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The preparation of substituted bithiophenyl aldehydes via the ring opening of dithieno[2,3-*b*:3′,2′-*d*]thiophene in the presence of *n*-BuLi

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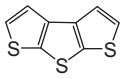
ABSTRACT

In the presence of *n*-BuLi in THF at low temperature, the phenomena of ring opening of symmetric substituted dithieno[2,3-*b*:3′,2′-*d*]thiophenes were observed. After quenching the organolithium intermediates with dry DMF, a series of substituted novel bithiophenyl aldehydes were prepared in good to excellent yields. The mechanism shows the key step for the ring opening of dithieno[2,3-*b*:3′,2′-*d*]thiophene is the nucleophilic attack of butyl anion onto the sulfur atom of the central ring. Total ten samples of symmetric substituted dithieno[2,3-*b*:3′,2′-*d*]thiophenes and their ring-opened products, the substituted bithiophenyl aldehydes were characterized by ^{1}H NMR, ^{13}C NMR, and HRMS. Two ring-opened products were confirmed by X-ray single crystal analysis.

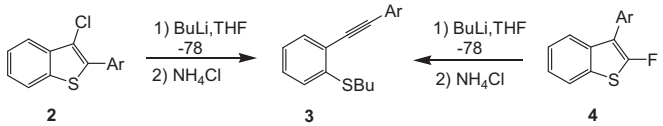
1. Introduction

In recent years, isomeric dithienothiophenes have been applied widely in the fields of organic semiconductors,[1] photosensitive materials,[2] and organic field effect transistors (OFETs).[3] As one of six isomeric dithienophenes, dithieno[2,3-*b*:3′,2′-*d*]thiophene (**1a**) has received attention in its preparation[4] and higher homologs syntheses of carbon–sulfur (C_2S) helicene with **1a** as building blocks in recent years.[5,6]



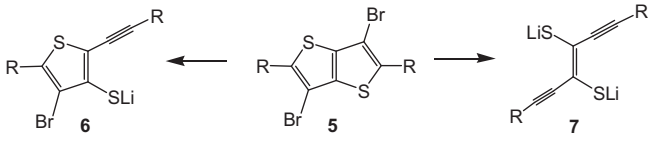
1a

The chemical stability is one of most important properties for fused oligothiophenes. It has been reported that ring-opening process could be happened on both α position[7] and β position[8] of halogen substituted benzo[*b*]thiophene rings. The ring-opening process could generate the derivatives of 1-butylsulfanyl-2-ethynylbenzene (**3**) in the presence of *n*-BuLi in THF at −78 °C (Eq. 1).



2 **3** **4**

Iddon[9] et al. reported the tandem ring-opening reactions of substituted thienothiophenes (**5**) with one or two equivalents of butyllithium in THF at −78 °C to form the derivatives of ethynylthiophene (**6**) or enediyne (**7**) (Eq. 2).



The ring-opening of highly fused thiophenes, such as dithienothiophenes has not been reported up to now. However, the chemical stability of dithienothiophenes is important in organic chemistry and material science. In our previous work,[10] we made the efficient formylation and diformylation of dithieno[3,2-*b*:2′,3′-*d*]thiophene, an isomer of **1a** in the presence of *n*-BuLi in THF at −78 °C and quenching with dry DMF subsequently. At meanwhile, none of ring-opening products were observed. However, we found the ring-opening reaction happened to **1a** at same conditions. In this paper, we try to report the unexpected ring-opening reaction happened to **1a** and its symmetric substituted compounds in the presence of *n*-BuLi in THF at −78 °C. After the organolithium intermediates were quenched with dry DMF, a series of novel substituted bithiophenyl aldehydes were obtained.

2. Results and discussion

The preparation of substituted bithiophenyl aldehydes via ring-opening reaction of **1a** with 1.1 and 2.2 equiv of *n*-BuLi.

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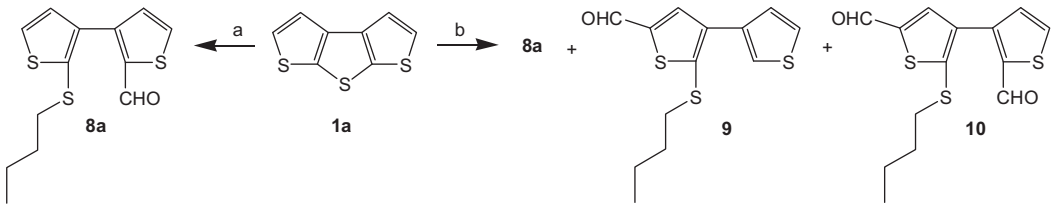


Scheme 1. The synthetic routes to **8a**, **9**, and **10**. Reagents and conditions: (a) (i)1.1 equiv *n*-BuLi, THF, −78 °C/2 h (ii) 2 equiv DMF. **8a**, 90%; (b) (i) 2.1 equiv *n*-BuLi, THF, −78 °C/2 h, (ii) 3 equiv DMF, **8a**, 23%; **9**, 13%; **10**, 55%.

2.1. Process of preparation

As we known that *n*-BuLi could be used as S-butylation[7] or strong base[11] agent in organic synthesis. One part of our previous work was to make the efficient formylation and diformylation of **1a** by using LDA to treat with **1a**, and then quenching with dry DMF.[10] However, with 1.1 equiv or 2.2 equiv *n*-BuLi used as base to instead of LDA, none of the products of formylation or diformylation of **1a** were obtained. Instead, we obtained the ring-opened products, 2′-butylsulfanyl-[3,3′]bithiophenyl-2-carbaldehyde (**8a**), 2-butylsulfanyl-[3,3′]bithiophenyl-5-carbaldehyde (**9**), and 2′-butylsulfanyl-[3,3′]bithiophenyl-2,5′-dicarbaldehyde (**10**) in reasonable yields (Scheme 1).

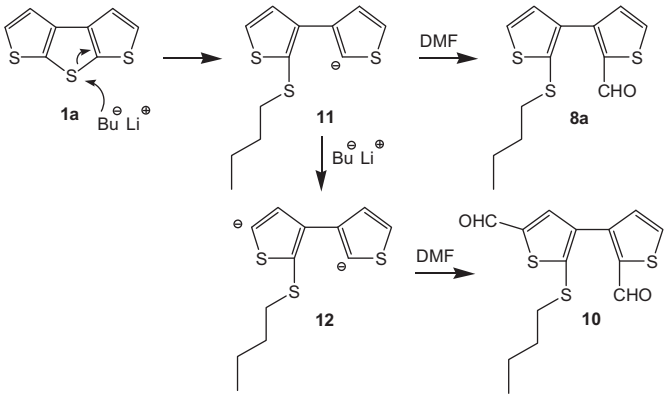
2.2. Reaction conditions

The reaction conditions and the relative distribution of products are shown in Table 1. It is clear that temperature is one of the factors affecting the selection of the reaction. If 1.1 equiv of *n*-BuLi is used at −78 °C for 2 h, only **8a** is obtained in 90% yield after quenching with DMF (Entry 1). If the reaction temperature is kept up to 0 °C for 0.5 h after addition of *n*-BuLi, and then changed back to −78 °C, both **8a** and **9** are afforded in 78% and 12% yield, respectively after quenching with DMF (Entry 3), and **8a** is the main product. It is concluded that the precursor of **9** might be formed easier from the precursor of **8a** at 0 °C than −78 °C.

