Synthesis and Fungicidal Activity of *(1Z, 3Z)*-4,4-Dimethyl-1-substituted-phenyl-2-(1*H*-1,2,4-triazol-1-yl)-pent-1-en-3-one *O*-[2,4-dimethylthiazole (or 4-methyl-1,2,3-thiadiazole)]-5-carbonyl Oximes

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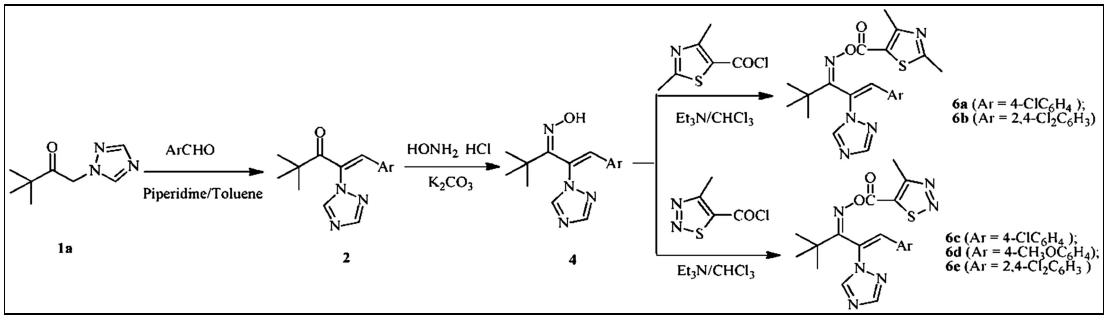

A series of novel (*Z*)-1-tert-butyl (or phenyl)-2-(1*H*-1,2,4-triazol-1-yl)-ethanone *O*-[2,4-dimethylthiazole (or 4-methyl-1,2,3-thiadiazole) −5-carbonyl] oximes **5a**–**5c** and *(1Z, 3Z)*-4,4-dimethyl-1-substitutedphenyl-2-(1*H*-1,2,4-triazol-1-yl)-pent-1-en-3-one *O*-[2,4-dimethylthiazole (or 4-methyl-1,2,3-thiadiazole)-5-carbonyl] oximes **6a**–**6e** were synthesized by the condensations of (*Z*)-1-tert-butyl (or phenyl)-2-(1*H*-1,2,4-triazol-1-yl)-ethanone oximes **3** or *(1Z, 3Z)*-4,4-dimethyl-1-substitutedphenyl-2-(1*H*-1,2,4-triazol-1-yl)-pent-1-en-3-one oximes **4** with 2,4-dimethylthiazole-5-carbonyl chloride or 4-methyl-1,2,3-thiadiazole-5-carbonyl chloride in the basic condition. Their structures were confirmed by IR, ^{1}H NMR, mass spectroscopy, and elemental analyses. The results of preliminary bioassays showed the title compounds **5** and **6** exhibited moderate to good fungicidal activities. For example, compound **6c** possessed 86.4% inhibition against *Fusarium oxysporum*, and compound **6b** exhibited 86.4 and 100% inhibition against *Fusarium oxysporum* and *Cercospora arachidicola Hori* at the concentration of 50 mg/L, respectively.

