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Simple and efficient approach to synthesis of [1,2,4]triazolo[4,3-*b*][1,2,4,6]thiatriazine-1-oxides from *N*-triazol-3-ylamidines

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Abstract: A facile method for the synthesis of [1,2,4]triazolo[4,3-*b*][1,2,4,6]thiatriazine 1-oxides **3a–h** is presented. The approach involves a reaction between *N*-triazol-3-ylamidines **2a–h** and thionyl chloride in the presence of pyridine. The structures of the synthesized compounds were confirmed by spectral studies including IR, ^{1}H NMR, ^{13}C NMR, MS and elemental analysis.

Keywords: amidines; iminoester; oxides; synthesis; thiatriazine; thionyl chloride; [1,2,4]triazole.

Introduction

1,2,4-Triazoles possess antimicrobial [1], antifungal [2], anti-inflammatory [3], antioxidant [4, 5], antiviral [6], anticancer [7] and anticonvulsant activity [8] depending on the substituents in the ring system. Interestingly, the 1,2,4,6-thiatriazine 1-oxides containing sulfur and nitrogen atoms, demonstrate excellent fungicidal [9] and anti-HIV activities [10]. The aim of the present work is to develop a synthesis of some new heterocyclic compounds [1,2,4]triazolo[4,3-*b*][1,2,4,6]thiatriazine 1-oxides **3** (Scheme 1).

Results and discussion

The synthesis of triazolothiatriazine 1-oxide derivatives **3a–h** was carried out according to the two steps outlined in Scheme 1. These products were obtained by treatment of *N*-triazol-3-ylamidines **2a–h** with thionyl chloride in the presence of two equivalents of pyridine in dioxane under reflux. The substrates **2a–h** were prepared by reaction of *N*-triazol-3-yl imidates **1** with a primary amine at room temperature. In turn, the imidates **1** were obtained by condensation of 3-amino[1,2,4]triazole with orthoesters according to a previously reported method [11]. The structures of all synthesized compounds **2a–h** and **3a–h** are fully consistent with infra-red (IR), ^{1}H NMR, ^{13}C NMR, MS and elemental analysis data. From a mechanistic viewpoint, it can be suggested that intermediate products **A** are final precursors to the observed products **3a–h**. Compounds **A** could not be isolated because their intramolecular cyclization appears to be fast.

Conclusion

A facile and efficient procedure for the synthesis of novel [1,2,4]triazolo[4,3-*b*][1,2,4,6]thiatriazine 1-oxides from *N*-triazol-3-ylamidines and thionyl chloride in the presence of pyridine as a catalyst was developed. The yields ranged from good to excellent.

Experimental

All chemicals, reagents and solvents were obtained from Sigma-Aldrich Company and were used without any purification. The imidate **1** was prepared as previously reported [11].

IR spectra were recorded in KBr pellets with a Nicolet IR200 instrument. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in DMSO-d_6 on a Brüker 300 spectrometer. Melting points were determined on an Electrothermal 9100 melting point apparatus. Elemental microanalysis was performed on a model 2400 series II Perkin-Elmer analyzer. The electron-spray ionization (ESI) positive MS spectra were recorded on a Brüker Daltonics LC–MS spectrometer.

General procedure for the synthesis of *N*-triazol-3-ylamidines 2a–h

A solution of *N*-triazol-3-ylimidate (**1**, 0.2 mol) and primary amine (0.21 mol) in absolute ethanol (20 ml) was stirred at room temperature for 3 days. The resultant precipitate of **2** was collected by filtration and crystallized from methanol.

