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Convenient preparation of 4-arylmethyl- and 4-hetarylmethyl thiazoles by regioselective cycloaddition reactions of 3-sulfanyl- and selanylpropargyl alcohols

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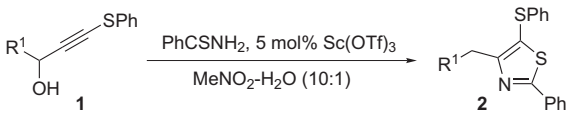
ABSTRACT

Complete details of thiazole syntheses by scandium-catalyzed cycloaddition reactions of 1-aryl- and 1,1-bisaryl-3-phenylsulfanylpropargyl alcohols with thioamides are described. Reactions of 1,1-bisarylpropargyl alcohols with thioamides and selenamide in $MeNO_2/H_2O$ resulted in 4-bisarylmethyl-1,3-thiazoles **4aa**–**ic** and 4H-4,4-bisaryl-1,3-thiazines **5ea**–**ga** in high yields. Reactions in $MeNO_2/D_2O$ resulted in 4-bisaryldeuteriomethyl-1,3-thiazoles **10ca**–**ia** with high deuterium purity. Reactions of dialkyl and alkyl aryl propargyl alcohols are also described.

1. Introduction

Hantzsch thiazole synthesis[1] is one of the best and most widely used routes to thiazoles, consisting of cyclization between a S–C–N fragment and a C–C fragment. The most common reagents providing S–C–N fragments[2] are the readily available and very stable starting materials, thioureas or thioamides. Useful reagents for providing C–C fragments are α-halo ketones[3] and similar compounds.[4] Other reagents providing C–C fragments, acceptors of thioamides, have been reported as alkynyliodonium salts,[5] α-haloacetonitriles,[6] α-diazoketones,[7] and propargyl bromides.[8] Recently, we reported a highly regioselective thiazole synthesis by cycloaddition reactions of 3-sulfanyl propargyl alcohols **1** with thioamides under mild scandium-catalyzed conditions (Scheme 1).[9]



2a (R^1=*p*-$MeOC_6H_4$), **2b** (3,4-$(MeO)_2C_6H_3$), **2c** (3,4-$(OCH_2O)C_6H_3$), **2d** (*p*-F-C_6H_4), **2e** (2-thienyl)

Scheme 1. Synthesis of thiazoles from propargyl alcohols.

The excellent regioselectivity of these reactions is due to a combination of the remarkable solvent effect of $MeNO_2/H_2O/Bu_4NHSO_4$ and the γ-substituent effect of the sulfur or selenium functional groups on the propargyl alcohols.[10] However, details of the reaction mechanism for 1,3-thiazole synthesis were not completely understood. In addition, reactions of disubstituted propargyl alcohols, such as 1,1-bisarylpropargyl alcohols and 1-ethynylcycloalkanols, were far more complex than those of the mono-aryl propargyl alcohols.[9] To clarify the mechanisms and limitations of these cycloaddition reactions, we performed cycloadditions of 1,1-bisarylpropargyl alcohols and 1,1-bisalkyl derivatives. Here, we report the complete details of efficient scandium-catalyzed cycloaddition reactions in $MeNO_2/H_2O$.

2. Results and discussion

First, we investigated the reactions of 1,1-bisaryl and 1,1-bis(hetaryl) propargyl alcohols **3**, which were easily obtained by reactions of phenylsulfanyl and phenylselanylethynes and the corresponding bisaryl or bis(hetaryl) ketones with thiobenzamide, thioacetamide, and benzselenamide (Table 1). Reaction of 1,1-diphenyl-3-(phenylsulfanyl)propargyl alcohol **3a** with thioacetamide resulted in 4-diphenylmethyl-2-methyl-5-(phenylsulfanyl)-1,3-thiazole **4aa** in 78% yield (entry 1). The structure of **4aa** was determined from the spectral features: the ^1H NMR spectrum shows a benzylic proton at δ 5.93 ppm, the ^{13}C NMR spectrum shows a benzylic carbon at δ 49.7 ppm, and the mass spectrum shows a molecular ion peak at *m*/*z* 373. Reaction of **3a**

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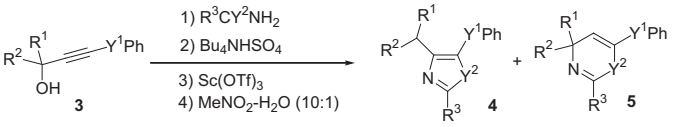
Table 1
Scandium-catalyzed cycloaddition of propargyl alcohol in $MeNO_2/H_2O$



Entry	Alcohol	R^1	R^2	Y^1	R^3	Y^2	Products	(% Yields)
1	**3a**	Ph	Ph	S	Me	S	**4aa** (78)	
2	**3a**	Ph	Ph	Se	Ph	Se	**4ba** (55)	
3	**3b**	Ph	Ph	Se	Ph	S	**4bb** (75)	
4	**3c**	*p*-FC_6H_4	*p*-FC_6H_4	S	Me	S	**4ca** (77)	
5	**3c**	*p*-FC_6H_4	*p*-FC_6H_4	S	Ph	S	**4cb** (99)	
6	**3d**	*p*-FC_6H_4	*p*-FC_6H_4	Se	Ph	S	**4da** (88)	
7	**3e**	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	S	Ph	S	**4ea** (9)	**5ea** (70)
8	**3f**	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	Se	Ph	S	**4fa** (35)	**5fa** (35)
9	**3g**	Ph	Me	S	Ph	S	**4ga** (78)	
10	**3g**	Ph	Me	S	Ph	S	**4ga** (18)[a]	**5ga** (44)
11	**3h**	2-Thienyl	2-Thienyl	S	Ph	S	**4ha** (66)	
12	**3i**	2-Thienyl	2-Thienyl	Se	Me	S	**4ia** (57)	
13	**3i**	2-Thienyl	2-Thienyl	Se	Ph	S	**4ib** (68)	
14	**3i**	2-Thienyl	2-Thienyl	Se	Ph	Se	**4ic** (68)	

[a] The reaction in the absence of H_2O gave 4,5-Dihydro-5-methyl-2,5-diphenyl-4-(phenylsulfanylmethylene)-1,3-thiazole (**6ga**) in 35% yield.

with benzselenamide under approximately same conditions resulted in the corresponding 4-diphenylmethyl 1,3-selenazole **4ba** as the sole product (entry 2). Reactions of bisarylpropargyl alcohols **3c** and **3h** and selenium derivatives **3d** and **3i** resulted in bisarylmethyl-1,3-thiazoles (entries 2–8, 10–13), respectively. However, reactions of bis(*p*-methoxyphenyl)propargyl alcohols **3e** and **3f** resulted in a mixture of two compounds, the targeted cycloadduct and an unexpected cycloadduct. To determine the structures of the two cycloadduct products, we performed desulfanylation by treating **4ea** with tributyltin hydride/AIBN in toluene under reflux conditions. The reaction resulted in two products: 4,4-bis(*p*-methoxyphenyl)-4,4-dihydro-2-phenyl-1,3-thiazin **8ea** and 4-[bis(*p*-methoxyphenyl)methyl]-2-phenyl-5-(tributylstannyl)-1,3-thiazole, which upon transmetalation with MeLi easily provided 4-[bis(*p*-methoxyphenyl)methyl]-2-phenyl-1,3-thiazole **7ea** (Fig. 1). The result demonstrates that the reaction of **4ea** produces both 1,3-thiazole **4ea** and the unexpected thiazine **5ea** via different pathways: 5-*exo*- or 6-*endo*-mode cyclization. In particular, entry 7 contains a dramatically increased proportion of 1,3-thiazine **5ea**. These different selectivities are undoubtedly responsible for the electronic natures of the propargylic carbocations. In contrast, although the reaction of alcohol **3g** (R^1=phenyl; R^2=methyl) also provided phenylethyl derivative **4ga** (entry 9) in good yield, the reaction without H_2O provided compounds **4ga**, **5ga**, and **6g** (entry 10). These products were confirmed by the same desulfanylation reaction that resulted in thiazine **8ga** and thiazole **9ga** (Fig. 1). Reactions of thienyl derivatives **3h** and **3i** with

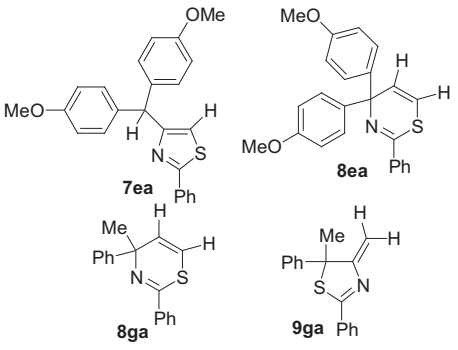
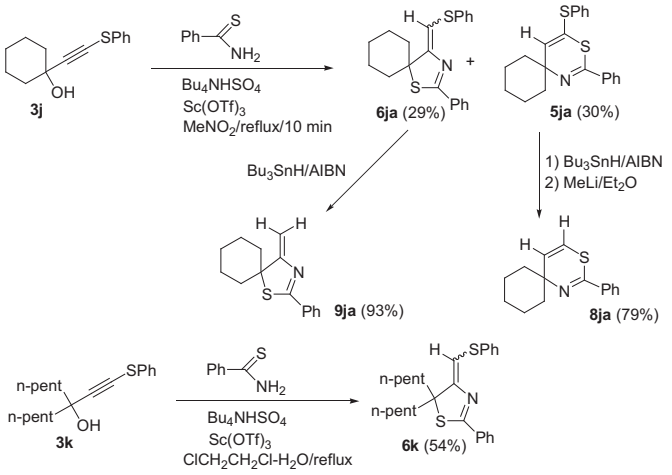


Figure 1.

thioamides and selenamide exclusively provided thiazoles **4ha**, **4ia**, **4ib**, and **4ic** (entries 11–14), regioselectively.

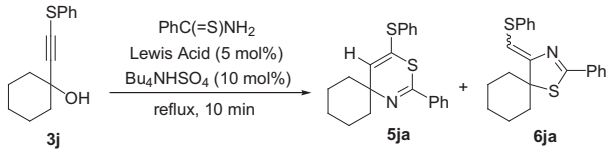
Next, we investigated the reactions of 1,1-dialkylpropargyl alcohols with thioamides (Scheme 2). Reaction of 1-(phenylsulfanylethynyl)cyclohexanol **3j** treated with thiobenzamide under the same conditions resulted in two types of spiro compounds, **6ja** and **5ja**, by 5-*exo*-mode cycloaddition of the propargyl cation and 6-*endo*-mode cycloaddition of the α-sulfanyl allenyl cation intermediates, respectively. Product structures of both **6ja** and **5ja** were confirmed as described above. The identification of compound **6ja** was demonstrated by conversion to 4-methylene-1-thia-3-azaspiro[4.5]dec-2-ene **9ja** and observation of the spectral features, which show *exo*-methylene at δ 5.15 (d, *J*=1 Hz) and 5.27 (d, *J*=1 Hz). Desulfanylation of **5ja** was achieved by successive transmetalation with MeLi in ether via 4-tributylstannyl-2-phenyl-3-thia-1-azaspiro[5.5]undec-2-ene to provide **8ja**, whose structure was determined by the characteristic vicinal protons at δ 5.80 and 6.41 ppm (*J*=10 Hz) because of thiazine. However, both products **6ja** and **5ja** contain other unknown compounds that might be regioisomers or *E*- and *Z*-stereoisomers. Reaction in $Sc(OTf)_3/MeNO_2/H_2O$ is ineffective for regioselective cycloaddition of the dialkyl derivatives. We investigated reaction conditions for the cycloaddition of cyclohexanol **3j** with thiobenzamide by varying the Lewis acid (e.g., BF_3/Et_2O, Yb(OTf)$_3$, Sc(OTf)$_3$, Hf(OTf)$_4$, Cu(OTf)$_2$, Sn(OTf)$_2$, Ln(OTf)$_3$, TMSOTf, …), solvent ($MeNO_2$, CH_2Cl_2, $ClCH_2CH_2Cl$, DMF, DMSO with or without H_2O), and reaction temperature. Surprisingly, the best combination of the conditions for conversion of bicyclic compounds **6ja** and **5ja** to spirothiazoles is reflux for 10 min in hafnium triflate (5 mol %)/$ClCH_2CH_2Cl$ (entry 7 of Table 2). These optimized conditions also apply to the reactions of other cycloalkanols and the undecanol **3k** (Scheme 2 and Table 3). Reaction of **3j** with thioacetamide exclusively provided (*E*)- and (*Z*)-2-methyl-4-(phenylsulfanylmethylene)-1-thia-3-azaspiro[4.5]dec-2-ene **6jb** in 65% yield (entry 1). Reactions of cyclopentanol **3l** resulted in spiro compounds **6la** and **6lb** in good yields. Thiazole formation proceeded without formation of β-elimination products to provide 1-thia-3-azaspiro[4.4]non-2-enes **6la** and **6lb**. Selenium analogs **6m** and spirocyclododecane **6n** were also obtained in moderate yield.



Scheme 2. Reaction of 1,1-dialkylpropargyl alcohols with thiobenzamides.

We also investigated studied the reactions of propargyl alcohols **3** with thioamides in $MeNO_2/D_2O$ (10:1) as a mechanistically intriguing and powerful approach to thiazole synthesis from propargyl alcohols (Table 4). Reaction of **3c** with thiobenzamide in $MeNO_2/D_2O$ resulted in the deuterated product 1,1-bis(*p*-fluorophenyl)methyl-5-phenylsulfanyl-1,3-thiazole **10ca** (entry 1) in 75% yield with 87% deuterium purity. Reactions of **3c** and **3d** with thioacetamides and benzselenamide produced various thiazoles

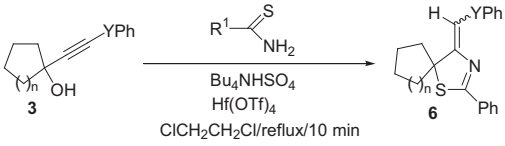
Table 2
Discovering reaction conditions for cycloaddition of cyclohexanol **3j** with thiobenzamide



3j 5ja 6ja

Entry	Condition	**5ja** (% yield)	**6ja** (% yield)(*Z*:*E*)
1	$Sc(OTf)_3$, $MeNO_2$	28	33 (10:1)
2	BF_3-Et_2O, $MeNO_2/H_2O$ (10:1)	20	25 (8:1)
3	$Yb(OTf)_3$, $MeNO_2/H_2O$ (10:1)	22	21 (3:1)
4	$Cu(OTf)_2$, $MeNO_2/H_2O$ (10:1)	11	11 (5:3)
5	$Y(OTf)_3$, $MeNO_2/H_2O$ (10:1)	16	24 (9:1)
6	$Hf(OTf)_4$, $MeNO_2/H_2O$ (10:1)	33	28 (13:1)
7	$Hf(OTf)_4$, $ClCH_2CH_2Cl$	4	56 (99:1)
8	$Hf(OTf)_4$, $ClCH_2CH_2Cl/H_2O$ (10:1)	11	45 (99:1)
9	$Hf(OTf)_4$, $CHCl_3/H_2O$ (10:1)	5	37 (99:1)

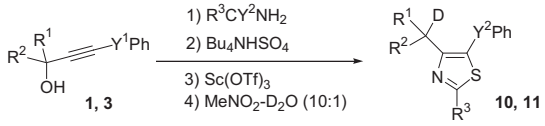
Table 3
Reactions of phenylsulfanyl and phenylselanyl cycloalkanols in $ClCH_2CH_2Cl$



Entry	Cycloalkanol **3** (Y/*n*=)	Amide (R^1)	**6ja** (% yield)(*Z*:*E*)
1	**3j** (S/2)	Me	**6jb** (65) (88:12)
2	**3l** (S/1)	Ph	**6la** (43) (99:1)
3	**3l** (S/1)	Me	**6lb** (47) (99:1)
4	**3m** (Se/2)	Ph	**6m** (50) (99:1)
5	**3n** (S/8)	Ph	**6n** (43) (77:23)

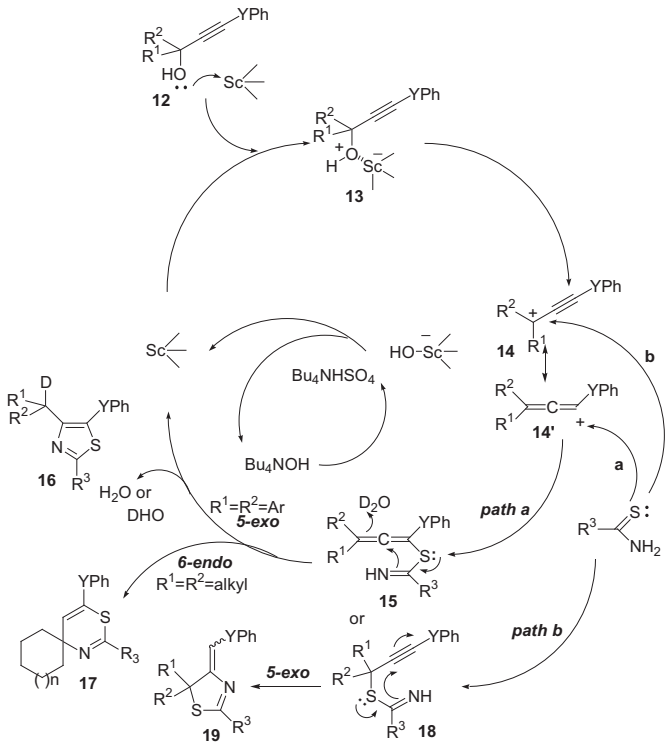
10cb and selenazole **10cc** (entries 2–4 of Table 4). Cycloaddition reactions of the monoaryl derivatives provided **11aa** and **11ea** in high yields but with lower deuterium purity than that for the bisaryl derivatives (entries 5 and 6). Reactions of most of the disubstituted alcohols provided deuterated products **10ea**, **10b–c**, and **10ia** with high deuterium purity (entries 7–11). Our previous findings suggest that cycloaddition may be a stepwise process (Scheme 3). Reaction of propargyl alcohol **12** by activation and departure of its hydroxyl group resulted in intermediates α-sulfanyl and selanylpropargyl cation **14** and propadienyl cation **14′**. In the case of the alcohol (R^1=R^2=aryl), the latter intermediate **14′** is stabilized by both two aromatic groups and an α-sulfanyl group. A

