5-N-Arylaminothiazoles as Highly Twisted Fluorescent Monocyclic Heterocycles: Synthesis and Characterization

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Ⓢ *Supporting Information*

ABSTRACT: A series of 5-N-arylaminothiazoles was prepared by reacting thioamide dianions derived from secondary thioamides with thioformamides, followed by sequential oxidation with iodine. X-ray analyses demonstrated that they adopt structures that are highly twisted from planar conformations. Their orientations were tuned by the steric and/or electronic interactions of the substituents at their 2-, 4-, and 5-positions. The 5-aminothiazoles exhibited a range of fluorescent emissions, from blue to orange. Although the absorption spectra were independent of the polarity of the solvent, fluorescent emissions were influenced by the polarity of the solvent: in more polar solvents, the emissions were red-shifted. These phenomena were examined in terms of Lippert−Mataga plots and the change in the dipole moment between the ground and excited states. They also exhibited emissions in the solid state, again from blue to orange. Cyclic voltammetry of the 5-aminothiazoles showed reversible waves of one-electron oxidation. The half-potential of the oxidation was reduced by the introduction of electron-donating groups to the phenyl groups on the nitrogen atom at the 5-position. DFT calculations were carried out to determine the energy levels of the HOMO and LUMO. Finally, the results of TG-DTA showed that they are thermally stable.
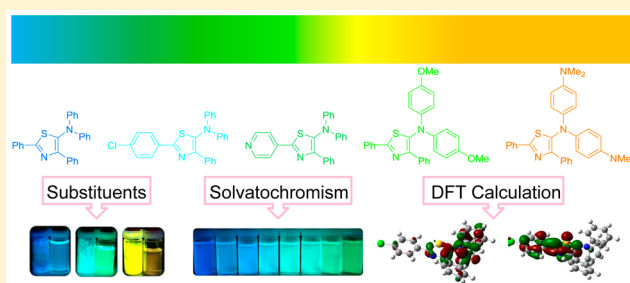
INTRODUCTION

Monocyclic 1,3-azoles, such as imidazoles, oxazoles, and thiazoles, are potential motifs for providing fluorescent molecules that can be used in OLED[1] and chemosensors.[2] Unlike condensed azoles, monocyclic 1,3-azoles possess a certain level of flexibility. As a result, the efficiency and wavelength range of fluorescence appear to be low and narrow, respectively, with single monocyclic units. However, those compounds possess three carbon atoms to which a wide variety of substituents can be attached. When these substituents are bulky and aromatic, they strongly affect the conformation of the whole molecule, since the core structural moieties are rather small compared with condensed 1,3-azoles. Due to the proximity of the introduced substituents in the core structures, they cannot be oriented in the same plane, but, instead, they adopt twisted three-dimensional structures.[3] This feature may give rise to their unique fluorescent properties. Furthermore, the introduction of electron-donating and -attracting groups to the appropriate positions of monocyclic heteroaromatic compounds provides D−A molecules.[4] Therefore, increasing attention has been paid to fluorescent 1,3-imidazoles,[5] oxazoles,[6] and thiazoles.[7] In this regard, we recently developed 5-N,N-diarylaminothiazoles[8] and -selenazoles[9] for the first time in a series of studies on the chemistry of C=S[10] and C=Se[11]

containing compounds. These are rare examples[12] of 1,3-azoles with diarylamino groups attached to the 5-position of 1,3-azoles. Their synthesis has been achieved with an unprecedented transition metal-free coupling reaction between secondary thioamides and thioformamides. This method is in marked contrast to the established method for preparing thiazoles using primary thioamides, which is known as Hantzsch thiazole synthesis.[13] The resulting 5-aminothiazoles adopt highly deviated conformations, but they show strong blue fluorescence. Due to the facile synthetic methods and the ready availability of the starting materials, a variety of 5-N-arylaminothiazoles can be obtained. We report herein the synthesis and characteristic photophysical, electrochemical, and thermal properties of a series of 5-N-arylaminothiazoles.

RESULTS AND DISCUSSION

Syntheses. For the synthesis of a 5-aminothiazole library, 5-amino-2-thiazolines were prepared by reacting secondary thioamides **1** with thioformamides **3**. The results are summarized in Table 1. First, thioamide dianion **2a**[14] was generated from secondary thioamide **1a** by treatment with *n-*

Table 1. Synthesis of 5-Amino-2-thiazolines 4−24[a]

entry	1	3	product	yield(%)[b]	entry	1	3	product	yield(%)[b]
1	Ar = Ar' = Ph **1a**	R = R' = Ph **3a**	**4**	97	12	Ar = 4-Py Ar' = Ph **1d**	R = Bn R' = Ph **3c**	**15**	64
2	Ar = 4-ClC₆H₄ Ar' = Ph **1b**		**5**	63	13	Ar = Ar' = Ph **1a**	R = 1-adamantyl R' = Ph **3d**	**16**	4[c,d]
3	Ar = 2-Py Ar' = Ph **1c**		**6**	66				**17**	19[c]
4	Ar = 4-Py Ar' = Ph **1d**		**7**	80	14	Ar = 4-ClC₆H₄ Ar' = Ph **1b**		**18**	50
5	Ar = 4-PhC₆H₄ Ar' = Ph **1e**		**8**	60	15	Ar = 2-Py Ar' = Ph **1c**		**19**	31
6	Ar = Ph Ar' = C₆H₄Me-2 **1f**		**9**	50	16	Ar = Ar' = Ph **1a**	R, R' = 4-MeC₆H₄ **3e**	**20**	71
7	Ar = Ph Ar' = C₆H₄OMe-2 **1g**		**10**	92	17	Ar = 4-PhC₆H₄ Ar' = Ph **1e**		**21**	72
8	Ar = 4-ClC₆H₄ Ar' = C₆H₄OMe-2 **1h**		**11**	34	18	Ar = Ar' = Ph **1a**	R, R' = C₆H₄OMe-4 **3b**	**22**	62
9	Ar = Ph Ar' = CH=CHPh **1i**		**12**	30	19	Ar = Ar' = Ph **1a**	R, R' = C₆H₄NMe₂-4 **3f**	**23**	58
10	Ar = 4-PhC₆H₄ Ar' = Ph **1e**	R = Bn R' = Ph **3c**	**13**	40	20	Ar = 4-PhC₆H₄ Ar' = Ph **1e**		**24**	66
11	Ar = 2-Py Ar' = Ph **1c**		**14**	58					

[a]The reaction was carried out as follows, unless otherwise noted: To a solution of thioamide **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 thioformamide **3** (1.0 equiv), and the mixture was stirred. To this was added iodine (2.0 or 3.0 equiv), and the mixture was stirred. [b]Isolated yields. [c]The reaction of **1a** and **3d** gave thiazole **18** as the main product in 19% yield. [d]Not isolated.

BuLi (2 equiv) at 0 °C. As an electrophile, N,N-diphenyl thioformamide (**3a**) was added to the reaction mixture, followed by the addition of iodine (3 equiv) to give *trans*-5-diphenylamino-2-thiazoline **4** in 97% yield (entry 1). A similar reaction enabled the introduction of a range of substituents to
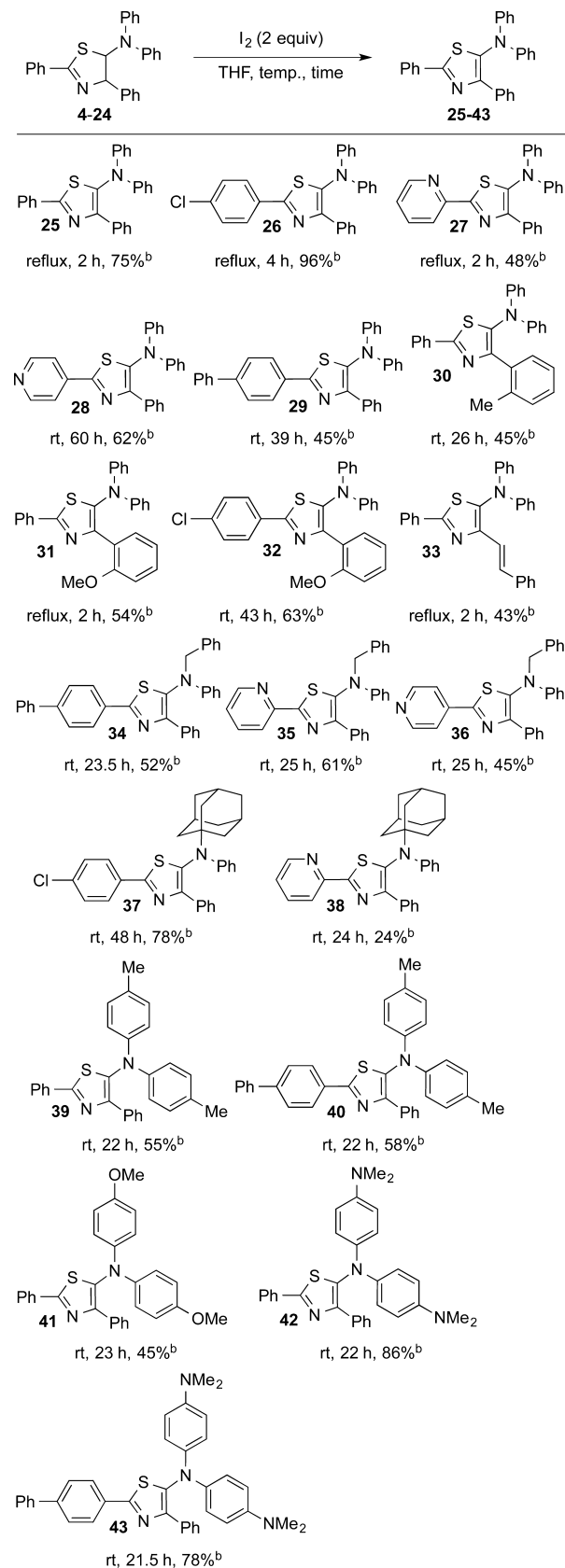
the 2-, 4-, and 5-positions. The reactions of thioamides **1b−e** and thioformamide **3a** gave 2-thiazolines **5−8** having 4-chlorophenyl-, 2-pyridyl-, 4-pyridyl-, and biphenyl groups at the 2-position in good yields (entries 2−5). A variety of aromatic substituents was introduced to the 4-positions with

the use of N-arylmethyl thioamides **1f–1h** to form **9–11** (entries 6–8). 4-Styryl-2-thiazoline **12** was obtained with N-cinnamyl thioamide **1i** and *s*-BuLi to generate the corresponding dianion **2i** (entry 9). Compounds with a wide variety of substituents on the nitrogen atoms were prepared. The use of N-benzyl, N-phenyl thioformamide (**3b**) led to 2-thiazolines **13–15** (entries 10–12). An adamantyl group on the nitrogen atom was successfully introduced with thioformamide **3c** to give **17–18** (entries 13–15). However, in the reaction of thioamide **1a**, desired product **16** was scarcely obtained, and, instead, thiazole **17**, probably formed by the oxidation of **16**, was isolated in 19% yield (entry 13). In contrast, the reaction of thioamide dianions, generated from **1b** and **1c** with *n*-BuLi, with **3d** yielded the corresponding 2-thiazolines **18** and **19** in respective yields of 50 and 31% (entries 14 and 15). Finally, 5-N-arylamino-2-thiazolines **20–24** with electron-donating groups, such as 4-methyl-, 4-methoxy-, and 4-dimethylamino-phenyl groups, on the nitrogen atom at the 5-position were also obtained in 58–72% yields (entries 16–20).

Oxidation of the resulting 2-thiazolines **4–15** and **18–24** was carried out with iodine as an oxidant (Table 2). The time required for the reaction to run to completion was dependent on the substituents attached to the thiazole rings. The reaction was then monitored by TLC. In some cases, the reaction under reflux in THF gave the desired products in better yields (e.g., thiazoles **31** and **33**). However, the oxidation of some 2-thiazolines at higher temperatures gave complex mixtures that included the desired thiazoles. Even so, all of the 2-thiazolines were converted to the corresponding 5-aminothiazoles in low to high yields. In particular, with our synthetic methods, a range of unprecedented 5-N-arylamino-2-thiazolines and -thiazoles with electron-donating and -withdrawing groups was provided. Additionally, fluorescent emission by all of the 5-N-arylaminothiazoles was visually confirmed under UV light.

Molecular Structures. The structures of thiazoles **17**, **29**, **32**, **33**, **35**, and **42** were determined by X-ray analyses. Representative bond lengths and torsion angles are summarized in Table 3. Their molecular structures are shown in Figure 1.

