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A one pot synthesis of annulated carbazole analogs

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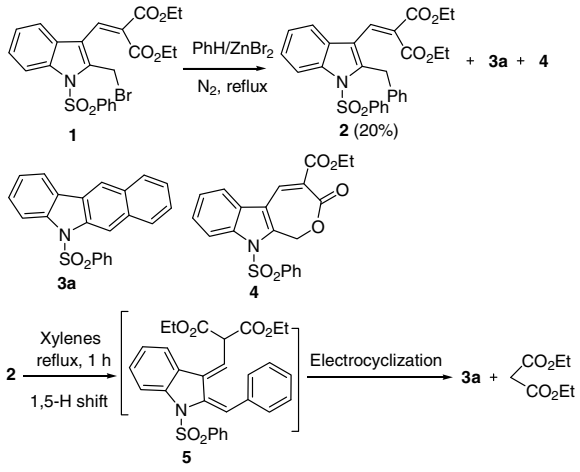
ABSTRACT

A $ZnBr_2$-mediated arylation of N-protected 2/3-bromomethylindoles containing an electron-deficient malonylidene unit with arenes at 80 °C led to the formation of arylated products, which on unprecedented 1,5-sigmatropic rearrangement followed by electrocyclization and subsequent aromatization with loss of diethylmalonate furnished the corresponding annulated carbazoles in reasonable yields.

The discovery of technologically promising electronic and optical properties in fused aromatic compounds necessitates the development of new synthetic routes to such systems.[1] Recently, a plethora of aromatic and heteroaromatic annulation reactions has been reported.[2] Ever since the first isolation of a carbazole alkaloid,[3] organic chemists have been interested in the synthesis of carbazole and its derivatives, due to their promising biological activities. Recently, Knölker and Reddy extensively reviewed the synthesis of biologically active carbazole alkaloids.[4] Carbazole and its annulated derivatives due to their unique optical, electrical, and chemical properties are often used as functional building blocks in the construction of organic materials for optoelectronic devices.[5–7] Very recently, several benzo and naphthocarbazole analogs have been explored as potential anticancer agents.[8]

Even though, a variety of arylation protocols are known for benzylic bromides,[9–12] they are yet to be adopted for the arylation of N-protected bromomethylindoles.[13] In continuation of our interest on synthetic elaboration of N-protected bromomethylindoles,[14] we wanted to prepare N-protected-2-benzylindole **2** from the bromo compound **1**. However, the direct phenylation of bromo compound **1**[15] in the presence of $ZnBr_2$ in dry benzene at reflux was found to be troublesome. Careful column chromatographic separation of the reaction mixture led to the isolation of benzo[*b*]carbazole **3a** (25%) and lactone **4** (5%), in addition to the expected 2-benzylindole **2** (20%). The formation of benzo[*b*]carbazole **3a** might only occur from the benzylindole **2**. Hence, the *N*-phenylsulfonyl-2-benzylindole **2** was refluxed in xylenes for 1 h. Removal of the solvent, followed by column chromatographic purification led to the isolation of carbazole **3a** (60%) and diethyl malonate. It is apparent that compound **2** underwent, a thermally facile 1,5-hydrogen shift to form intermediate **5**, which on electrocyclization followed by subsequent elimination of diethyl malonate[16] afforded carbazole **3a** (Scheme 1). The formation of seven-membered lactone **4** might be realized through loss of ethyl bromide from bromo compound **1**, which was confirmed via the formation of **4** (40%) upon refluxing



Scheme 1. Phenylation of bromo compound **1**.

