Synthetic Procedure for Various Selenium-Containing Electron Donors of the Bis(Ethylenedithio)tetrathiafulvalene (BEDT-TTF) Type

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Received December 19, 2001

Six selenium variants of BEDT-TTF have been successfully synthesized by a newly developed synthetic method that involves a combination of two key reactions for the construction of two kinds of heterocyclic rings: the first is a one-pot formation of 1,3-dichalcogenole-2-chalcogenones from a common starting material, THP-protected 2-(ethynylthio)ethanol, leading to the inner five-membered rings, and the other is the annelation of the outer six-membered heterocyclic ring onto the inner ring by an intramolecular transalkylation reaction on a chalcogen atom. This method turned out to be widely applicable to the syntheses of the electron donors of bis(ethylenedithio)- and bis(ethyleneselenothio)-substituted types. However, synthetic attempts to form analogous donors of the bis(ethylenediseleno)-substituted type from THP-protected 2-(ethynylseleno)ethanol were unsuccessful. This is attributable to the predominance of side-reactions via a seleniranium (episelenonium) salt over the desired six-membered ring formation by transalkylation via a seleninium salt.

Introduction

Since the discovery of the very high conductivity of tetrathiafulvalene (TTF)-tetracyanoquinodimethane, structural modifications of TTF have been extensively carried out in search of better electron donors, and as a result, more than 1000 TTF derivatives have been prepared.[1] The most successful compound is bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF, **1a**), which has provided more than fifty superconducting radical cation salts,[2] involving κ-(BEDT-TTF)$_2$·Cu[N(CN)$_2$]Cl with the highest transition temperature T_c = 12.8 K at 0.3 kbar among organic superconductors except for those of A_3C_{60} type.[3] As the replacement of skeletal sulfur atoms of TTF derivatives by selenium atoms is generally recognized as an effective approach to superior electron donors with enhanced intermolecular interactions,[4] selenium variants of BEDT-TTF have aroused much interest. Considering partial replacement of the eight sulfur atoms of BEDT-TTF by selenium, there are nearly fifty selenium variants. Even if unsymmetrical types with respect to the central double bond are excluded,[5] nine selenium-containing compounds (**1b**−**j**) can be designed as shown in Chart 1. Among them, the three highly symmetrical compounds bis(ethylenedithio)tetraselenafulvalene (BETS, **1b**),[6] bis(ethylenediseleno)tetrathiafulvalene (BEDSe-TTF, **1h**),[7] and bis(ethylenediseleno)tetraselenafulvalene (BEDSe-TSF, **1i**)[8] have been synthesized and recognized to possess remarkable abilities to form highly conductive radical cation salts. In particular, BETS is a unique organic donor in that it can give unprecedented magnetic organic superconductors.[6d] However, the previous meth-

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(2) For comprehensive reviews on organic superconductors, see: (a) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties, and Theory*; Prentice Hall: Englewood Cliffs, NJ, 1992. (b) Ishiguro, T.; Yamaji, K.; Saito, G. *Organic Superconductors*, 2nd ed.; Springer-Verlag: Berlin, 1998.

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(7) (a) Lee, V. Y. *Synth. Met.* **1987**, *20*, 161−167. (b) Hsu, S.-Y.; Chiang, L. Y. *Synth. Met.* **1988**, *27*, B651−B656. (c) Kini, A. M.; Gates, B. D.; Beno, M. A.; Williams, J. M. *J. Chem. Soc., Chem. Commun.* **1989**, 169−171.

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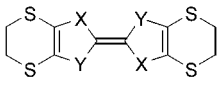
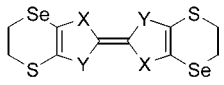
10.1021/jo016393h CCC: $22.00
Published on Web 05/15/2002

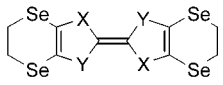
Chart 1



X = Y =S BEDT-TTF **1a**
X = Y = Se BETS **1b**
X = S, Y = Se BEDT-STF **1c**

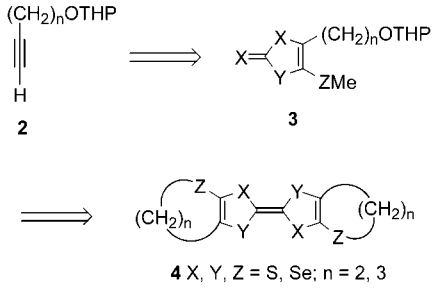


X = Y =S BEST-TTF **1d**
X = Y = Se BEST-TSF **1e**
X = S, Y = Se BEST-STF(t) **1f**
X = Se, Y = S BEST-STF(g) **1g**



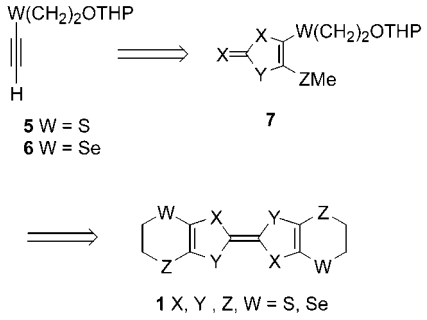
X = Y =S BEDSe-TTF **1h**
X = Y = Se BEDSe-TSF **1i**
X = S, Y = Se BEDSe-STF **1j**

Scheme 1



4 X, Y, Z = S, Se; n = 2, 3

Scheme 2



1 X, Y , Z, W = S, Se

ods for synthesizing these selenium compounds are not necessarily easy and lack generality. More specifically, the synthesis of BETS was carried out only by lengthy and difficult routes with low total yields. In addition, these methods are hardly applicable to the syntheses of the less symmetrical selenium variants of the ethylenedithio (BEDT)-substituted type or of the ethylenethiaselenathio (BEST)-substituted type or of the diselenadithiafulvalene (STF) skeleton type. For the STF skeleton type, only bis(ethylenedithio)diselenadithiafulvalene (BEDT-STF, **1c**) has been reported, but its synthetic yield was very low (<0.5%), allowing the study of neither its physical properties nor those of its radical cation salts.[9] Thus, it is desirable to develop a general synthetic method that is not only superior to the preceding ones of BETS but also applicable to the syntheses of all the selenium variants of BEDT-TTF.

Recently, we developed a general synthetic method for novel TTF- and TSF-type electron donors (**4**) fused with five- or six-membered heterocycles containing one chalcogen atom according to the outline shown in Scheme 1.[10] This method involves one-pot formation of 1,3-dichalcogenole-2-chalcogenones (**3**) from tetrahydropyran (THP)-protected 3-butyn-1-ol or 4-pentyn-1-ol (**2**)[11] followed by the outer heterocycle formation via an intramolecular transalkylation reaction on a chalcogen atom. A great merit of this method lies in the fact that a series of heterocycle-fused TTF-type donors are available from just limited starting acetylene compounds by choosing the appropriate chalcogen reagents.

Another merit of this method is that it enables the design of versatile donors with different outer ring sizes or different heterocyclic rings by adopting appropriate starting acetylene compounds. One may thus expect that BEDT-TTF-type electron donors fused with six-membered heterocycles containing two chalcogen atoms (**1**) are similarly accessible by starting with THP-protected 2-(ethynylthio)ethanol (**5**) or 2-(ethynylseleno)ethanol (**6**), as shown in Scheme 2. We have then examined the potential of this approach for the syntheses of not only BEDT-TTF itself (**1a**) but also its selenium variants (**1b**−**j**). In this paper, we report the scope and limitation of the present method.[12]

Results and Discussion

The 10 donors drawn in Chart 1 are roughly categorized into three classes of BEDT, BEST, and BEDSe types, according to the structures of the outer heterocycles. The present synthetic approaches to these types are justly linked to the starting THP-protected 2-(ethynylchalcogeno)ethanols **5** and **6**: the BEDT type can only be derived from the sulfur-containing acetylene **5**, the BEDSe type only from the selenium-containing acetylene (**6**), and the BEST type from either **5** or **6**. The validity and versatility of the present synthetic method are described in the respective classes of BEDT, BEST, and BEDSe.

Synthesis of BEDT-Substituted Donors (1a−c). Although all the BEDT-type compounds, BEDT-TTF (**1a**),[13] BETS (**1b**),[6a,b] and BEDT-STF (**1c**),[9] are known, we first tried to evaluate the validity of our synthetic method for these compounds. The synthesis of the key starting compound, THP-protected 2-(ethynylthio)ethanol **5**, as well as its synthetic application to BEDT-TTF is demonstrated in Scheme 3. A reaction of 2-iodoethyl tetrahydropyranyl ether (**8**)[14] with potassium thiocyanate gave the corresponding thiocyanate **9** (85% yield), which then reacted with ethynylmagnesium chloride to give **5** in 54% yield. The lithium acetylide derived from **5** with equimolar *n*-BuLi in the presence of tetramethylethylenediamine (TMEDA) was successively reacted with sulfur, carbon disulfide, and finally methyl thiocyanate to give the thione **7a** in 76% yield, which was then

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(10) (a) Jigami, T.; Takimiya, K.; Aso, Y.; Otsubo, T. *Chem. Lett.* **1997**, 1091−1092. (b) Jigami, T.; Takimiya, K.; Otsubo, T.; Aso, Y. *J. Org. Chem*. **1998**, *63*, 8865−8872. (c) Jigami, T.; Takimiya, K.; Aso, Y.; Otsubo, T. *Synth. Met.* **1999**, *102*, 1714−1715. (d) Kodani, M.; Murakami, S.; Jigami, T.; Takimiya, K.; Aso, Y.; Otsubo, T. *Heterocycles* **2001**, *54*, 225−234. (e) Jigami, T.; Kodani, M.; Murakami, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *J. Mater. Chem*. **2001**, *11*, 1026−1033.

(11) Takimiya, K.; Morikami, A.; Otsubo, T. *Synlett* **1997**, 319−321.

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(13) Mizuno, M.; Garito, A. F.; Cava, M. P. *J. Chem. Soc., Chem. Commun*. **1978**, 18−19.

