

## Synthesis and Systemic Fungicidal Activity of Silicon-Containing Azole Derivatives

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Received March 1, 2000; accepted May 12, 2000

**A new series of azole derivatives containing silicon were synthesized and evaluated for fungicidal activity against rice sheath blight by submerged application. Among them, 2-(4-fluorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)-3-trimethylsilylpropan-2-ol (9a) exhibited satisfactory efficacy at 12.5 grams per 10 ares.**

**Key words** fungicidal activity; 1*H*-1,2,4-triazole; silicon; synthesis; *Rhizoctonia solani*

The azoles, comprising 1,2,4-triazoles and imidazoles, are the largest and most commercially valuable family of fungicides for agricultural crops<sup>1)</sup> (Fig. 1, e.g. triadimenol<sup>2)</sup> **1**, hexaconazole<sup>3)</sup> **2**, flusilazole<sup>4)</sup> **3**). Azole fungicides inhibit the fungal biosynthesis of ergosterol, which is an important constituent of fungal cell membrane,<sup>5)</sup> and they are used to control a wide range of diseases in cereals, fruits, vegetables, and other agricultural products.<sup>1)</sup> Our interest in azole fungicide was sparked by the prospect of obtaining novel fungicidally active compounds for rice sheath blight, one of the most serious diseases afflicting rice crops in Japan.<sup>6)</sup> Thus for there have been no azole fungicides for controlling rice sheath blight and there is a great need for more persistent compounds possessing a novel mode of action and systemic activity in rice plants for the control of the disease.<sup>1,6)</sup> In the case of an agrochemical fungicide, the fungicide should have a systemic action, so that it may be applied indirectly to submerged crops and will be translocated throughout the plant. However, prior fungicides do not have sufficient activity. For example, flutolanil<sup>2)</sup> **4**, that is used for fungicide against rice sheath blight by submerged application, exhibits activity at high dosage (210 g/10a).

Our research began with the observation that the general structure of azole antifungals is represented as A (Fig. 2), constituting an azole ring, a substituted benzene ring, and a two-atom spacer between them. Another compound, flusilazole<sup>6)</sup> **3** (Fig. 1) is a very successful fungicide used to control powdery mildew of cereals around the world. The success of flusilazole demonstrates that a quaternary carbon atom can

be replaced with a silicon atom. Triadimenol **1** has another quaternary carbon atom as a *tert*-butyl group. Taking our earlier observation into account, the substitution of the *tert*-butyl group with the trimethylsilyl group **1** allows us to design an azole containing silicon **9**. In the literature,<sup>7)</sup> some derivatives that contain a silicon atom in part R of the general structure A are shown to have fungicidal properties. Specific examples of this are compounds **5** and **6** (Fig. 2). However, these compounds are not thoroughly optimized for activity against rice sheath blight and neither showed sufficient fungicidal activity in our evaluation system *vide infra*. In our synthetic program, new derivatives **9** containing a silicon atom in part R of the general structure A were synthesized and evaluated for fungicidal activity against rice sheath blight by submerged application.

### Synthesis

In the literature,<sup>7)</sup> compound **5** with a vinyl group adjacent to the trimethylsilyl group was synthesized by the reaction of phenacylazole **7** with organoaluminum prepared by the reaction of 1-bromoallyltrimethylsilane with aluminum and mercury(II) chloride. Simultaneously, compound **6** with an acetylene group between quaternary carbon and the silicon atom was synthesized by the reaction of phenacylazole **8** with ethynyltrimethylsilane and magnesium (Chart 1).

Using the simple trimethylsilylmethylmagnesium chloride,<sup>8)</sup> a compound easy to prepare by the reaction of chloromethyltrimethylsilane with magnesium, plans were made to prepare a new series of silicon-azoles **9** that have no sub-

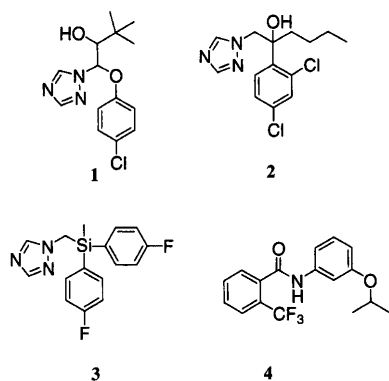


Fig. 1. Azole Fungicides and Flutolanil

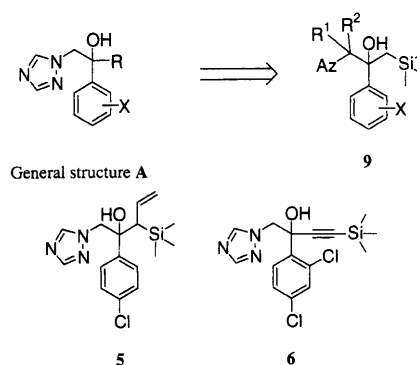


Fig. 2. General Structure of Reference Compounds **5**, **6**<sup>8)</sup> and Targeted Compound **9**

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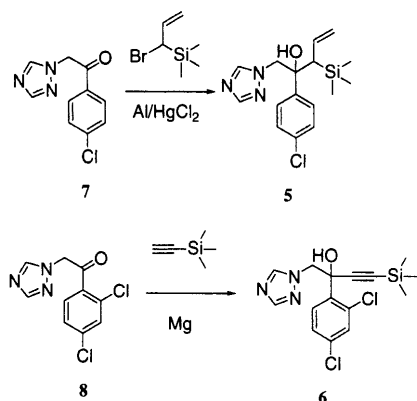


