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ORIGINAL PAPER

Synthesis, Crystal Structure and Biological Activity of N′-tert-butyl-N-(3-methoxylbenzoyl)-N-(4-methyl-1,2,3-thiadiazole-5-formylhydrazine

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Abstract The title compound, N′-tert-butyl-N-(3-methoxylbenzoyl)-N-(4-methyl-1,2,3-thiadiazole-5-formylhydrazine ($C_{16}H_{20}N_4O_3S$) was prepared from the reaction of 4-methyl-1,2,3-thiadiazole-5-carbonyl chloride with N′-tert-Butyl-3-methoxylbenzohydrazine, and its structure was characterized by ^{1}Hydrogen Nuclear Magnetic Resonance, High-Resolution Mass Spectrometry, IR spectra, and single crystal X-ray diffraction. The crystal of the title compound belongs to monoclinic system, space group *P 21/c* with cell parameters $a = 17.986(2)$ Å, $b = 8.0180(10)$ Å, $c = 12.0190(14)$ Å, $\alpha = 90°$, $\beta = 91.160(5)°$, $\gamma = 90°$, $V = 1732.9(4)$ Å^3, $Z = 4$, $D_c = 1.335$ g/cm^3, μ (Mo Ka) = 0.209 mm^{-1}, F (000) = 736, $R = 0.0367$ and $wR = 0.0932$. X-ray diffraction analysis indicates that all rings in the title compound are non-planar. The bioassay results indicated that, the title compound had good fungicide activity against *Sclerotinia sclerotiorum*, certain extent of insecticidal activity against *Plutella xylostella* L.

Keywords X-ray diffraction · Single crystal structure · Synthesis · Diacylhydrazine · Biological activity

Introduction

Diacylhydrazines are non-steroidal molting hormone agonists [1], which have been identified as one of the most important new class of insect growth regulators with unique action, simple structure, low toxicity to vertebrates, and high insecticidal selectivity [2–5]. N′-tert-butyl-N,N′-dibenzoylhydrazine (RH-5849) was the first nonsteroidal ecdysone agonist reported in 1988. Tebufenozide (RH-5992) was firstly commercialized by Rohm & Haas Company [6]. A variety of diacylhydrazine derivatives have been designed and synthesized for the purpose of obtaining new compounds with higher insecticidal activity afterwards. For example, methoxyfenozide (RH-2485), halofenozide (RH-0345), and chromafenozide (ANS-118) were commercialized as high ecdysone agonists [4]. Diacylhydrazines possess two phenyl groups in one molecule; Replacement of the phenyl group(s) by a heterocycle group is effective measures in novel pesticide development because heterocyclic groups are usually bioactive substructure. 1,2,3-Thiadiazoles as an important active substructure of heterocyclic compounds have various biological activities, some 1,2,3-thiadazoles are commercialized as plant activators [7, 8], many 1,2,3-thiadizole derivatives have been reported with antiviral [9, 10], antitumor [11], antibacterial [12], fungicidal [13–15], and insecticidal activities [16]. Moreover, 1,2,3-thiadiazole ring possesses the property of easy breakdown into low

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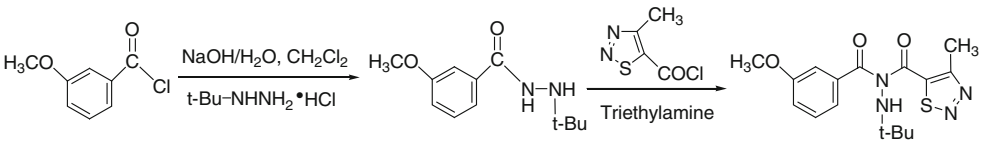
Scheme 1 Molecule structure and synthesis of the target compound



molecular weight compounds through release of N_2, it favors the characteristics of environmentally friendly pesticide candidates with low toxicity [17]. Our previous studies discovered some new 1,2,3-thiadizoles with fungicidal activity, antiviral activity and systemic acquired resistance [13, 18, 19], and two types of diacylhydrazines containing 1,2,3-thiadiazoles with carbonyl in N or N′ independently had good insecticidal activity [20, 21].

In this paper, another type of diacylhydrazines containing 1,2,3-thiadiazoles with two carbonyl in one N atom was designed and synthesized, the target compound N′-tert-butyl-N-(3-methoxylbenzoyl)-N-(4-methyl-1,2,3-thiadiazole-5-formyl)hydrazine was synthesized according to the routine described in Scheme 1, its crystal structure and biological activity were also detected.

