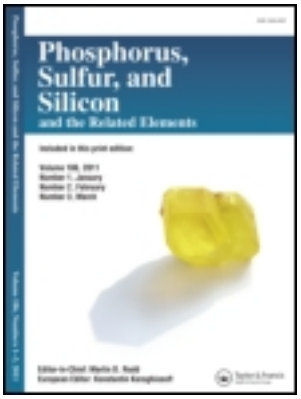

Phosphorus, Sulfur, and Silicon and the Related Elements

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Efficient Uncatalyzed Conversion of Primary and Secondary Thioamides into 1-Substituted, 5-Substituted, 1, 5-Disubstituted and Annulated Tetrazoles

Abdel-Aziz S. El-Ahl [a b], Fatty A. Amer [b] & Akram H. Elbeheery [b]

[a] Department of Chemistry, Makah University College, Umm Al-Qura University, Makah, Kingdom of Saudi Arabia

[b] Department of Chemistry, Faculty of Science, Mansoura University, Mansoura-, 35516, Egypt

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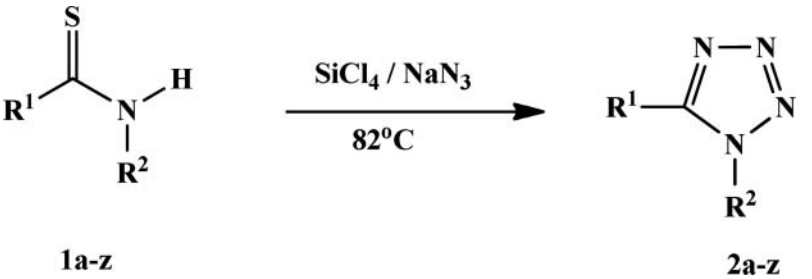
EFFICIENT UNCATALYZED CONVERSION OF PRIMARY AND SECONDARY THIOAMIDES INTO 1-SUBSTITUTED, 5-SUBSTITUTED, 1, 5-DISUBSTITUTED AND ANNULATED TETRAZOLES

Abdel-Aziz S. El-Ahl,[1,2] Fatty A. Amer,[2] and Akram H. Elbeheery[2]

[1]*Department of Chemistry, Makah University College, Umm Al-Qura University, Makah, Kingdom of Saudi Arabia*

[2]*Department of Chemistry, Faculty of Science, Mansoura University, Mansoura-35516, Egypt*

GRAPHICAL ABSTRACT



Abstract *Unprecedented high-yield simple and mild conversion of primary aliphatic and aromatic thioamides into 5-substituted tetrazoles on treatment with a combination of tetrachlorosilane and sodium azide in refluxing acetonitrile has been achieved. Secondary acyclic, cyclic, and heterocyclic thioamides could also be transformed in high yields into 1-substituted, 1,5-disubstituted, or annulated tetrazoles under the same reaction condition.*

Keywords Tetrachlorosilane; sodium azide; thioamides; tetrazoles

INTRODUCTION

Tetrazoles are a class of nitrogen-rich heterocycles with a wide range of applications.[1] They have found use in various material science applications, including photography,[2] special explosives for rocket propellants,[3] information recording systems,[4] and agricultural composition.[5] In addition, extensive work has been carried out in the field of medicinal chemistry where tetrazoles are frequently used as metabolically stable surrogates for carboxylic acids.[6–8]

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Address correspondence to Abdel-Aziz S. El-Ahl, Department of Chemistry, Makah University College, Umm Al-Qura University, P.O. Box 2064, Makah, Kingdom of Saudi Arabia. E-mail: elahl2002@yahoo.com

Tetrazoles serve as precursors for the synthesis of several interesting nitrogen heterocycles.[9,10] These are also employed as catalysts in asymmetric synthesis. Recently, proline-derived tetrazoles have been reported as a powerful enantioselective catalysts used in conjugate addition reactions, asymmetric aldol, Mannich reaction, and multi-component reactions.[11]

