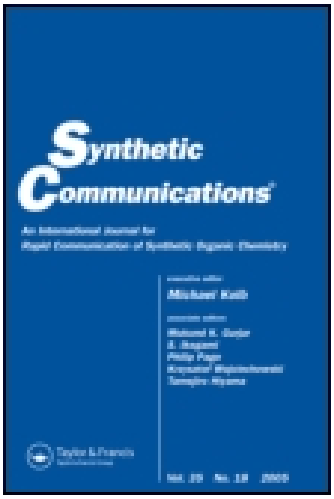


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Lewis Acid-Mediated Domino Reaction of 3-Bromomethylthiophenes with Arenes/Heteroarenes

Vasudevan Dhayalan [a] & Arasambattu K. Mohanakrishnan [a]

[a] Department of Organic Chemistry , University of Madras, Guindy Campus , Chennai , India

Accepted author version posted online: 19 Dec 2011.Published online: 26 Mar 2012.

To cite this article: Vasudevan Dhayalan & Arasambattu K. Mohanakrishnan (2012) Lewis Acid-Mediated Domino Reaction of 3-Bromomethylthiophenes with Arenes/Heteroarenes, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:14, 2149-2160, DOI: 10.1080/00397911.2011.554063

To link to this article: http://dx.doi.org/10.1080/00397911.2011.554063

Synthetic Communications®, 42: 2149–2160, 2012

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2011.554063

Taylor & Francis
Taylor & Francis Group

LEWIS ACID–MEDIATED DOMINO REACTION OF 3-BROMOMETHYLTHIOPHENES WITH ARENES/HETEROARENES

Vasudevan Dhayalan and Arasambattu K. Mohanakrishnan
Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai, India

GRAPHICAL ABSTRACT

Abstract *Lewis acid–mediated domino reaction of 3-bromomethylthiophenes with various types of arenes and heteroarenes is reported.*

Keywords Annulation; arylation; benzo[*b*]thiophene; domino reaction

INTRODUCTION

The electronic properties of π-conjugated oligothiophenes led to many important applications in molecular electronics.[1] Specifically, benz-annulation at the 2,3-position of thiophene rings leads to an important class of building blocks for the construction of optoelectronic materials.[1d,2] Design and synthesis of π-conjugated heteroacenes are being widely investigated because of their potential applications in organic thin-film transistors (OTFTs).[3] The densely packed solid-state structures of the planar π-conjugated heteroacenes are highly beneficial for efficient charge transport. Recently, a large number of thiophene-based heteroacenes have been explored because the heteroatom influences electronic as well as solid-state structures, that which them more attractive candidates for organic devices.[1d,4] Gao and coworkers reported conjugated ladder-type heteroacenes containing thiophene and pyrrole units as high-performance semiconducting materials.[5]

Wex and coworkers described the synthesis of dibenzothiophene analogs[6] via lithiation followed by formylation and subsequent reductive cyclization. Tedjamulia et al. established the synthesis of naphtho[*b*]thiophenes involving Friedel–Crafts phthaloylation of thiophene followed by successive reductions, oxidation, and

Received November 11, 2010.

Address correspondence to Arasambattu K. Mohanakrishnan, Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India. E-mail: mohan_67@hotmail.com

polyphosphoric acid (PPA)–mediated intramolecular cyclization reactions.[7] Takahashi et al. outlined a facile synthesis of thiophene-fused acenes,[8] via CuCl-mediated coupling between tetraiodothiophene and a zirconium-based organometallic reagent. The synthesis of dibenzothiophenes[9] involving intermolecular Diels–Alder reaction of bis-pyrrole with dimethyl acetylenedicarboxylate (DMAD) followed by an oxidative cleavage of the amine unit has been achieved by Sha and coworkers. Pouchain et al.[10] reported the synthesis of a thermally stable hybrid acene-thiophene organic semiconductor via Stille coupling between 2-bromoindeno[1,2-*b*]thiophene and 5,5′-bis(tributylstannyl)-2,2′-bithiophene.

RESULTS AND DISCUSSION

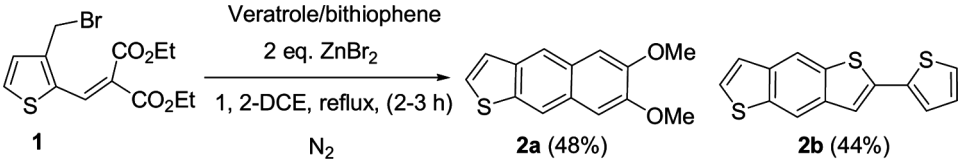
During our recent study of the synthesis of annulated heterocycles,[11] we observed that an interaction of malonylidene unit–tethered 3-bromomethylthiophene **1**[12] with veratrole or bithiophene in the presence of 2 eq. $ZnBr_2$ in 1,2-dichloroethane (DCE) at reflux afforded the annulated heterocycle **2a** or **2b** in 48%, and 44% yields, respectively (Scheme 1).

To further understand the synthetic utility of this domino reaction protocol, the vinylidene-tethered 3-bromomethylthiophenes **5a–c** were prepared, adopting published procedure,[12] via condensation of the 3-methylthiophene-2-carboxaldehyde **3** with active methylene compounds such as *N,N*-dimethylbarbituric acid, Meldrum's acid, or malononitrile followed by allylic bromination using N-bromosuccinimide (NBS). See Scheme 2.

