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J. Org. Chem., Just Accepted Manuscript • DOI: 10.1021/acs.joc.8b02382 • Publication Date (Web): 14 Nov 2018 Downloaded from http://pubs.acs.org on November 18, 2018

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Nosyl (2-nitrobenzenesulfonyl) annulation strategy toward winding vine-shaped bithiophenes

Shiomi Ashida,^a Naoki Tanaka,^a Yukiko Ito,^a Mitsuru Matsuoka,^a Takayoshi Hashimoto,^b Kentaro Okano,^a Yuji Miyazaki,^c Tohru Kobayashi,^c Tsuyoshi Yaita,^c Atsunori Mori*^a

^aDepartment of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan; ^bResearch Facility Center for Science and Technology, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan; ^cJapan Atomic Agency, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

ABSTRACT: Winding vine-shaped bithiophene was synthesized through the nosyl (2-nitorobenzene sulfonyl) cyclization protocol. The reaction of bithiophene bearing bromomethyl groups at the 3,3'-positions with nosylated 1,2-ethylenediamine in the presence of potassium carbonate afforded the annulated product in excellent yield. The obtained bithiophene was found to contain a 10-membered ring, which was confirmed by X-ray analysis. The related nosyldiamine bearing a tri- or tetramethylene group also reacted in a similar manner, affording 11- or 12-membered macrocycle, respectively.

The design and synthesis of structurally unique organic molecules are of great interest in organic chemistry. Cyclophanes represented as 1, in which a (hetero)aromatic structure strapped with alkylene chains forms a medium- to large-sized- ring structure, have been extensively studied due to their interesting properties such as aromaticity, chirality recognition, and spectroscopic understanding.¹ We have also shown that several heterobiaryls connected with a certain number of alkylene chains lead to medium-ring-sized molecules², and the formation of such structures was successfully achieved by ring-closing metathesis³ catalyzed by a ruthenium or molybdenum alkylidene complex through exclusive E-selectivity. Bisimidazoles 2 and bithiophenes 3 were indeed obtained, and we named these molecules as winding-vine-shaped heterobiaryls, some of which were revealed to show molecular asymmetry of axial, facial, and helical chiralities in a single structure. (Chart 1) We now turn to find a method for the preparation of a new class of vine-shaped molecules through a different cyclization pathway in which the undesired intermolecular reaction leading to oligomers should be avoided as much as possible.

Fukuyama and Kan showed that the 2-nitrobenzene sulfonyl (nosyl) group effectively serves as a protective group of amine derivatives suppressing exhaustive alkylation of the nitrogen atom to undergo selective monoalkylation.⁴ The treatment of the nosvl-protected primary amines with a base exclusively results in highly efficient monoalkylation. It has also been shown that the intramolecular alkylation of the nitrogen atom affords the cyclized product with a medium- to large-membered ring size despite the use of relatively concentrated conditions⁵ compared to the existing macrocyclization representative reactions, such as Yamaguchi's lactonization.⁶ The cyclization reaction has indeed been applied to the total synthesis of several natural products bearing a medium-sized ring structure.^{4,5} We envisaged that nosyl cyclization would be effective for the formation of winding vine-shaped molecules forming a 10-membered or higher ring size. If successful, this reaction can be an alternative protocol for achieving the generation of a new class of vineshaped molecules. Herein, we describe that the reaction of a bithiophene derivative bearing bromomethyl group at both thiophene rings with nosylated diamines induces smooth annulation to yield macrocyclic bithiophene.



Chart 1. Cyclophanes and winding vine-shaped heterobiaryls

Synthesis of the cyclization precursor with nosylated diamine was carried out by a slight modification of the previously described bithiophene synthesis.^{2d,7} The pathway to the cyclization precursor is represented in Scheme 1. Bromination of 3-methylthiophene with NBS afforded the 2-brominated product in a quantitative yield. The obtained bromothiophene was subjected to dimerization with a half amount of the Grignard reagent to give the corresponding thienyl magnesium by halogenmetal exchange followed by the addition of a nickel catalyst undergoing cross-coupling with the remaining bromothiophene. The coupling product **4** was obtained with 99% yield. Bromination of **4** at the 5, 5'-positions afforded dibromobithiophene **5** to allow further functionalization at the thiophene ring. Radical bromination of **5** with NBS/V70 was then performed to obtain bromothylated product **6** with 61% yield.

