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A Novel Radical Cyclization Approach to Thieno-Fused Heterocycles

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Dedicated to Professor Carmen Nájera on the occasion of her 60th birthday

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An efficient synthesis of novel aryl/heteroaryl-substituted thieno-fused heterocycles, that is, thieno[2,3-*b*]thiophenes, thieno[2,3-*b*]indoles, and pyrazolo[3,2-*c*]thiophenes, involving radical-mediated cyclization of 2-(2-bromoheteroaryl)-3-methylthio-3-aryl/heteroaryl acrylonitriles has been reported.

Introduction

Condensed thiophenes, especially heterocyclo-fused systems, have attracted considerable attention because several of these compounds display exceptional optoelectronic properties as well as a range of biological activities, thus finding applications as organic functional materials and as pharmaceuticals.[1–5] Thus, fused thienothiophenes such as thieno[2,3-*b*]thiophene (**1a**), thieno[3,2-*b*]thiophene (**1b**), and dithienothiophenes have been widely investigated as key components in several molecular structures for a variety of applications such as charge conducting materials,[2] organic field-effect transistors,[3] organic luminescence devices, nonlinear optics,[4] and as porous hydrogen storage hosts.[5] On the other hand, heterocyclo-fused thiophenes such as thieno[2,3-*b*]indole (**2**) have attracted great deal of interest due to its presence in natural products, and thienoindolin (**3**, Figure 1) isolated from the culture broth of *Streptomyces albogriseolus* (MJ 286–76F7) displays both growth promoting and inhibiting activities in rice seedlings.[6] Also, a number of thieno[2,3-*b*]indole derivatives are shown to display antifungal activity[7] and are useful in the treatment of central nervous system diseases such as epilepsy, senile dementia, Parkinson's disease, brain ischemia, and so on.[8] Some of the thieno[3,2-*b*]indole derivatives have also been found to be novel conducting polymers. Similarly, other five-membered heterocyclo-fused thiophenes such as thieno[3,2-*b*]pyrroles,[9a,9b] thieno[3,2-*d*]-imidazole, and thieno[2,3-*d*]imidazoles[9b] have been shown to be potential anti-inflammatory agents[9a] and are useful in the treatment of hepatitis C infection.[9a–9c] A thieno[3,2-*c*]pyrazole derivative A02011–1 (**4**) has been found to be a potent adenyl cyclase activator exhibiting an antiproliferative effect in rat vascular smooth muscle cells.[9d]

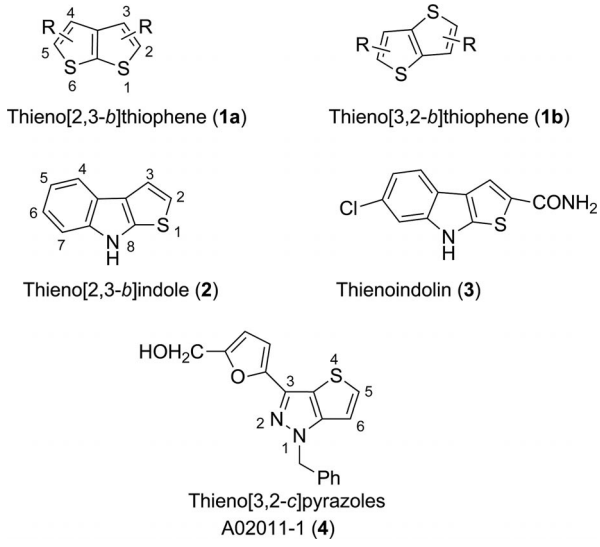

Figure 1. Important thieno-fused heterocycles.

A number of approaches have been reported in the literature for the synthesis of heterocyclo-fused thiophenes. Thus, symmetrically substituted thieno[2,3-*b*]thiophenes are usually synthesized by intramolecular cyclocondensation of in situ generated polarized ketene dithioacetals obtained by dialkylation of dithioate salts with activated halomethylene compounds involving construction of both thiophene rings in a one-pot reaction.[10] A similar general approach to

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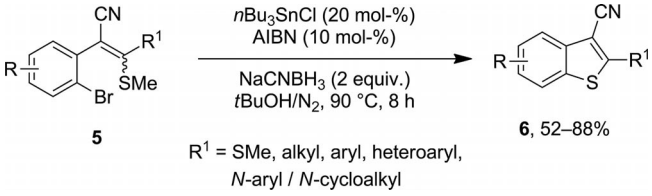
these heterocycles involves construction of a thiophene ring on vicinally substituted 2-formyl (or acyl)-3-thiomethylenethiophene derivatives through base-induced intramolecular cyclocondensation.[11] This methodology or its variants has also been employed for the synthesis of other thieno-fused heterocycles such as thieno[2,3-*c*]- and thieno[3,2-*c*]pyrazoles,[12] thieno[2,3-*b*]indole derivatives,[8,13,14] as well as in total synthesis of thienoindolin alkaloids by Bergman and co-workers.[15] Other preparative methods for aryl/heteroaryl-substituted thienothiophenes utilize palladium-catalyzed cross-coupling or selective metalation reactions[1c,11a–11d,16] including direct C–H arylation of thieno[2,3-*b*]thiophenes[17] and intramolecular cyclization of bisacetylene dithioate salts obtained by treatment of metalated bisacetylenes with carbon disulfide.[18] Thieno[2,3-*b*]indole and its derivatives have also been obtained by nitrene-mediated Cadogan cyclization of 3-(*o*-nitrophenyl)thiophene,[19] $AlCl_3$-induced electrophilic recyclization of 2-(2-furyl)arylisothiocyanates,[20] and tandem sigmatropic rearrangement of 2-(2′-butynylthio)indole sulfoxide derivative.[21a–21c] However, most of these methods suffer from some drawbacks and are limited in scope and generality. Therefore more flexible and efficient general methods for the preparation of thieno-fused heterocycles are desirable in view of their applications in materials science as well as pharmaceuticals.