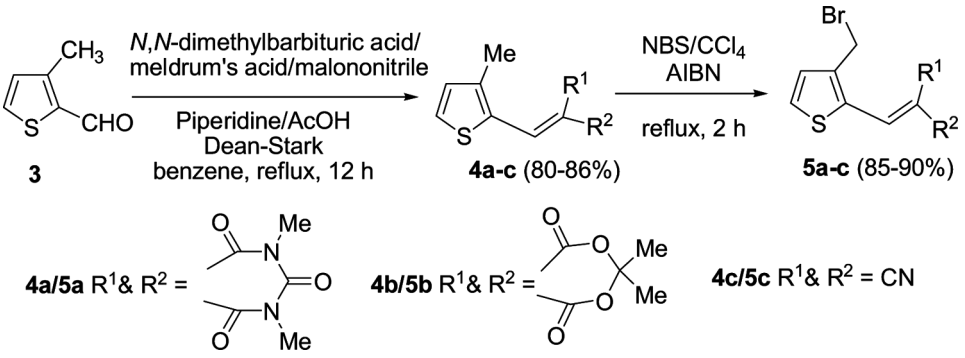
As expected, the interaction of bromo compounds **1**/**5a–c** with arenes as well as heteroarnes at room temperature followed by subsequent thermolysis at 80 °C and column chromatographic purification furnished annulated heterocycles **2a–f** in 40–67% yields (Scheme 3).

Details such as the nature of arenes/heteroarenes employed, the annulation products obtained, and their yields are summarized in Table 1. As expected, the annulation of bromo compound **1/5a** with veratrole in the presence of 1 eq. $ZnBr_2$ in 1,2-DCE at room temperature followed by reflux afforded the annulated product **2a** in 53% and 62% yields, respectively (entry 1).

The smooth annulation of bromo compounds **1/5a–c** could be successfully performed with bithiophene to afford the annulation product **2b** in 50%, 67%, 45%, and 43% yields (entry 2). The interaction of bromo compound **1/5a** with 1-methylnaphthalene in the presence of 1 eq. $ZnBr_2$ at room temperature followed by reflux led to the synthesis of the naphth-annulated benzo[*b*]thiophene **2c** in 46% and 62% yields (entry 3). Under identical conditions, the interaction of bromo compound **1/5a/5c**



Scheme 1. Domino reaction of bromo compound **1** with veratrole/bithiophene.



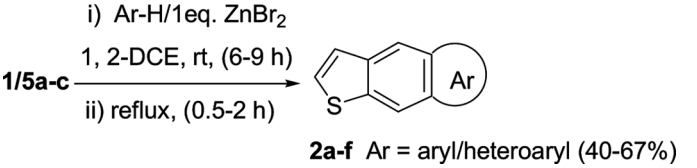
Scheme 2. Preparation of 3-bromomethylthiophenes **5a–c**.

with naphthalene afforded the phenanthro[2,3-*b*]thiophene **2d** in 47–60% yields (entry 4). A similar annulation of bromo compound **1/5a–c** with most of the heteroarenes using 1 eq. $ZnBr_2$ was problematic and always led to the formation of a complex mixture. However, upon interaction of bromo compound **1/5a–c** with a heteroarene, namely benzo[*b*]furan in the presence of 0.2 eq. of $ZnBr_2$ led to the synthesis of the mixed heterocycle **2e** in 46–63% yields (entry 5). Similarly, the annulation of bromo compound **1/5a/5c** could be successfully performed with 2-methylthiophene to furnish heterocycle **2f** in 40–55% yields (entry 6). Surprisingly, the interaction of bromo compound **1** or **5a–c** with 1-hexylindole in the presence of 0.2 eq. of $ZnBr_2$ failed to produce the expected heterocycle **2g**; instead, only a complex mixture was obtained.

The domino reaction of bromo compound **1** with benzo[*b*]thiophene in the presence of 0.2 eq. $ZnBr_2$ in 1,2-DCE at room temperature followed by reflux led to the generation of an inseparable mixture (1:0.4 based on ^1H NMR integration) of annulated heterocycles **6** and **7** in 54% yield (Scheme 4).

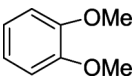
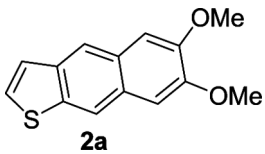
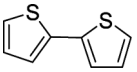
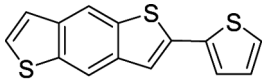
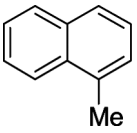
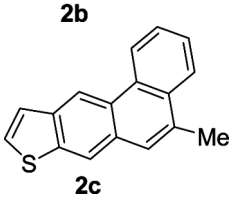
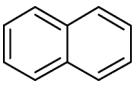
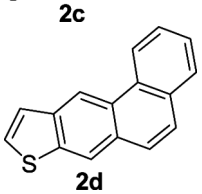
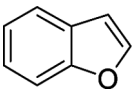
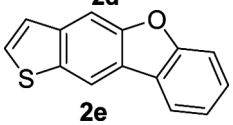
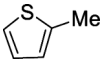
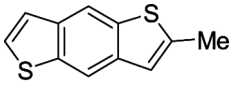
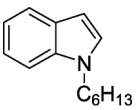
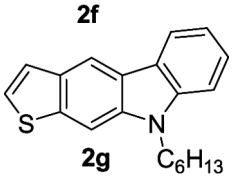
To understand mechanism of the annulation reaction, as a representative case the domino reaction of the bromo compound **1** in the presence of anhydrous K_2CO_3 was planned. Accordingly, the reaction of bromo compound **1** with arenes (anisole, veratrole, and *p*-xylene) using 2 eq. of $ZnBr_2$ in the presence of anhydrous K_2CO_3 at room temperature for 12 h afforded the arylated products **8a–c** in 70–80% yields. However, under identical conditions, the reaction of bromo compound **1** with heteroarenes (substituted thiophenes and benzo[*b*]furan) led to the synthesis of the heterocycles **2b, 2e**, and **2f** in 54–68% yields (Scheme 5).

Next, thermolysis of the intermediate veratrylmethylthiophene **8b** in the presence of 0.5 eq. of $ZnBr_2$ in 1,2-DCE at reflux furnished the heterocycle **2a** in 80%



Scheme 3. Domino reaction bromo compounds **1/5a–c** with arenes/heteroarenes.