Chart 1

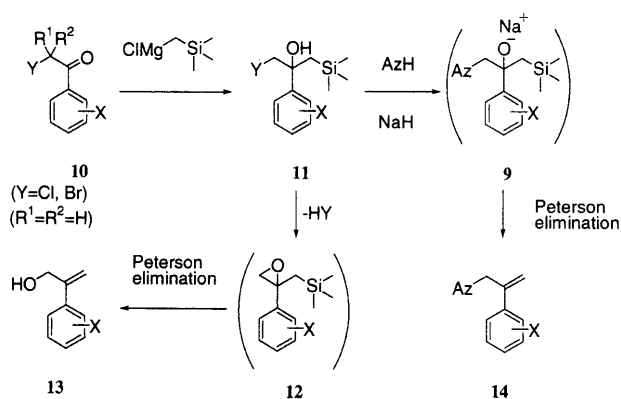


Chart 2

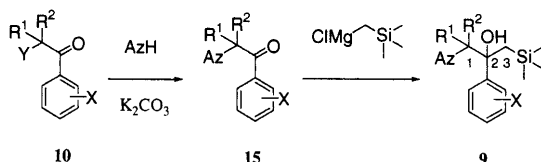


Chart 3

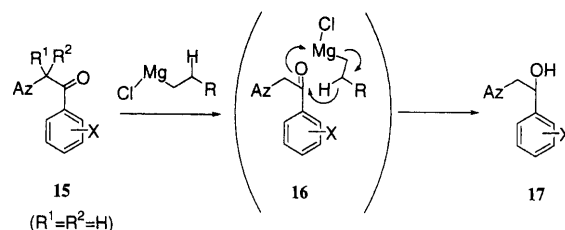


Chart 4

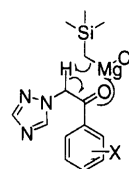


Fig. 3. The Enolization by the Grignard Reagent

of the lack of  $\beta$ -hydrogen necessary for reduction to **17**. In contrast, the majority of products **9** were given in only low yields and the unreacted starting materials **15** were almost completely recovered without side reactions. Triazole derivatives **9a–l**, **9r** and **9s** with no branch were formed in especially low yields, but an imidazole derivative **9p** was formed in a high yield. Under these conditions, a triazole ring presumably enhanced **15**, thereby facilitating enolization more readily than an imidazole ring and resulting in the recovery of the Grignard reagent (Fig. 3). Therefore, branched phenacylazoles **15m–o**, which have lower electronegativity on the  $\alpha$ -position, yielded **9m–o** in higher yields. The yields, physical data, spectroscopic data, and elementary analysis data of the derivatives **9** and **15** are summarized in Tables 1–4.

Phenacyltriazole **15a** was reacted with dimethylsulfoxonium methylide<sup>14)</sup> to prepare epoxide **18**, and then ethylenesilane **19** with an additional methylene group was synthesized by the Grignard reaction with **18** in the presence of cuprous bromide (Chart 5). Without cuprous bromide, the yield was decreased from 76% to 6%. Compounds **20** and **21**, that have a vinyl and an ethyl substituent adjacent to the silicon atom, were obtained in similar manners described in the literature<sup>8)</sup> (Chart 6).

### Systemic Fungicidal Activity and Discussion

The silicon-containing azole derivatives obtained above were examined for their fungicidal activity against rice sheath blight by submerged application in comparison with **2**, **5** and **6**. The results are shown in Table 5.

Among several mono- and di-substituted phenyl derivatives, fluorine substituent in the 4-position **9a** was more active than chlorine substituents **9b**, **9c**. Other substituents on phenyl ring **9d–j** failed to improve the activity. Moving the position of a fluorine atom around the phenyl ring demonstrated that 2- or 3-substituents **9k**, **9l** showed only moderate activities, while a 4-substituent **9a** showed markedly enhanced activity.

Once *p*-fluorophenyl was determined to be the optimum aryl group, a several kinds of azole rings in **9p–s** were investigated. As a result, the 1,2,4-triazol-1-yl group was essential for the fungicidal activity. All branched derivatives at the C-1 position **9m–o** and derivative **19** having an addi-

stituent adjacent to the trimethylsilyl group (Fig. 2). The first synthetic strategy involved addition of trimethylsilylmethylmagnesium chloride to phenacyl halides **10**, followed by substitution reaction with azoles in the presence of sodium hydride in *N,N*-dimethylformamide (shown in Chart 2). In the basic conditions, both the intermediates **11** and the target compounds **9** were easily decomposed to give styrenes **13** and **14**, respectively. The process by which this occurred was Peterson elimination and this synthetic route proved to be unsuitable for efficient synthesis of **9**. Therefore, another route was investigated as shown in Chart 3. By reversing the reaction steps, the initial treatment of **10** with azoles followed by the second reaction with trimethylsilylmethylmagnesium chloride can afford **9**. Before beginning our work, we found in our literature search that there are known Grignard reactions with azoles **15** that have an imidazole ring.<sup>9)</sup> Grignard reagents that have  $\beta$ -hydrogens have been reported to furnish little or no addition product, their predominant reaction being reduction of **15** to the secondary alcohol **17** (shown in Chart 4). On the other hand, trimethylsilylmethylmagnesium chloride was expected to undergo good conversion to **9** by virtue

Table 1. Synthesis of Phenacylazoles **15** and Silicon-Containing Azole Derivatives **9**

Entry No.	Y	X	R <sub>1</sub>	R <sub>2</sub>	Az	<b>15</b>		<b>9</b>	
						Yield (%)	mp (°C)	Yield (%)	mp (°C)
<b>a</b>	Cl	4-F	H	H	1,2,4-Triazol-1-yl	72	Ref. 10	7	118—119
<b>b</b>	Cl	4-Cl	H	H	1,2,4-Triazol-1-yl	81	Ref. 10	7	108—110
<b>c</b>	Cl	2,4-Cl <sub>2</sub>	H	H	1,2,4-Triazol-1-yl	31	Ref. 7	4	136—137
<b>d</b>	Cl	2,4-F <sub>2</sub>	H	H	1,2,4-Triazol-1-yl	27	Ref. 11	16	112—114
<b>e</b>	Br	H	H	H	1,2,4-Triazol-1-yl	64	Ref. 10	15	86—87
<b>f</b>	Cl	4-Me	H	H	1,2,4-Triazol-1-yl	89	Ref. 10	4	101
<b>g</b>	Br	4-OMe	H	H	1,2,4-Triazol-1-yl	55	Ref. 12	13	85—87
<b>h</b>	Br	4-CF <sub>3</sub>	H	H	1,2,4-Triazol-1-yl	78	117—119	8	144
<b>i</b>	Br	4-Br	H	H	1,2,4-Triazol-1-yl	53	Ref. 10	11	120—121
<b>j</b>	Cl	2-F, 4-Cl	H	H	1,2,4-Triazol-1-yl	60	136	6	129—130
<b>k</b>	Br	3-F	H	H	1,2,4-Triazol-1-yl	50	108—110	7	107—109
<b>l</b>	Br	2-F	H	H	1,2,4-Triazol-1-yl	42	106—107	14	97—98
<b>m</b>	Br	4-F	Me	H	1,2,4-Triazol-1-yl	74	Oil	58	183—184
<b>n</b>	Br	4-F	Et	H	1,2,4-Triazol-1-yl	79	50—52	91	117—118
<b>o</b>	Br	4-F	Me	Me	1,2,4-Triazol-1-yl	29	99—101	64	99—100
<b>p</b>	Cl	4-F	H	H	Imidazol-1-yl	38	Ref. 10	74	208
<b>q</b>	Cl	4-F	H	H	1,2,4-Triazol-4-yl	10*	255—256	22	273—274
<b>r</b>	Cl	4-F	H	H	1,2,3-Triazol-1-yl	57	Ref. 13	14	63—65
<b>s</b>	Cl	4-F	H	H	1,2,3-Triazol-2-yl	30*	Ref. 13	7	176—177

\*: **15q** and **15s** were by-products in the synthesis of **15a** and **15r**, respectively.