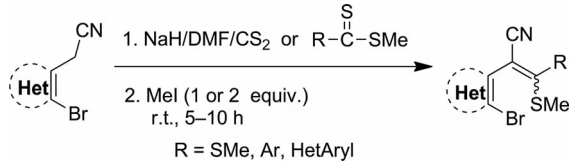
Our own interest in the synthesis of thienoheterocycles derives from our continued research program based on the development of new synthetic methods for five- and six-membered heterocycles by employing polarized ketene dithioacetals and other novel organosulfur precursors.[22] During the course of these studies, we recently reported a novel efficient approach for the synthesis of substituted 2-aryl/heteroaryl-3-cyano benzo[*b*]thiophenes through radical-mediated cyclization of 2-(*o*-bromoaryl)-3-aryl/heteroaryl/methylthioacrylonitriles (Scheme 1).[22d] The efficiency of this method along with the high yields of the product benzo[*b*]thiophenes prompted us to apply this radical cyclization protocol for the synthesis of novel thieno-fused heterocycles such as thieno[2,3-*b*]thiophenes, thieno[2,3-*b*]indoles, and pyrazolo[3,2-*c*]thiophenes from the appropriately substituted precursors. We have successively achieved this goal, and the results of these studies are presented in this paper.



Scheme 1. Synthesis of substituted benzo[*b*]thiophenes by radical cyclization.

Results and Discussion

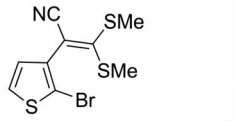
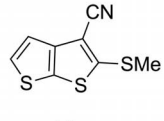
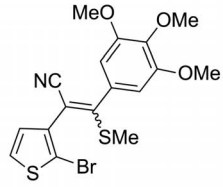
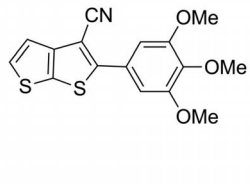
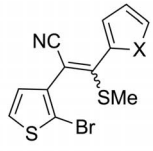
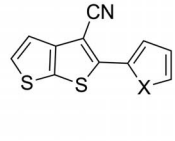
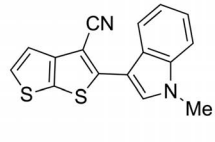
Desired acrylonitriles **9**, **11**, and **13** and related ketene dithioacetals **8**, **10**, and **12** were prepared according to previously developed methodology from our laboratory by base-induced condensation of the corresponding 2-bromo-3-thienylacetonitrile, 2-bromo-1-*N*-methyl-3-indolylacetonitrile, and 1,3-diphenyl-4-bromo-5-pyrazolylacetonitrile, respectively, with either aryl/heteroaryl dithioesters (or carbon disulfide) followed by in situ *S*-methylation of the resulting enethioates (Scheme 2).[22b] The structures of the known (i.e., **9b**, **9c**, **11b–e**, **13a**, and **13c**) and the unknown (i.e., **8**, **9a**, **9d**, **9e**, **10**, **11a**, **12**, **13b**, **13d**, **13e**) precursors were established with the help of spectral and analytical data. The ^1H and ^{13}C NMR spectra of these compounds showed them to be inseparable mixture of (*E*)/(*Z*) isomers, which also undergo thermal (*Z*)/(*E*) isomerization as reported in our previous paper.[22d]



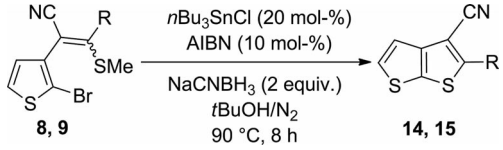
Scheme 2. Synthesis of 2-(bromoaryl/heteroaryl)-3-(methylthio)-3-aryl/heteroarylacrylonitriles.

A detailed investigation on the radical cyclization of substrate **8** with various reagents under different reaction conditions revealed that the best yield of **14** (Table 1, Entry 1)

Table 1. Synthesis of substituted thieno[2,3-*b*]thiophenes **14** and **15**.

