



Synthesis of Silicon-Containing Azole Derivatives with Magnesium Bromide Diethyl Etherate, and an Investigation of Their Fungicidal Activities

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Abstract—Enhancement of magnesium bromide diethyl etherate in addition reaction of trimethylsilylmethylmagnesium chloride **5** to 2-(1*H*-1,2,4-triazol-1-yl)acetophenones **6** allowed us to prepare silicon-containing azole derivatives, which were tested for fungicidal activity and phytotoxicity. Among them, 2-(4-fluorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)-3-trimethylsilylpropan-2-ol **1a** was determined to be the most effective and potential candidate for novel fungicide.

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Introduction

In the course of our research on azole fungicides, we synthesized a series of silicon-containing azole derivatives **1** and found that they exerted a remarkably potent activity against rice sheath blight in submerged application.¹ However, the low yields of **1** discourage us to allow any further evaluation.

Azole fungicides inhibit the fungal biosynthesis of ergosterol, an important constituent of fungal cell membrane, and this has led to their use for the control of a wide range of diseases.² Most of the azole fungicides have been developed for diseases on cereal crops, such as cyproconazole³ and tebuconazole⁴ for powdery mildew on cereal, and epoxiconazole⁵ and flusilazole⁶ for rust on cereal as shown in Figure 1. These situations prompted us to evaluate the synthesized derivatives for fungicidal activity against powdery mildew on cereal.

Powdery mildew on cereal is a disease caused by *Erysiphe graminis*. The fungus belongs to filamentous fungi, which contain ergosterol in their cell membrane. On the other hand, rice blast and rice sheath blight, which are devastating diseases to rice plant, caused by filamentous

fungi, *Pyricularia oryzae* and *Rhizoctonia solani*, respectively. Because these fungi also contain ergosterol in their cell membrane, azole fungicides were expected to show efficacy against these diseases on rice plant. Contrary to expectation, no azole fungicides were used for these diseases. Commercial azole fungicides were observed phytotoxicity for rice plant by our tests. It may be the reason why there have been no azole fungicides developed for rice plant so far. When we try to test the actions of the azole derivatives on rice plant, the phytotoxicity must be checked at the same time.

Disclosed herein is a convenient and efficient method to synthesize the silicon-containing azole derivatives and their evaluation for fungicidal activities against rice blast, rice sheath blight and powdery mildew on barley together with phytotoxicity.

Chemistry

The general synthetic method⁷ to prepare azole compounds such as **3** was to open the epoxides **2** with 1,2,4-triazole. However, under these conditions, our derivatives **1** were easily decomposed into allyl compounds **4**¹ (Fig. 2).

The addition of organometallic reagents to a (1-*H*-1,2,4-triazol-1-yl)acetophenone was attempted in special

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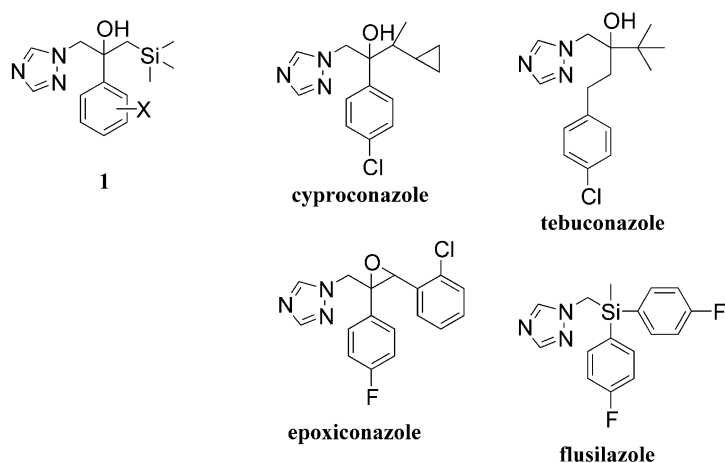


Figure 1. Silicon-containing azole derivatives **1** and other azole fungicides.