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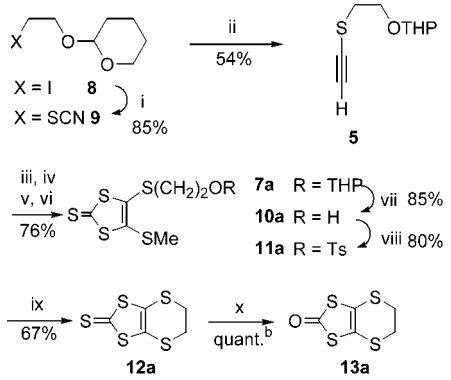
Scheme 3. Synthesis of THP-Protected 2-(Ethynylthio)ethanol (5) and BEDT-TTF (1a)[a]

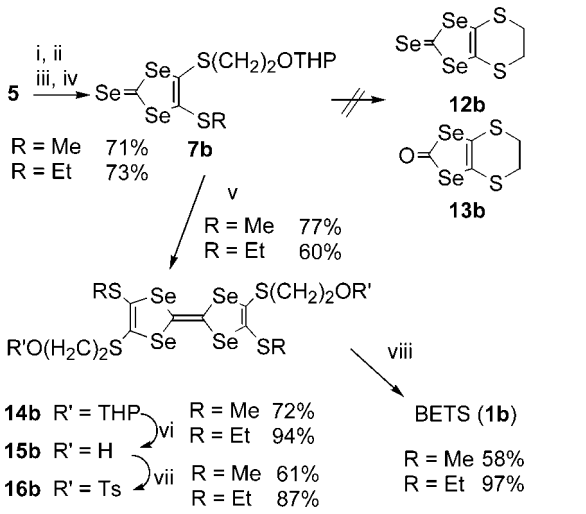


[a] Key: (i) KSCN, acetone, reflux; (ii) ethynylmagnesium chloride, THF, rt; (iii) *n*-BuLi, TMEDA, −70 °C; (iv) S, 0 °C; (v) CS_2, −90 °C; (vi) MeSCN; (vii) HCl aq MeOH−acetone, rt; (viii) TsCl, pyridine, 0 °C; (ix) NaI, DMF, 95 °C; (x) $Hg(OAc)_2$, $CHCl_3$, rt; (xi) $P(OMe)_3$, reflux. [b] From ref 15b. [c] From ref 19.

converted into 5,6-dihydro-2-thioxo-1,3-dithiolo[2,3-*d*]-[1,4]dithiin (**12a**)[15] via deprotection of THP group (**10a**, 85% yield), tosylation (**11a**, 80% yield), and finally ring-closing reaction (67% yield). Since the thione **12a** was already reported to be readily convertible to BEDT-TTF (**1a**) via the ketone **13a**,[15b] it follows that our synthetic method can be applicable to BEDT-TTF (**1a**). Here, we do not intend to assert that the present method is useful for the synthesis of BEDT-TTF, because since the first synthesis of BEDT-TTF by Cava's group,[13] several improved synthetic methods have already been developed.[16] In addition, BEDT-TTF itself and the precursors **12a** and **13a** are commercially available these days, though still expensive. Instead, we may emphasize that the intermediate **7a** is of special use as a counterpart for trialkyl phospite-mediated cross-coupling directed torward the synthesis of the hybrids consisting of half of the BEDT-TTF. When **12a** and **13a** are directly used for such cross-coupling reactions, cross-coupling hybrid products are often difficult to isolate from the homocoupling products by conventional purification techniques. However, use of **7a** with the polar functional group facilitates the chromatographic separation of the resulting cross-coupling product, which can be converted to the desired hybrid with the outer six-membered heterocyclic rings.[17]

A successful example of the synthetic route through the coupling reaction prior to the outer six-membered ring formation is demonstrated in the synthesis of BETS (**1b**), as shown in Scheme 4. The 1,3-diselenole-2-selone derivatives (**7b**, R = Me and Et) were prepared by successive treatments of **5** with an equimolar amount of *n*-BuLi, selenium, carbon diselenide, and methyl thiocyanate (or ethyl thiocyanate). However, it turned out that analogous conversions of **7b** to the 5,6-dihydro-2-selenoxo-1,3-diselenolo[2,3-*d*][1,4]dithiin (**12b**) or the oxo derivative (**13b**) were difficult because of the labile ethylenedithio-fused 1,3-diselenole-2-selone skeleton.[18] As an alternative approach, **7b** was first self-coupled into

Scheme 4. Synthesis of BETS (1b)[a]



[a] Key: (i) *n*-BuLi, TMEDA, −70 °C; (ii) Se, 0 °C; (iii) CSe_2, −90 °C; (iv) MeSCN or EtSCN; (v) $P(OMe)_3$, reflux; (vi) HCl aq, MeOH−THF, rt; (vii) TsCl, pyridine (R = Me) or Et_3N (R = Et), 0 °C; (viii) NaI, DMF, 80 °C.

the TSF derivative (**14b**) and then subjected to the construction of the outer six-membered rings. By this approach, both methylthio-substituted and ethylthio-substituted 1,3-diselenole-2-selone derivatives (**7b**, R = Me and Et) were successfully converted to BETS (**1b**). In the transformation sequence from **7b** with the methylthio group, however, poor solubility of the tosylate (**16b**) made its purification difficult and brought inadequate production and poor reproducibility in the final cyclization. In contrast, in the transformation sequence of **7b** with ethylthio groups, which can enhance the solubility, all reactions proceeded smoothly with high yields. The total yield of BETS from **8** is 16%, which is enhanced by 1 order of magnitude as compared to those of the preceding synthetic methods.[6]

To establish an effective synthetic method for the STF derivative (**1c**), the two possible synthetic methodologies from the key intermediate **7c** were examined as shown in Scheme 5. Analogously to the synthesis of BEDT-TTF (**1a**), the route involving the annelation of the outer heterocyclic ring onto **7c** was first tested. The preparation of 5,6-dihydro-2-thioxo-1,3-selenothia[2,3-*d*][1,4]dithiin (**12c**) from **7c** could be carried out without any problem, but the subsequent coupling reaction to BEDT-STF (**1c**) proceeded in a low yield (19%), although the yield was somewhat improved via the ketone (**13c**) (32% yield). On the other hand, the route involving a prior coupling from **7c**, as applied above to the synthesis of BETS (**1b**), gave a much better result. The direct self-coupling of **7c** gave the STF derivative (**14c**) only in 20% yield, but the yield was markedly improved to 85% by the two-step conversion via the ketone **17c**. The ensuing reactions for constructing the outer six-membered rings proceeded smoothly in high yields. Thus, it is suggested that for the synthesis of the heterocycle-fused STF system, the route through the construction of the STF skeleton prior to the annelation of the heterocyclic ring is advantageous,

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(16) Larsen, J.; Lenoir, C. *Org. Synth.* **1993**, *72*, 265−272 and references therein.

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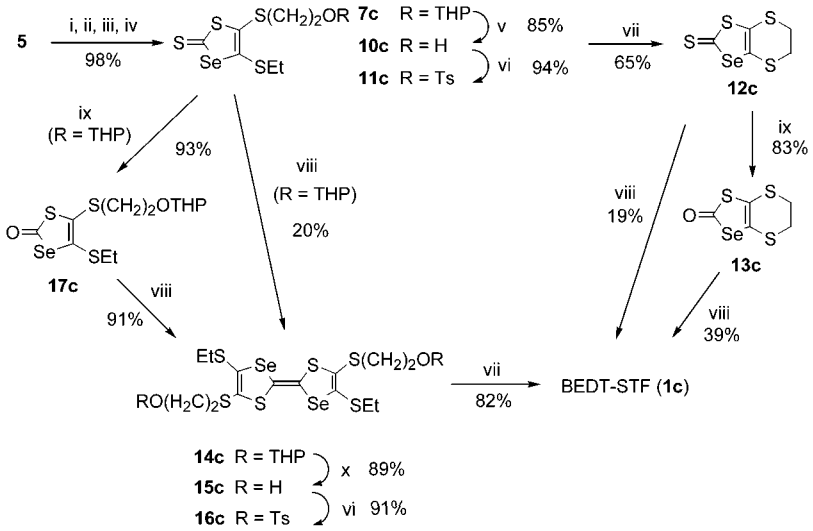
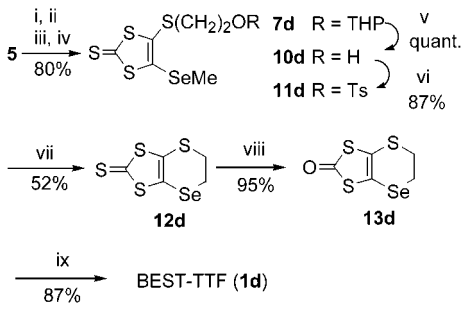
(18) We recently developed the facile synthetic method of 5,6-dihydro-2-selenoxo-1,3-diselenolo[2,3-*d*][1,4]dithiin (**12b**) and recognized that it is relatively labile. Morikami, A.; Takimiya, K.; Aso, Y.; Otsubo, T. *Org. Lett.* **1999**, *1*, 23−25.

Scheme 5. Synthesis of BEDT-STF (1c)[a]



[a] Key: (i) *n*-BuLi, TMEDA, −70 °C; (ii) Se, 0 °C; (iii) CS_2, −90 °C; (iv) EtSCN; (v) HCl aq, MeOH−acetone, rt; (vi) TsCl, Et_3N, 0 °C; (vii) NaI, DMF, 80 °C; (viii) $P(OMe)_3$, reflux; (ix) $Hg(OAc)_2$, $CHCl_3$, rt; (x) HCl aq, MeOH−THF, rt.

Scheme 6. Synthesis of BEST-TTF (1d)[a]



[a] Key: (i) *n*-BuLi, TMEDA, −70 °C; (ii) S, 0 °C; (iii) CS_2, −90 °C; (iv) Se, then MeI, 0 °C; (v) HCl aq, MeOH−acetone, rt; (vi) TsCl, pyridine, 0 °C; (vii) NaI, DMF, 80 °C; (viii) $Hg(OAc)_2$, $CHCl_3$, rt; (ix) $P(OMe)_3$, reflux.

similar to that of the TSF system. As generally seen for this type of unsymmetrical TTFs, the STF derivatives existed as a mixture of *E* and *Z* conformational isomers due to the ready rotation around the central double bond, being supported by the observation of some nonequivalent signals in ^{13}C NMR spectra of **14c**, **15c**, and **16c** (see the Experimental Section).

Synthesis of BEST-Substituted Donors (1d−g). The synthesis of BEST-TTF (**1d**) was accomplished as shown in Scheme 6, basically following the same pathway as that of BEDT-TTF (**1a**), except that the initial one-pot formation reaction of **5** to **7d** was quenched with a mixed reagent of selenium powder and iodomethane instead of methyl thiocyanate as a source of the selenium atom in the outer six-membered ring.

The syntheses of BEST-TSF (**1e**) and BEST-STF (**1f** and **1g**)[19] are outlined in Scheme 7, following the routes similar to those of BETS (**1b**) and BEDT-STF (**1c**). In BEST-STF, two regioisomers with different positions of chalcogen atoms regarding the inner-ring double bonds of the fused rings exist, both of which can be selectively synthesized by appropriately choosing the kinds of chalcogen reagents in the synthetic protocol in the first one-pot formation of 1,3-dichalcogenole-2-chalcogenones (**7f**,**g**). The successful syntheses of these complicated BEDT-TTF derivatives evidently demonstrate the great versatility of the present method.

