Heteroatom Chemistry
Volume 18, Number 3, 2007

A New Method for the Synthesis of Dinaphtho[1,2-*b*;2′,1′-*d*]thiophenes and Selenophenes

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Received 6 January 2006; revised 2 April 2006

ABSTRACT: *Naphthalene-1-sulfonic acid dimethylamides were treated with n-BuLi and elemental sulfur or selenium to afford dinaphtho[1,2-b:2′,1′-d]thiophenes and selenophenes, respectively. This is the first example of making two C—S/Se bonds and a C—C bond in a single step at room temperature and also demonstrates a useful method for the synthesis of both thiophenes and selenophenes on naphthalene. In the case of the reactions of elemental selenium, diselenides were also obtained along with dinaphtho[1,2-b:2′,1′-d]selenophenes. The structure of dinaphtho[1,2-b:2′,1′-d]thiophene was characterized by X-ray crystallography as a representative molecule.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:239–248, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20291

INTRODUCTION

Thiophenes and selenophenes condensed to aromatic systems are promising building blocks for optoelectrical polymers due to their ability to form highly conductive charge transfer complexes [1–5]. Planar π-conjugated five-unit rings of dinaphtho[1,2-*b*:2′,1′-*d*]thiophenes and selenophenes are also an important class of compounds similar to pentacene analogues for organic field-effect transistors (OFETs) application [6]. Efficient and convenient methods for their preparation are, therefore, in demand to solve some remaining problems. For example, Tedjamulia and his coworkers [7] have synthesized dinaphtho[1,2-*b*:2′,1′-*d*]thiophene in seven steps including five other isomers of dinaphthothiophene. Sulfur-bridging reactions of 2,2′-binaphthyl (**A**) with hydrogen sulfide at 550°C [8a] and diphenyl thiophene containing unsaturated groups at 1000°C [8b] also afforded dinaphtho[1,2-*b*:2′,1′-*d*]thiophene (see Fig. 1). Some other multistep methods are also available in the literature for the synthesis of dinaphtho[1,2-*b*:2′,1′-*d*]thiophenes [9]. Binaphthyl (BINAP) derivatives

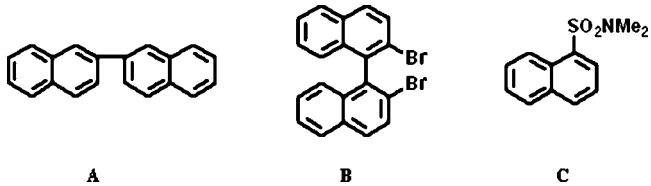

FIGURE 1 Typical substrates.

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Contract grant sponsor: Ministry of Education, Culture, Sports, Science and Technology, Japan.
Contract grant numbers: 16033205 and 15550023.

(**B**) are widely used for the synthesis of isomeric dinaphtho[2,1-*b*:1′,2′-*d*]thiophenes and selenophenes by selective lithiation and chalcogenization [10] as well as thermal rearrangement with intramolecular displacement [11]. Thermal cyclization with sulfur is the most common and well-known method to date, to produce sulfur linkage between two polyaromatic hydrocarbons.

Synthesis of thiophene and selenophene by the same method in a few steps remains unexplored, and only two examples [12,13] have been reported. Regioselective synthesis of thiophenes and selenophenes fused to two naphthalene cores via peri–peri C—S/Se linkage is the most difficult among all positional isomers of dinaphthothiophenes. Naphthalene-1-sulfonic acid dimethylamide (**C**) contains one functional group ($-SO_2NMe_2$) and has no C—C coupling between two naphthalene backbones like **A** or **B**. Thus, compound **C** is simple and inexpensive among substrates for one-step preparation of dinaphtho[1,2-*b*:2′,1′-*d*]thiophenes and selenophenes. Large π-conjugated isomeric chalcogenophenes are rare in the literature due to the limitations of selective synthesis, low reactivity, and poor tendency of polyaromatics to cyclize with various chalcogenating reagents.

RESULTS AND DISCUSSION

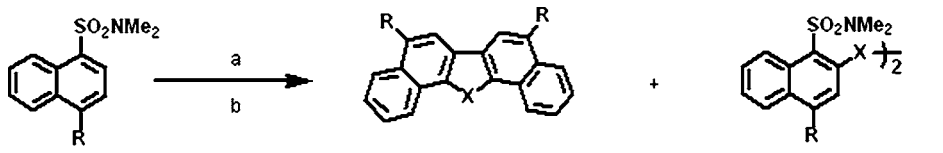
Here, we attempted to introduce a thiol group on sulfonamide **C** through selective ortholithiation, sulfurization, and acidification. Surprisingly, we isolated a thiophene fused to two naphthalene molecules on both sides. After ^{1}H NMR analysis of all six isomers of dinaphthothiophenes [14,15], initially the structure of unexpected product **3** was established (Scheme 1). Later, selenization of the same system also afforded dinaphtho[1,2-*b*:2′,1′-*d*]selenophene (**4**) [16]. Such curious results inspired us to study more about the novel synthetic methodology and also in detail about the formation of such chalcogenophenes.

Substrates **1** and **2** were prepared by conventional methods. 1-Bromo-naphthalene was lithiated with *n*-BuLi in dry ether and chlorosulfonated by SO_2Cl_2 at -20°C to afford naphthalene-1-sulfonyl chloride. On the other hand, 4-phenylnaphthalene-1-sulfonyl chloride was prepared from 1-phenylnaphthalene by direct chlorosulfonation with chlorosulfonic acid in CH_2Cl_2 at room temperature. Sulfonamides **1** and **2** were synthesized by the reaction of naphthalene-1-sulfonyl chloride and 4-phenylnaphthalene-1-sulfonyl chloride with an aqueous solution of dimethylamine both in 95% yields.

Both substrates, **1** and **2**, easily reacted with *n*-BuLi in tetramethyl ethylenediamine (TMEDA) at 0°C and with elemental sulfur or selenium to afford dinaphtho[1,2-*b*:2′,1′-*d*]thiophenes or selenophenes in moderate yields (Scheme 1). All of these chalcogenophenes are stable in air and also are easy to separate from the reaction mixture by column chromatography. Unfortunately, we did not succeed in preparation of analogous tellurophenes by this methodology because of the large size and/or low reactivity of metallic tellurium.

