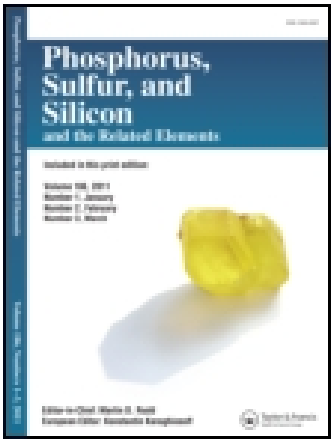

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Synthesis and Biological Activities of O,O-Dialkyl 1-((4,6-Dichloropyrimidin-2-yl)Carbamyloxy) Alkylphosphonates

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SYNTHESIS AND BIOLOGICAL ACTIVITIES OF *O,O*-DIALKYL 1-((4,6-DICHLOROPYRIMIDIN-2-YL)CARBAMYLOXY) ALKYLPHOSPHONATES

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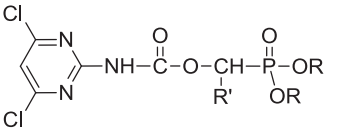
GRAPHICAL ABSTRACT



Abstract *A series of new 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy) alkylphosphonates were designed and synthesized. The structures of all the title compounds were confirmed by IR, ^{1}H-NMR, ^{31}P-NMR and elemental analysis. The results of the bioassay showed that all of title compounds exhibited weak herbicidal activities against monocotyledons and dicotyledons; however, some of them showed potential plant growth regulatory activities.*

Keywords Carbamyloxy; phosphonate; plant growth regulatory activity

INTRODUCTION

Pyrimidine compounds have received considerable attention over the past two decades in medicine and pesticide chemistry due to their biological activities.[1,2] Especially, more and more pyrimidine compounds have been used as insecticides and herbicides, such as pyrimidine amines, pyrimidine acrylic esters, pyrimidine sulfonylureas, and triazolopyrimidine sulfonamides.[3]

In our previous work, it was found that 1-(substituted phenoxyacetoxy)alkylphos phonates or phosphinates possess good herbicidal activities and plant growth regulatory activity.[2,3] In order to extend the structure type of alkylphosphonates and find more bioactive compounds, a pyrimidine amine structural unit was introduced into the molecule structure. Therefore, a novel series of *O,O*-dialkyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)alkylphosphonates were synthesized and screened for their herbicidal activities and plant growth regulatory activities. It is very interesting that all of these compounds have weak herbicidal activities, however, some of them showed potential plant growth regulating activities.

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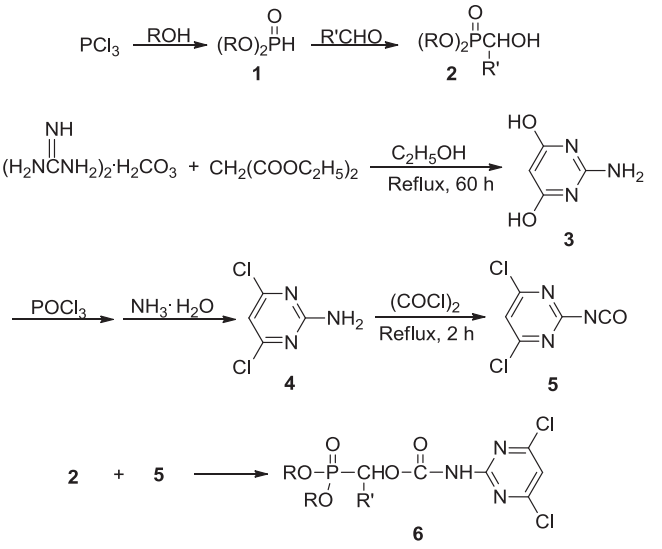


RESULTS AND DISCUSSION

Syntheses

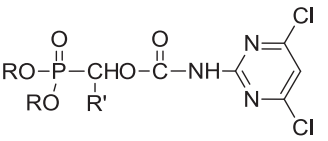
The multi-step procedure for the synthesis of the title phosphonates **6** is outlined in Scheme 1. *O,O*-Dialkyl phosphonate **1** was accomplished in a one-step reaction starting from phosphorus trichloride and the corresponding alcohol according to the literature.[4] 1-hydroxyalkylphosphonates **2** were prepared by the addition of **1** and several kinds of aldehydes using triethylamine as a catalyst and gave yields of 60%–90%. 4,6-Dichloro-2-isocyanatopyrimidine **5** were obtained by the reaction of 4,6-dichloropyrimidin-2-amine **4** with excess oxalyl chloride according to the literature.[5] The title compounds **6** were then obtained by the addition of compounds **2** with 4,6-dichloro-2-isocyanatopyrimidine **5**. The structures of **6a–p** (Table 1) were confirmed by comprehensive IR, ^{1}H-NMR, ^{31}P-NMR, and elemental analysis.

