Figure S19:

In this attached pdf file, all the results for the 84 OTPs found in wastewater treatment are visually shown. The following information is given for each OTP:

- Top left: OTP formation in ozonation batch experiments
- Top right: Fate of parent MP in wastewater treatment
- Middle: (left) Fate of OTP in post-treatment (% formed or abated) and (right) OTP peak area in all wastewater samples in the four WWTPs. The score and evaluation of MS^2 spectra match of WWTP OZO samples to batch samples is given below.
- Bottom: Information on OTP identification (exact mass, formula, atomic modification, proposed structure, confidence level, Massbank identifier, MS^2 spectra and interpretation of it)

This Figure is part of the *Supporting Information* document belonging to the following publication (citations of references can be found in the *SI* document):

Formation of transformation products during ozonation of secondary wastewater effluent and their fate in post-treatment: From laboratory- to full-scale

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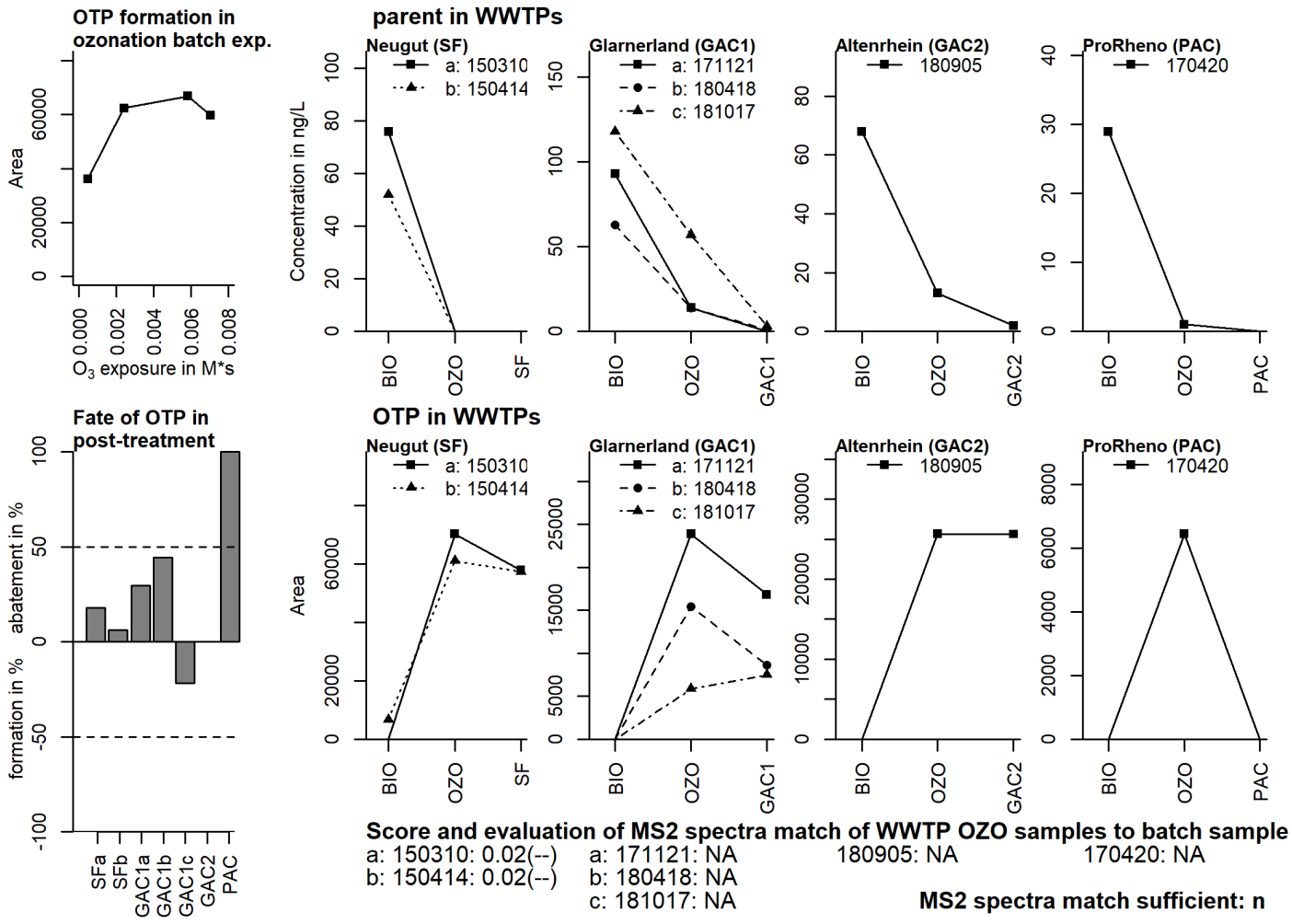
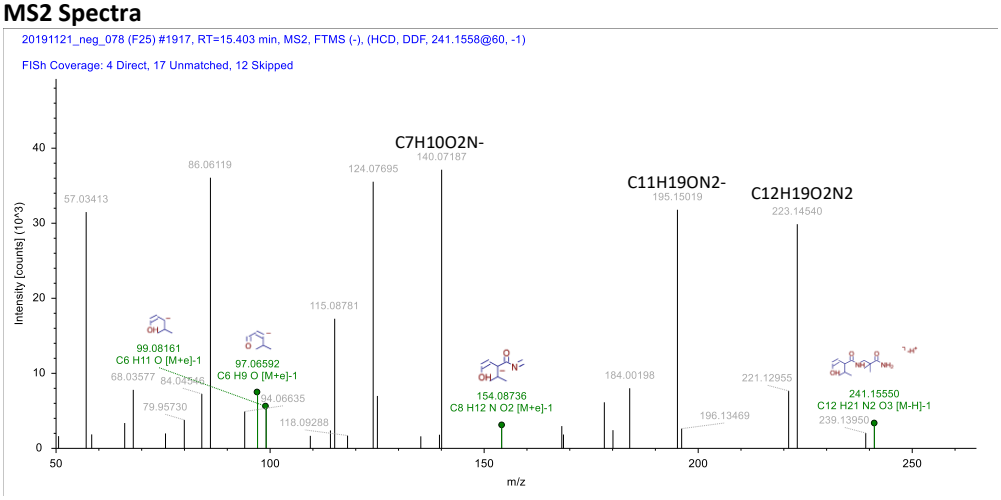
Name ALI_n_241.1556_15.2



MS Spectra

Neg	241.1556	[m-H]-
Neg	287.1611	m+FA-H

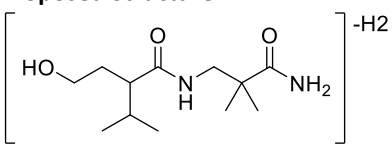
MS2 Spectra



Formula
C12H22O3N2

Atomic modification
-C18H31NO3

Proposed Structure

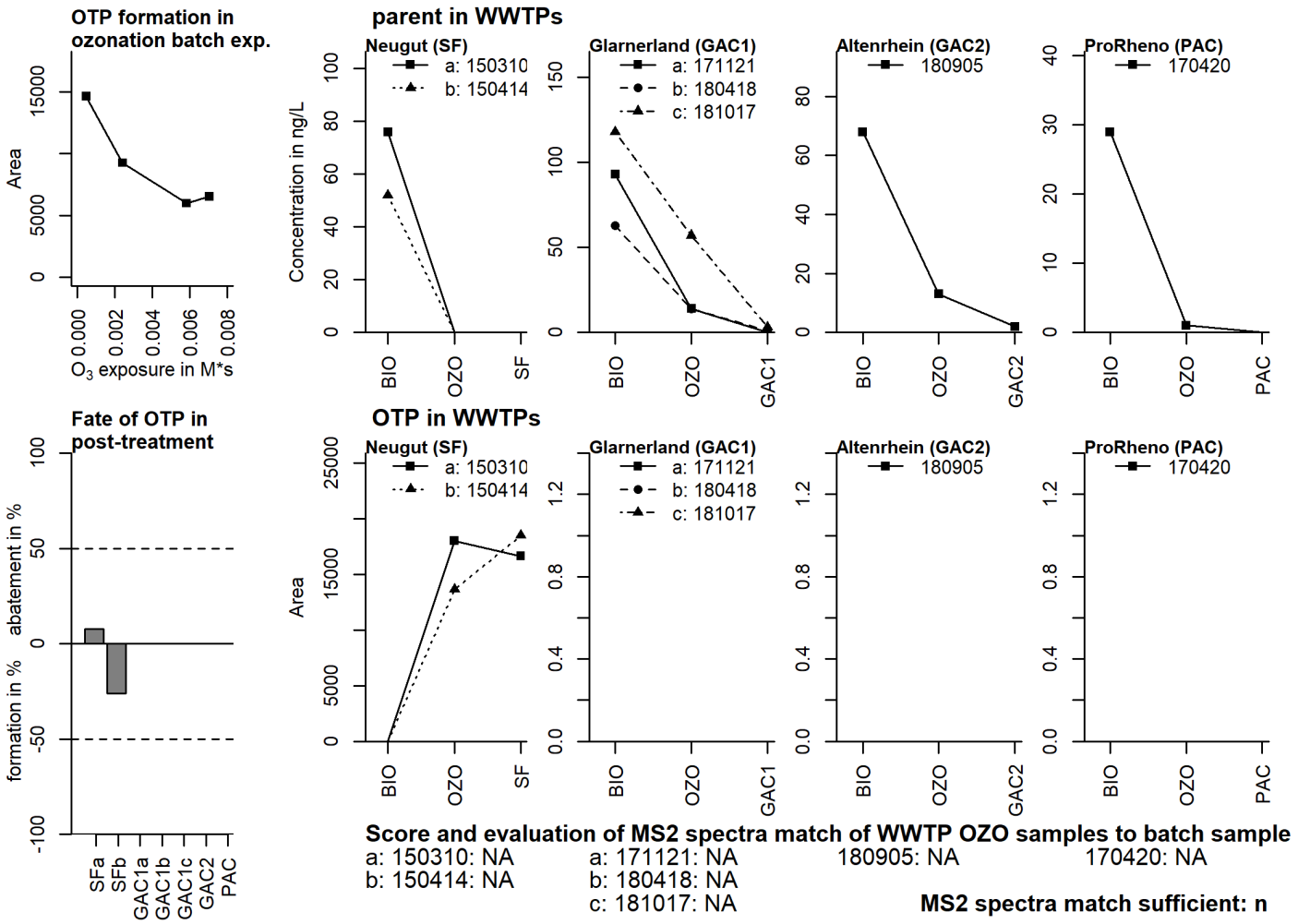


Confidence Level
Level 3

Additional Evidence for Structure Interpretation
The atomic modification from the elemental formula of the parent compound to this OTP is -C18H31NO3. This modification fits to a cleavage of the parent molecule at a C-C bond in the middle of the molecule, followed by an oxidation. Two hydrogen atoms need to be abstracted from the drawn structure to fit the chemical formula. This was probably done by oxidation of the primary alcohol to a carbonyl but there is no indication for this.
The exact type and position of the modification(s) remain unknown. The structures of the MS^2 fragments are drawn exemplarily.

Massbank ID
ET404601

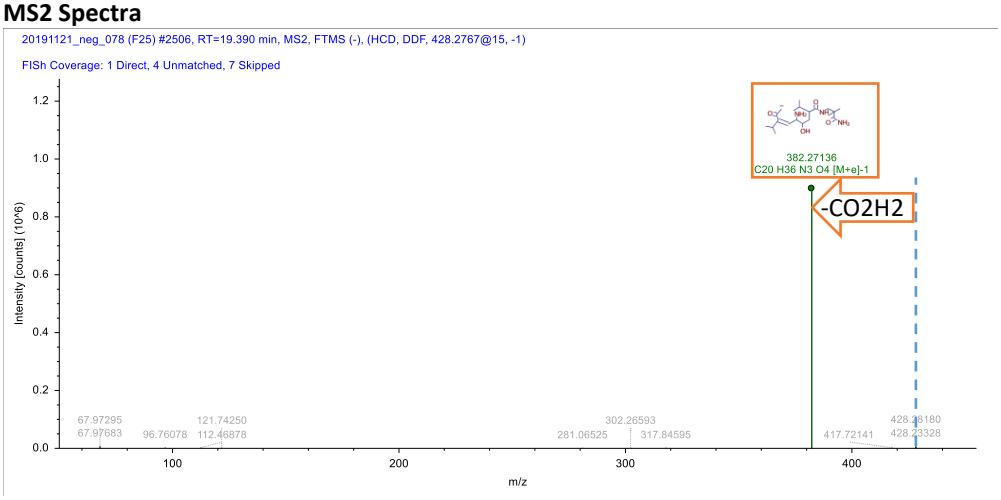
Name ALI_n_428.2762_19.1



MS Spectra

Neg 428.2762 [m-H]-

MS2 Spectra



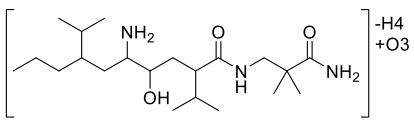
Formula

C21H39O6N3

Atomic modification

-C9H14

Proposed Structure



Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is -C9H14. This modification fits to a cleavage within the phenyl moiety and the addition of 3 oxygen atoms.

The neutral loss of –CO2H2 between the molecular ion and fragment 362 indicates that a carboxylic acid moiety was formed, likely where the cleavage occurred. The exact type and location of the modifications remain unknown. The structures of the MS^2 fragments are drawn exemplarily.

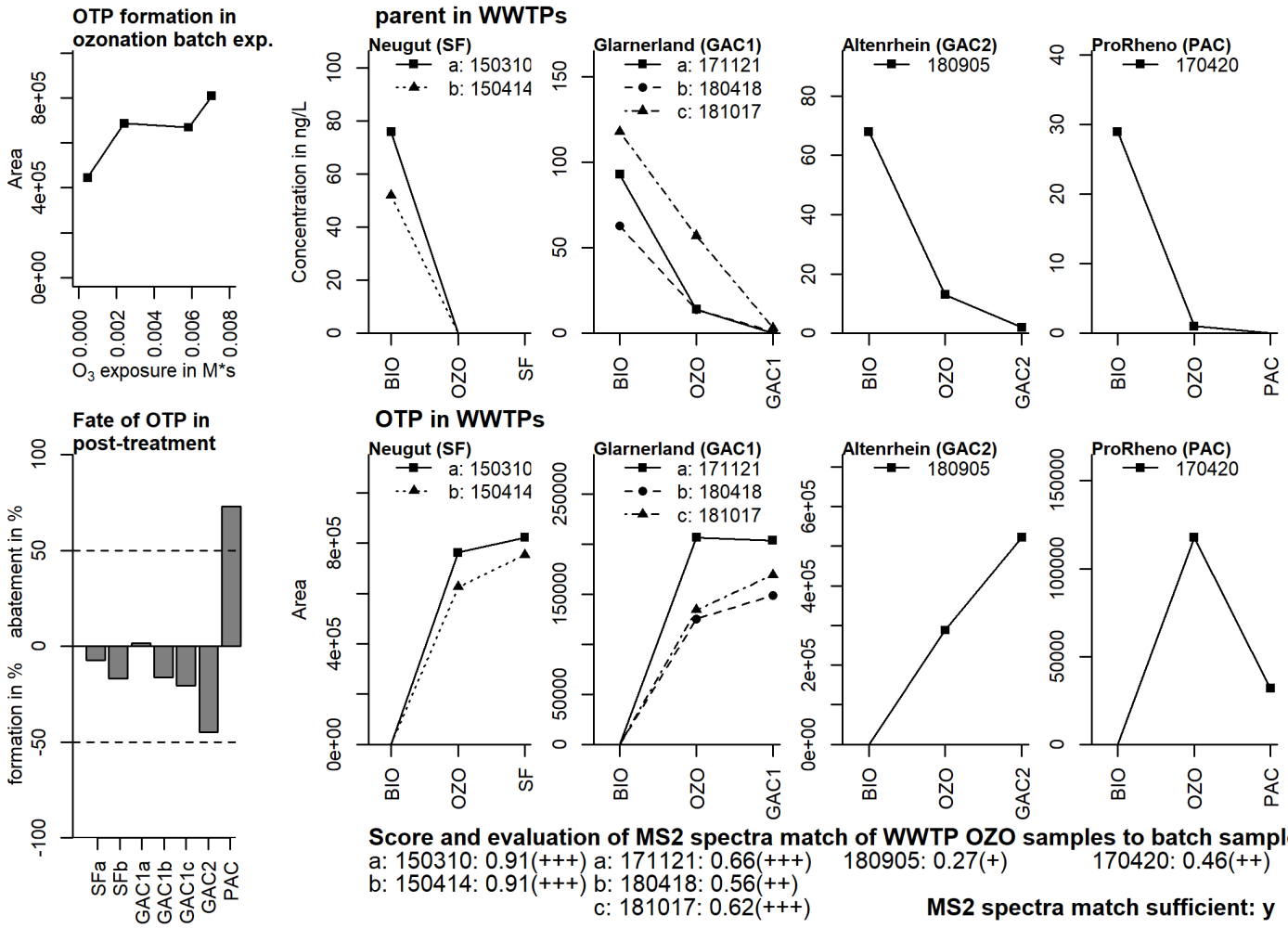
Confidence Level

Level 3

Massbank ID

ET404701

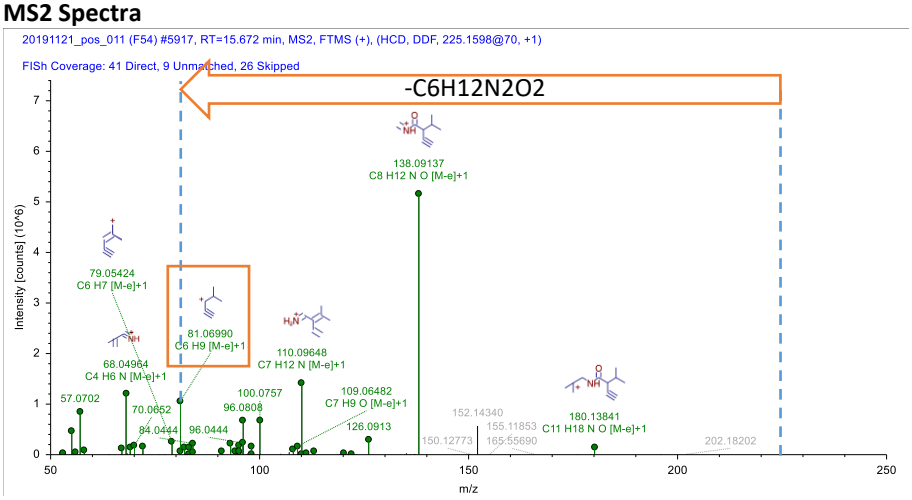
Name ALI_p_225.1597_15.3



MS Spectra

Pos 225.1597 [m+H]+

MS2 Spectra



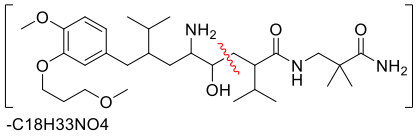
Formula

C12H20O2N2

Atomic modification

-C18H33NO4

Proposed Structure



-C18H33NO4

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is -C18H33NO4. This modification fits to a cleavage of the parent molecule at a C-C bond in the middle of the molecule, as shown by the red waved line. The part of the parent structure right of the line remained. To fit the molecular formula, four hydrogen atoms need to be abstracted. The exact type and position of the modification(s) remain unknown. The structures of the MS^2 fragments are drawn exemplarily.

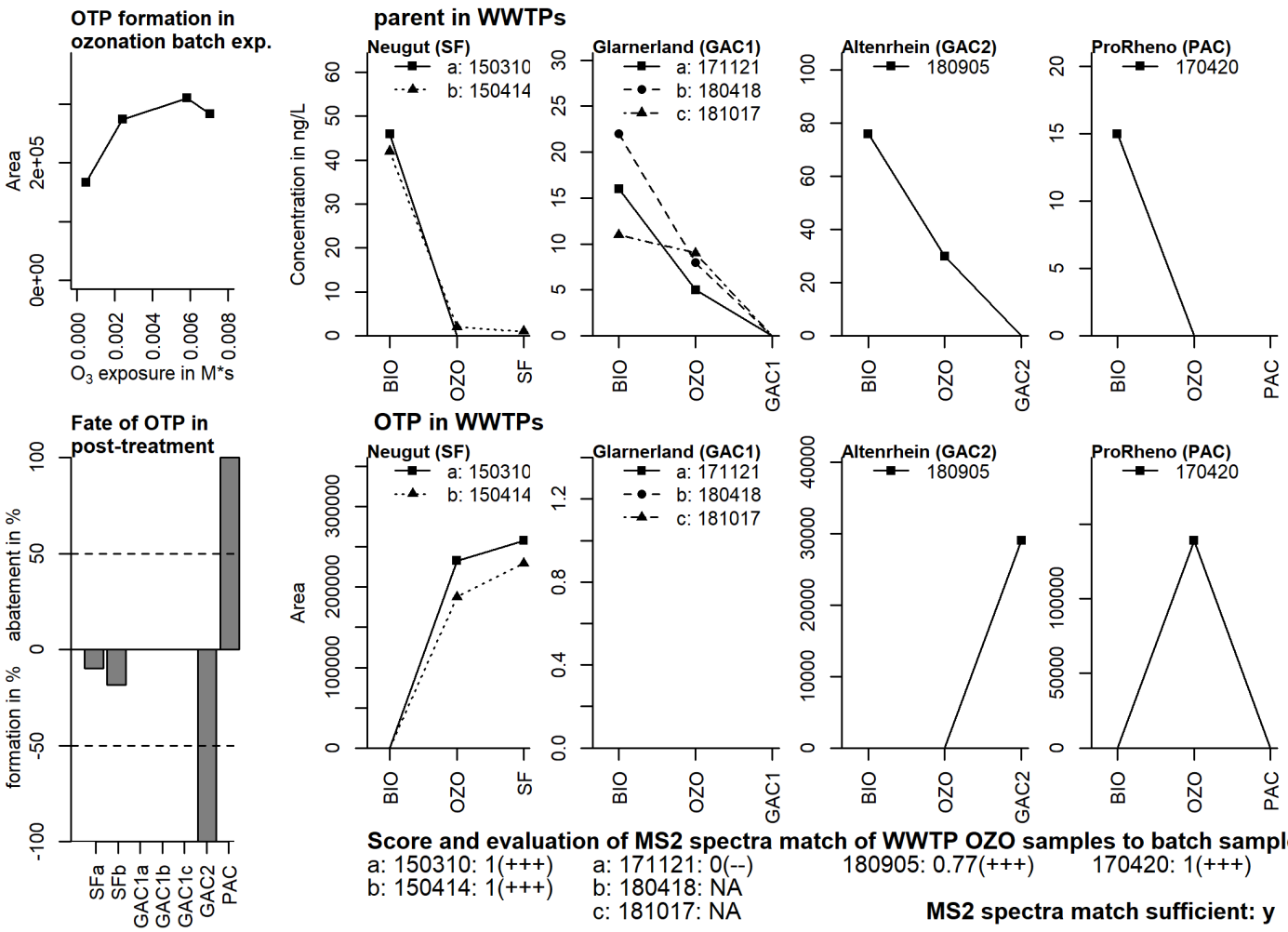
Confidence Level

Level 3

Massbank ID

ET400001

Name ASP_p_416.1486_12.8



Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

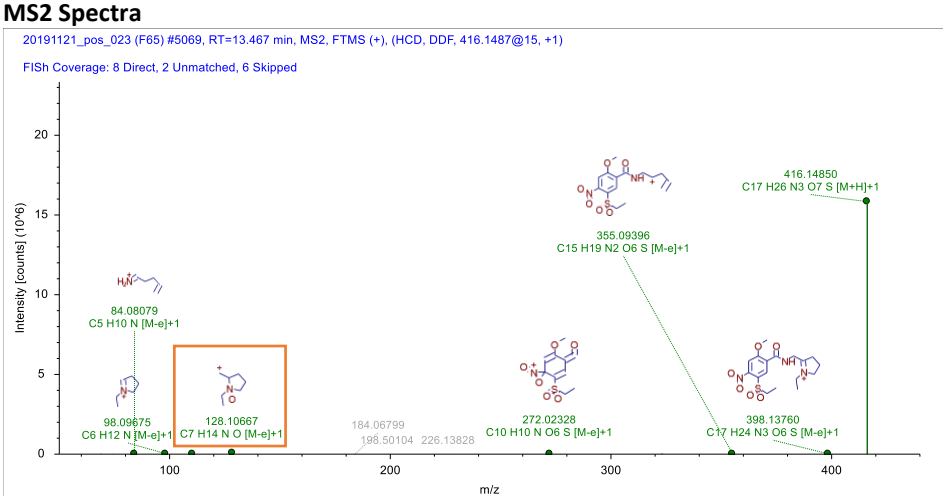
a: 150310: 1(+++) a: 171121: 0(--) 180905: 0.77(+++) 170420: 1(+++)
b: 150414: 1(+++) b: 180418: NA
c: 181017: NA

MS2 spectra match sufficient: y

MS Spectra

Pos 416.1486 [m+H]+

MS2 Spectra



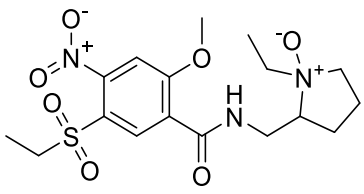
Formula

C17H25O7N3S

Atomic modification

-H2 +O3

Proposed Structure



Confidence Level

Level 3

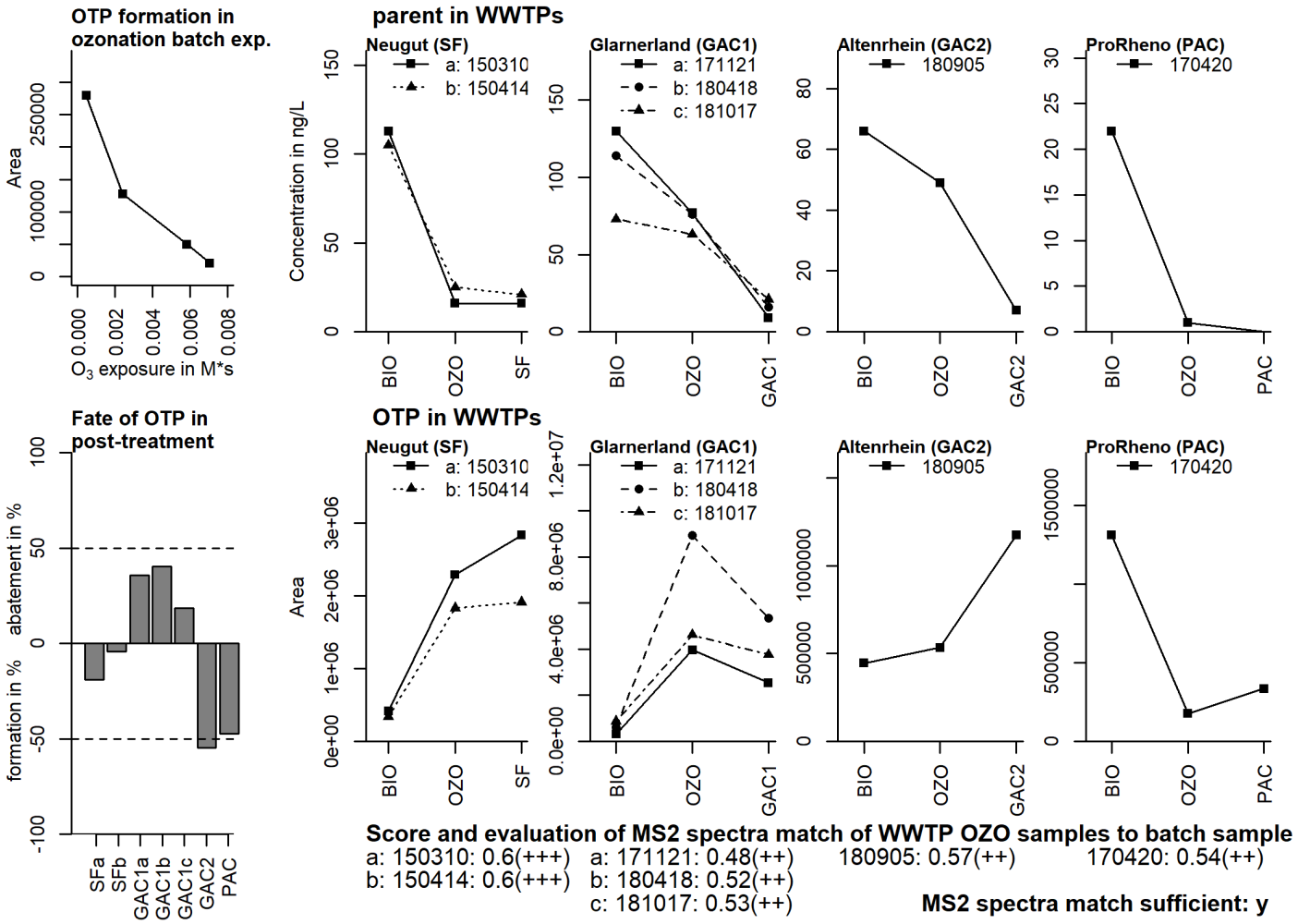
Massbank ID

ET400101

Additional Evidence for Structure Interpretation

A MS^2 fragment at the nominal mass of 112 was observed for the parent compound and corresponds to the ethylpyrrolidine moiety. The MS^2 fragment here at the nominal mass 128 corresponds to the fragment 112 of the parent with an addition of an oxygen atom. Tertiary amines are very reactive to form *N*-oxides during ozonation (von Sonntag & von Gunten 2012). Therefore, the formation of an *N*-oxide at the ethylpyrrolidine is very likely. A MS^2 fragment at the nominal mass 242 was observed for the parent compound and corresponds to the aromatic moiety. The fragment 272 corresponds to the fragment 242 at the parent moiety with an atomic modification of –H2 +O2. Aniline-like moieties are known to partially form nitro groups during ozonation (von Sonntag & von Gunten 2012), which would also fit here). Another possibility for an –H2 +O2 modification, namely the formation of a carboxylic acid of a terminal carbon, seems unlikely due to the absence of the characteristic neutral loss of water and carbon dioxide. Also, no matching signal was observed in negative mode.

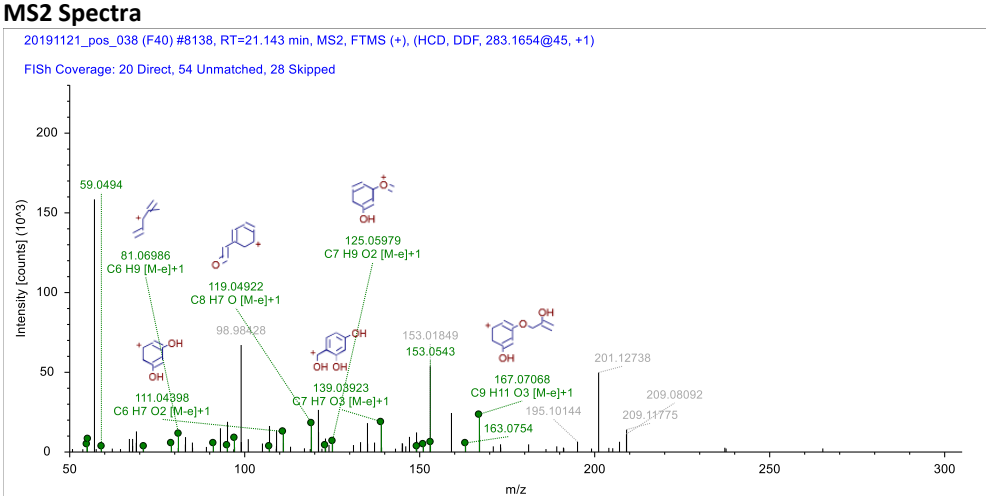
Name ATE_p_283.1666_21.2



MS Spectra

Pos 283.1666 [m+H]+

MS2 Spectra



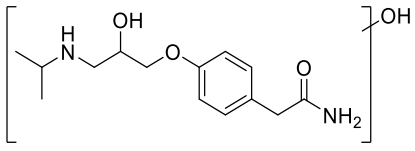
Formula

C14H22O4N2

Atomic modification

+O

Proposed Structure



Confidence Level

Level 3

Massbank ID

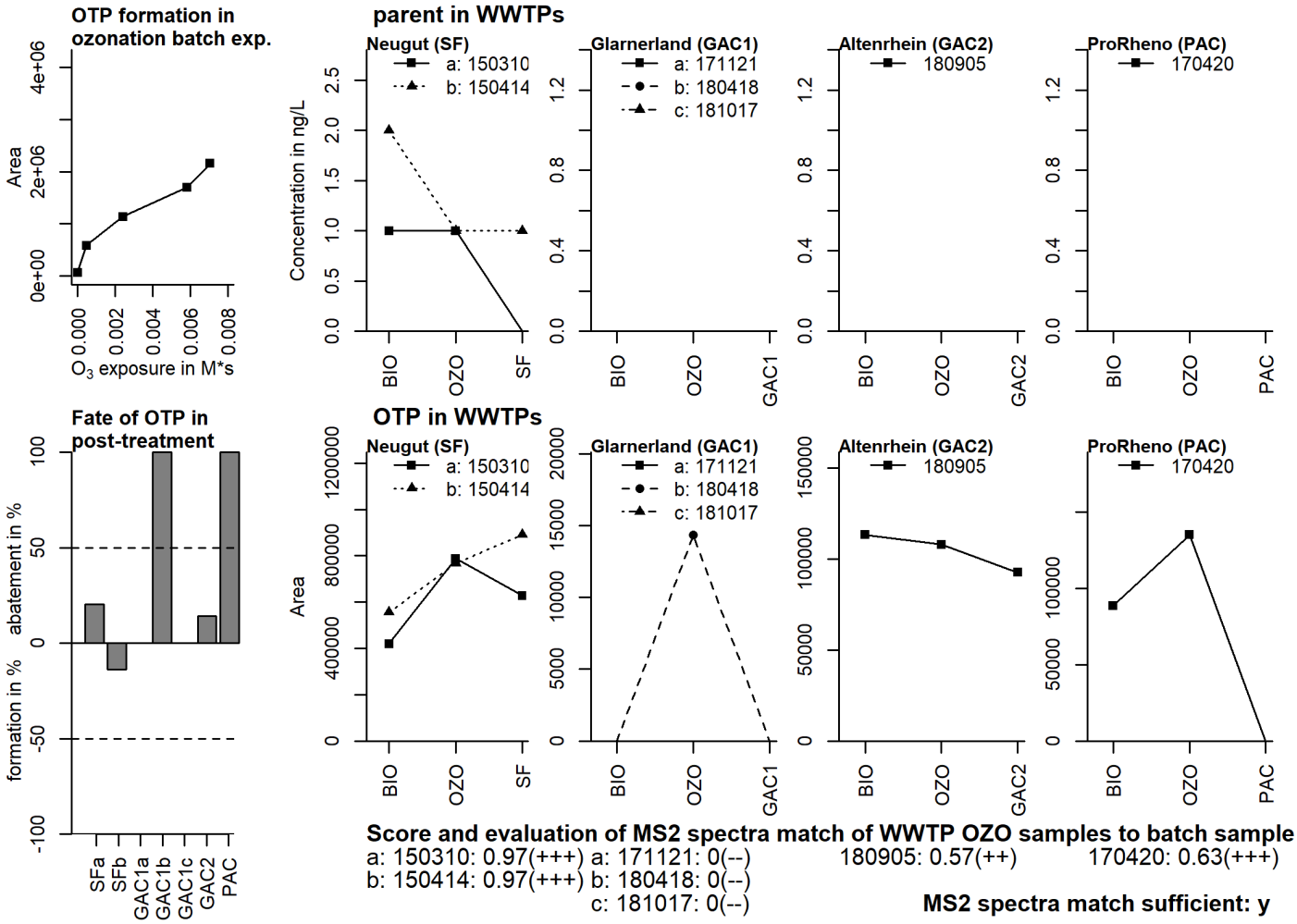
ET400201

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this TP is + O. This suggests a hydroxylation, which is known to happen during ozonation (von Sonntag & von Gunten 2012), likely by an OH radical. The hydroxylation likely occurred at an aliphatic C-atom, because once formed, phenol moieties react further quickly during ozonation. The exact location of the hydroxyl moiety remains unknown. The structures of the MS^2 fragments are drawn exemplarily.

Hydroxylated atenolol was suggested as OTP of atenolol in different studies (Quaresma et al. 2019, Tay et al. 2011, Xu et al. 2019).

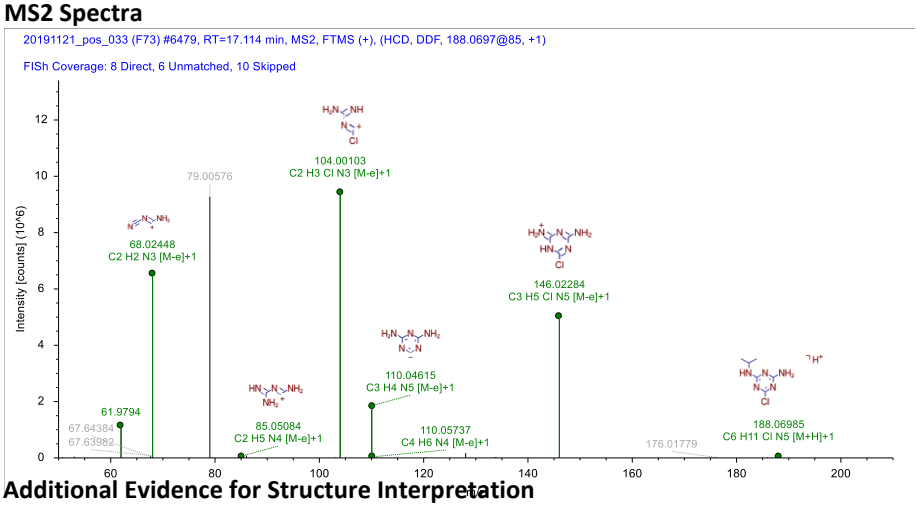
Name ATZ_p_188.0697_16.8



MS Spectra

Pos 188.0697 [m+H]+

MS2 Spectra



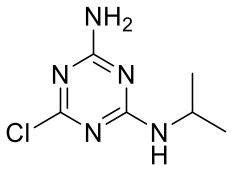
Formula

C6H10N5Cl

Atomic modification

-C2H4

Proposed Structure



Confidence Level

Level 3

Massbank ID

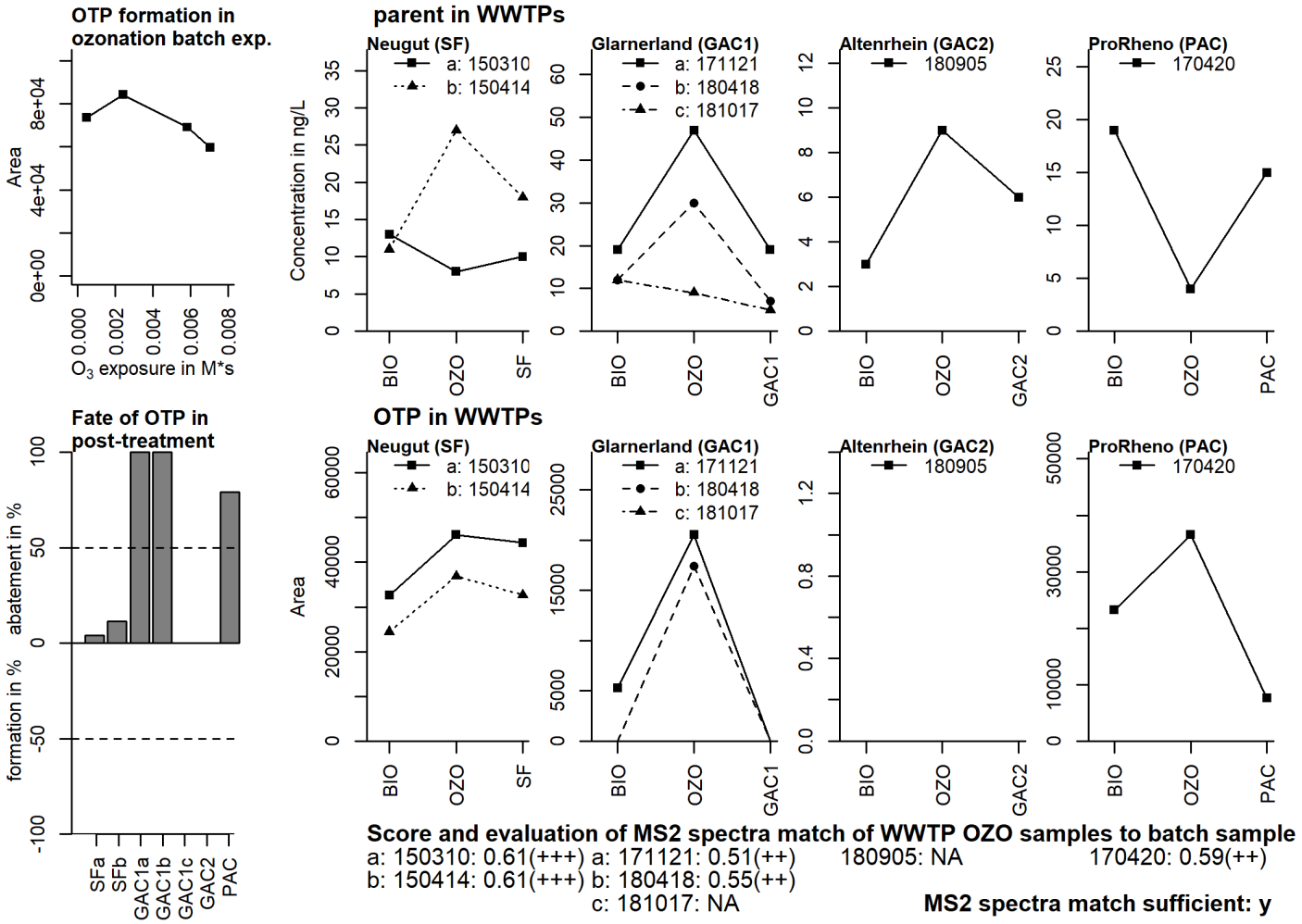
ET400301

Additional Evidence for Structure Interpretation

The MS^2 fragments at the nominal masses 146, 104, 79, 68, 61 were also observed for the parent compound and indicate that the chlorotriazineamine moiety is also part of this TP structure.

The atomic modification from the elemental formula of the parent compound to this TP is –C2H4, which suggests an *N*-deethylation, which is known to happen during ozonation (von Sonntag & von Gunten 2012). Deethylatrazine was suggested as ozone/hydroxyl radical transformation product in different studies (Acero et al. 2000, Beltran et al. 1998, Barletta et al. 2003).

Name BIT_n_215.9525_17.0



MS Spectra

Neg 215.9525 [m+Cl]-

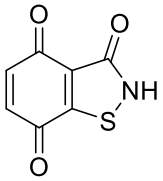
Formula

C7H3O3NS

Atomic modification

-H2 + O2

Proposed Structure



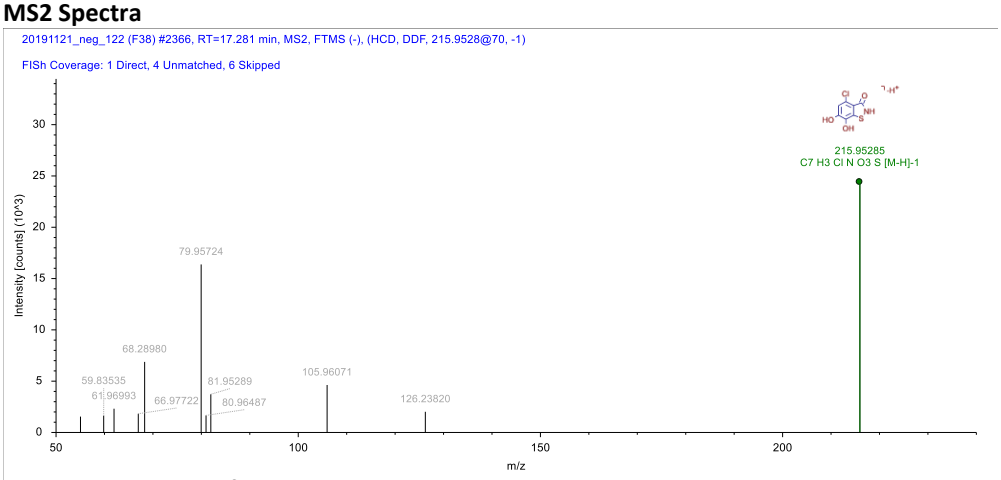
Confidence Level

Level 3

Massbank ID

ET404801

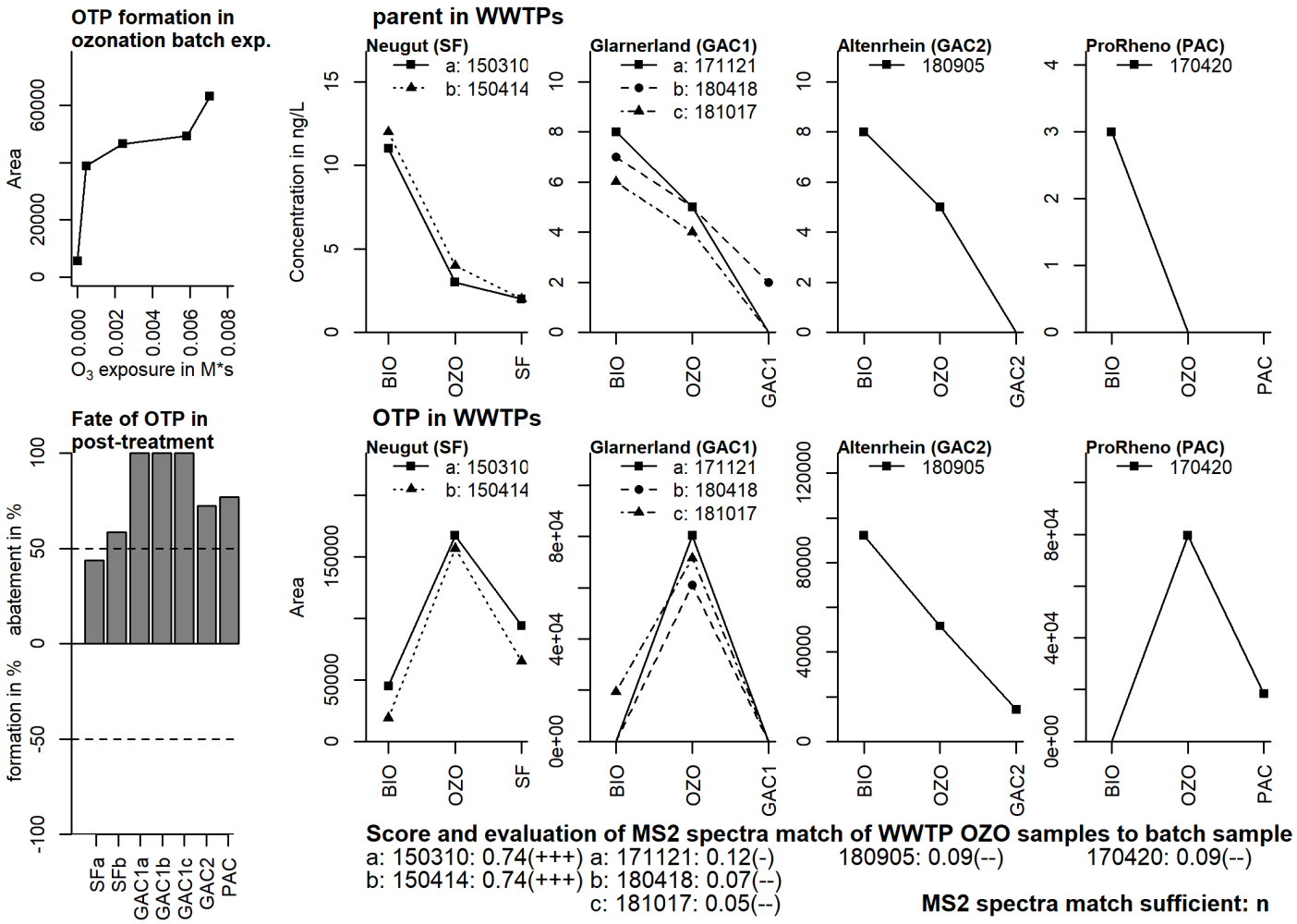
MS2 Spectra



Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this TP is –H2 +O2, which fits to the formation of a benzoquinone moiety after attack of OH radicals at the phenyl moiety to form a phenol intermediate, which can the be transformed to a benzoquinone (Tentscher et al. 2018, Ramseier and von Gunten 2009).

