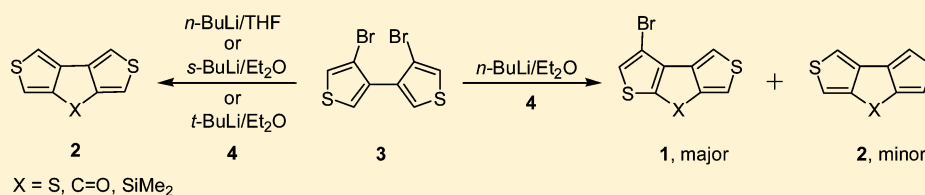


# Selectivity of Br/Li Exchange and Deprotonation of 4,4'-Dibromo-3,3'-bithiophene for Synthesis of Symmetrical and Unsymmetrical Dithienoheteroaromatic Rings

Hui Han, Wenling Zhao, Jinsheng Song, Chunli Li, and Hua Wang\*

Key Lab for Special Functional Materials of Ministry of Education, Henan University, Kaifeng 475004, China

**S** Supporting Information



**ABSTRACT:** The novel selective synthesis of symmetrical and unsymmetrical dithienoheteroaromatic rings (DTHAs) has been developed via intramolecular cyclization of 4,4'-dibromo-3,3'-bithiophene (3). Four reaction conditions including  $n\text{-BuLi/Et}_2\text{O}$ ,  $n\text{-BuLi/THF}$ ,  $s\text{-BuLi/Et}_2\text{O}$ , and  $t\text{-BuLi/Et}_2\text{O}$  were employed to react with 3 for selective formation of two types of dicarbanions, which generate the symmetrical and unsymmetrical DTHAs after quenching with three electrophilic reagents (4a–c). The possible mechanism of formation of DTHAs was proposed. In addition, two unsymmetrical DTHAs were confirmed by X-ray single-crystal analyses.

Due to versatile applications in organic field effect transistors (OFETs),<sup>1–3</sup> organic light-emitting diodes (OLEDs),<sup>4–6</sup> and dye-sensitized solar cells (DSSCs),<sup>7–9</sup> a variety of symmetric DTHA compounds, such as dithienothiophenes (DTTs), cyclopentadithiophenones (CDTs), and dithienosiloles (DTSs) derivatives have attracted considerable attention in recent years. Wong and Wu et al.<sup>9b</sup> reported two new sensitizers for DSSCs that adopted coplanar 4,4'-diphenyldithieno[3,2-*b*:2',3'-*d*]silole as the central linkage, and the best power conversion efficiency of those dyes achieved 7.6%. In our previous work, the synthesis of 2,5-distyryldithieno[2,3-*b*:3',2'-*d*]thiophene and its high field-effect mobility of 2.2 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> were studied.<sup>1d</sup> Most of these fused aromatic compounds have shown excellent properties in the organic electronic field, but there are only a few works regarding to the preparation of DTHAs and their derivatives, which will limit their applications in organic electronics. Further development on efficient synthesis of DTHAs is desirable for the realization of their diverse applications in materials science.

Some symmetric DTHA compounds have been synthesized and reported with several steps and low yields,<sup>10–12</sup> and in the literature they generally include two key steps: formation of dibromodithienyl intermediates (dibromodithienyl dimethylsilane, dibromodithienyl ketone, and dibromodithienyl sulfide) and intramolecular cyclization. Most of the methods are not efficient for the following reasons: hard to obtain intermediates, expensive reagent for ring closure, harsh reaction conditions, multiple steps, and low total yield. Our previous work improved the synthesis of *ss*-DTT in a total yield of 55–63% through introduction of trimethylsilyl (TMS) groups as protecting and solubilizing groups to 3,4-dibromothiophene.<sup>10b</sup> Although the