Therefore, many synthetic efforts have been made for the development of efficient routes to prepare tetrazoles. The most convenient routes to synthesize tetrazoles involved the addition of hydrazoic acid or inorganic azide salts into nitriles,[12] ketones,[13] oximes,[14] amides,[15] imidoyl chlorides,[16] and nitrlium triflates.[17] The use of Bronsted[18] or Lewis acids,[19] heterogeneous[20] or nanocrystalline catalysts,[21] or stoichiometric amounts of Zn II salts[22,23] have been reported as suitable additives in above-mentioned methodologies. As an alternative to inorganic azide salts, trimethylsilyl,[24] trialkyl tin,[25] and organoaluminum azides[26] have been introduced as comparatively safe azide sources (sometimes prepared in situ) that have the added benefit of being soluble in organic solvents. Unfortunately, with very few exceptions, several of these protocols included the use of toxic metals, expensive reagents, drastic reaction conditions, and/or the possible presence of dangerous hydrazoic acid or other explosive sublimates.

In this paper, we report a simple, safe, and cheap one-pot methodology for the uncatalyzed direct conversion of readily available primary and secondary thioamides into tetrazoles.

RESULTS AND DISCUSSION

During the last decade, we have being involved in developing a new methodology for the construction of tetrazole systems via reaction of $SiCl_4/NaN_3$ reagent system with ketones, α, ß-unsaturated ketones, and primary and secondary amides.[27–29]

To our knowledge the conversion of primary thioamides into 5-substituted tetrazoles has not been reported in the literature and only few reports on the conversion of secondary thioamides into tetrazoles have been reported using aluminum azide[30] or trimethylsilyl azide.[31]

Sulfur has lower electronegativity than oxygen. This means that thioamides should be less polar than amides, with more equable charge density, and less reactivity. In fact, thioamides are more polar (and especially more polarizable) compared with respective amides and participate in more reactions.[32]

Therefore, we envisioned that the investigation of the uncatalyzed reaction of the reagent system of tetrachlorosilane and sodium azide with wide varieties of thioamides as a new route for the synthesis of tetrazoles would be a new addition to the existing methods.

Thus, we have investigated the reaction of thiobenzamide **1a** with different stoichiometric amounts of tetrachlorosilane and sodium azide in dry acetonitrile under different conditions. It has been found that the reaction of **1a** with two equivalents of tetrachlorosilane and six equivalents of sodium azide in acetonitrile under reflux for 1.5 h to afford 5-phenyl-1*H*-tetrazole **2a** in 88% yield. This reaction is considered as the first direct conversion of primary thioamides into 5-substituted tetrazoles. The potency of this transformation came from the comparison with previously reported studies, which emphasized that 1*H*-tetrazoles could not be made directly from primary amides. They must be prepared using a cleavable N-substituent, e.g., ß-cyanoethyl group.[33]

We have found that dry acetonitrile is the best solvent of choice, which is unreactive toward this reagent system, and the possibility of liberation of hydrazoic acid is very low.

The risk of evolution of hydrazoic acid by pouring the reaction mixture into 5% ice-cooled sodium carbonate solution during work-up is minimal. By this method a variety of ring-substituted thiobezamides were converted into the corresponding tetrazoles (Scheme 1). The results of this reaction are summarized in Table 1.

As demonstrated in Table 1, the reaction tolerates both electron positive or electron negative groups on the aromatic ring. This is exemplified by the conversion of 4-methoxythiobenzamide **1e** and 4-nitrothiobenzamide **1f** into the corresponding tetrazoles **2e**,**f** in 90% and 80% yield, respectively. The reaction worked well with *ortho*-substituted thiobenzamides. In other methods, *ortho*-substituted substrates tend to be recalcitrant.[34] Of particular interest is *ortho*-chlorothiobenzamide **1c**, which produced 5-(2-chlorophenyl)-1*H*-tetrazole **2c** in 90% yield. The importance of this tetrazole is that it can be further elaborated into more complex structures using the fast possibilities of organometallic chemistry.