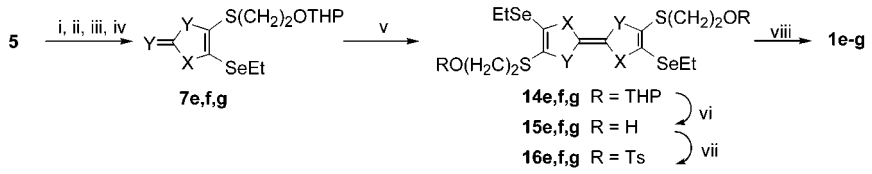
Synthetic Attempts for BEDSe-Substituted Donors (1h−j). The satisfactory syntheses of all the BEDT- and BEST-type donors (**1a**−**g**) have prompted us to apply the same approach to the syntheses of the remaining BEDSe-type counterparts (**1h**−**j**). In short, however, the synthetic strategy failed, and the results are detailed by the following synthetic investigations of BEDSe-TTF (**1h**). As already mentioned, the construction of the outer six-membered ring containing two selenium atoms requires the selenium-containing acetylene **6**, which was prepared by a procedure different from that of **5**, as outlined in Scheme 8. Trimethylsilyl (TMS) acetylene (**18**) was lithiated with butylllithum, in situ reacted with elemental selenium, and quenched with 2-iodoethyl tetrahydropyranyl ether to give 2-(trimethylethynylseleno)-ethanol (**19**). Without purification, it was treated with aqueous alkaline solution to give the desired **6** in a 74% two-step yield.

For the synthesis of BEDSe-TTF (**1h**), compound **6** was similarly cyclized to the 1,3-dithiole-2-thione derivative (**7h**) in 59% yield (Scheme 9). The THP protecting group of **7h** was readily removed (81% yield), and the resulting alcohol (**10h**) was treated with tosyl chloride as usual; however, no desired tosylate (**11h**) was obtained, and a trace amount of diselenide (**20**) was isolated instead. As an alternative route, **10h** was converted to the bromide **21** (24% yield), which was then treated with sodium iodide, in expectation of spontaneous annelation to 5,6-dihydro-2-thioxo-1,3-dithiolo[2,3-*d*][1,4]diselenin (**12h**). However, no formation of **12h** was detected, and the obtained products were the diselenide **20** (23%) when **21** was treated in DMF at 80 °C and 4-ethylseleno-1,3-dithiole-2-thione (**22**) (92%) when treated in refluxing 2-butanone.

In many attempts to synthesize BEDSe-TSF (**1i**) and STF (**1j**), the formation of the outer six-membered ring was also unsuccessful. Since it is already known that

(19) Abbreviated names of **1f** and **1g** are designated as BEST-STF-(t) and BEST-STF(g), respectively, because in **1f**, the relative position of selenium atoms on the inter-ring C=C bond in the dihydro-1,3-selenothia[1,4]thiaselenin moiety is trans, and, on the other hand, that in **1g** is geminal.

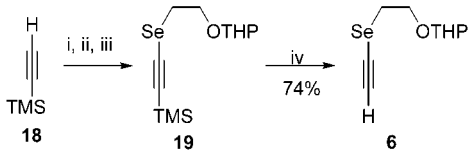
Scheme 7. Synthesis of BEST-TSF (1e) and BEST-STF (1f,g)[a]



X	Y	reagents		yield / % 7	14	15	16	1
Se	Se	Se, CSe_2	(e)	82	83	80	86	56
S	Se	S, CSe_2	(f)	73	50	92	72	55
Se	S	Se, CS_2	(g)	88	29	77	76	98

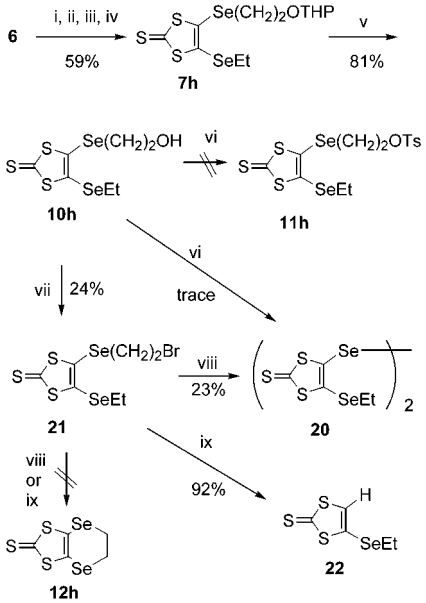
[a] Key: (i) *n*-BuLi, TMEDA, −70 °C; (ii) S or Se, 0 °C; (iii) CS_2 or CSe_2, −90 °C; (iv) Se, then EtI, 0 °C; (v) $P(OMe)_3$, reflux; (vi) HCl aq, MeOH−THF, rt; (vii) TsCl, Et_3N, 0 °C; (viii) NaI, DMF, 80 °C.

Scheme 8. Synthesis of Selenoacetylene 6[a]



[a] Key: (i) *n*-BuLi, −70 °C; (ii) Se, 0 °C; (iii) 2-iodoethyl tetrahydropyranyl ether (**8**), 0 °C; (iv) KOH aq, MeOH, rt.

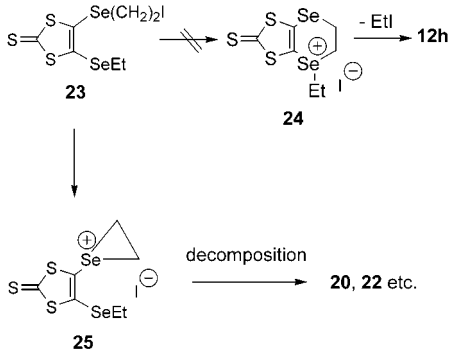
Scheme 9. Synthetic Attempts for BEDSe-TTF (1h)[a]



[a] Key: (i) *n*-BuLi, TMEDA, −70 °C; (ii) S, 0 °C; (iii) CS_2, −90 °C; (iv) Se, then EtI, 0 °C; (v) HCl aq, MeOH−THF, rt; (vi) TsCl, Et_3N, 0 °C; (vii) PBr_3, THF, rt; (viii) NaI, DMF, 80 °C; (ix) NaI, 2-butanone, reflux.

2-haloethylselenides tend to decompose via seleniranium (episelenonium) intermediates,[20] we thus speculate that the failure of the conversion of **21** into **12h** can be rationalized by decomposition of the resulting iodo compound **23** (or the bromo compound **21**) via the seleniranium salt **25** in preference to the formation of the outer six-membered ring by transalkylation via the seleninium salt **24** (Scheme 10). As a result, it is impossible to

Scheme 10. Suggested Reaction Path from 23



synthesize the BEDSe-type donors by this method involving the annelation of the outer six-membered heterocyclic ring by an intramolecular transalkylation reaction on a chalcogen atom.

Conclusion

We have established a synthetic method of BEDT-TTF (**1a**) and its six selenium variants (**1b**−**g**) from the common starting material **5**. The present method is quite valid and versatile in introducing selenium atoms at the desired positions of BEDT-TTF framework by changing the chalcogen reagents (elemental sulfur or selenium, carbon disulfide or carbon diselenide, alkyl thiocyanate or selenium powder and alkyl iodide) at the first one-pot formation of 1,3-dichalcogenole-2-chalcogenone. In addition, it may be emphasized that in combination with trialkyl phosphite-induced cross-coupling reactions, the present method has the potential of providing synthetic routes to numerous unprecedented TTF-type donors. However, it has the disadvantage of being inapplicable to the synthesis of BEDSe-type donors. In the previous syntheses of BEDSe-TTF[7] and BEDSe-TSF,[8] the construction of the outer BEDSe ring was accomplished by the reaction of either 1,3-dithiole (diselenole)-4,5-diselenium anion or TTF (TSF)-tetraselenium anion with 1,2-dibromoethane, but this ring formation is not straightforward because of the difficult in situ generation of these selenium anions. In this connection, we recently developed an improved synthetic method for BEDSe-TSF (**1i**) using the deprotection/realkylation protocol of a protected TSF tetraselenolate.[21]

(20) (a) Lindgren, B. *Acta Chem. Scand.* **1973**, *27*, 726−727. (b) Lindgren, B. *Tetrahedron Lett.* **1974**, 4347−4350.

(21) Kodani, M.; Takimiya, K.; Aso, Y.; Otsubo, T.; Nakayashiki, T.; Misaki, Y. *Synthesis* **2001**, 1614−1618.

Table 1. Half-Wave Oxidation Potentials[a] of BEDT-TTF-Type Donors

donor	$E_1^{1/2}$ (V)	$E_2^{1/2}$ (V)	ΔE (V)
BEDT-TTF (**1a**)	0.52	0.88	0.36
BETS (**1b**)	0.69	0.96	0.27
BEDT-STF (**1c**)	0.56	0.88	0.32
BEST-TTF (**1d**)	0.50	0.87	0.37
BEST-TSF (**1e**)	0.67	0.95	0.28
BEST-STF(t) (**1f**)	0.55	0.88	0.33
BEST-STF(g) (**1g**)	0.55	0.87	0.32
BEDSe-TSF (**1i**)	0.62	0.92	0.30
TTF	0.34	0.81	0.47
TSF	0.52	0.88	0.36

[a] Versus a Ag/AgCl electrode, in PhCN containing 0.1 M n-Bu_4NPF_6 as a supporting electrolyte. Pt working and counter electrodes, scan rate 100 mV/s, 23 °C.

This method nicely complements the present synthetic method of BEDT-TTF variants. All the selenium variants of BEDT-TTF thus obtained have strong electron-donating abilities similar to that of BEDT-TTF itself, which are estimated on the basis of their half-wave oxidation potentials as shown in Table 1. Now that these donors can be readily prepared in practical amounts by the present method, further investigations on the formation of their conductive radical cation salts are under way.[2]

Experimental Section

General. Melting points are uncorrected. NMR spectra were obtained in $CDCl_3$ at 400 MHz for ^1H and 100 MHz for ^{13}C with TMS as the internal reference. EI-MS spectra were obtained using an electron impact ionization procedure (70 eV). A FAB-MS spectrum was recorded using 3-nitrobenzyl alcohol as a matrix. The molecular ion peaks of selenium-containing compounds showed a typical selenium isotopic pattern, and all selenium-containing mass peaks are reported for ^{80}Se. All chemicals and solvents were reagent grade. All reactions were carried out under a nitrogen atmosphere with dry solvents. Column chromatography was carried out with silica gel (63−210 μm) or aluminum oxide (70−230 μm). Selenium powder (red)[23] and carbon diselenide[24] were synthesized according to the literature procedures.

