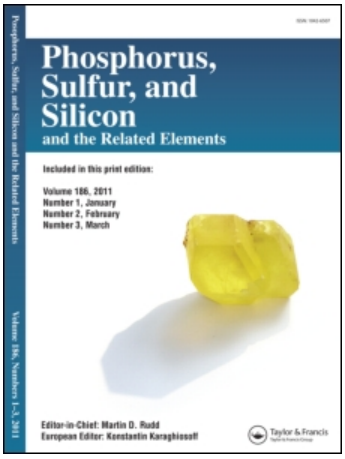

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Synthesis and Biological Activities of *O*-Alkyl, *O*-Aryl, *O*-{Z-[1-Phenyl-2-(1*H*-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioates

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Synthesis and Biological Activities of *O*-Alkyl, *O*-Aryl, *O*-{Z-[1-Phenyl-2-(1*H*-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioates

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A series of title compounds ***2*** *were efficiently synthesized via the condensation of 1-phenyl-2-(1H-1,2,4-triazol-1-yl)ethanone oxime with various asymmetric thiophosphoryl chlorides in sodium hydroxide powder and acetonitrile system. The structures of title compounds* ***2*** *were confirmed by IR,* ^{1}*H NMR,* ^{31}*P NMR, EI-MS, and elemental analysis. The results of preliminary bioassays indicated that the title compounds* ***2*** *possessed good to moderate insecticidal activity against aphides at the dosage of 250 mg/L, and some of them exhibited moderate fungicidal activities at the concentration of 100 mg/L.*

Keywords Biological activity; 1-phenyl-2-(1*H*-1,2,4-triazol-1-yl)ethanone oxime; phosphorothioate

INTRODUCTION

Oxime ester derivatives have attracted increasing attention because of their widespread biological activities. Some of them exhibit good fungicidal activities[1,2] or have been commercialized as insecticides[3,4] or herbicides,[5,6] which are widely used in worldwide plant protection. It is well known that many triazole-related molecules play an important role in the development of agrochemicals such as insecticides, nematocides, acaricide, and plant growth regulators.[7–11] As a continuation of our research work in attempt to find novel agrochemicals with high activity and low toxicity,[12,13] in this article, we report the synthesis and biological activities of novel oxime phosphorothioates containing

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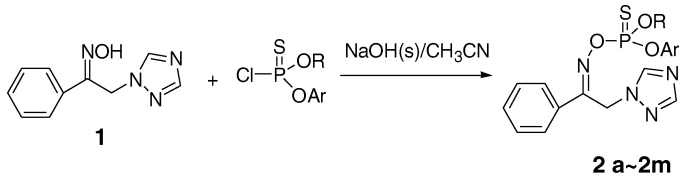
a triazole moiety **2**. The synthetic route is shown in Scheme 1. Characterization was done by IR, ^{1}H NMR, ^{31}P{^{1}H} NMR, MS, and elemental analyses. The results of preliminary bioassays showed that the title compounds possess insecticidal and fungicidal activities to some extent.



R = CH_3, C_2H_5; Ar = C_6H_5, 4-$CH_3C_6H_4$, 2-$CH_3OC_6H_4$, 4-FC_6H_4, 4-ClC_6H_4, 4-$NO_2C_6H_4$,

3-$CF_3C_6H_4$, 2-F,4-ClC_6H_3, 2-Cl,4-FC_6H_3, 2,4-$Cl_2C_6H_3$

SCHEME 1 Synthetic route of title compounds 2.

RESULTS AND DISCUSSION

Synthesis and Structure Determination

Oxime **1** reacted with various thiophosphoryl chlorides to yield the target compounds **2** in moderate yields. In order to optimize the reaction conditions, we scanned the different base and solvent systems, such as Et_3N/CH_2Cl_2, $Et_3N/CHCl_3$, pyridine/$CHCl_3$, K_2CO_3/CH_3CN, $NaHCO_3/H_2O$+THF, and NaOH (s)/CH_3CN. Finally, we found that the reaction gave the best result in mild reaction condition in the NaOH (s)/CH_3CN system, and no byproduct was detected by TLC.