IR spectra of the title compounds **6a–p** showed normal stretching absorption bands, indicating the existence N–H (3310–3347 cm^{-1}), P=O (~1220 cm^{-1}), P—C (750–820 cm^{-1}), P—O—C (1032–1070 cm^{-1}), C=O (~1770 cm^{-1}), C—O (~1170 cm^{-1}), Ar–H (~3050 cm^{-1}), and C—H (3002–3041 cm^{-1}). In the ^{1}H-NMR spectra of the title compounds **6a–p**, the chemical shifts of aromatic protons appeared at 7.06–7.78 ppm. As for compounds with aliphatic groups as R', the proton signal corresponding to OCHP displayed multiplets at 4.55–5.60 ppm; as for the compounds with aromatic groups as R', the proton signal appears at 6.11–6.81 ppm as doublets due to coupling with phosphorus. ^{31}P-NMR chemical shifts of compounds **6a–p** appeared as singlets at δ 13.3–23.6 ppm.

Biological Activity

The herbicidal activities of compounds **6a**–**p** were evaluated at a dosage of 2.25 kg/ha in greenhouse using the previously reported procedure.[6] They were tested for pre-emergence and post-emergence inhibitory effect against three monocotyledons (*Triticum aestivum L.*

Table 1 Structure and physical constants of compounds **6**



No.	R	R'	m.p. (°C)	Yield (%)
6a	Me	H	75–77	61
6b	Me	Me	148–149	68
6c	Me	Et	167–169	61
6d	Me	*n*-Bu	81–83	71
6e	Me	Fur-2-yl	194–195	61
6f	Me	Ph	161–163	71
6g	Me	*o*-ClPh	187–189	77
6h	Me	*p*-ClPh	151–153	75
6i	Me	*p*-NO_2Ph	185–187	71
6j	Et	Me	114–115	69
6k	Et	Ph	181–183	73
6l	Et	*o*-ClPh	173–175	75
6m	Et	*p*-ClPh	170–171	82
6n	*i*-Pr	Me	139–141	75
6o	*i*-Pr	Ph	195–196	83
6p	*i*-Pr	Fur-2-yl	181–183	62

(wheat), *Digitaria sanguinalis Scop* (ascendant crabgrass) and *Echinochloa crusgalli Beava* (barnyard grass)) and three dicotyledons (*Brassica napus L.* (rape), *Cucumis sativus L.* (cucumber), and *Amarantus mangestnus L.* (amaranth)). Unfortunately, compounds **6a**–**p** have almost no inhibitory activities against both monocotyledons and dicotyledons. However, it is very interesting that compounds **6a**–**p** present negative inhibition ratio (−2.3 to −68%) to some tested dicotyledonous plants. For example, **6c**, **6f**, **6l**, and **6o** showed promoting effect on the growth of dicotyledonous plants (Table S1 in Supplementary Materials).

Compounds **6a–p** were further tested for plant growth regulatory activity by cucumber cotyledon at the dosage of 10 ppm. As seen from Table S2, most of the compounds **6a–p** had stimulating activities to the growth of cucumber cotyledon. The regulatory growth index values clearly showed that **6a**, **6c**, **6n** inhibited the growth of cucumber cotyledons expansion. However, they displayed stimulating activities to the growth of cucumber cotyledons root. The compound **6i** inhibited both the growth of cucumber cotyledon expansion and cucumber cotyledon root, and **6k** exhibited higher stimulating activity to the growth of cucumber cotyledon root than indole acetic acid (**IAA)** at the dosage of 10 ppm, but their stimulating activity to the growth of cucumber cotyledon expansion at 10 ppm was lower compared with that of kinetin (**KT**).

Herbicidal activities (Table S1) and plant growth regulatory activities (Table S2) are presented in Supplementary Materials.

