# Efficient Synthesis of Substituted Dithieno[2,3-*b*:3',2'-*d*]siloles and A 10-Membered Silicon-Bridged Thiophene-Based Cyclophane

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**Abstract:** Two new substituted dithieno[2,3-*b*:3',2'-*d*]siloles, 7,7-diphenyl-2,5-bis(trimethylsilyl) dithieno[2,3-*b*:3',2'-*d*]silole (**1**) and 7,7-diphenyl-2,5-dichloro-dithieno[2,3-*b*:3',2'-*d*]silole (**2**) were synthesized in 79.4% and 31.6% yields, respectively *via* the cross-coupling of 1,4-dilithiobutadienes with dichlorodiphenylsilane. An unexpected tetrachloro-substituted 10-membered silicon-bridged thiophene-based cyclophane (**3**) was obtained in a high yield as 46.9% when the cross-coupling of 1,4-dilithiobutadiene reacted with dichlorodimethylsilane. In addition, the crystal structures of title compounds are described.

**Keywords:** Cross-coupling, dithieno[2,3-*b*:3',2'-*d*]silole, heterocycles, silicon-bridged thiophene-based cyclophane.

In recent years, particular attention has been paid to dithienosilole (DTS)-based polymers, promising functional organic materials in devices such as light-emitting diodes [1], field effect transistors [2], polymer solar cells [3], and dye sensitive solar cells (DSSCs) [4]. Among the DTS derivatives, great interest has been focused on dithieno[3,2-*b*:2',3'-*d*]silole (**4**) during the last twenty years. However, as one of the isomeric DTSs, there are few reports about the derivatives based on dithieno[2,3-*b*:3',2'-*d*]silole (**5**). Iyoda reported the preparation of 7,7-dimethyl-dithieno[2,3-*b*:3',2'-*d*]silole in good yields by using palladium-catalyzed intramolecular cross-coupling of organostannyl species [5a] or using $CuCl_2$-mediated cyclization of organozinc species [5b]. In our recent work, we have reported the synthesis of 7,7-dimethyl-2,5-bis(trimethylsilyl)-dithieno[2,3-*b*:3',2'-*d*] silole in 81% yield by using 2,2'-dilithium-5,5'-bis(trimethylsilyl)-3,3'-bithiophene with dichlorodimethylsilane and its halogenation ring opening in the presence of NXS (X = Cl, Br, I) [6].

Herein, we try to report the synthesis of dithieno[2,3-*b*:3',2'-*d*]silole based derivatives, 7,7-diphenyl-2,5-bis(trimethylsilyl)dithieno[2,3-*b*:3',2'-*d*]silole (**1**) and 7,7-diphenyl-2,5-dichloro-dithieno[2,3-*b*:3',2'-*d*]silole (**2**) *via* the cross-coupling of 1,4-dilithiobutadienes with dichloro-diphenyl-silane. In addition, an unexpected tetrachloro-substituted 10-membered silicon-bridged thiophene-based cyclophane (**3**) was obtained when 1,4-dilithiobutadiene reacted with dichlorodimethylsilane.

The synthetic route to **1** is shown in Scheme **2**. The efficient synthesis of 2,2'-dibromo-5,5'-bis(trimethylsilyl)-3,3'-bithiophene (**7**) was reported in our previous work [7]. With **7** as starting material, after double Br/Li-exchange, the reaction mixture was quenched with dichlorodiphenylsilane to generate **1** in 79.4 % isolated yield (Scheme **2**). Same case happened in the formation of 7,7-dimethyl-2,5-bis(trimethylsilyl)dithieno[2,3-*b*:3',2'-*d*]silole (**8**, 81.0%), in which dichlorodimethylsilane was used instead of dichlorodiphenylsilane [6]. Due to the presence of the two TMS groups, **7** has a very good solubility and there was no solubility problem in both Br/Li-exchange and subsequent ring close reaction. On the other hand, the TMS groups in **7** also prevent the possible side reactions occurred at the acidic α positions of thiophene during the Br/Li-exchange reaction. Based on such factors from the structure of **7**, our method offers a practical route to both **1** and **8** in good yields.

