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A Versatile Synthesis of Annulated Carbazole Analogs Involving a Domino Reaction of Bromomethylindoles with Arenes/Heteroarenes

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A $ZnBr_2$-mediated arylation of aryl/heteroaryl methyl bromides with arenes at 80 °C led to the formation of arylated products, which underwent subsequent 1,5-sigmatropic rearrangement followed by electrocyclization and aromatization with loss of a diethylmalonate unit to afford the corresponding annulated products.

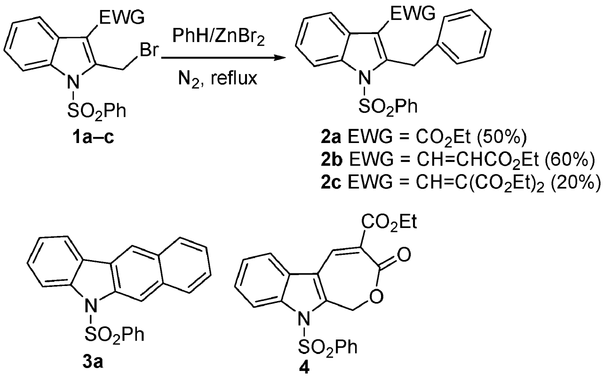
Introduction

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 have been reported.[2] Indole is one of the most important heterocycles, and its ring system is present in a large number of natural products of both marine and terrestrial origin. Among the indole alkaloids, carbazole is the most explored. Ever since the first isolation of carbazole alkaloids,[3] organic chemists have been interested in the synthesis of carbazole and its derivatives due to their promising biological activities. Knölker and Reddy extensively reviewed the synthesis of biologically active carbazole alkaloids.[4] Carbazole and its annulated derivatives, as a result of their unique optical, electrical, and chemical properties, are often used as functional building blocks in the construction of organic materials for optoelectronic devices.[5,6] A new class of semiconducting organic materials based on indolocarbazole and diindolocarbazole derivatives have also been reported.[7] Further, because of their intense luminescence, carbazole analogs have been widely used in OLEDs.[8] Recently, several benzo- and naphthocarbazole analogs have been explored as potential anticancer agents.[9]

Results and Discussion

A wide variety of arylation protocols for benzyl bromides with the use of aryl boronic acids/aryl Grignard reagents in the presence of a catalytic amount of Pd complexes,[10] $Co(acac)_3$,[11] and Cu^I[12] are reported. Lewis acid mediated arylation/heteroarylation of benzylic systems is usually explored with the use of arenes and heteroarenes.[13] Nevertheless, these recent developments are yet to be adopted for the arylation of *N*-protected bromomethylindoles.[14]

In continuation of our work on synthetic elaboration of *N*-protected bromomethylindoles,[15] we wanted to prepare *N*-protected-2-benzylindoles **2a**–**c** by starting from the respective bromides **1a**–**c** (Scheme 1).



Scheme 1. Phenylation of bromomethylindoles **1a**–**c**.

Direct phenylation of bromide **1a**/**1b** by using benzene in the presence of $ZnBr_2$ at reflux was found to be successful, affording expected products **2a**/**2b** in 50 and 60% yield, respectively. However, in the case of bromide **1c**,[16] a similar arylation reaction 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 expected 2-benzylindole **2c** (20%). The formation of seven-member lactone **4** might be realized only through the loss of ethyl bromide from bromide **1c**, which was confirmed by the formation of **4** (40%) upon refluxing **1c** with anhydrous $ZnBr_2$ (2 equiv.) in 1,2-

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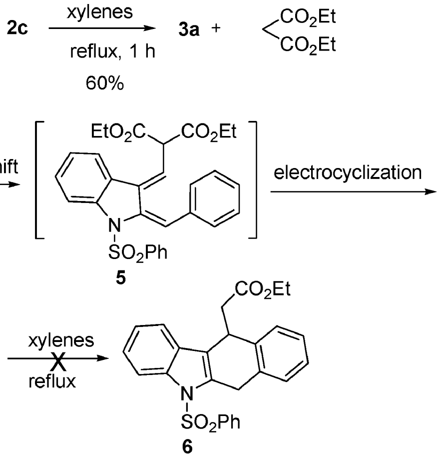
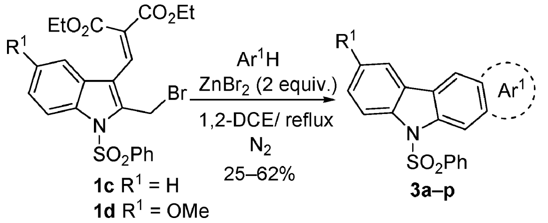
dichloroethane (1,2-DCE). In further support of our observation, survey of the literature also revealed that thermolysis of ethyl 2,4-diacetoxy-6-bromomethylbenzoate under vacuum led to the formation of 5,7-diacetoxyphthalide in excellent yield.[17] The formation of benzo[*b*]carbazole **3a** might occur only from benzylindole **2c**. Hence, *N*-phenylsulfonyl-2-benzylindole **2c** was heated at reflux 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 (Scheme 2). Obviously, compound **2c** underwent a thermally facile 1,5-hydrogen shift to form triene **5**, which upon electrocyclization followed by subsequent elimination of a diethyl malonate unit afforded carbazole **3a**. Survey of the literature revealed that Sha and coworkers achieved the syntheses of a large number of heteroaromatic pyrroles involving elimination of diethyl malonate during aromatization.[18] All our attempts to perform an annulation reaction of benzyl indole **2b** in refluxing xylenes were unsuccessful. Hence, it is clear that in the case of **2b**, the expected 1,5-hydrogen shift is not as feasible as that of **2c**.



Scheme 2. Thermolysis of 2-benzylindoles **2b** and **2c**.

It should be mentioned that base-mediated thermal electrocyclization methodology has been widely employed for the synthesis of carbazole alkaloids.[19] Indeed, thermal electrocyclization at very high temperature (460–500 °C) was utilized for the synthesis of pyrido[4,3-*b*]carbazole alkaloids.[20] In all these cases, the electrocyclization has to occur with *N*-free 2,3-divinylindole, and hence, an elevated temperature was essential. Only when the nitrogen lone pair was tightly held by an electron withdrawing phenylsulfonyl unit did the indole-2,3-divinyl system act as a typical triene, which in turn promotes smooth electrocyclization at moderate temperatures.[21]

Because of the high simplicity of the present annulation reaction, we tested this protocol with various arenes. To our delight, bromides **1c** and **1d** upon heating with arenes in the presence of $ZnBr_2$ (2 equiv.) led to the isolation of a variety of carbazole derivatives (Scheme 3). We recently reported[22] our preliminary results on annulation of bromide **1c** with arenes/heteroarenes.

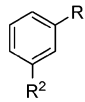
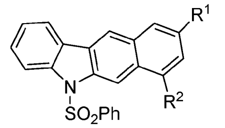
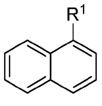
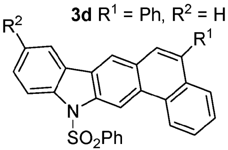
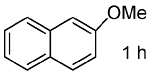
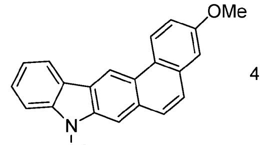
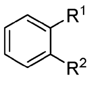
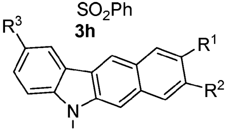
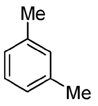
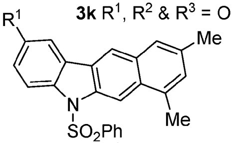
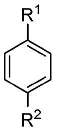
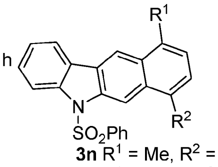


Scheme 3. Annulation of bromides **1c** and **1d** with arenes.

Details such as the nature of the arenes, 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 with benzene, an unactivated aryl system (Table 1, Entry 1). Annulations could be carried out with different types of arenes to afford benzannulated carbazoles **3a–p** in 25–62% yield (Table 1, Entries 1–6). The annulation of bromide **1c** with toluene led to the isolation of a 1:1 mixture of 1-methylbenzo[4,3-*b*]carbazole (**3b**) and 1-methylbenzo[2,3-*b*]carbazole (**3b′**). However, the annulation of **1c** with anisole furnished selectively 1-methoxybenzo[4,3-*b*]carbazole (**3c**) in a maximum yield of 62% (Table 1, Entry 1). In the case of biphenyl, in addition to annulation product **3d**, a considerable amount (22%) of arylated product was also isolated (Table 1, Entry 1). The annulation of bromide **1c** with naphthalene/1-methylnaphthalene furnished naphtho[*b*]carbazoles **3e**/**3f**, which contain an isosteric pentacyclic framework of calothrixins,[23] in 40 and 56% yield, respectively. Bromide **1d** containing a methoxy group at the indole 5-position upon similar annulation with 1-methylnaphthalene led to the isolation of product **3g** in a reduced yield of 44% (Table 1, Entry 2). The annulation of **1c** with 2-methoxynaphthalene led to the formation of isomeric annulated carbazole **3h** in 47% yield (Entry 3).

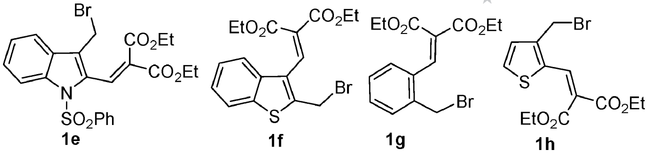
In the case of unactivated arenes such as benzene and naphthalene, seven-member lactone **4** was always isolated in minor amounts. The yields of annulated carbazoles **3i–p** obtained were moderate and almost comparable with 1,2-, 1,3-, and 1,4-disubstituted arenes (Table 1, Entries 4–6). However, a maximum annulation yield of 62% was obtained for a moderately active arene, namely, anisole. This confirms that the electron rich arenes may be favorable only for arylation and not for subsequent triene formation through 1,5-H transfer. As observed for 1-methylnaphthalene, in the case of 1,2-dimethoxybenzene an also in the presence of the 5-methoxy group of **1d** produced expected carbazole **3k** in a reduced yield of 44%. However, the annulation of bromides **1c**/**1d** with *m*-xylene formed respective carbazoles in almost identical yields. In the case of *p*-xylene, in addition to $ZnBr_2$, the annulation was also studied with the use of $InCl_3$ (20 mol-%) and anhydrous $FeCl_3$ (2 equiv.). The yield of annulation product **3n** was slightly enhanced with the use of expensive $InCl_3$ (20 mol-%), and reduced yields were always obtained with the use of anhydrous $FeCl_3$ (2 equiv.; Table 1, Entry 6). Finally, the structure of benzocarbazoles **3c** and **3l** were confirmed by X-ray analysis.[22,24]

Table 1. Annulation of bromides **1c** and **1d** with arenes.[a]

Entry	ArH	Time	Product	Yield [%][b]
1		24 h 1 h 1 h 4 h	 **3a** R^1& R^2 = H **3b** R^1 = Me, R^2 =H **3b'** R^1 = H, R^2 = Me **3c** R^1 = OMe, R^2 = H **3d** R^1 = Ph, R^2 = H	25[c-e] 50[f](**3b**+**3b'**) 62 35[e]
2		5 h 1 h 2 h	 **3e** R^1 = H, R^2 = H **3f** R^1 = Me, R^2 = H **3g** R^1 = Me, R^2 = OMe	40[d] 56 44
3		1 h	 **3h**	47
4		3 h 1 h 5 h	 **3i** R^1& R^2 = Me, R^3 = H **3j** R^1 & R^2 = OMe, R^3 = H **3k** R^1, R^2 & R^3 = OMe	56 57 44
5		1 h 2 h	 **3l** R^1 = H **3m** R^1 = OMe	55 53
6		1 h, 2 h, 4 h 2 h 2 h	 **3n** R^1 = Me, R^2 = Me **3o** R^1 = OMe, R^2 = OMe **3p** R^1 = Br, R^2 = OMe	50, 54,[g]47[h] 52 0[i]

[a] For products **3g**, **3k**, and **3m**, bromide **1d** was used. For all other cases, bromide **1c** was employed. [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. [f] Product was obtained as an inseparable 1:1 mixture of isomeric carbazoles **3b** and **3b′**. [g] Yield obtained by using 20 mol-% of InCl$_3$. [h] Yield obtained by using 2 equiv. of anhydrous of FeCl$_3$. [i] Only the corresponding arylated product was obtained in 63% yield.

The scope and limitations of the annulation reaction were further explored with isomeric bromomethylindole **1e**,[16] benzo[*b*]thienyl 3-methylbromide **1f**,[25] benzyl bromide **1g**,[26] as well as 3-bromomethylthiophene **1h** (Scheme 4).[18c]

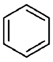
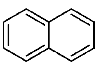
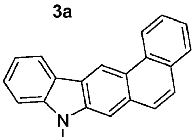
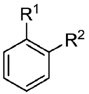
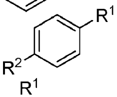
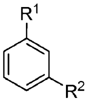
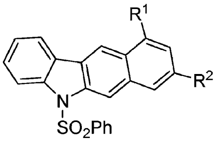
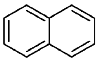
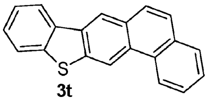
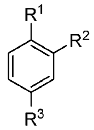
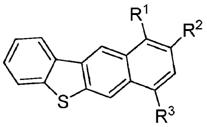
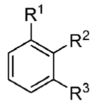
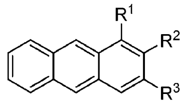
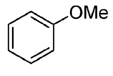
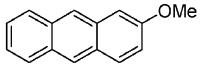
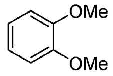
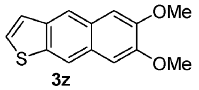


1e **1f** **1g** **1h**

Scheme 4.

Relatively, the yields of the annulation products were slightly better with isomeric 3-bromomethylindole **1e** (Table 2). The annulation of **1e** could be carried out with mono- and disubstituted arenes to afford the respective carbazoles. The ZnBr$_2$-mediated arylation of bromide **1e** with

Table 2. Annulation of bromides **1e**–**h** with arenes.

Substrate	Ar^{1}H	Time	Product	Yield [%][b]
1e		10 h	**3a**	25[b-d]
1e		6 h	 **3q**	43[c]
1e		1 h 4 h	**3i** R^1 & R^2 = Me **3j** R^1 & R^2 = OMe	58 58
1e		1 h 1 h	**3n** R^1 & R^2 = Me **3o** R^1 & R^2 = OMe	58[d] 56
1e		1 h 1 h	 **3r** R^1 & R^2 = Me **3s** R^1 = H, R^2 = OMe	54 45[d]
1f		3 h	 **3t**	46
1f		2 h 2 h	 **3u** R^1 = H, R^2, R^3 = Me **3v** R^1, R^3 = Me, R^2 = H	61 57
1g		3 h 2 h	 **3w** R^1 = H, R^2 & R^3 = Me **3x** R^1 & R^3 = Me, R^2 = H	30 35
1g		3 h	 **3y**	40
1h		3 h	 **3z**	48

[a] Isolated yield after column chromatography. [b] Benzene was used as the solvent. [c] Lactone **4** (5–10% yield) was also isolated. [d] Corresponding arylated product was also isolated.

naphthalene in 1,2-DCE at 80 °C led to the isolation of expected naphtho[*b*]carbazole **3q** in 43% yield. In comparison to isomeric bromomethylindole **1c**, the annulation of **1e** with 1,2- as well as 1,4-disubstituted benzenes proceeded in relatively better yields. In contrast, however, the annulation of **1e** with anisole provided only a reduced yield for carbazole **3s**.