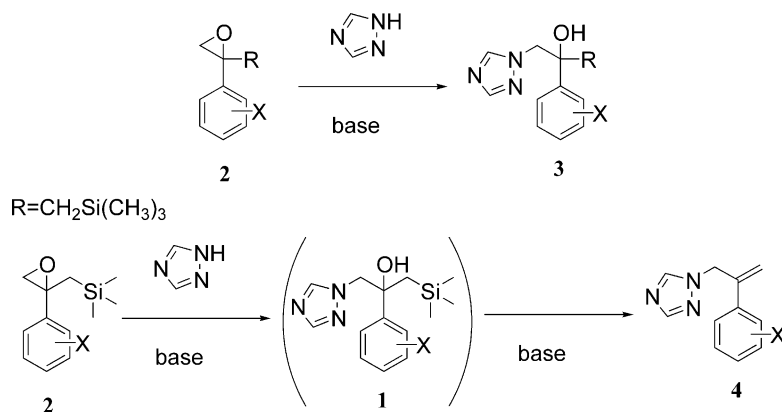


Figure 2. General synthetic method to prepare azole compound.

cases. For example, Chollet et al. reported the additions of alkenylaluminum halide and alkenylzinc halide to the acetophenones,⁸ and Dickinson et al. and Eto et al. reported the addition of heteroaralkyllithium.⁹

In our previous study,¹ we synthesized compounds **1** by adding trimethylsilylmethyl Grignard reagent **5** to (1H-1,2,4-triazol-1-yl)acetophenones **6** (Fig. 3). Regrettably, the compounds were formed in very low yields no matter how we varied the temperature, concentration of the Grignard reagent, and the ratio of the Grignard reagent and the acetophenone. On the other hand, the Grignard reaction with 2-(imidazol-1-yl)acetophenone **7** produced compounds **8** in fair yields (Fig. 4, Table 1).

Based on these observations, we presumed that the 2-nitrogen atom on the 1H-1,2,4-triazole ring is attributable to the failure of the Grignard reaction with **6**. A tentative explanation is that the magnesium atom of the Grignard reagent forms a chelate with the 2-nitrogen atom on the 1H-1,2,4-triazole ring (Fig. 5). The formation of this complex could facilitate deprotonation of the acetophenone to give the enolate species. Based on this hypothesis, we added the Grignard reagent **5** to **6** in the presence of magnesium bromide diethyl etherate¹⁰ in the hope that the magnesium ion would prevent the formation of such a chelate and increase the amount of the desired product.

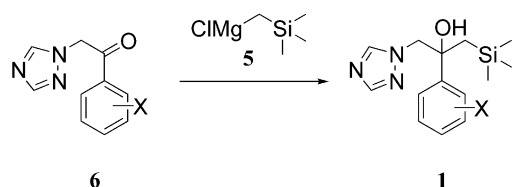


Figure 3. Silicon-containing triazole compounds prepared by the Grignard reaction.

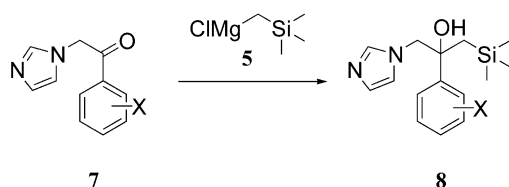
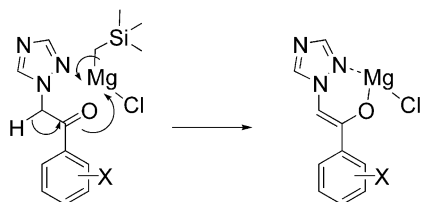


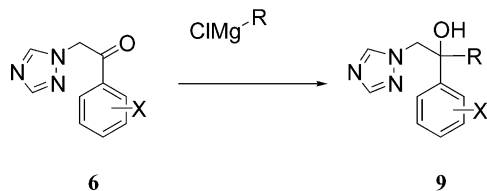
Figure 4. Silicon-containing imidazole compounds prepared by the Grignard reaction.