Experimental Procedures

Reagents and Measurements

All reagents and solvents for synthesis and analyses were of analytical grade, and commercially purchased from J&K Scientific Ltd. (China) which were used without further purification. Column chromatography purification was carried out by using silica gel with ethyl acetate and petroleum ether 1:2 (v/v) as mobile phase. The melting point was measured on an XT-4A apparatus without correction of the thermometer. Infrared (IR) spectra were recorded on a Bruker Tensor 27 Spectrophotometer in KBr pellet. Hydrogen Nuclear Magnetic Resonance (^{1}H NMR) spectra was measured on a Bruker AC-P500 Instrument (400 MHz) with deutero-chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as the internal standard. High-resolution mass spectrometry (HRMS) data was obtained on an FTICR-MS Varian 7.0T FTICR-MS instrument. The single crystal structure was determined on a Rigaku Saturn 724 CCD diffractometer. The equipment was operated using Mo-Kα radiation ($\lambda = 0.71075$ Å).

Synthesis of the Title Compound

To a stirred mixture of tert-butylhydrazine hydrochloride (2.9 g, 0.0234 mol) in 30 mL dichloromethane, sodium hydroxide (1.0 g, 96%, 0.024 mol) in water (2 mL) was added dropwise within 25 min at −10 °C, the reaction mixture was then stirred for 15 min. After the addition of 3-methoxylbenzoyl chloride (1.98 g, 0.116 mol) in batches, the mixture was further stirred in an ice-water bath for 0.5 h. Then the mixture was permitted to stir for another 5 h at room temperature. The reaction mixture was washed with water (3 × 10 mL) followed by brine (10 mL), the organic layer was dried over anhydrous sodium sulfate, after filtration, the solvent was removed under vacuum to give the compound N′-tert-Butyl-3-methoxylbenzohydrazine, yield was not optimized. According to the previous work, 4-methyl-1,2,3-thiadiazole-5-carbonyl chloride was synthesized from 4-methyl-1,2,3-thiadiazole-5-carboxylic acid according to Ref. [18]. A solution of 4-methyl-1,2,3-thiadiazole-5-carbonyl chloride (3.3 mmol) in dichloromethane (20 mL) was added dropwise to a stirred mixture of N-tert-butyl-N′-3-methoxylbenzoyl hydrazine(3.0 mmol), triethylamine (3.3 mmol), and dichloromethane (20 mL) in an ice bath for 1 h. Then remove the ice bath, the resultant mixture was stirred at room temperature for 5 h. The mixture was washed successively with water (3 × 20 mL) and brine (20 mL), the organic layer was dried over anhydrous sodium sulfate. After filtration the anhydrous sodium sulfate, the solvent was evaporated, the residue was then purified by column chromatography on silica gel using ethyl acetate and petroleum ether (60–90 °C) with 1:2 (v/v) as an eluent to obtain the target compound (0.09 g, 8.61%, mp = 194–196 °C) as a minor product, another product of N-tert-butyl-N-4-methyl-1,2,3-thiadiazole-5-yl-N′-3-methoxylphenyl diacylhydrazine as the main product(0.75 g, 71.75%) was obtained, 4-methyl-1,2,3-thiadiazole-5-carboxylic acid (0.07 g, 10.49%) was recovered. The solid was recrystallized in dichloromethane and petroleum ether which was then analyzed by single crystal techniques. ^{1}HNMR ($CDCl_3$, 400 MHz): δ 1.22 (s, 9H, $C(CH_3)_3$), 2.94 (s, 3H, thiadiazolyl-CH_3), 3.90 (s, 3H, –CH_3), 5.74 (s, 1H, NH), 7.20–7.49(m, 4H, Ph–H); HRMS (m/z): $(M + H)^+$: 349.1329, found: 349.1324; IR (KBr pellet press, ν, cm^{-1}): 3347 (NH, st), 2967, 1701 (C = O, st), 1677, 1598, 1488, 1468, 1457, 1372, 1264.

