Synthesis and Insecticidal Activity of Tetrazole-Linked Triazole Derivatives

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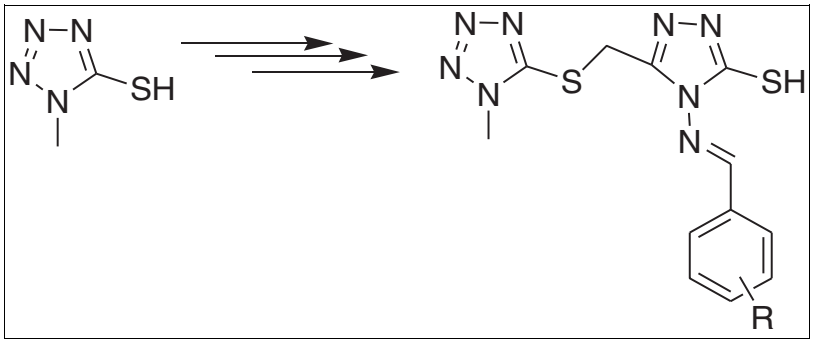

A new series of 4-(4-substitutedbenzylideneamino)-5-((1-methyl-1*H*-tetrazol-5-ylthio)methyl)-4*H*-1,2,4-triazole-3-thiol derivatives (**5a–k**) are prepared using 4-amino-5-((1-methyl-1*H*-tetrazol-5-ylthio)methyl-4*H*-1,2,4-triazole-3-thiol (**4**), as an intermediate compound. The structures of all the newly synthesized products are established supported by their spectral ^{1}H NMR, ^{13}C NMR, FTIR, electrospray ionization mass spectrometry (mass), and analytical data. All the compounds are screened for their insecticidal activity against *Plodia interpunctella*, and six compounds exhibited significant activity.

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INTRODUCTION

Insects often impact the comfort and health of humans and animals by biting and stinging activities and directly cause irritation, hypersensitivity, and loss of blood, toxicities, myiasis, and sometimes even death [1]. Indirect effect of insects is that they reduce several million tons of crop production every year. Unlike other insects, *Plodia interpunctella* is a cosmopolitan pest that infects wide range of stored products including nuts, beans, processed food, and dried foods [2].

To overcome the problems associated with *P. interpunctella*, several insect controls such as fumigants, which contain methyl or phosphine, were developed. Because of their stability in lower troposphere and impact on ozone depletion, those were banned since 2004 [3]. Now, the insecticidal control research is focused on development of new compounds that are highly potent, economical, and safe to use [4,5]. The current scenario highlights the need for the discovery of new lead compounds with simple structure, which exhibit optimal insecticidal activity against *P. interpunctella* and new mode of action. Tetrazole moiety derivatives represent an interesting class of compounds possessing a wide spectrum of biological activities. The antibacterial [6], antifungal [7], anticonvulsant [8,9], analgesic [10], anticancer [11], anti-amoebic [12], antagonist [13], antiviral [14], and antiproliferative [15] activities of various tetrazole derivatives have been reported in literature.

Similarly, several types of triazoles have been proved to possess valuable pharmacological properties, such as antiviral [16,17], antioxidant [18], antimalarial [19], anticonvulsant [20,21], Alzheimer's disease [22], antidepressant [23,24], antimicrobial [25,26], antitubercular [27,28], anti-inflammatory [29,30], antiplatelet [31], antibacterial [32], antifungal [33,34], anticancer [35,36], antiproliferative [37], and anti-HIV [38,39] activities. In the pursuit of design of new drugs, the development of hybrid molecules through the combination of different pharmacophores in one frame could lead to compounds with interesting biological properties. An integration of these two moieties has potential to show synergistic effect and could prove to be better insecticide. Hence, in the present study, an attempt is made to synthesize molecules containing both the tetrazole and triazole systems, and a series of new derivatives (**5a–k**) of hybrid molecules were synthesized, and their insecticidal activity was investigated.

RESULTS AND DISCUSSION

Chemistry. Compound **1** was treated with chloro acetic acid **2** with acetone as solvent and in the presence of K_2CO_3 to give 2-(1-methyl-1*H*-tetrazol-5-ylthio)acetic acid (**3**). The synthesis of cyclic amino-triazole (**4**) was performed by the treatment of compound **3** with thiocarbohydrazide in solvent-free condition. Finally, compound **4** was reacted with different substituted aldehydes in the presence of few

drops of concentrated sulfuric acid as a catalyst which upon condensation gave a Schiff base in good yields (**5a–k**) (Scheme 1). The structures of the newly synthesized compounds were established and confirmed from their spectral ^{1}H NMR, ^{13}C NMR, FTIR, electrospray ionization mass spectrometry (ESIMS), and analytical data. The physical data, ^{1}H NMR, ^{13}C NMR, ESIMS and analytical data for all the synthesized compounds are reported in experimental protocols.