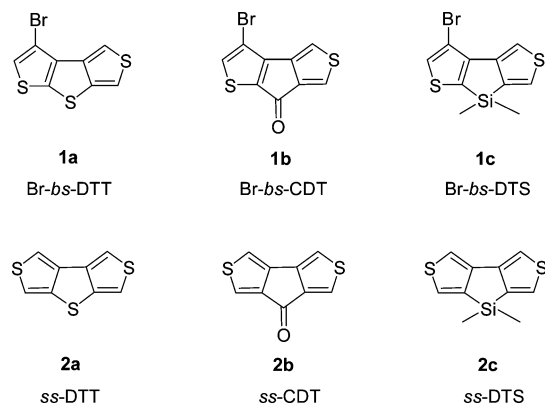
yield has been greatly improved, there are still four steps in that route. Iyoda et al.<sup>13</sup> showed the efficient synthesis of 2c in which 3 was dilithiated with  $n\text{-BuLi}$  at  $-100$  °C and then treated with 4c in tetrahydrofuran (THF) with a yield of 89%. Nevertheless, those reports on improving the yields were mainly focused on the symmetrical DTHAs, and it is rare to find efficient methods for unsymmetrical DTHAs synthesis. Recently, our group reported the first example in preparation of an unsymmetrical DTHA, dithieno[2,3-*b*:4',3'-*d*]silole (*bs*-DTS).<sup>14</sup> The efficient and novel method for the preparation of *bs*-DTSs in high yields occurred by intramolecular silole formation in which 4,4'-dibromo-2,2',5,5'-tetrakis(trimethylsilyl)[3,3']bithienyl was employed to react with  $t\text{-BuLi}$  and then quenched with water without addition of dichlorodimethylsilane or any other silicon source. The unsymmetrical DTHAs are novel building blocks in organic synthesis and important to be applied to organic electric materials because of their low LUMO energy level.<sup>15</sup>

In this work, the novel selectivity of the Br/Li exchange (including mono and double Br/Li exchanges) and deprotonation of 3 were observed when 3 was treated with 2 equiv of  $n\text{-BuLi}$  in Et<sub>2</sub>O. By using this kind of selectivity, both symmetrical DTHAs (*ss*-DTT, *ss*-CDT and *ss*-DTS) and unsymmetrical DTHAs (*bs*-DTT, *bs*-CDT and *bs*-DTS, Scheme 1) have been developed via intramolecular cyclization of 3 using three electrophilic reagents. In addition, it is fascinating to find that the kinds of BuLi and the solvent

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Scheme 1. Molecular Structures of DTHAs



systems will greatly influence this kind of selectivity and further determine the final components of the products.

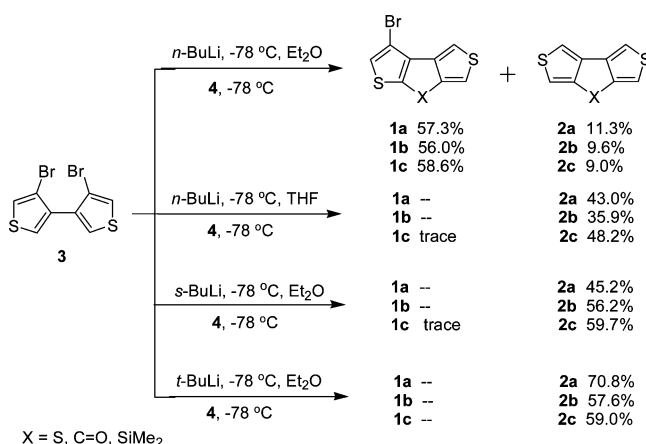
Compound **3** was synthesized by the homocoupling of 3,4-dibromothiophene.<sup>16</sup> In this paper, the Br/Li exchange reaction of **3** was first carried out with *n*-BuLi (2.2 equiv) in ethyl ether at  $-78\text{ }^{\circ}\text{C}$  for 2 h, followed by addition of an electrophilic reagent, bis(phenylsulfonyl)sulfide (**4a**), and after workup, it was interesting to find out that both unsymmetrical **1a** and symmetrical **2a** were obtained in one pot with isolated yields of 57.3% and 11.3%, respectively. To compare the influence of reaction temperature, parallel experiments were set up from  $-78$  to  $-45$  and  $-20\text{ }^{\circ}\text{C}$ , and the yield of **1a** decreased and the yield of **2a** increased accordingly, but the total yield decreased (entries 1–3, Table 1). In the meantime, the polymerization

