

A Preparation of Alkyl or Alkenyl *N*,*N*-Dimethylchalcogenocarbamates and Their One-Step Conversion into Symmetrical Dialkyl or Dialkenyl Dichalcogenides

Kazuaki Shimada,* Seiji Oikawa, Hidenori Nakamura, Akiko Moro-oka, Miho Kikuchi, Akiko Maruyama, Takahiro Suzuki, Hisashi Kogawa, Yukiko Inoue, Yaling Gong, Shigenobu Aoyagi, and Yuji Takikawa

Department of Chemical Engineering, Faculty of Engineering, Iwate University, Morioka, Iwate 020-8551

Received October 25, 2004; E-mail: shimada@iwate-u.ac.jp

Alkyl or alkenyl *N*,*N*-dimethylchalcogenocarbamates were easily prepared by a stepwise treatment of bis(*N*,*N*-dimethylcarbamoyl) dichalcogenides with NaH or $NaBH_4$, followed by various alkylating agents or acetylenes bearing electron-withdrawing substituents. The one-step conversion of alkyl or alkenyl *N*,*N*-dimethylselenocarbamates or *N*,*N*-dimethyltellurocarbamates into the corresponding symmetrical dialkyl or dialkenyl dichalcogenides was also achieved efficiently by treating with $SnCl_4$.

The preparation of organic chalcogenols and polychalcogenides has been extensively studied within the past few decades concerning synthetic use for the efficient chalcogenation of organic compounds. Among them, recent interest has been concentrated on the synthesis of dialkenyl dichalcogenides[1] and alkenechalcogenols[2] in light of novel intermediates and precursors for carbon chain homologation and the synthesis of various chalcogen-containing heterocycles. During our studies on the novel synthetic use of elemental selenium and tellurium as air-stable chalcogenide ion equivalents, we have already found a convenient preparation of symmetrical and nonsymmetrical dialkyl tellurides by a sequential repeating of reduction–alkylation–reduction–alkylation, starting from bis(*N*,*N*-dimethylcarbamoyl) ditelluride **2**.[3] It was expected that this method could be applied to the selenium series and the generation of alkanechalcogenols, or that their synthetic equivalents could be achieved by a soft Lewis acid-assisted hydrolytic cleavage of chalcogenocarbamates through a pathway involving complexation and subsequent decarbamoylation.[4,5] Along with such expectation, we attempted the convenient syntheses of *N*,*N*-dimethylchalcogenocarbamates (**3**, **4**) and subsequent reactions of compounds with various Lewis acids to give the corresponding chalcogenols, their $SnCl_4$ complexes, or a symmetrical dichalcogenides. In this paper, we would like to give a full account on the convenient preparation of alkyl or alkenyl *N*,*N*-dimethylchalcogenocarbamates (**3**, **4**) from bis(*N*,*N*-dimethylcarbamoyl) dichalcogenides (**1**, **2**) and the one-step conversion of *N*,*N*-dimethylchalcogenocarbamates into the corresponding symmetrical diselenides **7** and ditellurides **8** only by treating with $SnCl_4$ under mild reaction conditions.

Results and Discussion

Preparation of Bis(*N*,*N*-dimethylcarbamoyl) Diselenide and Bis(*N*,*N*-dimethylcarbamoyl) Ditelluride. Bis(*N*,*N*-dimethylcarbamoyl) diselenide **1** (X = Se)[4] was prepared by a stepwise treatment of dry DMF with sodium metal and elemental selenium at 100 °C, followed by aerobic exposure at R.T., and bis(*N*,*N*-dimethylcarbamoyl) ditelluride **2** (X = Te) was also efficiently synthesized in a similar manner to the preparation of **1**, as shown in Scheme 1.[3,6] The physical and spectral data of these products were identical in all respects to those of the reported data of **1** and **2**. A one-pot treatment of DMF with sodium metal and elemental selenium or tellurium at high temperature, followed by an alkylating agent (hexyl bromide or benzyl bromide), afforded the corresponding *Se*- or *Te*-alkyl *N*,*N*-dimethylchalcogenocarbamates (**3**, **4**) in moderate yields, besides **1** or **2** and several uncharacterized products. These results supported the in situ generation of *N*,*N*-dimethylcarbamoylchalcogenide ions **A** through the reaction of DMF with sodium metal and elemental chalcogen at high temperature. However, in all cases the maximum yields of **3** and **4** through these reactions remained 60% and 58%, respectively, based on the amount of elemental chalcogen, maybe due to their further thermal decomposition along with the extrusion of elemental chalcogen under an aerobic condition.[7]

The formation mechanism of *N*,*N*-dimethylchalcogenocar-

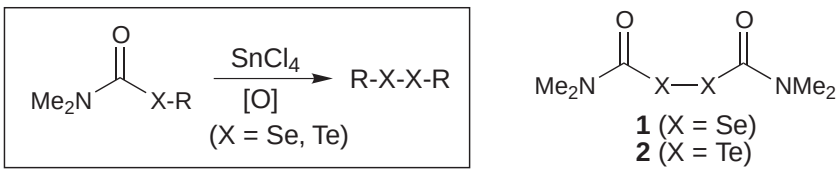

Chart 1.

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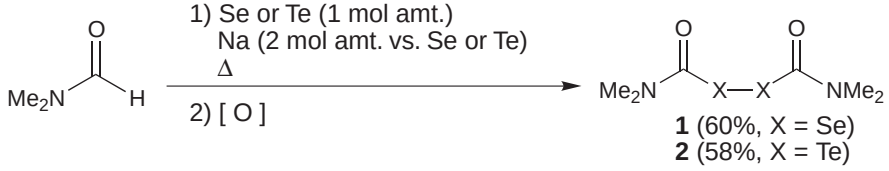
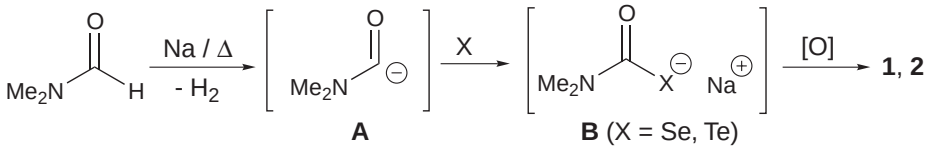


Scheme 1. Preparation of bis(*N*,*N*-dimethylcarbamoyl) diselenide (**1**) and bis(*N*,*N*-dimethylcarbamoyl) ditelluride (**2**).



Scheme 2. Plausible formation mechanism of *N*,*N*-dimethylchalcogenocarbamate ions **B** through the reacion of DMF with sodium metal and elemental chalcogen.

