Supplementary Information

Design, Synthesis, Insecticidal Activity, and Mechanism of Novel Diamide Derivatives Containing Acylthiourea Targeting Insect Ryanodine Receptors

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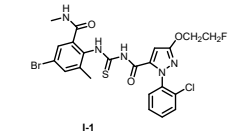
Content

1.Chemical structures of the title compounds I-1~17 and II-1~13



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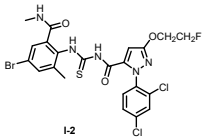

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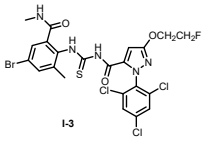

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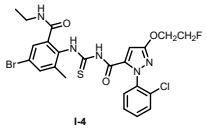

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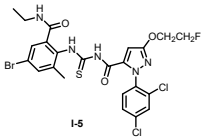

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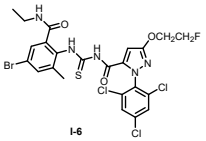

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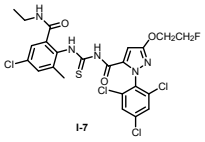

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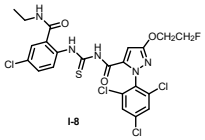

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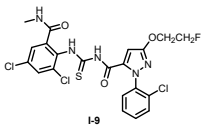

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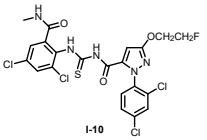

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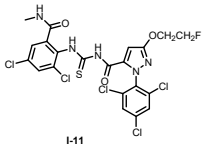

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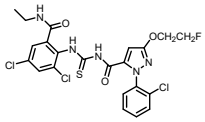

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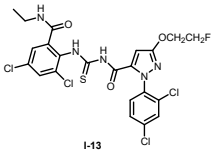

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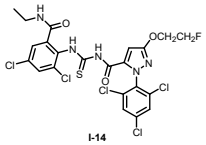

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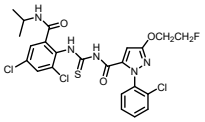

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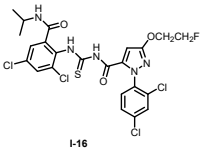

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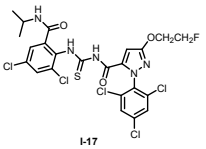

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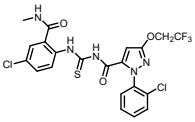

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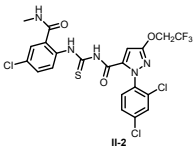

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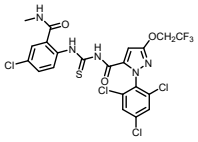

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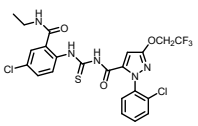

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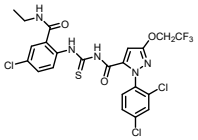

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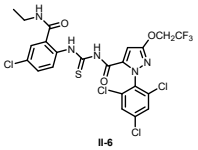

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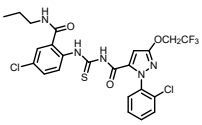

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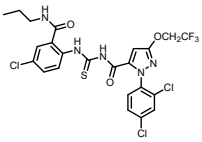

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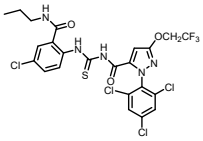

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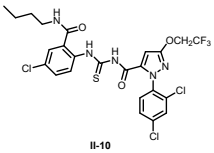

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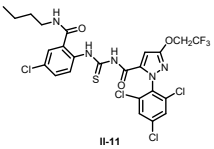

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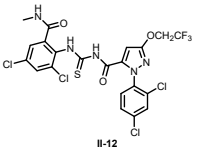

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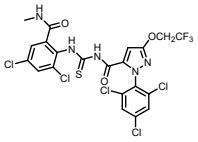
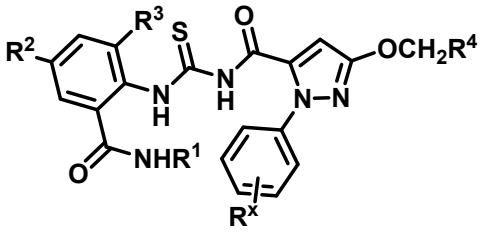


II-13

2.The results of a virtual screen of 30 compounds with the wild-type *Spodoptera frugiperda* RyR.



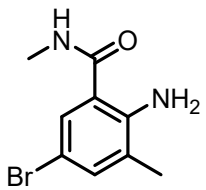
Compd.	R^1	R^2	R^3	R^4	R^X	Binding Energy (Kcal/mol)
I-1	Me	Br	Me	CH_2F	2-Cl	-8.4
I-2	Me	Br	Me	CH_2F	2,4-*di*Cl	-8.5
I-3	Me	Br	Me	CH_2F	2,4,6-*tri*Cl	-7.9
I-4	Et	Br	Me	CH_2F	2-Cl	-8.3
I-5	Et	Br	Me	CH_2F	2,4-*di*Cl	-8.2
I-6	Et	Br	Me	CH_2F	2,4,6-*tri*Cl	-7.8
I-7	Et	Cl	Me	CH_2F	2,4,6-*tri*Cl	-7.8
I-8	Et	Cl	H	CH_2F	2,4,6-*tri*Cl	-9.4

I-9	Me	Cl	Cl	CH_2F	2-Cl	-8.2
I-10	Me	Cl	Cl	CH_2F	2,4-*di*Cl	-8.1
I-11	Me	Cl	Cl	CH_2F	2,4,6-*tri*Cl	-8.2
I-12	Et	Cl	Cl	CH_2F	2-Cl	-8.2
I-13	Et	Cl	Cl	CH_2F	2,4-*di*Cl	-8.1
I-14	Et	Cl	Cl	CH_2F	2,4,6-*tri*Cl	-8.2
I-15	^{i}Pr	Cl	Cl	CH_2F	2-Cl	-8.2
I-16	^{i}Pr	Cl	Cl	CH_2F	2,4-*di*Cl	-8.2
I-17	^{i}Pr	Cl	Cl	CH_2F	2,4,6-*tri*Cl	-8.4
II-1	Me	Cl	H	CF_3	2-Cl	-9.9
II-2	Me	Cl	H	CF_3	2,4-*di*Cl	-10.0
II-3	Me	Cl	H	CF_3	2,4,6-*tri*Cl	-10.0
II-4	Et	Cl	H	CF_3	2-Cl	-9.8

II-5	Et	Cl	H	CF_3	2,4-*di*Cl	-8.9
II-6	Et	Cl	H	CF_3	2,4,6-*tri*Cl	-9.9
II-7	^{n}Pr	Cl	H	CF_3	2-Cl	-9.7
II-8	^{n}Pr	Cl	H	CF_3	2,4-*di*Cl	-10.0
II-9	^{n}Pr	Cl	H	CF_3	2,4,6-*tri*Cl	-10.0
II-10	^{n}Bu	Cl	H	CF_3	2,4-*di*Cl	-10.0
II-11	^{n}Bu	Cl	H	CF_3	2,4,6-*tri*Cl	-10.0
II-12	Me	Cl	Cl	CF_3	2,4-*di*Cl	-8.4
II-13	Me	Cl	Cl	CF_3	2,4,6-*tri*Cl	-8.8

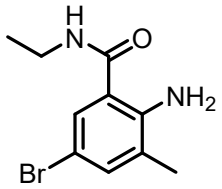
3.Chemical structures, yields, and ^{1}H NMR data of the intermediates

3.1 Chemical structures, yields, and ^{1}H NMR data of the intermediates 3a~i



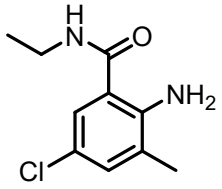
2-amino-5-bromo-*N*,3-dimethylbenzamide(3a, yield: 80%)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.32 (s, 1H, -CON**H**-), 7.50 (d, J = 2.2 Hz, 1H, Ph-**H**), 7.23 (d, J = 1.8 Hz, 1H, Ph-**H**), 6.37 (s, 2H, Ph-N**H**$_2$), 2.71 (d, J = 4.5 Hz, 3H, Ph-C**H**$_3$), 2.07 (s, 3H, -NHC**H**$_3$).



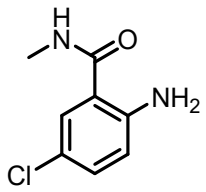
2-amino-5-bromo-*N*-ethyl-3-methylbenzamide(3b, yield: 79%)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.34 (s, 1H, -CON**H**-), 7.51 (s, 1H, Ph-**H**), 7.23 (s, 1H, Ph-**H**), 6.34 (s, 2H, Ph-N**H**$_2$), 3.22 (p, J = 7.0 Hz, 2H, -C**H**$_2$CH$_3$), 2.07 (s, 3H, Ph-C**H**$_3$), 1.09 (t, J = 7.2 Hz, 3H, -CH$_2$C**H**$_3$).



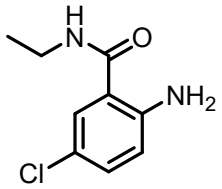
2-amino-5-chloro-*N*-ethyl-3-methylbenzamide(3c, yield: 76%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 (d, J = 2.0 Hz, 1H, Ph-**H**), 7.09 (d, J = 2.0 Hz, 1H, Ph-**H**), 6.01 (s, 2H, Ph-N**H**$_2$), 3.48 – 3.39 (m, 2H, -C**H**$_2$CH$_3$), 2.13 (s, 3H, Ph-C**H**$_3$), 1.23 (t, J = 7.3 Hz, 3H, -CH$_2$C**H**$_3$).



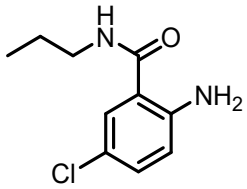
2-amino-5-chloro-*N*-methylbenzamide(3d, yield: 83%)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.32 – 8.25 (m, 1H, -CON**H**-), 7.50 (d, J = 2.4 Hz, 1H, Ph-**H**), 7.15 (dd, J = 8.8, 2.4 Hz, 1H, Ph-**H**), 6.71 (d, J = 8.8 Hz, 1H, Ph-**H**), 6.53 (s, 2H, Ph-N**H**$_2$), 2.71 (d, J = 4.5 Hz, 3H, -NHC**H**$_3$).



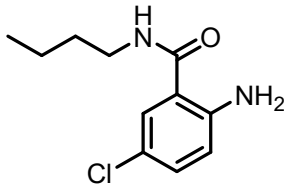
2-amino-5-chloro-*N*-ethylbenzamide(3e, yield: 78%)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.33 (s, 1H, -CON**H**-), 7.53 (s, 1H, Ph-**H**), 7.14 (d, J = 7.8 Hz, 1H, Ph-**H**), 6.72 (d, J = 8.6 Hz, 1H, Ph-**H**), 6.53 (s, 2H, Ph-N**H**$_2$), 3.29 – 3.17 (m, 2H, -C**H**$_2$CH$_3$), 1.10 (t, J = 6.8 Hz, 3H, -CH$_2$C**H**$_3$).



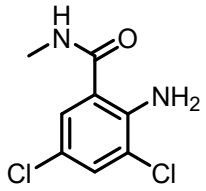
2-amino-5-chloro-*N*-propylbenzamide(3f, yield: 77%)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.32 (t, J = 5.1 Hz, 1H, -CON**H**-), 7.52 (d, J = 2.4 Hz, 1H, Ph-**H**), 7.14 (dd, J = 8.8, 2.4 Hz, 1H, Ph-**H**), 6.70 (d, J = 8.8 Hz, 1H, Ph-**H**), 6.50 (s, 2H, Ph-N**H**$_2$), 3.15 (q, J = 6.8 Hz, 2H, -C**H**$_2$CH$_2$CH$_3$), 1.50 (h, J = 7.4 Hz, 2H, -CH$_2$C**H**$_2$CH$_3$), 0.87 (t, J = 7.4 Hz, 3H, -CH$_2$CH$_2$C**H**$_3$).



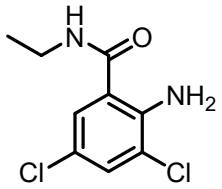
2-amino-*N*-butyl-5-chlorobenzamide(3g, yield: 80%)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 (t, J = 5.2 Hz, 1H, -CON**H**-), 7.51 (d, J = 2.5 Hz, 1H, Ph-**H**), 7.14 (dd, J = 8.8, 2.5 Hz, 1H, Ph-**H**), 6.70 (d, J = 8.8 Hz, 1H, Ph-**H**), 6.51 (s, 2H, Ph-N**H**$_2$), 3.19 (q, J = 7.0 Hz, 2H, -C**H**$_2$CH$_2$CH$_2$CH$_3$), 1.48 (p, J = 7.2 Hz, 2H, -CH$_2$C**H**$_2$CH$_2$CH$_3$), 1.31 (dq, J = 14.3, 7.1 Hz, 2H, -CH$_2$CH$_2$C**H**$_2$CH$_3$), 0.89 (t, J = 7.3 Hz, 3H, -CH$_2$CH$_2$CH$_2$C**H**$_3$).



2-amino-3,5-dichloro-*N*-methylbenzamide(3h, yield: 77%)

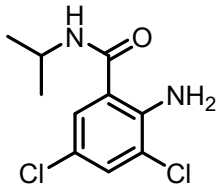
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.50 (s, 1H, -CON**H**-), 7.55 (s, 1H, Ph-**H**), 7.50 (s, 1H, Ph-**H**), 6.65 (s, 2H, Ph-N**H**$_2$), 2.74 (d, J = 3.3 Hz, 3H, -NHC**H**$_3$).



2-amino-3,5-dichloro-*N*-ethylbenzamide(3i, yield: 79%)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.53 (s, 1H, -CON**H**-), 7.56 (d, J = 2.3 Hz, 1H, Ph-**H**), 7.50 (d, J = 2.3 Hz, 1H, Ph-**H**), 6.64 (s, 2H, Ph-N**H**$_2$), 3.29 – 3.18 (m, 2H, -C**H**$_2$CH$_3$), 1.10 (t, J = 7.2 Hz, 3H, -CH$_2$C**H**$_3$).

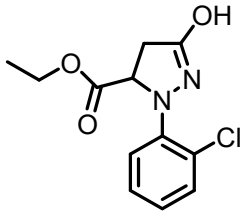
3.2 Chemical structure, yield, and ^{1}H NMR data of the intermediate 3j



2-amino-3,5-dichloro-*N*-isopropylbenzamide(3j, yield: 69%)

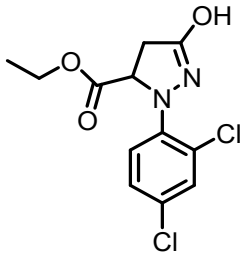
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 2.2 Hz, 1H, Ph-**H**), 7.19 (d, *J* = 2.1 Hz, 1H, Ph-**H**), 5.95 (s, 2H, Ph-N**H**$_2$), 5.81 (s, 1H, -CON**H**-), 4.21 (dq, *J* = 13.4, 6.6 Hz, 1H, -C**H**$(CH_3)_2$), 1.25 (d, *J* = 6.5 Hz, 6H, -CH(C**H**$_3)_2$).

3.3 Chemical structures, yields, and ^{1}H NMR data of the intermediates 5a~c、6a~c、7a~f, and 8a~f



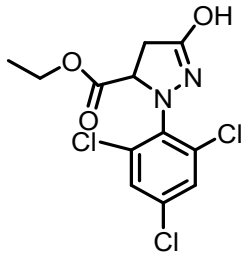
ethyl 1-(2-chlorophenyl)-3-hydroxy-4,5-dihydro-1H-pyrazole-5-carboxylate(5a, yield: 68%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (s, 1H, 2-Pyrazoline-O**H**), 7.36 (d, *J* = 7.9 Hz, 1H, Ph-**H**), 7.15 (d, *J* = 6.9 Hz, 2H, Ph-**H**), 6.96 (s, 1H, Ph-**H**), 4.37 – 4.28 (m, 3H, -C**H**$_2$CH$_3$, -COC**H**CH$_2$-), 3.04 (dd, *J* = 17.0, 9.8 Hz, 1H, 2-Pyrazoline-**H**), 2.51 (dd, *J* = 17.0, 3.0 Hz, 1H, 2-Pyrazoline-**H**), 1.31 (t, 3H, -CH$_2$C**H**$_3$).



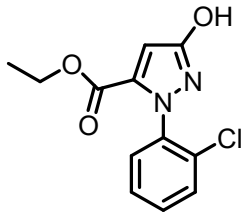
ethyl 1-(2,4-dichlorophenyl)-3-hydroxy-4,5-dihydro-1H-pyrazole-5-carboxylate(5b, yield: 52%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.90 (s, 1H, 2-Pyrazoline-O**H**), 7.29 (d, *J* = 8.5 Hz, 1H, Ph-**H**), 7.15 (s, 1H, Ph-**H**), 7.13 (s, 1H, Ph-**H**), 4.34 (q, *J* = 7.1 Hz, 2H, -C**H**$_2$CH$_3$), 4.26 (d, *J* = 9.5 Hz, 1H, -COC**H**CH$_2$), 3.02 (dd, *J* = 17.1, 9.8 Hz, 1H, -2-Pyrazoline-**H**), 2.52 (d, *J* = 17.1 Hz, 1H, 2-Pyrazoline-**H**), 1.30 (t, *J* = 7.1 Hz, 3H, -CH$_2$C**H**$_3$).



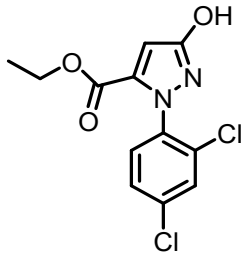
ethyl 3-hydroxy-1-(2,4,6-trichlorophenyl)-4,5-dihydro-1H-pyrazole-5-carboxylate(5c, yield: 70%)

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.64 (s, 1H, 2-Pyrazoline-O**H**), 7.35 (s, 2H, Ph-**H**), 4.29 – 4.17 (m, 3H, -C**H**$_2$CH$_3$, -COC**H**CH$_2$-), 3.21 (dd, *J* = 17.4, 10.8 Hz, 1H, 2-Pyrazoline-**H**), 2.88 (dd, *J* = 17.3, 4.6 Hz, 1H, 2-Pyrazoline-**H**), 1.26 (t, *J* = 7.1 Hz, 3H, -OCH$_2$C**H**$_3$).



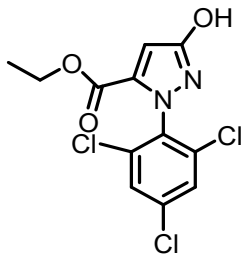
ethyl 1-(2-chlorophenyl)-3-hydroxy-1H-pyrazole-5-carboxylate(6a, yield: 85%)

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 10.93 (s, 1H, Pyrazole-O**H**), 7.52 – 7.49 (m, 1H, Ph-**H**), 7.43 (dq, *J* = 7.5, 3.9 Hz, 3H, Ph-**H**), 6.32 (s, 1H, Pyrazole-**H**), 4.18 (dd, *J* = 7.1, 2.9 Hz, 2H, -C**H**$_2$CH$_3$), 1.17 (t, *J* = 7.1 Hz, 3H, -CH$_2$C**H**$_3$).



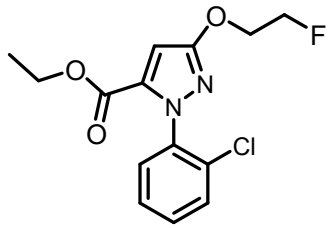
ethyl 1-(2,4-dichlorophenyl)-3-hydroxy-1H-pyrazole-5-carboxylate(6b, yield: 88%)

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 11.00 (s, 1H, Pyrazole-O**H**), 7.55 – 7.49 (m, 1H, Ph-**H**), 7.38 (d, *J* = 1.8 Hz, 2H, Ph-**H**), 6.32 (s, 1H, Pyrazole-**H**), 4.21 (q, *J* = 7.0 Hz, 2H, -C**H**$_2$CH$_3$), 1.22 (t, *J* = 7.1 Hz, 3H, -CH$_2$C**H**$_3$).



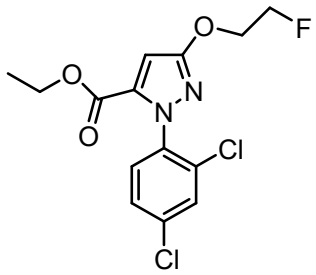
ethyl 3-hydroxy-1-(2,4,6-trichlorophenyl)-1H-pyrazole-5-carboxylate(6c, yield: 89%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.74 (s, 1H, Pyrazole-O**H**), 7.47 (s, 2H, Ph-**H**), 6.37 (s, 1H, Pyrazole-**H**), 4.22 (q, *J* = 7.1 Hz, 2H, -C**H**$_2$CH$_3$), 1.23 (t, *J* = 7.1 Hz, 3H, -CH$_2$C**H**$_3$).



