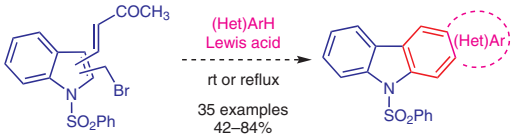
Synthesis V. Saravanan, A. K. Mohanakrishnan Paper

Synthesis of Annulated Carbazoles via $FeCl_3$/$SnCl_4$-Mediated Domino Reaction of Vinyl Ketone Tethered Bromomethylindoles with Arenes and Heteroarenes

Velu Saravanan
Arasambattu K. Mohanakrishnan*

Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, Tamil Nadu, India
mohan_67@hotmail.com
mohanakrishnan@unom.ac.in



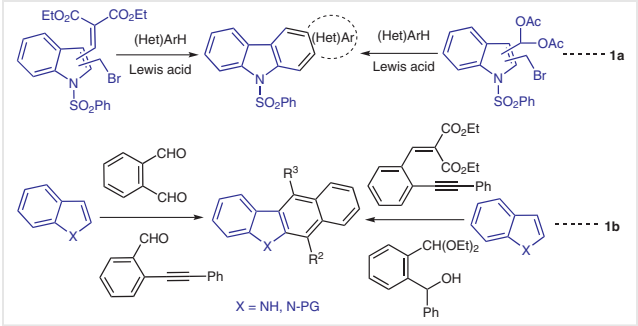
Received: 12.01.2021
Accepted after revision: 10.02.2021
Published online: 10.02.2021
DOI: 10.1055/a-1387-9479; Art ID: ss-2021-t0014-op

Abstract One-pot synthesis of aryl- as well as heteroaryl-annulated carbazoles was achieved from 2/3-bromomethylindoles involving Lewis acid mediated domino reaction with arenes as well as heteroarenes via successive Friedel–Crafts intermolecular as well as intramolecular alkylations followed by elimination of acetone. Further, the bis-domino reaction of 2,5-bis(bromomethyl)pyrrole was also carried out with selected heteroarenes. Additionally, the synthesized thienocarbazoles and thienodibenzofurans were successfully utilized for a second-generation domino reaction.

Key words carbazole, indole, pyrrole, Friedel–Crafts alkylation, Michael addition

Carbazole and its derivatives constitute an important class of bio-active natural products.[1] Substituted and annulated carbazole derivatives are an important class of anticancer agents that have been increased significantly in the past few decades.[2] Recent interest on aryl- and heteroaryl-fused carbazoles are due to their potent biological activities and also to their wide applications in materials science.[3,4] In addition, the annulated carbazole derivatives are also widely applied in optical devices owing to their photorefractive, hole transporting, and light-emitting properties.[5]

Our first report on the syntheses of aryl- and heteroaryl-annulated carbazoles employed a $ZnBr_2$-mediated domino reaction of N-protected 2/3-bromomethylindoles containing malonylidene unit with arenes as well as heteroarenes.[6] Later on, the methodology could be successfully extended with diacetoxymethine-tethered bromomethylindoles to afford the cyclo[*b*]annulated carbazoles[7] (Scheme 1a). In these methods, we have exploited the respective *N*-phenylsulfonyl 2/3-bromomethylindoles containing a masked aldehyde unit as an electrophilic bidentate synthon undergoing successive arylation with a wide variety of arenes as well as heteroarenes followed by intramolecular cyclization and aromatization. After these reports, synthesis of various types of benzannulated carbazoles are realized through umpolung strategy, that is, by reacting a nucleophilic indole unit with electrophilic bidentate benzene counter parts[8] (Scheme 1b).



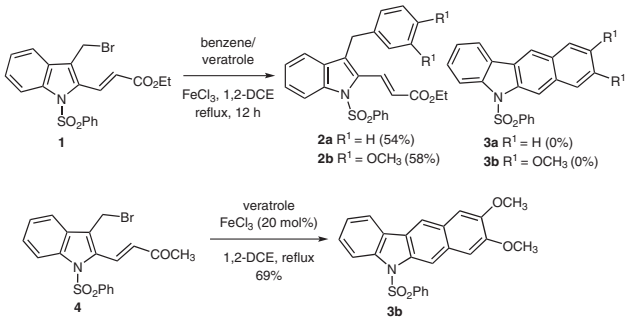
Scheme 1 Summary of recent annulated carbazole syntheses from indoles

Recently, we also achieved a straightforward synthesis of annulated cyclo[*b*]carbazoles involving the $SnCl_4$-mediated one-pot arylation, cyclization, and aromatization reaction sequence from 3-acetyl/aroyl-2-pivaloyloxymethylindoles.[9] The main drawbacks of our methodologies are moderate reactivity of the malonylidene-tethered bromomethylindoles and the stability as well as arylation selectivity associated with the bromomethylindoles containing acetoxymethine unit.

In a further continuation of our studies on the domino reaction, we wish to extend the synthesis of highly π-conjugated heteroacenes by modifying the leaving group for increasing the yield of the products. Initially, when we tested the reaction of 3-bromomethylindole **1**[10] containing a vinyl ester unit with benzene/veratrole in the presence of 20

Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany

mol% $FeCl_3$ in 1,2-dichloroethane (1,2-DCE) at reflux it furnished the respective 2-benzylindoles **2a** and **2b** in moderate yields. Under these reaction conditions, the benzylated indoles failed to undergo any further cyclization to produce the expected carbazole **3a**/**3b** (Scheme 2).



Scheme 2 Reaction of 3-bromomethylindole **1** with benzene/veratrole

It has been observed that an intermolecular Michael addition of cinnamic ester with veratrole could be successfully performed using an excess of $FeCl_3$.[11] However, the observed intramolecular Michael addition failure in the case of **2a**/**2b** even with excess of $FeCl_3$ might be due to the less reactivity of vinyl ester. Hence, we planned to change the aldehyde masking unit from vinyl ester into more reactive methyl vinyl ketone. As expected, the reaction of bromomethylindole **4**[10] with veratrole in the presence of $FeCl_3$ led to the isolation of annulated carbazole **3b** in 69% yield (Scheme 2).

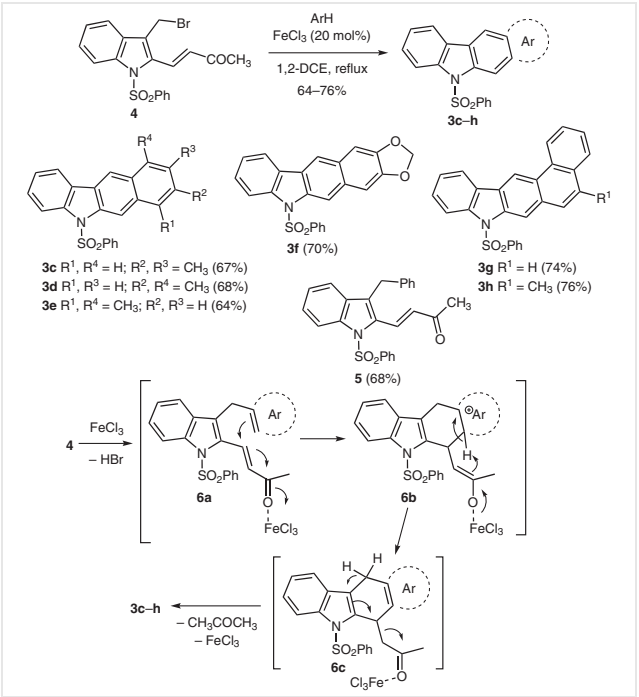
Next, we initiated our study to understand the effect of Lewis acids on the observed domino reaction. The domino reaction of 3-bromomethylindole **4** in the presence of $ZnBr_2$ and $ZnCl_2$ in 1,2-DCE at reflux afforded annulated carbazole in a very low yield. Further prolonging the reaction by refluxing for 24 hours also did not increase the yield (Table 1, entries 1, 2). Similarly, the cascade reaction of bromomethylindole **4** with veratrole using $BF_3{\cdot}OEt_2$, $SnCl_4$, $Zn(OTf)_2$, $InBr_3$, and $InCl_3$ gave aza-tetracene **3b** in 54%, 56%, 62%, 69% and 67% yield, respectively (entries 3–5, 7, 8). The use $Sc(OTf)_3$ and $Yb(OTf)_3$ did not give the annulated product, it failed to induce even the initial veratrylation, only the starting material **4** could be recovered unchanged (entries 9, 10).

Adopting the standard procedure, next, we extended the scope of the reaction with different arenes. The domino reaction of 3-bromomethylindole **4** with xylenes and benzodioxole using 20 mol% $FeCl_3$ afforded the corresponding annulated carbazoles **3c–f** in 64–70% yields (Scheme 3). Similarly, the synthesis of naphtho[*b*]carbazoles **3g**,**h** has also been achieved in 74% and 76% yields. However, the reaction of bromomethylindole **4** with benzene produced only the 3-benzylindole **5**. Obviously, the subsequent $FeCl_3$-catalyzed intramolecular Friedel–Crafts alkylation of **5** is not occurring with phenyl ring. The mechanism of formation of carbazoles **3c–h** from **4** is depicted in Scheme 3. The tentative mechanistic visualization for the formation of carbazole has been explained (Scheme 3). The initially formed arylmethylindoles **6a** underwent $FeCl_3$-catalyzed intramolecular Friedel–Crafts alkylation at the β-position of methyl vinyl ketone (MVK) unit followed by aromatization to afford

Table 1 Catalytic Efficiency of Lewis Acids as a Catalyst in the Domino Reaction of 3-Bromomethylindole **4** with Veratrole

Entry	LA (20 mol%)[a]	Time (h)	Yield (%)[b]
1	$ZnBr_2$	24	10
2	$ZnCl_2$	24	10
3	$BF_3{\cdot}OEt_2$	8	54
4	$SnCl_4$	4	56
5	$Zn(OTf)_2$	6	62
6	$FeCl_3$	4	69
7	$InCl_3$	8	69
8	$InBr_3$	8	67
9	$Sc(OTf)_3$	24	0[c]
10	$Yb(OTf)_3$	24	0[c]

[a] Synthesis of dimethoxybenzo[*b*]carbazole **3b** was accomplished using 3-bromomethylindole **4** (1 equiv), veratrole (1.1 equiv), and Lewis acid (LA; 0.2 equiv) in 1,2-DCE at reflux.
[b] Isolated yield of **3b** after column chromatography.
[c] Unreacted bromomethylindole **4**.



Scheme 3 Synthesis of benzo[*b*]annulated carbazoles **3c–h** and 3-benzylindole **5**

intermediate dihydrocrbazoles **6c**. The dihydrocrbazoles **6c** upon aromatization via $FeCl_3$-induced elimination of acetone unit[12] lead to the carbazoles **3c–h**.

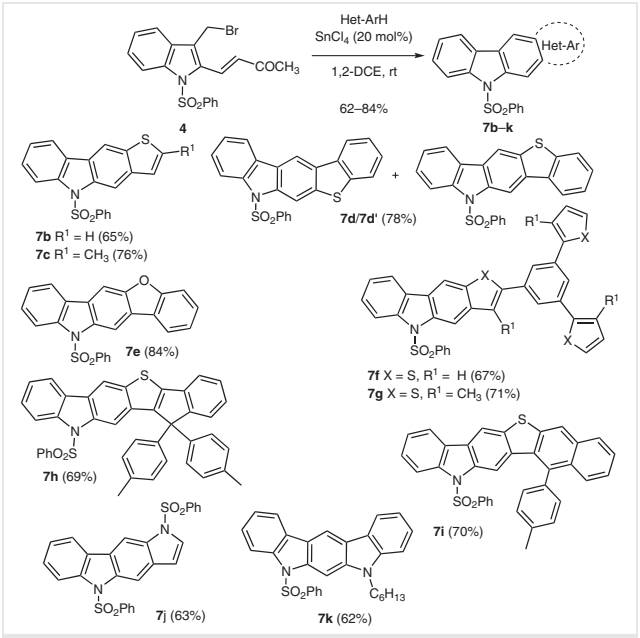
Next, the reaction of bromomethylindole **4** with heteroarene, bithiophene using 20 mol% $FeCl_3$ at reflux produced the annulated carbazole **7a** only in 30% yield (Table 2, entry 1). However, the annulation of the bromomethylindole **4** using 20 mol% of $ZnBr_2$, $FeCl_3$, $BF_3{\cdot}OEt_2$, $Zn(OTf)_2$, $InBr_3$, and $InCl_3$ in 1,2-DCE at room temperature led to the isolation of the thieno[*b*]carbazole **7a** in 48%, 46%, 64%, 68%, 70% and 68% yield, respectively (entries 2–5, 8, 9). The reaction of **4** with bithiophene in the presence of Lewis acids such as $Sc(OTf)_3$ and $Yb(OTf)_3$ failed to produce the annulated product **7a** (entries 10, 11). Among the various Lewis acids employed, the use of 20 mol% of $SnCl_4$ in 1,2-DCE at room temperature afforded annulated product **7a** in a comparatively better yield (entry 7). Thus, the above-mentioned results clearly indicate that the thiophene/bithiophene in the presence of Lewis acids at a refluxing condition of 1,2-DCE may induce an unwanted self-polymerization (entry 1). Hence, the Lewis acids could be used as a suitable catalyst for domino reaction of the bromomethylindole **4** with bithiophene only at room temperature.

Table 2 Effect of Different Lewis Acids on the Domino Reaction of 3-Bromomethylindole **4** with Bithiophene

Entry	LA (20 mol%)[a]	Time (h)	Yield (%)[b]
1	$FeCl_3$[c]	0.5	30
2	$ZnCl_2$	0.5	36
3	$ZnBr_2$	6	48
4	$FeCl_3$	6	64
5	$Zn(OTf)_2$	3	68
6	$BF_3{\cdot}OEt_2$	6	64
7	**$SnCl_4$**	**3**	**72**
8	$InCl_3$	6	70
9	$InBr_3$	6	68
10	$Sc(OTf)_3$	24	0[d]
11	$Yb(OTf)_3$	24	0[d]

[a] Annulation of 3-bromomethylindole **4** (1 equiv) with bithiophene (1.1 equiv) using Lewis acid (20 mol%) in 1,2-DCE at rt.
[b] Isolated yield of **7a** after column chromatography.
[c] Reaction was carried at reflux.
[d] Unreacted bromomethylindole **4**.