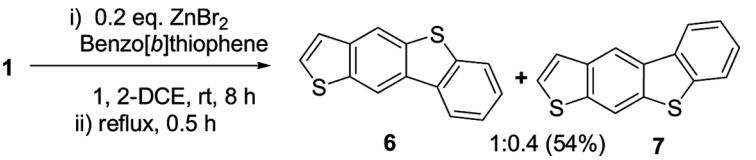
Table 1. Domino reaction of bromo compounds **1**/**5a–c** with arenes/heteroarenes

Entry	Substrate	Arene/heteroarene	Product	Yield (%)[a]
1	**1**/**5a**		 **2a**	53/62
2	**1**/**5a–c**		 **2b**	50/67/45/43
3	**1**/**5a**		 **2c**	46/62
4	**1**/**5a**/**5c**		 **2d**	48/60/47
5	**1**/**5a–c**		 **2e**	50/63/52/46
6	**1**/**5a**/**5c**		 **2f**	40/55/42
7	**1**/**5a–c**		 **2g**	0

[a]Isolated yield after column chromatography.

yield. However, under identical conditions, the thermolysis of either anisylmethythiophene **8a** or *p*-xylenylmethylthiophene **8c** failed to produce the expected annulated heterocycle **9** or **10**; instead only the starting material was recovered unchanged (Scheme 6).

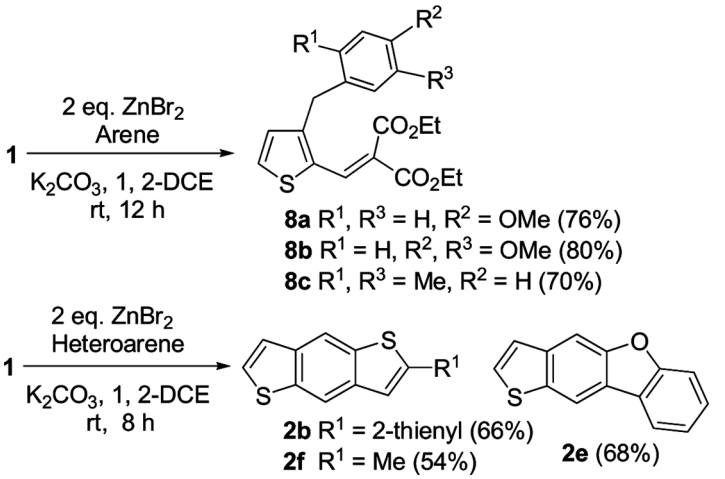
Now, it is clear that the nucleophilic character of the aryl/heteroaryl unit plays a crucial role in the formation of annulated heterocycles. Obviously, in the case of **8a** or **8c**, the moderately electron-rich nature of the aryl unit does not favor the subsequent Friedel–Crafts-type intramolecular cyclization reaction. Hence, the mechanism of the domino reaction involves the initial arylation followed by $ZnBr_2$-mediated intramolecular cyclization of **11** to produce intermediate **13**. Aromatization of the



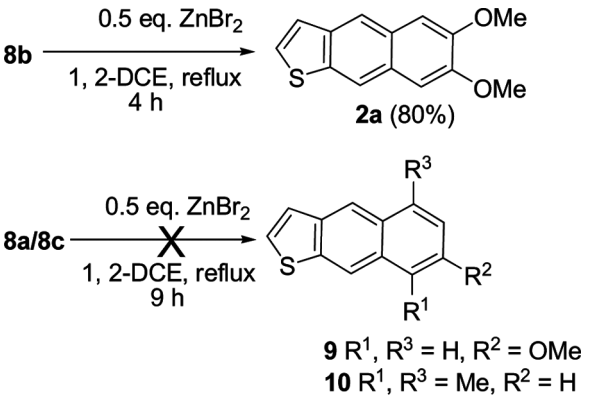
Scheme 4. Domino reaction of bromo compound **1** with benzo[*b*]thiophene.

intermediate **13** via elimination of diethyl malonate led to the formation of annulated heterocycles **2a–f** (Scheme 7).

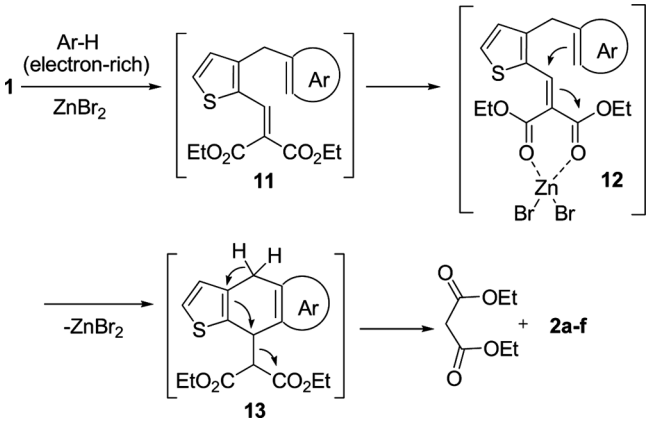
In conclusion, a facile $ZnBr_2$-mediated domino reaction of 3-bromomethylthiophenes containing the vinylidene unit has been successfully performed with arenes as well as heteroarenes to afford the respective aryl/heteroaryl annulated benzo[*b*]



Scheme 5. The reaction of bromo compound **1** with arenes/heteroarenes.



Scheme 6. Thermolysis of arylmethylthiophenes **8a–c**.



Scheme 7. Mechanism of domino reaction.

thiophene analogs. A suitable mechanism for the formation of annulated heterocycles via arylation followed by intramolecular cyclization and subsequent aromatization reactions has been proposed.

