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ORIGINAL PAPER

Synthesis and larvicidal activity of 1,3,4-oxadiazole derivatives containing a 3-chloropyridin-2-yl-1*H*-pyrazole scaffold

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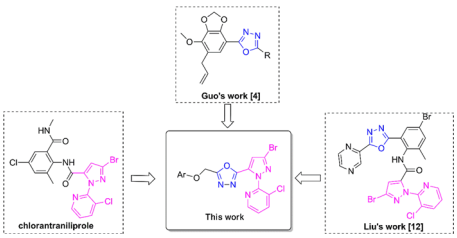
Abstract A new series of 1,3,4-oxadiazole derivatives with a 3-chloropyridin-2-yl-1*H*-pyrazole moiety was designed, synthesized, and characterized. The results of bioassay against *Helicoverpa armigera* and *Plutella xylostella* indicated that some of the synthesized compounds showed remarkable larvicidal activity. In particular, the LC_{50} values of the most active compounds against *P. xylostella* were 46.5, 23.9, and 13.9 mg/dm^3, and against *Helicoverpa armigera* were 88.3 and 69.5 mg/dm^3, the latter being slightly better than commercial chlorpyrifos (LC_{50} 103.77 mg/dm^3). Preliminary SAR was also discussed.

Graphical abstract



Yanyan Wang and Xiumian Lu are Co-first authors.

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Keywords 1,3,4-Oxadiazole derivatives · 3-Chloropyridin-2-yl-1*H*-pyrazole · Synthesis · Larvicidal activity

Introduction

In recent years, because of the continued warming weather and the resistance of insecticide, the pests in agriculture have become more and more difficult to prevent and control, which brought about enormous economic losses all over the world annually [1]. For example, the diamondback moth (*Plutella xylostella*) is a seriously harmful pest in many countries [2] and has caused a significant loss to oilseed plants and crucifers [3]. Hence, the discovery of novel molecules with excellent insecticidal activity has been attracting more and more attention in recent years.

1,3,4-Oxadiazole, a highly active pharmacophore, is widely used in pesticide design. Many compounds containing such a scaffold with excellent activity have been reported as insecticides (such as compounds **1**–**5** in Fig. 1) [4–14], fungicides [15–17], and herbicides [18–21]. For example, Liu and co-workers developed a series of anthranilic diamides analogs containing 1,3,4-oxadiazole that showed excellent insecticidal activity against *P. xylostella* [11]. As well as some insecticidal sarisan analogues with an 1,3,4-oxadiazole scaffold were developed by Guo et al. [4–6].

3-Chloropyridin-2-yl-1*H*-pyrazole is another important heterocyclic group and appears in many insecticidal molecules [22–27], the commercial chlorantraniliprole [22], cyantraniliprole [23, 24], and SYP-9080 (Fig. 2) [25] containing this type of scaffold. And in recent years, a large number of 3-chloropyridin-2-yl-1*H*-pyrazole derivatives

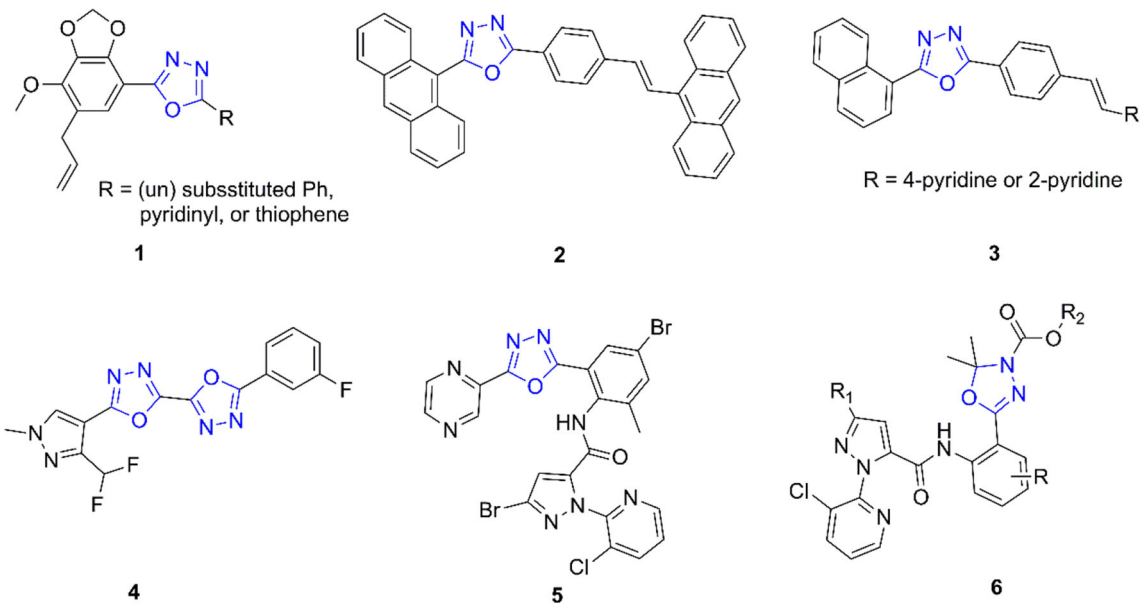


Fig. 1 The structures of insecticidal molecules containing a structure of 1,3,4-oxadiazole

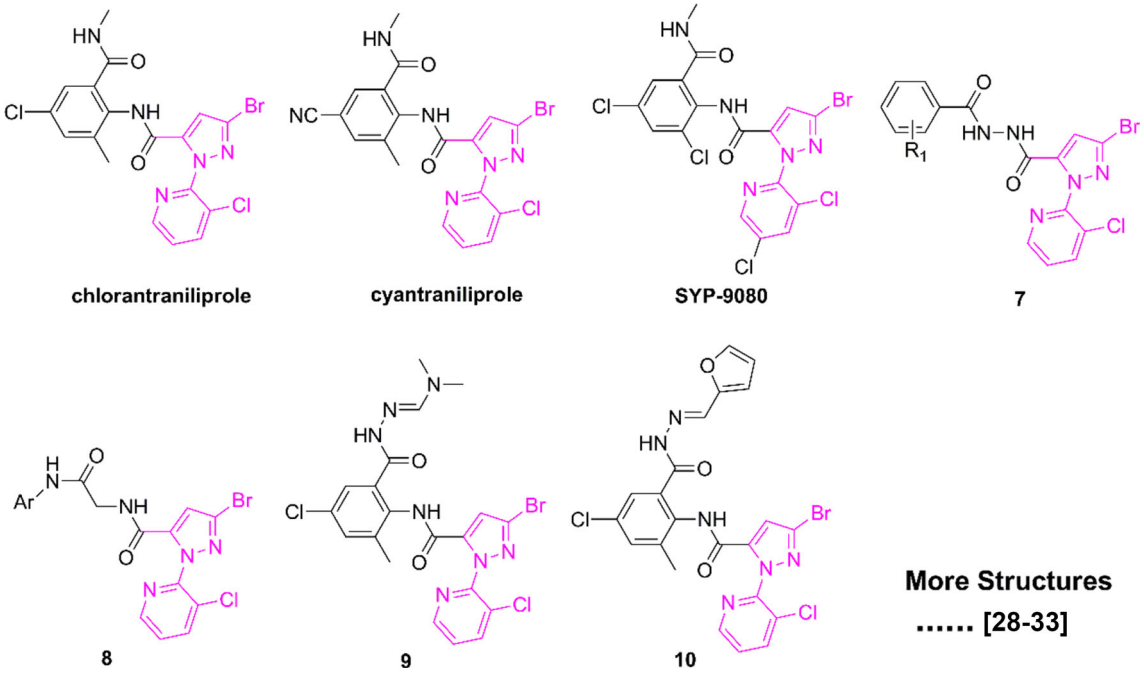


Fig. 2 The structures of commercial insecticides and insecticidal molecules containing the substructures of 3-chloropyridin-2-yl-1*H*-pyrazole

with excellent larvicidal activity were reported (such as compounds **5**, **6** in Fig. 1 and compounds **6–10** in Fig. 2) [9, 10, 25–27]. Most of them are anthranilic diamide derivatives and shown excellent insecticidal activities against various pests including diamondback moth, cotton bollworm, beet armyworm, oriental leafworm moth, etc. in our previous work [28–33]. A series of diamide derivatives containing a 3-chloropyridin-2-yl-1*H*-pyrazole scaffold and 1,3,4-oxadiazole substructure has been developed; some of them (such compounds **9** and **10** in Fig. 2) showed excellent larvicidal activity against not only lepidoptera but also diptera and homoptera.