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INTRODUCTION

The application of agrochemicals to protect vegetable and cereal crops is a virtual and convenient approach for modern agriculture. This has provided healthy crops and increased yields as well as economic benefits for decades. The main purpose of the research for agrochemicals is to develop novel active compounds with lower application doses, high selectivity, and benign environment [1,2]. The triazole fungicides, as an important class of agrochemicals, have played a major role in crop protection [3–5]. The introduction of these sterol biosynthesis inhibitors represented a significant progress in the chemical control of fungal diseases. More than 30 triazole fungicides such as uniconazole, diniconazole, paclobutrazol, and flusilazole, have been commercialized. Recently, heterocyclic compounds containing nitrogen, such as thiazole and 1,2,3-thiadiazole derivatives as two kinds of heterocyclic compounds with a wide spectrum of remarkable biological activities, are widely used in agrochemicals [6–13]. For example, clothianidin was developed as one of neonicotinoid insecticides, and methidathion was used cholinesterase inhibitor, which acts as nonsystemic insecticide and acaricide with contact and stomach action, whereas flurazole has been used as herbicides or their safeners, and ethaboxam acted as fungicides. acibenzolar-S-methyl and tiadinil were developed and used as plant activators, which induces fungicide resistance in rice plants; however, thidiazuron was used as plant growth regulator (see Fig. 1). On the other hand, oxime ester derivatives are very important agrochemicals and are receiving more and more attention due to their widespread biological activities[14], some of them can be used as insecticides [15,16], fungicides [17,18], herbicides (such as trifopsime and pyribenzoxim)[19], and plant virucides (for example, antiviral agent against tobacco mosaic virus [20]), which are widely used in the worldwide plant protection. To find novel fungicide lead compounds with high activity and low toxicity, we designed and synthesized a series of novel target compounds **5** and **6**, which

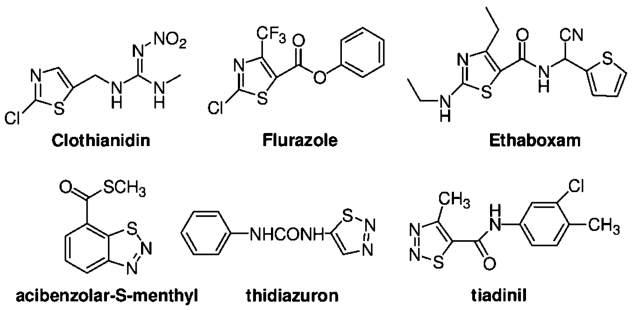


Figure 1. Some commercialized pesticides containing thiazole and thiadiazole moieties.

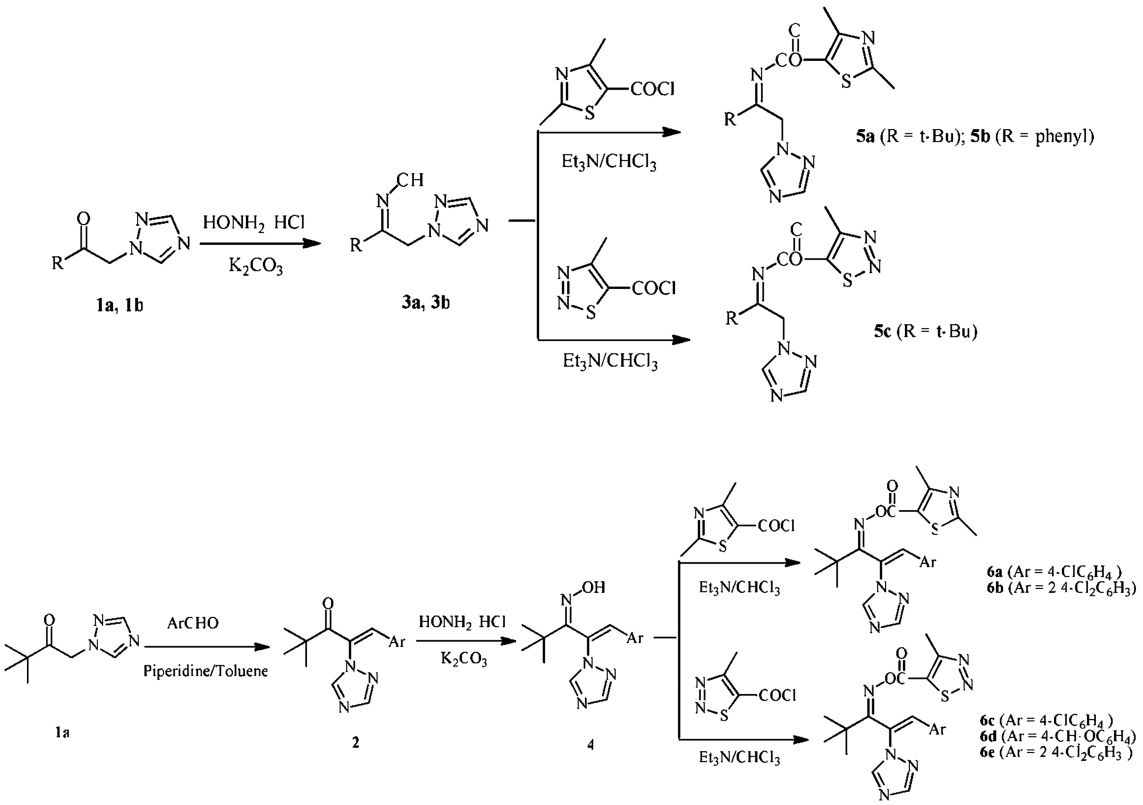
the triazole ring is bound *via* an oxime ester bridge to a 2,4-dimethylthiazole or 4-methyl-1,2,3-thiadiazole units. Herein, we report the synthesis and fungicide activities of the title compounds **5** and **6** in this article (Scheme 1).

