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# FORMATION OF SEVEN-MEMBERED-RING FUSED BITHIOPHENE DERIVATIVES BY NOSYL ANNULATION

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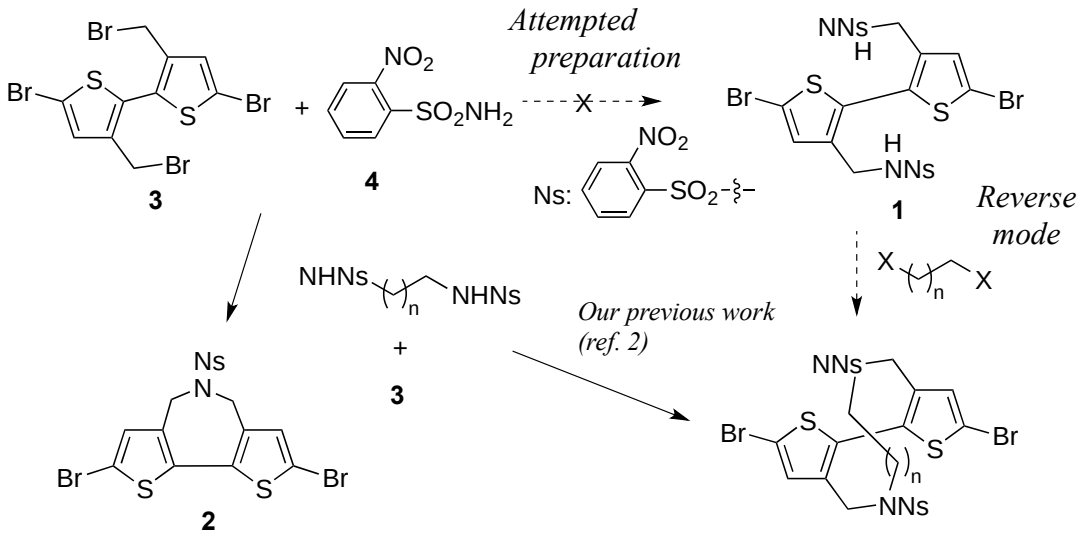
‡This paper is dedicated to Professor Kaoru Fuji on celebration of his 80th birthday.

**Abstract** – Nosyl annulation of a bithiophene derivative with nosylamide ($NsNH_2$) gives a 5-7-5 fused N, S-heterocyclic compound. The detailed molecular structure of the obtained nosylamide was analyzed by single-crystal X-ray crystallography. The obtained product was transformed into several amines and amides. The C−Br bond at the fused heterocycle was also subjected to cross-coupling reactions, where the nosyl group was found to be tolerant.

## INTRODUCTION

Heterocyclic compounds bearing a fused ring structure have attracted much attention in organic chemistry because a variety of such structures show application to advanced organic materials as well as biologically important molecules.[1] We have recently shown that a bithiophene derivative bearing two bromomethyl groups at the 3- and 3'-positions smoothly reacts with several 1,ω-dinosylated diamines to give annulated products of winding vine-shaped heterobiaryls, which suggest potential generation of molecular asymmetry.[2,3] The annulation was shown to form 10-12 membered-rings smoothly. During the course of our detailed study on the cyclization reaction, we have been interested in the nosyl annulation[4] of the *reverse mode* employing a bithiophene diamine with 1,ω-dihalides. We thus attempted the formation of starting diamine derivative **1** as illustrated in Scheme 1, however, diamine **1** was hardly

obtained to furnish the annulated product **2** bearing 5-7-5 membered-ring fused structure (Scheme 1). Herein, we report a new class of nosyl annulation employing nosyl amide and transformation of thus obtained fused heterocycles.




**Scheme 1.** Nosyl annulation of bithiophene derivatives

## RESULTS AND DISCUSSION

We first studied the reaction of bromomethylated bithiophene **3**[2,5] with Ns–$NH_2$ (**4**) under several conditions. Despite use of 2.2 equivalents of **4** dinosylated diamine **1** was not obtained at all, while the 5-7-5 membered ring-fused **2** was afforded as a sole product. It was also confirmed that the use of 1.0 equivalent of nosylamide **4** gave **2** also in excellent yield. Even by the slow addition of bithiophene **3** into the solution of **4**, diamine derivative **1** was hardly obtained probably because of the ease of seven-membered-ring formation allowing the intramolecular attack of the formed mononosylated intermediate. These results are summarized in Table 1.

