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ORIGINAL PAPER

Synthesis and insecticidal activity of anthranilic diamides with hydrazone substructure

[a,b]Jian Wu*‡, [a,b]Dan-Dan Xie‡, [c]Wei-Li Shan, [c]Yong-Hui Zhao, [c]Wei Zhang, [a,b]Baoan Song, [a,b]Song Yang, [a,b]Juan Ma

[a]*State Key Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering, Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education,* [b]*Research and Development Centre for Fine Chemicals, Guizhou University, Guiyang 550025, China*

[c]*Institute for the Control of Agrochemicals, Ministry of Agriculture, Beijing 100125, China*

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A series of anthranilic diamides with a hydrazone substructure was synthesised and characterised using ^{1}H NMR, ^{13}C NMR, IR and elemental analyses. The in vitro insecticidal activity of all the compounds was tested against *Plutella xylostella*. The results showed the synthesised compounds to possess good insecticidal activity. The LC_{50} values of compounds *VIIg*, *VIIl*, *VIIm*, *VIIn* exhibited excellent insecticidal activities, with the LC_{50} affording 7.92 mg L^{-1}, 12.01 mg L^{-1}, 0.62 mg L^{-1} and 10.71 mg L^{-1}, respectively. These may prove to be useful as potential insecticidal agents.

Keywords: anthranilic diamides, hydrazone, insecticidal activity, synthesis

Introduction

In recent years, pests in crops have become increasingly difficult to control; more and more resistant pests have been developed due to the continued and widespread application of traditional pesticides, thereby leading to enormous losses in worldwide crop production each year (Oerke, 2006). The diamondback moth (*Plutella xylostella* L.) can serve as an example: it is a serious pest in many parts of the world (Hasanshahi et al., 2013), and significant losses to crucifers and oilseed crops have become more common (Furlong et al., 2013). Hence, the development of new insecticidal molecules against the insects has attracted increased attention.

In recent decades, several insecticides with a structure containing phthalic diamides (such as fluobendiamide, chlorantraniliprole and cyantraniliprole; Fig. 1) have been developed and commercialised (Lahm et al., 2006, 2007, 2009; Selby et al., 2013; Seo et al., 2007; Tohnishi et al., 2000, 2005). These anthranilic diamides represent a new class of insecticides that binds to the ryanodine receptor, resulting in the uncontrolled release of calcium stores from the sarcoendoplasmic reticulum (Lahm et al., 2009, 2007). The anthranilic diamide insecticides have exhibited a high efficacy against various pests including the diamondback moth. In recent years, the phthalic diamides insecticides have become the focus for the development of novel insecticidal molecules, the skeletons of the commercial phthalic diamides insecticides were selected as lead structures, and a large number of phthalic diamides with high insecticidal activity have been reported (Chen et al., 2013; Clark et al., 2008; Feng et al., 2010, 2011; Selby et al., 2013; Koyanagi et al., 2006; Lahm et al., 2006; Ikegami et al., 2007, 2008a, 2008b; Zhao et al., 2012; Yackman & Sanemitsu, 2007; Yasuyuki et al., 2005; Zhang et al., 2012, 2014; Zhou et al., 2014), such as compounds *A*–*F* in Fig. 1 (Clark et al., 2008; Ikegami et al., 2007, 2008a; Selby et al., 2013; Zhang et al., 2014; Zhou et al., 2014); some of the highly active

*Corresponding author, e-mail: wujian2691@126.com
‡The first and the second authors contributed equally to this work.

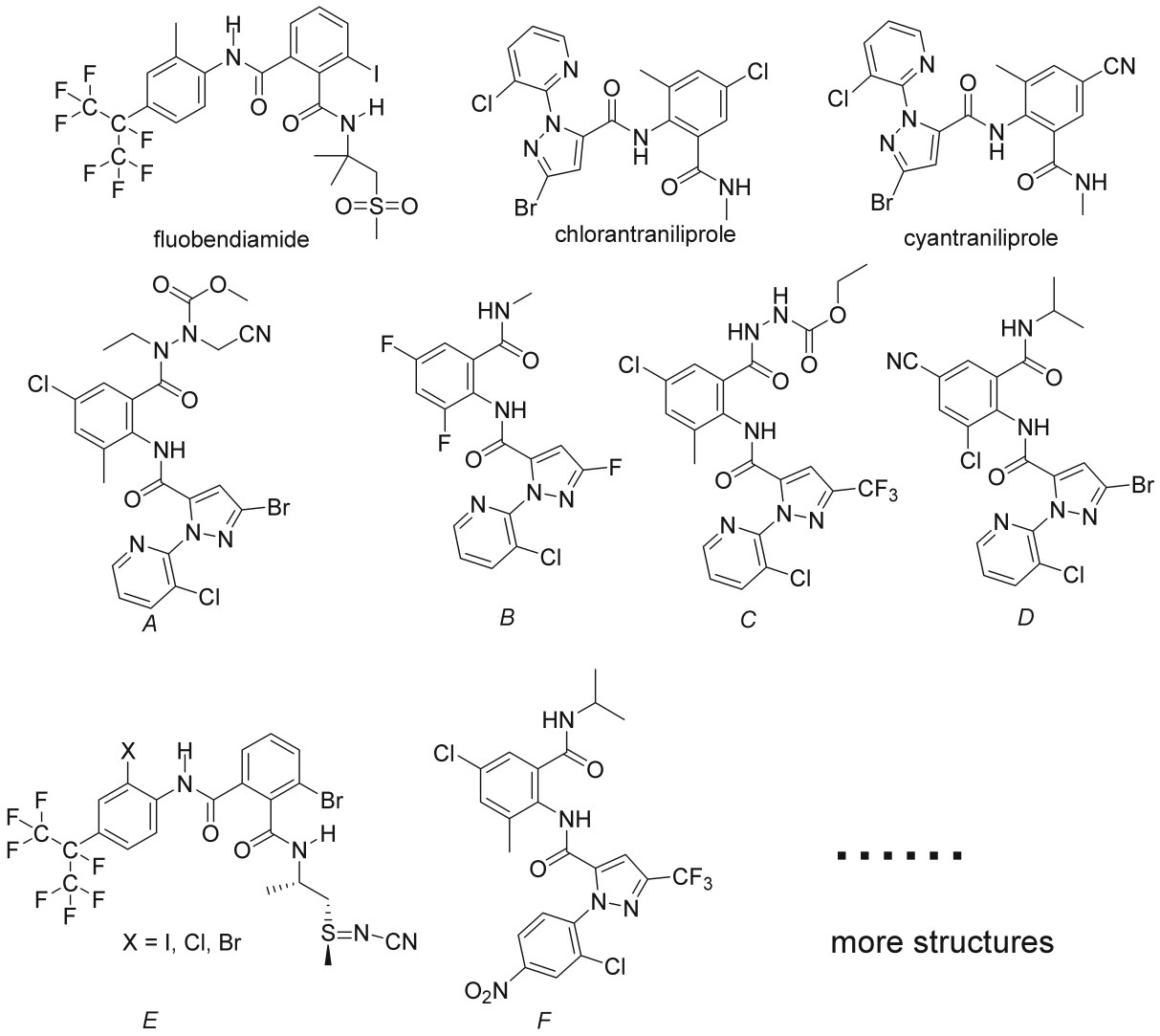


Fig. 1. Structures of phthalic diamides with insecticidal activity.

compounds are at the stage of industrial production.

