Electronic Supplementary Information (ESI) for

Synthesis, insecticidal ictivity, and structure-sctivity relationship (SAR) of anthranilic diamides analogous containing oxadiazole ring

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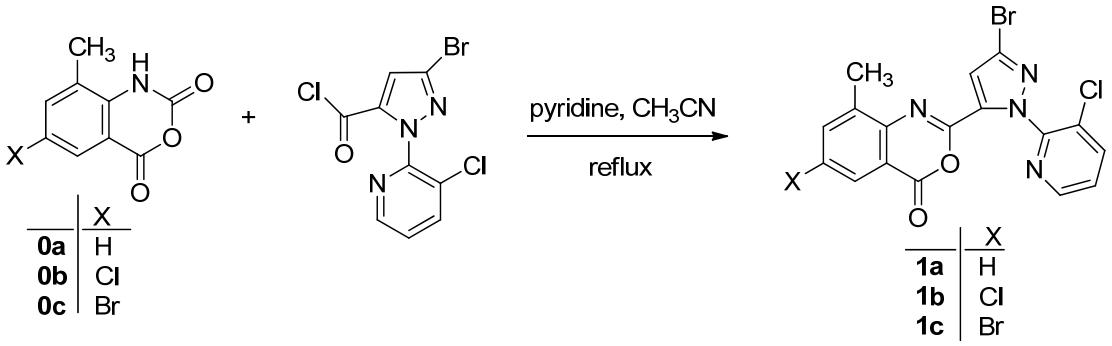
1. **Scheme S1.** General synthetic route for intermediates **1a-1c**



	X
0a	H
0b	Cl
0c	Br

	X
1a	H
1b	Cl
1c	Br

2. General synthetic method for intermediates **1a-1c**:

0a, **0b** or **0c** (0.10 mol) was added slowly to a mixture of 3-bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carbonyl chloride (0.12 mol), pyridine (40 mL) and acetonitrile (40 mL) at 70 ^{o}C about 0.5 h, then allowed to react 4 h. The mixture was cooled to room temperature and flitered to afford off-white solid, washed with a small quantity of acetonitrile and dried at room temperature to get product without further purification.

*2.1 2-(3-Bromo-1-(3-chloro-2-pyridinyl)-1H-pyrazol-5-yl)-8-methyl-4H-1,3-benzoxazin-4-one (**1a**)*

Yield 85.7%; mp 230-233 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (d, J = 4.6 Hz, 1H, Py-H), 8.00 (dd, J_1 = 16.9 Hz, J_2 = 7.8 Hz, 2H, Ar-H, Py-H), 7.55 (s, 1H, Ar-H), 7.52 (s, 1H, Ar-H), 7.51-7.46 (m, 1H, Py-H), 7.39 (s, 1H, CHCBr), 1.82 (s, 3H, ph-CH_3). MS *m/z* calcd for $C_{17}H_{10}BrClN_4O_2$ $(M+H)^+$ 418.64, Found 418.6.

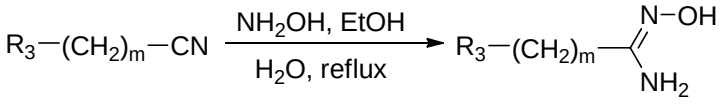
*2.2 2-(3-Bromo-1-(3-chloro-2-pyridinyl)-1H-pyrazol-5-yl)-6-chloro-8-methyl-4H-1,3-benzoxazin-4-one (**1b**)*

Yield 70.3%; mp 238-240 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.58 (dd, J = 4.7, 1.5 Hz, 1H, Py-H), 8.30 (dd, J = 8.1, 1.5 Hz, 1H, Py-H), 7.84 (d, J = 2.5 Hz, 1H, Ar-H), 7.72 (dd, J = 2.7, 1.9 Hz, 1H, Ar-H), 7.70 (d, J = 4.7 Hz, 1H, Py-H), 7.47 (s, 1H, CHCBr), 1.67 (s, 3H, Ph-CH_3). MS *m/z* calcd for $C_{17}H_9BrCl_2N_4O_2$ $(M+H)^+$ 453.09, Found 452.9.

*2.3 2-(3-Bromo-1-(3-chloro-2-pyridinyl)-1H-pyrazol-5-yl)-6-bromo-8-methyl-4H-1,3 -benzoxazin-4-one (**1c**)*

Yield 85.6%; mp 215-219 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.62 (d, J = 4.7 Hz, 1H, Py-H), 8.34 (dd, J = 8.1 Hz, 1H, Py-H), 8.00 (d, J = 2.2 Hz, 1H, Ar-H), 7.88 (d, J = 1.53 Hz, 1H, Ar-H), 7.76 (q, J = 8.1 Hz, 1H, Py-H), 7.51 (s, 1H, CHCBr), 1.71 (s, 3H, Ph-CH_3). MS *m/z* calcd for $C_{17}H_9Br_2ClN_4O_2$ $(M+H)^+$ 494,9, $(M+H+2)^+$ 496.9. Found $(M+H)^+$ 495.0, $(M+H+2)^+$ 497.0.

3. **Scheme S2.** General synthetic route of different amidoximes **M1**-**M7.**



	m	R_3
M1	1	H
M2	1	Ph
M3	0	2-CH_3Ph
M4	0	4-BrPh
M5	0	2,6-$(F)_2$Ph
M6	1	4-NO_2Ph
M7	0	3-Py

4. General synthetic method for different amidoximes **M1**-**M7**

A 50% aqueous solution of hydroxylamine (1 to 2.5 equiv.) was added to a solution of the nitrile (1 equiv.) in ethanol. The reaction was refluxed for 1 to 24 h. After this period, the reaction was cooled to r.t., resulting in some cases in the formation of a solid which was collected by filtration, washed with water, dried, and used without further purification. In other cases, most of the ethanol was removed by distillation in vacuo, and the aqueous residue was extracted with dichloromethane for three times. The combined organic layer was dried over anhydrous magnesium sulfate and evaporated to afford the desired product. This procedure was applied for the synthesis of the following amidoximes.

*4.1 N-Hydroxyacetimidamide (**M1**)*

Yield 78%; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.64 (s, 1H, OH), 5.32 (s, 2H, NH_2), 1.63 (s, 3H, CH_3). MS *m/z* calcd for $C_6H_7N_3O$ $(M+H)^+$ 137.1. Found 137.1.

*4.2 N-Hydroxy-2-phenylacetimidamide (**M2**)*

Yield 85%; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.85(s, 1H, OH), 7.26-7.28 (m, 4H, Ar-H), 7.18-7.21 (m, 1H, Ar-H), 5.34 (s, 2H, NH_2), 3.26 (s, 2H, CH_2). MS *m/z* calcd for $C_8H_{10}N_2O$ $(M+H)^+$ 151.2. Found 151.1.

*4.3 N-Hydroxy-2-methylbenzimidamide (**M3**)*

Yield 83%; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.27 (s, 1H, OH), 7.25-7.27 (m, 4H, Ar-H), 7.16-7.21 (m, 1H, Ar-H), 5.68 (s, 2H, NH_2), 2.34 (s, 3H, CH_3). MS *m/z* calcd for $C_8H_{10}N_2O$ $(M+H)^+$ 150.2. Found 150.1.

*4.4 N-hydroxy-4-bromobenzimidamide (**M4**)*

Yield 87%; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.70 (s, 1H, OH), 7.61 (d, J = 8.7 Hz, 2H, Ar-H), 7.55 (d, J = 8.8 Hz, 2H, Ar-H), 5.83 (s, 2H, NH_2). MS *m/z* calcd for $C_7H_7BrN_2O$ $(M+H)^+$ 215.0, $(M+H+2)^+$ 217. Found $(M+H)^+$ 215.0, $(M+H+2)^+$ 217.

*4.5 N-Hydroxy-2,6-difluorobenzimidamide (**M5**)*

Yield 81%; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.56 (s, 1H, OH), 7.48 (m, 1H, Ar-H), 7.13 (m, 2H, Ar-H), 5.96 (s, 2H, NH_2). MS *m/z* calcd for $C_7H_6F_2N_2O$ $(M+H)^+$ 171.1. Found 171.1.