By adopting the established conditions, syntheses of distinctively substituted hetero-annulated carbazoles were achieved (Scheme 4). The cascade reaction of 3-bromomethylindole **4** with 2-methylthiophene as well as thiophene using $SnCl_4$ at room temperature furnished the corresponding thienocarbazoles **7b**,**c** in 65% and 76% yield, respectively. Ambiguously, the annulation of bromomethylindole **4** with benzo[*b*]thiophene led to an inseparable mixture of carbazoles **7d** and **7d′** (1:0.4 ratio based on ^1H NMR) in 78% yield. The structures of the carbazoles **7d** and **7d′** were assigned based on our earlier report.[6b]

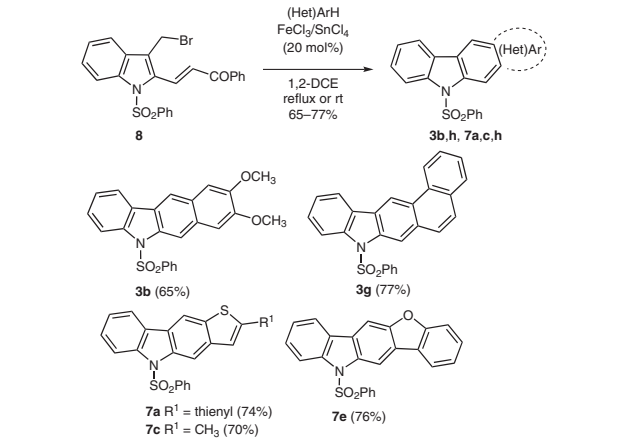


Scheme 4 Synthesis of hetero-annulated carbazoles **7b–k**

Annulation of 2-bromomethylindole **4** with benzo[*b*]furan produced the expected benzofuranocarbazole **7e** in 84% yield.[13] To our delight, the reaction of bromomethylindole **4** with trithienylbenzenes using $SnCl_4$ at room temperature led to the isolation of the corresponding mono-annulated thienocarbazole **7f** as well as **7g** in 67% and 71% yield, respectively. Further domino reaction of bromomethylindole **4** with thiophene-, indole-, and pyrrole-based heteroarenes led to the formation of corresponding annulated carbazoles **7h–k** in 62–70% yields (Scheme 4).[14]

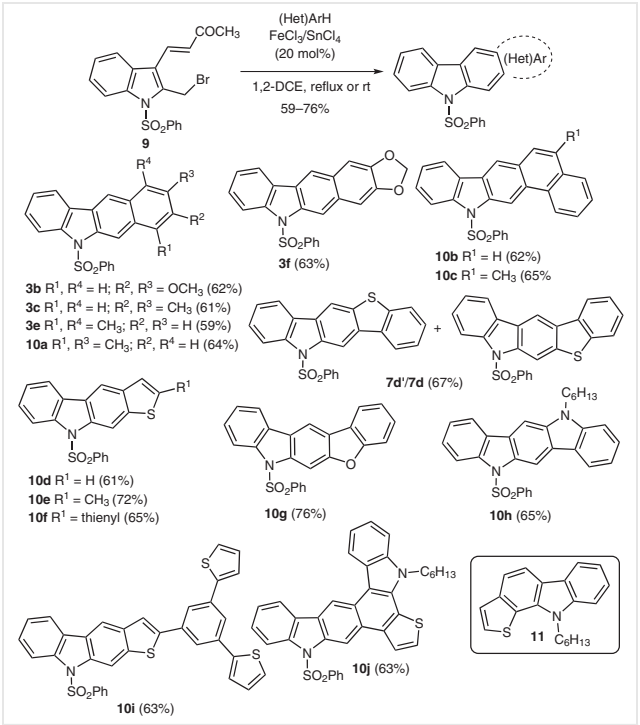
To understand the role of leaving group, the annulation of 3-bromomethylindole bearing phenyl vinyl ketone (PVK) was planned. Accordingly, Wittig reaction of the 1-phenylsulfonyl-2-methylindole-3-carboxaldehyde[6b] with (benzoylmethylene)triphenylphosphorane followed by benzylic bromination afforded the required bromo compound **8**. Next, the annulation of the bromo compound **8** with 1,2-dimethoxybenzene and naphthalene using 20 mol% $FeCl_3$ in 1,2-DCE at reflux gave the corresponding annulated carbazoles **3b** and **3g** in 65% and 77% yield, respectively (Scheme 5). The domino reaction of the bromo compound **8** with heteroarenes, bithiophene and 2-methylthiophene, in 1,2-DCE at room temperature furnished the corresponding known annulated heterocycles **7a** and **7c** in 74% and 70% yield, respectively. Similarly, the annulation of the bromo compound **8** with benzo[*b*]furan using 20 mol% $SnCl_4$ in 1,2-DCE afforded the benzofuranocarbazole **7e** in a good

yield. Comparatively, the domino reaction of the 3-bromomethylindoles **4** and **8** containing MVK as well as PVK produced the annulated carbazoles in almost comparable yields. Hence, it may be concluded that the leaving group (acetone/acetophenone) is not having any significant role on the yields of the domino reaction (Scheme 5).



Scheme 5 Annulation of phenyl vinyl ketone-tethered 3-bromomethylindole **8**. *Reagents and conditions*: The reaction of **8** with arenes (ArH) was performed using 20 mol% of $FeCl_3$ in 1,2-DCE at reflux. The reaction of **8** with heteroarenes (Het-ArH) was performed using 20 mol% of $SnCl_4$ in 1,2-DCE at rt.

With a working catalytic system, next, we investigated the domino reaction of isomeric 2-bromomethylindole **9**[10] with arenes and heteroarenes. As expected, the domino reaction of the 2-bromomethylindole **9** with 1,2-dimethoxybenzne and xylenes in 1,2-DCE at reflux furnished the corresponding annulated carbazoles **3b**,**c**, **10a**, and **3e** in 59–64% yields (Scheme 6). Similarly, the annulation of 2-bromomethylindole **9** with 1,3-benzoxazole and naphthalenes also produced the respective carbazoles **3f** and **10b**,**c** in 62–65% yields. As observed for isomeric 3-bromomethylindole **4**, 2-bromomethylindole **9** also reacts with thiophenes in the presence of 20 mol% $SnCl_4$ at room temperature to afford thieno[*b*]carbazoles **10d–f** in 61–72% yields (Scheme 6). Similar to the case of 3-bromomethylindole **4**, the cascade reaction of 2-bromomethylindole **9** with benzothiophene gave only an inseparable mixture of carbazoles **7d′** and 7**d** (1:0.4 ratio based on ^1H NMR) in 67% yield. The tandem annulation of 2-bromomethylindole **9** could be successfully performed with benzofuran, *N*-hexylindole, and 1,3,5-trithienylbenzene to give the corresponding annulated carbazoles **10g–i** in 65–76% yields. Surprisingly, the annulation of 2-bromomethylindole **9** with thienocarbazole **11** using $SnCl_4$ at room temperature furnished the bent heptacene **10j** as an exclusive product in 63% yield (Scheme 6). Obviously, the preferential indolylmethylation at the carbazole 6-position of **11** is favored by the combined electronic influence of thiophene as well as carbazole units. The structures of the representative annulated carbazoles **3g** and **10j** were confirmed by single crystal X-ray analyses (Figure 1 and Figure 2).[15]



Scheme 6 Domino reaction of 2-bromomethylindole **9** with arenes and heteroarenes. *Reagents and conditions*: The reaction of **9** with arenes (ArH) was performed using 20 mol% of $FeCl_3$ in 1,2-DCE at reflux. The reaction of **9** with heteroarenes (Het-ArH) was performed using 20 mol% of $SnCl_4$ in 1,2-DCE at rt.

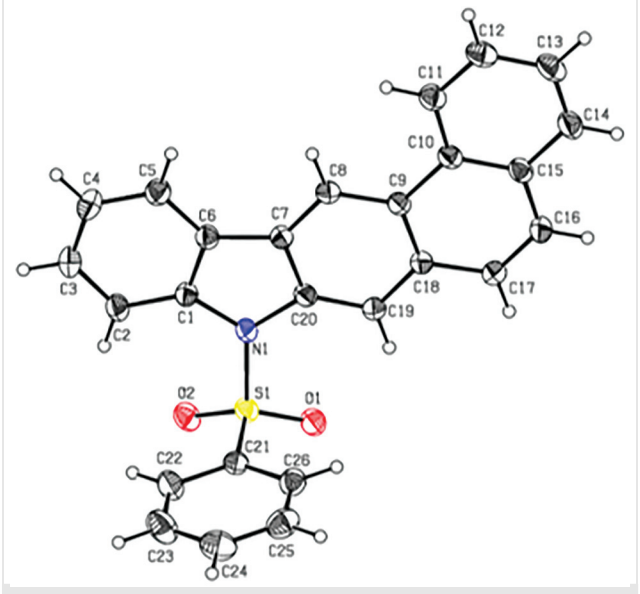


Figure 1 Molecular structure of carbazole **3g** in the crystal (triclininc, p1): ORTEP plot showing thermal ellipsoids at the 50% probability level.[15]

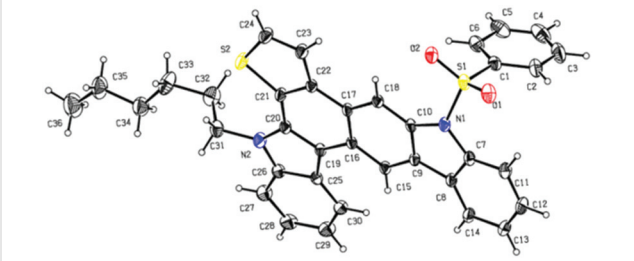
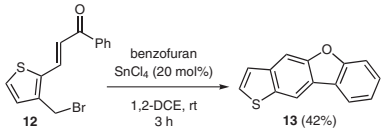


Figure 2 Molecular structure of carbazole **10j** in the crystal (triclininc, p1): ORTEP plot showing thermal ellipsoids at the 50% probability level.[15]

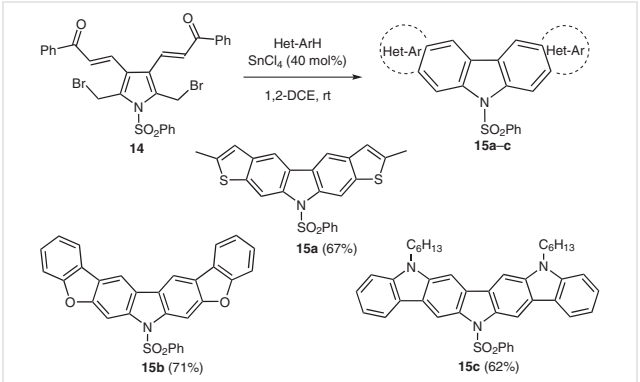
Further, as a representative case, the domino reaction of 3-bromomethylthiophene **12** containing a phenyl vinyl ketone unit with benzofuran using 20 mol% of $SnCl_4$ at room temperature for 6 hours gave thienodibenzofuran **13** in 42% yield (Scheme 7).



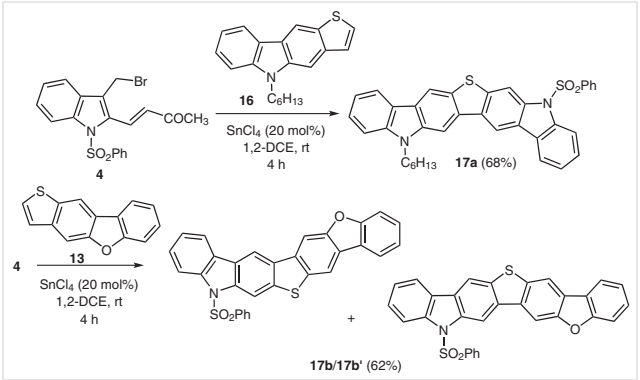
Scheme 7 Synthesis of thienodibenzofuran **13**

To further extend the scope of the reaction, the synthesis of C_2-symmetric carbazoles was investigated. Due to the difficulty associated with the separation of MVK analogue of 1-phenylsulfonyl-2,5-dimethylpyrrole 3,4-dicarboxaldehyde from triphenylphosphene oxide, a phenyl vinyl ketone tethered 2,5-bis(bromomethyl)pyrrole **14** was prepared from pyrrole 3,4-dialdehyde[9] via Wittig reaction with (benzoylmethylene)triphenylphosphorane at reflux in toluene followed by benzylic bromination. To our delight, the domino reaction of bis(bromomethyl)pyrrole **14** with 2-methylthiophene, benzofuran, and *N*-hexylindole using 40 mol% of $SnCl_4$ at room temperature produced the symmetric thienocarbazole, benzofuranocarbazole, and indolocarbazole **15a–c** in 67%, 71% and 62% yield, respectively (Scheme 8).

Finally, a second-generation domino reaction was carried out utilizing the synthesized annulated carbazole **13** and **16** (Scheme 9). Serendipitously, the cascade reaction of 3-bromomethylindole **4** with thienocarbazole **16** (prepared from carbazole **7b** via desulfonation and N-hexylation) using $SnCl_4$ afforded the linear heptacene **17a** as an exclusive product in 68% yield. It is obvious that on the contrary to thienocarbazole **11**, in the case of isomeric thioenocarbazole **13**, the nucleophilicity is enriched at the thiophene 2-position favoring the formation of the linear heptacene **17a**. However, the domino reaction of bromomethyindole **4** with thienodibenzofuran **13** furnished only an inseparable mixture of isomers **17b** and **17b′** (1:1 ration based on ^1H NMR spectrum) in 62% yield.