Table 1. Synthesis of imidazole derivatives **8**

Entry no.	X	8	
		Yield (%)	mp (°C)
a	4-F	74 ^a	123 ^a
b	4-Cl	84	108–10
c	2,4-Cl ₂	59	125–127
d	2,4-F ₂	97	112–114
e	H	93	86–87
f	4-Me	89	101

^aData from our previous work.¹**Figure 5.** Chelation by the Grignard reagent.**Table 2.** Synthesis of triazole derivatives **1**

Entry no.	X	1 Yield (%)	
		Additive (–) ^a	Additive (+)
a	4-F	7	45
b	4-Cl	7	41
c	2,4-Cl ₂	10	35
d	2,4-F ₂	16	55
e	H	15	32
f	4-Me	4	27
g	4-OMe	13	23
h	4-CF ₃	8	32
i	4-Br	11	23
j	2-F,4-Cl	6	52

^aData from our previous work.¹**Figure 6.** Triazole compounds prepared by the Grignard reaction.**Table 3.** Synthesis of triazole derivatives **9** X = 4-F

Entry no.	R	Yield (%)
a	Ethyl	70
b	Butyl	68
c	Isobutyl	39
d	Neopentyl	37

Our trial produced promising results, in which **5** reacted with the carbonyl group of **6** to give adducts **1** in better yields (Table 2). Moreover, the other aliphatic Grignard reagents also provided addition products **9** in fair yields (Fig. 6, Table 3).

Magnesium bromide diethyl etherate has the potential to work as a Lewis acid and activate the carbonyl group.¹¹ However, the use of the other Lewis acids such as aluminum chloride, zinc chloride and boron trifluoride resulted in only the recovery of the starting material.

From the results described above, we surmised that the magnesium bromide diethyl etherate improved the yields mainly by preventing the formation of chelation.

Thus, we have discovered a novel and efficient method to synthesize triazolyl derivatives from (1,2,4-triazol-1-yl)acetophenones with Grignard reagents in the presence of magnesium bromide diethyl etherate.

Fungicidal Activities and Discussion

We performed tests on the silicon-containing azole derivatives obtained by the above-described methods in order to assess their fungicidal activities against rice blast, rice sheath blight and powdery mildew of barley, and also their phytotoxicity and EC₅₀ values against the phytopathogenic fungi *P. oryzae* and *R. solani*. The results are shown in Table 4.

The data for imidazolyl derivatives **8a–8f** indicate generally low fungicidal activities. The substituted compounds on phenyl ring derivatives that appeared active in vitro were the 2,4-dichloro, 2,4-difluoro derivatives **8c** and **8d**.

On the other hand, the data for triazolyl derivatives **1a–1j** suggest that the 2-nitrogen atom on the 1*H*-1,2,4-triazole ring is critical for good activity. Compounds **1c**, **1d** and **1j** with dihalogen substitution on the phenyl ring inhibited the mycelia extension of *P. oryzae* more potently than the unsubstituted and mono-substituted compounds **1a**, **1b**, **1e**, **1f**, **1g**, **1h** and **1i**. In our in vitro tests against *R. solani*, all triazolyl derivatives were found to be highly active. Halogen-substituted derivatives applied by foliar spraying had more favorable fungicidal activities against both rice blast and powdery mildew on barley. The 4-fluoro derivative **1a** was proved to show maximum activity against rice sheath blight by submerged application. Some of the substituted compounds were nearly the same active as **1a**, but only **1a** was free of phytotoxic effects against rice plant (Table 4). This is a very important point for the development of an adequate fungicide.

Among silicon-free compounds, compounds with a straight alkyl chain **9a**, **9b** exerted weak fungicidal activities. Compounds with a branched alkyl chain **9c**, **9d** exhibited enhanced fungicidal activities but phytotoxicity was observed in these compounds.