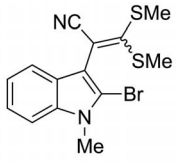
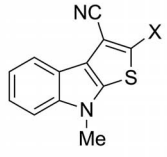
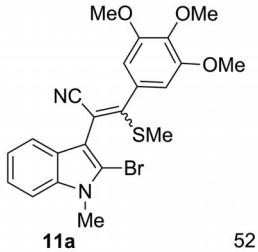
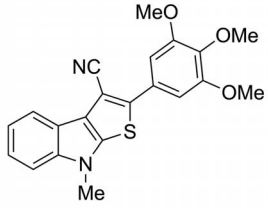
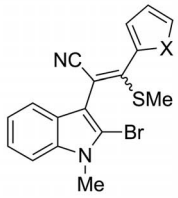
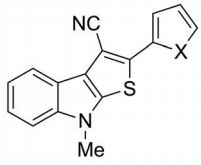
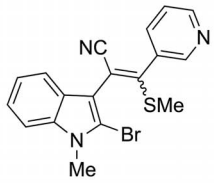
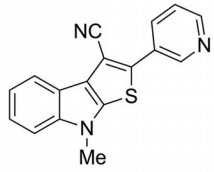
Entry	% Yield (**8**, **9**)		% Yield (**14**, **15**)	
1	 **8**	78	 **14**	76
2	 **9a**	72	 **15a**	89
3	 **9b**: X = S	72	 **15b**: X = S	70
4	**9c**: X = O	84	**15c**: X = O	65
5	**9d**: X = NMe	72	**15d**: X = NMe	84
6	 **9e**	60	 **15e**	80

was obtained under catalytic tin hydride conditions by using 20 mol-% of tributyltin chloride in the presence of $NaCNBH_3$ and AIBN (10 mol-%) in refluxing *tert*-butyl alcohol as reported in our previous paper.[22d] These optimized reaction conditions were applied throughout our studies of radical cyclization of various 2,3-aryl/heteroaryl-substituted 3-(methylthio)acrylonitriles **8**–**13**. Thus, ketene dithioacetal **8** and acrylonitriles **9a**–**e** underwent smooth radical cyclization under these conditions to furnish thiophenes **14** and **15a**–**e** in overall high yields (Scheme 3; Table 1, Entries 2–6), and no trace of the formation of debrominated products was observed in these reactions.

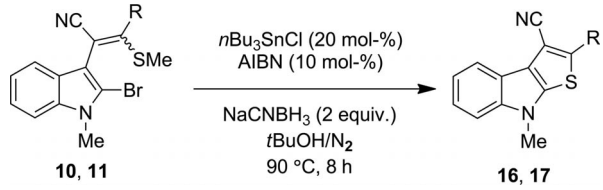


Scheme 3. Synthesis of substituted thieno[2,3-*b*]thiophenes **14** and **15**.

Table 2. Synthesis of 2,3-substituted thieno[2,3-*b*]indoles **16** and **17**.

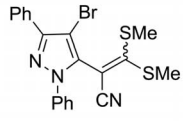
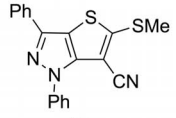
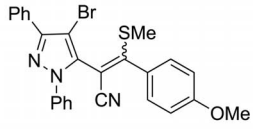
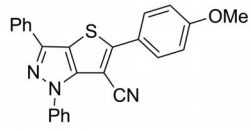
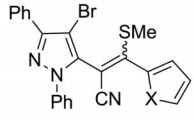
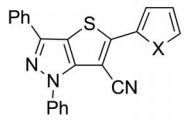
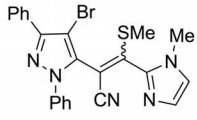
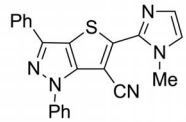
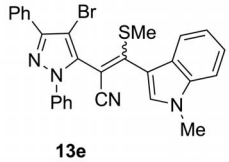
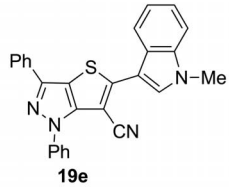
Entry		% Yield (**10**, **11**)		% Yield (**16**, **17**)
1	 **10**	81	 **16a**: X = H **16b**: X = SMe	69 0
2	 **11a**	52	 **17a**	73
3 4 5	 **11b**: X = S **11c**: X = O **11d**: X = NMe	80 79 80	 **17b**: X = S **17c**: X = O **17d**: X = NMe	75 72 74
6	 **11e**	77	 **17e**	73

The radical cyclization protocol was found to be equally facile for the construction of the thieno[2,3-*b*]indole ring system from the corresponding precursors **10** and **11a**–**e**, as shown in Scheme 4 and Table 2. Interestingly, treatment of ketene dithioacetal **10** with $nBu_3SnCl/NaCNBH_3$ under previously reported reaction conditions yielded exclusively **16a** (69%), which is apparently formed by further reductive dethiomethylation of the corresponding 2-(methylthio) derivative **16b** under these conditions (Table 2, Entry 1). On the other hand, novel thieno[2,3-*b*]indole-3-carbonitriles **17a**–**e** bearing an aryl or heteroaryl group in the 2-position could be synthesized in excellent yields by exposing **11a**–**e** to $nBu_3SnCl/NaCNBH_3$ under optimized reaction conditions (Table 2, Entries 2–6).



Scheme 4. Synthesis of 2,3-substituted thieno[2,3-*b*]indoles **16** and **17**.