Scheme 8 Synthesis of C_2-symmetric heterocycles **15a–c**



Scheme 9 Second-generation domino reaction

In summary, we have developed a simple annulation protocol for 2/3-(bromomethyl)indoles containing methyl vinyl ketone unit at the adjacent position. The observed annulation was initiated by a Lewis acid mediated arylation/heteroarylation at the bromomethyl carbon followed by an intramolecular Michael addition and subsequent aromatization via an elimination of acetone unit. The present protocol employing bromomethylindole containing masked aldehyde unit as an electrophilic bidentate synthon furnished a wide variety of aryl- as well as heteroaryl-annulated benzo[*b*]carbazoles in good yields. Compared to the existing methods wherein indole is used as nucleophilic counter parts,[8] our method is more advantageous since the domino reaction could be successfully performed with different types of arenes as well as heteroarenes to furnish structurally diverse type of annulated carbazoles.

All melting points were uncorrected. Solvents were dried by standard procedures. All the experiments carried out under N_2 atmosphere, unless otherwise stated. The progression of all the reaction was monitored by TLC using hexanes/EtOAc mixture. Column chromatography was carried out on silica gel (230–400 mesh, Merck) by increasing polarity. ^1H, ^{13}C and DEPT spectra were recorded in $CDCl_3$ using TMS as

an internal standard on Bruker 300 MHz and 400 MHz spectrometer at rt. Chemical shift values were quoted in parts per million (ppm) and coupling constants were quoted in hertz (Hz). HRMS were recorded on JEOL GC Mate II (EI) and Xevo G2S QTof instruments.

Ethyl (*E*)-3-[3-Benzyl-1-(phenylsulfonyl)-1*H*-indol-2-yl]acrylate (2a)

To a solution bromo compound **1** (0.2 g, 0.446 mmol) in anhyd benzene (20 mL) was added anhyd $FeCl_3$ (0.01 g, 0.089 mmol) and the reaction mixture was refluxed for 12 h. After completion of the reaction (monitored by TLC), the mixture was washed with H_2O (2 × 10 mL) and dried (Na_2SO_4). Evaporation of the solvent followed by column chromatographic purification (silica gel, EtOAc/hexane 1:9) afforded **2a** as a colorless solid; yield: 0.107 g (54%); mp 146–148 °C.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.25 (d, *J* = 8.4 Hz, 1 H), 8.19 (d, *J* = 15.9 Hz, 1 H), 7.67–7.64 (m, 2 H), 7.52 (t, *J* = 7.5 Hz, 1 H), 7.40–7.32 (m, 3 H), 7.24 (d, *J* = 6.9 Hz, 1 H), 7.21–7.14 (m, 4 H), 6.85–6.82 (m, 2 H), 6.00 (d, *J* = 16.2 Hz, 1 H), 4.27 (q, *J* = 7.2 Hz, 2 H), 4.10 (s, 2 H), 1.34 (t, *J* = 7.05 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.2, 138.5, 137.7, 137.4, 134.1, 133.8, 133.3, 131.3, 129.0, 128.7, 127.7, 126.7, 126.6, 126.4, 126.0, 124.5, 122.2, 120.4, 115.9, 60.9, 30.7, 14.3.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{26}H_{24}NO_4S$ [M + H]$^+$: 446.1426; found: 446.1417.

Ethyl (*E*)-3-[3-(3,4-Dimethoxybenzyl)-1-(phenylsulfonyl)-1*H*-indol-2-yl]acrylate (2b)

A mixture of bromo compound **1** (0.2 g, 0.446 mmol), veratrole (0.07 g, 0.491 mmol), and anhyd $FeCl_3$ (0.01 g, 0.089 mmol) in anhyd 1,2-DCE (10 mL) was refluxed for 12 h. Then, the usual workup as described above, followed by column chromatographic purification (silica gel, EtOAc/hexane 1:9) afforded arylated product **2b** as a colorless solid; yield: 0.14 g (58%); mp 136–138 °C.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.27–8.19 (m, 2 H), 7.69 (d, *J* = 7.2 Hz, 2 H), 7.51 (t, *J* = 7.35 Hz, 1 H), 7.42–7.35 (m, 3 H), 7.33–7.26 (m, 2 H), 7.23–7.17 (m, 1 H), 6.63 (d, *J* = 8.1 Hz, 1 H), 6.54 (s, 1 H), 6.30 (d, *J* = 8.4 Hz, 1 H), 6.03 (d, *J* = 16.2 Hz, 1 H), 4.28 (q, *J* = 7.11 Hz, 2 H), 4.05 (s, 2 H), 3.81 (s, 3 H), 3.67 (s, 3 H), 1.35 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.2, 149.1, 147.6, 137.6, 137.5, 134.0, 133.8, 133.1, 131.2, 129.0, 126.7, 126.6, 125.9, 124.5, 124.5, 122.4, 120.4, 119.6, 115.7, 111.4, 111.3, 60.9, 55.9, 55.8, 30.3, 14.3.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{28}H_{28}NO_6S$ [M + H]$^+$: 506.1637; found: 506.1631.

(*E*)-4-[3-(Bromomethyl)-1-(phenylsulfonyl)-1*H*-indol-2-yl]but-3-en-2-one (4)

To a solution of 1-phenylsulfonyl-2-methylindole[10] (2.0 g, 8.85 mmol) in anhyd CCl_4 (50 mL) were added AIBN (0.05 g) and finely powdered NBS (1.89 g, 10.62 mmol). The reaction mixture was refluxed for 2 h and cooled to rt. The floated succinimide was filtered off and washed with CCl_4 (15 mL). The combined filtrates were concentrated in vacuo to afford **4** as a light brown solid; yield: 3.40 g (92%); mp 134–136 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.4 Hz, 1 H), 8.10 (d, *J* = 16.5 Hz, 1 H), 7.69 (d, *J* = 7.8 Hz, 2 H), 7.61 (d, *J* = 7.8 Hz, 1 H), 7.53 (d, *J* = 7.35 Hz, 1 H), 7.46–7.33 (m, 4 H), 6.61 (d, *J* = 16.5 Hz, 1 H), 4.60 (s, 2 H), 2.51 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.9, 137.7, 137.0, 134.3, 133.5, 132.9, 132.5, 129.3, 128.8, 127.0, 126.6, 124.6, 122.0, 119.8, 115.2, 27.2, 22.9.

For further spectroscopic data, see ref. 10.

Annulated Carbazoles; General Procedure

To a mixture of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) and anhyd $FeCl_3$ (0.015 g, 0.01 mmol) in anhyd 1,2-DCE (10 mL) was added the respective arene (0.53 mmol), and the mixture was refluxed under N_2 atmosphere until the reaction was completed (TLC). After completion of the reaction (TLC), the mixture was poured into ice-water (30 mL) containing concd HCl (3 mL). The organic layer was separated and the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layers were washed with H_2O (2 × 20 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (silica gel, hexane/EtOAc) furnished the required annulated benzo[*b*]carbazole.

8,9-Dimethoxy-5-(phenylsulfonyl)-5*H*-benzo[*b*]carbazole (3b)

To a solution of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) and veratrole (0.073 g, 0.53 mmol) in anhyd 1,2-DCE (10 mL) was added anhyd $FeCl_3$ (0.015 g, 0.096 mmol) and the mixture was refluxed under N_2 atmosphere for 4 h. The usual workup following the above-mentioned general procedure gave annulated carbazole **3b** as a colorless solid; yield: 0.137 g (69%); mp 136–138 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (s, 1 H), 8.21 (d, *J* = 8.4 Hz, 1 H), 8.03 (s, 1 H), 7.81 (d, *J* = 7.5 Hz, 1 H), 7.72 (d, *J* = 7.5 Hz, 2 H), 7.40–7.35 (m, 1 H), 7.32–7.25 (m, 2 H), 7.21–7.14 (m, 3 H), 7.10 (s, 1 H), 3.97 (s, 3 H), 3.92 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.9, 149.2, 139.5, 137.7, 136.3, 133.7, 129.1, 129.0, 127.7, 126.7, 126.5, 125.2, 124.2, 120.2, 116.8, 115.3, 110.9, 106.6, 106.0, 55.9 (2 C).

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{24}H_{19}NO_4S$ [M + H]$^+$: 418.1113; found: 418.1104.

For further spectroscopic data, see ref. 7.

8,9-Dimethyl-5-(phenylsulfonyl)-5*H*-benzo[*b*]carbazole (3c)

Domino reaction of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) with *o*-xylene (0.076 g, 0.718 mmol) using anhyd $FeCl_3$ (0.015 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) at reflux for 4 h, followed by workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) adopting the above mentioned general procedure afforded carbazole **3c** as a colorless solid; yield: 0.123 g (67%); mp 202–204 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.51 (s, 1 H), 8.22 (d, *J* = 8.4 Hz, 1 H), 8.03 (s, 1 H), 7.82 (d, *J* = 7.5 Hz, 1 H), 7.72–7.69 (m, 3 H), 7.55 (s, 1 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 7.28–7.22 (m, 2 H), 7.15–7.10 (m, 2 H), 2.37 (s, 3 H), 2.33 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.8, 137.6, 136.7, 136.0, 135.0, 133.6, 132.0, 129.6, 128.9, 128.0, 127.8, 127.3, 126.7, 126.5, 126.1, 124.2, 120.4, 117.3, 115.3, 111.3, 20.3, 20.1.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{24}H_{19}NO_2S$ [M$^+$]: 385.1136; found: 385.1125.

For further spectroscopic data, see ref. 7.

8,10-Dimethyl-5-(phenylsulfonyl)-5*H*-benzo[*b*]carbazole (3d)

The reaction of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) with *m*-xylene (0.076 g, 0.718 mmol) using anhyd $FeCl_3$ (0.015 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) at reflux for 4 h, followed by workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) adopting the above-mentioned general procedure afforded annulated carbazole **3d** as a colorless solid; yield: 0.125 g (68%); mp 206–208 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.54 (s, 1 H), 8.29 (s, 1 H), 8.24 (d, *J* = 8.4 Hz, 1 H), 7.91 (d, *J* = 7.5 Hz, 1 H), 7.72 (d, *J* = 7.8 Hz, 2 H), 7.59 (s, 1 H), 7.41 (t, *J* = 7.65 Hz, 1 H), 7.31–7.23 (m, 2 H), 7.18–7.13 (m, 2 H), 7.08 (s, 1 H), 2.64 (s, 3 H), 2.43 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.9, 137.7, 137.2, 135.5, 134.1, 133.7, 133.6, 129.0, 128.4, 12832, 128.0, 126.9, 126.5, 125.9, 125.8, 124.2, 120.4, 115.4, 114.7, 112.1, 21.8, 19.6.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{24}H_{20}NO_2S$ [M + H]$^+$: 386.1215; found: 386.1199.

For further spectroscopic data, see ref. 7.

7,10-Dimethyl-5-(phenylsulfonyl)-5*H*-benzo[*b*]carbazole (3e)

To a solution of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) and *p*-xylene (0.076 g, 0.718 mmol) in anhyd 1,2-DCE (10 mL) was added anhyd $FeCl_3$ (0.015 g, 0.096 mmol) and the mixture was refluxed under N_2 atmosphere for 4 h. The usual workup following the above-mentioned general procedure gave annulated carbazole **3e** as a colorless solid; yield: 0.118 g (64%); mp 184–186 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (s, 1 H), 8.37 (s, 1 H), 8.27 (d, *J* = 8.4 Hz, 1 H), 7.95 (d, *J* = 7.8 Hz, 1 H), 7.73 (d, *J* = 7.5 Hz, 2 H), 7.44 (t, *J* = 7.65 Hz, 1 H), 7.30 (t, *J* = 7.5 Hz, 2 H), 7.20–7.12 (m, 4 H), 2.74 (s, 3 H), 2.66 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.1, 137.6, 137.0, 133.7, 132.7, 132.5, 132.4, 130.0, 129.0, 128.2, 126.6, 126.5, 126.0, 125.5, 124.2, 120.5, 115.4, 115.3, 109.3, 20.0, 19.7.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{24}H_{19}NO_2S$ [M$^+$]: 385.1136; found: 385.1128.

For further spectroscopic data, see ref. 7.

8,9-Dihydro[1,3]dioxo-5-(phenylsulfonyl)-5*H*-benzo[*b*]carbazole (3f)

To a solution of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) and 1,3-benzodioxole (0.064 g, 0.53 mmol) in anhyd 1,2-DCE (10 mL) was added anhyd $FeCl_3$ (0.015 g, 0.096 mmol) and the mixture was refluxed for 4 h. Then, the usual workup and column chromatographic purification (silica gel, EtOAc/hexane 2:8) adopting the above mentioned general procedure furnished annulated carbazole **3f** as a colorless solid; yield: 0.134 g (70%); mp 250–252 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 8.44 (s, 1 H), 8.24 (d, *J* = 8.1 Hz, 1 H), 8.13 (d, *J* = 7.5 Hz, 1 H), 7.86 (d, *J* = 7.5 Hz, 2 H), 7.61–7.56 (m, 3 H), 7.48–7.40 (m, 4 H), 6.16 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.0, 147.3, 138.6, 136.4, 135.5, 134.6, 130.1, 129.6, 128.2, 127.5, 126.2, 125.9, 124.6, 124.4, 120.7, 118.0, 114.7, 111.1, 104.0, 103.2, 101.4.

Anal. Calcd for $C_{23}H_{15}NOS$: C, 68.81; H, 3.77; N, 3.49; S, 7.99. Found: C, 68.66; H, 3.79; N, 3.23; S, 7.76.

8-(Phenylsulfonyl)-8*H*-naphtho[2,1-*b*]carbazole (3g)

Annulation of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) with naphthalene (0.068 g, 0.53 mmol) using anhyd $FeCl_3$ (0.015 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) at reflux for 4 h, followed by usual work up and column chromatographic purification (silica gel, EtOAc/hexane 1:9) afforded annulated carbazole **3g** as a colorless solid; yield: 0.144 g (74%); mp 184–186 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.99 (s, 1 H), 8.65–8.61 (m, 2 H), 8.26 (d, *J* = 8.1 Hz, 1 H), 7.97 (d, *J* = 7.5 Hz, 1 H), 7.79–7.73 (m, 4 H), 7.65–7.62 (m, 1 H), 7.58–7.41 (m, 3 H), 7.34–7.25 (m, 2 H), 7.18–7.13 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.6, 137.6, 137.4, 133.8, 131.9, 131.6, 130.2, 129.0, 128.6, 128.1, 127.4, 127.3, 126.7, 126.5 (2 C), 126.4, 126.3, 124.2, 122.4, 120.4, 115.3, 113.6, 113.3.