Crystal Data and Structure Determination

The crystal of the target compound was cultured from dichloromethane and petroleum ether. The colorless crystal of the title compound with dimensions of 0.24 × 0.22 × 0.20 mm^3 was selected and mounted on a glass fiber for

X-ray diffraction analysis. All measurements were made on a Rigaku Saturn 724 CCD diffractometer Mo$K\alpha$ radiation ($\lambda = 0.71075$ Å). The data were collected at a temperature of -160 ± 1 °C to a maximum 2θ value of 56°. A total of 540 oscillation images were collected. Three sweeps of data were done using w scans from –110.0 to 70.0° in 1.0° step, at $\chi = 45.0°$ and $\phi = 0$, 90 and 180°. The exposure rate was 5.0 [sec/°]. The detector swing angle was $-19.92°$. The crystal-to-detector distance was 45.08 mm. The crystal is monoclinic system, space group *P 1 21/c 1,* with unit cell parameters: $a = 17.986$ (2), $b = 8.0180$ (10), $c = 12.0190(14)$ Å, $V = 1732.9(4)$ Å^3, $Z = 4$, density (calculated) = 1.335 g/cm^3, and linear absorption coefficient 0.209 mm^{-1}. In total 19,940 integrated reflections were collected, reducing to a data set of 4,135 unique with $R_{int} = 0.0404$, and completeness of data (to $\theta = 27.89°$) of 99.8%. Data were collected and processed using Crystal Clear (Rigaku). An empirical absorption correction was applied using Crystal Clear (Rigaku). The Structure was solved by direct methods with the SHELXS-97 program [22]. Refinements were done by the full-matrix least-squares on F^2 with SHELXL-97 [23]. All of the non-H atoms were refined anisotropically by full-matrix least-squares to give the final $R = 0.0367$ and $wR = 0.0932$ ($w = 1/[\sigma^2\ ((F_o^2) + (0.0614P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$ with $(\Delta/\sigma)\text{max} = 0.998$ and $S = 1.035$ by using the SHELXL program. The hydrogen atoms were located from a difference Fourier map and refined isotropically. The corrections for absorption is multi-scan, Tmin = 0.9516, Tmax = 0.9594, various relevant details of the crystallographic experiment are given in Table 1.

Biological Screening

Fungicide Screening

Preliminary screening was conducted by fungi growth inhibition method according to the reference using potato dextrose agar (PDA) as cultivation medium [13]. A stock solution of each compound was prepared at 500 μg/mL using sterilized water containing 2 drops of N,N-dimethylformamide (DMF) as a solvent, then 1 mL of the stock solution was transferred into a 10 cm diameter of Petri dish, 9 mL of PDA was then added to prepare the plate containing 50 μg/mL of the test compound. Before the plate solidification, the PDA was thoroughly mixed by turning around the petri dish in the sterilized operation desk 5 times to scatter the compound in PDA evenly. Then, 4 mm of diameter of fungi cake was inoculated on the plate and cultured in the culture tank at 24–26 °C. The diameter of fungi spread was measured 2 days later. Growth inhibition was then calculated using the corresponding control. Fungi used in this study included *Alternaria solan*i (AS), *Botrytis cinerea* (BC), *Cercospora arachidicola* (CA), *Gibberella zeae* (GZ), *Phytophthora infestans* (Mont) de Bary (PI), *Physalospora piricola* (PP), *Pellicularia sasakii* (PS), *Sclerotinia sclerotiorum* (SS), and *Rhizoctonia cerealis* (RC).

Insecticide Activity of the Target Compound Against Plutella xylostella L (PXL)

The larvicidal activity of the target compound and the positive control tebufenozide (RH-5992) against PXL were tested by leaf film feeding method according to the reported procedure [20]. Fresh cabbage leaves were dipped into the 200 μg/mL test water solution for 10 s which was prepared with a 5% of acetone to help the compound to dissolve. After air-drying for evaporating off the acetone and water, the treated leaves were cut into small pieces and placed in the Petri dishes with 9 cm diameter. Ten indviduals of 2nd instar larvae of PXL were transferred into the 10 cm diameter of Petri dish. The Petri dishes were finally fastened with rubbers and placed in the standard culturation room for 96 h or 120 h at 25 °C with 80% of humidity. The percentage of mortalities was evaluated according to the corresponding CK which uses water to dispose only. The insects which had no reaction when touched by brush pen were regarded as death insect. Each treatment was repeated for three times.