EXPERIMENTAL

All melting points were uncorrected. Reagents were purchased from commercial sources and used as received without purification. Solvents were dried by standard procedures. Column chromatography was carried out on silica gel (grade 60, mesh size 230–400, Merck). Infrared (IR) spectra were recorded on a Shimadzu Fourier transform (FT)–IR 8300 instrument. ^{1}H and ^{13}CNMR spectra were recorded in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard on a Bruker-300 spectrometer. Chemical shift values were quoted in parts per million (ppm), and coupling constants were quoted in hertz (Hz). Chemical shift multiplicities were reported as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were recorded on a Jeol DX 303 HF spectrometer. Elemental analyses were carried out on Perkin-Elmer series II 2400 (IIT Madras) equipment.

Diethyl-2-((3-(bromomethyl)thiophen-2-yl)methylene)malonate (1)[12]

Allylic bromination of diethyl-2-((3-(methyl)thiophen-2-yl)methylene)malonate (2.68 g, 10 mmol) using NBS (2.12 g, 12 mmol) and azobisisobutyronitrile (AIBN, 0.05 g) in dry carbon tetrachloride (50 mL) using the published procedure[13] afforded bromo compound **1** as a yellow solid. Yield: 2.96 g (85%). Mp: 59 °C (lit.[13] 58–59 °C). ν_{max} (KBr): 1725, 1710, 1610 cm^{-1}. δ_H ($CDCl_3$, 300 MHz): 7.94 (s, 1H, Ar-H), 7.46 (d, $J = 5.1$ Hz, 1H, Ar-H), 7.11 (d, $J = 5.1$ Hz, 1H, Ar-H), 4.59 (s, 2H, -CH_2), 4.39 (q, $J = 7.2$ Hz, 2H, -OCH_2), 4.31 (q, $J = 7.2$ Hz, 2H, -OCH_2), 1.39–1.31 (m, 6H, -CH_3). δ_C ($CDCl_3$, 75 MHz): 166.1, 164.1, 142.6, 132.7, 130.6, 130.4, 129.7, 123.7, 62.0, 61.8, 25.1, 14.1, 13.9.

1,3-Dimethyl-5-((3-methylthiophen-2-yl)methylene)pyrimidine-2,4,6-(1*H*, 3*H*, 5*H*)-trione (4a)

N,N-Dimethylbarbituric acid (4.08 g, 26.13 mmol), piperidine (0.3 mL), and acetic acid (0.2 mL) were added to a solution of 3-methyl-2-thiophenecarboxaldehyde **3** (3.0 g, 23.77 mmol) in dry benzene (80 mL), and refluxed in a 250 mL RB flask fitted with a Dean–Stark apparatus for 12 h. Removal of solvent followed by crystallization from methanol afforded the compound **4a** as a yellow solid. Yield: 5.0 g (80%). Mp: 142–144 °C. ν_{max} (KBr): 1722, 1656, 1552 cm^{-1}. δ_H ($CDCl_3$, 300 MHz): 8.79 (s, 1H, Ar-H), 7.83 (d, $J = 4.8$ Hz, 1H, Ar-H), 7.04 (d, $J = 5.1$ Hz, 1H, Ar-H), 3.32 (s, 6H, -NCH_3), 2.52 (s, 3H, -CH_3). δ_C ($CDCl_3$, 75 MHz): 163.0, 161.9, 154.5, 151.4, 145.9, 140.4, 131.6, 131.2, 109.1, 28.9, 28.1, 15.8.

1,3-Dimethyl-5-((3-bromomethylthiophen-2-yl)methylene) pyrimidine-2,4,6(1*H*, 3*H*, 5*H*)-trione (5a)

AIBN (0.05 g) and finely powdered NBS (0.70 g, 3.93 mmol) were added to a solution of compound **4a** (1.0 g, 3.78 mmol) in dry carbon tetrachloride (20 mL), refluxed for 2 h, and cooled to room temperature. The floated succinimide was filtered off and washed with carbon tetrachloride (10 mL). The combined filtrate was concentrated in vacuo to afford the bromo compound **5a** as a yellow solid. Yield: 1.1 g (85%). Mp: 204–206 °C. ν_{max} (KBr): 1721, 1654, 1557 cm^{-1}. δ_H ($CDCl_3$, 300 MHz): 8.84 (s, 1H, Ar-H), 7.85 (d, $J = 5.1$ Hz, 1H, Ar-H), 7.25 (d, $J = 5.1$ Hz, 1H, Ar-H), 4.70 (s, 2H, -CH_2), 3.36 (s, 3H, -NCH_3) 3.35 (s, 3H, -NCH_3). δ_C ($CDCl_3$, 75 MHz): 162.6, 161.7, 151.2, 150.8, 143.9, 139.7, 132.8, 130.5, 111.0, 29.0, 28.2, 23.4.

2,2-Dimethyl-5-((3-methylthiophen-2-yl)methylene)-1,3-dioxane-4, 6-dione (4b)

Condensation of 3-methylthiophene-2-carboxaldehyde **3** (3.0 g, 23.77 mmol) with Meldrum's acid (3.76 g, 26.08 mmol) in the presence of piperidine (0.3 mL), and acetic acid (0.2 mL) following the procedure described for **4a**, furnished compound **4b** as a yellow solid. Yield: 5 g (84%). Mp: 134–136 °C. ν_{max} (KBr): 1707, 1551 cm^{-1}. δ_H ($CDCl_3$, 300 MHz): 8.70 (s, 1H, Ar-H), 7.85 (d, $J = 5.1$ Hz, 1H, Ar-H), 7.03 (d, $J = 4.2$ Hz, 1H, Ar-H), 2.51 (s, 3H, -CH_3), 1.70 (s, 6H, -CH_3). δ_C ($CDCl_3$, 75 MHz): 164.0, 161.3, 154.5, 146.2, 140.4, 131.2, 131.0, 105.4, 104.4, 27.5, 15.7.