The ^{1}H NMR spectra of compound (**3**) showed peak at δ 11.94 ppm as a singlet for –COOH proton and a singlet at δ 3.90 ppm for –NCH_3 group protons. Similarly, compound **4** showed four singlets at δ 3.60, δ 3.96, δ 5.15 and δ 13.57 ppm because of –SCH_2, –NCH_3, –NH_2, and SH group protons, respectively.

Biological assay results. The insecticidal activities against *P. interpunctella* of the library were investigated using toosendanin, a commercial product as a standard (100% activity). Table 1 summarizes the insecticidal activity (%) of each compound as function of the exposure duration. An examination of the results (Table 1) reveals that compounds **5e**, **5j**, **5g**, **5h**, **5d**, and **5f** exhibited significant activity of 94 ± 1.5, 92 ± 1.2, 91 ± 1.9, 91 ± 1.5, 90 ± 2.2, and 90 ± 1.8, respectively, at 15 μL/L comparable with the standard. Furthermore, **5k**, **5i**, and **5c** showed good insecticidal activity of 84 ± 1.7, 83 ± 1.5, and 76 ± 1.5, respectively, under similar conditions. The least insecticidal activity was associated with compounds **5a** and **5b** with moderate values of 73 ± 1.6 and 76 ± 1.2, respectively. The demonstration of synergic insecticidal activity by the new compounds validates the proposed hypothesis.

CONCLUSION

In conclusion, we have described an efficient and benign procedure for the synthesis of tetrazole-linked with triazole systems containing substituted phenyl rings, which gave excellent yields. The compounds, **5e**, **5j**, **5g**, **5h**, **5d**, and **5f**, showed significant insecticidal activity, whereas compounds **5k**, **5i**, and **5c** showed good activity. Thus, this novel class of new tetrazole-linked triazole-containing substituted phenyl derivatives emerges as a valuable lead series with great potential as insecticidal agents. A systematic study on the structure–activity relationships and the efficacy of evaluation might further improve the insecticidal activity of these title compounds.

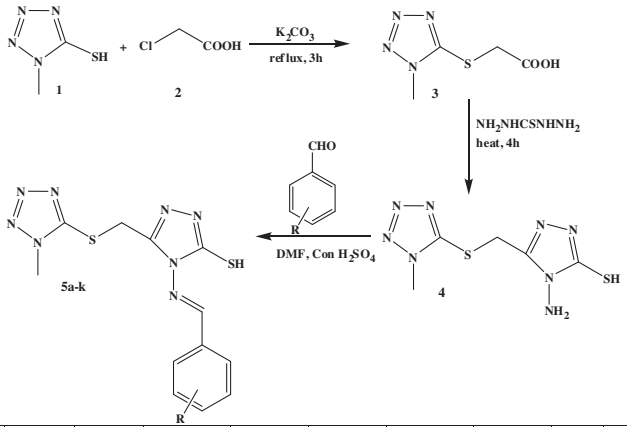
EXPERIMENTAL

Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected. All the reactions were monitored by TLC. The silica gel F_{254} plates were used for TLC in which the spots were examined under UV light and then developed by an iodine vapor. Column chromatography was performed with silica gel (BDH 100–200 mesh). Solvents were purified according to standard procedures. The spectra were recorded with the following instruments: NMR, Varian Gemini 400 MHz (^{1}H), 75 MHz (^{13}C) spectrometer (Thermo Fisher, San Jose, CA); ESIMS, VG-Autospec micromass, analyses of all the compounds were recorded in LCQ Fleet, Thermo Fisher Instruments Limited. Organic extracts were dried over anhydrous Na_2SO_4.

Biological assay

Insecticidal assay. A total of 30 insects of *P. interpunctella* (24 h age) were taken and placed into a 1000-mL glass jar. The dose for different compounds was calculated on the basis of nominal concentration and assumed 100% in the exposure glass jar [40]. Filter paper was placed inside the jar, and the compounds were transferred onto it. Then, varied concentrations ranging from 3, 6, 9, 12, to 15 μL/L were prepared from the stock. For the control, 15 μL/L toosendanin was prepared, and it was considered as standard. All experiments performed were executed in triplicate runs at constant temperature (27 ± 1°C), photo period (14L:10D) and relative humidity (65% ± 5). The values were measured averages ± SE. All chemicals and reagents used were of analytical grade and obtained from Sigma.