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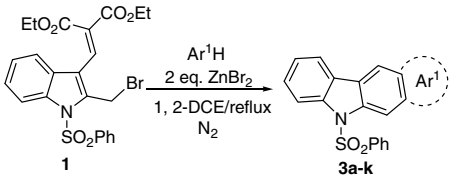
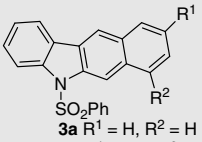
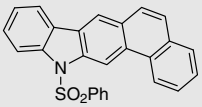
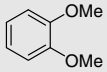
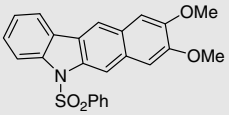
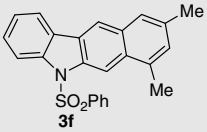
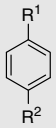
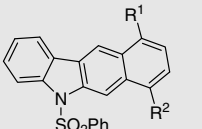
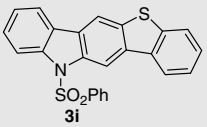
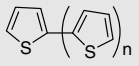
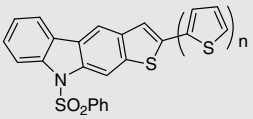


Scheme 2. Annulation of bromo compound **1** with arenas.

Table 1
Annulation of bromo compound **1** with arenes/heteroarenes[a]

Entry	ArH	Time (h)	Product[24]	Yield[b] (%) mp
1		24 1 1	 **3a** R^1 = H, R^2 = H **3b** R^1 = Me, R^2 = H **3b′** R^1 = H, R^2 = Me **3c** R^1 = OMe, R^2 = H	25[c–e] (158 °C) 50[f] (180–184 °C) 62 (200 °C)
2		5	 **3d**	40[d] (212 °C)
3		2	 **3e**	57 (210 °C)
4		1	 **3f**	55 (208 °C)
5		1, 2, 4 2	 **3g** R^1, R^2 = Me **3h** R^1, R^2 = OMe	50, 54,[g] 47[h] (182 °C) 52 (170 °C)
6		1	 **3i**	0
7		1.5 2	 **3j** n = 1 **3k** n = 2	48 (188 °C) 40 (244 °C)

[a] Reaction conditions: bromo compound **1** (0.57 mmol), Ar^1H (0.68 mmol), $ZnBr_2$ (1.15 mmol), 1,2-DCE (10 mL), 80 °C.
[b] Isolated yield after column chromatography.
[c] Benzene was used as solvent.
[d] Lactone **4** (5–10% yield) was also isolated.
[e] The corresponding arylated product was also isolated.
[f] Product **3b** was obtained as an inseparable 1:1 mixture of **3b** + **3b′** (based on ^1H NMR integration) of isomeric carbazoles.
[g] Yield obtained using 20 mol % $InCl_3$.
[h] Yield obtained using 2 equiv of anhydrous $FeCl_3$.

1 with 2 equiv of anhydrous $ZnBr_2$ in dry 1,2-DCE. A survey of the literature revealed that thermolysis of ethyl 2,4-diacetoxy-6-bromomethylbenzoate under vacuum led to the formation of 5,7-diacetoxyphthalide in excellent yield.[17]

Hibino and co-workers utilized base-mediated thermal electrocyclization of in situ generated N-protected-2,3-divinylindole at a moderate temperature for the synthesis of carbazole alkaloids.[18] Nevertheless, thermal electrocyclization of the in situ generated 2,3-divinylindole was observed only at very high temperature (460–500 °C).[19] Since, under thermal conditions, the electrocyclization has to occur with N-free-2,3-divinylindole, an elevated temperature was essential. Only when the nitrogen lone pair was tightly held by an electron withdrawing phenylsulfonyl unit, can the indole-2,3-divinyl system act as a typical triene, which in turn promotes smooth electrocyclization at a moderate temperature.[20]

Being surprised by this annulation sequence promoted by a facile 1,5-sigmatropic hydrogen shift, we tested this protocol with