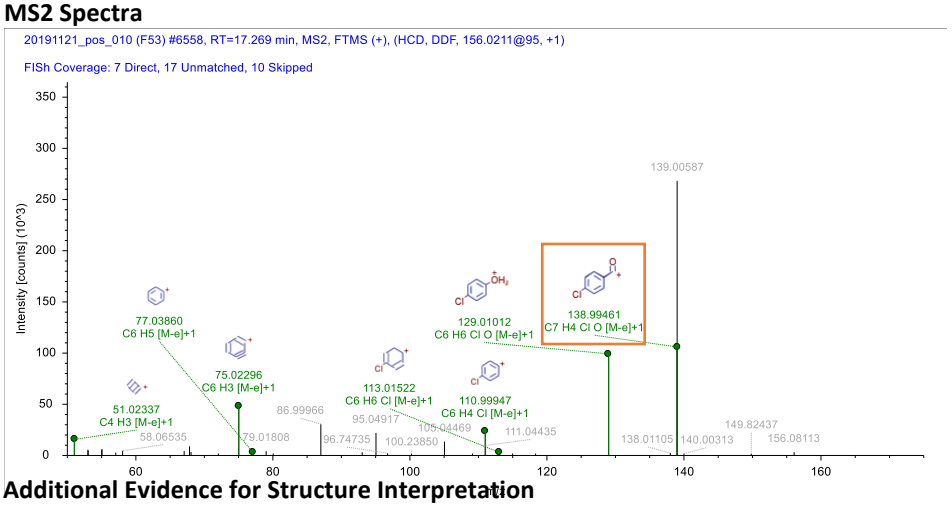
Name BZF_p_156.0209_16.9



MS Spectra

Pos 156.0209 [m+H]+

MS2 Spectra



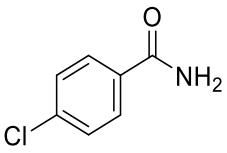
Formula

C7H6ONCl

Atomic modification

-C12H14O3

Proposed Structure



Confidence Level

Level 3

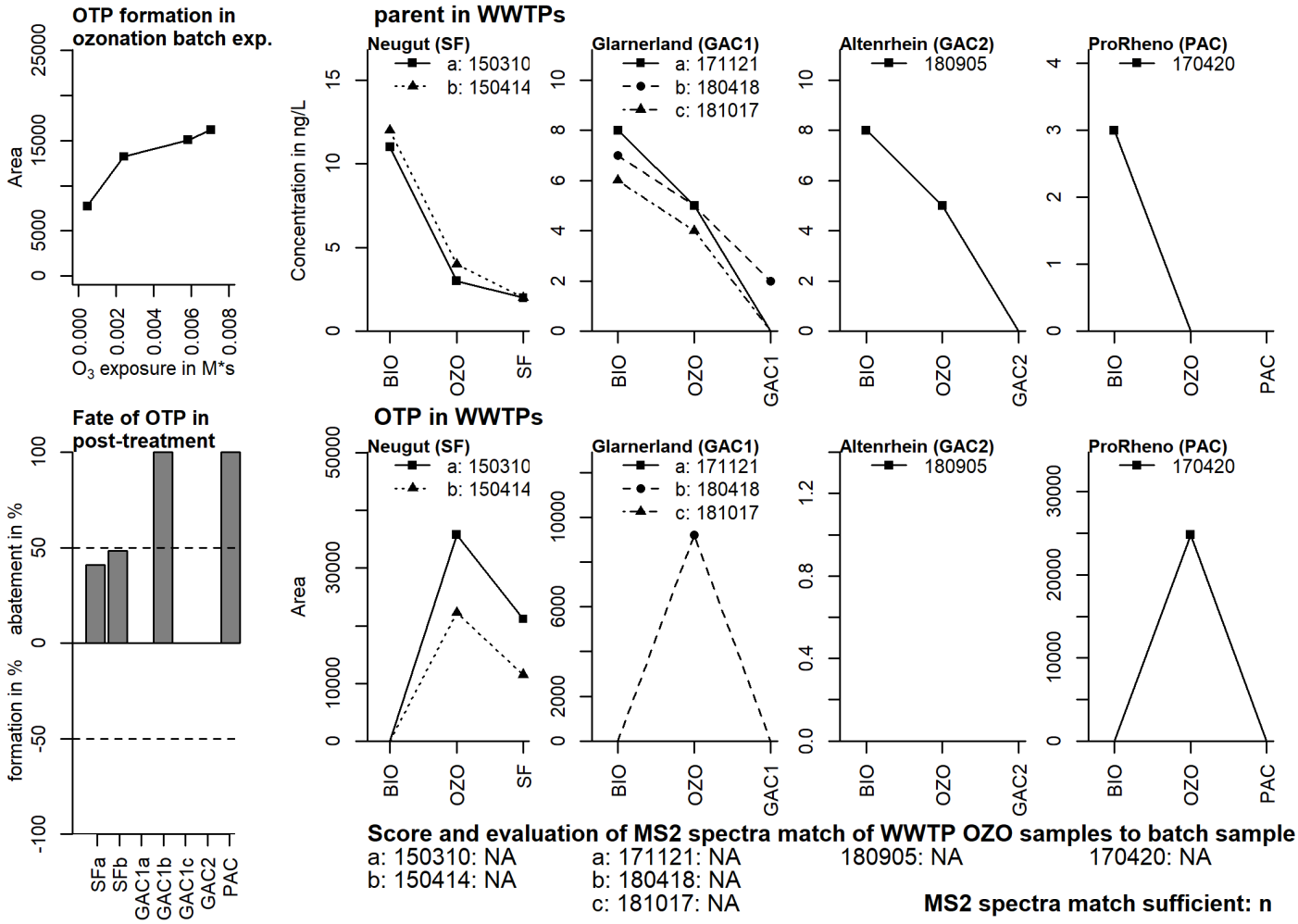
Massbank ID

ET400401

Additional Evidence for Structure Interpretation

The MS^2 fragment at the nominal mass 138 was also observed for the parent compound. It indicates that the drawn structure of the MS^2 fragment 138 is a substructure of this TP. The atomic modification from the elemental formula of the parent compound to this TP is -C12H14O3. This modification fits to a cleavage of the parent molecule at the N-CH2 bond in the middle of the molecule, whereby the proposed structure remains. Sui et al. (2017) also suggested the formation of this TP after ozonation of bezafibrate.

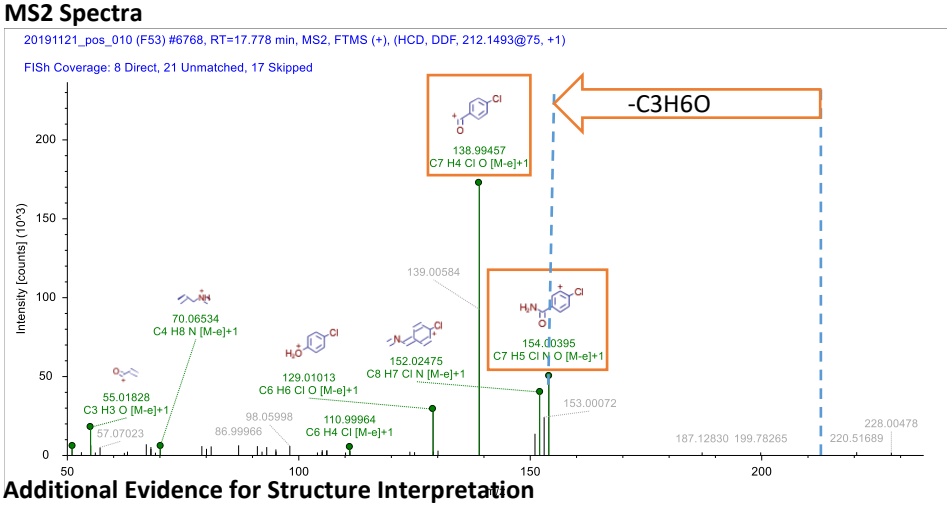
Name BZF_p_212.0469_17.1



MS Spectra

Pos 212.0469 [m+H]+

MS2 Spectra



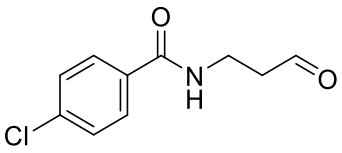
Formula

C10H10O2NCl

Atomic modification

-C9H10O2

Proposed Structure



Confidence Level

Level 3

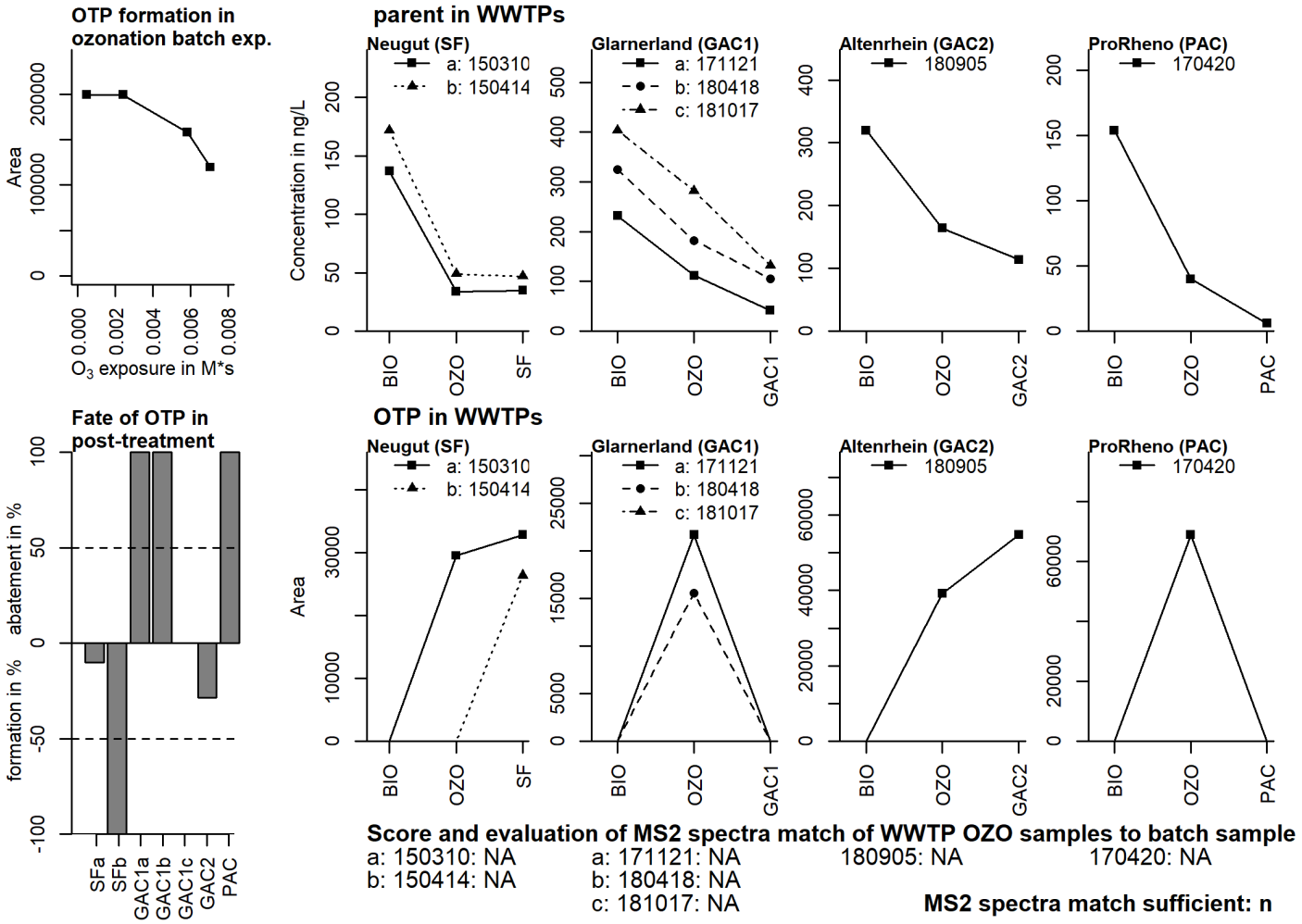
Massbank ID

ET400501

Additional Evidence for Structure Interpretation

The MS^2 fragment at the nominal mass 138 was also observed for the parent compound and for BZF_p_156.0209_16.9. It indicates that the structure drawn for the fragment 138 is a substructure of this TP. The fragment 55, which corresponds to a C3H3O moiety, indicates that neutral loss of –C3H6O between the precursor and the fragment 154 were one single moiety. In the structure of the parent compound a phenylethyl moiety is connected to the cholorobenzamide substructure. Therefore, it is likely that the C3H6O moiety is also connected to the nitrogen of the chlorobenzeamide substructure. The formula of this TP fits to a Criegee mechanism on the phenoxy moiety of the parent compound, followed by a C-C bond cleavage, which is known to occur during ozonation (von Sonntag & von Gunten 2012).

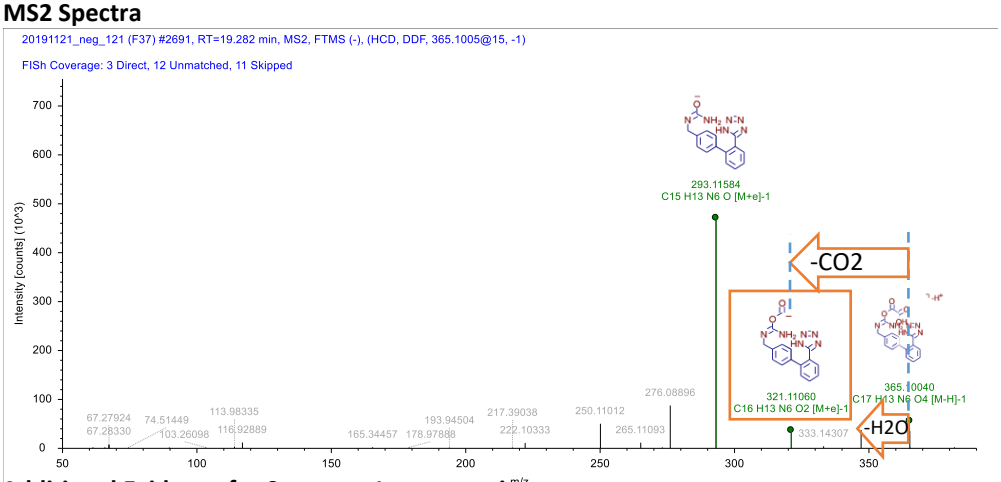
Name CAN_n_365.1000_18.9



MS Spectra

Neg 365.1000 [m-H]-

MS2 Spectra



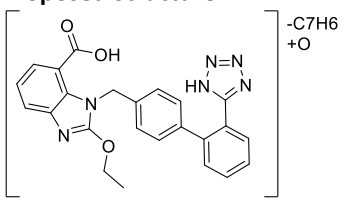
Formula

C17H14O4N6

Atomic modification

-C7H6 +O

Proposed Structure



Confidence Level

Level 3

Massbank ID

ET404801

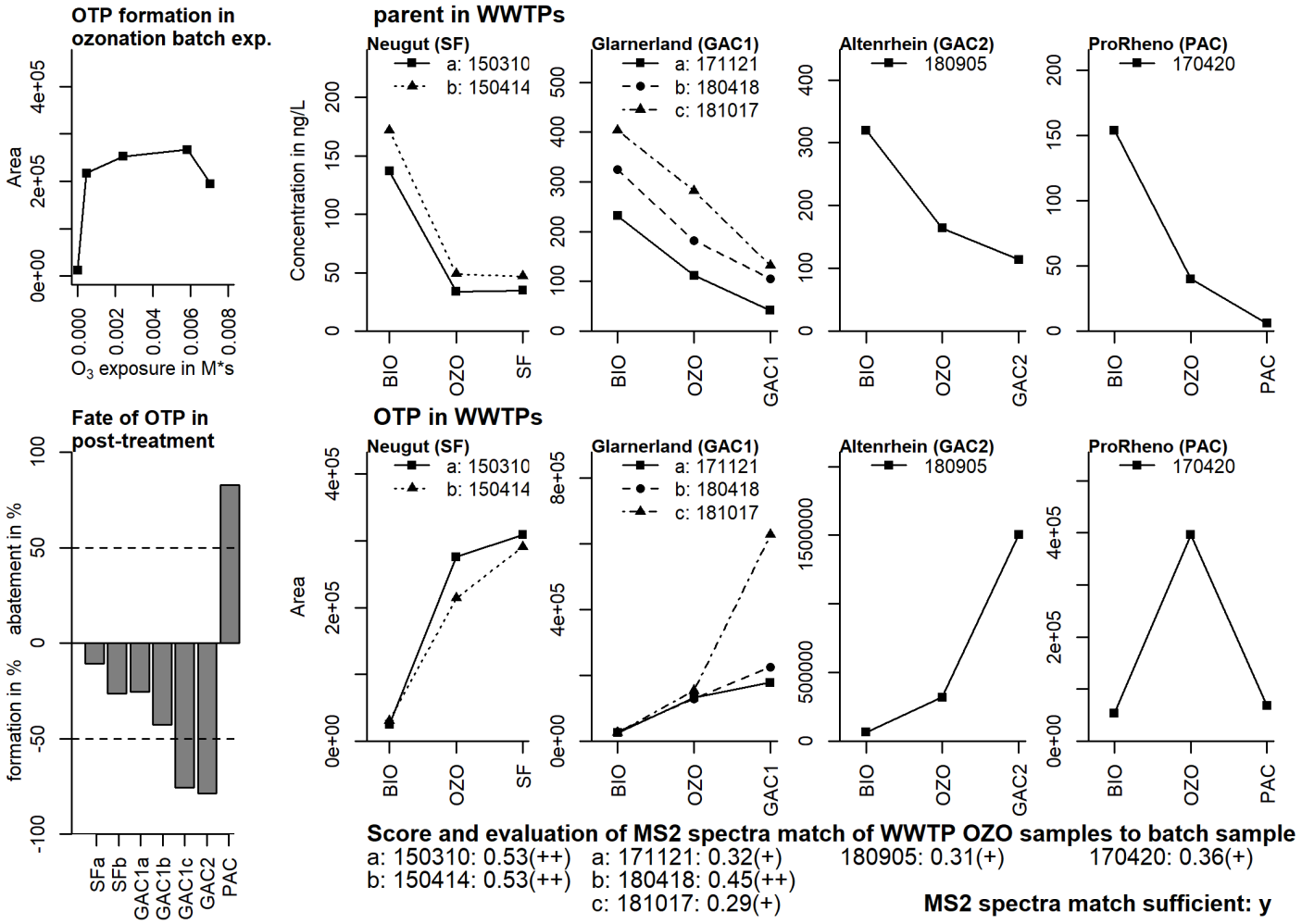
Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this TP is –C7H6 +O. Since no nitrogen atom was cleaved off, the methylbiphenyltriazole moiety probably remained intact after reaction with ozone.

The neutral loss of CO2 between the molecular ion and fragment 321 as well as the neutral loss of H2O between the molecular ion and fragment 347 indicate the presence of a carboxylic moiety.

The exact type and location of the modifications remain unknown. The structures of the MS^2 fragments are drawn exemplarily.

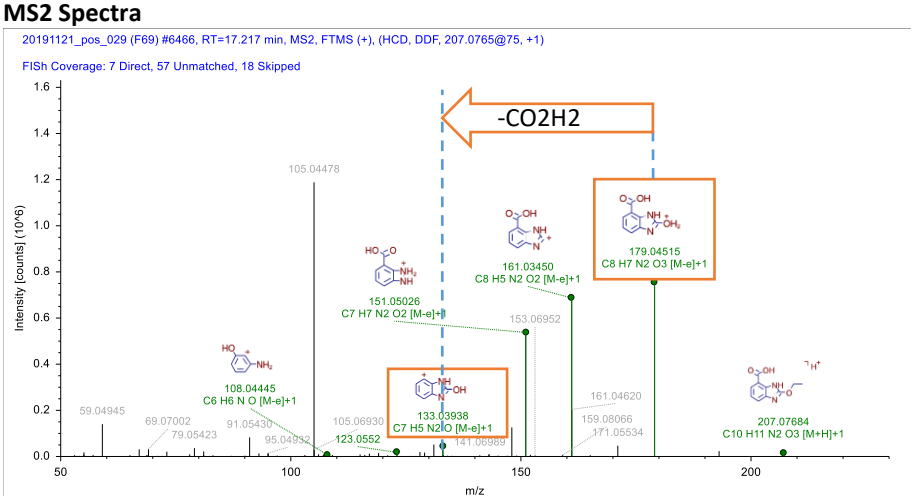
Name CAN_p_207.0766_17.0



MS Spectra

Pos	207.0766	[m+H]+
Neg	205.0616	[m-H]-

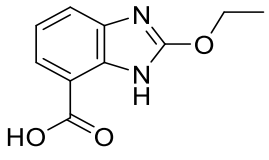
MS2 Spectra



Formula
C10H10O3N2

Atomic modification
-C14H10N4

Proposed Structure



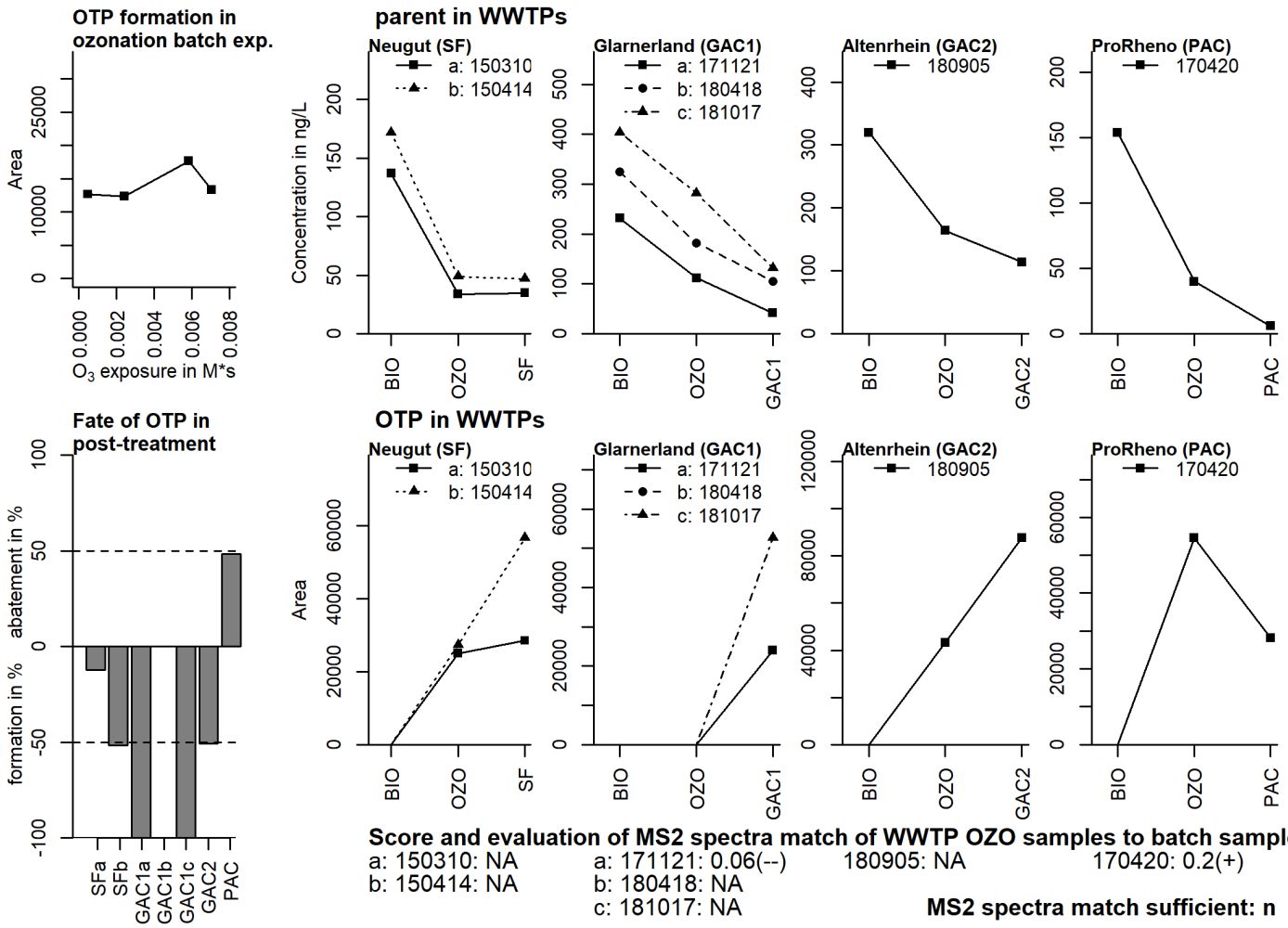
Confidence Level
Level 3

Massbank ID
ET400601

Additional Evidence for Structure Interpretation

The atomic modification of C14H10N4 from the parent structure to this TP fits to a cleavage of the moiety, which is common for all sartans (tetrazolebiphenylmethyl). The remaining part of the molecule fits to the formula for this TP. Furthermore, this TP was also detected in the negative MS spectrum and a neutral loss between fragments 179 and 133 indicates the presence of a carboxylic acid moiety, meaning that the carboxylic acid moiety is conserved. The proposed structure of the TP Sartan_p_251.0924_17.9 fits to the cleaved tetrazolebiphenylmethyl moiety, to which an oxygen atom was added.

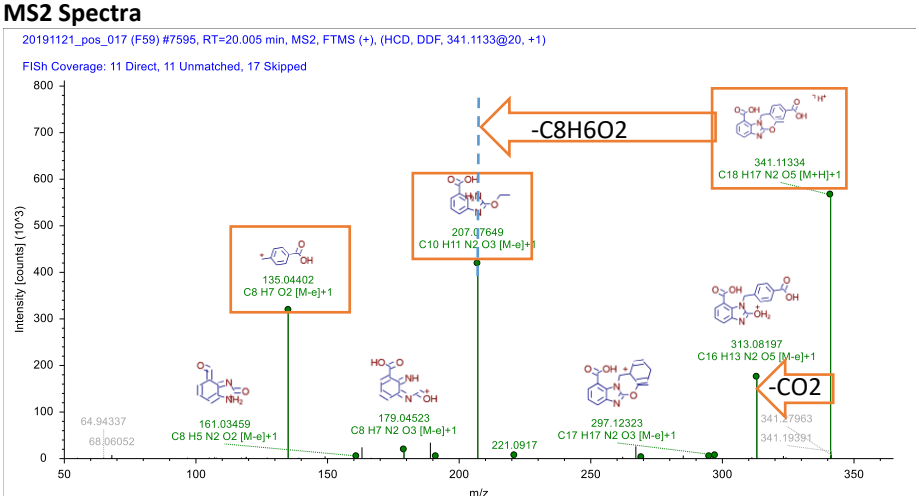
Name CAN_p_341.1130_19.6



MS Spectra

Pos	341.1130	[m+H]+
Neg	339.0983	[m-H]-

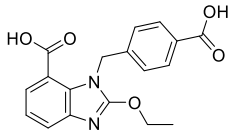
MS2 Spectra



Formula
C18H16O5N2

Atomic modification
-C6H4N4 +O2

Proposed Structure



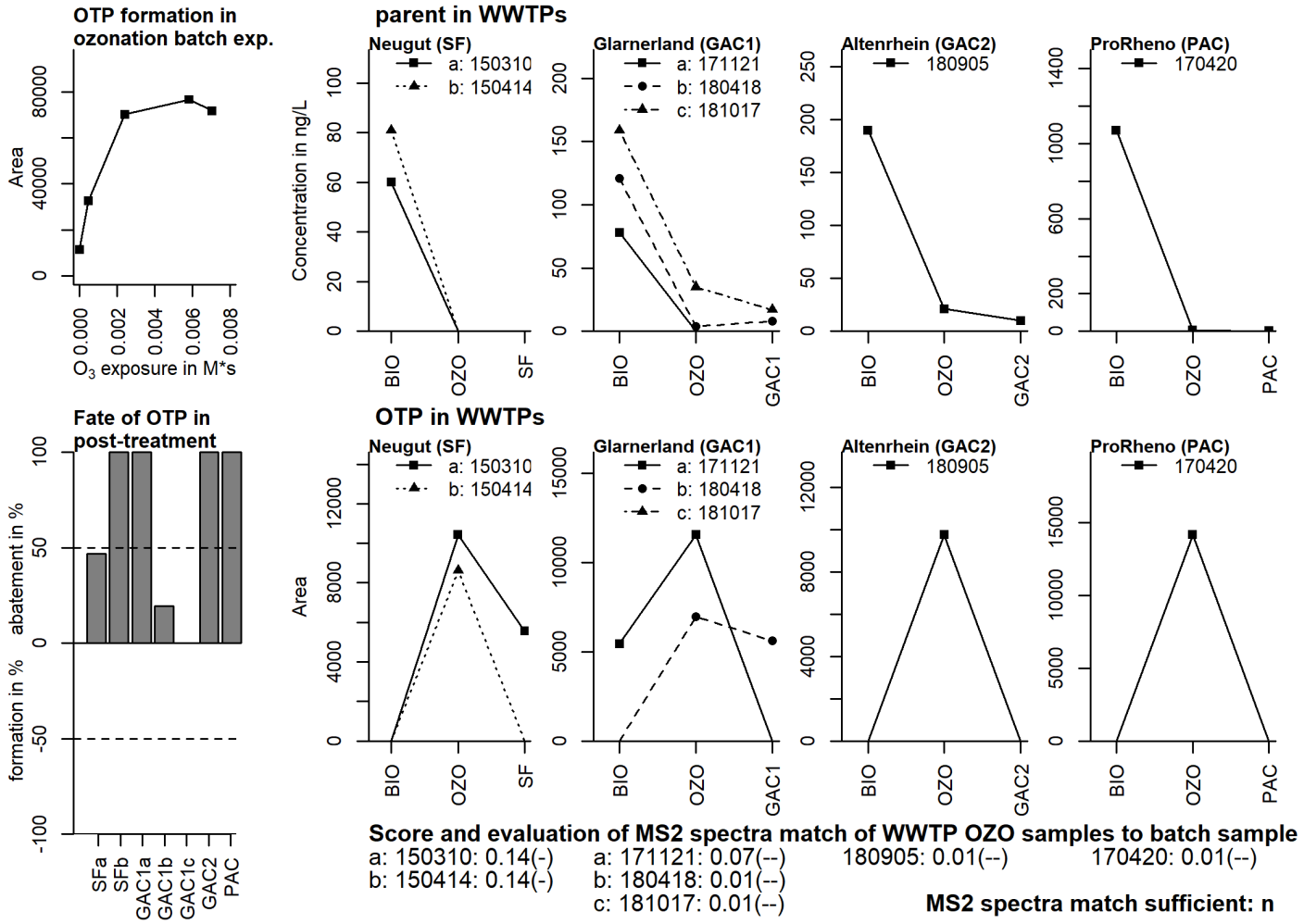
Confidence Level
Level 3

Massbank ID
ET400701

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this TP is -C6H4N4 +O2. This fits to a cleavage within the benzol moiety of the tetrazolebiphenylmethyl part and the modification of –H2 +O2 atoms. The fragment 135 as well as the neutral loss of C8H6O2 between the precursor and fragment 207 indicate that the two oxygens are connected to the p-methylbenzyl moiety. The exact type and position remain unknown. Aromatic compounds are known to form cis,cis-Muconic acid like structures (von Sonntag & von Gunten 2012). Therefore, the formation of this kind of structure, followed by a C-C bond cleavage, resulting in a p-benzoic acid moiety, is probable. There is however no further evidence. The structures of the MS^2 fragments are drawn exemplarily.

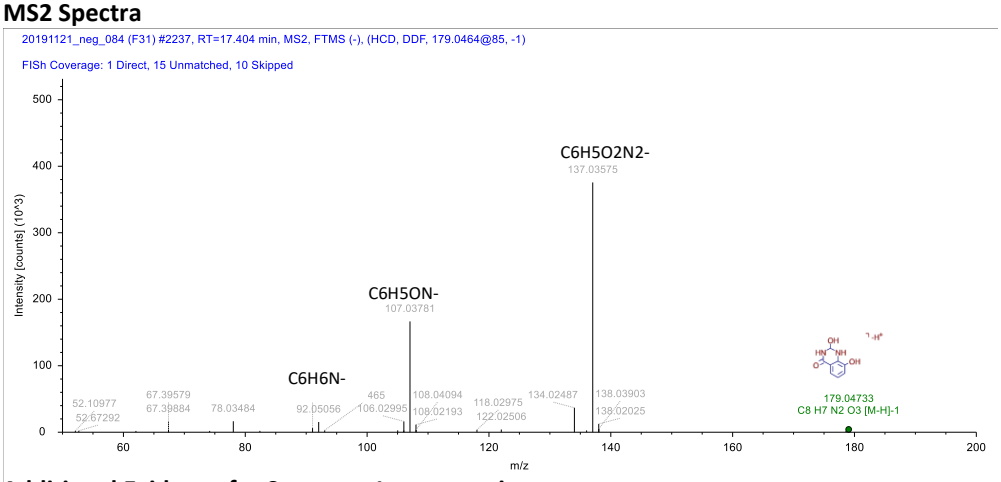
Name CBZ_n_179.0461_17.2



MS Spectra

Neg 179.0461 [m-H]-

MS2 Spectra



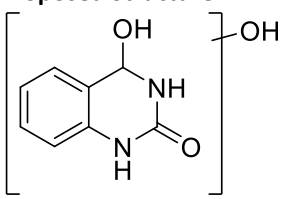
Formula

C8H8O3N2

Atomic modification

-C7H4 +O2

Proposed Structure



Confidence Level

Level 3

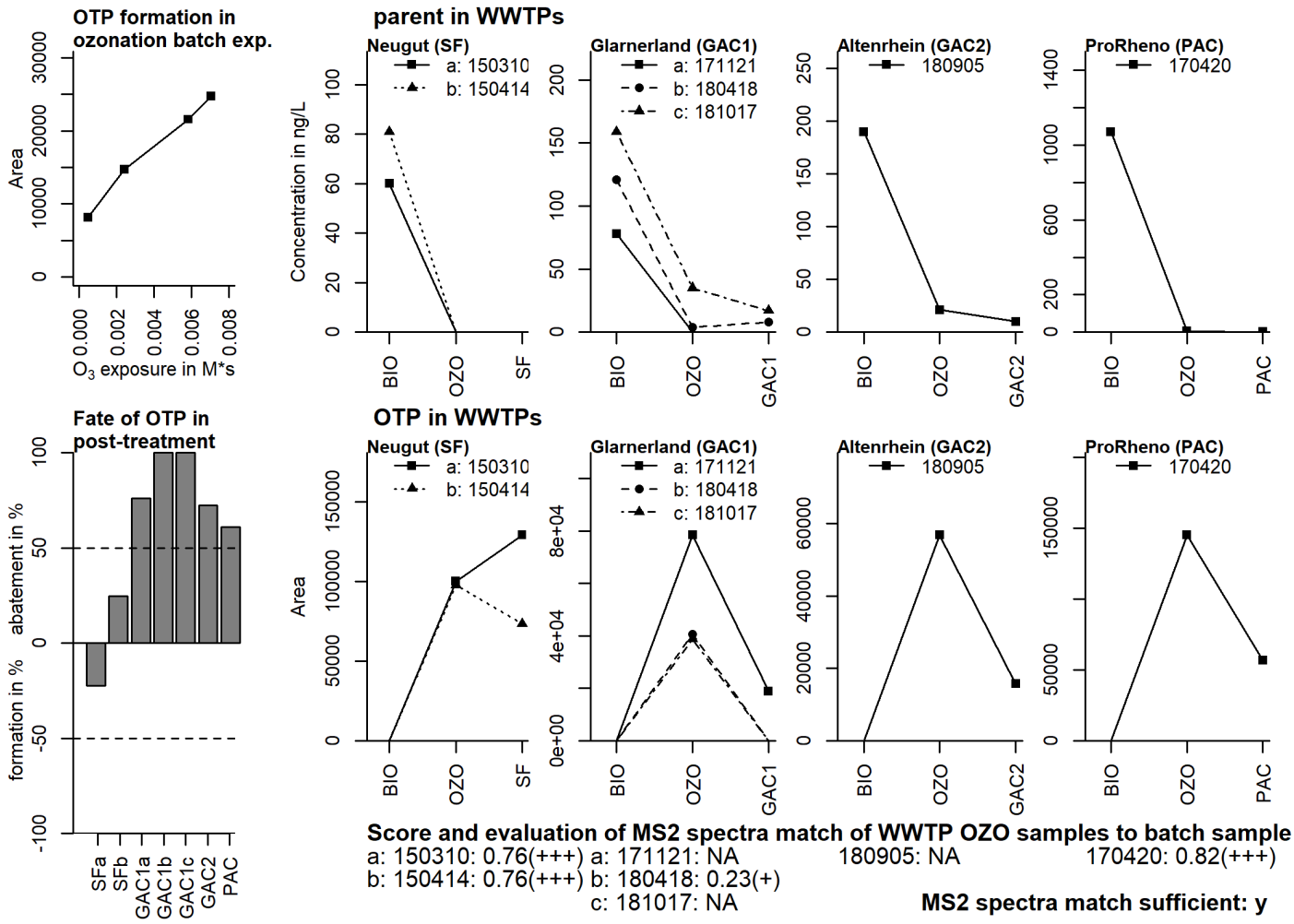
Massbank ID

ET405001

Additional Evidence for Structure Interpretation

Azais et al. (2017) identified the drawn structure on the MS^2 spectra as ozonation transformation product of carbamazepine, more precisely as degradation product of BQD and/or BaQD. Since both BQD and BaQD were detected, it is possible that these structures further reacted to form this TP. Another possibility is the formation a hydroxylamine moiety. Both the hydroxylamine and the phenol moiety quickly react further during ozonation. Therefore, the exact structure of this TP remains unclear. The structures of the MS^2 fragments are drawn exemplarily.

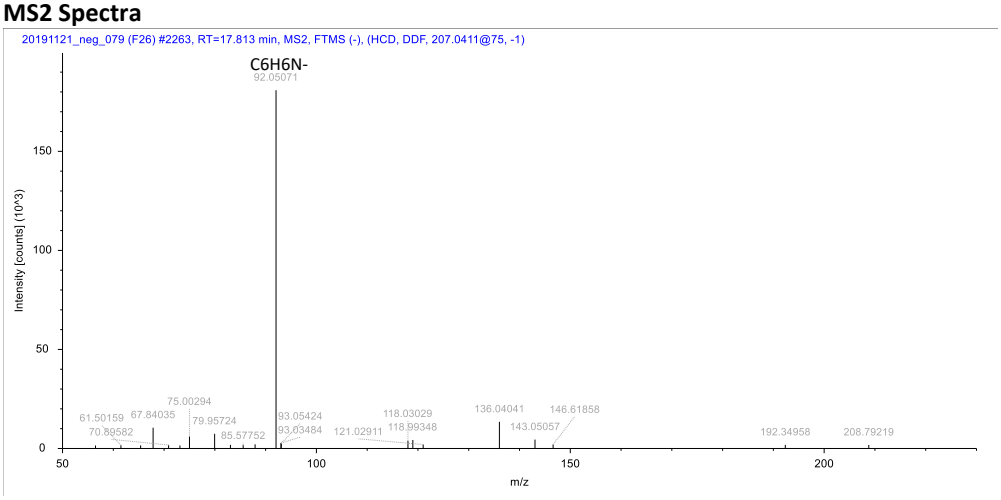
Name CBZ _n_207.0409_17.6



MS Spectra

Neg 207.0409 [m-H]-

MS2 Spectra



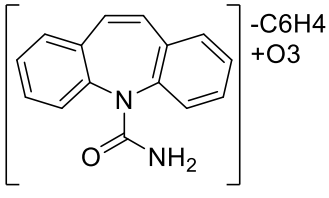
Formula

C9H8O4N2

Atomic modification

-C6H4 +O3

Proposed Structure



Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this TP is –C6H4 +O3. This modification fits to a cleavage of a phenyl moiety and the addition of 3 oxygen atoms. There is however no further evidence. The exact type and location of the modifications remain unknown.

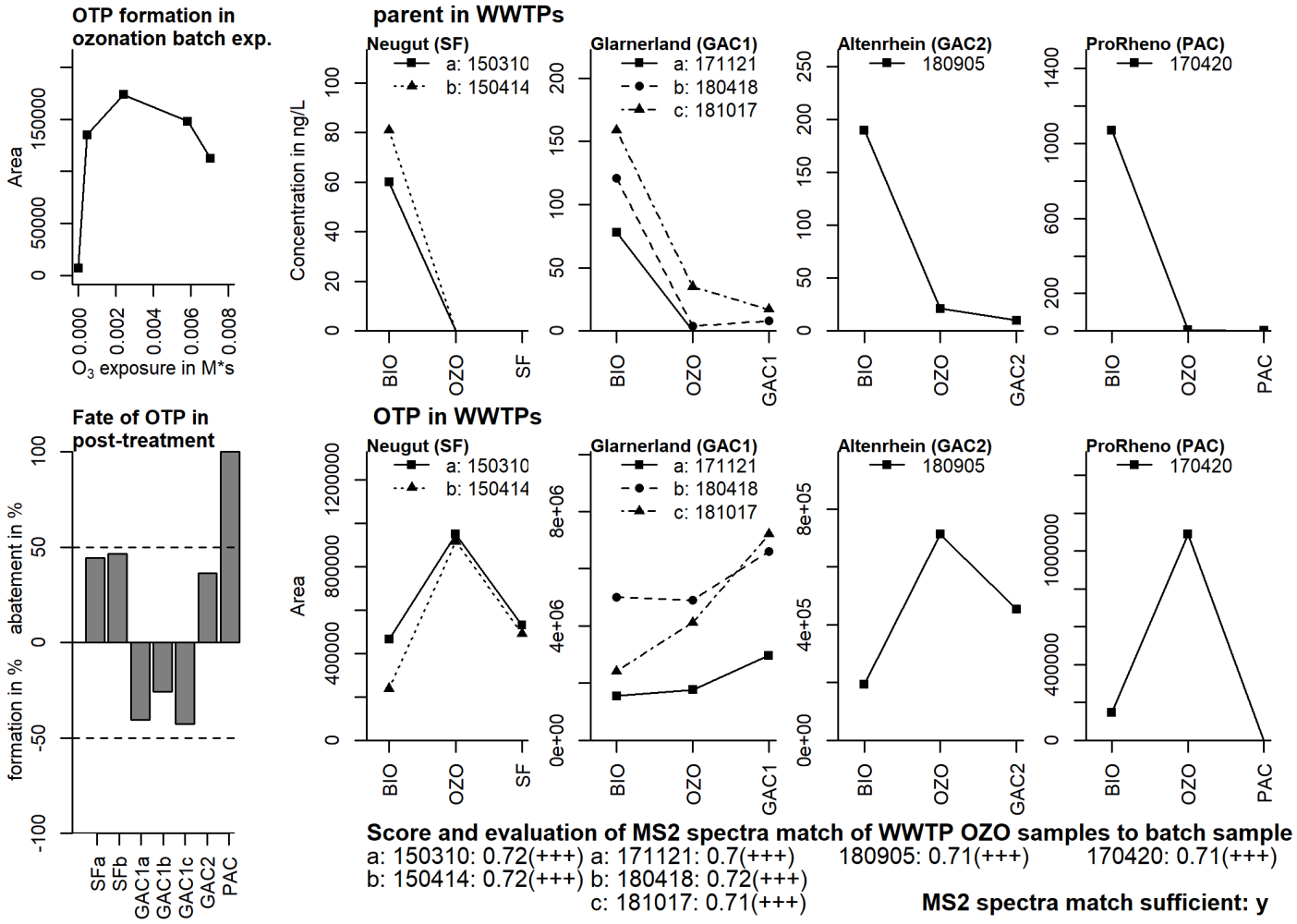
Confidence Level

Level 3

Massbank ID

ET405101

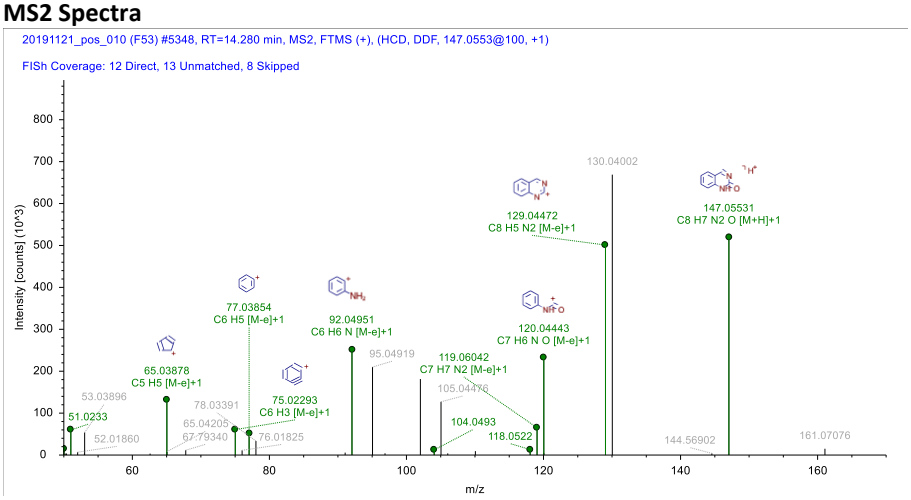
Name CBZ_p_147.0552_14.3



MS Spectra

Pos 147.0552 [m+H]+

MS2 Spectra



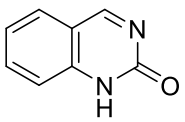
Formula

C8H6ON2

Atomic modification

-C7H4

Proposed Structure



Additional Evidence for Structure Interpretation

A fragment with the mass 147 and the elemental formula C8H6ON2 was observed in the MS^2 spectrum of CBZ_p_251.0812_17.9, which was identified as BQM. This indicates that this OTP structure is a substructure of BQM. This fits a cleavage of the benzaldehyde moiety, which was suggested by Azaïs et al. (2017) as a degradation product of BQM.

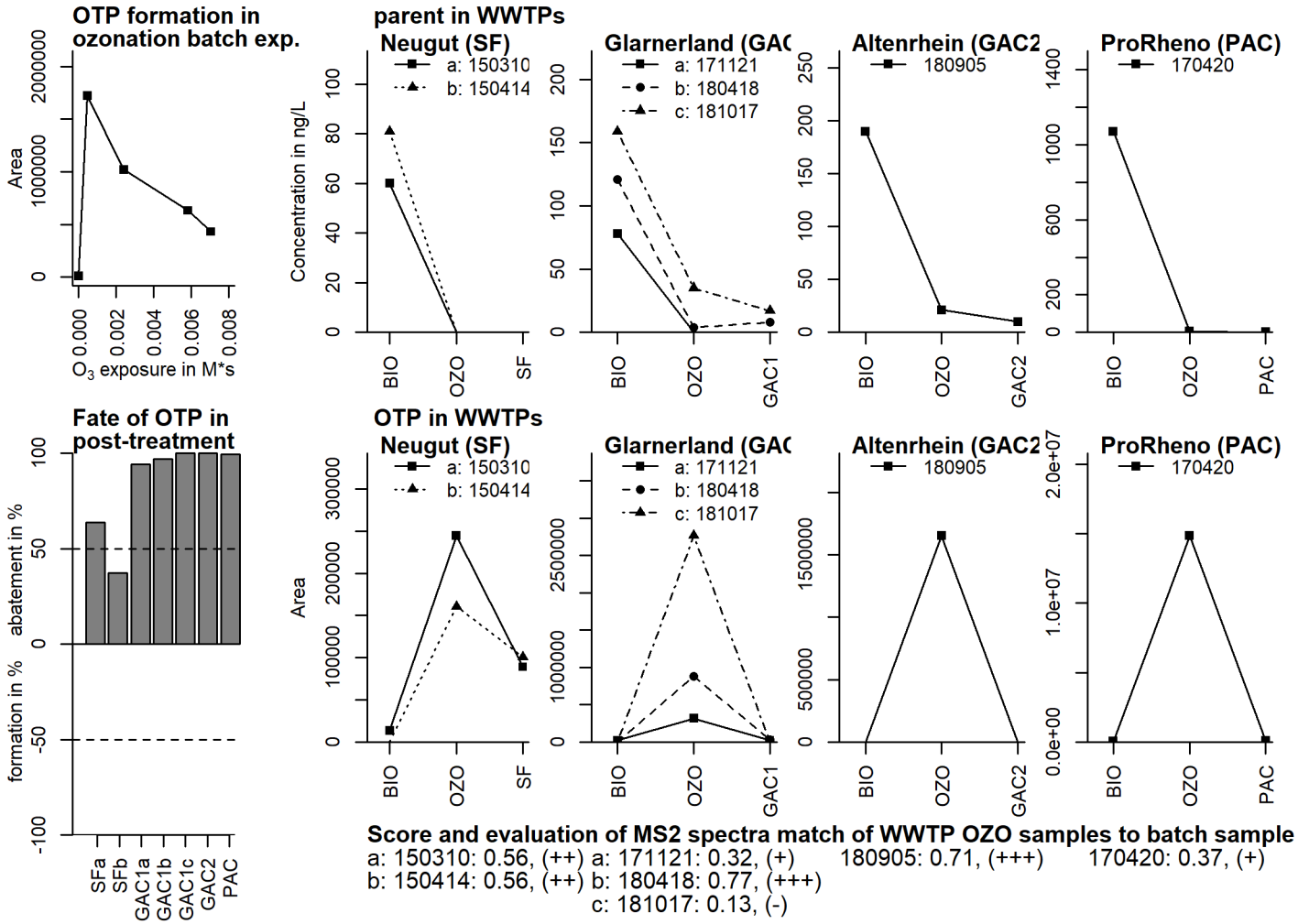
Confidence Level

Level 3

Massbank ID

ET400801

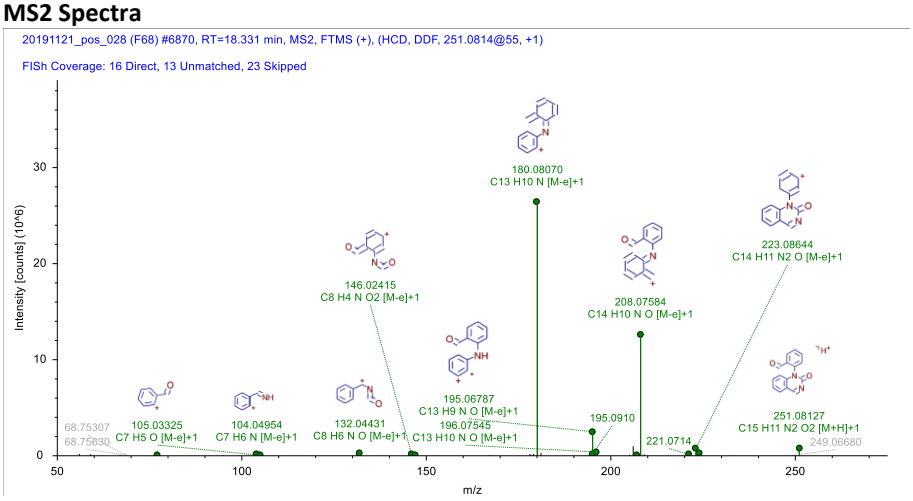
Name CBZ_p_251.0812_17.9



MS Spectra

Pos 251.0812 [m+H]+

MS2 Spectra



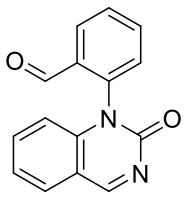
Formula

C15H10O2N2

Atomic modification

-H2 +O

Proposed Structure



Additional Evidence for Structure Interpretation

McDowell et al. (2005) identified 1-(2-benzaldehyde)-4-hydro-(1H,3H)-quinazoline-2-one (BQM) as an OTP for carbamazepine. The observed evidence from our MS and MS^2 spectrum match the one from McDowell et al. (2005). This OTP was later identified in two further studies (Hübner et al. 2014, Azais et al. 2017).