When TMS groups were replaced with Cl groups in 2,2'-dibromo-5,5'-dichloro-3,3'-bithiophene (**9**) [8], after double Br/Li exchange and quenching with dichlorodiphenylsilane, **2** could be obtained in 31.6% isolated yield. However, 7,7-dimethyl-2,5-dichlorodithieno[2,3-*b*:3',2'-*d*]silole (**10**) can not be obtained when dichlorodimethylsilane is used for the formation of silole ring. Instead of **10**, an unexpected 10-membered silicon-bridged thiophene-based cyclophane (**3**) was generated in pretty good yield (46.9%, Scheme **3**).

Compared with the case in Schemes **2** and **3**, when the starting material was changed from **7** to **9**, and the TMS groups (EDG, electron donating group) in **7** were replaced with Cl groups (EWG, electron withdrawing group) in **9**. After Br/Li exchange, the stability of dianion **9** is better than that of dianion **7**, which means that nucleophilicity of dianion **9** is worse than that of dianion **7**. As a result, the yield of formation of **1** is much higher than that of **2** when the dianions were quenched with dichlorodiphenylsilane.

The formation of two C-Si bonds for silole ring should be carried out step by step. With the weaker nucleophilicity, dianion **9** attacked Si atom of dichlorodimethylsilane, the main product is unexpectedly **3**, a silicon-bridged thiophene-based 10-membered ring cyclophane, instead of expected **10**. The yield of 46.9% in forming **3** is much higher than that of normal formation of macrocylces in organic synthesis. The formation of **3** is different from the case of dianion **7** reacting with dichlorodimethylsilane or dichlorodiphenylsilane to generate dithieno[2,3-*b*:3',2'-*d*]siloles, **8** and **1**. On

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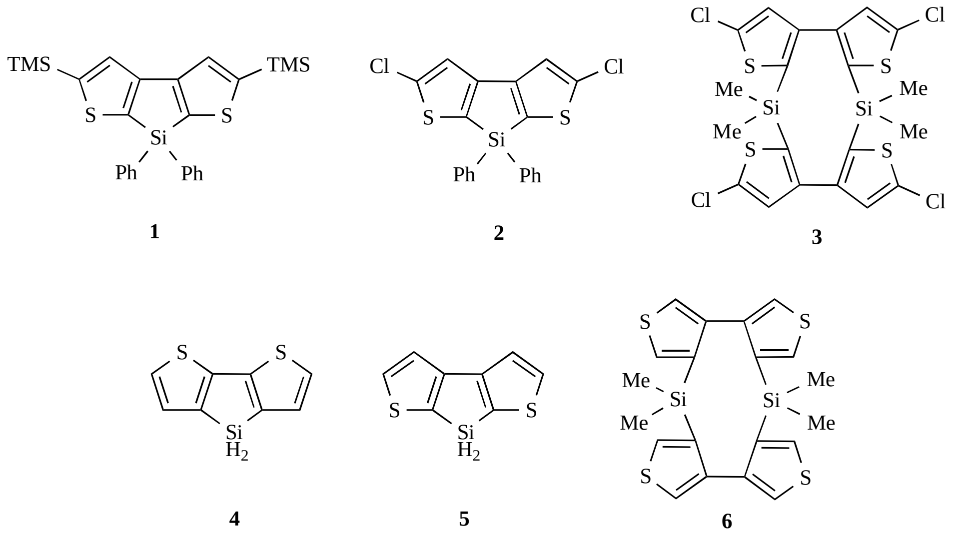
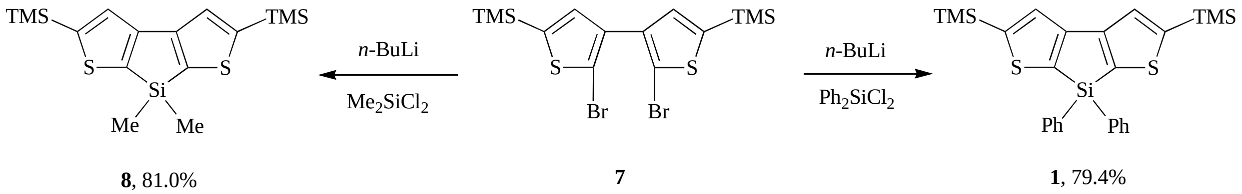
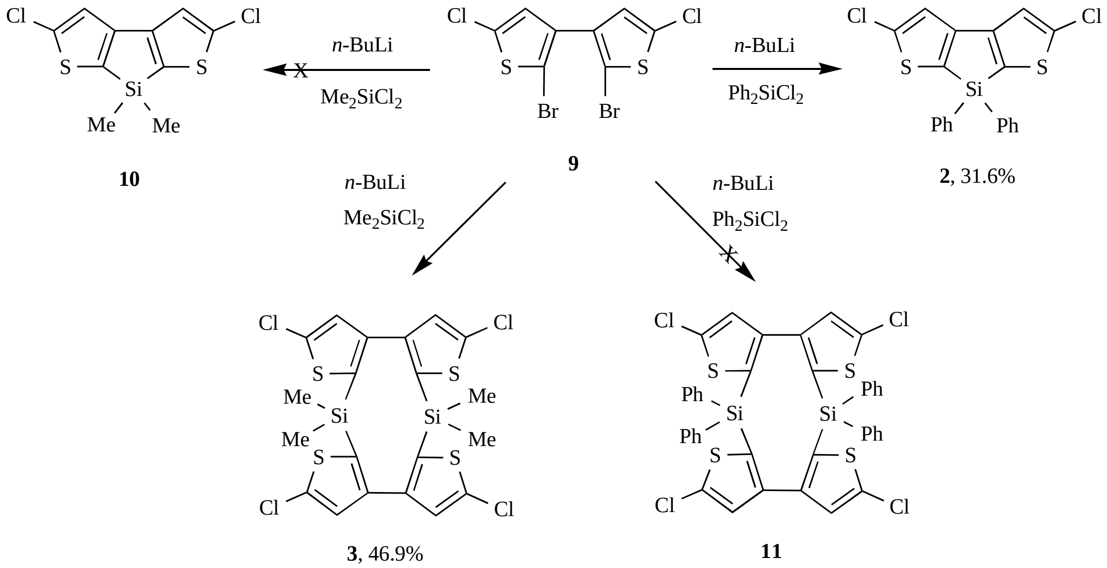