Scheme 1. Synthesis pathway of tetrazole-linked triazole derivatives.



Compd	5a	5b	5c	5d	5e	5f	5g	5h	5i	5j	5k
R	H	4-Me	4-OH	3,4-OH	3,4,5-F	2,4-Cl	2-NO_2, 4-CF_3	3-NO_2, 4-Cl	4-F	3-F, 4-Cl	4-NO_2

Table 1

Insecticidal activity of compounds (**5a–k**).

Compounds	Insecticidal assay ±SE				
	Concentration in μL/L				
	3 h	6 h	9 h	12 h	15 h
5a	55.0 ± 1.2	67.0 ± 1.7	69.0 ± 1.3	70.0 ± 1.0	73.0 ± 1.6
5b	60.0 ± 1.7	70.0 ± 1.3	70.0 ± 1.9	75.0 ± 1.4	76.0 ± 1.2
5c	69.0 ± 1.3	72.0 ± 1.2	75.0 ± 1.1	77.0 ± 1.6	76.0 ± 1.5
5d	81.0 ± 2.7	83.0 ± 2.2	84.0 ± 2.2	86.0 ± 2.2	90.0 ± 2.2
5e	86.0 ± 1.7	88.0 ± 1.4	89.0 ± 1.8	92.0 ± 1.9	94.0 ± 1.5
5f	80.0 ± 1.2	82.0 ± 1.5	83.0 ± 1.1	85.0 ± 1.4	90.0 ± 1.8
5g	83.0 ± 1.2	85.0 ± 1.5	87.0 ± 2.0	88.0 ± 1.3	91.0 ± 1.9
5h	82.0 ± 1.0	84.0 ± 1.6	85.0 ± 1.6	87.0 ± 1.1	91.0 ± 1.9
5i	72.0 ± 1.5	75.0 ± 1.4	78.0 ± 1.6	79.0 ± 1.4	83.0 ± 1.5
5j	85.0 ± 1.1	86.0 ± 1.8	88.0 ± 1.1	90.0 ± 1.0	92.0 ± 1.2
5k	72.0 ± 1.2	77.0 ± 1.1	79.0 ± 1.0	80.0 ± 1.6	84.0 ± 1.7
Toosendanin	100.0 ± 00	100.0 ± 00	100.0 ± 00	100.0 ± 00	100.0 ± 00

$n = 3$; SE, standard error.

Statistical analysis. The data obtained from the test was applied to Abbot's formula for mortality determination [41]. Mortality values in average for 24 h exposure were submitted to analysis for variance (one-way ANOVA) using the statistical program (SPSS ver. 2012) for probit assay [42]. The outcomes with $p < 0.05$ were considered as statistically significant.

2-(1-Methyl-1H-tetrazol-5-ylthio)acetic acid (3). To the mixture of 5-mercapto-1-methyl-1*H*-tetrazole, **1** (10 mmol) in acetone (20 mL), K_2CO_3 (25 mmol) was added at room temperature. This was followed by the addition of chloroacetic acid, **2** (12 mmol). The reaction mixture was heated under reflux for 3 h, and the completion of reaction was regularly monitored by TLC. The reaction mixture was cooled to room temperature and poured into ice water followed by extraction with ethyl acetate. The combined organic layer was evaporated, recrystallized to obtain 2-(1-methyl-1*H*-tetrazol-5-ylthio) acetic acid as solid.

Yield 86%; mp 167–169°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.94 (brs, 1H, COOH), 3.90 (s, 3H, NCH_3), 3.58 (s, 2H, SCH_2); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.5, 120.5, 38.9, 30.2; ESIMS: *m/z* 197 $(M + Na)^+$. *Anal*. Calcd for $C_4H_6N_4O_2S$: C, 27.58; H, 3.47; N, 32.17%; Found: C, 27.61; H, 3.44; N, 32.19%.

4-Amino-5-((1-methyl-1H-tetrazol-5-ylthio)methyl-4H-1,2,4-triazole-3-thiol (4). To a stirred solution of compound **3** (10 mmol), the thiocarbohydrazide (10 mmol) liquid was added and heated in solvent-free condition for 4 h. The completion of reaction was monitored by TLC. The reaction mixture was cooled to room temperature, and the excess of acid compound was removed with sodium bicarbonate solution. The solid was filtered, dried, and recrystallized with DMF to give 4-amino-5-((1-methyl-1*H*-tetrazol-5-ylthio)methyl-4*H*-1,2,4-triazole-3-thiol (**4**).