The structures of compounds **2a–2m** were deduced from their spectral data (IR, ^{1}H NMR, ^{31}P NMR, MS) and elemental analyses. In the ^{1}H NMR spectra of **2**, the two protons of the methylene moiety linking with triazole displayed as a singlet, the signal in the Z isomer is shifted downfield relative to that of the E isomer owing to the unshielded effect of a phosphoryl group, and in ^{31}P NMR spectra, the P signal in all of the title compounds displayed as a singlet, giving chemical shifts in δ 62–64; the C=N in all of compounds **2** are in Z configuration, which can be deduced by NMR analysis and further by compared with one of its ether analog determined by X-ray diffraction.[14] IR spectra of compounds **2** showed normal stretching absorption bands, indicating the existence Ar-H (~3000 cm^{-1}), C=N (~1600 cm^{-1}), P-O-Ar (~1230 cm^{-1}), P—O—C (~1035 cm^{-1}), and P=S (~690 cm^{-1}). The EI mass spectra of compounds **2** revealed the existence of the molecular ion peaks

and anticipant fragmentation peaks, which were in good accordance with the given structures of products.

Biological Activities

Insecticidal Activity

Compounds **2a–2m** were tested for insecticidal activity against aphides by dipping at the dosage of 250 mg/L. Preliminary bioassay results show that the title compounds possess good insecticidal activity. For example, compounds **2a** and **2l** exhibited 86.7% and 78.9% inhibitory rates against aphides, respectively. The structure–activity relationships are not very clear and are under investigation. The results of the insecticidal activities are listed in Table I.

Fungicidal Activities

The preliminary fungicidal activity of the target compounds **2** was evaluated by the classic plate method at a concentration of 100 mg/L. The six fungi used, *Fusarium oxysporium*, *Rhizoctonia solani*, *Botrytis cinereapers*, *Gibberella zeae*, *Dothiorella gregaria*, and *Colletotrichum gossypi*, belong to the group of field fungi and were isolated from corresponding crops. The activity data were also listed in Table I. The results indicated that most of compounds **2** exhibit moderate to weak inhibitory activities against the above six fungi. For example, compound **2l** exhibited 87.5%, 81.0%, 73.9%, 48.3%, 81.8%, and 83.3% inhibitory activity against the six fungi, respectively.

In conclusion, a series of novel oxime phosphorothioates containing a triazole moiety **2** were synthesized, and their biological activities were tested. The results showed that some of the title compounds **2** possessed good insecticidal activity against aphides at the dosage of 250 mg/L, and some of them displayed moderate fungicidal activity.

EXPERIMENTAL

Melting points were determined with a WRS-1B digital melting point apparatus and are uncorrected. ^{1}H and ^{31}P NMR spectra were recorded on Varian MERCURY-PLUS400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and TMS and 85% H_3PO_4 as the internal and external references, respectively; mass spectra were obtained with a Finnigan TRACEMS2000 spectrometer using the EI method; IR spectra were measured by a Nicolet NEXUS470 spectrometer; elemental analyses were performed with an Elementar Vario EL CHNSO elementary analyzer. All of the solvents and materials were reagent grade and purified

TABLE I The Insecticidal and Fungicidal Activities of Compounds 2 (Inhibitory Rate%)

Compd.	Insectcidal activity (250 mg/L) Aphides	Fungicidal activity (100 mg/L)					
		Fusarium oxysporium	*Rhizoctonia solani*	*Botrytis cinereapers*	*Gibberella zeae*	*Dothiorella gregaria*	*Colletotrichum gossypii*
2a	86.7	45.8	52.0	39.1	51.7	22.7	50.0
2b	48.9	40.5	36.0	29.0	37.4	15.7	38.0
2c	56.3	37.5	43.0	43.5	51.7	18.2	54.2
2d	34.0	37.5	48.0	56.5	44.8	27.3	41.7
2e	35.6	37.5	64.0	56.5	34.5	13.6	45.8
2f	44.8	16.7	5.0	17.4	24.1	31.8	37.5
2g	30.8	33.3	55.0	52.2	48.3	27.3	54.2
2h	66.7	41.7	56.0	52.2	37.9	27.3	45.8
2i	57.1	37.5	66.0	73.9	55.2	31.8	54.2
2j	49.8	33.3	57.0	47.8	37.9	31.8	58.3
2k	47.4	20.8	38.0	8.7	20.7	4.5	37.5
2l	78.9	87.5	81.0	73.9	48.3	81.8	83.3
2m	65.3	25.0	38.0	30.4	0	18.2	29.2

as required. Asymmetric thiophosphoric chlorides were prepared according to the procedures in the literature.[15–16]