**Table 1.** The reaction of dibromobithiophene **3** with nosylamide **4**[a]

| entry | **3** (eq) | **4** (eq) | conditions<br>temp (°C), time (h) | yield of **2**<br>% |
|---|---|---|---|---|
| 1 | 1 | 2.2 | 60 °C, 17 h | 91% |
| 2 | 1 | 1 | 60 °C, 18 h | 86% |
| 3 | 1 | 1 | rt, 3 h | 98% |
| 4[b] | 1 | 1 | rt, 26 h | 83% |

[a] The reaction was carried out with $K_2CO_3$ as a base in DMF as described in the experimental section.

[b] Slow addition of **3** into a mixture of **4** and $K_2CO_3$.

To confirm the molecular structure of the obtained product, single crystals of **2** were prepared by a solvent-evaporation method from a dichloromethane solution and single-crystal X-ray crystallography was performed (Figure 1). In the crystal, two thienyl rings have the same orientation by the nosyl annulation. These thienyl rings form a planar structure with the dihedral angle between two thienyl rings of 4º. The nitrogen atom locates out of the aromatic plane with the angle of 113º. The distance between N and S atoms was estimated to be 1.61 Å. In the packing structure, bithiophene groups form intermolecular π-π interaction with plane-to-plane distance of 3.73 Å.[6] The spectroscopic properties of **2** were measured by UV-vis absorption and photoluminescence spectroscopy in a THF solution indicating maximum absorption wavelength at 338 nm. Although photoluminescence (PL) was observed at 392 nm, the PL intensity was rather low with less than 1% the quantum yield because of the quench by the effect of the $SO_2$ or $NO_2$ group.

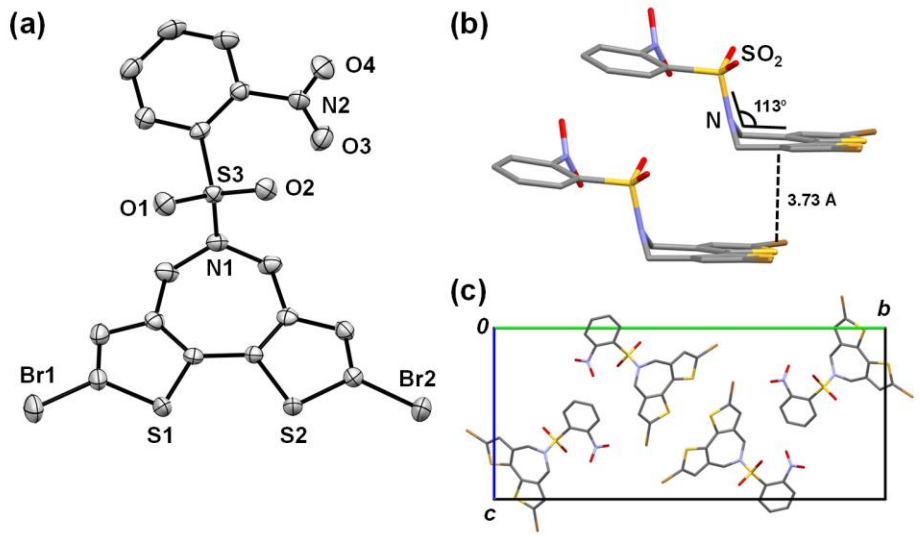
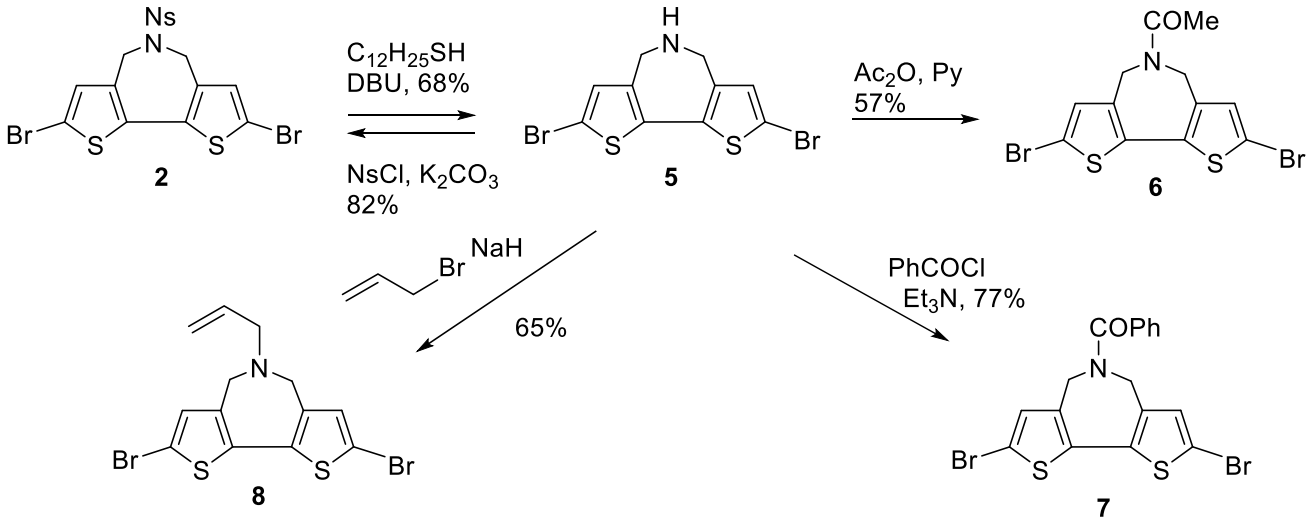