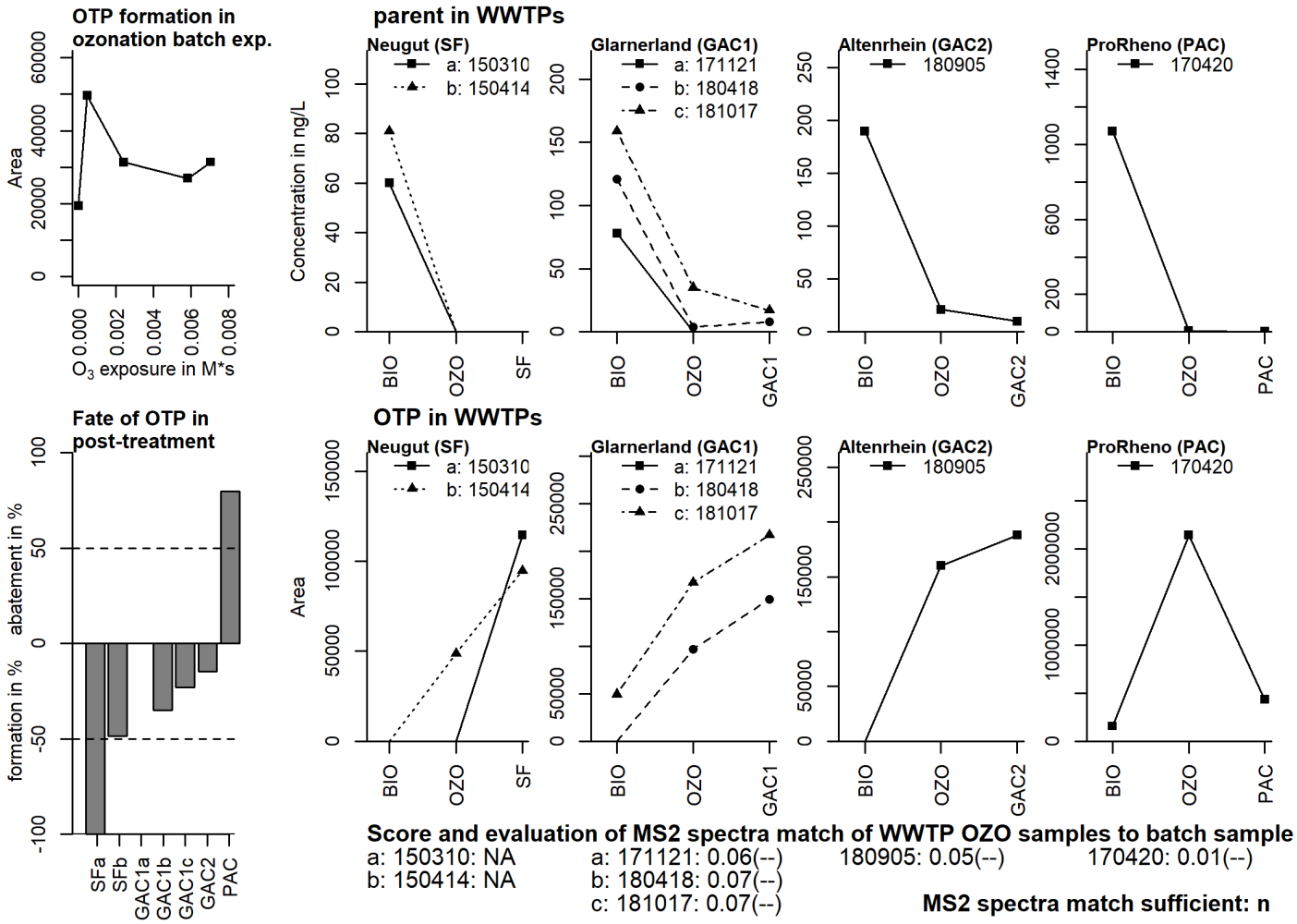
Confidence Level

Level 2a

Massbank ID

ET400901

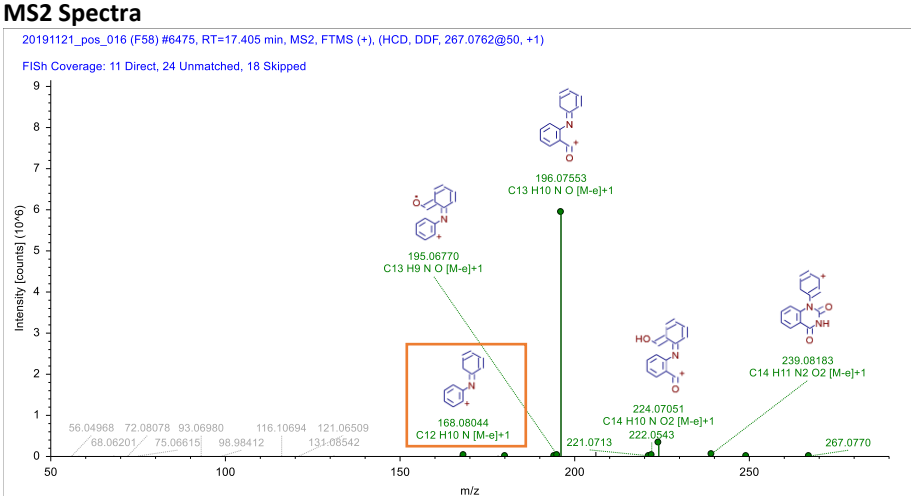
Name CBZ_p_267.0762_17.7



MS Spectra

Pos	267.0762	[m+H]+
Neg	265.0617	[m-H]-

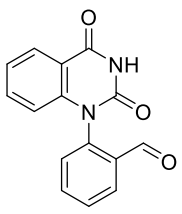
MS2 Spectra



Formula
C15H10O3N2

Atomic modification
-H2 +O2

Proposed Structure



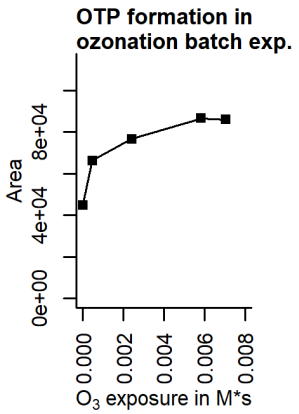
Confidence Level
Level 2a

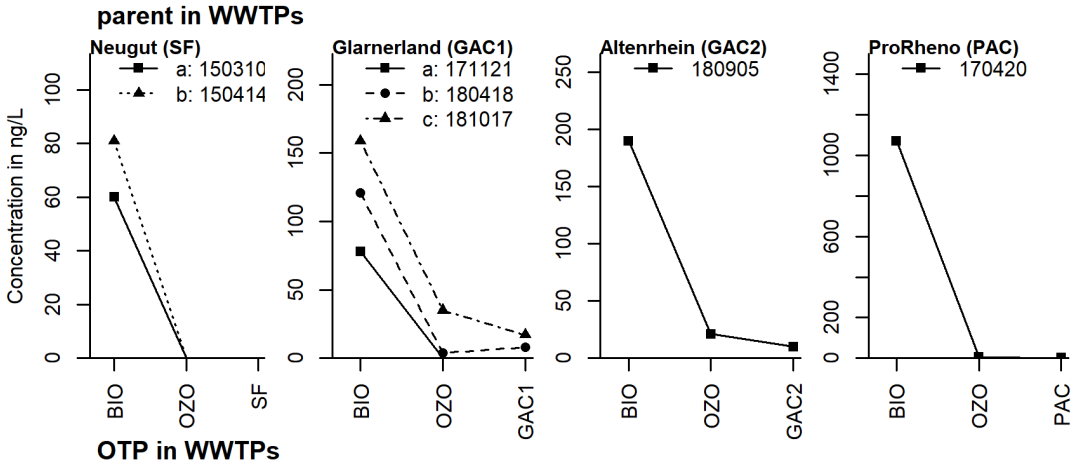
Massbank ID
ET401001

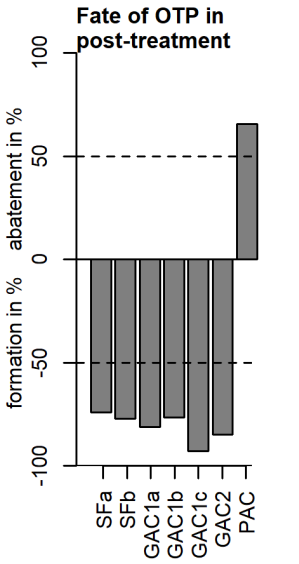
Additional Evidence for Structure Interpretation

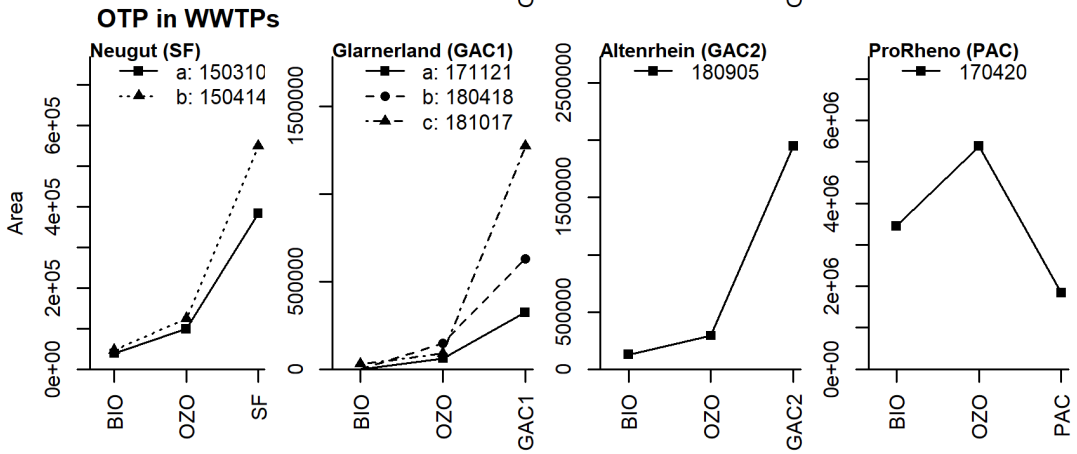
The MS^2 fragment at the nominal mass 168 was also observed for the parent compound. It indicates that the structure drawn for fragment 168 is a substructure of this TP. McDowell et al. (2005) identified 1-(2-benzaldehyde)-(1H,3H)-quinazoline-2,4-dione (BQD) as an OTP for carbamazepine. The evidence from our MS and MS^2 spectrum match the one from McDowell et al. (2005). This OTP was later identified in two further studies (Hübner et al. 2014, Azais et al. 2017).

Name CBZ_p_283.0711_17.3









Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

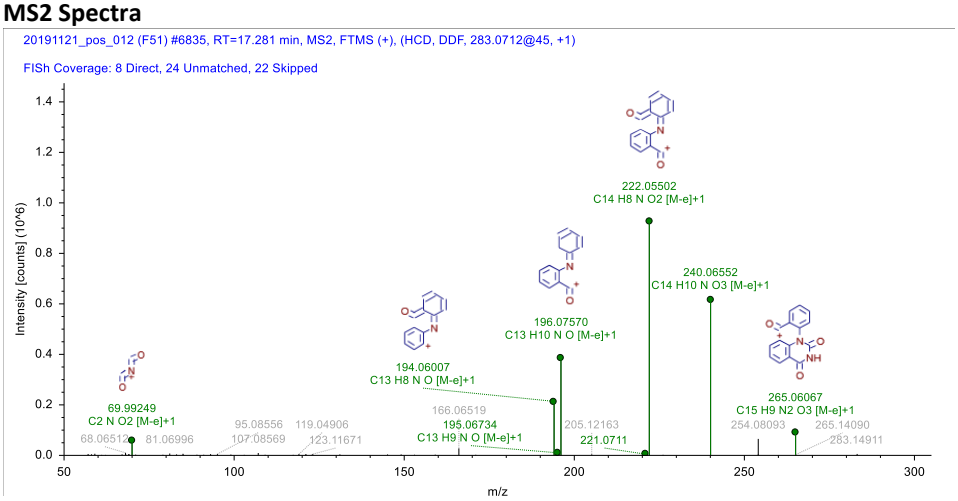
a: 150310: 0.78(+++) a: 171121: 0.86(+++) 180905: 0.84(+++) 170420: 1(+++)
b: 150414: 0.78(+++) b: 180418: 0.64(+++)
c: 181017: 0.65(+++)

MS2 spectra match sufficient: y

MS Spectra

Pos	283.0711	[m+H]+
Neg	281.0565	[m-H]-

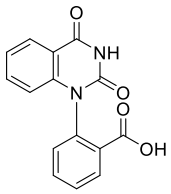
MS2 Spectra



Formula
C15H10O4N2

Atomic modification
-H2 +O3

Proposed Structure



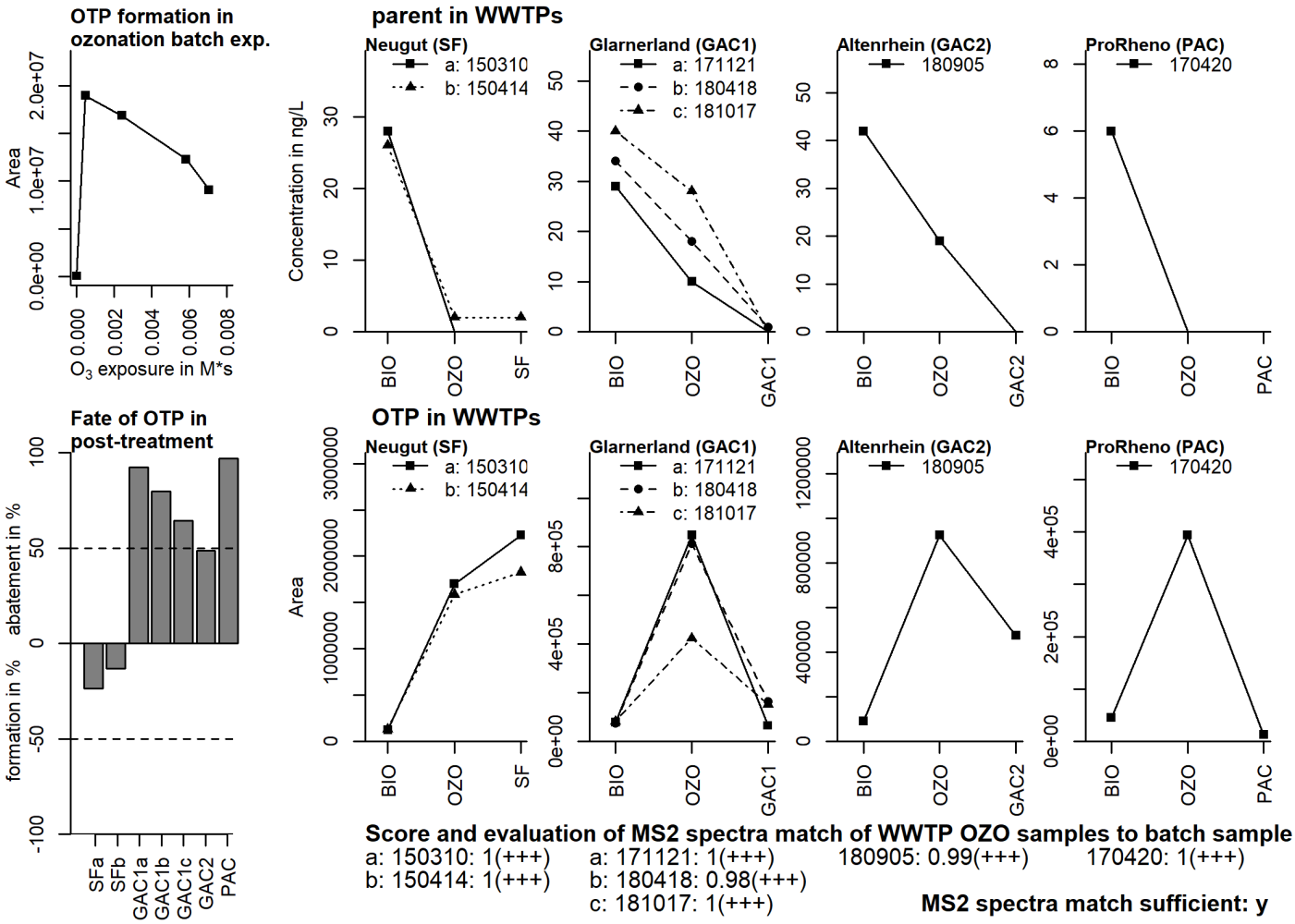
Additional Evidence for Structure Interpretation

1-(2-benzoic acid)-(1H,3H)-quinazoline-2,4-dione (BaQD) was identified by McDowell et al. (2005) as an oxidation product of carbamazepine after ozonation. The observed evidence from our MS and MS^2 spectrum match the one from by McDowell et al. (2005).

Confidence Level
Level 2a

Massbank ID
ET401101

Name CIT_p_341.1661_16.2



Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

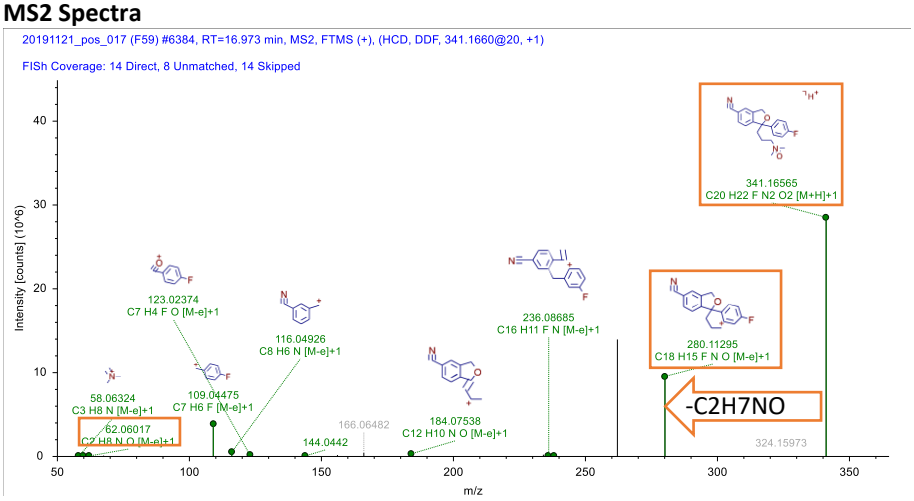
a: 150310: 1(+++) a: 171121: 1(+++) 180905: 0.99(+++) 170420: 1(+++)
b: 150414: 1(+++) b: 180418: 0.98(+++)
c: 181017: 1(+++)

MS2 spectra match sufficient: y

MS Spectra

Pos 341.1661 [m+H]+

MS2 Spectra



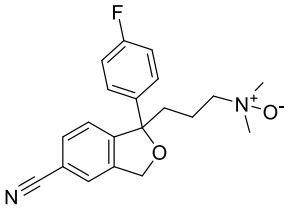
Formula

C20H21O2N2F

Atomic modification

+O

Proposed Structure



Confidence Level

Level 1

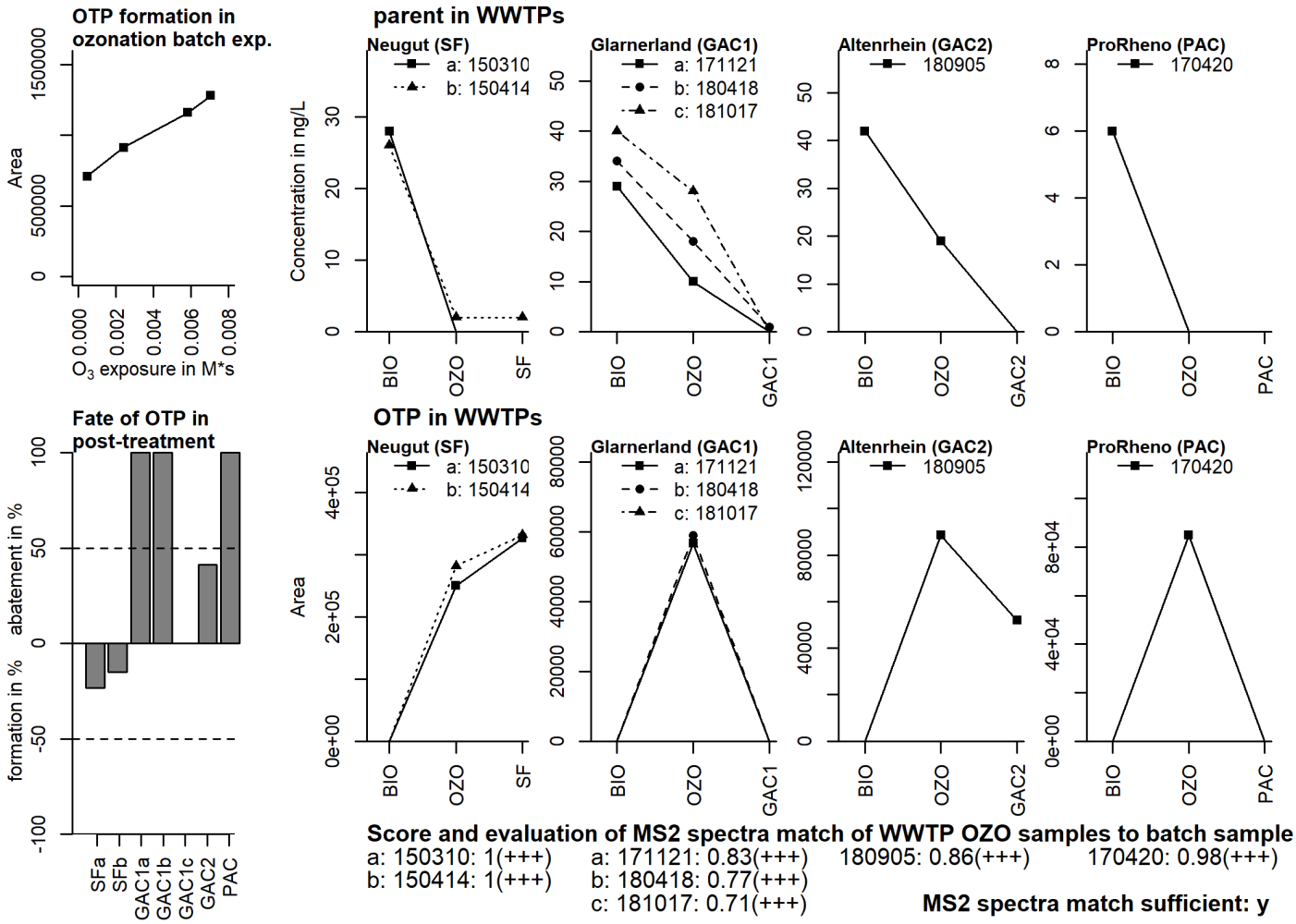
Massbank ID

ET401201

Additional Evidence for Structure Interpretation

The MS^2 fragments at the nominal masses 280, 236, 184, 144, 123, 116, 109 and 58 were also observed for the parent compound. This indicates that the structure drawn for the fragment 280 is a substructure of this OTP. The atomic modification from the parent compound to this OTP is +O. This would fit to an N-oxidation or a hydroxylation. Tertiary amines are very reactive to form *N*-oxides during ozonation (von Sonntag & von Gunten 2012). Therefore, the formation of a *N*-oxide at the dimethylpropylamine is very likely. Hörsing et al. (2012) identified Citalopram *N*-oxide as major OTP. The neutral loss of C2H7NO between the precursor and fragment 280 as well as the fragment 62 indicate that the modification of +O took place at the dimethylamine moiety.

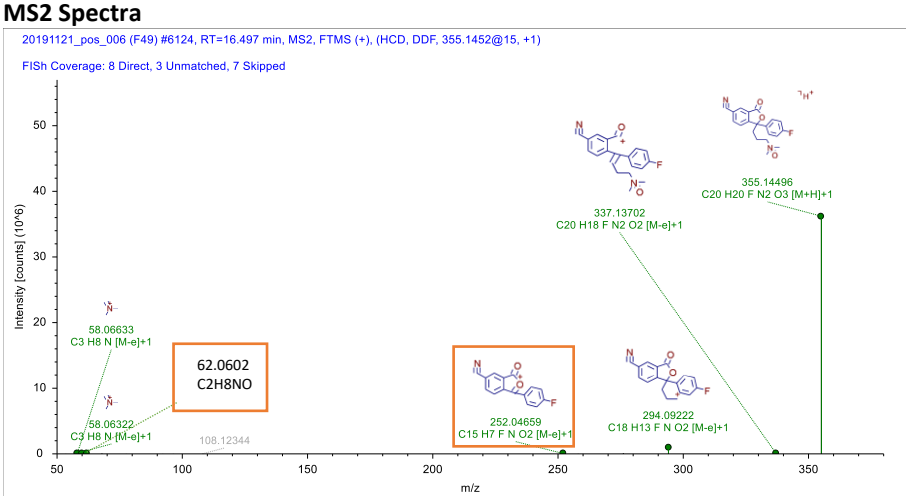
Name CIT_p_355.1451_15.9



MS Spectra

Pos	355.1451	[m+H]+
Neg	399.1359	[m+FA-H]-

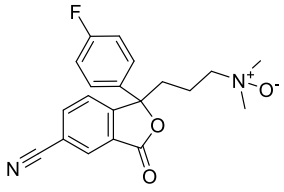
MS2 Spectra



Formula
C20H19O3N2F

Atomic modification
-H2 +O2

Proposed Structure



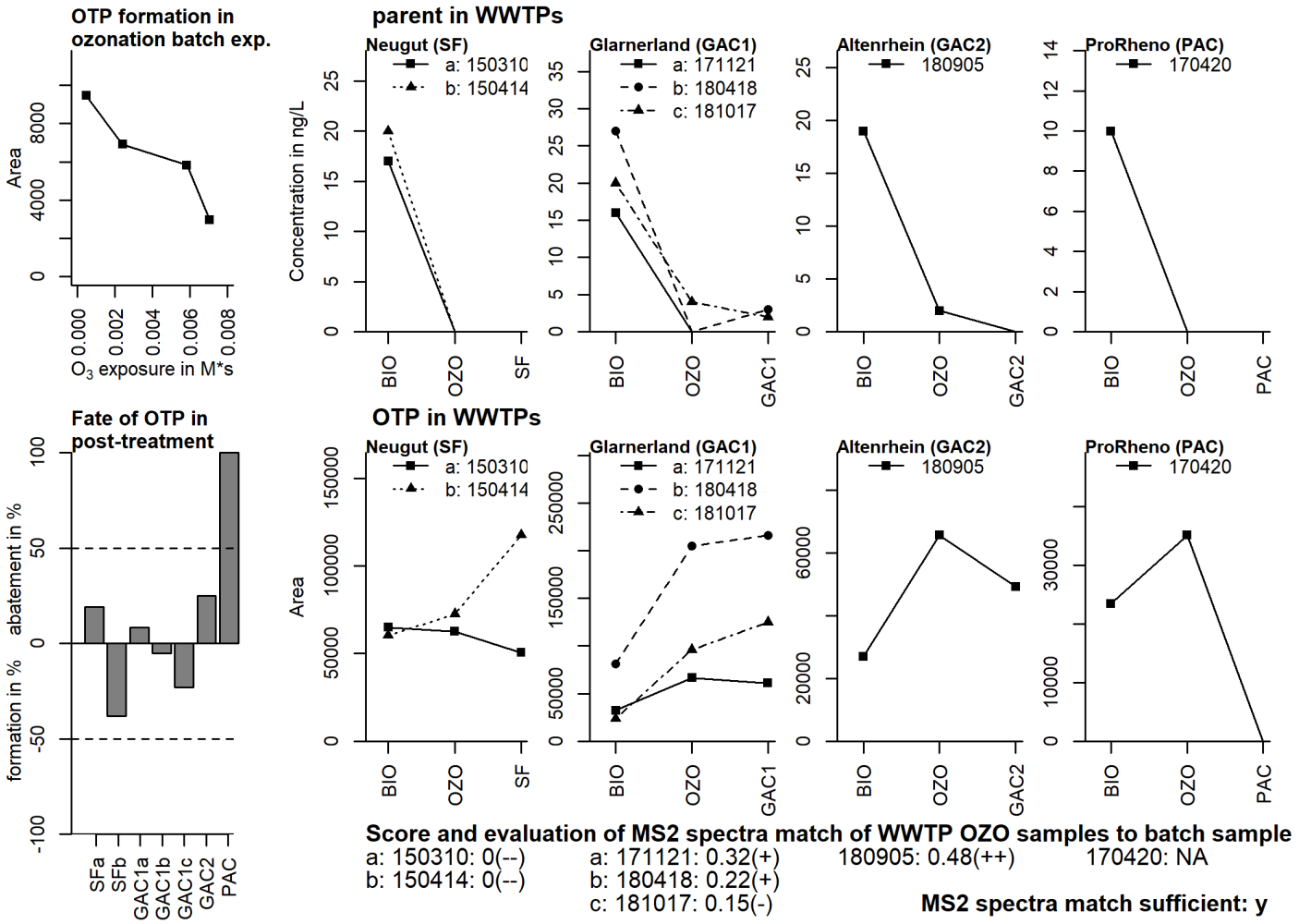
Confidence Level
Level 3

Massbank ID
ET401301

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this TP is –H2 +O2. A fragment at the exact mass of 62.0602 corresponding to an elemental formula of C2H8NO was observed in this MS^2 spectrum as well as in the MS^2 spectrum of CIT_p_341.1661_16.2, which was identified as citalopram *N*-oxide. This indicates that an *N*-oxide moiety is also likely for this TP. Fragment 252 with a formula of C15H7NO2 indicates that a second oxygen atom was added at the citalopram carbon backbone without the propyldimethylamine moiety. The modification of –H2 +O fits to the formation of a carbonyl group. Hörsing et al. (2012) suggested that the methylene group of the benzofuran moiety is a likely location for the formation of a carbonyl group. However, this mechanism is not entirely understood.

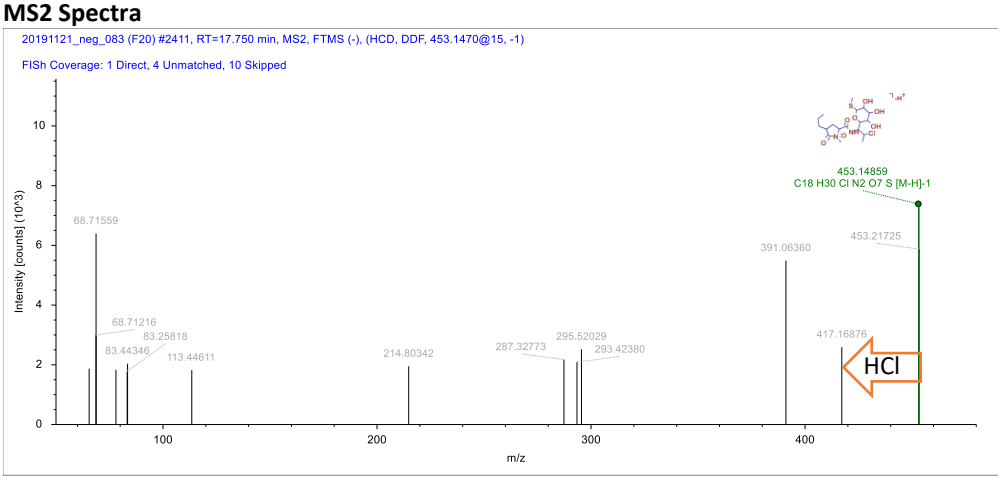
Name CLI_n_453.1466_17.7



MS Spectra

Neg 453.1466 [m-H]-

MS2 Spectra



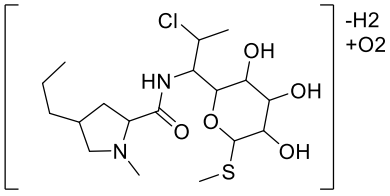
Formula

C18H31O7N2ClS

Atomic modification

-H2 +O2

Proposed Structure



Confidence Level

Level 3

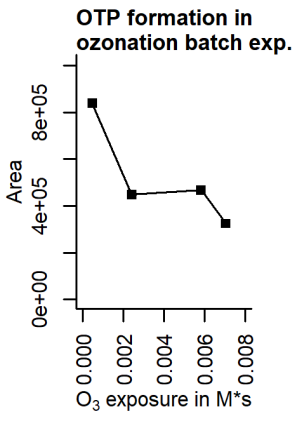
Massbank ID

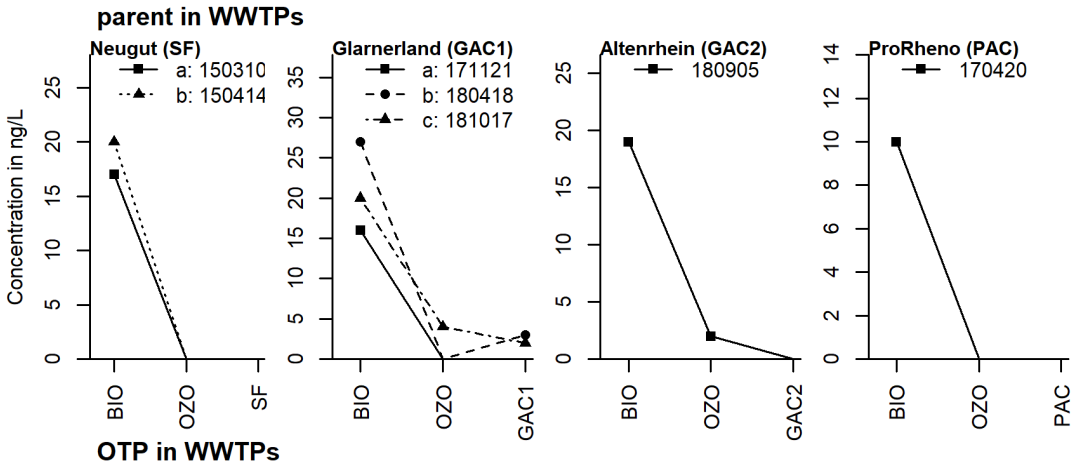
ET405201

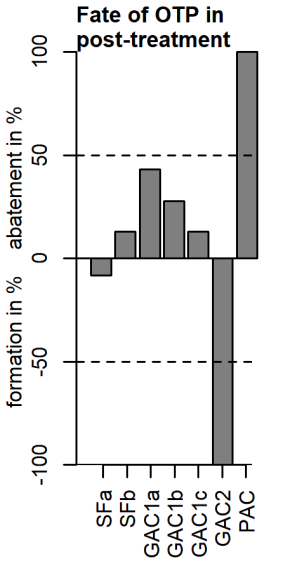
Additional Evidence for Structure Interpretation

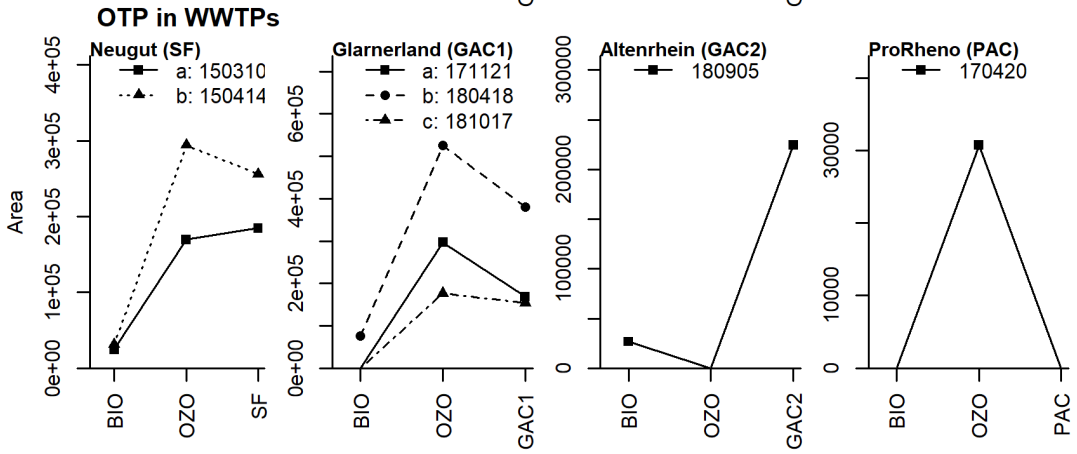
The atomic modification from the elemental formula of the parent compound to this TP is –H2 +O2. This modification fits to multiple known reactions with ozone such as the formation of an *N*-oxide (+O), a sulfoxide (+O) or the addition of a hydroxyl group after attack of a hydroxyl radical on a CH2 group (+O) (von Sonntag & von Gunten 2012). A possibility would be one of the mentioned reactions and the formation of a carbonyl moiety (-H2 +O) at a CH2 group of the mother substance. There is however no further evidence for the exact type and location of the modifications. The structures of the MS^2 fragments are drawn exemplarily.

Name CLI_p_457.1769_14.7









Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

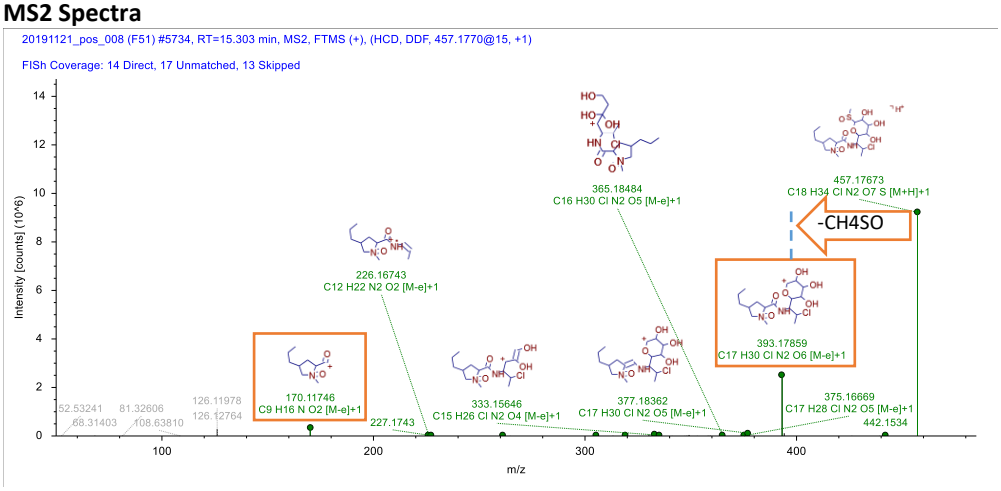
a: 150310: 1(+++) a: 171121: 1(+++) 180905: 0.96(+++) 170420: 0.64(+++)
b: 150414: 1(+++) b: 180418: 1(+++)
c: 181017: 0.91(+++)

MS2 spectra match sufficient: y

MS Spectra

Pos	457.1769	[m+H]+
Neg	455.1623	[m-H]-

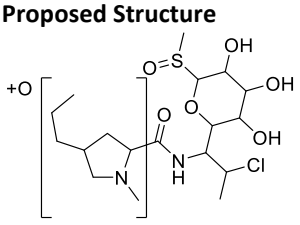
MS2 Spectra



Formula
C18H33O7N2ClS

Atomic modification
+O2

Proposed Structure



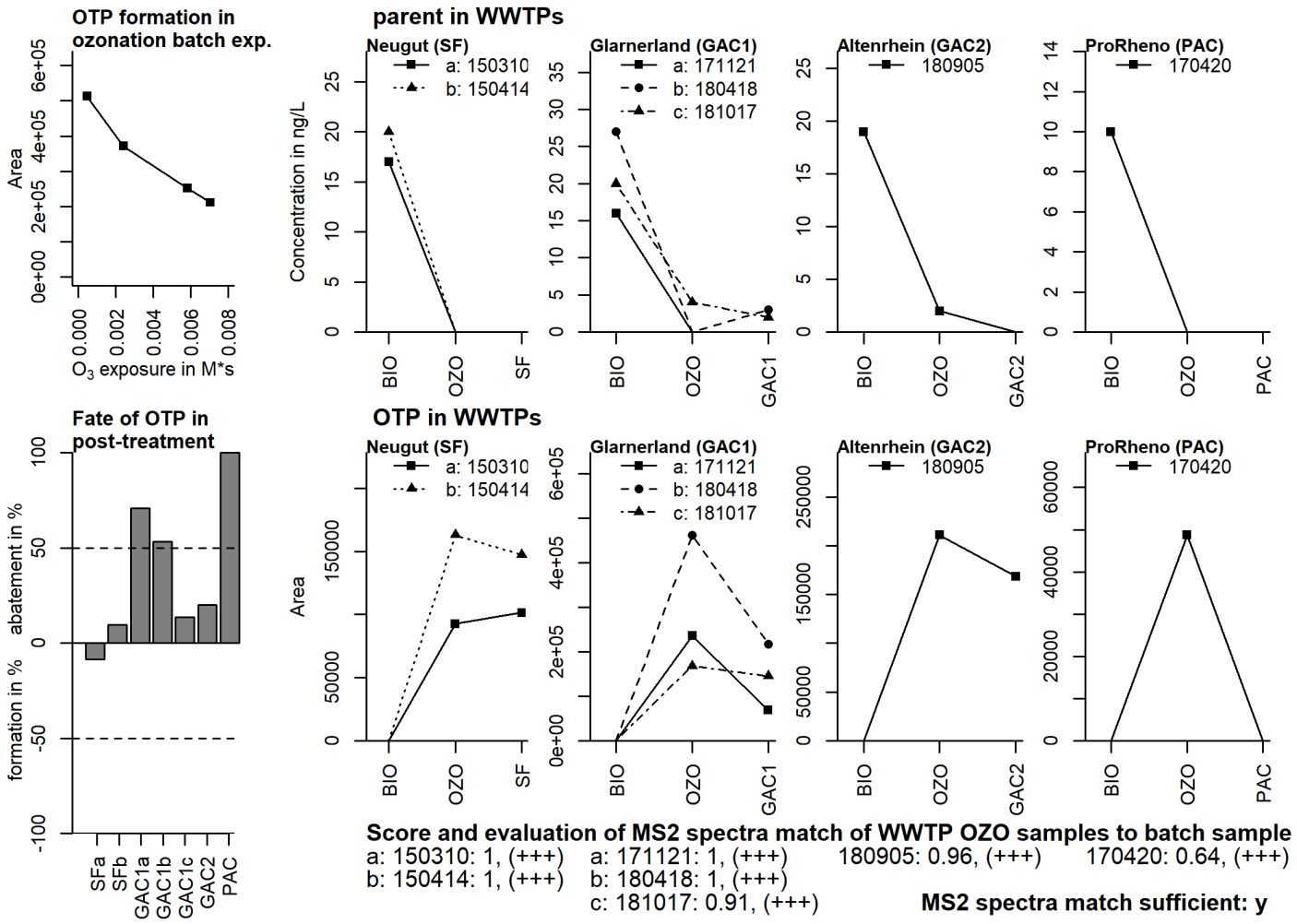
Confidence Level
Level 3

Massbank ID
ET401401

Additional Evidence for Structure Interpretation

For the parent compound clindamycin two OTPs (CLI_p_457.1769_14.7 and CLI_p_457.1769_15.1) with the exact mass of 457.1769 were observed at different retention times (14.7 and 15.1 min). The MS^2 spectra of these OTPs are very similar. The atomic modification from the elemental formula of the parent compound to theses OTPs is +O2. A modification of +O can be realized by the formation of sulfoxides from thioethers, by the formation of *N*-oxides from tertiary amines, or by hydroxylation. All three reactions are known to occur during ozonation (von Sonntag & von Gunten 2012).
The neutral loss of CH4SO between the precursor and fragment 393 fits to the cleavage of a methylsulfoxide moiety and indicates the formation of this substructure. Fragment 170 indicates that the second oxygen was added at the methylpropylpirolidine moiety. One OTP could for example have been formed by N-oxidation and the other by hydroxylation.

Name CLI_p_457.1769_15.1



Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

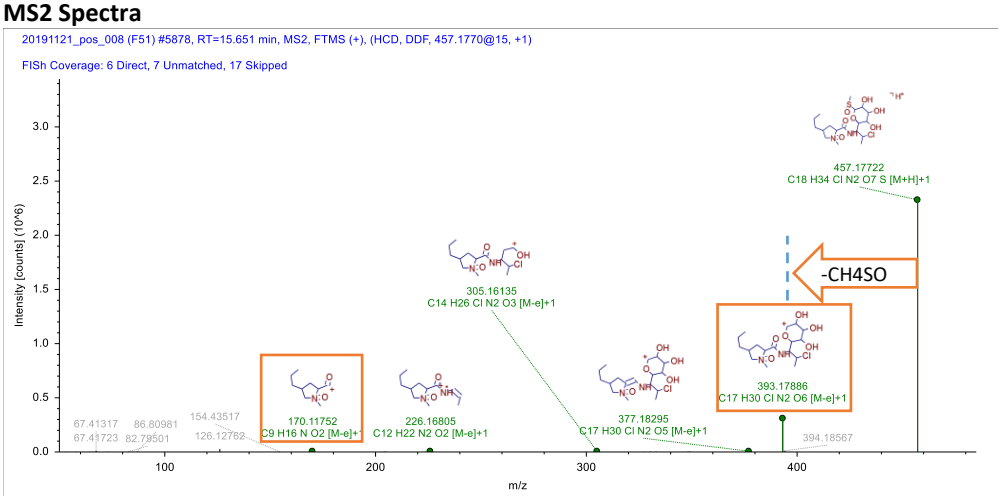
a: 150310: 1, (+++) a: 171121: 1, (+++) 180905: 0.96, (+++) 170420: 0.64, (+++)
b: 150414: 1, (+++) b: 180418: 1, (+++)
c: 181017: 0.91, (+++)

MS2 spectra match sufficient: y

MS Spectra

Pos	457.1769	[m+H]+
Neg	455.1623	[m-H]-

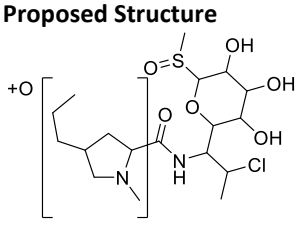
MS2 Spectra



Formula
C18H33O7N2ClS

Atomic modification
+O2

Proposed Structure



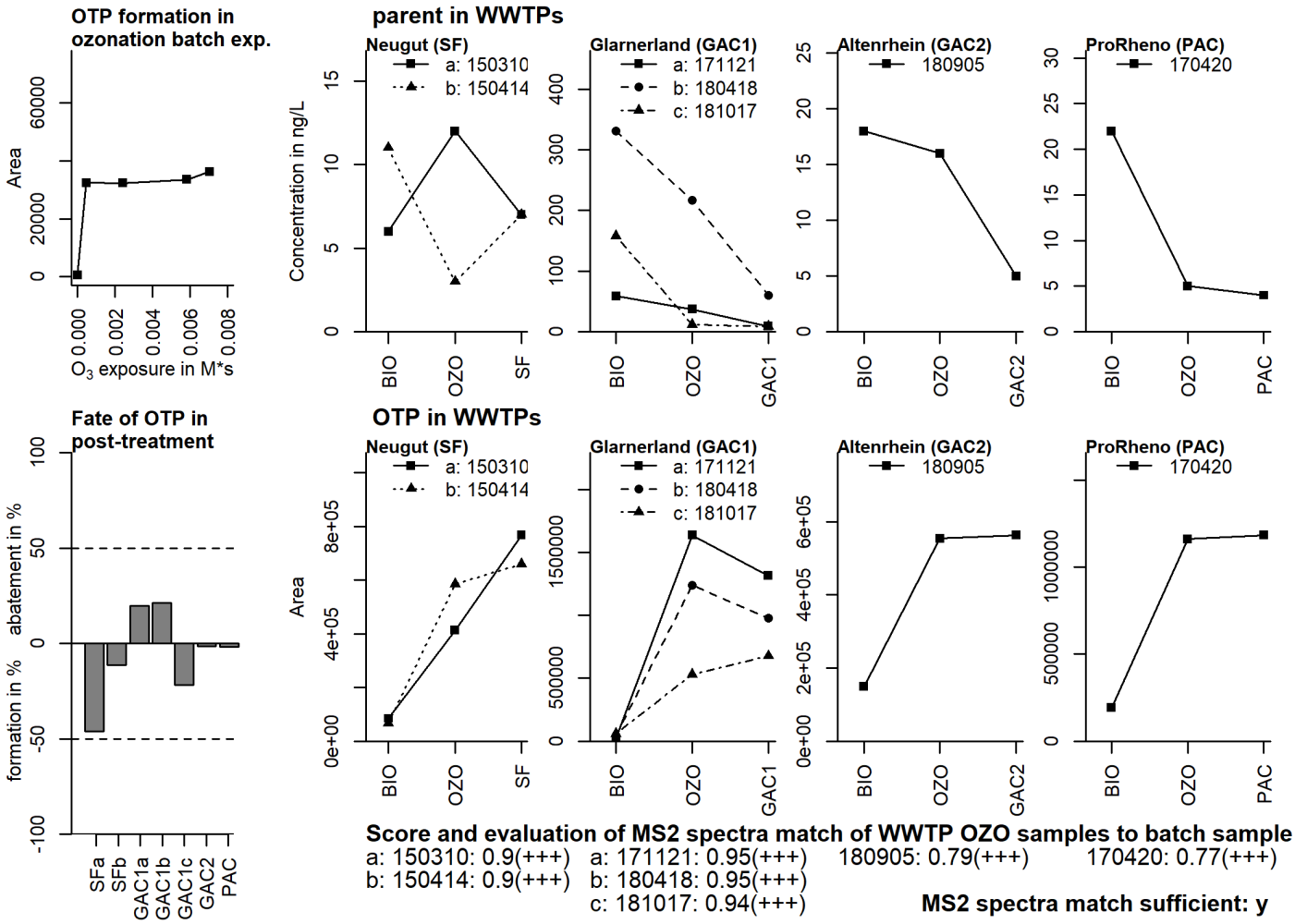
Confidence Level
Level 3

Massbank ID
ET401501

Additional Evidence for Structure Interpretation

For the parent compound clindamycin two OTPs (CLI_p_457.1769_14.7 and CLI_p_457.1769_15.1) with the exact mass of 457.1769 were observed at different retention times (14.7 and 15.1 min). The MS^2 spectra of these OTPs are very similar. The atomic modification from the elemental formula of the parent compound to theses OTPs is +O2. A modification of +O can be realized by the formation of sulfoxides from thioethers, by the formation of *N*-oxides from tertiary amines, or by hydroxylation. All three reactions are known to occur during ozonation (von Sonntag & von Gunten 2012).
The neutral loss of CH4SO between the precursor and fragment 393 fits to the cleavage of a methylsulfoxide moiety and indicates the formation of this substructure. Fragment 170 indicates that the second oxygen was added at the methylpropylpirolidine moiety. One OTP could for example have been formed by N-oxidation and the other by hydroxylation.