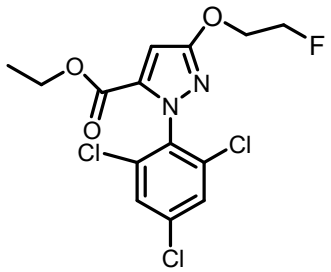
ethyl 1-(2-chlorophenyl)-3-(2-fluoroethoxy)-1H-pyrazole-5-carboxylate(7a, yield: 73%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 6.9 Hz, 1H, Ph-**H**), 7.27 – 7.21 (m, 3H, Ph-**H**), 6.32 (s, 1H, Pyrazole-**H**), 4.58 (d, *J* = 47.5 Hz, 2H, -CH$_2$C**H**$_2$F), 4.33 (d, *J* = 28.7 Hz, 2H, -C**H**$_2$CH$_2$F), 4.04 (q, *J* = 7.0 Hz, 2H, -C**H**$_2$CH$_3$), 1.03 (t, *J* = 7.1 Hz, 3H, -CH$_2$C**H**$_3$).



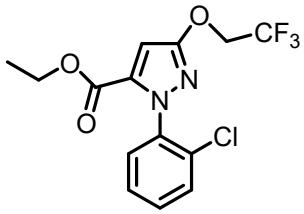
ethyl 1-(2,4-dichlorophenyl)-3-(2-fluoroethoxy)-1H-pyrazole-5-carboxylate(7b, yield: 71%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (s, 1H, Ph-**H**), 7.34 (s, 2H, Ph-**H**), 6.46 (s, 1H, Pyrazole-**H**), 4.62 (d, *J* = 47.5 Hz, 2H, -CH$_2$C**H**$_2$F), 4.37 (d, *J* = 28.7 Hz, 2H, -C**H**$_2$CH$_2$F), 4.19 (q, *J* = 7.1 Hz, 2H, -C**H**$_2$CH$_3$), 1.21 (t, *J* = 7.1 Hz, 3H, -CH$_2$C**H**$_3$).



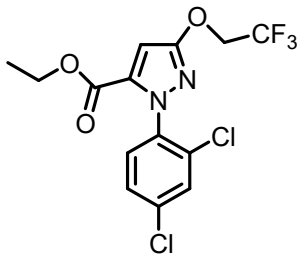
ethyl 3-(2-fluoroethoxy)-1-(2,4,6-trichlorophenyl)-1H-pyrazole-5-carboxylate(7c, yield: 77%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (s, 2H, Ph-**H**), 6.31 (s, 1H, Pyrazole-**H**), 4.60 (t, 1H, -C**H**$_2$CH$_2$F), 4.48 (t, 1H, -C**H**$_2$CH$_2$F), 4.32 (t, 1H, -CH$_2$C**H**$_2$F), 4.25 (t, 1H, -CH$_2$C**H**$_2$F), 4.03 (q, *J* = 7.1 Hz, 2H, -C**H**$_2$CH$_3$), 1.05 (t, *J* = 7.1 Hz, 3H, -CH$_2$C**H**$_3$).



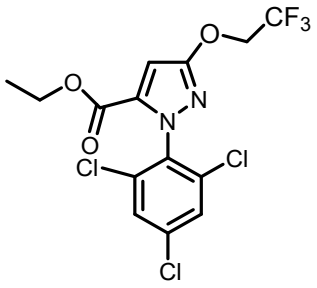
ethyl 1-(2-chlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxylate(7d, yield: 76%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 6.9 Hz, 1H, Ph-**H**), 7.27 – 7.21 (m, 3H, Ph-**H**), 6.52 (s, 1H, Pyrazole-**H**), 4.62 (q, *J* = 8.3 Hz, 2H, -C**H**$_2$CF$_3$), 4.22 (q, *J* = 7.1 Hz, 2H, -C**H**$_2$CH$_3$), 1.23 (t, *J* = 7.1 Hz, 3H, -CH$_2$C**H**$_3$).



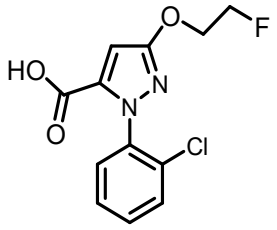
ethyl 1-(2,4-dichlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxylate(7e, yield: 69%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.47 (m, 1H, Ph-**H**), 7.36 (d, *J* = 1.7 Hz, 2H, Ph-**H**), 6.52 (s, 1H, Pyrazole-**H**), 4.62 (q, *J* = 8.3 Hz, 2H, -C**H**$_2$CF$_3$), 4.22 (q, *J* = 7.1 Hz, 2H, -C**H**$_2$CH$_3$), 1.23 (t, *J* = 7.1 Hz, 3H, -CH$_2$C**H**$_3$).



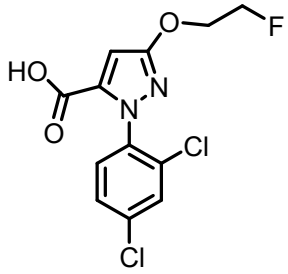
ethyl 1-(2,4,6-trichlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxylate(7f, yield: 70%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (s, 2H, Ph-**H**), 6.53 (s, 1H, Pyrazole-**H**), 4.62 (q, *J* = 8.3 Hz, 2H, -C**H**$_2$CF$_3$), 4.23 (q, *J* = 7.1 Hz, 2H, -C**H**$_2$CH$_3$), 1.24 (t, *J* = 7.1 Hz, 3H, -CH$_2$C**H**$_3$).



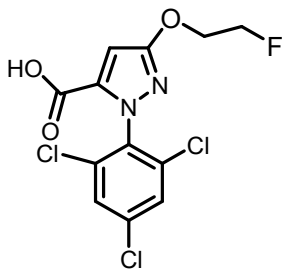
(2-chlorophenyl)-3-(2-fluoroethoxy)-1H-pyrazole-5-carboxylic acid(8a, yield: 89%)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60 (d, J = 7.5 Hz, 1H, Ph-**H**), 7.55 – 7.45 (m, 3H, Ph-**H**), 6.55 (s, 1H, Pyrazole-**H**), 4.72 (dt, J = 47.9, 3.7 Hz, 2H, -$CH_2C\mathbf{H}_2F$), 4.37 (dt, J = 30.3, 3.6 Hz, 2H, -$C\mathbf{H}_2CH_2F$).



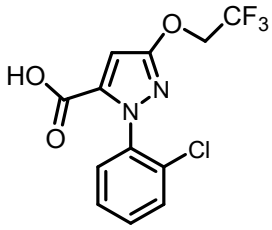
(2,4-dichlorophenyl)-3-(2-fluoroethoxy)-1H-pyrazole-5-carboxylic acid(8b, yield: 89%)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.82 (d, J = 2.0 Hz, 1H, Ph-**H**), 7.61 – 7.55 (m, 2H, Ph-**H**), 6.58 (s, 1H, Pyrazole-**H**), 4.72 (dt, 2H, -$C\mathbf{H}_2CH_2F$), 4.37 (dt, 2H, -$CH_2C\mathbf{H}_2F$).



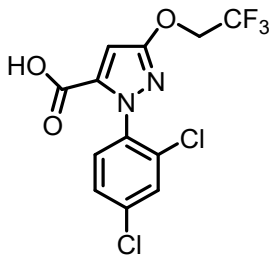
(2-fluoroethoxy)-1-(2,4,6-trichlorophenyl)-1H-pyrazole-5-carboxylic acid(8c, yield 90%)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 (s, 2H, Ph-**H**), 6.63 (s, 1H, Pyrazole-**H**), 4.72 (dt, 2H, -$C\mathbf{H}_2CH_2F$), 4.37 (dt, 2H, -$CH_2C\mathbf{H}_2F$).



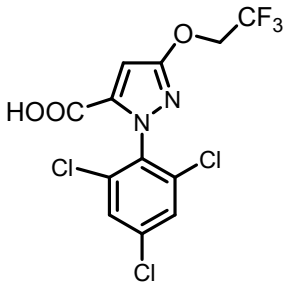
(2-chlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxylic acid(8d, yield: 91%)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62 (d, J = 7.5 Hz, 1H, Ph-**H**), 7.55 – 7.46 (m, 3H, Ph-**H**), 6.69 (s, 1H, Pyrazole-**H**), 4.87 (q, J = 8.8 Hz, 2H, -$C\mathbf{H}_2CF_3$).



(2,4-dichlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxylic acid(8e, yield: 89%)

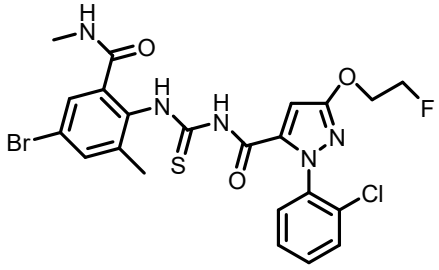
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 (d, J = 1.8 Hz, 1H, Ph-**H**), 7.62 – 7.57 (m, 2H, Ph-**H**), 6.72 (s, 1H, Pyrazole-**H**), 4.87 (q, J = 8.9 Hz, 2H, -C**H**$_2$CF$_3$).



(2,4,6-trichlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxylic acid(8f, yield: 90%)

^{1}H NMR (400 MHz, Acetone-d_6) δ 9.43 (s, 1H, -COO**H**), 7.66 (s, 2H, Ph-**H**), 6.73 (s, 1H, Pyrazole-**H**), 4.86 (q, J = 8.5 Hz, 2H, -C**H**$_2$CF$_3$).

4. Chemical structures, yields, and ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and HRMS data of the title compounds I-1~17 and II-1~13



I-1

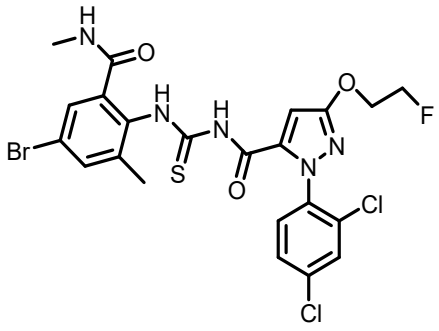
***N*-((4-bromo-2-methyl-6-(methylcarbamoyl)phenyl)carbamothioyl)-1-(2-chlorophenyl)-3-(2-fluoroethoxy)-1H-pyrazole-5-carboxamide(I-1, yield: 29%, melting point: 128-139 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.76 (s, 1H, -CON**H**CS-), 11.59 (s, 1H, -Ph-N**H**CS-), 8.30 (d, J = 4.8 Hz, 1H, -CON**H**-), 7.60 – 7.58 (m, 2H, Ph-**H**), 7.52 – 7.47 (m, 4H, Ph-**H**), 7.17 (d, J = 4.5 Hz, 1H, Pyrazole-**H**), 4.75 (d, J = 47.8 Hz, 2H, -$CH_2C\mathbf{H}_2F$), 4.40 (d, J = 30.2 Hz, 2H, -$C\mathbf{H}_2CH_2F$), 2.63 (s, 3H, -NHC$\mathbf{H}_3$), 2.17 (s, 3H, Ph-C$\mathbf{H}_3$).

^{13}C NMR (101 MHz, DMSO) δ 180.1, 165.9, 162.2, 158.7, 139. 7, 138.5, 134.6, 134.5, 130.9, 130.2, 129.8, 129. 8, 128.8, 128.4, 128.1,120.5, 96.6, 83.2(d), 79.6, 69.0, 26.4, 18.1.

^{19}F NMR (376 MHz, DMSO-d_6) δ -222.44 – -222.86 (m).

HRMS (ESI) Calculated for $C_{22}H_{21}BrClFN_5O_3S$ ([M + H]$^+$)= 568.0216, found 568.0211.



I-2

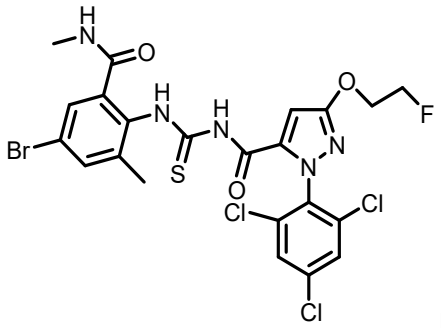
***N*-((4-bromo-2-methyl-6-(methylcarbamoyl)phenyl)carbamothioyl)-1-(2,4-dichlorophenyl)-3-(2-fluoroethoxy)-1H-pyrazole-5-carboxamide(I-2, yield: 30%, melting point: 138-157 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.77 (s, 1H, -CON**H**CS-), 11.57 (s, 1H, -Ph-N**H**CS-), 8.22 (d, J = 4.7 Hz, 1H, -CON**H**-), 7.84 (d, J = 2.2 Hz, 1H, Ph-**H**), 7.66 – 7.58 (m, 3H, Ph-**H**), 7.45 (d, J = 2.1 Hz, 1H, Ph-**H**), 7.22 (s, 1H, Pyrazole-**H**), 4.83 – 4.68 (m, 2H, -$CH_2C\mathbf{H}_2F$), 4.46 – 4.34 (m, 2H, -$C\mathbf{H}_2CH_2F$), 2.62 (d, J = 4.6 Hz, 3H, -NHC$\mathbf{H}_3$), 2.18 (s, 3H, Ph-C$\mathbf{H}_3$).

^{13}C NMR (101 MHz, DMSO) δ 180.1, 165. 9, 162.4, 158. 6, 139.7, 137.7, 136.4, 134.6, 134.6, 134.6, 132.3, 131.1, 129.8, 128.8, 128.6, 120.5, 96.9, 83.1(d), 69.1, 68.9, 26.4, 18.1.

^{19}F NMR (376 MHz, DMSO-d_6) δ -222.72 (tt, J = 48.0, 30.3 Hz).

HRMS (ESI) Calculated for $C_{22}H_{20}BrCl_2FN_5O_3S$ ([M + H]$^+$)= 601.9826, found 601.9821.



I-3

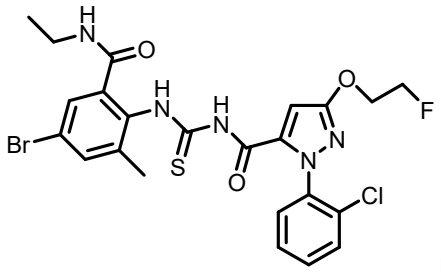
***N*-((4-bromo-2-methyl-6-(methylcarbamoyl)phenyl)carbamothioyl)-3-(2-fluoroethoxy)-1-(2,4,6-trichlorophenyl)-1H-pyrazole-5-carboxamide(I-3, yield: 30%, melting point: 117-123 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.81 (s, 1H, -CON**H**CS-), 11.51 (s, 1H, -Ph-N**H**CS-), 8.18 (d, J = 4.6 Hz, 1H, -CON**H**-), 7.94 (d, J = 2.0 Hz, 2H, Ph-**H**), 7.59 (d, J = 1.8 Hz, 1H, Ph-**H**), 7.44 (d, J = 2.0 Hz, 1H, Ph-**H**), 7.37 (s, 1H, Pyrazole-**H**), 4.83 – 4.68 (m, 2H, -$CH_2C\mathbf{H}_2F$), 4.40 (dt, J = 30.1, 3.7 Hz, 2H, -$C\mathbf{H}_2CH_2F$), 2.61 (d, J = 4.6 Hz, 3H, -NHC$\mathbf{H}_3$), 2.17 (s, 3H, Ph-C$\mathbf{H}_3$).

^{13}C NMR (101 MHz, DMSO) δ 180.0, 165.9, 163.0, 158.1, 139.7, 136.9, 136.3, 135.9, 135.5, 134.8, 134.6, 129.8, 129.1, 128.8, 127.9, 120.5, 97.1, 83.1(d), 69.2, 69.0, 26.3, 18.1.

^{19}F NMR (376 MHz, DMSO-d_6) δ -222.76 (tt, J = 48.2, 30.2 Hz).

HRMS (ESI) Calculated for $C_{22}H_{18}BrCl_3FN_5O_3S$ ([M + H]$^+$)= 657.9256, found 657.9247.



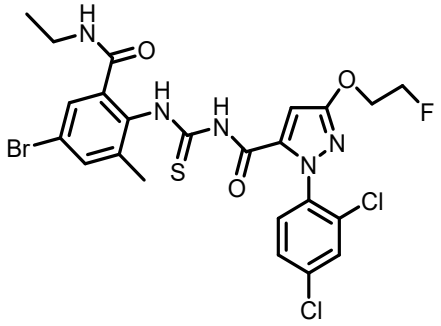
I-4

***N*-((4-bromo-2-(ethylcarbamoyl)-6-methylphenyl)carbamothioyl)-1-(2-chlorophenyl)-3-(2-fluoroethoxy)-1H-pyrazole-5-carboxamide(I-4, yield: 31%, melting point: 171-179 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.79 (s, 1H, -CON**H**CS-), 11.56 (s, 1H, -Ph-N**H**CS-), 8.17 (s, 1H, -CON**H**-), 7.58 (d, J = 8.3 Hz, 3H, Ph-**H**), 7.52 – 7.46 (m, 2H, Ph-**H**), 7.42 (s, 1H, Ph-**H**), 7.17 (s, 1H, Pyrazole-**H**), 4.75 (d, J = 48.0 Hz, 2H, -$CH_2C\mathbf{H}_2F$), 4.40 (d, J = 30.2 Hz, 2H, -$C\mathbf{H}_2CH_2F$), 3.12 (dq, J = 12.7, 6.5 Hz, 2H, -$C\mathbf{H}_2CH_3$), 2.17 (s, 3H, Ph-C$\mathbf{H}_3$), 0.97 (t, J = 7.0 Hz, 3H, -$CH_2C\mathbf{H}_3$).

^{13}C NMR (101 MHz, DMSO) δ 180.3, 165.2, 162.2, 158.6, 139.5, 138.5, 137.4, 136.2, 134.4, 134.4, 131.1, 130.2, 129.8, 128.8, 128.4, 120.6, 96.6, 83.2(d), 69.0, 68.8, 34.3, 18.0, 14.8.

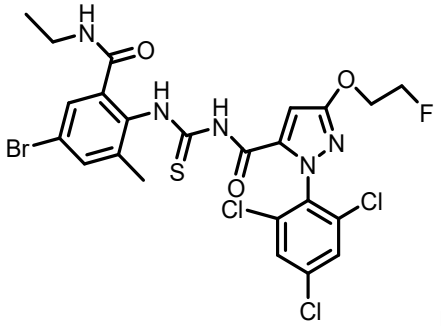
^{19}F NMR (376 MHz, DMSO-d_6) δ -222.62 (tt, J = 47.6, 30.3 Hz).
HRMS (ESI) Calculated for $C_{23}H_{22}BrClFN_5O_3S$ ([M + H]$^+$)= 582.0372, found 582.0375.



I-5

***N*-((4-bromo-2-(ethylcarbamoyl)-6-methylphenyl)carbamothioyl)-1-(2,4-dichlorophenyl)-3-(2-fluoroethoxy)-1H-pyrazole-5-carboxamide(I-5, yield: 32%, melting point: 142-163 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.87 (s, 1H, -CON**H**CS-), 11.49 (s, 1H, -Ph-N**H**CS-), 8.17 – 8.10 (m, 1H, -CON**H**-), 7.98 – 7.89 (m, 3H, Ph-**H**), 7.61 – 7.56 (m, 1H, Ph-**H**), 7.44 – 7.40 (m, 1H, Ph-**H**), 7.37 (s, 1H, Pyrazole-**H**), 4.76 (dt, J = 47.8, 3.5 Hz, 2H, -CH_2C**H**$_2$F), 4.40 (dt, J = 30.1, 3.5 Hz, 2H, -C**H**$_2$$CH_2$F), 3.09 (tq, J = 13.2, 6.0 Hz, 2H, -C**H**$_2$$CH_3$), 2.17 (s, 3H, Ph-C**H**$_3$), 0.95 (t, J = 7.2 Hz, 3H, -CH_2C**H**$_3$).
^{13}C NMR (101 MHz, DMSO) δ 180.1, 165.1, 163.0, 159.9, 158.0, 139.6, 137.5, 136.3, 135.9, 135.5, 134.9, 134.8, 134.4, 129.1, 128.8, 120.6, 97.1, 83.1(d), 69.2, 69.0, 34.3, 18.0, 14.8.
^{19}F NMR (376 MHz, DMSO-d_6) δ -222.74 (tt, J = 47.6, 30.2 Hz).
HRMS (ESI) Calculated for $C_{23}H_{21}BrCl_2FN_5O_3S$ ([M + K]$^+$)= 653.9541, found 653.9536.



I-6

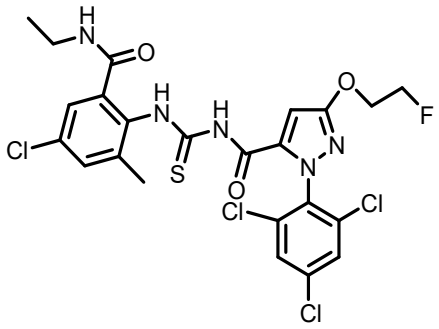
***N*-((4-bromo-2-(ethylcarbamoyl)-6-methylphenyl)carbamothioyl)-3-(2-fluoroethoxy)-1-(2,4,6-trichlorophenyl)-1H-pyrazole-5-carboxamide(I-6, yield: 34%, melting point: 150-161 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.84 (s, 1H, -CON**H**CS-), 11.49 (s, 1H, -Ph-N**H**CS-), 8.11 (t, J = 5.2 Hz, 1H, -CON**H**-), 7.93 – 7.90 (m, 2H, Ph-**H**), 7.58 (s, 1H, Ph-**H**), 7.41 (s, 1H, Ph-**H**), 7.37 (s, 1H, Pyrazole-**H**), 4.76 (d, J = 47.9 Hz, 2H, -CH_2C**H**$_2$F), 4.40 (d, J = 30.0 Hz, 2H, -C**H**$_2$$CH_2$F), 3.09 (dt, J = 13.5, 6.8 Hz, 2H, -C**H**$_2$$CH_3$), 2.17 (s, 3H, Ph-C**H**$_3$), 0.96 (t, J = 7.2 Hz, 3H, -CH_2C**H**$_3$).