**Scheme 1.** The molecular structures of **1**-**6**.



**Scheme 2.** The synthetic route to **1** and **8**.



**Scheme 3.** The synthetic route to **2** and **3**.

one hand, the absence of **10** means that the macrocyclic structure of **3** is more stable than that of **10** in the nucleophilic reaction of dianion **9** with of dichlorodimethylsilane. On the other hand, the nucleophilic reaction of dianion **9** with dichlorodiphenylsilane, which bears bulky phenyl groups, can not generate macrocyclic compound **11**, but only **2** in low yield (Scheme **3**).

Another silicon-bridged thiophene-based 10-membered ring cyclophane, **6** (Scheme **1**) was reported by Iyoda [9] in 18-50% yield. In his work, three steps were involved. The first step was Br/Li exchange of bis(3-bromothiophen-2-yl)dimethylsilane to form the aryl lithium species; the second step was the aryl lithium species combined with CuCN to afford the Lipshutz cuprate and the last step was the Lipshutz cuprate oxidated by 1,4-benzoquinone to result in target compound **6**. Compared with the Iyoda method, our method for making **3** is more facile. In addition, the structure of **3** is obviously different from that of **6**.

The structure of **2** was confirmed by single crystal X-ray analysis (Fig. **1**). In the structure of **2**, the frame of dithienosilole shows slight torsion. The crystal of **2** belongs to monoclinic, space group P2 (1). The torsional angle between two thiophene rings is 10.1° (C4-C2-C6-C8) and the dihedral angle between the two thiophene rings is 7.3°. The two benzene rings are out of the plane of dithienosilole. The dihedral angles between the plane of the dithienosilole and the two planes of the benzene rings are 64.5° and 83.2°, respectively and meanwhile the dihedral angle between the two benzene planes is 66.0°.

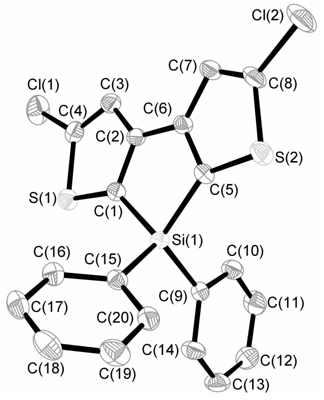


**Fig. (1).** Molecular structure and conformation for **2**. Carbon, silicon, chlorine and sulfur atoms are depicted with thermal ellipsoids set at 50% probability level and all hydrogen atoms are omitted for clarity.

