Tetrahedron 68 (2012) 5283–5289

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of benzothieno[2,3-*b*]thiophenes, [2,3-*b*:3′,2′-*d*]-dithienothiophenes and their selenium derivatives via electrophilic cyclization and McMurry cyclization

Weizhi Geng [a], Hanliu Wang [a], Zitao Wang [a], Shaoguang Zhang [a], Wen-Xiong Zhang [a], Zhenfeng Xi [a,b,*]

[a] *Beijing National Laboratory of Molecular Sciences (BNLMS) and Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Haidian District, Beijing 100871, China*
[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry (SIOC), CAS, Shanghai 200032, China*

ARTICLE INFO

Article history:
Received 17 November 2011
Received in revised form 16 December 2011
Accepted 23 December 2011
Available online 3 February 2012

Keywords:
Benzothieno[2,3-*b*]thiophene
Dilithio reagent
Dithienothiophene
Electrophilic cyclization
McMurry cyclization

ABSTRACT

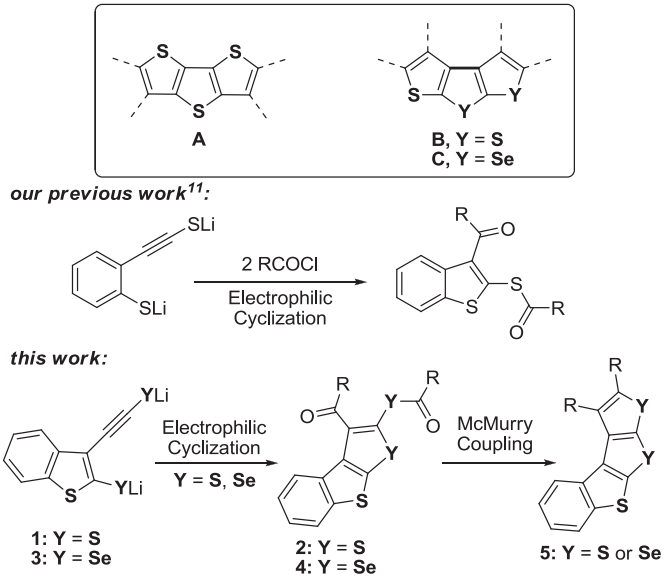
Benzothieno[2,3-*b*]thiophenes, [2,3-*b*:3′,2′-*d*]-dithienothiophenes, and their selenium derivatives were synthesized in good yields from readily available 3-ethynyllithio-benzo[*b*]thiophenyllithio compounds, sulfur or selenium, and 2 equiv of acid chlorides. Two heteroarene rings were constructed by a twofold cyclization via an acid chloride-induced electrophilic ring closing and the McMurry cyclization using Zn/$TiCl_4$ reagents.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Benzothieno[2,3-*b*]thiophenes, dithienothiophenes, and their selenium derivatives have been increasingly attractive due to their utility for electronic materials.[1] For the further development of new materials based on thienothiophenes, it is of primary importance to develop effective synthetic methods to construct thiophene rings. Chalcogen elements, such as sulfur and selenium, are among the cheapest and simplest sources.[2] A challenge topic is the efficient cyclization of sulfur- and selenium-containing species. Sashida and co-workers employed the thiol- or selenol-induced electrophilic cyclization to construct benzothiophenes and their analogs.[2a] Yamaguchi and co-workers developed a double/triple cyclization to construct thiophene or selenophene-fused polycyclic aromatic hydrocarbons.[3]

Although the synthetic methods of dithieno[3,2-*b*: 2′,3′-*d*] thiophenes (**A**) are well established,[1h,3a,4] the synthetic method toward [2,3-*b*:3′,2′-*d*]-dithienothiophenes (**B**) or its seleno derivative (**C**) is limited (Scheme 1).[5–7] In principle, the reported methods for **B** type of compounds can be categorized into two pathways: one is the cyclization of bithiophenyl and $(PhSO_2)_2S$ as



Scheme 1. Synthetic strategy for benzothieno[2,3-*b*]thiophenes and their selenium derivatives via electrophilic cyclization and the McMurry coupling.

* Corresponding author. Tel.: +86 10 6275 9728; fax: +86 10 6275 1708; e-mail address: zfxi@pku.edu.cn (Z. Xi).

0040-4020/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2012.01.088

reported by Rajca and co-workers,[6] the other is the coupling of two C(sp^2)–Br bonds in bis(3-bromothiophen-2-yl)sulfanes.[7] Therefore, it is of great importance to develop general and efficient methods to synthesize **B** type of compounds and their selenium derivatives such as (**C**) (Scheme 1).

Recently, we reported the synthesis of benzothiophene derivatives from *o*-lithiophenylethynyllithium via electrophilic cyclization (Scheme 1).[11] On the basis of this work, we developed a step-by-step method to construct unsymmetric benzothieno[2,3-*b*]thiophenes **2**, [2,3-*b*:3′,2′-*d*]-dithienothiophenes **5**, and their selenium derivatives from commercially available 3-ethynylbenzo[*b*]thiophene. The first thiophene ring was constructed by using the electrophilic cyclization and the other one was formed by McMurry coupling (Scheme 1).

2. Results and discussion

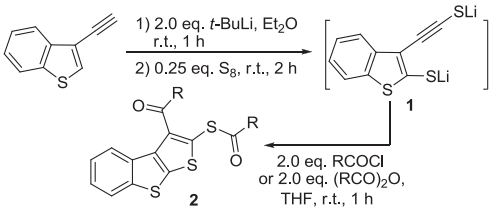
3-Ethynylbenzo[*b*]thiophene was treated with 2 equiv of *t*-BuLi in Et_2O for 1 h to afford 3-ethynyllithia-benzo[*b*]thiophen-2-yl-lithium **1**, a dilithio reagent,[12] to which was then added 0.25 equiv of S_8 (Table 1). After stirring at room temperature for 2 h, the intermediate **1** was formed and applied for further reactions.

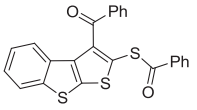
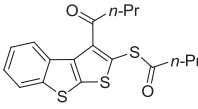
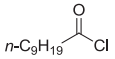
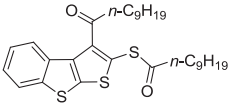
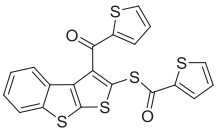
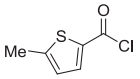
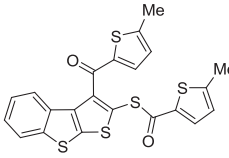
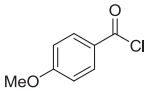
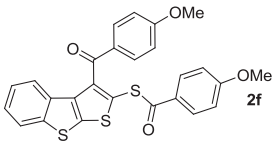
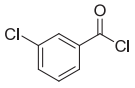
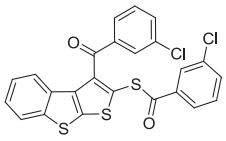
When 2 equiv of an acyl chloride was added to **1**, an electrophilic cyclization occurred to afford the corresponding disubstituted benzothieno[2,3-*b*]thiophene **2**. Acyl chloride with either alkyl or aromatic substituents could all afford their corresponding benzothieno[2,3-*b*]thiophenes **2a**–**2c** in moderate to high isolated yields. Benzoic anhydride and butyric anhydride could also induce this electrophilic cyclization, leading to the cyclized products **2a** and **2b** in 90% and 63% isolated yields, respectively. The structure of **2a** has been determined by single-crystal X-ray structural analysis (Fig. 1). Heteroaromatic acyl chlorides, such as thiophene-2-carbonyl chloride and 5-methylthiophene-2-carbonyl chloride, were also applicable, yielding **2d**, **2e** in good yields. Aryl acyl chlorides bearing either electron-donating or electron-withdrawing substituents on the phenyl ring could also afford their corresponding products **2f** and **2g** in good isolated yields.