Table 4
Scandium-catalyzed cycloaddition of propargyl alcohol in $MeNO_2/D_2O$



Entry	Alcohol	R^1	R^2	Y^1	R^3	Y^2	Product (% yields/D%)
1	**3c**	*p*-FC_6H_4	*p*-FC_6H_4	S	Ph	S	**10ca** (75/87)
2	**3c**	*p*-FC_6H_4	*p*-FC_6H_4	S	Me	S	**10cb** (62/91)
3	**3c**	*p*-FC_6H_4	*p*-FC_6H_4	S	Ph	Se	**10cc** (43/88)
4	**3d**	*p*-FC_6H_4	*p*-FC_6H_4	Se	Ph	S	**10da** (80/88)
5	**1a**	*p*-$MeOC_6H_4$	H	S	Ph	S	**11aa** (70/46)
6	**1e**	*p*-FC_6H_4	H	S	Ph	S	**11ea** (90/49)
7	**3e**	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	S	Ph	S	**10ea** (49/90)
8	**3h**	2-Thienyl	2-Thienyl	S	Ph	S	**10ha** (59/90)
9	**3h**	2-Thienyl	2-Thienyl	S	Me	S	**10hb** (54/92)
10	**3h**	2-Thienyl	2-Thienyl	S	Ph	Se	**10hc** (57/85)
11	**3i**	2-Thienyl	2-Thienyl	Se	Ph	S	**10ia** (59/90)

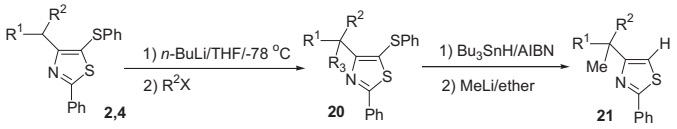
reaction medium, such as $MeNO_2/H_2O$ fully stabilizes both the intermediates. Therefore, thioamides regioselectively attack the α-sulfanyl allenyl cation **14′**, which is thermodynamically more stable than **14**, and intramolecular cyclization then occurs in 5-*exo* mode to provide 1,3-thiazole **16** (*path a*). In contrast, because dialkyl **14** is not stabilized by aromatic substituents, the reactions of dialkylpropargyl alcohols (R^1=R^2=alkyl) proceed via both intermediate **14** and **14′** to give two types of products, thiazole **19** (through *path b*) and thiazine **17** (through *path a*). Thus, we attempted to control the reaction path by which cycloalkanols react with thioamides by using chlorinated solvents, such as CH_2Cl_2 or 1,2-dichloroethane, which could activate the propargyl cation **14**. In the final step, reaction by intramolecular 5-*exo*-mode cyclization of iminyl propadienyl sulfide **18** results in 4-methylene-1,3-thiazole **19**. Biaryl derivatives (R^1=R^2=aryl) undergo smooth 5-*exo*-mode attack of the nitrogen of intramolecular imine **15**, providing **16** because of the strong stabilizing effect of the one or two aromatic groups on the benzylic anions. This mechanism for the formation of thiazoles is supported by the fact that protonation in the anionic cyclization of imine **15** would occur with both the higher deuterium purity and the exclusive deuteration on the 4-benzylic position of the thiazoles. These would be the most suitable mechanisms for formation of thiazoles. It is very interesting that the cycloadditions of dialkyl allenyl imine **15** (R^1=R^2=alkyl) exclusively undergo 6-*endo*-mode cyclization to provide thiazine **17**.



Scheme 3. Mechanism for formations of thiazoles and thiazines.

Finally, we examined the alkylation reactions of 4-benzylthiazoles with *n*-BuLi/alkyl halides, some of which were reported in the previous communication (Table 5) to investigate the transformation of the thiazoles obtained. First, we reacted lithiated 1,3-thiazoles with some electrophiles (entries 1–6). Reaction of 4-*p*-methoxybenzyl-5-phenylsulfanyl-1,3-thiazole **2a** with *n*-BuLi at −78 °C easily resulted in a versatile lithiated 1,3-thiazole. Reactions with alkyl halides, such as methyl iodide, ethyl iodide, benzyl bromide, and isopropyl iodide provided alkylated products **20a–d** in moderate to high yields. Reaction of lithiated **2a** with methanol-

Table 5
Alkylations of lithiated thiazoles with alkyl halides



Entry	Thiazole	R^1	R^2	*n*-BuLi (equiv)	R^3X (equiv)	Product (% yield)	Product (% yield)[a]
1	**2a**	*p*-$MeOC_6H_4$	H	3	MeI (10)	**20a** (Me) (79)	**21a** (69/72)
2	**2a**	*p*-$MeOC_6H_4$	H	1.5	EtI (1.5)	**20b** (Et) (87)	
3	**2a**	*p*-$MeOC_6H_4$	H	1.5	CD_3OD (10)	**20c** (D) (69)	
4	**2a**	*p*-$MeOC_6H_4$	H	1.5	*i*-PrI (3)	**20d** (*i*-Pr) (69)	
5	**2b**	3,4-$(MeO)_2C_6H_3$	H	1.2	MeI (10)	**20e** (Me) (63)	**21e** (58/74)
6	**2b**	*p*-FC_6H_4	H	3	Bn (3)	**20f** (Bn) (50)	
7	**2c**	*p*-$MeOC_6H_4$	H	1.5	Bn (3)	**20g** (Bn) (78)	
8	**2d**	*p*-$MeOC_6H_4$	H	1.5	MeI (10)	**20h** (Me) (63)	**21h** (96/75)
9	**2e**	Ph	H	1.2	MeI (10)	**20i** (Me) (74)	**21i** (93/75)
10	**4aa**	Ph	Ph	1.2	MeI (10)	—	

[a] The yields of both stannylation and transmetalation are, respectively, shown.

d_4 resulted in mono deuterated thiazole **20c** in almost pure form. Some 4-benzylthiazoles also underwent lithiation and alkylation to provide a wide variety of substituted thiazoles in good yields. In contrast, alkylation of 4-bisarylmethyl-1,3-thiazole **4aa** did not proceed under some conditions. Next, we examined the desulfanylation of methylated thiazoles, because neither sulfanyl nor selanyl functional groups are necessary to provide other useful compounds. Methylated thiazoles underwent desulfanylation to provide thiazoles **21a**–**i** by the two-step process described above. A representative example is described as follows. The desulfanylation of **20a** by using tributyltin hydride/AIBN, one of the usual methods for the desulfanylation and deselanylation of bis(aryl) sulfides and bis(aryl) selenides, failed to hydrate the thiazoles, forming stannylated thiazoles instead. Therefore, we performed transmetalation of the stannanes using MeLi. The same procedures for the alkylated thiazoles **20e**, **20h**, and **20i** were also examined, as shown in entries 5, 8, and 9. These investigations demonstrate that the thiazole of propargyl alcohols bearing sulfur and selenium functional groups with thioamides is one of the most practical leading compounds because of its useful functionalities.

3. Conclusion

In conclusion, we demonstrated a useful thiazole synthesis by reaction of 3-sulfanyl and selanylpropargyl alcohols with some thioamides and selenamides. 1-Aryl and 1,1-bis(aryl)propargyl alcohols resulted in 4-benzyl and 4-bisarylmethyl-1,3-thiazoles in good-to-high yields. 1,1-Dialkyl derivatives provided two types of products, by 5-*exo*- or 6-*endo*-mode cyclization reactions, which we could control by choosing an appropriate solvent. We further investigated cyclization reactions in $MeNO_2/D_2O$ and showed details of the mechanisms for scandium-catalyzed cycloaddition reactions of 3-sulfanyl and selanylpropargyl alcohols with thioamides and selenamide.

4. Experimental

4.1. General

Melting points were determined on a J-Science Labo micro-melting point apparatus and uncorrected. Elemental analyses were performed at the Center of Instrumentation of Gifu University. ^1H and ^{13}C NMR spectra were determined with JEOL ECA600 (600 MHz) spectrometer at Gifu University. Chemical shift are expressed in parts par million (ppm) with respect to tetramethylsilane as the internal standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet. IR spectra were recorded with a JASCO FT-IR 460PLUS infrared spectrometer and are expressed in reciprocal centimeters. EI mass spectra (MS) were obtained using a JEOL MS-700 spectrometer with a direct-insertion probe at 70 eV. All high-resolution mass spectra were obtained using a JMSD300 JMA2000 on-line system.

4.2. Preparations of 2-phenylthiazole (2a–e)

*Preparations of 4-(4-methoxybenzyl)-2-phenyl-5-(phenylsulfanyl) thiazole (**2a**). Typical procedure*. To a nitromethane (0.5 ml)/water (0.05 ml) solution of 1-(*p*-methoxyphenyl)-3-(phenylsulfanyl) prop-2-yn-1-ol (**1a**) (50 mg, 0.18 mmol) was added thiobenzamide (50 mg, 0.37 mmol) and tetrabutylammonium hydrogensulfate (6 mg, 0.018 mmol). Then scandium triflate (4 mg, 0.009 mmol) was added to a mixture. The whole was stirred under a reflux condition for 10 min and poured into a saturated $NaHCO_3$ (50 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt/*n*-hexane (1:20) to give the title compound **2a** (65 mg, 93%) as a yellow oil.

Compound **2a**: IR (KBr, cm^{-1}) ν 3063, 3031, 2999, 2951, 2930, 2909, 2832, 1610, 1582, 1510, 1478, 1454, 1440, 1427, 1301, 1245, 1175, 1107, 1082, 1070, 1036, 1001, 985, 847, 817, 763, 741, 687, 661, 620; ^1H NMR (600 MHz, $CDCl_3$) δ 3.75 (3H, s, OMe), 4.19 (2H, s, CH_2), 6.77 (2H, d, J=9 Hz, ArH), 7.14–7.17 (3H, m, ArH), 7.22–7.24 (4H, m, ArH), 7.40–7.41 (3H, m, ArH), 7.90–7.91 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.7 (t), 55.2 (q), 113.7 (d×2), 120.9 (s), 126.2 (d), 126.5 (d×2), 127.1 (d×2), 128.9 (d×2), 129.1 (d×2), 129.9 (d×2), 130.4 (d), 131.1 (s), 133.4 (s), 137.3 (s), 158.0 (s), 162.3 (s), 170.5 (s); MS *m*/*z* 389 (M^+), 374 (M^+–Me), 312 (M^+–Ph), 280 (M^+–PhS). Anal. Calcd for $C_{23}H_{16}NOS_2$: C, 70.92; H, 4.92; N, 3.60. Found: C, 70.79; H, 4.98; N, 3.60.

*4.2.1. 4-[(3,4-Dimethoxybenzyl)-2-phenyl-5-(phenylsulfanyl)-thiazole (**2b**).* IR (KBr, cm^{-1}) ν 2930, 1515, 1478, 1464, 1454, 1261, 1235, 1154, 1140, 1029, 764, 741, 689; ^1H NMR (600 MHz, $CDCl_3$) δ 3.65 (3H, s, MeO), 3.73 (3H, s, MeO), 4.11 (2H, s, CH_2), 6.65 (1H, d, J=9 Hz, ArH), 6.77 (1H, d, J=9 Hz, ArH), 6.78 (1H, s, ArH), 7.02–7.16 (6H, m, ArH), 7.31–7.33 (2H, m, ArH), 7.82 (2H, dd, J=3 and 7 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.1 (t), 55.6 (q), 55.8 (q), 111.1 (d), 112.3 (d), 120.7 (s), 120.9 (d), 126.2 (d), 126.4 (d×2), 127.0 (d×2), 128.9

(d×2), 129.1 (d×2), 130.4 (d), 131.5 (s), 133.4 (s), 137.3 (s), 147.4 (s), 148.7 (s), 162.3 (s), 170.6 (s); MS *m*/*z* 419 (M^+), 342 (M^+−Ph), 310 (M^+−SPh). Anal. Calcd for $C_{24}H_{21}S_2O_2N$: C, 68.71, H, 5.05; N, 3.34. Found: C, 68.52; H, 5.10; N, 3.30.

*4.2.2. 4-(3,4-Methylenedioxybenzyl)-2-phenyl-5-(phenyl-sulfanyl) thiazole (**2c**).* White powders, mp 63–65 °C, IR (KBr, cm^{-1}) ν 2886, 1712, 1581, 1502, 1487, 1442, 1361, 1245, 1185, 1039, 929, 978, 764, 740, 689; ^1H NMR (600 MHz, $CDCl_3$) δ 4.15 (2H, s, CH_2), 5.86 (2H, s, CH_2), 6.65 (1H, d, *J*=8 Hz, ArH), 6.74 (1H, d, *J*=8 Hz, ArH), 6.83 (1H, d, *J*=1 Hz, ArH), 7.14–7.16 (3H, m, ArH), 7.21–7.24 (2H, m, ArH), 7.39–7.40 (3H, m, ArH), 7.89–7.91 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.2 (t), 100.7 (t), 108.0 (d), 109.5 (d), 121.1 (s), 121.9 (d), 126.3 (d), 126.5 (d×2), 127.1 (d×2), 128.9 (d×2), 129.1 (d×2), 130.4 (d), 132.6 (s), 133.4 (s), 137.2 (s), 145.9 (s), 147.4 (s), 162.0 (s), 170.5 (s); MS *m*/*z* 403 (M^+), 326 (M^+−Ph), 294 (M^+−SPh). Anal. Calcd for $C_{23}H_{19}O_2S_2N$: C, 68.46, H, 4.25; N, 3.47. Found: C, 68.04; H, 4.36; N, 3.44.

*4.2.3. 4-(4-Fluorobenzyl)-2-phenyl-5-(phenylsulfanyl)thiazole (**2d**).* A yellow oil, IR (KBr, cm^{-1}) ν 3060, 2922, 1602, 1581, 1508, 1489, 1478, 1454, 1440, 1427, 1222, 1157, 1052, 1023, 986, 853, 835, 822, 778, 763, 739, 668, 661, 620; ^1H NMR (600 MHz, $CDCl_3$) δ 4.20 (2H, s, CH_2), 6.88 (2H, d, *J*=8 Hz, ArH), 7.13 (2H, d, *J*=8 Hz, ArH), 7.14–7.16 (1H, m, ArH), 7.19–7.26 (4H, m, ArH), 7.39–7.40 (3H, m, ArH), 7.88–7.90 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.7 (t), 114.9 (d), 115.1 (d), 121.2 (s), 126.3 (d×2), 126.5 (d×2), 127.1 (d×2), 128.9 (d×2), 129.1 (d×2), 130.3 (d), 130.4 (d), 130.5 (d), 133.3 (s), 137.1 (s), 161.5 (d, *J*=244 Hz), 161.7 (s), 170.6 (s); MS *m*/*z* 377 (M^+), 300 (M^+−Ph), 268 (M^+−PhS). Anal. Calcd for $C_{22}H_{16}NFS_2$: C, 67.00; H, 4.27; N, 3.71. Found: C, 69.86; H, 4.29; N, 3.69.

*4.2.4. 2-Phenyl-5-(phenylsulfanyl)-4-(2-thienylmethyl)thiazole (**2e**).* White prisms, from CH_2Cl_2/*n*-hexane, mp 63–64 °C, IR (KBr, cm^{-1}) ν 3104, 3064, 2914, 2901, 2852, 1713, 1579, 1579, 1504, 1491, 1476, 1454, 1439, 1419, 1359, 1308, 1284, 1237, 1177, 1156, 1120, 1075, 1050, 1026, 1000, 985, 923, 903, 849, 830, 763, 744, 687, 659, 625; ^1H NMR (600 MHz, $CDCl_3$) δ 4.43 (2H, s, CH_2), 6.87 (2H, d, *J*=3 Hz, ArH), 7.10–7.25 (5H, m, ArH), 7.39–7.41 (3H, m, ArH), 7.90–7.93 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 30.0 (t), 121.6 (s), 124.1 (d), 125.6 (d), 126.4 (d), 126.5 (d×2), 126.6 (d), 127.3 (d×2), 128.9 (d×2), 129.1 (d×2), 130.5 (d), 133.3 (s), 137.0 (s), 141.0 (s), 160.7 (s), 170.6 (s); MS *m*/*z* 365 (M^+), 280 (M^+−thienyl), 256 (M^+−PhS). Anal. Calcd for $C_{20}H_{14}NS_3$: C, 65.90; H, 3.87; N, 3.84. Found: C, 65.75; H, 4.20; N, 3.80.

