Synthesis and Fungicidal Activity of Novel 2-Heteroatomthiazole-based Carboxanilides

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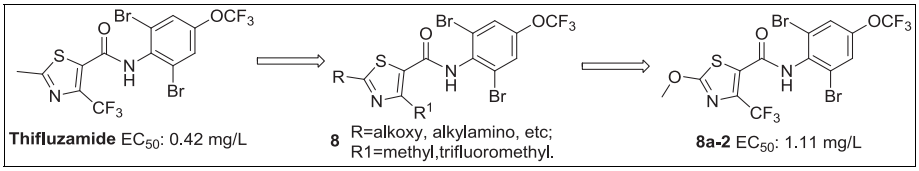

A new series of 2-heteroatomthiazole-based carboxanilides (**8**) are prepared by reacting 2-heteroatomthiazole-based carboxylic acid chlorides with 2,6-dibromo-4-(trifluoromethoxy)aniline. The structures of all the newly synthesized compounds were supported by spectroscopic data NMR, MS, and elemental analysis, etc. Bioassay showed that the compounds exhibited potent fungicidal activities against *Rhizoctonia solani*, etc. Particularly, N-(2,6-dibromo-4-(trifluoromethoxy)phenyl)-2-methoxy-4-(trifluoromethyl)thiazole-5-carboxamide (**8a-2**) showed fungicidal potency which was comparable to that of Thifluzamide, the only commercialized thiazole carboxanilide fungicides of succinate dehydrogenase inhibitor (SDHI).

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INTRODUCTION

The fungicide market has been dominated by strobilurins and triazoles, and consequently pathogen resistance to these fungicides has become a serious problem. The development of resistance to current treatments, along with newly evolving pathogens problems, and market environment, gives rise to an emerging demand of new fungicides that are not only active to resistance strains but also safe to humans and the environment.

Carboxanilides are a well-known class of fungicides whose mode of action has been determined to be inhibition of succinate dehydrogenase [1,2]. Eighteen examples of commercial fungicides with this mode of action include Carboxin (Fig. 1; I) [3], Boscalid (II) [4], Fluxapyroxad (III) [5], and Benzovindilfupyr (IV) [6], etc.

Thiazole carboxanilides are also well known as members of the carboxamide family of fungicides. Examples include Metsulfovax (Fig. 2; V) [7], Scedlavax (VI) [8], Ethaboxam (VII) [9], and Thifluzamide (VIII) [10], etc. However only one member of this group, N-(2,6-dibromo-4-(trifluoromethoxy)phenyl)-2-methyl-4-(trifluoromethyl)thiazole-5-carboxamide, has been developed as an agricultural fungicide of succinate dehydrogenase inhibitor (SDHI) under the trade name "Thifluzamide" by Rohm and Haas Company, USA in 1997 (Fig. 2; VIII) [10]. Thifluzamide (VIII) has been shown to be highly active against rice sheath blight. It is thus meaningful to develop new thiazole carboxanilide fungicides of SDHI that have fungicidal activities comparable to that of Thifluzamide but are better broad-spectrum control.

In our previous work, we found that 2-heteroatomthiazole-based compounds showed remarkable fungicidal activity. In order to obtain novel thiazole carboxanilides, a new series of 2-heteroatomthiazole-based carboxanilides (**8**) are prepared by replacing methyl in Thifluzamide with R (R = alkoxy, alkylamino, etc.). Bioassay results indicated that **8a-2**[N-(2,6-dibromo-4-(trifluoromethoxy)phenyl)-2-methoxy-4-(trifluoromethyl)thiazole-5-carboxamide] not only exhibited fungicidal activities against *Rhizoctonia solani* at the level to that of Thifluzamide, but also showed stronger fungicidal activities against *Botrytis cinerea* than that of Thifluzamide.