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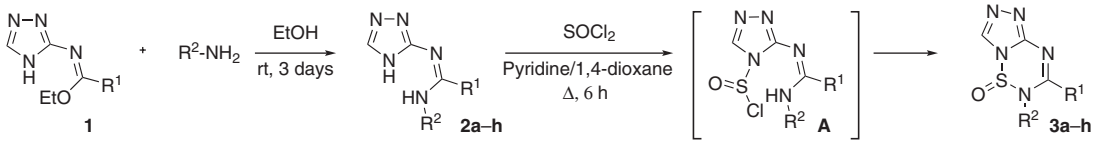

1 2a–h A 3a–h

3a: R^1 = Me; R^2 = Et
3b: R^1 = Et; R^2 = Et
3c: R^1 = Me; R^2 = *n*-Pr
3d: R^1 = Et; R^2 = *n*-Pr
3e: R^1 = Me; R^2 = cyclopentyl
3f: R^1 = Et; R^2 = cyclopentyl
3g: R^1 = Me; R^2 = Bn
3h: R^1 = Et; R^2 = Bn

Scheme 1

***N*-Ethyl-*N′*-(4*H*-1,2,4-triazol-3-yl)ethanamidine (2a)** Yield 70%; a white solid; mp 165–167°C; IR: ν 3420 ($NH_{triazolic}$), 3130 ($NH_{amidinic}$), 1645 cm^{-1} (C=N); ^{1}H NMR: δ 1.56 (t, 3H, *J*=6.2 Hz, C<u>H</u>$_3$-CH$_2$-NH), 2.14 (s, 3H, CH$_3$-C(N)=N), 3.07 (m, 2H, CH$_3$-C<u>H</u>$_2$-NH-), 7.86 (s, 1H, N=C<u>H</u>-NH), 9.10 (s 1H, CH$_3$-CH$_2$-N<u>H</u>), 10.88 (s, 1H, N=CH-N<u>H</u>); ^{13}C NMR: δ 15.2 (<u>C</u>H$_3$-CH$_2$-NH-), 18.6 (<u>C</u>H$_3$-C(N)=N), 38.7 (CH$_3$-<u>C</u>H$_2$-NH-), 153.8 (N=<u>C</u>H-NH-), 154.3 (N=<u>C</u>(N)-N), 161.5 (N=<u>C</u>(CH$_3$)-N). Anal. Calcd for $C_6H_{11}N_5$: C, 47.04; H, 7.24; N, 45.72. Found: C, 47.49; H, 7.25; N, 45.72.

***N*-Ethyl-*N′*-(4*H*-1,2,4-triazol-3-yl)propanamidine (2b)** Yield 80%; a white solid; mp 144–146°C; IR: ν 3445 ($NH_{triazolic}$), 3162 ($NH_{amidinic}$), 1648 cm^{-1} (C=N); ^{1}H NMR: δ 1.13 (t, 3H, *J*=6.2 Hz, C<u>H</u>$_3$-CH$_2$-C(NH)=N), 1.44 (t, 3H, *J*=9.0 Hz, C<u>H</u>$_3$-CH$_2$-NH), 2.62 (q, 2H, *J*=6.2 Hz, CH$_3$-C<u>H</u>$_2$-C(N)=N), 3.52 (m, 2H, CH$_3$-C<u>H</u>$_2$-NH), 7.66 (s, 1H, N=C<u>H</u>-NH-), 9.60 (s, 1H, CH$_3$-CH$_2$-N<u>H</u>-), 11.08 (s, 1H, N=CH-N<u>H</u>); ^{13}C NMR: δ 9.9 (<u>C</u>H$_3$-CH$_2$-C(N)=N), 14.2 (<u>C</u>H$_3$-CH$_2$-NH), 20.0 (CH$_3$-CH$_2$-<u>C</u>(N)=N), 42.8 (CH$_3$-<u>C</u>H$_2$-NH), 154.6 (N=<u>C</u>H-NH-), 157.0 (N=<u>C</u>(N)N), 167.0 (N=<u>C</u>(CH$_2$CH$_3$)-N). Anal. Calcd for $C_7H_{13}N_5$: C, 50.28; H, 7.84; N, 41.88. Found: C, 50.27; H, 7.26; N, 41.89.