4.3. Preparations of 1,1-bis(aryl)propargyl alcohols

*4.3.1. 1,1-Diphenyl-3-(phenylsulfanyl)prop-2-yn-1-ol (**3a**). Typical procedure.* *n*-BuLi was added dropwise to a THF (10 ml) solution of ethynyl phenyl sulfide (0.40 g, 2.98 mmol) at 0 °C under an Ar atmosphere. After stirring for 10 min, benzophenone (0.65 g, 3.58 mmol) in THF (5 ml) was added to the mixture. The whole was stirred 2 h at room temperature and poured into water (100 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt/*n*-hexane (1:10) to give the title compound (0.437 g, 46%) as a yellow oil.

IR (KBr, cm^{-1}) ν 3542, 3426, 3060, 3028, 2955, 2870, 2170, 1953, 1886, 1809, 1582, 1490, 1478, 1449, 1329, 1179, 1098, 1065, 1032, 999, 919, 890, 741, 699, 669, 643, 595, 532, 495, 464, 436; ^1H NMR (600 MHz, $CDCl_3$) δ 42.93 (1H, br s, OH), 7.20–7.21 (1H, m, ArH), 7.25–7.30 (4H, m, ArH), 7.33–7.38 (6H, m, ArH), 7.62–7.64 (4H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 73.8 (s), 74.9 (s), 101.3 (s), 125.7 (d×2), 125.8 (d×4), 126.2 (d), 127.3 (d×2), 127.9 (d×4), 128.9 (d×2), 130.1 (s), 144.4 (s×2); MS *m*/*z* 316 (M^+), 299 (M^+−OH), 239 (M^+−Ph), 207 (M^+−SPh). Anal. Calcd for $C_{21}H_{16}OS$: C, 79.71; H, 5.10. Found: C, 79.98; H, 5.31.

*4.3.2. 1,1-Diphenyl-3-(phenylselanyl)prop-2-yn-1-ol (**3b**).* A yellow oil, IR (KBr, cm^{-1}) ν 3433 (OH), 3059, 2170, 1953, 1577, 1490, 1477, 1449, 1440, 1327, 1179, 1162, 1058, 1031, 1021, 997, 918, 890, 776, 890, 642; ^1H NMR (600 MHz, $CDCl_3$) δ 2.95 (1H, br s, OH), 7.23–7.28 (5H, m, ArH), 7.31–7.34 (4H, m, ArH), 7.46–7.47 (2H, m, ArH), 7.62 (4H, br d, *J*=8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.3 (s), 75.5 (s), 106.0 (s), 126.1 (d×4), 127.2 (d), 127.8 (d×2), 128.3 (d×4), 128.5 (s), 129.1 (d×2), 129.5 (d×2), 144.6 (s×2); MS *m*/*z* 364 (M^+). Anal. Calcd for $C_{21}H_{16}OSe$: C, 66.12; H, 4.44. Found: C, 66.36; H, 4.27.

*4.3.3. 1,1-Bis(p-fluorophenyl)-3-(phenylsulfanyl)prop-2-yn-1-ol (**3c**).* Yield 69%, a yellow oil, IR (KBr, cm^{-1}) ν 3419 (OH), 3063, 2359, 2175, 1602, 1505, 1478, 1441, 1412, 1228, 1193, 1082, 999, 902, 836, 771, 740, 688, 638, 610; ^1H NMR (600 MHz, $CDCl_3$) δ 2.86 (1H, br s, OH), 7.01–7.04 (4H, m, ArH), 7.22–7.36 (5H, m, ArH), 7.56–7.58 (4H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 74.5 (s), 100.3 (s), 115.2 (d×2), 115.3 (d×2), 126.5 (d×2), 126.9 (d), 127.9 (d×2), 128.0 (d×2), 129.4 (d×2), 132.1 (s), 140.3 (s×2), 161.6 (s), 163.2 (s×2); MS *m*/*z* 352 (M^+), 335 (M^+−OH). Anal. Calcd for $C_{21}H_{14}F_2OS$: C, 71.58; H, 4.00. Found: C, 71.32; H, 4.11.

*4.3.4. 1,1-Bis(p-Fluorophenyl)-3-(phenylselanyl)propargyl alcohol (**3d**).* IR (KBr, cm^{-1}) ν 3405, 3063, 2186, 1897, 1603, 1505, 1440, 1411, 1327, 1227, 1158, 1071, 998, 903, 838, 736, 687, 581; ^1H NMR (600 MHz, $CDCl_3$) δ 2.99 (1H, br s, OH), 6.99–7.02 (4H, br t, *J*=9 Hz, ArH), 7.25–7.28 (3H, m, ArH), 7.45–7.47 (2H, m, ArH), 7.55–7.57 (4H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 69.0 (s), 74.5 (s), 105.3 (s), 115.1 (d×2), 115.2 (d×2), 127.4 (d), 127.9 (d×2), 128.0 (d×2), 128.1 (s), 129.2 (d×2), 129.6 (d×2), 140.4 (s×2), 161.5 (s×2); MS *m*/*z* 400 (M^+), 305 (M^+−C_6H_4F), 243 (M^+−SePh). Anal. Calcd for $C_{21}H_{14}F_2OSe$: C, 63.17; H, 3.53. Found: C, 62.95; H, 3.63.

*4.3.5. 1,1-Bis(p-Methoxyphenyl)-3-(phenylsulfanyl)propargyl alcohol (**3e**).* IR (KBr, cm^{-1}) ν 3449, 2933, 2837, 2179, 1604, 1508, 1463, 1417, 1305, 1252, 1171, 1082, 1033, 833, 770, 741; ^1H NMR (600 MHz, $CDCl_3$) δ 3.10 (1H, br s, OH), 3.78 (6H, s, OMe), 6.84 (4H, d, *J*=9 Hz, ArH), 7.17–7.20 (1H, m, ArH), 7.24–7.28 (2H, m, ArH), 7.35–7.36 (2H, m, ArH), 7.50 (4H, d, *J*=9 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.2 (q), 55.4 (q), 74.0 (s), 76.8 (s), 101.6 (s), 113.5 (d×4), 126.2 (d×2), 126.5 (d), 127.4 (d×4), 129.2 (d×2), 130.7 (s), 137.1 (s×2), 159.1 (s×2); MS *m*/*z* 375 (M^+−1), 359 (M^+−OH), 267 (M^+−SPh). Anal. Calcd for $C_{23}H_{20}O_3S$: C, 73.38; H, 5.35. Found: C, 73.17; H, 5.39.

*4.3.6. 1,1-Bis(p-Methoxyphenyl)-3-(phenylselanyl)propargyl alcohol (**3f**).* IR (KBr, cm^{-1}) ν 3438, 2933, 2837, 2170, 1604, 1508, 1462, 1417, 1305, 1252, 1169, 1070, 1032, 998, 929, 835, 771, 738, 687; ^1H NMR (600 MHz, $CDCl_3$) δ 2.81 (1H, br s, OH), 3.79 (6H, br s, MeO), 6.85 (4H, d, *J*=9 Hz, ArH), 7.24–7.27 (3H, m, ArH), 7.47–7.49 (2H, m, ArH), 7.51 (4H, d, *J*=9 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.3 (q×2), 67.2 (s), 74.9 (s), 106.6 (s), 113.6 (d×4), 126.9 (d), 127.3 (d×4), 128.5 (s), 128.8 (d×2), 129.4 (d), 132.1 (d), 137.2 (s×2), 158.8 (s×2); MS *m*/*z* 424 (M^+), 267 (M^+−SePh). Anal. Calcd for $C_{23}H_{20}O_3Se$: C, 65.25; H, 4.76. Found: C, 65.04; H, 4.93.

*4.3.7. 1-Methyl-1-phenyl-3-(phenylsulfanyl)prop-2-yn-1-ol (**3g**).* IR (KBr, cm^{-1}) ν 3335 (OH), 3060, 2984, 2360, 2173, 1703, 1583, 1479, 1442, 1363, 1228, 1164, 1092, 1071, 1024, 963, 921, 903, 764, 740, 700; ^1H NMR (600 MHz, $CDCl_3$) δ 1.85 (3H, s, Me), 2.53 (1H, br s, OH), 7.19–7.24 (1H, m, ArH), 7.29–7.33 (3H, m, ArH), 7.36–7.41 (4H, m, ArH), 7.61–7.68 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 32.9 (q), 70.7 (s), 71.8 (s), 101.7 (s), 124.9 (d×2), 126.2 (d×2), 126.6 (d), 127.9 (d), 128.4 (d×2), 129.3 (d×2), 132.4 (s), 145.1 (s); MS *m*/*z* 254

(M^+), 239 (M^+−Me), 177 (M^+−Ph), 145 (M^+−SPh). Anal. Calcd for $C_{16}H_{14}OS$: C, 75.56; H, 5.55. Found: C, 75.35; H, 5.81.

*4.3.8. 1,1-Bis(2-thienyl)-3-(phenylsulfanyl)propargyl alcohol (**3h**).* IR (KBr, cm^{-1}) ν 3525, 3310, 2170, 1700, 1582, 1515, 1477, 1414, 1361, 1297, 1231, 1140, 1088, 1033, 967, 838, 786, 739, 704; ^1H NMR (600 MHz, $CDCl_3$) δ 3.55 (1H, br s, OH), 6.93 (2H, dd, J=4 and 5 Hz, ArH), 7.18 (2H, dd, J=4 and 1 Hz, ArH), 7.19–7.23 (1H, m, ArH), 7.27 (2H, dd, J=4 and 5 Hz, ArH), 7.30–7.31 (2H, m, ArH), 7.40 (2H, br d, J=7 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 70.2 (s), 74.5 (s), 99.3 (s), 125.5 (d×2), 126.0 (d×2), 126.5 (d×2), 126.5 (d×2), 126.8 (d), 129.3 (d×2), 131.8 (s), 148.7 (s×2); MS m/z 328 (M^+), 219 (M^+−SPh). Anal. Calcd for $C_{17}H_{12}OS_3$: C, 62.20; H, 3.68. Found: C, 61.87; H, 3.92.

*4.3.9. 1,1-Bis(2-thienyl)-3-(phenylselanyl)propargyl alcohol (**3i**).* IR (KBr, cm^{-1}) ν 3403, 3072, 2924, 2169, 1704, 1613, 1577, 1477, 1439, 1362, 1230, 1143, 1067, 1033, 999, 964, 903, 851, 738, 707; ^1H NMR (600 MHz, $CDCl_3$) δ 3.46 (1H, br s, OH), 6.92 (2H, dd, J=4 and 5 Hz, ArH), 7.17 (2H, dd, J=4 and 1 Hz, ArH), 7.23–7.30 (5H, m, ArH), 7.50–7.52 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 68.2 (s), 70.3 (s), 104.2 (s), 125.5 (d×2), 126.0 (d×2), 126.5 (d×2), 127.3 (d), 128.0 (s), 129.3 (d×2), 129.6 (d×2), 148.8 (s×2); MS m/z 299 (M^+−Ph), 219 (M^+−SePh). Anal. Calcd for $C_{17}H_{12}OS_2Se$: C, 54.40; H, 3.22. Found: C, 54.49; H, 3.35.

*4.3.10. 3-n-Pentyl-3-(phenylsulfanyl)oct-1-yn-3-ol (**3k**).* Yield 96%, a yellow oil, IR (KBr, cm^{-1}) ν 3412, 3061, 2932, 2170, 1708, 1584, 1479, 1378, 1140, 1023, 946, 737, 687; ^1H NMR (600 MHz, $CDCl_3$) δ 0.91 (6H, t, J=7 Hz, Me×2), 1.32–1.35 (8H, m, CH_2), 1.52–1.60 (4H, m, CH_2), 1.67–1.76 (4H, m, CH_2), 2.02 (1H, br s, OH), 7.22 (1H, br t, J=7 Hz, ArH), 7.32 (2H, br t, J=8 Hz, ArH), 7.40–7.42 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0 (q×2), 22.6 (t×2), 24.1 (t×2), 32.0 (t×2), 42.0 (t×2), 70.6 (s), 72.4 (s), 102.1 (s), 126.1 (d×2), 126.4 (d), 129.1 (d×2), 132.9 (s); MS m/z 304 (M^+), 287 (M^+−OH), 195 (M^+−SPh). Anal. Calcd for $C_{19}H_{28}OS$: C, 74.95; H, 9.27. Found: C, 74.70; H, 9.26.

4.4. Syntheses of 1,3-thiazoles from 1,1-bis(aryl)-3-(phenylsulfanyl)propargyl alcohols

Scandium triflate (4 mg, 0.008 mmol) was added to a $MeNO_2$ (0.50 ml)/H_2O (0.10 ml) solution of **3a** (50 mg, 0.16 mmol), thioacetamide (24 mg, 0.32 mmol), and tetrabutylammonium hydrogensulfate (11 mg, 0.032 mmol). The reaction mixture was refluxed for 10 min and poured into a saturated $NaHCO_3$ (50 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt/*n*-hexane (1:50) to give 4-diphenylmethyl-2-methyl-5-(phenylsulfanyl)-1,3-thiazole (**4aa**) (46 mg, 78%) as a yellow oil.

*4.4.1. 4-(Diphenylmethyl)-2-methyl-5-(phenylsulfanyl)-1,3-thiazole (**4aa**).* IR (KBr, cm^{-1}) ν 3429, 3060, 3025, 2922, 1947, 1878, 1803, 1733, 1600, 1581, 1495, 1478, 1440, 1373, 1308, 1254, 1180, 1129, 1077, 1049, 1024, 999, 912, 844, 785, 740, 699. 637, 624, 582, 548; ^1H NMR (600 MHz, $CDCl_3$) δ 2.66 (3H, s, Me), 5.93 (1H, s, CH), 7.06–7.07 (2H, m, ArH), 7.10–7.27 (13H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.2 (q), 49.7 (d), 121.0 (s), 126.1 (d), 126.4 (d×2), 127.2 (d×2), 128.2 (d×4), 129.0 (d×2), 129.2 (d×4), 137.2 (s), 142.4 (s×2), 162.4 (s), 169.4 (s); MS m/z 373 (M^+) 296 (M^+−Ph) 264 (M^+−SPh). Anal. Calcd for $C_{23}H_{19}NS_2$: C, 74.00; H, 5.13; N, 3.75. Found: C, 73.64; H, 5.14; N, 3.48.

*4.4.2. 4-(Diphenylmethyl)-2-phenyl-5-(phenylselanyl)-1,3-selenazole (**4ba**).* Yield 55%, a yellow oil, IR (KBr, cm^{-1}) ν 3059, 3025, 2925, 1713, 1599, 1577, 1478, 1447, 1360, 1309, 1221, 1178, 1078, 1031, 998, 944, 917, 893, 841, 762, 737, 719, 701, 663, 633, 615; ^1H NMR (600 MHz, $CDCl_3$) δ 5.99 (1H, br s, CH), 7.15–7.46 (18H, m, ArH), 7.81–7.85 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 51.6 (s), 121.2 (s), 126.3 (d×2), 127.0 (d×2), 127.6 (d), 128.1 (d×4), 128.9 (d×2), 129.2 (d×4), 129.3 (d×2), 130.4 (d×2), 130.4 (d), 133.0 (s), 136.3 (s), 143.0 (s×2), 163.2 (s), 177.8 (s); MS m/z 531 (M^+), 454 (M^+−Ph), 374 (M^+−SePh). Anal. Calcd for $C_{28}H_{21}NSe_2$: C, 56.77; H, 3.57; N, 2.36. Found: C, 56.59; H, 3.57; N, 2.38.

*4.4.3. 4-(Diphenylmethyl)-2-phenyl-5-(phenylselanyl)-1,3-thiazole (**4bb**).* Yield 75%, white powders, mp 124–130 °C, IR (KBr, cm^{-1}) ν 3060, 3025, 1948, 1599, 1577, 1477, 1453, 1313, 1241, 1179, 1156, 1074, 1020, 910, 842, 762, 734, 688, 656, 619; ^1H NMR (600 MHz, $CDCl_3$) δ 5.99 (1H, br s, CH), 7.12 (5H, m, ArH), 7.21–7.29 (6H, m, ArH), 7.35–7.37 (7H, m, ArH), 7.90–7.91 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 51.0 (d), 115.3 (s), 126.3 (d×2), 126.5 (d×2), 127.0 (d×2), 128.1 (d×4), 128.8 (d×2), 129.2 (d×4), 129.3 (d×2), 130.3 (d×2), 132.1 (s), 133.5 (s), 142.8 (s×2), 163.1 (s), 171.4 (s); MS m/z 483 (M^+), 406 (M^+−Ph), 326 (M^+−SePh). Anal. Calcd for $C_{28}H_{21}NSSe$: C, 69.70; H, 4.39; N, 2.90. Found: C, 69.69; H, 4.48; N, 2.90.

