Design, Synthesis, and Insecticidal Activity of 1,5-Diphenyl-1-pentanone Analogues

Yang, Shaoxiang[a](杨绍祥) Kang, Tieniu[a](康铁牛) Rui, Changhui[b](芮昌辉)
Yang, Xinling[a](杨新玲) Sun, Yufeng[a](孙玉凤) Cui, Zining[a](崔紫宁)
Ling, Yun*,[a](凌云)

[a] *Key Laboratory of Pesticide Chemistry and Application, Ministry of Agriculture, Department of Applied Chemistry, College of Science, China Agricultural University, Beijing 100193, China*
[b] *Institute of Plant Protection, Chinese Academy of Agricultural Sciences, Beijing 100193, China*

Three series of novel 1,5-diphenyl-1-pentanone derivatives were designed and synthesized. Their structures were characterized by IR, ^{1}H NMR techniques, and elemental analysis. The insecticidal activities of the new compounds were preliminarily evaluated. The bioassay results indicated that the compounds **X11**—**X30** displayed better aphicidal activity against *Aphis gossypii* than compounds **X1**—**X10** and the lead compound (*E*)-1,5-diphenyl-1-penten-1-one (**A**). The inhibitory rates of compounds **X6** and **X29** were 100% against *Plutella xylostella* (L.) at 600 mg•L^{-1}. Compounds **X12**, **X13, X19**, **X24, X25**, **X26** and **X27** showed higher insecticidal activity against *Tetranychus cinnabarinus* (Boisduval) at 600 mg•L^{-1} than the lead compound (**A**).

Keywords *Stellera chamaejasme* L., (*E*)-1,5-diphenyl-1-penten-1-one, analogue, synthesis, design, insecticidal activity

Introduction

Synthetic insecticides play an essential role in agricultural pest management. Strategies to control pests with classic insecticides, such as pyrethroids, organophosphorus and carbamate insecticides, however, have led to some side effects, notably environmental contamination and resistant strains generation.[1] Therefore, the novel active molecule has become the focus in pesticide discovery for decades and continues to be an active area nowadays.[2] The active component with novel structure from a plant extract is often used as a lead for new insecticide discovery to overcome their drawbacks such as instability, complex structure and limited insecticidal spectrum. Pyrethroids and neonicotinoids are successful example insecticides discovered basically from the natural plant products.[3]

(*E*)-1,5-Diphenyl-2-penten-1-one (**A**), extracted from *Stellera chamaejasme* L, showed good insecticidal property and antifeedant activity against *Aphis gossypii* Glov, *Schizaphis graminum* Rondani[4] and *Myzus persicae* Sulzer.[5] Compound **A** is similar in structure to these active compounds possessing a phenyl-carbonyl-phenyl skeleton, such as daphneolone, chalcones, dihydrochalcones, 2-phenylethyl benzoate, dibenzyl ketone and flavonoids. Thus, **A** is regarded as a lead for new insecticide discovery. Hou *et al.*[6,7] reported some 1,5-diphenyl-1-pentanone analogues with better aphicidal activity when the electron density of carbonyl in the analogues increased. Eight new analogues in which the 1-phenyl was replaced by different nitrogen heterocycles, also exhibited good insecticidal activity against *Aphis gossypii* at 600 mg•L^{-1}.[8]

The reported insecticidal spectrum of 1,5-diphenyl-1-pentanone and its analogues is mainly limited in aphids. In order to find novel compounds with wide insecticidal spectra, the title compound **X** (Figure 1) was herein designed, in which the 1-phenyl of compound **A** was replaced with 3-substituent-4-nitroimino-1,3,5-oxadiazinanes, an active group of neonicotinoid insecticide, thiamethoxam.[13-18] In the meantime, the linkage length of compound **A** was reduced from five-carbon to three-carbon so as to investigate the biological effects of varying carbon number in linkage. The title compound **X** was synthesized with the method in Scheme 1. Their biological activities against different kinds of pests were preliminarily evaluated.

Experimental

Materials and methods

Melting points (m.p.) were recorded on a Yanagimoto MFG. Co., which was uncorrected. ^{1}H NMR spectra were obtained at 300 MHz using a Bruker

* E-mail: lyun@cau.edu.cn
Received April 15, 2011; revised June 23, 2011; accepted July 29, 2011.
Project supported by the National Key Project for Basic Research (No. 2010CB126104), the National Key Technology R&D Program (No. 2011BAE06B05-5) and Innovation Fund for Graduate Student of China Agricultural University.

CHINESE JOURNAL OF CHEMISTRY

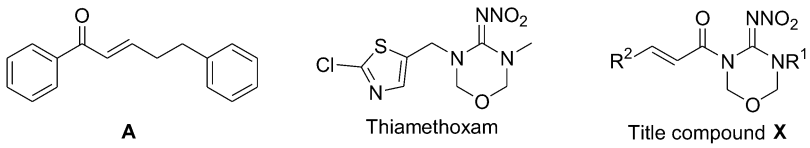
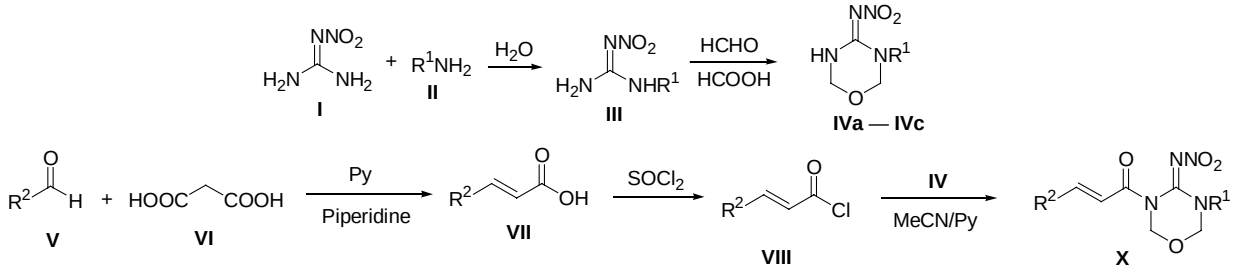


Figure 1 The structures of the lead compound **A**, thiamethoxam and title compound **X**.