Preparation of 1-Phenyl-2-(1*H*-1,2,4-triazol-1-yl)ethanone Oxime (1)

1-Phenyl-2-(1*H*-1,2,4-triazol-1-yl)ethanone (3.7 g, 20 mmol), hydroxyl ammonium chloride (2.3 g, 32 mmol), and ethanol (25 mL) were added to a 50 mL flask. The mixture was stirred at room temperature until the reaction was complete (monitored by thin layer chromatography), and the solid was filtered and recrystallized from methanol to give a light yellow solid (2.55 g, yield 56%), mp: 160–162°C. Anal. Calcd. for $C_{10}H_{10}N_4O$ (%): C, 59.40; H, 4.98; N, 27.71. Found: C, 59.56; H, 5.04; N, 27.53.

General Procedure of the Preparation of *O*-Alkyl, *O*-Aryl, *O*-{Z-[1-Phenyl-2-(1*H*-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioates (2)

1-Phenyl-2-(1*H*-1,2,4-triazol-1-yl)ethanone oxime (0.41 g, 2 mmol), NaOH powder (0.08 g, 2 mmol), and anhydrous acetonitrile (10 mL) were added into a three-necked flask at 298 K. After vigorously stirring for 5 ~ 10 min, then thiophosphoryl chloride (2 mmol) in acetonitrile (5 mL) was added dropwise. The mixture was allowed to stir at room temperature for 5–8 h until the reaction was complete (monitored by thin-layer chromatography). The solid was filtered off, and the filtrate was concentrated under vacuum. The residue was purified by column chromatography on silica gel using petroleum ether:acetone (2:1 *v*/*v*) as the eluent, giving a light yellow oil .

O-Ethyl, O-Phenyl, O-{Z-[1-Phenyl-2-(1H-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioate (2a)

Yellow oil, Yield: 63%; IR (KBr, cm^{-1}) υ: 3063, 2984 (Ar-H), 1592 (C=N), 1489, 1446 (Ar), 1203 (P-O-Ar), 1025 (P—O—C), 691 (P=S); ^1H NMR: δ 1.38 (t, $J = 7.2$ Hz, 3H, CH_3), 4.30–4.34 (m, 2H, $\underline{CH_2}CH_3$), 5.50 (s, 2H, CH_2), 7.18–7.88 (m, 10H, Ar-H), 7.92 (s, 1H, Tr-H), 8.23 (s, 1H, Tr-H); $^{31}P\{^1H\}$ NMR (162 MHz) δ: 62.16; MS *m*/*z* (%): 402 (M^+, 18.3), 309 (5.9), 218 (6.8), 186 (28.7), 171(36.4), 104 (71.8), 103 (100), 82 (58.3), 77 (93.6), 76 (79.2), 65 (52.8), 51 (72.7). Anal. Calcd. for $C_{18}H_{19}N_4O_3PS$: C 53.72, H 4.76, N 13.92. Found C 53.53, H 5.07, N 13.75.