Insecticide Activity of the Target Compound Against Larval Culex Pipiens Pallens (CPP)

The larvicidal activity of the target compound against CPP was evaluated according to the reported procedure [20]. The target compound of 2 mg was weighed into a 10 mL vial; 10 mL of acetone was added to dissolve the compound to prepare 200 μg/mL of mother solution. The working solution of 2 μg/mL was prepared by diluting 1 mL of mother solution with 89 mL of water and 10 mL of feeding solution into a 100 mL beaker. Ten CPP of 4th instar larvae were transfer into the beaker. Thereafter, the beakers with mosquito larvae were put into the standard conditioned rooms for further cultivation with temperature of 25 °C and humidity of 80%. After 24 h or 96 h of cultivation, the mortalities of the larval were calculated by the corresponding CK, which was prepared by 1 mL of acetone for substituting 1 mL of mother solution, the observation was conducted until all the larvae metamorphosized into pupation or died. Tebufenozide was chosen as a positive control.

Table 1 Crystal data and structure refinement for the title compound

Molecular formula	$C_{16}H_{20}N_4O_3S$
Formula weight	348.42
Temperature (K)	113 (2)
Crystal system, space group	Monoclinic, *P 21/c*
μ (MoKa)	0.71075 mm^{-1}
Unit cell dimensions	$a = 17.986(2)$ Å; $b = 8.0180(10)$ Å; c = 12.0190(14) Å; $\alpha = 90^\circ$; $\beta = 91.160(5)^\circ$; $\gamma = 90^\circ$
Volume (Å^3)	1732.9 (4)
Z, calculated density (g cm^{-3})	4, 1.335
Absorption coefficient (mm^{-1})	0.209
F (000)	736
Crystal size (mm)	0.24 × 0.22 × 0.20
Theta range/°	1.13–27.89
Index ranges	$-23 \le h \le 23$; $-10 \le k \le 10$; $-15 \le l \le 15$
Reflections collected	19940
Independent reflections	4135 [R (int) = 0.0404]
Completeness to θ max	99.8%
Max and min transmission	0.9594 and 0.9516
Observed data/restraints/parameters	4135/0/226
Goodness of fit on F^2	1.035
Final *R* indices [$I > 2$sigma (I)]	$R_1 = 0.0367$, $wR_2 = 0.0932$
R indices (all data)	$R_1 = 0.0445$, $wR_2 = 0.1008$
Largest difference peak and hole (e/Å^3)	0.314 and −0.306

Results and Discussion

Synthesis of the Title Compound

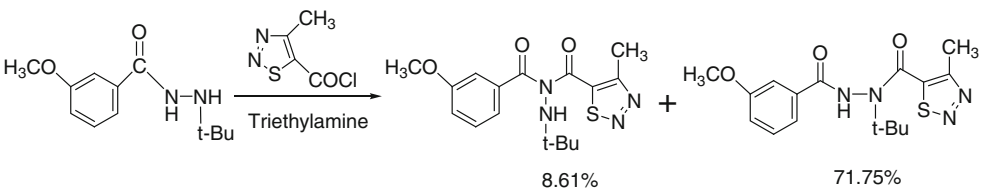
The title compound was synthesized according to Scheme 1. Intermediate 4-methyl-1,2,3-thiadiazole-5-carbonyl chloride was synthesized according to Ref. [18], $N(Et)_3$ as acid acceptor, 4-methyl-1,2,3-thiadiazole-5-carboxylic acid was found to be the main by-product when the reaction mixture contained excessive of 4-methyl-1,2,3-thiadiazole-5-carbonyl chloride, 10.49% of 4-methyl-1,2,3-thiadiazole-5-carboxylic acid was recovered. Another by-product $N(Et)_3$·HCl was easily to be removed by washing with water. The results of the column chromatography showed that, the title compound was produced as minor compound, another main product was obtained as shown in Scheme 2, the total yields of these two compounds added up to 80.36%, the structures of the title compound was confirmed by ^{1}H NMR, IR and HRMS determination [20].

Analysis of the Crystallographic Structure

The molecular structure and perspective view of the crystal packing in a unit cell of the title compound are shown in Figs. 1 and 2, respectively. The selected bond lengths, angles and torsion angles are listed in Table 2.