***N*-Propyl-*N′*-(4*H*-1,2,4-triazol-3-yl)ethanamidine (2c)** Yield 65%; a white solid; mp 130–132°C ; IR: ν 3440 ($NH_{triazolic}$), 3200 ($NH_{amidinic}$), 1640 cm^{-1} (C=N); ^{1}H NMR: δ 1.15 (t, 3H, *J*=8.0 Hz, C<u>H</u>$_3$-CH$_2$-CH$_2$-NH), 2.01 (m, 2H, CH$_3$-C<u>H</u>$_2$-CH$_2$-NH), 2.44 (s, 3H, C<u>H</u>$_3$-C(N)=N), 3.49 (m, 2H, CH$_3$-CH$_2$-C<u>H</u>$_2$-NH), 7.26 (s, 1H, N=C<u>H</u>-NH), 9.72 (s, 1H, CH$_3$-CH$_2$-CH$_2$-N<u>H</u>), 11.80 (s, 1H, N=CH-N<u>H</u>); ^{13}C NMR: δ 12.8 (<u>C</u>H$_3$-CH$_2$-CH$_2$-NH), 22.0 (CH$_3$-<u>C</u>H$_2$-CH$_2$-NH), 23.0 (<u>C</u>H$_3$-C(N)=N), 44.7 (CH$_3$-CH$_2$-<u>C</u>H$_2$-NH), 152.9 (N=<u>C</u>H-NH), 158.6 (N=<u>C</u>(N)-N), 166.6 (N=<u>C</u>(CH$_3$)-N). Anal. Calcd for $C_7H_{13}N_5$: C, 50.28; H, 7.84; N, 41.88. Found: C, 50.30 H, 7.85; N, 41.90.

***N*-Propyl-*N′*-(4*H*-1,2,4-triazol-3-yl)propanamidine (2d)** Yield 71%; a white solid; mp 170–172°C; IR: ν 3410 (NH_{cyclic}), 3180 ($NH_{amidinic}$), 1640 cm^{-1} (C=N); ^{1}H NMR: δ 1.14 (t, 3H, *J*=8.2 Hz, C<u>H</u>$_3$-CH$_2$-CH$_2$-NH), 1.31 (t, 3H, *J*=7.6 Hz, C<u>H</u>$_3$-CH$_2$-C(N)=N), 1.98 (m, 2H, CH$_3$-C<u>H</u>$_2$-CH$_2$-NH), 2.80 (q, 2H, *J*=7.6 Hz, CH$_3$-C<u>H</u>$_2$-C(N)=N), 3.50 (m, 2H, CH$_3$-CH$_2$-C<u>H</u>$_2$-NH), 7.29 (s, 1H, N=C<u>H</u>-NH), 9.54 (s, 1H, CH$_3$-CH$_2$-CH$_2$-N<u>H</u>), 11.04 (s, 1H, N=CH-N<u>H</u>); ^{13}C NMR: δ 11.6 (<u>C</u>H$_3$-CH$_2$-CH$_2$-NH), 12.9 (<u>C</u>H$_3$-<u>C</u>H$_2$-C(N)=N), 23.0 (CH$_3$-<u>C</u>H$_2$-CH$_2$-NH), 24.0 (CH$_3$-<u>C</u>H$_2$-C(N)=N), 45.9 (CH$_3$-CH$_2$-<u>C</u>H$_2$-NH), 152.8 (N=<u>C</u>H-NH), 156.9 (N=<u>C</u>(N)-N), 165.7 (N=<u>C</u>(CH$_2$CH$_3$)-N). Anal. Calcd for $C_8H_{15}N_5$: C, 53.02; H, 8.34; N, 38.64. Found: C, 53.02; H, 8.35; N, 38.63.