Indeed, the sequential reaction of bromides **1f–h** was studied with a large number of mono- and disubstituted arenes; however, the reaction was successful only with selected arenes. The structures of annulated products **3u–z** are listed in Table 2. As expected, the annulation of benzo[*b*]thienyl-3-methylbromide **1f** with naphthalene gave naphtho[1,2-*b*]dibenzothiophene (**3t**) in 46% yield. Similarly, the annulation of **1f** with *m*-xylene and *p*-xylene also furnished products **3u** and **3w** in 61 and 57% yield, respectively. The annulation of benzyl bromide **1g** with *o*-xylene, *m*-xylene, and anisole produced corresponding anthracenes **3w–y** in 30–40% yield. Obviously, the low yields of **3w–y** might be due to the lower reactivity of bromide **1g**. The annulation of 3-bromomethylthiophene **1h** was successful only in the case of an electron-rich arene, namely, 1,2-dimethoxybenzene, to furnish naphtho[*b*]thiophene **3z** in 48% yield. As a representative case, the structure of benzo[2,3-*b*]dibenzothiophene **3u** was confirmed by X-ray analysis (Figure 1).

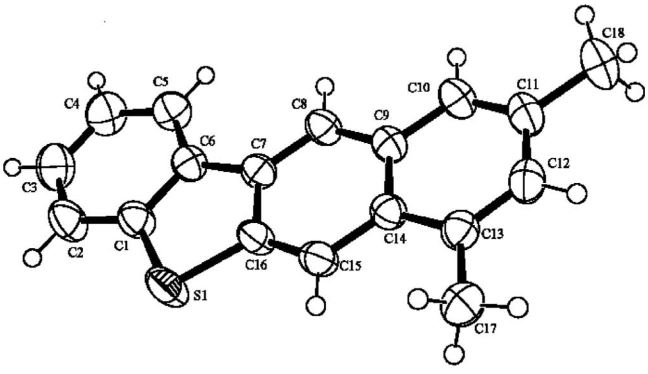
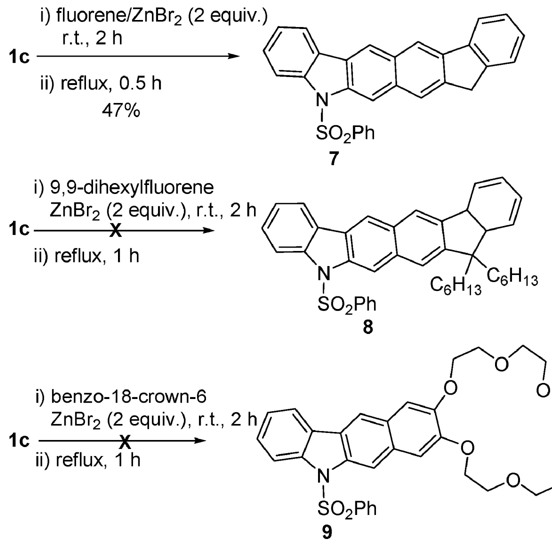


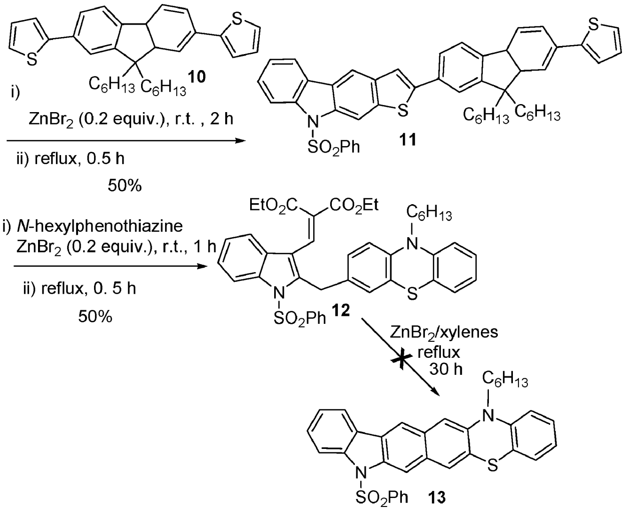
Figure 1. ORTEP view of benzo[2,3-*b*]dibenzothiophene **3u**.

The annulation of bromomethylindole **1c** with fluorene could be performed in a stepwise manner. The fluorenylation of **1c** at room temperature for 2 h followed by subsequent thermolysis at 80 °C for 0.5 h produced annulated carbazole **7** in 47% yield (Scheme 5). Surprisingly, all our attempts to carry out the annulation of **1c** with 9,9-dihexylfluorene did not give expected product **8**. Even though starting materials were consumed during arylation of **1c** with 9,9-dihexylfluorene at room temperature, subsequent thermolysis followed by column chromatographic purification did not afford any characterizable product. The observed failure to obtain **8** might be due to bis- or trisarylation of 9,9-dihexylfluorene. Similarly, the annulation of **1c** with benzo-18-crown-6 was also found to be unsuccessful (Scheme 5).



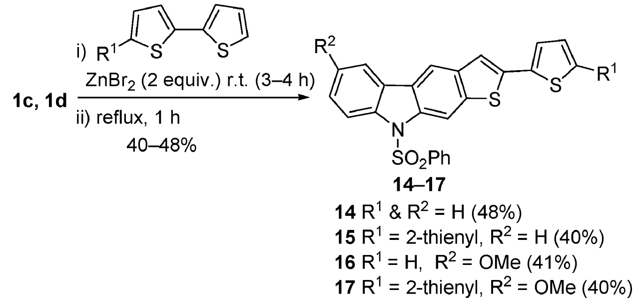
Scheme 5.

Even though the annulation of 9,9-dihexylfluorene was unsuccessful, the annulation of **1c** could be carried out successfully with heteroarene **10**[27] containing the 9,9-dihexylfluorenyl unit to furnish mixed heterocycle **11** in 50% yield (Scheme 6). The attempted annulation of **1c** with *N*-hexylphenothiazine under similar conditions led to the isolation of arylation product **12** in 50% yield. Attempted annulation of **12** in refluxing xylenes also failed to produce expected carbazole **13** (Scheme 6).



Scheme 6.

The annulation of **1c/1d** with bithiophene/terthiophene in 1,2-DCE at room temperature for 3–4 h followed by thermolysis at 80 °C for 1 h led to the formation of corresponding heterocycles **14–17** in 40–48% yields (Scheme 7). The structure of thieno[2,3-*b*]carbazole **16** was confirmed by single-crystal X-ray analysis (Figure 2).



Scheme 7.

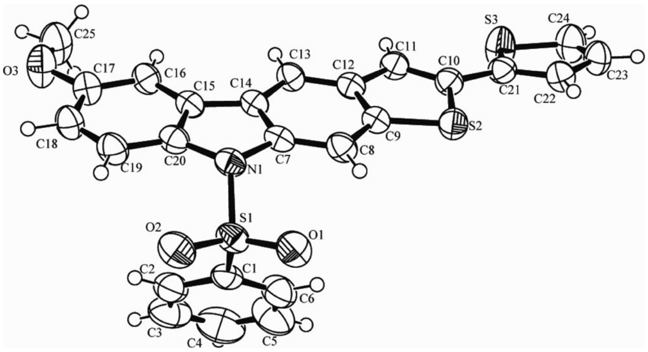
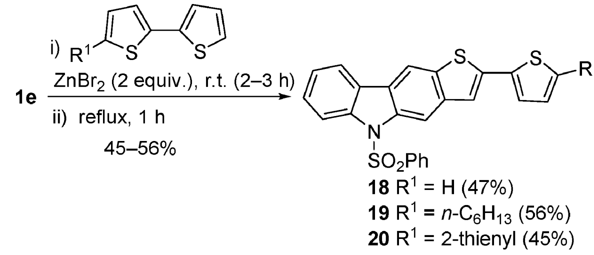


Figure 2. ORTEP view of thieno[2,3-*b*]carbazole **16**.

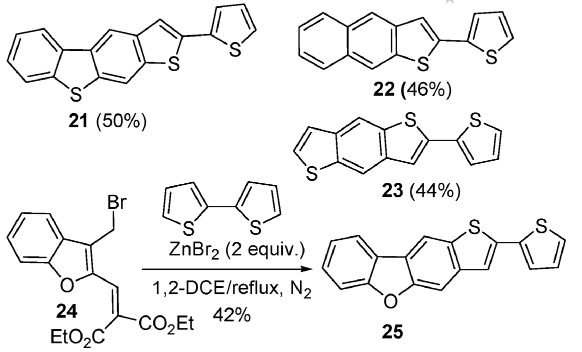
The interaction of isomeric 3-bromomethylindole **1e** with bithiophenes/terthiophene also gave expected carbazole analogs **18**–**20** in 45–56% yields (Scheme 8).



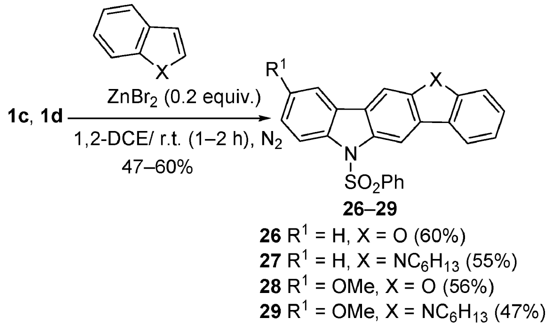
Scheme 8.

Under identical conditions, annulation of bromides **1f**–**h** with bithiophene yielded corresponding annulated compounds **21**–**23** in 44–50% yields (Scheme 9). 3-Bromomethylbenzo[*b*]furan **24**[28] upon heating at reflux with bithiophene in 1,2-DCE led to the isolation of mixed heterocycle **25** in 42% yield.

The annulation of bromomethylindoles **1c**/**1d** with benzo[*b*]heterocycles such as benzo[*b*]furan/*N*-hexylindole with ZnBr$_2$ (0.2 equiv.) in 1,2-DCE at room temperature for 1–2 h afforded expected annulated heterocycles **26**–**29** in 47–60% yield (Scheme 10).

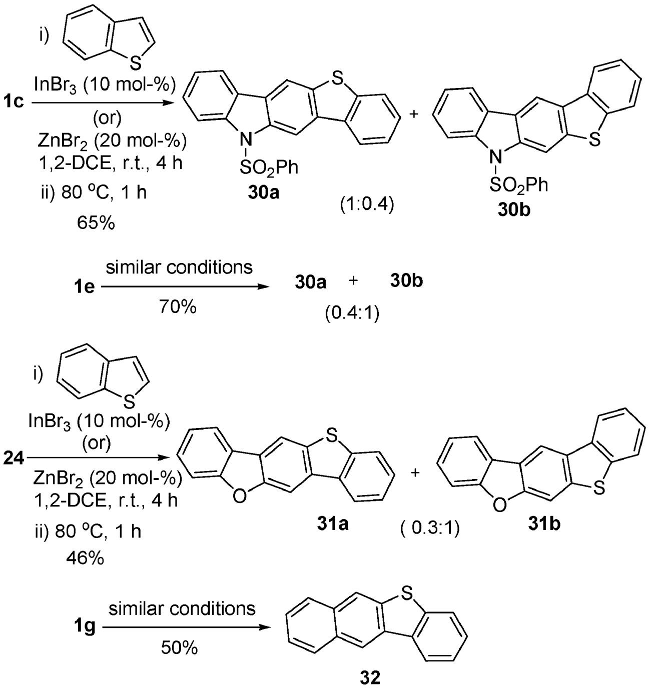


Scheme 9.



Scheme 10.

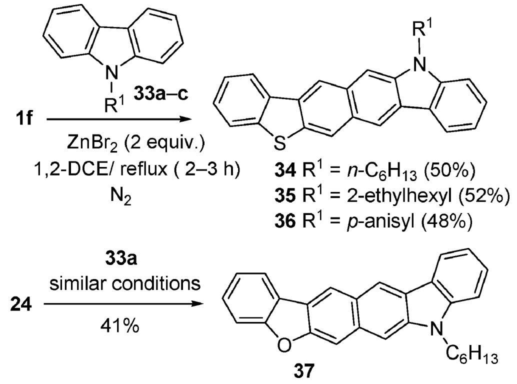
Initially, the annulation reaction of bromide **1c** with benzo[*b*]thiophene was tried in 1,2-DCE at reflux without any success. However, the same could be successfully performed in a stepwise manner (Scheme 11). The heteroarylation of 2-bromomethylindole **1c** with benzo[*b*]thiophene at room temperature followed by subsequent thermolysis at 80 °C for 1 h led to an inseparable mixture of annulated products **30a** and **30b** (1:0.4 based on ^{1}H NMR integration) in 65% yield. The annulation of isomeric bromide **1e** with benzo[*b*]thiophene under identical conditions led to the isolation of products **30a** and **30b** (0.4:1 based on ^{1}H NMR integration) as an inseparable mixture in 70% yield. Similarly, the annulation of 3-bromomethylbenzo[*b*]furan **24**



Scheme 11.

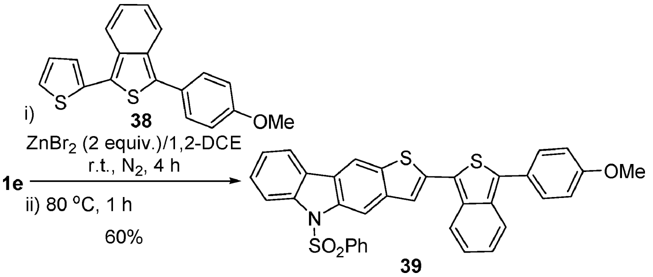
with benzo[*b*]thiophene also furnished an inseparable mixture of annulated heterocycles **31a** and **31b** in 46% yield (0.3:1 based on ^{1}H NMR integration). Even though the 3-position of the benzo[*b*]thiophene is relatively more nucleophilic than the 2-position, the reason for the formation of an isomeric mixture of annulated products **30/31** is not clear. However, as expected, the annulation of bromomethylbenzene **1g** with benzo[*b*]thiophene under similar conditions gave annulated product **32** in 50% yield (Scheme 11).

The heteroarylation of 2-bromomethylbenzo[*b*]thiophene **1f** with *N*-alkyl-/*N*-anisylcarbazole with the use of $ZnBr_2$ (2 equiv.) in 1,2-DCE at reflux for 2–3 h followed by usual workup and column chromatographic purification afforded annulated carbazoles **34**–**36** in 48–52% yield (Scheme 12). Similarly, the annulation of 3-bromomethylbenzo[*b*]furan **24** with *N*-hexylcarbazole **33a** furnished expected product **37** in 41% yield.



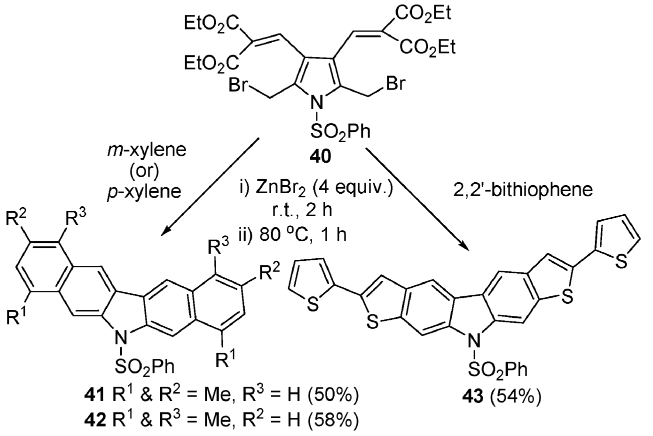
Scheme 12.

Heteroarylation of bromide **1e** with 1-(4-methoxyphenyl)-3-(thiophen-2-yl)benzo[*c*]thiophene (**38**)[29] at room temperature for 4 h followed by thermolysis at 80 °C for 1 h led to the isolation of annulation product **39** in 60% yield (Scheme 13).