^{13}C NMR (101 MHz, DMSO) δ 180.1, 165.1, 163.0, 159.8, 158.1, 139.6, 137.5, 136.3, 135.9, 135.5, 134.9, 134.8, 134.4, 129.1, 128.8, 120.6, 97.1, 83.1(d), 69.2, 69.0, 34.3, 18.0, 14.8.

^{19}F NMR (376 MHz, DMSO-d_6) δ -222.74 (tt, J = 47.6, 30.1 Hz).

HRMS (ESI) Calculated for $C_{23}H_{20}BrCl_3FN_5O_3S$ ([M + H]$^+$)= 649.9593, found 649.9595.



I-7

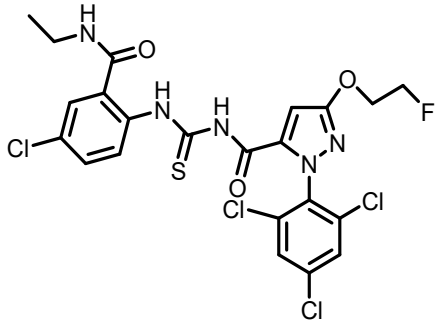
***N*-((4-chloro-2-(ethylcarbamoyl)-6-methylphenyl)carbamothioyl)-3-(2-fluoroethoxy)-1-(2,4,6-trichlorophenyl)-1H-pyrazole-5-carboxamide(I-7, yield: 32%, melting point: 147-151 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.86 (s, 1H, -CON**H**CS-), 11.49 (s, 1H, -Ph-N**H**CS-), 8.12 (s, 1H, -CON**H**-), 7.94 (s, 2H, Ph-**H**), 7.45 (s, 1H, Ph-**H**), 7.37 (s, 1H, Ph-**H**), 7.29 (s, 1H, Pyrazole-**H**), 4.76 (d, J = 47.9 Hz, 2H, -CH_2C**H**$_2$F), 4.40 (d, J = 29.8 Hz, 2H, -C**H**$_2$$CH_2$F), 3.14 – 3.04 (m, 2H, -C**H**$_2$$CH_3$), 2.17 (s, 3H, Ph-C**H**$_3$), 0.95 (t, J = 6.8 Hz, 3H, -CH_2C**H**$_3$).

^{13}C NMR (101 MHz, DMSO) δ 180.2, 165.2, 163.0, 160.0, 158.0, 139.3, 137.3, 136.3, 135.9, 135.5, 134.9, 133.9, 132.1, 129.1, 125.9, 100.0, 97.1, 83.1(d), 69.2, 69.0, 34.3, 18.1, 14.8.

^{19}F NMR (376 MHz, DMSO-d_6) δ -222.73 (tt, J = 48.1, 30.4 Hz).

HRMS (ESI) Calculated for $C_{23}H_{20}Cl_4FN_5O_3S$ ([M + H]$^+$)= 606.0098, found 606.0095.



I-8

***N*-((4-chloro-2-(ethylcarbamoyl)phenyl)carbamothioyl)-3-(2-fluoroethoxy)-1-(2,4,6-trichlorophenyl)-1H-pyrazole-5-carboxamide(I-8, yield: 34%, melting point: 140-152 ℃, white solid)**

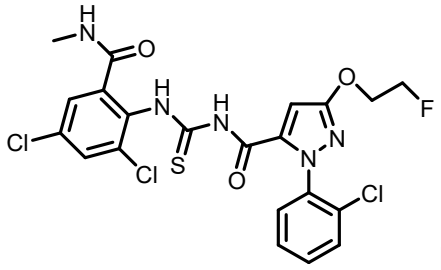
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.21 (s, 1H, -CON**H**CS-), 11.82 (s, 1H, -Ph-N**H**CS-), 8.52 (s, 1H, -CON**H**-), 7.93 (s, 3H, Ph-**H**), 7.53 (s, 2H, Ph-**H**), 7.35 (s, 1H, Pyrazole-**H**),

4.75 (d, *J* = 47.1 Hz, 2H, -$CH_2C\mathbf{H}_2F$), 4.39 (d, *J* = 29.3 Hz, 2H, -$C\mathbf{H}_2CH_2F$), 3.15 – 3.06 (m, 2H, -$C\mathbf{H}_2CH_3$), 1.00 (t, *J* = 6.7 Hz, 3H, -$CH_2C\mathbf{H}_3$).

^{13}C NMR (101 MHz, DMSO) *δ* 179.6, 172.3, 165.2, 163.0, 157.8, 136.3, 135.8, 135.5, 135.1, 134.8, 133.3, 130.9, 129.9, 129.4, 129.1, 128.0, 97.1, 83.1(d), 69.2, 69.0, 34.4, 14.7.

^{19}F NMR (376 MHz, DMSO-d_6) *δ* -222.73 (tt, *J* = 48.0, 30.3 Hz).

HRMS (ESI) Calculated for $C_{22}H_{18}Cl_4FN_5O_3S$ ([M + H]$^+$)= 591.9941, found 591.9943.



I-9

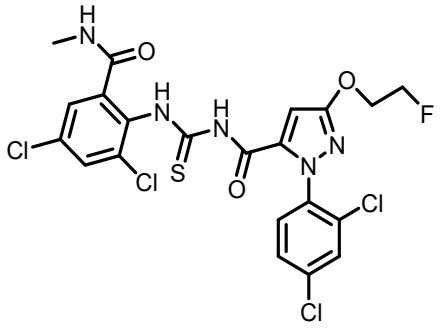
1-(2-chlorophenyl)-*N*-((2,4-dichloro-6-(methylcarbamoyl)phenyl)carbamothioyl)-3-(2-fluoroethoxy)-1H-pyrazole-5-carboxamide(I-9, yield: 34%, melting point: 174-182 ℃, white solid)

^{1}H NMR (400 MHz, DMSO-d_6) *δ* 11.90 (s, 1H, -CON**H**CS-), 11.60 (s, 1H, -Ph-N**H**CS-), 8.26 (d, *J* = 4.6 Hz, 1H, -CON**H**-), 7.80 (d, *J* = 2.2 Hz, 1H, Ph-**H**), 7.63 – 7.58 (m, 2H, Ph-**H**), 7.49 (dd, *J* = 5.3, 3.2 Hz, 3H, Ph-**H**), 7.17 (s, 1H, Pyrazole-**H**), 4.75 (dt, 2H, -$CH_2C\mathbf{H}_2F$), 4.40 (dt, *J* = 30.2, 3.5 Hz, 2H, -$C\mathbf{H}_2CH_2F$), 2.63 (d, *J* = 4.5 Hz, 3H, -NHC$\mathbf{H}_3$).

^{13}C NMR (101 MHz, DMSO) *δ* 180.9, 164.9, 162.2, 158.8, 138.5, 136.1, 134.3, 133.2, 133.0, 131.0, 131.0, 130.8, 130.2, 129.8, 128.5, 127.6, 96.7, 83.2(d), 69.0, 68.9, 26.4.

^{19}F NMR (376 MHz, DMSO-d_6) *δ* -222.66 (tt, *J* = 47.7, 30.0 Hz).

HRMS (ESI) Calculated for $C_{21}H_{17}Cl_3FN_5O_3S$ ([M + H]$^+$)= 544.0174, found 544.0176.

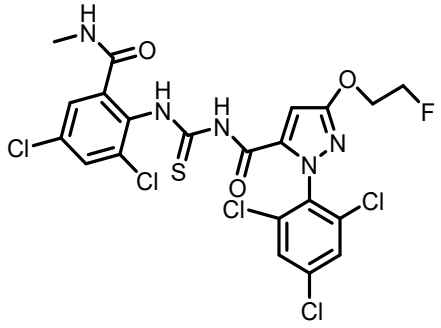


I-10

***N*-((2,4-dichloro-6-(methylcarbamoyl)phenyl)carbamothioyl)-1-(2,4-dichlorophenyl)-3-(2-fluoroethoxy)-1H-pyrazole-5-carboxamide(I-10, yield: 29%, melting point: 173-182 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) *δ* 11.92 (s, 1H, -CON**H**CS-), 11.61 (s, 1H, -Ph-N**H**CS-), 8.28 (s, 1H, -CON**H**-), 7.83 (s, 2H, Ph-**H**), 7.62 (d, *J* = 23.2 Hz, 2H, Ph-**H**), 7.51 (s, 1H, Ph-**H**), 7.24 (s, 1H, Pyrazole-**H**), 4.76 (d, *J* = 46.9 Hz, 2H, -$CH_2C\mathbf{H}_2F$), 4.41 (d, *J* = 29.5 Hz, 2H, -$C\mathbf{H}_2CH_2F$), 2.65 (s, 3H, -$C\mathbf{H}_3$).

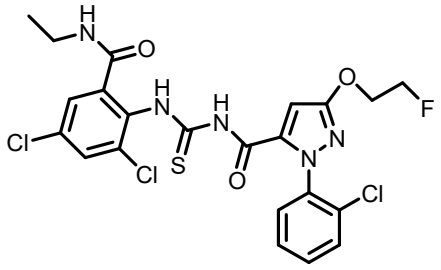
^{13}C NMR (101 MHz, DMSO-d_6) δ 180.8, 164.9, 162.4, 138.5, 137.7, 136.2, 134.7, 134.3, 133.3, 133.0, 132.4, 131.1, 130.8, 129.8, 128.6, 127.6, 97.0, 83.1(d), 69.1, 68.9, 26.5.
^{19}F NMR (376 MHz, DMSO-d_6) δ -222.66 (tt, J = 47.9, 30.2 Hz).
HRMS (ESI) Calculated for $C_{21}H_{16}Cl_4FN_5O_3S$ ([M + Na]$^+$)= 599.9604, found 599.9602.



I-11

***N*-((2,4-dichloro-6-(methylcarbamoyl)phenyl)carbamothioyl)-3-(2-fluoroethoxy)-1-(2,4,6-trichlorophenyl)-1H-pyrazole-5-carboxamide(I-11, yield: 30%, melting point: 125-134 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.98 (s, 1H, -CON**H**CS-), 11.54 (s, 1H, -Ph-N**H**CS-), 8.24 (d, J = 4.4 Hz, 1H, -CON**H**-), 7.94 (s, 2H, Ph-**H**), 7.81 (s, 1H, Ph-**H**), 7.51 – 7.47 (m, 1H, Ph-**H**), 7.39 (s, 1H, Pyrazole-**H**), 4.76 (d, J = 48.0 Hz, 2H, -$CH_2C\mathbf{H}_2F$), 4.40 (d, J = 29.8 Hz, 2H, -$C\mathbf{H}_2CH_2F$), 2.63 (d, J = 4.1 Hz, 3H, -$C\mathbf{H}_3$).
^{13}C NMR (101 MHz, DMSO) δ 180.6, 164.9, 163.0, 158.2, 138.5, 136.1, 135.9, 135.6, 135.0, 134.8, 134.3, 133.1, 130.8, 128.7, 127.6, 97.2, 83.1(d), 79.6, 69.2, 69.0, 26.4.
^{19}F NMR (376 MHz, DMSO-d_6) δ -222.75 (tt, J = 48.1, 30.1 Hz).
HRMS (ESI) Calculated for $C_{21}H_{15}Cl_5FN_5O_3S$ ([M + Na]$^+$)= 633.9214, found 633.9211.



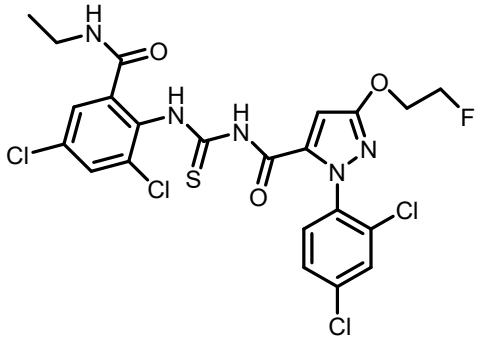
I-12

1-(2-chlorophenyl)-*N*-((2,4-dichloro-6-(ethylcarbamoyl)phenyl)carbamothioyl)-3-(2-fluoroethoxy)-1H-pyrazole-5-carboxamide(I-12, yield: 33%, melting point: 149-158 ℃, white solid)

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.92 (s, 1H, -CON**H**CS-), 11.58 (s, 1H, -Ph-N**H**CS-), 8.19 (t, J = 5.5 Hz, 1H, -CON**H**-), 7.81 (d, J = 2.4 Hz, 1H, Ph-**H**), 7.64 – 7.57 (m, 2H, Ph-**H**), 7.53 – 7.45 (m, 3H, Ph-**H**), 7.20 (s, 1H, Pyrazole-**H**), 4.85 – 4.67 (m, 2H, -$CH_2C\mathbf{H}_2F$), 4.47 – 4.34 (m, 2H, -$C\mathbf{H}_2CH_2F$), 3.16 (dd, 1H, -$C\mathbf{H}_2CH_3$), 3.07 (dd, J = 13.1, 6.5 Hz, 1H, -$C\mathbf{H}_2CH_3$), 0.96 (t, J = 7.2 Hz, 3H, -$CH_2C\mathbf{H}_3$).
^{13}C NMR (101 MHz, DMSO) δ 180.9, 164.1, 162.2, 158.7, 139.1, 138.6, 136.0, 134.2, 133.1, 131.2, 131.0, 130.6, 130.2, 129.9, 128.4, 127.6, 96.7, 83.2(d), 69.0, 68.8, 34.4, 14.8.

^{19}F NMR (376 MHz, DMSO-d_6) δ -222.69 (tt, J = 47.7, 30.3 Hz).

HRMS (ESI) Calculated for $C_{22}H_{19}Cl_3FN_5O_3S$ ([M + H]$^+$)= 558.0331, found 558.0328.



I-13

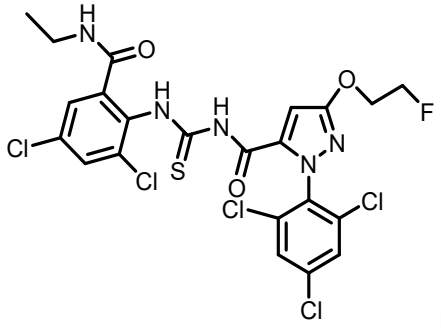
***N*-((2,4-dichloro-6-(ethylcarbamoyl)phenyl)carbamothioyl)-1-(2,4-dichlorophenyl)-3-(2-fluoroethoxy)-1H-pyrazole-5-carboxamide(I-13, yield: 33%, melting point: 156-163 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.95 (s, 1H, -CON**H**CS-), 11.59 (s, 1H, -Ph-N**H**CS-), 8.20 (s, 1H, -CON**H**-), 7.81 (d, J = 10.7 Hz, 2H, Ph-**H**), 7.64 (d, J = 8.5 Hz, 1H, Ph-**H**), 7.58 (d, J = 8.2 Hz, 1H, Ph-**H**), 7.48 (s, 1H, Ph-**H**), 7.25 (s, 1H, Pyrazole-**H**), 4.76 (d, J = 47.9 Hz, 2H, -$CH_2C\mathbf{H}_2$F), 4.41 (d, J = 30.1 Hz, 2H, -$C\mathbf{H}_2CH_2$F), 3.13 (ddd, J = 30.8, 12.6, 6.1 Hz, 2H, -$C\mathbf{H}_2CH_3$), 0.98 (t, J = 7.1 Hz, 3H, -$CH_2C\mathbf{H}_3$).

^{13}C NMR (101 MHz, DMSO) δ 180.9, 164.1, 162.4, 158.6, 139.1, 137.7, 136.2, 134.8, 134.2, 133.1, 132.6, 131.2, 130.6, 129.8, 128.6, 127.6, 97.0, 83.1(d), 69.1, 68.9, 34.4, 14.8.

^{19}F NMR (376 MHz, DMSO-d_6) δ -222.66 (tt, J = 48.0, 30.2 Hz).

HRMS (ESI) Calculated for $C_{22}H_{18}Cl_4FN_5O_3S$ ([M + Na]$^+$)= 613.9761, found 613.9762.



I-14

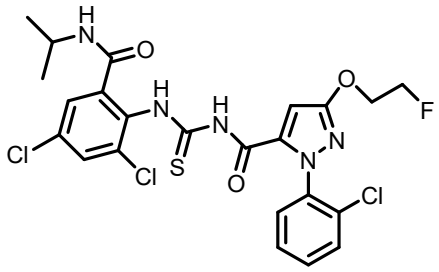
***N*-((2,4-dichloro-6-(ethylcarbamoyl)phenyl)carbamothioyl)-3-(2-fluoroethoxy)-1-(2,4,6-trichlorophenyl)-1H-pyrazole-5-carboxamide(I-14, yield: 32%, melting point: 147-167 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.00 (s, 1H, -CON**H**CS-), 11.52 (s, 1H, -Ph-N**H**CS-), 8.15 (s, 1H, -CON**H**-), 7.93 (s, 2H, Ph-**H**), 7.81 (s, 1H, Ph-**H**), 7.46 (s, 1H, Ph-**H**), 7.38 (s, 1H, Pyrazole-**H**), 4.75 (d, J = 47.7 Hz, 2H, -$CH_2C\mathbf{H}_2$F), 4.40 (d, J = 30.3 Hz, 2H, -$C\mathbf{H}_2CH_2$F), 3.11 (dd, J = 38.6, 5.9 Hz, 2H, -$C\mathbf{H}_2CH_3$), 0.95 (t, 3H, -$CH_2C\mathbf{H}_3$)

^{13}C NMR (101 MHz, DMSO) δ 180.7, 164.0, 163.0, 158.2, 139.1, 136.1, 135.9, 135.6, 134.9, 134.2, 133.2, 130.6, 129.1, 127.6, 97.2, 83.1(d), 69.2, 34.4, 31.4, 22.5, 14.7, 14.4.

^{19}F NMR (376 MHz, DMSO-d_6) δ -222.77 (tt, J = 47.7, 30.1 Hz).

HRMS (ESI) Calculated for $C_{22}H_{17}Cl_5FN_5O_3S$ ([M + Na]$^+$)= 647.9371, found 647.9372.



I-15

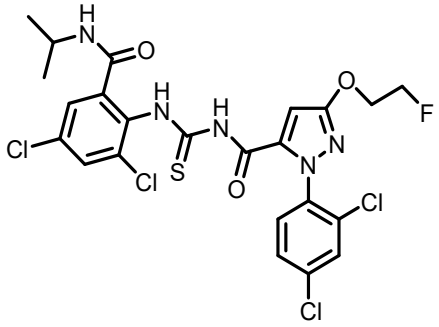
1-(2-chlorophenyl)-*N*-((2,4-dichloro-6-(isopropylcarbamoyl)phenyl)carbamothioyl)-3-(2-fluoroethoxy)-1H-pyrazole-5-carboxamide(I-15, yield: 33%, melting point: 177-182 ℃, white solid)

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.96 (s, 1H, -CON**H**CS-), 11.58 (s, 1H, -Ph-N**H**CS-), 8.01 (d, J = 7.6 Hz, 1H, -CON**H**-), 7.78 (d, J = 2.1 Hz, 1H, Ph-**H**), 7.63 – 7.54 (m, 2H, Ph-**H**), 7.49 (dd, J = 6.8, 3.5 Hz, 2H, Ph-**H**), 7.44 (d, J = 2.1 Hz, 1H, Ph-**H**), 7.19 (s, 1H, Pyrazole-**H**), 4.75 (dt, J = 47.8, 3.4 Hz, 2H, -$CH_2C\mathbf{H}_2$F), 4.40 (dt, J = 30.2, 3.4 Hz, 2H, -$C\mathbf{H}_2CH_2$F), 3.87 (dt, J = 13.3, 6.6 Hz, 1H, -C**H**$(CH_3)_2$), 1.00 (d, J = 6.6 Hz, 6H, -CH(C**H**$_3)_2$).

^{13}C NMR (101 MHz, DMSO) δ 181.0, 163.4, 162.2, 158.6, 139.4, 138.6, 136.0, 134.0, 133.2, 131.1, 130.5, 130.2, 129.9, 128.4, 127.7, 96.7, 83.2(d), 69.0, 68.9, 41.6, 41.2, 23.7, 22.5.

^{19}F NMR (376 MHz, DMSO-d_6) δ -222.65 (tt, J = 47.3, 29.6 Hz).

HRMS (ESI) Calculated for $C_{23}H_{21}Cl_3FN_5O_3S$ ([M + H]$^+$)= 572.0487, found 572.0487.