As shown in Table 2. Bond lengths and bond angles within the thiadiazole ring agree well with the values reported [24]. The sum of O(1–C(4)–N(3), O(1)–C(4)–C(1) and N(3)–C(4)–C(1) angles are 360°, indicating the sp^2 hybridizationstate of C(4) atom; The sum of O(2)–C(9)–N(3), O(2)–C(9)–C(10) and N(3)–C(9)–C(10) angles are 360°, indicating the sp^2 hybridization state of C(9) atom. Due to the conjugation of thiadiazole ring and C(4) = O(1) bond, the bond lengths of C(1) = C(2) (1.3821(18) Å) and N(1) = N(2) (1.3079(16) Å) are slightly longer than that of typical C = C bond (1.34 Å) [25] and N = N bond (1.24 Å) [26], respectively, and the bond lengths of C(1)–C(4) (1.4958(17) Å) and C(2)–N(2) (1.3720(18) Å) are slightly shorter than typical C–C bond(1.54 Å) [27] and

Scheme 2 Another product of the reaction



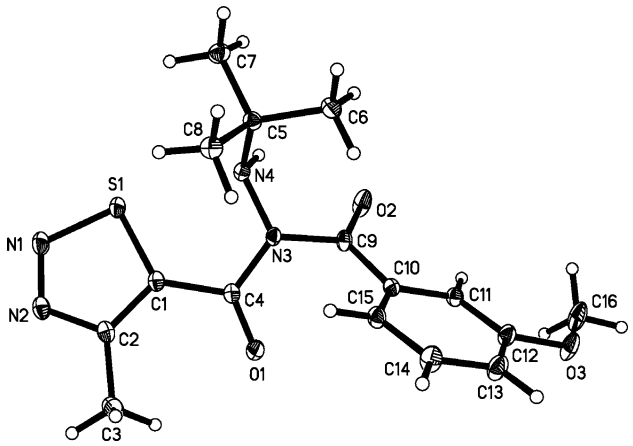


Fig. 1 Molecular structure of the title compound

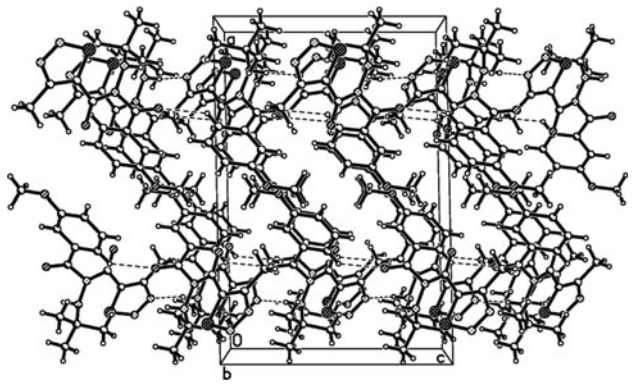


Fig. 2 Crystal packing of the title compound

C–N bond (1.47 Å) [28]. Because of the P-π conjugate effect, the N(3)–C(9) bond (1.4529(15) Å) and N(3)–C(4) bond (1.3903(16) Å) is shorter than the typical C–N single bond (1.47 Å). The torsion angles of C(2)–C(1)–C(4)–O(1) and S(1)–C(1)–C(4)–N(3) are 16.4 (2)° and 22.38 (17)°, respectively, indicating that the acyl amide group and the thiadiazole ring are non-planar. The torsion angles of C(16)–O(3)–C(12)–C(11) is −0.2(2)°, indicating that the methoxyl group and the benzene ring are coplanar. The dihedral angle formed by the thiadiazole ring and benzene ring is 52.85°. There are two intermolecular hydrogen bonds in the structure, C (15)–H (15)···O (2) and N (4)−H (1)···N (2) as detailed in Table 3.

Biological Activity of the Title Compound

The results of insecticidal activity of the title compound against the PXL is 25% at 400 μg/mL and 10% against CPP at 2 μg/mL, the corresponding positive control RH-5992 has 40% of insecticidal activity against the PXL at 200 μg/mL and 100% activity against CPP at 2 μg/mL respectively. This demonstrates that the compound has a certain extent insecticidal activity, its insecticidal activity is lower than that of N or N′ carbonyl substituted 1,2,3-thiadiazole containing diacylhydrazines. Fungicide activity against the typical fungi commonly occurring in the Chinese agro-ecosystem was detected at 50 μg/mL in vitro. The results of the target compound has inhibition of 37%, 44%, 90% against BC, RC, SS respectively, this indicated that the target compound has a good growth inhibition to BC, and comparatively good growth inhibition to SS (Table 4), while the control compound RH5992 only had 30%, 46%, 54% of inhibition against PI, RC, SS respectively.