Substituents on substrates have an impact on the cyclization. Thiophenes and selenophenes are not formed when R is changed from phenyl to methyl. An electron-donating methyl group on the substrate at the opposite peri position of the sulfonamide group renders cyclization, while hydrogen or phenyl group on the same position accelerates the reaction. To clarify the formation mechanism of such chalcogenophenes, we attempted to trap related intermediates from the reaction mixture.

During the synthesis of selenophene, we also observed simultaneous formation of **5** and **8** as side products (Scheme 1). The reaction mixture was quenched over water or methanol during 2 to 6 h reaction time in the presence or absence of elemental



1 (R = H)

2 (R = Ph)

3 (30%, X = S, R = H)
4 (31%, X = Se, R = H)
6 (37%, X = S, R = Ph)
7 (11%, X = Se, R = Ph)

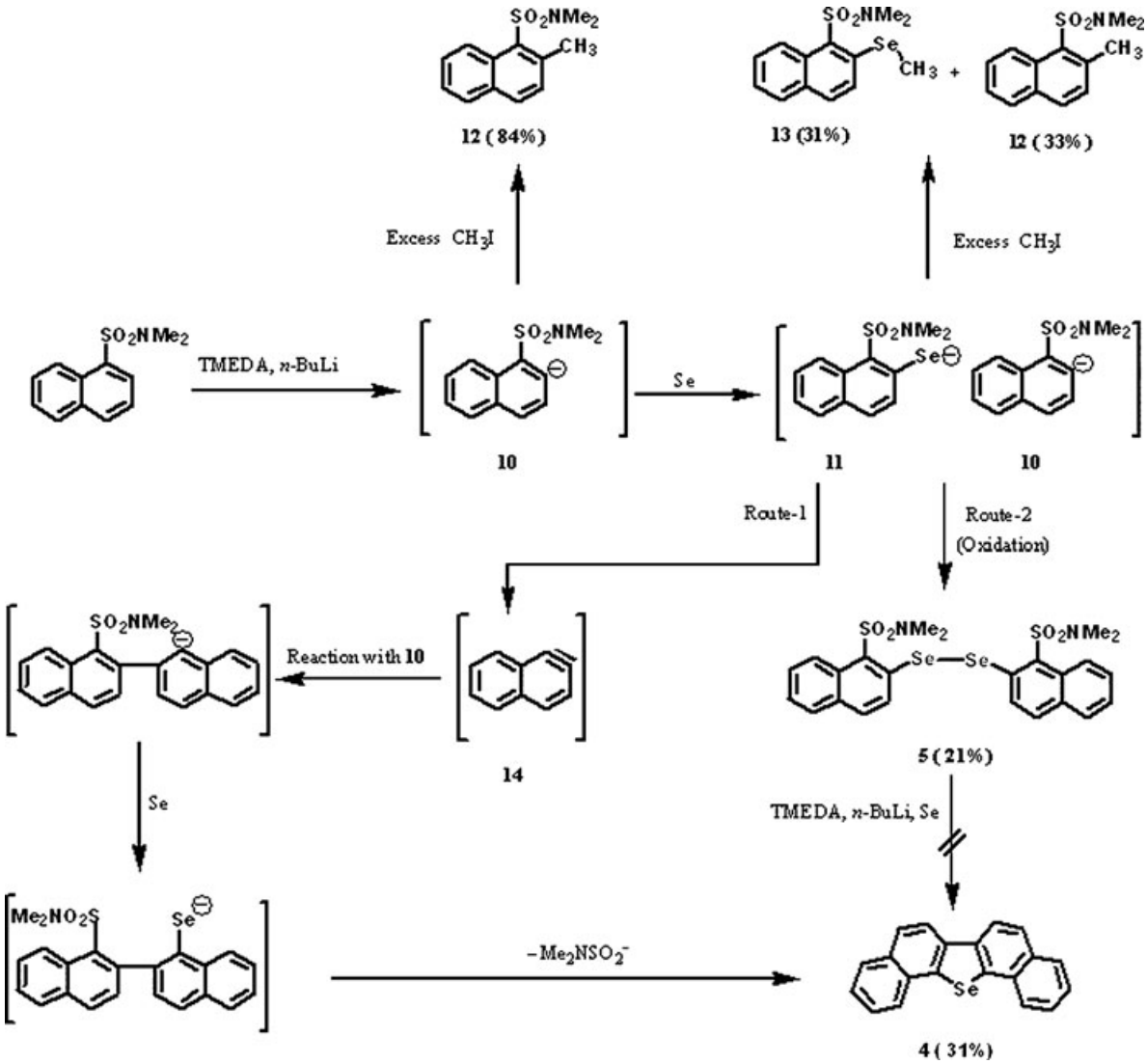
5 (21%, X = Se, R = H)
8 (15%, X = Se, R = Ph)

SCHEME 1 (a) TMEDA, *n*-BuLi, 0°C, 6 h; (b) S_8/Se, RT, 3 h.

sulfur and selenium. In these cases, no specific intermediates were isolated except recovery of substrates. Initially, there were two ideas about the mechanism: (a) oxidative coupling of naphthalene-1-sulfonic acid dimethylamide carbanion (**10**) results in the formation of a C—C bond between two naphthalene backbones. Later, elimination of the functional groups and cyclization with elemental sulfur or selenium make C—S/Se—C bonds or (b) via intermediate formation of 1,2-naphthalyne (**14**) in strong basic condition (Scheme 2, route 1). Isolation of products, **5** and **8**, during selenophene formation, has strengthened our second speculation. It was expected to get other isomers of dinaphthochalcogenophenes if the reaction proceeded through an intermediate 1,2-naphthalyne (**14**), but we isolated a single cyclized product in all cases.