RESULTS AND DISCUSSION

Chemistry. The synthesis scheme shown in Figure 3 provides moderate to high yields of the test compounds. The structures of all synthesized compounds were analyzed and confirmed by ^{1}H NMR and MS. Because of the structural similarity of compounds **8**, only some representative compounds, such as **8a-1**, **8a-2**, **8a-3**, **8b-2**, and **8c-2**, were analyzed and confirmed by ^{13}C NMR

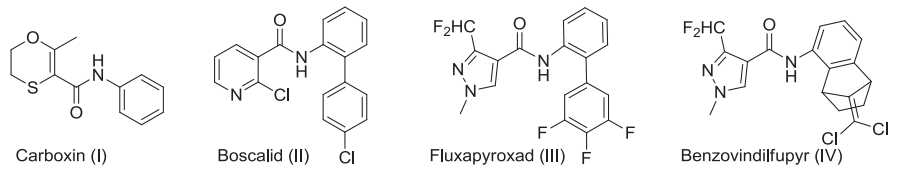


Figure 1. Carboxanilides referred to in text.

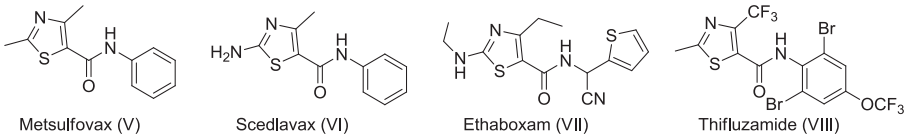


Figure 2. Thiazole carboxanilides referred to in text.

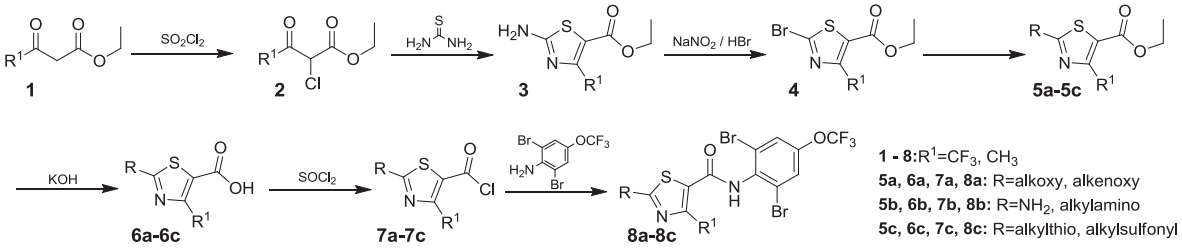


Figure 3. Synthesis pathway of thiazole carboxanilides.

and elemental analysis; **8a-2** was analyzed and confirmed by IR analysis. Table 1 summarizes the chemical structures, MS data, and physical characteristics of compounds **8.** NMR and elemental analysis data are listed in Table 2.

Because of the presence of heteroatom on the 2-position of thiazole ring, we expected to observe different δ_H of the same group in ^{1}H NMR data. When the heteroatom is oxygen, the hydrogen on 2-position of thiazole ring has the highest chemical shift value; while the heteroatom is sulfur, the hydrogen on 2-position of thiazole ring has the lowest chemical shift value. For example, $\delta_H = 4.17$ ppm for **8a-2**, $\delta_H = 3.04$ ppm for **8b-2**, and $\delta_H = 2.75$ ppm for **8c-2**.

Fungicidal activity. All compounds prepared were evaluated for initial activity against *R. solani* at 500 mg/L by typical assay above, and LC_{50} was calculated through further assay in which five to six different concentrations were used and listed in Table 1. The representative compound **8a-2** was evaluated against *B. cinerea* at 500 mg/L. The activities of Thifluzamide were also shown in Table 1.

As shown in Table 1**,** only **8a-2**, **8a-3**, and **8c-2** exhibit 100% fungicidal activity against *R. solani* at 500 mg/L, and **8a-2** has shown potent fungicidal activities when compared with commercial fungicides. For example, **8a-2** has LC_{50} (mg L^{-1}) values of 1.11 which is comparable to that of Thifluzamide.

As shown in Table 1, **8a-2** also exhibit 90% fungicidal activity against *B. cinerea* at 500 mg/L.

Apparent structure–activity relationship. The general structure of compounds **8** (Fig. 3) was optimized through R and R^1 moieties. Different choices of R and R^1 can greatly affect fungicidal activity (Table 1).