When 2.2 equiv of *n*-BuLi used in the reaction at −78 °C, a mixture of **8a**, **9** and **10** is obtained at same time in the yields of 23%, 13%, and 55%, respectively (Entry 2, Table 1), and **10** is the main product. Similar to entry 3, high temperature (0 °C) makes different distribution of products (Entry 4). Only **9** and **10** are given in yields of 13% and 77%, respectively. However, none of **8a** is observed at same time. Therefore, it is also concluded that higher temperature is helpful to generate **10**. All three ring-opening products are regarded as alkyl and formyl thiophene derivatives, but the synthetic method is different from what reported.[12]

2.3. Possible mechanisms

Based on the results in Table 1, the possible mechanisms for generation of **8a** and **10** are proposed in Scheme 2. Different from the case of deprotonation at α position of **1a** with LDA,[10] the butyl anion from *n*-BuLi attacks on the sulfur atom of central ring directly for nucleophilic substitution. After the central ring opened, carbanion **11** is generated, and the charge is transferred to the right thiophene ring (Scheme 2). Carbanion **11** should be stable at −78 °C, which generates **8a** when quenched with DMF. Carbanion **11** could also be changed into dicarbanion **12** when another equivalent of *n*-BuLi is employed. When second deprotonation happened at α position on left thiophene ring of **11** (Scheme 2), dicarbanion **12** is generated, which gives **10** after quenching with DMF. Higher temperature (such as 0 °C) is helpful in the process of making **12** from **11** (Entry 4, Table 1).



Scheme 2. The possible mechanism for generating **8a** and **10**.

The possible mechanism for making **9** could be regarded as an intermolecular anion exchange process. After the charge equilibrium between carbanion **11** and **13** formed,[13] the side product, **9** is obtained when the reaction mixture was quenched with dry DMF.

2.4. Crystal structure of 2-butylsulfanyl-[3,3′]bithiophenyl-5-carbaldehyde (9)

The structure of **9** was confirmed by X-ray crystal analysis[14] (Fig. 1). The two linked thiophene rings are coplanar with the torsion angle (C5–C4–C7–C8) of 8.11°. The dihedral angle between the two thiophenes is 7.964°. The butylsulfanyl groups is also coplanar with the linked thiophene ring, the dihedral angle between them is 1.656°. The torsion angle (S1–C5–S3–C10) is 1.88°. The crystal packing is in the order of layer by layer with a distance of 2.703 Å (O–H10A). In each layer, there are short contacts including hydrogen bonding among the molecules. The distances of O1···H3, O1···H9, and H1···H8 are 2.569, 2.710 and 2.243 Å, respectively.

Table 1
The conditions of the ring-opening reaction and the distribution of products

Entry	**1a** (g)	*n*-BuLi (equiv)	Temperature (°C)	DMF (equiv)	**8a**[a] (g/%)	**9**[a] (g/%)	**10**[a] (g/%)
1	0.26	1.1	−78	2.0	0.33/90%	—	—
2	0.30	2.2	−78	3.0	0.10/23%	0.056/13%	0.26/55%
3	0.30	1.1	−78 to 0	2.0	0.34/78%	0.052/12%	—
4	0.30	2.2	−78 to 0	3.0	—	0.057/13%	0.37/77%

[a] isolated yields.

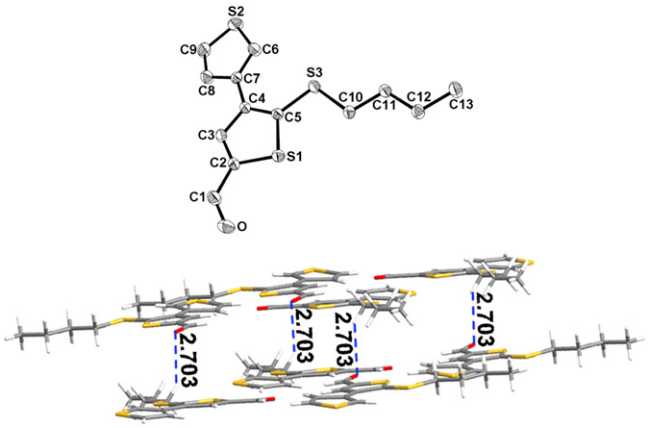


Figure 1. Crystallographic structure of **9** (top) and its crystal packing (bottom).

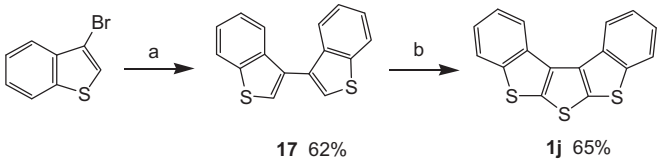
The preparation of substituted thiophene aldehyes via the ring opening of symmetric 2,5-disubstituted dithieno[2,3-*b*:3′,2′-*d*]thiophene in the presence of 1.1 equiv *n*-BuLi.

2.5. The preparation of symmetric 2,5-disubstitued dithieno[2,3-*b*:3′,2′-*d*]thiophenes

In order to have a further study on the ring-opening phenomenon of **1a**, a series of symmetric 2,5-disubstitued dithieno[2,3-*b*:3′,2′-*d*]thiophene were synthesized (Scheme 4). **1c**[9] and **1d**[4c] were obtained according to the methods from the literatures.

With **1a** as starting material, 2,5-dimethyldithieno[2,3-*b*:3′,2′-*d*]thiophene (**1b**) was obtained in 85% yield by dilithiation of **1a** with LDA (2.2 equiv) first and then quenching with iodomethane. 2,5-Dibromodithieno[2,3-*b*:3′,2′-*d*]thiophene (**14**) and dithieno[2,3-*b*:3′,2′-*d*]thiophene-2,5-dicarbaldehyde (**15**) were obtained according to our previous work.[10] Oxidation of **15** with $KMnO_4$ in 1,4-dioxane to obtained dithieno[2,3-*b*:3′,2′-*d*]thiophene-2,5-dicarboxylic acid (**16**) in 86% yield. Esterification of **16** in dry ethanol with concentrated H_2SO_4 as catalyst could obtain dithieno[2,3-*b*:3′,2′-*d*] thiophene-2,5-dicarboxylic acid diethyl ester (**1e**) in 83% yield. Suzuki coupling reactions were employed to generate 2,5-diaryldithieno[2,3-*b*:3′,2′-*d*]thiophene (**1f**–**i**) by using **14** with relative boric acids in yield range of 62–66% (Scheme 3).