Scheme 1 General synthetic route for the title compounds **X1**—**X30**



X1: R^1 = Me, R^2 = 4-F-C_6H_4; **X2**: R^1 = Me, R^2 = 4-Cl-C_6H_4; **X3**: R^1 = Me, R^2 = 4-Br-C_6H_4; **X4**: R^1 = Me, R^2 = 2,4-Cl_2-C_6H_3;
X5: R^1 = Me, R^2 = 4-OMe-C_6H_4; **X6**: R^1 = Me, R^2 = 4-OEt-C_6H_4; **X7**: R^1 = Me, R^2 = 3-Me-C_6H_4; **X8**: R^1 = Me, R^2 = Phenyl;
X9: R^1 = Me, R^2 = 2-Furyl; **X10**: R^1 = Me, R^2 = Thienyl; **X11**: R^1 = Et, R^2 = 4-F-C_6H_4; **X12**: R^1 = Et, R^2 = 4-Cl-C_6H_4;
X13: R^1 = Et, R^2 = 4-Br-C_6H_4; **X14**: R^1 = Et, R^2 = 2,4-Cl_2-C_6H_3; **X15**: R^1 = Et, R^2 = 4-OMe-C_6H_4; **X16**: R^1 = Et, R^2 = 4-OEt-C_6H_4;
X17: R^1 = Et, R^2 = 3-Me-C_6H_4; **X18**: R^1 = Et, R^2 = Phenyl; **X19**: R^1 = Et, R^2 = 2-Furyl; **X20**: R^1 = Et, R^2 = Thienyl;
X21: R^1 = *i*-Pr, R^2 = 4-F-C_6H_4; **X22**: R^1 = *i*-Pr, R^2 = 4-Cl-C_6H_4; **X23**: R^1 = *i*-Pr, R^2 = 4-Br-C_6H_4; **X24**: R^1 = *i*-Pr, R^2 = 2,4-di-Cl-C_6H_3;
X25: R^1 = *i*-Pr, R^2 = 4-OMe-C_6H_4; **X26**: R^1 = *i*-Pr, R^2 = 4-OEt-C_6H_4; **X27**: R^1 = *i*-Pr, R^2 = 3-Me-C_6H_4; **X28**: R^1 = *i*-Pr, R^2 = Phenyl;
X29: R^1 = *i*-Pr, R^2 = 2-Furyl; **X30**: R^1 = *i*-Pr, R^2 = Thienyl

Avance DPX300 spectrometer in $CDCl_3$ solution with tetramethylsilane as the internal standard. Elemental analyses were determined on ST-Carloerba. Co. elemental analyzer.

Synthetic procedure for 1-methyl-2-nitroguanidine IIIa

Take **IIIa** as the example,[19] 21.0 g (0.2 mol) of nitroguanidine and 40% aqueous methylamine (20 g, 0.25 mol) were added to absolute water (150 mL) in a 500 mL three-necked round-bottomed flask. The solution was stirred at room temperature for 24 h. The solid was collected by filtration, and then dried to obtain compound **IIIa** in white crystal (20.7 g, 88.2%), m.p. 160.0—162.0 ℃ (Lit.[19] 160.0—161.0 ℃). **IIIb** and **IIIc** were obtained by the similar method.

IIIb: white crystals (22.7 g, 86.8%), m.p. 146.0—148.0 ℃ (Lit.[19] 145.0—146.0 ℃).

IIIc: white crystals (18.5 g, 46.2%), m.p. 128.0—130.0 ℃ (Lit.[19] 126.0—127.0 ℃).

Synthetic procedure for *N*-(3-methyl-1,3,5-oxadiazinan-4-ylidene)nitramide IVa

1∶1 mixture of formaldehyde (37%, 20 mL) and formic acid (80%, 20 mL) was added to 1-methyl-2-nitroguanidine (**IIIa**, 2.4 g) in a 100 mL three-necked round-bottomed flask. The resulting mixture was heated to 75 ℃ for 12 h. After cooled to 0 ℃, and adjusted to pH 8.0 with concentrated hydrochloric acid, the white solid was filtered and dried to get compound **IVa**. White crystals (2.6 g, 81.2%), m.p. 140.0—141.0 ℃ (Lit.[19] 143.0—144.0 ℃). **IVb** and **IVc** were obtained by the similar method.

IVb: white crystals (2.8 g, 86.8%), m.p. 120.0—122.0 ℃ (Lit.[19] 117.0—118.0 ℃).

IVc: white crystals (1.5 g, 38.2%), m.p. 108.0—110.0 ℃ (Lit.[19] 108.0—109.0 ℃).

Synthetic procedure for cinnamic acid VII

0.3 g (2.86 mmol) of malonic acid was added to stirred solution of the corresponding aldehyde (1.3 mmol) in pyridine (15 mL) and piperidine (1.5 mL). The mixture was heated to reflux for 1 h. The reaction mixture was neutralized with 1 mol•L^{-1} hydrochloric acid in an ice bath. White crystals were separated out, filtered and washed with cooled water. Recrystallization from aqueous ethanol (V_{water}∶V_{etanol}=1∶1) afforded the corresponding acids **VII** with yields of 90%—96%.[20]

Synthetic procedure for the title compounds X

A mixture containing intermediate **VII** (7 mmol) and thionyl chloride (100 mmol) was added into a 50 mL flask equipped with a condenser and refluxed for 8 h. After cooled to room temperature, the excess thionyl chloride was distilled off via vacuum. The residue was reacted with **III** (7 mmol) in 20 mL acetonitrile for 8 h at refluxing temperature with pyridine as an acid acceptor. The solvent was removed under reduced pressure to give crude products. The products were purified by column chromatography on silica gel with ethyl acetate and petroleum (60—90 ℃) at a volume ratio of 1∶1 as an eluent. The yields and melting points of the title

compounds **X1**—**X30** are listed as follows. Their structures were confirmed by IR, ^{1}H NMR techniques and elemental analysis.

N-{3-[(*E*)-3-(4-Fluorophenyl)acryloyl]-5-methyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X1**): White powdery crystals, yield 71.4%, m.p. 110—112 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.05 (s, 3H, NCH_3), 5.10 (s, 2H, OCH_2N), 5.38 (s, 2H, NCH_2O), 7.01 (d, J=15.57 Hz, 1H, =CHC=O), 7.27—7.34 (m, 2H, ArH-2,6), 7.69 (d, J=15.63 Hz, 1H, CH=C), 7.73—7.80 (m, 2H, ArH-3,5); IR (KBr) ν: 3085, 1679, 1616, 1599, 1547, 1507, 1336 cm^{-1}. Anal. calcd for $C_{13}H_{13}FN_4O_4$: C 50.65, H 4.25, N 18.17; found C 50.45, H 4.51, N 18.50.

