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Reaction of Selenoamide Dianions with Thio- and Selenoformamides Leading to the Formation of 5-Aminoselenazoles: Photophysical and Electrochemical Properties

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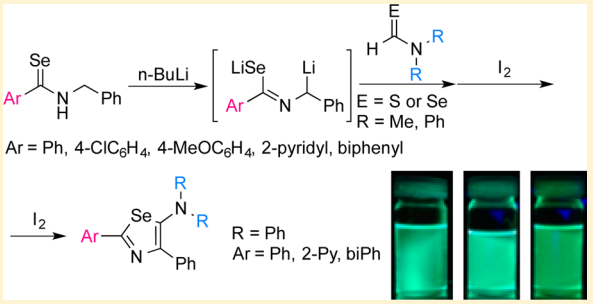
Supporting Information

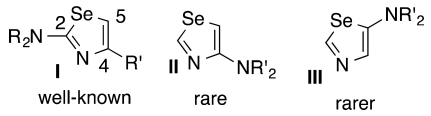
ABSTRACT: 5-Amino-2-selenazolines were synthesized by reacting selenoamide dianions generated from secondary selenoamides and BuLi with tertiary thio- and selenoformamides followed by treatment with iodine. The resulting 5-amino-2-selenazolines were further oxidized with iodine to give 5-aminoselenazoles in moderate to good yields. The general tendencies in the ^{77}Se NMR spectra of the starting selenoamides, 5-amino-2-selenazolines, and 5-aminoselenazoles were determined. The chemical shifts of these compounds were highly influenced by the skeletons involving the selenium atom as well as the substituents on the carbon atoms of each skeleton. The molecular structures of 5-aminoselenazoles were clarified by X-ray analyses, and their electronic structures were elucidated by DFT calculations. Finally, UV−vis and fluorescence spectroscopy and cyclic voltammetry (CV) of 5-aminoselenazoles were performed, and their properties are discussed in relation to the substituents on the selenazole rings.



INTRODUCTION

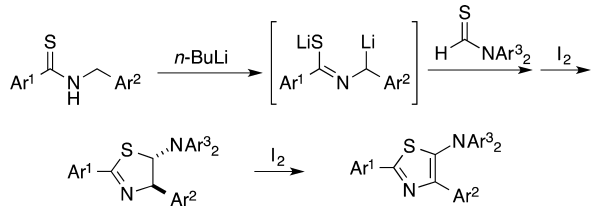
2-Selenazolines[1] and selenazoles[2,3] are an interesting class of selenium- and nitrogen-containing heterocycles in view of their unique properties, although they have received less attention than other selenium-containing heterocycles[4] such as selenophenes[5] and ebselen.[6] It is partly due to the lack of the diversity of the substitution patterns in the known derivatives. In fact, selenazole cores possess three carbon atoms, to which a wide range of substituents can be introduced. For example, compounds with amino groups at the 2-positions of selenazoles **I** have been studied to some extent[7] (Chart 1).

Chart 1. A Range of Aminoselenazoles



In contrast, little is known about those aminoselenazoles with amino groups at the 4- and 5-positions of general structures **II**[8] and **III**. In particular, to the best of our knowledge, only one example of a 5-*N*,*N*-disubstituted aminoselenazole has been reported.[9,10] One method that is frequently used for the synthesis of selenazoles is the condensation reaction of primary selenoureas and selenoamides with α-halo carbonyl compounds.[11] However, with these methods, amino groups cannot be introduced at the 5-positions of selenazoles. Very recently, sulfur isologues[12] of 5-*N*,*N*-diarylaminoselenazoles were prepared for the first time in our studies on chalcogenocarbonyl[13] and chalcogenophosphoryl compounds.[14] In this reaction, thioamide dianions were generated from secondary thioamides and treated with thioformamides (Scheme 1).

Scheme 1. Synthesis of 5-Aminothiazoles



Notably, 5-*N*,*N*-diarylaminothiazoles have been shown to possess strong fluorescence properties and are considered to be candidates for use in thiazole-based organic light-emitting diodes (OLED) and fluorescent chemosensors.[15] In contrast, to the best of our knowledge, only metal complexes have been examined in studies on fluorescence properties of selenazole-containing compounds.[16] Our synthetic studies on selenoamides have shown that selenoamide dianions[17] similar to thioamide dianions can be generated. We report here the reactions of selenoamide dianions with thio- and selenoforma-

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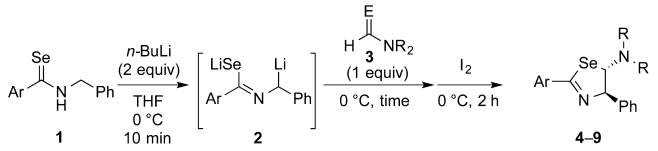
Table 1. Synthesis of 5-Amino-2-selenazolines 4–9[a]



entry	1	Ar	electrophile	time(h)	I_2(equiv)	product	yield(%)[b]
1	**1a**	Ph	**3a**	0.5	1	**4**	91
2	**1b**	MeO	**3a**	1	1	**5**	53
3	**1c**	Cl	**3a**	1.3	1	**6**	47
4	**1a**	Ph	**3b**	0.5	2	complex mixture	
5	**1a**	Ph	**3c**	0.5	2	**7**	47
6	**1d**		**3c**	1	2	**8**	78
7	**1e**	Ph	**3c**	1	2	**9**	44

[a]The reaction was carried out as follows, unless otherwise noted: To a solution of selenoamide **1** (1.0 equiv) in THF (2.0 mL) was slowly added *n*-BuLi (2.0 equiv), and the mixture was stirred. To this was added thio- or selenoformamide **3** (1.0 equiv), and the mixture was stirred. To this was added iodine (1.0 or 2.0 equiv), and the mixture was stirred. [b]Isolated yields.

mides leading to the formation of unprecedented 5-amino-selenazoles. The photophysical and electrochemical properties of the obtained compounds are also described along with the results of computational studies.