Furthermore, selenium and tellurium were also investigated. As given in Table 2, when 3-ethynyllithia-benzo[*b*]-thiophen-2-yl-lithium was treated with 2 equiv of selenium powder for 2 h, the intermediate **3** was formed as yellow precipitation and then the solvent was changed to THF. When 2 equiv of an acyl chloride was added, a same type of electrophilic cyclization occurred to afford the corresponding product **4** in this condition. Both alkyl and aromatic acyl chloride could all afford their corresponding benzo[*b*]selenopheno[3,2-*d*]thiophenes **4a**–**4d** in moderate yields. Heteroaromatic acyl chloride, such as thiophene-2-carbonyl chloride could also give corresponding product **4e** in 68% yields. However, due to the low solubility of tellurium, when *o*-lithiophenylethynyllithium was treated with 2 equiv of tellurium powder, the reaction was messy.

The compounds **2** and **4** featuring two carbonyl groups were further applied to the synthesis of another thiophene ring. It is well known that McMurry reaction is an efficient method to construct C=C and C=X (X=O, N) bonds.[8] The use of low-valent titanium species for C=C bond formation by intramolecular reductive coupling between carbonyl groups and esters or amides resulted in the formation of nitrogen-containing heterocycles. However, the formation of chalcogen-containing heterocycles via reductive coupling is unknown in the literature. The Mukaiyama reagent ($TiCl_4$/Zn) was found effective for reductive coupling of two carbonyl groups in benzothiophenes **2** (and **4**). To a well stirred and cooled solution of **2** in dry dioxane, $TiCl_4$ was added dropwise under nitrogen atmosphere (Scheme 2). After the

Table 1
Synthesis of benzothieno[2,3-*b*]thiophene derivatives **2** via electrophilic cyclization



RCOCl	Product **2**		Yield[a] (%)
		**2a**	92[b] (90%)
		**2b**	71[b] (63%)
		**2c**	71
		**2d**	61
		**2e**	70
		**2f**	81
		**2g**	77

[a] Isolated yields.
[b] The yields in parenthesis were obtained with anhydride.

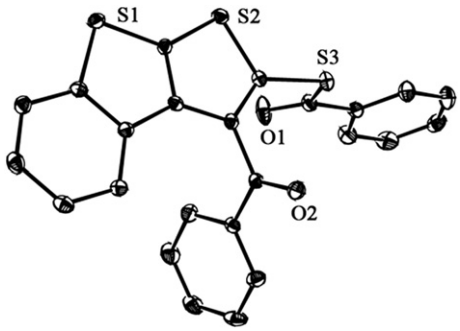
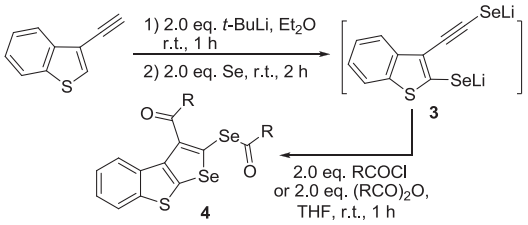
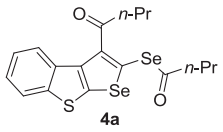
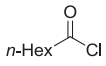
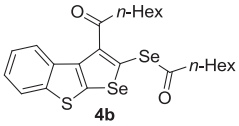
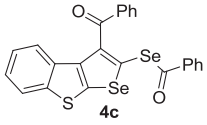
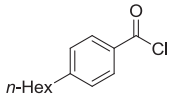
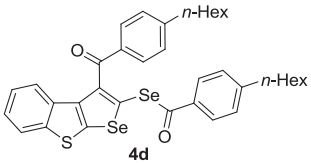
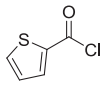
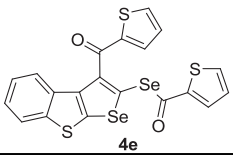
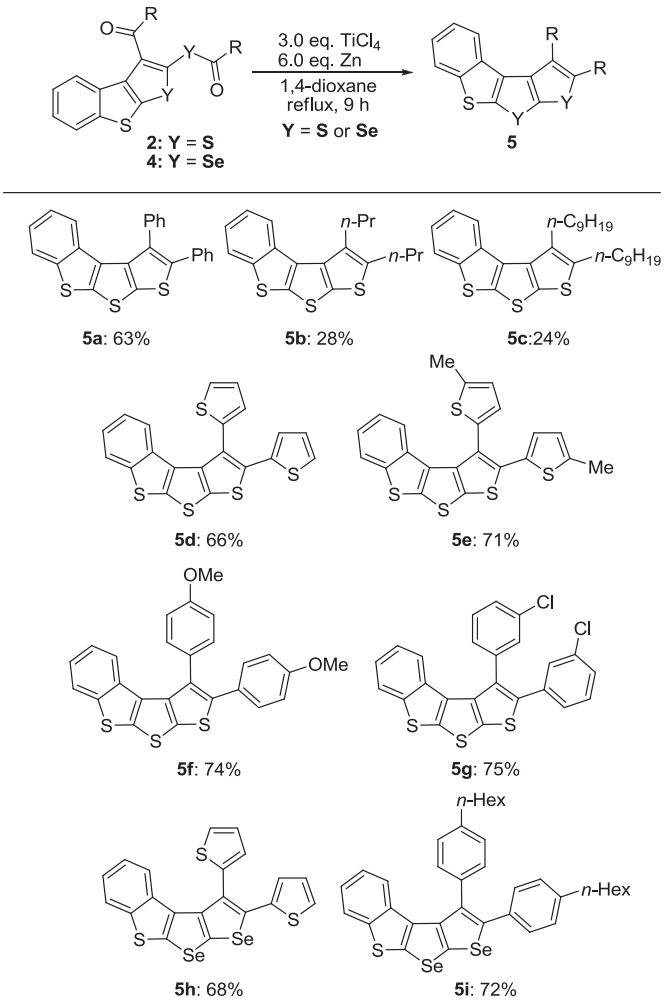


Fig. 1. Single-crystal X-ray structure of **2a** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2
Synthesis of benzo[*b*]selenopheno[3,2-*d*]thiophene derivatives **4** via electrophilic cyclization



RCOCl	Product **4**	Yield (%)
	 **4a**	62
	 **4b**	57
	 **4c**	77
	 **4d**	65
	 **4e**	68



Scheme 2. Synthesis of [2,3-*b*:3′,2′-*d*]-dithienothiophenes **5a**–**g** and their selenium derivatives **5h**–**i** via the McMurry cyclization from **2** and **4**.

mixture was stirred for 30 min, activated Zn powder was added and then the mixture was refluxed for 9 h. Compounds **2a**–**g** were applied, aiming at the synthesis of the corresponding [2,3-*b*:3′,2′-*d*]-dithienothiophenes **5a**–**g**. As given in Scheme 2, the yields of **5b** and **5c** were much lower than those of aromatic **5a**, **5d**–**g**. With these results, we supposed that the stability of thioesters caused by the aromatic substituted groups showed significant influence in the reductive cyclization.[9] The electron-donating or electron-withdrawing substituents on the aromatic rings did not greatly affect the cyclization. The structure of **5b** was determined by single-crystal X-ray structural analysis (Fig. 2). Under the same condition, the benzo[*b*]selenopheno[3,2-*d*]thiophenes **4d**, **4e** could also afford their corresponding [2,3-*b*]-thieno-[3′,2′-*d*]-seleno-selenophenes **5h**, **5i** in good isolated yields.