Table 1. Formation of **1a** and **2a** through Cyclization at Different Temperatures

entry	<i>n</i> -BuLi (equiv)	reaction temp ( $^{\circ}\text{C}$ )/time (h)	<b>1a</b> (%)	<b>2a</b> (%)
1	2.2	$-78/2$	57.3	11.3
2	2.2	$-45/2$	36.9	15.7
3	2.2	$-20/2$	28.4	26.1

was increased and confirmed by  $^1\text{H}$  NMR. Finally, 2.2 equiv of *n*-BuLi at  $-78\text{ }^{\circ}\text{C}$  in ethyl ether were chosen as the optimal reaction conditions for preparation of unsymmetrical DTHAs. Under these optimal reaction conditions, **1b** and **1c** were efficiently obtained in 56.0% and 58.6% yields, respectively, when dimethylcarbamic chloride (**4b**) and dichlorodimethylsilane (**4c**) were employed (Scheme 2). In the meantime, the symmetrical DTHAs, **2b**, and **2c** were also obtained in low yields of 9.6% and 9.0%, respectively.

In order to better understand such novel selectivity, the influence of BuLi types and solvent effects were taken into account. As shown in Scheme 2, when ethyl ether was replaced by THF, **2** was generated in moderate yields (43.0%, 35.9%, and 48.2% yields for **2a**, **2b**, and **2c**, respectively), and only a trace **1c** was observed by GCMS. On the other hand, if *s*-BuLi or *t*-BuLi was used instead of *n*-BuLi in ethyl ether, no **1** was observed, and only **2** was formed in good yields (Scheme 2). For example, in the case of *s*-BuLi/ $\text{Et}_2\text{O}$ , 45.2%, 56.2%, and 59.7% yields for **2a**, **2b**, and **2c** were obtained, respectively; in

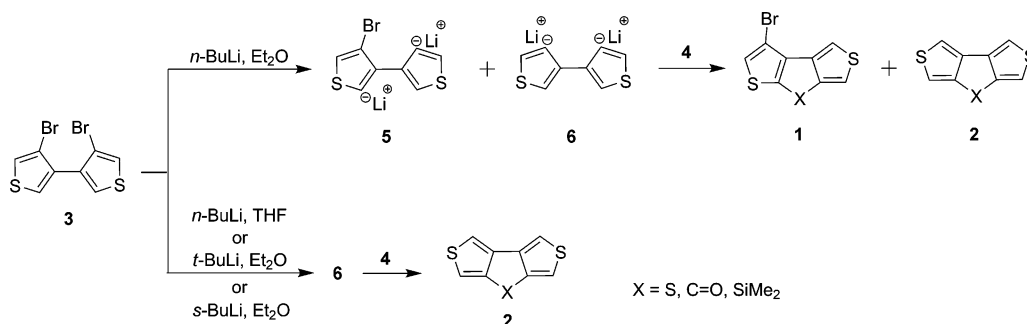
Scheme 2. Synthesis of **1** and **2** under Different Reaction Conditions

the case of *t*-BuLi/ $\text{Et}_2\text{O}$ , 70.8%, 57.6%, and 59.0% yields for **2a**, **2b**, and **2c** were obtained, respectively.

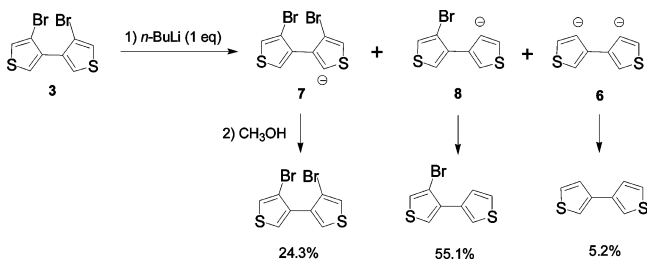
It is interesting to note that the kinds of BuLi and the solvent systems will greatly influence this type of selectivity and further decide the final components of the products. It is known that *n*-BuLi exists as a hexameric aggregate in hydrocarbons,<sup>17</sup> a tetrameric aggregate in diethyl ether,<sup>18</sup> and a temperature-dependent equilibrium of dimeric and tetrameric aggregates in THF.<sup>18b,19</sup> The reactivity of *n*-BuLi depends on its aggregation types. The tetrameric aggregate of *n*-BuLi in ethyl ether means weaker reactivity with the novel selectivity of both Br/Li exchange and deprotonation took place at the same time in our case, which generated both **1** and **2**. However, *n*-BuLi in THF gives lower oligomers assigned as a mixture of tetramer and dimer, which means higher reactivity with the selectivity of only double Br/Li exchanges of **3**. As a result, only **2** could be generated in this case. From the reactions in our work, we can conclude that the aggregation state of *n*-BuLi in ethyl ether or THF really plays a role to control the reaction selectivity.