*4.6 N-Hydroxy-2-(4-nitrophenyl)acetimidamide (**M6**).*

Yield 80%; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.98 (s, 1H, OH), 8.15-8.18 (m, 2H, Ar-H), 7.53-7.56 (m, 2H, Ar-H), 5.51 (s, 2H, NH_2), 3.43 (s, 2H, CH_2). MS *m/z* calcd for $C_8H_9N_3O_3$ $(M+H)^+$ 196.2. Found 196.0.

*4.7 N-Hydroxynicotinimidamide (**M7**)*

Yield 85%; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.89 (s, 1H, OH), 8.89-8.91 (m, 1H, Ar-H), 8.57-8.59 (m, 1H, Ar-H), 8.03-8.07 (m, 1H, Ar-H), 7.40-7.44 (m, 1H, Ar-H), 6.01 (s, 2H, NH_2). MS *m/z* calcd for $C_6H_7N_3O$ $(M+H)^+$ 138.1. Found 138.1.

Reference:

(1) A. Hamze, J. F. Hernandez, P. Fulcrand, J. Martinez, *J. Org. Chem.*, 2003, **68**, 7316-7321.

5. **Table S1**. Crystal and structure refinement data of compound **18**.

Compound	**18**
Chemical formula	$C_{24}H_{14}Br_2Cl_2N_6O_2$
Formula weight	649.13
Crystal system	triclinic
Space group	*P-1*
a (Å)	9.229 (18)
b (Å)	11.142 (2)
c (Å)	12.526 (3)
α (°)	76.53 (3)
β (°)	80.97 (3)
γ (°)	86.17 (3)
V (Å^3), Z	1236.5 (4) / 2
D_{calc} (g cm^{-3})	1.744
μ (mm^{-1})	3.530
F (0 0 0)	640
θ range (°)	1.69-25.38
Index range	$0 \le h \le 11$
	$-13 \le k \le 13$
	$-14 \le l \le 15$
Reflns collected	4844
Unique reflns (R_{int})	4538 (0.054)
Refinement mothod on F^2	Full-matrix least-squares
GOF on F^2	1.001
R_1 [$I > 2\sigma(I)$]	0.0657
wR_2 [$I > 2\sigma(I)$]	0.1490
R_1 (all data)	0.1293
wR_2 (all data)	0.1713
Residual (e Å^{-3})	1.118 and -0.875