According to Scheme 2, the formation of product **5** easily proves in situ generation of naphthalene-1-sulfonic acid dimethylamide carbanion (**10**) and naphthalene-1-sulfonic acid dimethylamide-2-selenolate anion (**11**) in the system. The intermediate 1,2-naphthalyne (**14**) may be formed from either **11** or **10**, as a strong basic condition always accelerates benzyne [17] formation even by elimination of aromatic protons. Analogous 1,2-naphthalyne (**14**) has also been reported from 1-bromo-2-fluoronaphthalene [18] and 1-bromonaphthalene [19], respectively.

Oxygen accelerates the generation of 1,1′-bis(*N*,*N*-dimethylaminosulfonylnaphthyl)-2,2′-diselenide (**5**). That is why on increasing the reaction time the yields of both products **5** and **8** increase due to more contact of oxygen with the reaction



SCHEME 2 Plausible mechanism for the generation of **4** and **5**.

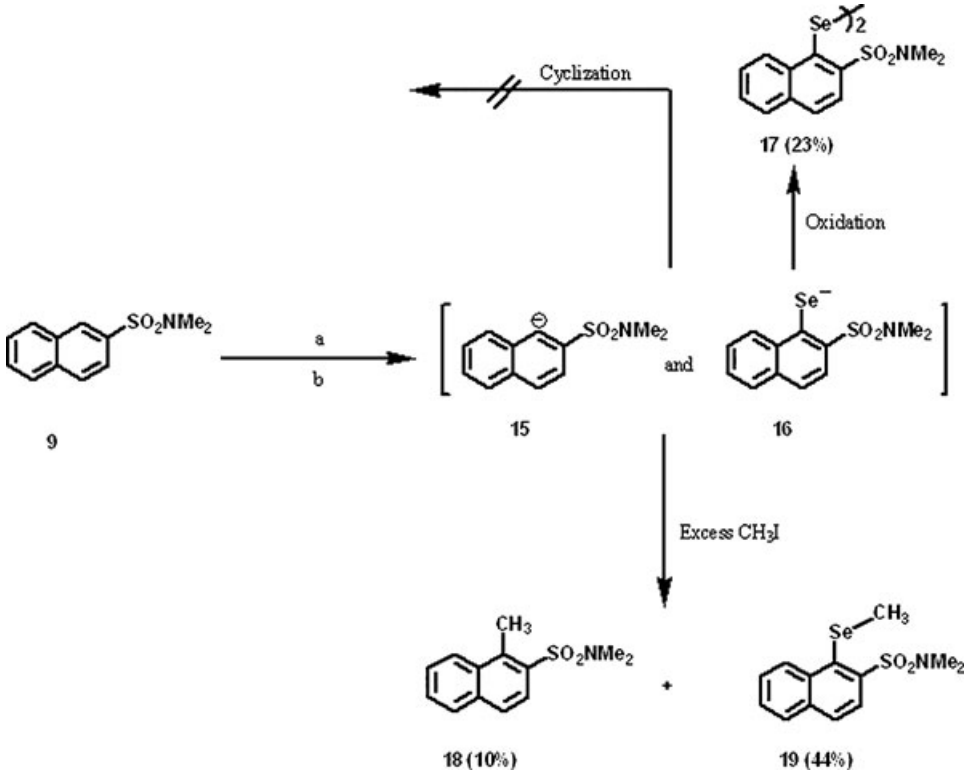
mixture. But under the same cyclization condition, **5** alone does not go to the respective dinaphtho[1,2-*b*:2′,1′-*d*]selenophene (Scheme 2, route 2).

Trapping experiments also gave clear evidence for the generation of intermediates **10** and **11**. Quenching of a lithiated mixture of the substrate with CH_3I afforded product **12** in 84% yield. Later, we inserted elemental selenium into the solution of carbanion (**10**) and trapping with CH_3I afforded four products in **11** (22%), **13** (31%), **5** (8%), and **4** (4%) yield, respectively. So, the substrate excessively generates the intermediates **10** and **11** in this system (Scheme 2).

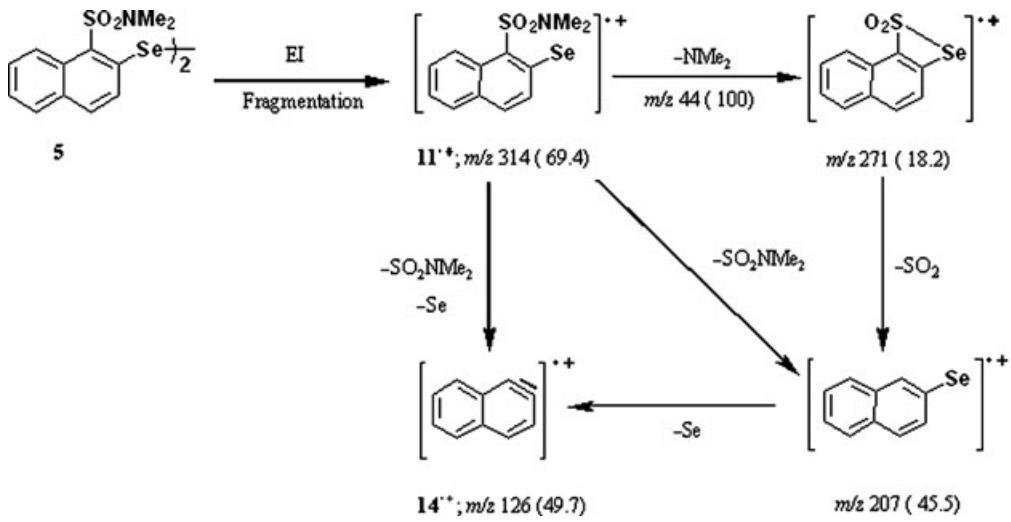
Naphthalene-2-sulfonic acid dimethylamide (**9**) did not give any dinaphthothiophene and selenophene under the same conditions (Scheme 3), but it afforded 2,2′-bis(*N*,*N*-dimethylaminosulfonylnaphthyl)-1,1′-diselenide (**17**) in 23% yield. In a trapping experiment, isolation of products **18** (10%) and **19** (44%) easily clarified the generation of intermediates **15** and **16**. The generation of carbanion and selenolate anions is not only essential criteria for the synthesis of chalcogenephenes. The isomeric position of the sulfonamide group on naphthalene and its activity in terms of conversion to other intermediates, like **14**, are also important factors for cyclization. Carbanion (**15**) and selenolate anion (**16**) produced in Scheme 3 are less active than the corresponding intermediates **10** and **11** of Scheme 2 to convert them to respective thiophenes or selenophenes. The peri-position of the sulfonamide group on naphthalene is essential for cyclization.