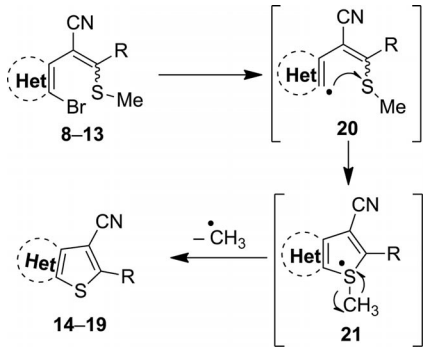
Table 3. Synthesis of 5,6-substituted thieno[3,2-*c*]pyrazoles **18** and **19**.

Entry		% Yield (**12**, **13**)		% Yield (**18**, **19**)
1	 **12**	68	 **18**	62
2	 **13a**	72	 **19a**	76
3 4	 **13b**: X = S **13c**: X = O	72 84	 **19b**: X = S **19c**: X = O	78 73
5	 **13d**	71	 **19d**	71
6	 **13e**	90	 **19e**	74

The scope and generality of this efficient radical-mediated thiophene annulation protocol was further evident by extending the methodology for the synthesis of tetrasubstituted thieno[3,2-*c*]pyrazoles **18** and **19a**–**e** as depicted in Scheme 5. Thus, a number of 1,3-diphenyl-6-cyano-5-methylthio- (**18**), 5-aryl-/5-heteroarylthieno[3,2-*c*]pyrazoles **19a**–**e** were obtained in excellent yields when acrylonitrile precursors **12** and **13a**–**e** were subjected to radical cyclization under identical conditions (Table 3, Entries 1–6).

Scheme 5. Synthesis of 5,6-substituted thieno[3,2-*c*]pyrazoles **18** and **19**.

A probable mechanism for the formation of thieno-fused heterocycles **14**–**19** from acrylonitrile precursors **8**–**13** is shown in Scheme 6. Thus, carbon-centered heterocyclic radical intermediate **20** (formed through abstraction of a bromine radical by a tributyltin radical) undergoes intramolecular addition to the favorably located methylthio group to give fused five-membered radical intermediate **21**, which undergoes homolytic C–S bond cleavage to furnish thieno-fused heterocycles **14**–**19** in good yields (Scheme 6).



Scheme 6. Mechanism for the formation of **14**–**19** from **8**–**13**.

Conclusions

In summary, we have reported an efficient, general, high-yielding synthesis of novel aryl/heteroaryl-substituted thieno-fused heterocyclic motifs by a radical cyclization process involving unusual intramolecular addition of a carbon-centered radical to a neighboring sulfide as the key step. The methodology utilizes readily accessible precursors and proceeds under simple and mild reaction conditions without formation of any side products. The broad scope of the reaction for the synthesis of other thieno-fused heterocycles is currently under investigation.

Experimental Section

General: Unless otherwise noted, all reactions were carried out in oven-dried glassware under an N_2 atmosphere in anhydrous solvents. Wherever appropriate, all reagents were purified prior to use according to the appropriate guidelines.[23] ^{1}H NMR (300, 400, or 500 MHz) and ^{13}C NMR (75, 100, or 125 MHz) spectra were recorded with a Jeol JNM-LA 400 FT NMR or a Jeol JNM-LA 500 FT NMR spectrometer with $CDCl_3$ as the solvent. Tetramethylsilane was used as an internal reference. Melting points were recorded with a Mel-Temp melting point apparatus (capillary method). IR spectra were recorded with a Perkin–Elmer 1320 spectrophotometer. The FAB mass spectra were recorded with a JEOL SX 102/DA-6000 Mass Spectrometer/Data system. HRMS (ESI) data were recorded with a Waters Micromass Q-TOF Premier Mass Spectrometer and a Bruker Daltonics APEXII FTICR spectrometer. Chromatographic purification was conducted by column chromatography on 100–200 mesh size silica gel obtained from Acme Synthetic Chemicals (India).

General Procedure for the Preparation of 2-(2-Bromoheteroaryl)-3-aryl/heteroaryl-3-(methylthio)-2-propenenitriles (9, 11 and 13):[22b,22d,22e] To a stirred suspension of NaH (0.44 g, 11 mmol, 60%) in dry THF or DMF (25 mL) under a N_2 atmosphere was added a solution of the corresponding 2,4-bromoheteroarylacetonitrile (5.0 mmol) in dry THF or DMF (50 mL) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 1 h and a solution of the corresponding dithioester (5.0 mmol) in dry THF or DMF (15 mL) was added dropwise over a period of 15–20 min at 0 °C. The reaction mixture was further stirred for 3 h at room temperature and MeI (0.46 mL, 7.5 mmol) was then added dropwise at 0 °C. The mixture was further stirred for 3 h and then poured into ice-cold water. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extract was washed with H_2O (3 × 50 mL) and brine (50 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure to give crude adducts **9**, **11**, and **13**, which were purified by column chromatography (hexane/EtOAc).