RESULTS AND DISCUSSION

Synthesis. Initially, *N*-benzyl aromatic selenoamides were prepared by the selenation reaction of the corresponding amides with Woollins reagent[18] and/or the combination of $HSiCl_3$/Se/amines developed by us[19] in moderate to high yields. *N*-Benzyl selenobenzamide (**1a**) was then treated with BuLi at 0 °C for 10 min (Table 1). The reaction mixture turned deep purple, which was indicative of the formation of selenoamide dianion **2a**. To the reaction mixture was added *N*,*N*-dimethyl thioformamide (**3a**), and the mixture was stirred at the same temperature for 1 h. Iodine was added to the reaction mixture, and stirring was continued for 2 h to give the first example of 5-amino-2-selenazoline **4** in 91% yield (entry 1). A similar reaction was carried out with secondary selenoamides **1b** and **1c** to give the corresponding 2-selenazolines **5** and **6** in moderate yields (entries 2 and 3). In all cases, products that contained a sulfur atom were not observed. The trans stereochemistry of **4**–**6** was determined by comparing their ^{1}H NMR spectra with those of the corresponding 2-thiazolines.[12] Additionally, the J^3 coupling constants (J^3 = 1.4–4.5 Hz) between the protons on two carbon atoms adjacent to NR_2 and N=C groups supported the trans configuration. *N*,*N*-Diphenyl thioformamide (**3b**) was then treated with selenoamide dianion **2a**, but the reaction gave a complex mixture that included the 2-selenazoline and 2-thiazoline (entry 4). Instead, the reaction of selenoamide dianion **2a** with *N*,*N*-diphenyl selenoformamide (**3c**) was carried out to successfully give the desired 2-seleanazoline **7** with high purity in moderate yield (entry 5). The introduction of 2-pyridyl and biphenyl groups at the 2-position of the 2-selenazoline ring was achieved with the use of the corresponding secondary selenoamides **1d** and **1e** (entries 6 and 7). In all cases, the formation of cis isomers was not observed probably because of the steric hindrance of the substituents at the 4- and 5-positions.

Further oxidation of the resulting 2-selenazolines **4**–**9** with iodine was carried out to give the corresponding selenazoles **10**–**15** in low to good yields (Table 2). The completion of the reaction was monitored by TLC, and the use of 2 equiv of I_2

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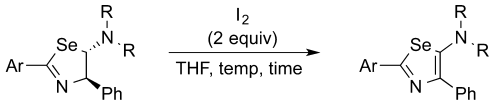
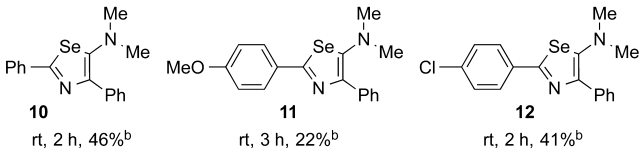
Table 2. Synthesis of 5-Aminoselenazoles 10−15[a]





[a]The reaction was carried out as follows, unless otherwise noted: To a solution of selenazoline **4**−**9** (1.0 equiv) in THF was added iodine, and the mixture was stirred. [b]Isolated yields.

facilitated the reaction. In all cases, when the starting 2-selenazolines were completely consumed, the reaction mixtures were subjected to aqueous workup. In some cases, during this procedure, the products partially decomposed, and the isolated yields of the products were highly dependent on the substituents. Nevertheless, once they were isolated, they could be stored at least within 1 month in a refrigerator.

Molecular Structures. The structures of 5-aminoselenazoles were unequivocally determined by X-ray structure analyses. An ORTEP drawing of **13** is shown in Figure 1.

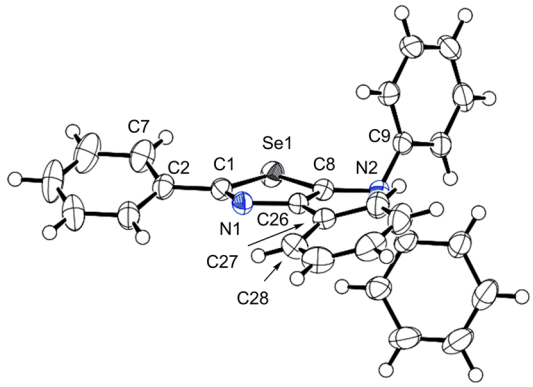


Figure 1. ORTEP drawing of 5-aminoselenazole **13**.

Phenyl groups at the 2- and 4-positions are located within nearly the same plane as the selenazole ring, with dihedral angles of −22.85° and 18.54° for C7−C2−C1−Se1 and N1−C21−C27−C26, respectively, although they are more deviated than those in the corresponding thiazole **16**. In contrast, the diphenylamino group and selenazole ring are highly deviated, with a dihedral angle of 60.86° for Se1−C8−N2−C9. Figure 2 shows a comparison of the bond lengths and bond angles of the selenazoyl moiety of **13** and those of its sulfur isologue **16**. Due to the longer ionic radius of the selenium atom, the bond lengths of the C−Se bonds in **13** are ca. 1.09 times longer than the C−S bonds in the corresponding thiazole **16**. The bond angle of C−Se−C in **13** was more acute than that of C−S−C in **16**.

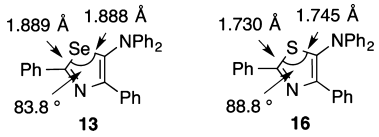


Figure 2. Structures of selenazoyl and thiazoly moieties of **13** and **16**.

To further compare the structures of the 5-aminoselenazoles, DFT calculations of selenazoles **10** and **13** were carried out with the B3LYP/6-31G(d) basis set.[20] The calculated molecular structures are shown in Figure 3. For **10**, almost no deviation

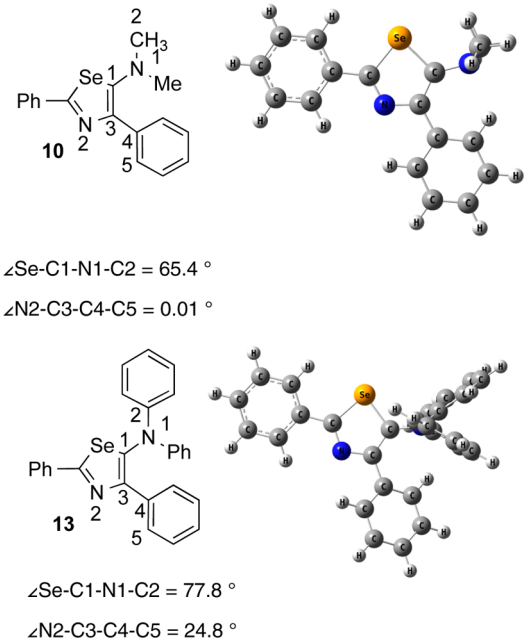


Figure 3. Molecular structures of **10** and **13** derived from DFT calculations (B3LYP/6-31G(d)).

was observed for the two phenyl groups at the 2- and 4-positions and the selenazole ring. Although the calculated dihedral angle for Se−C1−N1−C2 of **13** did not match the results of X-ray analyses, the deviation of diphenylamino group was confirmed. Likewise, even for **10**, the amino group at the 5-position was deviated, with the dihedral angle of 65.4° for Se−C1−N1−C2.