From the experimental results above, it is obvious that the selectivity of Br/Li exchange and deprotonation of **3** depends on the reaction conditions. When *n*-BuLi and ethyl ether were utilized in the reaction, both Br/Li exchange and deprotonation reactions took place at the same time. During this process, two possible dicarbanions, **5** and **6** (Scheme 3), were generated after *n*-BuLi was added at  $-78\text{ }^{\circ}\text{C}$  in  $\text{Et}_2\text{O}$ . Intermediate **5** was formed by both Br/Li exchange and deprotonation, and **6** was generated via double Br/Li exchanges of **3**. From the ratio ( $\sim 5:1$ ) of the final yields of **1** and **2**, we can conclude that **5** was the favorite intermediate. When THF was utilized instead of ethyl ether, **2** was obtained in good yields and only a trace of **1c** was observed. This result implies that dianionic intermediate **6** should be the favorite intermediate. From the experimental results, we can conclude that the reactivity of the  $\alpha$ -H and  $\beta$ -Br on the thiophene ring was greatly influenced by the solvent system utilized in the reaction and result in the reaction selectivity difference between deprotonation and Br/Li exchange due to the reactivity difference between the aggregative types of *n*-BuLi in ethyl ether and THF. On the basis of this idea, it is easy to understand the temperature effect in Table 1. High temperature decreases the aggregation of *n*-BuLi in  $\text{Et}_2\text{O}$ , which increases its reactivity and the ratio of **2** in the products.

## Scheme 3. Possible Mechanism for the Formation of 1 and 2



In order to further understand the mechanism of the reaction, another reaction of 3 with 1 equiv of *n*-BuLi in ethyl ether was employed. After quenching with CH<sub>3</sub>OH, 4-bromo-3,3'-bithiophene (55.1%), 4,4'-dibromo-3,3'-bithiophene (24.3%), and 3,3'-bithiophene (5.2%) were observed by GCMS (see the Supporting Information). The possible mechanism was proposed in Scheme 4. The carbanions 7 and

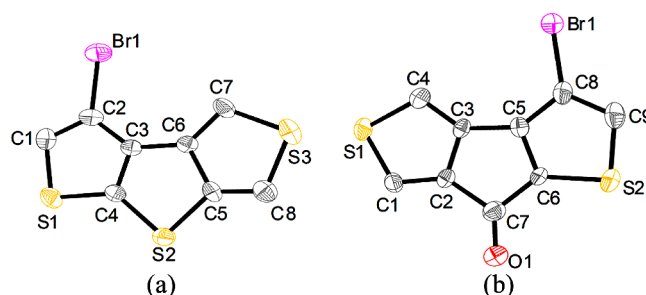
Scheme 4. Reaction of 3 with 1 equiv of *n*-BuLi in Et<sub>2</sub>O

8 were the main intermediates, which were generated from protonation and Br/Li exchange of 3, respectively, and the Br/Li exchange was the favorite path. When another 1 equiv of *n*-BuLi was employed in our work, the second carbanion should be formed on the neighboring thiophene, which means that Br/Li exchange should occur on 7 and deprotonation occur on 8. Both of the changes formed dicarbanion 5, which generated 1 as major product after quenching with 4. There was some byproduct 2 as a minor product observed due to dicarbanion 6 from the double Br/Li exchange (Schemes 3 and 4).