In all cases, amino groups at the 5-position are twisted from the thiazole rings. The torsion angles at the 2-, 4-, and 5-positions (i.e., S1–C2–C6–C7, N3–C4–C8–C9, and S1–C5–N10–C11) were sensitive to the substituents at these positions, even if there appears to be almost no inter- and intramolecular interactions between the substituents at the 2- and 5-positions. The torsion angles of S1–C5–N10–C11 were affected by the substituents at the 2-position. In particular, the introduction of a biphenyl group to the 2-position deviated the torsion angle of S1–C5–N10–C11 to almost 90°, as in **29**. In this case, the phenyl group at the 4-position also deviated from the thiazole ring by more than 30°. The 2-methoxyphenyl group at the 4-position in **32** was deviated from the thiazolyl ring. It was oriented close to the diphenylamino group, but it did not influence the torsion angle of N3–C4–C8–C9 (33.0(3)°) in **32**, which was nearly the same as that in **29** (34.1(3)°). In thiazole **33** with an *E*-2-phenylethenyl group, the substituent at the 2-position was nearly in the same plane as that of the thiazole ring. The deviation of a diphenylamino group at the 5-position in **33** was slightly smaller than those in other thiazoles (49.0(3)°). The nitrogen atom in the pyridyl group in **35** was located close to the sulfur atom, and the pyridine ring was nearly in the same plane as that of the thiazole ring. Likewise, the deviation of the phenyl group on the nitrogen atom in **35** was slightly smaller than those in **17**, **29**,

Table 2. Synthesis of 5-Aminothiazoles 25–43[a]

25 Ph–thiazole–N(Ph)₂, reflux, 2 h, 75%[b]

26 Cl-C₆H₄–thiazole–N(Ph)₂, reflux, 4 h, 96%[b]

27 2-pyridyl–thiazole–N(Ph)₂, reflux, 2 h, 48%[b]

28 4-pyridyl–thiazole–N(Ph)₂, rt, 60 h, 62%[b]

29 biphenyl–thiazole–N(Ph)₂, rt, 39 h, 45%[b]

30 Ph–thiazole(4-(2-Me-C₆H₄))–N(Ph)₂, rt, 26 h, 45%[b]

31 Ph–thiazole(4-(2-MeO-C₆H₄))–N(Ph)₂, reflux, 2 h, 54%[b]

32 Cl-C₆H₄–thiazole(4-(2-MeO-C₆H₄))–N(Ph)₂, rt, 43 h, 63%[b]

33 Ph–thiazole(4-CH=CH-Ph)–N(Ph)₂, reflux, 2 h, 43%[b]

34 biphenyl–thiazole–N(CH₂Ph)(Ph), rt, 23.5 h, 52%[b]

35 2-pyridyl–thiazole–N(CH₂Ph)(Ph), rt, 25 h, 61%[b]

36 4-pyridyl–thiazole–N(CH₂Ph)(Ph), rt, 25 h, 45%[b]

37 Cl-C₆H₄–thiazole–N(adamantyl)(Ph), rt, 48 h, 78%[b]

38 2-pyridyl–thiazole–N(adamantyl)(Ph), rt, 24 h, 24%[b]

39 Ph–thiazole–N(4-Me-C₆H₄)₂, rt, 22 h, 55%[b]

40 biphenyl–thiazole–N(4-Me-C₆H₄)₂, rt, 22 h, 58%[b]

41 Ph–thiazole–N(4-MeO-C₆H₄)₂, rt, 23 h, 45%[b]

42 Ph–thiazole–N(4-NMe₂-C₆H₄)₂, rt, 22 h, 86%[b]

43 biphenyl–thiazole–N(4-NMe₂-C₆H₄)₂, rt, 21.5 h, 78%[b]

[a]The reaction was carried out as follows, unless otherwise noted: To a solution of thiazoline **4–24** (1.0 equiv) in THF was added iodine, and the mixture was stirred. [b]Isolated yields.

Table 3. Dihedral Angles and Bond Lengths of Thiazoles 18, 29, 32, 33, 36, and 42

		dihedral angles			bond lengths			
	thiazole	S1–C2–C6–C7	N3–C4–C8–C9	S1–C5–N10–C11	C2–C6	C4–C8	C5–N10	S1–C2
18	R^1, R^2, R^4 = H R^3 = Admanthyl	8.5(5)	10.3(5)	86.7(3)	1.469(5)	1.481(4)	1.408(4)	1.726(4)
29	R^1, R^3 = Ph R^2, R^4 = H	13.6(3)	**34.1(3)**	**92.3(2)**	1.471(3)	1.485(3)	**1.413(3)**	1.721(2)
32	R^1 = Cl R^2 = OMe R^3 = Ph R^4 = H	22.7(4)	**33.0(3)**	62.0(3)	**1.457(3)**	1.470(3)	1.392(3)	1.726(3)
33	Styryl	**0.3(3)**	5.9(4)	**49.0(3)**	1.475(4)	**1.446(4)**	1.398(3)	1.737(3)
35	2-2Py 5-BnPh	**1.6(8)**	31.4(8)	57.3(6)	1.472(7)	1.480(9)	1.398(7)	1.713(6)
42	R^1, R^2 = H R^3 = $C_6H_4NMe_2$-4 R^4 = NMe_2	21.1(2)	21.4(2)	61.3(2)	1.471(2)	1.475(2)	1.394(2)	1.733(1)
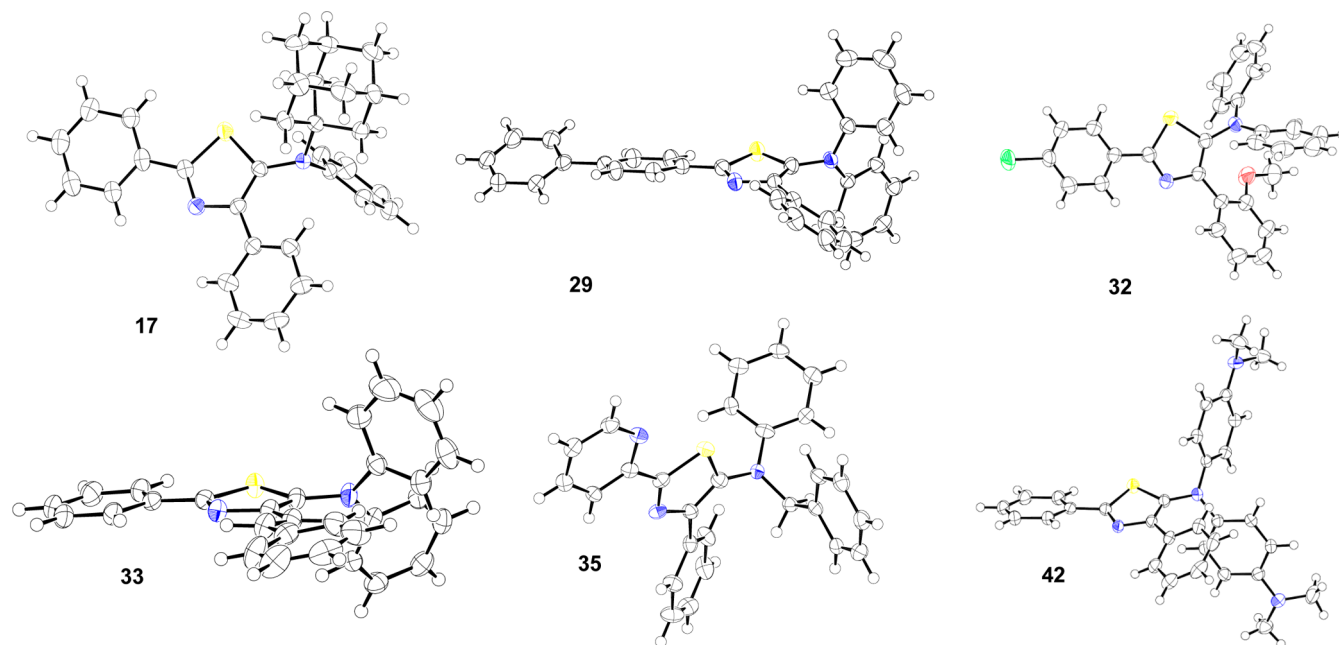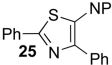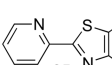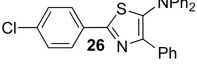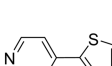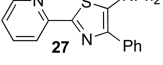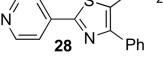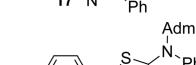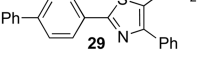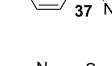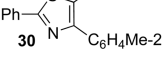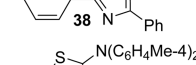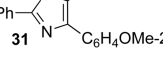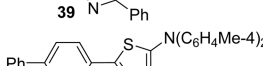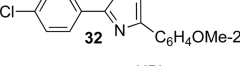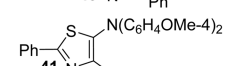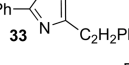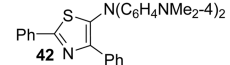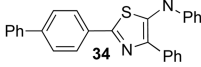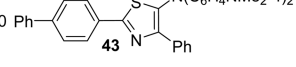
Figure 1. Molecular structures of (a) **17**, (b) **29**, (c) **32**, (d) **33**, (e) **35**, and (f) **42**. Ellipsoids are drawn at 50% probability.

32, and **42**. On the other hand, the phenyl group at the 4-position in **35** (1.6(8)°) was deviated from the thiazole ring by more than 30°. Finally, the introduction of Me_2N groups on the phenyl ring attached to the nitrogen atom at the 5-position also influenced the deviation of the substituents at the 2- and 4-positions, as shown in **42**. These X-ray analysis results of the 5-aminothiazoles clearly show that they adopt twisted structures in the ground state. Hence, the fluorescence shown below does not follow a twisted intramolecular charge transfer mechanism,

in which fluorescent molecules with planar structures in the ground state twist to deviated structures in excited states.[15]

Electronic Absorption and Fluorescence Spectroscopy. The photophysical properties of 5-aminothiazoles were examined. Table 4 shows their UV−visible and fluorescence spectra in $CHCl_3$ solutions. All of the compounds exhibited strong absorption bands from 249 to 420 nm depending on the substituents. Generally, electron-donating groups at the 5-positions and electron-withdrawing groups at the 2-positions shifted the absorptions and emissions to longer wavelengths.

Table 4. UV−Vis and Fluorescence Spectra of Thiazoles 25−43[a]

entry	Thiazole	UV-vis λ$_{abs}$ (nm)	log ε	fluorescence λ$_{em}$ (nm)	Φ$_F$	Stokes shift (cm⁻¹) [nm]	entry	Thiazole	UV-vis λ$_{abs}$ (nm)	log ε	fluorescence λ$_{em}$ (nm)	Φ$_F$	Stokes shift (cm⁻¹) [nm]
1	25	249 286 367	4.57 4.41 4.02	463	0.43	5650 [96]	11	35	288 322 378	4.13 4.04 3.78	471	0.39	5224 [93]
2	26	256 281 371	4.62 4.50 4.05	474	0.56	5860 [103]	12	36	298 320 378	4.05 3.91 3.68	479	0.23	5578 [101]
3	27	289 328 388	4.33 3.99 4.00	**482**	**0.86**	5026 [96]	13	17	288 304 **334**	4.12 4.07 3.97	**471**	0.04	**8709 [137]**
4	28	288 328 394	4.34 3.97 3.98	**492**	**0.80**	5056 [98]	14	37	286 318 **342**	4.15 4.11 4.03	**471**	0.06	**8008 [129]**
5	29	310 332 378	4.39 4.18 4.02	472	0.44	5269 [94]	15	38	278 320 **354**	4.15 3.97 3.95	**476**	0.10	**7240 [122]**
6	30	294 370	4.33 3.93	461	0.63	5335 [91]	16	39	288 322 376	4.29 3.92 3.75	474	0.44	5498 [98]
7	31	296 **378**	4.32 4.06	461	0.50	4763 [83]	17	40	312 336 **388**	4.43 4.19 4.07	**488**	0.51	5281 [100]
8	32	296 **384**	4.38 4.16	468	0.61	4674 [84]	18	41	292 **388**	4.47 3.87	**507**	0.21	6049 [119]
9	33	292 366	4.48 4.16	466	0.03	5863 [100]	19	42	304 342 **412**	4.44 4.02 3.74	**554**	0.01	6221 [142]
10	34	272 326 360	4.70 4.30 4.02	468	0.23	6410 [108]	20	43	272 312 420	4.65 4.53 3.74	509	0.01	4163 [89]

[a]In CHCl₃, c = 10⁻⁵ M, excited at 350 nm. Qunine sulfate was used as a reference for Φ$_F$.

The longest wavelengths of N,N-diphenylaminothiazoles 25−33 are in the range of 366−394 nm (entries 1−9). The replacement of an aromatic substituent at the 2-position with a 2- or 4-pyridyl group shifted the wavelengths from 367 to 388 and 394 nm, respectively (25 vs 27 and 28) (entries 1, 3, and 4). The introduction of chlorine or a phenyl group to the para-position of the phenyl group at the 2-position slightly shifted the longest wavelengths to a longer region by 4 and 11 nm (25 vs 26 and 29) (entries 1, 2, and 5). The methoxy group at the ortho-position of the phenyl group at the 4-position also affected the wavelengths by ca. 12 nm (25 vs 31 and 26 vs 32) (entries 1, 7, 2, and 8). Notably, replacement of the phenyl group on the nitrogen atom with an alkyl substituent showed a hypsochromic effect for the longest wavelengths (entries 10−15). In particular, those of N-adamantyl thiazoles 17, 37, and 38 were observed at 344 ± 10 nm (entries 13−15). Thiazoles 39−43, which have electron-donating groups, such as methyl, methoxy, and dimethylamino groups, at the para-positions of the phenyl groups on the nitrogen atom showed red shifts of the longest wavelengths (entries 16−20), and those of 42 and 43 were observed at 412 and 420 nm, respectively (entries 19 and 20).

As in the UV−vis spectra, fluorescence spectra and their efficiencies could also be finely tuned by the substituents at the 2-, 4-, and 5-positions. Replacement of an aromatic group at the 4-position with a 2-phenylethenyl group quenched the efficiency of the emission, as shown in 33 (entry 9). Likewise, the adamantyl group in 17, 37, and 38 highly decreased the emission (entries 13−15). On the other hand, the benzyl group in 34−36 did not have an influence as strong as the adamantyl group (entries 10−12). The UV−vis spectra of 31 and 32 showed bathochromic shifts, but their fluorescence spectra were in regions almost identical to those of 25 and 26, resulting in the observation of smaller Stokes shifts (entries 7 and 8). Thiazoles 27 and 28, which have pyridyl groups at the 2-position, showed emission with a high efficiency at wavelengths longer than that of 25 (entries 3 and 4). Thiazoles 39, 40, and 41, which have methyl and methoxy groups at the para-position of the phenyl group on the nitrogen atom, also exhibited bathochromic shifts in fluorescence (entries 17 and 18). Therefore, a change in emissions from light blue to deep yellow was achieved by changing the substituents attached to the N,N-diarylaminothiazole cores (Figure 2). The emission spectra of thiazoles 42 and 43, which have a dimethylamino group at the para-position, showed excitation wavelength-dependent luminescence[15] (entries 19 and 20). For 42, excitation at 310 nm resulted in lower-energy emission at 450 and 554 nm, whereas excitation at 410 nm exhibited the emission at 616 nm (Figure 3). Although further elucidation is necessary, the phenomena may be due to multiple molecular conformations and/or several singlet states with similar energy levels.