Primary thioamides with a bulkier C-aryl group afforded the corresponding tetrazoles in high yields. This is demonstrated by the conversion of 4-phenylthiobenzamide **1g**, which has a bulky biphenyl nucleus, to the corresponding tetrazole **2g** in 85% yield (1.5-h reflux in acetonitrile). Several highly potent AT1 selective antagonists contain a biphenyltetrazole moiety appended to a five-membered or a six-membered heterocycle. The biphenyl-tetrazole moiety is considered to be an essential acidic functional group for antagonism.[35]

While the conversion of aliphatic nitriles into tetrazoles has been reported to require very high temperature using a sealed glass pressure reactor,[36] aliphatic thioamides such as phenoxythioacetamide **1h** was readily converted to the corresponding tetrazole **2h** in 85% yield (2-h reflux in acetonitrile).

We have also investigated the reaction of secondary thioamides with $SiCl_4/NaN_3$ reagent system. The reaction of *N*-aryl thioformamides **1i–r** with $SiCl_4/NaN_3$ in acetonitrile under reflux conditions afforded 1-aryl-1*H*-tetrazoles **2i–r** in 80–90% yields (cf. Table 1). The reaction tolerates various substituents at the aryl group such as chloro-, methoxy-, and methyl- or nitro- groups. The reaction rate was retarded as the N-substituent gets bulkier.

Similarly, N-aryl thioacetamides **1s–z** furnished the corresponding 1,5-disubstituted tetrazoles **2s–z** in yields ranging from 86–92% under the same reaction conditions (cf. Table 1).

For steric reasons N-(1-naphthyl)thioacetamide **1y** and N-benzyl-2-phenyl-thioacetamide **1z** required relatively longer reaction time to be completely converted into the corresponding **2y** and **2z** tetrazoles (6–7-h reflux in acetonitrile).

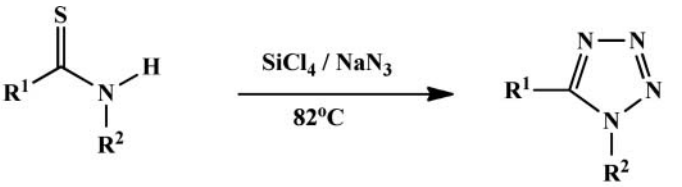
In order to investigate the potentiality and generality of this reaction in the synthesis of different tetrazoles, we have investigated the reaction of $SiCl_4/NaN_3$ with both aliphatic and aromatic heterocyclic thioamides (Scheme 2). Thus, the reaction of $SiCl_4/NaN_3$ reagent system with azepan-2-thione **3** in refluxing acetonitrile afforded 6,7,8,9-tetrahydro-5*H*-tetrazolo-[1,5-a]azepine **4** in 88% yield.

Also, the reaction of 4-methylquinoline-2(1*H*)-thione **5** with $SiCl_4/NaN_3$ under the same conditions furnished 5-methyl tetrazolo[1,5-a]quinoline **6** in 86% yield.

The structures of the previously reported tetrazoles **2a–f**, **2h–p**, and **2r–x** and the four hitherto unknown tetrazoles **2g**, **2q**, **2y**, and **2z** have been confirmed by analytical and spectral methods and comparison of their spectroscopic data with those reported in the literature. The ^{1}H-NMR of 5-methyl-1-(1-naphthyl)-1*H*-tetrazole **2y** displayed a three-proton singlet at δ 2.43 ppm assigned for the 5-CH_3 group, three two-proton doublets each at δ 8.11, 8.0, 7.17 ppm and a four-proton multiplet at δ 7.67–7.47 ppm assigned for aromatic

Table 1 Analytical data, physical characteristics, and reaction time of tetrazoles **2a–z**