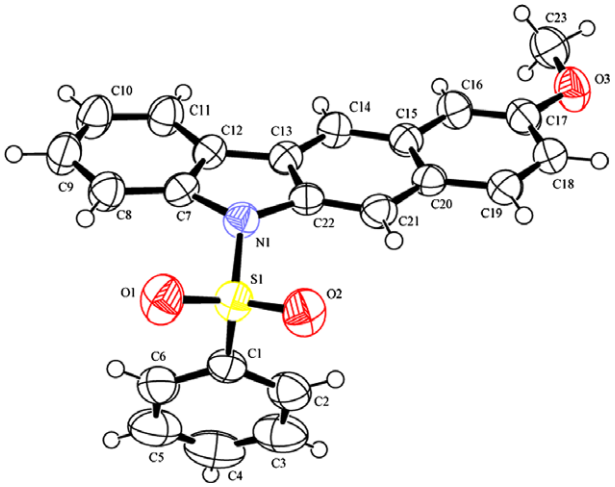


Figure 1. ORTEP diagram of carbazole **3c**.

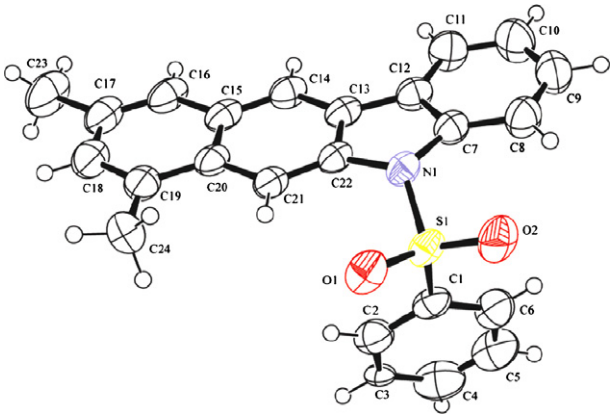
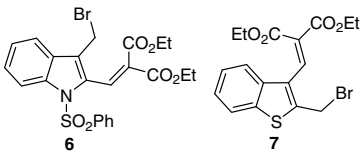
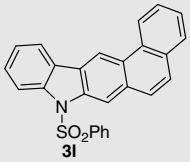
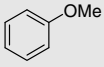
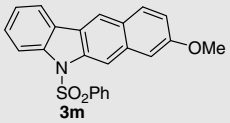
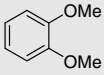
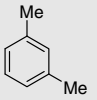
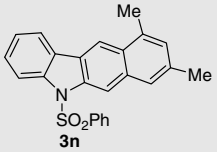
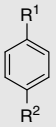
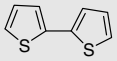
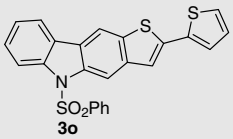
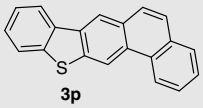
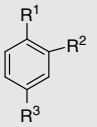
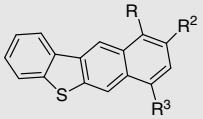
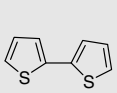
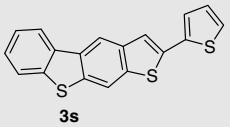


Figure 2. ORTEP diagram of carbazole **3f**.



Scheme 3.

Table 2
Annulation of bromo compounds **6** and **7** with arenes/heteroarenes[a]

Substrate	ArH	Time (h)	Product[24]	Yield[b] (%) mp
6		10	**3a**	25[c–e] (158 °C)
6		4	 **3l**	43[d] (186 °C)
6		1	 **3m**	45[e] (214 °C)
6		2	**3e**	58[e] (210 °C)
6		1	 **3n**	54 (228 °C)
6		1 2	**3g** R^1, R^2 = Me **3h** R^1, R^2 = OMe	58[e] (182 °C) 56 (170 °C)
6		2	 **3o**	47 (228 °C)
7		3	 **3p**	46 (220 °C)
7		2 2	 **3q** R^1 = H, R^2, R^3 = Me **3r** R^1, R^3 = Me, R^2 = H	61 (148 °C) 57 (150 °C)
7		2	 **3s**	49 (208 °C)

[a] Reaction conditions: bromo compound (0.57 mmol), Ar[1]H (0.68;mmol), $ZnBr_2$ (1.15 mmol), 1,2-DCE (10 mL), 80 °C.
[b] Isolated yield after column chromatography.
[c] Benzene was used as solvent.
[d] Lactone **4** (5–10% yield) was also isolated.
[e] Corresponding arylated product was also isolated.