CONCLUSIONS

In conclusion, a series of 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)alkylphospho nates were synthesized via the key intermediates 4,6-dichloro-2-isocyanatopyrimidine

and 1-hydroxyphosphonates with satisfactory yields. Most of the synthesized compounds showed weak herbicidal activities against the tested weeds for pre- or post-emergence, but some of them showed promoting effect on the growth of dicotyledonous plants. The plant growth regulatory activities of these compounds were tested on cucumber cotyledon at the dosage of 10 ppm. The primary bioassay results indicated that compounds **6a–p** showed good to moderate plant growth regulatory activities. Especially, compound **6k** exhibited higher stimulating activity to the growth of cucumber cotyledon root than **IAA**, but their stimulating activity to the growth of cucumber cotyledon expansion at 10 ppm was lower compared with **KT**.

EXPERIMENTAL

^{1}H, ^{13}C-NMR, and ^{31}P-NMR spectra were recorded on a Varian Mercury-Plus 200 spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard. Infrared spectra were recorded in potassium bromide disks on a Nicolet Avatar 360 FTIR spectrometer. Elemental analysis was performed by Elementar Vario EL III elementary analyzer. Mass spectra were measured on Finnigan Trace MS 2000 spectrometer. Melting points (m.p.) were measured on an electrothermal melting point apparatus and temperature uncorrected.

Synthesis

Synthesis of 2-aminopyrimidine-4,6-diol (3). 2-aminopyrimidine-4,6-diol **3** was prepared by the nucleophilic addition–elimination reaction of guanidine carbonate and diethyl malonate using ethanol as solvent in 93% yield after refluxing 60 h.[7]

Synthesis of 4,6-dichloropyrimidin-2-amine (4) and 4,6-dichloro-2-isocyanatopyrimidine (5). 4,6-dichloropyrimidin-2-amine **4** was synthesized by a standard method.[8] 4,6-dichloro-2-isocyanatopyrimidine **5** was obtained as a reddish brown liquid in 70% yield by treated compound **4** with four equivalent oxalyl chloride under 110°C for 2 h.[5]

General Procedure for the Synthesis of Compounds 6

1-hydroxylalkylphosphonates **2** were obtained by the general method of our previously published papers.[9–11] To a three-necked flask, compounds **2** (0.005 mol), 4,6-dichloro-2-isocyanatopyrimidine **5** (0.005 mol), and 1,2-dichloroethane (15 mL) were added. The resulting mixture was stirred at ambient temperature about 15 min, and then evaporated. The residue was chromatographed on silica gel using acetone–petroleum ether (1:2) as the eluent to afford the pure title compounds **6a**–**p** as solid in 61%–81% yields.

***O,O*-Dimethyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)methylphosphonates (6a).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 3.83$ (d, 6H, $2OCH_3$, $J = 7.0$ Hz), 4.55 (d, 2H, OCH_2P, $J = 8.4$ Hz), 4.99 (s, 1H, Ar-H), 9.48 (s, 1H, NH); ^{31}P-NMR ($CDCl_3$, 81 MHz): $\delta = 21.6$; IR (υ/cm^{-1}): 3447 (N—H), 3002 (Ar-H), 1764 (C=O), 1560, 1512, 1462 (C=C), 1230 (P=O), 1185 (C—O), 1039 (P—O—C); Anal. Calcd. for $C_8H_{10}Cl_2N_3O_5P$: C, 29.19; H, 3.03; N, 12.02. Found: C, 30.07; H, 3.24; N, 11.97.

***O,O*-Dimethyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)ethylphosphonates (6b).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 1.51$–1.55 (m, 3H, CH_3), $\delta = 3.84$ (d, 6H, $2OCH_3$, $J = 3.4$ Hz), 5.30–5.32 (m, 1H, -OCHP), 7.27 (s, 1H, Ar–H), 8.70 (s, 1H, NH); ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 15.7$, 54.0, 54.5, 54.6, 54.7, 64.7, 68.2, 116.1,

150.6, 150.8, 157.8, 162.9; ^{31}P NMR ($CDCl_3$, 81 MHz): δ = 23.6; IR (υ/cm^{-1}): 3344 (N—H), 3030 (Ar–H), 1765 (C=O), 1622, 1582, 1558 (C=C), 1245 (P=O), 1181 (C-O), 1037 (P—O—C); Anal. Calcd. for $C_9H_{12}Cl_2N_3O_5P$: C, 31.39; H, 3.48; N, 12.20. Found: C, 31.72; H, 3.54; N, 11.65.