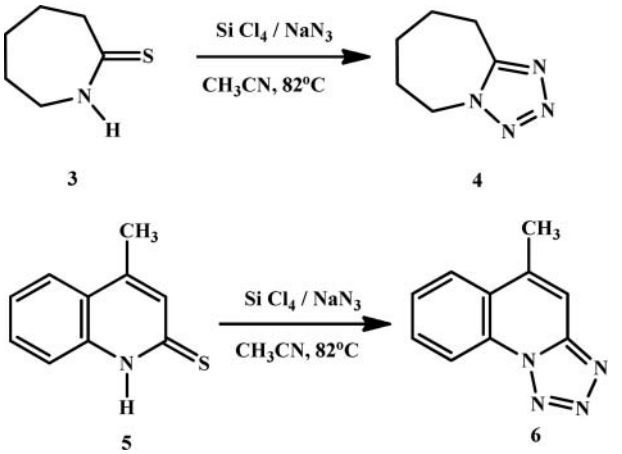
Compound no.	Time (h)	Yield (%)	mp °C (Lit mp °C)	M. F (Mol. wt)	Elemental analyses: found (Calculated)		
					C	H	N
2a	1.5	88	248–250 (249–250)[37a]	$C_7H_6N_4$ (146.16)	57.52 (57.27)	4.14 (3.99)	38.34 (38.25)
2b	1.5	92	261–262 (262–263)[37b]	$C_7H_5ClN_4$ (180.59)	46.55 (46.50)	2.79 (2.90)	31.02 (31.30)
2c	1.5	90	180 (179–180)[37b]	$C_7H_5ClN_4$ (180.59)	46.55 (46.42)	2.79 (2.61)	31.02 (31.21)
2d	1.5	92	250 (249–250)[37c]	$C_8H_8N_4$ (160.18)	59.99 (60.10)	5.03 (4.90)	34.98 (34.90)
2e	1.5	90	233 (232–233)[37d]	$C_8H_8N_4O$ (176.18)	54.54 (54.70)	4.58 (4.70)	31.80 (32.10)
2f	2	80	219 (219)[37c]	$C_7H_5N_5O_2$ (191.15)	43.98 (43.62)	2.64 (2.50)	36.64 (36.75)
2g	1.5	85	253	$C_{13}H_{10}N_4$ (222.25)	70.26 (70.30)	4.54 (4.63)	25.21 (25.07)
2h	2	85	127(127.5)[37e]	$C_8H_8N_4O$ (176.18)	54.54 (54.69)	4.58 (4.87)	31.80 (31.71)
2i	8	90	215 (215)[37f]	$C_7H_6N_4$ (146.15)	57.53 57.30	4.14 (4.00)	38.34 38.20
2j	6	92	155 (155–156)[37f]	$C_7H_5ClN_4$ (180.59)	46.55 (46.51)	2.79 (2.82)	31.02 (31.08)
2k	7	86	102 (101–102)[37f]	$C_7H_5ClN_4$ (180.59)	46.55 (46.57)	2.79 (2.83)	31.02 (31.05)
2l	6	90	116 (116–117)[37g]	$C_8H_8N_4O$ (176.18)	54.54 (54.60)	4.58 (4.60)	31.80 (31.80)
2m	8	85	65 (65)[37f]	$C_8H_8N_4O$ (176.18)	54.54 (54.50)	4.58 (4.60)	31.80 (32.00)
2n	6	90	94 (93–94)[37g]	$C_8H_8N_4$ (160.18)	59.99 (59.72)	5.03 (5.31)	34.98 (34.75)
2o	8	83	53 (53–54)[37f]	$C_8H_8N_4$ (160.18)	59.99 (59.80)	5.03 (4.90)	34.98 (34.90)
2p	10	80	205 (205)[37g]	$C_7H_5N_5O_2$ (191.15)	43.98 (44.10)	2.64 (2.70)	36.64 (36.61)
2q	9	85	96	$C_{11}H_8N_4$ (196.21)	67.34 (67.50)	4.11 (3.96)	28.55 (28.54)
2r	10	80	59 (59–60)[38a]	$C_8H_8N_4$ (160.18)	59.99 (60.10)	5.03 (5.00)	34.98 (34.80)
2s	6	87	98 (97–98)[38b]	$C_8H_8N_4$ (160.18)	59.99 (60.10)	5.03 (5.10)	34.98 (34.80)
2t	6	92	106 (106)[38c]	$C_9H_{10}N_4$ (174.20)	62.05 (61.95)	5.79 (5.81)	32.16 (32.24)
2u	6	89	87 (87)[38c]	$C_9H_{10}N_4$ (174.20)	62.05 (61.86)	5.79 (5.93)	32.16 (32.42)
2v	6	92	90 (90)[13]	$C_9H_{10}N_4O$ (190.20)	56.83 (57.00)	5.30 (5.20)	29.46 (29.60)
2w	6	92	119 (119–120)[38d]	$C_8H_7ClN_4$ (194.62)	49.37 (49.23)	3.63 (3.71)	28.79 (28.80)
2x	6	90	119 (119)[38e]	$C_8H_7BrN_4$ (239.07)	40.19 (39.95)	2.95 (2.87)	23.44 (23.68)
2y	7	86	106	$C_{12}H_{10}N_4$ (210.23)	68.56 (68.38)	4.79 (4.81)	26.65 (26.81)
2z	6	88	84–86	$C_{15}H_{14}N_4$ (250.30)	71.98 (71.64)	5.64 (5.82)	22.38 (22.26)
4	8	88	60 (60)[21]	$C_6H_{10}N_4$ 138.17	52.16 (52.25)	7.29 (7.19)	40.55 (40.51)
6	8	86	207 (207)[38f]	$C_{10}H_8N_4$ (184.20)	65.21 (65.38)	4.38 (4.46)	30.42 (30.10)