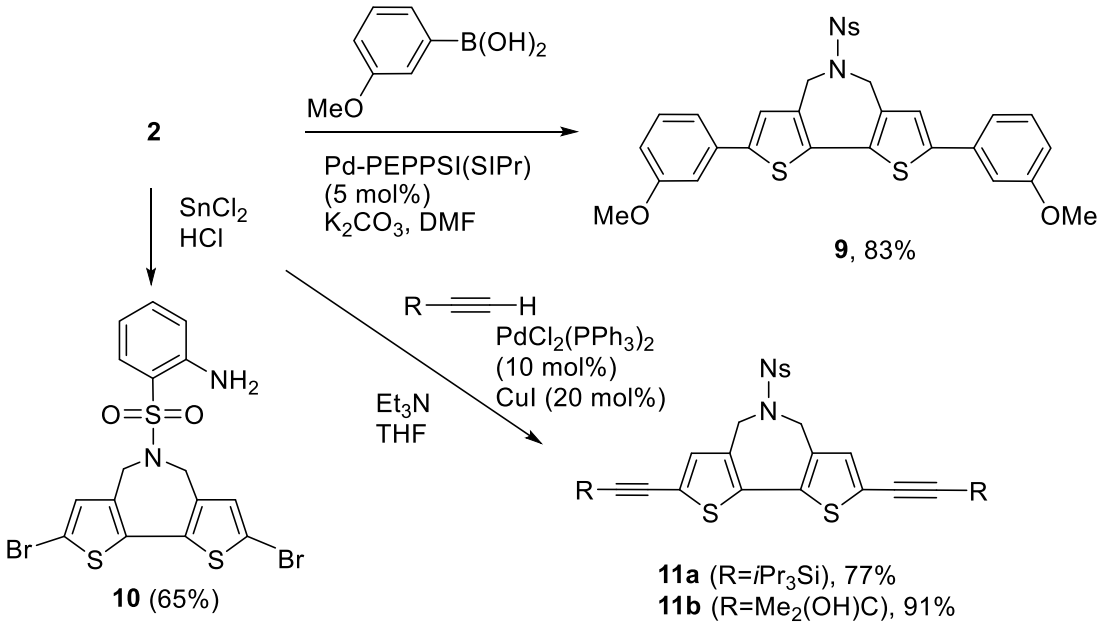

**Figure 1.** Molecular structure of **2** (CCDC-1923036)[6] (a) ORTEP drawn with 50% probability. (b) Side view. (c) Packing structure. Hydrogen atoms are omitted for clarity.