2-Thiocyanatoethyl Tetrahydropyranyl Ether (9). A mixture of 2-iodoethyl tetrahydropyranyl ether (**8**)[14] (79 g, 0.31 mol) and potassium thiocyanate (45 g, 0.47 mol) in acetone (1.3 L) was refluxed for 18 h. Precipitated inorganic salts were filtered off, and the filtrate was concentrated to about one-third of the original volume, diluted with water (200 mL), and extracted with dichloromethane (150 mL × 3). The extract was washed with water (300 mL × 3) and brine (300 mL × 2), dried (Na_2SO_4), and concentrated in vacuo to give the crude product, which was then purified by distillation (bp 115 °C at 3 mmHg) to give **9** (58.2 g, 85% yield) as a colorless oil: ^1H NMR δ 1.50−1.80 (m, 6H, CH_2), 3.19 (m, 2H, CH_3), 3.50−4.08 (m, 4H, CH), 4.67 (m, 1H, CH); ^{13}C NMR δ 18.67, 24.90, 29.85, 33.84, 61.77, 64.94, 98.50, 111.85; IR (neat) 2155 cm^{-1} (SCN); MS m/z 187 (M^+). Anal. Calcd for $C_8H_{13}NO_2S$: C, 51.31; H, 7.00; N, 7.48. Found: C, 51.08; H, 7.01; N, 7.38.

2-Ethynylthioethyl Tetrahydropyranyl Ether (5). To freshly prepared ethynylmagnesium chloride (0.3 mol) in THF (200 mL) was slowly added **9** (40 g, 0.23 mol) in THF (30 mL) at 0 °C, and the resulting reaction mixture was further stirred for 12 h at room temperature and then poured onto ice−water (ca. 1 L). The mixture was extracted with dichloromethane (300 mL × 3), and the extract was washed with water (300 mL × 3) and brine (200 mL × 2), dried (Na_2SO_4), and concentrated in vacuo. The oily residue was purified by distillation (bp 96 °C at 2 mmHg) to give **5** (23 g, 54% yield) as a colorless oil: ^1H NMR δ 1.50−1.80 (m, 6H, CH_2), 2.79 (s, 1H, CH), 2.94 (m, 2H, CH_3), 3.50−4.10 (m, 4H, CH), 4.67 (m, 1H, CH); ^{13}C NMR δ 19.00, 25.18, 30.22, 34.64, 61.82, 65.15, 73.86, 81.86, 98.60; IR (neat) 2043 cm^{-1} (C≡C). This compound was thermally unstable and immediately used in the following step without further purification.

2-Ethynylselenoethyl Tetrahydropyranyl Ether (6). To a solution of trimethylsilylacetylene (**18**) (9.8 g, 0.1 mol) in THF (200 mL) was slowly added a hexane solution of n-BuLi (1.54 M, 65 mL, 0.1 mol) at −70 °C, and the resulting solution was stirred for 30 min at the same temperature. To the resulting lithium acetylide solution was added selenium powder (7.95 g, 0.1 mol) in one portion, and the resulting mixture was allowed to warm to 0 °C over a period of 2 h. Then, the mixture was cooled again to −70 °C, and 2-iodoethyl tetrahydropyranyl ether (**8**) (28.16 g, 0.11 mol) was added. The mixture was allowed to warm to room temperature over a period of 2 h and then concentrated in vacuo. The residue was diluted with water (250 mL) and extracted with dichloromethane (100 mL × 3), and the extract was washed with water (100 mL × 2) and brine (100 mL × 2), dried (Na_2SO_4), and concentrated in vacuo. The residual 2-(trimethylethynylseleno)ethyl tetrahydropyranyl ether (**19**) was dissolved in methanol (250 mL) and then treated with an aqueous potassium hydroxide solution (5.5 g in 30 mL of water). The mixture was concentrated, and the residue was diluted with dichloromethane (250 mL), was washed with water (100 mL × 2) and brine (100 mL × 2), and dried (Na_2SO_4). The solution was passed through a short column of alumina and concentrated in vacuo to give the crude product, which was then purified by distillation (bp 88−92 °C at 10^{-2} mmHg) to give **6** (17.3 g, 74% yield) as a colorless oil: ^1H NMR δ 1.40−1.70 (m, 6H, CH_2), 2.66 (s, 1H, CH), 2.88 (m, 2H, CH_3), 3.40−3.90 (m, 4H, CH), 4.54 (m, 1H, CH); ^{13}C NMR δ 19.11, 25.26, 28.26, 30.32, 62.00, 64.90, 66.07, 87.97, 98.63; IR (neat) 2031 cm^{-1} (C≡C). This compound was not sufficiently thermally stable to be microanalyzed.

General One-Pot Synthetic Method of 1,3-Dichalcogenole-2-chalcogenones (7). 4-Methylthio-5-[2-(tetrahydropyran-2-yloxy)ethylthio]-1,3-dithiole-2-thione (7a). To a mixture of **5** (4.6 g, 25 mmol) and TMEDA (7.4 mL, 49 mmol) in THF (100 mL) cooled to −70 °C was added a hexane solution of n-BuLi (1.61 M, 15 mL, 25 mmol), and the solution was stirred for 30 min to form the lithium acetylide species. Sulfur (780 mg, 25 mmol) was added in one portion, and the reaction mixture was warmed to 0 °C over a period of 1 h and stirred for additional 2 h at 0 °C. The mixture was cooled again to −90 °C, and then carbon sulfide (1.5 mL, 25 mmol) and methyl thiocyanate (5.1 mL, 74 mmol) were added. The resulting mixture was allowed to warm to 0 °C over a period of 2 h and stirred for an additional 0.5 h at 0 °C. Then, the mixture was diluted with water (100 mL) and extracted with dichloromethane (100 mL × 3). The extract was washed with brine (100 mL × 2), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified with column chromatography on silica gel eluted with benzene to afford **7a** as a yellow oil (R_f = 0.4, 6.3 g, 76%): ^1H NMR δ 1.48−1.90 (m, 6H, CH_2), 2.52 (s, 3H, CH_3), 3.09 (t, J = 6.4 Hz, 2H, CH_2), 3.50−4.00 (m, 4H, CH), 4.63 (m, 1H, CH); ^{13}C NMR δ 18.87, 18.93, 25.02, 30.08, 36.14, 61.85, 65.88, 98.56, 132.02, 139.30, 210.24; IR (neat) 1064 cm^{-1} (C═S); MS m/z 340 (M^+). Anal. Calcd for $C_{11}H_{16}O_2S_5$: C, 38.80; H, 4.74. Found: C, 38.76; H, 4.72.

4-Methylthio-5-[2-(tetrahydropyran-2-yloxy)ethylthio]-1,3-diselenole-2-selone (7b, R = Me): red oil (71% yield from **5**); ^1H NMR δ 1.48−1.88 (m, 6H, CH_2), 2.55 (s, 3H, CH_3), 3.12 (t, J = 6.6 Hz, 2H, CH_2), 3.50−4.10 (m, 4H, CH_2), 4.64 (m, 1H, CH); ^{13}C NMR δ 19.24, 20.47, 25.27, 30.36, 37.36, 62.24, 66.16, 98.97, 140.38, 148.20, 206.18; IR (neat) 905 cm^{-1}

(22) Some conductive radical cation salts of BEDT-STF (**1c**) have been reported in a preliminary report: Mori, H.; Okano, T.; Kamiya, M.; Haemori, M.; Suzuki, H.; Tnanaka, S.; Tamura, M.; Nishio, Y.; Kajita, K.; Kodani, M.; Takimiya, K.; Otsubo, T.; Moriyama, H. *Synth. Met.* **2001**, *120*, 979−980.

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(C═Se); MS *m*/*z* 484 (M^+). Anal. Calcd for $C_{11}H_{16}O_2S_2Se_3$: C, 27.45; H, 3.35. Found: C, 27.45; H, 3.35.

4-Ethylthio-5-[2-(tetrahydropyran-2-yloxy)ethylthio]-1,3-diselenole-2-selone (7b, R = Et): red oil (73% yield from **5**); ^{1}H NMR δ 1.37 (t, J = 7.3 Hz, 3H, CH_3), 1.49−1.88 (m, 6H, CH_2), 2.95 (q, J = 7.3 Hz, 2H, CH_2), 3.12 (t, J = 6.6 Hz, 2H, CH_2), 3.50−4.05 (m, 64H, CH_2), 4.64 (m, 1H, CH); ^{13}C NMR δ 14.73, 19.09, 25.13, 30.21, 31.90, 37.33, 62.03, 65.97, 98.76, 143.61, 145.20, 206.37; IR (neat) 907 cm^{-1} (C═Se); MS *m*/*z* 498 (M^+). Anal. Calcd for $C_{12}H_{18}O_2S_2Se_3$: C, 29.10; H, 3.66. Found: C, 29.40; H, 3.58.

4-Ethylthio-5-[2-(tetrahydropyran-2-yloxy)ethylthio]-1,3-thiaselenole-2-thione (7c): red oil (98% yield from **5**); ^{1}H NMR δ 1.38 (t, J = 7.4 Hz, 3H, CH_3), 1.50−1.88 (m, 6H, CH_2), 2.93 (q, J = 7.4 Hz, 2H, CH_2), 3.10 (t, J = 6.6 Hz, 2H, CH_2), 3.45−4.00 (m, 4H, CH_2), 4.64 (m, 1H, CH); ^{13}C NMR δ 14.71, 19.07, 25.16, 30.23, 31.83, 36.31, 62.01, 66.05, 98.72, 133.30, 142.31, 213.15; IR (neat) 1054 cm^{-1} (C═S); MS *m*/*z* 402 (M^+). Anal. Calcd for $C_{12}H_{18}O_2S_4Se$: C, 35.90; H, 4.52. Found: C, 36.10; H, 4.66.

4-Methylseleno-5-[2-(tetrahydropyran-2-yloxy)ethylthio]-1,3-dithiole-2-thione (7d): yellow oil (80% yield from **5**); ^{1}H NMR δ 1.49−1.89 (m, 6H, CH_2), 2.42 (s, 3H, CH_3), 3.09 (t, J = 6.6 Hz, 2H, CH_2), 3.50−4.00 (m, 4H, CH), 4.64 (m, 1H, CH); ^{13}C NMR δ 9.61, 19.13, 25.20, 30.28, 36.54, 62.13, 66.07, 98.84, 131.12, 132.55, 212.77; IR (neat) 1067 cm^{-1} (C═S); MS *m*/*z* 388 (M^+). Anal. Calcd for $C_{11}H_{16}O_2S_4Se$: C, 34.10; H, 4.16. Found: C, 34.13; H, 4.14.

4-Ethylseleno-5-[2-(tetrahydropyran-2-yloxy)ethylthio]-1,3-diselenole-2-selone (7e): red oil (82% yield from **5**); ^{1}H NMR δ 1.51 (t, J = 7.4 Hz, 3H, CH_3), 1.5−1.9 (m, 6H, CH_2), 3.01 (q, J = 7.4 Hz, 2H, CH_2), 3.13 (t, J = 6.6 Hz, 2H, CH_2), 3.45−4.00 (m, 4H, CH_2), 4.64 (m, 1H, CH); ^{13}C NMR δ 15.56, 18.97, 24.84, 25.02, 30.09, 37.46, 61.86, 65.81, 98.58, 136.06, 143.22, 208.70; IR (neat) 909 cm^{-1} (C═Se); MS *m*/*z* 546 (M^+). Anal. Calcd for $C_{12}H_{18}O_2SSe_4$: C, 26.53; H, 3.53. Found: C, 26.73; H, 3.52.