Yield 82%; mp 189–191°C; IR (cm^{-1}): 3458 (COOH), 1489 (N=N), 1258 (–N–N=N–), 1168 (tetrazole); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.57 (s, 1H, SH), 5.15 (s, 2H, NH_2), 3.96 (s, 3H, NCH_3), 3.60 (s, 2H, SCH_2); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 172.1, 168.2, 160.5, 34.7, 30.4; ESIMS: *m/z* 245 $(M + H)^+$. *Anal*. Calcd for $C_5H_8N_8S_2$: C, 24.58; H, 3.30; N, 45.87%: Found: C, 24.54; H, 3.27; N, 45.91%.

4-(4-Substitutedbenzylideneamino)-5-((1-methyl-1H-tetrazol-5-ylthio)methyl)-4H-1,2,4-triazole-3-thiol derivatives (5a–k). An equimolar mixture of compound **5** (10 mmol) and substituted aldehydes (10 mmol), plus 3–4 drops of concentrated sulfuric acid in *N*,*N*-dimethyl formamide (10 mL) medium were stirred at room temperature for 5–8 h. The reaction mixture was then poured into ice-cold water to give a solid product, which was collected by suction filtration and dried. The crude product was then recrystallized from ethyl acetate to obtain pure compounds (**5a–k**).

4-(Benzylideneamino)-5-((1-methyl-1H-tetrazol-5-ylthio)methyl)-4H-1,2,4-triazole-3-thiol (5a). Yield 92%; mp 236–238°C; IR (cm^{-1}): 1583 (C=C), 1496 (N=N), 1275 (–N–N=N–), 1189 (tetrazole); ^{1}H NMR (DMSO-d_6, 400 MHz): δ 13.60 (s, 1H, SH), 10.02 (s, 1H, CH), 7.70–7.45 (m, 5H, Ar-H), 3.85 (s, 3H, NCH_3), 3.58 (s, 2H, SCH_2); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 168.4, 160.2, 156.8, 148.4, 134.6, 131.2, 129.4, 128.9, 34.2, 30.1; ESIMS: *m/z* 355 $(M + Na)^+$. *Anal*. Calcd for $C_{12}H_{12}N_8S_2$: C, 43.36; H, 3.63; N, 33.71%; Found: C, 43.39; H, 3.61; N, 33.73%.

4-(4-Methylbenzylideneamino)-5-((1-methyl-1H-tetrazol-5-ylthio)methyl)-4H-1,2,4-triazole-3-thiol (5b). Yield 77%; mp 253–255°C; IR (cm^{-1}): 1578 (C=C), 1504 (N=N), 1282 (–N–N=N–), 1197 (tetrazole); ^{1}H NMR (DMSO-d_6, 400 MHz): δ 13.56 (s, 1H, SH), 9.86 (s, 1H, CH), 7.59 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.27 (d, $J = 8.0$ Hz, 2H, Ar-H), 3.86 (s, 3H, NCH_3), 3.55 (s, 2H, SCH_2), 2.38 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 168.2, 159.28, 156.6, 148.2, 140.8, 130.9, 129.2, 33.4, 30.1, 24.3; ESIMS: *m/z* 369 $(M + Na)^+$. *Anal*. Calcd for $C_{13}H_{14}N_8S_2$: C, 45.07; H, 4.07; N, 32.34%; Found: C, 45.05; H, 4.09; N, 32.36%.

4-(4-Hydroxybenzylideneamino)-5-((1-methyl-1H-tetrazol-5-ylthio)methyl)-4H-1,2,4-triazole-3-thiol (5c). Yield 83%; mp 221–223°C; IR (cm^{-1}): 3293 (OH), 1575 (C=C), 1498 (N=N), 1265 (–N–N=N–), 1178 (tetrazole); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.68 (s, 1H, SH), 10.86 (s, 1H, CH), 7.52 (s, 2H, Ar-H), 6.96 (s, 2H, Ar-H), 3.98 (s, 3H, NCH_3), 3.90 (brs, 1H, OH), 3.59 (s, 2H, SCH_2); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.4,

160.8, 160.2, 156.9, 148.3, 130.8, 126.4, 116.2, 33.8, 30.2; ESIMS: *m/z* 349 $(M+H)^+$. *Anal*. Calcd for $C_{12}H_{12}N_8OS_2$: C, 41.37; H, 3.47; N, 32.16%; Found: C, 41.39; H, 3.49; N, 32.13%.