Since we have been successful in nosyl cyclization to give **2** smoothly, our interest was turned to the transformation of **2**. The nosyl group of **2** was found to be removed by usual denosylation protocol[4,7] affording **5** (68% yield), which was re-nosylated by the reaction of nosyl chloride to give **2** in 82% yield. The N−acylation reaction of **5** also proceeded to afford **6** and **7** in good yields 57% and 77%, respectively. The allylated product was also obtained in 65% yield by the reaction of allyl bromide (Scheme 2).




**Scheme 2.** Removal of the nosyl group of **2** and transformation of the thus deprotected amine **5**

The reaction at the carbon–bromine bond of the thiophene ring in the presence of a palladium catalyst was found to take place with the $NO_2$ group of **2** being intact.[8] The reaction of **2** with arylboronic acid[9] in the presence of 5 mol% Pd-PEPPSI-SIPr, 1,3-bis(2,6-diisopropylphenyl)imidazolidene)(3-chloropyridyl)-palladium(II) dichloride,[10] afforded the arylation product **9** in 83% yield. On the other hand, attempted reduction of the nitro group by hydrogenation resulted in giving the corresponding aniline derivative accompanied by partial debromination. The selective reduction to give aniline **10** was found to proceed with $SnCl_2$/HCl in 65% yield. The Sonogashira coupling was also found to proceed with **2** catalyzed by a palladium/copper system. The reaction of triisopropylsilylacetylene afforded the alkynylated product **11a** in 77% yield and the use of 2-methyl-3-butyn-2-ol gave **11b** (91% yield).[11]




**Scheme 3.** Transformation of the carbon-bromine bond of **2**

In summary, we have shown that the reaction of bithiophene bearing bromomethyl group at the 3,3'-positions with nosylamide gives annulated fused 5-7-5 membered tricyclic product. The annulation occurred preferentially despite use of two equivalents of nosylamide. The obtained product bearing the carbon-bromine bond was found to undergo transition metal-catalyzed coupling reaction such as Suzuki-Miyaura and Sonogashira coupling reactions to introduce aryl and alkynyl groups.

## EXPERIMENTAL

**General.** High-resolution mass spectra (HRMS) were performed on a JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. X-Ray crystal structure analysis was carried out with Bruker Single Crystal D8 Venture diffractometer and SHELXL-97 software at National Tsing-Hua University, Taiwan. All the reactions were performed in a flame-dried glassware prior to use under nitrogen atmosphere using standard Schlenk technique. Unless otherwise specified, chemicals were purchased and used as such without further purification. THF (anhydrous grade) was purchased from Kanto Chemical. Co. Ltd. and passed through alumina and copper column (Nikko Hansen & Co. Ltd.) or distilled from sodium dispersion in a mineral oil/benzophenone ketyl[12] prior to the use. Flash column chromatography was performed on Wakogel® C-300 (45–75 μm, Wako Pure Chemical Industries, Ltd.). Recycling preparative SEC (size exclusion chromatography) was performed with LC-9201 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL-1H/JAIGEL-2H.

**6-Aza-[2,1-b:3,4-b']bis(5-bromothieno)-6-(2-nitrobenzene)sulfonylcycloheptane (2):** To a solution of 5,5'-dibromo-3,3'-bis(bromomethyl)-2,2'-bithiophene (**3**, 1.5 g, 3.0 mmol) in 9 mL of DMF were successively added potassium carbonate (1.0 g, 7.2 mmol) and 2-nitrobenzenesulfonamide (0.61 g, 3.0 mmol) at room temperature. After stirring at room temperature for 3 h, the mixture was poured into water and the organic product was extracted three times with $CH_2Cl_2$. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give **2** as a colorless solid (1.61 g, 98%). Mp 214–216 °C; IR (ATR, $cm^{-1}$) 1537, 1371, 1352, 1158, 1078, 933, 818, 794; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.69 (dt, $J$ = 1.4, 7.8 Hz, 1H), 7.62 (dt, $J$ = 1.8, 7.8 Hz, 1H), 7.49 (ddd, $J$ = 8.2, 7.8, 1.4 Hz, 1H), 7.48 (dd, $J$ = 8.2, 1.8 Hz, 1H), 6.86 (s, 2H), 4.73 (s, 4H); $^{13}$C{$^1$H} NMR (101 MHz, DMSO-$d_6$) δ 147.3, 136.7, 134.7, 132.3, 132.2, 131.5, 131.1, 129.8, 124.3, 109.6, 49.1; HRMS (DART$^+$) *m/z* calcd. for $C_{16}H_{11}{}^{79}Br^{81}BrN_2O_4S_3$, 550.8227 $[M+H]^+$; found, 550.8208.