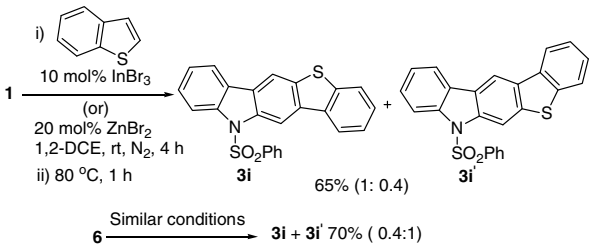
various arenes/heteroarenes. To our delight, bromo compound **1** on heating with arenes in the presence of 2 equiv of $ZnBr_2$ led to the isolation of a variety of carbazole derivatives **3a–k**, (Scheme 2).

Details such as the nature of the arenes/heteroarenes, conditions employed, and the annulation products obtained along with their yields are summarized in Table 1. Annulation product **3a** was obtained in only 25% yield on reaction with benzene, an unactivated aryl system (Table 1, entry 1). Annulations could be carried out with different types of aryl/heteroaryl systems to afford the respective products **3a–k** in 25–62% yields. The annulation of **1** with toluene led to an inseparable 1:1 (based on ^{1}H NMR integration value) isomeric mixture of carbazoles **3b** and **3b′** (Table 1, entry 1). However, the annulation was found to be selective with anisole affording carbazole **3c** (Table 1, entry 1).

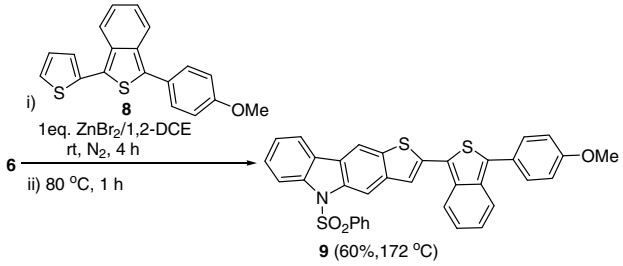
The annulation of **1** with naphthalene furnished the corresponding naphtho[*b*]carbazole **3d**, which represents an iso-steric pentacyclic framework of calothrixins.[21] In the case of unactivated aryl systems such as benzene and naphthalene, the seven-membered lactone **4** was always isolated in minor amounts. As expected, the annulation yield was found to be better with activated arenes (entries 1, 3–5). A maximum annulation yield of 62% was observed for anisole. In the case of *o*/*p*-xylene, in addition to $ZnBr_2$, the annulation was also studied using 20 mol % $InCl_3$ as well as 2 equiv of anhydrous $FeCl_3$. Under these conditions, the yield of the annulation product **3g** was only slightly enhanced with 20 mol % of expensive $InCl_3$. Reduced yields were obtained with 2 equiv of anhydrous $FeCl_3$ (entry 5). Attempted annulation of bromo compound **1** with benzo[*b*]thiophene led to a complex mixture (entry 6). However, the annulation of **1** was carried out successfully with other heterocycles. Annulation of **1** with bi-thiophene/ter-thiophene led to the isolation of products **3j** and **3k** in 48% and 40% yields, respectively (entry 7). The structure of carbazoles **3c** and **3f** was confirmed by X-ray analysis[22] (Figs. 1 and 2).

The scope and limitations of the annulation reaction were further explored with bromo compounds **6** and **7**[23] (Scheme 3).