I-16

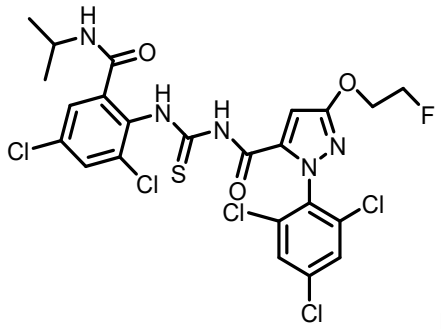
***N*-((2,4-dichloro-6-(isopropylcarbamoyl)phenyl)carbamothioyl)-1-(2,4-dichlorophenyl)-3-(2-fluoroethoxy)-1H-pyrazole-5-carboxamide(I-16, yield: 34%, melting point: 166-180 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.97 (s, 1H, -CON**H**CS-), 11.56 (s, 1H, -Ph-N**H**CS-), 8.00 (d, J = 7.6 Hz, 1H, -CON**H**-), 7.86 – 7.83 (m, 1H, Ph-**H**), 7.80 (d, J = 2.2 Hz, 1H, Ph-**H**), 7.66 – 7.56 (m, 2H, Ph-**H**), 7.45 (d, J = 2.2 Hz, 1H, Ph-**H**), 7.24 (s, 1H, Pyrazole-**H**), 4.75 (dt, J = 47.8, 3.4 Hz, 2H, -$CH_2C\mathbf{H}_2$F), 4.40 (dt, J = 30.1, 3.4 Hz, 2H, -$C\mathbf{H}_2CH_2$F), 3.87 (dq, J = 13.4, 6.6 Hz, 1H, -C**H**$(CH_3)_2$), 0.99 (dd, J = 13.0, 6.5 Hz, 6H, -CH(C**H**$_3)_2$).

^{13}C NMR (101 MHz, DMSO) δ 180.9, 172.3, 163.3, 162.4, 158.5, 139.4, 137.7, 136.1, 134.8, 133.1, 132.7, 131.3, 130.5, 129.8, 128.6, 127.7, 100.0, 97.0, 83.1(d), 69.1, 68.9, 41.5, 22.5.

^{19}F NMR (376 MHz, DMSO-d_6) δ -222.72 (tt, J = 47.6, 30.3 Hz).

HRMS (ESI) Calculated for $C_{23}H_{20}Cl_4FN_5O_3S$ ([M + Na]$^+$)= 627.9917, found 627.9918.



I-17

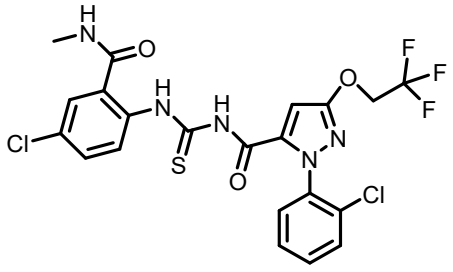
***N*-((2,4-dichloro-6-(isopropylcarbamoyl)phenyl)carbamothioyl)-3-(2-fluoroethoxy)-1-(2,4,6-trichlorophenyl)-1H-pyrazole-5-carboxamide(I-17, yield: 30%, melting point: 154-165 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.03 (s, 1H, -CON**H**CS-), 11.52 (s, 1H, -Ph-N**H**CS-), 7.98 (d, J = 6.3 Hz, 1H, -CON**H**-), 7.92 (d, J = 14.4 Hz, 2H, Ph-**H**), 7.79 (s, 1H, Ph-**H**), 7.45 (s, 1H, Ph-**H**), 7.38 (s, 1H, Pyrazole-**H**), 4.75 (d, J = 47.9 Hz, 2H, -CH_2C**H**$_2$F), 4.40 (d, J = 29.9 Hz, 2H, -C**H**$_2$$CH_2$F), 3.90 – 3.81 (m, 1H, -C**H**$(CH_3)_2$), 0.98 (dd, J = 11.8, 5.8 Hz, 6H, -CH(C**H**$_3)_2$).

^{13}C NMR (101 MHz, DMSO-d_6) δ 180.8, 163.3, 163.0, 158.1, 139.5, 136.1, 135.9, 135.6, 135.1, 134.9, 133.2, 131.5, 130.5, 129.1, 127.7, 97.3, 83.1(d), 69.2, 69.0, 41.5, 22.5, 22.3, 14.8.

^{19}F NMR (376 MHz, DMSO-d_6) δ -222.74 (tt, J = 47.8, 30.3 Hz).

HRMS (ESI) Calculated for $C_{23}H_{19}Cl_5FN_5O_3S$ ([M + Na]$^+$)= 661.9527, found 661.9525.

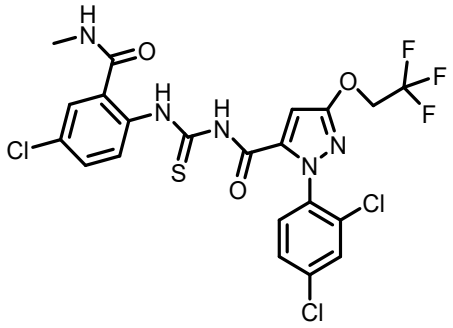


II-1

***N*-((4-chloro-2-(methylcarbamoyl)phenyl)carbamothioyl)-1-(2-chlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxamide(II-1, yield: 32%, melting point: 171-180 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.42 (s, 1H, -CON**H**CS-), 11.78 (s, 1H, -Ph-N**H**CS-), 8.63 – 8.54 (m, 1H, -CON**H**-), 8.03 (d, J = 8.7 Hz, 1H, Ph-**H**), 7.65 – 7.48 (m, 6H, Ph-**H**), 7.23 (s, 1H, Pyrazole-**H**), 4.90 (q, J = 8.7 Hz, 2H, -C**H**$_2$$CF_3$), 2.64 (d, J = 4.2 Hz, 3H, -NHC**H**$_3$).

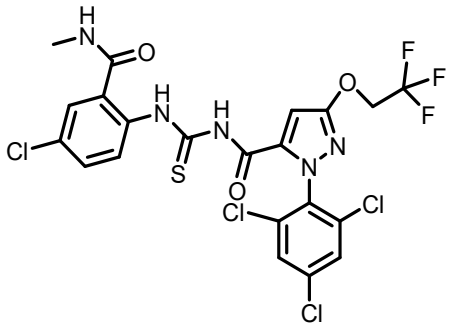
^{13}C NMR (101 MHz, DMSO) δ 179.5, 166.0, 161.0, 158.1, 138.2, 136.9, 135.4, 132.0, 131.1, 130.9(t), 129.8, 128.5, 125.4, 124.3, 122.7, 120.2, 100.0, 96.7, 65.8, 65.5, 26.5.
^{19}F NMR (376 MHz, DMSO-d_6) δ -72.73 (t, J = 9.0 Hz).
HRMS (ESI) Calculated for $C_{21}H_{16}Cl_2F_3N_5O_3S$ ([M + H]$^+$)= 546.0376, found 546.0372.



II-2

***N*-((4-chloro-2-(methylcarbamoyl)phenyl)carbamothioyl)-1-(2,4-dichlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxamide(II-2, yield: 31%, melting point: 175-191 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.41 (s, 1H, -CON**H**CS-), 11.79 (s, 1H, -Ph-N**H**CS-), 8.59 (d, J = 4.5 Hz, 1H, -CON**H**-), 8.03 (d, J = 8.7 Hz, 1H, Ph-**H**), 7.85 (d, J = 1.8 Hz, 1H, Ph-**H**), 7.65 – 7.53 (m, 4H, Ph-**H**), 7.26 (s, 1H, Pyrazole-**H**), 4.90 (q, J = 8.8 Hz, 2H, -C**H**$_2$CF$_3$), 2.64 (d, J = 4.4 Hz, 3H, -NHC**H**$_3$).
^{13}C NMR (101 MHz, DMSO) δ 179.4, 166.0, 161.2, 158.0, 137.3, 135.4, 134.9, 132.2, 131.1(t), 129.3, 128.7, 125.4, 122.6, 97.0, 79.6, 65.9, 65.5, 60.2, 26.4, 21.2, 14.6.
^{19}F NMR (376 MHz, DMSO-d_6) δ -72.75 (t, J = 9.0 Hz).
HRMS (ESI) Calculated for $C_{21}H_{15}Cl_3F_3N_5O_3S$ ([M + Na]$^+$)= 601.9805, found 601.9804.



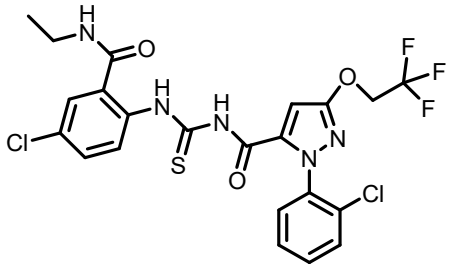
II-3

***N*-((4-chloro-2-(methylcarbamoyl)phenyl)carbamothioyl)-1-(2,4,6-trichlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxamide(II-3, yield: 31%, melting point: 166-172 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.31 (s, 1H, -CON**H**CS-), 11.86 (s, 1H, -Ph-N**H**CS-), 8.59 (s, 1H, -CON**H**-), 8.01 (d, J = 8.6 Hz, 1H, Ph-**H**), 7.94 (s, 2H, Ph-**H**), 7.60 – 7.52 (m, 2H, Ph-**H**), 7.43 (s, 1H, Pyrazole-**H**), 4.91 (q, J = 8.7 Hz, 2H, -C**H**$_2$CF$_3$), 2.64 (d, J = 4.1 Hz, 3H, -NHC**H**$_3$).
^{13}C NMR (101 MHz, DMSO) δ 179.4, 166.0, 161.8, 157.5, 136.9, 135.7, 135.5, 135.3, 134.7, 132.2, 130.8(t), 129.1, 127.9, 125.4, 122.6, 97.1, 66.2, 65.9, 65.5, 65.2, 26.4.

^{19}F NMR (376 MHz, DMSO-d_6) δ -72.67 (t, J = 8.9 Hz).

HRMS (ESI) Calculated for $C_{21}H_{14}Cl_4F_3N_5O_3S$ ([M + Na]$^+$)= 635.9416, found 635.9413.



II-4

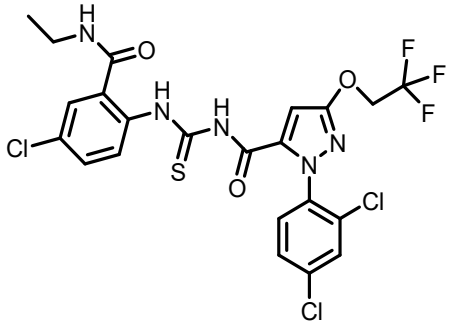
***N*-((4-chloro-2-(ethylcarbamoyl)phenyl)carbamothioyl)-1-(2-chlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxamide(II-4, yield: 29%, melting point: 127-136 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.31 (s, 1H, -CON**H**CS-), 11.78 (s, 1H, -Ph-N**H**CS-), 8.55 (t, J = 5.2 Hz, 1H, -CON**H**-), 7.98 (d, J = 8.3 Hz, 1H, Ph-**H**), 7.65 – 7.51 (m, 6H, Ph-**H**), 7.22 (s, 1H, Pyrazole-**H**), 4.90 (q, J = 8.8 Hz, 2H, -C**H**$_2$CF$_3$), 3.12 (p, J = 7.0 Hz, 2H, -C**H**$_2$CH$_3$), 1.01 (t, J = 7.2 Hz, 3H, -CH$_2$C**H**$_3$).

^{13}C NMR (101 MHz, DMSO) δ 179.7, 165.3, 161.0, 158.1, 138.1, 136.9, 135.3, 132.8, 131.1, 130.9, 130.8(t), 130.2, 130.0, 129.8, 129.4, 128.5, 128.0, 96.7, 65.8, 65.5, 34.4, 14.8.

^{19}F NMR (376 MHz, DMSO-d_6) δ -72.73 (t, J = 8.7 Hz).

HRMS (ESI) Calculated for $C_{22}H_{18}Cl_2F_3N_5O_3S$ ([M + Na]$^+$)= 582.0352, found 582.0346.



II-5

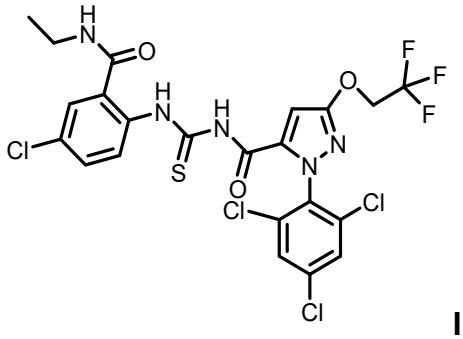
***N*-((4-chloro-2-(ethylcarbamoyl)phenyl)carbamothioyl)-1-(2,4-dichlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxamide(II-5, yield: 30%, melting point: 151-164 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.36 (s, 1H, -CON**H**CS-), 11.81 (s, 1H, -Ph-N**H**CS-), 8.58 (s, 1H, -CON**H**-), 8.02 (d, J = 8.4 Hz, 1H, Ph-**H**), 7.82 (s, 1H, Ph-**H**), 7.65 – 7.51 (m, 4H, Ph-**H**), 7.27 (s, 1H, Pyrazole-**H**), 4.90 (q, J = 8.4 Hz, 2H, -C**H**$_2$CF$_3$), 3.18 – 3.06 (m, 2H, -C**H**$_2$CH$_3$), 1.01 (t, J = 6.8 Hz, 3H, -CH$_2$C**H**$_3$).

^{13}C NMR (101 MHz, DMSO) δ 179.5, 165.3, 161.2, 158.0, 140.8, 137.3, 136.9, 135.3, 134.9, 132.2(t), 129.8, 128.0, 125.4, 122.6, 119.9, 100.0, 97.0, 65.9, 65.5, 65.2, 34.5, 14.7.

^{19}F NMR (376 MHz, DMSO-d_6) δ -72.74 (t, J = 8.8 Hz).

HRMS (ESI) Calculated for $C_{22}H_{17}Cl_3F_3N_5O_3S$ ([M + Na]$^+$)= 615.9962, found 615,9956.



II-6

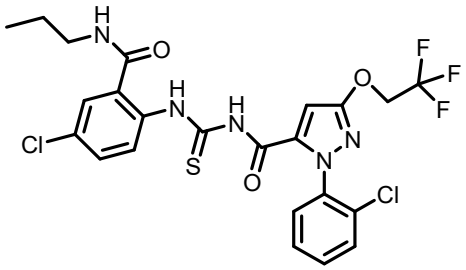
***N*-((4-chloro-2-(ethylcarbamoyl)phenyl)carbamothioyl)-1-(2,4,6-trichlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxamide(II-6, yield 34%, melting point: 108-117 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.23 (s, 1H, -CON**H**CS-), 11.88 (s, 1H, -Ph-N**H**CS-), 8.54 (s, 1H, -CON**H**-), 7.97 (d, J = 8.3 Hz, 1H, Ph-**H**), 7.92 (s, 2H, Ph-**H**), 7.53 (d, J = 8.3 Hz, 2H, Ph-**H**), 7.44 (s, 1H, Pyrazole-**H**), 4.91 (q, J = 8.6 Hz, 2H, -C**H**$_2$CF$_3$), 3.17 – 3.07 (m, 2H, -C**H**$_2$CH$_3$), 1.00 (t, J = 7.1 Hz, 3H, -CH$_2$C**H**$_3$).

^{13}C NMR (101 MHz, DMSO) δ 179.5, 165.2, 161.8, 157.6, 136.8, 135.7, 135.5, 134.7, 133.2, 130.9, 130.0(t), 129.3, 129.1, 128.0, 125.4, 122.6, 120.5, 97.1, 65.9, 65.5, 34.4, 14.7.

^{19}F NMR (376 MHz, DMSO-d_6) δ -72.71 (t, J = 8.7 Hz).

HRMS (ESI) Calculated for $C_{22}H_{16}Cl_4F_3N_5O_3S$ ([M + Na]$^+$)= 649.9572, found 649.9569.



II-7

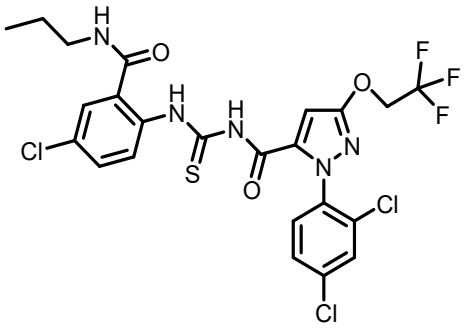
***N*-((4-chloro-2-(propylcarbamoyl)phenyl)carbamothioyl)-1-(2-chlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxamide(II-7, yield: 30%, melting point: 137-148 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.29 (s, 1H, -CON**H**CS-), 11.79 (s, 1H, -Ph-N**H**CS-), 8.56 (t, J = 5.4 Hz, 1H, -CON**H**-), 7.95 (d, J = 8.2 Hz, 1H, Ph-**H**), 7.64 – 7.50 (m, 6H, Ph-**H**), 7.22 (s, 1H, Pyrazole-**H**), 4.90 (q, J = 8.8 Hz, 2H, -C**H**$_2$CF$_3$), 3.06 (q, J = 6.5 Hz, 2H, -C**H**$_2$CH$_2$CH$_3$), 1.42 (q, J = 7.2 Hz, 2H , -CH$_2$C**H**$_2$CH$_3$), 0.83 (t, J = 7.3 Hz, 3H , -CH$_2$CH$_2$C**H**$_3$).

^{13}C NMR (101 MHz, DMSO) δ 179.8, 165.5, 161.0, 158.1, 138.2, 136.9, 135.3, 133.0, 131.1, 130.9, 130.8, 130.2(t), 130.0, 129.8, 129.6, 128.4, 128.0, 96.7, 65.8, 65.5, 41.3, 22.5, 11.9.

^{19}F NMR (376 MHz, DMSO-d_6) δ -72.77 (t, J = 8.9 Hz).

HRMS (ESI) Calculated for $C_{23}H_{20}Cl_2F_3N_5O_3S$ ([M + Na]$^+$)= 596.0508, found 596.0503.



II-8

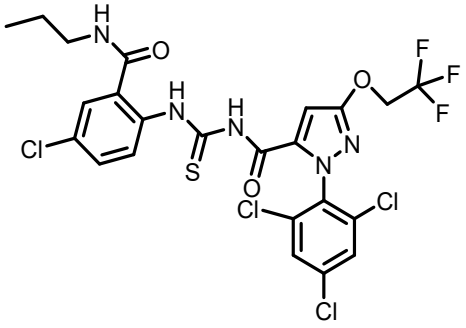
***N*-((4-chloro-2-(propylcarbamoyl)phenyl)carbamothioyl)-1-(2,4-dichlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxamide(II-8, yield: 31%, melting point: 184-195 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.29 (s, 1H, -CON**H**CS-), 11.81 (s, 1H, -Ph-N**H**CS-), 8.56 (t, J = 5.5 Hz, 1H, -CON**H**-), 7.97 (d, J = 9.4 Hz, 1H, Ph-**H**), 7.83 (d, J = 2.1 Hz, 1H, Ph-**H**), 7.65 – 7.51 (m, 4H, Ph-**H**), 7.25 (s, 1H, Pyrazole-**H**), 4.90 (q, J = 8.8 Hz, 2H, -C**H**$_2$CF$_3$), 3.06 (q, J = 6.7 Hz, 2H, -C**H**$_2$CH$_2$CH$_3$), 1.42 (h, J = 7.2 Hz, 2H, -CH$_2$C**H**$_2$CH$_3$), 0.83 (t, J = 7.4 Hz, 3H, -CH$_2$CH$_2$C**H**$_3$).

^{13}C NMR (101 MHz, DMSO) δ 179.6, 165.5, 161.2, 158.0, 141.8, 137.3, 136.9, 135.2, 134.8, 132.9, 132.2(t), 129.8, 129.4, 128.6, 128.0, 125.4, 122.6, 96.9, 65.9, 65.5, 41.3, 22.5, 11.9.

^{19}F NMR (376 MHz, DMSO-d_6) δ -72.73 (t, J = 8.8 Hz).

HRMS (ESI) Calculated for $C_{23}H_{19}Cl_3F_3N_5O_3S$ ([M + Na]$^+$)= 630.0118, found 630.0116.



II-9

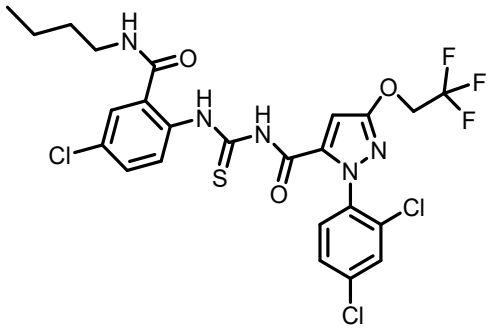
***N*-((4-chloro-2-(propylcarbamoyl)phenyl)carbamothioyl)-1-(2,4,6-trichlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxamide(II-9, yield: 31%, melting point: 141-149 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.17 (s, 1H, -CON**H**CS-), 11.87 (s, 1H, -Ph-N**H**CS-), 8.51 (t, J = 5.1 Hz, 1H, -CON**H**-), 7.91 (d, J = 6.5 Hz, 3H, Ph-**H**), 7.53 (d, J = 6.4 Hz, 2H, Ph-**H**), 7.43 (s, 1H, Pyrazole-**H**), 4.91 (q, J = 8.7 Hz, 2H, -C**H**$_2$CF$_3$), 3.06 (q, J = 6.4 Hz, 2H, -C**H**$_2$CH$_2$CH$_3$), 1.42 (h, J = 7.0 Hz, 2H, -CH$_2$C**H**$_2$CH$_3$), 0.83 (t, J = 7.3 Hz, 3H, -CH$_2$CH$_2$C**H**$_3$).