Mass spectra of **5** and **8** also showed important information regarding possible intermediates. For compound **5**, radical cationic peaks for both plausible intermediates $\mathbf{11}^{\bullet+}$(*m*/*z* 314) and $\mathbf{14}^{\bullet+}$ (*m*/*z* 126) were observed in 69.4% and 49.7% intensity, respectively (Scheme 4). Fragmentation patterns and simultaneous generation of various radical cations from **5** suggest that energetically it is favorable to form 1,2-naphthalyne (**14**) from the respective selenolate anion by sequential elimination of selenium and functional group.

We also tried to understand the unique role of the selenolate anion (**11**) in the cyclization. For independent generation of the selenolate anion (**11**) in TMEDA, compound **5** was reduced with $LiAlH_4$ at 0°C (not shown in the scheme). Later, intermediate **11** was trapped by the excess CH_3I from the reducing mixture. Quantitative isolation of **13** easily indicated the excessive formation of intermediate **11** in TMEDA solution. But, this intermediate **11** did not go to the respective selenophene in the presence of elemental selenium. Thus, intermediate **11** is not independently responsible for the generation



SCHEME 3 (a) TMEDA, *n*-BuLi, 0°C, 6 h; (b) Se, RT, 3 h.



SCHEME 4 Possible fragmentation pattern of **5**. Relative intensities are shown in parentheses.

of dinaphtho[1,2-*b*:2′,1′-*d*] selenophene (**4**). Intermediate **10** has also an important role in this reaction.

Intermediate **10** is a less possible precursor than intermediate **11** for the generation of 1,2-naphthalyne (**14**). Heavy atom such as iodine elimination is a traditional process for the generation of benzyne in aromatic systems. As selenium is also a heavy atom, so intermediate **11** is a more expectable precursor for the formation of 1,2-naphthalyne (**14**). Experimental results suggest that both intermediates are essential for the generation of cyclized products. We assume that selenolate or thiolate anion is responsible for the generation of 1,2-naphtahlyne (**14**), and the reaction of carbanion **10** with 1,2-naphthalyne (**14**) results a C—C bond. Finally, elimination of the sulfonamide group from C—C coupled dinaphthoselenolate anion results C—Se—C linkage between two naphthalene molecules (Scheme 2, route 1).

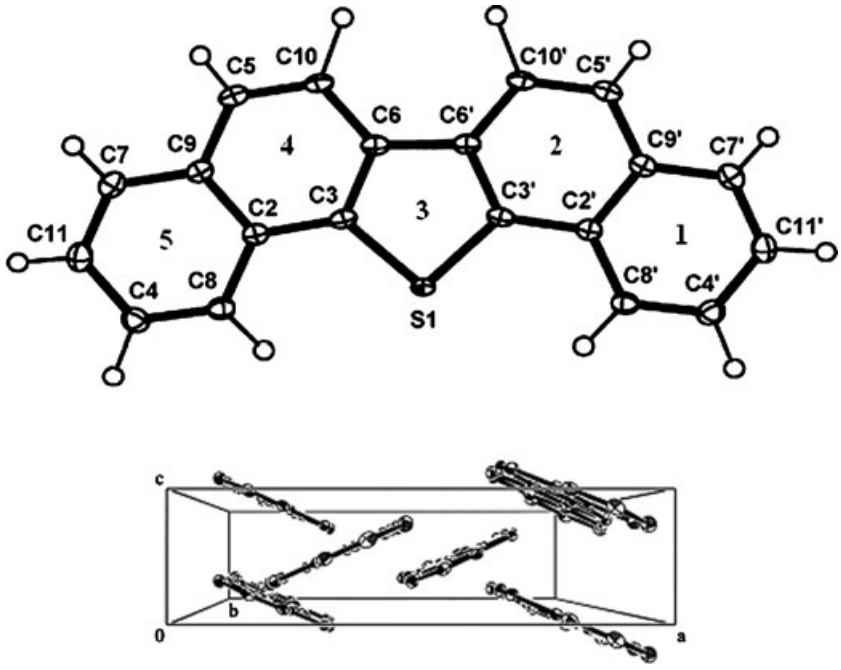


FIGURE 2 ORTEP drawing and crystal packings of compound 4.

The thiolate anion does not afford any specific isolable disulfide but the selenolate anion does (Scheme 1). The structure and reactivity of thiolate and selenolate anions generated in the reaction mixtures are not the same. But sulfur-containing reaction mixtures generally afford thiophenes in higher overall yield than selenophenes. Specifically, diselenides have no role in the cyclization; these side products are due to oxidation. The results of Scheme 3 also clarify more about this assumption as substrate **9** gave only diselenide (**17**) and no cyclized product. We also tried to trap 1,2-naphthalyne (**14**) from the reaction mass by using the excess furan under the same reaction condition. But unfortunately, cycloadduct of 1,2-naphthalyne (**14**) has not yet been isolated.

Although several authors [7–9] have reported dinaphtho[1,2-*b*:2′,1′-*d*]thiophenes, at first we characterized and analyzed its structure by X-ray crystallography (Fig. 2). Valle has analyzed the structure of another isomer, dinaphtho[1,2-*b*:1′,2′-*d*]thiophene, in terms of planarity [20]. Dinaphtho[1,2-*b*:1′,2′-*d*]thiophene is thermodynamically stable but is a nonplanar molecule due to peri–peri C—C linkage between the naphthalene backbones. On the other hand, dinaphtho[1,2-*b*:2′,1′-*d*]thiophene is both planar and stable. The value of dihedral angles among five units of its crystal structure emphasizes its flat nature (Table 3). This is may be due to the relaxation of strain energy by peri–peri C—S—C linkage between two naphthalene cores. Crystal packing and molecular arrangement on the plane also indicate low molecule-to-molecule interactions in solid state.