RESULTS AND DISCUSSION

1-(*t*-Butyl)-2-(1*H*-1,2,4-triazol-1-yl)ethanone (**1a**) reacted with aromatic aldehydes in the presence of piperidine to obtain 3-(substitutedphenyl)-1-*t*-butyl-2-(1*H*-1,2,4-triazol-1-yl)prop-2-en-1-ones (**2**) as *Z*- and *E*-isomer mixtures. After purified by flash column chromatography, pure *Z*-isomers 2 were obtained; Treatment of **1**(**1a**, and **1b**) and **2** with hydroxylamine hydrochloride in the presence of potassium carbonate and methanol afforded (*Z*)-1-tert-butyl (or phenyl)-2-(1*H*-1,2,4-triazol-1-yl)-ethanone oximes **3** or (*1Z, 3Z*)-4, 4-dimethyl-1-substitutedphenyl-2-(1*H*-1,2,4-triazol-1-yl)-pent-1-en-3-one oximes **4** in 75–89% yields, which reacted with 2,4-dimethylthiazole-5-carbonyl chloride or 4-methyl-1,2,3-thiadiazole-5-carbonyl chloride in the presence of triethylamine in chloroform at 10–15°C to get the title compounds **5** and **6** in moderate to excellent yields.

The structures of compounds **5** and **6** were deduced from their spectral data (IR, ^{1}H NMR, and ESI-MS) and elemental analyses, which were listed in the experimental part. Because of the C=C or (and) C=N bonds, it probably existed in *E*- and *Z*-isomers in compounds **3** and **4** and target molecules **5** and **6**. In the ^{1}H NMR spectra of **5** and **6**, the *t*-butyl protons displayed as a singlet with chemical shift δ between 1.0 and 1.3; the protons of two methyl linking with thiazole and 1,2,3-thiadiazole also showed two singlet and a singlet with chemical shifts δ 2.7, 2.8, and the methyl protons linking with 1,2,3-thiadiazole displayed as a singlet with chemical shifts δ between 2.9 and 3.1; the alkene proton also exhibited as a singlet in δ 7.6; whereas the 1,2,4-triazole protons showed two singlets with chemical shifts δ 8.0 and 8.2, respectively. These data indicated

Scheme 1. Synthetic route to compounds **5** and **6.**



compounds **5** and **6** are existed as single isomers. According to the reported literatures [21,22], the *t*-butyl protons and alkene proton of the Z-isomer of **2** are shifted downfield with chemical shifts δ 1.2–1.5 and 7.5, respectively; whereas these protons in *E*-isomer are presented in 1.0 and 6.8, respectively. So, in this article, the C=C bonds in both compounds **4** and **6** are existed as Z-isomer. Moreover, according to the related literature report [23] and our previous X-ray diffraction data [24], the C=N bonds of compounds **5** and **6** are all existed as Z configurations. IR spectra of compounds **5** and **6** showed normal stretching absorption bands, indicating the existence Ar-H (∼3050 cm^{-1}), C=O (∼1750 cm^{-1}), C=N (∼1650 cm^{-1}), and Ar (1580, 1510, and 1480 cm^{-1}). The ESI mass spectra of compounds **5** and **6** revealed the existence of the molecular ion peaks and strong M+K or M+Na peaks, which were in good accordance with the given structures of products.