Encouraged by above reports and as a continuation of work on finding potential insecticidal molecule, an attempt was made in this work by incorporation of the scaffolds of 3-chloropyridin-2-yl-1*H*-pyrazole and 1,3,4-oxadiazole, then structural variation by the introduction of different kinds of moiety via an ether linkage, resulting in 1,3,4-

oxadiazole derivatives containing a 3-chloropyridin-2-yl-1*H*-pyrazole scaffold with good insecticidal activity (Fig. 3). Structures of the synthesized compounds were characterized by ^{1}H NMR, ^{19}F NMR, ^{13}C NMR, and HR-MS. Results of larvicidal assays indicated that some of synthesized compounds exhibited good larvicidal activities. In particular, the compounds **16u**, **16v**, and **16w** exhibited good larvicidal activities against *P. xylostella* and *H. armigera*; the LC_{50} values of them against *P. xylostella* were 46.5, 23.9, and 13.9 mg/dm^3, respectively, and the LC_{50} values of compounds **16u**, **16v** against *H. armigera* were 88.3, 69.5 mg/dm^3, respectively.

Results and discussion

Synthesis

The synthetic route for the title compounds are depicted in Scheme 1. First, the key intermediates substituted ethyl 2-phenoxyacetates **13** were easily obtained in good yield via reactions of ethyl 2-chloroacetate with different substituted phenols in the present of K_2CO_3 in solvent of acetonitrile, which further reacted with hydrazine hydrate (80%) to yield substituted 2-phenoxyacetohydrazides **14** in > 90% yields. Subsequent treatment of substituted 2-phenoxyacetohydrazides **14**, with 3-bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxylic acid (**15**, prepared according to reported protocols [19, 26, 27]) in the presence of phosphorus oxychloride at refluxing temperature afforded the title compounds **16** with excellent yield by employed known protocol [34].

In the ^{1}H NMR spectra, the proton at position 5 of pyridine ring appeared as a doublet of doublets near $\delta = 8.45$ ppm due to the coupling coefficients from the protons at positions 3 and 4 of the pyridine; the coupling constants were 4.6 and 1.5 Hz, respectively. Pyrazole-H exhibited a singlet near 7.15 ppm. The two protons (–CH_2–) appeared as a singlet near 5.10 ppm; in the ^{13}C NMR of F-contained compound, because of the coupling coefficient from F, the carbon was split into multiplet. For instance, the carbon connected to F resonance frequency is near $\delta = 155$ ppm as a doublet and with the coupling constant ($^{1}J_{C–F}$) range from 240 to 250 Hz; and the carbon at *ortho* position of fluorine atom was also split into doublet with coupling constant ($^{2}J_{C–F}$) ranged from 20 to 26 Hz; for the compound with a group of trifluoromethyl (–CF_3), the carbon (in –CF_3) was split as a quartet, the coupling coefficient ranged from 256 to 275 Hz, as well as the carbon linked to –CF_3 was split into a quartet with $^{2}J_{F–C}$ was about 31 Hz. The properties, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and HR-MS data of the synthesized compounds **16a** to **16ad** are summarized in more detail in the "Experimental".

Insecticidal activity

The larvicidal activities of the synthesized compounds against both *H. armigera* and *P. xylostella* were evaluated using procedures reported previously [29, 30, 33, 35, 36] and summarized in Tables 1 and 2, respectively.

The results listed in Table 1 revealed that some of the synthesized compounds showed weak to good larvicidal activity against *H. armigera* at the corresponding concentration. For example, the larvicidal activities of compounds

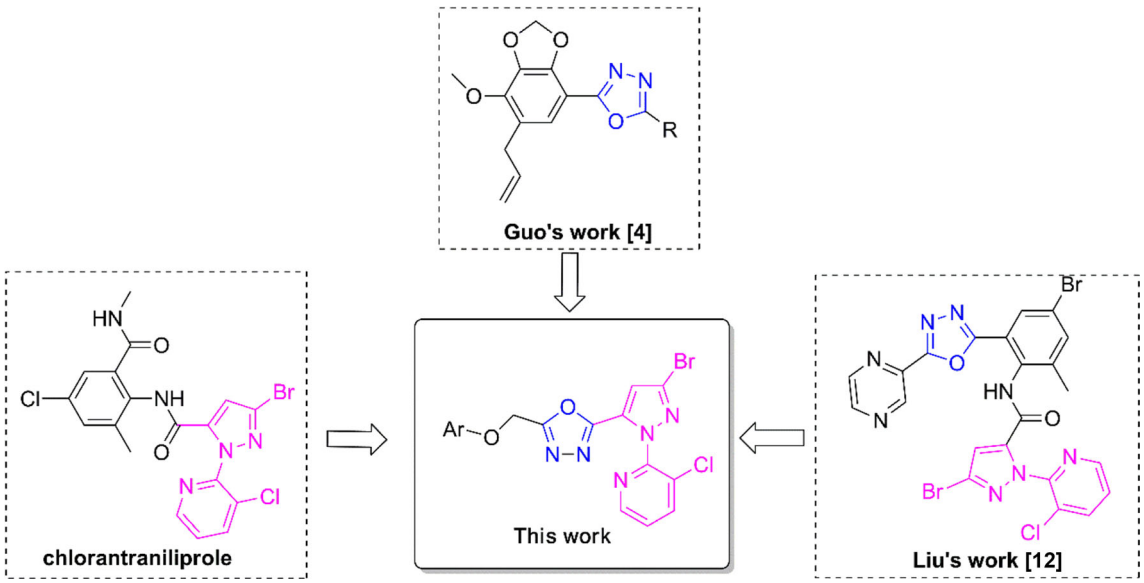
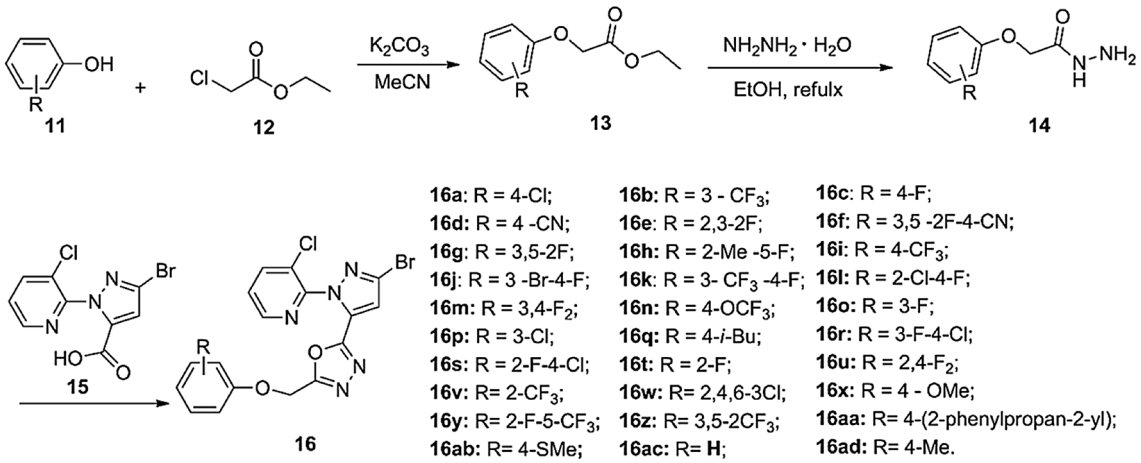


Fig. 3 The design of title compound

Scheme 1



16i, **16 s**, **16u**-**16w**, **16z**, and **16ab** were > 50% at 500 mg/dm^3 and the larvicidal activities of compounds **16u**, **16v**, **16w**, and **16ab** were 80.0, 83.3, 66.7, and 70.0%, respectively. Whereas the concentration was 100 mg/dm^3, the mortalities of compounds **16u** and **16w** were still over 50%. These results indicated that compounds **16u** and **16w** showed equivalent activity to that of commercial chlorpyrifos.

As shown in Table 2, some of the synthesized compounds showed no or weak larvicidal activity against *P. xylostella*. But several title compounds showed moderate to good larvicidal activity, for instance, the larvicidal activities of compounds **16f**, **16i**, **16k**, **16l**, **16r**, **16s**, **16u**, **16v**, **16w**, **16aa**, and **16ab** at 500 mg/dm^3 were 63.3, 80.0, 76.7, 73.3, 83.3, 90.0, 96.7, 100, 100, 63.3, and 93.3%, respectively. And compounds **16u**, **16v**, **16w** showed > 70% activities at 100 mg/dm^3. In particularly, the activity of compound **16w** was up to 93.3%. When the concentration decreased to 50 mg/dm^3, the activities of compounds **16u**, **16v**, and **16w** were 56.7, 73.3, and 80%, respectively. And compounds **16v**, **16w** showed moderated larvicidal activity at 25 mg/dm^3.