O-Methyl, O-Phenyl, O-{Z-[1-Phenyl-2-(1H-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioate (2b)

Yellow oil, Yield: 70%; IR (KBr, cm^{-1}) υ: 3061, 2934 (Ar-H), 1585 (C=N), 1492, 1451 (Ar), 1228 (P-O-Ar), 1175 (P—O—C), 698 (P=S); ^1H NMR: δ 3.93 (d, $J = 14.4$ Hz, 3H, OCH_3), 5.50 (s, 2H, CH_2), 7.18–7.87 (m, 10H, Ar-H), 7.92 (s, 1H, Tr-H), 8.23 (s, 1H, Tr-H); $^{31}P\{^1H\}$ NMR (162 MHz) δ: 62.35; MS *m/z* (%): 389 (M+1, 13.3), 343 (41.7), 341 (66.9), 297 (34.4), 295 (58.6), 251 (23.7), 232 (33.1), 218 (68.5), 185 (80.2), 109 (14.8), 103 (35.2), 82 (42.7), 77 (100), 65 (47.3), 55 (80.3). Anal. Calcd. for $C_{17}H_{17}N_4O_3PS$: C 52.57, H 4.41, N 14.43. Found C 52.67, H 4.29, N 14.17.

O-Ethyl, O-(4-Totyl), O-{Z-[1-Phenyl-2-(1H-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioate (2c)

Yellow oil, Yield: 66%; IR (KBr, cm^{-1}) υ: 3061, 2983 (Ar-H), 1584 (C=N), 1492, 1446 (Ar), 1227 (P-O-Ar), 1177, 1035 (P—O—C), 694 (P=S); ^1H NMR: δ 1.37 (t, $J = 7.2$ Hz, 3H, $CH_2\underline{CH_3}$), 2.33 (s, 3H, CH_3Ar), 4.28–4.37 (m, 2H, $\underline{CH_2}CH_3$), 5.49 (s, 2H, CH_2), 7.05–7.14 (m, 4H, Ar-H), 7.43–7.51 (m, 3H, Ar-H), 7.86 (d, $J = 7.2$ Hz, 2H, Ar-H), 7.93 (s, 1H, Tr-H), 8.25 (s, 1H, Tr-H); $^{31}P\{^1H\}$ NMR (162 MHz) δ: 62.28; MS *m/z* (%): 417 (M+1, 29.6), 185 (14.4), 103 (19.8), 97 (17.0), 77 (100), 65 (18.0), 55 (26.4), 51 (30.7). Anal. Calcd. for $C_{19}H_{21}N_4O_3PS$: C 54.80, H 5.08, N 13.45. Found C 54.64, H 5.17, N 13.61.

O-Ethyl, O-(2-Methoxyphenyl), O-{Z-[1-Phenyl-2-(1H-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioate (2d)

Yellow oil, Yield: 65%; IR (KBr, cm^{-1}) υ: 2983 (Ar-H), 1583 (C=N), 1486, 1446 (Ar), 1209 (P-O-Ar), 1035 (P—O—C), 677 (P=S); ^1H NMR: δ 1.40 (t, $J = 7.2$ Hz, 3H, $CH_2\underline{CH_3}$), 3.83 (s, 3H, $ArOCH_3$), 4.30–4.41 (m, 2H, $\underline{CH_2}CH_3$), 5.56 (s, 2H, CH_2), 6.92–7.94 (m, 9H, Ar-H), 8.01 (s, 1H, Tr-H), 8.51 (s, 1H, Tr-H); $^{31}P\{^1H\}$ NMR (162 MHz) δ: 62.55; MS *m/z* (%): 432 (M^+, 5.5), 309 (57.9), 294 (14.9), 286 (23.1), 276 (21.6), 248 (43.5), 218 (36.8), 186 (39.2), 138 (37.7), 125 (25.8), 103 (53.3), 95 (37.1), 82 (68.9), 77 (100), 65 (46.1), 55 (61.2), 51 (70.8). Anal. Calcd. for $C_{19}H_{21}N_4O_4PS$: C 52.77, H 4.89, N 12.96. Found C 52.90, H 4.63, N 13.17.