HRMS (EI, Q-TOF): *m*/*z* calcd for $C_{26}H_{18}NO_2S$ [M$^+$]: 407.0980; found: 407.0968.

For further spectroscopic data, see ref. 7.

X-ray Crystallographic Data for Compound 3g[15]

Single-crystal of compound **3g** was obtained by crystallization from $CHCl_3$ and all calculations were performed with the SHELXL-97 program.[16] $C_{26}H_{17}NO_2S$, MW = 407.46 gmol^{-1}, triclinic crystal system, space group *P-1*, Z = 2. *a* = 7.7051 (2) Å, *b* = 10.4586 (2) Å, *c* = 12.1532 (3) Å, *α* = 100.599 (1)°, *β* = 91.487 (1)°, *γ* = 93.818 (1)°, *V* = 959.79 (4) Å^3 and D_{calc} = 1.410 Mg m^{-3}. In total, 3762 independent reflections were collected, of which 3045 were considered as observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least-squares procedures to final *R*-value of 3.70%.

5-Methyl-8-(phenylsulfonyl)-8*H*-naphtho[2,1-*b*]carbazole (3h)

The domino reaction of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) with 1-methylnaphthalene (0.075 g, 0.53 mmol) using anhyd $FeCl_3$ (0.015 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) at reflux for 4 h, followed by usual workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) gave naphtho[*b*]carbazole **3h** as a colorless solid; yield: 0.153 g (76%); mp 210–212 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.93 (s, 1 H), 8.64 (d, *J* = 7.5 Hz, 1 H), 8.55 (s, 1 H), 8.25 (d, *J* = 8.4 Hz, 1 H), 7.96–7.92 (m, 2 H), 7.75 (d, *J* = 7.5 Hz, 2 H), 7.61 (s, 1 H), 7.58–7.53 (m, 2 H), 7.42 (t, *J* = 7.8 Hz, 1 H), 7.33–7.26 (m, 2 H), 7.18–7.13 (m, 2 H), 2.63 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.5, 137.7, 137.5, 133.7, 132.9, 131.9, 131.7, 130.3, 129.0, 127.8, 127.3, 126.7 (2 C), 126.4 (2 C), 125.7, 124.7, 124.2, 122.8, 120.2, 115.3, 113.5, 112.6, 20.1.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{27}H_{19}NO_2SNa$ [M + Na]$^+$: 444.1034; found: 444.1032.

For further spectroscopic data, see ref. 7.

(*E*)-4-[3-Benzyl-1-(phenylsulfonyl)-1*H*-indol-2-yl]but-3-en-2-one (5)

A mixture of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) and anhyd $FeCl_3$ (0.015 g, 0.096 mmol) in anhyd benzene (10 mL) was refluxed for 24 h. Then, the usual workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) adopting the above mentioned general procedure produced 3-benzylindole **5** as a colorless solid; yield: 0.135 g (68%); mp 128–130 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 8.4 Hz, 1 H), 8.08 (d, *J* = 16.5 Hz, 1 H), 7.62 (d, *J* = 7.5 Hz, 2 H), 7.52 (t, *J* = 7.2 Hz, 1 H), 7.41–7.32 (m, 3 H), 7.27–7.20 (m, 2 H), 7.15–7.13 (m, 3 H), 6.82–6.79 (m, 2 H), 6.21 (d, *J* = 16.8 Hz, 1 H), 4.10 (s, 2 H), 2.43 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.5, 138.4, 137.9, 137.2, 134.0, 133.7, 133.2, 131.5, 131.0, 129.1, 128.7, 127.7, 126.8, 126.6, 124.8, 120.5, 116.0, 30.7, 26.8.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{24}H_{22}NO_3S$ [M + H]$^+$: 416.1302; found: 416.1309.

Hetero-Annulated Carbazoles; General Procedure

A solution of 3-bromomethylindole **4** (0.48 mmol), the respective heteroarene (0.53 mmol), and anhyd $SnCl_4$ (0.096 mmol) in anhyd 1,2-DCE (10 mL) was stirred at rt under N_2 atmosphere. After the completion of the reaction (TLC), the mixture was poured into ice-water

(30 mL) containing concd HCl (3 mL). The organic layer was separated and the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layers were washed with H_2O (2 × 20 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (silica gel, hexane/EtOAc) afforded the required heteroannulated carbazole.

5-(Phenylsulfonyl)-2-(thiophen-2-yl)-5*H*-thieno[3,2-*b*]carbazole (7a)

The domino reaction of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) with bithiophene (0.087 g, 0.53 mmol) using anhyd $SnCl_4$ (0.025 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) adopting the above-mentioned general procedure followed by column chromatographic purification (silica gel, EtOAc/hexane 1:9) furnished annulated carbazole **7a** as a colorless solid; yield: 0.153 g (72%); mp 230–232 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.57 (s, 1 H), 8.24 (d, *J* = 8.1 Hz, 1 H), 8.10 (s, 1 H), 7.79 (d, *J* = 7.5 Hz, 1 H), 7.73 (d, *J* = 7.5 Hz, 2 H), 7.46 (s, 1 H), 7.43–7.33 (m, 3 H), 7.31–7.17 (m, 4 H), 7.01–6.98 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.1, 139.3, 138.5, 137.6, 137.3, 137.0, 135.5, 133.8, 129.0, 128.0, 127.6, 126.5, 126.1, 125.8, 125.3, 125.1, 124.2, 120.2 (2 C), 115.3, 113.0, 109.3.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{24}H_{15}NO_2S_3Na$ [M + Na]$^+$: 468.0163; found: 468.0143.

For further spectroscopic data, see ref. 7.

5-(Phenylsulfonyl)-5*H*-thieno[3,2-*b*]carbazole (7b)

The domino reaction of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) with thiophene (0.08 g, 0.957 mmol) using anhyd $SnCl_4$ (0.025 g, 0.096 mmol) at rt for 3 h, followed by workup and column chromatographic purification (silica gel, EtOAc/hexane 5:95) afforded thieno[*b*]carbazole **7b** as a colorless solid; yield: 0.113 g (65%); mp 176–178 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (s, 1 H), 8.24 (d, *J* = 8.4 Hz, 1 H), 8.21 (s, 1 H), 7.80 (d, *J* = 7.5 Hz, 1 H), 7.71 (d, *J* = 7.5 Hz, 2 H), 7.43–7.38 (m, 3 H), 7.32–7.23 (m, 2 H), 7.16 (t, *J* = 7.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.5, 139.4, 137.7, 136.8, 136.2, 133.8, 129.0, 127.7, 126.5, 126.2, 125.1, 124.3, 124.2, 120.1, 115.4, 113.4, 109.6.

Anal. Calcd for $C_{20}H_{13}NO_2S_2$: C, 66.09; H, 3.61; N, 3.85; S, 17.64. Found: C, 65.82; H, 3.43; N, 3.69; S, 17.52.

2-Methyl-5-(phenylsulfonyl)-5*H*-thieno[3,2-*b*]carbazole (7c)

The annulation of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) with 2-methylthiophene (0.025 g, 0.53 mmol) in the presence of anhyd $SnCl_4$ (0.151 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) at rt for 3 h, followed by workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) led to the isolation of thieno[*b*]carbazole **7c** as a colorless solid; yield: 0.137 g (76%); mp 196–198 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56 (s, 1 H), 8.30 (d, *J* = 8.4 Hz, 1 H), 8.20 (s, 1 H), 7.82 (d, *J* = 7.5 Hz, 1 H), 7.77 (d, *J* = 7.8 Hz, 2 H), 7.44 (t, *J* = 7.8 Hz, 1 H), 7.38–7.28 (m, 2 H), 7.25–7.20 (m, 2 H), 7.09 (s, 1 H), 2.59 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.5, 140.3, 139.1, 137.7, 136.7, 136.2, 133.7, 129.0, 127.3, 124.5, 126.4, 124.2, 122.1, 119.8, 115.3, 113.0, 108.6, 16.5.

HRMS (ESI-Ion trap, MeOH): *m*/*z* calcd for $C_{21}H_{15}NO_2S_2Na$ [M + Na]$^+$: 400.0442; found: 400.0437.

For further spectroscopic data, see ref. 7.

7-(Phenylsulfonyl)benzo[*b*]thieno[3,2-*b*]carbazole (7d)/11-(Phenylsulfonyl)benzo[*b*]thieno[2,3-*b*]carbazole (7d′)

To a solution of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) in anhyd 1,2-DCE (10 mL) were added anhyd $SnCl_4$ (0.025 g, 0.096 mmol) and benzo[*b*]thiophene (0.071 g, 0.53 mmol) and the mixture was stirred at rt under N_2 atmosphere for 3 h. The usual workup adopting the above mentioned general procedure, followed by column chromatographic purification (silica gel, EtOAc/hexane 1:9) gave an inseparable mixture of carbazoles **7d** and **7d′** as a colorless solid; yield: 0.154 g (78%); mp 174–176 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.96 (s), 8.67 (s), 8.40 (s), 8.22 (d, *J* = 8.1 Hz), 8.09–8.03 (m), 7.86 (d, *J* = 7.5 Hz), 7.77–7.71 (m), 7.42–7.25 (m), 7.71 (t, *J* = 7.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.1, 139.5, 139.4, 139.3, 138.9, 137.8, 137.7, 137.6, 134.9, 133.9 (2 C), 132.4, 129.1 (2 C), 127.9, 127.6, 127.2, 126.7 (2 C), 126.5 (2 C), 126.4, 124.7, 124.6, 124.3, 124.2, 122.9, 122.8, 121.9, 121.3, 120.1, 120.0, 115.4, 115.3, 113.6, 112.3, 108.8, 107.9.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{24}H_{15}NO_2S_2Na$ [M + Na]$^+$: 436.0442; found: 436.0442.

For further spectroscopic data, see ref. 6b.

11-(Phenylsulfonyl)-11*H*-benzofuro[3,2-*b*]carbazole (7e)

The domino reaction of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) with benzo[*b*]furan (0.062 g, 0.53 mmol) using anhyd $SnCl_4$ (0.025 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) adopting the above mentioned general procedure, followed by column chromatographic purification (silica gel, EtOAc/hexane 1:9) furnished benzofurano[*b*]carbazole **7e** as a colorless solid; yield: 0.160 g (84%); mp 208–210 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.89 (s, 1 H), 8.35 (d, *J* = 8.1 Hz, 1 H), 8.12 (d, *J* = 7.2 Hz, 1 H), 7.95 (s, 1 H), 7.92 (d, *J* = 7.8 Hz, 1 H), 7.80 (d, *J* = 7.5 Hz, 2 H), 7.58–7.51 (m, 3 H), 7.42–7.35 (m, 3 H), 7.29–7.26 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.2, 153.6, 139.4, 137.6, 134.9, 133.8, 129.0, 127.8, 127.7, 126.7 (2 C), 126.5, 124.6, 124.5, 124.2, 122.9, 121.0, 120.1, 115.6, 111.7, 107.1, 102.2.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{24}H_{16}NO_3S$ [M + H]$^+$: 398.0851; found: 398.0849.

For further spectroscopic data, see ref. 7.

2-[3,5-Di(thiophen-2-yl)phenyl]-5-(phenylsulfonyl)-5*H*-thieno-[3,2-*b*]carbazole (7f)

The domino reaction of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) with 2,2′-(5-(thiophen-3-yl)-1,3-phenylene)dithiophene (0.17 g, 0.53 mmol) using anhyd $SnCl_4$ (0.025 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) at rt for 6 h, followed by workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) adopting the general procedure as mentioned above afforded **7f** as a light brown solid; yield: 0.193 g (67%); mp 176–178 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.65 (s, 1 H), 8.25 (d, *J* = 8.1 Hz, 1 H), 8.17 (s, 1 H), 7.82 (d, *J* = 7.5 Hz, 1 H), 7.75–7.69 (m, 6 H), 7.43–7.36 (m, 4 H), 7.32–7.25 (m, 3 H), 7.22–7.18 (m, 2 H), 7.08–7.07 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.5, 143.3, 140.3, 139.4, 137.7, 137.0, 136.0, 135.9, 135.5, 133.8, 129.1, 128.2, 127.8, 126.5, 126.1, 125.6, 125.3, 124.2, 124.0, 123.6, 123.1, 120.7, 120.1, 115.4, 113.2, 109.6.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{34}H_{21}NO_2S_4$ [M$^+$]: 603.0455; found: 603.0458.

2-[3,5-Bis(3-methylthiophen-2-yl)phenyl]-3-methyl-5-(phenylsulfonyl)-5*H*-thieno[3,2-*b*]carbazole (7g)

The annulation of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) with 1,3,5-tris(3-methylthiophen-2-yl)benzene (0.193 g, 0.53 mmol) using anhyd $SnCl_4$ (0.025 g, 0.096 mmol) in anhyd 1,2-DCE at rt for 6 h, followed by workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) adopting the above mentioned general procedure afforded carbazole **7g** as a colorless solid; yield: 0.219 g (71%); mp 174–176 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.60 (s, 1 H), 8.27 (d, *J* = 8.4 Hz, 1 H), 8.23 (s, 1 H), 7.86 (d, *J* = 7.5 Hz, 1 H), 7.74 (d, *J* = 7.5 Hz, 2 H), 7.56–7.53 (m, 3 H), 7.45–7.40 (m, 1 H), 7.36–7.31 (m, 2 H), 7.24 (d, *J* = 7.8 Hz, 2 H), 7.20–7.18 (m, 2 H), 6.90 (d, *J* = 8.1 Hz, 2 H), 2.62 (s, 3 H), 2.37 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.2, 139.4, 138.8, 137.7, 137.0, 136.9, 135.6, 135.4, 135.2, 133.9, 133.8, 131.4, 129.1, 129.0, 128.8, 128.4, 127.7, 126.5, 126.3, 125.2, 124.3, 1240.0, 120.1, 115.4, 113.,2, 108.4, 15.2, 13.3.