5-((3-Bromomethylthiophen-2-yl)methylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (5b)

Allylic bromination of compound **4b** (2.0 g, 7.93 mmol) using NBS (1.55 g, 8.70 mmol) in the presence of AIBN (0.05 g) in dry CCl_4 (30 mL), following the procedure described for **5a**, furnished the bromo compound **5b** as a yellow solid. Yield: 2.30 g (88%). Mp: 174–176 °C. ν_{max} (KBr): 1706, 1566 cm^{-1}. δ_H ($CDCl_3$, 300 MHz): 8.70 (s, 1H, Ar-H), 7.87 (d, $J = 5.1$ Hz, 1H, Ar-H), 7.24 (d, $J = 5.1$ Hz, 1H, Ar-H), 4.66 (s, 2H, -CH_2), 1.71 (s, 6H, -CH_3). δ_C ($CDCl_3$, 75 MHz): 163.3, 161.0, 150.9, 144.0, 139.8, 132.3, 130.4, 107.7, 104.8, 27.6, 23.1.

2-((3-Methylthiophen-2-yl)methylene)malononitrile (4c)

Condensation of 3-methylthiophene-2-carboxaldehyde **3** (3.0 g, 23.77 mmol) with malononitrile (1.64 g, 24.88 mmol) in the presence of piperidine (0.3 mL) and acetic acid (0.2 mL) following the procedure described for **4a**, furnished compound **4c** as a yellow solid. Yield: 3.56 g (86%). Mp: 196 °C. ν_{max} (KBr): 2215, 1569 cm^{-1}. δ_H ($CDCl_3$, 300 MHz): 7.93 (s, 1H, Ar-H), 7.78 (d, $J = 4.8$ Hz, 1H, Ar-H), 7.07 (d, $J = 5.1$ Hz, 1H, Ar-H), 2.46 (s, 3H, -CH_3). δ_C ($CDCl_3$, 75 MHz): 150.3, 149.1, 135.8, 131.2, 130.7, 114.5, 113.2, 14.8.

2-((3-Bromomethylthiophen-2-yl)methylene)malononitrile (5c)

Allylic bromination of compound **4c** (1.0 g, 5.74 mmol) using NBS (1.12 g, 6.29 mmol) in the presence of AIBN (0.05 g) in dry CCl_4 (15 mL), following the procedure described for **5a**, furnished the bromo compound **5c** as a yellow solid. Yield: 1.30 g (90%). Mp: 104–106 °C. ν_{max} (KBr): 2215, 1568 cm^{-1}. δ_H ($CDCl_3$, 300 MHz): 8.06 (s, 1H, Ar-H), 7.82 (d, $J = 5.1$ Hz, 1H, Ar-H), 7.27 (d, $J = 4.8$ Hz, 1H, Ar-H), 4.58 (s, 2H, -CH_2). δ_C ($CDCl_3$, 75 MHz): 149.2, 147.7, 135.8, 132.1, 131.2, 130.5, 114.4, 113.2, 29.6.

$ZnBr_2$-Mediated Domino Reaction of Bromo Compounds 1/5a–c with Arenes/Heteroarenes

Anhydrous $ZnBr_2$ (3 mmol), and arene/heteroarene (3.6 mmol) were added to a solution of bromo compound **1/5a–c** (3 mmol) in dry dichloroethane (DCE, 15 mL). The mixiture was then stirred at room temperature for 8 h and then refluxed for 1 h under N_2 atmosphere. The solvent was removed, and the residue was quenched with icewater (50 mL) containing 1 mL of concentrated HCl, extracted with chloroform (3×10 mL), and dried (Na_2SO_4). Removal of solvent followed by flash column chromatographic purification (*n*-hexane/ethyl acetate) led to the isolation of annulated product.

6,7-Dimethoxynaphtho[2,3-*b*]thiophene (2a). Mp: 210–212 °C (lit.[11] 210 °C). δ_H ($CDCl_3$, 300 MHz): 8.18 (s, 1H, Ar-H), 8.14 (s, 1H, Ar-H), 7.41 (d, $J = 5.4$ Hz, 1H, Ar-H), 7.35 (d, $J = 5.4$ Hz, 1H, Ar-H), 7.19 (s, 1H, Ar-H), 7.14 (s, 1H, Ar-H), 4.03 (s, 6H, -OCH_3). δ_C ($CDCl_3$, 75 MHz): 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. MS (*m/z*) %: 244 (M^+, 63%). Anal. calcd. for $C_{14}H_{12}O_2S$: C, 68.83; H, 4.95; S, 13.12%. Found: C, 68.99; H, 4.73; S, 13.39%.

5-(2′-Thienyl)thieno[3,2-*d*]benzothiophene (2b). Mp: 252–254 °C (lit.[11] 252 °C). δ_H ($CDCl_3$, 300 MHz): 8.45 (s, 2H, Ar-H), 7.80 (d, $J = 5.4$ Hz, 1H, Ar-H), 7.68 (s, 1H, Ar-H), 7.65 (d, $J = 5.1$ Hz, 1H, Ar-H), 7.48 (d, $J = 4.8$ Hz, 2H, Ar-H), 7.17 (t, $J = 4.5$ Hz, 1H, Ar-H). δ_C ($CDCl_3$, 75 MHz): 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. MS (*m/z*) %: 272 (M^+, 73%). Anal. calcd. for $C_{14}H_8S_3$: C, 61.73; H, 2.96; S, 35.31%. Found: C, 61.53; H, 2.80; S, 35.53%.