In **5b**, the dihedral angles of C4–C5–C6–C7 and C5–C6–C7–C8 were 178.92° and 181.73°, indicating that all aromatic rings were nearly coplanar. From the crystal packing of **5b** (Fig. 3A and B), the distances of S1–S2# (3.579 Å) and S1–S3# (3.509 Å) reveal that there exist strong interactions between those S atoms of neighboring enantiomers. The head-to-head S–S interactions are expected to provide new packing mode for charge transport.[1f]

Particularly, the compound **5e** bearing two methyl-thiophenyl groups was an interesting precursor to construct larger planar π-conjugated systems as demonstrated by Pei and co-workers.[10] Thus, when **5e** was treated with $FeCl_3$, the oxidative C–C bond formation between two α-positions of the thiophene units produced the compound **6** in 87% isolated yield (Scheme 3). According to the literature, such a large planar π-conjugated compound could show helical structure and potential application in organic materials.[6]

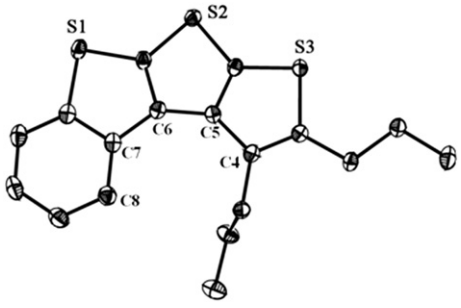


Fig. 2. Single-crystal X-ray structure **5b** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

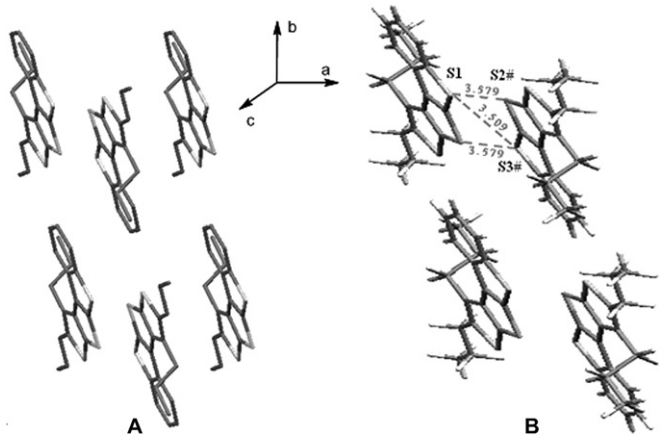
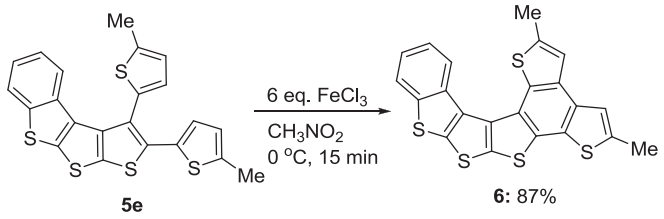


Fig. 3. S–S interaction in crystal packing in **5b**. (A) Top view of crystal packing (B) S···S distance in crystal packing.



Scheme 3. Synthesis of compound **6** via oxidative coupling of **5e**.

3. Conclusion

In summary, we reported the synthesis of benzothieno[2,3-*b*] thiophenes, [2,3-*b*:3′,2′-*d*]-dithienothiophenes, and their selenium derivatives from readily available dilithio reagents, sulfur or selenium, and 2 equiv of acid chlorides. By carefully controlling the amount of sulfur or selenium, the first 2-thio-thiophene ring could be conveniently constructed by acid chloride-induced electrophilic cyclization. The second thiophene ring was achieved by C=C double bond formation via the McMurry reaction. Study on the opto-electronic property of these derivatives will be reported in due course.

4. Experimental section

4.1. General information

Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. *t*-BuLi was obtained from Acros. All reactions were carried out under a dry and oxygen-free nitrogen atmosphere in slight positive pressure by using Schlenk techniques or under a nitrogen atmosphere in a Mikrouna Super (1220/750) Glovebox. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieve catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer to ensure both were always below 1 ppm.

Single crystals of **2a** and **5b** suitable for X-ray analysis were grown in CH_2Cl_2/hexane at room temperature for 3 days. Data collections for **2a** and **5b** were performed at −100 °C on a RIGAKU CCD SATURN 724 diffractometer, using graphite-monochromated Mo Kα radiation (λ=0.71073 Å). The determination of crystal class and unit cell parameters was carried out by Rapid-AUTO (Rigaku 2000) program package for **2a** and **5b**. The raw frame data were processed using Crystal Structure (Rigaku/MSC 2000) for **2a** and **5b** to yield the reflection data file. The structures of **2a** and **5b** were solved by use of SHELXTL program. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. **2a** (CCDC-790434) and **5b** (CCDC-790435). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (FT, 300 MHz for ^1H; 75 MHz for ^{13}C), a Varian Mercury 300 spectrometer (FT, 300 MHz for ^1H; 75 MHz for ^{13}C) or a Bruker ARX400 spectrometer (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) at room temperature, unless otherwise noted. Infrared spectra (IR) were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization).

4.2. Typical procedure for the preparation of benzothieno [2,3-*b*]thiophenes 2a–g

In a 25 mL flask, *t*-BuLi (2 mmol, 1.6 M in pentane) was added dropwise at −78 °C to a stirred solution of 3-ethynylbenzo[*b*] thiophene (1 mmol, 158 mg) in Et_2O (5 mL) and the reaction mixture was allowed to warm to room temperature. After stirring at room temperature for 1 h, S_8 (0.25 mmol, 64 mg) was added and the reaction was stirred at room temperature for 2 h. The solvent of the reaction mixture was evaporated under vacuum and THF (5 mL) was added. After that, acid chloride (2 mmol) was added dropwise at room temperature. After stirring at room temperature for 1 h, the solvent of the reaction mixture was evaporated under vacuum. The residue was purified by chromatography to give products **2a**–**l**.

*4.2.1. S-3-Benzoylbenzothieno[2,3-b]thiophen-2-yl benzothioate (**2a**).* Yellow solid (mp 152.2–153.2 °C), isolated yield 92% (396 mg); ^1H NMR (400 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=7.16–8.16 (m, 14H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=122.24 (1 CH), 122.97 (1 CH), 124.75 (1 CH), 124.86 (1 CH), 126.68 (1 quat. C), 127.59 (2 CH), 128.72 (4 CH), 129.91 (2 CH), 131.56 (1 quat. C), 134.00 (1 CH), 134.09 (1 CH), 135.31 (1 quat. C), 137.06 (1 quat. C), 139.35 (1 quat. C), 140.71 (1 quat. C), 142.88 (1 quat. C), 143.12 (1 quat. C), 188.50 (1 quat. C), 192.33 (1 quat. C). HRMS calcd for $C_{24}H_{14}O_2S_3$ $[M+H]^+$: 431.0229, found 431.0237.