HRMS (ESI-Ion trap, MeOH): *m*/*z* calcd for $C_{37}H_{27}NO_2S_4Na$ [M + Na]$^+$: 668.0822; found: 668.0827.

4,4-Di-(*p*-tolyl)-4*H*-indeno[1,2-*b*]thiophenocarbazole (7h)

The domino reaction of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) with 4,4-di-*p*-tolyl-4*H*-indeno[1,2-*b*]thiophene (0.185 g, 0.53 mmol) in the presence of anhyd $SnCl_4$ (0.025 g, 0.096 mmol) in anhyd 1,2-DCE at r.t. for 6 h followed by workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) furnished hetero-annulated carbazole **7h** as a colorless solid; yield: 0.208 g (69%); mp 182–184 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.42 (s, 1 H), 8.26 (d, *J* = 8.4 Hz, 1 H), 8.21 (s, 1 H), 7.80 (d, *J* = 7.5 Hz, 1 H), 7.48–7.38 (m, 5 H), 7.28 (t, *J* = 7.8 Hz, 3 H), 7.21–7.19 (m, 6 H), 7.06–6.98 (m, 5 H), 2.25 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.8, 148.3, 143.3, 140.6, 139.8, 139.3, 137.4, 137.1, 136.7, 136.6, 133.8, 133.6, 129.2, 128.7, 128.5, 127.6, 127.5, 127.1, 126.6, 126.3, 125.3, 124.5, 124.3, 120.0, 119.8, 115.5 114.8, 108.5, 63.9, 21.1.

HRMS (ESI, Q-TOF): *m*/*z* calcd for $C_{41}H_{29}NO_2S_2$ [M$^+$]: 631.1640; found: 631.1642.

For further spectroscopic data, see ref. 7.

9-(Phenylsulfonyl)-7-(*p*-tolyl)naphtho[*b*]thieno[3,2-*b*]carbazole (7i)

The reaction of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) with naphtho[*b*]thiophene (0.144 g, 0.53 mmol) using anhyd $SnCl_4$ (0.025 g, 0.096 mmol) in anhyd 1,2-DCE at rt for 4 h followed by workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) gave carbazole **7i** as a colorless solid; yield: 0.185 g (70%); mp 202–204 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.62 (s, 1 H), 8.57 (s, 2 H), 8.25 (d, *J* = 8.4 Hz, 1 H), 8.01–7.94 (m, 2 H), 7.73 (d, *J* = 7.5 Hz, 3 H), 7.45–7.40 (m, 3 H), 7.37–7.32 (m, 6 H), 7.23–7.18 (m, 2 H), 2.45 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.5, 138.9, 138.7, 138.4, 138.1, 137.7, 135.7, 133.9, 133.4, 132.5, 131.6, 131.0, 129.8, 129.7, 129.1, 128.5, 127.5, 126.5, 126.4, 126.0, 125.2, 125.1, 124.6, 124.3, 119.9, 119.2, 115.3, 112.8, 108.7, 21.5.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{35}H_{24}NO_2S_2$ [M + H]$^+$: 554.1248; found: 554.1248.

1,9-Bis(phenylsulfonyl)-1,9-dihydropyrrolo[2,3-*b*]carbazole (7j)

The annulation of 3-bromomethylindole **4** (0.2 g, 0.48 mmol) with 1-phenylsulfonylpyrrole (0.109 g, 0.53 mmol) using anhyd $SnCl_4$ (0.025 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) at rt for 3 h followed workup and column chromatographic purification (silica gel, EtOAc/hexane 2:8) adopting the general procedure yielded pyrrolocarbazole **7j** as a colorless solid; yield: 0.130 g (63%); mp 254–256 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 7.8 Hz, 2 H), 8.30 (d, *J* = 8.4 Hz, 1 H), 8.00 (d, *J* = 7.5 Hz, 1 H), 7.88 (d, *J* = 7.5 Hz, 2 H), 7.77 (d, *J* = 7.5 Hz, 2 H), 7.64 (d, *J* = 4.2 Hz, 1 H), 7.51–7.46 (m, 2 H), 7.43–7.36 (m, 4 H), 7.29–7.24 (m, 2 H), 6.82 (d, *J* = 4.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.2, 138.2, 137.7, 135.6, 133.9, 133.8, 132.5, 131.1, 129.4, 129.0, 127.8, 127.6, 126.7, 126.5, 125.0, 124.1, 120.1, 115.3, 110.2, 107.3, 104.6.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{26}H_{18}N_2O_4S_2$ [M]$^+$: 486.0708; found: 486.0703.

5-Hexyl-7-(phenylsulfonyl)-5,7-dihydroindolo[2,3-*b*]carbazole (7k)

The domino reaction 3-bromomethylindole **4** (0.2 g, 0.48 mmol) with 1-hexylindole (0.132 g, 0.53 mmol) using anhyd $SnCl_4$ (0.025 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) at rt for 3 h followed workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) adopting the general procedure gave indolo[*b*]carbazole **7k** as a colorless solid; yield: 0.142 g (62%); mp 260–262 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.96 (s, 1 H), 8.29 (d, *J* = 8.4 Hz, 1 H), 8.21 (d, *J* = 7.5 Hz, 1 H), 7.90 (d, *J* = 7.5 Hz, 1 H), 7.72 (d, *J* = 7.5 Hz, 2 H), 7.68 (s, 1 H), 7.47–7.27 (m, 6 H), 7.23 (t, *J* = 7.5 Hz, 1 H), 7.18–7.13 (m, 2 H), 4.27 (t, *J* = 7.35 Hz, 2 H), 1.83 (q, *J* = 7.35 Hz, 2 H), 1.36–1.29 (m, 2 H), 1.25–1.23 (m, 4 H) 0.79 (d, *J* = 6.9 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.7, 139.4, 138.4, 137.6, 133.5, 132.7, 128.8, 127.4, 127.2, 126.5, 126.3, 125.9, 129.0, 123.6, 112.9, 120.7, 119.8, 118.9, 115.7, 108.7, 106.9, 98.5, 43.3, 31.6, 28.8, 27.0, 22.5, 14.0.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{30}H_{29}N_2O_2S$ [M + H]$^+$: 481.1950; found: 481.1943.

For further spectroscopic data, see ref. 7.

(*E*)-3-[3-Methyl-1-(phenylsulfonyl)-1*H*-indol-2-yl]-1-phenylprop-2-en-1-one

A solution of 1-phenylsulfonyl-3-methylindole-2-carboxaldehyde (3 g, 10.03 mmol) and benzoylmethylenetriphenylphosphorane (5.71 g, 15.05 mmol) in anhyd toluene (70 mL) was refluxed for 12 h. After completion of the reaction (monitored by TLC), removal of solvent in vacuo followed by crystallization of the crude product from MeOH afforded the title vinyl indole as a colorless solid; yield: 3.54 g (84%); mp 150–151 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25–8.22 (m, 1 H), 7.97–7.91 (m, 3 H), 7.83–7.80 (m, 1 H), 7.75 (d, *J* = 7.8 Hz, 1 H), 7.51 (d, *J* = 15.6 Hz, 1 H), 7.52–7.37 (m, 6 H), 7.34–7.31 (m, 3 H), 2.71 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.3, 1414.0, 138.9, 138.3, 136.8, 135.7, 134.2, 132.8, 129.5, 128.7, 128.4, 127.4, 126.5, 125.0, 124.4, 122.3, 120.0, 116.8, 114.8, 13.4.

Anal. Calcd for $C_{24}H_{19}NO_3S$: C, 71.80; H, 4.77; N, 3.49; S, 7.99. Found: C, 71.61; H, 4.64; N, 3.26; S, 7.73.

(*E*)-3-[3-(Bromomethyl)-1-(phenylsulfonyl)-1*H*-indol-2-yl]-1-phenylprop-2-en-1-one (8)

To a solution of the above prepared (*E*)-3-[3-methyl-1-(phenylsulfonyl)-1*H*-indol-2-yl]-1-phenylprop-2-en-1-one (3.0 g, 7.48 mmol) and AIBN (0.05 g) in anhyd CCl_4 (30 mL), finely powdered NBS (1.7 g, 9.72 mmol) was added. The reaction mixture was refluxed for 2 h and then cooled to rt. The floated succinimide was filtered off and washed with CCl_4 (10 mL). The combined filtrates were concentrated in vacuo and the crude product was washed with MeOH (10 mL) to afford bromo compound **8** as a pale yellow solid; yield: 3.30 g (87%); mp 128–130 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31–8.26 (m, 2 H), 8.09 (d, *J* = 7.5 Hz, 2 H),), 7.76 (d, *J* = 7.5 Hz, 2 H), 7.62 (t, *J* = 7.5 Hz, 2 H), 7.56–7.47 (m, 4 H), 7.44–7.35 (m, 4 H), 4.69 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.2, 138.4, 137.6, 137.3, 134.8, 134.2, 133.3, 132.6, 129.3, 128.9, 128.8, 128.7, 128.6, 127.0, 126.8, 124.6, 121.5, 119.6, 115.4, 23.8.

Anal. Calcd for $C_{24}H_{18}BrNO_3S$: C, 60.01; H, 3.78; N, 2.92; S, 6.68. Found: C, 59.84; H, 3.53; N, 2.69; S, 6.46.

8,9-Dimethoxy-5-(phenylsulfonyl)-5*H*-benzo[*b*]carbazole (3b)

The domino reaction of 3-bromomethylindole **8** (0.2 g, 0.417 mmol) with veratrole (0.058 g, 0.459 mmol) using anhyd $FeCl_3$ (0.014 g, 0.084 mmol) in anhyd 1,2-DCE (10 mL) at rt for 4 h, followed by workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) gave benzo[*b*]carbazole **3b** as a colorless solid; yield: 0.113 g (65%).

8-(Phenylsulfonyl)-8*H*-naphtho[2,1-*b*]carbazole (3g)

A mixture of 3-bromomethylindole **8** (0.2 g, 0.48 mmol), naphthalene (0.059 g, 0.459 mmol), and anhyd $FeCl_3$ (0.014 g, 0.084 mmol) in anhyd 1,2-DCE (10 mL) was refluxed for 4 h. Then, the usual work up, followed by column chromatographic purification (silica gel, EtOAc/hexane 1:9) afforded carbazole **3g** as a colorless solid; yield: 0.130 g (77%).

2-Methyl-5-(phenylsulfonyl)-5*H*-thieno[3,2-*b*]carbazole (7a)

The annulation of 3-bromomethylindole **8** (0.2 g, 0.417 mmol) with 2-methylthiophene (0.045 g, 0.459 mmol) using anhyd $SnCl_4$ (0.151 g, 0.58 mmol) in anhyd 1,2-DCE (10 mL) at rt for 3 h, followed by usual workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) afforded thieno[*b*]carbazole **7a** as a colorless solid; yield: 0.116 g (74%).

5-(Phenylsulfonyl)-2-(thiophen-2-yl)-5*H*-thieno[3,2-*b*]carbazole (7c)

A solution of 3-bromomethylindole **8** (0.2 g, 0.417 mmol), bithiophene (0.054 g, 0.459 mmol), and anhyd $SnCl_4$ (0.025 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) was stirred at rt for 3 h. Then, the usual workup, followed by column chromatographic purification (silica gel, EtOAc/hexane 1:9), furnished annulated carbazole **7c** as a colorless solid; yield: 0.130 g (70%).

11-(Phenylsulfonyl)-11*H*-benzofuro[3,2-*b*]carbazole (7e)

The reaction of 3-bromomethylindole **8** (0.2 g, 0.417 mmol) with benzofuran (0.054 g, 0.459 mmol) in the presence of anhyd $SnCl_4$ (0.025 g, 0.096 mmol) at rt for 3 h, followed by workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) furnished benzofurano[*b*]carbazole **7e** as a colorless solid; yield: 0.126 g (76%).

(*E*)-4-[2-(Bromomethyl)-1-(phenylsulfonyl)-1*H*-indol-3-yl]but-3-en-2-one (9)

To a solution of 1-phenylsulfonyl-2-methylindole[10] (3.0 g, 8.85 mmol) in anhyd CCl_4 (50 mL) were added AIBN (0.05 g) and finely powdered NBS (1.89 g, 10.62 mmol). The reaction mixture was refluxed for 2 h and cooled to rt. The floated succinimide was filtered off and washed with CCl_4 (15 mL). The combined filtrates were concentrated in vacuo to afford bromo compound **9** as a light brown solid; yield: 2.84 g (76%); mp 122–124 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.4 Hz, 1 H), 7.96 (d, *J* = 7.5 Hz, 2 H), 7.80–7.70 (m, 2 H), 7.60–7.55 (m, 1 H), 7.48–7.32 (m, 4 H), 6.93 (d, *J* = 16.2 Hz, 1 H), 5.20 (s, 2 H), 2.42 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.8, 138.8, 137.1, 136.8, 134.4, 132.1, 129.9, 129.4, 127.1, 127.0,126.6, 124.7, 120.6, 119.4, 115.21, 28.1, 21.5.

For further spectroscopic data, see ref. 10.

7,9-Dimethyl-5-(phenylsulfonyl)-5*H*-benzo[*b*]carbazole (10a)

To a solution of 2-bromomethylindole **9** (0.2 g, 0.48 mmol) and *m*-xylene (0.076 g, 0.718 mmol) in anhyd 1,2-DCE (10 mL) was added anhyd $FeCl_3$ (0.01 g, 0.096) and the mixture was refluxed under N_2 atmosphere for 6 h. Then, the usual workup, followed by column chromatographic purification (silica gel, EtOAc/hexane 1:9) gave benzo[*b*]carbazole **10a** as a colorless solid; yield: 0.118 g (64%); mp 206–208 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.72 (s, 1 H), 8.25 (d, *J* = 8.1 Hz, 1 H), 8.09 (s, 1 H), 7.86 (d, *J* = 7.8 Hz, 1 H), 7.70 (d, *J* = 7.5 Hz, 2 H), 7.47–7.40 (m, 2 H), 7.30–7.25 (m, 2 H), 7.17–7.12 (m, 3 H), 2.73 (s, 3 H), 2.40 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.1, 137.6, 136.8, 134.5, 134.3, 133.7, 131.1, 130.6, 129.3, 129.0 (2 C), 128.2, 126.6, 126.5, 125.2, 124.3, 120.6, 118.2, 115.5, 108.8, 21.6, 19.9.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{24}H_{19}NO_2S$ [M$^+$]: 385.1136; found: 385.1130.