Compared with the case of *n*-BuLi, *t*-BuLi exists as a dimeric aggregate in Et<sub>2</sub>O<sup>20</sup> and primarily as a solvated monomer in THF,<sup>19b</sup> so *t*-BuLi normally shows much higher reactivity priority than *n*-BuLi in the selection of Br/Li exchange.<sup>21,22</sup> In general, *s*-BuLi shows a moderate reactivity between *n*-BuLi and *t*-BuLi. From the experimental data, the case of *s*-BuLi showed behavior similar to that of *t*-BuLi under the reaction conditions. In the case of *s*-BuLi and *t*-BuLi, instead of protonation, only double Br/Li exchanges occurred on 3 and only 2 was generated in good yields in ethyl ether (Scheme 2).

In all, because of the selectivity of the deprotonation and Br/Li exchange in the reaction, we have found an efficient and general way to obtain the symmetrical and unsymmetrical DTHAs in which new bonds (C–S, C–C, and C–Si) could be formed efficiently.

The molecular structures of 1a and 1b were confirmed by single-crystal X-ray analysis (Figure 1). Compound 1a belongs to monoclinic space group *P*2(1)/*c*, with four molecules in one unit cell. From the single-crystal structure of 1a, it is obvious that all of the thiophene rings are approximately coplanar. The



**Figure 1.** Molecular structures and conformations (top view) for 1a (a) and 1b (b). Carbon, bromine, oxygen, and sulfur atoms are depicted with thermal ellipsoids set at the 30% probability level, and all hydrogen atoms are omitted for clarity.

dihedral angle between the two side thiophenes is 2.6°, and the torsion angles are 3.8° (C2–C3–C6–C7) and 4.9° (Br1–C2–C7–H7A). In crystal packing of 1a, the S···S and Br···Br interactions can be clearly observed. The distances of S2···S2 and Br1···Br1 are 3.482 and 3.620 Å, respectively. Compound 1b belongs to triclinic space group *P*-1 with four molecules in one unit cell. In the crystal packing of 1b, each of two molecules stack orthogonally together and the dihedral angle of the two molecules is 85.6°. Each molecule is approximately coplanar with torsions of –1.3° (C4–C3–C5–C8) and –5.2° (C11–C12–C16–C17). The S···O, C···H, and Br···Br interactions are clearly observed in crystal packing. The distances of S1···O1, S4···O2, H18···C1, and Br2···Br1 are 3.193, 3.140, 2.886, and 3.690 Å, respectively.

In summary, we have established a novel and efficient way to selectively synthesize unsymmetrical DTHAs (1a, 1b, and 1c) and symmetrical DTHAs (2a, 2b, and 2c) via intramolecular cyclization. The product distribution depends on the selectivity of deprotonation and/or Br/Li exchange occurred on 3 due to the reaction conditions including the kinds of BuLi and the solvent systems. The aggregation state of BuLi in different solvent system plays a role to control the reaction selectivity. The presence of *n*-BuLi/Et<sub>2</sub>O gives an efficient yield of unsymmetrical DTHAs due to the selectivity of the deprotonation and Br/Li exchange reactions. When the reaction conditions change to *n*-BuLi/THF, *s*-BuLi/Et<sub>2</sub>O, or *t*-BuLi/Et<sub>2</sub>O, only symmetrical DTHAs could be obtained efficiently. Both symmetrical and unsymmetrical DTHAs are important to materials science; however, the synthetic method in making unsymmetrical DTHAs gives a simple and efficient manner that may show a wide application in both synthetic chemistry and organic electronics.