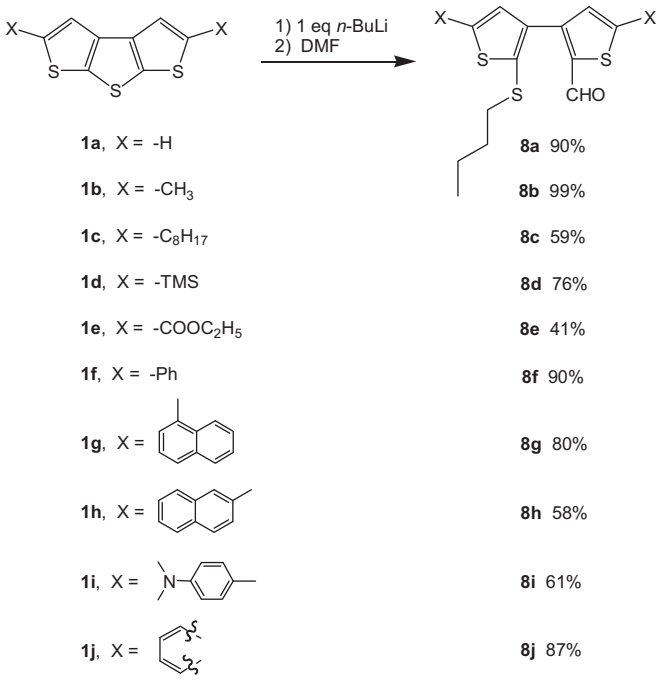
The synthesis of bis(benzo[4,5]thieno)[2,3-*b*:3′,2′-*d*]thiophene (**1j**) was different from others. Bromination of benzo[*b*]thiophene to generate 3-bromobenzo[*b*]thiophene was made according to the method of literature.[15] After Br/Li exchange and treatment of $CuCl_2$, the coupling product, [3,3′]bi[benzo[*b*]thiophenyl] (**17**) [15b] was obtained in 62% yield. With *n*-BuLi as base to deproton **17** and $(PhSO_2)_2S$ used for annelation, **1j** was obtained in 65% yield (Scheme 4).



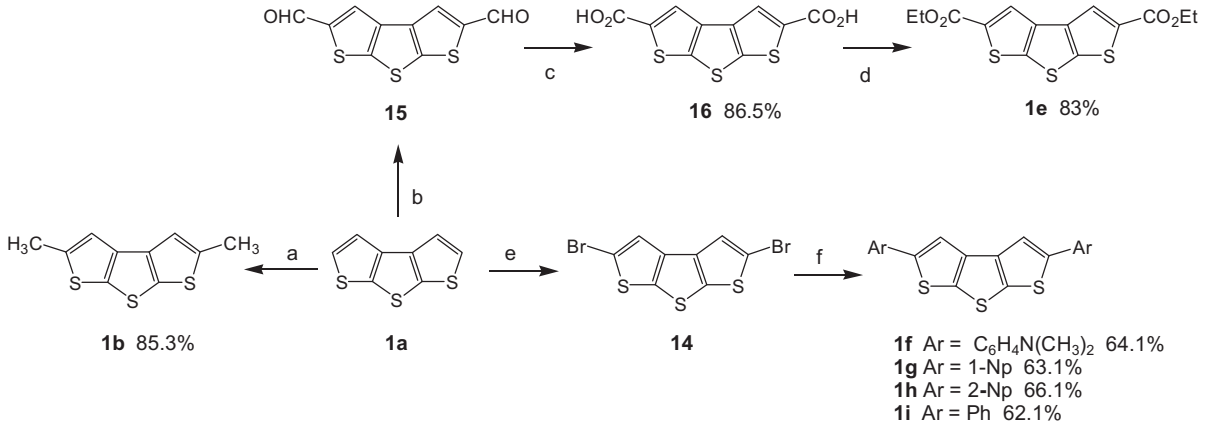
Scheme 4. The synthetic route to **1j**. Reagents and conditions: (a) (i) *n*-BuLi (1.05 equiv), Et_2O, −78 °C; (ii) dry $CuCl_2$; (b) (i) *n*-BuLi (3.2 equiv), Et_2O, −78 °C, then reflux 2 h; (ii) $(PhSO_2)_2S$ (1.0 equiv), −78 °C to rt overnight.

2.6. The preparation of substituted thiophene aldehyes via the ring opening of symmetric 2,5-disubstitued dithieno[2,3-*b*:3′,2′-*d*]thiophenes

Using same conditions for making **8a**, a series of substituted bithiophenyl aldehyes (**8b**–**j**) were obtained via the ring opening of symmetric 2,5-disubstitued dithieno[2,3-*b*:3′,2′-*d*]thiophenes (**1b**–**j**)



Scheme 5. The substituted thiophene aldehyes (**8a**–**j**) were obtained via the ring opening of symmetric 2,5-disustituted dithieno[2,3-*b*:3′,2′-*d*]thiophenes (**1a**–**j**).



Scheme 3. The synthetic route to substituted dithieno[2,3-*b*:3′,2′-*d*]thiophenes. Reagents and conditions: (a) (i) LDA (2.2 equiv), Et_2O, 0 °C; (ii) CH_3I (3.0 equiv), −78 °C; (b) see Ref. 11; (c) $KMnO_4$ (15 equiv), 1,4-dioxane; (d) Anhyd EtOH (excess), concentrated H_2SO_4, reflux; (e) see Ref. 11; (f) $ArB(OH)_2$ (2.2 equiv), $Pd(PPh_3)_4$ (6% mol), K_2CO_3 aq (10 equiv, 2 M), THF, reflux.

in the presence of *n*-BuLi at −78 °C and then quenching with excess dry DMF (Scheme 5). The ring-opened products are type of novel bithiophenyl aldehydes with butylsulfanyl group.

As shown in Scheme 5, with different substituted groups, including alkyl groups, aryl groups, and electron-withdrawing group, all of the reactions proceeded smoothly to give the corresponding substituted thiophene aldehyes (**8a**–**j**) with yields ranging from 41–99%. Obvious low yield (41%) of making **8e** may due to the side reaction happened by the two ester groups in **1e** with *n*-BuLi.

