Synthesis of Unsymmetrical Tetrathiafulvalene Derivatives via Me_3Al-Promoted Reactions of Organotin Compounds with Esters

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Efficient synthetic methods for the construction of a wide variety of unsymmetrical tetrathiafulvalenes (TTFs) via the Me_3Al-promoted reactions of organotin thiolates or selenolates with esters are described. Reaction of tin thiolates (**3a-c** and **10**) and selenolates (**3d**, **5**, and **7**) with esters (**11a**,**b**) in the presence of Me_3Al as a Lewis acid gave dihydrotetrathiafulvalene derivatives (**12**, **14**, **15**, and **17-20**) and 1,3-dithiane derivatives (**13** and **16**). In addition, the synthesis of diselenadithiafulvalene derivatives (**25-28**) could be accomplished by Me_3Al-mediated reaction of tin thiolate (**2a**) or selenolates (**3d** and **5**) with esters (**22a**, **22d**, and **24**). Furthermore, the application of the Me_3Al-promoted reaction of tin thiolate (**34**) with esters (**11a-b**, **22a-d**, and **35a-b**) for the synthesis of unsymmetrical TTFs-fused donors enabled us to obtain various TTFs-fused systems (**29-33**) in short steps.

Introduction

Recently, remarkable progress has been made in the development of organic metals based on radical cation salts of unsymmetrical tetrathiafulvalene (TTF) derivatives. Following the discovery of superconductivities in $(DMET)_2X$[1] and $(MDT\text{-}TTF)_2AuI_2$,[2] the Ni(dmit)$_2$ (dmit = 4,5-dimercapto-1,3-dithiole-2-thione) salt of EDT-TTF (ethylenedithiotetrathiafulvalene) has been found to be an ambient pressure superconductor.[3] In addition, a new current appeared in the area of TTF chemistry in 1992. Through the synthetic investigations on the bis-fused TTF molecule[4] and its analogs by Misaki,[5] production of a variety of TTFs-fused donors has become feasible, and many charge-transfer complexes composed of unsymmetrical TTFs-fused donors have been organic metals stable at the low temperature.[6] Subsequently, (DTEDT)$[Au(CN)_2]_{0.4}$ has been ascertained to exhibit superconductivity with the transition temperature of 4 K.[7] Thus, in order to pursue further research on new organic metals derived from unsymmetrical TTFs, the development of synthetic methods that enable the efficient construction of unsymmetrical TTFs is very important.

In the conventional synthesis of TTF derivatives, the coupling reaction utilizing trialkyl phosphite is a synthetic approach to the construction of symmetrical TTFs.[8] However, when this coupling reaction is applied to the synthesis of unsymmetrical TTFs, two symmetrical self-coupling products are formed along with the unsymmetrical cross-coupling product (eq 1, Scheme 1). Especially, in the case of the synthesis of diselenadithiafulvalene (DSDTF) derivatives, the separation of the desired cross-coupling product from self-coupling products is often troublesome.[9] Meanwhile, we have found that the non-phosphite coupling syntheses of unsymmetrical TTFs such as DHTTF (dihydrotetrathiafulvalene) derivatives, 1,3-dithiane derivatives, and DSDTFs are accomplished by Me_3Al-promoted reaction of organotin compounds with esters (eq 2).[10,11] If this Me_3Al-promoted reaction could be applicable to the synthesis of unsymmetrical TTFs-fused donors, further extension

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(1) DMET = dimethyl(ethylenedithio)diselenadithiafulvalene, X = $Au(CN)_2$: Kikuchi, K.; Kikuchi, M.; Namiki, T.; Saito, K.; Ikemoto, I.; Murata, K.; Ishiguro, T.; Kobayashi, K. *Chem. Lett.* **1987**, 931−932. X = $AuCl_2$ and AuI_2: Kikuchi, K.; Murata, K.; Honda, Y.; Namiki, T; Saito, K.; Anzai, H.; Kobayashi, K.; Ishiguro, T.; Ikemoto, I. *J. Phys. Soc. Jpn.* **1987**, *56*, 4241−4244. X = I_3 and IBr_2: Kikuchi, K.; Murata, K.; Honda, Y.; Namiki, T.; Saito, K.; Ishiguro, T.; Kobayashi, K.; Ikemoto, I. *J. Phys. Soc. Jpn.* **1987**, *56*, 3436−3439. X = $AuBr_2$: Kikuchi, K.; Murata, K.; Honda, Y.; Namiki, T.; Saito, K; Kobayashi, K.; Ishiguro, T.; Ikemoto, I. *J. Phys. Soc. Jpn.* **1987**, *56*, 2627−2628.

(2) MDT-TTF = (methylenedithio)tetrathiafulvalene: (a) Kini, A. M.; Beno, M. A.; Son, D.; Wang, H. H.; Carlson, K. D.; Porter, L. C.; Welp, U.; Vogt, B. A.; Williams, J. M.; Jung, D.; Evain, M.; Whangbo, M.-H.; Overmyer, D. L.; Schirber, J. E. *Solid State Commun.* **1989**, *69*, 503−507. (b) Papavassiliou, G. C.; Mousdis, G. A.; Zameounis, J. S.; Terzis, A.; Hountas, A.; Hilti, B.; Mayer, C. W.; Pfeiffer, J. *Synth. Metals* **1988**, *27*, B379-B383.

(3) Tajima, H.; Inokuchi, M.; Kobayashi, A.; Ohta, T.; Kato, R.; Kobayashi, H.; Kuroda, H., *Chem. Lett.* **1993**, 1235−1238.

(4) This compound was initially proposed by Schumaker: Schumaker, R. R.; Engler, E. M. *J. Am. Chem. Soc.* **1977**, *99*, 5519−5521.

(5) (a) Misaki, Y.; Kawakami, K.; Mastui, T.; Yamabe, T.; Shiro, M. *J. Chem. Soc., Chem. Commun.* **1994**, 459−340. (b) Misaki, Y.; Nishikawa, H.; Kawakami, K.; Yamabe, T; Mori, T.; Inokuchi, H; Mori, H.; Tanaka, S. *Chem. Lett.* **1993**, 2073−2076. (c) Misaki, Y.; Matsui, T.; Kawakami, K.; Nishikawa, H.; Yamabe, T.; Shiro, M. *Chem. Lett.* **1993**, 1337−1340. (d) Misaki, Y.; Nishikawa, H.; Yamabe, T.; Mori, T.; Inokuchi, H.; Mori, H.; Tanaka, S. *Chem. Lett.* **1993**, 729−732. (e) Misaki, Y.; Kawakami, K.; Nishikawa, H.; Fujiwara, H.; Yamabe, T.; Shiro, M. *Chem. Lett.* **1993**, 445−448. (f) Misaki, Y.; Nishikawa, H.; Kawakami, K.; Koyanagi, S.; Yamabe, T.; Shiro, M. *Chem. Lett.* **1992**, 2321−2324. (g) Misaki, Y.; Nishikawa, H.; Fujiwara, H.; Kawakami, K.; Yamabe, T.; Yamoti, H.; Saito, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1408−1409. (h) Misaki, Y.; Nishikawa, H.; Kawakami, K.; Uehara, T.; Yamabe, T. *Tetrahedron Lett.* **1992**, *33*, 4321−4324.

(6) (a) Misaki, Y; Kawakami, K; Fujiwara, H; Yamabe, T; Mori, T; Mori, H; Tanaka, S. *Chem. Lett.* **1995**, 1125−1126. (b) Mori, T.; Misaki, Y.; Yamabe, T. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3187−3190. (c) Mori, T.; Inokuchi, H.; Misaki, Y.; Nishikawa, H.; Yamabe, T.; Mori, H.; Tanaka, S. *Chem. Lett.* **1993**, 2085−2088. (d) Misaki, Y.; Nishikawa, H.; Yamabe, T.; Mori, T.; Inokuchi, H.; Mori, H.; Tanaka, S. *Chem. Lett.* **1993**, 1341−1344. (e) Mori, T.; Inokuchi, H.; Misaki, Y.; Nishikawa, H.; Yamabe, T.; Mori, H.; Tanaka, S. *Chem. Lett.* **1993**, 733−736.

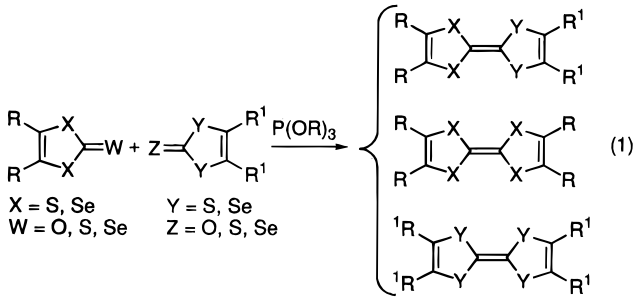
(7) DTEDT = 2-(1,3-dithiol-2-ylidene)-5-(2-ethanediylidene-1,3-dithiole)-1,3,4,6-tetrathiapentalene, which belongs to the vinylogous bis-fused TTF system: Misaki, Y.; Higuchi, N.; Fujiwara, H.; Yamabe, T.; Mori, T.; Mori, H.; Tanaka, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1222−1225.

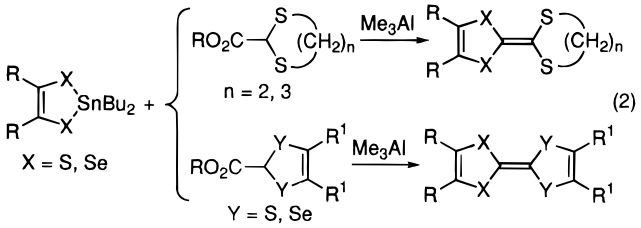
(8) For general reviews, see: (a) Krief, A. *Tetrahedron* **1986**, *42*, 1209−1252. (b) Bryce, M. R. *Aldrichimica Acta* **1985**, *18*, 73−77. (c) Schumaker, R. R.; Lee, V. Y.; Engler, E. M. *J. Phys.* **1983**, *44*, C-1139−C-1145. (d) Narita, M.; Pittman, C. U. *Synthesis* **1976**, 489−514.

(9) (a) Aonuma, S.; Okano, Y.; Sawa, H.; Kato, R.; Kobayashi, H. *J. Chem. Soc., Chem. Commum.* **1992**, 1193−1195. (b) Kobayashi, K.; Kikuchi, K.; Namiki, T.; Ikemoto, I. *Synth. Metals* **1987**, *19*, 555−558. (c) Kikuchi, K.; Namiki, T.; Ikemoto, I.; Kobayashi, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1472−1473.