Table 2. Analytical Data of **9**

Entry No.	Formula	Calcd (%)			Found (%)		
		C	H	N	C	H	N
<b>9a</b>	C <sub>14</sub> H <sub>20</sub> FN <sub>3</sub> OSi	57.31	6.87	14.32	57.32	6.78	14.33
<b>9b</b>	C <sub>14</sub> H <sub>20</sub> ClN <sub>3</sub> OSi	54.27	6.51	13.56	54.20	6.33	13.64
<b>9c</b>	C <sub>14</sub> H <sub>19</sub> Cl <sub>2</sub> N <sub>3</sub> OSi	48.84	5.56	12.20	48.86	5.46	11.96
<b>9d</b>	C <sub>14</sub> H <sub>19</sub> F <sub>2</sub> N <sub>3</sub> OSi	54.00	6.15	13.49	54.27	6.45	13.24
<b>9e</b>	C <sub>14</sub> H <sub>21</sub> N <sub>3</sub> OSi	61.05	7.69	15.26	61.01	7.46	15.08
<b>9f</b>	C <sub>15</sub> H <sub>23</sub> N <sub>3</sub> OSi	62.24	8.01	14.52	62.14	8.08	14.82
<b>9g</b>	C <sub>15</sub> H <sub>23</sub> N <sub>3</sub> O <sub>2</sub> Si	58.98	7.59	13.76	58.99	7.61	13.72
<b>9h</b>	C <sub>15</sub> H <sub>20</sub> F <sub>3</sub> N <sub>3</sub> OSi	52.46	5.87	12.24	52.43	5.84	12.54
<b>9i</b>	C <sub>14</sub> H <sub>20</sub> BrN <sub>3</sub> OSi	47.46	5.69	11.86	47.62	5.93	11.76
<b>9j</b>	C <sub>14</sub> H <sub>19</sub> ClFN <sub>3</sub> OSi	51.29	5.84	12.82	51.50	5.83	12.58
<b>9k</b>	C <sub>14</sub> H <sub>20</sub> FN <sub>3</sub> OSi	57.31	6.87	14.32	57.33	6.65	14.57
<b>9l</b>	C <sub>14</sub> H <sub>20</sub> FN <sub>3</sub> OSi	57.31	6.87	14.32	57.25	6.83	14.48
<b>9m</b>	C <sub>15</sub> H <sub>22</sub> FN <sub>3</sub> OSi	58.60	7.21	13.67	58.30	7.03	13.58
<b>9n</b>	C <sub>16</sub> H <sub>24</sub> FN <sub>3</sub> OSi	59.78	7.53	13.07	59.88	7.42	13.13
<b>9o</b>	C <sub>16</sub> H <sub>24</sub> FN <sub>3</sub> OSi	59.78	7.53	13.07	59.57	7.58	13.06
<b>9p</b>	C <sub>15</sub> H <sub>21</sub> FN <sub>2</sub> OSi	61.61	7.24	9.58	61.31	7.44	9.86
<b>9q</b>	C <sub>14</sub> H <sub>20</sub> FN <sub>3</sub> OSi	57.31	6.87	14.32	57.02	6.56	14.60
<b>9r</b>	C <sub>14</sub> H <sub>20</sub> FN <sub>3</sub> OSi	57.31	6.87	14.32	57.38	6.70	14.10
<b>9s</b>	C <sub>14</sub> H <sub>20</sub> FN <sub>3</sub> OSi	57.31	6.87	14.32	57.11	6.75	14.34

tional methylene group reduced fungicidal activity. Two other branched derivatives at the C-3 position **20**, **21** exhibited less activity than **9a**. The reference compounds **2**, **5** and **6** were also less active than **9a**.

In summary, we have discovered a series of novel silicon-containing azole derivatives that have systemic fungicidal activity against rice sheath blight by submerged application. Most notably, 2-(4-fluorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)-3-trimethylsilylpropan-2-ol (**9a**) exhibited very promising efficacy at 12.5 grams per 10 ares and is under development as novel fungicide.

#### Experimental

All melting points (mp) were determined on a Yamato micro melting point apparatus and were uncorrected. IR was recorded on a JASCO A-102 spectrometer and <sup>1</sup>H-NMR spectra were recorded on a Varian EM-200L

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 Silica gel 60 F<sub>254</sub> precoated with a 0.25 mm-thick layer (E. Merck) and 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 plates of Silica gel 60 F<sub>254</sub> with a layer thickness of 2 mm (E. Merck). The following abbreviations are used: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet; br, broad.

**1-Chloro-2-(4-fluorophenyl)-3-trimethylsilylpropan-2-ol (11a: R<sup>1</sup>=R<sup>2</sup>=H, X=4-F, Y=Cl)** A solution of trimethylsilylmethylmagnesium chloride (1.0M) in diethyl ether (200 ml, 57.0 mmol) was added to a solution of 2-chloro-1-(4-fluorophenyl)ethanone **10a** (R<sup>1</sup>=R<sup>2</sup>=H, X=4-F, Y=Cl) (8.63 g, 50.07 mmol) in diethyl ether (60 ml). After stirring for 0.5 h, the mixture was refluxed for 1 h, poured into ice, quenched with an aqueous solution of ammonium chloride, and extracted with ethyl acetate. The organic layer was