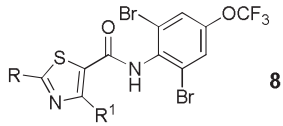
When R was kept OCH_3, the fungicidal activity against *R. solani* was influenced by the nature of the R^1 group. Changing the R^1 group from methyl to trifluoromethyl increased the fungicidal activity. For example, the fungicidal activities of **8a-2** were much stronger than that of **8a-1**.

When R^1 was kept CF_3, the fungicidal activity against *R. solani* was influenced by the nature of the R group. Changing the R group from 2-alkoxy to 2-alkylthio slightly reduced the fungicidal activity; changing the R group from 2-alkoxy or 2-alkylthio to 2-alkylamino reduced the fungicidal activity. For example, the fungicidal activities were correlated as following: **8b-2** $<<$ **8c-2** $<$ **8a-2**. For 2-substituted analogues, the results in Table 1 showed that a C_1 saturated chain alkyl was required for the development of optimal fungicidal activity. As the chain length increased, the fungicidal activities of corresponding compounds decreased: **8a-2** $>$ **8a-3** $>>$ **8a-4**, **8a-5**, **8a-6**, **8a-7**.

For R^1=CF_3, R=OCH_3, the resulting compound **8a-2** showed the highest activity among compounds **8**, and it possessed comparable levels of fungicidal activity to that of Thifluzamide.

Table 1

Chemical structures, MS, physical characteristics, fungicidal activity (%) against *Rhizoctonia solani*, and *Botrytis cinerea* at 500 mg/L and LC_{50} (mg/L) of compounds **8.**



8

						Botrytis cinerea	*Rhizoctonia solani*			
No.	R^1	R	Formula	MS	mp (°C)	500 mg/L	500 mg/L	Regression equation	*r*	LC_{50}
8a-1	CH_3	OCH_3	$C_{13}H_9Br_2F_3N_2O_3S$	488	158.2–162.7	—[a]	10.0	—	—	>500
8a-2	CF_3	OCH_3	$C_{13}H_6Br_2F_6N_2O_3S$	542	184.7–185.9	90	100	Y = 4.9277 + 1.5918x	0.9629	1.11
8a-3	CF_3	OCH_2CH_3	$C_{14}H_8Br_2F_6N_2O_3S$	556	165.9–166.5	—	100	Y = 4.7866 + 0.5326x	0.8455	2.52
8a-4	CF_3	$OCH_2CH_2CH_3$	$C_{15}H_{10}Br_2F_6N_2O_3S$	570	131.0–132.4	—	15.7	—	—	>500
8a-5	CF_3	$OCH(CH_3)_2$	$C_{15}H_{10}Br_2F_6N_2O_3S$	570	133.8–136.4	—	11.1	—	—	>500
8a-6	CF_3	$O(CH_2)_3CH_3$	$C_{16}H_{12}Br_2F_6N_2O_3S$	584	Viscous solid	—	11.1	—	—	>500
8a-7	CF_3	$OCH_2CH=CH_2$	$C_{15}H_8Br_2F_6N_2O_3S$	568	Viscous solid	—	3.43	—	—	>500
8b-1	CF_3	NH_2	$C_{12}H_5Br_2F_6N_3O_2S$	527	243.0–246.3	—	46.8	—	—	≈500
8b-2	CF_3	$NHCH_3$	$C_{13}H_7Br_2F_6N_3O_2S$	541	273.0–273.2	—	0	—	—	>500
8c-1	CH_3	SCH_3	$C_{13}H_9Br_2F_3N_2O_2S_2$	504	164.0–165.6	—	50.0	—	—	≈500
8c-2	CF_3	SCH_3	$C_{13}H_6Br_2F_6N_2O_2S_2$	558	181.0–181.3	—	100	Y = 4.3562 + 1.2359x	0.9902	3.32
Thifluzamide						65	100	Y = 5.5993 + 1.5733x	0.9934	0.42

[a]No test.

Table 2

^{1}H NMR data of the synthesized 2-heteroatomthiazole-based carboxanilides.