***N*-Cyclopentyl-*N′*-(4*H*-1,2,4-triazol-3-yl)ethanamidine (2e)** Yield 63%; mp 185–186°C; IR: ν 3430 ($NH_{triazolic}$), 3170 ($NH_{amidinic}$), 1642 cm^{-1} (C=N); ^{1}H NMR: δ 1.26 (m, 4H, CH$_2$-C<u>H</u>$_2$-C<u>H</u>$_2$-CH$_2$-CH-NH), 2.40 (s, 3H, C<u>H</u>$_3$-C(N)=N), 2.87 (m, 4H, C<u>H</u>$_2$-CH$_2$-CH$_2$-C<u>H</u>$_2$-CH-NH), 4.49 (m, 1H, CH$_2$-CH$_2$-CH$_2$-CH$_2$-C<u>H</u>-NH), 6.98 (s, 1H, N=C<u>H</u>-NH), 9.41 (s, 1H, CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH-N<u>H</u>), 12.08 (s, 1H, N=CH-N<u>H</u>); ^{13}C NMR: δ 22.9 (<u>C</u>H$_3$-C(N)=N), 23.8 (CH$_2$-<u>C</u>H$_2$-<u>C</u>H$_2$-CH$_2$-CH-N), 33.1 (<u>C</u>H$_2$-CH$_2$-CH$_2$-<u>C</u>H$_2$-CH-NH), 62.6 (CH$_2$-CH$_2$-CH$_2$-CH$_2$-<u>C</u>H-N), 152.8 (N=<u>C</u>H-NH), 155.3 (N=<u>C</u>(N)-N), 165.75 (N=<u>C</u>(CH$_3$)-N). Anal. Calcd for $C_9H_{15}N_5$: C, 55.94; H, 7.82; N, 36.24. Found: C, 55.92; H, 7.84; N, 36.25.

***N*-Cyclopentyl-*N′*-(4*H*-1,2,4-triazol-3-yl)propanamidine (2f)** Yield 65%; mp 158–159°C; IR: ν 3438 ($NH_{triazolic}$), 3190 ($NH_{amidinic}$), 1641 cm^{-1} (C=N); ^{1}H NMR: δ 1.18 (t, *J*=6.8 Hz, 3H, C<u>H</u>$_3$-CH$_2$-C(N)=N), 1.68 (m, 4H, CH$_2$-C<u>H</u>$_2$-C<u>H</u>$_2$-CH$_2$-CH-NH), 2.80 (m, 4H, C<u>H</u>$_2$-CH$_2$-CH$_2$-C<u>H</u>$_2$-CH-NH), 3.18 (q, 2H, *J*=6.8 Hz, CH$_3$-C<u>H</u>$_2$-C(N)=N), 4.43 (m, 1H, CH$_2$-CH$_2$-CH$_2$-CH$_2$-C<u>H</u>-NH), 6.98 (s, 1H, N=C<u>H</u>-NH), 9.22 (s, 1H, CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH-N<u>H</u>), 12.20 (s, 1H, N=C<u>H</u>-NH); ^{13}C NMR: δ 18.0 (<u>C</u>H$_3$-CH$_2$-C(N)=N), 23.6 (CH$_2$-<u>C</u>H$_2$-<u>C</u>H$_2$-CH$_2$-CH-NH), 26.8 (CH$_3$-<u>C</u>H$_2$-C(N)=N), 32.8 (<u>C</u>H$_2$-CH$_2$-CH$_2$-<u>C</u>H$_2$-CH-NH), 63.0 (CH$_2$-CH$_2$-CH$_2$-CH$_2$-<u>C</u>H-NH),152.7 (N=<u>C</u>H-NH), 155.0 (N=<u>C</u>(N)-N), 166.9 (N=<u>C</u>(CH$_2$CH$_3$)-N). Anal. Calcd for $C_{10}H_{17}N_5$: C, 57.95; H, 8.27; N, 33.79. Found: C, 57.96; H, 8.27; N, 33.80.

***N*-Benzyl-*N′*-(4*H*-1,2,4-triazol-3-yl)ethanamidine (2g)** Yield 78%; a white solid, mp 172–174°C, IR: ν 3452 ($NH_{triazolic}$), 3185 ($NH_{amidinic}$), 1643 cm^{-1} (C=N); ^{1}H NMR: δ 2.33 (s, 3H, C<u>H</u>$_3$-C(N)=N), 4.81 (s, 2H, Ph-C<u>H</u>$_2$-NH), 6.79 (s, 1H, N=C<u>H</u>-NH), 7.40–7.80 (m, 5H, C<u>H</u>$_{aromatic}$), 9.77 (s, 2H, Ph-CH$_2$-N<u>H</u>), 11.67 (s, 1H, N=CH-N<u>H</u>); ^{13}C NMR: δ 22.0 (<u>C</u>H$_3$-C(N)=N), 49.0 (Ph-<u>C</u>H$_2$-NH), 126.6, 127.8, 132.4, 134.5(C$_{arom,}$ <u>C</u>$_6$H$_5$), 154.0 (N=<u>C</u>H-NH), 157.9 (N=<u>C</u>(N)-N), 166.8 (N=<u>C</u>(CH$_3$)-N). Anal. Calcd for $C_{11}H_{13}N_5$: C, 61.38; H, 6.09; N, 32.45. Found: C, 61.40; H, 6.11; N, 32.45.