Table 4. Fungicidal activities of azole derivatives

Compd	P.O. IC ₅₀ (ppm)	R.B. MIC (g/10a)	R.S. IC ₅₀ (ppm)	S.B. MIC (g/10a)	P.M. MIC (ppm)	Phytotoxicity
8a	6.00	30	> 10	> 100 ^a	1	nt
8b	3.53	30	> 10	> 100	1	nt
8c	0.24	30	6.50	> 100	1	nt
8d	0.27	30	6.50	> 100	1	nt
8e	6.60	30	> 10	> 100	> 3	nt
8f	> 10	30	> 10	> 100	> 3	nt
1a	1.09	3	0.04	12.5 ^a	0.3	—
1b	2.70	3	0.08	25 ^a	0.1	++
1c	0.26	> 100	0.01	> 100 ^a	nt	++
1d	0.38	3	0.02	100 ^a	> 3	++
1e	2.26	> 100	0.09	50 ^a	0.3	nt
1f	> 10	nt	0.13	> 100 ^a	3	nt
1g	> 10	> 100	nt	> 100 ^a	> 3	nt
1h	> 10	3	0.13	100 ^a	1	nt
1i	5.89	> 100	0.12	> 100 ^a	0.1	++
1j	0.76	3	0.04	50 ^a	0.3	++
9a	> 10	> 100	5.19	> 100	nt	—
9b	> 10	> 100	2.47	> 100	nt	+
9c	6.38	30	0.35	25	1	++
9d	1.82	100	0.05	25	1	++

P.O., *Pyricularia oryzae*; R.B., Rice blast; R.S., *Rhizoctonia solani*; S.B., Sheath blight; P.M., Powdery mildew; nt, not tested.

^aData from our previous work.¹

Conclusion

In conclusion, we discovered a novel and efficient method to synthesize silicon-containing triazolyl derivatives from (1,2,4-triazol-1-yl)acetophenones **6** with Grignard reagents in the presence of magnesium bromide diethyl etherate. The obtained silicon-containing azole derivatives showed broad fungicidal activities. Among them, 2-(4-fluorophenyl)-3-(1*H*-1,2,4-triazol-1-yl)-1-trimethylsilylpropan-2-ol **1a** exhibited the most promising efficacy and safety for rice plant. As a result of this work, **1a** was advanced to commercial development for the control of fungal infections of rice and other crops.

Experimental

All melting points (mp) were uncorrected. IR was recorded on a Perkin-Elmer 1600 spectrometer and ¹H NMR spectra were recorded on a Varian Gemini 200 spectrometer using tetramethylsilane as an internal standard. MS were obtained on a JEOL JMS-D300 spectrometer and a VG Auto Spec M mass spectrometer. TLC was performed on a plate of precoated with a 0.25 mm-thick layer of silica gel (E. Merck), and the spots were made visible by ultraviolet (UV) irradiation or by spraying with a solution made of 25 g ammonium molybdate and 1 g ceric sulfate in 500 mL of 10% sulfuric acid followed by heating. Silica gel (350–250 mesh, Yamamura Chemical Laboratories Co., Ltd.) was used for column chromatography and preparative TLC was carried out on a plate of precoated with a 2 mm-thick layer of silica gel (E. Merck). The following abbreviations are used hereafter: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet; br, broad.

General procedure for the Grignard reaction in the absence of magnesium bromide diethyl etherate

This general procedure used for our previous work¹ was applied to this work. A solution of trimethylsilylmethylmagnesium chloride (1.0 M) in diethyl ether (13.5 mL, 13.5 mmol) was added to a solution of acetophenones (2.7 mmol) in diethyl ether (60 mL). After stirring for 0.5 h, the mixture was refluxed for 6 h, poured into ice, quenched with an aqueous solution of ammonium chloride, and extracted with ethyl acetate. After drying over magnesium sulfate and evaporation of the solvent, the residue was purified by chromatography and crystallized from diisopropyl ether.

The same general method was used to prepare the derivatives described below. The yields are given in Table 1.

2-(4-Chlorophenyl)-1-(imidazol-1-yl)-3-trimethylsilylpropan-2-ol (8b). Mp 173–174 °C. IR (KBr) cm⁻¹: 2957, 2700, 1592, 1511, 1491, 1431, 1411, 1289, 1247, 1226, 1178, 1090. ¹H NMR (200 MHz, CDCl₃) δ: -0.17 (9H, s), 1.19 (1H, d, *J* = 14.8 Hz), 1.39 (1H, d, *J* = 14.8 Hz), 4.09 (2H, s), 6.66 (1H, s), 6.92 (1H, s), 7.25 (1H, s), 7.29–7.35 (4H, m). MS *m/z*: 309 (M⁺), 293, 227, 219, 137. Anal. calcd for C₁₅H₂₁N₂OClSi: C, 58.33; H, 6.85; N, 9.07. Found: C, 58.38; H, 6.65; N, 9.08.