5-Methyl phenanthro[2,3-*b*]thiophene (2c). Mp: 146 °C. δ_H ($CDCl_3$, 300 MHz): 9.02 (s, 1H, Ar-H), 8.72 (d, $J = 7.8$ Hz, 1H, Ar-H), 8.19 (s, 1H, Ar-H), 7.96 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.58–7.44 (m, 5H, Ar-H), 2.65 (s, 3H,-CH_3). δ_C ($CDCl_3$, 75 MHz): 138.6, 138.5, 132.2, 132.0, 130.7, 129.7, 127.3, 126.5, 126.4, 126.3, 124.7, 124.1, 122.8, 120.6, 117.1, 20.1. MS (m/z) %: 248 (M^+, 43%). Anal. Calcd. for $C_{17}H_{12}S$: C, 82.22; H, 4.87; S, 12.91%. Found: C, 82.02; H, 4.99; S, 12.73%.

Phenanthro[2,3-*b*]thiophene (2d). Mp: 148 °C. δ_H ($CDCl_3$, 300 MHz): 9.13 (s, 1H, Ar-H), 8.76 (d, $J = 8.1$ Hz, 1H, Ar-H), 8.36 (s, 1H, Ar-H), 7.87 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.77–7.54 (m, 6H, Ar-H). δ_C ($CDCl_3$, 75 MHz): 139.1, 138.6, 131.8, 130.6, 129.6, 128.6, 127.9, 127.8, 126.8, 126.7, 126.6, 126.5, 124.1, 122,6, 121.5, 117.2. MS (m/z) %: 234 (M^+, 73%). Anal. calcd. for $C_{16}H_{10}S$: C, 82.01; H, 4.30; S, 13.68%. Found: C, 82.20; H, 4.13; S, 13.89%.

Thieno[3,2-*b*]dibenzofuran (2e). Mp 166 °C. δ_H ($CDCl_3$, 300 MHz): 8.32 (s, 1H, Ar-H), 7.92 (t, $J = 4.8$ Hz, 1H, Ar-H), 7.86 (s, 1H, Ar-H), 7.50–7.34 (m, 4H, Ar-H), 7.28 (t, $J = 7.5$ Hz, 1H, Ar-H). δ_C ($CDCl_3$, 75 MHz): 157.1, 154.6, 139.3, 134.4, 127.7, 127.5, 123.8, 123.1, 122.7, 120.7, 113.8, 111.6, 105.1, 104.5. MS (m/z) %: 224 (M^+, 43%). Anal. calcd. for $C_{14}H_8OS$: C, 74.97; H, 3.60; S, 14.30%. Found: C, 74.80; H, 3.85; S, 14.45%.

2-Methylthieno[3,2-*b*]benzothiophene (2f). Mp: 168–170 °C. δ_H ($CDCl_3$, 300 MHz): 8.09 (s, 1H, Ar-H), 8.05 (s, 1H, Ar-H), 7.33 (d, $J = 5.7$ Hz, 1H, Ar-H), 7.24 (d, $J = 5.7$ Hz, 1H, Ar-H), 6.91 (s, 1H, Ar-H), 2.53 (s, 3H, -CH_3). δ_C ($CDCl_3$, 75 MHz): 141.6, 138.4, 137.2, 136.9, 136.7, 126.2, 123.0, 120.6, 116.4, 115.6, 16.5. MS (EI) m/z (%): 204 (M^+, 33%). Anal. calcd. for $C_{11}H_8S_2$: C, 64.66; H, 3.95; S, 31.39. Found: C, 64.50; H, 3.79; S, 31.58.

Annulation of Bromo Compound 1 with Benzo[*b*]thiophene

Domino reaction of bromo compound **1** (1 g, 2.88 mmol) with benzo[*b*]thiophene (0.46 g, 3.42 mmol) in dry DCE (15 mL) in the presence of anhydrous $ZnBr_2$ (0.13 g, 0.57 mmol) was performed at room temperature for 8 h followed by refluxing for 0.5 h. The usual workup, followed by flash column chromatographic purification (*n*-hexane/ethyl acetate 99:1), led to the isolation of an inseparable mixture of isomeric thieno[3,2-*b*]dibenzothiophene **6** and thieno[2,3-*b*]dibenzothiophene **7** as a colorless solid. Yield: 372 mg (54%). Mp: 142–144 °C. δ_H ($CDCl_3$, 300 MHz): 8.64 (s, Ar-H), 8.58 (s, Ar-H), 8.31 (s, Ar-H), 8.26 (s, Ar-H), 8.23–8.19 (m, Ar-H), 7.87–7.84 (m, Ar-H), 7.55–7.39 (m, Ar-H). δ_C ($CDCl_3$, 75 MHz): 139.9, 139.5, 139.2, 137.4, 137.0, 136.6, 136.5, 135.3, 134.9, 133.5, 133.4, 127.7, 127.0, 126.9, 126.2, 124.4, 123.8, 123.1, 122.9, 121.5, 121.4, 117.0, 115.9, 115.8, 115.1.

$ZnBr_2$-Mediated Arylation of Bromo Compound 1 with Arenes

Anhydrous $ZnBr_2$ (6.0 mmol), K_2CO_3 (6.0 mmol) and arene (6.0 mmol) were added To a solution of bromo compound **1** (3.0 mmol), in dry DCE (15 mL). The reaction mixture was stirred at room temperature for 12 h under N_2 atmosphere. The solvent was removed, and the residue was quenched with icewater (50 mL),

extracted with chloroform (3×10 mL), and dried (Na_2SO_4). Removal of solvent followed by flash column chromatographic purification (*n*-hexane/ethyl acetate) led to the isolation of arylated product **8a–c.**