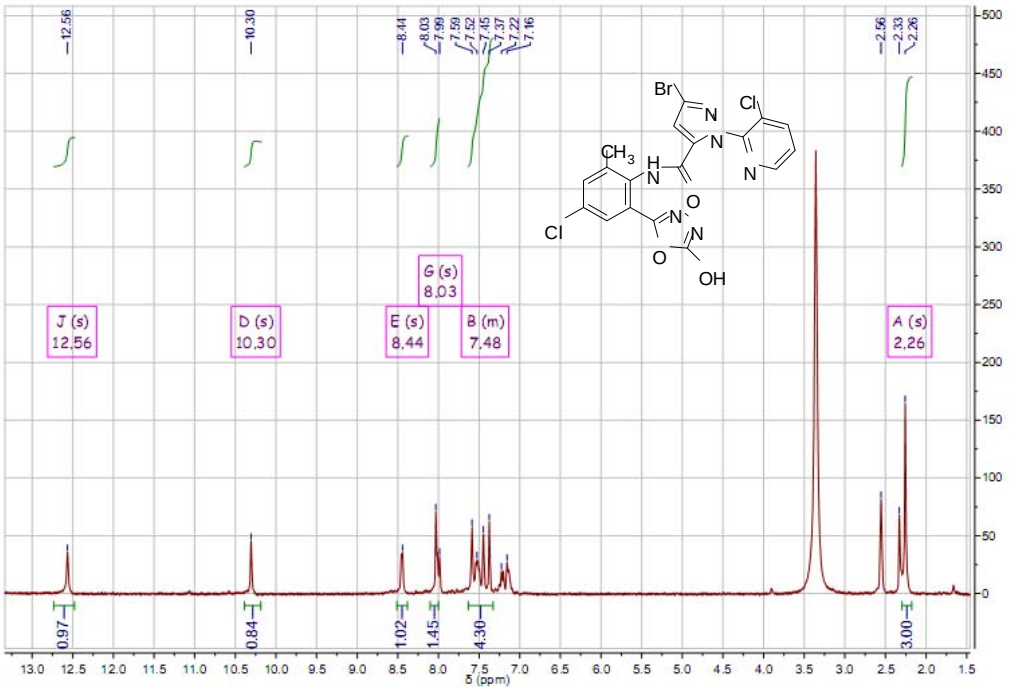


Figure S1 ^{1}H NMR of compound **3**

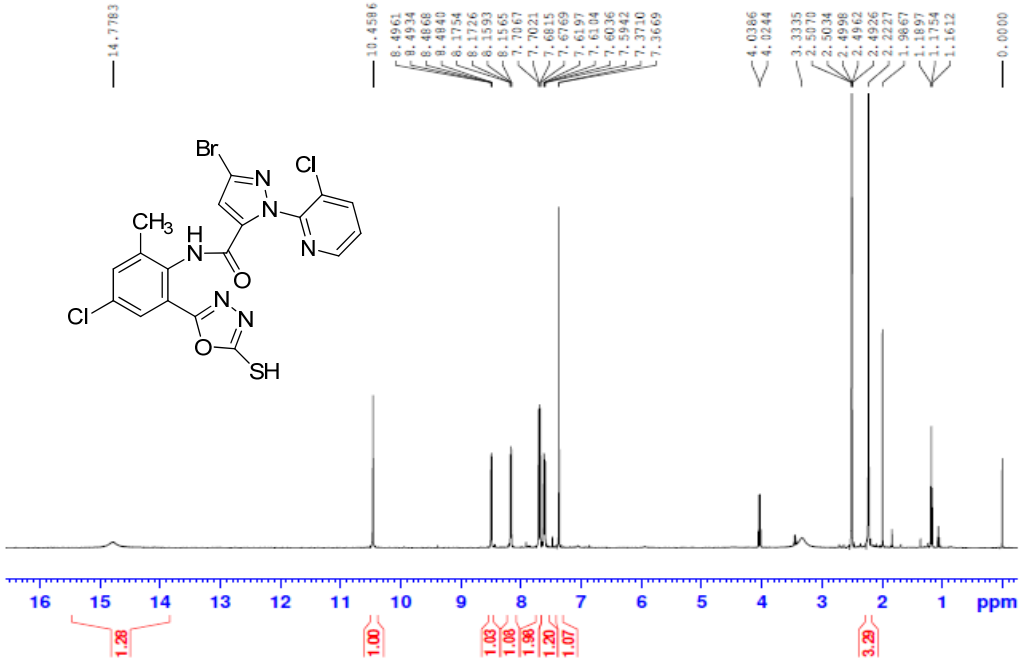


Figure S2 ^{1}H NMR of compound **4**

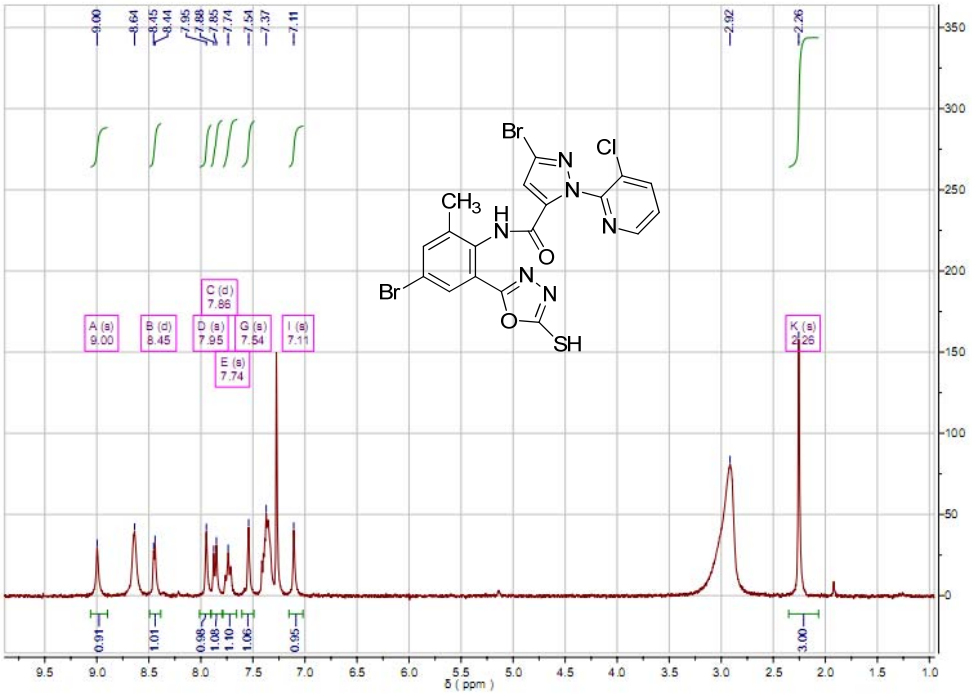


Figure S3 ^{1}H NMR of compound **5**

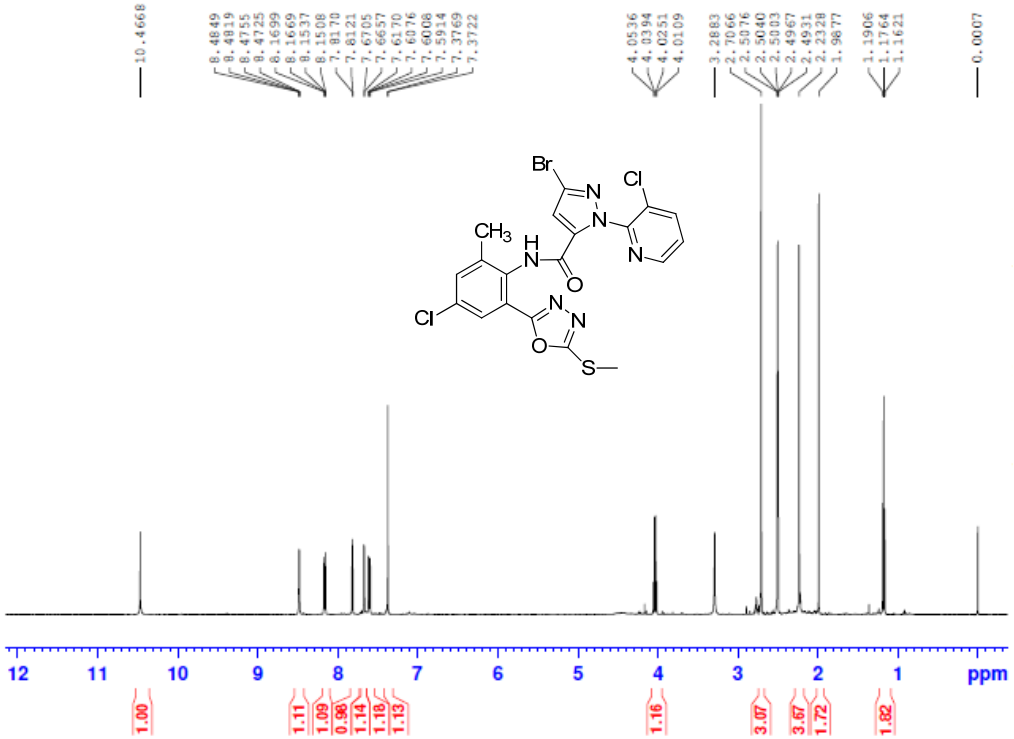


Figure S4 ^{1}H NMR of compound **6**