TABLE 1 Selected Bond Lengths, Angles, and Torsion Angles

Bond Lengths (Å)		*Bond Angles (°)*	
S(1)—C(3)	1.743(2)	C(3)—S(1)—C(3′)	90.91(7)
C(3)—C(6)	1.394(3)	S(1)—C(3)—C(6)	112.6(1)
		C(3)—C(6)—C(6′)	112.1(1)

TABLE 2 Crystal properties

Crystal's Data	
Crystal system	Orthorhombic
Space group	Pnma (#62)
Temperature	123 K
a (Å)	13.044(6)
b (Å)	25.97(1)
c (Å)	3.859(2)
V (Å^3)	1306(1)
Z	2
D_{cak} (g cm^{-1})	1.445
μ(MoKα) (cm^{-1})	2.35
*R*I	0.049
Rw	0.182
GOF	1.002

TABLE 3 Dihedral Angles between Least-Squares Plane

Plane	*Plane*	*Angle (°)*	*esd*
1	2	0.333	0.068
1	3	1.234	0.055
1	4	179.365	0.067
1	5	0.842	0.069
2	3	1.022	0.050
2	4	179.653	0.066
2	5	0.635	0.067

CONCLUSION

As mentioned above, we have synthesized some novel compounds by developing a new synthetic approach. This method is intriguing and challenging for its simplicity, mechanism, and minimum steps. In respect of the formation of chalcogenophenes, it is an extraordinary and scarce model of making three bonds in a single step at room temperature. Further studies regarding confirmation of the mechanism and photophysical properties of these products are continuing in the laboratory.

EXPERIMENTAL

General

Melting points were measured with a MEL-TEMP capillary melting point apparatus and are uncorrected. ^{1}H-(400 MHz) and ^{13}C-(101 MHz) NMR spectra are recorded on a Bruker AC-400P instrument with $CDCl_3$ as a solvent. ^{1}H NMR chemical shifts are given in relative ppm from internal TMS ($\delta = 0.0$). ^{13}C NMR chemical shifts are given in relative ppm from the internal $CDCl_3$ ($\delta = 77.0$). Mass spectra are recorded with a Hitachi M-2000 or JEOL JMSSX 102 spectrometer under electron ionization (70 eV). High-resolution mass spectra were measured on an Applied Biosystems Japan QSTARXL Hybrid LC/MS/MS system under atmospheric pressure chemical ionization (APCI) condition. IR spectra were recorded on KBr disks with a JASCO FT/IR-7300 spectrometer. Ether and THF were freshly distilled from Na-benzophenone prior to use. Commercial grade TMEDA was purified by atmospheric distillation before use. Wakogel C-200 was used for silica gel column chromatography. Elemental analyses were recorded using Yanaco MT-5 apparatus at the elemental analysis division of Iwate University.

Synthesis of Naphthalene-1-sulfonyl Chloride

To a solution of 1-bromo-naphthalene (2.134 g, 10.0 mmol) in dry ether (55 mL) under nitrogen, *n*-BuLi (1.1 eq.) was added slowly at −20°C. Within 2 min, the solution became a white suspension and stirred for 20 min. SO_2Cl_2 (1.5 eq.) was added into the reaction mixture at −20°C and it was stirred for 1.5 h from −20°C to room temperature. The resultant reaction mixture was poured into ice water and quenched over 30 min with constant stirring. The organic layer was extracted with ether, dried over anhydrous $MgSO_4$ and the excess solvent was removed in vacuo. Column chromatography on silica gel eluting with *n*-hexane/chloroform (1:1) gave pure naphthalene-1-sulfonyl chloride (1.160 g, 51%). The compound was found as a white solid [21]; mp 70°C; ^{1}H NMR ($CDCl_3$) δ 7.61 (t, 1H, $J = 7.9$ Hz, ArH), 7.70 (t, 1H, $J = 7.5$ Hz, ArH), 7.81 (t, 1H, $J = 7.9$ Hz, ArH), 8.01 (d, 1H, $J = 7.9$ Hz, ArH), 8.22 (d, 1H, $J = 8.2$ Hz, ArH), 8.38 (d, 1H, $J = 7.5$ Hz, ArH), 8.79 (d, 1H, $J = 8.6$ Hz, ArH).

4-Phenylnaphthalene-1-sulfonyl Chloride

To a solution of 1-phenylnaphthalene (4.085 g, 20.0 mmol) in dry CH_2Cl_2, HSO_3Cl (4.0 eq.) was gradually added at 0°C. The resultant reaction mixture was stirred for 2 h at room temperature. Saturated brine solution was added to quench the reaction mixture and also stirred for more 30 min. Insoluble and inorganic precipitates were removed by suction filtration. Organic products were extracted by the excess chloroform from the filtrate, dried over anhydrous $MgSO_4$, and the excess solvent was removed by evaporation. 4-Phenylnaphthalene-1-sulfonyl chloride was obtained after silica gel column chromatography by using *n*-hexane/$CHCl_3$(2:1) as eluents (2.41 g, 40%). Colorless needles; mp 110.5–111.0°C; ^{1}H NMR ($CDCl_3$) δ 7.46 (m, 1H, ArH), 7.47 (d, 1H, $J = 7.7$ Hz, ArH), 7.51–7.56 (m, 4H, ArH), 7.62 (m, 1H, ArH), 7.81 (m, 1H, ArH), 8.02 (d, 1H, $J = 8.5$ Hz, ArH), 8.41 (d, 1H, $J = 7.7$ Hz, ArH), 8.88 (d, 1H, $J = 8.7$ Hz, ArH); ^{13}C NMR ($CDCl_3$) δ 124.3, 124.9, 127.6, 127.7, 127.9, 128.5, 128.6, 128.9, 129.1, 129.7, 132.8, 138.6, 138.8, 149.5; IR (KBr) 1365, 1167 cm^{-1} (SO_2); EIMS (70 eV) *m*/*z* 302 (M^+); Anal. Calcd for $C_{16}H_{11}ClO_2S$: C, 63.47; H, 3.66. Found: C, 63.65; H, 3.94.