The median lethal concentrations (LC_{50}) for parts of the synthesized compounds were further evaluated by using previous protocols [33, 35, 36]. For comparison, the LC_{50} value of chlorpyrifos (a commonly used insecticide) was also evaluated. The LC_{50} values given in Table 3 indicated that the compounds **16r**, **16s**, **16u**, **16v**, **16w**, **16ab** against *P. xylostella* were 162.5, 100.6, 46.5, 23.9, 13.9, 69.7 mg/dm^3, respectively. And the LC_{50} values of compounds **16u**, **16v**, **16w** were 88.3, 69.5, and 190.1 mg/dm^3, in particularly, compounds **16u** and **16v** showed slightly better activity than commercial chlorpyrifos.

As revealed by data in Tables 1 and 2, the larvicidal activity of the title compound was affected by R group on benzene. When R was a hydrogen (**16ac**), the compound showed very weak larvicidal activity, and the activity could be further deceased by introduction of a monosubstitution group at 4 position of benzene (such as compounds **16a**, **16c**, **16d**, **16n**, and **16q**), as well as the compounds containing a monosubstitution at 3 position of benzene showed weak activities (e.g. compounds **16b**, **16g**, **16o**, **16p**, and **16q** etc.). In addition, the activity was disfavored when benzene was substituted by two groups at 3 and 5 positions, as well as decreased by introducing other substituents, such as 2-fluorine-5-(trifluoromethyl), 3,4-difluorine, and 3-bromine-4-fluorine. However, the activities could be slightly improved by introducing an appropriate bulky group at 4 position (**16i** > **16c**, **16q** > **16ad**) or 2 position (**16v** > **16t**) of benzene, but a much larger group was not favored (**16i** > **16n**). Moreover, the introduction of a methoxyl (**16x**) could slightly improve the activity, and the methylthio (**16ab**) was much more favored than methoxyl. Furthermore, the larvicidal activity could be enhanced by two fluorines at 2 and 4 positions (**16u**) or three chlorines at 2, 3, and 5 positions (**16w**) on benzene ring, simultaneously. And a compound containing a 4-(2-phenylpropan-2-yl) (**16aa**) was found to show moderate larvicidal activity.

Conclusions

Thirty novel 1,3,4-oxadiazole derivatives containing a 3-chloropyridin-2-yl-1*H*-pyrazole scaffold (**16a**–**16ad**) were designed and synthesized based on combination of the sub-structures of chlorantraniliprole and 1,3,4-oxadiazole. The structures of these compounds were characterized and confirmed by ^{1}H NMR, ^{19}F NMR, ^{13}C NMR, HR-MS. A preliminary evaluation of the larvicidal activities of the synthesized compounds against both *H. armigera* and *P.*

Table 1 Larvicidal activity of compounds **16a–16ad** against *H. armigera*

Comp.	Insecticidal activity/% at different concentrations/mg dm^{-3}				
	500	200	100	50	25
16a	0.0	–	–	–	–
16b	0.0	–	–	–	–
16c	0.0	–	–	–	–
16e	16.7	–	–	–	–
16f	33.3	5.6	–	–	–
16g	0.0	–	–	–	–
16h	0.0	–	–	–	–
16i	50.0	27.8	22.2	–	–
16j	0.0	–	–	–	–
16k	37.5	11.1	5.6	–	–
16l	33.3	5.6	–	–	–
16m	0.0	–	–	–	–
16n	0.0	–	–	–	–
16o	0.0	–	–	–	–
16p	0.0	–	–	–	–
16q	4.2	–	–	–	–
16r	41.7	16.7	11.1	–	–
16s	50.0	27.8	22.2	6.7	–
16t	0.0	–	–	–	–
16u	80.0	66.7	50.0	30.0	16.7
16v	83.3	72.2	56.7	40.0	23.3
16w	66.7	50.0	30.0	20	6.7
16x	8.3	–	–	–	–
16y	16.7	–	–		
16z	54.2	33.3	27.8	6.7	
16aa	33.3	5.6	0.0	–	–
16ab	70.0	56.7	40.0	23.3	6.7
16ac	4.2	–	–	–	–
16ad	0.0	–	–	–	–
Chlorantraniliprole	100	100	100	100	100
Chlorpyrifos	100	83.3	66.7	36.7	20
Avermectins	100	100	100	100	100

xylostella was conducted. The results indicated that some of the synthesized compounds exhibited good larvicidal activity against the tested pests. In particular, the LC_{50} values of compounds **16r**, **16s**, **16u**, **16v**, **16w**, and **16ab** against *P. xylostella* were 162.5, 100.6, 46.5, 23.9, 13.9, and 69.7 mg/dm^3, respectively. And the LC_{50} values of compounds **16u**, **16v**, and **16w** against *H. armigera* were 88.3, 69.5, and 190.1 mg/dm^3, respectively. Compounds **16u** and **16v** showed slightly better activity against *H. armigera* than commercial chlorpyrifos (LC_{50} 103.77 mg/dm^3). Preliminary SAR study revealed that an appropriate bulky group at 4 position or 2 position of benzene can slightly improve the activities, and the larvicidal activity could be enhanced by 2,4-difluorine and 2,3,5-trichlorine on benzene ring. Further structural modifications and biological evaluation to explore the full potential of this kind of 1,3,4-oxadiazole derivatives containing a 3-chloropyridin-2-yl-1*H*-pyrazole scaffold are currently in progress in our laboratory.

Experimental

All chemical reagents were of analytical grade and purchased from Accela ChemBio Co., Ltd. (Shanghai, China). Melting points were determined using a XT-4 melt point

Table 2 Larvicidal activity of compounds **16a–16ad** against *P. xylostella*

Comp.	Insecticidal activity/% at different concentrations/mg dm^{-3}				
	500	200	100	50	25
16a	20.0	–	–	–	–
16b	20.0	–	–	–	–
16c	16.7	3.3	–	–	–
16d	30				
16e	16.7	0	–	–	–
16f	63.3	30	6.7	–	–
16g	0.0	–	–	–	–
16h	0.0	–	–	–	–
16i	80.0	57.8	42.2	–	–
16j	0.0	–	–	–	–
16k	76.7	53.3	36.7	26.7	3.3
16l	73.3	25.6	6.7	–	–
16m	13.3	–	–	–	–
16n	0.0	–	–	–	–
16o	3.3	–	–	–	–
16p	0.0	–	–	–	–
16q	4.2	0.0	0.0	–	–
16r	83.3	56.7	33.3	20.0	3.3
16s	90.0	70.0	43.3	30	16.7
16t	6.7	–	–	–	–
16u	96.7	86.7	70.0	56.7	30
16v	100	96.7	86.7	73.3	56.7
16w	100	100	93.3	80	67.7
16x	28.3	13.3	–	–	–
16y	56.7	30.0	6.7		
16z	50.0	33.3	27.8		
16aa	63.3	35.6	20.0	6.7	
16ab	93.3	76.7	60.0	40	23.3
16ac	14.2	4.0	1.0	–	–
16ad	25.0	6.7	–	–	–
Chlorpyrifos	100	100	100	90	83
Chlorantraniliprole	100	100	100	100	100

instrument (Beijing Tech Instrument Co., China). ^{1}H and ^{13}C NMR were gauged on an AVANCE III HD 400 M NMR (Bruker corporation, Switzerland) or JEOL ECX 500 NMR spectrometer (JEOL Ltd., Japan) operating at room temperature using DMSO-d_6 or $CDCl_3$ as solvents. HR-MS was collected on an Orbitrap LC–MS instrument (Q-Exative, Thermo Scientific™, American). The course of the reactions was monitored by TLC.

*General procedure for intermediates **14***

Intermediates **14** were prepared by following the known procedure [22, 29, 30]. The mixture of ethyl 2-chloroacetate (1 mmol), substituted phenols (1 mmol), and K_2CO_3 (1.2 mmol) in acetonitrile was stirred in refluxing for 2 h (the course of the reactions was monitored by TLC), then filtered, and the mother liquid was evaporated in vacuo to afford corresponding substituted ethyl 2-phenoxyacetates, which were then reacted with hydrazine hydrate (80%) to yield substituted 2-phenoxyacetohydrazides **14** in > 90% yield.