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60

6, 61%

Figure 1. X-ray structure of macrocyclic bithiophene **8a**, in which the nosyl group is omitted for clarity. (CCDC-1838596)

As shown in Scheme 3, removal of the nosyl group was performed by the treatment of **8a** with *n*-dodecanethiol in the presence of DBU at room temperature for 18 h to afford the denosylated product **9a** in 85% yield.^{5c,10} ¹H NMR measurements suggested the presence of a thiophene ring, while the aromatic protons derived from the nosyl group completely disappeared. The reaction of **9a** with nosyl chloride in the presence of K₂CO₃ was also found to reproduce the nosylated bithiophene **8a** with 74% yield.



Scheme 3. Denosylation of macrocyclic **8a** and renosylation leading to **8a**

The related cyclization of **6** with nosylated $1,\omega$ -diamines **7b** (n = 3) and **7c** (n = 4) was also examined.⁸ When the reaction was carried out with **7b** at 60 °C in DMF for 3 h, the annulated product **8b** composed of the 11-membered ring was obtained with 83% yield. It was found that use of nosylated 1,4-diamine led to the corresponding product with the 12-membered ring **8c** with 62% yield under similar conditions. (Scheme 4)



Scheme 4. Reaction of bithiophene 6 with nosylated $1,\omega$ -diamines 7.

The key for the successful annulation is the ease of macrocyclization by the nosyl group. The reaction of **6** with **7a** was examined under several conditions, as summarized in Table 1. The nosyl cyclization, which we initially examined under the conditions shown in the literature to form the medium-sized ring, proceeded to give the cyclized product **8a** in a quantitative yield at 60 °C under the concentration of ca. 0.2 M (Scheme 2; entry 1 of Table 1).^{4,5} The reaction was found to occur within shorter time periods to afford **8a** in excellent yields (3 h, 84%; 0.5 h, 91%: entry 2 and 3). It was also found that the reaction was completed smoothly under diluted conditions (0.02 M, 97%: entry 4). It is noteworthy that the reaction at a much higher concentration (0.1 M, 92%: entry 4) gave **8a**. This result is in marked contrast to the ring-closing metathesis in the formation of the vine-shaped compound **3** under diluted conditions. The

Scheme 1. Preparation of tetrabromobithiophene 6

Ъ

5.75%

NBS

ref s1

Dinosylated diamine was prepared by the reaction of 1,2-ethvlenediamine with 2 equivalents of 2-nitro-benzenesulfonyl chloride to give the nosylated ethylenediamine 7a.8 We first examined the standard reaction conditions of the nosyl alkylation for the reaction of bithiophene bearing two bromomethyl groups 6 with 7a in the presence of potassium carbonate. This reaction was found to occur at 60 °C in DMF as a solvent for 24 h to result in the consumption of bithiophene 6, as was confirmed by the analysis, leading to the cyclized product 8a in 99% yield after chromatographic purification. The measurement of ¹H NMR suggested the involvement of both bithiophene- and nosyl-derived signals, the ratio of which was confirmed to be ca. 1:1. The methylene protons adjacent to the thiophene ring was observed as different doublet signals at 3.98 and 4.81 ppm, respectively and another methylene protons derived from the ethylenediamine moiety was shown as two broad singlets at 3.05 and 3.38 ppm. These broad signals were found to be coalesced at 77 °C. (See Supporting Information) Mass spectrometry analysis found the m/Z peak of 778.8456 (M+H), showing reasonable agreement with the cyclized product $(C_{24}H_{19}^{79}Br_2N_4O_8S_4).$



Scheme 2. Annulation of bithiophene 6 with nosylated ethylenediamine 7a

X-ray crystal structure analysis also supported the formation of the cyclized product. As shown in Figure 1, **8a** shows the structure of the cyclized product consisting of the 10-membered ring. Two thiophene rings were found to form anti-conformation, and the torsion angle of the carbon–carbon bond between the two thiophene rings was found to be 76.9°, thus displaying the winding vine-shaped structure, in which the *N*-nosyl containing alkylene chain is located across the thiophene–thiophene bond.⁹