*Naphthalene-1-sulfonic Acid Dimethylamide (**1**)*

To a solution of naphthalene-1-sulfonyl chloride (1.133 g, 5.0 mmol) in dry THF, 50% aqueous solution of dimethylamine (4–5 eq.) was added at room temperature. The resultant reaction mixture was stirred for 1.5 h at room temperature, poured into ice water, and extracted with chloroform. The organic phase was dried over anhydrous $MgSO_4$ and the excess solvent was removed in vacuo. Running silica gel column chromatography with *n*-hexane/chloroform (1:1) as eluents afforded **1** (1.117 g, 95%). The product was found as white solid; mp 88.0–89.0°C; ^{1}H NMR ($CDCl_3$) δ 2.82 (s, 6H, NMe_2), 7.54 (d, 1H, $J = 7.6$ Hz, ArH), 7.58 (m, 1H, ArH), 7.65 (m, 1H, ArH), 7.92 (d, 1H, $J = 7.6$ Hz, ArH), 8.06 (d, 1H, $J = 8.3$ Hz, ArH), 8.19 (m, 1H, ArH), 8.78 (d, 1H, $J = 8.7$ Hz, ArH); ^{13}C NMR ($CDCl_3$) δ 37.4, 124.0, 125.3, 126.8, 128.0, 128.8, 129.1, 130.3, 132.7, 134.2, 134.3; IR (KBr) 1334, 1153 cm^{-1} (SO_2); EIMS (70 eV) *m*/*z* 235 (M^+); Anal. Calcd for $C_{12}H_{13}NO_2S$: C, 61.25; H, 5.57; N, 5.95. Found: C, 60.99; H, 5.55; N, 5.96.

*4-Phenylnaphthalene-1-sulfonic Acid Dimethylamide (**2**)*

The synthetic procedure of substrate **2** was the same as that of substrate **1**. Compound **2** was isolated as colorless needles in 95% yield. mp 106.9–107.7°C; ^{1}H NMR ($CDCl_3$) δ 2.88 (s, 6H, NMe_2), 7.45–7.48 (m, 3H, ArH), 7.49–7.54 (m, 4H, ArH), 7.65 (m, 1H, ArH), 7.95 (m, 1H, ArH), 8.24 (m, 1H, ArH), 8.85 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$) δ 37.4, 125.1, 125.5, 126.7, 127.1, 127.7, 128.1, 128.4, 129.5, 129.75, 129.77, 132.0, 132.7, 139.5, 146.4; IR (KBr) 1335, 1154 cm^{-1} (SO_2); EIMS (70 eV) *m*/*z* 311 (M^+); Anal. Calcd for $C_{18}H_{17}NO_2S$: C, 69.43; H, 5.50; N, 4.50. Found: C, 69.52; H, 5.55; N, 4.53.

*Naphthalene-2-sulfonic Acid Dimethylamide (**9**)*

Compound **9** was synthesized in 96% yield from naphthalene-2-sulfonyl chloride by following the above procedure. Bright white crystal [22]; mp 96.5–97.0°C; ^{1}H NMR ($CDCl_3$) δ 2.76 (s, 6H, NMe_2), 7.60–7.67 (m, 2H, ArH), 7.77 (dd, 1H, $J = 8.7$, 1.8 Hz, ArH), 7.93 (d, 1H, $J = 8.3$ Hz, ArH), 7.98 (m, 2H, ArH), 8.35 (s, 1H, ArH).

*Dinaphtho[1,2-b:2′,1′-d]thiophene (**3**)*

General procedure: Compound **1** (0.235 g, 1.0 mmol) was dissolved in TMEDA (10 mL) under nitrogen and *n*-BuLi in *n*-pentane (1.1 eq.) was added at 0°C. The resultant reaction mixture was stirred for next 6 h at the same temperature. Two equivalents of elemental sulfur was added into the mixture, and was stirred for 3 h at room temperature. The resultant reaction mixture was quenched with 1 M aqueous solution of NH_4Cl and oxidized by air for 30 min. The

organic products were extracted twice with the excess chloroform, dried over anhydrous $MgSO_4$, and the residual solvent was removed in vacuo. The product was isolated after dry bed column chromatography by using *n*-hexane 100% as an eluent (40 mg, 29%). All spectral data are similar to those reported in the literature [7,14].

Colorless plates; mp 256.7–257.2°C; ^{1}H NMR ($CDCl_3$) δ 7.55 (m, 2H, ArH), 7.63 (m, 2H, ArH), 7.88 (d, 2H, $J = 8.7$ Hz, ArH), 7.98 (d, 2H, $J = 8.2$ Hz, ArH), 8.20 (d, 2H, $J = 8.7$ Hz, ArH), 8.23 (d, 2H, $J = 8.4$ Hz, ArH); EIMS (70 eV) m/z 284 (M^+).

*Dinaphtho[1,2-b:2′,1′-d]selenophene (**4**)*

The product was synthesized in 31% yield by the procedure mentioned above. Two equivalents of elemental selenium was used in place of sulfur. Silky white plates; mp 292.5–293°C; ^{1}H NMR ($CDCl_3$) δ 7.54–7.64 (m, 4H, ArH), 7.92 (d, 2H, $J = 8.5$ Hz, ArH), 7.97 (m, 2H, ArH), 8.05 (m, 2H, ArH), 8.20 (d, 2H, $J = 8.5$ Hz, ArH); ^{13}C NMR ($CDCl_3$) δ 121.1, 126.1, 126.2, 126.3, 127.0, 128.9, 131.5, 132.3, 136.9, 139.3; IR (KBr) 3049, 1511, 1378, 1309, 1251, 806, 741, 652, 527 cm^{-1}; EIMS (70 eV) m/z 332 (M^+), 252 (M^+–Se); Anal. Calcd for $C_{20}H_{12}Se$: C, 72.51; H, 3.65. Found: C, 72.29; H, 3.97.