N-{3-[(*E*)-3-(4-Chlorophenyl)acryloyl]-5-methyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X2**): White powdery crystals, yield 72.1%, m.p. 160—161 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.08 (s, 3H, NCH_3), 5.11 (s, 2H, OCH_2N), 5.39 (s, 2H, NCH_2O), 7.07 (d, J=15.62 Hz, 1H, =CHC=O), 7.51—7.55 (m, 2H, ArH-2,6), 7.65—7.73 (m, 3H, ArH-3,5, CH=C); IR (KBr) ν: 3032, 1684, 1621, 1580, 1491, 1333, 1096 cm^{-1}. Anal. calcd for $C_{13}H_{13}ClN_4O_4$: C 48.08, H 4.04, N 17.25; found C 48.35, H 4.16, N 17.44.

N-{3-[(*E*)-3-(4-Bromophenyl)acryloyl]-5-methyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X3**): White powdery crystals, yield 69.0%, m.p. 148—150 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.08 (s, 3H, NCH_3), 5.10 (s, 2H, OCH_2N), 5.38 (s, 2H, NCH_2O), 7.08 (d, J=15.56 Hz, 1H, =CHC=O), 7.62—7.68 (m, 5H, ArH-2,3,5,6, CH=C); IR (KBr) ν: 3031, 1684, 1621, 1582, 1484, 1399, 1069 cm^{-1}. Anal. calcd for $C_{13}H_{13}BrN_4O_4$: C 42.29, H 3.55, N 15.18; found C 42.57, H 3.60, N 15.30.

N-{3-[(*E*)-3-(2,4-Dichlorophenyl)acryloyl]-5-methyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X4**): Light yellow powdery crystals, yield 73.0%, m.p. 180—181 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.08 (s, 3H, NCH_3), 5.11 (s, 2H, OCH_2N), 5.39 (s, 2H, NCH_2O), 7.15 (d, J=15.49 Hz, 1H, =CHC=O), 7.58—7.59 (m, 1H, ArH-6), 7.77—7.86 (m, 3H, ArH-3,5, CH=C); IR (KBr) ν: 3076, 1682, 1623, 1585, 1498, 1378, 1097 cm^{-1}. Anal. calcd for $C_{13}H_{12}Cl_2N_4O_4$: C 43.47, H 3.37, N 15.60; found C 43.71, H 3.60, N 15.64.

N-{3-[(*E*)-3-(4-Methoxyphenyl)acryloyl]-5-methyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X5**): Yellow powdery crystals, yield 72.0%, m.p. 131—133 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.07 (s, 3H, NCH_3), 3.81 (s, OCH_3), 5.09 (s, 2H, OCH_2N), 5.36 (s, 2H, NCH_2O), 6.89 (d, J=15.54 Hz, 1H, =CHC=O), 6.99—7.02 (d, J=8.79 Hz, 2H, ArH-2,6), 7.63—7.68 (m, 3H, ArH-3,5, CH=C); IR (KBr) ν: 2941, 1697, 1622, 1596, 1513, 1343, 1099 cm^{-1}. Anal. calcd for $C_{14}H_{16}N_4O_5$: C 52.50, H 5.03, N 17.49; found C 52.69, H 5.25, N 17.41.

N-{3-[(*E*)-3-(4-Ethoxyphenyl)acryloyl]-5-methyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X6**): Yellow powdery crystals, yield 68.0%, m.p. 120—122 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.31—1.36 (t, J=8.62 Hz, CH_2CH_3,), 3.07 (s, 3H, NCH_3), 4.05—4.12 (t, J=6.96 Hz, CH_2CH_3), 5.10 (s, 2H, OCH_2N), 5.36 (s, 2H, NCH_2O), 6.88 (d, J=15.46 Hz, 1H, =CHC=O), 6.97—7.01 (m, 2H, ArH-2,6), 7.60—7.68 (m, 3H, ArH-3,5, CH=C); IR (KBr) ν: 3070, 1675, 1598, 1571, 1512, 1338, 1106 cm^{-1}. Anal. calcd for $C_{14}H_{16}N_4O_5$: C 53.89, H 5.43, N 16.76; found C 53.78, H 5.49, N 16.49.

N-[3-Methyl-5-((*E*)-3-*m*-tolylacryloyl)-1,3,5-oxadiazinan-4-ylidene]nitramide (**X7**): Yellow powdery crystals, yield 68.0%, m.p. 100—102 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.34 (s, 3H, Ar-CH_3), 3.08 (s, 3H , NCH_3), 5.10 (s, 2H, OCH_2N), 5.38 (s, 2H, NCH_2O), 7.25 (d, J=15.57 Hz, 1H, =CHC=O), 7.26—7.50 (m, 4H, ArH-2,4,5,6), 7.63 (d, J=15.54 Hz, 1H, CH=C); IR (KBr) ν: 3023, 1672, 1613, 1568, 1504, 1334, 1103 cm^{-1}. Anal. calcd for $C_{14}H_{16}N_4O_4$: C 55.26, H 5.30, N 18.41; found C 55.33, H 5.44, N 18.43.

N-(3-Cinnamoyl-5-methyl-1,3,5-oxadiazinan-4-ylidene)nitramide (**X8**): White powdery crystals, yield 71.0%, m.p. 120—121 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.08 (s, 3H, NCH_3), 5.10 (s, 2H, OCH_2N), 5.38 (s, 2H, NCH_2O), 7.05 (d, J=15.64 Hz, 1H, =CHC=O), 7.43—7.71 (m, 6H, Ph, CH=C); IR (KBr) ν: 3077, 1677, 1616, 1573, 1505, 1338, 1028 cm^{-1}. Anal. calcd for $C_{13}H_{14}N_4O_4$: C 53.79, H 4.86, N 19.30; found C 53.75, H 4.98, N 19.32.

N-{3-[(*E*)-3-(Furan-2-yl)acryloyl]-5-methyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X9**): Brown powdery crystals, yield 56.0%, m.p. 113—115 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.07 (d, J=2.69 Hz,, 3H, NCH_3), 5.09 (d, J=1.70 Hz, 2H, OCH_2N), 5.33 (d, J=1.11 Hz, NCH_2O), 6.65—6.75 (m, 2H, Fu-4 H, =CHC=O), 7.00—7.09 (m, 1H, Fu-3 H), 7.44 (d, J=15.32 Hz, 1H, CH=C), 7.89 (t, J=1.17 Hz, 1H, Fu-5 H); IR (KBr) ν: 3031, 1679, 1616, 1575, 1329, 1100 cm^{-1}. Anal. calcd for $C_{11}H_{12}N_4O_5$: C 47.15, H 4.32, N 19.99; found C 47.42, H 4.39, N 19.90.