^{13}C NMR (101 MHz, DMSO) δ 179.7, 165.4, 161.8, 157.6, 136.8, 135.7, 135.5, 135.1, 134.8, 133.5(t), 129.1, 128.0, 125.4, 122.6, 97.1, 79.6, 65.9, 65.5, 65.2, 41.3, 22.5, 11.9, 11.8.

^{19}F NMR (376 MHz, DMSO-d_6) δ -72.69 (t, J = 8.9 Hz).

HRMS (ESI) Calculated for $C_{23}H_{18}Cl_4F_3N_5O_3S$ ([M + Na]$^+$)= 663.9729, found 663.9727.



II-10

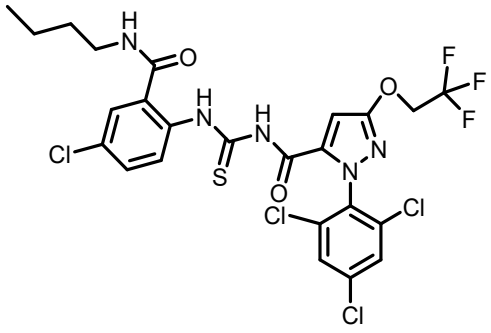
***N*-((2-(butylcarbamoyl)-4-chlorophenyl)carbamothioyl)-1-(2,4-dichlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxamide(II-10, yield: 32%, melting point: 179-191 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.28 (s, 1H, -CON**H**CS-), 11.80 (s, 1H, -Ph-N**H**CS-), 8.53 (t, J = 5.4 Hz, 1H, -CON**H**-), 7.95 (d, J = 9.4 Hz, 1H, Ph-**H**), 7.82 (d, J = 2.0 Hz, 1H, Ph-**H**), 7.65 – 7.52 (m, 4H, Ph-**H**), 7.26 (s, 1H, Pyrazole-**H**), 4.90 (q, J = 8.8 Hz, 2H, -C**H**$_2$CF$_3$), 3.10 (q, J = 6.6 Hz, 2H, -C**H**$_2$CH$_2$CH$_2$CH$_3$), 1.40 (p, J = 6.9 Hz, 2H, -CH$_2$C**H**$_2$CH$_2$CH$_3$), 1.29 – 1.23 (m, 2H, -CH$_2$CH$_2$C**H**$_2$CH$_3$), 0.85 (t, J = 7.3 Hz, 3H, -CH$_2$CH$_2$CH$_2$C**H**$_3$).

^{13}C NMR (101 MHz, DMSO) δ 179.7, 175.1, 165.4, 161.2, 158.0, 137.3, 136.9, 135.2, 134.8, 133.0, 132.2(t), 129.8, 129.5, 128.7, 128.0, 125.4, 122.6, 120.5, 97.0, 65.9, 65.5, 31.3, 20.0, 14.1.

^{19}F NMR (376 MHz, DMSO-d_6) δ -72.73 (t, J = 8.8 Hz).

HRMS (ESI) Calculated for $C_{24}H_{21}Cl_3F_3N_5O_3S$ ([M + Na]$^+$)= 644.0275, found 644.0274.



II-11

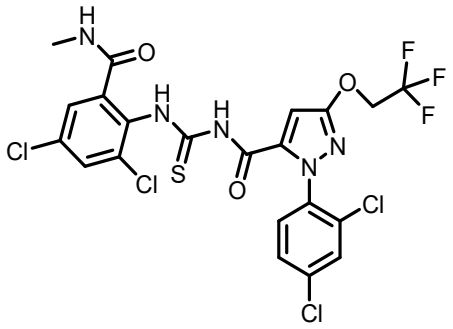
***N*-((2-(butylcarbamoyl)-4-chlorophenyl)carbamothioyl)-1-(2,4,6-trichlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxamide(II-11, yield: 33%, melting point: 169-172 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.16 (s, 1H, -CON**H**CS-), 11.87 (s, 1H, -Ph-N**H**CS-), 8.48 (t, J = 5.3 Hz, 1H, -CON**H**-), 7.96 – 7.87 (m, 3H, Ph-**H**), 7.57 – 7.50 (m, 2H, Ph-**H**), 7.44 (s, 1H, Pyrazole-**H**), 4.91 (q, J = 8.8 Hz, 2H, -C**H**$_2$CF$_3$), 3.10 (q, J = 6.5 Hz, 2H, -C**H**$_2$CH$_2$CH$_2$CH$_3$), 1.40 (p, J = 6.8 Hz, 2H, -CH$_2$C**H**$_2$CH$_2$CH$_3$), 1.30 – 1.23 (m, 2H, -CH$_2$CH$_2$C**H**$_2$CH$_3$), 0.85 (t, J = 7.3 Hz, 3H, -CH$_2$CH$_2$CH$_2$C**H**$_3$).

^{13}C NMR (101 MHz, DMSO) δ 179.7, 165.4, 161.8, 157.5, 136.8, 135.7, 135.6, 135.2, 134.8, 133.5, 131.0(t), 130.0, 129.6, 129.1, 128.0, 125.4, 122.6, 97.1, 65.9, 65.5, 39.1, 31.3, 20.0, 14.1.

^{19}F NMR (376 MHz, DMSO-d_6) δ -72.70 (t, J = 9.0 Hz).

HRMS (ESI) Calculated for $C_{24}H_{20}Cl_4F_3N_5O_3S$ ([M + Na]$^+$)= 677.9885, found 677.9880.



II-12

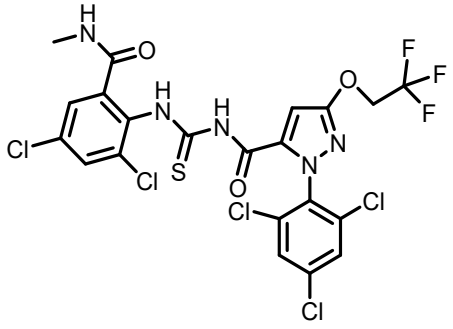
***N*-((2,4-dichloro-6-(methylcarbamoyl)phenyl)carbamothioyl)-1-(2,4-dichlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxamide(II-12, yield: 31%, melting point: 127-130 ℃, white solid)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.00 (s, 1H, -CON**H**CS-), 11.57 (s, 1H, -Ph-N**H**CS-), 8.27 (d, J = 4.6 Hz, 1H, -CON**H**-), 7.87 (d, J = 2.1 Hz, 1H, Ph-**H**), 7.83 (d, J = 2.2 Hz, 1H, Ph-**H**), 7.67 (d, J = 8.5 Hz, 1H, Ph-**H**), 7.61 (dd, J = 8.5, 2.1 Hz, 1H, Ph-**H**), 7.50 (d, J = 2.2 Hz, 1H, Ph-**H**), 7.32 (s, 1H, Pyrazole-**H**), 4.90 (q, J = 8.8 Hz, 2H, -C**H**$_2$CF$_3$), 2.64 (d, J = 4.5 Hz, 3H, -NHC**H**$_3$).

^{13}C NMR (101 MHz, DMSO) δ 180.7, 164.9, 161.2, 158.5, 138.5, 137.4, 136.6, 134.9, 134.3, 133.2, 133.0, 132.3, 131.1(t), 129.8, 128.7, 127.6, 97.0, 65.9, 65.5, 40.6, 26.4.

^{19}F NMR (376 MHz, DMSO-d6) δ -72.71 (t, J = 8.8 Hz).

HRMS (ESI) Calculated for $C_{21}H_{14}Cl_4F_3N_5O_3S$ ([M + Na]$^+$)= 635.9416, found 635.9410.



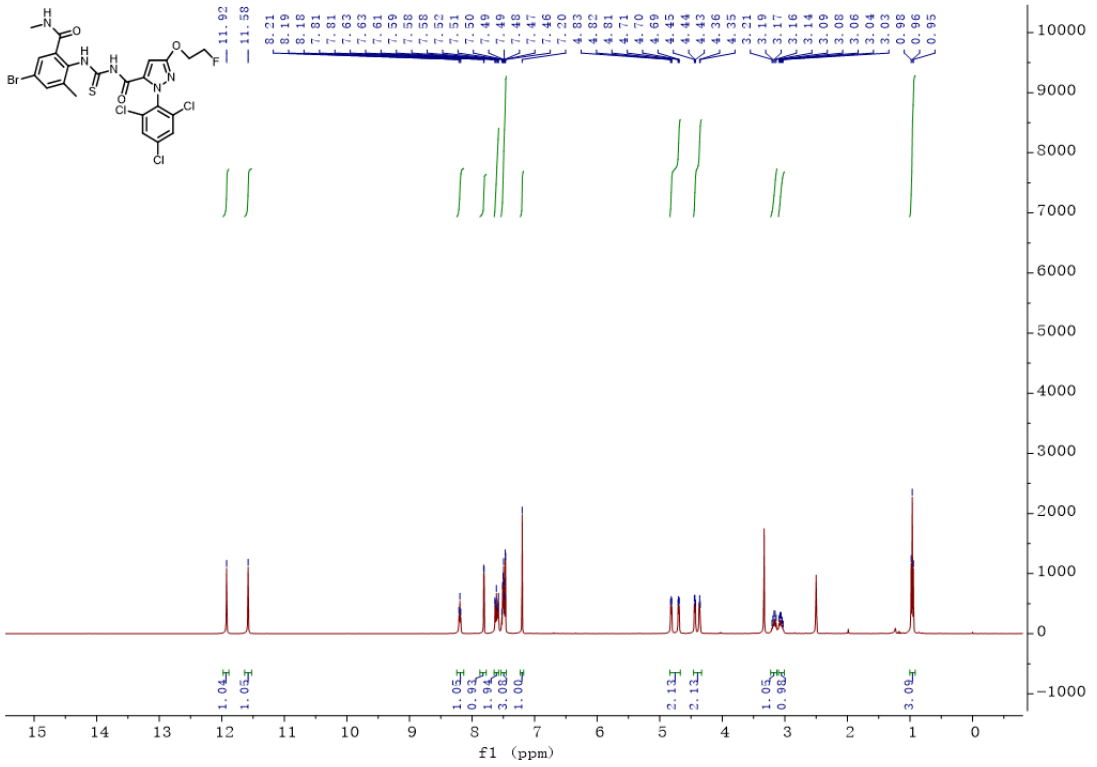
II-13

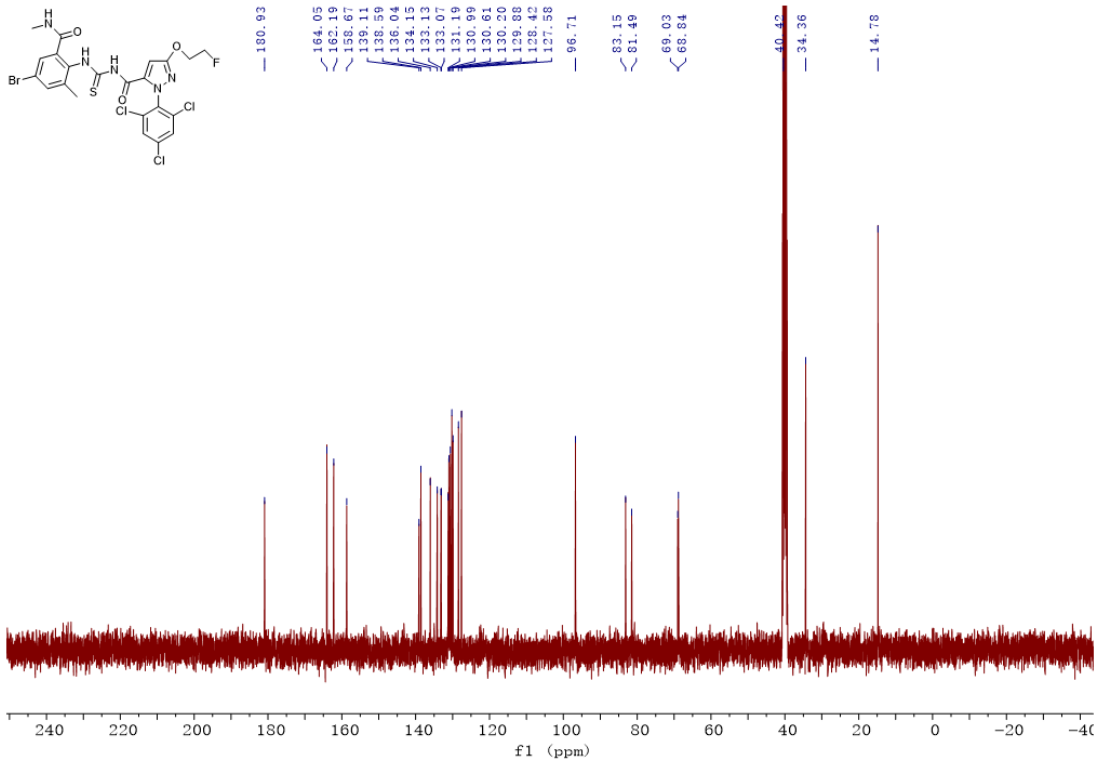
***N*-((2,4-dichloro-6-(methylcarbamoyl)phenyl)carbamothioyl)-1-(2,4,6-trichlorophenyl)-3-(2,2,2-trifluoroethoxy)-1H-pyrazole-5-carboxamide(II-13, yield: 31%, melting point: 148-159 ℃, white solid)**

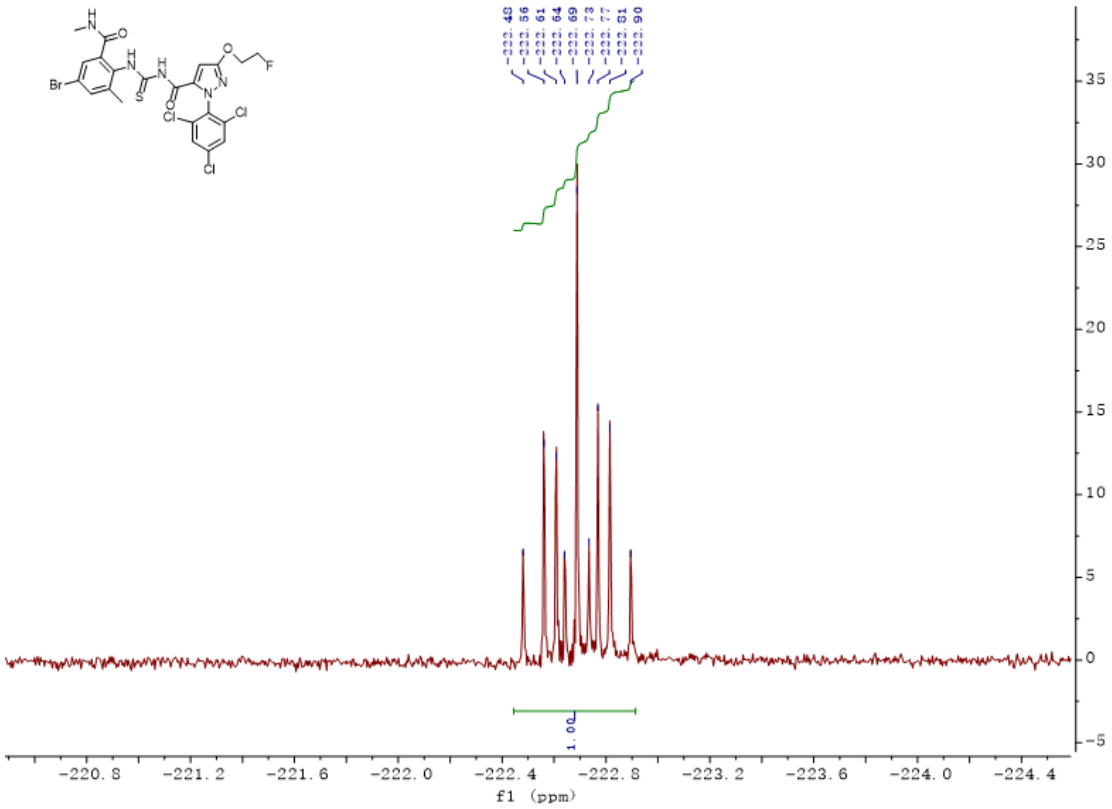
^{1}H NMR (400 MHz, DMSO-d_6) δ 13.68 (s, 2H, -CON**H**CS-), 10.42 (s, 1H, -Ph-N**H**CS-), 8.45 – 8.22 (m, 1H, -CON**H**-), 7.83 (d, J = 5.5 Hz, 3H, Ph-**H**), 7.48 (s, 1H, Ph-**H**), 6.98 (s, 1H, Pyrazole-**H**), 4.98 – 4.81 (m, 2H, -C**H**$_2$CF$_3$), 2.82 – 2.59 (m, 3H, -NHC**H**$_3$).

^{13}C NMR (101 MHz, DMSO) δ 172.4, 165.5, 161.8, 156.5, 138.8, 138.7, 135.8, 135.3, 135.0, 134.0, 132.5, 131.0(t), 128.7, 127.2, 94.8, 65.7, 65.4, 31.4, 26.5, 22.5, 14.4.
^{19}F NMR (376 MHz, DMSO-d_6) δ -72.77 (t, J = 9.0 Hz).
HRMS (ESI) Calculated for $C_{21}H_{13}Cl_5F_3N_5O_3S$ ($[M + Na]^+$)= 669.9026, found 669.9024.

5. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectrum of some title compounds I-1~17 and II-1~13