S0022-3263(95)02255-9 CCC: $12.00

Scheme 1





of the TTFs-fused systems would be possible. We now report a full account of the Me_3Al-promoted reaction and application of this reaction to the synthesis of new unsymmetrical TTFs-fused donors.

Results and Discussion

Preparation of Organotin Thiolates and Selenolates. Organotin thiolates **3a-c** and selenolate **3d** could be prepared by trapping the corresponding dimagnesium salts with Cl_2SnBu_2 (eq 3, Scheme 2). Treatment of thiones **1a-c** and selone **1d** with $Hg(OAc)_2$/THF−AcOH gave ketones **2a-d** (**2a**, 92% yield; **2b**, 82% yield; **2c**, 62% yield; **2d**, 72% yield). Grignard reaction of **2a-d** in THF followed by trapping with Cl_2SnBu_2 at −78 °C produced organotin thiolates **3a-c** and selenolate **3d**. However, direct transformation of thione **1a** into tin thiolate **3a** via Grignard reaction was not successful. Although tin thiolates **3a-c** could not be purified by column chromatography on silica gel, purification of tin selenolate **3d** in the same way was possible (81% yield). Organotin selenolates **5** and **7** could be prepared via insertion reaction of selenium into the carbon−lithium bond (eqs 4 and 5). Two consecutive stepwise reactions of 1,2-dibromocyclopentene (**4**) in THF with 2 equiv of ^{t}BuLi and 1 equiv of elemental selenium[12] followed by trapping with Cl_2SnBu_2 at −78 °C enabled us to prepare **5** (eq 4). Tin selenolate **5** tended to decompose through silica gel. Preparation of tin selenolate **7** was carried out by successive treatment of 2,3-dihydro-1,4-dithiin (**6**) with

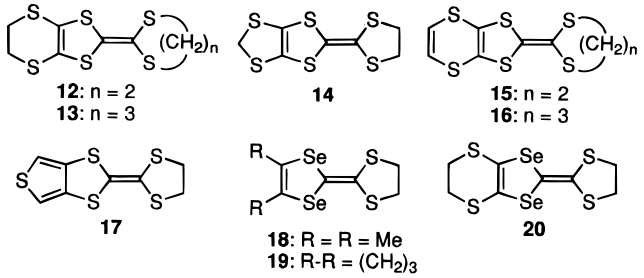
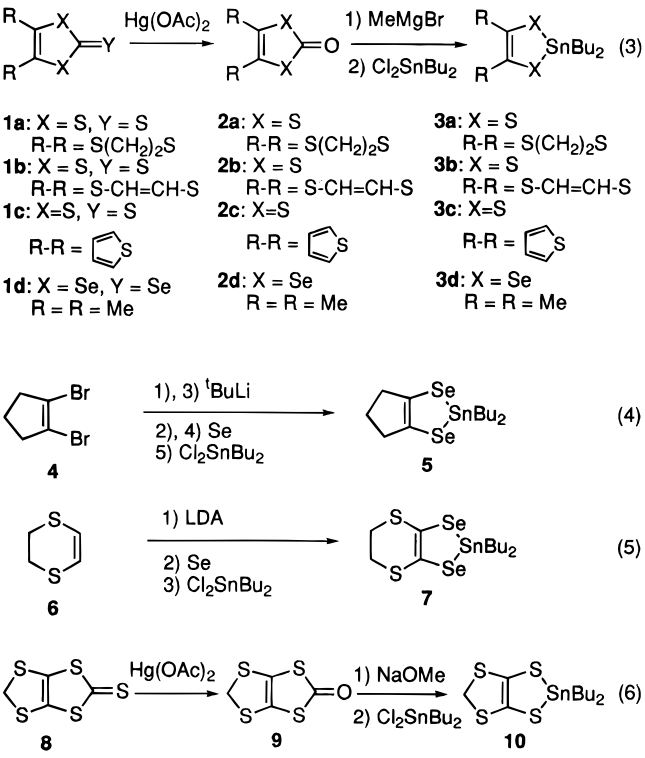


Figure 1. DHTTF derivatives and 1,3-dithiane derivatives.

Scheme 2



LDA and elemental selenium[13] followed by trapping with Cl_2SnBu_2 in 60% yield (eq 5). Finally, though tin thiolate **10** could not be obtained via Grignard reaction of ketone **9** derived from **8**, basic cleavage of **9** with NaOMe/MeOH followed by treatment with Cl_2SnBu_2/THF gave **10** (eq 6). Tin thiolate **10** was used without purification through silica gel. Conversion of ketone **2c** into tin thiolate **3c** could also be carried out by basic cleavage with NaOMe/MeOH, whereas transformation of **2a** into **3a** by a similar procedure led to a decrease in yield of **3a**.

Synthesis of DHTTF Derivatives and 1,3-Dithiane Derivatives. The results of Me_3Al-promoted coupling synthesis of DHTTF derivatives[14] and 1,3-dithiane derivatives (Figure 1) are summarized in Table 1. Tin thiolate **3a** reacted with **11a** in the presence of Lewis acids such as $TiCl_4$, Me_2AlCl, and Me_3Al (entries 1−3). However, reaction of **3a** with **11a** using $BF_3{\cdot}OEt_2$ as a Lewis acid afforded only trace amounts of **12**. Trimethyl-

(10) (a) Yamada, J.; Amano, Y.; Takasaki, S.; Nakanishi, R.; Matsumoto, K.; Satoki, S.; Anzai, H. *J. Am. Chem. Soc.* **1995**, *117*, 1149−1150. (b) Yamada, J.; Takasaki, S.; Kobayashi, M.; Anzai, H.; Tajima, N.; Tamura, M.; Nishio, Y.; Kajita, K. *Chem. Lett.* **1995**, 1069−1070.

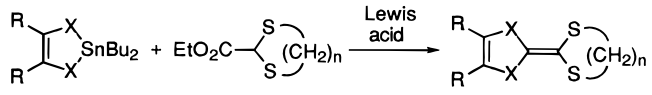
(11) For the other non-phosphite coupling reactions, see: (a) Gimber, Y.; Moradpour, A.; Dive, G.; Dehareng, D.; Lahlii, K. *J. Org. Chem.* **1993**, *58*, 4685−4690. (b) Sudmale, I. V.; Tormos, G. V.; Khodorkovsky, V. Yu.; Edzine, A. S.; Neilands, O. J.; Cava, M. P. *J. Org. Chem.* **1993**, *58*, 1355−1358. (c) Mori, T.; Inokuchi, H. *Chem. Lett.* **1992**, 1873−1876. (d) Khodorkovsky, V. Yu.; Tormos, G. V.; Neilands, O. Ya.; Kolotilo, N. V.; II′chenko, A. Ya. *Tetrahedron Lett.* **1992**, *33*, 973−976. (e) Jørgensen, M.; Lerstrup, K. A.; Bechgaard, K. *J. Org. Chem.* **1991**, *56*, 5684−5688. (f) Mizuno, M.; Cava, M. P. *J. Org. Chem.* **1978**, *43*, 416−418. (g) Gonnella, N. C.; Cava, M. P. *J. Org. Chem.* **1978**, *43*, 369−370.

(12) Okano, Y.; Sawa, H.; Aonuma, S.; Kato, R. *Chem. Lett.* **1993**, 1851−1854.

(13) Kato, R.; Kobayashi, H.; Kobayashi, A. *Synth. Metals* **1991**, *41*−43, 2093.

(14) The synthesis and electrochemistry of DHTTF itself was reported: Coffen, D. L.; Chambers, J. Q.; Williams, D. R.; Garrett, P. E.; Canfield, N. D. *J. Am. Chem. Soc.* **1971**, *93*, 2258−2268. For some recent works involving DHTTF derivatives, see: (a) Lorcy, D.; Paillard, M.-P. L.; Robert, A. *Tetrahedron Lett.* **1993**, *34*, 5289−5292. (b) Salle, M.; Gorgues, A.; Jubault, M.; Gouriou, Y. *Synth. Metals* **1991**, *41*−43, 2575−2578.

Table 1. Syntheses of DHTTF Derivatives and 1,3-Dithiane Derivatives



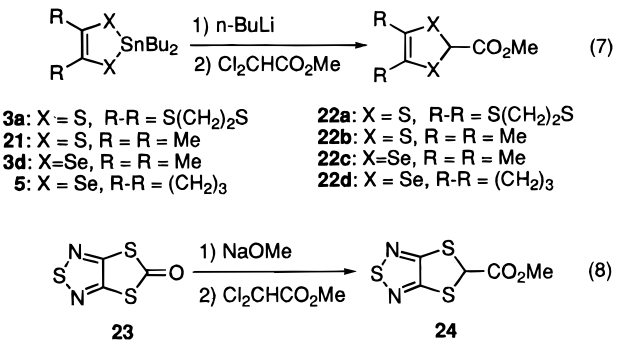
entry	organotin compound	ester	Lewis acid	temp, °C	reaction time	product	yield (%)
1	**3a**	**11a**	$TiCl_4$	−78 → rt[a]	overnight	**12**	28[b,c]
2	**3a**	**11a**	Me_2AlCl	−78 → rt	overnight	**12**	44[b,c]
3	**3a**	**11a**	Me_3Al	−78 → rt	overnight	**12**	57[b,c]
4	**3a**	**11b**	Me_3Al	−78 → rt	overnight	**13**	61[b,c]
5	**10**	**11a**	Me_3Al	−78 → rt	overnight	**14**	26[d,e]
6	**3b**	**11a**	Me_3Al	−78 → rt	overnight	**15**	9[d,f]
7	**3b**	**11a**	Me_3Al	−78 → 15	3 h	**15**	36[d,f]
8	**3b**	**11b**	Me_3Al	−78 → rt	6 h	**16**	22[b,f]
9	**3c**	**11a**	Me_3Al	rt	3 days	**17**	67[b,g]
10	**3d**	**11a**	Me_3Al	rt	6 days	**18**	83[b]
11	**5**	**11a**	Me_3Al	rt	5 days	**19**	33[b,h]
12	**7**	**11a**	Me_3Al	rt	6 days	**20**	42[b]

[a] Room temperature. [b] After column chromatography on silica gel. [c] Overall yield from **2a**. [d] After column chromatography followed by recrystallization. [e] Overall yield from **9**. [f] Overall yield from **2b**. [g] Overall yield from **2c**. [h] Overall yield from **4**.