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metathesis reaction required diluted conditions (<0.05 M) to undergo smooth cyclization that avoided the undesired intermolecular side reactions,^{2d} while the approach employing nosyl annulation resulted in giving 8a without any serious side reactions despite the high concentration. The reaction at room temperature and 0 °C proceeded to afford 8a in 86% and 63% yields, respectively (0.2 M, 0.5 h). Incomplete cyclization was found at an even lower temperature (-30 °C, 3 h: 33%), whereas uncyclized byproduct was hardly observed to accompany the recovery of bithiophene 6 (58%). Such smooth cyclization was found to proceed specifically with nosyl diamine 7a. This result 10 suggests that the second intramolecular nucleophilic substitu-11 tion to form a 10-membered ring occurred much faster. In con-12 trast, the attempted reaction with diamines of different carbon 13 numbers **7b** (C3) and **7c** (C4) gave a much lower yield despite a high conversion of 6 under similar conditions as shown in en-14 tries 10 and 11 (40% yield at 89% conv; 46% yield at 92% conv, 15 respectively) whereas the detection of uncyclized intermediate 16 was unsuccessful so far. The reaction of unprotected 1,2-eth-17 ylenediamine under similar conditions resulted in little cycliza-18 tion affording a complex mixture of unidentified byproducts 19 (entry 12). The related reaction of the N-boc analog was also 20 found to be unsuccessful (entry 13). These results demonstrate 21 that the use of nosyl macrocyclization of bithiophene 6 with di-22 amines 7 is a practical synthetic tool for obtaining winding vine-23 shaped heterobiaryls. 24

Table 1. Reaction of nosylated diamine 7 with bithiophene 6 under several different conditions^a

entry	Diamine	conc (M) ^b	time (h)	temp (°C)	yield	
1	7a	0.2	24	60	>99%	
2	7a	0.2	3	60	84%	
3	7a	0.2	0.5	60	91%	
4	7a	0.02	3	60	97%	
5	7a	0.1	3	60	92%	
6	7a	0.2	0.5	rt	86%	
7	7a	0.2	0.5	0	63% (67%) ^c	
8	7a	0.2	3	-20	53% (76%) ^c	
9	7a	0.2	3	-30	33% (42%) ^c	
10	7b	0.2	3	-20	40% (89%) ^c	
11	7c	0.2	3	-20	46% (92%) ^c	
12	H ₂ (en) ^d	0.1	19	60	0%	
13 ^d	Boc ₂ (en) ^{d,e}	0.02	1.5	rt	0%	

^a The reaction was carried out with 6 (0.11 mmol), ethylenediamine derivative (0.10 mmol), and K₂CO₃ (0.4 mmol) in DMF at 60 °C. ^b Amount of 6 (mmol)/DMF (mL). ^c The yield based on ¹H NMR measurement. Recovery of 6 is shown (¹H NMR) in parentheses: 42%. d en: -NHCH2CH2NH- .e The reaction was performed with NaH (0.8 mmol) as a base.

The attempted separation of the enantiomer by HPLC analysis with a chiral column was found to be unsuccessful so far, most likely because of the insufficiently high isomerization barrier due to the ease of rotation of the strapped chain between the 3, 3'-positions of bithiophene compared to the related chain bearing a C-C double bond. Computational studies of 8a indicated that the isomerization barrier to *ent*-**8a** is 71.07 kJmol^{-1} , whose value showed reasonable agreement with that estimated by the measurement of variable-temperature NMR study indicating coalesce temperature at 77 °C (ΔG^{\dagger} (25 °C) = 66.95 kJmol⁻¹). These values are much lower than that of the related winding vine-shaped bithiophene 3a (106.91 kJmol⁻¹) formed by ring-closing metathesis.^{2f, 11} Considering that the enantiopurity of 3a (70% ee) was decreased to 38% ee after 7 h at room temperature, racemization of 8a would occur much faster despite the existence of the sterically bulky nosyl groups. (Chart 2)



3a (Y: CH₂, Z: (*E*)-CH=CH), X = H △G[#] = 106.91 kJ·mol⁻¹) **8a** (Y: NHNs, Z: C_2H_4), X = Br $\Delta G^{\#}$ = 71.07 kJ·mol⁻¹)

Chart 2. Calculated racemization barrier of winding-vine shaped bithiophenes

In summary, we have shown that nosvl cyclization is an effective annulation protocol affording winding vine-shaped heterobiaryls in addition to its existing applications to natural product syntheses.^{4,5} Although the formation of 10-membered macrocyclic heterobiaryls has only been successfully carried out by ring-closing metathesis, the nosyl strategy was found to be applicable for the synthesis of derivatives extended to larger ring sizes of 11- and 12-membered rings. The post-transformation of the thus-obtained vine-shaped bithiophenes would allow the functionalization of the nitrogen substituent and the thiophene ring to a variety of bithiophene derivatives among which molecular asymmetry would be observed with an appropriate structural modification.