For further spectroscopic data, see ref. 7.

12-(Phenylsulfonyl)-12*H*-naphtho[1,2-*b*]carbazole (10b)

A mixture of 2-bromomethylindole **9** (0.2 g, 0.48 mmol), anhyd $FeCl_3$ (0.015 g, 0.096 mmol), and naphthalene (0.076 g, 0.53 mmol) in anhyd 1,2-DCE (10 mL) was refluxed for 4 h. Then, the usual workup, followed by the column chromatographic purification (silica gel, EtOAc/hexane 1:9) gave naphthocarbazole **10b** as a colorless solid; yield: 0.121 g (62%); mp 210–212 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.58 (s, 1 H), 8.84 (d, *J* = 8.1 Hz, 1 H), 8.31 (d, *J* = 8.1 Hz, 1 H), 8.26 (s, 1 H), 7.94 (d, *J* = 7.2 Hz, 1 H), 7.84 (d, *J* = 7.5 Hz, 1 H), 7.78–7.73 (m, 3 H), 7.70–7.64 (m, 2 H), 7.58 (t, *J* = 7.2 Hz, 1 H), 7.47 (t, *J* = 7.65 Hz, 1 H), 7.36–7.29 (m, 2 H), 7.20–7.15 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.8, 137.9, 137.6, 133.8, 132.1, 130.6, 130.3, 130.1, 129.1, 129.0, 128.6, 128.2, 127.0, 126.9, 126.8, 126.5, 126.4, 126.3, 124.3, 123.2, 120.5, 119.2, 115.5, 108.2.

HRMS (EI, Q-TOF): *m*/*z* calcd for $C_{26}H_{17}NO_2S$ [M$^+$]: 407.0980; found: 407.0971.

For further spectroscopic data, see ref. 7.

5-Methyl-12-(phenylsulfonyl)-12*H*-naphtho[1,2-*b*]carbazole (10c)

The domino reaction of 2-bromomethylindole **9** (0.2 g, 0.48 mmol) with 1-methylnaphthalene (0.082 g, 0.53 mmol) using anhyd $FeCl_3$ (0.015 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) at reflux for 4 h, followed by the usual workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) furnished naphtho[*b*]carbazole **10c** as a colorless solid; yield: 0.131 g (65%); mp 204–206 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.42 (s, 1 H), 8.76 (d, *J* = 7.8 Hz, 1 H), 8.22 (d, *J* = 8.4 Hz, 1 H), 7.90 (s, 1 H), 7.86 (d, *J* = 8.1 Hz, 1 H), 7.73 (d, *J* = 7.8 Hz, 1 H), 7.68 (d, *J* = 7.5 Hz, 2 H), 7.61–7.49 (m, 2 H), 7.38–7.35 (m, 2 H), 7.22–7.13 (m, 2 H), 7.06–7.01 (m, 2 H), 2.51 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.7, 137.7, 137.3, 133.8, 132.2, 131.9, 130.6, 129.5, 129.1, 129.0, 128.0, 126.9, 126.6, 126.5, 126.4, 124.8, 124.3, 123.4, 120.5, 118.3, 115.5, 108.0, 20.0.

Anal. Calcd for $C_{27}H_{19}NO_2S$: C, 76.93; H, 4.54; N, 3.32; S, 7.61. Found: C, 76.71; H, 4.37; N, 3.09; S, 7.46.

For further spectroscopic data, see ref. 7.

9-(Phenylsulfonyl)-9*H*-thieno[2,3-*b*]carbazole (10d)

To a solution of 2-bromomethylindole **9** (0.2 g, 0.48 mmol) and thiophene (0.08 g, 0.957 mmol) in anhyd 1,2-DCE (10 mL) was added anhyd $SnCl_4$ (0.025 g, 0.096 mmol) and the reaction mixture was stirred at rt for 3 h. Then, the mixture was poured into ice-water (30 mL) containing concd HCl (3 mL). The organic layer was separated and the aqueous layer was extracted with DCM (2 × 20 mL). The combined extracts were washed with H_2O (3 × 30 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (silica gel, EtOAc/hexane 1:9) afforded thieno[*b*]carbazole **10d** as a colorless solid; yield: 0.106 g (61%); mp 170–172 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.76 (s, 1 H), 8.25 (d, *J* = 7.8 Hz, 1 H), 8.19 (s, 1 H), 7.85 (d, *J* = 7.5 Hz, 1 H), 7.73 (d, *J* = 7.5 Hz, 3 H), 7.44–7.39 (m, 2 H), 7.33–7.26 (m, 2 H), 7.20 (t, *J* = 7.8 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.7, 139.1, 137.6, 136.5, 133.8, 129.0, 127.6, 126.6, 126.5 (2 C), 125.2, 124.1, 123.4, 120.1 115.3, 114.1, 108.5.

Anal. Calcd for $C_{20}H_{13}NO_2S_2$: C, 66.09; H, 3.61; N, 3.85; S, 17.64. Found: C, 65.87; H, 3.49; N, 3.92; S, 17.38.

2-Methyl-9-(phenylsulfonyl)-9*H*-thieno[2,3-*b*]carbazole (10e)

The domino reaction of 2-bromomethylindole **9** (0.2 g, 0.48 mmol) with 2-methylthiophene (0.052 g, 0.53 mmol) using anhyd $SnCl_4$ (0.025 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) at rt for 3 h, followed by workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) gave thieno[*b*]carbazole **10e** as a colorless solid; yield: 0.130 g (72%); mp 206–208 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.62 (s, 1 H), 8.22 (d, *J* = 8.1 Hz, 1 H), 7.96 (s, 1 H), 7.79 (d, *J* = 7.5 Hz, 1 H), 7.70 (d, *J* = 7.5 Hz, 2 H), 7.38 (t, *J* = 7.65 Hz, 1 H), 7.32–7.23 (m, 2 H), 7.19–7.14 (m, 2 H), 6.91 (s, 1 H), 2.51 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.1, 139.7, 138.9, 137.7, 137.4, 135.8, 133.7, 129.0, 127.3, 126.8, 126.4, 124.9, 124.0, 121.0, 119.9, 115.3, 112.9, 108.2, 16.3.

Anal. Calcd for $C_{21}H_{15}NO_2S_2$: C, 66.82; H, 4.01; N, 3.71; S, 16.99. Found: C, 66.58; H, 3.86; N, 3.69; S, 16.73.

For further spectroscopic data, see ref. 7.

9-(Phenylsulfonyl)-2-(thiophen-2-yl)-9*H*-thieno[2,3-*b*]carbazole (10f)

Annulation of 2-bromomethylindole **9** (0.2 g, 0.48 mmol) with bithiophene (0.087 g, 0.53 mmol) using anhyd $SnCl_4$ (0.025 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) adopting the above mentioned general procedure, followed by workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) furnished thienocarbazole **10f** as a colorless solid; yield: 0.138 g (65%); mp 186–188 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.61 (s, 1 H), 8.20 (d, *J* = 8.4 Hz, 1 H), 7.95 (s, 1 H), 7.75–7.69 (m, 3 H), 7.37 (t, *J* = 7.65 Hz, 1 H), 7.30–7.20 (m, 3 H), 7.18–7.13 (m, 4 H), 6.93 (t, *J* = 7.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.0, 138.9, 137.5, 137.3, 137.2, 137.1, 136.4, 133.8, 129.0, 128.0, 127.6, 126.4, 125.6, 125.4, 125.1, 124.1, 120.0, 119.0, 115.3, 113.8, 108.2.

Anal. Calcd for $C_{24}H_{15}NO_2S_3$: C, 64.69; H, 3.39; N, 3.14; S, 21.59. Found: C, 64.47; H, 3.12; N, 3.02; S, 21.37.

For further spectroscopic data, see ref. 7.

7-(Phenylsulfonyl)benzo[*b*]thieno[3,2-*b*]carbazole (7d)/11-(Phenylsulfonyl)benzo[*b*]thieno[2,3-*b*]carbazole (7d′)

To a solution of 2-bromomethylindole **9** (0.2 g, 0.48 mmol) in anhyd 1,2-DCE (10 mL) were added anhyd $SnCl_4$ (0.025 g, 0.096 mmol) and benzo[*b*]thiophene (0.071 g, 0.53 mmol) and the mixture was stirred at rt for 3 h. Then, the usual workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) led to the isolation of an inseparable mixture of isomeric carbazoles **7d** and **7d′** as a colorless solid; yield: 0.132 g (67%); mp 230–232 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.99 (s), 8.69 (s), 8.45 (s), 8.24 (d, *J* = 7.8 Hz), 8.14 (s), 8.09–8.08 (m), 7.91–7.88 (m), 7.80 (d, *J* = 7.8 Hz), 7.75–7.71 (m), 7.41–7.34 (m), 7.32–7.25 (m), 7.22–7.14 (m).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.5, 139.4 (2 C), 137.7, 137.6, 136.7, 135.7, 135.5, 135.4, 133.9, 133.8, 129.1 (2 C), 127.9, 127.6, 127.1, 126.8, 126.7, 126.5 (2 C), 126.0, 124.7, 124.6, 124.3, 124.2, 122.9, 122.8, 121.9, 121.3, 120.1, 115.5, 115.3, 113.6, 112.3, 108.8, 108.0.

Anal. Calcd for $C_{24}H_{15}NO_2S_2$: C, 69.71; H, 3.66; N, 3.39; S, 15.51. Found: C, 69.47; H, 3.39; N, 3.24; S, 15.24.

For further spectroscopic data, see ref. 7.

7-(Phenylsulfonyl)-7*H*-benzofuro[2,3-*b*]carbazole (10g)

The domino reaction of 2-bromomethylindole **9** (0.2 g, 0.48 mmol) with benzofuran (0.062 g, 0.53 mmol) using anhyd $SnCl_4$ (0.025 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) adopting the general procedure, followed by workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) gave benzofuranocarbazole **10g** as a colorless solid; yield: 0.144 g (76%); mp 190–192 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.44 (s, 1 H), 8.27–8.25 (m, 2 H), 7.87 (t, *J* = 6.9 Hz, 2 H), 7.75 (d, *J* = 7.8 Hz, 2 H), 7.49 (d, *J* = 8.1 Hz, 1 H), 7.42–7.26 (m, 5 H), 7.24–7.16 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.0, 156.1, 138.9, 138.0, 137.6, 133.9, 129.0, 127.1, 126.9, 126.5, 126.4, 124.2, 123.9, 122.9, 122.8, 121.6, 120.4, 119.7, 115.2, 111.6, 111.1, 98.9.

Anal. Calcd for $C_{24}H_{15}NO_3S$: C, 72.53; H, 3.80; N, 3.52; S, 8.07. Found: C, 72.29; H, 3.58; N, 3.27; S, 7.81.

For further spectroscopic data, see ref. 7.

5-Hexyl-11-(phenylsulfonyl)-5,11-dihydroindolo[3,2-*b*]carbazole (10h)

The domino reaction of 2-bromomethylindole **9** (0.2 g, 0.48 mmol) with 1-hexylindole (0.106 g, 0.53 mmol) using anhyd $SnCl_4$ (0.025 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) following the general procedure gave indolocarbazole **10h** as a colorless solid; yield: 0.149 g (65%); mp 164–166 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.93 (s, 1 H), 8.26 (d, *J* = 8.1 Hz, 1 H), 8.18 (d, *J* = 7.8 Hz, 1 H), 7.85 (d, *J* = 7.5 Hz, 1 H), 7.69 (d, *J* = 7.5 Hz, 2 H), 7.62 (s, 1 H), 7.43–7.34 (m, 2 H), 7.31–7.16 (m, 4 H), 7.10 (t, *J* = 7.65 Hz, 2 H), 4.20 (t, *J* = 7.2 Hz, 2 H), 1.80–1.73 (m, 4 H), 1.31–1.27 (m, 2 H), 1.20–1.19 (m, 4 H), 0.76 (d, *J* = 6.3 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.7, 139.4, 138.4, 137.6, 133.6, 132.7, 128.9, 127.4, 127.2, 126.5, 126.3, 125.9, 124.0, 123.6, 122.9, 120.7, 119.8, 118.9, 115.7, 108.7, 106.9, 98.6, 43.3, 31.6, 28.9, 27.0, 22.6, 14.1.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{30}H_{29}N_2O_2S$ [M + H]$^+$: 481.1950; found: 481.1948.

For further spectroscopic data, see ref. 7.

2-[3,5-Di(thiophen-2-yl)phenyl]-9-(phenylsulfonyl)-9*H*-thieno-[2,3-*b*]carbazole (10i)

The annulation of 2-bromomethylindole **9** (0.2 g, 0.48 mmol) with 1,3,5-tri(thiophen-2-yl)benzene (0.170 g, 0.53 mmol) using anhyd $SnCl_4$ (0.025 g, 0.096 mmol) adopting the general procedure, followed by workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) gave carbazole **10i** as a colorless solid; yield: 0.182 g (63%); mp 128–130 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.69 (s, 1 H), 8.22 (d, *J* = 8.1 Hz, 1 H), 8.07 (s, 1 H), 7.79 (d, *J* = 7.8 Hz, 1 H), 7.75–7.63 (m, 5 H), 7.52 (s, 1 H), 7.41–7.33 (m, 4 H), 7.26–7.16 (m, 5 H), 7.05–7.02 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.4, 143.3, 139.5, 139.0, 137.7, 137.4, 136.6, 135.8, 135.4, 133.9, 129.1, 128.2, 128.1, 127.7, 126.5, 125.5 (2 C), 124.2, 124.0, 123.4, 123.0, 120.0, 119.7, 115.3, 114.2, 108.4.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{15}H_{10}S_2$ [M$^+$]: 603.0455; found: 603.0453.