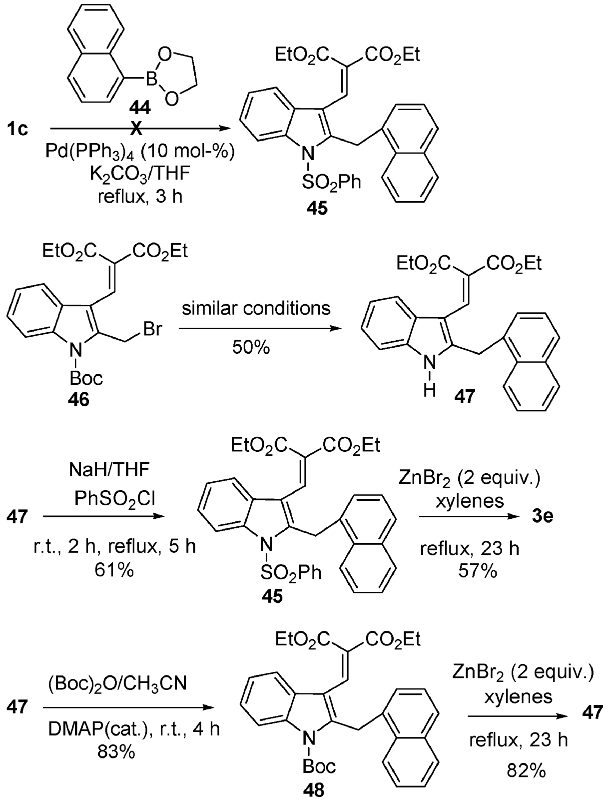
Scheme 13.

Finally, the bisannulation of bromide **40**[30] was performed with *m*-xylene and *p*-xylene with the use of $ZnBr_2$ (4 equiv.) to afford heterocycles **41** and **42** in 50 and 58% yield, respectively. Similarly, the annulation of **40** with bithiophene also furnished mixed heterocycle **43** in 54% yield (Scheme 14).



Scheme 14.

Having succeeded in the synthesis of a wide range of annulated carbazoles through Lewis acid mediated arylation, finally, an attempt was made to effect smooth annulation of bromide **1c** by a coupling reaction with the use of a zero-valent Pd catalyst. However, as a representative case, Suzuki coupling reaction of bromomethylindole **1c** with freshly prepared 1-naphthylboronate (**44**)[31] by using $Pd(PPh_3)_4$ as a catalyst in dry THF at room temperature did not afford arylated product **45**. Even under refluxing conditions of dry THF, the expected Suzuki coupling of **1c** was unsuccessful (Scheme 15). However, when bromide **46** was subjected to Suzuki coupling reaction in dry THF at reflux, arylated

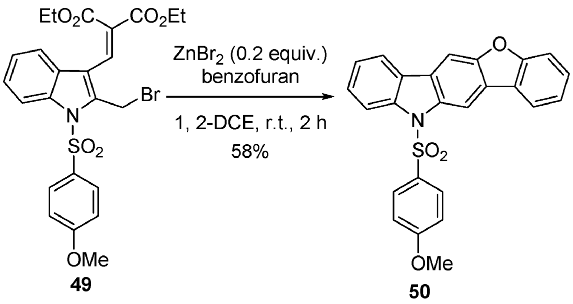


Scheme 15.

compound **47** was isolated in 50% yield with cleavage of the Boc unit.

Next, conventional 1-phenylsulfonation of **47** afforded compound **45** in 61% yield. As expected, thermolysis of **45** with the use of $ZnBr_2$ in dry xylenes at reflux for 23 h furnished known naphtho[*b*]carbazole **3e** in 57% yield (Scheme 15). As expected, *tert*-butoxycarbonylation of **47** by using Boc anhydride in dry acetonitrile gave compound **48** in 83% yield. However, the attempted annulation of **48** in dry xylenes at reflux did not afford the annulated carbazole; only Boc-cleaved product **47** was isolated in 82% yield (Scheme 15). Obviously, the Boc unit underwent thermal cleavage[32] in refluxing xylenes rather than the expected 1,5-H shift to form the required triene. This confirms that the presence of a Boc unit on the indole nitrogen atom is detrimental to the observed annulation reaction.

It should be mentioned that the presence of a methoxy group at the indole 5-position did not have any significant influence on the annulation yields of carbazoles **3g**, **3k**, **3m**, **16**, **17**, **28**, and **29**. To further understand the nature of the observed annulation reaction, the preparation of bromide **49**[16] containing a 4-methoxybenzenesulfonyl group at the indole nitrogen atom was carried out by using conventional reactions. As a representative case, the annulation of bromide **49** with benzo[*b*]furan led to the isolation of mixed heterocycle **50** in 58% yield (Scheme 16).



Scheme 16.

The yields of benzofuranylcarbazoles **26**, **28**, and **50** obtained from the respective bromomethylindoles **1c**, **1d**, and **49** were only formed in 56–60% yield. This clearly confirms the presence of a methoxy group either at the indole 5-position or at the 4-position of a phenylsulfonyl group did not have any significant effect on the annulation reaction.

Conclusions

We developed a simple and versatile annulation protocol for indolyl-2/3-methylbromides, benzo[*b*]thienyl methylbromide, benzo[*b*]furanyl methylbromide benzyl bromide, bromomethyl thiophene, and pyrrolyl-2,5-bis(methylbromide)s containing an electron-deficient malonylidene unit at the adjacent position. The observed annulation was triggered by a Lewis acid mediated arylation of benzyl bromides with arenes. The resulting arylated products at 80 °C led to the formation of an in situ generated triene, which upon electrocyclization followed by subsequent aromatization through elimination of diethyl malonate afforded the respective annulated products in reasonable yields. The annulation reactions of these bromides with a variety of heteroarenes were also performed at moderate temperature (room temperature in some cases!) to afford hitherto inaccessible mixed heterocycles in moderate yields. Attempts to perform a similar annulation of bromomethylindoles involving a Suzuki coupling reaction were unsuccessful. Hence, the optimum reaction condition for the domino reaction of benzyl bromides with an arene in the presence of Lewis acid at 80 °C. For heteroarenes, the entire sequence can be performed at room temperature or 0 °C followed by slightly elevated temperature depending upon its nucleophilic character.

It should be mentioned that considering the number of chemical events taking place in these annulation reactions, the isolation of the heterocycles in moderate yields is acceptable. Application of the annulation methodology to the synthesis of highly complex heterocyclic systems is in progress. In particular, the electron-deficient malonylidene group with the less electron-deficient vinylidene unit is also being explored in our laboratory.

Experimental Section

General Methods: All reactions were carried out in oven-dried apparatus by using dry solvent under anhydrous conditions, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on silica and components were visualized by observation under iodine or UV light. Flash chromatography was performed by using silica gel (230–400 mesh). All melting points are uncorrected. IR spectra were recorded with a Shimadzu FT-IR 8300 instrument. NMR spectra (JEOL 400 MHz and Bruker 300 MHz) were determined in $CDCl_3$ solution containing tetramethylsilane as an internal standard, unless otherwise stated. Organic extracts were dried with anhydrous Na_2SO_4. The following abbreviations explain the multiplicity s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Carbon types were determined from ^{13}C NMR and DEPT experiments. Elemental analyses were performed with a Perkin–Elmer series II 2400 (IIT Madras) elemental analyzer. Mass spectra were recorded with a JEOL DX 303 HF mass spectrometer. All bromomethyl compounds **1a**–**h**, **24**, **40**, **46**, and **49** were prepared from the corresponding aldehydes by using a published procedure in two steps through diethyl malonate condensation followed by allylic bromination (see the Supporting Information for a detailed procedure).

2a: To a suspension of bromide **1a** (0.5 g, 1.18 mmol) in dry benzene (20 mL) was added anhydrous $ZnBr_2$ (0.53 g, 2.35 mmol), and the reaction mixture was heated at reflux for 20 h under a nitrogen atmosphere. The solvent was removed, and the reaction mixture was then quenched with ice water (50 mL) containing concentrated HCl (2 mL). The mixture was extracted with chloroform (3 × 10 mL) and dried (Na_2SO_4). The solvent was removed in vacuo, and the crude product was then purified by flash column chromatography (*n*-hexane/ethyl acetate, 96:4) to afford **2a** (0.25 g, 50%) as a colorless solid. M.p. 138 °C. IR (KBr): $\tilde{\nu}$ = 1705, 1378, 1187 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.13–8.06 (m, 2 H), 7.33–7.25 (m, 5 H), 7.16–7.07 (m, 7 H), 4.96 (s, 2 H), 4.28 (q, J = 7.2 Hz, 2 H), 1.27 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 164.6, 146.3, 138.4, 137.8, 135.9, 133.8, 129.0, 128.5, 128.3, 127.3, 126.6, 126.2, 125.1, 124.4, 122.0, 114.6, 113.3, 60.6, 31.8, 14.3 ppm. MS (EI): *m*/*z* (%) = 419 (67) [M]$^{+}$. $C_{24}H_{21}NO_4S$ (419.12): calcd. C 68.72, H 5.05, N 3.34, S 7.64; found C 68.60, H 5.24, N 3.58, S 7.38.

2b: Phenylation of bromide **1b** (0.5 g, 1.11 mmol) with dry benzene (20 mL) by using anhydrous $ZnBr_2$ (0.50 g, 2.22 mmol) following the same procedure as that of **2a** afforded compound **2b** (0.3 g, 60%) as a colorless solid. M.p. 114 °C. IR (KBr): $\tilde{\nu}$ = 1722, 1638, 1379, 1174 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, J = 6.9 Hz, 1 H), 7.84–7.79 (m, 2 H), 7.37–7.02 (m, 12 H), 6.51 (d, J = 15.9 Hz, 1 H), 4.60 (s, 2 H), 4.18 (q, J = 7.2 Hz, 2 H), 1.25 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 166.6, 140.7, 137.8, 137.1, 136.2, 134.8, 133.2, 128.5, 128.1, 127.9, 126.7, 126.0, 125.9, 124.7, 123.8, 119.6, 119.2, 117.2, 114.8, 60.0, 30.8, 13.8 ppm. MS (EI): *m*/*z* (%) = 445 (54) [M]$^{+}$. $C_{26}H_{23}NO_4S$ (445.13): calcd. C 70.09, H 5.20, N 3.14, S 7.20; found C 70.34, H 5.40, N 3.30, S 7.32.

2c: To a suspension of bromide **1c** (0.3 g, 0.57 mmol) in dry benzene (15 mL) was added anhydrous $ZnBr_2$ (0.26 g, 1.15 mmol), and the reaction mixture was heated to reflux for 24 h under a nitrogen atmosphere. Usual workup as in the case of **2a** followed by flash column chromatography (*n*-hexane to *n*-hexane/ethyl acetate, 99:1) afforded compounds **3a** (0.05 g, 25%) and **2c** (0.06 g, 20%). Data for **2c**: Colorless solid. M.p.124 °C. IR (KBr): $\tilde{\nu}$ = 1730, 1714, 1624, 1372, 1173 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.14 (d, J = 6.0 Hz,1 H), 7.87 (s, 1 H), 7.43–7.14 (m, 13 H), 4.54 (s, 2 H), 4.28 (q, J = 7.2 Hz, 2 H), 3.86 (q, J = 7.2 Hz, 2 H), 1.31 (t, J = 6.9 Hz, 3 H), 0.63 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 165.3, 164.0, 139.2, 138.4, 137.5, 136.9, 136.3, 133.6, 127.9, 128.9, 128.7, 128.5, 127.6, 126.6, 126.5, 125.1, 124.0, 119.7, 117.9, 114.9, 61.7, 61.3, 32.6, 14.1, 13.1 ppm. MS (EI): *m*/*z* (%) = 517 (81) [M]$^{+}$. $C_{29}H_{27}NO_6S$ (517.16): calcd. C 67.29, H 5.26, N 2.71, S 6.20; found C 67.49, H 5.43, N 2.95, S 6.04. Data for **3a**: Colorless solid. M.p. 158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.67 (s, 1 H), 8.26 (d, J = 8.4 Hz, 1 H), 8.25 (s, 1 H), 7.97–7.87 (m, 3 H), 7.75 (d, J = 8.1 Hz, 2 H), 7.48–7.42 (m, 3 H), 7.33–7.30 (m, 2 H), 7.19 (t, J = 8.1 Hz, 2 H) ppm. ^{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 ppm. MS (EI): *m*/*z* (%) = 357 (58) [M]$^{+}$. $C_{22}H_{15}NO_2S$ (357.08): calcd. 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.

4: To a solution of bromide **1c** (0.5 g, 0.96 mmol) in dry 1,2-DCE (15 mL) was added $ZnBr_2$ (0.43 g, 1.90 mmol). The reaction mixture was then heated at reflux for 10 h under a nitrogen atmosphere. The mixture was then poured over ice water (50 mL) containing concentrated HCl (1 mL), extracted with chloroform (2 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatography (*n*-hexane/ethyl acetate, 95:5) led to the isolation of lactone **4** (0.16 g, 40%) as a colorless solid. M.p. 176 °C. IR (KBr): $\tilde{\nu}$ = 1744, 1701, 1579, 1385, 1186 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20 (s, 1 H), 8.16 (d, J = 8.4 Hz, 1 H), 7.86 (d, J = 7.5 Hz, 2 H), 7.62 (d, J = 7.8 Hz, 1 H), 7.53 (t, J = 7.5 Hz, 1 H), 7.46–7.39 (m, 3 H), 7.32 (t, J = 7.2 Hz, 1 H), 5.62 (s, 2 H), 4.33 (q, J = 7.2 Hz, 2 H), 1.33 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 164.9, 164.4, 137.9, 137.3, 136.5, 135.5, 134.8, 129.8, 126.9, 126.7, 126.6, 125.1, 121.2, 119.2, 115.2, 62.2, 59.4, 14.1 ppm. MS (EI): *m*/*z* (%) = 411 (63) [M]$^{+}$. $C_{21}H_{17}NO_6S$ (411.08): calcd. C 61.30, H 4.16, N 3.40, S 7.79; found C 61.45, H 4.04, N 3.60, S 7.56.

3b′: To a solution of substrate **1c** (0.5 g, 0.96 mmol) in dry 1,2-DCE (15 mL) was added $ZnBr_2$ (0.43 g, 1.90 mmol) and toluene (0.11 mL, 1.08 mmol). The reaction mixture was then heated at reflux for 1 h under a nitrogen atmosphere. The mixture was then poured over ice water (50 mL) containing concentrated HCl (2 mL), extracted with chloroform (3 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatography (*n*-hexane/ethyl acetate, 99:1) afforded a mixture of **3b** and **3b′** (0.18 g, 50%) as a colorless solid. M.p. 180–184 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.91 (s, 1 H), 8.73 (s, 1 H), 8.39 (d, J = 8.4 Hz, 1 H), 8.33 (d, J = 9.6 Hz, 1 H), 8.21 (s, 1 H), 8.00 (d, J = 8.1 Hz, 3 H), 7.86–7.83 (m, 5 H), 7.71 (s, 1 H), 7.56–7.51 (m, 2 H), 7.43–7.36 (m, 8 H), 7.30–7.24 (m, 4 H), 2.89 (s, 3 H), 2.56 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.1, 139.9, 137.6, 137.3, 136.7, 135.8, 134.9, 134.5, 133.8, 133.7, 132.3, 131.3, 130.9, 130.7, 129.0, 128.4, 128.3, 128.2, 126.9, 126.8, 126.7 126.6, 126.5 (2 C), 126.4, 126.3, 124.9, 124.3, 124.2, 120.6 (2 C), 119.0, 117.6, 115.4 (2 C), 112.1, 108.8, 21.7, 20.0 ppm. ^{13}C NMR (DEPT 135, 75.4 MHz, $CDCl_3$): δ = 133.8, 133.7, 129.0, 128.9, 128.4, 128.3 (2 C), 128.2, 126.8, 126.7, 126.6, 126.5 (2 C), 124.9, 124.3, 124.2, 120.7, 120.6, 119.0, 117.6, 115.4 (2 C), 112.1, 108.8, 21.7, 20.0 ppm.