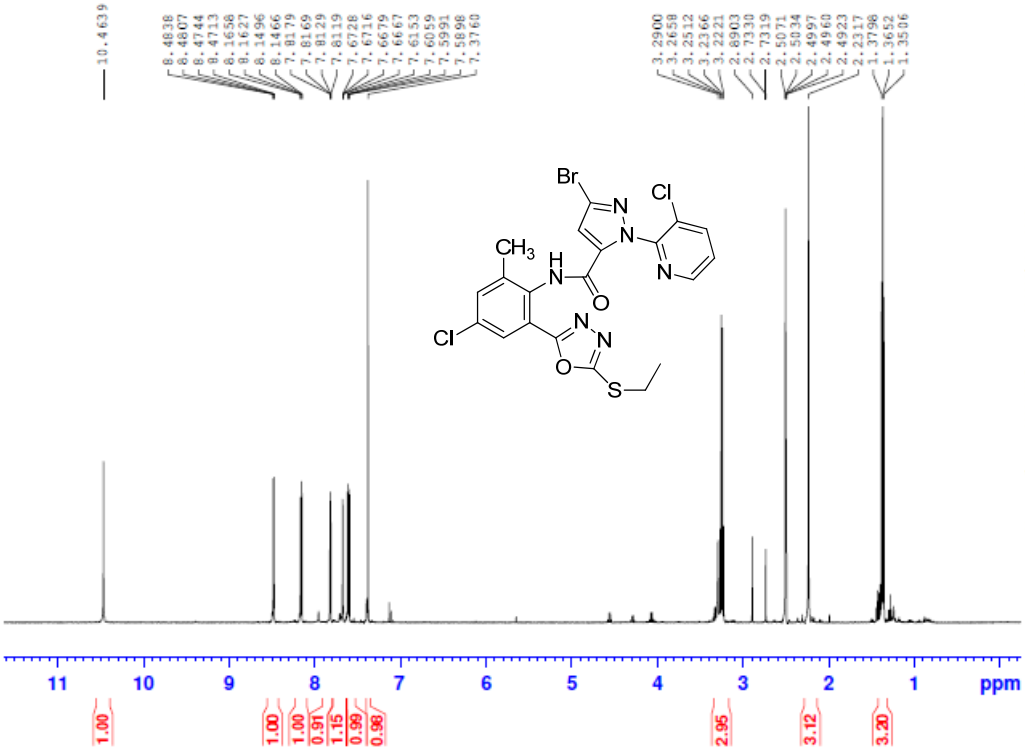


Figure S5 ^{1}H NMR of compound **7**

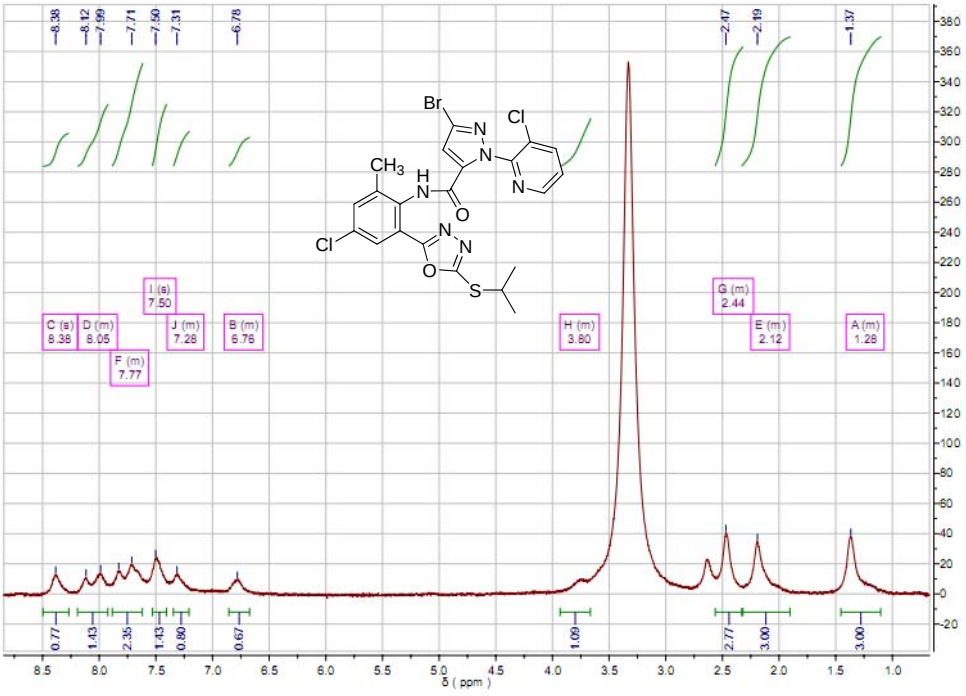


Figure S6 ^{1}H NMR of compound **8**

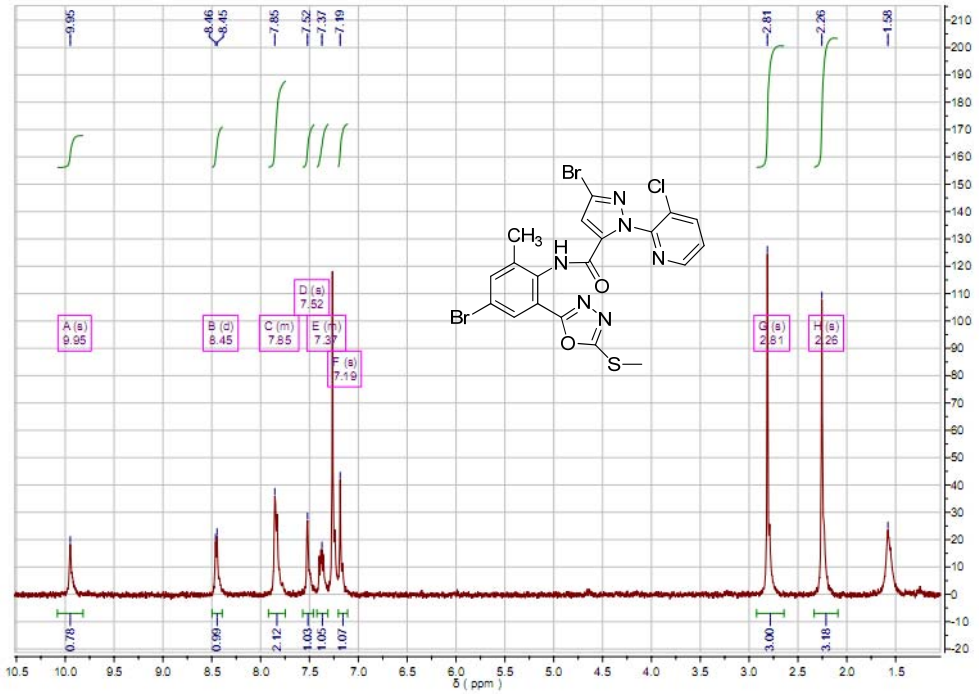


Figure S7 ^{1}H NMR of compound **9**

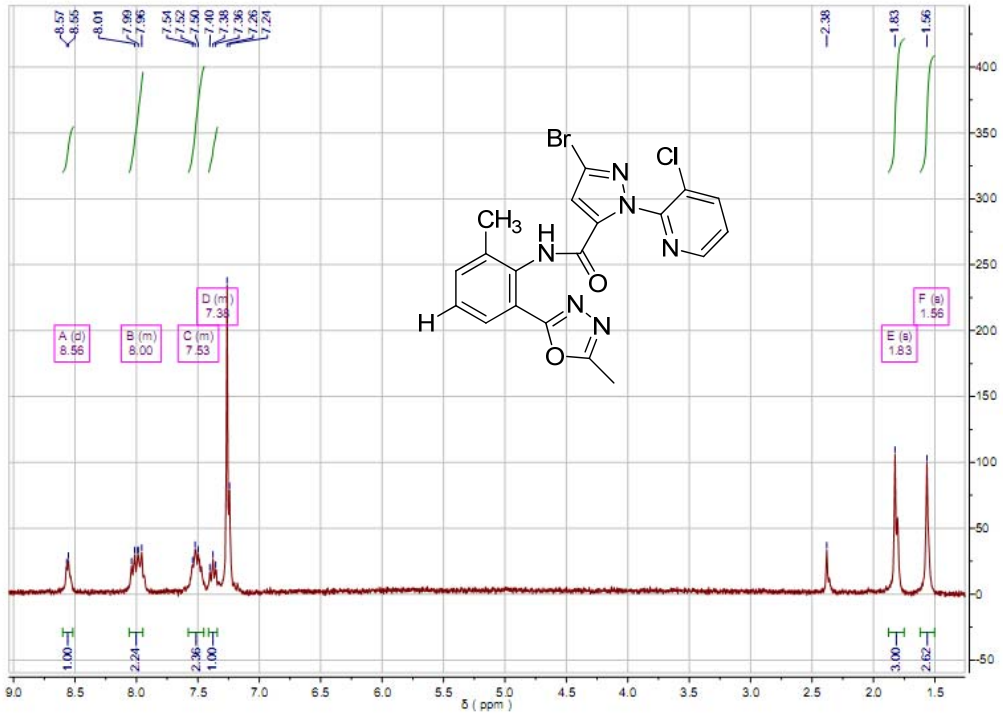


Figure S8 ^{1}H NMR of compound **10**