Diethyl-2-((3-(4-methoxybenzyl)thiophen-2-yl)methylene)malonate (8a). Yield: 0.82 g (76%). Mp: 82–84 °C. ν_{max} (KBr): 1722, 1610 cm^{-1}. δ_H ($CDCl_3$, 300 MHz): 8.19 (s, 1H, Ar-H), 7.36 (d, $J = 5.1$ Hz, 1H, Ar-H), 7.18 (d, $J = 7.8$ Hz, 1H, Ar-H), 7.06 (d, $J = 7.8$ Hz, 1H, Ar-H), 6.89–6.83 (m, 3H, Ar-H), 4.40 (q, $J = 6.9$ Hz, 2H, -OCH_2), 4.29 (q, $J = 6.9$ Hz, 2H, -OCH_2), 4.06 (s, 2H, -CH_2), 3.82 (s, 3H, -OCH_3), 1.40–1.29 (m, 6H, CH_3). δ_C ($CDCl_3$, 75 MHz): 166.7, 164.6, 157.1, 147.6, 133.0, 130.2, 129.9, 129.8, 127.9, 120.6, 119.1, 110.4, 61.8, 61.4, 55.2, 25.2, 14.2, 13.9. MS (EI) ***mlz*** (%): 374 (M^+, 77%). Anal. calcd. for $C_{20}H_{22}O_5S$: C, 64.15; H, 5.92; S, 8.56. Found: C, 64.37; H, 5.78; S, 8.79.

Diethyl-2-((3-(3,4-dimethoxybenzyl)thiophen-2-yl)methylene)malonate (8b). Thick liquid; yield: 0.93 g (80%). ν_{max} (KBr): 1706, 1609 cm^{-1}. δ_H ($CDCl_3$, 300 MHz): 8.03 (s, 1H, Ar-H), 7.42 (d, $J = 5.1$ Hz, 1H, Ar-H), 6.85–6.77 (m, 2H, Ar-H), 6.68 (d, $J = 6.3$ Hz, 2H, Ar-H), 4.41 (q, $J = 7.2$ Hz, 2H, -OCH_2), 4.29 (q, $J = 7.2$ Hz, 2H, -OCH_2), 4.05 (s, 2H, -CH_2), 3.85 (s, 3H, -OCH_3), 3.83 (s, 3H, -OCH_3), 1.40-1.29 (m, 6H, CH_3). δ_C ($CDCl_3$, 75 MHz): 166.6, 164.5, 149.1, 147.8, 147.6, 132.4, 132.0, 130.4, 130.2, 130.1, 122.1, 120.6, 111.8, 111.3, 61.9, 61.6, 55.9, 55.8, 34.3, 14.2, 13.9. MS (EI) *m/z* (%): 404 (M^+, 89%). Anal. calcd. for $C_{21}H_{24}O_6S$: C, 62.36; H, 5.98; S, 7.93. Found: C, 62.21; H, 5.80; S, 7.73.

Diethyl-2-((3-(2,5-dimethylbenzyl)thiophen-2-yl)methylene)malonate (8c). Thick liquid; yield: 0.75 g (70%). ν_{max} (KBr): 1719, 1603 cm^{-1}. δ_H ($CDCl_3$, 300 MHz): 8.01 (s, 1H, Ar-H), 7.37 (d, $J = 4.8$ Hz, 1H, Ar-H), 7.06–6.81 (m, 3H, Ar-H), 6.67 (d, $J = 5.1$ Hz, 1H, Ar-H), 4.41 (q, $J = 6.9$ Hz, 2H, -OCH_2), 4.30 (q, $J = 6.9$ Hz, 2H, -OCH_2), 4.01 (s, 2H, -CH_2), 2.26 (s, 3H, -CH_3), 2.21 (s, 3H, -CH_3), 1.40–1.29 (m, 6H, CH_3). δ_C ($CDCl_3$, 75 MHz): 166.6, 164.5, 147.3, 137.4, 135.7, 133.1, 132.3, 130.3, 130.2, 130.1, 130.0 (2C), 127.5, 122.0, 62.0, 61.5, 32.5, 21.0, 19.2, 14.2, 13.9. MS (EI) *m/z* (%): 372 (M^+, 90%). Anal. calcd. for $C_{21}H_{24}O_4S$: C, 67.72; H, 6.49; S, 8.61. Found: C, 67.56; H, 6.67; S, 8.48.

$ZnBr_2$-Mediated Domino Reaction of Bromo Compound 1 with Heteroarenes in the Presence of K_2CO_3

Anhydrous $ZnBr_2$ (6.0 mmol), K_2CO_3 (6.0 mmol), and heteroarene (6.0 mmol) were added to a solution of bromo compound **1** (3.0 mmol) in dry DCE (15 mL). The reaction mixture was stirred at room temperature for 8 h under N_2 atmosphere. The solvent was removed, and the residue was quenched with icewater (50 mL), extracted with chloroform (3×10 mL), and dried (Na_2SO_4). Removal of solvent followed by flash column chromatographic purification (*n*-hexane/ethyl acetate) led to the isolation of annulated product **2b, 2e**, and **2f.**

ACKNOWLEDGMENTS

We thank the University Grants Commission, New Delhi (32-194/2006/SR), for financial support. V. D. thanks the Council for Scientific and Industrial

Research, New Delhi, for a senior research fellowship. We thank the Department of Science and Technology (DST-FIST) for a 300-MHz NMR facility.