*4.4.4. 4-[Bis(p-fluorophenyl)methyl]-2-methyl-5-(phenylsulfanyl)-1,3-thiazole (**4ca**).* Yield 77%, orange powders, mp 81–86 °C, IR (KBr, cm^{-1}) ν 3465, 3062, 1715, 1603, 1581, 1506, 1478, 1440, 1290, 1226, 1181, 1158, 1097, 1050, 1016, 998, 839, 798, 786, 755, 740, 689, 619, 573, 528, 502; ^1H NMR (600 MHz, $CDCl_3$) δ 2.67 (3H, s, Me), 5.86 (1H, s, CH), 6.90–6.93 (4H, m, ArH), 7.03–7.04 (2H, m, ArH), 7.11–7.20 (7H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.0 (q), 48.2 (d), 115.0 (d×2), 115.1 (d×2), 121.2 (s), 126.2 (d), 127.1 (d×2), 129.0 (d×2), 130.5 (d×2), 130.5 (d×2), 137.0 (s), 138.0 (s×2), 161.5 (d×2, J=244 Hz), 161.9 (s), 169.7 (s); MS m/z 409 (M^+), 300 (M^+−SPh). Anal. Calcd for $C_{23}H_{17}F_2NS_2$: C, 67.50; H, 4.18; N, 3.42. Found: C, 67.39; H, 4.30; N, 3.37.

*4.4.5. 4-[Bis(p-fluorophenyl)methyl]-2-phenyl-5-(phenylsulfanyl)-1,3-thiazole (**4cb**).* Yield 99%, a yellow oil, IR (KBr, cm^{-1}) ν 3062, 1714, 1603, 1581, 1506, 1479, 1455, 1431, 1295, 1227, 1158, 1098, 1048, 1016, 1001, 917, 838, 791, 762, 740, 688, 608, 573, 529; ^1H NMR (600 MHz, $CDCl_3$) δ 5.89 (1H, s, CH), 6.91–6.94 (4H, m, ArH), 7.08–7.19 (6H, m, ArH), 7.27–7.29 (4H, m, ArH), 7.39–7.41 (2H, m, ArH), 7.89–7.90 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 48.5 (d), 114.9 (d×2), 115.1 (d×2), 122.1 (s), 126.5 (d×2), 126.5 (d×2), 127.4 (d×2), 128.9 (d×2), 129.1 (d×2), 130.5 (d×2), 130.6 (d×2), 133.4 (s), 136.8 (s), 138.1 (s×2), 160.8 (s), 162.4 (s), 162.7 (s), 170.6 (s); MS m/z 471 (M^+), 362 (M^+−SPh). Anal. Calcd for $C_{28}H_{19}NF_2S_2$: C, 71.31; H, 4.06; N, 2.97. Found: C, 71.26; H, 4.25; N, 2.95.

*4.4.6. 4-[Bis(p-fluorophenyl)methyl]-2-phenyl-5-(phenylselanyl)-1,3-thiazole (**4da**).* Yield 88%, mp 76–80 °C, IR (KBr, cm^{-1}) ν 3422, 3060, 1889, 1713, 1603, 1577, 1506, 1478, 1453, 1438, 1361, 1302, 1225, 1158, 1097, 1068, 1020, 1000, 981, 943, 917, 879, 839, 790, 762, 736, 688, 607; ^1H NMR (600 MHz, $CDCl_3$) δ 5.93 (1H, s, CH), 6.90–6.93 (4H, m, ArH), 7.13–7.19 (3H, m, ArH), 7.21–7.28 (6H, m, ArH), 7.39–7.40 (3H, m, ArH), 7.89–7.90 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 49.4 (d), 114.9 (d×2), 115.1 (d×2), 115.3 (s), 126.5 (d×2), 127.1 (d), 128.9 (d×2), 129.4 (d×2), 130.2 (d×2), 130.5 (d), 130.5 (d×2), 130.6 (d×2), 131.9 (s), 133.3 (s), 138.4 (s), 138.4 (s), 160.5 (d×2, J=246 Hz), 162.6 (s), 171.7 (s); MS m/z 519 (M^+). Anal. Calcd for $C_{28}H_{19}F_2NSSe$: C, 64.86; H, 3.69; N, 2.70. Found: C, 64.47; H, 3.80; N, 2.68.

*4.4.7. 4-[Bis(p-methoxyphenyl)methyl]-2-phenyl-5-(phenylsulfanyl)-1,3-thiazole (**4ea**) and 4,4-bis(p-methoxyphenyl)-4,4-dihydro-2-phenyl-6-(phenylsulfanyl)-1,3-thiazine (**5ea**).* Compounds **4ea**/**5ea**=1:8, white powders, mp 79–83 °C, IR (KBr, cm^{-1}) ν 3434, 3059, 2928, 2834, 2359, 1772, 1685, 1606, 1580, 1508, 1475, 1459, 1441, 1302,

1250, 1173, 1083, 1036, 995, 961, 906, 888, 830, 805, 767, 745, 690, 609; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.76 (s, 4-Me), 3.77 (s, 5-Me), 5.85 (br s, 4-CH), 6.57 (s, 5-olefinic H), 6.78 (br d, J=8 Hz, ArH), 6.84 (br d, J=8 Hz, ArH), 7.13–7.42 (m, ArH), 7.87 (br d, J=7 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 48.4 (4-d), 55.2 (4- and 5-q), 71.2 (5-s), 113.5 (d), 113.5 (d), 125.7 (s), 127.5 (d), 128.4 (d), 128.5 (d), 129.1 (d), 130.3 (d), 131.1 (d), 132.2 (d), 133.3 (s), 135.2 (s), 137.2 (s), 138.9 (s), 155.5 (s), 158.4 (s); MS m/z 495 (M^+), 386 (M^+–SPh). Anal. Calcd for $C_{30}H_{25}NO_2S_2$: C, 72.70; H, 5.08; N, 2.83. Found: C, 72.49; H, 5.06; N, 2.83.

*4.4.8. 4-[Bis(p-methoxyphenyl)methyl]-2-phenyl-5-(phenylselanyl)-1,3-thiazole (**4fa**) and 4,4-bis(p-methoxyphenyl)-4,4-dihydro-2-phenyl-6-(phenylselanyl)-1,3-thiazine (**5fa**).* Compounds **4fa**/**5fa**=1:1, a yellow oil, IR (KBr, cm^{-1}) ν 3449, 3060, 3000, 2953, 2904, 2833, 2366, 1699, 1607, 1578, 1508, 1477, 1462, 1439, 1302, 1250, 1174, 1086, 1036, 988, 906, 832, 789, 765, 738, 689, 611; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.75 (s, OMe), 3.77 (s, OMe), 5.88 (s, 4-CH), 6.62 (s, 5-CH), 6.78 (d, J=8 Hz, ArH), 6.82 (d, J=8 Hz, ArH), 7.15–7.53 (m, ArH), 7.87 (d, J=8 Hz, ArH), 7.91 (br d, J=4 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 49.4 (d, 4-CH), 55.2 (q), 55.2 (q), 70.8 (s, 5-C), 113.5 (d), 113.5 (d), 114.7 (s), 118.9 (s), 126.5 (d), 126.9 (d), 127.4 (d), 127.9 (d), 128.4 (d), 128.5 (d), 128.8 (d), 129.3 (d), 129.3 (d), 130.0 (d), 130.2 (d), 131.0 (d), 132.7 (d), 133.1 (d), 133.5 (s), 135.4 (s), 135.4 (s), 137.2 (s), 139.0 (s), 155.6 (s), 158.0 (s), 163.7 (s), 171.4 (s); MS m/z 543 (M^+), 528 (M^+–Me), 436 (M^+–$MeOC_6H_4$). Anal. Calcd for $C_{30}H_{25}NO_2SSe$: $C_{30}H_{25}NO_2SSe$: C, 70.58; H, 4.94; N, 2.74. Found: C, 70.79; H, 4.94; N, 2.68.

*4.4.9. Pure **5fa**.* IR (KBr, cm^{-1}) ν 3058, 2928, 2834, 1606, 1578, 1507, 1462, 1440, 1303, 1249, 1173, 1089, 1036, 989, 960, 906, 861, 829, 767, 740, 690; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.78 (3H, s, OMe), 6.62 (1H, s, olefinic H), 6.82 (4H, d, J=8 Hz, ArH), 7.27 (4H, m, ArH), 7.30–7.31 (2H, m, ArH), 7.35–7.38 (2H, m, ArH), 7.42–7.43 (1H, m, ArH), 7.53–7.54 (2H, m, ArH), 7.87–7.88 (2H, br d, J=8 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.2 (q×2), 70.8 (s), 113.5 (d×4), 118.9 (s), 127.5 (d×2), 127.9 (d), 128.4 (d×2), 128.5 (d×4), 129.3 (s and d×2), 131.0 (d), 132.7 (d×2), 133.1 (d), 137.2 (s), 139.0 (s×2), 155.6 (s), 158.3 (s×2); MS m/z 511 (M^+). Anal. Calcd for $C_{24}H_{21}NO_2S$: C, 66.41; H, 4.64; N, 2.58. Found: C, 66.22; H, 4.68; N, 2.58.

4.5. Structure determination by reaction of 4fa and 5fa with tributyltin hydride/AIBN

A toluene (1.5 ml) solution of **4fa** and **5fa** (33 mg, 0.07 mmol), tributyltin hydride (0.17 ml, 0.70 mmol), and AIBN (2 mg) was stirred under reflux condition for 4 h. The solvent was evaporated under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt/n-hexane (1:40) to give 4-[bis(p-methoxyphenyl)methyl]-2-phenyl-5-(tributylstannyl)-1,3-thiazole (24 mg, 55%) as a yellow oil and 4,4-bis(p-methoxyphenyl)-4,4-dihydro-2-phenyl-1,3-thiazine (8 mg, 32%) as a yellow oil.

4.5.1. 4-[Bis(p-methoxyphenyl)methyl]-2-phenyl-5-(tributylstannyl)-1,3-thiazole. IR (KBr, cm^{-1}) ν 2955, 2928, 2852, 1608, 1509, 1478, 1302, 1250, 1176, 1110, 1074, 1038, 962, 831, 811, 790, 762, 690; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.85 (9H, t, J=7 Hz, Me×3), 1.25–1.30 (12H, m, CH_2), 1.47–1.52 (6H, m, CH_2), 3.76 (6H, s, OMe×2), 5.26 (1H, s, CH), 6.80 (4H, d, J=8 Hz, ArH), 7.26 (4H, d, J=8 Hz, ArH), 7.25–7.38 (3H, m, ArH), 7.95 (2H, d, J=8 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 11.2 (t×3), 13.6 (q×3), 29.0 (t×3), 53.5 (d), 55.2 (q×2), 113.4 (d×4), 125.1 (s), 126.6 (d×2), 128.6 (d×2), 129.3 (d), 129.9 (d×4), 134.3 (s), 136.6 (s×2), 157.9 (s×2), 164.9 (s), 172.3 (s); MS m/z 676 (small M^+), 620 (M^+–Bu).

The compound underwent transmetalation by MeLi in ether at −78 °C to give 4-bis(p-methoxyphenyl)methyl-2-phenyl-1,3-thiazole (**7ea**) (36%) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.78 (3H, s, OMe), 5.64 (1H, s, CH), 6.69 (1H, s, olefinic H), 6.84 (2H, d, J=8 Hz, ArH), 7.13 (2H, d, J=8 Hz, ArH), 7.38–7.40 (3H, m, ArH), 7.91–7.93 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 52.1 (d), 55.2 (q), 113.7 (d×2), 116.0 (d), 126.6 (d×2), 128.8 (d×2), 130.0 (d×2), 133.8 (s), 135.4 (s), 158.1 (s×2), 160.7 (s); MS m/z 387 (M^+).

*4.5.2. 4,4-Bis(p-methoxyphenyl)-4,4-dihydro-2-phenyl-1,3-thiazine (**8ea**).* IR (KBr, cm^{-1}) ν 2954, 2930, 1607, 1579, 1508, 1463, 1445, 1302, 1249, 1114, 1069, 1036, 984, 956, 830, 811, 767, 961; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.77 (6H, s, OMe), 6.13 (1H, d, J=10 Hz, olefinic H), 6.67 (1H, d, J=10 Hz, olefinic H), 6.83 (4H, d, J=8 Hz, ArH), 7.32 (4H, d, J=8 Hz, ArH), 7.25–7.44 (3H, m, ArH), 7.96 (2H, d, J=7 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.2 (q×2), 67.4 (d), 113.4 (d×2), 117.7 (d×4), 117.8 (d), 126.8 (d), 127.3 (d×2), 128.4 (d×2), 128.6 (d×4), 130.8 (d), 137.8 (s), 139.4 (s×2), 154.2 (s), 158.2 (s×2); MS 387 (M^+), 380 (M^+–p-$MeOC_6H_4$). Anal. Calcd for $C_{24}H_{21}NO_2S$: C, 74.39; H, 5.46; N, 3.61. Found: C, 73.71; H, 5.66; N, 3.53.

*4.5.3. 4-(1-Phenylethyl)-2-phenyl-5-(phenylsulfanyl)-1,3-thiazole (**4ga**).* Yield 78%, a yellow oil, IR (KBr, cm^{-1}) ν 3060, 3026, 2969, 2928, 2868, 2360, 1946, 1801, 1581, 1478, 1450, 1371, 1316, 1242, 1179, 1157, 1076, 1025, 1001, 792, 914, 840, 763, 738, 713, 688, 662, 610; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.73 (3H, d, J=7 Hz, Me), 4.63 (1H, q, J=7 Hz, CH), 7.07–7.23 (8H, m, ArH), 7.39–7.47 (5H, m, ArH), 7.93–7.95 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.8 (q), 39.2 (d), 119.7 (s), 126.1 (d), 126.2 (d), 126.5 (d×2), 127.0 (d×2), 127.8 (d×2), 128.2 (d×2), 128.8 (d×2), 129.0 (d×2), 130.3 (d), 133.6 (s), 137.4 (s), 144.5 (s), 166.0 (s), 170.3 (s); MS m/z 373 (M^+), 358 (M^+–Me), 264 (M^+–SPh). Anal. Calcd for $C_{23}H_{19}NS_2$: C, 73.96; H, 5.13; N, 3.75. Found: C, 73.65; H, 5.15; N, 3.75.

*4.5.4. 4H-4-Methyl-2,4-diphenyl-6-(phenylsulfanyl)-1,3-thiazole (**5ga**).* IR (KBr, cm^{-1}) ν 3059, 3024, 2975, 2883, 1954, 1685, 1617, 1580, 1476, 1445, 1368, 1312, 1275, 1230, 1178, 1072, 1026, 1001, 948, 893, 829, 764, 741, 689, 664, 629, 609; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.84 (3H, s, Me), 6.44 (1H, s, olefinic H), 7.30–7.50 (12H, m, ArH), 7.87 (2H, d, J=7 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.6 (q), 65.7 (s), 124.9 (s), 125.9 (d×2), 126.9 (d), 127.3 (d), 127.5 (d), 128.3 (d×2), 128.5 (d×2), 129.1 (d×2), 129.8 (d×2), 131.1 (d), 133.6 (d), 137.2 (s), 133.6 (s), 146.6 (s), 156.4 (s); MS m/z 373 (M^+), 358 (M^+–Me), 296 (M^+–Ph), 264 (M^+–SPh). High-resolution mass calcd for $C_{23}H_{19}NS_2$: 373.0959, found m/z: 373.0964.

4.5.5. 4H-6-Methyl-2,4-diphenyl-6-tributylstannyl-1,3-thiazine. A colorless oil, IR (KBr, cm^{-1}) ν 2956, 2925, 2852, 2360, 2341, 1601, 1578, 1558, 1490, 1457, 1446, 1417, 1376, 1287, 1232, 1177, 1073, 1028, 952, 939, 881, 839, 764, 691, 668; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.89 (9H, t, J=7 Hz, Me×3), 1.06–1.09 (6H, m, CH_2), 1.32–1.37 (6H, m, CH_2), 1.55–1.59 (6H, m, CH_2), 6.02 (1H, s, olefinic H), 7.20–7.22 (1H, m, ArH), 7.29–7.39 (2H, m, ArH), 7.39–7.45 (4H, m, ArH), 7.51 (2H, br d, J=9 Hz, ArH), 7.95 (2H, br d, J=8 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 10.3 (t×3), 13.7 (q×3), 27.2 (t×3), 28.9 (t×3), 29.2 (q), 62.0 (s), 126.2 (d×2), 126.4 (d), 127.4 (d×2), 127.9 (d×2), 128.4 (d×2), 130.3 (s), 130.5 (d), 135.8 (d), 138.2 (s), 147.7 (s), 158.1 (s); MS m/z 540 (M^+–Bu).

*4.5.6. 4H-6-Methyl-2,4-diphenyl-1,3-thiazine (**8ga**).* A yellow oil, IR (KBr, cm^{-1}) ν 3083, 3058, 3025, 2971, 2924, 2860, 1633, 1577, 1490, 1445, 1368, 1254, 1220, 1178, 1157, 1093, 1073, 930, 878, 765, 730, 691, 655; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.78 (3H, s, Me), 6.01 (1H, d, J=10 Hz, olefinic H), 6.50 (1H, d, J=10 Hz, olefinic H), 7.22–7.24 (1H, m, ArH), 7.32–7.35 (2H, m, ArH), 7.40–7.47 (3H, m, ArH), 7.51–7.52 (2H, m, ArH), 7.93–7.95 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.3 (q), 61.9 (s), 117.0 (d), 125.9 (d×2), 126.7 (d), 127.2 (d), 127.3 (d×2), 128.2 (d×2), 128.5 (d×2), 130.8 (d), 137.8 (s), 147.2 (s), 155.0

(s); MS *m*/*z* 265 (M^+), 250 (M^+−Me). Anal. Calcd for $C_{17}H_{15}NS$: C, 76.94; H, 5.70; H, 5.28. Found: C, 76.47; H, 5.81; N, 5.24.