No.	^{1}H NMR ($CDCl_3$ or DMSO, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm; elemental analysis; IR (KBr)
8a-1	^{1}H NMR ($CDCl_3$): 2.662 (s, 3H, CH_3), 4.128 (s, 3H, CH_3), 7.010 (bs, 1H, NH), 7.526 (d, J = 0.9 Hz, 2H, Ph H); ^{13}C NMR ($CDCl_3$): 17.76, 58.82, 114.90, 116.58, 118.36, 121.81, 123.94, 124.78, 133.51, 147.80, 153.92, 159.95, 174.33; Anal. Calcd. for $C_{13}H_9Br_2F_3N_2O_3S$: C31.86, H 1.85, N 5.72; found: C 31.69, H 1.82, N 5.79.
8a-2	^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.171 (s, 3H, CH_3), 7.521 (s, 2H, Ph H), 7.669 (s, 1H, NH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 59.31, 118.04, 118.36, 121.65, 121.81, 123.98, 124.87, 125.00, 126.16, 132.61, 148.28, 156.80, 175.04; calc for $C_{13}H_6Br_2F_6N_2O_3S$: C 28.70, H 1.11, N 5.15; found: C 28.62, H 1.15, N 5.12; IR (KBr) cm^{-1}: 1653 (C=O), 3204 (NH).
8a-3	^{1}H NMR($CDCl_3$): 1.475 (t, J = 7.1 Hz, 1H, CH_3), 4.533–4.604 (q, J = 7.1 Hz, 2H, CH_2), 7.529 (d, J = 0.9 Hz, 2H, Ph H), 7.578 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): 14.21, 69.18, 118.02, 118.35, 121.63, 121.80, 124.00, 124.80, 125.24, 125.82, 132.65, 148.20, 156.93, 174.47; calc for $C_{14}H_8Br_2F_6N_2O_3S$: C 30.13, H 1.44, N 5.02; found: C 30.09, H 1.38, N 5.11.
8a-4	^{1}H NMR($CDCl_3$): 1.043 (t, J = 7.5 Hz, 3H, CH_3), 1.804–1.922 (m, 2H, CH_2), 4.462 (t, J = 6.6 Hz, 2H, CH_2), 7.527 (s, 2H, Ph H), 7.536 (s, 1H, NH).
8a-5	^{1}H NMR($CDCl_3$): 1.447 (d, J = 6.0 Hz, 6H, 2*CH_3), 5.268–5.351 (m, 1H, CH), 7.516 (d, J = 1.2 Hz, 2H, Ph H), 7.581 (s, 1H, NH).
8a-6	^{1}H NMR($CDCl_3$): 0.986 (t, J = 7.4 Hz, 3H, CH_3), 1.420–1.545 (m, 2H, CH_2), 1.767–1.861 (m, 2H, CH_2), 4.504 (t, J = 6.5 Hz, 2H, CH_2), 7.529 (s, 2H, Ph H), 7.533 (s, 1H, NH).
8a-7	^{1}H NMR($CDCl_3$): 4.987–5.014 (m, 2H, CH_2), 5.368–5.521 (m, 2H, CH_2), 5.996–6.127 (m, 1H, CH), 7.528 (s, 2H, Ph H), 7.559 (s, 1H, NH).
8b-1	^{1}H NMR(DMSO): 7.840 (s, 2H, NH_2), 7.896–7.940 (m, 2H, Ph H), 10.301(s, 1H, NH); ^{13}C NMR(DMSO): 14.21, 69.18, 118.02, 118.35, 121.63, 121.80, 124.00, 124.80, 125.24, 125.82, 132.65, 148.20, 156.93, 174.47; 118.02, 118.35, 121.44, 121.81, 124.32, 125.26, 135.05, 147.30, 156.38, 157.45, 160.98, 168.54.
8b-2	^{1}H NMR(DMSO): 3.048 (s, 3H, CH_3), 7.500 (s, 1H, NH), 7.525 (s, 2H, Ph H); ^{13}C NMR(DMSO): 30.90, 117.80, 118.02, 118.29, 121.44, 121.90, 124.85, 125.12, 125.24, 135.04, 147.09, 157.56, 168.93; Anal. Calcd. for $C_{13}H_7Br_2F_6N_3O_2S$: C 28.75, H 1.30, N 7.74; found: C 28.82, H 1.22, N 7.86.
8c-1	^{1}H NMR($CDCl_3$): 2.724 (s, 3H, CH_3), 2.748 (s, 3H, CH_3), 7.136 (bs, 1H, NH), 7.527 (d, J = 0.9 Hz, 2H, Ph H).
8c-2	^{1}H NMR($CDCl_3$): 2.758 (s, 3H, CH_3), 7.535 (d, J = 0.9 Hz, 2H, Ph H), 7.573 (s, 1H, NH); ^{13}C NMR: 16.59, 118.04, 118.34, 121.66, 121.79, 124.00, 124.83, 125.27, 125.30, 132.47, 148.30, 156.50, 171.56; Anal. Calcd. for $C_{13}H_6Br_2F_6N_2O_2S_2$: C 27.88, H 1.08, N 5.00; found: C 27.79, H 1.02, N 4.96.