Name COF_n_225.0627_12.2



Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

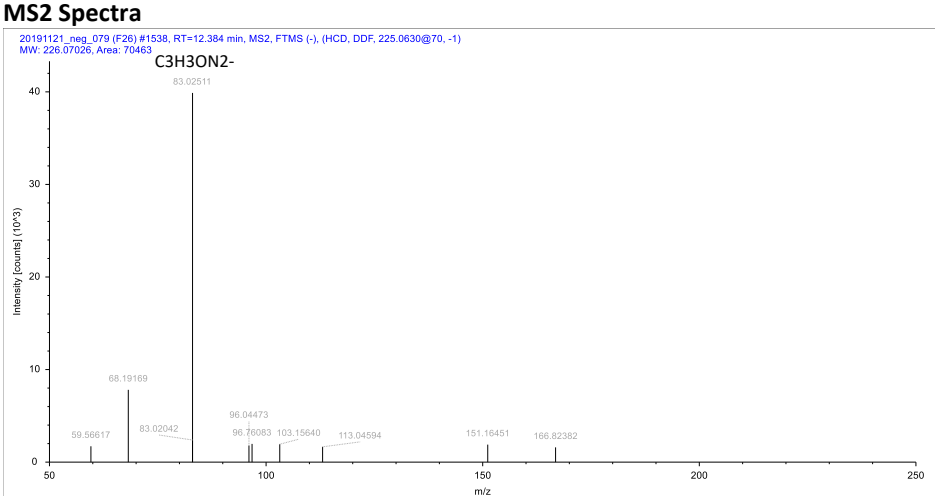
a: 150310: 0.9(+++) a: 171121: 0.95(+++) 180905: 0.79(+++) 170420: 0.77(+++)
b: 150414: 0.9(+++) b: 180418: 0.95(+++)
c: 181017: 0.94(+++)

MS2 spectra match sufficient: y

MS Spectra

Neg 225.0627 [m-H]-

MS2 Spectra



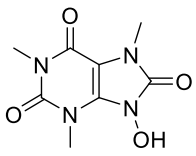
Formula

C8H10O4N4

Atomic modification

+O2

Proposed Structure



Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this TP is +O2. This modification fits to multiple reactions with ozone and/or hydroxyl radicals. Rosal et al. (2009) detected an OTP of caffeine with this mass and suggested the formation of a carbonyl group at the C-2 and the addition of an hydroxyl group at the N-2 of the methylimidazole moiety. There is however no further evidence for the exact type and location of the modifications.

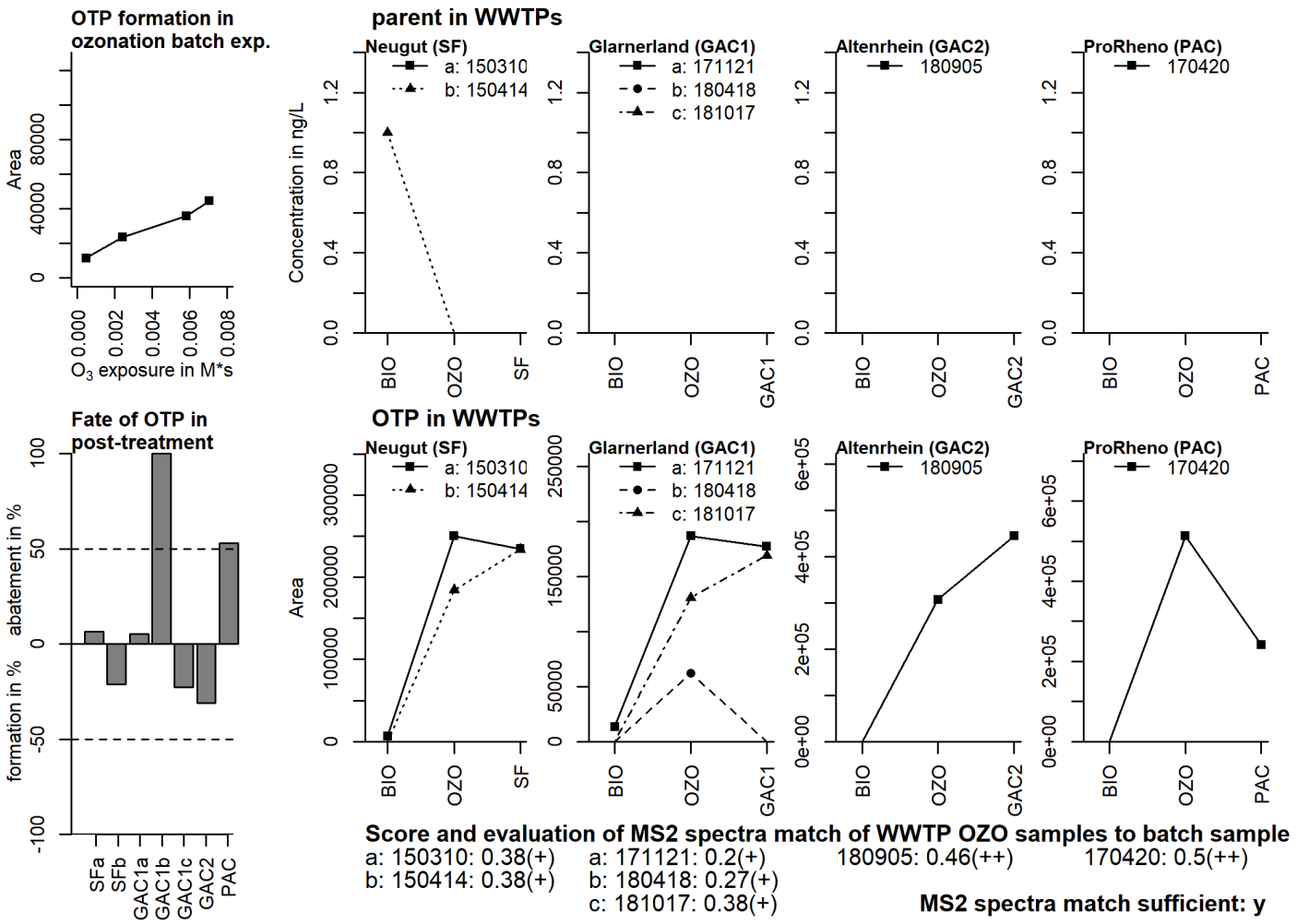
Confidence Level

Level 3

Massbank ID

ET405301

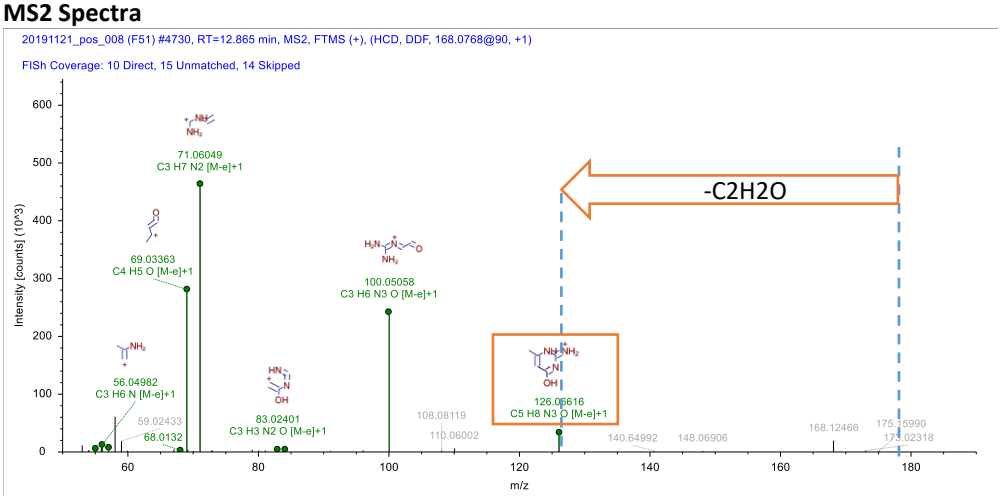
Name CYP_p_168.0767_12.4



MS Spectra

Pos 168.0766 [m+H]+

MS2 Spectra



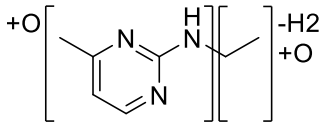
Formula

C7H9O2N3

Atomic modification

-C7H6+O2

Proposed Structure



Confidence Level

Level 3

Massbank ID

ET401601

Additional Evidence for Structure Interpretation

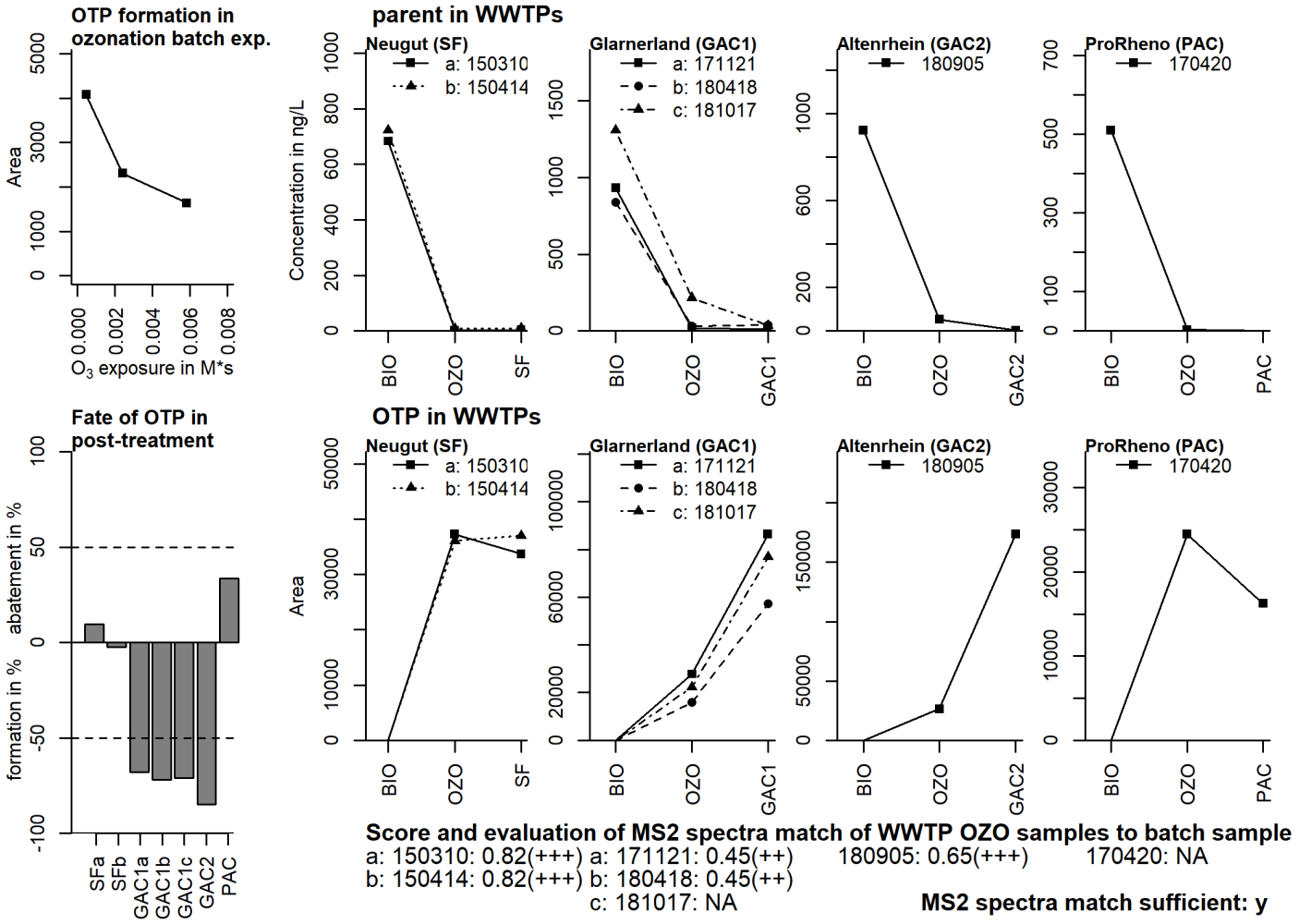
The atomic modification from the elemental formula of the parent compound to this OTP is -C7H6+O2. This fits to a cleavage within the phenyl moiety and the cleavage of the cyclopropyl moiety.

The neutral loss of C2H2O between the precursor and fragment 126 indicates that an oxygen atom was added at a C2H2 moiety. This fits to a Criegee addition, which is known to occur within phenyl moieties (von Sonntag & von Gunten 2012), followed by a C-C bond cleavage.

Fragment 126 indicates that the second oxygen atom was added at the methylpyrimidin-amine like moiety of the TP.

The exact type and position of the modifications remain unknown. The structures of the MS^2 fragments are drawn exemplarily.

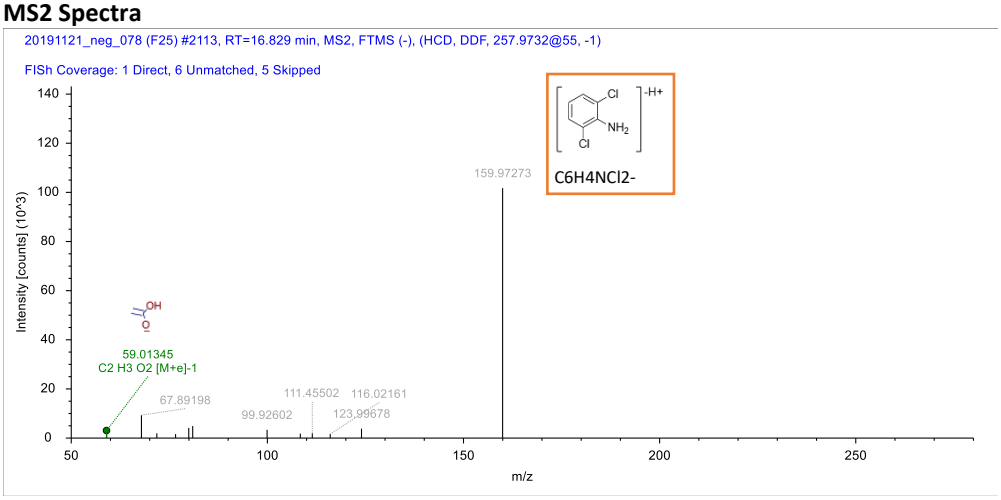
Name DIC_n_257.9729_16.7



MS Spectra

Neg 257.9729 [m-H]-

MS2 Spectra



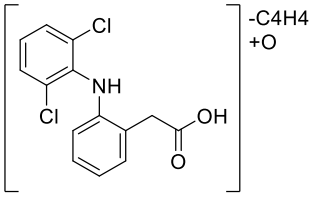
Formula

C10H7O3NCl2

Atomic modification

-C4H4+O

Proposed Structure



Additional Evidence for Structure Interpretation

Fragment 159 corresponds to the dichloroaniline moiety and indicates the modification did not take place at this part of the molecule.

There is no further indication for the exact type and location of the modification(s).

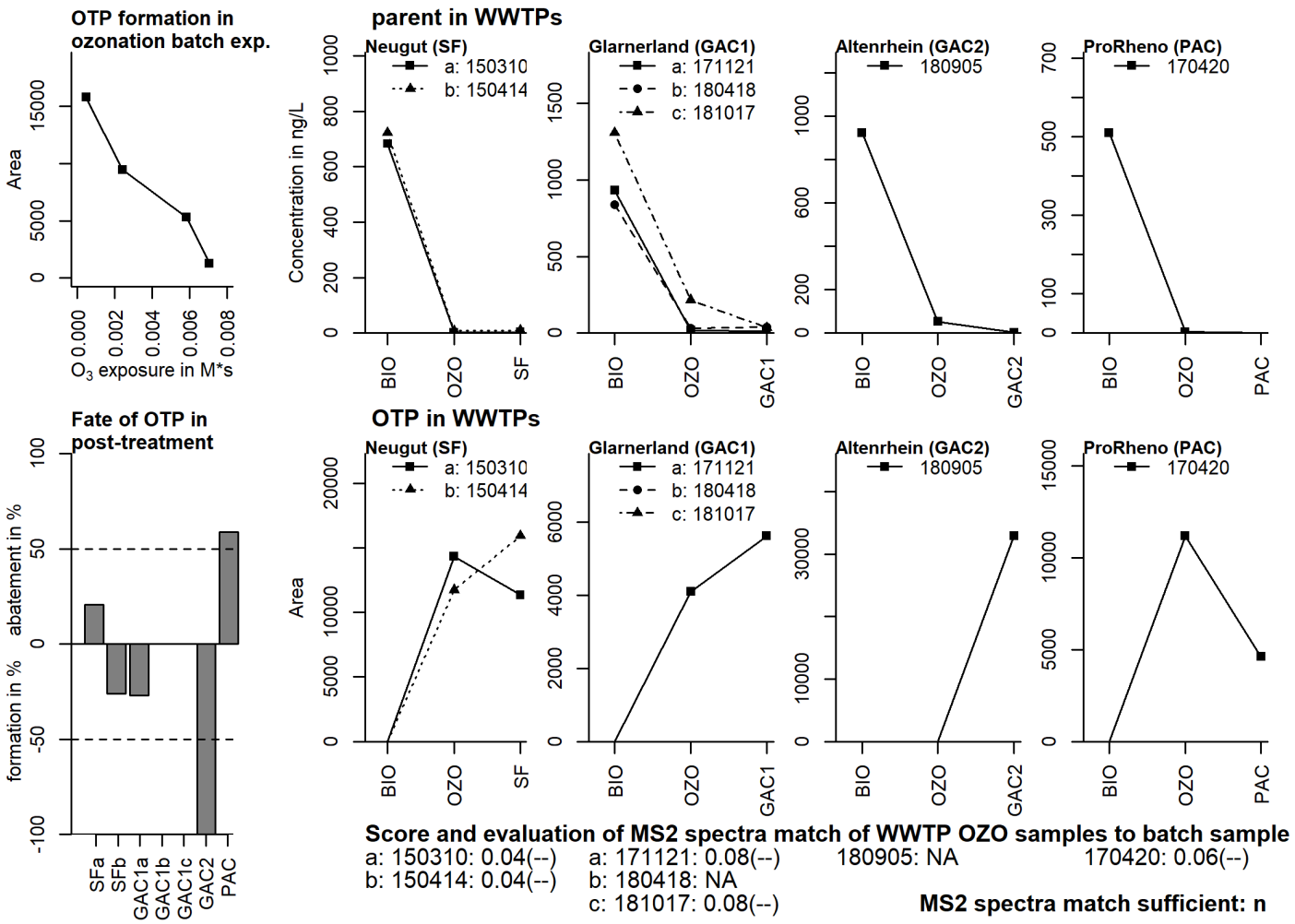
Confidence Level

Level 3

Massbank ID

ET405401

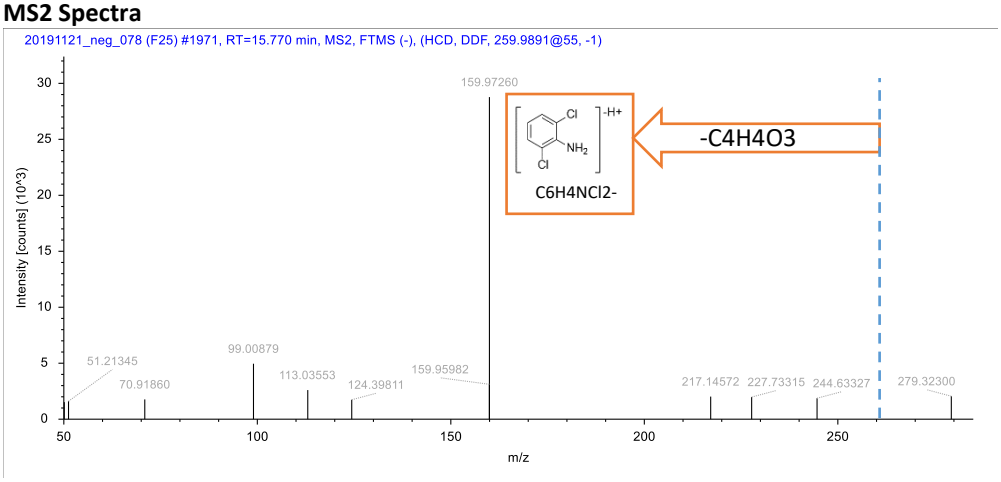
Name DIC_n_259.9873_15.6



MS Spectra

Neg 259.9873 [m-H]-

MS2 Spectra



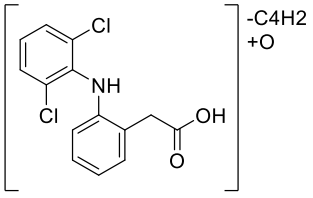
Formula

C10H9O3NCl2

Atomic modification

-C4H2+O

Proposed Structure



Confidence Level

Level 3

Massbank ID

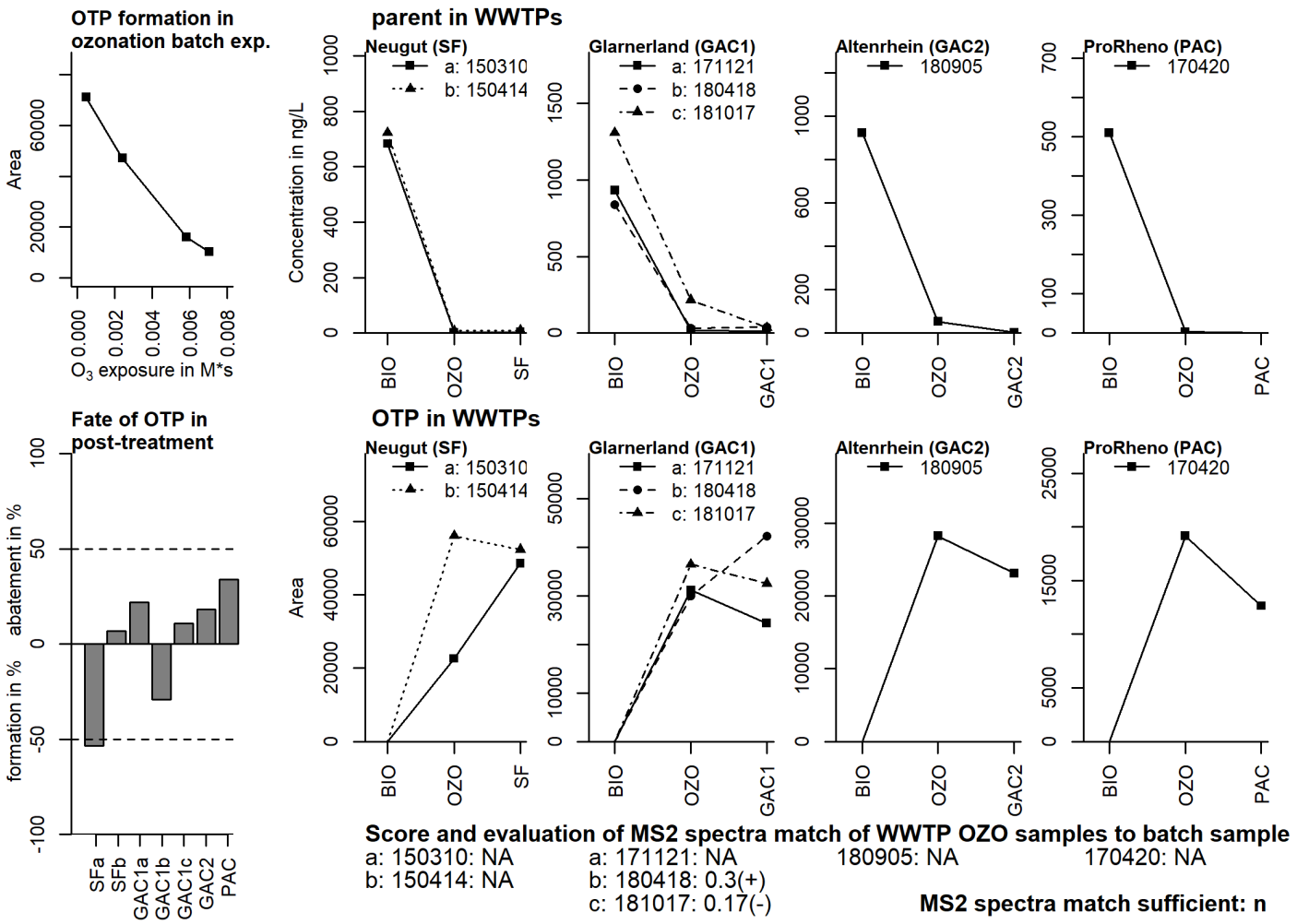
ET405501

Additional Evidence for Structure Interpretation

Fragment 159 corresponds to the dichloroaniline moiety and indicates that the modification did not take place at this part of the molecule.

The neutral loss of C4H4O3 between the precursor and fragment 159 fits to the fragment 99 and also indicates, that the atomic modification did not take place at the dichloroaniline moiety. It is likely that the modification occurred by a phenyl ring opening reaction, which is known to happen during ozonation (von Sonntag & von Gunten 2012). Coelho et al. (2009) detected an OTP of diclofenac with the exact same mass as we did, but did not provide any structural suggestion. The detection of this OTP in the negative mode MS spectrum indicates the presence of a carboxylic acid moiety.

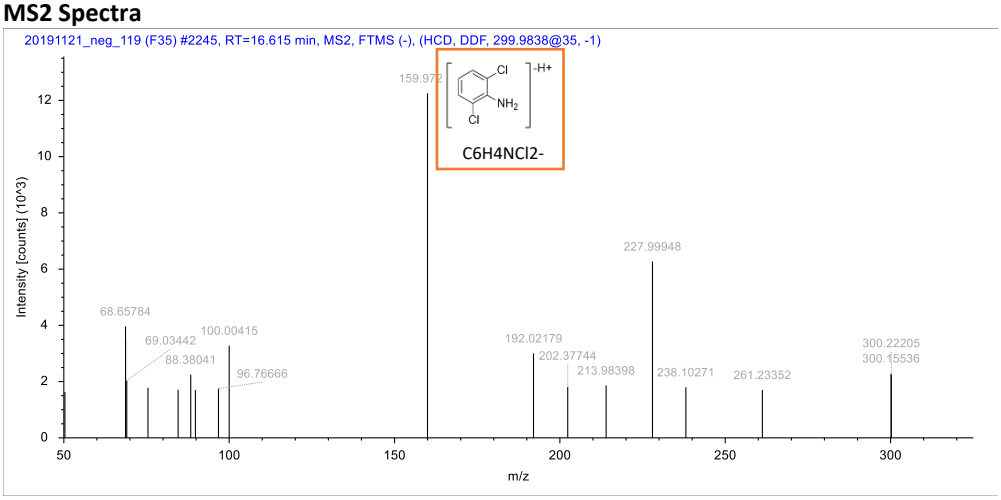
Name DIC_n_299.9834_16.4



MS Spectra

Neg 299.9834 [m-H]-

MS2 Spectra



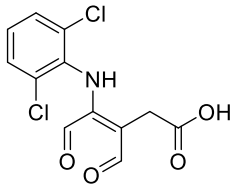
Formula

C12H9O4NCl2

Atomic modification

-C2H2 +O2

Proposed Structure



Confidence Level

Level 3

Massbank ID

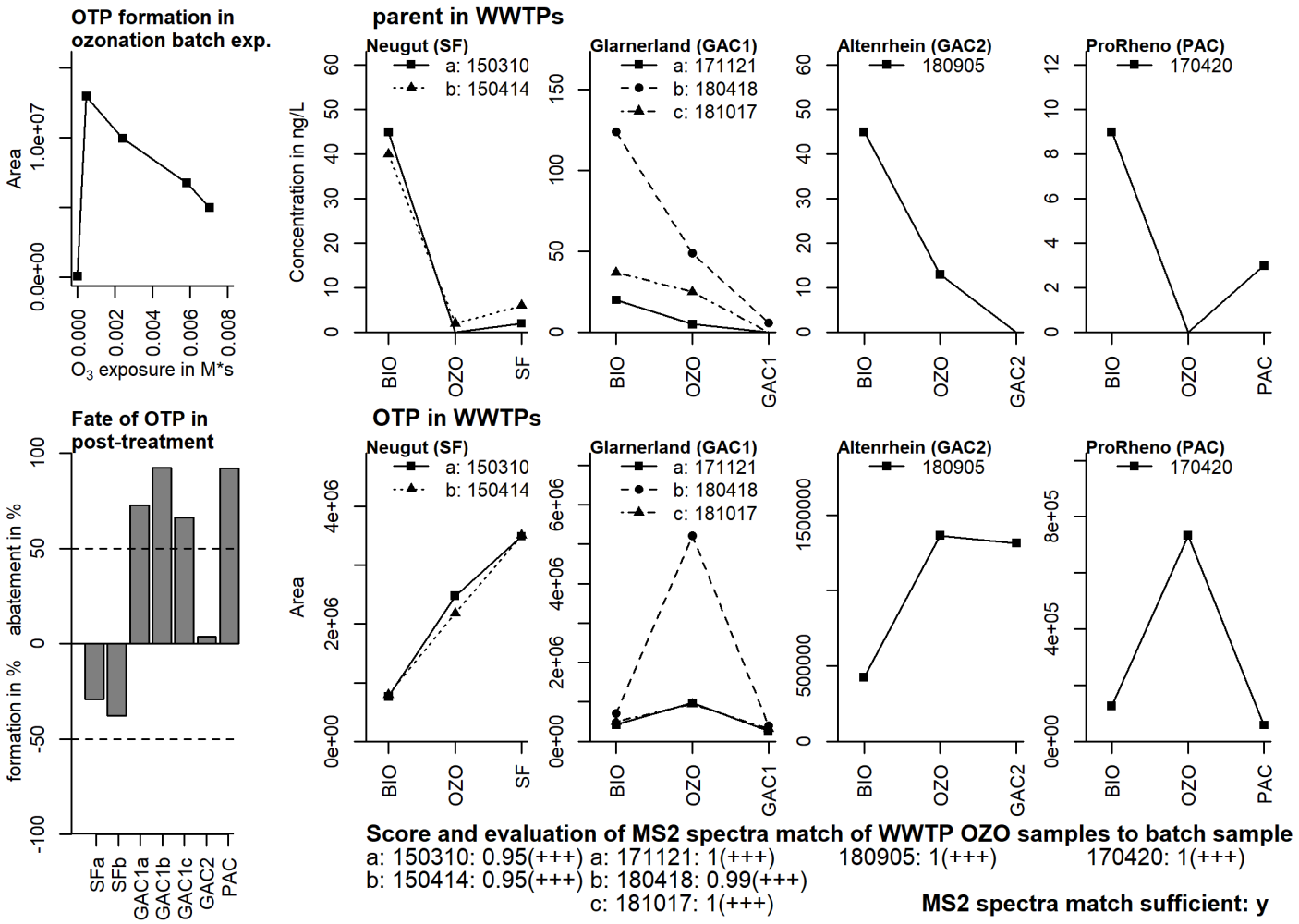
ET405601

Additional Evidence for Structure Interpretation

Fragment 159 corresponds to the dichloroaniline moiety and indicates the modification didn't take place at this part of the molecule.

The atomic modification fits to a cleavage within the other aromatic moiety and the addition of 2 oxygen atoms. Ozone is known to react with phenyl moieties to form malealdehyde type moieties (Tay et al. 2013, Müller et al. 2012). Therefore, the formation of this TP is likely. There is however no further evidence.

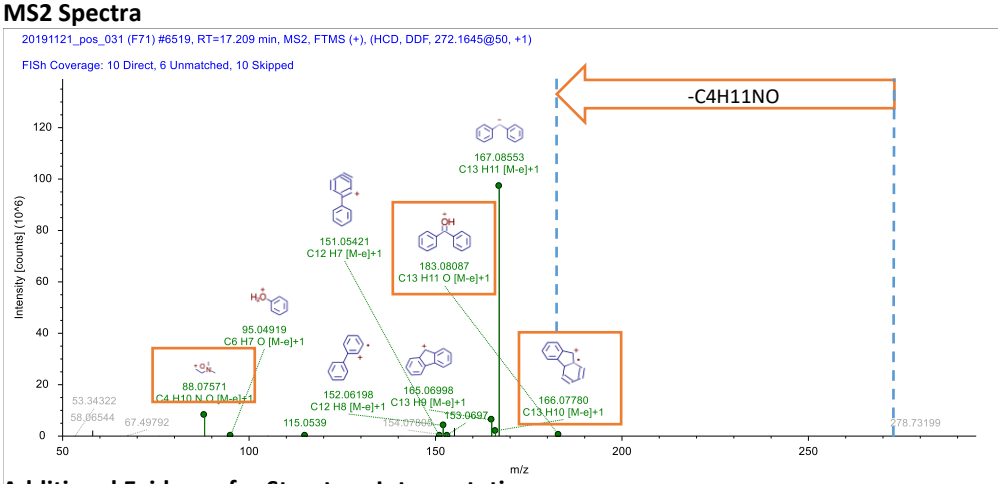
Name DIP_p_272.1644_16.5



MS Spectra

Pos 272.1664 [m+H]+

MS2 Spectra



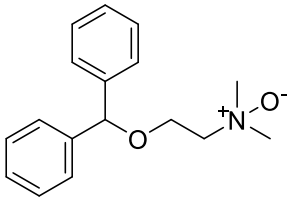
Formula

C17H21O2N

Atomic modification

+O

Proposed Structure



Confidence Level

Level 2a

Massbank ID

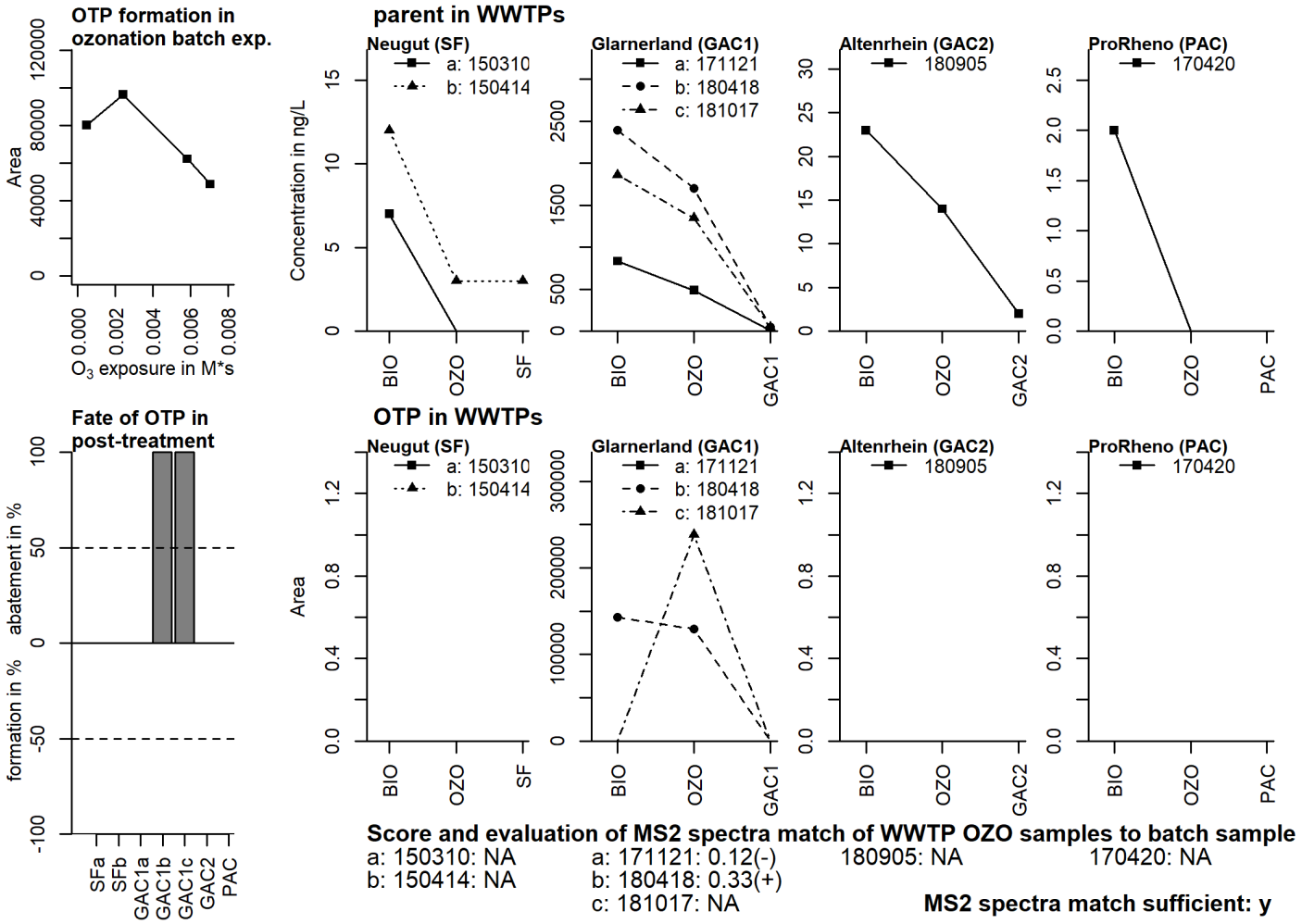
ET401701

Additional Evidence for Structure Interpretation

The MS^2 fragments at the nominal masses 183, 167, 166, 165, 152, 151 were also observed for the parent compound. It indicates that the structure drawn for the fragment 183 is a substructure of this OTP. The neutral loss of C4H11NO as well as the fragment 88 with corresponding formula of C4H10NO indicate that the modification took place on the dimethylethyl moiety and not at the diphenyl moiety of the parent structure.

Tertiary amines are very reactive to form *N*-oxides during ozonation (von Sonntag & von Gunten 2012). Therefore, the formation of a *N*-oxide at the dimethylethylamine is very likely. Merel et al. (2017) identified diphenhydramine *N*-oxide as major OTP.

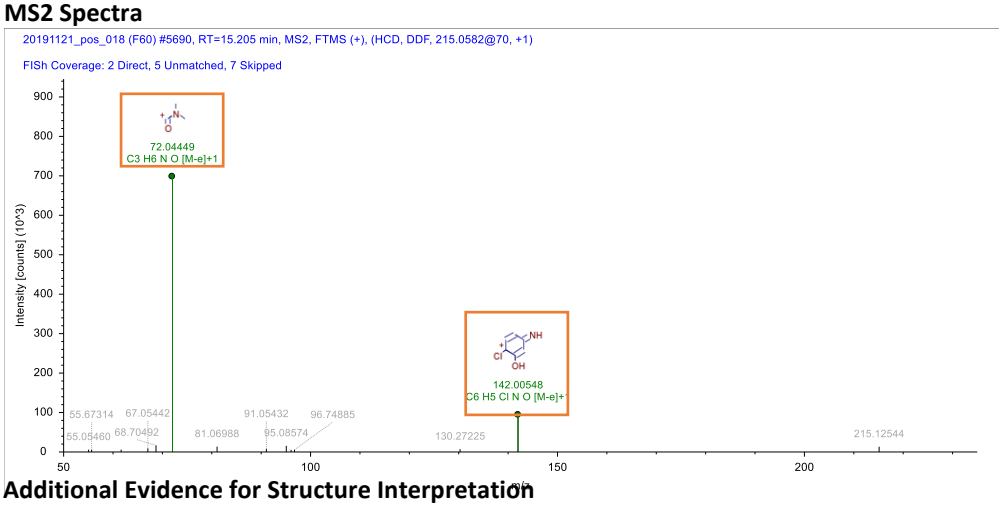
Name DIU_p_215.0582_14.8



MS Spectra

Pos 215.0582 [m+H]+

MS2 Spectra



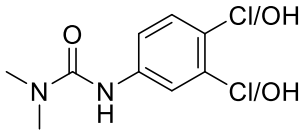
Formula

C9H11O2N2Cl

Atomic modification

-Cl +OH

Proposed Structure



Confidence Level

Level 3

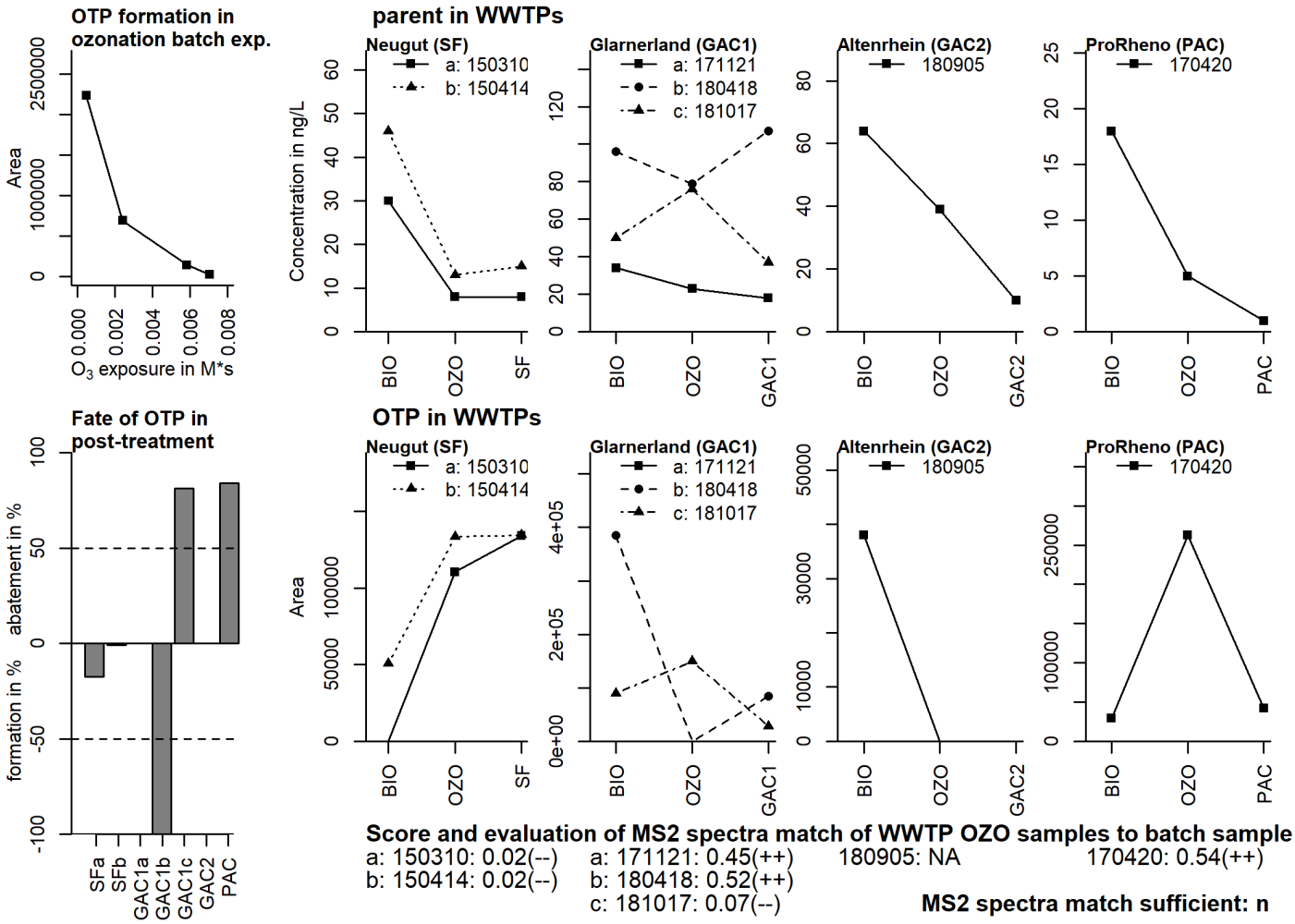
Massbank ID

ET401801

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is –Cl +OH. This fits to an abstraction of the chlorine atom and the addition of a hydroxy group. The MS^2 fragment at the nominal mass 72 was also observed for the parent compound. It indicates that the structure drawn for the fragment 72 is a substructure of this TP. The MS^2 fragment at the nominal mass 142 corresponds to the fragment 159 of the parent with an addition of an oxygen and hydrogen atom and abstraction of a chlorine. This indicates that the hydroxy group was added on the aromatic moiety. Feng et al. (2008) suggested a structure where a chlorine atom is replaced by a hydroxyl group as OTP of diuron (likely by hydroxyl reaction). It is likely that one chlorine was replaced by a hydroxyl group. However, it is unclear at which position. The structures of the MS^2 fragments are drawn exemplarily.

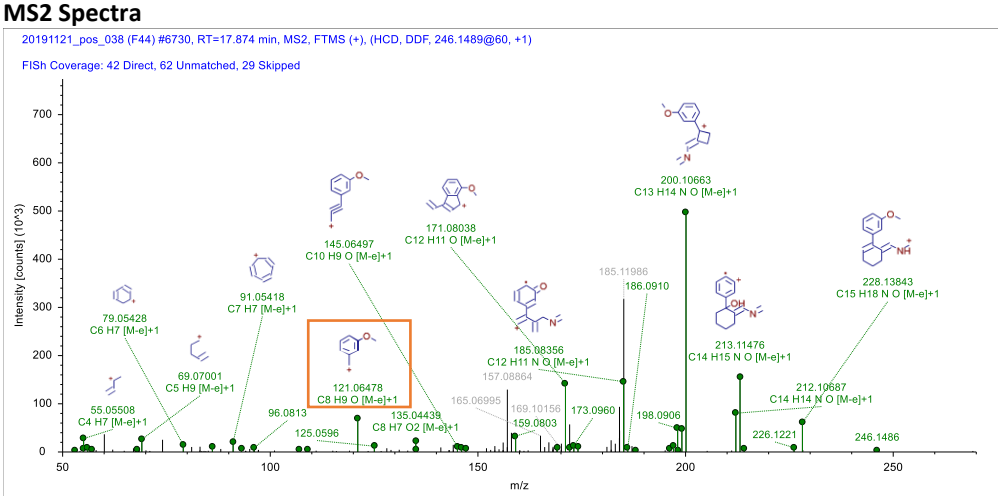
Name DMT_p_246.1489_17.5



MS Spectra

Pos 246.1489 [m+H]+

MS2 Spectra



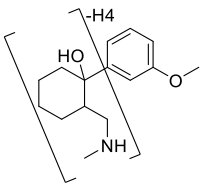
Formula

C15H19NO2

Atomic modification

-H4

Proposed Structure



Additional Evidence for Structure Interpretation

Fragment 121 was also observed for the parent compound. It indicates that the methoxybenzyl moiety is a substructure of this TP.