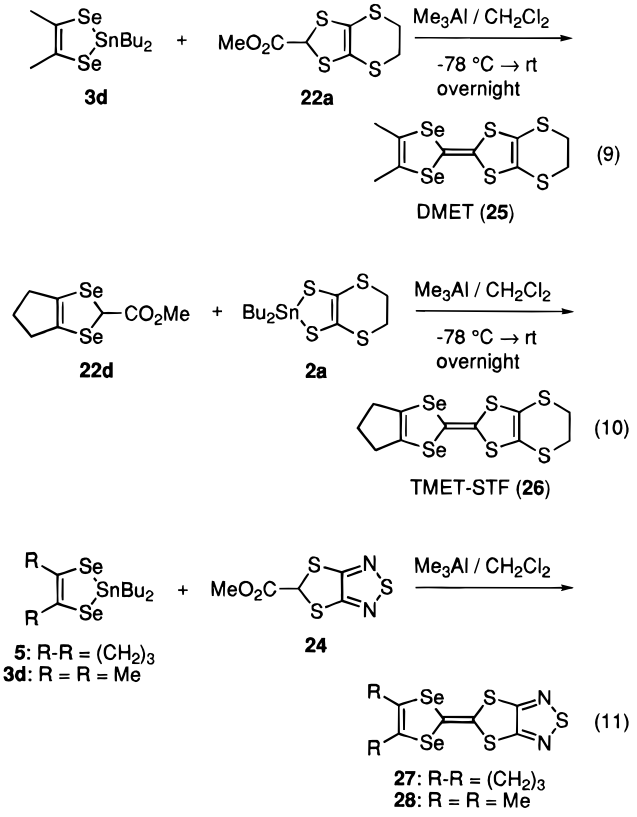
aluminum gave the best result among the Lewis acids examined. Similarly, the Me_3Al-mediated reaction of **3a** with **11b** produced the 1,3-dithiane derivative **13** in 61% yield based on **3a** (entry 4). A dihydro-analog of MDT-TTF **14** could also be prepared by the Me_3Al-mediated reaction of **10** with **11a** (entry 5). A vinylenedithio-annelated DHTTF **15** seems to be sensitive to the acidic conditions, since the treatment of **3b** with **11a** for a prolonged period resulted in a decrease in yield of **15** (entry 6). Therefore, we shortened the reaction time when treatment of **3b** with both **11a** and **11b** was carried out (entries 7 and 8). A thieno-annelated DHTTF **17** could be formed slowly by reaction of **3c** with **11a** (entry 9). An alternative synthetic method of **17** is as follows. Similarly to preparation of **5** (eq 4, Scheme 2), except for the addition of elemental sulfur instead of Se powder, two consecutive stepwise reactions of 3,4-dibromothiophene followed by treatment with Cl_2SnBu_2 gave **3c**. Reaction of **3c** with **11a** in the presence of Me_3Al afforded **17** in *ca.*19% overall yield from 3,4-dibromothiophene. However, the isolated **17** via this synthetic route contained small amounts of impurities. The reaction of tin selenolates **3d**, **5**, and **7** was relatively very slow in comparison with the reaction of tin thiolates, but the selenium analog of DHTTF derivatives **18**-**20** could be prepared by this Me_3Al-mediated coupling reaction (entries 10−12).

Preparation of Esters. We investigated the synthetic method for the preparation of esters **22** and **24** (Scheme 3) so as to construct the other unsymmetrical TTFs, *i.e.*, DSDTF derivatives and unsymmetrical TTFs-fused donors, by the Me_3Al-promoted reactions. Transmetalation of organotin compounds **3a**, **21** (prepared from 4,5-dimethyl-1,3-dithiol-2-one via Grignard reaction), **3d**, and **5** with 2 equiv of *n*-butyllithium at −78 °C followed by treatment with methyl dichloroacetate gave the desired esters **22a**-**d** (eq 7: **22a**, 35% yield based on **2a**; **22b**, 41% yield based on 4,5-dimethyl-1,3-dithiol-2-one; **22c**, 73% yield; **22d**, 54% yield based on **4**). Ester **22d** could also be prepared by direct reaction of the dilithium salt of cyclopentene-1,2-diselenol with methyl dichloroacetate in 50% overall yield from **4**. In the case of preparation of ester **24** with a 1,2,5-thiadiazole ring (eq 8), basic cleavage of TDA-DTC (**23**)[15] with NaOMe/MeOH

Scheme 3



Scheme 4



followed by treatment with methyl dichloroacetate in THF was carried out (44% yield).

Synthesis of DSDTF Derivatives. Tin selenolate **3d** reacted smoothly with **22a** in the presence of Me_3Al, and DMET (**25**) was obtained in 43% yield (eq 9, Scheme 4). Similarly, the Me_3Al-promoted reaction of ester **22d** with tin thiolate **2a** produced TMET-STF[16] (**26**) in 37% yield (eq 10). On the other hand, under the same operating conditions as used for synthesis of **25** and **26**, the yield of a thiadiazolo-fused DSDTF derivative **27** was only 3% even though the reaction time was prolonged. Accordingly, preparation of **27** and **28** was carried out under alternative operating conditions. Tin selenolate **3d** or **5** was first reacted with Me_3Al at room temperature in CH_2Cl_2, and then ester **24** was added. Under these operating conditions the yields of **27** and **28** were 27% and 12%, respectively. Although, at present, there exists no direct

(15) TDA-DTC = thiadiazole(dithiocarbonate): Underhill, A. E.; Hawkins, I.; Edge, S.; Wilkes, S. B.; Varma, K. S.; Kobayashi, A.; Kobayashi, H. *Synth. Metals* **1993**, *55*−57, 1914−1019.

(16) TMET-STF = Trimethylene(ethylenedithio)diselenadithiafulvalene, see ref 12.

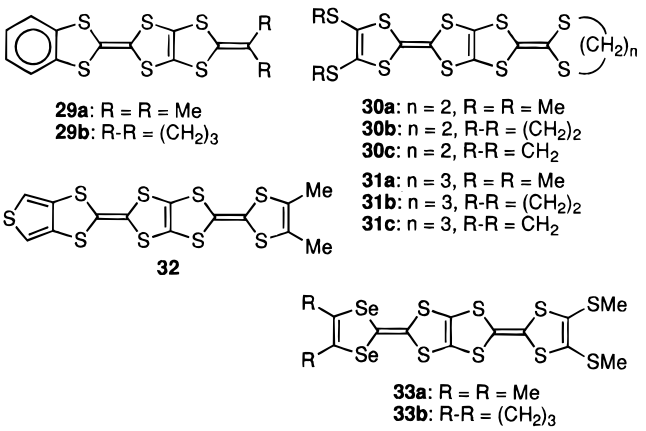
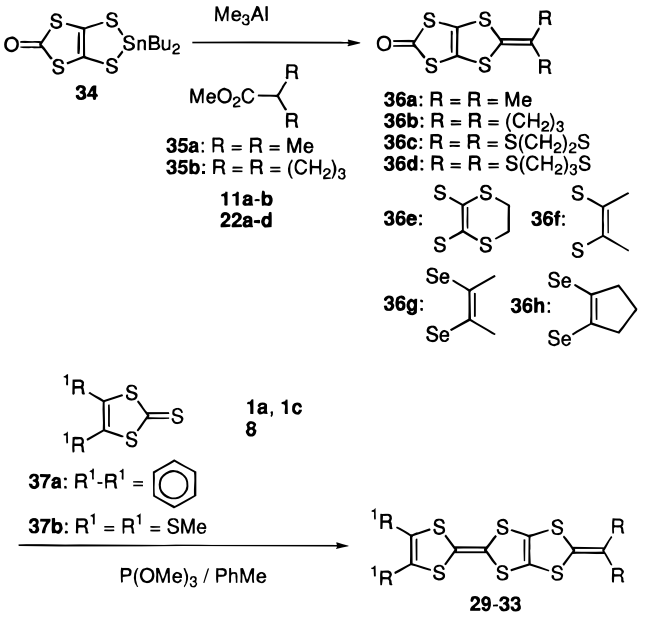


Figure 2. Unsymmetrical TTFs-fused donors.

Scheme 5



evidence for the mechanism of this reaction, the initially formed aluminium selenolate by the tin−aluminium exchange reaction of **3d** or **5** with Me_3Al presumably reacted with ester **24**.

Synthesis of Unsymmetrical TTFs-Fused Donors via the Me_3Al-Promoted Reaction. As mentioned above, we have established an efficient synthetic method for the construction of DHTTFs, 1,3-dithiane derivatives, and DSDTFs without separation from self-coupling products. Our next target is to develop a method for the new, and short-step synthesis of TTFs-fused systems **29-33** (Figure 2) via the Me_3Al-promoted reaction of the organotin thiolate (**34**, Scheme 5) with esters (**35a-b**, **11a-b**, and **22a-d**).

Scheme 5 outlines our synthetic method for the construction of TTFs-fused systems. Treatment of thiapendione[17] with NaOMe (2 equiv)/MeOH[18] followed by trapping with Cl_2SnBu_2/THF at −78 °C gave organotin thiolate **34** in 96% yield. Reaction of **34** with esters **35a-b**, **11a-b**, and **22a-d** in the presence of Me_3Al was examined, and the results are summarized in Table 2. In all cases, tin thiolate **34** was reacted with Me_3Al at room temperature for 40 min prior to addition of esters. Preparation of ketones **36a** and **36b** in five steps from the Zn(dmit)$_2$ complex is known,[5h] while we demonstrated that these compounds can be prepared in two steps from thiapendione via the Me_3Al-mediated coupling reactions (entries 1 and 2). Reaction of **34** with ester **11a** gave ketone **36c** as a key intermediate for the formation of the TTFs-DHTTF fused system (entry 3). Changing the solvent used for the reaction with **11b** from dichloromethane to 1,2-dichloroethane led to a increase in yield of **36d** (entries 4 and 5). On the other hand, the yield of **36e** was not influenced by the solvent employed for the reaction with **22a** (entries 6 and 7), although the length of the reaction time had some effect (entry 8). Similarly to preparation of **36e**, reaction with **22b** afforded ketone **36f**[5a] leading to the bis-fused TTFs system (entry 9). Furthermore, the Me_3Al-promoted reaction of **34** with both **22c** and **22d** produced the selenium-introduced ketones **36g** and **36h** (entries 10 and 11). Such ketones have not so far been prepared by conventional synthetic methods.