1a-z 2a-z

1,2	R^1	R^2	1,2	R^1	R^2	1,2	R^1	R^2
a	Ph	H	j	H	4-ClC_6H_4	s	CH_3	Ph
b	4-ClC_6H_4	H	k	H	3-ClC_6H_4	t	CH_3	4-$CH_3C_6H_4$
c	2-ClC_6H_4	H	l	H	4-$CH_3OC_6H_4$	u	CH_3	3-$CH_3C_6H_4$
d	4-$CH_3C_6H_4$	H	m	H	3-$CH_3OC_6H_4$	v	CH_3	4-$CH_3OC_6H_4$
e	4-$CH_3OC_6H_4$	H	n	H	4-$CH_3C_6H_4$	w	CH_3	4-ClC_6H_4
f	4-$O_2NC_6H_4$	H	o	H	3-$CH_3C_6H_4$	x	CH_3	4-BrC_6H_4
g	4-PhC_6H_4	H	p	H	4-$O_2NC_6H_4$	y	CH_3	1-Naphthyl
h	$PhOCH_2$	H	q	H	1-Naphthyl	z	$PhCH_2$	$PhCH_2$
i	H	Ph	r	H	$PhCH_2$			

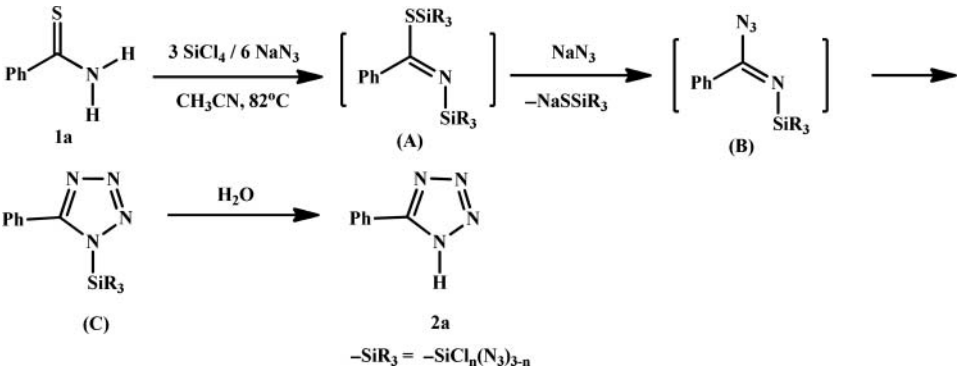
Scheme 1 Reaction of primary and secondary aromatic thioamides with $SiCl_4/NaN_3$ reagent system.