**6-Aza-[2,1-b:3,4-b']bis(5-bromothieno)cycloheptane (5):** To a solution of **2** (0.67 g, 1.2 mmol) in DMF (12 mL) were added 1-dodecanethiol (1.23 g, 6.1 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU: 0.93 g, 6.1 mmol). The mixture was stirred at room temperature for 3 h. The resulting mixture was poured

into 6 M aqueous hydrochloric acid to form a precipitate, which was washed with $Et_2O$ repeatedly to leave a crude solid. The residue was recrystallized from MeOH to provide **5** as a colorless solid of hydrogen chloride salt (330 mg, 68%). Mp 234 °C (decomp); IR (ATR, $cm^{-1}$) 2950, 2770, 2622, 2575, 1577, 1457, 1417, 962; $^1H$ NMR (400 MHz, DMSO-$d_6$) δ 9.71 (s, 2H), 7.29 (s, 2H), 4.46 (s, 4H); $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-$d_6$) δ 133.1, 132.3x2, 110.6, 46.1; HRMS (DART$^+$) *m/z* calcd. for $C_{10}H_8{}^{79}Br_2NS_2$, 363.8465 $[M+H]^+$; found, 363.8459 (as dehydrochlorinated fragment).

**Reinstallation of the nosyl group to 5 leading to 2:** To a solution of **5** (40 mg, 0.1 mmol) and 2-nitrobenzenesulfonyl chloride (NsCl, 22 mg, 0.1 mmol) in $CH_2Cl_2$ (0.3 mL) was added triethylamine (35 μL, 0.25 mmol) and the resulting mixture was stirred at room temperature for 16 h. The resulting mixture was poured into water and the organic product was extracted three times with $CH_2Cl_2$. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give 45 mg of **2** as a colorless solid (82%), which was confirmed to be identical with the authentic sample.

**6-Aza-[2,1-b:3,4-b']bis(5-bromothieno)-6-acetylcycloheptane (6):** To a solution of **5** (40 mg, 0.1 mmol) in pyridine (3.0 mL) was added acetic anhydride (19 μL, 0.2 mmol) and the resulting mixture was stirred at room temperature for 3 h. The resulting mixture was poured into water and the organic product was extracted three times with $CH_2Cl_2$. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a crude solid. Purification by silica gel chromatography (hexane/MeOAc = 1:1) to provide **7** as a colorless solid (23 mg, 57%). Mp 185–187 °C; IR (ATR, $cm^{-1}$) 1634, 1473, 1447, 1429, 1412, 1384, 1280, 1251, 1207, 991, 961, 938, 835; $^1H$ NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.83 (s, 1H), 4.77 (s, 2H), 4.63 (s, 2H), 2.10 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.2, 136.9, 135.1, 134.0, 132.1, 131.7, 130.4, 111.2, 110.9, 50.1, 47.0, 21.5; HRMS (DART$^+$) *m/z* calcd. for $C_{12}H_{10}{}^{79}Br^{81}BrNOS_2$, 407.8550 $[M+H]^+$; found, 407.8532.

**6-Aza-[2,1-b:3,4-b']bis(5-bromothieno)-6-benzoylcycloheptane (7):** To a solution of **5** (40 mg, 0.1 mmol) in THF (3.0 mL) were added triethylamine (40 μL, 0.31 mmol) and benzoyl chloride (12 μL, 0.1 mmol). After stirring at room temperature for 5 h, the resulting mixture was poured into water and the organic product was extracted three times with $CH_2Cl_2$. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a crude solid. Purification by column chromatography on silica gel (hexane/MeOAc = 5:1) followed by preparative SEC using $CHCl_3$ as an eluent provided **7** as a colorless solid (36 mg, 77%). Mp 180–181 °C; IR (ATR, $cm^{-1}$) 1637, 1454, 1414, 1294, 1260, 1203, 1138, 995, 960, 927; $^1H$ NMR (400 MHz, DMSO-$d_6$) δ 7.38–