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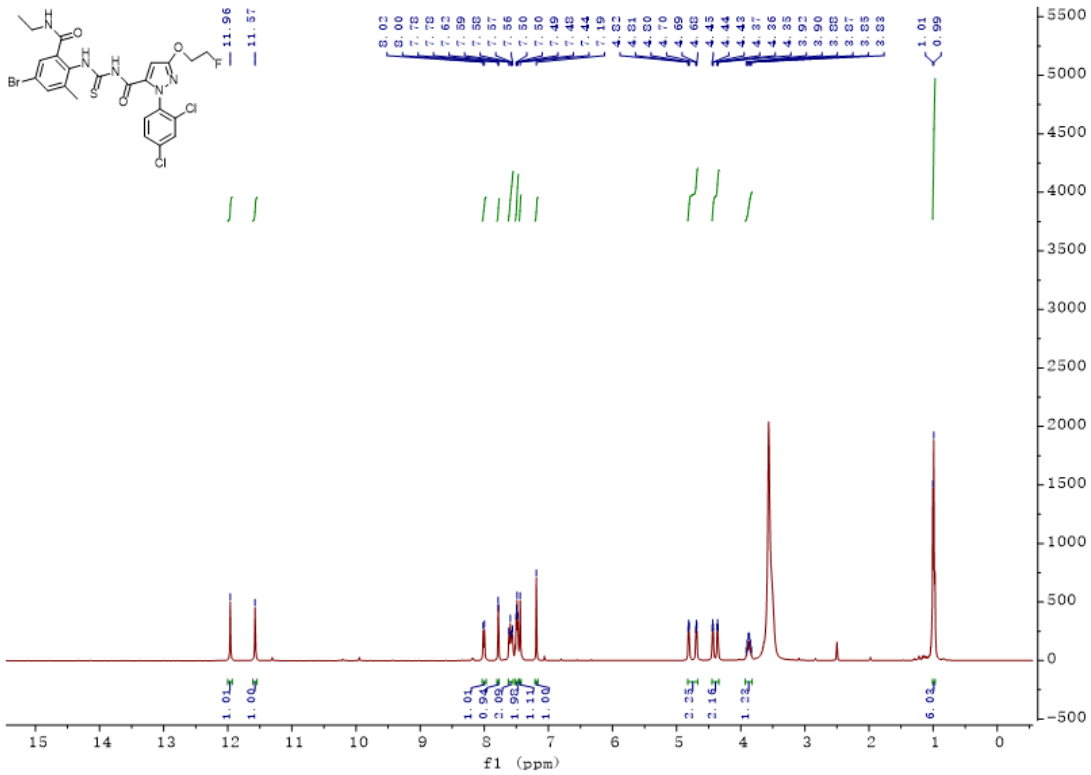
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1.01
1.00
1.01
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1.98
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1.00
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1.32
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4
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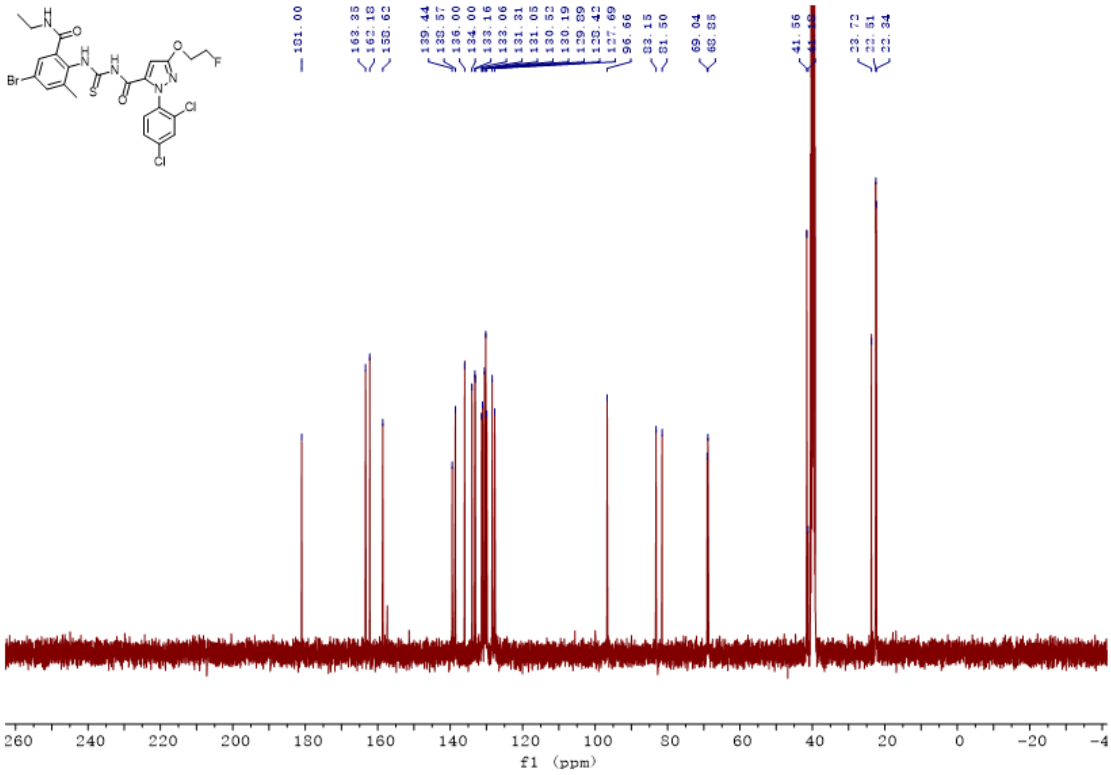
f1 (ppm)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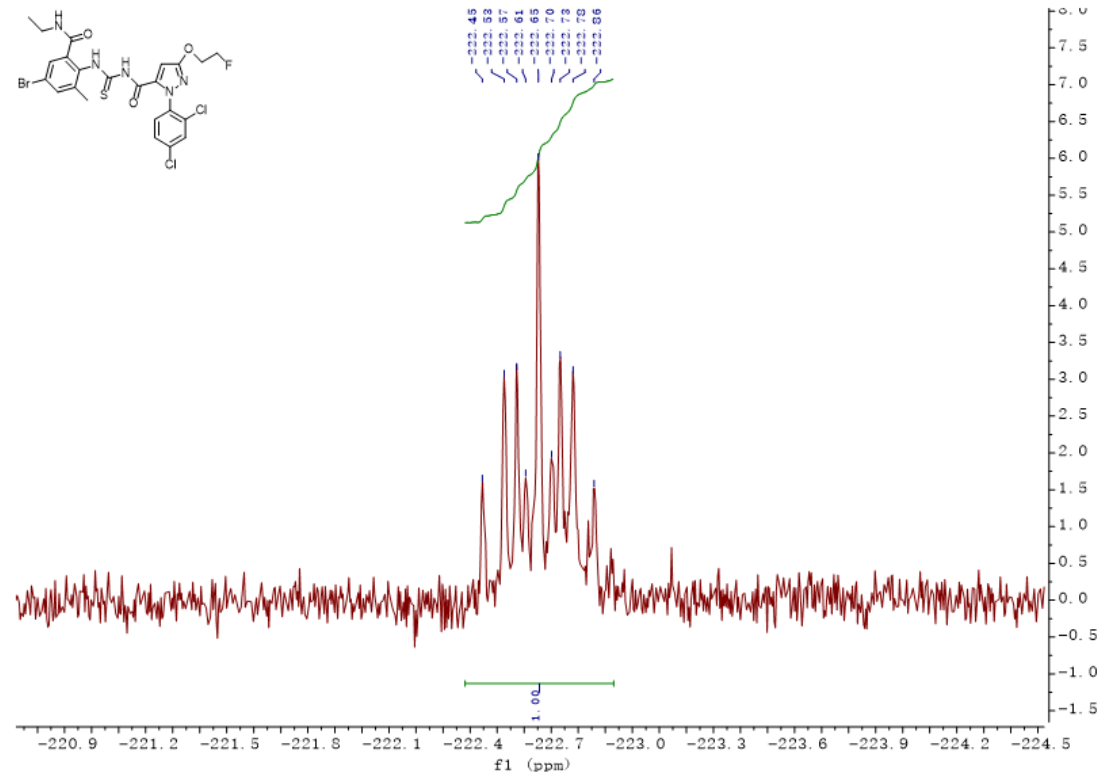
f1 (ppm)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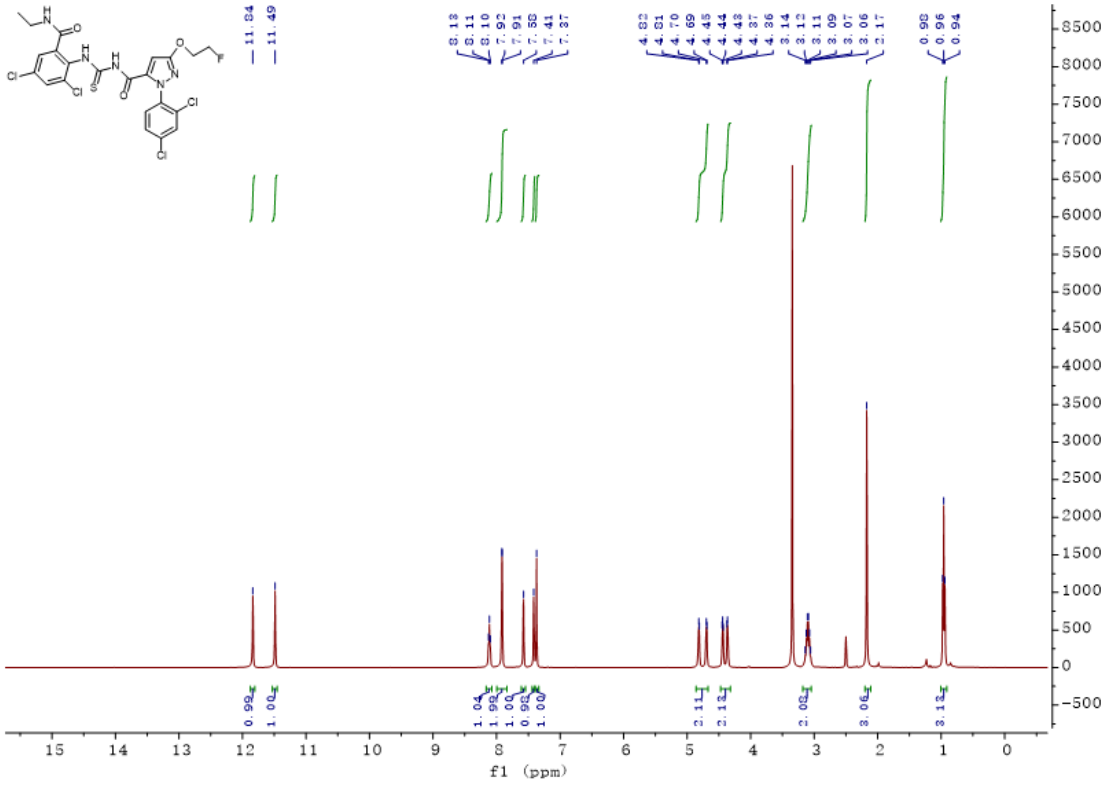
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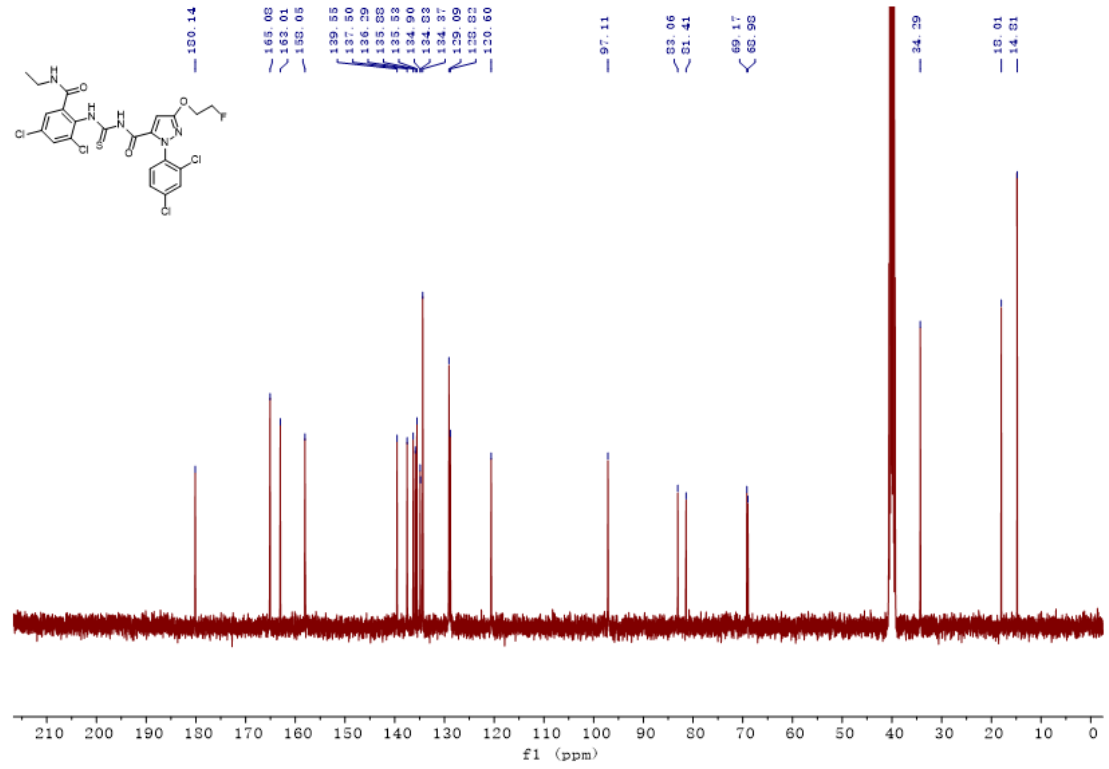
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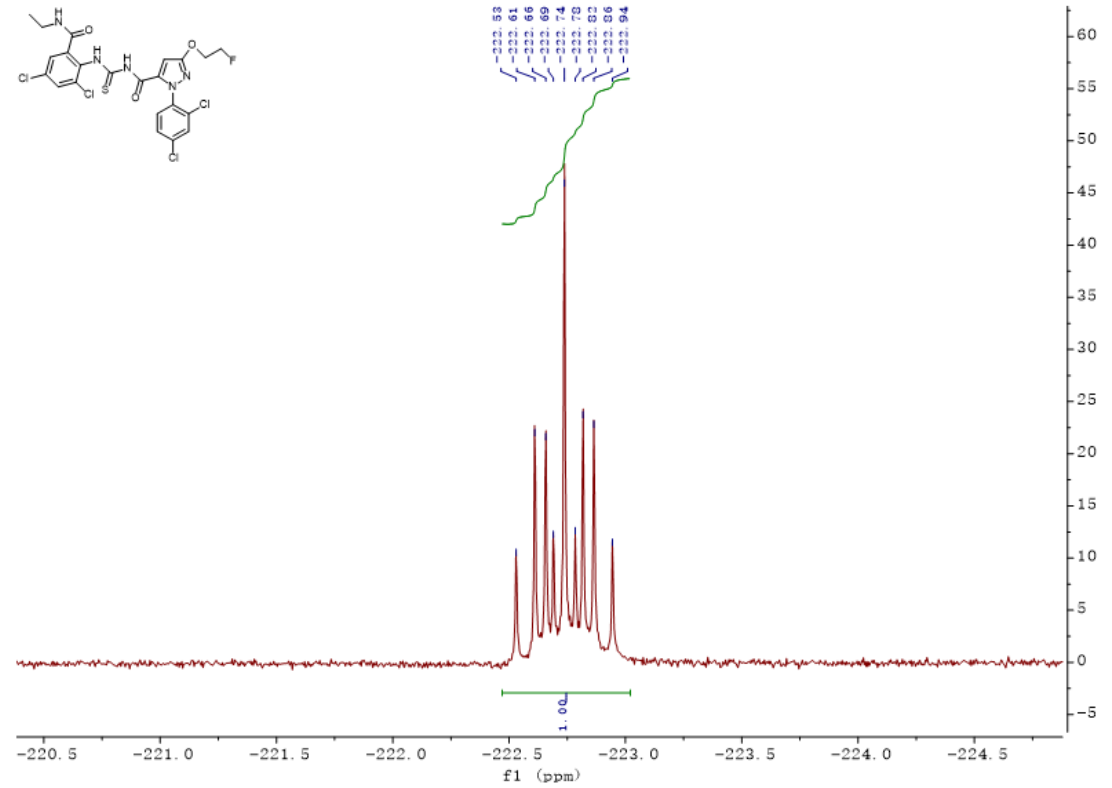
f1 (ppm)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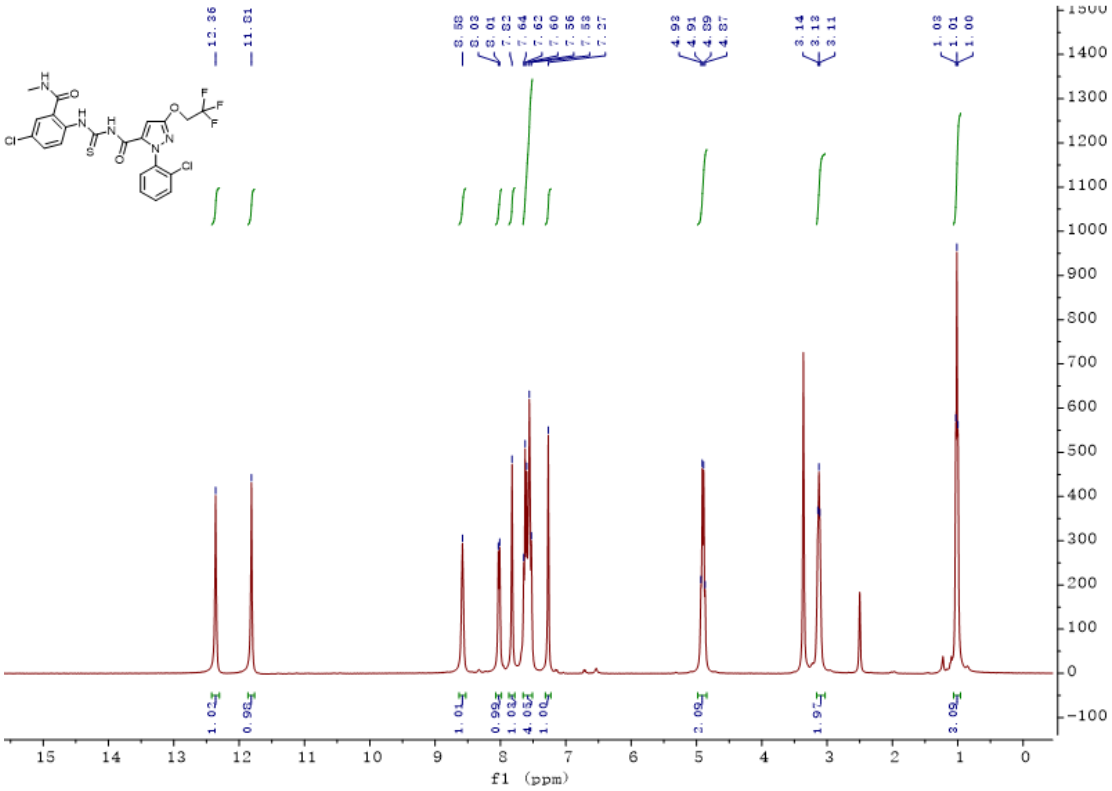
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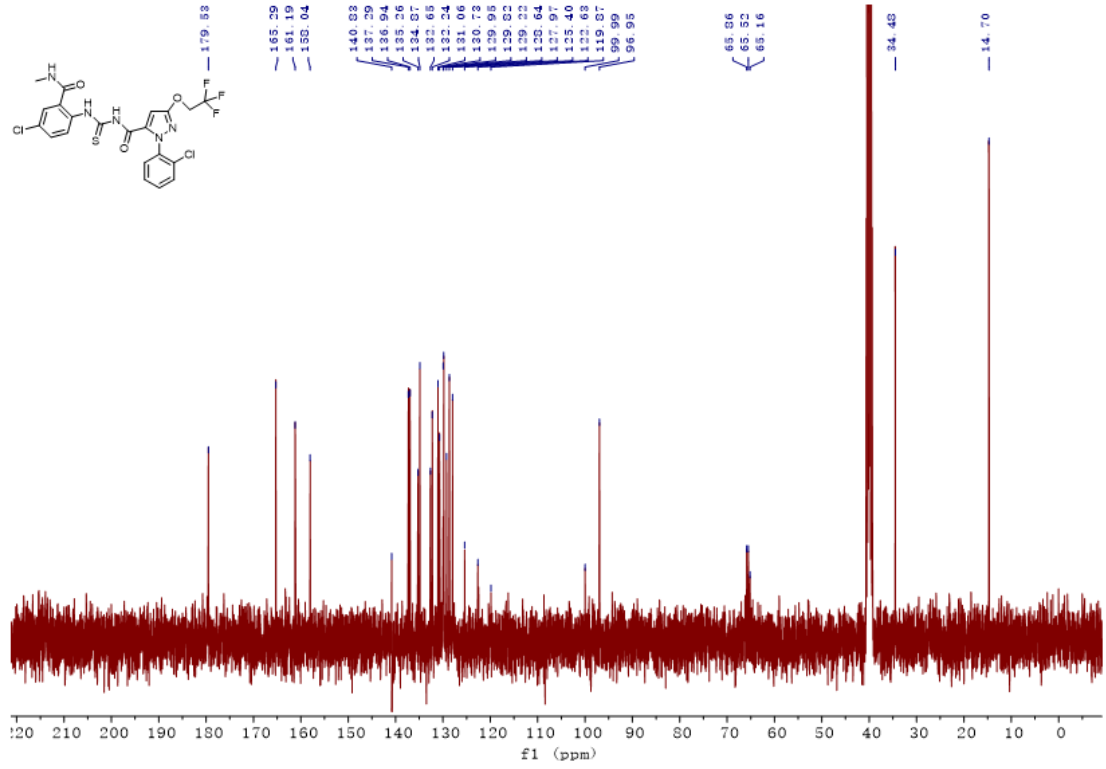