The influence of the solvent on the photophysical properties of 5-aminothiazoles 26, 27, and 40 was elucidated. Nine
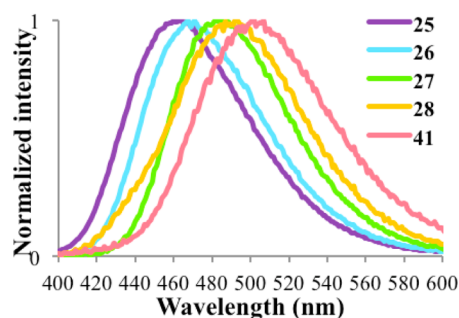
Figure 2. Normalized fluorescence spectra of thiazoles 25−28 and 41 in CHCl$_3$ (10^{-5} M); excitation wavelength λ_{ex} = 350 nm.
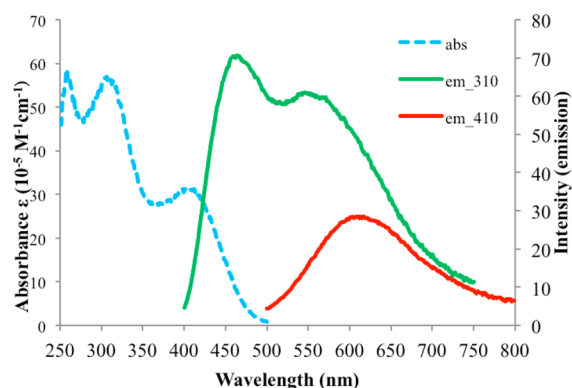

Figure 3. Absorbance and fluorescence spectra of thiazole 42 in CHCl$_3$ (10^{-5} M). Absorbance spectrum (blue dashed line) and fluorescence spectra under excitation at 310 nm (green solid line) and 410 nm (red solid line).

solvents with different Reichardt polarity indices ($E_T(30)$)[16] were used, and the results are shown in Table 5. The thiazoles dissolved in all of the solvents with low concentrations except for glycerol. 1% methanol in glycerol was then used as the most polar solvent. The absorption spectra of 26, 27, and 40 were independent of the solvent polarity except for those in 1% methanol in glycerol, in which the absorption was shifted to longer wavelengths by about 5 to 12 nm. In contrast, solvent-dependent bathochromic shifts of more than 45 nm were observed for fluorescent spectra. Normalized spectra are shown in Figure 4. As the solvents became more polar, the emissions became more red-shifted, except that the emission of 40 in 1% methanol in glycerol was shifted to a shorter wavelength by 6 nm compared with that in methanol. Notably, the relatively high emission was maintained even in polar solvents.[17] The fluorescence lifetime was also solvent-dependent. In all cases, the lifetimes in less polar solvents, such as cyclohexane and toluene, were shorter than those in other solvents. These results suggest that the thiazoles are less polar in the ground state and more polar in the excited state. Intramolecular charge transfer may take place in the excited state.

To further elucidate the solvent effects and to clarify the difference in polarity between the ground and excited states, the Lippert−Mataga correlation[18] was determined. Plots of the Stokes shifts of the thiazoles 26, 27, and 40 versus the orientation polarization of the solvents (Δf)[19] are shown in Figure 5.

A linear correlation was observed, which indicated a solvent effect in the excited state, although the standard deviation for 27 was greater than those of the other compounds. This may be due to the hydrogen-bonding interaction between the nitrogen

Table 5. Solvatochromism of Thiazoles 26, 27, and 40

entry	Thiazole	solvent[a] Et (30)	C$_6$H$_{12}$ 30.9	toluene 33.9	Et$_2$O 34.5	THF 37.4	CHCl$_3$ 39.1	CH$_2$Cl$_2$ 40.7	CH$_3$CN 45.6	MeOH 55.4	glycerol[b] 57.0[b]
1	26	λ_{abs} (nm)	**371**	374	370	371	372	371	371	**370**	380
		λ_{em} (nm)	**454**	466	466	478	477	480	489	**493**	499
		Stokes shift (cm^{-1})	4928	5279	5568	6033	5917	6121	6504	6743	6276
		Φ_F[c]	**0.33**	0.52	0.50	0.61	0.62	0.65	0.52	**0.48**	0.62
		χ^2[d]	1.07	1.11	1.13	1.23	1.37	1.04	1.46	1.16	1.05
		τ (ns)[d]	**2.41**	3.46	3.77	4.47	4.60	4.93	5.02	**5.16**	5.06
2	27	λ_{abs} (nm)	**381**	385	378	381	385	383	379	**382**	393
		λ_{em} (nm)	**459**	471	472	480	489	490	500	**523**	526
		Stokes shift (cm^{-1})	4460	4743	5269	5413	5524	5701	6385	7057	6434
		Φ_F[c]	**0.60**	0.66	0.67	0.66	0.69	0.68	0.47	**0.35**	0.48
		χ^2[d,e]	1.27	1.11	1.35	1.25	1.29	1.11	1.19	1.07	0.97
		τ (ns)[d,e]	**3.94**	4.42	4.97	5.16	5.60	5.60	5.08	**4.49**	3.93
3	40	λ_{abs} (nm)	**382**	386	380	382	383	383	382	**380**	387
		λ_{em} (nm)	**467**	480	481	492	495	499	511	**516**	510
		Stokes shift (cm^{-1})	4765	5073	5526	5853	5908	6070	6609	6936	6232
		Φ_F[c]	**0.35**	0.55	0.55	0.63	0.65	0.67	0.50	**0.46**	0.47
		χ^2[d,e]	1.84	1.58	1.66	1.20	1.28	1.31	1.41	1.30	0.92
		τ (ns)[d,e]	**1.85**	2.97	3.30	3.84	4.21	4.44	4.22	**4.22**	3.42

[a]c = 10^{-5} M. [b]1% of methanol in glycerol. [c]Excited at maxmum absorption wavelength. [d]Excited at 365 nm. [e]Excited at 405 nm.
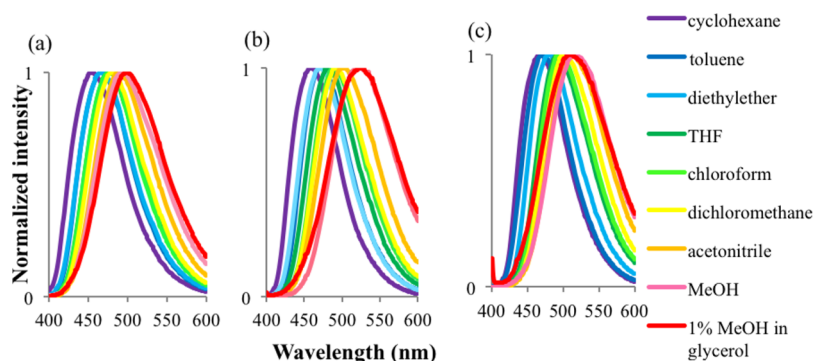
Figure 4. Normalized solvent-dependent fluorescence spectra of (a) **26**, (b) **27**, and (c) **40**. Recorded in cyclohexane, toluene, diethyl ether, THF, chloroform, dichloromethane, acetonitrile, methanol, and 1% MeOH in glycerol (10^{-5} M); excitation wavelength λ_{ex} = corresponding longest-wavelength absorption maximum.
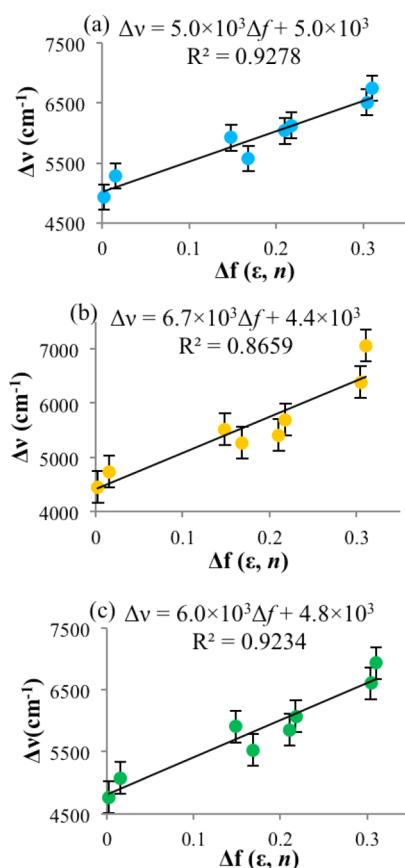

Figure 5. Lippert−Mataga plot of (a) **26**, (b) **27**, and (c) **40** in solvents of different polarity.

atom in **27** and the hydrogen atom in MeOH. In fact, plots without MeOH clearly showed a better standard deviation (Figure S1, Supporting Information). The change in the dipole moment between the ground and excited states was further estimated on the basis of the plots, and the results are shown in Table S1. Radiative and nonradiative decay rate constants of thiazoles **26**, **27**, and **40** are also shown in Figure S2. A large change in the dipole moment indicates a more pronounced intramolecular charge transfer for these molecules in the excited state. For fluorescent molecules that show intramolecular charge transfer, these are generally planar in the ground state and twisted in the excited state.[20] On the other hand, our 5-aminothiazoles highly deviate in the ground state, as shown in

X-ray analyses. Therefore, they may be planarized[21] to some extent in the excited state to enable more efficient delocalization of the electrons on the nitrogen atom to the thiazole ring and the substituent at the 2-position.

The photoluminescence properties of 5-aminothiazoles in the solid state were also elucidated. The results for **26−28**, **37**, and **42** are shown in Table 6. Unlike the absorptions and emissions in solution, general trends could not be determined, partly because of the difficulty in obtaining reproducible data in the solid state. Nevertheless, photographs of 5-aminothiazoles show emission from blue to yellow in the solid state (Figure 6 and Figures S3 and S4, Supporting Information).

Electrochemical Properties. To determine the redox properties of 5-aminothiazoles, cyclic voltammetry measurements were carried out in acetonitrile. In particular, 5-aminothiazoles **26** and **40−42** were chosen as representative examples since they possess different electron-donating groups on the aromatic rings at the 5-positions, and they were expected to be highly influential to electrochemical oxidations. Representative cyclic voltammograms at a scan rate of 100 mV/s are shown in Figures 7 and 8, and the relevant data are listed in Table 7. 5-Aminothiazoles **26**, **40**, and **41** exhibited reversible one-electron oxidation below +0.7 V (vs Fc/Fc+ ([n-Bu4N]ClO4/MeCN). Notably, the introduction of electron-donating groups, such as methyl and methoxy groups, to the para-position of the phenyl rings on the nitrogen atom at the 5-position reduced the oxidation potential by more than 0.1 V, from +0.635 to +0.523 and +0.407 V.[22] On the other hand, the cyclic voltammogram of **42** exhibited two reversible oxidation processes at more negative potentials than those observed for **41**. The first oxidation wave can be attributed to the formation of a cation-radical species, and the second is ascribed to the successive oxidation of the cation radical to its corresponding cation. This is probably due to the introduction of more electron-donating dimethylamino groups to the aromatic rings on the nitrogen atom at the 5-position, which may be able to accept two electron oxidations. A similar two reversible oxidation process has been observed for 4-aminophenyl diphenylamine.[23]

Theoretical Calculations. To gain further insight into the electronic structures of 5-aminothiazoles, DFT calculations were performed for compounds **26** and **40−42** at the B3LYP/6-31+G(d,p) level[24] (Figure 9 and Table 7).

As shown in Figure 9, the HOMO of diphenylaminothiazoles **26** and **42** is localized on the diphenylamino groups at the 5-position, whereas the LUMO of these compounds is

Table 6. UV−Vis and Fluorescence Spectra of Thiazoles 26, 27, 28, 37, and 42 in the Solid State

entry	Thiazole	λ_{ex} (nm)	λ_{em}[a] (nm)	Φ_F[b]	Stokes Shift (cm^{-1}) [nm]
1	26	347	453	0.14	6743 [106]
2	27	395	466	0.15	3857 [71]
3	28	410	464 576	0.07	7029 [166]
4	37	373	452	0.06	4685 [79]
5	42	415	558	0.06	6175 [143]

[a]Excited at λ_{ex}. [b]Absolute fluorescent quantum yield.

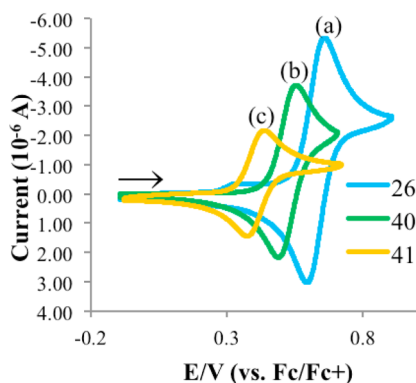**Figure 6.** Photograph showing the emission colors of **26−28**, **37**, and **42** when excited with a UV lamp (365 nm).

Figure 7. Cyclic voltammograms of (a) **26**, (b) **40**, and (c) **41** recorded in acetonitrile; 0.1 M electrolyte [n-Bu$_4$N][ClO$_4$]; v = 100 mVs^{-1}; Pt working electrode, Ag/AgCl reference electrode, and Pt counter electrode.

Figure 8. Cyclic voltammogram of **42** recorded in acetonitrile; 0.1 M electrolyte [n-Bu$_4$N][ClO$_4$]; v = 100 mVs^{-1}; Pt working electrode, Ag/AgCl reference electrode, and Pt counter electrode.

delocalized on both the thiazole ring and aromatic substituents at the 2-position. These orbital environments also support an intramolecular donor−acceptor-type π-electron system in which the substituents at the 5-position act as donors and both the thiazoles and the substituents at the 2-position are acceptors. The longest wavelength calculated for 5-amino-thiazole **26** is 418 nm with a large oscillator strength, which is red-shifted compared to the experimental values (371 nm in CHCl$_3$ in Table 4, and 347 nm in the solid state in Table 7) (entry 1). Nevertheless, the calculated HOMO−LUMO gap for **26** (2.97 eV) is almost identical to that derived from the onset between the absorption and emission spectra. This similarity of the HOMO−LUMO gaps between calculated and experimental values was also observed for 5-aminothiazoles **40−42** (entries 2−4). Likewise, the tendency of a red-shift in the longest absorption wavelengths on going from **26** to **40−42** is also
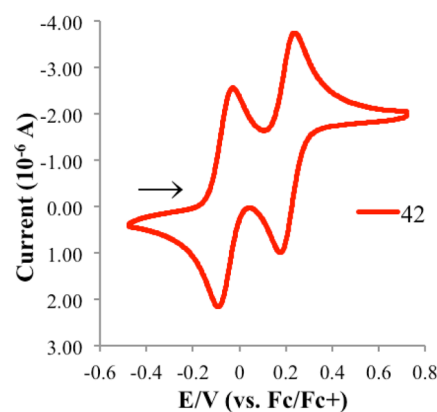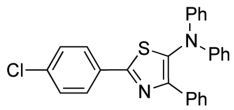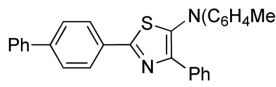
reflected in the calculated results. In all cases, the main contributions to these S$_0$ to S$_1$ electron transitions are from HOMO−LUMO (π−π^*) transitions.