The hydrazone substructure has been widely used in pesticide design. Many compounds (such as compounds *G*–*J*; Fig. 2) with hydrazone and a wide spectrum of activities have been reported as insecticidal agents (Böger et al., 2001; Hollingshaus, 1987; Li et al., 2014; Liu et al., 2010a, 2010b; Tabanca et al., 2013; Wang et al., 2006), including the metaflumizone (Fig. 2), which was developed by BASF (Germany) (Takagi et al., 1992; Klein, 2005). More recently, a series of nalidixic acid derivatives containing hydrazone (*K*; Fig. 2) was reported as possessing excellent insecticidal activity against *Spodoptera litura* (Fabricius) (Aggarwal et al., 2010). Liu et al. (2010a) disclosed a series of hydrazone derivatives (*L*; Fig. 2) with good insecticidal activity by using fluobendiamide as a lead structure. In a previous work, a series of novel insecticidal molecules was developed containing a hydrazone substructure (*M*; Fig. 2), which exhibited excellent activity against *Plutella xylostella* (Linnaeus), *Helicoverpa armigera* (Hübner), *Culex pipiens pallens, Laphygma exigua* (Hübner), *Spodoptera litura* (Fabricius), *Nilaparvata lugens* (Stål) and *Rhopalosiphum maidis* (Fitch). In particular, compound *N* (Fig. 2) exhibits excellent activity (IC_{50} = 0.71 mg L^{-1}) against *Plutella xylostella* (Wu et al., 2012). Accordingly, an attempt was made to carry out some modifications via changed substituent groups on the benzene ring, as well as in the hydrazone substructure, which may result in new phthalic diamides with better insecticidal activity than that of the compounds previously reported (Wu et al., 2012). In addition, this modification may enhance information on the structure-activity relationship (SAR) to this type of substructure. In the present work, a series of new anthranilic diamides with a hydrazone substructure was synthesised (Fig. 3). Biological assays revealed that some of the synthesised compounds exhibited good insecticidal activity against *Plutella xylostella* (Linnaeus).

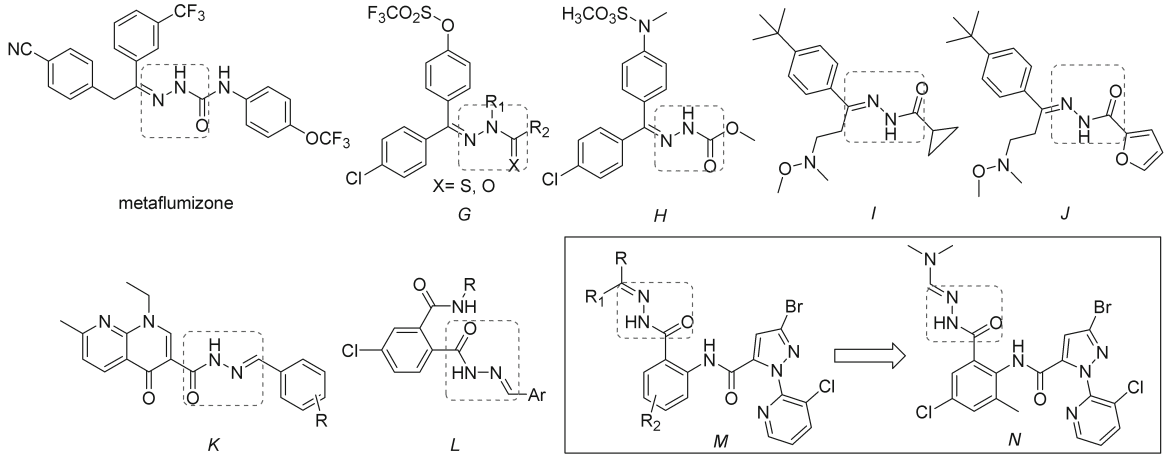
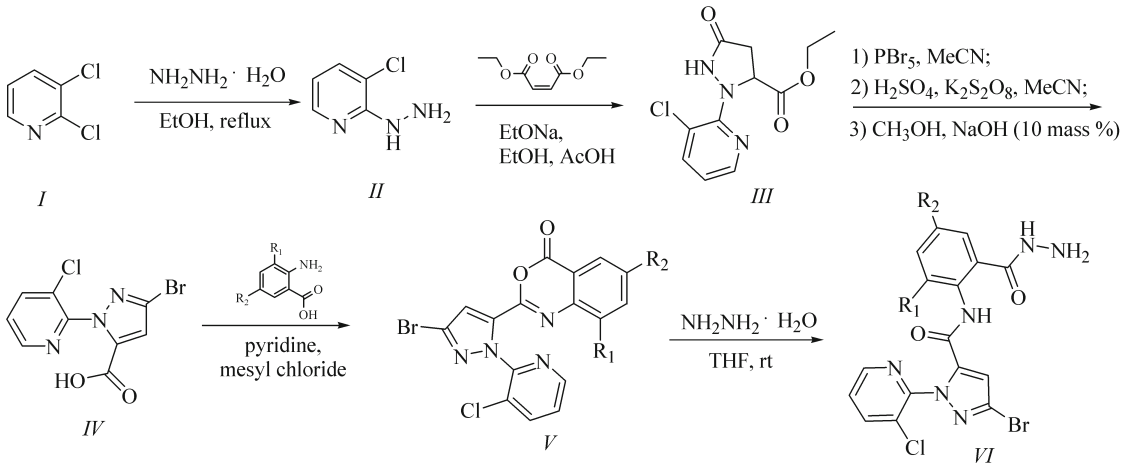


Fig. 2. Insecticidal molecules containing hydrazone group.



VIIa: R_1 = H, R_2 = Cl, R_3 = H, R_4 = -$N(CH_3)_2$
VIIb: R_1 = H, R_2 = Cl, R_3 = H, R_4 = furan-2-yl
VIIc: R_1 = H, R_2 = Cl, R_3 = H, R_4 = CH_2CH_3
VIId: R_1 = H, R_2 = Cl, R_3 = CH_3, R_4 = CH_3
VIIe: R_1 = H, R_2 = Cl, R_3 = R_4 = -$(CH_2)_5$-
VIIf: R_1 = H, R_2 = Cl, R_3 = H, R_4= 4-CF_3-C_6H_4-
VIIg: R_1 = R_2 = Cl, R_3 = H, R_4 = furan-2-yl
VIIh: R_1 = R_2 = Cl, R_3 = H, R_4 = 2,4-di-Cl-C_6H_3-
VIIi: R_1 = R_2 = Cl, R_3 = H, R_4 = 2-((5-chloro-1,3-dimethyl-1*H*-pyrazol-4-yl)
VIIj: R_1 = R_2 = Cl, R_3 = H, R_3 = R_4 = -$(CH_2)_5$-
VIIk: R_1 = CH_3, R_2 = Cl, R_3 = R_4 = -$(CH_2)_5$-
VIIl: R_1 = R_2 = Cl, R_3 = H, R_4 = 1*H*-imidazol-2-yl
VIIm: R_1= R_2= Cl, R_3 = H, R_4 = -$N(CH_3)_2$
VIIn: R_1 = R_2 = Cl, R_3 = H, R_4 = 3-CH_3-C_6H_4-
VIIo: R_1 = CH_3, R_2 = R_3 = H, R_4 = furan-2-yl
VIIp: R_1 = CH_3, R_2 = Cl, R_3 = H, R_4 = 2-F-C_6H_4-
VIIq: R_1 = CH_3, R_2 = R_3 = H, R_4 = 2-F-C_6H_4-
VIIr: R_1 = CH_3, R_2 = Cl, R_3 = H, R_4 = 3-CH_3O-C_6H_4-
VIIs: R_1 = CH_3, R_2 = R_3 = H, R_4 = 3-CH_3O-C_6H_4-

Fig. 3. Synthesis of compounds *VIIa*–*VIIs*.