2.7. The crystal structure of 2′-butylsulfanyl-[3,3′]bi[benzo[*b*]thiophenyl]-2-carbaldehyde (8j)

The structure of **8j** was confirmed by X-ray crystal analysis (Fig. 2).[16] The two moieties of benzo[*b*] thiophenyl rings are linked together in the molecule with the torsion angle (C6–C7–C10–C11) of 70.97° and a dihedral angle of 73.14°. There are short contacts of hydrogen bonding are found in the crystal packing. The distances of S···H and O···H are 2.869 Å (S2–H9A) and 2.511 Å (O1–H12), respectively. In the crystal packing, the neighbored benzo[*b*]thiophenyls with aldehyde groups are parallel with distances of 3.635 Å (C8–C8) and 3.895 Å (C8–S1). At the meanwhile, the neighbored benzo[*b*]thiophenyls with butylsulfanyl groups are also parallel with 3.889 Å (S2–S2) and 3.868 Å (S2–C17).

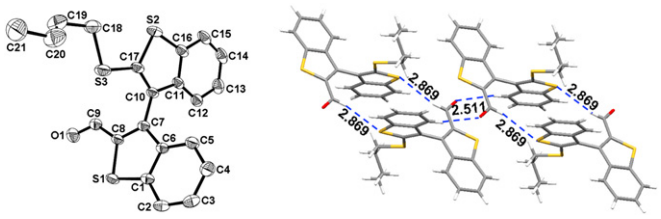


Figure 2. Crystallographic structure of **8j** (left) and its crystal packing (right).

3. Conclusions

In summary, we have synthesized a series of symmetric substituted dithieno[2,3-*b*:3′,2′-*d*]thiophene (**1a**–**j**) and prepared the corresponding novel substituted bithiophenyl aldehydes (**8a**–**j**) in good to excellent yields via the ring-opening reactions of **1a**–**j** in the presence of *n*-BuLi at −78 °C in THF. The crystal structures of two ring-opened products showed interesting crystal packing with some short contacts including hydrogen bonding interactions, S···S interactions and π···π interactions. The ring-opening reactions of **1a**–**j** are important in theoretical understanding for the stability of dithienothiophenes. The symmetric substituted dithieno[2,3-*b*:3′,2′-*d*]thiophenes (**1a**–**j**) could be used in organic functional materials.[3,17] The substituted bithiophenyl aldehydes (**8a**–**j**) could be derived from their aldehyde groups and used as pharmaceutical and pesticide intermediates.

4. Experimental

4.1. General

Ether and tetrahydrofuran (THF) for use were freshly distilled from sodium/benzophenone prior to use. Bis(phenylsulfonyl)sulfide was obtained according to the literature method.[18] Concentration of *n*-BuLi (hexane) was determined by titration with *N*-pivaloyl-*o*-toluidine.[19] Column chromatography was carried out on silica gel (300–400 mesh). Analytical thin-layer chromatography was performed on glass plates of Silica Gel GF-254 with detection by UV. Standard techniques for synthesis under inert atmosphere, using gasbag and Schlenk glassware equipped with an 8 mm PTFE vacuum stop-cock, were employed. All starting materials and reagents were commercially available.

NMR spectra were obtained using chloroform-*d* ($CDCl_3$) as solvent. The chemical shift references were as follows: (^{1}H) $CDCl_3$, 7.26 ppm ($CHCl_3$); (^{13}C) $CDCl_3$, 77.00 ppm ($CDCl_3$); (^{1}H) DMSO-d_6, 2.50 ppm; (^{13}C) DMSO-d_6, 39.50 ppm; IR spectra were obtained using an FTIR instrument, equipped with an ATR sampling accessory. MS analysis was carried out at 70 eV, using a direct insertion technique or a GC insertion. HRMS spectra were recorded on a mass spectrometer equipped with TOF (EI^+). Melting point determination was taken on a Melt-Temp apparatus and was uncorrected.

The X-ray crystallographic analyses were performed using crystals of compounds **9** and **8j** with the size 0.24×0.14×0.05 mm and 0.18×0.12×0.09 mm, respectively. The intensity data were collected with the ω scan mode (207 K) on a diffractometer with CCD detector using Mo Kα radiation (λ=0.71073 Å). The data were corrected for Lorentz and polarization effects and absorption corrections were performed using SADABS program.[20] The crystal structures were solved using the SHELXTL program and refined using full matrix least squares.[21] The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons. Further details are in the deposited CIFs. Slow evaporation of solutions of **8j** and **9** in $CHCl_3/CH_3OH$ (1:1, 1:5 v/v) were employed, respectively for growing single crystals.

4.2. Synthesis of 2,5-dimethyldithieno[2,3-*b*:3′,2′-*d*]-thiophene (1b)

n-BuLi (2.5 M in hexane, 0.9 mL, 2.25 mmol, 2.2 equiv) was added dropwise to diisopropyl amine (0.33 mL, 2.34 mmol, 2.3 equiv) in dry ethyl ether (10 mL) at 0 °C. After keeping at 0 °C for 0.5 h, the prepared LDA solution was transferred into a solution of **1a** (0.20 g, 1.03 mmol) in dry Et_2O (40 mL) at −78 °C, then warmed slowly to 0 °C. After keeping at 0 °C for 2 h, the reaction mixture was cooled to −78 °C, CH_3I (0.2 mL, 3.09 mmol, 3.0 equiv) was added dropwise. The reaction mixture was kept at −78 °C for 1 h and then warmed slowly to ambient temperature overnight. After quenched with H_2O (30 mL), extracted with Et_2O (2×30 mL) and then washed with H_2O (30 mL). After drying over $MgSO_4$, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with petrol ether (60–90 °C) as eluent to yield **1b** (0.197 g, 85.3%) as a white solid. Mp: 150–151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=6.98 (s, 2H), 2.59 (s, 6H), ^{13}C NMR (100 MHz, $CDCl_3$): δ=142.29, 138.13, 135.29, 116.93, 16.37. IR (KBr): 2910, 2848 (C–H) cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{10}H_8S_3$ $[M]^+$: 223.9788, found: 223.9790.

4.3. Synthesis of dithieno[2,3-b:3′,2′-*d*]thiophene-2,5-dicarboxylic acid diethyl ester (1e)

*4.3.1. Synthesis of dithieno[2,3-b:3′,2′-d]thiophene-2,5-dicarboxylic acid (**16**).* A solution of $KMnO_4$ (1.40 g, 15 equiv) in water (30 mL) was added into a solution of dithieno[2,3-*b*:3′,2′-*d*]thiophene-2,5-dicarbaldehyde (**15**)[10] (150 mg, 0.59 mmol) in dioxane (70 mL). The reaction mixture was stirred at ambient temperature overnight. After the brown precipitate was filtered, the filtrate was treated with NaOH (5%) until pH=12, then extracted with ethyl ether (3×40 mL) and the water phase was acidified with HCl (2 M) until pH=1. The acidified water phase was extracted with ethyl ether (4×50 mL), washed with water (3×50 mL) and dried over $MgSO_4$. After removing the solvent in vacuo, a white powder of **16** (125 mg, 74.5%) was obtained. Mp >300 °C, ^{1}H NMR (400 MHz, DMSO-d_6): δ=13.30 (s, 2H), 8.25 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=163.06, 145.97, 137.48, 136.91, 124.97. IR (KBr): 2963, 2853, 2809 (C–H), 1673 (C=O) cm^{-1}.