2-(2-Bromo-3-thienyl)-3-(1-*N*-methyl-2-pyrrolyl)-3-methylthio-2-propenenitrile (9d): Obtained as a 1:1 inseparable mixture of geometrical isomers; yield: 72% (1.22 g); viscous liquid; R_f = 0.46 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 3090, 2925, 2204, 1556, 1500 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.32 (d, J = 5.6, 0.5 Hz, 0.5 H, HetArH), 7.02–7.03 (m, 1 H, HetArH), 6.79 (dd, J = 2.2, 2.2 Hz, 0.5 H, HetArH), 6.61 (dd, J = 2.2, 2.2 Hz, 0.5 H, HetArH), 6.44 (dd, J = 3.6, 1.7 Hz, 0.5 H, HetArH), 6.25 (d, J = 5.6 Hz, 0.5 H, HetArH), 6.21–6.19 (m, 1 H, HetArH), 6.10 (dd, J = 3.7, 2.7 Hz, 0.5 H, HetArH), 3.63 (s, 1.5 H, NMe), 3.17 (s, 1.5 H, NMe), 2.05 (s, 1.5 H, SMe), 1.79 (s, 1.5 H, SMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 155.1, 152.5, 133.5, 128.5, 128.3, 126.7, 126.1, 125.8, 125.4, 117.0, 116.5, 114.6, 113.8, 113.6, 112.1, 108.7, 102.4, 101.8, 34.4, 34.3, 16.5, 15.9 ppm. HRMS (ESI): calcd. for $C_{13}H_{12}N_2S_2$ $[M + H]^+$ 338.9625; found 338.9623.

General Procedure for the Radical Cyclization of 2-(2-Bromo-3-thienyl)-/2-(2-Bromo-1-*N*-methyl-3-indolyl)-/2-(4-Bromo-1,3-diphenyl-1*H*-5-pyrazolyl)-3-aryl/heteroaryl/methylthio-3-(methylthio)-2-propenenitriles (8, 9a–e, 10, 11a–e, 12, and 13a–e):[22d] To a solution of the appropriate propenenitrile **8**–**13** (2.5 mmol), AIBN (10 mmol-%), and $NaCNBH_3$ (5.0 mmol) in degassed *t*BuOH (25 mL) was added nBu$_3$SnCl (20 mmol-%), and the reaction mixture was heated at reflux for 5–8 h. It was then cooled to room temperature and the solvent was evaporated followed by the addition of water (25 mL). It was extracted with ethyl acetate (3 × 25 mL), the combined organic extracts were washed with H_2O (2 × 50 mL) and brine (50 mL), dried (Na_2SO_4), and evaporated under reduced pressure to afford the crude product, which was purified by column chromatography over silica gel (EtOAc/hexane) to give pure thieno-fused heterocycles **14**–**19**.

2-Methylthiothieno[2,3-*b*]thiophene-3-carbonitrile (14): Yield: 76% (0.40 g); colorless liquid; R_f = 0.58 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 3102, 2923, 2223, 1506, 1461, 1429, 1374, 1262 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.45 (d, J = 5.2 Hz, 1 H, HetArH), 7.23 (d, J = 5.2 Hz, 1 H, HetArH), 2.62 (s, 3 H, SMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.2, 144.9, 136.6, 129.8, 118.5, 113.6, 106.4, 21.2 ppm. HRMS (ESI): calcd. for $C_8H_5NS_3$ [M + H]$^+$ 211.9662; found 211.9666.

2-(3,4,5-Trimethoxyphenyl)thieno[2,3-*b*]thiophene-3-carbonitrile (15a): Yield: 89% (0.74 g); white solid; m.p. 136–137 °C; R_f = 0.51 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 3096, 2937, 2217, 1584, 1501, 1413, 1331, 1247 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.48 (d, J = 5.4 Hz, 1 H, HetArH), 7.35 (d, J = 5.4 Hz, 1 H, HetArH), 6.99 (s, 2 H, ArH), 3.93 (s, 6 H, 2 OMe), 3.90 (s, 3 H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 157.2, 153.6, 146.3, 139.6, 135.0, 129.8, 127.2, 119.1, 115.4, 105.0, 98.7, 61.0, 56.3 ppm. HRMS (ESI): calcd. for $C_{16}H_{14}NS_2O_3$ [M + H]$^+$ 332.0333; found 332.0334.

2-(2-Thienyl)thieno[2,3-*b*]thiophene-3-carbonitrile (15b): Yield: 70% (0.43 g); white solid; m.p. 97–98 °C; R_f = 0.81 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 3100, 2924, 2215, 1247, 1087 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.58 (dd, J = 5.0, 1.0 Hz, 1 H, HetArH), 7.45 (d, J = 5.0 Hz, 1 H, HetArH), 7.43 (dd, J = 5.0, 1.0 Hz, 1 H, HetArH), 7.31 (d, J = 5.0 Hz, 1 H, HetArH), 7.12 (dd, J = 5.0, 3.9 Hz, 1 H, HetArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 149.8, 146.1, 134.7, 133.6, 130.1, 128.0, 127.5, 119.1, 115.1, 98.1 ppm. HRMS (ESI): calcd. for $C_{11}H_6NS_3$ [M + H]$^+$ 247.9662; found 247.9665.

2-(2-Furyl)thieno[2,3-*b*]thiophene-3-carbonitrile (15c): Yield: 65% (0.37 g); white solid; m.p. 115–116 °C; R_f = 0.78 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 3108, 2924, 2216, 1607, 1388, 1287, 1255, 1075 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.51 (d, J = 1.7 Hz, 1 H, HetArH), 7.45 (d, J = 5.4 Hz, 1 H, HetArH), 7.30 (d, J = 5.4 Hz, 1 H, HetArH), 7.16 (d, J = 3.6 Hz, 1 H, HetArH), 6.57 (dd, J = 3.6, 1.7 Hz, 1 H, HetArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 146.4, 145.6, 145.5, 143.3, 134.8, 130.1, 118.8, 114.8, 112.5, 109.7, 95.8 ppm. HRMS (ESI): calcd. for $C_{11}H_6NOS_2$ [M + H]$^+$ 231.9891; found 231.9893.