Experimental

Unless stated otherwise, all reagents were of analytical grade or chemically pure and purchased from Bangcheng chemical (China) and Nuotai chemical (China). All anhydrous solvents were dried and purified in accordance with the standard techniques immediately prior to use. Melting points were left un-

Table 1. Physical properties and analytical data for newly synthesised compounds

Compound	Formula	Appearance	M_r	w_i(calc.)/% w_i(found)/%			Yield	M.p.
				C	H	N	%	°C
VIIa	$C_{19}H_{16}BrCl_2N_7O_2$	yellow solid	525.19	43.45 43.43	3.07 3.18	18.67 18.82	91	227–230
VIIb	$C_{21}H_{13}BrCl_2N_6O_3$	white solid	548.18	46.01 46.12	2.39 2.43	15.33 15.27	85	169–173
VIIc	$C_{19}H_{15}BrCl_2N_6O_2$	yellow solid	510.17	44.73 44.56	2.96 3.02	16.47 16.51	83	126–131
VIId	$C_{19}H_{15}BrCl_2N_6O_2$	yellow solid	510.17	44.73 44.66	2.96 2.89	16.47 16.38	81	220–224
VIIe	$C_{22}H_{19}BrCl_2N_6O_2$	yellow solid	550.24	48.02 48.23	3.48 3.53	15.27 15.31	85	213–216
VIIf	$C_{24}H_{14}BrCl_2F_3N_6O_2$	yellow solid	626.21	46.03 45.98	2.25 2.31	13.42 13.51	80	243–247
VIIg	$C_{21}H_{12}BrCl_3N_6O_3$	yellow solid	582.62	43.29 43.28	2.08 2.14	14.42 14.36	80	162–164
VIIh	$C_{23}H_{12}BrCl_5N_6O_2$	white solid	661.55	41.76 41.85	1.83 1.92	12.70 12.75	78	238–240
VIIi	$C_{22}H_{15}BrCl_4N_8O_2$	white solid	645.12	40.96 41.03	2.34 2.52	17.37 17.54	85	220–223
VIIj	$C_{22}H_{18}BrCl_3N_6O_2$	white solid	584.68	45.19 45.24	3.10 3.34	14.37 14.43	94	126–128
VIIk	$C_{23}H_{21}BrCl_2N_6O_2$	white solid	564.26	48.96 29.03	3.75 3.68	14.89 14.83	96	126–128
VIIl	$C_{20}H_{12}BrCl_3N_8O_2$	white solid	582.62	49.19 48.98	2.48 2.53	11.47 11.23	96	223–224
VIIm	$C_{19}H_{15}BrCl_3N_7O_2$	white solid	559.63	40.78 40.82	2.70 2.71	17.52 17.39	90	220–224
VIIn	$C_{24}H_{16}BrCl_3N_6O_3$	white solid	622.69	46.29 46.44	2.59 2.48	13.50 13.56	90	235–237
VIIo	$C_{22}H_{16}BrClN_6O_3$	white solid	527.76	50.07 50.21	3.06 3.11	15.92 15.88	92	190–192
VIIp	$C_{24}H_{16}BrCl_2FN_6O_2$	white solid	590.23	48.84 48.89	2.73 2.72	14.24 14.17	79	> 250
VIIq	$C_{24}H_{16}BrClFN_6O_2$	white solid	555.79	51.86 51.83	3.08 3.12	15.12 15.09	88	153–155
VIIr	$C_{25}H_{19}BrCl_2N_6O_3$	white solid	590.23	48.84 48.89	2.73 2.72	14.24 14.17	79	150–152
VIIs	$C_{25}H_{20}BrClN_6O_3$	white solid	567.82	52.88 52.76	3.55 3.54	14.80 14.78	96	210–211

corrected and determined on a XT-4 binocular microscope (Beijing Tech Instrument, China). The ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL ECX 500 NMR spectrometer (Japan) at ambient temperature operating at 500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR by using $CDCl_3$ or DMSO as solvents and TMS as an internal standard. Chemical shifts are given in δ relative to TMS. Infrared spectra were recorded using KBr technique on an IR Pristige-21 spectrometer (Shimadzu, Japan) elemental analysis was performed on an Elemental Vario-III CHN analyser (Elementar, German). The course of the reactions was monitored by TLC; analytical TLC was performed on silica gel GF 254 (Merck, Germany). The key intermediate pyrazole-5-carboxylic acid (*IV*) was obtained in five steps by following the recognised procedure using 2,3-dichloropyridine and hydrazine as starting materials with good yields (Lahm et al., 2006, 2007).

General procedure for synthesis of substituted-4H-benzo[d][1,3]oxazin-4-one (V)

To a solution of acid (*IV*; 0.6 g, 2 mmol) in acetonitrile (10 mL) methanesulphonyl chloride (0.27 mL, 3.6 mmol) and pyridine (0.6 g) were added, the resulting mixture was then stirred at ambient temperature for 10 min. Next, the substituted 2-amino-benzoic acid (3 mmol) was added, followed by pyridine (0.4 mL, 5 mmol), and the mixture was stirred at ambient temperature for a further 20 min. Methanesulphonyl chloride (0.4 mL, 5.2 mmol) was then added, the mixture