In general, for compounds **8**:

Activity order of R^1: $CF_3 > > CH_3$.

Activity order of R: $OCH_3 > SCH_3 > OCH_2CH_3 > > NH_2$, $SO_2CH_3 > > OCH(CH_3)_2$, $OCH_2CH_2CH_3$, $O(CH_2)_3CH_3$, $OCH_2CH{=}CH_2$, $NHCH_3$.

CONCLUSION

The above results demonstrate that besides methyl group in Thifluzamide (*6*), a methoxy group on the 2-position of the thiazole ring is also viable for the development of optimal fungicidal activity. Further studies on the biological activity and structure–activity relationships of this series of compounds are in progress.

EXPERIMENTAL

Unless otherwise noted, reagents and solvents were used as received from commercial suppliers. NMR spectra were obtained with a Varian INOVA-300 spectrometer using tetramethylsilane (TMS) as the internal standard and deuteriochloroform ($CDCl_3$) or deuteriodimethylsulfoxide (DMSO) as the solvent. LC-MS were recorded with an Agilent 1260/6120 Series and GC-MS with an Agilent 7890-5975C Series. Uncorrected melting points were taken in a WRS-1A digital melting points apparatus. Elemental analyses were obtained with a Vario EL III from Elementar.

Synthesis. The general synthetic methods for the target compounds **8** are shown in Figure 3. Representative procedures are given below. Yields were not optimized. All reactions were carried out under a protective atmosphere of dry nitrogen or utilizing a calcium chloride tube.

Ethyl 2-chloro-4,4,4-trifluoro-3-oxobutanoate (2). Sulfuryl dichloride (1.05 mol) was added dropwise to ethyl 4,4,4-trifluoro-3-oxobutanoate (0.95 mol) at room temperature. The reaction was stirred overnight at the same temperature. Ethyl 2-chloro-4,4,4-trifluoro-3-oxobutanoate **(2)** was obtained after the extra sulfuryl dichloride was removed, yield 94.7%.

Ethyl 2-amino-4-(trifluoromethyl)thiazole-5-carboxylate (3). The mixture of compound **2** (0.18 mol) and thiourea (0.18 mol) in ethanol (200 mL) was heated under reflux for 4–6 h. The reaction mixture was cooled to room temperature and poured into ice water to give ethyl 2-amino-4-(trifluoromethyl)thiazole-5-carboxylate **(3)** as a solid which was collected by suction filtration and dried, yield 88.5%.

Ethyl 2-bromo-4-(trifluoromethyl)thiazole-5-carboxylate (4). To the mixture of compound **3** (0.16 mol) and hydrobromide (40%, 120 mL) in water (100 mL), sodium nitrite (0.18 mol) in water (30 mL) was added dropwise at −5–0°C. The reaction mixture was stirred for 2–3 h at the same temperature, then for 1 h at room temperature followed by being poured into ice water to give ethyl 2-bromo-4-(trifluoromethyl)thiazole-5-carboxylate **(4)** as a solid which was collected by suction filtration and dried, yield 79.8%.