*4.2.2. S-3-Butyrylbenzothieno[2,3-b]thiophen-2-yl butanethioate (**2b**).* Yellow oil, isolated yield 71% (257 mg); ^1H NMR (400 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=0.99 (t, *J*=7.4 Hz, 3H, CH_3), 1.00 (t, *J*=7.4 Hz, 3H, CH_3), 1.73–1.83 (m, 4H, CH_2), 2.68 (t, *J*=7.3 Hz, 2H, CH_2), 2.96 (t, *J*=7.3 Hz, 2H, CH_2), 7.34–7.38 (m, 2H, CH), 7.78–7.87 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=13.39 (1 CH_3), 13.79 (1 CH_3), 17.53 (1 CH_2), 18.87 (1 CH_2), 45.06 (1 CH_2), 46.12 (1 CH_2), 122.27 (1 CH), 123.01 (1 CH), 124.86 (1 CH), 125.00 (1 CH), 125.84 (1 quat. C), 131.76 (1 quat. C), 138.85 (1 quat. C), 142.32 (1 quat. C), 142.57 (1 quat. C), 143.17 (1 quat. C), 195.96 (1 quat. C), 201.42 (1 quat. C). HRMS calcd for $C_{18}H_{18}O_2S_3$ $[M+Na]^+$: 385.0361, found 385.0359.

*4.2.3. S-3-Decanoylbenzothieno[2,3-b]thiophen-2-yl decanethioate (**2c**).* Yellow oil, isolated yield 71% (376 mg); ^1H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=0.84–0.90 (m, 6H, CH_3), 1.27 (br s, 24H,

CH_2), 1.69–1.79 (m, 4H, CH_2), 2.68 (t, J=7.5 Hz, 2H, CH_2), 2.96 (t, J=7.2 Hz, 2H, CH_2), 7.34–7.37 (m, 2H, CH), 7.77–7.86 (m, 2H, CH), ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=14.47 (2 CH_3), 23.03 (2 CH_2), 24.44 (1 CH_2), 25.74 (1 CH_2), 29.29 (1 CH_2), 29.58 (1 CH_2), 29.60 (1 CH_2), 29.63 (1 CH_2), 29.72 (1 CH_2), 29.78 (1 CH_2), 29.81 (1 CH_2), 30.07 (1 CH_2), 32.20 (1 CH_2), 32.22 (1 CH_2), 43.72 (1 CH_2), 44.65 (1 CH_2), 122.71 (1 CH), 123.40 (1 CH), 125.26 (1 CH), 125.40 (1 CH), 126.28 (1 quat. C), 132.18 (1 quat. C), 139.28 (1 quat. C), 142.74 (1 quat. C), 142.96 (1 quat. C), 143.58 (1 quat. C), 196.48 (1 quat. C), 201.95 (1 quat. C). UV–vis (CH_2Cl_2): λ_{max}=233 nm. HRMS calcd for $C_{30}H_{42}O_2S_3$ $[M+H]^+$: 531.2420, found 531.2420.

*4.2.4. S-3-(Thiophene-2-carbonyl)benzothieno[2,3-b]thiophen-2-yl thiophene-2-carbothioate (**2d**).* Yellow solid (mp 69.7–71.5 °C), isolated yield 61% (267 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=6.92–7.82 (m, 10H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=122.16 (1 CH), 123.04 (1 CH), 124.89 (1 CH), 124.99 (1 CH), 128.19 (1 CH), 128.70 (1 CH), 131.44 (1 quat. C), 132.66 (1 CH), 133.79 (1 quat. C), 134.44 (1 CH), 135.56 (1 quat. C), 136.22 (1 CH), 136.74 (1 CH), 138.93 (1 quat. C), 139.59 (1 quat. C), 140.49 (1 quat. C), 143.08 (1 quat. C), 143.81 (1 quat. C), 180.49 (1 quat. C), 184.22 (1 quat. C). HRMS calcd for $C_{20}H_{10}O_2S_5$ $[M+H]^+$: 442.9357, found 442.9359.

*4.2.5. S-3-(5-Methylthiophene-2-carbonyl)benzothieno[2,3-b] thiophen-2-yl 5-methylthiophene-2-carbothioate (**2e**).* Yellow solid, isolated yield 70% (329 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=2.46 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 6.65–7.72 (m, 8H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=15.86 (1 CH_3), 16.18 (1 CH_3), 122.02 (1 CH), 122.93 (1 CH), 126.70 (1 CH), 126.91 (1 CH), 127.55 (1 CH), 131.41 (1 CH), 133.27 (1 quat. C), 135.42 (1 CH), 136.43 (1 quat. C), 136.93 (1 quat. C), 137.617 (1 CH), 138.87 (1 quat. C), 140.37 (1 quat. C), 141.54 (1 quat. C), 143.00 (1 quat. C), 149.82 (1 quat. C), 150.81 (1 quat. C), 152.80 (1 quat. C), 179.93 (1 quat. C), 183.646(1 quat. C). HRMS calcd for $C_{22}H_{14}O_2S_5$ $[M+H]^+$: 470.9676, found 470.9667.

*4.2.6. S-3-(4-Methoxybenzoyl)benzothieno[2,3-b]thiophen-2-yl 4-methoxybenzothioate (**2f**).* Yellow solid, isolated yield 81% (397 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=3.78 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 6.84–6.88 (m, 4H, CH), 7.16–7.45 (m, 4H, CH), 7.77–8.00 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=55.43 (1 CH_3), 55.52 (1 CH_3), 113.93 (2 CH), 114.01 (2 CH), 122.18 (1 quat. C), 122.96 (1 quat. C), 124.74 (2 CH), 126.28 (1 quat. C), 128.08 (1 quat. C), 129.98 (2 CH), 130.06 (1 quat. C), 131.63 (1 quat. C), 132.50 (2 CH), 139.23 (1 quat. C), 141.05 (1 quat. C), 142.69 (1 quat. C), 143.09 (1 quat. C), 164.31 (1 quat. C), 164.34 (1 quat. C),186.99 (1 quat. C), 190.97 (1 quat. C). HRMS calcd for $C_{26}H_{18}O_4S_3$ $[M+H]^+$: 491.0440, found 491.0449.

*4.2.7. S-3-(3-Chlorobenzoyl)benzothieno[2,3-b]thiophen-2-yl 3-chlorobenzothioate (**2g**).* Yellow solid, isolated yield 77% (383 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=7.19–7.98 (m, 12H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=122.12 (1 CH), 123.08 (1 CH), 124.87 (1 CH), 125.07 (1 CH), 125.68 (1 quat. C), 126.22 (1 CH), 127.45 (1 CH), 128.24 (1 CH), 129.37 (1 CH), 130.07 (1 CH), 130.08 (1 CH), 131.26 (1 quat. C), 134.00 (1 quat. C), 134.09 (1 quat. C), 135.03 (2 quat. C), 136.50 (1 quat. C), 138.46 (1 quat. C), 139.23 (1 quat. C), 140.07 (1 quat. C), 143.07 (1 quat. C), 143.33 (1 quat. C),187.35 (1 quat. C), 190.90 (1 quat. C). HRMS calcd for $C_{24}H_{12}Cl_2O_2S_3$ $[M+H]^+$: 498.9449, found 498.9449.