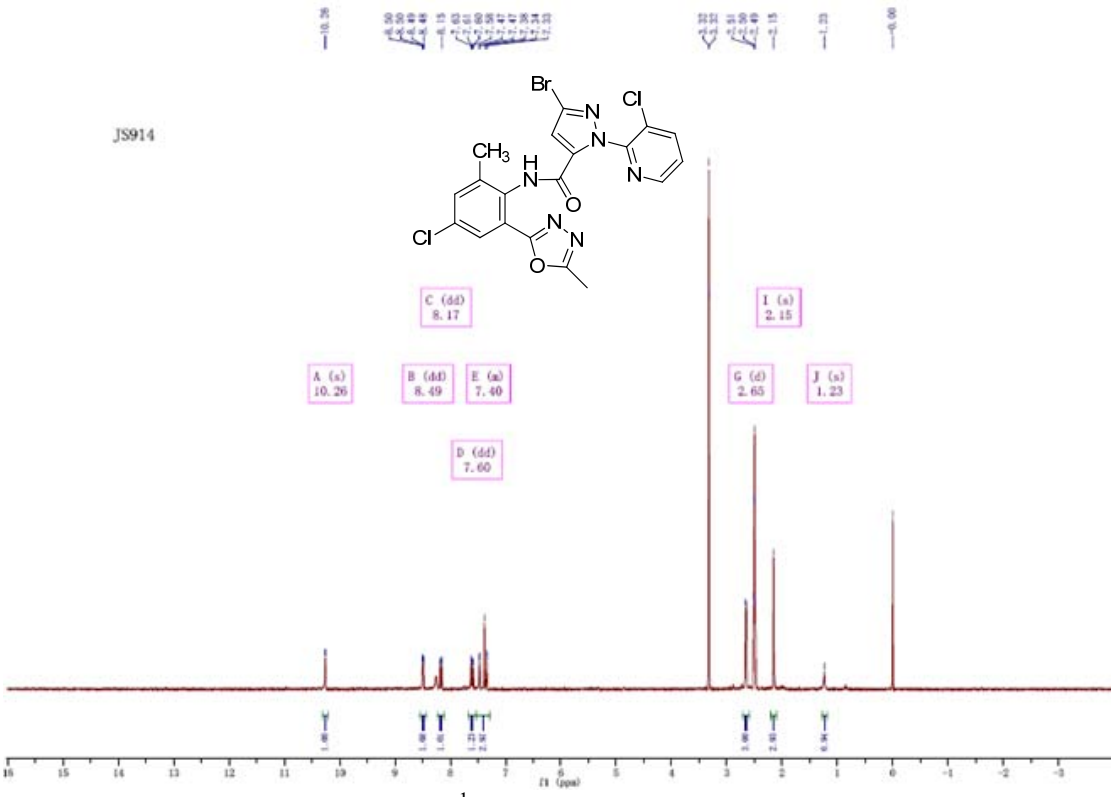


Figure S9 ^{1}H NMR of compound **11**

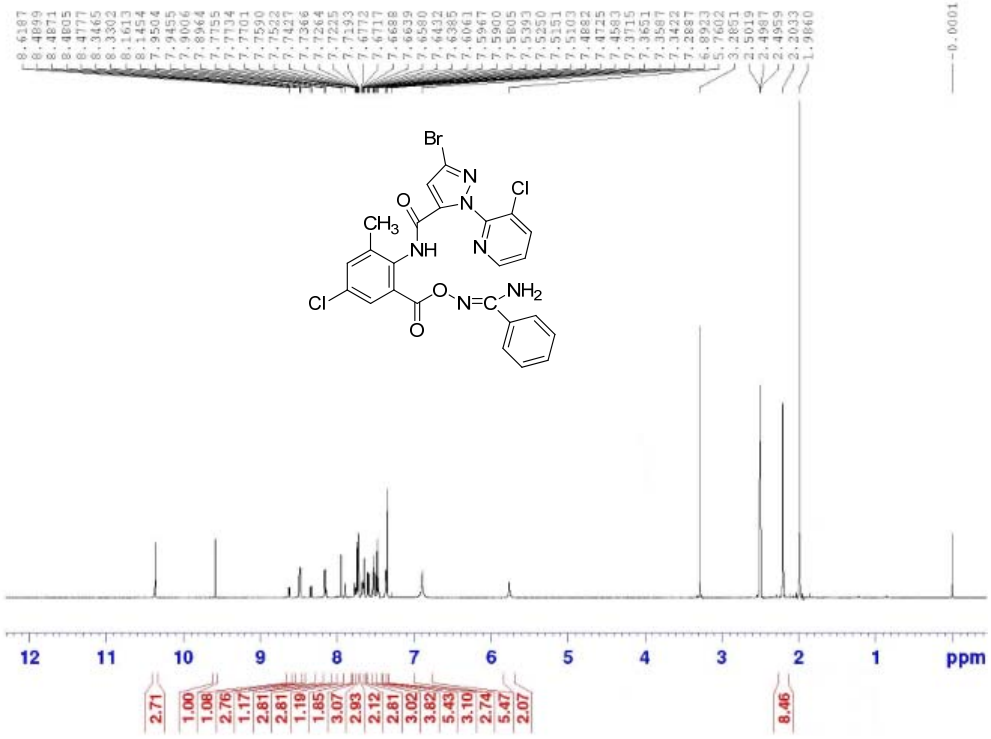


Figure S10 ^{1}H NMR of compound **12**

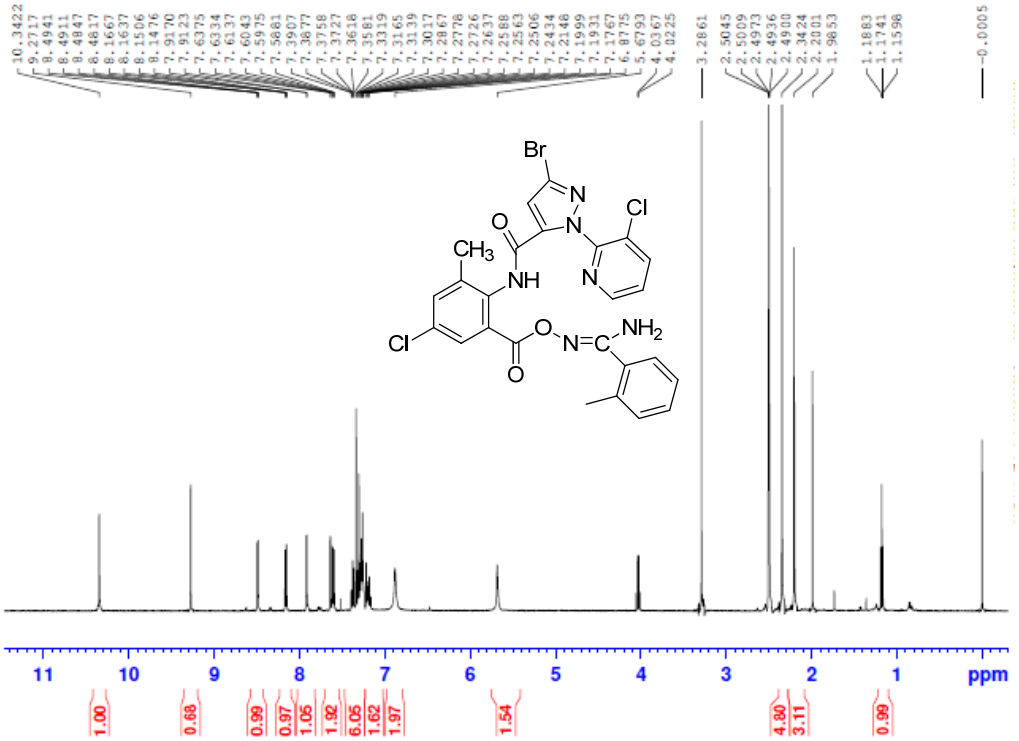


Figure S11 ^{1}H NMR of compound **13**

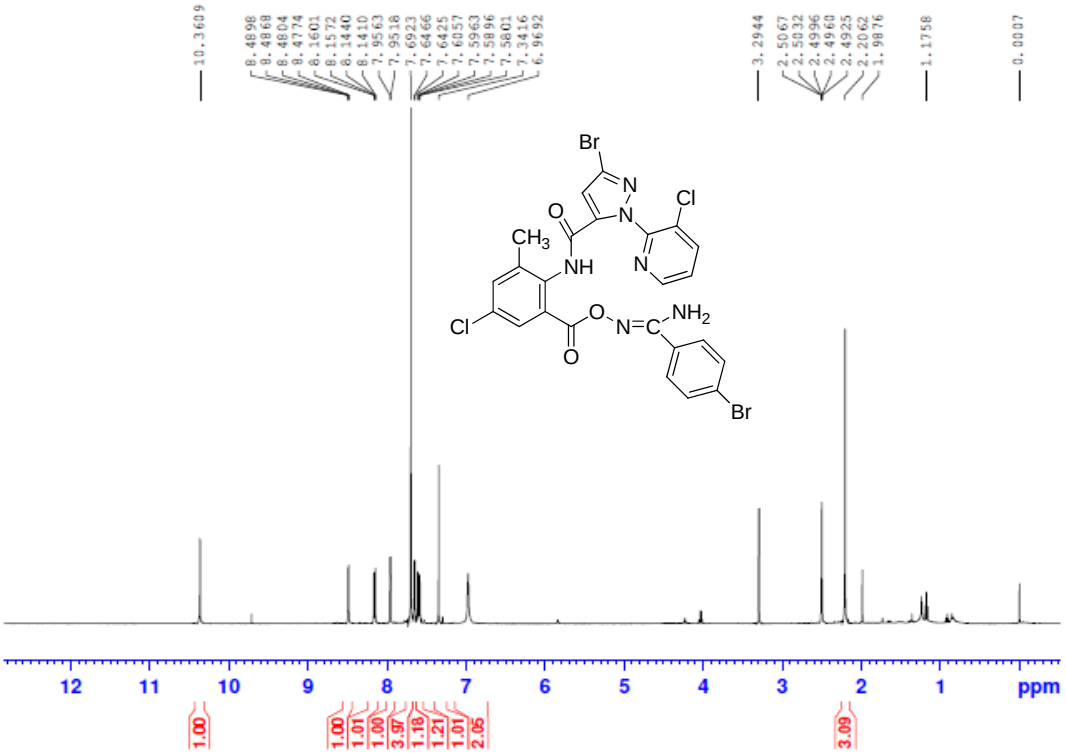
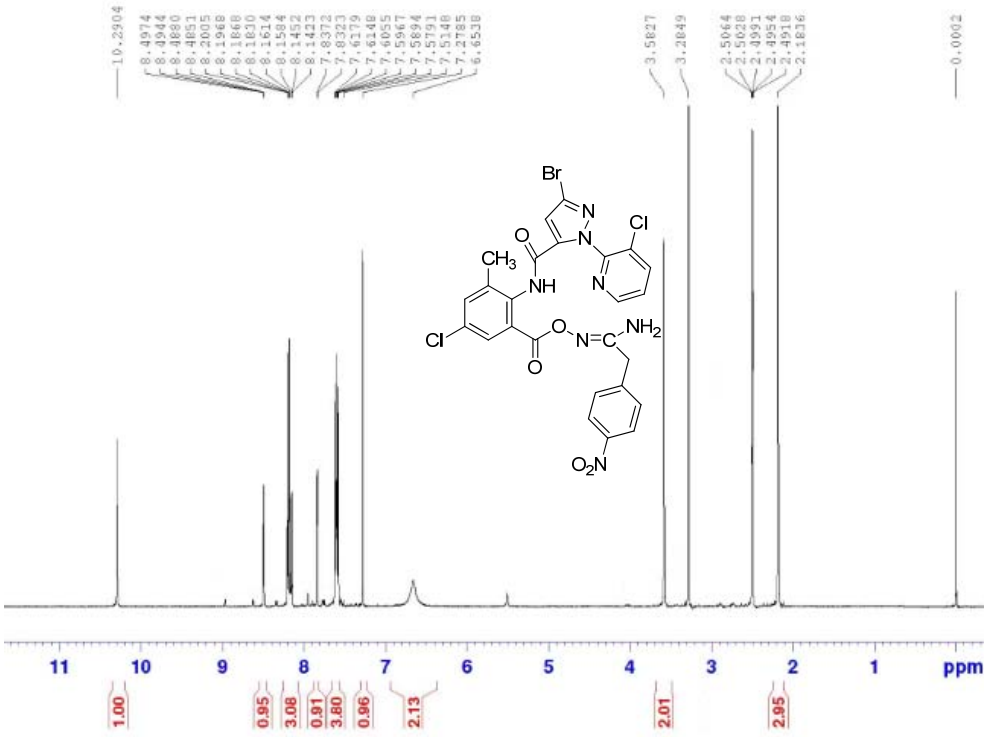