***N*-Benzyl-*N′*-(4*H*-1,2,4-triazol-3-yl)propanamidine (2h)** Yield 74%; a white solid; mp 180–182°C, IR: ν 3449 (NH_{cyclic}), 3190 ($NH_{amidinic}$), 1646 cm^{-1} (C=N); ^{1}H NMR: δ 1.26 (t, 3H, *J*=6.2 Hz, C<u>H</u>$_3$-CH$_2$-C(N)=N), 3.32 (q, 2H, *J*=6.2 Hz, CH$_3$-C<u>H</u>$_2$-C(N)=N), 4.98 (s, 2H, Ph-C<u>H</u>$_2$-NH), 6.99 (s, 1H, N=C<u>H</u>-NH), 7.64-7.88 (m, 5H, C<u>H</u>$_{aromatic}$), 9.43 (s, 2H, Ph-CH$_2$-N<u>H</u>), 11.92 (s, 1H, N=CH-N<u>H</u>); ^{13}C NMR: δ 11.8 (<u>C</u>H$_3$-CH$_2$-C(N)=N), 27.1 (CH$_3$-<u>C</u>H$_2$-C(N)=N), 50.7 (Ph-<u>C</u>H$_2$-N), 125.2, 126.7, 130.8, 131.1 (C$_{arom,}$ <u>C</u>$_6$H$_5$), 153.6 (N=<u>C</u>H-NH), 159.1 (N=<u>C</u>(N)-N), 166.0 (N=<u>C</u>(CH$_2$CH$_3$)-N); MS: *m/z*=276 $[M+1]^+$. Anal. Calcd for $C_{12}H_{15}N_5$: C, 62.86; H, 6.59; N, 30.54. Found: C, 62.87; H, 6.60; N, 30.55.

General procedure for synthesis of [1,2,4]triazolo[4,3-*b*][1,2,4,6]thiatriazine 1-oxides 3a–h

Thionyl chloride (0.12 mol) was added dropwise to a mixture of *N*-triazol-3-ylamidine **2a–h** (0.12 mmol) and pyridine (0.24 mol) in anhydrous 1,4-dioxane (40 ml). The mixture was heated under reflux

for 6 h and then left to cool. The precipitate of pyridinium chloride was filtered. The solvent was removed under reduced pressure and the resulting solid was filtered off and crystallized from a mixture of dichloromethane and ethanol (v/v, 8:2) to give an analytically pure product **3a–h**.

2-Ethyl-3-methyl-2*H*-[1,2,4]triazolo[4,3-*b*][1,2,4,6]thiatriazine 1-oxide (3a) Yield 52%; a yellow solid; mp 240–242°C, IR: ν 1080 (S=O), 1612 cm^{-1} (C=N); ^1H NMR: δ 1.40 (t, 3H, *J*=9.0 Hz, C$\underline{H}_3$-CH_2-N), 2.54 (s, 3H, C$\underline{H}_3$-C(N)=N), 3.47 (q, 2H, *J*=9.0 Hz, CH_3-C$\underline{H}_2$-N), 7.52 (s, 1H, N=C$\underline{H}$-N-SO); ^{13}C NMR: δ 14.2 ($\underline{C}H_3$-CH_2-N), 19.3 ($\underline{C}H_3$-C(N)=N), 40.3 (CH_3-$\underline{C}H_2$-N), 151.4 (N=$\underline{C}$H-N-SO), 156.2 (N=$\underline{C}$(N)-N),163.8 (N=$\underline{C}$(CH_3)-N); ESI-MS : *m/z* 200 $[M+1]^+$. Anal. Calcd for $C_6H_9N_5OS$: C, 36.17; H, 4.55; N, 35.15; O, 8.03; S, 16.09. Found: C, 36.18; H, 4.56; N, 35.17; O, 8.04; S, 16.10.