Biological activity. ***Fungicidal activity.*** The preliminary fungicidal activity of the target compounds **5** and **6** was evaluated by the classic plate method at the concentration of 50 mg/L, which was described in the experimental part. The five fungi used, *Fusarium oxysporium*, *Physalospora piricola Nose*, *Alternaria solani*, *Cercospora arachidicola Hori*, and *Gibberella sanbinetti*, belong to the group of field fungi and were isolated from corresponding crops. The activities data were also listed in Table 1. The results indicated that most of compounds **5** and **6** exhibit moderate to good inhibitory activities against the above five fungi. For example, compound **6c** possessed 86.4% inhibition against *Fusarium oxysporum*, and compound **6b** exhibited 86.4 and 100% inhibition against *Fusarium oxysporum* and *Cercospora arachidicola Hori* at the concentration of 50 mg/L, respectively. As for preliminary structure-activity relationship, first, most of compounds **6** exhibited better fungicidal activity than compounds **5**, this result indicated that C=C moiety introduced to the target molecular skeleton was useful for the improvement of fungicidal activity, and compound **6b** showed the best activities against the five fungi. Second, compounds **6** containing 2,4-dimethylthiazole moiety seems to display better activities than that of 4-methyl-1,2,3-thiadiazole moiety. Further exploring of structure-activity relationship need more experimental results to support. Further biological activity (*in vivo*) investigations are on the way.

In conclusion, a series of novel (*Z*)-1-tert-butyl (or phenyl)-2-(1*H*-1,2,4-triazol-1-yl)-ethanone *O*-[2,4-dimethylthiazole (or 4-methyl-1,2,3-thiadiazole)-5-carbonyl] oximes **5a–5c** and *(1Z, 3Z)*-4,4-dimethyl-1-substituted-phenyl-2-(1*H*-1,2,4-triazol-1-yl)-pent-1-en-3-one *O*-[2,4-dimethylthiazole (or 4-methyl-1,2,3-thiadiazole)-5-carbonyl] oximes **6a–6e** were designed and synthesized. The results of preliminary bioassays showed the title compounds **5** and **6** exhibited moderate to good fungicidal activities. For example, compound **6c** possessed 86.4% inhibition against *Fusarium oxysporum*, and compound **6b** exhibited 86.4 and 100% inhibition against *Fusarium oxysporum* and *Cercospora arachidicola Hori* at the concentration of 50 mg/L, respectively.

EXPERIMENTAL

Melting points were determined with a WRS-1B digital melting point apparatus and are uncorrected. ^{1}H NMR spectra was recorded with a Varian Mercury PLUS 400 (400 MHz) and Varian Mercury PLUS 600 (600 MHz) spectrometer with TMS as the internal reference and $CDCl_3$ as the solvent, whereas mass spectra were obtained with an Applied Biosystems API 2000 LC/MS/MS (ESI-MS) spectrometer. IR spectra were measured by a Nicolet NEXUS470 spectrometer. Elemental analyses were performed with an Elementar Vario ELIII CHNSO elemental analyzer. *(1Z, 3Z)*-4,4-dimethyl-1-substitutedphenyl-2-(1*H*-1,2,4-triazol-1-yl)-pent-1-en-3-one was prepared by the Knoevenagel reactions of 1-tert-butyl-2-(1*H*-1,2,4-triazol-1-yl)-ethanone (**1a**) with aromatic aldehydes in the presence of piperidine according to the literature procedure [25]. 2,4-Dimethylthiazole-5-carbonyl chloride and 4-methyl-1,2,3-thiadiazole-5-carbonyl chloride were synthesized according to the reported methods [26,27], respectively. All of the solvents and materials were reagent grade and purified as required.