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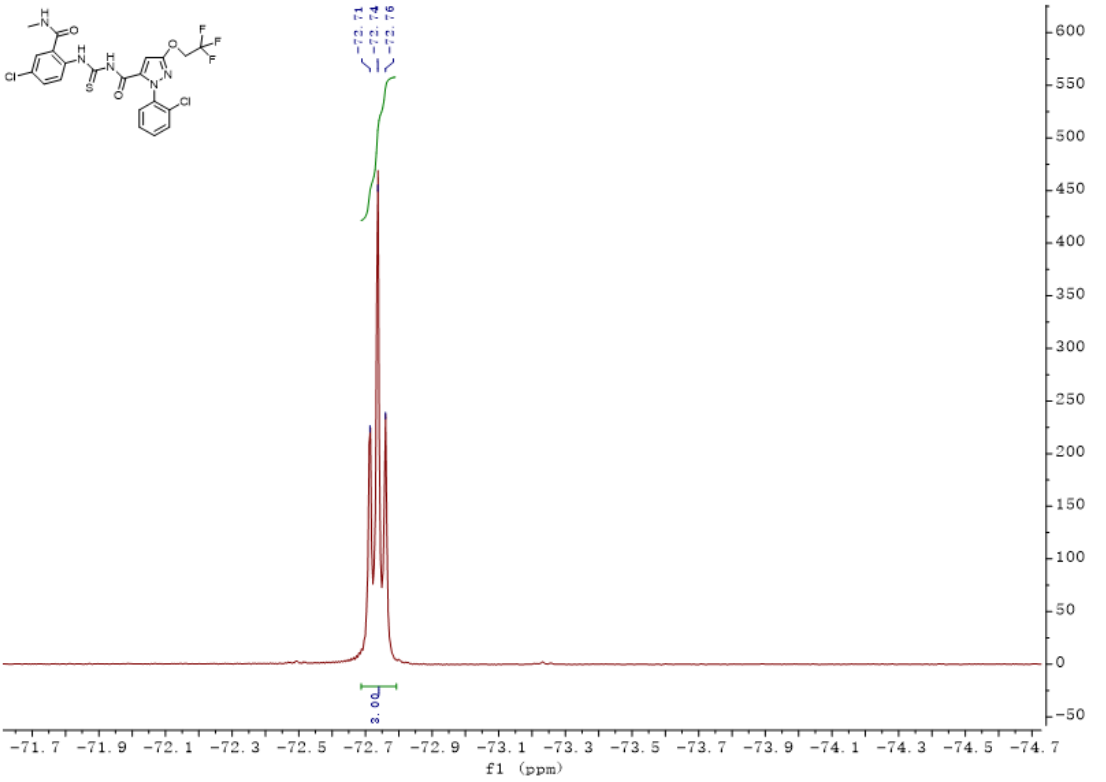
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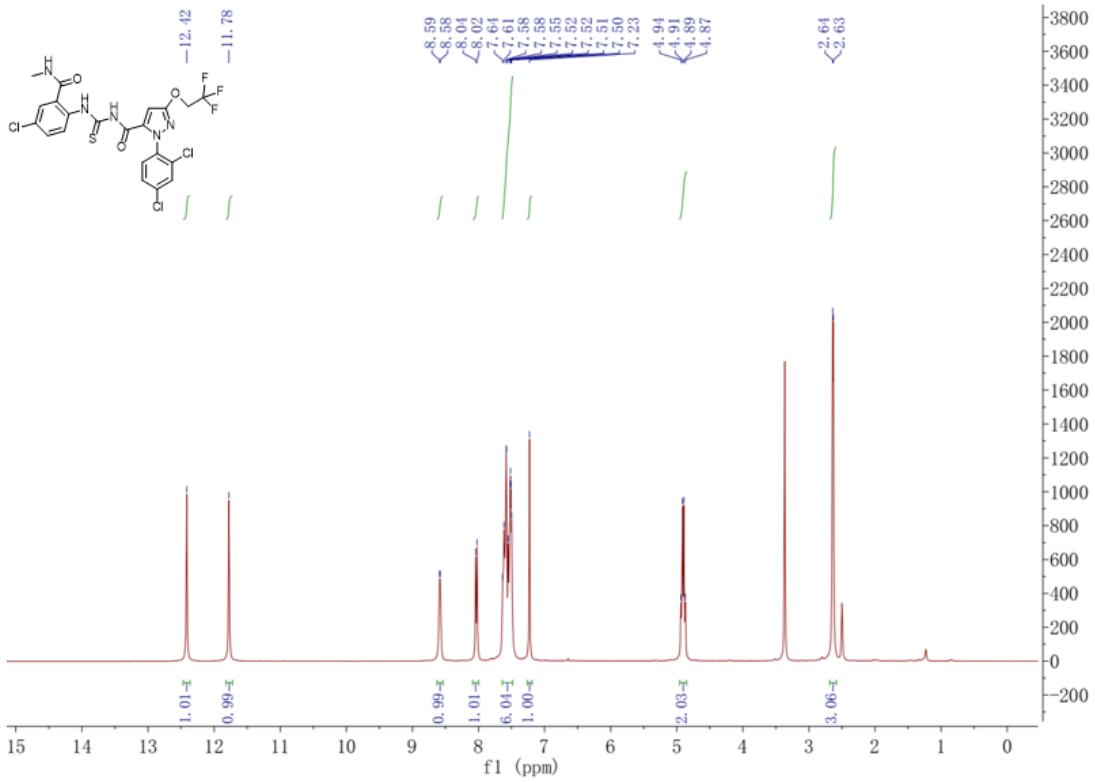
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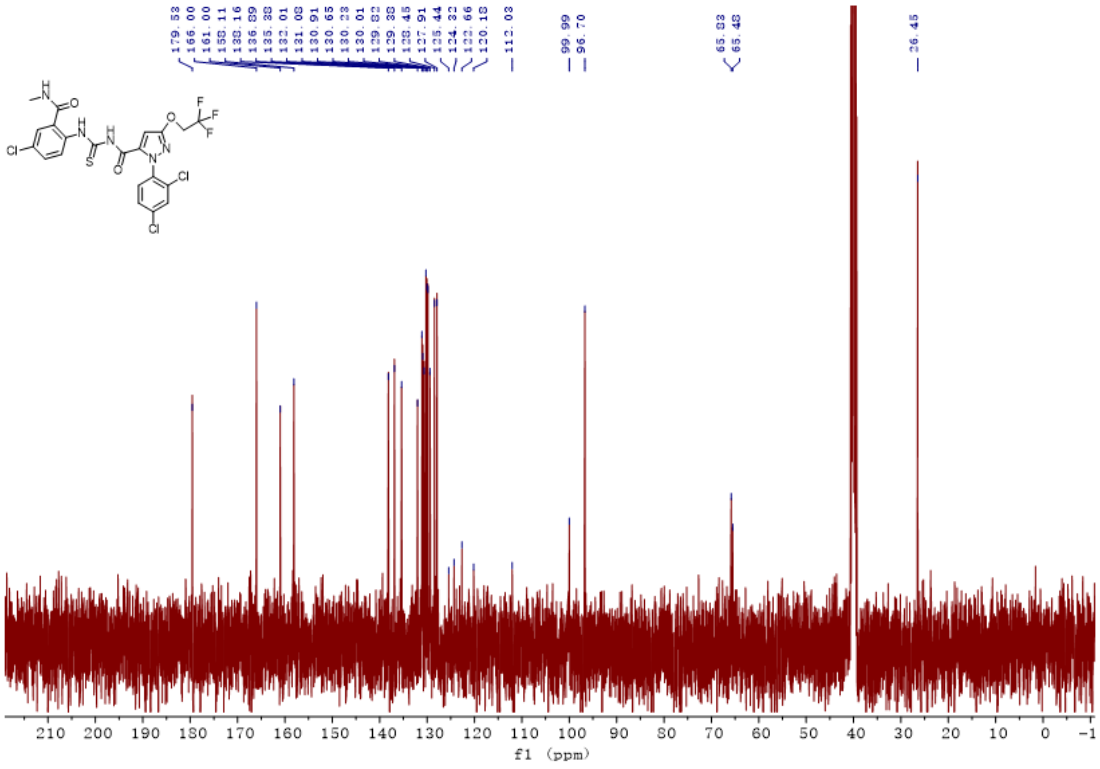
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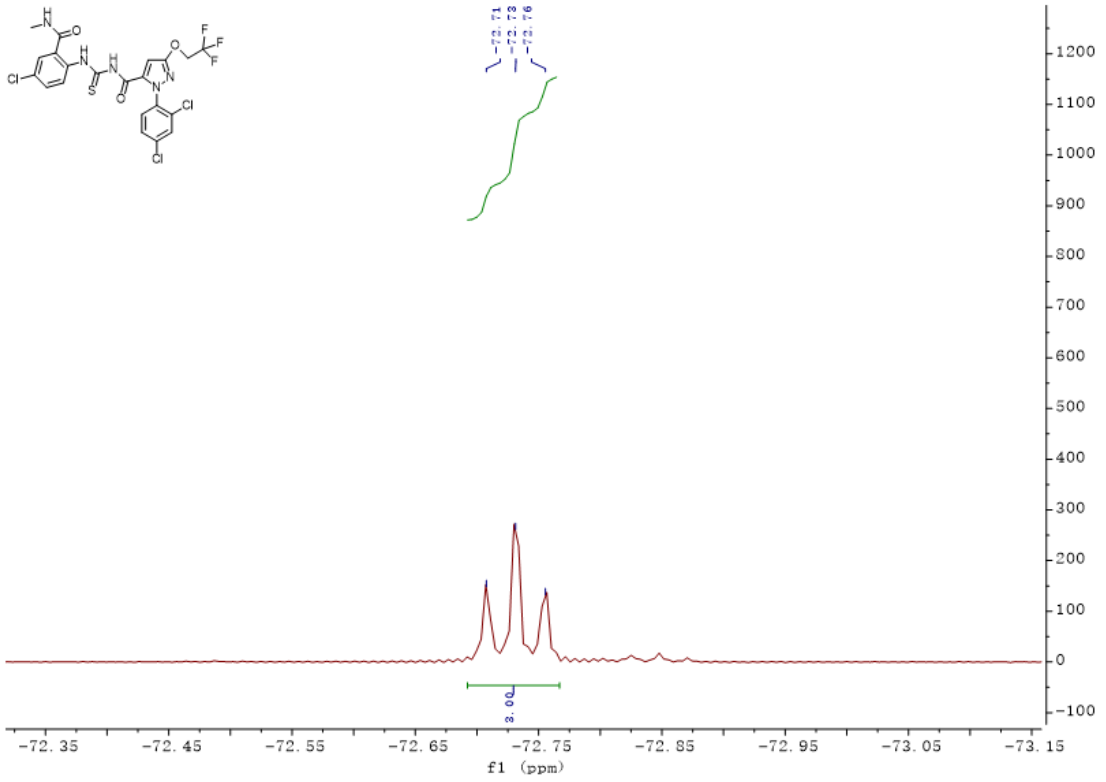
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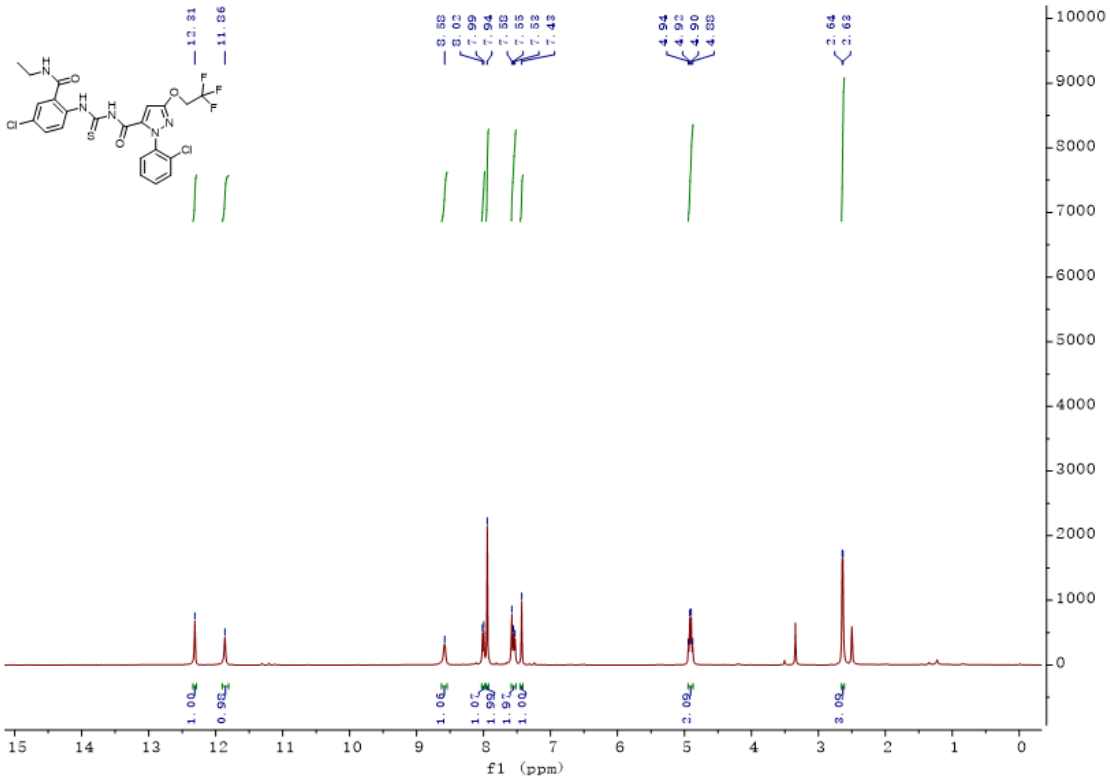
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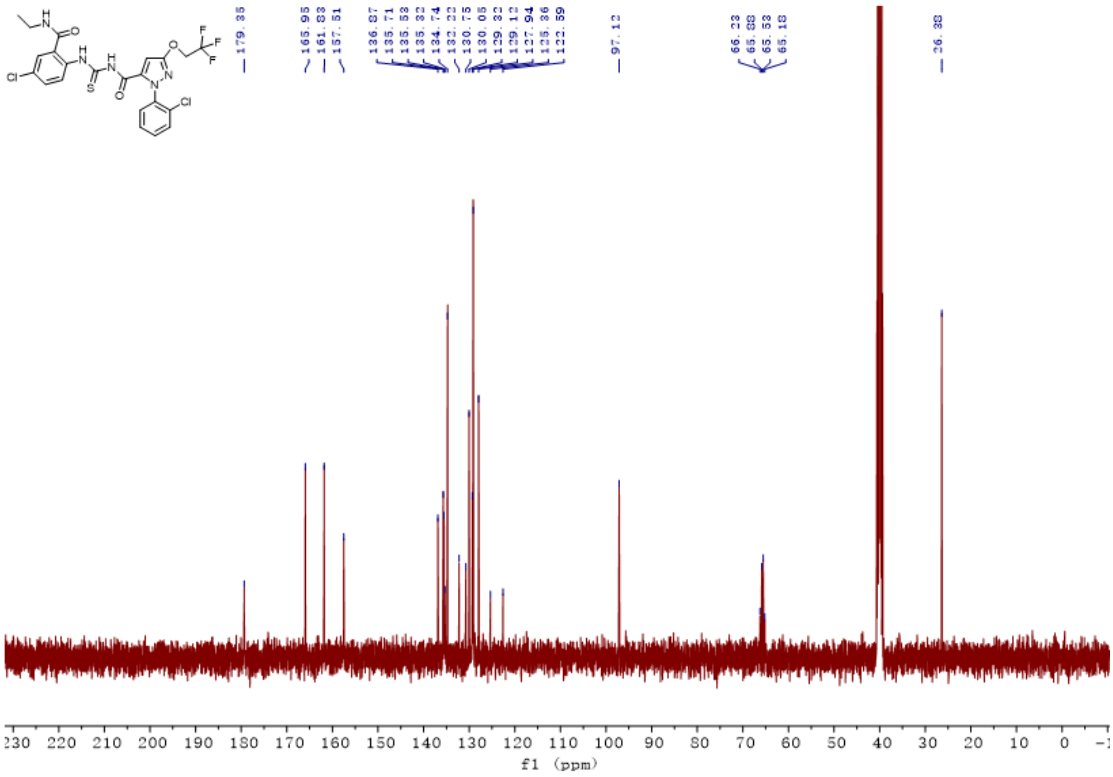
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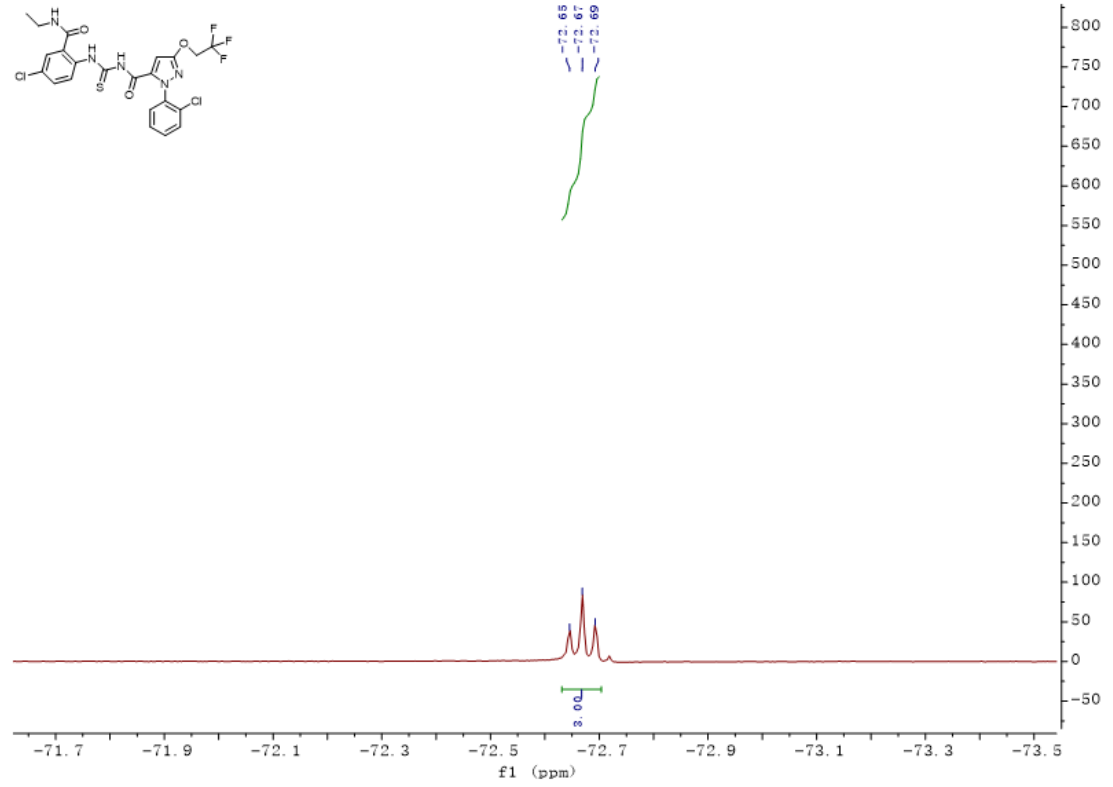
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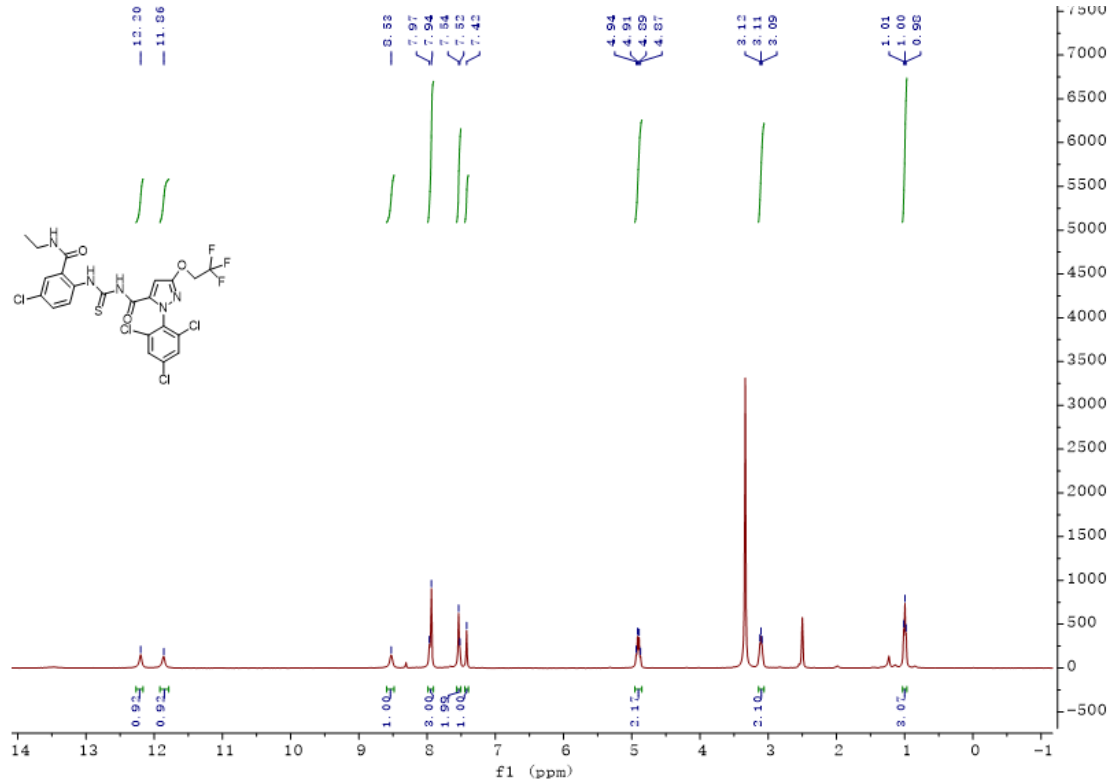
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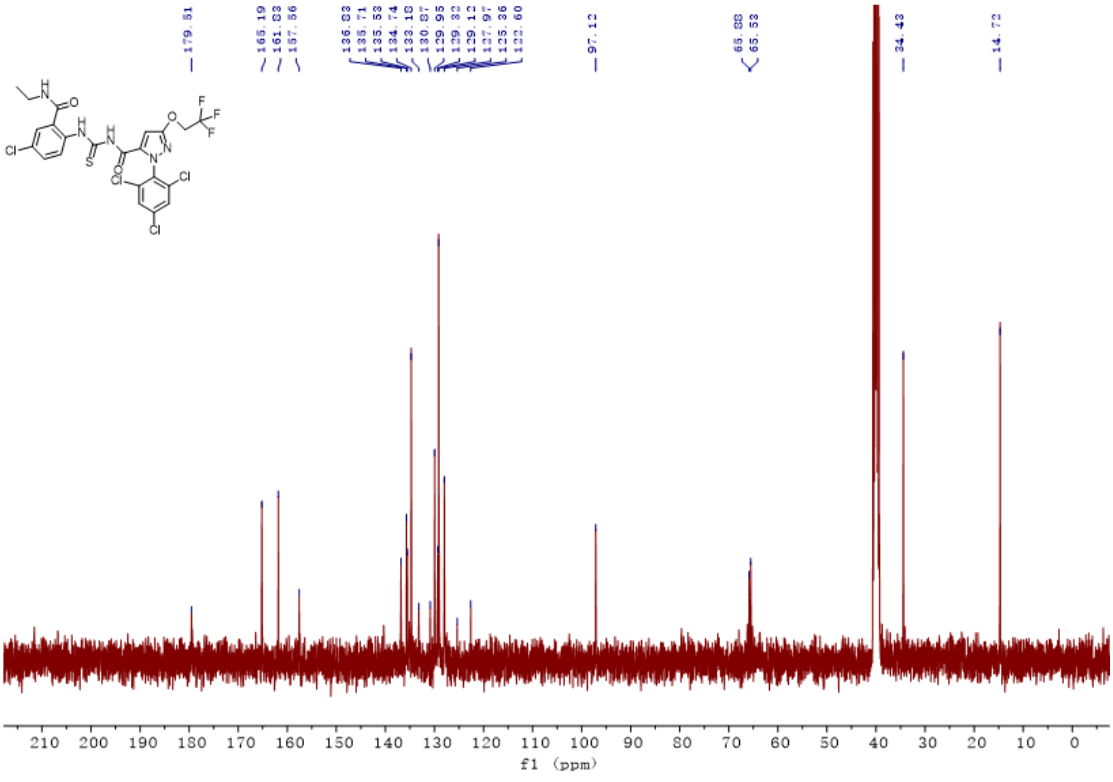
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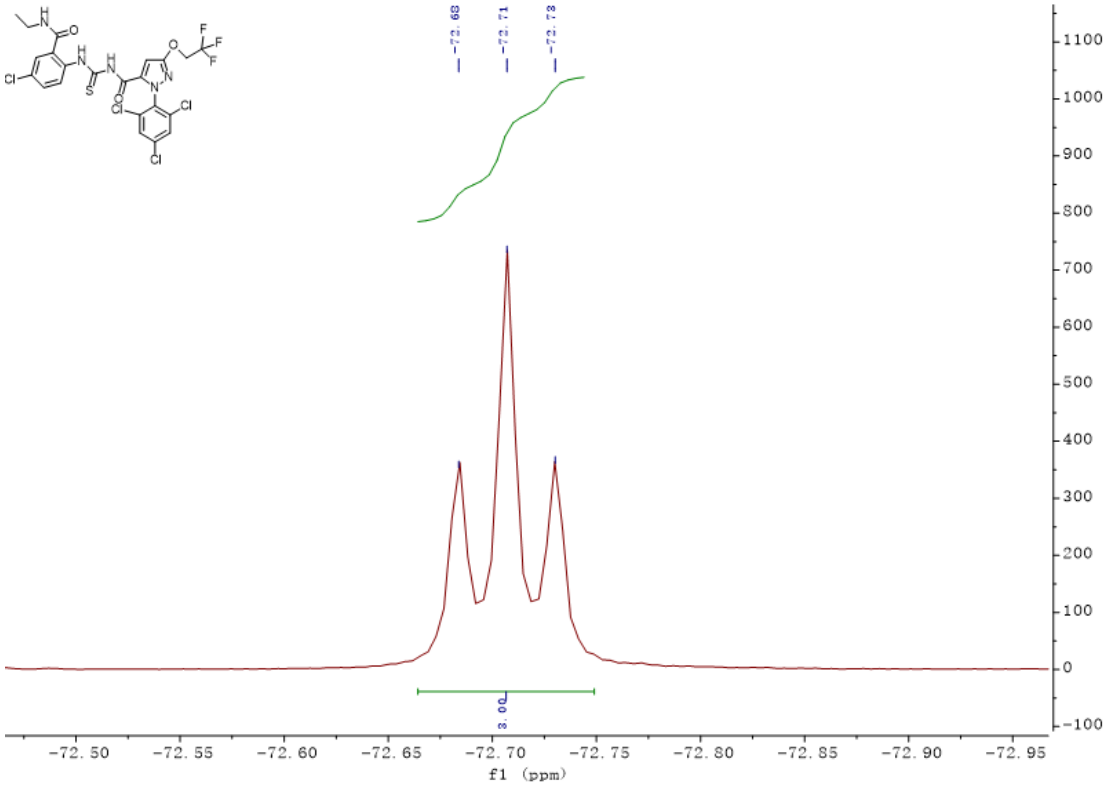
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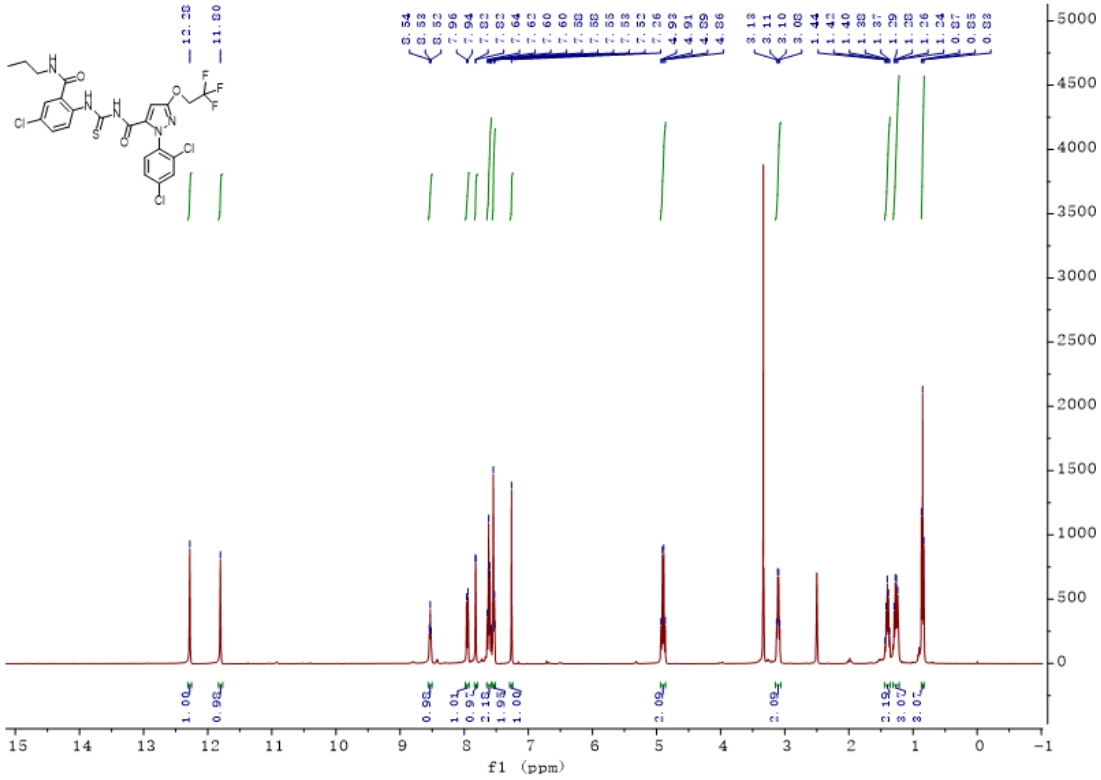