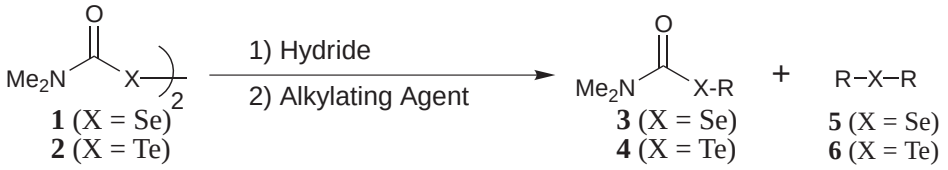
bamate ions **A** in these reactions was not clear. However, the fact that the treatment of sodium metal with dry DMF at 100 °C resulted in a facile changing of the color of the reaction mixture along with the evolution of some gas, maybe H_2 gas, might suggest the in situ formation of some reactive species as *N*,*N*-dimethylcarbamoyl anion **A**. Therefore, **1** and **2** were assumed to be afforded through a pathway involving the reaction of *N*,*N*-dimethylcarbamoyl anion **A** with elemental chalcogen to give *N*,*N*-dimethylchalcogenocarbamate ions **B** and the subsequent aerobic oxidation of **B**, as shown in Scheme 2.

Stepwise Preparation of Alkyl or Alkenyl *N*,*N*-Dimethylchalcogenocarbamates (3, 4) Starting from Bis(*N*,*N*-dimethylcarbamoyl) Dichalcogenides (1, 2). A DMF solution of bis(*N*,*N*-dimethylcarbamoyl) diselenide **1** was treated with NaH (2.2 mol amt.)[8] and then with an alkylating agent (hexyl bromide, benzyl bromide, allyl bromide, methallyl bromide, cyclohexyl bromide) or an acetylenic compound (methyl propiolate or *p*-(trifluoromethyl)phenylacetylene) to afford the corresponding *Se*-alkyl or *Se*-alkenyl *N*,*N*-dimethylselenocarbamates **3** in good-to-moderate yields.[3,7,9] Trace amounts of dialkenyl selenides **5** were obtained as by-products in some cases of the reactions. In cases starting from terminal acetylenes bearing an electron-withdrawing group, the geometry of the newly-formed double bonds of **3** was Z.[10] However, no addition product was obtained by using phenylacetylene as a substrate, even if the reaction was carried out at a higher temperature, and the use of 4-phenyl-3-butyn-2-one only gave a complex mixture, even under a mild reaction condition. These results suggested that an electron-withdrawing group on the acetylenic moiety is necessary for the nucleophilic addition of the in situ generated *N*,*N*-dimethylselenocarbamate anion. In contrast with the use of NaH as a reducing agent for **1**, the treatment of **1** with $NaBH_4$ in DMF–C_2H_5OH (1:1) gave monoselenides **5** as the main products. These results suggested a further conversion elimination of alkane- or alkeneselenolate ions through a nucleophilic attack of $NaBH_4$ or alkoxide ion toward **3** in an alcoholic media. Bis(*N*,*N*-dimethylcarbamoyl) ditelluride (**2**) was also converted into the corresponding *Te*-alkyl or *Te*-alkenyl *N*,*N*-dimethyltellurocarbamates **4** through a similar stepwise reduction–alkylation or reduction–alkenylation using $NaBH_4$ as a reducing agent in an alcoholic media in place of NaH and an alkylating agent or an acetylenic compound (methyl propiolate, *p*-(trifluoromethyl)phenylacetylene, or 4-phenyl-3-butyn-2-one).[11] A small amount of dialkenyl selenides **5** or dialkenyl tellurides **6** were found as by-products of these reactions. All results of the reactions are given in Table 1.

$SnCl_4$-Induced Cleavage of *N*,*N*-Dimethylchalcogenocarbamates (3, 4) to Afford the Corresponding Symmetrical Diselenides 5 and Ditellurides 6. A CH_2Cl_2, $CHCl_3$, or $C_2H_4Cl_2$ solution of **3** or **4** was treated with $SnCl_4$ (1–1.5 mol amt.) under an Ar atmosphere at R.T. or heating at refluxing temperature to afford symmetrical dialkyl or dialkenyl dichalcogenides (**7**, **8**)[12,13] in high yields without the contamination of **5** or **6**. Interestingly, the Z geometry of the double bonds of **3** and **4** was completely retained in products **5**–**8** during the reactions. However, in all cases, selenols or tellurols were not found at all in the crude reaction mixture, and a trace amount of monoselenide **5b** (**7b**:**5b** = 95:5, determined by the integration of the ^{1}H NMR spectrum of the mixture) was found in the crude product when the reaction was carried out using selenocarbamate **3b** in a similar manner. However, the use of another Lewis acid, such as $Et_2O \cdot BF_3$, $TiCl_4$, or *p*-toluenesulfonic acid, in place of $SnCl_4$, only gave the recovery of substrates (**3**, **4**). All of the results are given in Table 2.

When the reaction of **3b** (R = $CH_2C_6H_5$) and $SnCl_4$ (2.0 mol amt.) was monitored by using ^{1}H NMR in $CDCl_3$ in an NMR tube at 25 °C, the singlet signals of **3b** ($\delta = 2.81$, 2.93, and 4.09) just disappeared as soon as adding $SnCl_4$ to the solution of **3b** and three new singlets ($\delta = 3.14$ ($\Delta\delta = +0.33$) and 3.39 ($\Delta\delta = +0.46$), assigned to the *N*,*N*-dimethylcarbamoyl group, and $\delta = 4.61$ ($\Delta\delta = +0.51$), assigned to the benzyl methylene group) were observed. However, no signals assigned to benzeneselenol or dibenzyl diselenide (**7b**) were observed at all through NMR monitoring of the reaction. The ^{13}C NMR spectrum of the reaction mixture also showed a slight downfield shift of the benzylic carbon signal ($\delta = 30.4$ for **3b** and $\delta = 33.9$ for the reaction mixture ($\Delta\delta = +3.5$)) in contrast with a slight downfield shift of the carbamoyl carbon signal ($\delta = 165.0$ for the starting **3b** and $\delta = 175.7$ for the reaction mixture ($\Delta\delta = +10.7$)), and the ^{77}Se NMR spectrum of the reaction mixture also showed a small degree of downfield shift of the selenium signal

Table 1. Preparation of *N*,*N*-Dimethylchalcogenocarbamates **3** and **4**

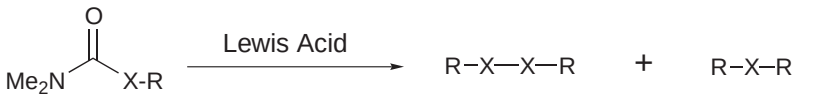


1 (X = Se) **2** (X = Te) **3** (X = Se) **4** (X = Te) **5** (X = Se) **6** (X = Te)

