



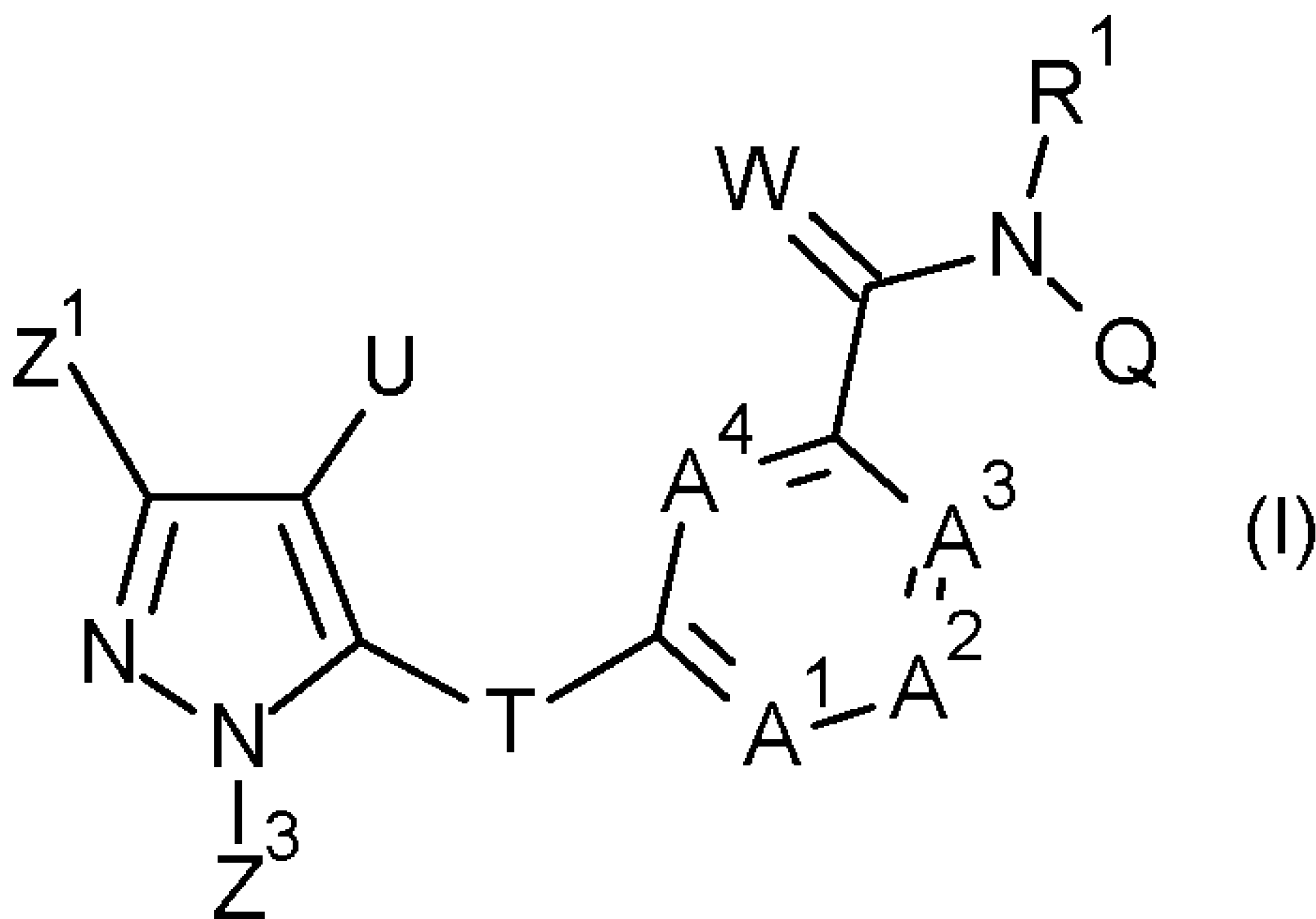
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(54) Titre : DERIVES DE PYRAZOLE A ACTIVITE PESTICIDE
(54) Title: PESTICIDALLY ACTIVE PYRAZOLE DERIVATIVES



(57) Abrégé/Abstract:

Compounds of formula (I), as defined herein, to processes for preparing them, to pesticidal, in particular insecticidal, acaricidal, molluscicidal and nematocidal compositions comprising them and to methods of using them to combat and control pests such as insect, acarine, mollusc and nematode pests.

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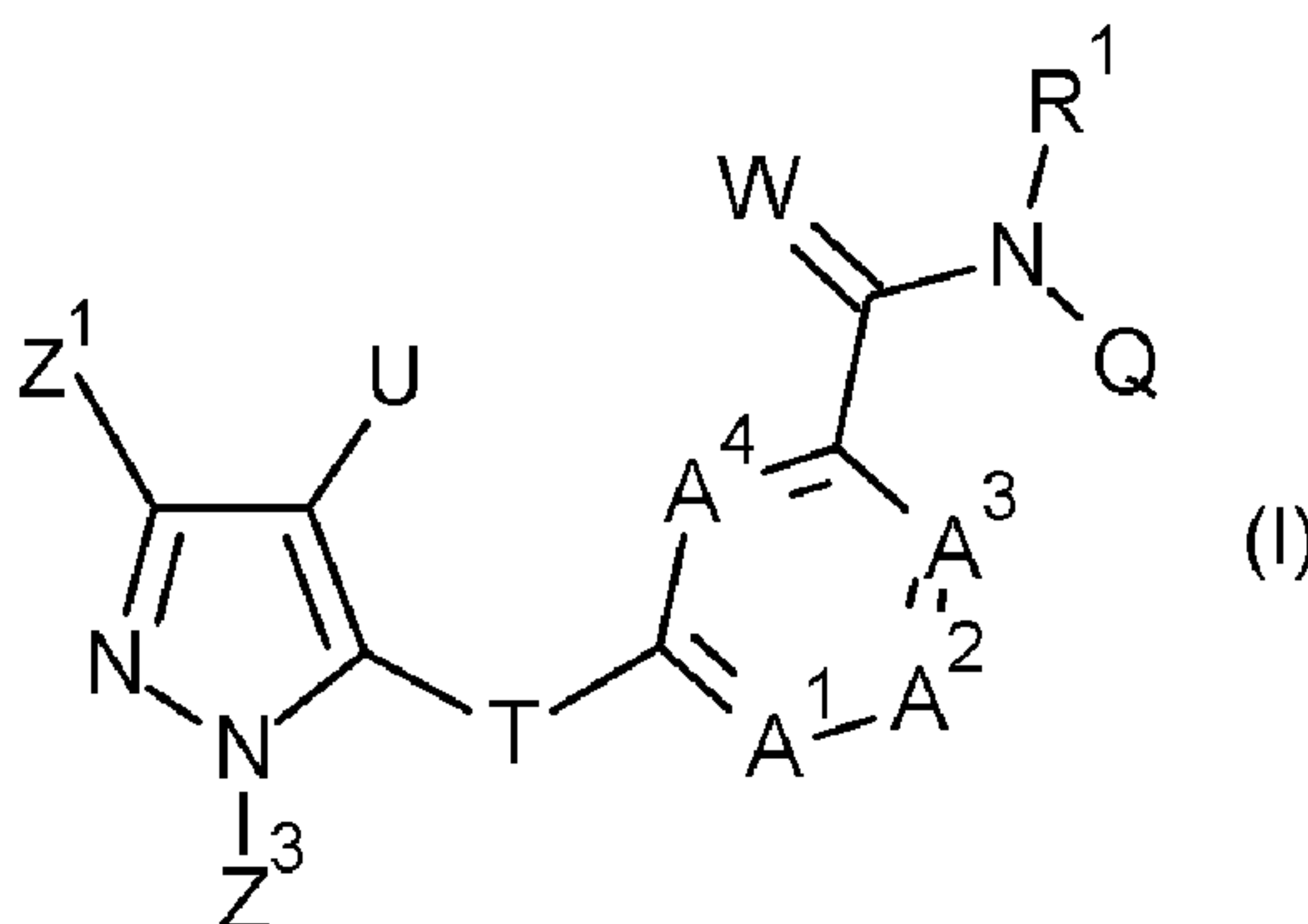
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(54) Title: PESTICIDALLY ACTIVE PYRAZOLE DERIVATIVES



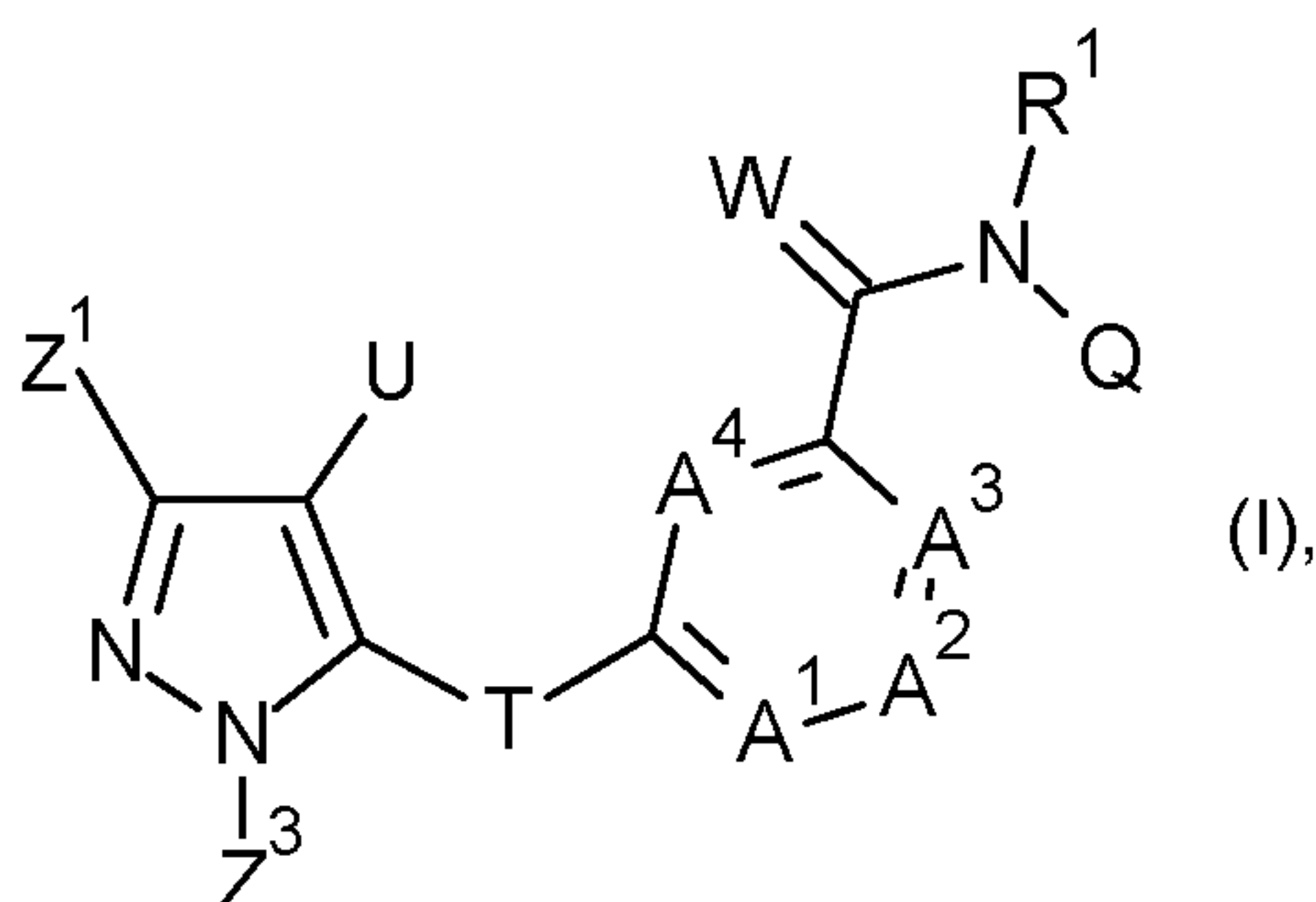
(57) Abstract: Compounds of formula (I), as defined herein, to processes for preparing them, to pesticidal, in particular insecticidal, acaricidal, molluscicidal and nematocidal compositions comprising them and to methods of using them to combat and control pests such as insect, acarine, mollusc and nematode pests.

Pesticidally active pyrazole derivatives

The present invention relates to pyrazole derivatives, to processes for preparing them, to intermediates for preparing them, to pesticidal, in particular insecticidal, acaricidal, molluscicidal and nematocidal compositions comprising those derivatives and to methods of using them to combat and control pests such as insect, acarine, mollusc and nematode pests.

It has now surprisingly been found that certain pyrazole derivatives have highly potent insecticidal properties. Other compounds in this area are known from WO2014/122083, WO2012/107434, WO2015/067646, WO2015/067647, WO2015/067648, WO2015/150442, WO2015/193218 and WO2010/051926.

Thus, as embodiment 1, the present invention relates to a compound of formula (I),



wherein

R¹ is selected from H, C₁-C₆-alkyl, C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₃-C₇ cycloalkyl, C₃-C₇ cycloalkyl- C₁-C₃-alkyl, C₁-C₆-alkylcarbonyl, C₁-C₆-alkoxycarbonyl, aryl(C₀-C₃)-alkyl and heteroaryl(C₀-C₃)-alkyl, wherein each of C₁-C₆-alkyl, C₃-C₆ alkenyl, C₃-C₆ alkynyl, C₃-C₇ cycloalkyl, C₃-C₇ cycloalkyl- C₁-C₃-alkyl, C₁-C₆-alkylcarbonyl, C₁-C₆-alkoxycarbonyl, aryl(C₀-C₃)-alkyl and heteroaryl(C₀-C₃)-alkyl is unsubstituted or substituted with 1 to 5 substituents independently selected from halogen, cyano, C₁-C₆-alkoxy and C₁-C₆-alkoxycarbonyl;

Q is selected from H, hydroxy, HC(=O)-, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₃-C₇ cycloalkyl, C₃-C₇ heterocycloalkyl, C₃-C₇ cycloalkyl- C₁-C₃-alkyl, C₁-C₃-alkyl-C₃-C₇ cycloalkyl, aryl(C₀-C₃)-alkyl, heteroaryl(C₀-C₃)-alkyl, N- C₁-C₆-alkylamino, N- C₁-C₆-alkylcarbonylamino and N,N-di (C₁-C₆-alkyl)amino, wherein each of C₁-C₆-alkyl, C₁-C₆-alkoxy, C₃-C₆ alkenyl, C₃-C₆ alkynyl, C₃-C₇ cycloalkyl, C₃-C₇ heterocycloalkyl, C₃-C₇ cycloalkyl- C₁-C₃-alkyl, C₁-C₃-alkyl-C₃-C₇ cycloalkyl, aryl(C₀-C₃)-alkyl, heteroaryl(C₀-C₃)-alkyl, N- C₁-C₆-alkylamino, N- C₁-C₆-alkylcarbonylamino and N,N-di (C₁-C₆-alkyl)amino is unsubstituted or substituted with 1 to 5 substituents independently selected from halogen, hydroxyl, nitro, amino, cyano, C₁-C₆-alkoxy, C₁-C₆-alkoxycarbonyl, hydroxycarbonyl, C₁-C₆-alkylcarbonyl, C₃-C₆-cycloalkylcarbonyl and phenyl;

W is O or S;

A^1 is CR^2 or N;

A^2 is CR^3 or N;

A^3 is CR^4 or N;

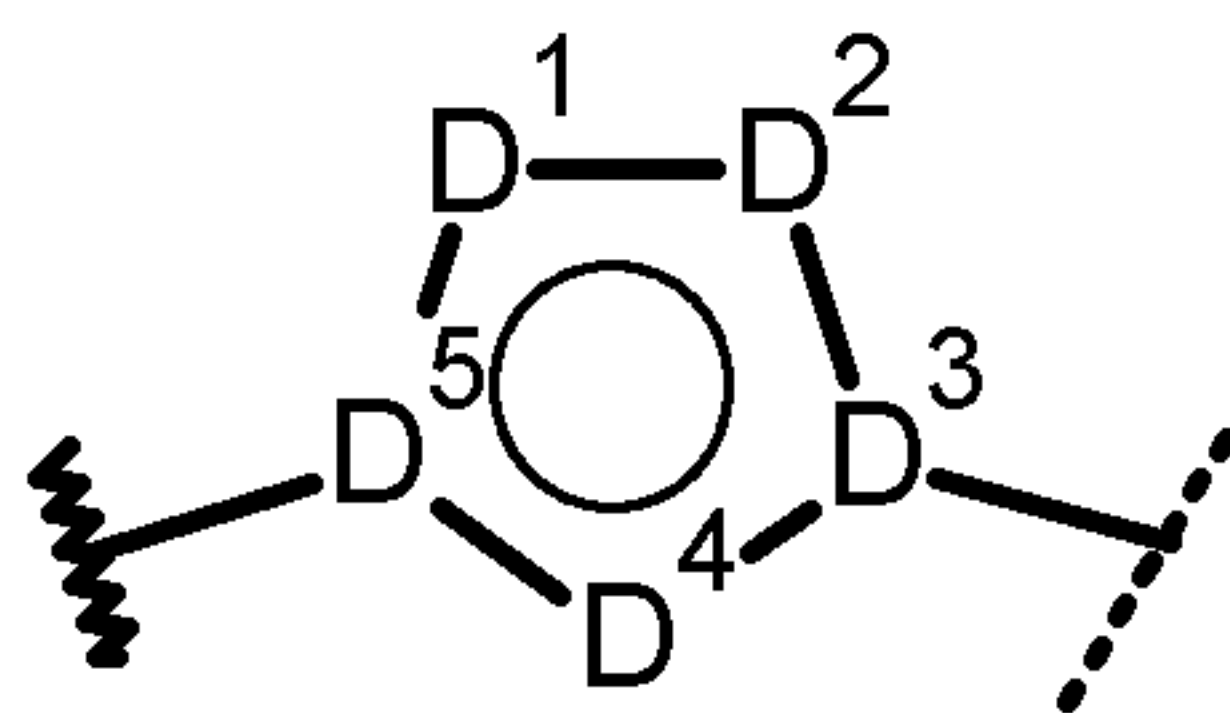
A^4 is CR^5 or N;

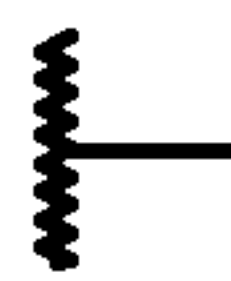
5 with the proviso that no more than 3 of A^1 , A^2 , A^3 and A^4 are N;

R^2 , R^3 , R^4 and R^5 are independently selected from H, halogen, cyano, nitro, C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy, *N*- C_1 - C_6 -alkoxy-imino- C_1 - C_3 -alkyl, C_1 - C_6 -alkylsulfanyl, C_1 - C_6 -alkylsulfinyl, C_1 - C_6 -alkylsulfonyl, *N*- C_1 - C_6 -alkylamino and *N,N*-di- C_1 - C_6 -alkylamino, wherein each of C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy, *N*- C_1 - C_6 -alkoxy-

10 imino- C_1 - C_3 -alkyl, C_1 - C_6 -alkylsulfanyl, C_1 - C_6 -alkylsulfinyl, C_1 - C_6 -alkylsulfonyl, *N*- C_1 - C_6 -alkylamino and *N,N*-di- C_1 - C_6 -alkylamino is unsubstituted or substituted with 1 to 5 substituents independently selected from halogen, hydroxy, nitro, amino, cyano, C_1 - C_6 -alkoxy, C_1 - C_6 -alkoxycarbonyl, hydroxycarbonyl, C_1 - C_6 -alkylcarbamoyl, C_3 - C_6 -cycloalkylcarbamoyl and phenyl;

T is a 5-membered heteroaryl of formula



15 wherein  indicates the bond to the pyrazole group;

D^1 is selected from CR^{6a} , N, NR^{6b} , O and S;

D^2 is selected from CR^{7a} , N, NR^{7b} , O and S;

D^3 is C or N;

D^4 is selected from CR^{8a} , N, NR^{8b} and O;

20 D^5 is C or N;

with the proviso that at least one of D^1 , D^2 , D^3 , D^4 and D^5 is selected from N, O and S, and that no more than one of D^1 , D^2 and D^4 is O or S, and that at least one of D^3 and D^5 is C;

R^{6a} , R^{7a} and R^{8a} are independently selected from H, halogen, cyano, nitro, amino, C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy, C_1 - C_6 -alkylcarbonyl, C_1 - C_6 -alkylsulfanyl, C_1 - C_6 -alkylsulfinyl and C_1 - C_6 -alkylsulfonyl, wherein each

25 of C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy, C_1 - C_6 -alkylcarbonyl, C_1 - C_6 -alkylsulfanyl, C_1 - C_6 -alkylsulfinyl, C_1 - C_6 -alkylsulfonyl is unsubstituted or substituted with 1 to 5 halogen;

R^{6b} , R^{7b} and R^{8b} are independently selected from H and C_1 - C_6 -alkyl, wherein each of C_1 - C_6 -alkyl is unsubstituted or substituted with 1 to 5 halogen;

Z^1 is selected from C_1 - C_6 -alkyl, C_3 - C_7 heterocycloalkyl, C_1 - C_6 -haloalkyl, C_3 - C_6 -cycloalkyl and C_3 - C_6 -

30 halocycloalkyl, wherein each of C_1 - C_6 -alkyl, C_3 - C_7 heterocycloalkyl, C_1 - C_6 -haloalkyl, C_3 - C_6 -cycloalkyl and C_3 - C_6 -halocycloalkyl is unsubstituted or substituted with 1 to 5 substituents independently selected from halogen, hydroxy, nitro, amino, cyano, C_1 - C_6 -alkoxy, C_1 - C_6 -alkoxycarbonyl, hydroxycarbonyl, C_1 - C_6 -alkylcarbamoyl, C_3 - C_6 -cycloalkylcarbamoyl and phenyl;

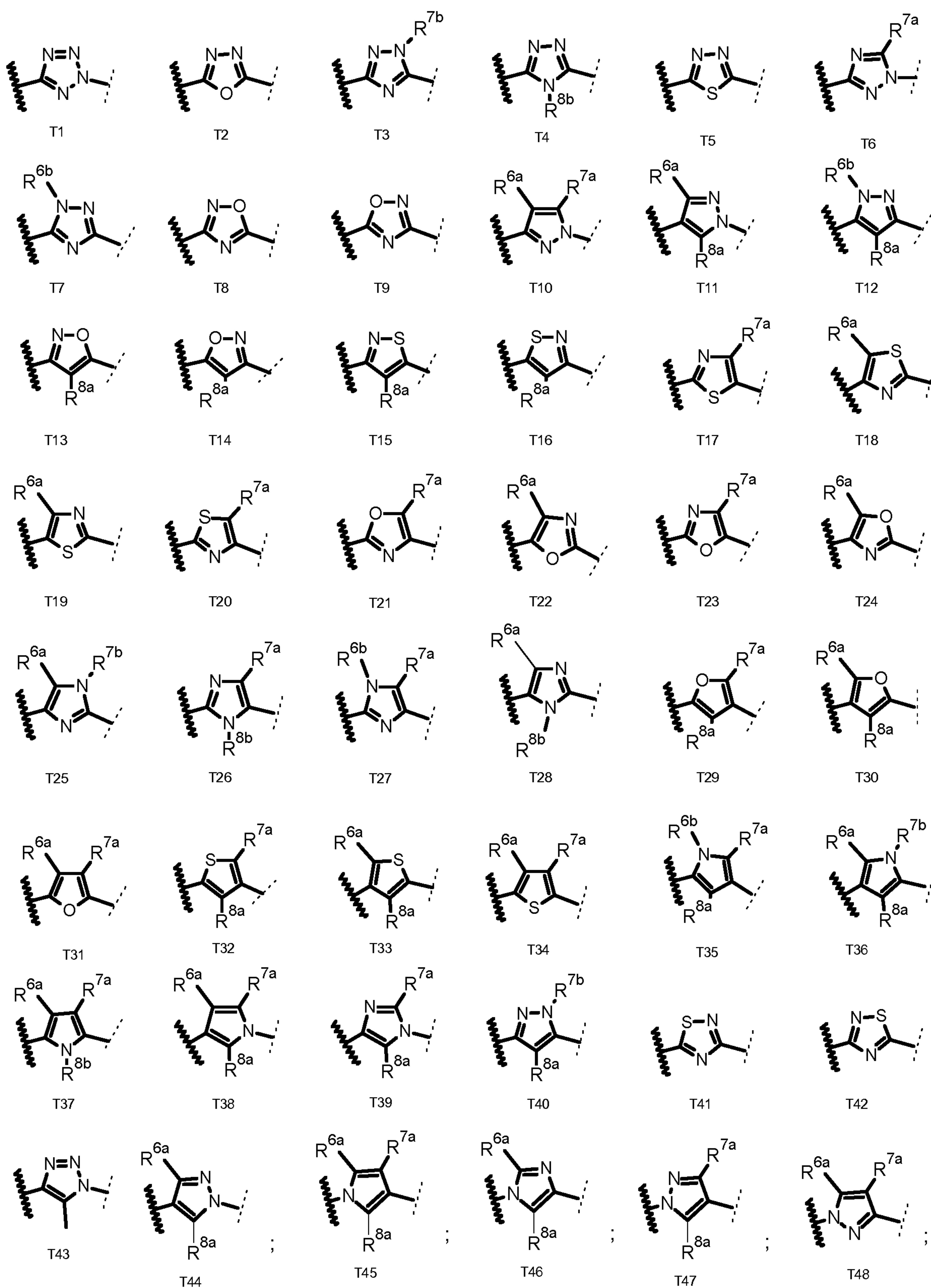
U is selected from C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₃-C₅-cycloalkoxy, C₃-C₅-halocycloalkoxy, C₃-C₅-cycloalkyl, C₃-C₅-halocycloalkyl, C₂-C₄-alkenyl, C₂-C₄-haloalkenyl, C₂-C₃-alkynyl, -S-C₃-C₅-cycloalkyl, -S-C₃-C₅-halocycloalkyl, -SO-C₃-C₅-cycloalkyl, -SO-C₃-C₅-halocycloalkyl, -SO₂-C₃-C₅-cycloalkyl, -SO₂-C₃-C₅-halocycloalkyl, -O-C₂-C₄-alkenyl, -O-C₂-C₄-haloalkenyl, -NHCN, -SO₂F, -O-SO₂-C₁-C₄-alkyl, -O-SO₂-C₁-C₄-haloalkyl and OH;

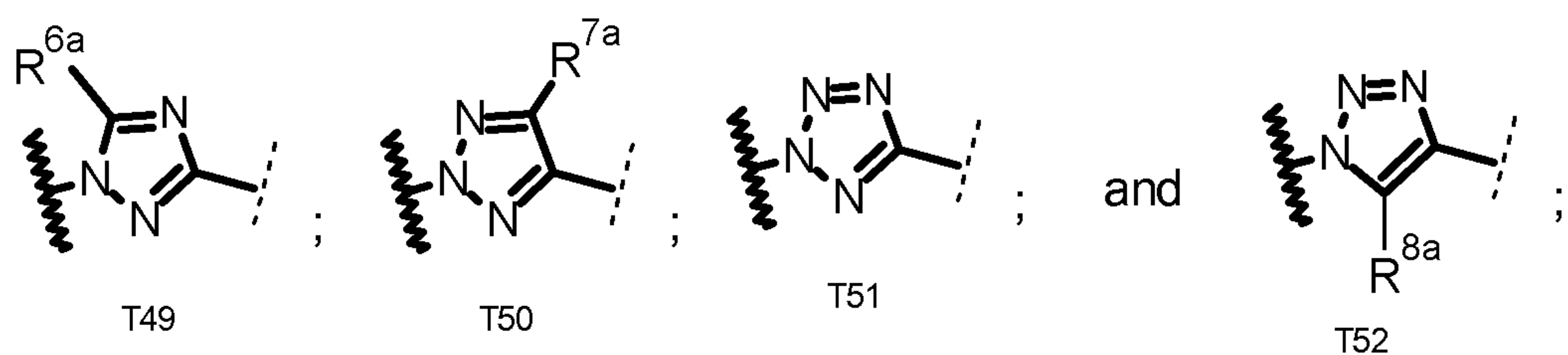
Z³ is selected from H, C₁-C₆-alkyl, C₁-C₆-cycloalkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, aryl and heteroaryl, wherein each of C₁-C₆-alkyl, C₁-C₆-cycloalkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, aryl and heteroaryl is unsubstituted or substituted with 1 to 5 substituents independently selected from halogen, hydroxy, nitro, amino, cyano, C₁-C₆-alkoxy, C₁-C₆-alkoxycarbonyl, hydroxycarbonyl, C₁-C₆-alkylcarbamoyl, C₃-C₆-cycloalkylcarbamoyl and phenyl;
or an agrochemically acceptable salt or N-oxide thereof.

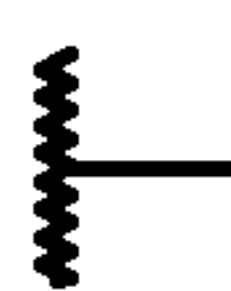
Preferred values of A¹, A², A³, A⁴, D¹, D², D³, D⁴, D⁵, R¹, R², R³, R⁴, R⁵, R^{6a}, R^{6b}, R^{7a}, R^{7b}, R^{8a}, R^{8b}, Q, Z¹, U and Z³ in relation to each compound of the present invention, including the intermediate compounds, are as set out below in embodiments 2 to 25.

As used herein, when one embodiment refers to several other embodiments by using the term "according to any one of", for example "according to any one of embodiments 1 to 23", then said embodiment refers not only to embodiments indicated by integers such as 1 and 2 but also to embodiments indicated by numbers with a decimal component such as for example 23.1, 23.2, 23.3, 23.4, 23.20, 23.25, 23.30.

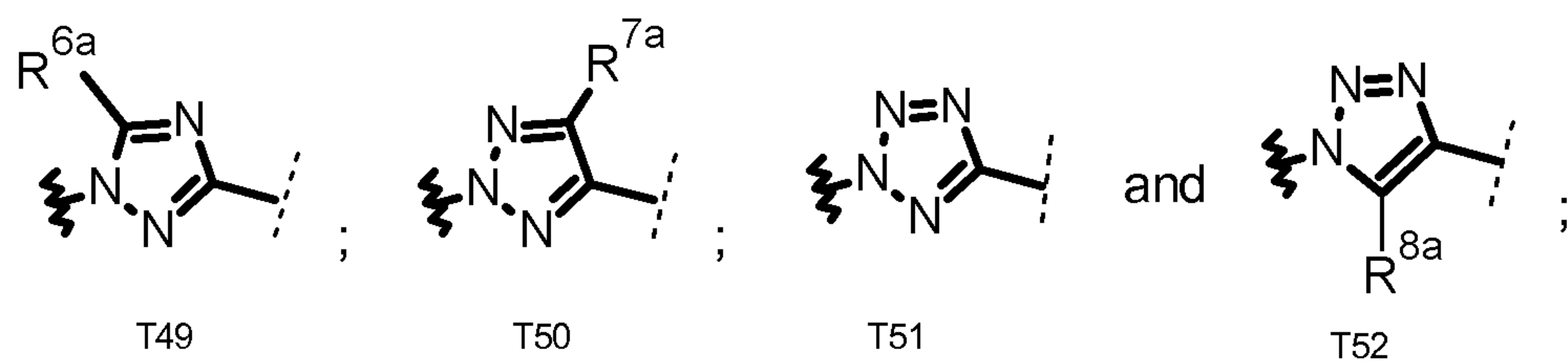
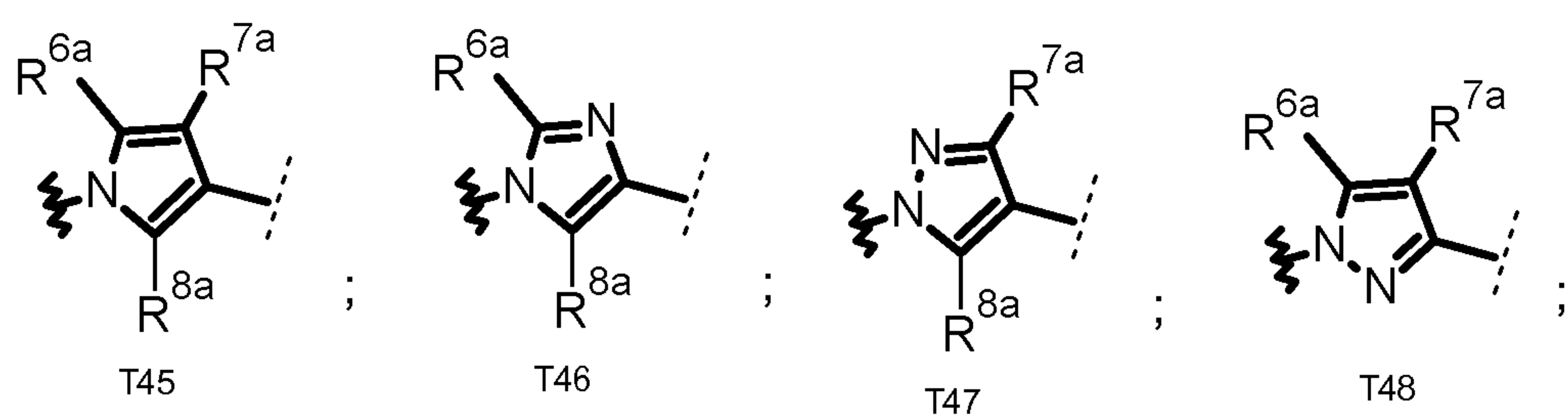
Embodiment 2: A compound or salt according to embodiment 1, wherein T is selected from



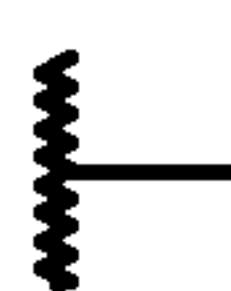


wherein  indicates the bond to the pyrazole group.

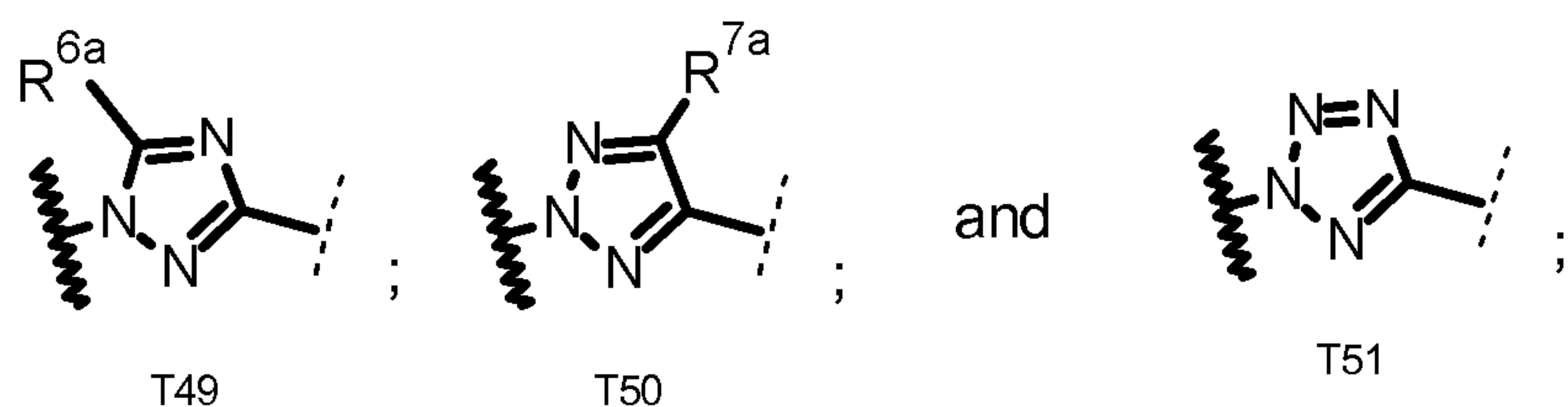
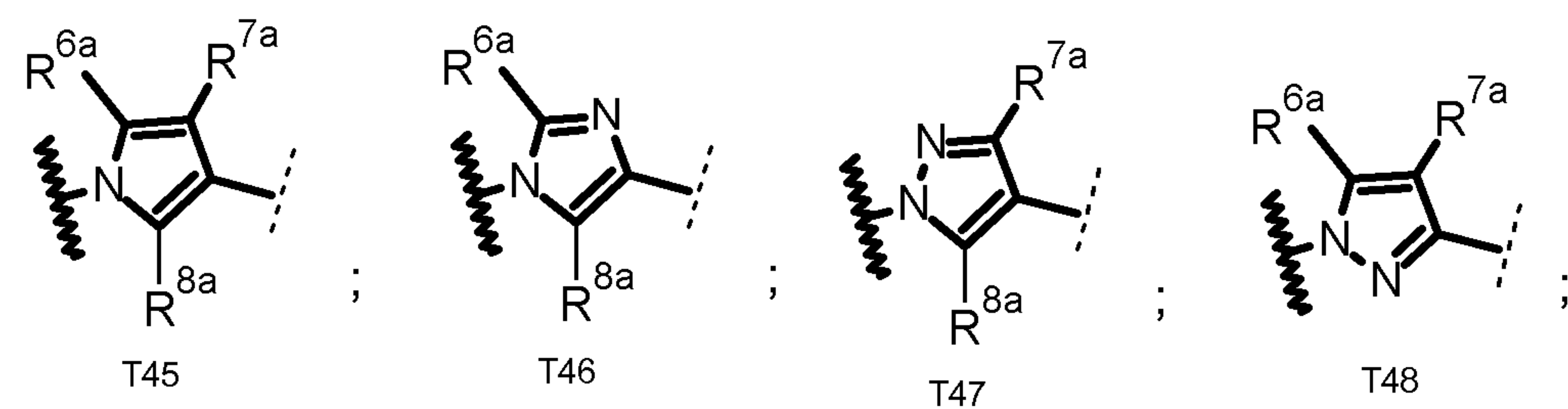
Embodiment 3: A compound or salt according to embodiment 1, wherein T is selected from



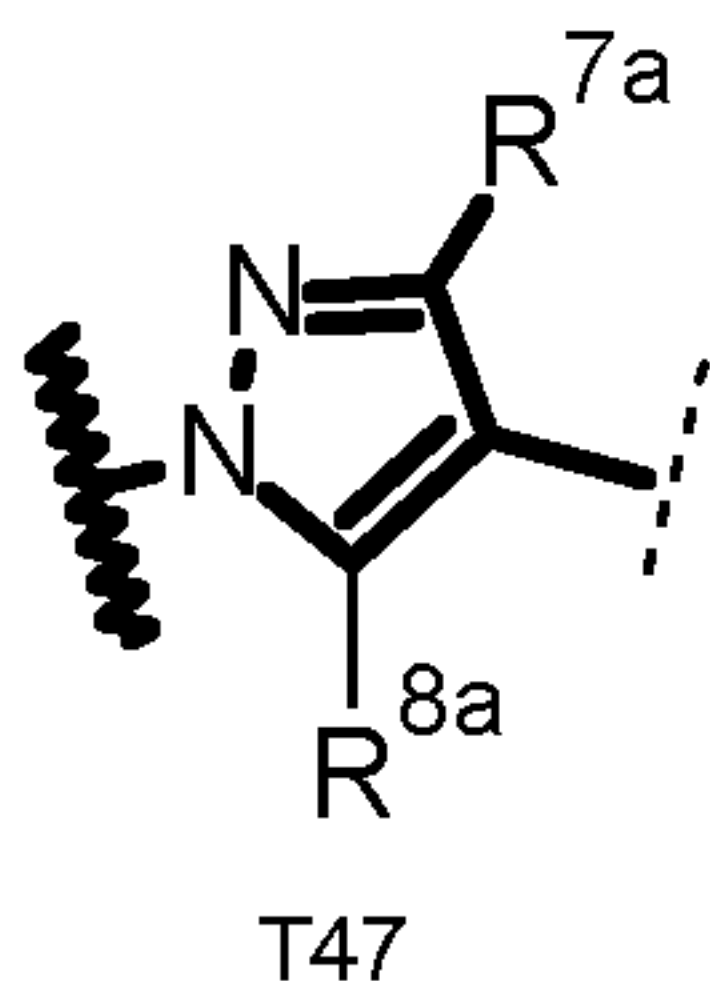
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wherein  indicates the bond to the pyrazole group.

Embodiment 3.1: A compound or salt according to embodiment 1, wherein T is selected from



Embodiment 4: A compound or salt according to embodiment 1, wherein T is



5 wherein  indicates the bond to the pyrazole group.

Embodiment 5: A compound or salt according to any one of embodiments 1 to 4, wherein

R¹ is selected from H, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, s-butyl, t-butyl, propenyl, propargyl, methoxymethyl, ethoxymethyl, propoxymethyl, methylcarbonyl, ethylcarbonyl, n-
 10 propylcarbonyl, isopropylcarbonyl, s-butylcarbonyl, t-butylcarbonyl, methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, isopropoxycarbonyl, s-butoxycarbonyl, t-butoxycarbonyl, cyanomethyl, 2-cyanoethyl, benzyl, 4-methoxybenzyl, pyrid-2-yl-methyl, pyrid-3-yl-methyl, pyrid-4-yl-methyl and 4-chlor-pyrid-3-yl-methyl.

15 Embodiment 6: A compound or salt according to any one of embodiments 1 to 5, wherein R¹ is selected from H, methyl, ethyl, n-propyl, n-propylcarbonyl and propenyl.

Embodiment 6.1: A compound or salt according to any one of embodiments 1 to 5, wherein R¹ is selected from H, methyl and ethyl.

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Embodiment 7: A compound or salt according to any one of embodiments 1 to 5, wherein R¹ is H or methyl.

Embodiment 8: A compound or salt according to any one of embodiments 1 to 7, wherein

25 Q is selected from H, hydroxy, HC(=O)-, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₃-C₇ cycloalkyl, C₃-C₇ heterocycloalkyl, C₃-C₇ cycloalkyl- C₁-C₃-alkyl, C₁-C₃-alkyl-C₃-C₇ cycloalkyl, aryl(C₀-C₃)-alkyl, heteroaryl(C₀-C₃)-alkyl, N- C₁-C₆-alkylamino, N- C₁-C₆-alkylcarbonylamino and N,N-di (C₁-C₆-alkyl)amino, wherein each of C₁-C₆-alkyl, C₁-C₆-alkoxy, C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₃-C₇ cycloalkyl, C₃-C₇ heterocycloalkyl, C₃-C₇ cycloalkyl- C₁-C₃-alkyl, C₁-C₃-alkyl-C₃-C₇ cycloalkyl, aryl(C₀-C₃)-alkyl,
 30 heteroaryl(C₀-C₃)-alkyl, N- C₁-C₆-alkylamino, N- C₁-C₆-alkylcarbonylamino and N,N-di (C₁-C₆-alkyl)amino is unsubstituted or substituted with 1 to 5 substituents independently selected from halogen, hydroxyl,

nitro, amino, cyano, C₁-C₆-alkoxy, C₁-C₆-alkoxycarbonyl, hydroxycarbonyl, C₁-C₆-alkylcarbamoyl, C₃-C₆-cycloalkylcarbamoyl and phenyl.

Embodiment 9: A compound or salt according to any one of embodiments 1 to 8, wherein

- 5 Q is selected from H, methyl, ethyl, n-propyl, 1-methylethyl, 1,1-dimethylethyl, 1-methylpropyl, n-butyl, 2-methylpropyl, 2-methylbutyl, hydroxyethyl, 2-hydroxypropyl, cyanomethyl, 2-cyanoethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 1-trifluoromethylethyl, 2,2-difluoropropyl, 3,3,3-trifluoropropyl, 2,2-dimethyl-3-fluoropropyl, cyclopropyl, 1-cyano-cyclopropyl, 1-methoxycarbonyl-cyclopropyl, 1-(N-methylcarbamoyl)cyclopropyl, 1-carbamoyl-cyclopropyl, 1-carbamothioyl-cyclopropyl, 1-(N-cyclopropylcarbamoyl)cyclopropyl, cyclopropyl-methyl, cyclobutyl, cyclopentyl, cyclohexyl, 1-cyclopropylethyl, bis(cyclopropyl)methyl, 2,2-dimethylcyclopropyl-methyl, 2-phenylcyclopropyl, 2,2-dichlorocyclopropyl, trans-2-chlorocyclopropyl, cis-2-chlorocyclopropyl, 2,2-difluorocyclopropyl, trans-2-fluorocyclopropyl, cis-2-fluorocyclopropyl, trans-4-hydroxycyclohexyl, 4-trifluoromethylcyclohexyl, prop-2-enyl, 2-methylprop-2-enyl, prop-2-ynyl, 1,1-dimethylbut-2-ynyl, 3-chloro-prop-2-enyl, 3-fluoro-prop-2-enyl, 3,3-dichloro-prop-2-enyl, 3,3-dichloro-1,1-dimethylprop-2-enyl, oxetan-3-yl, thietan-3-yl, 1-oxido-thietan-3-yl, 1,1-dioxido-thietan-3-yl, isoxazol-3-ylmethyl, 1,2,4-triazol-3-ylmethyl, 3-methyloxetan-3-ylmethyl, benzyl, 2,6-difluorophenylmethyl, 3-fluorophenylmethyl, 2-fluorophenylmethyl, 2,5-difluorophenylmethyl, 1-phenylethyl, 4-chlorophenylethyl, 2-trifluoromethylphenylethyl, 1-pyridin-2-ylethyl, pyridin-2-ylmethyl, 5-fluoropyridin-2-ylmethyl, (6-chloro-pyridin-3-yl)methyl, pyrimidin-2-ylmethyl, methoxy, 2-ethoxyethyl, 2-methoxyethyl, 2-(methylsulfanyl)ethyl, 1-methyl-2-(ethylsulfanyl)ethyl, 2-methyl-1-(methylsulfanyl)propan-2-yl, methoxycarbonyl, methoxycarbonylmethyl, NH₂, N-ethylamino, N-allylamino, N,N-dimethylamino, N,N-diethylamino, 2-thienylmethyl, isopropyl, isobutyl, methylsulfonyl, methylsulfinyl, 3-(methylsulfanyl)-cyclobutyl, 2-oxo-2[(2,2,2-trifluoroethyl)amino]ethyl, 1-(CF₃)cyclopropyl, 2-methylcyclopropyl, 1,1,1-trifluoropropan-2-yl, buta-2,3-dien-1-yl, 3-chloroprop-2-en-1-yl, 3-cyanothientan-3-yl, 3-(methylsulfonyl)cyclobutyl, 4-fluorophenyl, 2-[(methylsulfinyl)methyl]cyclobutyl, 3-methylbutan-2-yl, 2-(methylsulfonyl)cyclobutyl, 2-(dimethylamino)ethyl and 2-methoxyethyl; or
- 10 Q is selected from phenyl, naphthyl, pyridazine, pyrazine, pyrimidine, triazine, pyridine, pyrazole, thiazole isothiazole, oxazole, isoxazole, triazole, imidazole, furan, thiophene, pyrrole, oxadiazole, thiadiazole, tetrazole and tetrahydrofuran, each of which is unsubstituted or substituted with 1 to 4 substituents independently selected from V;
- 15 V is selected from fluoro, chloro, bromo, iodo, cyano, nitro, methyl, ethyl, difluoromethyl, hydroxyl, trichloromethyl, chlorodifluoromethyl, dichlorofluoromethyl, trifluoromethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 1,2,2,2-tetrafluoroethyl, 1-chloro-1,2,2,2-tetrafluoroethyl, 2,2,2-trichloroethyl, 2-chloro-2,2-difluoroethyl, 1,1-difluoroethyl, pentafluoroethyl heptafluoro-n-propyl, heptafluoro-isopropyl, nonafluoro-n-butyl, cyclopropyl, cyclobutyl, methoxy, ethoxy, n-propoxy, 1-methylethoxy, fluoromethoxy, difluoromethoxy, chloro-difluoromethoxy, dichloro-fluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 2-chloro-2,2-difluoroethoxy, pentafluoroethoxy, N-
- 20 25 30 35

methoxyiminomethyl, 1-(N-methoxyimino)-ethyl, methylsulfanyl, methylsulfonyl, methylsulfinyl, trifluoromethylsulfonyl, trifluoromethylsulfinyl, trifluoromethylsulfanyl and N,N-dimethylamino.

Embodiment 10: A compound or salt according to any one of embodiments 1 to 9, wherein

5 Q is selected from 1 -cyano-cyclopropyl, benzyl, cyclopropyl, 2-thienylmethyl, carbamothioylcyclopropyl, pyrid-4-yl, 2,2,2-trifluorethyl, methylsulfonyl, thietan-3-yl and 1- carbamoylcyclopropyl.

Embodiment 10.1: A compound or salt according to any one of embodiments 1 to 9, wherein

Q is selected from 1 -cyano-cyclopropyl, benzyl and cyclopropyl.

10

Embodiment 11: A compound or salt according to any one of embodiments 1 to 10, wherein W is O.

Embodiment 12: A compound or salt according to any one of embodiments 1 to 11, wherein

15 A^1 is CR^2 or N;

A^2 is CR^3 or N;

A^3 is CR^4 or N;

A^4 is CR^5 or N;

with the proviso that no more than 3 of A^1 , A^2 , A^3 and A^4 are N;

20 R^2 and R^5 are independently selected from H, methyl, methoxy, fluoro and chloro;

R^3 and R^4 are independently selected from H, fluoro, chloro, bromo, iodo, cyano, nitro, methyl, ethyl, fluoromethyl, difluoromethyl, chlordifluoromethyl, trifluoromethyl, 2,2,2-trifluoroethyl, methoxy, ethoxy, n-propoxy, 1 -methylethoxy, fluoromethoxy, difluoromethoxy, chloro-difluoromethoxy, dichloro-fluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 2-chloro-2,2-difluoroethoxy, pentafluoroethoxy, N-methoxyiminomethyl, 1-(N-methoxyimino)-ethyl, methylsulfanyl, trifluoromethylsulfanyl, methylsulfonyl, methylsulfinyl, trifluoromethylsulfonyl and trifluoromethylsulfinyl.

25

Embodiment 13: A compound or salt according to any one of embodiments 1 to 12, wherein

A^1 and A^4 are CH;

30 A^2 is CH, N or CF;

A^3 is CH, CF or CCl.

Embodiment 13.1: A compound or salt according to any one of embodiments 1 to 12, wherein

A^1 is CH or CF;

35 A^2 is CH or N;

A^3 is CCN or CCl.

A^4 is CH.

Embodiment 14: A compound or salt according to any one of embodiments 1 to 13, wherein R^{6a} , R^{7a} and R^{8a} are independently selected from H, halogen, cyano, nitro, amino, methyl, ethyl, propyl, 1-methylethyl, tert-butyl, trifluoromethyl, difluoromethyl, methoxy, ethoxy, trifluoromethoxy, 2,2-difluoroethoxy, 2,2,2-trifluoroethoxy, methylcarbonyl, ethylcarbonyl, trifluoromethylcarbonyl, methylsulfanyl, methylsulfinyl, methylsulfonyl, trifluoromethylsulfonyl, trifluoromethylsulfanyl and trifluoromethylsulfinyl;
 R^{6b} , R^{7b} and R^{8b} are independently selected from H or methyl.

Embodiment 15: A compound or salt according to any one of embodiments 1 to 14, wherein R^{6a} , R^{7a} and R^{8a} are independently selected from H, F, methyl and trifluoromethoxy; R^{6b} , R^{7b} and R^{8b} are independently selected from H and methyl.

Embodiment 15.1: A compound or salt according to any one of embodiments 1 to 14, wherein R^{6a} , R^{7a} , R^{8a} , R^{6b} , R^{7b} and R^{8b} are H.

Embodiment 16: A compound or salt according to any one of embodiments 1 to 15, wherein Z^1 is selected from methyl, ethyl, 1,1-dimethylethyl, difluoromethyl, trichloromethyl, chlorodifluoromethyl, dichlorofluoromethyl, trifluoromethyl, bromodichloromethyl, 1-fluoroethyl, 1-fluoro-1-methylethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 1,2,2,2-tetrafluoroethyl, 1-chloro-1,2,2,2-tetrafluoroethyl, 2,2,2-trichloroethyl, 2-chloro-2,2-difluoroethyl, 1,1-difluoroethyl, pentafluoroethyl, heptafluoro-n-propyl, heptafluoro-isopropyl, nonafluoro-n-butyl, cyclopropyl, 1-chlorocyclopropyl, 1-fluorocyclopropyl, 1-bromocyclopropyl, 1-cyano-cyclopropyl, 1-trifluoromethyl-cyclopropyl, cyclobutyl and 2,2-difluoro-1-methyl-cyclopropyl.

Embodiment 17: A compound or salt according to any one of embodiments 1 to 15, wherein Z^1 is $-\text{CF}_2\text{CF}_3$.

Embodiment 18: A compound or salt according to any one of embodiments 1 to 17, wherein U is selected from C_{1-3} -haloalkoxy and C_{2-4} -alkenyl.

Embodiment 18.1: A compound or salt according to any one of embodiments 1 to 17, wherein U is selected from C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_3 - C_5 -cycloalkoxy, C_3 - C_5 -cycloalkyl, C_2 - C_4 -alkenyl, C_2 - C_4 -haloalkenyl, C_2 - C_3 -alkynyl, $-\text{S}-\text{C}_3$ - C_5 -cycloalkyl, $-\text{SO}-\text{C}_3$ - C_5 -cycloalkyl, $-\text{SO}_2$ - C_3 - C_5 -cycloalkyl, $-\text{O}-\text{C}_2$ - C_4 -alkenyl, $-\text{O}-\text{C}_2$ - C_4 -haloalkenyl, $-\text{NHCN}$, $-\text{SO}_2\text{F}$ and OH.

Embodiment 19: A compound or salt according to any one of embodiments 1 to 17, wherein

U is selected from $-\text{OCHF}_2$, $-\text{OCH}_2\text{CF}_3$, $-\text{OCH}_3$, $-\text{O-cyclopropyl}$, cyclopropyl, OH, $-\text{O-CH=CH}_2$, $-\text{CH=CH}_2$, $-\text{C}\equiv\text{CH}$, $-\text{S-cyclopropyl}$, $-\text{O-CF=CF}_2$, $-\text{O-SO}_2\text{-F}$, $-\text{NHCN}$, $-\text{SO}_2\text{-cyclopropyl}$, $-\text{SO-cyclopropyl}$, $-\text{O-CF}_2\text{-CF}_2\text{H}$, $-\text{OEt}$, $-\text{O-CH}_2\text{-CF}_2\text{H}$, $-\text{O-CF}_2\text{CF}_2\text{CF}_3$, $-\text{O-CF}_2\text{CFHCF}_3$ and $-\text{CF}_2\text{CF}_3$.

- 5 Embodiment 20: A compound or salt according to any one of embodiments 1 to 17, wherein U is selected from $-\text{OCHF}_2$, $-\text{CH=CH}_2$ and $-\text{C}\equiv\text{CH}$, in particular $-\text{OCHF}_2$.

Embodiment 21: A compound or salt according to any one of embodiments 1 to 20, wherein Z^3 is selected from H, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, s-butyl, t-butyl, ethenyl, 1-propenyl, cyclopropyl, 1-propinyl, 1-butylinyl, difluoromethyl, trichloromethyl, chlorodifluoromethyl, dichlorofluoromethyl, trifluoromethyl, 1-fluoroethyl, 1-fluoro-1-methylethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, phenyl, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl, 2,5-dichlorophenyl, 3,4-dichlorophenyl, 2,6-dichlorophenyl, 2,6-dichloro-4-trifluoromethylphenyl, 3-chloro-5-trifluoromethylpyridin-2-yl, 4- NO_2 -phenyl and 3-chloro-pyridin-2-yl.

15 Embodiment 22: A compound or salt according to any one of embodiments 1 to 20, wherein Z^3 is methyl.

Embodiment 23: A compound or salt according to any one of embodiments 1 to 4, wherein

20 R^1 is H;

Q is selected from 1-cyano-cyclopropyl, benzyl, cyclopropyl, 2-thienylmethyl, carbamothioylcyclopropyl, pyrid-4-yl, 2,2,2-trifluoroethyl, methylsulfonyl, thietan-3-yl and 1-carbamoylcyclopropyl;

W is O;

A^1 is CR^2 or N;

25 A^2 is CR^3 or N;

A^3 is CR^4 or N;

A^4 is CR^5 or N;

with the proviso that no more than 3 of A^1 , A^2 , A^3 and A^4 are N;

R^2 and R^5 are independently selected from H, methyl, methoxy, fluoro and chloro;

30 R^3 and R^4 are independently selected from H, fluoro, chloro, bromo, iodo, cyano, nitro, methyl, ethyl, fluoromethyl, difluoromethyl, chlorodifluoromethyl, trifluoromethyl, 2,2,2-trifluoroethyl, methoxy, ethoxy, n-propoxy, 1-methylethoxy, fluoromethoxy, difluoromethoxy, chloro-difluoromethoxy, dichloro-fluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 2-chloro-2,2-difluoroethoxy, pentafluoroethoxy, N-methoxyiminomethyl, 1-(N-methoxyimino)-ethyl, methylsulfonyl, trifluoromethylsulfonyl, methylsulfonyl,

35 methylsulfinyl, trifluoromethylsulfonyl and trifluoromethylsulfinyl;

Z^1 is selected from methyl, ethyl, 1,1-dimethylethyl, difluoromethyl, trichloromethyl, chlorodifluoromethyl, dichlorofluoromethyl, trifluoromethyl, bromodichloromethyl, 1-fluoroethyl, 1-fluoro-1-methylethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 1,2,2,2-tetrafluoroethyl, 1-chloro-1,2,2,2-

tetrafluoroethyl, 2,2,2-trichloroethyl, 2-chloro-2,2-difluoroethyl, 1,1 -difluoroethyl, pentafluoroethyl, heptafluoro-n-propyl, heptafluoro-isopropyl, nonafluoro-n-butyl, cyclopropyl, 1 -chlorocyclopropyl, 1 -fluorocyclopropyl, 1 -bromocyclopropyl, 1 -cyano-cyclopropyl, 1-trifluoromethyl-cyclopropyl, cyclobutyl and 2,2-difluoro-1-methyl-cyclopropyl;

- 5 U is selected from $-\text{OCHF}_2$, $-\text{OCH}_2\text{CF}_3$, $-\text{OCH}_3$, $-\text{O-cyclopropyl}$, cyclopropyl, OH, $-\text{O-CH=CH}_2$, $-\text{CH=CH}_2$, $-\text{C}\equiv\text{CH}$, $-\text{S-cyclopropyl}$, $-\text{O-CF=CF}_2$, $-\text{O-SO}_2\text{-F}$, $-\text{NHCN}$, $-\text{SO}_2\text{-cyclopropyl}$, $-\text{SO-cyclopropyl}$, $-\text{O-CF}_2\text{-CF}_2\text{H}$, $-\text{OEt}$, $-\text{O-CH}_2\text{-CF}_2\text{H}$, $-\text{O-CF}_2\text{CF}_2\text{CF}_3$, $-\text{O-CF}_2\text{CFHCF}_3$ and $-\text{CF}_2\text{CF}_3$;
 Z^3 is selected from H, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, s-butyl, t-butyl, ethenyl, 1-propenyl, 1-propinyl, cyclopropyl, 1-butylnyl, difluoromethyl, trichloromethyl, chlorodifluoromethyl,
 10 dichlorofluoromethyl, trifluoromethyl, 1-fluoroethyl, 1-fluoro-1-methylethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, phenyl, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl, 2,5-dichlorophenyl, 3,4-dichlorophenyl, 2,6-dichlorophenyl 2,6-dichloro-4-trifluoromethylphenyl, 3- chlor-5-trifluoromethylpyridin-2-yl, 4- NO_2 -phenyl and 3-chloro-pyridin-2-yl.
- 15 Embodiment 24: A compound or salt according to any one of embodiments 1 to 4, wherein
 R^1 is H;
 Q is selected from 1 -cyano-cyclopropyl, benzyl, cyclopropyl, 2-thienylmethyl, carbamothioylcyclopropyl, pyrid-4-yl, 2,2,2-trifluoroethyl, methylsulfonyl, thietan-3-yl and 1- carbamoylcyclopropyl;
 W is O;
 20 A^1 is CR^2 or N;
 A^2 is CR^3 or N;
 A^3 is CR^4 or N;
 A^4 is CR^5 or N;
 with the proviso that no more than 3 of A^1 , A^2 , A^3 and A^4 are N;
 25 R^2 and R^5 are independently selected from H, methyl, fluoro and chloro;
 R^3 and R^4 are independently selected from H, fluoro, chloro, bromo, iodo, cyano, nitro, methyl, ethyl, fluoromethyl, difluoromethyl, chlordifluoromethyl, trifluoromethyl, 2,2,2-trifluoroethyl, methoxy, ethoxy, n-propoxy, 1 -methylethoxy, fluoromethoxy, difluoromethoxy, chloro-difluoromethoxy, dichloro-fluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 2-chloro-2,2-difluoroethoxy, pentafluoroethoxy, N-methoxyiminomethyl, 1-(N-methoxyimino)-ethyl, methylsulfonyl, trifluoromethylsulfonyl, methylsulfonyl,
 30 methylsulfinyl, trifluoromethylsulfonyl and trifluoromethylsulfinyl;
 Z^1 is $-\text{CF}_2\text{CF}_3$;
 U is selected from $-\text{OCHF}_2$, $-\text{CH=CH}_2$ and $-\text{C}\equiv\text{CH}$, in particular $-\text{OCHF}_2$;
 Z^3 is methyl.
- 35 Embodiment 25: A compound or salt according to any one of embodiments 1 to 24, wherein
 R^{6a} , R^{7a} and R^{8a} are independently selected from H, methyl and trifluoromethoxy;
 R^{6b} , R^{7b} and R^{8b} are independently selected from H and methyl.

R¹ is H;

Q is selected from 1- cyano-cyclopropyl, benzyl, cyclopropyl, 2-thienylmethyl, carbamothioylcyclopropyl, pyrid-4-yl, 2,2,2-trifluorethyl, methylsulfonyl, thietan-3-yl and 1-carbamoylcyclopropyl;

W is O;

5 A¹ and A⁴ are CH;

A² is N, CH or CF;

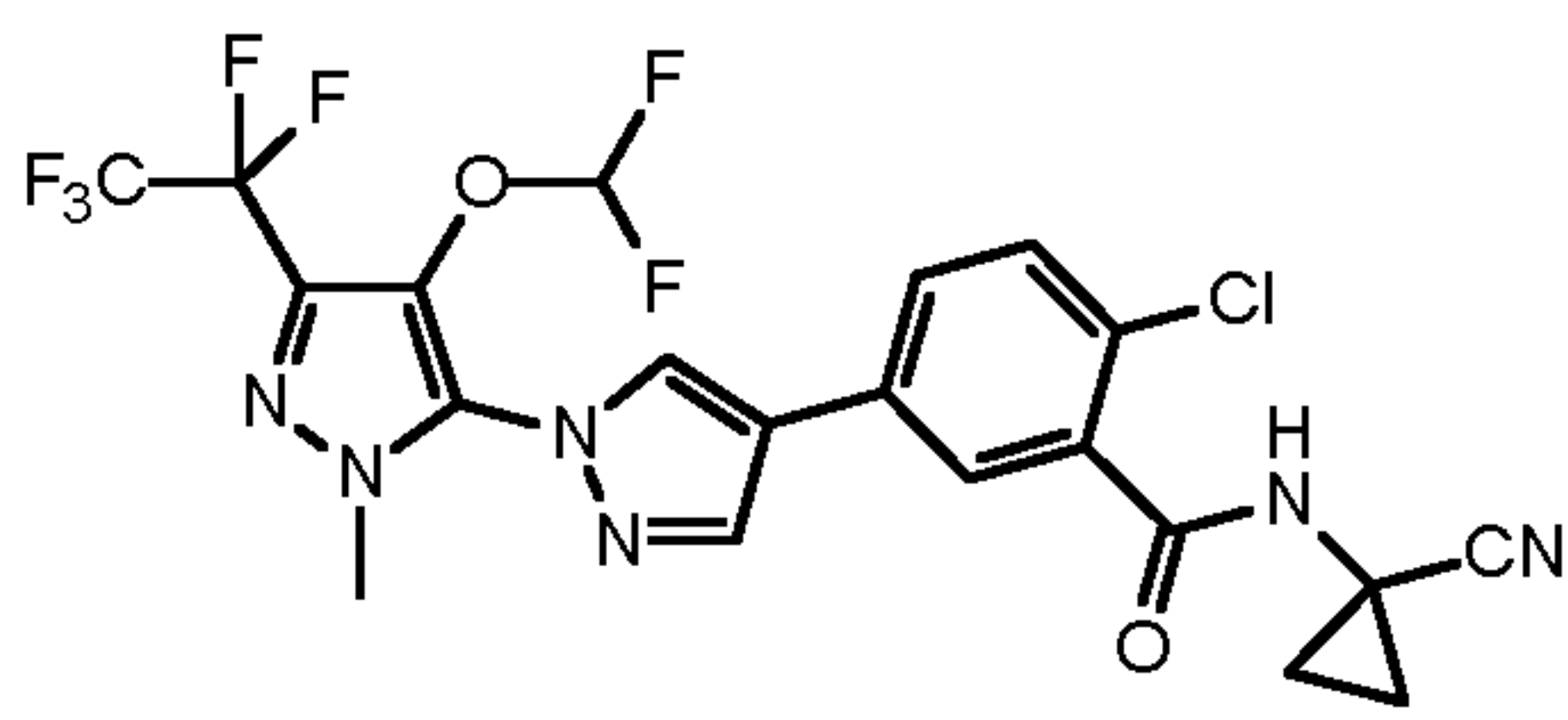
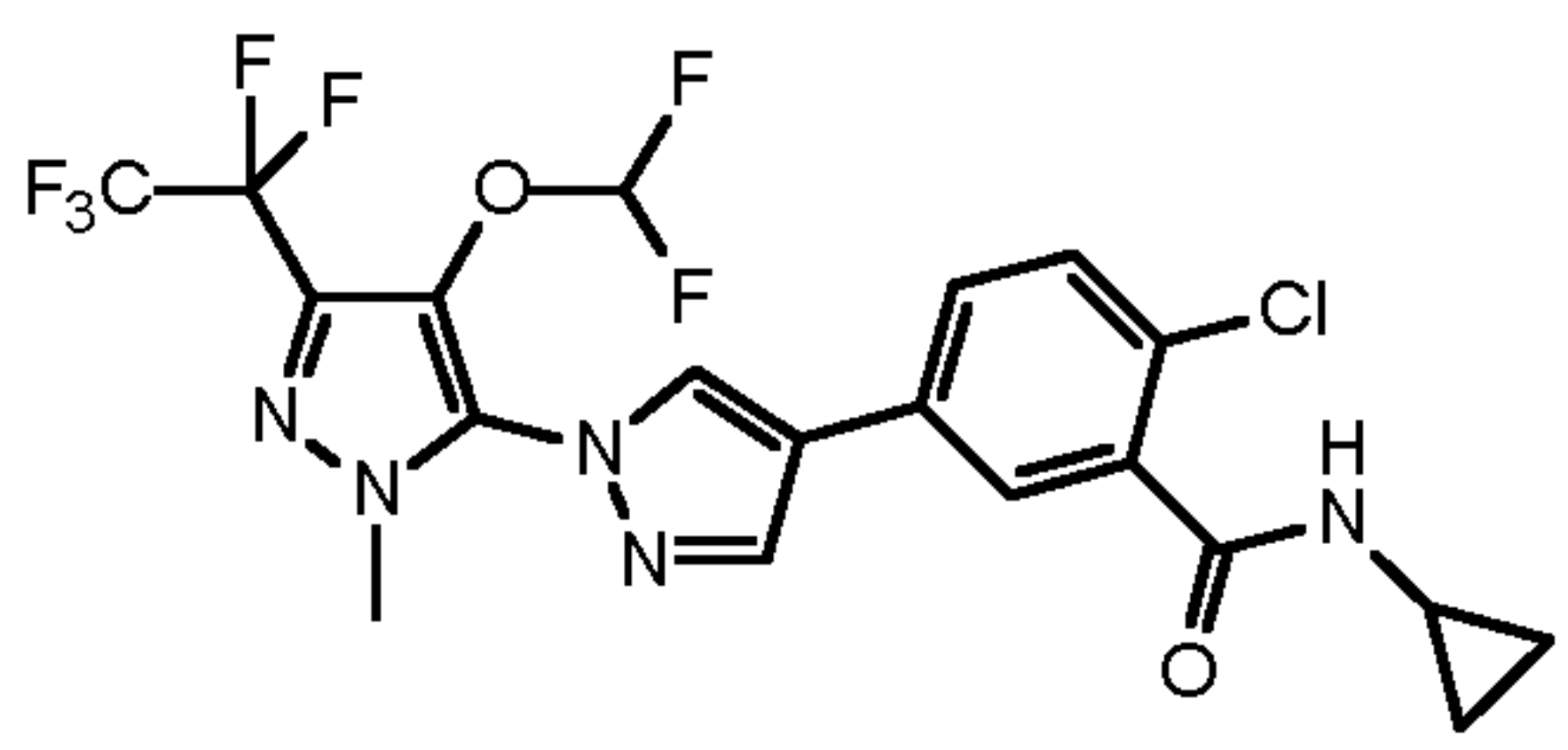
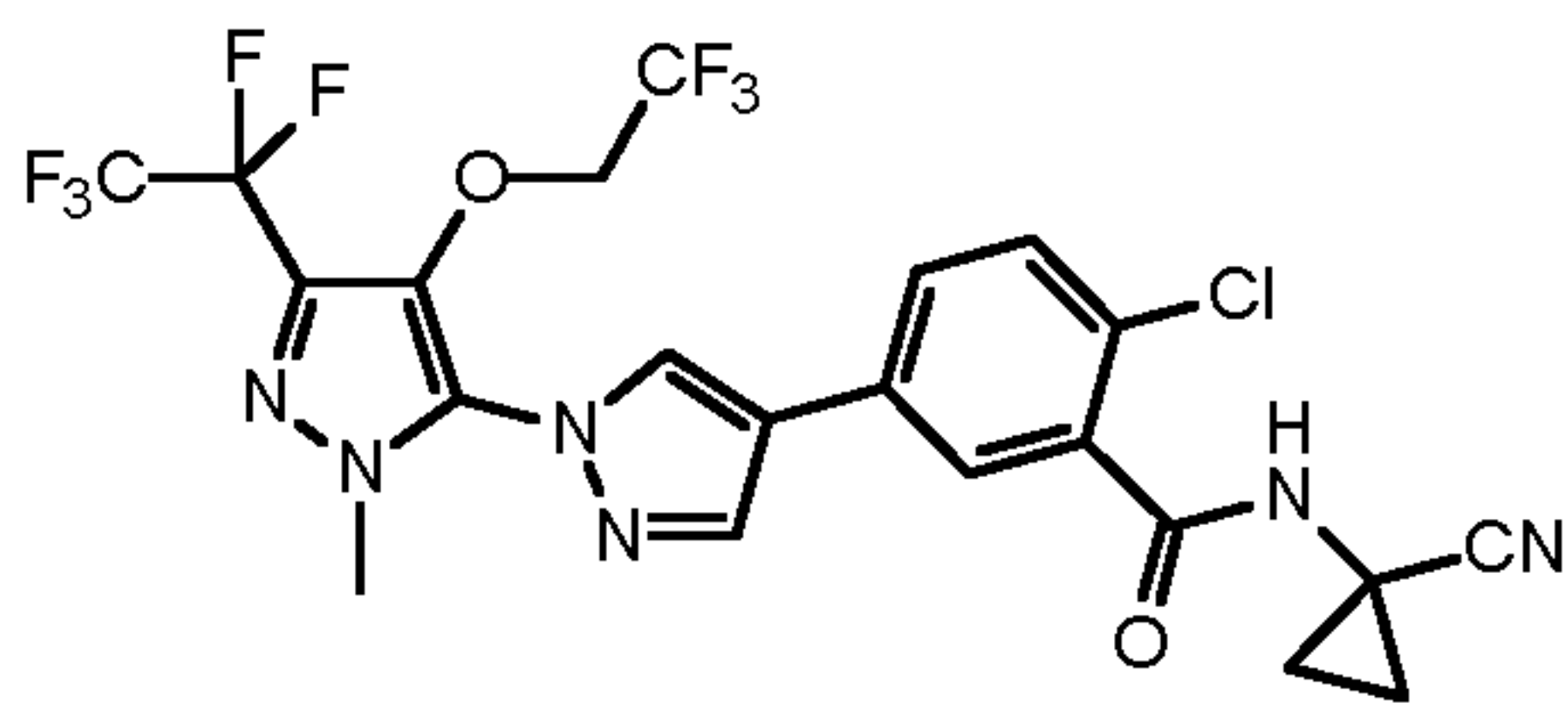
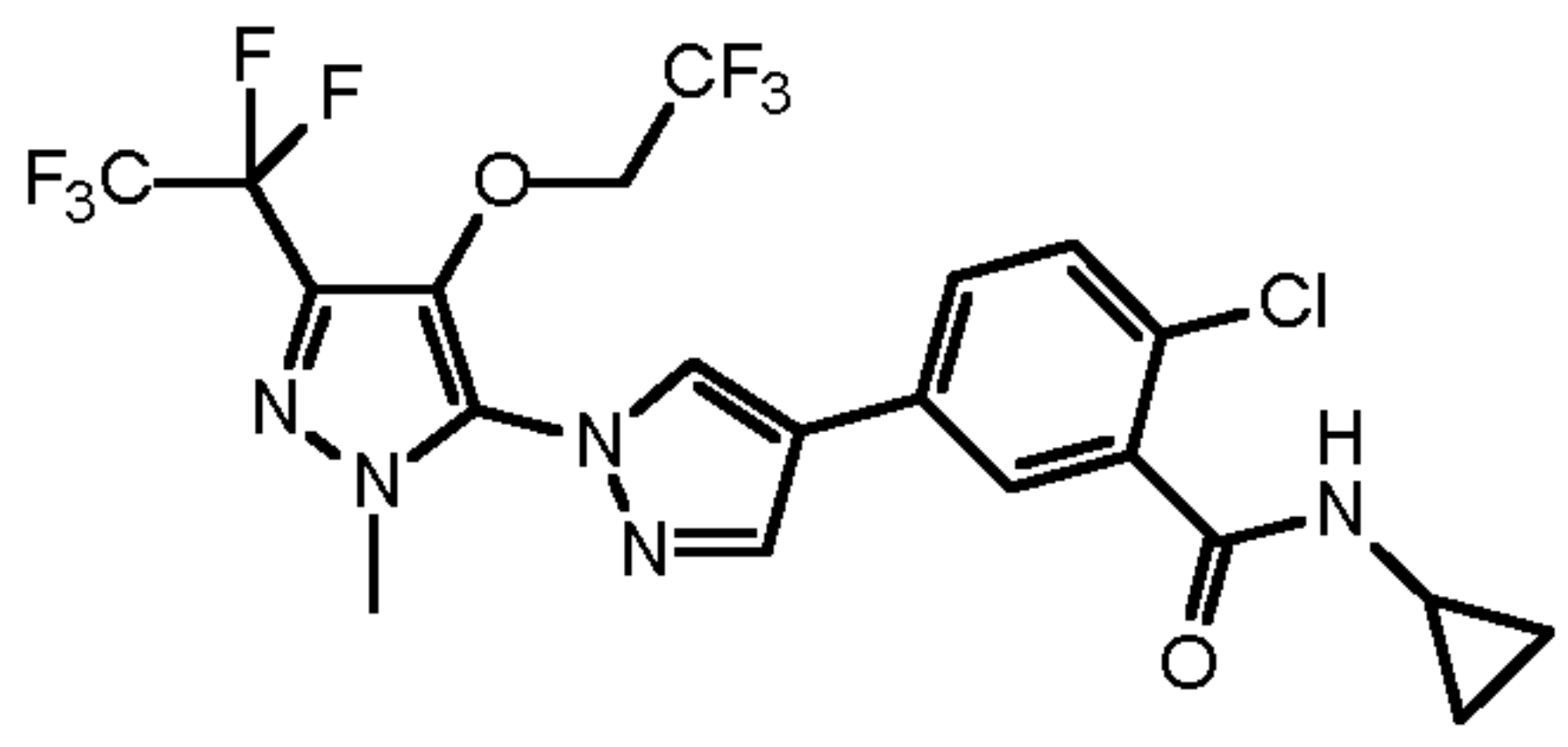
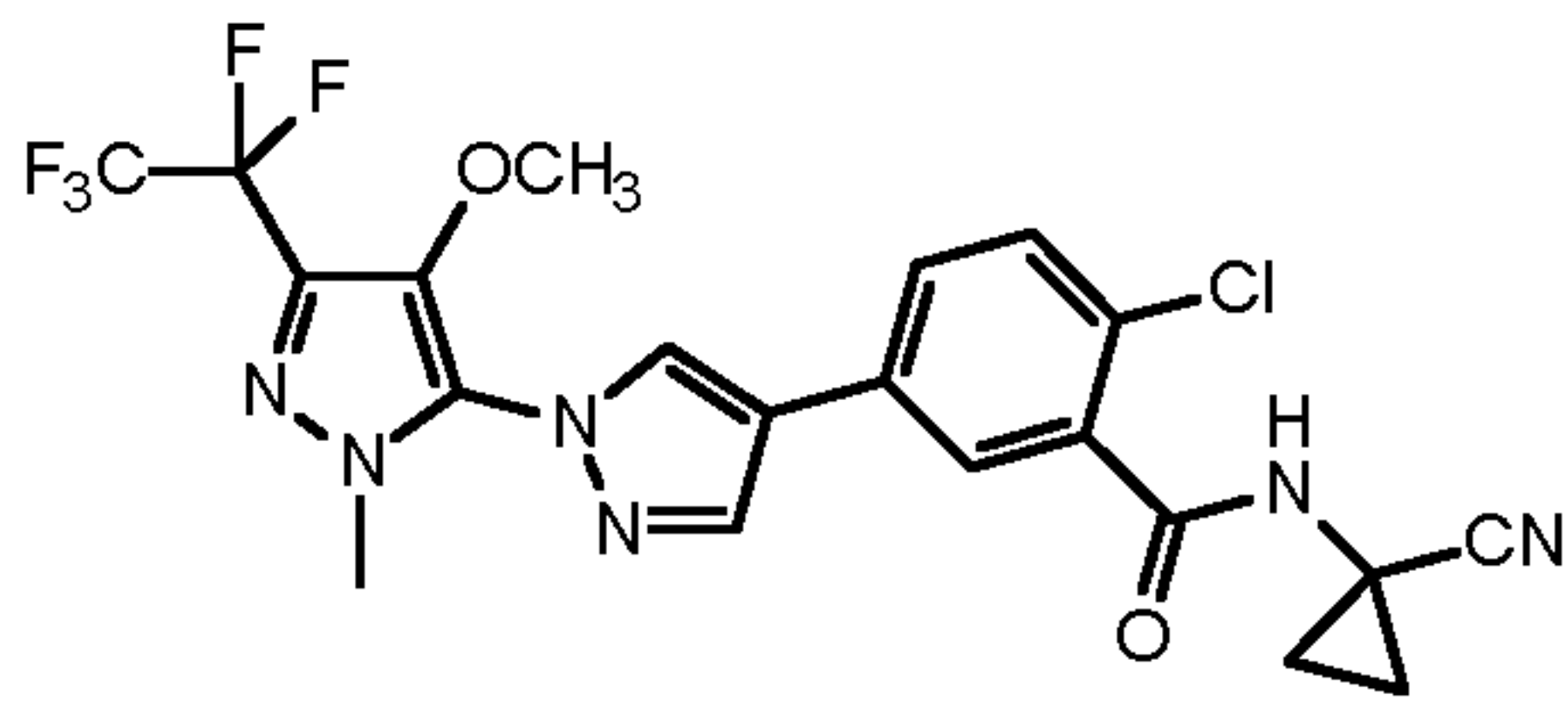
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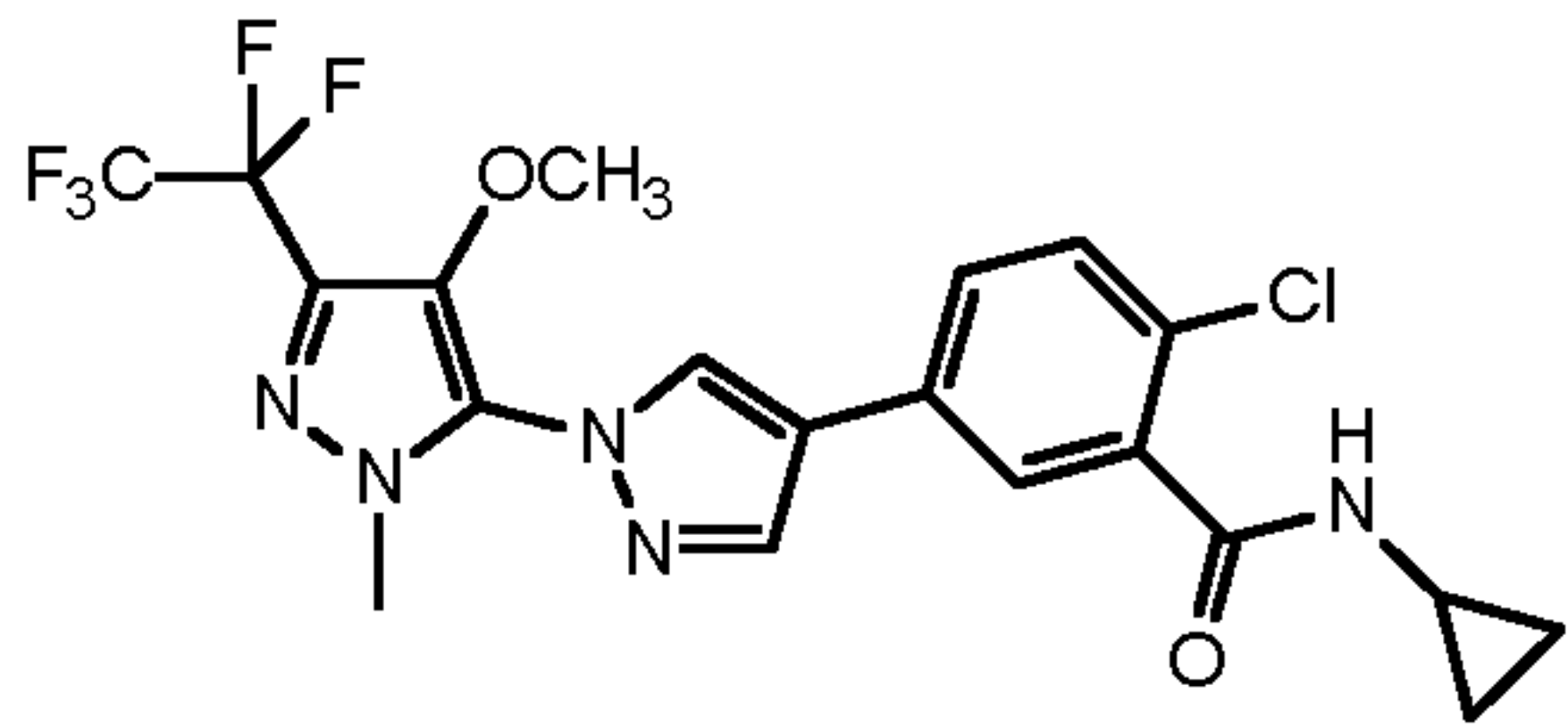
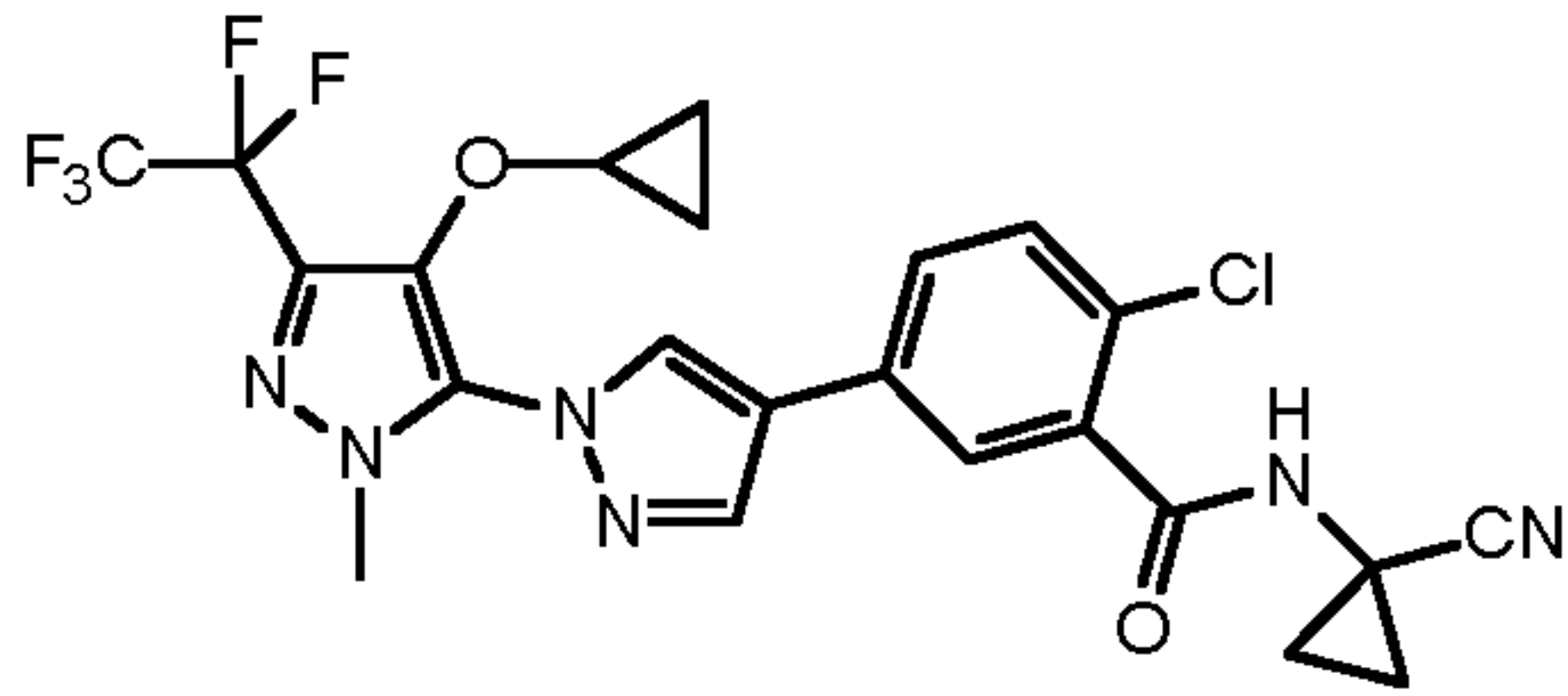
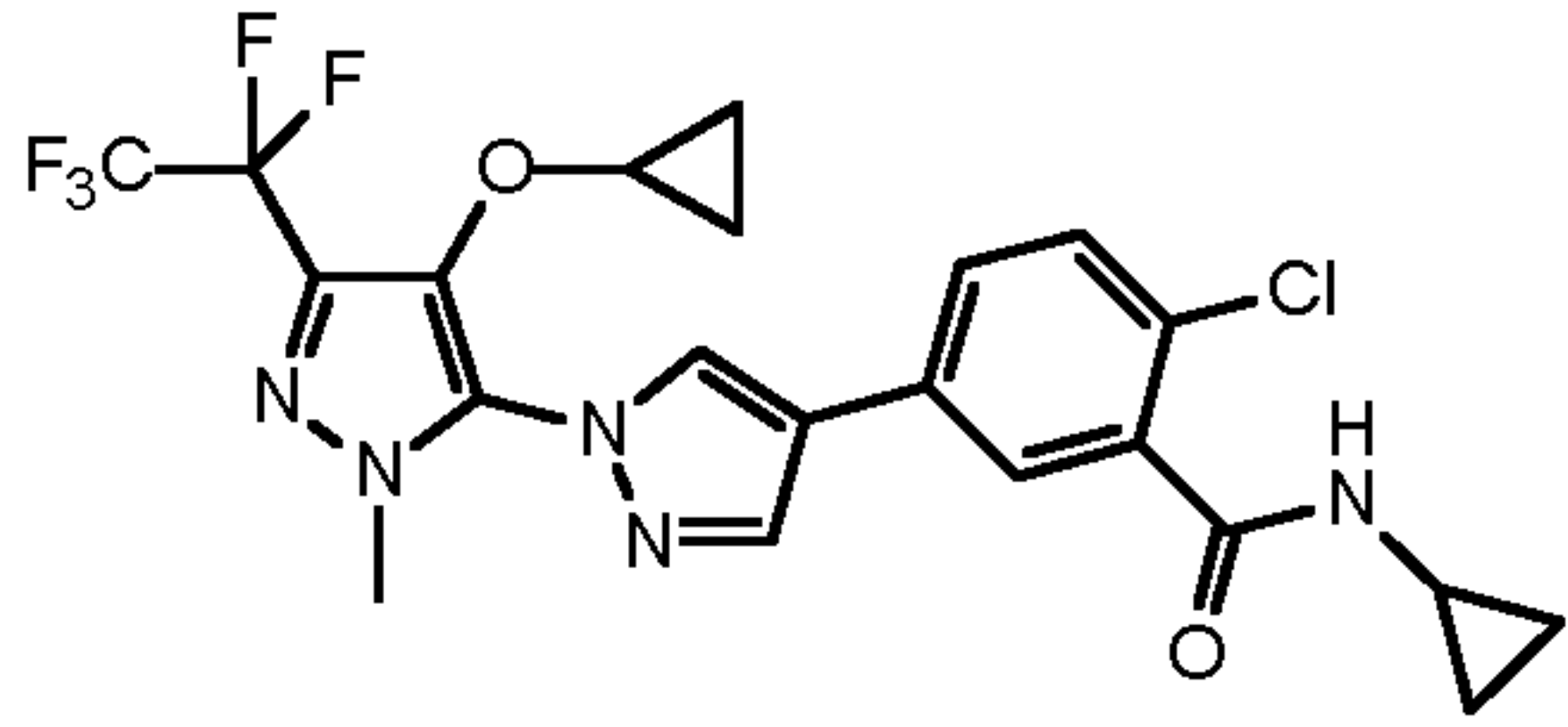
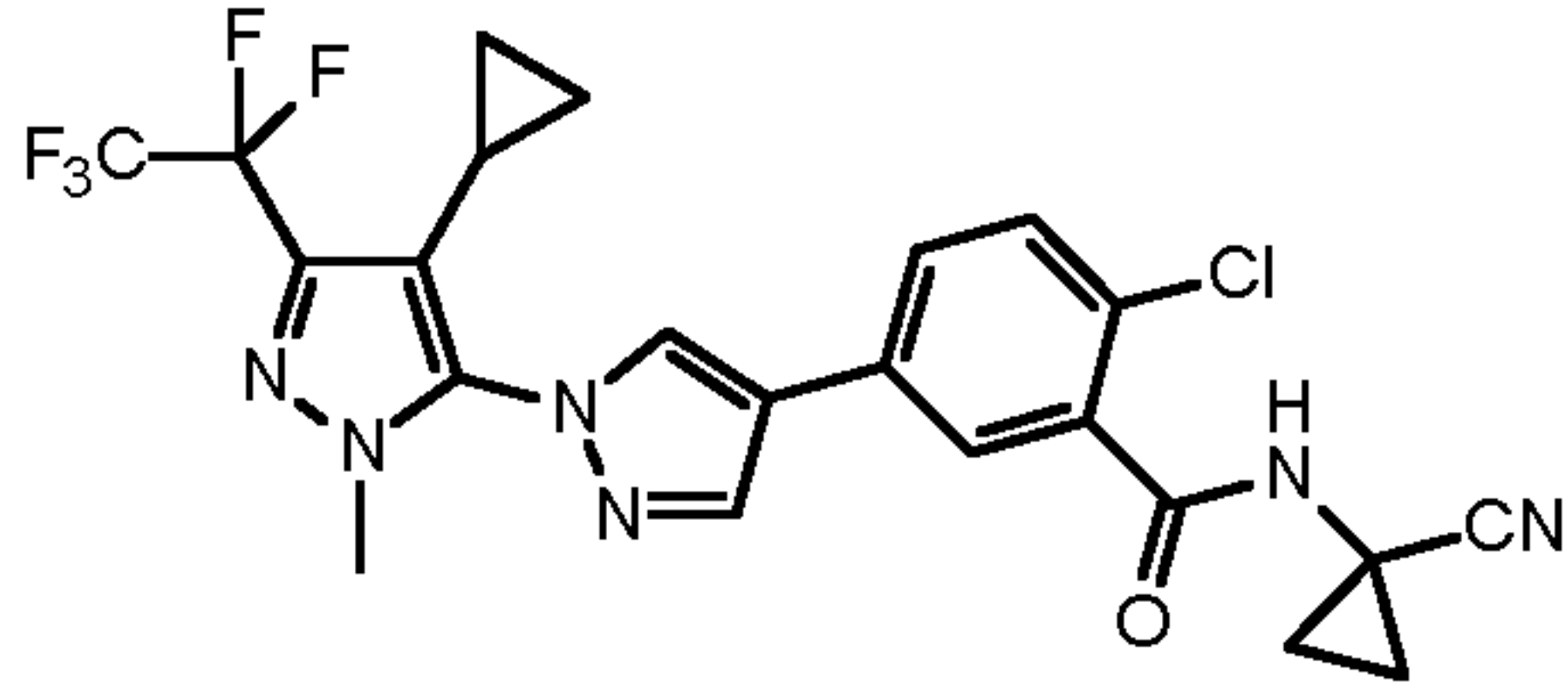
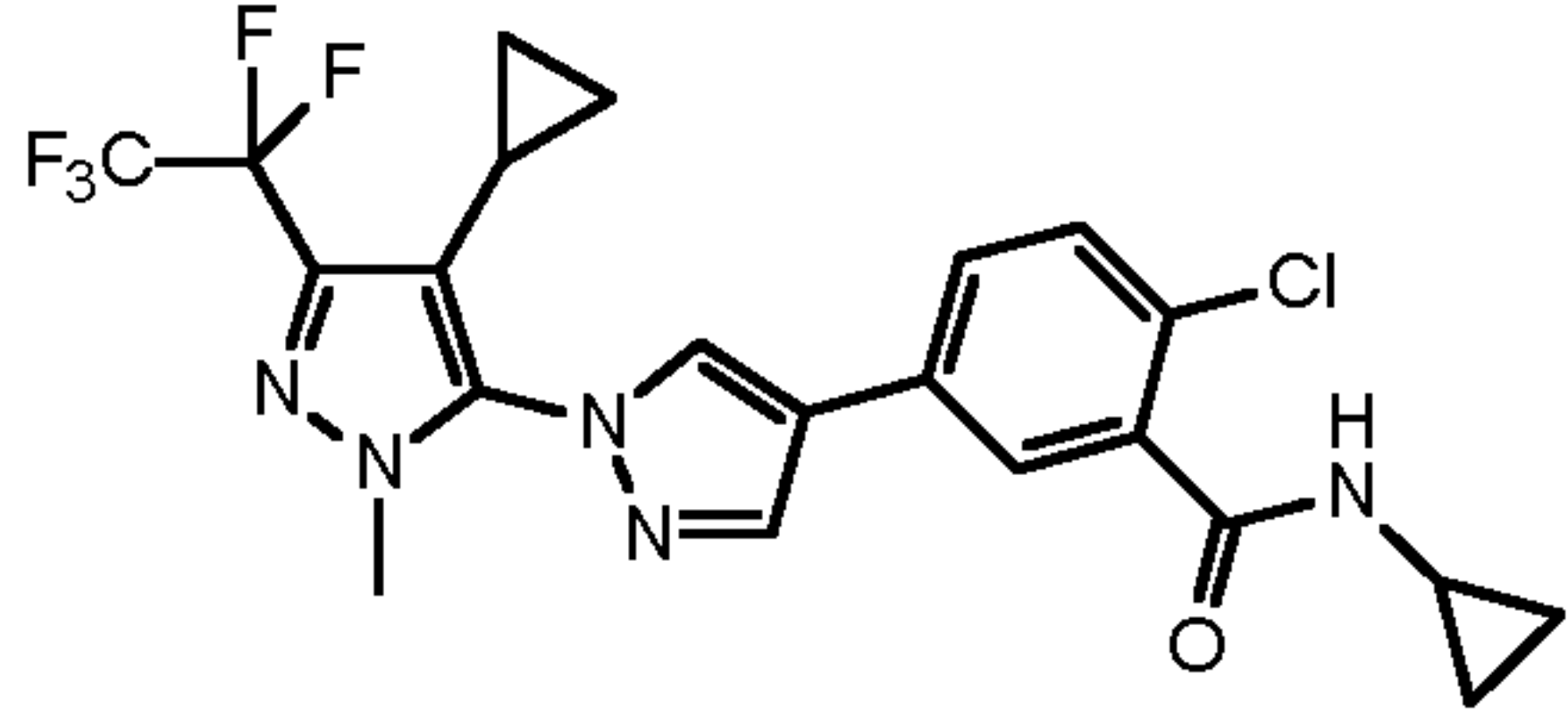
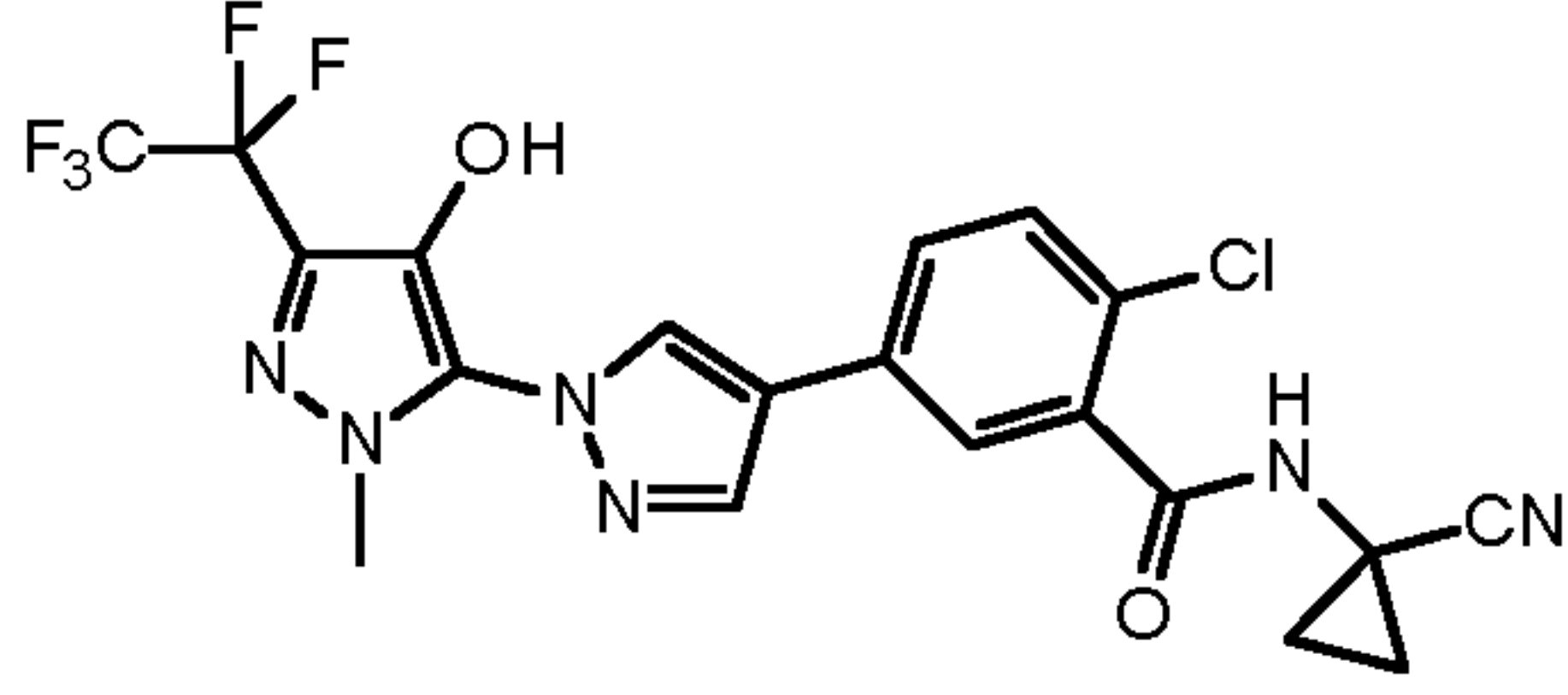
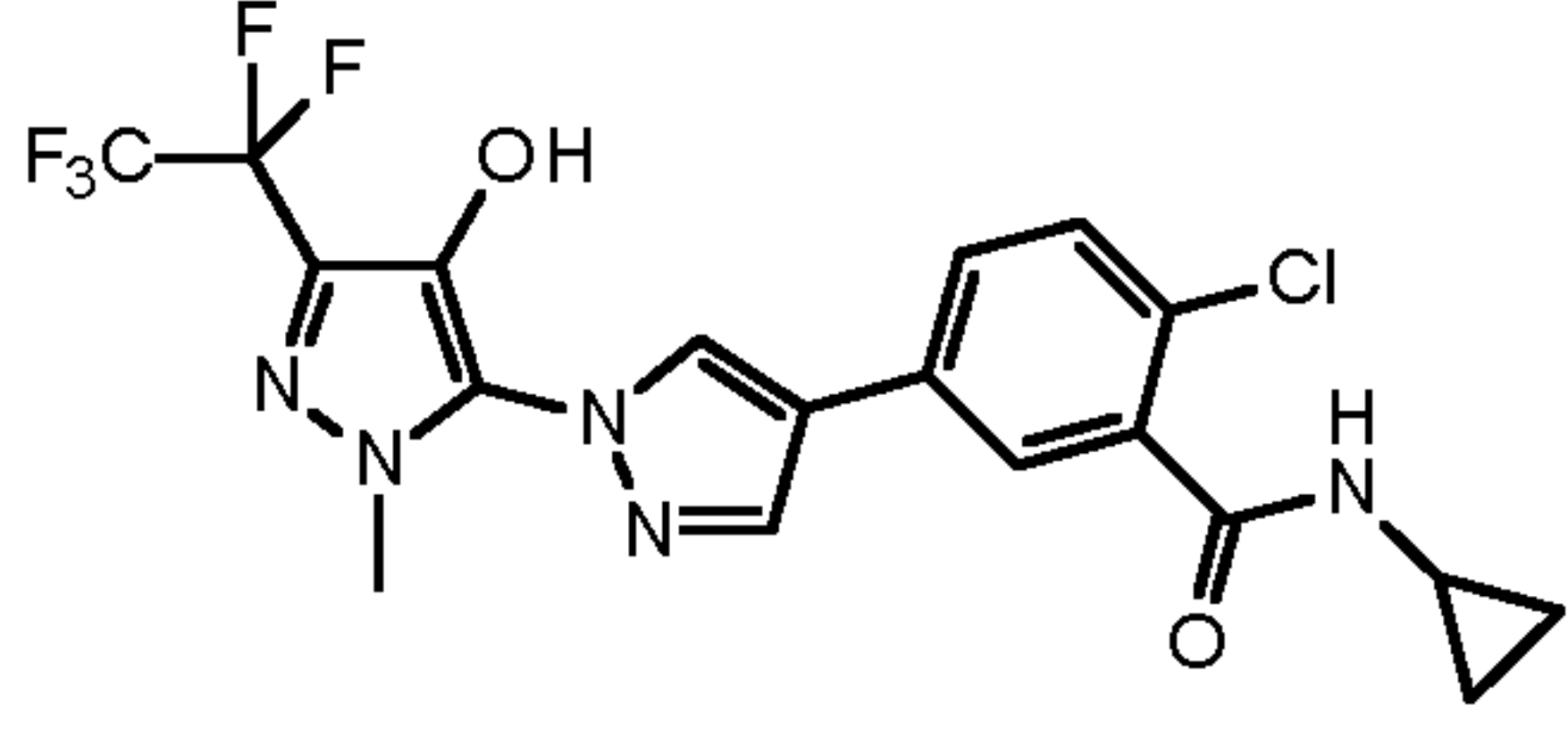
Z¹ is -CF₂CF₃;

