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Synthesis of Isochalcogenazole Rings by Treating β-(*N*,*N*-Dimethylcarbamoylchalcogenenyl)alkenyl Ketones with Hydroxylamine-*O*-sulfonic Acid

Kazuaki Shimada,*[1] Akiko Moro-oka,[1] Akiko Maruyama,[1] Hiroyuki Fujisawa,[1] Toshio Saito,[1] Ryo Kawamura,[1] Hisashi Kogawa,[1] Maiko Sakuraba,[1] Yukichi Takata,[1] Shigenobu Aoyagi,[1] Yuji Takikawa,[1] and Chizuko Kabuto[2]

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

[2]Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University, Aramaki, Aoba-ku, Sendai 980-8578

Received August 3, 2006; E-mail: shimada@iwate-u.ac.jp

β-(*N*,*N*-Dimethylcarbamoylselenenyl)- and β-(*N*,*N*-dimethylcarbamoyltellurenyl)alkenyl ketones were converted into isoselenazoles and isotellurazole *Te*-oxides, respectively, simply by treating with hydroxylamine-*O*-sulfonic acid, and deoxygenation of the latter products was successfully carried out by treating with PPh_3. Alternative treatment of ynone oxime tosylates with hydrochalcogenide ions or *N*,*N*-dimethylchalcogenocarbamate ions also gave the same isochalcogenazole rings. These reactions were assumed to proceed through intramolecular nucleophilic substitution on the nitrogen atom of oxime sulfonates by the attack of in situ generated chalcogen nucleophiles.

Recently, hetero Diels–Alder reactions have become one of the most effective methods for the syntheses of various heterocycles, and especially, the thermal reactions of cyclic heterodienes possessing removable heteroatom-bridges, such as O, S, SO_2, and N=N atoms, have been widely used as preparable and treatable heterodynes with a cisoid structure.[1–5] Especially, chalcogen-containing five-membered heterocycles have been regarded as novel bridged heterodienes, and the synthetic use of these compounds have been extensively studied in the light of their potentiality of novel 4π components for hetero Diels–Alder reactions. However, the synthetic pathways to construct complicated compounds have been limited because of the thermal stability of the oxygen-, sulfur-, or nitrogen-bridged compounds, and less reactive isothiazole *S*,*S*-dioxides as potential SO_2-bridged heterodienes for hetero Diels–Alder reactions have also been reported.[6–9] It has been assumed that selenium or tellurium analogues of such substrates would be more reactive because of the weak *C*-chalcogen or *N*-chalcogen bonds and the enhanced ring strain of these five-membered heterocylces along with a decrease in aromaticity.[10,11] Moreover, subsequent heteroatom extrusion from these compounds should also be possible under much milder reaction conditions than those of the oxygen or sulfur derivatives.[12,13]

In the course of our studies on the syntheses and chemical conversion of heavy chalcogen-containing heterocyclic compounds, we have preliminarily reported the thermal reaction of 1,2,4-selenadiazoles, a 1,2,5-selenadiazole, and a 1,3-selenazoles in the presence of acetylenic dienophiles to afford the corresponding nitrogen-containing six-membered heterocycles in high yields via hetero Diels–Alder reactions and the subsequent selenium extrusion.[14] Extension of the synthetic methods to heavy isochalcogenazoles became a challenging target. However, to date, only limited methods for the preparation of isoselenazoles and isotellurazoles have been reported[15–27] in spite of their potential as acceptors for nucleophiles,[17,28] electrophiles,[29] and reactive heterodienes, and thus, new and efficient synthetic methods for these compounds are required. Actually, we have already reported a convenient preparation of *Se*-alkenyl selenocarbamates **4** and *Te*-alkenyl tellurocarbamates **5** involving a stepwise reduction–alkylation reaction starting from bis(*N*,*N*-dimethylcarbamoyl) dichalcogenides **1** and **2**,[30–32] and the Lewis acid-induced removal of dimethylcarbamoyl group from **4** (X = Se) and **5** (X = Te) forming dialkenyl diselenides and ditellurides, respectively. These results suggested that in situ generated *Z*-alkenechalcogenol derivatives **A** bearing a leaving group on the oxime nitrogen atom would undergo facile ring closure to give isochalcogenazoles **6** and **7** via intramolecular nucleophilic substitution on the nitrogen atom. Here, we describe a new and convenient synthetic route for isoselenazole and isotellurazole ring systems starting from chalcogenocarbamates **4** (X = Se) or **5** (X = Te), hydroxylamine-*O*-sulfonic acid, and ynones **3** as shown in Scheme 1. Alternative attempts to prepare **6** and **7** from ynone oxime tosylates **12** and chalcogen nucleophiles are also mentioned in this paper.

Results and Discussion

Preparation of *Se*-Alkenyl Selenocarbamates 4 and *Te*-Alkenyl Tellurocarbamates 5. Initially, bis(*N*,*N*-dimethylcarbamoyl) diselenide (**1**), bis(*N*,*N*-diethylcarbamoyl) diselenide (**1′**), and bis(*N*,*N*-dimethylcarbamoyl) ditelluride (**2**) were prepared according to Sonoda's method[30,31] or by ours.[32] Acetylenic compounds were efficiently converted into the corresponding ynones **3a–3h** through a two-step procedure: (1)

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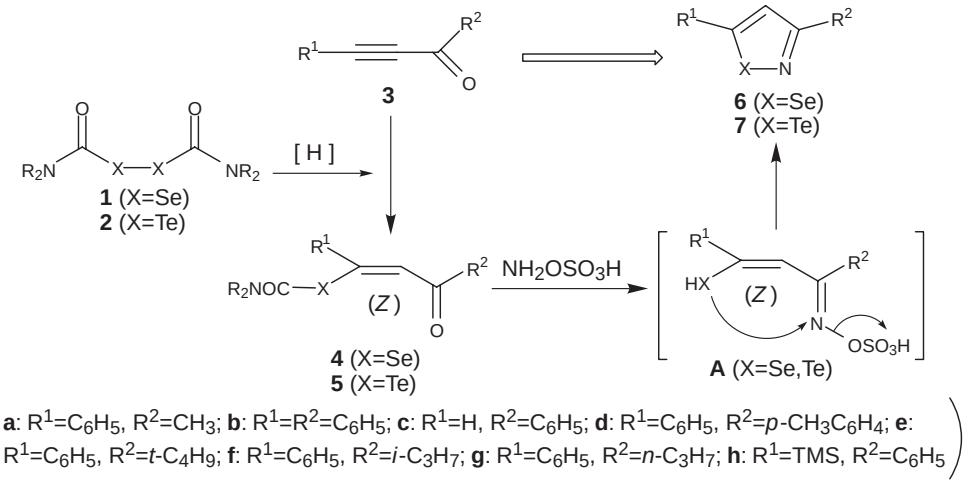
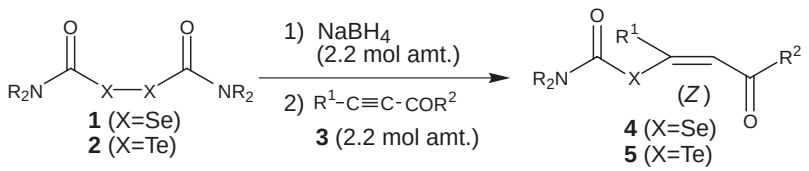


Scheme 1. General strategy for preparation of isochalcogenazoles **6** and **7**.

Table 1. Preparation of *Se*-Alkenyl Selenocarbamates **4** and *Te*-Alkenyl Tellurocarbamates **5**[a)]

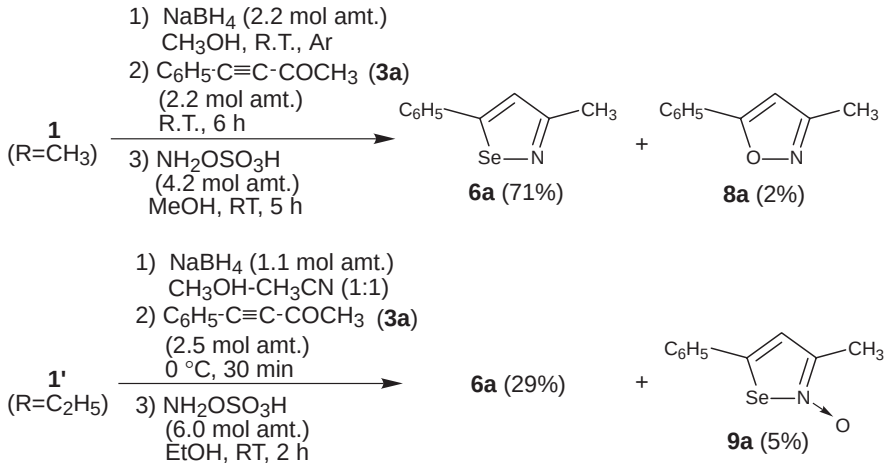


Substrate			Ynone **3**		Temp	Time	Yield of **4** or **5**[c)]/%[b)]
1 or **2**	X	R	R^1	R^2	/°C	/h	
1	Se	CH_3	C_6H_5	CH_3	−50	0.25	Complex mixture[c)]
1	Se	CH_3	C_6H_5	C_6H_5	−50	0.25	Complex mixture[d)]
1	Se	CH_3	H	C_6H_5	−50–R.T.	2	20 (**4c**)[e),f)]
1′	Se	C_2H_5	C_6H_5	CH_3	−50	0.25	61 (**4a′**)[e),g)]
2	Te	CH_3	C_6H_5	CH_3	−50–R.T.	7	94 (**5a**)[e)]
2	Te	CH_3	C_6H_5	C_6H_5	−50–R.T.	7	74 (**5b**)[e)]
2	Te	CH_3	C_6H_5	p-$CH_3C_6H_4$	0	1	61 (**5d**)[e)]
2	Te	CH_3	C_6H_5	t-C_4H_9	−50–R.T.	7	37 (**5e**)[e),f)]
2	Te	CH_3	C_6H_5	i-C_3H_7	−50–R.T.	7	47 (**5f**)[e)]
2	Te	CH_3	CH_3	C_6H_5	−50–R.T.	4	Complex mixture
2	Te	CH_3	TMS	C_6H_5	−50–R.T.	4	Complex mixture