Table 1

Fungicidal activity of compounds **5** and **6** (relative inhibitory rate %).

Compounds	*Fusarium oxysporium*	*Physalospora piricola Nose*	*Alternaria solani*	*Cercospora arachidicola Hori*	*Gibberella sanbinetti*
5a	27.3	0.0	3.6	23.1	17.2
5b	27.3	25.0	14.3	76.9	37.9
5c	22.7	0.0	3.6	15.4	22.4
6a	68.2	10.7	39.3	7.7	27.6
6b	86.4	71.4	60.7	100.0	51.7
6c	86.4	0.0	25.0	69.2	19.0
6d	22.7	21.4	21.4	0.0	15.5
6e	0.0	0.0	10.7	53.8	17.2
Difenoconazole	100	100	100	100	98.3

General procedure for the synthesis of (*Z*)-1-tert-butyl (or phenyl)-2-(1*H*-1,2,4-triazol-1-yl)-ethanone oximes 3 or (1*Z*, 3*Z*)-4,4-dimethyl-1-substitutedphenyl-2-(1*H*-1,2,4-triazol-1-yl)-pent-1-en-3-one oximes 4. To the stirred mixture of **1** or **2** (12.8 mmol), K_2CO_3 (2.33 g, 16.9 mmol) in anhydrous methanol (20 mL) and hydroxylamine hydrochloride (1.08 g, 15.4 mmol) in H_2O (6 mL) were added slowly at 0∼5°C. After the addition completed, the solution was stirring under reflux for 8–10 h. The mixture was concentrated under vacuum, the residue was poured to water (10 mL). The solid was collected by filtration, and recrystallized from the mixture of methanol and petroleum ether (*V/V* 1:1) to get **3** and **4** as a white solid.

3,3-Dimethyl-1-(1*H*-1,2,4-triazol-1-yl)butan-2-one oxime (3a). White solid, yield: 89%, m.p. 123.4–124.7 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.17 (s, 9H, *t*-Bu), 5.05 (s, 2H, CH_2), 7.91 (s, 1H, triazole-H), 8.31 (s, 1H, triazole-H), 9.41 (s, 1H, OH). *Anal*. Calcd for $C_8H_{14}N_4O$: C, 52.73; H, 7.74; N, 30.75. Found: C, 52.57; H, 7.61; N, 30.53.

1-(Phenyl)-2-(1*H*-1,2,4-triazol-1-yl)ethanone oxime (3b). White solid, yield: 82%, m.p. 153.3–155.4°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.56 (s, 2H, CH_2), 7.42–7.81 (m, 5H, ArH), 7.93 (s, 1H, triazole-H), 8.16 (s, 1H, triazole-H), 9.38 (s, 1H, OH). *Anal*. Calcd for $C_{10}H_{10}N_4O$: C, 59.40; H, 4.98; N, 27.71. Found: C, 59.25; H, 5.14; N, 27.90.

(1*Z*, 3*Z*)-1-(2,4-Dichlorophenyl)-4,4-dimethyl-2-(1*H*-1,2,4-triazol-1-yl)pent-1-en-3-one oxime (4a). White solid, yield: 70%, m.p. 147.6–148.7°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.17 (s, 9H, *t*-Bu), 6.36 (d, *J* = 9.0 Hz, 1H, ArH), 7.19 (d, *J* = 9.0 Hz, 1H, ArH), 7.45 (s, 1H, ArH), 7.48 (s, 1H, =CH), 7.89 (s, 1H, triazole-H), 8.23 (s, 1H, triazole-H), 9.42 (s, 1H, OH). *Anal*. Calcd for $C_{15}H_{16}Cl_2N_4O$: C, 53.11; H, 4.75; N, 16.52. Found: C, 53.27; H, 4.78; N, 16.63.