5-Ethylseleno-4-[2-(tetrahydropyran-2-yloxy)ethylthio]-1,3-thiaselenole-2-selone (7f): red oil (73% yield from **5**); ^{1}H NMR δ 1.51 (t, J = 7.5 Hz, 3H, CH_3), 1.49−1.86 (m, 6H, CH_2), 3.00 (q, J = 7.5 Hz, 2H, CH_2), 3.13 (t, J = 6.4 Hz, 2H, CH_2), 3.45−4.05 (m, 4H, CH_2), 4.64 (m, 1H, CH); ^{13}C NMR δ 15.71, 19.15, 24.36, 25.15, 30.23, 37.68, 62.13, 66.00, 98.88, 130.84, 144.76, 207.24; IR (neat) 932 cm^{-1} (C═Se); MS *m*/*z* 498 (M^+). Anal. Calcd for $C_{12}H_{18}O_2S_2Se_3$: C, 29.10; H, 3.66. Found C, 29.13; H, 3.65.

4-Ethylseleno-5-[2-(tetrahydropyran-2-yloxy)ethylthio]-1,3-thiaselenole-2-thione (7g): yellow oil (88% yield from **5**); ^{1}H NMR δ 1.52 (t, J = 7.5 Hz, 3H, CH_3), 1.50−1.85 (m, 6H, CH_2), 2.98 (q, J = 7.5 Hz, 2H, CH_2), 3.09 (t, J = 6.4 Hz, 2H, CH_2), 3.48−4.00 (m, 4H, CH_2), 4.64 (m, 1H, CH); ^{13}C NMR δ 15.73, 19.23, 24.89, 25.30, 30.40, 36.67, 62.22, 66.19, 98.95, 133.76, 134.07, 215.63; IR (neat) 1055 cm^{-1} (C═S); MS *m*/*z* 450 (M^+). Anal. Calcd for $C_{12}H_{18}O_2S_3Se_2$: C, 32.14; H, 4.05. Found: C, 32.11; H, 4.07.

4-Ethylseleno-5-[2-(tetrahydropyran-2-yloxy)ethylseleno]-1,3-dithiole-2-thione (7h). This compound was similarly prepared using 2-ethynylselenoethyl tetrahydropyranyl ether (**6**) instead of **5**: yellow oil (59% yield from **6**); ^{1}H NMR δ 1.51 (t, J = 7.6 Hz, 3H, CH_3), 1.45−1.80 (m, 6H, CH_2), 2.98 (q, J = 7.5 Hz, 2H, CH_2), 3.16 (t, J = 6.7 Hz, 2H, CH_2), 3.45−4.10 (m, 4H, CH_2), 4.64 (m, 1H, CH); ^{13}C NMR δ 15.71, 19.11, 24.47, 25.19, 30.19, 30.26, 62.11, 66.53, 98.72, 128.01, 128.29, 215.27; IR (neat) 1063 cm^{-1} (C═S); MS *m*/*z* 450 (M^+). Anal. Calcd for $C_{12}H_{18}O_2S_3Se_2$: C, 32.14; H, 4.05. Found: C, 32.08; H, 4.12.

General Synthetic Method for 10. 4-Methylthio-5-(2-hydroxyethylthio)-1,3-dithiole-2-thione (10a). A mixture of **7a** (5.8 g, 17 mmol), hydrochloric acid (1 M, 20 mL), methanol (30 mL), and acetone (30 mL) was stirred at room temperature for 24 h. The mixture was diluted with dichloromethane (300 mL), and the solution was washed with water (100 mL × 3) and brine (100 mL × 2), dried ($MgSO_4$), and then concentrated. The residue was purified by column chromatography (silica gel; eluent, 9:1 v/v dichloromethane/ethyl acetate) to **10a** as a yellow solid (R_f = 0.2 (CH_2Cl_2), 3.7 g, 85%): ^{1}H NMR δ 2.43 (s, 1H, OH), 2.54 (s, 3H, CH_3), 3.03 (t, J = 5.4 Hz, 2H, CH_2), 3.81 (t, J = 5.4 Hz, CH_2); ^{13}C NMR δ 19.16, 39.72, 60.21, 130.10, 141.98, 210.61; IR (neat) 3000−3700 (OH), 1063 cm^{-1} (C═S); MS *m*/*z* 256 (M^+). Anal. Calcd for $C_6H_8OS_5$: C, 28.10; H, 3.14. Found: C, 28.12; H, 3.15.

4-Ethylthio-5-(2-hydroxyethylthio)-1,3-thiaselenole-2-thione (10c): yellow oil (85% yield from **7c**); ^{1}H NMR δ 1.40 (t, J = 7.4 Hz, 3H, CH_3), 2.32 (s, 1H, OH), 2.96 (q, J = 7.4 Hz, 2H, CH_2), 3.01 (t, J = 5.5 Hz, 2H, CH_2), 3.80 (t, J = 5.5 Hz, CH_2); ^{13}C NMR δ 14.85, 32.20, 39.97, 59.95, 131.21, 144.97, 213.15; IR (neat) 3100−3700 (OH), 1051 cm^{-1} (C═S); MS *m*/*z* 318 (M^+). Anal. Calcd for $C_7H_{10}OS_4Se$: C, 26.49; H, 3.12. Found: C, 26.64; H, 3.14.

4-Methylseleno-5-(2-hydroxyethylthio)-1,3-dithiole-2-thione (10d): yellow oil (quantitative from **7d**); ^{1}H NMR δ 2.28 (t, J = 6.4 Hz, 1H, OH), 2.45 (s, 3H, CH_3), 3.02 (t, J = 5.9 Hz, CH_2), 3.81 (dt, J = 6.4, 5.9 Hz, 2H, CH_2); ^{13}C NMR δ 10.00, 40.03, 60.20, 130.01, 133.47, 212.83; IR (neat) 3000−3500 (OH), 1057 cm^{-1} (C═S); MS *m*/*z* 304 (M^+). Anal. Calcd for $C_6H_8OS_4Se$: C, 23.76; H, 2.66. Found: C, 23.76; H, 2.61.

4-Ethylseleno-5-(2-hydroxyethylseleno)-1,3-dithiole-2-thione (10h): yellow oil (81% yield from **7h**); ^{1}H NMR δ 1.53 (t, J = 7.6 Hz, 3H, CH_3), 2.25 (J = 5.8 Hz, 1H, OH), 3.00 (t, J = 7.6 Hz, 2H, CH_2), 3.10 (t, J = 6.0 Hz, 2H, CH_2), 3.88 (dt, J = 5.8, 6.0 Hz, 2H, CH_2); ^{13}C NMR δ 15.80, 24.83, 34.20, 60.86, 125.85, 130.96, 215.39; IR (neat) 3000−3500 (OH), 1059 cm^{-1} (C═S); MS *m*/*z* 366 (M^+). Anal. Calcd for $C_7H_{10}OS_3Se_2$: C, 23.08; H, 2.77. Found: C, 23.09; H, 2.78.

General Synthetic Method for 11. 4-Methylthio-5-(2-tosyloxyethylthio)-1,3-dithiole-2-thione (11a). To a solution of **10a** (3.2 g, 12 mmol) in pyridine (24 mL) was added tosyl chloride (2.4 g, 37 mmol) at 0 °C. After being stirred for 36 h at 0 °C, the mixture was poured into ice containing 1 M hydrochloric acid (30 mL). The mixture was extracted with dichloromethane (100 mL × 3), and the extract was washed successively with water (100 mL × 2) and brine (50 mL × 2) and dried ($MgSO_4$). The concentrated extract was purified by column chromatography on silica gel eluted with dichloromethane to give **10a** as yellow oil (R_f = 0.5, 4.0 g, 80% yield): ^{1}H NMR δ 2.41 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.01 (t, J = 6.6 Hz, 2H, CH_2), 4.16 (t, J = 6.6 Hz, 2H, CH_2), 7.33 (d, J = 8.3 Hz, 2H, ArH), 7.73 (d, J = 8.3 Hz, 2H, ArH); ^{13}C NMR δ 18.88, 21.64, 34.75, 67.47, 127.82, 129.93, 130.22, 132.25, 143.23, 145.32, 210.05; IR (KBr) 1354, 1188 (O═S═O), 1072 cm^{-1} (C═S); MS *m*/*z* 410 (M^+). Anal. Calcd for $C_{13}H_{14}O_3S_6$: C, 38.03; H, 3.44. Found: C, 37.98; H, 3.38.

4-Ethylthio-5-(2-tosyloxyethylthio)-1,3-thiaselenole-2-thione (11c): yellow needles from chloroform−hexane (94% yield from **10c**); mp 69−70 °C; ^{1}H NMR δ 1.36 (t, J = 7.4 Hz, 3H, CH_3), 2.47 (s, 3H, CH_3), 2.92 (q, J = 7.4 Hz, 2H, CH_2), 3.05 (t, J = 6.8 Hz, 2H, CH_2), 4.21 (t, J = 6.8 Hz, 2H, CH_2), 7.38 (d, J = 8.2 Hz, 2H, ArH), 7.80 (d, J = 8.2 Hz, 2H, ArH); ^{13}C NMR δ 14.85, 21.74, 32.05, 34.83, 67.55, 127.97, 129.38, 130.02, 132.46, 145.36, 145.92, 210.65; IR (KBr) 1354, 1171 (O═S═O), 1055 cm^{-1} (C═S); MS *m*/*z* 472 (M^+). Anal. Calcd for $C_{14}H_{16}O_3S_5Se$: C, 35.66; H, 3.42. Found: C, 35.43; H, 3.36.

4-Methylseleno-5-(2-tosyloxyethylthio)-1,3-dithiole-2-thione (11d): yellow oil (87% yield from **10d**); ^{1}H NMR δ 2.41 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 3.05 (t, J = 6.8 Hz, 2H, CH_2), 4.22 (t, J = 6.8 Hz, 2H, CH_2), 7.38 (d, J = 8.0 Hz, 2H, ArH), 7.80 (d, J = 8.0 Hz, 2H, ArH); ^{13}C NMR δ 9.70, 21.73, 30.90, 67.47, 126.23, 127.97, 129.11, 130.02, 132.50, 145.42, 212.32; IR (KBr) 1361, 1174 (O═S═O), 1063 cm^{-1} (C═S); MS *m*/*z* 458 (M^+). Anal. Calcd for $C_{13}H_{14}O_3S_5Se$: C, 34.13; H, 3.08. Found: C, 34.00; H, 3.05.