a) All reactions were carried out by treating a C_2H_5OH solution of **1** (X = Se) or a DMF–C_2H_5OH solution of **2** (X = Te) with $NaBH_4$ (2.2 mol amt.) followed by ynone **3** (2.2 mol amt.) to the reaction mixture at the recorded temperature under an Ar atmosphere. b) Isolated yields based on the starting ynones **3**. c) Small amount of plausible **4a** ($R^1 = C_6H_5$, $R^2 = CH_3$) was detected in the mixture by ^{1}H NMR measurement. d) Small amount of plausible **4b** ($R^1 = R^2 = C_6H_5$) was detected in the mixture by ^{1}H NMR measurement. e) Single geometrical isomers were obtained. f) **4** or **5** was isolated after chromatographic separation of the complex mixture afforded by the reaction. g) Crude yield after rough chromatographic purification.

C_2H_5MgBr, $(CH_3)_3SiCl$, (2) acetyl chloride, pivaloyl chloride, isobutyryl chloride, butanoyl chloride, benzoyl chloride, or *p*-toluoyl chloride, $AlCl_3$.[33] Subsequent treatment of **1** or **1′** with NaH or $NaBH_4$[32,34] (2.2 mol amt.) and ynones **3** only afforded complex mixtures in all cases. However, in the ^{1}H NMR spectra, the presence of *Se*-alkenyl selenocarbamates **4** (R = CH_3) or **4′** (R = C_2H_5), respectively,[32,35] was observed in the crude mixture. Compounds **4** (R = CH_3) were not stable and underwent gradual decomposition during the usual workup, chromatographic separation, and storage. Compound **4a′** (R = C_2H_5) was relatively stable and was isolated by chromatography; however, it gradually decomposed. Therefore, subsequent heterocyclic ring forming reactions were carried out by using a one-pot method without isolation and purification of **4** and **4′**. On the other hand, *Te*-alkenyl tellurocarbamates **5** were isolated in high to moderate yields as single *Z*-isomers from the reaction of **2**,[36,37] $NaBH_4$, and **3**. The results are summarized in Table 1.

Synthesis of Isoselenazoles 6 and Isotellurazoles 7 by Treating *Se*-Alkenyl Selenocarbamates 4 or *Te*-Alkenyl Tellurocarbamates 5 with Hydroxylamine-*O*-sulfonic Acid. Treatment of a CH_3OH solution of crude selenocarbamates **4** with hydroxylamine-*O*-sulfonic acid (4.4 mol amt.) at reflux under an Ar atmosphere only gave a complex mixture maybe due to the facile decomposition of **4** during the reaction. However, a one-pot treatment of a CH_3OH solution of **1** (R = CH_3)



Scheme 2. One-pot synthesis of isoselenazole **6a**, isoxazole **8a**, and isoselenazole *N*-oxide **9a** starting from **1** or **1′**.

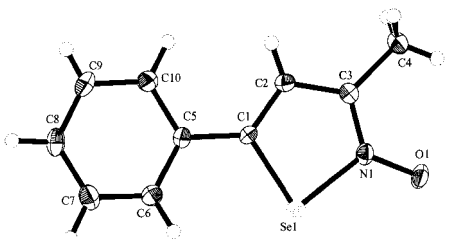


Fig. 1. ORTEP drawing of isoselenazole *N*-oxide **9a**.

with $NaBH_4$, ynone **3a**, and hydroxylamine-*O*-sulfonic acid afforded isoselenazole **6a** (71%)[21,22] and isoxazole **8a** (2%)[38–41] as well as complex mixture, and a similar treatment of a CH_3CN solution of **1′** (R = C_2H_5) afforded a mixture of isoselenazole **6a** (29%) and its *N*-oxide **9a** (5%), as shown in Scheme 2. These results indicated that the crude mixture obtained from the reaction of **3** with **1**/$NaBH_4$ contained **4** as the main components. The structure of **9a** was determined by X-ray crystallographic analysis, and an ORTEP drawing of **9a** is shown in Fig. 1. Compound **9a** was converted into **6a** in 88% yield by treating with PPh_3 (1.1 mol amt.) in $CHCl_3$ at refluxing temperature for 50 h. Compound **6a** was reasonably stable in air, and treatment of **6a** with *m*-chloroperbenzoic acid (*m*CPBA) or an aqueous hydrogen peroxide solution only caused decomposition affording a complex mixture containing isoxazole **8a** as a minor component. The actual pathway for the formation of **9a** is still unclear at this time, but this result clearly showed that the oxidation of **6a** is not involved.

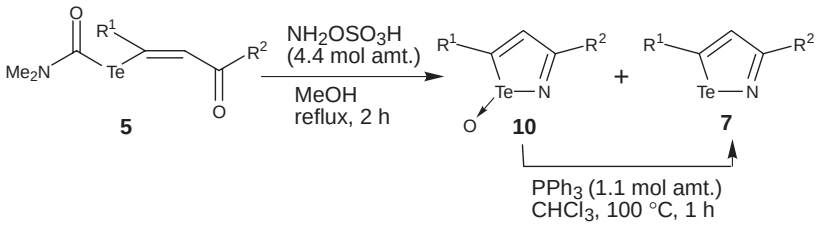
A similar treatment of a CH_3OH solution of *Te*-alkenyl tellurocarbamates **5** with hydroxylamine-*O*-sulfonic acid afforded air-stable isotellurazole *Te*-oxides **10** as well as a trace amount of isotellurazoles **7**.[21,22] In the mass spectra, the parent ion peaks of **10** were observed along with the isotope distribution pattern for one tellurium atom. The ^{1}H NMR spectra of **10** also showed a new signal assigned to the vinyl proton of the C-4 position of isotellurazole ring, and the ^{125}Te NMR signal of **10b** ($\delta = 3831$) was shifted significantly downfield compared to that of **7b** ($\delta = 1676$). The similarity in the patterns of ^{1}H NMR and ^{13}C NMR spectra of **10b** to those of **7b**, except for the downfield shift of the ^{125}Te NMR signal, strongly indicated the existence of telluroxide moiety, not *N*-oxide, in **10**. However, attempts to prepare a single crystal of **10** for X-ray crystallographic analysis were unsuccessful. Deoxygenation of **10** was also performed by using PPh_3 (1.1 mol amt.) in $CHCl_3$ in a sealed tube to afford **7** in almost quantitative yields. The results of the synthesis and the subsequent deoxygenation of isotellurazole *Te*-oxides **10** are given in Table 2.

It was presumed that isochalcogenazole rings would be formed through a pathway involving acid-induced removal of a *N*,*N*-dialkylcarbamoyl cation from **4** or **5** and subsequent nucleophilic substitution of the resulting alkeneselenols or alkenetellurols **A** (X = Se and Te)[32] on the nitrogen atoms of the in situ formed oxime sulfonates.[42–47] However, no methanolysis products, *O*-methyl *N*,*N*-dimethylselenocarbamate, were found in the crude reaction mixture, and thus, this pathway was negligible. In addition, reaction of crude selenocarbamate **4a′** (R = C_2H_5, $R^1 = C_6H_5$, $R^2 = CH_3$) with hydroxylamine-*O*-sulfonic acid in the presence of allyltrimethylsilane (10 mol amt.) in methanol to trap the *N*,*N*-dialkylcarbamoyl cation only afforded a mixture containing isoxazole **8a** (35%), isoselenazole **6a** (13%), and an intractable mixture, and *N*,*N*-diethylbutenamide, the allylation product of *N*,*N*-diethylcarbamoyl cation, was not found in the crude mixture.

Isoselenazoles **6** and isotellurazoles **7** were reasonably stable toward exposure to air, and further treatment of isotellurazole **7a** with an excess amount of hydroxylamine-*O*-sulfonic acid under a similar condition (methanol, reflux, 2 h) only resulted in the complete recovery of **7a**. On the other hand, *m*CPBA oxidation of **7** in $CHCl_3$ at 0 °C only resulted in forming a complex mixture containing isoxazoles **8**. These results suggest that the formation pathway of **9** and **10** does not involve the oxidation of **6** and **7**, respectively. The formation pathway of isoselenazole *N*-oxide **9** and isotellurazole *Te*-oxides **10** through the reaction of **4** and **5** with hydroxylamine-*O*-sulfonic acid is still unclear.