*4.5.7. 4,5-Dihydro-5-methyl-2,5-diphenyl-4-(phenylsulfanylmethylene)-1,3-thiazole (**6ga**).* A yellow oil, IR (KBr, cm^{-1}) ν 2925, 2854, 2360, 2342, 1610, 1579, 1541, 1491, 1478, 1447, 1368, 1313, 1256, 1177, 1160, 1132, 1070, 1027, 953, 840, 765, 741, 689, 669; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.96 (3H, s, Me), 6.06 (1H, s, olefinic H), 7.15–7.16 (3H, m, ArH), 7.23–7.28 (2H, m, ArH), 7.28–7.34 (1H, m, ArH), 7.41–7.45 (4H, m, ArH), 7.49–7.51 (1H, m, ArH), 7.90–7.91 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 27.8 (q), 86.8 (s), 111.8 (d), 125.8 (d×2), 126.4 (d), 127.6 (d), 128.0 (d×2), 128.3 (d×2), 128.5 (d×2), 128.6 (d×2), 128.7 (d×2), 129.1 (d×2), 131.6 (d), 132.8 (s), 135.7 (s), 143.8 (s), 154.9 (s), 162.2 (s); MS *m*/*z* 373 (M^+), 358 (M^+−Me), 296 (M^+−Ph); high resolution mass calcd for $C_{23}H_{19}NS_2$: 373.0955, found *m*/*z* 373.0941.

4.5.8. 4,5-Dihydro-5-methyl-2,5-diphenyl-4-(tributylstannyl-methylene)-1,3-thiazole. A yellow oil, IR (KBr, cm^{-1}) ν 2956, 2926, 2853, 1606, 1579, 1561, 1492, 1448, 1417, 1375, 1339, 1312, 1256, 1217, 1176, 1134, 1073, 1028, 1001, 956, 864, 765, 690, 657, 628; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.87 (9H, t, *J*=7 Hz, Me×3), 0.99 (6H, t, *J*=7 Hz, CH_2×3), 1.27–1.31 (6H, m, CH_2×3), 1.47–1.52 (6H, m, CH_2×3), 5.87 (1H, s, olefinic H), 7.24–7.26 (1H, m, ArH), 7.31–7.35 (2H, m, ArH), 7.41–7.48 (10H, m, ArH), 7.86–7.87 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 9.9 (t×3), 13.7 (q×3), 27.3 (t×3), 28.2 (q), 29.1 (t×3), 88.3 (s), 118.9 (d), 125.9 (d×2), 127.1 (d), 128.2 (d×3), 128.5 (d×2), 131.3 (d), 133.5 (s), 144.7 (s), 163.0 (s), 165.1 (s); MS *m*/*z* 496 (M^+−Bu).

*4.5.9. 4,5-Dihydro-5-methyl-2,5-diphenyl-4-methylene-1,3-thiazole (**9ga**).* A yellow oil, IR (KBr, cm^{-1}) ν 3059, 3027, 2979, 2928, 2851, 2382, 2349, 2316, 1603, 1578, 1493, 1447, 1258, 1131, 1073, 1028, 956, 921, 866, 767, 690, 627; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.91 (3H, s, Me), 5.13 (1H, d, *J*=2 Hz, olefinic H), 5.37 (1H, d, *J*=2 Hz, olefinic H), 7.26–7.29 (2H, m, ArH), 7.33–7.36 (2H, m, ArH), 7.42–7.49 (4H, m, ArH), 7.86 (2H, br d, *J*=7 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.1 (q), 87.0 (s), 106.0 (t), 125.6 (d×2), 127.4 (d), 128.2 (d×2), 128.4 (d×2), 128.6 (d×2), 131.4 (d), 133.1 (s), 144.3 (s), 155.6 (s), 162.7 (s); MS *m*/*z* 265 (M^+), 250 (M^+−Me). High resolution mass calcd for $C_{17}H_{15}NS$: 265.0925, found *m*/*z* 265.0898.

*4.5.10. 4-[Bis(2-thienyl)methyl]-2-phenyl-5-(phenylsulfanyl)-1,3-thiazole (**4ha**).* White prisms, mp 119–123 °C, IR (KBr, cm^{-1}) ν 3064, 2919, 2360, 1716, 1579, 1505, 1477, 1455, 1433, 1320, 1230, 1178, 1074, 1047, 1023, 1001, 987, 919, 853, 763, 740, 688, 615. 524; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.41 (1H, br s, CH), 6.88 (2H, dd, *J*=3 and 5 Hz, ArH), 6.93–7.01 (2H, m, ArH), 7.14–7.23 (6H, m, ArH), 7.36–7.51 (4H, m, ArH), 7.96–7.97 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 41.2 (d), 121.7 (s), 125.0 (d×2), 125.9 (d×2), 126.3 (d×2), 126.5 (d), 126.6 (d×2), 127.6 (d×2), 128.9 (d×2), 129.1 (d×2), 130.6 (d), 133.4 (s), 136.7 (s), 145.4 (s×2), 161.8 (s), 170.8 (s); MS *m*/*z* 447 (M^+); Anal. Calcd for $C_{24}H_{17}NS_4$: C, 64.40; H, 3.83; N, 3.13. Found: C, 64.07; H, 3.82; N, 3.11.

*4.5.11. 4-[Bis(2-thienyl)methyl]-2-methyl-5-(phenylselanyl)-1,3-thiazole (**4ia**).* Yield 57%, a yellow oil, IR (KBr, cm^{-1}) ν 3442, 3069, 2922, 2359, 1793, 1734, 1616, 1577, 1503, 1476, 1438, 1415, 1361, 1275, 1229, 1176, 1067, 1020, 983, 853, 785, 736, 700, 614, 537; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.70 (3H, s, Me), 6.40 (1H, br s, CH), 6.87–6.89 (4H, m, ArH), 7.16–7.18 (5H, m, ArH), 7.26–7.27 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.8 (q), 42.0 (d), 114.1 (s), 124.9 (d×2), 125.9 (d×2), 126.4 (d×2), 127.1 (d), 129.3 (d×2), 130.3 (d×2), 131.9 (s), 145.6 (s×2), 160.9 (s), 170.9 (s); MS *m*/*z* 433 (M^+), 276 (M^+−SePh). Anal. Calcd for $C_{19}H_{15}NS_3Se$: C, 52.80; H, 3.50; N, 3.24. Found: C, 52.61; H, 3.48; N, 3.04.

*4.5.12. 4-[Bis(2-thienyl)methyl]-2-phenyl-5-(phenylselanyl)-1,3-thiazole (**4ib**).* Yield 68%, white prisms, mp 132–135 °C, IR (KBr, cm^{-1}) ν 3430, 3065, 2924, 2853, 2388, 2349, 2285, 1712, 1631, 1577, 1477, 1437, 1361, 1316, 1222, 1178, 1068, 1039, 1020, 1000, 980, 920, 853, 763, 737, 689, 637, 617; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.44 (1H, br s, CH), 6.87 (2H, br t, *J*=4 Hz, ArH), 6.96 (2H, br s, ArH), 7.18 (5H, br t, *J*=5 Hz, ArH), 7.31 (2H, br t, *J*=4 Hz, ArH), 7.38–7.41 (3H, m, ArH), 7.96–7.97 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 42.4 (d), 114.9 (s), 125.0 (d×2), 125.8 (d×2), 126.2 (d×2), 126.6 (d×2), 127.2 (d), 128.9 (d×2), 129.4 (d×2), 130.4 (d×2), 130.5 (d), 131.8 (s), 133.3 (s), 145.8 (s×2), 161.9 (s), 172.1 (s); MS *m*/*z* 495 (M^+), 338 (M^+−SePh). High-resolution mass calcd for $C_{24}H_{17}NS_3Se$: 494.9703, found *m*/*z*: 494.9688.

*4.5.13. 4-[Bis(2-thienyl)methyl]-2-phenyl-5-(phenylselanyl)-1,3-selenazole (**4ic**).* Yield 68%, white prisms, mp 119–124 °C, IR (KBr, cm^{-1}) ν 3448, 3067, 2925, 2853, 2388, 2349, 2285, 1712, 1625, 1577, 1507, 1476, 1455, 1437, 1361, 1279, 1227, 1177, 1069, 1021, 999, 943, 851, 762, 736, 689, 619; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.46 (1H, br s, CH), 6.87 (2H, br d, *J*=3 Hz, ArH), 6.88 (2H, br s, ArH), 7.31–7.53 (6H, m, ArH), 7.88 (2H, dd, *J*=2 and 4 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 43.0 (d), 120.6 (s), 125.0 (d×2), 126.2 (d×2), 127.1 (d×2), 127.2 (d), 128.6 (s), 128.9 (d×2), 129.4 (d×2), 130.4 (d×2), 130.6 (d), 136.1 (s), 145.9 (s×2), 162.0 (s), 178.6 (s); MS *m*/*z* 543 (M^+). Anal. Calcd for $C_{24}H_{17}NS_2Se_2$: C, 53.20; H, 3.16; N, 2.59. Found: C, 53.24; H, 2.95; N, 2.56.

4.6. Reactions of phenylsulfanylethynylcycloalkanols with thiobenzamide

*4.6.1. Reaction of phenylsulfanylethynylcyclohexanol (**3j**) with thiobenzamide. Typical procedure.* Haffnium triflate (33 mg, 0.04 mmol) was added to a 1,2-dichloroethane (1.0 ml)/H_2O (0.10 ml) solution of **3j** (50 mg, 0.22 mmol), thiobenzamide (59 mg, 0.43 mmol), and tetrabutylammonium hydrogensulfate (15 mg, 0.04 mmol) at room temperature. The reaction mixture was heated under reflux condition for 20 min. The cooled mixture was poured into a saturated $NaHCO_3$ (50 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with CH_2Cl_2/*n*-hexane (1:10) to give (*Z*)-2-phenyl-4-(phenylsulfanylmethylene)-1-thia-3-azaspiro[4.5]dec-2-ene (**6ja**) (0.034 g, 45%) as a yellow oil and 2-phenyl-4-phenylsulfanyl-3-thia-1-azaspiro[5.5]undec-2-ene (**5ja**) (8.0 mg, 11%) as a yellow oil.

*4.6.1.1. (E)- and (Z)-4-(phenylsulfanylmethylene)-1-thia-3-azaspiro[4.5]dec-2-ene (**6ja**).* IR (KBr, cm^{-1}) ν 3436, 3060, 3025, 2930, 2853, 1614, 1580, 1478, 1446, 1313, 1281, 1252, 1178, 1157, 1115, 1087, 1025, 968, 944, 904, 870, 834, 765, 740, 689, 643, 615, 470, 445, 420; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.40–1.44 (m, *E*- and *Z*-CH_2), 1.63–1.74 (m, *E*- and *Z*-CH_2), 1.87–2.04 (m, *E*- and *Z*-CH_2), 6,14 (s, *Z*-olefinic H), 6.97 (s, *E*-olefinic H), 7.18–7.7.21 (m, ArH), 7.30–7.31 (m, ArH), 7.40–7.47 (m, ArH), 7.84–7.92 (m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) of *Z*-5a δ 23.3 (t×2), 26.0 (t), 39.9 (t×2), 85.6 (s), 108.0 (d), 126.2 (d), 128.0 (d×2), 128.2 (d×2), 128.5 (d×2), 129.1 (d×2), 131.1 (d), 133.4 (s), 136.1 (s), 157.7 (s), 158.6 (s); MS *m*/*z* 351 (M^+) 242 (M^+−SPh). Anal. Calcd for $C_{21}H_{21}NS_2$: C, 71.75; H, 6.02; N, 3.98. Found: C, 71.57; H, 6.03; N, 4.01.

*4.6.1.2. 4-Phenylsulfanyl-2-phenyl-3-thia-1-azaspiro[5.5]undec-2-ene (**5ja**).* IR 3060, 2930, 2854, 2663, 1735, 1617, 1580, 1476, 1445, 1301, 1228, 1195, 1176, 1142, 1103, 1070, 1025, 979, 941, 904, 886, 822, 761, 740, 689, 671, 527, 469, 431, 405; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.55–1.61 (4H, m, CH_2), 1.79–1.86 (4H, m, CH_2), 1.93–1.94 (2H, m, CH_2), 6.23 (1H, s, olefinic H), 7.22–7.25 (1H, m, ArH), 7.28–7.37 (6H, m, ArH), 7.40–7.53 (1H, m, ArH), 7.80–7.81 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) **5ja** δ 21.8 (t×2), 25.8 (t), 36.0

(t×2), 63.1 (s), 124.1 (s), 127.0 (d), 127.6 (d×2), 128.5 (d×2), 128.8 (d×2), 129.1 (d×2), 129.2 (d×2), 130.9 (d), 134.1 (s), 137.3 (s), 155.1 (s); MS *m*/*z* 351 (M^+) 238 (M^+−Ph). High-resolution mass calcd for $C_{21}H_{21}NS_2$: 351.1115, found *m*/*z*: 373.1093.

4.7. Desulfanylation of 6ja with tributyltin hydride

IR (KBr, cm^{-1}) ν 2930, 2853, 1607, 1579, 1490, 1446, 1395, 1252, 1177, 1156, 1051, 970, 953, 921, 850, 764, 709, 689, 642, 615, 569; ^1H NMR (600 MHz, $CDCl_3$) δ 1.38–1.44 (1H, m, CH_2), 1.52–1.57 (2H, m, CH_2), 1.69–1.71 (2H, m, CH_2), 1.83–1.88 (3H, m, CH_2), 1,94–2.00 (2H, m, CH_2), 5.15 (1H, d, *J*=1 Hz, olefinic H), 5.27 (1H, d, *J*=1 Hz, olefinic H), 7.40–7.46 (3H, m, ArH), 7.80–7.82 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.5 (t×2), 26.0 (t), 39.6 (t×2), 85.4 (s), 102.2 (t), 128.1 (d×2), 128.4 (d×2), 130.1 (d), 133.6 (s), 157.5 (s), 159.2 (s); MS *m*/*z* 243 (M^+). Anal. Calcd for $C_{15}H_{17}NS$: C, 74.00; H, 7.04; N, 5.76. Found: C, 73.93; H, 6.95; N, 5.73.

4.8. Reaction of 5ja with tributyltin hydride and the following MeLi

A toluene (2.0 ml) solution of **5ja** (200 mg, 0.57 mmol), tributyltin hydride (0.75 ml, 2.84 mmol), and AIBN (19 mg, 0.11 mmol) was heated under reflux condition for 1.5 h. The evaporated mixture was purified by preparative TLC on silica gel eluting with CH_2Cl_2/*n*-hexane (1:4) to give a mixture of 8a and 2-phenyl-10-tributylstannyl-3-thia-1-azaspiro[5.5]undec-2-ene (0.20 g).

IR (KBr, cm^{-1}) 3650, 3526, 3447, 2929, 2361, 1716, 1654, 1602, 1559, 1507, 1457, 1418, 1361, 1295, 1219, 1176, 1074, 976, 939, 766, 691; ^1H NMR (600 MHz, $CDCl_3$) δ 0.90 (9H, t, *J*=7 Hz, Me), 1.04–1.07 (6H, m, CH_2), 1.32–1.36 (6H, m, CH_2), 1.54–1.57 (8H, m, CH_2), 1.61–1.94 (6H, m, CH_2), 5.78 (1H, s, olefinic H), 7.26–7.41 (3H, m, ArH), 7.89 (2H, d, *J*=8 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 10.2 (t×3), 13.6 (q×3), 22.2 (t×2), 26.1 (t), 27.2 (t×3), 28.9 (t×3), 35.5 (t×2), 59.2 (s), 127.5 (d×2), 128.3 (d×2), 129.1 (s), 130.3 (d), 135.9 (s), 138.4 (d), 156.6 (s); MS *m*/*z* 533 (small M^+). The mixture of **5ja** and tributylstannylated product was not further purified and used in the next step.

*4.8.1. 2-Phenyl-3-thia-1-azaspiro[5.5]undec-2-ene (**8ja**).* IR (KBr, cm^{-1}) ν 3430, 3060, 2929, 2854, 1716, 1623, 1489, 1446, 1333, 1228, 1177, 1075, 973, 931, 851, 765, 736, 690, 611, 411; ^1H NMR (600 MHz, $CDCl_3$) δ 1.54–1.56 (4H, m.CH_2), 1.72–1.74 (2H, m, CH_2), 1.84–1.85 (4H, m, CH_2), 5.80 (1H, d, *J*=10 Hz, olefinic H), 6.41 (1H, d, *J*=9 Hz, olefinic H), 7.36–7.44 (3H, m, ArH), 7.88–7.90 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.8 (t×2), 25.9 (t), 36.0 (t×2), 59.3 (s), 116.7 (d), 127.5 (d×2), 128.4 (d×2), 130.6 (d), 138.0 (s); MS *m*/*z* 243 (M^+). High resolution mass could not be measured by the same peak of the standard PFK.