Substrate		Hydride	Solvent	Alkylating agent	Yield/%[a]	
1, **2**	X	(2.2 mol amt.)		(2.4 mol amt.)	**3**, **4**	**5**, **6**
1	Se	NaH	DMF[b]	*n*-$C_6H_{13}Br$	89 (**3a**)	0
1	Se	$NaBH_4$	DMF–C_2H_5OH (1:1)[c]	*n*-$C_6H_{13}Br$	27 (**3a**)	34 (**5b**)
1	Se	NaH	DMF[b]	$C_6H_5CH_2Br$	82 (**3b**)	0
1	Se	$LiAlH_4$	THF	$C_6H_5CH_2Br$	complex mixture	
1	Se	DIBAL	THF	$C_6H_5CH_2Br$	0[d]	0
1	Se	NaH	DMF[b]	$H_2C{=}CHCH_2Br$	95 (**3c**)	0
1	Se	$NaBH_4$	DMF–C_2H_5OH (1:1)[c]	$H_2C{=}CHCH_2Br$	72 (**3c**)	8 (**5c**)
1	Se	NaH	DMF[b]	$H_2C{=}CH(CH_3)CH_2Br$	53 (**3d**)	0
1	Se	NaH	DMF[b]	*c*-$C_6H_{11}Br$	13 (**3e**)	0
1	Se	NaH	DMF[b]	$BrCH_2CO_2$–*t*-C_4H_9	52 (**3f**)	0
1	Se	NaH	DMF[b]	$BrCH_2CO_2$–*l*-menthyl	82 (**3g**)	0
1	Se	NaH	DMF[b]	$HC{\equiv}CCO_2CH_3$	46 (**3h**)[e]	0
1	Se	NaH	DMF[b]	$C_6H_5C{\equiv}CCOCH_3$	complex mixture	
2	Te	$NaBH_4$	DMF–C_2H_5OH (1:1)[c]	*n*-$C_6H_{13}Br$	92 (**4a**)[f]	0
2	Te	$NaBH_4$	DMF–C_2H_5OH (1:1)[c]	$C_6H_5CH_2Br$	92 (**4b**)[f]	0
2	Te	$NaBH_4$	DMF–C_2H_5OH (1:1)[c]	$H_2C{=}CHCH_2Br$	89 (**4c**)[f]	0
2	Te	$NaBH_4$	DMF–C_2H_5OH (1:1)[c]	$HC{\equiv}CCO_2CH_3$	88 (**4h**)[e,f]	trace (**6h**)
2	Te	$NaBH_4$	DMF–C_2H_5OH (1:1)[c]	*p*-$CF_3C_6H_4C{\equiv}CH$	42 (**4i**)[e,f]	trace (**6i**)
2	Te	$NaBH_4$	DMF–C_2H_5OH (1:1)[c]	2,6-$Cl_2C_6H_3C{\equiv}CH$	61 (**4j**)[e,f]	trace (**6g**)
2	Te	$NaBH_4$	DMF–C_2H_5OH (1:1)[c]	$C_6H_5C{\equiv}CCOCH_3$	94 (**4k**)[e]	0

a) Yields were based on the two molar formation of **3**–**6** from substrates **1**, **2** for these reactions. b) A DMF solution of **1** was treated with NaH (2.2 mol amt.) at 0 °C to R.T. for 2 h and then with an alkylating agent (2.4 mol amt.) at 0 °C for 1–1.5 h. c) A solution of **1** or **2** was treated with $NaBH_4$ (2.2 mol amt.) at −50 °C for 15 min and then with an alkylating agent (2.4 mol amt.) at −50 °C, and the reaction mixture was warmed gradually to 0 °C for 1 h. d) Diselenide **1** was quantitatively recovered. e) The geometry of the newly-formed double bond was exclusively Z. f) Ref. 3.

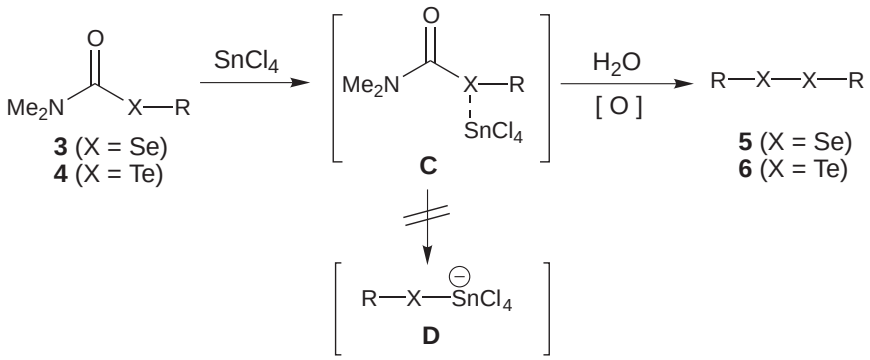
Table 2. Reaction of *N*,*N*-Dimethylchalcogenocarbamates (**3**, **4**) with a Lewis Acid



3 (X = Se) **4** (X = Te) **7** (X = Se) **8** (X = Te) **5** (X = Se) **6** (X = Te)

Substrate		Lewis acid	Solvent	Temp	Time/h	Yield/%[a]	
R	X	(mol amt.)				**7**, **8**	**5**, **6**
n-C_6H_{13} (**3a**)	Se	$Et_2O{\cdot}BF_3$ (1.5)	$C_2H_4Cl_2$	Reflux	4	0[b]	0
n-C_6H_{13} (**3a**)	Se	$SnCl_4$ (1.5)	$C_2H_4Cl_2$	Reflux	4	quant (**7a**)	0
$C_6H_5CH_2$ (**3b**)	Se	$SnCl_4$ (1.5)	$C_2H_4Cl_2$	Reflux	4	90 (**7b**)	5 (**5b**)[c]
$H_2C{=}CHCH_2$ (**3c**)	Se	$SnCl_4$ (1.5)	$C_2H_4Cl_2$	Reflux	4	complex mixture	
CH_2CO_2–*t*-C_4H_9 (**3f**)	Se	$SnCl_4$ (1.5)	$CHCl_3$	Reflux	4	complex mixture	
CH_2CO_2–*l*-menthyl (**3g**)	Se	$SnCl_4$ (1.5)	$CHCl_3$	Reflux	18	23 (**7g**)[d]	0
Z-$CH{=}CHCO_2CH_3$ (**3h**)	Se	$SnCl_4$ (1.5)	$CHCl_3$	Reflux	4	0[b]	0
Z-$CH{=}CHCO_2CH_3$ (**3h**)	Se	$SnCl_4$ (1.5)	$C_2H_4Cl_2$	Reflux	4	65 (**7h**)[e]	0
n-C_6H_{13} (**4a**)	Te	$SnCl_4$ (1.5)	CH_2Cl_2	Reflux	0.25	96 (**8a**)	0
Z-$CH{=}CHCO_2CH_3$ (**4h**)	Te	$SnCl_4$ (1.5)	CH_2Cl_2	Reflux	0.25	88 (**8h**)[e]	0
Z-$CH{=}CH$–2,6-$Cl_2C_6H_3$ (**4j**)	Te	$SnCl_4$ (1.5)	CH_2Cl_2	Reflux	0.25	97 (**8j**)[e]	0
n-C_6H_{13} (**3a**)	Se	$LiAlH_4$ (1.5)	THF	R.T.	5	87 (**7a**)	0

a) Isolated yields. b) Substrate was quantitatively recovered. c) Determined by integration of the signals of the ^1H NMR spectrum of the mixture. d) Compound **3g** was recovered in 70% yield. e) The geometry of the double bonds was completely retained in Z.