Next we attempted to construct the TTFs-fused systems from **36** by the Me_3Al-promoted reaction; however, for example, conversion of **36c** into the corresponding tin thiolate was unsuccessful due to its insolubility in appropriate solvents used for the Grignard reaction. In general, ketones **36c-h** were not sufficiently soluble in common organic solvents, except for carbon disulfide. Thus, transformations of **36a-h** into the unsymmetrical TTFs-fused donors **29-33** were performed by the cross-coupling reactions with 2 equiv of the appropriate 1,3-dithiole-2-thiones **37a**,**b**, **1a**, **1c**, and **8** in P(OMe)$_3$/boiling PhMe (v/v = 1/1) for 2 h.[5a−d] The isolated products by either column chromatography on silica gel or column

Table 2. Me_3Al-Promoted Reaction of the Tin Thiolate 34 with Esters

		reaction conditions				isolated
entry	ester	solvent	temp	time	product	yield (%)
1	**35a**	CH_2Cl_2	rt[a]	4 days	**36a**	35[b]
2	**35b**	CH_2Cl_2	rt	3 days	**36b**	52[b]
3	**11a**	CH_2Cl_2	rt	2 days	**36c**	48[b]
4	**11b**	CH_2Cl_2	rt	5 days	**36d**	9[b]
5	**11b**	$ClCH_2CH_2Cl$	rt	5 days	**36d**	23[c]
6	**22a**	$ClCH_2CH_2Cl$	rt	overnight	**36e**	9[c]
7	**22a**	CH_2Cl_2	rt	overnight	**36e**	11[c]
8	**22a**	CH_2Cl_2	rt	2 days	**36e**	trace
9	**22b**	CH_2Cl_2	rt	overnight	**36f**	12[b]
10	**22c**	CH_2Cl_2	rt	4 days	**36g**	33[c]
11	**22d**	CH_2Cl_2	rt	overnight	**36h**	16[c]

[a] Room temperature. [b] After column chromatography on silica gel. [c] After column chromatography on silica gel followed by recrystallization.

Table 3. Cross-Coupling Reaction between Ketones and Thiones

ketone	thione	product	yield (%)
36a	**37a**	**29a**	20[a]
36b	**37a**	**29b**	26[a]
36c	**37b**	**30a**	47[a]
36c	**1a**	**30b**	80[b]
36c	**8**	**30c**	28[a]
36d	**37b**	**31a**	43[b]
36d	**1a**	**31b**	62[a]
36d	**8**	**31c**	16[a]
36f	**1c**	**32**	7[a]
36g	**37b**	**33a**	46[a]
36h	**37b**	**33b**	36[a]

[a] After column chromatography on silica gel followed by recrystallization. [b] After column chromatography on silica gel.

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chromatography followed by recrystallization were the desired cross-coupling products **29**−**33** (Table 3). Under similar conditions, cross-coupling reaction of **36e** with **37a** or **1c** (a 0.16 or 0.39 mmol scale) gave trace amounts of the desired product. Eventually, we have accomplished the three-step synthesis of unsymmetrical TTFs-fused donors, including **33a** and **33b** as one of the two TTFs-DSDTFs systems respectively, via the Me_3Al-mediated reaction.

Conclusion

The conversion of esters into dithioketene acetals by the use of aluminium thiolates[19] and the application of this transformation for the synthesis of unsymmetrical TTFs[20] have been already reported. In contrast to these reports, our synthetic concept is as follows. Magnesium, lithium, or sodium chalcogenides are transformed to the stable tin chalcogenides (stabilization), which are subsequently reacted with esters in the presence of Me_3Al (activation). The present work reveals that this stabilization−activation procedure[21] is not only useful for the synthesis of various unsymmetrical TTFs, but also applicable for the preparation of a variety of highly desirable analogs since both tin compounds and esters are readily obtainable by standard procedures.

Experimental Section

General Methods. Melting points are uncorrected. ^{1}H-NMR spectra were run at 400 MHz. ^{13}C-NMR spectra were recorded at 100 MHz. ^{1}H-NMR chemical shifts are expressed in parts per million (δ) relative to $CHCl_3$ (δ 7.26) as an internal reference. For ^{13}C-NMR chemical shifts, reference was the center peak of chloroform-*d* (δ 77.1). Air- and/or moisture-sensitive reactions were carried out in a dry reaction flask under nitrogen.

Materials. Tetrahydrofuran was distilled from sodium benzophenone ketyl under an argon atmosphere unless otherwise noted. Diisopropylamine was distilled from CaH_2 and stored under an argon atmosphere. All other solvents were dried by appropriate procedures, and stored over molecular sieves. Trimethylaluminium/hexane, *n*-butyllithium/hexane, t-butyllithium/pentane, sodium methylate/methanol, and methylmagnesium bromide/tetrahydrofuran were purchased from Kanto Chemical Co. 4,5-(Ethylenedithio)-1,3-dithiole-2-thione (**1a**), 4,5-(methylenedithio)-1,3-dithiole-2-thione (**8**), ethyl 1,3-dithiolane-2-carboxylate (**11a**), ethyl 1,3-dithiane-2-carboxylate (**11b**), and thiapendione (1,3,4,6-tetrathiapentalene-2,5-dione) were purchased from Tokyo Kasei Kogyo Co. 4,5-(Vinylenedithio)-1,3-dithiole-2-thione (**1b**) and thieno[3,4-*d*]-1,3-dithiole-2-thione (**1c**) were prepared essentially according to the literature.[22] 4,5-Dimethyl-1,3-diselenole-2-selone (**1d**) was prepared by the known method.[23] 4,5-Dimethyl-1,3-dithiol-2-one was synthesized by reaction of 3-bromo-2-butanone with potassium isopropylxanthate followed by treatment with concd H_2SO_4. Methyl cyclopentanecarboxylate (**35b**) was obtained by esterification (concd H_2SO_4/MeOH) of cyclopentanecarboxylic acid. Benzo[*d*]-1,3-dithiole-2-thione (**37a**) was synthesized by reaction of 1,2-benzenedithiol with thiophosgene in the presence of triethylamine. 4,5-Bis(methylthio)-1,3-dithiole-2-thione (**37b**) was prepared according to the literature.[24]

A Typical Procedure for Conversion of Thiones into Ketones. Conversion of thione **1a** into ketone **2a** is representative. In a 300-mL flask were placed 80 mL of THF (distilled from CaH_2) and 1.12 g (5.0 mmol) of **1a**. A solution of $Hg(OAc)_2$ (2.39 g, 7.5 mmol) in acetic acid (80 mL) was added, and the mixture was stirred vigorously at room temperature for 30 min. The reaction mixture was filtered through Celite, and the solution was diluted with dichloromethane and water. The organic layer was washed successively with several portions of water and saturated aqueous $NaHCO_3$ solution, dried over $MgSO_4$, and then concentrated under reduced pressure. Purification of the residue with silica gel column chromatography by using dichloromethane as an eluent followed by recrystallization from ethanol gave 0.96 g (92% yield) of **2a**.

4,5-(Ethylenedithio)-1,3-dithiol-2-one (2a): pale yellow needles; mp 127−128 °C (lit.[18] mp 127−128 °C); ^{1}H NMR ($CDCl_3$) δ 3.43 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 31.2, 113.5, 188.9; MS, *m*/*z* (% relative intensity) 210 ($M^+ + 2$, 17), 208 (M^+, 100), 182 (8), 180 (42); HRMS (EI) calcd for $C_5H_4OS_4$ 207.9145, measured 207.9145.

4,5-(Vinylenedithio)-1,3-dithiol-2-one (2b): pale orange needles; mp 98−99 °C from ethanol (lit.[22] mp 99 °C); ^{1}H NMR ($CDCl_3$) δ 6.62 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 117.3, 124.0, 192.4; MS, *m*/*z* (% relative intensity) 208 ($M^+ + 2$, 22), 206 (M^+, 100), 180 (14), 178 (63), HRMS (EI) calcd for $C_5H_2OS_4$ 205.8989, measured 205.8987.

Thieno[3,4-*d*]-1,3-dithiol-2-one (2c): brownish white needles; mp 103−104 °C from ethanol (lit.[23] mp 107−108 °C); ^{1}H NMR ($CDCl_3$) δ 7.31 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 115.4, 128.5, 193.9; MS, *m*/*z* (% relative intensity) 176 ($M^+ + 2$, 55), 174 (M^+, 100), 148 (25), 146 (50); HRMS (EI) calcd for $C_5H_2OS_3$ 173.9268, measured 173.9270.

4,5-Dimethyl-1,3-diselenol-2-one (2d): pale yellow needles; mp 42−43 °C from ethanol; ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 15.8, 128.6, 188.4; MS, *m*/*z* (% relative intensity) 244 ($M^+ + 4$, 32), 242 ($M^+ + 2$, 100), 240 (M^+, 88), 238 ($M^+ - 2$, 53), 216 (18), 214 (45), 212 (42), 210 (27); HRMS (EI) calcd for $C_5H_6OSe_2$ 241.8749, measured 241.8744.

4,5-(Methylenedithio)-1,3-dithiol-2-one (9). The same procedure as described above in A Typical Procedure was employed except for using 2 equiv of $Hg(OAc)_2$. Purification of the product with column chromatograpy on silica gel gave **9** in 92% yield from **8**: pale brown needles; mp 101−102 °C from ethanol; ^{1}H NMR ($CDCl_3$) δ 4.74 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 38.4, 114.0, 193.0; MS, *m*/*z* (% relative intensity) 196 ($M^+ + 2$, 20), 194 (M^+, 100), 168 (7), 166 (30); HRMS (EI) calcd for $C_4H_2OS_4$ 193.8989, measured 193.8990.

A Typical Procedure for Conversion of Ketones into Tin Compounds via Grignard Reaction. Transformation of ketone **2a** into tin thiolate **3a** is representative. To a solution of **2a** (1.04 g, 5.0 mmol) in THF (50 mL) was added dropwise a THF solution of MeMgBr (0.90 M × 18.3 mL, 16.5 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 2 h. After the reaction mixture was cooled to −78 °C, a solution of Cl_2SnBu_2 (1.67 g, 5.3 mmol) in THF (25 mL) was added dropwise for 30 min, and stirring was continued for 1 h at that temperature. The mixture was allowed to warm to 0 °C, and the reaction was quenched by the addition of saturated aqueous NaCl solution. The resulting suspension was filtered through Celite, and the aqueous layer was extracted with three portions of chloroform. The organic extracts were combined and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the crude **3a** as a yellow solid.