2-(2,4-Dichlorophenyl)-1-(imidazol-1-yl)-3-trimethylsilylpropan-2-ol (8c). Mp 154–156 °C. IR (KBr) cm⁻¹: 3141, 2948, 2892, 1588, 1551, 1511, 1463, 1435, 1287, 1247, 1235, 1110. ¹H NMR (200 MHz, CDCl₃) δ: -0.18 (9H, s), 1.08 (1H, d, *J* = 15.1 Hz), 2.12 (1H, d, *J* = 15.1 Hz), 4.30 (1H, d, *J* = 14.3 Hz), 4.64 (1H, d, *J* = 14.3 Hz), 6.74 (1H, s), 6.89 (1H, s), 7.21 (1H, dd, *J* = 2.2, 8.6 Hz), 7.34 (1H, s), 7.40 (1H, d, *J* = 2.2 Hz), 7.63 (1H, d, *J* = 8.6 Hz). MS *m/z*: 343 (M⁺), 327, 253, 171. Anal. calcd for

$C_{15}H_{20}N_2OCl_2Si$: C, 52.48; H, 5.87; N, 8.16. Found: C, 52.48; H, 5.60; N, 8.26.

2-(2,4-Difluorophenyl)-1-(imidazol-1-yl)-3-trimethylsilylpropan-2-ol (8d). Mp 147–148 °C. IR (KBr) cm^{-1} : 3122, 2957, 2900, 1620, 1596, 1515, 1499, 1431, 1415, 1283, 1271, 1247, 1231, 1130, 1094, 1078. 1H NMR (200 MHz, $CDCl_3$) δ : –0.19 (9H, s), 1.12 (1H, d, $J=15.0$ Hz), 1.64 (1H, d, $J=15.0$ Hz), 4.19 (1H, d, $J=14.2$ Hz), 4.31 (1H, d, $J=14.2$ Hz), 6.742–6.89 (4H, m), 7.38–7.50 (2H, m). MS m/z : 310 (M^+), 295, 229, 131. Anal. calcd for $C_{15}H_{20}F_2N_2OSi$: C, 58.04; H, 6.49; N, 9.02. Found: C, 58.02; H, 6.44; N, 9.19.

1-(Imidazol-1-yl)-2-phenyl-3-trimethylsilylpropan-2-ol (8e). Mp 178–179 °C. IR (KBr) cm^{-1} : 2957, 2707, 1596, 1511, 1443, 1407, 1343, 1283, 1247, 1190, 1108, 1078. 1H NMR (200 MHz, $CDCl_3$) δ : –0.20 (9H, s), 1.19 (1H, d, $J=14.7$ Hz), 1.42 (1H, d, $J=14.7$ Hz), 4.09 (1H, d, $J=14.0$ Hz), 4.17 (1H, d, $J=14.0$ Hz), 6.64 (1H, s), 6.90 (1H, s), 7.23 (1H, s), 7.29–7.35 (5H, m). MS m/z : 275 (M^+), 259, 193, 185, 103. Anal. calcd for $C_{15}H_{22}N_2OSi$: C, 65.65; H, 8.08; N, 10.21. Found: C, 65.61; H, 8.11; N, 10.23.

1-(Imidazol-1-yl)-2-(4-methylphenyl)-3-trimethylsilylpropan-2-ol (8f). Mp 172–173 °C. IR (KBr) cm^{-1} : 3144, 2956, 1511, 1428, 1400, 1283, 1244, 1111, 1078. 1H NMR (200 MHz, $CDCl_3$) δ : –0.19 (9H, s), 1.17 (1H, d, $J=14.7$ Hz), 1.41 (1H, d, $J=14.7$ Hz), 2.34 (3H, s), 4.06 (1H, d, $J=15.0$ Hz), 4.14 (1H, d, $J=15.0$ Hz), 6.67 (1H, s), 6.93 (1H, s), 7.11–7.22 (5H, m). MS m/z : 288 (M^+), 273, 207, 199, 117. Anal. calcd for $C_{16}H_{24}N_2OSi$: C, 66.62; H, 8.39; N, 9.71. Found: C, 66.88; H, 8.14; N, 9.84.