Scheme 3. Plausible pathway for the formation of symmetrical dialkenyl dichalcogenides (**5**, **6**).

($\delta = 466.2$ for the starting **3b** and $\delta = 487.5$ for the reaction mixture ($\Delta\delta = +21.3$)). Furthermore, even after standing the reaction mixture for 240 h at R.T., the singlet of the methylene signal in the ^{1}H NMR spectrum remained unchanged, and no signal assigned to diselenide **7b**, monoselenide **5b**, possible alkanechalcogenol, or their $SnCl_4$ complexes like **D**, was observed at all.

These results indicated that the interaction between **3b** and $SnCl_4$ was very weak in contrast with the reported complexation of bis(*N*,*N*-dimethylcarbamoyl) diselenide with $SnCl_4$ or $HgCl_2$.[4] Furthermore, the coordinating feature of **3b** and $SnCl_4$, in which either the selenium atom or the oxygen atom of selenocarbamate group may have an interaction with $SnCl_4$, was not clear enough due to unexpected slight downfield shifts of both the carbonyl carbon signal and the selenium signal of **3b** through monitoring the ^{13}C NMR and ^{77}Se NMR spectra of the reaction mixture. However, it was noteworthy that the conversion of **3** or **4** into **5** or **6**, respectively, was efficiently achieved by using a soft Lewis acid, $SnCl_4$. Therefore, these results suggested a preferred interaction of selenium or tellurium atom of **3** or **4** with $SnCl_4$ to form some complexes **C** that might cause a facile hydrolytic removal of the *N*,*N*-dimethylcarbamoyl moiety from **3** and **4** through contact with moisture, quenching of the reactions, or subsequent aerobic oxidation during the usual workup, as shown in Scheme 3.

Conclusion

In conclusion, we found a highly convenient synthesis of symmetrical dialkyl and dialkenyl dichalcogenides (**7**, **8**) only by treating *N*,*N*-dimethylchalcogenocarbamates (**3**, **4**) with $SnCl_4$. Further attempts for synthetic applications of these dichalcogenides, as well as the generation of alkeneselenols and alkenetellurols through anaerobic cleavage of **3** and **4**, are under way in our laboratory.

Experimental

Instruments. The melting points were determined with a Büchi 535 micro-melting-point apparatus. ^{1}H NMR spectra were recorded on a Hitachi R-22 (90 MHz) or a Bruker AC-400P (400 MHz) spectrometer, and the chemical shifts of the ^{1}H NMR spectra are given in δ relative to internal tetramethylsilane (TMS). ^{13}C NMR spectra were recorded on a Bruker AC-400P (100 MHz). ^{77}Se NMR spectra were recorded on a Bruker AC-400P (76 MHz). Mass spectra were recorded on a Hitachi M-2000 mass spectrometer with electron-impact ionization at 20 or 70 eV using a direct inlet system. IR spectra were recorded for thin-film (neat) or KBr disks on a JASCO FT/IR-7300 spectrometer. Elemental analyses were performed using a Yanagimoto CHN corder MT-5.

Materials. Column chromatography was performed using silica gel (Merck, Cat. No. 7734 or 9385) without a pretreatment. Dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), and 1,2-dichloroethane were dried over P_4O_{10}, and were freshly distilled before use. Benzene, hexane, acetonitrile, and *N*,*N*-dimethylformamide (DMF) were dried over calcium hydride (CaH_2) and freshly distilled before use. Diethyl ether and tetrahydrofuran (THF) were dried over lithium tetrahydroaluminate ($LiAlH_4$) and was freshly distilled before use. Ethanol and methanol were dried over anhydrous magnesium sulfate ($MgSO_4$), and were freshly distilled before use. All of the substrates and reagents, including hexyl bromide, benzyl bromide, allyl bromide, methallyl bromide, bromocyclohexane, *t*-butyl alcohol, *l*-menthol, bromoacetyl chloride, methyl propiolate, *p*-trifluorobenzaldehyde, 2,6-dichlorobenzaldehyde, elemental selenium, elemental tellurium, diethyl ether–boron trifluoride (1/1) ($Et_2O\cdot BF_3$), titanium(IV) chloride ($TiCl_4$), *p*-toluenesulfonic acid, tin(IV) chloride ($SnCl_4$), sodium metal, lithium tetrahydroaluminate ($LiAlH_4$), sodium tetrahydroborate ($NaBH_4$), sodium hydride (NaH), diisobutylaluminum hydride (DIBAL), anhydrous sodium sulfate, and sodium hydrogen carbonate were commercially available reagent grade, and were used without any pretreatment.

Preparation of Bis(*N*,*N*-dimethylcarbamoyl) Diselenide (1). Dry *N*,*N*-dimethylformamide (DMF, 100 mL) was treated with sodium metal (2.300 g, 6.60 mmol) at 110 °C for 15 min in a three-necked flask under an Ar atmosphere. After cooling the reaction mixture to 80 °C, selenium powder (261 mg, 3.30 mmol) was added to the reaction mixture and then the reaction mixture was heated again up to 130 °C for 24 h under an Ar atmosphere. The reaction mixture was cooled again to R.T., and an excess amount of water was added to the reaction mixture. The reaction mixture was exposed to air by vigorous stirring under an aerobic condition for 24 h at room temperature. After removal of unreacted elemental selenium by suction filtration, the filtrate was extracted with benzene. The organic layer was washed with water, and dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the residual crude solid was recrystallized from benzene–hexane to obtain bis(*N*,*N*-dimethylcarbamoyl) diselenide (**1**, 4.624 g, 60% overall yield from elemental selenium).

1 (X = Se): Pale yellow needles, mp 102.0–103.0 °C (dec.); MS (*m*/*z*) 304 (M^+; 5%, ^{80}Se), 72 (bp); IR (KBr) 2937, 1686, 1357, 1246, 1083, 877, 666, 447 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.06 (6H, br.s), 3.14 (6H, br.s); ^{13}C NMR ($CDCl_3$) δ 37.5 (q), 38.2 (q), 159.3 (s). Found: C, 24.39; H, 3.76; N, 9.30%. Calcd

for $C_6H_{12}N_2O_2Se_2$: C, 23.85; H, 4.00; N, 9.27%.