7.49 (m, 3H), 7.31 (s, 1H), 7.20 (d, *J* = 6.9, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 6.85 (s, 1H), 4.85 (s, 2H), 4.71 (s, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.2, 136.563, 135.557, 135.4, 133.6, 132.5, 131.9, 130.4, 130.1, 128.6, 127.0, 111.0x2, 51.6, 46.8; HRMS (DART$^+$) *m/z* calcd. for $C_{17}H_{12}{}^{79}Br^{81}BrNOS_2$, 469.8707 $[M+H]^+$; found, 469.8717.

**6-Aza-[2,1-b:3,4-b']bis(5-bromothieno)-6-(2-propen-1-yl)cycloheptane (8):** To a solution of **3** (54 mg, 0.14 mmol) and sodium hydride (16 mg, 0. 39 mmol) in THF (3 mL) was added 3-bromo-1-propene (23 μL, 0.27 mmol) and stirring was continued at 40 °C for 72 h. The resulting mixture was poured into water and the organic product was extracted three times with $CH_2Cl_2$. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a crude solid. Purification by silica gel chromatography (hexane/MeOAc = 5:1) to provide **8** as a yellow solid (36 mg, 65%). Mp 96–98 °C; IR (ATR, $cm^{-1}$) 1452, 1416, 1368, 1300, 1181, 1124, 952, 922, 826; $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 6.68 (s, 2H), 5.85 (ddt, *J* = 16.9, 10.5, 6.4 Hz, 1H), 5.12 (dd, *J* = 10.1, 1.4 Hz, 1H), 5.05 (dd, *J* = 17.4, 1.4 Hz, 1H), 4.07 (s, 4H), 3.13 (d, *J* = 6.4 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 137.7, 135.4, 132.9, 132.2, 118.5, 109.7, 55.3, 55.1; HRMS (DART$^+$) *m/z* calcd. for $C_{13}H_{12}{}^{79}Br^{81}BrNS_2$, 405.8757 $[M+H]^+$; found, 405.8739.

**6-Aza-[2,1-b:3,4-b']bis(5-(3-methoxyphenyl)thieno)-6-(2-nitrobenzene)sulfonylcycloheptane (9):** To a solution of **2** (55 mg, 0.10 mmol) and 3-(methoxyphenyl)boronic acid (30 mg, 0.20 mmol) in THF (1 mL) were added potassium carbonate (111 mg, 0.8 mmol) and (1,3-bis(2,6-diisopropylphenyl)-imidazolidene)(3-chloropyridyl)palladium(II) dichloride (3 mg, 5 μmol). The mixture was stirred at 100 °C for 19 h. The resulting mixture was poured into water and the organic product was extracted three times with $Et_2O$. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a crude solid. Purification by silica gel chromatography (hexane/MeOAc = 5:1) to provide **9** as a yellow solid (37 mg, 83%). Mp 159–161 °C; IR (ATR, $cm^{-1}$) 2958, 2927, 2855, 1600, 1544, 1467, 1353, 1081, 1048, 921; $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.49 (ddd, *J* = 7.8, 7.6, 1.4, Hz, 1H), 7.37 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.36 (ddd, *J* = 7.8, 7.8, 1.8 Hz, 1H), 7.30 (t, *J* = 7.8, Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.12 (s, 2H), 7.07 (dd, *J* = 2.3, 1.8 Hz, 2H), 6.86 (ddd, *J* = 7.8, 2.3, 1.8 Hz, 2H), 4.89 (s, 4H), 3.87 (s, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 160.2, 141.9, 135.0, 134.7, 133.5, 132.4, 131.8, 131.1, 130.3, 130.2, 124.8, 123.5, 118.2, 113.8, 111.2, 55.5, 50.4, 29.9; HRMS (DART$^+$) *m/z* calcd. for $C_{30}H_{24}N_2O_6S_3$, 605.0874 $[M+H]^+$; found, 605.0910.