^{77}Se NMR Spectroscopy. The ^{77}Se nucleus is NMR active. Indeed, it is three times more sensitive than the ^{13}C nucleus, and the chemical shifts are highly influenced by the fundamental skeletons of organoselenium compounds and the substituents close to the selenium atom.[21] These data for the starting selenoamides, 2-selenazolines, and 5-aminoselenazoles are listed in Chart 2. The signals of selenoamides **1** were observed in the region from 517 to 638 ppm, and replacement of the phenyl group with a 2-pyridyl group at the 2-position shielded the signal by 120 ppm (see **1a** and **1d**). The signals of 5-amino-2-selenazolines are found from 346 to 541 ppm, whereas those of 5-aminoselenazoles range from 629 to 707 ppm. Unlike the effect of the 2-pyridyl group in selenoamide **1d**, introduction of a 2-pyridyl group at the 2 positions in 2-selenazolyl and selenazole rings deshielded the signals (see **1d**, **8**, and **14**). The signals of 5-amino-2-selenazolines and 5-aminoselenazoles with an *N*,*N*-dimethylamino group are in higher field regions than those with an *N*,*N*-diphenylamino

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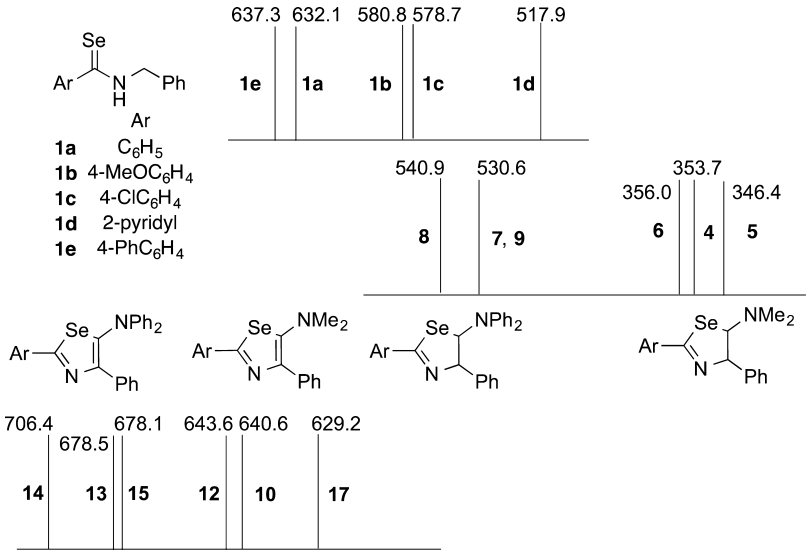
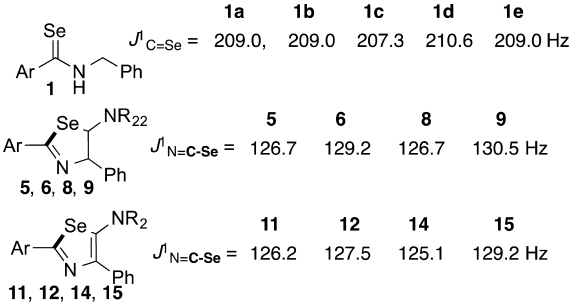
Chart 2. ^{77}Se NMR Spectra of Selenoamides, 2-Selenazolines, and Selenazoles



group, and the signals for 5-amino-2-selenazolines are highly sensitive to the substituents on the nitrogen atom.

The coupling constants between the carbon and selenium atoms are also informative. Those of selenoamides, selenazolines, and selenazoles (Chart 3) were mainly dependent on the

Chart 3. J^1 Coupling Constants of C═Se and C−Se Bonds of Selenoamides, 2-Selenazolines, and Selenazoles



molecular skeletons to which the selenium atom was introduced. For selenoamides, $J^1_{C=Se}$ values were ca. 210 Hz, whereas in 2-selenazolines and selenazoles, $J^1_{N=C-Se}$ values ranged from 125 to 131 Hz.

Electronic Absorption and Fluorescence Spectroscopy. The photophysical properties of selenazoles **10**−**15** and thiazole **17** are summarized in Table 3. The absorption spectra and fluorescence spectra of **13**−**15** and **17** are shown in Figure 4. In the UV−visible spectra, the longest wavelengths of compounds **10** and **11** were observed at around 333 nm, whereas those of **12**−**15** were shifted to longer wavelengths. Those of 5-aminoselenazoles **13**−**15** appeared at 395 ± 11 nm. These results implied that the substituents at not only the 2-positions of selenazoles but also on the nitrogen atom at the 5-position strongly influenced the absorption spectra. In a series of *N*,*N*-diphenylaminoselenazoles **13**−**15**, bathochromic shifts of the longest wavelengths and absorption onset (λ_{onset}) were observed when the phenyl group at the 2-position in **13** was replaced with a 2-pyridyl group as in **14**. The fluorescence spectra were also dependent on the substituents and were observed from 438 to 498 nm. *N*,*N*-Dimethyl selenazoles **10**−**12** were only slightly fluorescent. In contrast, the introduction of phenyl groups to the nitrogen atom at the 5-position enhanced the fluorescence quantum yields of selenazoles **13**−**15**. Replacement of the selenium atom in **14** with a sulfur atom as in **17** shifted the absorption and emission spectra to shorter wavelengths by ca. 10 nm, and thiazole **17** was more fluorescent.

Theoretical Calculations. To gain further insights into the electronic properties, DFT and time-dependent (TD) DFT calculations were carried out for compounds **10**−**15** and **17**. The results at the TD-B3LYP/6-31G(d)//B3LYP/6-31(d) level of theory with the ground-state geometries are shown in Tables 3 and 4 and Figure 5. The HOMOs of *N*,*N*-dimethylaminoselenazoles **10**−**12** are delocalized mainly at the aromatic ring at the 4-positions and selenazole rings, whereas those of *N*,*N*-diphenylaminoselenazoles **13**−**15** are localized on the *N*,*N*-diphenyl amino groups. In contrast, the LUMOs of all the selenazoles are delocalized on the selenazole rings and the aromatic rings at the 2-positions. The calculated λ_{max} values of **10**−**12** are close to the observed values. In contrast, those of **13**−**15** were red-shifted by 20−32 nm compared with the observed values, although the general tendencies of the absorption wavelengths for the observed and calculated values were identical. The absorption maxima in the low-energy region of all the selenazoles **10**−**15** were attributed to the transitions from the HOMO to the LUMO.

Cyclic Voltammograms. To experimentally estimate energy levels of HOMO, electrochemical measurements were carried out on selenazoles **13**−**15** and thiazole **17**. In all cases, reversible one-electron oxidation waves were observed at around $E^{1/2}_{ox}$ = +0.59 eV (vs F_c/F_c^+([nBu$_4$N]ClO$_4$/MeCN). Replacement of the sulfur atom in **17** with a selenium atom slightly reduced the oxidation potential (**14** vs **17**).