The structure of **3** was also confirmed by single crystal X-ray analysis (Fig. **2**). The crystal of **3** belongs to monoclinic, space group P1. In **3**, the central 10-membered ring has a "U"-shaped cycle containing both convex and concave U-shapes linked together. The average dihedral angle between the two thiophene rings in the bithienyl unit is 66.8°. The two homochiral bithienyl moieties of **3** have transoid conformation. The torsional angles between the neighboring thiophene rings are 109.3° (C4-C3-C14-C13) and 111.9° (C5- C6-C10-C9). Two oppositing thiophenes have an average dihedral angle of 19.4°.

In summary, we have successfully synthesized disubstituted dithieno[2,3-*b*:3',2'-*d*]siloles, **1** and **2** by the cross-coupling of 1,4-dilithiobutadienes with dichlorosilane. The efficient synthesis of the dithieno[2,3-*b*:3',2'-*d*]siloles makes them possible to be used as the building blocks in the application of organic functional materials, such as organic semiconductor, OLED, etc. More interesting is that we provide an efficient method for making a new tetrachloro-substituted 10-membered silicon-bridged thiophene-based cyclophane, **3**, which might show its application as a new type of host molecule in supramolecular chemistry.

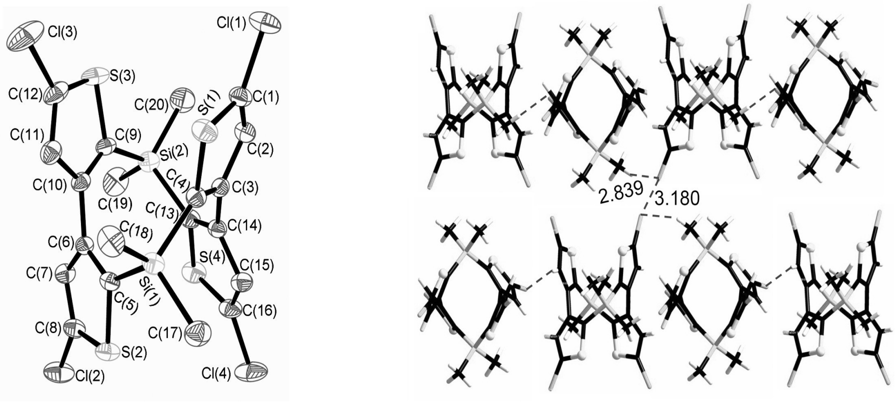
## EXPERIMENTAL

### Preparation of 1

In a Schlenk flask, a solution of **7** (477.3 mg, 1.02 mmol) in anhyd THF (20 mL) was added under Ar, then *n*-BuLi (2.57 M, 0.83 mL, 2.1 equiv) was added dropwise at –78 °C. After keeping at –78 °C for 2 h, $Ph_2SiCl_2$ (0.24 mL, 1.12 mmol, 1.1 equiv) was added, then the reaction mixture was warmed slowly to ambient temperature and heated at 120 °C overnight. After quenching with $H_2O$ (20 mL), the reaction mixture was extracted with $CHCl_3$ (3 × 20 mL) and then the organic layer was washed with sat. $NaHCO_3$ (40 mL) and $H_2O$ (2 × 30 mL). After drying over $MgSO_4$, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with PE (60–90 °C) as eluent to yield **1** (397.1 mg, 79.4 %) as a white solid. Mp: 149-150 ℃. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, $J_1$=8.0Hz, $J_2$=1.6Hz, 2H), 7.46 (s, 1H), 7.35-7.43(m, 3H), 0.36 (s, 1H); $^{13}$CNMR(100 MHz, $CDCl_3$): δ 154.68, 152.60, 138.59, 135.33, 131.61, 130.32, 128.14, 128.11, 0.02; HRMS (TOF MS EI$^+$) *m/z* calcd for [$C_{26}H_{30}S_2Si_3$] 490.1097 (Exact Mass), found 490.1102. IR (KBr): 3060.7, 3001.7, 2954.6, 2887.7, 1657.6, 1658.9, 1484.7, 1429.7 (C-H) cm$^{-1}$.