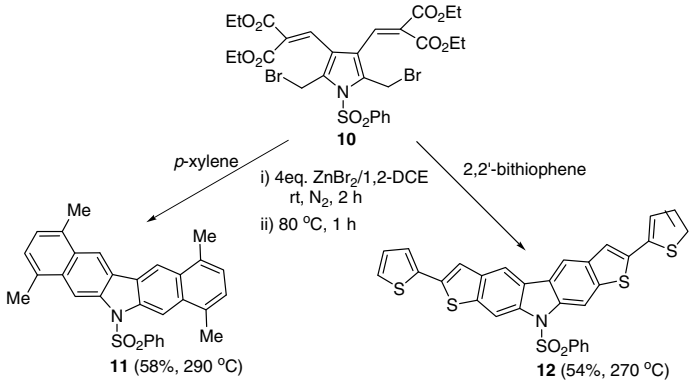
Similar to the case of bromo compound **1**, annulation of isomeric 3-bromomethylindole **6** could be performed with unactivated mono- and di-substituted arenes to afford the respective products **3a–o** (Table 2). The $ZnBr_2$-mediated arylation of bromo compound **6** with naphthalene in 1,2-DCE at 80 °C for 10 h furnished the isomeric naphtho[*b*]carbazole **3l** in 43% yield. Compared to the bromo compound **1**, annulation of **6** with anisole furnished isomeric carbazole **3g** in low yield (45%). However, the annulation of **6** could be achieved in relatively better yields with *p*-xylene/1,4-dimethoxybenzene to afford the respective carbazoles **3g**/**3h**. The



Scheme 4. Annulation of bromo compounds **1** and **6** with benzo[*b*]thiophene.



Scheme 5. Annulation of bromo compound **6** with benzo[*c*]thiophene **8**.



Scheme 6. Bis-annulation of bromo compound **10**.

annulation of **6** with bi-thiophene afforded expected product **3o** in 47% yield. The structures and yields of the annulated products **3p–s** obtained using benzo[thienyl]-2-bromomethylindole **7** are also presented in Table 2. As expected, the annulation of bromo compound **7** proceeded smoothly with arenes as well as heteroarenes using $ZnBr_2$ in 1,2-DCE at reflux to afford products **3p–s** in 46–61% yields (Table 2).

Even though annulation of bromo compound **1** was unsuccessful with benzo[*b*]thiophene in 1,2-DCE at reflux (Table 1, entry 6), the same could be performed in a stepwise manner. The heteroarylation of 2-bromomethylindole **1** with benzo[*b*]thiophene at room temperature followed by subsequent thermolysis at 80 °C for 1 h led to an inseparable mixture of annulated products **3i** and **3i′** (1:0.4 based on ^{1}H NMR integration) in 65% yield (Scheme 4). Annulation of 3-bromomethylindole **6** with benzo[*b*]thiophene under identical conditions also produced **3i** and **3i′** (0.4:1 based on ^{1}H NMR integration) in a slightly enhanced 70% yield (Scheme 4).

Heteroarylation of bromo compound **6** with 1-(4-methoxyphenyl)-3-(thiophen-2-yl)benzo[*c*]thiophene **8**[25] followed by thermolysis at 80 °C for 1 h led to the isolation of annulation product **9**[26] in 60% yield (Scheme 5).

Finally, the bis-annulation of bromo compound **10**[27] was performed with *p*-xylene/bi-thiophene using 4 equiv of $ZnBr_2$ to afford heterocycles **11** and **12**[28] in 58 and 54% yields, respectively (Scheme 6).

In summary, we have developed a one pot annulation protocol for indolyl-2/3-methylbromides and benzo[thienyl]-2-bromomethylindole containing an electron-deficient malonylidene unit at the adjacent position. The observed annulation was triggered by a simple $ZnBr_2$-mediated arylation at 80 °C. The resulting arylated products, at the same temperature, led to the formation of an in situ generated triene, which on electrocyclization followed by subsequent aromatization with loss of diethyl malonate afforded the respective annulated products in reasonable yields. The annulation methodology developed herein can be utilized with a wide variety of aryl and heteroaryl systems under mild conditions.