Attempts at an Alternative Synthesis of Isoselenazoles 6 and Isotellurazoles 7. Ynones **3** have generally been recognized as Michael accepters, and therefore, nucleophilic 1,4-attack of chalcogenide ions to ynone oxime derivatives bearing a leaving group on the oxime nitrogen should result in further cyclization to form isochalcogenazoles **6** and **7** via intramolecular nucleophilic substitution on the oxime nitrogen.

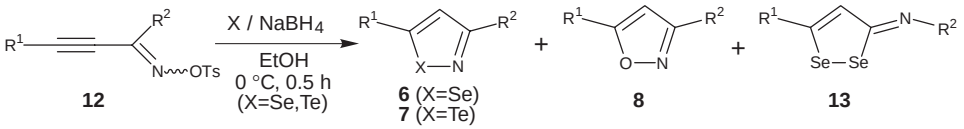
Table 2. Syntheses of Isotellurazole *Te*-Oxides **10** and Isotellurazoles **7**[a)]



Substrate			Yield/%		Yield/% of deoxygenation[b)]	
R^1	R^2	**5**	**10**	**7**	**10** to **7**	$Ph_3P{=}O$
C_6H_5	CH_3	**5a**	79 (**10a**)	4 (**7a**)	91 (**7a**)	quant.
C_6H_5	C_6H_5	**5b**	86 (**10b**)	trace (**7b**)	94 (**7b**)	quant.
C_6H_5	p-$CH_3C_6H_5$	**5d**	74 (**10d**)	0	89 (**7d**)	quant.
C_6H_5	t-C_4H_9	**5e**	67 (**10e**)	0	—[c)]	

a) All reactions were carried out under an Ar atmosphere. b) Carried out in a sealed tube. c) Not attempted.

Table 3. Reaction of Ynone Oxime Tosylates **12** with NaSeH or NaTeH



Substrate				Chalcogen X	Yield/%[a)]		
R^1	R^2	**12**	Major:Minor[b)]		**6**	**8**	**13**
C_6H_5	CH_3	**12a**	10:1	Se	41 (**6a**)	38 (**8a**)	0
C_6H_5	C_6H_5	**12b**	10:1	Se	0	59 (**8b**)	38 (**13b**)
C_6H_5	n-C_3H_7	**12g**	5:1	Se	43 (**6g**)	40 (**8g**)	0
C_6H_5	CH_3	**12a**	10:1	Te	0[c)]	Trace (**8a**)	—
C_6H_5	C_6H_5	**12b**	10:1	Te	0[c)]	Trace (**8b**)	—

a) Isolated yields. b) Determined by integration of the signals of the ^{1}H NMR spectrum of oxime tosylates **12**. c) Complex mixture was obtained.

Ynone oximes **11** were easily prepared by the reaction of ynones **3**, hydroxylamine hydrochloride, and sodium acetate, and oximes **11** were easily converted into the mixtures of *syn–anti* geometrical isomers of oxime tosylates **12** by treating them with *p*-toluenesulfonyl chloride and triethylamine. It was noteworthy that oxazoles **8** were formed as byproducts of the tosylation in most cases through base-induced ring closure of **11**. Subsequently, when an oxime tosylate **12** was treated with NaSeH, generated in situ by treating elemental selenium with $NaBH_4$ in ethanol, isoselenazole **6** and isoxazole **8** were mainly obtained. All the results of reactions of oxime tosylates **12** with NaSeH are shown in Table 3. Interestingly, 1,2-diselenole **13b**, instead of isoselenazole **6b**, was obtained along with isoxazole **8b** by starting from oxime tosylate **12b** ($R^1 = R^2 = C_6H_5$). All the spectral data of **13b**, involving MS, IR, ^{1}H NMR, and ^{13}C NMR spectra, as well as elemental analysis data, were fully consistent with the structure. Selena-Beckmann rearrangement of oxime sulfonates has already been reported by Segi and Nakajima which involves the treatment of oxime mesylates with $(Me_2Al)_2Se$,[48] and **13b** was also regarded as a selena-Beckmann product of **12b**. The structure of **13b** was determined by X-ray crystallographic analysis, and an ORTEP drawing of **13b** is shown in Fig. 2. It was worth noting that

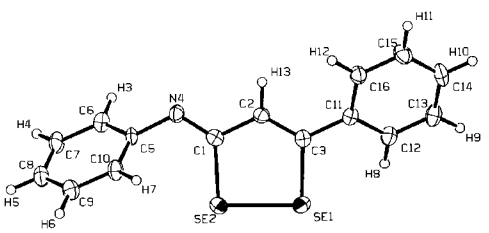


Fig. 2. ORTEP drawing of **13b**.

the some intermolecular attractive Se–N–Se interaction, i.e. Se(1)–N = 3.52 Å and Se(2)–N = 3.58 Å, respectively, was found in the crystal packing structure of **13b** as shown in Fig. 3.

On the other hand, similar reactions of **12** with NaTeH only gave intractable mixtures, and isotellurazoles **7** were not found in the crude products. NaTeH is widely known to behave as a reducing agent and as a divalent tellurium nucleophile to afford dialkenyl ditellurides from the reactions with various substrates having acetylenic moieties, imine moieties, and hydroxylamine derivatives,[49–59] and this might have caused the complicated mixture in our case.

In contrast, when ynone oxime tosylate **12a** was treated with *N*,*N*-dimethylcarbamoylchalcogenide ion, generated in situ

through reductive cleavage of **1** or **2** using $NaBH_4$, the corresponding isochalcogenazole **6a** or **7a**, respectively, was mainly afforded without the formation of isoxazole **8a** and oxidation products (**9a** and **10a**). In addition, tosylate **15a** was obtained in low yield as the sole geometrical isomer in the case starting from **2** as shown in Table 4.

It should be noted that **13b** was not unexpected from selena-Beckmann rearrangement of **12b**. Presumably, conversion of **12b** into **13b** is initiated by Michael addition of NaSeH to the β-position of ynone oxime tosylates **12** to form general intermediates **B**, and the formation of **6** can be explained by intramolecular nucleophilic substitution of intermediary alkeneselenolate ions **C** to the nitrogen atom of the oxime sulfonates. However, when an aryl group is bound at the R^2 position, subsequent 1,2-shift of aryl group from the oxime carbon atom to the nitrogen atom along with elimination of tosyloxy group might proceed predominantly,[46,60–62] and further addition of hydroselenide ion (SeH^-) to the newly formed iminocarbon of ketenimine **D** occurs. The final aerobic oxidation during the usual workup would afford 1,2-diselenole **13b**. The formation of **8** through the reaction of **12** with NaSeH can also be explained by the cleavage of tosyloxy group to generate free oximes **11** through the nucleophilic attack of hydroselenide ion (SeH^-) to the sulfur atom of the tosyloxy moiety of **12**. A plausible reaction pathway for the formation of isoselenazoles **6**, isoxazoles **8**, and 1,2-diselenole **13b** is summarized as shown in Scheme 3.

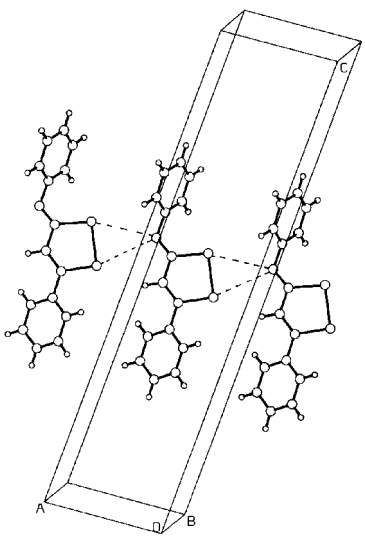


Fig. 3. Crystal structure of **13b**.

Conclusion

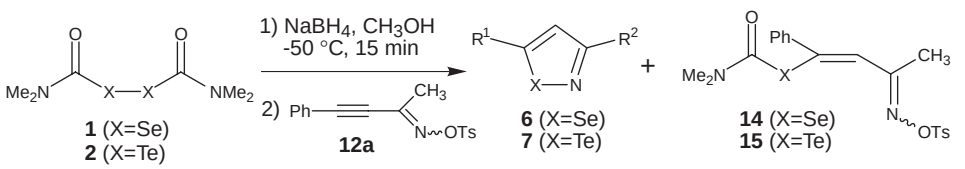
In conclusion, we found several new methods for the synthesis of isochlcogenazoles **6** and **7** starting from bis(*N*,*N*-dialkylcarbamoyl) dichalcogenides **1**, **1′**, and **2** and ynones **4** involving the intramolecular nucleophilic substitution of enechalcogenolate ions on the nitrogen atoms of in situ generated ynone oxime sulfonates. Especially, the reactions of *Te*-alkenyl tellurocarbamates **5** with hydroxylamine-*O*-sulfonic acid gave the best results for the formation of isotellurazole ring system among these new methods. Further attempts to synthesize various fused heterocycles via hetero Diels–Alder approach using these higher-row isochalcogenazoles as novel 4π components bridged with a heavy chalcogen atom are under way in our laboratory.