4.3. Typical procedure for the preparation of benzo[*b*] selenopheno[3,2-*d*]thiophenes 4a–e

In a 25 mL flask, *t*-BuLi (2 mmol, 1.6 M in pentane) was added dropwise at −78 °C to a stirred solution of 3-ethynylbenzo[*b*] thiophene (1 mmol, 158 mg) in Et_2O (5 mL) and the reaction mixture was allowed to warm to room temperature. After stirring at room temperature for 1 h, Se (2 mmol, 160 mg) was added and the reaction was stirred at room temperature for 2 h. The solvent of the reaction mixture was evaporated under vacuum and THF (5 mL) was added. After that, acid chloride (2 mmol) was added dropwise at room temperature. After stirring at room temperature for 1 h, the solvent of the reaction mixture was evaporated under vacuum. The residue was purified by chromatography to give products **4a**–**e**.

*4.3.1. Se-3-Butyrylbenzoylbenzo[b]selenopheno[3,2-d]thiophen-2-yl butanethioate (**4a**).* Yellow oil, isolated yield 62% (284 mg); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=0.87–1.17 (m, 6H, CH_3), 1.16–1.77 (m, 4H, CH_2), 2.61–2.84 (m, 4H, CH_2), 7.20–7.29 (m, 2H, CH), 7.55–7.73 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=13.30 (1 CH_3), 13.80 (1 CH_3), 17.33 (1 CH_2), 18.72 (1 CH_2), 46.47 (1 CH_2), 48.62 (1 CH_2), 121.41 (1 CH), 122.91 (1 CH), 123.47 (1 quat. C), 124.25 (1 CH), 124.64 (1 CH), 132.63 (1 quat. C), 139.39 (1 quat. C), 144.17 (1 quat. C), 144.20 (1 quat. C), 144.64 (1 quat. C), 199.41 (1 quat. C), 204.14 (1 quat. C). HRMS calcd for $C_{18}H_{18}O_2SSe_2$ $[M+H]^+$: 458.9441, found 458.9433.

*4.3.2. Se-(3-Heptanoyl)benzoylbenzo[b]selenopheno[3,2-d] thiophen-2-yl heptaneselenoate (**4b**).* Yellow oil, isolated yield 57% (309 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=0.77–0.83 (m, 6H, CH_3), 1.18–1.32 (m, 12H, CH_2), 1.58–1.72 (m, 4H, CH_2), 2.64–2.69 (t, J=7.5 Hz, 2H, CH_2), 2.82–2.87 (t, J=7.5 Hz, 2H, CH_2), 7.24–7.28 (m, 2H, CH), 7.56–7.76 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=13.96 (1 CH_3), 14.00 (1 CH_3), 22.35 (1 CH_2), 22.47 (1 CH_2), 23.81 (1 CH_2), 25.14 (1 CH_2), 28.44 (1 CH_2), 28.85 (1 CH_2), 31.33 (1 CH_2), 31.53 (1 CH_2), 44.64 (1 CH_2), 46.94 (1 CH_2), 121.50 (1 CH), 122.95 (1 CH), 123.56 (1 quart. C), 124.30 (1 CH), 124.69 (1 CH), 132.73 (1 quart. C), 139.48 (1 quart. C), 144.25 (1 quart. C), 144.30 (1 quart. C), 144.66(1 quart. C), 199.52 (1 quart. C), 204.28 (1 quart. C). HRMS calcd for $C_{24}H_{30}O_2SSe_2$ $[M+H]^+$: 543.0373, found 543.0386.

*4.3.3. Se-3-Benzoylbenzo[b]selenopheno[3,2-d]thiophen-2-yl benzothioate (**4c**).* Yellow solid, isolated yield 77% (405 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=7.10–7.60 (m, 10H, CH), 7.77–7.81 (m, 2H, CH), 7.96–7.98 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=121.98 (1 CH), 122.76 (1 CH), 124.13 (1 CH), 124.51 (1 CH), 125.46 (1 quat. C), 127.39 (2 CH), 128.85 (2 CH), 129.04 (2 CH), 130.05 (2 CH), 132.73 (1 quat. C), 134.13 (1 CH), 134.40 (1 CH), 136.74 (1 quat. C), 137.26 (1 quat. C), 140.25 (1 quat. C), 141.53 (1 quat. C), 144.25 (1 quat. C), 144.40 (1 quat. C), 192.28 (1 quat. C), 194.43 (1 quat. C). HRMS calcd for $C_{24}H_{14}O_2SSe_2$ $[M+Na]^+$: 548.8940, found 548.8948.

*4.3.4. Se-3-(4-Hexylbenzoyl)benzoylbenzo[b]selenopheno[3,2-d]thiophen-2-yl-4-hexylbenzothioate (**4d**).* Yellow oil, isolated yield 65% (451 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=0.89–0.92 (m, 6H, CH_3), 1.28–1.33 (m, 12H, CH_2), 1.58–1.63 (m, 4H, CH_2), 2.60–2.66 (m, 4H, CH_2), 7.15–7.43 (m, 8H, CH) , 7.71–7.95 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=13.99 (2 CH_3), 22.44 (1 CH_2), 22.46 (1 CH_2), 28.77 (2 CH_2), 30.75 (1 CH_2), 30.81 (1 CH_2), 31.51 (2 CH_2), 35.94 (1 CH_2), 35.99 (1 CH_2), 121.96 (1 CH), 122.62 (1 CH), 123.94 (1 CH), 124.34 (1 CH), 122.55 (1 quart. C), 127.46 (2 CH), 128.83 (2 CH), 128.92 (2 CH), 130.15 (2 CH), 132.74 (1 quart. C), 134.48 (1 quart. C), 134.82 (1 quart. C), 140.16 (1 quart. C), 141.33(1 quart. C), 144.05 (1 quart. C), 144.18 (1 quart. C), 149.98 (1 quart. C), 150.39 (1 quart. C), 191.59 (1 quart. C), 194.02 (1 quart. C). HRMS calcd for $C_{36}H_{38}O_2SSe_2$ $[M+H]^+$: 695.1001, found 695.1016.

*4.3.5. Se-3-(Thiophene-2-carbonyl) benzoylbenzo[b]selenopheno [3,2-d]thiophen-2-yl thiophene-2-carbothioate (**4e**).* Yellow solid, isolated yield 68% (366 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si,

25 °C): δ=6.98–7.79 (m, 10H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): 121.91 (1 CH), 122.77 (1 CH), 124.23 (1 CH), 124.60 (1 CH), 125.14 (1 quart. C), 128.24 (1 CH), 128.74 (1 CH), 132.62 (1 quart. C), 132.82 (1 CH), 134.82 (1 CH), 136.24 (1 CH), 136.69 (1 CH), 139.80 (1 quart. C), 141.15 (1 quart. C), 141.33 (1 quart. C), 143.68 (1 quart. C), 144.17(1 quart. C), 144.72 (1 quart. C), 182.50 (1 quart. C), 186.28 (1 quart. C). HRMS calcd for $C_{20}H_{10}O_2S_3Se_2$ $[M+H]^+$: 538.8254, found 538.8246.

4.4. Typical procedure for the preparation of compound 5

To a solution of **2** or **4** (1 mmol) in dry dioxane (50 mL), the mixture was cooled to 0 °C and $TiCl_4$ (0.33 mL, 3 mmol) was added dropwise under nitrogen atmosphere. After stirring at 0 °C for 0.5 h, Zn powder (0.39 g, 6 mmol) was added in small lots and then the mixture was refluxed for 9 h. The reaction mixture was quenched by H_2O and the product was extracted by Et_2O. The solvent of the organic layer was evaporated under vacuum. The residue was purified by chromatography to give the products **5a**–**i**.