Scheme 2 Reaction of aliphatic and aromatic heterocyclic thioamides with $SiCl_4/NaN_3$ reagent system.

protons. The mass spectra of compounds **2a**, **2n**, **2t**, and **6** were found to show a regular fragmentation giving molecular ion peaks at m/z of 146, 160, 174, and 184, respectively, along with fragment results from elimination of nitrogen or hydrazoic acid molecules. In the Infrared (IR) spectra, the bands due to –N=N- and C=N group, which are present in all studied compounds, were observed at about 1595 and 1516 cm^{-1}, respectively. The bands at about 1185 and 1086 cm^{-1} were characteristic for the CN_4 (tetrazole ring).

The mechanism of transformation of thioamides into tetrazoles may be explained by the in situ formation of an azidochlorosilane species, represented as $SiCl_n(N_3)_{4-n}$, from tetrachlorosilane and sodium azide in 1:3 ratio, respectively.[27b] In this example the azidosilane reagent forms N,S-bis silyl imidate A,[39] which in turn reacts with an equivalent of sodium azide to give the imidoyl azide B via a nucleophilic addition elimination mechanism. The intermediate imidoyl azide B tautomerizes to N-silyl tetrazole C (presumably as the N-1 regioisomer), which is hydrolyzed in the workup to provide 5-substituted tetrazoles (Scheme 3). A similar mechanism has been proposed for the reaction of amides with tetrachlorosilane and sodium azide.[29] Also, the reported formation of tetrazoles via desulfurization of thiourea derivatives in presence of sodium azide gives support for the proposed reaction mechanism.[40] It is interesting to note that this reagent apparently does not react with the acetonitrile solvent.



Scheme 3 Mechanism of reaction of thioamides with $SiCl_4/NaN_3$ reagent system.

CONCLUSION

In conclusion, a very simple and convenient chemoselective method has been developed for the synthesis of different substituted and annulated tetrazoles from primary and secondary cyclic and acyclic thioamides. The isolation and purification steps were particularly straightforward in comparison to other methods. This method has advantages in terms of yields, short reaction times, ease of operation, absence of any catalyst, and making a useful and important addition to the present methodologies. This methodology might also find widespread use in organic synthesis for the preparation of different substituted tetrazoles. In addition, we demonstrated that primary thioamides are much more reactive toward $SiCl_4/NaN_3$ reagent system than nitriles exemplified by the solvent.