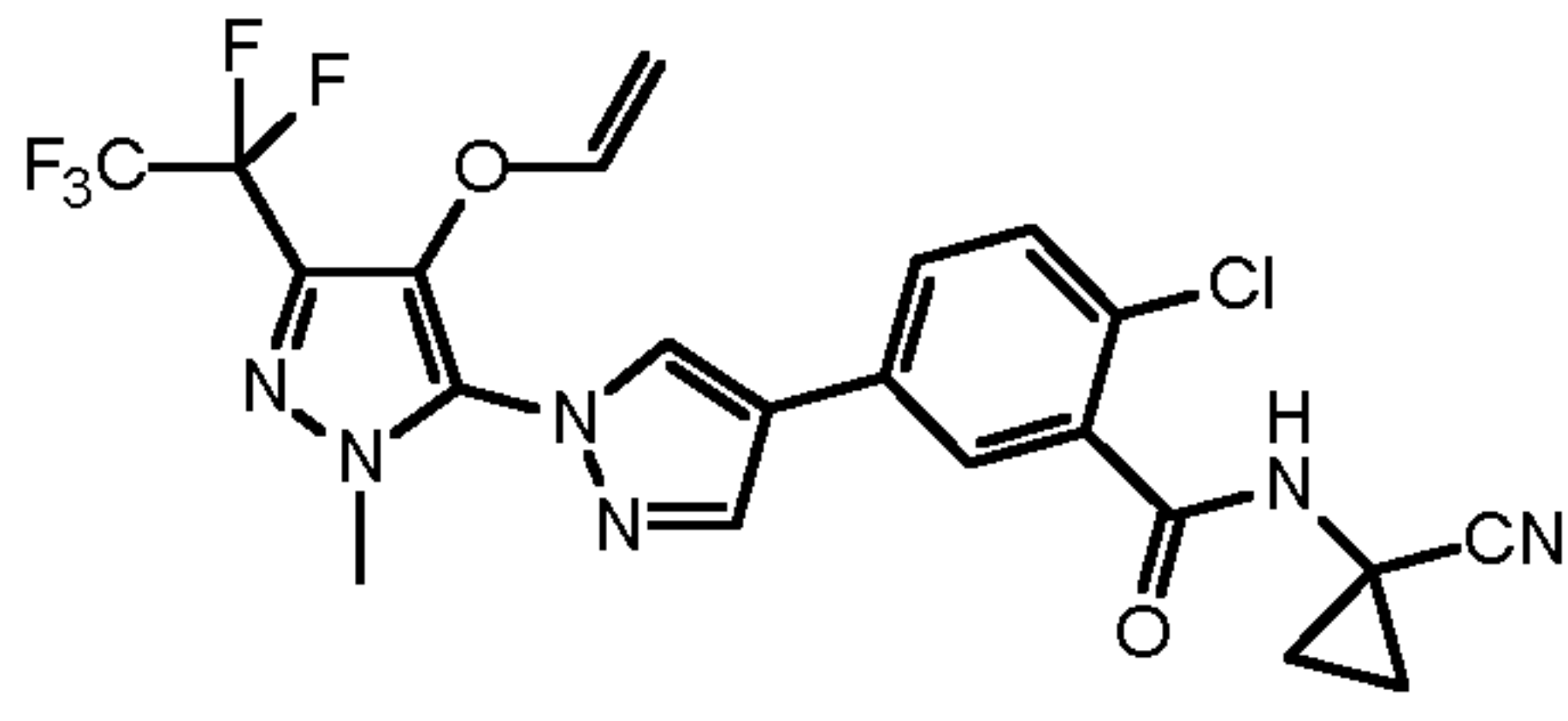
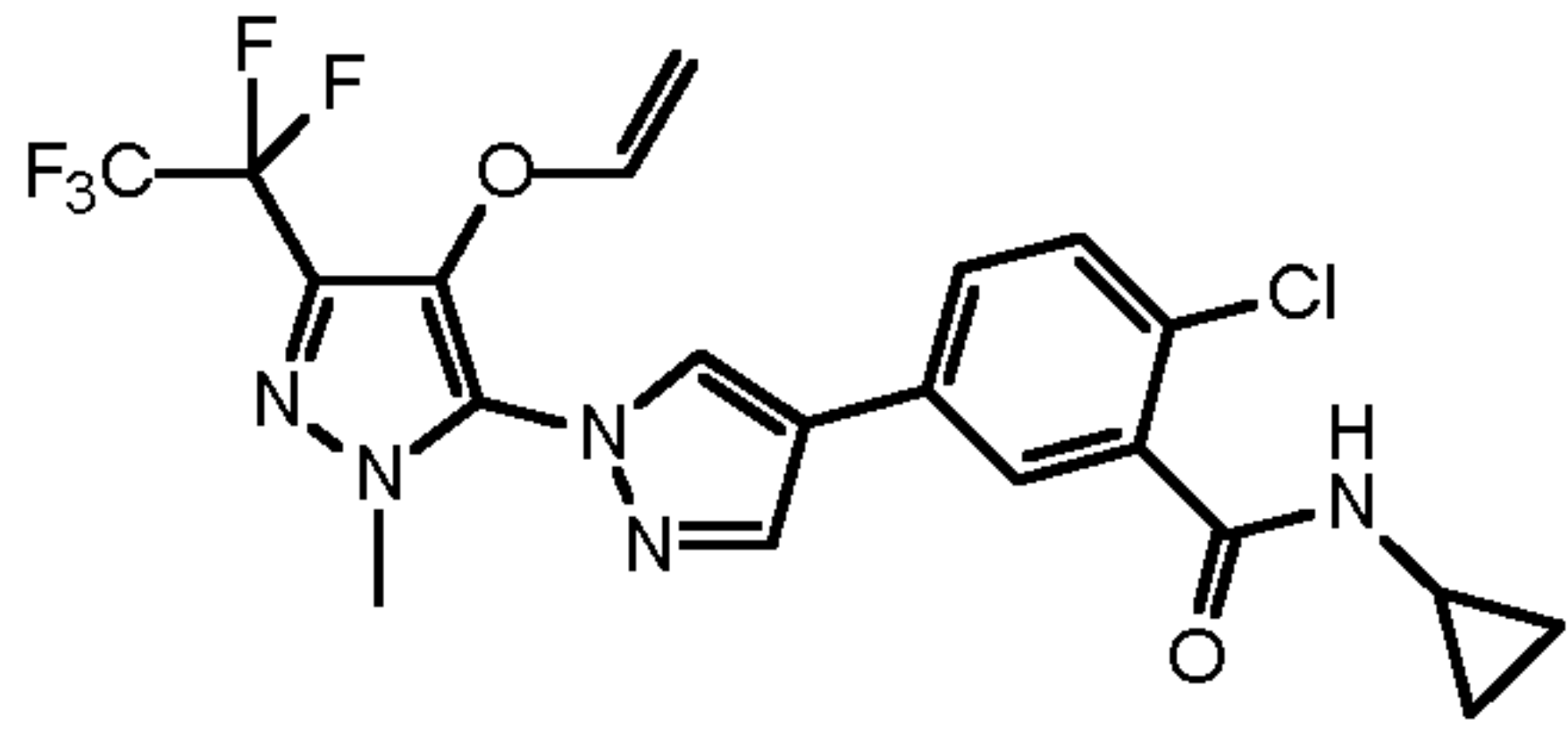
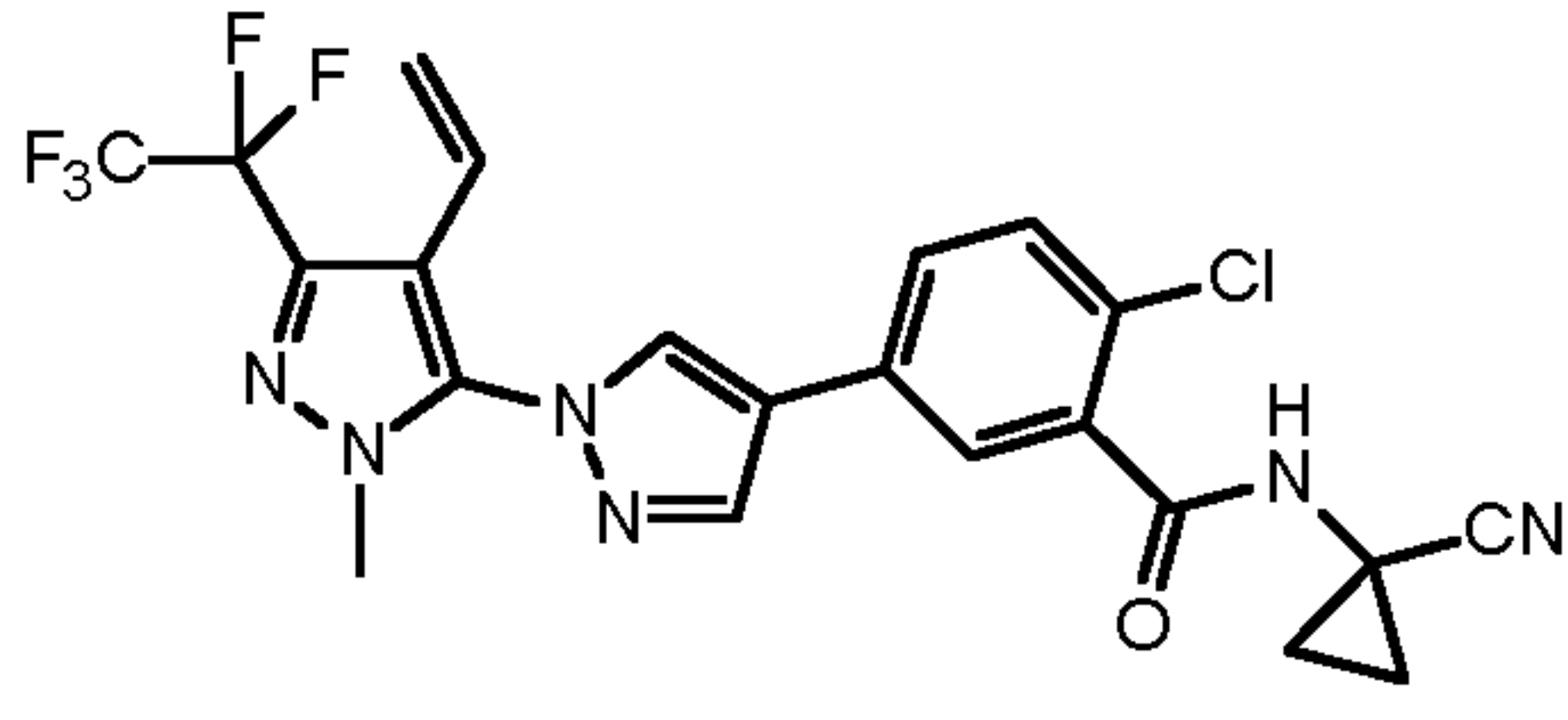
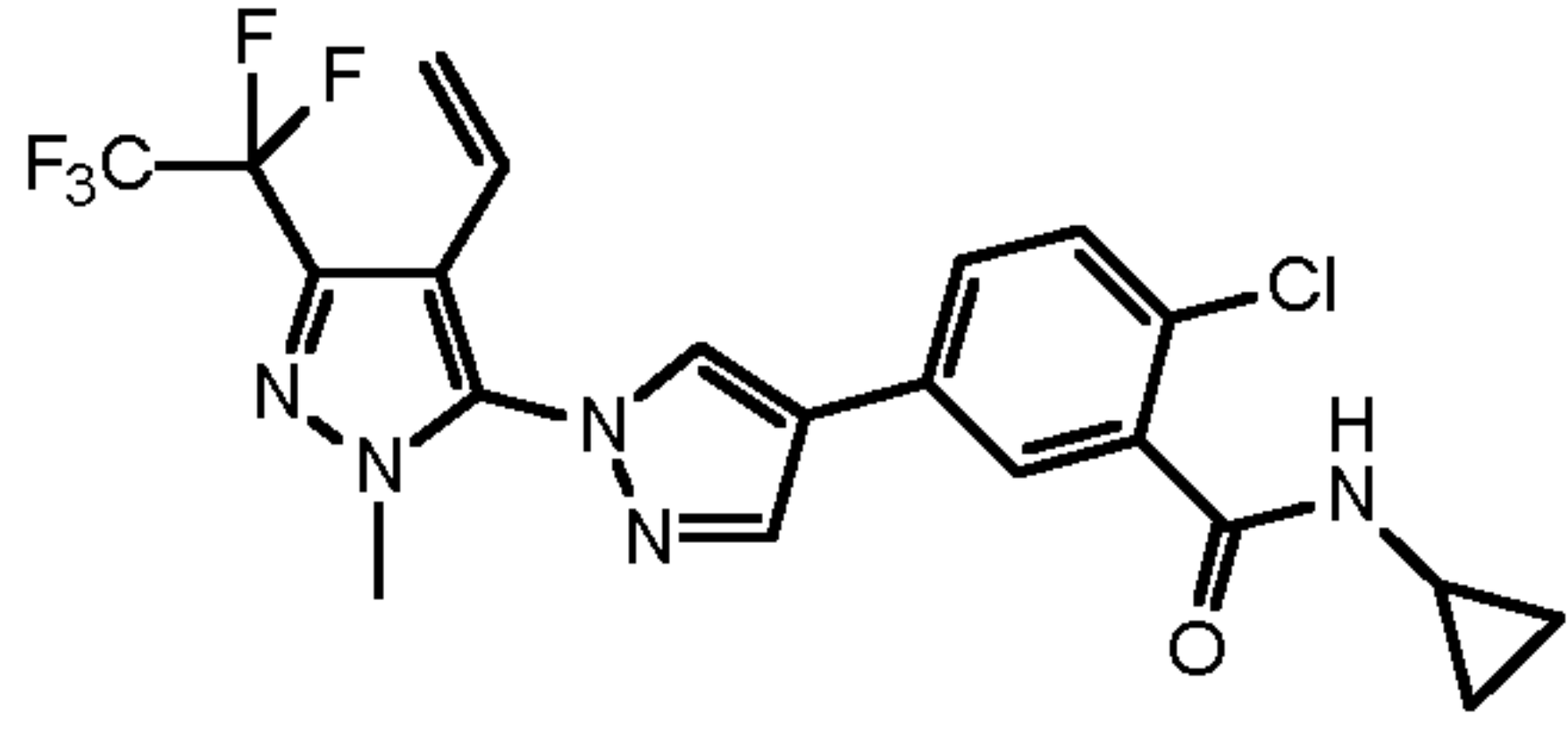
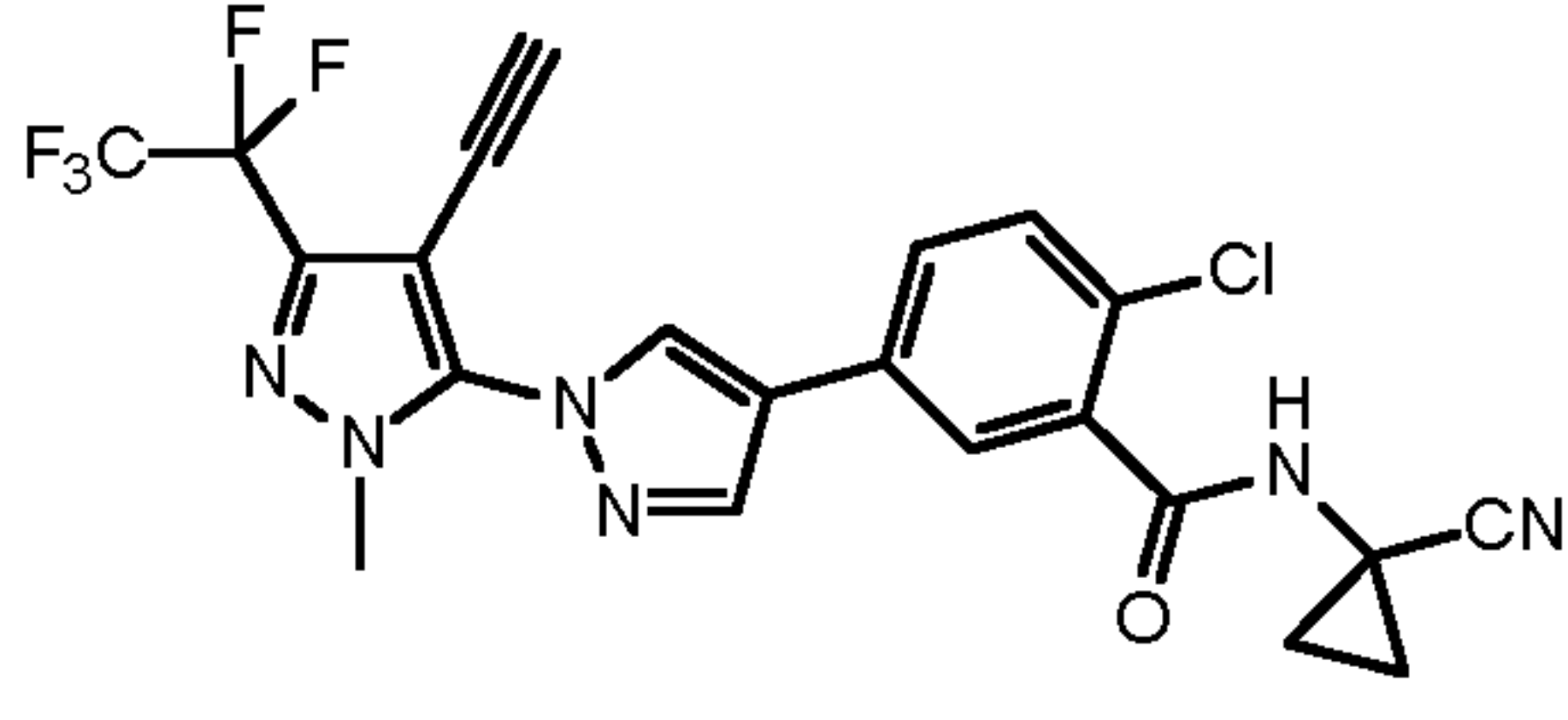
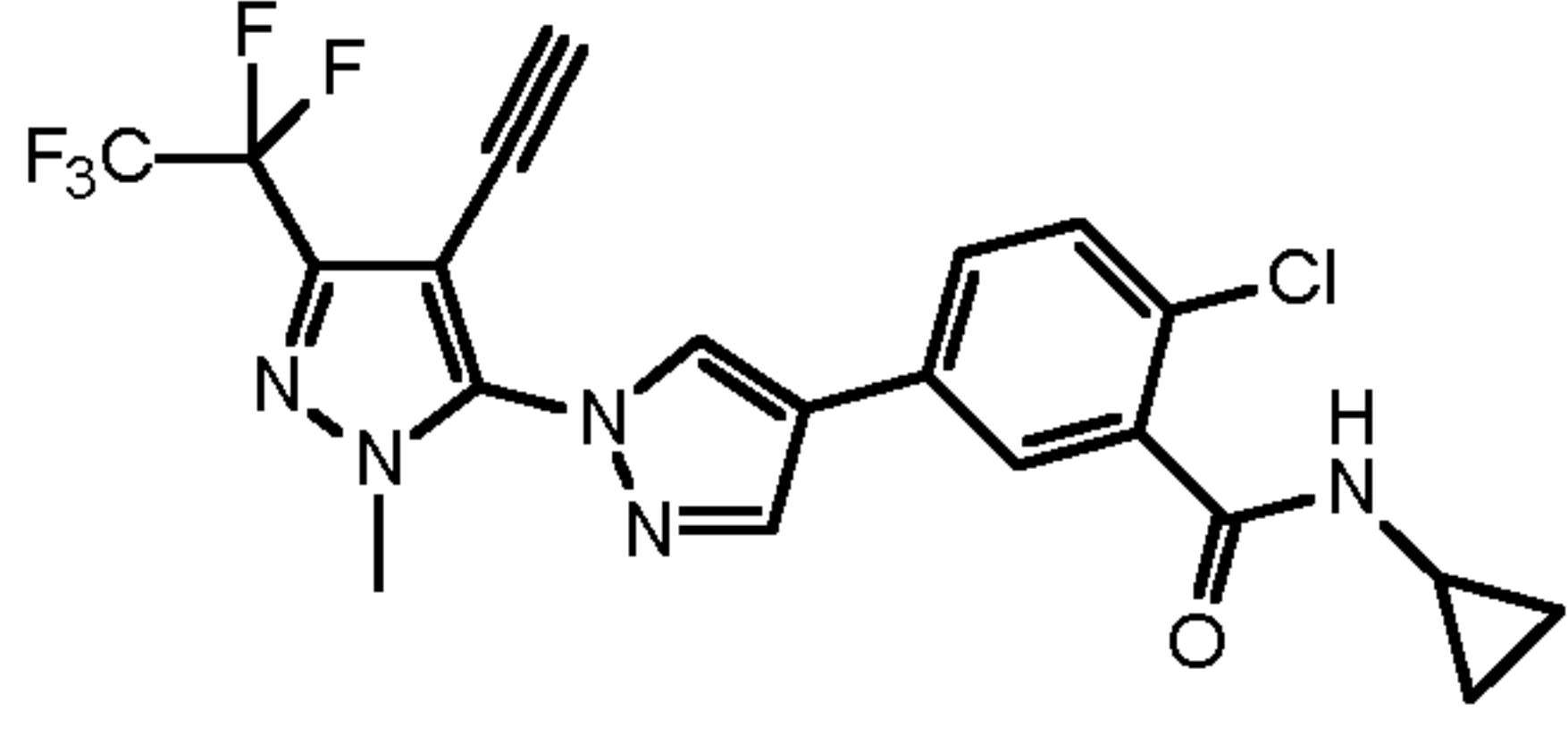
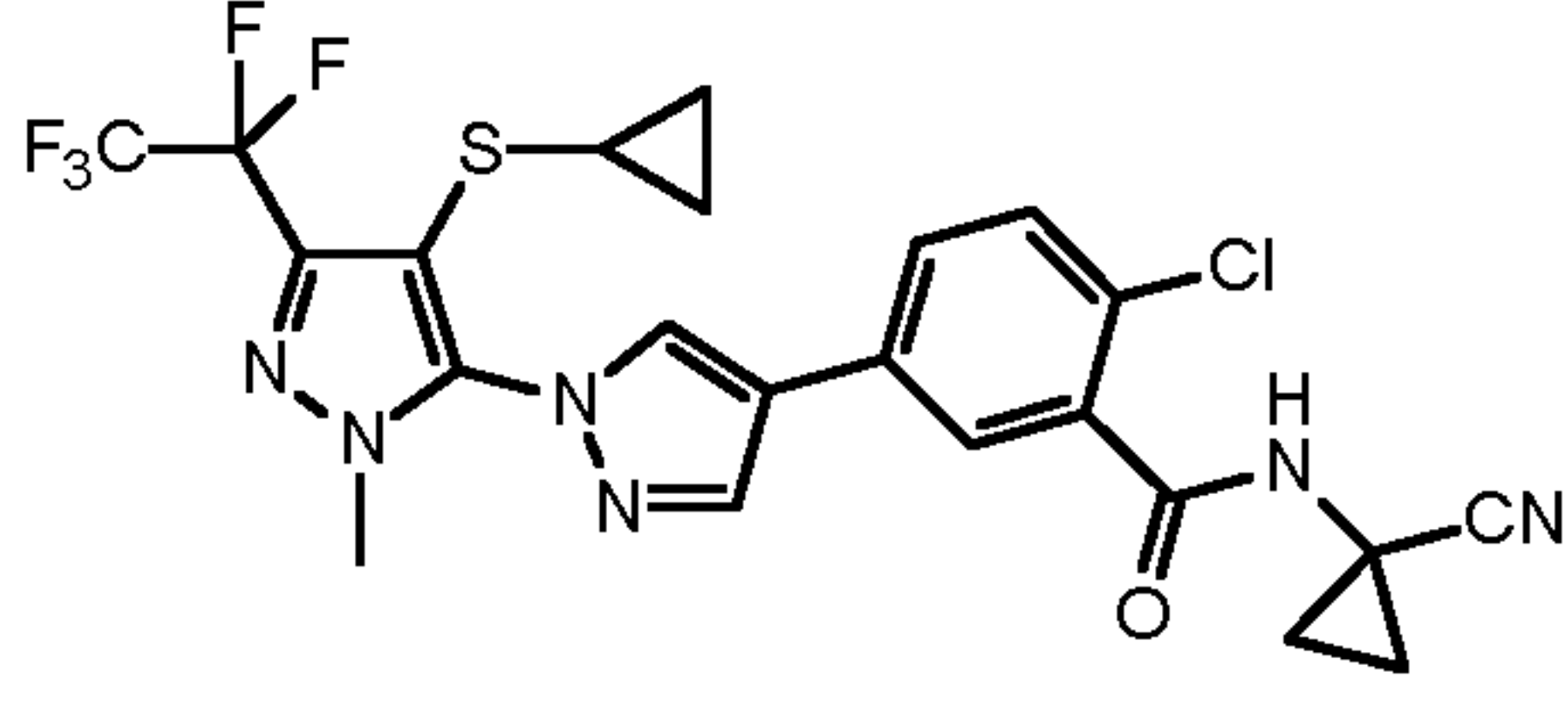
U is selected from -OCHF₂, -CH=CH₂ and -C≡CH, in particular -OCHF₂;

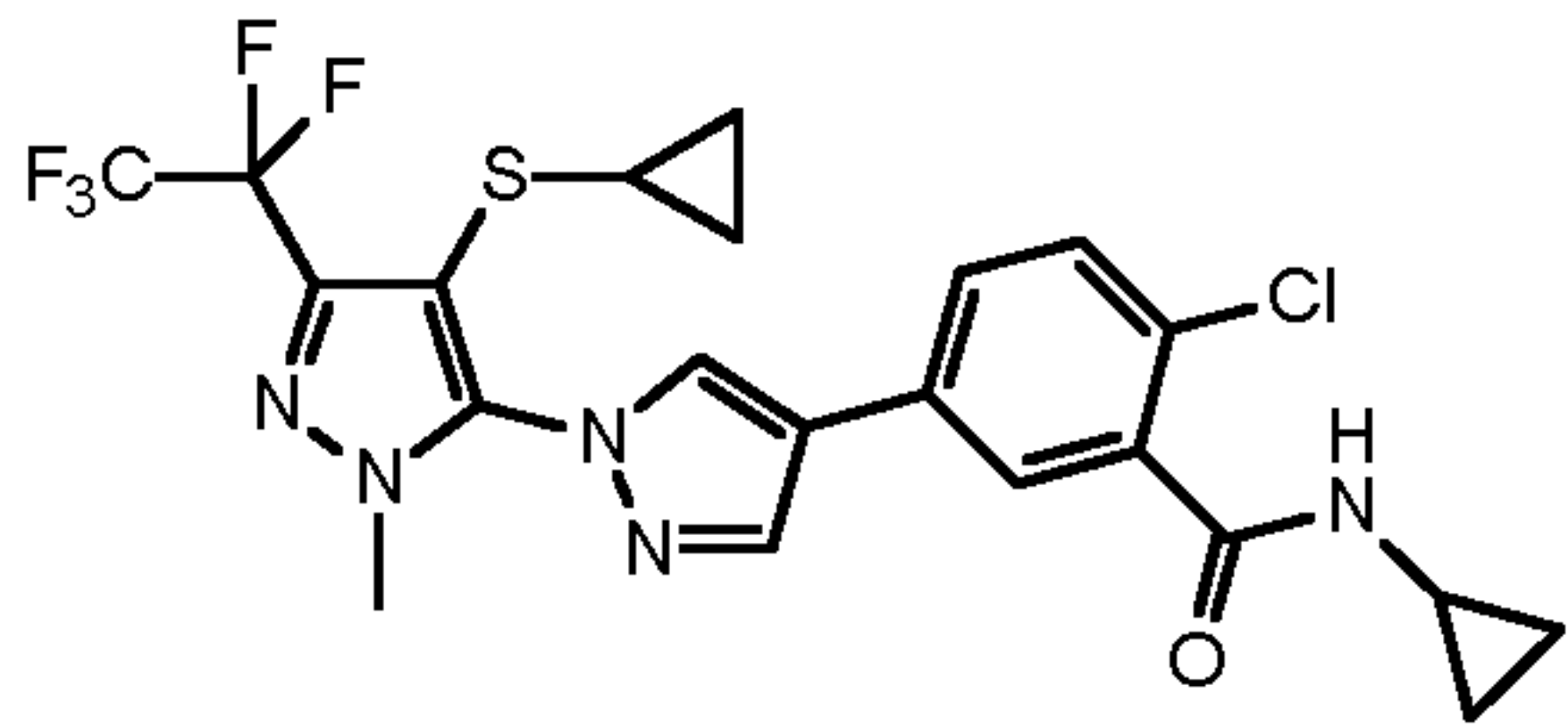
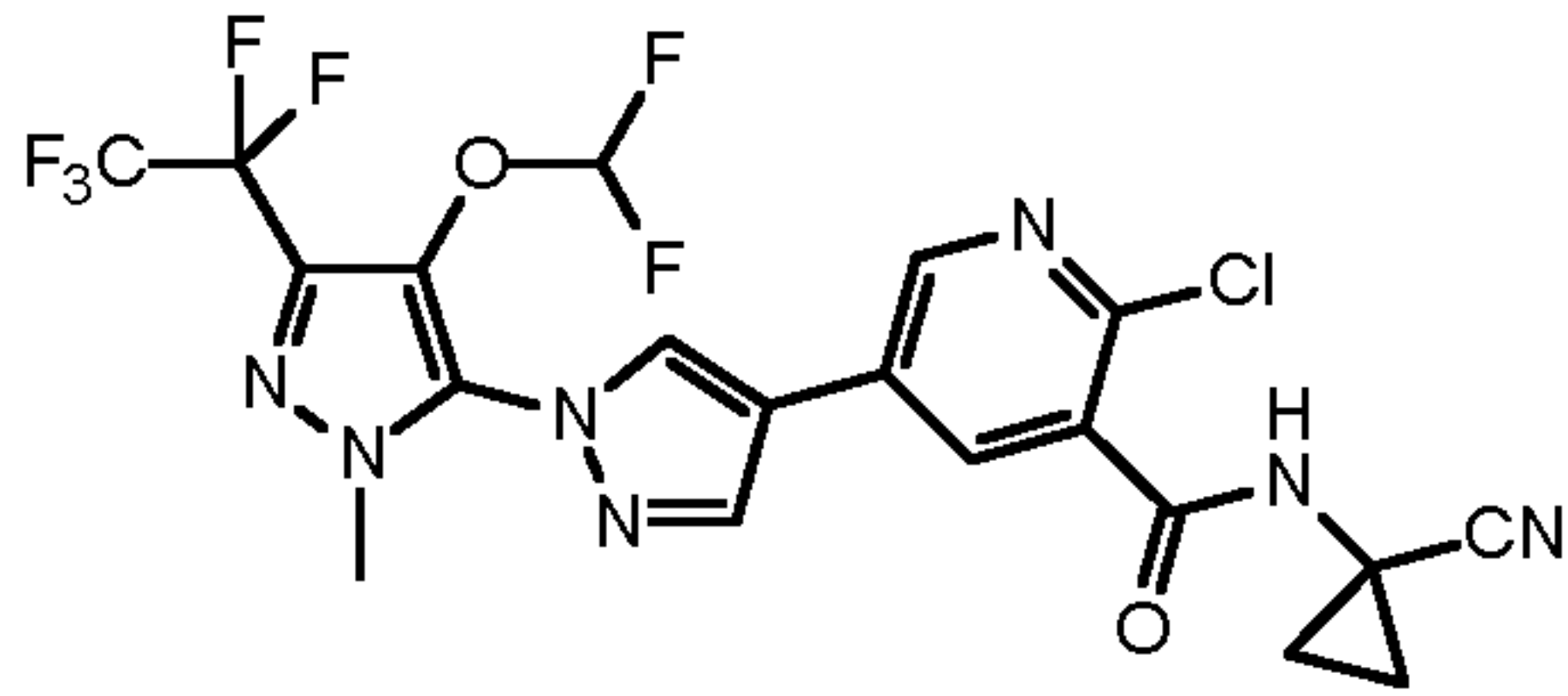
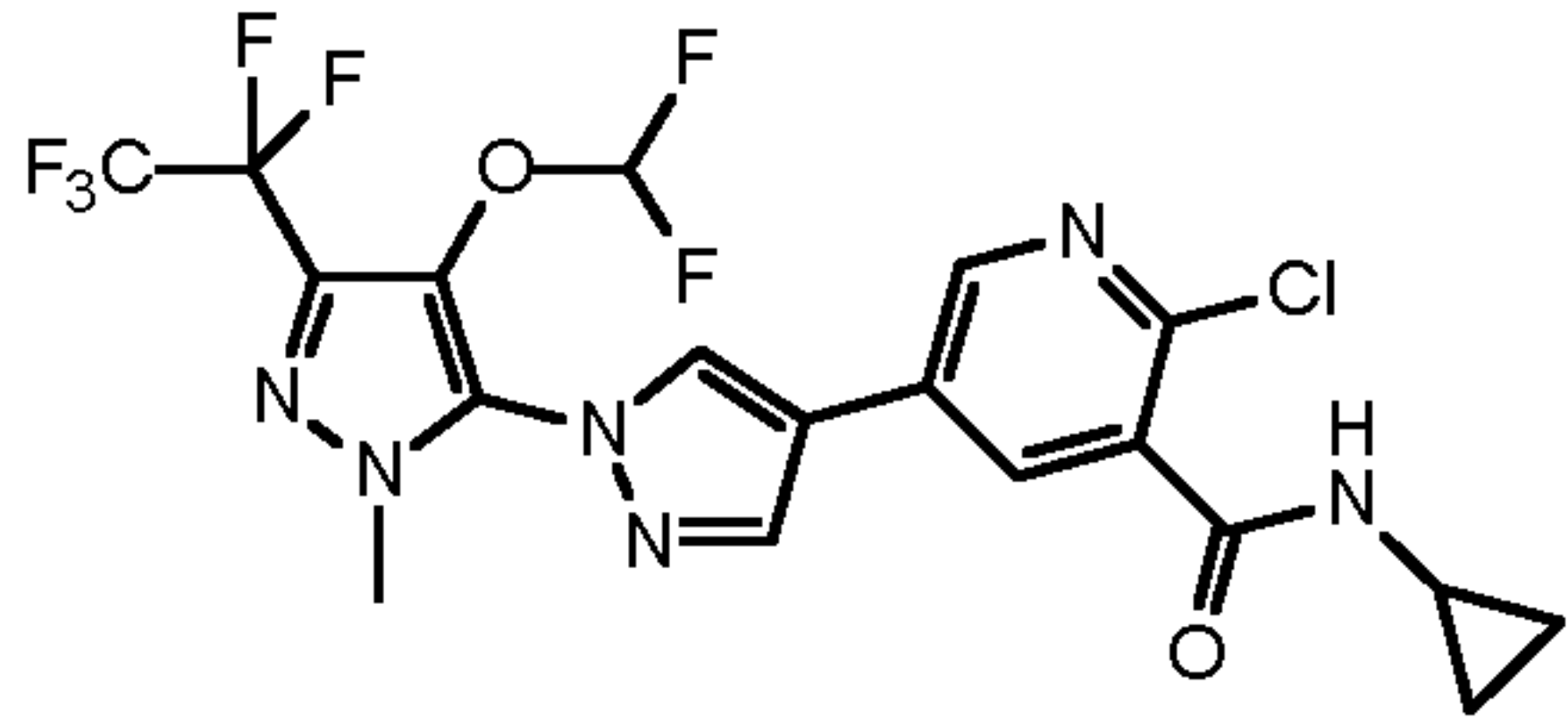
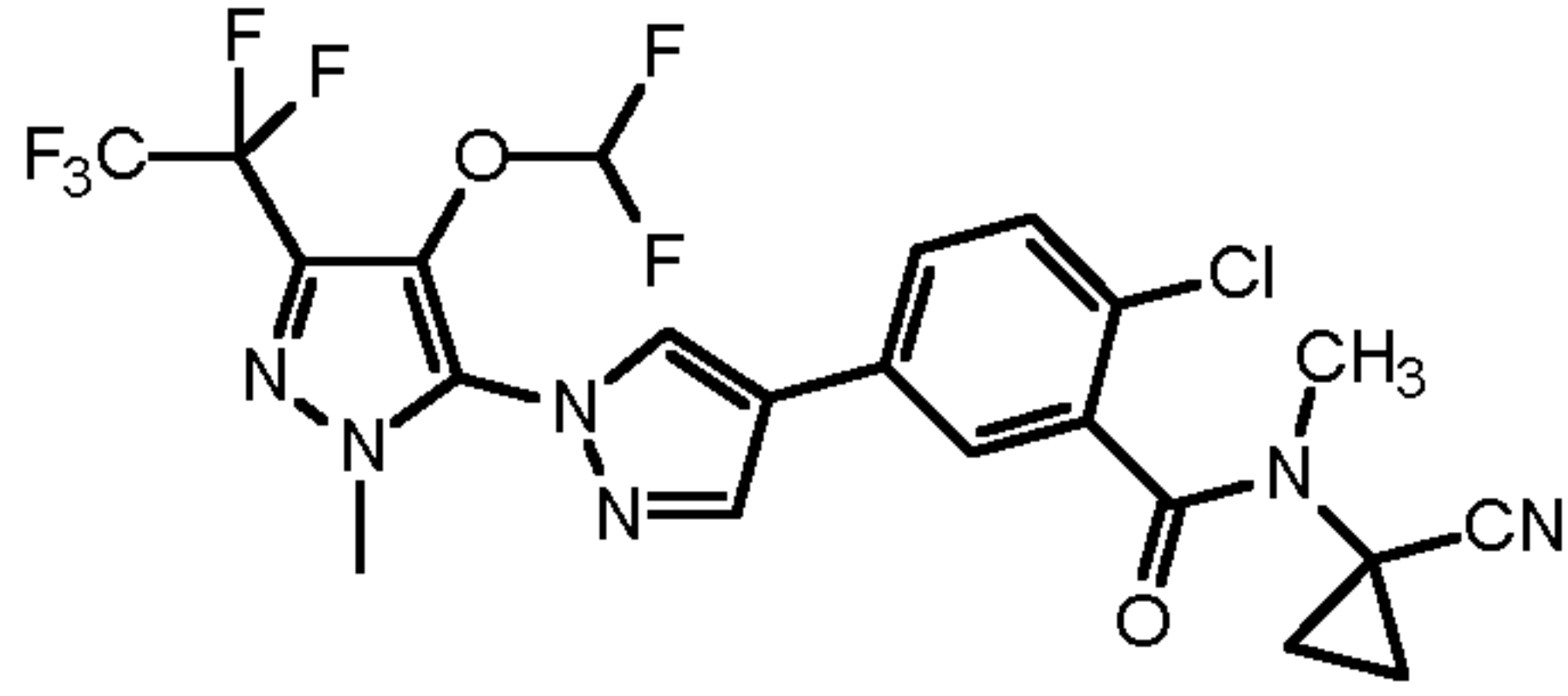
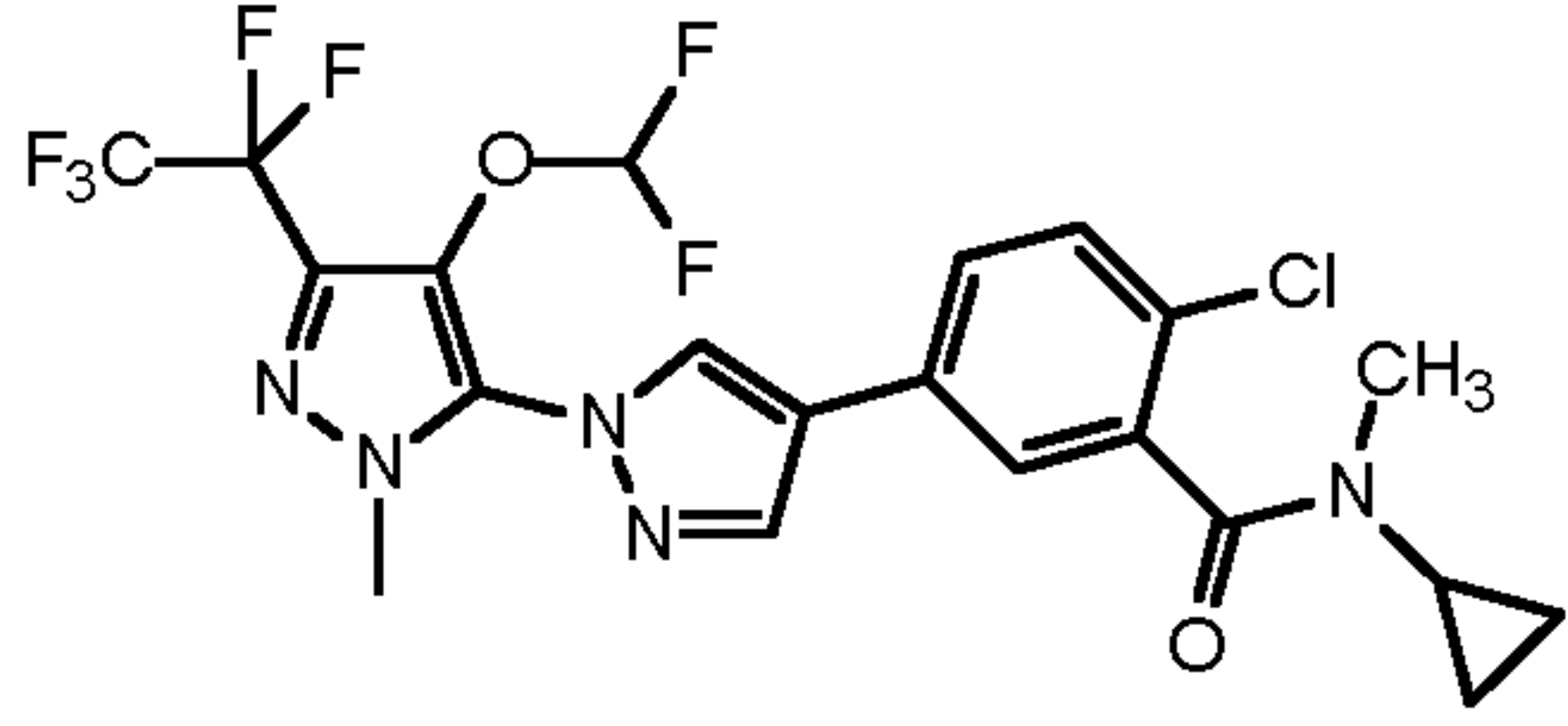
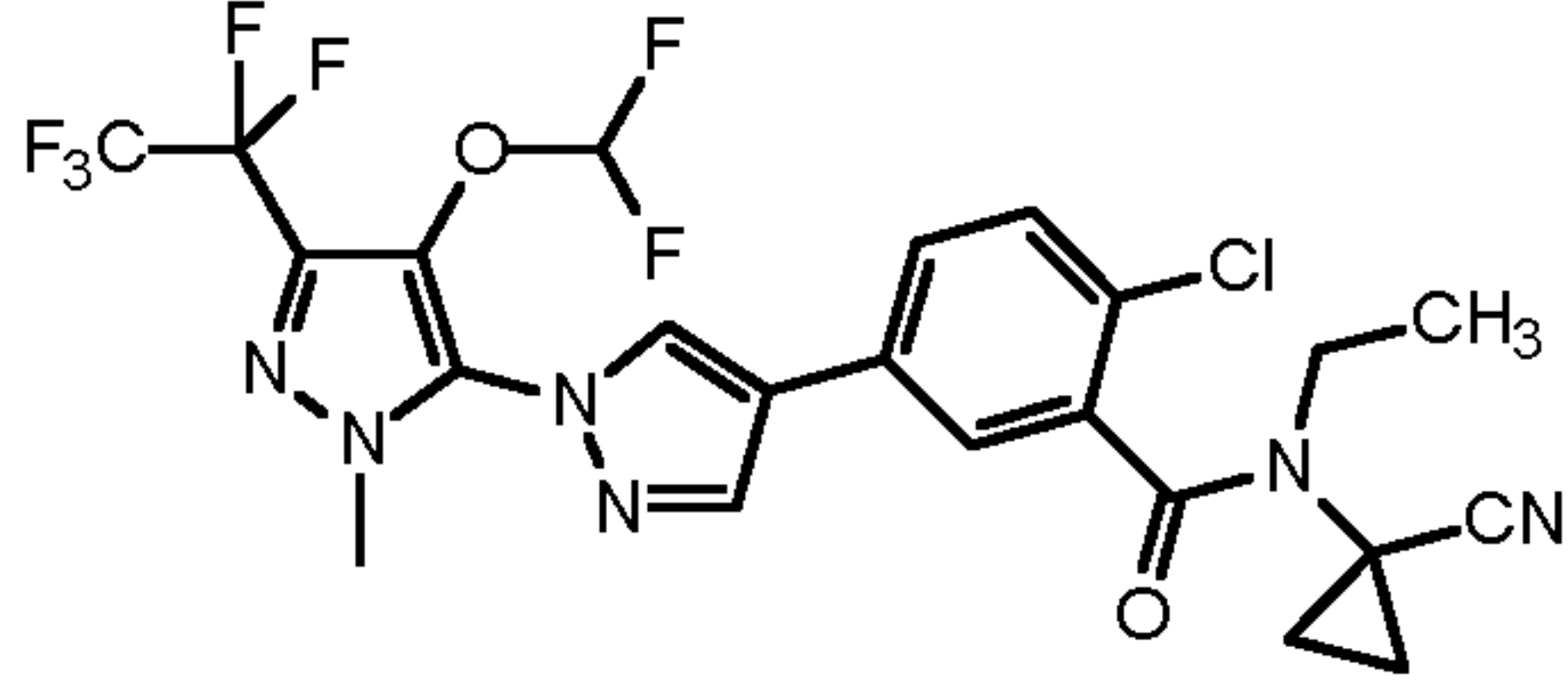
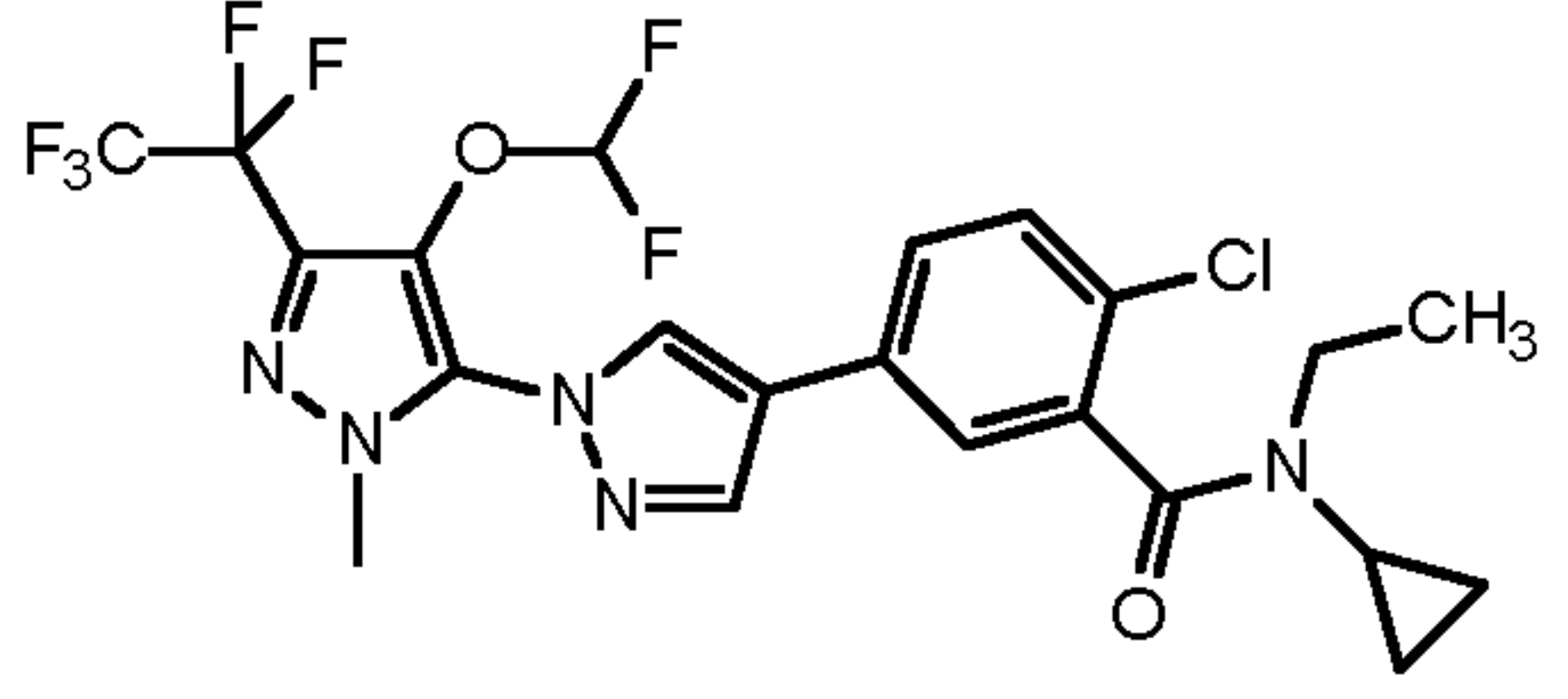
10 Z³ is methyl.

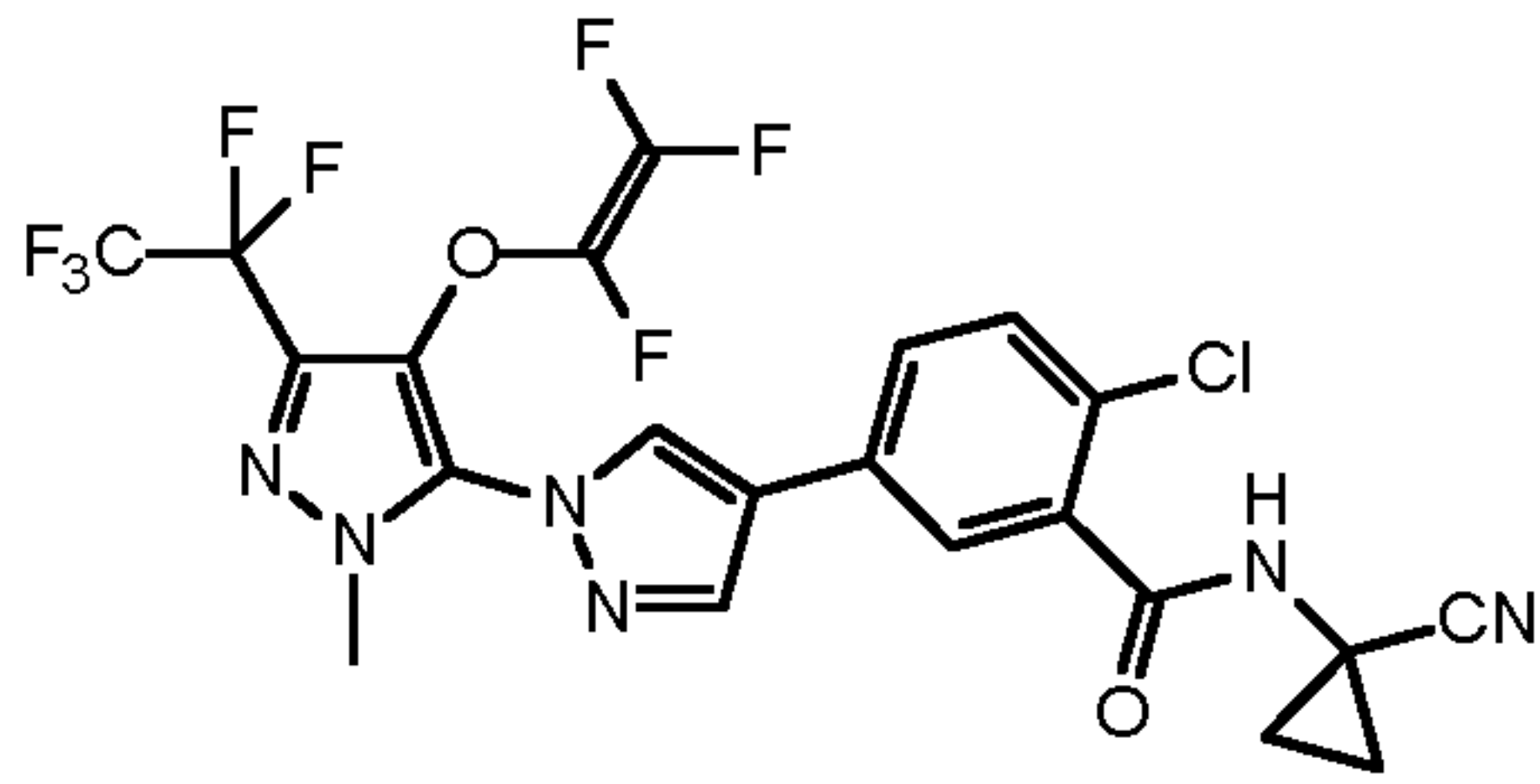
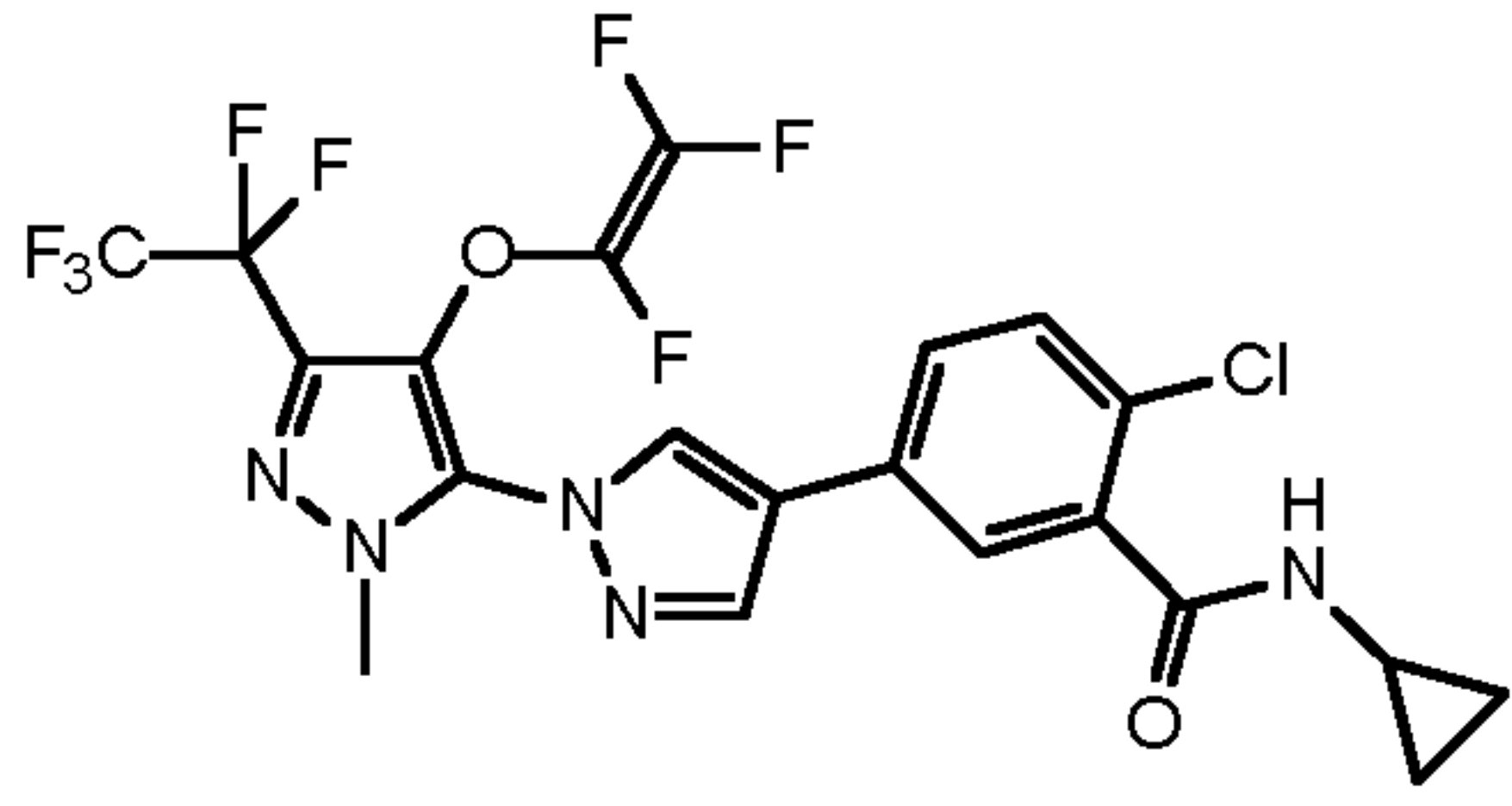
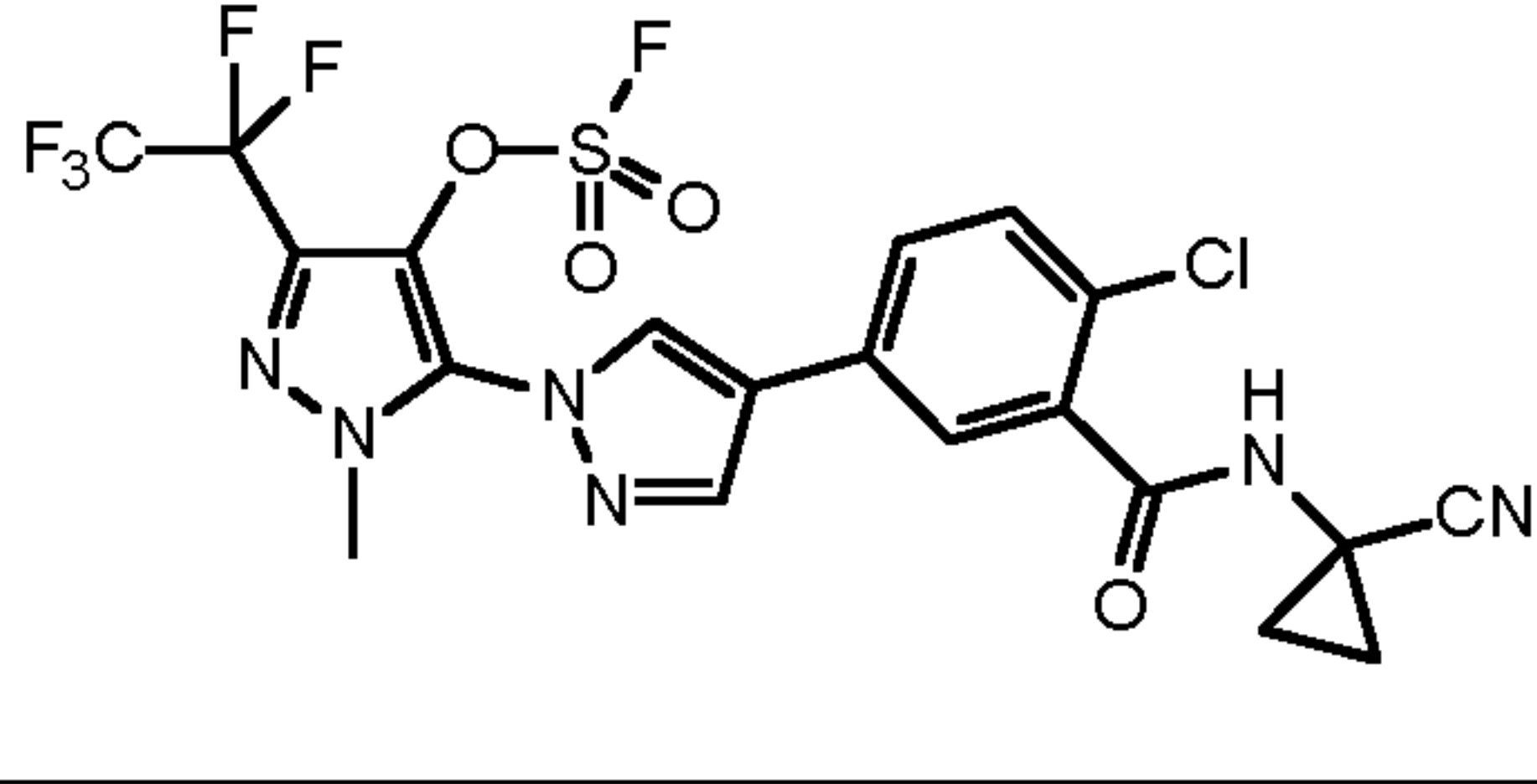
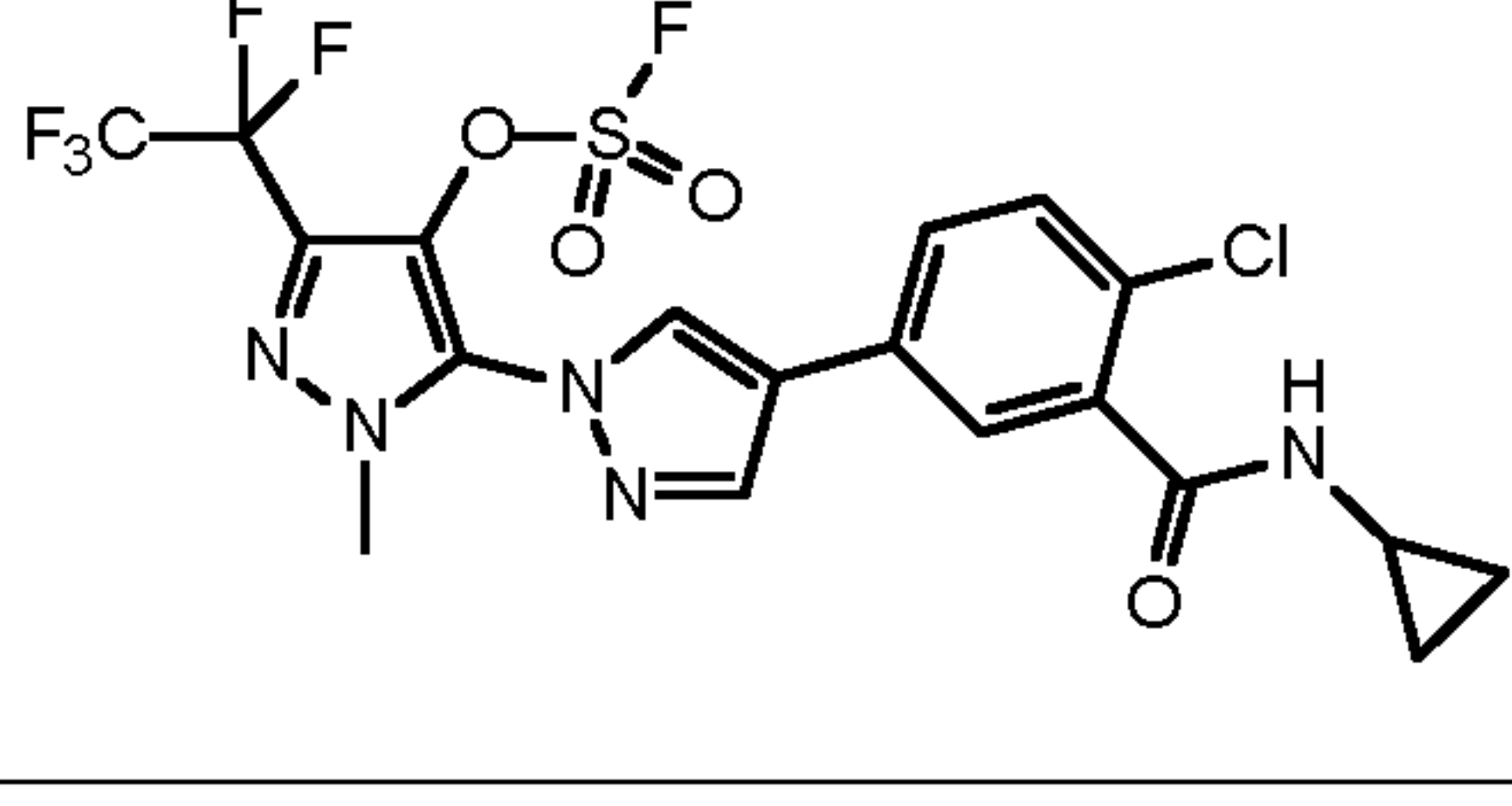
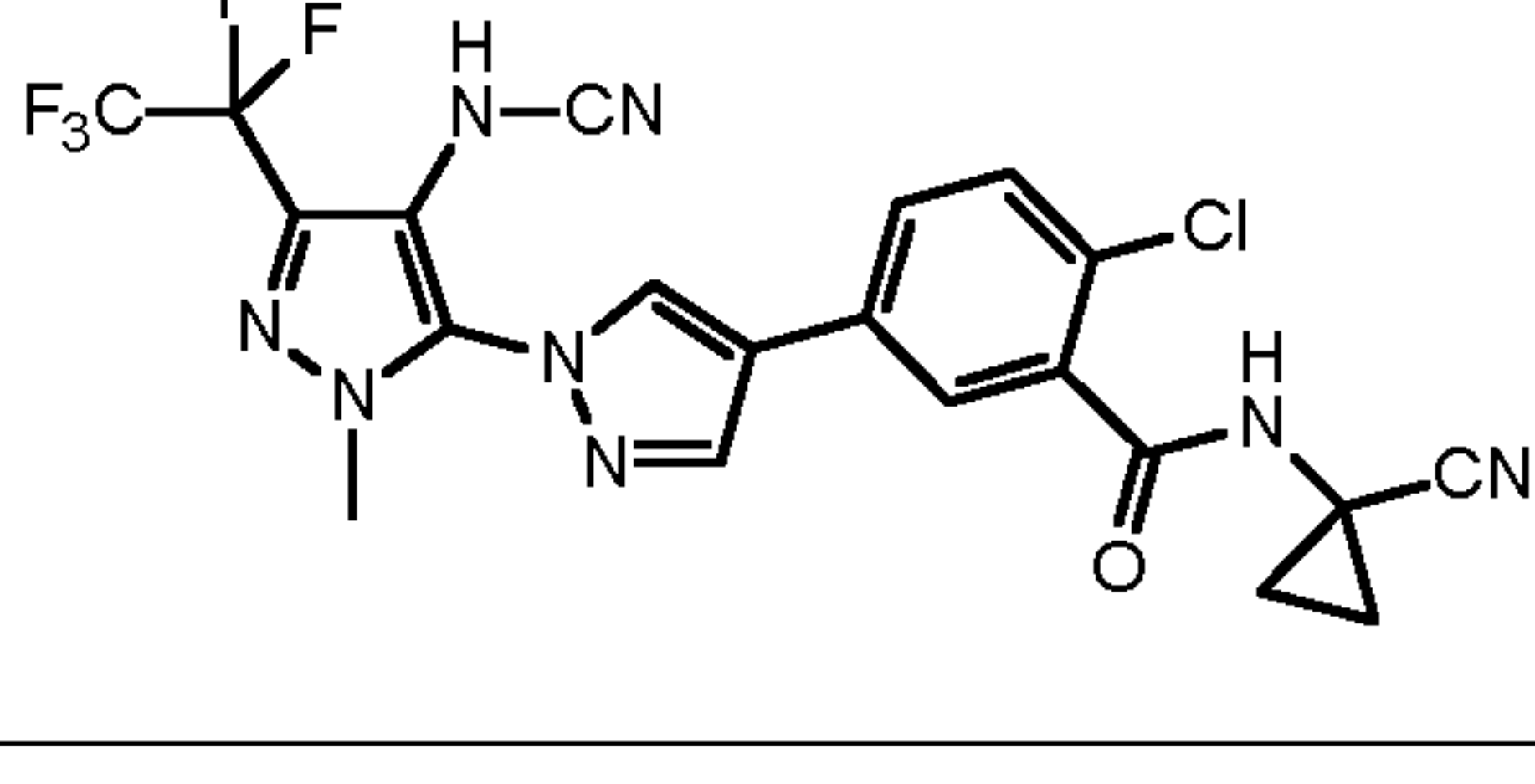
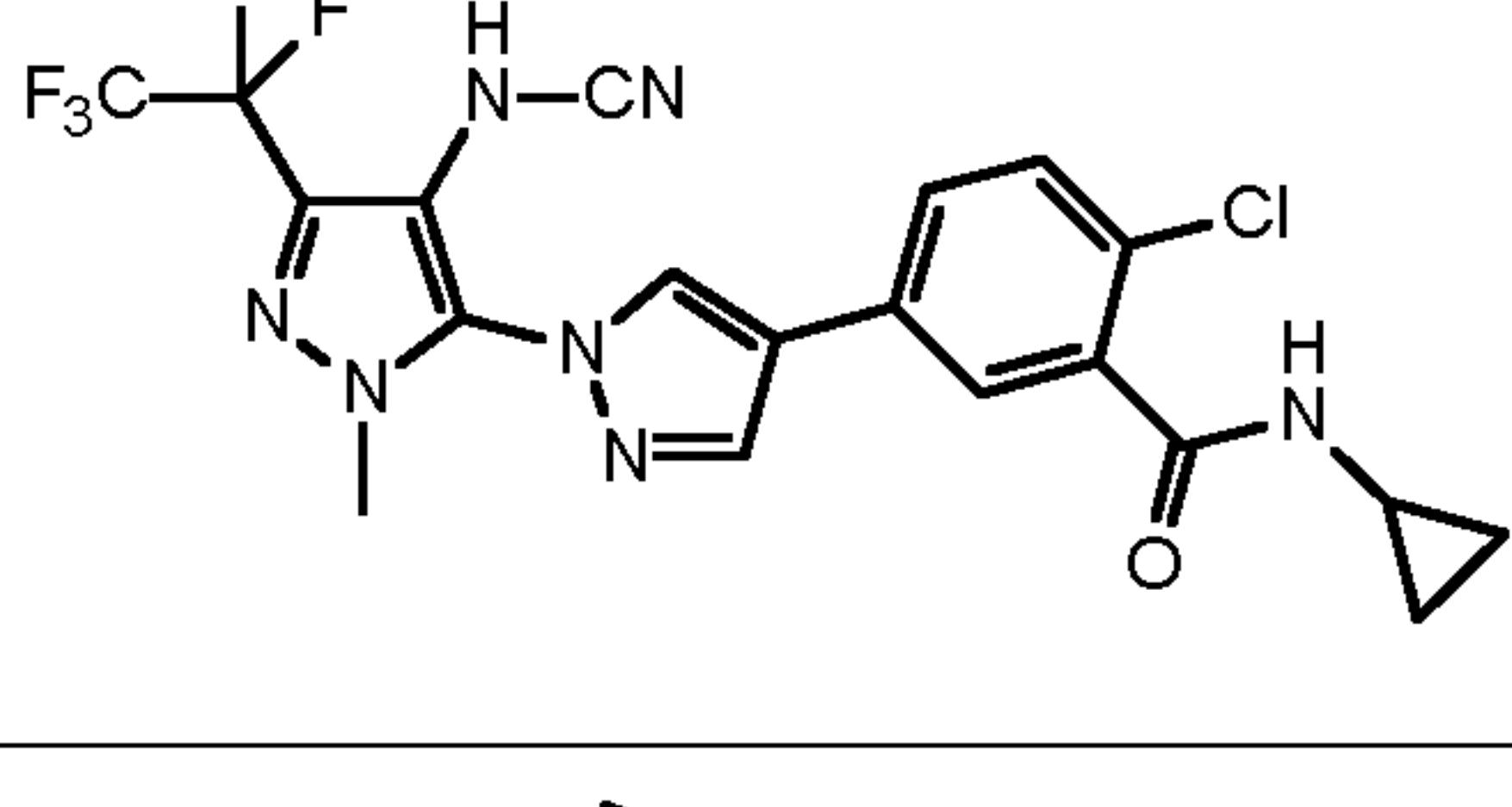
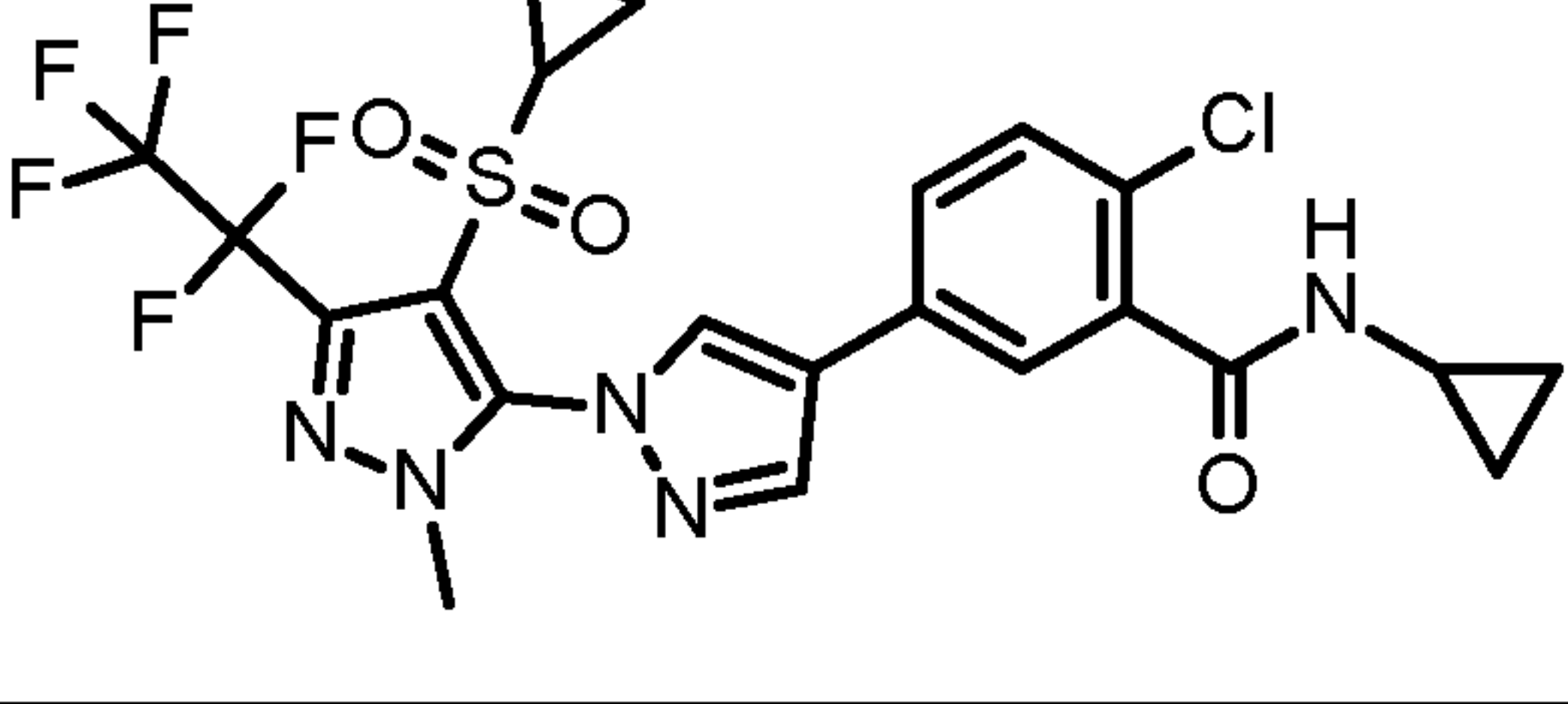
Embodiment 25.1: A compound or salt according to embodiment 1 selected from