*4.3.2. Synthesis of dithieno[2,3-b:3′,2′-d]thiophene-2,5-dicarboxylic acid diethyl ester (**1e**).* Compound **16** (167 mg, 0.59 mmol) and

H_2SO_4 (0.1 mL, 98%) was added to absolute EtOH (10 mL), the reaction mixture was refluxed for four days at 110 °C. After cooling to ambient temperature, H_2O (30 mL) was added, the reaction mixture was extracted with $CHCl_3$ (2×30 mL) and then washed with H_2O (2×30 mL). After drying over $MgSO_4$, the solvent was removed in vacuo. The residue was purified by column chromatography twice on silica gel with chloroform as eluent to yield **1e** (166 mg, 83%). Mp: 192–194 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.05 (s, 2H), 4.40 (q, J=7.2 Hz, 4H), 1.41 (t, J=7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=161.96, 145.51, 137.89, 136.56, 124.36, 61.57, 14.33. IR (KBr): 3096, 2980, 2928 (C–H), 1718 (C=O) cm^{-1}. HRMS (EI): m/z calcd for $C_{14}H_{12}O_4S_3$ [M]$^+$: 339.9898, found: 339.9901.

4.4. General procedure for the preparation of compounds 1f–i

*4.4.1. 2,5-Diphenyldithieno[2,3-b:3′,2′-d]thiophene (**1f**).* A mixture of 2,5-dibromodithieno[2,3-*b*:3′,2′-*d*]thiophene (**14**) (500 mg, 1.4 mmol), phenyl boronic acid (379.4 mg, 3.1 mmol, 2.2 equiv), tetrakis(triphenyl-phosphine)palladium (99 mg, 0.043 mmol, 6% equiv), and K_2CO_3 aq (7 mL, 2 M) in THF (60 mL) was refluxed and stirred under argon for 20 h. After cooling, the mixture was quenched with H_2O (50 mL), extracted with $CHCl_3$ (2×50 mL) and then washed with H_2O (50 mL). After drying over $MgSO_4$, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with petrol ether (60–90 °C) and chloroform (1:1, v/v) to yield **1f** as white solid (0.306 g, 62.1%). Mp: 207–208 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.65 (d, J=7.6 Hz, 4H), 7.60 (s, 2H), 7.43 (t, J=7.6 Hz, 4H), 7.33 (t, J=7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=147.01, 139.18, 137.68, 134.65, 129.03, 127.80, 125.79, 114.69. IR (KBr): 2953, 2923, 2847 (C–H) cm^{-1}. HRMS (EI): m/z calcd for $C_{20}H_{12}S_3$ [M]$^+$: 348.0101, found: 348.0104.

*4.4.2. 2,5-Dinaphthalen-1-yl-dithieno[2,3-b:3′,2′-d]thiophene (**1g**).* From the reaction on the 100 mg scale of **14**, 80.0 mg (63.1%) of **1g** was obtained as white solid. Mp: 162–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.38–8.31 (m, 2H), 7.96–7.89 (m, 4H), 7.67 (dd, J=7.2 Hz, 1.2 Hz, 2H), 7.51–7.58 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=144.26, 138.66, 138.33, 133.83, 132.31, 131.91, 128.86; 128.56, 128.37, 126.68, 126.16, 125.66, 125.21, 119.22. IR (KBr): 2958, 2926, 2854 (C–H) cm^{-1}. HRMS (EI): m/z calcd for $C_{28}H_{16}S_3$ [M]$^+$: 448.0414, found: 448.0417.

*4.4.3. 2,5-Dinaphthalen-2-yl-dithieno[2,3-b:3′,2′-d]thiophene (**1h**).* From the reaction on the 150 mg scale of **14**, 125.6 mg (66.1%) of **1h** was obtained as pale yellow solid. Mp: 243–245 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.08 (s, 2H), 7.92–7.87 (m, 4H), 7.85 (d, J=8.0 Hz, 2H), 7.80 (d, J=8.0 Hz, 2H), 7.75 (s, 2H), 7.50 (qn, J=8.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=147.13, 139.31, 137.92, 133.61, 132.86, 132.02, 128.75; 128.04, 127.76, 126.73, 126.17, 124.18, 124.04, 115.10. IR (KBr): 2955, 2922, 2851 (C–H) cm^{-1}. HRMS (EI): m/z calcd for $C_{28}H_{16}S_3$ [M]$^+$: 448.0414, found: 448.0418.

*4.4.4. 2,5-bis[4-(dimethylamino)phenyl]dithieno[2,3-b:3′,2′-d]thiophene (**1i**).* From the reaction on the 250 mg scale of **14**, 198.0 mg (64.1%) of **1i** was obtained as white pale gray solid. Mp: 270–272 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.52 (d, J=8.4 Hz, 4H), 7.41 (s, 2H), 6.77 (d, J=8.4 Hz, 4H), 3.00 (s, 12H) . IR (KBr): 2883, 2853, 2798 (C–H) cm^{-1}. HRMS (EI): m/z calcd for $C_{24}H_{22}N_2S_3$ [M]$^+$: 434.0945, found: 434.0949.

*4.4.5. Synthesis of bis(benzo[4,5]thieno)[2,3-b:3′,2′-d]thiophene (**1j**).*

*4.4.5.1. Synthesis of 3,3′-bibenzo[b]thiophene (**17**).* To a solution of 3-bromobenzo[*b*]thiophene (0.8853 g, 4.15 mmol) in dry ethyl ether (50 mL), *n*-BuLi (1.74 mL, 1.05 equiv) was added dropwise at −78 °C. After keeping at same time for 3 h, dry $CuCl_2$ (1.008 g, 1.8 equiv) was added. The reaction temperature was kept at −78 °C for 1 h, −50 °C for 3 h, and then warmed slowly to ambient temperature overnight. The reaction was quenched with water. After HCl (2 M, 40 mL) was added, the reaction mixture was extracted with ethyl ether (4×40 mL), and the organic phase was washed with saturated $NaHCO_3$ (50 mL), saturated NaCl (50 mL) and then dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel with petroleum ether (60–90 °C) as eluent and then recrystallization from hexane to yield **17** (343.2 mg, 62.0%). Mp: 80–82 °C (lit.[15b] 72 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.98–7.94 (m, 2H), 7.77–7.73 (m, 2H), 7.57 (s, 2H), 7.45–7.33 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=140.17, 138.55, 131.39, 124.72, 124.60, 124.29, 123.21, 122.82. IR (KBr): 3091, 3060, (C–H) cm^{-1}. MS (CI, 70 eV): m/z=265.94 [M$^+$].