Thermal Properties. To determine the thermal stability of 5-aminothiazoles, thermogravimetric and differential thermal analyses of **26**, **27**, and **31** were carried out under a N$_2$ atmosphere at a heating rate of 5 K min^{-1} (Figure 10). These 5-aminothiazoles are thermally stable below 280 °C at least, which is about 100 °C above their melting temperatures.

■ CONCLUSIONS

In summary, we have described the syntheses, structures, and photophysical properties of a series of 5-N-arylaminothiazoles and have presented a theoretical elucidation of their electronic structures. The reactions of thioamide dianions with thioformamides followed by sequential oxidation with iodide gave 5-aminothiazoles via 5-amino-2-thiazolines. They adopted highly varied structures due to subtle interactions between the substituents at the 2-, 4-, and 5-positions, as determined by X-ray analyses. The longest wavelengths in their UV−vis spectra were within the range from 360 to 420 nm, whereas their emissions ranged from 460 to 610 nm. The introduction of electron-donating groups to the aromatic groups attached to

Table 7. Results of Cyclic Voltammetry and DFT Calculations

entry	Thiazole		HOMO–LUMO gap (eV)		$E_{1/2}$ (V)[c]	HOMO (eV)		LUMO[b] (eV)	excited state	contribution	λ_{abs} (nm)	f
			onset[a]	TD-DFT[b]		CV[d]	DFT[b]					
1	(structure)	26	2.96	2.97	+0.635	-5.44	-5.51	-2.00	HOMO–LUMO	0.70	418	0.23
2	(structure)	40	2.87	2.84	+0.523	-5.32	-5.24	-1.89	HOMO–LUMO	0.70	436	0.32
3	(structure)	41	2.88	2.81	+0.407	-5.21	-5.06	-1.71	HOMO–LUMO	0.70	441	0.20
4	(structure)	42	2.84	2.55	-0.058 +0.209	-5.01	-4.59	-1.55 -0.78[e]	HOMO–LUMO	0.70	486	0.20

[a]In CHCl$_3$, excited at 350 nm, $c = 10^{-5}$ M. [b]The first oxidation potential is shown. [c]DFT, TD-DFT (TD/B3LYP/6-31+G(d,p)) calculations were carried out with the use of optimized structures at B3LYP/6-31+G(d,p). Gas-phase energies are shown. [d]E_{HOMO} (eV) = $-4.8 - E_{1/2ox}$, based on ferrocene.[25] [e]LUMO + 1.
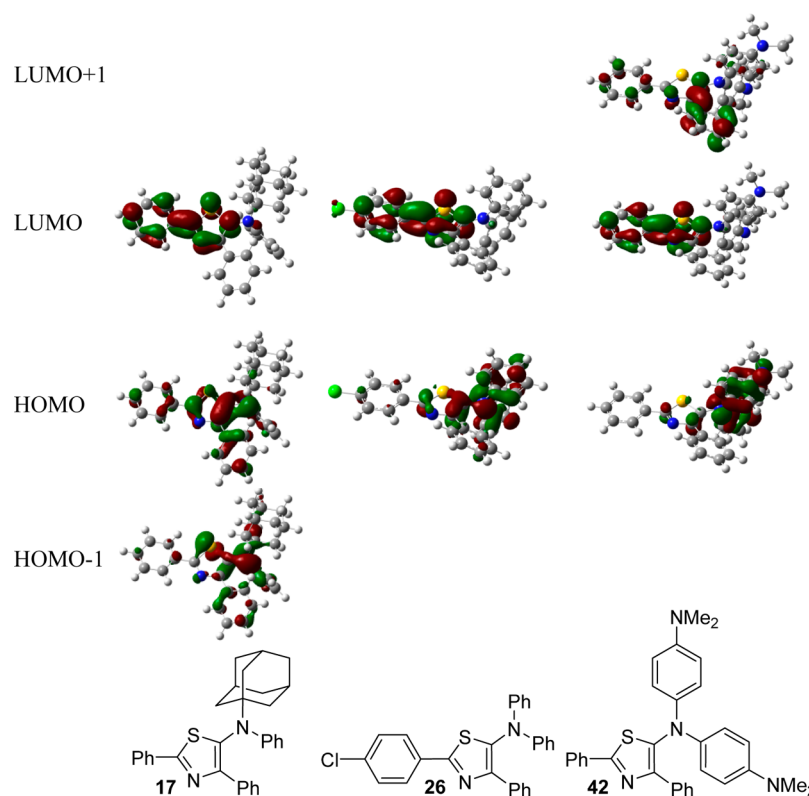

Figure 9. Frontier orbitals (HOMO − 1, HOMO, LUMO, and LUMO + 1) for **17** (left), **26** (middle), and **42** (right).

the nitrogen atom at the 5-position shifted both the absorption and emission wavelengths, whereas the substituents at the 4-position had almost no influence on these spectra. The absorption spectra were not affected by the polarity of the solvent, whereas solvatochromism was observed for fluorescence spectra. In this regard, the relationship between solvent polarity and Stokes shifts was elucidated on the basis of Lippert−Mataga plots. The change in the dipole moments of the 5-aminothiazoles between the ground and excited states was evaluated, and the compounds were more polarized in the latter state. Cyclic voltammograms exhibited reversible one-electron oxidation curves, except for 5-N,N-dimethylamino-phenylthiazoles. Again, oxidation potentials were controlled by the substituents at the 5-position. DFT calculations for 5-aminothiazoles showed that the HOMO is localized on the amino groups, whereas the LUMO is delocalized on both the thiazole rings and the substituents at the 2-position. Finally, TG/DTA showed that the 5-aminothiazoles are thermally stable below 280 °C. These characteristic features and the ready availability of a variety of 5-aminothiazoles suggest that they may be highly useful as fluorescent chemo- and biosensors. One of the next steps in demonstrating the usefulness of these 5-aminothiazoles is to produce them with a hydroxy group, which should enable the formation of inter- and intramolecular hydrogen-bonding networks.
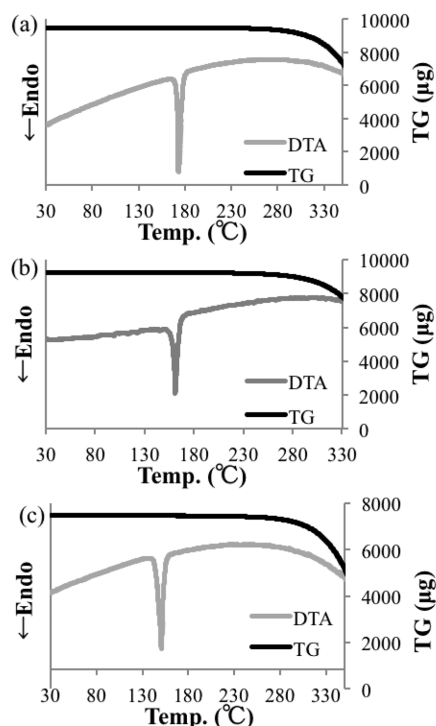
Figure 10. TG-DTA curve of (a) **26**, (b) **27**, and (c) **31** at heating rate of 5 K min^{-1} under a N$_2$ atmosphere.

■ EXPERIMENTAL SECTION

General Remarks. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$. Chemical shifts of protons are reported in δ values referenced to tetramethylsilane as an internal standard in CDCl$_3$, and the following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet. All spectra were acquired in the proton-decoupled mode. HRMS were recorded on a double-focusing mass spectrometer (EI). IR spectra were obtained using KBr pellets or neat films. UV–vis absorption, fluorescence, and absolute fluorescence quantum yields were obtained on the respective spectrometers. Electrochemical measurements were performed using a platinum working electrode, a platinum wire counter electrode, and an Ag/Ag$^+$ [0.01 M AgCl] reference electrode in 0.1 M n-Bu$_4$NClO$_4$ (MeCN). The potentials were calibrated with ferrocene/ferrocenium (Fc/Fc$^+$). DMF was distilled from calcium hydride. All other chemicals were used without further purification. Column chromatography was performed on silica gel 60 N (spherical neutral), 100−210 μm. Flash column chromatography was performed on silica gel 60 N (spherical neutral), 40−50 μm. All manipulations were carried out under an argon atmosphere. The compounds **1a**,[8] **1b**,[8] **1c**,[9] **1g**,[26] **1i**,[27] **3a**,[8] **3b**,[8] **3c**[28] **4−6**,[8] and **25−27**[8] were prepared according to literature procedures.

General Procedure for the Preparation of Thiazolines. To a solution of thioamide (1 equiv) in THF was added slowly a 1.25 M solution of n- or s-butyllithium in n-hexane (2 equiv) at 0 °C, and the mixture was stirred for 10 min at this temperature. To this was added thioformamide (1 equiv) at 0 °C, and the mixture was stirred for 0−0.5 h at this temperature. To this was added iodine (2−3 equiv) at 0 °C, and the mixture was stirred for 2−3 h at 0 °C or room temperature. The resulting mixture was poured into a saturated aqueous solution of Na$_2$S$_2$O$_3$ and extracted with Et$_2$O. 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 thiazolines.

General Procedure for the Preparation of Thiazoles. To a solution of thiazoline (1 equiv) in THF was added iodine (2 equiv) at room temperature, and the mixture was stirred for 2−4 h under reflux or for 21.5−60 h at room temperature. The resulting mixture was poured into a saturated aqueous solution of Na$_2$S$_2$O$_3$ and extracted

with Et$_2$O. 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 thiazoles.

***N*-[(2-Methylphenyl)methyl]benzenecarbothioamide (1f).** To a solution of benzaldehyde (0.21 mL, 2.0 mmol) in DMF (1.0 mL) was added elemental sulfur (0.07 g, 2.2 mmol) at room temperature. To this was added 2-methylbenzylamine (0.27 mL, 2.2 mmol), and the mixture was stirred for 2 h at 85 °C. The mixture was cooled to room temperature, 2-methylbenzylamine (0.24 mL, 2.0 mmol), elemental sulfur (0.06 g, 2.0 mmol), and DMF (1.0 mL) were added, and the mixture was stirred for 1 h at 85 °C. The combined organic phase was washed with a saturated aqueous solution of NaHCO$_3$ and extracted with Et$_2$O. The organic layer was dried over MgSO$_4$ and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 8:1) to give **1f** (0.52 g, 99%) as a yellow solid (mp 88−92 °C): IR (KBr) 3220, 2908, 1530, 1213, 944, 920, 748, 691 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.37 (s, 3H), 4.94 (d, J = 4.9 Hz, 2H), 7.19−7.27 (m, 3H, 7.28−7.37 (m, 3H), 7.44 (tt, J = 7.3 Hz, 1H), 7.55 (br, 1H), 7.71−7.73 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 19.1, 49.4, 126.4, 126.6, 128.46, 128.52, 129.4, 130.8, 131.1, 134.0, 137.0, 141.5, 198.8; MS (EI) m/z 241 (M$^+$); HRMS (EI) calcd for C$_{15}$H$_{15}$NS, 241.0925; found, 241.0899.

***N*-(Phenylmethyl)-4-pyridinecarbothioamide (1d).** According to the synthetic procedure for **1f**. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 1:2) to give **1d** (1.20 g, 90%) as a yellow solid (mp 136−137 °C): IR (KBr) 3187, 1594, 1559, 1436, 1401, 1347, 1063, 943, 829, 706, 696 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.97 (d, J = 4.9 Hz, 2H), 7.26−7.50 (m, 7H, Ar), 8.34−8.36 (m, 2H, Ar), 8.73 (br, 1H, NH); ^{13}C NMR (CDCl$_3$) δ 51.1, 120.8, 128.4, 128.5, 129.1, 135.7, 148.3, 149.8, 196.3; MS (EI) m/z 228 (M$^+$); Anal. Calcd for C$_{13}$H$_{12}$N$_2$S$_2$: C, 68.39; H, 5.30; N, 1.27. Found: C, 68.16; H, 5.39; N, 12.20.

***N*-[(Phenylmethyl)-(1,1′-biphenyl)-4-carbothioamide (1e).** According to the synthetic procedure for **1f**. The crude material was purified by recrystallized from CH$_2$Cl$_2$/hexane to give **1d** (2.31 g, 95%) as a yellow solid (mp 191−192 °C): IR (KBr) 3310, 3079, 3053, 3028, 2928, 1601, 1529, 1514, 1482, 1404, 1386, 1324, 1197, 1070, 933, 842, 768, 758, 742, 725, 694 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.03 (d, J = 4.9 Hz, 2H), 7.42−7.45 (m, 8H), 7.58−7.62 (m, 4H), 7.75 (br, 1H), 7.84−7.86 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 51.2, 127.1, 127.2, 127.2, 128.0, 128.3, 128.4, 128.9, 129.0, 129.5, 139.9, 140.2, 144.1, 175.3; MS (EI) m/z 303 (M$^+$); HRMS (EI) calcd for C$_{20}$H$_{17}$NS, 303.1082; found, 303.1076.