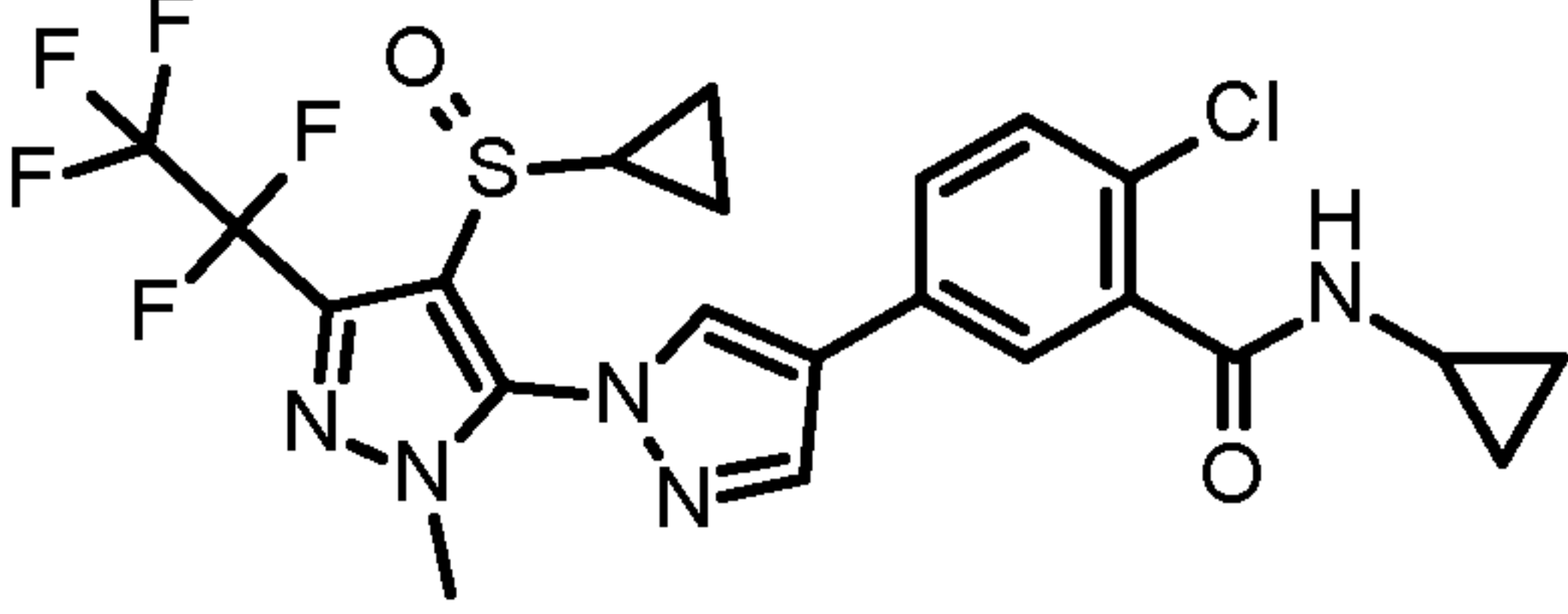
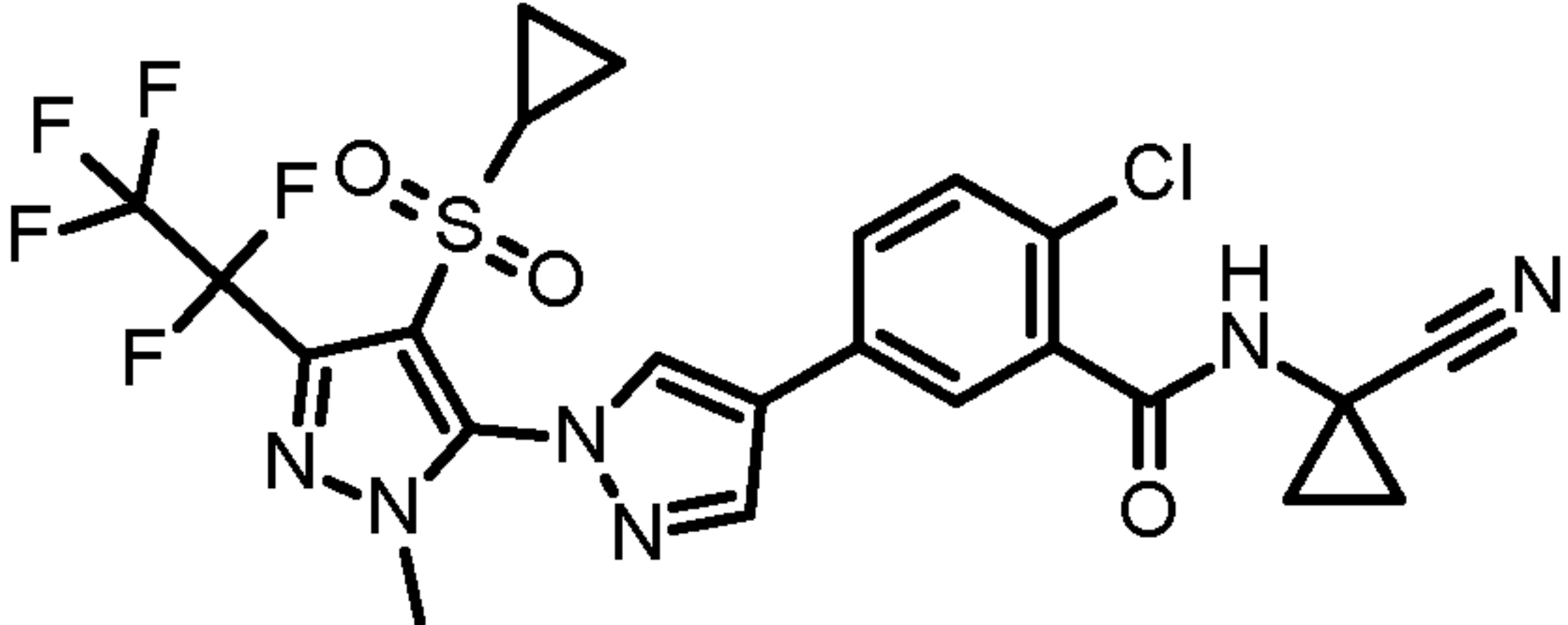
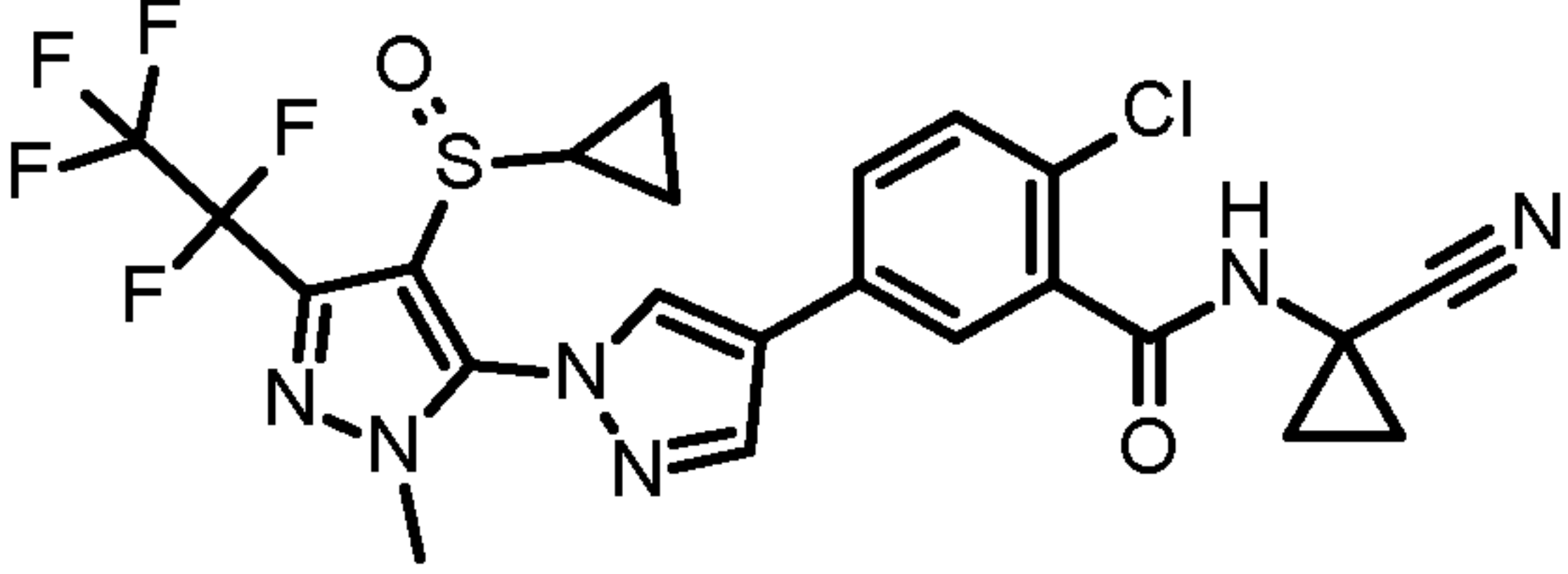
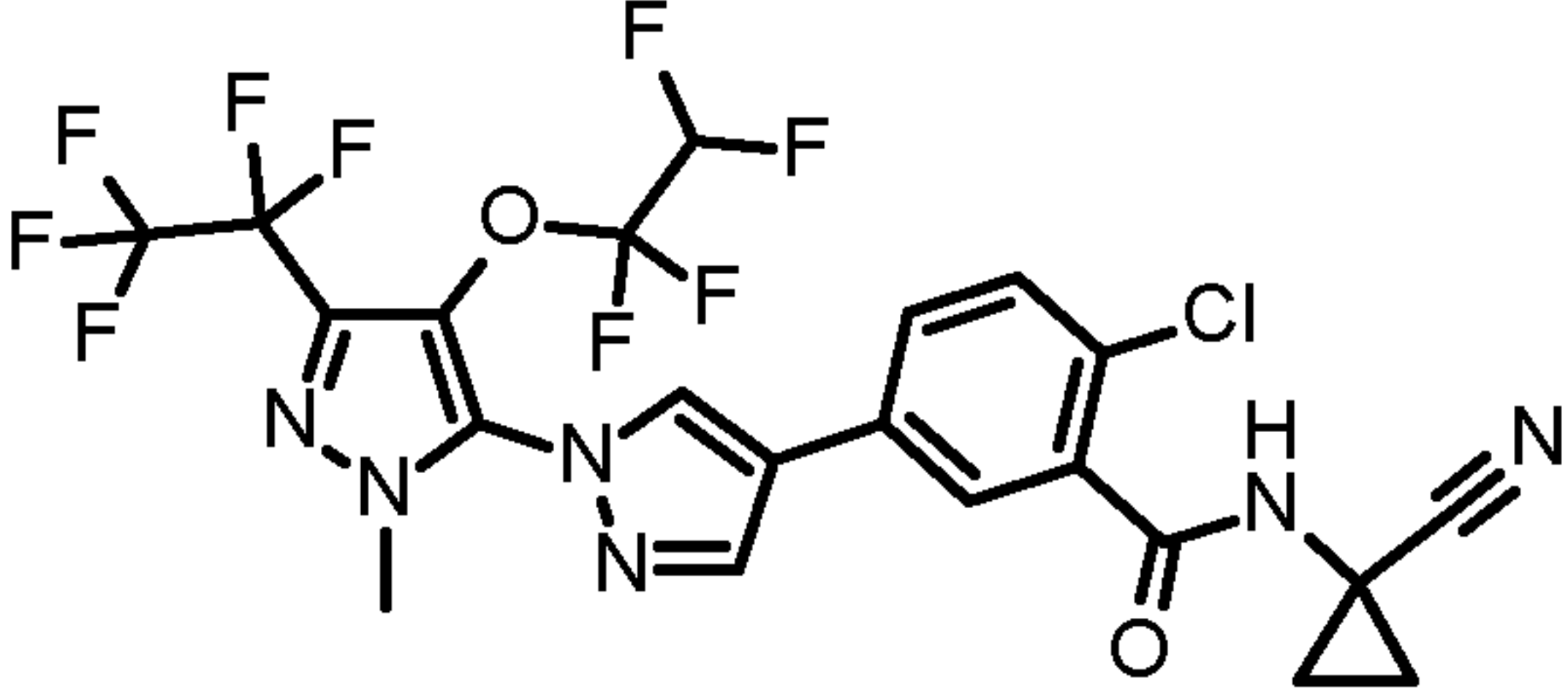
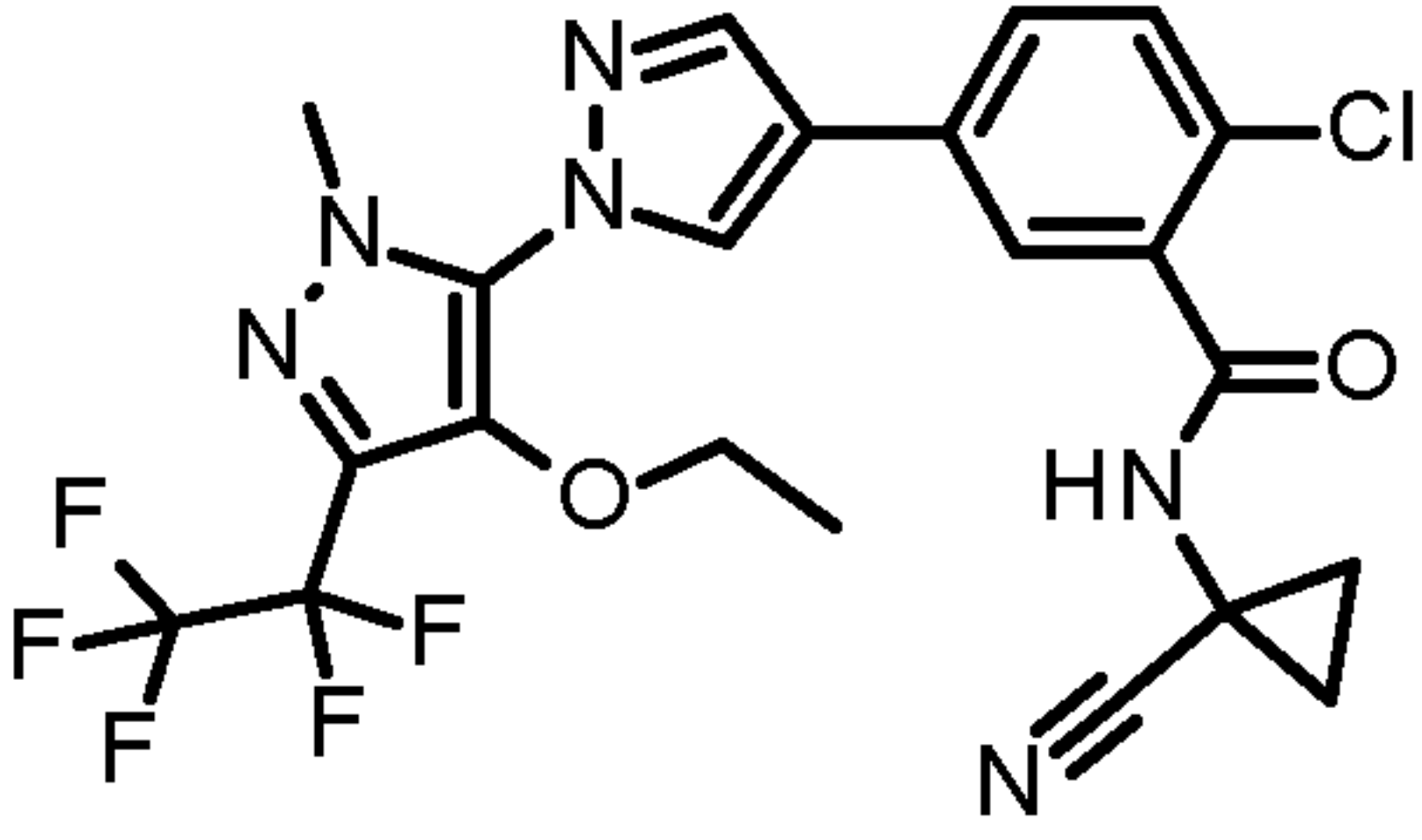
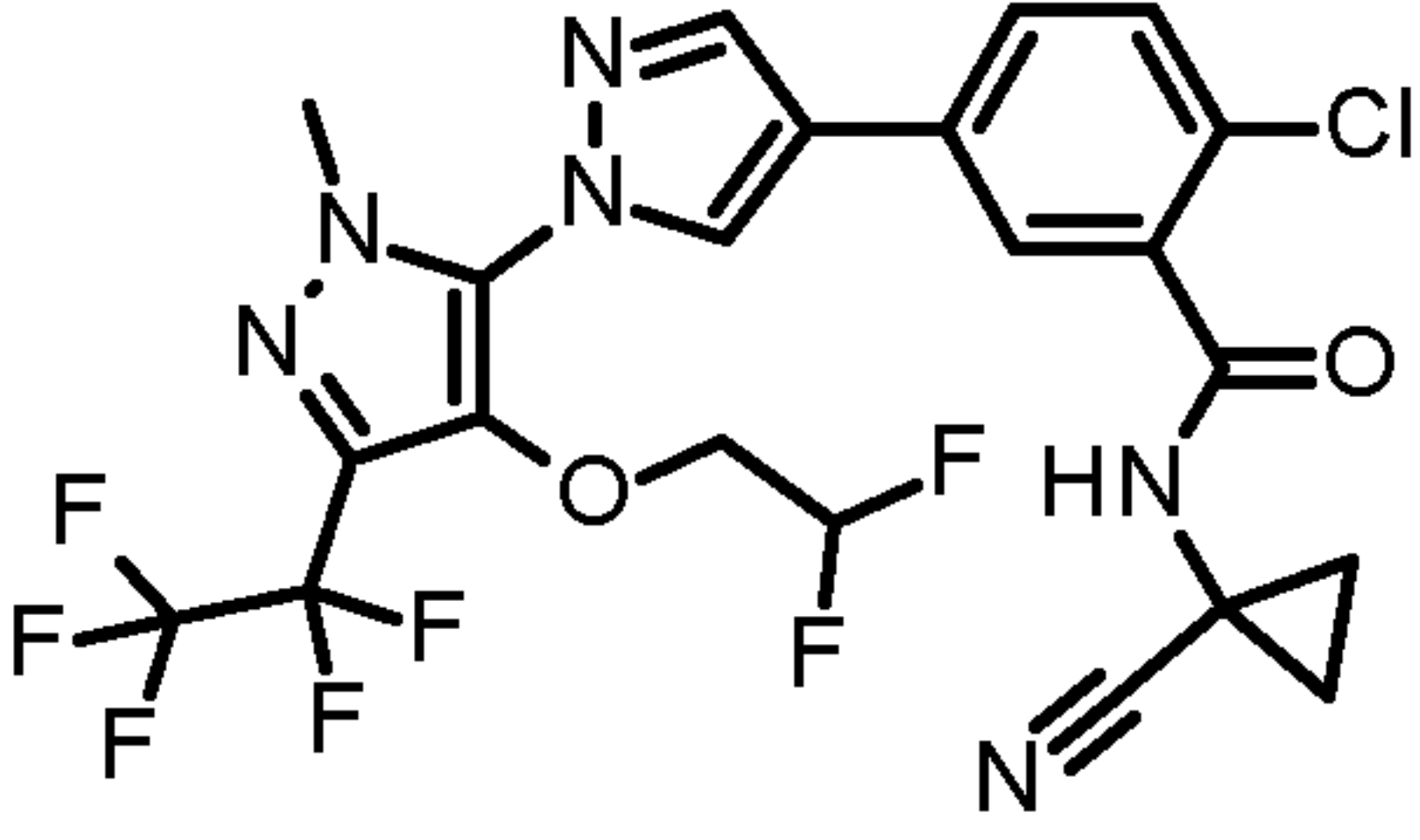
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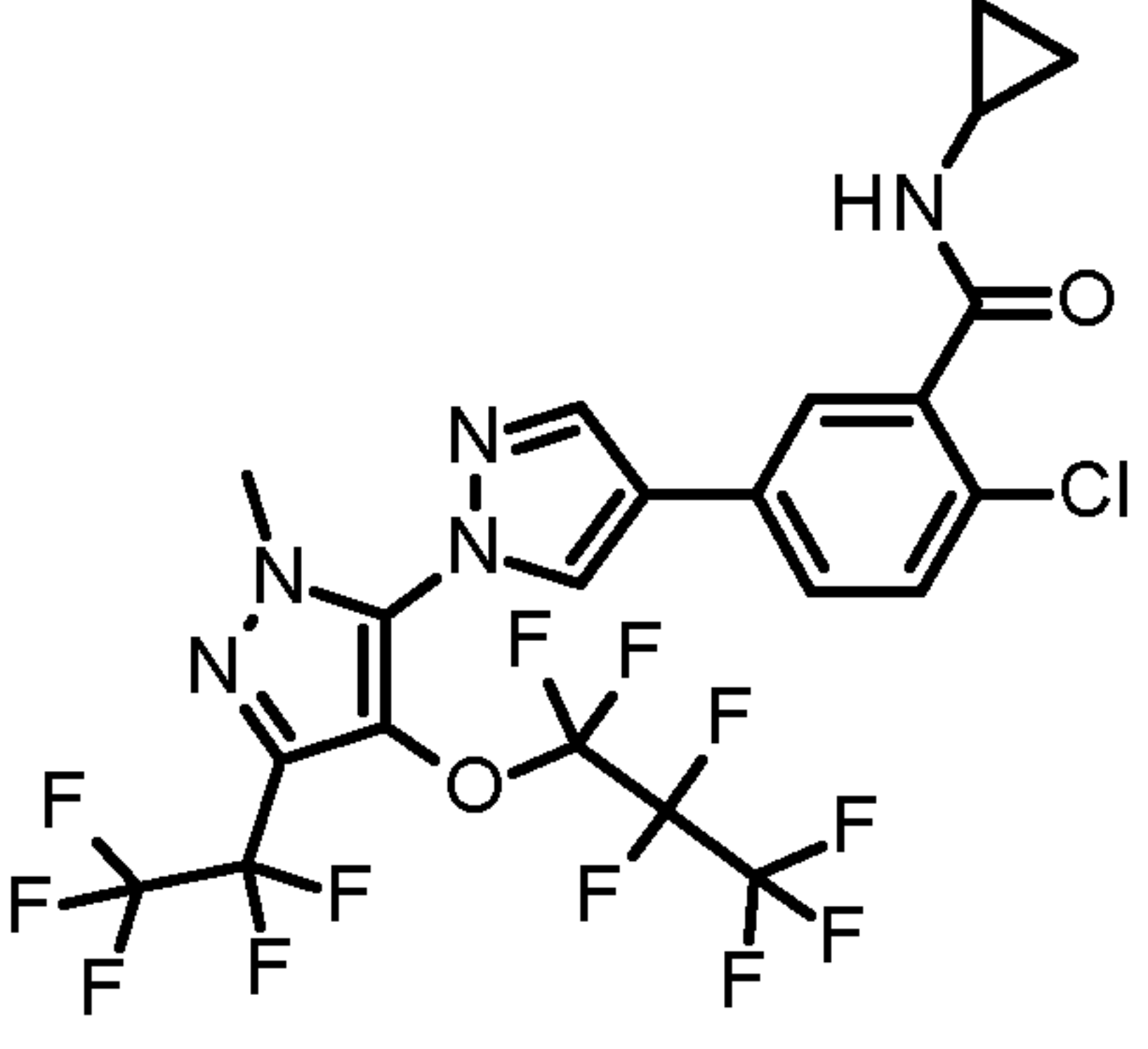
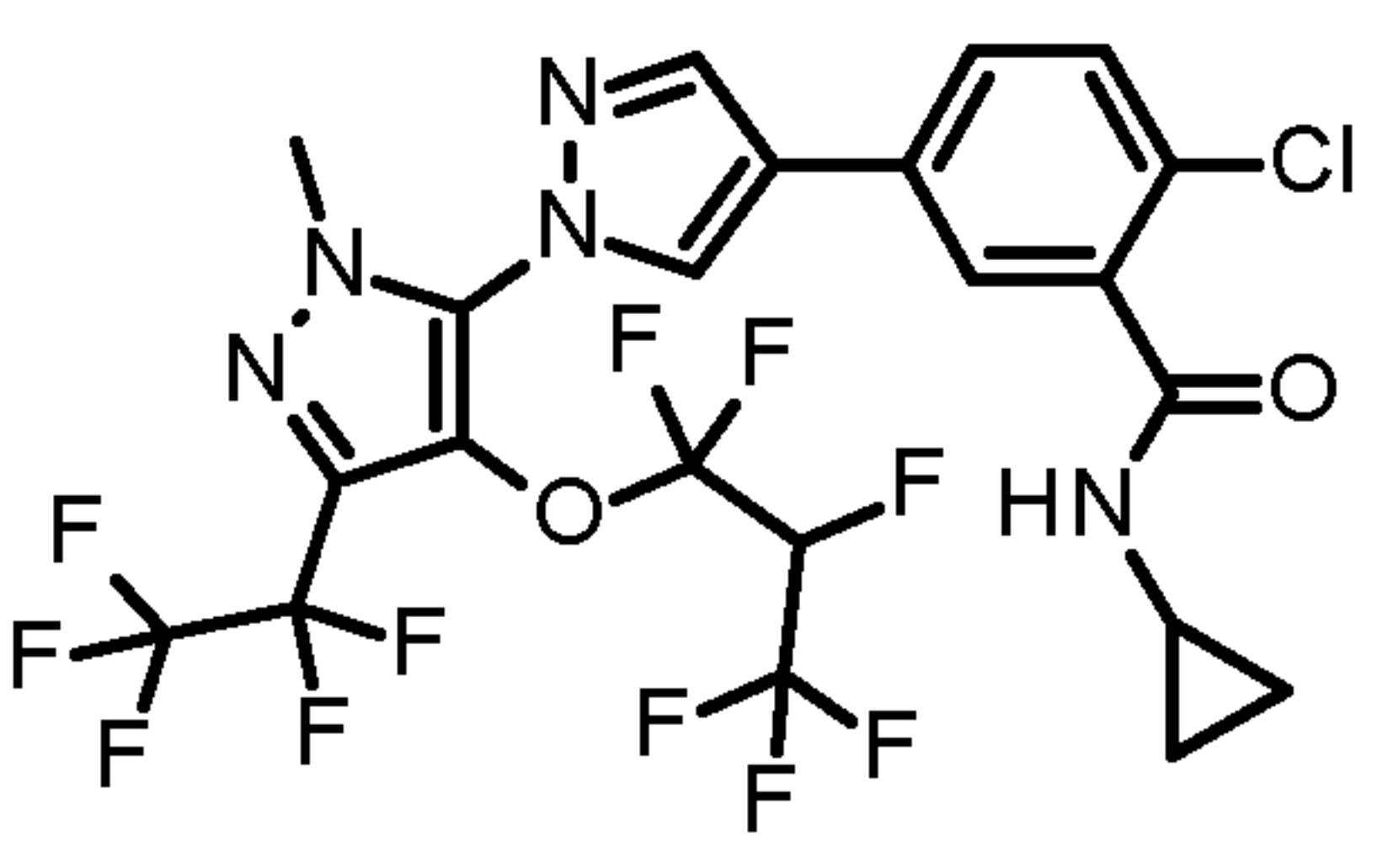
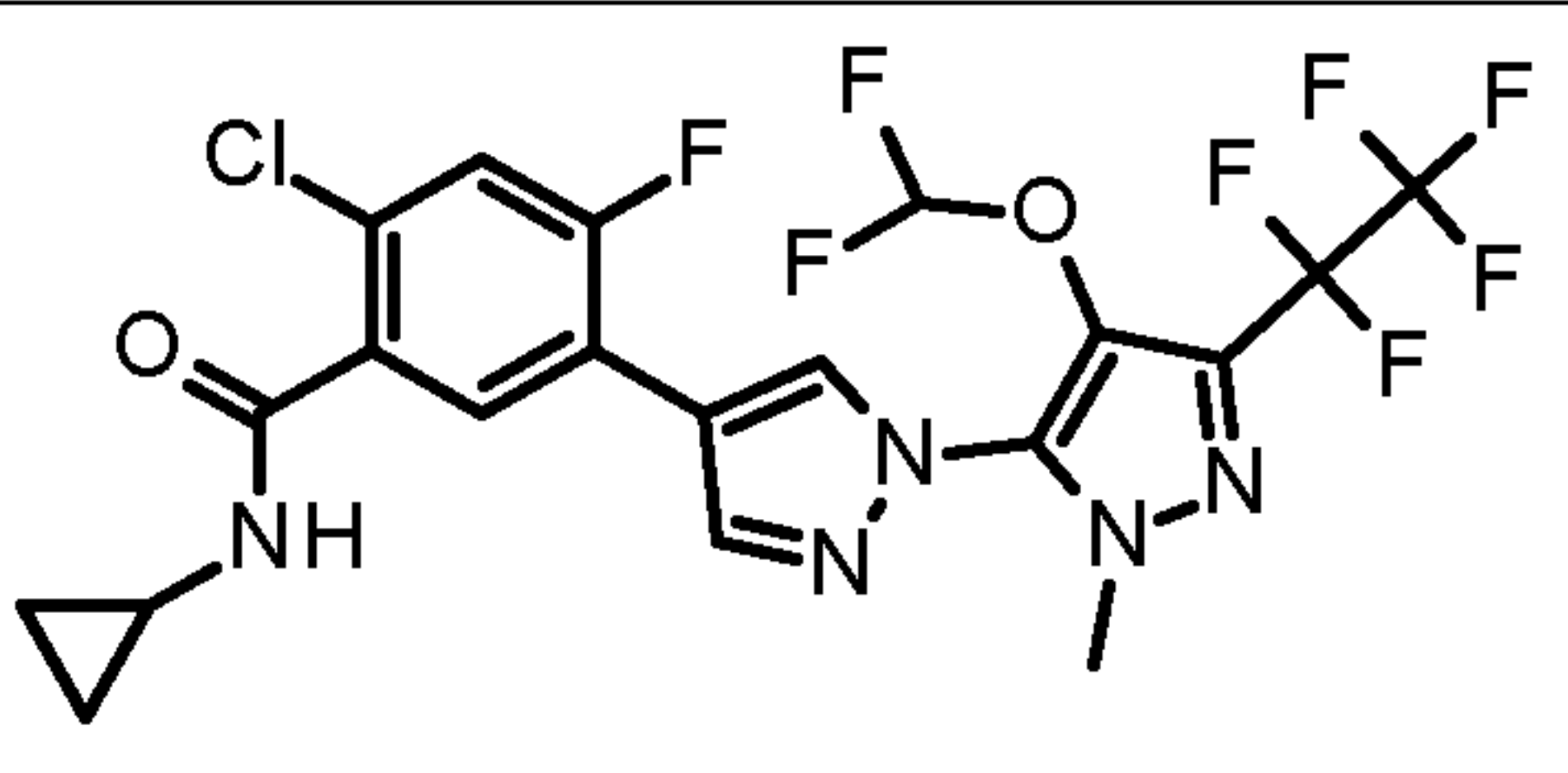
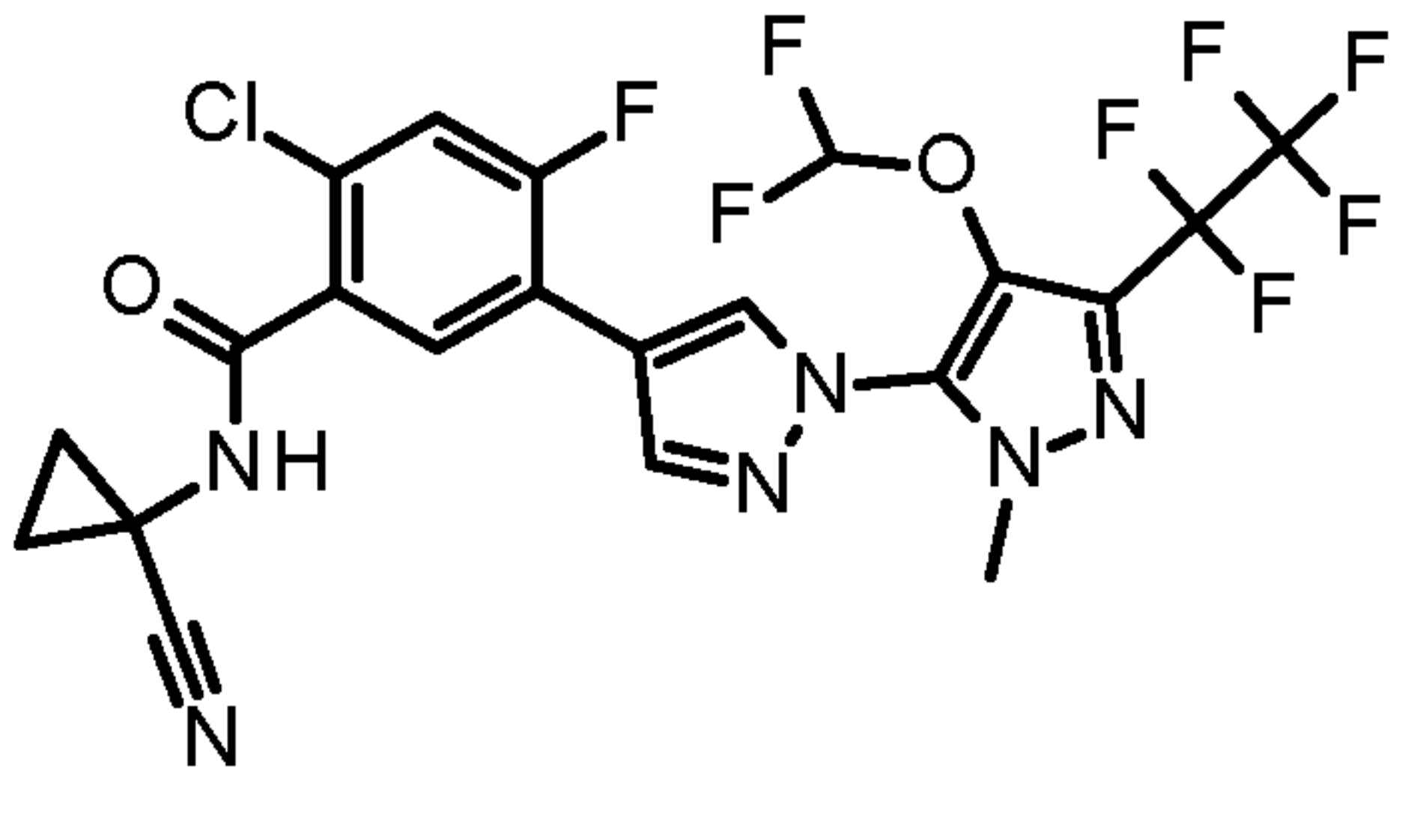
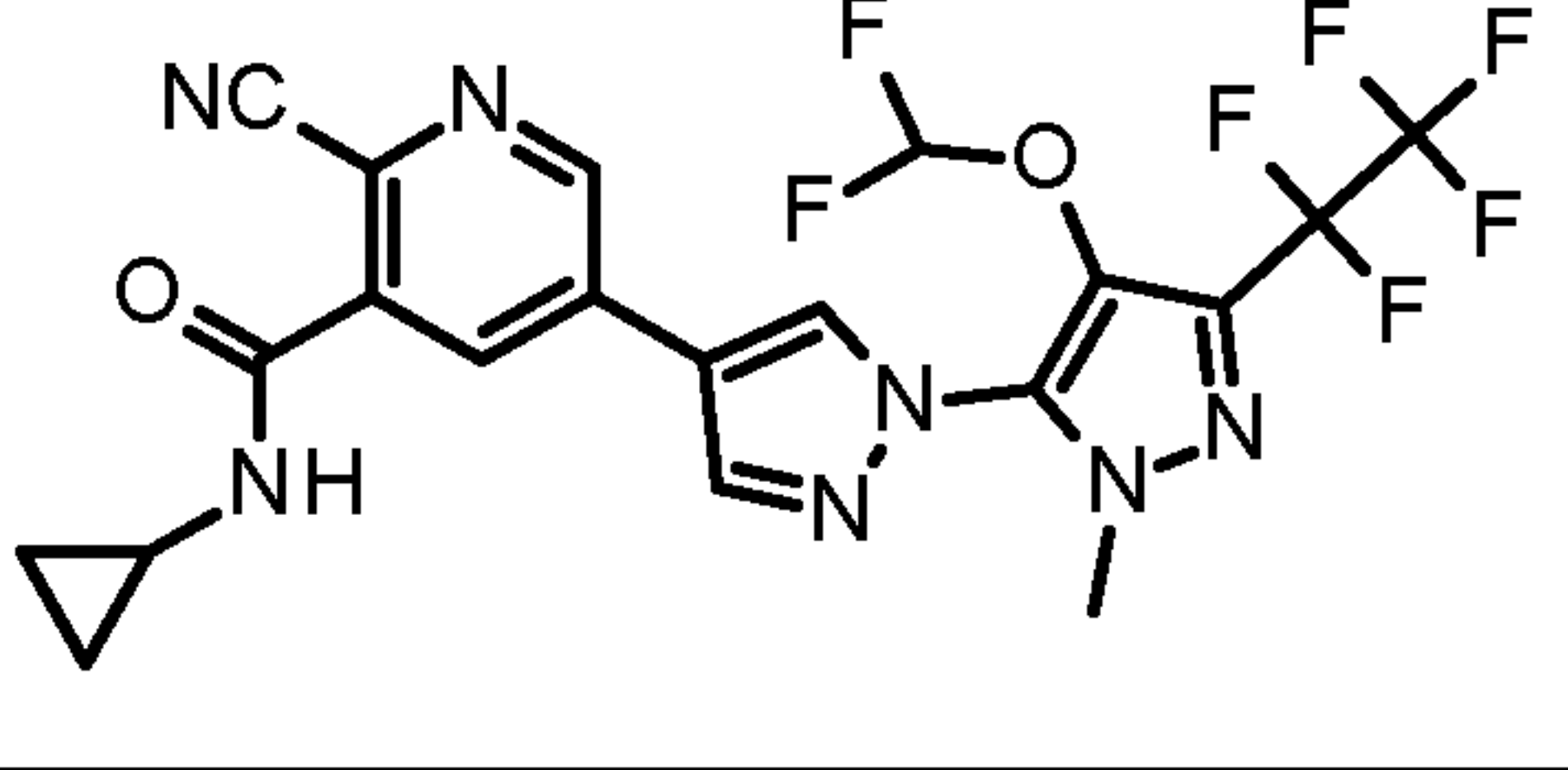
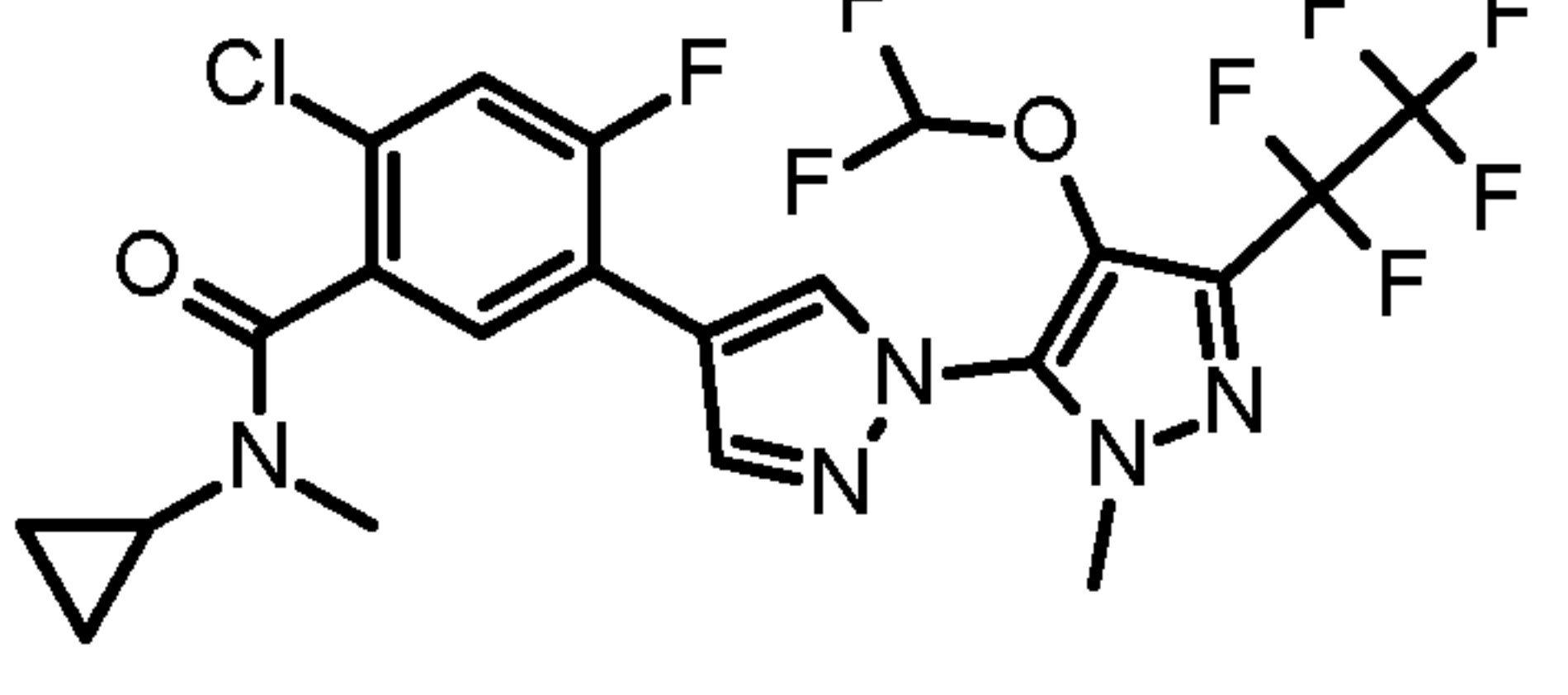
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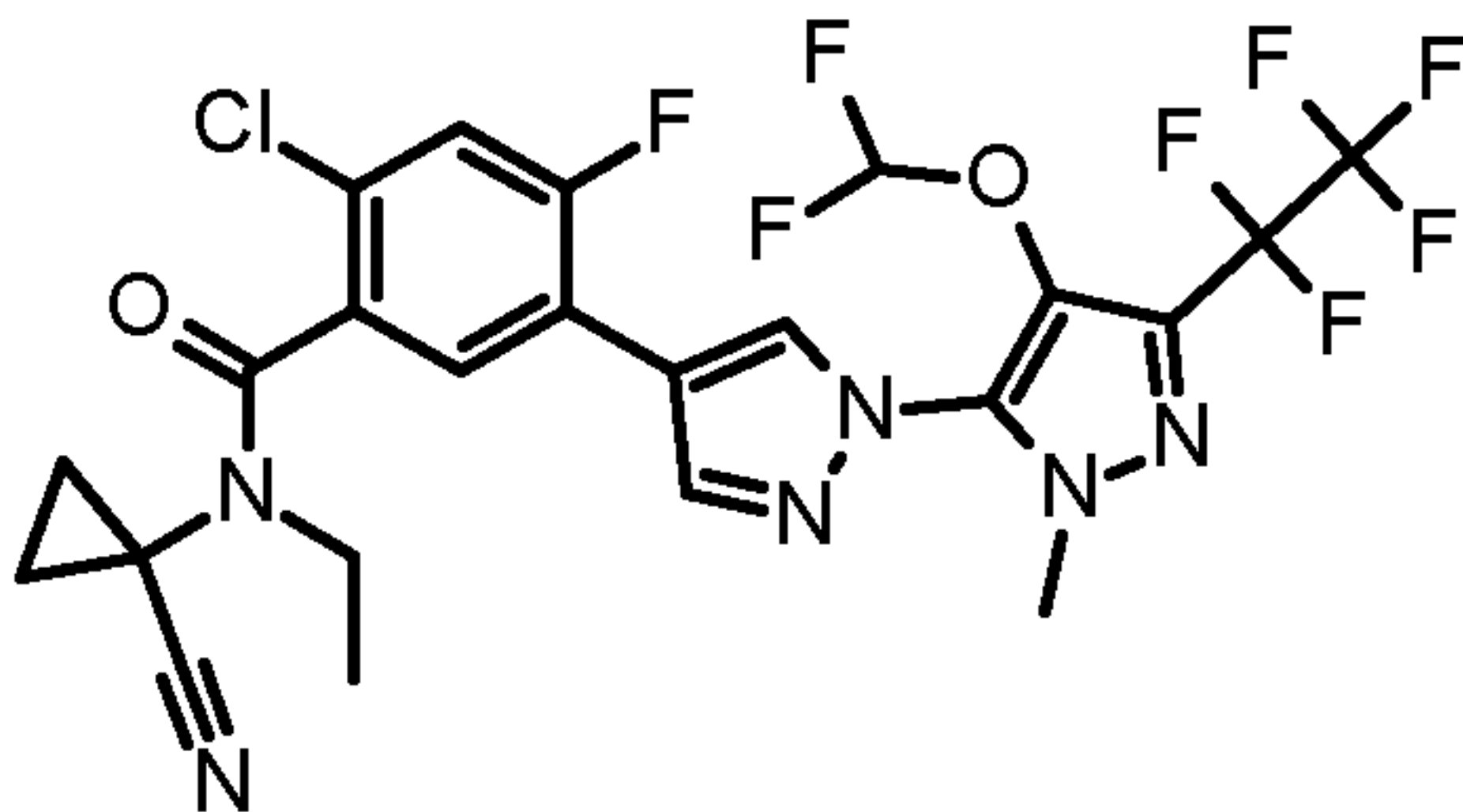
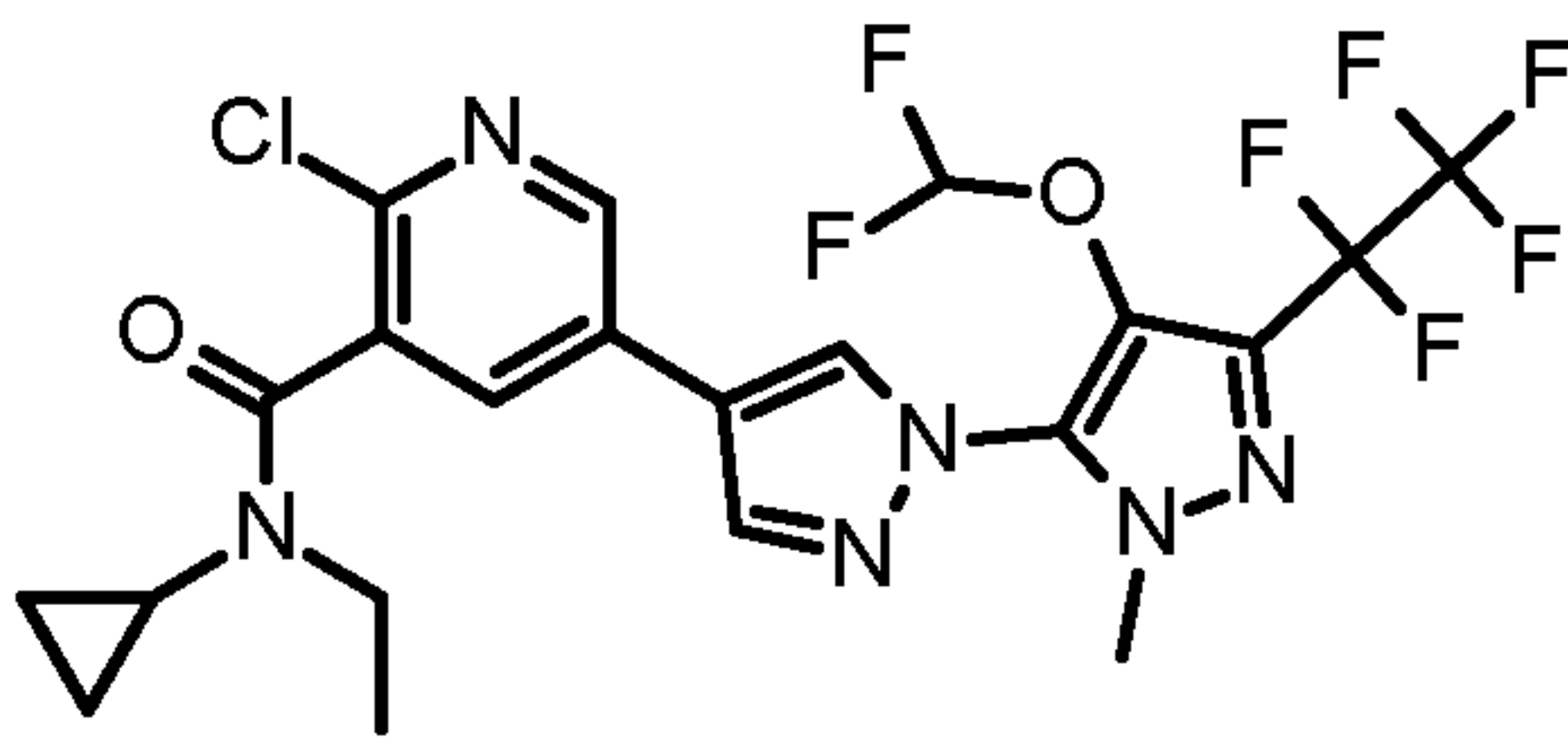
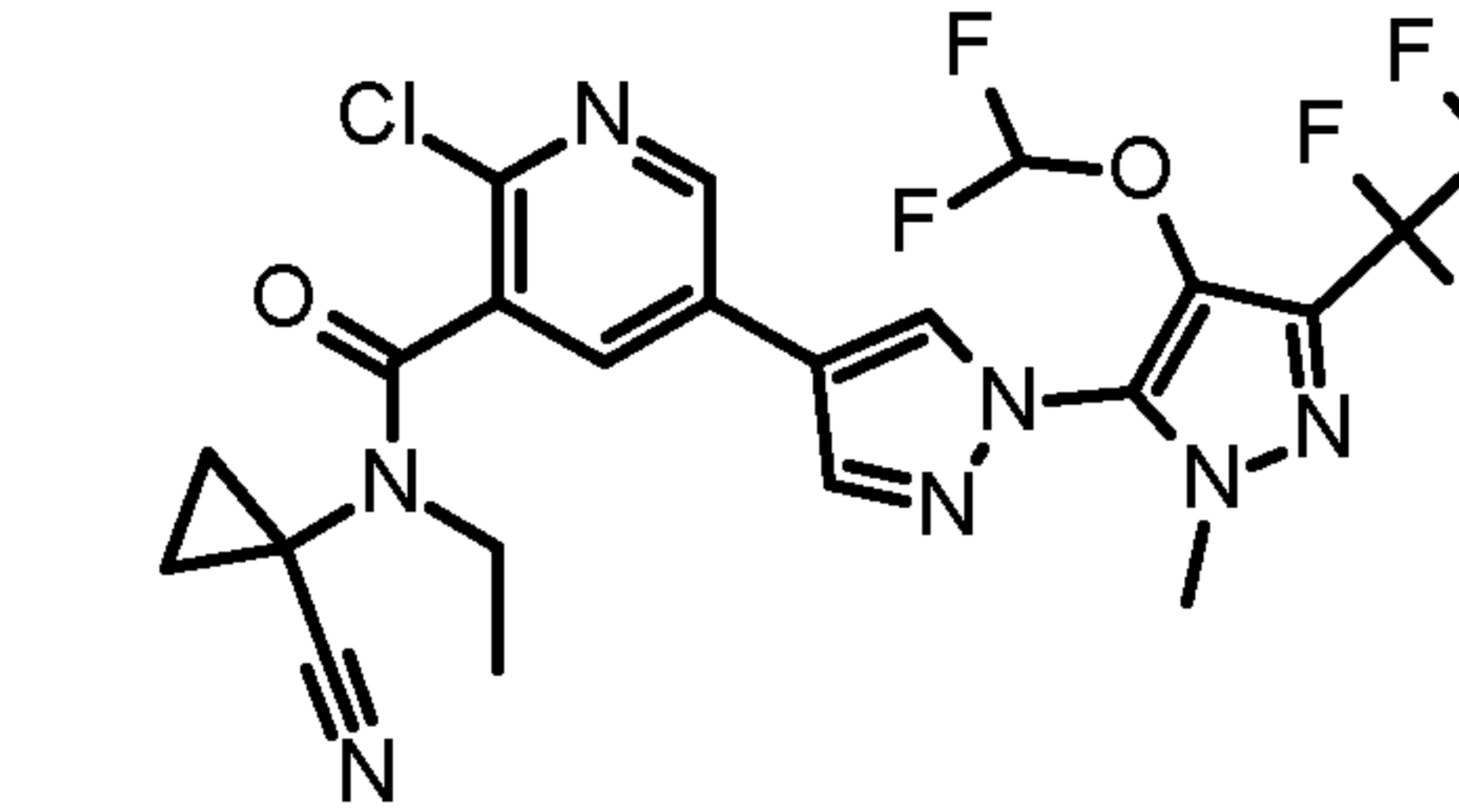
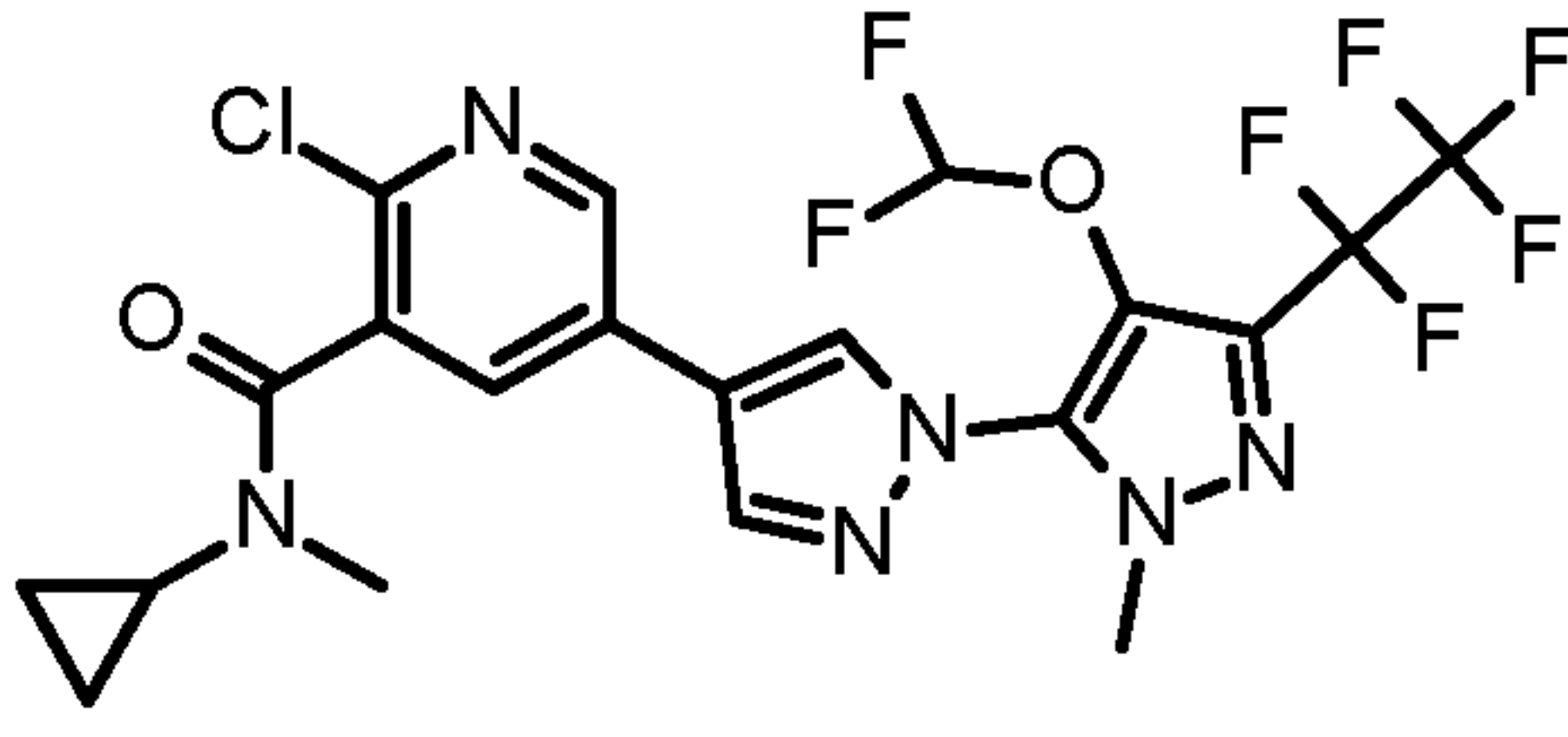
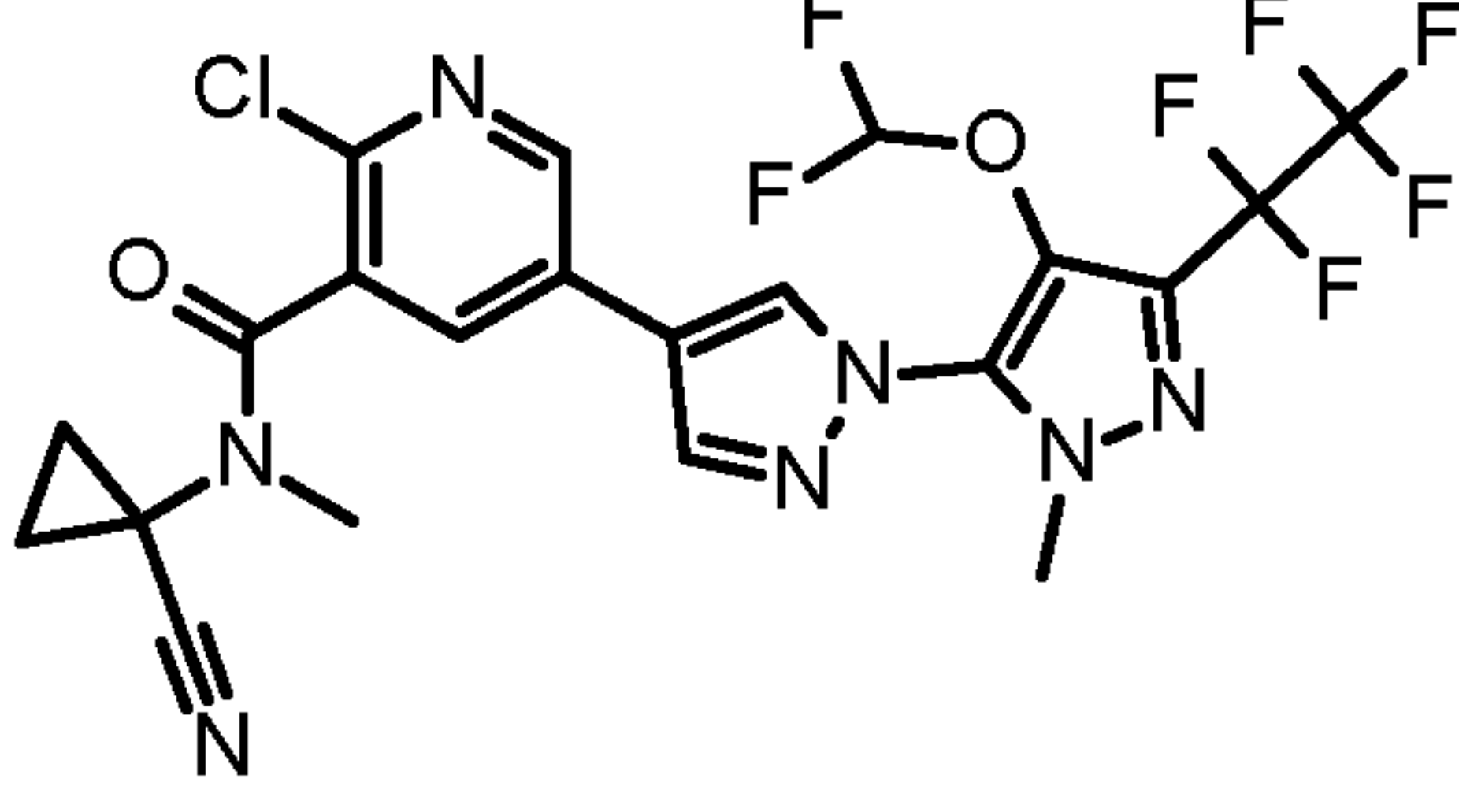
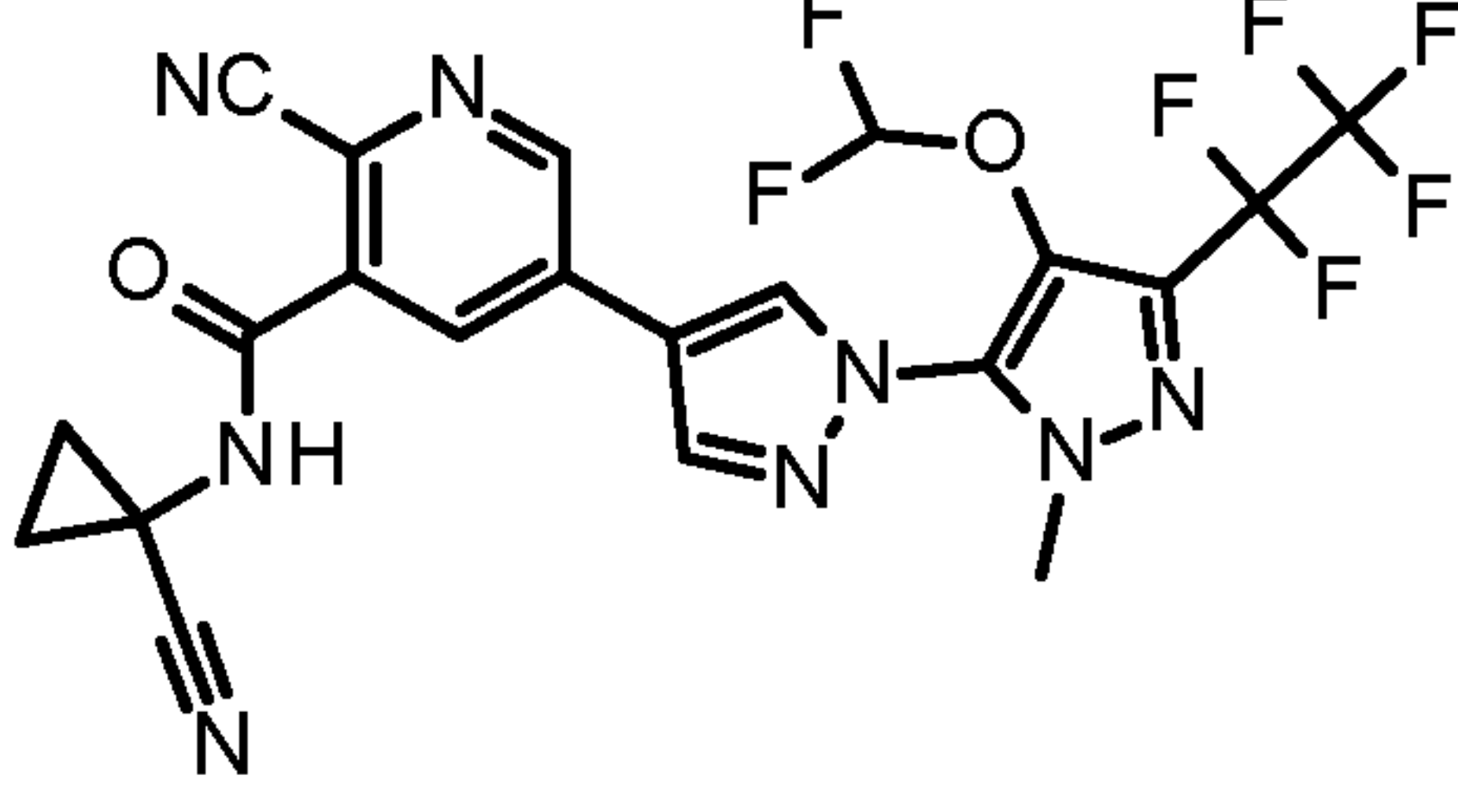
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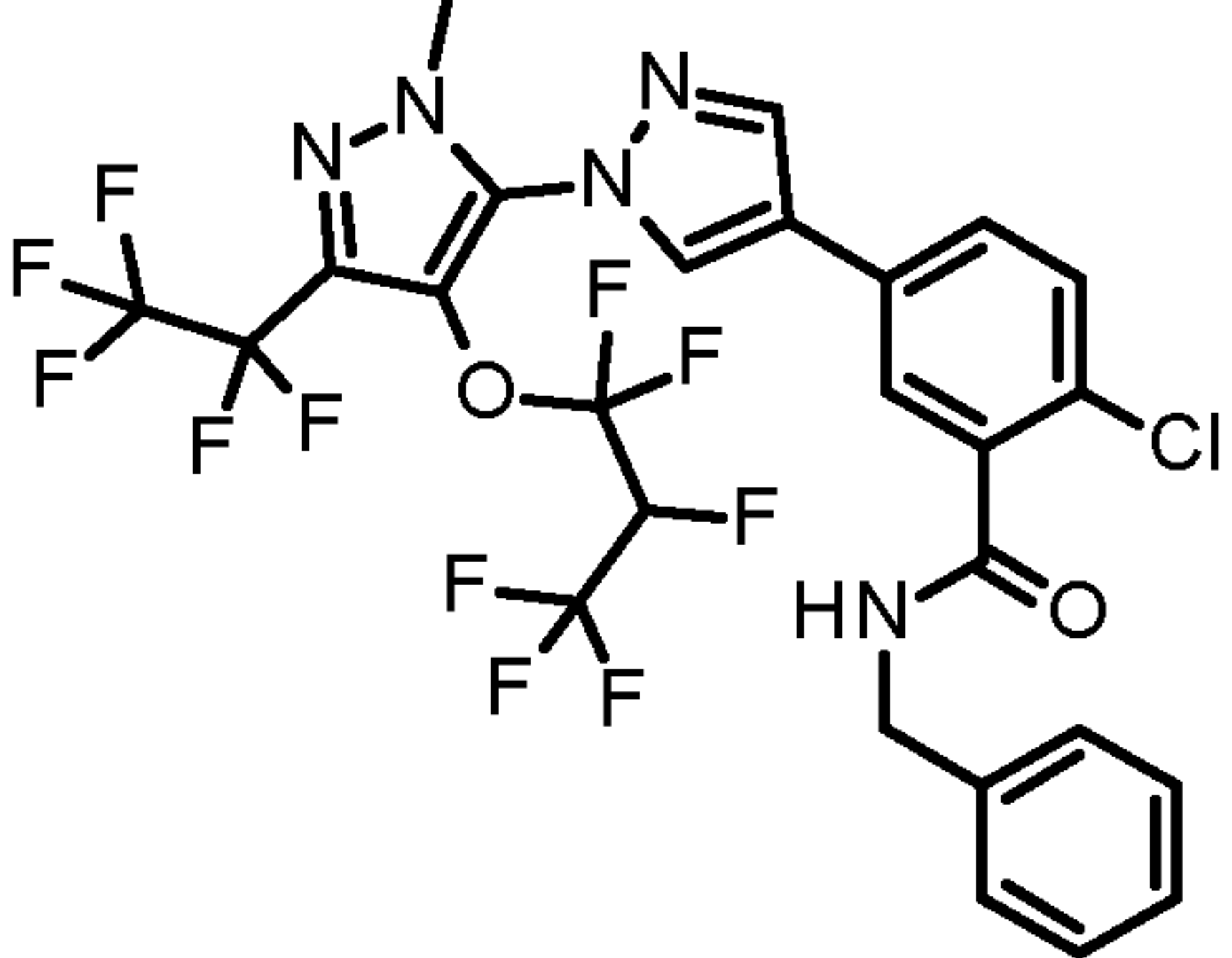
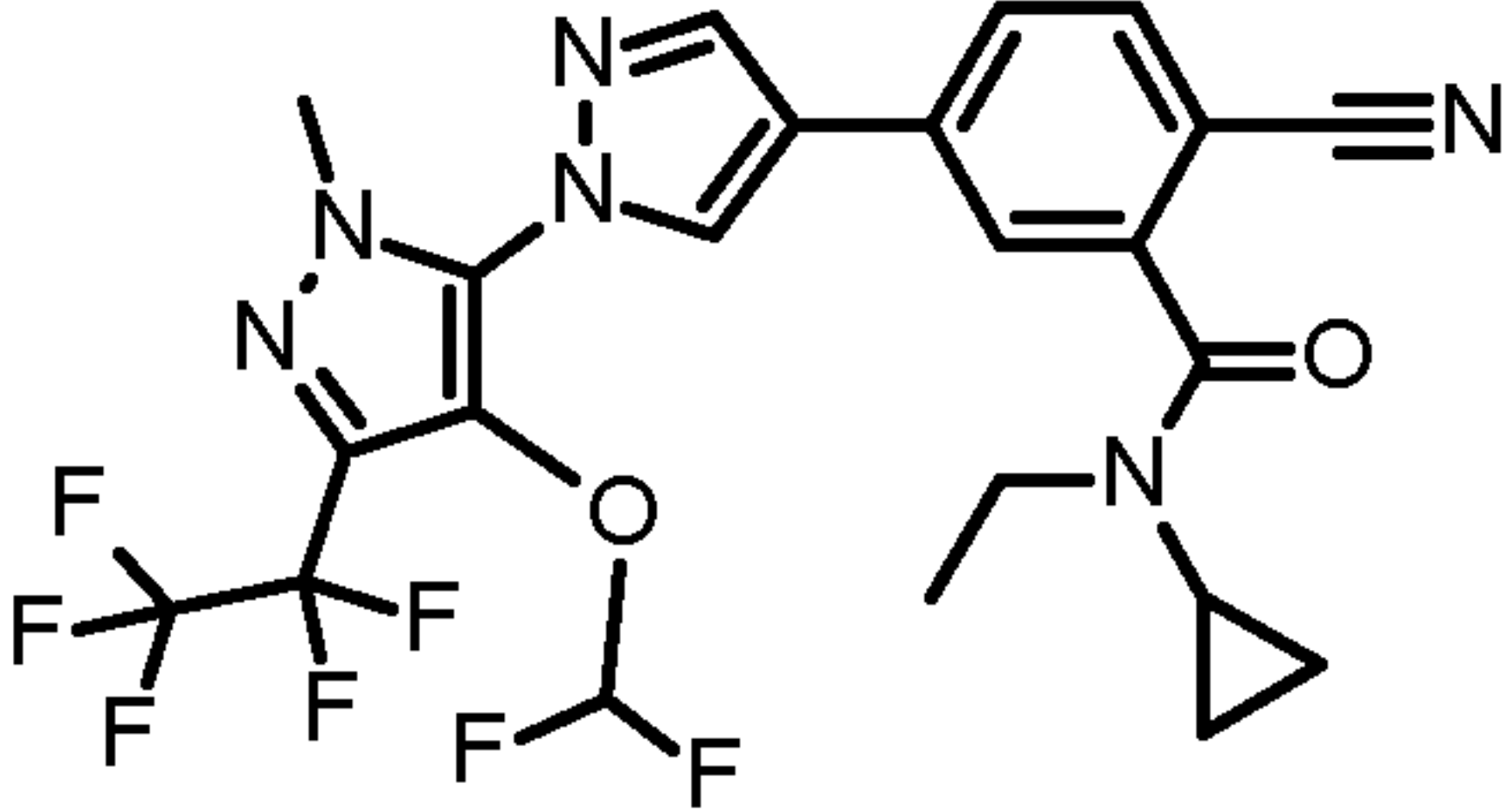
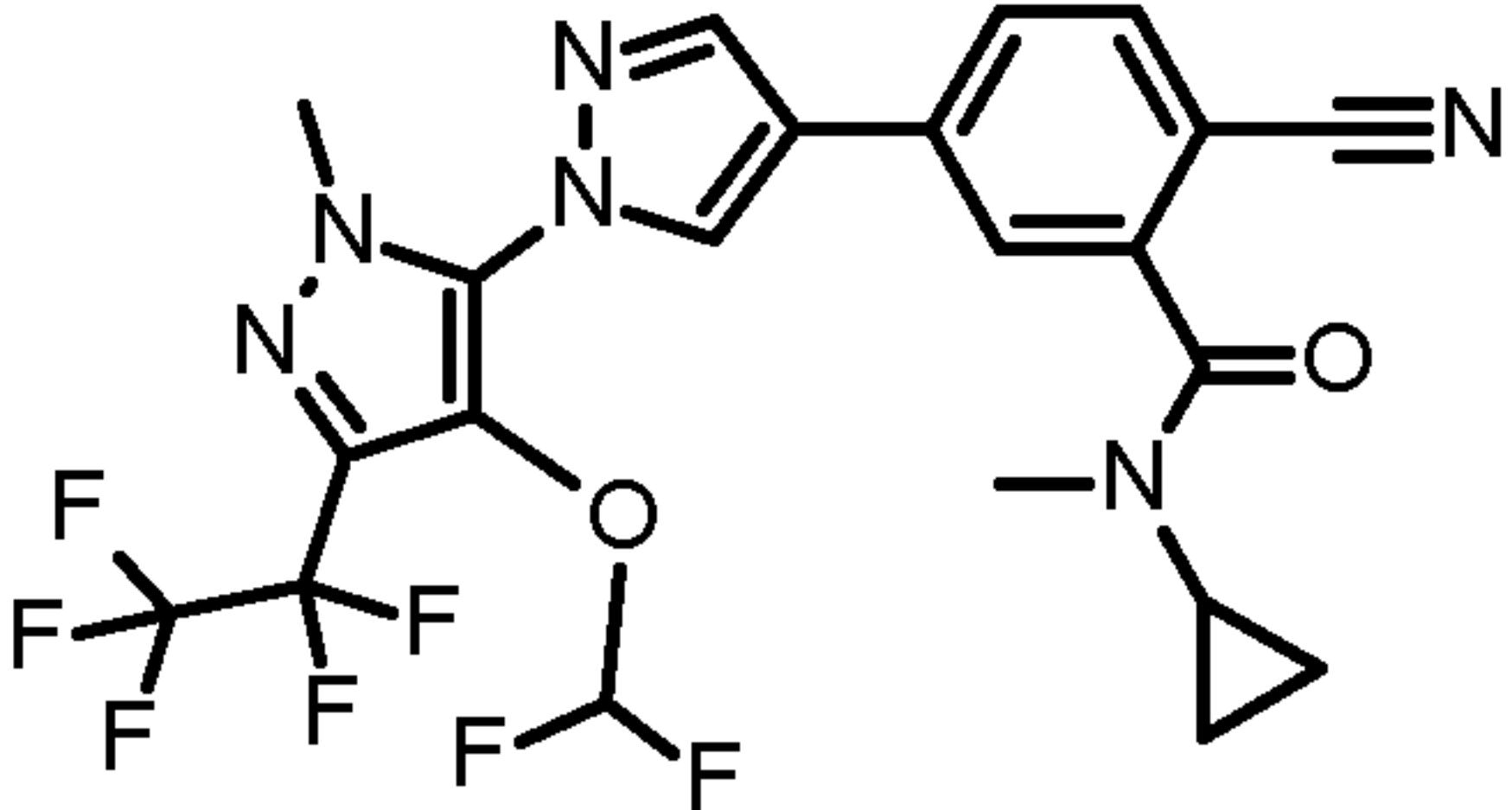
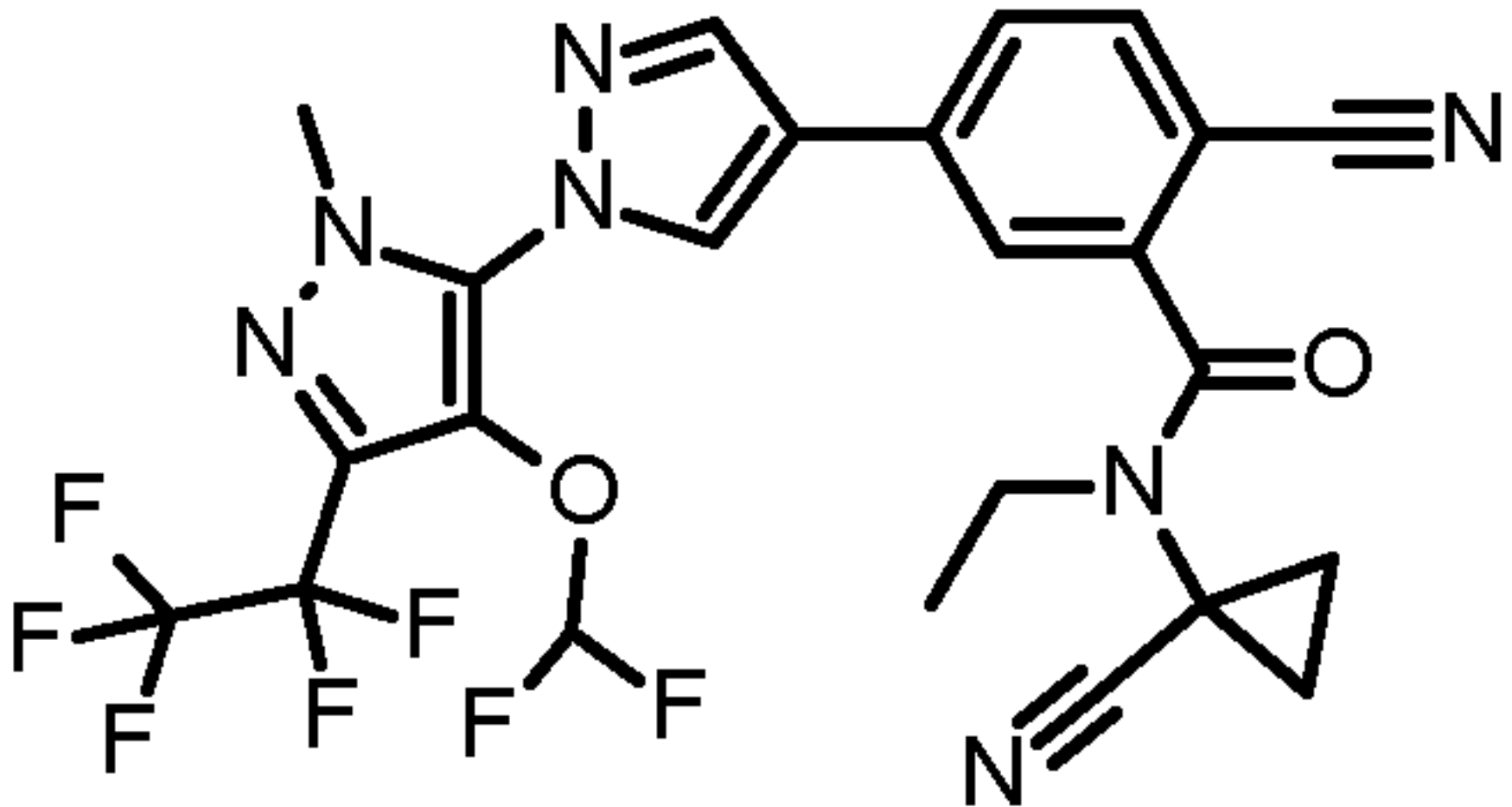
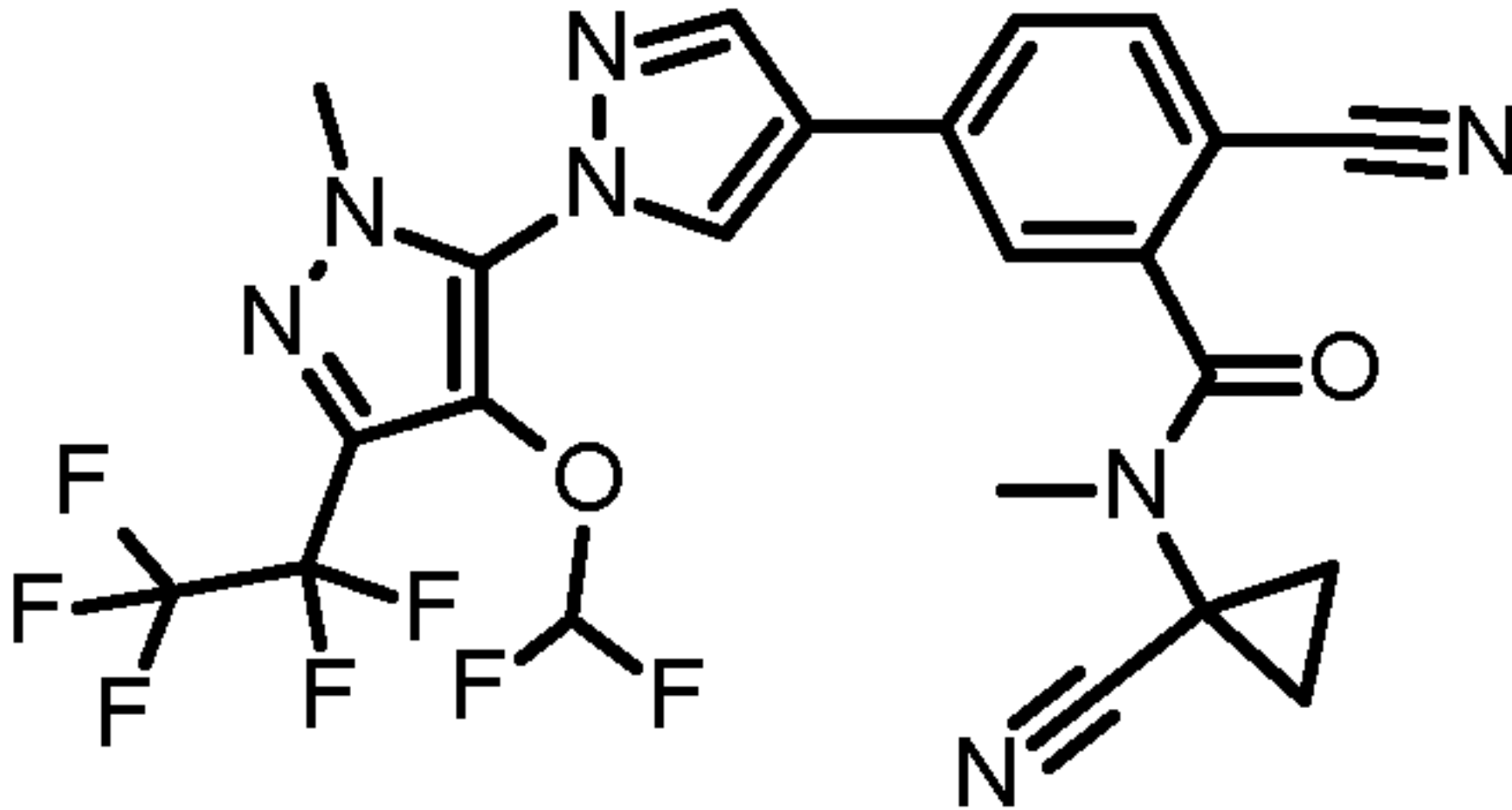
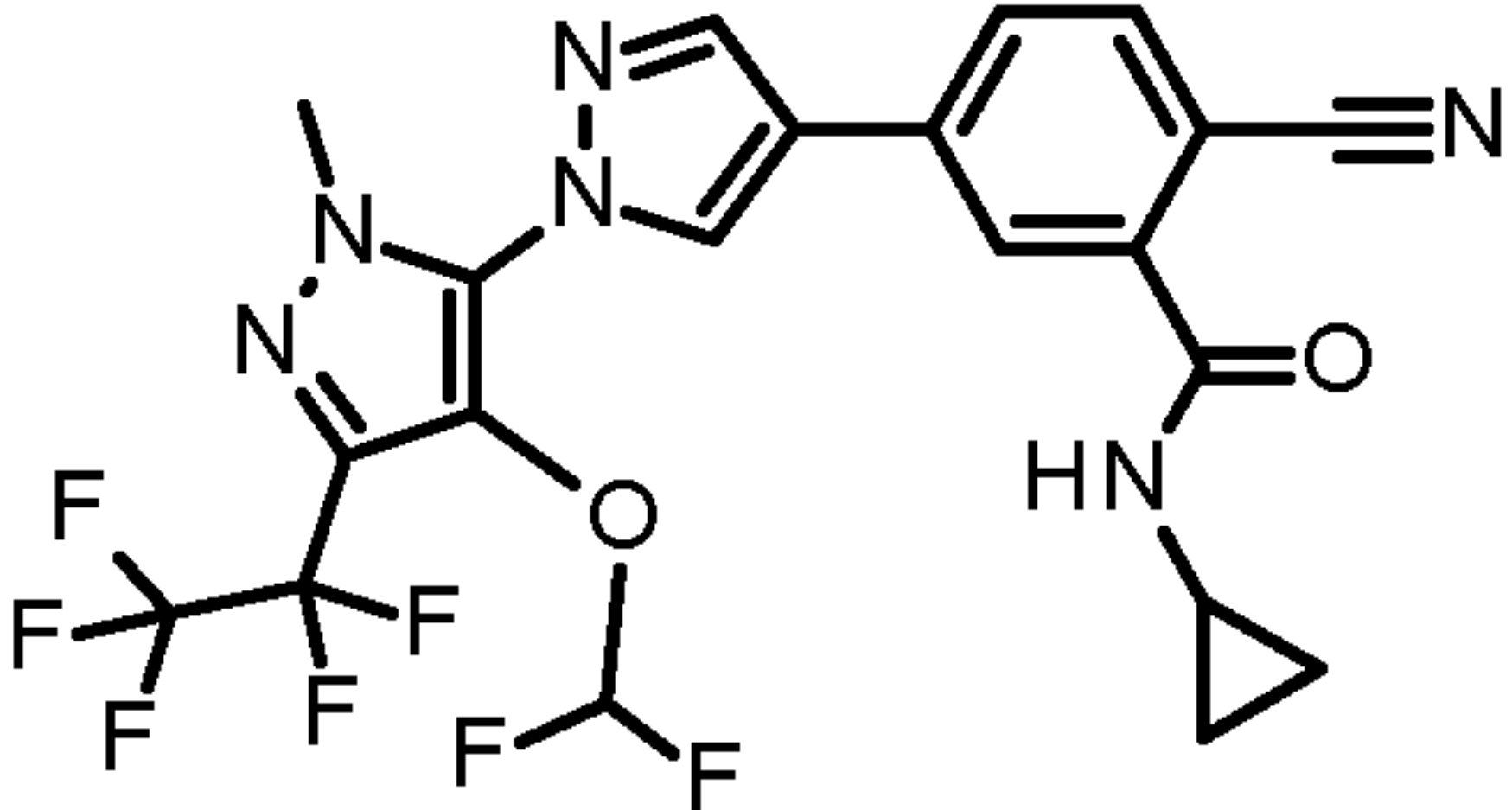
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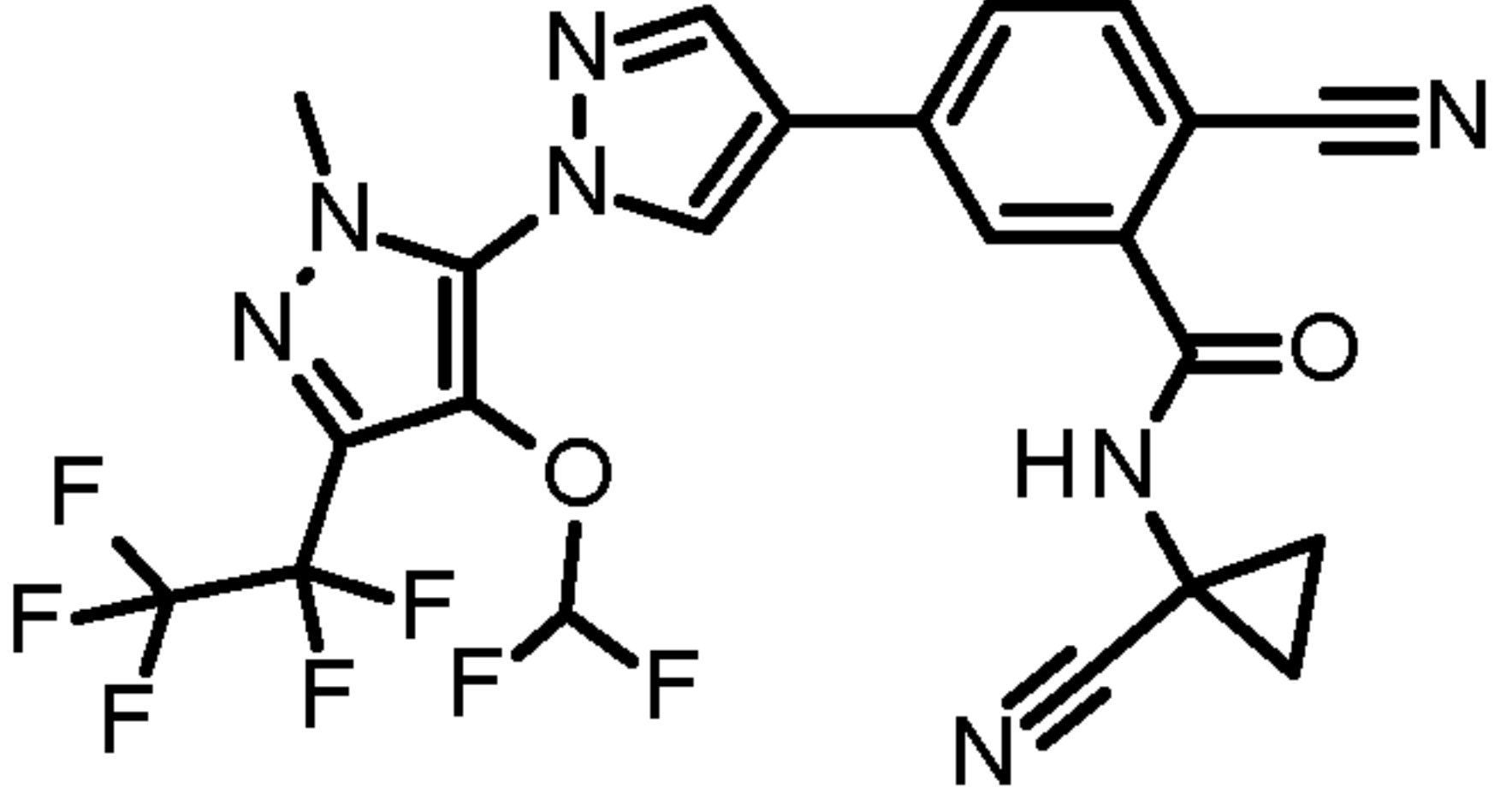
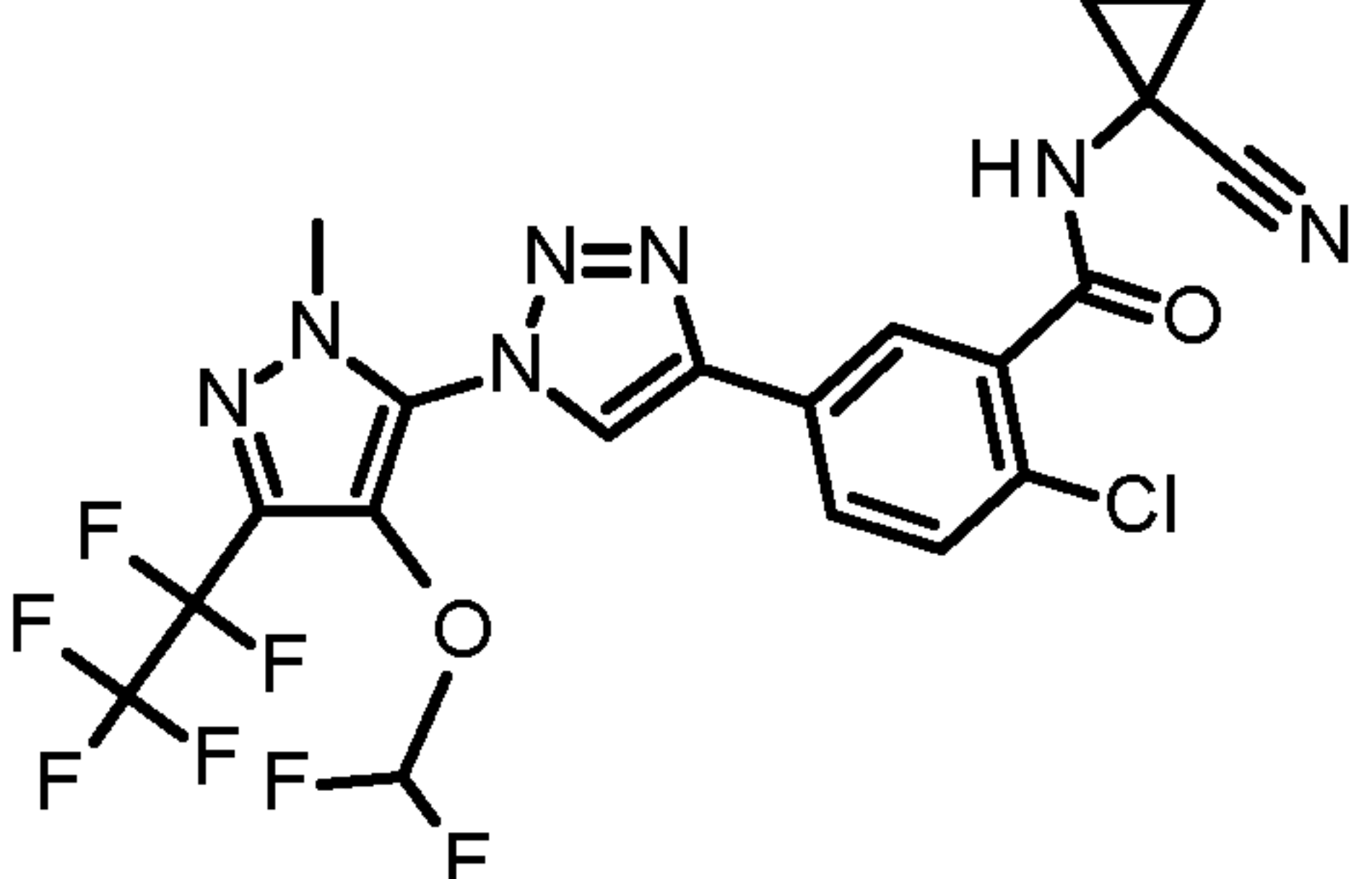
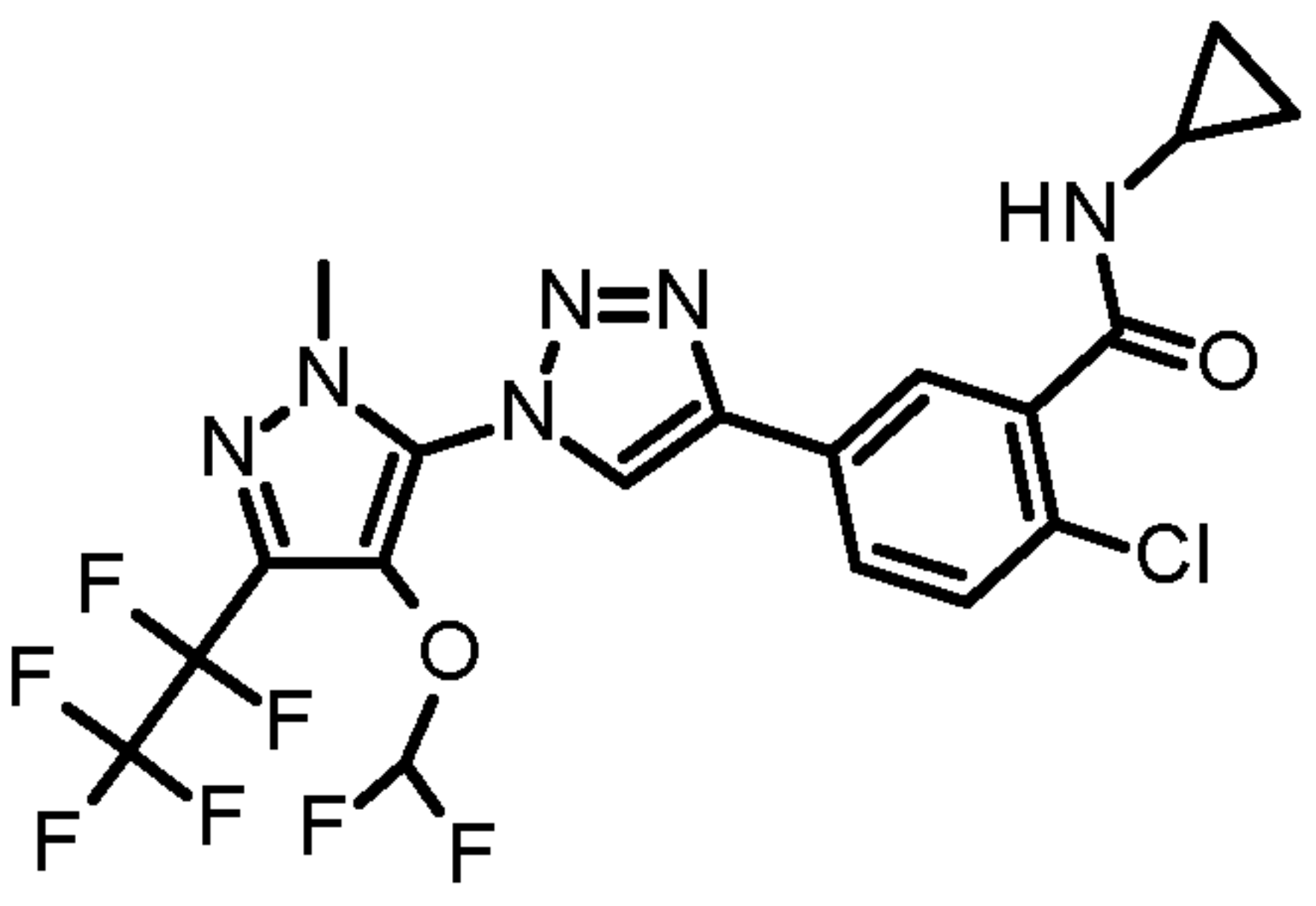
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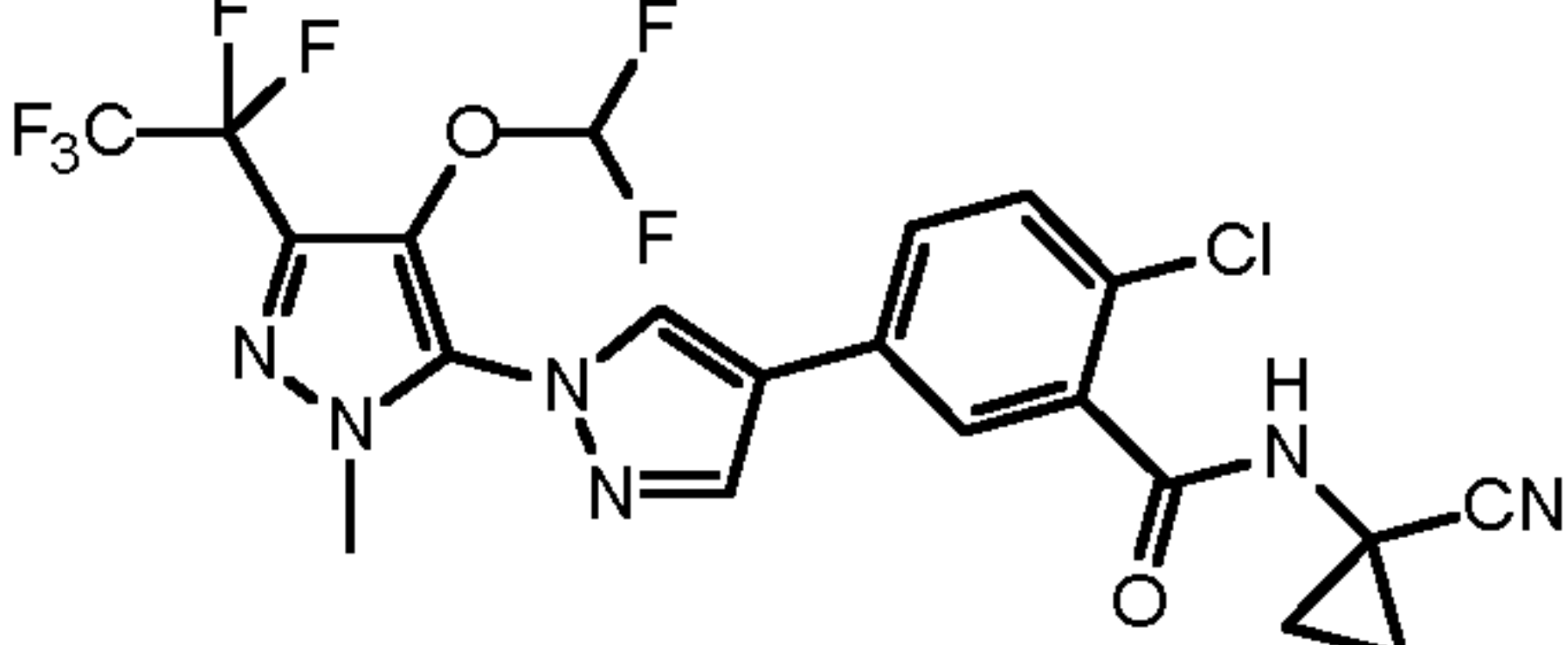
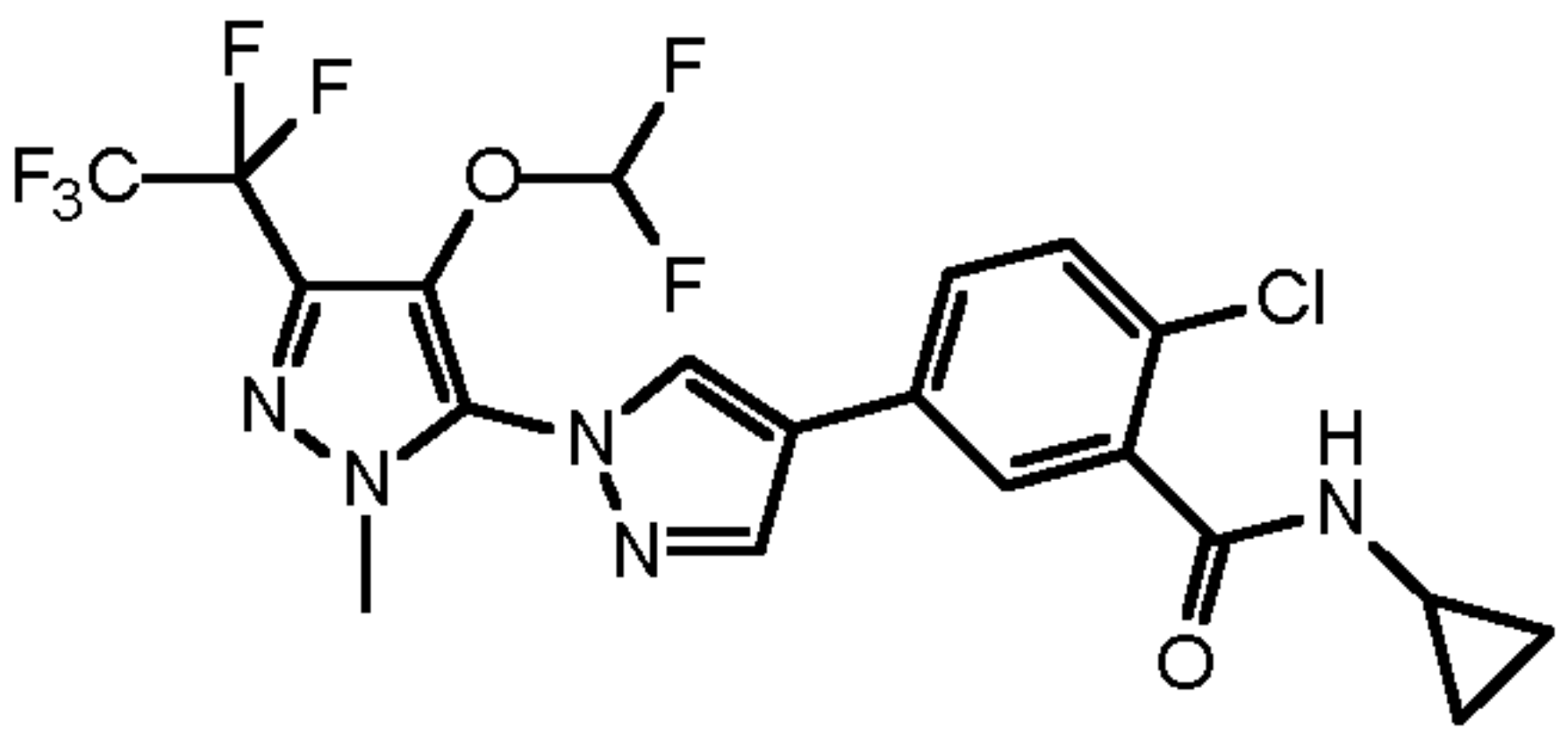
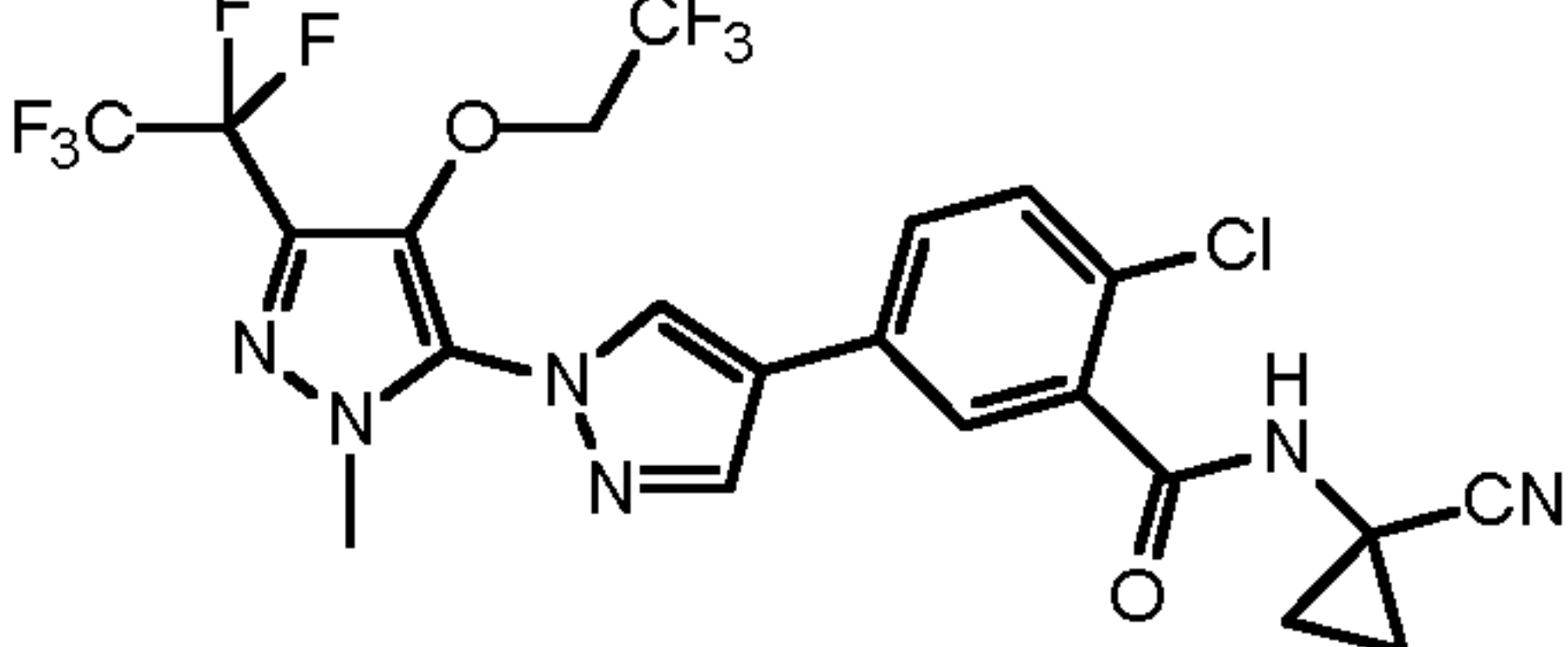
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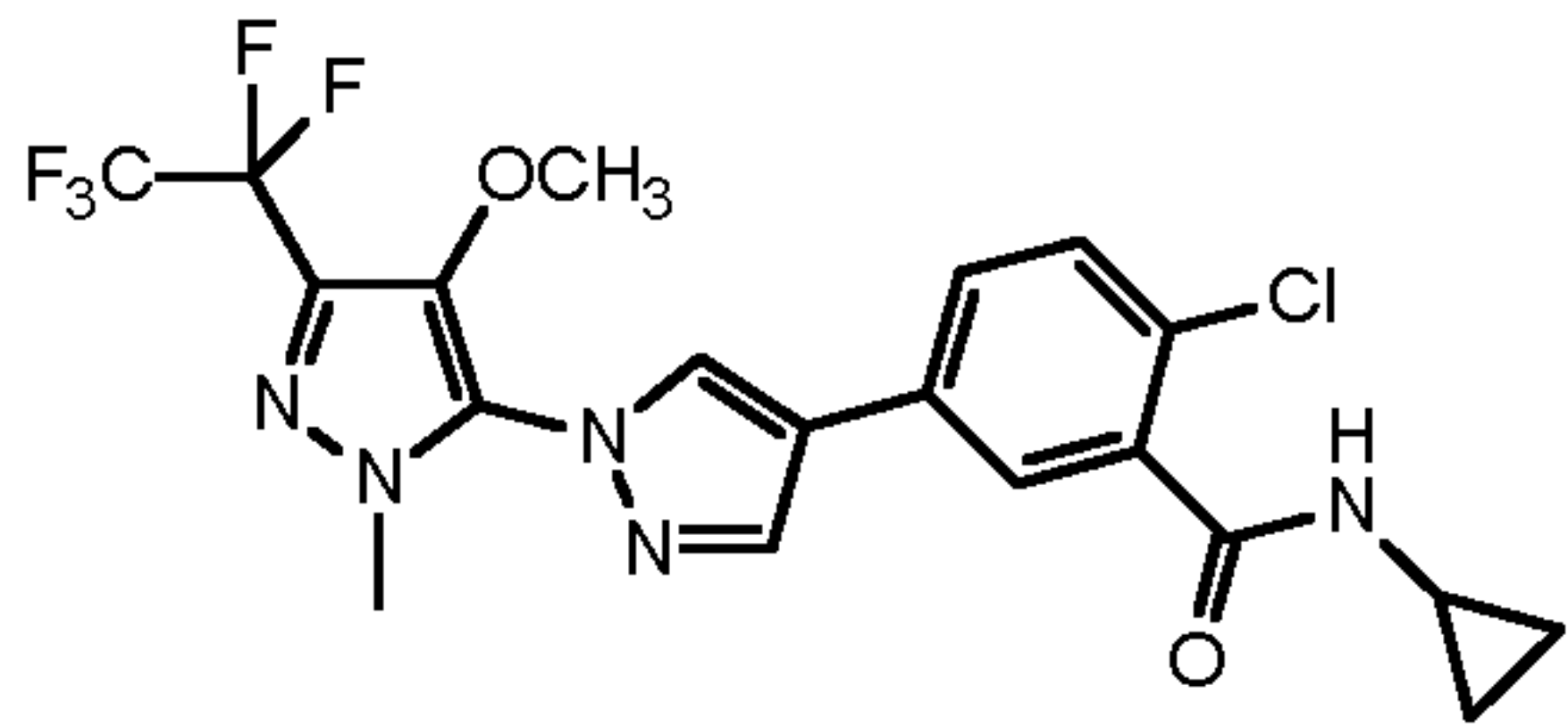
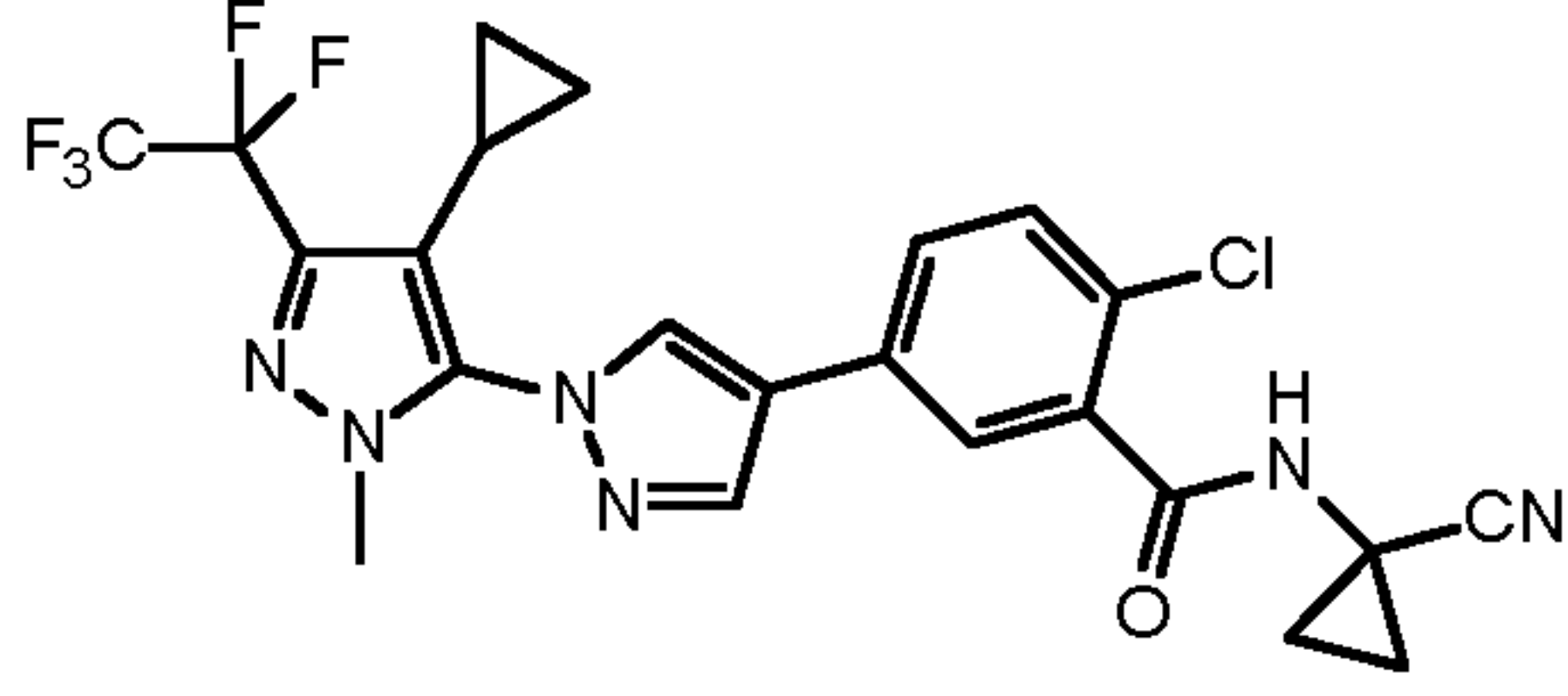
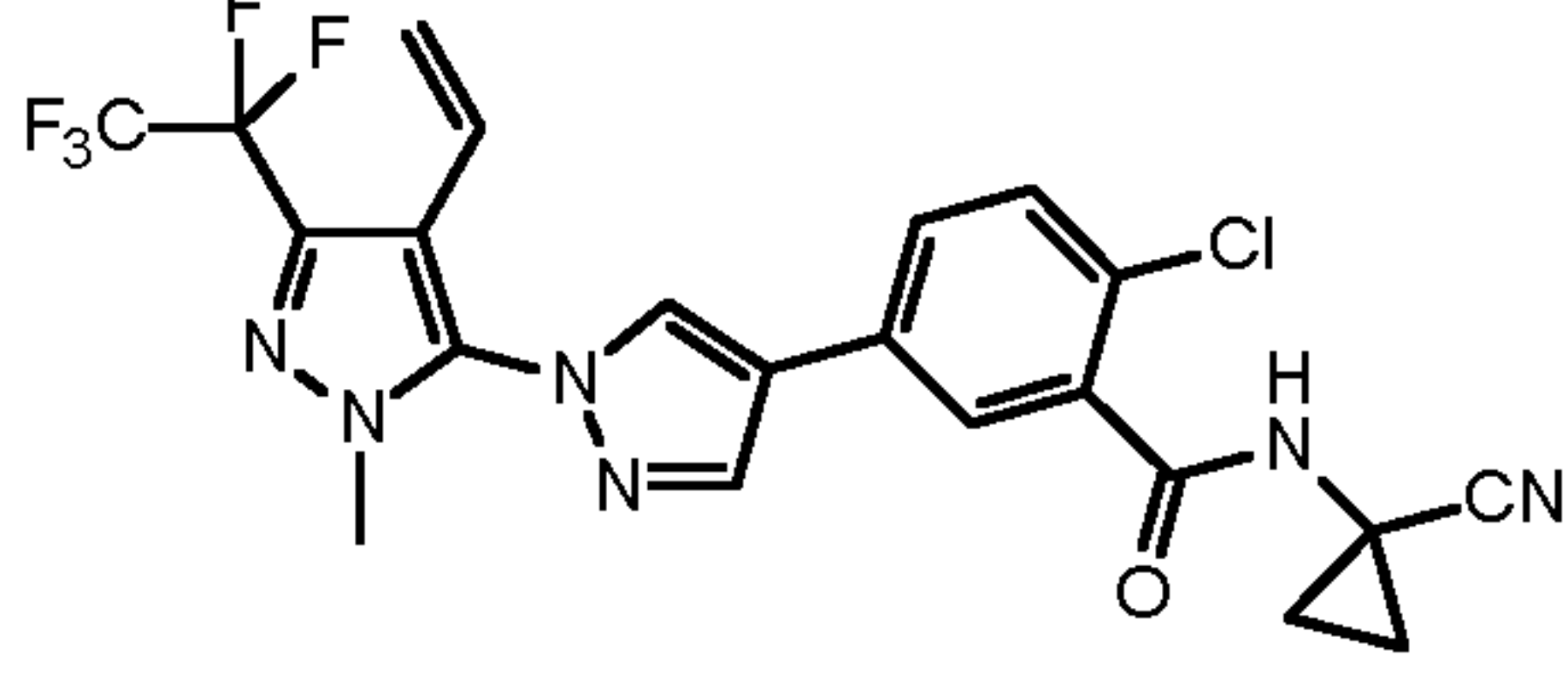
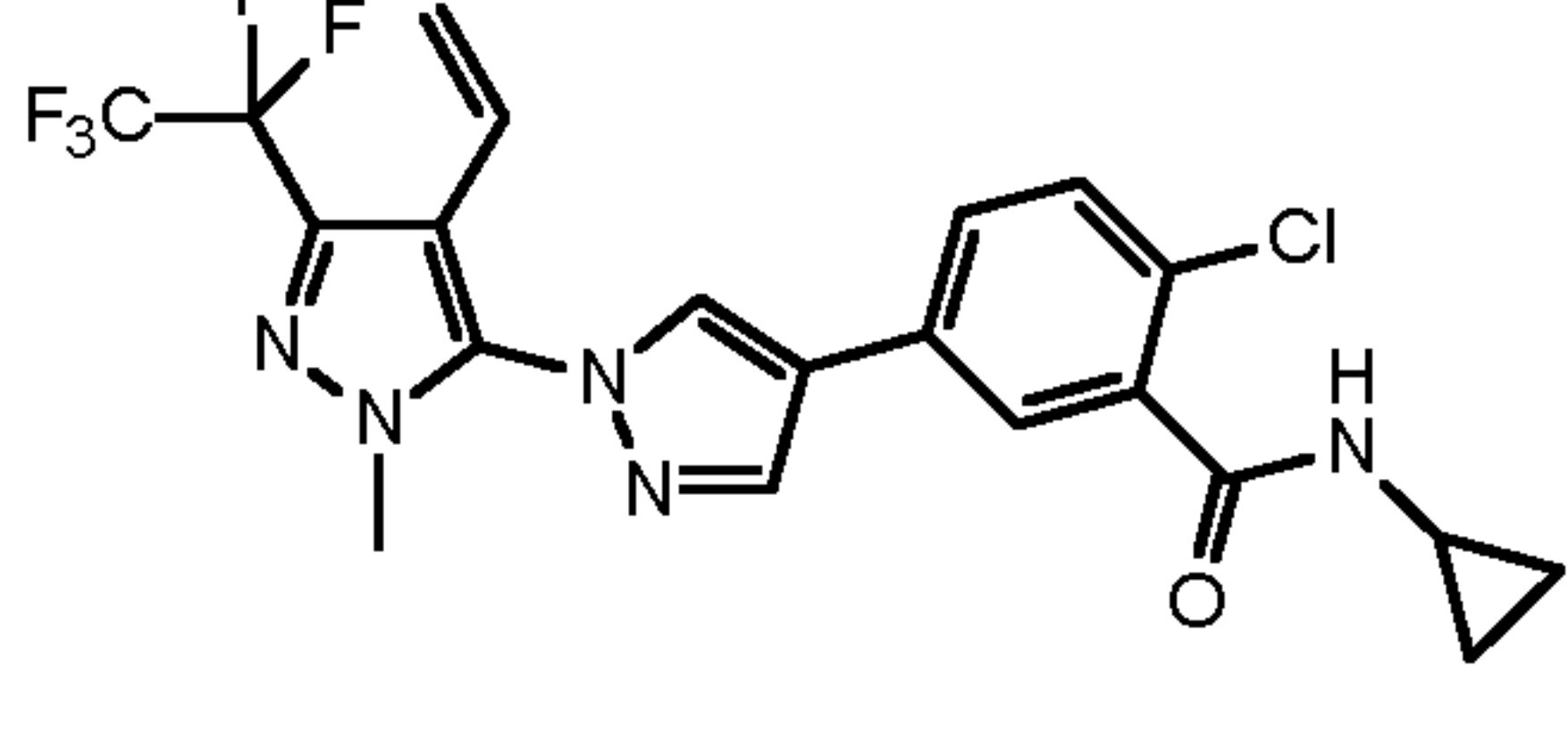
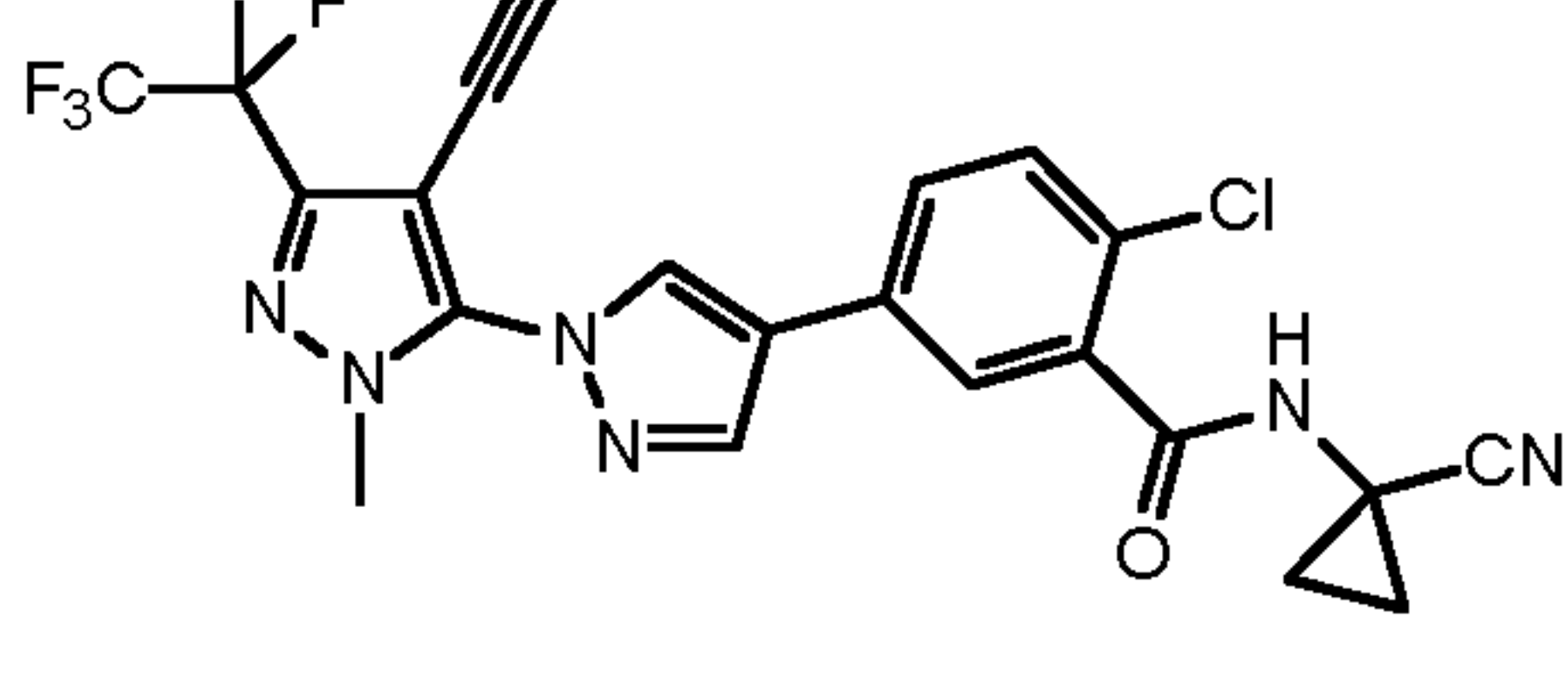
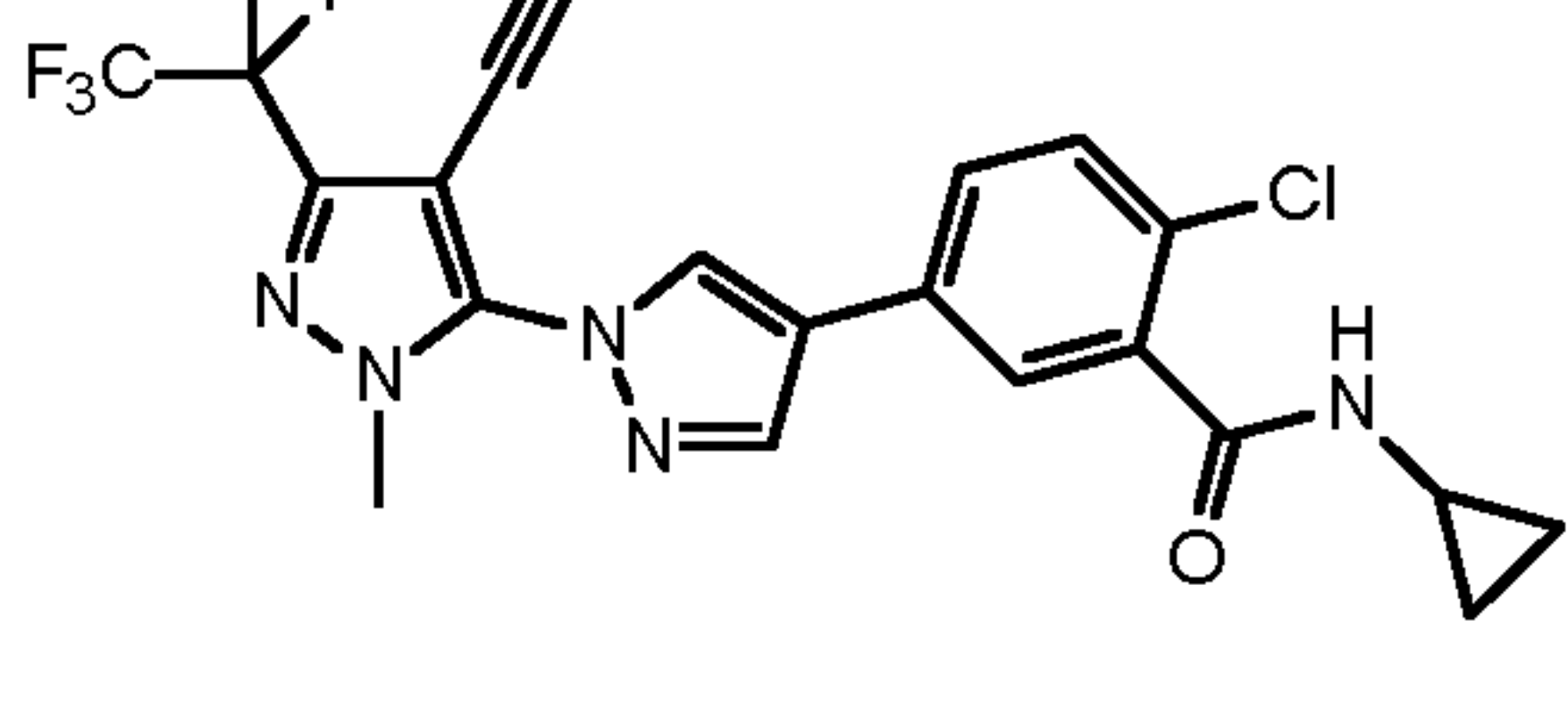
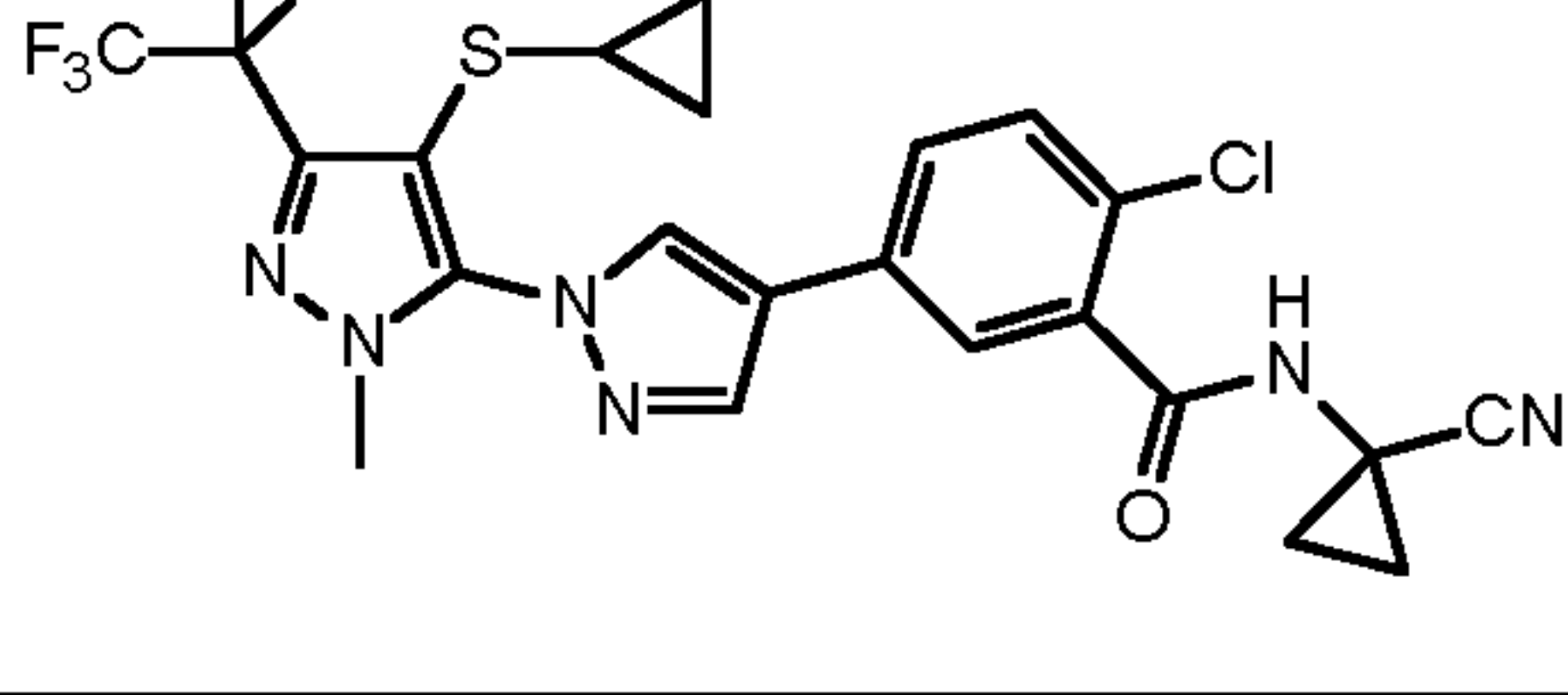
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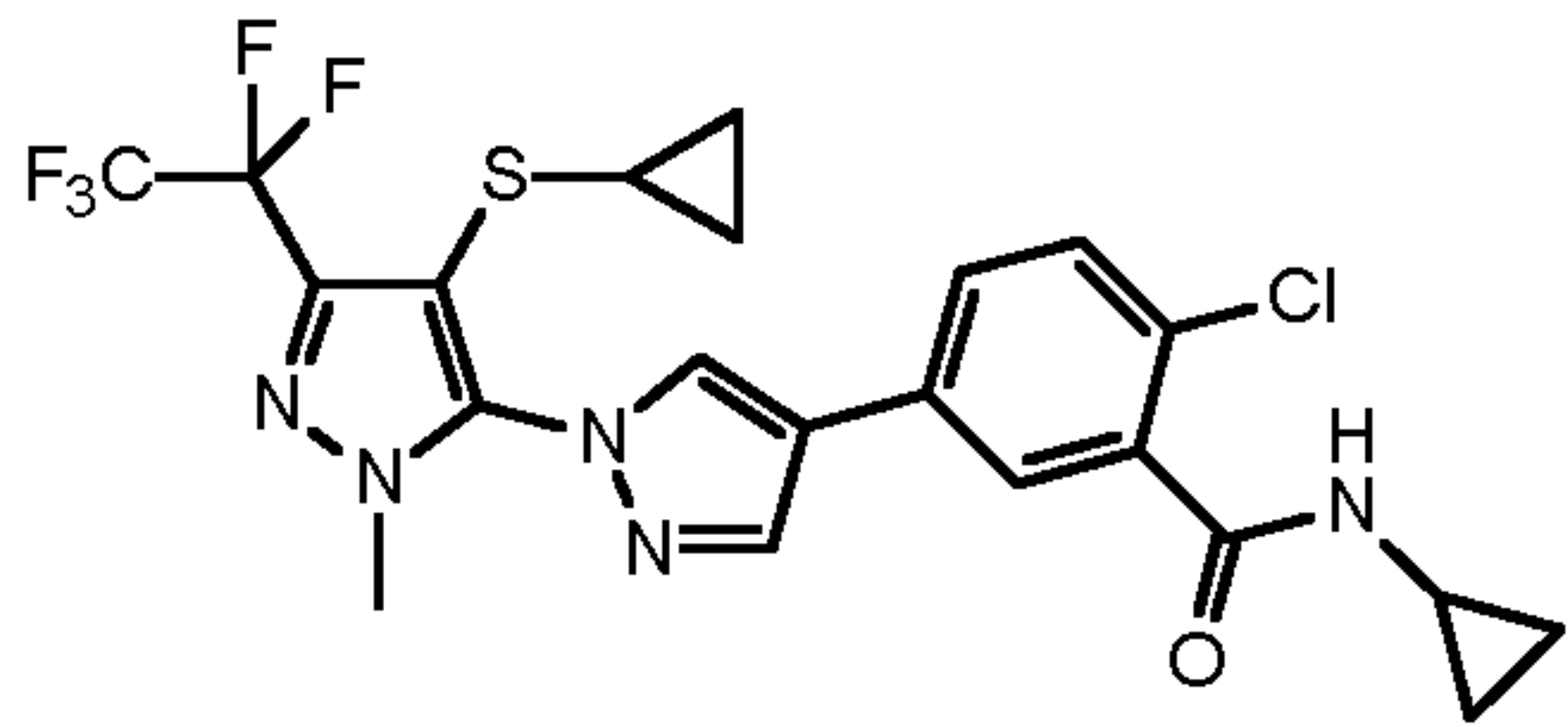
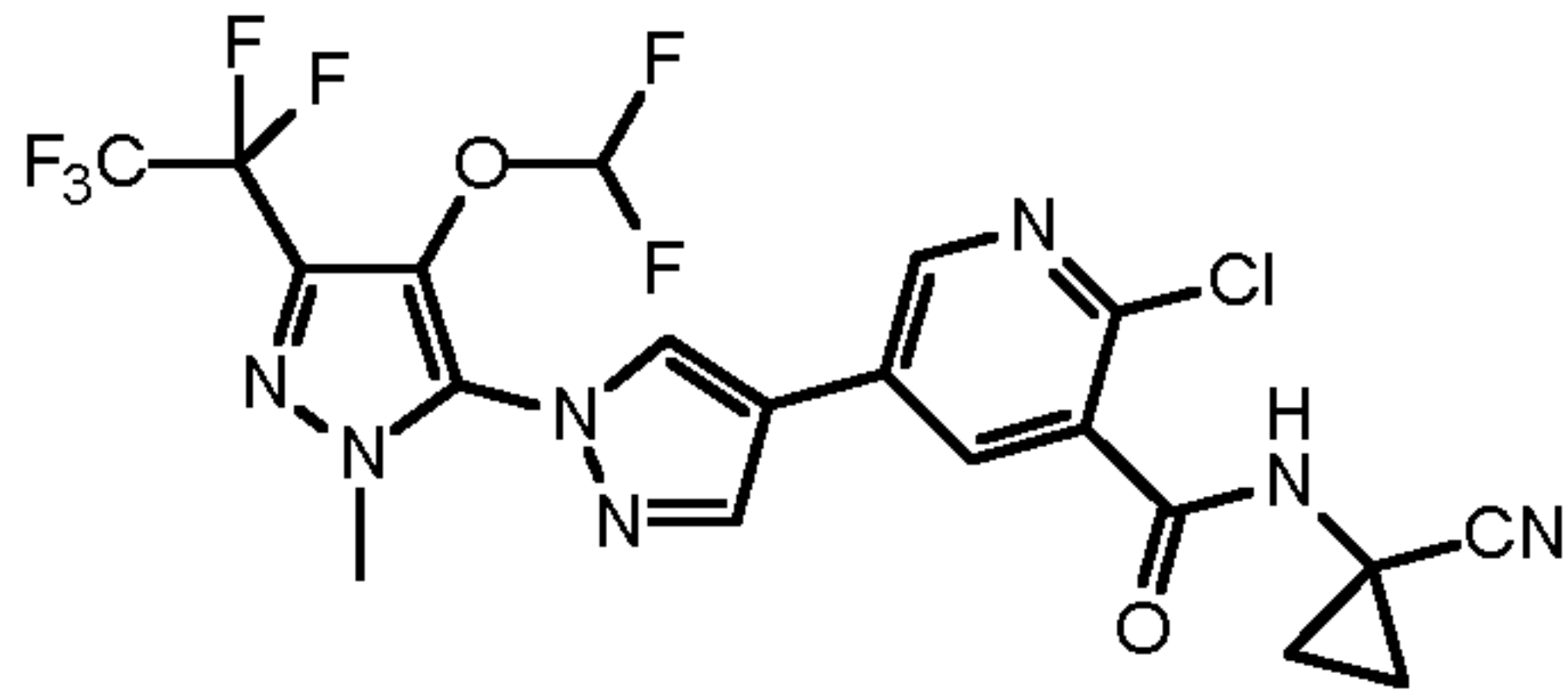
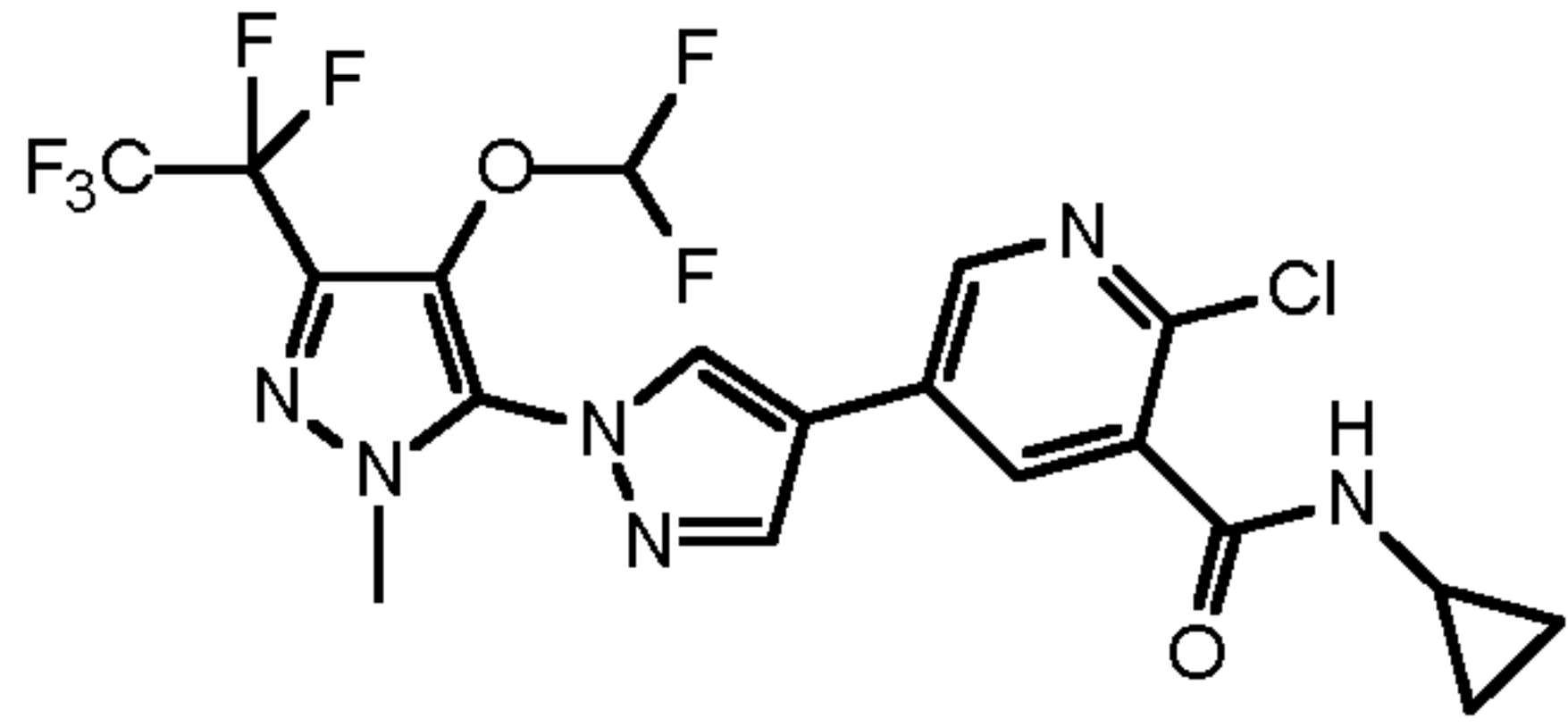
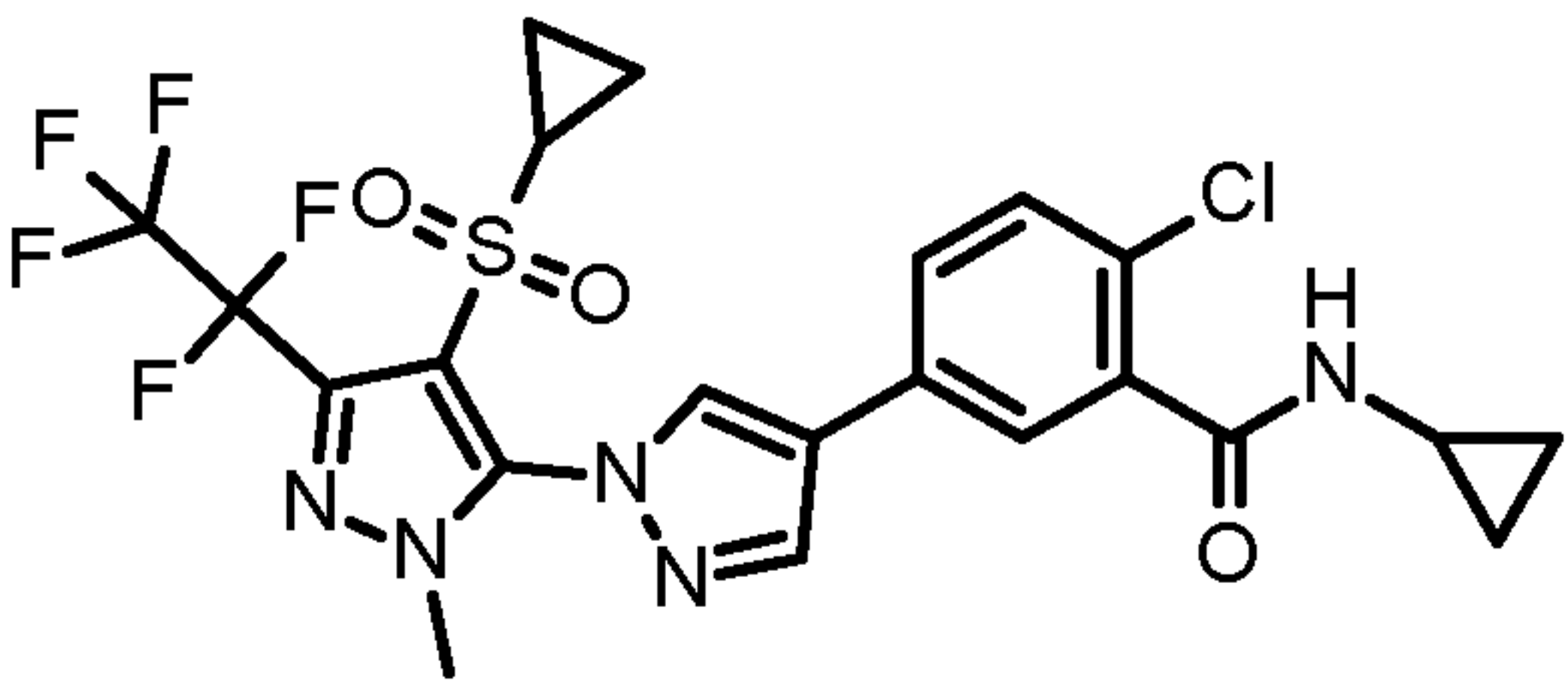
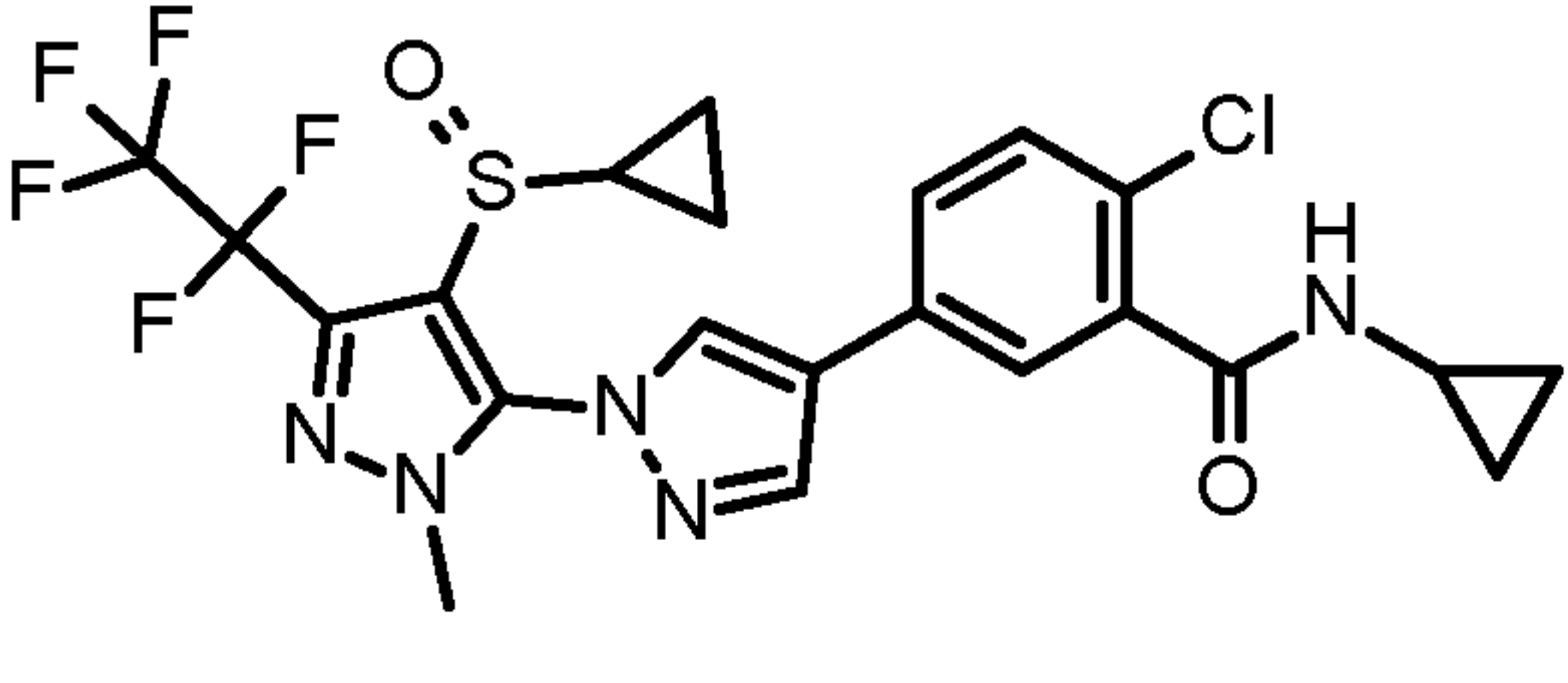
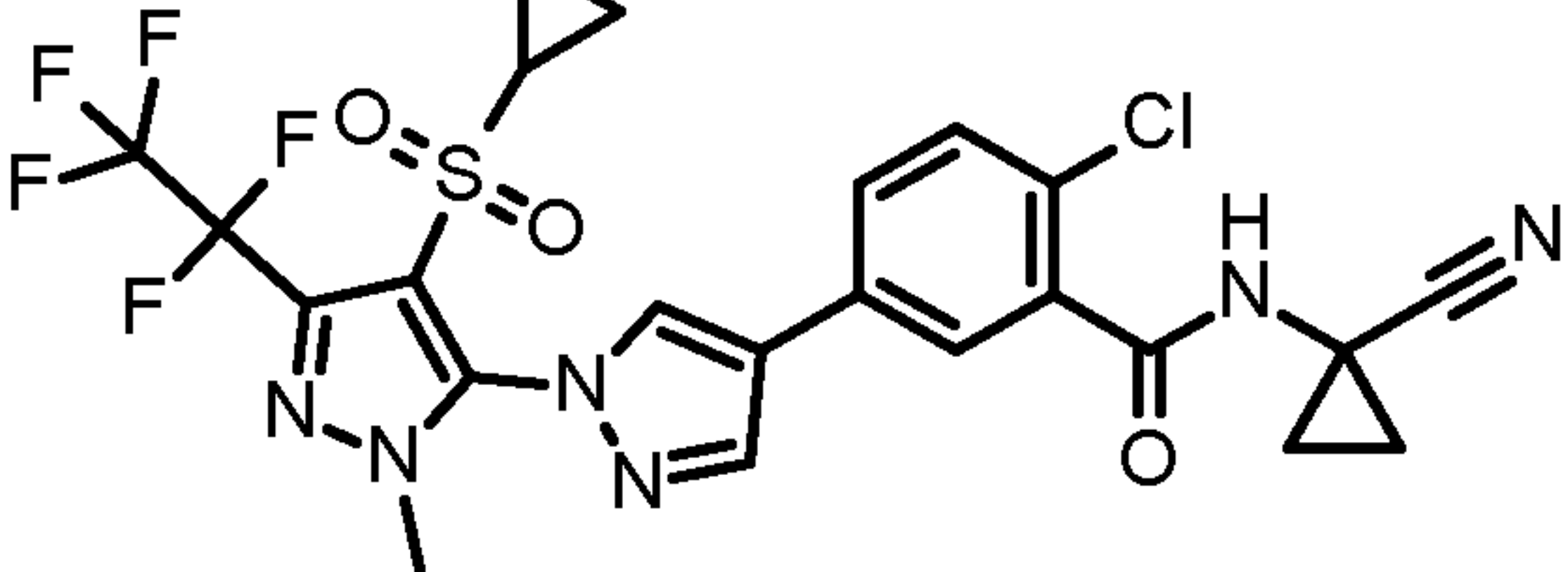
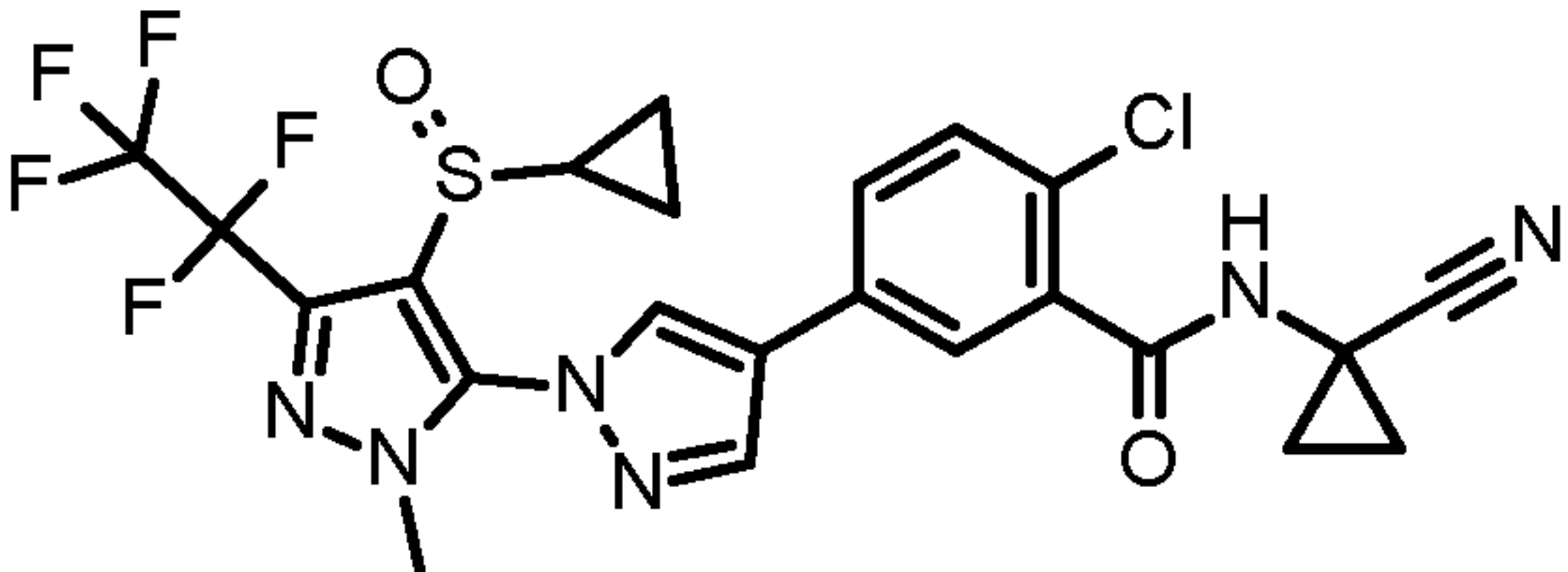
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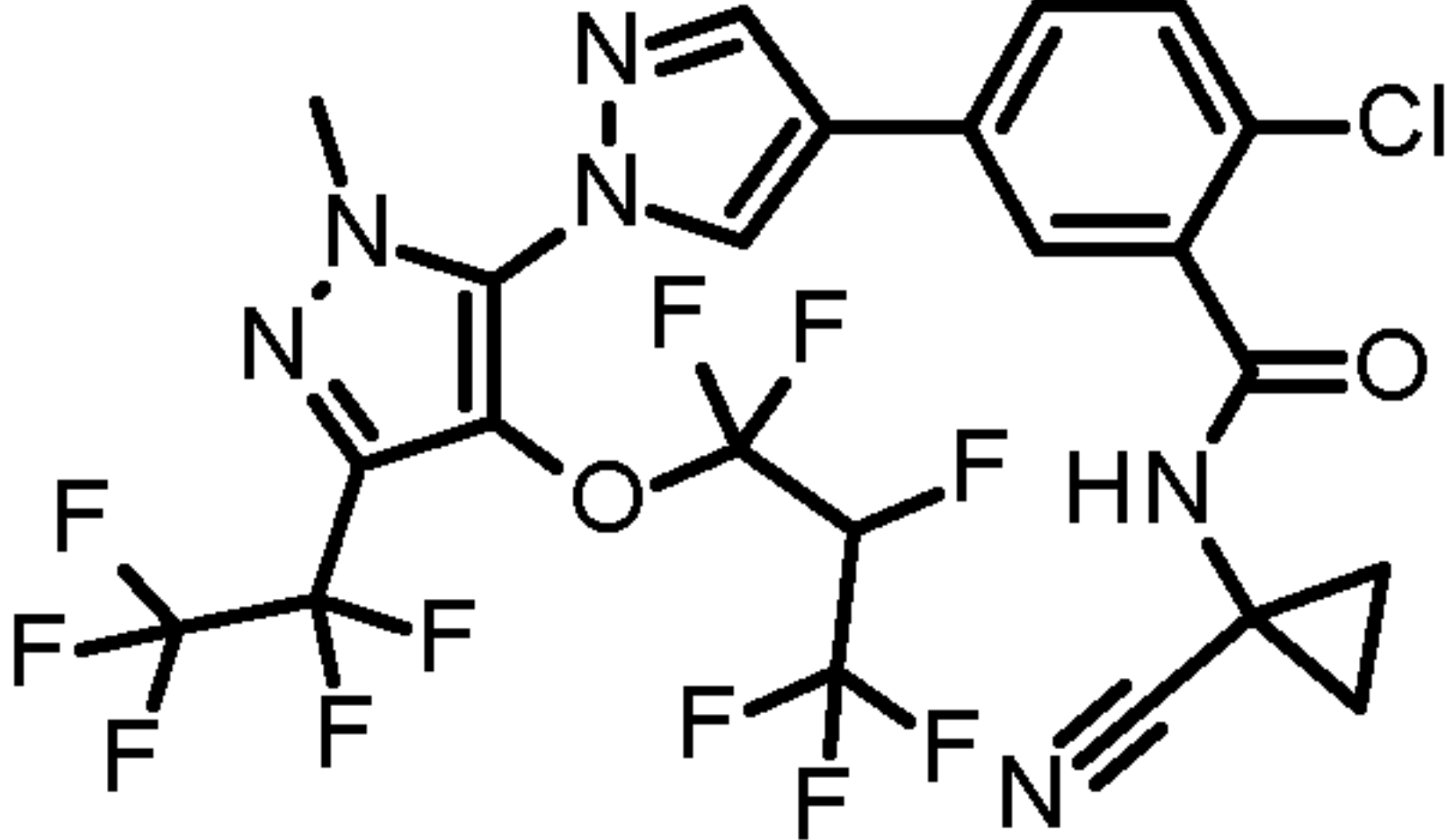
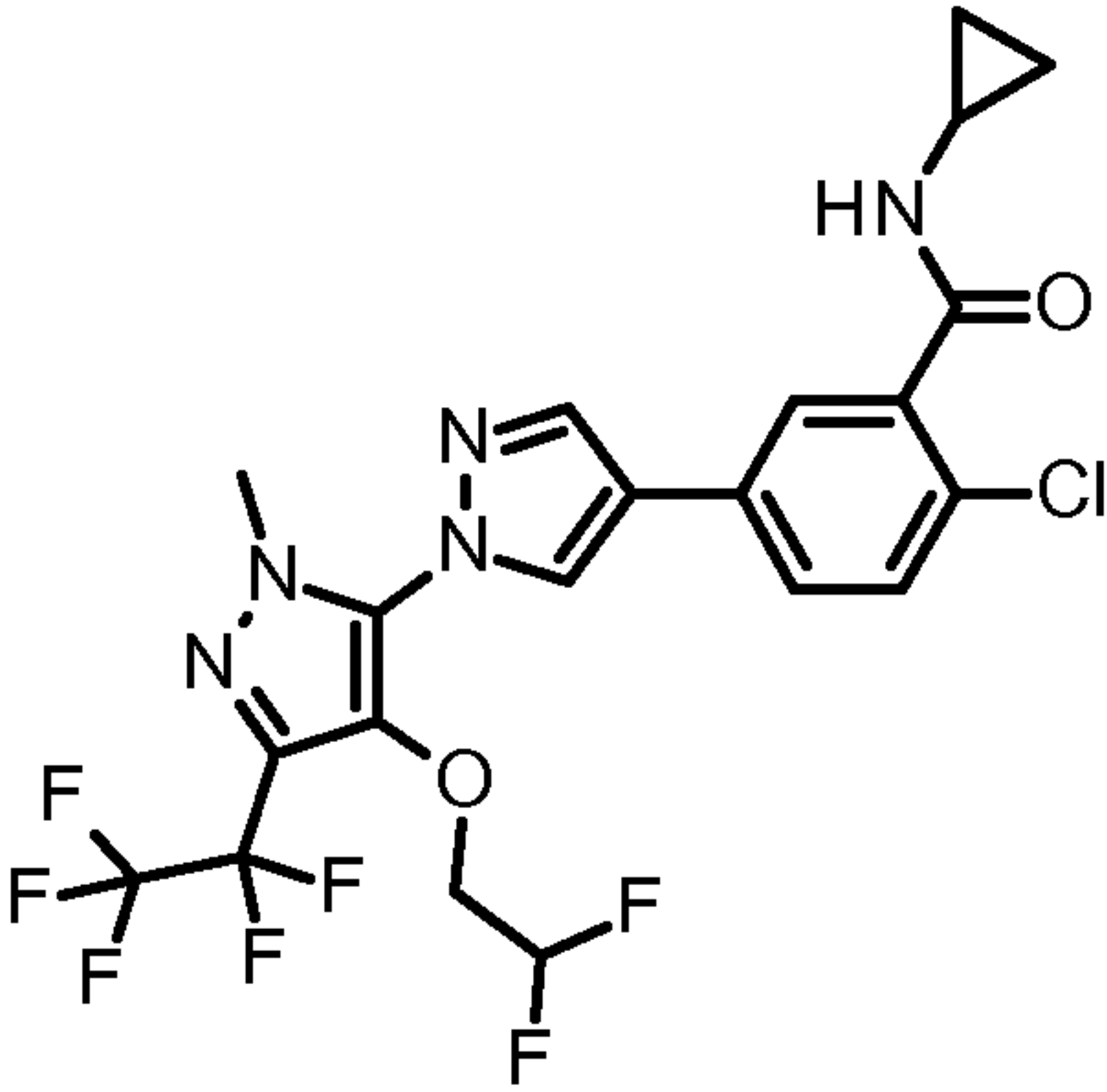
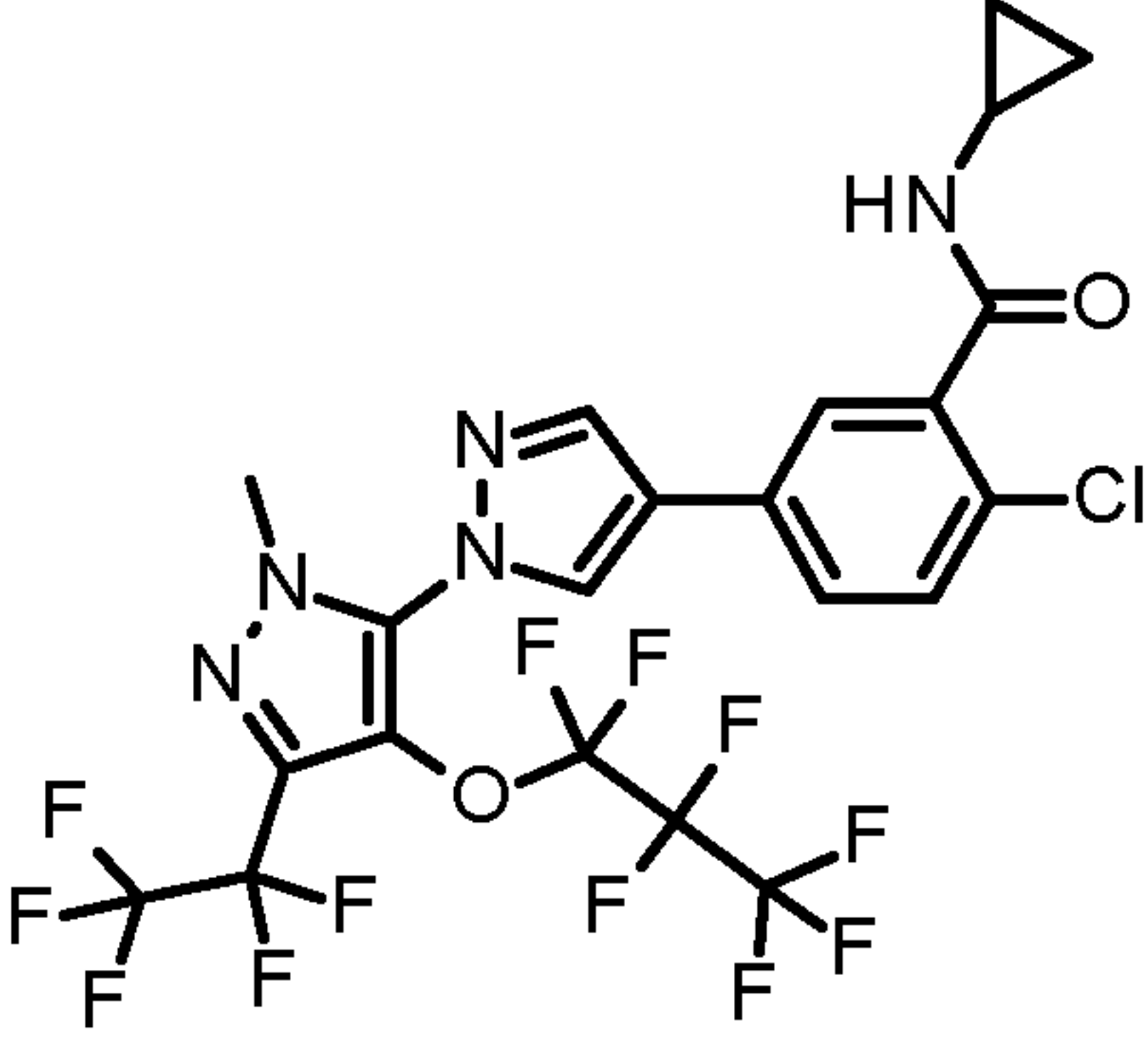
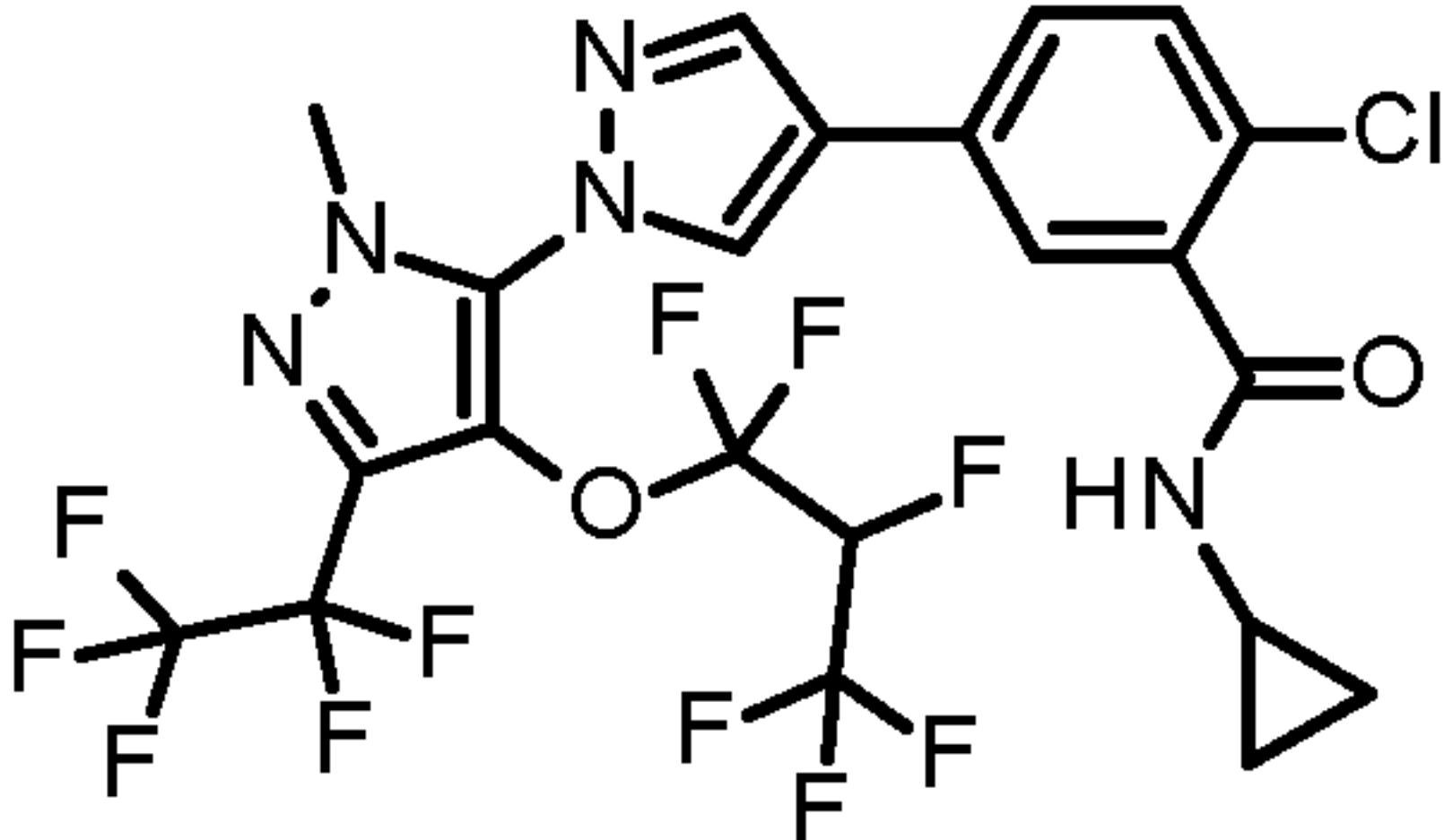
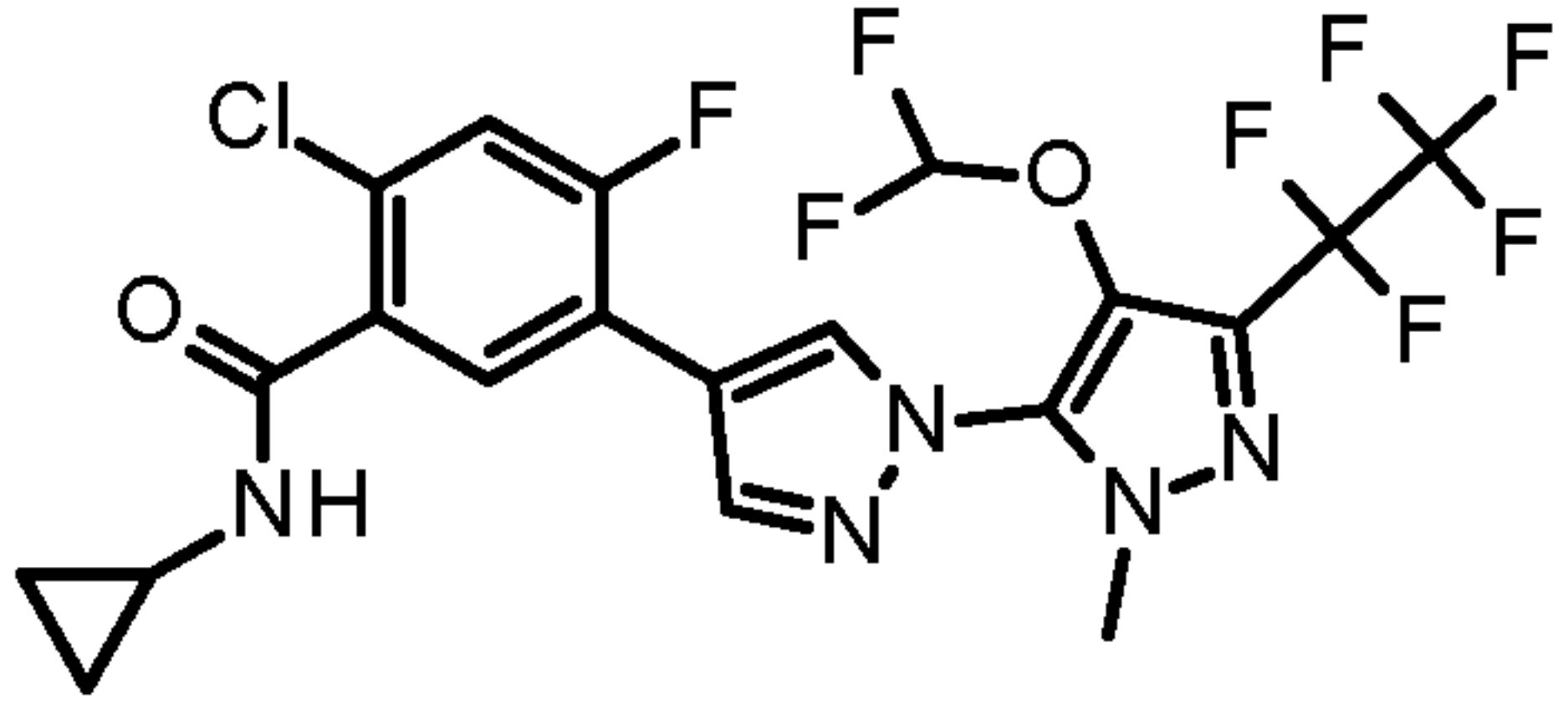
Embodiment 25.2: A compound or salt according to embodiment 1 selected from