4,5-(Ethylenedithio)-2,2-dibutyl-2-stanna-1,3-dithiole (3a): mp 113−115 °C; ^{1}H NMR ($CDCl_3$); δ 0.93 (t, J = 7.3 Hz, 6 H), 1.36 (sixtet, J = 7.3 Hz, 4 H), 1.66 (m, 4 H), 1.73 (m, 4 H); ^{13}CMR ($CDCl_3$) δ 13.6, 22.3, 26.7, 27.9, 33.3, 116.8.

4,5-(Vinylenedithio)-2,2-dibutyl-2-stanna-1,3-dithiole (3b): viscous brown solid; ^{1}H NMR ($CDCl_3$); δ 0.92 (t, J = 7.3 Hz, 6 H), 1.36 (sixtet, J = 7.3 Hz, 4 H), 1.66−1.77(m, 8 H) 6.47 (s, 2 H); ^{13}CMR ($CDCl_3$) δ 13.6, 23.9, 26.6, 27.7, 121.0, 125.2.

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Thieno[3,4-*d*]-2,2-dibutyl-2-stanna-1,3-dithiole (3c). The same procedure as described above in A Typical Procedure was used except that reaction of **2c** with MeMgBr was carried out for 3 h: brownish-white solid; mp 49−50 °C; ^{1}H NMR ($CDCl_3$); δ 0.92 (t, J = 7.3 Hz, 6 H), 1.37 (sixtet, J = 7.3 Hz, 4 H), 1.67 (m, 4 H), 1.73 (m, 4 H); ^{13}CMR ($CDCl_3$) δ 13.6, 22.7, 26.7, 27.9, 117.6, 136.9.

4,5-Dimethyl-2,2-dibutyl-2-stanna-1,3-diselenole (3d). The same procedure as described above in A Typical Procedure was performed except that (i) reaction of **2d** with MeMgBr was carried out for 4.5 h, and (ii) the product was purified by silica gel column chromatography using hexane−dichloromethane as an eluent: orange oil; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 6 H), 1.37 (sixtet, J = 7.3 Hz, 4 H), 1.58 (m, 4 H), 1.70 (m, 4 H), 2.07 (s, 6 H); ^{13}CMR ($CDCl_3$) δ 13.6, 20.4, 23.7, 26.6, 28.7, 124.4.

4,5-Dimethyl-2,2-dibutyl-2-stanna-1,3-dithiole (21). The same procedure as described above in A Typical Procedure was employed except that (i) reaction of 4,5-dimethyl-1,3-dithiol-2-one with MeMgBr was carried out for 4 h and (ii) purification by silica gel column chromatography (hexane-dichloromethane) could be carried out (80% yield from 4,5-dimethyl-1,3-dithiol-2-one): pale yellow powder; mp 65−66 °C; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 6 H), 1.36 (sixtet, J = 7.3 Hz, 4 H), 1.55 (m, 4 H), 1.70 (m, 4 H), 2.01 (s, 6 H); ^{13}CMR ($CDCl_3$) δ 13.6, 21.3, 22.7, 26.7, 27.9, 123.0.

4,5-Trimethylene-2,2-dibutyl-2-stanna-1,3-diselenole (5). In a 100-mL flask with a septum inlet were placed 0.60 mL (5.0 mmol) of 1,2-dibromocyclopentene and 30 mL of THF, and the mixture was cooled to −78 °C. A pentane solution of ^{t}BuLi (1.60 M × 6.3 mL, 10 mmol) was added via a syringe, and the mixture was stirred at −78 °C for 2.5 h. After the reaction solution was warmed to −20 °C, selenium powder (395 mg, 5 mmol) was added and the resulting mixture was stirred at −20 °C for an additional 0.5 h. Once again, the reaction solution was cooled to −78 °C, and the addition of a solution of ^{t}BuLi in pentane (1.60 M × 6.3 mL, 10 mmol) was repeated. After stirring at −78 °C for 2.5 h, the mixture was warmed up to room temperature, and then selenium powder (395 mg, 5 mmol) was added. The resulting mixture was stirred at room temperature for 30 min, and a solution of Cl_2SnBu_2 (1.52 g, 5.0 mmol) in THF (20 mL) was added dropwise for 40 min at −78 °C. The reaction mixture was allowed to warm up to room temperature and stirred at that temperature overnight. The reaction was quenched by the addition of saturated aqueous NaCl solution, and the resulting suspension was filtered through Celite. After the aqueous layer was extracted with three portions of dichloromethane, the extracts were combined and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a deep brown oil: ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 6 H), 1.36 (sixtet, J = 7.3 Hz, 4 H), 1.61 (m, 4 H), 1.68 (m, 4 H), 2.14 (quintet, J = 7.3 Hz, 2 H), 2.47 (t, J = 7.3 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 21.8, 26.5, 27.0, 28.5, 38.7, 132.0.

4,5-(Ethylenedithio)-2,2-dibutyl-2-stanna-1,3-diselenole (7). In a 30-mL flask with a septum inlet were placed 0.42 mL (3.0 mmol) of diisopropylamine and 2 mL of THF, and the mixture was cooled to 0 °C. A hexane solution of ^{n}BuLi (1.71 M × 1.75 mL, 3.0 mmol) was added via a syringe, and the mixture was stirred at 0 °C for 10 min. The reaction solution was cooled to −78 °C, a solution of 2,3-dihydro-1,4-dithiin (118 mg, 1.0 mmol) in THF (3 mL) was added dropwise slowly. After stirring at −78 °C for 15 min, selenium powder (158 mg, 2.0 mmol) was added and the resulting mixture was warmed to −40 °C gradually. The reaction solution was maintained at −40 °C for 20 min to afford a pale yellow solution. A solution of Cl_2SnBu_2 (608 mg, 2.0 mmol) in THF (10 mL) was added dropwise at −78 °C for 20 min, and the mixture was allowed to warm to 0 °C. The reaction was quenched by the addition of saturated aqueous NaCl solution, and the resulting suspension was filtered through Celite. After the aqueous layer was extracted with three portions of chloroform, the extracts were combined, dried over $MgSO_4$, and then concentrated under reduced pressure. Purification with silica gel column chromatography by using hexane−dichloromethane as an eluent gave 303 mg (60 % yield) of **7**. The purification was carried out within a short period, since **7** was sensitive to silica gel: reddish brown powder; mp 77−79 °C; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 6 H), 1.36 (sixtet, J = 7.3 Hz, 4 H), 1.71 (m, 8 H), 3.20 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 21.3, 26.6, 28.6, 33.3, 112.6.

4,5-(Methylenedithio)-2,2-dibutyl-2-stanna-1,3-dithiole (10). A 100-mL flask with a septum inlet containing 389 mg (2.0 mmol) of **9** was cooled in a water bath, and a methanol solution of NaOMe (1 M × 4.0 mL, 4.0 mmol) was added in one portion via a syringe. After stirring for 10 min, the water bath was removed, and the mixture was diluted with 10 mL of THF. A solution of Cl_2SnBu_2 (608 mg, 2.0 mmol) in THF (20 mL) was added dropwise at −78 °C for 30 min, and the resulting mixture was warmed to 0 °C gradually. The reaction was quenched by the addition of saturated aqueous NaCl solution, and the aqueous layer was extracted with three portions of dichloromethane. The extracts were combined and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a viscous deep violet oil. When **10** was kept at room temperature for a prolonged time, decomposition of **10** took place gradually: ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 6 H), 1.37 (sixtet, J = 7.3 Hz, 4 H), 1.63−1.78 (m, 8 H), 4.55 (s, 2 H). The exact assignment for **10** could not be made on the basis of ^{13}C NMR analysis due to impurities.

Thieno[3,4-*d*]-2,2-dibutyl-2-stanna-1,3-dithiole (3c). The same procedure as described above was used. The usual workup led to the crude tin thiolate **3c**, which was identical with the sample prepared via Grignard reaction of **2c**.

A Typical Procedure for Syntheses of DHTTF Derivatives and Related Compounds. Entry 3 in Table 1 is representative. In a 50-mL flask with a septum inlet were placed 2.0 mmol (based on **2a**) of tin thiolate **3a** and 30 mL of dichloromethane, and the mixture was cooled to −78 °C. A hexane solution of Me_3Al (1.02 M × 4.0 mL, 4.1 mmol) and 0.28 mL (2.0 mmol) of ester **11a** were successively added via syringes, and the reaction mixture was allowed to warm up to room temperature. After stirring at room temperature overnight, the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ solution at 0 °C, and the resulting suspension was filtered through Celite. The aqueous layer was extracted with three portions of chloroform. The extracts were combined, dried over $MgSO_4$, and then concentrated in vacuo. Purification of the residue with silica gel column chromatography by using hexane followed by hexane-dichloromethane as eluents gave 338 mg (57% yield) of **12**.

(Ethylenedithio)dihydrotetrathiafulvalene (12): orange powder; mp 223.5 °C dec from ethanol−chloroform; ^{1}H NMR ($CDCl_3$) δ 3.28 (s, 4 H), 3.47 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 30.2, 40.0, 109.3, 113.3, 118.9; MS, *m/z* (% relative intensity) 298 (M^+ + 2, 30), 296 (M^+, 100), 268 (51), 192 (30), 148 (30), 83 (70); HRMS (EI) calcd for $C_8H_8S_6$ 295.8950, measured 295.8951.

2-[4,5-(Ethylenedithio)-1,3-dithiol-2-ylidene]-1,3-dithiane (13): yellow powder; mp 152−153 °C from ethanol−chloroform; ^{1}H NMR ($CDCl_3$) δ 2.17 (m, 2 H), 2.85 (m, 4 H), 3.29 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 24.7, 29.6, 31.9, 104.6, 112.4, 137.3; MS, *m/z* (% relative intensity) 312 (M^+ + 2, 28), 310 (M^+, 100), 282 (43), 236 (14), 162 (17), 88 (9); HRMS (EI) calcd for $C_9H_{10}S_6$ 309.9107, measured 309.9104. Anal. Calcd for $C_9H_{10}S_6$: C, 34.80; H, 3.25. Found: C, 34.69; H, 3.03.