*4.4.1. 2,3-Diphenylbenzo[2,3-b:3′,2′-d]-dithienothiophene (**5a**).* White solid (mp 192.0–193.5 °C), isolated yield 63% (249 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=5.74–5.77 (m, 1H, CH), 6.63–7.51(m, 13H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=122.64 (1 CH), 123.38 (1 CH), 123.51 (1 CH), 124.05 (1 CH), 127.42 (1 CH), 128.14 (1 CH), 128.30 (2 CH), 128.72 (2 CH), 129.11 (2 CH), 131.20 (2 CH), 131.55 (1 quat. C), 132.24 (1 quat. C), 133.77 (1 quat. C), 134.37 (1 quat. C), 136.41 (1 quat. C), 137.18 (1 quat. C), 139.87 (1 quat. C), 140.96 (1 quat. C), 141.51 (1 quat. C), 142.84(1 quat. C). HRMS calcd for $C_{24}H_{14}S_3$ $[M+H]^+$: 399.0330, found 399.0324.

*4.4.2. 2,3-Dipropylbenzo[2,3-b:3′,2′-d]-dithienothiophene (**5b**).* Colorless solid (mp 78.0–81.2 °C): isolated yield 28% (95 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=1.04–1.14 (m, 6H, CH_3), 1.72–1.83 (m, 4H, CH_2), 2.86 (t, J=7.5 Hz, 2H, CH_2), 3.10 (t, J=7.8 Hz, 2H, CH_2), 7.32–7.47 (m, 2H, CH), 7.85 (d, J=7.8 Hz, 1H, CH), 8.19 (d, J=7.8 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=13.69 (1 CH_3), 13.90 (1 CH_3), 24.81 (1 CH_2), 25.17 (1 CH_2), 30.86 (1 CH_2), 31.15 (1 CH_2), 122.61 (1 CH), 123.33 (1 CH), 123.38 (1 CH), 124.44 (1 CH), 130.52 (1 quat. C), 132.66 (1 quat. C), 133.69 (1 quat. C), 134.77 (1 quat. C), 139.57 (1 quat. C), 139.83 (1 quat. C), 141.55 (1 quat. C), 143.06 (1 quat. C). HRMS calcd for $C_{18}H_{18}S_3$ $[M+H]^+$: 331.0643, found 331.0639.

*4.4.3. 2,3-Didecanoylbenzo[2,3-b:3′,2′-d]-dithienothiophene (**5c**).* Yellow oil, isolated yield 24% (119 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=0.84–0.90 (m, 6H, CH_3), 1.25–1.49 (m, 24H, CH_2), 1.68–1.73 (m, 4H, CH_2), 2.80 (t, J=7.8 Hz, 2H, CH_2), 3.03 (t, J=7.8 Hz, 2H, CH_2), 7.25–7.40 (m, 2H, CH), 7.76–7.78 (m, 1H, CH), 8.12–8.15 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=14.12 (2 CH_3), 22.67 (2 CH_2), 22.69 (2 CH_2), 29.03 (1 CH_2), 29.09 (1 CH_2), 29.30 (1 CH_2), 29.35 (1 CH_2), 29.36 (1 CH_2), 29.45 (1 CH_2), 29.55 (1 CH_2), 29.59 (1 CH_2), 31.70 (1 CH_2), 31.87 (1 CH_2), 31.90 (1 CH_2), 31.94 (1 CH_2), 122.62 (1 CH), 123.23 (1 CH), 123.29 (1 CH), 124.33 (1 CH), 130.55 (1 quat. C), 132.63 (1 quat. C), 133.68 (1 quat. C), 134.70 (1 quat. C), 139.50 (1 quat. C), 139.79 (1 quat. C), 141.50 (1 quat. C), 143.02 (1 quat. C). HRMS calcd for $C_{30}H_{42}S_3$ $[M+H]^+$: 498.2449, found 498.2447.

*4.4.4. 2,3-Di(thiophen-2-yl)benzo[2,3-b:3′,2′-d]-dithienothiophene (**5d**).* Yellow solid, isolated yield 66% (269 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=6.13 (d, J=7.5 Hz, 1H, CH), 6.92–7.32 (m, 7H, CH), 7.62–7.74 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=122.43 (1 quat. C), 122.68 (1 CH), 123.03 (1 CH), 123.61 (1 CH), 124.42 (1 CH), 125.94 (1 CH), 126.43 (1 CH), 126.75 (1 CH), 127.79 (1 CH), 128.12 (1 CH), 130.64 (1 CH), 132.18 (1 quat. C), 133.60 (1 quat. C), 135.20 (1 quat. C), 135.89 (1 quat. C), 136.22 (1 quat. C), 138.52 (1 quat. C), 140.07 (1 quat. C), 141.33 (1 quat. C), 142.77 (1 quat. C). HRMS calcd for $C_{20}H_{10}S_5$ $[M+H]^+$: 410.9459, found 410.9454.

*4.4.5. 2,3-Bis(5-methylthiophen-2-yl)benzo[2,3-b:3′,2′-d]-dithienothiophene (**5e**).* White solid, isolated yield 71% (310 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=2.39 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 6.30–7.22 (m, 8H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=15.28 (1 CH_3), 15.63 (1 CH_3), 122.12 (1 quat. C), 122.59 (1 CH), 123.27 (1 CH), 123.48 (1 CH), 124.25 (1 CH), 125.02 (1 CH), 125.73 (1 CH), 125.75 (1 CH), 130.47 (2 CH), 132.23 (1 quat. C), 133.64 (1 quat. C), 133.69 (1 quat. C), 134.48 (1 quat. C), 138.90 (1 quat. C), 139.80 (1 quat. C), 141.09 (1 quat. C), 141.39 (1 quat. C), 142.58 (1 quat. C), 142.74 (1 quat. C), 144.26(1 quat. C). HRMS calcd for $C_{22}H_{14}S_5$[M+H]$^+$: 438.9772, found 438.9763.

*4.4.6. 2,3-Bis(4-methoxyphenyl)benzo[2,3-b:3′,2′-d]-dithienothiophene (**5f**).* Yellow solid, isolated yield 74% (339 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=3.75 (s, 3H, CH_3), 3.89 (s, 3H, CH_3), 6.15 (d, J=8.1 Hz, 1H, CH), 6.75 (d, J=8.7 Hz, 2H, CH), 6.84–6.88 (m, 3H, CH), 7.13–7.19 (m, 3H, CH), 7.32 (d, J=8.4 Hz, 2H, CH), 7.71 (d, J=8.1 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=55.14 (1 CH_3), 55.38 (1 CH_3), 113.68 (2 CH), 114.05 (2 CH), 122.63 (1 CH), 123.29 (1 CH), 123.54 (1 CH), 124.04 (1 CH), 126.91 (1 quat. C), 129.24 (1 quat. C), 130.08 (1 quat. C), 130.25 (2 CH), 130.51 (1 quat. C), 132.21 (2 CH), 133.79 (1 quat. C), 135.47 (1 quat. C), 139.60 (1 quat. C), 141.01 (1 quat. C), 141.47 (1 quat. C), 142.79 (1 quat. C), 158.79 (1 quat. C), 159.46 (1 quat. C). HRMS calcd for $C_{26}H_{18}O_2S_3$ $[M+H]^+$: 459.0542, found 459.0548.