*General procedure for the synthesis of title compounds **16a–16ad***

Different fresh substituted 2-phenoxyacetohydrazides **14** (0.5 mmol), 3-bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxylic acid (0.5 mmol), and phosphorus

Table 3 IC_{50} values of parts of the title compounds and chlorpyrifos against *P. xylostella* and *H. armigera*

Insects	Comp.	IC_{50}/mg dm^{-3}	$y = a + bx$	r
P. xylostella	**16r**	162.5	$y = 0.4463 + 2.0598x$	0.99
	16s	100.6	$y = 1.5190 + 1.7383x$	0.99
	16u	46.5	$y = 2.05354 + 1.7674x$	0.99
	16v	23.9	$y = 2.3172 + 1.94551x$	0.99
	16w	13.9	$y = 3.0665 + 1.6907x$	0.99
	16ab	69.7	$y = 1.8632 + 1.7020x$	0.99
	Chlorpyrifos	7.6	$y = 3.730 + 1.44x$	0.98
H. armigera	**16u**	88.3	$y = 2.802 + 1.130x$	0.98
	16v	69.5	$y = 2.787 + 1.202x$	0.98
	16w	190.1	$y = 2.722 + 1.000x$	0.97
	Chlorpyrifos	103.77	$y = 2.228 + 1.375x$	0.98

oxychloride (3 cm^3) were added to a flask. The resulting mixture was stirred for 120 min at refluxing temperature; the resulting mixture was poured into crushed ice, neutralized with 10% NaOH, and then filtered and recrystallized from ethanol in good yield.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(4-chlorophenoxy)methyl]-1,3,4-oxadiazole
(**16a**, $C_{17}H_{10}BrCl_2N_5O_2$)
Yield 78.2%; white solid; m.p.: 82–83 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.44$ (dd, $^3J = 4.6$ Hz, $^4J = 1.6$ Hz, 1H, pyridine-H), 7.90 (dd, $^3J = 8.1$ Hz, $^4J = 1.6$ Hz, 1H, pyridine-H), 7.46 (dd, $^3J = 8.1$ Hz, $^4J = 4.6$ Hz, 1H, pyridine-H), 7.26 (d, $J = 7.0$ Hz, 2H, benzene-H), 7.11 (s, 1H, pyrazole-H), 6.87 (d, $J = 7.0$ Hz, 2H, benzene-H), 5.20 (s, 2H, $–CH_2–$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 162.16$, 156.59, 155.95, 147.86, 147.31, 139.71, 129.92, 129.78, 129.45, 128.99, 127.54, 126.66, 116.20, 112.58, 59.90 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{17}H_{10}BrCl_2N_5O_2$ ($[M+H]^+$) 465.94677, found 465.94672.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(3-(trifluoromethyl)phenoxy]methyl)-1,3,4-oxadiazole
(**16b**, $C_{18}H_{10}BrClF_3N_5O_2$)
Yield 78.2%; white solid; m.p.: 97–98 °C; ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 8.51$ (dd, $^3J = 4.7$ Hz, $^4J = 1.4$ Hz, 1H, pyridine-H), 8.25 (dd, $^3J = 8.1$ Hz, $^4J = 1.4$ Hz, 1H, pyridine-H), 7.69 (dd, $^3J = 8.1$ Hz, $^4J = 4.7$ Hz, 1H, pyridine-H), 7.55 (d, $^4J = 3.3$ Hz, 1H, benzene-H), 7.53 (t, $^3J = 8.3$ Hz, 1H, benzene-H), 7.36-7.33 (m, 2H, benzene-H + pyrazole-H), 7.29 (dd, $^3J = 8.1$ Hz, $^4J = 2.2$ Hz, 1H, benzene-H), 5.52 (s, 2H, $–CH_2–$) ppm; ^{19}F NMR (471 MHz, DMSO-d_6): $\delta = -61.01$ ppm; ^{13}C NMR (126 MHz, DMSO-d_6): $\delta = 163.23$, 157.91, 156.17, 148.28, 147.49, 140.70, 131.45, 131.06 (q, $J = 31.7$ Hz), 130.25, 128.88, 128.71, 128.24, 123.29 (q, $J = 272.6$ Hz), 119.74, 119.04, 119.01, 112.91, 112.11, 112.08, 60.19, 40.53, 40.36, 40.19, 40.03, 39.86, 39.69, 39.53 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{18}H_{10}BrClF_3N_5O_2$ ($[M+H]^+$) 499.97313, found 499.97275.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(4-fluorophenoxy)methyl]-1,3,4-oxadiazole
(**16c**, $C_{17}H_{10}BrClFN_5O_2$)
Yield 78.2%; white solid; m.p.: 85–87 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.45$ (dd, $^3J = 4.7$ Hz, $^4J = 1.6$ Hz, 1H), 7.90 (dd, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, 1H), 7.44 (dd, $^3J = 8.1$ Hz, $^4J = 4.7$ Hz, 1H), 7.11 (s, 1H, pyrazole-H), 7.00-6.95 (m, 2H, benzene-H), 6.91-6.87 (m, 2H, benzene-H), 5.19 (s, 2H, $–CH_2–$) ppm; ^{19}F NMR (471 MHz, $CDCl_3$): $\delta = -121.29$ ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 162.33$, 159.18, (d, $J = 240.8$ Hz), 156.56, 153.50, 147.91, 147.31, 139.68, 129.97, 129.72 (d, $J = 63.9$ Hz), 128.96, 126.62, 116.42, 116.29, 116.23, 112.52, 60.42 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{17}H_{10}BrClFN_5O_2$ ($[M+H]^+$) 499.97632, found 499.97635.

4-[[5-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-1,3,4-oxadiazol-2-yl]methoxy]benzonitrile
(**16d**, $C_{18}H_{10}BrClN_6O_2$)
Yield 78.2%; white solid; m.p.: 88–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.47$ (dd, $^3J = 4.7$ Hz, $^4J = 1.5$ Hz, 1H), 7.93 (dd, $^3J = 8.1$ Hz, $^4J = 1.5$ Hz, 1H), 7.62 (d, $^3J = 8.9$ Hz, 2H, benzene-H), 7.47 (dd, $^3J = 8.1$ Hz, $^4J = 4.7$ Hz, 1H), 7.12 (s, 1H, pyrazole-H), 7.05 (d, $^3J = 8.9$ Hz, 2H, benzene-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 164.60$, 162.63, 161.57, 156.66, 147.84, 139.72, 129.84, 129.41, 128.96, 126.70, 112.62, 99.00, 98.77, 98.16, 97.96, 59.92 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{18}H_{10}BrClN_6O_2$ ($[M+H]^+$) 446.98099, found 446.98092.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(2,3-difluorophenoxy)methyl]-1,3,4-oxadiazole
(**16e**, $C_{17}H_9BrClF_2N_5O_2$)
Yield 78.2%; white solid; m.p.: 103–104 °C; ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 8.54$ (dd, $^3J = 4.6$ Hz, $^4J = 1.4$ Hz, 1H, pyridine-H), 8.26 (dd, $^3J = 8.1$ Hz, $^4J = 1.4$ Hz, 1H, pyridine-H), 7.69 (dd, $^3J = 8.1$ Hz, $^4J = 4.6$ Hz, 1H, pyridine-H), 7.58–7.51 (m, 1H, benzene-H, pyridine-H), 7.17–6.98 (m, 3H, benzene-H), 5.53 (s, 2H, –CH_2–) ppm; ^{19}F NMR (471 MHz, DMSO-d_6): $\delta = -137.60$, -159.54 ppm; ^{13}C NMR (126 MHz, DMSO-d_6): $\delta = 162.99$, 156.24, 150.97 (dd, $J = 245.1$, 10.1 Hz), 148.28, 147.47, 140.83 (dd, $J = 246.3$, 14.6 Hz), 140.71, 130.21, 128.92, 128.70, 124.82 (d, $J = 8.8$ Hz), 124.78, 112.99, 111.77, 111.74, 111.07 (d, $J = 17.2$ Hz), 61.20 ppm; HR-MS (ESI$^+$): *m/z* calcd for $C_{17}H_9BrClF_2N_5O_2$ ([M+H]$^+$) 467.96690, found 467.96698.