Table 2. Spectral data of newly prepared compounds

Compounds	Spectral data
VIIa	IR, $\tilde{\nu}$/cm^{-1}: 3232.7, 3124.6 (NH), 3064.8 (ArH), 2954.0, 2910.5 (CH_3), 1687.7, 1645.2 (C═O), 1585.4, 1517.9, 1506.4, 1465.9 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d$_6$), δ: 12.58 (s, 1H, -CON*H*Ar), 11.09 (s, 1H, -ArCON*H*), 8.51 (dd, ^4J = 4.6 Hz, ^3J = 1.2 Hz, 1H, pyridine-H), 8.21–8.18 (m, 2H, -C*H*═N + Ph-*H*), 7.88–7.83 (m, 2H, Ph-H), 7.64 (dd, ^4J = 8.1 Hz, ^3J = 5.2 Hz, 1H, pyridine-H), 7.48 (dd, ^4J = 7.5 Hz, ^3J = 1.2 Hz, 1H, pyridine-H), 7.15 (s, 1H, 4-pyrazole-H), 2.84 (s, 6H, CH_3—N—CH_3) ^{13}C NMR (DMSO-d$_6$), δ: 162.1, 156.2, 155.1, 153.7, 149.7,148.6, 147.8, 140.0, 137.4, 131.8, 128.4, 127.9, 127.7, 127.4, 122.8, 119.4, 110.3, 33.7
VIIb	IR, $\tilde{\nu}$/cm^{-1}: 3250.0, 3178.6 (NH), 3064.8, 2951.0 (ArH), 1689.6, 1645.2 (C═O), 1622.1, 1595.1, 1577.7, 1506.4 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d$_6$), δ: 12.04 (s, 1H, -CON*H*Ar), 11.67 (s, 1H, -ArCON*H*), 8.48 (d, J = 4.6 Hz, 1H, pyridine-H), 8.25 (s, 1H, -C*H*═N), 8.17 (d, J = 8.0 Hz, 1H, Ph-H), 8.04 (dd, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 1H, pyridine-H), 7.91 (s, 1H, Ph-H), 7.87 (s, 1H, furan-H), 7.61 (dd, ^4J = 4.6 Hz, ^3J = 7.5 Hz, 1H), 7.57 (d, ^4J = 8.6 Hz, Ph-H), 7.23 (s, 1H, pyrazole-H), 6.98 (s, 1H, furan-H), 6.64 (t, ^3J = 1.7 Hz, 1H, furan-H) ^{13}C NMR (DMSO-d$_6$), δ: 163.4, 162.8, 156.2, 155.3, 149.6, 148.6, 147.8, 146.2, 140.0, 139.9, 139.3, 136.7, 132.5, 128.7, 128.3, 127.7, 127.3, 124.5, 124.5, 124.4, 115.0, 112.9, 110.8
VIIc	IR, $\tilde{\nu}$/cm^{-1}: 3298.3, 3232.6 (NH), 3087.8, 3012.0 (ArH), 2934.2, 2889.5 (CH_2CH_3), 1700.6, 1678.2 (C═O), 1632.4, 1600.4, 1578.7, 1536.4 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d$_6$), δ: 11.78 (s, 1H, -CON*H*Ar), 11.74 (s, 1H, -ArCON*H*), 8.53 (dd, J = 4.6 Hz, J = 2.3 Hz,1H, pyridine-H), 7.68–7.55 (m, 2H, Ph-H), 7.44 (dd, ^4J = 8.1 Hz, ^3J = 5.2 Hz, 1H, pyridine-H), 7.35 (dd, ^4J = 7.5 Hz, ^3J = 1.2 Hz, 1H, pyridine-H), 7.23 (s, 1H, 4-pyrazole-H), 2.31 (q, J = 5.5 Hz, 2H, -CH_2-), 1.09 (t, J = 5.5 Hz, 2H, -CH_3) ^{13}C NMR (DMSO-d$_6$), δ: 162.4, 155.2, 153.4, 149.3, 148.4, 146.8, 140.2, 137.4, 133.2, 128.6, 126.7, 127.4, 121.8, 120.4, 110.3, 20.5, 17.7
VIId	IR, $\tilde{\nu}$/cm^{-1}: 3275.3, 3244.2 (NH), 3138.1, 3126.6 (ArH), 2968.4 (CH_3), 1685.7, 1660.7 (C═O), 1595.1, 1577.7, 1521.8, 1506.4 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d$_6$), δ: 11.69 (s, 1H, -CON*H*Ar), 10.82 (s, 1H, -ArCON*H*), 8.50 (s, 1H, -C*H*═N), 8.19 (d, ^3J = 8.1 Hz, 1H, Ph-H), 8.01 (d, ^3J = 5.8 Hz, 1H, pyridine-H), 7.81 (s, 1H, Ar-H), 7.45–7.64 (m, 3H, Ar-H), 7.20 (s, 1H, pyrazole-H), 2.00 (s, 3H, CH_3), 1.91 (s, 3H, CH_3) ^{13}C NMR (DMSO-d$_6$), δ: 163.5, 163.3, 155.4, 148.6, 147.8, 140.0, 139.9, 136.5, 132.1, 129.1, 128.6, 128.4, 127.7, 127.4, 124.8, 124.0, 110.6, 25.6, 18.9
VIIe	IR, $\tilde{\nu}$/cm^{-1}: 3267.4 (NH), 3122.7 (ArH), 2935.6, 2845.0 (-CH_2-), 1670.3, 1660.7 (C═O), 1595.1, 1575.8, 1519.1, 1469.7 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d$_6$), δ: 11.72 (s, 1H, -CON*H*Ar), 11.00 (s, 1H, -ArCON*H*), 8.54 (d, ^3J = 4.6 Hz, 1H, pyridine-H), 8.20 (d, ^3J = 8.0 Hz, 1H, Ph-H), 8.02 (d,^3J = 8.6 Hz, 1H, Ar-H), 7.63–7.51 (m, 3H, Ar-H), 7.19 (s, 1H, pyrazole-H), 2.35–2.29 (m, 4H, hexamethylene-H), 1.70–1.38 (m, 6H, hexamethylene-H) ^{13}C NMR (DMSO-d$_6$), δ: 168.6, 163.6, 160.4, 155.4, 148.6, 147.8, 140.0, 136.5, 132.1, 129.0, 128.5, 127.7, 127.4, 124.7, 124.0, 110.7, 35.5, 28.8, 27.4, 26.3, 25.5, 19.1
VIIf	IR, $\tilde{\nu}$/cm^{-1}: 3323.3, 3209.5 (NH), 3197.9, 3170.9 (ArH), 1695.4, 1683.8 (C═O), 1585.4, 1558.4, 1521.8, 1506.4, 1490.9 (skeleton vibration of aromatic ring), 1295.4 (—C—N) ^{1}H-NMR (DMSO-d$_6$), δ: 11.60 (s, 1H, -CON*H*Ar), 9.98 (s, 1H, -ArCON*H*), 8.52 (dd, ^4J = 1.2 Hz, ^3J = 4.6 Hz, 1H, Pyridine-H), 8.48 (s, 1H, ═CH), 8.10 (dd, ^4J = 1.7 Hz, ^3J = 8.0 Hz, 1H, pyridine-H), 7.75 (dd, ^4J = 1.2 Hz, ^3J = 4.6 Hz, 1H, pyridine-H), 7.56 (d, J = 8.1 Hz, 2H, Ph-H), 7.25–7.48 (m, 3H, Ph-H), 7.23 (d, J = 8.06 Hz, 2H, Ph-H) ^{13}C NMR (DMSO-d$_6$), δ: 165.3, 162.5, 160.4, 158.2, 155.6, 149.2, 148.2, 147.3, 144.4, 142.0, 138.4, 137.6, 136.3, 132.5, 128.7, 128.4, 122.7, 126.4, 124.1, 121.4, 115.2, 111.9
VIIg	IR, $\tilde{\nu}$/cm^{-1}: 3242.3, 3134.3 (N-H), 3064.9 (Ar-H), 1670.4, 1660.7 (C═O), 1622.1, 1573.9, 1539.2, 1463.9 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d$_6$), δ: 11.77 (br, 1H, NH), 10.59 (br, 1H, NH), 8.40 (dd, 1H, ^4J = 1.8 Hz, ^3J = 4.6 Hz, pyridine-H), 8.06 (s, 1H, C═NH), 8.04 (dd, 1H, ^4J = 1.7 Hz, ^3J = 8.0 Hz, pyridine-H), 7.88 (d, 1H, ^3J = 4.6 Hz, furan-H), 7.83 (s, 1H, Ph-H), 7.63 (s, 1H, Ph-H), 7.50 (dd, ^4J = 5.2 Hz, ^3J = 8.0 Hz, 1H, pyridine-H), 7.37 (d, ^3J = 1.7 Hz, 1H, furan-H), 6.92 (s, 1H, pyrazole-H), 6.61 (t, ^3J = 1.7 Hz, 1H, furan-H) ^{13}C NMR (DMSO-d$_6$), δ: 161.6, 157.2, 148.9, 148.9, 148.7, 147.2, 143.3, 138.6, 138.2, 136.6, 135.5, 134.3, 133.3, 132.6, 132.1, 131.3, 131.2, 129.9, 128.4, 128.2, 127.7, 127.3, 111.3
VIIh	IR, $\tilde{\nu}$/cm^{-1}: 3223.0, 3187.8 (N—H), 3001.2 (Ar—H), 1672.0, 1651.0 (C═O), 1618.2, 1587.0, 1570.0, 1463.0 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d$_6$), δ: 12.09 (br, 1H, NH), 10.62 (br, 1H, NH), 8.51 (s, 1H, C═NH), 8.44 (d, 1H, J = 3.4 Hz, pyridine-H), 8.00–7.82 (m, 3H, J = 4.6 Hz, pyridine-H + 2Ph-H), 7.71 (d, 1H, J = 9.8 Hz, pyridine-H), 7.54–7.49 (m, 2H, 2Ph-H), 7.39 (s, 1H, pyrazole-H), 7.29–7.20 (m, 1H, Ph-H) ^{13}C NMR (DMSO-d$_6$), δ: 161.6, 157.2, 148.9, 148.9, 148.7, 147.2, 143.3, 138.6, 138.2, 136.6, 135.5, 134.3, 133.3, 132.6, 132.1, 131.3, 131.2, 129.9, 128.4, 128.2, 127.7, 127.3, 111.3