*4.4.7. 2,3-Bis(3-chlorophenyl)benzo[2,3-b:3′,2′-d]-dithienothiophene (**5g**).* Yellow solid, isolated yield 75% (350 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=6.94–7.62 (m, 12H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=122.84 (1 CH), 123.06 (1 CH), 123.61 (1 CH), 124.28 (1 CH), 127.26 (1 CH), 127.77 (1 CH), 128.58 (1 CH), 129.11 (1 CH), 129.31 (1 CH), 129.63 (1 CH), 130.05 (1 CH), 130.46 (2 quat. C), 131.01 (1 quat. C), 131.98 (1 quat. C), 133.30 (1 quat. C), 134.26 (1 quat. C), 134.72 (1 quat. C), 135.63 (1 quat. C), 137.14 (1 quat. C), 138.47 (1 quat. C),140.18 (1 quat. C), 140.32 (1 quat. C), 142.82 (1 quat. C). HRMS calcd for $C_{24}H_{12}Cl_2S_3$ $[M+H]^+$: 466.9556, found 466.9556.

*4.4.8. 2,3-Bis(5-methylthiophen-2-yl)benzo[2,3-b]-thieno-[3′,2′-d]-seleno-selenophene (**5h**).* White solid (mp 218.2–219.5 °C, decomposed), isolated yield 68% (344 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=6.88–7.72 (m, 10H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=122.30 (1 CH), 123.13 (1 CH), 123.51 (1 CH), 123.97 (1 CH), 126.58 (1 CH), 126.74 (1 CH), 126.76 (1 CH), 127.81 (1 CH), 128.16 (1 CH), 130.87 (1 CH), 133.54 (2 quat. C), 133.78 (1 quat. C), 136.97 (1 quat. C), 137.96 (1 quat. C), 137.97 (1 quat. C), 140.51 (1 quat. C), 143.48(1 quat. C), 143.83 (1 quat. C), 14.38 (1 quat. C). HRMS calcd for $C_{20}H_{10}S_3Se_2$ $[M+H]^+$: 506.8348, found 506.8354.

*4.4.9. 2,3-Bis(4-hexylphenyl)benzo[2,3-b]-thieno-[3′,2′-d]-seleno-selenophene (**5i**).* Yellow solid (mp 152.4–153.8 °C), isolated yield 72% (477 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=0.83–0.93 (m, 6H, CH_3), 1.23–1.69 (m, 16H, CH_2), 2.49 (t, J=7.5 Hz, 2H, CH_2), 2.67 (t, J=7.5 Hz, 2H, CH_2), 5.77 (d, J=6 Hz, 1H, CH), 6.71 (t, J=7.5 Hz, 1H, CH), 6.94–7.27 (m, 9H, CH), 7.66 (d, J=6 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ=14.09 (1 CH_3), 14.18 (1 CH_3), 22.59 (1 CH_2), 22.70 (1 CH_2), 28.90 (1 CH_2), 29.00 (1 CH_2), 31.14 (1 CH_2), 31.67 (1 CH_2), 31.81 (1 CH_2), 31.94 (1 CH_2), 35.56 (1 CH_2), 35.85 (1 CH_2),122.16 (1 CH), 122.82 (1 CH), 123.43 (1 CH), 124.20 (1 CH), 128.12 (2 CH), 128.84 (2 CH), 129.15 (2 CH), 131.08 (2 CH), 133.51 (1 quart. C), 133.80 (1 quart. C), 134.45 (1 quart. C), 135.32 (1 quart. C), 135.59(1 quart. C), 137.30 (1 quart. C), 140.02 (1 quart. C), 141.99 (1 quart. C), 142.83 (1 quart. C), 143.98 (1

quart. C), 144.22 (1 quart. C) 147.39 (1 quart. C). HRMS calcd for $C_{36}H_{38}SSe_2$ $[M+H]^+$: 663.1109, found 663.1103.

4.5. Preparation of compound 6

To a solution of **5e** (88 mg, 0.1 mmol) in 150 mL of dry dichloromethane was added a solution of $FeCl_3$ (98 mg, 0.6 mmol) in CH_3NO_2 (1 mL) at 0 °C. After 15 min, 30 mL of anhydride methanol was added to quench the reaction. The mixture was washed by brine, saturated aqueous NH_4Cl, and then dried over Na_2SO_4. After removal of the solvents under reduced pressure, the residue was recrystallized by CH_2Cl_2 to give **6** as a white solid.

*4.5.1. Compound **6**.* White solid (mp 210.0–211.2 °C, decomposed), isolated yield 87% (76 mg); UV–vis (CH_2Cl_2): λ_{max}=291, 324 nm. HRMS calcd for $C_{22}H_{14}S_5[M+H]^+$: 436.9615, found 436.9617. Anal. calcd for $C_{22}H_{14}S_5$: C, 60.51; H, 2.77. Found C, 60.47; H, 2.78.

Acknowledgements

The authors thank Prof. Jian Pei and Mr. Yan Zhou at Peking University for discussion and support on experiments. This work was supported by the Natural Science Foundation of China and the Major State Basic Research Development Program (2011CB808705).

Supplementary data

Supplementary data (experimental procedures, X-ray single-crystal structural data for **2a** and **5b**, characterization data for all new compounds, and copies of NMR spectra). Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.01.088.