General Synthetic Method for 12. 5,6-Dihydro-2-thioxo-1,3-dithiolo[2,3-*d*][1,4]dithiin (12a). A mixture of **11a** (0.40 g, 0.96 mmol) and sodium iodide (0.29 g, 1.9 mmol) in DMF (4 mL) was heated at 95 °C for 20 h. The mixture was then diluted with water (30 mL) and extracted with carbon disulfide (50 mL × 3), and the extract was successively washed with water (50 mL × 3) and brine (50 mL × 2) and finally dried ($MgSO_4$). Column chromatography of the concentrated extract on silica gel eluted with carbon disulfide gave **12a** as yellow

needles (0.14 g, 67% yield): mp 121−122 °C (recrystallization from chloroform; lit.[15b] 119−121 °C); ^{1}H NMR δ 3.38 (s, 4H, CH_2); MS *m*/*z* 224 (M^+); IR (KBr) 1061 cm^{-1} (C═S).

5,6-Dihydro-2-thioxo-1,3-thiaselenolo[2,3-*d*][1,4]-dithiin (12c): yellow needles from carbon disulfide−hexane (65% yield from **11c**); mp 122 °C; ^{1}H NMR δ 3.41 (s, 4H, CH_2); ^{13}C NMR δ 29.95, 30.88, 122.58, 124.63, 209.18; IR (KBr) 1020 cm^{-1} (C═S); MS *m*/*z* 272 (M^+). Anal. Calcd for $C_5H_4S_4Se$: C, 22.14; H, 1.49. Found: C, 22.32; H, 1.56.

5,6-Dihydro-2-thioxo-1,3-dithiolo[2,3-*d*][1,4]-thiaselenin (12d): yellow needles from chloroform−hexane (52% yield from **11d**); mp 124−125 °C; ^{1}H NMR δ 3.33 (m, 2H, CH_2), 3.52 (m, 2H, CH_2); ^{13}C NMR δ 25.17, 31.50, 118.38, 126.61, 210.33; IR (KBr) 1059 cm^{-1} (C═S); MS *m*/*z* 272 (M^+). Anal. Calcd for $C_5H_4S_4Se$: C, 22.14; H, 1.49. Found: C, 22.12; H, 1.46.

General Synthetic Method for 13. 5,6-Dihydro-2-oxo-1,3-dithiolo[2,3-*d*][1,4]thiaselenin (13d). A mixture of **12d** (0.59 g, 2.2 mmol) and mercury acetate (0.17 g, 5.5 mmol) in chloroform (44 mL) was stirred for 8 h. The resulting white solid was filtered off and washed with chloroform (10 mL × 3), and the combined filtrate was washed with water (50 mL × 3) and brine (50 mL × 3) and dried ($MgSO_4$). Evaporation of the solvent gave a pale yellow solid, which was then purified by recrystallization from chloroform−hexane to give **13d** as pale yellow needles (533 mg, 95%): mp 119−120 °C; ^{1}H NMR δ 3.31 (m, 2H, CH_2), 3.56 (m, 2H, CH_2); ^{13}C NMR δ 27.06, 32.37, 109.69, 117.12, 191.00; IR (KBr) 1613 cm^{-1} (C═O); MS *m*/*z* 256 (M^+). Anal. Calcd for $C_5H_4OS_3Se$: C, 23.53; H, 1.58. Found: C, 23.56; H, 1.52.

5,6-Dihydro-2-oxo-1,3-thiaselenolo[2,3-*d*][1,4]dithiin (13c): colorless fine crystals from carbon disulfide−hexane (83% yield from **12c**); mp 110 °C (lit.[9] 110 °C); ^{1}H NMR δ 3.43 (s, 4H, CH_2); ^{13}C NMR δ 32.77, 34.06 100.52, 118.40, 189.65; IR (KBr) 1635 cm^{-1} (C═O); MS *m*/*z* 256 (M^+). Anal. Calcd for $C_5H_4OS_3Se$: C, 23.53; H, 1.58. Found: C, 23.43; H, 1.62.

General Synthetic Method for 14. 2,6(7)-Bis(methylthio)-3,7(6)-bis[2-(tetrahydropyran-2-yloxy)ethylthio]-tetraselenafulvalene (14b, R = Me). To a refluxing solution of **7b** (R = Me, 2.0 g, 4.2 mmol) in benzene (20 mL) was added trimethyl phosphite (2.0 mL, 17 mol), and the resulting mixture was refluxed for 1 h. Evaporation of the solvent and excess trimethyl phosphite gave an oily residue, which was purified by column chromatography on silica gel with dichloromethane−ethyl acetate (9:1, v/v) as an eluent to give **14b** (R = Me) as a red oil (R_f = 0.3, 1.3 g, 77%): ^{1}H NMR δ 1.48−1.90 (m, 12H, CH_2), 2.460 and 2.462 (s, 6H, CH_3), 3.056 (t, *J* = 7.0 Hz, 2H, CH_2), 3.063 (t, *J* = 6.2 Hz, 2H, CH_2), 3.48−3.98 (m, 8H, CH_2), 4.65 (m, 2H, CH); ^{13}C NMR δ 19.25, 20.52, 25.34, 30.40, 37.00, 62.15, 66.30 and 66.32, 98.88, 107.39 and 107.45, 127.49 and 127.63, 133.27 and 133.39; MS (FAB) *m*/*z* 808 (M^+). Anal. Calcd for $C_{22}H_{32}O_4S_4Se_4$: C, 32.84; H, 4.01. Found: C, 32.80; H, 4.00.

2,6(7)-Bis(ethylthio)-3,7(6)-bis[2-(tetrahydropyran-2-yloxy)ethylthio]-tetraselenafulvalene (14b, R = Et): red oil (60% yield from **7b**, R = Et); ^{1}H NMR δ 1.33 (t, *J* = 7.3 Hz, 6H, CH_3), 1.45−1.90 (m, 12H, CH_2), 2.88 (q, *J* = 7.3 Hz, 4H, CH_2), 3.062 (t, *J* = 6.8 Hz, 2H, CH_2), 3.068 (t, *J* = 6.6 Hz, 2H, CH_2), 3.45−3.90 (m, 8H, CH_2), 4.65 (m, 2H, CH); ^{13}C NMR δ 14.99, 19.23, 23.31, 30.39, 31.72, 37.01 and 37.02, 62.12, 66.28, 98.85, 106.88, 129.89 and 129.95, 131.29 and 131.34; MS (FAB) *m*/*z* 836 (M^+). Anal. Calcd for $C_{24}H_{36}O_4S_4Se_4$: C, 34.62; H, 4.36. Found: C, 34.70; H, 4.36.

2,6(7)-Bis(ethylthio)-3,7(6)-bis[2-(tetrahydropyran-2-yloxy)ethylthio]-diselenadithiafulvalene (14c): yellow oil (R_f = 0.2, 0.88 g, 91% from **17c**); ^{1}H NMR δ 1.329 and 1.331 (t, *J* = 7.5 Hz, 6H, CH_3), 1.50−1.85 (m, 12H, CH_2), 2.846 and 2.849 (q, *J* = 7.5 Hz, 4H, CH_2), 3.05−3.09 (m, 4H, CH_2), 3.48−3.98 (m, 8H, CH_2), 4.65 (m, 2H, CH); ^{13}C NMR δ 15.04 and 15.07, 19.25 and 19.27, 25.36, 30.44, 31.74 and 31.79, 35.86 and 35.89, 62.16 and 62.19, 66.36, 98.88 and 98.91, 108.38 and 109.13, 127.99 and 128.57, 128.88 and 129.77; MS *m*/*z* 740 (M^+). Anal. Calcd for $C_{24}H_{36}O_4S_6Se_2$: C, 39.02; H, 4.91. Found: C, 38.85; H, 4.96.

2,6(7)-Bis(ethylseleno)-3,7(6)-bis[2-(tetrahydropyran-2-yloxy)ethylthio]-tetraselenafulvalene (14e): red oil (83% yield from **7e**); ^{1}H NMR δ 1.48 (t, *J* = 7.4 Hz, 6H, CH_3), 1.45−1.90 (m, 12H, CH_2), 2.95 (q, *J* = 7.4 Hz, 4H, CH_2), 3.04 (t, *J* = 6.8 Hz, 2H, CH_2), 3.05 (t, *J* = 6.6 Hz, 2H, CH_2), 3.45−3.98 (m, 8H, CH_2), 4.65 (m, 2H, CH); ^{13}C NMR δ 15.91, 19.22, 24.64, 25.29, 30.36, 37.07, 62.11, 66.21, 98.82, 108.70, 108.75, 122.43 and 122.70, 128.40 and 128.66; MS (FAB) *m*/*z* 932 (M^+). Anal. Calcd for $C_{24}H_{36}O_4S_2Se_6$: C, 31.12; H, 3.92. Found: C, 30.84; H, 3.77.

3,7-Bis(ethylseleno)-2,6-bis[2-(tetrahydropyran-2-yloxy)-ethylthio]-diselenadithiafulvalene (14f): red oil (50% yield from **7f**); ^{1}H NMR δ 1.48 (t, *J* = 7.6 Hz, 6H, CH_3), 1.46−1.89 (m, 12H, CH_2), 2.956 and 2.964 (q, *J* = 7.6 Hz, 4H, CH_2), 3.02 (m, 4H, CH_2), 3.48−3.96 (m, 8H, CH_2), 4.65 (m, 2H, CH); ^{13}C NMR δ 15.91, 19.29, 23.74, 25.35, 30.44, 37.08 and 37.15, 62.20, 66.30, 98.95, 110.44 and 111.05, 122.13 and 123.06, 125.36 and 126.03; MS (FAB,) *m*/*z* 836 (M^+). Anal. Calcd for $C_{24}H_{36}O_4S_4Se_4$: C, 34.62; H, 4.36. Found: C, 34.59; H, 4.37.

2,6-Bis(ethylseleno)-3,7-bis[2-(tetrahydropyran-2-yloxy)-ethylthio]-diselenadithiafulvalene (14g): red oil (67% yield from **7g**); ^{1}H NMR δ 1.48 (t, *J* = 7.6 Hz, 6H, CH_3), 1.48−1.80 (m, 12H, CH_2), 2.91 (q, *J* = 7.6 Hz, 4H, CH_2), 3.05 (m, 4H, CH_2), 3.48−3.90 (m, 8H, CH_2), 4.65 (m, 2H, CH); ^{13}C NMR δ 15.91, 19.18, 24.49 and 24,53, 25.27, 30.35, 35.90 and 35.93, 62.04 and 62.07, 66.21, 98.76, 109.54 and 110.37, 119.20 and 120.26, 127.72 and 129.04; MS (FAB) *m*/*z* 836 (M^+). Anal. Calcd for $C_{24}H_{36}O_4S_4Se_4$: C, 34.62; H, 4.36. Found: C, 34.44; H, 4.34.