Table 3. IR and MS Spectrum Data of **9**

Entry No.	IR (cm <sup>-1</sup> )	MS (m/z)
<b>9a</b>	3167, 3119, 2945, 1506, 1228, 1139	293 (M <sup>+</sup> ), 278, 211
<b>9b</b>	3143, 3095, 2953, 1517, 1489, 1250, 1089	309 (M <sup>+</sup> ), 294, 227, 211
<b>9c</b>	3156, 3100, 2956, 1517, 1489, 1244, 1089	344 (M <sup>+</sup> ), 326, 261, 214
<b>9d</b>	3244, 3114, 2956, 1512, 1500, 1272, 1139	312 (M <sup>+</sup> +1), 296, 229
<b>9e</b>	3143, 3119, 2956, 1506, 1456, 1244, 1133	276 (M <sup>+</sup> +1), 260, 193
<b>9f</b>	3178, 3111, 2956, 1517, 1278, 1139, 1089	289 (M <sup>+</sup> ), 274, 256, 207
<b>9g</b>	3222, 3122, 2944, 1511, 1244, 1133, 1022	305 (M <sup>+</sup> ), 290, 274, 133
<b>9h</b>	3178, 3100, 2967, 1617, 1517, 1328, 1244, 1117, 1067	344 (M <sup>+</sup> +1), 328, 261, 234, 171
<b>9i</b>	3156, 3100, 2956, 1517, 1489, 1244, 1089	355 (M <sup>+</sup> +2), 353 (M <sup>+</sup> ), 273, 257
<b>9j</b>	3167, 3100, 2956, 1606, 1517, 1483, 1394, 1250, 1094	327 (M <sup>+</sup> ), 312, 245, 155
<b>9k</b>	3189, 2956, 2900, 1589, 1511, 1278, 1250, 1206, 1139	293 (M <sup>+</sup> ), 278, 260, 211, 121
<b>9l</b>	3189, 3122, 2959, 1511, 1461, 1283, 1244, 1205, 1133	293 (M <sup>+</sup> ), 278, 211, 121
<b>9m</b>	3278, 3143, 2956, 1594, 1506, 1211, 1139, 1044	306 (M <sup>+</sup> -1), 292, 220, 211
<b>9n</b>	3245, 3197, 2967, 1600, 1506, 1228, 1217, 1139, 1017	322 (M <sup>+</sup> +1), 306, 211
<b>9o</b>	3311, 3155, 2967, 1606, 1506, 1278, 1244, 1200, 1156	322 (M <sup>+</sup> +1), 288, 207
<b>9p</b>	3134, 2956, 1605, 1506, 1222, 1111, 1084	293 (M <sup>+</sup> +1), 277, 211
<b>9q</b>	3234, 3095, 2956, 1600, 1511, 1234, 1134, 1089	294 (M <sup>+</sup> +1), 278, 211, 121
<b>9r</b>	3500, 2945, 1600, 1511, 1411, 1361, 1234, 1172	293 (M <sup>+</sup> ), 278, 211
<b>9s</b>	3189, 2956, 1600, 1506, 1422, 1222, 1083	294 (M <sup>+</sup> +1), 278, 211, 121