A possible abstraction of H2 is the formation of an imine moiety, which then undergo hydrolysis. It is unclear where the two remaining hydrogen atoms were abstracted. The exact type and location remain unknown. The structures of the MS^2 fragments are drawn exemplarily.

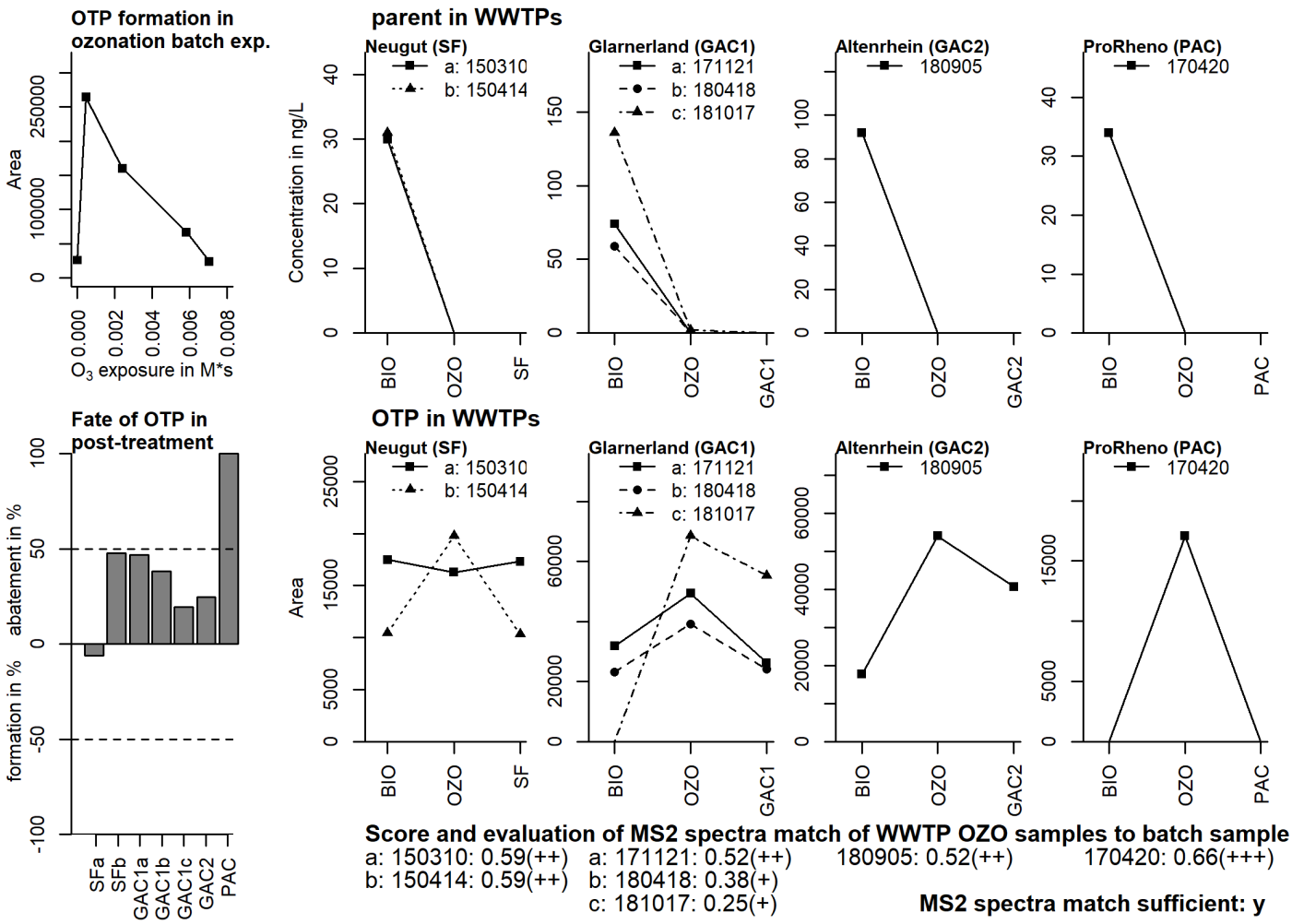
Confidence Level

Level 3

Massbank ID

ET401901

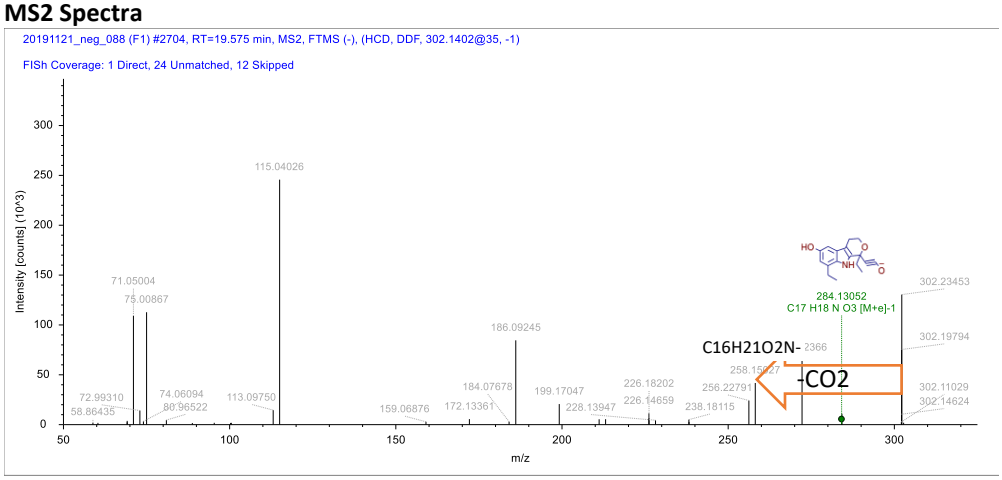
Name ETO_n_302.1395_19.6



MS Spectra

Neg 302.1395 [m-H]-

MS2 Spectra



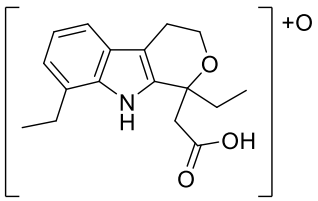
Formula

C17H21O4N

Atomic modification

+O

Proposed Structure



Confidence Level

Level 3

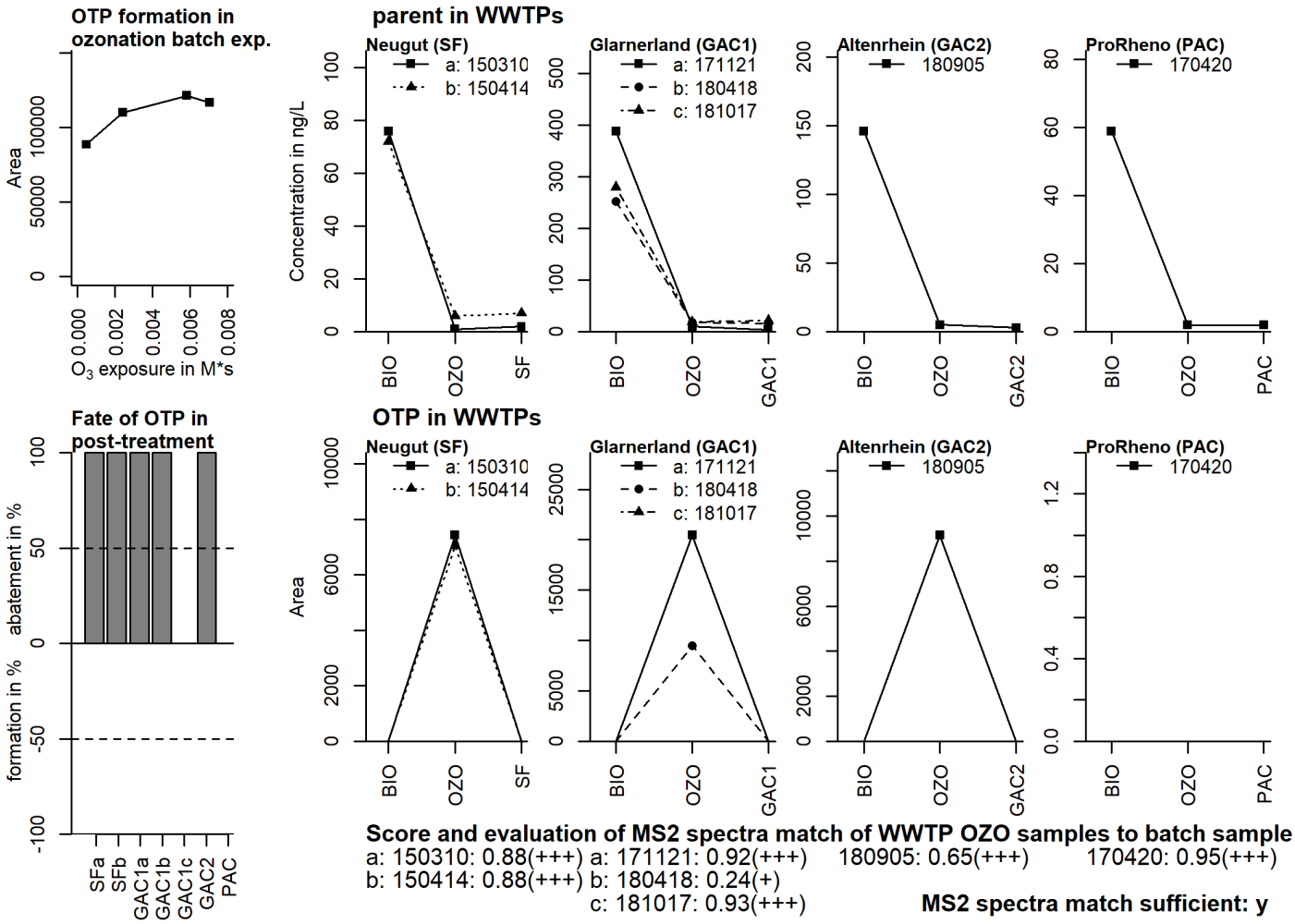
Massbank ID

ET405701

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this TP is +O. This fits to the addition of a hydroxy group via an OH radical. This likely did not occur at the benzene moiety, because once formed, phenol moieties react further quickly during ozonation. There is no further evidence for the exact type and location of the modification. The structures of the MS^2 fragments are drawn exemplarily.

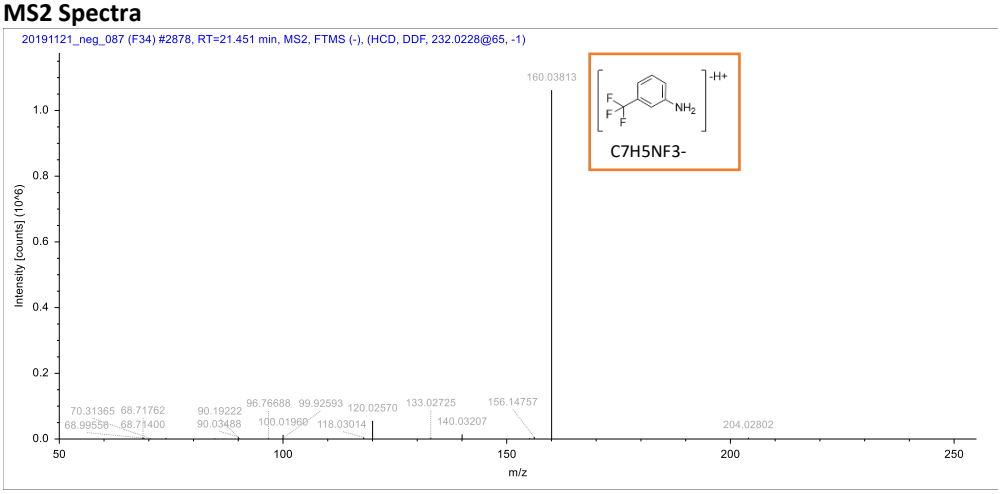
Name FAD_n_232.0224_21.7



MS Spectra

Neg 232.0224 [m-H]-

MS2 Spectra



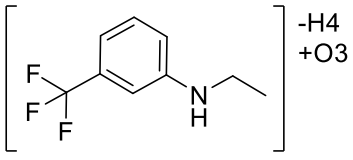
Formula

C9H6O3NF3

Atomic modification

-C5H4 +O

Proposed Structure



Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this TP is –C5H4 +O. Fragment 160 indicates that the 5 C atoms were cleaved off from the benzoic acid moiety. There is no further evidence for the location of the oxygen atoms.

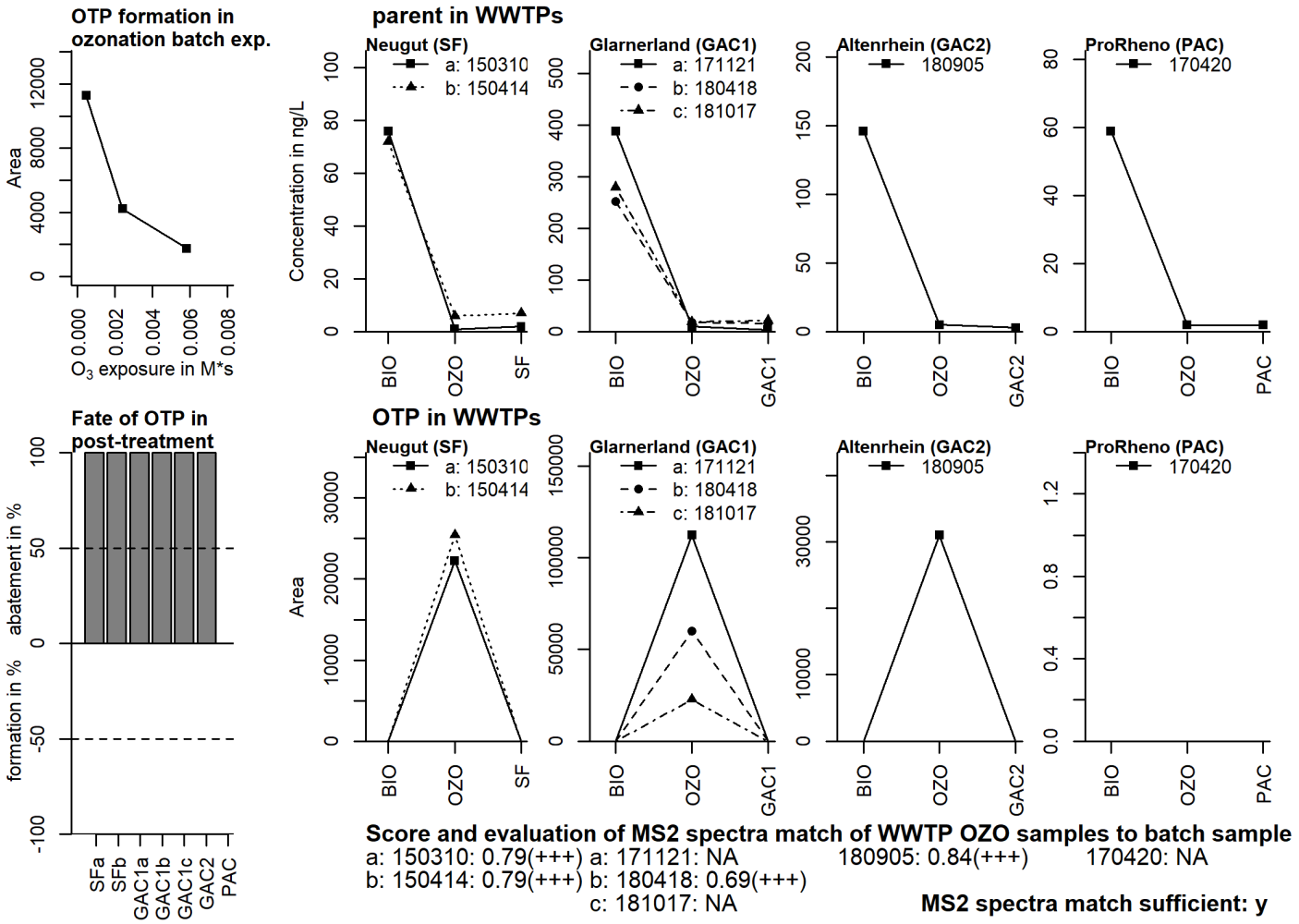
Confidence Level

Level 3

Massbank ID

ET405901

Name FAD_n_258.0384_19.6



Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

a: 150310: 0.79(+++) a: 171121: NA 180905: 0.84(+++) 170420: NA

b: 150414: 0.79(+++) b: 180418: 0.69(+++)

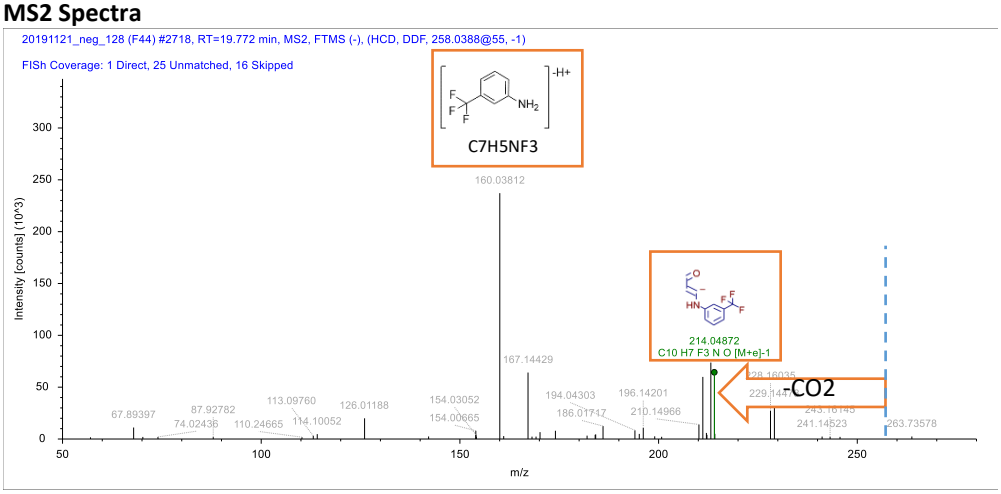
c: 181017: NA

MS2 spectra match sufficient: y

MS Spectra

Neg 258.0384 [m-H]-

MS2 Spectra



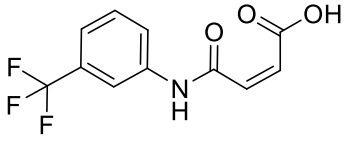
Formula

C11H8O3NF3

Atomic modification

-C3H2 +O

Proposed Structure



Confidence Level

Level 3

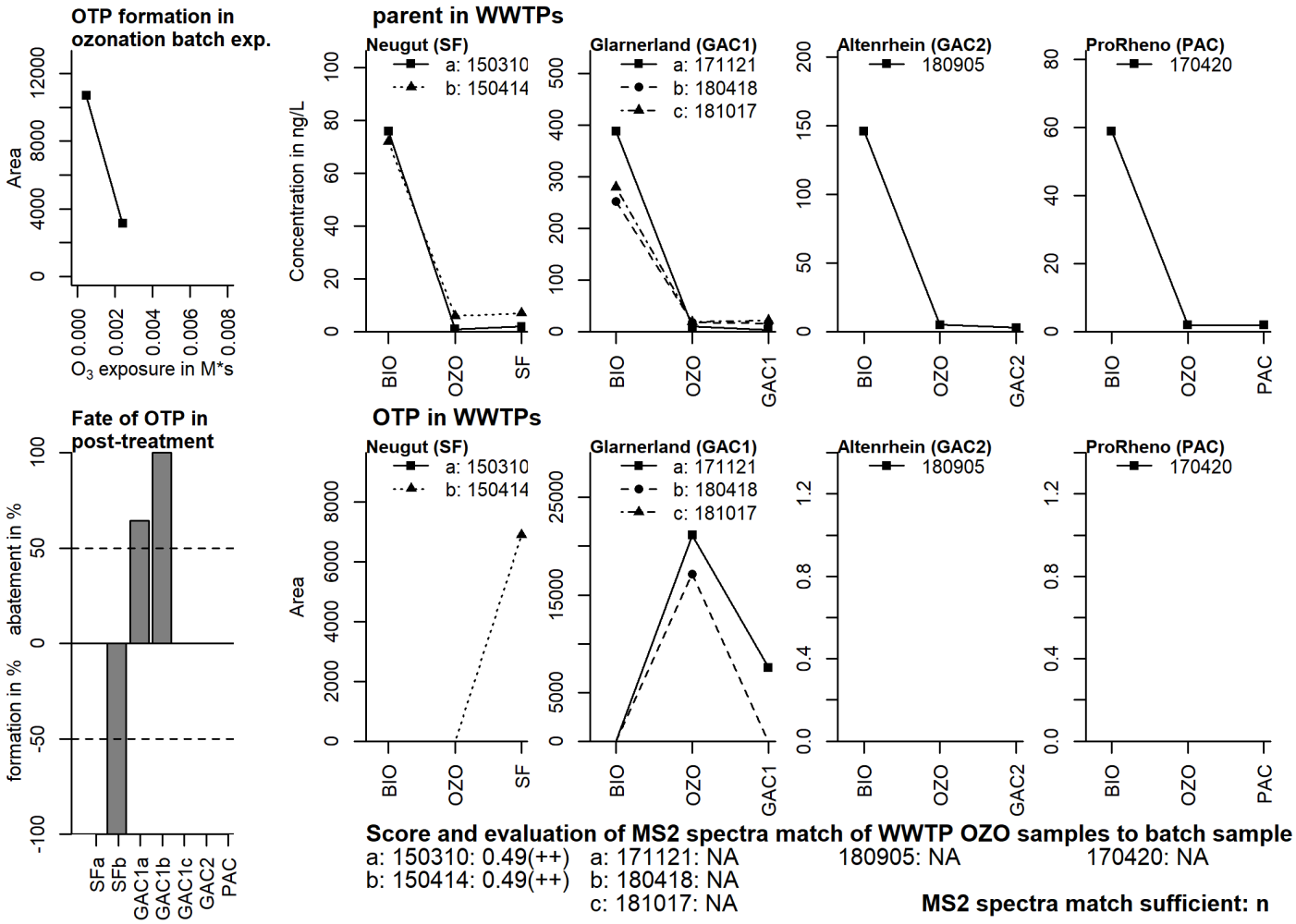
Massbank ID

ET406001

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this TP is –C3H2 +O. Fragment 160 indicates that the 3 C atoms were cleaved off from the benzoic acid moiety. The neutral loss of CO2 between the molecular ion and fragment 214 indicates the presence of a carboxylic acid moiety. The drawn suggested structure fits the molecular formula of this OTP and could have been formed after two Criegee additions on the benzoic acid moiety, leading to the cleaving off of three carbon atoms, including the carboxylic acid moiety. The exact type and location of the modification remain unknown. The structures of the MS^2 fragments are drawn exemplarily.

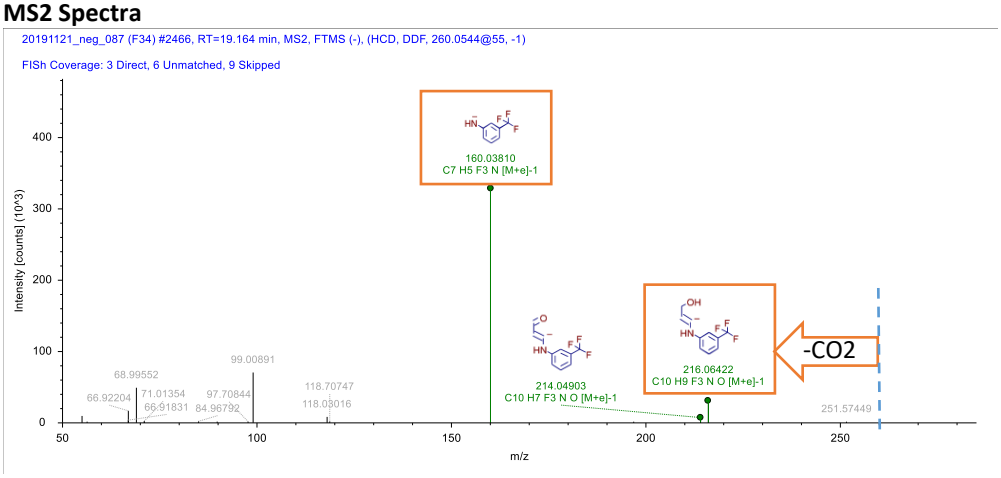
Name FAD_n_260.0537_19.0



MS Spectra

Neg 260.0537 [m-H]-

MS2 Spectra



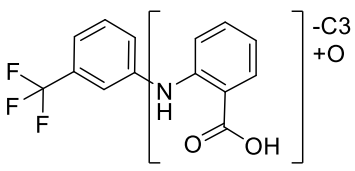
Formula

C11H10O3NF3

Atomic modification

-C3 +O

Proposed Structure



Confidence Level

Level 3

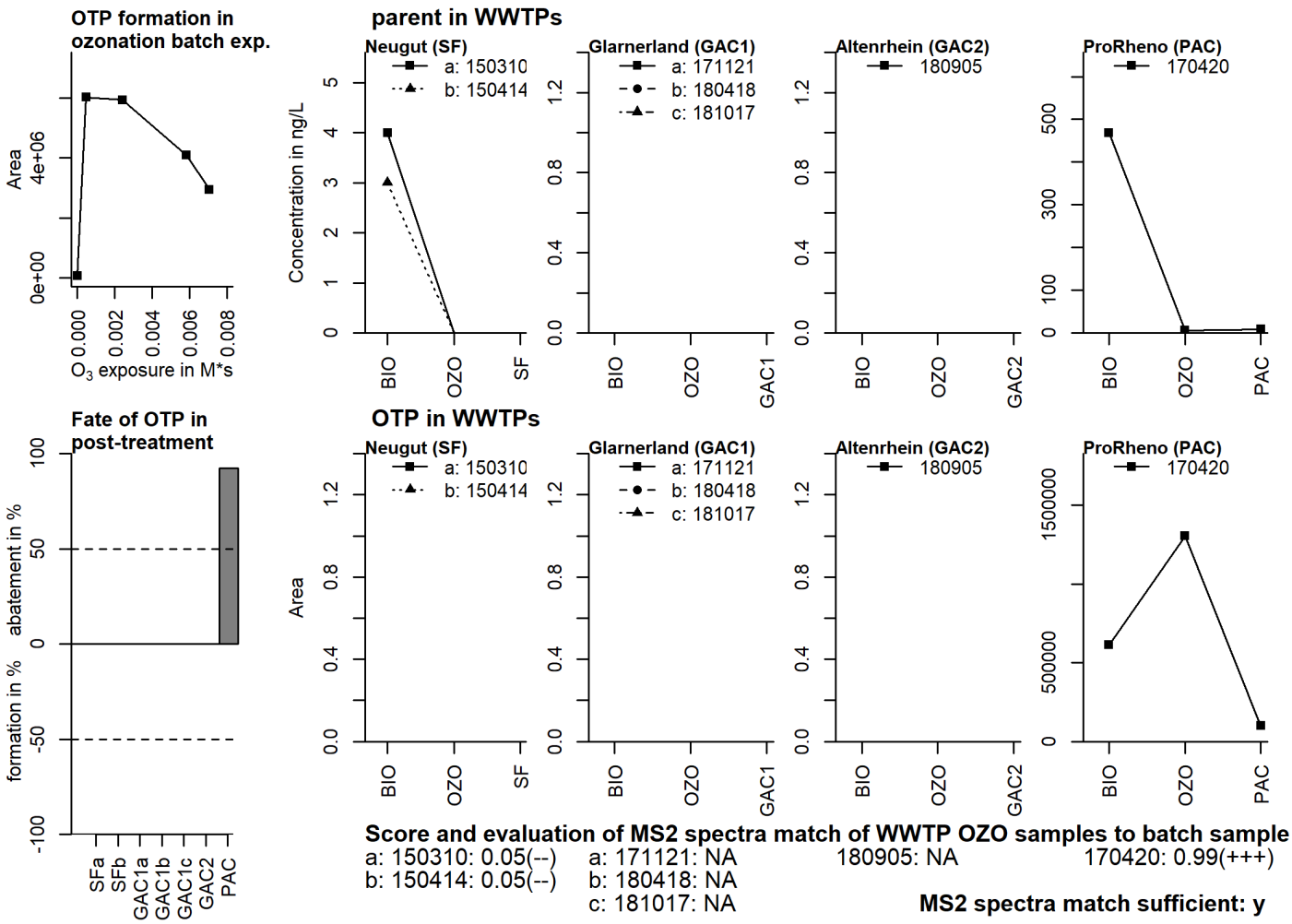
Massbank ID

ET406101

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this TP is –C3 +O. Fragment 160 indicates that the 3 C atoms were cleaved off from the benzoic acid moiety. The neutral loss of CO2 between the molecular ion and fragment 216 as well as the fact that this OTP was detected in the negative MS spectrum suggest the presence of a carboxylic acid moiety. The exact type and location of the cleavage/modification remain unknown. The structures of the MS^2 fragments are drawn exemplarily.

Name FEN_p_290.2478_18.3



Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

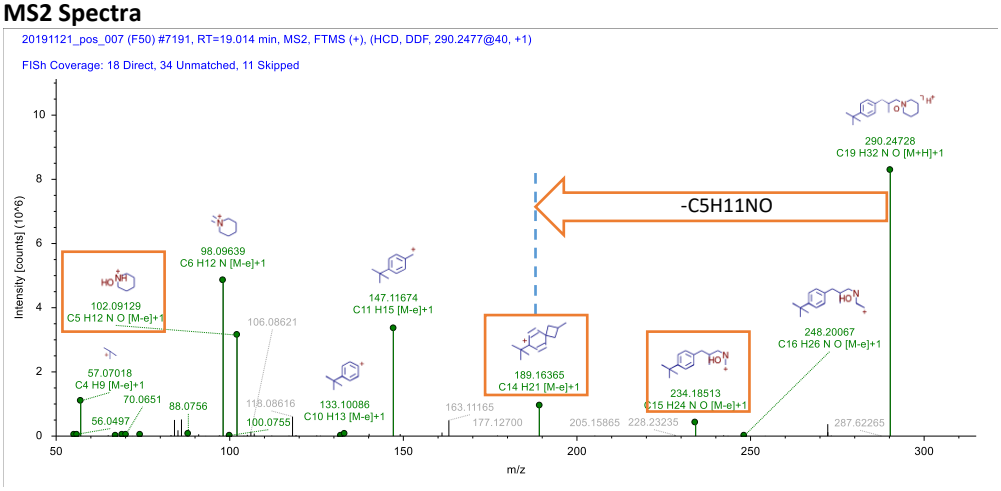
a: 150310: 0.05(--) a: 171121: NA 180905: NA 170420: 0.99(+++)
b: 150414: 0.05(--) b: 180418: NA
c: 181017: NA

MS2 spectra match sufficient: y

MS Spectra

Pos 290.2478 [m+H]+

MS2 Spectra



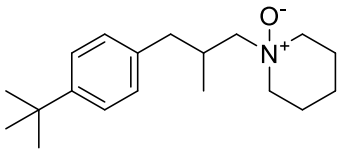
Formula

C19H31ON

Atomic modification

+O

Proposed Structure



Confidence Level

Level 3

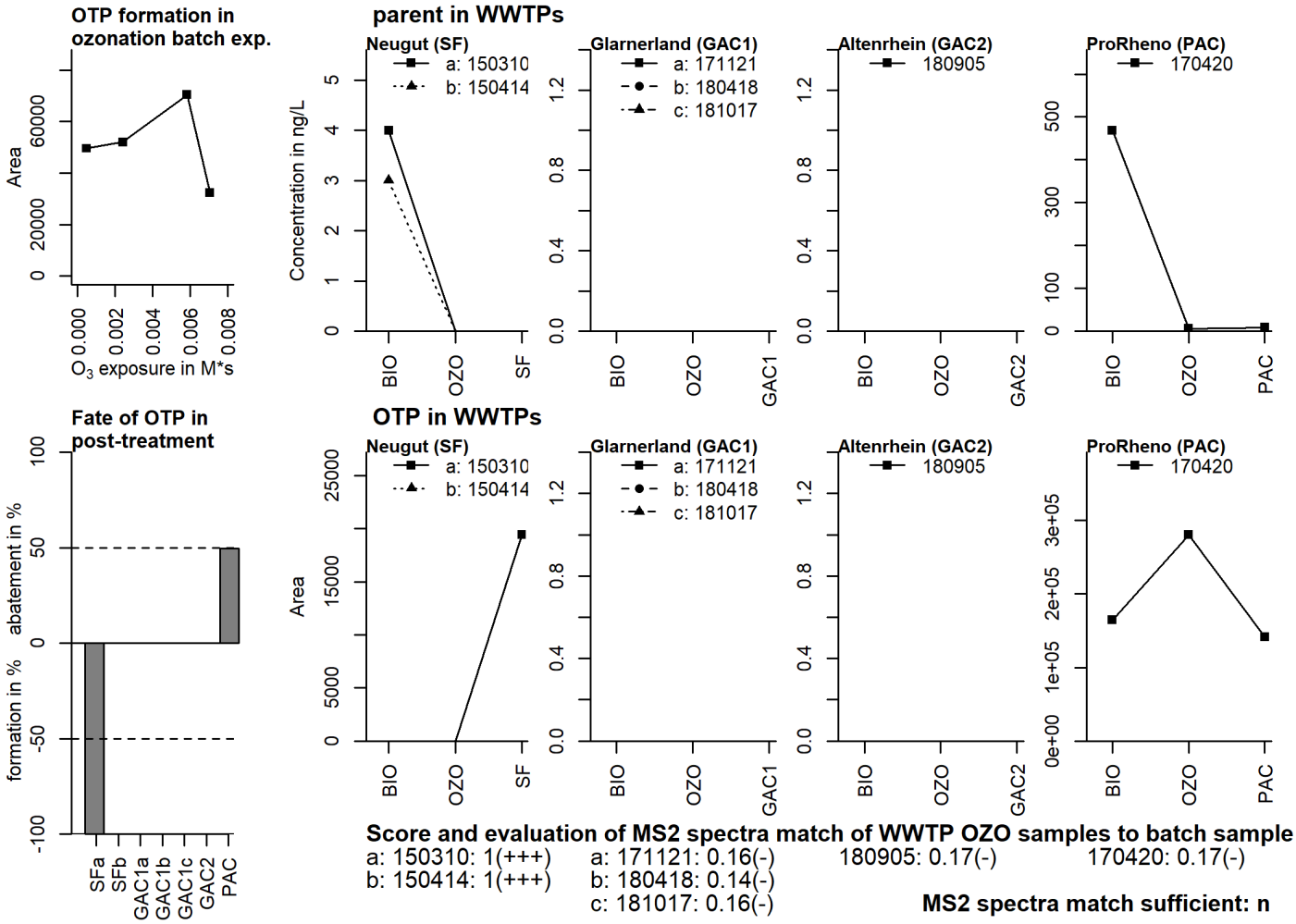
Massbank ID

ET402001

Additional Evidence for Structure Interpretation

The MS^2 fragments at the nominal masses 189, 147, 133, 69 and 57 were also observed for the parent compound. The atomic modification from the elemental formula of the parent compound to this TP is +O. The neutral loss of C5H11NO between the precursor and fragment 189 as well as fragment 102 indicate that the modification took place at the piperidine moiety. Tertiary amines are very reactive to form *N*-oxides during ozonation (von Sonntag & von Gunten 2012). Therefore, the formation of a *N*-oxide at the piperidine moiety is very likely (Borowska et al. 2016).

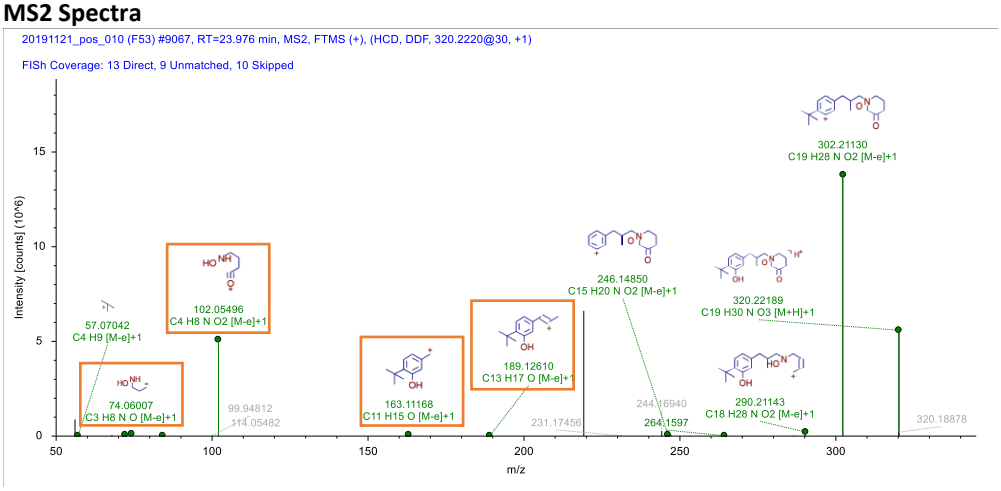
Name FEN_p_320.2220_22.5



MS Spectra

Pos	320.2220	[m+H]+
Neg	318.2072	[m-H]-

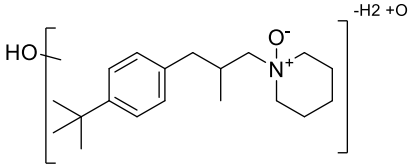
MS2 Spectra



Formula
C19H29O3N

Atomic modification
-H2 +O3

Proposed Structure



Confidence Level
Level 3

Massbank ID
ET402101

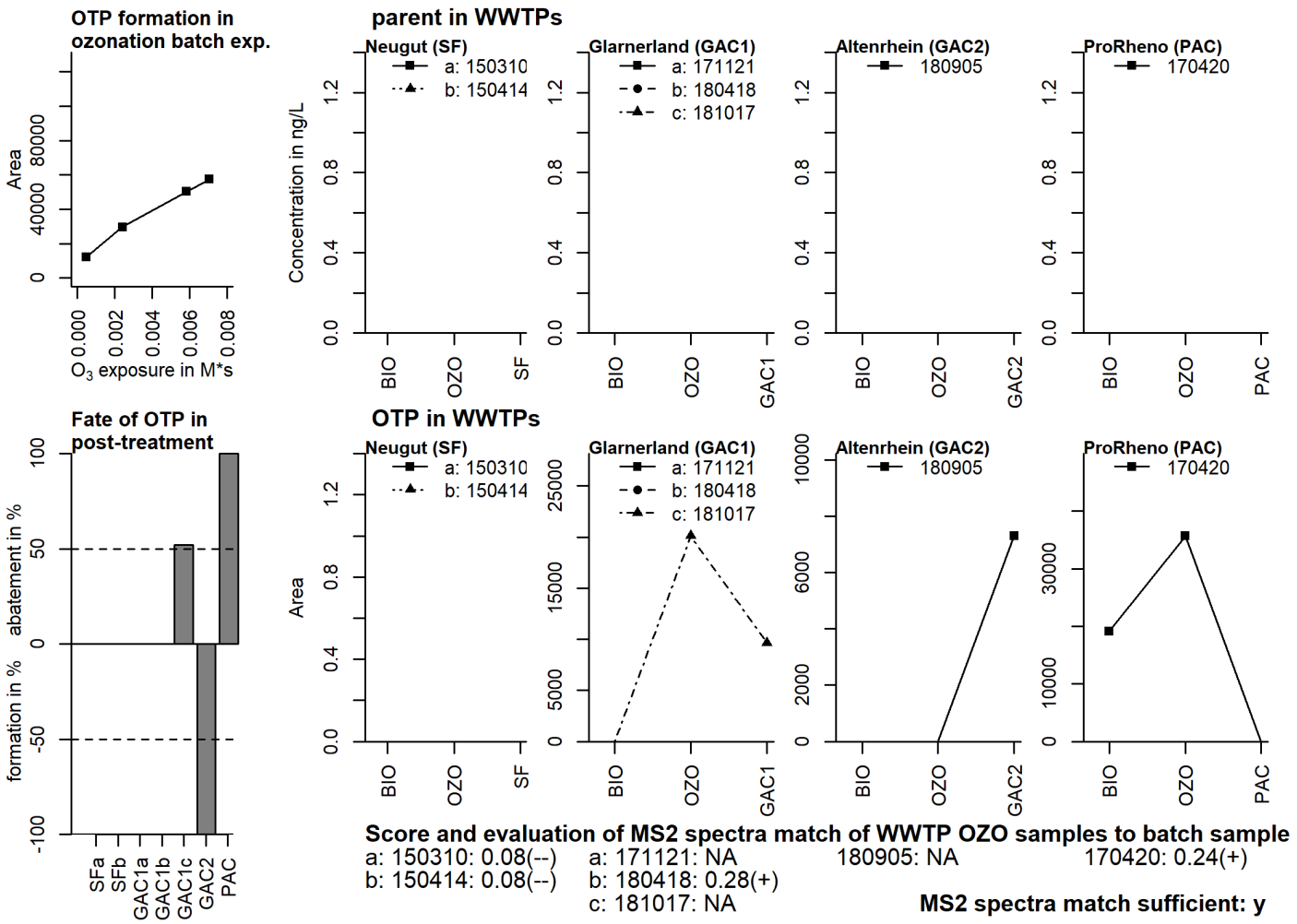
Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this TP is –H2 +O3. Fragment 74 was also found in the MS^2 spectrum of FEN_p_290.2478_18.3, which was identified as fenpropidin *N*-oxide. This indicates that a *N*-oxide formation is also likely for this TP.

The second oxygen atom was likely added by hydroxylation of an aliphatic C- atom with an OH radical. Hydroxylation of the benzene moiety is unlikely because once formed, phenol moieties react further quickly during ozonation. Fragments 163 and 189 suggest that an oxygen atom was added at the 1-(tert-Butyl)-4-methylbenzyl moiety.

Fragment 102 indicates that the third oxygen atom was added at the piperidine moiety. The exact position and type of modification remain unknown. The structures of the MS^2 fragments are drawn exemplarily.

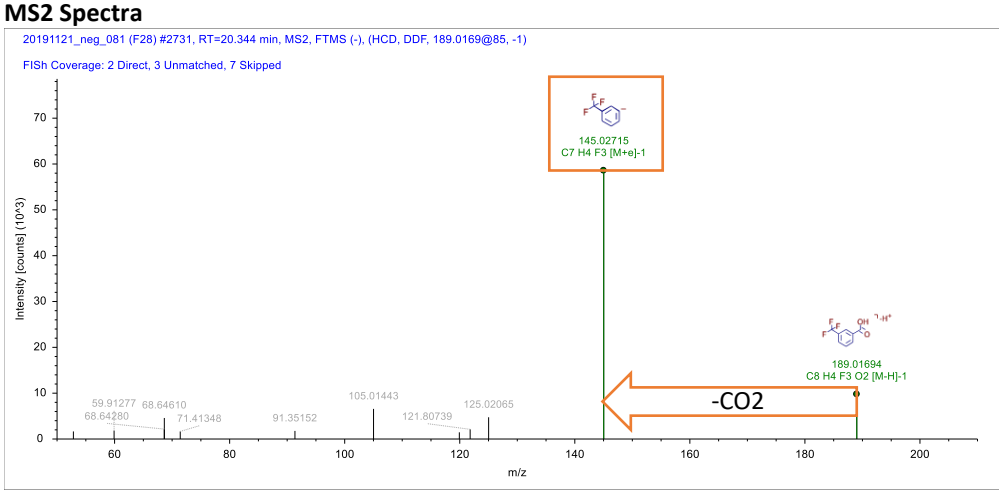
Name FFA_n_189.0167_20.1



MS Spectra

Neg 189.0168 [m-H]-

MS2 Spectra



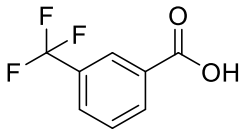
Formula

C8H5O2F3

Atomic modification

-C4H9N +O2

Proposed Structure



Additional Evidence for Structure Interpretation

The atomic modification fits for fenfluramine to a cleavage of the diethylamine moiety. The addition of 2 oxygen atoms fits to the formation of carboxylic acid moiety on the remaining C atom of the side chain. The neutral loss of 44 between the proposed structure and fragment 145 also indicates the formation of a carboxylic acid moiety.