Figure S12 ^{1}H NMR of compound **14**



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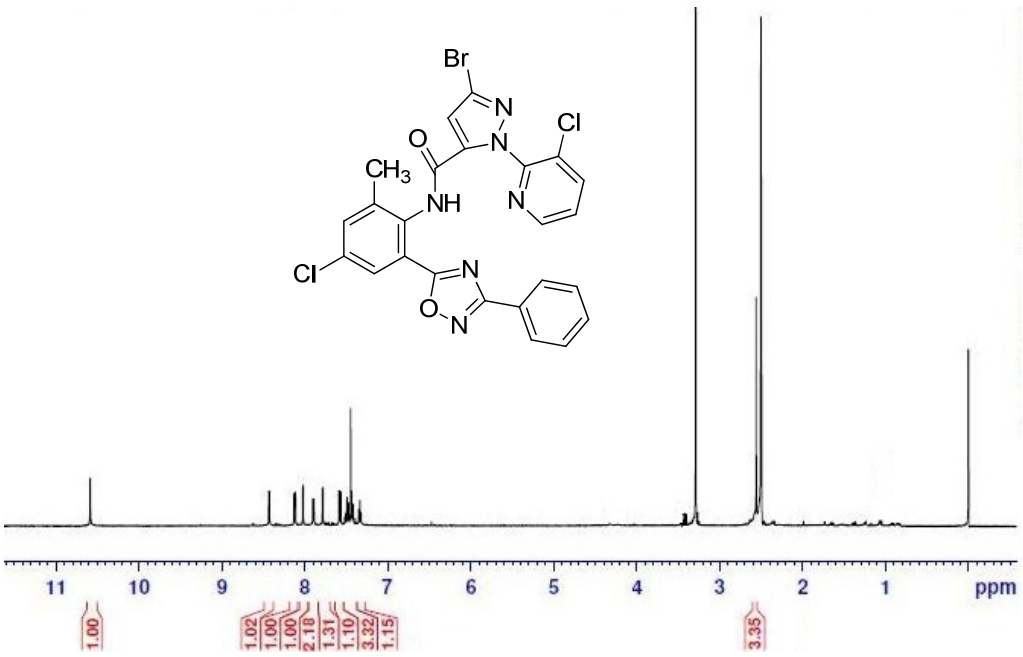