Table 4. <sup>1</sup>H-NMR Spectrum Data of **9**

Entry No.	<sup>1</sup> H-NMR (200 MHz), $\delta$ (ppm)
<b>9a</b>	(CDCl <sub>3</sub> ) -0.18 (9H, s), 1.16 (1H, d, <i>J</i> =14.5 Hz), 1.33 (1H, d, <i>J</i> =14.5 Hz), 4.36 (1H, d, <i>J</i> =14.0 Hz), 4.43 (1H, d, <i>J</i> =14.0 Hz), 6.97 (2H, t, <i>J</i> =8.7 Hz), 7.30 (2H, dd, <i>J</i> =5.3, 8.7 Hz), 7.91 (1H, s), 7.99 (1H, s)
<b>9b</b>	(CDCl <sub>3</sub> ) -0.19 (9H, s), 1.15 (1H, d, <i>J</i> =14.5 Hz), 1.31 (1H, d, <i>J</i> =14.5 Hz), 4.35 (2H, s), 7.17—7.33 (4H, m), 7.80 (1H, s), 7.88 (1H, s)
<b>9c</b>	(CDCl <sub>3</sub> ) -0.16 (9H, s), 1.36 (1H, d, <i>J</i> =14.5 Hz), 2.04 (1H, d, <i>J</i> =14.5 Hz), 4.60 (1H, d, <i>J</i> =14.0 Hz), 5.38 (1H, d, <i>J</i> =14.0 Hz), 7.30 (1H, dd, <i>J</i> =2.2, 8.4 Hz), 7.31 (1H, d, <i>J</i> =2.2 Hz), 7.62 (1H, d, <i>J</i> =8.4 Hz), 7.98 (1H, s), 8.04 (1H, s)
<b>9d</b>	(CDCl <sub>3</sub> ) -0.17 (9H, s), 1.23 (1H, d, <i>J</i> =14.5 Hz), 1.48 (1H, d, <i>J</i> =14.5 Hz), 4.41 (1H, d, <i>J</i> =13.7 Hz), 4.43—4.72 (1H, bs), 4.69 (1H, d, <i>J</i> =13.7 Hz), 6.69—6.79 (2H, m), 7.40—7.49 (1H, m), 7.83 (1H, s), 7.87 (1H, s)
<b>9e</b>	(CDCl <sub>3</sub> ) -0.20 (9H, s), 1.20 (1H, d, <i>J</i> =14.5 Hz), 1.41 (1H, d, <i>J</i> =14.5 Hz), 4.48 (1H, d, <i>J</i> =14.8 Hz), 4.58 (1H, d, <i>J</i> =14.8 Hz), 7.24—7.35 (5H, m), 7.97 (1H, s), 8.59 (1H, s)
<b>9f</b>	(CDCl <sub>3</sub> ) -0.19 (9H, s), 1.15 (1H, d, <i>J</i> =14.4 Hz), 1.36 (1H, d, <i>J</i> =14.4 Hz), 2.30 (3H, s), 4.35 (1H, d, <i>J</i> =14.0 Hz), 4.43 (1H, d, <i>J</i> =14.0 Hz), 7.07 (2H, dd, <i>J</i> =1.8, 8.3 Hz), 7.18 (2H, dd, <i>J</i> =1.8, 8.3 Hz), 7.90 (2H, s)
<b>9g</b>	(CDCl <sub>3</sub> ) -0.14 (9H, s), 1.72 (1H, d, <i>J</i> =14.5 Hz), 1.93 (1H, d, <i>J</i> =14.5 Hz), 3.81 (3H, s), 4.11 (1H, d, <i>J</i> =11.9 Hz), 4.33 (1H, d, <i>J</i> =11.9 Hz), 6.88 (2H, dd, <i>J</i> =2.2, 9.0 Hz), 7.08 (2H, dd, <i>J</i> =2.2, 9.0 Hz), 8.01 (1H, s), 8.19 (1H, s)
<b>9h</b>	(CDCl <sub>3</sub> ) -0.19 (9H, s), 1.20 (1H, d, <i>J</i> =14.5 Hz), 1.34 (1H, d, <i>J</i> =14.5 Hz), 4.44 (1H, d, <i>J</i> =14.8 Hz), 4.45 (1H, d, <i>J</i> =14.8 Hz), 7.42 (2H, d, <i>J</i> =8.6 Hz), 7.58 (2H, d, <i>J</i> =8.6 Hz), 7.93 (1H, s), 8.10 (1H, s)
<b>9i</b>	(CDCl <sub>3</sub> ) -0.18 (9H, s), 1.20 (1H, d, <i>J</i> =14.5 Hz), 1.35 (1H, d, <i>J</i> =14.5 Hz), 4.43 (1H, d, <i>J</i> =13.9 Hz), 4.51 (1H, d, <i>J</i> =13.9 Hz), 7.25 (2H, d, <i>J</i> =8.1 Hz), 7.41 (2H, d, <i>J</i> =8.1 Hz), 7.96 (1H, s), 8.50 (1H, s)
<b>9j</b>	(CDCl <sub>3</sub> ) -0.16 (9H, s), 1.20 (1H, d, <i>J</i> =14.6 Hz), 1.50 (1H, dd, <i>J</i> =1.9, 14.6 Hz), 4.48 (1H, d, <i>J</i> =13.7 Hz), 4.74 (1H, d, <i>J</i> =13.7 Hz), 6.99—7.05 (2H, m), 7.37—7.45 (1H, m), 7.87 (1H, s), 8.21 (1H, s)
<b>9k</b>	(CDCl <sub>3</sub> ) -0.17 (9H, s), 1.17 (1H, d, <i>J</i> =14.5 Hz), 1.32 (1H, d, <i>J</i> =14.5 Hz), 4.37 (2H, s), 6.85—6.91 (1H, m), 6.94—7.00 (2H, m), 7.10—7.31 (1H, m), 7.76 (1H, s), 7.88 (1H, s)
<b>9l</b>	(CDCl <sub>3</sub> ) -0.18 (9H, s), 1.19 (1H, d, <i>J</i> =14.4 Hz), 1.52 (1H, d, <i>J</i> =14.4 Hz), 4.43 (1H, d, <i>J</i> =13.7 Hz), 4.54 (1H, bs), 4.76 (1H, d, <i>J</i> =13.7 Hz), 6.92—7.06 (2H, m), 7.15—7.21 (1H, m), 7.41—7.45 (1H, m), 7.81 (1H, s), 7.82 (1H, s)
<b>9m</b>	(CDCl <sub>3</sub> ) -0.32 (9H, s), 0.52 (1H, d, <i>J</i> =15.3 Hz), 1.17 (1H, d, <i>J</i> =15.3 Hz), 1.23 (3H, d, <i>J</i> =6.9 Hz), 4.07 (1H, s), 4.49 (1H, q, <i>J</i> =6.9 Hz), 7.01—7.10 (2H, m), 7.40—7.47 (2H, m), 8.05 (1H, s), 8.14 (1H, s)
<b>9n</b>	(CDCl <sub>3</sub> ) -0.34 (9H, s), 0.44 (1H, d, <i>J</i> =14.5 Hz), 0.52 (3H, t, <i>J</i> =7.4 Hz), 1.11 (1H, d, <i>J</i> =14.5 Hz), 1.21—1.42 (1H, m), 1.84—2.08 (1H, m), 4.07 (1H, m), 7.02—7.11 (2H, m), 7.43—7.50 (2H, m), 8.04 (1H, s), 8.17 (1H, s)
<b>9o</b>	(CDCl <sub>3</sub> ) -0.29 (9H, s), 0.57 (1H, d, <i>J</i> =15.2 Hz), 1.47 (1H, d, <i>J</i> =15.2 Hz), 1.50 (3H, s), 1.66 (3H, s), 5.23 (1H, s), 7.01—7.29 (2H, m), 7.29—7.37 (2H, m), 7.99 (1H, s), 8.03 (1H, s)
<b>9p</b>	(CD <sub>3</sub> OD) -0.21 (9H, s), 1.22 (1H, d, <i>J</i> =14.7 Hz), 1.49 (1H, d, <i>J</i> =14.7 Hz), 4.17 (1H, d, <i>J</i> =15.0 Hz), 4.25 (1H, d, <i>J</i> =15.0 Hz), 6.94 (1H, s), 6.98 (1H, s), 6.94—7.03 (2H, m), 7.27 (1H, s), 7.35—7.42 (2H, m)
<b>9q</b>	(DMSO- <i>d</i> <sub>6</sub> ) -0.28 (9H, s), 1.10 (1H, d, <i>J</i> =12.0 Hz), 1.92 (1H, d, <i>J</i> =12.0 Hz), 4.28 (1H, d, <i>J</i> =12.0 Hz), 4.35 (1H, d, <i>J</i> =12.0 Hz), 7.12 (2H, t, <i>J</i> =8.8 Hz), 7.40 (2H, dd, <i>J</i> =5.5, 8.8 Hz), 8.05 (2H, s)
<b>9r</b>	(CDCl <sub>3</sub> ) -0.20 (9H, s), 1.03 (1H, d, <i>J</i> =14.6 Hz), 1.28 (1H, d, <i>J</i> =14.6 Hz), 4.63 (1H, d, <i>J</i> =14.1 Hz), 4.67 (1H, s), 4.72 (1H, d, <i>J</i> =14.1 Hz), 6.94 (2H, t, <i>J</i> =8.9 Hz), 7.37 (2H, dd, <i>J</i> =5.4, 8.9 Hz), 7.51 (2H, s)
<b>9s</b>	(CD <sub>3</sub> OD) -0.21 (9H, s), 1.24 (1H, d, <i>J</i> =14.8 Hz), 1.51 (1H, d, <i>J</i> =14.8 Hz), 4.65 (1H, d, <i>J</i> =13.5 Hz), 4.75 (1H, d, <i>J</i> =13.5 Hz), 6.99 (2H, t, <i>J</i> =8.9 Hz), 7.42 (2H, dd, <i>J</i> =5.3, 8.9 Hz), 7.55 (1H, s), 7.64 (1H, s)

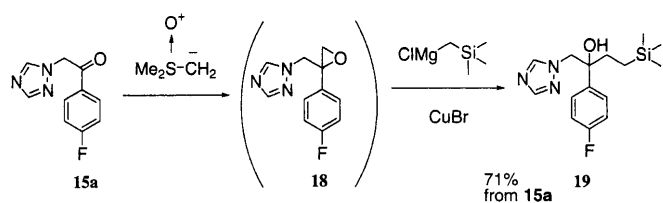


Chart 5

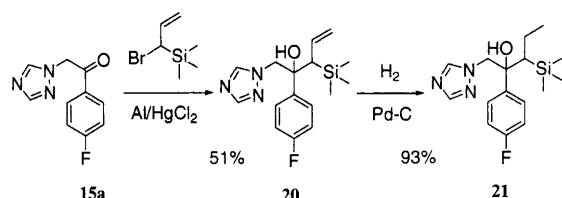


Chart 6

Table 5. Fungicidal Activity of Silicon-Containing Azole Derivatives and Comparative Compounds against Rice Sheath Blight by Submerged Application