## EXPERIMENTAL SECTION

**Synthesis of 3-Bromodithieno[2,3-*b*:3',4'-*d*]thiophene (1a) and Dithieno[3,4-*b*:3',4'-*d*]thiophene (2a).** To a solution of **3** (211.8 mg, 0.65 mmol) in dry ethyl ether (20 mL) was added *n*-BuLi (2.38 M, 0.60 mL, 1.43 mmol, 2.2 equiv) dropwise at  $-78^{\circ}\text{C}$ . After 2 h at  $-78^{\circ}\text{C}$ , **4a** (207.4 mg, 0.66 mmol, 1.01 equiv) was added under argon. The reaction mixture was kept at  $-78^{\circ}\text{C}$  for 1 h and  $-55^{\circ}\text{C}$  for 2 h and then warmed slowly to ambient temperature overnight. After being quenched with  $\text{H}_2\text{O}$  (20 mL), the reaction mixture was extracted with  $\text{CHCl}_3$  ( $3 \times 20$  mL), and the organic phase was washed with  $\text{H}_2\text{O}$  (40 mL), saturated NaCl solution (40 mL), and  $\text{H}_2\text{O}$  (40 mL) and dried over anhydrous  $\text{MgSO}_4$ . After the solvent was removed in vacuo, the residue was purified by column chromatography on silica gel (300–400 mesh) with petroleum ether ( $60$ – $90^{\circ}\text{C}$ ) as eluent to yield **1a** (103.1 mg, 57.3%) as a white solid and **2a** (14.5 mg, 11.3%) as a white solid. From the other two reactions on the 489.0 mg and 513.3 mg scales of **3**, 203.7 mg (49.0%) and 222.8 mg (51.2%) of **1a** and 24.7 mg (8.3%) and 34.3 mg (11.1%) of **2a** were obtained, respectively. **1a**: mp  $89$ – $91^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 2.8$  Hz, 1 H), 7.26 (d,  $J = 2.8$  Hz, 1 H), 7.19 (s, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.7, 141.5, 137.7, 133.3, 123.2, 111.9, 111.3, 104.1; IR (KBr) 3109.1 (CH)  $\text{cm}^{-1}$ ; HRMS (TOF MS EI $^+$ )  $m/z$  calcd for  $[\text{C}_8\text{H}_3\text{S}_3\text{Br}]$  273.8580, found 273.8583  $[\text{C}_8\text{H}_3\text{S}_3^{79}\text{Br}]$  and 275.8564  $[\text{C}_8\text{H}_3\text{S}_3^{81}\text{Br}]$ . **2a**: mp  $71$ – $72^{\circ}\text{C}$  (lit.<sup>10a</sup> mp  $87$ – $87.5^{\circ}\text{C}$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J = 2.4$ , 2 H), 7.04 (d,  $J = 2.8$ , 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.9, 136.1, 114.0, 111.6 (this analysis is in agreement with the literature data<sup>10b</sup>); IR (KBr) 3091.7 (CH)  $\text{cm}^{-1}$ .

Parallel experiments were set up following procedures similar to those described above. When the reaction temperature was set at  $-45^{\circ}\text{C}$ , **1a** (47.2 mg, 36.9%) and **2a** (14.3 mg, 15.7%) were obtained from **3** (150.6 mg, 0.46 mmol). When the reaction temperature was set at  $-20^{\circ}\text{C}$ , **1a** (40.1 mg, 28.4%) and **2a** (26.3 mg, 26.1%) were obtained from **3** (166.4 mg, 0.51 mmol).

**Synthesis of 3-Bromo-7H-cyclopenta[1,2-*b*:3,4-*c'*]dithiophen-7-one (1b) and 7H-Cyclopenta[1,2-*c*:3,4-*c'*]dithiophen-7-one (2b).** To a solution of **3** (350.5 mg, 1.08 mmol) in dry ethyl ether (50 mL) was added *n*-BuLi (1.59 M, 1.50 mL, 2.38 mmol, 2.2 equiv) dropwise at  $-78^{\circ}\text{C}$ . After the solution was kept at  $-78^{\circ}\text{C}$  for 2 h, **4b** (0.10 mL, 1.09 mmol, 1.0 equiv) was added dropwise under argon. The reaction mixture was warmed up slowly to ambient temperature overnight. The workup the same as that for preparation of **1a** and **1b**. The crude product was purified by column chromatography on silica gel (200–300 mesh) with petroleum ether ( $60$ – $90^{\circ}\text{C}$ )/chloroform (1:1, v/v) as eluent to yield **1b** (164.1 mg, 56.0%) as a yellow solid and **2b** (20.0 mg, 9.6%) as a yellow solid. **1b**: mp  $140$ – $142^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J = 1.6$  Hz, 1 H), 7.55 (s, 1 H), 7.12 (d,  $J = 2.0$  Hz, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  177.6, 152.9, 144.1, 143.6, 138.5, 135.1, 127.6, 115.1, 105.2; IR (KBr) 3076.3 (CH), 1697.3 (C=O)  $\text{cm}^{-1}$ ; HRMS (TOF MS EI $^+$ )  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $[\text{C}_9\text{H}_3\text{BrOS}_2]$  269.8803, found 269.8809. **2b**: mp  $165$ – $167^{\circ}\text{C}$  (lit.<sup>11</sup> mp  $172$ – $173^{\circ}\text{C}$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 2.0$  Hz, 2 H), 7.09 (d,  $J = 2.0$  Hz, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.2, 148.3, 140.9, 127.0, 115.4; IR (KBr) 3083.1 (CH)  $\text{cm}^{-1}$ , 1704.3 (C=O)  $\text{cm}^{-1}$ .