Table 2. (continued)

Compounds	Spectral data
VIIi	IR, $\tilde{\nu}$/cm^{-1}: 3277.0, 3226.9 (N—H), 3049.4 (Ar—H), 2933.2, 2905.5 (CH_3), 1697.4, 1683.9 (C═O), 1616.3, 1573.9, 1525.6, 1479.4 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d$_6$), δ: 11.63 (br, 1H, NH), 10.59 (br, 1H, NH), 8.44 (dd, 1H, ^4J = 1.7 Hz, ^3J = 4.6 Hz, pyridine-H), 8.13 (s, 1H, C═NH), 8.06 (dd, 1H, ^4J = 4.6 Hz, ^3J = 8.6 Hz, pyridine-H), 7.90 (d, 1H,^{4} J = 2.3 Hz, Ph-H), 7.68 (d, 1H, ^4J = 1.7 Hz, Ph-H), 7.56 (dd, 1H, ^4J = 4.6 Hz, ^3J = 8.0 Hz, pyridine-H), 7.44 (s, 1H, pyrazole-H), 3.77 (s, 3H, -CH_3), 2.35 (s, 3H, -CH_3) ^{13}C NMR (DMSO-d$_6$), δ: 160.6, 156.2, 148.8, 147.5, 147.0, 141.3, 139.6, 137.4, 136.6, 134.3, 132.8, 132.2, 131.5, 131.2, 129.9, 18.4, 128.2, 127.7, 127.3, 111.3, 36.4, 19.0
VIIj	IR, $\tilde{\nu}$/cm^{-1}: 3275.3 (N—H), 3003.0 (ArH), 2935.4, 2861.0 (-CH_3 or -CH_2-), 1689.8, 1678.3 (C═O), 1637.6, 1575.8, 1485.0 (skeleton vibration of aromatic ring). ^{1}H-NMR (DMSO-d$_6$), δ: 10.73 (br, 1H, NH), 10.27 (br, 1H, NH), 8.49 (dd, 1H, ^4J = 1.2 Hz, ^3J = 4.6 Hz, pyridine-H), 8.14 (dd, 1H, ^4J = 1.7 Hz, ^3J = 8.0 Hz, pyridine-H), 7.59 (dd, 1H, ^4J = 4.6 Hz, ^3J = 8.0 Hz, pyridine-H), 7.50 (d, 1H, ^4J = 2.3 Hz, Ph-H), 7.38 (d, 1H, ^4J = 2.3 Hz, Ph-H), 7.36 (s, 1H, pyrazole-H), 2.24–2.28 (m, 4H, 2CH_2), 1.64–1.49 (m, 6H, 3CH_2) ^{13}C NMR (DMSO-d$_6$), δ: 167.3, 162.5, 159.3, 154.2, 147.5, 146.6, 138.9, 135.4, 130.9, 127.9, 127.4, 126.5, 126.2, 123.6, 122.8, 109.5, 34.3, 27.2, 26.3, 25.2, 24.4, 17.9
VIIk	IR, $\tilde{\nu}$/cm^{-1}: 3228.7 (N—H), 3000.0 (ArH), 2937.5, 2860.0 (-CH_3 or -CH_2-), 1702.8, 1675.6 (C═O), 1575.8, 1489.0 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d$_6$), δ: 10.47 (br, 1H, NH), 10.24 (br, 1H, NH), 8.46 (dd, 1H, ^4J = 1.2 Hz, ^3J = 4.6 Hz, pyridine-H), 8.13 (dd, 1H, ^4J = 1.7 Hz, ^3J = 8.0 Hz, pyridine-H), 7.58 (dd, 1H, ^4J = 4.6 Hz, ^3J = 8.0 Hz, pyridine-H), 7.47 (d, 1H, ^4J = 2.3 Hz, Ph-H), 7.36 (d, 1H, ^4J = 2.3 Hz, Ph-H), 7.33 (s, 1H, pyrazole-H), 2.21–2.27 (m, 4H, 2CH_2), 2.14 (s, 3H, -CH_3), 1.62–1.41 (m, 6H, 3CH_2) ^{13}C NMR (125 MHz), δ: 161.4, 156.2, 149.7, 148.8, 147.5, 146.0, 139.2, 138.2, 137.3, 134.4, 132.8, 131.5, 127.6, 127.3, 114.5, 111.4, 29.1, 28.1, 26.2, 25.3, 20.2
VIIl	IR, $\tilde{\nu}$/cm^{-1}: 3224.7 (N—H), 3000.0 (ArH), 2937.5, 2860.0 (-CH_3 or -CH_2-), 1683.8, 1667.8 (C═O), 1635.6, 1575.8, 1489.0 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d$_6$), δ: 12.82 (br, 1H, NH), 11.89 (br, 1H, NH), 10.65 (br, 1H, NH), 8.39 (d, 1H, ^3J = 2.9 Hz, pyridine-H), 8.10 (s, 1H, -CH═N), 8.03 (d, 1H, ^3J = 8.0 Hz, pyridine-H), 7.89 (s, 1H, Ph-H), 7.68 (s, 1H, Ph-H), 7.49 (dd, 1H, ^4J = 4.6 Hz, ^3J = 8.0 Hz, pyridine-H), 7.39 (d, 1H, imidazole-H), 7.10–7.26 (m, 2H, pyrazole-H + imidazole-H) ^{13}C NMR (DMSO-d$_6$), δ: 161.1, 156.3, 148.8, 147.6, 142.7, 140.4, 139.6, 139.2, 137.3, 134.4, 132.9, 131.9, 131.5, 131.3, 18.4, 127.6, 127.3, 127.0, 111.4