***N*-[(2-Methylphenyl)methyl]-4-chlorobenzenecarbothioamide (1h).** According to the synthetic procedure for **1f**. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 8:1) to give **1h** (0.33 g, 56%) as a yellow solid (mp 102−104 °C): IR (KBr) 3218, 3001, 2836, 1603, 1436, 1536, 1486, 1086, 753, 723 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.88 (s, 3H), 5.00 (d, J = 5.4 Hz, 2H), 6.94−7.00 (q, 2H), 7.33−7.37 (m, 3H), 7.40 (dd, J = 1.5 Hz, 1.5 Hz, 1H), 7.78 (tt, J = 2.4 Hz, 2.2 Hz, 2H), 7.99 (br, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 47.3, 55.5, 110.2, 120.9, 123.9, 128.0, 128.6, 129.8, 131.0, 137.1, 140.2, 157.6, 196.8; MS (EI) m/z 291 (M$^+$); HRMS (EI) calcd for C$_{15}$H$_{14}$ClNOS, 291.0485; found, 291.0476.

***N*-(1-Adamantyl)-*N*-phenylmethanethioamide (3d).** To a solution of *N*-(1-adamanthyl)-*N*-phenylmethaneamide (0.13 g, 0.5 mmol) in toluene (0.5 mL) were added elemental sulfur (0.02 g, 0.55 mmol), DABCO (0.06 g, 0.55 mmol), and trichlorosilane (0.06 mL, 0.55 mmol), and the mixture was stirred for 6 h at 115 °C. The combined organic phase was washed with a saturated aqueous sodium bicarbonate, dried over MgSO$_4$, and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 8:1) to give **3d** (0.09 g, 69%) as a white solid (mp 213−215 °C): IR (KBr) 2905, 2850, 1592, 1492, 1452, 1384, 1359, 1344, 1272, 1195, 1075, 1004, 714, 697, 651 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.64−1.69 (m, 6H), 1.96 (d, J = 2.4 Hz, 6H), 2.19 (s, 3H), 7.06−7.08 (m, 2H), 7.36−7.52 (m, 3H), 9.90 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 29.7, 35.5, 42.7, 62.9, 128.3, 129.1,

139.5, 188.3; MS (EI) *m/z* 271 (M⁺); HRMS (EI) calcd for C₁₇H₂₁NS, 271.1395; found, 271.1403.

N,N-Bis(4-methylphenyl)methanethioamide (3e). According to the synthetic procedure for **3d**, the crude material was purified by column chromatography (SiO₂, hexane/EtOAc = 8:1) to give **3e** (6.94 g, 94%) as a yellow solid (mp 114–115 °C): IR (KBr) 3036, 2922, 1507, 1422, 1354, 1303, 1002, 915, 814, 587 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.34 (s, 3H), 2.38 (s, 3H), 7.03–7.05 (m, 2H), 7.14–7.21 (m, 4H), 7.25–7.29 (m, 2H), 9.94 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 20.9, 21.2, 122.5, 127.3, 130.1, 130.3, 137.2, 138.3, 139.0, 143.6, 189.7; MS (EI) *m/z* 241 (M⁺); HRMS (EI) calcd for C₁₅H₁₅NS, 241.0925; found, 241.0918.

N,N-Bis(4-dimethylaminophenyl)methanethioamide (3f). According to the synthetic procedure for **3d**, the crude material was purified by column chromatography (SiO₂, hexane/EtOAc = 5:1) to give **3f** (0.20 g, 67%) as a yellow solid (mp 171–172 °C): IR (KBr) 2990, 2884, 2803, 1606, 1518, 1438, 1419, 1354, 1223, 1147, 1122, 1013, 992, 818, 808, 580 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.95 (s, 6H), 2.98 (s, 6H), 6.62–6.66 (m, 2H), 6.71–6.75 (m, 2H), 7.01–7.06 (m, 2H), 7.16–7.20 (m, 2H), 9.79 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 40.3, 40.4, 112.2, 112.3, 123.7, 127.6, 130.6, 136.1, 149.3, 149.5, 188.0; MS (EI) *m/z* 299 (M⁺); HRMS (EI) calcd for C₁₇H₂₁N₃S, 299.1456; found, 299.1447.

(4R*,5S*)-4,5-Dihydro-2-(4-pyridyl)-N,N,4-triphenyl-5-thiazolamine (7). According to the general procedure for thiazolines, compound **7** was prepared. The crude material was purified by column chromatography (SiO₂, hexane/EtOAc/Et₃N = 5:1:0.01) to give **7** (0.65 g, 80%) as an orange solid (mp 52–55 °C): IR (KBr) 3054, 3026, 3005, 1591, 1548, 1491, 1448, 1410, 1266, 1236, 1213, 1032, 1002, 992, 963, 831, 753, 728, 694 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.97 (d, *J* = 3.4 Hz, 1H), 6.32 (d, *J* = 3.4 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 4H), 7.00–7.05 (m, 2H), 7.18–7.29 (m, 9H), 7.58 (d, *J* = 5.9 Hz, 2H), 8.62 (d, *J* = 5.9 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 82.1, 82.6, 119.8, 121.6, 121.9, 123.4, 124.0, 126.2, 127.4, 128.1, 128.8, 129.3, 129.4, 139.2, 140.4, 145.4, 150.3, 166.8; MS (EI) *m/z* 407 (M⁺); HRMS (EI) calcd for C₂₆H₂₁N₃S, 407.1456; found, 407.1449.

(4R*,5S*)-2-[1,1′-Biphenyl]-4-yl-4,5-dihydro-N,N,4-triphenyl-5-thiazolamine (8). According to the general procedure for thiazolines, compound **8** was prepared. The crude material was purified by column chromatography (SiO₂, hexane/EtOAc = 15:1) to give **8** (0.87 g, 60%) as a brown liquid: IR (KBr) 3059, 3029, 2956, 2926, 1686, 1597, 1491, 1450, 1276, 1241, 1034, 948, 908, 846, 751, 728, 696 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.03 (d, *J* = 3.9 Hz, 1H), 6.32 (d, *J* = 3.9 Hz, 1H), 7.04–7.07 (m, 5H), 7.28–7.41 (m, 12H), 7.44–7.48 (m, 2H), 7.61–7.66 (m, 4H), 7.96 (d, *J* = 6.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 81.5, 82.4, 117.7, 121.4, 123.4, 123.8, 125.0, 126.1, 126.3, 127.1, 127.9, 128.8, 128.9, 129.4, 129.6, 140.0, 144.0, 145.6, 161.7; MS (EI) *m/z* 482 (M⁺); HRMS (EI) calcd for C₃₃H₂₆N₂S, 482.1817; found, 482.1811.

(4R*,5S*)-4,5-Dihydro-4-(2-methylphenyl)-N,N,2-triphenyl-5-thiazolamine (9). According to the general procedure for thiazolines, compound **9** was prepared. The crude material was purified by column chromatography (SiO₂, hexane/EtOAc/Et₃N = 45:1:0.01) to give **9** (0.21 g, 50%) as a brown solid (mp 128–137 °C): IR (KBr) 2923, 1596, 1587, 1490, 1034, 949, 766, 754, 704, 689 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.43 (s, 3H), 6.09 (d, *J* = 2.4 Hz, 1H), 6.20 (d, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.96–7.02 (m, 7H), 7.10–7.21 (m, 6H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.38–7.42 (m, 1H), 7.76 (d, *J* = 3.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 20.0, 79.5, 80.4, 123.3, 123.9, 125.7, 126.2, 127.8, 128.5, 128.6, 129.5, 131.0, 131.4, 133.7, 135.2, 137.5, 145.6, 169.4; MS (EI) *m/z* 420 (M⁺); HRMS (EI) calcd for C₂₈H₂₄N₂S, 420.1660; found, 420.1648.

(4R*,5S*)-4,5-Dihydro-4-(2-methoxyphenyl)-N,N,2-triphenyl-5-thiazolamine (10). According to the general procedure for thiazolines, compound **10** was prepared. The crude material was purified by column chromatography (SiO₂, hexane/EtOAc/Et₃N = 8:1:0.01) to give **10** (2.00 g, 92%) as a yellow solid (mp 194–195 °C): IR (KBr) 2838, 1586, 1490, 1286, 1241, 1110, 1094, 1068, 767, 752, 702, 690 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.86 (s, 3H), 6.21 (d, *J* = 2.4 Hz, 1H), 6.41 (d, *J* = 2.4 Hz, 1H), 6.86 (t, *J* = 7.3 Hz, 1H), 6.93

(d, *J* = 7.3 Hz, 1H), 6.94–7.07 (m, 7H), 7.24–7.29 (m, 5H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.45–7.48 (m, 1H), 7.80–7.82 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 55.6, 79.8, 80.1, 110.6, 120.5, 122.0, 122.8, 123.3, 123.4, 125.1, 125.7, 126.1, 126.6, 126.7, 127.4, 128.3, 128.4, 128.8, 129.2, 129.5, 131.0, 133.7, 137.9, 144.2, 145.5, 146.2, 156.5, 169.3; MS (EI) *m/z* 436 (M⁺); HRMS (EI) calcd for C₂₈H₂₄N₂OS, 436.1609; found, 436.1595.

(4R*,5S*)-4,5-Dihydro-2-(4-chlorophenyl)-4-(2-methoxyphenyl)-N,N-diphenyl-5-thiazolamine (11). According to the general procedure for thiazolines, compound **11** was prepared. The crude material was purified by column chromatography (SiO₂, hexane/EtOAc/Et₃N = 30:1:0.01) to give **11** (0.16 g, 34%) as a yellow solid (mp 176–181 °C): IR (KBr) 2838, 1588, 1488, 1239, 757, 748, 701, 688, 607 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.87 (s, 3H), 6.23 (d, *J* = 2.4 Hz, 1H), 6.40 (d, *J* = 2.4 Hz, 1H), 6.86 (t, *J* = 7.3 Hz, 1H), 6.92–6.95 (m, 2H), 7.02 (dd, *J* = 1.0, 9.3 Hz, 6H), 7.26 (t, *J* = 7.8 Hz, 5H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 55.7, 77.0, 80.7, 110.8, 120.6, 123.4, 123.6, 126.7, 127.2, 128.8, 129.0, 129.3, 129.7, 132.3, 137.3, 145.6, 156.6, 168.2; MS (EI) *m/z* 470 (M⁺); HRMS (EI) calcd for C₂₈H₂₃N₂OSCl, 470.1220; found, 470.1202.

(4R*,5S*)-4,5-Dihydro-4-(2-phenylethenyl)-N,N,2-triphenyl-5-thiazolamine (12). According to the general procedure for thiazolines, compound **12** was prepared. The crude material was purified by column chromatography (SiO₂, hexane/EtOAc/Et₃N = 45:1:0.01) to give **12** (0.06 g, 30%) as a yellow oil: IR (KBr) 2955, 2926, 2857, 1597, 1520, 1489, 1450, 1387, 768, 746, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.55 (td, *J* = 1.0 Hz, 7.3 Hz, 1H), 6.24–6.31 (m, 2H), 6.70 (d, *J* = 16.1 Hz, 1H), 7.03–7.09 (m, 6H), 7.24–7.32 (m, 7H), 7.35–7.40 (m, 4H), 7.43–7.44 (m, 1H), 7.72–7.74 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 78.9, 81.7, 113.8, 116.6, 117.8, 121.0, 121.8, 123.2, 126.3, 126.5, 126.7, 127.7, 128.2, 128.5, 128.8, 128.9, 129.0, 129.2, 129.3, 129.3, 129.4, 130.1, 147.2; MS (EI) *m/z* 432 (M⁺); HRMS (EI) calcd for C₂₉H₂₄N₂S, 432.1660; found, 432.1630.

(4R*,5S*)-2-[1,1′-Biphenyl]-4-yl-4,5-dihydro-N-phenylmethyl-N,4-diphenyl-5-thiazolamine (13). According to the general procedure for thiazolines, compound **13** was prepared. The crude material was purified by column chromatography (SiO₂, hexane/EtOAc/Et₃N = 20:1:0.01) to give **13** (0.01 g, 40%) as a yellow solid (mp 168–169 °C): IR (KBr) 3057, 3030, 1591, 1502, 1487, 1323, 1230, 1158, 1149, 1033, 1018, 956, 767, 749, 727, 694 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.48 (q, *J* = 24.0 Hz, 2H), 5.97 (d, *J* = 3.4 Hz, 1H), 6.20 (d, *J* = 3.4 Hz, 1H), 6.85–6.90 (m, 3H), 7.19–7.59 (m, 15H), 7.63–7.72 (m, 4H), 8.05–8.07 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 51.7, 83.1, 83.8, 116.6, 120.4, 120.6, 126.1, 126.5, 127.0, 127.1, 127.2, 127.6, 127.9, 128.6, 128.9, 129.2, 129.2, 132.2, 139.0, 140.1, 140.2, 144.3, 148.2, 168.7; MS (EI) *m/z* 496 (M⁺); HRMS (EI) calcd for C₃₄H₂₈N₂S, 496.1973; found, 496.1987.

(4R*,5S*)-4,5-Dihydro-2-(2-pyridyl)-N-phenylmethyl-N,4-diphenyl-5-thiazolamine (14). According to the general procedure for thiazolines, compound **14** was prepared. The crude material was purified by column chromatography (SiO₂, hexane/EtOAc = 15:1) to give **14** (0.12 g, 58%) as a yellow liquid: IR (KBr) 3249, 3059, 2923, 2857, 1952, 1673, 1597, 1495, 1465, 1452, 1150, 1029, 996, 963, 752, 730, 617, 607 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.48 (s, 2H), 5.97 (d, *J* = 3.4 Hz, 1H), 6.15 (d, *J* = 3.0 Hz, 1H), 6.85–6.87 (m, 3H), 7.18 (t, *J* = 8.1 Hz, 2H), 7.25–7.44 (m, 11H), 7.81 (ddd, *J* = 1.5 Hz, 1.5 Hz, 1.5 Hz, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 8.71–8.73 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 51.7, 81.8, 84.5, 116.8, 120.4, 121.8, 123.9, 125.6, 126.1, 126.5, 126.9, 127.9, 128.4, 128.9, 129.1, 136.6, 139.0, 140.1, 148.3, 149.4, 151.2, 162.3; MS (EI) *m/z* 419 (M⁺ −2); HRMS (EI) calcd for C₂₇H₂₃N₃S, 421.1613; found, 421.1604.