Finally, the energy levels of HOMO and LUMO derived from absorption and fluorescence spectroscopy, cyclic voltammetry, and DFT calculations are compared in Table 4. The experimental values of HOMO−LUMO band gaps derived from λ_{onset} and of the energy levels of HOMO derived from cyclic voltammograms were comparable to those obtained from TD-DFT and DFT calculations.

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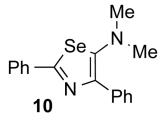
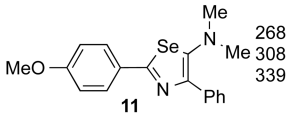
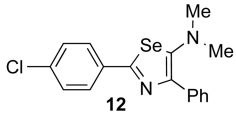
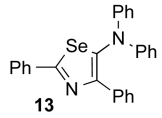
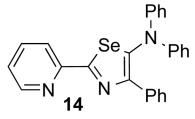
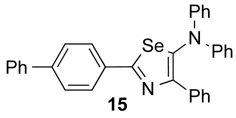
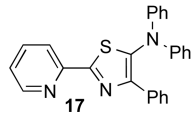
Table 3. Photophysical Properties and DFT Calculation of Selenazoles 10−15 and Thiazole 17

compound	λ_{abs}/nm[a]	λ_{onset}/nm[a]	λ_{em}/nm[a]	Φ_F[a]	calcd λ_{max}/nm (f)[b]	composition of band[b]
 **10**	278 326	-	470	0.029	334 (0.1754)	H → L, 69% H → L+1, 10%
 **11**	268 308 339	-	438	0.039	333 (0.2986)	H → L, 69%
 **12**	260 320 360	402	455	0.002	353 (0.2032)	H → L, 68% H-1 → L, 13%
 **13**	252 282 384	422	480	0.068	413 (0.1528)	H → L, 69% H-1 → L, 11%
 **14**	296 406	442	498	0.113	439 (0.1489)	H → L, 70%
 **15**	310 332 394	410	468	0.159	426 (0.2530)	H → L, 69% H-1 → L, 10%
 **17**	289 328 388	431	482	0.863	424 (0.2062)	H → L, 70%

[a]In $CHCl_3$, excited at 350 nm, $c = 10^{-5}$ M. [b]TD-DFT (TD/B3LYP/6-31G(d)) calculations were carried out with the use of optimized structures at B3LYP/6-31G(d).

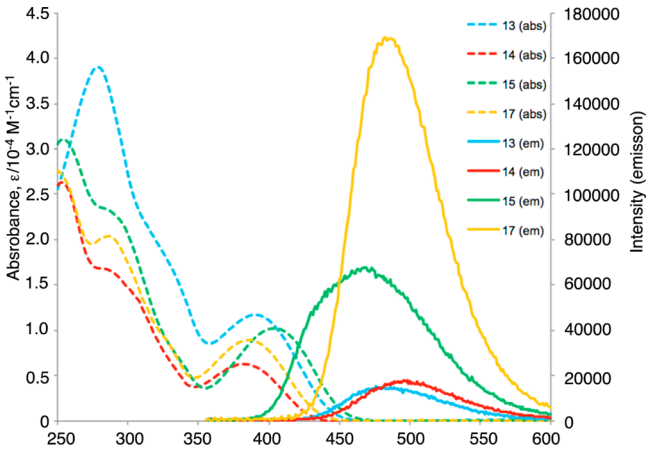


Figure 4. UV and fluorescent spectra of **13**−**15** and **17**.

CONCLUSION

N,*N*-Disubstituted selenazoles were synthesized, and their properties were demonstrated. The addition reaction of selenoamide dianions to thio- and selenoformamides followed by treatment with iodine gave 5-amino-2-selenazolines. Their further oxidation with iodine gave the corresponding 5-aminoselenazoles. On the basis of X-ray analyses and DFT calculations, the 5-amino groups on 5-aminoselenazoles were found to be highly deviated from the plane of the selenazolyl ring. The photophysical properties of 5-aminoselenazoles were elucidated by UV−visible and fluorescence spectroscopy. In the cyclic voltammograms of 5-*N*,*N*-diphenylaminoselenazoles, reversible one-electron oxidation was observed. The experimental and calculated values of the HOMO−LUMO band gaps and the energy levels of HOMO are self-consistent. Further studies on the reactivity of chalcogenoamide dianions and the properties of 5-aminochalcogenazoles and the application of their fluorescent properties are in progress.

EXPERIMENTAL SECTION

General Remarks. All reagents and solvents were purchased from commercial sources and were used without purification. ^{1}H NMR and ^{13}C NMR spectra were measured with tetramethylsilane and $CDCl_3$ as an internal standard, respectively. ^{77}Se NMR spectra were measured with Me_2Se as an external standard. All experiments were carried out under an argon atmosphere in dried glassware.

*N-(Phenylmethyl)benzenecarboselenoamide (**1a**).*[22] To a solution of *N*-phenylmethyl phenylamide (1.06 g, 5.0 mmol) in toluene (5.0 mL) were added elemental selenium (0.43 g, 5.5 mmol), dibenzylamine (1.06 mL, 5.5 mmol), and trichlorosilane (0.52 mL, 5.5 mmol), and the mixture was stirred for 3 h at 115 °C. The combined organic

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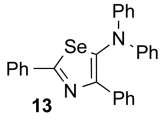
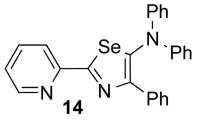
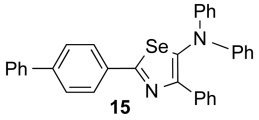
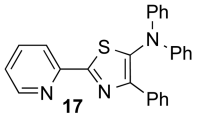
Table 4. Electrochemical Properties and HOMO−LUMO Energy Gaps of Selenazoles 13−15 and Thiazole 17

entry	compound	λ_{onset}/nm[a]	HOMO-LUMO band gap [eV]		$E^{1/2}_{ox}$/eV[d]	HOMO/eV	
			onset[b]	TD-DFT[c]		CV[e]	DFT[f]
1	 **13**	422	2.94	3.00	0.585	-5.39	-5.14
2	 **14**	442	2.81	2.82	0.604	-5.40	-5.11
3	 **15**	410	3.02	2.91	0.567	-5.37	-5.14
4	 **17**	432	2.87	2.92	0.642	-5.44	-5.09