4-(3,4-Difluorobenzylideneamino)-5-((1-methyl-1H-tetrazol-5-ylthio)methyl)-4H-1,2,4-triazole-3-thiol (5d). Yield 86%; mp 261–263°C; IR (cm^{-1}): 1585 (C=C), 1503 (N=N), 1276 (–N–N=N–), 1189 (tetrazole); ^1H NMR ($CDCl_3$, 400 MHz): δ 13.72 (s, 1H, SH), 10.89 (s, 1H, CH), 7.60 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.34 (s, 1H, Ar-H), 3.98 (s, 3H, NCH_3), 3.62 (s, 2H, SCH_2); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.4, 160.3, 156.9, 151.8, 149.7, 148.2, 131.0, 126.5, 117.4, 115.6, 34.0, 30.1; ESIMS: *m/z* 391 $(M+Na)^+$. *Anal*. Calcd for $C_{12}H_{10}F_2N_8S_2$: C, 39.12; H, 2.74; N, 30.42%; Found: C, 39.09; H, 2.75; N, 30.44%.

4-(3,4,5-Trifluorobenzylideneamino)-5-((1-methyl-1H-tetrazol-5-ylthio)methyl)-4H-1,2,4-triazole-3-thiol (5e). Yield 93%; mp 243–245°C; IR (cm^{-1}): 1566 (C=C), 1503 (N=N), 1287 (–N–N=N–), 1195 (tetrazole); ^1H NMR (DMSO-d_6, 400 MHz): δ 13.75 (s, 1H, SH), 10.92 (s, 1H, CH), 7.64 (s, 1H, Ar-H), 7.52 (s, 1H, Ar-H), 3.99 (s, 3H, NCH_3), 3.64 (s, 2H, SCH_2); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 168.3, 160.5, 157.1 151.3, 148.2, 142.5, 132.6, 111.4, 34.1, 30.0; ESIMS: *m/z* 409 $(M+Na)^+$. *Anal*. Calcd for $C_{12}H_9F_3N_8S_2$: C, 37.30; H, 2.35; N, 29.0%; Found: C, 37.28; H, 2.37; N, 29.03%.

4-(2,4-Dichlorobenzylideneamino)-5-((1-methyl-1H-tetrazol-5-ylthio)methyl)-4H-1,2,4-triazole-3-thiol (5f). Yield 89%; mp 229–231°C; IR (cm^{-1}): 1573 (C=C), 1508 (N=N), 1280 (–N–N=N–), 1176 (tetrazole); ^1H NMR ($CDCl_3$, 400 MHz): δ 13.74 (s, 1H, SH), 10.86 (s, 1H, CH), 7.74–7.51 (m, 3H, Ar-H), 3.97 (s, 3H, NCH_3), 3.62 (s, 2H, SCH_2); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.2, 160.1, 156.9, 148.0, 138.1, 135.4, 131.6, 130.5, 127.0, 34.2, 30.0; ESIMS: *m/z* 402 $(M+H)^+$. *Anal*. Calcd for $C_{12}H_{10}Cl_2N_8S_2$: C, 35.92; H, 2.51; N, 27.92%; Found: C, 35.95; H, 2.53; N, 27.90%.

4-(2-Nitro-4-(trifluoromethyl)benzylideneamino)-5-((1-methyl-1H-tetrazol-5-ylthio)methyl)-4H-1,2,4-triazole-3-thiol (5g). Yield 90%; mp 216–218°C; IR (cm^{-1}): 1592 (C=C), 1502 (N=N), 1287 (–N–N=N–), 1198 (tetrazole); ^1H NMR ($CDCl_3$, 400 MHz): δ 13.75 (s, 1H, SH), 10.88 (s, 1H, CH), 7.93–7.80 (m, 2H, Ar-H), 7.56 (s, 1H, Ar-H), 3.99 (s, 1H, NCH_3), 3.64 (s, 2H, SCH_2); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.3, 160.1, 156.9, 148.0, 134.3, 131.6, 131.3, 130.5, 123.2, 121.8, 34.2, 30.1; ESIMS: *m/z* 446 $(M+H)^+$. *Anal*. Calcd for $C_{13}H_{10}F_3N_9O_2S_2$: C, 35.06; H, 2.26; N, 28.30%; Found: C, 35.04; H, 2.28; N, 28.32%.