(Methylenedithio)dihydrotetrathiafulvalene (14). The same procedure as described above in A Typical Procedure was employed except that (i) the aqueous layer was extracted with dichloromethane, (ii) removal of the solvent was performed below 40 °C, and (iii) purification with silica gel column chromatography was carried out by using pentane and pentane−dichloromethane as eluents: brown needles; mp 129 °C dec from hexane−carbon disulfide; ^{1}H NMR ($CDCl_3$) δ 3.47 (s, 4 H), 4.91 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 40.0, 44.8, 117.2, 117.3, 119.5; MS, *m/z* (% relative intensity) 284 (M^+ + 2, 26), 282 (M^+, 100), 178 (58), 88 (54); HRMS (EI) calcd for $C_7H_6S_6$ 281.8794, measured 281.8795. Anal. Calcd for $C_7H_6S_6$: C, 29.76; H, 2.14. Found: C, 29.77; H, 2.08.

(Vinylenedithio)dihydrotetrathiafulvalene (15). The same procedure as described above in A Typical Procedure was used except that purification with silica gel column chroma-

tography was carried out by using hexane and hexane−chloroform as eluents: orange needles; mp 184 °C dec from ethanol−chloroform; ^{1}H NMR ($CDCl_3$) δ 3.46 (s, 4 H), 6.53 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 39.7, 114.7, 118.3, 121.3, 124.6; MS, *m/z* (% relative intensity) 296 ($M^+ + 2$, 27), 294 (M^+, 100), 190 (44), 148 (23), 114 (18), 88 (15); HRMS (EI) calcd for $C_8H_6S_6$ 293.8794, measured 293.8793.

2-[4,5-(Vinylenedithio)-1,3-dithiol-2-ylidene]-1,3-dithiane (16). The same procedure as described in the procedure for preparation of **15** was employed: yellow powder; mp 148−149 °C from ethanol−chloroform; ^{1}H NMR ($CDCl_3$) δ 2.18 (m, 2 H), 2.86 (m, 4 H), 6.55 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.7, 31.8, 106.5, 118.0, 124.3, 143.0; MS, *m/z* (% relative intensity) 310 ($M^+ + 2$, 33), 308 (M^+, 100), 234 (25), 202 (24), 162 (18), 88 (10); HRMS (EI) calcd for $C_9H_8S_6$ 307.8950, measured 307.8949; Anal. Calcd for $C_9H_8S_6$: C, 35.03; H, 2.61. Found: C, 34.88; H, 2.56.

Thienodihydrotetrathiafulvalene (17): yellow powder; mp 105.5−106 °C from hexane-dichloromethane; ^{1}H NMR ($CDCl_3$) δ 3.49 (s, 4 H), 6.82 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 39.8, 111.6, 117.8, 118.9, 136.8; MS, *m/z* (% relative intensity) 264 ($M^+ + 2$, 20), 262 (M^+, 89), 234 (18), 202 (37), 158 (100). Anal. Calcd for $C_8H_6S_5$: C, 36.61; H, 2.30. Found: C, 36.63; H, 2.20.

Dimethyldihydrodiselenadithiafulvalene (18): orange powder; mp 155.5−156.0 °C from ethanol−chloroform; ^{1}H NMR ($CDCl_3$) δ 1.97 (s, 6 H), 3.51 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 16.0, 41.2, 99.8, 118.9, 126.1; MS, *m/z* (% relative intensity) 332 ($M^+ + 4$, 36), 330 ($M^+ + 2$, 100), 328 (M^+, 86), 326 ($M^+ - 2$, 50), 226 (33), 224 (29). Anal. Calcd for $C_8H_{10}S_2Se_2$: C, 29.27; H, 3.07. Found: C, 29.28; H, 2.86.

Trimethylenedihydrodiselenadithiafulvalene (19): pale orange plate; mp 196 °C dec from ethanol-chloroform; ^{1}H NMR ($CDCl_3$) δ 2.34 (quintet, J = 7.3 Hz, 2 H), 2.56 (t, J = 7.3 Hz, 4 H), 3.52 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 27.2, 33.1, 40.8, 107.7, 120.4, 135.1; MS, *m/z* (% relative intensity) 344 ($M^+ + 4$, 47), 342 ($M^+ + 2$, 100), 340 (M^+, 87), 338 ($M^+ - 2$, 60), 238 (26), 236 (20); Anal. Calcd for $C_9H_{10}S_2Se_2$: C, 31.77; H, 2.96. Found: C, 31.89; H, 2.95.

(Ethylenedithio)dihydrodiselenadithiafulvalene (20). The same procedure as described above in A Typical Procedure was employed except that (i) the aqueous layer was extracted with carbon disulfide and (ii) purification with silica gel column chromatography was carried out by using hexane and hexane−carbon disulfide as eluents: light-red needles; mp 201 °C dec from ethanol−carbon disulfide; ^{1}H NMR ($CDCl_3$) δ 3.29 (s, 4 H), 3.52 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 31.1, 40.9, 97.6, 114.0, 125.6; MS, *m/z* (% relative intensity) 394 ($M^+ + 4$, 42), 392 ($M^+ + 2$, 100), 390 (M^+, 85), 388 ($M^+ - 2$, 48), 336 (22), 276 (28); HRMS (EI) calcd for $C_8H_8S_4{}^{80}Se_2$ 391.7839, measured 391.7812. Anal. Calcd for $C_8H_8S_4Se_2$: C, 24.61; H, 2.07. Found: C, 24.53; H, 2.00.

A Typical Procedure for Preparation of Esters via Transmetalation. Preparation of **22a** from tin thiolate **3a** is representative. In a 200-mL flask with a septum inlet were placed 5.0 mmol (based on **2a**) of the crude tin thiolate **3a** and 50 mL of THF, and the mixture was cooled to −78 °C. A hexane solution of ^{n}BuLi (1.61 M × 6.2 mL, 10 mmol) was added dropwise for 10 min via a syringe, and stirring was continued for 30 min at that temperature. After a solution of methyl dichloroacetate (0.52 mL, 5.0 mmol) in THF (25 mL) was added dropwise for 30 min, the reaction mixture was allowed to warm to 0 °C, and the reaction was quenched by saturated aqueous NH_4Cl solution. The aqueous layer was extracted with three portions of dichloromethane. The extracts were combined, dried over $MgSO_4$, and then concentrated in vacuo. Chromatography of the residue on silica gel by using hexane followed by hexane−dichloromethane as eluents gave 446 mg (35% yield based on **2a**) of **22a**.

Methyl 4,5-(ethylenedithio)-1,3-dithiole-2-carboxylate (22a): pale reddish-orange oil; ^{1}H NMR ($CDCl_3$) δ 3.17 (m, 2 H), 3.27 (m, 2 H), 3.76 (s, 3 H), 5.11 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 30.2, 48.8, 53.6, 111.7, 168.5; MS, *m/z* (% relative intensity) 254 ($M^+ + 2$, 15), 252 (M^+, 88), 195 (32), 193 (100), 167 (12), 165 (68); HRMS (EI) calcd for $C_7H_8O_2S_4$ 251.9407, measured 251.9394.

Methyl 4,5-dimethyl-1,3-dithiole-2-carboxylate (22b): orange oil; ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 6 H), 3.71 (s, 3 H), 4.98 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.5, 47.6, 53.2, 119.5, 169.9; MS, *m/z* (% relative intensity) 192 ($M^+ + 2$, 8), 190 (M^+, 80), 133 (29), 131 (100); HRMS (EI) calcd for $C_7H_{10}O_2S_2$ 190.0122, measured 190.0134.

Methyl 4,5-dimethyl-1,3-diselenole-2-carboxylate (22c): pale orange oil; ^{1}H NMR ($CDCl_3$) δ 1.87 (s, 6 H), 3.76 (s, 3 H), 5.15 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 15.9, 26.6, 53.5, 122.9, 171.7; MS, *m/z* (% relative intensity) 288 ($M^+ + 4$, 20), 286 ($M^+ + 2$, 65), 284 (M^+, 57), 282 ($M^+ - 2$, 34), 229 (31), 227 (100), 225 (87), 223 (51); HRMS (EI) calcd for $C_7H_{10}O_2{}^{80}Se_2$ 285.9011, measured 285.9022.

Methyl 4,5-trimethylene-1,3-diselenole-2-carboxylate (22d): brownish-yellow solid; mp 50−51 °C; ^{1}H NMR ($CDCl_3$) δ 2.3−2.5 (m, 6 H), 3.76 (s, 3 H), 5.84 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 28.9, 32.8, 38.9, 53.5, 133.8, 171.3; MS, *m/z* (% relative intensity) 300 ($M^+ + 4$, 15), 298 ($M^+ + 2$, 39), 296 (M^+, 31), ($M^+ - 2$, 18), 241 (30), 239 (100), 237 (91), 235 (54); HRMS (EI) calcd for $C_8H_{10}O_2{}^{80}Se_2$ 297.9011, measured 297.9021.

Methyl 1,2,5-Thiadiazolo[3,4-*d*]-1,3-dithiole-2-carboxylate (24). In a 200-mL flask with a septum inlet was placed 0.88 g (5.0 mmol) of **23**, and this flask was cooled in a water bath. A methanol solution of NaOMe (1 M × 10 mL, 10 mmol) was added in one portion via a syringe, and the mixture was stirred for 10 min. After removal of the water bath, a solution of methyl dichloroacetate (0.52 mL, 5.0 mmol) in THF (50 mL) was added dropwise for 30 min, and stirring was continued for 3 days. The reaction was quenched by saturated aqueous NH_4Cl solution, and the usual workup was carried out. Purification of the product with silica gel column chromatography by using hexane−dichloromethane as an eluent gave 478 mg (44% yield) of **24**: pale yellow plate: mp 82.5−83.0 °C from hexane−dichloromethane; ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 3 H), 5.84 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 54.1, 55.2, 161.2, 168.1; MS, *m/z* (% relative intensity) 222 ($M^+ + 2$, 12), 220 (M^+, 84), 163 (46), 161 (100); HRMS (EI) calcd for $C_5H_4O_2N_2S_3$ 219.9435, measured 219.9437.