4-[[5-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-1,3,4-oxadiazol-2-yl]methoxy]-2,6-difluorobenzonitrile
(**16f**, $C_{18}H_8BrClF_2N_6O_2$)
Yield 78.2%; white solid; m.p.: 76–77 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.48$ (dd, $^3J = 4.5$ Hz, $^4J = 1.5$ Hz, 1H, pyridine-H), 7.87 (d, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz, 1H, pyridine-H), 7.40 (dd, $^3J = 8.0$ Hz, $^4J = 4.6$ Hz, 1H, pyridine-H), 7.07 (s, 1H, pyrazole-H), 6.64 (s, 1H, benzene-H), 6.62 (s, 1H, benzene-H), 4.87 (s, 2H, –CH_2–) ppm; ^{19}F NMR (471 MHz, $CDCl_3$): $\delta = -101.86$ ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 163.74$ (d, $J = 247.9$ Hz), 163.62 (d, $J = 247.9$ Hz), 159.04 (t, $J = 13.5$ Hz), 156.66, 147.84, 147.32, 139.72, 129.84, 129.41, 128.96, 126.70, 115.17, 112.62, 98.98 (d, $J = 7.2$ Hz), 98.81 (d, $J = 7.2$ Hz), 98.37, 98.16, 97.96, 59.92 ppm; HR-MS (ESI$^+$): *m/z* calcd for $C_{18}H_8BrClF_2N_6O_2$ ([M+H]$^+$) 492.96215, found 492.96211.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(3,5-difluorophenoxy)methyl]-1,3,4-oxadiazole
(**16g**, $C_{17}H_9BrClF_2N_5O_2$)
Yield 78.2%; white solid; m.p.: 91–92 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.43$ (dd, $^3J = 4.6$ Hz, $^4J = 1.4$ Hz, 1H, pyridine-H), 7.90 (d, $^3J = 8.1$ Hz, $^4J = 1.4$ Hz, 1H, pyridine-H), 7.44 (dd, $^3J = 8.1$ Hz, $^4J = 4.6$ Hz, 1H, pyridine-H), 7.10 (s, 1H, pyrazole-H), 6.51–6.39 (m, 3H, benzene-H), 5.18 (s, 2H, –CH_2–) ppm; ^{19}F NMR (471 MHz, $CDCl_3$): $\delta = -107.64$ ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 163.74$ (d, $J = 247.9$ Hz), 163.62 (d, $J = 247.9$ Hz), 159.04 (t, $J = 13.5$ Hz), 156.66, 147.84, 147.32, 139.72, 129.84, 129.41, 128.96, 126.70, 112.62, 98.97 (d, $J = 7.2$ Hz), 98.80 (d, $J = 7.2$ Hz), 98.37, 98.16, 97.96, 59.92 ppm; HR-MS (ESI$^+$): *m/z* calcd for $C_{17}H_9BrClF_2N_5O_2$ ([M+H]$^+$) 467.96690, found 467.96698.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(5-fluoro-2-methylphenoxy)methyl]-1,3,4-oxadiazole
(**16h**, $C_{18}H_{12}BrClFN_5O_2$)
Yield 78.2%; white solid; m.p.: 95–97 °C; ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 8.49$ (dd, $^3J = 4.7$ Hz, $^4J = 1.5$ Hz, 1H, pyridine-H), 8.24 (dd, $^3J = 8.1$ Hz, $^4J = 1.5$ Hz, 1H, pyridine-H), 7.68 (dd, $^3J = 8.1$ Hz, $^4J = 4.7$ Hz, 1H, pyridine-H), 7.56 (s, 1H, pyrazole-H), 7.16 (dd, $^3J_{F–H} = 11.3$ Hz, $^4J_{H–H} = 4.0$ Hz, 1H, benzene-H), 6.95 (dd, $^3J_{F–H} = 11.1$ Hz, $^4J_{H–H} = 2.5$ Hz, 1H, benzene-H), 6.72 (td, $^3J_{H–H} = 8.4$ Hz, $^4J_{H–H} = 2.5$ Hz, 1H, benzene-H), 5.43 (s, 2H, –CH_2–), 2.04 (s, 3H, –CH_3) ppm; ^{19}F NMR (471 MHz, DMSO-d_6): $\delta = -114.33$ ppm; ^{13}C NMR (126 MHz, DMSO-d_6): $\delta = 161.70$ (d, $J = 244.2$ Hz), 162.22, 156.59, 156.12, 156.04, 147.86, 147.30, 139.71, 131.58, 131.50, 129.98, 129.41, 128.98, 126.66, 122.74, 122.71, 112.57, 108.44 (d, $J = 20.7$ Hz), 100.08 (d, $J = 25.9$ Hz), 59.95, 15.64 ppm; HR-MS (ESI$^+$): *m/z* calcd for $C_{18}H_{12}BrClFN_5O_2$ ([M+H]$^+$) 463.99197, found 463.99213.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(4-(trifluoromethyl)phenoxy]methyl)-1,3,4-oxadiazole
(**16i**, $C_{18}H_{10}BrClF_3N_5O_2$)
Yield 78.2%; white solid; m.p.: 97–98 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.44$ (dd, $^3J = 4.6$ Hz, $^4J = 1.3$ Hz, 1H, pyridine-H), 7.89 (dd, $^3J = 8.0$ Hz, $^4J = 1.3$ Hz, 1H, pyridine-H), 7.56 (d, $^3J = 8.6$ Hz, 2H, benzene-H), 7.42 (dd, $^3J = 8.0$ Hz, $^4J = 4.6$ Hz, 1H, pyridine-H), 7.11 (s, 1H, pyrazole-H), 7.02 (d, $^3J = 8.6$ Hz, 2H, benzene-H), 5.27 (s, 2H, –CH_2–) ppm; ^{19}F NMR (471 MHz, $CDCl_3$): $\delta = -61.60$ ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 161.84$, 159.67, 156.66, 147.86, 147.29, 139.69, 129.86, 129.42, 128.97, 127.34, 127.31, 126.65, 124.68 (q, $J = 32.8$ Hz), 124.17 (d, $J = 271.2$ Hz), 114.85, 112.61, 59.59 ppm; HR-MS (ESI$^+$): *m/z* calcd for $C_{18}H_{10}BrClF_3N_5O_2$ ([M+H]$^+$) 499.97313, found 499.97339.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(3-bromo-4-fluorophenoxy)methyl]-1,3,4-oxadiazole
(**16j**, $C_{17}H_9Br_2ClFN_5O_2$)
Yield 78.2%; white solid; m.p.: 117–118 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.44$ (dd, $^3J = 4.6$ Hz, $^4J = 1.5$ Hz, 1H), 7.90 (dd, $^3J = 8.1$ Hz, $^4J = 1.5$ Hz, 1H), 7.44 (dd, $^3J = 8.1$ Hz, $^4J = 4.6$ Hz, 1H), 7.12 (dd, $^3J = 5.4$ Hz, $^4J = 3.1$ Hz, 1H), 7.11 (s, 1H, pyrazole-H), 7.03 (t, $J = 8.5$ Hz, 1H, benzene-H), 6.85 (dt, $J = 9.0$, 3.4 Hz, 1H, benzene-H), 5.18 (s, 2H, –CH_2–) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 161.87$, 156.61, 154.82 (d, $J = 242.2$ Hz), 153.68, 147.85, 147.32, 139.71, 129.88, 129.42, 128.97, 126.67, 119.99, 116.98 (d, $J = 24.3$ Hz), 115.26, 112.60, 109.51 (d, $J = 22.9$ Hz), 60.42 ppm; HR-

MS (ESI^+): *m/z* calcd for $C_{17}H_9Br_2ClFN_5O_2$ ($[M+H]^+$) 527.88683, found 527.88596.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[[4-fluoro-3-(trifluoromethyl)phenoxy]methyl]-1,3,4-oxadiazole (**16k**, $C_{18}H_9BrClF_4N_5O_2$)

Yield 78.2%; white solid; m.p.: 86–88 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.43$ (dd, $^3J = 4.5$ Hz, $^4J = 1.7$ Hz, 1H, pyridine-H), 7.89 (dd, $^3J = 8.0$ Hz, $^4J = 1.7$ Hz, 1H, pyridine-H), 7.43 (dd, $^3J = 8.0$ Hz, $^4J = 4.6$ Hz, 1H, pyridine-H), 7.15 (s, 1H, pyrazole-H), 7.13–7.05 (m, 3H, benzene-H), 5.22 (s, 2H, $–CH_2–$) ppm; ^{19}F NMR (471 MHz, $CDCl_3$): $\delta = -61.50, -122.78$ ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 161.72, 156.64, 154.87$ (d, $J = 249.6$ Hz), 153.07, 147.83, 147.32, 139.73, 129.84, 129.42, 128.95, 126.73, 122.16 (q, $J = 271.2$ Hz), 119.18 (dq, $J = 33.3, 14.3$ Hz) 119.10, 118.22 (d, $J = 22.5$ Hz), 113.80, 112.57, 60.37 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{18}H_9BrClF_4N_5O_2$ ($[M+H]^+$) 517.96371, found 517.96412.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(2-chloro-4-fluorophenoxy)methyl]-1,3,4-oxadiazole (**16l**, $C_{17}H_9BrCl_2FN_5O_2$)