Experimental

Instruments. 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 as δ relative to internal tetramethylsilane (TMS). ^{13}C NMR spectra were recorded on a Bruker AC-400P (100 MHz). ^{77}Se NMR spectra and ^{125}Te NMR spectra were recorded on a Bruker AC-400P (76 and 125 MHz), and the chemical shifts of the ^{77}Se NMR and ^{125}Te NMR spectra are given in δ relative to external standard of dimethyl selenide and dimethyl telluride, respectively. 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.

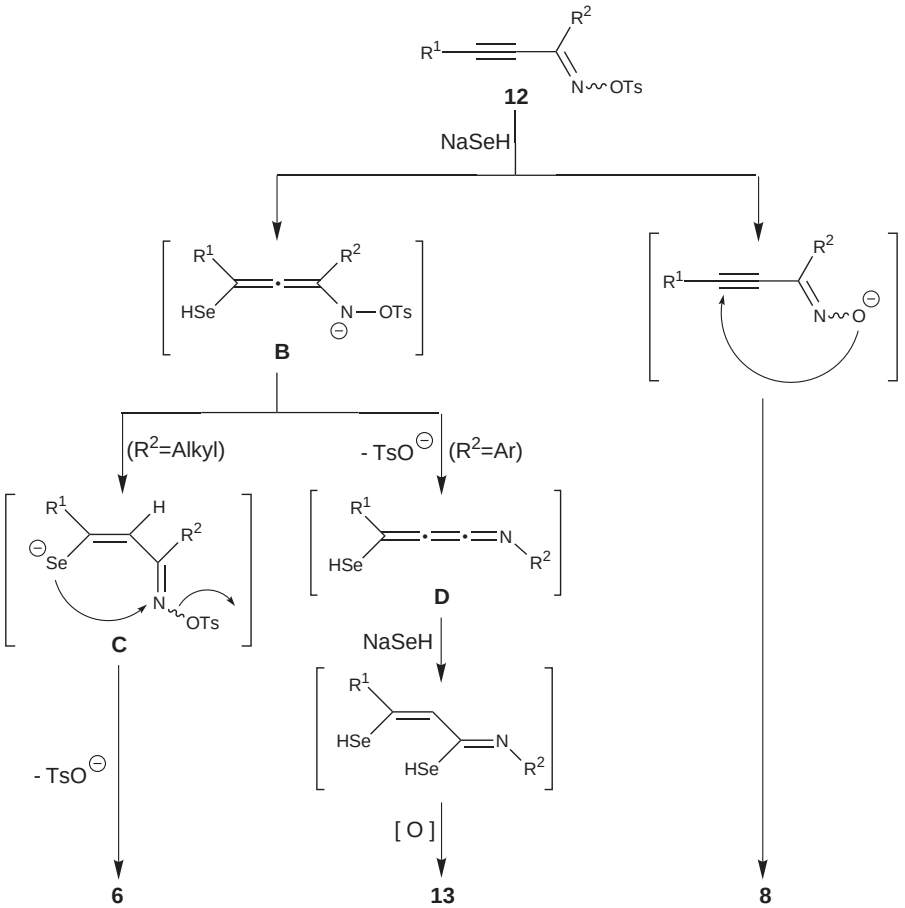
Materials. Column chromatography was performed using silica gel (Merck, Cat. No. 7734 or 9385) without pretreatment. Dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4) were dried over P_4O_{10} and were freshly

Table 4. Reaction of Ynone Oxime Tosylate **12a** with Bis(*N*,*N*-dimethylcarbamoyl) Dichalcogenide **1** and **2** and $NaBH_4$



1 or **2**	X	$NaBH_4$ /mol amt.	Temp /°C	Time /h	Yield/%[b] **6** or **7**	Yield/%[b] **14** or **15**
1	Se	2.2	R.T.	4	14 (**6a**)	0[c]
2	Te	2.2	R.T.	7	12 (**7a**)	23 (**15a**)
2	Te	4.4	40	7	30 (**7a**)	22 (**15a**)

a) A methanolic solution of **1** or **2** was treated with $NaBH_4$ at -50 °C for 15 min, and the resulting reaction mixture was treated with ynone oxime tosylate **12a** under the condition described in the table. b) Isolated yields. c) Complex mixture was obtained.



Scheme 3. Plausible formation pathway of isoselenazoles **6**, 1,2-diselenole **13a**, and isoxazoles **8** through the reaction of oxime tosylates **12** with NaSeH.

distilled before use. Benzene, hexane, acetonitrile, triethylamine, 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 tetrahydridoaluminate ($LiAlH_4$) 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, NMR solvents, and reagents, including elemental selenium, elemental tellurium, sodium metal, diethylamine, carbon monoxide (gas), phenylacetylene, trimethylsilylacetylene, ethyl bromide, magnesium metal, trimethylchlorosilane, anhydrous aluminium trichloride ($AlCl_3$), acetyl chloride, pivaloyl chloride, butanoyl chloride, isobutyryl chloride, benzoyl chloride, *p*-toluoyl chloride, sodium hydride (NaH) in a mineral oil (about 50%), sodium tetrahydroborate ($NaBH_4$), lithium tetrahydridoaluminate ($LiAlH_4$), hydroxylamine-*O*-sulfonic acid, hydroxylamine hydrochloride, sodium acetate, *p*-toluenesulfonyl chloride, triphenylphosphine, *m*-chloroperbenzoic acid (*m*CPBA), anhydrous sodium sulfate (Na_2SO_4), anhydrous magnesium sulfate ($MgSO_4$), 34.5% aqueous hydrogen peroxide solution, acetic acid, concentrated hydrochloric acid, and deuteriochloroform ($CDCl_3$), were commercially available reagent grade and were used without any pretreatment.

General Procedure for Preparation of *Se*-Alkenyl Selenocarbamates 4. To a DMF solution (10 mL) of bis(*N*,*N*-dimethylcarbamoyl) diselenide (**1**, 616 mg, 2.00 mmol)[30–32] or bis(*N*,*N*-diethylcarbamoyl) diselenide (**1′**, 716 mg, 2.00 mmol)[30,32] was added a methanolic solution (5 mL) of $NaBH_4$ (168 mg, 2.2 mol amt.) at −50 °C, and the reaction mixture was then treated with ynone **3** (2.2 mol amt.) at 0 °C for 7 h. The reaction was quenched with water, and the reaction mixture was extracted with benzene. The organic layer was washed twice with water and was dried over anhydrous Na_2SO_4 powder. The organic solvent was removed in vacuo, and the residual crude mixtures were subjected to chromatographic separation. However, purification of unstable *Se*-alkenyl *N*,*N*-dimethylselenocarbamates **4** was not successful even after repeated column chromatography on silica gel. On the other hand, the corresponding *N*,*N*-diethylselenocarbamates **4′** were relatively stable and were isolated in low yield as an yellow oil.

4a′ (R = C_2H_5, R^1 = C_6H_5, R^2 = CH_3): Yellow oil; IR (neat) 2975, 1665, 1548, 1402, 1245, 1212, 1111, 842, 750, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t, J = 7.0 Hz), 1.25 (3H, t, J = 7.0 Hz), 2.33 (3H, s), 3.18 (2H, q, J = 7.0 Hz), 3.46 (2H, q, J = 7.0 Hz), 6.90 (1H, s), 7.32–7.34 (3H, m), 7.50–7.52 (2H, m).

4c (R = CH_3, R^1 = H, R^2 = C_6H_5): Yellow plates, mp 103.5–104.8 °C (dec.); MS (*m*/*z*) 283 (M^+; 5%, ^{80}Se), 131 (C_6H_5-COCH=CH; 31%), 72 (Me_2NCO; bp); IR (KBr) 1618, 1600, 1503, 1332, 1211, 1089, 828, 766, 700, 560 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.11 (3H, s), 3.12 (3H, s), 7.47–7.51 (2H, m), 7.56–7.59 (1H, m), 7.72 (1H, d, J = 9.3 Hz), 8.02–8.03 (2H, m), 8.79 (1H, d, J = 9.3 Hz); ^{13}C NMR ($CDCl_3$) δ 33.7 (q), 37.3 (q), 120.1 (d), 128.2 (d), 128.9 (d), 132.9 (d), 137.4 (s), 146.7 (d), 164.6 (s), 189.5 (s). Calcd for $C_{12}H_{13}NO_2Se$: C, 51.07; H, 4.64; N, 4.96%. Found: C, 50.91; H, 4.53; N, 4.72%.

General Procedure for Preparation of *Te*-Alkenyl Telluro-

carbamates 5. To a DMF solution (10 mL) of bis(*N*,*N*-dimethylcarbamoyl) ditelluride (**2**, 398 mg, 1.00 mmol) was added a methanolic solution (5 mL) of $NaBH_4$ (84 mg, 2.2 mol amt.) at −50 °C, and the reaction mixture was then treated with ynone **3** (2.2 mol amt.) at 0 °C for 7 h. The reaction was quenched with water, and the reaction mixture was extracted with benzene. The organic layer was washed twice with water and was dried over anhydrous Na_2SO_4 powder. The organic solvent was removed in vacuo, and the residual crude products were subjected to column chromatography on silica gel to obtain *Te*-alkenyl *N*,*N*-dimethyltellurocarbamates **5** in high to moderate yields as yellow crystals.