Preparation of Bis(*N*,*N*-dimethylcarbamoyl) Ditelluride (2). Dry *N*,*N*-dimethylformamide (DMF, 50 mL) was treated with sodium metal (1.840 g, 80 mmol) at 110 °C for 30 min in a three-necked flask under an Ar atmosphere, and the reaction mixture was treated with tellurium powder (2.552 g, 20 mmol) at 110 °C for 1 h under an Ar atmosphere. The reaction mixture was cooled to 0 °C and an excess amount of water was added to the reaction mixture. The reaction mixture was exposed to air by vigorous stirring under an aerobic condition for 1 h at 0 °C. After removal of unreacted elemental tellurium by suction filtration, the filtrate was extracted with benzene. The organic layer was washed with water, and dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the residual crude solid was recrystallized from hexane–dichloromethane to obtain bis(*N*,*N*-dimethylcarbamoyl) ditelluride (**2**, 2.334 g, 58% overall yield from elemental tellurium, yellow needles). Compound **2** was unstable and caused a gradual decomposition with the extrusion of elemental tellurium under aerobic exposure and light. Compound **2** should be kept dried in an Ar atmosphere in a dark position for the storage.

2 (X = Te):[3,6] Yellow needles, mp 121.0–122.0 °C (dec.); MS (*m*/*z*) 404 (M^+; 0.5%, ^{130}Te), IR (KBr) 1655, 1340, 1235, 1060, 860, 655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.08 (6H, s), 3.11 (6H, s); ^{13}C NMR ($CDCl_3$) δ 36.1 (q), 40.6 (q), 145.4 (s). Found: C, 17.58; H, 3.01; N, 6.86%. Calcd for $C_6H_{12}N_2O_2Te_2$: C, 18.04; H, 3.03; N, 7.01%.

General Method for Preparation of *Se*-Alkyl and *Se*-Alkenyl *N*,*N*-Dimethylselenocarbamates 3. A 20 mL DMF solution of diselenide **1** (1510 mg, 5.0 mmol) was treated with NaH (422 mg, 11.0 mmol) at 0 °C to room temperature for 2 h, and then with an alkyl halide or a terminal acetylenic compound (12.0 mmol) at 0 °C to room temperature for 1–1.5 h. The reaction was quenched with an excess amount of water, and the reaction mixture was extracted with benzene. The organic layer was washed with brine, and dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the crude mixture was subjected to column chromatographic separation on silica gel to afford the corresponding *Se*-alkyl *N*,*N*-dimethylselenocarbamates **3** in high yields.

3a (**R = hexyl**): Pale yellow oil; MS (*m*/*z*) 237 (M^+; bp, ^{80}Se), 72 (C_3H_6NO; 70%); IR (neat) 2927, 1666, 1363, 1260, 1094, 898, 558 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, J = 6.8 Hz), 1.25–1.42 (6H, m), 1.70 (2H, quintet, J = 7.5 Hz), 2.92 (2H, t, J = 7.5 Hz), 2.97 (3H, br.s), 3.01 (3H, br.s); ^{13}C NMR ($CDCl_3$) δ 13.9 (q), 22.4 (t), 27.0 (t), 29.6 (t), 30.8 (t), 31.2 (t), 36.4 (q), 37.1 (q), 165.2 (s). Found: C, 45.76; H, 8.10; N, 5.92%. Calcd for $C_9H_{19}NOSe$: C, 45.84; H, 8.38; N, 5.92%.

3b (**R = benzyl**): Pale green solid, mp 55.1–55.6 °C; MS (*m*/*z*) 243 (M^+; 12%, ^{80}Se), IR (KBr) 3025, 2940, 1656, 1493, 1363, 1257, 1091, 896, 756, 694, 610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.91 (3H, br.s), 3.02 (3H, br.s), 4.19 (2H, s), 7.17–7.20 (1H, m), 7.25–7.28 (2H, m), 7.33–7.35 (2H, m); ^{13}C NMR ($CDCl_3$) δ 30.4 (t), 30.6 (q), 37.1 (q), 126.7 (d), 128.4 (d), 128.9 (d), 139.5 (s), 165.0 (s). Found: C, 49.68; H, 5.41; N, 5.72%. Calcd for $C_{10}H_{13}NOSe$: C, 49.38; H, 5.80; N, 5.72%.

3c (**R = allyl**): Pale yellow oil; MS (*m*/*z*) 193 (M^+; bp, ^{80}Se), 120 (C_3H_5Se: 35%, ^{80}Se), 72 (C_3H_6NO; 99%); IR (neat) 2932, 1664, 1363, 1259, 1094, 896, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.96 (3H, br.s), 3.02 (3H, br.s), 3.59 (2H, d, J = 7.3 Hz), 5.00 (1H, dd, J = 10.6, 0.9 Hz), 5.20 (1H, dd, J = 16.8, 1.3 Hz), 5.95 (1H, ddt, J = 16.8, 10.6, 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 29.1 (t), 36.5 (q), 37.1 (q), 116.6 (t), 135.1 (d), 164.5 (s). Found: C, 37.24; H, 5.60; N, 7.17%. Calcd for $C_6H_{11}NOSe$: C, 37.51; H, 5.77; N, 7.29%.

3d (**R = methallyl**): Pale yellow oil; MS (*m*/*z*) 207 (M^+; 81%, ^{80}Se), 134 (C_4H_7Se; 10%, ^{80}Se), 72 (C_3H_6NO; bp); IR (neat) 3080, 2930, 1667, 1362, 1260, 1095, 897, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.83 (3H, s), 2.98 (3H, br.s), 3.03 (3H, br.s), 3.65 (2H, s), 4.80 (1H, br.s), 4.99 (1H, br.s); ^{13}C NMR ($CDCl_3$) δ 21.4 (q), 34.0 (t), 36.7 (q), 37.2 (q), 113.5 (t), 142.6 (s), 165.0 (s). Found: C, 41.02; H, 6.55; N, 6.53%. Calcd for $C_7H_{13}NOSe$: C, 40.78; H, 6.35; N, 6.79%.

3e (**R = cyclohexyl**): Pale green oil; MS (*m*/*z*) 235 (M^+; bp, ^{80}Se), 72 (C_3H_6NO; 84%); IR (neat) 2929, 1660, 1361, 1092 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30–1.35 (2H, m), 1.41–1.50 (2H, m), 1.56–1.64 (2H, m), 1.66–1.71 (2H, m), 2.04–2.09 (2H, m), 2.94 (3H, br.s), 3.00 (3H, br.s), 3.58 (1H, ddd, J = 9.6, 7.6, 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 25.6 (t), 26.8 (t), 34.3 (t), 36.2 (t), 37.1 (t), 43.6 (d), 165.5 (s). Found: C, 46.20; H, 7.34; N, 5.83%. Calcd for $C_9H_{17}NOSe$: C, 46.16; H, 7.32; N, 5.98%.