Yield 78.2%; white solid; m.p.: 110–112 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.46$ (dd, $^3J = 4.7$ Hz, $^4J = 1.6$ Hz, 1H, pyridine-H), 7.92 (dd, $^3J = 8.1$ Hz, $^4J = 1.6$ Hz, 1H, pyridine-H), 7.46 (dd, $^3J = 8.1$ Hz, $^4J = 4.7$ Hz, 1H, pyridine-H), 7.26 (s, 1H, pyrazole-H), 6.97 (d, $J = 4.8$ Hz, 1H, benzene-H), 6.91 (d, $J = 3.0$ Hz, 1H, benzene-H), 6.85 (dd, $^3J = 9.1$ Hz, $^4J = 4.9$ Hz, 2H, benzene-H) ppm; ^{19}F NMR (471 MHz, $CDCl_3$): $\delta = -119.23$ ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 163.04, 159.02$ (d, $J = 246.1$ Hz), 157.68, 157.60, 156.18, 148.29, 147.48, 140.70, 131.42, 130.23, 128.90, 128.72, 128.26, 112.99 (d, $J = 14.1$ Hz), 112.53, 104.82 (d, $J = 24.6$ Hz), 60.46 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{17}H_9BrCl_2FN_5O_2$ ($[M+H]^+$) 483.93735, found 483.93530.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(3,4-difluorophenoxy)methyl]-1,3,4-oxadiazole (**16m**, $C_{17}H_9BrClF_2N_5O_2$)

Yield 78.2%; white solid; m.p.: 85–86 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.42$ (dd, $^3J = 4.7$ Hz, $^4J = 1.5$ Hz, 1H, pyridine-H), 7.89 (dd, $^3J = 8.1$ Hz, $^4J = 1.5$ Hz, 1H), 7.43 (dd, $^3J = 8.1$ Hz, $^4J = 4.9$ Hz, 1H), 7.09 (s, 1H, pyrazole-H), 7.04 (dd, $J_{F–H} = 18.7$ Hz, $J_{F–H} = 9.2$ Hz, 1H), 6.76 (ddd, $J_{F–H} = 11.4$ Hz, $J_{F–H} = 6.4$ Hz, $J_{F–H} = 2.9$ Hz, 1H, benzene-H), 6.67-6.61 (m, 1H, benzene-H), 5.16 (s, 2H, $–CH_2–$) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): $\delta = -134.08$ (d, $J = 21.2$ Hz), -145.50 (d, $J = 21.1$ Hz) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 161.91, 156.59, 153.53, 150.51$ (dd, $J = 249.2, 14.0$ Hz), 147.84, 147.32, 146.05 (dd, $J = 242.6, 12.6$ Hz), 139.72, 129.89, 129.42, 128.93, 126.72, 117.74, 117.66 (d, $J = 18.6$ Hz), 112.56, 110.26, 105.15 (d, $J = 20.6$ Hz), 60.33 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{17}H_9BrClF_2N_5O_2$ ($[M + H]^+$) 467.96690, found 467.96674.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[[4-(trifluoromethoxy)phenoxy]methyl]-1,3,4-oxadiazole (**16n**, $C_{18}H_{10}BrClF_3N_5O_3$)

Yield 78.2%; white solid; m.p.: 62–64 °C; ^1H NMR (500 MHz, DMSO-d_6): $\delta = 8.51$ (dd, $^3J = 4.6$ Hz, $^4J = 1.4$ Hz, 1H, pyridine-H), 8.27 (dd, $^3J = 8.1$ Hz, $^4J = 1.3$ Hz, 1H, pyridine-H), 7.71 (dd, $^3J = 8.1$ Hz, $^4J = 4.8$ Hz, 1H, pyridine-H), 7.56 (s, 1H, pyrazole-H), 7.30 (d, $^3J = 9.0$ Hz, 2H, benzene-H), 7.08 (d, $^3J = 9.1$ Hz, 2H, benzene-H), 5.43 (s, 2H) ppm; ^{19}F NMR (471 MHz, $CDCl_3$): $\delta = -58.18$ ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 162.12, 156.57, 155.80, 147.84, 147.30, 143.92, 139.70, 129.94, 129.39, 128.93, 126.69, 122.76, 120.56$ (q, $J = 256.5$ Hz), 115.85, 112.54, 60.00 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{18}H_{10}BrClF_3N_5O_3$ ($[M+H]^+$) 515.96804, found 515.96674.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(3-fluorophenoxy)methyl]-1,3,4-oxadiazole (**16o**, $C_{17}H_{10}BrClFN_5O_2$)

Yield 78.2%; white solid; m.p.: 78–79 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.40$ (dd, $^3J = 4.7$ Hz, $^4J = 1.5$ Hz, 1H, pyridine-H), 7.86 (dd, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, 1H, pyridine-H), 7.40 (dd, $^3J = 8.1$ Hz, $^4J = 4.8$ Hz, 1H, pyridine-H), 7.21 (dd, $^3J = 8.3$ Hz, $^4J = 6.8$ Hz, 1H, benzene-H), 7.09 (s, 1H, pyrazole-H), 5.18 (s, 2H, $–CH_2–$) ppm; ^{19}F NMR (471 MHz, $CDCl_3$): $\delta = -110.37$ ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 163.52$ (d, $J = 246.7$ Hz), 162.11, 158.56, 156.55, 147.81, 147.31, 139.7, 130.77, 129.96, 129.36, 128.92, 126.72, 112.56, 110.33, 109.37 (d, $J = 21.3$ Hz), 103.00 (d, $J = 25.2$ Hz), 59.79 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{17}H_{10}BrClFN_5O_2$ ($[M+H]^+$) 449.97632, found 449.97424.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(3-chlorophenoxy)methyl]-1,3,4-oxadiazole (**16p**, $C_{17}H_{10}BrCl_2N_5O_2$)

Yield 78.2%; white solid; m.p.: 98–99 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.43$ (dd, $^3J = 4.7$ Hz, $^4J = 1.6$ Hz, 1H, pyridine-H), 7.89 (dd, $^3J = 8.1$ Hz, $^4J = 1.6$ Hz, 1H, pyridine-H), 7.44 (dd, $^3J = 8.1$ Hz, $^4J = 4.7$ Hz, 1H, pyridine-H), 7.21 (d, $^3J = 8.2$ Hz, 1H, benzene-H), 7.12 (s, 1H, pyrazole-H), 7.01 (dd, $^3J = 8.1$ Hz, $^4J = 1.9$ Hz, 1H, benzene-H), 6.94–6.92 (m, 1H, benzene-H), 6.82 (dd, $^3J = 8.3$ Hz, $^4J = 2.5$ Hz, 1H, benzene-H), 5.21 (s, 2H, -CH_2-) ppm; ^{13}C NMR