5a ($R^1 = C_6H_5$, $R^2 = CH_3$):[32] Yellow solid, mp 67.0–67.5 °C; MS (*m*/*z*) 347 (M^+; 3%, ^{130}Te), 345 (M^+; 2%, ^{128}Te), 275 ($M^+ - Me_2NCO$; 55%, ^{130}Te), 273 ($M^+ - Me_2NCO$; 53%, ^{128}Te), 271 ($M^+ - Me_2NCO$; 31%, ^{126}Te), 43 (CH_3CO; bp); IR (KBr) 2924, 1637, 1609, 1522, 1483, 1359, 1089, 822, 761, 702, 646 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.34 (3H, s), 2.60 (3H, br s), 2.77 (3H, br s), 7.35–7.65 (6H, m). Calcd for $C_{13}H_{15}NO_2Te$: C, 45.28; H, 4.38; N, 4.06%. Found: C, 44.97; H, 4.38; N, 3.77%.

5b ($R^1 = R^2 = C_6H_5$): Orange needles, mp 101.3–102.7 °C; MS (*m*/*z*) 409 (M^+; 3%, ^{130}Te), 330 ($M^+ - C_6H_5$; 84%, ^{128}Te), 251 ($M^+ - 2(C_6H_5)$; 24%, ^{126}Te), 202 (Me_2NCO, 81%), 172 (NCOTe; 1%, ^{130}Te), 72 (Me_2NCO; bp); IR (KBr) 1606, 1481, 1238, 1086, 758, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.59 (3H, s), 2.80 (3H, s), 7.36–7.40 (3H, m), 7.47–7.51 (4H, m), 7.55–7.58 (1H, m), 8.04–8.06 (2H, m), 8.13 (1H, s); ^{13}C NMR ($CDCl_3$) δ 33.6 (q), 41.7 (q), 126.5 (d), 127.8 (d), 128.2 (d), 128.4 (d), 128.7 (d), 129.0 (d), 132.9 (d), 137.3 (s), 143.8 (s), 161.4 (s), 162.0 (s), 188.5 (s). Calcd for $C_{18}H_{17}NO_2Te$: C, 53.13; H, 4.21; N, 3.44%. Found: C, 53.00; H, 4.18; N, 3.30%.

5d ($R^1 = C_6H_5$, $R^2 = p\text{-}CH_3C_6H_4$): Orange plates, mp 130.5–131.0 °C (dec.); MS (*m*/*z*) 423 (M^+; 5%, ^{130}Te), 73 ($Me_2NCO + 1$; bp); IR (KBr) 1618, 1600, 1503, 1332, 1211, 1089, 828, 766, 700, 560 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.41 (3H, s), 2.59 (3H, br s), 2.81 (3H, br s), 7.28–7.30 (2H, m), 7.36–7.38 (3H, m), 7.48–7.50 (2H, m), 7.90–7.95 (2H, m), 8.11 (1H, s); ^{13}C NMR ($CDCl_3$) δ 21.7 (q), 33.7 (q), 41.7 (q), 126.6 (d), 127.8 (d), 128.4 (d), 128.5 (d), 128.9 (d), 129.5 (d), 134.9 (s), 160.6 (s), 162.2 (s), 188.2 (s). ^{125}Te NMR ($CDCl_3$) $\delta = -192.7$. Calcd for $C_{19}H_{19}NO_2Te$: C, 54.21; H, 4.55; N, 3.33%. Found: C, 54.02; H, 4.38; N, 3.21%.

5e ($R^1 = C_6H_5$, $R^2 = t\text{-}C_4H_9$): Yellow prisms, mp 89.0–89.3 °C (dec.); MS (*m*/*z*) 392 (M^+; 5%, ^{130}Te), 389 (M^+; 3%, ^{128}Te), 317 (bp); IR (KBr) 2966, 1687, 1618, 1512, 1484, 1364, 1248, 1217, 1087, 1013, 948, 761, 699, 663 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (9H, s), 2.59 (3H, br s), 2.80 (3H, br s), 7.34–7.35 (3H, m), 7.41–7.43 (2H, m), 7.58 (1H, s); ^{13}C NMR ($CDCl_3$) δ 25.6 (q), 33.7 (q), 41.7 (q), 42.9 (q), 126.5 (d), 127.8 (d), 128.4 (d), 128.8 (d), 143.8 (s), 158.3 (s), 161.7 (s), 204.6 (s). Calcd for $C_{16}H_{21}NO_2Te$: C, 49.66; H, 5.48; N, 3.62%. Found: C, 49.45; H, 5.53; N, 3.54%.

5f ($R^1 = C_6H_5$, $R^2 = i\text{-}C_3H_7$): Yellow needles, mp 97.4–97.6 °C (dec.); MS (*m*/*z*) 375 (M^+; 5%, ^{130}Te), 299 (bp); IR (KBr) 2960, 1701, 1637, 1488, 1362, 1249, 1084, 881, 759, 696, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.19 (3H, br d, $J = 7.0$ Hz), 1.21 (3H, br d, $J = 7.0$ Hz), 2.59 (3H, br s), 2.80 (3H, br s), 2.80 (1H, septet, $J = 7.0$ Hz), 7.33–7.43 (6H, m); ^{13}C NMR ($CDCl_3$) δ 18.4 (q), 33.8 (q), 40.7 (q), 41.6 (q), 127.8 (d), 128.4 (d), 128.7 (d), 128.8 (d), 143.5 (s), 157.5 (s), 161.4 (s), 203.2 (s). Calcd for $C_{15}H_{19}NO_2Te$: C, 48.31; H, 5.14; N, 3.76%. Found: C, 48.19; H, 5.04; N, 3.65%.

General Procedure for Synthesis of Isoselenazoles 6 and Their *N*-Oxides 11 from Bis(*N*,*N*-dialkylcarbamoyl) Diselenide (1 or 1′). An acetonitrile solution (10 mL) of bis(*N*,*N*-dimethylcarbamoyl) diselenide (**1**) or bis(*N*,*N*-diethylcarbamoyl) diselenide (**1′**) was treated with $NaBH_4$ (1.0–2.2 mol amt.) at room temperature for 30 min under an Ar atmosphere, and the reaction mixture was treated with ynone **3** (2.20–2.50 mol amt.) at room temperature for 2–6 h. The reaction was quenched with water and was extracted with $CHCl_3$. The organic layer was washed with water, and was dried over anhydrous Na_2SO_4 powder. The organic solvent was removed in vacuo, and ethanol (20 mL) was added to the residual crude products. Then, a methanolic or an ethanolic solution of the crude products was then treatment with hydroxylamine-*O*-sulfonic acid (4.0–6.0 mol amt.) at room temperature for a few hours. The reaction was quenched by large amount of water, and the reaction mixture was extracted with chloroform. The organic layer was washed with water, and was dried over anhydrous Na_2SO_4 powder. The organic solvent was removed in vacuo, and the residual crude products were subjected to column chromatography on silica gel to obtain isoselenazoles **6a**, isoxazole **8a**, and isoselenazole *N*-oxides **9a**.

6a ($R^1 = C_6H_5$, $R^2 = CH_3$): Pale yellow needles, mp 72.1–72.9 °C (lit.,[37] 73.0–75.0 °C); MS (*m*/*z*) 223 (M^+; bp, ^{80}Se), 182 ($M^+ - CH_3CN$; 36%, ^{80}Se), 102 ($C_6H_5C{=}CH$; 48%); IR (KBr) 3059, 2925, 1546, 1491, 1448, 1377, 1344, 827, 762, 732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.48 (3H, s), 7.35–7.39 (4H, m), 7.50–7.52 (2H, m); ^{13}C NMR ($CDCl_3$) δ 21.6 (q), 123.1 (d), 126.9 (d), 129.1 (d), 133.6 (s), 171.5 (s), 172.5 (s); ^{77}Se NMR ($CDCl_3$) δ 602.6. Calcd for $C_{10}H_9NSe$: C, 54.07; H, 4.08; N, 6.31%. Found: C, 54.18; H, 4.10; N, 6.06%.

8a ($R^1 = C_6H_5$, $R^2 = CH_3$):[38–41,63] Colorless needles, mp 64.5–66.0 °C (lit.,[38] 65.0–67.0 °C).

9a ($R^1 = C_6H_5$, $R^2 = CH_3$): Yellow plates, mp 135.3–136.0 °C; MS (*m*/*z*) 239 (M^+; 34%, ^{80}Se), 223 ($M^+ - O$; 67%, ^{80}Se); IR (KBr) 3067, 2994, 1543, 1412, 1247, 1200, 939, 882, 823, 758 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.27 (3H, s), 6.78 (1H, s), 7.28–7.38 (5H, m); ^{13}C NMR ($CDCl_3$) δ 14.5 (q), 116.2 (d), 125.7 (d), 129.2 (d), 132.8 (s), 148.2 (s), 149.3 (s). Calcd for $C_{10}H_9NOSe$: C, 50.43; H, 3.81; N, 5.88%. Found: C, 50.85; H, 3.87; N, 5.94%.