All the results indicated that, 1,2,3-thiadiazole was a very good active substructure for novel pesticide development. Changing phenyl group into 1,2,3-thiadiazole kept the insecticidal activity of diacylhydrazine insecticides.

Table 2 Selected bond lengths, angles and torsion angles of the title compound

Bond lengths (Å)					
S(1)–N(1)	1.6611 (12)	N(3)–N(4)	1.4202 (15)	C(1)–C(4)	1.4958 (17)
S(1)–C(1)	1.7075 (13)	N(2)–C(2)	1.3720 (18)	O(1)–C(4)	1.2142 (15)
N(3)–C(4)	1.3903 (16)	O(2)–C(9)	1.2079 (15)	N(3)–C(9)	1.4529 (15)
O(3)–C(12)	1.3719 (15)	N(4)–C(5)	1.4929 (17)	O(3)–C(16)	1.4321 (17)
N(1)–N(2)	1.3079 (16)	C(1)–C(2)	1.3821 (18)	C(12)–C(13)	1.3946 (19)
Bond angles (°)					
N(1)–S(1)–C(1)	93.19 (6)	N(1)–N(2)–C(2)	113.93 (11)	C(4)–N(3)–N(4)	117.01 (10)
C(4)–N(3)–C(9)	119.99 (11)	N(4)–N(3)–C(9)	116.82 (10)	N(3)–N(4)–C(5)	114.24 (10)
O(1)–C(4)–N(3)	121.83 (11)	O(1)–C(4)–C(1)	121.33 (11)	N(3)–C(4)–C(1)	116.82 (11)
O(2)–C(9)–N(3)	117.65 (11)	O(2)–C(9)–C(10)	123.25 (12)	N(3)–C(9)–C(10)	118.84 (10)
Torsion angles (°)					
C(4)–N(3)–N(4)–C(5)	124.41 (11)	C(9)–N(3)–N(4)–C(5)	−83.15 (13)	N(4)–N(3)–C(4)–O(1)	168.56 (11)
C(9)–N(3)–C(4)–O(1)	17.03 (18)	N(4)–N(3)–C(4)–C(1)	−9.96 (16)	C(2)–C(1)–C(4)–O(1)	16.4 (2)
S(1)–C(1)–C(4)–N(3)	22.38 (17)	C(16)–O(3)–C(12)–C(11)	−0.2 (2)	N(4)–N(3)–C(9)–O(2)	−29.56 (17)

Table 3 Intermolecular hydrogen bonds of the title compound

D–H···A	dD–H/Å	dH···A/Å	dD···A/Å	∠DHA/(°)
C(15)–H(15)···O(2)^{i}	0.950	2.440	3.1422 (16)	131.0
N(4)−H(1)···N(2)^{ii}	0.878 (14)	2.235 (15)	3.0407 (16)	152.5 (14)

Symmetry codes: (i) x, 3/2 − y, 1/2 + z; (ii) x, 1/2 − y, −1/2 + z

Table 4 Insecticidal and fungicidal activity of the title compound (%)

Compd.	AS	BC	CA	GZ	PI	PP	PS	RC	SS	PXL	CPP
Titile compound	14 ± 3	37 ± 2	18 ± 2	16 ± 4	43 ± 4	5 ± 3	18 ± 2	44 ± 2	90 ± 4	25 ± 6[a]	10 ± 4
RH-5992	8 ± 2	29 ± 5	15 ± 0	9 ± 1	30 ± 4	24 ± 5	10 ± 3	46 ± 1	54 ± 3	40 ± 5	100 ± 0

AS *Alternaria solani*, PI *Phytophthora infestans*, BC *Botrytis cinerea*, CA *Cercospora arachidicola*, GZ *Gibberella zea,* PP *Physalospora piricola*, PS *Pellicularia sasakii*, RC *Rhizoctonia cerealis*, SS *Sclerotinia sclerotiorum*, PXL *Plutella xylostella* L., 96 h, 200 μg/mL, *CPP Culex pipiens pallens* 2 μg/mL

[a] Results of 400 μg/mL

Supplementary Information

Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 819047. Copy of the data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).

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