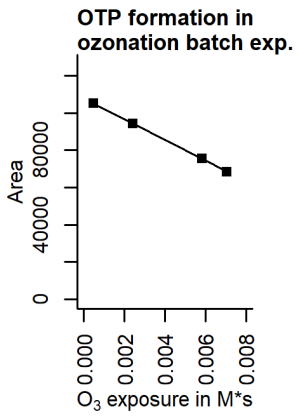
Confidence Level

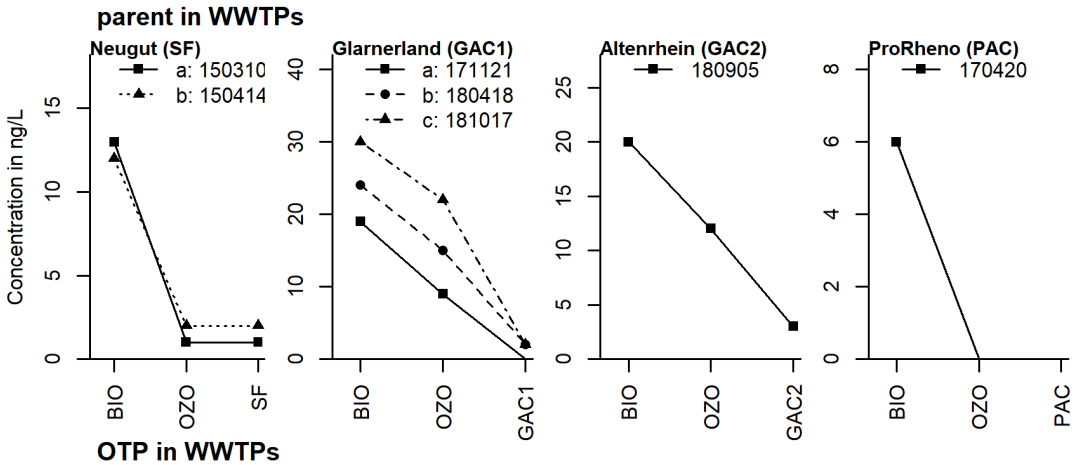
Level 3

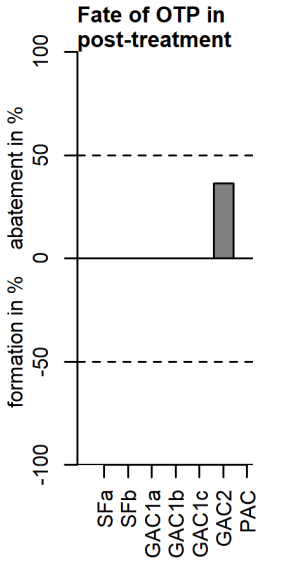
Massbank ID

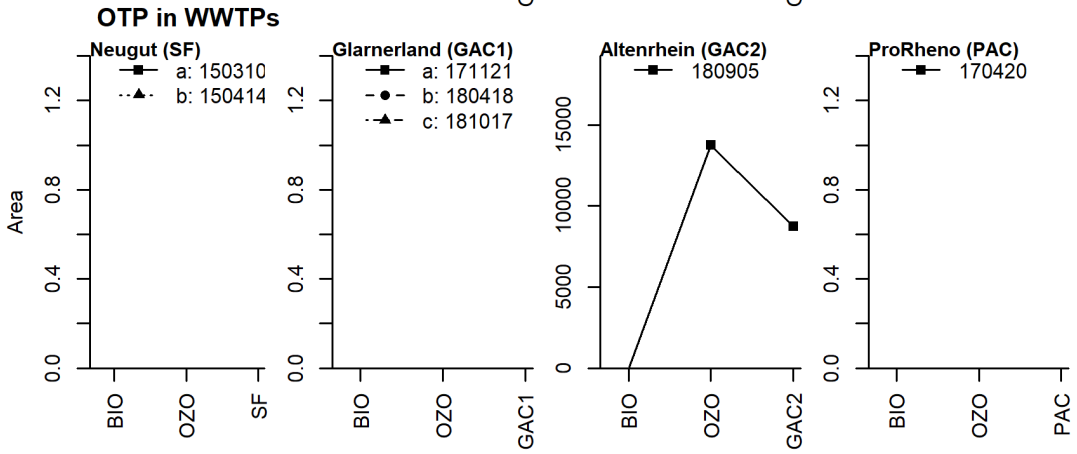
ET405801

Name FLE_n_362.04655_19.2









Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

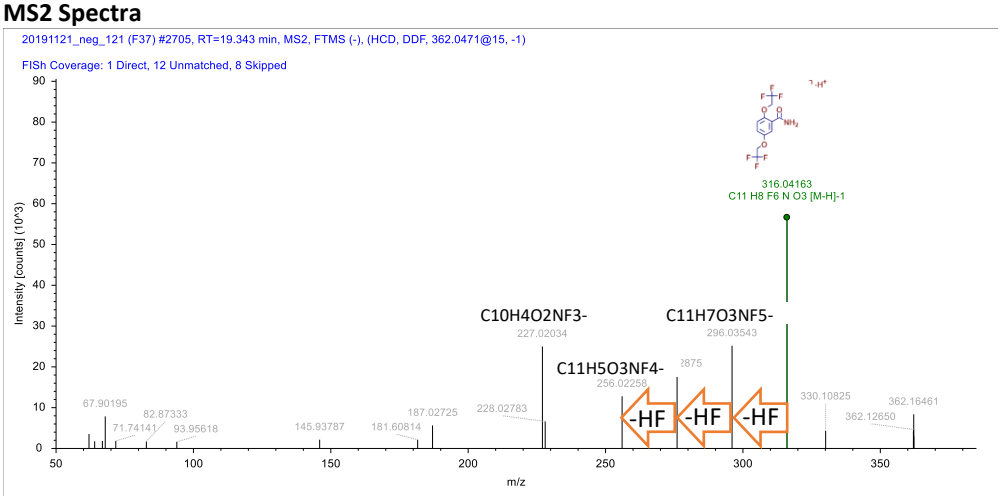
a: 150310: NA
b: 150414: NA
a: 171121: NA
b: 180418: NA
c: 181017: NA
180905: NA
170420: NA

MS2 spectra match sufficient: n

MS Spectra

Neg	362.0466	[m+FA-H]-
Neg	316.0415	[m-H]-

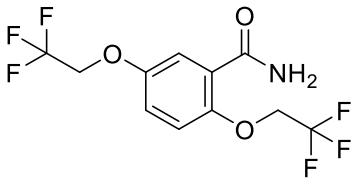
MS2 Spectra



Formula
C11H9O3NF6

Atomic modification
-C6H11N

Proposed Structure

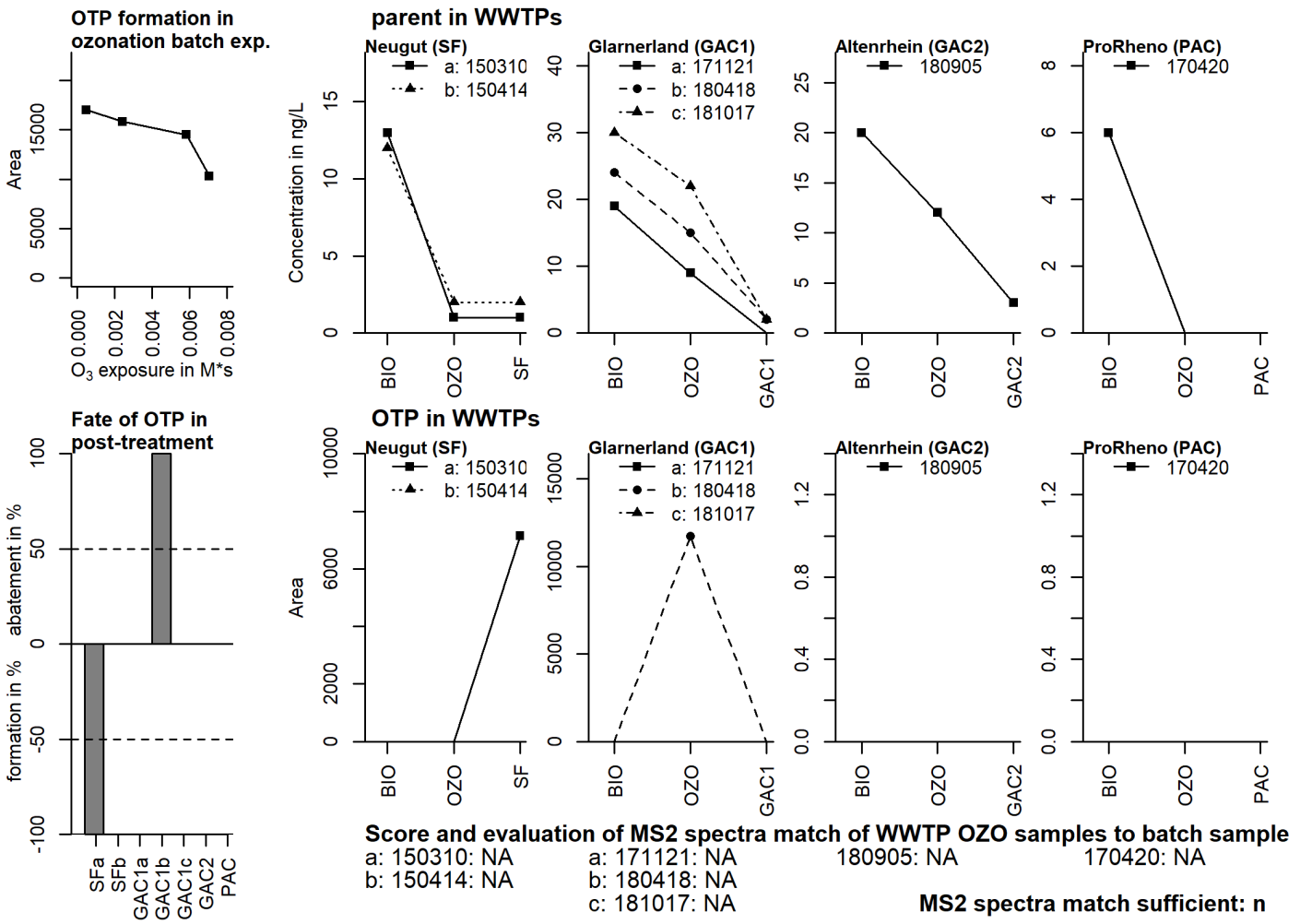


Additional Evidence for Structure Interpretation
The atomic modification from the elemental formula of the parent compound to this OTP is -C6H11N. This modification fits to a splitting-off of the methylpiperidine moiety of the parent compound. A N-dealkylation reaction is known to occur during ozonation (von Sonntag & von Gunten 2012). Therefore, for this reaction the proposed structure is likely.

Confidence Level
Level 3

Massbank ID
ET406267

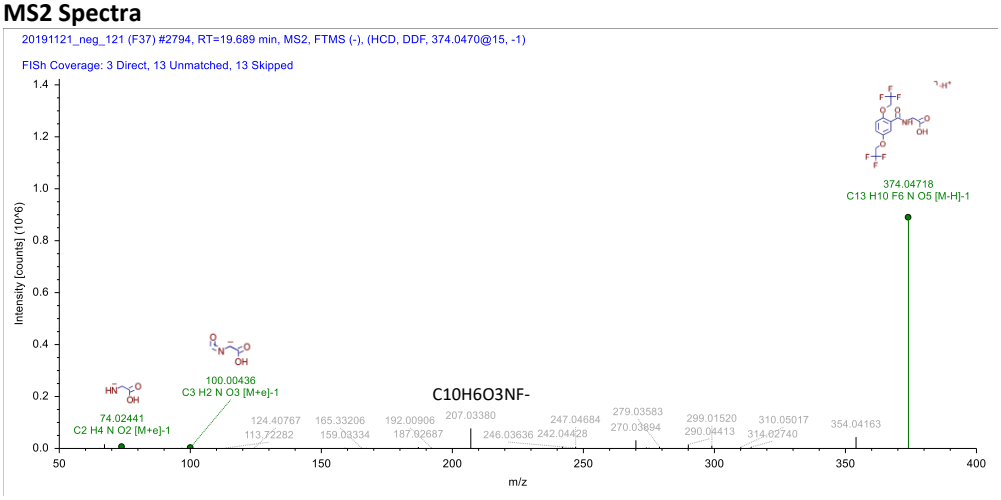
Name FLE_n_374.0465_19.4



MS Spectra

Neg 374.0465 [m-H]-

MS2 Spectra



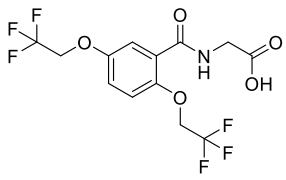
Formula

C13H11O5NF6

Atomic modification

-C4H9N +O2

Proposed Structure



Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is -C4H9N +O2. This modification fits to a cleavage within the piperidine moiety and the addition of two oxygen atoms at the location of the cleavage, as indicated by fragment 74.

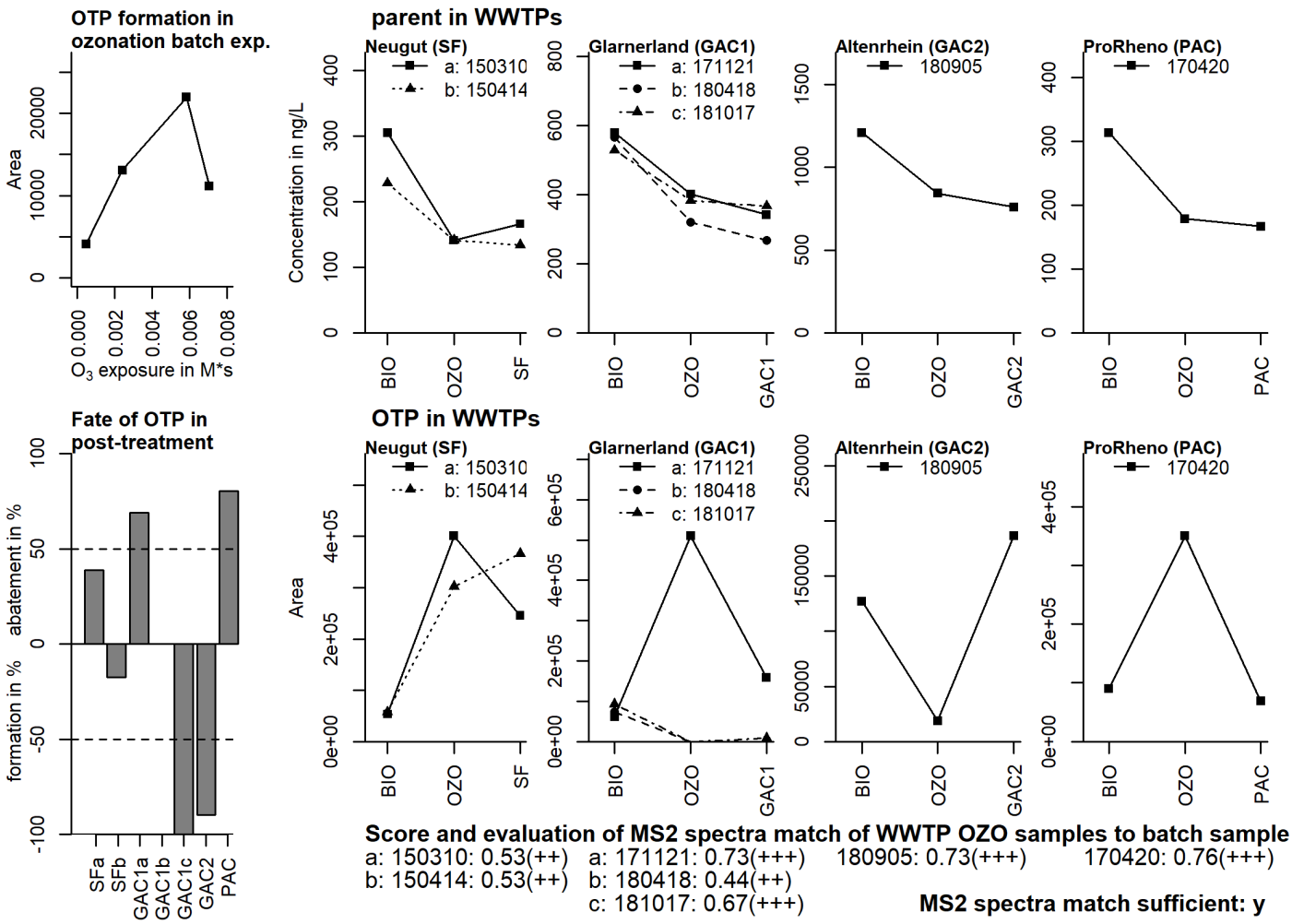
Confidence Level

Level 3

Massbank ID

ET406301

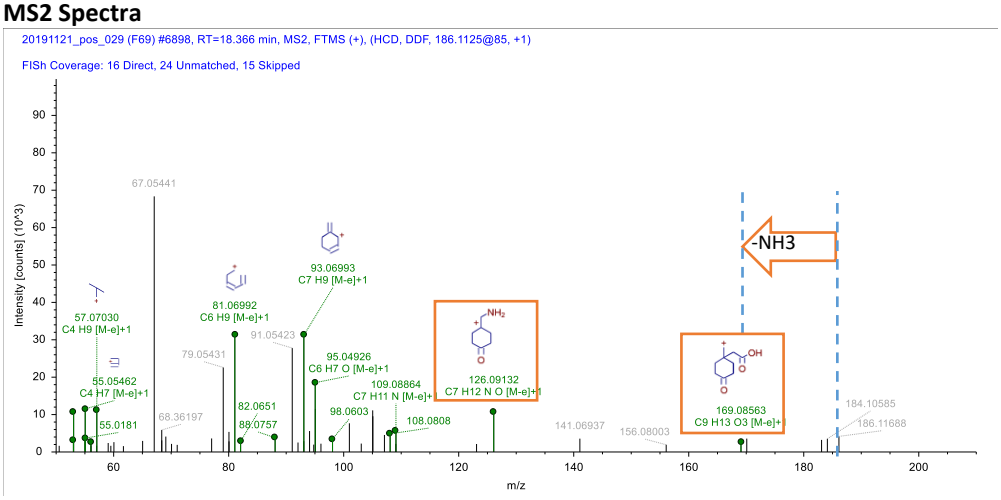
Name GAB_p_186.1124_17.5



MS Spectra

Pos 186.1124 [m+H]+

MS2 Spectra



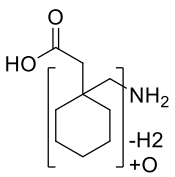
Formula

C9H15O3N

Atomic modification

-H2 +O

Proposed Structure



Confidence Level

Level 3

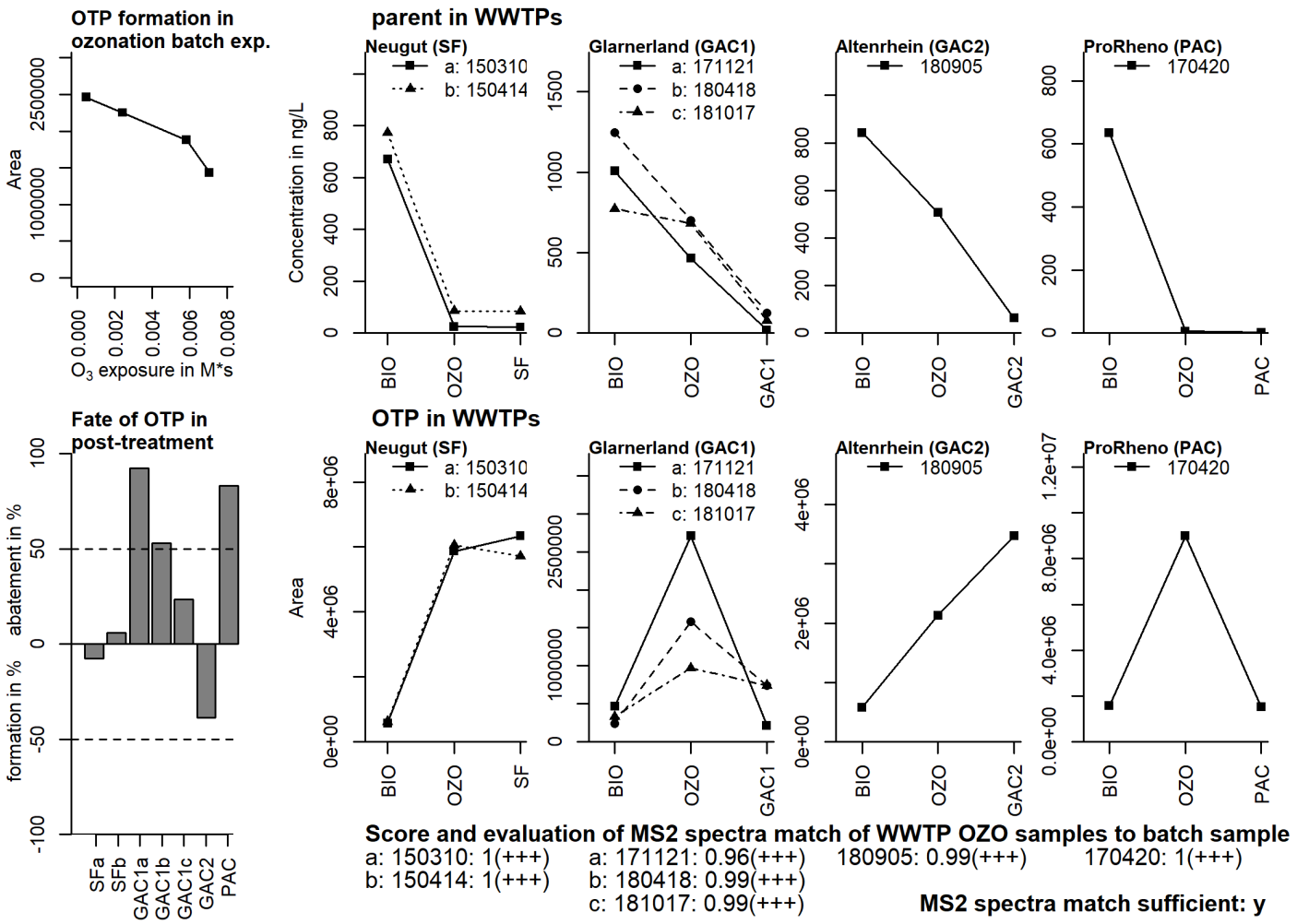
Massbank ID

Et402201

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is –H2 +O. The neutral loss of NH3 between the precursor and fragment 169 indicates that the oxidation did not take place at the primary amine. Fragment 126 indicates that the oxidation took place at the methylcyclohexyl moiety. Different reactions could have led to this molecular formula, most likely the formation of a carbonyl moiety at the α-C atom of the primary amine. However, the exact position and type of modification remain unknown. The structures of the MS^2 fragments are drawn exemplarily.

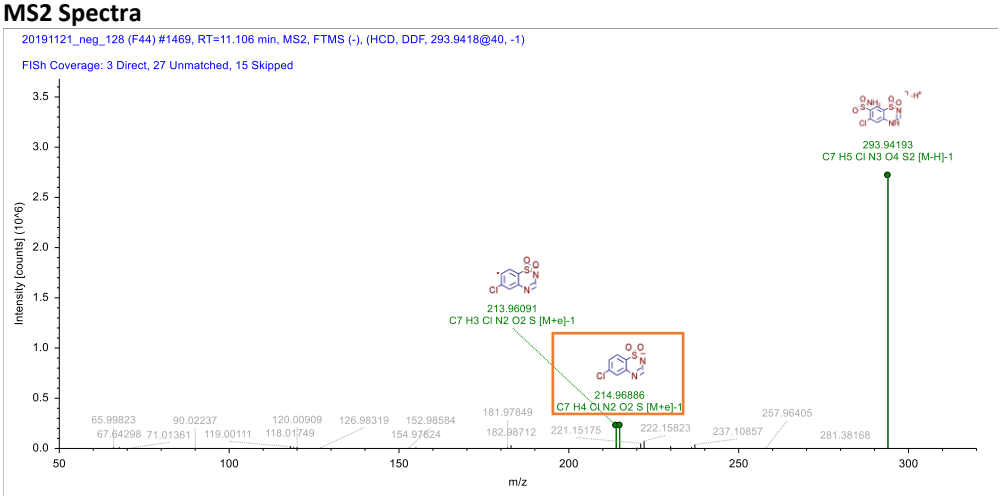
Name HCT_n_293.9415_10.8



MS Spectra

Neg	293.9415	[m-H]-
Pos	295.9561	[m+H+]

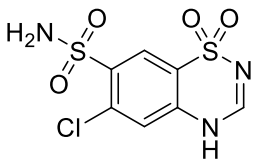
MS2 Spectra



Formula
C7H6O4N3ClS2

Atomic modification
-H2

Proposed Structure

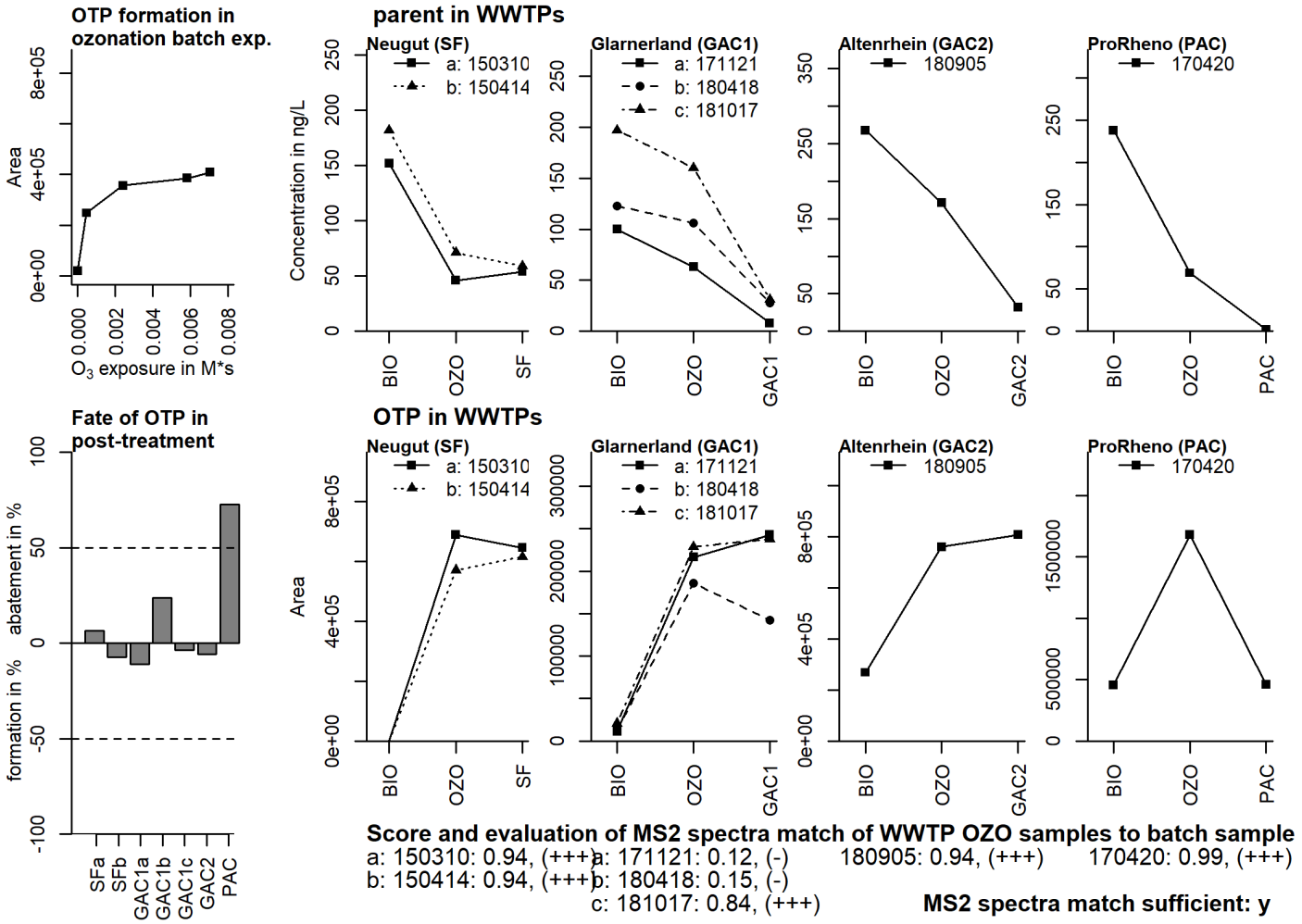


Additional Evidence for Structure Interpretation
The atomic modification from the elemental formula of the parent compound to this OTP is –H2. This fits to the oxidation of a C-N bond. A fragment with mass 216 was observed for the parent compound and corresponds to fragment 214 here with abstraction of 2 hydrogen atoms.
The drawn structure, chlorthiazide, was identified as OTP of hydrochlorthiazide by Borowska et al. (2016). The structure was confirmed with a reference standard.

Confidence Level
Level 1

Massbank ID
ET406401

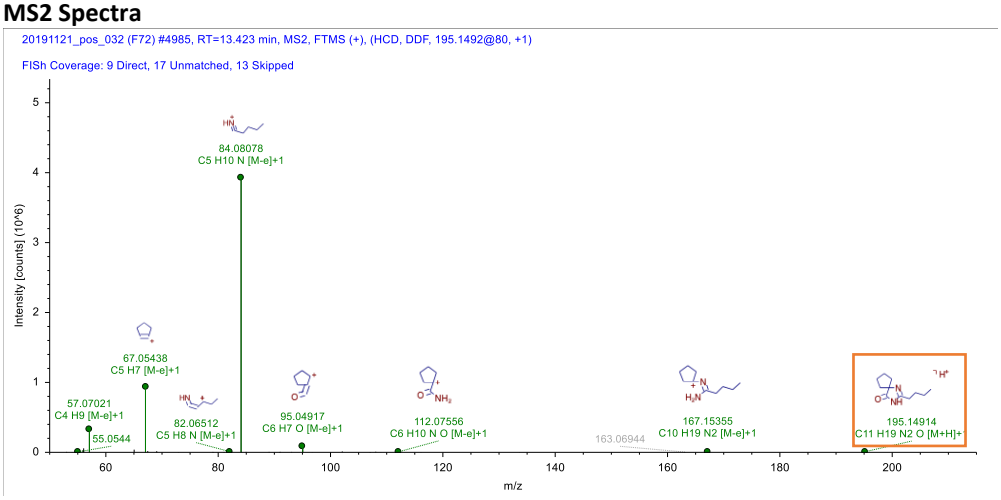
Name IRB_p_195.1491_12.8



MS Spectra

Pos 195.1491 [m+H]+

MS2 Spectra



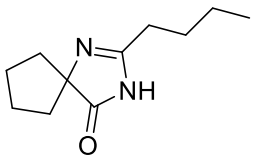
Formula

C11H18ON2

Atomic modification

-C14H10N4

Proposed Structure



Additional Evidence for Structure Interpretation

A fragment with the nominal mass 195 was also observed for the parent compound and corresponds to this precursor. It indicates that the proposed structure was conserved. The atomic modification from the elemental formula of the parent compound to this OTP fits to a cleavage of the tetrazolebiphenylmethyl moiety, which is common for all sartans.

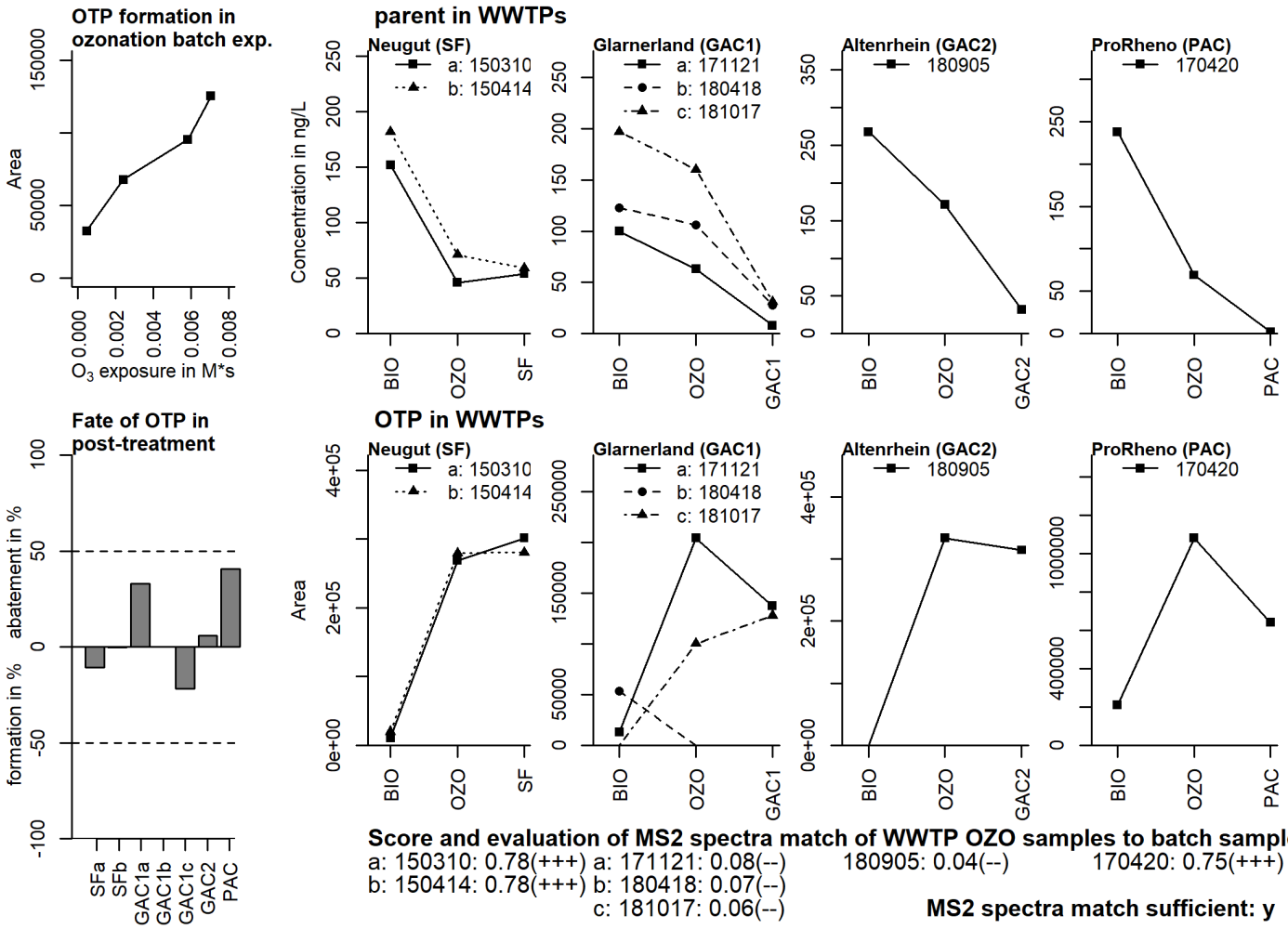
Confidence Level

Level 3

Massbank ID

ET402301

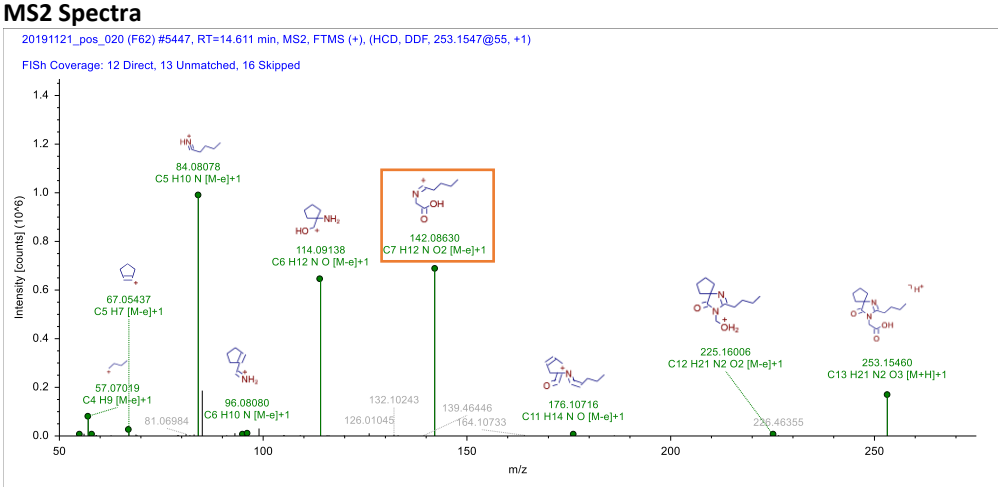
Name IRB_p_253.1545_14.2



MS Spectra

Pos	253.1445	[m+H]+
Neg	251.1399	[m-H]-

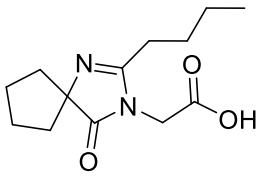
MS2 Spectra



Formula
C13H20O3N2

Atomic modification
-C12H8N4 +O2

Proposed Structure



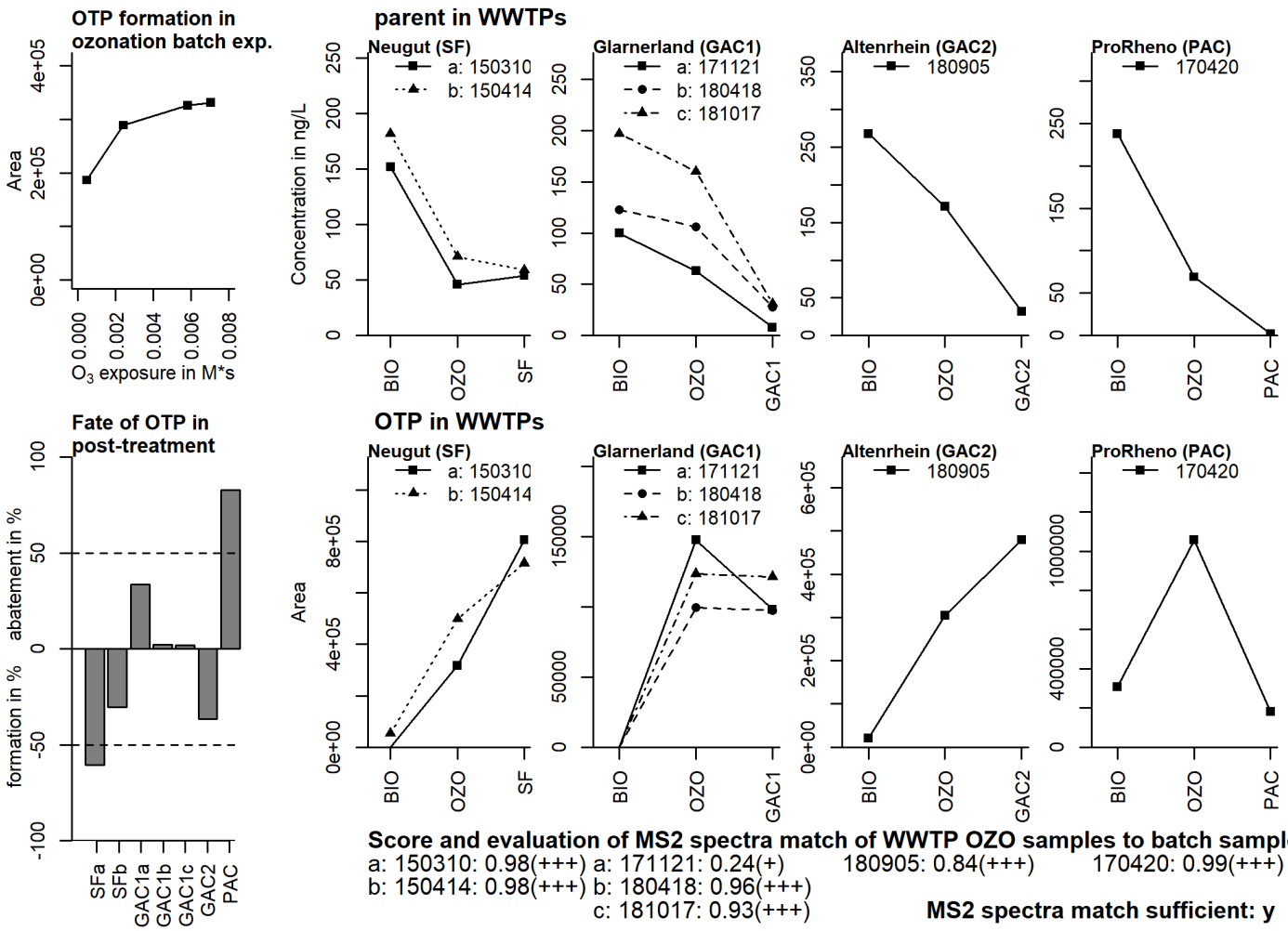
Confidence Level
Level 3

Massbank ID
ET402401

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is - C12H8N4 +O2. This fits to a cleavage within the benzene moiety of the tetrazolebiphenylmethyl part, which is common for all sartans, and the addition of two oxygen atoms. Fragment 142 indicates that the two oxygens are connected to the ethylpentylamine moiety. This TP was detected in negative MS spectrum, which indicates the presence of a carboxylic acid moiety. There is no further evidence in the MS^2 spectrum about the exact position. However, aromatic compounds are known to form cis,cis-muconic acid like structures (von Sonntag & von Gunten 2012). Therefore, the formation of this kind of structure, followed by a C-C bond cleavage, resulting in an aminoacetic acid structure, is likely.

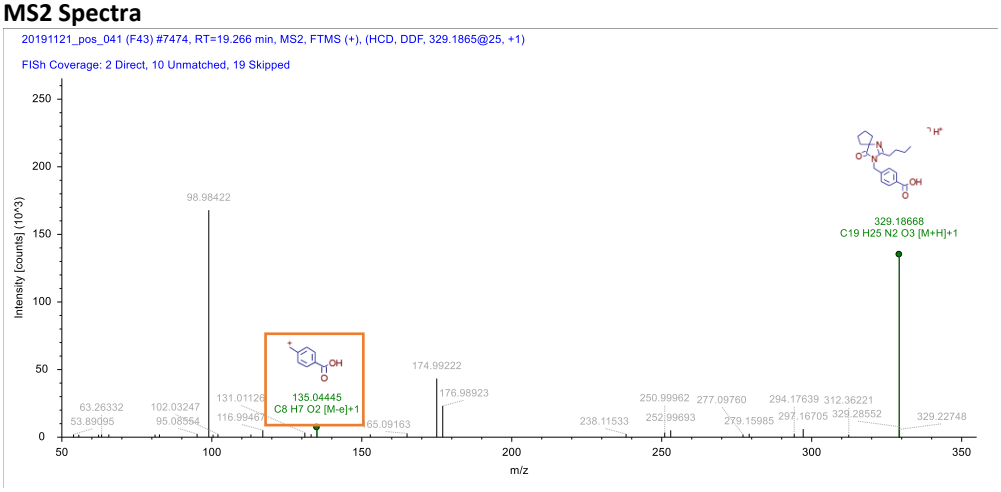
Name IRB_p_329.1858_19.4



MS Spectra

Pos	329.1858	[m+H]+
Neg	327.1713	[m-H]-

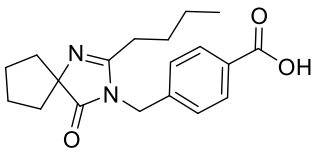
MS2 Spectra



Formula
C19H24N2O3

Atomic modification
-C6H4N4 +O2

Proposed Structure



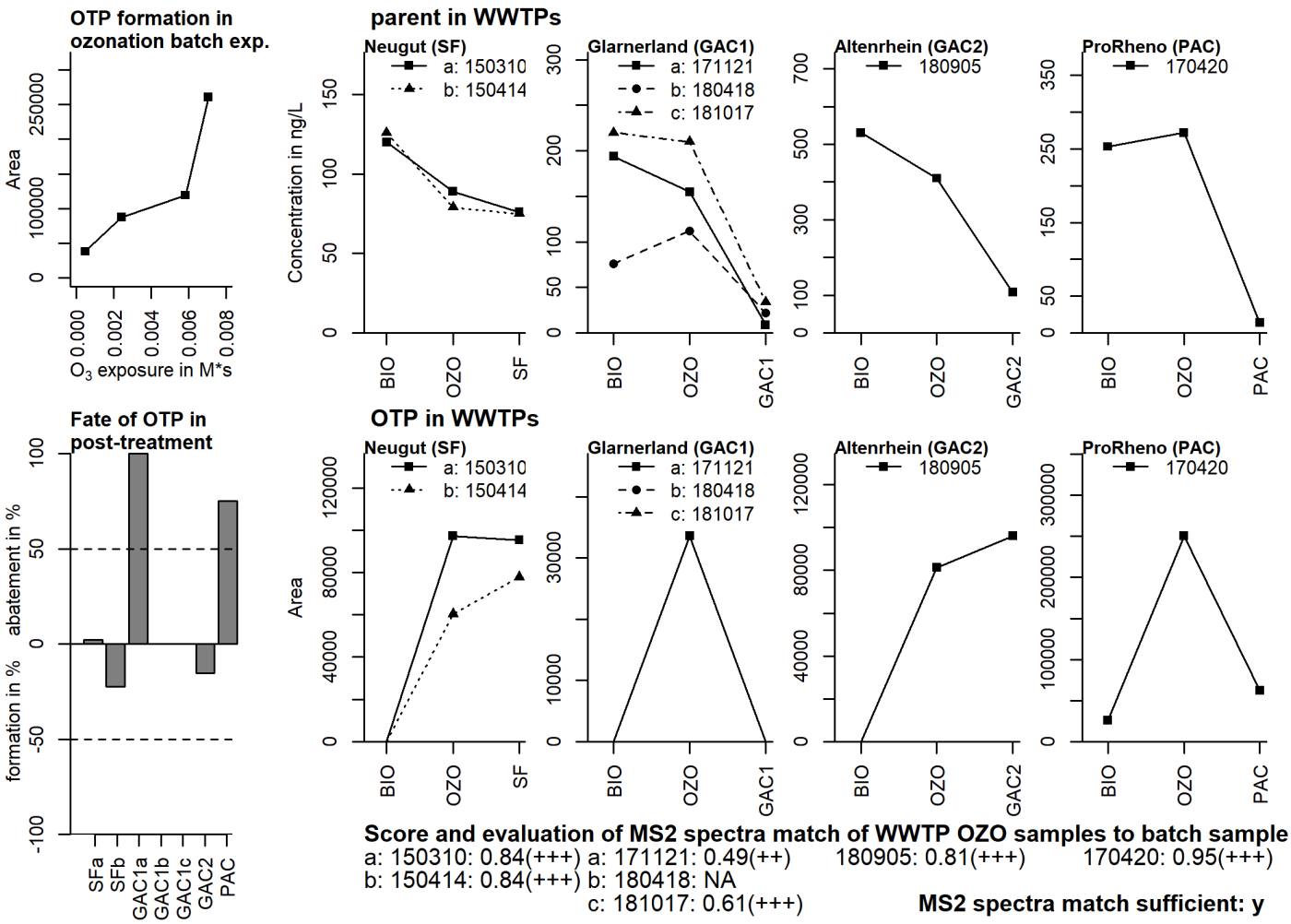
Confidence Level
Level 3

Massbank ID
ET402501

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is -C6H4N4 +O2. This fits to a cleavage within the benzene moiety of the tetrazolebiphenylmethyl part, which is common for all sartans, and the addition of two oxygen atoms. Fragment 135 indicates that the two oxygens are connected to the dimethylphenyl moiety. This OTP was also detected in negative MS spectrum, which indicates the presence of a carboxylic acid moiety. Furthermore, the precursor showed a neutral loss of CO2 in the negative MS spectrum. There is no further evidence in the MS^2 spectrum about the exact position. However, aromatic compounds are known to form cis,cis-muconic acid like structures (von Sonntag & von Gunten 2012). Therefore, the formation of this kind of structure, followed by a C-C bond cleavage, resulting in a benzoic acid structure, is likely.

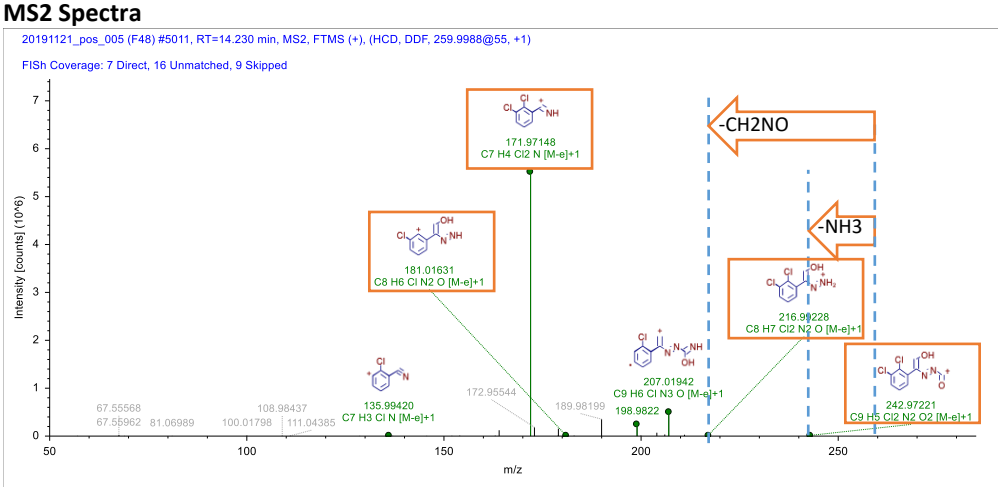
Name LAM_p_259.9988_13.7



MS Spectra

Pos	259.9988	[m+H]+
Neg	257.9842	[m-H]-

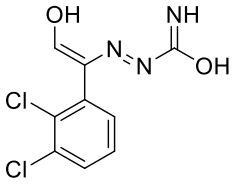
MS2 Spectra



Formula
C9H7O2N3Cl2

Atomic modification
-N2 +O2

Proposed Structure



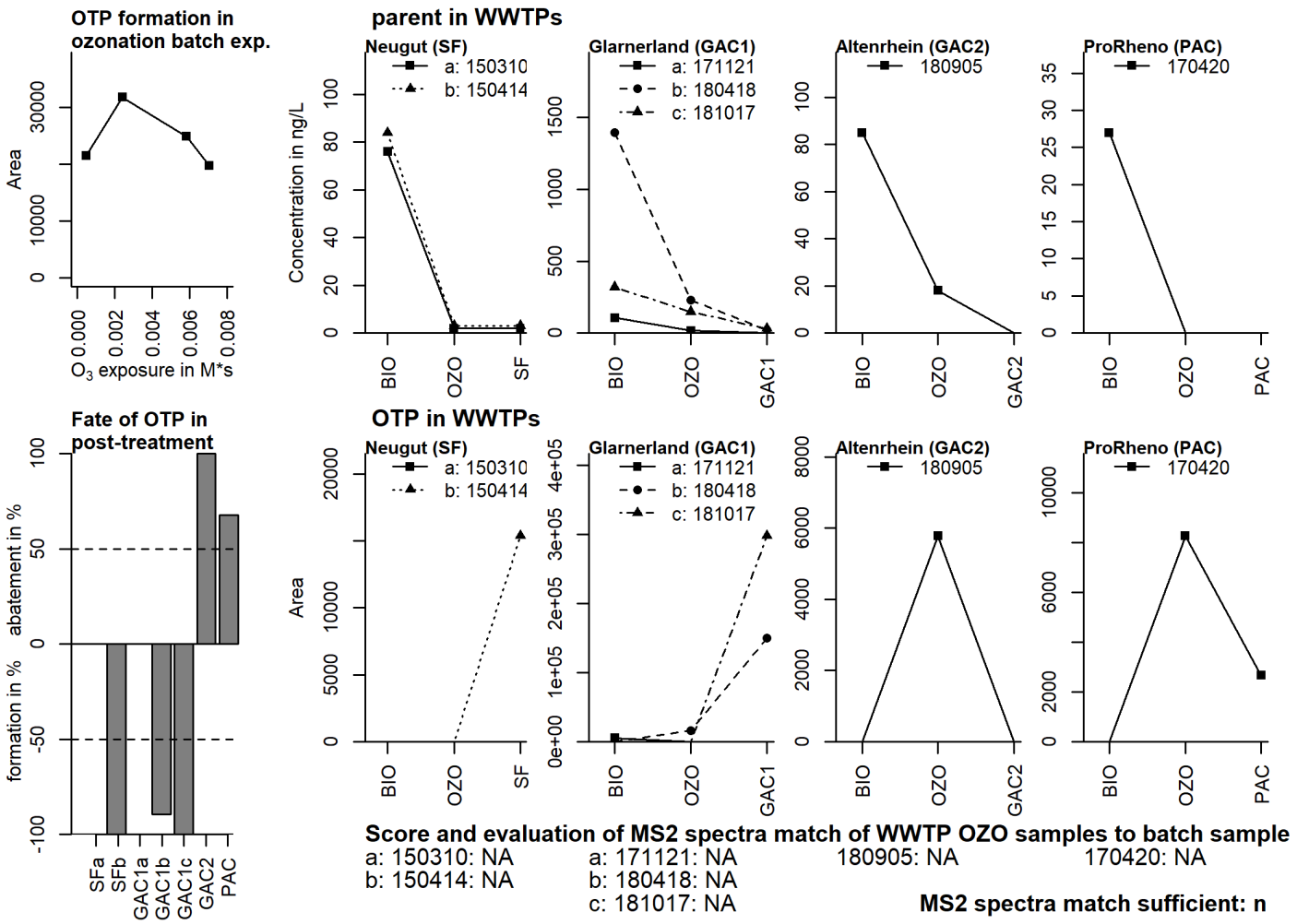
Confidence Level
Level 3

Massbank ID
ET402601

Additional Evidence for Structure Interpretation

The MS^2 fragment at the nominal mass 171 was also observed for the parent compound. It indicates that the structure drawn for the fragment 171 is a substructure of this OTP. The atomic modification from the elemental formula of the parent compound to this OTP is –N2 +O2. This fits to a cleavage of two nitrogen atoms within the triazinediamine moiety and the addition of two oxygen atoms. Keen et al. (2014) suggested this structure as OTP of lamotrigine. The neutral loss of NH3 between the precursor and fragment 242 indicates that this OTP contains a terminal nitrogen atom. The neutral loss of CH2NO between the precursor and fragment 216 fits to a cleavage of a formimidic acid like moiety. Bollmann et al. (2016) however suggested the formation of the N2–oxide. What is an N2-oxide?