X-ray Crystallographic Analysis of Isoselenazole *N*-Oxide 9a. A single crystal with sizes of $0.25 \times 0.10 \times 0.04$ mm^3 was mounted on a Rigaku MSC Mercury CCD diffractometer, equipped with a rotating anode (50 kV, 40 mA), using graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). Crystal data are as follows: $a = 8.942(2)$, $b = 5.817(1)$, $c = 17.812(4)$ Å, $\beta = 102.016(5)°$, $V = 906.2(3)$ Å^3, space group $= P2_1/n$ (No. 14), $Z = 4$, $D_{calcd} = 1.745$ g cm^{-3}, μ(Mo Kα) $= 40.98$ cm^{-1}. The 2θ–ω scan mode with a scan rate of 8° min^{-1} (ω) was employed with a scan range ($1.20 + 0.30 \tan\theta$). A total of 8316 reflection within $2\theta = 55.0°$ was collected. The structure was solved by the direct method and refined by the full-matrix least-square method. All non-hydrogen atoms were refined anisotropically and hydrogen atoms found in the successive D-Fourier map were refined isotropically. The final cycle of refinement was carried out using 1521 observed reflections within $I_o > 2.5\sigma(I_o)$ converged to the final $R = \Sigma||F_o| - |F_c||/\Sigma F_o|$ value of 0.032 and $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2)]^{1/2}$ of 0.098. The maximum and minimum peaks on the final difference Fourier map correspond to 0.46 and −0.54 eÅ^{-3}, respectively. Selected bond lengths and bond angles are listed in Table 5. Crystallographic data have been deposited at the CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK, and the copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC-620036.

Table 5. Bond Lengths and Bond Angles for Isoselenazole *N*-Oxide **9a**

Bond lengths/Å		Bond angles/deg	
Se(1)–N(1)	1.898(2)	N(1)–Se(1)–C(1)	86.4(1)
Se(1)–C(1)	1.874(2)	Se(1)–N(1)–O(1)	121.1(2)
O(1)–N(1)	1.284(3)	Se(1)–N(1)–C(3)	112.0(2)
N(1)–C(3)	1.317(3)	O(1)–N(1)–C(3)	126.9(2)
C(1)–C(2)	1.353(4)	Se(1)–C(1)–C(2)	109.8(2)
C(1)–C(5)	1.472(4)	Se(1)–C(1)–C(5)	121.3(2)
C(2)–C(3)	1.414(4)	C(2)–C(1)–C(5)	128.8(2)
C(3)–C(4)	1.498(4)	C(1)–C(2)–C(3)	117.3(2)
		N(1)–C(3)–C(2)	114.5(2)
		N(1)–C(3)–C(4)	119.7(2)
		C(2)–C(3)–C(4)	125.7(2)
		C(1)–C(5)–C(6)	121.3(2)
		C(1)–C(5)–C(10)	120.2(2)

General Procedure for Deoxygenation of Isoselenazole *Se*-Oxide 9a Using Triphenylphosphine. A $CHCl_3$ solution of isoselenazole *N*-oxide **9a** ($R^1 = C_6H_5$, $R^2 = CH_3$, 238 mg, 1.00 mmol) was treated with triphenylphosphine (289 mg, 1.1 mol amt.) at reflux for 50 h, and the reaction was quenched by cooling the reaction mixture at 0 °C in an ice bath. The organic solvent was then removed in vacuo, and the residual crude products were subjected to column chromatography on silica gel to obtain isoselenazole **6a** (198 mg, 89% yield) along with the formation of quantitative amount of triphenylphosphine oxide.

General Procedure for Synthesis of Isotellurazole *Te*-Oxides 10 by Treating *Te*-Alkenyl Tellurocarbamates 5 with Hydroxylamine-*O*-sulfonic Acid. A methanolic solution (10 mL) of *Te*-alkenyl *N*,*N*-dimethyltellurocarbamates **5** was treated with hydroxylamine-*O*-sulfonic acid (4.4 mol amt.) at reflux for 1 h. The reaction mixture was cooled to room temperature and was quenched with water, and the crude reaction mixture was extracted with benzene. The organic layer was washed with water and was dried over anhydrous Na_2SO_4 powder. The organic solvent was removed in vacuo, and the residual crude products were subjected to column chromatography on silica gel to obtain isotellurazole *Te*-oxides **10** as main products besides a small amount of isotellurazoles **7**.

10a ($R^1 = C_6H_5$, $R^2 = CH_3$): Ivory powder, mp 210.3–211.8 °C (dec.); MS (*m*/*z*) 289 (M^+; 10%, ^{130}Te), 287 (M^+; 13%, ^{128}Te), 285 (M^+; 9%, ^{126}Te), 273 ($M^+ - O$; 61%, ^{130}Te), 271 ($M^+ - O$; 60%, ^{128}Te), 269 ($M^+ - O$; 76%, ^{126}Te), 102 (C_6H_5-C_2H; bp); IR (KBr) 3050, 2917, 1570, 1492, 1467, 1441, 1372, 1342, 1221, 1164, 1022, 925, 905, 868, 831, 758, 694, 616 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.68 (3H, s), 7.05 (1H, s), 7.24–7.28 (3H, m), 7.39–7.41 (2H, m); ^{13}C NMR ($CDCl_3$) δ 15.5 (q), 126.8 (d), 127.5 (d), 127.6 (d), 129.3 (d), 140.0 (s), 153.0 (s), 157.3 (s); ^{125}Te NMR ($CDCl_3$) δ 3806. Calcd for $C_{10}H_9NOTe$: C, 41.88; H, 3.16; N, 4.88%. Found: C, 41.47; H, 3.16; N, 4.61%.

10b ($R^1 = R^2 = C_6H_5$): Yellow amorphous solids, mp 107.5–108.0 °C (dec.); MS (*m*/*z*) 351 (M^+; 10%, ^{130}Te), 349 (M^+; 13%, ^{128}Te), 347 (M^+; 9%, ^{126}Te), 335 ($M^+ - O$; 61%, ^{130}Te), 333 ($M^+ - O$; 60%, ^{128}Te), 331 ($M^+ - O$; 76%, ^{126}Te), 102 (C_6H_5-C_2H; bp); IR (KBr) 1485, 1353, 1238, 1134, 1060, 756, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.23–7.31 (7H, m), 7.36 (1H, s), 7.48–7.50 (2H, m), 7.58 (1H, s); ^{13}C NMR ($CDCl_3$) δ 97.4 (d), 125.8 (d), 126.7 (d), 127.2 (d), 128.6 (d), 128.7 (d), 130.3 (s), 162.9 (s), 170.3 (s); ^{125}Te NMR ($CDCl_3$) δ 3831. Calcd for $C_{15}H_{11}NOTe$: C, 51.64; H, 3.18; N, 4.02%. Found: C, 51.09; H, 3.01; N, 3.89%.

10d ($R^1 = C_6H_5$, $R^2 = p$-$CH_3C_6H_4$): Orange oil; MS (*m*/*z*) 365 (M^+; 2%, ^{130}Te), 102 ($C_6H_5C_2H$; bp); IR (oil) 2922, 1537, 1486, 1444, 1341, 1276, 758, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.39 (3H, s), 7.24–7.26 (3H, m), 7.39–7.42 (3H, m), 7.50–7.52 (2H, m), 7.83–7.85 (1H, m), 8.62 (1H, s); ^{13}C NMR ($CDCl_3$) δ 21.5 (q), 127.1 (d), 127.4 (d), 127.6 (d), 128.3 (d), 128.55 (d), 128.63 (d), 129.1 (s), 129.6 (s), 139.3 (s), 140.8 (s), 165.9 (s). Calcd for $C_{16}H_{13}NOTe$: C, 52.96; H, 3.61; N, 3.86%. Found: C, 52.53; H, 3.46; N, 3.74%.

10e ($R^1 = C_6H_5$, $R^2 = t$-C_4H_9): Pale yellow oil; MS (*m*/*z*) 331 (M^+; 6%, ^{130}Te), 329 (M^+; 6%, ^{128}Te), 327 (M^+; 3%, ^{126}Te), 315 ($M^+ - O$; bp, ^{130}Te), 313 ($M^+ - O$; 72%, ^{128}Te), 311 ($M^+ - O$; 34%, ^{126}Te); IR (KBr) 2924, 1573, 1493, 1468, 1375, 1344, 1219, 1105, 928, 871, 835, 759, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.09 (9H, s), 7.36–7.52 (6H, m); ^{125}Te NMR ($CDCl_3$) δ 3782. Calcd for $C_{13}H_{15}NOTe$: C, 47.48; H, 4.60; N, 4.26%. Found: C, 47.12; H, 4.43; N, 4.15%.

General Procedure for Deoxygenation of Isotellurazole *Te*-Oxides 10 Using Triphenylphosphine. A $CHCl_3$ solution of isotellurazole *Te*-oxides **10** (1.00 mmol) was treated with triphenylphosphine (1.1 mol amt.) at 100 °C for 12 h in a sealed tube, and the reaction vessel was cooled to 0 °C in an ice bath to quench the reaction. The organic solvent was then removed in vacuo, and the residual crude products were subjected to column chromatography on silica gel to obtain isotellurazoles **7** in high yields along with quantitatively formed triphenylphosphine oxide.