3c: To a solution of substrate **1c** (0.5 g, 0.96 mmol) in dry 1,2-DCE (15 mL) was added $ZnBr_2$ (0.43 g, 1.90 mmol) and anisole (0.12 mL, 1.10 mmol). The reaction mixture was then heated at reflux for 1 h under a nitrogen atmosphere. The mixture was then poured over ice water (50 mL) containing concentrated HCl (2 mL), extracted with chloroform (3 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatography (*n*-hexane/ethyl acetate, 96:4) afforded **3c** (0.23 g, 62%) as a colorless solid. M.p. 200 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (s, 1 H), 8.30 (d, J = 8.4 Hz, 1 H), 8.18 (s, 1 H), 7.93 (t, J = 9.1 Hz, 2 H), 7.77 (d, J = 9.6 Hz, 2 H), 7.48 (t, J = 8.6 Hz, 1 H), 7.40–7.32 (m, 2 H), 7.26–7.18 (m, 4 H), 3.91 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.3, 140.0, 137.6, 135.9, 133.7, 131.8, 129.9, 129.0, 128.6, 128.3, 127.3, 126.5, 124.2, 120.6, 119.4, 117.0, 115.4, 112.4, 105.5, 55.4 ppm. MS (EI): *m*/*z* (%) = 387 (44) [M]$^{+}$. $C_{23}H_{17}NO_3S$ (387.09): calcd. C 71.30, H 4.42, N 3.62, S 8.28; found C 71.08, H 4.59, N 3.82, S 8.03.

3d: The annulation of bromide **1c** (0.2 g, 0.38 mmol) with biphenyl (0.07 g, 0.45 mmol) by using $ZnBr_2$ (0.17 g, 0.75 mmol) in dry 1,2-DCE (8 mL) following the same procedure as that of **3c** afforded compound **3d** (0.06 g, 35%) as a colorless thick liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.77 (s, 1 H), 8.38 (s, 1 H), 8.35 (d, J = 8.1 Hz, 1 H), 8.16 (s, 1 H), 8.13 (d, J = 8.7 Hz, 1 H), 8.02 (d, J = 6.9 Hz, 1 H), 7.85–7.81 (m, 3 H), 7.75 (d, J = 8.1 Hz, 2 H), 7.57–7.48 (m, 4 H), 7.44–7.28 (m, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 141.0, 140.1, 138.0, 137.7, 137.4, 133.8, 132.2, 130.9, 129.0 (2C), 128.9, 128.5, 127.7, 127.4, 126.7, 126.5, 126.4, 125.9, 125.8, 124.5, 124.3, 124.0, 120.7, 118.7, 115.4, 112.1 ppm. MS (EI): *m*/*z* (%) = 433 (60) [M]$^{+}$. $C_{28}H_{19}NO_2S$ (433.11): calcd. C 77.57, H 4.42, N 3.23, S 7.40; found C 77.40, H 4.57, N 3.01, S 7.63.

3e: The annulation of bromide **1c** (0.6 g, 1.15 mmol) with naphthalene (0.17 g, 1.32 mmol) by using $ZnBr_2$ (0.52 g, 2.30 mmol) in dry 1,2-DCE (15 mL) following the same procedure as that of **3c** afforded compound **3e** (0.19 g, 40%) as a colorless solid. M.p. 212 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.59 (s, 1 H), 8.85 (d, J = 8.1 Hz, 1 H), 8.32 (d, J = 8.4 Hz, 1 H), 8.28 (s, 1 H), 7.96 (d, J = 8.4 Hz, 1 H), 7.82 (d, J = 7.8 Hz, 1 H), 7.79–7.74 (m, 3 H), 7.72–7.65 (m, 2 H), 7.59 (t, J = 6.9 Hz, 1 H), 7.48 (t, J = 7.6 Hz, 1 H), 7.37–7.30 (m, 2 H), 7.18 (t, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.8, 137.9, 137.7, 133.8, 132.1, 130.6, 130.2, 129.4, 129.2, 129.0, 128.4, 128.2, 127.0, 126.9, 126.8, 126.6, 126.5, 126.4 ppm. 126.3, 124.3, 123.2, 120.5, 119.2, 115.5, 108.3 ppm. MS (EI): *m*/*z* (%) = 407 (61) [M]$^{+}$. $C_{26}H_{17}NO_2S$ (407.10): calcd. C 76.64, H 4.21, N 3.44, S 7.87; found C 76.82, H 4.35, N 3.72, S 7.65.

3f: The annulation of bromide **1c** (0.2 g, 0.38 mmol) with 1-methylnaphthalene (0.06 mL, 0.42 mmol) by using $ZnBr_2$ (0.17 g, 0.75 mmol) in dry 1,2-DCE (8 mL) following the same procedure as that of **3c** afforded compound **3f** (0.09 g, 56%) as a colorless solid. M.p. 206 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.56 (s, 1 H), 8.89 (d, *J* = 8.1 Hz, 1 H), 8.34 (d, *J* = 8.4 Hz, 1 H), 8.10 (s, 1 H), 8.01 (d, *J* = 7.8 Hz, 1 H), 7.90 (d, *J* = 7.8 Hz, 1 H), 7.80 (d, *J* = 7.5 Hz, 2 H), 7.74–7.46 (m, 4 H), 7.36–7.15 (m, 4 H), 2.67 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.7, 137.6, 137.4, 133.8, 132.1, 131.9, 130.6, 129.5, 129.1, 129.0, 128.0, 126.9, 126.6, 126.5, 124.8, 124.2, 123.5, 120.5, 118.3, 115.5, 108.0, 20.0 ppm. MS (EI): *m*/*z* (%) = 421 (65) $[M]^+$. $C_{27}H_{19}NO_2S$ (421.11): calcd. C 76.93, H 4.54, N 3.32, S 7.61; found C 76.66, H 4.62, N 3.57, S 7.93.

3g: The annulation of bromide **1d** (0.3 g, 0.54 mmol) with 1-methylnaphthalene (0.09 mL, 0.63 mmol) by using anhydrous $ZnBr_2$ (0.25 g, 1.11 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **3c** afforded compound **3g** (0.11 g, 44%) as a colorless solid. M.p. 276–278 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.60 (s, 1 H), 8.95 (d, *J* = 7.8 Hz, 1 H), 8.27 (d, *J* = 9.0 Hz, 1 H), 8.19 (s, 1 H), 8.09 (d, *J* = 7.8 Hz, 1 H), 7.80–7.65 (m, 6 H), 7.46 (d, *J* = 7.2 Hz, 1 H), 7.37 (t, *J* = 7.5 Hz, 1 H), 7.26–7.19 (m, 1 H), 7.11 (dd, *J* = 2.7, 9.0 Hz, 1 H), 3.93 (s, 3 H), 2.75 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.2, 138.1, 137.4, 134.0, 133.6, 132.2, 132.0, 130.1, 129.1, 128.9, 127.0, 126.7, 126.6, 126.5, 124.8, 123.5, 118.3, 116.7, 115.7, 108.6, 104.0, 55.8, 20.0 ppm. MS (EI): *m*/*z* (%) = 451 (15) $[M]^+$. $C_{28}H_{21}NO_3S$ (451.12): calcd. C 74.48, H 4.69, N 3.10, S 7.10; found C 74.69, H 4.52, N 3.28, S 7.34.

3h: The annulation of bromide **1c** (0.2 g, 0.38 mmol) with 2-methoxynaphthalene (0.07 g, 0.44 mmol) by using $ZnBr_2$ (0.17 g, 0.75 mmol) in dry 1,2-DCE (8 mL) following the same procedure as that of **3c** afforded compound **3h** (0.08 g, 47%) as a colorless solid. M.p. 172–174 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.03 (s, 1 H), 8.74 (s, 1 H), 8.65 (d, *J* = 8.7 Hz, 1 H), 8.35 (d, *J* = 8.4 Hz, 1 H), 8.09 (d, *J* = 7.8 Hz, 1 H), 7.90 (d, *J* = 9.0 Hz, 1 H), 7.84 (d, *J* = 7.8 Hz, 2 H), 7.69 (d, *J* = 9.0 Hz, 1 H), 7.54 (t, *J* = 7.5 Hz, 2 H), 7.45–7.38 (m, 3 H), 7.32–7.24 (m, 2 H), 3.97 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 158.4, 139.7, 137.7, 136.9, 133.8, 133.1, 131.0, 129.0, 128.1 (2 C), 126.9, 126.7, 126.6, 126.5, 124.6, 124.3, 124.1, 120.4, 117.1, 115.4, 113.5, 113.1, 108.9, 55.5 ppm. MS (EI): *m*/*z* (%) = 437 (43) $[M]^+$. $C_{27}H_{19}NO_3S$ (437.11): calcd. C 74.12, H 4.38, N 3.20, S 7.33; found C 74.34, H 4.18, N 3.43, S 7.12.

3i: The annulation of bromide **1c** (0.31 g, 0.59 mmol) with *o*-xylene (0.09 mL, 0.75 mmol) by using anhydrous $ZnBr_2$ (0.27 g, 1.19 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **3c** afforded compound **3i** (0.13 g, 56%) as a colorless solid. M.p. 204 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.65 (s, 1 H), 8.30 (d, *J* = 8.1 Hz, 1 H), 8.11 (s, 1 H), 7.9 (d, *J* = 7.5 Hz, 1 H), 7.78 (d, *J* = 8.7 Hz, 3 H), 7.63 (s, 1 H), 7.47 (t, *J* = 7.2 Hz, 1 H), 7.37–7.30 (m, 2 H), 7.20 (t, *J* = 9 Hz, 2 H), 2.63 (s, 3 H), 2.48 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.9, 137.7, 136.8, 136.0, 135.0, 133.6, 132.0, 129.7, 128.9, 128.0, 127.8, 127.3, 126.8, 126.5, 126.1, 124.2, 120.4, 117.3, 115.4, 111.3, 20.3, 20.2 ppm. MS (EI): *m*/*z* (%) = 385 (81) $[M]^+$. $C_{24}H_{19}NO_2S$ (385.11): calcd. C 74.78, H 4.97, N 3.63, S 8.32; found C 74.88, H 4.76, N 3.87, S 8.50.

3j: The annulation of bromide **1c** (0.41 g, 0.78 mmol) with veratrole (0.12 mL, 0.94 mmol) by using $ZnBr_2$ (0.35 g, 1.55 mmol) in dry 1,2-DCE (12 mL) following the same procedure as that of **3c** afforded compound **3j** (0.19 g, 57%) as a colorless solid. M.p. 210 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 8.29 (d, *J* = 8.1 Hz, 1 H), 8.14 (s, 1 H), 7.92 (d, *J* = 7.2 Hz, 1 H), 7.80 (d, *J* = 7.2 Hz, 2 H), 7.50–7.28 (m, 7 H), 4.06 (s, 3 H), 4.01 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 150.0, 149.3, 139.5, 137.7, 136.4, 133.7, 129.1, 129.0, 127.7, 126.8, 126.5, 125.2, 124.2, 120.1, 116.8, 115.4, 111.0, 106.7, 106.0, 56.0, 55.9 ppm. MS (EI): *m*/*z* (%) = 417 (59) $[M]^+$. $C_{24}H_{19}NO_4S$ (417.10): calcd. C 69.05, H 4.59, N 3.36, S 7.68; found C 69.25, H 4.82, N 3.65, S 7.46.

3k: The annulation of bromide **1d** (0.2 g, 0.36 mmol) with veratrole (0.06 mL, 0.43 mmol) by using $ZnBr_2$ (0.16 g, 0.71 mmol) in dry 1,2-DCE (8 mL) following the same procedure as that of **3c** afforded compound **3k** (0.07 g, 44%) as a colorless solid. M.p. 240–242 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56 (s, 1 H), 8.19 (d, *J* = 9.0 Hz, 1 H), 8.09 (s, 1 H), 7.75 (d, *J* = 8.1 Hz, 2 H), 7.40–7.20 (m, 6 H), 7.05 (dd, *J* = 1.8, 9.0 Hz, 1 H), 4.07 (s, 3 H), 4.02 (s, 3 H), 3.90 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.1, 150.0, 149.3, 137.5, 137.0, 133.7, 133.5, 129.2, 128.9, 128.0, 126.5, 125.4, 116.8, 116.5, 115.0, 111.4, 106.7, 106.1, 104.0, 55.9 (2 C), 55.8 ppm. MS (EI): *m*/*z* (%) = 447 (24) $[M]^+$. $C_{25}H_{21}NO_5S$ (447.11): calcd. C 67.10, H 4.73, N 3.13, S 7.17; found C 67.30, H 4.61, N 3.32, S 7.43.

3l: The annulation of bromide **1c** (0.3 g, 0.57 mmol) with *m*-xylene (0.08 mL, 0.65 mmol) by using $ZnBr_2$ (0.26 g, 1.15 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **3c** afforded compound **3l** (0.12 g, 55%) as a colorless solid. M.p. 208 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.85 (s, 1 H), 8.38 (d, *J* = 8.1 Hz, 1 H), 8.20 (s, 1 H), 7.98 (d, *J* = 7.5 Hz, 1 H), 7.85–7.82 (m, 2 H), 7.58–7.52 (m, 2 H), 7.39 (t, *J* = 7.3 Hz, 2 H), 7.29–7.24 (m, 3 H), 2.85 (s, 3 H), 2.52 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.1, 137.6, 136.8, 134.4, 134.3, 133.7, 131.1, 130.6, 129.2, 128.9, 128.2, 126.5, 126.4, 125.2, 124.2, 120.6, 118.2, 115.4, 108.7, 21.5, 19.9 ppm. MS (EI): *m*/*z* (%) = 385 (38) $[M]^+$. $C_{24}H_{19}NO_2S$ (385.11): calcd. C 74.78, H 4.97, N 3.63, S 8.32; found C 74.48, H 5.09, N 3.90, S 8.60.

3m: The annulation of bromide **1d** (0.2 g, 0.36 mmol) with *m*-xylene (0.06 mL, 0.47 mmol) by using $ZnBr_2$ (0.16 g, 0.71 mmol) in dry 1,2-DCE (8 mL) following the same procedure as that of **3c** afforded compound **3m** (0.08 g, 53%) as a colorless solid. M.p. 186–188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (s, 1 H), 8.23 (d, *J* = 9.0 Hz, 1 H), 8.15 (s, 1 H), 7.73 (d, *J* = 7.5 Hz, 2 H), 7.57 (s, 1 H), 7.43–7.34 (m, 2 H), 7.25–7.20 (m, 3 H), 7.08 (dd, *J* = 2.7, 9.0 Hz, 1 H), 3.91 (s, 3 H), 2.82 (s, 3 H), 2.50 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.1, 137.5, 137.4, 134.5, 134.4, 134.3, 133.6, 131.1, 130.7, 129.3, 128.8, 127.8, 126.7, 126.5, 125.2, 118.2, 116.6, 115.7, 109.2, 104.2, 55.8, 21.6, 19.9 ppm. MS (EI): *m*/*z* (%) = 415 (77) $[M]^+$. $C_{25}H_{21}NO_3S$ (415.12): calcd. C 72.27, H 5.09, N 3.37, S 7.72; found C 72.03, H 5.30, N 3.53, S 7.53.