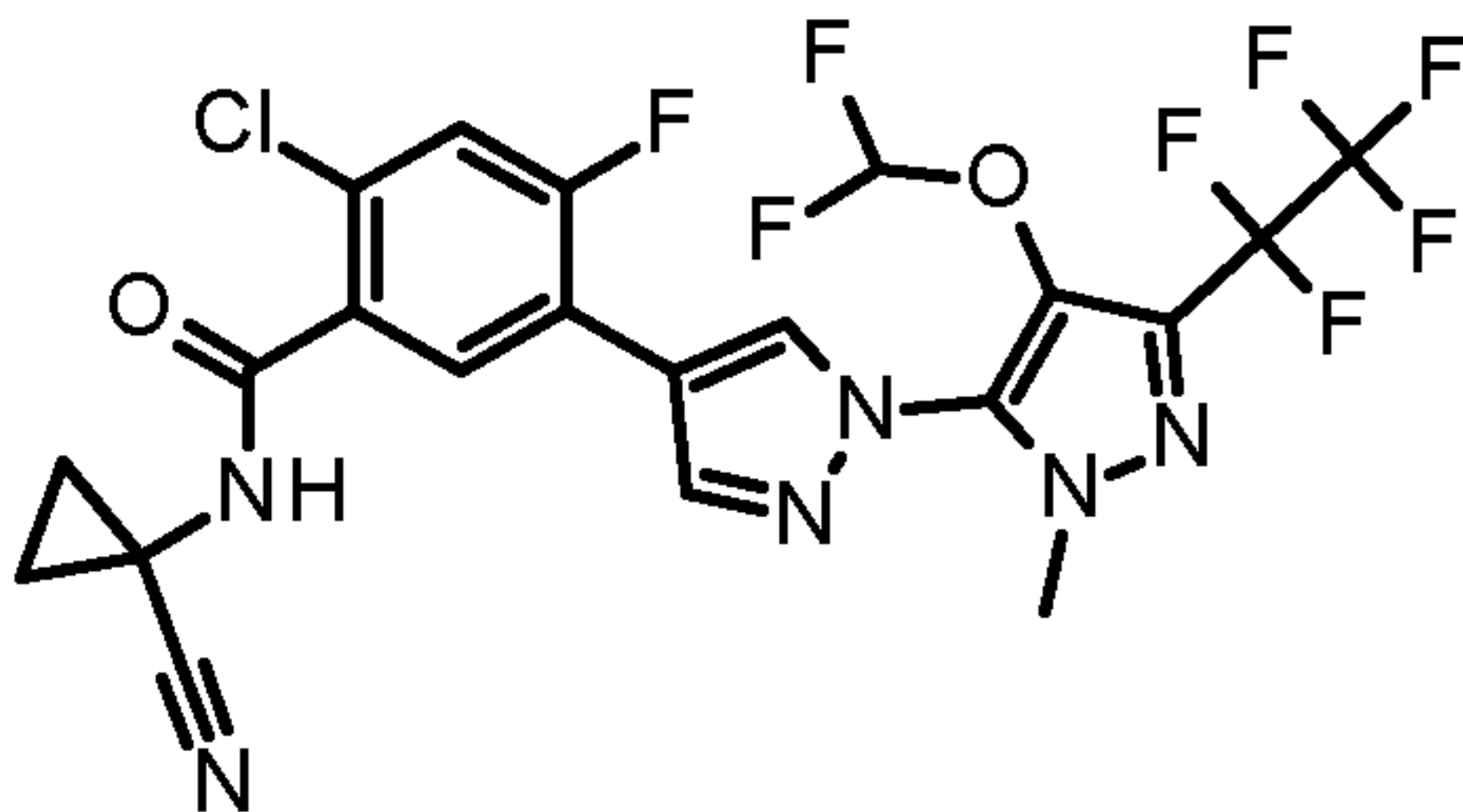
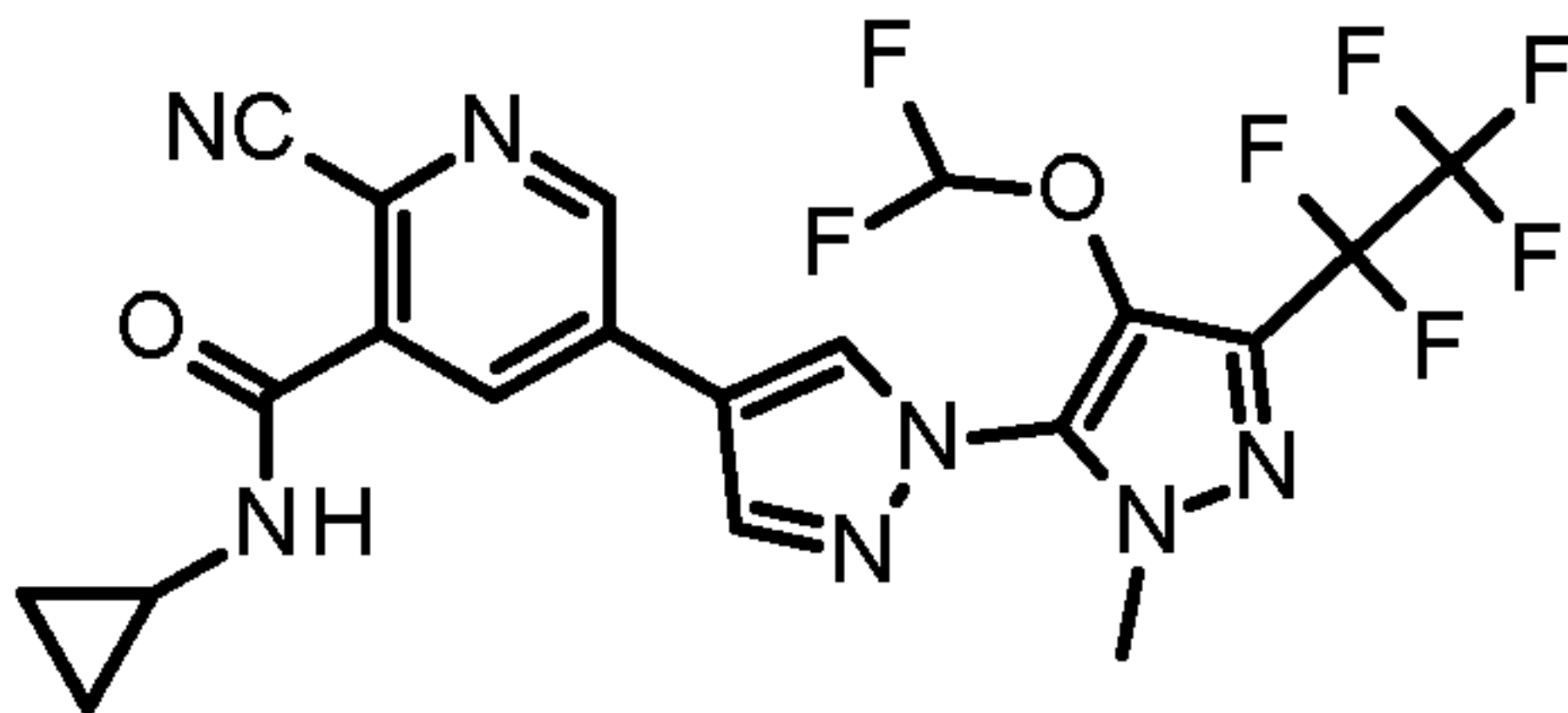
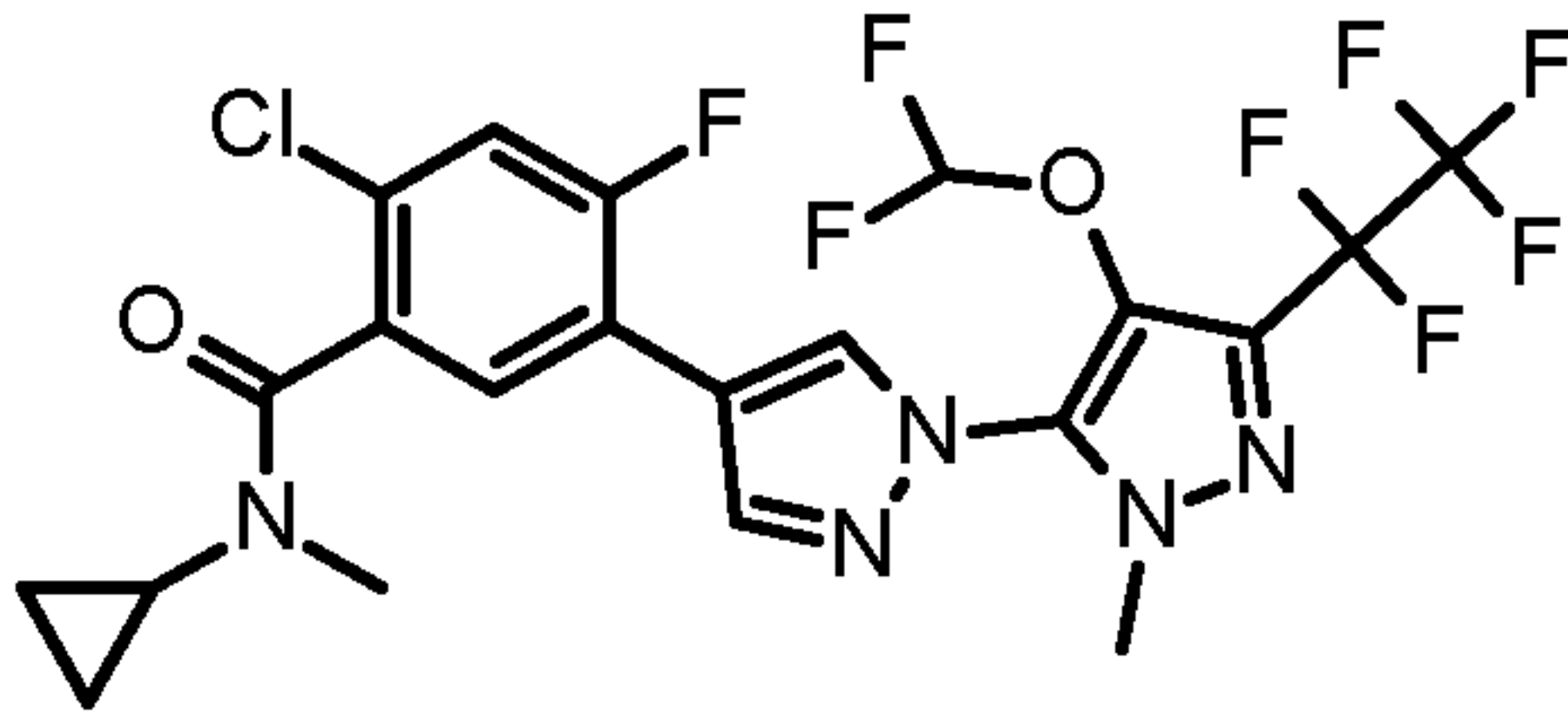
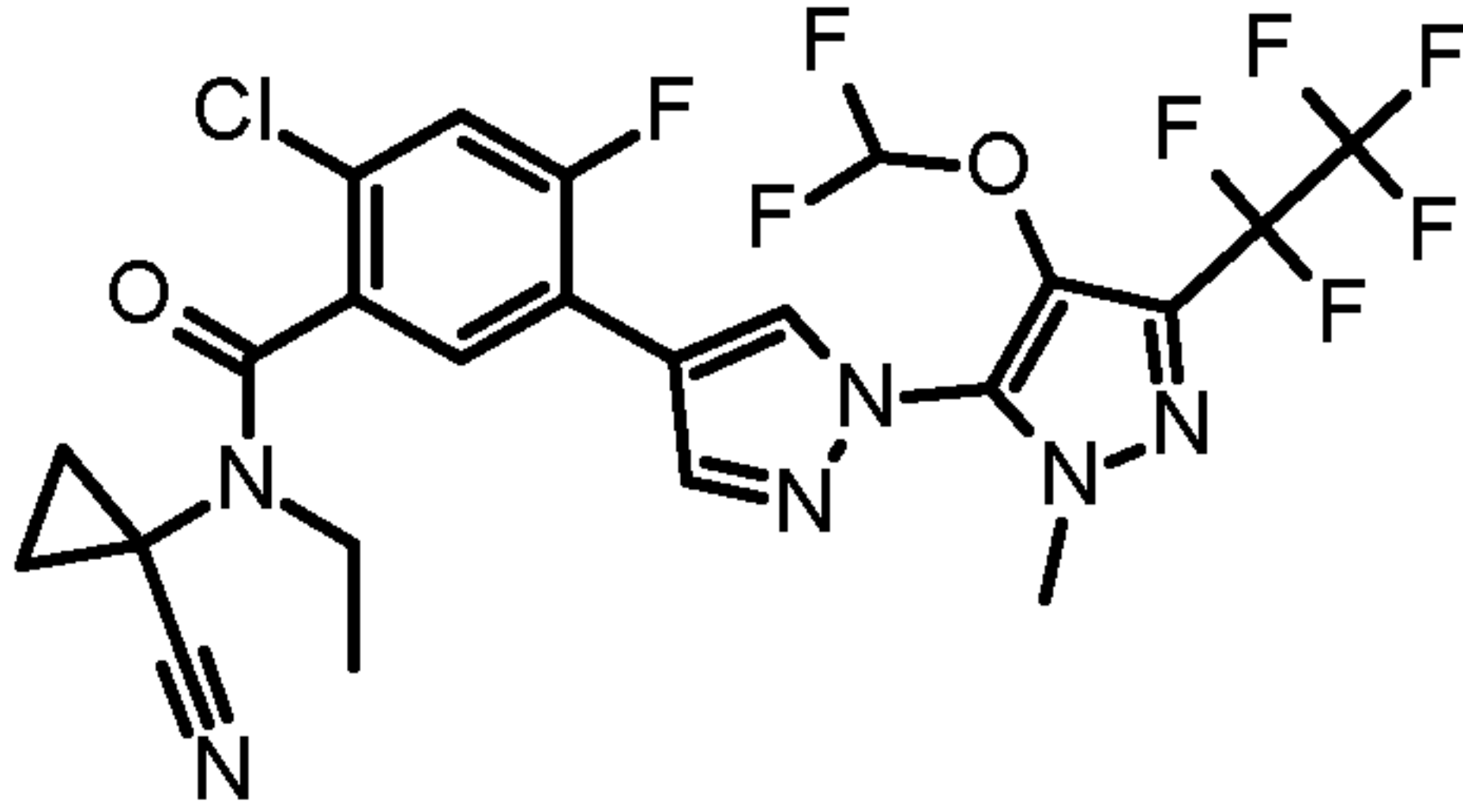
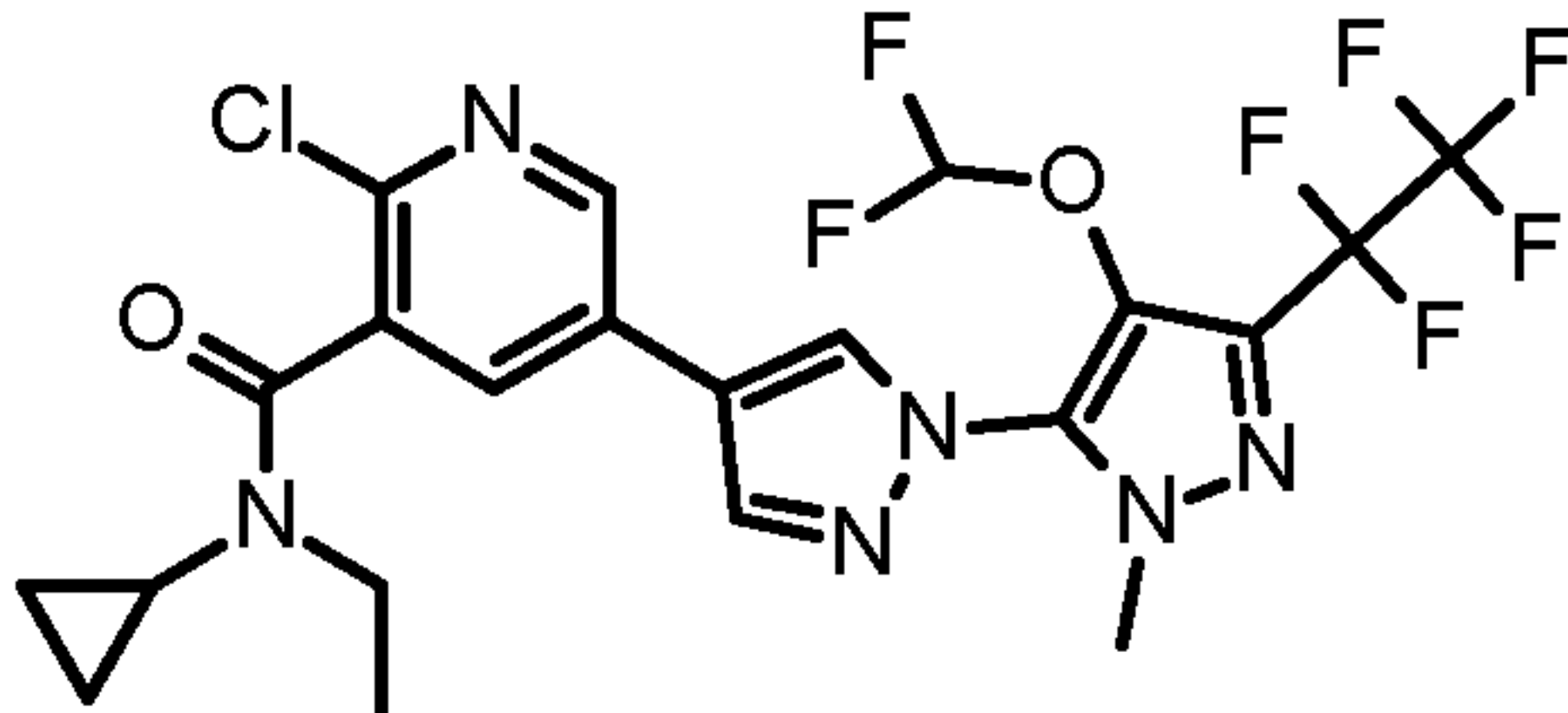
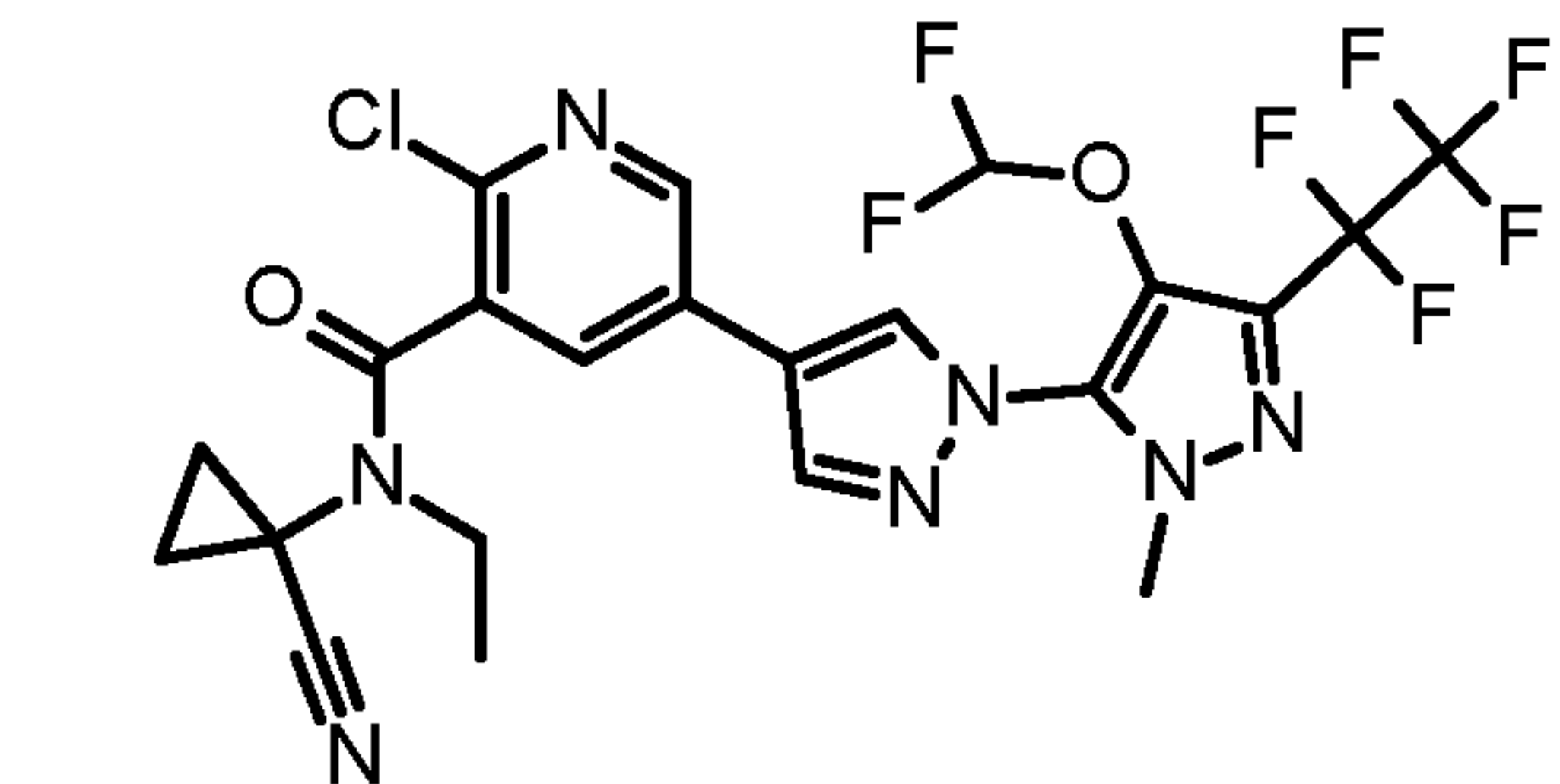
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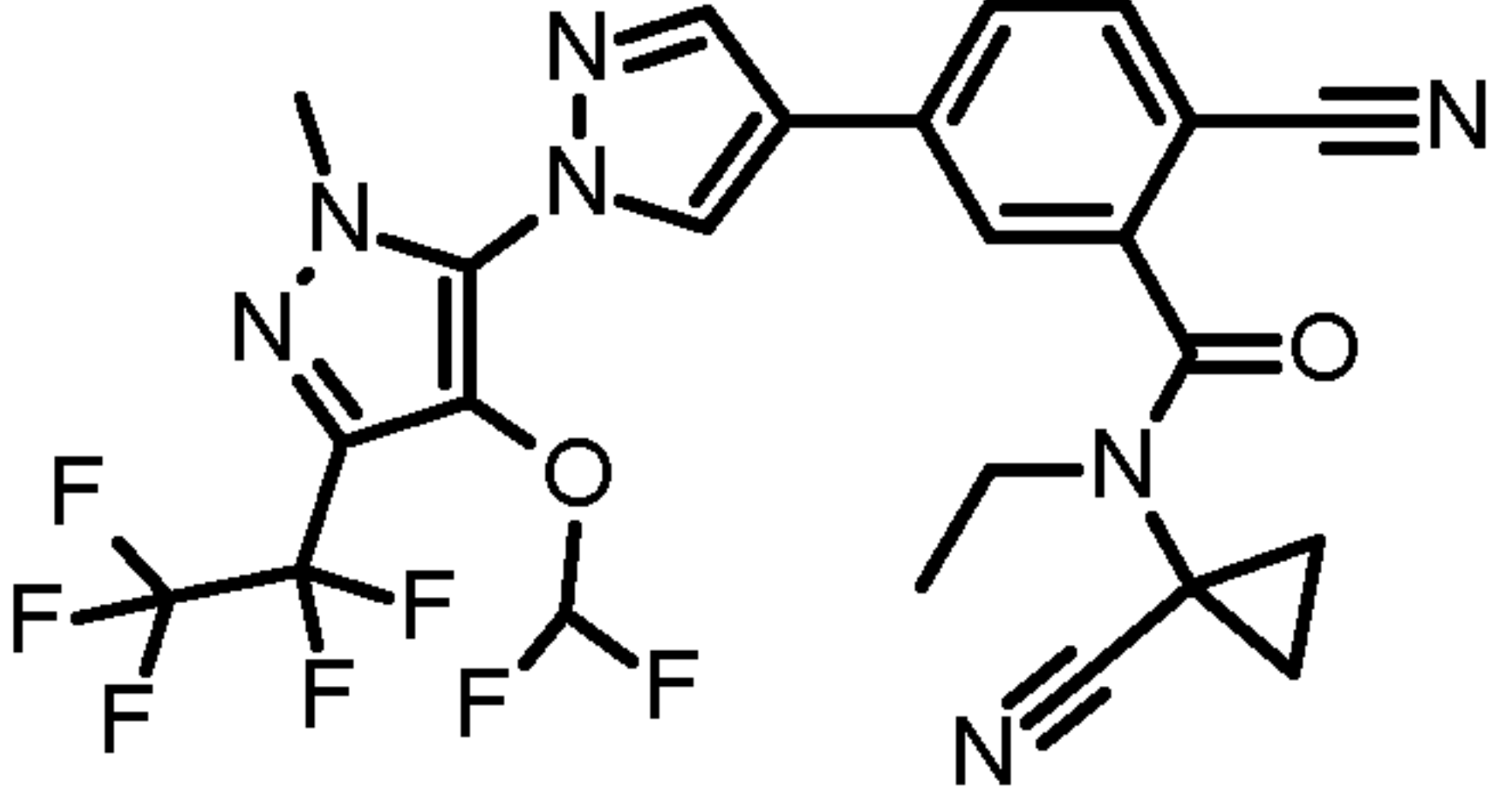
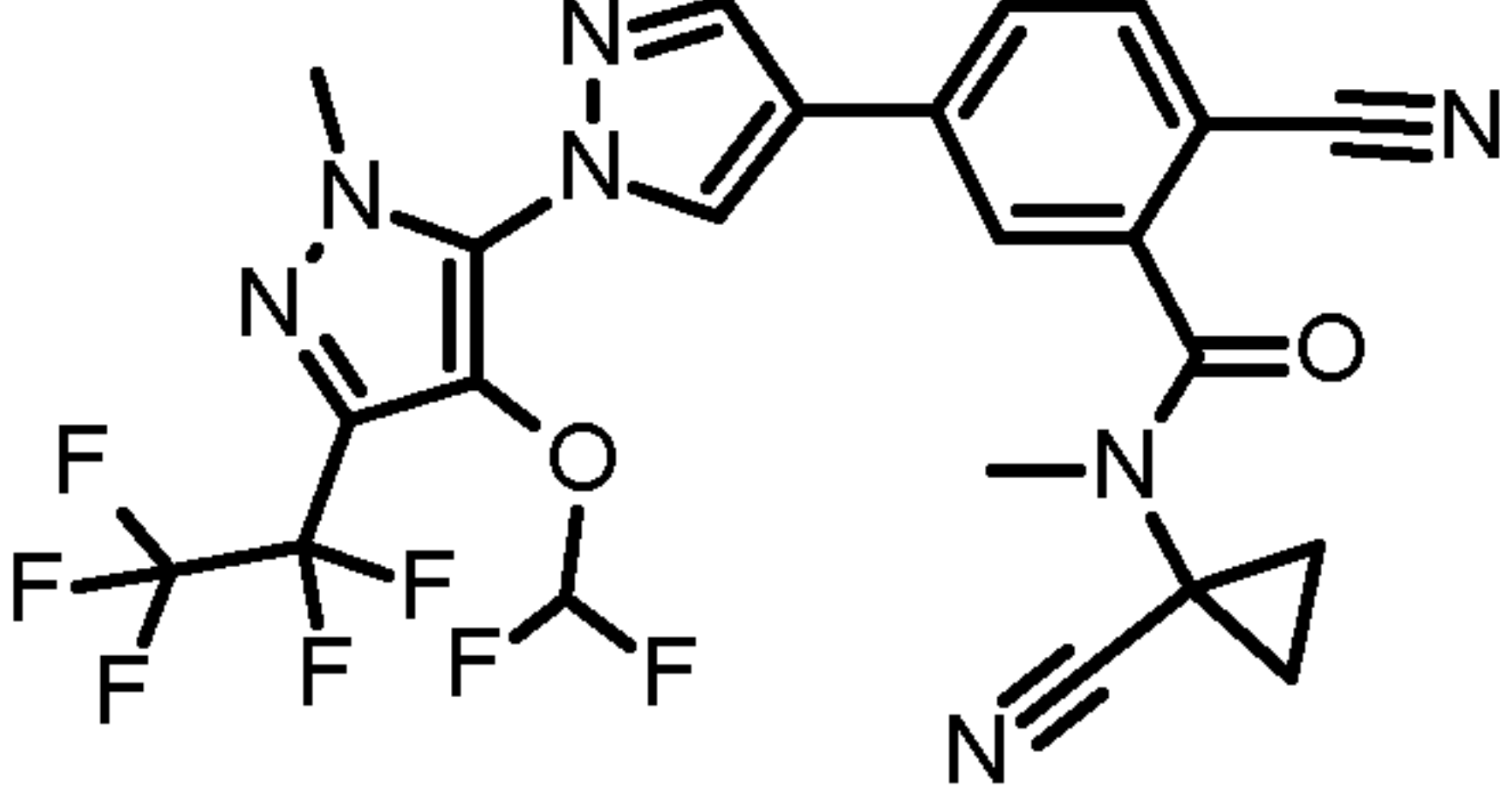
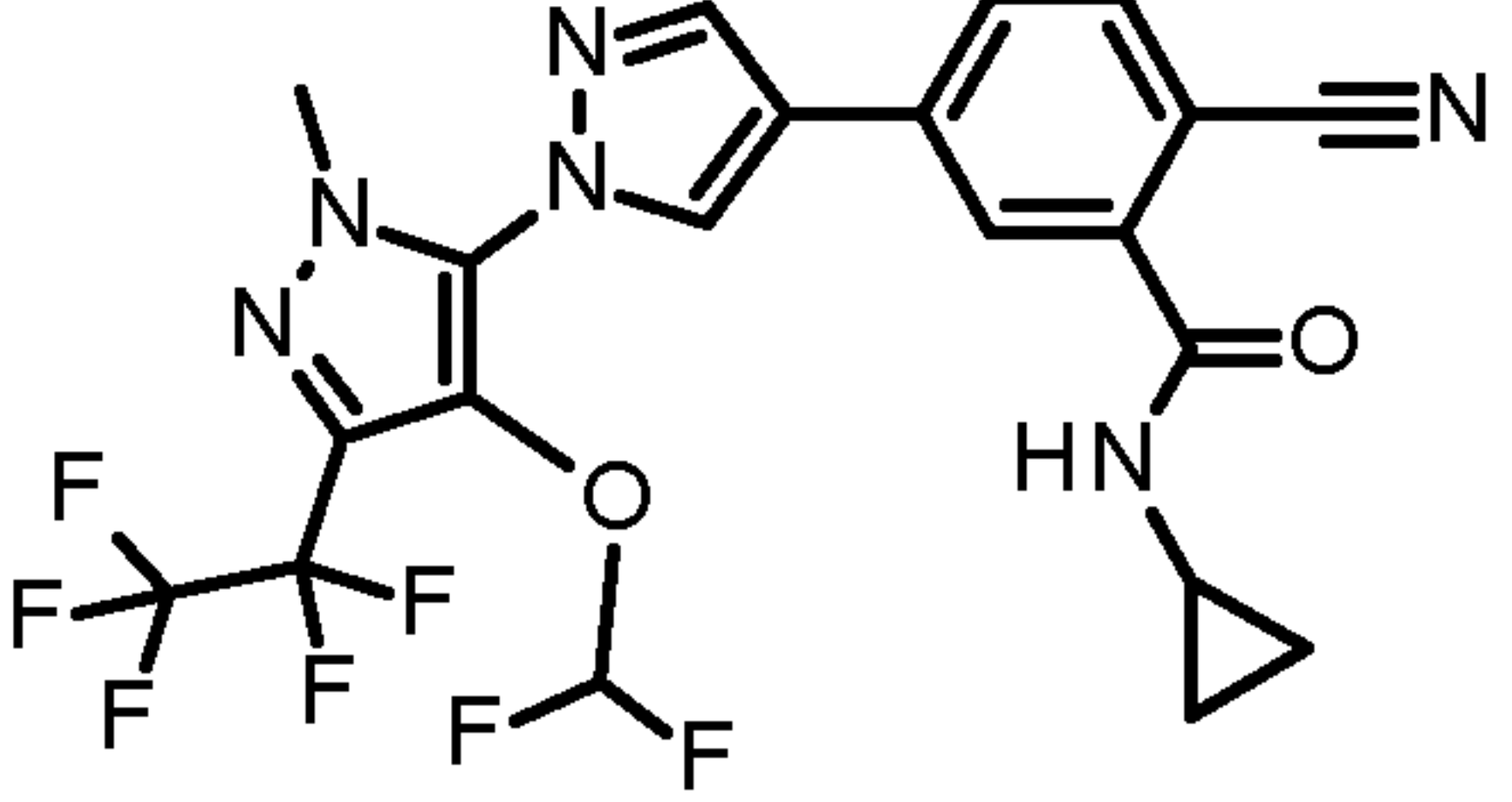
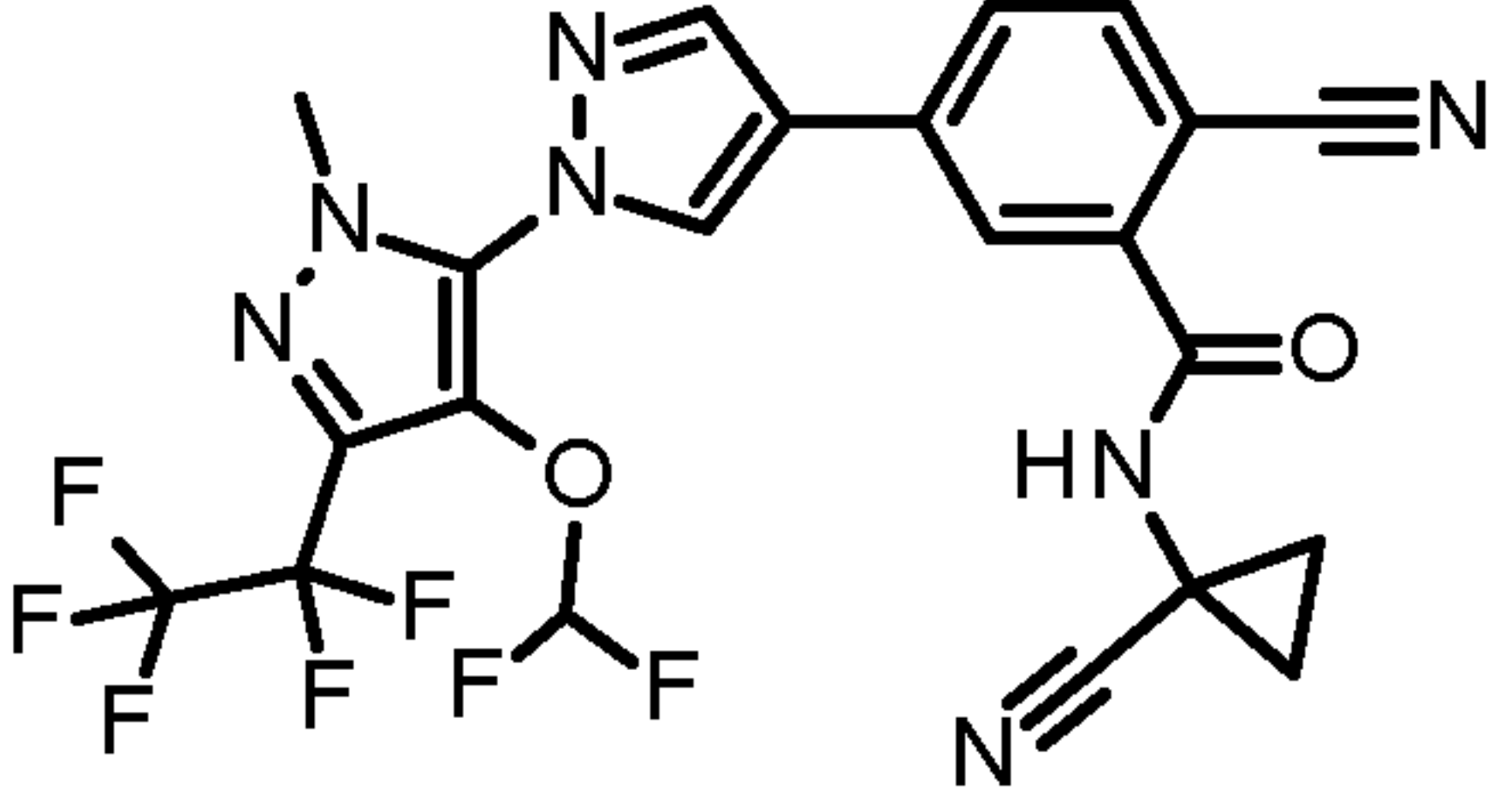
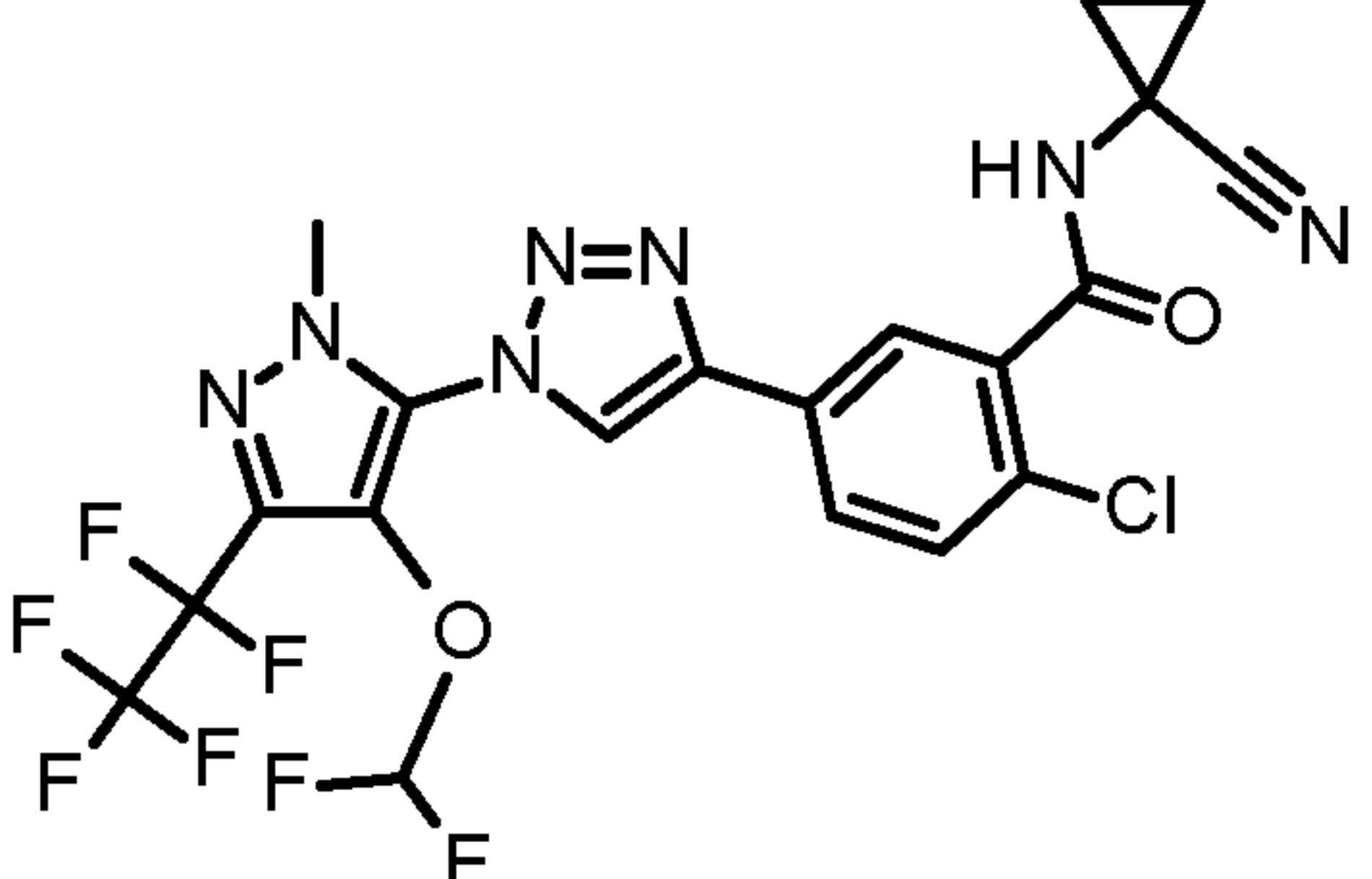
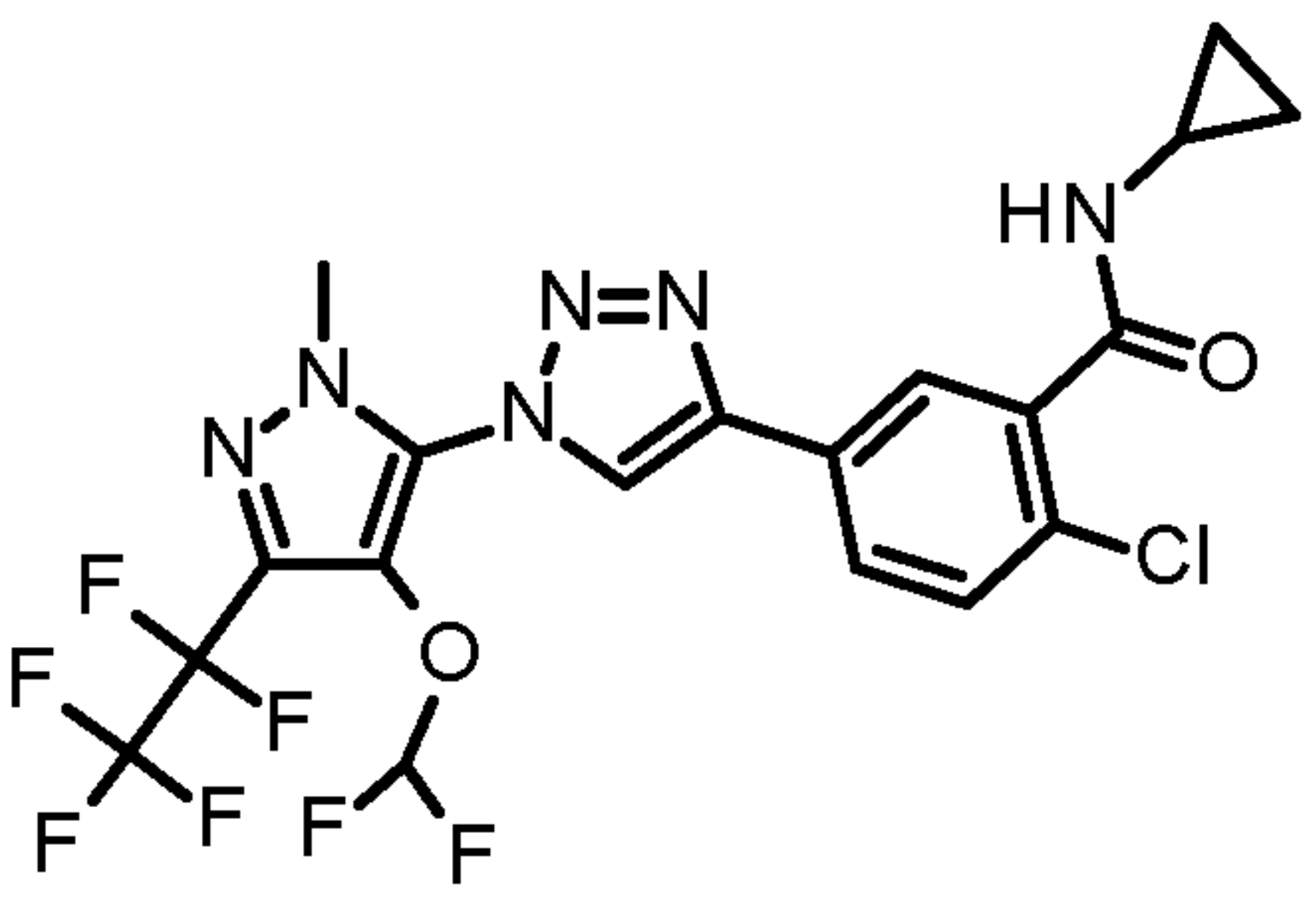
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Definitions:

The term "Alkyl" as used herein- in isolation or as part of a chemical group – represents straight-chain or
 5 branched hydrocarbons, preferably with 1 bis 6 carbon atoms, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, s-butyl, t-butyl, pentyl, 1- methylbutyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 1,1 -dimethylpropyl, 2,2- dimethylpropyl, 1 -ethylpropyl, hexyl, 1 -methylpentyl, 2-methylpentyl, 3-methylpentyl, 4- methylpentyl, 1,2-dimethylpropyl, 1,3-dimethylbutyl, 1,4-dimethylbutyl, 2,3-dimethylbutyl, 1,1- dimethylbutyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-
 10 trimethylpropyl, 1- ethylbutyl and 2-ethylbutyl. Alkyl groups with 1 to 4 carbon atoms are preferred, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, s-butyl or t-butyl.

The term "Alkenyl" - in isolation or as part of a chemical group - represents straight-chain or branched hydrocarbons, preferably with 2 bis 6 carbon atoms and at least one double bond, for example vinyl, 2-
 15 propenyl, 2-butenyl, 3-butenyl, 1- methyl-2-propenyl, 2-methyl-2-propenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-2-butenyl, 2- methyl-2-butenyl, 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1,1 - dimethyl-2-propenyl, 1,2-dimethyl-2-propenyl, 1 -ethyl-2-propenyl, 2-hexenyl, 3-hexenyl, 4- hexenyl, 5-hexenyl, 1 -methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2- pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1 -methyl-4-pentenyl, 2-
 20 methyl-4-pentenyl, 3- methyl-4-pentenyl, 4-methyl-4-pentenyl, 1, 1 -dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl, 1,2- dimethyl-2-butenyl, 1,2-dimethyl-3-butenyl, 1,3-dimethyl-2-butenyl, 2,2-dimethyl-3-butenyl, 2,3- dimethyl-2-butenyl, 2,3-dimethyl-3-butenyl, 1 -ethyl-2-butenyl, 1-ethyl-3-butenyl, 2-ethyl-2-butenyl, 2-ethyl-3-butenyl, 1, 1,2-trimethyl-2-propenyl, 1 -ethyl- 1 -methyl-2-propenyl und 1-ethyl-2-methyl-2-propenyl. Alkenyl groups with 2 to 4 carbon atoms are preferred, for example 2-propenyl, 2-butenyl or 1-
 25 methyl-2-propenyl.

The term "Alkynyl" - in isolation or as part of a chemical group - represents straight-chain or branched hydrocarbons, preferably with 2 bis 6 carbon atoms and at least one triple bond, for example 2-propynyl, 2-butynyl, 3-butynyl, 1-methyl-2- propynyl, 2-pentynyl, 3-pentynyl, 4-pentynyl, 1-methyl-3-butynyl, 2-
 30 methyl-3-butynyl, 1-methyl-2- butynyl, 1,1 -dimethyl-2-propynyl, 1 -ethyl-2-propynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, 5-hexynyl, 1- methyl-2-pentynyl, 1-methyl-3-pentynyl, 1 -methyl-4-pentynyl, 2-methyl-3-pentynyl, 2-methyl-4- pentynyl, 3 -methyl-4-pentynyl, 4-methyl-2-pentynyl, 1,1 -dimethyl-3 -butynyl, 1,2-dimethyl-3 -butynyl, 2,2- dimethyl-3-butynyl, 1-ethyl-3-butynyl, 2-ethyl-3-butynyl, 1-ethyl-1-methyl-2-propynyl and 2,5-hexadiynyl. Alkynyls with 2 to 4 carbon atoms are preferred, for example
 35 ethynyl, 2- propynyl or 2-butynyl-2-propenyl.

The term "cycloalkyl" - in isolation or as part of a chemical group - represents saturated or partially unsaturated mono-, bi- or tricyclic hydrocarbons, preferably 3 to 10 carbon atoms, for example

cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, bicyclo[2.2.1]heptyl, bicyclo[2.2.2]octyl or adamantyl.

Cycloalkyls with 3, 4, 5, 6 or 7 carbon atoms are preferred, for example cyclopropyl or cyclobutyl.

- 5 The term "heterocycloalkyl" - in isolation or as part of a chemical group - represents saturated or partially unsaturated mono-, bi- or tricyclic hydrocarbons, preferably 3 to 10 carbon atoms, for example cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, bicyclo[2.2.1]heptyl, bicyclo[2.2.2]octyl or adamantyl, wherein one or more of the ring atoms, preferably 1 to 4, more preferably 1, 2 or 3 of the ring atoms are independently selected from N, O, S, P, B, Si and Se, more
10 preferably N, O and S, wherein no O atoms can be located next to each other.

The term "Alkylcycloalkyl" represents mono-, bi- oder tricyclic alkylcycloalkyl, preferably with 4 to 10 or 4 to 7 carbon atoms, for example ethylcyclopropyl, isopropylcyclobutyl, 3-methylcyclopentyl und 4-methyl-cyclohexyl. Alkylcycloalkyls with 4, 5 or 7 carbon atoms are preferred, for example ethylcyclopropyl or 4-
15 methyl-cyclohexyl.

The term "cycloalkylalkyl" represents mono, bi- or tricyclic cycloalkylalkyls, preferably 4 to 10 or 4 to 7 carbon atoms, for example cyclopropylmethyl, cyclobutylmethyl, cyclopentylmethyl, cyclohexylmethyl and cyclopentylethyl. Cycloalkylalkyls with 4, 5 or 7 carbon atoms are preferred, for example
20 cyclopropylmethyl or cyclobutylmethyl.

The term "halogen" or "halo" represents fluoro, chloro, bromo or iodo, particularly fluoro, chloro or bromo. The chemical groups which are substituted with halogen, for example haloalkyl, halocycloalkyl, haloalkyloxy, haloalkylsulfanyl, haloalkylsulfinyl or haloalkylsulfonyl are substituted one or up to the
25 maximum number of substituents with halogen. If "alkyl", "alkenyl" or "alkynyl" are substituted with halogen, the halogen atoms can be the same or different and can be bound at the same carbon atom or different carbon atoms.

The term "halocycloalkyl" represents mono-, bi- or tricyclic halocycloalkyl, preferably with 3 to 10
30 carbon atoms, for example 1 -fluoro-cyclopropyl, 2-fluoro- cyclopropyl or 1 -fluoro-cyclobutyl. Preferred halocycloalkyl mit 3, 5 oder 7 carbon atoms.

The term "haloalkyl", "haloalkenyl" or "haloalkynyl" represents alkyls, alkenyls or alkynyls substituted with halogen, preferably with 1 to 9 halogen atoms that are the same or different, for example monohaloalkyls (= monohaloalkyl) like $\text{CH}_2\text{CH}_2\text{Cl}$, $\text{CH}_2\text{CH}_2\text{F}$, CHClCH_3 , CHFCH_3 , CH_2Cl , CH_2F ;
35 perhaloalkyls like CCl_3 or CF_3 or CF_2CF_3 ; polyhaloalkyls like CHF_2 , CH_2F , CH_2CHFCl , $\text{CF}_2\text{CF}_2\text{H}$, CH_2CF_3 . The same applies for haloalkenyl and other groups substituted by halogen. Examples of haloalkoxy are for example OCF_3 , OCHF_2 , OCH_2F , OCF_2CF_3 , OCH_2CF_3 , OCF_3 , OCHF_2 , OCH_2F , OCF_2CF_3 , OCH_2CF_3 .

Further examples of haloalkyls are trichloromethyl, chlorodifluoromethyl, dichlorofluoromethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2,2,2-trichloroethyl, 2-chloro-2,2-difluoroethyl, pentafluoroethyl and pentafluoro-t-butyl.

Haloalkyls having 1 to 4 carbon atoms and 1 to 9, preferably 1 to 5 of the same or different halogen atoms selected from fluoro, chloro or bromo, are preferred.

Haloalkyls having 1 or 2 carbon atoms and 1 to 5 gleichen of the same or different halogen atoms selected from fluoro or chloro, for example difluoromethyl, trifluoromethyl or 2,2-difluoroethyl, are particularly preferred.

- 10 The term "hydroxyalkyl" represents straight or branched chain alcohols, preferably with 1 to 6 carbon atoms, for example methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, s-butanol and t-butanol. Hydroxyalkyls having 1 to 4 carbon atoms are preferred.

- 15 The term "alkoxy" represents straight or branched chain O-alkyl, preferably having 1 to 6 carbon atoms, for example methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, s-butoxy und t-butoxy. Alkoxy having 1 to 4 carbon atoms are preferred.

- The term "haloalkoxy" represents straight or branched chain O-alkyl substituted with halogen, preferably with 1 to 6 carbon atoms, for example difluoromethoxy, trifluoromethoxy, 2,2-difluoroethoxy, 1,1,2,2-tetrafluoroethoxy, 2,2,2-Trifluoroethoxy and 2-Chloro-1,1,2-trifluoroethoxy.
20 Haloalkoxy having 1 to 4 carbon atoms are preferred.

- The term "alkylsulfanyl" represents straight or branched chain S-alkyl, preferably with 1 to 6 carbon atoms, for example methylthio, ethylthio, n-propylthio, isopropylthio, n-butylthio, isobutylthio, s-butylthio and t-butylthio. Alkylsulfanyl having 1 to 4 carbon atoms are preferred. Examples for haloalkylsulfanyl, i.e. with halogen substituted alkylsulfanyl, are for example difluoromethylthio, trifluoromethylthio, trichloromethylthio, chlorodifluoromethylthio, 1-fluoroethylthio, 2-fluoroethylthio, 2,2-difluoroethylthio, 1,1,2,2-tetrafluoroethylthio, 2,2,2-trifluoroethylthio or 2-chloro-1,1,2-trifluoroethylthio.

- 30 The term "alkylsulfinyl" represents straight or branched chain alkylsulfinyl, preferably having 1 to 6 carbon atoms, for example methylsulfinyl, ethylsulfinyl, n-propylsulfinyl, isopropylsulfinyl, n-butylsulfinyl, isobutylsulfinyl, s-butylsulfinyl und t-butylsulfinyl.
Alkylsulfinyls having 1 to 4 carbon atoms are preferred.
Examples of haloalkylsulfinyls, i.e. with halogen substituted alkylsulfinyls, are difluoromethylsulfinyl, trifluoromethylsulfinyl, trichloromethylsulfinyl, chlorodifluoromethylsulfinyl, 1-fluoroethylsulfinyl, 2-fluoroethylsulfinyl, 2,2-difluoroethylsulfinyl, 1,1,2,2-tetrafluoroethylsulfinyl, 2,2,2-trifluoroethylsulfinyl and 2-chloro-1,1,2-trifluoroethylsulfinyl.
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The term "alkylsulfonyl" represents straight or branched chain alkylsulfonyl, preferably having 1 to 6 carbon atoms, for example methylsulfonyl, ethylsulfonyl, n-propylsulfonyl, isopropylsulfonyl, n-butylsulfonyl, isobutylsulfonyl, s-butylsulfonyl and t-butylsulfonyl.

Alkylsulfonyls having 1 to 4 carbon atoms are preferred.

- 5 Examples of haloalkylsulfonyls, i.e. with halogen substituted alkylsulfonyls, are for example difluoromethylsulfonyl, trifluoromethylsulfonyl, trichloromethylsulfonyl, chlorodifluoromethylsulfonyl, 1-fluoroethylsulfonyl, 2-fluoroethylsulfonyl, 2,2-difluoroethylsulfonyl, 1,1,2,2-tetrafluoroethylsulfonyl, 2,2,2-trifluoroethylsulfonyl and 2-chloro- 1,1,2-trifluoroethylsulfonyl.

- 10 The term "alkylcarbonyl" represents straight or branched chain alkyl-C(=O), preferably having 2 to 7 carbon atoms, for example methylcarbonyl, ethylcarbonyl, n-propylcarbonyl, isopropylcarbonyl, s-butylcarbonyl and t-butylcarbonyl.

Alkylcarbonyls having 1 to 4 carbon atoms are preferred.

- 15 The term "cycloalkylcarbonyl" represents cycloalkyl-carbonyl, preferably 3 to 10 carbon atoms in the cycloalkyl part, for example cyclopropylcarbonyl, cyclobutylcarbonyl, cyclopentylcarbonyl, cyclohexylcarbonyl, cycloheptyl-carbonyl, cyclooctylcarbonyl, bicyclo[2.2.1]heptyl, bicyclo[2.2.2]octylcarbonyl and adamantylcarbonyl. Cycloalkylcarbonyls having 3, 5 or 7 carbon atoms in the cycloalkyl part are preferred.

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The term "alkoxycarbonyl" " - in isolation or as part of a chemical group - represents straight or branched chain alkoxycarbonyl, preferably having 1 to 6 carbon atoms or 1 to 4 carbon atoms in the alkoxy part, for example methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, isopropoxycarbonyl, s-butoxycarbonyl and t-butoxycarbonyl.

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The term "alkylaminocarbonyl" represents straight or branched chain alkylaminocarbonyl having preferably 1 to 6 carbon atoms or 1 to 4 carbon atoms in the alkyl part, for example methylaminocarbonyl, ethylaminocarbonyl, n-propylaminocarbonyl, isopropylaminocarbonyl, s-butylaminocarbonyl and t-butylaminocarbonyl.

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The term "N,N-Dialkylamino-carbonyl" " represents straight or branched chain N,N-dialkylaminocarbonyl with preferably 1 to 6 carbon atoms or 1 to 4 carbon atoms in the alkyl part, for example N,N-Dimethylamino-carbonyl, N,N-diethylamino-carbonyl, N,N-di(n-propylamino)-carbonyl, N,N-di(isopropylamino)-carbonyl and N,N-di(s-butylamino)-carbonyl.

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The term "aryl" represents a mono-, bi- or polycyclical aromatic system with preferably 6 to 14, more preferably 6 to 10 ring-carbon atoms, for example phenyl, naphthyl, anthryl, phenanthrenyl, preferably phenyl. "Aryl" also represents polycyclic systems, for example tetrahydronaphthyl, indenyl, indanyl,

fluorenyl, biphenyl. Arylalkyls are examples of substituted aryls, which may be further substituted with the same or different substituents both at the aryl or alkyl part. Benzyl and 1-phenylethyl are examples of such arylalkyls.

- 5 The term "heterocyclyl", "heterocyclic ring" or "heterocyclic ring system" represents a carbocyclic ring system with at least one ring, in which ring at least one carbon atom is replaced by a heteroatom, preferably selected from N, O, S, P, B, Si, Se, and which ring is saturated, unsaturated or partially saturated, and which ring is unsubstituted or substituted with a substituent Z, wherein the connecting bond is located at a ring atom. Unless otherwise defined, the heterocyclic ring has preferably 3 to 9 ring
10 atoms, preferably 3 to 6 ring atoms, and one or more, preferably 1 to 4, more preferably 1, 2 or 3 heteroatoms in the heterocyclic ring, preferably selected from N, O, and S, wherein no O atoms can be located next to each other. The heterocyclic rings normally contain no more than 4 nitrogens, and/or no more than 2 oxygen atoms and/or no more than 2 sulfur atoms. In case that the heterocyclic substituent or the heterocyclic ring are further substituted, it can be further annulated with other heterocyclic rings.

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The term „heterocyclic“ also includes polycyclic systems, for example 8-aza-bicyclo[3.2.1]octanyl or 1-aza-bicyclo[2.2.1]heptyl.

The term „heterocyclic“ also includes spirocyclic systems, for example 1-oxa-5-aza-spiro[2.3]hexyl.

20

Examples of heterocyclyls are for example piperidinyl, piperazinyl, morpholinyl, thiomorpholinyl, dihydropyranyl, tetrahydropyranyl, dioxanyl, pyrrolinyl, pyrrolidinyl, imidazolinyl, imidazolidinyl, thiazolidinyl, oxazolidinyl, dioxolanyl, dioxolyl, pyrazolidinyl, tetrahydrofuranyl, dihydrofuranyl, oxetanyl, oxiranyl, azetidiny, aziridinyl, oxazetidiny, oxaziridinyl, oxazepanyl, oxazinanyl, azepanyl, oxopyrrolidinyl, dioxopyrrolidinyl, oxomorpholinyl, oxopiperazinyl und oxepanyl.

25

Particularly important are heteroaryls, i.e. heteroaromatic systems.

The term „heteroaryl“ represents heteroaromatic groups, i.e. completely unsaturated aromatic heterocyclic groups, which fall under the above definition of heterocycles. „Heteroaryls“ with 5 to 7-membered rings with 1 to 3, preferably 1 or 2 of the same or different heteroatoms selected from N, O, and S. Examples of “heteroaryls” are furyl, thienyl, pyrazolyl, imidazolyl, 1,2,3- and 1,2,4-triazolyl, isoxazolyl, thiazolyl, isothiazolyl, 1,2,3-, 1,3,4-, 1,2,4- and 1,2,5-oxadiazolyl, azepinyl, pyrrolyl, pyridyl, pyridazinyl, pyrimidinyl, pyrazinyl, 1,3,5-, 1,2,4- and 1,2,3-triazinyl, 1,2,4-, 1,3,2-, 1,3,6- and 1,2,6-oxazinyl, oxepinyl, thiopinyl, 1,2,4-triazolonyl und 1,2,4-diazepinyl.

35

Halogen is generally fluorine, chlorine, bromine or iodine. This also applies, correspondingly, to halogen in combination with other meanings, such as haloalkyl or halophenyl.

Haloalkyl groups preferably have a chain length of from 1 to 6 carbon atoms. Haloalkyl is, for example, fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, pentafluoroethyl, 1,1-difluoro-2,2,2-trichloroethyl, 2,2,3,3-tetrafluoroethyl and 2,2,2-trichloroethyl.

5

Alkoxy is, for example, methoxy, ethoxy, propoxy, i-propoxy, n-butoxy, isobutoxy, sec-butoxy and tert-butoxy and also the isomeric pentyloxy and hexyloxy radicals.

Alkoxyalkyl groups preferably have a chain length of 1 to 6 carbon atoms.

10 Alkoxyalkyl is, for example, methoxymethyl, methoxyethyl, ethoxymethyl, ethoxyethyl, n-propoxymethyl, n-propoxyethyl, isopropoxymethyl or isopropoxyethyl.

Alkoxycarbonyl is for example methoxycarbonyl (which is C₁alkoxycarbonyl), ethoxycarbonyl, propoxycarbonyl, isopropoxycarbonyl, n-butoxycarbonyl, tert-butoxycarbonyl, n-pentoxycarbonyl or
15 hexoxycarbonyl.

The cycloalkyl groups preferably have from 3 to 6 ring carbon atoms, for example cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

20 A compound according to any one of embodiments 1 to 25 which has at least one basic centre can form, for example, acid addition salts, for example with strong inorganic acids such as mineral acids, for example perchloric acid, sulfuric acid, nitric acid, nitroic acid, a phosphorus acid or a hydrohalic acid, with strong organic carboxylic acids, such as C₁-C₄alkanecarboxylic acids which are unsubstituted or substituted, for example by halogen, for example acetic acid, such as saturated or unsaturated
25 dicarboxylic acids, for example oxalic acid, malonic acid, succinic acid, maleic acid, fumaric acid or phthalic acid, such as hydroxycarboxylic acids, for example ascorbic acid, lactic acid, malic acid, tartaric acid or citric acid, or such as benzoic acid, or with organic sulfonic acids, such as C₁-C₄alkane- or arylsulfonic acids which are unsubstituted or substituted, for example by halogen, for example methane- or p-toluenesulfonic acid. A compounds according to any one of embodiments 1 to 25 which have at
30 least one acidic group can form, for example, salts with bases, for example mineral salts such as alkali metal or alkaline earth metal salts, for example sodium, potassium or magnesium salts, or salts with ammonia or an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower-alkylamine, for example ethyl-, diethyl-, triethyl- or dimethylpropylamine, or a mono-, di- or trihydroxy-lower-alkylamine, for example mono-, di- or triethanolamine.

35

Compounds according to any one of embodiments 1 to 25 also include hydrates which may be formed during the salt formation.

The compounds according to any one of embodiments 1 to 25 may be made by a variety of methods well known to a person skilled in the art or as shown in Schemes 1 to 4. Further instructions regarding the preparation can be found in WO2015/067646, WO2015/150442, WO2015/193218, WO2014/122083 and WO2012/107434.

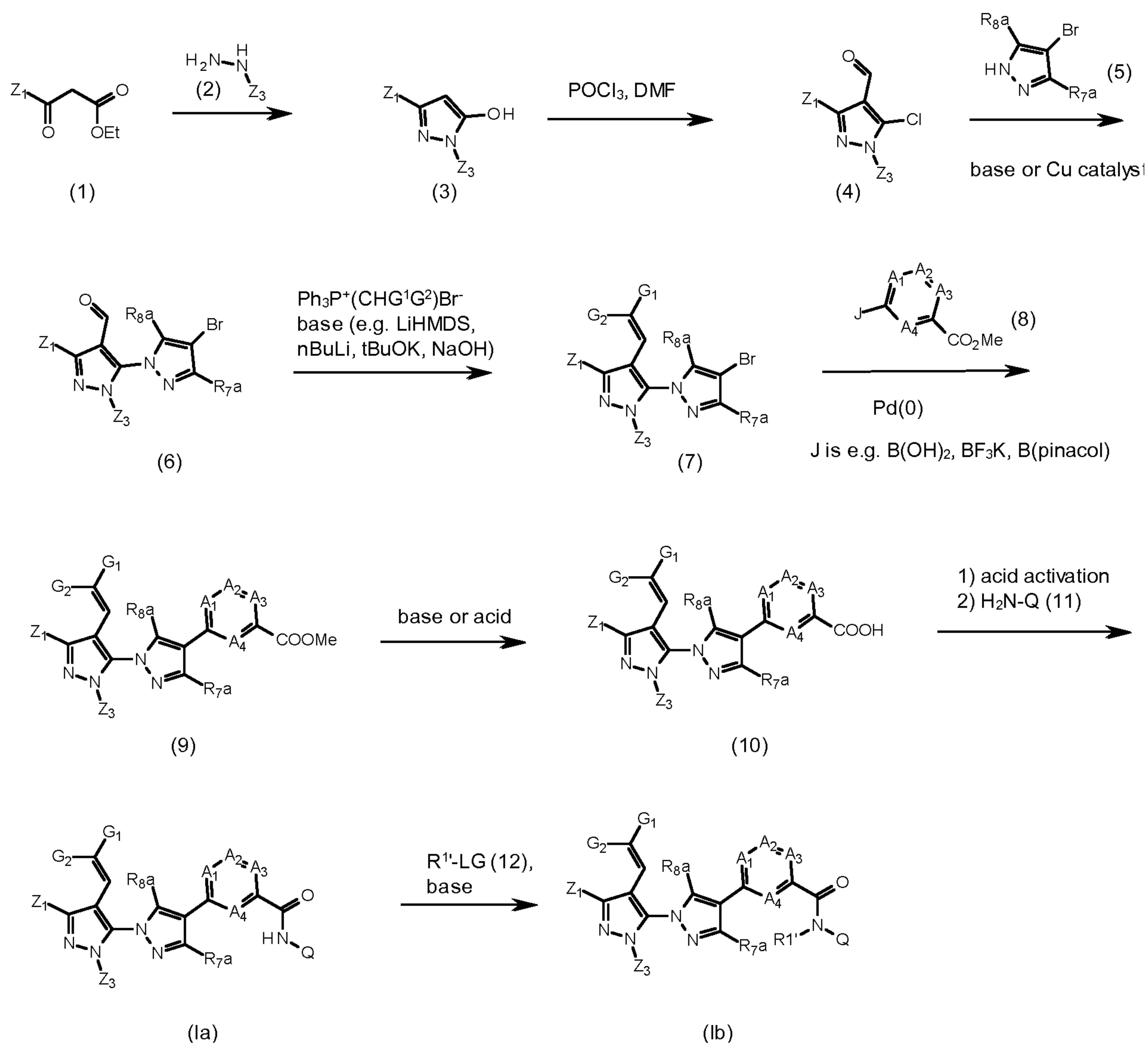
5

The compounds according to any one of embodiments may be made by a variety of methods known to a person skilled in the art or as shown in Schemes 1 to 4.

For example, compounds of formula (Ia) or (Ib) can be prepared according to Scheme 1.

10

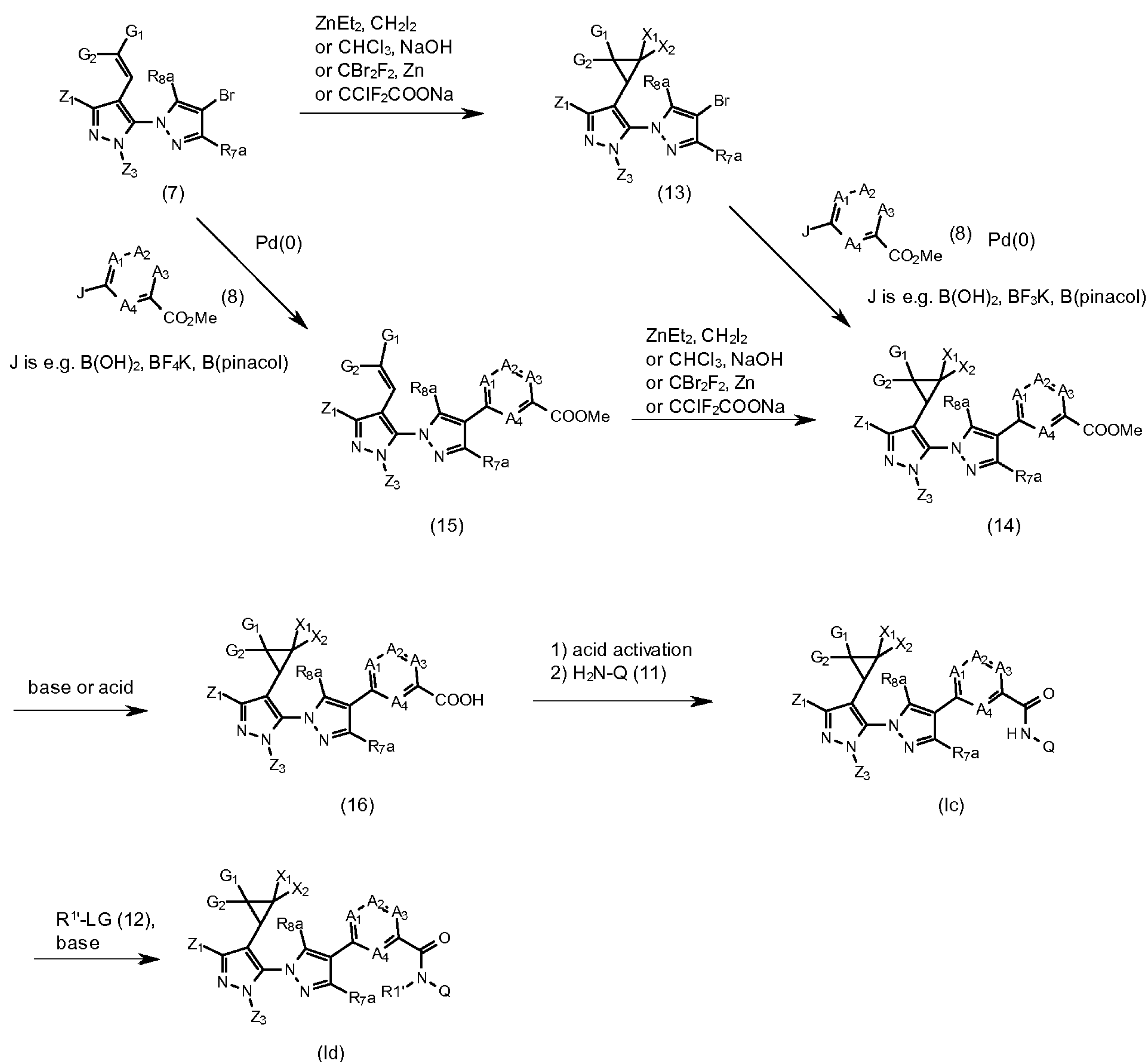
Scheme 1:



wherein R^1 , Q, A^1 , A^2 , A^3 , A^4 , R^{7a} , R^{8a} , Z^1 and Z^3 are as defined in any one of embodiments 1 to 25, G^1 and G^2 are independently selected from H, halogen, C_{1-2} -alkyl or C_{1-2} -haloalkyl, $R^{1'}$ is as R^1 but not H. Compounds of formula (1), (2), (5), (8), (11) or $Ph_3P(CHG^1G^2)Br$ are commercially available or are known from the chemistry literature. Compounds of formula (3) can be prepared according to processes
5 described e.g. in US5536701. Compounds of formula (4) can be prepared according to *Synth. Commun.* **2004**, 34, 1541 (Vilsmeier reaction). Compounds of formula (7) can be prepared according to *Org. Lett.* **2014**, 16, 6120 or WO2012/069948 (Wittig olefination). Compounds of formula (9) can be obtained by classical Suzuki coupling between compound of formula (7) and a boronic acid, ester (e.g. pinacol ester) or trifluoroborate of formula (8) as described in N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**,
10 95, 2457–2483 or in G. A. Molander, L. Jean-Gérard, *Org. React.* **2013**, 79, 1 - 316.

Compounds of formula (lc) or (ld) can be prepared according to Scheme 2.

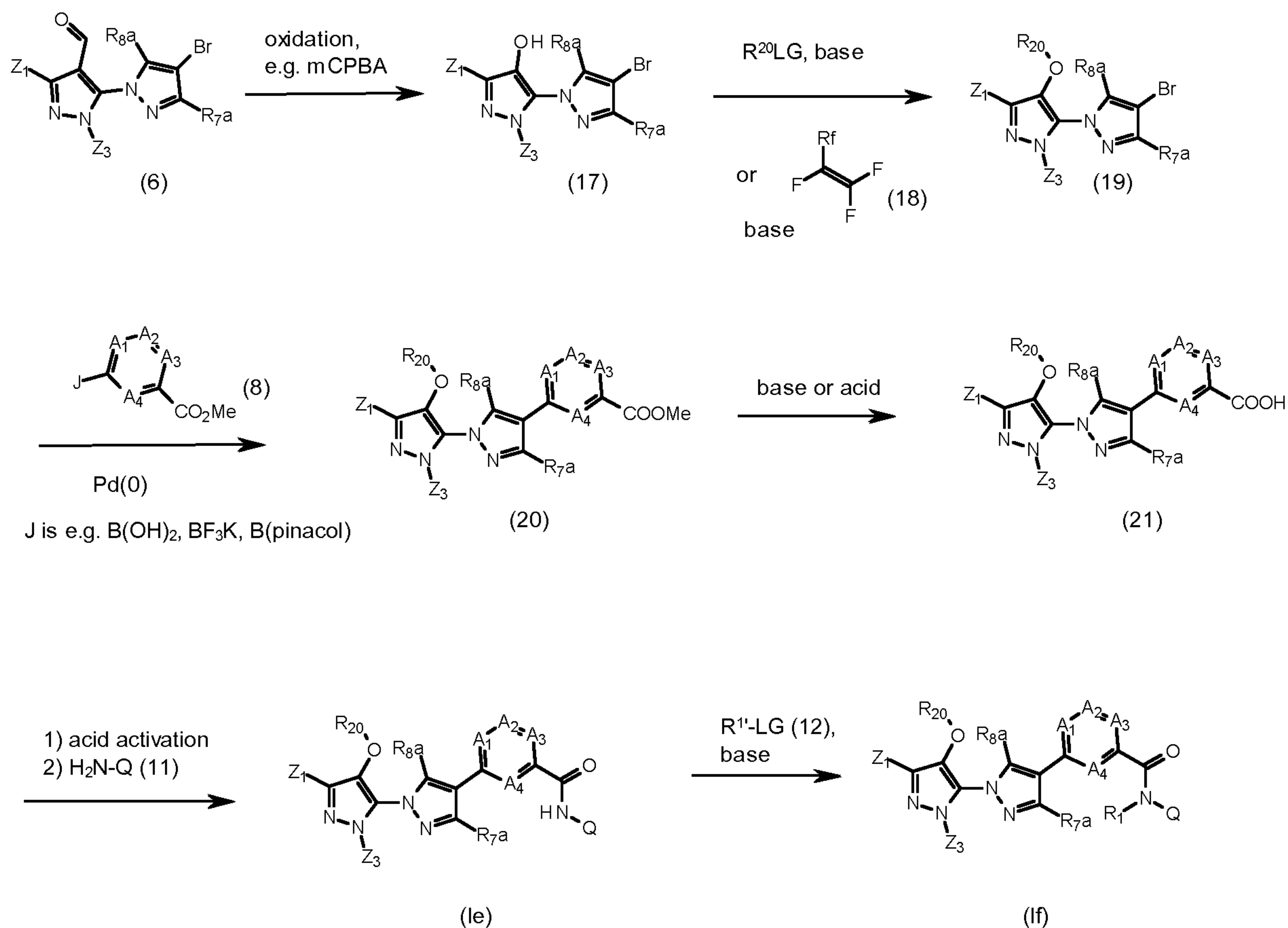
Scheme 2:



wherein R¹, Q, A¹, A², A³, A⁴, R^{7a}, R^{8a}, Z¹ and Z³ are as defined in any one of embodiments, G¹ and G² are independently selected from H, halogen, C₁₋₂-alkyl or C₁₋₂-haloalkyl, X¹ and X² are independently selected from H, Cl, F or Br, R^{1'} is as R¹ but not H. Preparation of compounds of formula (7) is described in scheme 1. Compounds of formula (13) or (14) can be prepared from compounds of formula (7) or (15) according to known processes described e.g. in WO03097637, *Synthesis* **2015**, 47, 1593 (ZnEt₂, CH₂I₂, Simmons-Smith reaction), WO09024614, *Organometallics*, **2009**, 28, 2646 (CHCl₃, NaOH, TBAB), WO06082001, *J. Fluorine Chem.* **2002**, 115, 79 (CBr₂F₂, Zn) or WO04042845 (CCIF₂COONa). Compounds of formula (14) or (15) can be obtained by classical Suzuki coupling between compound of formula (13) or (7) and a boronic acid, ester (e.g. pinacol ester) or trifluoroborate of formula (8) as described in N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, 95, 2457–2483 or in G. A. Molander, L. Jean-Gérard, *Org. React.* **2013**, 79, 1 - 316.

Compounds of formula (Ie) or (If) can be prepared according to Scheme 3.

Scheme 3:

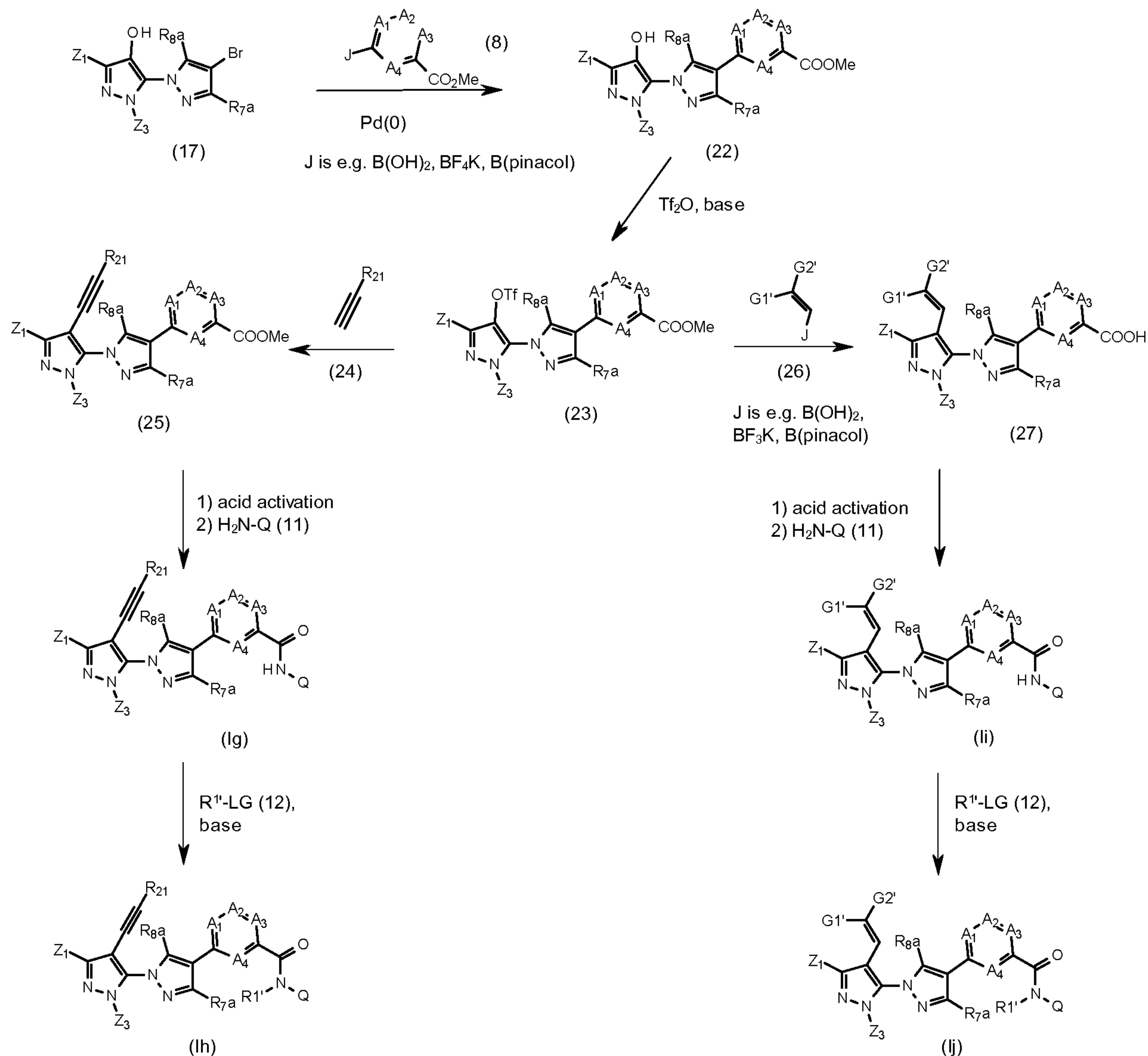


wherein R¹, Q, A¹, A², A³, A⁴, R^{7a}, R^{8a}, Z¹ and Z³ are as defined in any one of embodiments 1 to 25, R^{1'} is as R¹ but not H. R²⁰ is C₁₋₃-alkyl, C₁₋₃-haloalkyl, C₃₋₅-cycloalkyl, C₃₋₅-halocycloalkyl. R_f is F or a fluorinated C₁₋₃-alkyl, LG is a leaving group as for example halogen, OMs (mesylate), OTs (tosylate), OTf (triflate).

Preparation of compounds of formula (6) is described in scheme 1. Compounds of formula (17) can be prepared according to processes described e.g. in WO07060525 (Bayer-Villiger oxidation). Compounds of formula (19) can be obtained by reacting compound of formula (17) with R²⁰LG or a compound of formula (18) in the presence of a base such as NaH, NaHCO₃, Na₂CO₃, DBU in a solvent such as THF, CH₃CN, DMF, DMA. LG is a leaving group as for example halogen, OMs, OTs, OTf. Compounds of formula (20) can be obtained by classical Suzuki coupling between compounds of formula (19) and a boronic acid, ester (e.g. pinacol ester) or trifluoroborate of formula (8) as described in N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, 95, 2457–2483 or in G. A. Molander, L. Jean-Gérard, *Org. React.* **2013**, 79, 1 - 316.

Compounds of formula (lg), (lh), (li) or (lj) can be prepared according to Scheme 4.

Scheme 4:



5

wherein R^1 , Q, A^1 , A^2 , A^3 , A^4 , R^{7a} , R^{8a} , Z^1 and Z^3 are as defined in any one of embodiments, $\text{G}^{1'}$ and $\text{G}^{2'}$ are independently H or C_{1-2} -alkyl, R^{21} is H or CH_3 ; $\text{R}^{1'}$ is as R^1 but not H.

Preparation of compounds of formula (17) is described in scheme 3. Compounds of formula (22) can be obtained by classical Suzuki coupling between compounds of formula (17) and a boronic acid, ester or trifluoroborate of formula (8) as described in N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, 95, 2457–2483 or in G. A. Molander, L. Jean-Gérard, *Org. React.* **2013**, 79, 1 - 316. Compound of formula (25) can be obtained by cross-coupling of compounds of formula (23) and a compound of formula (24) (e.g. *Chem. Rev.* **2007**, 107, 874–922, Sonogashira reaction). Compound of formula (27) can be obtained by cross-coupling of compounds of formula (26) with a compound of formula (26) (Suzuki coupling).

A compound according to any one of embodiments 1 to 25 can be converted in a manner known per se into another compound according to any one of embodiments 1 to 25 by replacing one or more substituents of the starting compound according to any one of embodiments 1 to 25 in the customary manner by (an)other substituent(s) according to the invention.

Depending on the choice of the reaction conditions and starting materials which are suitable in each case, it is possible, for example, in one reaction step only to replace one substituent by another substituent according to the invention, or a plurality of substituents can be replaced by other substituents according to the invention in the same reaction step.