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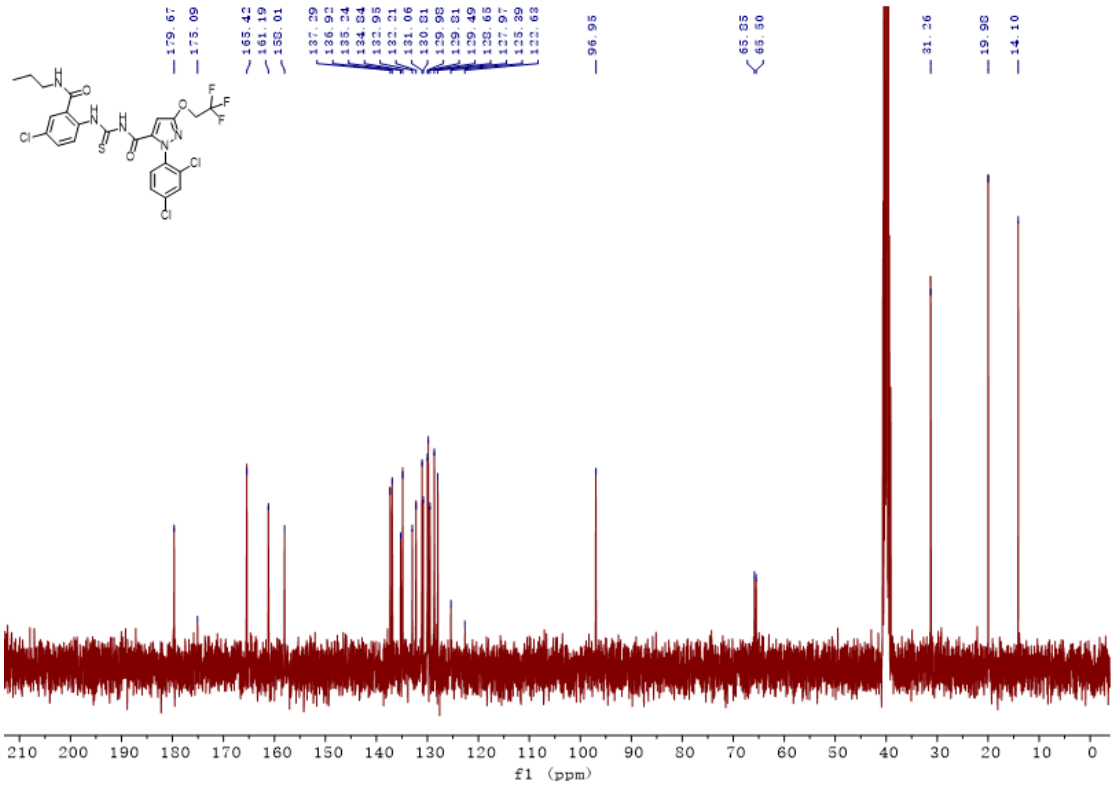
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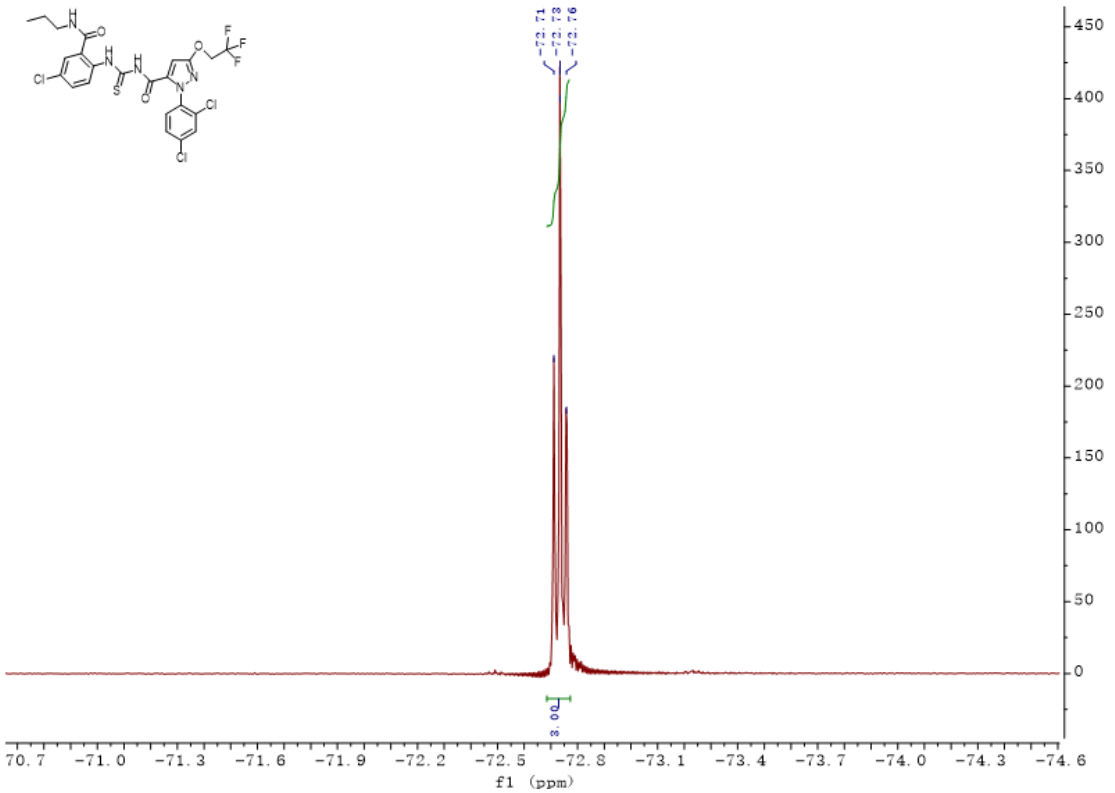
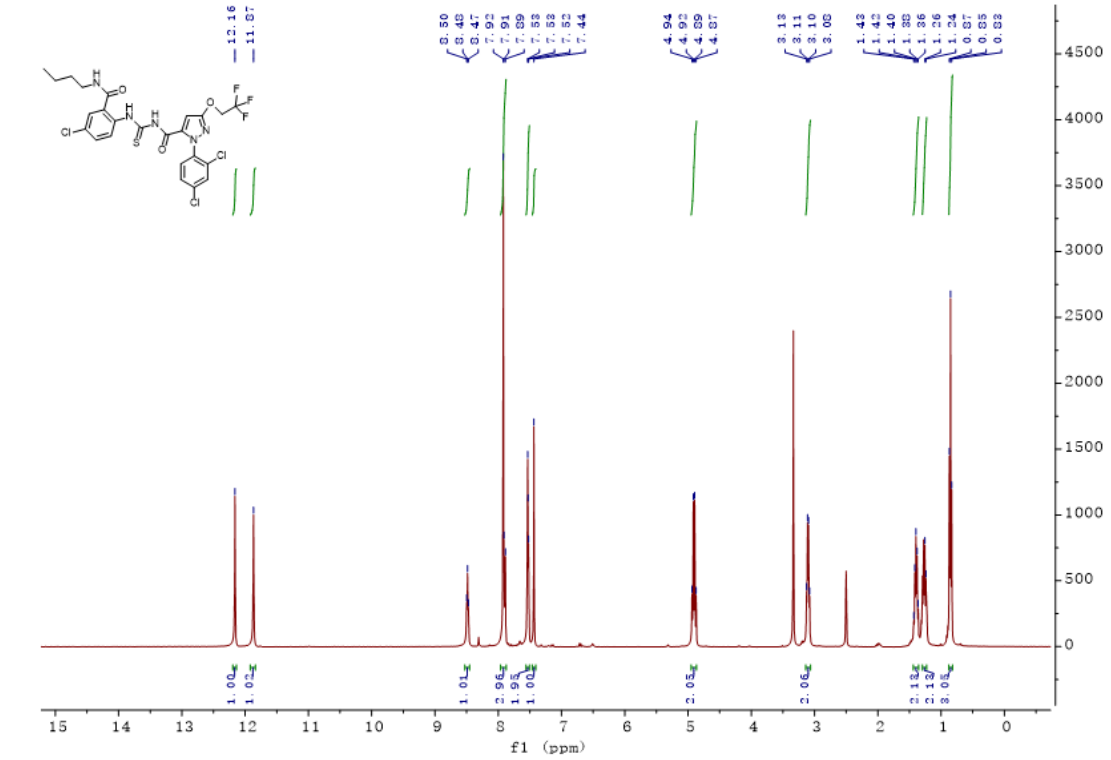
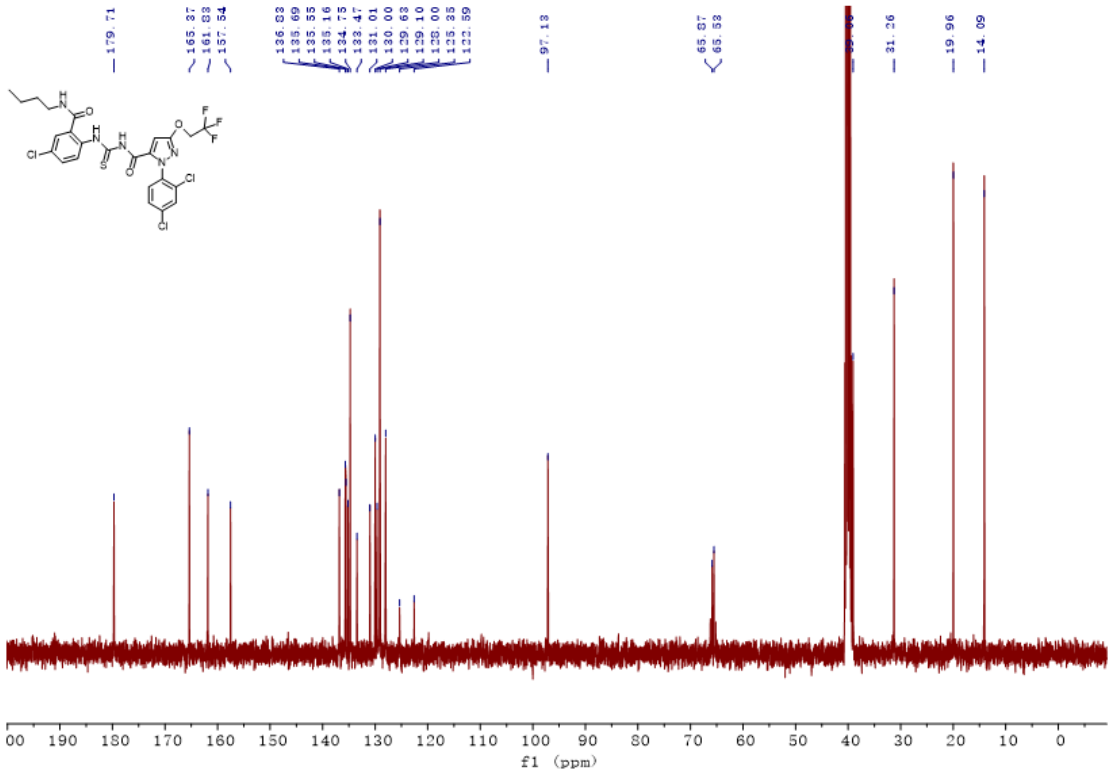
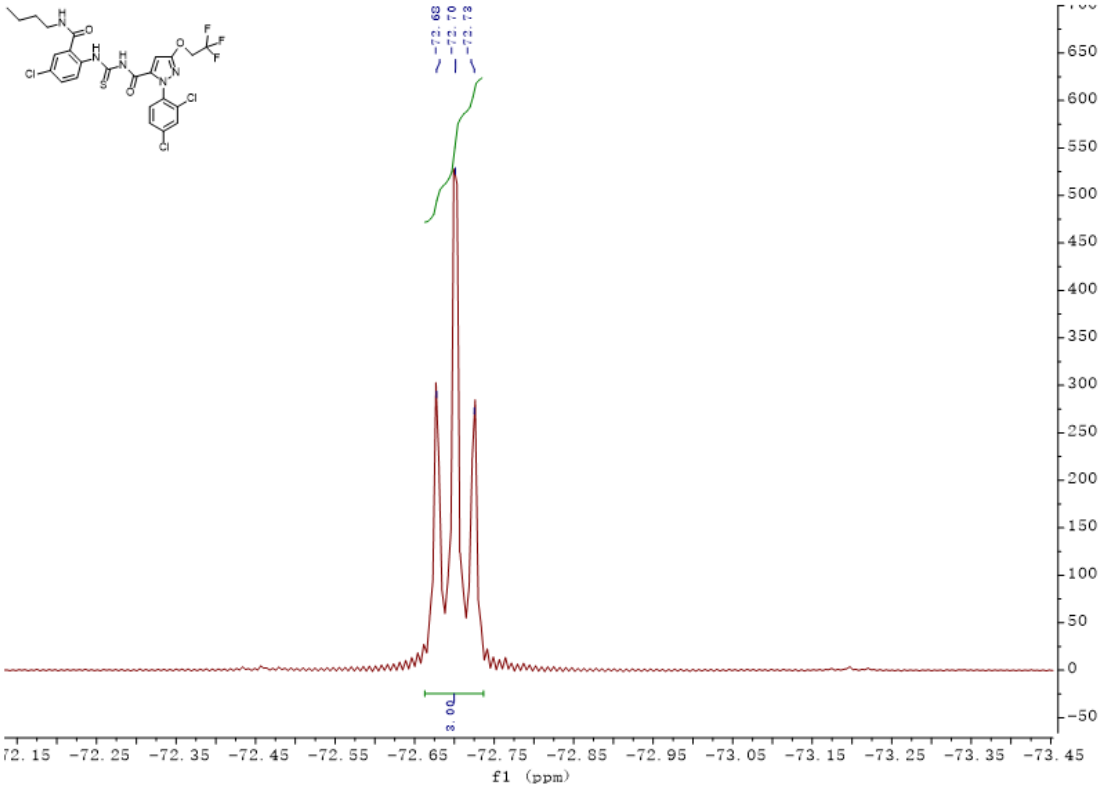
125.39
122.63
96.95
65.85
65.50
31.26
19.98
14.10
f1 (ppm)


-72.71
-72.73
-72.76
3.00
f1 (ppm)


12.16
11.87
8.50
8.48
8.47
7.92
7.91
7.89
7.53
7.52
7.44
4.94
4.93
4.89
4.87
3.13
3.11
3.10
3.08
1.43
1.42
1.40
1.38
1.36
1.26
1.24
0.87
0.85
0.83
f1 (ppm)


179.71
165.37
161.83
157.54
136.83
135.69
135.55
135.16
134.75
133.47
131.01
130.00
129.63
129.10
128.00
125.35
122.59
97.18
65.87
65.53
31.26
19.96
14.09
f1 (ppm)



6. The original data of the LC_{50} value of CHL's insecticidal activity against *P. xylostella*.

Compd.	Insecticidal activities at a concentration of (mg/L) (%)						
	50	**25**	**10**	**5**	**0.5**	**0.05**	**0.01**
I-14	100	100	100	100	77 ± 5	50 ± 5	0
I-15	100	100	100	83 ± 5	60 ± 7	37 ± 5	0
I-17	100	100	100	90 ± 0	73 ± 6	40 ± 4	0
CHL	100	100	100	100	100	53 ± 3	13 ± 5