Ethyl 2-methoxy-4-(trifluoromethyl)thiazole-5-carboxylate (5). The mixture of compound **4** (0.10 mol) and sodium methanolate (30%, 0.14 mol) in tetrahydrofuran (120 mL) was heated under reflux for 2.5–3.5 h. The reaction mixture was cooled to room temperature and then poured into ice water followed by extraction with ethyl acetate. The combined organic layer was dried and evaporated to give ethyl 2-methoxy-4-(trifluoromethyl)thiazole-5-carboxylate **(5)** which was used directly without purification.

2-Methoxy-4-(trifluoromethyl)thiazole-5-carboxylic acid (6) and 2-methoxy-4-(trifluoromethyl)thiazole-5-carboxylic acid chlorode (7). The thiazole carboxylic acid **(6)** was synthesized by base hydrolysis of the corresponding ethyl ester **(5)**. The thiazole acid chloride **(7)** was synthesized from the corresponding carboxylic acid **(6)** and excess (1.2 equivalents) sulfurous dichloride in toluene under reflux. After 4–6 h, the excess sulfurous dichloride and toluene were removed to yield the acid chloride **(7)** which was used directly without purification.

N-(2,6-dibromo-4-(trifluoromethoxy)phenyl)-4-methoxy-2-(trifluoromethyl)thiazole-5-carboxamide (8a-2). To the mixture of 2,6-dibromo-4-(trifluoromethoxy)aniline (0.010 mol) and xylene (20 mL), the compound **7** (0.010 mol) in xylene (5 mL) was added dropwise at room temperature. The reaction mixture was stirred for 3–5 h at 90–100°C. The reaction mixture was cooled to room temperature and poured into ice water followed by extraction with ethyl acetate. The combined organic layer was dried with anhydrous sodium sulfate. After the solvent was removed, the crude product was separated by silica-gel column chromatography using petroleum ether and ethyl acetate (50:1 to 20:1 by volume) as eluant to give 98.6% (HPLC) **8a-2** as a white solid 3.08 g, yield 56.8%. IR (KBr) cm^{-1}: 1653 (C=O), 3204 (NH); GC-MS (EI, 70Ev) (m/z) 465 (30% $M^+ - 79 + 2$), 463 (30% $M^+ - 79$), 210 (100% $M^+ - 332$); calc for $C_{13}H_6Br_2F_6N_2O_3S$: C 28.70, H 1.11, N 5.15; found: C 28.62, H 1.15, N 5.12; ^1H NMR ($CDCl_3$, 300 MHz) δ: 4.171 (s, 3H, CH_3), 7.521 (s, 2H, Ph H), 7.669 (s, 1H, NH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 59.31, 118.04, 118.36, 121.65, 121.81, 123.98, 124.87, 125.00, 126.16, 132.61, 148.28, 156.80, 175.04.

The synthesis of **8a-1, 8a-3 – 8a-7, 8b-1 – 8b-2,** and **8c-1 – 8c-2** with ≥95.0% purity (HPLC) was similar to that of **8a-2**, and **th**eir structures were supported by spectroscopic data in Tables 1 and 2.

Biological assay [11–15]

Test compounds. Stock solution of every test compound was prepared in DMF at a concentration of 1.0 g L^{-1}, and then diluted to the required test

concentrations (0.10–200 mg L^{-1}) with water containing Tween 80 (0.002 g L^{-1}).

***The activity against R. solani* or *B. cinerea*.** Cucumber plants were grown under greenhouse conditions (T = 22° C, 60 (±5)% relative humidity and a 12-h light cycle). Plants were maintained in plastic pots (6-cm diameter × 10 cm). Test compound solutions were sprayed over the plants. One day later plants were inoculated by a spore suspension of *R. solani* or *B. cinerea* (1.0×10^5 spores mL^{-1}). One or two weeks later the symptoms were examined. Each bioassay was conducted in triplicate, and the biological effect was reported as the average of the triplicates. The dose–response data were analyzed by probit analysis as described by Bliss [16], and the activities were evaluated as EC_{50} values (95% FL).

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