***O,O*-Dimethyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)propylphosphonates (6c).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 1.23–1.30 (m, 3H, CH_3), 2.16–2.31 (m, 2H, CH_2), 3.83 (d, 6H, 2OCH_3, J = 3.6 Hz), 5.24 (d, 2H, OCHP, J = 4.0 Hz), 7.12 (s, 1H, Ar–H), 9.05 (s, 1H, NH); ^{31}P-NMR ($CDCl_3$, 81 MHz): δ = 23.2; IR (υ/cm^{-1}): 3440 (N—H), 3108 (Ar–H), 1755 (C=O), 1546, 1509 (C=C), 1218 (P=O), 1180 (C—O), 1044 (P—O—C); Anal. Calcd. for $C_{10}H_{14}Cl_2N_3O_5P$: C, 33.51; H, 3.91; N, 11.73. Found: C, 33.11; H, 3.79; N, 12.18.

***O,O*-Dimethyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)pentylphosphonates (6d).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 0.85–0.89 (m, 3H, CH_3), 1.36–1.40 (m, 4H, 2CH_2), 1.87–1.90 (m, 2H, CH_2), 3.84 (d, 6H, 2OCH_3, J = 4.8 Hz), 5.28 (d, 1H, OCHP, J = 5.6 Hz), 7.30 (s, 1H, Ar–H), 9.35 (s, 1H, NH); ^{31}P NMR ($CDCl_3$, 81 MHz): δ = 23.4; IR (υ/cm^{-1}): 3310 (N—H), 3020 (Ar–H), 1769 (C=O), 1553, 1511 (C=C), 1216 (P=O), 1182 (C—O), 1032 (P—O—C); Anal. Calcd. for $C_{12}H_{18}Cl_2N_3O_5P$: C, 37.30; H, 4.60; N, 10.08. Found: C, 37.45; H, 4.48; N, 9.77.

***O,O*-Dimethyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)-1-(furan-2-yl) methylphosphonates (6e).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 3.86 (d, 6H, 2OCH_3, J = 9,6 Hz), 6.39 (d, H, OCHP, J = 15.8 Hz), 7.05–7.47 (m, 4H, Ar–H), 8.65 (s, 1H, NH); ^{31}P-NMR ($CDCl_3$, 81 MHz): δ = 16.7; IR (υ/cm^{-1}): 3409 (N—H), 3034 (Ar–H), 1769 (C=O), 1571, 1552, 1509 (C=C), 1218 (P=O), 1178 (C—O), 1033 (P—O—C); Anal. Calcd. for $C_{12}H_{12}Cl_2N_3O_6P$: C, 33.51; H, 3.91; N, 11.73. Found: C, 33.11; H, 3.79; N, 12.18.

***O,O*-Dimethyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)-1-(phenyl)methylphosphonates (6f).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 3.73 (d, 6H, 2OCH_3, J = 10.8 Hz), 6.22 (d, 1H, OCHP, J = 14.0 Hz), 7.32–7.60 (m, 6H, Ar–H), 9.90 (s, 1H, NH); ^{31}P NMR ($CDCl_3$, 81 MHz): δ = 20.1; IR (υ/cm^{-1}): 3432 (N—H), 3036 (Ar–H), 1772 (C=O), 1554, 1510, 1454 (C=C), 1215 (P=O), 1171 (C—O), 1052 (P—O—C); Anal. Calcd. for $C_{14}H_{14}Cl_2N_3O_5P$: C, 41.37; H, 3.44; N, 10.34. Found: C, 41.03; H, 3.81; N, 10.30. MS (*m/z*,%): 405 (M^+ 7.90), 216 (57.60), 191 (55.00), 190 (56.50), 110 (100.00), 105 (54.00), 91 (9.05), 77 (54.45).