*1,1′-Bis(N,N-dimethylaminosulfonyldinaphthyl)-2,2′-diselenide (**5**)*

This product was isolated along with product **4**. Recrystallization from CH_2Cl_2 afforded pure **5** in 25% yield. Light yellow powder; mp 235°C; ^{1}H NMR ($CDCl_3$) δ 2.93 (s, 12H, $-NMe_2$), 7.52 (t, 2H, $J = 7.4$ Hz, ArH), 7.63 (t, 2H, $J = 7.4$ Hz, ArH), 7.77 (m, 2H, ArH), 7.80 (m, 2H, ArH), 8.05 (d, 2H, $J =$ 8.8 Hz, ArH), 8.31 (d, 2H, $J = 8.8$ Hz, ArH); ^{13}C NMR ($CDCl_3$) δ 36.9, 124.5, 126.4, 127.6, 128.3, 128.8, 130, 131.2, 133.1, 133.9, 134.6; IR (KBr) 1332, 1315, 1148 cm^{-1}; EIMS (70 eV) m/z 628 (M^+); Anal. Calcd for $C_{24}H_{24}N_2O_4S_2Se_2$: C, 46.01; H, 3.86; N, 4.47. Found: C, 46.29; H, 4.17; N, 4.27.

*4,4′-Diphenyldinaphtho[1,2-b:2′,1′-d]thiophene (**6**)*

The product was synthesized in 37% yield according to the above procedure. Compound **2** was used as the starting material. Colorless needles; mp 213–213.5°C; ^{1}H NMR ($CDCl_3$) δ 7.44–7.53 (m, 8H, ArH), 7.55–7.58 (m, 4H, ArH), 7.64 (m, 2H, ArH), 8.00 (m, 2H, ArH), 8.14 (s, 2H, ArH), 8.31 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 120.7, 124.6, 126.2, 126.7, 127.4, 127.5, 128.3, 129.3, 130.3, 130.7, 133.4, 136.5, 138.3, 140.7; IR (KBr) 3052, 2927, 1603, 1494, 1406, 1364, 871, 759, 703 cm^{-1}; EIMS (70 eV) m/z 436 (M^+); Anal. Calcd for $C_{32}H_{20}S$: C, 88.04; H, 4.62; S, 7.35. Found: C, 87.87; H, 4.62; S, 7.53.

*4,4′-Diphenyldinaphtho[1,2-b:2′,1′-d]selenophene (**7**)*

The product was also synthesized in 11% yield by following the above procedure. Two equivalents of elemental selenium was used in place of sulfur. Colorless needles; mp 231–231.2°C; ^{1}H NMR ($CDCl_3$) δ 7.43–7.54 (m, 8H, ArH), 7.55–7.59 (m, 4H, ArH), 7.63 (m, 2H, ArH), 7.99 (m, 2H, ArH), 8.11 (m, 2H, ArH), 8.13 (s, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 121.4, 126.4, 126.5, 126.6, 126.9, 127.5, 128.3, 129.8, 130.0, 132.4, 132.9, 133.0, 140.2, 141.6; IR (KBr) 3050, 1492, 1407, 871, 759, 695 cm^{-1}; EIMS (70 eV) m/z 484 (M^+); HR-APCI-TOFMS Calcd for $C_{32}H_{20}Se[M]^+$: 484.0724. Found: 484.0717.

*1,1′-Bis(N,N-dimethylaminosulfonylnaphthyl)-4,4′-bis(phenyl)-2,2′-diselenide (**8**)*

The experimental procedure was the same as the above procedure. Two equivalents of elemental selenium was used in place of sulfur. Both products **7** and **8** were isolated in 11% and 15% yield, respectively, by eluting with chloroform on silica gel column chromatography. Recrystallization from ether afforded pure **8**. Silky white solid; mp 226°C; ^{1}H NMR ($CDCl_3$) δ 2.75 (s, 12H, $-NMe_2$), 7.05 (m, 4H, ArH), 7.19 (m, 4H, ArH), 7.30 (m, 2H, ArH), 7.44 (t, 2H, $J = 7.5$ Hz, ArH), 7.62 (t, 2H, $J = 7.8$ Hz, ArH), 7.83 (d, 2H, $J = 8.4$ Hz, ArH), 7.94 (s, 2H, ArH), 8.79 (d, 2H, $J = 8.4$ Hz, ArH); ^{13}C NMR (CDCl3) δ 36.8, 124.8, 126.3, 127.1, 127.9, 128.1, 128.4, 129.0, 129.5, 129.9, 131.5, 131.8, 133.8, 139.0, 145.4; IR (KBr) 1323, 1151, 961, 714 cm^{-1}; EIMS (70 eV) m/z 700 (M^+-Se); Anal. Calcd for $C_{36}H_{32}N_2O_4S_2Se_2$: C, 55.53; H, 4.14; N, 3.60. Found: C, 55.83; H, 4.04; N, 3.31.

*2-Methylnaphthalene-1-sulfonic Acid Dimethylamide (**12**)*

Substrate **1** was dissolved in TMEDA, and *n*-BuLi was added into the solution. The resulted lithiated mixture was stirred for 6 h in ice bath at 0°C. The excess (10 eq.) CH_3I was added slowly into the reactor, and suddenly the solution turned into a pasty mass. Dried THF was added into the reactor, and after 30 min unreacted CH_3I was removed by evaporation. The resultant reaction mixture was quenched over aqueous $NaHSO_3$ solution. The organic product was extracted with $CHCl_3$, dried over $MgSO_4$, and the solvent was removed in vacuo. Running a silica gel

column chromatography with $CHCl_3$ gave the product **12** in 84% yield. Silky white solid, mp 72°C; ^{1}H NMR ($CDCl_3$) δ 2.90 (s, 3H, $-CH_3$), 2.79 (s, 6H, $-NMe_2$), 7.35 (d, $J = 8.4$ Hz, 1H, ArH), 7.49 (t, $J = 7.4$ Hz, 1H, ArH), 7.59 (t, 1H, $J = 7.2$ Hz, ArH), 7.82 (d, 1H, $J = 8.6$ Hz, ArH), 7.92 (d, 1H, $J = 8.4$ Hz, ArH), 8.88 (d, 1H, $J = 8.9$ Hz, ArH); ^{13}C NMR ($CDCl_3$) δ 24.1, 36.4, 125.6, 125.7, 127.7, 128.5, 130.2, 130.6, 130.7, 133.1, 133.7, 141.5; IR (KBr) 1302, 1134, 932, 604 cm^{-1}; EIMS (70 eV) *m/z* 249 (M^+); Anal. Calcd for: $C_{13}H_{15}NO_2S$: C, 62.62; H, 6.06; N, 5.62. Found: C, 62.56; H, 6.06; N, 5.64.