4-(4-Chloro-3-nitrobenzylideneamino)-5-((1-methyl-1H-tetrazol-5-ylthio)methyl)-4H-1,2,4-triazole-3-thiol (5h). Yield 82%; mp 277–279°C; IR (cm^{-1}): 1566 (C=C), 1510 (N=N), 1283 (–N–N=N–), 1180 (tetrazole); ^1H NMR ($CDCl_3$, 400 MHz): δ 13.72 (s, 1H, SH), 10.84 (s, 1H, CH), 7.78–7.56 (m, 3H, Ar-H), 3.97 (s, 3H, NCH_3), 3.62 (s, 2H, SCH_2); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.2, 160.0, 156.9, 148.2, 136.8, 132.7, 131.8, 130.0, 124.3, 34.1, 30.0; ESIMS: *m/z* 412 $(M+H)^+$. *Anal*. Calcd for $C_{12}H_{10}ClN_9O_2S_2$: C, 35.01; H, 2.46; N, 30.62%; Found: C, 35.03; H, 2.44; N, 30.65%.

4-(4-Fluorobenzylideneamino)-5-((1-methyl-1H-tetrazol-5-ylthio)methyl)-4H-1,2,4-triazole-3-thiol (5i). Yield 81%; mp 209–211°C; IR (cm^{-1}): 1578 (C=C), 1499 (N=N), 1280 (–N–N=N–), 1192 (tetrazole); ^1H NMR ($CDCl_3$, 400 MHz): δ 13.74 (s, 1H, SH), 10.85 (s, 1H, CH), 7.74 (d, $J = 8.3$ Hz, 2H, Ar-H), 7.56 (d, $J = 8.3$ Hz, 2H, Ar-H), 3.99 (s, 3H, NCH_3), 3.63 (s, 2H, SCH_2); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.4, 165.2, 160.1, 156.8, 148.0, 130.8, 129.5, 115.6, 34.2, 33.0; ESIMS: *m/z* 373 $(M+Na)^+$. *Anal*. Calcd for $C_{12}H_{11}FN_8S_2$: C, 41.13; H, 3.17; N, 32.02%; Found: C, 41.16; H, 3.15; N, 32.05%.

4-(4-Chloro-3-fluorobenzylideneamino)-5-((1-methyl-1H-tetrazol-5-ylthio)methyl)-4H-1,2,4-triazole-3-thiol (5j). Yield 80%; mp 218–220°C; IR (cm^{-1}): 1592 (C=C), 1508 (N=N), 1280 (–N–N=N–), 1173 (tetrazole); ^1H NMR ($CDCl_3$, 400 MHz): δ 13.72 (s, 1H, SH), 10.83 (s, 1H, CH), 7.58–7.27 (m, 3H, Ar-H), 3.97 (s, 3H, NCH_3), 3.64 (s, 2H, SCH_2); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.3, 162.9, 160.0, 156.9, 148.1, 133.5, 130.8, 126.2, 123.0, 115.5, 34.2, 33.0; ESIMS: *m/z* 385 $(M+H)^+$. *Anal*. Calcd for $C_{12}H_{10}ClFN_8S_2$: C, 37.46; H, 2.64; N, 29.20%; Found: C, 37.48; H, 2.61; N, 29.22%.

4-(4-Nitrobenzylideneamino)-5-((1-methyl-1H-tetrazol-5-ylthio)methyl)-4H-1,2,4-triazole-3-thiol (5k). Yield 90%; mp 198–200° C; IR (cm^{-1}): 1583 (C=C), 1514 (N=N), 1291 (–N–N=N–), 1179 (tetrazole); ^1H NMR ($CDCl_3$, 400 MHz): δ 13.74 (s, 1H, SH), 10.82 (s, 1H, CH), 8.31 (d, $J = 8.5$ Hz, 2H, Ar-H), 7.96 (d, $J = 9.0$ Hz, 2H, Ar-H), 4.0 (s, 3H, NCH_3), 3.63 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.2, 160.1, 156.8, 150.2, 148.1, 140.0, 130.2, 124.0, 34.0, 30.1; ESIMS: *m/z* 400 $(M+Na)^+$. *Anal*. Calcd for $C_{12}H_{11}N_9O_2S_2$: C, 38.20; H, 2.95; N, 33.42%; Found: C, 38.23; H, 2.93; N, 33.44%.

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