[a] λ_{onset} are taken as the intersection of spectrum baseline and a tangent line to edge of the absorption band. [b] HOMO−LUMO energy gaps calculated from λ_{onset}. [c] HOMO−LUMO energy gaps calculated from TD-DFT (TD/B3LYP/6-31G(d)) calculations. [d] V vs F_c/F_c^+ in acetonitrile containing tetrabutylammonium perchlorate (Bu_4NClO_4, 0.1 M) as supporting electrolyte at a scan rate of 100 mV/s. Counter and working electrodes were made of Pt. Halfwave oxidation potentials are shown. [e] E_{HOMO} (eV) = −4.8 − $E^{1/2}_{ox}$, ref 23. [f] E_{HOMO} (eV) calculated from DFT calculations (B3LYP/6-31G(d)).

phase was washed with a saturated aqueous solution of NaOH and NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO_2, hexane:EtOAc = 10:1) to give **1a** (0.52 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.99 (d, J = 5.4 Hz, 2H), 7.33−7.48 (m, 8H), 7.73−7.76 (m, 2H), 8.20 (br, 1H).

*4-Methoxy-N-(phenylmethyl)benzenecarboselenoamide (**1b**).*[22] According to the synthetic procedure of **1a**, compound **1b** was prepared, and the crude material was purified by column chromatography (SiO_2, hexane:EtOAc = 10:1) to give **1b** (0.52 g, 85%) as an orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.00 (d, J = 4.9 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 7.25−7.40 (m, 8H), 7.77 (d, J = 8.8 Hz, 2H), 8.14 (br, 1H).

*4-Chloro-N-(phenylmethyl)benzenecarboselenoamide (**1c**).* To a solution of Woollins reagent (0.09 g, 0.17 mmol) in toluene (0.5 mL) was added *N*-phenylmethyl 4-chlorobenzamide (0.07 g, 0.27 mmol), and the mixture was stirred for 2 h at 130 °C. The resulting mixture was concentrated in vacuo. The crude material was purified by column chromatography (SiO_2, dichloromethane) to give **1c** (0.06 g, 71%) as an orange liquid. IR (KBr) 3084, 3061, 3025, 2920, 2836, 1949, 1877, 1811, 1602, 1495, 1453, 1254, 1174, 1027, 834, 747, 735, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (d, J = 5.4 Hz, 2H), 7.11−7.35 (m, 7H), 7.62 (d, J = 8.8 Hz, 1H), 7.74−7.76 (m, 1H), 8.07 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.9, 113.4, 126.7, 127.9, 128.2, 128.3, 128.6, 128.7, 140.0, 202.8; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 578.7; MS (EI) m/z 308 (M^+); HRMS (EI) Calcd for $C_{14}H_{12}ClNSe$: 308.9823; found: 308.9843.

*N-(Phenylmethyl)-2-pyridinecarboselenoamide (**1d**).* According to the synthetic procedure of **1c**, compound **1d** was prepared. The crude material was purified by column chromatography (SiO_2, dichloromethane) to give **1d** (0.09 g, 61%) as an orange solid. (mp 59−61 °C); IR (KBr) 3217, 3065, 3044, 3024, 2924, 1519, 1454, 1434, 1373, 1329, 1053, 1044, 913, 743, 733, 695, 686 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.04 (d, J = 5.4 Hz, 2H), 7.35−7.47 (m, 6H), 7.82−7.86 (m, 1H), 8.43 (d, J = 4.4 Hz, 1H), 8.82 (d, J = 7.8 Hz, 1H), 10.97 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.4, 126.1, 127.7, 128.2, 128.4, 128.9, 135.6, 137.3, 146.9, 153.0, 195.4; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 517.9; MS (EI) m/z 276 (M^+); HRMS (EI) Calcd for $C_{13}H_{12}N_2Se$: 276.0166; found: 276.0164.

*N-(Phenylmethyl)[1,1′-biphenyl]-4-carboselenoamide (**1e**).* According to the synthetic procedure of **1c**, compound **1e** was prepared. The crude material was purified by column chromatography (SiO_2, dichlorometane) to give **1e** (0.26 g, 75%) as an orange solid (mp 174−177 °C): IR (KBr) 3276, 3026, 2923, 1601, 1528, 1512, 1483, 1403, 1321, 1194, 1063, 911, 891, 841, 767, 752, 696, 687 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02 (d, J = 5.4 Hz, 2H), 7.36−7.47 (m, 8H), 7.57−7.60 (m, 4H), 7.85 (d, J = 8.8 Hz, 2H), 8.20 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.7, 127.0, 127.1, 127.2, 128.0, 128.4, 128.5, 128.9, 129.1, 135.4, 139.8, 143.2, 143.9, 203.7; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 637.3; MS (EI) m/z 351 (M^+); HRMS (EI) Calcd for $C_{20}H_{17}NSe$: 351.0526; found: 351.0523.

General Procedure for the Preparation of 2-Selenazolines. To a solution of selenoamide (1 equiv) in THF was added slowly 1.25 M solution of *n*-butyllithium in *n*-hexane (2 equiv) at 0 °C, and the mixture was stirred for 10 min at this temperature. To this was added thio- or selenoformamide (1 equiv) at 0 °C, and the mixture was stirred for 0.5−1.3 h at this temperature. To this was added iodine (1−2 equiv) at 0 °C, and the mixture was stirred for 2 h at 0 °C. The resulting mixture was poured into a saturated aqueous solution of $Na_2S_2O_3$ and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (SiO_2) to give the corresponding 2-selenazolines.

(4R,5S*)-4,5-Dihydro-N,N-dimethyl-2,4-diphenyl-5-selenazolamine (**4**).* According to the general procedure for selenazolines, compound **4** was prepared. The crude material was purified by column chromatography (SiO_2, hexane:EtOAc:Et_3N = 7:1:0.01) to give **4** (0.15 g, 91%) as an orange solid (mp 97−98 °C): IR (KBr) 2952, 2823, 1599, 1448 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.11 (s, 6H), 5.61 (d, J = 2.0 Hz, 1H), 5.67 (d, J = 2.0 Hz, 1H), 7.16−7.27 (m, 5H), 7.31−7.40 (m, 3H), 7.89 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.4, 86.5, 95.9, 126.3, 127.6, 128.5, 128.6, 129.1, 131.1, 136.1, 139.2, 168.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 291.2; MS (EI) m/z 330 (M^+); HRMS (EI) Calcd for $C_{17}H_{18}N_2Se$ (M^+) 330.0635, found: 330.0631.