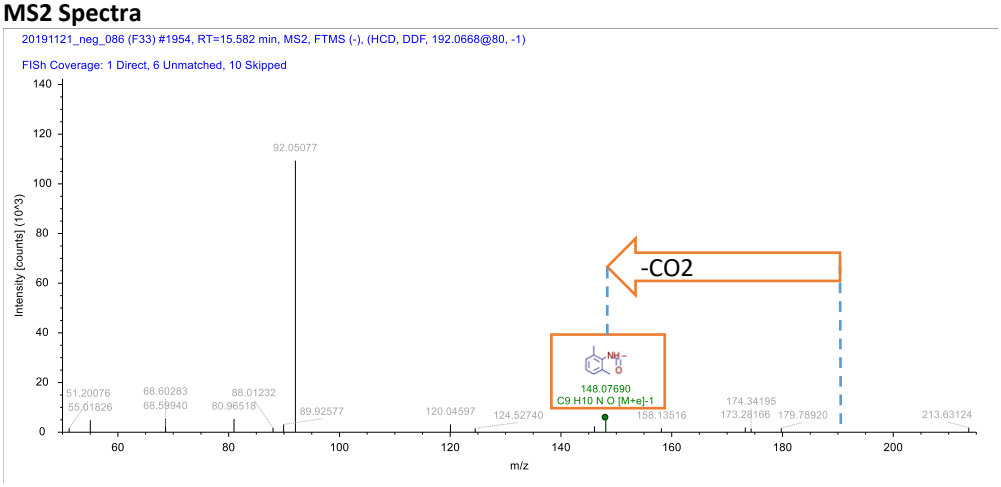
Name LID_n_192.0665_16.0



MS Spectra

Neg 192.0665 [m-H]-

MS2 Spectra



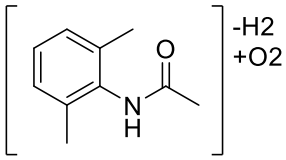
Formula

C10H11O3N

Atomic modification

-C4H11N +O2

Proposed Structure



Additional Evidence for Structure Interpretation

The loss of C4H11N fits to the cleavage of diethylamine moiety. Two oxygen atoms were added on the remaining dimethylacetanilide moiety.

The neutral loss of CO2 (-44) between the proposed structure and fragment 148 indicates the presence of a carboxylic acid. Its exact location remains unknown.

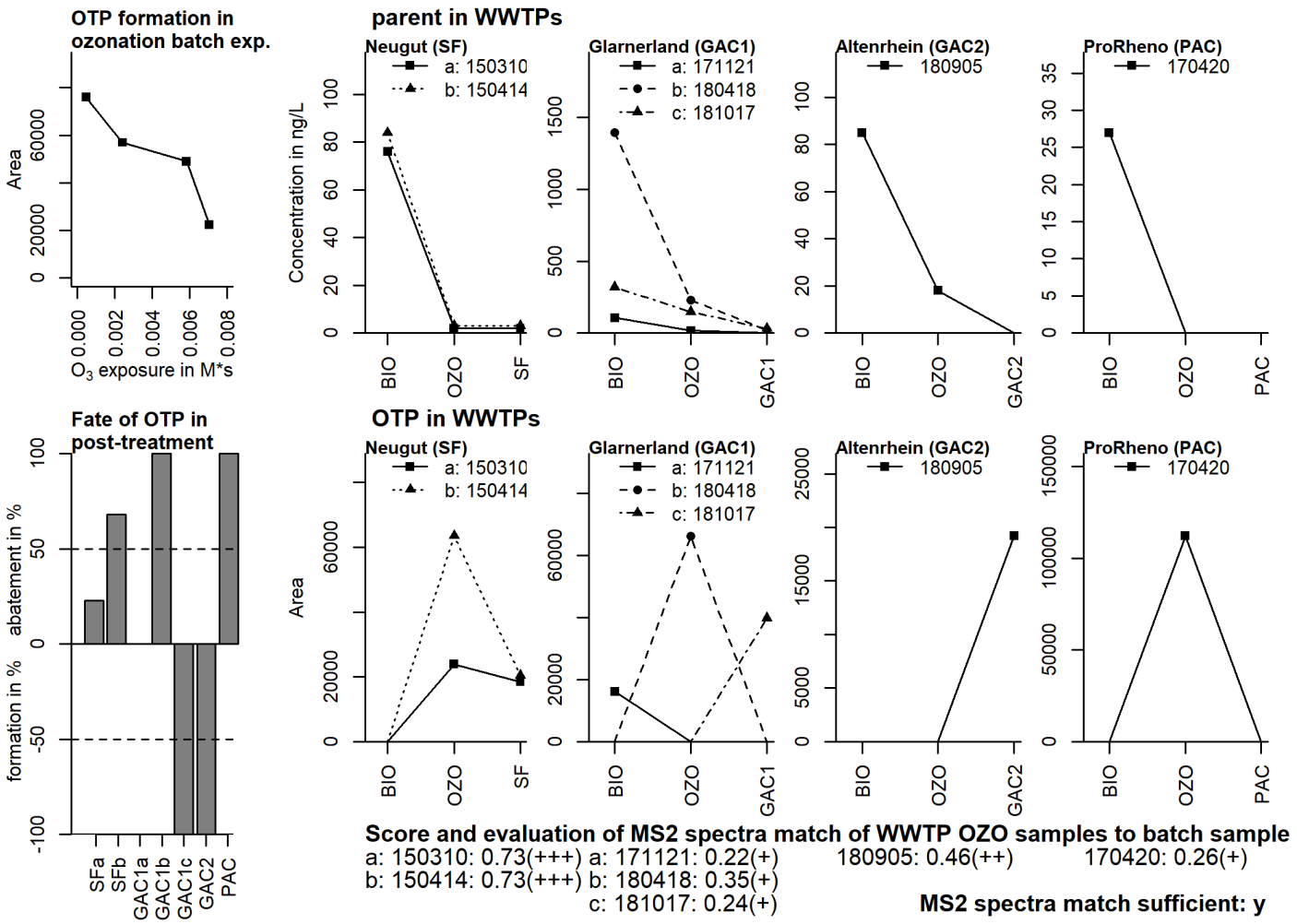
Confidence Level

Level 3

Massbank ID

ET407001

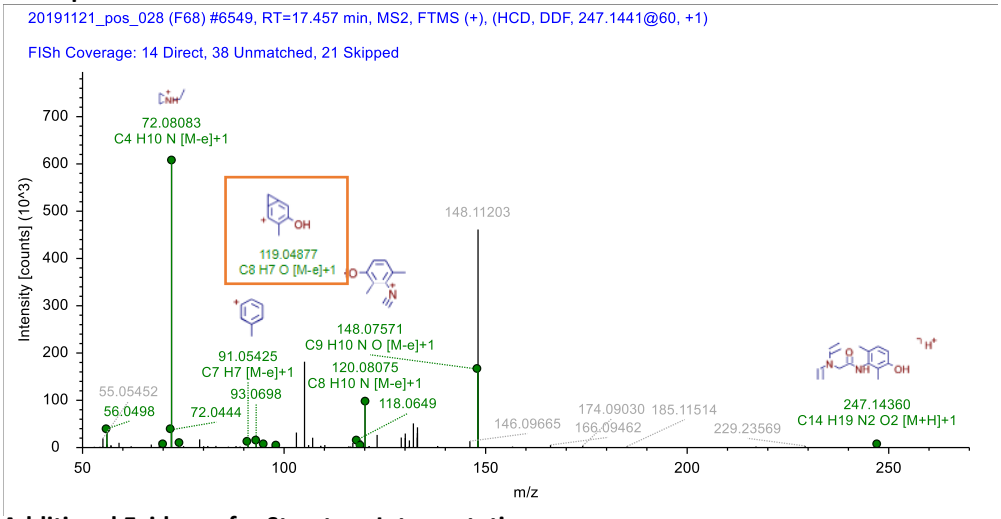
Name LID_p_247.1438_17.8



MS Spectra

Pos 247.1438 [m+H]+

MS2 Spectra



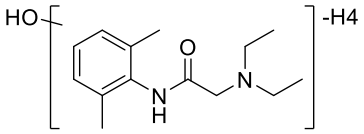
Formula

C14H18O2N2

Atomic modification

-H4 +O

Proposed Structure



Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is –H4 +O. The oxygen atom was likely added by hydroxylation via an OH radical. Fragment 191 suggests that the oxygen atom was added at the dimethylphenyl moiety, in this case most likely at a methyl moiety, because once formed, phenol moieties quickly further react during ozonation.

To fit the molecular formula, four hydrogen atoms need to be abstracted from the drawn structure. The exact type and location of the modifications remain unknown. The structures of the fragments are drawn exemplarily.

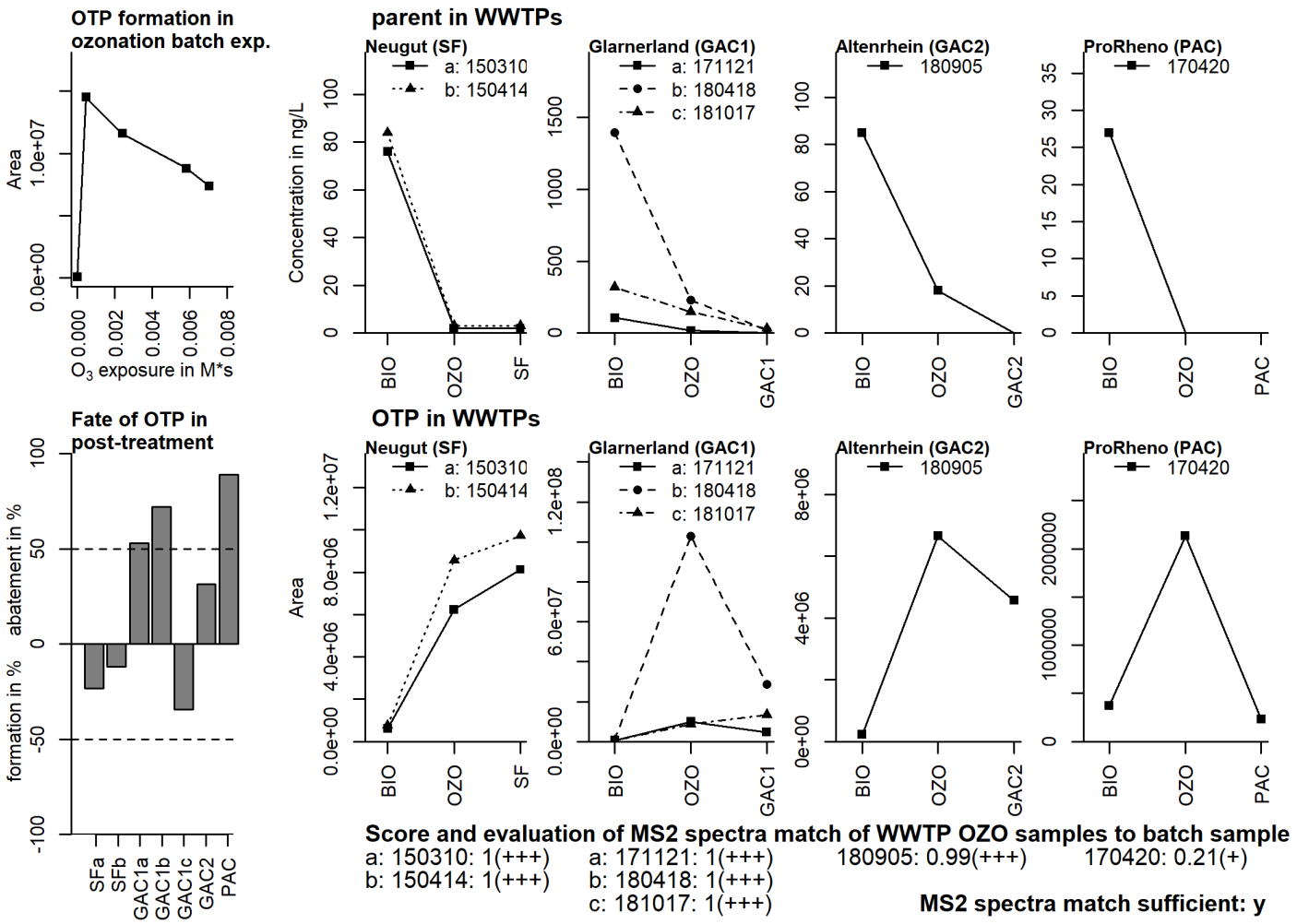
Confidence Level

Level 3

Massbank ID

ET402701

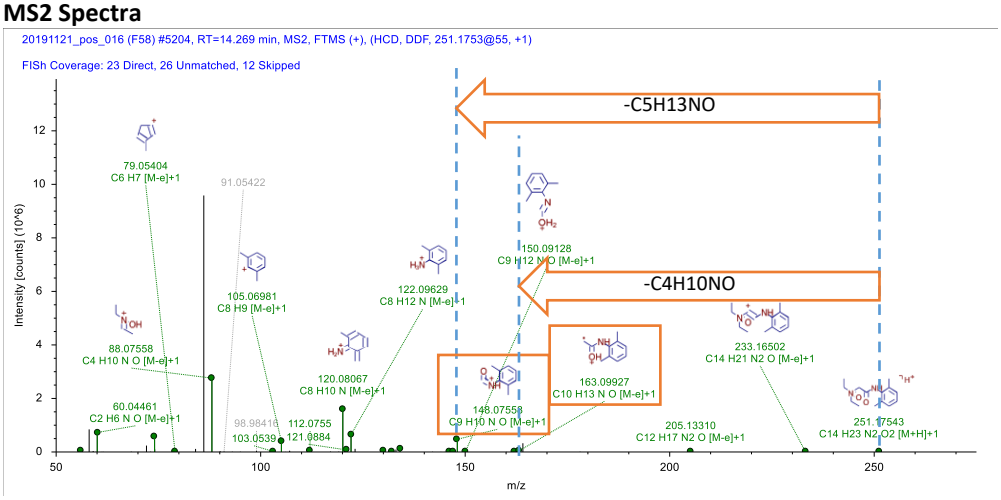
Name LID_p_251.1752_13.6



MS Spectra

Pos 251.1752 [m+H]+

MS2 Spectra



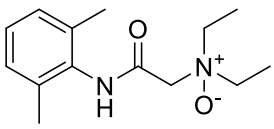
Formula

C14H22O2N2

Atomic modification

+O

Proposed Structure



Confidence Level

Level 1

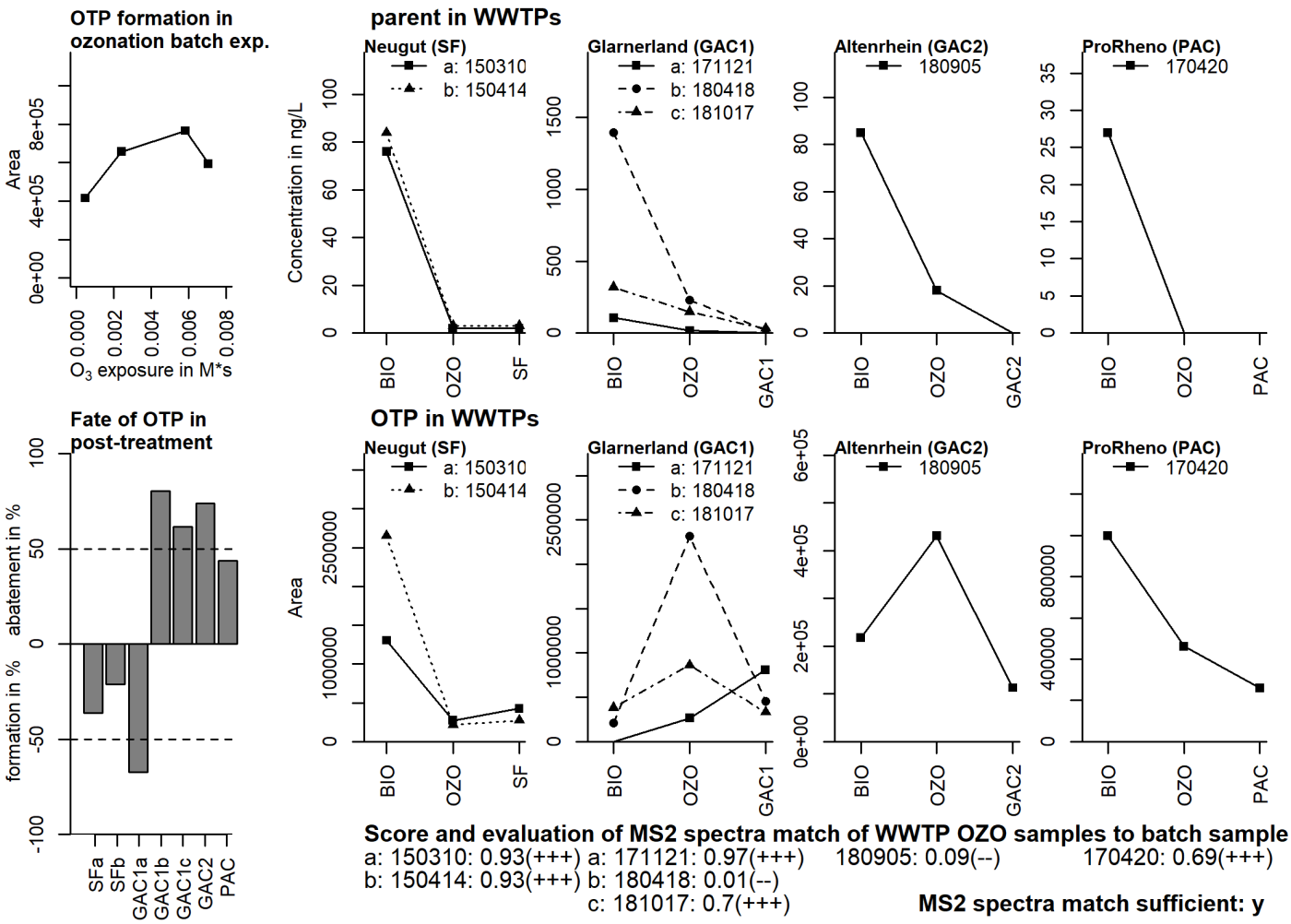
Massbank ID

ET402801

Additional Evidence for Structure Interpretation

Tertiary amines are very reactive to form *N*-oxides during ozonation (von Sonntag & von Gunten 2012). Therefore, the formation of a *N*-oxide at the diethylmethylamine moiety is very likely. The neutral loss of C5H13NO between the precursor and fragment 148 fits to a cleavage of the diethylmethylamine *N*-oxide moiety. The neutral loss of C5H10NO between the precursor and fragment 148 fits to a cleavage of the diethylamine N-oxide moiety. Merel et al. (2017) identified lidocaine *N*-oxide as major ozone transformation product. The MS^2 spectrum here matches the reference spectrum we recorded for lidocaine *N*-oxide.

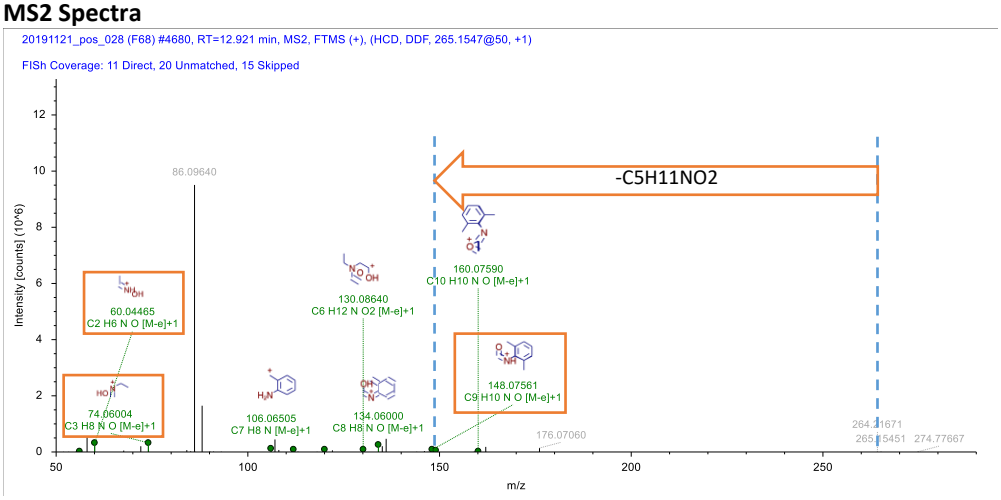
Name LID_p_265.1545_12.4



MS Spectra

Pos 265.1545 [m+H]+

MS2 Spectra



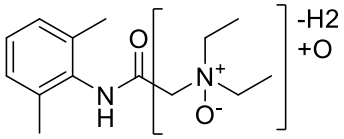
Formula

C14H20O3N2

Atomic modification

-H2 +O2

Proposed Structure



Confidence Level

Level 3

Massbank ID

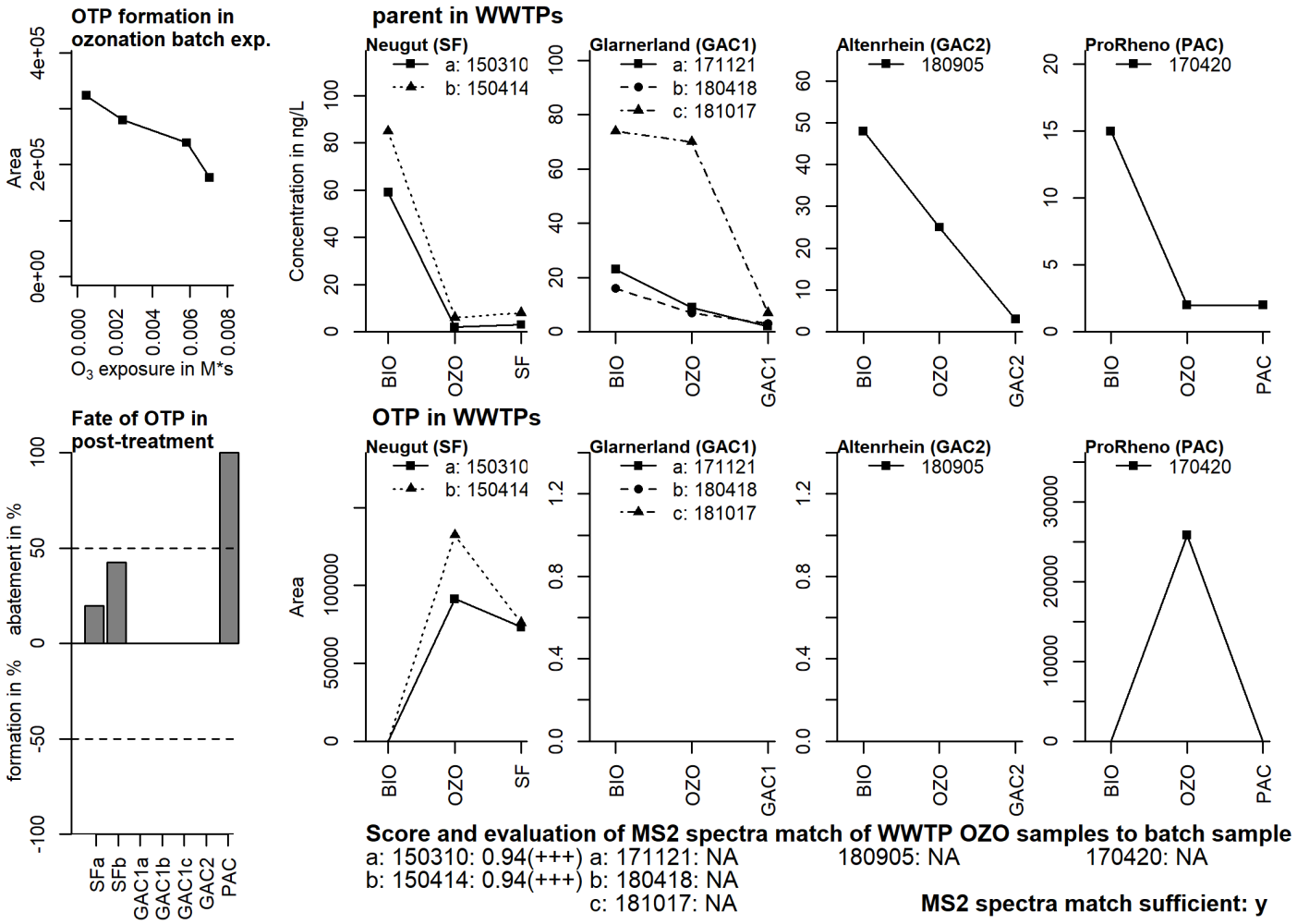
ET402901

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is –H2 +O2. Since tertiary amines are very reactive to form *N*-oxides during ozonation (von Sonntag & von Gunten 2012), it is probable that the *N*-oxide was formed in this OTP as well, which is supported by fragments 74 and 60. The OTP LID_p_251.1752_13.6 was identified as lidocaine *N*-oxide.

The neutral loss of C5H11NO2 between precursor and fragment 148 indicates also that the modification +O2 –H2 occurred at the diethylmethylamine. This modification fits to an N-oxidation in combination with a formation of a carbonyl group, likely at a CH2 of an ethyl moiety. The exact type and position of the modification remain unknown. The structures of the MS^2 fragments are drawn exemplarily.

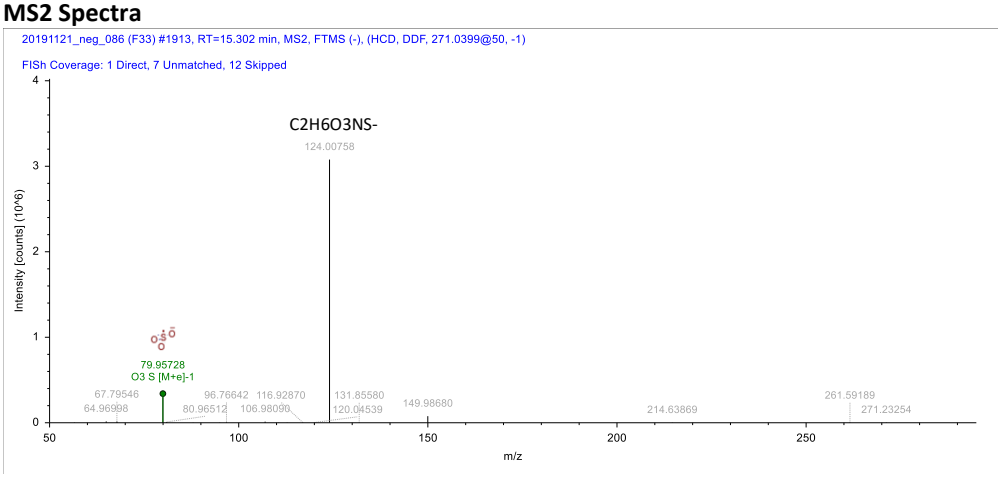
Name LVI_n_271.0392_15.1



MS Spectra

Neg 272.0392 [m-H]-

MS2 Spectra



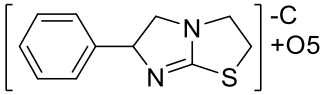
Formula

C10H12O5N2S

Atomic modification

-C +O5

Proposed Structure



Additional Evidence for Structure Interpretation

Fragment 79 indicates the formation of a sulfonic acid moiety. The exact type and location of the remaining modification(s) remain unknown.

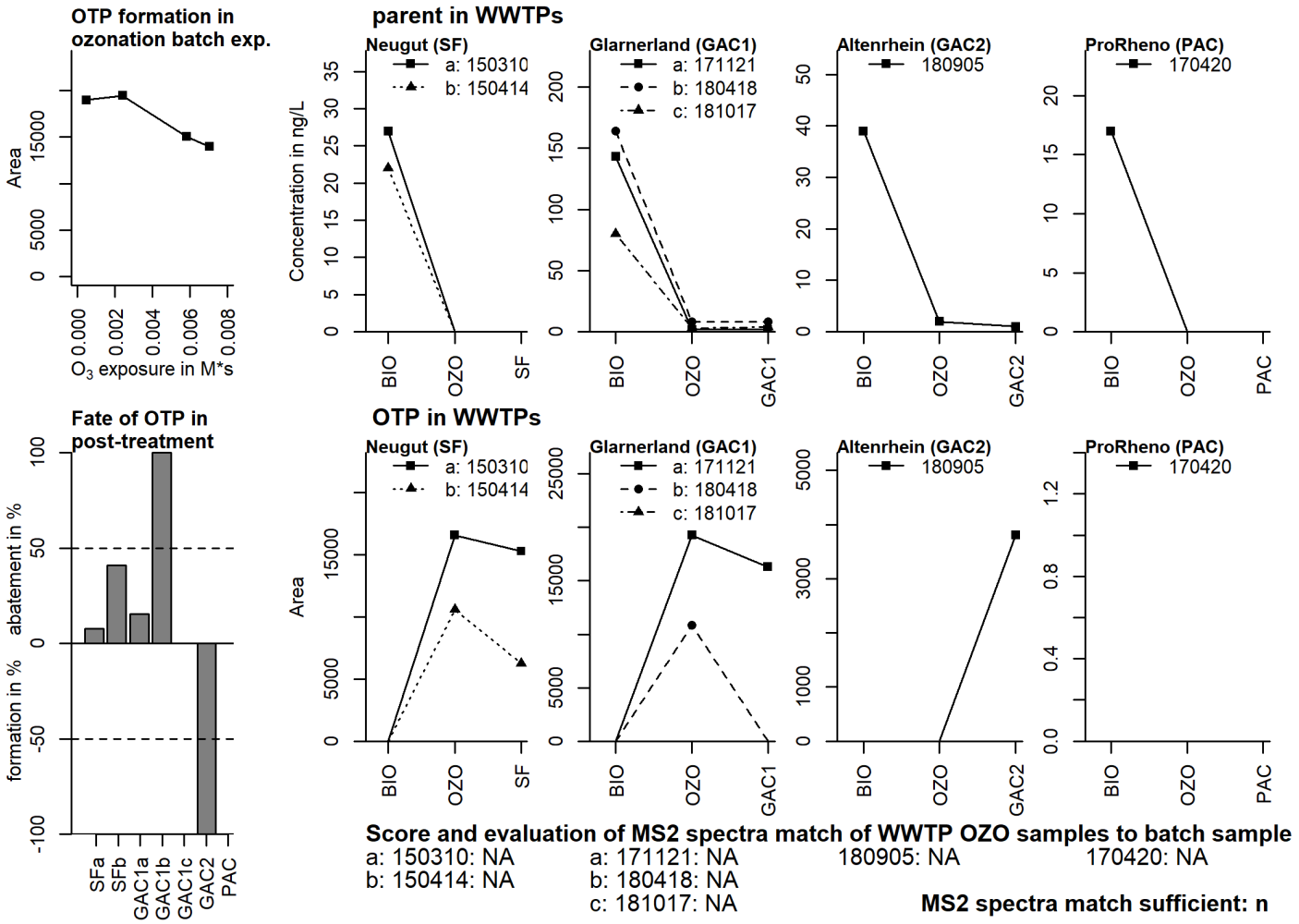
Confidence Level

Level 3

Massbank ID

ET406501

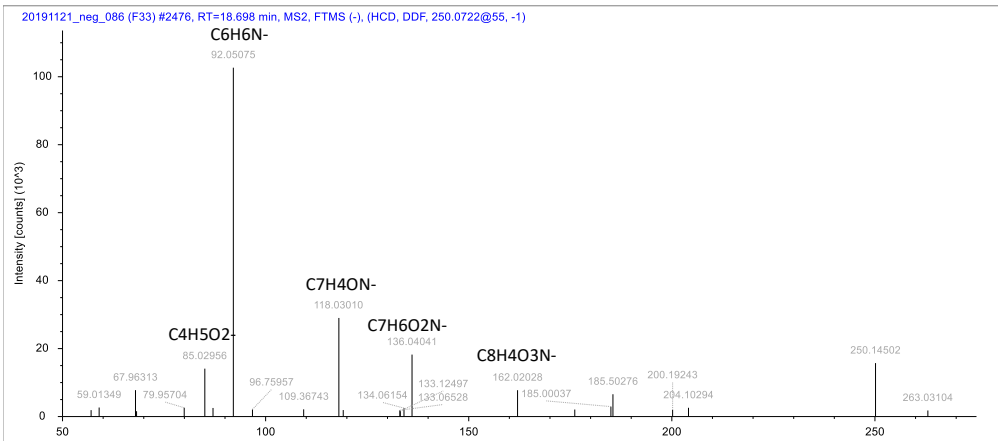
Name MAA_n_250.0719_18.5



MS Spectra

Neg 250.0719 [m-H]-

MS2 Spectra



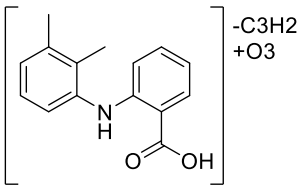
Formula

C12H13O5N

Atomic modification

-C3H2 +O3

Proposed Structure



Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is –C3H2 +O3. This OTP was likely formed by opening of an aromatic ring, which is known to happen during ozonation (von Sonntag & von Gunten 2012). Fragment 92 with formula C6H6N indicates that one of the two rings was not cleaved. The exact type and location of the modifications remain unknown.

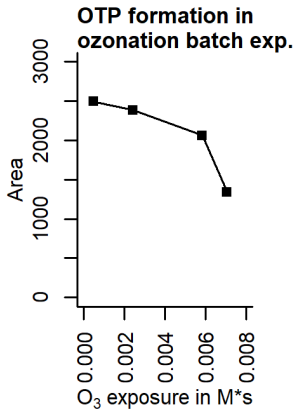
Confidence Level

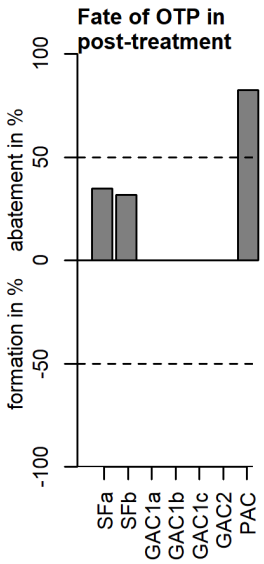
Level 3

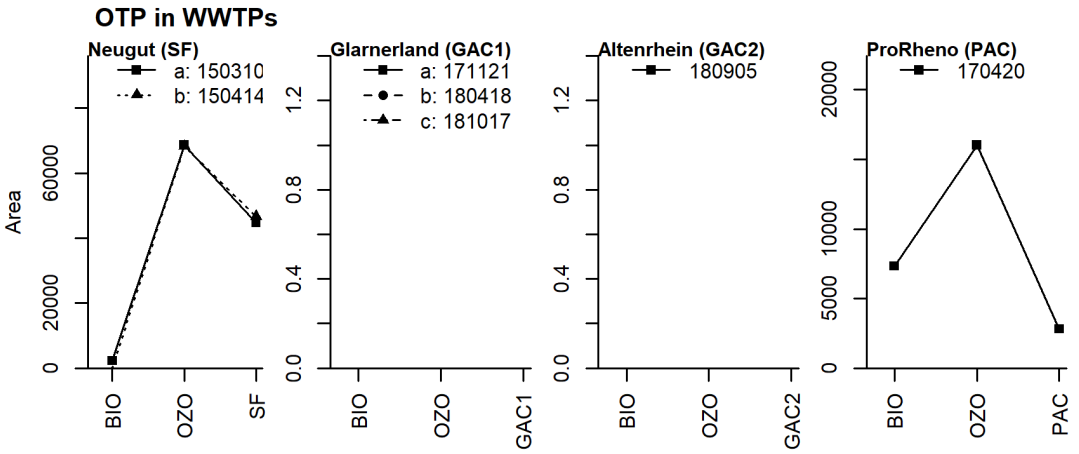
Massbank ID

ET406601

Name nk_n_293.1148_16.2







Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

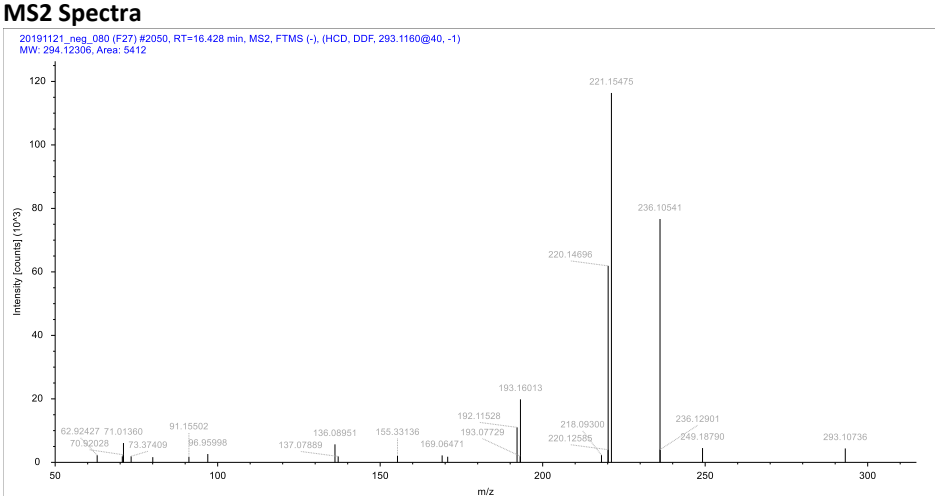
a: 150310: 0.94(+++) a: 171121: NA 180905: NA 170420: 0.96(+++)
b: 150414: 0.94(+++) b: 180418: 0.92(+++)
c: 181017: NA

MS2 spectra match sufficient: y

MS Spectra

Neg 293.1148 ?

MS2 Spectra



Formula

?

Atomic modification

?

Proposed Structure

Additional Evidence for Structure Interpretation

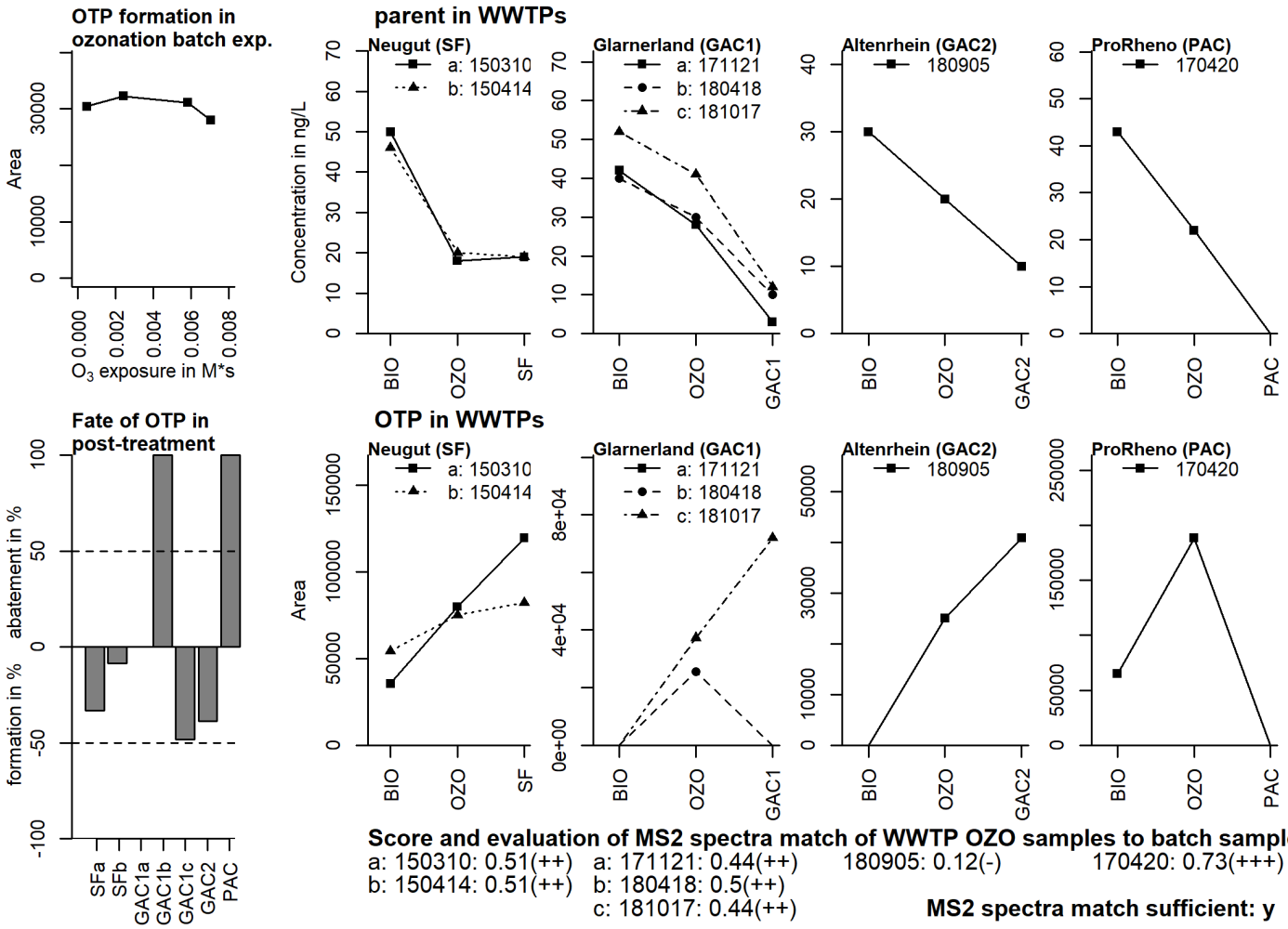
Confidence Level

Level 5

Massbank ID

ET406901

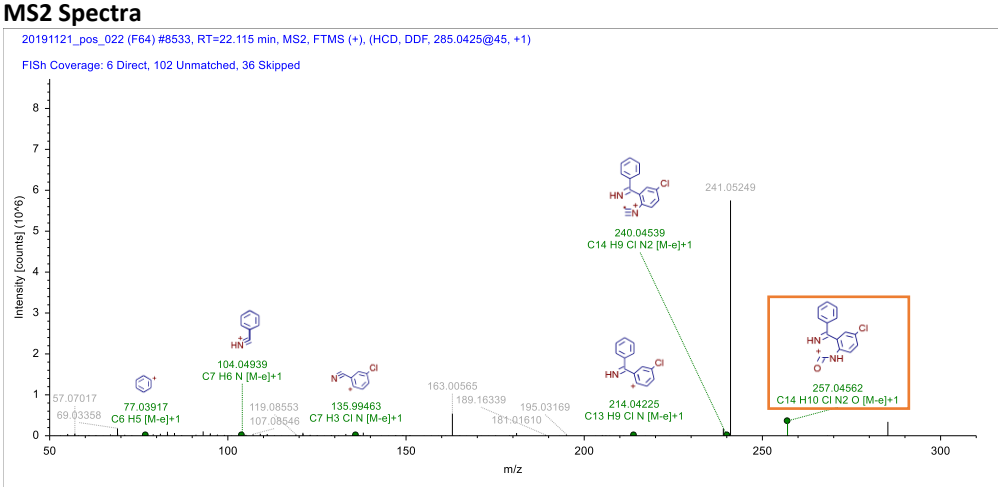
Name OXA_p_285.0423_21.9



MS Spectra

Pos 285.0423 [m+H]+

MS2 Spectra



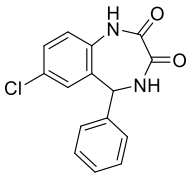
Formula

C15H9O2N2Cl

Atomic modification

-H2

Proposed Structure



Additional Evidence for Structure Interpretation

The MS^2 fragments at the nominal masses 257, 214 and 104 were also observed for the parent compound. They indicate that the structure drawn for the fragment 257 is a substructure of this OTP. This OTP probably was formed by oxidation of the C-OH bond to a carbonyl group.