Experimental section

General. Melting points were uncorrected. ¹H NMR (400, 500 MHz) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100, 125 MHz) spectra were measured on JEOL ECZ400 or Bruker Avance 500 spectrometer. Unless noted, NMR spectra were measured at room temperature. The chemical shift was expressed in ppm with $CHCl_3$ (7.26 ppm for ¹H), $CDCl_3$ (77.0 ppm for ¹³C{¹H}) as internal standards. High resolution mass spectra (HRMS) were measured by JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F254) were used. Purification by HPLC with preparative SEC column (JAI-GEL-2H) was performed by JAI LC-9201. Infrared spectra were recorded on Bruker Alpha with an ATR attachment (Ge). X-ray structure analysis was performed by Rigaku Saturn CCD area detector with graphite monochromated Mo-Ka radiation at Japan Atomic Energy Agency. HPLC analyses with a chiral column were carried out with JASCO LC-2000 Plus with chiral column Daicel Chiralpak IF or IC (0.46 cm I.D. x 25 cm, flow rate: 1.0 mL/min) using UV (297 nm) detector. DFT calculation study was carried out with SPARTAN version 16 or Gaussian version 9.0 in a B3LYP/6-31G level. Unless specified, chemicals were purchased and used without furhter purification. Preparation of 3,3'-dimethyl-2,2'-bithiophene (**4**) and 5,5'-Dibromo-3,3'-dimethyl-2,2'-bithiophene (**5**) were performed in a manner shown in the literature.¹² *N*,*N*-Bis(2-nitrobenzenesulfonyl)-1,2-ethylenediamine (**7a**) and *N*,*N*-Bis(2-nitrobenzenesulfonyl)-1,4-butanediamine (7c) were prepared in a manner as shown in the literature.^{13,14} V70 (2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile)) was purchased from TCI Co Ltd. and stored in the freezer.

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5,5'-Dibromo-3,3'-bis(bromomethyl)-2,2'-bithiophene (6): To a solution of bromobithiophene **5** in 40 mL carbon tetrachloride was added NBS (11.1 g, 36 mmol) followed by addition of V70 (11.1 g, 36 mmol). After stirring at room temperature for 5 h, the mixture was concentrated under reduced pressure to leave a crude oil, which was purifeid by column chromatography on silica gel to afford 12.3 g of 6 (61% yield) as a colorless solid. ¹H NMR (400 MHz, CDCl₃) δ 4.31 (s, 4H), 7.15 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 24.77, 65.0, 130.5, 132.1, 139.2. IR (ATR) 3091, 3061, 3026, 1652, 1518, 1434, 1204, 1185, 994, 932, 829 cm⁻¹. HRMS (DART+) calcd for C₁₀H₇⁷⁹Br₂⁸¹Br₂S₂ (M+H): 510.6682, Found: 510.6702.

21 6.9-Diaza-[2.1-b:3.4-b']bis(5-bromothieno)-6.9-bis(2-nitro-22 benzenesulfonyl)-cyclodecane (8a): To 20 mL Schlenk tube 23 equipped with a magnetic stirring bar were dissolved 5,5'-di-24 bromo-3,3'-bis(bromomethyl)-2,2'-bithiophene (6, 1.1 g, 2.0 25 mmol) and N,N-bis(2-nitrobenzenesulfonyl)-1,2-ethylenedia-26 mine (7a, 43 mg, 2.0 mmol) in 10 mL DMF. K₂CO₃ (1.1 g, 8.0 27 mmol) was added to the resulting solution at room temperature 28 and stirring was continued for 0.5 h at 60 °C. The resulting mixture was poured into water to form a precipitate, which was 29 washed with water, methanol, and diethyl ether repeatedly to 30 leave a crude solid. Purification by chromatography on silica 31 gel using dichlorome-methanol = 5:1 as an eluent afforded 1.43 32 g of **8a** (92% yield) as a colorless solid. Mp. 222.4-223.9 °C. ¹H 33 NMR (CDCl₃) δ 3.05 (brs, 2H), 3.38 (brs, 2H), 3.98 (d, J = 14.834 Hz, 2H), 4.81 (d, J = 14.8 Hz, 2H), 7.20 (s, 2H), 7.66-7.77 (m, 35 6H), 7.98-8.05 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 36 147.9, 139.1, 134.0, 132.7, 132.2, 132.0, 131.9, 130.8, 124.5, 37 115.5, 31.6, 22.6; IR (ATR) 1531, 1350, 1163, 1123, 1065, 975, 926, 851, 812 cm⁻¹; HRMS (ESI+): calcd 38 for C₂₄H₁₉⁷⁹Br⁸¹BrN₄O₈S₄ (M+H): 778.8432, Found: 778.8456. 39