For further spectroscopic data, see ref. 7.

5-Hexyl-10-(phenylsulfonyl)-5,10-dihydrocarbazolo[2,3-*c*]thieno-[2,3-*a*]carbazole (10j)

The domino reaction of 2-bromomethylindole **9** (0.20 g, 0.48 mmol) with thienocarbazole **11**[17] (0.16 g, 0.52 mmol) using anhyd $SnCl_4$ (0.025 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) at rt for 2 h, followed by usual workup and column chromatographic purification (silica gel; EtOAc/hexane 3:97) furnished benzo[*b*]carbazole **10j** as a colorless solid; yield: 0.177 g (63%); mp 144–148 °C.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.30 (s, 1 H, ArH), 9.16 (s, 1 H, ArH), 8.58 (d, *J* = 7.5 Hz, 1 H, ArH), 8.37 (d, *J* = 8.4 Hz, 1 H, ArH), 8.32 (d, *J* = 5.4 Hz, 1 H, ArH), 8.13 (d, *J* = 7.2 Hz, 1 H, ArH), 7.81 (d, *J* = 7.5 Hz, 2 H, ArH), 7.67 (d, *J* = 5.4 Hz, 1 H, ArH), 7.57–7.30 (m, 6 H, ArH), 7.25–7.20 (m, 2 H, ArH), 4.63 (t, *J* = 7.6 Hz, CH_2), 1.96–1.94 (m, 2 H, CH_2), 1.93–1.36 (m, 6 H, CH_2), 0.92–0.90 (m, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 139.5, 139.0, 137.7, 137.4, 136.7, 133.7, 129.0, 128.4, 127.4, 127.0, 126.5, 124.2, 123.9, 123.7, 123.2, 123.0, 122.7, 121.6, 120.9, 120.0, 115.4, 115.2, 112.5, 109.5, 108.3, 44.9, 31.6, 30.7, 26.7, 22.6, 14.0.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{36}H_{31}N_2O_2S_2$ [M + H]$^+$: 587.1827; found: 587.1819.

X-ray Crystallographic Data for Compound 10j[15]

Single-crystal of compound **10j** was obtained by crystallization from $CHCl_3$ and all calculations were performed with the SHELXL-97 program.[16] $C_{36}H_{30}N_2O_2S_2$, MW = 586.74 gmol^{-1}, triclinic crystal system, space group *P-1*, Z = 2. *a* = 8.6065 (3) Å, *b* = 12.5672 (4) Å, *c* = 13.8313 (4) Å, α = 98.402 (2)°, β = 97.736 (2), γ = 99.150 (2)°, V = 1441.89 (8) Å^3 and D_{calc} = 1.351 Mg m^{-3}. In total, 8914 independent reflections were collected, of which 4614 were considered as observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least-squares procedures to final *R*-value of 5.95%.

10-Hexyl-10*H*-thieno[2,3-*a*]carbazole (11)

To a solution of thieno[*a*]carbazole (0.8 g, 2.20 mmol) in DMSO (15 mL) was added 30% aq NaOH (10 mL) and the heterogeneous solution was stirred at rt for 6 h. After completion of the reaction (TLC), the mixture was poured over crushed ice (50 g) containing concd HCl (5 mL). The solid obtained was filtered, washed with H_2O (30 mL), and dried. The crude product was washed with 5% EtOAc/hexane (10 mL) to afford N-free carbazole. To a solution of N-free carbazole (0.35 g, 1.56 mmol) in toluene (10 mL) were added 1-bromohexane (0.3 mL, 2.03 mmol), Bu_4NBr (0.05 g) and 50% aq NaOH (10 mL). Then, the reaction mixture was heated at 80 °C for 8 h. After completion of hexylation, the organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with H_2O (2 × 20 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification led to the isolation of **11** as a colorless liquid; yield: 0.40 g (85%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.03 (d, *J* = 7.6 Hz, 1 H, ArH), 7.97 (d, *J* = 8.0 Hz, 1 H, ArH), 7.57 (d, *J* = 8.4 Hz, 1 H, ArH), 7.43 (d, *J* = 5.6 Hz, 2 H, ArH), 7.37–7.34 (m, 3 H, ArH), 4.48 (t, *J* = 7.8 Hz, 2 H, NCH_2), 1.83 (t, *J* = 7.6 Hz, 2 H, CH_2), 1.42–1.20 (m, 6 H, CH_3), 0.78 (t, *J* = 6.8 Hz, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 139.7, 139.4, 135.4, 125.1, 124.8, 123.8, 123.4, 120.0, 119.3, 118.5, 117.3, 115.2, 109.0, 44.8, 31.5, 30.7, 26.7, 22.5, 14.0.

Anal. Calcd for $C_{20}H_{21}NS$; C, 78.13; H, 6.88; N, 4.56; S, 10.43. Found: C, 78.26; H, 6.61; N, 4.52; S, 10.20.

(*E*)-3-(3-Methylthiophen-2-yl)-1-phenylprop-2-en-1-one

To a stirred solution of 3-methylthiophene-2-carboxaldehyde (90%; 2.2 g, 15.9 mmol) and acetophenone (2 g, 16.6 mmol) in EtOH (30 mL) at 0–10 °C was slowly added a solution of NaOH (2 g) in H_2O (2 mL). The reaction mixture was then stirred at the same temperature for 2 h and then poured over crushed ice (200 g) and acidified with concd HCl (10 mL). The yellow solid obtained was then filtered and dried to afford the title compound; yield: 3.1 g (86%); mp 52–53 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08–8.01 (m, 3 H), 7.61–7.48 (m, 3 H), 7.33–7.27 (m, 2 H), 6.91 (d, *J* = 5.1 Hz, 1 H), 2.41 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.7, 142.5, 138.5, 135.5, 134.6, 132.5, 131.4, 128.5, 128.3, 127.2, 120.1, 14.2.

(*E*)-3-(3-Bromomethylthiophen-2-yl)-1-phenylprop-2-en-1-one (12)

To a solution of thze above prepared(*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one (2.5 g, 10.95 mmol) in anhyd CCl_4 (40 mL) were added a catalytic amount of AIBN (0.1 g) and finely powdered NBS (2.34 g, 13.14 mmol). The reaction mixture was then refluxed for 2 h and cooled to rt. The floated succinimide was filtered off and washed with CCl_4 (10 mL). The solvent was then removed in vacuo to afford bromo compound **12** as a thick liquid; yield: 2.9 g (86%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06–8.01 (m, 3 H), 7.62–7.58 (m, 1 H), 7.53–7.48 (m, 2 H), 7.47–7.35 (m, 2 H), 7.12–7.11 (d, *J* = 5.1 Hz, 1 H), 4.62 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.5, 140.8, 137.9, 133.6, 133.0, 130.6, 128.7, 128.5, 127.9, 121.9, 24.1.

Anal. Calcd for $C_{14}H_{11}BrOS$: C, 54.74; H, 3.61; S, 10.44. Found: C, 54.56; H, 3.52; S, 10.61.

Benzo[*b*]thieno[2,3-*f*]benzofuran (13)

To a solution of bromo compound **12** (0.2 g, 0.65 mmol) in anhyd 1,2-DCE (5 mL) were added anhyd $SnCl_4$ (0.033 g, 0.13 mmol) and benzofuran (0.085 g, 0.71 mmol). Then, the reaction mixture was stirred at rt under N_2 atmosphere for 3 h. The subsequent workup, followed by column chromatographic purification (silica gel, EtOAc/hexane 2:98) afforded dibenzothiophene **13** as a red solid; yield: 0.06 g (42%); mp 178–180 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.41 (s, 1 H), 8.03–7.99 (m, 1 H), 7.95 (s, 1 H), 7.58–7.54 (m, 2 H), 7.50–7.46 (m, 1 H), 7.44–7.43 (m, 1 H), 7.38–7.34 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.1, 154.7, 139.1, 134.9, 127.8, 127.5, 123.8, 123.2, 122.7, 120.7 113.8, 111.6, 105.1.

Anal. Calcd for $C_{14}H_8OS$: C, 74.98; H, 3.60; S, 14.29. Found: C, 74.83; H, 3.48; S, 14.06.

For further spectroscopic data, see ref. 6d.

(2*E*,2′*E*)-3,3′-[2,5-Dimethyl-1-(phenylsulfonyl)-1*H*-pyrrole-3,4-diyl]bis(1-phenylprop-2-en-1-one)

A solution of pyrrole-3,4-dicarbaldehyde[9] (1 g, 3.43 mmol) and (benzoylmethylene)triphenylphosphorane (3.91 g, 10.31 mmol) in anhyd toluene (60 mL) was refluxed for 8 h. After completion of the reaction (monitored by TLC), the solvent was evaporated under vacuo. The resulting crude product upon crystallization from MeOH afforded 3,4-divinylpyrrole as colorless solid; yield: 1.53 g (90%); mp 128–130 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.5 Hz, 4 H), 7.86 (d, *J* = 15.6 Hz, 2 H), 7.78 (d, *J* = 7.5 Hz, 2 H), 7.68 (t, *J* = 7.2 Hz, 1 H), 7.60–7.52 (m, 4 H), 7.47–7.42 (m, 4 H), 7.22 (d, *J* = 15.6 Hz, 2 H), 2.60 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.8, 139.5, 138.0, 136.4, 134.3, 134.0, 132.9, 129.8, 128.7, 128.4, 126.5, 125.1, 120.5, 13.4.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{30}H_{26}NO_4S$ [M + H]$^+$: 496.1583; found: 496.1580.

(2*E*,2′*E*)-3,3′-[2,5-Bis(bromomethyl)-1-(phenylsulfonyl)-1*H*-pyrrole-3,4-diyl]bis(1-phenylprop-2-en-1-one) (14)

To a solution of the above prepared 2,5-dimethylpyrrole (1.0 g, 2.02 mmol) in anhyd CCl_4 (50 mL) were added AIBN (0.05 g) and finely powdered NBS (0.86 g, 4.84 mmol). The reaction mixture was refluxed for 2 h and cooled to rt. The floated succinimide was filtered off and washed with CCl_4 (15 mL). The combined filtrates were concentrated in vacuo to afford 2,5-bis(bromomethyl)pyrrole **14** as a brown solid; yield: 1.23 g (93%); mp 134–136 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.5 Hz, 6 H), 7.86 (d, *J* = 15.9 Hz, 2 H), 7.72 (t, *J* = 7.5 Hz, 1 H), 7.66–7.58 (m, 6 H), 7.51 (t, *J* = 7.5 Hz, 4 H), 5.01 (s, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.1, 138.6, 137.4, 135.0, 133.4, 133.1, 129.9, 128.9, 128.7, 127.6, 127.4, 124.7, 22.4.

Anal. Calcd for $C_{30}H_{23}Br_2NO_4S$: C, 55.15; H, 3.55; N, 2.14; S, 4.91. Found: C, 54.97; H, 3.38; N, 2.26; S, 4.72.

2,7-Dimethyl-10-(phenylsulfonyl)-10*H*-dithieno[2,3-*b*:3′,2′-*h*]carbazole (15a)

To a solution of 2,5-bis(bromomethyl)pyrrole **14** (0.2 g, 0.31 mmol) and 2-methylthiophene (0.066 g, 0.67 mmol) in anhyd 1,2-DCE (10 mL), was added anhyd $SnCl_4$ (0.032 g, 0.12 mmol) and the mixture stirred at rt for 3 h. Then, the mixture was poured into ice-water (50 mL). The organic layer was separated and the aqueous layer was extracted with DCM (2 × 20 mL). The combined extracts were washed with H_2O (3 × 50 mL) and dried (Na_2SO_4). Removal of solvent, followed by column chromatographic purification (silica gel, EtOAc/hexane 1:9) afforded hetero-annulated carbazole **15a** as a colorless solid; yield: 0.092 g (67%); mp 290–292 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.70 (s, 2 H), 8.13 (s, 2 H), 7.79 (d, *J* = 7.8 Hz, 2 H), 7.41 (t, *J* = 7.35 Hz, 1 H), 7.30–7.25 (m, 2 H), 7.06 (s, 2 H), 2.64 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.2, 139.6, 137.4, 136.4, 133.7, 129.0, 126.5, 125.2, 121.0, 112.8, 108.5, 96.1, 16.4.

HRMS (ESI-Ion trap, MeOH): *m*/*z* calcd for $C_{24}H_{17}NO_2S_3Na$ [M + Na]$^+$: 470.0319; found: 470.0311.

7-(Phenylsulfonyl)-7*H*-dibenzofuro[2,3-*b*:3′,2′-*h*]carbazole (15b)

The domino reaction of 2,5-bis(bromomethyl)pyrrole **14** (0.2 g, 0.31 mmol) with benzofuran (0.08 g, 0.67 mmol) in anhyd 1,2-DCE (10 mL) using anhyd $SnCl_4$ (0.032 g, 0.12 mmol) adopting the procedure similar to that of **15a**, followed by workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) furnished benzofuranocarbazole **15b** as colorless solid; yield: 0.106 g (71%); mp 298–300 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 6.3 Hz, 2 H), 8.30 (d, *J* = 6.3 Hz, 2 H), 7.91 (t, *J* = 6.6 Hz, 2 H), 7.77 (t, *J* = 6.9 Hz, 2 H), 7.52–7.48 (m, 2 H), 7.42–7.37 (m, 2 H), 7.33–7.28 (m, 3 H), 7.23–7.16 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.0, 155.8, 138.5, 137.4, 134.0, 129.1, 127.1, 126.6, 123.9, 123.0, 122.8, 121.7, 120.4, 111.7, 110.7, 99.2.

HRMS (ESI-Ion trap, MeOH): *m*/*z* calcd for $C_{30}H_{17}NO_4SNa$ [M + Na]$^+$: 510.0776; found: 510.0768.

