*; Moody, C. J., Ed.; JAI Press: Greenwich, CT, 1995; Vol. *1*, p 173. (e) Knölker, H.-J. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 1998; Vol. *1*, Chapter 3.13, p 534. (f) Knölker, H.-J. *Chem. Soc. Rev.* **1999**, *28*, 151. (g) Knölker, H.-J.; Braier, A.; Bröcher, D. J.; Cömmerer, S.; Fröhner, W.; Gonser, P.; Hermann, H.; Herzberg, D.; Reddy, K. R.; Rohde, G. *Pure Appl. Chem.* **2001**, *73*, 1075.

(2) (a) Knölker, H.-J.; Reddy, K. R. In *The Alkaloids*; Cordell, G. A., Ed.; Academic Press: Amsterdam, 2008; Vol. *65*, pp 1−430. (b) Agarwal, S.; Cömmerer, S.; Filali, S.; Fröhner, W.; Knöll, J.; Krahl, M. P.; Reddy, K. R.; Knölker, H.-J. *Curr. Org. Chem.* **2005**, *9*, 1601. (c) Schmidt, A. W.; Reddy, K. R.; Knölker, H.-J. *Chem. Rev.* **2012**, *112*, 3193. (d) Knölker, H.-J.; Reddy, K. R. *Chem. Rev.* **2002**, *102*, 4303. (e) Knölker, H.-J. *Chem. Lett.* **2009**, *38*, 8. (f) Bauer, I.; Knölker, H.-J. *Top. Curr. Chem.* **2011**, *309*, 203. (g) Roy, J.; Jana, A. K.; Mal, D. *Tetrahedron* **2012**, *68*, 6099.

(3) (a) Remers, W. A.; Dorr, R. T. *Chemistry Biology and Therapeutics of the Mytomycins In Alkaloids: Chemical and Biological Perspectives*; Pelletier, S. W., Ed.; John Wiley & Sons: New York, 1988; Vol. *6*, pp 1−74. (b) Nettleton, D. E.; Doyle, T. W.; Krishnan, B.; Matsumoto, G. K.; Clardy, J. *Tetrahedron Lett.* **1985**, *26*, 4011. (c) Díaz, J. L.; Dobarro, A.; Villacampa, B.; Velasco, D. *Chem. Mater.* **2001**, *13*, 2528. (d) Knölker, H.-J.; Reddy, K. R. *Tetrahedron* **2000**, *56*, 4733. (e) Kober, U.; Knölker, H.-J. *Synlett* **2015**, *26*, 1549. (f) Fröhner, W.; Krahl, M. P.; Reddy, K. R.; Knölker, H.-J. *Heterocycles* **2004**, *63*, 2393. (g) Forke, R.; Krahl, M. P.; Krause, T.; Schlechtingen, G.; Knölker, H.-J. *Synlett* **2007**, *2007*, 268. (h) Krahl, M. P.; Schmidt, A. W.; Knölker, H.-J. *Heterocycles* **2012**, *86*, 357.

(4) Pindur, U.; Haber, M.; Sattler, K. *J. Chem. Educ.* **1993**, *70*, 263.