*4.4.5.2. Synthesis of bis(benzo[4,5]thieno)[2,3-b:3′,2′-d]thiophene (**1j**).* To a solution of **17** (100.9 mg, 0.38 mmol) in dry Et_2O (35 mL), *n*-BuLi (2.34 M, 0.52 mL, 1.21 mmol, 3.2 equiv) was added dropwise at −78 °C, and then warmed to ambient temperature and refluxed for 2 h. After cooling to −78 °C again, $(PhSO_2)_2S$ (120 mg, 0.38 mmol, 1.0 equiv) was added, the reaction mixture was kept at −78 °C for 1 h, and then slowly warmed to −55 °C. After keeping at −55 °C for 2 h, slowly warmed to ambient temperature overnight. The reaction mixture was quenched with H_2O (50 mL), extracted with Et_2O (3×40 mL), washed with H_2O (50 mL), and finally dried over $MgSO_4$. After removing the solvent in vacuo, the residue was purified by column chromatography on silica gel with petroleum ether (60–90 °C) as eluent to yield **1j** as white solid (73 mg, 65%). Mp: 200–202 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.63 (d, J=8.0 Hz, 2H), 7.91 (d, J=8.4 Hz, 2H), 7.57 (td, J=7.6 Hz, 0.8 Hz, 2H), 7.42 (td, J=7.6 Hz, 0.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=143.11, 139.53, 134.52, 132.48, 124.68, 123.92, 123.44, 123.14. IR(KBr): 3110, 3051, 3030 (C–H) cm^{-1}. HRMS (EI): m/z calcd for $C_{16}H_8S_3$ [M]$^+$: 295.9788, found: 295.9790.

4.5. General procedure for the preparation of compounds 8a–j

*4.5.1. 2′-Butylsulfanyl-[3,3′]bithiophenyl-2-carbaldehyde (**8a**).* Compound **1a** (0.255 g, 1.30 mmol) was dissolved in dry THF (40 mL) and cooled to −78 °C under argon. *n*-BuLi (2.62 M in hexane, 0.55 mL, 1.44 mmol, 1.1 equiv) was added dropwise at −78 °C. After keeping at −78 °C for 2 h, DMF (0.20 mL, 2.60 mmol, 2.0 equiv) was added dropwise, then kept at −78 °C for 1 h, the reaction mixture was warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with H_2O (30 mL), extracted with $CHCl_3$ (2×30 mL) and then washed with H_2O (30 mL). After drying over $MgSO_4$, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with petrol ether (60–90 °C) and chloroform (1:1, v/v) as eluents to yield **8a** (0.33 g, yield: 90.0%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.78 (d, J=1.2 Hz, 1H), 7.74 (dd, J=5.2 Hz, 1.2 Hz, 1H), 7.41 (d, J=5.6 Hz, 1H), 7.23 (d, J=5.2 Hz, 1H), 7.10 (d, J=5.2 Hz, 1H), 2.67 (t, J=7.2 Hz, 2H), 1.42 (qn, J=7.2 Hz, 2H), 1.25 (sx, J=7.2 Hz, 2H), 0.80 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=183.82, 144.31, 139.05, 137.06, 133.98, 133.50, 130.93, 130.05, 127.66, 38.16, 31.02, 21.36, 13.47. IR (KBr): 2957, 2923, 2870 (C–H), 1661 (C=O) cm^{-1}. HRMS (ESI): m/z calcd for $C_{13}H_{15}OS_3$ [M+H]$^+$: 283.0285, found: 283.0282; $C_{13}H_{14}NaOS_3$ [M+Na]$^+$: 305.0104, found: 305.0096.

*4.5.2. 2′-Butylsulfanyl-5,5′-dimethyl-[3,3′]bithiophenyl-2-carbaldehyde (**8b**).* From the reaction on the 103 mg scale of **1b**, 140.2 mg (99.0%) of **8b** was obtained yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ=9.68 (s, 1H), 6.88 (s, 1H), 6.73 (s, 1H), 2.62 (t, J=7.2 Hz, 2H), 2.57 (s, 3H), 2.47 (s, 3H), 1.42 (qn, J=7.2 Hz, 2H), 1.25 (sx, J=7.2 Hz, 2H), 0.80 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=183.41, 149.29, 145.26, 142.15, 137.83, 137.10, 130.54, 129.63, 128.35, 38.38, 31.11,

21.38, 16.21, 15.48, 13.47. IR (KBr): 2956, 2925, 2870 (C–H), 1659 (C=O) cm^{-1}. HRMS (EI): *m/z* calcd for $C_{15}H_{18}OS_3$ $[M]^+$: 310.0520, found:310.0522.

*4.5.3. 2′-Butylsulfanyl-5,5′-dioctyl-[3,3′]bithiophenyl-2-carbaldehyde (**8c**).* From the reaction on the 160 mg scale of **1c**, 110.3 mg (59.3%) of **8c** was obtained as yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ=9.70 (s, 1H), 6.91 (s, 1H), 6.75 (s, 1H), 2.86 (t, *J*=7.6 Hz, 2H), 2.77 (t, *J*=7.6 Hz, 2H), 2.63 (t, *J*=7.2 Hz, 2H), 1.76–1.64 (m, 4H), 1.44–1.21 (m, 24H), 0.88 (t, *J*=6.8 Hz, 6H), 0.80 (t, *J*=7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=183.58, 155.39, 148.25, 145.24, 137.64, 136.63, 130.22, 128.55, 127.21, 38.35, 31.80, 31.26, 31.12, 30.77, 30.29, 29.24, 29.23, 29.15, 29.07, 28.99, 22.62, 21.38, 14.06, 13.50. IR (KBr): 2955, 2927, 2854 (C–H), 1662 (C=O) cm^{-1}. HRMS (EI): *m/z* calcd for $C_{29}H_{46}OS_3$ $[M]^+$: 506.2711, found: 506.2714.

*4.5.4. 2′-Butylsulfanyl-5,5′-bis-trimethylsilanyl-[3,3′]bithiophenyl-2-carbaldehyde (**8d**).* From the reaction on the 200 mg scale of **1d**, 190.2 mg (75.6%) of **8d** was obtained as yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ=9.75 (s, 1H), 7.31 (s, 1H), 7.17 (s, 1H), 2.72 (t, *J*=7.2 Hz, 2H), 1.45 (qn, *J*=7.2 Hz, 2H), 1.27 (sx, *J*=7.2 Hz, 2H), 0.80 (t, *J*=7.2 Hz, 3H), 0.37 (s, 9H), 0.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=183.70, 150.64, 145.20, 143.17, 142.93, 139.03, 137.60, 137.09, 136.53, 37.98, 31.13, 21.45, 13.52, −0.24, −0.46. IR (KBr): 2957, 2930, 2872 (C–H), 1667 (C=O) cm^{-1}. HRMS (EI): *m/z* calcd for $C_{19}H_{30}OSi_2S_3$ $[M]^+$: 426.0997, found:426.1001.