3f (**R = CH_2CO_2–*t*-C_4H_9**): Pale yellow oil; MS (*m*/*z*) 267 (M^+; 0.1%, ^{80}Se), 211 ($M^+ - t$-C_4H_9; 28%), 57 (*t*-C_4H_9; bp); IR (neat) 2981, 1732, 1668, 1259, 1096, 897, 676 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 (9H, s), 2.98 (3H, s), 3.02 (3H, s), 3.63 (2H, s); ^{13}C NMR ($CDCl_3$) δ 27.8 (q), 28.7 (t), 36.8 (q), 37.0 (q), 81.5 (s), 163.4 (s), 169.5 (s). Found: C, 40.93; H, 6.69; N, 5.20%. Calcd for $C_9H_{17}NO_3Se$: C, 40.61; H, 6.44; N, 5.26%.

3g (**R = CH_2CO_2–*l*-menthyl**): Pale yellow oil; MS (*m*/*z*) 349 (M^+; 3%, ^{80}Se), 83 (C_6H_{11}; bp); IR (neat) 2956, 2870, 1725, 1678, 1456, 1367, 1265, 1095, 986, 896, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.74–2.02 (18H, m), 2.97 (3H, s), 3.69 (2H, s), 4.68 (1H, dt, J = 10.9, 4.4 Hz); ^{13}C NMR ($CDCl_3$) δ 16.1 (q), 20.6 (q), 21.8 (q), 23.2 (t), 25.9 (d), 27.3 (t), 31.2 (d), 34.0 (t), 36.7 (q), 37.0 (q), 40.0 (dd), 46.8 (d), 163.0 (s), 169.0 (s). Found: C, 51.97; H, 7.99; N, 3.86%. Calcd for $C_{15}H_{27}NO_3Se$: C, 51.72; H, 7.81; N, 4.02%.

3h (**R = (*Z*)-CH=CH–CO_2CH_3**): Pale yellow solid, mp 76.5–76.7 °C; MS (*m*/*z*) 237 (M^+; bp, ^{80}Se), 72 (C_3H_6NO; 70%); IR (neat) 2952, 1698, 1663, 1585, 1435, 1209, 1091 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.06 (3H, br.s), 3.09 (3H, br.s), 3.78 (3H, s), 6.45 (1H, d, J = 9.7 Hz), 8.37 (1H, d, J = 9.7 Hz); ^{13}C NMR ($CDCl_3$) δ 36.6 (q), 37.0 (q), 51.7 (q), 117.1 (d), 144.4 (d), 163.3 (s), 167.8 (s). Found: C, 35.75; H, 4.70; N, 5.93%. Calcd for $C_7H_{11}NO_3Se$: C, 35.61; H, 4.70; N, 5.93%.

General Method for Preparation of *Te*-Alkyl and *Te*-Alkenyl *N*,*N*-Dimethyltellurocarbamates 4. A 15 mL 1:2 ethanol–DMF solution of ditelluride **2** (602 mg, 1.50 mmol) was treated with $NaBH_4$ (127 mg, 3.30 mmol) at −50 °C for 0.5 h, and then with an alkyl halide or a terminal acetylenic compound (3.60 mmol); the reaction mixture was then gradually warmed up to 0 °C for 1 h. The reaction was quenched with water, and the reaction mixture was extracted with benzene. The organic layer was washed with brine, and dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the crude mixture was subjected to column chromatographic separation on silica gel to afford the corresponding *Te*-alkyl or *Te*-alkenyl *N*,*N*-dimethyltellurocarbamates **4** in high to moderate yields.

4a (**R = hexyl**): Pale yellow oil; MS (*m*/*z*) 287 (M^+; bp, ^{130}Te), 215 ($C_6H_{13}Te$; 28%, ^{130}Te); IR (neat) 2900, 1620, 1330, 1235, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, J = 7.0 Hz), 1.25–1.42 (6H, m), 1.80–1.88 (2H, m), 2.88 (3H, br.s), 2.93 (2H, t, J = 7.5 Hz), 3.05 (3H, br.s); ^{13}C NMR ($CDCl_3$) δ 12.9 (t), 13.9 (q), 22.4 (t), 31.1 (t), 31.8 (t), 32.0 (t), 35.6 (q), 38.3 (q), 155.8 (s). Found: C, 37.63; H, 6.45; N, 4.61%. Calcd for

$C_9H_{19}NOTe$: C, 37.95; H, 6.72; N, 4.92%.

4b (**R = benzyl**): Yellow oil; MS (*m*/*z*) 293 (M^+; 52%, ^{130}Te), 91 (C_7H_7; bp); IR (neat) 3020, 2915, 1640, 1350, 1250, 1060, 880, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.81 (3H, br.s), 3.07 (3H, br.s), 4.03 (2H, s), 7.11–7.15 (1H, m), 7.21–7.25 (2H, m), 7.31–7.33 (2H, m); ^{13}C NMR ($CDCl_3$) δ 15.7 (t), 35.9 (q), 38.2 (q), 126.1 (d), 128.4 (d), 141.6 (s), 157.0 (s). Found: C, 41.04; H, 4.37; N, 4.76%. Calcd for $C_{10}H_{13}NOTe$: C, 41.30; H, 4.51; N, 4.82%.

4c (**R = allyl**): Yellow oil; MS (*m*/*z*) 243 (M^+; 42%, ^{130}Te), 72 (C_3H_6NO; bp); IR (neat) 2990, 1630, 1345, 1240, 1060, 875 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.85 (3H, br.s), 3.03 (3H, br.s), 3.65 (2H, d, $J = 8.0$ Hz), 4.86 (1H, br.d, $J = 10.0$ Hz), 5.11 (1H, br.d, $J = 17.0$ Hz), 6.05 (1H, ddt, $J = 17.0$, 10.0, 8.0 Hz). Found: C, 37.12; H, 5.58; N, 7.14%. Calcd for $C_6H_{11}NOTe$: C, 37.51; H, 5.77; N, 7.29%.

4d (**R = methallyl**): Yellow oil; MS (*m*/*z*) 257 (M^+; 99%, ^{130}Te), 255 (M^+; bp, ^{128}Te), 185 (C_4H_7Te; 27%, ^{130}Te); IR (neat) 2929, 1651, 1356, 1245, 1084, 885, 666 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.78 (3H, s), 2.87 (3H, br.s), 3.05 (3H, br.s), 3.72 (2H, s), 4.72 (1H, br.s), 4.98 (1H, br.s). Found: C, 40.35; H, 6.23; N, 6.65%. Calcd for $C_7H_{13}NOTe$: C, 40.78; H, 6.36; N, 6.79%.

4e (**R = cyclohexyl**): Yellow oil; MS (*m*/*z*) 285 (M^+; 26%, ^{130}Te), 72 (C_3H_6NO; bp); IR (neat) 2890, 2825, 1620, 1430, 1335, 1240, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–1.80 (6H, m), 1.80–2.40 (4H, m), 2.87 (3H, br.s), 3.40 (3H, br.s), 3.50–3.90 (1H, m). Found: C, 45.98; H, 7.17; N, 5.79%. Calcd for $C_9H_{17}NOTe$: C, 46.16; H, 7.32; N, 5.98%.