General Synthetic Method for 15. 2,6(7)-Bis(methylthio)-3,7(6)-bis(2-hydroxyethylthio)-tetraselenafulvalene (15b R = Me): A mixture of **14b** (R = Me, 1.3 g, 1.6 mmol), hydrochloric acid (1.0 M, 4.0 mL), methanol (30 mL), and THF (30 mL) was stirred at room temperature for 24 h. The mixture was diluted with water (50 mL) and extracted with dichloromethane (50 mL × 3). The extract was washed with water (50 mL × 3) and brine (50 mL × 3) and dried ($MgSO_4$). Evaporation of the solvent gave crude **15b** (R = Me), which was purified by silica gel column chromatography eluted with dichloromethane−ethyl acetate (9:1, v/v) to give a red oil (R_f = 0.1, 0.74 g, 72% yield): ^{1}H NMR δ 2.50 (s, 3H, CH_3), 2.62 (s, 2H, OH), 2.96 (t, *J* = 5.6 Hz, 4H, CH_2), 3.76 (t, *J* = 5.6 Hz, 4H, CH_2); ^{13}C NMR δ 20.72, 40.19, 59.97, 107.22, 125.10 and 125.30, 136.53 and 136.70; IR (KBr) 3300 cm^{-1} (OH); MS *m*/*z* 640 (M^+). Anal. Calcd for $C_{12}H_{16}O_2S_4Se_4$: C, 22.65; H, 2.53. Found: C, 22.64; H, 2.53.

2,6(7)-Bis(ethylthio)-3,7(6)-bis(2-hydroxyethylthio)-tetraselenafulvalene (15b, R = Et): pink plates from chloroform−hexane (94% yield from **14b**, R = Et); mp 84−85 °C; ^{1}H NMR δ 1.35 (t, *J* = 7.4 Hz, 6H, CH_3), 2.46, (t, *J* = 6.3 Hz, 2H, OH), 2.92 (t, *J* = 7.4 Hz, 4H, CH_2), 2.97 (t, *J* = 5.6 Hz, 4H, CH_2), 3.75 (dt, *J* = 6.3, 5.6 Hz, 4H, CH_2); ^{13}C NMR δ 15.08, 32.15, 40.35, 59.88, 106.87, 127.18 and 127.32, 135.04 and 135.17; IR (KBr) 3400 cm^{-1} (OH); MS *m*/*z* 668 (M^+). Anal. Calcd for $C_{14}H_{20}O_2S_4Se_4$: C, 25.31; H, 3.03. Found: C, 25.04; H, 2.80.

2,6(7)-Bis(ethylthio)-3,7(6)-bis(2-hydroxyethylthio)-diselenadithiafulvalene (15c): red powder from chloroform−hexane (89% yield from **14c**); mp 79−81 °C; ^{1}H NMR δ 1.353 and 1.354 (t, *J* = 7.5 Hz, 6H, CH_3), 2.42−2.49 (m, 2H, OH), 2.885 and 2.889 (q, *J* = 7.5 Hz, 4H, CH_2), 2.95−3.10 (m, 4H, CH_2), 3.71−3.78 (m, 4H, CH_2); ^{13}C NMR δ 15.13, 32.10 and 32.16, 39.34, 59.98 and 60.04, 108.30 and 109.11, 126.07 and 127.33, 131.30 and 132.23; IR (KBr) 3400 cm^{-1} (OH); MS *m*/*z* 572 (M^+). Anal. Calcd for $C_{14}H_{20}O_2S_6Se_2$: C, 29.47; H. 3.53. Found: C, 29.48; H, 3.42.

2,6(7)-Bis(ethylseleno)-3,7(6)-bis(2-hydroxyethylthio)-tetraselenafulvalene (15e): red plate from dichloromethane−hexane (80% yield from **14e**); mp 89−90 °C; ^{1}H NMR δ 1.50 (t, *J* = 7.5 Hz, 6H, CH_3), 2.54, (t, *J* = 5.3 Hz, 2H, OH), 2.95 (t, *J* = 5.3 Hz, 4H, CH_2), 3.00 (q, *J* = 7.5 Hz, 4H, CH_2), 3.75 (q, *J* = 5.3 Hz, 4H, CH_2); ^{13}C NMR δ 16.00, 25.33, 40.43, 59.71, 108.73, 126.17 and 126.45, 126.50 and 126.77; IR (KBr) 3400 cm^{-1} (OH); MS *m*/*z* 764 (M^+). Anal. Calcd for $C_{14}H_{20}O_2S_2Se_6$: C, 22.18; H, 2.66. Found: C, 21.98; H, 2.56.

3,7-Bis(ethylseleno)-2,6-bis(2-hydroxyethylthio)-diselenadithiafulvalene (15f): red powder from chloroform−hexane (92% yield from **14f**); mp 110−112 °C; ^{1}H NMR δ 1.50 (t, J = 7.6 Hz, 6H, CH_3), 2.40 (t, J = 6.8 Hz, 2H, OH), 2.93 (t, J = 6.6 Hz, 4H, CH_2), 3.01 (q, J = 7.6 Hz, 4H, CH_2), 3.74 (dt, J = 6.8, 6.6 Hz, 4H, CH_2); ^{13}C NMR δ 15.91, 24.29, 40.34, 59.71, 110.51, 123.81, 125.88; IR (KBr) 3400 cm^{-1} (OH); MS m/z 668 (M^+). Anal. Calcd for $C_{14}H_{20}O_2S_4Se_4$: C, 25.31; H, 3.03. Found: C, 25.30; H, 3.01.

2,6-Bis(ethylseleno)-3,7-bis(2-hydroxyethylthio)-diselenadithiafulvalene (15g): red powder from chloroform−hexane (77% yield from **14g**); mp 68−70 °C; ^{1}H NMR δ 1.503 and 1.505 (t, J = 7.6 Hz, 6H, CH_3), 2.51 (s, 2H, OH), 2.951 and 2.955 (q, J = 7.6 Hz, 4H, CH_2), 2.96 (t, J = 5.6 Hz, 4H, CH_2), 3.73 (t, J = 5.6 Hz, 4H, CH_2); ^{13}C NMR δ 15.95, 25.07 and 25.11, 39.28, 59.80 and 59.85, 109.47 and 110.39, 122.33 and 123,40, 125.98 and 127.30; IR (KBr) 3300 cm^{-1} (OH); MS m/z 668 (M^+). Anal. Calcd for $C_{14}H_{20}O_2S_4Se_4$: C, 25.31; H, 3.03. Found: C, 25.30; H, 3.00.

General Synthetic Method for 16. 2,6(7)-Bis(methylthio)-3,7(6)-bis(2-tosyloxyethylthio)tetraselenafulvalene (16b, R = Me). To a solution of **15b** (R = Me, 0.21 g, 0.33 mmol) in pyridine (5 mL) was added tosyl chloride (0.19 g, 2.0 mmol) at 0 °C. The mixture was stirred for 12 h, and then poured onto a mixture of ice and hydrochloric acid (1 M, 10 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (50 mL × 3). The combined dichloromethane solution was washed successively with hydrochloric acid (1 M, 50 mL × 2), water (50 mL × 3), and brine (50 mL × 2) and dried ($MgSO_4$). Evaporation of the solvent gave crude **16b** (R = Me), which was purified by column chromatography on silica gel eluted with dichloromethane followed by recrystallization from dichloromethane−hexane (1:1, v/v) as an orange solid (0.19 g, 61%): mp 117−119 °C (from dichloromethane−methanol); ^{1}H NMR δ 2.45 (s, 6H, CH_3), 2.46 (s, 6H, CH_3), 3.03 (t, J = 7.0 Hz, 4H, CH_2), 4.20 (t, J = 7.0 Hz, 4H, CH_2), 7.36 (d, J = 8.3 Hz, 4H, ArH), 7.80 (d, J = 8.3 Hz, 4H, ArH); IR (KBr) 1363, 1175 cm^{-1} (O═S═O). Anal. Calcd for $C_{26}H_{28}O_6S_6Se_4$: C, 33.06; H, 2.99. Found: C, 33.10; H, 2.93.

2,6(7)-Bis(ethylthio)-3,7(6)-bis(2-tosyloxyethylthio)tetraselenafulvalene (16b, R = Et): pale red solid from chloroform−hexane (87% yield from **15b**, R = Et); mp 118−120 °C; ^{1}H NMR δ 1.29 (t, J = 7.4 Hz, 6H, CH_3), 2.46 (s, 6H, CH_3), 2.86 (q, J = 7.4 Hz, 4H, CH_2), 3.04 (t, J = 7.0 Hz, 4H, CH_2), 4.19 (t, J = 7.0 Hz, 4H, CH_2), 7.36 (d, J = 8.1 Hz, 4H, ArH), 7.80 (d, J = 8.1 Hz, 4H, ArH); ^{13}C NMR δ 14.05 and 15.04, 21.66 and 22.55, 31.89 and 31.91, 35.32 and 35.37, 67.79 and 67.80, 106.87, 126.23 and 126.38, 127.90, 129.91, 132.64, 135.19 and 135.27, 145.02; IR (KBr) 1350, 1177 cm^{-1} (O═S═O). Anal. Calcd for $C_{28}H_{32}O_6S_6Se_4$: C, 34.57; H, 3.32. Found: C, 34.35; H, 3.21.

2,6(7)-Bis(ethylthio)-3,7(6)-bis(2-tosyloxyethylthio)diselenadithiafulvalene (16c): pink powder from dichloromethane−hexane (91% yield from **15c**); mp 110−112 °C; ^{1}H NMR δ 1.293 and 1.297 (t, J = 7.5 Hz, 6H, CH_3), 2.46 (s, 6H, CH_3), 2.83 (q, J = 7.5 Hz, 4H, CH_2), 3.037 (t, J = 7.2 Hz, 2H, CH_2), 3.044 (t, J = 7.1 Hz, 2H, CH_2), 4.186 (t, J = 7.1 Hz, 2H, CH_2), 4.190 (t, J = 7.1 Hz, 2H, CH_2), 7.35 (d, 4H, J = 8.1 Hz, ArH), 7.80 (d, 4H, J = 8.2 Hz, ArH); ^{13}C NMR δ 15.14, 21.74, 31.94 and 31.98, 34.32 and 34.38, 67.97, 108.40 and 109.24, 125.38, 127.99, 129.97, 131.41 and 132,36, 132.79, 145.10; IR (KBr) 1348, 1177 cm^{-1} (O═S═O). Anal. Calcd for $C_{28}H_{32}O_6S_8Se_2$: C, 38.26; H, 3.67. Found: C, 38.15; H, 3.56.