(4R*,5S*)-4,5-Dihydro-2-(4-pyridyl)-N-phenylmethyl-N,4-diphenyl-5-thiazolamine (15). According to the general procedure for thiazolines, compound **15** was prepared. The crude material was purified by column chromatography (SiO₂, hexane/EtOAc = 4:1) to give **15** (0.13 g, 64%) as an orange liquid: IR (KBr) 3061, 3028, 2920, 2857, 1947, 1595, 1494, 1452, 1408, 1323, 1229, 1151, 1029, 963, 908, 824, 747, 732, 699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.43 (s, 2H),

5.96 (d, J = 2.4 Hz, 1H), 6.25 (d, J = 2.4 Hz, 1H), 6.85–6.92 (m, 3H), 7.19–7.30 (m, 5H), 7.33–7.41 (m, 7H), 7.80–7.81 (m, 2H), 8.75–8.76 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 52.0, 84.0, 84.2, 117.0, 121.1, 122.4, 126.2, 126.7, 127.3, 128.3, 128.8, 129.2, 129.4, 138.8, 139.6, 140.4, 148.1, 150.6, 167.6; MS (EI) m/z 421 (M$^+$); HRMS (EI) calcd for C$_{27}$H$_{23}$N$_3$S, 421.1613; found, 421.1618.

N,2,4-Triphenyl-N-(1-adamanthyl)-5-thiazolamine (17). According to the general procedure for thiazolines, compound **17** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 30:1) to give **17** (0.04 g, 19%) as a pale red solid (mp 40–42 °C): IR (KBr) 2903, 2849, 1592, 1486, 1443, 1303, 1227, 1180, 1071, 981, 909, 760, 734, 691 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.47–1.55 (m, 6H), 1.89 (s, 6H), 2.01 (s, 3H), 6.96–7.00 (m, 1H), 7.12–7.26 (m, 6H), 7.32–7.37 (m, 4H), 7.92–7.95 (m, 2H), 8.10–8.13 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 29.8, 36.1, 40.7, 58.4, 124.3, 126.3, 127.7, 128.0, 128.3, 128.4, 128.5, 128.8, 129.8, 134.3, 135.1, 141.5, 144.8, 150.6, 162.6; MS (EI) m/z 462 (M$^+$); HRMS (EI) calcd for C$_{31}$H$_{30}$N$_2$S, 462.2130; found, 462.2137.

(4R*,5S*)-4,5-Dihydro-2-(4-chlorophenyl)-N-(1-adamanthyl)-N,4-diphenyl-5-thiazolamine (18). According to the general procedure for thiazolines, compound **18** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 30:1) to give **18** (0.12 g, 50%) as a yellow solid (mp 161–163 °C): IR (KBr) 3059, 3026, 2931, 2901, 2846, 1602, 1487, 1449, 1306, 1279, 1237, 1216, 1126, 1114, 1100, 1090, 1026, 952, 708, 695, 606 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.54–1.63 (m, 9H), 1.77–1.80 (m, 3H), 2.05 (s, 3H), 5.55 (d, J = 4.4 Hz, 1H), 6.14 (d, J = 4.6 Hz, 1H), 7.18–7.25 (m, 3H), 7.27–7.28 (m, 2H), 7.29–7.36 (m, 5H), 7.42 (s, 2H), 7.71–7.73 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 29.7, 36.2, 41.9, 56.2, 82.5, 83.4, 126.2, 126.9, 127.4, 128.1, 128.4, 128.5, 129.4, 132.9, 133.0, 136.7, 140.7, 141.7, 167.4; MS (EI) m/z 498 (M$^+$); HRMS (EI) calcd for C$_{31}$H$_{31}$ClN$_2$S, 498.1896; found, 498.1876.

(4R*,5S*)-4,5-Dihydro-2-(2-pyridyl)-N-(1-adamanthyl)-N,4-diphenyl-5-thiazolamine (19). According to the general procedure for thiazolines, compound **19** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 10:1) to give **19** (0.07 g, 31%) as an orange liquid: IR (KBr) 3054, 2905, 2850, 1584, 1492, 1473, 1434, 1304, 1229, 1183, 1072, 1003, 782, 741, 697 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.43–1.59 (m, 2H), 1.78–1.81 (m, 2H), 1.88–1.89 (m, 4H), 2.04 (s, 2H), 2.11 (s, 2H), 5.52 (d, J = 4.4 Hz, 1H), 6.14 (d, J = 4.4 Hz, 1H), 7.05–7.45 (m, 11H), 7.60–7.63 (m, 1H), 7.83–7.85 (m, 1H), 8.63–8.64 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 29.8, 36.2, 41.9, 56.1, 80.5, 83.4, 121.3, 123.6, 125.1, 126.4, 126.7, 127.4, 127.9, 128.1, 128.3, 128.5, 133.4, 136.3, 142.2, 149.1, 152.1, 172.1; MS (EI) m/z 465 (M$^+$); HRMS (EI) calcd for C$_{30}$H$_{31}$N$_3$S, 465.2239; found, 465.2245.

(4R*,5S*)-4,5-Dihydro-2,4-diphenyl-N,N-bis(4-methylphenyl)-5-thiazolamine (20). According to the general procedure for thiazolines, compound **20** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc/Et$_3$N = 30:1:0.01) to give **20** (0.16 g, 71%) as an orange oil: IR (KBr) 3058, 3025, 2918, 2859, 1604, 1508, 1345, 1232, 1032, 946, 808, 765, 729, 690 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.27 (s, 6H), 6.00 (d, J = 3.4 Hz, 1H), 6.30 (d, J = 3.4 Hz, 1H), 6.93 (d, J = 8.3 Hz, 4H), 7.07 (d, J = 7.8 Hz, 4H), 7.25–7.29 (m, 1H), 7.32–7.33 (m, 4H), 7.40–7.54 (m, 3H), 7.83–7.86 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 41.2, 81.9, 82.1, 121.4, 122.5, 123.2, 126.3, 127.3, 127.8, 128.4, 128.7, 129.9, 130.0, 130.3, 131.3, 133.2, 140.2, 143.6, 144.8, 189.7; MS (EI) m/z 434 (M$^+$); HRMS (EI) calcd for C$_{29}$H$_{26}$N$_2$S, 434.1817; found, 434.1805.

(4R*,5S*)-2-[1,1′-Biphenyl]-4-yl-4,5-dihydro-4-phenyl-N,N-bis(4-methylphenyl)-5-thiazolamine (21). According to the general procedure for thiazolines, compound **21** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 30:1) to give **21** (0.19 g, 72%) as an orange solid (mp 57–58 °C): IR (KBr) 3057, 3027, 2918, 1600, 1508, 1486, 1277, 1241, 1078, 1035, 948, 847, 808, 765, 728, 698 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.29 (s, 6H), 6.03 (d, J = 2.4 Hz, 1H), 6.32 (d, J = 2.5 Hz, 1H), 6.96 (d, J = 7.8 Hz, 4H), 7.08 (d, J = 7.8 Hz, 4H), 7.34–7.48 (m,

8H), 7.62–7.65 (m, 4H), 7.91–7.94 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 20.7, 81.9, 82.3, 123.3, 126.3, 127.0, 127.1, 127.2, 127.8, 127.9, 128.7, 128.8, 128.9, 129.9, 133.2, 140.1, 140.4, 143.4, 143.9, 168.2; MS (EI) m/z 508 (M$^+$ −2H); HRMS (EI) calcd for C$_{35}$H$_{30}$N$_2$S, 510.2130; found, 510.2126.

(4R*,5S*)-4,5-Dihydro-2,4-diphenyl-N,N-bis(4-methoxyphenyl)-5-thiazolamine (22). According to the general procedure for thiazolines, compound **22** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 15:1) to give **22** (0.15 g, 62%) as a brown oil: IR (KBr) 3059, 2954, 2930, 2834, 1603, 1578, 1504, 1443, 1358, 1180, 1032, 948, 828, 768, 736, 693 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.75 (s, 6H), 6.00 (d, J = 3.4 Hz, 1H), 6.26 (d, J = 3.4 Hz, 1H), 6.80–6.82 (m, 4H), 6.98–7.00 (m, 4H), 7.38–7.47 (m, 8H), 7.91–7.93 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.6, 82.7, 82.8, 114.7, 124.7, 126.5, 127.9, 128.5, 128.6, 128.9, 131.3, 133.9, 139.7, 140.5, 156.1, 168.5; MS (EI) m/z 464 (M$^+$ − 2H); HRMS (EI) calcd for C$_{29}$H$_{26}$N$_2$ O$_2$S, 466.1715; found, 466.1694.

(4R*,5S*)-4,5-Dihydro-2,4-diphenyl-N,N-bis(4-dimethylaminophenyl)-5-thiazolamine (23). According to the general procedure for thiazolines, compound **23** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 5:1) to give **23** (0.14 g, 58%) as an orange solid (mp 58–59 °C): IR (KBr) 3041, 2881, 2795, 1603, 1512, 1444, 1348, 1225, 1088, 1074, 1037, 947, 817, 701, 688 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.86 (s, 12H), 5.98 (d, J = 3.9 Hz, 1H), 6.27 (d, J = 3.9 Hz, 1H), 6.65 (d, J = 9.3 Hz, 4H), 6.95 (d, J = 8.8 Hz, 4H), 7.33–7.47 (m, 8H), 7.85 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 41.1, 82.3, 83.3, 113.7, 124.2, 126.4, 127.6, 128.3, 128.4, 128.6, 130.9, 134.1, 136.7, 140.9, 147.2, 168.4; MS (EI) m/z 492 (M$^+$); HRMS (EI) calcd for C$_{31}$H$_{32}$N$_4$S, 492.2348; found, 492.2349.

(4R*,5S*)-2-[1,1′-Biphenyl]-4-yl-4,5-dihydro-4-phenyl-N,N-bis(4-dimethylaminophenyl)-5-thiazolamine (24). According to the general procedure for thiazolines, compound **24** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 7:1) to give **24** (0.12 g, 66%) as a brown solid (mp 114–116 °C): IR (KBr) 3026, 2880, 2795, 1605, 1510, 1485, 1444, 1339, 1227, 947, 845, 813, 765, 696 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.86 (s, 12H), 5.98 (d, J = 3.9 Hz, 1H), 6.27 (d, J = 3.9 Hz, 1H), 6.66–6.72 (m, 2H), 6.95–7.01 (m, 5H), 7.34–7.39 (m, 4H), 7.44–7.47 (m, 3H), 7.61–7.66 (m, 4H), 7.91–7.93 (m, 2H), 8.00–8.04 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 41.1, 82.3, 83.4, 113.7, 113.8, 122.6, 124.3, 126.4, 127.0, 127.1, 127.6, 127.8, 128.1, 128.7, 128.8, 128.9, 128.9, 133.0, 136.8, 140.3, 140.9, 143.7, 147.2, 168.0; MS (EI) m/z 568 (M$^+$); HRMS (EI) calcd for C$_{37}$H$_{36}$N$_4$S, 568.2661; found, 568.2685.

2-(4-Pyridyl)-N,N,4-triphenyl-5-thiazolamine (28). According to the general procedure for thiazoles, compound **28** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc/Et$_3$N = 5:1:0.01) to give **28** (0.10 g, 62%) as an orange solid (mp 168–170 °C): IR (KBr) 3036, 1587, 1488, 1442, 1407, 1344, 1266, 1233, 998, 819, 759, 694 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.02 (t, J = 7.4 Hz, 2H), 7.12 (d, J = 7.2 Hz, 4H), 7.21–7.27 (m, 7H), 7.84 (d, J = 5.4 Hz, 2H), 7.91 (d, J = 7.2 Hz, 2H), 8.70 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 119.9, 121.2, 121.6, 122.2, 122.8, 123.4, 123.8, 124.2, 125.9, 127.3, 127.4, 128.2, 128.3, 128.4, 128.5, 129.3, 129.5, 132.9, 138.5, 140.6, 142.1, 146.3, 149.2, 150.4, 150.5, 159.8; MS (EI) m/z 405 (M$^+$); HRMS (EI) calcd for C$_{26}$H$_{19}$N$_3$S, 405.1300; found, 405.1285.

2-[1,1′-Biphenyl]-4-yl-N,N,4-triphenyl-5-thiazolamine (29). According to the general procedure for thiazoles, compound **29** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 40:1) to give **29** (0.77 g, 45%) as a yellow solid (mp 154–155 °C): IR (KBr) 3026, 1716, 1587, 1528, 1487, 1443, 1272, 1233, 1074, 978, 911, 843, 751, 693 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.01 (t, J = 8.0 Hz, 2H), 7.15 (s, J = 8.0 Hz, 4H), 7.25–7.30 (m, 6H), 7.37–7.49 (m, 4H), 7.65–7.69 (m, 4H), 7.95–7.97 (m, 2H), 8.05–8.08 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 121.4, 123.1, 126.6, 126.9, 127.4, 127.5, 127.7, 127.9, 128.2, 128.8, 129.2, 132.8, 133.3, 139.8, 140.1, 142.6, 146.4, 148.8, 163.1; MS (EI)

m/z 480 (M$^+$); HRMS (EI) calcd for C$_{33}$H$_{24}$N$_2$S, 480.1660; found, 480.1663.

4-(2-Methylphenyl)-*N,N,*2-triphenyl-5-thiazolamine (30). According to the general procedure for thiazoles, compound **30** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 30:1, 10:1) to give **30** (0.05 g, 45%) as an pale yellow liquid: IR (KBr) 3959, 2923, 1588, 1492, 1291, 1277, 751, 692 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.03 (s, 3H), 6.85–6.96 (m, 8H), 6.99–7.04 (m, 1H), 7.06–7.13 (m, 5H), 7.32–7.37 (m, 3H), 7.85–7.88 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 20.0, 117.8, 121.8, 122.9, 125.2, 126.1, 128.2, 128.8, 128.9, 129.3, 129.6, 129.9, 130.1, 133.3, 134.0, 137.2, 141.5, 146.7, 150.7, 162.0; MS (EI) *m/z* 418 (M$^+$); HRMS (EI) calcd for C$_{28}$H$_{22}$N$_2$S, 418.1504; found, 418.1526.