2,3-Diethyl-2*H*-[1,2,4]triazolo[4,3-*b*][1,2,4,6]thiatriazine 1-oxide (3b) Yield 45%; a yellow solid; mp 230–233°C; IR: ν 1080 (S=O), 1612 cm^{-1} (C=N); ^1H NMR: δ 1.06 (t, 3H, *J*=6.0 Hz, C$\underline{H}_3$-CH_2-C(N)=N), 1.42 (t, 3H, *J*=9.0 Hz, C$\underline{H}_3$-CH_2-N), 2.58 (q, 2H, *J*=6.0 Hz, CH_3-C$\underline{H}_2$-C(N)=N), 3.49 (q, 2H, *J*=9.0 Hz, CH_3-C$\underline{H}_2$-N), 7.66 (s, 1H, N=C$\underline{H}$-N-SO); ^{13}C NMR: δ 10.7 ($\underline{C}H_3$-CH_2-C(N)=N), 15.0 ($\underline{C}H_3$-CH_2-N), 20.1 (CH_3-CH_2-$\underline{C}$(N)=N), 41.0 (CH_3-$\underline{C}H_2$-N), 152.60 (N=$\underline{C}$H-N-SO), 155.8 (N=$\underline{C}$(N)N), 165.1 (N=$\underline{C}$ (CH_2CH_3) N); ESI-MS: *m/z* 214 $[M+1]^+$. Anal. Calcd for $C_7H_{11}N_5OS$: C, 39.42; H, 5.20; N, 32.84; O, 7.50; S, 15.04. Found: C, 39.44; H, 5.21; N, 32.86, O; 7.51; S, 15.05.

3-Methyl-2-propyl-2*H*-[1,2,4]triazolo[4,3-*b*][1,2,4,6]thiatriazine 1-oxide (3c) Yield 36%; a beige solid; mp 192–194°C; IR: ν 1081 (S=O), 1616 cm^{-1} (C=N); ^1H NMR: δ 1.13 (t, 3H, *J*=7.2 Hz, C$\underline{H}_3$-CH_2-CH_2-N), 1.90 (m, 2H, CH_3-C$\underline{H}_2$-CH_2-N), 2.42 (s, 3H, C$\underline{H}_3$-C(N)=N), 3.46 (t, 2H, J=6.3 Hz, CH_3-CH_2-C$\underline{H}_2$-N), 7.20 (s, 1H, N=C$\underline{H}$-N-SO); ^{13}C NMR: δ 12.1 ($\underline{C}H_3$-CH_2-CH_2-N), 21.1 (CH_3-$\underline{C}H_2$-CH_2-N), 22.8 ($\underline{C}H_3$-C(N)=N), 43.7 (CH_3-CH_2-$\underline{C}H_2$-N), 152.3 (N=$\underline{C}$H-N-SO), 157.6 (N=$\underline{C}$(N)-N), 166.2 (N=$\underline{C}$(CH_3)-N); ESI-MS: *m/z* 214 $[M+1]^+$. Anal. Calcd for $C_7H_{11}N_5OS$: C, 39.42; H, 5.20; N, 32.84; O, 7.50; S, 15.04. Found: C, 36.43; H, 5.42; N, 32.86; O, 7.05; S, 15.08.