*4.5.5. 2′-Butylsulfanyl-2-formyl-[3,3′]bithiophenyl-5,5′-dicarboxylic acid diethyl ester (**8e**).* From the reaction on the 100 mg scale of **1e**, 51.2 mg (40.7%) of **8e** was obtained as yellow liquid. ^1H NMR ($CDCl_3$, 400 MHz): δ=9.81 (s, 1H), 7.82, (s, 1H), 7.71 (s, 1H), 4.38 (sx, *J*=7.2 Hz, 4H), 2.87 (t, *J*=7.2 Hz, 2H), 1.57 (qn, *J*=7.2 Hz, 2H), 1.40–1.32 (m, 8H), 0.87 (t, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ=183.61, 161.33, 161.07, 144.14, 143.13, 142.10, 140.18, 135.14, 134.86, 133.69, 133.34, 62.11, 61.61, 37.21, 30.96, 21.62, 14.31, 14.21, 13.46. IR (KBr): 2957, 2926, 2854 (C–H), 1716, 1673 (C=O) cm^{-1}. HRMS (EI): *m/z* calcd for $C_{19}H_{22}O_5S_3$ $[M]^+$: 426.0629, found:426.0633.

*4.5.6. 2′-Butylsulfanyl-5,5′-diphenyl-[3,3′]bithiophenyl-2-carbaldehyde (**8f**).* From the reaction on the 111 mg scale of **1f**, 124.6 mg (89.8%) of **8f** was obtained as yellow liquid. ^1H NMR ($CDCl_3$, 400 MHz): δ=9.85 (s, 1H), 7.74–7.69 (m, 2H), 7.62–7.57 (m, 2H), 7.49–7.31 (m, 8H), 2.76 (t, *J*=7.2 Hz, 2H), 1.51 (qn, *J*=7.2 Hz, 2H), 1.31 (sx, *J*=7.6 Hz, 2H), 0.817 (t, *J*=7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ=183.55, 152.22, 145.86, 145.13, 138.04, 137.82, 133.31, 133.17, 132.95, 129.44, 129.19, 129.09, 128.27, 126.63, 126.34, 125.63, 125.53, 38.33, 31.19, 21.47, 13.53. IR (KBr): 3059, 2955, 2928, 2870 (C–H), 1651 (C=O) cm^{-1}. HRMS(ESI): *m/z* calcd for $C_{25}H_{22}OS_3$ $[M+H]^+$: 435.0911, found: 435.0901.

*4.5.7. 2′-Butylsulfanyl-5,5′-di-naphthalen-1-yl-[3,3′]bithiophenyl-2-carbaldehyde (**8g**).* From the reaction on the 158 mg scale of **1g**, 150.4 mg (79.9%) of **8g** was obtained as yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ=10.04 (s, 1H), 8.37–8.27 (m, 2H), 7.98–7.88 (m, 4H), 7.69 (d, *J*=7.2 Hz, 1H), 7.63 (d, *J*=6.8 Hz, 1H), 7.60–7.50 (m, 7H), 7.36 (s, 1H), 2.89 (t, *J*=7.2 Hz, 2H), 1.61 (qn, *J*=7.2 Hz, 2H), 1.39 (sx, *J*=7.2 Hz, 2H), 0.88 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=183.61, 150.39, 144.39, 143.79, 138.74, 137.18, 134.23, 133.86, 131.33, 131.29, 131.13, 131.05, 129.97, 129.78, 129.06, 128.59, 128.52, 128.27, 128.17, 127.06, 126.86, 126.39, 126.25, 125.25, 125.20, 125.15, 38.47, 31.30, 21.54, 13.60. IR (KBr): 3051, 2954, 2924, 2854 (C–H), 1658 (C=O) cm^{-1}. HRMS(ESI): *m/z* calcd for $C_{33}H_{26}OS_3$ $[M]^+$: 534.1146, found: 534.1148.

*4.5.8. 2′-Butylsulfanyl-5,5′-di-naphthalen-2-yl-[3,3′]bithiophenyl-2-carbaldehyde (**8h**).* From the reaction on the 96 mg scale of **1h**, 66.2 mg (57.7%) of **8h** was obtained as yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ=9.91 (s, 1H), 8.21 (d, *J*=1.2 Hz, 1H), 8.06 (d, *J*=1.2 Hz, 1H), 7.94–7.83 (m, 6H), 7.81 (dd, *J*=8.6 Hz, 1.8 Hz, 1H), 7.73 (dd, *J*=8.6 Hz, 1.8 Hz, 1H), 7.64 (s, 1H), 7.58–7.46 (m, 5H), 2.82 (t, *J*=7.2 Hz, 2H), 1.56 (qn, *J*=7.2 Hz, 2H), 1.34 (sx, *J*=7.2 Hz, 2H), 0.84 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=183.51, 152.30, 145.88, 145.21, 138.11, 137.96, 133.68, 133.58, 133.52, 133.35, 133.01, 130.55, 130.30, 129.01, 128.87, 128.41, 128.09, 127.80, 127.77, 127.01, 126.99, 126.93, 126.82, 126.41, 125.90, 125.57, 124.31, 123.90, 123.66, 38.39, 31.25, 21.52, 13.55. IR (KBr): 3055, 3016, 2957, 2928, 2858 (C–H), 1655 (C=O) cm^{-1}. HRMS (EI): *m/z* calcd for $C_{33}H_{26}OS_3$ $[M]^+$: 534.1146, found: 534.1151.

*4.5.9. 2′-Butylsulfanyl-5,5′-bis(4-dimethylamino-phenyl)-[3,3′]bithiophenyl-2-carbaldehyde (**8i**).* From the reaction on the 120 mg scale of **1i**, 87.6 mg (61.4%) of **8i** was obtained as yellow solid. Mp: 197–200 °C. ^1H NMR (400 MHz, $CDCl_3$): δ=9.78 (s, 1H), 7.59 (d, *J*=8.8 Hz, 2H), 7.46 (d, *J*=8.8 Hz, 2H), 7.32 (s, 1H), 7.17 (s, 1H), 6.72 (d, *J*=8.8 Hz, 4H), 3.03 (s, 6H), 3.00 (s, 6H), 2.71 (t, *J*=7.2 Hz, 2H), 1.48 (qn, *J*=7.2 Hz, 2H), 1.29 (sx, *J*=7.2 Hz, 2H), 0.80 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=183.39, 153.64, 151.08, 150.33, 146.95, 146.15, 138.89, 135.48, 129.97, 127.40, 126.61, 124.23, 123.38, 121.52, 120.86, 112.38, 112.10, 40.36, 40.21, 38.47, 31.20, 21.46, 13.55. IR (KBr): 2957, 2924, 2857 (C–H), 1643 (C=O) cm^{-1}. HRMS (EI): *m/z* calcd for $C_{29}H_{32}N_2OS_3$, $[M]^+$: 520.1677, found: 520.1680.