**Synthesis of 3-Bromo-7,7-dimethyl-7H-silolo[2,3-*b*:4,5-*c'*]dithiophene (1c) and 7,7-Dimethyl-7H-silolo[2,3-*c*:4,5-*c'*]dithiophene (2c).** To a solution of **3** (105.0 mg, 0.32 mmol) in dry ethyl ether (10 mL) was added *n*-BuLi (2.59 M, 0.26 mL, 0.68 mmol, 2.1 equiv) dropwise at  $-78^{\circ}\text{C}$ . After the solution was kept at  $-78^{\circ}\text{C}$  for 2 h, **4c** (0.04 mL, 0.33 mmol, 1.0 equiv) was added dropwise. The reaction mixture was warmed slowly to ambient temperature overnight. The workup was same as that for preparation of **1a** and **2a**. The crude product was purified by column chromatography on silica gel (300–400 mesh) with petroleum ether ( $60$ – $90^{\circ}\text{C}$ ) as eluent to yield **1c** (57.2 mg, 58.6%) as a white solid and **2c** (6.5 mg, 9.0%) as a colorless solid. From the other reaction on the 108.0 mg scale of **3**, 54.1 mg (53.9%) of **1c** and 6.7 mg (9.0%) of **2c** were obtained respectively. **1c**: mp  $45$ – $47^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J = 2.4$  Hz, 1 H), 7.52 (s, 1 H), 7.41 (d,  $J = 2.4$  Hz, 1 H), 0.47 (s, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.0, 145.6,

143.9, 141.0, 132.2, 130.0, 114.7, 107.4,  $-1.8$ ; IR (KBr) 3100.4 (CH)  $\text{cm}^{-1}$ ; HRMS (FTMS ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $[\text{C}_{10}\text{H}_{10}\text{SiS}_2\text{Br}]$  300.9177, found 300.9171. **2c**: mp  $102$ – $104^{\circ}\text{C}$  (lit.<sup>13</sup> mp  $104.2$ – $105.0^{\circ}\text{C}$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 2.0$  Hz, 2 H), 7.32 (d,  $J = 2.4$  Hz, 2 H), 0.45 (s, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.7, 146.4, 129.9, 114.5,  $-1.5$  (this analysis is in agreement with the literature data<sup>13</sup>); IR (KBr) 3083.7 (CH)  $\text{cm}^{-1}$ .

**Synthesis of Dithieno[3,4-*b*:3',4'-*d*]thiophene (2a).** *Method A (n-BuLi in THF).* The procedure was same as that for the preparation of **2a** in ethyl ether. The only difference was that the reaction solvent was changed to THF. From the reaction on a 115.3 mg (0.36 mmol) scale of **3**, 10 mL of dry THF was employed. A 30.0 mg (43.0%) portion of **2a** was obtained by column chromatography on silica gel (200–300 mesh) with petroleum ether ( $60$ – $90^{\circ}\text{C}$ ) as eluent.

*Method B (s-BuLi in Ethyl Ether).* The procedure was same as that for the preparation of **2a** in ethyl ether. The only difference was that *n*-BuLi was used instead of *s*-BuLi. From the reaction on a 201.4 mg (0.65 mmol) scale of **3**, 57.7 mg (45.2%) of **2a** was obtained by column chromatography on silica gel (200–300 mesh) with petroleum ether ( $60$ – $90^{\circ}\text{C}$ ) as eluent.