*4.8.2. (E)- and (Z)-2-Methyl-4-(phenylsulfanylmethylene)-1-thia-3-azaspiro[4.5]dec-2-ene (**6lb**).* *E*/*Z*=1:7, a orange oil, IR (KBr, cm^{-1}) ν 3073, 2930, 2854, 2359, 1734, 1646, 1582, 1507, 1478, 1440, 1373, 1261, 1160, 1086, 1024, 976, 941, 904, 876, 830, 741, 689, 637, 602; ^1H NMR (600 MHz, $CDCl_3$) δ 1.31–1.36 (m, *E*- and *Z*-CH_2), 1.52–1.57 (m, *E*- and *Z*-CH_2), 1.69–1.71 (m, *E*- and *Z*-CH_2), 1.80–1.87 (m, *E*- and *Z*-CH_2), 2.22 (s, *Z*-Me), 2.28 (s, *E*-Me), 6.05 (s, *E*-olefinic H), 6.19 (s, *Z*-olefinic H), 7.26–7.30 (m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) of *Z*-**6lb** δ 20.8 (q), 23.2 (t×2), 25.7 (t), 39.5 (t×2), 85.3 (s), 107.4 (d), 126.2 (d), 127.8 (d×2), 129.0 (d×2), 136.0 (s), 157.7 (s), 158.9 (s); MS *m*/*z* 289 (M^+) 180 (M^+−SPh). High-resolution mass calcd for $C_{16}H_{19}NS_2$: 289.0957, found *m*/*z*: 289.0938.

*4.8.3. (Z)-2-Phenyl-4-(phenylsulfanylmethylene)-1-thia-3-azaspiro [4.4]non-2-ene (**6la**).* *Z*:*E*=99:1, a yellow oil, IR (KBr, cm^{-1}) ν 3442, 3060, 3026, 2959, 2868, 2386, 2349, 2284, 1609, 1581, 1478, 1447, 1316, 1256, 1207, 1176, 1157, 1087, 1024, 1000, 953, 887, 826, 765, 740, 689, 613, 522, 501, 470, 435, 411; ^1H NMR (600 MHz, $CDCl_3$) δ 1.92 (4H, m, CH_2), 2.04–2.07 (2H, m, CH_2), 2.19–2.21 (2H, m, CH_2), 6.19 (1H, s, olefinic H), 7.20–7.21 (1H, m, ArH), 7.29–7.31 (4H, m, ArH), 7.40–7.46 (3H, m, ArH), 7.82 (2H, d, *J*=7 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 25.6 (t×2), 43.4 (t×2), 92.2 (s), 107.6 (d), 126.3 (d), 128.0 (d×2), 128.1 (d×2), 128.5 (d×2), 129.1 (d×2), 131.1 (d), 133.1 (s), 136.0 (s), 156.9 (s), 159.4 (s); MS *m*/*z* 259 (M^+−1), 228 (M^+−SPh). Anal. Calcd for $C_{20}H_{19}NS_2$: C, 71.18; H, 5.67; N, 4.15. Found: C, 71.13; H, 5.81; N, 3.95.

*4.8.4. (Z)-2-Methyl-4-(phenylsulfanylmethylene)-1-thia-3-azaspiro-[4.4]ron-2-ene (**6lb**).* *Z*:*E*=99:1, a orange oil, IR (KBr, cm^{-1}) ν 3422, 3058, 2959, 2869, 1639, 1582, 1478, 1440, 1371, 1303, 1206, 1150, 1086, 1068, 1024, 1000, 974, 945, 903, 889, 823, 740, 690, 615; ^1H NMR (600 MHz, $CDCl_3$) δ 1.82–1.88 (4H, m, CH_2), 1.97–1.99 (2H, m, CH_2), 2.04–2.07 (2H, m, CH_2), 2.27 (3H, s, Me), 6.11 (1H, s, olefinic H), 7.18–7.21 (1H, m, ArH), 7.27–7.31 (4H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.5 (q), 25.5 (t×2), 43.2 (t×2), 91.7 (s), 107.1 (d), 126.3 (d), 127.9 (d×2), 129.1 (d×2), 135.9 (s), 158.0 (s), 158.4 (s); MS *m*/*z* 275 (M^+). Anal. Calcd for $C_{15}H_{17}NS_2$: C, 65.41; H, 6.22; N, 5.09. Found: C, 65.03; H, 6.19; N, 4.21.

*4.8.5. (Z)-2-Phenyl-4-(phenylselanylmethylene)-1-thia-3-azaspiro-[4.5]dec-2-ene (**6m**).* *Z*:*E*=99:1, a yellow oil, IR (KBr, cm^{-1}) ν 3448, 3059, 3029, 2930, 2853, 1614, 1577, 1476, 1446, 1313, 1281, 1252, 1220, 1178, 1157, 1107, 1070, 1022, 968, 943, 904, 859, 817, 764, 736, 688, 642, 616, 525, 491, 469, 417; ^1H NMR (600 MHz, $CDCl_3$) δ 1.37–1.43 (1H, m CH_2), 1.59–1.66 (2H, m, CH_2), 1.71–1.73 (2H, m, CH_2), 1.86–1.91 (3H, m, CH_2), 1.96–2.04 (2H, m, CH_2), 6.42 (1H, s, olefinic H), 7.21–7.29 (3H, m, ArH), 7.39–7.46 (5H, m, ArH), 7.83–7.84 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.3 (t×2), 25.9 (t), 39.8 (t×2), 85.4 (s), 103.4 (d), 126.8 (d), 128.2 (d×2), 128.5 (d×2), 129.3 (d×2), 130.7 (d×2), 131.1 (d), 131.4 (s), 133.4 (s), 158.2 (s), 160.2 (s); MS *m*/*z* 399 (M^+). Anal. Calcd for $C_{21}H_{21}NS_2$: C, 63.31; H, 5.31; N, 3.52. Found: C, 63.47; H, 5.37; N, 3.51.

*4.8.6. (E)- and (Z)- 2-Phenyl-4-(phenylsulfanylmethylene)-1-thia-3-azaspiro[4.11]-dec-2-ene (**6n**).* *Z*:*E*=77:23, a orange oil, IR (KBr, cm^{-1}) ν 3589, 3453, 3369, 3197, 3060, 2937, 2852, 2360, 1734, 1715, 1685, 1580, 1471, 1445, 1352, 1258, 1218, 1025, 1000, 940, 899, 764, 742, 690; ^1H NMR (600 MHz, $CDCl_3$) δ 1.39–1.42 (m, CH_2), 1.56–1.60 (m, CH_2), 1.75–1.80 (m, CH_2), 1.89–1.94 (m, CH_2) 6.13(s, *E*-olefinic H), 6.19 (s, *Z*-olefinic H), 7.23–7.26 (m, ArH), 7.29–7.36 (m, ArH), 7.40–7.45 (m, ArH), 7.77.81 (m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) of *Z*-7e δ 19.0 (t×2), 22.2 (t×2), 22.7 (t×2), 26.1 (t), 26.5 (t×2), 32.7 (t×2), 66.1 (s×2), 123.3 (s), 127.0 (d), 127.5 (d×2), 128.4 (d×2), 129.1 (d×2), 129.3 (d×2), 130.8 (d), 134.0 (d), 137.4 (s×2); MS *m*/*z* 435 (M^+) 358 (M^+−Ph), 326 (M^+−SPh). High-resolution mass calcd for $C_{27}H_{33}NS_2$: 435.2054, found *m*/*z*: 435.2040.

4.9. Reaction of 3k with thiobenzamide

*4.9.1. Reaction of 5-phenylsulfanylethynyl-5-undecanol with thiobenzamide (**3k**).*

*4.9.1.1. 5-Methyl-4,5-dihydro-2,5-diphenyl-4-(phenylsulfanylmethyl-ene)-1,3-thiazole (**6k**).* IR (KBr, cm^{-1}) ν 3419, 3062, 2930, 2857, 1715, 1627, 1581, 1458, 1377, 1227, 1154, 1073, 1025, 1001, 941, 885, 763, 739, 689, 661, 617; ^1H NMR (600 MHz, $CDCl_3$) δ 0.86–0.92 (6H, t, *J*=7 Hz, Me×2), 1.24–1.36 (12H, m, CH_2), 1.62–1.67 (2H, m, CH_2), 1.81–1.86 (2H, m, CH_2), 6.05 (1H, s, olefinic H), 7.15–7.43 (8H, m, ArH), 7.75–7.76 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1 (q×2), 22.6 (t×2), 24.1 (t×2), 32.3 (t×2), 41.6 (t×2), 66.6 (s), 123.1 (s), 126.8 (d×2), 127.0 (d), 128.4 (d×2), 129.1 (d×2), 129.4 (d×2), 130.6 (d), 132.3 (d), 133.8 (s), 137.8 (s), 154.1 (s); MS *m*/*z* 352 (M^+−$(CH_2)_4$Me), 313 (M^+−PhSH).

4.10. Reactions of 1-aryl- and 1,1-bisaryl-3-(phenylsulfanyl) propargyl alcohols 1 and 3 with thiobenzamide in $MeNO_2/D_2O$

*4.10.1. Bis(p-fluorophenyl)-3-(phenylsulfanyl)propargyl ALCOHOL (**3c**) with thiobenzamide in $MeNO_2/D_2O$. Typical procedure*. Scandium triflate (3.5 mg, 0.007 mmol) was added to a mixture of **3c** (50 mg, 0.14 mmol), benzthioamide (39 mg, 0.28 mmol), and Bu_4NHSO_4 (10 mg, 0.03 mmol) in $MeNO_2$ (0.50 ml)/D_2O (0.1 ml). The reaction mixture was heated under reflux condition for 10 min and poured into a saturated $NaHCO_3$ (50 ml). The work-up procedure gave 4-[bis(*p*-fluorophenyl)deuteriomethyl]-2-phenyl-5-(phenylsulfanyl)-1,3-thiazole (**10ca**) (50 mg, 75%).

Compound **10ca**: yield 75%, 87% D purity, a yellow oil, IR (KBr, cm^{-1}) ν 3062, 2925, 1887, 1603, 1581, 1507, 1478, 1453, 1440, 1313, 1300, 1280, 1227, 1179, 1159, 1098, 1071, 1048, 1023, 1000, 981, 917, 838, 784, 761, 739, 688, 658, 608; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.89 (s, a trace of benzyl H), 6.91–6.94 (m, ArH), 7.08–7.19 (m, ArH), 7.24–7.30 (m, ArH), 7.39–7.41 (m, ArH), 7.90–7.91 (m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 114.9 (d×2), 115.1 (d×2), 121.9 (s), 126.4 (d), 126.5 (d×2), 127.3 (d×2), 128.9 (d×2), 129.1 (d×2), 130.5 (d×2), 130.5 (d×2), 130.6 (d), 133.4 (s), 136.8 (s), 138.1 (s), 161.1 (d×2, *J*=244 Hz), 162.7 (s), 170.6 (s×2), 171.1 (s); MS *m*/*z* 472 (M^+), 395 (M^+−Ph), 363 (M^+−SPh). High-resolution mass calcd for $C_{28}H_{18}DF_2NS_2$: 472.0990, found *m*/*z*: 472.0991.

*4.10.1.1. 4-[Bis(p-fluorophenyl)deuteriomethyl]-2-methyl-5-(phenyl-sulfanyl)-1,3-thiazole (**10cb**).* Yield 62%, 91% D purity, white prisms, mp 79–84 °C, IR (KBr, cm^{-1}) ν 3421, 3060, 2924, 1889, 1603, 1581, 1507, 1478, 1440, 1374, 1290, 1227, 1178, 1159, 1098, 1075, 1017, 838, 780, 740, 689, 638, 611, 570, 553, 526; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.68 (br s, *D*- and *H*–Me), 5.86 (br s, *H*–CH), 6.90–6.93 (m, H- and D-ArH), 7.03–7.04 (m, *D*- and *H*-ArH), 7.10–7.20 (m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.0 (q), 115.0 (d×2), 115.1 (d×2), 121.1 (s), 126.3 (d), 127.1 (d×2), 129.0 (d×2), 130.5 (d×2), 130.5 (d×2), 137.0 (s), 137.9 (s), 161.5 (d×2, *J*=246 Hz), 161.9 (s), 169.7 (s×2); MS *m*/*z* 410 (M^+), 301 (M^+−SPh). Anal. Calcd for $C_{23}H_{16}DF_2NS_2$: C, 67.50; H, 4.18; N, 3.42. Found: C, 67.39; H, 4.30; N, 3.37.

*4.10.1.2. 4-[Bis(p-fluorophenyl)deuteriomethyl]-2-phenyl-5-(phenyl-sulfanyl)-1,3-selenazole (**10cc**).* Yield 43%, 88% D purity, white powders, mp 108–113 °C, IR (KBr, cm^{-1}) ν 3434, 3060, 1888, 1602, 1581, 1507, 1479, 1439, 1301, 1277, 1227, 1158, 1097, 1065, 1023, 987, 954, 835, 780, 761, 739, 689, 661, 586, 560, 524, 500; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.90 (br s, *H*–CH), 6.92–6.95 (m, *D*- and *H*-ArH), 7.15–7.17 (m, *D*- and *H*-ArH), 7.19–7.22 (m, *D*- and *H*-ArH), 7.27–7.30 (m, *D*- and *H*-ArH), 7.36–7.44 (m, *D*- and *H*-ArH), 7.81–7.83 (m, *D*- and *H*-ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 114.9 (d×2), 115.0 (d×2), 126.4 (d), 127.0 (d×2), 127.4 (d×2), 128.4 (d), 129.0 (d×2), 129.1 (d×2), 130.5 (d×2), 130.6 (d×2), 130.8 (d), 136.2 (s), 137.7 (s), 138.3 (s), 161.5 (d×2, *J*=244 Hz), 163.1 (s), 177.3 (s); MS *m*/*z* 520 (M^+), 411 (M^+−SPh). Anal. Calcd for $C_{28}H_{18}DF_2NSSe$: C, 64.74; H, 3.49; N, 2.70. Found: C, 64.87; H, 3.72; N, 2.54.

*4.10.1.3. 4-[Bis(p-fluorophenyl)deuteriomethyl]-2-phenyl-5-(phenylselanyl)-1,3-thiazole (**10da**).* Yield 80%, 88% D purity, a yellow oil, IR (KBr, cm^{-1}) ν 3062, 1888, 1603, 1577, 1507, 1476, 1438, 1300, 1273, 1227, 1159, 1098, 1063, 1019, 980, 917, 838, 783, 762, 735, 713, 688, 648, 606, 571, 523; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.93 (s, *H*-CH), 6.90–6.93 (m, *D*- and *H*-ArH), 7.13–7.28 (m, *D*- and *H*-ArH), 7.39–7.40 (m, *D*- and *H*-ArH), 7.89–7.91 (m, *D*- and *H*-ArH); ^{13}C NMR (150 MHz, $CDCl_3$) of D-14da δ 49.4 (d), 114.9 (d×2), 115.1 (d×2), 115.2 (s), 126.5 (d×4), 127.1 (d), 128.9 (d×2), 129.4 (d×2), 130.2 (d), 130.4 (d×2), 130.5 (d×2), 131.9 (s), 133.3 (s×2), 138.3 (s), 161.5 (s×2, *J*=245 Hz), 162.6 (s), 171.7 (s); MS *m*/*z* 520 (M^+), 443 (M^+−Ph). Anal. Calcd for $C_{28}H_{18}DF_2NSSe$: C, 64.74; H, 3.49; N, 2.70. Found: C, 64.44; H, 3.52; N, 2.72.

*4.10.1.4. 4-(p-Methoxyphenyldeuteriomethyl)-2-phenyl-5-(phenylsulfanyl)-1,3-thiazole (**11aa**).* Yield 70%, 46% D purity, mp 66–69 °C, IR (KBr, cm^{-1}) ν 3060, 3001, 2931, 2833, 1610, 1582, 1510, 1478, 1454, 1440, 1301, 1246, 1177, 1108, 1067, 1037, 1001, 971, 916, 843, 809, 764, 740, 689, 620, 583, 566; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.73 (s, OMe), 4.17 (s, CH_2), 4.19 (s, CHD), 6.77 (d, *J*=8 Hz, ArH), 7.13–7.16 (m, ArH), 7.21–7.24 (m, ArH), 7.38–7.39 (m, ArH), 7.89–7.92 (m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.4 (d, *J*=20 Hz), 34.7 (t, CH_2), 55.2 (q), 113.7 (d×2), 120.8 (s), 126.2 (d), 126.5 (d×2), 127.1 (d×2), 128.9 (d×2), 129.1 (d×2), 129.9 (d×2), 130.4 (d), 131.0 (s), 133.4 (s), 137.3 (s), 158.0 (s), 162.3 (s), 170.5 (s); MS *m*/*z* 472 (M^+), 363 (M^+−SPh). Anal. Calcd for $C_{23}H_{18}DNOS_2$: 70.70; 4.65; N, 3.59. Found: C, 70.71; H, 5.02; N, 3.57.

*4.10.1.5. 4-(2-Thienyldeuteriomethyl)-2-phenyl-5-(phenyl-sulfanyl)-1,3-thiazole (**11ea**).* Yield 90%, 49% D purity, a yellow oil, IR (KBr, cm^{-1}) ν 3446, 3062, 2925, 2363, 1713, 1636, 1580, 1541, 1506, 1488, 1478, 1455, 1439, 1362, 1317, 1229, 1177, 1157, 1072, 1052, 1024, 1001, 988, 968, 918, 850, 763, 740, 688, 623, 577, 529; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.41 (br s, CH_2), 4.44 (br s, CHD), 6.88 (d, *J*=3 Hz, ArH), 7.11–7.12 (m, ArH), 7.15–7.18 (m, ArH), 7.22–7.25 (m, ArH), 7.40–7.41 (m, ArH), 7.91–7.92 (m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.7 (t, *J*=18 Hz, CDH), 29.9 (t, CH_2), 121.6 (s), 124.1 (d), 125.5 (d), 126.4 (d), 126.5 (d×2), 126.6 (d), 127.3 (d×2), 128.9 (d×2), 129.1 (d×2), 130.5 (d), 133.3 (s), 137.0 (s), 140.9 (s), 160.7 (s), 170.7 (s); MS *m*/*z* 366 (M^+), 257 (M^+−SPh). Anal. Calcd for $C_{20}H_{14}DNS_2$: C, 65.50; H, 3.85; N, 3.82. Found: C, 65.25; H, 4.20; N, 3.82.