VIIm	IR, $\tilde{\nu}$/cm^{-1}: 3232.7 (NH), 3124.5, 3068.8 (ArH), 2954.0, 2910.5 (CH_3), 1688.7, 1685.2 (C═O), 1575.4, 1517.9, 1506.4, 1465.5 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d$_6$), δ: 11.93 (s, 1H, -CON*H*Ar), 10.92 (s, 1H, -ArCON*H*), 8.31 (d, ^3J = 4.1 Hz, 1H, pyridine-H), 8.16 (d, 1H, ^3J = 8.1 Hz, pyridine-H), 7.98 (s, 1H, -C*H*═N), 7.93 (s, 1H, Ph-H), 7.70 (s, 1H, Ph-H), 7.50 (dd, 3H, ^3J = 8.0 Hz, ^4J = 4.6 Hz, Ar-H), 7.18 (s, 1H, pyrazole-H), 2.91 (s, 3H, CH_3), 2.89 (s, 3H, CH_3) ^{13}C NMR (DMSO-d$_6$), δ: 163.8, 158.4, 148.6, 147.4, 145.4, 141.1, 140.7, 138.8, 132.6, 131.7, 130.0, 126.4, 124.9, 123.5, 111.5, 34.7
VIIn	IR, $\tilde{\nu}$/cm^{-1}: 3288.6, 3122.7 (N—H), 3061.0 (ArH), 2810 (-CH_3), 1687.7, 1670.3 (C═O), 1647.2, 1573.9, 1554.63, 1485.1 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d$_6$), δ: 11.87 (br, 1H, NH), 10.61 (br, 1H, NH), 8.39 (dd, 1H, J = 4.0 Hz, pyridine-H), 8.16 (s, 1H, C═NH), 8.06 (d, 1H, J = 8.0 Hz, pyridine-H), 7.89 (d, 1H, Ph-H), 7.65 (s, 1H, Ph-H), 7.51 (dd, 1H, ^4J = 4.6 Hz, ^3J = 7.5 Hz, pyridine-H), 7.40 (s, 1H, Ph-H), 7.36 (t, 1H, J = 7.5 Hz, Ph-H), 7.18–7.24 (m, 2H, Ph-H + pyrazole-H)), 7.00 (d, J = 8.0 Hz, 1H, Ph-H), 3.77 (s, 3H, -CH_3) ^{13}C NMR (DMSO-d$_6$), δ: 161.2, 160.0, 159.7, 156.2, 148.8, 148.5, 147.5, 139.6, 139.4, 139.1, 137.2, 136.0, 134.3, 13.8, 131.3, 130.5, 128.4, 127.8, 127.3, 127.0, 120.7, 117.0, 111.6, 55.7
VIIo	IR, $\tilde{\nu}$/cm^{-1}: 3242.3 (NH), 3067.2, 3025.2 (ArH), 2889.3 (CH_3), 1689.6, 1667.0 (C═O), 1558.5, 1541.1, 1464.0, 1458.2 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d$_6$), δ: 11.07 (bs, 1H, –CONHAr), 10.05 (bs, 1H, –CONHN═), 8.41 (s, 1H, ═CH), 8.33 (dd, 1H, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 4.6 Hz, 6-pyridine-H), 8.05 (dd, 1H, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 8.1 Hz, 4-pyridine-H), 7.88 (s, 1H, 5-Ph-H), 7.56 (dd, 1H, $^3J_{HH}$ = 4.6 Hz, $^3J_{HH}$ = 8.1 Hz, 1H, 5-pyridine-H), 7.37 (s, 1H, 3-Ph-H), 6.54–7.72 (m, 4H, pyrazole-H + 3 furan-H), 2.18 (s, 3H, CH_3) ^{13}C NMR (DMSO-d$_6$), δ: 162.5, 161.9, 157.1, 154.3, 148.6, 147.2, 147.3, 144.1, 142.0, 138.9, 138.3, 136.7, 132.8, 128.7, 128.1, 122.7, 126.3, 123.5, 124.1, 121.4, 115.2, 111.9, 110.8, 18.9
VIIp	IR, $\tilde{\nu}$/cm^{-1}: 3402.4, 3383.1 (NH), 3007.2, 2998.2 (ArH), 2889.3(CH_3), 1687.6, 1662.0 (C=O), 1648.3, 1627.8, 1558.5, 1458.2 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d$_6$), δ: 11.92 (br, 1H, NH),10.37 (br, 1H, NH), 8.49 (s, 1H, ═CH), 8.43 (dd, ^4J = 1.7 Hz, ^3J = 4.6 Hz, 1H, pyridine-H), 8.07 (dd, ^4J = 1.7 Hz, ^3J = 8.0 Hz, 1H, pyridine-H), 7.92 (t, J = 6.3 Hz, 1H, Ph-H), 7.46–7.51 (m, 5H, Ar-H), 7.39 (s, 1H, pyrazole-H), 7.29–7.33 (m, 2H, Ph-H), 2.20 (s, 3H, Ph-CH_3) ^{13}C NMR (DMSO-d$_6$), δ: 161.5, 160.5, 159.5, 156.1, 148.9, 148.6, 146.5, 139.8, 139.3, 139.1, 135.8, 135.2, 134.3, 132.8, 131.2, 130.6, 128.2, 127.5, 127.1, 128.8, 120.7, 117.0, 111.4, 19.2