***O,O*-Dimethyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)-1-(2-chlorphenyl)methylphosphonates (6g).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 3.72 (d, 6H, 2OCH_3, J = 11.0 Hz), 6.73 (d, 1H, OCHP, J = 14.2 Hz), 7.22–7.77 (m, 5H, Ar–H), 9.90 (s, 1H, NH); ^{31}P-NMR ($CDCl_3$, 81 MHz): δ = 19.1; IR (υ/cm^{-1}): 3434 (N—H), 3037, 3004 (Ar–H), 1762 (C=O), 1579, 1552, 1515 (C=C), 1219 (P=O), 1191 (C—O), 1054 (P—O—C); Anal. Calcd. for $C_{14}H_{13}Cl_3N_3O_5P$: C, 38.18; H, 2.95; N, 9.54. Found: C, 38.59; H, 3.13; N, 9.01.

***O,O*-Dimethyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)-1-(4-chlorophenyl) methylphosphonates (6h).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 3.89 (d, 6H, 2OCH_3, J = 9.2 Hz), 6.81 (d, 1H, OCHP, J = 14.0 Hz), 7.15–7.39 (m, 5H, Ar–H), 10.35 (s, 1H, NH); ^{31}P-NMR ($CDCl_3$, 81 MHz): δ = 19.6; IR (υ/cm^{-1}): 3430 (N—H), 3032 (Ar–H), 1781 (C=O), 1581, 1555, 1511 (C=C), 1213 (P=O), 1172 (C—O), 1039 (P—O—C); Anal. Calcd. for $C_{14}H_{13}Cl_3N_3O_5P$: C, 38.18; H, 2.95; N, 9.54. Found: C, 38.40; H, 2.94; N, 9.52.

***O,O*-Dimethyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)-1-(4-nitrophenyl) methylphosphonates (6i).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 3.86 (d, 6H, $2OCH_3$, J = 11.0 Hz), 6.23 (d, 1H, OCHP, J = 15.2 Hz), 7.30–7.55 (m, 5H, Ar–H), 9.90 (s, 1H, NH); ^{31}P-NMR ($CDCl_3$, 81 MHz): δ = 18.5; IR (υ/cm^{-1}): 3426 (N—H), 3041 (Ar–H), 1764 (C=O), 1608, 1581, 1554 (C=C), 1216 (P=O), 1184 (C—O), 1040 (P—O—C); Anal. Calcd. for $C_{14}H_{13}Cl_2N_4O_7P$: C, 37.25; H, 2.88; N, 12.41. Found: C, 37.12; H, 2.94; N, 12.08.

***O,O*-Diethyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)ethylphosphonates (6j).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 1.65 (m, 3H, CH_3), 1.44–1.48 (m, 6H, $2CH_3$), 4.27–4.30 (m, 4H, $2OCH_2$), 5.43–5.45 (m, 1H, OCHP), 7.06 (s, 1H, Ar–H), 10.23 (s, 1H, NH); ^{31}P-NMR ($CDCl_3$, 81 MHz): δ = 21.5; IR (υ/cm^{-1}): 3350 (N—H), 3010 (Ar–H), 1767 (C=O), 1612, 1580, 1556 (C=C), 1216 (P=O), 1182 (C-O), 1050 (P—O—C); Anal. Calcd. for $C_{11}H_{16}Cl_2N_3O_5P$: C, 35.48; H, 4.30; N, 11.29. Found: C, 35.41; H, 4.34; N, 10.81.

***O,O*-Diethyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)-1-(phenyl)methylphosphonates (6k).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 1.15–1.17 (m, 6H, $2CH_3$), 4.15–4.17 (m, 4H, $2OCH_2$), 6.18 (d, 1H, OCHP, J = 15.2 Hz), 7.38–7.61 (m, 6H, Ar–H), 9.80 (s, 1H, NH); ^{31}P-NMR ($CDCl_3$, 81 MHz): δ = 18.1; IR (υ/cm^{-1}): 3416 (N—H), 3026 (Ar–H), 1774 (C=O), 1577, 1555, 1508 (C=C), 1216 (P=O), 1172 (C—O), 1047 (P—O—C); Anal. Calcd. for $C_{16}H_{18}Cl_2N_3O_5P$: C, 44.23; H, 4.14; N, 9.67. Found: C, 44.36; H, 4.17; N, 9.56.