Figure S14 ^{1}H NMR of compound **16**

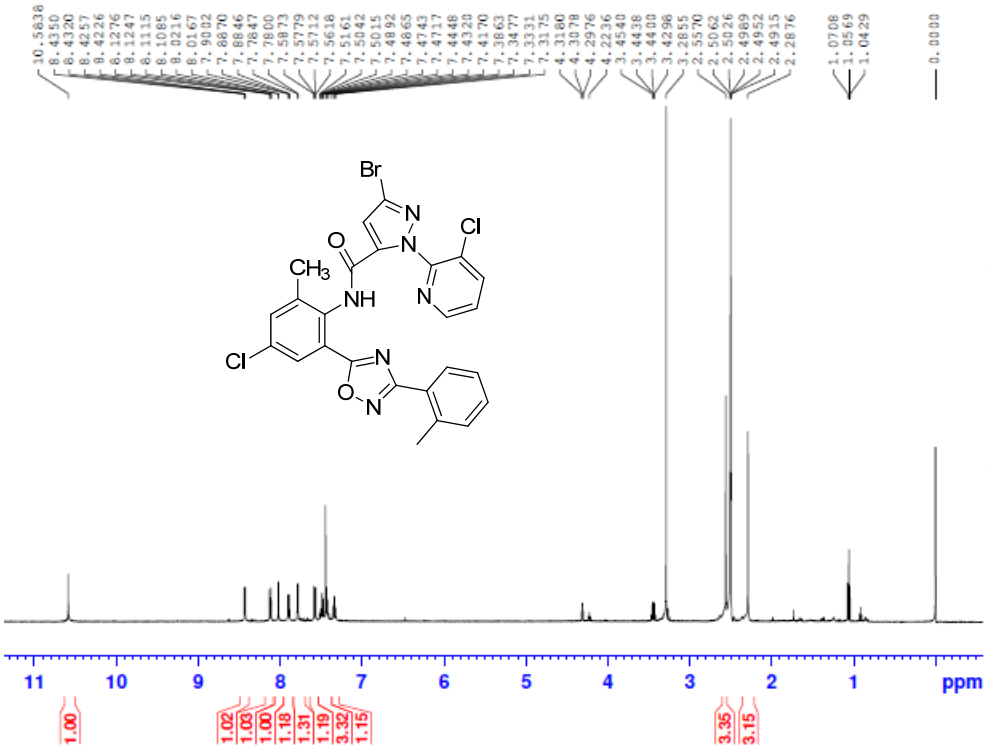


Figure S15 ^{1}H NMR of compound **17**

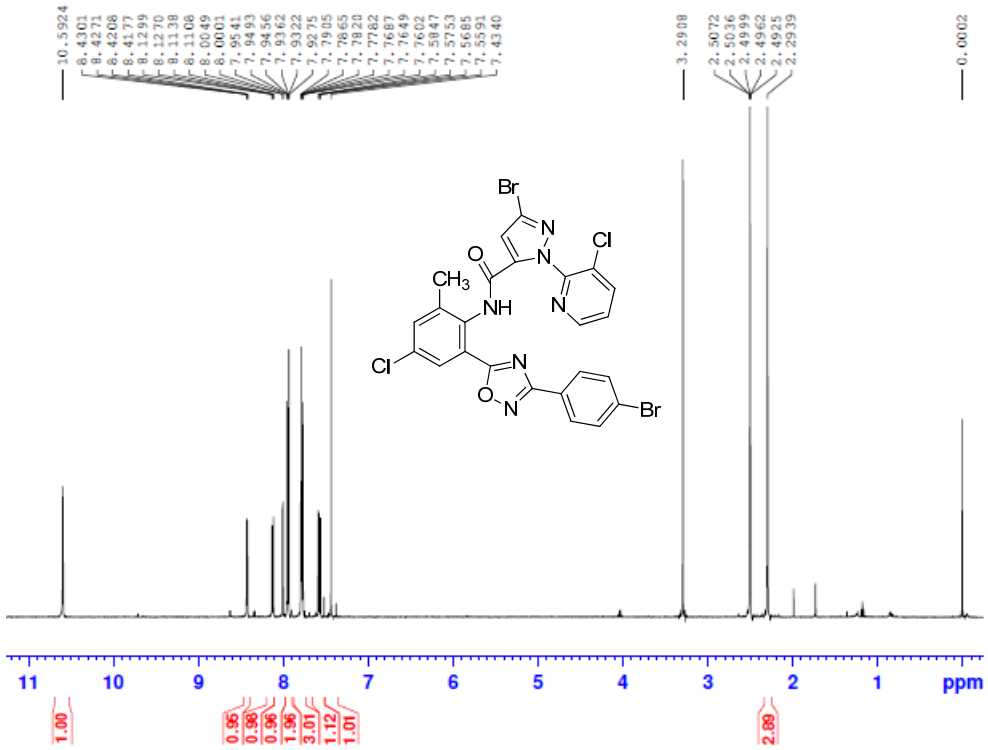


Figure S16 ^{1}H NMR of compound **18**

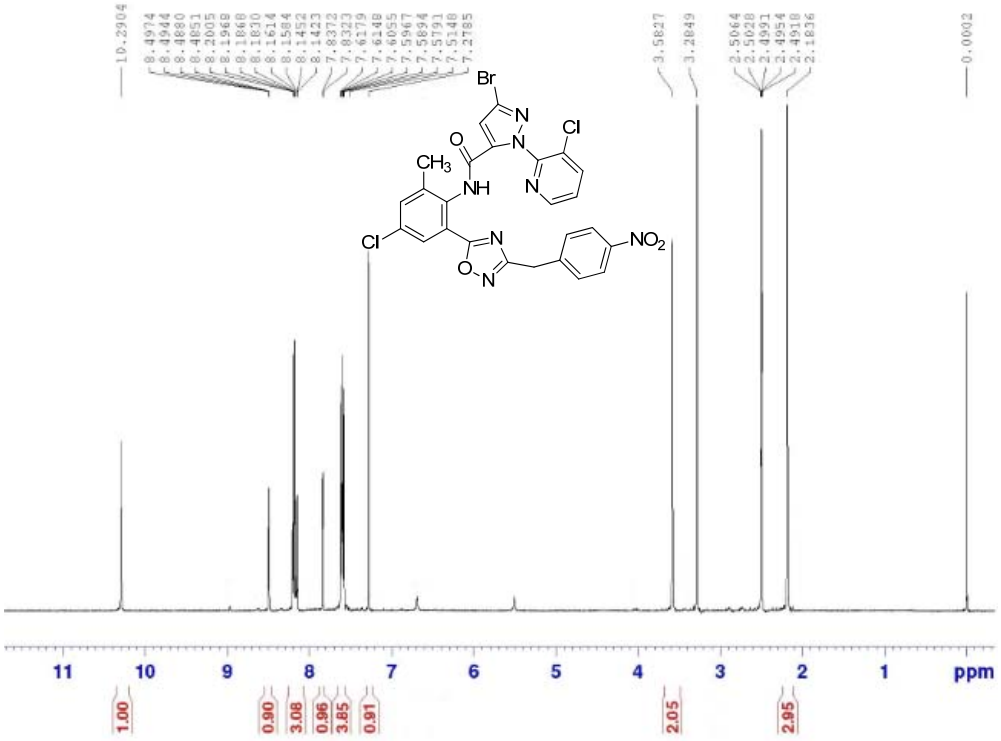


Figure S17 ^{1}H NMR of compound **19**

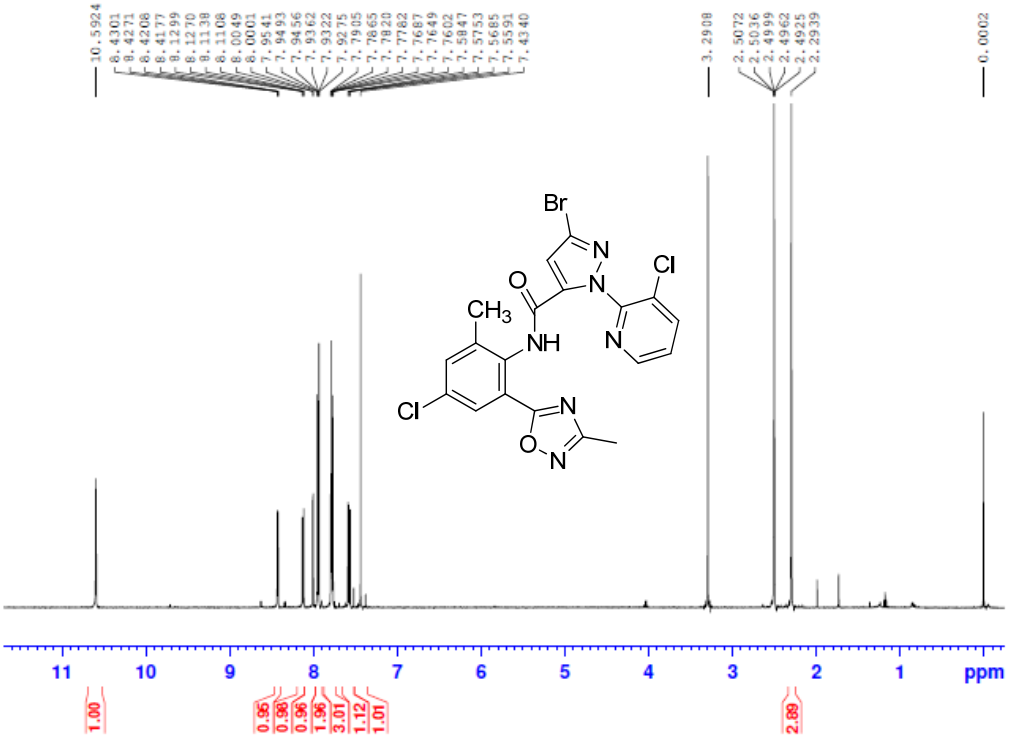


Figure S18 ^{1}H NMR of compound **20**