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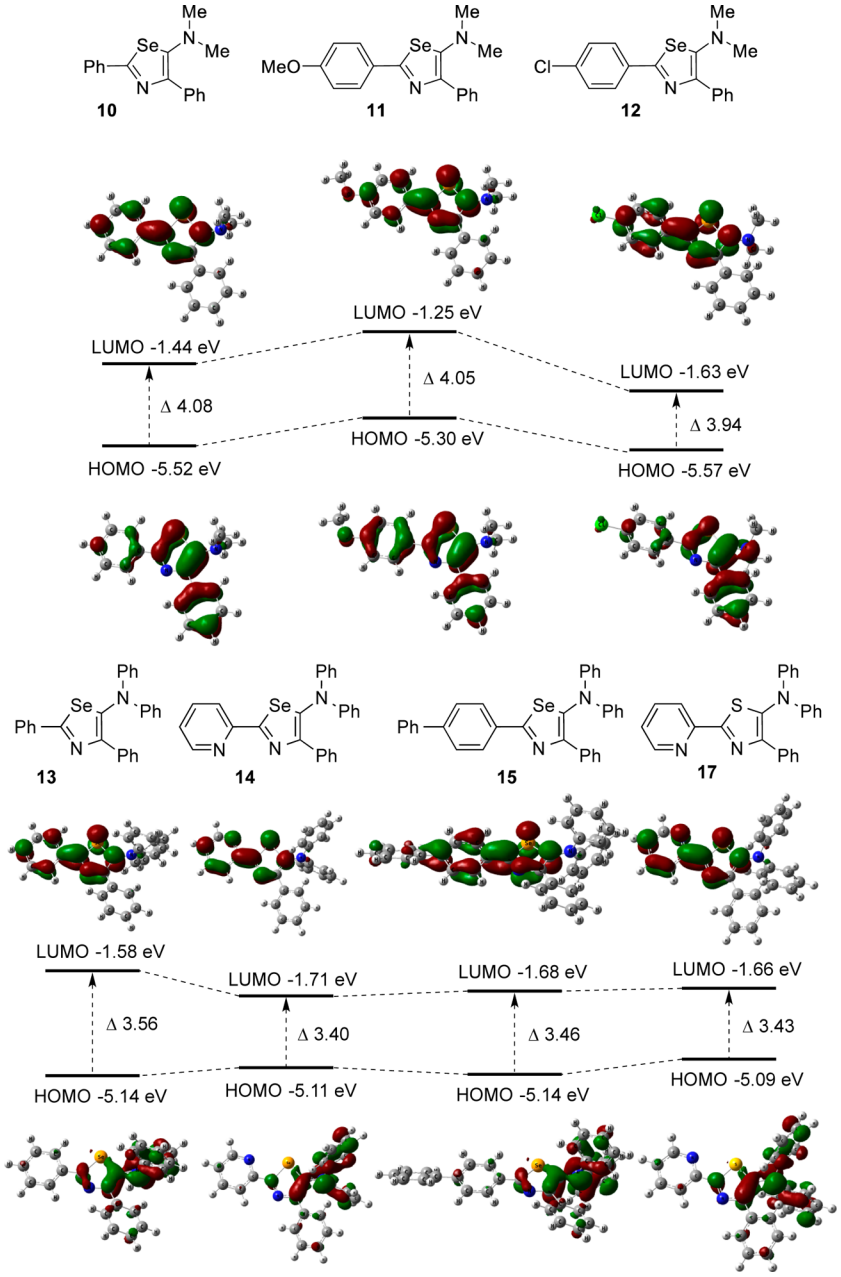

Figure 5. Molecular orbital plots and energy levels of HOMOs and LUMOs of **10**−**15** and **17**.

(4R,5S*)-4,5-Dihydro-N,N-dimethyl-2-(4-methoxyphenyl)-4-phenyl-5-selenazolamine (**5**).* According to the general procedure for selenazolines, compound **5** was prepared. The crude material was purified by column chromatography (SiO_2, hexane:EtOAc:Et_3N = 5:1:0.01) to give **5** (0.09 g, 51%) as an orange solid (mp 97−100 °C): IR (KBr) 1598, 1508, 1447, 1301 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.19 (s, 6H), 3.85 (s, 3H), 5.66 (d, J = 1.5 Hz, 1H), 5.72 (d, J = 1.4 Hz, 1H), 6.92−6.95 (m, 2H), 7.25−7.34 (m, 5H), 7.89−7.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.4, 55.4, 86.5, 95.8, 113.8, 126.4, 127.6, 128.6, 128.9, 130.8, 139.5, 162.0, 167.4; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 346.4; MS (EI) m/z 360 (M^+); HRMS (EI) Calcd for $C_{18}H_{20}N_2OSe$: 360.0741; found: 360.0736.

(4R,5S*)-4,5-Dihydro-N,N-dimethyl-2-(4-chlorophenyl)-4-phenyl-5-selenazolamine (**6**).* According to the general procedure for selenazolines, compound **6** was prepared. The crude material was purified by column chromatography (SiO_2, hexane:EtOAc = 10:1) to give **6** (0.085 g, 47%) as an orange oil: IR (KBr) 3082, 3060, 3027, 2949, 2861, 2930, 2788, 1601, 1485 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 6H), 5.63−5.69 (m, 2H), 7.19−7.25 (m, 5H), 7.34 (d, J = 8.3 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.5, 86.5, 96.7, 126.3, 127.8, 128.6, 128.7, 130.3, 134.7, 137.2, 139.0, 167.0; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 356.0; MS (EI) m/z 364 (M^+); HRMS (EI) Calcd for $C_{17}H_{17}ClN_2Se$: 364.0245; found: 364.0223.

(4R,5S*)-4,5-Dihydro-N,N,2,4-tetraphenyl-5-selenazolamine (**7**).* According to the general procedure for selenazolines, compound **7** was prepared. The crude material was purified by column chromatography (SiO_2, hexane:EtOAc:Et_3N = 30:1:0.01) to give **7** (0.213 g, 47%) as a yellow solid (mp 157−158 °C): IR (KBr) 3437, 1492, 1229, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.98 (d, J = 3.9 Hz, 1H), 6.57 (d, J = 3.9 Hz, 1H), 6.98−7.04 (m, 6H), 7.18−7.24 (m, 5H), 7.25−7.29 (m, 4H), 7.31 (t, J = 7.3 Hz, 2H), 7.38 (t, J = 7.3 Hz, 1H), 7.67 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.4, 84.3, 123.2, 123.8, 126.5, 127.8, 128.4, 128.7, 128.8, 129.3, 131.0, 136.1, 139.6, 145.7, 167.8; ^{77}Se NMR (76 MHz, $CDCl_3$) δ −114.0; MS (EI) m/z 454 (M^+); HRMS (EI) Calcd for $C_{27}H_{22}N_2Se$ (M^+) 454.0948, found: 454.0971.