N-{3-Methyl-5-[(*E*)-3-(thiophen-2-yl)acryloyl]-1,3,5-oxadiazinan-4-ylidene}nitramide (**X10**): Brown powdery crystals, yield 76.0%, m.p. 106—108 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.07 (s, 3H, NCH_3), 5.09 (d, J=2.51 Hz, 2H, OCH_2N), 5.34 (s, 2H, NCH_2O), 6.72 (d, J=15.27 Hz, 1H, =CHC=O), 7.15—7.18 (m, 1H, Thiophene-4 H), 7.56—7.58 (m, 1H, Thiophene-3 H), 7.76 (d, J=5.07 Hz, 1H, Thiophene-5 H), 7.87 (d, J=15.26 Hz, 1H, CH=C); IR (KBr) ν: 3080, 1670, 1597, 1570, 1323, 1103 cm^{-1}. Anal. calcd for $C_{11}H_{12}N_4O_4S$: C 44.59, H 408, N 18.91; found C 44.53, H 4.10, N 18.65.

N-{3-Ethyl-5-[(*E*)-3-(4-fluorophenyl)acryloyl]-1,3,5-oxadiazinan-4-ylidene}nitramide (**X11**): White powdery crystals, yield 31.5%, m.p. 168—170 ℃; ^{1}H NMR ($DCCl_3$, 300 MHz) δ: 1.35 (t, J=7.23 Hz, 3H, CCH_3), 3.67—3.71 (m, 2H, CH_2C), 4.93 (s, 2H, OCH_2N), 5.36 (s, 2H, NCH_2O), 6.90 (d, J=15.00 Hz, 1H, =CHC=O), 7.03—7.11 (m, 2H, ArH-2,6), 7.53—7.59 (m, 2H, ArH-3,5), 7.81 (d, J=15.42 Hz, 1H, CH=C); IR (KBr) ν: 3006, 1679, 1616, 1570, 1511, 1270, 1041 cm^{-1}. Anal. calcd for $C_{14}H_{15}FN_4O_4$: C 52.17, H 4.69, N 17.18; found C 52.13, H 4.61, N 17.36.

N-{3-[(*E*)-3-(4-Chlorophenyl)acryloyl]-5-ethyl-1,3,5-

oxadiazinan-4-ylidene}nitramide (**X12**): White powdery crystals, yield 22.4%, m.p. 172—174 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.26 (t, J=7.20 Hz, 3H, CCH_3), 3.69—3.73 (m, 3H, CH_2C), 4.93 (s, 2H, OCH_2N), 5.37 (s, 2H, NCH_2O), 6.96 (d, J=15.39 Hz, 1H, =CHC=O), 7.44 (d, J=8.49 Hz, 2H, ArH-2,6), 7.52 (d, J=8.55 Hz, 2H, ArH-3,5), 7.78 (d, J=15.48 Hz, 1H, CH=C); IR (KBr) ν: 3076, 1702, 1628, 1589, 1570, 1226, 1092 cm^{-1}. Anal. calcd for $C_{14}H_{15}ClN_4O_4$: C 49.64, H 4.46, N 16.54; found C 49.69, H 4.35, N 16.63.

N-{3-[(*E*)-3-(4-Bromophenyl)acryloyl]-5-ethyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X13**): White powdery crystals, yield 25.0%, m.p. 174—176 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.36 (t, J=7.20 Hz, 3H, CCH_3), 3.65—3.76 (m, 2H, CH_2C), 4.93 (s, 2H, OCH_2N), 5.37 (s, 2H, NCH_2O), 6.94 (d, J=15.39 Hz, 1H, =CHC=O), 7.26—7.38 (m, 2H, ArH-2,6), 7.48—7.52 (m, 2H, ArH-3,5), 7.80 (d, J=15.48 Hz, 1H, CH=C); IR (KBr) ν: 3077, 1700, 1628, 1586, 1486, 1295, 1071 cm^{-1}. Anal. calcd for $C_{14}H_{15}BrN_4O_4$: C 43.88, H 3.95, N 14.62; found C 43.80, H 3.94, N 14.63.

N-{3-[(*E*)-3-(2,4-Dichlorophenyl)acryloyl]-5-ethyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X14**): White powdery crystals, yield 45.5%, m.p. 139—140 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.36 (t, J=7.20 Hz, 3H, CCH_3), 3.65—3.76 (m, 2H, CH_2C), 4.93 (s, 2H, OCH_2N), 5.37 (s, 2H, NCH_2O), 6.94 (d, J=15.39 Hz, 1H, =CHC=O), 7.24 (d, J=8.52 Hz, 1H, ArH-5), 7.43 (d, J=2.07 Hz, 1H, ArH-2), 7.63 (d, J=8.52 Hz, 1H, ArH-4), 7.80 (d, J=15.48 Hz, 1H, CH=C); IR (KBr) ν: 3083, 1708, 1625, 1584, 1504, 1228, 1050 cm^{-1}. Anal. calcd for $C_{14}H_{14}Cl_2N_4O_4$: C 45.06, H 3.78, N 15.01; found C 45.11, H 3.74, N 15.10.

N-{3-Ethyl-5-[(*E*)-3-(4-methoxyphenyl)acryloyl]-1,3,5-oxadiazinan-4-ylidene}nitramide (**X15**): Yellow powdery crystals, yield 17.2%, m.p. 142—144 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.35 (t, J=7.22 Hz, 3H, CCH_3), 3.66—3.68 (m, 2H, CH_2C), 3.84 (s, 3H, OCH_3), 4.96 (s, 2H, OCH_2N), 5.36 (s, 2H, NCH_2O), 6.80—6.91 (m, 3H, =CHC=O, ArH-2,6), 7.51—7.54 (m, 2H, ArH-3,5), 7.83 (d, J=15.32 Hz, 1H, CH=C); IR (KBr) ν: 3081, 1674, 1602, 1569, 1515, 1308, 1027 cm^{-1}. Anal. calcd for $C_{15}H_{18}N_4O_5$: C 53.89, H 5.43, N 16.76; found C 53.76, H 5.49, N 16.61.

N-{3-[(*E*)-3-(4-Ethoxyphenyl)acryloyl]-5-ethyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X16**): Yellow powdery crystals, yield 22.3%, m.p. 126—128 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.35 (t, J=7.22 Hz, 3H, CCH_3), 1.43 (t, J=7.02 Hz, 3H, $OCCH_3$), 3.64—3.68 (m, 2H, CH_2C), 4.04—4.08 (m, 2H, OCH_2), 4.91 (s, 2H, OCH_2N), 5.35 (s, 2H, NCH_2O), 6.80—6.89 (m, 3H, =CHC=O, ArH-2,6), 7.49—7.52 (m, 2H, ArH-3,5), 7.82 (d, J=15.36 Hz, 1H, CH=C); IR (KBr) ν: 3081, 1696, 1600, 1570, 1512, 1294, 1040 cm^{-1}. Anal. calcd for $C_{16}H_{20}N_4O_5$: C 55.17, H 5.79, N 16.08; found C 55.07, H 5.63, N 16.00.