***O,O*-Diethyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)-1-(2-chlorophenyl)methylphosphonates (6l).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = δ = 1.15–1.19 (m, 6H, $2CH_3$), 4.15–4.17 (m, 4H, $2OCH_2$), 5.60 (d, 1H, OCHP, J = 14.2 Hz), 7.22–7.78 (m, 5H, Ar–H), 9.40 (s, 1H, NH); ^{31}P NMR ($CDCl_3$, 81 MHz): δ = 21.2; IR (υ/cm^{-1}): 3422 (N—H), 3030 (Ar–H), 1772 (C=O), 1577, 1551, 1476 (C=C), 1216 (P=O), 1177 (C—O), 1051 (P—O—C); Anal. Calcd. for $C_{16}H_{17}Cl_3N_3O_5P$: C, 41.02; H, 3.62; N, 9.09. Found: C, 40.82; H, 3.58; N, 8.57.

***O,O*-Diethyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)-1-(4-chlorophenyl)methylphosphonates (6m).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 1.18–1.21 (m, 6H, $2CH_3$), 4.24–4.28 (m, 4H, $2OCH_2$), 6.14 (d, 1H, OCHP, J = 14.2 Hz), 7.28–7.57 (m, 5H, Ar–H), 9.90 (s, 1H, NH); ^{31}P-NMR ($CDCl_3$, 81 MHz): δ = 17.0; IR (υ/cm^{-1}): 3321 (N—H), 3029 (Ar–H), 1781 (C=O), 1575, 1552, 1509 (C=C), 1216 (P=O), 1165 (C—O), 1051 (P—O—C); Anal. Calcd. for $C_{16}H_{17}Cl_3N_3O_5P$: C, 41.02; H, 3.62; N, 9.09. Found: C, 41.07; H, 3.67; N, 8.54.

***O,O*-Diisopropyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)ethylphosphonates (6n).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 1.06–1.65 (m, 15H, $5CH_3$), 4.80–4.87 (m, 2H, 2CH), 5.18–5.21 (m, 1H, OCHP), 7.30 (s, 1H, Ar–H), 9.70 (s, 1H, NH); ^{31}P-NMR ($CDCl_3$, 81 MHz): δ = 19.4; IR (υ/cm^{-1}): 3310 (N—H), 3022 (Ar–H), 1768 (C=O), 1576, 1546, 1507 (C=C), 1212 (P=O), 1180 (C—O), 1039 (P—O—C); Anal. Calcd. for $C_{13}H_{20}Cl_2N_3O_5P$: C, 39.02; H, 5.02; N, 10.50. Found: C, 39.07; H, 4.87; N, 10.33.

***O,O*-Diisopropyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)-1-(phenyl)methylphosphonates (6o).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 1.31–1.41 (m, 12H, $4CH_3$), 4.78–4.98 (m, 2H, 2CH), 6.11 (d, 1H, OCHP, J = 14.2 Hz), 7.27–7.64 (m, 6H, Ar–H), 10.10 (s, 1H, NH); ^{31}P NMR ($CDCl_3$, 81 MHz): δ = 15.7; IR (υ/cm^{-1}): 3426 (N—H), 3026 (Ar–H), 1772 (C=O), 1576, 1553, 1455 (C=C), 1217 (P=O), 1172 (C—O),

1073 (P—O—C); Anal. Calcd. for $C_{18}H_{22}Cl_2N_3O_5P$: C, 46.77; H, 4.80; N, 9.09. Found: C, 46.75; H, 4.76; N, 8.57.

***O,O*-Diisopropyl 1-((4,6-dichloropyrimidin-2-yl)carbamyloxy)-1-(furan-2-yl)methylphosphonates (6p).** White solid: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 1.01–1.13 (m, 12H, 4CH_3), 4.89–5.06 (m, 2H, 2CH), 6.21 (d, 1H, OCHP, J = 14.2 Hz), 6.68–7.28 (m, 4H, Ar–H), 9.90 (s, 1H, NH); ^{31}P-NMR ($CDCl_3$, 81 MHz): δ = 13.3; IR (υ/cm^{-1}): 3406 (N—H), 3022 (Ar–H), 1774 (C=O), 1578, 1551, 1509 (C=C), 1215 (P=O), 1173 (C—O), 1074 (P—O—C); Anal. Calcd. for $C_{16}H_{20}Cl_2N_3O_6P$: C, 42.49; H, 4.46; N, 9.29. Found: C, 42.44; H, 4.72; N, 8.90.

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SUPPLEMENTAL MATERIAL

Supplementary data of this article can be accessed on the publisher's website, www.tandfonline.com/gpss

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