5,8-Dihexyl-14-(phenylsulfonyl)-8,14-dihydro-5*H*-pyrrolo[3,2-*b*:4,5-*b*′]dicarbazole (15c)

The domino reaction of 2,5-bis(bromomethyl)pyrrole **14** (0.2 g, 0.31 mmol) with *N*-hexylcarbazole (0.169 g, 0.67 mmol) in anhyd 1,2-DCE (10 mL) using anhyd $SnCl_4$ (0.032 g, 0.12 mmol) adopting the procedure similar to that of **15a**, followed by workup and column chromatographic purification (Silica gel, EtOAc/hexane 1:9) furnished benzofuranocarbazole **15c** as colorless solid; yield: 0.124 g (62%); mp 298–300 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.01 (s, 2 H), 8.27 (d, *J* = 7.8 Hz, 2 H), 7.74–7.72 (m, 4 H), 7.50 (t, *J* = 7.5 Hz, 2 H), 7.41–7.38 (m, 2 H), 7.31–7.25 (m, 2 H), 7.31–7.25 (m, 3 H), 7.11 (t, *J* = 7.8 Hz, 2 H), 4.34 (t, *J* = 7.05 Hz, 4 H), 1.93 (t, *J* = 6.3 Hz, 4 H), 1.46–1.29 (m, 12 H), 0.88 (t, *J* = 6.75 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.6, 138.5, 137.1, 133.6, 133.2, 128.7, 126.9, 126.6, 126.1, 123.3, 123.0, 120.7, 118.9, 108.7, 107.6, 98.3, 43.3, 31.6, 28.9, 27.1, 22.6, 14.1.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{42}H_{44}N_3O_2S$ [M$^+$]: 654.3154; found: 654.3157.

5-Hexyl-5*H*-thieno[3,2-b]carbazole (16)

To a solution of 5-(phenylsulfonyl)-5*H*-thieno[3,2-*b*]carbazole (**7b**; 0.5 g, 1.37 mmol) in DMSO (15 mL) was added aq 30% NaOH (5 mL) and the heterogeneous solution was stirred for 3 h. After the completion of the reaction (TLC), the mixture was poured over crushed ice (50 mL) containing concd HCl (5 mL). The solid obtained was filtered, washed with H_2O (30 mL) and dried (Na_2SO_4). The crude product was washed with 5% EtOAc/hexane (10 mL) to afford 5*H*-thieno[3,2-*b*]carbazole (0.27 g). The thieno[3,2-*b*]carbazole was used as such in the next step without any further purification. To a suspension of NaH (0.107 g, 2.24 mmol) in anhyd THF (mL) at 0 °C, 5*H*-thieno[3,2-*b*]carbazole (0.25 g, 1.12 mmol) was added. After the addition was completed, the reaction mixture was stirred at rt for 2 h and then cooled to 0 °C. To this, a solution of hexyl bromide (0.22 g, 1.13 mmol) in THF (2 mL) was added and stirred for 10 min. Then, the mixture was stirred at rt for 12 h and poured over crushed ice (50 g) containing NH_4Cl (5 g). The mixture was extracted with DCM (30 mL) and the DCM layer was washed with H_2O (3 × 20 mL) and dried (Na_2SO_4). The solvent was removed under vacuo and the crude product was purified by column chromatography (silica gel, EtOAc/hexane 1:9) to afford 5-hexylthieno[3,2-*b*]carbazole **16** as a white solid; yield: 0.23 g (56%); mp 86–88 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.51 (s, 1 H), 8.11–8.09 (d, *J* = 7.5 Hz, 1 H), 7.71 (s, 1 H), 7.48–7.33 (m, 4 H), 7.22–7.17 (m, 1 H), 4.29 (t, *J* = 7.2 Hz, 2 H), 1.92–1.84 (m, 2 H), 1.43–1.29 (m, 6 H), 0.88–0.83 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.1, 139.8, 138.5, 131.6, 126.6, 126.2, 123.6, 123.0, 122.4, 120.5, 118.7, 113.6, 108.4, 101.8, 43.4, 31.7, 28.7, 27.1, 22.6, 14.0.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{20}H_{21}NS$ [M$^+$]: 307.1395; found: 307.1402.

Annulated Carbazole (17a)

The domino reaction 3-bromomethylindole **4** (0.2 g, 0.48 mmol) with 5-hexyl-5*H*-thieno[3,2-*b*]carbazole (**16**; 0.22 g, 0.72 mmol) using anhyd $SnCl_4$ (0.025 g, 0.096 mmol) in anhyd 1,2-DCE (10 mL) at rt for 4 h, followed by usual workup and column chromatographic purification (silica gel, EtOAc/hexane 1:9) adopting the above mentioned general procedure afforded carbazole **17a** as a colorless solid; yield: 0.191 g (68%); mp 148–150 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.85 (s, 1 H), 8.64–8.63 (m, 2 H), 8.46 (s, 1 H), 8.33 (d, *J* = 8.1 Hz, 1 H), 8.00 (d, *J* = 7.5 Hz, 1 H), 7.89 (d, *J* = 7.8 Hz, 2 H), 7.80 (s, 1 H), 7.69 (s, 1 H), 7.57–7.46 (m, 3 H), 7.43–7.37 (m, 2 H), 7.32–7.27 (m, 2 H), 4.35 (t, *J* = 7.05 Hz, 2 H), 2.03–1.98 (m, 2 H), 1.46–1.36 (m, 4 H), 0.94 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.0, 139.8, 139.5, 137.8, 137.3, 133.7, 132.8, 131.4, 129.0, 127.7, 127.3, 127.0, 126.6, 125.4, 124.8, 124.3 (2 C), 123.7, 122.4, 120.2,118.9, 118.8, 115.3, 114.4, 110.8, 102.8, 101.4, 43.5, 31.7, 28.2, 27.2, 22.7, 14.1.

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{36}H_{31}N_2O_2S_2$ [M + H]$^+$: 587.1827; found: 587.1824.

5-(Phenylsulfonyl)-5*H* benzo[2′,3′]benzofuro[6′,5′:4,5]thieno-[2,3-*b*]carbazole (17b)/8-(Phenylsulfonyl)-8*H*-benzo[2′,3′]benzofuro[6′,5′:4,5]thieno[3,2-*b*]carbazole (17b′)

To a solution of bromo compound **4** (0.2 g, 0.48 mmol) in anhyd 1,2-DCE (5 mL) were added anhyd $SnCl_4$ (0.025 g, 0.096 mmol) and benzo[*b*]thiophene **13** (0.118 g, 0.53 mmol). The reaction mixture was stirred at rt for 4 h, followed by usual workup column chromatographic purification (silica gel; EtOAc/hexane 3:97) to afford an inseparable mixture of benzothieno[3,2-*b*]dibenzothiophene **17b** and **17b′** as a colorless solid; yield: 0.149 g (62%); mp 296–298 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.28 (s, 1 H), 9.19 (s, 1 H), 8.92 (s, 1 H), 8.86 (s, 4 H), 8.77–8.75 (m, 4 H), 8.34–8.28 (m, 4 H), 8.24–8.23 (m, 3 H), 8.02 (d, *J* = 7.2 Hz, 2 H), 7.96 (t, *J* = 8.1 Hz, 2 H), 7.78–7.73 (m, 2 H), 7.62–7.58 (m, 2 H), 7.54–7.47 (m, 7 H).

HRMS (ESI-TOF, MeOH): *m*/*z* calcd for $C_{30}H_{18}NO_3S_2$ [M$^+$]: 504.0728; found: 504.0727.

Conflict of Interest

The authors declare no conflict of interest.

Funding Information

This work was funded by the Council of Scientific and Industrial Research (CSIR) Project [02(0376)/19/EMR-II] and University Grants Commission (UGC)-Mid Career Award [F-19-230/2018(BSR)], New Delhi.

Acknowledgment

V. S. thanks Council of Scientific and Industrial Research (CSIR) New Delhi for a fellowship. The authors thank the Department of Science and Technology Funds for the Improvement of Science and Technology (DST-FIST) New Delhi for NMR and HRMS facilities.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1387-9479.

References

(1) (a) Knölker, H.-J.; Reddy, K. R. In *The Alkaloids, Vol. 65*; Cordell, G. A., Ed.; Academic Press: Amsterdam, **2008**, 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.* **2012**, *309*, 203. (g) Roy, J.; Jana, A. K.; Mal, D. *Tetrahedron* **2012**, *68*, 6099.

(2) (a) Juret, P.; Tanguy, A.; Girard, A.; Le Talaer, J. Y.; Abbatucci, J. S.; Dat-Xuong, N.; Le Pecq, J.-B.; Paoletti, C. *Eur. J. Cancer* **1978**, *14*, 205. (b) Paoletti, C.; Le Pecq, J.-B.; Dat-Xuong, N.; Juret, P.; Garnier, H.; Amiel, J.-L.; Rouesse, J. *Recent Results Cancer Res.* **1980**, *74*, 107. (c) Juret, P.; Heron, J. F.; Couette, J. E.; Delozier, T.; Le Talaer, J. Y. *Cancer Treat. Rep.* **1982**, *66*, 1909. (d) Dodion, P.; Rozencweig, M.; Nicaise, C.; Piccart, M.; Cumps, E.; Crespeigne, N.; Kisner, D.; Kenis, Y. *Eur. J. Cancer Clin. Oncol.* **1982**, *18*, 519.

(3) (a) Remers, W. A.; Dorr, R. T. *Chemistry Biology and Therapeutics of the Mytomycins*, In *Alkaloids: Chemical and Biological Perspectives, Vol. 6: Pelletier S. W*; Wiley: New York, **1988**, 1–74. (b) Nettleton, D. E.; Doyle, T. W.; Krishnan, B.; Matsumoto, G. K.; Clardy, J. *Tetrahedron Lett.* **1985**, *26*, 4011.

(4) Díaz, J. L.; Dobarro, A.; Villacampa, B.; Velasco, D. *Chem. Mater.* **2001**, *13*, 2528.

(5) (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) Guan, M.; Chen, Z.; Bian, Z.; Liu, Z.; Gong, G.; Baik, W.; Lee, H.; Huang, C. *Org. Electron.* **2006**, *7*, 330. (e) Levick, M. T.; Coote, S. C.; Grace, I.; Lambert, C.; Turner, M. L.; Procter, D. J. *Org. Lett.* **2012**, *14*, 5744. (f) 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. (g) Gratia, P.; Magomedov, A.; Malinauskas, T.; Daskeviciene, M.; Abate, A.; Ahmad, S.; Grätzel, M.; Getautis, V.; Nazeeruddin, M. K. *Angew. Chem. Int. Ed.* **2015**, *54*, 11409. (h) Konidena, R. K.; Chung, W. J.; Lee, J. Y. *Org. Lett.* **2020**, *22*, 2786. (i) Xu, P.; Zhang, C.-R.; Wu, Y.-Z.; Yuan, L.-H.; Chen, Y.-H.; Liu, Z.-J.; Chen, H. S. *J. Phys. Chem. A* **2020**, *124*, 3626.

(6) (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., Sect. B: Org. Chem. Incl. Med. Chem.* **2011**, *50*, 843. (d) Dhayalan, V.; Mohanakrishnan, A. K. *Synth. Commun.* **2012**, *42*, 2149.

(7) Sureshbabu, R.; Saravanan, V.; Dhayalan, V.; Mohanakrishnan, A. K. *Eur. J. Org. Chem.* **2011**, *5*, 922.

(8) (a) Tang, R.-Y.; Li, J.-H. *Chem. Eur. J.* **2010**, *16*, 4733. (b) Suarez, A.; Garcia, P. P.; Manuel, A.; Rodriguez, F.; Sanz, R. *Adv. Synth. Catal.* **2014**, *356*, 374. (c) Zou, J.-F.; Wang, H.; Li, L.; Xu, Z.; Yang, K-F.; Wen, L. *RSC Adv.* **2014**, *4*, 47272. (d) Wu, J.; Halong, D.; Wu, F.; Li, X.; Wan, B. *Org. Biomol. Chem.* **2014**, *12*, 6806.

(9) Saravanan, V.; Mageshwaran, T.; Mohanakrishnan, A. K. *J. Org. Chem.* **2016**, *81*, 8633.

(10) Mohanakrishnan, A. K.; Srinivasan, P. C. *J. Org. Chem.* **1995**, *60*, 1939.

(11) Suchand, B.; Krishna, J.; Mritunjoy, K.; Satyanarayana, G. *RSC Adv.* **2014**, *4*, 13941.

(12) For aromatization via elimination of acetone, see: Uchuskin, M. G.; Pilipenko, A. S.; Serdyuk, O. V.; Trushkov, I. V.; Butin, A. V. *Org. Biomol. Chem.* **2012**, *10*, 7262.

(13) Frohner, W.; Krahl, M. P.; Reddy, K. R. *Heterocycles* **2004**, *63*, 2393.

(14) (a) Grotta, H. M.; Riggle, C. J.; Bearse, A. E. *J. Org. Chem.* **1961**, *26*, 1509. (b) Kistenmacher, A.; Mullen, K. *J. Heterocycl. Chem.* **1992**, *29*, 1237. (c) Knölker, H.-J.; Reddy, K. R. *Tetrahedron* **2000**, *56*, 4733.

(15) CCDC 1812297 (**3g**) and CCDC 1825263 (**10j**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

(16) (a) Sheldrick, G. M. *SHELXS97*; University of Göttingen: Göttingen, **1997**. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

(17) Sankar, E.; Raju, P.; Karunakaran, J.; Mohanakrishnan, A. K. *J. Org. Chem.* **2017**, *82*, 13583.

(18) Matthews, J. M.; Qin, N.; Colburn, R. W.; Dax, S. L.; Hawkin, M.; McNally, J. J.; Reany, L.; Youngman, M. A.; Baker, J.; Hutchinson, T.; Liu, Y.; Lubin, M. L.; Neeper, M.; Brandt, M. R.; Stone, D. J.; Flores, C. M. *Bioorg. Med. Chem. Lett.* **2012**, *22*, 2922.