(1*Z*, 3*Z*)-4,4-Dimethyl-1-(4-chlorophenyl)-2-(1*H*-1,2,4-triazol-1-yl)pent-1-en-3-one oxime (4b). White solid, yield: 65%, m.p. 119.5–120.5°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.18 (s, 9H, *t*-Bu), 7.34 (d, *J* = 8.0 Hz, 2H, ArH), 7.50 (d, *J* = 8.0 Hz, 2H, ArH), 7.61 (s, 1H, =CH), 7.92 (s, 1H, triazole-H), 8.33 (s, 1H, triazole-H), 10.11 (s, 1H, OH). *Anal*. Calcd for $C_{15}H_{17}ClN_4O$: C, 59.11; H, 5.62; N, 18.38. Found: C, 59.02; H, 5.49; N, 18.30.

(1*Z*, 3*Z*)-1-(4-Methoxyphenyl)-4,4-dimethyl-2-(1*H*-1,2,4-triazol-1-yl)pent-1-en-3-one oxime (4c). White solid, yield: 79%, m.p. 121.3–122.4°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.19 (s, 9H, *t*-Bu), 3.86 (s, 3H, OCH_3), 6.97 (d, *J* = 7.6 Hz, 2H, ArH), 7.75 (d, *J* = 7.2 Hz, 2H, ArH), 7.83 (s, 1H, =CH), 7.91 (s, 1H, triazole-H), 8.38 (s, 1H, triazole-H), 10.05 (s, 1H, OH). *Anal*. Calcd for $C_{16}H_{20}N_4O_2$: C, 63.98; H, 6.71; N, 18.65. Found: C, 63.83; H, 6.54; N, 18.77.

General procedure for the synthesis of (*Z*)-1-tert-butyl (or phenyl)-2-(1*H*-1,2,4-triazol-1-yl)-ethanone *O*-[2,4-dimethylthiazole (or 4-methyl-1,2,3-thiadiazole)-5-carbonyl] oximes 5 and (1*Z*, 3*Z*)-4,4-dimethyl-1-substitutedphenyl-2-(1*H*-1,2,4-triazol-1-yl)-pent-1-en-3-one *O*-[2,4-dimethylthiazole (or 4-methyl-1,2,3-thiadiazole)-5-carbonyl] oximes 6. Oxime **3** or **4** (2.0 mmol), triethylamine (2.4 mmol) and anhydrous chloroform (7.5 mL) were added to a three-necked flask, a solution of 2,4-dimethylthiazole-5-carbonyl chloride [or 4-methyl-1,2,3-thiadiazole)-5-carbonyl chloride] (2.2 mmol) in anhydrous chloroform (5 mL) was added dropwise slowly at 5–10°C. After the addition completed, the mixture was stirred at room temperature for 10–12 h till the reaction was complete (monitored by TLC). The workup involved washing with water and 5% $NaHCO_3$, respectively. After phase separation, drying over anhydrous sodium sulphate, filtration, and evaporation, the crude product was purified by column chromatography on silica gel using petroleum ether and acetone (3:1 *v/v*) as the eluent, giving the target compounds **5** and **6** in 65–84% yields.

Data for **5a** (R = *t*-Bu): light yellow solid, yield: 65%, m.p. 129.5–130.6°C; IR: C=O 1742, C=N 1526, 1506, C—O 1250, 1048, N—O—C 1033; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.32(s, 9H, *t*-Bu), 2.69 (s, 3H, CH_3), 2.71 (s, 3H, CH_3), 5.10 (s, 2H, CH_2), 7.95 (s, 1H, triazole-H), 8.15 (s, 1H, triazole-H); ESI-MS: *m/z* 343.5 (M+Na, 100), 322 (M+1, 5). *Anal*. Calcd for $C_{14}H_{19}N_5O_2S$: C, 52.32; H, 5.96; N, 21.79. Found: C, 52.37; H, 5.71; N, 21.94.