4-(2-Methoxyphenyl)-*N,N,*2-triphenyl-5-thiazolamine (31). According to the general procedure for thiazoles, compound **31** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc/Et$_3$N = 45:1:0.01) to give **31** (0.09 g, 54%) as a yellow solid (mp 145−147 °C): IR (KBr) 1587, 1489, 1348, 1292, 1276, 1252, 753, 692 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.49 (s, 3H), 6.64 (d, *J* = 8.3 Hz, 1H), 6.76–6.80 (td, *J* = 1.0 Hz, 6.8 Hz, 1H), 6.89–6.94 (m, 2H), 7.03–7.05 (dd, *J* = 1.0 Hz, 7.8 Hz, 4H), 7.10–7.16 (m, 5H), 7.24–7.27 (m, 1H), 7.39–7.43 (m, 3H), 7.91–7.94 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.1, 110.3, 120.1, 122.1, 122.7, 123.6, 126.2, 128.7, 128.8, 129.3, 129.7, 131.1, 134.3, 141.9, 146.2, 146.5, 156.9, 161.6; MS (EI) *m/z* 434 (M$^+$); HRMS (EI) calcd for C$_{28}$H$_{22}$N$_2$OS, 434.1453; found, 434.1461.

2-(4-Chlorophenyl)-4-(2-metoxyphenyl)-*N,N*-diphenyl-5-thiazolamine (32). According to the general procedure for thiazoles, compound **32** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 20:1) to give **32** (0.03 g, 63%) as a yellow solid (mp 141−146 °C): IR (KBr) 2923, 2853, 1586, 1527, 1488, 1291, 1276, 1248, 754, 697 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.57 (s, 3H), 6.63 (d, *J* = 8.3 Hz, 1H), 6.77–6.80 (dd, *J* = 1.0 Hz, 6.4 Hz, 1H), 6.92 (t, *J* = 7.3 Hz, 2H), 7.02–7.04 (dd, *J* = 1.0 Hz, 7.8 Hz, 4H), 7.10–7.16 (m, 5H), 7.23–7.26 (dd, *J* = 1.5 Hz, 7.6 Hz, 1H), 7.35–7.39 (dt, *J* = 2.4 Hz, 8.8 Hz, 2H), 7.84–7.88 (dt, *J* = 2.4 Hz, 8.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.1, 104.8, 110.3, 117.9, 120.1, 122.2, 122.8, 123.4, 127.4, 128.8, 129.0, 129.4, 131.0, 132.8, 135.5, 142.3, 146.2, 146.4, 156.9, 160.0; MS (EI) *m/z* 468 (M$^+$); HRMS (EI) calcd for C$_{28}$H$_{21}$ClN$_2$OS, 468.1063; found, 468.1050.

4-(2-Phenylethenyl)-*N,N,*2-triphenyl-5-thiazolamine (33). According to the general procedure for thiazoles, compound **33** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc/Et$_3$N = 8:1:0.01) to give **33** (0.05 g, 43%) as a yellow solid (mp 138−148 °C): IR (KBr) 1589, 1489, 1354, 1310, 1274, 1231, 961, 754, 695, 675, 494 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.90 (d, *J* = 16.0 Hz, 1H), 7.07 (t, *J* = 7.3 Hz, 2H), 7.17–7.38 (m, 13H), 7.43–7.48 (m, 3H), 7.55–7.65 (m, 1H), 7.97–7.99 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 118.7, 121.9, 123.4, 126.4, 126.8, 127.9, 128.7, 129.0, 129.5, 130.2, 131.9, 134.1, 137.3, 140.8, 147.3, 148.3, 163.9; MS (EI) *m/z* 430 (M$^+$); HRMS (EI) calcd for C$_{29}$H$_{22}$N$_2$S, 430.1504; found, 430.1482.

2-[1,1′-Biphenyl]-4-yl-*N,*4-diphenyl-*N*-phenylmethyl-5-thiazolamine (34). According to the general procedure for thiazoles, compound **34** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc/Et$_3$N = 40:1:0.01) to give **34** (0.05 g, 52%) as a yellow solid (mp 109−110 °C): IR (KBr) 3027, 2925, 2226, 1594, 1496, 1486, 1443, 1363, 1202, 995, 977, 842, 764, 749, 695 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.80 (s, 2H), 6.90 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 7.21–7.48 (m, 11H), 7.47 (t, *J* = 4.0 Hz, 2H), 7.65 (t, *J* = 8.0 Hz, 4H), 7.90 (d, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 56.6, 114.5, 119.5, 126.7, 127.0, 127.2, 127.4, 127.6, 127.7, 128.1, 128.5, 128.6, 128.8, 129.1, 129.3, 132.5, 132.8, 133.7, 137.0, 140.1, 142.7, 148.1, 149.4, 163.2; MS (EI) *m/z* 494 (M$^+$); HRMS (EI) calcd for C$_{34}$H$_{26}$N$_2$S, 494.1817; found, 494.1803.

2-(2-Pyridyl)-*N,*4-diphenyl-*N*-phenylmethyl-5-thiazolamine (35). According to the general procedure for thiazoles, compound **35**

was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc/Et$_3$N = 10:1:0.01) to give **35** (0.05 g, 61%) as a yellow solid (mp 126−128 °C): IR (KBr) 3038, 1595, 1583, 1530, 1495, 1479, 1433, 1002, 781, 770, 753, 736, 715, 694 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.72 (s, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 2H), 7.13–7.18 (m, 7H), 7.23–7.32 (m, 4H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 2H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.51 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 56.7, 114.7, 119.5, 119.6, 124.5, 127.0, 127.2, 127.5, 128.2, 128.6, 129.3, 133.7, 135.1, 135.3, 136.9, 137.0, 148.0, 149.2, 149.6, 151.4, 162.0; MS (EI) *m/z* 419 (M$^+$); HRMS (EI) calcd for C$_{27}$H$_{21}$N$_3$S, 419.1456; found, 419.1456.

2-(4-Pyridyl)-*N,*4-diphenyl-*N*-phenylmethyl-5-thiazolamine (36). According to the general procedure for thiazoles, compound **36** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 2:1) to give **36** (0.05 g, 49%) as an orange solid (mp 51−52 °C): IR (KBr) 3058, 3028, 1594, 1527, 1495, 1443, 1406, 1355, 1297, 1283, 1203, 993, 820, 749, 723, 693, 664 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.79 (s, 2H), 6.92 (t, *J* = 7.0 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 2H), 7.16–7.28 (m, 7H), 7.32–7.40 (m, 3H), 7.80–7.81 (d, *J* = 5.4 Hz, 2H), 7.85–7.87 (m, 2H), 8.67–8.69 (d, *J* = 4.9 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 56.6, 114.9, 116.9, 120.1, 127.2, 127.4, 127.6, 128.5, 128.6, 128.7, 129.4, 133.2, 136.6, 141.0, 142.3, 147.9, 150.0, 150.1, 159.9; MS (EI) *m/z* 419 (M$^+$); HRMS (EI) calcd for C$_{27}$H$_{21}$N$_3$S, 419.1456; found, 419.1481.

2-(4-Chlorophenyl)-*N,*4-diphenyl-*N*-(1-adamanthyl)-5-thiazolamine (37). According to the general procedure for thiazoles, compound **37** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc/Et$_3$N = 40:1:0.01) to give **37** (0.11 g, 78%) as a white solid (mp 84−86 °C): IR (KBr) 2903, 2849, 1592, 1484, 1443, 1303, 1228, 1090, 1074, 981, 831, 697 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.55−1.64 (m, 6H), 1.93 (s, 6H), 2.10 (s, 3H), 7.09–7.22 (m, 5H), 7.35–7.36 (m, 1H), 7.42–7.44 (m, 4H), 8.02–8.07 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 29.8, 36.1, 40.7, 58.4, 124.5, 127.3, 127.7, 128.0, 128.3, 128.4, 128.6, 128.9, 132.8, 134.8, 135.6, 141.9, 144.6, 150.6, 161.0; MS (EI) *m/z* 496 (M$^+$); HRMS (EI) calcd for C$_{31}$H$_{29}$ClN$_2$S, 496.1740; found, 496.1730.

2-(2-Pyridyl)-*N,*4-diphenyl-*N*-(1-adamanthyl)-5-thiazolamine (38). According to the general procedure for thiazoles, compound **38** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc/Et$_3$N = 30:1:0.01) to give **38** (0.03 g, 24%) as a white solid (mp 188−189 °C): IR (KBr) 2905, 2851, 1583, 1490, 1473, 1434, 1303, 1228, 1181, 1072, 1003, 781, 739, 697 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.55−1.62 (m, 6H), 2.14 (m, 6H), 2.14 (s, 3H), 7.04–7.08 (m, 1H), 7.17–7.21 (m, 2H), 7.27–7.34 (m, 4H), 7.41–7.43 (m, 2H), 7.76–7.81 (m, 1H), 8.16–8.19 (m, 2H), 8.24–8.26 (m, 1H), 8.62–8.63 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 29.8, 36.1, 40.7, 58.3, 119.4, 124.2, 124.8, 127.6, 127.9, 128.2, 128.4, 129.4, 135.0, 136.9, 144.0, 144.4, 149.3, 151.1, 151.8, 162.6; MS (EI) *m/z* 463 (M$^+$); HRMS (EI) calcd for C$_{30}$H$_{29}$N$_3$S, 463.2082; found, 463.2082.

2,4-Diphenyl-*N,N*-bis(4-methylphenyl)-5-thiazolamine (39). According to the general procedure for thiazoles, compound **39** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 40:1) to give **39** (0.07 g, 55%) as a brown solid (mp 104−105 °C): IR (KBr) 3025, 2956, 2920, 2860, 1609, 1515, 1446, 1310, 923, 808, 761, 695 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.26 (s, 6H), 7.01–7.03 (m, 7H), 7.19–7.29 (m, 5H), 7.41–7.42 (m, 3H), 7.96–7.98 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 20.7, 121.3, 126.1, 127.4, 127.8, 128.1, 128.8, 129.8, 129.9, 132.4, 133.5, 134.0, 140.5, 144.3, 148.3, 163.2; MS (EI) *m/z* 432 (M$^+$); HRMS (EI) calcd for C$_{29}$H$_{24}$N$_2$S, 432.1660; found, 432.1671.

2-[1,1′-Biphenyl]-4-yl-4-phenyl-*N,N*-bis(4-methylphenyl)-5-thiazolamine (40). According to the general procedure for thiazoles, compound **40** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc/Et$_3$N = 50:1:0.01) to give **40** (0.07 g, 55%) as a yellow solid (mp 75−76 °C): IR (KBr) 3025, 2918, 1606, 1505, 1485, 1444, 1287, 1266, 1235, 978, 843, 811, 764, 694 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.27 (s, 6H), 7.00–

7.05 (m, 7H), 7.22−7.31 (m, 4H), 7.37−7.40 (m, 1H), 7.46 (t, J = 8.4 Hz, 2H), 7.63−7.67 (m, 4H), 7.98 (d, J = 6.8 Hz, 2H), 8.05 (d, J = 2.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 20.7, 121.3, 126.6, 126.9, 127.4, 127.5, 127.7, 127.8, 128.1, 128.8, 129.7, 132.5, 132.9, 133.4, 140.2, 140.5, 142.5, 144.3, 148.3, 162.8; MS (EI) m/z 508 (M$^+$); HRMS (EI) calcd for C$_{35}$H$_{28}$N$_2$S, 508.1973; found, 508.1965.

2,4-Diphenyl-*N*,*N*-bis(4-methoxyphenyl)-5-thiazolamine (41). According to the general procedure for thiazoles, compound **41** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 20:1) to give **41** (0.04 g, 45%) as a brown liquid: IR (KBr) 3054, 2949, 2832, 1503, 1460, 1441, 1240, 1178, 1033, 824, 761, 685 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.75 (s, 6H), 6.75−6.78 (m, 4H), 7.01−7.04 (m, 4H), 7.22−7.28 (m, 3H), 7.40−7.43 (m, 3H), 7.95−7.99 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.4, 114.5, 114.6, 122.6, 126.1, 127.8, 128.1, 128.8, 129.9, 133.4, 133.9, 140.6, 141.3, 147.5, 155.5, 162.7; MS (EI) m/z 464 (M$^+$); HRMS (EI) calcd for C$_{29}$H$_{24}$N$_2$O$_2$S, 464.1558; found, 464.1562.

2,4-Diphenyl-*N*,*N*-bis(4-dimethylaminophenyl)-5-thiazolamine (42). According to the general procedure for thiazoles, compound **42** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc/Et$_3$N = 10:1:0.01) to give **42** (0.10 g, 86%) as a yellow green solid (mp 198−199 °C): IR (KBr) 3037, 2877, 2836, 2790, 1611, 1509, 1486, 1441, 1344, 1274, 945, 818, 808, 765, 695, 683, 555 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.87 (s, 12H), 6.61−6.64 (d, J = 8.8 Hz, 4H), 6.98−7.00 (d, J = 8.8 Hz, 4H), 7.18−7.21 (m, 1H), 7.27−7.29 (m, 2H), 7.40−7.42 (m, 3H), 7.94−7.96 (m, 2H), 8.01−8.03 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 41.2, 113.8, 122.6, 128.2, 127.5, 127.6, 128.2, 128.8, 129.8, 133.9, 134.4, 138.3, 142.3, 146.8, 147.1, 162.2; MS (EI) m/z 490 (M$^+$); HRMS (EI) calcd for C$_{31}$H$_{30}$N$_4$S, 490.2191; found, 490.2178.

2-[1,1′-Biphenyl]-4-yl-4-phenyl-*N*,*N*-bis(4-dimethylaminophenyl)-5-thiazolamine (43). According to the general procedure for thiazoles, compound **43** was prepared. The crude material was purified by column chromatography (SiO$_2$, hexane/EtOAc = 5:1) to give **43** (0.08 g, 78%) as an orange solid (mp 147−151 °C): IR (KBr) 3025, 2878, 2794, 1608, 1509, 1483, 1443, 1341, 1271, 1222, 946, 841, 813, 764, 694 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.81 (s, 12H), 6.56 (d, J = 9.3 Hz, 4H), 6.93 (d, J = 9.3 Hz, 4H), 7.13−7.15 (m, 1H), 7.18−7.22 (m, 2H), 7.29−7.31 (m, 1H), 7.36−7.40 (m, 2H), 7.56−7.58 (m, 4H), 7.93−7.97 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 41.0, 113.6, 113.8, 122.2, 122.5, 126.4, 126.9, 127.3, 127.4, 127.6, 128.0, 128.8, 133.2, 133.8, 138.0, 140.2, 142.2, 146.7, 146.9, 161.5; MS (EI) m/z 566 (M$^+$); HRMS (EI) calcd for C$_{37}$H$_{34}$N$_4$S, 566.2504; found, 566.2498.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01963.