(126 MHz, $CDCl_3$): δ = 162.05, 157.98, 156.61, 147.84, 147.32, 139.72, 135.28, 130.69, 129.92, 129.41, 129.00, 126.65, 122.74, 115.64, 112.93, 112.61, 59.75 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{17}H_{10}BrCl_2N_5O_2$ ($[M+H]^+$) 465.94677, found 465.94492.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[[4-(tert-butyl)phenoxy]methyl]-1,3,4-oxadiazole
(**16q**, $C_{21}H_{19}BrClN_5O_2$)
Yield 78.2%; white solid; m.p.: 53–54 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.43 (dd, ^3J = 4.7 Hz, ^4J = 1.6 Hz, 1H), 7.85 (d, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1H), 7.39 (dd, ^3J = 8.0 Hz, ^4J = 4.7 Hz, 1H), 7.30 (d, ^3J = 7.2 Hz, 2H, benzene-H), 7.11 (s, 1H, pyrazole-H), 6.86 (d, J = 7.2 Hz, 2H, benzene-H), 5.18 (s, 2H, –CH_2–), 1.28 (s, 9H, –CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.78, 156.46, 155.20, 147.86, 147.33, 145.21, 139.72, 130.13, 129.38, 128.91, 126.72, 126.66, 114.39, 112.49, 77.61, 77.36, 77.10, 59.79, 34.29, 31.61 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{21}H_{19}BrClN_5O_2$ ($[M+H]^+$) 488.04835, found 488.04849.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(4-chloro-3-fluorophenoxy)methyl]-1,3,4-oxadiazole
(**16r**, $C_{17}H_9BrCl_2FN_5O_2$)
Yield 78.2%; white solid; m.p.: 124–126 °C; ^1H NMR (500 MHz, DMSO-d_6): δ = 8.58–8.46 (dd, 1H, ^3J = 4.7 Hz, ^4J = 1.5 Hz, pyridine-H), 8.32 (dd, 1H, ^3J = 7.9, ^4J = 1.5 Hz, 1H, pyridine-H), 7.70 (dd, ^3J = 7.9 Hz, ^4J = 4.7 Hz, 1H, pyridine-H), 7.56 (s, 1H, pyrazole-H), 7.48 (t, J = 8.8 Hz, 1H, benzene-H), 7.17 (dd, J = 11.2, 2.6 Hz, 1H, benzene-H), 6.87 (d, J = 8.6 Hz, 1H, benzene-H), 5.45 (s, 2H, –CH_2–) ppm; ^{19}F NMR (471 MHz, DMSO-d_6): δ = −113.29 ppm; ^{13}C NMR (126 MHz, DMSO-d_6): δ = 163.04, 159.02 (d, J = 246.1 Hz), 157.68, 157.60, 156.18, 148.29, 147.48, 140.70, 131.42, 130.23, 128.90, 128.72, 128.26, 112.99 (d, J = 14.1 Hz), 112.53, 104.82 (d, J = 24.6 Hz), 60.46 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{17}H_9BrCl_2FN_5O_2$ ($[M+H]^+$) 483.93735, found 483.93729.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(4-chloro-2-fluorophenoxy)methyl]-1,3,4-oxadiazole
(**16s**, $C_{17}H_9BrCl_2FN_5O_2$)
Yield 78.2%; white solid; m.p.: 83–84 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.46 (dd, ^3J = 4.7 Hz, ^4J = 1.5 Hz, 1H), 7.92 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H), 7.45 (dd, ^3J = 7.8 Hz, ^4J = 4.9 Hz, 1H), 7.13 (s, 1H, pyrazole-H), 7.12 (s, 1H, benzene-H), 7.04 (dt, J = 6.2, 2.0 Hz, 2H, benzene-H), 5.26 (s, 2H, –CH_2–) ppm; ^{19}F NMR (471 MHz, $CDCl_3$): δ = −129.45 ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.73, 153.80, 152.97 (d, J = 208.9 Hz), 147.32, 139.71, 129.87, 128.17, 126.65, 125.25, 124.70, 118.92, 117.82 (d, J = 6.5 Hz), 117.59 (d, J = 7.9 Hz), 112.65, 111.17, 61.49 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{17}H_9BrCl_2FN_5O_2$ ($[M+H]^+$) 483.93735, found 483.93515.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(2-fluorophenoxy)methyl]-1,3,4-oxadiazole
(**16t**, $C_{17}H_{10}BrClFN_5O_2$)
Yield 78.2%; white solid; m.p.: 74–75 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.39 (dd, ^3J = 4.6 Hz, ^4J = 1.3 Hz, 1H), 7.86 (dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz, 1H), 7.40 (dd, ^3J = 8.1 Hz, ^4J = 4.6 Hz, 1H), 7.09 (s, 1H, pyrazole-H), 7.06-6.92 (m, 4H, benzene-H), 5.24 (s, 2H, –CH_2–) ppm; ^{19}F NMR (471 MHz, $CDCl_3$): δ = −132.95 ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.16, 156.60, 152.93 (d, J = 247.0 Hz), 147.78, 147.33, 145.26 (d, J = 10.7 Hz), 139.73, 130.00, 129.32, 128.92, 126.74, 124.72, 123.57, 116.86 (d, J = 18.1 Hz) 116.54, 112.55, 61.19 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{17}H_{10}BrClFN_5O_2$ ($[M+H]^+$) 449.97632, found 449.97446.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(2,4-difluorophenoxy)methyl]-1,3,4-oxadiazole
(**16u**, $C_{17}H_9BrClF_2N_5O_2$)
Yield 78.2%; white solid; m.p.: 93–94 °C; ^1H NMR (500 MHz, DMSO-d_6): δ = 8.51 (dd, ^3J = 4.5 Hz, ^4J = 1.2 Hz, 1H, pyridine-H), 8.26 (dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz, 1H, pyridine-H), 7.70 (dd, ^3J = 8.1 Hz, ^4J = 4.7 Hz, 1H, pyridine-H), 7.56 (s, 1H, pyrazole-H), 7.33–7.20 (m, 2H, benzene-H), 7.01 (t, J = 8.7 Hz, 1H, benzene-H), 5.45 (s, 2H, –CH_2–) ppm; ^{19}F NMR (471 MHz, DMSO-d_6): δ = −117.96, −129.00 ppm; ^{13}C NMR (126 MHz, DMSO-d_6): δ = 163.15, 157.08 (dd, J = 240.8, 10.8 Hz), 156.21, 152.22 (dd, J = 247.9, 12.7 Hz),148.30, 147.48, 142.14 (dd, J = 10.7, 3.3 Hz), 140.71, 130.23, 128.91, 128.71, 128.29, 117.78, 117.77, 117.71, 117.69, 112.94, 111.63 (dd, J = 22.6, 3.9 Hz), 105.70 (dd, J = 27.5, 22.4 Hz), 61.56 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{17}H_9BrClF_2N_5O_2$ ($[M+H]^+$) 467.96690, found 467.96680.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[[2-(trifluoromethyl)phenoxy]methyl]-1,3,4-oxadiazole
(**16v**, $C_{18}H_{10}BrClF_3N_5O_2$)
Yield 78.2%; white solid; m.p.: 76–77 °C; ^1H NMR (500 MHz, DMSO-d_6): δ = 8.46 (dd, ^3J = 4.6 Hz, ^3J = 1.5 Hz, 1H, pyridine-H), 8.23 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H, pyridine-H), 7.70–7.64 (dd, ^3J = 8.1 Hz, ^4J = 4.6 Hz, 1H, pyridine-H), 7.61 (t, J = 7.7 Hz, 2H, benzene-H), 7.50 (s, 1H, benzene-H), 7.34 (dd, ^3J = 8.6 Hz, ^4J = 3.1 Hz, 1H, benzene-H), 7.19 (s, 1H, pyrazole-H), 5.58 (s, 2H, –CH_2–) ppm; ^{19}F NMR

(471 MHz, DMSO-d_6): $\delta = -60.62$ ppm; ^{13}C NMR (126 MHz, DMSO-d_6): $\delta = 163.12$, 156.21, 155.33, 148.24, 147.39, 140.70, 134.84, 130.21, 128.92, 128.60, 128.23, 127.53, 127.49, 123.95 (q, $J = 272.6$ Hz),122.35, 118.17 (q, $J = 30.6$ Hz), 114.91, 112.91, 60.64 ppm; HR-MS (ESI$^+$): *m/z* calcd for $C_{18}H_{10}BrClF_3N_5O_2$ ([M+H]$^+$) 499.97313, found 499.97113.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(2,4,6-trichlorophenoxy)methyl]-1,3,4-oxadiazole (**16w**, $C_{17}H_8BrCl_4N_5O_2$)

Yield 78.2%; white solid; m.p.: 123–124 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.48$ (d, $^3J = 4.7$ Hz, 1H, pyridine-H), 7.92 (d, $^3J = 8.0$ Hz, 1H, pyridine-H), 7.45 (dd, $^3J = 8.0$ Hz, $^4J = 4.7$ Hz, 1H, pyridine-H), 7.29 (d, $^4J = 0.9$ Hz, 2H, benzene-H), 7.13 (s, 1H, pyrazole-H), 5.18 (s, 2H, –CH_2–) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 161.53$, 156.76, 148.76, 147.91, 147.38, 139.72, 131.19, 130.03, 129.51, 129.14, 128.98, 126.73, 112.57, 63.50 ppm; HR-MS (ESI$^+$): *m/z* calcd for $C_{17}H_8BrCl_4N_5O_2$ ([M+H]$^+$) 533.86883, found 533.86873.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(4-methoxyphenoxy)methyl]-1,3,4-oxadiazole (**16x**, $C_{18}H_{13}BrClN_5O_3$)

Yield 78.2%; white solid; m.p.: 94–95 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.42$ (dd, $^3J = 4.3$ Hz, $^4J = 1.6$ Hz, 1H, pyridine-H), 7.88 (dd, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, 1H, pyridine-H), 7.42 (dd, $^3J = 8.0$ Hz, $^4J = 4.3$ Hz, 1H, pyridine-H), 7.10 (s, 1H, pyrazole-H), 6.86 (d, $J = 9.0$ Hz, 2H, benzene-H), 6.81 (d, $J = 9.1$ Hz, 2H, benzene-H), 5.15 (s, 2H, –CH_2–), 3.74 (s, 3H, –CH_3–) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 162.74$, 156.46, 155.08, 151.51, 147.90, 147.32, 139.68, 130.09, 129.43, 128.92, 126.64, 116.22, 114.90, 112.47, 60.64, 55.78 ppm; HR-MS (ESI$^+$): *m/z* calcd for $C_{18}H_{13}BrClN_5O_3$ ([M+H]$^+$) 461.99631, found 461.99411.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[[2-fluoro-5-(trifluoromethyl)phenoxy]methyl]-1,3,4-oxadiazole (**16y**, $C_{18}H_9BrClF_4N_5O_2$)

Yield 78.2%; white solid; m.p.: 64–66 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.44$ (d, $^3J = 4.6$ Hz, $^4J = 1.5$ Hz, 1H), 7.89 (dd, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz, 1H), 7.43 (dd, $^3J = 8.0$ Hz, $^4J = 4.6$ Hz, 1H), 7.29 (d, $^3J = 5.9$ Hz, 2H, benzene-H), 7.20 (t, $^3J = 9.2$ Hz, 1H, benzene-H), 7.13 (s, 1H, pyrazole-H), 5.31 (s, 2H, –CH_2–) ppm; ^{19}F NMR (471 MHz, $CDCl_3$): $\delta = -61.90$, -126.72 ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 161.43$, 156.74, 154.79 (d, $J = 253.7$ Hz), 147.80, 147.34, 145.53 (d, $J = 11.5$ Hz), 139.74, 129.85, 129.37, 128.96, 127.25 (d, $J = 29.5$ Hz), 126.74, 123.37 (q, $J = 272.4$ Hz), 120.91, 117.40 (d, $J = 19.4$ Hz) 113.87, 112.62, 61.33 ppm; HR-MS (ESI$^+$): *m/z* calcd for $C_{18}H_9BrClF_4N_5O_2$ ([M+H]$^+$) 517.96371, found 517.96343.