Data for **5b** (R = Ph): light yellow crystals, yield: 77%, m.p. 113.5–114.8°C; IR: Ph-H 3098, 2961, C=O 1754, Ph 1660, 1449, C=N 1519, 1314, C—O 1244, 1194, N—O—C 1019; ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.75 (s, 3H, CH_3), 2.78 (s, 3H, CH_3), 5.58 (s, 2H, CH_2), 7.43–7.46 (m, 2H, ArH), 7.49–7.50 (m, 1H, ArH), 7.84 (d, *J* = 7.2 Hz, 2H, ArH), 7.95 (s, 1H, triazole-H), 8.20 (s, 1H, triazole-H); ESI-MS: *m/z* 364 (M+Na, 100). *Anal*. Calcd for $C_{16}H_{15}N_5O_2S$: C, 56.29; H, 4.43; N, 20.51. Found: C, 56.05; H, 4.34; N, 20.30.

Data for **5c** (R = *t*-Bu): yellow solid, yield: 82%, m.p. 70.6–72.4°C; IR: C=O 1751, C=N 1533, 1496, C—O 1245, 1052, N—O—C 1030; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.36 (s, 9H, *t*-Bu), 2.98 (s, 3H, CH_3), 5.12 (s, 2H, CH_2), 7.95 (s, 1H, triazole-H), 8.15 (s, 1H, triazole-H); ESI-MS: *m/z* 330.6 (M+Na, 100), 328 (48), 183 (55). *Anal*. Calcd for $C_{12}H_{16}N_6O_2S$: C, 46.74; H, 5.23; N, 27.25. Found: C, 46.96; H, 5.28; N, 27.17.

Data for **6a** (Ar = 4-ClC_6H_4): yellow crystals, yield: 84%, m.p. 133.0–133.8°C; IR: Ph-H 3095, 2938, C=O 1754, Ph 1588, 1485, 1433, C=N 1510, C—O 1203, 1024, N—O—C 1001; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.62 (s, 9H, *t*-Bu), 2.74 (s, 3H, CH_3), 2.78 (s, 3H, CH_3), 7.36 (d, *J* = 8.4 Hz, 2H, ArH), 7.67 (s, 1H, =CH), 7.73 (d, *J* = 8.4 Hz, 2H, ArH), 8.10 (s, 1H, triazole-H), 8.44 (s, 1H, triazole-H); ESI-MS: *m/z* 443 (M^+, 100). *Anal*. Calcd for $C_{21}H_{22}ClN_5O_2S$: C, 56.81; H, 4.99; N, 15.78. Found: C, 56.64; H, 5.07; N, 16.02.

Data for **6b** (Ar = 2,4-$Cl_2C_6H_3$): yellow crystals, yield: 75%, m.p. 117.5–118.4°C; IR: Ph-H 3074, 2915, C=O 1751, Ph 1545, 1438, 1407, C=N 1524, C—O 1235, 1026, N—O—C 1013; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.59 (s, 9H, *t*-Bu), 2.74 (s, 3H, CH_3), 2.79 (s, 3H, CH_3), 7.27 (s, 1H, =CH), 7.29 (s, 1H, triazole-H), 7.34 (d, *J* = 9.0 Hz, 1H, ArH), 7.48 (s, 1H, ArH), 8.10 (d, *J* = 9.0 Hz, 1H, ArH), 8.83 (s, 1H, triazole-H); ESI-MS: *m/z* 518 (M+K+2, 100), 516 (M+K, 78), 498 (M+Na−1, 63). *Anal*. Calcd for $C_{21}H_{21}Cl_2N_5O_2S$: C, 52.72; H, 4.42; N, 14.64. Found: C, 52.59; H, 4.50; N, 14.71.