4h (**R = (*Z*)-CH=CHCO$_2$CH$_3$**): Colorless needles, mp 104.0–105.0 °C; MS (*m*/*z*) 287 (M^+; bp, ^{130}Te), 215 ($C_4H_5O_2Te$; 94%, ^{130}Te); IR (KBr) 1690, 1630, 1560, 1320, 1205 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.96 (3H, br.s), 3.09 (3H, br.s), 3.81 (3H, br.s), 6.97 (1H, br.d, $J = 9.5$ Hz), 8.94 (1H, br.d, $J = 9.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 35.8 (q), 37.4 (q), 52.2 (q), 123.2 (d), 140.6 (d), 159.8 (s), 169.1 (s). Found: C, 29.30; H, 3.71; N, 4.91%. Calcd for $C_7H_{11}NO_3Te$: C, 29.53; H, 3.89; N, 4.92%.

4i (**R = (*Z*)-CH=CH–(*p*-CF$_3$C$_6$H$_4$)**): Colorless plates, mp 109.0–110.0 °C; MS (*m*/*z*) 373 (M^+; 27%, ^{130}Te), 301 ($C_9H_6F_3Te$; 21%, ^{130}Te), 171 ($C_9H_6F_3$; 38%), 151 ($C_9H_5F_2$, bp); IR (KBr) 1650, 1329, 1112, 1067, 853 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.86 (3H, br.s), 3.08 (3H, br.s), 7.35 (2H, d, $J = 8.1$ Hz), 7.42–7.50 (2H, m), 7.60 (2H, d, $J = 8.1$ Hz); ^{13}C NMR ($CDCl_3$) δ 36.1 (q), 37.1 (q), 115.3 (d), 125.2 (dq, $J_{C-F} = 4$ Hz), 127.5 (d), 129.0 (q, $J_{C-F} = 32$ Hz), 135.7 (d), 142.5 (s), 155.3 (s). Found: C, 38.95; H, 3.18; N, 3.71%. Calcd for $C_{12}H_{12}F_3NOTe$: C, 38.87; H, 3.26; N, 3.78%.

4j (**R = (*Z*)-CH=CH–(2,6-Cl$_2$C$_6$H$_3$)**): Yellow plates, mp 91.5–92.0 °C (dec.); MS (*m*/*z*) 373 (M^+; 5%, ^{130}Te, ^{35}Cl), 171 ($C_8H_5Cl_2$; bp, ^{35}Cl); IR (KBr) 1655, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.79 (3H, br.s), 3.05 (3H, br.s), 7.16 (1H, t, $J = 8.0$ Hz), 7.25 (1H, d, $J = 10.5$ Hz), 7.31 (2H, d, $J = 8.0$ Hz), 7.58 (1H, d, $J = 10.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 35.9 (q), 37.5 (q), 120.0 (d), 128.0 (br.d), 129.1 (br.d), 133.1 (d), 134.0 (s), 137.5 (s), 155.8 (s). Found: C, 35.71; H, 2.96; N, 3.77%. Calcd for $C_{11}H_{11}Cl_2NOTe$: C, 35.54; H, 2.98; N, 3.77%.

4k (**R = (*Z*)-C$_6$H$_5$C=CHCOCH$_3$**): Yellow solid, mp 67.0–67.5 °C; MS (*m*/*z*) 347 (M^+; 3%, ^{130}Te), 275 ($M^+ - Me_2NCO$; 55%, ^{130}Te), 43 (bp); IR (neat) 2924, 1638, 1608, 1522, 1483, 1360, 1310, 1222, 1182, 1090, 981, 823, 762, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.33 (3H, s), 2.57 (3H, s), 2.77 (3H, s), 7.36–7.65 (6H, m). Found: C, 44.97; H, 4.38; N, 3.77%. Calcd for $C_{13}H_{15}NOTe$: C, 45.28; H, 4.38; N, 4.06%.

Synthesis of Symmetrical Diselenides 7 by Treating *N,N*-Dimethylselenocarbamates 3 with Tin(IV) Chloride. A 15 mL CH_2Cl_2, $CHCl_3$, or $C_2H_4Cl_2$ solution of *Se*-alkyl or *Se*-alkenyl *N,N*-dimethylselenocarbamate **3** (0.25 mmol) was treated with $SnCl_4$ (35 mg, 0.5 mmol) at refluxing temperature for 0.5 h. The reaction was then quenched with an excess amount of aqueous sodium hydrogen carbonate solution, and the mixture was extracted with chloroform. The organic layer was washed with water, and dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the crude mixture was subjected to column chromatographic separation on silica gel to afford the corresponding symmetrical diselenide **7** in high-to-moderate yields along with the contamination of monoselenide **5b** in the case of the reaction starting from **3b**.

7g (**R = CH$_2$CO$_2$–*l*-menthyl**): Pale yellow needles, mp 42.1–43.9 °C; MS (*m*/*z*) 552 (M^+; 1%, ^{80}Se), 276 ($M^+/2$; 2%, ^{80}Se), 69 (C_5H_9; bp, ^{80}Se); IR (KBr) 2948, 1709, 1386, 1288, 1102, 990, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76–2.04 (36H, m), 3.73 (4H, br.s), 4.70 (2H, dt, $J = 10.9$, 4.4 Hz); ^{13}C NMR ($CDCl_3$) δ 16.2 (q), 20.8 (q), 21.9 (q), 23.2 (t), 26.0 (d), 29.9 (t), 31.3 (d), 34.1 (t), 40.6 (dd), 46.9 (d), 75.4 (br.s), 170.1 (s). Found: C, 52.20; H, 7.71%. Calcd for $C_{24}H_{42}O_4Se_2$: C, 52.17; H, 7.66%.

7h (**R = (*Z*)-CH=CHCO$_2$CH$_3$**): Pale yellow needles, mp 71.0–72.0 °C (dec.); MS (*m*/*z*) 330 (M^+; 39%, ^{80}Se), 165 ($M^+/2$; 64%, ^{80}Se), 163 ($M^+/2$; bp, ^{78}Se); IR (KBr) 1680, 1570, 1436, 1343, 1213, 1145, 1006, 922 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.79 (6H, s), 6.28 (2H, d, $J = 9.4$ Hz), 8.06 (2H, d, $J = 9.4$ Hz); ^{13}C NMR ($CDCl_3$) δ 51.7 (q), 118.7 (d), 148.5 (d), 167.2 (s). Found: C, 29.71; H, 3.23%. Calcd for $C_8H_{10}O_4Se_2$: C, 29.29; H, 3.07%.

Synthesis of Symmetrical Ditellurides 11 by Treating *N,N*-Dimethyltellurocarbamates 4 with Tin(IV) Chloride. A 15 mL CH_2Cl_2 or $CHCl_3$ solution of *Te*-alkyl or *Te*-alkenyl *N,N*-dimethyltellurocarbamate **4** (0.25 mmol) was treated with $SnCl_4$ (35 mg, 0.5 mmol) at refluxing temperature for 0.5 h. The reaction was then quenched with an excess amount of aqueous sodium hydrogen carbonate solution, and the mixture was extracted with $CHCl_3$. The organic layer was washed with water and then with brine, and dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the crude mixture was subjected to column chromatographic separation on silica gel to afford the corresponding symmetrical ditelluride **8** in high-to-moderate yields along with the formation of a trace amount of monotelluride **6**.