2-[[3,5-Bis(trifluoromethyl)phenoxy]methyl]-5-[3-bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-1,3,4-oxadiazole (**16z**, $C_{19}H_9BrClF_6N_5O_2$)

Yield 78.2%; white solid; m.p.: 73–74 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.44$ (dd, $^3J = 4.7$ Hz, $^4J = 1.5$ Hz, 1H, pyridine-H), 7.90 (dd, $^3J = 8.1$ Hz, $^4J = 1.5$ Hz, 1H, pyridine-H), 7.54 (s, 1H, benzene-H), 7.44 (dd, $^3J = 8.1$ Hz, $^4J = 4.7$ Hz, 1H, pyridine-H), 7.39 (s, 2H, benzene-H), 7.10 (s, 1H, pyrazole-H), 5.33 (s, 2H, –CH_2–) ppm; ^{19}F NMR (471 MHz, $CDCl_3$): $\delta = -62.93$ ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 161.16$, 157.82, 156.76, 147.84, 147.32, 139.72, 133.33 (q, $J = 33.7$ Hz), 129.74, 129.42, 128.97, 126.70, 124.01, 121.84, 116.13, 115.28, 112.64, 60.02 ppm; HR-MS (ESI$^+$): *m/z* calcd for $C_{19}H_9BrClF_6N_5O_2$ ([M+H]$^+$) 567.96051, found 567.96055.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[[4-(2-phenylpropan-2-yl)phenoxy]methyl]-1,3,4-oxadiazole (**16aa**, $C_{26}H_{21}BrClN_5O_2$)

Yield 78.2%; white solid; m.p.: 191–192 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.42$ (d, $^3J = 4.6$ Hz, 1H, pyridine-H), 7.87 (d, $^3J = 8.0$ Hz, 1H, pyridine-H), 7.40 (dd, $^3J = 8.0$ Hz, $^4J = 4.6$ Hz, 1H, pyridine-H), 7.32–7.22 (m, 5H, benzene-H), 7.17 (d, $J = 7.7$ Hz, 2H, benzene-H), 7.12 (s, 1H, pyrazole-H), 6.84 (d, $J = 7.9$ Hz, 2H, benzene-H), 5.20 (s, 2H, –CH_2–), 1.67 (s, 6H, –CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 162.69$, 156.50, 155.32, 150.61, 147.91, 147.35, 144.89, 139.73, 130.10, 129.43, 128.97, 128.20, 128.06, 126.80, 126.67, 125.83, 114.93, 114.30, 112.52, 59.74, 42.51, 30.94 ppm; HR-MS (ESI$^+$): *m/z* calcd for $C_{26}H_{21}BrClN_5O_2$ ([M+H]$^+$) 550.06400, found 550.06398.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[[4-(methylthio)phenoxy]methyl]-1,3,4-oxadiazole (**16ab**, $C_{18}H_{13}BrClN_5O_2S$)

Yield 78.2%; white solid; m.p.: 78–80 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.43$ (dd, $^3J = 4.7$ Hz, $^4J = 1.6$ Hz, 1H), 7.89 (dd, $^3J = 8.1$ Hz, $^4J = 1.6$ Hz, 1H), 7.42 (dd, $^3J = 8.0$ Hz, $^4J = 4.6$ Hz, 1H), 7.22 (d, $^3J = 8.7$ Hz, 2H, benzene-H), 7.11 (s, 1H, pyrazole-H), 6.87 (d, $^3J = 8.8$ Hz, 2H, benzene-H), 5.19 (s, 2H, –CH_2–), 2.43 (s, 3H, CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 162.41$, 156.53, 155.68, 147.87, 147.30, 139.69, 131.38, 129.99, 129.57, 129.42, 128.95, 126.64, 115.72, 115.60, 112.53, 59.87, 17.45 ppm; HR-MS (ESI$^+$): *m/z* calcd for $C_{18}H_{13}BrClN_5O_2S$ ([M+H]$^+$) 477.97347, found 477.97360.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-(phenoxymethyl)-1,3,4-oxadiazole
(**16ac**, $C_{17}H_{11}BrClN_5O_2$)
Yield 78.2%; white solid; m.p.: 72–73 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.42$ (dd, $^3J = 4.6$ Hz, $^4J = 1.0$ Hz, 1H, pyridine-H), 7.87 (dd, $^3J = 8.0$ Hz, $^4J = 1.0$ Hz, 1H, pyridine-H), 7.41 (dd, $^3J = 8.1$ Hz, $^4J = 4.7$ Hz, 1H, pyridine-H), 7.29 (t, $J = 7.6$ Hz, 2H, benzene-H), 7.11 (s, 1H, pyrazole-H), 7.02 (t, $J = 7.4$ Hz, 1H, benzene-H), 6.92 (d, $J = 8.7$ Hz, 2H, benzene-H), 5.21 (s, 2H, $–CH_2–$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 162.58$, 157.40, 156.51, 147.87, 147.32, 139.70, 130.05, 129.88, 129.41, 128.94, 126.66, 122.47, 114.82, 112.51, 59.65 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{17}H_{11}BrClN_5O_2$ ($[M+H]^+$) 431.98574, found 431.98380.

2-[3-Bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl]-5-[(p-tolyloxy)methyl]-1,3,4-oxadiazole
(**16ad**, $C_{18}H_{13}BrClN_5O_2$)
Yield 78.2%; white solid; m.p.: 61–62 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.41$ (d, $^3J = 4.4$ Hz, 1H), 7.86 (d, $^3J = 8.0$ Hz, 1H), 7.40 (dd, $^3J = 7.9$ Hz, $^4J = 4.7$ Hz, 1H), 7.10 (s, 1H, pyrazole-H), 7.07 (d, $J = 8.1$ Hz, 2H, benzene-H), 6.81 (d, $J = 8.4$ Hz, 2H, benzene-H), 5.17 (s, 2H, $–CH_2–$), 2.27 (s, 3H, $–CH_3$) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 162.63$, 156.41, 155.28, 147.84, 147.24, 139.60, 131.82, 130.20, 130.03, 130.01, 129.38, 128.86, 126.53, 114.69, 112.41, 77.40, 77.08, 76.76, 59.84, 20.53 ppm; HR-MS (ESI^+): *m/z* calcd for $C_{18}H_{13}BrClN_5O_2$ ($[M+H]^+$) 446.00139, found 446.00139.

Insecticidal activity

The larvicidal activity was conducted on organism reared in the lab and repeated at 25 ± 1 °C according to statistical requirements. Mortalities were disposed according to Abbott's formula [37]. Evaluations were based on a percentage scale (0 = no activity and 100 = complete eradication).

Insecticidal activity against *H. armigera*

The insecticidal activity of the synthesized compounds against *H. armigera* was tested by the diet-incorporated method [29]. A quantity of 3 cm^3 of solution containing the synthesized compound was added to the prepared forage (27 g), subsequently diluted to corresponding concentrations, and then placed in a 24-pore plate. One larva of *H. armigera* was placed in each of the pores on the plate. Mortalities were calculated after 72–96 h. Commercial insecticides chlorantraniliprole (with a 3-chloropyridin-2-yl-1*H*-pyrazole scaffold) and chlorpyrifos (an effective organophosphorus pesticide against lepidoptera) were used as positive controls under the same conditions.

Insecticidal activity against *P. xylostella*

The insecticidal activities against the *P. xylostella* were determined according to previously determined protocols [29, 30, 33]. Fresh cabbage discs (diameter was 2 cm) were dipped into the prepared solutions containing compounds **16a–16ad** for 10 s, dried in the air, and then placed in a Petri dish (diameter 9 cm) lined with filter paper. Then, ten third instar larvae were carefully transferred to the Petri dish. Each assay was conducted in triplicate. Mortalities were determined after 72 h. The commercial chlorantraniliprole, chlorpyrifos, and avermectins were tested under the same condition for positive controls.

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