REFERENCES

1. (a) Müllen, K.; Wegner, G.; Eds. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, Germany, 1998; (b) Gronowitz, S.; Hornfeldt, A.-B. *Thiophenes*. Elsevier Academic Press, San Diego, CA, 2004 (c) Roncali, J. Oligothienylenevinylenes as a new class of multinanometer linear π-conjugated systems for micro-and nanoelectronics. *Acc. Chem. Res.* **2000**, *33*, 147–156; (d) Mishra, A.; Ma, C.-Q.; Bäuerle, P. Functional oligothiophenes: Molecular design for multidimensional nanoarchitectures and their applications. *Chem. Rev.* **2009**, *109*, 1141–1276.
2. (a) Wex, B.; Kaafarani, B. R.; Krischbaum, K.; Neckers, D. C. Synthesis of the *anti* and *syn* isomers of thieno[*f,f′*]bis[1]benzothiophene: Comparison of the optical and electrochemical properties of the *anti* and *syn* isomers. *J. Org. Chem.* **2005**, *70*, 4502–4505 (b) Ebata, H.; Izawa, T.; Miyazaki, E.; Takimiya, K.; Ikeda, M.; Kuwabara, H.; Yui, T. Highly soluble [1]benzothieno[3,2-*b*]benzothiophene (BTBT) derivatives for high-performance, solution-processed organic field-effect transistors. *J. Am. Chem. Soc.* **2007**, *129*, 15732–1573; (c) Ebata, H.; Miyazaki, E.; Yamamoto, T.; Takimiya, K. Synthesis, properties, and structures of benzo[1,2-b:4,5-b′]bis[b]benzothiophene and benzo[1,2-b:4,5-b′]bis[b] benzoselenophene. *Org. Lett.* **2007**, *9*, 4499–4502; (d) Ni, Y.; Nakajima, K.; Kanno, K.-I.; Takahashi, T. Zirconium-mediated coupling reaction for synthesis of substituted thiophene-fused acenes. *Org. Lett.* **2009**, *11*, 3702–3705.
3. (a) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. Synthesis, morphology, and field-effect mobility of anthradithiophenes. *J. Am. Chem. Soc.* **1998**, *120*, 664–672; (b) Payne, M. M.; Odom, S. A.; Parkin, S. R.; Anthony, J. E. Stable, crystalline acenedithiophenes with up to seven linearly fused rings. *Org. Lett.* **2004**, *6*, 3325–3328; (c) Yamamoto, T.; Takimiya, K. Facile synthesis of highly π-extended heteroarenes, dinaphtho[2,3-b:2′,3′-f] chalcogenopheno[3,2-b]chalcogenophenes, and their application to field-effect transistors. *J. Am. Chem. Soc.* **2007**, *129*, 2224–2225; (d) Nicolas, Y.; Blanchard, P.; Roncali, J.; Allain, M.; Mercier, N.; Deman, A. L.; Tardy, J. Synthesis of a thermally stable hybrid acene-thiophene organic semiconductor via a soluble precursor. *Org. Lett.* **2005**, *7*, 3513–3516; (e) Gao, J.; Li, R.; Li, L.; Meng, Q.; Jiang, H.; Li, H.; Wu, H. High-performance field-effect transistor based on dibenzo[*d,d′*]thieno[3,2:4,5-*b′*]dithiophene, an easily synthesized semiconductor with high ionization potential. *Adv. Mater.* **2007**, *19*, 3008–3011; (f) Sun, Y.; Liu, Y.; Zhu, D. Advances in organic field-effect transistors. *J. Mater. Chem.* **2005**, *15*, 53–65.
4. (a) Katz, H. F.; Bao, Z.; Gilat, S. L. Synthetic chemistry for ultrapure, processable, and high-mobility organic transistor semiconductors. *Acc. Chem. Res.* **2001**, *34*, 359–369; (b) Watson, M. D.; Fechtenkötter, A.; Müllen, K. Big is beautiful—"Aromaticity" revisited from the viewpoint of macromolecular and supramolecular benzene chemistry. *Chem. Rev.* **2001**, *101*, 1267–1300; (c) Anthony, J. E. Functionalized acenes and heteroacenes for organic electronics. *Chem. Rev.* **2006**, *106*, 5028–5048; (d) Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J.-L. Charge transport in organic semiconductors. *Chem. Rev.* **2007**, *107*, 926–952.
5. Gao, P.; Feng, X.; Yang, X.; Enkelmann, V.; Baumgarten, M.; Müllen, K. Conjugated ladder-type heteroacenes bearing pyrrole and thiophene ring units: Facile synthesis and characterization. *J. Org. Chem.* **2008**, *73*, 9207–9213.
6. Wex, B.; Kaafarani, B. R.; Neckers, D. C. Efficient isomer-pure synthesis of a benzo[*b*] thiophene analogue of pentacene. *J. Org. Chem.* **2004**, *69*, 2197–2199.

7. Tedjamulia, M. L.; Tominaga, Y.; Castle, R. N.; Lee, M. L. The synthesis of dinaphthothiophenes. *Heterocycl. Chem.* **1983**, *20*, 1143–1148.
8. Ni, Y.; Nakajima, K.; Kanno, K. I.; Takahashi, T. Zirconium-mediated coupling reaction for synthesis of substituted thiophene-fused acenes. *Org. Lett.* **2009**, *11*, 3702–3705.
9. Sha, C.-K.; Tsou, C.-P. Synthesis and Diels–Alder reaction of thieno[2,3-*c*:4,5-c′]-dipyrroles. *Tetrahedron* **1993**, *49*, 6831–6836.
10. Pouchain, L.; Aleveque, O.; Nicolas, Y.; Oger, A.; Regent, C. H. L.; Allain, M.; Blanchard, P.; Roncali, J. Quaterthiophenes with terminal indeno[1,2-*b*]thiophene units as *p*-type organic semiconductors. *J. Org. Chem.* **2009**, *74*, 1054–1064.
11. (a) Mohanakrishnan, A. K.; Dhayalan, V.; Arul Clement, J.; Balamurugan, R.; Sureshbabu, R.; Senthil Kumar, N. A one-pot synthesis of annulated carbazole analogs. *Tetrahedron Lett.* **2008**, *49*, 5850–5854; (b) Dhayalan, V.; Arul Clement, J.; Jegan, R.; Mohanakrishnan, A. K. A versatile synthesis of annulated carbazole analogs involving a domino reaction of bromomethylindoles with arenes/heteroarenes. *Eur. J. Org. Chem.* **2009**, 4, 531–546.
12. Sha, C.-K.; Tsou, C.-P. Thieno[2,3-*c*]pyrroles: Synthesis, Diels–Alder reaction, and synthetic utility. *J. Org. Chem.* **1990**, *55*, 2446–2450.