2-(1-*N*-Methyl-2-pyrrolyl)thieno[2,3-*b*]thiophene-3-carbonitrile (15d): Yield: 84% (0.51 g); white solid; m.p. 88–89 °C; R_f = 0.67 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 3096, 2953, 2216, 1554, 1488, 1457, 1304 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.46 (d, J = 5.2 Hz, 1 H, HetArH), 7.34 (d, J = 5.2 Hz, 1 H, HetArH), 6.82 (dd, J = 2.4, 2.2 Hz, 1 H, HetArH), 6.58 (dd, J = 3.6, 1.8 Hz, 1 H, HetArH), 6.23 (dd, J = 3.6, 2.7 Hz, 1 H, HetArH), 3.77 (s, 3 H, NMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 147.8, 145.5, 135.5, 129.7, 126.6, 123.6, 119.0, 115.1, 113.8, 109.0, 100.8, 35.4 ppm. HRMS (ESI): calcd. for $C_{12}H_9N_2S_2$ [M + H]$^+$ 245.0207; found 245.0209.

2-(1-*N*-Methyl-3-indolyl)thieno[2,3-*b*]thiophene-3-carbonitrile (15e): Yield: 80% (0.58 g); white solid; m.p. 139–140 °C; R_f = 0.48 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 3123, 3050, 2908, 2210, 1534, 1227, 1163 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.01 (d, J = 7.8 Hz, 1 H, ArH), 7.80 (s, 1 H, HetArH), 7.46 (d, J = 5.4 Hz, 1 H, HetArH), 7.41 (d, J = 7.8 Hz, 1 H, ArH), 7.37–5.25 (m, 3 H, ArH), 3.89 (s, 3 H, NMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.1, 145.4, 137.0, 133.4, 129.2, 129.0, 125.5, 123.0, 121.2, 119.9, 118.7, 116.5, 110.0, 107.7, 95.8, 33.2 ppm. HRMS (ESI): calcd. for $C_{16}H_{10}N_2S_2$ [M]$^+$ 294.0285; found 294.0282.

8-Methyl-8*H*-thieno[2,3-*b*]indole-3-carbonitrile (16a): Yield: 69% (0.37 g); white solid; m.p. 118–120 °C; R_f = 0.42 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 2937, 2218, 1497, 1325 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.01 (d, J = 7.8 Hz, 1 H, ArH), 7.44 (s, 1 H, HetArH), 7.37–7.23 (m, 3 H, ArH), 3.81 (s, 3 H, NMe) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 168.8, 143.3, 142.3, 126.1, 123.4, 121.2, 120.2, 119.2, 115.3, 109.3, 102.1, 32.2 ppm. HRMS (ESI): calcd. for $C_{12}H_9N_2S$ [M + H]$^+$ 213.0486; found 213.0485.

8-Methyl-2-(3,4,5-trimethoxyphenyl)-8*H*-thieno[2,3-*b*]indole-3-carbonitrile (17a): Yield: 73% (0.69 g); yellow solid; m.p. 170–171 °C; R_f = 0.50 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 2932, 2831, 2214, 1581, 1490, 1328, 1258, 1133 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.08 (d, J = 7.8 Hz, 1 H, ArH), 7.38 (d, J = 6.2 Hz, 2 H, ArH), 7.30–7.26 (m, 1 H, ArH), 7.02 (s, 2 H, ArH), 3.96 (s, 6 H, 2 OMe), 3.91 (s, 3 H, OMe), 3.86 (s, 3 H, NMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 153.6, 145.1, 141.7, 141.0, 138.9, 128.0, 123.4, 122.4, 120.7, 120.4, 119.1, 116.1, 109.3, 104.6, 97.0, 61.0, 56.2, 32.2 ppm. HRMS (ESI): calcd. for $C_{21}H_{19}N_2SO_3$[M + H]$^+$ 379.1116; found 379.1137.

8-Methyl-2-(2-thienyl)-8*H*-thieno[2,3-*b*]indole-3-carbonitrile (17b): Yield: 75% (0.55 g); white solid; m.p. 139–140 °C; R_f = 0.38 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 3098, 3084, 2928, 2209, 1493, 1461, 1410, 1324, 1052 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.97 (d, J = 7.6 Hz, 1 H, ArH), 7.50 (dd, J = 3.6, 1.2 Hz, 1 H, HetArH), 7.34–7.20 (m, 4 H, ArH/ArHetArH), 7.08 (dd, J = 5.0, 1.2 Hz, 1 H, HetArH), 3.75 (s, 3 H, NMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 141.7, 140.5, 138.1, 134.5, 128.1, 126.3, 126.1, 123.4, 121.7, 120.5, 120.4, 119.1, 115.7, 109.3, 96.6, 32.2 ppm. HRMS (ESI): calcd. for $C_{16}H_{11}N_2S_2$ [M + H]$^+$ 295.0364; found 295.0389.