3n: The annulation of bromide **1c** (0.3 g, 0.57 mmol) with *p*-xylene (0.08 mL, 0.65 mmol) by using $ZnBr_2$ (0.26 g, 1.15 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **3c** afforded compound **3n** (0.11 g, 50%) as a colorless solid. M.p. 182 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.90 (s, 1 H), 8.48 (s, 1 H), 8.39 (d, *J* = 8.4 Hz, 1 H), 8.07 (d, *J* = 7.8 Hz, 1 H), 7.85 (d, *J* = 7.5 Hz, 2 H), 7.58–7.53 (m, 1 H), 7.45–7.39 (m, 2 H), 7.34–7.32 (m, 4 H), 2.86 (s, 3 H), 2.78 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.1, 137.6, 137.0, 133.8, 132.7, 132.5, 132.4, 130.0, 129.0, 128.2, 126.7, 126.5, 126.0, 125.5, 124.3, 120.6, 115.4 (2 C), 109.4, 20.0, 19.7 ppm. MS (EI): *m*/*z* (%) = 385 (47) $[M]^+$. $C_{24}H_{19}NO_2S$ (385.11): calcd. C 74.78, H 4.97, N 3.63, S 8.32; found C 74.58, H 4.85, N 3.92, S 8.59.

3o: The annulation of bromide **1c** (0.31 g, 0.59 mmol) with 1,4-dimethoxybenzene (0.10 g, 0.72 mmol) by using $ZnBr_2$ (0.27 g, 1.19 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **3c** afforded compound **3o** (0.13 g, 52%) as a colorless solid. M.p. 170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.03 (s, 1 H), 8.64 (s, 1 H), 8.27 (d, J = 8.1 Hz, 1 H), 7.97 (d, J = 7.8 Hz, 1 H), 7.76 (d, J = 8.4 Hz, 2 H), 7.44 (t, J = 8.4 Hz, 1 H), 7.35–7.28 (m, 1 H), 7.19 (t, J = 7.8 Hz, 3 H), 6.70–6.61 (m, 2 H), 3.98 (s, 3 H), 3.94 (s, 3 H) ppm. ^{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 ppm. MS (EI): m/z (%) = 417 (81) [M]$^+$. $C_{24}H_{19}NO_4S$ (417.10): calcd. 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.

3p: To a solution of bromide **1c** (0.2 g, 0.38 mmol) in dry DCE (8 mL) was added anhydrous $ZnBr_2$ (0.17 g, 0.75 mmol) and 4-bromoanisole (0.06 mL, 0.46 mmol). The mixture was then heated at reflux for 2 h under a nitrogen atmosphere. The solvent was removed, and the reaction mixture was quenched with ice water (20 mL) containing concentrated HCl (1 mL), extracted with chloroform (2 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by column chromatographic purification (*n*-hexane/ethyl acetate, 95:5) afforded the arylated product (0.15 g, 63%) as a colorless thick liquid. IR (KBr): $\tilde{\nu}$ = 1728, 1712, 1626, 1380, 1186 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, J = 8.4 Hz, 1 H), 7.74 (s, 1 H), 7.55 (d, J = 7.5 Hz, 2 H), 7.50–7.35 (m, 3 H), 7.32–7.22 (m, 4 H), 6.75–6.72 (m, 2 H), 4.47 (s, 2 H), 4.27 (q, J = 7.2 Hz, 2 H), 3.88 (q, J = 7.2 Hz, 2 H), 3.87 (s, 3 H), 1.31 (t, J = 6.9 Hz, 3 H), 0.58 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 165.2, 164.1, 156.3, 138.5, 137.7, 136.7, 136.5, 134.0, 131.5, 130.4, 129.5, 129.1, 128.5, 127.7, 126.4, 125.1, 124.0, 119.7, 118.4, 115.0, 112.9, 111.9, 61.7, 61.2, 55.8, 26.6, 14.1, 13.1 ppm. MS (EI): m/z (%) = 627 (33) [M]$^{+2}$, 625 (33) [M]$^+$. $C_{30}H_{28}BrNO_7S$ (625.08): calcd. C 57.51, H 4.50, N 2.24, S 5.12; found C 57.71, H 4.64, N 2.48, S 5.31.

3q: The annulation of bromide **1e** (0.3 g, 0.57 mmol) with naphthalene (0.08 g, 0.62 mmol) by using $ZnBr_2$ (0.26 g, 1.15 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **3c** afforded compound **3q** (0.1 g, 43%) as a colorless solid. M.p. 186 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.05 (s, 1 H), 8.69 (s, 1 H), 8.67 (d, J = 7.8 Hz, 1 H), 8.28 (d, J = 8.4 Hz, 1 H), 8.02 (d, J = 7.8 Hz, 1 H), 7.84–7.67 (m, 5 H), 7.63–7.44 (m, 3 H), 7.37–7.29 (m, 2 H), 7.21–7.16 (m, 2 H) ppm. ^{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 (2 C), 126.5, 126.4, 124.3, 122.5, 120.4, 115.4, 113.7, 113.4 ppm. MS (EI): m/z (%) = 407 (39) [M]$^+$. $C_{26}H_{17}NO_2S$ (407.10): calcd. 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.

3r: The annulation of bromide **1e** (0.3 g, 0.57 mmol) with *m*-xylene (0.08 mL, 0.65 mmol) by using $ZnBr_2$ (0.26 g, 1.15 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **3c** afforded compound **3r** (0.12 g, 54%) as a colorless solid. M.p. 228 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.62 (s, 1 H), 8.38 (s, 1 H), 8.32 (d, J = 8.4 Hz, 1 H), 8.0 (d, J = 7.5 Hz, 1 H), 7.80 (d, J = 7.2 Hz, 2 H), 7.67 (s, 1 H), 7.49 (t, J = 7.5 Hz, 1 H), 7.42–7.34 (m, 2 H), 7.26–7.17 (m, 3 H), 2.73 (s, 3 H), 2.51 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.9, 137.7, 137.2, 135.5, 134.0, 133.7, 129.0, 128.4, 128.3, 128.0, 126.9, 126.5, 125.9, 125.8, 124.2, 120.4, 115.5, 114.7, 112.2, 21.7, 19.6 ppm. MS (EI): m/z (%) = 385 (37) [M]$^+$. $C_{24}H_{19}NO_2S$ (385.11): calcd. C 74.78, H 4.97, N 3.63, S 8.32; found C 74.60, H 4.77, N 3.90, S 8.49.

3s: The annulation of bromide **1e** (0.3 g, 0.57 mmol) with anisole (0.07 mL, 0.68 mmol) by using $ZnBr_2$ (0.26 g, 1.15 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **3c** afforded compound **3s** (0.1 g, 45%) as a colorless solid. M.p. 214 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (s, 1 H), 8.31 (d, J = 8.4 Hz, 1 H), 8.24 (s, 1 H), 7.96 (d, J = 7.8 Hz, 1 H), 7.86–7.81 (m, 3 H), 7.52–7.29 (m, 6 H), 7.17 (dd, J = 2.7, 2.4 Hz, 1 H), 3.99 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.9, 139.6, 137.9, 137.7, 134.4, 133.7, 130.2, 129.4, 120.0, 127.8, 126.7, 126.5, 126.3, 124.9, 124.2, 120.2, 118.7, 118.4, 115.3, 113.6, 111.0, 106.0, 55.4 ppm. MS (EI): m/z (%) = 387 (74) [M]$^+$. $C_{23}H_{17}NO_3S$ (387.09): calcd. C 71.30, H 4.42, N 3.62, S 8.28; found C 71.52, H 4.57, N 3.36, S 8.49.

3t: The annulation of bromide **1f** (0.33 g, 0.83 mmol) with naphthalene (0.13 g, 1.01 mmol) by using $ZnBr_2$ (0.37 g, 1.64 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **3c** afforded compound **3t** (0.11 g, 46%) as a colorless solid. M.p. 220 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.12 (s, 1 H), 8.74 (d, J = 8.1 Hz, 1 H), 8.62 (s, 1 H), 8.31–8.28 (m, 1 H), 7.92–7.87 (m, 3 H), 7.74–7.62 (m, 3 H), 7.52–7.49 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.2, 138.5, 135.2, 135.0, 132.2, 129.7, 129.7, 129.5, 128.6, 127.4, 127.3, 126.9, 126.7, 126.5, 124.6, 122.9, 122.8, 121.9, 120.7, 116.2 ppm. HRMS: calcd. for $C_{20}H_{12}S$ [M]$^+$ 284.0660; found 284.0663.

3u: The annulation of bromide **1f** (0.35 g, 0.88 mmol) with *m*-xylene (0.13 mL, 1.03 mmol) by using $ZnBr_2$ (0.39 g, 1.73 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **3c** afforded compound **3u** (0.14 g, 61%) as a colorless solid. M.p.148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.51 (s, 1 H), 8.39 (s, 1 H), 8.27–8.24 (m, 1 H), 7.88–7.84 (m, 1 H), 7.67 (s, 1 H), 7.54–7.47 (m, 2 H), 7.24 (s, 1 H), 2.75 (s, 3 H), 2.55 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.2, 136.8, 135.3, 134.7, 134.3, 133.0, 131.4, 130.5, 129.2, 127.5, 125.6, 124.4, 122.8, 121.9, 119.9, 117.0, 21.7, 19.6 ppm. MS (EI): m/z (%) = 262 (61) [M]$^+$. $C_{18}H_{14}S$ (262.08): calcd. C 82.40, H 5.38, S 12.22; found C 82.65, H 5.28, S 12.46. For single-crystal X-ray analysis of **3u**, all calculations were performed with the SHELXL-97 program.[33] Crystal data of **3u**: $C_{18}H_{14}S$, MW = 262.35 g mol^{-1}, monoclinic crystal system, space group $P2_1/n$, Z = 4. a = 10.0219(3) Å, b = 5.8692(5) Å, c = 22.8554(5) Å, α = 90°, β = 99.787(1)°, γ = 90°, V = 1324.80(12) Å^3, $D_{\text{calcd.}}$ = 1.315 mg m^{-3}. In total, 3030 independent reflections were collected of which 2574 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 4.58%. CCDC-705388 (for **3u**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3v: The annulation of bromide **1f** (0.32 g, 0.80 mmol) with *p*-xylene (0.11 mL, 0.94 mmol) by using $ZnBr_2$ (0.36 g, 1.60 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **3c** afforded compound **3v** (0.12 g, 57%) as a colorless solid. M.p. 150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (s, 1 H), 8.34 (s, 1 H), 8.23–8.20 (m, 1 H), 7.79–7.76 (m, 1 H), 7.44–7.39 (m, 2 H), 7.16 (d, J = 7.8 Hz, 2 H), 2.74 (s, 3 H), 2.66 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.3, 137.4, 135.5, 134.4, 132.7, 132.1, 131.4, 130.3, 127.5, 126.3, 125.5, 124.5, 122.9, 121.9, 117.7, 116.8, 19.8, 19.7 ppm. MS (EI): m/z (%) = 262 (29) [M]$^+$. $C_{18}H_{14}S$ (262.08): calcd. C 82.40, H 5.38, S 12.22; found C 82.23, H 5.59, S 12.46.

3w: The annulation of bromide **1g** (0.33 g, 0.96 mmol) with *o*-xylene (0.14 mL, 1.13 mmol) by using $ZnBr_2$ (0.43 g, 1.90 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **3c** afforded compound **3w** (0.06 g, 30%) as a colorless solid. M.p. 248 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31 (s, 2 H), 8.01–7.97 (m, 2 H), 7.77 (s, 2 H), 7.45–7.42 (m, 2 H), 2.50 (s, 6 H) ppm. ^{13}C

NMR (75.4 MHz, $CDCl_3$): δ = 135.6, 131.4, 131.2, 128.0, 126.9, 124.8, 20.4 ppm. MS (EI): *m*/*z* (%) = 206 (19) $[M]^+$. $C_{16}H_{14}$ (206.11): calcd. C 93.16, H 6.84; found C 93.38, H 6.60.

3x: The annulation of bromide **1g** (0.33 g, 0.96 mmol) with *m*-xylene (0.14 mL, 1.13 mmol) by using $ZnBr_2$ (0.43 g, 1.90 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **3c** afforded compound **3x** (0.07 g, 35%) as a colorless solid. M.p. 78 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.53 (s, 1 H), 8.35 (s, 1 H), 8.08–8.01 (m, 2 H), 7.66 (s, 1 H), 7.51–7.48 (m, 2 H), 7.20 (s, 1 H), 2.83 (s, 3 H), 2.55 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 134.6, 134.0, 132.3, 131.6, 131.2, 130.1, 128.6, 128.6, 127.9, 125.7, 125.3, 124.9, 122.6, 21.9, 19.6 ppm. MS (EI): *m*/*z* (%) = 206 (27) $[M]^+$. $C_{16}H_{14}$ (206.11): calcd. C 93.16, H 6.84; found C 93.01, H 6.96.

3y: The annulation of bromide **1g** (0.32 g, 0.93 mmol) with anisole (0.12 mL, 1.10 mmol) by using $ZnBr_2$ (0.42 g, 1.86 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **3c** afforded compound **3y** (0.08 g, 40%) as a colorless solid. M.p. 176 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.35 (s, 1 H), 8.28 (s, 1 H), 7.96 (t, *J* = 7.4 Hz, 2 H), 7.90 (d, *J* = 9 Hz, 1 H), 7.47–7.38 (m, 2 H), 7.20–7.14 (m, 2 H), 3.97 (s, 3 H) ppm. MS (EI): *m*/*z* (%) = 208 (53) $[M]^+$. $C_{15}H_{12}O$ (208.09): calcd. C 86.51, H 5.81; found C 86.23, H 5.59.

3z: The annulation of bromide **1h** (0.3 g, 0.86 mmol) with veratrole (0.13 mL, 1.01 mmol) by using $ZnBr_2$ (0.38 g, 1.68 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **3c** afforded compound **3z** (0.1 g, 48%) as a colorless solid. M.p. 210 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.18 (s, 1 H), 8.14 (s, 1 H), 7.41 (d, *J* = 5.4 Hz, 1 H), 7.35 (d, *J* = 5.4 Hz, 1 H), 7.19 (s, 1 H), 7.14 (s, 1 H), 4.03 (s, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 149.6, 149.3, 137.6, 136.7, 127.4, 127.1, 126.6, 123.3, 120.1, 118.8, 105.8, 105.0, 55.9, 55.8 ppm. MS (EI): *m*/*z* (%) = 244 (63) $[M]^+$. $C_{14}H_{12}O_2S$ (244.06): calcd. C 68.83, H 4.95, S 13.12; found C 68.99, H 4.73, S 13.39.

7: To a solution of bromide **1c** (0.2 g, 0.38 mmol) in dry DCE (8 mL) was added anhydrous $ZnBr_2$ (0.17 g, 0.75 mmol) and fluorene (0.08 g, 0.48 mmol). The mixture was stirred at room temperature for 2 h and then heated at reflux for 0.5 h under a nitrogen atmosphere. The solvent was removed, and the reaction mixture was quenched with ice water (20 mL) containing concentrated HCl (1 mL), extracted with chloroform (2 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatography (*n*-hexane/ethyl acetate, 99:1) led to the isolation of **7** (0.08 g, 47%) as a colorless solid. M.p. 242–244 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.72 (s, 1 H), 8.33 (s, 1 H), 8.32 (d, *J* = 8.1 Hz, 1 H), 8.24 (s, 1 H), 8.10 (s, 1 H), 7.97 (d, *J* = 7.5 Hz, 1 H), 7.90 (d, *J* = 7.2 Hz, 1 H), 7.83 (d, *J* = 7.2 Hz, 2 H), 7.57–7.47 (m, 2 H), 7.43–7.32 (m, 4 H), 7.28–7.23 (m, 2 H), 4.09 (s, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 143.7, 141.6, 140.9, 140.2, 140.0, 137.8, 137.0, 133.7, 132.8, 130.3, 129.0, 128.2, 127.7, 127.0, 126.5, 125.3, 124.3, 123.8, 120.6, 120.5, 118.5, 117.7, 115.4, 112.2, 36.4 ppm. MS (EI): *m*/*z* (%) = 445 (41) $[M]^+$. $C_{29}H_{19}NO_2S$ (445.11): calcd. C 78.18, H 4.30, N 3.14, S 7.20; found C 78.03, H 4.58, N 3.32, S 7.42.