6,9-Diaza-[2,1-b:3,4-b']bis(5-bromothieno)-cyclodecane

41 (9a): To a solution of 8a (78 mg, 0.1 mmol) in DMF (1.5 mL) 42 was added 1-dodecanethiol (0.12 mL, 0.5 mmol) and DBU (0.07 mL, 0.5 mmol). The mixture was stirred at room temper-43 ature for 17 h. The resulting reaction mixture was poured into 44 aq sodium hydrogen carbonate to result in phase separation. The 45 aqueous layer was extracted three times with dichloromethane 46 and the organic layer was dried over anhydrous sodium sulfate. 47 Removal of the solvent left a crude oil, which was subjected to 48 purification by column chromatography on silica gel to afford 49 35 mg of 9a (85%) as a colorless oil. ¹H NMR (400 MHz, 50 $CDCl_3$ δ 2.67 (s, 4H), 3.75 (s, 4H), 6.99 (s, 2H), ¹³C{¹H} NMR 51 (100 MHz, CDCl₃) δ 41.7, 42.5, 113.9, 131.0, 131.5, 142.3, IR 52 (ATR) 3367, 2923, 2850, 1723, 1586, 1451, 1127, 837 cm⁻¹, HRMS (DART+): calcd for $C_{12}H_{13}^{81}Br_2N_2S_2$ (M+H): 410.8846, 53 Found: 410.8862. 54

Reinstallation of Ns group leading to 9a: To a solution of 9a
(91 mg, 0.22 mmol) and 2-nitrobenzenesulfonyl chloride (NsCl, 100 mg, 0.45 mmol) in a mixture of THF/H₂O (0.5 mL/0.5 mL)

was added sodium hydrogen carbonate (54 mg, 0.6 mmol) and the resulting mixture was stirred at room temperature for 24 h. The resulting mixture was poured into aq ammonium chloride and the organic product was extacted three times with dichloromethane. The solution was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil. Purification by chromatography on silica gel using hexane/methyl acetate = 1:1 afforded 126 mg of **8a** (74% yield), which was confirmed to be identical with the authentic sample.

N,*N*-Bis(2-nitrobenzenesulfonyl)-1,3-propanediamine (7b): To a solution of 1,3-propanediamine (231 mg, 3.1 mmol) in THF (6.2 mL)/H₂O (6.2 mL) were added sodium hydrogen carbonate (712 mg, 8.5 mmol) and 2-nitrobenzenesulfonyl chloride (NsCl, 1.30 g, 5.9 mmol). The resulting mixture was stirred at room temperature for 18 h. The resulting mixture was poured into water and the organic product was extracted three times with dichloromethane. The solution was dried over anhydrous sodium sulfate and concentration of the solvent under reduced pressure afforded 1.09 g of 7b (84% yield). ¹H NMR (400 MHz, $CDCl_3$) δ 1.81 (quint, J = 6.4 Hz, 2H), 3.25 (dt, J = 6.4, 6.4 Hz, 4H), 5.56 (t, J = 6.4 Hz, 2H), 7.73-7.81 (m, 4H), 7.86-7.90 (m, 2H), 8.14-8.18 (m, 2H). ${}^{13}C{}^{1}H{}$ NMR δ 30.4, 40.1, 125.5, 131.0, 133.0, 133.4, 133.7, 148.0; IR (ATR) 1536, 1413, 1339, 1163, 1162, 1064, 855 cm⁻¹; HRMS (DART+): calcd for C₁₅H₁₇N₄O₈S₂ (M+H): 445.0488, Found: 445.0490.