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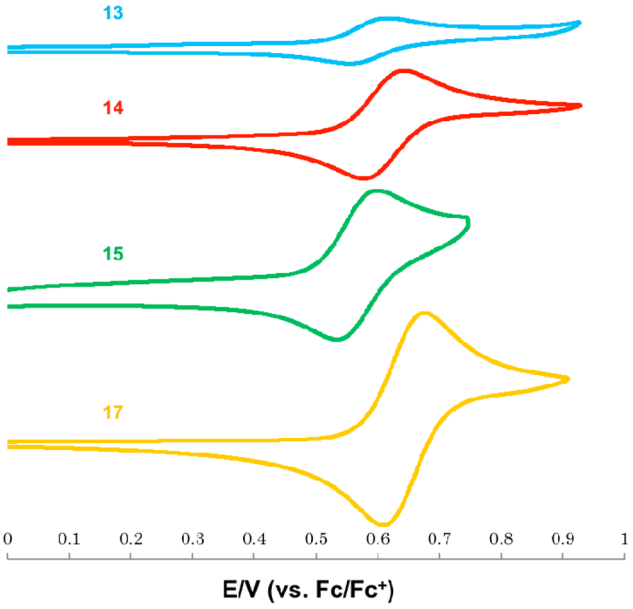

Figure 6. Cyclic voltammogram of **13**−**15** and **17**.

(4R,5S*)-4,5-Dihydro-2-(2-pyridyl)-N,N,4-triphenyl-5-selenazolamine (**8**).* According to the general procedure for selenazolines, compound **8** was prepared. The crude material was purified by column chromatography (SiO_2, hexane:EtOAc = 8:1) to give **8** (0.14 g, 61%) as a brown oil: IR (KBr) 3058, 2923, 2854, 1687, 1588, 1493 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.06 (d, J = 4.4 Hz, 1H), 6.59 (d, J = 4.4 Hz, 1H), 7.05−7.07 (m, 5H), 7.17 (d, J = 7.8 Hz, 1H), 7.27−7.34 (m, 10H), 7.69−7.73 (m, 1H), 7.92 (d, J = 7.8 Hz, 1H), 8.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.5, 84.9, 120.7, 121.9, 123.4, 123.7, 125.4, 126.6, 127.1, 127.9, 128.8, 129.0, 129.3, 130.3, 136.4, 139.8, 146.0, 149.4, 153.2, 171.2; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 540.9; MS (EI) m/z 455 (M^+); HRMS (EI) Calcd for $C_{26}H_{21}N_3Se$: 455.0901; found: 455.0913.

(4R,5S*)-2-[1,1′-Biphenyl]-4-yl-4,5-dihydro--N,N,4-triphenyl-5-selenazolamine (**9**).* According to the general procedure for selenazolines. The crude material was purified by column chromatography (SiO_2, hexane:EtOAc = 25:1) to give **9** (0.12 g, 44%) as a brown oil: IR (KBr) 3055, 3026, 1600, 1490 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.07 (d, J = 4.4 Hz, 1H), 6.66 (d, J = 4.4 Hz, 1H), 7.07−7.08 (m, 6H), 7.27−7.38 (m, 10H), 7.44−7.46 (m, 2H), 7.61 (d, J = 7.8 Hz, 4H), 7.82 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.5, 84.4, 123.3, 123.9, 125.7, 126.5, 126.6, 126.9, 127.1, 127.8, 127.9, 128.7, 128.8, 129.3, 135.0, 139.6, 140.1, 143.9, 145.8; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 530.6; MS (EI) m/z 530 (M^+); HRMS (EI) Calcd for $C_{33}H_{26}N_2Se$: 530.1261; found: 530.1274.

Preparation of (4R,5S*)-4,5-Dihydro-2-(2-pyridyl)-N,N,4-triphenyl-5-thiazolamine.* To a solution of *N*-phenylmethyl-2-pyridinecarbothioamide (0.23 g, 1.0 mmol) in THF (3.0 mL) was added slowly a 1.25 M solution of *n*-butyllithium in *n*-hexane (1.28 mL, 2.0 mmol) at 0 °C, and the mixture was stirred for 10 min at this temperature. To this was added *N*,*N*-diphenylthioformamide (0.21 g, 1.0 mmol) at 0 °C, and the mixture was stirred for 20 min at this temperature. To this was added iodine (0.76 g, 3.0 mmol) at 0 °C, and the mixture was stirred for 3 h at room temperature. The resulting mixture was poured into a saturated aqueous solution of $Na_2S_2O_3$ and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude material was purified by column chromatography (SiO_2, hexane:EtOAc:Et_3N = 30:1:0.01) to give thiazoline (0.27 g, 66%) as a brown liquid: IR (KBr) 3060, 2956, 2930, 2871, 2246, 1950, 1874, 1686, 1591 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.02 (d, J = 4.4 Hz, 1H), 6.30 (d, J = 4.4 Hz, 1H), 7.02−7.06 (m, 6H), 7.23−7.34 (m, 10H), 7.69 (ddd, J = 1.7 Hz, J = 1.7 Hz, J = 1.7 Hz, 1H), 7.97 (d, J = 7.0 Hz, 1H), 8.65−8.67 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 80.1, 82.9, 121.4, 123.6, 123.7, 125.0, 126.0, 126.4, 126.8, 126.9, 127.9, 128.2, 128.8, 129.1, 129.3, 129.6, 136.5, 145.8, 149.2, 161.7; MS (EI) m/z 407(M^+); HRMS (EI) Calcd for $C_{26}H_{21}N_3S$: 407.1456, found: 407.1431.

General Procedure for Preparation of Selenazoles. To a solution of selenazoline (1 equiv) in THF was added iodine (2 equiv) at room temperature, and the mixture was stirred for 2 h at this temperature. The resulting mixture was poured into a saturated aqueous solution of $Na_2S_2O_3$ and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (SiO_2) to give the corresponding selenazoles.

*N,N-Dimethyl-2,4-diphenyl-5-selenazolamine (**10**).* According to the general procedure of selenazoles, compound **10** was prepared. The crude material was purified by column chromatography (SiO_2, hexane:EtOAc:Et_3N = 10:1:0.01) to give **10** (0.09 g, 46%) as a yellow oil: IR (KBr) 3487, 2943, 2859, 1530, 1489 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.63 (s, 6H), 7.17−7.39 (m, 6H), 7.74−7.88 (m, 2H), 8.04−8.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.1, 125.7, 126.5, 126.9, 128.3, 128.8, 129.5, 135.6, 137.2, 143.3, 160.2, 164.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 654.6; MS (EI) m/z 328 (M^+); HRMS (EI) Calcd for $C_{17}H_{16}N_2Se$: 328.0479; found: 328.0466.