11: To a solution of bromide **1c** (0.2 g, 0.38 mmol) in dry DCE (8 mL) was added anhydrous $ZnBr_2$ (0.02 g, 0.09 mmol) and fluorene **10**[27] (0.23 g, 0.46 mmol). The mixture was stirred at room temperature for 2 h and then heated at reflux for 0.5 h under a nitrogen atmosphere. The solvent was removed, and the reaction mixture was quenched with ice water (20 mL) containing concentrated HCl (1 mL), extracted with chloroform (2 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatography (*n*-hexane/ethyl acetate, 99:1) led to the isolation of **11** (0.15 g, 50%) as a pale-yellow solid. M.p. 108–110 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.74 (s, 1 H), 8.26 (d, *J* = 8.1 Hz, 1 H), 8.15 (s, 1 H), 7.87 (d, *J* = 7.2 Hz, 1 H), 7.75 (d, *J* = 7.8 Hz, 2 H), 7.64–7.52 (m, 7 H), 7.45–7.22 (m, 7 H), 7.04 (t, *J* = 4.2 Hz, 1 H), 1.99 (t, *J* = 7.5 Hz, 4 H), 1.49–0.66 (m, 22 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 151.9, 151.8, 145.1 (2 C), 141.2, 140.0, 139.5, 139.1, 137.8, 137.7, 136.4, 133.8, 133.6, 132.9, 129.1, 128.1, 127.6, 126.6, 126.5, 125.6, 125.4, 125.1, 124.7, 124.2, 123.0, 120.7, 120.3, 120.2, 120.0, 118.5, 115.5, 113.9, 108.5, 55.4, 40.4, 31.5, 29.7, 23.8, 22.6, 14.0 ppm. $C_{49}H_{47}NO_2S_3$ (777.28): calcd. C 75.64, H 6.09, N 1.80, S 12.36; found C 75.83, H 6.16, N 1.60, S 12.20. HRMS: calcd. for $C_{49}H_{47}NO_2S_3$ $[M]^+$ 777.2769; found 777.2765.

12: To a solution of bromide **1c** (0.2 g, 0.38 mmol) in dry DCE (8 mL) was added anhydrous $ZnBr_2$ (0.02 g, 0.09 mmol) and *N*-hexylphenothiazine (0.13 g, 0.46 mmol). The mixture was stirred at room temperature for 1 h and then heated at reflux for 0.5 h under a nitrogen atmosphere. The solvent was removed, and the reaction mixture was quenched with ice water (20 mL) containing concentrated HCl (1 mL), extracted with chloroform (2 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatography (*n*-hexane/ethyl acetate, 95:5) led to the isolation of **12** [0.14 g (50%)] as a colorless thick liquid. IR (KBr): $\tilde{\nu}$ = 1733, 1715, 1630, 1375, 1180 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.1 Hz, 1 H), 7.89 (s, 1 H), 7.43 (d, *J* = 6.9 Hz, 1 H), 7.36–7.23 (m, 4 H), 7.18–6.84 (m, 8 H), 6.68 (d, *J* = 8.1 Hz, 2 H), 4.41 (s, 2 H), 4.29 (q, *J* = 6.9 Hz, 2 H), 3.93 (q, *J* = 7.2 Hz, 2 H), 3.78 (t, *J* = 7.2 Hz, 2 H), 1.79–1.75 (m, 2 H), 1.42–1.28 (m, 9 H), 0.86 (t, *J* = 6.9 Hz, 3 H), 0.62 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 165.3, 164.0, 145.3, 144.0, 139.0, 138.5, 136.9, 136.5, 133.5, 131.3, 129.8, 128.7, 127.8, 127.5, 127.3, 127.2, 126.2, 125.1, 125.0, 124.9, 124.0, 122.3, 119.7, 117.7, 115.3, 115.2, 114.9, 61.8, 61.3, 47.4, 31.5, 31.4, 26.9, 26.7, 22.6, 14.1, 14.0, 13.1 ppm. $C_{41}H_{42}N_2O_6S_2$ (722.25): calcd. C 68.12, H 5.86, N 3.88, S 8.87; found C 68.00, H 5.98, N 3.65, S 8.96. HRMS: calcd. for $C_{41}H_{42}N_2O_6S_2$ $[M]^+$ 722.2484; found 722.2481.

14: To a solution of bromide **1c** (0.31 g, 0.59 mmol) in dry DCE (10 mL) was added anhydrous $ZnBr_2$ (0.26 g, 1.15 mmol) and bithiophene (0.12 g, 0.72 mmol). The mixture was stirred at room temperature for 3 h and then heated at reflux for 1 h under a nitrogen atmosphere. The solvent was removed, and the reaction mixture was quenched with ice water (30 mL) containing concentrated HCl (1 mL), extracted with chloroform (3 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatography (*n*-hexane/ethyl acetate, 99:1) led to the isolation of **14** (0.13 g, 48%) as a pale-yellow solid. M.p. 188 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.67 (s, 1 H), 8.45 (d, *J* = 8.4 Hz, 1 H), 8.09 (s, 1 H), 7.85 (d, *J* = 7.5 Hz, 1 H), 7.74 (d, *J* = 8.4 Hz, 2 H), 7.44–7.18 (m, 8 H), 7.02 (t, *J* = 4.5 Hz, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.1, 139.0, 137.6, 137.4, 137.3, 137.2, 136.5, 133.8, 129.1, 128.0, 127.6, 126.5, 125.6, 125.5, 125.2, 124.1, 120.0, 119.0, 115.4, 113.8, 108.3 ppm. HRMS: calcd. for $C_{24}H_{15}NO_2S_3$ $[M]^+$ 445.0265; found 445.0269.

15: The annulation of bromide **1c** (0.3 g, 0.57 mmol) with terthiophene (0.17 g, 0.68 mmol) by using $ZnBr_2$ (0.26 g, 1.15 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **14** afforded compound **15** (0.12 g, 40%) as a pale-yellow solid. M.p. 244 °C. ^1H NMR (300 MHz, [D_6]DMSO): δ = 8.83 (s, 1 H), 8.53 (s, 1 H), 8.27 (d, *J* = 8.4 Hz, 1 H), 8.20 (d, *J* = 7.5 Hz, 1 H), 7.93 (d, *J* = 7.5 Hz, 2 H), 7.76 (s, 1 H), 7.60 (t, *J* = 6.8 Hz, 3 H), 7.51–7.42 (m, 5 H), 7.37 (d, *J* = 3.9 Hz, 1 H), 7.15 (t, *J* = 3.8 Hz, 1 H) ppm. ^{13}C NMR (DEPT 90, 75.4 MHz, $CDCl_3$): δ = 133.8, 129.1, 127.9, 127.6, 126.5, 125.9, 124.9, 124.5, 124.2, 124.0, 120.0, 118.9, 115.4, 113.9, 108.3 ppm. HRMS: calcd. for $C_{28}H_{17}NO_2S_4$ [M]$^+$ 527.0142; found 527.0147.

16: The annulation of bromide **1d** (0.2 g, 0.36 mmol) with bithiophene (0.07 g, 0.42 mmol) by using $ZnBr_2$ (0.16 g, 0.71 mmol) in dry 1,2-DCE (8 mL) following the same procedure as that of **14** afforded compound **16** (0.07 g, 41%) as a pale-yellow solid. M.p. 180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.71 (s, 1 H), 8.20 (d, *J* = 9.0 Hz, 1 H), 8.10 (s, 1 H), 7.75 (d, *J* = 7.5 Hz, 2 H), 7.44–7.25 (m, 7 H), 7.09–7.05 (m, 2 H), 3.90 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.1, 139.1, 137.4, 137.2 (2 C), 137.1, 133.7, 133.3, 129.0, 128.0, 127.7, 126.5, 125.6, 125.2, 119.0 116.5, 115.2, 113.8, 108.6, 103.6, 55.8 ppm. MS (EI): *m*/*z* (%) = 475 (66) [M]$^+$. $C_{25}H_{17}NO_3S_3$ (475.04): calcd. C 63.13, H 3.60, N 2.95, S 20.23; found C 63.29, H 3.42, N 2.75, S 20.45. For single-crystal X-ray analysis of **16**, all calculations were made with the SHELXL-97 program.[33] Crystal data of **16**: $C_{25}H_{17}NO_3S_3$, MW = 475.58 g mol^{-1}, orthorhombic crystal system, space group *Pbca*, $Z = 8$. $a = 15.3900(12)$ Å, $b = 10.1269(7)$ Å, $c = 28.2330(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 4400.20(6)$ Å^3, $D_{\text{calcd.}} = 1.436$ mg m^{-3}. In total, 5212 independent reflections were collected, of which 2068 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 5.27%. CCDC-704773 (for **16**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

17: The annulation of bromide **1d** (0.2 g, 0.36 mmol) with terthiophene (0.10 g, 0.40 mmol) by using $ZnBr_2$ (0.16 g, 0.71 mmol) in dry 1,2-DCE (8 mL) following the same procedure as that of **14** afforded compound **17** (0.08 g, 40%) as a pale-yellow solid. M.p. 212 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.70 (s, 1 H), 8.20 (d, *J* = 9.0 Hz, 1 H), 8.09 (s, 1 H), 7.75 (d, *J* = 7.2 Hz, 2 H), 7.45–7.36 (m, 3 H), 7.31–7.20 (m, 5 H), 7.13–7.03 (m, 3 H), 3.91 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.1, 139.1, 137.6, 137.4, 137.2, (2 C), 137.1, 136.9, 135.8, 133.7, 133.3, 129.0, 128.0, 127.7, 126.5, 125.9, 125.7, 124.9, 124.4, 124.1, 118.9, 116.5, 115.3, 113.8, 108.6, 103.6, 55.8 ppm. HRMS: calcd. for $C_{29}H_{19}NO_3S_4$ [M]$^+$ 557.0248; found 557.0244.

18: The annulation of bromide **1e** (0.2 g, 0.38 mmol) with bithiophene (0.08 g, 0.48 mmol) by using $ZnBr_2$ (0.17 g, 0.75 mmol) in dry 1,2-DCE (8 mL) following the same procedure as that of **14** afforded compound **18** (0.08 g, 47%) as a pale-yellow solid. M.p. 228 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (s, 1 H), 8.32 (d, *J* = 8.4 Hz, 1 H), 8.16 (s, 1 H), 7.87–7.79 (m, 3 H), 7.52 (s, 1 H), 7.50–7.25 (m, 7 H), 7.06 (t, *J* = 4.4 Hz, 1 H) ppm. ^{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 ppm. MS (EI): *m*/*z* (%) = 445 (29) [M]$^+$. $C_{24}H_{15}NO_2S_3$ (445.03): calcd. 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.

19: The annulation of bromide **1e** (0.25 g, 0.48 mmol) with hexylbithiophene (0.14 g, 0.56 mmol) by using $ZnBr_2$ (0.21 g, 0.93 mmol) in dry 1,2-DCE (8 mL) following the same procedure as that of **14** afforded compound **19** (0.14 g, 56%) as a pale-yellow solid. M.p. 190 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (s, 1 H), 8.34 (d, *J* = 8.4 Hz, 1 H), 8.16 (s, 1 H), 7.88–7.81 (m, 3 H), 7.52–7.26 (m, 6 H), 7.13 (d, *J* = 3.6 Hz, 1 H), 6.75 (d, *J* = 3.6 Hz, 1 H), 2.85 (t, *J* = 7.5 Hz, 2 H), 1.76–1.71 (m, 2 H), 1.45–1.32 (m, 6 H), 0.93 (t, *J* = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 147.2, 140.3, 139.2, 139.1, 137.7, 137.0, 135.3, 134.8, 133.7, 139.0, 127.5, 126.4, 126.2, 125.1, 125.0, 124.8, 124.2, 119.9, 119.0, 115.3, 112.9, 109.0, 31.6, 31.5, 30.3, 28.8, 22.6, 14.1 ppm. HRMS: calcd. for $C_{30}H_{27}NO_2S_3$ [M]$^+$ 529.1204; found 529.1208.

20: The annulation of bromide **1e** (0.31 g, 0.59 mmol) with terthiophene (0.18 g, 0.72 mmol) by using $ZnBr_2$ (0.26 g, 1.15 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **14** afforded compound **20** (0.14 g, 45%) as a pale-yellow solid. M.p. 240 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 8.25 (d, *J* = 7.8 Hz, 1 H), 8.14 (s, 1 H), 7.83 (d, *J* = 7.8 Hz, 1 H), 7.73 (d, *J* = 8.7 Hz, 2 H), 7.46 (s, 1 H), 7.45–7.23 (m, 6 H), 7.20–7.14 (m, 2 H), 7.06 (d, *J* = 3.6 Hz, 1 H), 6.98 (t, *J* = 3.9 Hz, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.1, 139.3, 138.1, 137.8, 137.6, 137.1, 136.8, 135.8, 135.5, 133.8, 129.0, 128.0, 127.7, 126.5, 126.1, 125.9, 125.2, 124.9, 124.5, 124.2, 124.1, 120.0, 119.9, 115.3, 113.0, 109.3 ppm. MS (EI): *m*/*z* (%) = 527 (66) [M]$^+$. $C_{28}H_{17}NO_2S_4$ (527.01): calcd. C 63.73, H 3.25, N 2.65, S 24.31; found C 63.83, H 3.03, N 2.91, S 24.60.

21: The annulation of bromide **1f** (0.3 g, 0.75 mmol) with bithiophene (0.15 g, 0.90 mmol) by using $ZnBr_2$ (0.34 g, 1.50 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **14** afforded compound **21** (0.12 g, 50%) as a pale-yellow solid. M.p. 208 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.46 (s, 1 H), 8.19 (t, *J* = 4.5 Hz, 2 H), 7.85–7.82 (m, 1 H), 7.52 (s, 1 H), 7.50–7.45 (m, 2 H), 7.32 (d, *J* = 4.8 Hz, 1 H), 7.26 (s, 1 H), 7.08 (t, *J* = 4.5 Hz, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.4, 138.5, 138.1, 137.4, 137.0, 136.7, 135.2, 133.9, 128.0, 127.0, 125.6, 125.2, 124.5, 122.9, 121.4, 119.5, 115.6, 115.5 ppm. MS (EI): *m*/*z* (%) = 322 (71) [M]$^+$. $C_{18}H_{10}S_3$ (321.99): calcd. C 67.04, H 3.13, S 29.83; found C 67.14, H 3.29, S 29.61.

22: The annulation of bromide **1g** (0.31 g, 0.90 mmol) with bithiophene (0.18 g, 1.08 mmol) by using $ZnBr_2$ (0.40 g, 1.80 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **14** afforded compound **22** (0.11 g, 46%) as a pale-yellow solid. M.p. 270 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 (s, 1 H), 8.19 (s, 1 H), 7.92 (t, *J* = 6 Hz, 1 H), 7.87 (t, *J* = 6 Hz, 1 H), 7.47 (s, 1 H), 7.46–7.42 (m, 2 H), 7.33 (d, *J* = 4.8 Hz, 2 H), 7.08 (t, *J* = 3.9 Hz, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.7, 138.4, 137.7, 137.4, 131.3, 131.2, 128.1 128.0, 127.2, 126.0, 125.7, 125.3, 125.0, 121.5, 120.2, 118.9 ppm. MS (EI): *m*/*z* (%) = 266 (53) [M]$^+$. $C_{16}H_{10}S_2$ (266.02): calcd. C 72.14, H 3.78, S 24.07; found C 72.40, H 3.93, S 24.30.