7a ($R^1 = C_6H_5$, $R^2 = CH_3$): Pale yellow needles, mp 147.5–148.0 °C (lit.,[22] 149.0–150.0 °C), MS (*m*/*z*) 273 (M^+; 67%, ^{130}Te), 271 (M^+; 63%, ^{128}Te), 269 (M^+; 63%, ^{126}Te), 268 (M^+; bp, ^{125}Te), 228 (88%); IR (KBr) 1551, 1314, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.51 (3H, s), 7.36–7.38 (3H, m), 7.43–7.45 (2H, m), 8.01 (1H, s); ^{13}C NMR ($CDCl_3$) δ 25.7 (q), 127.5 (d), 129.1 (d), 129.2 (d), 132.8 (d), 137.9 (s), 170.2 (s), 177.0 (s). ^{125}Te NMR ($CDCl_3$) δ 1676.

7b ($R^1 = R^2 = C_6H_5$): Pale yellow powder, mp 140.5–141.0 °C; MS (*m*/*z*) 335 (M^+; ^{130}Te), 333 (M^+; ^{128}Te), 205 ($M^+ - Te$; bp); IR (KBr) 1535, 1482, 1442, 1392, 1098, 1028, 847, 837, 753, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.35–7.50 (6H, m), 7.73–7.75 (2H, m), 7.94–7.95 (2H, m), 8.65 (1H, s); ^{13}C NMR ($CDCl_3$) δ 129.2 (d), 129.3 (d), 130.6 (d), 131.50 (d), 131.52 (d), 132.1 (d), 132.6 (d), 138.1 (d), 140.5 (s), 171.4 (s), 176.6 (s). Calcd for $C_{15}H_{11}NTe$: C, 54.13; H, 3.33; N, 4.21%. Found: C, 54.01; H, 3.15; N, 4.09%.

7d ($R^1 = C_6H_5$, $R^2 = p$-$CH_3C_6H_4$): Orange oil; MS (*m*/*z*) 349 (M^+; 35%, ^{130}Te), 219 ($M^+ - Te$; bp); IR (oil) 2922, 1537, 1486, 1444, 1341, 1276, 758, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.39 (3H, s), 7.4–7.26 (3H, m), 7.39–7.42 (3H, m), 7.50–7.52 (2H, m), 7.83–7.85 (1H, m), 8.62 (1H, s). ^{13}C NMR ($CDCl_3$) δ 21.3 (q), 127.3 (d), 127.5 (s), 128.9 (d), 129.0 (d), 129.1 (d), 129.2 (d), 129.6 (d), 130.4 (d), 137.8 (s), 138.1 (s), 139.0 (s). Calcd for $C_{16}H_{13}NTe$: C, 55.40; H, 3.78; N, 4.04%. Found: C, 55.11; H, 3.62; N, 3.99%.

Reaction of *Se*-Alkenyl Selenocarbamate 4a with Hydroxylamine-*O*-sulfonic Acid in the Presence of Allyltrimethylsilane. An acetonitrile solution (10 mL) of crude *Se*-alkenyl selenocarbamate **4a** (573 mg), obtained from the reaction of bis(*N*,*N*-diethylcarbamoyl) diselenide (**1′**), $NaBH_4$ and ynone **3** (366 mg, 2.50 mmol), was treated with hydroxylamine-*O*-sulfonic acid (673 mg, 2.4 mol amt.) at room temperature for 6 h in the presence of allyltrimethylsilane (2852 mg, 10 mol amt.). The reaction was quench-

ed by large amount of water, and the reaction mixture was extracted with chloroform. The organic layer was washed with water and was dried over anhydrous Na_2SO_4 powder. The organic solvent was removed in vacuo, and the residual crude products were subjected to column chromatography on silica gel to obtain isoselenazoles **6a** (48 mg, 13%) and isoxazole **8a** (125 mg, 35%) along with several uncharacterizable products.

Conversion of Ynones 3 into the Corresponding Ynone Oxime Tosylates 12. A methanolic solution of ynone **3** (3.00 mmol) was treated with a solution of hydroxylamine hydrochloride (462 mg, 2.2 mol amt.) and sodium acetate (270 mg, 1.1 mol amt.) in H_2O/methanol at room temperature for 5 h. The reaction was quenched by adding a large amount of water to the reaction mixture, and the mixture was extracted with CH_2Cl_2. The organic layer was washed twice with water and was dried over anhydrous Na_2SO_4 powder. The organic solvent was removed in vacuo, and the residual crude products were subjected to column chromatography on silica gel to obtain a *syn–anti* geometrical mixture of ynone oximes **11** (98% for **11a**, 47% for **11b**, and 50% for **11g**, respectively) as a main products as colorless powders or oils besides isoxazole **8** as a byproduct. Subsequently, a CH_2Cl_2 solution of **11** (9 mmol) was treated with *p*-toluenesulfonyl chloride (1891 mg, 1.1 mol amt.) and triethylamine (2001 mg, 2.2 mol amt.) at room temperature for 24 h. The reaction was quenched with 10% aqueous hydrochloric acid, and the reaction mixture was extracted with CH_2Cl_2. The organic layer was washed with a saturated aqueous $NaHCO_3$ solution and was dried over anhydrous Na_2SO_4 powder. The solvent was removed in vacuo, and the residual crude products were subjected to column chromatography on silica gel to obtain the corresponding oxime tosylates **12** in high yields (87% for **12a**, 79% for **12b**, and 84% for **12g**, respectively). In most cases, the major byproducts were the corresponding isoxazoles **8**.

11a ($R^1 = C_6H_5$, $R^2 = CH_3$, approximately 10:1 geometrical mixture): Pale yellow oil; IR (oil) 3261, 3059, 2922, 2218, 1616, 1327, 1184, 1172, 1028, 979, 756, 689 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer δ 2.21 (3H, s), 7.20–7.80 (5H, m), 8.60–9.20 (1H, br s), minor isomer δ 2.38 (3H, s), 7.20–7.80 (5H, m), 8.60–9.20 (1H, br s).

11b ($R^1 = R^2 = C_6H_5$): colorless oil; IR (oil) 3266, 2219, 1498, 1451, 1401, 1334, 1061, 956, 751, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.00–8.20 (10H, m), 9.20–9.50 (1H, m).

11g ($R^1 = C_6H_5$, $R^2 = n\text{-}C_3H_7$, approximately 1:1 geometrical mixture): IR (oil) 3322, 2966, 2876, 2215, 1491, 1443, 1314, 993, 757, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (3H, t, $J = 6.9$ Hz), 1.01 (3H, t, $J = 6.9$ Hz), 1.40–1.90 (2H, m), 2.43 (2H, br t, $J = 7.0$ Hz), 7.20–7.60 (3H, m), 7.70–8.00 (2H, m).

12a ($R^1 = C_6H_5$, $R^2 = CH_3$, approximately 10:1 geometrical mixture): Pale yellow powder, mp 69.7–70.1 °C; IR (KBr) 3060, 2925, 2202, 1378, 1194, 1180, 817 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer δ 2.20 (3H, s), 2.43 (3H, s), 7.20–7.40 (5H, m), 7.48 (2H, br d, $J = 8.0$ Hz), 7.92 (2H, br d, $J = 8.0$ Hz), minor isomer δ 2.14 (3H, s), 2.43 (3H, s), 7.20–7.40 (5H, m), 7.49 (2H, br d, $J = 8.0$ Hz), 7.93 (2H, br d, $J = 8.0$ Hz); ^{13}C NMR ($CDCl_3$, major isomer) δ 18.3 (q), 20.8 (q), 21.6 (q), 95.1 (s), 120.6 (s), 128.4 (d), 128.5 (d) 128.77 (d), 128.82 (d), 129.6 (d), 132.0 (s), 132.2 (s), 145.3 (s), 151.7 (s). Calcd for $C_{17}H_{15}NO_3S$: C, 65.16; H, 4.82; N, 4.47%. Found: C, 65.01; H, 4.88; N, 4.45%.

12b ($R^1 = R^2 = C_6H_5$, approximately 10:1 geometrical mixture: Pale yellow solid, mp 99.1–100.9 °C; IR (KBr) 3064, 2206, 1760, 1380, 1194, 1179, 766, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.50 (3H, s), 7.20–7.80 (12H, m), 8.00–8.30 (2H, m).

12g ($R^1 = C_6H_5$, $R^2 = n\text{-}C_3H_7$, approximately 5:1 geometrical mixture): Pale yellow oil; IR (oil) 2963, 2934, 2210, 1598, 1491, 1444, 1378, 1193, 1179, 1095 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer δ 0.89–1.11 (3H, m), 1.47–1.83 (2H, m), 2.29–2.57 (2H, m), 2.43 (3H, s), 7.35–7.40 (7H, m), 7.83–7.97 (2H, m).

Preparation of Isoselenazoles 6 by Treating Oxime Tosylates 12 with Sodiumhydrogen Selenide. An ethanolic solution of $NaBH_4$ (425 mg, 11 mmol) was treated with elemental selenium (237 mg, 3.0 mmol) under an argon atmosphere at 0 °C, and then, ynone oxime tosylate **12** (2.2 mmol) was added to the colorless solution. The reaction mixture was stirred at room temperature for 2 h. The reaction was quenched with a large amount of water, and the reaction mixture was extracted with benzene. The organic layer was washed with water and was dried over anhydrous Na_2SO_4 powder. The solvent was removed in vacuo, and the residual crude products were subjected to column chromatography on silica gel to obtain isoselenazoles **6** and isoxazoles **8**. Exceptionally, in case the reaction starting from oxime tosylate **12b** ($R^1 = R^2 = C_6H_5$, 818 mg, 2.2 mmol), unexpected 1,2-diselenole **13b** (304 mg, 38% yield) was obtained besides isoxazole **8b** (431 m, 59% yield).