**6-Aza-[2,1-b:3,4-b']bis(5-bromothieno)-6-(2-aminobenzene)sulfonylcycloheptane (10):** To 10 mL screw-capped test tube equipped with a magnetic stirring bar was dissolved tin(II) chloride dihydrate

(0.23 g, 1.0 mmol**)** in 1.0 mL of 12 M hydrochloric acid at 0 °C. The reaction temperature was raised to room temperature and **2** (0.11 g, 0.20 mmol) dissolved in 3 mL of THF was added. The resulting mixture was allowed to stir for 28 h. The aqueous phase was extracted with $CH_2Cl_2$ and the combined organic layer was dried over anhydrous sodium sulfate. Purification by column chromatography on silica gel using hexane/$CH_2Cl_2$ (2:3) as an eluent afforded 68 mg of **10** (65%). Mp 186–188 °C; IR (ATR, $cm^{-1}$) 2923, 2854, 1615, 1483, 1452, 1418, 1322, 1141, 1067, 751; $^1$H-NMR (400 MHz, DMSO-$d_6$) δ 7.06–7.18 (m, 3H), 7.10 (s, 2H), 6.64 (d, $J$ = 8.2 Hz, 1H), 6.40 (dd, $J$ = 8.2, 6.9 Hz, 1H), 5.89 (s, 2H), 4.69 (s, 4H); $^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 145.5, 134.5, 134.3, 133.1, 131.2, 129.2, 120. 6, 117.4, 117.3, 110.5, 49.6; HRMS (DART$^+$) *m/z* calcd. for $C_{16}H_{13}{}^{79}Br^{81}BrN_2O_2S_3$, 520.8485 $[M+H]^+$; found, 520.8467.

**6-Aza-[2,1-b:3,4-b']bis(5-(2-triisopropylsilylethynyl)thieno)-6-nitrobenzenesulfonylcycloheptane (11a):** To a solution of **2** (55 mg, 0.10 mmol) in 2 mL of THF were added bis(triphenylphosphine)palladium(II) dichloride (7 mg, 0.010 mmol), copper(I) iodide (4 mg, 0.020 mmol), (triisopropylsilyl)acetylene (49 μmL, 0.22 mmol) and triethylamine (0.28 mL, 2.0 mmol). The mixture was stirred at room temperature for 5 h and filtered through a pad of celite. The filtrate was concentrated under reduced pressure to leave a crude solid. Purification by silica gel chromatography (hexane/MeOAc = 5:1) to provide **11a** as a yellow solid (58 mg, 77%). Mp 178–180 °C; IR (ATR, $cm^{-1}$) 2943, 2865, 2143, 1548, 1463, 1371, 1169, 920, 748, 681; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, $J$ = 7.8, 1.4, Hz, 1H), 7.58 (dt, $J$ = 1.4, 7.8 Hz, 1H), 7.44–7.49 (m, 2H), 6.98 (s, 2H), 4.75 (s, 4H), 1.12 (s, 36H), 1.11 (s, 6H); $^{13}$C{$^1$H} NMR (101 MHz, DMSO-$d_6$) δ 148.1, 134.7, 133.7, 133.6, 132.8, 132.5, 131.4, 130.6, 123.9, 122.1, 98.7, 98.4, 49.8, 18.8, 11.4; HRMS (DART$^+$) *m/z* calcd. for $C_{16}H_{11}{}^{79}Br^{81}BrN_2O_4S_3$, 550.8227 $[M+H]^+$; found, 550.8208.

**6-Aza-[2,1-b:3,4-b']bis(5-(2-(3-hydroxy-3-methylbutyn-1-yl)thieno)-6-nitrobenzenesulfonylcyclohe-ptane (11b):** To a solution of **2** (55 mg, 0.10 mmol) in 2 mL of THF were added bis(triphenylphosphine)palladium(II) dichloride (7 mg, 0.010 mmol), copper(I) iodide (4 mg, 0.020 mmol), 2-methyl-3-butyn-2-ol (21 μmL, 0.22 mmol) and triethylamine (0.28 mL, 2.0 mmol). The mixture was stirred at room temperature for 5 h and filtered through a pad of celite. The filtrate was concentrated under reduced pressure to leave a crude solid. Purification by silica gel chromatography (hexane/MeOAc = 1:1) to provide **11b** as a yellow solid (51 mg, 91%). Mp 149–151 °C; IR (ATR, $cm^{-1}$) 3288, 2976, 2961, 1543, 1353, 1171, 1074, 1027, 955, 881; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, $J$ = 8.0, 1.4, Hz, 1H), 7.55 (ddd, $J$ = 8.0, 7.8, 1.4 Hz, 1H), 7.46 (dt, $J$ = 1.4, 7.8 Hz, 1H), 7.45 (dd, $J$ = 7.8, 1.4 Hz, 1H), 6.94 (s, 2H), 4.77 (s, 4H) , 1.99 (s, 2H), 1.61 (s, 12H); $^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 148.1, 134.6, 133.7,