3-Ethyl-2-propyl-2*H*-[1,2,4]triazolo[4,3-*b*][1,2,4,6]thiatriazine 1-oxide (3d) Yield 40%; a beige solid; mp 212–214°C; IR: ν 1083 (S=O), 1616 cm^{-1} (C=N); ^1H NMR: δ 1.10 (t, 3H, *J*=8.2 Hz, C$\underline{H}_3$-CH_2-CH_2-N), 1.28 (t, 3H, *J*=8.9 Hz, C$\underline{H}_3$-CH_2-C(N)=N), 1.96 (m, 2H, CH_3-C$\underline{H}_2$-CH_2-N), 2.80 (q, 2H, J=8.9 Hz, CH_3-C$\underline{H}_2$-C(N)=N), 3.46 (t, 2H, J=8.4 Hz, CH_3-CH_2-C$\underline{H}_2$-N), 7.13 (s, 1H, N=C$\underline{H}$-N-SO); ^{13}C NMR: δ 11.2 ($\underline{C}H_3$-CH_2-CH_2-N), 12.6 ($\underline{C}H_3$-$\underline{C}H_2$-C(N)=N), 22.4 (CH_3-$\underline{C}H_2$-CH_2-N), 23.2 (CH_3-$\underline{C}H_2$-C(N)=N), 45.7 (CH_3-CH_2-$\underline{C}H_2$-N), 152.0 (N=$\underline{C}$H-N-SO), 156.5 (N=$\underline{C}$(N)-N), 166.8 (N=$\underline{C}$(CH_2CH_3)-N); ESI-MS: *m/z* 228 $[M+1]^+$. Anal. Calcd for $C_8H_{13}N_5OS$: C, 42.28; H, 5.77; N, 30.81; O, 7.04; S, 14.11. Found: C, 42.29; H, 5.78; N, 30.84; O, 7.05; S, 14.10.

2-Cyclopentyl-3-methyl-2*H*-[1,2,4]triazolo[4,3-*b*][1,2,4,6]thiatriazine 1-oxide (3e) Yield 28%; a yellowish solid; mp 216–2018°C; IR: ν 1082 (S=O), 1615 cm^{-1} (C=N); ^1H NMR: δ 1.24 (m, 4H, CH_2-C$\underline{H}_2$-C$\underline{H}_2$-CH_2-CH-N), 2.38 (s, 3H,C$\underline{H}_3$-C(N)=N), 2.85(m, 4H, C$\underline{H}_2$-CH_2-CH_2-C$\underline{H}_2$-CH N), 4.48 (m, 1H, CH_2-CH_2-CH_2-CH_2-C$\underline{H}$ N), 6.88(s, 1H, N=C$\underline{H}$-N-SO); ^{13}C NMR: δ 22.8 ($\underline{C}H_3$-C(N)=N), 23.6 (CH_2-$\underline{C}H_2$-$\underline{C}H_2$-CH_2-CH-N), 32.2 ($\underline{C}H_2$-CH_2-CH_2-$\underline{C}H_2$-CH-N), 62.0 (CH_2-CH_2-CH_2-CH_2-$\underline{C}$H-N), 151.8 (N=$\underline{C}$H-N-SO), 155.5 (N=$\underline{C}$(N)-N), 165.3 (N=$\underline{C}$(CH_3)-N). ESI-MS : *m/z* 240 $[M+1]^+$. Anal. Calcd for $C_9H_{13}N_5OS$: C, 45.17; H, 5.48; N, 29.27; O, 6.69; S, 13.40. Found: C, 45.18; H, 5.50; N, 29.28; O, 6.71; S, 13.41.