N-[3-Ethyl-5-((*E*)-3-*m*-tolylacryloyl)-1,3,5-oxadiazinan-4-ylidene]nitramide (**X17**): Yellow powdery crystals, yield 28.2%, m.p. 147—148 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.33—1.37 (m, 3H, CCH_3), 2.37 (s, 3H, $ArCH_3$), 3.64—3.76 (m, 2H, CH_2C), 4.92 (s, 2H, OCH_2N), 5.36 (s, 2H, NCH_2O), 6.93 (d, J=15.39 Hz, 1H, =CHC=O), 7.20—7.23 (m, 1H, ArH-2), 7.24—7.30 (m, 1H, ArH-4), 7.36—7.38 (m, 2H, ArH-5,6), 7.83 (d, J=15.48 Hz, 1H, CH=C); IR (KBr) ν: 2945, 1676, 1611, 1562, 1506, 1272, 1039 cm^{-1}. Anal. calcd for $C_{15}H_{18}N_4O_4$: C 56.60, H 5.70, N 17.60; found C 56.60, H 5.58, N 17.68.

N-(3-Cinnamoyl-5-ethyl-1,3,5-oxadiazinan-4-ylidene)nitramide (**X18**): Yellow powdery crystals, yield 18.3%, m.p. 168—170 ℃.; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.35 (t, J=7.26 Hz, 3H, CCH_3), 3.65—3.69 (m, 2H, CH_2C), 4.92 (s, 2H, OCH_2N), 5.36 (s, 2H, NCH_2O), 6.96 (d, J=15.39 Hz, 1H, =CHC=O), 7.37—7.41 (m, 3H, ArH-2,3,4), 7.55—7.58 (m, 2H, ArH-5,6), 7.86 (d, J=15.39 Hz, 1H, CH=C); IR (KBr) ν: 3081, 1678, 1614, 1568, 1271, 1503, 1040 cm^{-1}. Anal. calcd for $C_{14}H_{16}N_4O_4$: C 55.26, H 5.30, N 18.41; found C 55.25, H 5.22, N 18.69.

N-{3-Ethyl-5-[(*E*)-3-(furan-2-yl)acryloyl]-1,3,5-oxadiazinan-4-ylidene}nitramide (**X19**): Brown powdery crystals, yield 19.8%, m.p. 131—133 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.34 (t, J=7.22 Hz, 3H, CCH_3), 3.65—3.68 (m, 3H, CH_2C), 4.91 (s, 2H, OCH_2N), 5.34 (s, 2H, NCH_2O), 6.47—6.49 (m, 1H, Fu-3 H) , 6.71 (d, J=3.45 Hz, 1H, Fu-4 H), 6.82 (d, J=15.03 Hz, 1H, =CHC=O), 7.48—7.52 (m, 1H, Fu-5 H), 7.59 (d, J=15.06 Hz, 1H, CH=C); IR (KBr) ν: 3093, 1675, 1613, 1567, 1273, 1040 cm^{-1}. Anal. calcd for $C_{12}H_{14}N_4O_5$: C 48.98, H 4.80, N 19.04; found C 48.91, H 4.63, N 19.09.

N-{3-Ethyl-5-[(*E*)-3-(thiophen-2-yl)acryloyl]-1,3,5-oxadiazinan-4-ylidene}nitramide (**X20**): Brown powdery crystals, yield 15.2%, m.p. 165—167 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.35 (t, J=7.22 Hz, 3H, CCH_3), 3.65—3.69 (m, 3H, CH_2C), 4.92 (s, 2H, OCH_2N), 5.35 (s, 2H, NCH_2O), 6.74 (d, J=15.06 Hz, 1H, =CHC=O), 7.03—7.09 (m, 1H, Thiophene-4 H), 7.34 (d, J=3.41 Hz, 1H, Thiophene-3 H), 7.44 (d, J=5.10 Hz, 1H, Thiophene-5 H), 7.94 (d, J=15.09 Hz, 1H, CH=C); IR (KBr) ν: 3119, 1674, 1599, 1566, 1280, 1043 cm^{-1}. Anal. calcd for $C_{12}H_{14}N_4O_4S$: C 46.44, H 4.55, N 18.05; found C 46.40, H 4.41, N 18.12.

N-{3-[(*E*)-3-(4-Fluorophenyl)acryloyl]-5-isopropyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X21**): White powdery crystals, yield 45.5%, m.p. 131—132 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.33 (d, J=6.84 Hz, 6H, $C(CH_3)_2$), 4.78—4.82 (m, 1H, CHC_2), 4.86 (s, 2H, OCH_2N), 5.34 (s, 2H, NCH_2O), 6.89 (d, J=15.39 Hz, 1H, =CHC=O), 7.04—7.10 (m, 2H, ArH-2,6), 7.53—7.58 (m, 2H, ArH-3,5), 7.82 (d, J=15.39 Hz, 1H, CH=C); IR (KBr) ν: 3110, 1674, 1617, 1597, 1544, 1240, 1006 cm^{-1}. Anal. calcd for $C_{15}H_{17}FN_4O_4$: C 53.57, H 5.09, N 16.66; found C 53.60, H 4.93, N 16.78.

N-{3-[(*E*)-3-(4-Chlorophenyl)acryloyl]-5-isopropyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X22**): White

powdery crystals, yield 30.2%, m.p. 155—157 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.33 [d, J=6.81 Hz, 6H, $C(CH_3)_2$], 4.76—4.80 (m, 1H, CHC_2), 4.86 (s, 2H, OCH_2N), 5.34 (s, 2H, NCH_2O), 6.93 (d, J=15.39 Hz, 1H, =CHC=O), 7.33—7.37 (m, 2H, ArH-2,6), 7.46—7.52 (m, 2H, ArH-3,5), 7.79 (d, J=15.42 Hz, 1H, CH=C); IR (KBr) ν: 3067, 1697, 1623, 1592, 1557, 1289, 1091 cm^{-1}. Anal. calcd for $C_{15}H_{17}ClN_4O_4$: C 51.07, H 4.86, N 15.88; found C 51.19, H 4.68, N 15.98.