2,6(7)-Bis(ethylseleno)-3,7(6)-bis(2-tosyloxyethylthio)-tetraselenafulvalene (16e): brown solid from dichloromethane−hexane (86% yield from **15e**); mp 147−148 °C; ^{1}H NMR δ 1.44 (t, J = 7.2 Hz, 6H, CH_3), 2.46 (s, 6H, CH_3), 2.93 (q, J = 7.2 Hz, 4H, CH_2), 3.02 (t, J = 7.0 Hz, 4H, CH_2), 4.20 (t, J = 7.0 Hz, 4H, CH_2), 7.36 (d, J = 8.2 Hz, 4H, ArH), 7.80 (d, J = 8.2 Hz, 4H, ArH); ^{13}C NMR δ 16.02, 21.77, 25.05, 35.49, 67.87, 108.74, 125.36, 126.69, 128.03, 130.00, 132.73, 145.12; IR (KBr) 1348, 1177 cm^{-1} (O═S═O). Anal. Calcd for $C_{28}H_{32}O_6S_4Se_6$: C, 31.53; H, 3.02. Found: C, 31.55; H, 3.00.

3,7-Bis(ethylseleno)-2,6-bis(2-tosyloxyethylthio)diselenadithiafulvalene (16f): pink powder from dichloromethane−hexane (72% yield from **15f**); mp 134−136 °C; ^{1}H NMR δ 1.43−1.46 (m, 6H, CH_3), 2.46 (s, 6H, CH_3), 2.92−3.01 (m, 8H, CH_2), 4.17−4.21 (m, 4H, CH_2), 7.36 (d, J = 8.3 Hz, 4H, ArH), 7.80 (d, J = 8.3 Hz, 4H, ArH); ^{13}C NMR δ 15.96, 21.75, 24.04, 35.48, 67.85, 107.04, 122.88, 125.94, 128.03, 130.00, 132,80, 145.14; IR (KBr) 1348, 1177 cm^{-1} (O═S═O). Anal. Calcd for $C_{28}H_{32}O_6S_6Se_4$: C, 34.57; H, 3.32. Found: C, 34.53; H, 3.29.

2,6-Bis(ethylseleno)-3,7-bis(2-tosyloxyethylthio)diselenadithiafulvalene (16g): pink powder from dichloromethane−hexane (76% yield from **15g**); mp 107−109 °C; ^{1}H NMR δ 1.450 and 1.452 (t, J = 7.4 Hz, 6H, CH_3), 2.45 (s, 6H, CH_3), 2.89 (q, J = 7.4 Hz, 4H, CH_2), 3.024 and 3.029 (t, J = 7.3 Hz, 4H, CH_2), 4.19 (t, J = 7.3 Hz, 4H, CH_2); 7.35 (d, 4H, J = 8.5 Hz, ArH), 7.80 (d, 4H, J = 8.5 Hz, ArH); ^{13}C NMR δ 16.04, 21.75, 24.92, 34.47 and 34.53, 67.97, 109.12 and 110.09, 122.65 and 123.78, 125.15, 128.02, 129.99, 132,84, 145.10; IR (KBr) 1348, 1177 cm^{-1} (O═S═O). Anal. Calcd for $C_{28}H_{32}O_6S_6Se_4$: C, 34.57; H, 3.32. Found: C, 34.52; H, 3.26.

4-Ethylthio-5-[2-(tetrahydropyran-2-yloxy)ethylthio]-1,3-thiaselenol-2-one (17c). Transchalcogenation reaction of **7c** to **17c** was carried out in a manner similar to that described for the conversion of **12d** to **13d**: colorless oil (93% yield); ^{1}H NMR δ 1.30 (t, J = 7.4 Hz, 3H, CH_3), 1.50−1.85 (m, 6H, CH_2), 2.91 (q, J = 7.4 Hz, 2H, CH_2), 3.07 (t, J = 6.8 Hz, 2H, CH_2), 3.45−3.97 (m, 4H, CH_2), 4.64 (m, 1H, CH); ^{13}C NMR δ 14.65, 19.00, 25.10, 30.17, 31.83, 36.08, 61.85, 65.94, 98.58, 124.66, 132.72, 188.46; IR (neat) 1700 cm^{-1} (C═O); MS m/z 386 (M^+). Anal. Calcd for $C_{12}H_{18}O_3S_3Se$: C, 37.40; H, 4.71. Found: C, 37.68; H, 4.76.

Bis(ethylenedithio)tetraselenafulvalene (BETS, 1b). A mixture of **16b** (R = Et, 102 mg, 0.11 mmol) and sodium iodide (63 mg, 4.2 mmol) in DMF (0.9 mL) was stirred at 80 °C for 4.5 h. The reaction mixture was cooled, diluted with water (30 mL), and then extracted with carbon disulfide (30 mL × 3). The extract was washed with water (50 mL × 2) and brine (50 mL × 2) and dried ($MgSO_4$). Evaporation of the solvent gave a red solid, which was purified by recrystallization from carbon disulfide−hexane to afford reddish purple needles (97% yield): mp 269−270 °C (lit.[5b] 275 °C dec.); ^{1}H NMR δ 3.30 (s, 8H, CH_2); MS m/z 576 (M^+).

Bis(ethylenedithio)diselenadithiafulvalene (BEDT-STF, 1c). Three approaches shown in Scheme 5 were examined, and the best result was obtained from **16c** using the same procedure described for the synthesis of **1b** from **16b**: red needles from chlorobenzene (82% yield); mp 250 °C (lit.[11] 250 °C dec.); ^{1}H NMR δ 3.28 (s, 8H, CH_2); MS m/z 480 (M^+). Anal. Calcd for $C_{10}H_8S_6Se_2$: C, 25.10; H, 1.69. Found: C, 25.28; H, 1.69.

Bis(ethyleneselenothio)tetrathiafulvalene (BEST-TTF, 1d). This compound was obtained by trimethyl phosphite-induced homocoupling of **13d**: orange needles from chlorobenzene (87% yield); mp 260 °C dec.; ^{1}H NMR δ 3.18 (m, 4H, CH_2), 3.37 (m, 4H, CH_2); MS m/z 480 (M^+). Anal. Calcd for $C_{10}H_8S_6Se_2$: C, 25.10; H, 1.69. Found: C, 25.19; H, 1.68.

Bis(ethyleneselenothio)tetraselenafulvalene (BEST-TSF, 1e). Compounds **1e**−**g** were obtained from **16e**−**g**, respectively, by using the same procedure described for the synthesis of **1b**. **1e**: purple needles from chlorobenzene (56% yield from **16e**); mp 245 °C dec.; ^{1}H NMR δ 3.19 (m, 4H, CH_2), 3.40 (m, 4H, CH_2); MS m/z 672 (M^+). Anal. Calcd for $C_{10}H_8S_2Se_6$: C, 18.03; H, 1.21. Found: C, 18.07; H, 1.29.

Bis(ethyleneselenothio)diselenadithiafulvalene (BEST-STF(t), 1f): red needles from carbon disulfide−hexane (55% yield from **16f**); mp 240 °C dec.; ^{1}H NMR δ 3.19 (m, 4H, CH_2), 3.39 (m, 4H, CH_2); MS m/z 576 (M^+). Anal. Calcd for $C_{10}H_8S_4Se_4$: C, 20.99; H, 1.41. Found: C, 20.99; H, 1.43.

Bis(ethyleneselenothio)diselenadithiafulvalene (BEST-STF(g), 1g): red needles from carbon disulfide−hexane (98% yield from **16g**); mp 250 °C dec.; ^{1}H NMR δ 3.19 (m, 4H, CH_2), 3.37 (m, 4H, CH_2); MS m/z 576 (M^+). Anal. Calcd for $C_{10}H_8S_4Se_4$: C, 20.99; H, 1.41. Found: C, 20.93; H, 1.49.

4-Ethylseleno-5-(2-bromoethylseleno)-1,3-dithiole-2-thione (21). To a solution of **10h** (433 mg, 1.18 mmol) in THF (10 mL) was slowly added phosphorus tribromide (0.14 mL, 1.42 mmol) at −10 °C, and the resulting mixture was stirred for 5 h at room temperature. The reaction mixture was diluted with water (50 mL) and extracted with dichloromethane (100 mL × 3). The extract was washed with water (200 mL × 3) and brime (200 mL × 3), dried ($MgSO_4$), and concentrated in vacuo. The resulting residue was purified with a silica gel column chromatography eluted with dichloromethane to give the bromide (**21**) (R_f = 0.85, 119 mg, 24% yield) as a yellow oil: ^{1}H NMR δ 1.53 (t, J = 7.6 Hz, 3H, CH_3), 3.00 (t, J = 7.6 Hz, 2H, CH_2), 3.29−3.69 (AA′BB′, 4H, CH_2); ^{13}C NMR δ 15.82, 24.71, 29.94, 31.11, 124.33, 131.82, 214.93; IR (neat) 1053 cm^{-1} (C═S); MS m/z 428 (M^+). Anal. Calcd for $C_7H_9BrS_3Se_2$: C, 19.68; H, 2.12. Found: C, 19.64; H, 2.16.

Attempted Cyclization Reactions of 21: Reaction A. A mixture of **21** (58 mg, 0.13 mmol) and sodium iodide (40 mg, 0.27 mmol) in DMF (1.1 mL) was stirred at 80 °C for 5 h. Water (30 mL) was then added, and the resulting mixture was extracted with carbon disulfide (30 mL × 3). The extract was washed with water (50 mL × 2) and brine (50 mL × 2), dried ($MgSO_4$), and concentrated in vacuo. Silica gel column chromatography of the residue eluted with carbon disulfide gave 4,4′-bis(5-ethylseleno-2-thioxo-1,3-dithiolo)-diselenide (**20**) (R_f = 0.3, 10 mg, 23% yield) as a pink solid: mp 108 °C; ^{1}H NMR δ 1.53 (t, J = 7.6 Hz, 6H, CH_3), 2.99 (t, J = 7.6 Hz, 4H, CH_2); ^{13}C NMR δ 15.93, 25.58, 128.25, 130.25, 214.04; IR (neat) 1078 cm^{-1} (C═S); MS m/z 642 (M^+). Anal. Calcd for $C_{10}H_{10}S_6Se_4$: C, 18.81; H, 1.58. Found: C, 18.46; H, 1.67.

Reaction B. A similar reaction was carried out in refluxing 2-butanone as a solvent. In this case, the main product was 4-ethylseleno-1,3-dithiole-2-thione (**22**, 92% yield): ^{1}H NMR δ 1.50 (t, J = 7.5 Hz, 3H, CH_3), 2.92 (t, J = 7.5 Hz, 2H, CH_2), 7.12 (s, 1H, CH); ^{13}C NMR δ 15.79, 24.73, 125.11, 133.01, 215.95; IR (neat) 1059 cm^{-1} (C═S); MS m/z 242 (M^+). Anal. Calcd for $C_5H_6S_3Se$: C, 24.89; H, 2.51. Found: C, 24.89; H, 2.54.

Acknowledgment. The authors are greatly indebted to the Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology for financial support.

Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for compounds **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO016393H