General procedure for the Grignard reaction in the presence of magnesium bromide diethyl etherate

A solution of (1*H*-1,2,4-triazol-1-yl)acetophenone (1.5 mmol) in dichloromethane (2.0 mL) was added to a suspension of magnesium bromide diethyl etherate (775 mg, 3.0 mmol) in dichloromethane (3.0 mL) and diethyl ether (3 mL) at room temperature and stirred for 0.5 h. A solution of trimethylsilylmethylmagnesium chloride (1.5 M) in diethyl ether (2.0 mL, 3.0 mmol) was added at 0 °C. After stirring for 0.5 h, the mixture was poured into ice, quenched with an aqueous solution of ammonium chloride, and extracted with ethyl acetate. The organic layer was washed with water and dried over magnesium sulfate. The solvent was then evaporated, and the solid remaining was partitioned between toluene and 1 N HCl. The organic layer was washed with water and concentrated to yield a residue, and this residue was purified by chromatography and crystallized from diisopropyl ether. The yields are given in Table 3.

The same general method was used to prepare the derivatives described below.

2-(4-Fluorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)butan-2-ol (9a). Mp 94–96 °C. IR (KBr) cm^{-1} : 3205, 3110, 2970, 2931, 1602, 1521, 1460, 1415, 1286, 1217, 1163, 1134, 1099, 1016. 1H NMR (200 MHz, $CDCl_3$) δ : 0.80 (3H, t,

$J=7.6$ Hz), 1.75 (1H, dt, $J=7.6, 14.3$ Hz), 1.90 (1H, dt, $J=7.6, 14.3$ Hz), 4.37 (1H, d, $J=14.3$ Hz), 4.45 (1H, d, $J=14.3$ Hz), 7.00 (2H, t, $J=8.7$ Hz), 7.28 (2H, dd, $J=5.3, 8.7$ Hz), 7.84 (1H, s), 7.88 (1H, s). MS m/z : 235 (M^+), 206, 164, 123, 109. Anal. calcd for $C_{12}H_{14}FN_3O$: C, 61.26; H, 6.00; N, 17.86. Found: C, 61.41; H, 5.97; N, 17.71.

2-(4-Fluorophenyl)-4-methyl-1-(1*H*-1,2,4-triazol-1-yl)pentan-2-ol (9c). Mp 126–129 °C. IR (KBr) cm^{-1} : 3190, 2958, 2873, 1606, 1512, 1425, 1357, 1224, 1207, 1141, 1031. 1H NMR (200 MHz, $CDCl_3$) δ : 0.68 (3H, d, $J=6.3$ Hz), 0.92 (3H, d, $J=6.3$ Hz), 1.53–1.70 (2H, m), 1.80–1.88 (1H, m), 4.04 (1H, s), 4.31 (1H, d, $J=14.0$ Hz), 4.40 (1H, d, $J=14.0$ Hz), 6.99 (2H, t, $J=8.5$ Hz), 7.31 (2H, dd, $J=5.5, 8.5$ Hz), 7.79 (1H, s), 7.89 (1H, s). MS m/z : 263 (M^+), 206, 181, 164, 139, 121, 109. Anal. calcd for $C_{14}H_{18}FN_3O$: C, 63.86; H, 6.89; N, 15.96. Found: C, 63.90; H, 6.87; N, 15.70.

4,4-Dimethyl-2-(4-fluorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)pentan-2-ol (9d). Mp 129–133 °C. IR (KBr) cm^{-1} : 3184, 2954, 2858, 1604, 1515, 1361, 1277, 1209, 1143, 1124, 1022. 1H NMR (200 MHz, $CDCl_3$) δ : 0.79 (9H, s), 1.72 (1H, d, $J=14.5$ Hz), 1.95 (1H, d, $J=14.5$ Hz), 4.14 (1H, s), 4.27 (1H, d, $J=13.7$ Hz), 4.38 (1H, d, $J=13.7$ Hz), 6.96 (2H, t, $J=6.8$ Hz), 7.32 (2H, dd, $J=7.5, 8.8$ Hz), 7.73 (1H, s), 7.87 (1H, s). MS m/z : 277 (M^+), 206, 195, 164, 139, 123, 109. Anal. calcd for $C_{15}H_{20}FN_3O$: C, 64.96; H, 7.27; N, 15.15. Found: C, 64.87; H, 7.23; N, 14.93.