Preparation of Isochalcogenazole 6a and 7a by Treating Oxime Tosylates 12a with Bis(*N*,*N*-dimethylcarbamoyl) Dichalcogenide 1 and 2 with $NaBH_4$. A methanolic solution of bis(*N*,*N*-dimethylcarbamoyl) dichalcogenide (X = Se, Te, 0.7 mmol) was treated with $NaBH_4$ 58 mg (2.2 mol amt.) or 116 mg (4.4 mol amt.) under an argon atmosphere at −50 °C for 15 min, and then oxime tosylate **12a** (488 mg, 2.20 mol amt.) was treated with the resulting mixture at R.T. or 40 °C for several hours. The reaction was quenched with a large amount of water, and the reaction mixture was extracted with benzene. The organic layer was washed with water and was dried over anhydrous Na_2SO_4 powder. The solvent was removed in vacuo, and the residual crude products were subjected to column chromatography on silica gel to obtain isoselenazoles **6a** or isotellurazole **7a** in moderate yields. In case the reaction starting from **2**, oxime tosylate **15a** was obtained as the main byproduct.

6g ($R^1 = C_6H_5$, $R^2 = n\text{-}C_3H_7$): Red oil; MS (*m/z*) 251 (M^+; 31%, ^{80}Se), 102 ($C_6H_5C{=}CH$; bp); IR (oil) 2961, 1548, 1446, 758, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (3H, t, $J = 7.3$ Hz), 1.78 (2H, sextet, $J = 7.3$ Hz), 2.75 (2H, t, $J = 7.3$ Hz), 7.33–7.38 (3H, m), 7.47–7.48 (2H, m), 7.67 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 13.9 (q), 22.0 (t), 37.9 (t), 122.3 (d), 126.9 (d), 129.1 (d), 129.3 (d), 133.6 (s), 172.2 (s), 175.9 (s). Calcd for $C_{12}H_{13}NSe$: C, 57.61; H, 5.24; N, 5.60%. Found: C, 57.85; H, 5.29; N, 5.50%.

8b ($R^1 = R^2 = C_6H_5$): Colorless needles, mp 141.2–141.7 °C (lit.,[64] 141 °C).

8g ($R^1 = C_6H_5$, $R^2 = n\text{-}C_3H_7$):[41,65] Pale yellow solids, IR (KBr) 3059, 2961, 1575, 1452, 1072, 893 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (3H, t, $J = 6.8$ Hz), 1.40–2.00 (2H, m), 2.20–2.80 (2H, m), 6.39 (1H, s), 7.30–7.80 (5H, m).

13b ($R^1 = R^2 = C_6H_5$): Red prisms, mp 127.4–127.7 °C; MS (*m/z*) 365 (M^+; 26%, ^{80}Se), 363 (M^+; 21%, ^{78}Se), 102 (bp); IR (KBr) 1548, 1479, 1443, 1150, 823, 757, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.10–7.76 (11H, m); ^{13}C NMR ($CDCl_3$) δ 118.9 (s), 125.4 (d), 126.7 (d), 126.9 (d), 129.1 (d), 130.0 (d), 130.3 (d), 135.4 (s), 153.2 (a), 159.4 (a), 171.2 (s); ^{77}Se NMR ($CDCl_3$) δ 459.4 (s), 569.0 (s). Calcd for $C_{15}H_{11}NSe_2$: C, 49.61; H, 3.05; N, 3.86%. Found: C, 49.61; H, 3.00; N, 3.70%.

15a ($R^1 = C_6H_5$, $R^2 = CH_3$): Orange powder, mp 115.2–117.3 °C; MS (*m/z*) 273 ($M^+ - Me_2NCO - OTs$; 2%, ^{130}Te), 271 ($M^+ - Me_2NCO - OTs$; 2%, ^{128}Te), 269 ($M^+ - Me_2NCO -$

Table 6. Bond Lengths, Bond Angles, and Torsion Angles for 1,2-Diselenole **13b**

Bond lengths/Å		Bond angles/deg		Torsion angles/deg[a)]	
Se(1)–Se(2)	2.3225(8)	Se(2)–Se(1)–C(3)	91.6(2)	Se(1)–Se(2)–C(1)–N(4)	172.6(4)
Se(1)–C(3)	1.887(5)	Se(1)–Se(2)–C(1)	92.6(2)	Se(1)–Se(2)–C(1)–C(2)	−3.8(4)
Se(2)–C(1)	1.943(5)	C(1)–N(4)–C(5)	121.0(4)	Se(1)–C(3)–C(2)–C(1)	−3.4(7)
N(4)–C(1)	1.276(4)	Se(2)–C(1)–N(4)	125.2(4)	Se(1)–C(3)–C(11)–C(12)	34.1(6)
N(4)–C(5)	1.421(6)	Se(2)–C(1)–C(2)	112.7(3)	Se(1)–C(3)–C(11)–C(16)	−144.5(4)
C(1)–C(2)	1.49(7)	N(4)–C(1)–C(2)	122.0(4)	Se(2)–Se(1)–C(3)–C(2)	0.1(4)
C(2)–C(3)	1.339(7)	C(1)–C(2)–C(3)	124.2(4)	Se(2)–Se(1)–C(3)–C(11)	179.6(4)
C(3)–C(11)	1.473(7)	Se(1)–C(3)–C(2)	118.7(4)	Se(2)–C(1)–N(4)–C(5)	2.3(7)
C(5)–C(6)	1.377(7)	Se(1)–C(3)–C(11)	116.4(4)	Se(2)–C(1)–C(2)–C(3)	5.2(7)
C(5)–C(10)	1.400(7)	C(2)–C(3)–C(11)	124.9(5)	N(4)–C(1)–C(2)–C(3)	−171.4(5)
C(11)–C(12)	1.392(7)	N(4)–C(5)–C(6)	118.0(5)	N(4)–C(5)–C(6)–C(7)	−178.7(5)
C(11)–C(16)	1.396(7)	N(4)–C(5)–C(10)	122.9(5)	N(4)–C(5)–C(10)–C(9)	179.0(5)
				C(1)–Se(2)–Se(1)–C(3)	1.9(2)
				C(1)–N(4)–C(5)–C(6)	−131.7(5)
				C(1)–N(4)–C(5)–C(10)	51.8(7)
				C(1)–C(2)–C(3)–C(11)	177.2(5)
				C(2)–C(1)–N(4)–C(5)	178.4(5)
				C(2)–C(3)–C(11)–C(12)	−146.5(5)
				C(2)–C(3)–C(11)–C(16)	34.9(8)

a) The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.

OTs; 1%, ^{126}Te), 102 (bp); IR (KBr) 2924, 1662, 1596, 1378, 1364, 1189, 1174, 1083, 803, 788, 667 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.08 (3H, s), 2.32 (3H, s), 2.68 (3H, s), 2.77 (3H, s), 6.66 (1H, s), 7.02–7.36 (5H, m), 7.43–7.45 (2H, m), 7.74–7.79 (2H, m); ^{13}C NMR ($CDCl_3$) δ 19.6 (q), 21.6 (q), 35.7 (q), 38.3 (q), 128.1 (d), 128.5 (d), 128.6 (d), 128.8 (d), 129.45 (s), 129.48 (d), 132.7 (s), 133.6 (d), 143.0 (s), 144.8 (s), 155.9 (s), 164.0 (s). Calcd for $C_{20}H_{22}N_2O_4STe$: C, 46.73; H, 4.31; N, 5.45%. Found: C, 47.05; H, 4.50; N, 5.41%.

X-ray Crystallographic Analysis of 1,2-Diselenole 13b. A single crystal with sizes of $0.25 \times 0.15 \times 0.4\,mm^3$ used for the data collection on a Rigaku automated four circle diffractometer (AFC5PR), equipped with a rotating anode (45 kV, 200 mA), using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Crystal data are as follows: $a = 6.448(1)$, $b = 7.728(4)$, $c = 26.989(2)$ Å, $\beta = 96.52(1)^\circ$, $V = 1336.1(8)$ Å^3, space group = $P2_1/c$ (No. 14), $Z = 4$, $D_{calcd} = 1.81\,g\,cm^{-3}$, μ(Mo Kα) = 54.58 cm^{-1}. The 2θ–ω scan mode with a scan rate of $8^\circ\,min^{-1}$ (ω) was employed with a scan range ($1.20 + 0.30\tan\theta$). A total of 4830 reflection within $2\theta = 60^\circ$ was collected. The structure was solved by the direct method and refined by the full-matrix least-square method. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms found in the successive D-Fourier map were refined isotropically. The final cycle of refinement was carried out using 2148 observed reflections within $I_o > 2.5\sigma(I_o)$ converged to the final $R = \Sigma||F_o| - |F_c||/\Sigma F_o|$ value of 0.046 and $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2)]^{1/2}$ of 0.044. The maximum and minimum peaks on the final difference Fourier map correspond to 0.28 and $-0.31\,e$Å^{-3}, respectively. Selected bond lengths and bond angles are listed in Table 6.

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