*2-Methylselanylnaphthalene-1-sulfonic Acid Dimethylamide (***13***)*

Dark nontransparent solution of carbanion **10** was generated over 6 h by the reaction of **1** and *n*-BuLi. Two equivalents of elemental selenium was poured into the reaction mixture and allowed to stir for 30 min. The reaction mixture was quenched with the excess (10 eq.) CH_3I. Unreacted CH_3I was removed by evaporation, and the resultant reaction mixture was requenched with aqueous $NaHSO_3$ solution. The organic products were extracted with CH_2Cl_2, dried over $MgSO_4$, and remaining solvent was removed in vacuo. On TLC, the crude showed four spots on the *n*-hexane/chloroform (1:1) solvent system. Running a silica gel column by the same solvent system resulted four products **12** (33%), **13** (31%), **5** (8%), and **4** (4%), respectively. Product **13** was found as a brown crystal, mp 121°C; ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3H, $-CH_3$), 2.84 (s, 6H, $-NMe_2$), 7.47–7.51 (m, 2H, ArH), 7.58 (t, 1H, $J = 7.3$ Hz, ArH), 7.81 (d, 1H, $J = 8.7$ Hz, ArH), 7.85 (d, 1H, $J = 8.9$ Hz, ArH), 8.73 (d, 1H, $J = 8.9$ Hz, ArH); ^{13}C NMR (CDCl3) δ 8.5, 36.7, 124.5, 124.6, 125.8, 128.1, 128.6, 129.1, 131.5, 131.8, 133.1, 139.8; IR (KBr) 1315, 1135, 935, 720 cm^{-1}; EIMS (70 eV) *m/z* 329 (M^+); Anal. Calcd for $C_{13}H_{15}NO_2SSe$: C, 57.56; H, 4.61; N, 4.27. Found: C, 57.59; H, 4.75; N, 4.38.

*2,2′-Bis(N,N-dimethylaminosulfonylnaphthyl)-1,1′-diselenide (***17***)*

The product was synthesized by following the above procedure. Two equivalents of elemental selenium was used for the selenium source. Only product **17** was isolated as a yellow powder in 23% yield. mp 221.5°C; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 12H, $-NMe_2$), 7.22 (m, 2H, ArH), 7.52 (m, 2H, ArH), 7.85 (m, 2H, ArH), 7.93 (m, 2H, ArH), 8.01 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ 36.7, 125.9, 127.3, 128.4, 128.6, 129.9, 130.6, 132.1, 135.2, 135.7, 140.8; IR (KBr) 1323, 1133, 973 cm^{-1}; EIMS (70 eV) *m/z* 628 (M^+); Anal. Calcd for $C_{24}H_{24}N_2O_4S_2Se_2$: C, 46.01; H, 3.86; N, 4.47. Found: C, 45.75; H, 4.00; N, 4.47.

*1-Methylnaphthalene-2-sulfonic Acid Dimethylamide (***18***)*

The trapping experiment of product **13** was also used for **18**. Two trapping products **18** (10%) and **19** (44%) were isolated. Product **18** was isolated as a white solid, mp 64°C; ^{1}H NMR ($CDCl_3$) δ 3.05 (s, 3H, $-CH_3$), 2.81 (s, 6H, $-NMe_2$), 7.60–7.64 (m, 2H, ArH), 7.79 (d, $J = 8.8$ Hz, 1H, ArH), 7.88 (m, 1H, ArH), 7.97 (d, 1H, $J = 8.8$ Hz, ArH), 8.24 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$) δ 15.6, 37.2, 125.2, 125.4, 126.5, 127.1, 127.5, 128.1, 128.6, 129.0, 129.1, 133.2; IR (KBr) 1313, 1151, 950, 715 cm^{-1}; EIMS (70 eV) *m/z* 249 (M^+); Anal. Calcd for $C_{13}H_{15}NO_2S$: C, 62.62; H, 6.06; N, 5.62. Found: C, 62.66; H, 6.07; N, 5.97.

*1-Methylselanylnaphthalene-2-sulfonic Acid Dimethylamide (***19***)*

Brown crystal, mp 98°C; ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 3H, $-CH_3$), 2.95 (s, 6H, $-NMe_2$), 7.61–7.70 (m, 2H, ArH), 7.89 (d, $J = 7.9$ Hz, 1H, ArH), 7.92 (d, 1H, $J = 8.7$ Hz, ArH), 8.12 (d, 1H, $J = 8.7$ Hz, ArH), 8.84 (d, 1H, $J = 8.2$ Hz, ArH); ^{13}C NMR ($CDCl_3$) δ 11.4, 37.4, 125.7, 128.0 128.4, 128.7, 129.3, 130.4, 131.7, 135.1, 135.3, 141.7; IR (KBr) 1327, 1160, 974, 720 cm^{-1}; EIMS (70 eV) *m/z* 329 (M^+); Anal. Calcd for $C_{13}H_{15}NO_2SSe$: C, 47.56; H, 4.61; N, 4.27. Found: C, 47.72; H, 4.52; N, 4.28.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 601484 for compound **3**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).

ACKNOWLEDGEMENT

We are grateful to Ms. Shiduko Nakajo (Division of Elemental Analysis, Iwate University) for elemental analyses.

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