2-Cyclopentyl-3-ethyl-2*H*-[1,2,4]triazolo[4,3-*b*][1,2,4,6]thiatriazine 1-oxide (3f) Yield 25%; a yellowish solid; mp 200–202°C; IR: ν 1080 (S=O), 1616 cm^{-1} (C=N); ^1H NMR: δ 1.16 (t, J=6.4 Hz, 3H, C$\underline{H}_3$-CH_2-C(N)=N), 1.62 (m, 4H, CH_2-C$\underline{H}_2$-C$\underline{H}_2$-CH_2-CH-N), 2.77 (m, 4H, C$\underline{H}_2$-CH_2-CH_2-C$\underline{H}_2$-CH-N), 3.10 (q, 2H, J=6.4 Hz, CH_3-C$\underline{H}_2$-C(N)=N), 4.40 (m, 1H, CH_2-CH_2-CH_2-CH_2-C$\underline{H}$-N), 6.92 (s, 1H, N=C$\underline{H}$-N-SO); ^{13}C NMR: δ 17.0 ($\underline{C}H_3$-CH_2-C(N)=N), 23.0 (CH_2-$\underline{C}H_2$-$\underline{C}H_2$-CH_2-CH-N), 26.2 (CH_3-$\underline{C}H_2$-C(N)=N) 31.9 ($\underline{C}H_2$-CH_2-CH_2-$\underline{C}H_2$-CH-N), 62.8 (CH_2-CH_2-CH_2-CH_2-$\underline{C}$H-N), 152.5 (N=$\underline{C}$H-N-SO), 154.8 (N=$\underline{C}$(N)-N), 166.2 (N=$\underline{C}$(CH_2CH_3)-N); ESI-MS: *m/z* 254 $[M+1]^+$. Anal. Calcd for $C_{10}H_{15}N_5OS$: C, 47.41; H, 5.97; N, 27.65; O, 6.32; S, 12.66. Found: C, 45.18; H, 5.50; N, 29.28; O, 6.71; S, 13.41.

2-Benzyl-3-methyl-2*H*-[1,2,4]triazolo[4,3-*b*][1,2,4,6]thiatriazine 1-oxide (3g) Yield 47%; a brown solid; mp 209–201°C; IR: ν 1080 (S=O), 1614 cm^{-1} (C=N); ^1H NMR: δ 2.30 (s, 3H, C$\underline{H}_3$-C(N)=N), 4.78 (s, 2H, Ph-C$\underline{H}_2$-N), 6.70 (s, 1H, N=C$\underline{H}$-N-SO), 7.02–7.30 (m, 5H, C$\underline{H}_{aromatic}$); ^{13}C NMR: δ 21.2 ($\underline{C}H_3$-C(N)=N), 48.5 (Ph-$\underline{C}H_2$-N), 125.6, 126.4, 130.4, 132.02 ($C_{arom,}$ $\underline{C}_6H_5$), 153.0 (N=$\underline{C}$H-N-SO), 157.1 (N=$\underline{C}$(N)-N), 166.2 (N=$\underline{C}$(CH_3)-N); ESI-MS: *m/z* 262 $[M+1]^+$. Anal. Calcd for $C_{11}H_{11}N_5OS$: C, 50.56; H, 4.24; N, 26.80; O, 6.12; S, 12.27. Found: C, 50.57; H, 4.27; N, 26.79; O, 6.10; S, 12.30.

2-Benzyl-3-ethyl-2*H*-[1,2,4]triazolo[4,3-*b*][1,2,4,6]thiatriazine 1-oxide (3h) Yield 50%; a dark brown solid; mp 242–242°C; IR: ν 1083 (S=O), 1614 cm^{-1} (C=N); ^1H NMR: δ 1.23 (t, 3H, *J*=6.8 Hz, C$\underline{H}_3$-CH_2-C(N)=N), 3.22 (q, 2H, *J*=6.8 Hz, CH_3-C$\underline{H}_2$-C(N)=N), 4.90 (s, 2H, Ph-C$\underline{H}_2$-N), 6.75 (s, 1H, N=C$\underline{H}$-N-SO), 7.30-7.81 (m, 5H, C$\underline{H}_{aromatic}$); ^{13}C NMR: δ 11.2 ($\underline{C}H_3$-CH_2-C(N)=N), 26.0 (CH_3-$\underline{C}H_2$-C(N)=N), 50.01 (Ph-$\underline{C}H_2$-N), 124.6, 125.9, 129.8, 131.6 ($C_{arom,}$ $\underline{C}_6H_5$), 152.64 (N=$\underline{C}$H-N-SO),157.6 (N=$\underline{C}$(N)-N), 165.0 (N=$\underline{C}$(CH_2CH_3)-N); ESI-MS: *m/z* 276 $[M+1]^+$. Anal. Calcd for $C_{12}H_{13}N_5OS$: C, 52.35; H, 4.76; N, 25.44; O, 5.81; S, 11.65. Found: C, 52.36; H, 4.78; N, 25.45; O, 5.82; S, 11.66.

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