*Method C (t-BuLi in Ethyl Ether).* The procedure was same as that for the preparation of **2a** in ethyl ether. The only difference was that 4.0 equiv of *t*-BuLi was used instead of 2.0 equiv of *n*-BuLi. From the reaction on a 1.9654 g (6.04 mmol) scale of **3**, 842.5 mg (70.8%) of **2a** was obtained by column chromatography on silica gel (200–300 mesh) with petroleum ether ( $60$ – $90^{\circ}\text{C}$ ) as eluent. From the other reaction on a 2.2620 g scale of **3**, 836.2 mg (61.0%) of **2a** was obtained.

**Synthesis of 7H-Cyclopenta[1,2-*c*:3,4-*c'*]dithiophen-7-one (2b).** *Method A (n-BuLi in THF).* The procedure was the same as that for the preparation of **2b** in ethyl ether. The only difference was that the reaction solvent was changed to THF. From the reaction on a 111.4 mg (0.34 mmol) scale of **3** with 10 mL dry THF, 23.7 mg (35.9%) of **2b** was obtained by column chromatography on silica gel (200–300 mesh) with petroleum ether ( $60$ – $90^{\circ}\text{C}$ )/chloroform = 1:1 (v/v) as eluent.

*Method B (s-BuLi in Ethyl Ether).* The procedure was the same as that for the preparation of **2b** in ethyl ether. The only difference was that *s*-BuLi was used instead of *n*-BuLi. From the reaction on a 213.0 mg (0.66 mmol) scale of **3**, 71.3 mg (56.2%) of **2b** was obtained by column chromatography on silica gel (200–300 mesh) with petroleum ether ( $60$ – $90^{\circ}\text{C}$ )/chloroform (1:1, v/v) as eluent.

*Method B (t-BuLi in Ethyl Ether).* The procedure was same as that for the preparation of **2b** in ethyl ether. The only difference is that 4.0 equiv of *t*-BuLi was used instead of 2.0 equiv of *n*-BuLi. From the reaction on the 350.8 mg (1.08 mmol) scale of **3**, 119.6 mg (57.6%) of **2b** was obtained by column chromatography on silica gel (200–300 mesh) with petroleum ether ( $60$ – $90^{\circ}\text{C}$ ): chloroform (1:1, v/v) as eluent. From the other two reactions on the 480.2 mg and 509.0 mg scales of **3**, 168.0 mg (59.0%) and 170.0 mg (56.3%) of **2b** were obtained respectively.

**Synthesis of 7,7-Dimethyl-7H-silolo[2,3-*c*:4,5-*c'*]dithiophene (2c).** *Method A (n-BuLi in THF).* The procedure was same as that for the preparation of **2c** in ethyl ether. The only difference was that the reaction solvent was changed to THF. From the reaction on the 262.8 mg (0.81 mmol) scale of **3**, and using 20 mL of dry THF, 86.8 mg (48.2%) of **2c** was obtained by column chromatography on silica gel (200–300 mesh) with petroleum ether ( $60$ – $90^{\circ}\text{C}$ ) as eluent and then precipitation twice by  $\text{CHCl}_3$ – $\text{CH}_3\text{OH}$  (1:5, v/v).

*Method B (s-BuLi in Ethyl Ether).* The procedure was same as that for the preparation of **2c** in ethyl ether. The only difference was that *s*-BuLi was used instead of *n*-BuLi. From the reaction on the 397.8 mg (1.23 mmol) scale of **3**, 163.4 mg (59.7%) of **2c** was obtained by column chromatography on silica gel (200–300 mesh) with petroleum ether ( $60$ – $90^{\circ}\text{C}$ ) as eluent.

*Method B (t-BuLi in Ethyl Ether).* The procedure was same as that for the preparation of **2c** in ethyl ether. The only difference was that 4.0 equiv of *t*-BuLi was used instead of 2.0 equiv of *n*-BuLi. From the reaction on a 204.2 mg (0.63 mmol) scale of **3**, 82.6 mg (59.0%) of **2c** was obtained by column chromatography on silica gel (200–300

mesh) with petroleum ether (60–90 °C) as eluent. From the other reaction on a 212.4 mg scale of **3**, 82.2 mg (56.4%) of **2c** was obtained.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Characterization of all compounds and crystallographic files of **1a** and **1b** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Tel: (0086)-378-3897112. Fax: 3881358. E-mail: [hwang@henu.edu.cn](mailto:hwang@henu.edu.cn).

### Notes

The authors declare no competing financial interest.

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