6h (**R = (*Z*)-CH=CHCO$_2$CH$_3$**): Pale yellow plates, mp 138.5–139.5 °C; MS (*m*/*z*) 300 (M^+; 50%, ^{130}Te), 215 ($C_4H_5O_2$; bp, ^{130}Te); IR (KBr) 1680, 1540, 1400, 1315, 1200, 990, 800, 630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80 (6H, s), 5.98 (2H, d, $J = 10.0$ Hz), 8.53 (2H, d, $J = 10.0$ Hz). Found: C, 32.11; H, 3.19%. Calcd for $C_8H_{10}O_4Te$: C, 32.27; H, 3.39%.

8i (**R = (*Z*)-CH=CHCO$_2$CH$_3$**): Yellow plates; MS (*m*/*z*) 430 (M^+; 10%, ^{130}Te), 215 ($M^+/2$; bp, ^{130}Te); IR (KBr) 1670, 1561, 1432, 1334, 1203, 1003, 803 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.81 (6H, s), 6.65 (2H, d, $J = 10.0$ Hz), 8.99 (2H, d, $J = 10.0$ Hz). Found: C, 23.04; H, 2.53%. Calcd for $C_8H_{10}O_4Te_2$: C, 22.59; H, 2.37%.

8j (**R = (*Z*)-CH=CH–(2,6-Cl$_2$C$_6$H$_3$)**): Red plates, mp 111.5–112.5 °C (dec.); MS (*m*/*z*) 606 (M^+; 8%, ^{130}Te, 35Cl), 303 ($M^+/2$; 4%, ^{130}Te, ^{35}Cl), 173 ($C_8H_5Cl_2$; bp); IR (KBr) 2925, 1556, 1425, 1297, 1193, 1085, 790, 776, 712 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.87 (2H, d, $J = 10.5$ Hz), 7.20 (2H, t, $J = 8.0$ Hz), 7.33 (4H, d, $J = 8.0$ Hz), 7.88 (2H, d, $J = 10.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 109.4 (d), 128.2 (br.d), 129.4 (br.d), 134.2 (br.s), 135.5 (d), 136.2 (br.s). Found: C, 32.01; H, 1.74%. Calcd for $C_{16}H_{10}Cl_4Te_2$: C, 32.07; H, 1.68%.

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References

1 a) L. Testaferri, M. Tiecco, T. Marcello, M. Tingoli, and D. Chianelli, *Tetrahedron*, **42**, 4577 (1986). b) M. J. Dabdoub and J. V. Comasseto, *J. Organomet. Chem.*, **344**, 167 (1988). c) J. V. Comasseto, W. L. Lo, N. Petragnani, and H. A. Stefani, *Synthesis*, **1997**, 373, and references cited therein. d) K. Shimada, M. Asahida, K. Takahashi, Y. Sato, Y. Takikawa, and C. Kabuto, *Chem. Lett.*, **1998**, 513. e) X. Huang and J.-H. Wang, *Synth. Commun.*, **30**, 301 (2000).

2 J.-C. Guillemin, A. Bouayad, and D. Vijykumar, *Chem. Commun.*, **2000**, 1163.

3 K. Shimada, S. Oikawa, and Y. Takikawa, *Chem. Lett.*, **1992**, 1389.

4 K. Kondo, N. Sonoda, K. Yoshida, M. Koishi, and S. Tsutsumi, *Chem. Lett.*, **1972**, 401.

5 S. Fujiwara, A. Ogawa, N. Kambe, I. Ryu, and N. Sonoda, *Tetrahedron Lett.*, **29**, 6121 (1988).

6 H. Suzuki, H. Manabe, and M. Inouye, *Chem. Lett.*, **1985**, 1671.

7 S. Kato, T. Kawachi, K. Ibi, S. Nakaiida, K. Kawai, T. Kanda, T. Murai, and H. Ishihara, *Heteroat. Chem.*, **6**, 215 (1995).

8 P. Dowd and P. Kennedy, *Synth. Commun.*, **11**, 935 (1981).

9 K. Kondo, M. Takarada, S. Murai, and N. Sonoda, *Synthesis*, **1979**, 598.

10 W. E. Truce and J. A. Simms, *J. Am. Chem. Soc.*, **78**, 2756 (1956).

11 T. Inoue, T. Mogami, N. Kambe, A. Ogawa, and N. Sonoda, *Heteroat. Chem.*, **4**, 471 (1993).

12 a) C. Engler, *Ber. Dtsch. Chem. Ges.*, **11**, 930 (1878). b) E. Baumann and E. Fromm, *Ber. Dtsch. Chem. Ges.*, **28**, 907 (1895). c) W. H. H. Günther, *J. Org. Chem.*, **32**, 3929 (1967). d) V. I. Cohen, *J. Org. Chem.*, **42**, 2510 (1977). e) J. W. Lewicki, W. H. H. Günther, and J. Y. C. Chu, *J. Org. Chem.*, **43**, 2672 (1978). f) J. A. Gadysz, J. L. Hornby, and J. E. Galbe, *J. Org. Chem.*, **43**, 1204 (1978). g) D. Klayman and T. S. Griffin, *J. Am. Chem. Soc.*, **95**, 197 (1973). h) L. Syper and J. Mlochowski, *Synthesis*, **1984**, 439. i) A. Krief, A. F. DeMahieu, W. Dumont, and M. Trabelsi, *Synthesis*, **1988**, 131. j) J. X. Wang, W. Cui, and Y. Hu, *J. Chem. Soc., Perkin Trans. 1*, **1994**, 2341. k) P. Salama and C. Bernard, *Tetrahedron Lett.*, **36**, 5711 (1995).

13 a) W. S. Haller and K. J. Irgolic, *J. Organomet. Chem.*, **38**, 97 (1972). b) H. Suzuki, K. Miyoshi, and A. Osuka, *Nippon Kagaku Kaishi*, **1981**, 472. c) G. Merker, H. Berge, and P. Jeroschewski, *J. Prakt. Chem.*, **326**, 467 (1984). d) D. H. R. Barton, L. Bohé, and X. Lusinchi, *Tetrahedron Lett.*, **28**, 6609 (1987). e) D. H. R. Barton, L. Bohé, and X. Lusinchi, *Tetrahedron Lett.*, **29**, 2571 (1988). f) D. H. R. Barton, L. Bohé, and X. Lusinchi, *Tetrahedron Lett.*, **31**, 93 (1990). g) M. J. Dabdoub and J. V. Comasseto, *Organometallics*, **7**, 84 (1988). h) L. Engman, *Organometallics*, **8**, 1997 (1989).