*4.10.1.6. 4-[Bis(p-methoxyphenyl)deuteriomethyl]-2-phenyl-5-(phenyl-sulfanyl)-1,3-thiazole (**10ea**).* Yield 49%, 90% D purity, mp 133–135 °C, IR (KBr, cm^{-1}) ν 3431, 3060, 3000, 2925, 2853, 1608, 1580, 1509, 1477, 1440, 1298, 1248, 1177, 1113, 1071, 1036, 1000, 982, 835, 809, 783, 763, 741, 717, 688, 658, 627, 608, 583, 548; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.75 (s, D-OMe), 3.78 (s, H-OMe), 5.84 (s, CH), 6.79 (d, *J*=8 Hz, D-ArH), 6.84 (d, *J*=8 Hz, H-ArH), 7.11–7.20 (m, ArH), 7.24–7.31 (m, ArH), 7.34–7.42 (m, ArH), 7.87–7.92 (m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.2 (q×2), 113.5 (d×4), 121.3 (s), 126.2 (d), 126.5 (d×2), 127.3 (d×2), 128.8 (d×2), 129.1 (d×2), 130.0 (d×4), 130.4 (d), 133.6 (s), 135.1 (s×2), 137.2 (s), 158.0 (s×2), 163.9 (s), 170.3 (s); MS *m*/*z* 496 (M^+), 310 (M^+−Ph−SPh). Anal. Calcd for $C_{30}H_{24}DNO_2S_2$: C, 72.60; H, 4.87; N, 2.82. Found: C, 72.42; H, 4.89; N, 2.81.

*4.10.1.7. 4-[Bis(2-thienyl)deuteriomethyl]-2-phenyl-5-(phenyl-sulfanyl)-1,3-thiazole (**10ha**).* Yield 59%, 90% D purity, mp 126–129 °C, IR (KBr, cm^{-1}) ν 3343, 3063, 2923, 2853, 1656, 1579, 1478, 1453, 1432, 1314, 1232, 1158, 1080, 1040, 1024, 1001, 978, 917, 849, 763, 740, 688, 613; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.41 (br s, CH), 6.88 (dd, *J*=4 and 5 Hz, ArH), 6.97–6.98 (m, ArH), 7.14–7.22 (m, ArH), 7.40–7.41 (m, ArH), 7.96–7.97 (m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 121.7 (s), 125.0 (d×2), 125.9 (d×2), 126.3 (d×2), 126.5 (d×2), 126.6 (d×2), 127.6 (d×2), 128.9 (d×2), 129.1 (d×2), 130.6 (d), 133.4 (s), 136.7 (s), 145.3 (s×2), 161.8 (s), 170.8 (s); MS *m*/*z* 448 (M^+). Anal. Calcd for $C_{24}H_{16}DNS_4$: C, 64.30; H, 3.59; N, 3.12. Found: C, 63.94; H, 3.65; N, 3.11.

*4.10.1.8. 4-[Bis(2-thienyl)deuteriomethyl]-2-methyl-5-(phenyl-sulfanyl)-1,3-thiazole (**10hb**).* Yield 54%, 92% D purity, IR (KBr, cm^{-1}) ν 3430, 3103, 3071, 2922, 2853, 1733, 1617, 1580, 1500, 1478, 1439, 1415, 1360, 1290, 1233, 1179, 1081, 1067, 1042, 1023, 997, 900, 849, 830, 785, 740, 699, 616, 549; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.70 (br s, *D*- and *H*-Me), 6.36 (br s, *H*-CH), 6.88 (dd, *J*=3 and 5 Hz, *D*- and *H*-ArH), 6.91 (d, *J*=3 Hz, *D*- and *H*-ArH), 7.12–7.24 (m, *D*- and *H*-ArH), 7.68–7.69 (m, *H*–ArH), 7.90–7.91 (m, *H*-ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.0 (q), 124.9 (d×2), 126.0 (d×2), 126.4 (d×2), 127.4 (d×2), 127.9 (d), 129.1 (d×2), 133.1 (s), 133.5 (s), 136.8 (s), 145.2 (s×2), 160.9

(s), 170.0 (s); MS *m/z* 386 (M^+), 277 (M^+−SPh). Anal. Calcd for $C_{19}H_{14}DNS_4$: $C_{19}H_{14}DNS_4$: C, 59.00; H, 3.65; N, 3.62. Found: C, 58.82; H, 3.86; N, 3.14.

*4.10.1.9. 4-[Bis(2-thienyl)deuteriomethyl]-2-phenyl-5-(phenylsulfanyl)-1,3-selenazole (**10hc**).* Yield 57%, 85% D purity, mp 113–118 °C, IR (KBr, cm^{-1}) ν 3421, 3062, 2924, 2852, 1793, 1712, 1580, 1505, 1479, 1454, 1437, 1310, 1232, 1177, 1075, 1023, 1000, 953, 917, 850, 761, 740, 688, 664, 597, 513; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.43 (br s, *H*-CH), 6.89 (dd, *J*=6 and 8 Hz, ArH), 6.98 (dd, *J*=2 and 6 Hz, ArH), 7.18 (d, *J*=5 Hz, ArH), 7.21–7.22 (m, ArH), 7.31–7.42 (m, ArH), 7.90–7.91 (m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) of D-14hc δ 41.9 (d, *H*-CH), 125.0 (d×2), 125.8 (d×2), 126.2 (d×2), 126.5 (d), 127.1 (d×2), 127.6 (d×2), 127.9 (s), 129.0 (d×2), 129.1 (d×2), 130.8 (d), 136.2 (s), 137.6 (s), 145.6 (s×2), 162.1 (s), 177.6 (s); MS *m/z* 496 (M^+). Anal. Calcd for $C_{24}H_{16}DNS_3Se$: C, 58.20; H, 3.25; N, 2.83. Found: C, 58.03; H, 3.28; N, 2.82.

*4.10.1.10. 4-[Bis(2-thienyl)deuteriomethyl]-2-phenyl-5-(phenylselanyl)-1,3-thiazole (**10ia**).* Yield 59%, 90% D purity, mp 136–140 °C, IR (KBr, cm^{-1}) ν 3066, 2925, 2855, 2382, 2348, 2300, 1577, 1504, 1477, 1453, 1436, 1313, 1232, 1179, 1157, 1074, 1020, 1000, 978, 916, 849, 763, 736, 688, 615; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.44 (br s, *H*-CH), 6.87 (dd, *J*=4 and 5 Hz, *D*- and *H*-ArH), 6.96 (dd, *J*=1 and 3 Hz, *D*- and *H*-ArH), 7.17–7.23 (m, *D*- and *H*-ArH), 7.30–7.31 (m, *D*- and *H*-ArH), 7.40–7.41 (m, *D*- and *H*-ArH), 7.96–7.98 (m, *D*- and *H*-ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 114.7 (s), 125.0 (d×2), 125.8 (d×2), 126.3 (d×2), 126.6 (d×2), 127.2 (d×2), 128.9 (d×2), 129.4 (d×2), 130.4 (d×2), 130.5 (d), 131.8 (s), 133.3 (s), 145.6 (s×2), 161.8 (s), 172.0 (s); MS *m/z* 496 (M^+). Anal. Calcd for $C_{24}H_{16}NS_3Se$: C, 58.17; H, 3.25; N, 2.83. Found: C, 57.84; H, 3.31; N, 2.82.

4.11. Alkylations of 4-benzyl-2-phenyl-5-(phenylsulfanyl)-1,3-thiazoles 2 and 4 with *n*-BuLi/electrophiles

*4.11.1. Reaction of p-methoxyphenyl-2-phenyl-5-phenylsulfanyl-1,3-thiazole (**2a**) with n-BuLi/methyl iodide. Typical procedure.* *n*-BuLi (0.15 ml of 2.6 M *n*-hexane solution, 0.39 mmol) was added dropwise to a THF (1.0 ml) solution of **2a** (0.05 g, 0.13 mmol) at −78 °C under an Ar atmosphere. The reaction mixture was stirred for 10 min. Methyl iodide (0.18 g, 1.30 mmol) in THF (1.0 ml) was added to the mixture. The whole was stirred for 10 min and poured into water (50 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with *n*-hexane/EtOAc (50:1) to give 4-[1-(4-methoxyphenyl)ethyl]-2-phenyl-5-(phenylsulfanyl)thiazole (**20a**) (42 mg, 79%) as a yellow oil.

Compound **20a**: IR (KBr, cm^{-1}) ν 2962, 2927, 1610, 1582, 1511, 1478, 1460, 1440, 1264, 1245, 1177, 1036, 763, 739, 688; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.70 (3H, d, *J*=7 Hz, Me), 3.75 (3H, m, MeO), 6.77 (2H, q, *J*=7 Hz, CHMe), 6.77 (2H, d, *J*=7 Hz, ArH), 7.08–7.21 (5H, m, ArH), 7.33 (2H, d, *J*=9 Hz, ArH), 7.41–7.44 (2H, m, ArH), 7.94–7.96 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 22.0 (q), 38.4 (q), 55.2 (d), 113.6 (d×2), 119.3 (s), 126.1 (d), 126.5 (d×2), 126.9 (d×2), 128.7 (d×2), 128.9 (d×2), 129.0 (d×2), 130.3 (d), 133.7 (s), 136.8 (s), 137.5 (s), 158.0 (s), 166.5 (s), 170.4 (s); MS *m/z* 403 (M^+), 388 (M^+−Me), 326 (M^+−Ph), 294 (M^+−SPh). High-resolution mass calcd for $C_{24}H_{21}S_2NO$: 403.1064, found *m/z* 403.0996.

*4.11.1.1. 4-[1-(4-Methoxyphenyl)propyl]-2-phenyl-5-(phenylsulfanyl)-thiazole (**20b**).* White prisms, mp 59–61 °C, IR (KBr, cm^{-1}) ν 2925, 2854, 1714, 1611, 1583, 1511, 1478, 1455, 1441, 1362, 1247, 1221, 1177, 1036, 764, 740, 689; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.83 (3H, t, *J*=7 Hz, Me), 2.07–2.12 (1H, m, CH_2), 2.23–2.27 (1H, m, CH_2), 3.75 (3H, s, OMe), 4.26 (1H, t, *J*=7 Hz, CH), 6.76 (2H, d, *J*=9 Hz, ArH), 7.08–7.21 (5H, m, ArH), 7.34 (2H, d, *J*=9 Hz, ArH), 7.42–7.44 (3H, m, ArH), 7.96 (2H, dd, *J*=2 and 7 Hz, ArH); MS *m/z* 417 (M^+), 388 (M^+−Et). Anal. Calcd for $C_{24}H_{21}NS_2$: C, 74.38; H, 5.46; N, 3.61. Found: C, 74.43; H, 5.37; N, 3.71.

*4.11.1.2. 4-(1-Deutrio-4-methoxybenzyl)-2-phenyl-5-(phenylsulfanyl)-thiazole (**20c**).* White powders, mp 60–62 °C, IR (KBr, cm^{-1}) ν 2925, 2854, 1714, 1512, 1478, 1465, 1441, 1362, 1247, 1221, 1177, 1036, 764, 689; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.74 (s, MeO), 4.16 (s, CH_2), 4.19 (s, CHD), 6.77 (d, *J*=8 Hz, ArH), 7.14–7.16 (m, ArH), 7.21–7.24 (m, ArH), 7.39–7.40 (m, ArH), 7.90–7.91 (m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.5 (t, *J*=20 Hz, CHD), 34.7 (t), 55.2 (q), 113.7 (d×2), 120.8 (s), 126.2 (d), 126.5 (d×2), 127.1 (d×2), 128.9 (d×2), 129.1 (d×2), 129.9 (d×2), 130.4 (d), 131.0 (s), 133.4 (s), 137.3 (s), 158.0 (s), 162.3 (s), 170.5 (s); MS *m/z* 390 (M^+), 375 (M^+−Me), 313 (M^+−Ph), 312 (M^+−Ph), 281 (M^+−SPh), 280 (M^+−SPh). High-resolution mass calcd for $C_{23}H_{18}S_2NOD$: 390.0971, found *m/z* 390.0896.

*4.11.1.3. 4-[1-(4-Methoxyphenyl)-2-methylpropyl]-2-phenyl-5-(phenyl-sulfanyl)thiazole (**20d**).* A yellow oil, IR (KBr, cm^{-1}) ν 2956, 2927, 2855, 2361, 2343, 1610, 1582, 1510, 1479, 1440, 1247, 1177, 762, 739, 688; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.81 (3H, d, *J*=7 Hz, Me), 0.84 (3H, d, *J*=7 Hz, Me), 2.68–2.70 (1H, m, CH), 3.74 (3H, s, MeO), 3.94 (1H, d, *J*=11 Hz, CH), 6.76 (2H, d, *J*=9 Hz, ArH), 7.07–7.08 (2H, m, ArH), 7.11–7.13 (1H, m, ArH), 7.17–7.19 (4H, m, ArH), 7.36 (2H, d, *J*=8 Hz, ArH), 7.42–7.44 (3H, m, ArH), 7.96–7.47 (4H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.2 (q), 21.7 (q), 33.4 (d), 52.4 (d), 55.1 (q), 113.4 (d×2), 120.0 (s), 126.0 (d), 126.5 (d×2), 127.0 (d×2), 128.9 (d×2), 128.9 (d×2), 129.7 (d×2), 130.3 (d), 133.8 (s), 135.0 (s), 137.6 (s), 157.9 (s), 165.5 (s), 170.0 (s); MS *m/z* 431(M^+), 388 (M^+−CH$(CH_2)_2$), 322 (M^+−SPh). Anal. Calcd for $C_{26}H_{25}NOS_2$: C, 72.35; 5.84; N, 3.25. Found: C, 72.07; H, 5.79; N, 3.23.

*4.11.1.4. 4-[1-(3,4-Dimethoxyphenyl)ethyl]-2-phenyl-5-(phenyl-sul-fanyl)thiazole (**20e**).* white powder, mp 46–48 °C, IR (KBr, cm^{-1}) ν 2960, 2930, 1583, 1515, 1478, 1463, 1450, 1440, 1261, 1235, 1156, 1143, 1029, 764, 741, 689; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.72 (3H, d, *J*=7 Hz, Me), 3.75 (3H, s, MeO), 3.82 (3H, s, MeO), 4.59 (1H, q, *J*=7 Hz, CH), 6.73 (1H, d, *J*=8 Hz, ArH), 6.96 (1H, d, *J*=8 Hz, ArH), 6.98 (1H, s, ArH), 7.07 (2H, d, *J*=8 Hz, ArH), 7.11–7.13 (1H, m, ArH), 7.16–7.19 (2H, m, ArH), 7.40–7.41 (3H, m, ArH), 7.94–7.95 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.9 (q), 38.7 (d), 55.6 (q), 56.0 (q), 110.9 (d), 111.2 (d), 119.0 (s), 119.5 (d), 126.0 (d), 126.4 (d×2), 126.7 (d×2), 128.8 (d×2), 129.0 (d×2), 130.3 (d), 133.6 (s), 137.1 (s), 137.5 (s), 147.3 (s), 148.5 (s), 166.4 (s), 170.4 (s); MS *m/z* 433(M^+), 418 (M^+−Me), 356 (M^+−Ph), 324 (M^+−SPh). High-resolution mass calcd for $C_{25}H_{23}S_2O_2N$: 433.1170, found *m/z* 433.1177.

*4.11.1.5. 4-[1-(3,4-Dimethoxyphenyl)-2-phenylethyl]-2-phenyl-5-(phenylsulfanyl)thiazole (**20f**).* white powders, mp 130–132 °C, IR (KBr, cm^{-1}) ν 2925, 1714, 1516, 1362, 1262, 1222, 1142, 1030, 765, 742, 691; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.33 (1H, dd, *J*=6 and 13 Hz, CH_2), 3.68 (1H, dd, *J*=10 and 13 Hz, CH), 3.78 (3H, s, OMe), 3.81 (3H, s, MeO), 4.66 (1H, dd, *J*=6 and 10 Hz, CH_2), 6.74–6.78 (3H, m, ArH), 7.03–7.08 (7H, m, ArH), 7.12–7,17 (3H, m, ArH), 7.43–7.44 (3H, m, ArH), 7.98–8.00 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 42.6 (t), 46.9 (d), 55.6 (q), 55.8 (q), 111.0 (d), 111.5 (d), 120.3 (d), 121.0 (s), 125.9 (d), 126.4 (d×2), 126.9 (d×2), 128.1 (d×2), 128.9 (d×5), 129.1 (d×2), 130.3 (d), 133.7 (s), 135.6 (s), 137.2 (s), 140.2 (s), 147.5 (s), 148.5 (s), 164.2 (s), 170.2 (s); MS *m/z* 509 (M^+), 418 (M^+−CH_2Ph), 310 (M^+−PhS−CH_2Ph), 308 (M^+−PhS−CH_2Ph). High-resolution mass calcd for $C_{31}H_{27}S_2O_2N$: 509.1483, found *m/z* 509.1515.