Salts of compounds of formula (I) can be prepared in a manner known per se. Thus, for example, acid addition salts of compounds according to any one of embodiments 1 to 25 are obtained by treatment with a suitable acid or a suitable ion exchanger reagent and salts with bases are obtained by treatment with a suitable base or with a suitable ion exchanger reagent.

Salts of compounds according to any one of embodiments 1 to 25 can be converted in the customary manner into the free compounds, acid addition salts, for example, by treatment with a suitable basic compound or with a suitable ion exchanger reagent and salts with bases, for example, by treatment with a suitable acid or with a suitable ion exchanger reagent.

Salts of compounds according to any one of embodiments 1 to 25 can be converted in a manner known per se into other salts of compounds according to any one of embodiments 1 to 25, acid addition salts, for example, into other acid addition salts, for example by treatment of a salt of inorganic acid such as hydrochloride with a suitable metal salt such as a sodium, barium or silver salt, of an acid, for example with silver acetate, in a suitable solvent in which an inorganic salt which forms, for example silver chloride, is insoluble and thus precipitates from the reaction mixture.

Depending on the procedure or the reaction conditions, the compounds according to any one of embodiments 1 to 25, which have salt-forming properties can be obtained in free form or in the form of salts.

The compounds according to any one of embodiments 1 to 25 and, where appropriate, the tautomers thereof, in each case in free form or in salt form, can be present in the form of one of the stereoisomers which are possible or as a mixture of these, for example in the form of pure stereoisomers, such as antipodes and/or diastereomers, or as stereoisomer mixtures, such as enantiomer mixtures, for example racemates, diastereomer mixtures or racemate mixtures, depending on the number, absolute and relative configuration of asymmetric carbon atoms which occur in the molecule and/or depending on

the configuration of non-aromatic double bonds which occur in the molecule; the invention relates to the pure stereoisomers and also to all stereoisomer mixtures which are possible and is to be understood in each case in this sense hereinabove and hereinbelow, even when stereochemical details are not mentioned specifically in each case.

5

Diastereomer mixtures or racemate mixtures of compounds according to any one of embodiments 1 to 25, in free form or in salt form, which can be obtained depending on which starting materials and procedures have been chosen can be separated in a known manner into the pure diastereomers or racemates on the basis of the physicochemical differences of the components, for example by fractional
10 crystallization, distillation and/or chromatography.

Enantiomer mixtures, such as racemates, which can be obtained in a similar manner can be resolved into the optical antipodes by known methods, for example by recrystallization from an optically active solvent, by chromatography on chiral adsorbents, for example high-performance liquid chromatography
15 (HPLC) on acetyl cellulose, with the aid of suitable microorganisms, by cleavage with specific, immobilized enzymes, via the formation of inclusion compounds, for example using chiral crown ethers, where only one enantiomer is complexed, or by conversion into diastereomeric salts, for example by reacting a basic end-product racemate with an optically active acid, such as a carboxylic acid, for example camphor, tartaric or malic acid, or sulfonic acid, for example camphorsulfonic acid, and
20 separating the diastereomer mixture which can be obtained in this manner, for example by fractional crystallization based on their differing solubilities, to give the diastereomers, from which the desired enantiomer can be set free by the action of suitable agents, for example basic agents.

Pure diastereomers or enantiomers can be obtained according to the invention not only by separating
25 suitable stereoisomer mixtures, but also by generally known methods of diastereoselective or enantioselective synthesis, for example by carrying out the process according to the invention with starting materials of a suitable stereochemistry.

N-oxides can be prepared by reacting a compound according to any one of embodiments 1 to 25 with a suitable oxidizing agent, for example the H_2O_2 /urea adduct in the presence of an acid anhydride, e.g.
30 trifluoroacetic anhydride. Such oxidations are known from the literature, for example from J. Med. Chem., 32 (12), 2561-73, 1989 or WO 00/15615.

It is advantageous to isolate or synthesize in each case the biologically more effective stereoisomer, for example enantiomer or diastereomer, or stereoisomer mixture, for example enantiomer mixture or diastereomer mixture, if the individual components have a different biological activity.

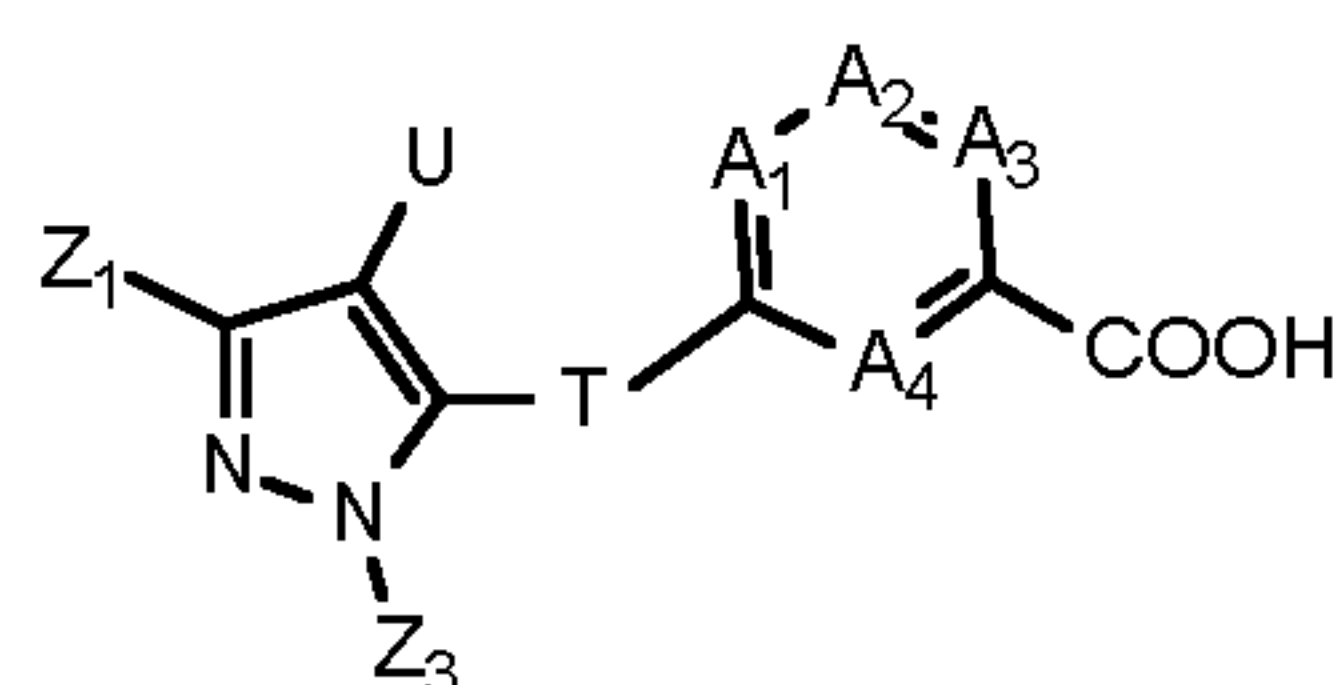
35 The compounds according to any one of embodiments 1 to 25 and, where appropriate, the tautomers thereof, in each case in free form or in salt form, can, if appropriate, also be obtained in the form of hydrates and/or include other solvents, for example those which may have been used for the crystallization of compounds which are present in solid form.

The following Examples illustrate, but do not limit, the invention.

The compounds of the invention can be distinguished from known compounds by virtue of greater efficacy at low application rates, which can be verified by the person skilled in the art using the experimental procedures outlined in the Examples, using lower application rates if necessary, for example 50 ppm, 12.5 ppm, 6 ppm, 3 ppm, 1.5 ppm or 0.8 ppm.

The present invention also provides intermediates useful for the preparation of compounds according to any one of embodiments 1 to 25. Certain intermediates are novel and as such form a further aspect of the invention.

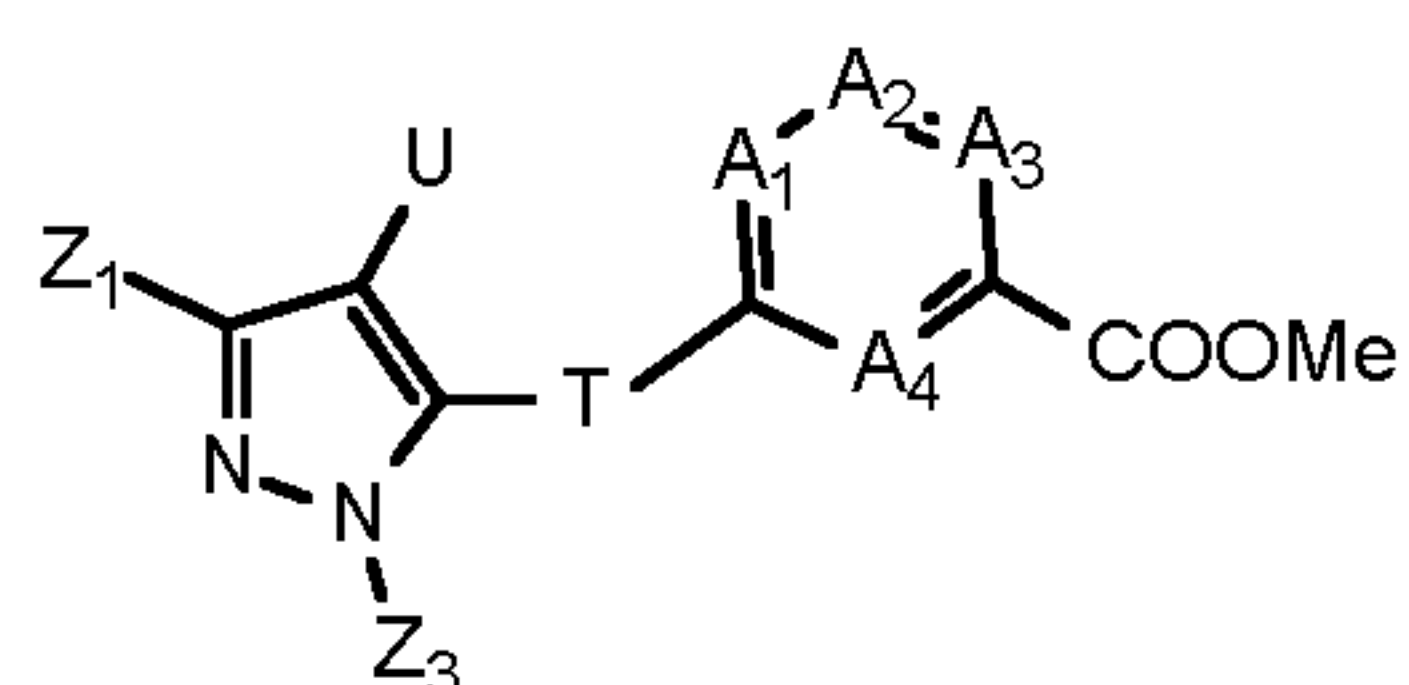
One group of novel intermediates are compounds of formula (II)



(II)

wherein A¹, A², A³, A⁴, T, U, Z¹ and Z³ are as defined in any one of embodiments 1 to 25. The preferences for A¹, A², A³, A⁴, U, Z¹ and Z³ are the same as the preferences set out for the corresponding substituents of a compound according to any one of embodiments 1 to 25.

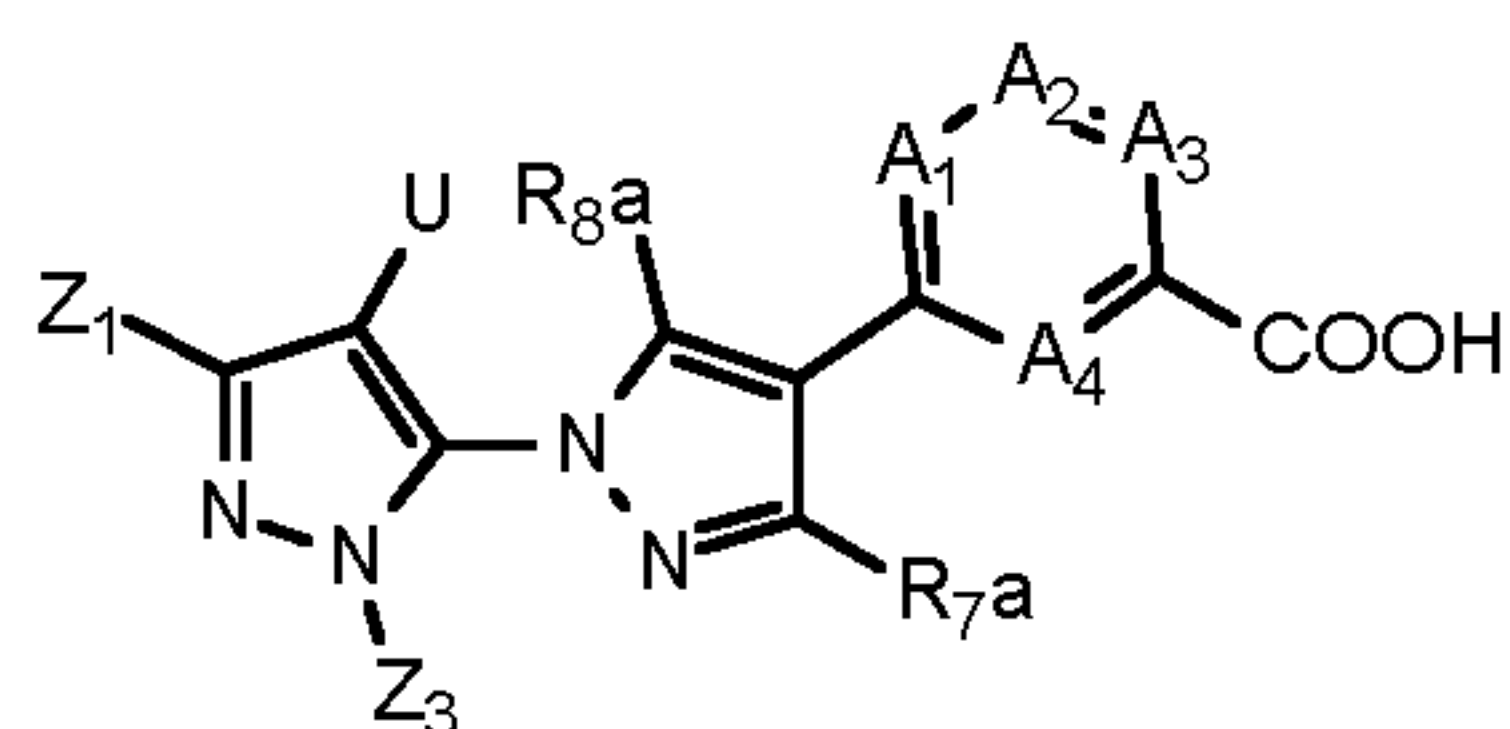
Another group of novel intermediates are compounds of formula (III)



(III)

wherein A¹, A², A³, A⁴, U, Z¹ and Z³ are as defined in any one of embodiments 1 to 25. The preferences for A¹, A², A³, A⁴, U, Z¹ and Z³ are the same as the preferences set out for the corresponding substituents of a compound according to any one of embodiments 1 to 25.

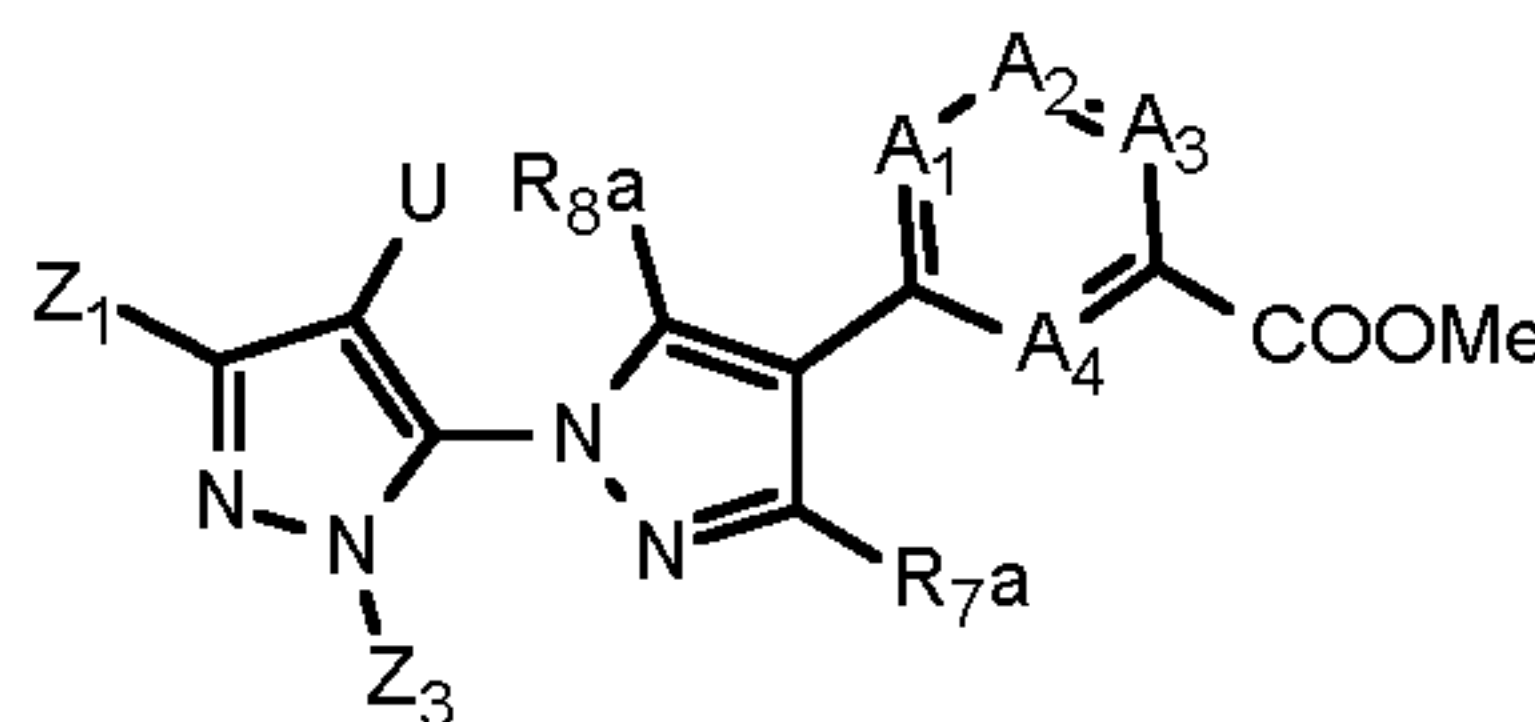
One group of novel intermediates are compounds of formula (IV)



(IV)

wherein A^1 , A^2 , A^3 , A^4 , U , R^{7a} , R^{8a} , Z^1 and Z^3 are as defined in any one of embodiments 1 to 25. The preferences for A^1 , A^2 , A^3 , A^4 , U , R^{7a} , R^{8a} , Z^1 and Z^3 are the same as the preferences set out for the corresponding substituents of a compound according to any one of embodiments 1 to 25.

5 Another group of novel intermediates are compounds of formula (V)



(V)

wherein A^1 , A^2 , A^3 , A^4 , U , R^{7a} , R^{8a} , Z^1 and Z^3 are as defined in any one of embodiments 1 to 25. The preferences for A^1 , A^2 , A^3 , A^4 , U , R^{7a} , R^{8a} , Z^1 and Z^3 are the same as the preferences set out for the corresponding substituents of a compound according to any one of embodiments 1 to 25.

The compounds according to any one of embodiments 1 to 25 are preventively and/or curatively valuable active ingredients in the field of pest control, even at low rates of application, which have a very favorable biocidal spectrum and are well tolerated by warm-blooded species, fish and plants. The active ingredients according to the invention act against all or individual developmental stages of normally sensitive, but also resistant, animal pests, such as insects or representatives of the order Acarina. The insecticidal or acaricidal activity of the active ingredients according to the invention can manifest itself directly, i. e. in destruction of the pests, which takes place either immediately or only after some time has elapsed, for example during ecdysis, or indirectly, for example in a reduced oviposition and/or hatching rate.

Examples of the above mentioned animal pests are:

from the order *Acarina*, for example,

Acalitus spp, Aculus spp, Acaricalus spp, Aceria spp, Acarus siro, Amblyomma spp., Argas spp., Boophilus spp., Brevipalpus spp., Bryobia spp, Calipitrimerus spp., Chorioptes spp., Dermanyssus gallinae, Dermatophagoides spp, Eotetranychus spp, Eriophyes spp., Hemitarsonemus spp, Hyalomma spp., Ixodes spp., Olygonychus spp, Ornithodoros spp., Polyphagotarsonus latus, Panonychus spp., Phyllocoptruta oleivora, Phytionemus spp, Polyphagotarsonemus spp, Psoroptes spp., Rhipicephalus spp., Rhizoglyphus spp., Sarcoptes spp., Steneotarsonemus spp, Tarsonemus spp. and Tetranychus spp.;

from the order *Anoplura*, for example,

Haematopinus spp., Linognathus spp., Pediculus spp., Pemphigus spp. and Phylloxera spp.;

from the order *Coleoptera*, for example,

Agriotes spp., Amphimallon majale, Anomala orientalis, Anthonomus spp., Aphodius spp, Astylus
 atromaculatus, Ataenius spp, Atomaria linearis, Chaetocnema tibialis, Cerotoma spp, Conoderus spp,
 Cosmopolites spp., Cotinis nitida, Curculio spp., Cyclocephala spp, Dermestes spp., Diabrotica spp.,
 Diloboderus abderus, Epilachna spp., Eremnus spp., Heteronychus arator, Hypothenemus hampei,
 5 Lagria vilosa, Leptinotarsa decemLineata, Lissorhoptrus spp., Liogenys spp, Maecolaspis spp,
 Maladera castanea, Megascelis spp, Meligethes aeneus, Melolontha spp., Myochrous armatus,
 Orycaephilus spp., Otiorhynchus spp., Phyllophaga spp, Phlyctinus spp., Popillia spp., Psylliodes spp.,
 Rhyssomatus aubtilis, Rhizopertha spp., Scarabeidae, Sitophilus spp., Sitotroga spp., Somaticus spp,
 Sphenophorus spp, Sternechus subsignatus, Tenebrio spp., Tribolium spp. and Trogoderma spp.;

10 from the order *Diptera*, for example,

Aedes spp., Anopheles spp, Antherigona soccata, Bactrocea oleae, Bibio hortulanus, Bradysia spp,
 Calliphora erythrocephala, Ceratitis spp., Chrysomyia spp., Culex spp., Cuterebra spp., Dacus spp.,
 Delia spp, Drosophila melanogaster, Fannia spp., Gastrophilus spp., Geomyza tripunctata, Glossina
 spp., Hypoderma spp., Hyppobosca spp., Liriomyza spp., Lucilia spp., Melanagromyza spp., Musca
 15 spp., Oestrus spp., Orseolia spp., Oscinella frit, Pegomyia hyoscyami, Phorbia spp., Rhagoletis spp,
 Rivelia quadrifasciata, Scatella spp, Sciara spp., Stomoxys spp., Tabanus spp., Tannia spp. and Tipula
 spp.;

from the order *Hemiptera*, for example,

Acanthocoris scabrator, Acrosternum spp, Adelphocoris lineolatus, Amblypelta nitida, Bathycoelia
 20 thalassina, Blissus spp, Cimex spp., Clavigralla tomentosicollis, Creontiades spp, Distantiella
 theobroma, Dichelops furcatus, Dysdercus spp., Edessa spp, Euchistus spp., Eurydema pulchrum,
 Eurygaster spp., Halyomorpha halys, Horcias nobilellus, Leptocorisa spp., Lygus spp, Margarodes spp,
 Murgantia histrionic, Neomegalotomus spp, Nesidiocoris tenuis, Nezara spp., Nysius simulans, Oebalus
 insularis, Piesma spp., Piezodorus spp, Rhodnius spp., Sahlbergella singularis, Scaptocoris castanea,
 25 Scotinophara spp. , Thyanta spp , Triatoma spp., Vatica illudens;

Acyrtosium pisum, Adalges spp, Agalliana ensigera, Agonoscena targionii, Aleurodicus spp,
 Aleurocanthus spp, Aleurolobus barodensis, Aleurothrixus floccosus, Aleyrodes brassicae, Amarasca
 biguttula, Amritodus atkinsoni, Aonidiella spp., Aphididae, Aphis spp., Aspidiotus spp., Aulacorthum
 solani, Bactericera cockerelli, Bemisia spp, Brachycaudus spp, Brevicoryne brassicae, Cacopsylla spp,
 30 Cavariella aegopodii Scop., Ceroplaster spp., Chrysomphalus aonidium, Chrysomphalus dictyospermi,
 Cicadella spp, Cofana spectra, Cryptomyzus spp, Cicadulina spp, Coccus hesperidum, Dalbulus maidis,
 Dialeurodes spp, Diaphorina citri, Diuraphis noxia, Dysaphis spp, Empoasca spp., Eriosoma larigerum,
 Erythroneura spp., Gascardia spp., Glycaspis brimblecombei, Hyadaphis pseudobrassicae, Hyalopterus
 spp, Hyperomyzus pallidus, Idioscopus clypealis, Jacobiasca lybica, Laodelphax spp., Lecanium corni,
 35 Lepidosaphes spp., Lopaphis erysimi, Lyogenys maidis, Macrosiphum spp., Mahanarva spp, Metcalfa
 pruinosa, Metopolophium dirhodum, Myndus crudus, Myzus spp., Neotoxoptera sp, Nephrotettix spp.,
 Nilaparvata spp., Nippolachnus piri Mats, Odonaspis ruthae, Oregma lanigera Zehnter, Parabemisia
 myricae, Paratrioza cockerelli, Parlatoria spp., Pemphigus spp., Peregrinus maidis, Perkinsiella spp,

- Phorodon humuli, Phylloxera spp, Planococcus spp., Pseudaulacaspis spp., Pseudococcus spp.,
Pseudatomoscelis seriatus, Psylla spp., Pulvinaria aethiopica, Quadraspidiotus spp., Quesada gigas,
Recilia dorsalis, Rhopalosiphum spp., Saissetia spp., Scaphoideus spp., Schizaphis spp., Sitobion spp.,
Sogatella furcifera, Spissistilus festinus, Tarophagus Proserpina, Toxoptera spp, Trialeurodes spp,
5 Tridiscus sporoboli, Trionymus spp, Trioza erytreae , Unaspis citri, Zyginia flammigera, Zyginidia
scutellaris, ;
from the order *Hymenoptera*, for example,
Acromyrmex, Arge spp, Atta spp., Cephus spp., Diprion spp., Diprionidae, Gilpinia polytoma, Hoplo-
campa spp., Lasius spp., Monomorium pharaonis, Neodiprion spp., Pogonomyrmex spp, Slenopsis
10 invicta, Solenopsis spp. and Vespa spp.;
from the order *Isoptera*, for example,
Coptotermes spp, Cornitermes cumulans, Incisitermes spp, Macrotermes spp, Mastotermes spp,
Microtermes spp, Reticulitermes spp.; Solenopsis geminata
from the order *Lepidoptera*, for example,
15 Acleris spp., Adoxophyes spp., Aegeria spp., Agrotis spp., Alabama argillaceae, Amylois spp.,
Anticarsia gemmatilis, Archips spp., Argyresthia spp, Argyrotaenia spp., Autographa spp., Bucculatrix
thurberiella, Busseola fusca, Cadra cautella, Carposina nipponensis, Chilo spp., Choristoneura spp.,
Chrysoteuchia topiaria, Clysia ambiguella, Cnaphalocrocis spp., Cnephasia spp., Cochylis spp.,
Coleophora spp., Colias lesbia, Cosmophila flava, Crambus spp, Crocidolomia binotalis, Cryptophlebia
20 leucotreta, Cydalima perspectalis, Cydia spp., Diaphania perspectalis, Diatraea spp., Diparopsis
castanea, Earias spp., Eldana saccharina, Ephestia spp., Epinotia spp, Estigmene acrea, Etiella
zinckinella, Eucosma spp., Eupoecilia ambiguella, Euproctis spp., Euxoa spp., Feltia jaculiferia, Gra-
pholita spp., Hedya nubiferana, Heliothis spp., Hellula undalis, Herpetogramma spp, Hyphantria cunea,
Keiferia lycopersicella, Lasmopalpus lignosellus, Leucoptera scitella, Lithocollethis spp., Lobesia
25 botrana, Loxostege bifidalis, Lymantria spp., Lyonetia spp., Malacosoma spp., Mamestra brassicae,
Manduca sexta, Mythimna spp, Noctua spp, Operophtera spp., Orniodes indica, Ostrinia nubilalis,
Pammene spp., Pandemis spp., Panolis flammea, Papaipema nebris, Pectinophora gossypiella,
Perileucoptera coffeella, Pseudaletia unipuncta, Phthorimaea operculella, Pieris rapae, Pieris spp.,
Plutella xylostella, Prays spp., Pseudoplusia spp, Rachiplusia nu, Richia albicosta, Scirpophaga spp.,
30 Sesamia spp., Sparganothis spp., Spodoptera spp., Sylepta derogate, Synanthedon spp.,
Thaumetopoea spp., Tortrix spp., Trichoplusia ni, Tuta absoluta, and Yponomeuta spp.;
from the order *Mallophaga*, for example,
Damalinae spp. and Trichodectes spp.;
from the order *Orthoptera*, for example,
35 Blatta spp., Blattella spp., Gryllotalpa spp., Leucophaea maderae, Locusta spp., Neocurtilla
hexadactyla, Periplaneta spp. , Scapteriscus spp, and Schistocerca spp.;
from the order *Psocoptera*, for example,
Liposcelis spp.;

from the order *Siphonaptera*, for example,

Ceratophyllus spp., Ctenocephalides spp. and Xenopsylla cheopis;

from the order *Thysanoptera*, for example,

Calliothrips phaseoli, Frankliniella spp., Heliothrips spp, Hercinothrips spp., Parthenothrips spp,

5 Scirtothrips aurantii, Sericothrips variabilis, Taeniothrips spp., Thrips spp;

from the order *Thysanura*, for example, Lepisma saccharina.

The active ingredients according to the invention can be used for controlling, i. e. containing or

destroying, pests of the abovementioned type which occur in particular on plants, especially on useful

10 plants and ornamentals in agriculture, in horticulture and in forests, or on organs, such as fruits, flowers, foliage, stalks, tubers or roots, of such plants, and in some cases even plant organs which are formed at a later point in time remain protected against these pests.

Suitable target crops are, in particular, cereals, such as wheat, barley, rye, oats, rice, maize or sorghum;

15 beet, such as sugar or fodder beet; fruit, for example pomaceous fruit, stone fruit or soft fruit, such as apples, pears, plums, peaches, almonds, cherries or berries, for example strawberries, raspberries or blackberries; leguminous crops, such as beans, lentils, peas or soya; oil crops, such as oilseed rape, mustard, poppies, olives, sunflowers, coconut, castor, cocoa or ground nuts; cucurbits, such as pumpkins, cucumbers or melons; fibre plants, such as cotton, flax, hemp or jute; citrus fruit, such as
20 oranges, lemons, grapefruit or tangerines; vegetables, such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes or bell peppers; Lauraceae, such as avocado, Cinnamomum or camphor; and also tobacco, nuts, coffee, eggplants, sugarcane, tea, pepper, grapevines, hops, the plantain family, latex plants and ornamentals.

25 The active ingredients according to the invention are especially suitable for controlling Aphis craccivora, Diabrotica balteata, Heliothis virescens, Myzus persicae, Plutella xylostella and Spodoptera littoralis in cotton, vegetable, maize, rice and soya crops. The active ingredients according to the invention are further especially suitable for controlling Mamestra (preferably in vegetables), Cydia pomonella (preferably in apples), Empoasca (preferably in vegetables, vineyards), Leptinotarsa (preferably in
30 potatos) and Chilo suppressalis (preferably in rice).

In a further aspect, the invention may also relate to a method of controlling damage to plant and parts thereof by plant parasitic nematodes (Endoparasitic-, Semiendoparasitic- and Ectoparasitic nematodes), especially plant parasitic nematodes such as root knot nematodes, Meloidogyne hapla, Meloidogyne

35 incognita, Meloidogyne javanica, Meloidogyne arenaria and other Meloidogyne species; cyst-forming nematodes, Globodera rostochiensis and other Globodera species; Heterodera avenae, Heterodera glycines, Heterodera schachtii, Heterodera trifolii, and other Heterodera species; Seed gall nematodes, Anguina species; Stem and foliar nematodes, Aphelenchoides species; Sting nematodes, Belonolaimus

longicaudatus and other Belonolaimus species; Pine nematodes, Bursaphelenchus xylophilus and other Bursaphelenchus species; Ring nematodes, Criconema species, Criconemella species, Criconemoides species, Mesocriconema species; Stem and bulb nematodes, Ditylenchus destructor, Ditylenchus dipsaci and other Ditylenchus species; Awl nematodes, Dolichodorus species; Spiral nematodes, 5 Helicotylenchus multicinctus and other Helicotylenchus species; Sheath and sheathoid nematodes, Hemicyclophora species and Hemicriconemoides species; Hirshmanniella species; Lance nematodes, Hoploaimus species; false rootknot nematodes, Nacobbus species; Needle nematodes, Longidorus elongatus and other Longidorus species; Pin nematodes, Pratylenchus species; Lesion nematodes, Pratylenchus neglectus, Pratylenchus penetrans, Pratylenchus curvatus, Pratylenchus goodeyi and 10 other Pratylenchus species; Burrowing nematodes, Radopholus similis and other Radopholus species; Reniform nematodes, Rotylenchus robustus, Rotylenchus reniformis and other Rotylenchus species; Scutellonema species; Stubby root nematodes, Trichodorus primitivus and other Trichodorus species, Paratrichodorus species; Stunt nematodes, Tylenchorhynchus claytoni, Tylenchorhynchus dubius and other Tylenchorhynchus species; Citrus nematodes, Tylenchulus species; Dagger nematodes, 15 Xiphinema species; and other plant parasitic nematode species, such as Subanguina spp., Hypsoperine spp., Macroposthonia spp., Melinius spp., Punctodera spp., and Quinisulcius spp..

The compounds according to any one of embodiments 1 to 25 may also have activity against the molluscs. Examples of which include, for example, Ampullariidae; Arion (*A. ater*, *A. circumscriptus*, *A. hortensis*, *A. rufus*); Bradybaenidae (*Bradybaena fruticum*); Cepaea (*C. hortensis*, *C. Nemoralis*); 20 ochlodina; Deroceras (*D. agrestis*, *D. empiricorum*, *D. laeve*, *D. reticulatum*); Discus (*D. rotundatus*); Euomphalia; Galba (*G. trunculata*); Helicelia (*H. itala*, *H. obvia*); Helicidae *Helicigona arbustorum*); Helicodiscus; Helix (*H. aperta*); Limax (*L. cinereoniger*, *L. flavus*, *L. marginatus*, *L. maximus*, *L. tenellus*); Lymnaea; Milax (*M. gagates*, *M. marginatus*, *M. sowerbyi*); Opeas; Pomacea (*P. canaticulata*); Vallonia and Zanioides. 25

The term "crops" is to be understood as including also crop plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising one or more selectively acting toxins, such as are known, for example, from toxin-producing bacteria, especially those of the 30 genus *Bacillus*.

Toxins that can be expressed by such transgenic plants include, for example, insecticidal proteins, for example insecticidal proteins from *Bacillus cereus* or *Bacillus popilliae*; or insecticidal proteins from *Bacillus thuringiensis*, such as δ -endotoxins, e.g. Cry1Ab, Cry1Ac, Cry1F, Cry1Fa2, Cry2Ab, Cry3A, 35 Cry3Bb1 or Cry9C, or vegetative insecticidal proteins (Vip), e.g. Vip1, Vip2, Vip3 or Vip3A; or insecticidal proteins of bacteria colonising nematodes, for example *Photorhabdus* spp. or *Xenorhabdus* spp., such as *Photorhabdus luminescens*, *Xenorhabdus nematophilus*; toxins produced by animals, such as scorpion toxins, arachnid toxins, wasp toxins and other insect-specific neurotoxins; toxins

produced by fungi, such as Streptomyces toxins, plant lectins, such as pea lectins, barley lectins or snowdrop lectins; agglutinins; proteinase inhibitors, such as trypsin inhibitors, serine protease inhibitors, patatin, cystatin, papain inhibitors; ribosome-inactivating proteins (RIP), such as ricin, maize-RIP, abrin, luffin, saporin or bryodin; steroid metabolism enzymes, such as 3-hydroxysteroidoxidase, ecdysteroid-
 5 UDP-glycosyl-transferase, cholesterol oxidases, ecdysone inhibitors, HMG-COA-reductase, ion channel blockers, such as blockers of sodium or calcium channels, juvenile hormone esterase, diuretic hormone receptors, stilbene synthase, bibenzyl synthase, chitinases and glucanases.

In the context of the present invention there are to be understood by δ -endotoxins, for example Cry1Ab, Cry1Ac, Cry1F, Cry1Fa2, Cry2Ab, Cry3A, Cry3Bb1 or Cry9C, or vegetative insecticidal proteins (Vip),
 10 for example Vip1, Vip2, Vip3 or Vip3A, expressly also hybrid toxins, truncated toxins and modified toxins. Hybrid toxins are produced recombinantly by a new combination of different domains of those proteins (see, for example, WO 02/15701). Truncated toxins, for example a truncated Cry1Ab, are known. In the case of modified toxins, one or more amino acids of the naturally occurring toxin are replaced. In such amino acid replacements, preferably non-naturally present protease recognition
 15 sequences are inserted into the toxin, such as, for example, in the case of Cry3A055, a cathepsin-G-recognition sequence is inserted into a Cry3A toxin (see WO 03/018810).

Examples of such toxins or transgenic plants capable of synthesising such toxins are disclosed, for example, in EP-A-0 374 753, WO93/07278, WO95/34656, EP-A-0 427 529, EP-A-451 878 and WO 03/052073.

20 The processes for the preparation of such transgenic plants are generally known to the person skilled in the art and are described, for example, in the publications mentioned above. CryI-type deoxyribonucleic acids and their preparation are known, for example, from WO 95/34656, EP-A-0 367 474, EP-A-0 401 979 and WO 90/13651.

The toxin contained in the transgenic plants imparts to the plants tolerance to harmful insects. Such
 25 insects can occur in any taxonomic group of insects, but are especially commonly found in the beetles (Coleoptera), two-winged insects (Diptera) and moths (Lepidoptera).

Transgenic plants containing one or more genes that code for an insecticidal resistance and express one or more toxins are known and some of them are commercially available. Examples of such plants are: YieldGard® (maize variety that expresses a Cry1Ab toxin); YieldGard Rootworm® (maize variety
 30 that expresses a Cry3Bb1 toxin); YieldGard Plus® (maize variety that expresses a Cry1Ab and a Cry3Bb1 toxin); Starlink® (maize variety that expresses a Cry9C toxin); Herculex I® (maize variety that expresses a Cry1Fa2 toxin and the enzyme phosphinothricine N-acetyltransferase (PAT) to achieve tolerance to the herbicide glufosinate ammonium); NuCOTN 33B® (cotton variety that expresses a Cry1Ac toxin); Bollgard I® (cotton variety that expresses a Cry1Ac toxin); Bollgard II® (cotton variety
 35 that expresses a Cry1Ac and a Cry2Ab toxin); VipCot® (cotton variety that expresses a Vip3A and a Cry1Ab toxin); NewLeaf® (potato variety that expresses a Cry3A toxin); NatureGard®, Agrisure® GT

Advantage (GA21 glyphosate-tolerant trait), Agrisure® CB Advantage (Bt11 corn borer (CB) trait) and Protecta®.

Further examples of such transgenic crops are:

1. **Bt11 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Genetically modified *Zea mays* which has been rendered resistant to attack by the European corn borer (*Ostrinia nubilalis* and *Sesamia nonagrioides*) by transgenic expression of a truncated Cry1Ab toxin. Bt11 maize also transgenically expresses the enzyme PAT to achieve tolerance to the herbicide glufosinate ammonium.

2. **Bt176 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Genetically modified *Zea mays* which has been rendered resistant to attack by the European corn borer (*Ostrinia nubilalis* and *Sesamia nonagrioides*) by transgenic expression of a Cry1Ab toxin. Bt176 maize also transgenically expresses the enzyme PAT to achieve tolerance to the herbicide glufosinate ammonium.

3. **MIR604 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Maize which has been rendered insect-resistant by transgenic expression of a modified Cry3A toxin. This toxin is Cry3A055 modified by insertion of a cathepsin-G-protease recognition sequence. The preparation of such transgenic maize plants is described in WO 03/018810.

4. **MON 863 Maize** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/DE/02/9. MON 863 expresses a Cry3Bb1 toxin and has resistance to certain Coleoptera insects.

5. **IPC 531 Cotton** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/ES/96/02.

6. **1507 Maize** from Pioneer Overseas Corporation, Avenue Tedesco, 7 B-1160 Brussels, Belgium, registration number C/NL/00/10. Genetically modified maize for the expression of the protein Cry1F for achieving resistance to certain Lepidoptera insects and of the PAT protein for achieving tolerance to the herbicide glufosinate ammonium.

7. **NK603 × MON 810 Maize** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/GB/02/M3/03. Consists of conventionally bred hybrid maize varieties by crossing the genetically modified varieties NK603 and MON 810. NK603 × MON 810 Maize transgenically expresses the protein CP4 EPSPS, obtained from *Agrobacterium sp.* strain CP4, which imparts tolerance to the herbicide Roundup® (contains glyphosate), and also a Cry1Ab toxin obtained from *Bacillus thuringiensis subsp. kurstaki* which brings about tolerance to certain Lepidoptera, include the European corn borer.

Transgenic crops of insect-resistant plants are also described in BATS (Zentrum für Biosicherheit und Nachhaltigkeit, Zentrum BATS, Clarastrasse 13, 4058 Basel, Switzerland) Report 2003, (<http://bats.ch>). The term "crops" is to be understood as including also crop plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising antipathogenic

substances having a selective action, such as, for example, the so-called "pathogenesis-related proteins" (PRPs, see e.g. EP-A-0 392 225). Examples of such antipathogenic substances and transgenic plants capable of synthesising such antipathogenic substances are known, for example, from EP-A-0 392 225, WO95/33818 and EP-A-0 353 191. The methods of producing such transgenic plants are generally known to the person skilled in the art and are described, for example, in the publications mentioned above.

Crops may also be modified for enhanced resistance to fungal (for example Fusarium, Anthracnose, or Phytophthora), bacterial (for example Pseudomonas) or viral (for example potato leafroll virus, tomato spotted wilt virus, cucumber mosaic virus) pathogens.

Crops also include those that have enhanced resistance to nematodes, such as the soybean cyst nematode.

Crops that are tolerant to abiotic stress include those that have enhanced tolerance to drought, high salt, high temperature, chill, frost, or light radiation, for example through expression of NF-YB or other proteins known in the art.

Antipathogenic substances which can be expressed by such transgenic plants include, for example, ion channel blockers, such as blockers for sodium and calcium channels, for example the viral KP1, KP4 or KP6 toxins; stilbene synthases; bibenzyl synthases; chitinases; glucanases; the so-called "pathogenesis-related proteins" (PRPs; see e.g. EP-A-0 392 225); antipathogenic substances produced by microorganisms, for example peptide antibiotics or heterocyclic antibiotics (see e.g. WO95/33818) or protein or polypeptide factors involved in plant pathogen defence (so-called "plant disease resistance genes", as described in WO 03/000906).

Further areas of use of the compositions according to the invention are the protection of stored goods and store rooms and the protection of raw materials, such as wood, textiles, floor coverings or buildings, and also in the hygiene sector, especially the protection of humans, domestic animals and productive livestock against pests of the mentioned type.

The present invention also provides a method for controlling pests (such as mosquitoes and other disease vectors; see also http://www.who.int/malaria/vector_control/irs/en/). In one embodiment, the method for controlling pests comprises applying the compositions of the invention to the target pests, to their locus or to a surface or substrate by brushing, rolling, spraying, spreading or dipping. By way of example, an IRS (indoor residual spraying) application of a surface such as a wall, ceiling or floor surface is contemplated by the method of the invention. In another embodiment, it is contemplated to

apply such compositions to a substrate such as non-woven or a fabric material in the form of (or which can be used in the manufacture of) netting, clothing, bedding, curtains and tents.

In another embodiment, the method for controlling such pests comprises applying a pesticidally effective amount of the compositions of the invention to the target pests, to their locus, or to a surface or substrate so as to provide effective residual pesticidal activity on the surface or substrate. Such application may be made by brushing, rolling, spraying, spreading or dipping the pesticidal composition of the invention. By way of example, an IRS application of a surface such as a wall, ceiling or floor surface is contemplated by the method of the invention so as to provide effective residual pesticidal activity on the surface. In another embodiment, it is contemplated to apply such compositions for residual control of pests on a substrate such as a fabric material in the form of (or which can be used in the manufacture of) netting, clothing, bedding, curtains and tents.

Substrates including non-woven, fabrics or netting to be treated may be made of natural fibres such as cotton, raffia, jute, flax, sisal, hessian, or wool, or synthetic fibres such as polyamide, polyester, polypropylene, polyacrylonitrile or the like. The polyesters are particularly suitable. The methods of textile treatment are known, e.g. WO 2008/151984, WO 2003/034823, US 5631072, WO 2005/64072, WO2006/128870, EP 1724392, WO2005113886 or WO 2007/090739.

Further areas of use of the compositions according to the invention are the field of tree injection/trunk treatment for all ornamental trees as well all sort of fruit and nut trees.

In the field of tree injection/trunk treatment, the compounds according to the present invention are especially suitable against wood-boring insects from the order *Lepidoptera* as mentioned above and from the order *Coleoptera*, especially against woodborers listed in the following tables A and B:

Table A. Examples of exotic woodborers of economic importance.

Family	Species	Host or Crop Infested
Buprestidae	<i>Agrilus planipennis</i>	Ash
Cerambycidae	<i>Anoplura glabripennis</i>	Hardwoods
	<i>Xylosandrus crassiusculus</i>	Hardwoods
Scolytidae	<i>X. mutilatus</i>	Hardwoods
	<i>Tomicus piniperda</i>	Conifers

Table B. Examples of native woodborers of economic importance.

Family	Species	Host or Crop Infested
Buprestidae	<i>Agrilus anxius</i>	Birch
	<i>Agrilus politus</i>	Willow, Maple
	<i>Agrilus sayi</i>	Bayberry, Sweetfern

Family	Species	Host or Crop Infested
	<i>Agrilus vittaticollis</i>	Apple, Pear, Cranberry, Serviceberry, Hawthorn
	<i>Chrysobothris femorata</i>	Apple, Apricot, Beech, Boxelder, Cherry, Chestnut, Currant, Elm, Hawthorn, Hackberry, Hickory, Horsechestnut, Linden, Maple, Mountain-ash, Oak, Pecan, Pear, Peach, Persimmon, Plum, Poplar, Quince, Redbud, Serviceberry, Sycamore, Walnut, Willow
	<i>Texania campestris</i>	Basswood, Beech, Maple, Oak, Sycamore, Willow, Yellow-poplar
	<i>Goes pulverulentus</i>	Beech, Elm, Nuttall, Willow, Black oak, Cherrybark oak, Water oak, Sycamore
	<i>Goes tigrinus</i>	Oak
	<i>Neoclytus acuminatus</i>	Ash, Hickory, Oak, Walnut, Birch, Beech, Maple, Eastern hophornbeam, Dogwood, Persimmon, Redbud, Holly, Hackberry, Black locust, Honeylocust, Yellow-poplar, Chestnut, Osage-orange, Sassafras, Lilac, Mountain-mahogany, Pear, Cherry, Plum, Peach, Apple, Elm, Basswood, Sweetgum
	<i>Neoptychodes trilineatus</i>	Fig, Alder, Mulberry, Willow, Nettleaf hackberry
	<i>Oberea ocellata</i>	Sumac, Apple, Peach, Plum, Pear, Currant, Blackberry
	<i>Oberea tripunctata</i>	Dogwood, Viburnum, Elm, Sourwood, Blueberry, Rhododendron, Azalea, Laurel, Poplar, Willow, Mulberry
	<i>Oncideres cingulata</i>	Hickory, Pecan, Persimmon, Elm, Sourwood, Basswood, Honeylocust,
Cerambycidae		

Family	Species	Host or Crop Infested
Scolytidae		Dogwood, Eucalyptus, Oak, Hackberry, Maple, Fruit trees
	<i>Saperda calcarata</i>	Poplar
	<i>Strophiona nitens</i>	Chestnut, Oak, Hickory, Walnut, Beech, Maple
	<i>Corthylus columbianus</i>	Maple, Oak, Yellow-poplar, Beech, Boxelder, Sycamore, Birch, Basswood, Chestnut, Elm
	<i>Dendroctonus frontalis</i>	Pine
	<i>Dryocoetes betulae</i>	Birch, Sweetgum, Wild cherry, Beech, Pear
	<i>Monarthrum fasciatum</i>	Oak, Maple, Birch, Chestnut, Sweetgum, Blackgum, Poplar, Hickory, Mimosa, Apple, Peach, Pine
	<i>Phloeotribus liminaris</i>	Peach, Cherry, Plum, Black cherry, Elm, Mulberry, Mountain-ash
	<i>Pseudopityophthorus pruinus</i>	Oak, American beech, Black cherry, Chickasaw plum, Chestnut, Maple, Hickory, Hornbeam, Hophornbeam
	<i>Paranthrene simulans</i>	Oak, American chestnut
	<i>Sannina uroceriformis</i>	Persimmon
	<i>Synanthedon exitiosa</i>	Peach, Plum, Nectarine, Cherry, Apricot, Almond, Black cherry
	<i>Synanthedon pictipes</i>	Peach, Plum, Cherry, Beach, Black Cherry
	<i>Synanthedon rubrofascia</i>	Tupelo
	<i>Synanthedon scitula</i>	Dogwood, Pecan, Hickory, Oak, Chestnut, Beech, Birch, Black cherry, Elm, Mountain-ash, Viburnum, Willow, Apple, Loquat, Ninebark, Bayberry
Sesiidae	<i>Vitacea polistiformis</i>	Grape

In the hygiene sector, the compositions according to the invention are active against ectoparasites such as hard ticks, soft ticks, mange mites, harvest mites, flies (biting and licking), parasitic fly larvae, lice, hair lice, bird lice and fleas.

5 Examples of such parasites are:

Of the order Anoplurida: Haematopinus spp., Linognathus spp., Pediculus spp. and Phtirus spp., Solenopotes spp..

5 Of the order Mallophagida: Trimenopon spp., Menopon spp., Trinoton spp., Bovicola spp., Werneckiella spp., Lepikentron spp., Damalina spp., Trichodectes spp. and Felicola spp..

10 Of the order Diptera and the suborders Nematocerina and Brachycerina, for example Aedes spp., Anopheles spp., Culex spp., Simulium spp., Eusimulium spp., Phlebotomus spp., Lutzomyia spp., Culicoides spp., Chrysops spp., Hybomitra spp., Atylotus spp., Tabanus spp., Haematopota spp., Philipomyia spp., Braula spp., Musca spp., Hydrotaea spp., Stomoxys spp., Haematobia spp., Morellia spp., Fannia spp., Glossina spp., Calliphora spp., Lucilia spp., Chrysomyia spp., Wohlfahrtia spp., Sarcophaga spp., Oestrus spp., Hypoderma spp., Gasterophilus spp., Hippobosca spp., Lipoptena spp. and Melophagus spp..

15 Of the order Siphonaptera, for example Pulex spp., Ctenocephalides spp., Xenopsylla spp., Ceratophyllus spp..

Of the order Heteropterida, for example Cimex spp., Triatoma spp., Rhodnius spp., Panstrongylus spp..

20 Of the order Blattellidae, for example Blatta orientalis, Periplaneta americana, Blattella germanica and Supella spp..

25 Of the subclass Acaria (Acarida) and the orders Meta- and Meso-stigmata, for example Argas spp., Ornithodoros spp., Otobius spp., Ixodes spp., Amblyomma spp., Boophilus spp., Dermacentor spp., Haemophysalis spp., Hyalomma spp., Rhipicephalus spp., Dermanyssus spp., Raillietia spp., Pneumonyssus spp., Sternostoma spp. and Varroa spp..

30 Of the orders Actiniedida (Prostigmata) and Acaridida (Astigmata), for example Acarapis spp., Cheyletiella spp., Ornithocheyletia spp., Myobia spp., Psorergates spp., Demodex spp., Trombicula spp., Listerophorus spp., Acarus spp., Tyrophagus spp., Caloglyphus spp., Hypodectes spp., Pterolichus spp., Psoroptes spp., Chorioptes spp., Otodectes spp., Sarcoptes spp., Notoedres spp., Knemidocoptes spp., Cytodites spp. and Laminosioptes spp..

35 The compositions according to the invention are also suitable for protecting against insect infestation in the case of materials such as wood, textiles, plastics, adhesives, glues, paints, paper and card, leather, floor coverings and buildings.

The compositions according to the invention can be used, for example, against the following pests: beetles such as *Hylotrupes bajulus*, *Chlorophorus pilosis*, *Anobium punctatum*, *Xestobium rufovillosum*, *Ptilinuspecticornis*, *Dendrobium pertinex*, *Ernobius mollis*, *Priobium carpini*, *Lyctus brunneus*, *Lyctus africanus*, *Lyctus planicollis*, *Lyctus linearis*, *Lyctus pubescens*, *Trogoxylon aequale*, *Minthesrugicollis*,
 5 *Xyleborus spec.*, *Tryptodendron spec.*, *Apate monachus*, *Bostrychus capucins*, *Heterobostrychus brunneus*, *Sinoxylon spec.* and *Dinoderus minutus*, and also hymenopterans such as *Sirex juvencus*, *Urocerus gigas*, *Urocerus gigas taignus* and *Urocerus augur*, and termites such as *Kaloterme flavicollis*, *Cryptotermes brevis*, *Heterotermes indicola*, *Reticulitermes flavipes*, *Reticulitermes santonensis*, *Reticulitermes lucifugus*, *Mastotermes darwiniensis*, *Zootermopsis nevadensis* and
 10 *Coptotermes formosanus*, and bristletails such as *Lepisma saccharina*.

In one aspect, the invention therefore also relates to pesticidal compositions such as emulsifiable concentrates, suspension concentrates, microemulsions, oil dispersibles, directly sprayable or dilutable solutions, spreadable pastes, dilute emulsions, soluble powders, dispersible powders, wettable
 15 powders, dusts, granules or encapsulations in polymeric substances, which comprise - at least - one of the active ingredients according to any one of embodiments 1 to 25 and which are to be selected to suit the intended aims and the prevailing circumstances. In these compositions, the active ingredient is employed in pure form, a solid active ingredient for example in a specific particle size, or, preferably, together with - at least - one of the auxiliaries conventionally used in the art of formulation, such as
 20 extenders, for example solvents or solid carriers, or such as surface-active compounds (surfactants).

Examples of suitable solvents are: unhydrogenated or partially hydrogenated aromatic hydrocarbons, preferably the fractions C₈ to C₁₂ of alkylbenzenes, such as xylene mixtures, alkylated naphthalenes or tetrahydronaphthalene, aliphatic or cycloaliphatic hydrocarbons, such as paraffins or cyclohexane,
 25 alcohols such as ethanol, propanol or butanol, glycols and their ethers and esters such as propylene glycol, dipropylene glycol ether, ethylene glycol or ethylene glycol monomethyl ether or ethylene glycol monoethyl ether, ketones, such as cyclohexanone, isophorone or diacetone alcohol, strongly polar solvents, such as N-methylpyrrolid-2-one, dimethyl sulfoxide or N,N-dimethylformamide, water, unepoxidized or epoxidized vegetable oils, such as unexpodized or epoxidized rapeseed, castor,
 30 coconut or soya oil, and silicone oils.

Solid carriers which are used for example for dusts and dispersible powders are, as a rule, ground natural minerals such as calcite, talc, kaolin, montmorillonite or attapulgite. To improve the physical properties, it is also possible to add highly disperse silicas or highly disperse absorbitive polymers. Suitable adsorptive carriers for granules are porous types, such as pumice, brick grit, sepiolite or
 35 bentonite, and suitable non-sorptive carrier materials are calcite or sand. In addition, a large number of granulated materials of inorganic or organic nature can be used, in particular dolomite or comminuted plant residues.

Suitable surface-active compounds are, depending on the type of the active ingredient to be formulated, non-ionic, cationic and/or anionic surfactants or surfactant mixtures which have good emulsifying, dispersing and wetting properties. The surfactants mentioned below are only to be considered as examples; a large number of further surfactants which are conventionally used in the art of formulation and suitable according to the invention are described in the relevant literature.

Suitable non-ionic surfactants are, especially, polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, of saturated or unsaturated fatty acids or of alkyl phenols which may contain approximately 3 to approximately 30 glycol ether groups and approximately 8 to approximately 20 carbon atoms in the (cyclo)aliphatic hydrocarbon radical or approximately 6 to approximately 18 carbon atoms in the alkyl moiety of the alkyl phenols. Also suitable are water-soluble polyethylene oxide adducts with polypropylene glycol, ethylenediaminopolypropylene glycol or alkyl polypropylene glycol having 1 to approximately 10 carbon atoms in the alkyl chain and approximately 20 to approximately 250 ethylene glycol ether groups and approximately 10 to approximately 100 propylene glycol ether groups. Normally, the abovementioned compounds contain 1 to approximately 5 ethylene glycol units per propylene glycol unit. Examples which may be mentioned are nonylphenoxypolyethoxyethanol, castor oil polyglycol ether, polypropylene glycol/polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol or octylphenoxypolyethoxyethanol. Also suitable are fatty acid esters of polyoxyethylene sorbitan, such as polyoxyethylene sorbitan trioleate.

The cationic surfactants are, especially, quarternary ammonium salts which generally have at least one alkyl radical of approximately 8 to approximately 22 C atoms as substituents and as further substituents (unhalogenated or halogenated) lower alkyl or hydroxyalkyl or benzyl radicals. The salts are preferably in the form of halides, methylsulfates or ethylsulfates. Examples are stearyltrimethylammonium chloride and benzylbis(2-chloroethyl)ethylammonium bromide.

Examples of suitable anionic surfactants are water-soluble soaps or water-soluble synthetic surface-active compounds. Examples of suitable soaps are the alkali, alkaline earth or (unsubstituted or substituted) ammonium salts of fatty acids having approximately 10 to approximately 22 C atoms, such as the sodium or potassium salts of oleic or stearic acid, or of natural fatty acid mixtures which are obtainable for example from coconut or tall oil; mention must also be made of the fatty acid methyl taurates. However, synthetic surfactants are used more frequently, in particular fatty sulfonates, fatty sulfates, sulfonated benzimidazole derivatives or alkylaryl sulfonates. As a rule, the fatty sulfonates and fatty sulfates are present as alkali, alkaline earth or (substituted or unsubstituted) ammonium salts and they generally have an alkyl radical of approximately 8 to approximately 22 C atoms, alkyl also to be understood as including the alkyl moiety of acyl radicals; examples which may be mentioned are the sodium or calcium salts of lignosulfonic acid, of the dodecylsulfuric ester or of a fatty alcohol sulfate mixture prepared from natural fatty acids. This group also includes the salts of the sulfuric esters and sulfonic acids of fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonyl groups and a fatty acid radical of approximately 8 to approximately 22 C atoms. Examples of alkylarylsulfonates are the sodium, calcium or triethanolammonium salts of

decylbenzenesulfonic acid, of dibutylnaphthalenesulfonic acid or of a naphthalenesulfonic acid/formaldehyde condensate. Also possible are, furthermore, suitable phosphates, such as salts of the phosphoric ester of a p-nonylphenol/(4-14)ethylene oxide adduct, or phospholipids.

As a rule, the compositions comprise 0.1 to 99%, especially 0.1 to 95%, of active ingredient and 1 to 99.9%, especially 5 to 99.9%, of at least one solid or liquid adjuvant, it being possible as a rule for 0 to 25%, especially 0.1 to 20%, of the composition to be surfactants(% in each case meaning percent by weight). Whereas concentrated compositions tend to be preferred for commercial goods, the end consumer as a rule uses dilute compositions which have substantially lower concentrations of active ingredient.

Typically, a pre-mix formulation for foliar application comprises 0.1 to 99.9 %, especially 1 to 95 %, of the desired ingredients, and 99.9 to 0.1 %, especially 99 to 5 %, of a solid or liquid adjuvant (including, for example, a solvent such as water), where the auxiliaries can be a surfactant in an amount of 0 to 50 %, especially 0.5 to 40 %, based on the pre-mix formulation.

Normally, a tank-mix formulation for seed treatment application comprises 0.25 to 80%, especially 1 to 75 %, of the desired ingredients, and 99.75 to 20 %, especially 99 to 25 %, of a solid or liquid auxiliaries (including, for example, a solvent such as water), where the auxiliaries can be a surfactant in an amount of 0 to 40 %, especially 0.5 to 30 %, based on the tank-mix formulation.

Typically, a pre-mix formulation for seed treatment application comprises 0.5 to 99.9 %, especially 1 to 95 %, of the desired ingredients, and 99.5 to 0.1 %, especially 99 to 5 %, of a solid or liquid adjuvant (including, for example, a solvent such as water), where the auxiliaries can be a surfactant in an amount of 0 to 50 %, especially 0.5 to 40 %, based on the pre-mix formulation.

Whereas commercial products will preferably be formulated as concentrates (e.g., pre-mix composition (formulation)), the end user will normally employ dilute formulations (e.g., tank mix composition).

Preferred seed treatment pre-mix formulations are aqueous suspension concentrates. The formulation can be applied to the seeds using conventional treating techniques and machines, such as fluidized bed techniques, the roller mill method, rotostatic seed treaters, and drum coaters. Other methods, such as spouted beds may also be useful. The seeds may be presized before coating. After coating, the seeds are typically dried and then transferred to a sizing machine for sizing. Such procedures are known in the art.

In general, the pre-mix compositions of the invention contain 0.5 to 99.9 especially 1 to 95, advantageously 1 to 50 %, by mass of the desired ingredients, and 99.5 to 0.1, especially 99 to 5 %, by mass of a solid or liquid adjuvant (including, for example, a solvent such as water), where the auxiliaries (or adjuvant) can be a surfactant in an amount of 0 to 50, especially 0.5 to 40 %, by mass based on the mass of the pre-mix formulation.

Examples of foliar formulation types for pre-mix compositions are:

GR: Granules

WP: wettable powders

WG: water dispersable granules (powders)

SG: water soluble granules

5 SL: soluble concentrates

EC: emulsifiable concentrate

EW: emulsions, oil in water

ME: micro-emulsion

SC: aqueous suspension concentrate

10 CS: aqueous capsule suspension

OD: oil-based suspension concentrate, and

SE: aqueous suspo-emulsion.

Whereas, examples of seed treatment formulation types for pre-mix compositions are:

WS: wettable powders for seed treatment slurry

15 LS: solution for seed treatment

ES: emulsions for seed treatment

FS: suspension concentrate for seed treatment

WG: water dispersible granules, and

CS: aqueous capsule suspension.

20 Examples of formulation types suitable for tank-mix compositions are solutions, dilute emulsions, suspensions, or a mixture thereof, and dusts.

Preferred compositions are composed in particular as follows (% = percent by weight):

Emulsifiable concentrates:

25 active ingredient: 1 to 95%, preferably 5 to 20%
 surfactant: 1 to 30%, preferably 10 to 20 %
 solvent: 5 to 98%, preferably 70 to 85%

Dusts:

30 active ingredient: 0.1 to 10%, preferably 0.1 to 1%
 solid carrier: 99.9 to 90%, preferably 99.9 to 99%

Suspension concentrates:

active ingredient: 5 to 75%, preferably 10 to 50%
 35 water: 94 to 24%, preferably 88 to 30%
 surfactant: 1 to 40%, preferably 2 to 30%

Wettable powders:

active ingredient: 0.5 to 90%, preferably 1 to 80%
 surfactant: 0.5 to 20%, preferably 1 to 15%
 solid carrier: 5 to 99%, preferably 15 to 98%

5 Granulates:

active ingredient: 0.5 to 30%, preferably 3 to 15%
 solid carrier: 99.5 to 70%, preferably 97 to 85%

Examples:

10 The following compounds according to embodiment 1 may be prepared according to the methods described herein or according to known methods.

Experimental

15 The following examples are intended to illustrate the invention and are not to be construed as being limitations thereon.

“Mp” means melting point in °C. ¹H NMR measurements were recorded on a Bruker 400MHz spectrometer, chemical shifts are given in ppm relevant to a TMS standard. Spectra measured in deuterated solvents as indicated.

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LC MS Method A: Standard:

Spectra were recorded on a Mass Spectrometer from Waters (SQD or ZQ Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive or negative ions, Capillary: 3.00 kV, Cone range: 30-60 V, Extractor: 2.00 V, Source Temperature: 150 °C, Desolvation Temperature: 350 °C, Cone Gas Flow: 0 L/Hr, Desolvation Gas Flow: 650 L/Hr, Mass range: 100 to 900 Da) and an Acquity UPLC from Waters: Binary pump, heated column compartment and diode-array detector. Solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Waters UPLC HSS T3, 1.8 µm, 30 x 2.1 mm, Temp: 60 °C, DAD Wavelength range (nm): 210 to 500, Solvent Gradient: A = water + 5% MeOH + 0.05 % HCOOH, B= Acetonitrile + 0.05 % HCOOH: gradient: 25
 30 gradient: 0 min 0% B, 100%A; 1.2-1.5min 100% B; Flow (ml/min) 0.85.

LC MS Method B: Standard long:

Spectra were recorded on a Mass Spectrometer from Waters (SQD or ZQ Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive or negative ions, Capillary: 3.00 kV, Cone range: 30-60 V, Extractor: 2.00 V, Source Temperature: 150 °C, Desolvation Temperature: 350 °C, Cone Gas Flow: 0 L/Hr, Desolvation Gas Flow: 650 L/Hr, Mass range: 100 to 900 Da) and an Acquity UPLC from Waters: Binary pump, heated column compartment and diode-array detector. Solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Waters
 35

UPLC HSS T3, 1.8 μ m, 30 x 2.1 mm, Temp: 60 °C, DAD Wavelength range (nm): 210 to 500, Solvent Gradient: A = water + 5% MeOH + 0.05 % HCOOH, B= Acetonitrile + 0.05% HCOOH: gradient: gradient: 0 min 0% B, 100% A; 2.7-3.0min 100% B; Flow (ml/min) 0.85.

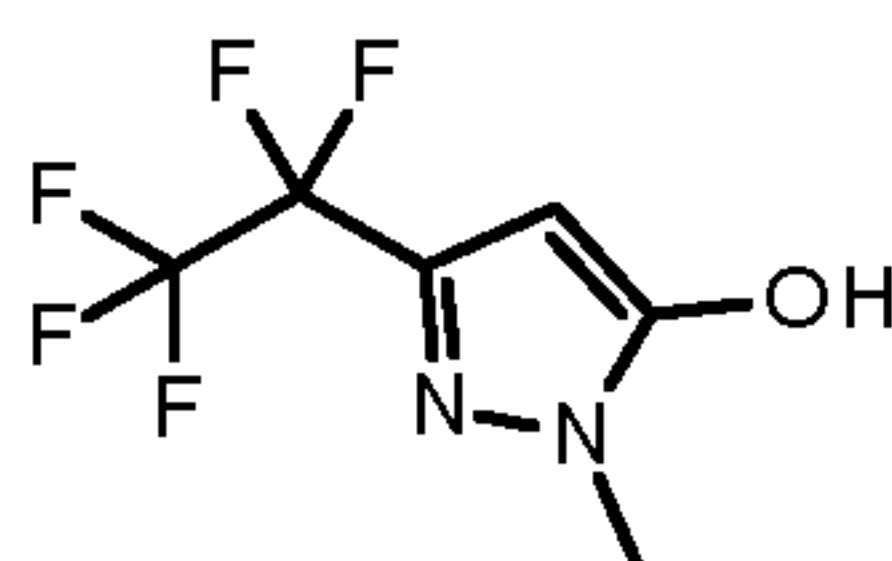
5 LC MS Method C: Unpolar:

Spectra were recorded on a Mass Spectrometer from Waters (SQD or ZQ Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive or negative ions, Capillary: 3.00 kV, Cone range: 30-60 V, Extractor: 2.00 V, Source Temperature: 150 °C, Desolvation Temperature: 350 °C, Cone Gas Flow: 0 L/Hr, Desolvation Gas Flow: 650 L/Hr, Mass range: 100 to 900 Da) and an
 10 Acquity UPLC from Waters: Binary pump, heated column compartment and diode-array detector. Solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Waters UPLC HSS T3, 1.8 μ m, 30 x 2.1 mm, Temp: 60 °C, DAD Wavelength range (nm): 210 to 500, Solvent Gradient: A = water + 5% MeOH + 0.05% HCOOH, B= Acetonitrile + 0.05% HCOOH: gradient: gradient: 0 min 40% B, 60% A; 1.2-1.5 min 100% B; Flow (ml/min) 0.85.

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Example 1: 2-chloro-N-(1-cyanocyclopropyl)-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]benzamide.

a) Preparation of 2-Methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-ol



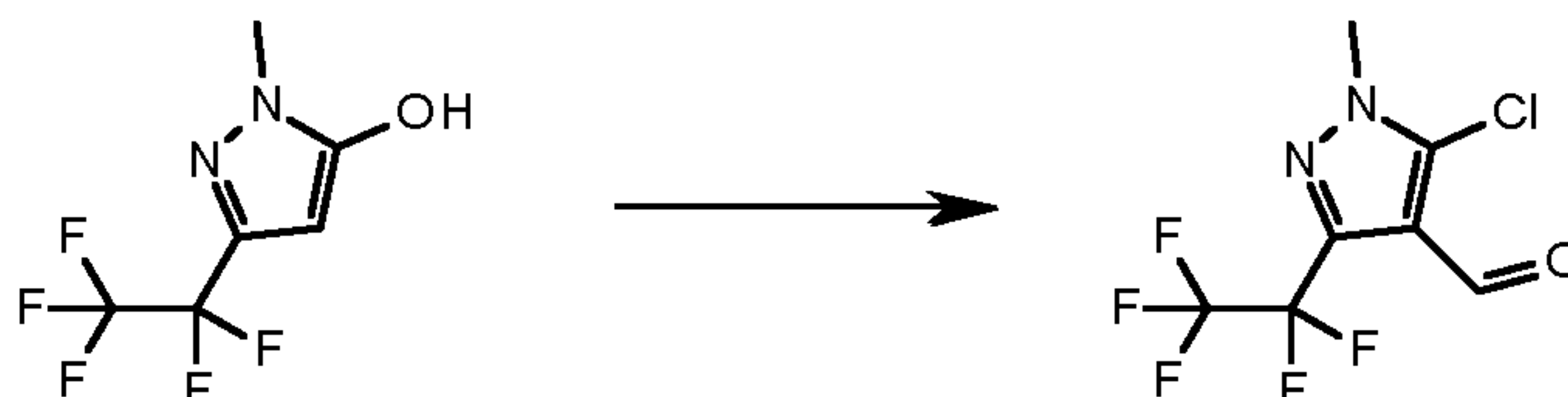
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A solution of ethyl 4,4,5,5,5-pentafluoro-3-oxo-pentanoate (30 g, 128 mmol) and methyl hydrazine (6.2 g, 135 mmol) in 120 ml of ethanol was stirred at RT overnight under Argon, the reaction mixture was then heated to 60°C for 24 h to have a complete conversion. The solvent was evaporated under vacuum and the residue purified by flash chromatography to give 2-methyl-5-(1,1,2,2,2-
 25 pentafluoroethyl)pyrazol-3-ol as a beige solid.

¹H NMR (400 MHz, DMSO-*d*₆) δ ppm 3.60 (s, 3 H) 5.71 (s, 1 H) 11.70 (s, 1 H).

LC-MS (Method B): *t*_R = 1.03 min, *m/z* = 215 [M-1], 217 [M+1].

b) Preparation of 5-Chloro-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazole-4-carbaldehyde

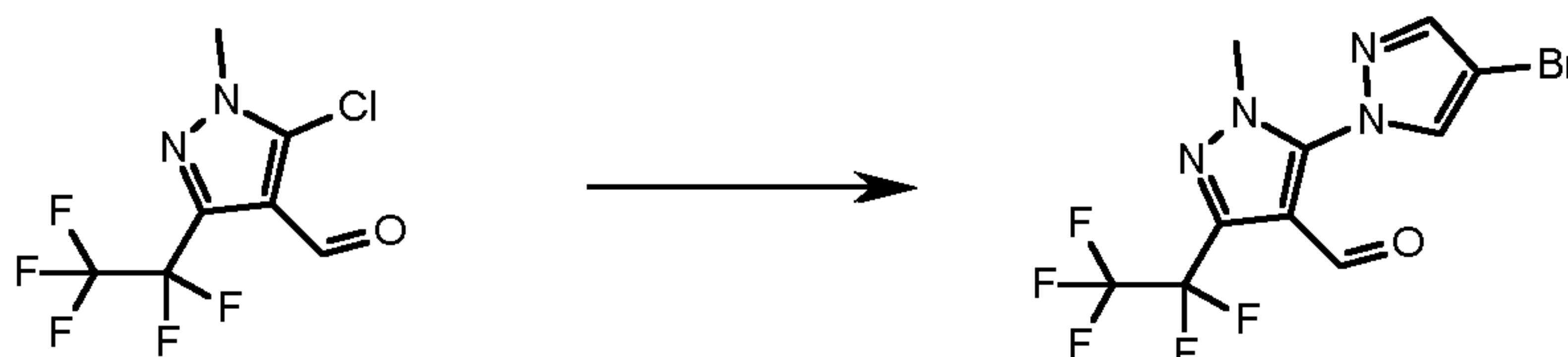


Under Argon and at 0°C, POCl₃ (16.3 ml, 175 mmol) was carefully added dropwise to 2.5 ml of N,N-dimethylformamide. To this reaction mixture was added 2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-ol (5 g, 23.1 mmol), the mixture was then heated at 100°C for 18 h. The reaction mixture was then cooled to RT and poured slowly on an aqueous solution of sodium hydrogen carbonate, the solution was extracted three time with ethyl acetate, dried over magnesium sulfate and evaporated under vacuum. The residue was purified by flash chromatography to give 5-chloro-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazole-4-carbaldehyde as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ ppm 4.00 (s, 3 H) 10.00 (s, 1 H)

LC-MS (Method B): t_R = 1.37 min, m/z = 263 [M+1].

c) Preparation of 5-(4-Bromopyrazol-1-yl)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazole-4-carbaldehyde

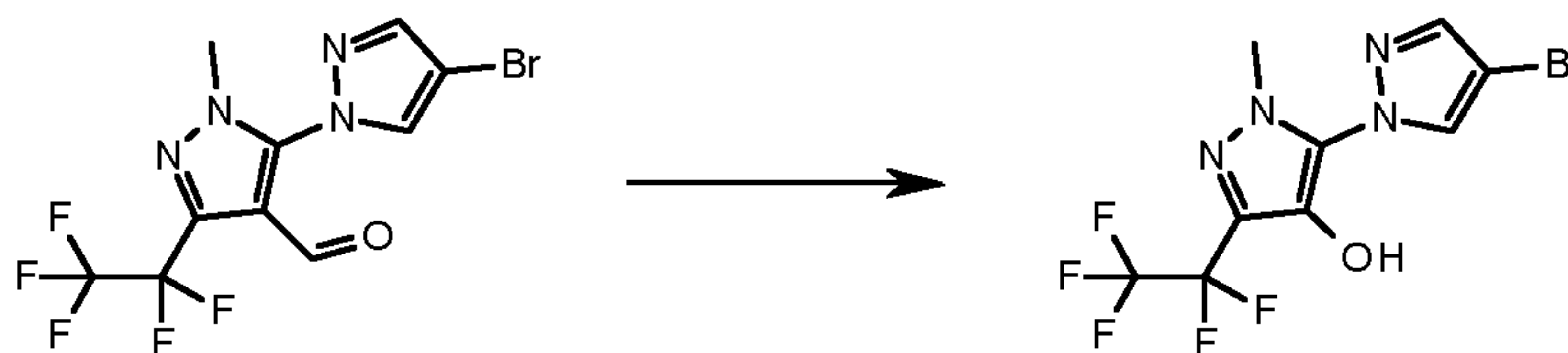


Under Argon, 5-chloro-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazole-4-carbaldehyde (12.85 g, 48.9 mmol) was dissolved in acetonitrile (500 ml), then cesium carbonate (31,89 g, 97,8 mmol) was added. To this mixture, 4-bromo-1H-pyrazole (7.9 g, 53.8 mmol) was added and the mixture was stirred at RT for 18 h. The mixture was diluted with ethyl acetate, washed with water and brine, the organic layers were dried over magnesium sulfate and evaporated under vacuum. The residue was purified by flash chromatography to give 5-(4-bromopyrazol-1-yl)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazole-4-carbaldehyde as a white solid.

¹H NMR (400 MHz, CDCl₃) δ ppm 3.98 (s, 3 H) 7.83 (s, 1 H) 8.09 (s, 1 H) 9.97 (s, 1 H).

LC-MS (Method B): t_R = 1.63 min, m/z = 371 [M-1], 373 [M+1].

d) Preparation of 5-(4-Bromopyrazol-1-yl)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazol-4-ol

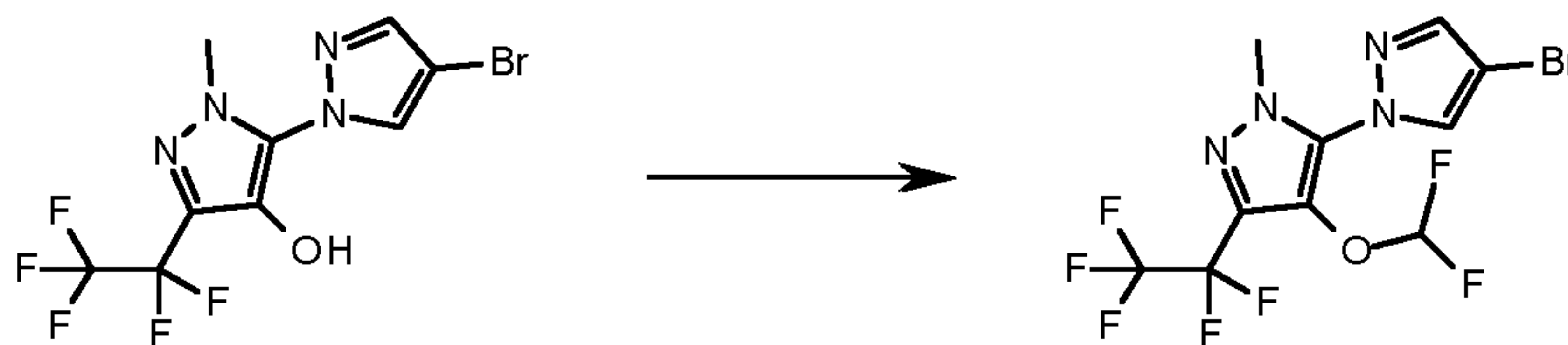


To a solution of 5-(4-bromopyrazol-1-yl)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazole-4-carbaldehyde (500 mg, 1.34 mmol) in dichloromethane (5 ml) was added meta-chloroperbenzoic acid (642 mg, 2.68 mmol). The mixture was stirred at RT for 5 days. The mixture was diluted with ethyl acetate, and

washed with water, and aqueous solutions of sodium hydrogen carbonate and sodium thiosulfate. The organic layers were dried over magnesium sulfate and reduced under vacuum. The residue was purified by flash chromatography to give 5-(4-bromopyrazol-1-yl)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazol-4-ol as a white solid.

- 5 ^1H NMR (400 MHz, CDCl_3) δ ppm 3.79 (s, 3 H) 6.35 (s, 1 H) 7.66 (s, 1 H) 7.75 (s, 1 H)
LC-MS (Method B): t_R = 1.39 min, m/z = 361 [M-1], 363 [M+1].

e) Preparation of 5-(4-Bromopyrazol-1-yl)-4-(difluoromethoxy)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazole



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To a solution of 5-(4-bromopyrazol-1-yl)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazol-4-ol (466 mg, 1.29 mmol) and potassium hydroxide (1.44 g, 25.81 mmol) in a mixture of 4 ml of acetonitrile/water (1:1) was added at -78°C 1-[[bromo(difluoro)methyl]-ethoxy-phosphoryl]oxyethane (689 mg, 2.58 mmol). The mixture was allowed to warm to RT and stirred in a closed vessel for 3 h. In order to complete the reaction, 1-[[bromo(difluoro)methyl]-ethoxy-phosphoryl]oxyethane (172 mg, 0.645 mmol) was added at -78°C and the reaction was stirred at RT for another 1 h. The reaction mixture was diluted with ether, washed with brine and water. The organic layers were dried over magnesium sulfate and reduced under vacuum. The residue was purified by flash chromatography to give 5-(4-bromopyrazol-1-yl)-4-(difluoromethoxy)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazole as a colourless oil.

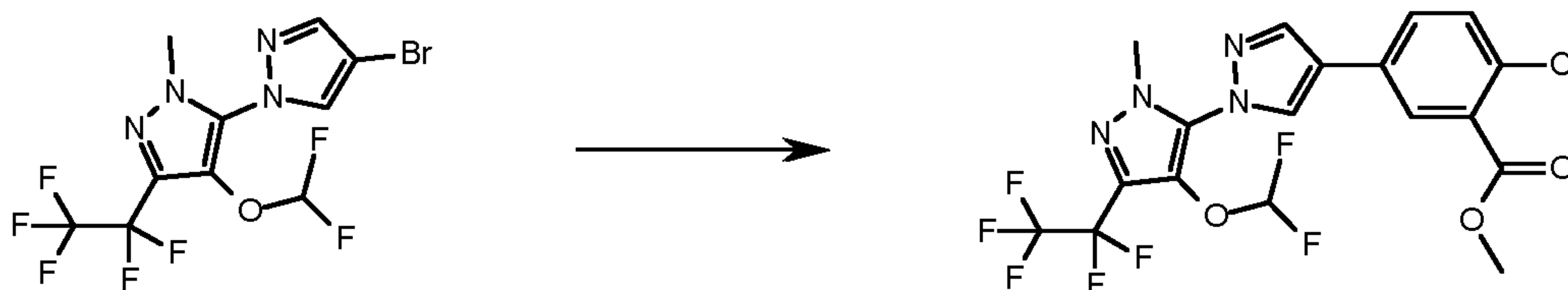
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^1H NMR (400 MHz, CDCl_3) δ ppm 3.87 (s, 3 H) 6.08 - 6.52 (m, 1 H) 7.78 (s, 1 H) 7.81 (s, 1 H).
LC-MS (Method B): t_R = 1.79 min, m/z = 409 [M-1], 411 [M+1].

f) Preparation of Methyl 2-chloro-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]benzoate

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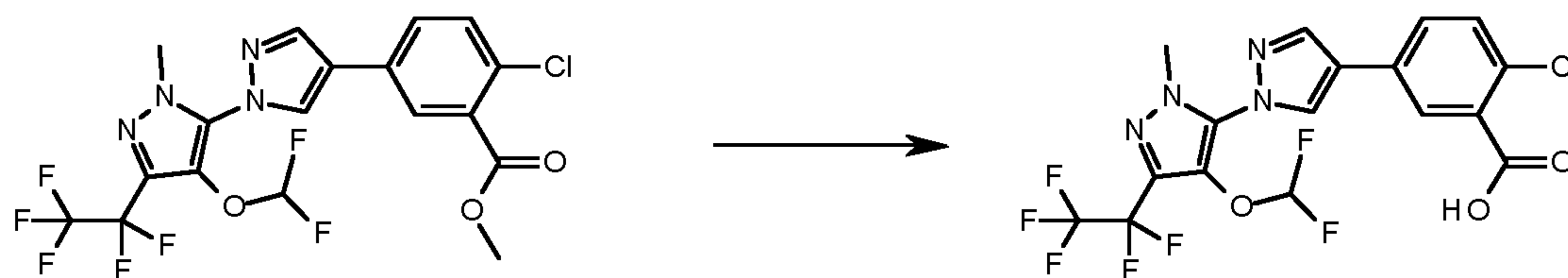
In a microwave tube, 5-(4-bromopyrazol-1-yl)-4-(difluoromethoxy)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazole (50 mg, 0.121 mmol), 5-(4-bromopyrazol-1-yl)-4-(difluoromethoxy)-1-methyl-

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3-(1,1,2,2,2-pentafluoroethyl)pyrazole (56 mg, 0.182 mmol) and cesium fluoride (37 mg, 0.243 mmol) were dissolved in 4 ml dioxane/water (3/1). The mixture was purged with argon for 5 min. Pd(dppf)Cl₂ (4.8 mg, 0.006 mmol) was added and the mixture was irradiated in the microwave oven at 160°C for 30 min. The mixture was evaporated, diluted with ethyl acetate, quenched with 25 ml water, extracted three times with ethyl acetate; the combined organic phases were washed with brine, dried over sodium sulfate, filtrated and evaporated. The black-brown resin was purified over silica gel to give methyl 2-chloro-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]benzoate as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ ppm 3.93 (s, 3 H) 3.98 (s, 3 H) 6.11 - 6.51 (m, 1 H) 7.49 - 7.54 (m, 1 H) 7.49 - 7.54 (m, 1 H) 7.55 - 7.60 (m, 1 H) 7.97 - 8.04 (m, 2 H) 8.13 (s, 1 H)
LC-MS (Method B): t_R = 1.98 min, m/z = 499 [M-1], 501 [M+1].

g) Preparation of 2-Chloro-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]benzoic acid

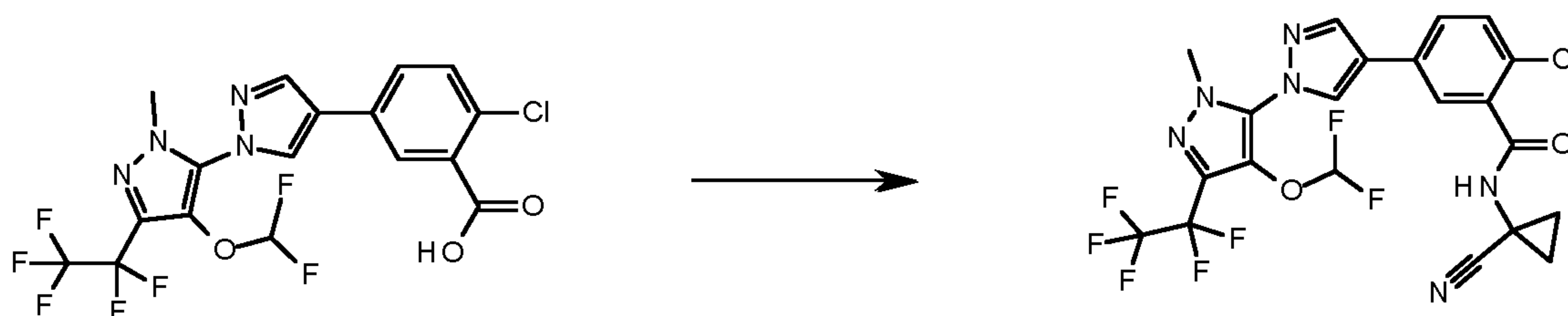


Methyl 2-chloro-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]benzoate (192 mg, 0.38 mmol) was dissolved in 5 ml tetrahydrofuran/water (4:1). LiOH monohydrate (46 mg, 1.9 mmol) was added in one portion and the reaction mixture was warmed at 50°C for 3h. The mixture was evaporated, diluted with ethyl acetate and 25 ml water. The water phase was acidified to pH 4, extracted with 3 x 30ml ethyl acetate; the organic phase was washed with brine, dried over sodium sulfate, filtrated and evaporated. The residue was purified by flash chromatography to give 2-chloro-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]benzoic acid as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ ppm 3.94 (s, 3 H) 6.13 - 6.51 (m, 1 H) 7.54 - 7.58 (m, 1 H) 7.61 - 7.66 (m, 1 H) 8.04 (s, 1 H) 8.13 - 8.18 (m, 2 H).

LC-MS (Method B): t_R = 1.73 min, m/z = 485 [M-1], 487 [M+1].

h) Preparation of 2-Chloro-N-(1-cyanocyclopropyl)-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]benzamide



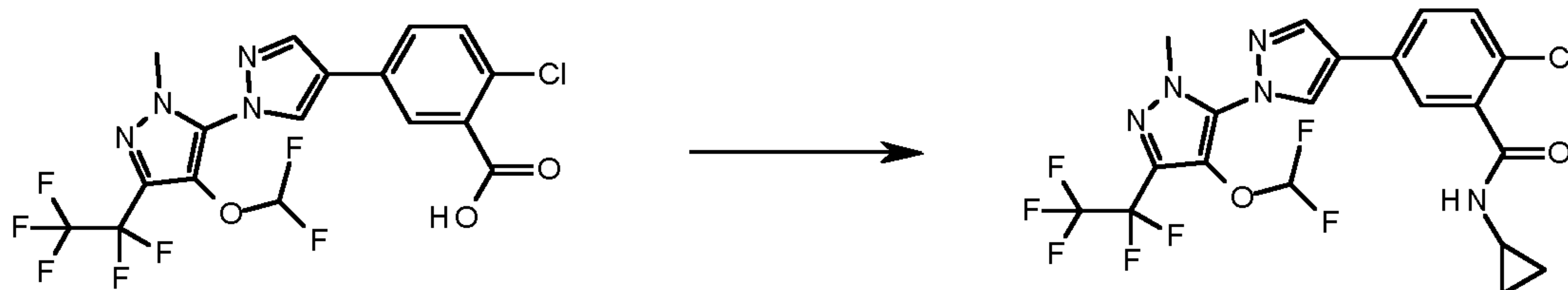
A mixture of 2-chloro-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]benzoic acid (45mg, 0.092 mmol), 1-amino-1-cyano-cyclopropane hydrochloride (33.5 mg, 0.277 mmol), EDCI (22.61 mg, 0.115 mmol), HOAT (16.39 mg, 0.115 mmol) and triethylamine (42.1 mg, 0.416 mmol) in 3 ml DMF was stirred at RT for 2 hours. The mixture was diluted with ethyl acetate, quenched with water; the organic phase was washed successively with water and once with brine. The organic phase was dried over magnesium sulfate, filtrated and evaporated. The crude product was purified by flash chromatography to give 2-chloro-N-(1-cyanocyclopropyl)-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]benzamide as a white solid.

¹H NMR (400 MHz, CDCl₃) δ ppm 1.41 - 1.46 (m, 2 H) 1.67 - 1.72 (m, 2 H) 3.93 (s, 3 H) 6.12 - 6.51 (m, 1 H) 7.46 (d, *J*=8.07 Hz, 1 H) 7.57 (dd, *J*=8.25, 2.38 Hz, 1 H) 7.96 (d, *J*=2.20 Hz, 1 H) 8.03 (s, 1 H) 8.12 (s, 1 H).

LC-MS (Method B): *t_R* = 1.74 min, *m/z* = 549 [M-1], 551 [M+1].

Mp: 138°-139°C

Example 2: 2-Chloro-N-cyclopropyl-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]benzamide



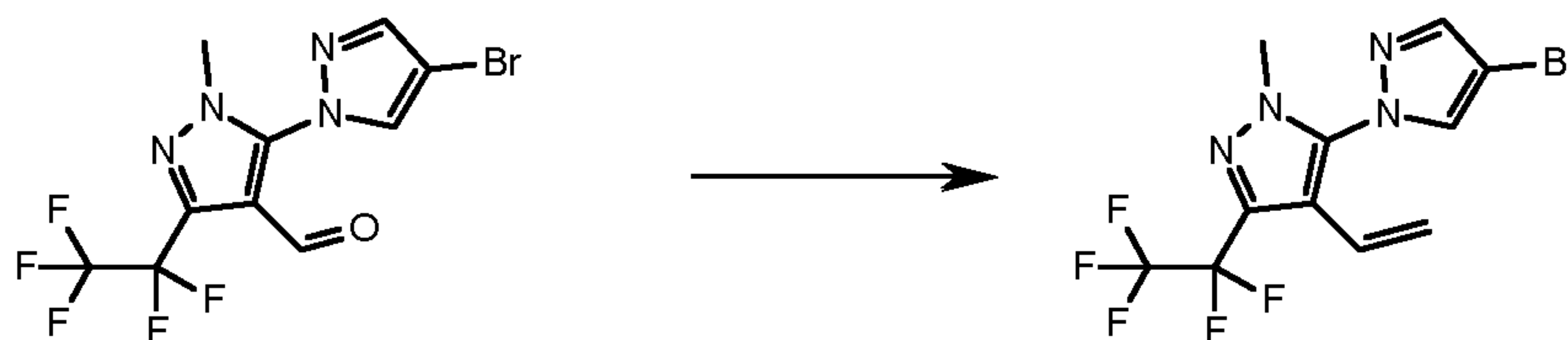
A mixture of 2-chloro-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]benzoic acid (45 mg, 0.092 mmol), cyclopropylamine (15.84 mg, 0.28 mmol), EDCI (22.61 mg, 0.115 mmol), HOAT (16.39 mg, 0.115 mmol) and triethylamine (32.75 mg, 0.323 mmol) in 3 ml DMF was stirred at RT for 2 hours. The mixture was diluted with ethyl acetate and water; the organic phase was washed successively with water and once with brine. The organic phase was dried over magnesium sulfate, filtrated and evaporated. The crude product was purified by flash chromatography to give 2-chloro-N-cyclopropyl-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]benzamide as a white solid.

¹H NMR (400 MHz, CDCl₃) δ ppm 0.56 - 0.63 (m, 2 H) 0.81 - 0.87 (m, 2 H) 2.88 (tq, *J*=7.08, 3.71 Hz, 1

H) 3.85 (s, 3 H) 6.02 - 6.46 (m, 2 H) 7.33 - 7.48 (m, 2 H) 7.75 - 7.96 (m, 2 H) 7.98 - 8.07 (m, 1 H).
LC-MS (Method B): t_R = 1.77 min, m/z = 524 [M-1], 526 [M+1].

Example 15: 2-Chloro-N-(1-cyanocyclopropyl)-5-[1-[2-methyl-5-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazol-3-yl]pyrazol-4-yl]benzamide

a) Preparation of 5-(4-Bromopyrazol-1-yl)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazole

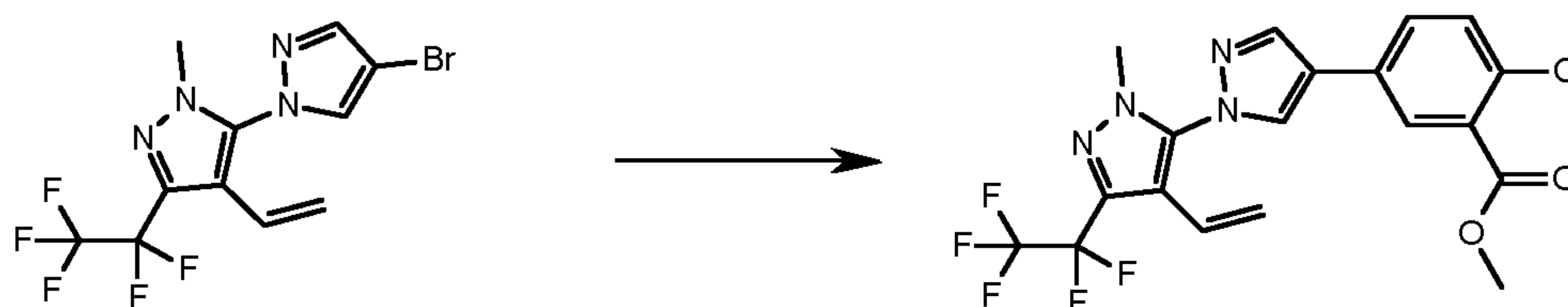


To a stirred mixture of methyl(triphenyl)phosphonium bromide (7.3 g, 20 mmol) in dry THF (100 ml) under argon at -78°C was added dropwise n-BuLi (1.6mol/L) in hexane (13 ml, 20 mmol). The resulting mixture was stirred at -78°C for 30 min. To this yellow mixture was added a solution of 5-(4-bromopyrazol-1-yl)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazole-4-carbaldehyde (5.0 g, 13 mmol) in THF. The mixture was allowed to warm to RT. The reaction mixture was quenched with aqueous ammonium chloride and then diluted with ethyl acetate; organic phase was washed with water and brine, dried over magnesium and evaporated under vacuum. The crude product was purified by flash chromatography to give 5-(4-bromopyrazol-1-yl)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazole as a white solid.

^1H NMR (400 MHz, CDCl_3) δ ppm 3.73 - 3.76 (m, 3 H) 4.91 (d, $J=17.97$ Hz, 1 H) 5.20 - 5.28 (m, 1 H) 6.44 - 6.53 (m, 1 H) 7.66 (s, 1 H) 7.85 (s, 1 H).

LC-MS (Method B): t_R = 1.89 min, m/z = 369 [M-1].

b) Preparation of Methyl 2-chloro-5-[1-[2-methyl-5-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazol-3-yl]pyrazol-4-yl]benzoate



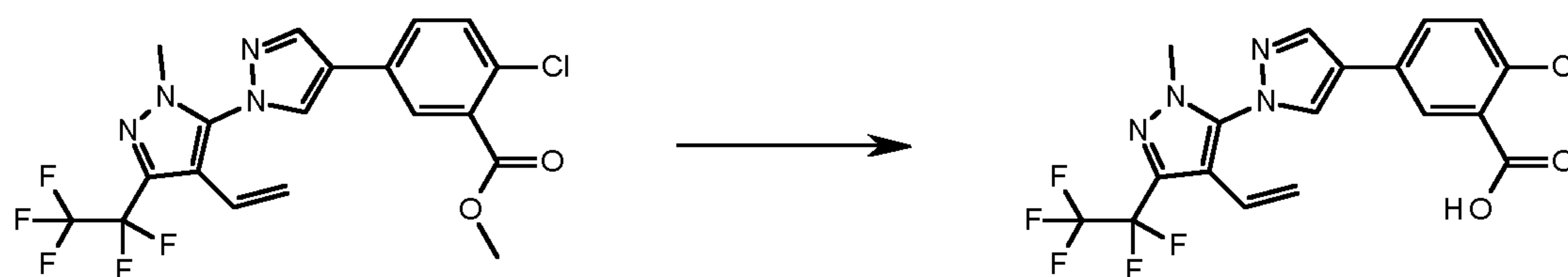
5-(4-Bromopyrazol-1-yl)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazole (1.2 g, 3.2 mmol), methyl 2-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (1.2 g, 3.9 mmol) and sodium carbonate (1.7 g, 16 mmol) were dissolved in 10 ml 1,2-dimethoxyethane and 2 ml water. The mixture was purged with argon for 5 min. Then $\text{Pd}(\text{P}(\text{Ph}_3))_4$ (560 mg, 0.49 mmol) was added and the mixture was irradiated in the microwave oven at 100°C for 40 min. The reaction was not complete and 0.05 eq. of $\text{Pd}(\text{P}(\text{Ph}_3))_4$ was added and the mixture was further irradiated in the microwave oven at 120°C for 20

min. The mixture was filtrated over celite and evaporated to dryness; crude mixture was separated over silica gel to give 2-chloro-5-[1-[2-methyl-5-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazol-3-yl]pyrazol-4-yl]benzoate as a yellow oil.

^1H NMR (400 MHz, CDCl_3) δ ppm 3.81 (s, 3 H) 3.99 (s, 3 H) 4.95 (d, $J=17.97$ Hz, 1 H) 5.20 - 5.25 (m, 1 H) 6.52 (dd, $J=17.97$, 11.74 Hz, 1 H) 7.52 - 7.55 (m, 1 H) 7.58 - 7.62 (m, 1 H) 7.91 (d, $J=0.73$ Hz, 1 H) 8.01 (d, $J=2.20$ Hz, 1 H) 8.17 (d, $J=0.73$ Hz, 1 H).

LC-MS (Method B): t_R = 2.09 min, m/z = 459 [M-1], 461 [M+1].

c) Preparation of 2-Chloro-5-[1-[2-methyl-5-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazol-3-yl]pyrazol-4-yl]benzoic acid

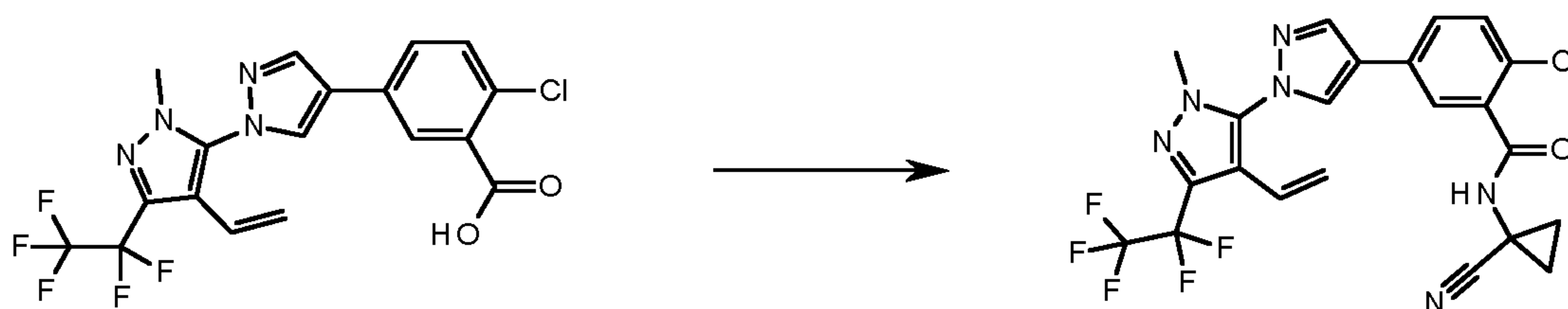


Methyl 2-chloro-5-[1-[2-methyl-5-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazol-3-yl]pyrazol-4-yl]benzoate (450 mg, 0.976 mmol) was dissolved in a mixture of THF and water (5 ml, 4:1). LiOH monohydrate (233 mg, 9.76 mmol) was added in one portion and the reaction mixture was stirred at RT overnight. The mixture was evaporated, diluted with ethyl acetate, quenched with 25 ml water and acidified to pH 4. The water phase was extracted 3 times with ethyl acetate; the combined organic phases were washed with brine, dried over sodium sulfate, filtrated and evaporated. The crude product was purified over silica gel to give 2-chloro-5-[1-[2-methyl-5-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazol-3-yl]pyrazol-4-yl]benzoic acid as a white solid.

^1H NMR (400 MHz, CDCl_3) δ ppm 3.82 (s, 3 H) 4.96 (d, $J=17.97$ Hz, 1 H) 5.23 (dd, $J=11.74$, 1.10 Hz, 1 H) 6.52 (dd, $J=17.97$, 11.74 Hz, 1 H) 7.56 - 7.59 (m, 1 H) 7.64 - 7.68 (m, 1 H) 7.93 (d, $J=0.73$ Hz, 1 H) 8.19 (dd, $J=3.30$, 1.47 Hz, 2 H).

LC-MS (Method B): t_R = 1.8 min, m/z = 445 [M-1], 447 [M+1].

d) Preparation of 2-Chloro-N-(1-cyanocyclopropyl)-5-[1-[2-methyl-5-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazol-3-yl]pyrazol-4-yl]benzamide

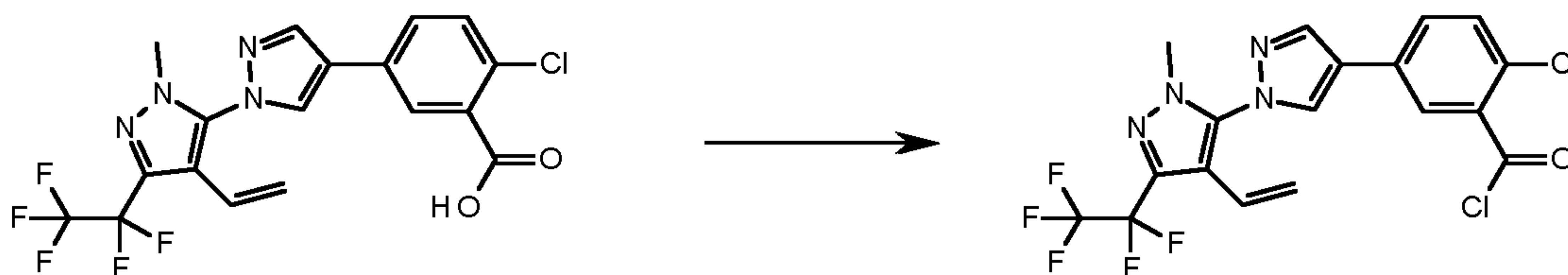


A mixture of 2-chloro-5-[1-[2-methyl-5-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazol-3-yl]pyrazol-4-yl]benzoic acid (158 mg, 0.353 mmol), 1-amino-1-cyano-cyclopropane hydrochloride (128 mg, 1.06 mmol), EDCI (86.47 mg, 0.44 mmol), HOAT (62 mg, 0.44 mmol) and triethylamine (161 mg, 1.6 mmol) in 5 ml DMF was stirred at RT for 16 hours. The mixture was diluted with ethyl acetate and water. The organic phase was washed successively with water and once with brine and a solution of hydrochloride acid (1N). The organic phase was dried over magnesium sulfate, filtrated and evaporated. The crude product was purified by chromatography to give 2-chloro-N-(1-cyanocyclopropyl)-5-[1-[2-methyl-5-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazol-3-yl]pyrazol-4-yl]benzamide as a white solid.

¹H NMR (400 MHz, CDCl₃) δ ppm 1.41 - 1.44 (m, 2 H) 1.68 - 1.72 (m, 2 H) 3.79 (s, 3 H) 4.92 (d, J=17.97 Hz, 1 H) 5.17 - 5.23 (m, 1 H) 6.49 (dd, J=17.79, 11.55 Hz, 1 H) 6.90 (s, 1 H) 7.45 (d, J=8.07 Hz, 1 H) 7.57 (dd, J=8.44, 2.20 Hz, 1 H) 7.90 (s, 1 H) 7.96 (d, J=2.20 Hz, 1 H) 8.14 (d, J=0.73 Hz, 1 H). LC-MS (Method B): t_R = 1.77 min, m/z = 509 [M-1], 511 [M+1].

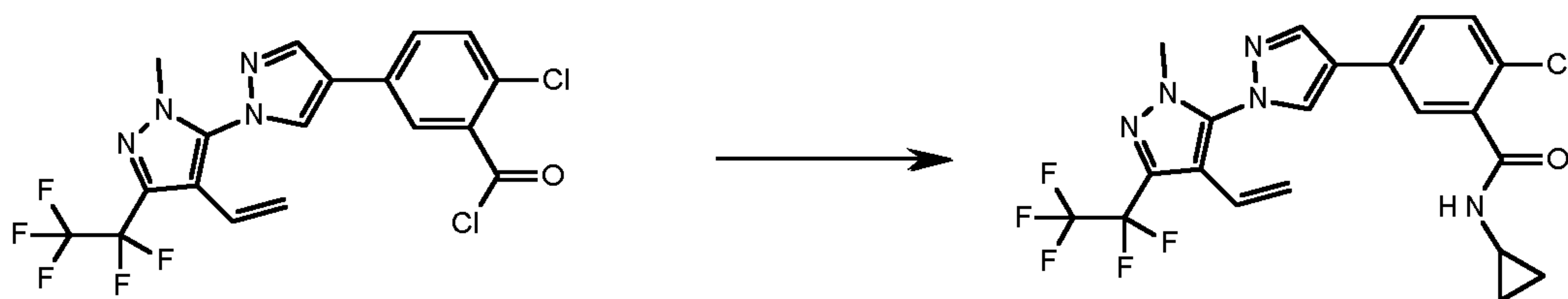
Example 16: Preparation of 2-Chloro-N-cyclopropyl-5-[1-[2-methyl-5-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazol-3-yl]pyrazol-4-yl]benzamide

a) Preparation of 2-Chloro-5-[1-[2-methyl-5-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazol-3-yl]pyrazol-4-yl]benzoyl chloride



To a suspension of 2-chloro-5-[1-[2-methyl-5-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazol-3-yl]pyrazol-4-yl]benzoic acid (example 3, step c; 50 mg, 0.111 mmol) in 5 ml dry dichloromethane was added sequentially oxalyl dichloride (2 ml) and one drops of DMF in argon atmosphere. The reaction mixture was stirred until gas evolution stopped. The solvent was removed under reduced pressure to dryness and the crude product was used directly for the next step.

b) Preparation of 2-Chloro-N-cyclopropyl-5-[1-[2-methyl-5-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazol-3-yl]pyrazol-4-yl]benzamide



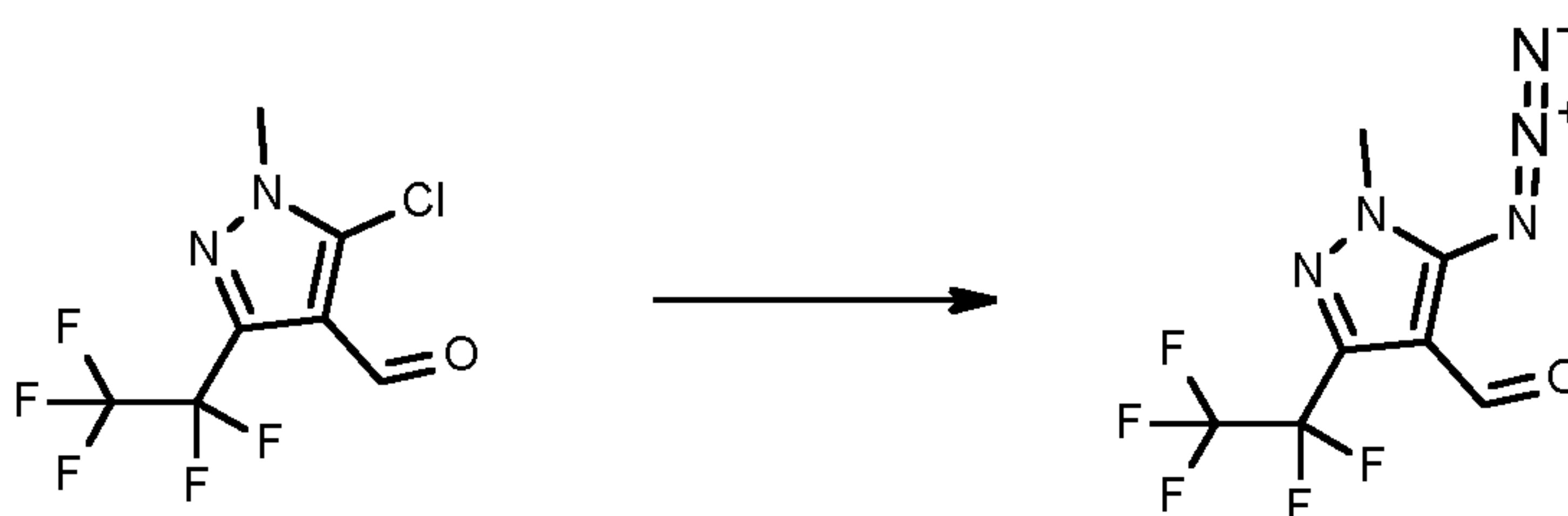
To a solution of cyclopropanamine (19 mg, 0.335 mmol) and 2-chloro-5-[1-[2-methyl-5-(1,1,2,2,2-pentafluoroethyl)-4-vinyl-pyrazol-3-yl]pyrazol-4-yl]benzoyl chloride (52 mg, 0.111 mmol) in 3 ml THF was added pyridine (44 mg, 0.0559 mmol) at RT. The reaction mixture was heated to 60°C for 16 hours. The mixture was diluted with water and ethyl acetate, washed with water/brine and with diluted hydrochloride acid (1N). The organic layer was dried over magnesium sulfate and evaporated under vacuum. The crude product was purified by flash chromatography to give a white solid.