23: The annulation of bromide **1h** (0.32 g, 0.92 mmol) with bithiophene (0.18 g, 1.08 mmol) by using $ZnBr_2$ (0.41 g, 1.82 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **14** afforded compound **23** (0.11 g, 44%) as a pale-yellow solid. M.p. 252 °C. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 8.45 (s, 2 H), 7.80 (d, *J* = 5.4 Hz, 1 H), 7.68 (s, 1 H), 7.65 (d, *J* = 5.1 Hz, 1 H), 7.48 (d, *J* = 4.8 Hz, 2 H), 7.17 (t, *J* = 4.5 Hz, 1 H) ppm. ^{13}C NMR (75.4 MHz, [D_6]DMSO): δ = 137.8, 137.5, 137.1, 136.6, 136.4, 135.5, 128.5, 128.2, 126.9, 125.7, 123.2, 118.9, 116.9, 116.7 ppm. MS (EI): *m*/*z* (%) = 272 (73) [M]$^+$. $C_{14}H_8S_3$ (271.98): calcd. C 61.73, H 2.96, S 35.31; found C 61.53, H 2.80, S 35.53.

25: To a solution of bromide **24** (0.3 g, 0.78 mmol) in dry DCE (10 mL) was added anhydrous $ZnBr_2$ (0.35 g, 1.55 mmol) and bithiophene (0.15 g, 0.90 mmol). The mixture was then heated at reflux for 4 h under a nitrogen atmosphere. The solvent was removed, and the reaction mixture was quenched with ice water (30 mL) containing concentrated HCl (1 mL), extracted with chloroform (3 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatography (*n*-hexane/ethyl acetate, 99:1) led to the isolation of **25** (0.1 g, 42%) as a pale-yellow solid. M.p. 228 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.29 (s, 1 H), 7.97 (d, *J* = 6.9 Hz, 1 H), 7.85 (s, 1 H), 7.57–7.26 (m, 6 H), 7.08 (s, 1 H) ppm.

^{13}C NMR (75.4 MHz, CDCl$_3$): δ = 157.1, 154.9, 139.8, 138.5, 137.4, 134.2, 128.0, 127.5, 125.7, 125.2, 123.8, 123.2, 122.7, 120.6, 119.6, 113.5, 111.5, 105.0 ppm. MS (EI): *m*/*z* (%) = 306 (55) [M]$^+$. $C_{18}H_{10}OS_2$ (306.02): calcd. C 70.56, H 3.29, S 20.93; found C 70.40, H 3.50, S 20.68.

26: To a solution of bromide **1c** (0.2 g, 0.38 mmol) in dry DCE (8 mL) was added anhydrous $ZnBr_2$ (0.02 g, 0.09 mmol) and 2,3-benzofuran (0.05 mL, 0.42 mmol). The mixture was then stirred at room temperature for 2 h under a nitrogen atmosphere. The solvent was removed, and the reaction mixture was quenched with ice water (20 mL) containing concentrated HCl (1 mL), extracted with chloroform (2 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatography (*n*-hexane/ethyl acetate, 99:1) led to the isolation of **26** (0.09 g, 60%) as a colorless solid. M.p. 192–194 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.49 (s, 1 H), 8.32 (d, *J* = 8.1 Hz, 1 H), 8.28 (s, 1 H), 7.91 (t, *J* = 7.5 Hz, 2 H), 7.81 (d, *J* = 7.2 Hz, 2 H), 7.54 (d, *J* = 8.1 Hz, 1 H), 7.47–7.22 (m, 7 H) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$): δ = 157.0, 156.2, 139.0, 138.0, 137.7, 133.9, 129.0, 127.1, 126.9, 126.5 (2 C), 124.2, 123.9, 122.9, 122.8, 121.7, 120.5, 119.7, 115.3, 111.6, 111.0, 98.9 ppm. MS (EI): *m*/*z* (%) = 397 (65) [M]$^+$. $C_{24}H_{15}NO_3S$ (397.08): calcd. C 72.53, H 3.80, N 3.52, S 8.07; found C 72.22, H 3.87, N 3.80, S 8.29.

27: The annulation of bromide **1c** (0.2 g, 0.38 mmol) with *N*-hexylindole (0.09 g, 0.44 mmol) by using $ZnBr_2$ (0.02 g, 0.09 mmol) in dry 1,2-DCE (8 mL) following the same procedure as that of **26** afforded compound **27** (0.1 g, 55%) as a colorless solid. M.p. 166 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.01 (s, 1 H), 8.35 (d, *J* = 8.4 Hz, 1 H), 8.26 (d, *J* = 7.8 Hz, 1 H), 7.94 (d, *J* = 7.8 Hz, 1 H), 7.78 (d, *J* = 8.1 Hz, 2 H), 7.72 (s, 1 H), 7.50–7.17 (m, 8 H), 4.30 (t, *J* = 7.2 Hz, 2 H), 1.90–1.85 (m, 2 H), 1.55–1.30 (m, 6 H), 0.85 (t, *J* = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$): δ = 141.7, 139.4, 138.4, 137.6, 133.5, 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, 98.5, 43.3, 31.6, 28.8, 27.0, 22.6, 14.0 ppm. MS (EI): *m*/*z* (%) = 480 (35) [M]$^+$. $C_{30}H_{28}N_2O_2S$ (480.19): calcd. C 74.97, H 5.87, N 5.83, S 6.67; found C 74.82, H 5.69, N 5.60, S 6.40.

28: The annulation of bromide **1d** (0.2 g, 0.36 mmol) with 2,3-benzofuran (0.05 mL, 0.42 mmol) by using $ZnBr_2$ (0.02 g, 0.09 mmol) in dry 1,2-DCE (8 mL) following the same procedure as that of **26** afforded compound **28** (0.09 g, 56%) as a colorless solid. M.p. 198–200 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.47 (s, 1 H), 8.24 (s, 1 H), 8.20 (d, *J* = 9.0 Hz, 1 H), 7.94 (d, *J* = 7.5 Hz, 1 H), 7.76 (d, *J* = 7.5 Hz, 2 H), 7.56 (d, *J* = 8.1 Hz, 1 H), 7.47–7.31 (m, 4 H), 7.25 (t, *J* = 7.5 Hz, 2 H), 7.03 (dd, *J* = 2.7, 9.0 Hz, 1 H), 3.90 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$): δ = 157.1, 157.0, 156.2, 138.7, 137.4, 133.8, 133.2, 129.0, 127.7, 127.1, 126.5, 123.9, 123.0, 122.9, 121.6, 120.4, 116.4, 114.6, 111.7, 111.0, 103.2, 99.2, 55.8 ppm. MS (EI): *m*/*z* (%) = 427 (51) [M]$^+$. $C_{25}H_{17}NO_4S$ (427.09): calcd. C 70.24, H 4.01, N 3.28, S 7.50; found C 70.37, H 4.26, N 3.12, S 7.73.

29: The annulation of bromide **1d** (0.2 g, 0.36 mmol) with *N*-hexylindole (0.09 g, 0.44 mmol) by using $ZnBr_2$ (0.02 g, 0.09 mmol) in dry 1,2-DCE (8 mL) following the same procedure as that of **26** afforded compound **29** (0.09 g, 47%) as a colorless solid. M.p. 172–174 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.00 (s, 1 H), 8.26 (t, *J* = 8.7 Hz, 2 H), 7.72 (d, *J* = 7.5 Hz, 2 H), 7.67 (s, 1 H), 7.52 (t, *J* = 8.1 Hz, 1 H), 7.42–7.17 (m, 6 H), 7.06 (dd, *J* = 2.4, 9.0 Hz, 1 H), 4.33 (t, *J* = 7.2 Hz, 2 H), 3.93 (s, 3 H), 1.95–1.85 (m, 2 H), 1.43–1.26 (m, 6 H), 0.86 (t, *J* = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$): δ = 157.0, 141.7, 138.4, 137.3, 133.7, 133.4, 128.7, 128.6, 126.5, 126.3, 126.1, 123.7, 122.9, 120.7, 118.9, 116.9, 114.9, 108.7, 107.3, 103.3, 98.4, 55.8, 43.3, 31.6, 28.8, 27.0, 22.5, 14.0 ppm. MS (EI): *m*/*z* (%) = 510 (78) [M]$^+$. $C_{31}H_{30}N_2O_3S$ (510.20): calcd. C 72.91, H 5.92, N 5.49, S 6.28; found C 72.73, H 5.68, N 5.72, S 6.47.

30a and 30b: To a solution of bromide **1c** (0.3 g, 0.57 mmol) in dry 1,2-DCE (10 mL) was added $InBr_3$ (0.02 g, 0.06 mmol) and benzo[*b*]thiophene (0.09 g, 0.67 mmol). The reaction mixture was stirred at room temperature for 4 h and then heated at reflux for 1 h under a nitrogen atmosphere. The mixture was then poured over ice water (30 mL) containing concentrated HCl (1 mL), extracted with chloroform (2 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatography (*n*-hexane/ethyl acetate, 99:1) afforded an inseparable mixture of products **30a** and **30b** (1:0.4, based on ^{1}H NMR integration) as a colorless solid (0.15 g, 65%). Data for the mixture of isomers: M.p. 230–232 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.05 (s), 8.77 (s), 8.54 (s), 8.33 (d, *J* = 7.8 Hz), 8.22 (s), 8.18–8.15 (m), 7.98 (d, *J* = 7.5 Hz), 7.89–7.79 (m), 7.53–7.22 (m) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$): δ = 140.1, 139.5, 139.4, 138.9, 137.8, 137.7, 137.6, 136.7, 135.6, 135.5, 135.4, 134.9, 133.9, 133.8, 132.4, 129.1, 129.0, 127.9, 127.5, 127.1, 126.8, 126.7, 126.5, 126.4, 126.0, 124.5, 124.3, 124.2, 122.9, 122.8, 121.9, 121.3, 120.1, 119.9, 115.4, 115.3, 113.6, 112.2, 108.8, 107.9 ppm. ^{13}C NMR (DEPT 90, 75.4 MHz, CDCl$_3$): δ = 133.9, 133.8, 129.1, 129.0, 127.9, 127.5, 127.1, 126.7, 126.5, 126.4, 124.5, 124.3, 124.2, 122.9, 122.8, 121.9, 121.3, 120.1, 119.9, 115.4, 115.3, 113.6, 112.2, 108.8, 107.9 ppm.

30a and 30b: The annulation of bromide **1e** (0.3 g, 0.57 mmol) with benzo[*b*]thiophene (0.09 g, 0.67 mmol) by using $InBr_3$ (0.02 g, 0.06 mmol) in dry 1,2-DCE (10 mL) following a similar procedure as mentioned above led to an inseparable mixture of products **30a** and **30b** (0.4:1, based on ^{1}H NMR integration) as a colorless solid (0.16 g, 70%). Data for the mixture of isomers: M.p. 192–194 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.03 (s), 8.74 (s), 8.47 (s), 8.29 (d, *J* = 8.4 Hz), 8.15 (s), 8.13–8.10 (m), 7.94 (d, *J* = 7.5 Hz), 7.84–7.76 (m), 7.49–7.35 (m), 7.33–7.19 (m) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$): δ = 140.1, 139.5, 139.4, 138.9, 137.8, 137.7, 137.6, 136.6, 135.6, 135.5, 135.3, 134.9, 133.9, 133.8, 132.4, 129.1, 129.0, 127.8, 127.5, 127.1, 126.7, 126.5, 126.4 (2 C), 126.0, 124.7, 124.5, 124.3, 124.2, 122.8, 122.7, 121.8 121.3, 120.1, 119.9, 115.4, 115.3, 113.6, 112.2, 108.8, 107.9 ppm. ^{13}C NMR (DEPT 90, 75.4 MHz, CDCl$_3$): δ = 133.9, 133.8, 129.1, 129.0, 127.8, 127.6, 127.1, 126.7, 126.5, 126.4, 124.5, 124.3, 124.2, 122.9, 122.8, 121.9, 121.3, 120.1, 119.9, 115.4, 115.3, 113.6, 112.2, 108.7, 107.9 ppm.

31a and 31b: The annulation of bromide **24** (0.33 g, 0.86 mmol) with benzo[*b*]thiophene (0.14 g, 1.04 mmol) by using $ZnBr_2$ (0.04 g, 0.17 mmol) in dry 1,2-DCE (10 mL) following the similar procedure as that of **30** afforded an inseparable mixture of products **31a** and **31b** (0.11 g, 46%) as a colorless solid (1:0.3, based on ^{1}H NMR integration) Data for the mixture of isomers: M.p. 170 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.58 (s), 8.28 (s), 8.20–8.13 (m), 7.99 (t, *J* = 6.3 Hz), 7.92 (s), 7.85–7.80 (m), 7.57–7.31 (m) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$): δ = 157.2, 156.8, 155.8, 154.6, 140.3, 139.1, 139.0, 135.4, 135.2, 135.1, 134.1, 131.5, 127.6, 127.3, 126.9, 126.3, 124.7, 124.5, 124.3, 124.1, 123.7, 122.9 (2 C), 122.8 (2 C), 122.6, 121.6, 121.2, 120.7, 120.5, 114.0, 112.8, 111.7, 105.1, 103.8 ppm. ^{13}C NMR (DEPT 90, 75.4 MHz, CDCl$_3$): δ = 127.7, 127.3, 126.9, 126.3, 124.5, 124.3, 122.9 (2 C), 122.8 (2 C), 121.6, 121.2, 120.8, 120.5, 114.0, 112.8, 117.7, 105.1, 103.8 ppm.

32: The annulation of bromide **1g** (0.3 g, 0.88 mmol) with benzo[*b*]thiophene (0.14 g, 1.04 mmol) by using $ZnBr_2$ (0.04 g, 0.17 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **30** afforded compound **32** (0.1 g, 50%) as a colorless solid. M.p.

140 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 8.25 (s, 1 H), 8.22 (d, J = 4.2 Hz, 1 H), 8.00 (t, J = 6.3 Hz, 1 H), 7.89 (t, J = 6.3 Hz, 1 H), 7.82–7.79 (m, 1 H), 7.53–7.45 (m, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.2, 137.7, 135.1, 132.6, 130.9, 128.4, 127.7, 127.1, 126.0, 125.2, 124.5, 122.8, 122.0, 120.6, 120.0 ppm. ^{13}C NMR (DEPT: 90, 75.4 MHz, $CDCl_3$): δ = 128.4, 127.7, 127.1, 126.0, 125.2, 124.5, 122.9, 122.0, 120.6, 120.0 ppm. MS (EI): *m*/*z* (%) = 234 (53) [M]$^+$. $C_{16}H_{10}S$ (234.05): calcd. C 82.01, H 4.30, S 13.68; found C 82.22, H 4.13, S 13.87.

34: To a solution of bromide **1f** (0.3 g, 0.75 mmol) in dry 1,2-DCE (10 mL) was added $ZnBr_2$ (0.34 g, 1.50 mmol) and *N*-hexylcarbazole (0.22 g, 0.87 mmol). The reaction mixture was then heated at reflux for 3 h under a nitrogen atmosphere. The solvent was removed, and the reaction mixture was quenched with ice water (30 mL) containing concentrated HCl (1 mL), extracted with chloroform (2 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatography (*n*-hexane/ethyl acetate, 99:1) afforded product **34** (0.15 g, 50%) as a yellow solid. M.p.188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.67 (s, 1 H), 8.52 (s, 1 H), 8.38 (s, 1 H), 8.24–8.17 (m, 2 H), 7.81–7.78 (m, 1 H), 7.76 (s, 1 H), 7.52 (t, J = 7.5 Hz, 1 H), 7.46–7.43 (m, 2 H), 7.32 (d, J = 7.8 Hz, 1 H), 7.23 (t, J = 7.4 Hz, 1 H), 4.26 (t, J = 7.4 Hz, 2 H), 1.96–1.86 (m, 2 H), 1.53–1.25 (m, 6 H), 0.87 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 143.5, 140.4, 140.3, 135.4, 134.7, 134.1, 130.2, 127.8, 127.5, 126.0, 124.4, 122.85, 122.7, 121.8, 121.1, 120.9, 118.9, 118.7, 117.5, 108.2, 103.1, 43.3, 31.7, 28.4, 27.1, 22.6, 14.1 ppm. HRMS: calcd. for $C_{28}H_{25}NS$ [M]$^+$ 407.1708; found 407.1713.