### Preparation of 2 and 3

**2** and **3** were prepared from **9**, respectively according to the method used for the preparation of **1** from **7**. For **2**, the reaction was carried out on 165.2 mg scale of **9**, 55.6 mg (31.6 %) of **2** was obtained. Mp: 191-193℃. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.63-7.62 (m, 2 H), 7.48 (t, *J*=7.2 Hz, 1 H), 7.40 (t, *J*=7.2 Hz, 2 H), 7.14 (s, 1H); $^{13}$CNMR(100 MHz, $CDCl_3$): δ 151.19, 139.39, 135.27, 130.89, 130.03, 129.94, 128.40, 121.53; HRMS (TOF MS EI$^+$) *m/z* calcd for



(**a**) side view (**b**) crystal packings

**Fig. (2).** Molecular structure and conformation for **3**: (**a**) side view; Carbon, silicon and sulfur atoms are depicted with thermal ellipsoids set at 50% probability level and all hydrogen atoms are omitted for clarity. (**b**) crystal packings in monoclinic, space group P1.

[$C_{20}H_{12}Cl_2S_2Si$] 413.9527 (Exact Mass), found 413.9531. IR (KBr): 3068.5, 3017.4, 2993.9, 1657.6, 1582.9, 1496.5, 1421.8 (C-H) $cm^{-1}$. For **3**, the reaction was carried out on 759.8 mg scale of **9**, 267.2 mg (46.9 %) of **3** was obtained. Mp: 263-264 ℃. $^1H$ NMR (400 MHz, $CDCl_3$) δ 6.72 (s, 1H), 0.40 (s, 1H); $^{13}$CNMR(100 MHz, $CDCl_3$): δ 144.81, 134.76, 132.73, 129.88, 0.82; HRMS (TOF MS $EI^+$) *m/z* calcd for [$C_{20}H_{16}Cl_4S_4Si_2$] 579.8428 (Exact Mass), found 579.8433. IR (KBr): 3088.2, 2978.1, 2954.6, 2899.5 (C-H) $cm^{-1}$.

## Crystal Data for 2 and 3

Crystal Data for **2**: M = 415.43, $C_{20}H_{12}Cl_2S_2Si$, monoclinic, space group P2 (1), a = 6.6297 (12) Å, b = 12.109 (2) Å, c = 11.969 (2) Å, α = 90°, β = 100.072 (2)°, γ = 90°, V = 946.1(3) $Å^3$, Z = 2, $D_{calcd}$ = 1.458 $Mg/cm^3$. A colorless crystal of dimensions 0.41 × 0.38 × 0.36 mm was used for measurement at 296 (2) K with the ω scan mode on a Bruker Smart APEX diffractometer with CCD detector using Mo–$K_a$ radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects and absorption corrections were performed using SADABS [a] program. The crystal structures were solved using the SHELXTL [b] 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 fullmatrix least-squares refinement was based on 3457 independent reflections [I >2s(I)] and 226 variable parameters with R1 = 0.0321, wR2 = 0.0771. [a] Sheldrick, G. M. SADABS; University of Göttingen: Germany, 1996. [b] Sheldrick, G. M. SHELXTL Version 5.1; Bruker Analytical X-ray Systems, Inc.: Madisonv / WI, 1997. Crystal Data for **3**: M = 582.58, $C_{20}H_{16}Cl_4S_4Si_2$, monoclinic, space group P1, a = 10.456 (2) Å, b = 18.845 (4) Å, c = 13.6551(3) Å, α = 90°, β = 106.440 (2)°, γ = 90°, V = 2580.6(9) $Å^3$, Z = 4, $D_{calcd}$ = 1.499 $Mg/cm^3$. A colorless crystal of dimensions 0.41 × 0.37 × 0.35 mm was used for measurement at 296 (2) K. The structure was solved by the same methods as used for **2**. The final cycle of fullmatrix least-squares refinement was based on 4781 observed reflections [I >2s(I)] and 275 variable parameters with R1 = 0.0390, wR2 = 0.0809.

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## SUPPLEMENTARY MATERIAL

Supplementary material is available on the publishers Web site along with the published article.

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