O-Ethyl, O-(4-Fluorophenyl), O-{Z-[1-Phenyl-2-(1H-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioate (2e)

Yellow oil, Yield: 68%; IR (KBr, cm^{-1}) υ: 2983 (Ar-H), 1585 (C=N), 1486, 1446 (Ar), 1210 (P-O-Ar), 1036 (P—O—C), 678 (P=S); ^1H NMR: δ 1.37 (t, $J = 7.2$ Hz, 3H, $CH_2\underline{CH_3}$), 4.28–4.37 (m, 2H, $\underline{CH_2}CH_3$), 5.50 (s,

2H, CH_2), 6.95–7.13 (m, 5H, Ar-H), 7.44–.52 (m, 2H, Ar-H), 7.86 (d, J = 7.6 Hz, 2H, Ar-H), 7.95 (s, 1H, Tr-H), 8.32 (s, 1H, Tr-H); $^{31}P\{^1H\}$ NMR (162 MHz) δ: 62.72; MS m/z (%): 421 (M+1, 30.4), 420 (M^+, 50.4), 191 (20.2), 143 (41.6), 114 (20.6), 104 (42.5), 95 (74.8), 91 (65.4), 76 (53.8), 67 (100). Anal. Calcd. for $C_{18}H_{18}FN_4O_3PS$: C 51.43, H 4.32, N 13.33. Found C 51.58, H 4.13, N 13.09.

O-(4-Fluorophenyl), O-Methyl, O-{Z-[1-Phenyl-2-(1H-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioate (2f)

Yellow oil, Yield: 89%; IR (KBr, cm^{-1}) υ: 3061, 2963 (Ar-H), 1600, 1582 (C=N), 1486, 1446 (Ar), 1210 (P-O-Ar), 1046 (P—O—C), 674 (P=S); ^1H NMR: δ 3.92 (d, J = 13.6 Hz, 3H, OCH_3), 5.51 (s, 2H, CH_2), 7.01–7.87 (m, 9H, Ar-H), 7.93 (s, 1H, Tr-H), 8.23 (s, 1H, Tr-H); $^{31}P\{^1H\}$ NMR (162 MHz) δ: 62.65; MS (70eV) m/z (%): 407 (M^+, 2.2), 205 (6.6), 158 (9.2), 135 (13.3), 125 (9.1), 111 (37.6), 103 (27.6), 95 (20.0), 83 (64.2), 77 (100), 63 (36.1), 55 (84.5). Anal. Calcd. for $C_{17}H_{16}FN_4O_3PS$: C 50.25, H 3.97, N 13.79. Found C 50.41, H 4.13, N 13.54.

O-(4-Chlorophenyl), O-Ethyl, O-{Z-[1-Phenyl-2-(1H-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioate (2g)

Yellow oil, Yield: 73%; IR (KBr, cm^{-1}) υ: 2983 (Ar-H), 1590 (C=N), 1486, 1446 (Ar), 1209 (P-O-Ar), 1036 (P—O—C), 677 (P=S); ^1H NMR: δ 1.37 (t, J = 7.2 Hz, 3H, $CH_2\underline{CH_3}$), 4.25–4.38 (m, 2H, $\underline{CH_2}CH_3$), 5.50 (s, 2H, CH_2), 7.11 (d, J = 7.2 Hz, 2H, Ar-H), 7.29 (d, J = 8.4 Hz, 2H, Ar-H), 7.45–7.52 (m, 3H, Ar-H), 7.85 (d, J = 7.2 Hz, 2H, Ar-H), 7.94 (s, 1H, Tr-H), 8.29 (s, 1H, Tr-H); $^{31}P\{^1H\}$ NMR (162 MHz) δ: 62.72; MS m/z (%): 437 (M+1, 4.9), 223 (8.4), 205 (23.2), 185 (11.8), 159 (14.0), 127 (12.6), 105 (29.3), 104 (46.1), 99 (55.9), 97 (39.4), 77 (100), 63 (41.8), 55 (83.8). Anal. Calcd. for $C_{18}H_{18}ClN_4O_3PS$: C 49.49, H 4.15, N 12.83. Found C 49.25, H 4.04, N 12.79.