Dimethyl(ethylenedithio)diselenadithiafulvalene (DMET, 25). To a solution of tin selenolate **3d** (139 mg, 0.31 mmol) in dichloromethane (1 mL) was added at −78 °C a hexane solution of Me_3Al (1.02 M × 0.6 mL, 0.61 mmol), and then a solution of ester **22a** (76 mg, 0.30 mmol) in dichloromethane (1 mL) was added. The mixture was allowed to warm up to room temperature, and stirring was continued overnight. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ solution at 0 °C, and the resulting suspension was filtered through Celite. The aqueous layer was extracted with three portions of chloroform. The extracts were combined, dried over $MgSO_4$, and then concentrated in vacuo. Purification of the residue with silica gel column chromatography by using hexane and hexane−chloroform as eluents gave 53 mg (43% yield) of **25**: mp 195 °C dec from hexane-chloroform; ^{1}H NMR ($CDCl_3$) δ 2.00 (s, 6 H), 3.28 (s, 4 H). Anal. Calcd for $C_{10}H_{10}S_4Se_2$: C, 28.84; H, 2.42. Found: C, 28.96; H, 2.35.

Trimethylene(ethylenedithio)diselenadithiafulvalene (TMET-STF, 26). To a solution of the crude tin thiolate **2a** (124 mg, 0.30 mmol) in dichloromethane (3 mL) were successively added at −78 °C a hexane solution of Me_3Al (1.02 M × 0.6 mL, 0.61 mmol) and a solution of ester **22d** (89 mg, 0.30 mmol) in dichloromethane (2 mL). The mixture was warmed up to room temperature gradually, and stirring was continued overnight. The same workup and purification as described above gave 47 mg (37% yield) of **26**: mp 198 °C dec from hexane−chloroform; ^{1}H NMR ($CDCl_3$−CS_2) δ 2.38 (quintet, J = 7.3 Hz, 2 H), 2.60 (t, J = 7.3 Hz, 4 H), 3.30 (s, 4 H). Anal. Calcd for $C_{11}H_{10}S_4Se_2$: C, 30.84; H, 2.35. Found: C, 30.95 H, 2.44.

Trimethylene(thiadiazolo)diselenadithiafulvalene (27). To an ice-cold solution of the crude tin selenolate **5** (2.7 mmol based on **4**) in dichloromethane (5.4 mL) was added dropwise a hexane solution of Me_3Al (1.02 M × 5.4 mL, 5.5 mmol), and the mixture was stirred at room temperature for 1 h. After the disappearance of **5** was monitored by an analytical TLC (Merck 60F-254), a solution of ester **24** (0.59 g, 2.7 mmol) in

dichloromethane (10.8 mL) was added at room temperature, and stirring was continued at that temperature for 2 days. The same workup and purification as described above gave 288 mg (27% yield) of **27**: orange needles; mp 220 °C dec from ethanol−chloroform; ^{1}H NMR ($CDCl_3$) δ 2.41 (quintet, J = 7.3 Hz, 2 H), 2.62 (t, J = 7.3 Hz, 4 H); MS, *m/z* (% relative intensity) 400 ($M^+ + 4$, 40), 398 ($M^+ + 2$, 100), 396 (M^+, 86), 394 ($M^+ - 2$, 50), 282 (26), 238 (28); HRMS (EI) calcd for $C_9H_6N_2S_3{}^{80}Se_2$ 397.8024, measured 397.8024.

Dimethyl(thiadiazolo)diselenadithiafulvalene (28). The same procedure as described above was used except that reaction of tin selenolate **3d** with Me_3Al was carried out for 4 h. Purification followed by recrystallization from ethanol−chloroform gave **28** in 14% yield: orange needles; mp 224−225 °C from ethanol−chloroform; ^{1}H NMR ($CDCl_3$) δ 2.04 (s, 6 H); MS, *m/z* (% relative intensity) 388 ($M^+ + 4$, 39), 386 ($M^+ + 2$, 100), 384 (M^+, 86), 382 ($M^+ - 2$, 50), 332 (18), 226 (42); HRMS (EI) calcd for $C_8H_6N_2S_3{}^{80}Se_2$ 385.8024, measured 385.8022.

2,2-Dibutyl-2-stanna-1,3-dithiolo[4,5-*d*]-1,3-dithiol-2-one (34). In a 200-mL flask with a septum inlet was placed 2.08 g (10 mmol) of thiapendione, and this flask was cooled in a water bath. A methanol solution of NaOMe (1 M × 20 mL, 20 mmol) was added in one portion via a syringe, and the mixture was stirred for 10 min. After the mixture was cooled to −78 °C, a solution of Cl_2SnBu_2 (3.04 g, 10 mmol) in THF (100 mL) was added dropwise for 50 min, and the reaction mixture was allowed to warm to 0 °C. The reaction was quenched by the addition of water, and the resulting mixture was extracted with three portions of dichloromethane. The extracts were combined, dried over $MgSO_4$, and then concentrated in vacuo. Chromatography of the residue on silica gel by using dichloromethane as an eluent gave 3.96 g (96% yield) of **34**: dark yellow plate; mp 97 °C dec from hexane−dichloromethane; ^{1}H-NMR ($CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 6 H), 1.40 (m, 4 H), 1.78 (m, 8 H); ^{13}C-NMR ($CDCl_3$) δ 13.6, 24.0, 26.6, 27.8, 116.9, 193.0.

A Typical Procedure for Reaction of 34 with Esters. Entry 3 in Table 2 is representative. In a 30-mL flask with a septum inlet were placed 413 mg (1.0 mmol) of tin thiolate **34** and dichloromethane (5 mL), and the mixture was cooled to 0 °C. After a hexane solution of Me_3Al (1.02 M × 2.0 mL, 2.0 mmol) was added, stirring was continued at room temperature for 40 min, and then 0.28 mL (2.0 mmol) of ester **11a** was added via a syringe. The reaction mixture was stirred at room temperature for 2 days, and the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ solution at 0 °C. The resulting suspension was filtered through Celite, and the aqueous layer was extracted with three portions of carbon disulfide. The extracts were combined, dried over $MgSO_4$, and then concentrated in vacuo. Purification of the product with silica gel column chromatography by using hexane followed by hexane−carbon disulfide as eluents gave 142 mg (48% yield) of **36c**.

2-Isopropylidene-1,3-dithiolo[4,5-*d*]-1,3-dithiol-2-one (36a). The same procedure as described above in A Typical Procedure was used except that (i) the aqueous layer was extracted with chloroform and (ii) purification with silica gel column chromatography was carried out by using hexane and hexane−dichloromethane as eluents: brownish-yellow powder; mp 180 °C dec from ethanol−chloroform: ^{1}H NMR ($CDCl_3$) δ 1.78 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 23.4, 111.9, 120.5, 122.8, 192.2; MS, m/z (% relative intensity) 236 ($M^+ + 2$, 12), 234 (M^+, 67), 208 (15), 206 (64), 86 (100); HRMS (EI) calcd for $C_7H_6OS_4$ 233.9302, measured 233.9295.

2-Cyclopentanylidene-1,3-dithiolo[4,5-*d*]-1,3-dithiol-2-one (36b). The same procedure as described above was employed except that purification with silica gel column chromatography was performed by using hexane and hexane−chloroform as eluents: brown needles; mp 170 °C dec from ethanol−chloroform; ^{1}H NMR ($CDCl_3$) δ 1.81 (m, 4 H), 2.15 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 27.5, 34.4, 111.9, 115.5, 133.5, 192.2; MS, m/z (% relative intensity) 262 ($M^+ + 2$, 13), 260 (M^+, 42), 234 (10), 232 (57), 112 (100); HRMS (EI) calcd for $C_9H_8OS_4$ 259.9458, measured 259.9458.

2-(1′,3′-Dithiolan-2′-ylidene)-1,3-dithiolo[4,5-*d*]-1,3-dithiol-2-one (36c): light green powder; mp 212 °C dec from carbon disulfide; ^{1}H NMR ($CDCl_3$-CS_2) δ 3.53 (s, 4 H); MS, m/z (% relative intensity) 298 ($M^+ + 2$, 28), 296 (M^+, 92), 270 (31), 268 (100), 148 (83); HRMS (EI) calcd for $C_7H_4OS_6$ 295.8586, measured 295.8581.

2-(1′,3′-Dithian-2′-ylidene)-1,3-dithiolo[4,5-d]-1,3-dithiol-2-one (36d): pale brown powder; mp 185 °C dec from ethanol−carbon disulfide; ^{1}H NMR ($CDCl_3$−CS_2) δ 2.22 (m, 2 H), 2.92 (m, 4 H); MS, m/z (% relative intensity) 312 ($M^+ + 2$, 33), 310 (M^+, 100), 284 (25), 282 (77), 162 (36); HRMS (EI) calcd for $C_8H_6OS_6$ 309.8743, measured 309.8753.

2-[4′,5′-(Ethylenedithio)-1′,3′-dithiol-2′-ylidene]-1,3-dithiolo[4,5-*d*]-1,3-dithiol-2-one (36e): orange needles; mp 245 °C dec from ethanol−carbon disulfide; ^{1}H NMR ($CDCl_3$−CS_2) δ 3.30 (s, 4 H); MS, m/z (% relative intensity) 386 ($M^+ + 2$, 38), 384 (M^+, 100), 358 (24), 356 (65), 192 (48); HRMS (EI) calcd for $C_9H_4OS_8$ 383.8028, measured 383.8076.

2-(4′,5′-Dimethyl-1′,3′-dithiol-2′-ylidene)-1,3-dithiolo-[4,5-*d*]-1,3-dithiol-2-one (36f): shiny brown powder; mp 189−190 °C from ethanol−carbon disulfide; ^{1}H NMR ($CDCl_3$−CS_2) δ 2.02 (s, 6 H); MS, *m/z* (% relative intensity) 324 ($M^+ + 2$, 16), 322 (M^+, 57), 296 (29), 294 (100), 174 (59); calcd for $C_9H_6OS_6$ 321.8743, measured 321.8746.

2-(4′,5′-Dimethyl-1′,3′-diselenol-2′-ylidene)-1,3-dithiolo-[4,5-d]-1,3-dithiol-2-one (36g): dark brown powder; mp 222 °C dec from chloroform−carbon disulfide; ^{1}H NMR ($CDCl_3$−CS_2) δ 2.06 (s, 6 H); MS, *m/z* (% relative intensity) 420 ($M^+ + 4$, 17), 418 ($M^+ + 2$, 41), 416 (M^+, 36), 414 ($M^+ - 2$, 20), 390 (100), 388 (95); HRMS (EI) calcd for $C_9H_6OS_4{}^{80}Se_2$ 417.7632, measured 417.7604.