> Crystallographic data for **17**, **29**, **32**, **33**, **35**, and **42** in CIF format (CIF, CIF, CIF, CIF, CIF, CIF)
> Calculation of dipole moments, radiative and non-radiative rate constants, structure refinement for **17**, **29**, **32**, **33**, **35**, and **42**, and copies of ^{1}H and ^{13}C NMR spectra of products (PDF)

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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) For recent reviews, see: (a) Mukherjee, S.; Thilagar, P. *Dyes Pigm.* **2014**, *110*, 2. (b) Jeong, H.; Shin, H.; Lee, J.; Kim, B.; Park, Y.-I.; Yook, K. S.; An, B.- K.; Park, J. *J. Photonics Energy* **2015**, *5*, 057608. (c) Jou, J.-H.; Kumar, S.; Singh, M.; Chen, Y.-H.; Chen, C.-C.; Lee, M.-T. *Molecules* **2015**, *20*, 13005.

(2) For recent reviews, see: (a) Yang, Z.; Cao, J.; He, Y.; Yang, J. H.; Kim, T.; Peng, X.; Kim, J. S. *Chem. Soc. Rev.* **2014**, *43*, 4563. (b) Pradhan, T.; Jung, H. S.; Jang, J. H.; Kim, T. W.; Kang, C.; Kim, J. S. *Chem. Soc. Rev.* **2014**, *43*, 4684. (c) Zhou, Y.; Zhang, J. F.; Yoon, J. *Chem. Rev.* **2014**, *114*, 5511. (d) Kaur, P.; Singh, K. *RSC Adv.* **2014**, *4*, 11980. (e) Ghale, G.; Nau, W. M. *Acc. Chem. Res.* **2014**, *47*, 2150. (f) Terenzi, A.; Lauria, A.; Almerico, A. M.; Barone, G. *Dalton Trans* **2015**, *44*, 3527. (g) Zhou, X.; Lee, S.; Xu, Z.; Yoon, J. *Chem. Rev.* **2015**, *115*, 7944.

(3) (a) Tsai, Y.-L.; Fan, Y. S.; Lee, C.-J.; Huang, C.-H.; Das, D.; Lin, W. *Chem. Commun.* **2013**, *49*, 10266. (b) Cardoso, F. S. P.; Abboud, K. A.; Aponick, A. *J. Am. Chem. Soc.* **2013**, *135*, 14548. (c) Francke, R.; Little, R. D. *J. Am. Chem. Soc.* **2014**, *136*, 427. (d) Li, R.; Xiao, R.; Li, Y.; Lin, Q.; Zhang, R.; Zhao, J.; Yang, C.; Zou, K.; Li, D.; Yi, T. *Chem. Sci.* **2014**, *5*, 3922. (e) Dhanunjayarao, K.; Mukundam, V.; Venkatasubbaiah, K. *J. Mater. Chem. C* **2014**, *2*, 8599.

(4) (a) Schwartz, P. O.; Biniek, L.; Zaborova, E.; Heinrich, B.; Brinkmann, M.; Leclerc, N.; Méry, S. *J. Am. Chem. Soc.* **2014**, *136*, 5981. (b) Li, T.; Gao, J.; Cui, Y.; Zhong, C.; Ye, Q.; Han, L. *J. Photochem. Photobiol., A* **2015**, *303-304*, 91. (c) Nakagawa, T.; Yamaji, M.; Maki, S.; Niwa, H.; Hirano, T. *Photochem. Photobiol.* **2015**, *91*, 807.

(5) (a) Martorana, A.; Pace, A.; Buscemi, S.; Piccionello, A. P. *Org. Lett.* **2012**, *14*, 3240. (b) Chen, C. Y.; Hu, W. P.; Yan, P. C.; Senadi, G. C.; Wang, J. J. *Org. Lett.* **2013**, *15*, 6116. (c) Leitl, M. J.; Krylova, V. A.; Djurovich, P. I.; Thompson, M. E.; Yersin, H. *J. Am. Chem. Soc.* **2014**, *136*, 16032. (d) Mutoh, K.; Nakagawa, Y.; Sakamoto, A.; Kobayashi, Y.; Abe, J. *J. Am. Chem. Soc.* **2015**, *137*, 5674. (e) Yamashita, H.; Ikezawa, T.; Kobayashi, Y.; Abe, J. *J. Am. Chem. Soc.* **2015**, *137*, 4952.

(6) (a) Charier, S.; Ruel, O.; Baudin, J.-B.; Alcor, D.; Allemand, J.-F.; Meglio, A.; Jullien, L. *Angew. Chem., Int. Ed.* **2004**, *43*, 4785. (b) Iliashenko, R. Y.; Zozulia, O. S.; Doroshenko, A. O. *Cent. Eur. J. Chem.* **2011**, *9*, 962. (c) Iliashenko, R. Y.; Gorobets, N. Y.; Doroshenko, A. O. *Tetrahedron Lett.* **2011**, *52*, 5086. (d) Mahuteau-Betzer, F.; Piguel, S. *Tetrahedron Lett.* **2013**, *54*, 3188. (e) Kwon, J. E.; Park, S.; Park, S. Y. *J. Am. Chem. Soc.* **2013**, *135*, 11239. (f) Borodin, O. O.; Il'yashenko, R.; Yu; Doroshenko, A. O. *Chem. Heterocycl. Compd.* **2014**, *50*, 379.

(7) For selected examples, see: (a) Helal, A.; Kim, H. G.; Ghosh, M. K.; Choi, C.-H.; Kim, S.-H.; Kim, H. S. *Tetrahedron* **2013**, *69*, 9600. (b) Nagura, K.; Saito, S.; Yusa, H.; Yamawaki, H.; Fujihisa, H.; Sato, H.; Shimoikeda, Y.; Yamaguchi, S. *J. Am. Chem. Soc.* **2013**, *135*, 10322. (c) Mishra, B.; Shekar, K. P. C.; Kumar, A.; Phukan, S.; Mitra, S.; Kumar, D. *J. Heterocyclic Chem.* **2013**, *50*, 125. (d) Zheng, M.-H.; Sun, W.; Jin, J.-Y.; Yan, C.-H. *J. Fluoresc.* **2014**, *24*, 1169. (e) Wolfram, S.; Würfel, H.; Habenicht, S. H.; Lembke, C.; Richter, P.; Birckner, E.; Beckert, R.; Pohnert, G. *Beilstein J. Org. Chem.* **2014**, *10*, 2470. (f) Gautam, D.; Chaudhary, R. P. *Spectrochim. Acta, Part A* **2015**, *143*, 256. (g) Zhang, X.; Jing, S. Y.; Huang, S. Y.; Zhou, X. W.; Bai, J. M.; Zhao, B. X. *Sens. Actuators, B* **2015**, *206*, 663. (h) Tanaka, S.; Ashida, K.; Tatsuta, G.; Mori, A. *Synlett* **2015**, *26*, 1496.

(8) Murai, T.; Hori, F.; Maruyama, T. *Org. Lett.* **2011**, *13*, 1718.

(9) Murai, T.; Yamaguchi, K.; Hori, F.; Maruyama, T. *J. Org. Chem.* **2014**, *79*, 4930.

(10) (a) Murai, T.; Mutoh, Y. *Chem. Lett.* **2012**, *41*, 2. (b) Murai, T.; Nagaya, E.; Miyahara, K.; Shibahara, F.; Maruyama, T. *Chem. Lett.*

2013, *42*, 828. (c) Murai, T.; Morikawa, K.; Maruyama, T. *Chem. - Eur. J.* **2013**, *19*, 13112.

(11) (a) Murai, T.; Nishi, D.; Hayashi, S.; Nakanishi, W. *Bull. Chem. Soc. Jpn.* **2014**, *87*, 677. (b) Murai, T.; Mizutani, T.; Maruyama, T.; Ebihara, M. *J. Org. Chem.* **2015**, *80*, 6903.

(12) (a) Kondrat'eva, G. Y.; Aitzhanova, M. A.; Bogdanov, V. S.; Ivanova, Z. N. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1978**, *27*, 773. (b) Abu Safieh, K. A.; Darras, F. H.; Ayoub, M. T.; El-Abadelah, M. M.; Sabri, S. S.; Voelter, W. *Heterocycles* **2007**, *71*, 2681.

(13) Kempson, J. In *Name Reactions in Heterocyclic Chemistry II*; Li, J. J., Ed.; Jon Wiley & Sons: New York, 2011; p 299.

(14) (a) Murai, T. *Pure Appl. Chem.* **2010**, *82*, 541. (b) Shibahara, F.; Kobayashi, S.; Maruyama, T.; Murai, T. *Chem. - Eur. J.* **2013**, *19*, 304.

(15) (a) Jin, X.-H.; Ren, C.-X; Sun, J.-K.; Zhou, X.-J.; Cai, L.-X.; Zhang, J. *Chem. Commun.* **2012**, *48*, 10422. (b) Chaudhuri, T.; Das, T. K.; Salampuria, S.; Pal, C.; Banerjee, M. J. *J. Lumin.* **2014**, *145*, 525.

(16) (a) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; Wiley-VCH: Weinheim, Germany, 1988. (b) Suman, G. R.; Bubbly, S. G.; Gudennavar, S. B.; Thipperudrappa, J.; Roopashree, B.; Gayathri, V.; Nanje Gowda, N. M. *Luminescence* **2015**, *30*, 611. (c) Li, X. Y. *Int. J. Quantum Chem.* **2015**, *115*, 700.

(17) (a) Giordano, L.; Shvadchak, V. V.; Fauerbach, J. A.; Jares-Erijman, E. A.; Jovin, T. M. *J. Phys. Chem. Lett.* **2012**, *3*, 1011. (b) Gilani, A. G.; Moghadam, M.; Zakerhamidi, M. S. *Dyes Pigm.* **2012**, *92*, 1052. (c) Benedetti, E.; Kocsis, L. S.; Brummond, K. M. *J. Am. Chem. Soc.* **2012**, *134*, 12418. (d) Niko, Y.; Kawauchi, S.; Konishi, G. *Chem. - Eur. J.* **2013**, *19*, 9760.

(18) (a) Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 465. (b) Lippert, V. E. *Z. Elektrochem.* **1957**, *61*, 962. (c) Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra*; Dekker: New York, 1970. (d) Lippert, E. L. *Organic Molecular Photophysics*; Wiley: New York, 1975.

(19) (a) Forziati, A. F.; Glasgow, A. R., Jr.; Willingham, C. B.; Rossini, F. D. *National Bureau of Standards* **1946**, *36*, 129. (b) Koshevar, V. D. *Colloid J.* **2005**, *67*, 734. (c) Delgado-Camón, A.; Garriga, R.; Mateos, E.; Cebolla, V. L.; Galbán, J.; Membrado, L.; Marcos, S.; Gálvez, E. M. *Chem. Phys. Lett.* **2011**, *501*, 547. (d) Fukazawa, A.; Yamaguchi, E.; Ito, E.; Yamada, H.; Wang, J.; Irle, S.; Yamaguchi, S. *Organometallics* **2011**, *30*, 3870.

(20) For twisted intramolecular charge transfer mechanism, see: (a) Rettig, W. *Appl. Phys. B: Photophys. Laser Chem.* **1988**, *45*, 145. (b) Freidzon, A. Y.; Safonov, A. A.; Bagaturyants, A. A.; Alfimov, M. V. *Int. J. Quantum Chem.* **2012**, *112*, 3059. (c) Ookubo, Y.; Wakamiya, A.; Yorimitsu, H.; Osuka, A. *Chem. - Eur. J.* **2012**, *18*, 12690. (d) Mao, M.; Ren, M. G.; Song, Q. H. *Chem. - Eur. J.* **2012**, *18*, 15512. (e) Debnath, T.; Maity, P.; Lobo, H.; Singh, B.; Shankarling, G. S.; Ghosh, H. N. *Chem. - Eur. J.* **2014**, *20*, 3510. (f) Zhong, C. *Phys. Chem. Chem. Phys.* **2015**, *17*, 9248.

(21) (a) Yuan, C.; Saito, S.; Camacho, C.; Irle, S.; Hisaki, I.; Yamaguchi, S. *J. Am. Chem. Soc.* **2013**, *135*, 8842. (b) Mishra, A.; Sahu, S.; Tripathi, S.; Krishnamoorthy, G. *Photochem. Photobiol. Sci.* **2014**, *13*, 1476. (c) Kautny, P.; Lumpi, D.; Wang, Y.; Tissot, A.; Bintinger, J.; Horkel, E.; Stöger, B.; Hametner, C.; Hagemann, H.; Ma, D.; Fröhlich, J. *J. Mater. Chem. C* **2014**, *2*, 2069.

(22) A similar effect of electron-donating groups in the one-electron oxidation potential has been observed. See: Moss, K. C.; Bourdakos, K. N.; Bhalla, V.; Kamtekar, K. T.; Bryce, M. R.; Fox, M. A.; Vaughan, H. L.; Dias, F. B.; Monkman, A. P. *J. Org. Chem.* **2010**, *75*, 6771.

(23) Chiu, K. Y.; Su, T. X.; Li, J. H.; Lin, T.-H.; Liou, G.-S.; Cheng, S.-H. *J. Electroanal. Chem.* **2005**, *575*, 95.

(24) Frisch, M. J. et al. *Gaussian 09*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

(25) Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C. *Adv. Mater.* **2011**, *23*, 2367.

(26) Murai, T.; Michigami, T.; Yamaguchi, M.; Mizuhata, N. *J. Sulfur Chem.* **2009**, *30*, 225.

(27) Engman, L. *J. Org. Chem.* **1991**, *56*, 3425.

(28) Hermant, F.; Urbanska, E.; de Mazancourt, S. S.; Maubert, T.; Nicolas, E.; Six, Y. *Organometallics* **2014**, *33*, 5643.