O-Ethyl, O-(4-Nitrophenyl), O-{Z-[1-Phenyl-2-(1H-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioate (2h)

Yellow oil, Yield: 60%; IR (KBr, cm^{-1}) υ: 3105, 2984 (Ar-H), 1532 (C=N), 1475, 1446 (Ar), 1216 (P-O-Ar), 1035 (P—O—C), 676 (P=S); ^1H NMR: δ 1.40 (t, J = 7.2 Hz, 3H, $CH_2\underline{CH_3}$), 4.28–4.36 (m, 2H, $\underline{CH_2}CH_3$), 5.54 (s, 2H, CH_2), 7.33 (d, J = 8.0 Hz, 2H, Ar-H), 7.48–7.54 (m, 3H, Ar-H), 7.84 (d, J = 7.2 Hz, 2H, Ar-H), 8.00 (s, 1H, Tr-H), 8.23 (d, J = 8.4 Hz, 2H, Ar-H), 8.47 (s, 1H, Tr-H); $^{31}P\{^1H\}$ NMR (162 MHz) δ: 62.86; MS m/z (%): 448 (M+1, 1.8), 218 (3.6), 188 (5.4), 153 (7.1), 148 (8.1), 125 (30.3), 109 (46.4), 97 (42.6), 63 (100); 51(68.9). Anal. Calcd. for $C_{18}H_{18}N_5O_5PS$: C 48.32, H 4.06, N 15.65. Found C 48.41, H 3.93, N 15.47.

O-Ethyl, O-[3-(Trifluoromethyl)phenyl], O-{Z-[1-Phenyl-2-(1H-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioate (2i)

Yellow oil, Yield: 65%; IR (KBr, cm^{-1}) υ: 3061, 2934 (Ar-H), 1583 (C=N), 1491, 1445, 1322 (Ar), 12226 (P-O-Ar), 1172, 1110 (P—O—C), 694 (P=S); ^{1}H NMR: δ 1.38 (t, J = 7.2 Hz, 3H, $CH_2\underline{CH_3}$), 4.31–4.40 (m, 2H, $\underline{CH_2}CH_3$), 5.55 (s, 2H, CH_2), 7.41–7.54 (m, 7H, Ar-H), 7.83 (d, J = 7.6 Hz, 2H, Ar-H), 8.00 (s, 1H, Tr-H), 8.55 (s, 1H, Tr-H); ^{31}P{^{1}H} NMR (162 MHz) δ: 63.07; MS m/z (%): 470 (M^+, 3.6), 286 (25.8), 239 (12.2), 237 (6.4), 193 (3.5), 186 (13.2), 178 (8.9), 162 (37.1), 145 (27.3), 143 (22.5), 114 (42.6), 97 (100), 82 (35.1), 75 (32.0), 65 (36.7), 56 (63.0). Anal. Calcd. for $C_{19}H_{18}F_3N_4O_3PS$: C 48.51, H 3.86, N 11.91. Found C 48.37, H 3.60, N 11.76.

O-(4-Chloro-2-fluorophenyl), O-Ethyl, O-{Z-[1-Phenyl-2-(1H-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioate (2j)

Yellow oil, Yield: 61%; IR (KBr, cm^{-1}) υ: 2982 (Ar-H), 1580 (C=N), 1476, 1446, 1387 (Ar), 1232 (P-O-Ar), 1034 (P—O—C), 694 (P=S); ^{1}H NMR: δ 1.42 (t, J = 7.6 Hz, 3H, $CH_2\underline{CH_3}$), 4.30–4.32 (m, 2H, $\underline{CH_2}CH_3$), 5.54 (s, 2H, CH_2), 7.28–7.97 (m, 8H, Ar-H), 8.04 (s, 1H, Tr-H), 8.35 (s, 1H, Tr-H); ^{31}P{^{1}H} NMR (162 MHz) δ: 63.26. Anal. Calcd. for $C_{18}H_{17}ClFN_4O_3PS$: C 47.53, H 3.77, N 13.32. Found C 47.69, H 3.92, N 13.20.