N-{3-[(*E*)-3-(4-Bromophenyl)acryloyl]-5-isopropyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X23**): White powdery crystals, yield 34.6%, m.p. 166—168 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.33 [d, J=6.81 Hz, 6H, $C(CH_3)_2$], 4.77—4.81 (m, 1H, CHC_2), 4.86 (s, 2H, OCH_2N), 5.34 (s, 2H, NCH_2O), 6.95 (d, J=15.30 Hz, 1H, =CHC=O), 7.40—7.44 (m, 2H, ArH-2,6), 7.49—7.53 (m, 2H, ArH-3,5), 7.78 (d, J=15.45 Hz, 1H, CH=C); IR (KBr) ν: 2982, 1694, 1626, 1560, 1508, 1237, 1070 cm^{-1}. Anal. calcd for $C_{15}H_{17}BrN_4O_4$: C 45.35, H 4.31, N 14.10; found C 45.60, H 4.25, N 14.25.

N-{3-[(*E*)-3-(2,4-Dichlorophenyl)acryloyl]-5-isopropyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X24**): White powdery crystals, yield 60.7%, m.p. 154—156 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.33 [d, J=6.81 Hz, 6H, $C(CH_3)_2$], 4.76—4.80 (m, 1H, CHC_2), 4.86 (s, 2H, OCH_2N), 5.35 (s, 2H, NCH_2O), 6.93 (d, J=15.39 Hz, 1H, =CHC=O), 7.25—7.28 (m, 1H, ArH-5), 7.39—7.45 (m, 1H, ArH-2), 7.60—7.66 (m, 1H, ArH-4), 8.17 (d, J=15.41 Hz, 1H, CH=C); IR (KBr) ν: 3059, 1695, 1635, 1584, 1557, 1236, 1101 cm^{-1}. Anal. calcd for $C_{15}H_{16}Cl_2N_4O_4$: C 46.35, H 4.16, N 14.47; found C 46.60, H 4.08, N 14.59.

N-{3-Isopropyl-5-[(*E*)-3-(4-methoxyphenyl)acryloyl]-1,3,5-oxadiazinan-4-ylidene}nitramide (**X25**): Yellow powdery crystals, yield 28.2%, m.p. 164—166 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.33 [d, J=6.81 Hz, 6H, $C(CH_3)_2$], 3.83 (s, 3H, OCH_3), 4.77—4.81 (m, 1H, HC=C), 4.85 (s, 2H, OCH_2N), 5.33 (s, 2H, NCH_2O), 6.83 (d, J=15.30 Hz, 1H, =CHC=O), 6.86—6.90 (m, 2H, ArH-2,6), 7.51—7.54 (m, 2H, ArH-3,5), 7.83 (d, J=15.30 Hz, 1H, CH=C); IR (KBr) ν: 3066, 1692, 1626, 1602, 1553, 1236, 1027 cm^{-1}. Anal. calcd for $C_{16}H_{20}N_4O_5$: C 55.17, H 5.79, N 16.08; found C 55.32, H 5.59, N 16.24.

N-{3-[(*E*)-3-(4-Ethoxyphenyl)acryloyl]-5-isopropyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X26**): Yellow powdery crystals, yield 47.4%, m.p. 162—164 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.32 [d, J=6.81 Hz, 6H, $C(CH_3)_2$], 1.40—1.43 (m, 3H, CCH_3), 4.06—4.08 (m, 2H, CH_2C), 4.77—4.80 (m, 1H, HC=C), 4.84 (s, 2H, OCH_2N), 5.33 (s, 2H, NCH_2O), 6.82 (d, J=15.30 Hz, 1H, =CHC=O), 6.86—6.90 (m, 2H, ArH-2,6), 7.48—7.54 (m, 2H, ArH-3,5), 7.81 (d, J=15.33 Hz, 1H, CH=C); IR (KBr) ν: 2981, 1679, 1620, 1597, 1544, 1294, 1047 cm^{-1}. Anal. calcd for $C_{17}H_{22}N_4O_5$: C 56.34, H 6.12, N 15.46; found C 56.36, H 5.93, N 15.20.

N-[3-isopropyl-5-((*E*)-3-*m*-tolylacryloyl)-1,3,5-oxadiazinan-4-ylidene]nitramide (**X27**): Yellow powdery crystals, yield 35.8%, m.p. 152—153 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.33 [d, J=6.81 Hz, 6H, $C(CH_3)_2$], 2.37 (s, 3H, $ArCH_3$), 4.79—4.81 (m, 1H, HC=C), 4.85 (s, 2H, OCH_2N), 5.34 (s, 2H, NCH_2O), 6.93 (d, J=15.39 Hz, 1H, =CHC=O), 7.22—7.29 (m, 2H, ArH-2,4), 7.36 (s, 2H, ArH-5,6), 7.83 (d, J=15.39 Hz, 1H, CH=C); IR (KBr) ν: 2978, 1678, 1614, 1586, 1539, 1272, 1092 cm^{-1}. Anal. calcd for $C_{16}H_{20}N_4O_4$: C 57.82, H 6.07, N 16.86; found C 57.81, H 5.92, N 16.94.

N-(3-Cinnamoyl-5-isopropyl-1,3,5-oxadiazinan-4-ylidene)nitramide (**X28**): Yellow powdery crystals, yield 32.8%, m.p. 136—138 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.33 [d, J=6.81 Hz, 6H, $C(CH_3)_2$], 4.78—4.81 (m, 1H, HC=C), 4.86 (s, 2H, OCH_2N), 5.34 (s, 2H, NCH_2O), 6.96 (d, J=15.39 Hz, 1H, =CHC=O), 7.37—7.40 (m, 3H, ArH-2,3,4), 7.55—7.58 (m, 2H, ArH-5,6), 7.86 (d, J=15.39 Hz, 1H, CH=C); IR (KBr) ν: 2972, 1676, 1614, 1548, 1499, 1240, 1008 cm^{-1}. Anal. calcd for $C_{15}H_{18}N_4O_4$: C 56.60, H 5.70, N 17.60; found C 56.72, H 5.57, N 17.80.