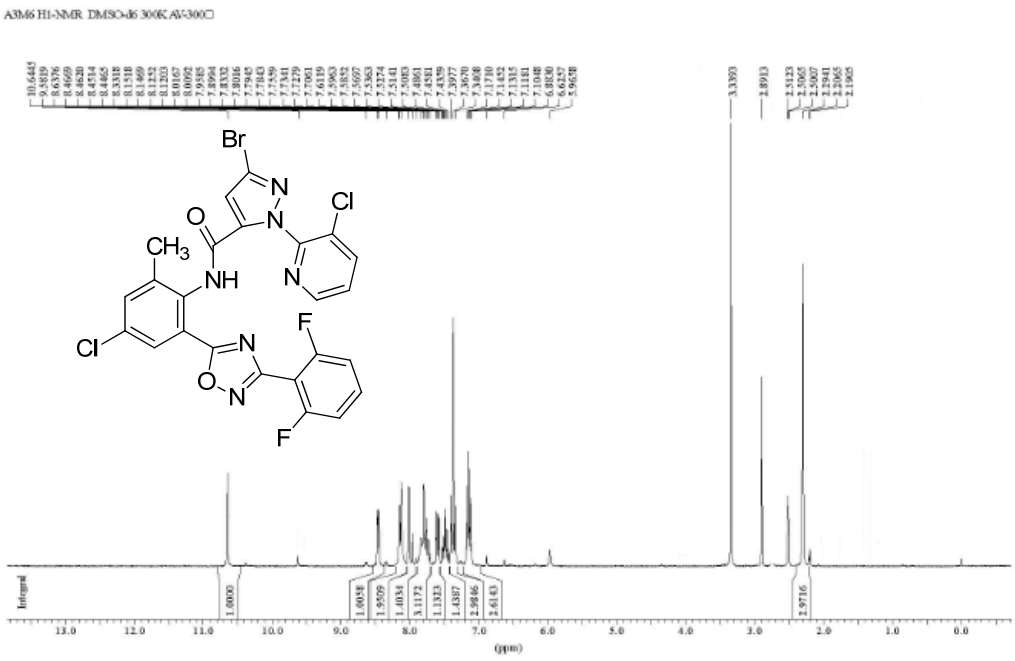


Figure S19 ^{1}H NMR of compound **21**

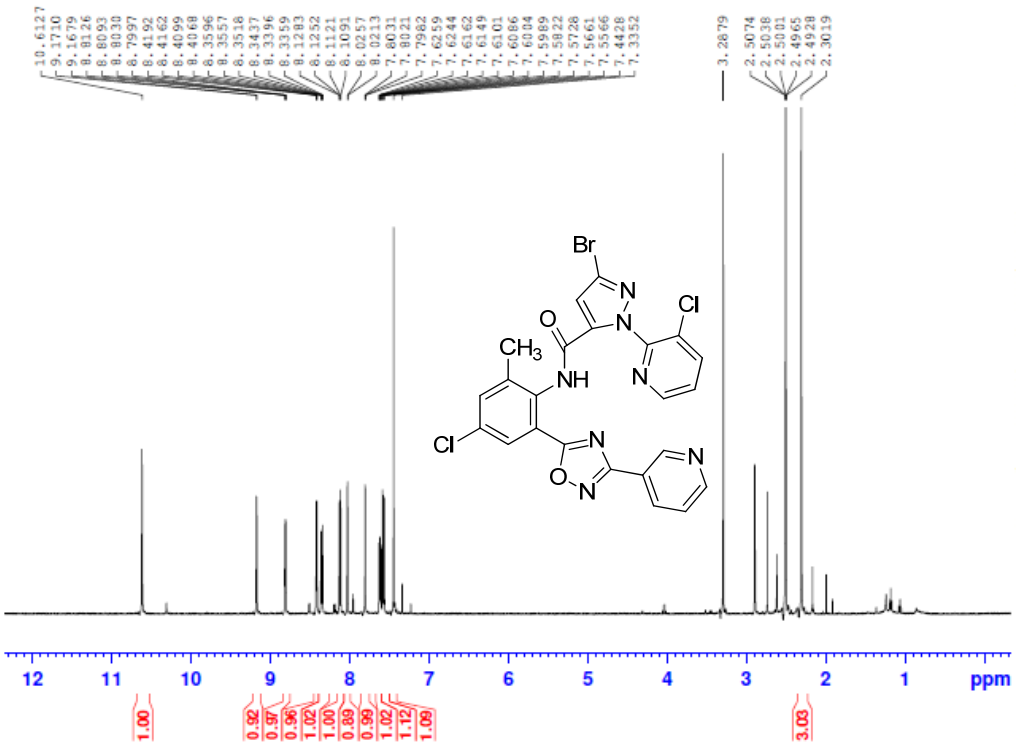
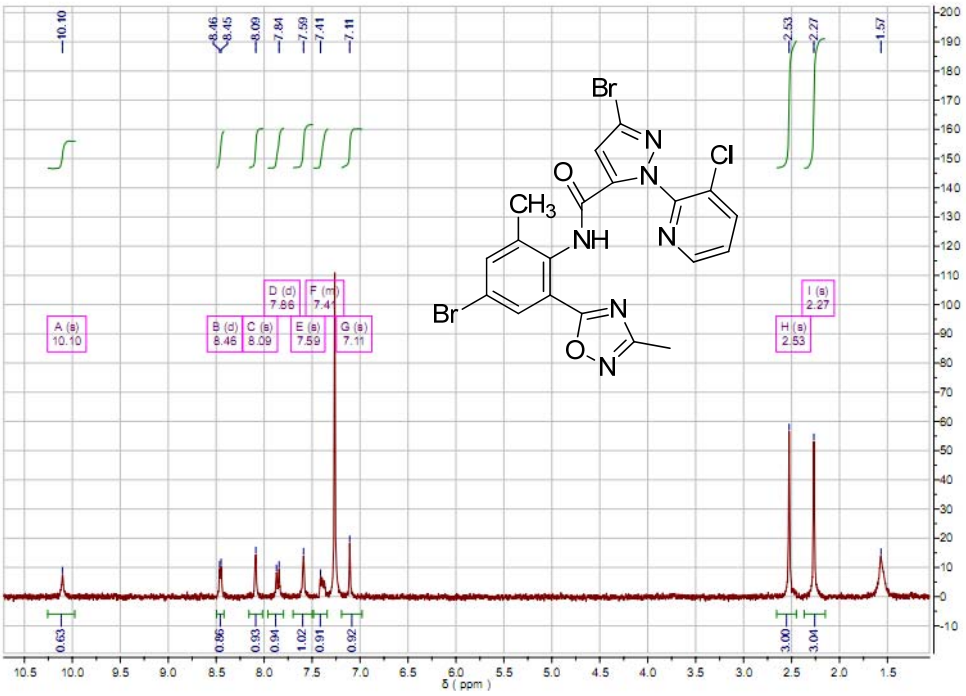


Figure S20 ^{1}H NMR of compound **22**



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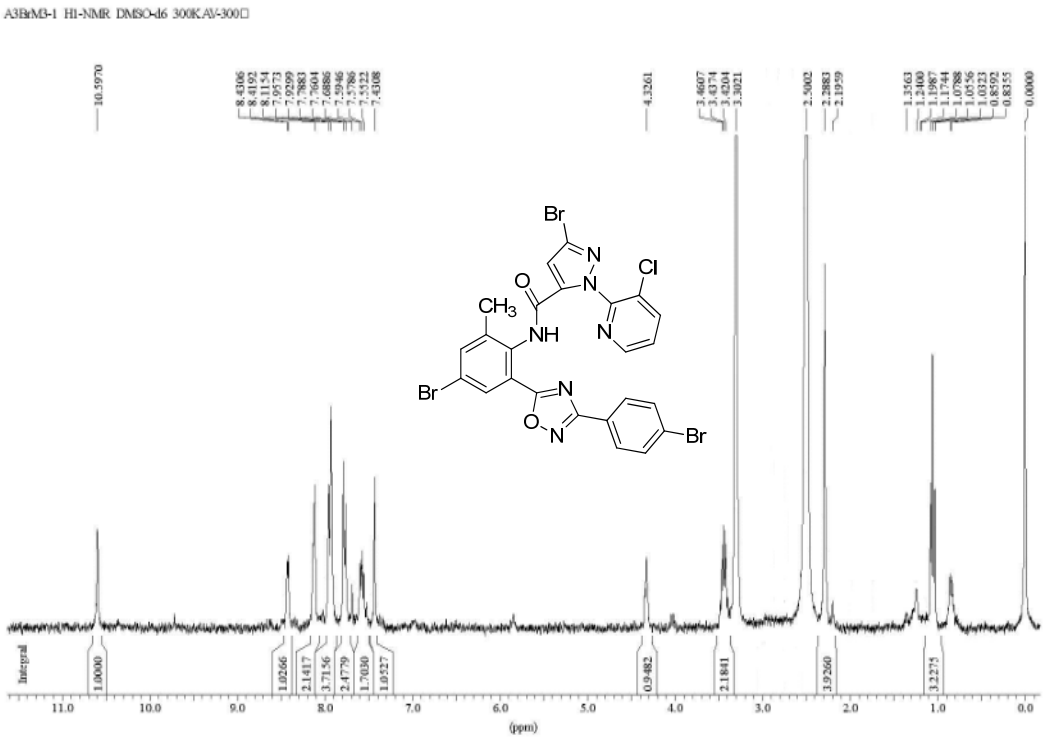

Figure S22 ^{1}H NMR of compound **24**