¹H NMR (400 MHz, CDCl₃) δ ppm 0.66 - 0.70 (m, 2 H) 0.89 - 0.94 (m, 2 H) 2.91 - 2.97 (m, 1 H) 3.78 (s, 3 H) 4.88 - 4.95 (m, 1 H) 5.19 (dd, *J*=11.55, 0.92 Hz, 1 H) 6.40 (br. s., 1 H) 6.49 (dd, *J*=17.97, 11.37 Hz, 1 H) 7.41 - 7.45 (m, 1 H) 7.49 - 7.53 (m, 1 H) 7.87 (d, *J*=0.73 Hz, 2 H) 8.13 (d, *J*=0.73 Hz, 1 H).

LC-MS (Method B): *t_R* = 1.86 min, *m/z* = 484 [M-1], 486 [M+1].

Example 64: Preparation of 2-Chloro-N-(1-cyanocyclopropyl)-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]triazol-4-yl]benzamide

a) Preparation of 5-Azido-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazole-4-carbaldehyde

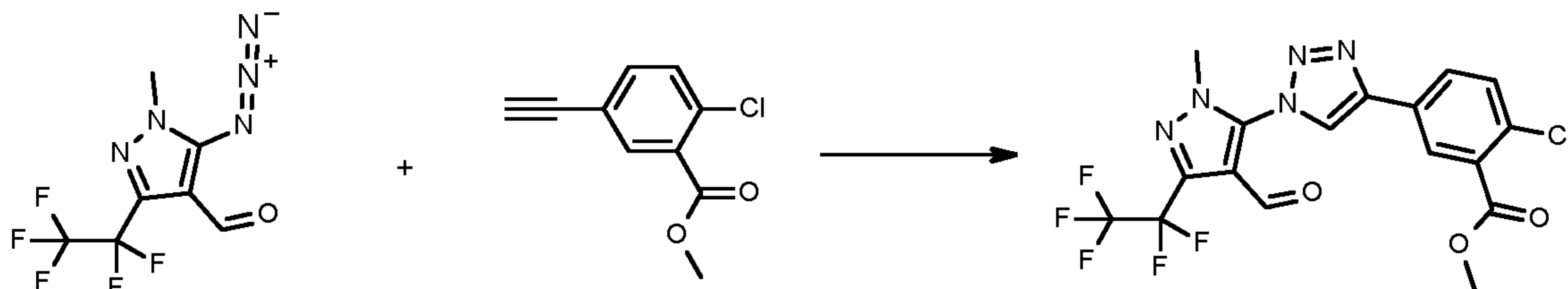


5-Chloro-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazole-4-carbaldehyde (1.0 g, 3.8 mmol) was dissolved in dimethyl sulfoxide (5.0 ml), then sodium azide (0.28 g, 4.2 mmol) was added. The mixture was stirred at RT overnight (18h). The mixture was diluted with diethyl ether, washed with water and brine, the organic layers were dried over magnesium sulfate and evaporated under vacuum to obtain the crude product which was taken forward to the next step.

¹H NMR (400 MHz, CDCl₃) δ ppm 3.78 (s, 3 H), 9.92 (s, 1 H).

LC-MS (Method A): *t_R* = 1.00 min.

b) Preparation of Methyl 2-chloro-5-[1-[4-formyl-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]triazol-4-yl]benzoate



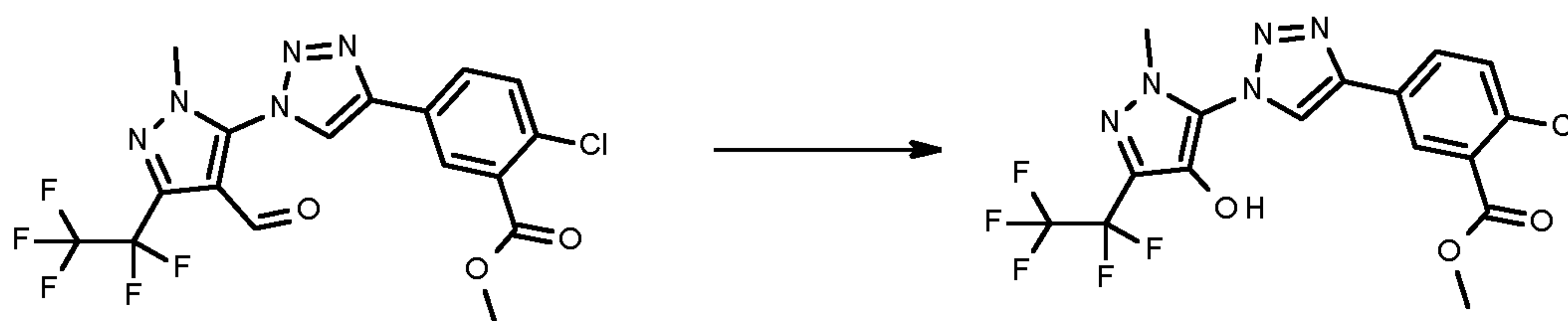
5

To a solution of 5-azido-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazole-4-carbaldehyde (1.0 g, 3.7 mmol) in a mixture of tert-butanol (4 ml) and water (2 ml) were added methyl 2-chloro-5-ethynylbenzoate (0.60 g, 3.1 mmol), L-Ascorbic acid sodium salt (0.062 g, 0.31 mmol) and copper(II) sulfate pentahydrate (0.0049 g, 0.031 mmol). The mixture was stirred at RT overnight (18h). The mixture was diluted with ethyl acetate, washed with water and brine, the organic layer were dried over magnesium sulfate, filtered and evaporated under vacuum. The crude product was purified by flash chromatography (Silica, Cyclohexane / gradient of ethyl acetate 0 to 25%) to afford a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ ppm 3.99 (s, 3 H), 4.08 (s, 3 H), 7.61 (d, *J*=8.4 Hz, 1 H), 8.02 (dd, *J*=8.4, 2.2 Hz, 1 H), 8.38 (d, *J*=2.2 Hz, 1H), 8.50 (s, 1H), 10.03 (s, 1 H).

LC-MS (Method A): *t_R* = 1.12 min, *m/z* = 464 [M+1].

c) Preparation of Methyl 2-chloro-5-[1-[4-hydroxy-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]triazol-4-yl]benzoate



20

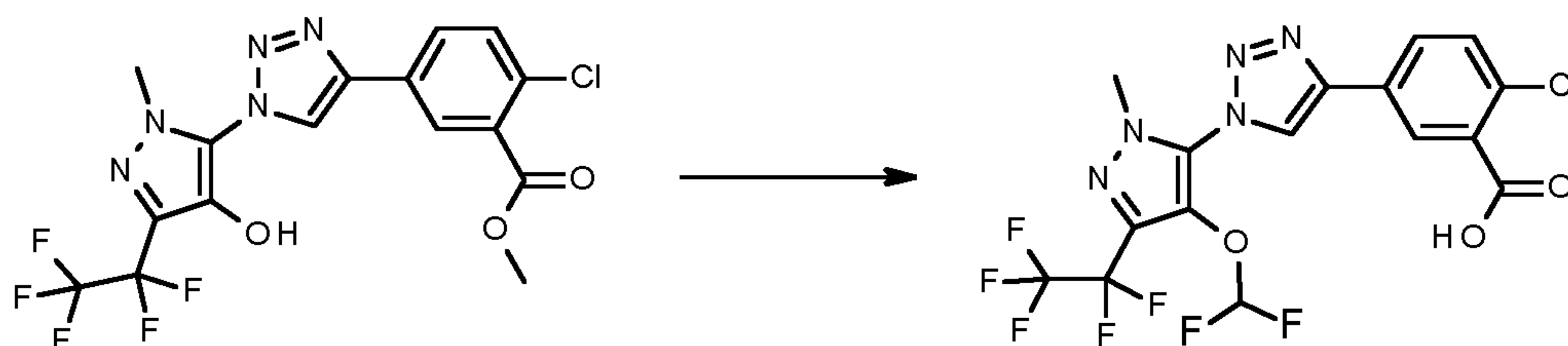
To a stirred solution of methyl 2-chloro-5-[1-[4-formyl-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]triazol-4-yl]benzoate (1.5 g, 3.2 mmol) in trifluoroacetic acid (4.2 ml) was added urea hydrogen peroxide (0.63 g, 6.5 mmol) in 5 portions over a period of 25 minutes at RT under argon. The reaction mixture was stirred at RT for 2 h and then at 40 °C for 1 h. The mixture was diluted with ethyl acetate, and consecutively washed with water, aqueous solutions of sodium hydrogen carbonate and saturated sodium metabisulfite solutions. The organic layer were dried over magnesium sulfate, filtered and evaporated under vacuum. The residue was purified by flash chromatography to give the title compound as a yellow solid.

25

^1H NMR (400 MHz, CDCl_3) δ ppm 3.99 (2x overlapped s, 6 H), 5.35 (br. s, 1H), 7.59 (d, $J=8.4$ Hz, 1 H), 7.97 (dd, $J=8.4, 2.2$ Hz, 1 H), 8.22 (s, 1H), 8.31 (d, $J=2.2$ Hz, 1H).

LC-MS (Method A): t_R = 1.04 min, m/z = 450 [M-1], 452 [M+1].

5 d) Preparation of 2-Chloro-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]triazol-4-yl]benzoic acid



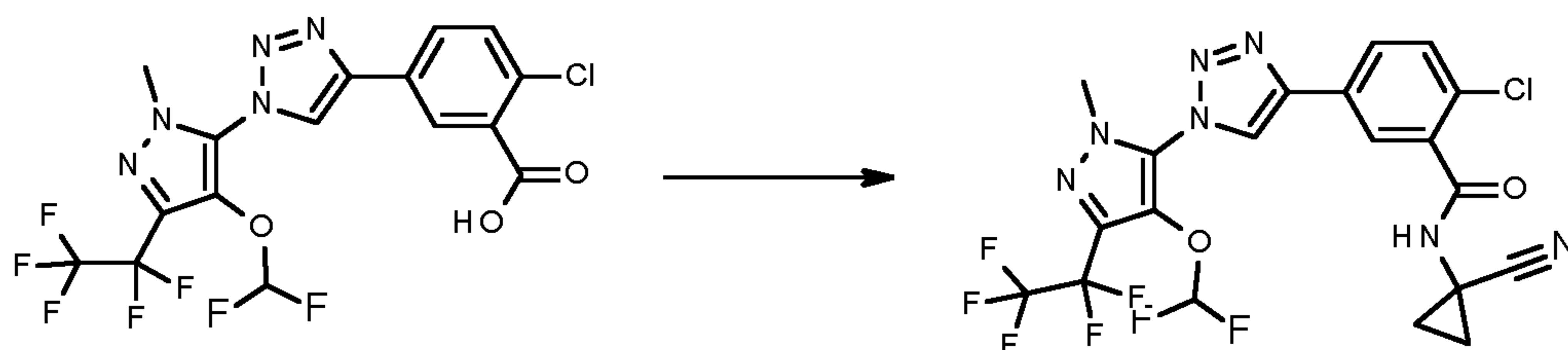
10 To a stirred solution of 2-chloro-5-[1-[4-hydroxy-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]triazol-4-yl]benzoate (0.24 g, 0.53 mmol) and potassium hydroxide (0.6 g, 11 mmol) in a mixture of acetonitrile/water = 1:1 (10.6 ml) cooled to -78°C was added diethyl (bromodifluoromethyl)phosphonate (0.29 g, 1.1 mmol). The reaction mixture was allowed to warm to RT and then it was stirred at this temperature over a weekend. The conversion was monitored by GCMS and UPLC. The reaction mixture was diluted with ethyl acetate and then consecutively washed with 1N HCl, water and brine. The organic layer was dried over magnesium sulfate, filtered and evaporated under vacuum to afford the title compound which was used in the next step without further purification.

^1H NMR (400 MHz, CDCl_3) δ ppm 3.98 (s, 3 H), 6.37 (t, $J=72.6$ Hz, 1H), 7.64 (d, $J=8.4$ Hz, 1 H), 8.08 (dd, $J=8.4, 2.2$ Hz, 1 H), 8.22 (s, 1H), 8.47 (d, $J=2.2$ Hz, 1H).

20 LC-MS (Method A): t_R = 1.04 min, m/z = 486 [M-1], 488 [M+1].

e) Preparation of 2-Chloro-N-(1-cyanocyclopropyl)-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]triazol-4-yl]benzamide

25



Oxalyl chloride (0.07 g, 0.53 mmol) was dissolved in dry dichloromethane (2.7 ml) followed by the addition of 1 drop of dimethylformamide and 2-chloro-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-

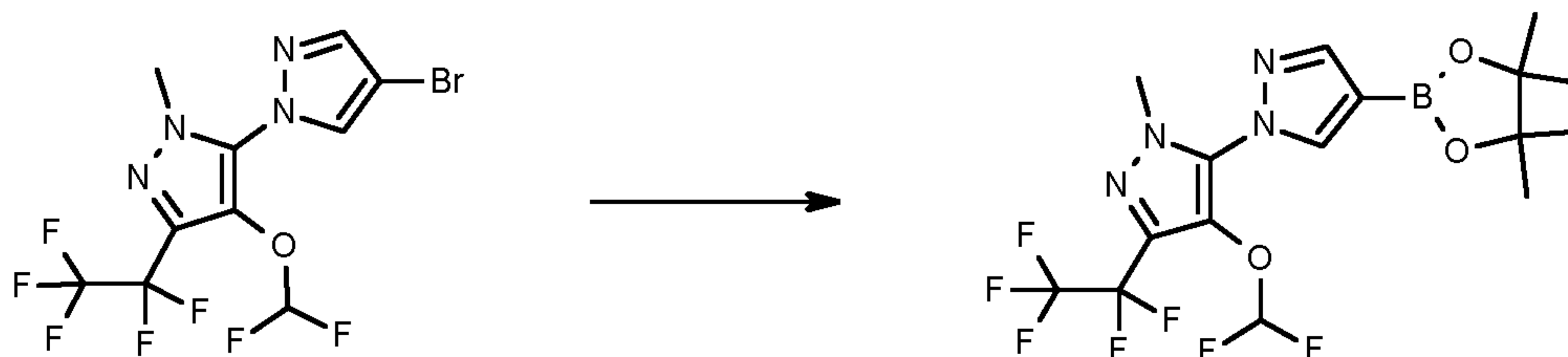
pentafluoroethyl)pyrazol-3-yl]triazol-4-yl]benzoic acid (0.13 g, 0.27 mmol). The reaction mixture was stirred at RT for 30 minutes and then at 35°C for 10 minutes. Afterwards the mixture was evaporated to dryness. The remaining acid chloride was dissolved in dry pyridine (1.3 ml) and 1-amino-1-cyano-cyclopropane hydrochloride (0.047 g, 0.40 mmol) was added at 0°C. The reaction mixture was stirred at

RT for 1h. The product was isolated by flash chromatography.
¹H NMR (400 MHz, CDCl₃) δ ppm 1.44 (m, 2 H), 1.72 (m, 2H), 3.99 (s, 3 H), 6.37 (t, *J*=72.4 Hz, 1H), 6.90 (br s, 1H), 7.56 (d, *J*=8.4 Hz, 1 H), 8.08 (dd, *J*=8.4, 2.2 Hz, 1 H), 8.21 (d, *J*=2.2 Hz, 1H), 8.22 (s, 1H), 8.47 (d, *J*=2.2 Hz, 1H).

LC-MS (Method A): *t*_R = 1.05 min, *m/z* = 550 [M-1], 552 [M+1].

Example 54: Preparation of 2-Chloro-N-cyclopropyl-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]-N-methyl-pyridine-3-carboxamide

a) Preparation of 4-(Difluoromethoxy)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)-5-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrazol-1-yl]pyrazole

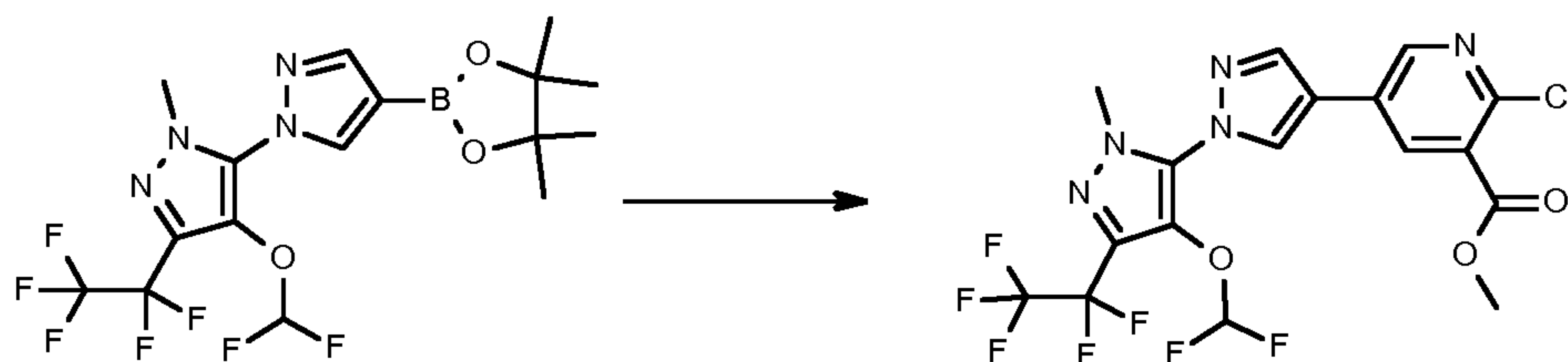


A microwave tube was charged with 5-(4-bromopyrazol-1-yl)-4-(difluoromethoxy)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)pyrazole (8.0 g, 18 mmol), 4,4,5,5-tetramethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolane (5.6 g, 22 mmol), potassium acetate (5.4 g, 55 mmol) and dioxane (37 ml). After purging with argon, Pd(PPh₃)₄ (1.1 g, 0.91 mmol) was added. The tube was sealed up and heated in the microwave reactor to 140 °C for 45 min. The reaction mixture was taken up in ethyl acetate, washed with water and brine. The organic layer were dried over magnesium sulfate, filtered and evaporated under vacuum to obtain the crude product which was used directly in the next step.

¹H NMR (400 MHz, CDCl₃) δ ppm 1.36 (s, 12 H), 3.85 (s, 3 H), 6.28 (t, *J*=72.8 Hz, 1H), 8.01 (s, 1H), 8.07 (s, 1H).

LC-MS (Method A): *t*_R = 1.18 min, *m/z* = 457 [M-1], 459 [M+1].

b) Preparation of Methyl 2-chloro-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]pyridine-3-carboxylate

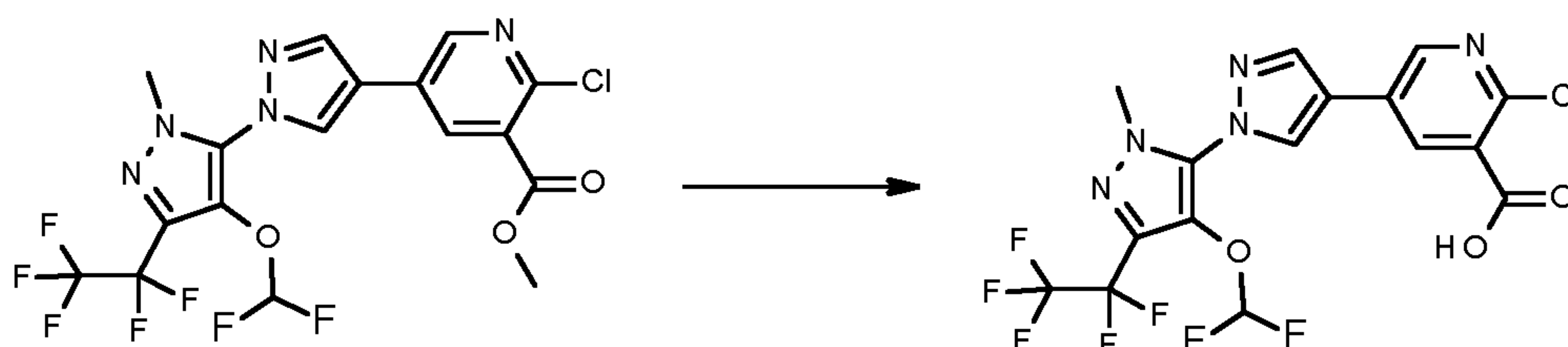


5 A microwave tube was charged with 4-(difluoromethoxy)-1-methyl-3-(1,1,2,2,2-pentafluoroethyl)-5-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrazol-1-yl]pyrazole (3.1 g, 4.4 mmol), methyl 5-bromo-2-chloro-pyridine-3-carboxylate (1.0 g, 4.0 mmol), tetrahydrofuran (53 ml), water (5.9 ml) and potassium hydrocarbonate (1.2 g, 12 mmol). After purging with argon, Pd(dppf)₂Cl₂ (0.17 g, 0.20 mmol, 0.050) was added. The tube was sealed up and heated in the microwave reactor to 120 °C for 45 min. The reaction mixture was taken up in ethyl acetate and filtered over a celite pad. The filtrate was washed with water and brine. The organic layer was dried over magnesium sulfate, filtered and evaporated under vacuum. The crude product was purified by flash chromatography (Silica, Cyclohexane / gradient of ethyl acetate 0 to 30%).

¹H NMR (400 MHz, CDCl₃) δ ppm 3.95 (s, 3 H), 4.02 (s, 3 H), 6.33 (t, *J*=73.0 Hz, 1H), 8.11 (s, 1H), 8.17 (s, 1H), 8.30 (d, *J*=2.6 Hz, 1H), 8.71 (d, *J*=2.6 Hz, 1H).

LC-MS (Method A): *t*_R = 1.12 min, *m/z* = 502 [M+1].

c) Preparation of 2-chloro-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]pyridine-3-carboxylic acid

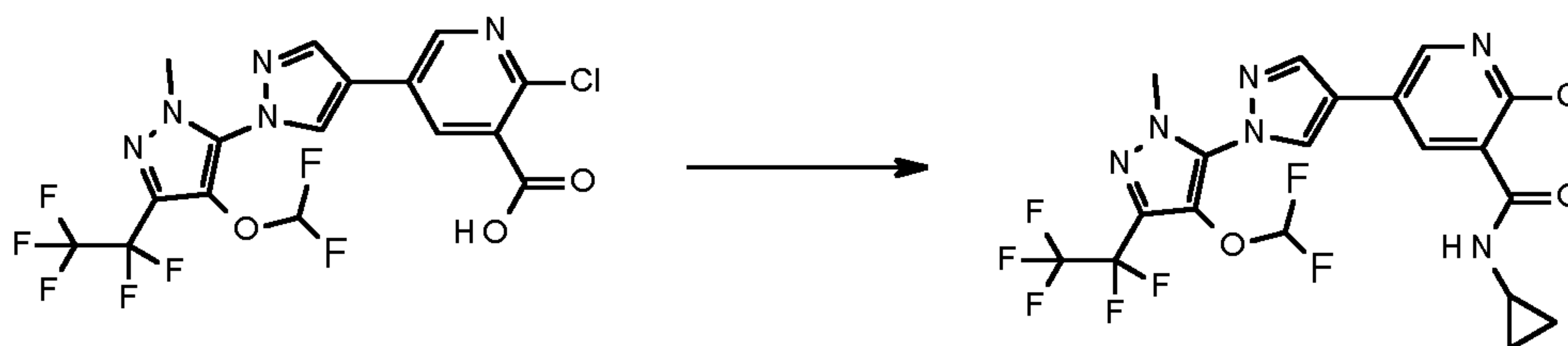


Methyl 2-chloro-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]pyridine-3-carboxylate (1.4 g, 2.8 mmol) was dissolved in tetrahydrofuran (14 mL). Water (3 mL) and lithium hydroxide monohydrate (0.29 g, 7.0 mmol, 2.5) were subsequently added and the mixture was stirred at RT for 1 h. Most of tetrahydrofuran was removed by rotary evaporation. The aqueous residue was acidified at 0°C with 32 % HCl and the product was extracted with ethyl acetate. The extract was washed with water and brine, dried over magnesium sulfate, filtered and evaporated to result in a yellow solid which was used as is in the next step.

^1H NMR (400 MHz, CDCl_3) δ ppm 3.96 (s, 3 H), 6.34 (t, $J=73.0$ Hz, 1H), 8.13 (s, 1H), 8.19 (s, 1H), 8.44 (d, $J=2.6$ Hz, 1H), 8.77 (d, $J=2.6$ Hz, 1H).

LC-MS (Method A): t_R = 1.00 min, m/z = 486 [M-1], 488 [M+1].

5 d) Preparation of 2-Chloro-N-cyclopropyl-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]pyridine-3-carboxamide



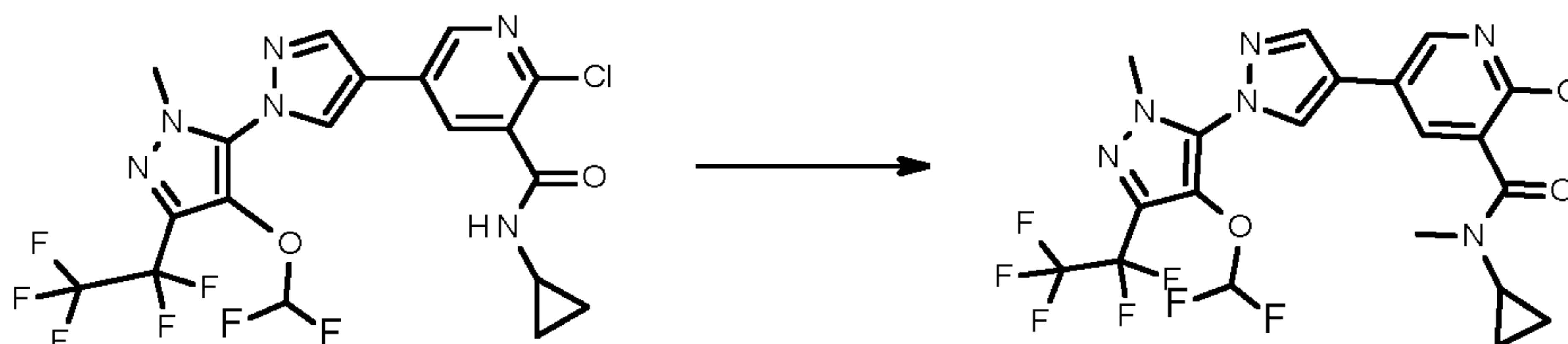
10 Oxalyl chloride (0.30 g, 2.3 mmol) was dissolved in dry dichloromethane (11 ml) followed by the addition of 1 drop of dimethylformamide and 2-chloro-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]pyridine-3-carboxylic acid (0.55 g, 1.1 mmol). The reaction mixture was stirred at RT for 30 minutes and then at 35°C for 10 minutes. Afterwards the mixture was evaporated to dryness. The remaining acid chloride was dissolved in dry pyridine (6 ml) and

15 cyclopropylamine (0.13 g, 2.3 mmol) was added at 0°C. The reaction mixture was stirred at RT for 1h. The product was isolated by flash chromatography.

^1H NMR (400 MHz, CDCl_3) δ ppm 0.71 (m, 2H), 0.95 (m, 2H), 2.98 (m, 1H), 3.95 (s, 3 H), 6.33 (t, $J=72.8$ Hz, 1H), 6.69 (br s, 1H), 8.10 (s, 1H), 8.17 (s, 1H), 8.29 (d, $J=2.6$ Hz, 1H), 8.64 (d, $J=2.6$ Hz, 1H).

LC-MS (Method A): t_R = 1.02 min, m/z = 525 [M-1], 527 [M+1].

20 e) Preparation of 2-Chloro-N-cyclopropyl-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]-N-methyl-pyridine-3-carboxamide



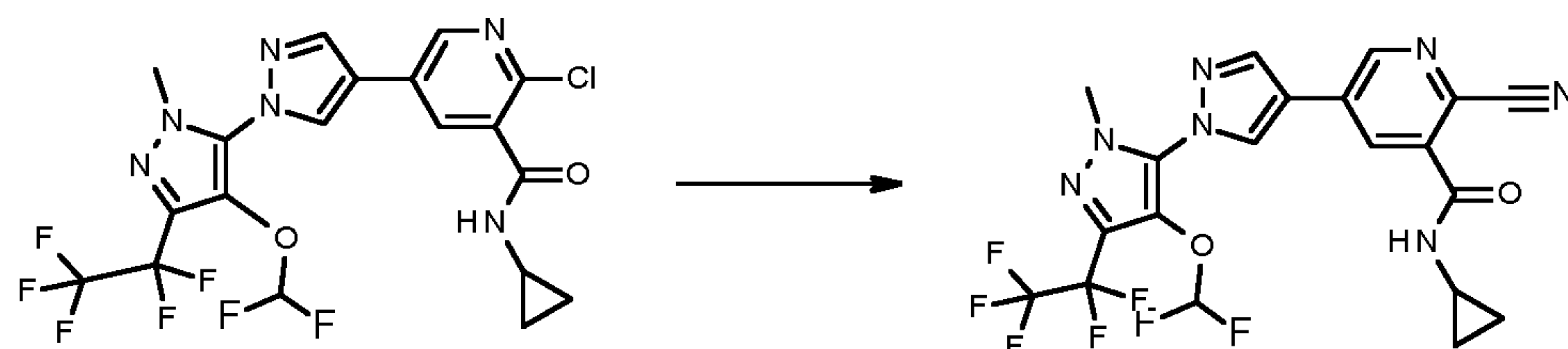
To a solution of 2-chloro-N-cyclopropyl-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]pyridine-3-carboxamide (0.15 g, 0.28 mmol) in N,N-dimethylformamide sodium hydride (0.014 g, 0.36 mmol, 60% dispersion in mineral oil) was added at

30 RT. The reaction mixture was stirred at RT for 30 minutes followed by the addition of iodomethane

(0.081 g, 0.57 mmol). The reaction mixture was stirred overnight at RT. The product was isolated by flash chromatography.

LC-MS (Method A): t_R = 1.08 min, m/z = 541 [M+1].

5 Example 49: Preparation of 2-Cyano-N-cyclopropyl-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]pyridine-3-carboxamide



A microwave tube was charged with 2-chloro-N-cyclopropyl-5-[1-[4-(difluoromethoxy)-2-methyl-5-(1,1,2,2,2-pentafluoroethyl)pyrazol-3-yl]pyrazol-4-yl]pyridine-3-carboxamide (0.05, 0.095 mmol), zinc cyanide (0.011 g, 0.095 mmol), zinc powder (1 mg, 0.011 mmol), 1,1'-bis(diphenylphosphino)ferrocene (2.1 mg, 0.0038 mmol), tris(dibenzylideneacetone)dipalladium(0) (1.8 mg, 0.0019 mmol) and dry N,N-dimethylacetamide (2.0 mL). The mixture was purged with argon, the tube was sealed up and heated in the microwave reactor to 140 °C for 1 h. The crude reaction mixture was subjected to flash chromatography on silica. The product decomposed on silica resulting in a product with the same molecular mass.

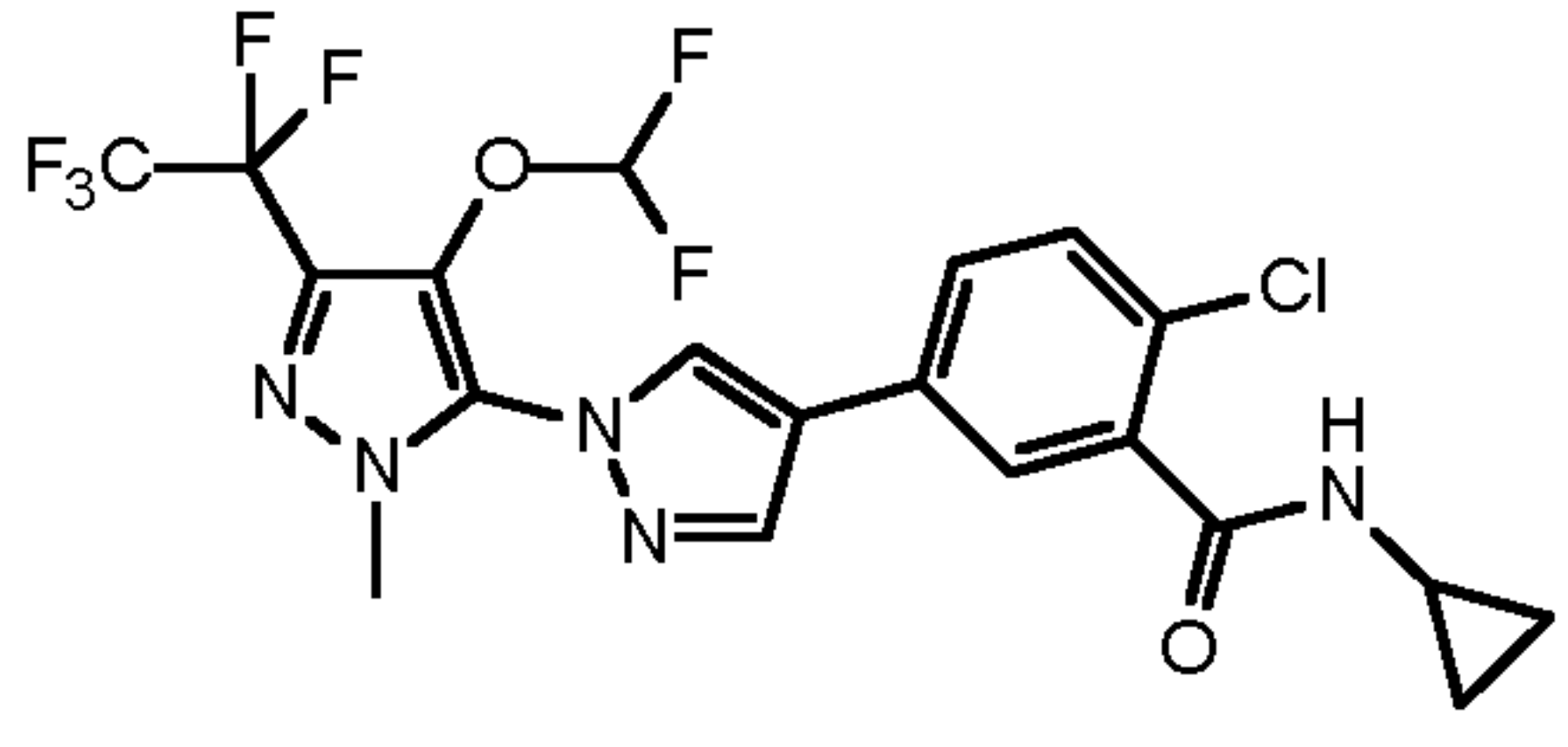
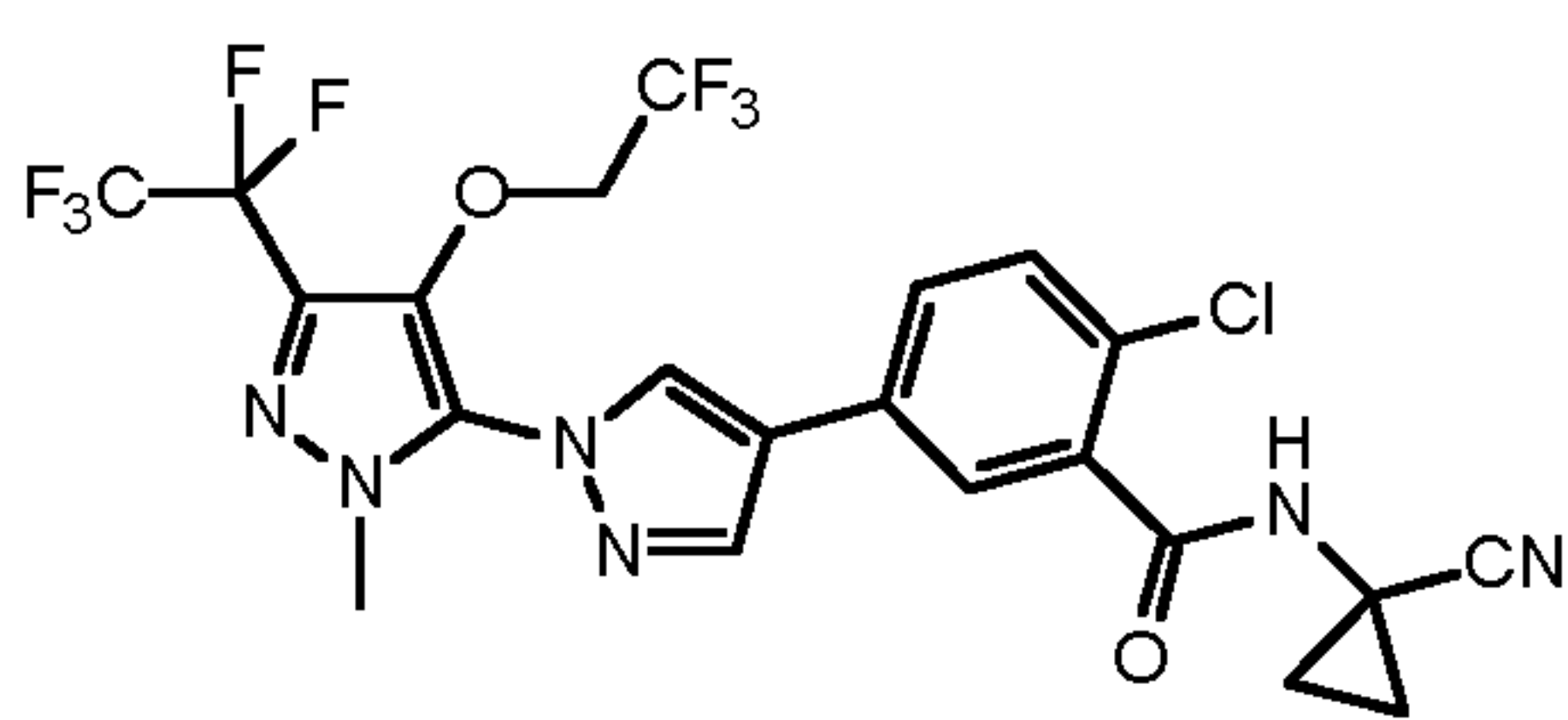
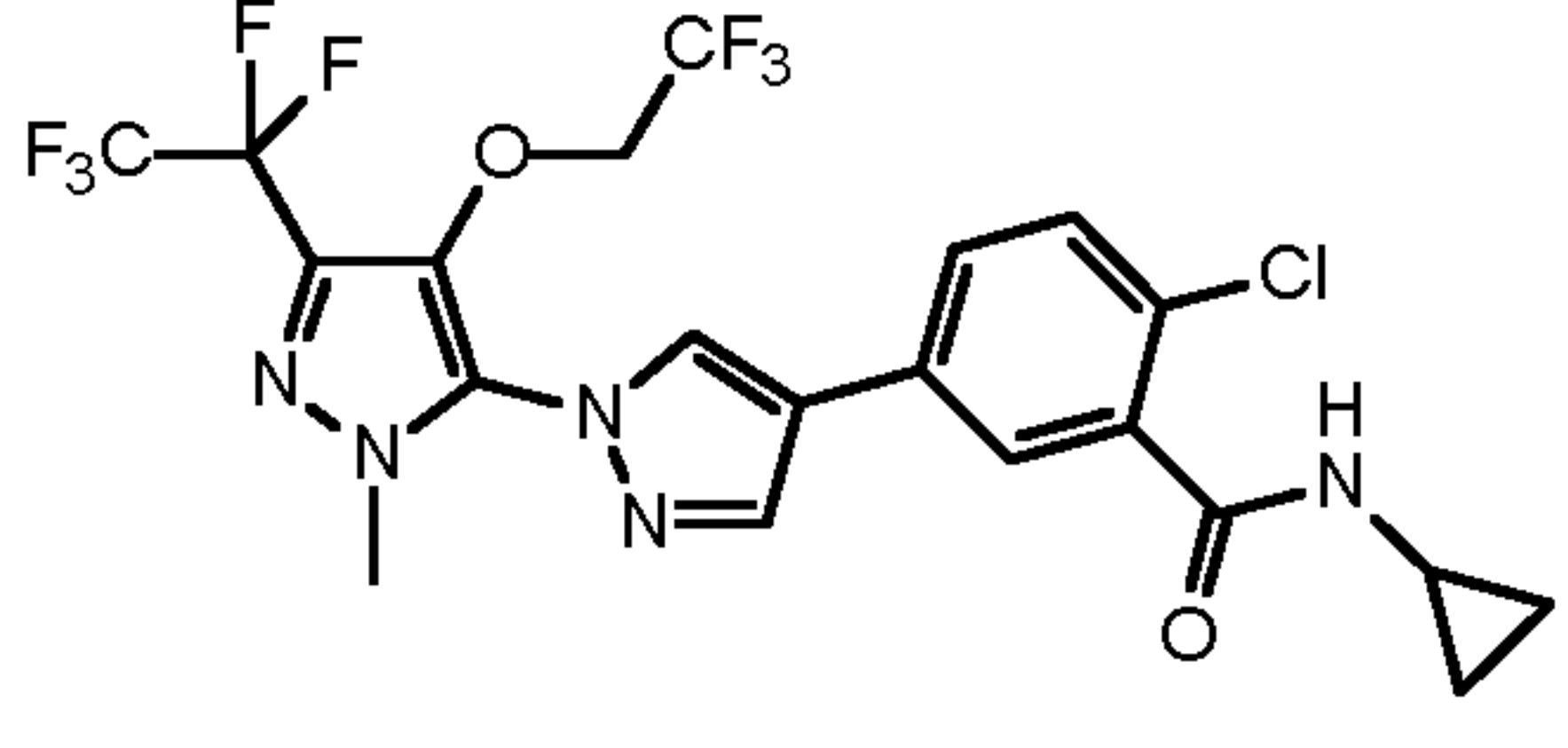
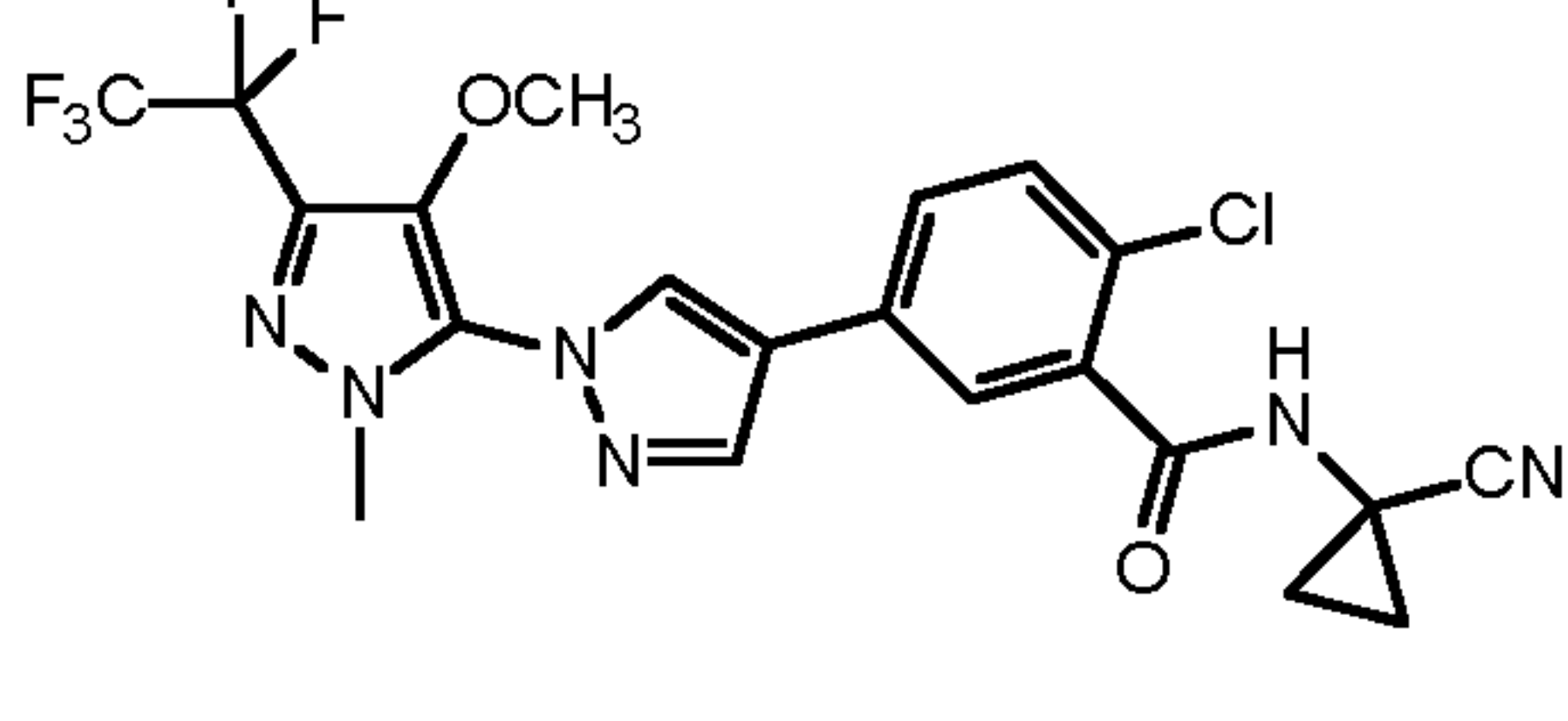
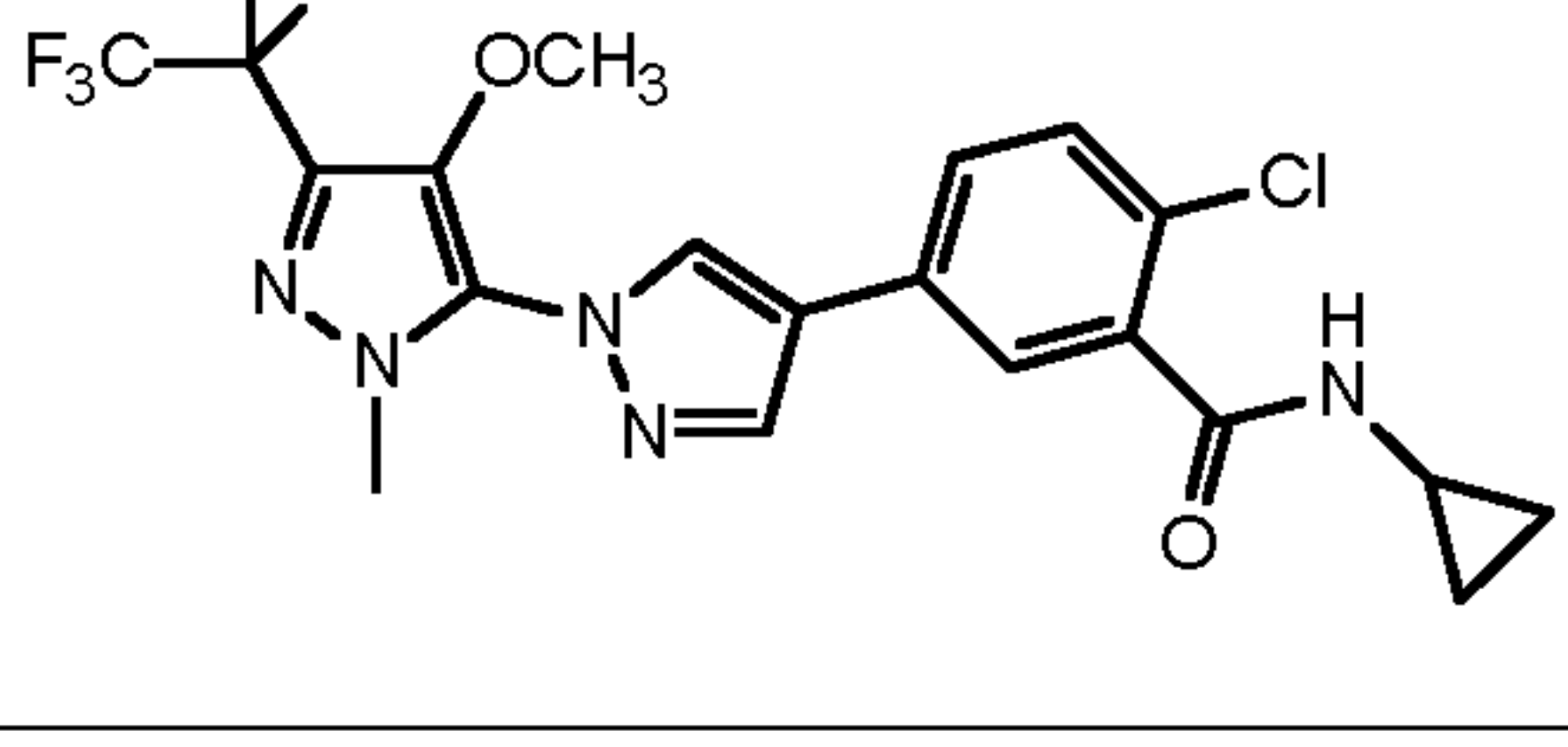
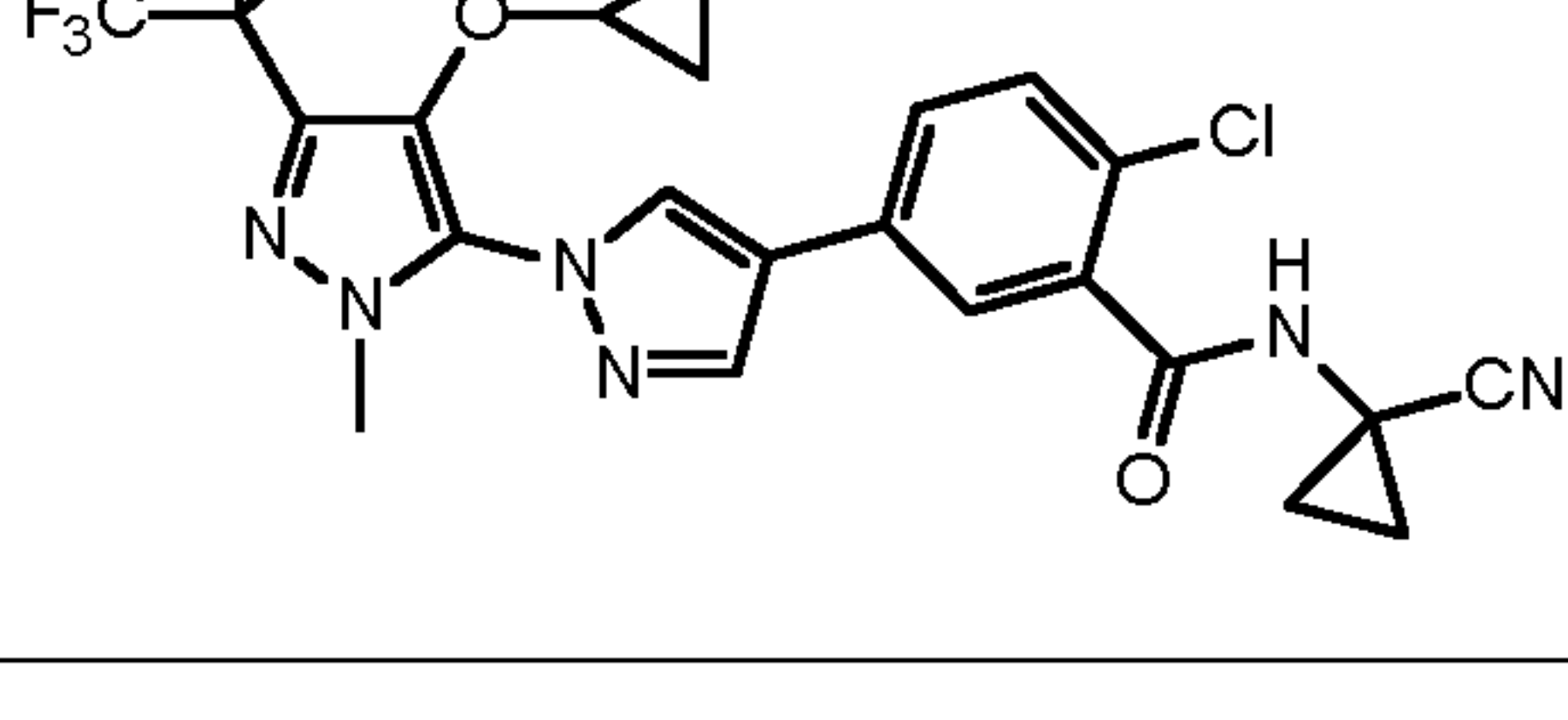
^1H NMR (400 MHz, CDCl_3) δ ppm 1.05 – 1.15 (m, 4H), 2.82 (m, 1H), 3.97 (s, 3 H), 6.35 (t, $J=72.8$ Hz, 1H), 8.21 (s, 1H), 8.25 (d, $J=1.8$ Hz, 1H), 8.26 (s, 1H), 9.14 (d, $J=2.2$ Hz, 1H).

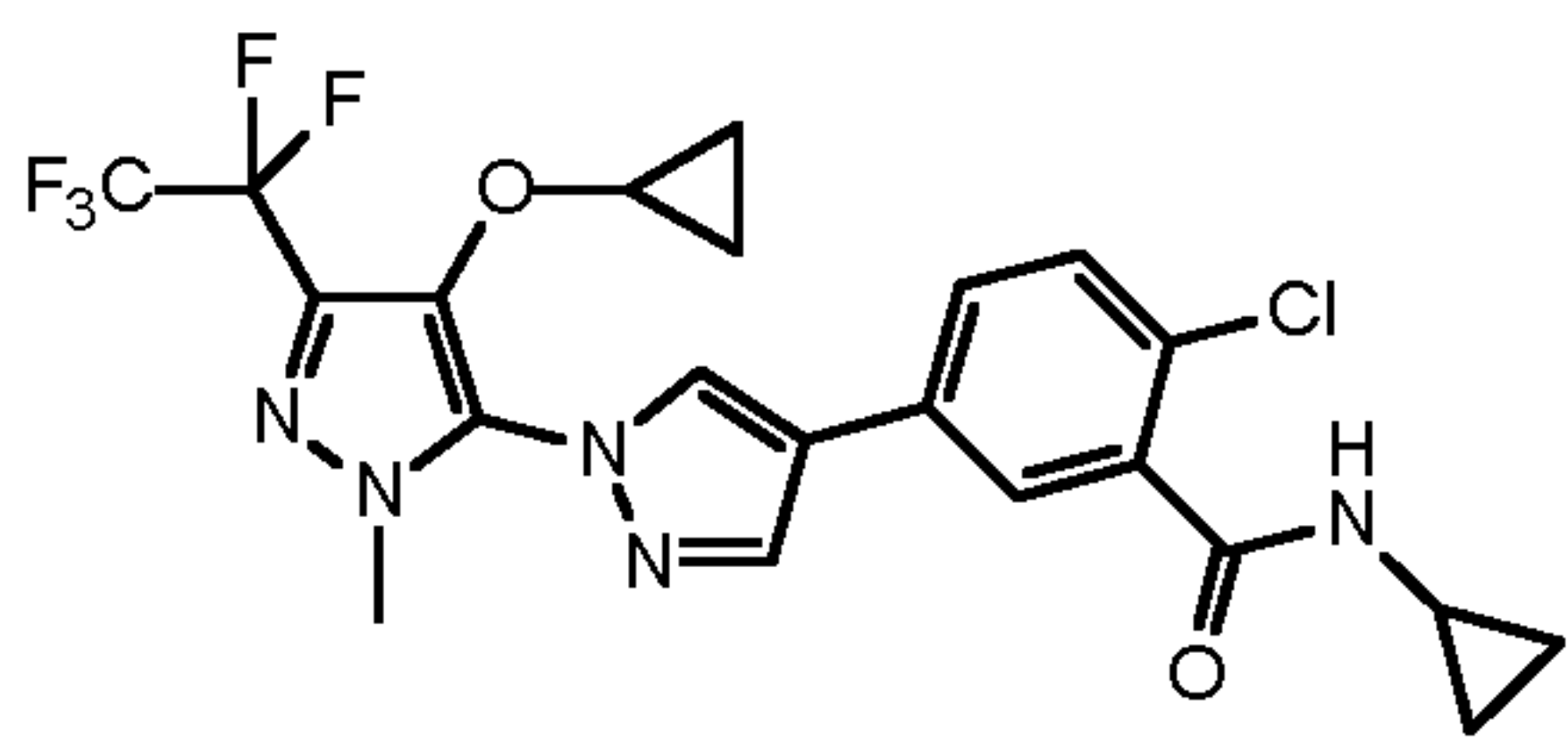
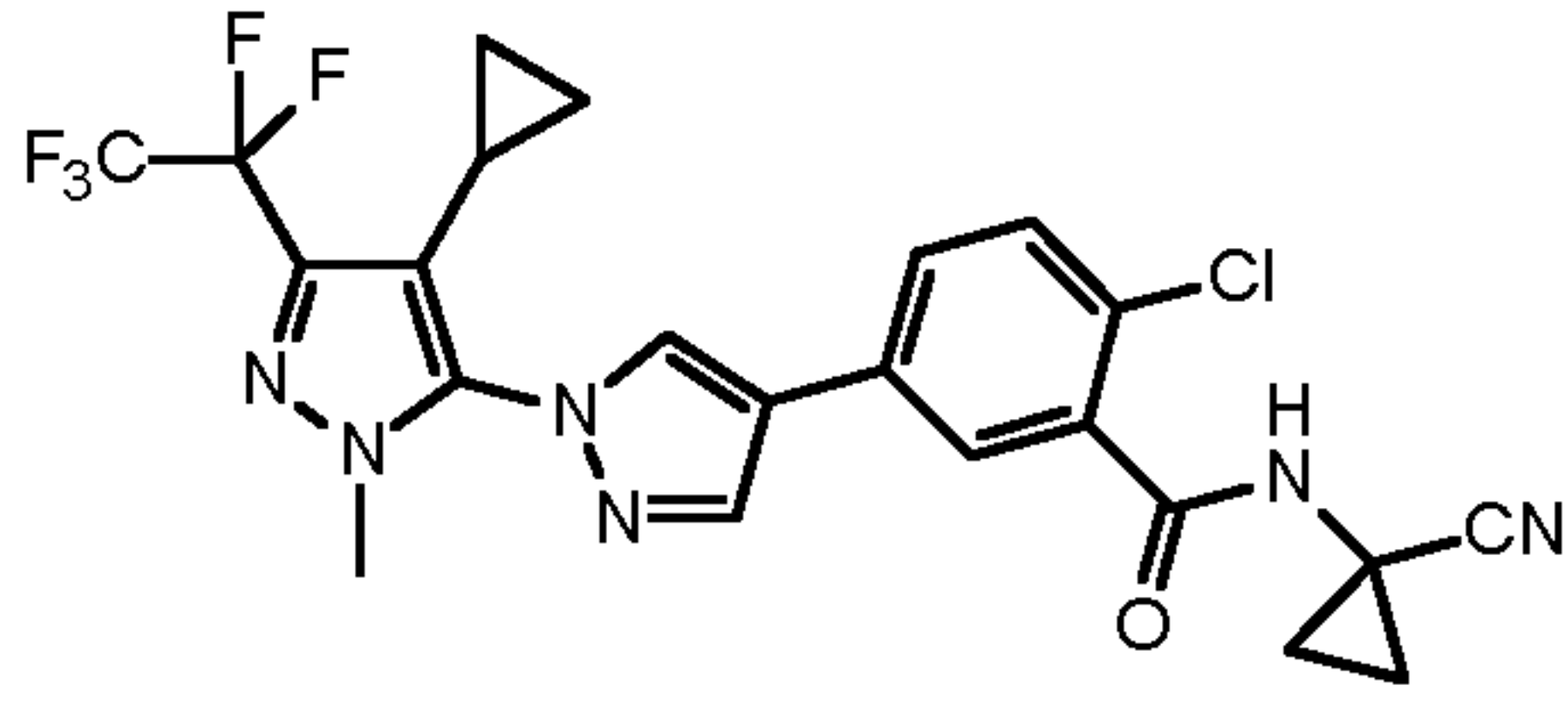
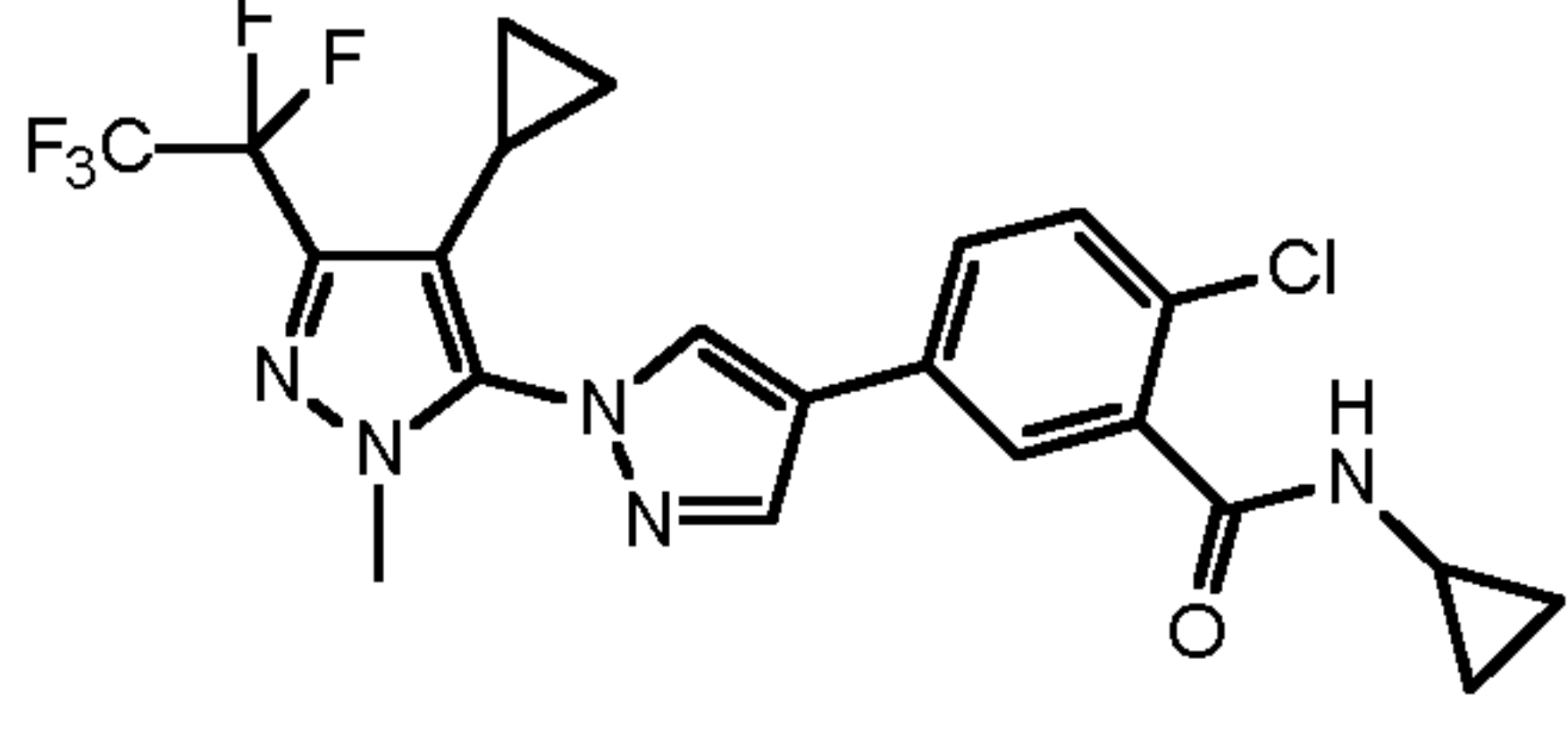
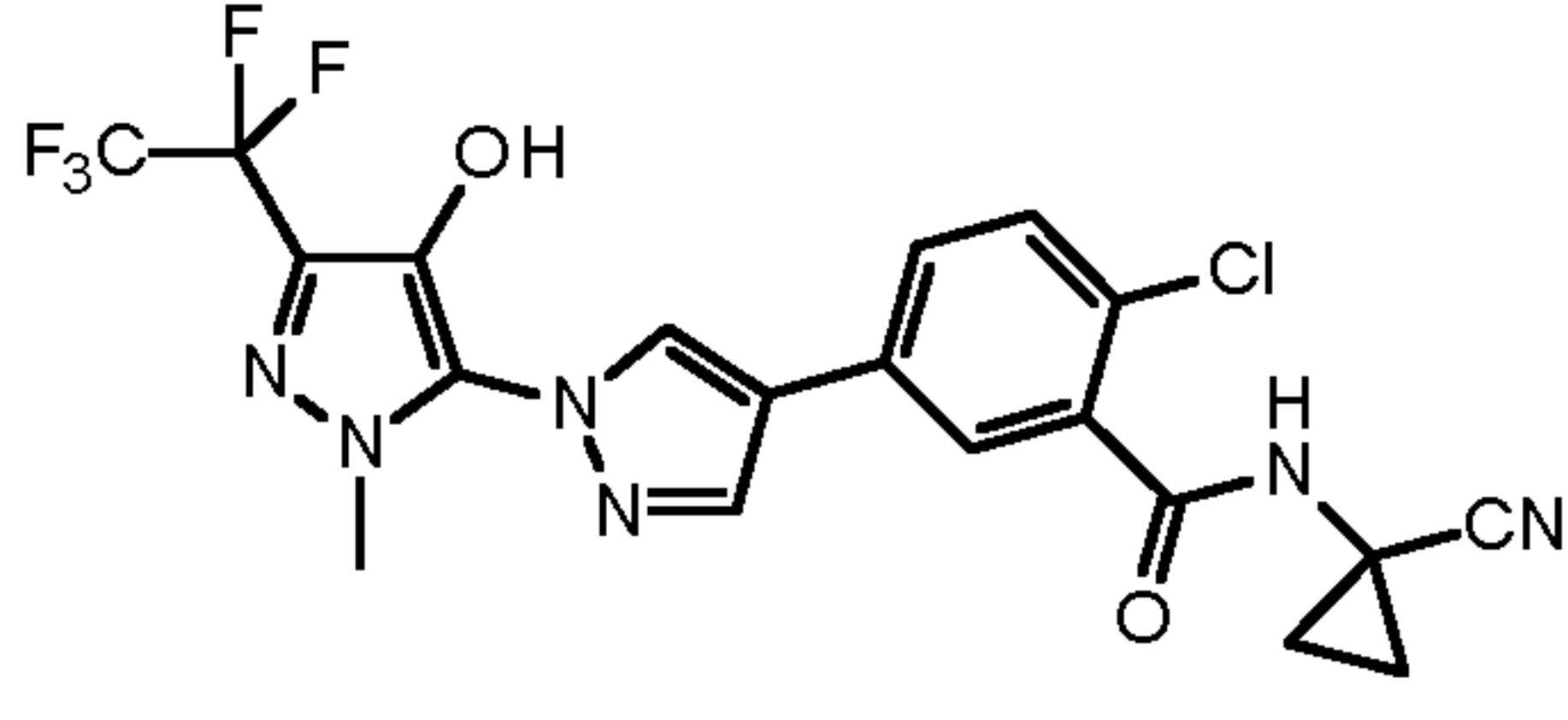
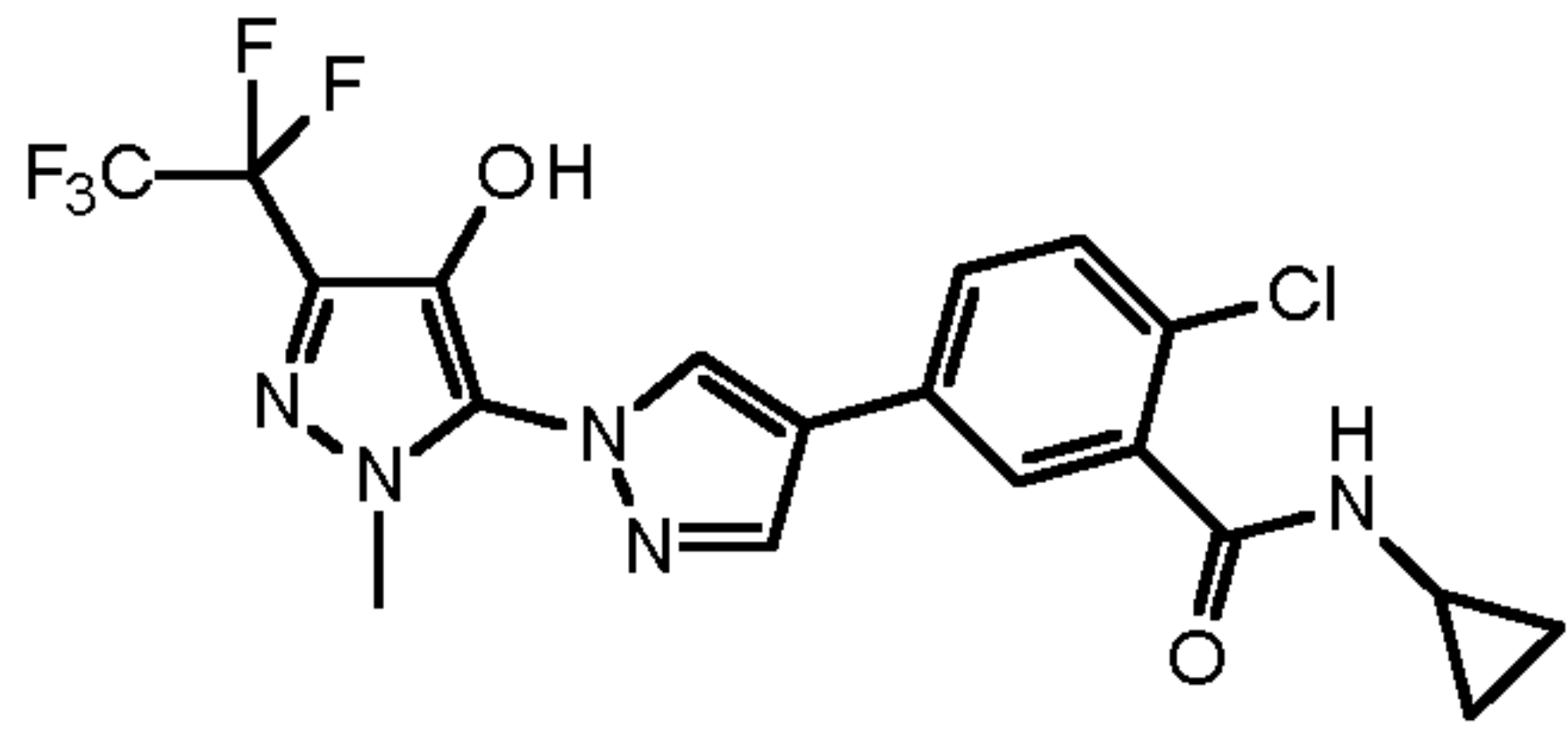
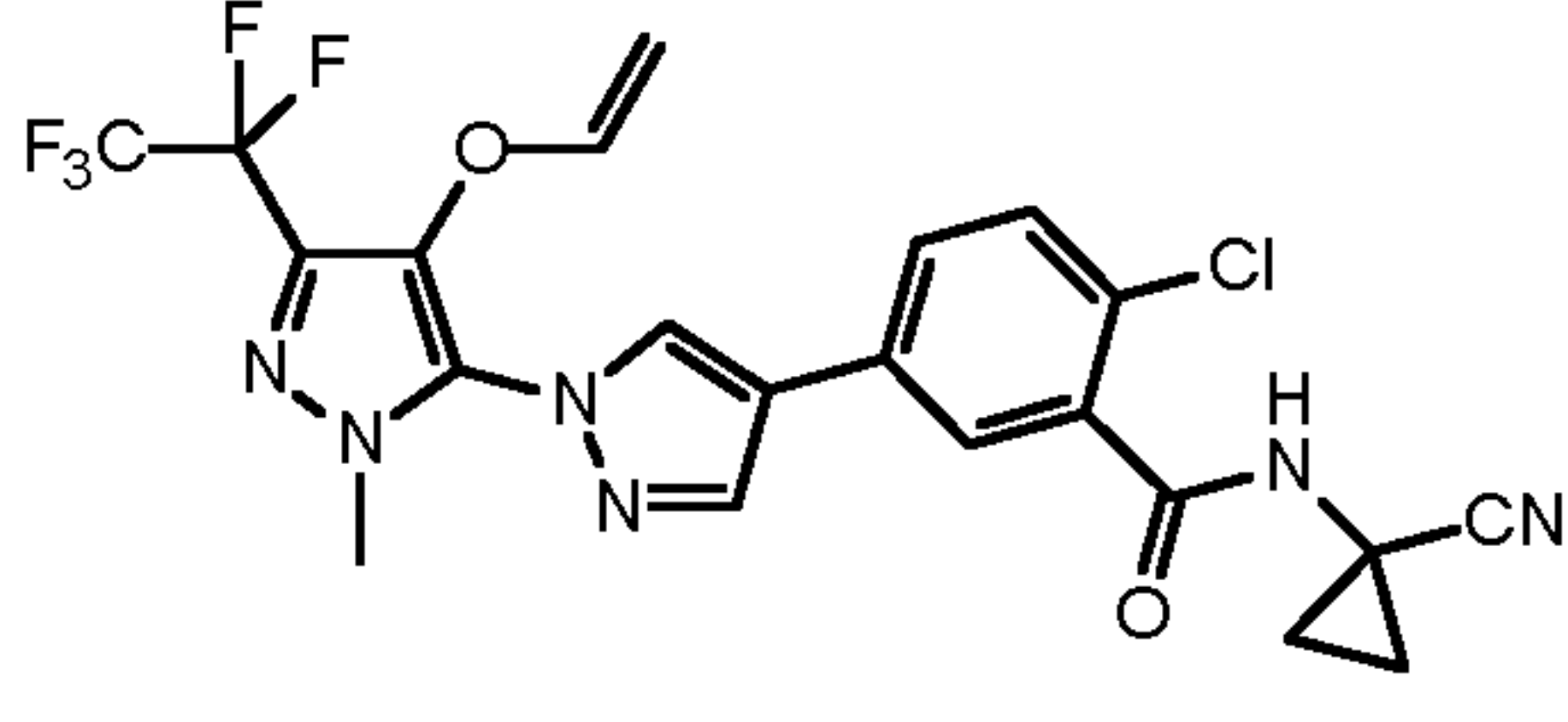
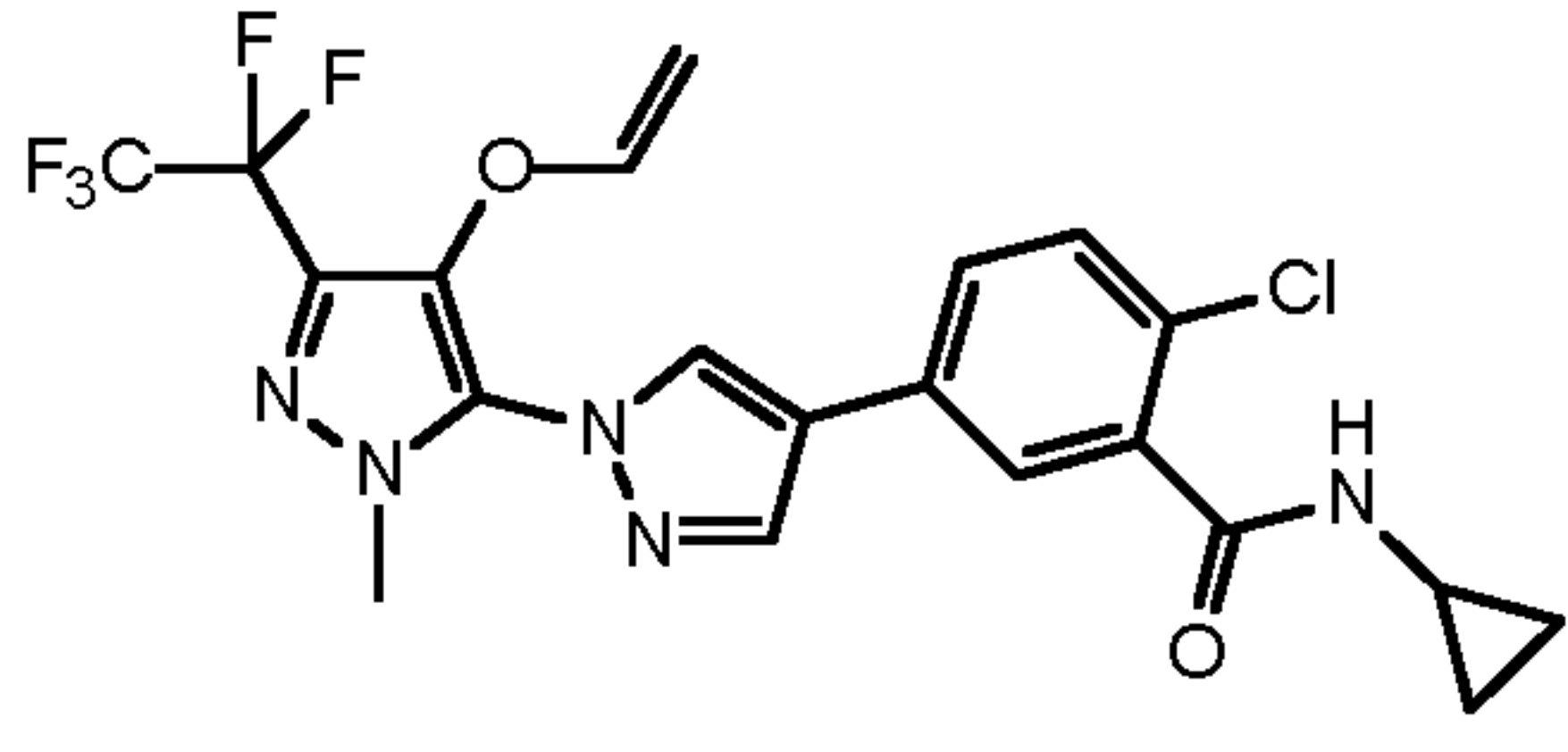
LC-MS (Method A): t_R = 1.02 min, m/z = 516 [M-1], 518 [M+1].

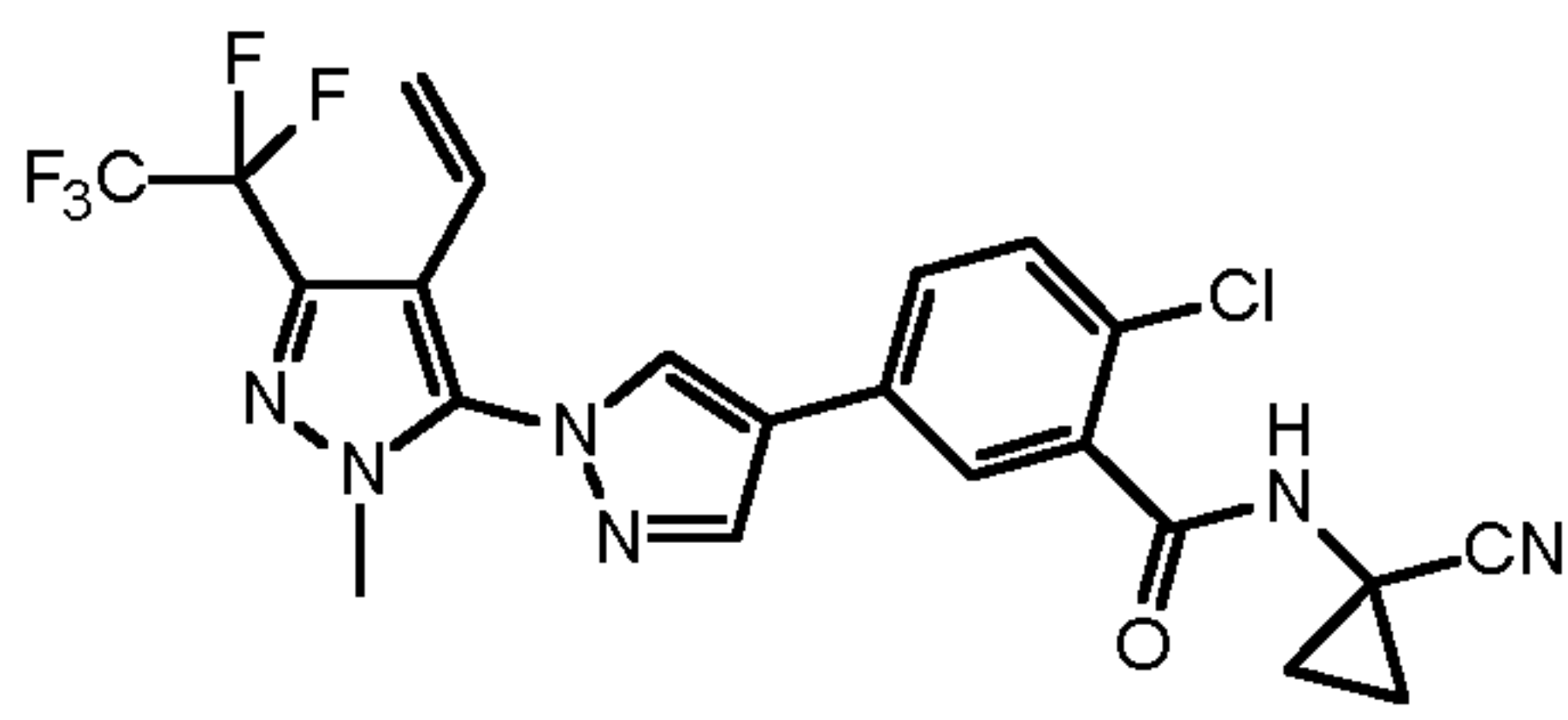
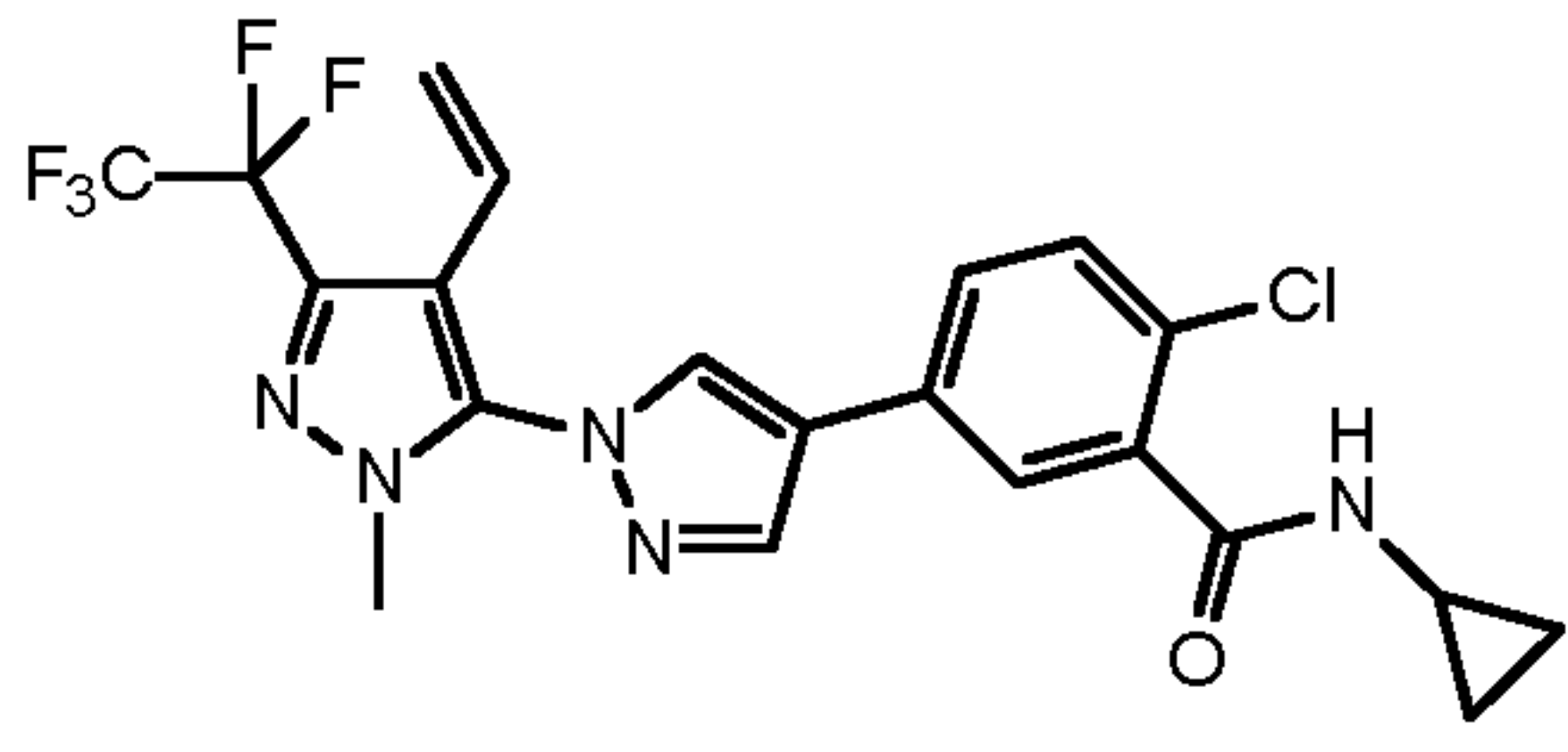
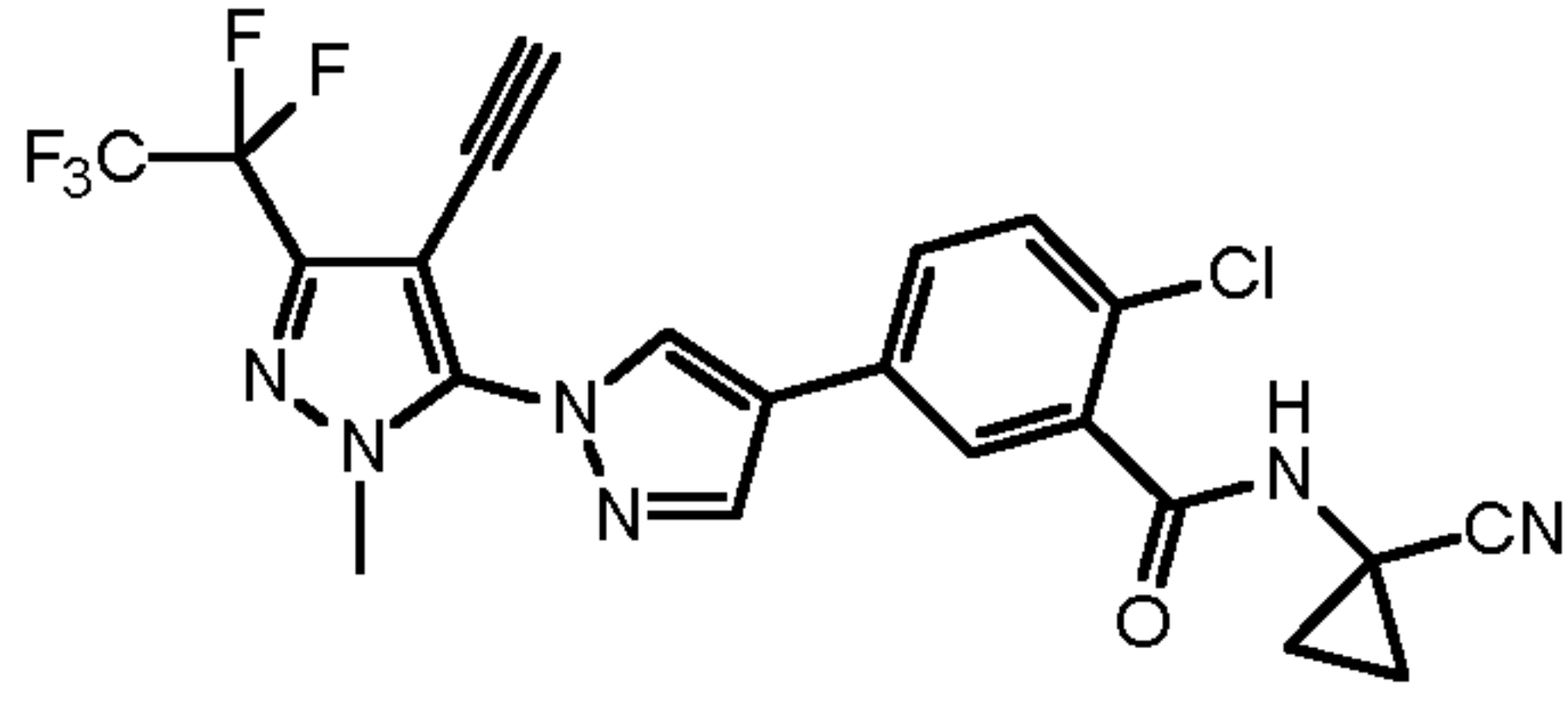
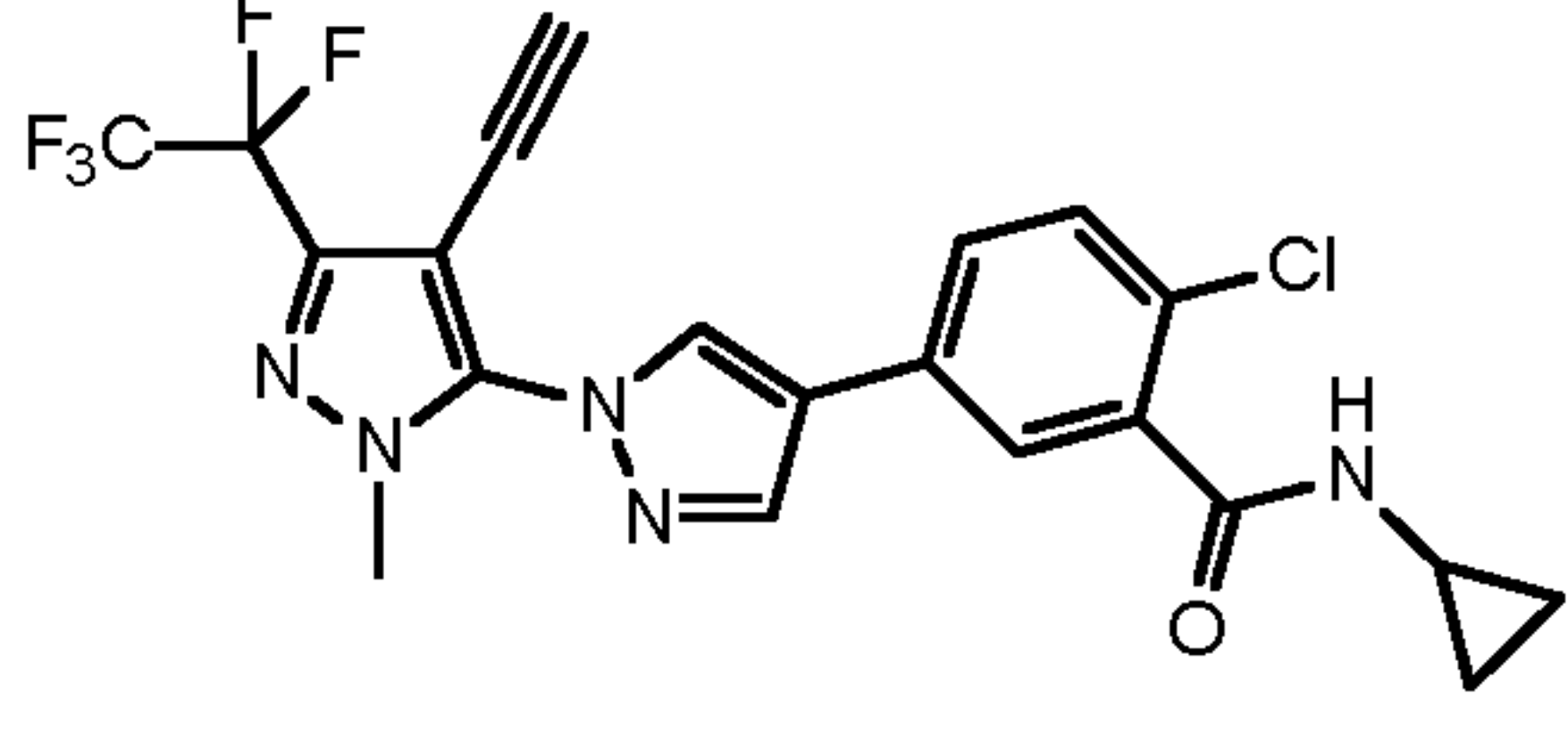
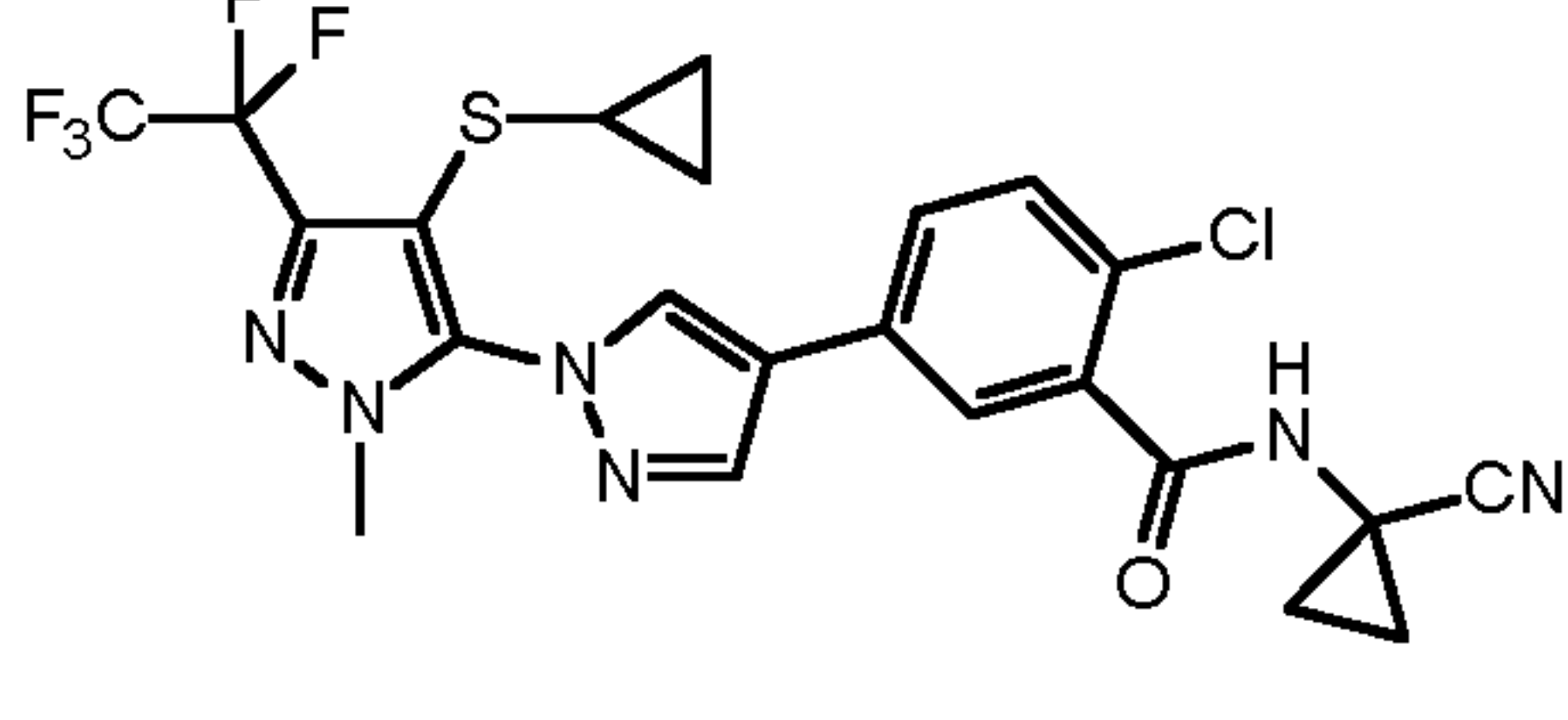
The following compounds which have been characterized were prepared in analogy to Examples 1, 2, 15, 16, 49, 54 and 64.