Table 2 Spectroscopic data of compounds **2a–z**, **4 and 6**

Compound no.	IR cm^{-1} (KBr, selected peaks)); MS (m/z)	^{1}H-NMR, δ ppm
2a	3060, 2600, 1608, 1563, 1163, 1057; MS (m/z,%) 146 (M^+, 22), 118 ($M^+ -N_2$, 100), 104 ($M^+ -N_3$, 11.9), 103 ($M^+ -HN_3$, 35.5)	δ (CD_3OD): 8.03–7.99 (m, 2H), 7.59–7.56 (m, 3H)
2b	3090, 2550, 1606, 1580, 1164, 1095, 744	δ (CD_3OD): 8.03–7.99 (d, $J = 7.8$ Hz, 2H), 7.61–7.57 (d, $J = 7.8$ Hz, 2H)
2c	3085, 2700, 1600, 1560, 1160, 1070, 744	δ (CD_3OD): 7.83–7.72 (m, 1H), 7.62–7.44 (m, 3H)
2d	3000, 2847, 2615, 1613, 1571, 1161, 1052	δ ($CDCl_3$): 7.73 (d, $J = 7.6$, 2H), 7.01–7.06 (d, $J = 7.6$, 2H), 2.18 (s, 3H)
2e	3090, 2925, 2720, 1613, 1590, 1178, 1055	δ ($CDCl_3$): 7.97 (d, $J = 8.2$ Hz, 2H), 7.14 (d, $J = 8.2$, 2H), 3.83 (s, 3H)
2f	3208, 3100 1610, 1565, 1161, 1549,1109, 1063	δ (CD_3OD): 8.43–8.38 (d, $J = 7.9$ Hz, 2H), 8.31–8.27 (d, $J = 7.9$, 2H)
2g	3092, 2847, 2800, 1660, 1607, 1159, 1092	δ ($CDCl_3$):7.94 (d, $J = 7.9$ Hz, 2H), 7.61–7.46 (m, 5H), 7.30 (d, $J = 7.9$ Hz, 2H)
2h	3050, 2750, 1597, 1570, 1108, 1077	δ (CD_3OD): 7.37–7.26 (m, 2H), 7.03–6.91 (m, 3H), 5.47 (s, 2H)
2i	3120, 1596, 1501, 1090, 1047	δ ($CDCl_3$): 9.0 (s, 1H), 7.75–7.52 (m, 5H)
2j	3123, 3040, 1503, 1091, 1037	δ ($CDCl_3$): 9.01 (s, 1H), 7.72–7.65 (m, 2H) 7.59–7.52 (m, 2H)
2k	3125, 3090, 1592, 1183, 1086, 776	δ ($CDCl_3$): 9.12 (s, 1H), 7.75–7.42 (m, 4H)
2l	3127, 3095, 2930 1607, 1517, 1093, 1046	δ ($CDCl_3$): 8.95 (s, 1H), 7.71 (d, $J = 8$, 2H), 7.5 (d, $J = 8$ Hz, 2H), 3.88 (s, 3H)
2m	3130, 3018, 2971 (CH_3) 1612, 1595, 1090	δ ($CDCl_3$): 8.95 (s, 1H), 7.5–7.44 (m, 2H), 6.98–6.95 (m, 2H), 3.85 (s, 3H)
2n	3131, 3086, 2920 (CH_3), 1594, 1514, 1090, 1043; MS (m/z,%) 160 (M^+, 3.4), 132 ($M+ -N_2$, 60.6), 131 ($M^+ -HN_2$, 100), 91 ($PhCH_2-$, 61.3), 77 (C_6H_5-, 30.9), 65 (C_5H_5-, 33.8)	δ ($CDCl_3$): 8.95 (s, 1H), 7.58–7.54 (m 2H), 7.39–7.7.35 (m, 2H), 2.44 (s, 3H)
2o	3107, 3066, 2970, 2929, 1610, 1588, 1171, 1094	δ ($CDCl_3$): 8.96 (s, 1H), 7.58 (s, 1H), 7.44 (m, 1H), 7.35 (m, 1H), 7.24 (m, 1H), 2.35 (s, 3H)
2p	3123, 3093, 1594, 1522, 1462, 1350, 1110, 1084	δ ($CDCl_3$): 9.13 (s, 1H), 8.53–8.46 (m 2H), 8.02–7.95 (m, 2H)
2q	3088, 1595, 1516, 1172, 1086	δ ($CDCl_3$): 8.94 (s, 1H), 8.1–8.05 (m, 1H), 8.01–7.96 (m, 1H), 7.64–7.40 (m, 5H)
2r	3109 3038, 2963 1478, 1456, 1101, 1075	δ ($CDCl_3$): 8.51 (s, 1H), 7.43–7.37 (m, 3H), 7.36–7.25 (m, 2H), 5.59 (s, 2H)
2s	3061, 2952 1592, 1500, 1113, 1083	δ ($CDCl_3$): 7.62–7.55 (m, 3H), 7.49–7.43 (m, 5H), 2.61 (s, 3H)
2t	3038, 2987, 2954 (CH_3) 1514, 1460, 1109, 1087; MS (m/z,%) 174 (M^+, 5.3), 146 ($M^+ -N_2$, 84.0), 145 ($M^+ -HN_2$, 100), 105 (52.3), 91 ($PhCH_2-$, 73.8), 77(C_6H_5-, 32), 65(43.3)	δ ($CDCl_3$): 7.30 (m, 4H), 2.57 (s, 3H), 2.44 (s, 3H)
2u	3061, 2920 1593, 1520, 1098, 1076	δ ($CDCl_3$): 7.45–7.25 (m, 4H), 2.59 (s, 3H), 2.45 (s, 3H)

(Continued on next page)