Acknowledgments

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References and notes

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22. Crystallographic data for **3c** and **3f** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 685765 and CCDC 685764. Copies of the data may be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 (0)1223 33603 or email: deposit@ccdc.cam.ac.uk).
23. The bromo compound **6** was prepared from the corresponding aldehyde via condensation with diethyl malonate using $TiCl_4$/pyridine, followed by allylic bromination using NBS. For the preparation of bromo compound **7** see: Sha, C.-K.; Hsu, H.-Y.; Cheng, S.-Y.; Kuo, Y.-L. *Tetrahedron* **2003**, *59*, 1477–1481.
24. *General procedure for annulation of benzylic bromo compounds* **1**, **6**, *and* **7**: To a solution of bromo compound (0.57 mmol) in dry 1,2-DCE (10 mL), $ZnBr_2$ (1.15 mmol) and arene/heteroarene (0.68 mmol) were added. The reaction mixture was then refluxed for the specified time (see Tables 1 and 2) under a N_2 atmosphere, then poured over ice-water (30 mL) containing 1 mL of concd HCl, extracted with chloroform (2 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatographic purification (silica gel, 230–420 mesh, *n*-hexane/ethyl acetate 99:1) afforded the annulation products.
5-(Phenylsulfonyl)-5H-benzo[b]carbazole (**3a**): Yield: 25%; mp 158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 8.25 (s, 1H), 7.97–7.87 (m, 3H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.48–7.42 (m, 3H), 7.33–7.30 (m, 2H), 7.19 (t, *J* = 8.1 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 134.8, 132.4, 132.0, 128.5, 127.8, 125.4, 123.8, 123.2, 123.1, 122.8, 121.7, 121.3, 121.1, 120.7, 120.0, 119.0, 115.4, 113.2, 110.1, 107.0; MS (EI) *m*/*z* (%): 357 (M^+, 58%); Anal. Calcd for $C_{22}H_{15}NO_2S$: C, 73.93; H, 4.23; N, 3.92; S, 8.97. Found: C, 73.77; H, 4.41; N, 3.79; S, 8.71.
7,10-Dimethoxy-5-(phenylsulfonyl)-5H-benzo[b]carbazole (**3h**): Yield: 52%; mp 170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.64 (s, 1H), 8.27 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.44 (t, *J* = 8.4 Hz, 1H), 7.35–7.28 (m, 1H), 7.19 (t, *J* = 7.8 Hz, 3H), 6.70–6.61 (m, 2H), 3.98 (s, 3H), 3.94 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 149.8, 149.6, 140.0, 137.7, 137.4, 133.7, 128.9, 128.2, 126.7, 126.6, 126.4, 126.1, 124.2, 123.8, 120.7, 115.4, 113.0, 107.0, 103.0, 102.0, 55.9, 55.8; MS (EI) *m*/*z* (%): 417 (M^+, 81%); Anal. Calcd for $C_{24}H_{19}NO_4S$: C, 69.05; H, 4.59; N, 3.36; S, 7.68. Found: C, 69.29; H, 4.43; N, 3.48; S, 7.86.
8-(Phenylsulfonyl)-8H-naphtho[2,1-b]carbazole (**3l**): Yield: 43%; mp 186 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.69 (s, 1H), 8.67 (d, *J* = 7.8 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.84–7.67 (m, 5H), 7.63–7.44 (m, 3H), 7.37–7.29 (m, 2H), 7.21–7.16 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 139.7, 137.7, 137.5, 133.8, 132.0, 131.7, 130.3, 129.0, 128.7, 128.1, 127.5, 127.4, 127.3, 126.8, 126.6 (2C), 126.5,126.4, 124.3, 122.5, 120.4, 115.4, 113.7, 113.4; MS (EI) *m*/*z* (%): 407 (M^+, 39%); Anal. Calcd for $C_{26}H_{17}NO_2S$: C, 76.64; H, 4.21; N, 3.44; S, 7.87. Found: C, 76.47; H, 4.39; N, 3.66; S, 7.65.