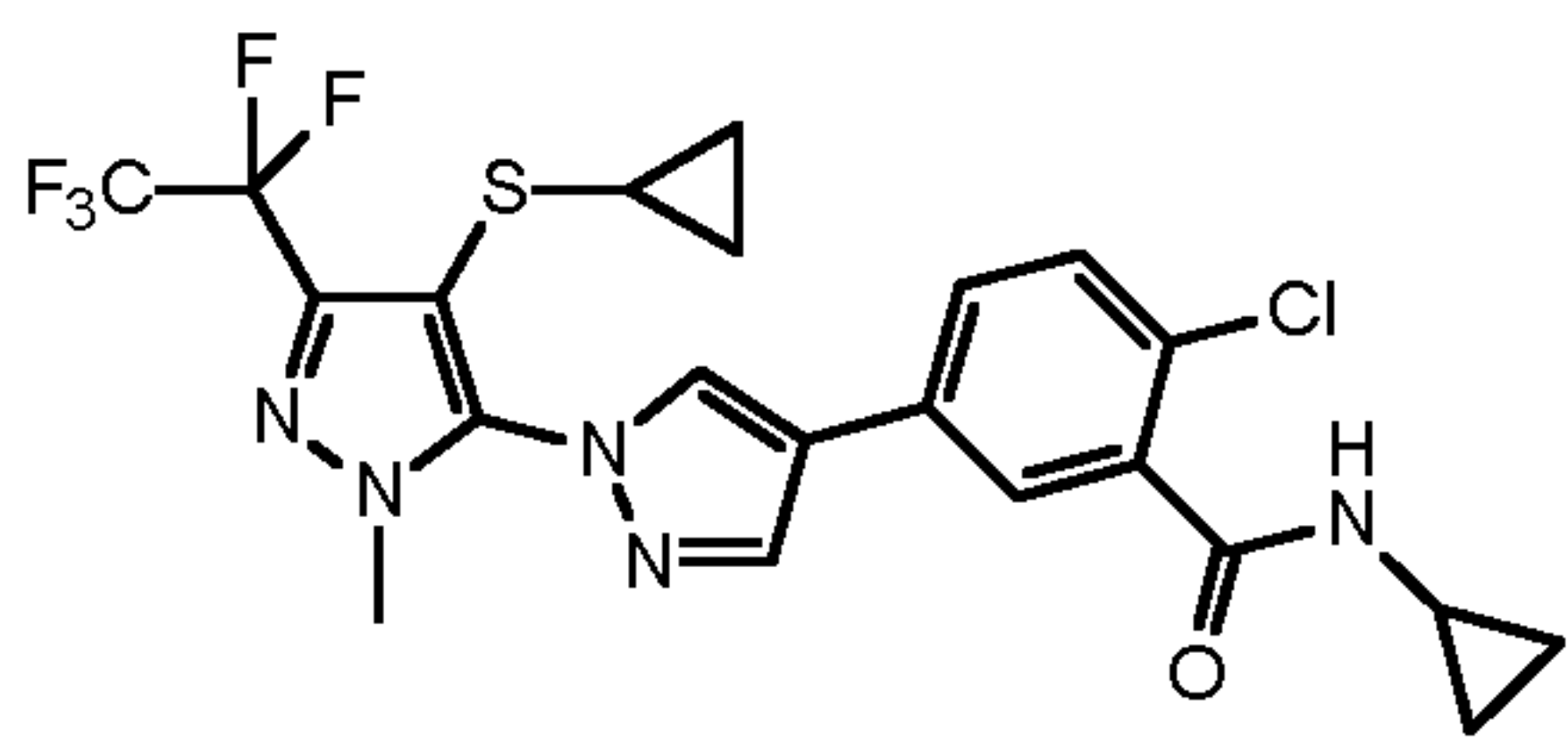
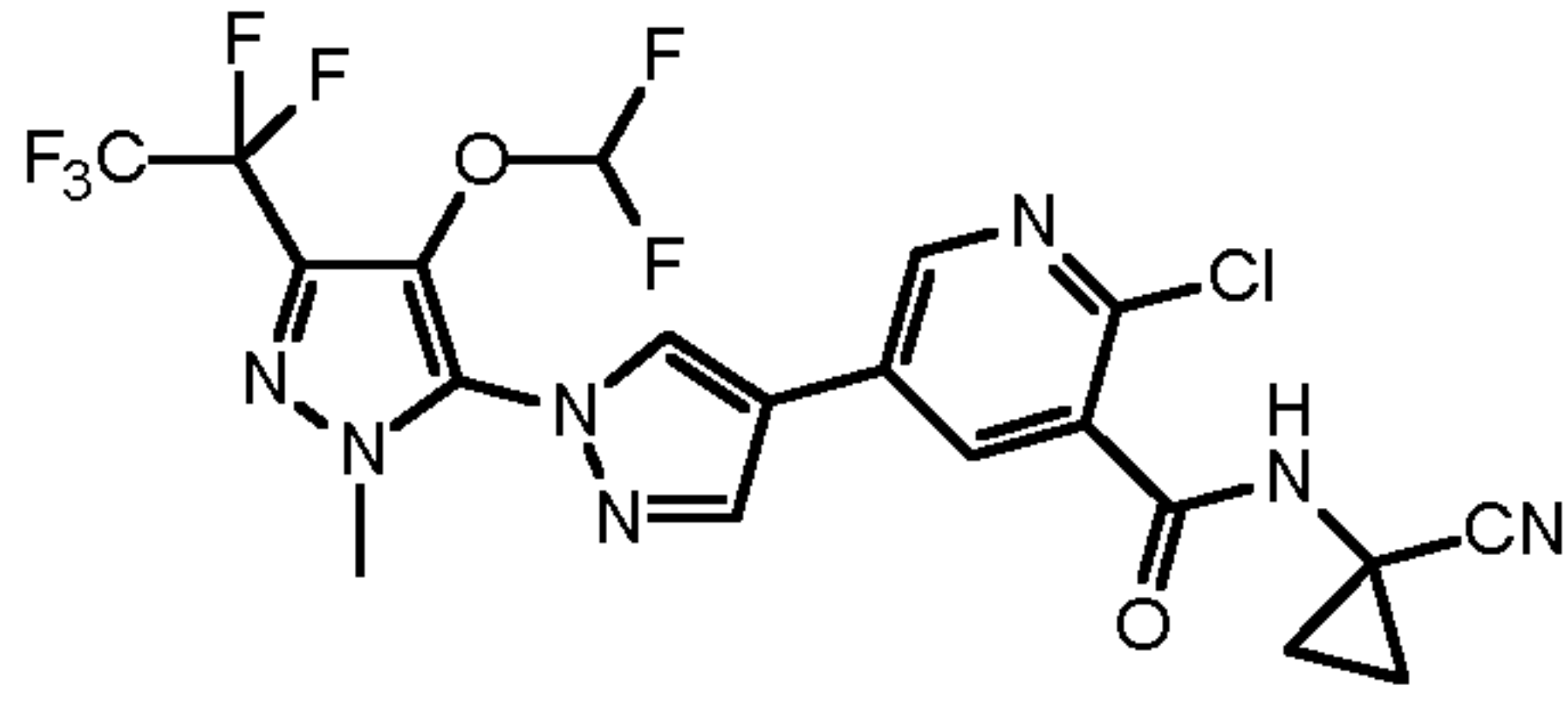
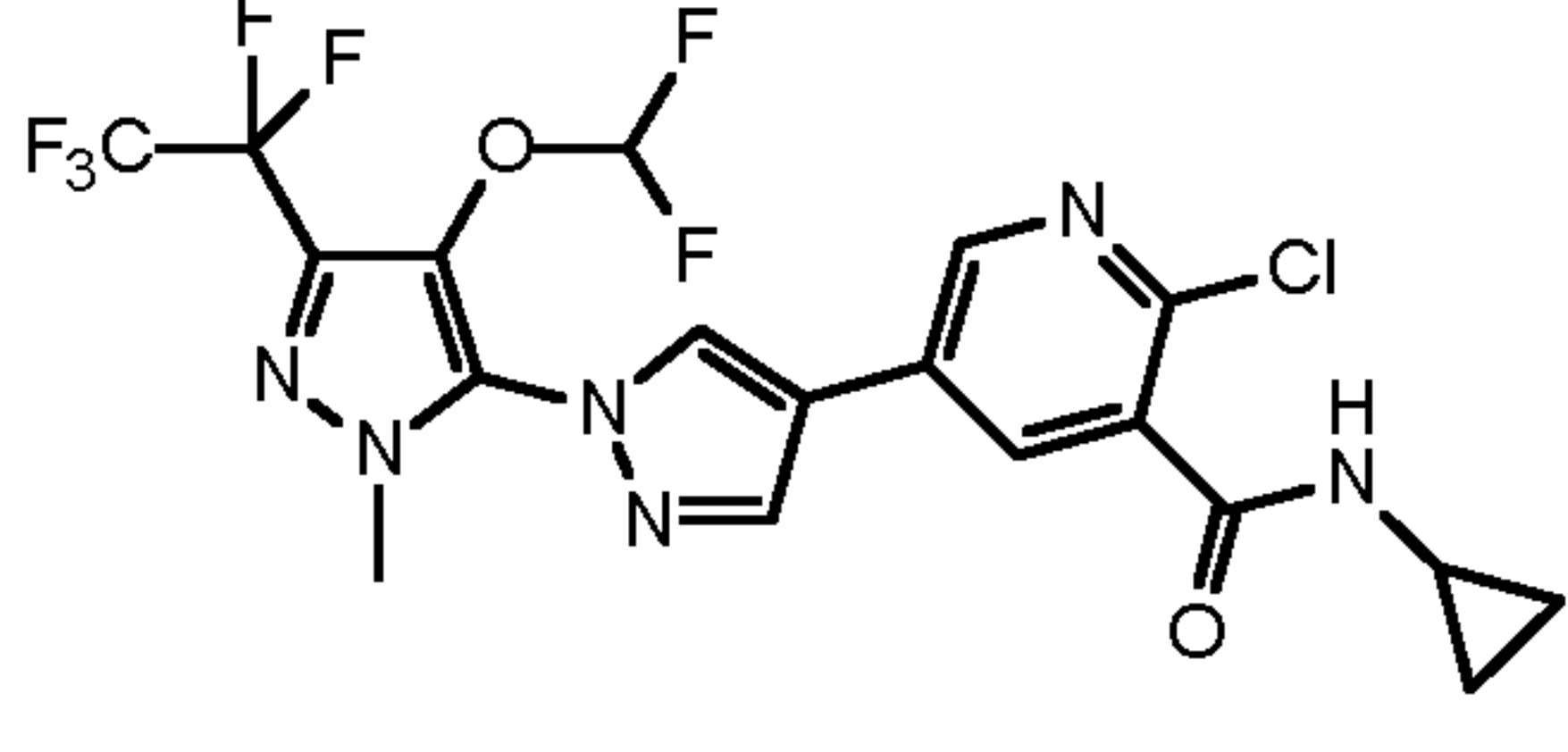
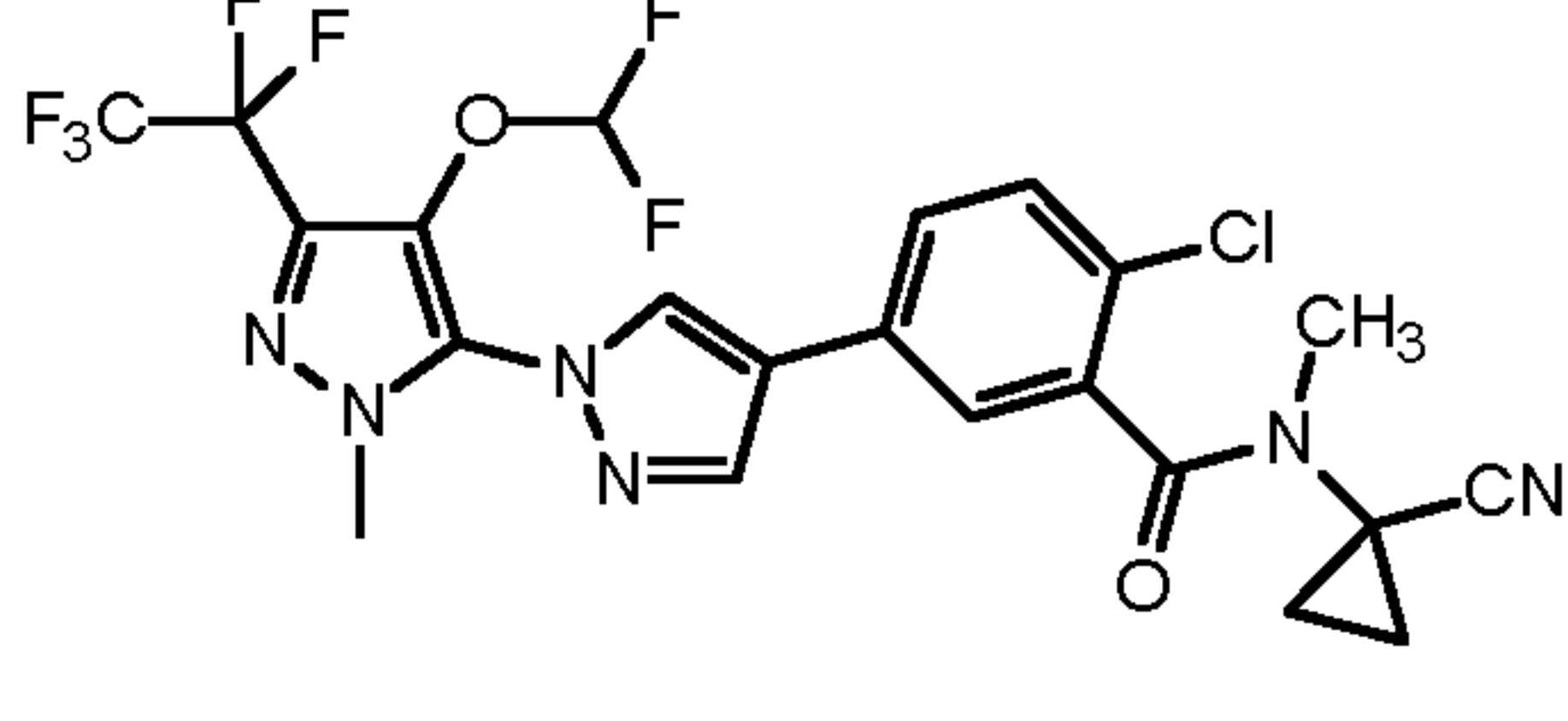
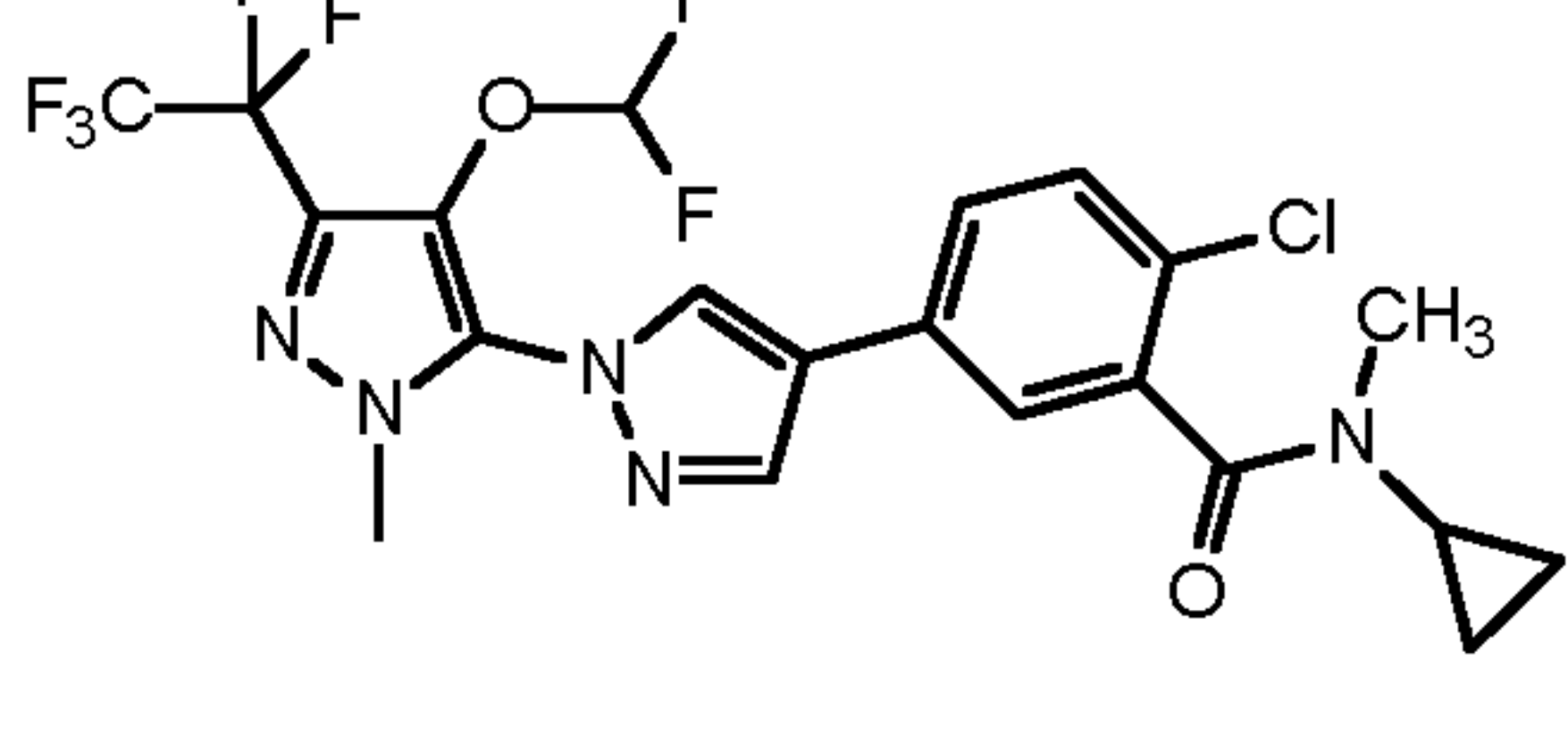
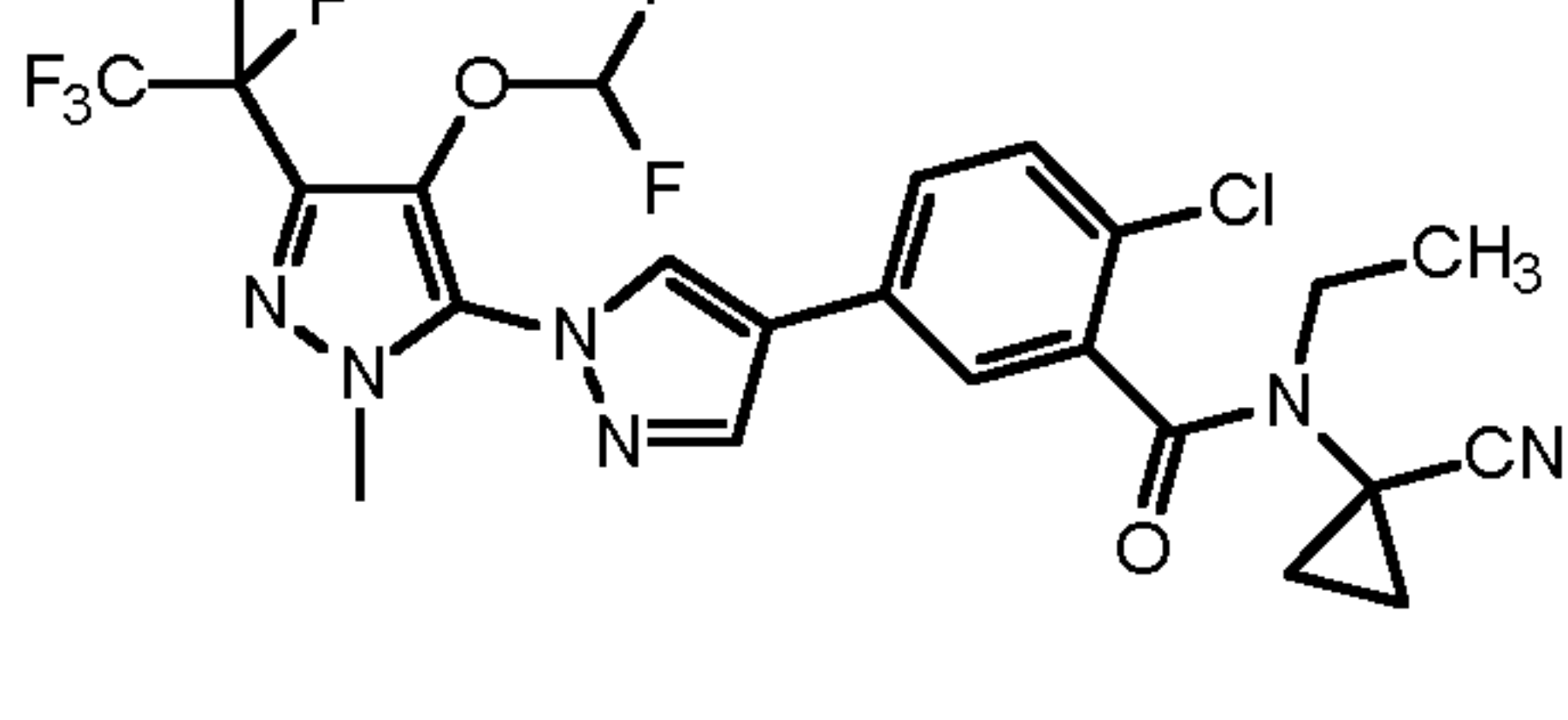
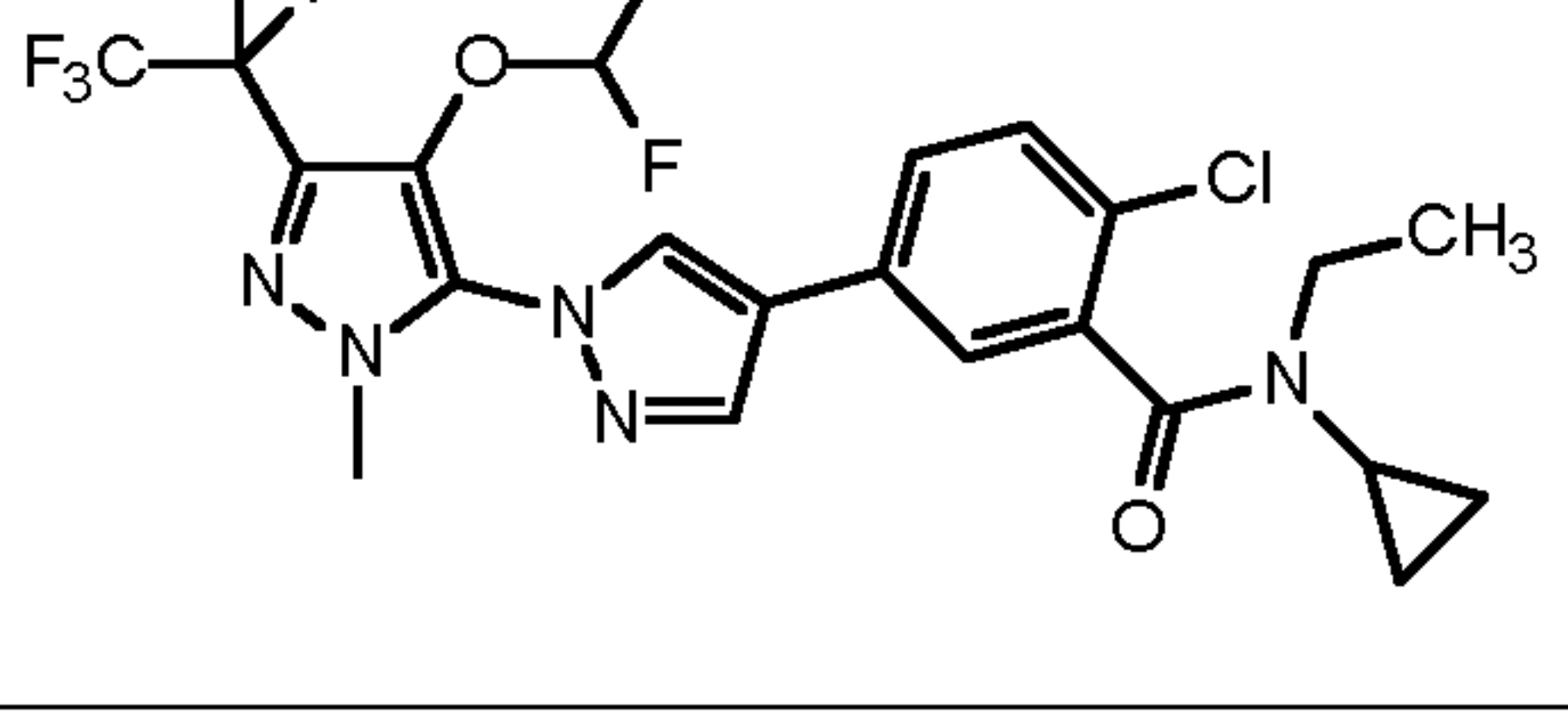
Table 1: Examples of compounds of formula (I):

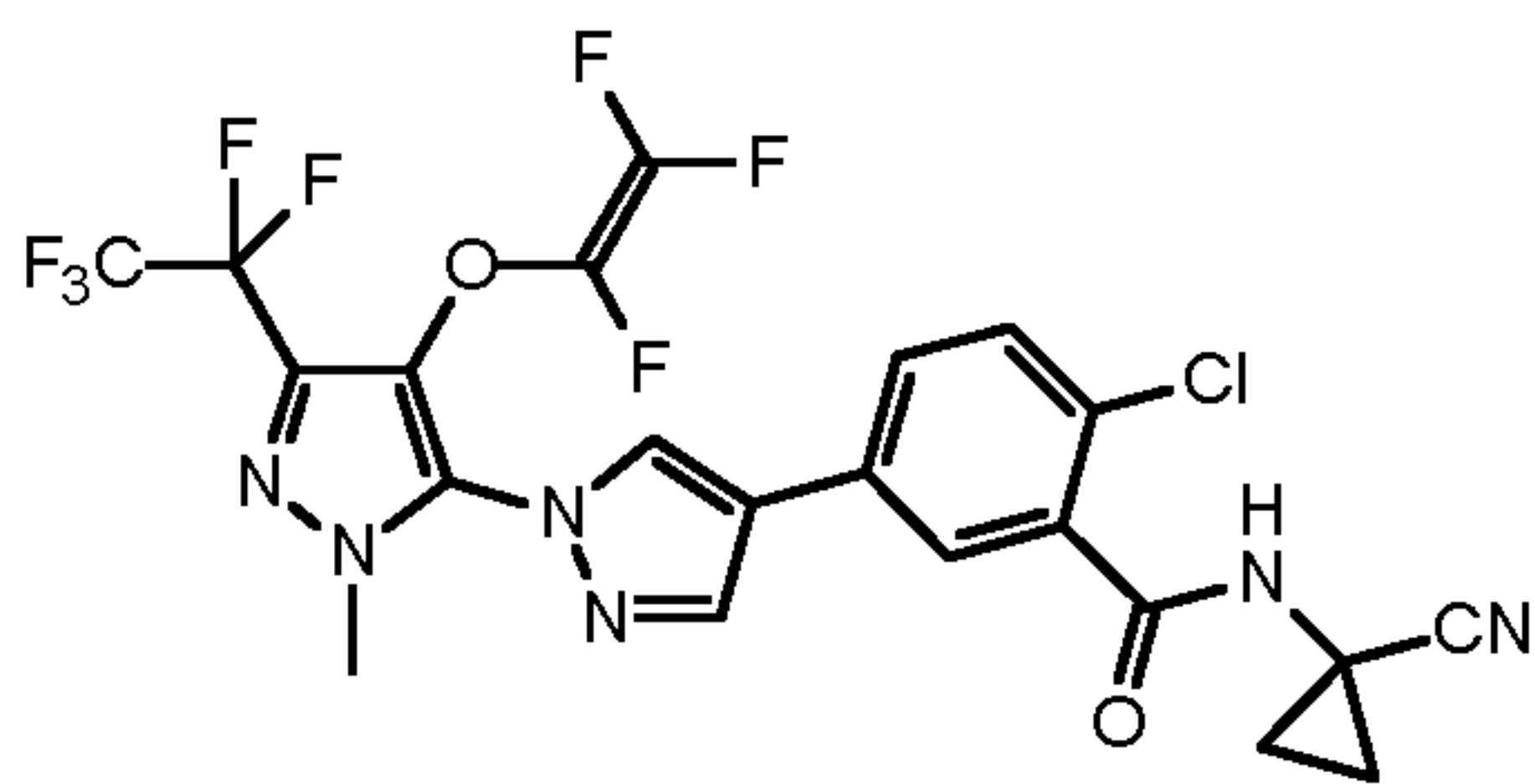
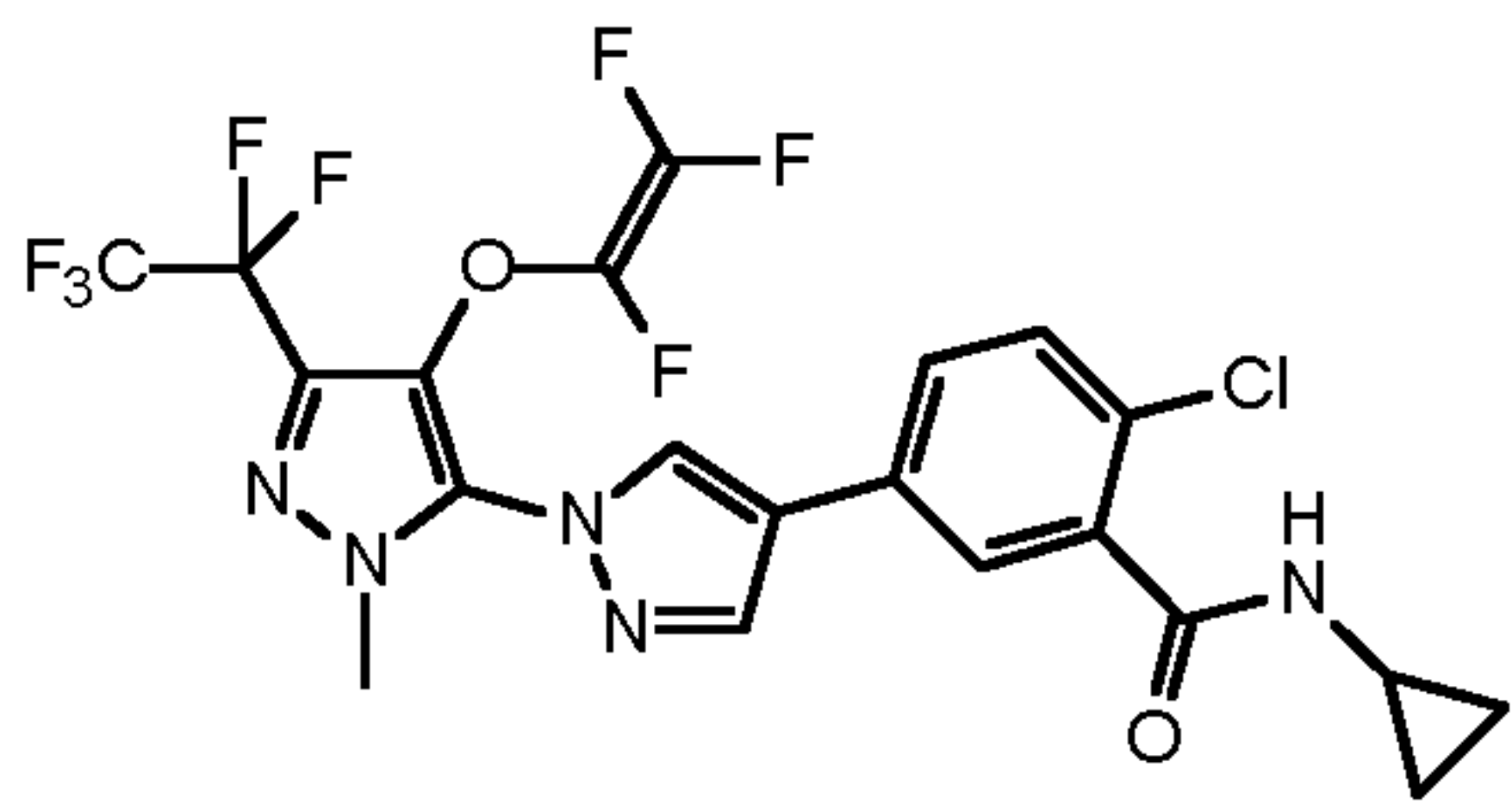
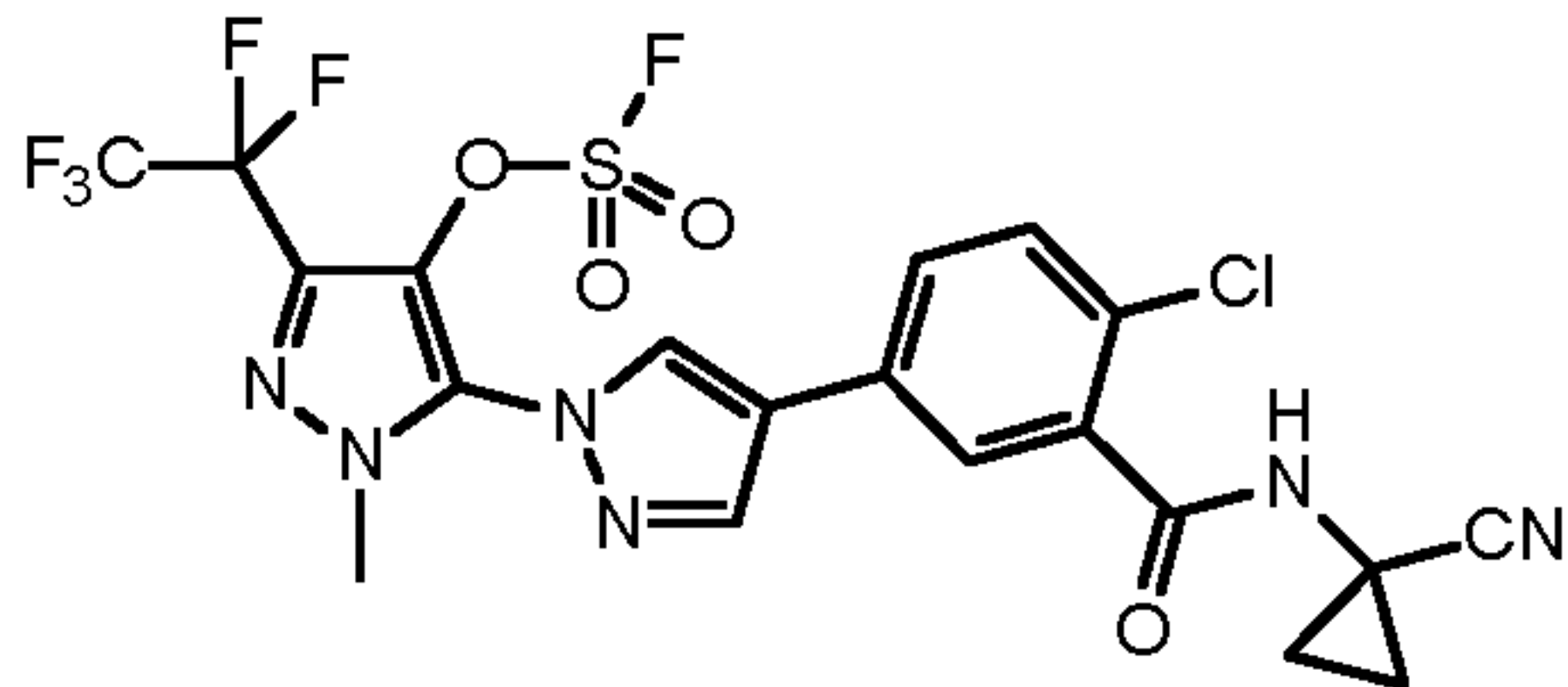
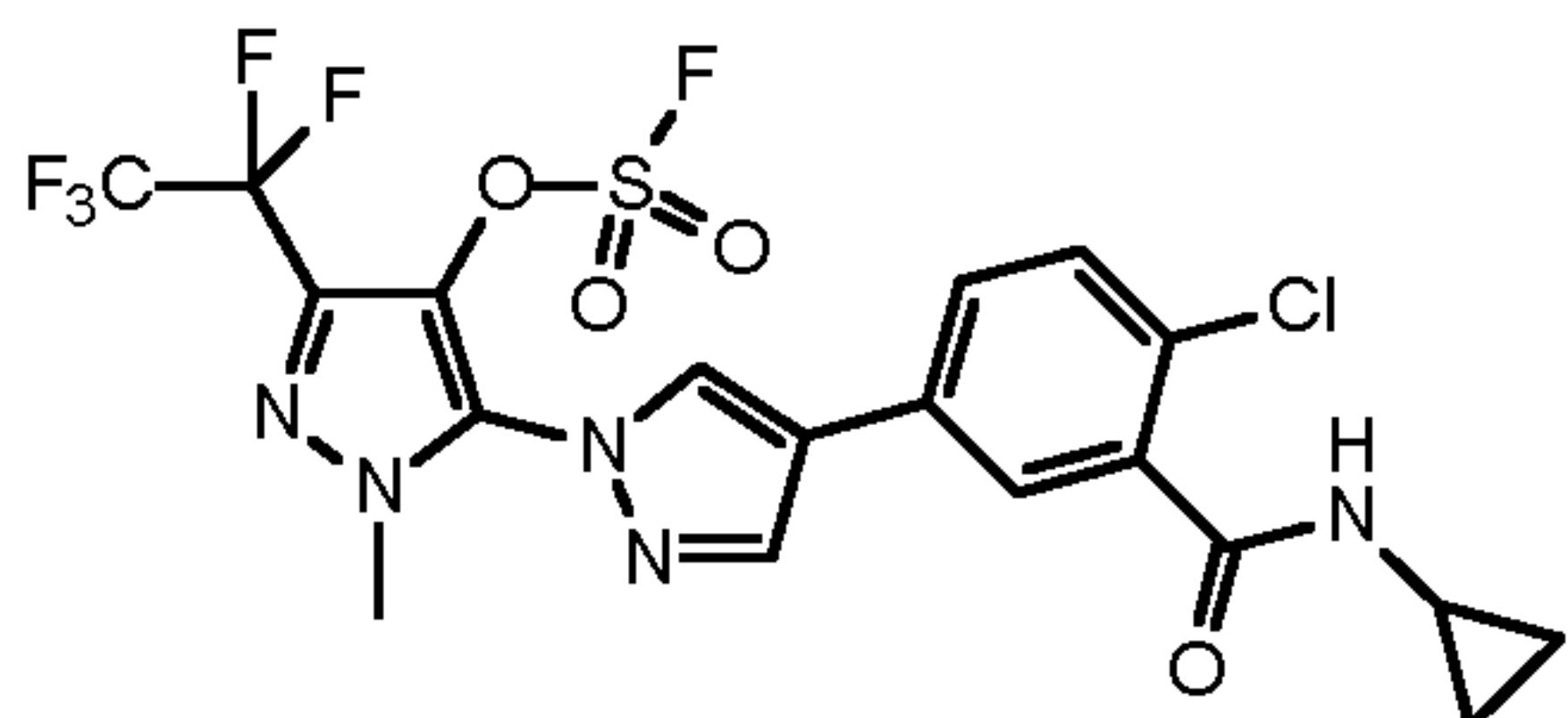
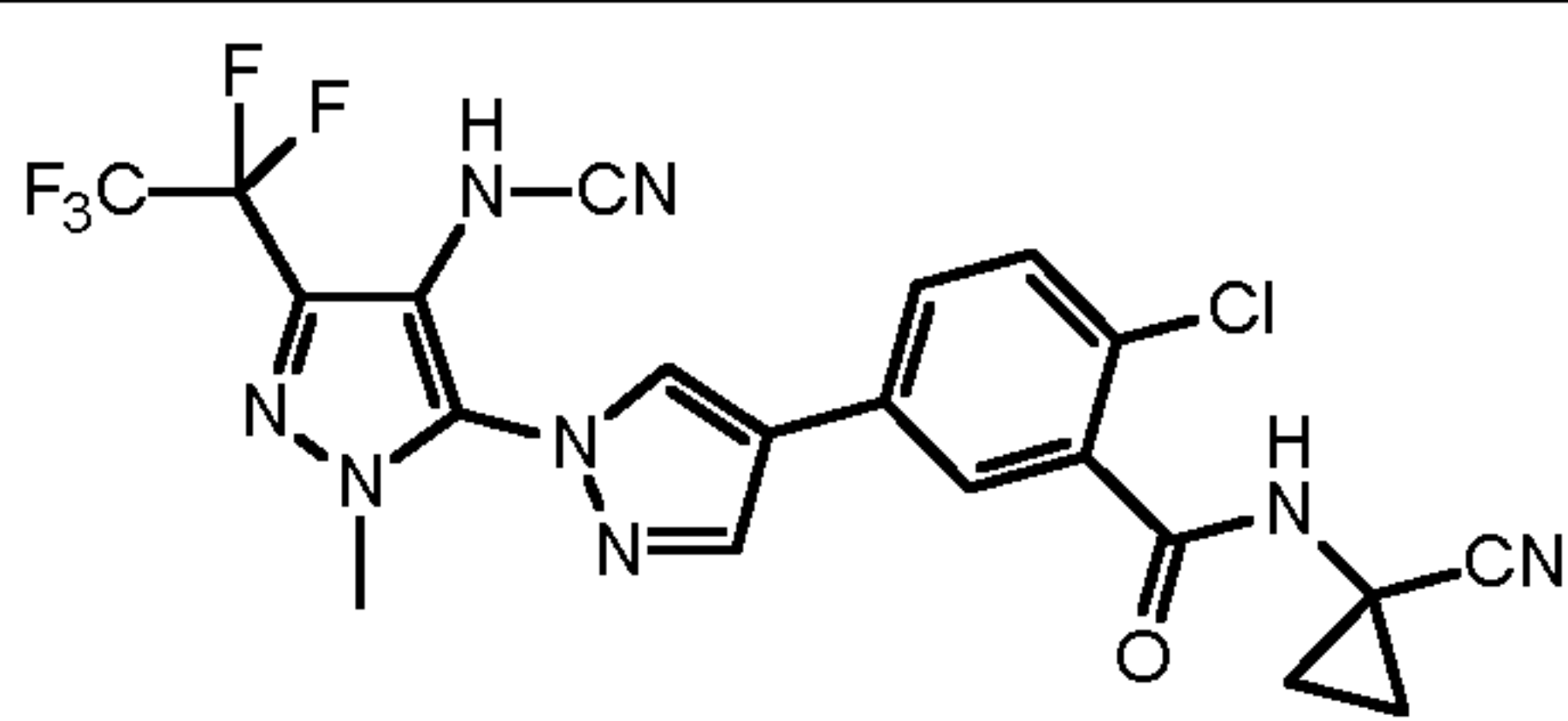
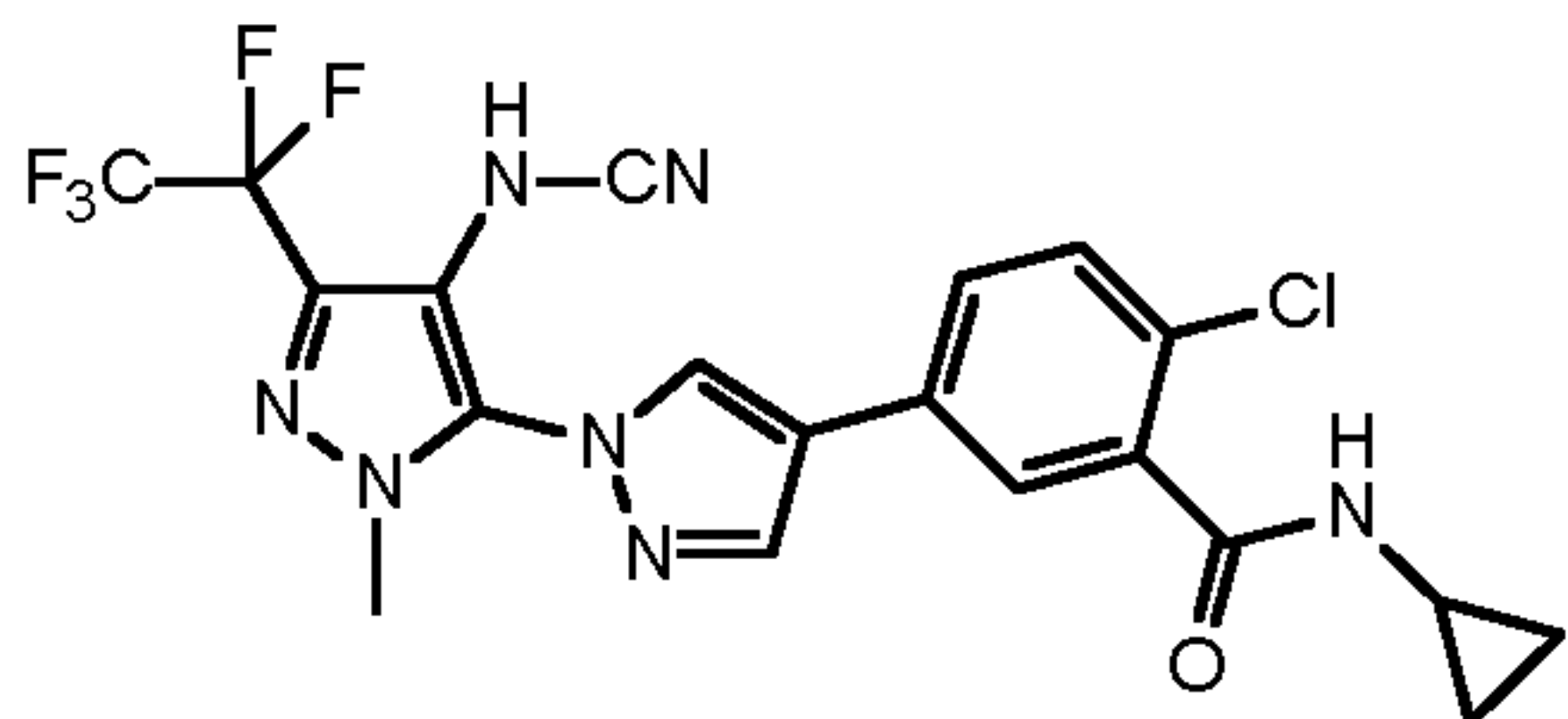
	Structure	^1H -NMR (400 MHz) LC MS (method)	Mp [°C]
1		(CDCl_3) δ ppm: 1.41 - 1.46 (m, 2 H) 1.67 - 1.72 (m, 2 H) 3.93 (s, 3 H) 6.12 - 6.51 (m, 1 H) 7.46 (d, $J=8.07$ Hz, 1 H) 7.57 (dd, $J=8.25, 2.38$ Hz, 1 H) 7.96	138-139

	Structure	1H-NMR (400 MHz) LC MS (method)	Mp [°C]
		(d, $J=2.20$ Hz, 1 H) 8.03 (s, 1 H) 8.12 (s, 1 H)	
2		(CDCl ₃) δ ppm 0.56 - 0.63 (m, 2 H) 0.81 - 0.87 (m, 2 H) 2.88 (tq, $J=7.08, 3.71$ Hz, 1 H) 3.85 (s, 3 H) 6.02 - 6.46 (m, 2 H) 7.33 - 7.48 (m, 2 H) 7.75 - 7.96 (m, 2 H) 7.98 - 8.07 (m, 1 H).	
3		LC-MS (A): $t_R = 1.09$ min, $m/z = 583/5$ [M+1] ⁺	
4			
5			
6		LC-MS (B): $t_R = 1.69$ min, $m/z = 490/2$ [M+1] ⁺	
7			

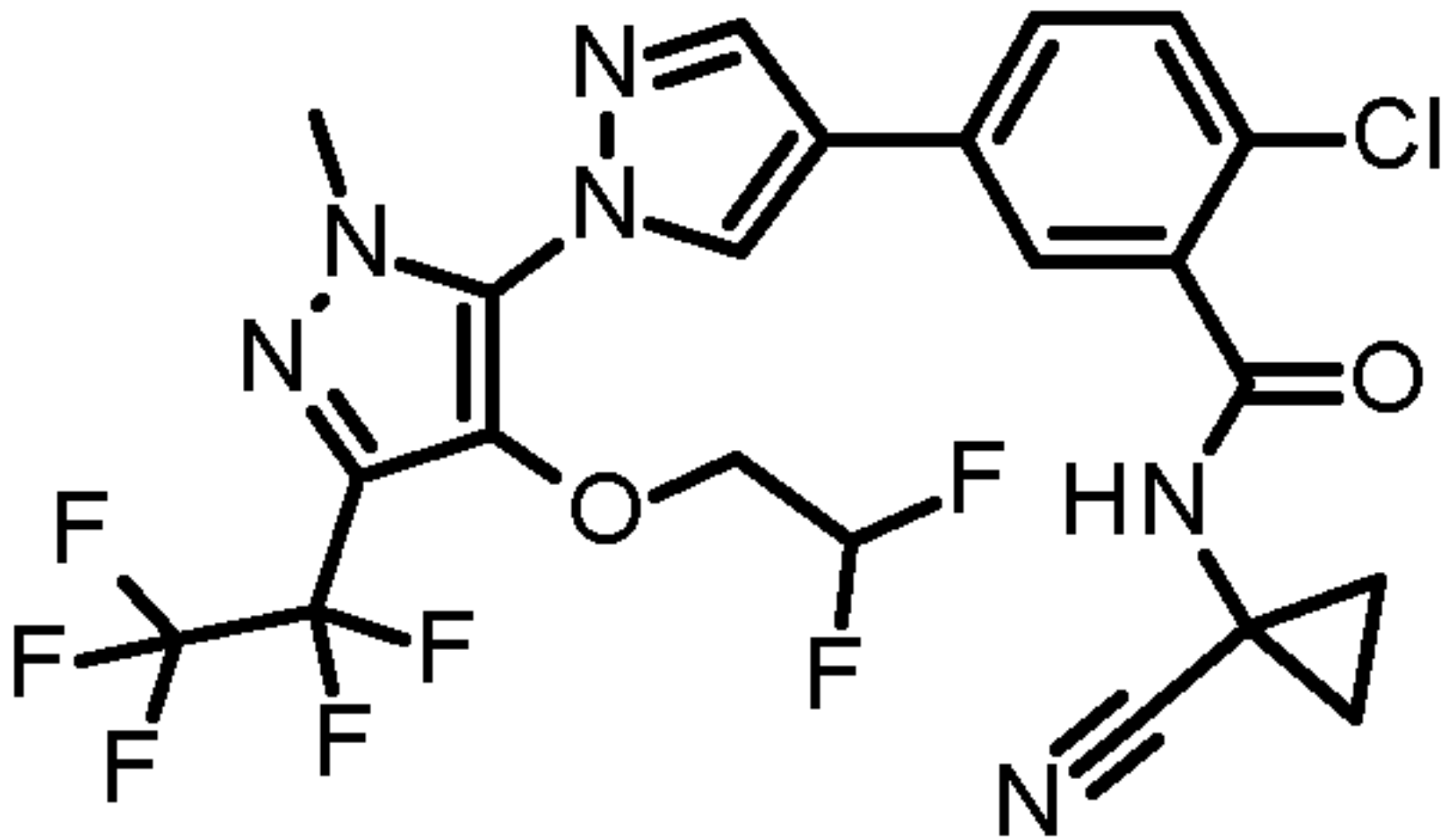
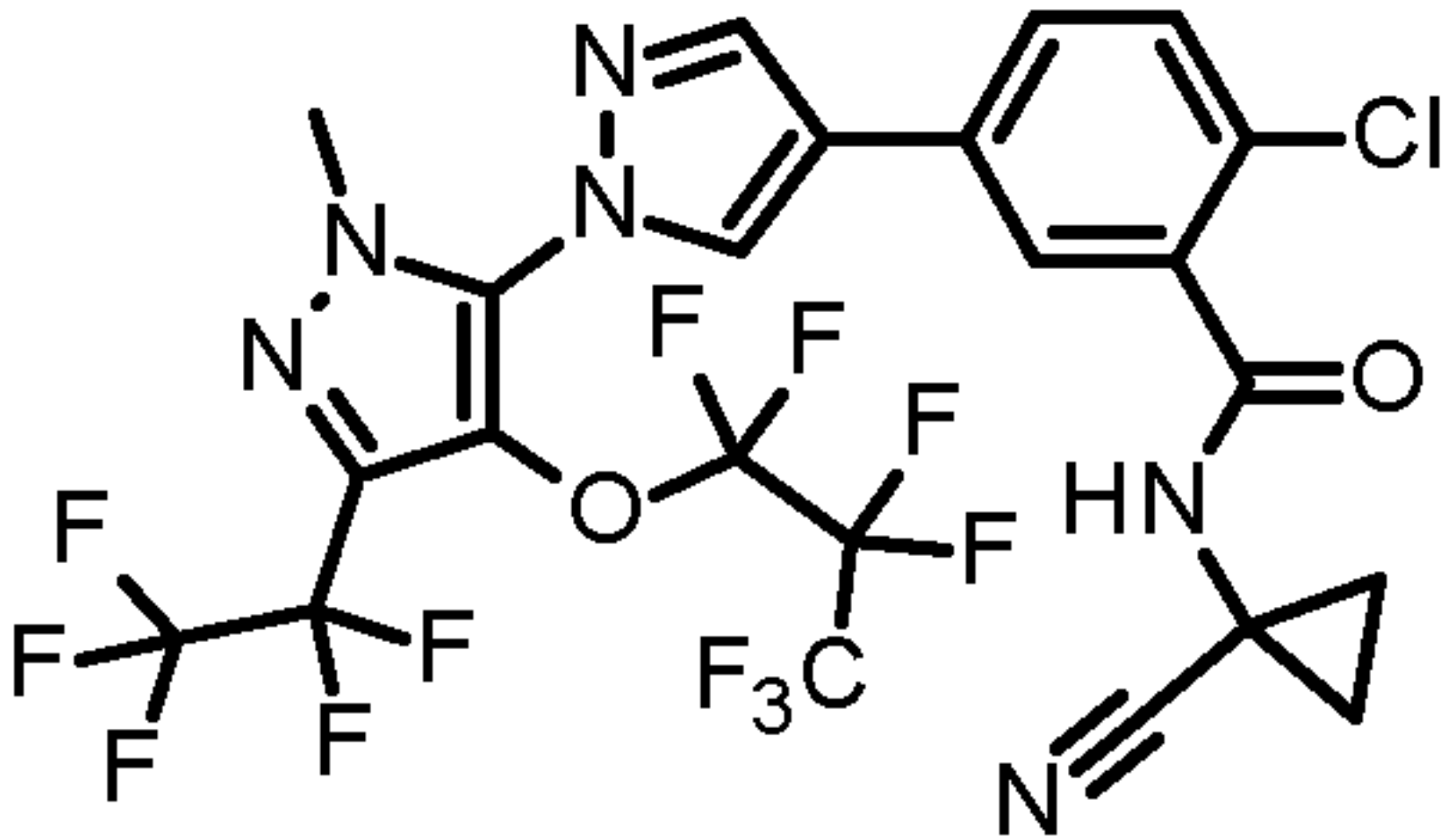
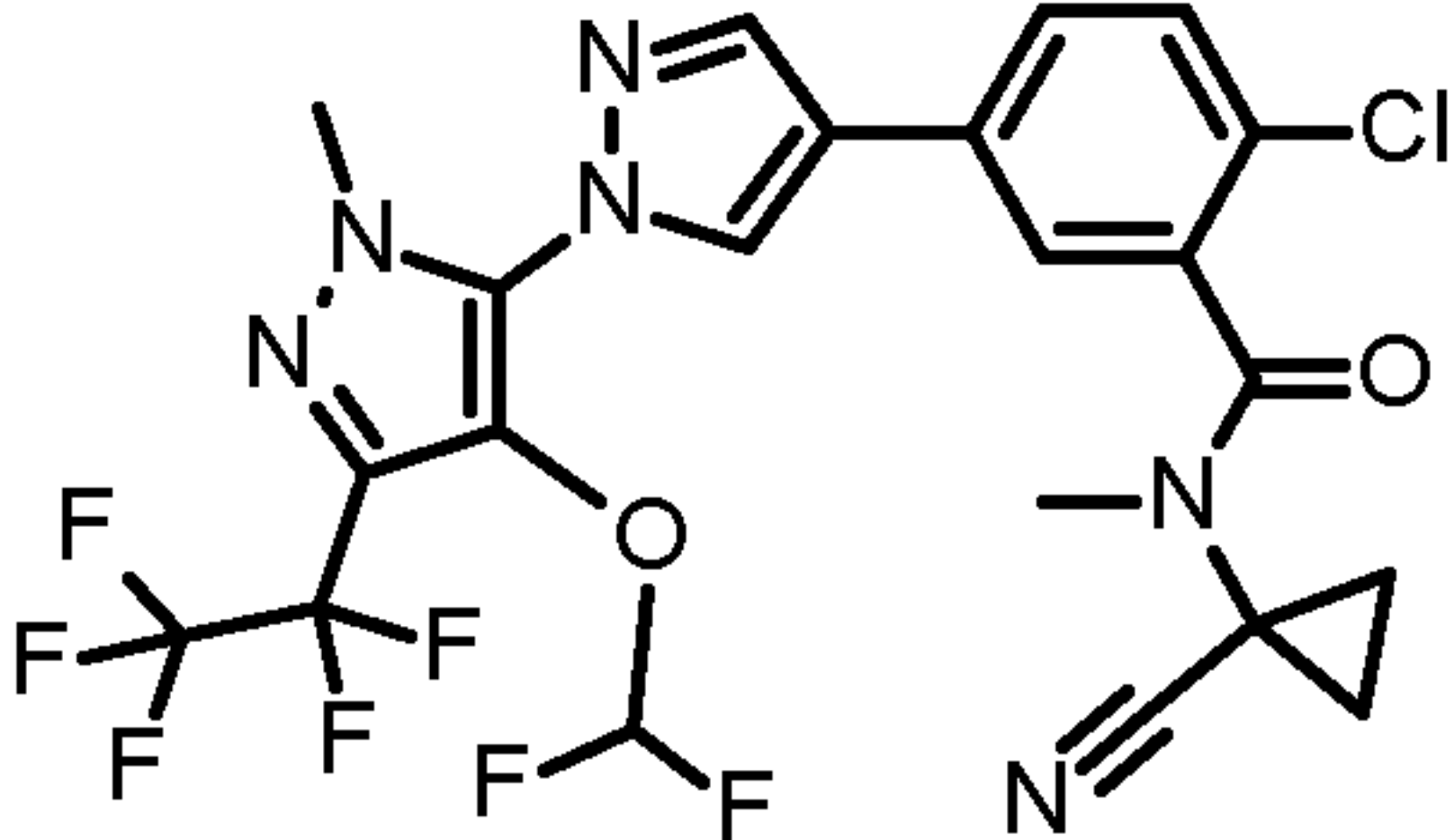
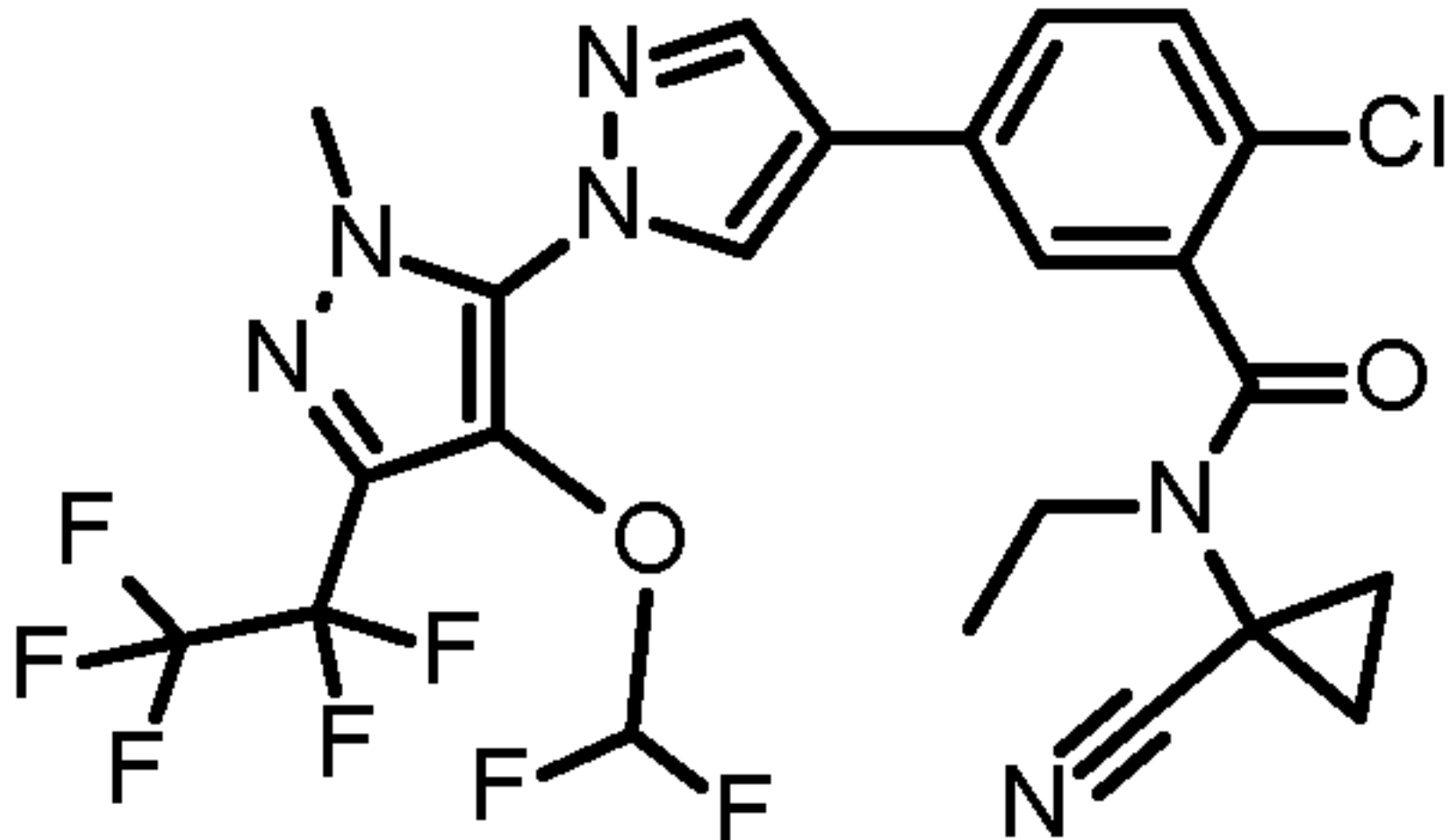
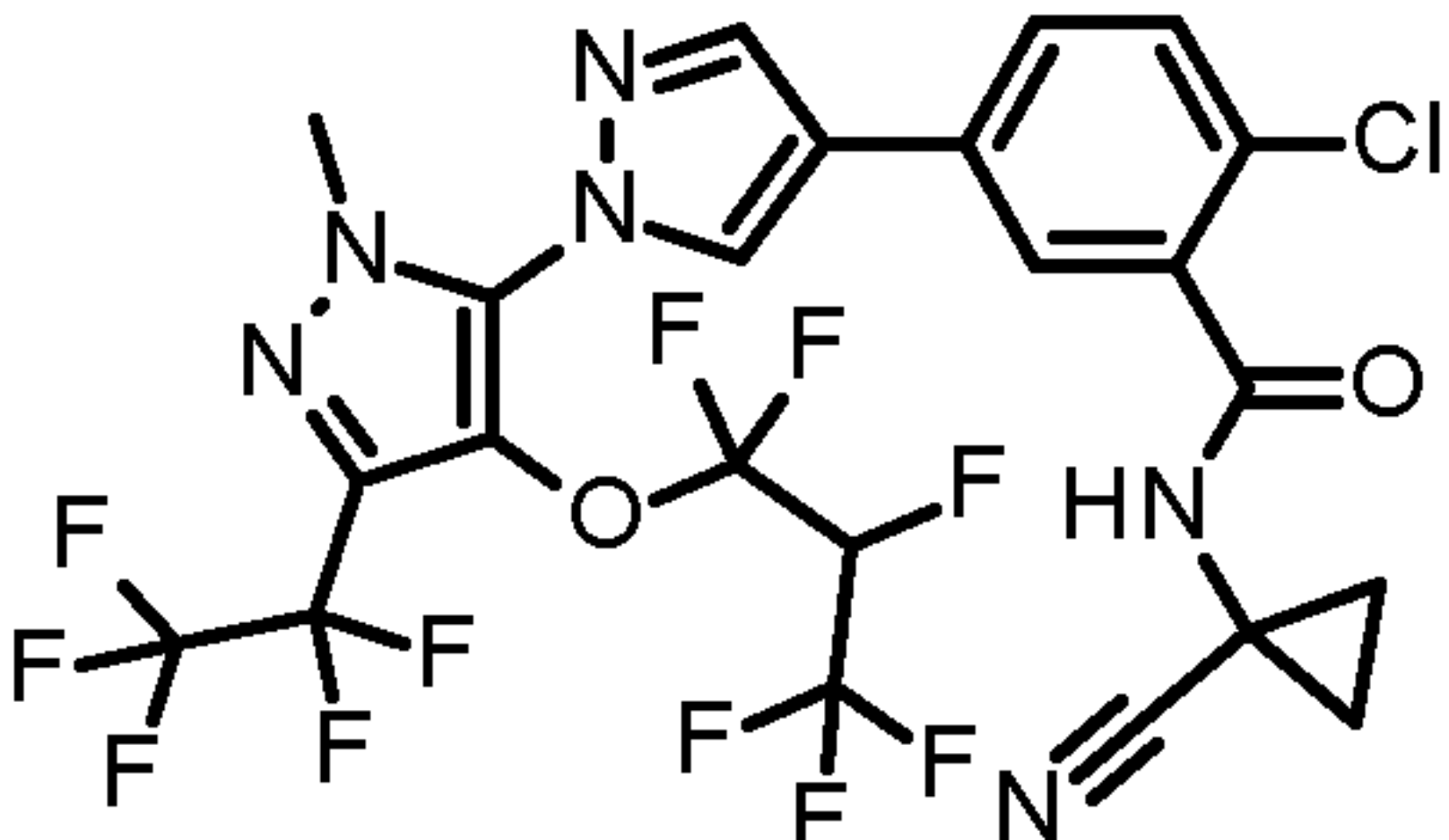
	Structure	1H-NMR (400 MHz) LC MS (method)	Mp [°C]
8			
9		LC-MS (B): t _R = 1.79 min, m/z = 525/7 [M+1] ⁺	
10			
11			
12			
13			
14			

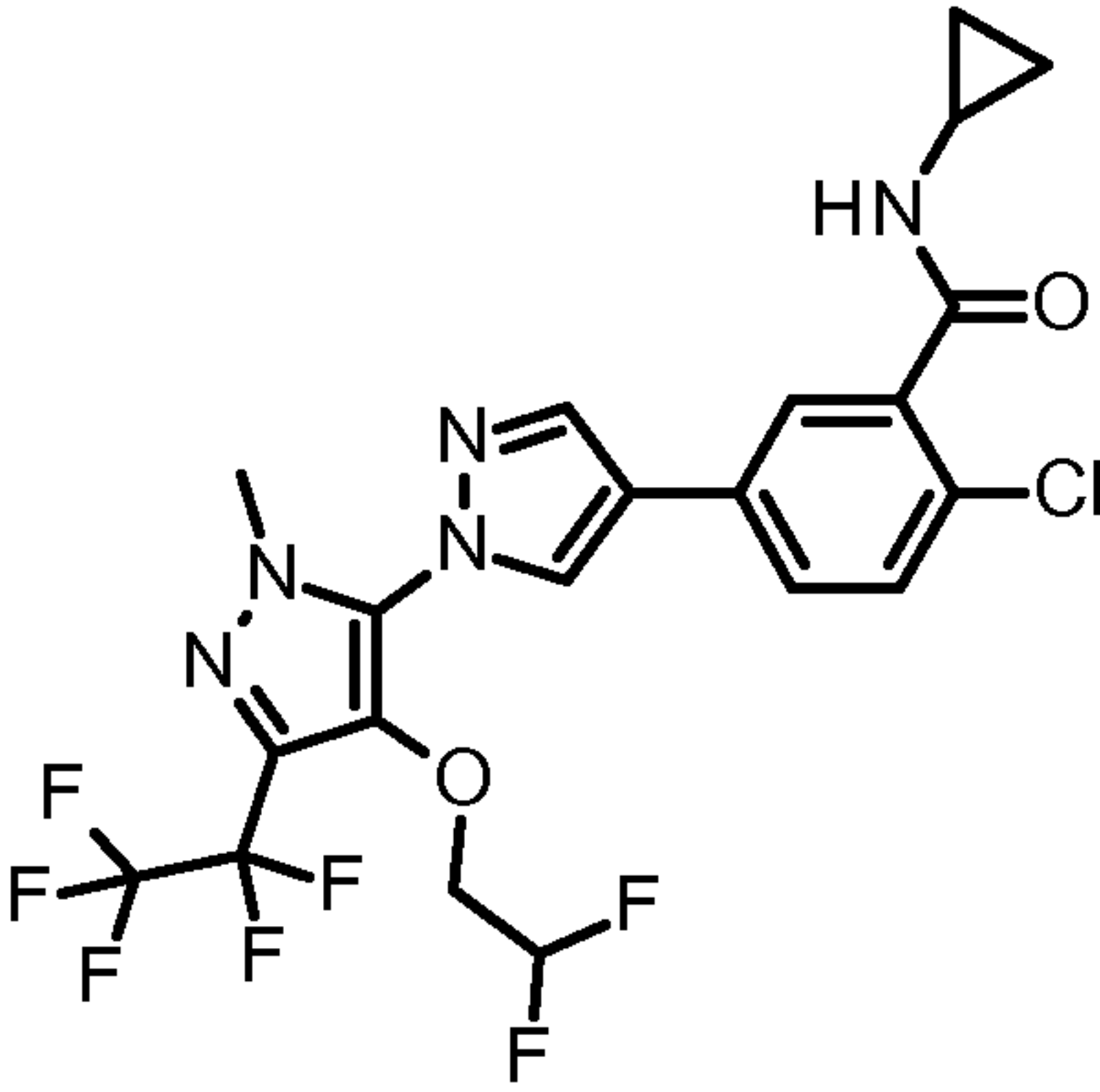
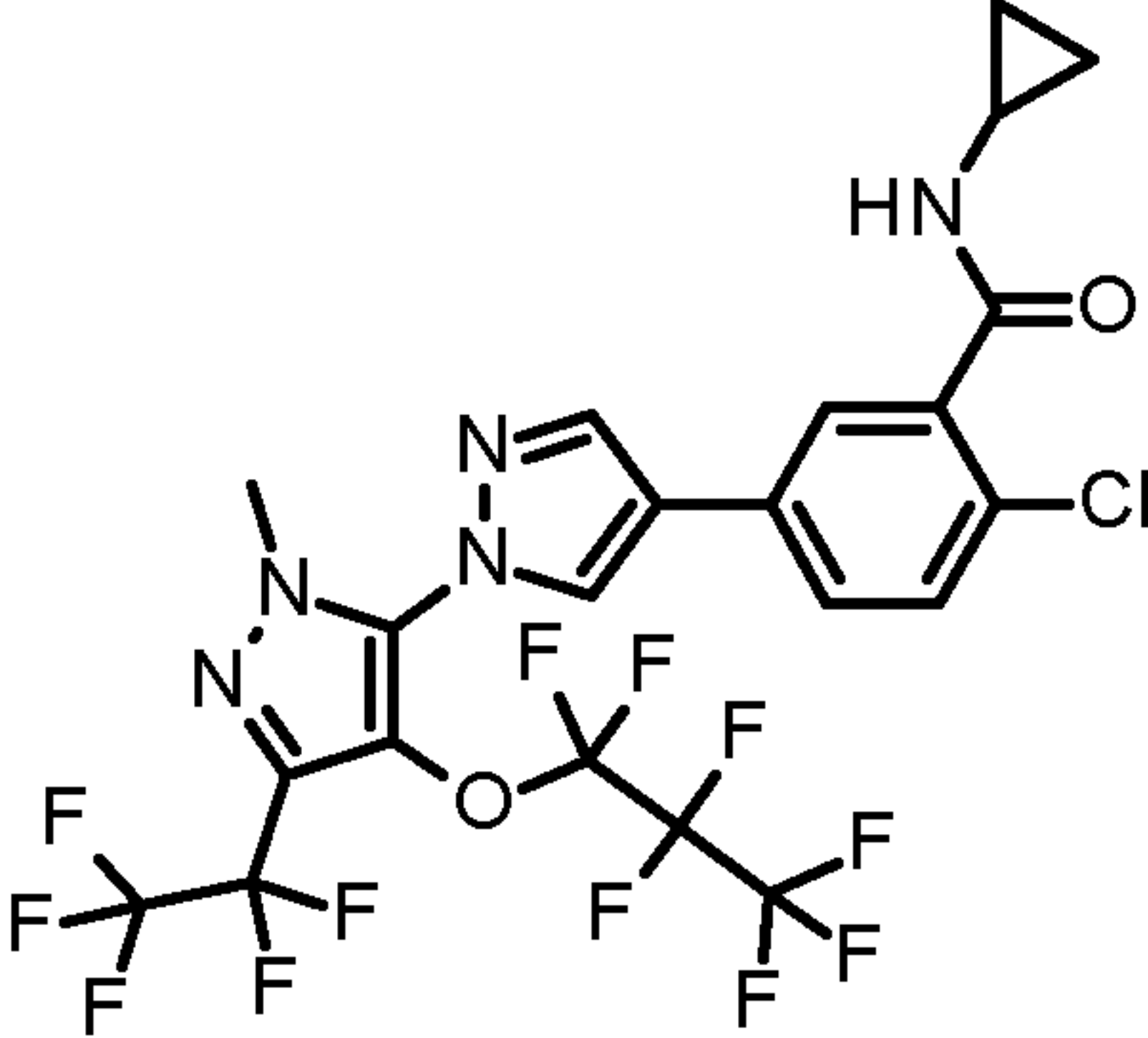
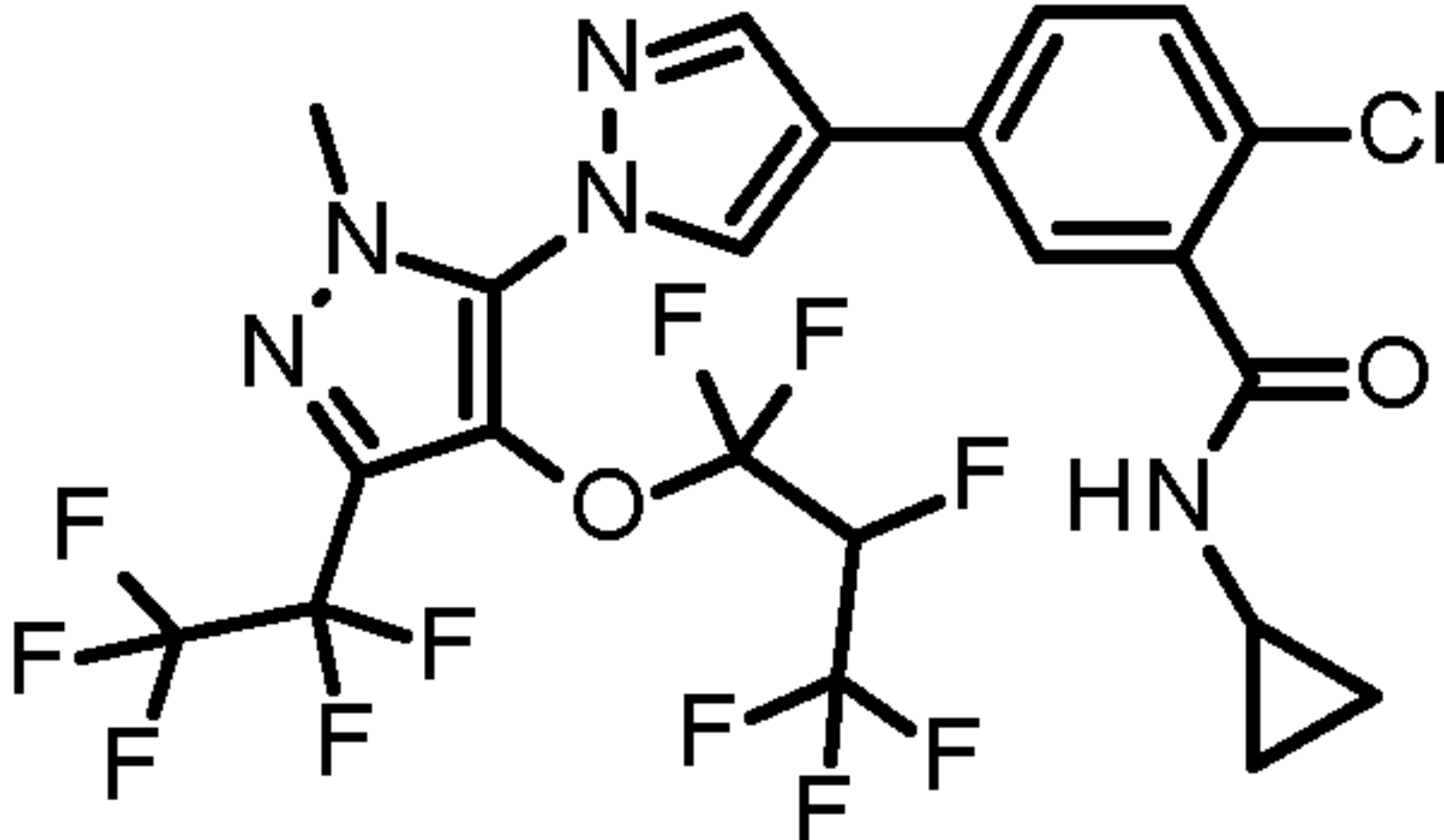
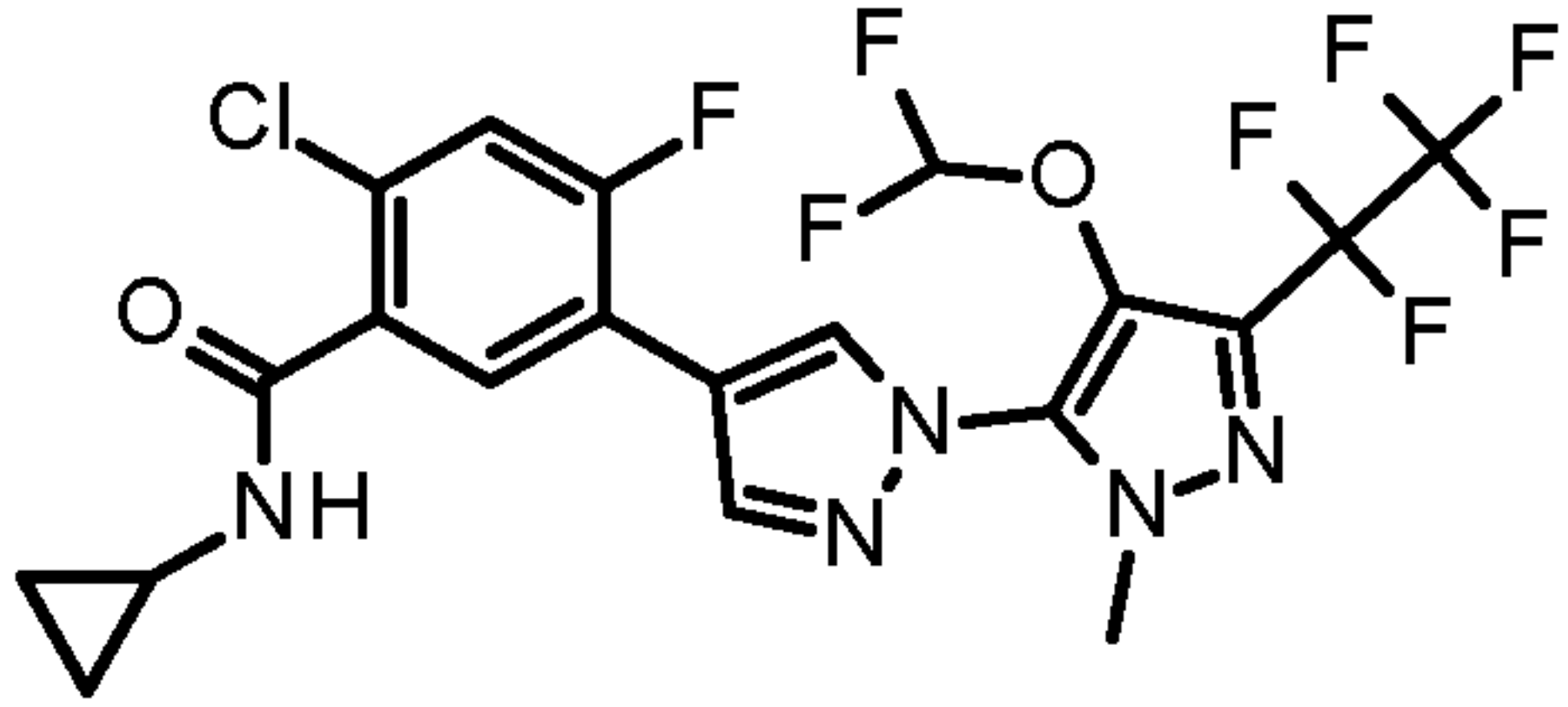
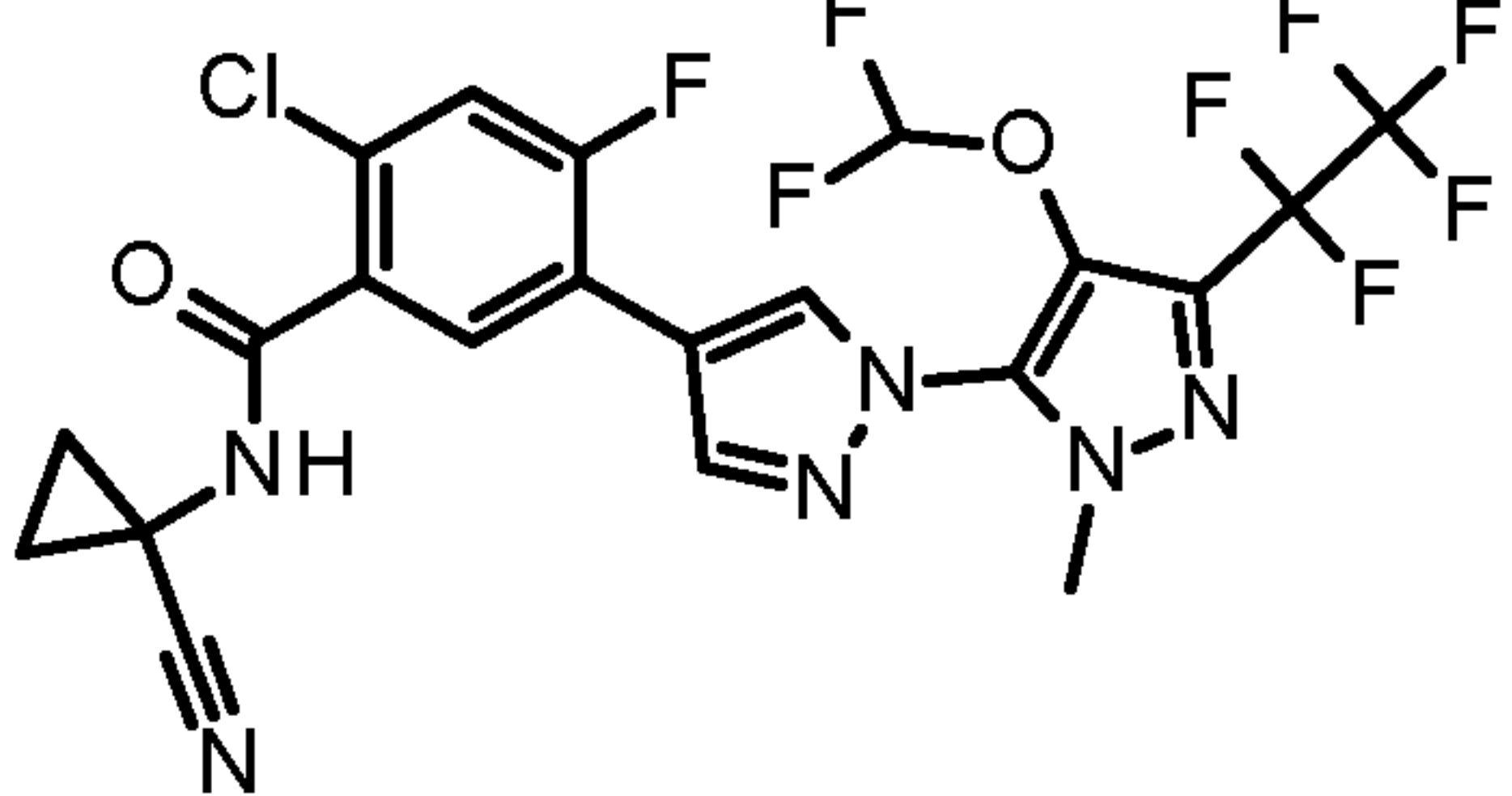
	Structure	1H-NMR (400 MHz) LC MS (method)	Mp [°C]
15		(CDCl ₃) δ ppm 1.41 - 1.44 (m, 2 H) 1.68 - 1.72 (m, 2 H) 3.79 (s, 3 H) 4.92 (d, <i>J</i> =17.97 Hz, 1 H) 5.17 - 5.23 (m, 1 H) 6.49 (dd, <i>J</i> =17.79, 11.55 Hz, 1 H) 6.90 (s, 1 H) 7.45 (d, <i>J</i> =8.07 Hz, 1 H) 7.57 (dd, <i>J</i> =8.44, 2.20 Hz, 1 H) 7.90 (s, 1 H) 7.96 (d, <i>J</i> =2.20 Hz, 1 H) 8.14 (d, <i>J</i> =0.73 Hz, 1 H).	
16		(CDCl ₃) δ ppm 0.66 - 0.70 (m, 2 H) 0.89 - 0.94 (m, 2 H) 2.91 - 2.97 (m, 1 H) 3.78 (s, 3 H) 4.88 - 4.95 (m, 1 H) 5.19 (dd, <i>J</i> =11.55, 0.92 Hz, 1 H) 6.40 (br. s., 1 H) 6.49 (dd, <i>J</i> =17.97, 11.37 Hz, 1 H) 7.41 - 7.45 (m, 1 H) 7.49 - 7.53 (m, 1 H) 7.87 (d, <i>J</i> =0.73 Hz, 2 H) 8.13 (d, <i>J</i> =0.73 Hz, 1 H).	
17		LC-MS (B): t _R = 1.75 min, m/z = 509/11 [M+1] ⁺	
18		LC-MS (B): t _R = 1.77 min, m/z = 484/6 [M+1] ⁺	
19			72-4

	Structure	1H-NMR (400 MHz) LC MS (method)	Mp [°C]
20			69-71
21		LC-MS (B): t _R = 1.64 min, m/z = 552/4 [M+1] ⁺	
22		LC-MS (B): t _R = 1.64 min, m/z = 527/9 [M+1] ⁺	
23			
24			
25			
26			

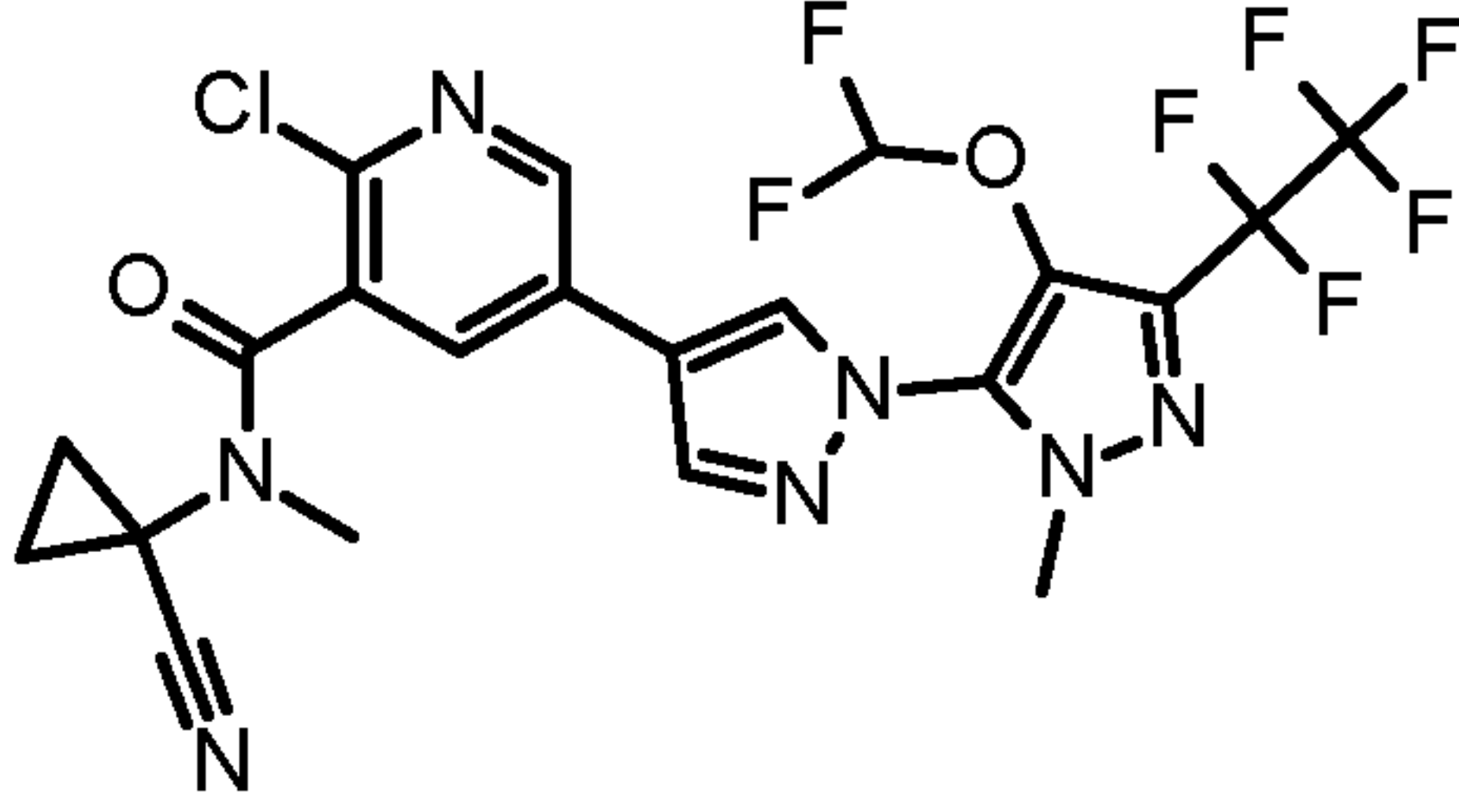
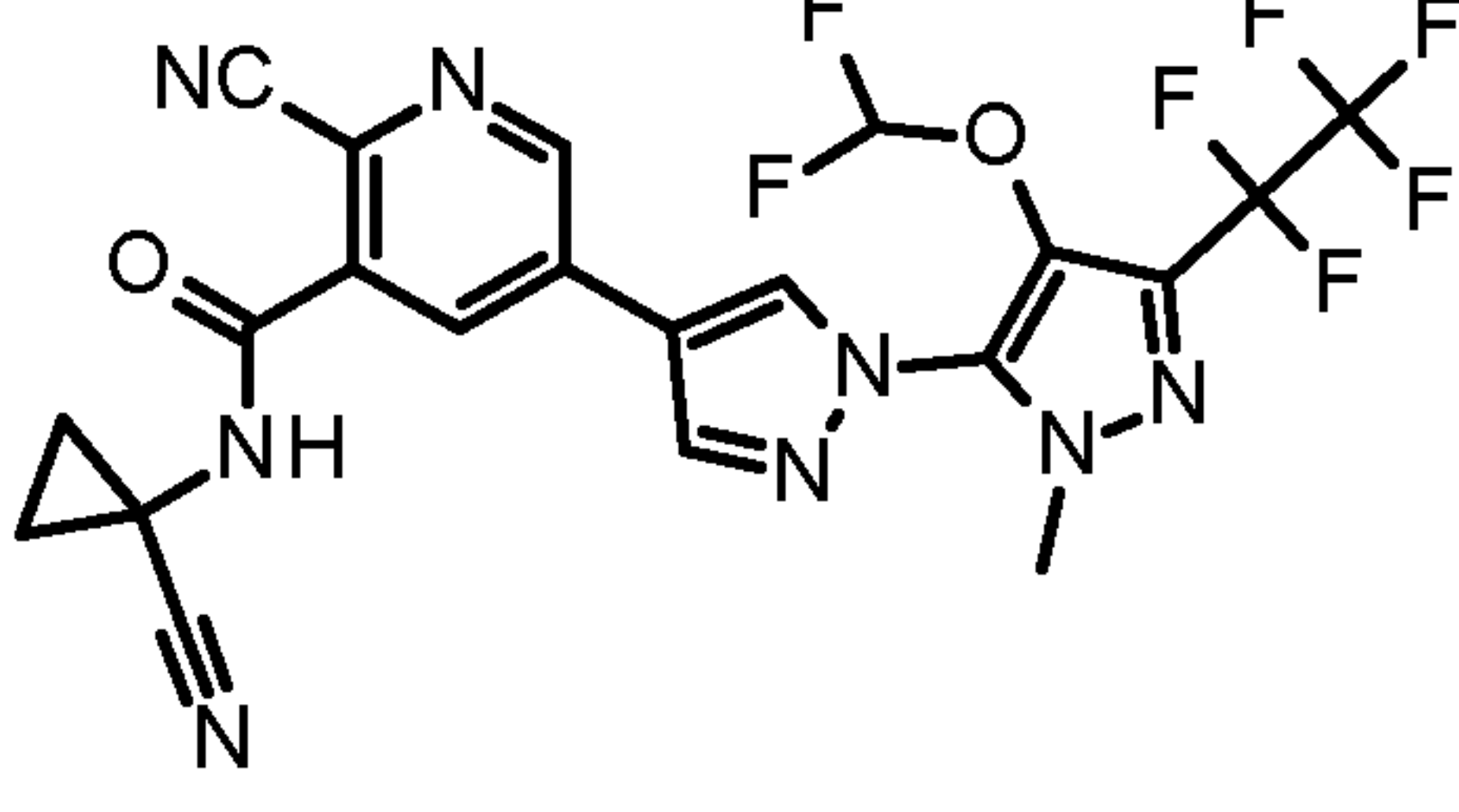
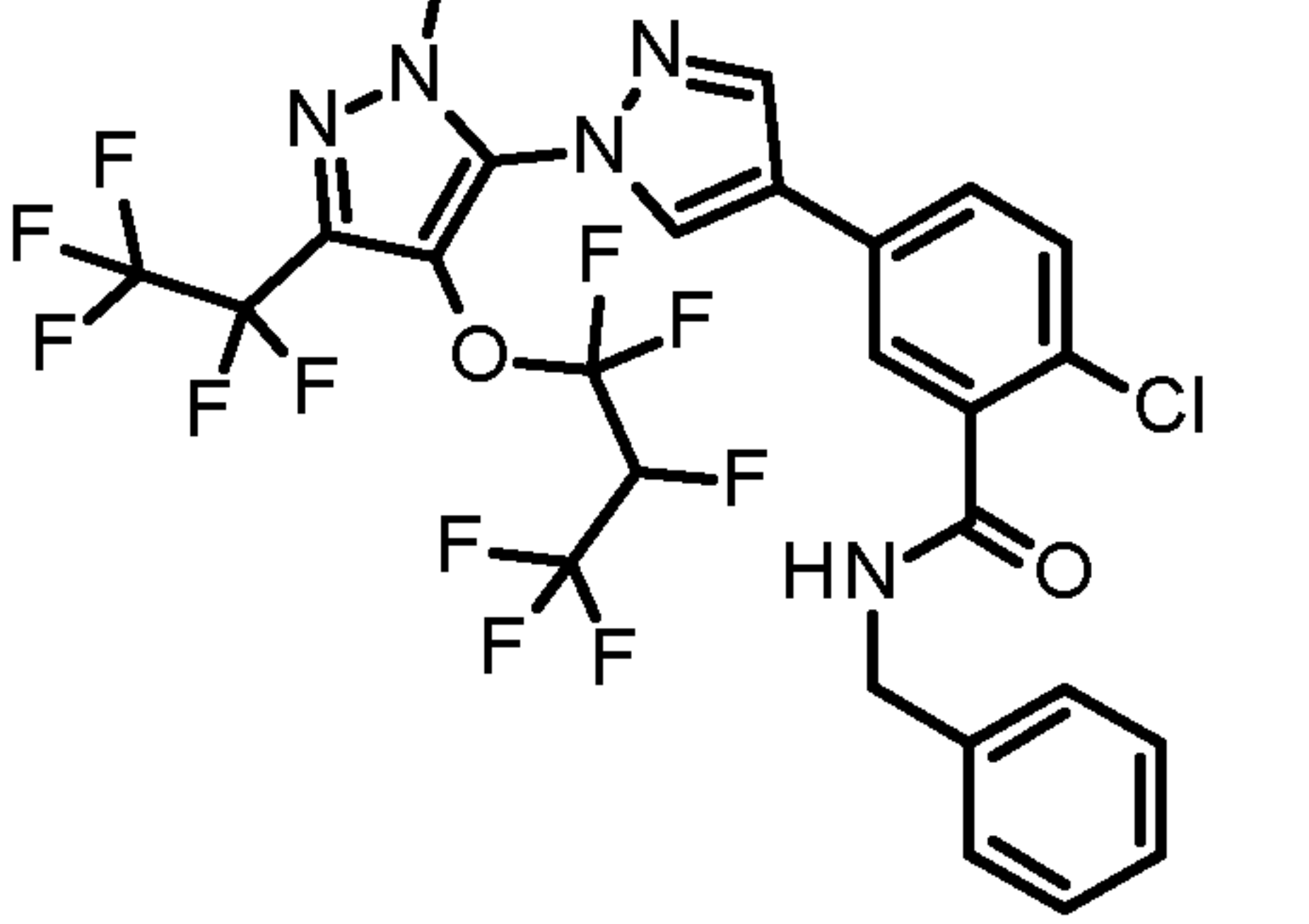
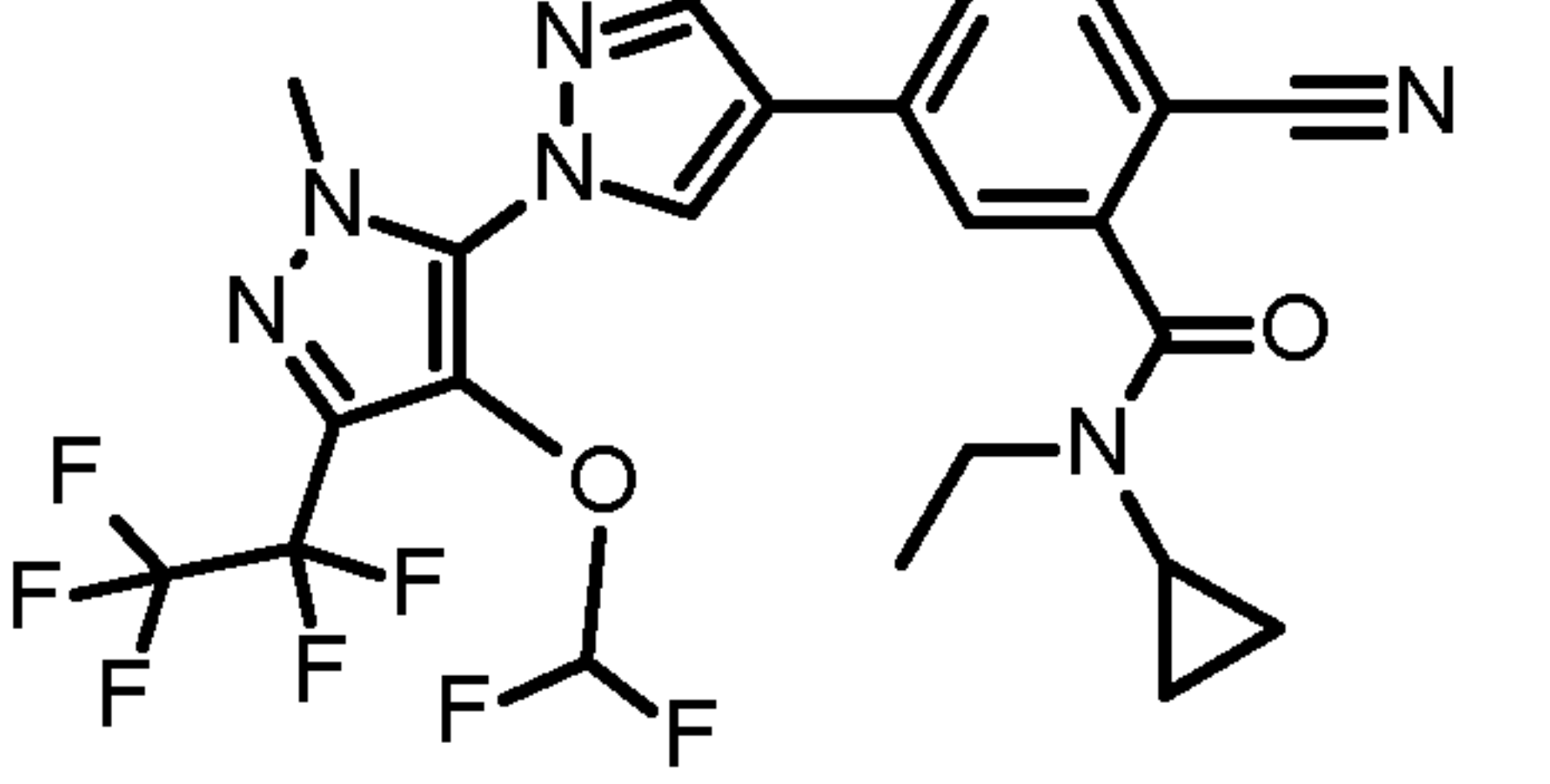
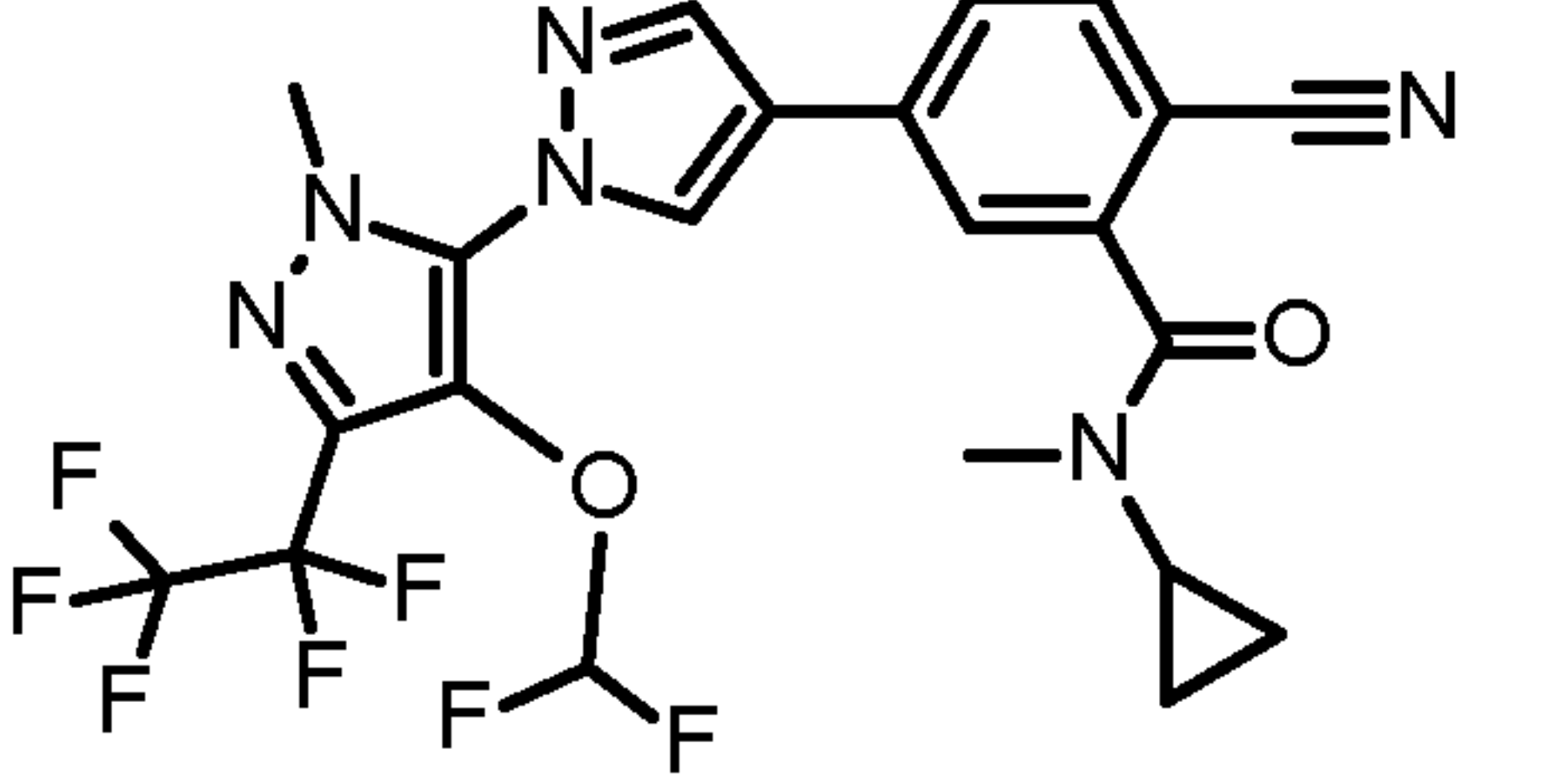
	Structure	1H-NMR (400 MHz) LC MS (method)	Mp [°C]
27			
28			
29			
30			
31			
32			

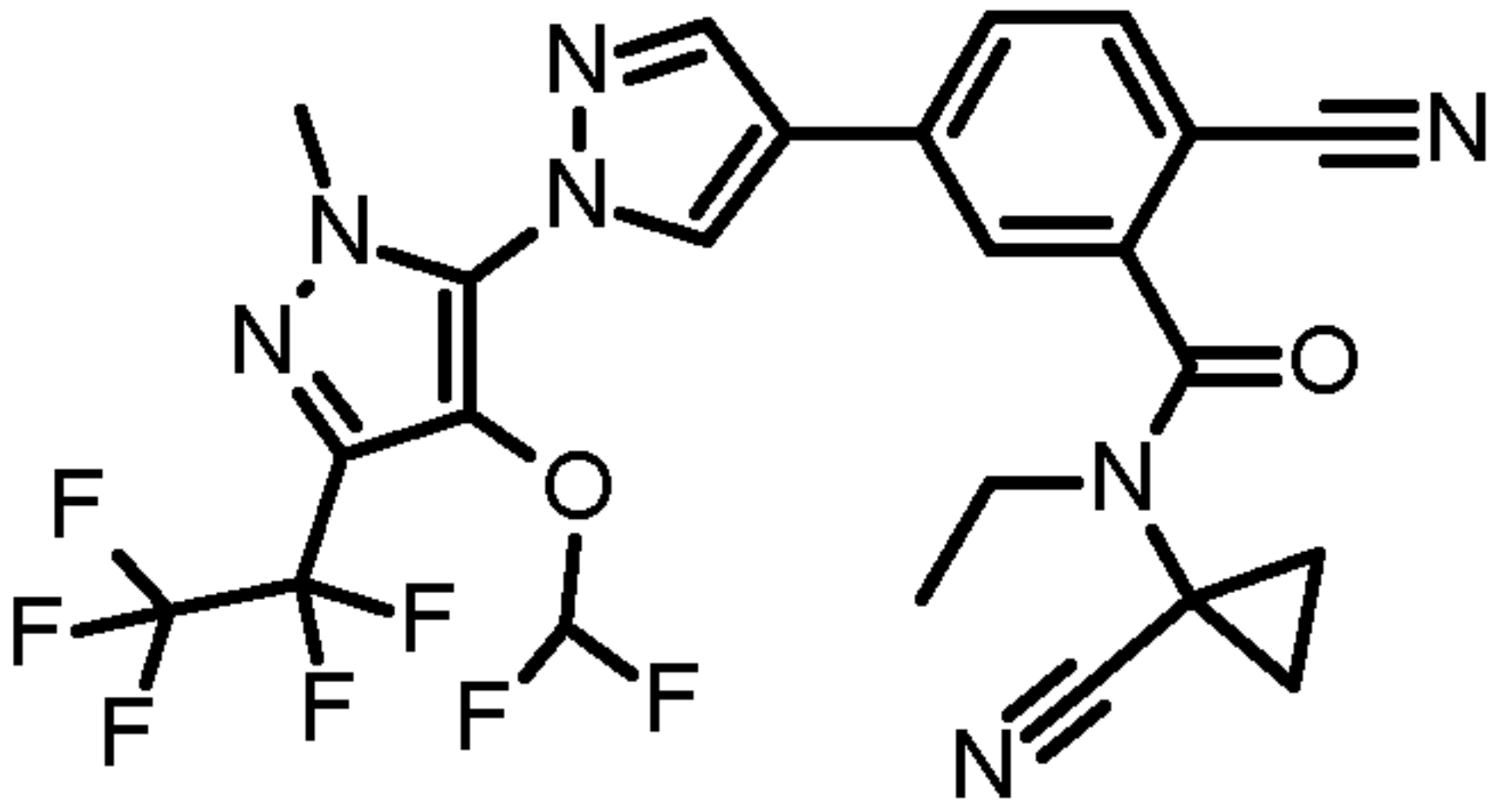
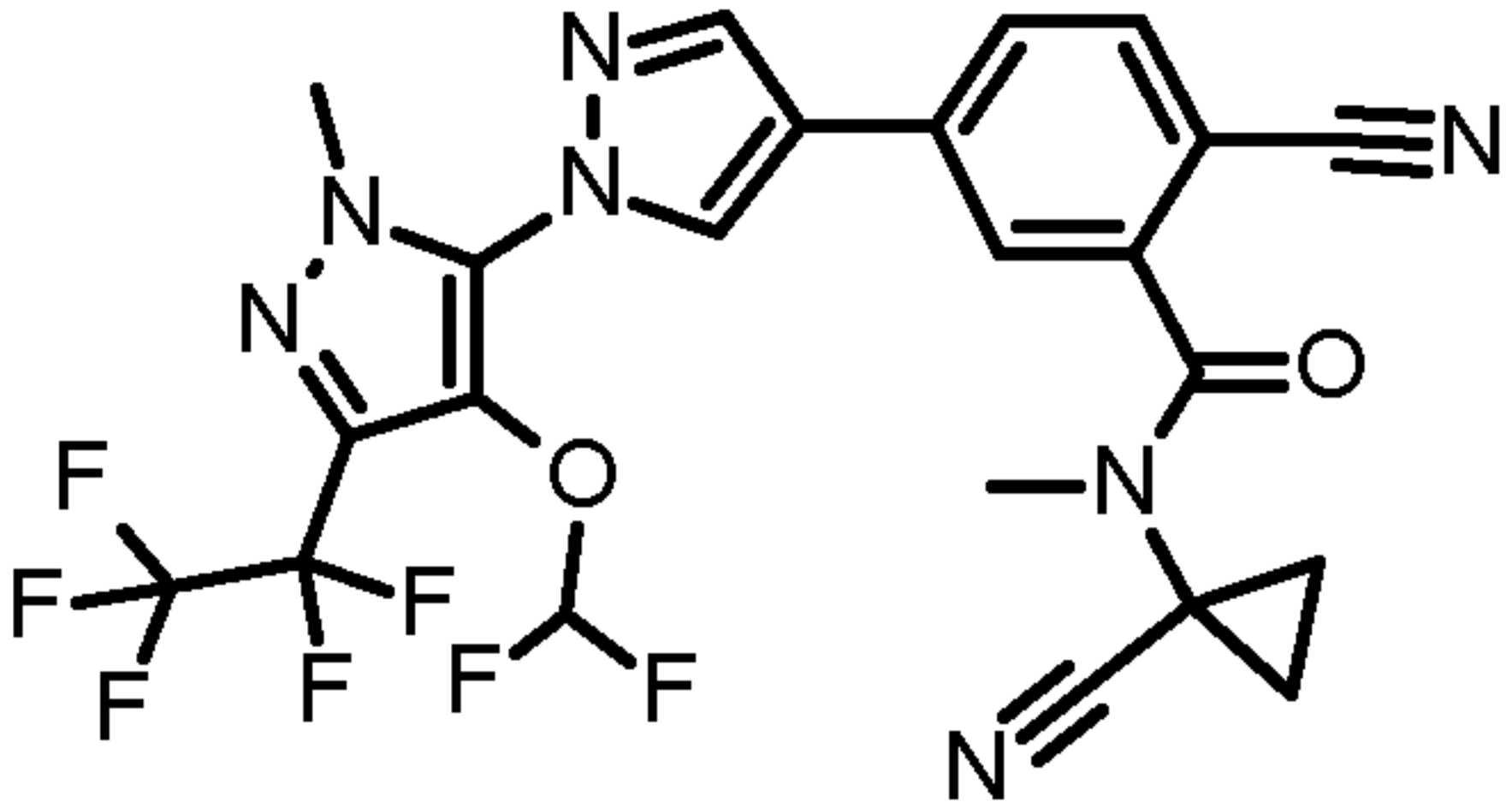
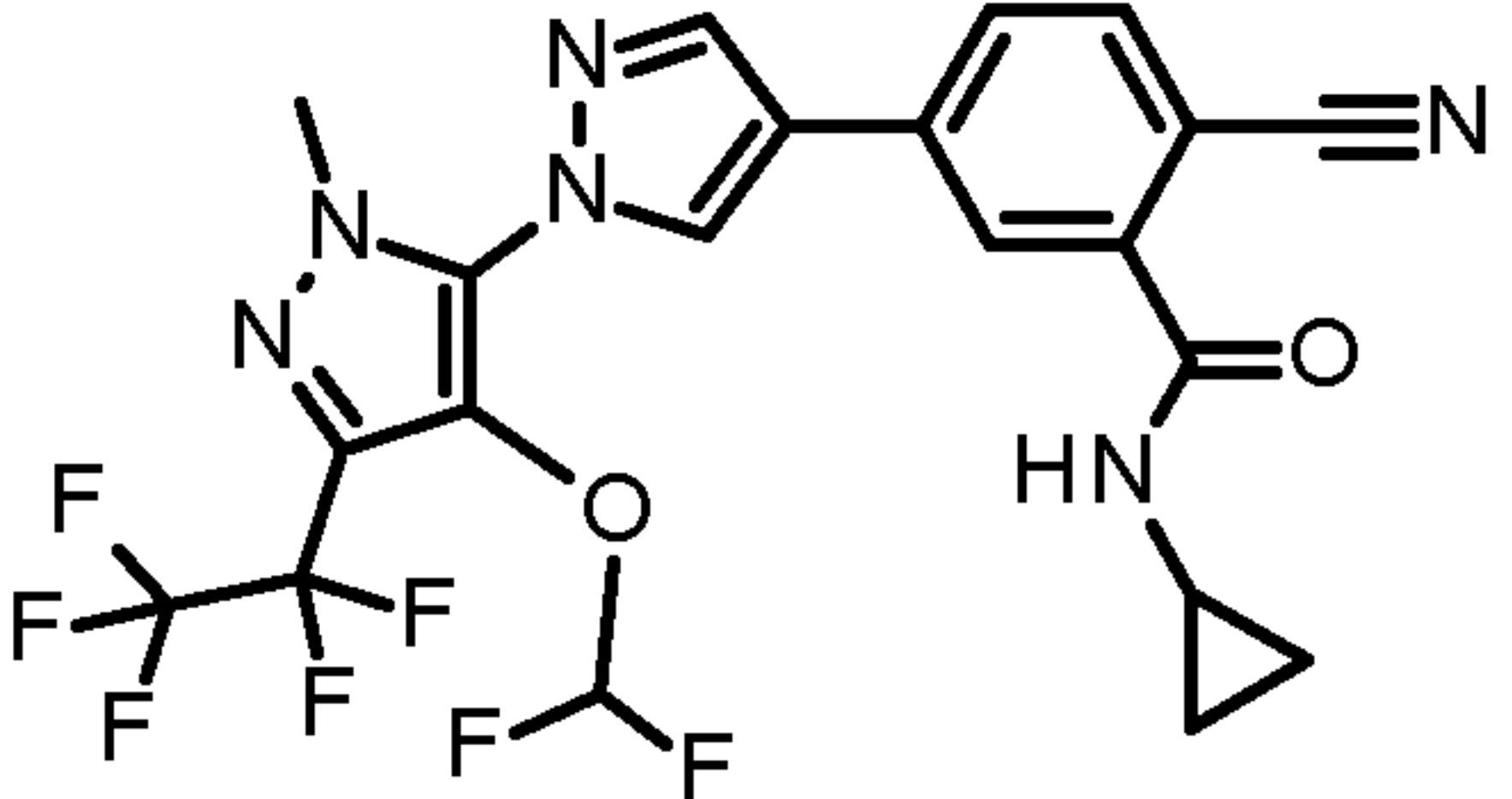
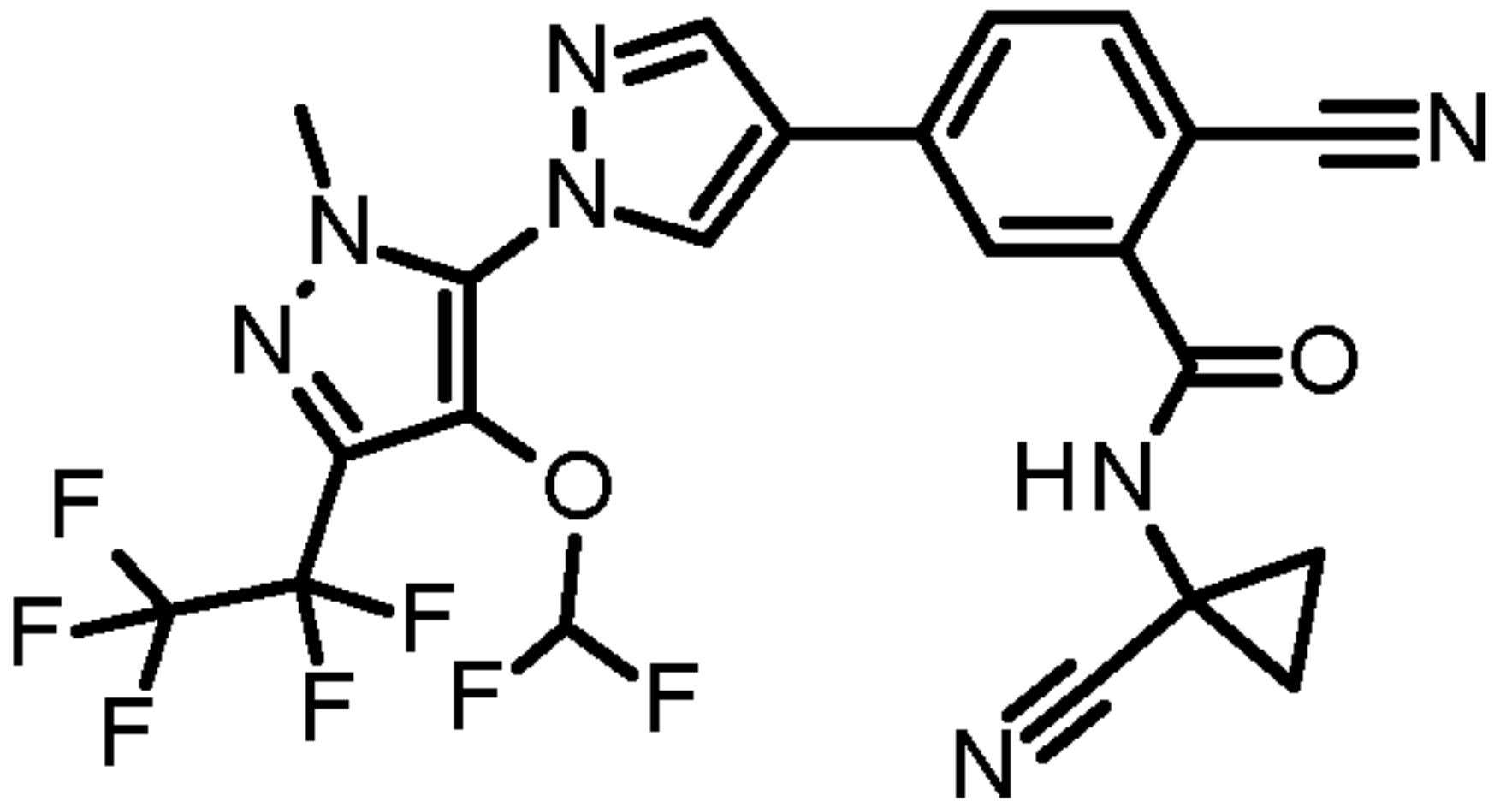
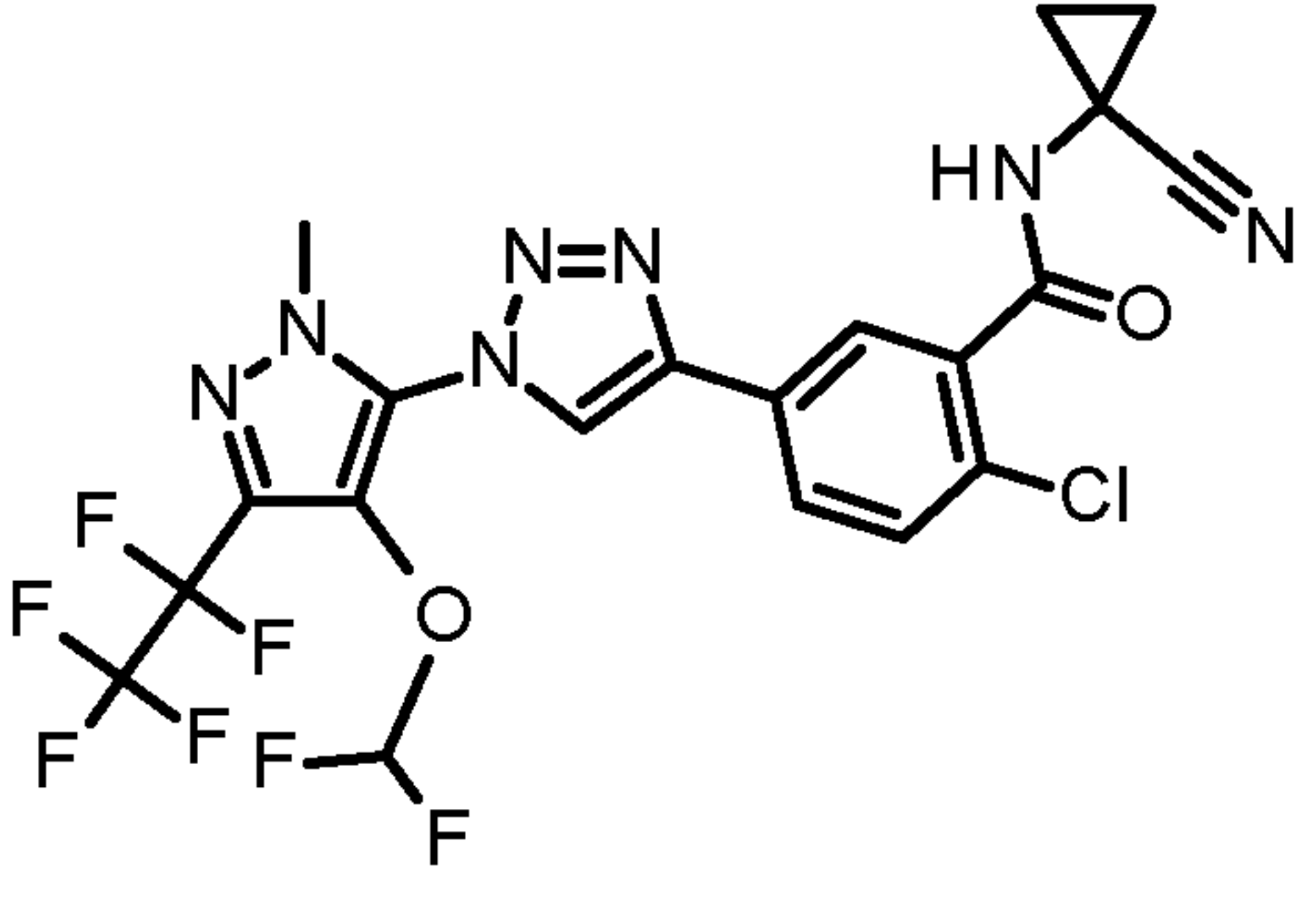
	Structure	¹ H-NMR (400 MHz) LC MS (method)	Mp [°C]
33			95-7
34			72-4
35			102-4
36			104-6
37		LC-MS (B): t _R = 1.80 min, m/z = 601/03 [M+1] ⁺	
38		LC-MS (B): t _R = 1.77 min, m/z = 529/31 [M+1] ⁺	169-70

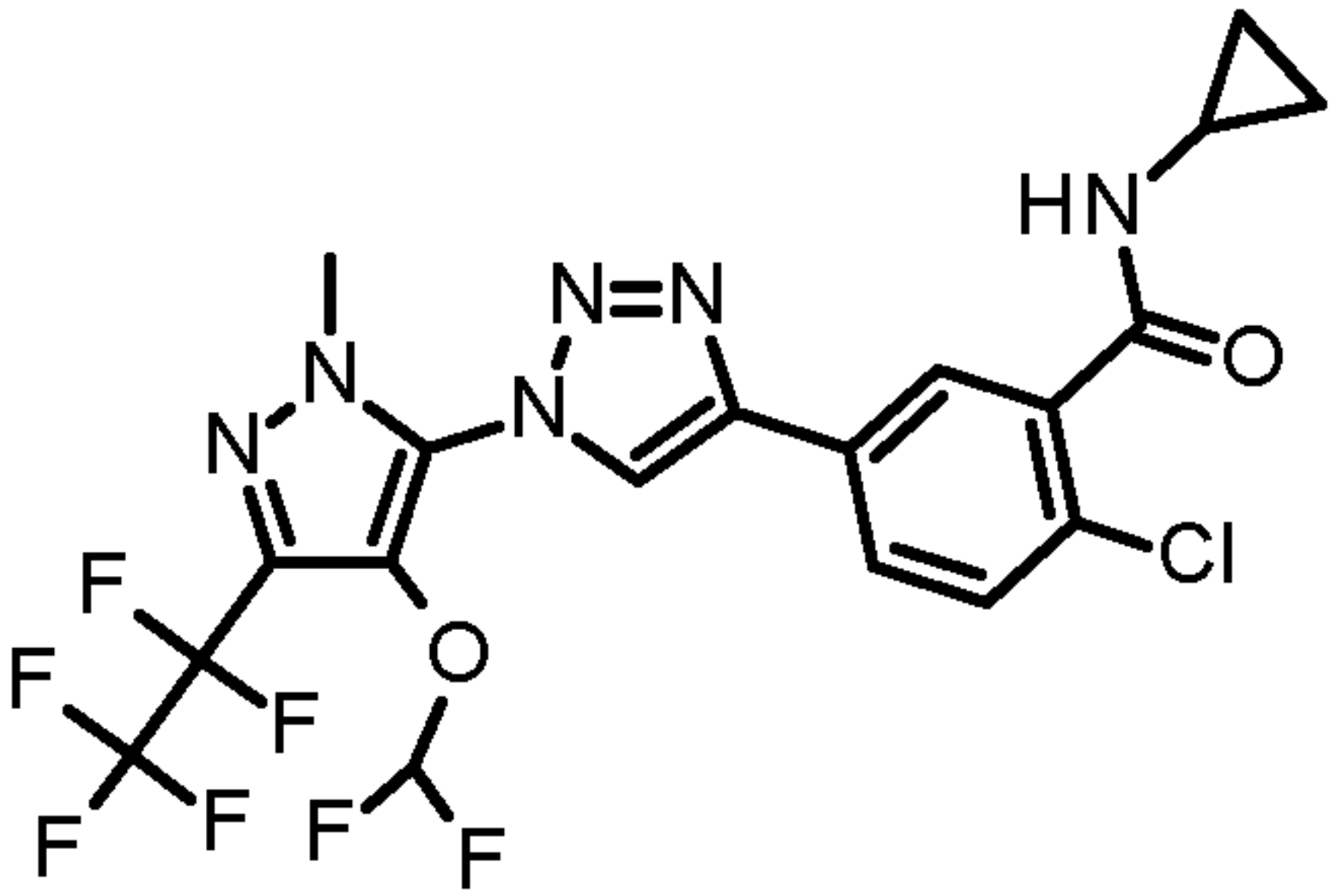
	Structure	¹ H-NMR (400 MHz) LC MS (method)	Mp [°C]
39		LC-MS (B): t _R = 1.75 min, m/z = 565/7 [M+1] ⁺	
40		LC-MS (B): t _R = 2.07 min, m/z = 669/71 [M+1] ⁺	
41		LC-MS (B): t _R = 1.86 min, m/z = 565/7 [M+1] ⁺	
42		LC-MS (B): t _R = 1.92 min, m/z = 579/81 [M+1] ⁺	
43		LC-MS (B): t _R = 1.92 min, m/z = 651/3 [M+1] ⁺	

	Structure	1H-NMR (400 MHz) LC MS (method)	Mp [°C]
44		LC-MS (B): $t_R = 1.76$ min, $m/z = 540/2$ $[M+1]^+$	
45		LC-MS (B): $t_R = 2.11$ min, $m/z = 644/6$ $[M+1]^+$	
46		LC-MS (B): $t_R = 1.94$ min, $m/z = 626/8$ $[M+1]^+$	
47		LC-MS (A): $t_R = 1.13$ min, $m/z = 544$ $[M+1]^+$, 542 $[M-1]^-$	
48		LC-MS (A): $t_R = 1.11$ min, $m/z = 569$ $[M+1]^+$, 567 $[M-1]^-$	

	Structure	1H-NMR (400 MHz) LC MS (method)	Mp [°C]
49		LC-MS (A): $t_R = 1.01$ min, m/z = 518 [M+1] ⁺ , 516 [M-1] ⁻	
50		LC-MS (A): $t_R = 1.17$ min, m/z = 558 [M+1] ⁺	
51		LC-MS (A): $t_R = 1.17$ min, m/z = 597 [M+1] ⁺	
52		LC-MS (A): $t_R = 1.07$ min, m/z = 566 [M+1] ⁺	
53		LC-MS (A): $t_R = 1.09$ min, m/z = 580 [M+1] ⁺	
54		LC-MS (A): $t_R = 1.08$ min, m/z = 541 [M+1] ⁺	

	Structure	¹ H-NMR (400 MHz) LC MS (method)	Mp [°C]
55		LC-MS (A): t _R = 1.12 min, m/z = 555 [M+1] ⁺ , 553 [M-1] ⁻	
56		LC-MS (A): t _R = 1.03 min, m/z = 543 [M+1] ⁺ , 541 [M-1] ⁻	
57		LC-MS (B): t _R = 2.09 min, m/z = 676/8 [M+1] ⁺	
58		LC-MS (A): t _R = 1.12 min, m/z = 545 [M+1] ⁺	
59		LC-MS (A): t _R = 1.08 min, m/z = 531 [M+1] ⁺	

	Structure	¹ H-NMR (400 MHz) LC MS (method)	Mp [°C]
60		LC-MS (A): t _R = 1.10 min, m/z = 570 [M+1] ⁺	
61		LC-MS (A): t _R = 1.07 min, m/z = 556 [M+1] ⁺	
62		LC-MS (A): t _R = 1.04 min, m/z = 517 [M+1] ⁺ , 516 [M-1] ⁻	
63		LC-MS (A): t _R = 1.03 min, m/z = 542 [M+1] ⁺ , 540 [M-1] ⁻	
64		LC-MS (A): t _R = 1.05 min, m/z = 552 [M+1] ⁺ , 550 [M-1] ⁻	

	Structure	1H-NMR (400 MHz) LC MS (method)	Mp [°C]
65		LC-MS (A): $t_R = 1.06$ min, $m/z = 527$ [M+1]	

Formulation examples (% = percent by weight)

Example F1: Emulsion concentrates

	a)	b)	c)
5 Active ingredient	25 %	40 %	50 %
Calcium dodecylbenzenesulfonate	5 %	8 %	6 %
Castor oil polyethylene glycol ether (36 mol of EO)	5 %	-	-
Tributylphenoxypolyethylene glycol ether (30 mol of EO)	-	12 %	4 %
10 Cyclohexanone	-	15 %	20 %
Xylene mixture	65 %	25 %	20 %

Emulsions of any desired concentration can be prepared from such concentrates by dilution with water.