8-Methyl-2-(2-furyl)-8*H*-thieno[2,3-*b*]indole-3-carbonitrile (17c): Yield: 72% (0.50 g); yellow solid; m.p. 111–112 °C; R_f = 0.41 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 2924, 2214, 1496, 1459 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$ 25 °C): δ = 8.02 (d, J = 7.8 Hz, 1 H, ArH), 7.47 (d, J = 1.7 Hz, 1 H, HetArH), 7.36–7.35 (m, 2 H, ArH), 7.28–7.24 (m, 1 H, ArH), 7.09 (d, J = 3.5 Hz, 1 H, HetArH), 6.56 (dd, J = 3.5, 1.7 Hz, 1 H, HetArH), 3.84 (s, 3 H, NMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 142.3, 142.2, 138.1, 134.5, 133.1, 128.0, 125.5, 123.5, 120.5, 119.3, 115.5, 112.5, 109.4, 108.2, 96.6, 32.3 ppm. HRMS (ESI): calcd. for $C_{16}H_{10}N_2OSNa$ [M + Na]$^+$ 301.0411; found 301.0418.

8-Methyl-2-(1-*N*-methyl-2-pyrrolyl)-8*H*-thieno[2,3-*b*]indole-3-carbonitrile (17d): Yield: 74% (0.54 g); m.p. 167–168 °C; R_f = 0.42 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 2925, 2854, 2214, 1491, 1460, 1403, 1331, 1302 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.08 (d, J = 7.8 Hz, 1 H, ArH), 7.40–7.38 (m, 2 H, ArH), 7.30–7.25 (m, 1 H, ArH), 6.83 (dd, J = 2.7, 1.8 Hz, 1 H, HetArH), 6.25 (dd, J = 3.8, 2.7 Hz, 1 H, HetArH), 5.68 (dd, J = 3.8, 1.8 Hz, 1 H, HetArH), 3.87 (s, 3 H, NCH_3), 3.78 (s, 3 H, NCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 141.8, 141.7, 135.6, 125.7, 123.8, 123.4, 121.3, 120.6, 120.3, 119.2, 115.7, 113.3, 109.3, 108.7, 100.2, 35.1, 32.3 ppm. HRMS (ESI): calcd. for $C_{17}H_{13}N_3S$ [M + H]$^+$ 292.0907; found 292.0907.

8-Methyl-2-(3-pyridyl)-8*H*-thieno[2,3-*b*]indole-3-carbonitrile (17e): Yield: 72% (0.52 g); white solid; m.p. 191–192 °C; R_f = 0.47 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 2921, 2219, 1495, 1469, 1410, 1327, 1089 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.60 (br. s, 1 H, HetArH), 8.28 (br. s, 1 H, HetArH), 7.87 (d, J = 8.0 Hz, 1 H, ArH), 7.70 (d, J = 7.6 Hz, 1 H, HetArH), 7.10 (dd, J = 7.6, 1.0 Hz, 1 H, HetArH), 7.06–7.01 (m, 1 H, ArH), 6.96–6.90 (m, 2 H, ArH), 3.51 (s, 3 H, NCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 149.0, 147.0, 142.1, 142.0, 139.5, 134.7, 129.2, 124.0, 123.9, 122.8,

120.7, 120.5, 119.3, 115.3, 109.5, 98.9, 32.4 ppm. HRMS (ESI): calcd. for $C_{17}H_{12}N_3S$ $[M + H]^+$ 290.0752; found 290.0750.

1,3-Diphenyl-5-(methylthio)-1*H*-thieno[3,2-*c*]pyrazole-6-carbonitrile (18): Yield: 62% (0.54 g); white solid; m.p. 221–222 °C; R_f = 0.65 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 2923, 2853, 2218, 1598, 1502, 1457, 1371, 1183, 1026 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.21 (d, J = 8.0 Hz, 2 H, ArH), 7.52–7.37 (m, 8 H, ArH), 2.49 (s, 3 H, SCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 166.3, 153.2, 140.6, 136.7, 133.4, 130.3, 129.7, 129.5, 129.4, 126.8, 125.3, 117.6, 108.3, 101.1, 19.6 ppm. HRMS (ESI): calcd. for $C_{19}H_{13}N_3S_2$ $[M]^+$ 347.055; found 347.054.

1,3-Diphenyl-5-(4-methoxyphenyl)-1*H*-thieno[3,2-*c*]pyrazole-6-carbonitrile (19a): Yield: 76% (0.77 g); white solid; m.p. 214–215 °C; R_f = 0.32 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 2923, 2851, 2219, 1606, 1522, 1497, 1458, 1262, 1173, 1032 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.94 (d, J = 7.9 Hz, 2 H, ArH), 7.77 (dd, J = 8.5 Hz, 4H ArH), 7.57 (dd, J = 7.9 Hz, 2 H, ArH), 7.48 (dd, J = 7.5 Hz, 2 H, ArH), 7.46–7.39 (m, 2 H, ArH), 7.03 (dd, J = 8.5, 1.5 Hz, 2H. ArH), 3.87 (s, 3 H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.4, 161.7, 145.1, 143.7, 138.7, 131.3, 129.7, 129.3, 129.1, 128.8, 128.4, 126.0, 124.5, 124.2, 118.1, 114.9, 114.2, 90.1, 55.6 ppm. HRMS (ESI): calcd. for $C_{25}H_{18}N_3SO$ $[M + H]^+$ 408.1171; found 408.1177.