5-(Phenylsulfonyl)-2-(thiophen-2-yl)-5H-thieno[3,2-b]carbazole (**3o**): Yield: 47%; mp 228 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.16 (s, 1H), 7.87–7.79 (m, 3H), 7.52 (s, 1H), 7.50–7.25 (m, 7H), 7.06 (t, *J* = 4.4 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 140.1, 139.3, 138.5, 137.7, 137.3, 137.0, 135.5, 133.8, 129.0, 128.0, 127.7, 126.5, 126.1, 125.9, 125.3, 125.1, 124.2, 120.0, 115.3, 113.0, 109.3; MS (EI) *m*/*z* (%): 445 (M^+, 29%); Anal. Calcd for $C_{24}H_{15}NO_2S_3$: C, 64.69; H, 3.39; N, 3.14; S, 21.59. Found: C, 64.84; H, 3.62; N, 3.01; S, 21.76.
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26. *Preparation of 2-(3-(4-methoxyphenyl)benzo[c]thiophen-1-yl)-5-(phenylsulfonyl)-5H-thieno[3,2-b]carbazole* **9**: To a solution of substrate **6** (0.3 g 0.57 mmol) in dry 1,2-DCE (10 mL), $ZnBr_2$ (0.26 g 1.15 mmol) and 1-(4-methoxyphenyl)-3-(thiophen-2-yl)benzo[*c*]thiophene **8**[25] (0.22 g, 0.68 mmol) were added. The reaction mixture was stirred at room temperature for 4 h and then refluxed for 1 h under N_2 atmosphere. It was then poured over ice-water (30 mL) containing 1 mL of concd HCl, extracted with chloroform (2 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatography (silica gel, 230–420 mesh, *n*-hexane/ethyl acetate 99:1) led to the isolation of compound **9** as a yellow solid (0.21 g, 60%); mp 172 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (s, 1 H), 8.26 (d, *J* = 8.1 Hz, 1H), 8.20 (s, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.78–7.70 (m, 3H), 7.65 (s, 1H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.45–7.12 (m, 6H), 7.05 (t, *J* = 8.7 Hz, 1H), 6.9 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 159.7, 140.1, 139.3, 137.7, 137.2, 136.2, 136.0, 135.9, 135.2, 133.8, 130.6, 129.0, 127.6, 126.5, 126.2, 126.1, 125.4, 125.3, 124.9, 124.3, 124.2, 121.6, 121.4, 121.0, 119.9, 115.3, 114.8, 112.9, 109.1, 55.5; Anal. Calcd for $C_{35}H_{23}NO_3S_3$: C, 69.86; H, 3.85; N, 2.33; S, 15.99. Found: C, 69.99; H, 3.63; N, 2.51; S, 15.75; HRMS (EI) Calcd for $C_{35}H_{23}NO_3S_3$ (M): 601.0840. Found: 601.0843.
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28. *Data for 10-(phenylsulfonyl)-2,7-di(thiophen-2-yl)-10H-dithieno[2,3-b:3′,2′-h]-carbazole* **12**: Yield: 54%; mp 270 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (s, 2H), 8.16 (s, 2H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.43 (s, 2), 7.40–7.26 (m, 7H), 7.06 (t, *J* = 3.9 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 139.2, 137.5, 137.3, 137.2, 137.0, 133.9, 129.1, 128.0, 126.5, 125.6, 125.4, 125.2, 119.0, 113.8, 108.5; Anal. Calcd for $C_{30}H_{17}NO_2S_5$: C, 61.72; H, 2.94; N, 2.40; S, 27.46. Found: C, 61.92; H, 2.76; N, 2.25; S, 27.61; HRMS (EI) Calcd for $C_{30}H_{17}NO_2S_5$ (M): 582.9863. Found: 582.9867.