Entry No.	Dose* (g/10a)	Entry No.	Dose* (g/10a)	Entry No.	Dose* (g/10a)
9a	12.5	9k	50	2	50
9b	25	9l	100	5	>100
9c	100	9m	50	6	>100
9d	100	9n	>100	19	>100
9e	50	9o	>100	20	100
9f	>100	9p	>100	21	50
9g	>100	9q	>100	4	>100
9h	100	9r	>100		
9i	>100	9s	>100		
9j	50				

\*: The minimum dose of each compound.

dried over magnesium sulfate and concentrated to give a solid, and the solid obtained was then chromatographed on silica gel (ethyl acetate–hexane, 1 : 10, v/v) to afford **11a** (8.8g, 68%) as an oil.

IR (neat)  $\text{cm}^{-1}$ : 3562, 2954, 2897, 1602, 1509, 1248, 1232, 1160.  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$ : -0.18 (9H, s), 1.23 (1H, d,  $J=14.7$  Hz), 1.45 (1H, d,  $J=14.7$  Hz), 3.70 (1H, d,  $J=11.0$  Hz), 3.80 (1H, d,  $J=11.0$  Hz), 6.99–7.09 (2H, m), 7.35–7.43 (2H, m). MS  $m/z$ : 170, 133, 121. *Anal.* Calcd for  $\text{C}_{11}\text{H}_8\text{F}_3\text{N}_3\text{O}$ : C, 55.26; H, 6.96; Cl, 13.59. Found: C, 55.02; H, 6.96; Cl, 13.58.

**Trial Procedure for Synthesis of 2-(4-Fluorophenyl)-1-(1H-1,2,4-triazol-1-yl)-3-trimethylsilylpropan-2-ol (9a) from 11a** To a solution of sodium hydride (60% mineral oil dispersion, 80 mg, 4.0 mmol) in  $N,N$ -dimethylformamide (10 ml) was added a suspension of 1H-1,2,4-triazole (280 mg, 4.0 mmol) in  $N,N$ -dimethylformamide (1 ml) at 0°C. After stirring the reaction mixture at room temperature for 0.5 h, **11a** (520 mg, 2.0 mmol) was added and the mixture was heated to 90°C for 3 h. The reaction mixture was partitioned between ethyl acetate and brine, the organic layer was dried over magnesium sulfate and concentrated to give a solid, and the solid obtained was chromatographed on silica gel (ethyl acetate–hexane, 1 : 4, v/v) to afford 2-(4-fluorophenyl)prop-2-en-1-ol **13a** ( $\text{R}^1=\text{R}^2=\text{H}$ ,  $\text{X}=\text{4-F}$ ,  $\text{Y}=\text{Cl}$ ) (170 mg, 56%) as an oil and 1-[2-(4-fluorophenyl)allyl]-1H-1,2,4-triazole **14a** ( $\text{R}^1=\text{R}^2=\text{H}$ ,  $\text{X}=\text{4-F}$ ,  $\text{Y}=\text{Cl}$ ) (110 mg, 27%) as colorless crystals (recrystallized from diisopropyl ether).

**13a**: IR (neat)  $\text{cm}^{-1}$ : 3355, 2925, 1602, 1510, 1233, 1161, 1044.  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.90 (1H, s), 4.44 (2H, s), 5.31 (1H, s), 5.40 (1H, s), 7.02 (2H, t,  $J=8.8$  Hz), 7.39 (2H, dd,  $J=5.4$ , 8.8 Hz). MS  $m/z$ : 152 ( $\text{M}^+$ ), 135, 121.

**14a**: mp 42–44°C. IR (KBr)  $\text{cm}^{-1}$ : 3087, 2996, 1630, 1602, 1510, 1452, 1268, 1227, 1161, 1138, 1018.  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.16 (3H, s), 5.55 (1H, s), 7.00 (2H, t,  $J=8.9$  Hz), 7.33 (2H, dd,  $J=5.2$ , 8.9 Hz), 7.92 (1H, s), 8.02 (1H, s). MS  $m/z$ : 203 ( $\text{M}^+$ ), 133, 121.

### General Procedure for Synthesis of 2-Azoly-1-phenylalkanones (15)

To a suspension of 1H-1,2,4-triazole (325 mg, 4.6 mmol) and potassium carbonate (325 mg, 2.3 mmol) in acetonitrile (5.0 ml) was added 2-halo-1-phenylalkanone **10** (4.6 mmol) at room temperature. After stirring the reaction mixture for 5 h and partitioning it between water and ethyl acetate, the organic layer was washed with brine, dried over magnesium sulfate, and concentrated to a solid. Chromatography of the solid on silica gel (ethyl acetate–hexane, 2 : 1, v/v) yielded **15** as colorless crystals (recrystallized from diisopropyl ether) without **15m** as an oil.

The same general method was used to prepare **15** described below.

**2-(1H-1,2,4-Triazol-1-yl)-1-(4-trifluoromethylphenyl)ethanone (15h)**: mp 117–119°C. IR (KBr)  $\text{cm}^{-1}$ : 3095, 2973, 1699, 1582, 1516, 1410, 1332, 1271.  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.75 (2H, s), 7.81 (2H, d,  $J=8.2$  Hz), 8.01 (1H, s), 8.11 (2H, d,  $J=8.2$  Hz), 8.28 (1H, s). MS  $m/z$ : 255 ( $\text{M}^+$ ), 236, 173, 145, 125. *Anal.* Calcd for  $\text{C}_{11}\text{H}_8\text{F}_3\text{N}_3\text{O}$ : C, 51.77; H, 3.16; N, 16.47. Found: C, 51.90; H, 3.17; N, 16.46.

**2-(1H-1,2,4-Triazol-1-yl)-1-(4-chloro-2-fluorophenyl)ethanone (15j)**: mp 136°C. IR (KBr)  $\text{cm}^{-1}$ : 3111, 3056, 2978, 1700, 1600, 1506, 1478, 1394, 1344, 1278, 1228, 1167, 1133, 1050, 1011.  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.64 (2H, s), 7.06–7.27 (2H, m), 7.76 (1H, dd,  $J=6.0$ , 8.8 Hz), 7.99 (1H, s), 8.23 (1H, s). MS  $m/z$ : 239 ( $\text{M}^+$ ), 204, 157, 129, 109. *Anal.* Calcd for  $\text{C}_{10}\text{H}_7\text{ClF}_2\text{N}_3\text{O}$ : C, 50.12; H, 2.94; N, 17.54. Found: C, 50.20; H, 2.98; N, 17.51.