6,10-Diaza-[2,1-b:3,4-b']bis(5-bromothieno)-cycloundecane (**8b**): Synthesis of **8b** was carried out in a manner to that of **8a** with **7b** (44 mg, 0.1 mmol) and bithiophene **6** (51 mg, 0.1 mmol) in 0.5 mL DMF at 60 °C for 3 h to afford 67 mg of **8b** (83% yield) as a colorless solid. Mp. 273.7-275.8 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 1.33 (quint, *J* = 6.6 Hz, 2H), 2.89-3.05 (m, 2H), 3.05-3.21 (m, 2H), 4.16 (d, *J* = 15.1 Hz, 2H), 4.59 (d, *J* = 15.1 Hz, 2H), 7.25 (s, 2H), 7.85 (ddd, *J* = 1.4, 7.8, 7.8 Hz, 2H), 7.91 (ddd, *J* = 1.4, 7.8 Hz, 2H), 8.01 (dd, *J* = 1.4, 7.8 Hz, 2H), 8.05 (dd, *J*=1.4, 7.8 Hz, 2H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆) δ 25.3, 44.2, 46.2, 114.2, 124.5, 130.0, 130.4, 130.8, 132.75 (HMQC correlation with ¹H δ 7.25), 5. Found: 792.8589.

6,11-Diaza-[2,1-b:3,4-b']bis(5-bromothieno)-cyclododecane (**8c**): Synthesis of **8b** was carried out in a manner to that of **8a** with **7c** (147 mg, 0.3 mmol) and bithiophene **6** (160 mg, 0.3 mmol) in 1.5 mL DMF at 60 °C for 3 h to afford 149 mg of **8c** as a colorless solid (62% yield). Mp. 237.8-239.3 °C. ¹H NMR (400 MHz, DMSO-*d*₆) 1.36-1.46 (brs, 4H), 3.02-3.10 (brs, 4H), 4.15 (d, J = 15.4 Hz, 2H), 4.80 (d, J = 15.4 Hz, 2H), 7.24 (s, 2H), 7.62-7.77 (m, 6H), 7.98-8.01 (m, 2H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆) δ 25.2, 45.1, 46.7, 145.5, 124.7, 129.7, 130.2, 131.0, 131.9, 132.9, 134.9, 139.3, 147.8. IR (ATR) 1543, 1347, 1159, 988, 924, 851 cm⁻¹. HRMS (ESI+): calcd for C₂₆H₂₃⁷⁹Br ⁸¹BrN₄O₈S₄ (M+H): 806.8745, Found: 806.8761.

Attempted cyclization of bithiophene 6 with N, N'-bis(tbutoxycarbonyl)-1,2-ethylenediamine (Boc-

NHCH₂CH₂NHBoc): To a 20 mL Schlenk tube were added N, $N^{-}t$ -butoxycarbonyl-1,2-ethlenediamine (26 mg, 0.1 mmol) and anhydrous DMF (5.0 mL) under nitrogen atmosphere. Sodium hydride (60% in mineral oil, 16 mg, 0.1 mmol) was then added at 0 °C, and resulting mixture were stirred for 0.5 h at room temperature. To the solution tetrabromobithiophene **6** (53.5 mg, 0.105 mmol) was added. After stirring at room tem-

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perature for 0.5 h, water was added to reaction mixture to terminate the reaction and organic layer was extracted three times with dichloromethane. The solution was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude product. No desired product was confirmed by TLC and ¹H NMR analyses.

Attempted cyclization of bithiophene 6 with 1,2-ethylenediamine: To a solution of 6 (268 mg, 0.5 mmol) and ethylenediamine (37 mg, 0.5 mmol) in 2.5 mL DMF was added potassium carbonate (276 mg, 0.5 mmol) and stirring was continued for 19 h at 60 °C. The resulting mixture was poured into water and the organic product was extacted three times with dichloromethane. The solution was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude solid, in which no desired product was confirmed by TLC analysis.

The Supporting Information is available free of charge on the ACS Publications website. Variable temperature NMR studies of **8a**, details on X-ray structure analysis of **8a**, DFT calculation of **8a** and **3**, 1 H/ 13 C{ 1 H} NMR spectra for all new compounds.

AUTHOR INFORMATION

Corresponding Author

*E-mail: amori@kobe-u.ac.jp

Acknowledgment. This work was supported by Kakenhi by JSPS (Exploratory Research no. 24655083), Naohiko Fukuoka Memorial Foundation, and Special Coordination Funds for Promoting Science and Technology, Creation of Innovation Centers for Advanced Interdisciplinary Research Areas (Innovative Bio-production Kobe).

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