*4.11.1.6. 4-[1-(Benzodioxol-5-yl)-2-phenylethyl]-2-phenyl-5-(phenyl-sulfanyl)thiazole (**20g**).* white powders, mp 113–114 °C, IR

(KBr, cm^{-1}) ν 1714, 1503, 1486, 1454, 1441, 1362, 1247, 1223, 1040, 933, 764, 741, 699, 689; ^1H NMR (600 MHz, $CDCl_3$) δ 3.29 (1H, dd, J=6 and 13 Hz, CH_2), 3.65 (1H, dd, J=10 and 13 Hz, CH_2), 4.63 (1H, dd, J=6 and 10 Hz, CH), 5.88 (2H, dd, J=1 and 10 Hz, CH_2), 6.65 (1H, d, J=8 Hz, ArH), 6.75–6.78 (3H, m, ArH), 6.85 (1H, d, J=8 Hz, ArH), 7.07–7.23 (8H, m, ArH), 7.42–7.47 (3H, m, ArH), 7.99–8.00 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 42.7 (t), 47.1 (d), 100.8 (t), 108.0 (d), 108.6 (d), 121.3 (d), 125.9 (d), 126.0 (d), 126.5 (d×2), 127.1 (d×2), 128.2 (d×2), 128.9 (d×4), 129.2 (d×2), 130.4 (d), 133.7 (s), 137.0 (s), 137.1 (s), 140.2 (s), 146.0 (s), 147.4 (s), 163.9 (s), 170.2 (s); MS m/z 493 (M^+), 402 (M^+-CH_2Ph), 294 ($M^+-PhS-CH_2Ph$). Anal. Calcd for $C_{30}H_{23}S_2O_2N$: C, 72.99, H, 4.70; N, 2.84. Found: C, 72.87; H, 4.71; N, 2.83.

*4.11.1.7. 4-[1-(4-Fluorophenyl)ethyl]-2-phenyl-5-(phenylsulfanyl)-thiazole (**20h**).* IR (KBr, cm^{-1}) ν 3061, 2970, 2928, 1603, 1582, 1508, 1478, 1449, 1440, 1429, 1224, 1158, 1054, 1041, 1024, 1001, 973, 837, 763, 738, 688; ^1H NMR (600 MHz, $CDCl_3$) δ 1.70 (3H, d, J=7 Hz, Me), 4.60 (1H, q, J=7 Hz, CH), 6.86–6.89 (1H, m, ArH), 7.04–7.05 (2H, m, ArH), 7.08–7.10 (1H, m, ArH), 7.14–7.16 (2H, m, ArH), 7.33–7.37 (5H, m, ArH), 7.92–7.93 (3H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 22.0 (q), 38.4 (d), 114.8 (d), 114.9 (d), 119.6 (s), 126.1 (d), 126.4 (d×2), 126.8 (d×2), 128.8 (d×2), 129.0 (d×2), 129.1 (d), 129.2 (d), 130.4 (d), 133.5 (s), 137.2 (s), 140.1 (s), 161.3 (s), 165.8 (s), 170.5 (s); MS m/z 391 (M^+), 376 (M^+-Me), 314 (M^+-Ph), 282 (M^+-SPh). Anal. Calcd for $C_{23}H_{18}FNS_2$: C, 70.56; H, 4.63; N, 3.58. Found: C, 70.33; H, 4.67; N, 3.49.

*4.11.1.8. 2-Phenyl-5-(phenylsulfanyl)-4-[1-(2-thienyl)ethyl]thiazole (**20i**).* A yellow oil, IR (KBr, cm^{-1}) ν 1714, 1581, 1488, 1478, 1449, 1439, 1431, 1361, 1220, 1024, 764, 740, 689; ^1H NMR (600 MHz, $CDCl_3$) δ 1.76 (3H, d, J=7 Hz, Me), 4.93 (1H, q, J=7 Hz, CH), 6.86–6.87 (2H, m, ArH), 7.12–7.18 (3H, m, ArH), 7.23–7.26 (3H, m, ArH), 7.42–7.43 (3H, m, ArH), 7.95 (2H, dd, J=3 and 6 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.0 (q), 34.9 (d), 119.9 (s), 123.7 (d), 123.9 (d), 126.2 (d×2), 126.4 (d×2), 127.0 (d×2), 128.8 (d×2), 129.0 (d×2), 130.3 (d), 133.4 (s), 137.2 (s), 147.9 (s), 165.1 (s), 170.6 (s); MS m/z 379 (M^+), 364 (M^+-Me), 302 (M^+-Ph), 269 (M^+-SPh). Anal. Calcd for $C_{21}H_{17}S_3N$: C, 66.45, H, 4.51; N, 3.69. Found: C, 65.66; H, 4.53; N, 3.66.

4.12. Desulfanylation of methylated 1,3-thiazoles 20

Typical procedure. A mixture of **20a** (70 mg, 0.17 mmol) and AIBN (12 mg, 0.07 mmol) in toluene (1.0 ml) was refluxed for 7 h. The cooled mixture was evaporated under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt/*n*-hexane (1:50) to give 4-[1-(4-methoxyphenyl)ethyl]-2-phenyl-5-(tributylstannyl)thiazole (68 mg, 69%) as a colorless oil.

4.12.1. 4-[1-(4-Methoxyphenyl)ethyl]-2-phenyl-5-(tributylstannyl)-thiazole. IR (KBr, cm^{-1}) ν 2956, 2926, 2871, 2852, 1611, 1510, 1480, 1463, 1303, 1245, 1177, 1074, 1038, 1008, 962, 830, 762, 689, 667, 602; ^1H NMR (600 MHz, $CDCl_3$) δ 0.87 (9H, t, J=7 Hz, Me×3), 1.10–1.14 (6H, m, CH_2×3), 1.27–1.35 (6H, m, CH_2×3), 1.44–1.53 (6H, m, CH_2×3), 1.73 (3H, d, J=7 Hz, Me), 3.75 (3H, s, MeO), 4.06 (1H, q, J=7 Hz, CH), 6.81 (2H, d, J=9 Hz, ArH), 7.33–7.41 (5H, m, ArH), 8.00 (2H, d, J=9 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 11.1 (t×3), 13.6 (q×3), 23.9 (d), 27.2 (t×3), 29.0 (t×3), 43.2 (t), 55.2 (q), 113.5 (d×2), 123.1 (s), 126.5 (d×2), 128.5 (d×2), 128.7 (d×2), 129.2 (d), 134.3 (s), 138.3 (s), 157.8 (s), 167.4 (s), 172.1 (s); MS m/z 528 (M^+-Bu), 526 (M^+-Bu), 470 (M^+-2Bu). Anal. Calcd for $C_{30}H_{43}SnSNO$: C, 61.66; H, 7.42; N, 2.40. Found: C, 61.32; H, 7.32; N, 2.39.

4.12.2. 4-[1-(3,4-Dimethoxyphenyl)ethyl]-2-phenyl-5-(tributylstannyl)thiazole. IR (KBr, cm^{-1}) ν 2956, 2926, 2871, 2853, 1517, 1480, 1464, 1261, 1234, 1155, 1144, 1031, 763, 690; ^1H NMR (600 MHz, $CDCl_3$) δ 0.88 (9H, t, J=7 Hz, Me×3), 1.10–1.18 (6H, m, CH_2×3), 1.29–1.37 (6H, m, CH_2×3), 1.48–1.54 (6H, m, CH_2×3), 1.74 (3H, d, J=7 Hz, Me), 3.83 (3H, s, MeO), 3.87 (3H, s, MeO), 4.04 (1H, q, J=7 Hz, ArH), 6.77 (1H, d, J=8 Hz, ArH), 6.91 (1H, d, J=8 Hz, ArH), 7.14 (1H, s, ArH), 7.34–7.37 (1H, m, CH), 7.39–7.42 (2H, m, ArH), 8.00 (2H, d, J=8 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 11.1 (t×3), 13.6 (q×3), 24.0 (d), 27.2 (t×3), 29.0 (t×3), 43.6 (q), 55.7 (q), 55.8 (d), 110.8 (d), 112.1 (d), 119.5. (d), 123.3 (s), 126.4 (d×2), 128.7 (d×2), 129.3 (d), 134.3 (s), 138.8 (s), 147.2 (s), 148.6 (s), 167.3 (s), 172.2 (s); MS m/z 558 (M^+-Bu), 556 (M^+-Bu), 444 ($M^+-3\times Bu$), 351 ($M^+-Ph-Me-3\times Bu$). Anal. Calcd for $C_{31}H_{45}NO_2SSn$: C, 60.60, H, 7.38; N, 2.28. Found: C, 60.38; H, 7.35; N, 2.27.

4.12.3. 2-Phenyl-4-[1-(2-thienyl)ethyl]-5-(tributylstannyl)thiazole. IR (KBr, cm^{-1}) ν 2957, 2927, 2871, 2852, 1716, 1508, 1482, 1463, 1376, 1231, 1074, 1046, 1023, 1007, 962, 868, 849, 763, 690, 604; ^1H NMR (600 MHz, $CDCl_3$) δ 0.88 (9H, t, J=7 Hz, Me×3), 1.14–1.17 (6H, m, CH_2), 1.28–1.36 (6H, m, CH_2), 1.48–1.66 (6H, m, CH_2), 1.80 (3H, d, J=7 Hz, Me), 4.34 (1H, d, J=7 Hz, CH), 6.86–6.87 (1H, m, ArH), 6.88 (1H, dd, J=4 and 5 Hz, ArH), 7.26 (2H, s, ArH), 7.35–7.42 (2H, m, ArH), 7.99 (2H, d, J=7 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 11.1 (t×3), 12.3 (q×3), 24.5 (d), 27.2 (t×3), 29.0 (t×3), 39.8 (d), 123.4 (s), 123.5 (d×2), 126.1 (d), 126.5 (d×2), 128.6 (d×2), 129.3 (d), 137.2 (s), 149.7 (s), 166.4 (s), 172.5 (s); MS m/z 504 (M^+-Bu), 502 (M^+-Bu), 379 ($M^+-SPh-Me-Bu$). Anal. Calcd for $C_{27}H_{39}S_2SnN$: C, 57.87, H, 7.01; N, 2.50. Found: C, 57.61; H, 6.97; N, 2.48.

4.12.4. 4-[1-(4-Fluorophenyl)ethyl]-2-phenyl-5-(tributylstannyl)-thiazole. IR (KBr, cm^{-1}) ν 2957, 2926, 2871, 2852, 1716, 1602, 1508, 1480, 1463, 1430, 1376, 1223, 1158, 1074, 1051, 1009, 962, 876, 835, 762, 739, 689, 667, 602; ^1H NMR (600 MHz, $CDCl_3$) δ 0.87 (9H, t, J=7 Hz, Me×3), 1.09–1.17 (6H, m, CH_2×3), 1.30–1.34 (6H, m, CH_2×3), 1.50–1.51 (6H, m, CH_2×3), 1.74–1.75 (3H, d, J=6 Hz, Me), 4.09 (1H, q, J=6 Hz, CH), 6.89–6.95 (2H, m, ArH), 7.33–7.40 (5H, m, ArH), 8.00 (2H, d, J=7 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 11.1 (t×3), 13.6 (q×3), 23.9 (d), 27.2 (t×3), 29.0 (t×3), 43.3 (d), 114.7 (d), 114.9 (d), 123.5 (s), 126.5 (d×2), 128.7 (d×2), 129.0 (d), 129.0 (d), 129.3 (d), 134.2 (s), 141.7 (s), 161.3 (d, J=244 Hz), 166.8 (s), 172.8 (s); MS m/z 516 (M^+-Bu), 458 ($M^+-2\times Bu$), 324 ($M^+-Ph-Bu$). Anal. Calcd for $C_{29}H_{40}FNSSn$: C, 60.85; H, 7.04; N, 2.45. Found: C, 60.91; H, 6.58; N, 2.51.

4.13. Destannylation of 4-[1-(4-methoxyphenyl)ethyl]-2-phenyl-5-(tributylstannyl)thiazole

Typical procedure. MeLi (1 M, 0.45 ml, 0.50 mmol) in ether was added dropwise to a THF (1.0 ml) solution of 4-[1-(4-methoxyphenyl)ethyl]-2-phenyl-5-(tributylstannyl)thiazole (56 mg, 0.10 mmol) at −72 °C under an Ar atmosphere. The reaction mixture was stirred for 10 min and poured into a saturated NH_4Cl (50 ml) solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt/*n*-hexane (1:30) to give **21a** (21 mg, 76%) as a yellow oil.

*4.13.1. 4-[1-(4-Methoxyphenyl)ethyl]-2-phenylthiazole (**21a**).* IR (KBr, cm^{-1}) ν 1611, 1511, 1497, 1462, 1439, 1302, 1247, 1178, 1035, 1002, 832, 766, 690; ^1H NMR (600 MHz, $CDCl_3$) δ 1.70 (3H, d, J=7 Hz, Me), 3.78 (3H, s, MeO), 4.31 (1H, q, J=7 Hz, CH), 6.75 (1H, s, CH), 6.86 (2H, dd, J=2 and 7 Hz, ArH), 7.26 (2H, dd, J=2 and 7 Hz, ArH), 7.38–7.42 (3H, m, ArH), 7.92–7.94 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.7 (q), 41.6 (d), 55.2 (q), 113.0 (d), 113.8 (d×2), 126.5 (d×2), 128.6 (d×2), 128.8 (d×2), 129.7 (d), 133.9 (s), 137.0 (s), 158.1 (s), 162.8 (s), 167.5 (s); MS m/z 295 (M^+), 280 (M^+-Me). Anal. Calcd for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74. Found: C, 73.11; H, 5.86; N, 4.68.

*4.13.2. 4-[1-(3,4-Dimethoxyphenyl)ethyl]-2-phenylthiazole (**21e**).* IR (KBr, cm^{-1}) ν 2963, 2930, 1591, 1516, 1463, 1417, 1259, 1236, 1160,

1143, 1030, 1005, 982, 767, 691; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.71 (3H, d, J=7 Hz, Me), 3.83 (3H, s, OMe), 3.89 (3H, s, OMe), 4.29 (1H, q, J=7 Hz, CH), 6.77 (1H, s, ArH), 6.81 (1H, d, J=8 Hz, ArH), 6.86–6.88 (1H, m, ArH), 6.92 (1H, d, J=2 Hz, ArH), 7.35–7.41 (3H, m, ArH), 7.92–7.94 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6 (q), 41.7 (d), 55.7 (q), 55.7 (q), 110.9 (d), 111.0 (d), 112.9 (d), 119.3 (d), 126.3 (d×2), 128.7 (d×2), 129.6 (d), 133.7 (s), 137.3 (s), 147.4 (s), 148.6 (s), 162.5 (s), 167.4 (s); MS m/z 403 (M^+), 388 (M^+–Me), 326 (M^+–Ph), 294 (M^+–SPh). High-resolution mass calcd for $C_{19}H_{19}NO_2S$: 325.1136, found m/z 325.1072.

*4.13.3. 4-[1-(4-Fluorophenyl)ethyl]-2-phenylthiazole (**21h**).* IR (KBr, cm^{-1}) ν 3063, 2970, 2930, 2872, 1603, 1508, 1461, 1437, 1223, 1159, 1052, 1003, 979, 915, 836, 766, 690, 609, 597, 548; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.70 (3H, d, J=8 Hz, Me), 4.31–4.34 (1H, q, J=8 Hz, CH), 6.77 (1H, s, ArH), 6.97–7.01 (2H, m, ArH), 7.28–7.30 (2H, m, ArH), 7.36–7.41 (3H, m, ArH), 7.91–7.93 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.7 (q), 41.5 (d), 113.1 (d), 115.0 (d), 115.2 (d), 126.5 (d×2), 128.8 (d×2), 129.0 (d), 129.1 (d), 129.8 (d), 133.8 (s), 140.5 (s), 161.4 (d, J=244 Hz), 162.1 (s), 167.7 (s); MS m/z 284 (M^+), 283, 269 (M^+–Me), 268 (M^+–Me). High-resolution mass calcd for $C_{17}H_{14}FNS$: 283.0831, found m/z 283.0828.

*4.13.4. 4-[1-(2-Thienyl)ethyl]-2-phenylthiazole (**21i**).* IR (KBr, cm^{-1}) ν 2971, 2928, 1713, 1510, 1497, 1458, 1437, 1362, 1222, 1002, 766, 690; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.80 (3H, d, J=8 Hz, Me), 4.64 (1H, q, J=7 Hz, CH), 6.87 (1H, d, J=8 Hz, ArH), 6.94–6.95 (2H, m, ArH), 7.17 (2H, dd, J=2 and 4 Hz, ArH), 7.37–7.42 (3H, m, ArH), 7.94–7.95 (1H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 22.6 (q), 37.7 (d), 113.2 (d), 123.6 (d), 124.0 (d), 126.5 (d×3), 128.8 (d×2), 129.8 (d), 133.8 (s), 148.4 (s), 161.7 (s), 167.7 (s); MS m/z 271 (M^+), 256 (M^+–Me). High resolution mass calcd for $C_{15}H_{13}NS_2$: 271.0489, found m/z 271.0409.

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