*N,N-Dimethyl-2-(4-methoxyphenyl)-4-phenyl-5-selenazolamine (**11**).* According to the general procedure of selenazoles, compound **11** was prepared. The crude material was purified by column chromatography (SiO_2, hexane:EtOAc = 25:1) to give **11** (0.02 g, 22%) as a pale yellow solid (mp 82−86 °C): IR (KBr) 3046, 3013, 2983, 2938, 2856, 2834, 2782, 1605, 1519, 1492 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.71 (s, 6H), 3.85 (s, 3H), 6.90−6.92 (m, 2H), 7.25−7.29 (m, 1H), 7.38−7.42 (m, 2H), 7.82−7.84 (m, 2H), 8.17−8.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.1, 55.4, 113.8, 114.1, 114.7, 127.1, 128.2, 129.0, 129.3, 129.7, 134.0, 134.7, 161.2; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 629.2; MS (EI) m/z 358 (M^+); HRMS (EI) Calcd for $C_{18}H_{18}N_2OSe$: 358.0584; found: 358.0560.

*N,N-Dimethyl-2-(4-chlorophenyl)-4-phenyl-5-selenazolamine (**12**).* According to the general procedure of selenazoles, compound **12** was prepared. The crude material was purified by column chromatography (SiO_2, hexane:EtOAc = 30:1) to give **12** (0.03 g, 41%) as a yellow oil: IR (KBr) 3051, 2987, 2944, 2795, 1527, 1487 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.73 (s, 6H), 7.25−7.28 (m, 1H), 7.34−7.42 (m, 4H), 7.81 (d, J = 8.3 Hz, 2H), 8.13 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.8, 48.3, 126.7, 127.2, 127.4, 127.7, 127.9, 128.6, 129.3, 135.3, 135.4, 143.2, 162.5; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 643.6; MS (EI) m/z 362 (M^+); HRMS (EI) Calcd for $C_{17}H_{15}ClN_2$ Se: 362.0089; found: 362.0079.

*N,N,2,4-Tetraphenyl-5-selenazolamine (**13**).* According to the general procedure of selenazoles, compound **13** was prepared. The crude material was purified by column chromatography (SiO_2, hexane:EtOAc:Et_3N = 10:1:0.01) to give **13** (0.16 g, 84%) as an orange yellow solid (mp 118−119 °C): IR (KBr) 2962, 1587, 1487, 1287 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.87 (t, J = 6.8 Hz, 2H), 7.04−7.15 (m, 12H), 7.28 (d, J = 2.0 Hz, 1H), 7.29 (d, J = 2.0 Hz, 1H), 7.80 (d, J = 6.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.6, 123.1, 126.7, 127.7, 127.8, 128.1, 128.8, 129.1, 130.1, 134.1, 136.8, 146.8, 147.6, 150.3, 170.0; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 692.5; MS (EI) m/z 452 (M^+); HRMS (EI) Calcd for $C_{27}H_{20}N_2Se$ (M^+) 452.0792, found: 452.0816.

*2-(2-Pyridyl)-N,N,4-triphenyl-5-selenazolamine (**14**).* According to the general procedure of selenazoles, compound **14** was prepared. The crude material was purified by column chromatography (SiO_2, hexane:EtOAc = 15:1) to give **14** (0.043 g, 46%) as a yellow solid (mp 85−88 °C): IR (KBr) 3049, 1583, 1485, 1472 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.96−6.99 (m, 2H), 7.14−7.22 (m, 11H), 7.32−7.33 (m, 1H), 7.76−7.84 (m, 3H), 8.22 (d, J = 7.8 Hz, 1H), 8.54 (d, J = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.5, 121.9, 123.1, 124.4, 127.6, 127.7, 128.0, 129.0, 129.3, 134.4, 136.8, 147.0, 149.5, 150.7, 153.5, 170.9; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 706.3; MS (EI) m/z 453 (M^+); HRMS (EI) Calcd for $C_{26}H_{19}N_3Se$: 453.0744; found: 453.0727.

*2-[1,1′-Biphenyl]-4-yl-N,N,4-triphenyl-5-selenazolamine (**15**).* According to the general procedure of selenazoles, compound **15** was prepared. The crude material was purified by column chromatography

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(SiO_2, hexane:EtOAc = 15:1) to give **15** (0.043 g, 46%) as a yellow solid (mp 148−152 °C): IR (KBr) 3024, 2920, 1589, 1487 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.05−7.07 (m, 2H), 7.22−7.30 (m, 12H), 7.43−7.53 (m, 2H), 7.69−7.71 (m, 4H), 7.96 (d, J = 7.8 Hz, 2H), 8.03 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.1, 121.7, 123.2, 123.5, 127.0, 127.2, 127.5, 127.8, 127.9, 128.1, 128.5, 128.9, 129.1, 129.5, 140.2, 142.9, 146.9, 147.6, 188.8; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 678.1; MS (EI) m/z 528 (M^+); HRMS (EI) Calcd for $C_{33}H_{24}N_2Se$: 528.1105; found: 528.1122.

*2-(2-Pyridyl)-N,N,4-triphenyl-5-thiazolamine (**17**).* To a solution of 2-(2-pyridyl)-4-phenyl-5-diphenylaminothiazoline (0.38 g, 0.94 mmol) in THF (8.0 mL) was added iodine (0.48 g, 1.88 mmol) at room temperature, and the mixture was stirred for 2 h under reflux. The resulting mixture was poured into a saturated aqueous solution of $Na_2S_2O_3$ and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, hexane:EtOAc = 30:1) to give **17** (0.18 g, 48%) as a yellow solid (mp 92−97 °C): IR (KBr) 3050, 1586, 1565, 1523, 1488 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.98 (t, J = 7.3 Hz, 2H), 7.12−7.14 (m, 4H), 7.19−7.31 (m, 8H), 7.80 (ddd, J = 2.0 Hz, J = 2.0 Hz, J = 1.5 Hz, 1H), 7.91−7.94 (m, 2H), 8.28 (d, J = 7.8 Hz, 1H), 8.56 (d, J = 4.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 119.3, 121.7, 123.1, 124.4, 127.3, 127.9, 128.1, 129.2, 133.4, 136.9, 142.6, 146.5, 148.9, 149.3, 151.4, 163.8; MS (EI) m/z 405 (M^+); HRMS (EI) Calcd for $C_{26}H_{19}N_3S$: 405.1300, found: 405.1320.

■ ASSOCIATED CONTENT

Supporting Information

X-ray data including a cif file, theoretical data, and ^1H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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