Data for **6c** (Ar = 4-ClC_6H_4): yellow solid, yield: 73%, m.p. 131.1–133.3°C; IR: Ph-H 3076, 2905, C=O 1742, Ph 1562, 1465, 1372, C=N 1524, C—O 1218, 1026, N—O—C 1017; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.18 (s, 9H, *t*-Bu), 3.07 (s, 3H, CH_3), 7.47 (d, *J* = 8.4 Hz, 2H, ArH), 7.74 (d, *J* = 9.0 Hz, 2H, ArH), 7.88 (s, 1H, =CH), 8.26 (s, 1H, triazole-H), 8.49 (s, 1H, triazole-H); ESI-MS: *m/z* 452 (M+Na−1, 15), 430.5 (M^+, 100). *Anal*. Calcd for $C_{19}H_{19}ClN_6O_2S$: C, 52.96; H, 4.44; N, 19.50. Found: C, 52.73; H, 4.53; N, 19.37.

Data for **6d** (Ar = 4-$CH_3OC_6H_4$): white solid, yield: 78%, m.p. 116.0–116.6°C; IR: Ph-H 3044, 2913, C=O 1757, Ph 1549, 1450, 1351, C=N 1545, C—O 1229, 1024, N—O—C 1026; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.65 (s, 9H, *t*-Bu), 3.06 (s, 3H, CH_3), 3.88 (s, 3H, OCH_3), 6.98 (d, *J* = 7.2 Hz, 2H, ArH), 7.74 (d, *J* = 7.2 Hz, 2H, ArH), 7.90 (s, 1H, =CH), 8.25 (s, 1H, triazole-H), 8.45 (s, 1H, triazole-H); ESI-MS: *m/z* 428 (7), 426 (M^+, 100). *Anal*. Calcd for $C_{20}H_{22}N_6O_3S$: C, 56.32; H, 5.20; N, 19.70. Found: C, 56.41; H, 5.35; N, 19.84.

Data for **6e** (Ar = 2,4-$Cl_2C_6H_3$): yellow crystals, yield: 69%, m.p. 102.2–103.8°C; IR: Ph-H 3042, 2915, C=O 1760, Ph 1536, 1440, C=N 1526, C—O 1234, 1045, N—O—C 1024; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.17 (s, 9H, *t*-Bu), 2.87 (s, 3H, CH_3), 6.95 (d, *J* = 9.0 Hz, 1H, ArH), 7.17 (d, *J* = 7.2 Hz, 1H, ArH), 7.36 (s, 1H, ArH), 7.46 (s, 1H, =CH), 7.79 (s, 1H, triazole-H), 8.13 (s, 1H, triazole-H); ESI-MS: *m/z* 505 507 (M+K+2, 65), (M+K, 100), 486 (M+Na−1, 8), 384 (26). *Anal*. Calcd for $C_{19}H_{18}Cl_2N_6O_2S$: C, 49.04; H, 3.90; N, 18.06. Found: C, 49.23; H, 3.77; N, 18.18.

Fungicidal activity testing. The fungicidal activity measurement method was adapted from the one described by Molina Torres [28]. The synthesized target compounds were dissolved in 0.5–1.0 mL of DMF to the concentration of 1000 mg/L. The solutions (1 mL) were mixed rapidly with thawed potato glucose agar culture medium (9 mL) under 50°C. The mixtures were poured into Petri dishes. After the dishes were cooled, the solidified plates were incubated with 4-mm mycelium disk, inverted, and incubated at 28°C for 48 h. Distilled water was used as the blank control and the commercially available fungicide difenoconazole as the control drug. Three replicates of each test were carried out. The mycelial elongation radius (mm) of fungi settlements was measured after 48 h of culture. The growth inhibitory rates were calculated with the following equation: $I = [(C - T)/C] \times 100\%$. Here, *I* is the growth inhibitory rate (%), *T* is the treatment group fungi settlement radius (mm), and *C* is the radius of the blank control. The results are listed in Table 1.

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