Table 2. (continued)

Compounds	Spectral data
VIIq	IR, $\tilde{\nu}/\mathrm{cm}^{-1}$: 3363.9, 3205.7 (NH), 3086.4 (ArH), 2949.3(CH_3), 1705.1, 1668.1 (C═O), 1527.6, 1489.1, 1458.2 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d_6), δ: 11.83, (br, 1H, NH)Ł10.29, (br, 1H, NH), 8.47 (s, 1H, ═CH), 8.39 (dd, 1H, $^4J = 1.2$ Hz, $^3J = 3.5$ Hz, pyridine-H), 8.02 (dd, 1H, $^4J = 1.7$ Hz, $^3J = 8.0$ Hz, pyridine-H), 7.89 (t, 1H, $J = 7.5$ Hz, Ph-H), 7.51 (dd, 1H, $^4J = 4.6$ Hz, $^3J = 8.0$ Hz, pyridine-H), 7.25–7.46 (m, 7H, Ar-H + pyrazole-H), 7.29–7.33 (m, 2H, Ph-H), 2.16 (s, 3H, Ph-CH_3) ^{13}C NMR (DMSO-d_6), δ: 162.7, 161.8, 159.6, 157.3, 149.2, 148.7, 147.4, 139.8, 139.2, 139.1, 135.2, 133.1, 132.3, 131.5, 130.2, 129.7, 128.2, 127.4, 127.1, 128.3, 120.2, 117.4, 110.4, 18.4
VIIr	IR, $\tilde{\nu}/\mathrm{cm}^{-1}$: 3385.1, 3242.3 (NH), 3132.4, 3066.8 (Ar-H), 2966.5, 2833.4 (CH_3), 1689.2, 1658.8 (C═O), 1579.7, 1541.1, 1489.1, 1460.1 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d_6), δ: 10.15 (1H, NH), 9.66 (1H, NH), 8.34 (dd, 1H, $^4J = 1.2$ Hz, $^3J = 4.6$ Hz, pyridine-H), 7.93(s, 1H, ═CH), 7.72 (dd, 1H, $^4J = 1.7$ Hz, $^3J = 8.0$ Hz, pyridine-H), 7.23–7.26 (m, 4H, Ar-H), 7.18 (d, $J = 7.4$ Hz, Ph-H), 7.14 (s, 1H, pyrazole-H), 7.05 (s, 1H, Ph-H), 7.02 (s, 1H, Ph-H), 6.93 (dd, 1H, $^4J = 1.2$ Hz, $^3J = 4.6$ Hz, pyridine-H), 3.80 (s, 3H, Ph-OCH_3), 2.07 (s, 3H, Ph-CH_3) ^{13}C NMR (DMSO-d_6), δ: 163.1, 162.3, 160.7, 158.3, 149.1, 147.4, 146.5, 139.6, 139.2, 139.1, 137.4, 136.3, 134.1, 132.8, 131.3, 130.1, 129.1, 128.3, 127.5, 128.1, 121.8, 118.2, 111.6, 55.7, 21.2
VIIs	IR, $\tilde{\nu}/\mathrm{cm}^{-1}$: 3377.4, 3219.2 (NH), 3136.3, 3064.9 (ArH), 2960.7, 2922.2 (CH_3), 1689.3, 1654.9 (C═O), 1608.3, 1587.5, 1554.6, 1464.0 (skeleton vibration of aromatic ring) ^{1}H-NMR (DMSO-d_6), δ: 11.74 (br, 1H, NH), 10.30 (br, 1H, NH), 8.43 (dd, 1H, $^4J = 1.7$ Hz, $^3J = 4.6$ Hz, pyridine-H), 8.22 (s,1H, ═CH), 8.05 (dd, 1H, $^4J = 1.2$ Hz, $^3J = 8.0$ Hz, pyridine-H), 7.55 (dd, 1H, $^4J = 5.2$ Hz, $^3J = 8.0$ Hz, pyridine-H), 7.24–7.43 (m, 8H, Ar-H), 7.01 (dd, 1H, $^4J = 2.3$ Hz, $^3J = 8.0$ Hz, pyridine-H), 3.80 (s, 3H, Ph-OCH_3), 2.19 (s, 3H, Ph-CH_3) ^{13}C NMR (DMSO-d_6), δ: 162.8, 162.4, 159.9, 158.4, 149.3, 147.2, 145.5, 138.6, 138.2, 138.1, 137.1, 136.6, 132.1, 131.5, 131.2, 129.5, 129.1, 127.2, 127.1, 126.8, 121.5, 117.3, 110.2, 58.4, 20.6

was stirred at ambient temperature and the reaction monitored by TLC. After completion of the reaction, water (5 mL) was added to the mixture to afford a crystalline solid which was filtered and recrystallised from ethanol.

General procedure for preparation of hydrazine (VI)

A suspension of *V* (1 mmol) in tetrahydrofuran (THF; 4 mL) was added to a mixture of hydrazine hydrate (80 %, 0.15 mL, 2.5 mmol) and THF (2 mL) under vigorous stirring, after the addition of *V*, and the mixture was stirred at ambient temperature for a further 40 min. The precipitated solid was filtered, washed with ethanol (3 mL) and dried to afford the intermediate *VI*.

General procedure for preparation of title compounds (VIIa–VIIs)

To a well-stirred solution of hydrazine (*VI*; 2 mmol) in ethanol (5 mL), ketones (or aldehydes and hemiacetals) (2 mmol) were added over 10 min. The resulting mixtures were stirred at ambient temperature to afford a solid; after completion of the reaction, the solids were filtered and recrystallised from a mixture of ethanol and *N*,*N*-dimethylformamide (DMF; $\varphi_r = 1:1$). The properties and analytical data for the synthesised compounds are listed in Table 1, and the spectral data are shown in Table 2.

Insecticidal bioassays

Previously reported procedures (Wu et al., 2014, 2012) were used to evaluate the insecticidal activity of the synthesised compounds *VIIa* to *VIIq* against *P. xylostella*. Fresh cabbage discs (diameter 2 cm) were dipped into the prepared solutions containing compounds *VIIa* to *VIIq* for 10 s, dried in air and placed in a Petri dish (diameter 9 cm) lined with filter paper. Ten larvae of second-instar *P. xylostella* were carefully transferred to the Petri dish. Chlorpyrifos, Chlorantraniliprole and compound *N* (Wu et al., 2012) were used as reference; three replicates were performed for each experiment. Mortalities were determined after 72 h. Evaluations were based on a percentage scale (0 = no activity and 100 = complete eradication), at intervals of 5 %. The results are summarised in Table 3.

Results and discussion

Synthesis

The synthetic protocol of the anthranilic diamides with a hydrazone group is depicted in Fig. 3. First, 3-chloro-2-hydrazinylpyridine (*II*) was synthesised with a good yield (up to 90 %) by the reaction of 2,3-dichloropyridine (*I*) with 80 % hydrazine hydrate, then compound *II* was allowed to further react with diethyl maleate under reflux in the presence of sodium ethoxide to af-

Table 3. Insecticidal activity of compounds *VIIa* to *VIIs*, chlorantraniliprole, compound *N* and chlorpyrifos against *P. xylostella*

	Insecticidal activity at different concentrations/(mg L^{-1})						
Compound	300	200	100	50	25	10	5
				%			
VIIa	20	–	–	–	–	–	–
VIIb	55	–	–	–	–	–	–
VIIc	60	30	–	–	–	–	–
VIId	45	–	–	–	–	–	–
VIIe	55	–	–	–	–	–	–
VIIf	15	–	–	–	–	–	–
VIIg	100	100	100	93	80	60	43
VIIh	100	93	73	50	33	17	–
VIIi	80	73	50	23	–	–	–
VIIj	90	73	56	33	20	–	–
VIIk	87	70	53	30	10	–	–
VIIl	100	100	100	95	73	33	23
VIIm	100	100	100	100	100	100	100
VIIn	100	100	100	90	67	50	30
VIIo	30	–	–	–	–	–	–
VIIp	100	100	97	63	43	20	–
VIIq	10	–	–	–	–	–	–
VIIr	100	100	90	50	20	–	–
VIIs	20	–	–	–	–	–	–
chlorpyrifos	100	100	100	90	83.3	60	40
chlorantraniliprole	100	100	100	100	100	100	100
compound *N*	100	100	100	100	100	100	100
blank control	0	0	0	0	0	0	0

ford ethyl 2-(3-chloropyridin-2-yl)-5-oxopyrazolidine-3-carboxylate (*III*) with a 50 % yield (Lahm et al., 2006, 2007). 3-Bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxylic acid (*IV*) was then obtained from *III* via bromination, oxydehydrogenation and acidolysis with good yields (Lahm et al., 2006, 2007). Next, substituted-4*H*-benzo[*d*][1,3]oxazin-4-one (*V*) was carried out in a single step by the treatment of *IV* with substituted-2-aminobenzoic acid in the presence of methanesulphonyl chloride and pyridine in acetonitrile at ambient temperature (Lahm et al., 2006, 2007). Subsequently, 3-bromo-1-(3-chloropyridin-2-yl)-*N*-(2-(hydrazinecarbonyl) substituted phenyl)-1*H*-pyrazole-5-carboxamide (*VI*) was readily obtained with an excellent yield (> 93 %) by the treatment of *V*with 80 % hydrazine hydrate in THF. Finally, the title compounds (*VIIa*–*VIIq*) were readily obtained with excellent yields by the treatment of intermediates *VI* with the corresponding different ketones, aldehydes or hemiacetals in ethanol at ambient temperature (Wu et al., 2012).