2-(4-Fluorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)hexan-2-ol (9b). Mp 94–95 °C. IR (KBr) cm^{-1} : 3178, 2921, 2864, 1604, 1510, 1461, 1427, 1276, 1220, 1136, 1089, 1031. 1H NMR (200 MHz, $CDCl_3$) δ : 0.82 (3H, t, $J=7.0$ Hz), 1.04 (1H, m), 1.15–1.32 (3H, m), 1.68 (1H, m), 1.83 (1H, m), 4.00 (1H, s), 4.36 (1H, d, $J=14.3$ Hz), 4.44 (1H, d, $J=14.3$ Hz), 6.99 (2H, t, $J=7.7$ Hz), 7.30 (2H, dd, $J=3.5, 7.7$ Hz), 7.83 (1H, s), 7.87 (1H, s). MS m/z : 263 (M^+), 206, 191, 164, 149, 138, 123, 109. Anal. calcd for $C_{14}H_{18}FN_3O$: C, 63.86; H, 6.89; N, 15.96. Found: C, 63.80; H, 6.80; N, 15.93.

Silicon-containing azole derivatives (**1a–1j**) were obtained in the same way. The yields are given in Table 2.

Antifungal activity

Four-millimeter mycelial agar discs were placed on potato dextrose agar plates containing test compounds. The plates were incubated at 25 °C for 7 days as for a test of *P. oryzae* or 3 days as for a test of *R. solani*, and the diameters of the mycelium colonies were then measured to examine the effects of the chemicals on fungal growth. The results are shown in Table 4.

Curative activity against rice blast

Rice seedlings (variety Sachikaze) at the 4–5 leaf stage were sprayed with a spore suspension of the fungus *P. oryzae* and kept in a moist chamber (relative humidity: 100%) at 20–22 °C. After 24 h, the rice seedlings were

sprayed with aqueous suspensions of the test compound at different concentrations. Placed back in the moist chamber. The concentration with the highest efficacy against rice sheath blight was identified after 6 days. The results are shown in Table 4.

Preventive activity against rice sheath blight by submerged application

Rice seedlings (variety Nipponbare) at the 3–4 leaf stage were flooded to a depth of 1 cm with water in pots, and then the test compound was applied to the water. After keeping the seedlings in a greenhouse for 7 days, 4–5 oat grains cultured with *R. solani* were placed around the base of each seedling. The seedlings were then kept in a moist chamber (relative humidity: 100%) for 5 days at 25–27 °C. The number of grams per 10 acres required to eradicate rice sheath blight was determined after 5 days. The results are shown in Table 4.

Curative activity against powdery mildew of barley

Barley seedlings (variety Sekishinriki) at the first leaf stage were inoculated with conidia of *Erysiphe graminis* f. sp. *hordei* by sprinkling spores of the fungus on the seedlings. After being kept in a greenhouse at 15–50 °C for 1 day, the seedlings were sprayed with an aqueous suspension of the test compound and kept in the greenhouse at the same temperature for 10 more days. On the 10th day, the most effective concentration against powdery mildew of barley was determined. The results are shown in Table 4.

Phytotoxicity test

Plastic pots (surface area 25 cm²) were filled with a clay loam soil and kept in a greenhouse. Rice seedlings that had reached the two-leaf stage were transplanted into the pots. After one day, the seedlings were sprayed with an aqueous suspension (500 g/10a) of the test compound and kept in the greenhouse at the same temperature. After 21 days, the phytotoxicity of each compound was judged by visual observation of the symptoms of the treated plants in comparison with untreated controls. Using the following criteria, the phytotoxicity was scored from ++ to – based on the extent of plant growth inhibition: ++, more than 30%

of growth inhibition; +, from 10 to 30% of growth inhibition; – less than 10% of growth inhibition. The results are shown in Table 4.

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References and Notes

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