Table 2 Spectroscopic data of compounds **2a–z, 4 and 6** *(Continued)*

Compound no.	IR cm^{-1} (KBr, selected peaks)); MS (m/z)	^{1}H-NMR, δ ppm
2v	3069, 2987, 2940 1606, 1513, 1103, 1020	δ ($CDCl_3$): 7.54 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0, 2H), 3.85 (s, 3H), 2.52 (s, 3H)
2w	3071, 2938 (CH_3) 1495, 1463, 1092, 1041, 850	δ ($CDCl_3$): 7.65 (d, J = 8.0 Hz 2H), 7.47 (d, J = 8.0, 2H), 2.59 (s, 3H)
2x	3055, 2945 (CH_3), 1490, 1463, 1111, 1072, 820	δ ($CDCl_3$): 7.72–7.68 (m, 2H), 7.37–7.33 (m, 2H), 2. 59 (s, 3H)
2y	3059, 2982 1595, 1517, 1113, 1083, 820	δ ($CDCl_3$): 8.13–8.09 (d, 1H, J = 8 Hz), 8.02–7.98 (d, 1H, J = 8 Hz), 7.67–7.47 (m, 4H), 7.17 (d, J = 8 Hz, 1H), 2.43 (s, 3H)
2z	3064, 2962 1618, 1555, 1153, 1091, 820	δ($CDCl_3$): 7.3–7.26 (m, 5H),7.04 (m,5H), 5.30 (s, 2H), 4.14 (s, 2H)
4	2955 (CH_2) 1590, 1490, 1117, 1089	δ ($CDCl_3$): 4.46 (t, 2H, J = 7.5 Hz), 3.10–3.04 (t, 2H, J = 7.5), 2.0–1.68 (m, 6H)
6	3079, 2920 1616, 1560, 1148, 1086; MS (m/z,%) 184 (M^+, 18.4), 156 ($M^+ - N_2$, 42.5), 129 (100), 102 (50), 77 (C_6H_5-, 20.5), 51 (38.4)	δ ($CDCl_3$): 8.88 (d, 1H, J = 8.2 Hz), 8.10 (d, 1H, J = 8.2 Hz, 7.9–7.85 (m, 2H), 7.65 (s, 1H), 2.85 (s, 3H)

EXPERIMENTAL

Infrared spectra were recorded on Thermo Nicolet nexus 470 FT-IR and Mattson 5000 FT-IR spectrophotometer with only selected absorptions being recorded. Absorption maxima were recorded in per centimeter. Nuclear magnetic resonance (NMR) spectra were run at ^{1}H-NMR Varian Mercury (200 MHz) FT-NMR spectrometer. Spectra were measured using $CDCl_3$ and CD_3OD as solvents with chemical shifts quoted in parts per million (δ ppm) using TMS as internal standard. The Mass Spectra (MS) were recorded on GC-MS QP-1000 EX Schmiadzu (Japan) mass spectrometer. Elemental analyses were obtained on a Heraeus CHN-OS Rapid analyzer in the elemental-analysis unit at the Faculty of Science, Cairo University, Egypt.

Melting points (uncorrected) were determined in an open capillary with a Griffin melting point apparatus. All thioamides were synthesized using Lawesson's reagent.

Tetrachlorosilane was used as obtained from commercial sources. The solvents were distilled and dried before use. Acetonitrile was dried by refluxing over phosphorus pentaoxide.

Reaction of $SiCl_4/NaN_3$ Reagent System with Primary and Secondary Thioamides (General Procedure)

Tetrachlorosilane (2.4 ml, 20 mmol) was added into a mixture of thioamide (10 mmol) and sodium azide (3.9 g, 60 mmol) in anhydrous acetonitrile (15 ml). The reaction mixture was stirred at room temperature for 10 min, then refluxed at 82°C until thioamide was consumed (TLC analyses). It was then poured into 5% cooled sodium carbonate solution (50 ml) and extracted with chloroform (2 × 50 ml). The organic extracts were dried

over anhydrous magnesium sulfate, filtered, and concentrated to give the corresponding substituted tetrazoles (cf. Tables 1 and 2).

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