35: The annulation of bromide **1f** (0.3 g, 0.75 mmol) with 2-ethylhexylcarbazole (0.25 g, 0.89 mmol) by using $ZnBr_2$ (0.34 g, 1.50 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **34** afforded compound **35** (0.17 g, 52%) as a yellow solid. M.p. 182 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.70 (s, 1 H), 8.54 (s, 1 H), 8.41 (s, 1 H), 8.28 (t, J = 5.1 Hz, 1 H), 8.23 (d, J = 7.8 Hz, 1 H), 7.84 (t, J = 4.8 Hz, 1 H), 7.76 (s, 1 H), 7.59–7.48 (m, 3 H), 7.36 (d, J = 8.1 Hz, 1 H), 7.28 (t, J = 7.8 Hz, 1 H), 4.15 (d, J = 7.5 Hz, 2 H), 2.22–2.18 (m, 1 H), 1.51–1.29 (m, 8 H), 1.01–0.90 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 143.9, 140.8, 140.4, 135.4, 134.7, 134.1, 130.2, 127.7, 127.5, 127.4, 125.9, 124.3, 122.8, 122.6, 121.8, 121.0, 120.8, 118.9, 118.7, 117.3, 108.5, 103.4, 47.7, 39.0, 31.1, 28.9, 24.6, 23.1, 14.0, 11.0 ppm. HRMS: calcd. for $C_{30}H_{29}NS$ [M]$^+$ 435.2021; found 435.2027.

36: The annulation of bromide **1f** (0.32 g, 0.80 mmol) with *p*-anisylcarbazole (0.26 g, 0.95 mmol) by using $ZnBr_2$ (0.36 g, 1.59 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **34** afforded compound **36** (0.17 g, 48%) as a pale-yellow solid. M.p. 225 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (s, 1 H), 8.65 (s, 1 H), 8.48 (s, 1 H), 8.29 (d, J = 7.8 Hz, 1 H), 8.21–8.18 (m, 1 H), 7.81 (t, J = 7.6 Hz, 2 H), 7.57 (d, J = 8.7 Hz, 2 H), 7.48–7.45 (m, 3 H), 7.32–7.30 (m, 2 H), 7.19 (d, J = 8.7 Hz, 2 H), 3.96 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 159.0, 144.3, 141.3, 140.3, 135.3, 134.8, 134.5, 130.5, 130.3, 128.7, 128.2, 127.6, 127.5, 126.0, 124.4, 123.0, 122.9, 121.8, 121.1, 120.9, 119.7, 119.1, 117.5, 115.3, 109.3, 104.3, 55.7 ppm. HRMS: calcd. for $C_{29}H_{19}NOS$ [M]$^+$ 429.1187; found 429.1182.

37: The annulation of bromide **24** (0.33 g, 0.86 mmol) with *N*-hexylcarbazole (0.26 g, 1.03 mmol) by using $ZnBr_2$ (0.39 g, 1.73 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **34** afforded compound **37** (0.14 g, 41%) as a pale-yellow solid. M.p. 132 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.73 (s, 1 H), 8.59 (s, 1 H), 8.24 (d, J = 7.5 Hz, 1 H), 8.07 (d, J = 7.5 Hz, 1 H), 8.00 (s, 1 H), 7.75 (s, 1 H), 7.57–7.48 (m, 4 H), 7.38 (d, J = 8.4 Hz, 2 H), 4.34 (t, J = 7.2 Hz, 2 H), 2.00–1.90 (m, 2 H), 1.50–1.30 (m, 6 H), 0.88 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.5, 155.0, 143.1, 140.9, 132.6, 127.7, 127.1, 125.2, 124.6, 124.4, 122.9, 127.8, 122.6, 120.9, 120.8, 119.6, 119.2, 118.8, 111.3, 108.2, 105.3, 102.5, 43.3, 31.6, 28.4, 27.1, 22.6, 14.0 ppm. HRMS: calcd. for $C_{28}H_{25}NO$ [M]$^+$ 391.1936; found 391.1934.

39: To a solution of substrate **1e** (0.3 g, 0.57 mmol) in dry 1,2-DCE (10 mL) was added $ZnBr_2$ (0.26 g, 1.15 mmol) and **38**[29] (0.22 g, 0.68 mmol). The reaction mixture was stirred at room temperature for 4 h and then heated at reflux for 1 h under a nitrogen atmosphere. The mixture was then poured over ice water (30 mL) containing concentrated HCl (1 mL), extracted with chloroform (2 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatography (*n*-hexane/ethyl acetate, 99:1) led to the isolation of **39** as a yellow solid (0.21 g, 60%). M.p. 172 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.65 (s, 1 H), 8.26 (d, J = 8.1 Hz, 1 H), 8.20 (s, 1 H), 8.06 (d, J = 8.7 Hz, 1 H), 7.85 (d, J = 7.5 Hz, 1 H), 7.78–7.70 (m, 3 H), 7.65 (s, 1 H), 7.57 (d, J = 8.6 Hz, 2 H), 7.45–7.12 (m, 6 H), 7.05 (t, J = 8.7 Hz, 1 H), 6.9 (d, J = 8.4 Hz, 2 H), 3.82 (s, 3 H) ppm. ^{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 ppm. $C_{35}H_{23}NO_3S_3$ (601.08): calcd. 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: calcd. for $C_{35}H_{23}NO_3S_3$ [M]$^+$ 601.0840; found 601.0843.

41: To a solution of bromide **40** (0.25 g, 0.34 mmol) in dry 1,2-DCE (10 mL) was added $ZnBr_2$ (0.3 g, 1.33 mmol) and *m*-xylene (0.1 mL, 0.84 mmol). The reaction mixture was stirred at room temperature for 2 h and then heated at reflux for 1 h under a nitrogen atmosphere. Usual workup followed by flash column chromatography (*n*-hexane/ethyl acetate, 99:1) afforded product **41** (0.08 g, 50%) as a colorless solid. M.p. 242 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.82 (s, 2 H), 8.32 (s, 2 H), 7.81 (d, J = 7.2 Hz, 2 H), 7.62 (s, 2 H), 7.39 (t, J = 6.0 Hz, 2 H), 7.26–7.14 (m, 3 H), 2.85 (s, 6 H), 2.53 (s, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 138.2, 134.6, 134.4, 133.6, 131.2, 131.0, 129.5, 129.0, 128.9, 126.5, 125.9, 125.3, 119.0, 109.0, 21.6, 19.9 ppm. HRMS: calcd. for $C_{30}H_{25}NO_2S$ [M]$^+$ 463.1606; found 463.1611.

42: The annulation of bromide **40** (0.3 g, 0.40 mmol) with *p*-xylene (0.12 mL, 0.94 mmol) by using $ZnBr_2$ (0.36 g, 1.59 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **41** afforded compound **42** (0.11 g, 58%) as a colorless solid. M.p. 290 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.89 (s, 2 H), 8.64 (s, 2 H), 7.84 (d, J = 8.4 Hz, 2 H), 7.41–7.21 (m, 7 H), 2.86 (s, 6 H), 2.84 (s, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 138.4, 133.7, 133.0, 132.8, 132.6, 130.2, 128.9, 126.8, 126.5, 126.2, 125.7, 116.1, 109.5, 20.0, 19.8 ppm. HRMS: calcd. for $C_{30}H_{25}NO_2S$ [M]$^+$ 463.1606; found 463.1612.

43: The annulation of bromide **40** (0.3 g, 0.40 mmol) with bithiophene (0.16 g, 0.96 mmol) by using $ZnBr_2$ (0.36 g, 1.59 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **41** afforded compound **43** (0.13 g, 54%) as a pale-yellow solid. M.p. 270 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.69 (s, 2 H), 8.16 (s, 2 H), 7.78 (d, J = 7.5 Hz, 2 H), 7.43 (s, 2 H), 7.40–7.26 (m, 7 H), 7.06 (t, J = 3.9 Hz, 2 H) ppm. ^{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 ppm. $C_{30}H_{17}NO_2S_5$ (582.99): calcd. 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: calcd. for $C_{30}H_{17}NO_2S_5$ [M]$^+$ 582.9863; found 582.9867.

47: To a mixture of **46** (0.5 g, 1.04 mmol) in dry THF (20 mL) was added **44** (0.25 g, 1.26 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol), and K_2CO_3 (0.29 g, 2.10 mmol), and the reaction mixture was heated to reflux for 48 h. The mixture was then quenched with ice water and extracted with $CHCl_3$, and the organic layer was washed with brine (2 × 10 mL). Removal of the solvent followed by column chromatography (*n*-hexane/ethyl acetate, 85:15) afforded compound **47** (0.22 g, 50%) as a yellow solid. M.p. 166–168 °C. IR (KBr): $\tilde{\nu}$ = 3284, 1700, 1601 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$: δ = 8.26 (s, 1 H), 8.03 (s, 1 H), 7.91–7.82 (m, 3 H), 7.55–7.44 (m, 4 H), 7.37 (d, *J* = 6.9 Hz, 1 H), 7.15–7.12 (m, 3 H), 4.57 (s, 2 H), 4.33 (q, *J* = 7.2 Hz, 2 H), 4.24 (q, *J* = 7.2 Hz, 2 H), 1.36 (t, *J* = 7.2 Hz, 3 H), 1.13 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 167.5, 165.7, 142.0, 137.7, 135.5, 134.1, 132.4, 131.9, 128.8, 128.5, 127.8, 126.9, 126.5, 126.2, 125.7, 123.6, 122.6, 121.2, 120.1, 115.8, 111.1, 108.7, 61.3 (2 C), 30.8, 14.3, 13.8 ppm. MS (EI): *m*/*z* (%) = 427 (51) $[M]^+$. $C_{27}H_{25}NO_4$ (427.18): calcd. C 75.86, H 5.89, N 3.28; found C 75.56, H 5.75, N 3.50.

45: To a stirred suspension of NaH (0.04 g, 0.83 mmol) in dry THF (10 mL) was slowly added compound **47** (0.2 g, 0.47 mmol) in dry THF (20 mL) under a nitrogen atmosphere at 0 °C. After the addition was complete, the reaction mixture was stirred at room temperature for 1 h and then heated at reflux for 1 h. The mixture was then cooled to 0 °C, and a solution of phenylsulfonyl chloride (0.09 mL, 0.67 mmol) in the same solvent (10 mL) was slowly added. The reaction mixture was stirred at room temperature for 1 h and then heated at reflux for 5 h. The mixture was then poured over crushed ice containing saturated NH_4Cl solution, extracted with $CHCl_3$ (2 × 10 mL), and dried (Na_2SO_4). Removal of the solvent followed by crystallization from methanol afforded **45** (0.16 g, 61%) as a colorless solid. M.p. 124–126 °C. IR (KBr): $\tilde{\nu}$ = 1728, 1713, 1624, 1376, 1177 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 8.4 Hz, 1 H), 8.08 (d, *J* = 8.1 Hz, 1 H), 7.87 (d, *J* = 7.5 Hz, 1 H), 7.66 (d, *J* = 8.1 Hz, 1 H), 7.57–7.35 (m, 8 H), 7.28 (t, *J* = 7.5 Hz, 1 H), 7.18 (t, *J* = 7.8 Hz, 2 H), 7.06 (t, *J* = 7.8 Hz, 1 H), 6.74 (d, *J* = 6.9 Hz, 1 H), 4.97 (s, 2 H), 4.18 (q, *J* = 7.2 Hz, 2 H), 3.87 (q, *J* = 6.9 Hz, 2 H), 1.23 (t, *J* = 6.9 Hz, 3 H), 0.73 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 164.7, 163.5, 138.0, 137.7, 136.1, 133.2, 132.6, 131.2, 129.0, 128.5, 128.2, 127.1, 126.8, 126.0, 125.9, 125.3, 125.1, 124.9, 124.6, 123.4, 122.7, 119.1, 117.8, 114.4, 61.1, 60.7, 29.0, 13.5, 12.8 ppm. MS (EI): *m*/*z* (%) = 567 (70) $[M]^+$. $C_{33}H_{29}NO_6S$ (567.17): calcd. C 69.82, H 5.15, N 2.47, S 5.65; found C 69.65, H 5.01, N 2.67, S 5.93.

48: To a solution of compound **47** (0.2 g, 0.46 mmol) in CH_3CN (10 mL) was added DMAP (0.01 g, 0.08 mmol) and di-*tert*-butyl dicarbonate (0.13 mL, 0.55 mmol), and the mixture was stirred at room temperature for 4 h. The solvent was removed in vacuo and then extracted with $CHCl_3$ (2 × 10 mL). The organic layer was washed with $NaHCO_3$ solution (2 × 10 mL) and then dried ($NaSO_4$). Removal of the solvent followed by crystallization from methanol afforded **48** (0.20 g, 83%) as a colorless solid. M.p. 137 °C. IR (KBr): $\tilde{\nu}$ = 1730, 1716, 1626 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.1 Hz, 1 H), 8.11 (d, *J* = 8.1 Hz, 1 H), 7.88 (d, *J* = 8.1 Hz, 1 H), 7.87 (s, 1 H), 7.71 (d, *J* = 8.4 Hz, 1 H), 7.62–7.50 (m, 3 H), 7.37–7.24 (m, 3 H), 6.75 (d, *J* = 6.9 Hz, 1 H), 4.89 (s, 2 H), 4.24 (q, *J* = 7.2 Hz, 2 H), 3.95 (q, *J* = 7.2 Hz, 2 H), 1.27 (t, *J* = 7.2 Hz, 3 H), 1.13 (s, 9 H), 0.96 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 165.8, 164.3, 149.8, 138.0, 137.2, 136.7, 134.8, 133.6, 131.7, 128.8, 127.2, 127.0, 126.2, 125.8, 125.6, 124.7, 124.1, 123.2, 123.1, 119.3, 116.6, 115.7, 84.6, 61.5, 61.3, 30.9, 27.5, 14.1, 13.6 ppm. MS (EI): *m*/*z* (%) = 527 (52) $[M]^+$. $C_{32}H_{33}NO_6$ (527.23): calcd. C 72.85, H 6.30, N 2.65; found C 72.70, H 6.49, N 2.90.

50: The annulation of bromide **49**[16] (0.24 g, 0.44 mmol) with benzo[*b*]furan (0.05 mL, 0.50 mmol) by using $ZnBr_2$ (0.02 g, 0.09 mmol) in dry 1,2-DCE (10 mL) following the same procedure as that of **26** afforded compound **50** (0.11 g, 58%) as a colorless solid. M.p. 176–178 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.49 (s, 1 H), 8.30 (d, *J* = 8.4 Hz, 1 H), 8.27 (s, 1 H), 7.90 (t, *J* = 6.0 Hz, 2 H), 7.72 (d, *J* = 8.4 Hz, 2 H), 7.53 (d, *J* = 8.1 Hz, 1 H), 7.46–7.28 (m, 4 H), 6.64 (d, *J* = 8.4 Hz, 2 H), 3.58 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 163.8, 157.0, 156.2, 139.0, 138.1, 129.3, 128.7, 127.1, 126.9, 126.4, 124.1, 123.9, 122.9, 122.8, 121.5, 120.5, 119.7, 115.3, 114.2, 111.6, 111.0, 98.9, 55.4 ppm. MS (EI): *m*/*z* (%) = 427 (75) $[M]^+$. $C_{25}H_{17}NO_4S$ (427.09): calcd. C 70.24, H 4.01, N 3.28, S 7.50; found C 70.03, H 4.15, N 3.04, S 7.30.

Supporting Information (see footnote on the first page of this article): Experimental procedure for the preparation of bromomethyl compounds **1a**–**h**, **24**, **40**, **46**, and **49**.

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