2-(4′,5′-Trimethylene-1′,3′-diselenol-2′-ylidene)-1,3-dithiolo[4,5-*d*]-1,3-dithiol-2-one (36h): brownish-orange powder; mp 198 °C dec from chloroform−carbon disulfide; ^{1}H NMR ($CDCl_3$−CS_2) δ 2.42 (m, 2 H), 2.64 (t, J = 7.3 Hz, 4 H); MS, *m/z* (% relative intensity) 432 ($M^+ + 4$, 31), 430 ($M^+ + 2$, 70), 428 (M^+, 60), 414 ($M^+ - 2$, 35), 402 (100), 400 (84); HRMS (EI) calcd for $C_{10}H_6OS_4{}^{80}Se_2$ 429.7632, measured 429.7620.

A Typical Procedure for Cross-Coupling Reactions. Reaction of **36c** with 4,5-(ethylenedithio)-1,3-dithiole-2-thione (**1a**) is representative. In a 30-mL flask with a septum inlet were placed 147 mg (0.5 mmol) of **36c**, 224 mg (1.0 mmol) of **1a**, toluene (5.0 mL), and trimethyl phosphite (5.0 mL). After the mixture was refluxed with stirring for 2 h, the resulting suspension was cooled to 0 °C and diluted with hexane. The suspension was filtered through a filter paper, and the residue was washed with hexane. The remaining solid was dissolved in carbon disulfide, and the solution was concentrated under reduced pressure. Purification of the residue with silica gel column chromatography by using carbon disulfide as an eluent gave 190 mg (80% yield) of **30b**.

2-(Benzo[*d*]-1′,3′-dithiol-2′-ylidene)-5-isopropylidene-1,3,4,6-tetrathiapentalene (29a): pale brown powder; mp 214 °C dec from ethanol−carbon disulfide; ^{1}H NMR ($CDCl_3$-CS_2) δ 1.75 (s, 6 H), 7.13 (m, 2 H), 7.24 (m, 2 H); MS, m/z (% relative intensity) 372 ($M^+ + 2$, 28), 370 (M^+, 100), 208 (21), 196 (28), 152 (12); HRMS (EI) calcd for $C_{14}H_{10}S_6$ 369.9107, measured 369.9099.

2-(Benzo[*d*]-1′,3′-dithiol-2′-ylidene)-5-cyclopentanylidene-1,3,4,6-tetrathiapentalene (29b): dark brown powder; mp 210 °C dec from ethanol−carbon disulfide; ^{1}H NMR ($CDCl_3$-CS_2) δ 1.81 (br, 4 H), 2.13 (br, 4 H), 7.13 (m, 2 H), 7.24 (m, 2 H); MS, m/z (% relative intensity) 398 ($M^+ + 2$, 28), 396 (M^+, 100), 208 (10), 196 (30), 152 (15); HRMS (EI) calcd for $C_{16}H_{12}S_6$ 395.9263, measured 395.9275.

2-[4′,5′-Bis(methylthio)-1′,3′-dithiol-2′-ylidene]-5-(1″,3″-dithiolan-2″-ylidene)-1,3,4,6-tetrathiapentalene (30a): yellow powder; mp 187 °C dec from ethanol−chloroform; ^{1}H NMR ($CDCl_3$-CS_2) δ 2.42 (s, 6 H), 3.50 (s, 4 H); MS, m/z (% relative intensity) 476 ($M^+ + 2$, 65), 474 (M^+, 100), 324 (23), 238 (21), 148 (26), 88 (29); HRMS (EI) calcd for $C_{12}H_{10}S_{10}$ 473.7990, measured 473.7999; Anal. Calcd for $C_{12}H_{10}S_{10}$: C, 30.35; H, 2.12. Found: C, 30.41; H, 2.08.

2-[4′,5′-(Ethylenedithio)-1′,3′-dithiol-2′-ylidene]-5-(1″,3″-dithiolan-2″-ylidene)-1,3,4,6-tetrathiapentalene (30b): dark red powder; mp 212 °C dec from chloroform−carbon disulfide;

^{1}H NMR ($CDCl_3$−CS_2) δ 3.30 (s, 4 H), 3.50 (s, 4 H); MS, m/z (% relative intensity) 474 ($M^+ + 2$, 45), 472 (M^+, 100), 444 (63), 148 (57), 88 (44); HRMS (EI) calcd for $C_{12}H_8S_{10}$ 471.7833, measured 471.7814; Anal. Calcd for $C_{12}H_8S_{10}$: C, 30.48; H, 1.70. Found: C, 30.35; H, 1.60.

2-[4′,5′-(Methylenedithio)-1′,3′-dithiol-2′-ylidene]-5-(1″,3″-dithiolan-2″-ylidene)-1,3,4,6-tetrathiapentalene (30c): brown powder; mp 199 °C dec from carbon disulfide; ^{1}H NMR (400 MHz, $CDCl_3$-CS_2) δ 3.50 (s, 4 H), 4.96 (s, 2 H); MS, m/z (% relative intensity) 460 ($M^+ + 2$, 45), 458 (M^+, 100), 338 (92), 234 (72), 148 (81); HRMS (EI) calcd for $C_{11}H_6S_{10}$ 457.7677, measured 457.7677.

2-[4′,5′-Bis(methylthio)-1′,3′-dithiol-2′-ylidene]-5-(1″,3″-dithian-2″-ylidene)-1,3,4,6-tetrathiapentalene (31a): dark orange powder; mp 205 °C dec from ethanol−carbon disulfide; ^{1}H NMR ($CDCl_3$−CS_2) δ 2.20 (m, 2 H), 2.43 (s, 6 H), 2.89 (m, 4 H); MS, m/z (% relative intensity) 490 ($M^+ + 2$, 63), 488 (M^+, 100), 338 (22), 236 (38); HRMS (EI) calcd for $C_{13}H_{12}S_{10}$ 487.8146, measured 487.8122.

2-[4′,5′-(Ethylenedithio)-1′,3′-dithiol-2′-ylidene]-5-(1″,3″-dithian-2″-ylidene)-1,3,4,6-tetrathiapentalene (31b): dark orange powder; mp 230 °C dec from ethanol−carbon disulfide; ^{1}H NMR ($CDCl_3$-CS_2) δ 2.21 (m, 2 H), 2.89 (m, 4 H), 3.31 (s, 4 H); MS, m/z (% relative intensity) 488 ($M^+ + 2$, 47), 486 (M^+, 100), 458 (64), 162 (63); HRMS (EI) calcd for $C_{13}H_{10}S_{10}$ 485.7990, measured 485.7983.

2-[4′,5′-(Methylenedithio)-1′,3′-dithiol-2′-ylidene]-5-(1″,3″-dithian-2″-ylidene)-1,3,4,6-tetrathiapentalene (31c): brown powder; mp 213 °C dec from ethanol−carbon disulfide; ^{1}H NMR ($CDCl_3$-CS_2) δ 2.20 (m, 2 H), 2.89 (m, 4 H), 4.97 (s, 2 H); MS, m/z (% relative intensity) 474 ($M^+ + 2$, 49), 472 (M^+, 100), 352 (80), 278 (51), 222 (39), 162 (41); HRMS (EI) calcd for $C_{12}H_8S_{10}$ 471.7833, measured 471.7834.

2-(Thieno[3,4-*d*]-1′,3′-dithiol-2′-ylidene)-5-(4″,5″-dimethyl-1″,3″-dithiol-2″-ylidene)-1,3,4,6-tetrathiapentalene (32): pale brown powder; mp 211 °C dec from ethanol−carbon disulfide; ^{1}H NMR ($CDCl_3$-CS_2) δ 1.97 (s, 6 H), 6.89 (s, 2 H); MS, m/z (% relative intensity); 466 ($M^+ + 2$, 42), 464 (M^+, 100), 288 (15), 202 (28), 174 (95); HRMS (EI) calcd for $C_{14}H_8S_9$ 463.8112, measured 463.8091.

2-(4′,5′-Dimethyl-1′,3′-diselenol-2′-ylidene)-5-[4″,5″-bis(methylthio)-1″,3″-dithiol-2″-ylidene]-1,3,4,6-tetrathiapentalene (33a): reddish-brown powder; mp 205 °C dec from ethanol−carbon disulfide; ^{1}H NMR ($CDCl_3$-CS_2) δ 2.09 (s, 6 H), 2.43 (s, 6 H); MS, m/z (% relative intensity) 598 ($M^+ + 4$, 59), 596 ($M^+ + 2$, 100), 594 (M^+, 91), 592 ($M^+ - 2$, 50), 446 (13), 444 (11), 270 (27), 268 (23), 238 (27); HRMS (EI) calcd for $C_{14}H_{12}S_8{}^{80}Se_2$ 595.7035, measured 595.7020.

2-(4′,5′-Trimethylene-1′,3′-diselenol-2′-ylidene)-5-[4″,5″-bis(methylthio)-1″,3″-dithiol-2″-ylidene]-1,3,4,6-tetrathiapentalene (33b): reddish-brown powder; mp 219.5 °C dec from carbon disulfide; ^{1}H NMR ($CDCl_3$−CS_2) δ 2.40 (quintet, J = 7.3 Hz, 2 H), 2.44 (s, 6 H), 2.62 (t, J = 7.3 Hz, 4 H); MS, m/z (% relative intensity) 610 ($M^+ + 4$, 52), 608 ($M^+ + 2$, 100), 606 (M^+, 85), 604 ($M^+ - 2$, 50), 458 (11), 456 (10), 282 (23), 280 (21), 238 (27); HRMS (EI) calcd for $C_{15}H_{12}S_8{}^{80}Se_2$ 607.7035, measured 607.7031. Anal. Calcd for $C_{15}H_{12}S_8Se_2$: C, 29.69; H, 1.99. Found: C, 29.71; H, 1.92.

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Supporting Information Available: ^{1}H NMR spectra of compounds **2d**, **9**, **3a-d**, **21**, **5**, **7**, **10**, **12**, **15**, **22a-d**, **24**, **27**, **28**, **34, 36a-h**, **29a-b**, **30c**, **31a-c**, **32**, and **33a** (36 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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