*4.5.10. 2′-Butylsulfanyl-[3,3′]bi[benzo[b]thiophenyl]-2-carbaldehyde (**8j**).* From the reaction on the 116 mg scale of **1j**, 130.6 mg (87.0%) of **8j** was obtained as yellow solid. Mp: 108–109 °C. ^1H NMR (400 MHz, $CDCl_3$): δ=9.81 (s, 1H), 7.98 (d, *J*=8.4 Hz, 1H), 7.86 (d, *J*=8.0 Hz, 1H), 7.57–7.47 (m, 2H), 7.41–7.24 (m, 4H), 2.88–2.75 (m, 2H), 1.56–1.42 (m, 2H), 1.30–1.13 (m, 2H), 0.75 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=185.35, 141.92, 140.43, 139.85, 139.81, 139.79, 138.92, 138.88, 128.80, 128.36, 125.50, 125.08, 124.93, 123.39, 122.63, 121.94, 36.60, 31.34, 21.49, 13.37. IR (KBr): 3053, 2956, 2927, 2912, 2843 (C–H), 1668 (C=O) cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{21}H_{18}OS_3$ $[M+H]^+$: 383.0598, found: 383.0596.

*4.5.11. The synthesis of 2-butylsulfanyl-[3,3′]bi- thiophenyl-5-carbaldehyde (**9**) and 2′-butylsulfanyl-[3,3′]bithiophenyl-2,5′-dicarbaldehyde (**10**) (Entry 4, Table 1).* To a solution of **1a** (0.30 g, 1.54 mmol) in THF (20 mL), *n*-BuLi (2.62 M in hexane, 1.29 mL, 3.38 mmol, 2.2 equiv) was added dropwise at −78 °C. After keeping at −78 °C for 1 h, the reaction mixture was warmed up slowly to 0 °C, and then cooled back to −78 °C. DMF (0.36 mL, 4.61 mmol, 3.0 equiv) was added dropwise at −78 °C, then kept at −78 °C for 1 h, the reaction mixture was warmed up slowly to ambient temperature over night. Workup is same to making **8a**. Light yellow solid **9** (0.057 g, 13%) and yellow liquid **10** (0.366 g, 77.2%) were obtained by column chromatography on silica gel with petrol ether (60–90 °C) and chloroform (1:1, v/v) as eluents.

Compound **9**, Mp: 55–57 °C. ^1H NMR (400 MHz, $CDCl_3$) δ=9.78 (s, 1H), 7.78 (s, 1H), 7.61–7.58 (m, 1H), 7.42–7.37 (m, 2H), 3.04 (t, *J*=7.2 Hz, 2H), 1.72 (qn, *J*=7.2 Hz, 2H), 1.45 (sx, *J*=7.2 Hz, 2H), 0.92 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=181.39, 145.99, 140.43, 137.76, 135.45, 134.76, 127.34, 125.79, 123.25, 36.41, 30.85, 20.87, 13.51. IR (KBr): 2956, 2925, 2867 (C–H), 1651 (C=O) cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{13}H_{15}OS_3$ $[M+H]^+$: 283.0285, found: 283.0282; $C_{13}H_{14}NaOS_3$ $[M+Na]^+$: 305.0104, found: 305.0098.

Compound **10**, ^1H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 9.79 (s, 1H), 7.80 (d, *J*=4.8 Hz, 1H), 7.68 (s, 1H), 7.24 (d, *J*=4.8 Hz, 1H), 2.99 (t, *J*=7.4 Hz, 2H), 1.67 (qn, *J*=7.5 Hz, 2H), 1.40 (sx, *J*=7.4 Hz, 2H), 0.90 (t, *J*=7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=182.85, 181.14, 149.86, 142.35, 141.20, 139.55, 138.41, 134.40, 132.75, 130.34, 36.32, 30.75, 21.74, 13.43. IR (KBr): 2957, 2928, 2857 (C–H), 1663 (C=O) cm^{-1}.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{15}O_2S_3$ $[M+H]^+$: 311.0234, found: 311.0230; $C_{13}H_{14}NaO_2S_3$ $[M+Na]^+$: 333.0054, found: 305.0038.

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Supplementary data

Electronic supplementary data available: ^{1}H NMR, ^{13}C NMR, HRMS, and X-ray crystallographic. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2010.01.056.

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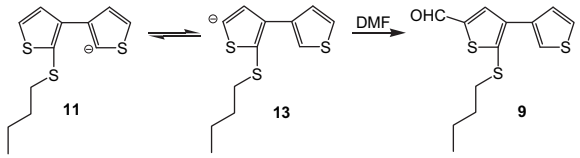
13. The possible mechanism for generating **9**.



14. Crystal data for **9**: M=282.42, $C_{13}H_{14}OS_3$, monoclinic, space group P2(1)/c, a=10.7974(15) Å, b=9.9673(14) Å, c=13.4751(18) Å, α=90°, β=111.692(2)°, γ=90°, V=1347.5(3) Å^3, Z=4, D_{calcd}=1.392 g/cm^3. A colorless crystal of dimensions 0.24×0.14×0.05 mm was used for measurement at 293(2) K with the ω scan mode on a Bruker Smart APEX diffractometer with CCD detector using Mo Kα radiation (λ=0.71073 Å). The data were corrected for Lorentz and polarization effects and absorption corrections were performed using *SADABS* program. The crystal structures were solved using the *SHELXTL* program and refined using full matrix least squares. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons. The final cycle of full-matrix least-squares refinement was based on 7224 independent reflections [$I>2\sigma(I)$] and 154 variable parameters with R_1=0.0498, wR_2=0.0781.
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16. Crystal data for **8j**: M=382.53, $C_{21}H_{18}OS_3$, triclinic, space group P-1, a=9.903(2) Å, b=10.102(2) Å, c=10.120(2) Å, α=90.205(4)°, β=103.568(4)°, γ=107.486(4)°, V=935.7(4) Å^3, Z=2, D_{calcd}=1.358 g/cm^3. A colorless crystal of dimensions 0.18×0.12×0.09 mm was used for measurement at 293(2) K. The structure was solved by the same methods of **9**. The final cycle of full-matrix least-squares refinement was based on 4833 observed reflections [$I>2\sigma(I)$] and 226 variable parameters with R_1=0.0441, wR_2=0.1238.
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