O-(2-Chloro-4-fluorophenyl), O-Ethyl, O-{Z-[1-Phenyl-2-(1H-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioate (2k)

Yellow oil, Yield: 65%; IR (KBr, cm^{-1}) υ: 2985 (Ar-H), 1577 (C=N), 1486, 1450, 1385 (Ar), 1230 (P-O-Ar), 1036 (P—O—C), 698 (P=S); ^{1}H NMR: δ 1.42 (t, J = 7.2 Hz, 3H, $CH_2\underline{CH_3}$), 4.20–4.24 (m, 2H, $\underline{CH_2}CH_3$), 5.64 (s, 2H, CH_2), 6.97–7.45 (m, 8H, Ar-H), 7.81 (s, 1H, Tr-H), 7.90 (s, 1H, Tr-H); ^{31}P{^{1}H} NMR (162 MHz) δ: 63.25; Anal. Calcd. for $C_{18}H_{17}ClFN_4O_3PS$: C 47.53, H 3.77, N 13.32. Found C 47.37, H 3.87, N 13.55.

O-(2,4-Dichlorophenyl), O-Ethyl, O-{Z-[1-Phenyl-2-(1H-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioate (2l)

Yellow oil, Yield: 82%; IR (KBr, cm^{-1}) υ: 2982 (Ar-H), 1578 (C=N), 1477, 1446, 1387 (Ar), 1230 (P-O-Ar), 1033 (P—O—C), 694 (P=S); ^{1}H NMR: δ 1.41 (t, J = 7.2 Hz, 3H, CH_3), 4.37–4.41 (m, 2H, $\underline{CH_2}CH_3$), 5.54 (s, 2H, CH_2), 7.20–7.25 (m, 2H, Ar-H), 7.43–7.51 (m, 4H, Ar-H), 7.83 (d, J = 6.0 Hz, 2H, Ar-H), 7.94 (s, 1H, Tr-H), 8.33 (s, 1H, Tr-H); ^{31}P{^{1}H} NMR (162 MHz) δ: 63.16; MS m/z (%): 473 (2.6), 471 (M^+, 6.7), 435 (5.0), 309 (13.8), 279 (15.4), 250 (23.5), 223 (13.5), 222 (22.9), 185 (24.9), 161

(19.3), 135 (29.0), 133 (45.9), 104 (67.7), 97 (45.1), 77 (89.7), 63 (78.7), 51 (100). Anal. Calcd. for $C_{18}H_{17}Cl_2N_4O_3PS$: C 45.87, H 3.64, N 11.89. Found C 45.97, H 3.33, N 12.10.

O-(2,4-Dichlorophenyl), O-Methyl, O-{Z-[1-Phenyl-2-(1H-1,2,4-triazol-1-yl)ethylidene]amino} Phosphorothioate (2m)

Yellow oil, Yield: 88%; IR (KBr, cm^{-1}) υ: 2963 (Ar-H), 1582 (C=N), 1508, 1446, 1364 (Ar), 1270 (P-O-Ar), 1208, 1172, 1137 (P—O—C), 678 (P=S); ^{1}H NMR: δ 3.83 (d, J = 13.6 Hz, 3H, OCH_3), 5.53 (s, 2H, CH_2), 7.13–7.82 (m, 8H, Ar-H), 7.84 (s, 1H, Tr-H), 7.95 (s, 1H, Tr-H); ^{31}P{^{1}H} NMR (162 MHz) δ: 63.04. Anal. Calcd. for $C_{17}H_{15}Cl_2N_4O_3PS$: C 44.65, H 3.31, N 12.25. Found C 44.51, H 3.37, N 12.05.

Insecticidal Bioassay Method Against Aphides by Dipping

Two cucumber leaves *ca*. 8 cm in diameter were dipped into a water solution of the test compound for a few seconds until the leaf surface was wet. After drying, the leaves were place on soil in a pet cup. Ten 2nd-instar larvae were released into the cup. The cup was covered with a lid and stored at 25°C, 50–55% relative humidity (RH), and 14 h light/10 h dark for 5 days. The mortality was assessed after treatment. The test was run three times, the results were averaged, 0 means no effect, and 100% means excellent insecticidal activity, and given as death rate in Table I.

Fungicidal Activity Testing

The fungicidal activity measurement method was adapted from the one described by Molina-Torres et al.[17] 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 dished 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. 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: $I = [(C - T)/C] * 100\%$, where I is the growth inhibitory rate (%) and T is the treatment group fungi settlement radius (mm). The results are also given in Table I.

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