**2-(1H-1,2,4-Triazol-1-yl)-1-(3-fluorophenyl)ethanone (15k)**: mp 108–110°C. IR (KBr)  $\text{cm}^{-1}$ : 3133, 2978, 2933, 1700, 1589, 1511, 1450, 1350, 1250, 1172, 1133.  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.66 (2H, s), 7.34–7.44 (1H, m), 7.50–7.60 (1H, m), 7.66–7.72 (1H, m), 7.76–7.81 (1H, m), 8.25 (1H, s), 8.54 (1H, s). MS  $m/z$ : 205 ( $\text{M}^+$ ), 177, 123, 95. *Anal.* Calcd for  $\text{C}_{10}\text{H}_8\text{FN}_3\text{O}$ : C, 58.54; H, 3.93; N, 20.48. Found: C, 58.56; H, 4.19; N, 20.50.

**2-(1H-1,2,4-Triazol-1-yl)-1-(2-fluorophenyl)ethanone (15l)**: mp 106–107°C. IR (KBr)  $\text{cm}^{-1}$ : 3122, 2987, 1700, 1611, 1572, 1511, 1483, 1372, 1317, 1272, 1206, 1187, 1100.  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.53 (2H, d,  $J=3.3$  Hz), 7.08–7.88 (2H, m), 7.48–7.60 (1H, m), 7.80–7.88 (1H, m), 7.87 (1H, s), 8.13 (1H, s). MS  $m/z$ : 205 ( $\text{M}^+$ ), 177, 123, 95. *Anal.* Calcd for  $\text{C}_{10}\text{H}_8\text{FN}_3\text{O}$ : C, 58.54; H, 3.93; N, 20.48. Found: C, 58.43; H, 4.17; N, 20.34.

**2-(1H-1,2,4-Triazol-1-yl)-1-(4-fluorophenyl)propanone (15m)**: IR (neat)  $\text{cm}^{-1}$ : 3122, 3067, 2989, 1694, 1600, 1506, 1450, 1405, 1300, 1278, 1228, 1161, 1139.  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.84 (3H, d,  $J=7.3$  Hz), 6.12 (1H, q,  $J=7.3$  Hz), 7.19 (2H, t,  $J=8.7$  Hz), 7.96 (1H, s), 8.03 (2H, dd,  $J=5.1$ , 8.7 Hz), 8.32 (1H, s). MS  $m/z$ : 219 ( $\text{M}^+$ ), 123, 95. *Anal.* Calcd for  $\text{C}_{11}\text{H}_{10}\text{FN}_3\text{O}$ : C, 57.14; H, 4.94; N, 18.17. Found: C, 57.15; H, 4.64; N, 18.00.

**2-(1H-1,2,4-Triazol-1-yl)-1-(4-fluorophenyl)butanone (15n)**: mp 50–52°C. IR (KBr)  $\text{cm}^{-1}$ : 3100, 2978, 1761, 1700, 1600, 1506, 1481, 1372, 1300, 1278, 1228, 1156, 1100.  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.98 (3H, t,  $J=7.4$  Hz), 2.05–2.37 (2H, m), 5.93 (1H, dd,  $J=5.6$ , 9.2 Hz), 7.19 (2H, t,  $J=8.8$  Hz), 7.95 (1H, s), 8.04 (2H, dd,  $J=5.3$ , 8.8 Hz), 8.36 (1H, s). MS  $m/z$ : 233 ( $\text{M}^+$ ), 123, 95. *Anal.* Calcd for  $\text{C}_{12}\text{H}_{12}\text{FN}_3\text{O}$ : C, 61.79; H, 5.19; N, 18.02. Found: C, 61.72; H, 4.98; N, 18.00.

**2-(1H-1,2,4-Triazol-1-yl)-1-(4-fluorophenyl)-2-methylpropanone (15o)**: mp 99–101°C. IR (KBr)  $\text{cm}^{-1}$ : 3122, 2989, 1683, 1600, 1500, 1467, 1411, 1372, 1283, 1233, 1211, 1156, 1128.  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.95 (6H, s), 6.97 (2H, t,  $J=8.4$  Hz), 7.38 (2H, dd,  $J=5.1$ , 8.4 Hz), 7.98 (1H, s), 8.24 (1H, s). MS  $m/z$ : 233 ( $\text{M}^+$ ), 123, 110. *Anal.* Calcd for  $\text{C}_{12}\text{H}_{12}\text{FN}_3\text{O}$ : C, 61.79; H, 5.19; N, 18.02. Found: C, 61.72; H, 5.04; N, 17.92.

**2-(4-Fluorophenyl)-1-(1H-1,2,4-triazol-1-yl)-3-trimethylsilylpropan-2-ol (9a)** A solution of trimethylsilylmethylmagnesium chloride (1.0 M) in diethyl ether (13.5 ml, 13.5 mmol) was added to a solution of **15a** (505 mg, 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. The organic layer was dried over magnesium sulfate and concentrated to give a solid, and the solid obtained was then chromatographed on silica gel (ethyl acetate–hexane, 2 : 1, v/v) to afford **9a** (30 mg, 7%) as colorless crystals (recrystallized from diisopropyl ether).

Other silicon-containing azole derivatives (**9b**–**s**) were prepared in the same way by the Grignard reaction. The yields, physical data, spectroscopic data, and elementary analysis data on the derivatives are summarized in Tables 1–4.

**2-(4-Fluorophenyl)-1-(1H-1,2,4-triazol-1-yl)-4-trimethylsilylbutan-2-ol (19)** A solution of sodium hydride (60% mineral oil dispersion, 520 mg, 13.0 mmol) in dimethyl sulfoxide (20 ml) was heated at 70°C for 1 h. When

the hydrogen gas ceased to evolve, the mixture was cooled to room temperature and trimethylsulfoxonium iodide (4.6 g, 21.0 mmol) was added. After stirring at room temperature for 0.5 h, **15a** (2.05 g, 10.0 mmol) was added and the mixture was stirred for 2 h at the same temperature. The reaction mixture was partitioned between ethyl acetate and brine, the organic layer was dried over magnesium sulfate and concentrated to give a solid, and the solid obtained was chromatographed on silica gel (ethyl acetate–hexane, 1 : 4, v/v) to afford 1-[2,3-epoxy-2-(4-fluorophenyl)propyl]-1*H*-1,2,4-triazole **18** (2.05 g, 94%) as an oil.

<sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>) δ: 2.81 (1H, d, *J*=4.8 Hz), 2.86 (1H, d, *J*=4.8 Hz), 4.60 (1H, d, *J*=14.9 Hz), 4.78 (1H, d, *J*=14.9 Hz), 7.02 (2H, t, *J*=8.8 Hz), 7.30 (2H, dd, *J*=5.3, 8.8 Hz), 7.89 (1H, s), 8.06 (1H, s).

This product was used for the next reaction without further purification.

Cuprous bromide (200 mg, 1.4 mmol) was added to a solution of **18** (290 mg, 1.4 mmol) in diethyl ether (5 ml) at 0 °C. A solution of trimethylsilylmethylmagnesium chloride in diethyl ether (5.0 ml, 4.2 mmol) was added dropwise to the mixture at room temperature for 0.5 h. The reaction mixture was poured into ice and quenched with a saturated 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 evaporated to give a solid, which was purified by column chromatography (ethyl acetate–hexane, 2 : 1, v/v) to afford **19** (314 mg, 76%) as colorless crystals (recrystallized from diisopropyl ether), mp 81 °C. IR (KBr) cm<sup>-1</sup>: 3256, 3133, 2945, 2889, 1600, 1511, 1428, 1278, 1250, 1233, 1200, 1161, 1133, 1073, 1029. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>) δ: -0.07 (9H, s), 0.12–0.27 (1H, m), 0.24–0.59 (1H, m), 1.61–1.92 (2H, m), 4.44 (2H, s), 6.94–7.04 (2H, m), 7.23–7.31 (2H, m), 7.87 (1H, s), 7.91 (1H, s). MS *m/z*: 308 (M<sup>+</sup>+1), 292, 225, 206. *Anal.* Calcd for C<sub>15</sub>H<sub>22</sub>FN<sub>3</sub>OSi: C, 58.60; H, 7.21; N, 13.67. Found: C, 58.76; H, 6.98; N, 13.71.

**2-(4-Fluorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)-3-trimethylsilylpent-4-en-2-ol (20)** A mixture of aluminum (180 mg, 6.7 mmol), mercury(II) chloride (40 mg, 6.7 mmol), and diethyl ether (2 ml) was stirred vigorously. As soon as the reaction started, a solution of 1-bromoallyltrimethylsilane (1.88 g, 9.9 mmol) in diethyl ether (5 ml) was added and the mixture was heated under reflux for 5 h. The mixture was diluted with diethyl ether (2 ml) and dichloromethane (6.5 ml), and then a solution of **15a** (616 mg, 3.0 mmol) in dichloromethane (7.5 ml) was added. After stirring at room temperature for 1 h, a saturated aqueous solution of ammonium chloride was added at 0 °C and the mixture was extracted with dichloromethane. The extract was washed with brine and dried over magnesium sulfate. The solvent was evaporated and the residue was purified by flash column chromatography (ethyl acetate–hexane, 2 : 1, v/v) to afford **20** (208 mg, 51%) as colorless crystals, mp 92–95 °C. IR (KBr) cm<sup>-1</sup>: 3167, 3111, 2956, 2900, 1606, 1511, 1417, 1278, 1239, 1161, 1133, 1100, 1028, 1006. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>) δ: -0.08 (9H, s), 2.09 (1H, d, *J*=11.3 Hz), 4.52 (2H, s), 4.89 (1H, dd, *J*=2.1, 16.8 Hz), 5.02 (1H, dd, *J*=2.1, 10.1 Hz), 5.65 (1H, ddd, *J*=10.1, 11.3, 16.8 Hz), 6.95 (2H, t, *J*=8.9 Hz), 7.29 (2H, dd, *J*=5.2, 8.9 Hz), 7.76 (1H, s), 7.83 (1H, s). MS *m/z*: 320 (M<sup>+</sup>+1), 304, 237, 229, 206; *Anal.* Calcd for C<sub>16</sub>H<sub>22</sub>FN<sub>3</sub>OSi: C, 60.16; H, 6.94; N, 13.15. Found: C, 59.99; H, 7.20; N, 13.20.

**2-(4-Fluorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)-3-trimethylsilyl-2-pentanol (21)** A solution of **20** (12.9 mg, 0.04 mmol) in ethanol (10 ml) was shaken with 10% palladium-charcoal (8.5 mg) under a hydrogen atmosphere at room temperature for 4 h. The solid was filtered off through Celite, the fil-

trate was concentrated under reduced pressure, and the residue was purified by column chromatography (ethyl acetate–hexane, 2 : 1, v/v) to afford **21** (10.5 mg, 93%) as colorless crystals (recrystallized from diisopropyl ether), mp 104–106 °C. IR (KBr) cm<sup>-1</sup>: 3278, 3131, 2956, 1600, 1511, 1378, 1250, 1222, 1161, 1133, 1050. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>) δ: -0.25 (9H, s), 1.13 (1H, t, *J*=4.8 Hz), 1.14 (3H, t, *J*=7.5 Hz), 1.16–2.03 (3H, m), 4.38 (1H, d, *J*=13.6 Hz), 4.69 (1H, d, *J*=13.6 Hz), 6.68 (2H, t, *J*=8.7 Hz), 7.18 (2H, dd, *J*=5.2, 8.7 Hz), 7.44 (1H, s), 7.80 (1H, s). MS *m/z*: 322 (M<sup>+</sup>+1), 306, 239, 206. *Anal.* Calcd for C<sub>16</sub>H<sub>24</sub>FN<sub>3</sub>OSi: C, 59.78; H, 7.53; N, 13.07. Found: C, 59.69; H, 7.46; N, 12.82.

**Preventive Activity against Rice Sheath Blight by Submerged Application** Rice seedlings (variety Nipponbare) at the 3–4-leaf stage grown in pots were flooded to a depth of 1 cm with water. The test compounds were then applied to the water in the pots. After keeping the seedlings in a greenhouse for 7 d, 4–5 oat grains previously cultured with *Rhizoctonia solani* were placed around the base of each seedling for inoculation with the fungus. The seedlings were then kept in a moist chamber (relative humidity: 100%) at 25–27 °C. After 5 d, the minimum effective dose of the each compound (g/10a) was evaluated (shown in Table 5).

**Acknowledgements** We are grateful to Drs. S. Sugai and T. Jojima, the current and former directors of our laboratories, for their encouragement throughout this work, and to Dr. K. Sato, our colleague in our laboratories, for his helpful discussion.

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