1,3-Diphenyl-5-(2-thienyl)-1*H*-thieno[3,2-*c*]pyrazole-6-carbonitrile (19b): Yield: 78% (0.75 g); white solid; m.p. 228–229 °C; R_f = 0.5 (hexane/EtOAc, 6:1). IR (KBr): $\tilde{\nu}$ = 3073, 2925, 2219, 1594, 1554, 1496, 1453, 1435 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.93 (d, J = 7.5 Hz, 2 H, ArH), 7.77–7.75 (m, 3 H, ArH), 7.60 (d, J = 8.0 Hz, 2 H, ArH), 7.54–7.42 (m, 5 H, ArH/HetArH), 7.19 (dd, J = 5.0, 3.8 Hz, 1 H, HetArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 154.8, 145.1, 144.0, 138.8, 134.1, 131.4, 129.6, 129.3, 129.1, 128.9, 128.8, 126.3, 124.4, 117.7, 114.1, 101.0, 90.1 ppm. MS: m/z (%) = 383 (75) $[M]^+$, 384 (100) $[M + H]^+$. HRMS (ESI): calcd. for $C_{22}H_{13}N_3S_2$ $[M]^+$ 383.0551; found 383.0554.

1,3-Diphenyl-5-(2-furyl)-1*H*-thieno[3,2-*c*]pyrazole-6-carbonitrile (19c): Yield: 73% (0.67 g); white solid; m.p. 231–232 °C; R_f = 0.45 (hexane/EtOAc, 6:1). IR (KBr): $\tilde{\nu}$ = 2923, 2853, 2218, 1598, 1502, 1457 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.93 (d, J = 8.5 Hz, 2 H, ArH); 7.75 (d, J = 8.5 Hz, 2 H, ArH), 7.59–7.57 (m, 3 H, ArH), 7.51–7.48 (m, 3 H, ArH), 7.47–7.40 (m, 2 H, HetArH), 6.32 (d, J = 3.4 Hz, 1 H, HetArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 150.0, 146.5, 144.6, 144.2, 143.8, 138.6, 131.1, 129.4, 129.1, 128.9, 128.5, 126.0, 124.0, 118.0, 113.8, 113.1, 111.8, 87.4 ppm. HRMS (ESI): calcd. for $C_{22}H_{14}N_3SO$ $[M + H]^+$ 368.0858; found 368.0858.

1,3-Diphenyl-5-(1-*N*-methylimidazol-2-yl)-1*H*-thieno[3,2-*c*]pyrazole-6-carbonitrile (19d): Yield: 71% (0.85 g); white solid; m.p. 214–215 °C; R_f = 0.2 (hexane/EtOAc, 4:1). IR (KBr): $\tilde{\nu}$ = 2923, 2218, 1598, 1502, 1457, 1371, 1183, 1026 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.93 (d, J = 8.0 Hz, 2 H, ArH), 7.76 (d, J = 8.0 Hz, 2 H, ArH), 7.59 (dd, J = 7.9 Hz, 2 H, ArH), 7.41–7.52 (m, 4 H, ArH), 7.22–7.25 (m, 2 H, HetArH), 3.94 (s, 3 H, NCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 144.1, 143.8, 138.5, 133.7, 131.0, 130.7, 129.4, 129.2, 129.0, 128.6, 126.0, 124.7, 124.0, 120.4, 118.9, 113.1, 94.1, 35.1 ppm. HRMS (ESI): calcd. for $C_{22}H_{16}N_5S$ $[M + H]^+$ 382.1126; found 382.1123.

1,3-Diphenyl-5-(1-*N*-methyindol-3-yl)-1*H*-thieno[3,2-*c*]pyrazole-6-carbonitrile (19e): Yield: 74% (0.80 g); white solid; m.p. 219–220 °C; R_f = 0.59 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 2921, 2214, 1598, 1527, 1458, 1377, 1259 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.15 (d, J = 7.8 Hz, 1 H, ArH), 7.99–7.96 (m, 3 H, ArH), 7.70 (d, J = 8.0 Hz, 2 H, ArH), 7.59–7.33 (m, 9 H, ArH), 3.88 (s, 3 H, NCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 157.3, 144.6, 143.7, 138.9, 137.2, 131.5, 130.1, 129.3, 129.1, 128.7, 128.2, 126.1, 125.6, 124.1, 123.4, 121.7, 120.3, 117.4, 115.5, 110.3, 108.0, 87.1, 33.6 ppm. HRMS (ESI): calcd. for $C_{27}H_{19}N_4S$ $[M + H]^+$ 431.1330; found 431.1358.

Supporting Information (see footnote on the first page of this article): General experimental procedure of **8**, **10**, and **12**; characterization data of **8**, **9a**, **9e**, **10**, **11a**, **12**, **13b**, **13d**, and **13e**; and copies of the ^1H NMR and ^{13}C NMR spectra of **14**, **15a**–**e**, **16a**, **17a**–**e**, **18**, and **19a**–**e**.

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