133.3, 132.9, 132.3, 131.3, 130.3, 123.8, 121.2, 99.8, 74.8, 65.9, 49.9, 31.4; HRMS (DART$^+$) *m/z* calcd. for $C_{26}H_{25}N_2O_6S_3$, 557.0847 $[M+H]^+$; found, 557.0875.

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## REFERENCES AND NOTES

1. T. Eicher, S. Hauptmann, and A. Speicher, *The Chemistry of Heterocycles : Structure, Reactions, Syntheses, and Applications*, Wiley-VCH, Berlin, 2003; A. F. Pozharskiĭ, A. T. Soldatenkov, and A. R. Katritzky, *Heterocycles in Life and Society : An Introduction to Heterocyclic Chemistry, Biochemistry and Applications*, Wiley, Hoboken, N. J., 2011; Y. Hayashi, K. Okano, and A. Mori, *Org. Lett.*, 2018, **20**, 958.
2. S. Ashida, N. Tanaka, Y. Ito, M. Matsuoka, T. Hashimoto, K. Okano, Y. Miyazaki, T. Kobayashi, T. Yaita, and A. Mori, *J. Org. Chem.*, 2018, **83**, 14797.
3. S. Nishio, T. Somete, A. Sugie, T. Kobayashi, T. Yaita, and A. Mori, *Org. Lett.*, 2012, **14**, 2476; Y. Okayama, S. Tsuji, Y. Toyomori, A. Mori, S. Arae, W.-Y. Wu, T. Takahashi, and M. Ogasawara, *Angew. Chem. Int. Ed.*, 2015, **54**, 4927; K. Maruhashi, Y. Okayama, R. Inoue, S. Ashida, Y. Toyomori, K. Okano, and A. Mori, *Sci. Rep.*, 2018, **8**, 1704.
4. T. Kan and T. Fukuyama, *Chem. Commun.*, 2004, 353; T. Kan, H. Kobayashi, and T. Fukuyama, *Synlett*, 2002, 697; T. Kan, A. Fujiwara, H. Kobayashi, and T. Fukuyama, *Tetrahedron*, 2002, **58**, 6267.
5. K. Fujita, Y. Sumino, K. Ide, S. Tamba, K. Shono, J. Shen, T. Nishino, A. Mori, and T. Yasuda, *Macromolecules*, 2016, **49**, 1259; Y. Toyomori, S. Tsuji, S. Mitsuda, Y. Okayama, S. Ashida, A. Mori, T. Kobayashi, Y. Miyazaki, T. Yaita, S. Arae, T. Takahashi, and M. Ogasawara, *Bull. Chem. Soc. Jpn.*, 2016, **89**, 1480; A. Mori, K. Ide, S. Tamba, S. Tsuji, Y. Toyomori, and T. Yasuda, *Chem. Lett.*, 2014, **43**, 640.
6. CCDC-1923036 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
7. P. Villo, L. Toom, E. Eriste, and L. Vares, *Eur. J. Org. Chem.*, 2013, 6886.
8. Q. Shao, J. He, Q.-F. Wu, and J.-Q. Yu, *ACS Catal.*, 2017, **7**, 7777.
9. A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147; N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.

10. E. A. B. Kantchev, C. J. O'Brien, and M. G. Organ, *Angew. Chem. Int. Ed.*, 2007, **46**, 2768.
11. K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.*, 1975, **16**, 4467; R. Chinchilla and C. Nájera, *Chem. Soc. Rev.*, 2011, **40**, 5084.
12. R. Inoue, M. Yamaguchi, Y. Murakami, K. Okano, and A. Mori, *ACS Omega*, 2018, **3**, 12703.