15

Example F2: Solutions

	a)	b)	c)	d)
Active ingredient	80 %	10 %	5 %	95 %
Ethylene glycol monomethyl ether	20 %	-	-	-
20 Polyethylene glycol MW 400	-	70 %	-	-
N-Methylpyrrolid-2-one	-	20 %	-	-
Epoxidized coconut oil	-	-	1 %	5 %
Petroleum ether (boiling range: 160-190°)	-	-	94 %	-
25				

The solutions are suitable for use in the form of microdrops.

Example F3: Granules

a)	b)	c)	d)
----	----	----	----

Active ingredient	5 %	10 %	8 %	21 %
Kaolin	94 %	-	79 %	54 %
Highly disperse silica	1 %	-	13 %	7 %
Attapulgate	-	90 %	-	18 %

- 5 The active ingredient is dissolved in dichloromethane, the solution is sprayed onto the carrier(s), and the solvent is subsequently evaporated in vacuo.

Example F4: Dusts a) b)

Active ingredient	2 %	5 %
10 Highly disperse silica	1 %	5 %
Talc	97 %	-
Kaolin	-	90 %

Ready-to-use dusts are obtained by intimately mixing the carriers and the active ingredient.

15	<u>Example F5: Wettable powders</u>	a)	b)	c)
	Active ingredient	25 %	50 %	75 %
	Sodium lignosulfonate	5 %	5 %	-
	Sodium lauryl sulfate	3 %	-	5 %
	Sodium diisobutyl-			
20	naphthalenesulfonate	-	6 %	10 %
	Octylphenoxypolyethylene glycol			
	ether (7-8 mol of EO)	-	2 %	-
	Highly disperse silica	5 %	10 %	10 %
	Kaolin	62 %	27 %	-

- 25 The active ingredient is mixed with the additives and the mixture is ground thoroughly in a suitable mill. This gives wettable powders, which can be diluted with water to give suspensions of any desired concentration.

Example F6: Extruder granules

30	Active ingredient	10 %
	Sodium lignosulfonate	2 %
	Carboxymethylcellulose	1 %
	Kaolin	87 %

- 35 The active ingredient is mixed with the additives, and the mixture is ground, moistened with water, extruded, granulated and dried in a stream of air.

Example F7: Coated granules

Active ingredient	3 %
-------------------	-----

Polyethylene glycol (MW 200)	3 %
Kaolin	94 %

In a mixer, the finely ground active ingredient is applied uniformly to the kaolin, which has been moistened with the polyethylene glycol. This gives dust-free coated granules.

5

Example F8: Suspension concentrate

Active ingredient	40 %
Ethylene glycol	10 %
Nonylphenoxypolyethylene glycol ether (15 mol of EO)	6 %
10 Sodium lignosulfonate	10 %
Carboxymethylcellulose	1 %
37 % aqueous formaldehyde solution	0.2 %
Silicone oil (75 % aqueous emulsion)	0.8 %
Water	32 %

15 The finely ground active ingredient is mixed intimately with the additives. Suspensions of any desired concentration can be prepared from the thus resulting suspension concentrate by dilution with water.

Example F9: Powders for dry seed treatment

	a)	b)	c)
active ingredient	25 %	50 %	75 %
light mineral oil	5 %	5 %	5 %
highly dispersed silicic acid	5 %	5 %	-
Kaolin	65 %	40 %	-
Talcum	-	-	20 %

The combination is thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording powders that can be used directly for seed treatment.

20

Example F10: Emulsifiable concentrate

active ingredient	10 %
octylphenol polyethylene glycol ether (4-5 mol of ethylene oxide)	3 %
calcium dodecylbenzenesulfonate	3 %
castor oil polyglycol ether (35 mol of ethylene oxide)	4 %
Cyclohexanone	30 %
xylene mixture	50 %

Emulsions of any required dilution, which can be used in plant protection, can be obtained from this concentrate by dilution with water.

Example F11: Flowable concentrate for seed treatment

active ingredients	40 %
propylene glycol	5 %
copolymer butanol PO/EO	2 %
Tristyrenephenole with 10-20 moles EO	2 %
1,2-benzisothiazolin-3-one (in the form of a 20% solution in water)	0.5 %
monoazo-pigment calcium salt	5 %
Silicone oil (in the form of a 75 % emulsion in water)	0.2 %
Water	45.3 %

The finely ground combination is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water. Using such dilutions, living plants as well as plant propagation material can be treated and protected against

5 infestation by microorganisms, by spraying, pouring or immersion.

The activity of the compositions according to the invention can be broadened considerably, and adapted to prevailing circumstances, by adding other insecticidally, acaricidally and/or fungicidally active ingredients. The mixtures of the compounds according to any one of embodiments 1 to 25 with other

10 insecticidally, acaricidally and/or fungicidally active ingredients may also have further surprising advantages which can also be described, in a wider sense, as synergistic activity. For example, better tolerance by plants, reduced phytotoxicity, insects can be controlled in their different development stages or better behaviour during their production, for example during grinding or mixing, during their storage or during their use.

15 Suitable additions to active ingredients here are, for example, representatives of the following classes of active ingredients: organophosphorus compounds, nitrophenol derivatives, thioureas, juvenile hormones, formamidines, benzophenone derivatives, ureas, pyrrole derivatives, carbamates, pyrethroids, chlorinated hydrocarbons, acylureas, pyridylmethyleamino derivatives, macrolides, neonicotinoids and *Bacillus thuringiensis* preparations.

20 The following mixtures of the compounds according to any one of embodiments 1 to 25 with active ingredients are preferred (the abbreviation "TX" means "one compound selected from the compounds according to any one of embodiments 1 to 25, preferably one compound from Table 1):

25 an adjuvant selected from the group of substances consisting of petroleum oils (alternative name) (628) + TX,

an acaricide selected from the group of substances consisting of 1,1-bis(4-chlorophenyl)-2-ethoxyethanol (IUPAC name) (910) + TX, 2,4-dichlorophenyl benzenesulfonate (IUPAC/Chemical Abstracts name) (1059) + TX, 2-fluoro-*N*-methyl-*N*-1-naphthylacetamide (IUPAC name) (1295) + TX,

30 4-chlorophenyl phenyl sulfone (IUPAC name) (981) + TX, abamectin (1) + TX, acequinocyl (3) + TX,

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(1167) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenoxuron (370) + TX, flumethrin (372) + TX, fluorbenside (1174) + TX, fluvalinate (1184) + TX, FMC 1137 (development code) (1185) + TX, formetanate (405) + TX, formetanate hydrochloride (405) + TX, formothion (1192) + TX, formparanate (1193) + TX, gamma-HCH (430) + TX, glyodin (1205) + TX, halfenprox (424) + TX, heptenophos (432) + TX, hexadecyl cyclopropanecarboxylate (IUPAC/Chemical Abstracts name) (1216) + TX, hexythiazox (441) + TX, iodomethane (IUPAC name) (542) + TX, isocarbophos (alternative name) (473) + TX, isopropyl O-(methoxyaminothiophosphoryl)salicylate (IUPAC name) (473) + TX, ivermectin (alternative name) [CCN] + TX, jasmolin I (696) + TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, lindane (430) + TX, lufenuron (490) + TX, malathion (492) + TX, malonoben (1254) + TX, mecarbam (502) + TX, mephosfolan (1261) + TX, mesulfen (alternative name) [CCN] + TX, methacrifos (1266) + TX, methamidophos (527) + TX, methidathion (529) + TX, methiocarb (530) + TX, methomyl (531) + TX, methyl bromide (537) + TX, metolcarb (550) + TX, mevinphos (556) + TX, mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime (alternative name) [CCN] + TX, mipafox (1293) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin (alternative name) [CCN] + TX, naled (567) + TX, NC-184 (compound code) + TX, NC-512 (compound code) + TX, nifluridide (1309) + TX, nikkomycins (alternative name) [CCN] + TX, nitrilacarb (1313) + TX, nitrilacarb 1:1 zinc chloride complex (1313) + TX, NNI-0101 (compound code) + TX, NNI-0250 (compound code) + TX, omethoate (594) + TX, oxamyl (602) + TX, oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, parathion (615) + TX, permethrin (626) + TX, petroleum oils (alternative name) (628) + TX, phenkapton (1330) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosphamidon (639) + TX, phoxim (642) + TX, pirimiphos-methyl (652) + TX, polychloroterpenes (traditional name) (1347) + TX, polynactins (alternative name) (653) + TX, proclonol (1350) + TX, profenofos (662) + TX, promacyl (1354) + TX, propargite (671) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothoate (1362) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, quinalphos (711) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, RA-17 (development code) (1383) + TX, rotenone (722) + TX, schradan (1389) + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, SI-0009 (compound code) + TX, sophamide (1402) + TX, spiroadiclofen (738) + TX, spiromesifen (739) + TX, SSI-121 (development code) (1404) + TX, sulfiram (alternative name) [CCN] + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulfur (754) + TX, SZI-121 (development code) (757) + TX, tau-fluvalinate (398) + TX, tebufenpyrad (763) + TX, TEPP (1417) + TX, terbam (alternative name) + TX, tetrachlorvinphos (777) + TX, tetradifon (786) + TX, tetranactin (alternative name) (653) + TX, tetrasul (1425) + TX, thiafenox (alternative name) + TX, thiocarboxime (1431) + TX, thiofanox (800) + TX, thiometon (801) + TX, thioquinox (1436) + TX, thuringiensin (alternative name) [CCN] + TX, triamiphos (1441) + TX, triarathene (1443) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, trichlorfon (824) + TX,

trifenofos (1455) + TX, trinactin (alternative name) (653) + TX, vamidothion (847) + TX, vaniliprole [CCN] and YI-5302 (compound code) + TX,

an algicide selected from the group of substances consisting of bethoxazin [CCN] + TX, copper dioctanoate (IUPAC name) (170) + TX, copper sulfate (172) + TX, cybutryne [CCN] + TX, dichlone (1052) + TX, dichlorophen (232) + TX, endothal (295) + TX, fentin (347) + TX, hydrated lime [CCN] + TX, nabam (566) + TX, quinoclamine (714) + TX, quinonamid (1379) + TX, simazine (730) + TX, triphenyltin acetate (IUPAC name) (347) and triphenyltin hydroxide (IUPAC name) (347) + TX,

an anthelmintic selected from the group of substances consisting of abamectin (1) + TX, crufomate (1011) + TX, doramectin (alternative name) [CCN] + TX, emamectin (291) + TX, emamectin

benzoate (291) + TX, eprinomectin (alternative name) [CCN] + TX, ivermectin (alternative name) [CCN] + TX, milbemycin oxime (alternative name) [CCN] + TX, moxidectin (alternative name) [CCN] + TX, piperazine [CCN] + TX, selamectin (alternative name) [CCN] + TX, spinosad (737) and thiophanate (1435) + TX,

an avicide selected from the group of substances consisting of chloralose (127) + TX, endrin (1122) + TX, fenthion (346) + TX, pyridin-4-amine (IUPAC name) (23) and strychnine (745) + TX,

a bactericide selected from the group of substances consisting of 1-hydroxy-1*H*-pyridine-2-thione (IUPAC name) (1222) + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide (IUPAC name) (748) + TX, 8-hydroxyquinoline sulfate (446) + TX, bronopol (97) + TX, copper dioctanoate (IUPAC name) (170) + TX, copper hydroxide (IUPAC name) (169) + TX, cresol [CCN] + TX, dichlorophen (232) + TX, dipyrithione (1105) + TX, dodicin (1112) + TX, fenaminosulf (1144) + TX, formaldehyde (404) + TX, hydrargaphen (alternative name) [CCN] + TX, kasugamycin (483) + TX, kasugamycin hydrochloride hydrate (483) + TX, nickel bis(dimethyldithiocarbamate) (IUPAC name) (1308) + TX, nitrapyrin (580) + TX, octhilinone (590) + TX, oxolinic acid (606) + TX, oxytetracycline (611) + TX, potassium hydroxyquinoline sulfate (446) + TX, probenazole (658) + TX, streptomycin (744) + TX, streptomycin sesquisulfate (744) + TX, tecloftalam (766) + TX, and thiomersal (alternative name) [CCN] + TX,

a biological agent selected from the group of substances consisting of *Adoxophyes orana* GV (alternative name) (12) + TX, *Agrobacterium radiobacter* (alternative name) (13) + TX, *Amblyseius* spp. (alternative name) (19) + TX, *Anagrapha falcifera* NPV (alternative name) (28) + TX, *Anagrus atomus* (alternative name) (29) + TX, *Aphelinus abdominalis* (alternative name) (33) + TX, *Aphidius colemani* (alternative name) (34) + TX, *Aphidoletes aphidimyza* (alternative name) (35) + TX, *Autographa californica* NPV (alternative name) (38) + TX, *Bacillus firmus* (alternative name) (48) + TX, *Bacillus sphaericus* Neide (scientific name) (49) + TX, *Bacillus thuringiensis* Berliner (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *aizawai* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *israelensis* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *japonensis* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *kurstaki* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *tenebrionis* (scientific name) (51) + TX, *Beauveria bassiana* (alternative name) (53) + TX, *Beauveria brongniartii* (alternative name) (54) + TX, *Chrysoperla carnea* (alternative name) (151) + TX, *Cryptolaemus montrouzieri* (alternative name) (178) + TX, *Cydia pomonella* GV (alternative

- name) (191) + TX, *Dacnusa sibirica* (alternative name) (212) + TX, *Diglyphus isaea* (alternative name) (254) + TX, *Encarsia formosa* (scientific name) (293) + TX, *Eretmocerus eremicus* (alternative name) (300) + TX, *Helicoverpa zea* NPV (alternative name) (431) + TX, *Heterorhabditis bacteriophora* and *H. megidis* (alternative name) (433) + TX, *Hippodamia convergens* (alternative name) (442) + TX, *Leptomastix dactylopii* (alternative name) (488) + TX, *Macrolophus caliginosus* (alternative name) (491) + TX, *Mamestra brassicae* NPV (alternative name) (494) + TX, *Metaphycus helvolus* (alternative name) (522) + TX, *Metarhizium anisopliae* var. *acridum* (scientific name) (523) + TX, *Metarhizium anisopliae* var. *anisopliae* (scientific name) (523) + TX, *Neodiprion sertifer* NPV and *N. lecontei* NPV (alternative name) (575) + TX, *Orius* spp. (alternative name) (596) + TX,
- 10 *Paecilomyces fumosoroseus* (alternative name) (613) + TX, *Phytoseiulus persimilis* (alternative name) (644) + TX, *Spodoptera exigua* multicapsid nuclear polyhedrosis virus (scientific name) (741) + TX, *Steinernema bibionis* (alternative name) (742) + TX, *Steinernema carpocapsae* (alternative name) (742) + TX, *Steinernema feltiae* (alternative name) (742) + TX, *Steinernema glaseri* (alternative name) (742) + TX, *Steinernema riobrave* (alternative name) (742) + TX, *Steinernema riobrave* (alternative name) (742) + TX, *Steinernema scapterisci* (alternative name) (742) + TX, *Steinernema* spp. (alternative name) (742) + TX, *Trichogramma* spp. (alternative name) (826) + TX, *Typhlodromus occidentalis* (alternative name) (844) and *Verticillium lecanii* (alternative name) (848) + TX,
- a soil sterilant selected from the group of substances consisting of iodomethane (IUPAC name) (542) and methyl bromide (537) + TX,
- 20 a chemosterilant selected from the group of substances consisting of apholate [CCN] + TX, bisazir (alternative name) [CCN] + TX, busulfan (alternative name) [CCN] + TX, diflubenzuron (250) + TX, dimatif (alternative name) [CCN] + TX, hemel [CCN] + TX, hempa [CCN] + TX, metepa [CCN] + TX, methiotepa [CCN] + TX, methyl apholate [CCN] + TX, morzid [CCN] + TX, penfluron (alternative name) [CCN] + TX, tepa [CCN] + TX, thiohempa (alternative name) [CCN] + TX, thiotepa (alternative name) [CCN] + TX, tretamine (alternative name) [CCN] and uredepa (alternative name) [CCN] + TX,
- 25 an insect pheromone selected from the group of substances consisting of (*E*)-dec-5-en-1-yl acetate with (*E*)-dec-5-en-1-ol (IUPAC name) (222) + TX, (*E*)-tridec-4-en-1-yl acetate (IUPAC name) (829) + TX, (*E*)-6-methylhept-2-en-4-ol (IUPAC name) (541) + TX, (*E,Z*)-tetradeca-4,10-dien-1-yl acetate (IUPAC name) (779) + TX, (*Z*)-dodec-7-en-1-yl acetate (IUPAC name) (285) + TX, (*Z*)-hexadec-11-enal (IUPAC name) (436) + TX, (*Z*)-hexadec-11-en-1-yl acetate (IUPAC name) (437) + TX, (*Z*)-hexadec-13-en-11-yn-1-yl acetate (IUPAC name) (438) + TX, (*Z*)-icos-13-en-10-one (IUPAC name) (448) + TX, (*Z*)-tetradec-7-en-1-al (IUPAC name) (782) + TX, (*Z*)-tetradec-9-en-1-ol (IUPAC name) (783) + TX, (*Z*)-tetradec-9-en-1-yl acetate (IUPAC name) (784) + TX, (*7E,9Z*)-dodeca-7,9-dien-1-yl acetate (IUPAC name) (283) + TX, (*9Z,11E*)-tetradeca-9,11-dien-1-yl acetate (IUPAC name) (780) + TX, (*9Z,12E*)-tetradeca-9,12-dien-1-yl acetate (IUPAC name) (781) + TX, 14-methyloctadec-1-ene (IUPAC name) (545) + TX, 4-methylnonan-5-ol with 4-methylnonan-5-one (IUPAC name) (544) + TX, alpha-multistriatin (alternative name) [CCN] + TX, brevicomin (alternative name) [CCN] + TX, codlelure
- 35

(alternative name) [CCN] + TX, codlemone (alternative name) (167) + TX, cuelure (alternative name) (179) + TX, disparlure (277) + TX, dodec-8-en-1-yl acetate (IUPAC name) (286) + TX, dodec-9-en-1-yl acetate (IUPAC name) (287) + TX, dodeca-8 + TX, 10-dien-1-yl acetate (IUPAC name) (284) + TX, dominicalure (alternative name) [CCN] + TX, ethyl 4-methyloctanoate (IUPAC name) (317) + TX, 5 eugenol (alternative name) [CCN] + TX, frontalinal (alternative name) [CCN] + TX, gossyplure (alternative name) (420) + TX, grandlure (421) + TX, grandlure I (alternative name) (421) + TX, grandlure II (alternative name) (421) + TX, grandlure III (alternative name) (421) + TX, grandlure IV (alternative name) (421) + TX, hexalure [CCN] + TX, ipsdienol (alternative name) [CCN] + TX, ipsenol (alternative name) [CCN] + TX, japonilure (alternative name) (481) + TX, lineatin (alternative name) [CCN] + TX, 10 litlure (alternative name) [CCN] + TX, looplure (alternative name) [CCN] + TX, medlure [CCN] + TX, megatomoic acid (alternative name) [CCN] + TX, methyl eugenol (alternative name) (540) + TX, muscalure (563) + TX, octadeca-2,13-dien-1-yl acetate (IUPAC name) (588) + TX, octadeca-3,13-dien-1-yl acetate (IUPAC name) (589) + TX, orfralure (alternative name) [CCN] + TX, oryctalure (alternative name) (317) + TX, ostramone (alternative name) [CCN] + TX, siglure [CCN] + 15 TX, sordidin (alternative name) (736) + TX, sulcatol (alternative name) [CCN] + TX, tetradec-11-en-1-yl acetate (IUPAC name) (785) + TX, trimedlure (839) + TX, trimedlure A (alternative name) (839) + TX, trimedlure B₁ (alternative name) (839) + TX, trimedlure B₂ (alternative name) (839) + TX, trimedlure C (alternative name) (839) and trunc-call (alternative name) [CCN] + TX, an insect repellent selected from the group of substances consisting of 2-(octylthio)ethanol (IUPAC 20 name) (591) + TX, butopyronoxyl (933) + TX, butoxy(polypropylene glycol) (936) + TX, dibutyl adipate (IUPAC name) (1046) + TX, dibutyl phthalate (1047) + TX, dibutyl succinate (IUPAC name) (1048) + TX, diethyltoluamide [CCN] + TX, dimethyl carbate [CCN] + TX, dimethyl phthalate [CCN] + TX, ethyl hexanediol (1137) + TX, hexamide [CCN] + TX, methoquin-butyl (1276) + TX, methylneodecanamide [CCN] + TX, oxamate [CCN] and picaridin [CCN] + TX, 25 an insecticide selected from the group of substances consisting of 1-dichloro-1-nitroethane (IUPAC/Chemical Abstracts name) (1058) + TX, 1,1-dichloro-2,2-bis(4-ethylphenyl)ethane (IUPAC name) (1056), + TX, 1,2-dichloropropane (IUPAC/Chemical Abstracts name) (1062) + TX, 1,2-dichloropropane with 1,3-dichloropropene (IUPAC name) (1063) + TX, 1-bromo-2-chloroethane (IUPAC/Chemical Abstracts name) (916) + TX, 2,2,2-trichloro-1-(3,4-dichlorophenyl)ethyl acetate 30 (IUPAC name) (1451) + TX, 2,2-dichlorovinyl 2-ethylsulfinylethyl methyl phosphate (IUPAC name) (1066) + TX, 2-(1,3-dithiolan-2-yl)phenyl dimethylcarbamate (IUPAC/ Chemical Abstracts name) (1109) + TX, 2-(2-butoxyethoxy)ethyl thiocyanate (IUPAC/Chemical Abstracts name) (935) + TX, 2-(4,5-dimethyl-1,3-dioxolan-2-yl)phenyl methylcarbamate (IUPAC/ Chemical Abstracts name) (1084) + TX, 2-(4-chloro-3,5-xylyloxy)ethanol (IUPAC name) (986) + TX, 2-chlorovinyl diethyl phosphate (IUPAC name) (984) + TX, 2-imidazolidone (IUPAC name) (1225) + TX, 2-isovalerylindan-1,3-dione (IUPAC name) (1246) + TX, 2-methyl(prop-2-ynyl)aminophenyl methylcarbamate (IUPAC name) (1284) + TX, 2-thiocyanatoethyl laurate (IUPAC name) (1433) + TX, 3-bromo-1-chloroprop-1-ene (IUPAC name) (917) + TX, 3-methyl-1-phenylpyrazol-5-yl dimethylcarbamate (IUPAC name) (1283) + TX, 4-

methyl(prop-2-ynyl)amino-3,5-xylyl methylcarbamate (IUPAC name) (1285) + TX, 5,5-dimethyl-3-oxocyclohex-1-enyl dimethylcarbamate (IUPAC name) (1085) + TX, abamectin (1) + TX, acephate (2) + TX, acetamiprid (4) + TX, acethion (alternative name) [CCN] + TX, acetoprole [CCN] + TX, acrinathrin (9) + TX, acrylonitrile (IUPAC name) (861) + TX, alanycarb (15) + TX, aldicarb (16) + TX, 5 aldoxycarb (863) + TX, aldrin (864) + TX, allethrin (17) + TX, allosamidin (alternative name) [CCN] + TX, allyxycarb (866) + TX, alpha-cypermethrin (202) + TX, alpha-ecdysone (alternative name) [CCN] + TX, aluminium phosphide (640) + TX, amidithion (870) + TX, amidothioate (872) + TX, aminocarb (873) + TX, amiton (875) + TX, amiton hydrogen oxalate (875) + TX, amitraz (24) + TX, anabasine (877) + TX, athidathion (883) + TX, AVI 382 (compound code) + TX, AZ 60541 10 (compound code) + TX, azadirachtin (alternative name) (41) + TX, azamethiphos (42) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azothoate (889) + TX, *Bacillus thuringiensis* delta endotoxins (alternative name) (52) + TX, barium hexafluorosilicate (alternative name) [CCN] + TX, barium polysulfide (IUPAC/Chemical Abstracts name) (892) + TX, barthrin [CCN] + TX, Bayer 22/190 (development code) (893) + TX, Bayer 22408 (development code) (894) + TX, bendiocarb 15 (58) + TX, benfuracarb (60) + TX, bensultap (66) + TX, beta-cyfluthrin (194) + TX, beta-cypermethrin (203) + TX, bifenthrin (76) + TX, bioallethrin (78) + TX, bioallethrin S-cyclopentenyl isomer (alternative name) (79) + TX, bioethanomethrin [CCN] + TX, biopermethrin (908) + TX, bioresmethrin (80) + TX, bis(2-chloroethyl) ether (IUPAC name) (909) + TX, bistrifluron (83) + TX, borax (86) + TX, brofenvalerate (alternative name) + TX, bromfenvinfos (914) + TX, bromocyclen 20 (918) + TX, bromo-DDT (alternative name) [CCN] + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bufencarb (924) + TX, buprofezin (99) + TX, butacarb (926) + TX, butathiofos (927) + TX, butocarboxim (103) + TX, butonate (932) + TX, butoxycarboxim (104) + TX, butylpyridaben (alternative name) + TX, cadusafos (109) + TX, calcium arsenate [CCN] + TX, calcium cyanide (444) + TX, calcium polysulfide (IUPAC name) (111) + TX, camphechlor (941) + TX, carbanolate 25 (943) + TX, carbaryl (115) + TX, carbofuran (118) + TX, carbon disulfide (IUPAC/Chemical Abstracts name) (945) + TX, carbon tetrachloride (IUPAC name) (946) + TX, carbophenothion (947) + TX, carbosulfan (119) + TX, cartap (123) + TX, cartap hydrochloride (123) + TX, cevadine (alternative name) (725) + TX, chlorbicyclen (960) + TX, chlordane (128) + TX, chlordecone (963) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, chlorethoxyfos (129) + TX, 30 chlorfenapyr (130) + TX, chlorfenvinphos (131) + TX, chlorfluazuron (132) + TX, chlormephos (136) + TX, chloroform [CCN] + TX, chloropicrin (141) + TX, chlorphoxim (989) + TX, chlorprazophos (990) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, chromafenozide (150) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, cis-resmethrin (alternative name) + TX, cismethrin (80) + TX, clocythrin (alternative name) + TX, 35 cloethocarb (999) + TX, closantel (alternative name) [CCN] + TX, clothianidin (165) + TX, copper acetoarsenite [CCN] + TX, copper arsenate [CCN] + TX, copper oleate [CCN] + TX, coumaphos (174) + TX, coumithoate (1006) + TX, crotamiton (alternative name) [CCN] + TX, crotoxyphos (1010) + TX, crufomate (1011) + TX, cryolite (alternative name) (177) + TX, CS 708 (development

code) (1012) + TX, cyanofenphos (1019) + TX, cyanophos (184) + TX, cyanthoate (1020) + TX, cyclethrin [CCN] + TX, cycloprothrin (188) + TX, cyfluthrin (193) + TX, cyhalothrin (196) + TX, cypermethrin (201) + TX, cyphenothrin (206) + TX, cyromazine (209) + TX, cythioate (alternative name) [CCN] + TX, *d*-limonene (alternative name) [CCN] + TX, *d*-tetramethrin (alternative name) (788) + TX, DAEP (1031) + TX, dazomet (216) + TX, DDT (219) + TX, decarbofuran (1034) + TX, deltamethrin (223) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037) + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-methylsulphon (1039) + TX, diafenthion (226) + TX, dialifos (1042) + TX, diamidafos (1044) + TX, diazinon (227) + TX, dicapthon (1050) + TX, dichlofenthion (1051) + TX, dichlorvos (236) + TX, dicliphos (alternative name) + TX, dicresyl (alternative name) [CCN] + TX, dicrotophos (243) + TX, dicyclanil (244) + TX, dieldrin (1070) + TX, diethyl 5-methylpyrazol-3-yl phosphate (IUPAC name) (1076) + TX, diflubenzuron (250) + TX, dilor (alternative name) [CCN] + TX, dimefluthrin [CCN] + TX, dimefox (1081) + TX, dimetan (1085) + TX, dimethoate (262) + TX, dimethrin (1083) + TX, dimethylvinphos (265) + TX, dimetilan (1086) + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinoprop (1093) + TX, dinosam (1094) + TX, dinoseb (1095) + TX, dinotefuran (271) + TX, diofenolan (1099) + TX, dioxabenzofos (1100) + TX, dioxacarb (1101) + TX, dioxathion (1102) + TX, disulfoton (278) + TX, dithicrofos (1108) + TX, DNOC (282) + TX, doramectin (alternative name) [CCN] + TX, DSP (1115) + TX, ecdysterone (alternative name) [CCN] + TX, EI 1642 (development code) (1118) + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, EMPC (1120) + TX, empenthrin (292) + TX, endosulfan (294) + TX, endothion (1121) + TX, endrin (1122) + TX, EPBP (1123) + TX, EPN (297) + TX, epofenonane (1124) + TX, eprinomectin (alternative name) [CCN] + TX, esfenvalerate (302) + TX, etaphos (alternative name) [CCN] + TX, ethiofencarb (308) + TX, ethion (309) + TX, ethiprole (310) + TX, ethoate-methyl (1134) + TX, ethoprophos (312) + TX, ethyl formate (IUPAC name) [CCN] + TX, ethyl-DDD (alternative name) (1056) + TX, ethylene dibromide (316) + TX, ethylene dichloride (chemical name) (1136) + TX, ethylene oxide [CCN] + TX, etofenprox (319) + TX, etrimfos (1142) + TX, EXD (1143) + TX, famphur (323) + TX, fenamiphos (326) + TX, fenazaflor (1147) + TX, fenchlorphos (1148) + TX, fenethacarb (1149) + TX, fenfluthrin (1150) + TX, fenitrothion (335) + TX, fenobucarb (336) + TX, fenoxacrim (1153) + TX, fenoxycarb (340) + TX, fenpirithrin (1155) + TX, fenpropathrin (342) + TX, fenpyrad (alternative name) + TX, fensulfothion (1158) + TX, fenthion (346) + TX, fenthion-ethyl [CCN] + TX, fenvalerate (349) + TX, fipronil (354) + TX, flonicamid (358) + TX, flubendiamide (CAS. Reg. No.: 272451-65-7) + TX, flucofuron (1168) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenerim [CCN] + TX, flufenoxuron (370) + TX, flufenprox (1171) + TX, flumethrin (372) + TX, fluvalinate (1184) + TX, FMC 1137 (development code) (1185) + TX, fonofos (1191) + TX, formetanate (405) + TX, formetanate hydrochloride (405) + TX, formothion (1192) + TX, formparanate (1193) + TX, fosmethilan (1194) + TX, fospirate (1195) + TX, fosthiazate (408) + TX, fosthietan (1196) + TX, furathiocarb (412) + TX, furethrin (1200) + TX, gamma-cyhalothrin (197) +

TX, gamma-HCH (430) + TX, guazatine (422) + TX, guazatine acetates (422) + TX, GY-81 (development code) (423) + TX, halfenprox (424) + TX, halofenozide (425) + TX, HCH (430) + TX, HEOD (1070) + TX, heptachlor (1211) + TX, heptenophos (432) + TX, heterophos [CCN] + TX, hexaflumuron (439) + TX, HHDN (864) + TX, hydramethylnon (443) + TX, hydrogen cyanide (444) + TX, hydroprene (445) + TX, hyquincarb (1223) + TX, imidacloprid (458) + TX, imiprothrin (460) + TX, indoxacarb (465) + TX, iodomethane (IUPAC name) (542) + TX, IPSP (1229) + TX, isazofos (1231) + TX, isobenzan (1232) + TX, isocarbophos (alternative name) (473) + TX, isodrin (1235) + TX, isofenphos (1236) + TX, isolane (1237) + TX, isoprocab (472) + TX, isopropyl O-(methoxyaminothiophosphoryl)salicylate (IUPAC name) (473) + TX, isoprothiolane (474) + TX, isothioate (1244) + TX, isoxathion (480) + TX, ivermectin (alternative name) [CCN] + TX, jasmolin I (696) + TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, juvenile hormone I (alternative name) [CCN] + TX, juvenile hormone II (alternative name) [CCN] + TX, juvenile hormone III (alternative name) [CCN] + TX, kelevan (1249) + TX, kinoprene (484) + TX, lambda-cyhalothrin (198) + TX, lead arsenate [CCN] + TX, lepimectin (CCN) + TX, leptophos (1250) + TX, lindane (430) + TX, lirimfos (1251) + TX, lufenuron (490) + TX, lythidathion (1253) + TX, *m*-cumenyl methylcarbamate (IUPAC name) (1014) + TX, magnesium phosphide (IUPAC name) (640) + TX, malathion (492) + TX, malonoben (1254) + TX, mazidox (1255) + TX, mecarbam (502) + TX, mecarphon (1258) + TX, menazon (1260) + TX, mephosfolan (1261) + TX, mercurous chloride (513) + TX, mesulfenfos (1263) + TX, metaflumizone (CCN) + TX, metam (519) + TX, metam-potassium (alternative name) (519) + TX, metam-sodium (519) + TX, methacrifos (1266) + TX, methamidophos (527) + TX, methanesulfonyl fluoride (IUPAC/Chemical Abstracts name) (1268) + TX, methidathion (529) + TX, methiocarb (530) + TX, methocrotophos (1273) + TX, methomyl (531) + TX, methoprene (532) + TX, methoquin-butyl (1276) + TX, methothrin (alternative name) (533) + TX, methoxychlor (534) + TX, methoxyfenozide (535) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, methylchloroform (alternative name) [CCN] + TX, methylene chloride [CCN] + TX, metofluthrin [CCN] + TX, metolcarb (550) + TX, metoxadiazone (1288) + TX, mevinphos (556) + TX, mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime (alternative name) [CCN] + TX, mipafox (1293) + TX, mirex (1294) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin (alternative name) [CCN] + TX, naftalofos (alternative name) [CCN] + TX, naled (567) + TX, naphthalene (IUPAC/Chemical Abstracts name) (1303) + TX, NC-170 (development code) (1306) + TX, NC-184 (compound code) + TX, nicotine (578) + TX, nicotine sulfate (578) + TX, nifluridide (1309) + TX, nitenpyram (579) + TX, nithiazine (1311) + TX, nitrilacarb (1313) + TX, nitrilacarb 1:1 zinc chloride complex (1313) + TX, NNI-0101 (compound code) + TX, NNI-0250 (compound code) + TX, nor nicotine (traditional name) (1319) + TX, novaluron (585) + TX, noviflumuron (586) + TX, O-5-dichloro-4-iodophenyl O-ethyl ethylphosphonothioate (IUPAC name) (1057) + TX, O,O-diethyl O-4-methyl-2-oxo-2*H*-chromen-7-yl phosphorothioate (IUPAC name) (1074) + TX, O,O-diethyl O-6-methyl-2-propylpyrimidin-4-yl phosphorothioate (IUPAC name) (1075) + TX, O,O,O',O'-tetrapropyl dithiopyrophosphate (IUPAC name) (1424) + TX, oleic acid (IUPAC name) (593) + TX, omethoate

(594) + TX, oxamyl (602) + TX, oxydemeton-methyl (609) + TX, oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, para-dichlorobenzene [CCN] + TX, parathion (615) + TX, parathion-methyl (616) + TX, penfluron (alternative name) [CCN] + TX, pentachlorophenol (623) + TX, pentachlorophenyl laurate (IUPAC name) (623) + TX, permethrin (626) + TX, petroleum oils (alternative name) (628) + TX, PH 60-38 (development code) (1328) + TX, phenkapton (1330) + TX, phenothrin (630) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosnichlor (1339) + TX, phosphamidon (639) + TX, phosphine (IUPAC name) (640) + TX, phoxim (642) + TX, phoxim-methyl (1340) + TX, pirimetaphos (1344) + TX, pirimicarb (651) + TX, pirimiphos-ethyl (1345) + TX, pirimiphos-methyl (652) + TX, polychlorodicyclopentadiene isomers (IUPAC name) (1346) + TX, polychloroterpenes (traditional name) (1347) + TX, potassium arsenite [CCN] + TX, potassium thiocyanate [CCN] + TX, prallethrin (655) + TX, precocene I (alternative name) [CCN] + TX, precocene II (alternative name) [CCN] + TX, precocene III (alternative name) [CCN] + TX, primidophos (1349) + TX, profenofos (662) + TX, profluthrin [CCN] + TX, promacyl (1354) + TX, promecarb (1355) + TX, propaphos (1356) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothiofos (686) + TX, prothoate (1362) + TX, protrifenbute [CCN] + TX, pymetrozine (688) + TX, pyraclofos (689) + TX, pyrazophos (693) + TX, pyresmethrin (1367) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridalyl (700) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, pyriproxyfen (708) + TX, quassia (alternative name) [CCN] + TX, quinalphos (711) + TX, quinalphos-methyl (1376) + TX, quinothion (1380) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, rafoxanide (alternative name) [CCN] + TX, resmethrin (719) + TX, rotenone (722) + TX, RU 15525 (development code) (723) + TX, RU 25475 (development code) (1386) + TX, ryania (alternative name) (1387) + TX, ryanodine (traditional name) (1387) + TX, sabadilla (alternative name) (725) + TX, schradan (1389) + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, SI-0009 (compound code) + TX, SI-0205 (compound code) + TX, SI-0404 (compound code) + TX, SI-0405 (compound code) + TX, silafluofen (728) + TX, SN 72129 (development code) (1397) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoride (IUPAC/Chemical Abstracts name) (1399) + TX, sodium hexafluorosilicate (1400) + TX, sodium pentachlorophenoxide (623) + TX, sodium selenate (IUPAC name) (1401) + TX, sodium thiocyanate [CCN] + TX, sophamide (1402) + TX, spinosad (737) + TX, spiromesifen (739) + TX, spirotetmat (CCN) + TX, sulcofuron (746) + TX, sulcofuron-sodium (746) + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulfuryl fluoride (756) + TX, sulprofos (1408) + TX, tar oils (alternative name) (758) + TX, tau-fluvalinate (398) + TX, tazimcarb (1412) + TX, TDE (1414) + TX, tebufenozide (762) + TX, tebufenpyrad (763) + TX, tebupirimfos (764) + TX, teflubenzuron (768) + TX, tefluthrin (769) + TX, temephos (770) + TX, TEPP (1417) + TX, terallethrin (1418) + TX, terbam (alternative name) + TX, terbufos (773) + TX, tetrachloroethane [CCN] + TX, tetrachlorvinphos (777) + TX, tetramethrin (787) + TX, theta-cypermethrin (204) + TX, thiacloprid (791) + TX, thiafenox (alternative name) + TX, thiamethoxam

(792) + TX, thicrofos (1428) + TX, thiocarboxime (1431) + TX, thiocyclam (798) + TX, thiocyclam hydrogen oxalate (798) + TX, thiodicarb (799) + TX, thiofanox (800) + TX, thiometon (801) + TX, thionazin (1434) + TX, thiosultap (803) + TX, thiosultap-sodium (803) + TX, thuringiensin (alternative name) [CCN] + TX, tolfenpyrad (809) + TX, tralomethrin (812) + TX, transfluthrin (813) + TX,

5 transpermethrin (1440) + TX, triamiphos (1441) + TX, triazamate (818) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, trichlorfon (824) + TX, trichlormetaphos-3 (alternative name) [CCN] + TX, trichloronat (1452) + TX, trifenofos (1455) + TX, triflumuron (835) + TX, trimethacarb (840) + TX, triprene (1459) + TX, vamidothion (847) + TX, vaniliprole [CCN] + TX, veratridine (alternative name) (725) + TX, veratrine (alternative name) (725) + TX, XMC (853) + TX, xylylcarb (854) + TX,

10 YI-5302 (compound code) + TX, zeta-cypermethrin (205) + TX, zetamethrin (alternative name) + TX, zinc phosphide (640) + TX, zolaprofos (1469) and ZXI 8901 (development code) (858) + TX, cyantraniliprole [736994-63-19 + TX, chlorantraniliprole [500008-45-7] + TX, cyenopyrafen [560121-52-0] + TX, cyflumetofen [400882-07-7] + TX, pyrifluquinazon [337458-27-2] + TX, spinetoram [187166-40-1 + 187166-15-0] + TX, spirotetramat [203313-25-1] + TX, sulfoxaflor [946578-00-3] + TX, flufiprole

15 [704886-18-0] + TX, meperfluthrin [915288-13-0] + TX, tetramethylfluthrin [84937-88-2] + TX, triflumezopyrim (disclosed in WO 2012/092115) + TX,

a molluscicide selected from the group of substances consisting of bis(tributyltin) oxide (IUPAC name) (913) + TX, bromoacetamide [CCN] + TX, calcium arsenate [CCN] + TX, cloethocarb (999) + TX, copper acetoarsenite [CCN] + TX, copper sulfate (172) + TX, fentin (347) + TX, ferric phosphate

20 (IUPAC name) (352) + TX, metaldehyde (518) + TX, methiocarb (530) + TX, niclosamide (576) + TX, niclosamide-olamine (576) + TX, pentachlorophenol (623) + TX, sodium pentachlorophenoxide (623) + TX, tazimcarb (1412) + TX, thiodicarb (799) + TX, tributyltin oxide (913) + TX, trifenmorph (1454) + TX, trimethacarb (840) + TX, triphenyltin acetate (IUPAC name) (347) and triphenyltin hydroxide (IUPAC name) (347) + TX, pyriprole [394730-71-3] + TX,

25 a nematicide selected from the group of substances consisting of AKD-3088 (compound code) + TX, 1,2-dibromo-3-chloropropane (IUPAC/Chemical Abstracts name) (1045) + TX, 1,2-dichloropropane (IUPAC/ Chemical Abstracts name) (1062) + TX, 1,2-dichloropropane with 1,3-dichloropropene (IUPAC name) (1063) + TX, 1,3-dichloropropene (233) + TX, 3,4-dichlorotetrahydrothiophene 1,1-dioxide (IUPAC/Chemical Abstracts name) (1065) + TX, 3-(4-chlorophenyl)-5-methylrhodanine (IUPAC name)

30 (980) + TX, 5-methyl-6-thioxo-1,3,5-thiadiazinan-3-ylacetic acid (IUPAC name) (1286) + TX, 6-isopentenylaminopurine (alternative name) (210) + TX, abamectin (1) + TX, acetoprole [CCN] + TX, alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, AZ 60541 (compound code) + TX, benclonthiaz [CCN] + TX, benomyl (62) + TX, butylpyridaben (alternative name) + TX, cadusafos (109) + TX, carbofuran (118) + TX, carbon disulfide (945) + TX, carbosulfan (119) + TX,

35 chloropicrin (141) + TX, chlorpyrifos (145) + TX, cloethocarb (999) + TX, cytokinins (alternative name) (210) + TX, dazomet (216) + TX, DBCP (1045) + TX, DCIP (218) + TX, diamidafofos (1044) + TX, dichlofenthion (1051) + TX, dicliphos (alternative name) + TX, dimethoate (262) + TX, doramectin (alternative name) [CCN] + TX, emamectin (291) + TX, emamectin benzoate (291) + TX,

eprinomectin (alternative name) [CCN] + TX, ethoprophos (312) + TX, ethylene dibromide (316) + TX, fenamiphos (326) + TX, fenpyrad (alternative name) + TX, fensulfothion (1158) + TX, fosthiazate (408) + TX, fosthietan (1196) + TX, furfural (alternative name) [CCN] + TX, GY-81 (development code) (423) + TX, heterophos [CCN] + TX, iodomethane (IUPAC name) (542) + TX, isamidofos (1230) + TX, isazofos (1231) + TX, ivermectin (alternative name) [CCN] + TX, kinetin (alternative name) (210) + TX, mecarphon (1258) + TX, metam (519) + TX, metam-potassium (alternative name) (519) + TX, metam-sodium (519) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, milbemycin oxime (alternative name) [CCN] + TX, moxidectin (alternative name) [CCN] + TX, *Myrothecium verrucaria* composition (alternative name) (565) + TX, NC-184 (compound code) + TX, oxamyl (602) + TX, phorate (636) + TX, phosphamidon (639) + TX, phosphocarb [CCN] + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, spinosad (737) + TX, terbam (alternative name) + TX, terbufos (773) + TX, tetrachlorothiophene (IUPAC/ Chemical Abstracts name) (1422) + TX, thiafenox (alternative name) + TX, thionazin (1434) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, xlenols [CCN] + TX, YI-5302 (compound code) and zeatin (alternative name) (210) + TX, fluensulfone [318290-98-1] + TX, a nitrification inhibitor selected from the group of substances consisting of potassium ethylxanthate [CCN] and nitrapyrin (580) + TX, a plant activator selected from the group of substances consisting of acibenzolar (6) + TX, acibenzolar-S-methyl (6) + TX, probenazole (658) and *Reynoutria sachalinensis* extract (alternative name) (720) + TX, a rodenticide selected from the group of substances consisting of 2-isovalerylindan-1,3-dione (IUPAC name) (1246) + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide (IUPAC name) (748) + TX, alpha-chlorohydrin [CCN] + TX, aluminium phosphide (640) + TX, antu (880) + TX, arsenous oxide (882) + TX, barium carbonate (891) + TX, bithiosemi (912) + TX, brodifacoum (89) + TX, bromadiolone (91) + TX, bromethalin (92) + TX, calcium cyanide (444) + TX, chloralose (127) + TX, chlorophacinone (140) + TX, cholecalciferol (alternative name) (850) + TX, coumachlor (1004) + TX, coumafuryl (1005) + TX, coumatetralyl (175) + TX, crimidine (1009) + TX, difenacoum (246) + TX, difethialone (249) + TX, diphacinone (273) + TX, ergocalciferol (301) + TX, flocoumafen (357) + TX, fluoroacetamide (379) + TX, flupropadine (1183) + TX, flupropadine hydrochloride (1183) + TX, gamma-HCH (430) + TX, HCH (430) + TX, hydrogen cyanide (444) + TX, iodomethane (IUPAC name) (542) + TX, lindane (430) + TX, magnesium phosphide (IUPAC name) (640) + TX, methyl bromide (537) + TX, norbormide (1318) + TX, phosacetim (1336) + TX, phosphine (IUPAC name) (640) + TX, phosphorus [CCN] + TX, pindone (1341) + TX, potassium arsenite [CCN] + TX, pyrinuron (1371) + TX, scilliroside (1390) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoroacetate (735) + TX, strychnine (745) + TX, thallium sulfate [CCN] + TX, warfarin (851) and zinc phosphide (640) + TX, a synergist selected from the group of substances consisting of 2-(2-butoxyethoxy)ethyl piperonylate (IUPAC name) (934) + TX, 5-(1,3-benzodioxol-5-yl)-3-hexylcyclohex-2-enone (IUPAC name) (903) +

TX, farnesol with nerolidol (alternative name) (324) + TX, MB-599 (development code) (498) + TX, MGK 264 (development code) (296) + TX, piperonyl butoxide (649) + TX, piprotal (1343) + TX, propyl isomer (1358) + TX, S421 (development code) (724) + TX, sesamex (1393) + TX, sesasmolin (1394) and sulfoxide (1406) + TX,

- 5 an animal repellent selected from the group of substances consisting of anthraquinone (32) + TX, chloralose (127) + TX, copper naphthenate [CCN] + TX, copper oxychloride (171) + TX, diazinon (227) + TX, dicyclopentadiene (chemical name) (1069) + TX, guazatine (422) + TX, guazatine acetates (422) + TX, methiocarb (530) + TX, pyridin-4-amine (IUPAC name) (23) + TX, thiram (804) + TX, trimethacarb (840) + TX, zinc naphthenate [CCN] and ziram (856) + TX,
- 10 a virucide selected from the group of substances consisting of imanin (alternative name) [CCN] and ribavirin (alternative name) [CCN] + TX,
a wound protectant selected from the group of substances consisting of mercuric oxide (512) + TX, octhilinone (590) and thiophanate-methyl (802) + TX,
and biologically active compounds selected from the group consisting of azaconazole (60207-31-0) + TX,
- 15 TX, bitertanol [70585-36-3] + TX, bromuconazole [116255-48-2] + TX, cyproconazole [94361-06-5] + TX, difenoconazole [119446-68-3] + TX, diniconazole [83657-24-3] + TX, epoxiconazole [106325-08-0] + TX, fenbuconazole [114369-43-6] + TX, fluquinconazole [136426-54-5] + TX, flusilazole [85509-19-9] + TX, flutriafol [76674-21-0] + TX, hexaconazole [79983-71-4] + TX, imazalil [35554-44-0] + TX, imibenconazole [86598-92-7] + TX, ipconazole [125225-28-7] + TX, metconazole
- 20 [125116-23-6] + TX, myclobutanil [88671-89-0] + TX, pefurazoate [101903-30-4] + TX, penconazole [66246-88-6] + TX, prothioconazole [178928-70-6] + TX, pyrifenoxy [88283-41-4] + TX, prochloraz [67747-09-5] + TX, propiconazole [60207-90-1] + TX, simeconazole [149508-90-7] + TX, tebuconazole [107534-96-3] + TX, tetraconazole [112281-77-3] + TX, triadimefon [43121-43-3] + TX, triadimenol [55219-65-3] + TX, triflumizole [99387-89-0] + TX, triticonazole [131983-72-7] + TX,
- 25 ancymidol [12771-68-5] + TX, fenarimol [60168-88-9] + TX, nuarimol [63284-71-9] + TX, bupirimate [41483-43-6] + TX, dimethirimol [5221-53-4] + TX, ethirimol [23947-60-6] + TX, dodemorph [1593-77-7] + TX, fenpropidine [67306-00-7] + TX, fenpropimorph [67564-91-4] + TX, spiroxamine [118134-30-8] + TX, tridemorph [81412-43-3] + TX, cyprodinil [121552-61-2] + TX, mepanipyrim [110235-47-7] + TX, pyrimethanil [53112-28-0] + TX, fenpiclonil [74738-17-3] + TX, fludioxonil
- 30 [131341-86-1] + TX, benalaxyl [71626-11-4] + TX, furalaxyl [57646-30-7] + TX, metalaxyl [57837-19-1] + TX, R-metalaxyl [70630-17-0] + TX, ofurace [58810-48-3] + TX, oxadixyl [77732-09-3] + TX, benomyl [17804-35-2] + TX, carbendazim [10605-21-7] + TX, debacarb [62732-91-6] + TX, fuberidazole [3878-19-1] + TX, thiabendazole [148-79-8] + TX, chlozolinate [84332-86-5] + TX, dichlozoline [24201-58-9] + TX, iprodione [36734-19-7] + TX, myclozoline [54864-61-8] + TX,
- 35 procymidone [32809-16-8] + TX, vinclozoline [50471-44-8] + TX, boscalid [188425-85-6] + TX, carboxin [5234-68-4] + TX, fenfuram [24691-80-3] + TX, flutolanil [66332-96-5] + TX, mepronil [55814-41-0] + TX, oxycarboxin [5259-88-1] + TX, penthiopyrad [183675-82-3] + TX, thifluzamide [130000-40-7] + TX, guazatine [108173-90-6] + TX, dodine [2439-10-3] [112-65-2] (free base) + TX,

iminoctadine [13516-27-3] + TX, azoxystrobin [131860-33-8] + TX, dimoxystrobin [149961-52-4] + TX, enestroburin {Proc. BCPC, Int. Congr., Glasgow, 2003, 1, 93} + TX, fluoxastrobin [361377-29-9] + TX, kresoxim-methyl [143390-89-0] + TX, metominostrobin [133408-50-1] + TX, trifloxystrobin [141517-21-7] + TX, orysastrobin [248593-16-0] + TX, picoxystrobin [117428-22-5] + TX,
 5 pyraclostrobin [175013-18-0] + TX, ferbam [14484-64-1] + TX, mancozeb [8018-01-7] + TX, maneb [12427-38-2] + TX, metiram [9006-42-2] + TX, propineb [12071-83-9] + TX, thiram [137-26-8] + TX, zineb [12122-67-7] + TX, ziram [137-30-4] + TX, captafol [2425-06-1] + TX, captan [133-06-2] + TX, dichlofluanid [1085-98-9] + TX, fluoroimide [41205-21-4] + TX, folpet [133-07-3] + TX, tolylfluanid [731-27-1] + TX, bordeaux mixture [8011-63-0] + TX, copperhydroxid [20427-59-2] + TX,
 10 copperoxychlorid [1332-40-7] + TX, coppersulfat [7758-98-7] + TX, copperoxid [1317-39-1] + TX, mancopper [53988-93-5] + TX, oxine-copper [10380-28-6] + TX, dinocap [131-72-6] + TX, nitrothal-isopropyl [10552-74-6] + TX, edifenphos [17109-49-8] + TX, iprobenphos [26087-47-8] + TX, isoprothiolane [50512-35-1] + TX, phosdiphen [36519-00-3] + TX, pyrazophos [13457-18-6] + TX, tolclofos-methyl [57018-04-9] + TX, acibenzolar-S-methyl [135158-54-2] + TX, anilazine [101-05-3] + TX,
 15 TX, benthiavalicarb [413615-35-7] + TX, blasticidin-S [2079-00-7] + TX, chinomethionat [2439-01-2] + TX, chloroneb [2675-77-6] + TX, chlorothalonil [1897-45-6] + TX, cyflufenamid [180409-60-3] + TX, cymoxanil [57966-95-7] + TX, dichlone [117-80-6] + TX, diclocymet [139920-32-4] + TX, diclomezine [62865-36-5] + TX, dicloran [99-30-9] + TX, diethofencarb [87130-20-9] + TX, dimetho-morph [110488-70-5] + TX, SYP-LI90 (Flumorph) [211867-47-9] + TX, dithianon [3347-22-6] + TX,
 20 ethaboxam [162650-77-3] + TX, etridiazole [2593-15-9] + TX, famoxadone [131807-57-3] + TX, fenamidone [161326-34-7] + TX, fenoxanil [115852-48-7] + TX, fentin [668-34-8] + TX, ferimzone [89269-64-7] + TX, fluazinam [79622-59-6] + TX, fluopicolide [239110-15-7] + TX, flusulfamide [106917-52-6] + TX, fenhexamid [126833-17-8] + TX, fosetyl-aluminium [39148-24-8] + TX, hymexazol [10004-44-1] + TX, iprovalicarb [140923-17-7] + TX, IKF-916 (Cyazofamid) [120116-88-3] + TX,
 25 + TX, kasugamycin [6980-18-3] + TX, methasulfocarb [66952-49-6] + TX, metrafenone [220899-03-6] + TX, pencycuron [66063-05-6] + TX, phthalide [27355-22-2] + TX, polyoxins [11113-80-7] + TX, probenazole [27605-76-1] + TX, propamocarb [25606-41-1] + TX, proquinazid [189278-12-4] + TX, pyroquilon [57369-32-1] + TX, quinoxifen [124495-18-7] + TX, quintozone [82-68-8] + TX, sulfur [7704-34-9] + TX, tiadinil [223580-51-6] + TX, triazoxide [72459-58-6] + TX, tricyclazole [41814-78-2] + TX,
 30 triformine [26644-46-2] + TX, validamycin [37248-47-8] + TX, zoxamide (RH7281) [156052-68-5] + TX, mandipropamid [374726-62-2] + TX, isopyrazam [881685-58-1] + TX, sedaxane [874967-67-6] + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (9-dichloromethylene-1,2,3,4-tetrahydro-1,4-methano-naphthalen-5-yl)-amide (disclosed in WO 2007/048556) + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (3',4',5'-trifluoro-biphenyl-2-yl)-amide (disclosed in WO
 35 2006/087343) + TX, [(3S,4R,4aR,6S,6aS,12R,12aS,12bS)-3-[(cyclopropylcarbonyl)oxy]-1,3,4,4a,5,6,6a,12,12a,12b-decahydro-6,12-dihydroxy-4,6a,12b-trimethyl-11-oxo-9-(3-pyridinyl)-2H,11Hnaphtho[2,1-b]pyrano[3,4-e]pyran-4-yl)methyl-

cyclopropanecarboxylate [915972-17-7] + TX and 1,3,5-trimethyl-N-(2-methyl-1-oxopropyl)-N-[3-(2-methylpropyl)-4-[2,2,2-trifluoro-1-methoxy-1-(trifluoromethyl)ethyl]phenyl]-1H-pyrazole-4-carboxamide [926914-55-8] + TX.

5 The references in brackets behind the active ingredients, e.g. [3878-19-1] refer to the Chemical Abstracts Registry number. The above described mixing partners are known. Where the active ingredients are included in "The Pesticide Manual" [The Pesticide Manual - A World Compendium; Thirteenth Edition; Editor: C. D. S. Tomlin; The British Crop Protection Council], they are described therein under the entry number given in round brackets hereinabove for the particular compound; for
10 example, the compound "abamectin" is described under entry number (1). Where "[CCN]" is added hereinabove to the particular compound, the compound in question is included in the "Compendium of Pesticide Common Names", which is accessible on the internet [A. Wood; Compendium of Pesticide Common Names, Copyright © 1995-2004]; for example, the compound "acetoprole" is described under the internet address <http://www.alanwood.net/pesticides/acetoprole.html>.

15 Most of the active ingredients described above are referred to hereinabove by a so-called "common name", the relevant "ISO common name" or another "common name" being used in individual cases. If the designation is not a "common name", the nature of the designation used instead is given in round brackets for the particular compound; in that case, the IUPAC name, the IUPAC/Chemical Abstracts
20 name, a "chemical name", a "traditional name", a "compound name" or a "development code" is used or, if neither one of those designations nor a "common name" is used, an "alternative name" is employed. "CAS Reg. No" means the Chemical Abstracts Registry Number.

The active ingredient mixture of the compounds according to any one of embodiments 1 to 25 with
25 active ingredients described above comprises a compound according to any one of embodiments 1 to 25 and an active ingredient as described above preferably in a mixing ratio of from 100:1 to 1:6000, especially from 50:1 to 1:50, more especially in a ratio of from 20:1 to 1:20, even more especially from 10:1 to 1:10, very especially from 5:1 and 1:5, special preference being given to a ratio of from 2:1 to 1:2, and a ratio of from 4:1 to 2:1 being likewise preferred, above all in a ratio of 1:1, or 5:1, or 5:2, or
30 5:3, or 5:4, or 4:1, or 4:2, or 4:3, or 3:1, or 3:2, or 2:1, or 1:5, or 2:5, or 3:5, or 4:5, or 1:4, or 2:4, or 3:4, or 1:3, or 2:3, or 1:2, or 1:600, or 1:300, or 1:150, or 1:35, or 2:35, or 4:35, or 1:75, or 2:75, or 4:75, or 1:6000, or 1:3000, or 1:1500, or 1:350, or 2:350, or 4:350, or 1:750, or 2:750, or 4:750. Those mixing ratios are by weight.

35 The mixtures as described above can be used in a method for controlling pests, which comprises applying a composition comprising a mixture as described above to the pests or their environment, with the exception of a method for treatment of the human or animal body by surgery or therapy and diagnostic methods practised on the human or animal body.

The mixtures comprising a compound of according to any one of embodiments 1 to 25 and one or more active ingredients as described above can be applied, for example, in a single “ready-mix” form, in a combined spray mixture composed from separate formulations of the single active ingredient components, such as a “tank-mix”, and in a combined use of the single active ingredients when applied in a sequential manner, i.e. one after the other with a reasonably short period, such as a few hours or days. The order of applying the compounds according to any one of embodiments 1 to 25 and the active ingredients as described above is not essential for working the present invention.

The compositions according to the invention can also comprise further solid or liquid auxiliaries, such as stabilizers, for example unepoxidized or epoxidized vegetable oils (for example epoxidized coconut oil, rapeseed oil or soya oil), antifoams, for example silicone oil, preservatives, viscosity regulators, binders and/or tackifiers, fertilizers or other active ingredients for achieving specific effects, for example bactericides, fungicides, nematocides, plant activators, molluscicides or herbicides.

The compositions according to the invention are prepared in a manner known per se, in the absence of auxiliaries for example by grinding, screening and/or compressing a solid active ingredient and in the presence of at least one auxiliary for example by intimately mixing and/or grinding the active ingredient with the auxiliary (auxiliaries). These processes for the preparation of the compositions and the use of the compounds I for the preparation of these compositions are also a subject of the invention.

The application methods for the compositions, that is the methods of controlling pests of the abovementioned type, such as spraying, atomizing, dusting, brushing on, dressing, scattering or pouring - which are to be selected to suit the intended aims of the prevailing circumstances - and the use of the compositions for controlling pests of the abovementioned type are other subjects of the invention. Typical rates of concentration are between 0.1 and 1000 ppm, preferably between 0.1 and 500 ppm, of active ingredient. The rate of application per hectare is generally 1 to 2000 g of active ingredient per hectare, in particular 10 to 1000 g/ha, preferably 10 to 600 g/ha.

A preferred method of application in the field of crop protection is application to the foliage of the plants (foliar application), it being possible to select frequency and rate of application to match the danger of infestation with the pest in question. Alternatively, the active ingredient can reach the plants via the root system (systemic action), by drenching the locus of the plants with a liquid composition or by incorporating the active ingredient in solid form into the locus of the plants, for example into the soil, for example in the form of granules (soil application). In the case of paddy rice crops, such granules can be metered into the flooded paddy-field.

The compounds of the invention and compositions thereof are also be suitable for the protection of plant propagation material, for example seeds, such as fruit, tubers or kernels, or nursery plants, against pests of the abovementioned type. The propagation material can be treated with the compound prior to planting, for example seed can be treated prior to sowing. Alternatively, the compound can be applied to seed kernels (coating), either by soaking the kernels in a liquid composition or by applying a layer of a solid composition. It is also possible to apply the compositions when the propagation material is planted to the site of application, for example into the seed furrow during drilling. These treatment methods for plant propagation material and the plant propagation material thus treated are further subjects of the invention. Typical treatment rates would depend on the plant and pest/fungi to be controlled and are generally between 1 to 200 grams per 100 kg of seeds, preferably between 5 to 150 grams per 100 kg of seeds, such as between 10 to 100 grams per 100 kg of seeds.

The term seed embraces seeds and plant propagules of all kinds including but not limited to true seeds, seed pieces, suckers, corns, bulbs, fruit, tubers, grains, rhizomes, cuttings, cut shoots and the like and means in a preferred embodiment true seeds.

The present invention also comprises seeds coated or treated with or containing a compound according to any one of embodiments 1 to 25. The term "coated or treated with and/or containing" generally signifies that the active ingredient is for the most part on the surface of the seed at the time of application, although a greater or lesser part of the ingredient may penetrate into the seed material, depending on the method of application. When the said seed product is (re)planted, it may absorb the active ingredient. In an embodiment, the present invention makes available a plant propagation material adhered thereto with according to any one of embodiments 1 to 25. Further, it is hereby made available, a composition comprising a plant propagation material treated with a compound according to any one of embodiments 1 to 25.

Seed treatment comprises all suitable seed treatment techniques known in the art, such as seed dressing, seed coating, seed dusting, seed soaking and seed pelleting. The seed treatment application of the compound according to any one of embodiments 1 to 25 can be carried out by any known methods, such as spraying or by dusting the seeds before sowing or during the sowing/planting of the seeds.

The pesticidal/insecticidal properties of the compounds according to any one of embodiments 1 to 25 can be illustrated via the following tests:

Diabrotica balteata (Corn root worm):

Maize sprouts placed onto an agar layer in 24-well microtiter plates were treated with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions by spraying. After drying, the plates were infested with L2 larvae (6 to 10 per well). The samples were assessed for mortality 4 days after infestation. The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: 1, 2, 6, 9, 15, 16, 17, 19, 20, 21, 22, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 58, 59, 61, 62, 64, and 65.

Euschistus heros (Neotropical Brown Stink Bug): Feeding/contact activity

Soybean leaves on agar in 24-well microtiter plates were sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaves were infested with N2 nymphs. The samples were assessed for mortality 5 days after infestation. The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: 1, 2, 6, 9, 15, 16, 17, 19, 20, 21, 22, 33, 34, 35, 36, 37, 38, 39, 40, 41 and 42.

Myzus persicae (Green peach aphid): Feeding/Contact activity

Sunflower leaf discs were placed onto agar in a 24-well microtiter plate and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying, the leaf discs were infested with an aphid population of mixed ages. The samples were assessed for mortality 6 days after infestation. The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: 1, 2, 9, 15, 16, 19, 20, 21, 22, 34, 17, 36, 42 and 57.

Plutella xylostella (Diamond back moth): Feeding/contact activity

24-well microtiter plates with artificial diet were treated with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions by pipetting. After drying, the plates were infested with L2 larvae (10 to 15 per well). The samples were assessed for mortality 5 days after infestation. The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: 1, 2, 6, 9, 15, 16, 17, 19, 20, 21, 22, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46 and 47.

Spodoptera littoralis (Egyptian cotton leaf worm): Feeding/contact activity

Cotton leaf discs were placed onto agar in 24-well microtiter plates and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf discs were infested with five L1 larvae. The samples were assessed for mortality 3 days after infestation. The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: 1, 2, 6, 9, 15, 16, 18, 18, 19, 20, 21, 22, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45 and 46.

Tetranychus urticae (Two-spotted spider mite): Feeding/contact activity

Bean leaf discs on agar in 24-well microtiter plates were sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf discs were infested with a mite population of mixed ages. The samples were assessed for mortality on mixed population (mobile stages) 8 days after infestation. The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: 1 , 2 , 6 , 9 , 15 , 16 , 17 , 19 , 20 , 21 , 22 , 33 , 34 , 35 , 36 , 37 , 38 , 39 , 41 , 42 and 44.

Thrips tabaci (Onion thrips): Feeding/Contact activity

Sunflower leaf discs were placed on agar in 24-well microtiter plates and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf discs were infested with a thrips population of mixed ages. The samples were assessed for mortality 6 days after infestation. The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: 6 , 9 , 16 , 19 , 20 , 22 , 22 , 33 , 34 , 35 , 36 , 37 , 40 , 41 , 42 , 43 , 45 and 46.

The compounds of the invention can be distinguished from known compounds by virtue of greater efficacy at low application rates, which can be verified by the person skilled in the art using the experimental procedures outlined in the Examples, using lower application rates if necessary, for example 50 ppm, 12.5 ppm, 6 ppm, 3 ppm, 1.5 ppm, 0.8 ppm or 0.2 ppm.

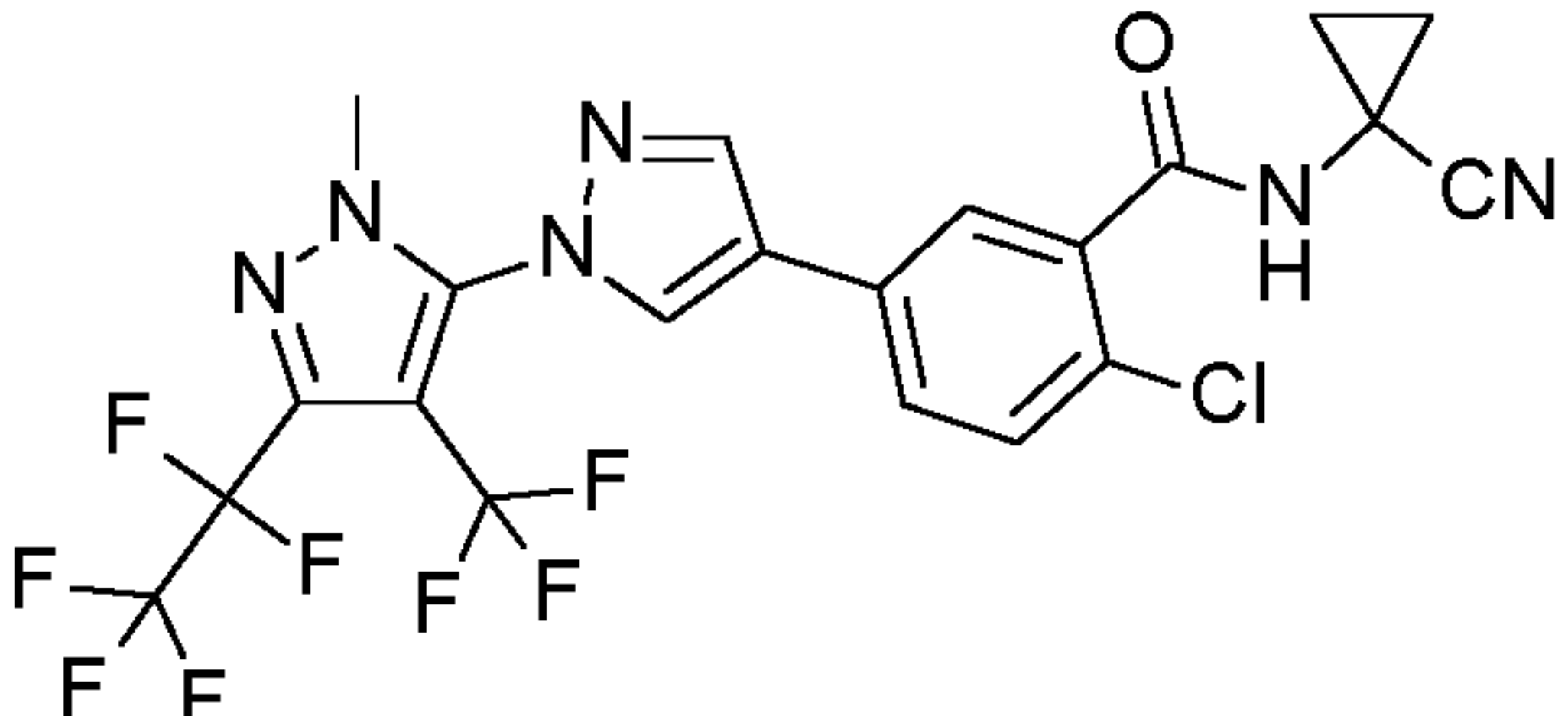
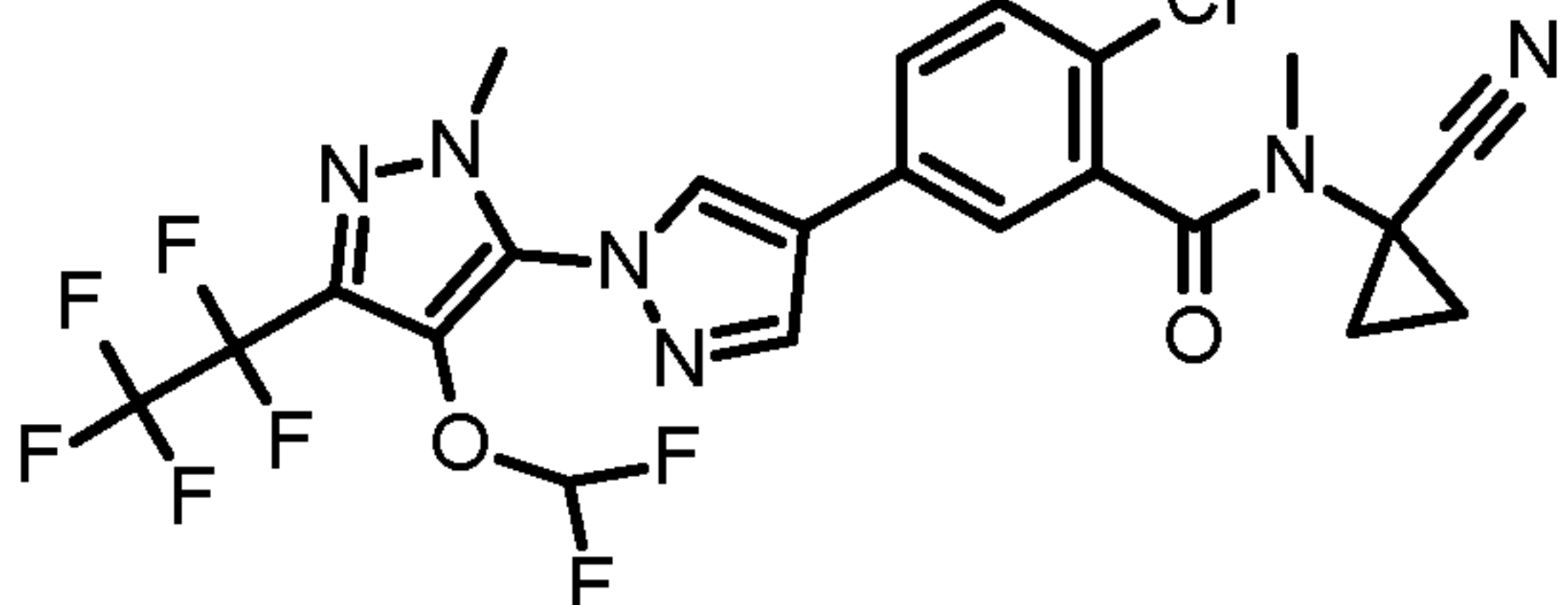
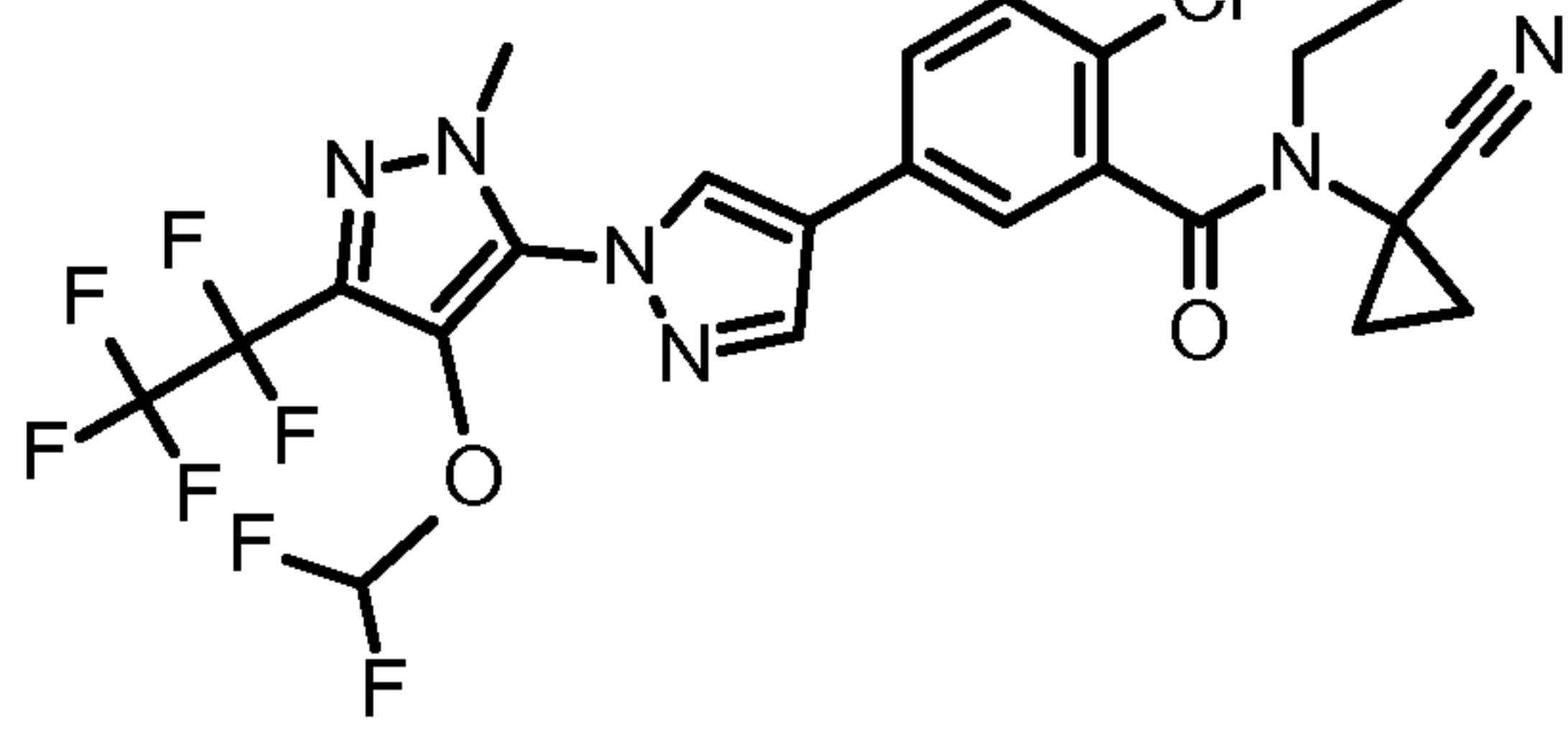
Biological comparison data:

Compound A is disclosed in WO2014/122083 as example (Ic-2) (p. 82, Table 3). The activities of compounds A is compared with the activities of compound 41 and 42, according to the present invention. The tests are carried out at different concentrations (ppm). It can be seen that compounds 41 and 42 of the present invention have surprisingly improved activity in comparison with compounds A.

a) Insecticidal activity against *Plutella xylostella* (Diamond back moth, larvicide L-2/3, feeding/contact)

Chinese cabbage plants are sprayed with diluted test solutions in an application chamber. 1 day after treatment, excised leaves are placed in petri dishes and infested with 10 L2 (2 replicates). Samples are checked 5 days after infestation for mortality, feeding behavior, and growth regulation.

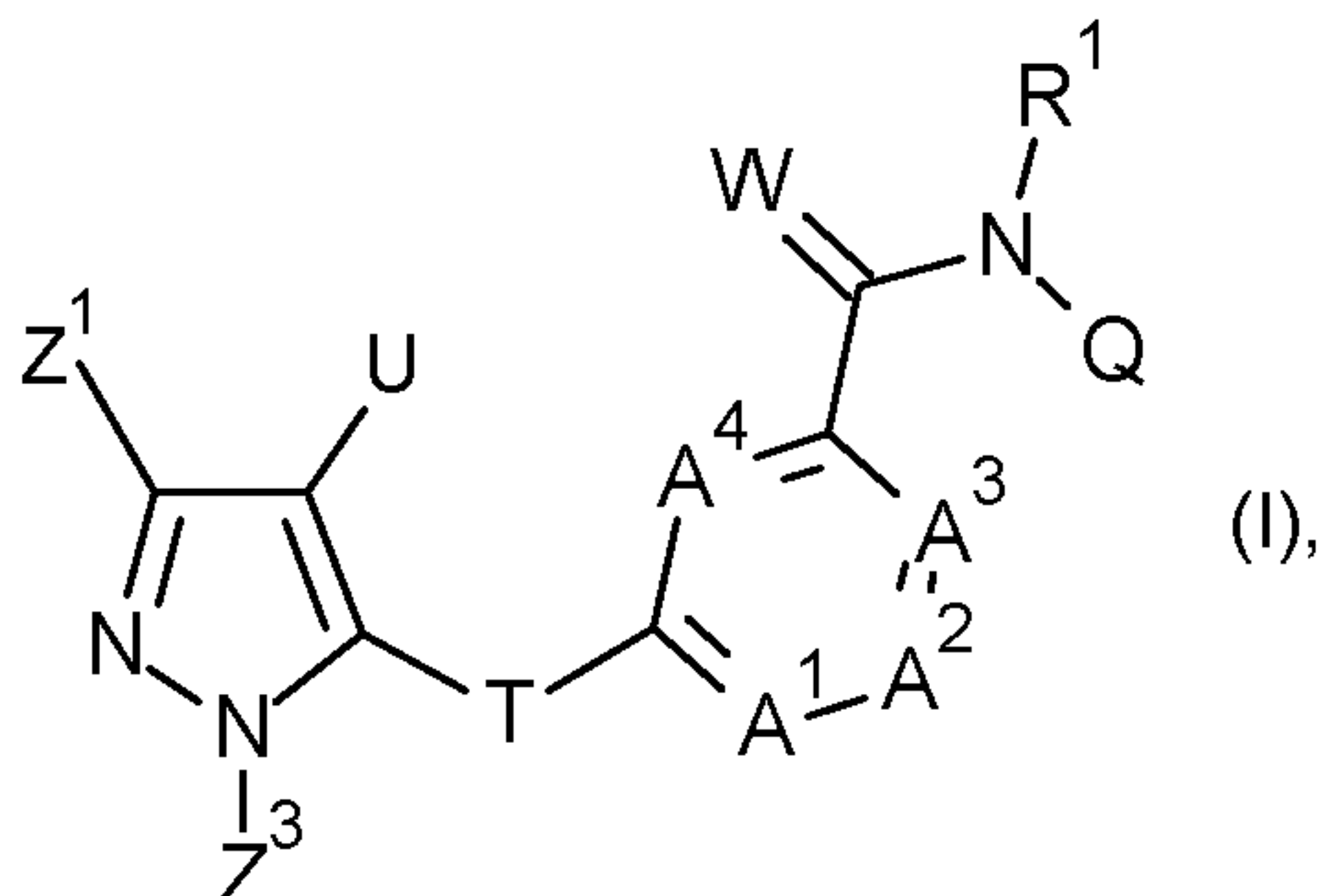
Compound	Compound structure	Concentration (ppm)	Mortality (%)
Cpd A		0.8	100
		0.2	100

Compound	Compound structure	Concentration (ppm)	Mortality (%)
		0.05	85
		0.0125	35
Cpd 41		0.8	100
		0.2	100
		0.05	100
		0.0125	90
Cpd 42		0.8	100
		0.2	100
		0.05	100
		0.0125	95

Furthermore, besides of the insecticidal properties, the compounds according to any one of
embodiments 1 to 25 have surprisingly shown to have improved degradation properties compared with
prior art compounds. Additionally, the compounds according to any one of embodiments 1 to 25 have
surprisingly shown to be less toxic to bees compared with prior art compounds.

Claims

1. A compound of formula (I),



5 wherein

R^1 is selected from H, C₁-C₆-alkyl, C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₃-C₇ cycloalkyl, C₃-C₇ cycloalkyl- C₁-C₃-alkyl, C₁-C₆-alkylcarbonyl, C₁-C₆-alkoxycarbonyl, aryl(C₀-C₃)-alkyl and heteroaryl(C₀-C₃)-alkyl, wherein each of C₁-C₆-alkyl, C₃-C₆ alkenyl, C₃-C₆ alkynyl, C₃-C₇ cycloalkyl, C₃-C₇ cycloalkyl- C₁-C₃-alkyl, C₁-C₆-alkylcarbonyl, C₁-C₆-alkoxycarbonyl, aryl(C₀-C₃)-alkyl and heteroaryl(C₀-C₃)-alkyl is unsubstituted or substituted with 1 to 5 substituents independently selected from halogen, cyano, C₁-C₆-alkoxy and C₁-C₆-alkoxycarbonyl;

Q is selected from H, hydroxy, HC(=O)-, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₃-C₇ cycloalkyl, C₃-C₇ heterocycloalkyl, C₃-C₇ cycloalkyl- C₁-C₃-alkyl, C₁-C₃-alkyl-C₃-C₇ cycloalkyl, aryl(C₀-C₃)-alkyl, heteroaryl(C₀-C₃)-alkyl, *N*- C₁-C₆-alkylamino, *N*- C₁-C₆-alkylcarbonylamino and *N,N*-di (C₁-C₆-alkyl)amino, wherein each of C₁-C₆-alkyl, C₁-C₆-alkoxy, C₃-C₆ alkenyl, C₃-C₆ alkynyl, C₃-C₇ cycloalkyl, C₃-C₇ heterocycloalkyl, C₃-C₇ cycloalkyl- C₁-C₃-alkyl, C₁-C₃-alkyl-C₃-C₇ cycloalkyl, aryl(C₀-C₃)-alkyl, heteroaryl(C₀-C₃)-alkyl, *N*- C₁-C₆-alkylamino, *N*- C₁-C₆-alkylcarbonylamino and *N,N*-di (C₁-C₆-alkyl)amino is unsubstituted or substituted with 1 to 5 substituents independently selected from halogen, hydroxyl, nitro, amino, cyano, C₁-C₆-alkoxy, C₁-C₆-alkoxycarbonyl, hydroxycarbonyl, C₁-C₆-alkylcarbonyl, C₃-C₆-cycloalkylcarbonyl and phenyl;

W is O or S;

A^1 is CR² or N;

A^2 is CR³ or N;

A^3 is CR⁴ or N;

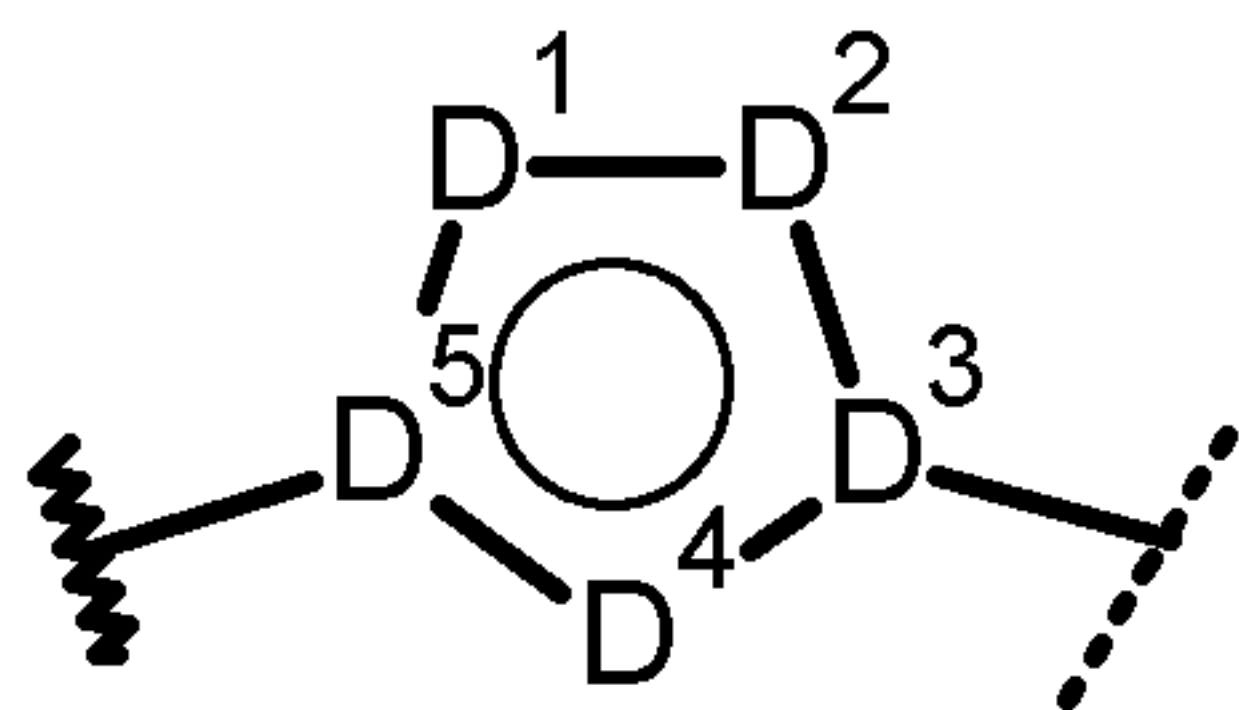
A^4 is CR⁵ or N;

with the proviso that no more than 3 of A^1 , A^2 , A^3 and A^4 are N;

R^2 , R^3 , R^4 and R^5 are independently selected from H, halogen, cyano, nitro, C₁-C₆-alkyl, C₁-C₆-alkoxy, *N*-C₁-C₆-alkoxy-imino-C₁-C₃-alkyl, C₁-C₆-alkylsulfanyl, C₁-C₆-alkylsulfinyl, C₁-C₆-alkylsulfonyl, *N*-C₁-C₆-alkylamino and *N,N*-di- C₁-C₆-alkylamino, wherein each of C₁-C₆-alkyl, C₁-C₆-alkoxy, *N*-C₁-C₆-alkoxy-imino-C₁-C₃-alkyl, C₁-C₆-alkylsulfanyl, C₁-C₆-alkylsulfinyl, C₁-C₆-alkylsulfonyl, *N*-C₁-C₆-alkylamino and *N,N*-di- C₁-C₆-alkylamino is unsubstituted or substituted with 1 to 5 substituents independently selected

from halogen, hydroxy, nitro, amino, cyano, C₁-C₆-alkoxy, C₁-C₆-alkoxycarbonyl, hydroxycarbonyl, C₁-C₆-alkylcarbamoyl, C₃-C₆-cycloalkylcarbamoyl and phenyl;

T is a 5-membered heteroaryl of formula



5 wherein  indicates the bond to the pyrazole group;

D¹ is selected from CR^{6a}, N, NR^{6b}, O and S;

D² is selected from CR^{7a}, N, NR^{7b}, O and S;

D³ is C or N;

D⁴ is selected from CR^{8a}, N, NR^{8b} and O;

10 D⁵ is C or N;

with the proviso that at least one of D¹, D², D³, D⁴ and D⁵ is selected from N, O and S, and that no more than one of D¹, D² and D⁴ is O or S, and that at least one of D³ and D⁵ is C;

R^{6a}, R^{7a} and R^{8a} are independently selected from H, halogen, cyano, nitro, amino, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-alkylcarbonyl, C₁-C₆-alkylsulfanyl, C₁-C₆-alkylsulfinyl and C₁-C₆-alkylsulfonyl, wherein each
15 of C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-alkylcarbonyl, C₁-C₆-alkylsulfanyl, C₁-C₆-alkylsulfinyl, C₁-C₆-alkylsulfonyl is unsubstituted or substituted with 1 to 5 halogen;

R^{6b}, R^{7b} and R^{8b} are independently selected from H and C₁-C₆-alkyl, wherein each of C₁-C₆-alkyl is unsubstituted or substituted with 1 to 5 halogen;

Z¹ is selected from C₁-C₆-alkyl, C₃-C₇ heterocycloalkyl, C₁-C₆-haloalkyl, C₃-C₆-cycloalkyl and C₃-C₆-

20 halocycloalkyl, wherein each of C₁-C₆-alkyl, C₃-C₇ heterocycloalkyl, C₁-C₆-haloalkyl, C₃-C₆-cycloalkyl and C₃-C₆-halocycloalkyl is unsubstituted or substituted with 1 to 5 substituents independently selected from halogen, hydroxy, nitro, amino, cyano, C₁-C₆-alkoxy, C₁-C₆-alkoxycarbonyl, hydroxycarbonyl, C₁-C₆-alkylcarbamoyl, C₃-C₆-cycloalkylcarbamoyl and phenyl;

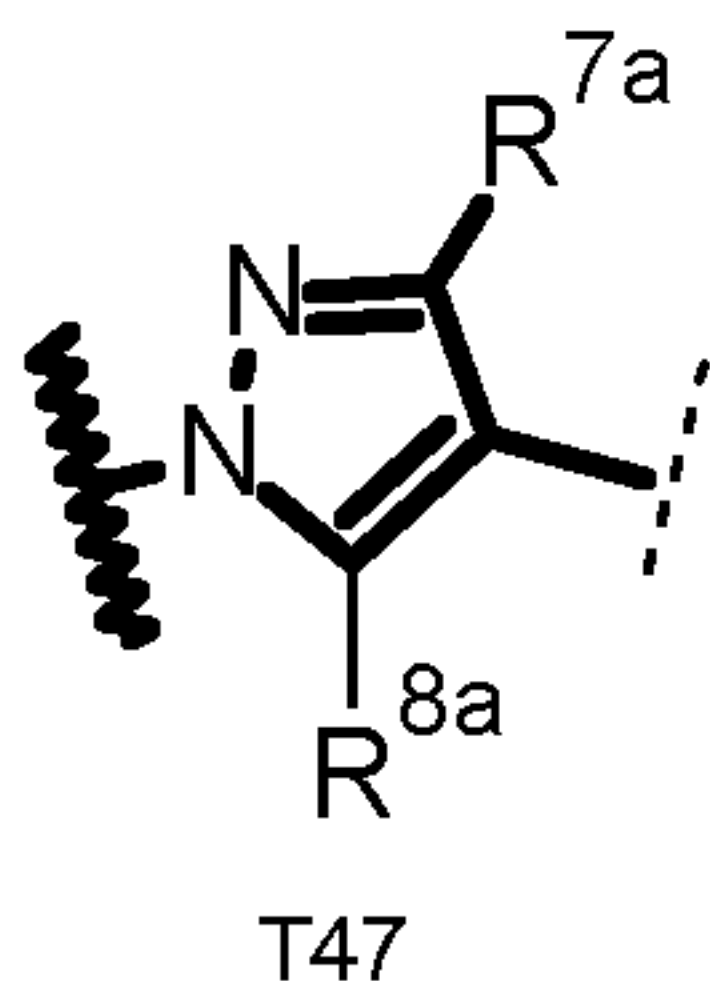
U is selected from C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₃-C₅-cycloalkoxy, C₃-C₅-halocycloalkoxy, C₃-C₅-cycloalkyl, C₃-C₅-halocycloalkyl, C₂-C₄-alkenyl, C₂-C₄-haloalkenyl, C₂-C₃-alkynyl, -S-C₃-C₅-cycloalkyl, -S-C₃-C₅-halocycloalkyl, -SO-C₃-C₅-cycloalkyl, -SO-C₃-C₅-halocycloalkyl, -SO₂-C₃-C₅-cycloalkyl, -SO₂-C₃-C₅-halocycloalkyl, -O-C₂-C₄-alkenyl, -O-C₂-C₄-haloalkenyl, -NHCN, -SO₂F, -O-SO₂-C₁-C₄-alkyl, -O-SO₂-C₁-C₄-haloalkyl and OH;

Z³ is selected from H, C₁-C₆-alkyl, C₁-C₆-cycloalkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, aryl and heteroaryl,

30 wherein each of C₁-C₆-alkyl, C₁-C₆-cycloalkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, aryl and heteroaryl is unsubstituted or substituted with 1 to 5 substituents independently selected from halogen, hydroxy, nitro, amino, cyano, C₁-C₆-alkoxy, C₁-C₆-alkoxycarbonyl, hydroxycarbonyl, C₁-C₆-alkylcarbamoyl, C₃-C₆-cycloalkylcarbamoyl and phenyl;

or an agrochemically acceptable salt or N-oxide thereof.

2. A compound or salt according to embodiment 1, wherein T is



5 wherein  indicates the bond to the pyrazole group.

3. A compound or salt according to claim 1 or 2, wherein

U is selected from $-\text{OCHF}_2$, $-\text{OCH}_2\text{CF}_3$, $-\text{OCH}_3$, $-\text{O-cyclopropyl}$, cyclopropyl, OH, $-\text{O-CH=CH}_2$, $-\text{CH=CH}_2$, $-\text{C}\equiv\text{CH}$, $-\text{S-cyclopropyl}$, $-\text{O-CF=CF}_2$, $-\text{O-SO}_2\text{-F}$, $-\text{NHCN}$, $-\text{SO}_2\text{-cyclopropyl}$, $-\text{SO-cyclopropyl}$, $-\text{O-CF}_2\text{-CF}_2\text{H}$, $-\text{OEt}$, $-\text{O-CH}_2\text{-CF}_2\text{H}$, $-\text{O-CF}_2\text{CF}_2\text{CF}_3$, $-\text{O-CF}_2\text{CFHCF}_3$ and $-\text{CF}_2\text{CF}_3$.

4. A compound or salt according to claim 1 or 2, wherein

U is selected from $-\text{OCHF}_2$, $-\text{CH=CH}_2$ and $-\text{C}\equiv\text{CH}$.

15 5. A compound or salt according to claim 1 or 2, wherein

U is $-\text{OCHF}_2$.

6. A compound or salt according to any one of claims 1 to 5, wherein

Z^1 is selected from methyl, ethyl, 1,1-dimethylethyl, difluoromethyl, trichloromethyl, chlorodifluoromethyl, dichlorofluoromethyl, trifluoromethyl, bromodichloromethyl, 1-fluoroethyl, 1-fluoro-1-methylethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 1,2,2,2-tetrafluoroethyl, 1-chloro- 1,2,2,2-tetrafluoroethyl, 2,2,2-trichloroethyl, 2-chloro-2,2-difluoroethyl, 1,1-difluoroethyl, pentafluoroethyl, heptafluoro-n-propyl, heptafluoro-isopropyl, nonafluoro-n-butyl, cyclopropyl, 1-chlorocyclopropyl, 1-fluorocyclopropyl, 1-bromocyclopropyl, 1-cyano-cyclopropyl, 1-trifluoromethyl-cyclopropyl, cyclobutyl and 2,2-difluoro-1-methyl-cyclopropyl.

7. A compound or salt according to any one of claims 1 to 6, wherein

Z^1 is $-\text{CF}_2\text{CF}_3$.

30 8. A compound or salt according to any one of claims 1 to 7, wherein

Z^3 is selected from H, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, s-butyl, t-butyl, ethenyl, 1-propenyl, 1-propinyl, cyclopropyl, 1-butylnyl, difluoromethyl, trichloromethyl, chlorodifluoromethyl,

dichlorofluoromethyl, trifluoromethyl, 1 -fluoroethyl, 1 fluoro- 1 -methylethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, phenyl, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl, 2,5-dichlorophenyl, 3,4-dichlorophenyl, 2,6-dichlorophenyl 2,6-dichloro-4-trifluoromethylphenyl, 3- chlor-5-trifluoromethylpyridin-2-yl, 4-NO₂-phenyl and 3-chloro-pyridin-2-yl.

5

9. A compound or salt according to any one of claims 1 to 8, wherein Z³ is methyl.

10. A pesticidal composition, which comprises at least one compound according to any one of claims 1 to 9, or an agrochemically acceptable salt or N-oxide thereof, as active ingredient and at least one auxiliary.

11. The composition according to claim 10, which further comprises one or more other insecticidally, acaricidally, nematocidally and/or fungicidally active agents.

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12. A method for controlling pests, which comprises applying a composition according to claim 10 or 11 to the pests or their environment with the exception of a method for treatment of the human or animal body by surgery or therapy and diagnostic methods practised on the human or animal body.

13. A method for the protection of plant propagation material from the attack by pests, which comprises treating the propagation material or the site, where the propagation material is planted, with a composition according to claim 10 or 11.

14. A coated plant propagation material, wherein the coating of the plant propagation material comprises a compound as defined in any one of claims 1 to 9.

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