References and notes

1. (a) Wudl, F.; Haddon, R. C.; Zellers, E. T.; Bramwell, F. B. *J. Org. Chem.* **1979**, *44*, 2491–2493; (b) Laquindanum, G. L.; Katz, H. E.; Lovinger, A. J.; Dodabalapur, A. *Adv. Mater.* **1997**, *9*, 36–39; (c) Mazzeo, M.; Vitale, V.; Sala, F. D.; Pisignano, D.; Anni, M.; Barbarella, G.; Favaretto, L.; Zanelli, A.; Cingolani, R.; Gigli, G. *Adv. Mater.* **2003**, *15*, 2060–2063; (d) Ebata, H.; Izawa, T.; Miyazaki, E.; Takimiya, K.; Ikeda, M.; Kuwabara, H.; Yui, T. *J. Am. Chem. Soc.* **2007**, *129*, 15732–15733; (e) Gao, J.; Li, R.; Li, L.; Meng, Q.; Jiang, H.; Li, H.; Hu, W. *Adv. Mater.* **2007**, *19*, 3008–3011; (f) Tan, L.; Zhang, L.; Jiang, X.; Yang, X.; Wang, L.; Wang, Z.; Li, L.; Hu, W.; Shuai, Z.; Li, L.; Zhu, D. *Adv. Funct. Mater.* **2009**, *19*, 272–276; (g) Fukazawa, A.; Yamaguchi, S. *Chem. Asian J.* **2009**, *4*, 1386–1400; (h) Shinamura, S.; Osaka, I.; Miyazaki, E.; Takimiya, K. *Heterocycles* **2011**, *83*, 1187–1204.
2. (a) Sashida, H.; Sadamori, K.; Tsuchiya, T. *Synth. Commun.* **1998**, *28*, 713–727 For recent benzothiophene synthesis, see: (b) Li, C.; Zhang, X.; Fang, R.; Zhong, P.; Li, J. H. *J. Org. Chem.* **2010**, *75*, 7037–7040; (c) Larock, R. C.; Mehta, S. *J. Org. Chem.* **2010**, *75*, 1652–1658; (d) Sanz, R.; Guilarte, V.; Hernando, E.; Sanjuan, A. M. *J. Org. Chem.* **2010**, *75*, 7443–7446; (e) Huang, H.; Li, J.; Zhao, W.; Mei, Y.; Duan, Z. *Org. Biomol. Chem.* **2011**, *9*, 5036–5038; (f) Shinamura, S.; Osaka, I.; Miyazaki, E.; Nakao, A.; Yamagishi, M.; Takeya, J.; Takimiya, K. *J. Am. Chem. Soc.* **2011**, *133*, 5024–5035; (g) Huang, H.; Li, J.; Lescop, C.; Duan, Z. *Org. Lett.* **2011**, *13*, 5252–5255.
3. (a) Okamoto, T.; Kudoh, K.; Wakamiya, A.; Yamaguchi, S. *Org. Lett.* **2005**, *7*, 5301–5304; (b) Mouri, K.; Wakamiya, A.; Yamada, H.; Kajiwara, T.; Yamaguchi, S. *Org. Lett.* **2007**, *9*, 93–96.
4. (a) Ghaisas, V. V.; Tilak, B. D. *Proc. Ind. Acad. Sci.* **1954**, *39A*, 14–19; (b) Fuller, L. S.; Iddon, B.; Smith, K. A. *J. Chem. Soc., Perkin Trans. 1* **1997**, *22*, 3465–3470; (c) Yamamoto, T.; Takimiya, K. *J. Am. Chem. Soc.* **2007**, *129*, 2224–2225; (d) Gao, P.; Beckmann, D.; Tsao, H. N.; Feng, X.; Enkelmann, V.; Pisula, W.; Müllen, K. *Chem. Commun.* **2008**, 1548–1550; (e) Henssler, J. T.; Matzger, A. J. *Org. Lett.* **2009**, *11*, 3144–3147; (f) Gao, P.; Beckmann, D.; Tsao, H. N.; Feng, X.; Enkelmann, V.; Baumgarten, M.; Pisula, W.; Müllen, K. *Adv. Mater.* **2009**, *21*, 213–216; (g) Kienle, M.; Unsinn, A.; Knochel, P. *Angew. Chem., Int. Ed.* **2010**, *49*, 4751–4754; (h) Saito, M.; Osaka, I.; Miyazaki, E.; Takimiya, K.; Kuwabara, H.; Ikeda, M. *Tetrahedron Lett.* **2011**, *52*, 285–288.
5. (a) Pandya, L. J.; Tilak, B. D. *Chem. Ind.* **1958**, 981–982; (b) Jong, F.; Janssen, M. J. *J. Org. Chem.* **1971**, *36*, 1645–1648.
6. (a) Rajca, A.; Wang, H.; Pink, M.; Rajca, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4481–4483; (b) Rajca, A.; Miyasaka, M.; Pink, M.; Wang, H.; Rajca, S. *J. Am. Chem. Soc.* **2004**, *126*, 15211–15222; (c) Miyasaka, M.; Rajca, A.; Pink, M.; Rajca, S. *J. Am. Chem. Soc.* **2005**, *127*, 13806–13807; (d) Miyasaka, M.; Pink, M.; Rajca, S.; Rajca, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 5954–5957.
7. (a) Iyoda, M.; Miura, M.; Sasaki, S.; Kabir, S. M. H.; Kuwatani, Y.; Yoshida, M. *Tetrahedron Lett.* **1997**, *38*, 4581–4582; (b) Kabir, S. M. H.; Miura, M.; Sasaki, S.; Harada, G.; Kuwatani, Y.; Yoshida, M.; Iyoda, M. *Heterocycles* **2000**, *52*, 761–774; (c) Iyoda, M.; Nakamura, N.; Todaka, M.; Ohtsu, S.; Hara, K.; Kuwatani, Y.; Yoshida, M.; Matsuyama, H.; Sugita, M.; Tachibana, H.; Inoue, H. *Tetrahedron Lett.* **2000**, *41*, 7059–7064; (d) Nenajdenko, V. G.; Gribkov, D. V.; Sumerin, V. V.; Balenkova, E. S. *Synthesis* **2003**, 124–128; (e) Sotgiu, G.; Favaretto, L.; Barbarella, G.; Antolini, L.; Gigli, G.; Mazzeo, M.; Bongini, A. *Tetrahedron* **2003**, *59*, 5083–5090; (f) Xu, L.; Wang, Z.; Xu, K.; Shi, J.; Wang, H. *Lett. Org. Chem.* **2009**, *6*, 474–477.
8. (a) McMurry, J. E.; Fleming, M. P. *J. Org. Chem.* **1976**, *41*, 896–897; (b) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3255–3266; (c) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405–411; (d) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513–1524; (e) McMurry, J. E.; Lectka, T.; Rico, J. G. *J. Org. Chem.* **1989**, *54*, 3748–3749; (f) Fürstner, A.; Bogdanovic, B. *Angew. Chem., Int. Ed.* **1996**, *35*, 2442–2469; (g) Dai, W.; Mak, W. L. *Tetrahedron Lett.* **2000**, *41*, 10277–10280.
9. (a) McMurry, J. E.; Miller, D. D. *J. Am. Chem. Soc.* **1983**, *105*, 1660–1661; (b) Banerji, A.; Nayak, S. K. *J. Chem. Soc., Chem. Commun.* **1990**, 150–151; (c) Fürstner, A.; Hupperts, A.; Ptock, A.; Janssen, E. *J. Org. Chem.* **1994**, *59*, 5215–5229.
10. (a) Pei, J.; Zhang, W.; Mao, J.; Zhou, X. *Tetrahedron Lett.* **2006**, *47*, 1551–1554; (b) Zhou, Y.; Liu, W.-J.; Zhang, W.; Cao, X.-Y.; Zhou, Q.-F.; Ma, Y.; Pei, J. *J. Org. Chem.* **2006**, *71*, 6822–6828; (c) Zhou, Y.; Liu, W.-J.; Ma, Y.; Wang, H.; Qi, L.; Cao, Y.; Wang, J.; Pei, J. *J. Am. Chem. Soc.* **2007**, *129*, 12386–12387.
11. Wang, Z.; Geng, W.; Wang, H.; Zhang, S.; Zhang, W.-X.; Xi, Z. *Tetrahedron Lett.* **2011**, *52*, 6997–6999.
12. For reviews, see: (a) Xi, Z. *Acc. Chem. Res.* **2010**, *43*, 1342–1351; (b) Wu, W.; Gu, D.; Wang, S.; Ning, Y.; Mao, G. *Chin. Sci. Bull.* **2011**, *56*, 1753–1769; (c) Ananikov, V. P.; Hazipov, O. V.; Beletskaya, I. P. *Chem. Asian J.* **2011**, *6*, 306–323; (d) Wang, Q.; Zhang, W.; Lin, C.; Xi, Z. *Chin. Sci. Bull.* **2010**, *55*, 2915–2923 See also: (e) Wang, Z.; Wang, Y.; Zhang, W.-X.; Hou, Z.; Xi, Z. *J. Am. Chem. Soc.* **2009**, *131*, 15108–15109; (f) Wang, Y.; Zhang, W.-X.; Wang, Z.; Xi, Z. *Angew. Chem., Int. Ed.* **2011**, *50*, 8122–8126.