N-{3-[(*E*)-3-(Furan-2-yl)acryloyl]-5-isopropyl-1,3,5-oxadiazinan-4-ylidene}nitramide (**X29**): Brown powdery crystals, yield 26.8%, m.p. 138—140 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.25 [d, J=6.81 Hz, 6H, $C(CH_3)_2$], 4.54—4.56 (m, 1H, HC=C), 5.10 (s, 2H, OCH_2N), 5.26 (s, 2H, NCH_2O), 6.64—6.68 (m, 1H, Fu-3 H), 6.75 (d, J=15.31 Hz, 1H, =CHC=O), 6.98—7.02 (m, 1H, Fu-4 H), 7.49 (d, J=15.30 Hz, 1H, CH=C), 7.87—7.91 (m, 1H, Fu-5 H); IR (KBr) ν: 2976, 1676, 1614, 1549, 1241, 1004 cm^{-1}. Anal. calcd for $C_{13}H_{16}N_4O_5$: C 50.65, H 5.23, N 18.17; found C 50.77, H 5.05, N 18.32.

N-{3-Isopropyl-5-[(*E*)-3-(thiophen-2-yl)acryloyl]-1,3,5-oxadiazinan-4-ylidene}nitramide (**X30**): Brown powdery crystals, yield 42.7%, m.p. 148—150 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.25 [d, J=6.81 Hz, 6H, $C(CH_3)_2$], 4.54—4.56 (m, 1H, HC=C), 5.10 (s, 2H, OCH_2N), 5.26 (s, 2H, NCH_2O), 6.73 (d, J=15.25 Hz, 1H, =CHC=O), 7.13—7.19 (m, 1H, Thiophene-4 H), 7.55—7.60 (m, 1H, Thiophene-3 H), 7.57 (m, 1H, Thiophene-5 H), 7.85 (d, J=15.27 Hz, 1H, CH=C); IR (KBr) ν: 3361, 1692, 1608, 1533, 1237, 1042 cm^{-1}. Anal. calcd for $C_{13}H_{16}N_4O_4S$: C 48.14, H 4.97, N 17.27; found C 48.36, H 4.86, N 17.47.

Biological activity

Insecticidal activities of the title compounds **X1**—**X30** against *Aphis gossypii*, *Plutella xylostella* (L.) and *Tetranychus cinnabarinus* (Boisduval) were evaluated (Table 1).

All bioassays were performed on representative test pests reared in the laboratory. The bioassay was repeated at (25±1) ℃ according to statistical requirements. All compounds were dissolved in acetone (AP, Beijing Chemical Reagent, Beijing, China) and diluted with distilled water containing Triton X-100 (0.1 mg•L^{-1}) to obtain gradient concentrations of 600 mg•L^{-1} and others for bioassays.[21] Assessments were made on a

CHINESE JOURNAL OF CHEMISTRY

dead/alive basis, and mortality rates were corrected using Abbott's formula.[22]

Insecticidal test for *Aphis gossypii* The insecticidal activity against *Aphis gossypii* was tested by leaf-dip method according to the following procedures. Cabbage leaves with 40—60 apterous adults were dipped for 5 s in diluted solutions of the title compounds containing Triton X-100 (0.1 mg•L^{-1}), and the excess dilution was removed with filter paper; the burgeons were placed in the conditioned room [(25±1) ℃]. Water containing Triton X-100 (0.1 mg•L^{-1}) was used as control. The mortality rates were evaluated 24 h after treatment. Each treatment was repeated three times, and the results were statistically analyzed.

Insecticidal test for *Tetranychus cinnabarinus* (Boisduval) The insecticidal activity against *Tetranychus cinnabarinus* (Boisduval) was tested by leaf-dip method according to the following procedures. Bean leaves with 20 adults were dipped for 5 s in diluted solutions of the chemicals containing Triton X-100 (0.1 mg•L^{-1}), and the excess dilution was dried by airing; the burgeons were placed in the conditioned room [(25±1) ℃]. Water containing Triton X-100 (0.1 mg•L^{-1}) was used as control. The mortality rates were evaluated 48 h after treatment. Each treatment was repeated three times, and the results were statistically analyzed.

Insecticidal test for *Plutella xylostella* (L.) The insecticidal activity against *Plutella xylostella* (L.) was tested by leaf-dip method according to the following procedures. Cabbage leaves of 2 cm diameter were dipped for 5 s in diluted solutions of the chemicals containing Triton X-100 (0.1 mg•L^{-1}), and the excess dilution was dried by airing, and then 10 2-instar-larvae were transferred on the leaf. The burgeons were placed in the conditioned room [(27±1) ℃]. Water containing Triton X-100 (0.1 mg•L^{-1}) was used as the control. The mortality rates were evaluated 72 h after treatment. Each treatment was repeated three times, and the results statistically analyzed.

Results and discussion

Chemical synthesis

The general synthetic route of title compounds **X** is shown in Scheme 1. Wherein, the key intermediate 3-substituent-4-nitroimino-1,3,5-oxadiazinanes **IV** and substituted cinnamic acid **VII** were prepared by the well-described routes, starting from the inexpensive commercial chemicals. The target compound **X** was synthesized by the reaction of different kinds of chloride **VIII** and intermediate **IV** in anhydrous acetonitrile under reflux with pyridine as an acid scavenger. Their structures were characterized by IR, ^{1}H NMR techniques and elemental analysis.

Bioactivity

The title compounds **X1**—**X30** were tested for their insecticidal activity against *Aphis gossypii*, *Plutella xylostella* (L.) and *Tetranychus cinnabarinus* (Boisduval). The results are listed in Table 1.

All compounds displayed good insecticidal activity against *Aphis gossypii*, except **X1**, **X8** and **X10**. For instance, the insecticidal activities of compounds **X11**—**X14**, **X19**, **X23**, **X24**, **X27** and **X30** against *Aphis gossypii* were 100%, which were much better than 70.1% of the lead compound **A**. Some title compounds, such as **X6** and **X29** with 100% inhibitory rate, exhibited good insecticidal activities against *Plutella xylostella* (L.). All compounds except **X4**, **X5**, **X8** and **X9** displayed better activity against *Tetranychus cinnabarinus* (Boisduval) than the lead compound **A**., for instance, the inhibitory rates of compounds **X12**, **X13**, **X19**, **X24**, **X25**, **X26** and **X27** were more than 80%, which were much higher than lead **A** (24.5%)

The preliminary structure-activity relationship showed that the compounds containing 3-ethyl-4-nitroimino-1,3,5-oxadiazinanes and 3-isopropyl-4-nitroimino-1,3,5-oxadiazinanes generally had better aphicidal activity than lead compound **A** and the compounds containing 3-methyl-4-nitroimino-1,3,5-oxadiazinanes. The title compounds **X**, in which the 1-phenyl of compound **A** was replaced with 3-substituent-4-nitroimino-1,3,5-oxadiazinanes, such as **X23** and **X29**, showed wider insecticidal spectra than lead **A**. And it also indicated that the title compounds with three-carbon linkage had broader insecticidal spectra than the compounds with five-carbon linkage reported in our previous literature.[8] Further studies on structural optimization and structure-activity relationships of this novel 1,5-diphenyl-1-pentanone derivatives are in progress.