The structures of the synthesised compounds (*VIIa*–*VIIs*) were established on the basis of the spectroscopic data. The IR (KBr) spectra indicated absorption bands around 3050 cm^{-1} for the Ar—H stretching vibrations. The absorption bands at 1445–1610 cm^{-1} were the skeletal vibration of the aromatic ring; all the compounds exhibited the characteristic N—H and C═O absorptions at 3150–3430 cm^{-1} and 1660–1710 cm^{-1}, respectively. In the ^{1}H-NMR spectra, taking compound *VIIa* as an example, two different N—H protons appeared as a broad singlet near δ 12.58 and 11.09, respectively. The proton at position 5 of pyridine appeared as a doublet of doublets at δ 8.51 due to the coupling coefficients from the protons at positions 3 and 4 of the pyridine ring; the coupling constants were 4.6 and 1.15 Hz (^4J = 4.6 Hz, ^3J = 1.2 Hz), respectively. 4-Pyrazole-H exhibited a singlet near δ 7.15. The six protons (-N(CH_3)$_2$) appeared as a singlet near δ 2.84; The properties, ^{1}H NMR, ^{13}C NMR, IR and the elemental analysis data of the title compounds *VIIa* to *VIIs* are listed in more detail in the Experimental section.

Insecticidal activity

The insecticidal activities of the synthesised compounds against *P. xylostella* were evaluated using procedures reported previously (Wu et al., 2012, 2014). Commercial chlorantraniliprole, chlorpyrifos and the active compound *N* were used as positive controls. The results listed in Table 3 indicate that some of the synthesised compounds *VIIa*–*VIIs* exhibited good insecticidal activities against *P. xylostella* at the test concentration. It can be seen that all the compounds *VIIg*, *VIIl*, *VIIm*, *VIIn*, *VIIp* and *VIIr* displayed 100 % activities against *P. xylostella* at 200 mg L^{-1}. When the concentration was 100 mg L^{-1}, the activities of com-

Table 4. LC_{50} values of parts of synthesised compounds, chlorantraniliprole, chlorpyrifos and compound *N* against *Plutella xylostella*

Compound	$y = a + bx$	LC_{50}/(mg L^{-1})	r	95 % Confidence interval
VIIg	$y = 3.31 + 1.87x$	7.92	0.99	5.88–10.65
VIIh	$y = 2.03 + 1.85x$	39.93	0.98	30.01–53.14
VIIi	$y = 0.49 + 2.20x$	110.76	0.99	80.90–141.19
VIIj	$y = 1.42 + 1.89x$	77.72	0.98	58.97–102.43
VIIk	$y = 0.83 + 2.10x$	96.23	0.99	75.20–123.12
VIIl	$y = 2.16 + 2.63x$	12.01	0.97	9.62–14.99
VIIm	$y = 5.32 + 1.60x$	0.62	0.96	0.42–0.92
VIIn	$y = 3.22 + 1.73x$	10.71	0.98	7.95–14.43
VIIp	$y = 1.72 + 2.36x$	24.41	0.96	19.25–30.97
VIIr	$y = 1.26 + 2.32x$	40.58	0.97	29.89–55.09
chlorpyrifos	$y = 3.56 + 1.65x$	7.39	0.99	5.28–10.33
chlorantraniliprole	$y = 6.20 + 0.93x$	0.05	0.95	0.024–0.11
compound *N*	$y = 5.28 + 1.88x$	0.71	0.95	0.52–0.97

pounds *VIIg*, *VIIl*, *VIIm* and *VIIn* attained 100 %, and their activities were over 90 % at 50 mg L^{-1}. In particular, compound *VIIm* exhibited excellent activity; the activity of *VIIm* still achieved 100 % at 5 mg L^{-1}, which was the same as for chlorantraniliprole and compound *N*. The LC_{50} values for some of the synthesised compounds, chlorantraniliprole and compound *N* were tested; the results are listed in Table 4. The table shows that the LC_{50} values of compounds *VIIg*, *VIIl*, *VIIm*, *VIIn* exhibited excellent insecticidal activities, with the LC_{50} of 7.92 mg L^{-1}, 12.01 mg L^{-1}, 0.62 mg L^{-1} and 10.71 mg L^{-1}, respectively. In particular, *VIIm* exhibited a much higher activity than that of chlorpyrifos (LC_{50} was 7.39 mg L^{-1}) and better than the compounds previously reported (Wu et al., 2012).

A previous study found that only compounds with a methyl group at the 2-position of benzene exhibited weak activity (Wu et al., 2012); similar results were also found in this work (such as *VIIo*, *VIIq* and *VIIs*). It was also found that compounds with only chorine at the 4-position (*VIIa*–*VIIf*) of benzene exhibited weak (or no) activities against *P. xylostella*. However, those compounds with both 2-methyl and 4-chorine on benzene (such as *VIIk*, *VIIp*) or 2,4-di-chorines on benzene (*VIIg*, *VIIh*, *VIIi*, *VIIj*, *VIIl*, *VIIm* and *VIIn*) exhibited excellent activities After combining these results with those reported previously (Wu et al., 2012), it may be concluded that the substituent at both the 2- and 4-positions of benzene can increase the activities of this type of compounds. It was also found that the activity could be enhanced by exchanging the methyl group (at 2-position of benzene) for chorine and decreased in the following order (*VIIm*, *N*, *VIIj*, *VIIk*, *VIIn, VIIr*). In addition, the substituent groups on the functional moiety of "N = R_3, R_4" were also a crucial factor that governed the activities; the activity was found to decrease when a bulky group was introduced (Wu et al., 2012), so that the activities of *VIIh*, *VIIi* and *VIIk* were much lower than that of *VIIg*.

Conclusions

In conclusion, nineteen new anthranilic diamides with a hydrazone group (*VIIa*–*VIIs*) were synthesised, characterised and confirmed by ^{1}H NMR, ^{13}C NMR, IR and elemental analyses. The preliminary insecticidal activities of the synthesised compounds were evaluated. The results indicated that some of the compounds exhibited a high efficiency against *Plutella xylostella*; in particular, compounds *VIIg*, *VIIl*, *VIIm* and *VIIn* exhibited excellent insecticidal activities, with the LC_{50} being 7.92 mg L^{-1}, 12.01 mg L^{-1}, 0.62 mg L^{-1} and 10.71 mg L^{-1}, respectively. In particular, compound *VIIm* exhibited a much higher activity than that of chlorpyrifos (LC_{50} was 7.39 mg L^{-1}) as well as higher than that of compound *N* (an active compound reported on previously). It may be concluded that the substituent groups on benzene at both the 2 and 4-positions could increase the activities of this type of compound. In addition, the substituent groups on the functional moiety of "$N = R_3$ R_4" were also a crucial factor that governing the activities; the activity was found to decrease when a bulky group was introduced. Further studies are currently underway to optimise the structure to obtain a better insecticidal activity in these new anthranilic diamides with a hydrazone group based on these findings.

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