DOI: 10.1021/acs.joc.6b01646
J. Org. Chem. 2016, 81, 8633−8646

(5) (a) Routier, S.; Mérour, J.-Y.; Dias, N.; Lansiaux, A.; Bailly, C.; Lozach, O.; Meijer, L. *J. Med. Chem.* **2006**, *49*, 789. (b) Routier, S.; Peixoto, P.; Mérour, J.-Y.; Coudert, G.; Dias, N.; Bailly, C.; Pierré, A.; Léonce, S.; Caignard, D.-H. *J. Med. Chem.* **2005**, *48*, 1401.
(6) (a) Liu, Y.; Nishiura, M.; Wang, Y.; Hou, Z. *J. Am. Chem. Soc.* **2006**, *128*, 5592. (b) Ding, J.; Gao, J.; Cheng, J.; Xie, Z.; Wang, L.; Ma, D.; Jing, X.; Wang, F. *Adv. Funct. Mater.* **2006**, *16*, 575. (c) Thomas, K. R. J.; Lin, J. T.; Tao, T.-Y.; Ko, C.-W. *J. Am. Chem. Soc.* **2001**, *123*, 9404. (d) Balandier, J.-Y.; Henry, N.; Arlin, J.-B.; Sanguinet, L.; Lemaur, V.; Niebel, C.; Chattopadhyay, B.; Kennedy, A. R.; Leriche, P.; Blanchard, P.; Cornil, J.; Geerts, Y. H. *Org. Lett.* **2013**, *15*, 302. (e) Grazulevicius, J. V.; Strohriegl, P.; Pielichowski, J.; Pielichowski, K. *Prog. Polym. Sci.* **2003**, *28*, 1297. (f) Promarak, V.; Pankuvang, A.; Ruchirawa, S. *Tetrahedron Lett.* **2007**, *48*, 1151.
(7) Kano, S.; Sugino, E.; Shibuya, S.; Hibino, S. *J. Org. Chem.* **1981**, *46*, 2979.
(8) (a) Bergman, J.; Pelcman, B. *Tetrahedron* **1988**, *44*, 5215. (b) Boogaard, A. T.; Pandit, U. K.; Koomen, G.-J. *Tetrahedron* **1994**, *50*, 4811. (c) Fraser, H. L.; Gribble, G. W. *Can. J. Chem.* **2001**, *79*, 1515.
(9) Martarello, L.; Joseph, D.; Kirsch, G. *Heterocycles* **1996**, *43*, 367.
(10) Asche, C.; Frank, W.; Albert, A.; Kucklaender, U. *Bioorg. Med. Chem.* **2005**, *13*, 819.
(11) Moody, C. J. J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2505.
(12) Gribble, G. W.; Keavy, D. J.; Davis, D. A.; Saulnier, M. G.; Pelcman, B.; Barden, T. C.; Sibi, M. P.; Olson, E. R.; BelBruno, J. J. *J. Org. Chem.* **1992**, *57*, 5878.
(13) (a) Sha, C.-K.; Chuang, K.-S.; Wey, S.-J. *J. Chem. Soc., Perkin Trans. 1* **1987**, 977. (b) Kreher, R. P.; Dyker, G. *Z. Naturforsch., B: J. Chem. Sci.* **1987**, *42*, 473.
(14) (a) Martínes-Esperón, M. F.; Rodríguez, D.; Castedo, L.; Saá, C. *Org. Lett.* **2005**, *7*, 2213. (b) Martínes-Esperón, M. F.; Rodríguez, D.; Castedo, L.; Saá, C. *Tetrahedron* **2008**, *64*, 3674.
(15) (a) Tang, R.-Y.; Li, J.-H. *Chem. - Eur. J.* **2010**, *16*, 4733. (b) Prakash, K. S.; Nagarajan, R. *Adv. Synth. Catal.* **2012**, *354*, 1566.
(16) Xing, Y.; Hu, B.; Yao, Q.; Lu, P.; Wang, Y. *Chem. - Eur. J.* **2013**, *19*, 12788.
(17) Wu, J.; Halong, D.; Wu, F.; Li, X.; Wan, B. *Org. Biomol. Chem.* **2014**, *12*, 6806.
(18) Paul, K.; Bera, K.; Jalal, S.; Sarkar, S.; Jana, U. *Org. Lett.* **2014**, *16*, 2166.
(19) Suárez, A.; García-García, P. P.; Fernández-Rodríguez, F.; Sanz, R. *Adv. Synth. Catal.* **2014**, *356*, 374.
(20) Boominathan, S. S. K.; Senadi, G. C.; Vandavasi, J. K.; Chen, J. Y-F.; Wang, J.-J. *Chem. - Eur. J.* **2015**, *21*, 3193.
(21) (a) Mohanakrishnan, A. K.; Dhayalan, V.; Arul Clement, J.; Balamurugan, R.; Sureshbabu, R.; Senthilkumar, N. *Tetrahedron Lett.* **2008**, *49*, 5850. (b) Dhayalan, V.; Arul Clement, J.; Jegan, R.; Mohanakrishnan, A. K. *Eur. J. Org. Chem.* **2009**, *4*, 531. (c) Dhayalan, V.; Sureshbabu, R.; Mohanakrishnan, A. K. *Indian J. Chem.* **2011**, *50B*, 843.
(22) Sureshbabu, R.; Saravanan, V.; Dhayalan, V.; Mohanakrishnan, A. K. *Eur. J. Org. Chem.* **2011**, *6*, 922.
(23) (a) Nobre, S. M.; Monteiro, A. L. *Tetrahedron Lett.* **2004**, *45*, 8225. (b) Kuwano, R.; Yokogi, M. *Org. Lett.* **2005**, *7*, 945. (c) Kuno, A.; Saino, N.; Kamachi, T.; Okamoto, S. *Tetrahedron Lett.* **2006**, *47*, 2591. (d) Kofink, C.; Knochel, P. *Org. Lett.* **2006**, *8*, 4121. (e) Mertins, K.; Iovel, I.; Kischel, J.; Zapf, A.; Beller, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 238. (f) Deshmukh, M. S.; Srivastava, A.; Das, B.; Jain, N. *J. Org. Chem.* **2015**, *80*, 10041.
(24) Muthu Ramalingam, B.; Saravanan, V.; Mohanakrishnan, A. K. *Org. Lett.* **2013**, *15*, 3726.
(25) Rajeshwaran, G. G.; Nandakumar, M.; Sureshbabu, R.; Mohanakrishnan, A. K. *Org. Lett.* **2011**, *13*, 1270.
(26) Dhayalan, V.; Mohanakrishnan, A. K. *Indian J. Chem.* **2010**, *49B*, 327.
(27) (a) Zhang, Z.; Zhang, Q.; Yan, Z.; Liu, Q. *J. Org. Chem.* **2007**, *72*, 9808. (b) Yang, Y.-H.; Shi, M. *Org. Lett.* **2006**, *8*, 1709.
(28) Rafiq, S. M.; Sivasakthikumaran, R.; Karunakaran, J.; Mohanakrishnan, A. K. *Eur. J. Org. Chem.* **2015**, *23*, 5099.
(29) Saravanan, V.; Ramalingam, B. M.; Mohanakrishnan, A. K. *Eur. J. Org. Chem.* **2014**, *6*, 1266.
(30) (a) CCDC No for the carbazole **14c** is 1483917. (b) CCDC No for the carbazole **16c** is 1483857.
(31) Seshadri, P. R.; Balakrishnan, B.; Ilangovan, K.; Sureshbabu, R.; Mohanakrishnan, A. K. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2009**, *E65*, o531.
(32) CCDC No for the carbazole **20** is 1488226.
(33) Gribble, G. W.; Keavy, D. J.; Davis, D. A.; Saulnier, M. G.; Pelcman, B.; Barden, T. C.; Sibi, M. P.; Olson, E. R.; BelBruno, J. J. *J. Org. Chem.* **1992**, *57*, 5879.

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J. Org. Chem. 2016, 81, 8633−8646