Table 1 Insecticidal activity of title compounds **X1**—**X30** at 600 mg•L^{-1}

Compd.	Insecticidal activity (relative inhibitory ratio)/%		
	Aphis gossypii	*Plutella xylostella*	*Tetranychus cinnabarinus* (Boisduval)
A	70.1	80.0	24.5
X1	42.1	38.9	44.1
X2	85.0	33.3	38.9
X3	61.4	5.6	70.3
X4	67.5	33.3	23.8
X5	75.0	66.7	17.2
X6	59.3	100	44.7
X7	57.6	50.0	56.0
X8	19.7	61.1	15.2
X9	62.7	55.6	17.4
X10	25.8	55.6	47.5
X11	100	30.0	69.1
X12	100	40.0	82.2
X13	100	0	80.8

Continued

Compd.	Insecticidal activity (relative inhibitory ratio)/%		
	Aphis gossypii	*Plutella xylostella*	*Tetranychus cinnabarinus* (Boisduval)
X14	100	0	73.3
X15	99.2	10.0	48.2
X16	98.0	20.0	57.0
X17	95.5	80.0	40.0
X18	96.8	40.0	72.8
X19	100	50.0	81.3
X20	89.3	30.0	47.2
X21	93.8	40.0	46.7
X22	98.4	40.0	37.6
X23	100	70.0	78.4
X24	100	50.0	86.3
X25	86.6	40.0	81.7
X26	83.5	30.0	86.9
X27	100	0	82.0
X28	97.8	70.0	47.2
X29	98.3	100	73.3
X30	100	20.0	43.0

Conclusions

Thirty novel 1,5-diphenyl-1-pentanone derivatives were synthesized by the reaction of substituted cinnamoyl chloride and 3-substituent-4-nitroimino-1,3,5-oxadiazinanes in acetonitrile under reflux with pyridine as an acid acceptor. The preliminary bioassay showed the target compounds exhibited good insecticidal activity against *Aphis gossypii*. Especially the compounds **X11**—**X30** displayed good insecticidal activity against *Aphis gossypii*, higher than the lead compound **A** and compounds **X1**—**X10**. Some of them also showed excellent activities against *Plutella xylostella* (L.) and *Tetranychus cinnabarinus* (Boisduval) at 600 mg•L^{-1}. In a summary, the designed title compounds, with 3-substituent-4-nitroimino-1,3,5-oxadiazinanes and three-carbon linkage, showed better aphicidal activity and broader insecticidal spectra than the lead compound **A**.

References

1 Qian, X.-H.; Lee, P.; Cao, S. *J. Agric. Food Chem*. **2010**, *58*, 2613.
2 Shang, E.-C.; Shang, Z.-W. *Modern Agrochem*. **2010**, *9*, 1 (in Chinese).
3 Nishimura, K.; Kanda, Y.; Okazawa, A.; Ueno, T. *Pestic. Biochem. Physiol*. **1994**, *50*, 51.
4 Gao, P.; Hou, T.-P.; Gao, R.; Cui, Q.; Liu, S.-G. *Pest Manag. Sci*. **2001**, *57*, 307.
5 Yang, S.-X.; Yang, X.-L.; Lu, Y.-Y.; Sun, Y.-F.; Ling, Y. *Chin. J. Org. Chem*. **2010**, *30*, 1543 (in Chinese).
6 Lu, T.; Chen, L.; Hou, T.-P. *Pestic. Biochem. Physiol*. **2007**, *89*, 60.
7 Chen, L.; Wang, X.; Lu, T.; Hou, T.-P. *Pest Manag. Sci*. **2007**, *63*, 928.
8 Yang, S.-X.; Kang, T.-N.; Yang, X.-L.; Sun, Y.-F.; Rui, C.-H.; Ling, Y. *Chin. J. Org. Chem*. **2010**, *30*, 1870 (in Chinese).
9 Liu, M.; Wang, Y.; Wangyang, W.-Z.; Liu, F.; Cui, Y.-L.; Duan, Y.-S.; Wang, M.; Liu, S.-Z.; Rui, C.-H. *J. Agric. Food Chem*. **2010**, *58*, 6858.
10 Lima, L. M. A.; Barreiro, E. J. *Curr. Med. Chem*. **2005**, *12*, 23.
11 Liu, Y.-X.; Cai, B.-L.; Li, Y.-H.; Song, H.-B.; Huang, R.-Q.; Wang, Q.-M. *J. Agric. Food Chem*. **2007**, *55*, 3011.
12 Zhao, Q.-Q.; Liu, S.-H.; Li, Y.-H.; Wang, Q.-M. *J. Agric. Food Chem*. **2009**, *57*, 2849.
13 Moriie, K.; Ootsu, J.; Hatsutori, Y.; Watanabe, A.; Ito, A. *JP 07224062*, **1995** [*Chem. Abstr*. **1995**, *124*, 8855].
14 Shiokawa, K.; Tsuboi, S.; Kagabu, S.; Sasaki, S.; Moriya, K.; Hattori, Y. *US 4849432*, **1987 [***Chem. Abstr*. **1988**, *108*, 21897].
15 Kiriyama, K.; Nishimura, K. *Pest. Manag. Sci*. **2002**, *58*, 669.
16 Ishimitsu, K.; Suzuki, J.; Ohishi, H.; Yamada, T.; Hatano, R.; Takakusa, N.; Mitsui, J. *WO 9104965 A1*, **1991** [*Chem. Abstr*. **1991**, *115*, 92085].
17 Aoki, I.; Tabuchi, T.; Minamida, I. *EP 381130*, **1990** [*Chem. Abstr*. **1991**, *114*, 61936].
18 Uneme, H.; Iwanaga, K.; Higuchi, N.; Kando, Y.; Okauchi, T.; Akayama, A.; Minamida, I. *Pestic. Sci*. **1999**, *55*, 202.
19 Peter, M. Z. *Naturforsch., B*: *Chem. Sci*. **2006**, *61*, 353.
20 Carolina, M.; Hugo, V.; Joao, X. *Eur. J. Pharm. Sci*. **2004**, *23*, 363.
21 Zhao, Y.; Li, Y.-Q.; Wang, S.-H.; Li, Z.-M. *Arkivoc* **2009**, (xi), 152.
22 Abbott, W. S. *J. Econ. Entomol*. **1925**, *18*, 265.

(E1104153 Zhao, C.; Lu, Z.)