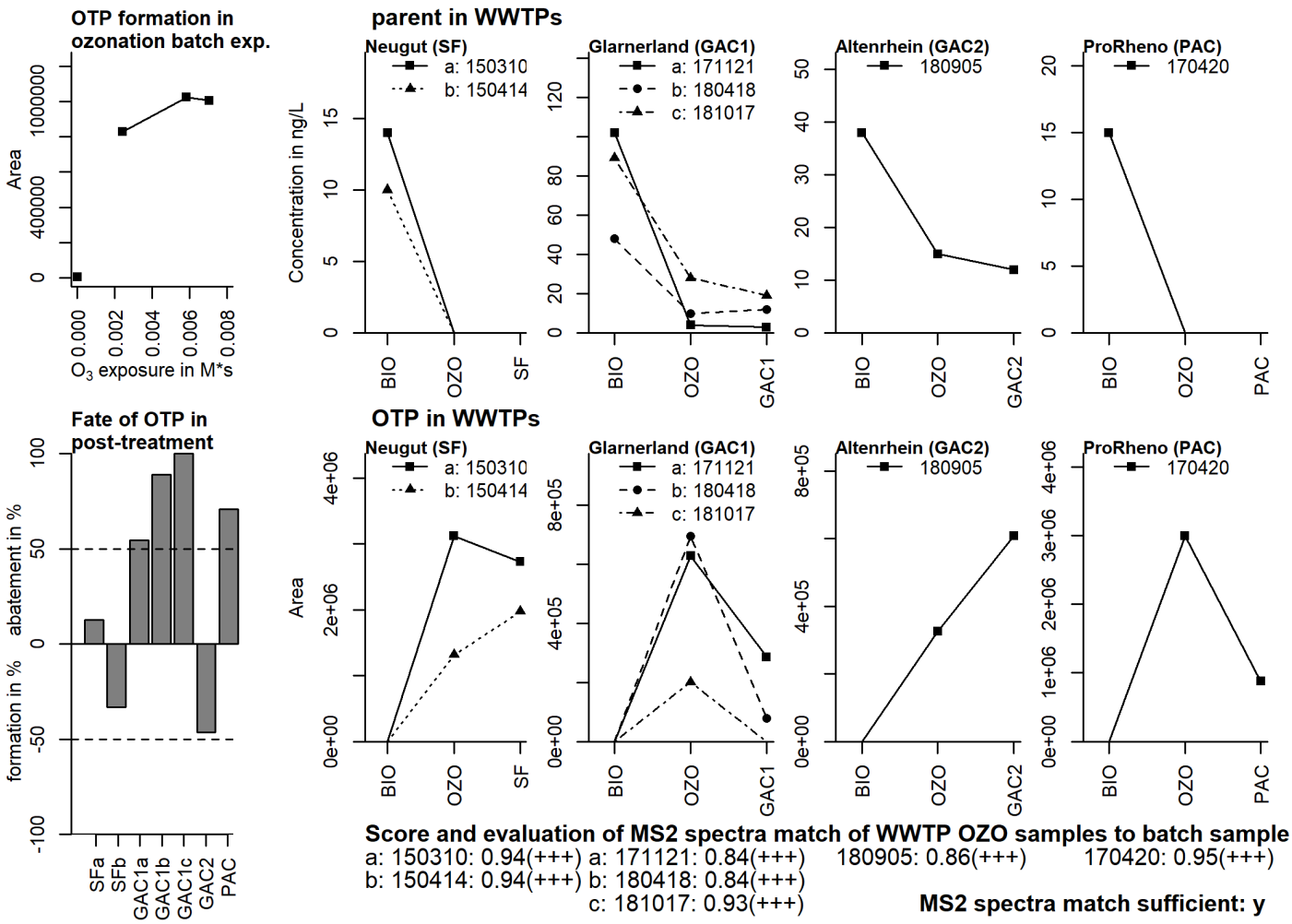
Confidence Level

Level 3

Massbank ID

ET403001

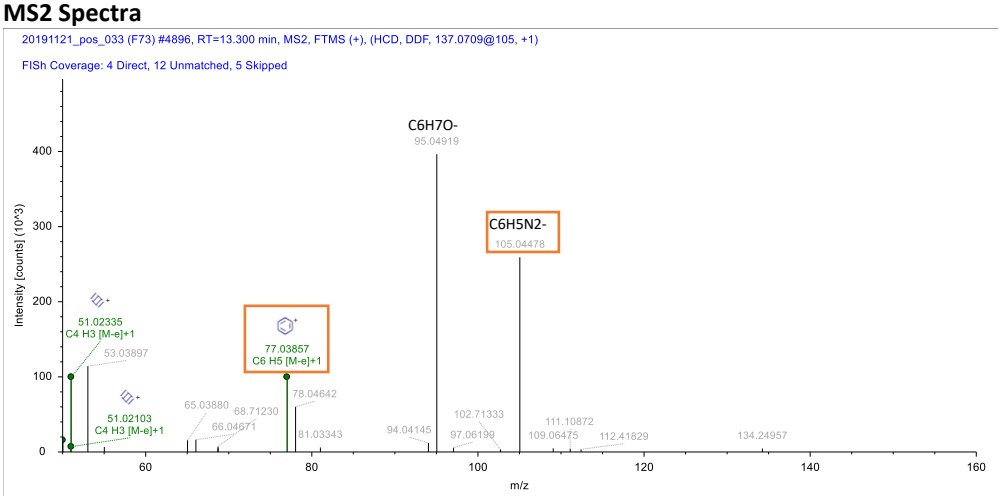
Name PHE_p_137.0709_12.9



MS Spectra

Pos 137.0708 [m+H]+

MS2 Spectra



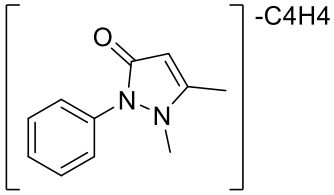
Formula

C7H8ON2

Atomic modification

-C4H4

Proposed Structure



Confidence Level

Level 3

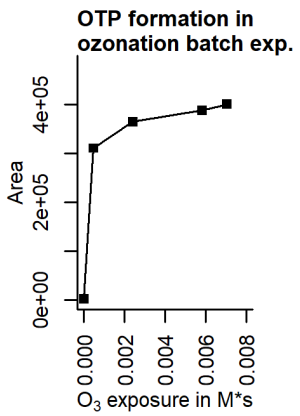
Massbank ID

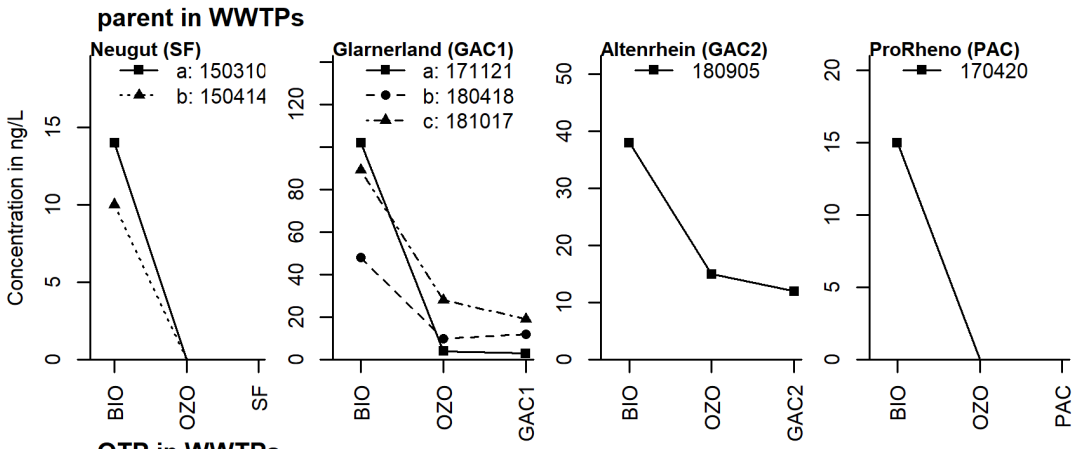
ET403101

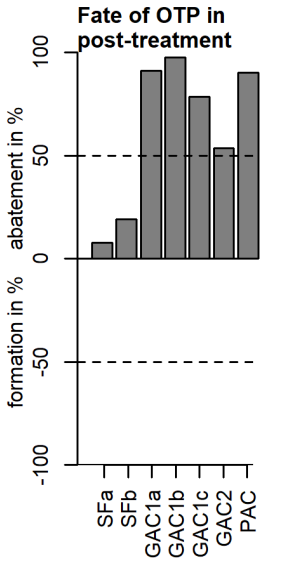
Additional Evidence for Structure Interpretation

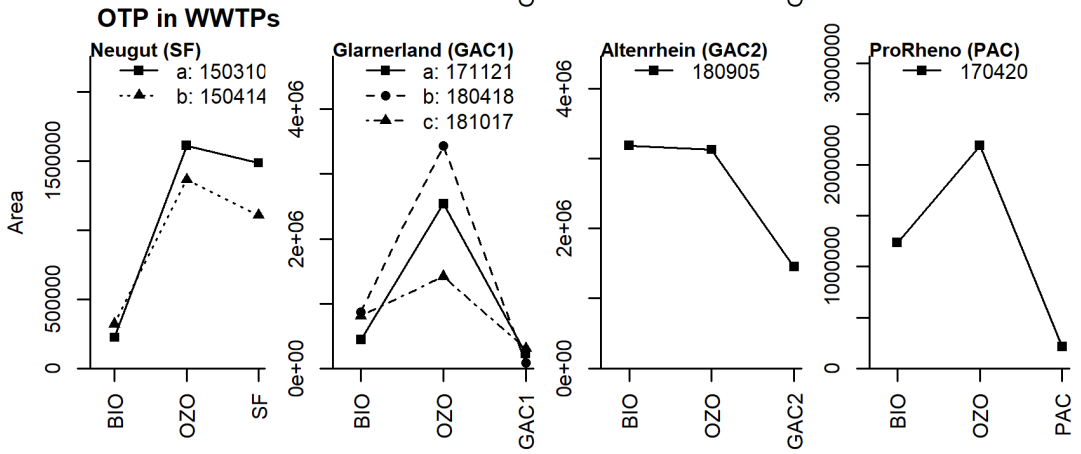
For the parent compound phenazone two OTPs (PHE_p_137.0709_14.1 and PHE_p_137.0709_12.9) with the exact mass of 137.0708 were observed at different retention times (14.1 and 12.9 min). The MS^2 spectra of these OTPs are very similar. The MS^2 fragment at the nominal masses 77 was also observed for the parent compound. It indicates that a phenyl moiety is a substructure of this TP. Fragment 92 and 105 fit to the formula C6H6N and C6H5N respectively. Both TPs were probably formed after a rearrangement, resulting in the formation of two isomers. The exact type of the modification remains unknown.

Name PHE_p_137.0709_14.1









Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

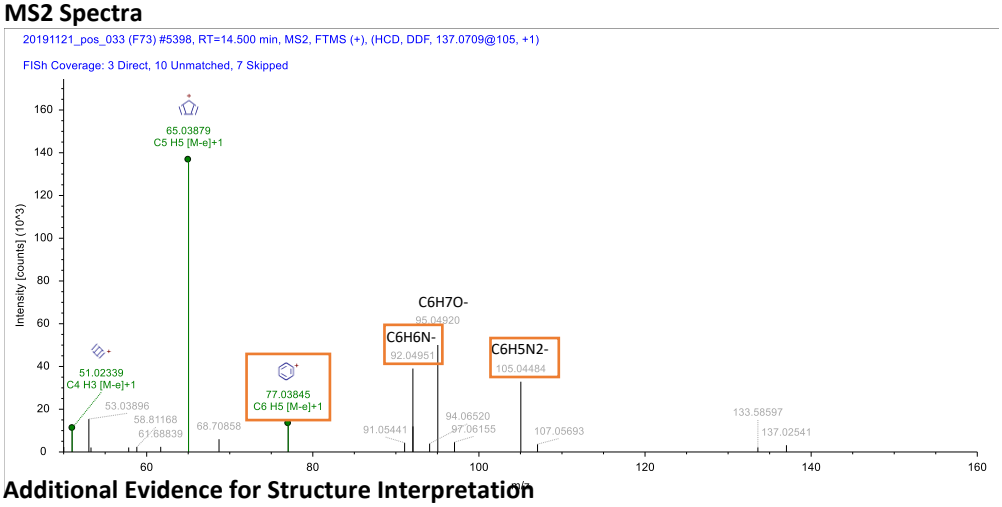
a: 150310: 0.57(++) a: 171121: 0.79(+++) 180905: 0.56(++) 170420: 0.84(+++)
b: 150414: 0.57(++) b: 180418: 0.94(+++)
c: 181017: 0.95(+++)

MS2 spectra match sufficient: y

MS Spectra

Pos 137.0708 [m+H]+

MS2 Spectra



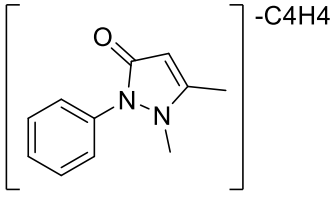
Formula

C7H8ON2

Atomic modification

-C4H4

Proposed Structure



Confidence Level

Level 3

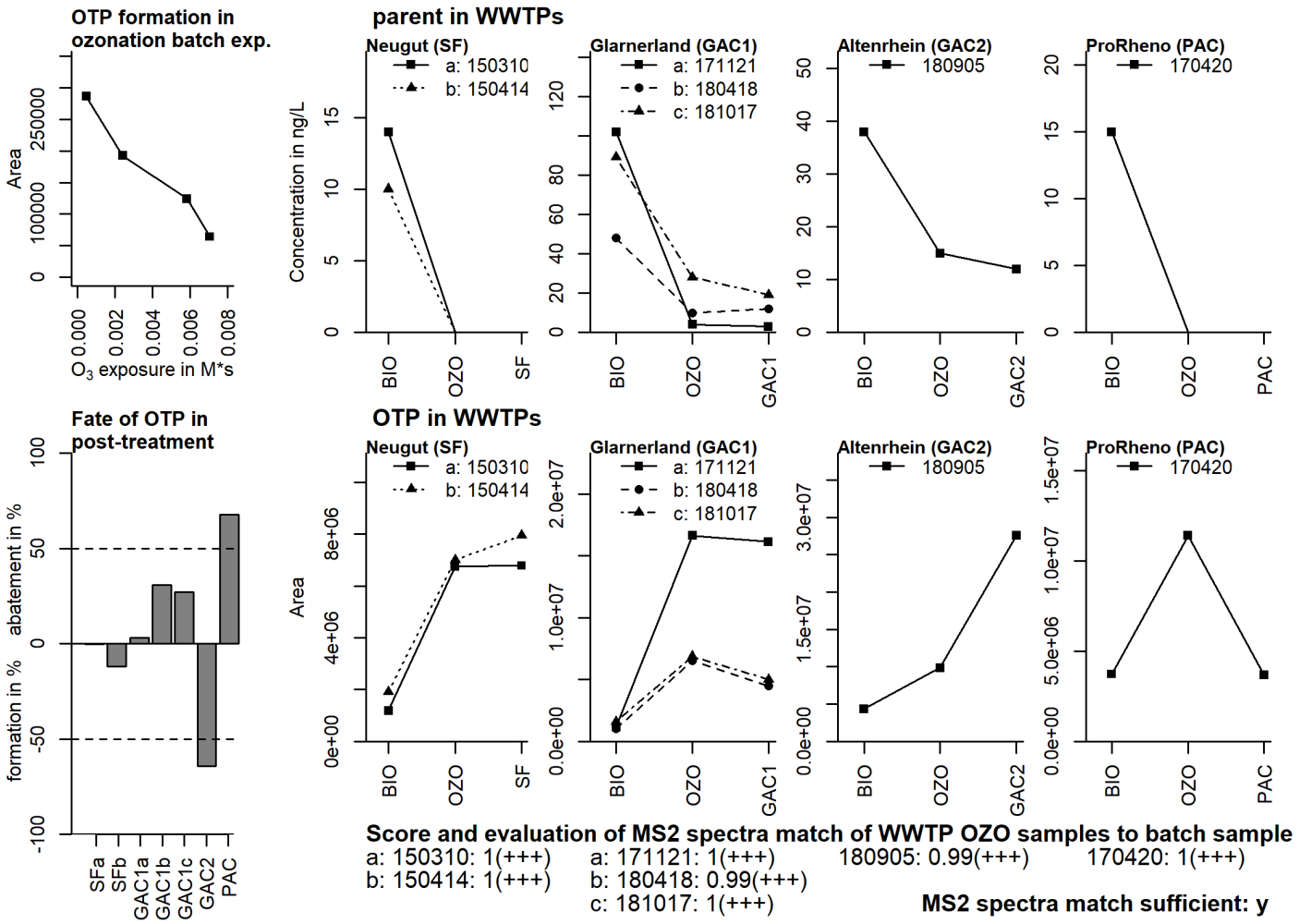
Massbank ID

ET403201

Additional Evidence for Structure Interpretation

For the parent compound phenazone two OTPs (PHE_p_137.0709_14.1 and PHE_p_137.0709_12.9) with the exact mass of 137.0708 were observed at different retention times (14.1 and 12.9 min). The MS^2 spectra of these OTPs are very similar. The MS^2 fragment at the nominal masses 77 was also observed for the parent compound. It indicates that a phenyl moiety is a substructure of this TP. Fragment 92 and 105 fit to the formula C6H6N and C6H5N respectively. Both TPs were probably formed after a rearrangement, resulting in the formation of two isomers. The exact type of the modification remains unknown.

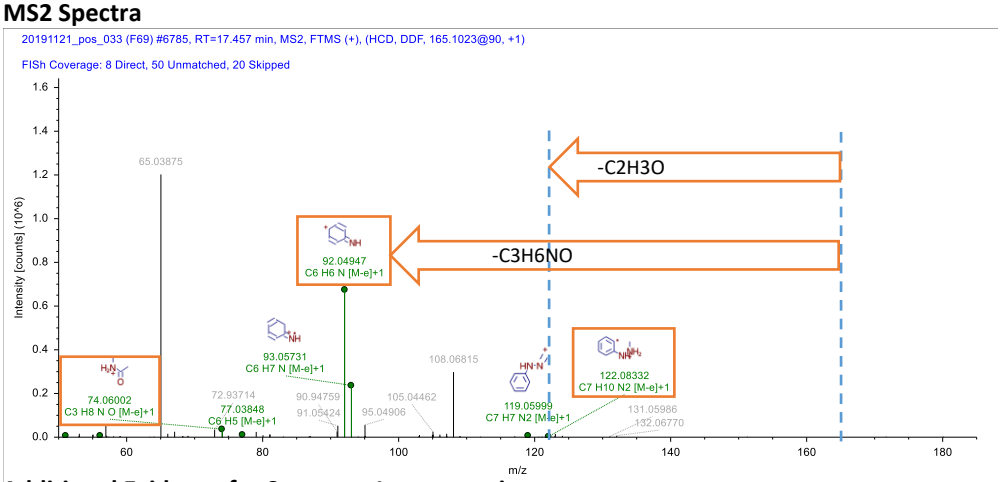
Name PHE_p_165.1021_17.6



MS Spectra

Pos	165.1021	[m+H]+
Neg	163.0876	[m-H]-

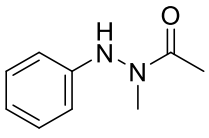
MS2 Spectra



Formula
C9H12ON2

Atomic modification
-C2

Proposed Structure



Confidence Level
Level 3

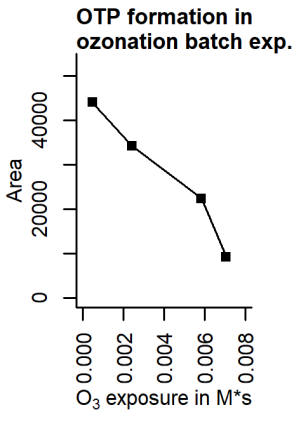
Massbank ID
ET403301

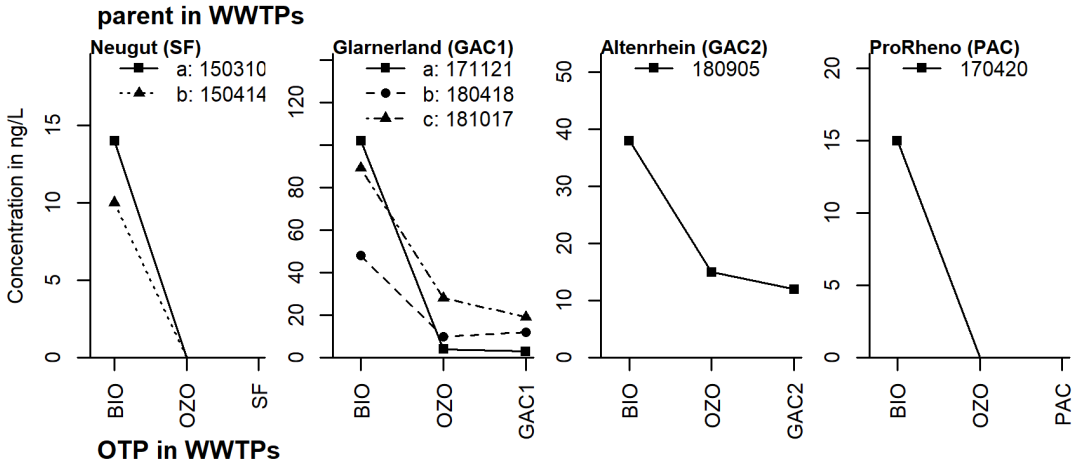
Additional Evidence for Structure Interpretation

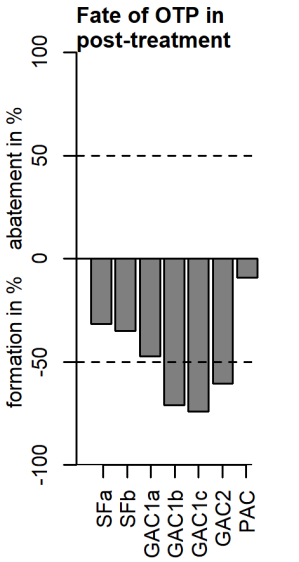
The MS^2 fragments at the nominal masses 92 and 77 were also observed for the parent compound. They indicate that the structure drawn for the fragment 92 is a substructure of this OTP.

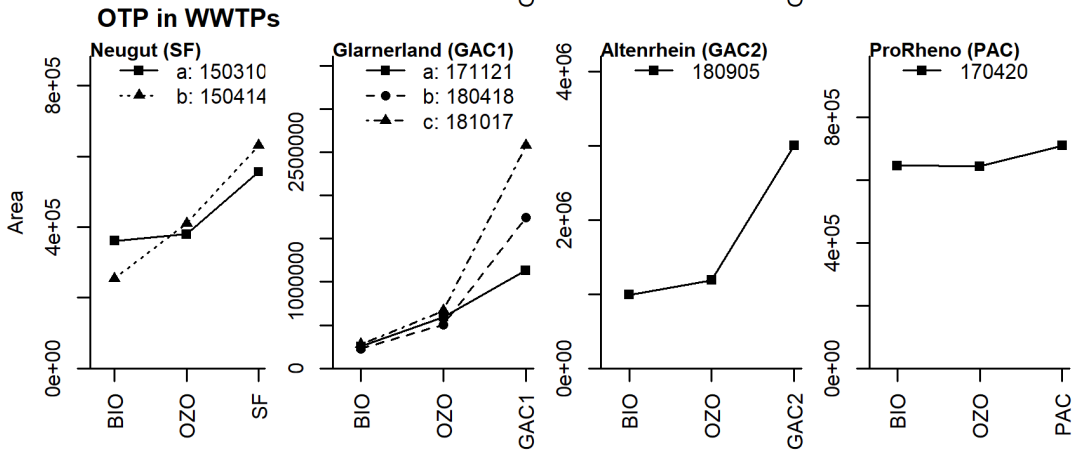
The neutral loss of C2H3O between the precursor and fragment 122 fits to a cleavage within the amide moiety. The neutral loss of C3H7NO between the precursor and fragment 92 fits to a cleavage of the N-N bond and fragment 74 corresponds to the cleaved moiety. This structure has been suggested as major ozone transformation product of phenazone in different studies (Miao et al. 2015, Favier et al. 2015).

Name PHE_p_237.0868_15.1









Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

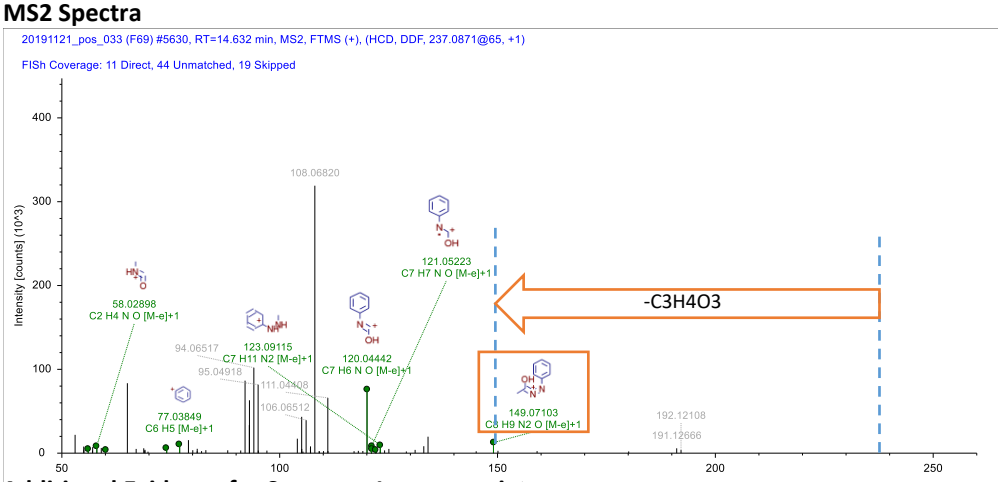
a: 150310: 0.85(+++) a: 171121: 0.71(+++) 180905: 0.88(+++) 170420: 0.83(+++)
b: 150414: 0.85(+++) b: 180418: 0.87(+++)
c: 181017: 0.76(+++)

MS2 spectra match sufficient: y

MS Spectra

Pos	237.0868	[m+H]+
Neg	235.0722	[m-H-]

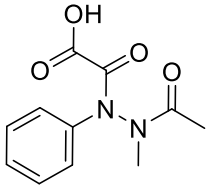
MS2 Spectra



Formula
C11H12O4N2

Atomic modification
+O3

Proposed Structure



Confidence Level
Level 3

Massbank ID
ET403401

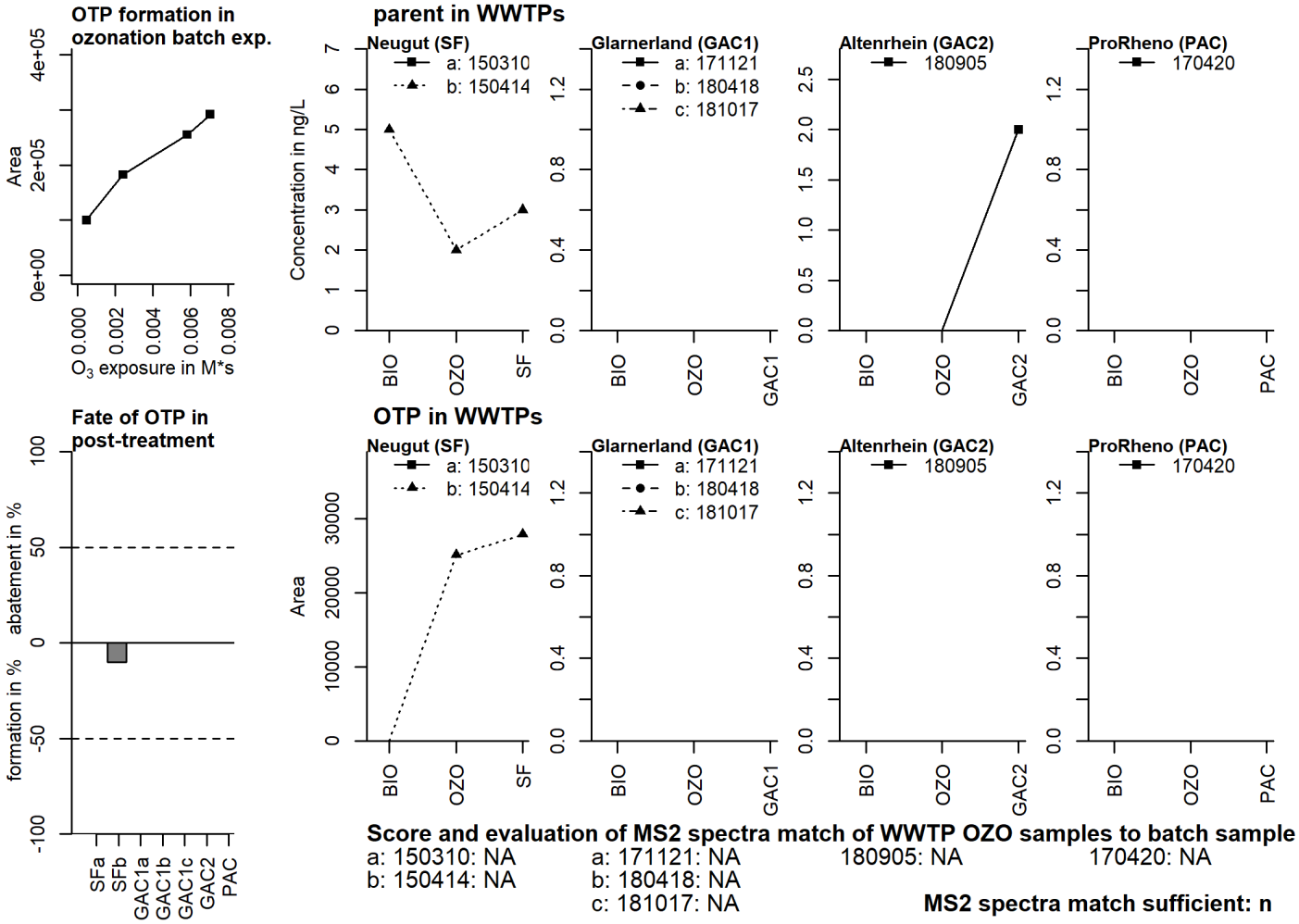
Additional Evidence for Structure Interpretation

The MS^2 fragments at the nominal masses 149 and 77 were also observed for the parent compound. They indicate that the structure drawn for the fragment 149 is a substructure of this OTP.

The neutral loss of C3H4O3 between the precursor and fragment 149 fits to the cleavage of a methyl group and an oxoacetic like structure.

This structure has been suggested as OTP of phenazone by Miao et al. (2015).

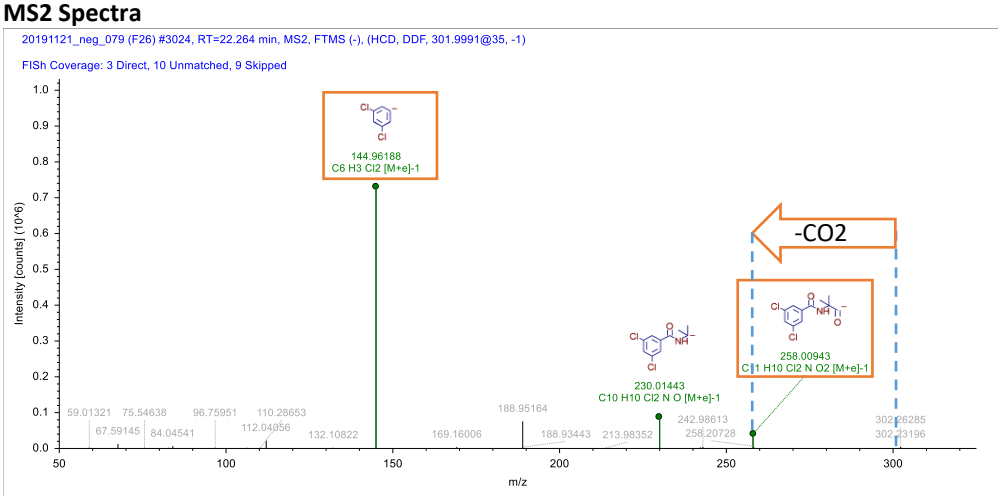
Name PYZ_n_301.9991_22.6



MS Spectra

Neg 301.9991 [m-H]-

MS2 Spectra



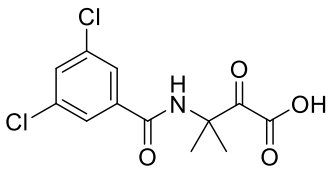
Formula

C12H11O4NCl2

Atomic modification

+O3

Proposed Structure



Additional Evidence for Structure Interpretation

The MS^2 fragment at the nominal mass 144 was also observed for the parent compound. It indicates that the drawn structure of the MS^2 fragment 144 is a substructure of this OTP and that the modification likely did not take place at the aromatic moiety.
Ozonolysis of alkynes are known to give diketone products (Bailey 1982). Furthermore, the neutral loss of CO2 between the proposed structure and fragment 148 indicates the presence of a carboxylic acid moiety. Therefore, the formation of the drawn structure is likely.

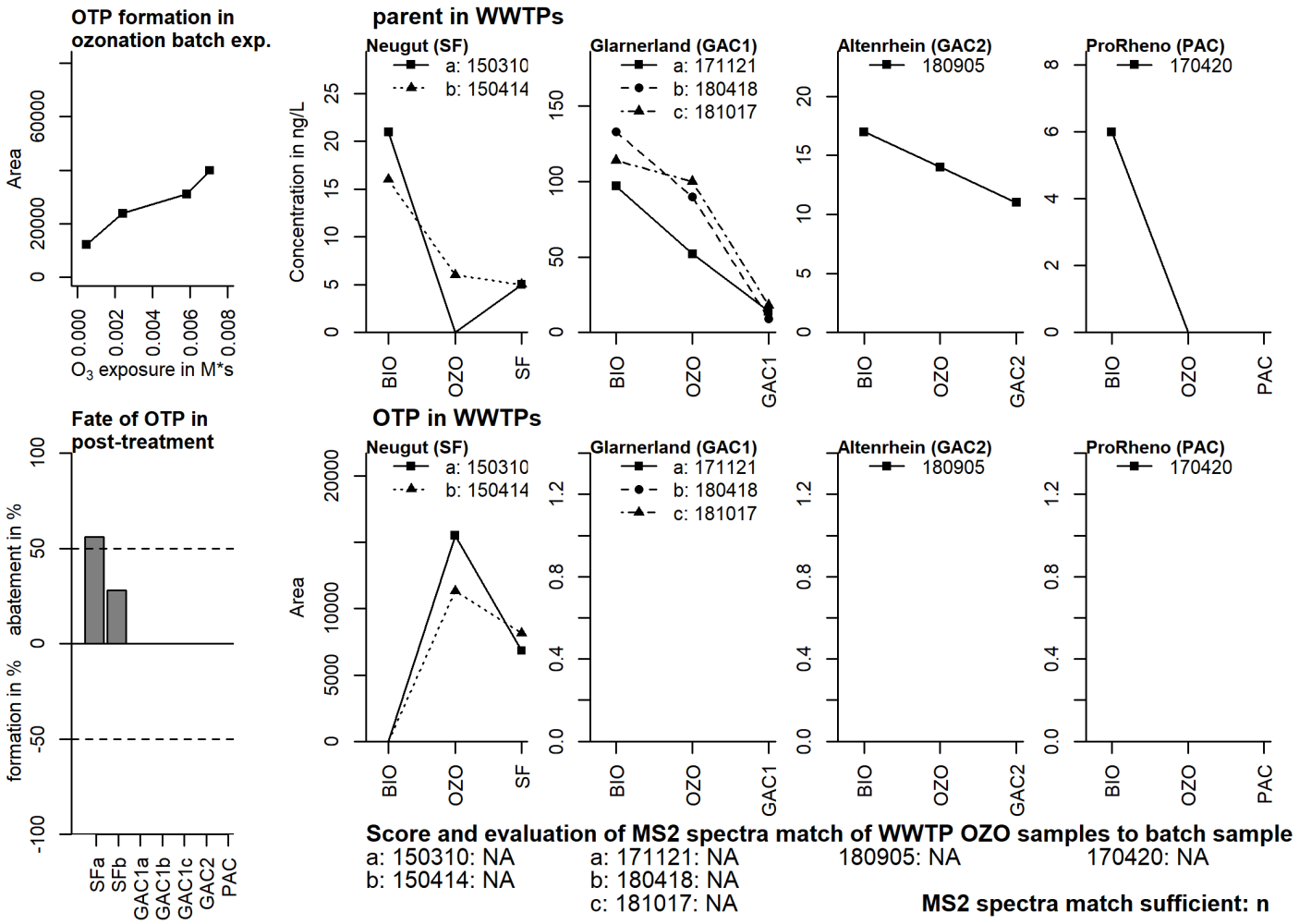
Confidence Level

Level 3

Massbank ID

ET407101

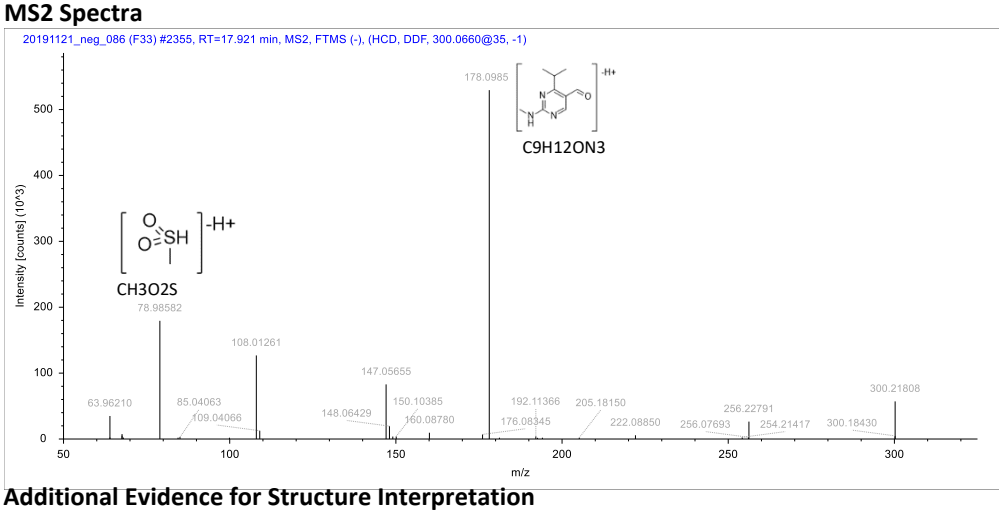
Name ROS_n_300.0656_17.7



MS Spectra

Neg 300.0656 [m-H]-

MS2 Spectra



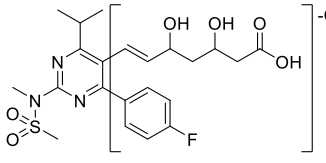
Formula

C11H15O5N3S

Atomic modification

-C11H13FO

Proposed Structure



Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is – C11H13FO. This fits to cleavages and the addition of oxygen atoms within the dihydroxyheptenoic acid moiety and the fluorophenyl moiety, likely at the C-C double bond since ozone is known to react with olefins (von Sonntag & von Gunten 2012). The exact type and location of the modification(s) remain unknown. The structures of the MS^2 fragments are drawn exemplarily.

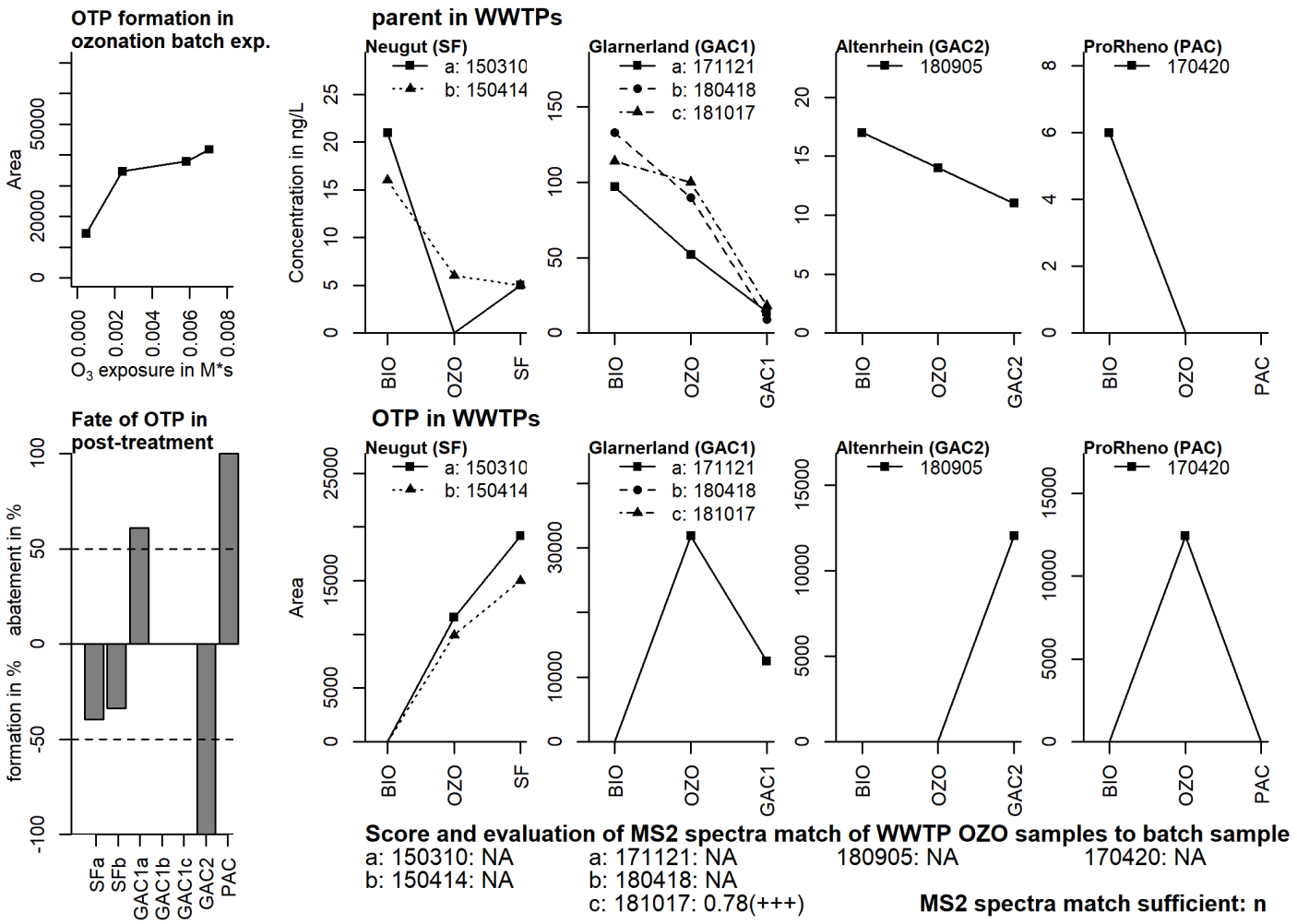
Confidence Level

Level 3

Massbank ID

ET407201

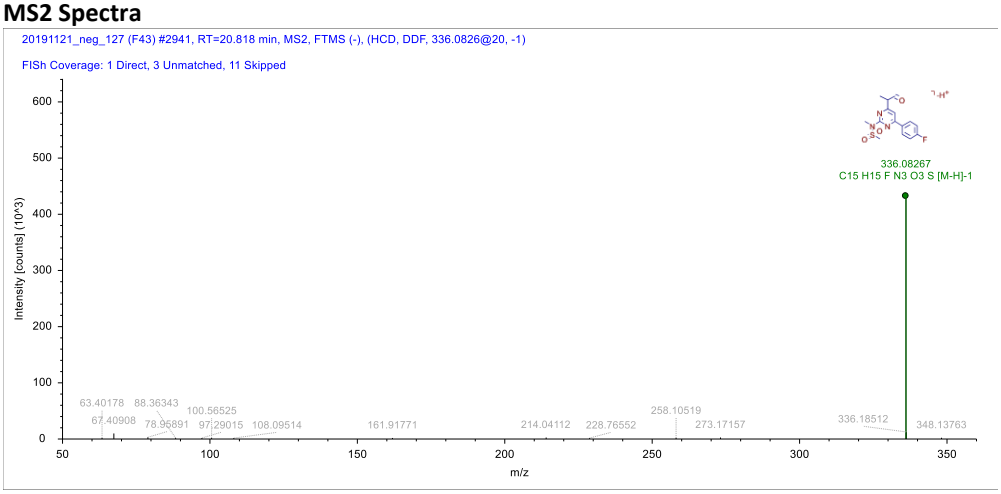
Name ROS_n_336.0821_20.7



MS Spectra

Neg 336.0821 [m-H]-

MS2 Spectra



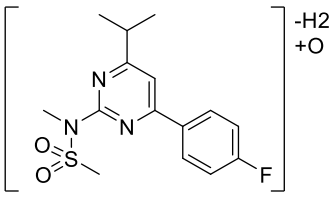
Formula

C15H16O3N3FS

Atomic modification

-C7H12O3

Proposed Structure



Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is –-C7H12O3. This fits the cleavage of the dihydroxyheptenoic acid moiety and likely the formation of a carbonyl group. The exact type and location of the modification(s) remain unknown. The structures of the MS^2 fragments are drawn exemplarily.

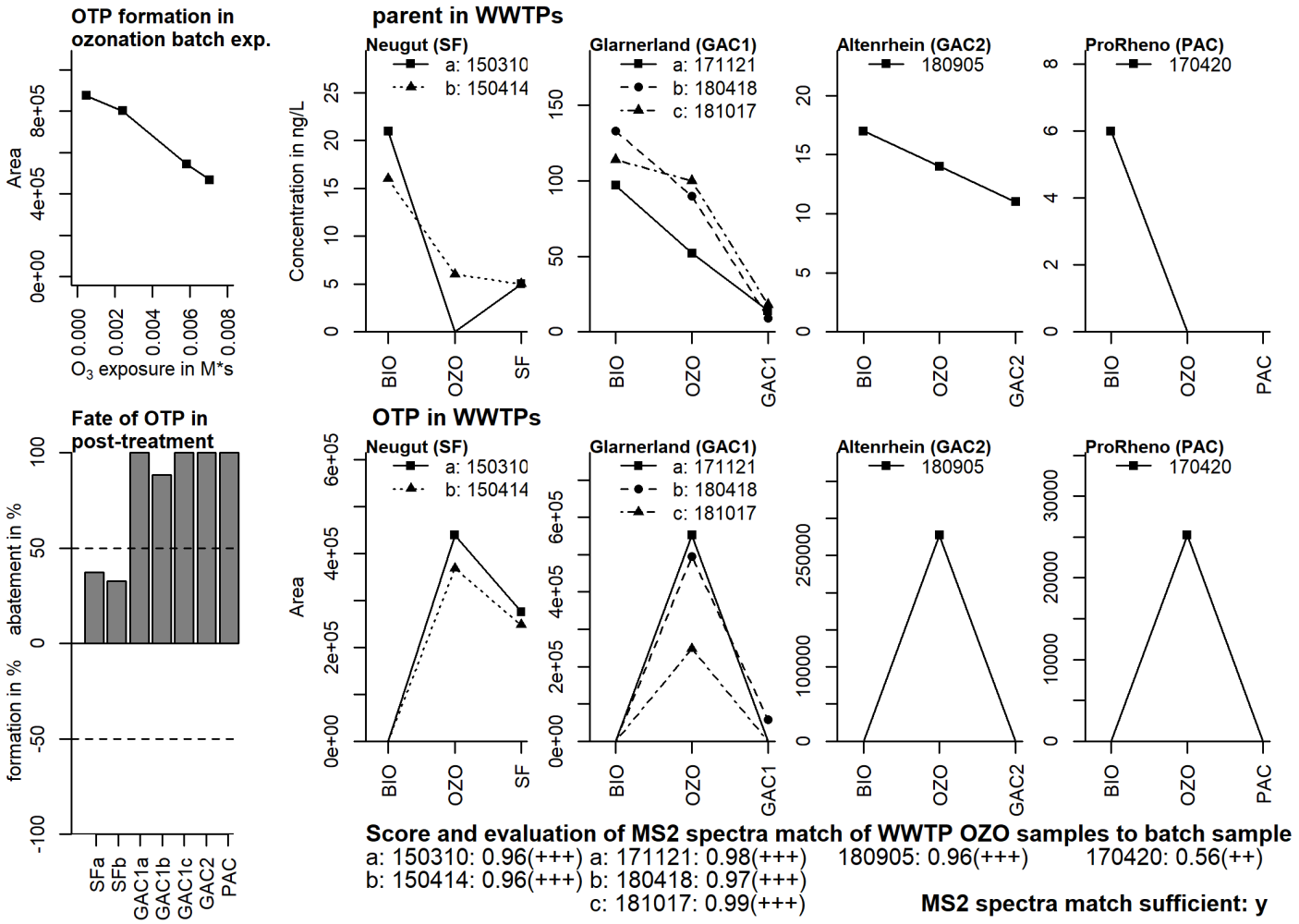
Confidence Level

Level 3

Massbank ID

ET407301

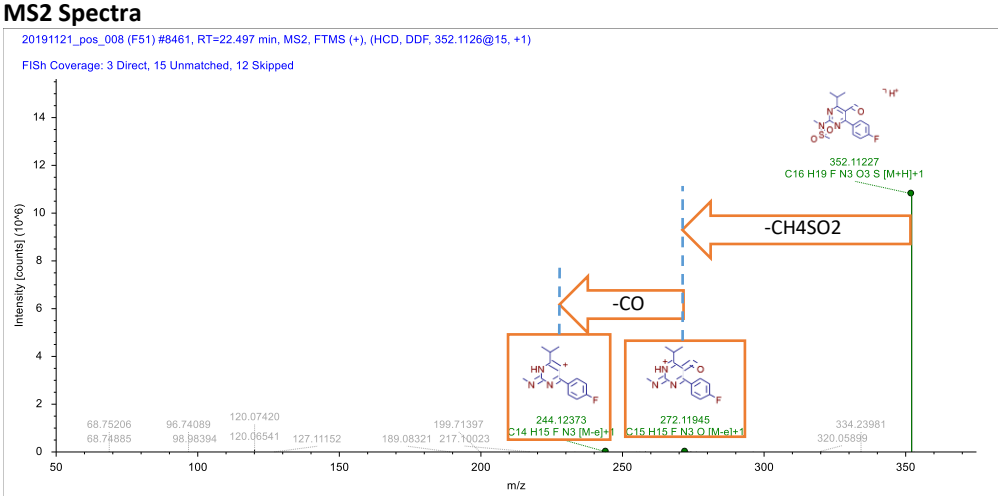
Name ROS_p_352.1124_22.0



MS Spectra

Pos 352.11236 [m+H]+

MS2 Spectra



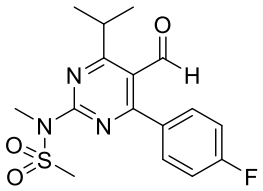
Formula

C16H18O3N3FS

Atomic modification

-C6H10O3

Proposed Structure



Confidence Level

Level 3

Massbank ID

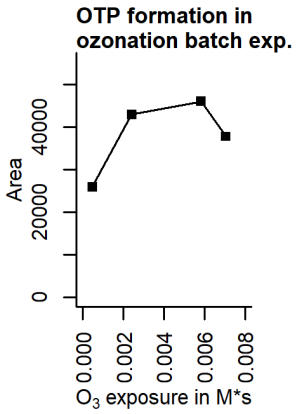
ET403501

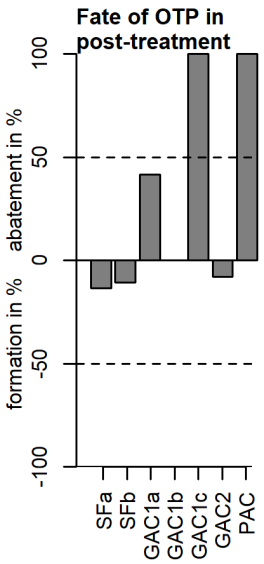
Additional Evidence for Structure Interpretation

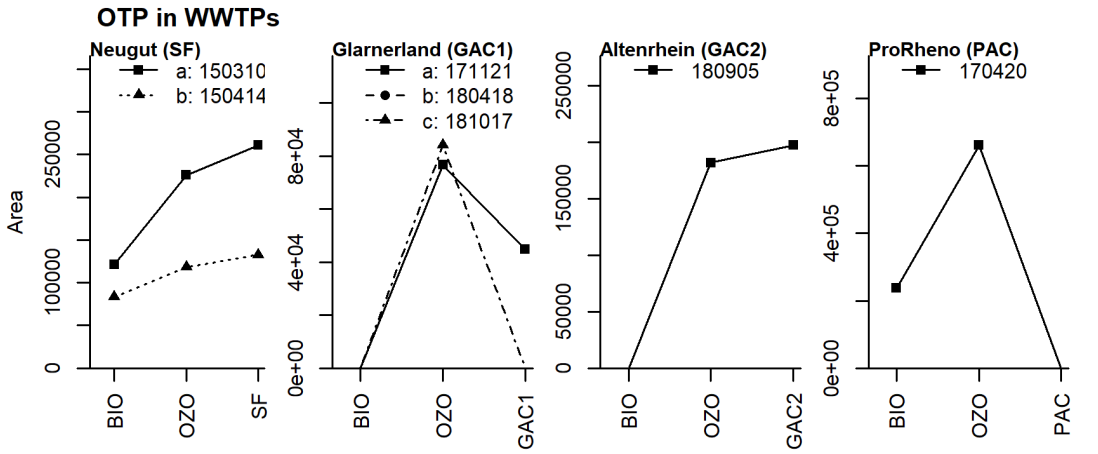
The atomic modification from the elemental formula of the parent compound to this OTP is -C6H10O3. This modification fits to a cleavage of the parent molecule at the C-C double bond of the dihydroxyheptenoic acid moiety and the addition of an oxygen atom. The neutral loss of CH4SO2 indicates that the modification did not occur at methylsulfonyl moiety. The CO loss between fragment 272 and fragment 244 indicates the formation of an aldehyde moiety.

Olefins are known to react with ozone, resulting in the oxidative cleavage of the C-C double bond and the formation of two terminal carbonyl moieties (von Sonntag & von Gunten 2012). This indicates that the formation of the proposed structure is likely.

Name Sartans_p_251.0924_17.9







Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

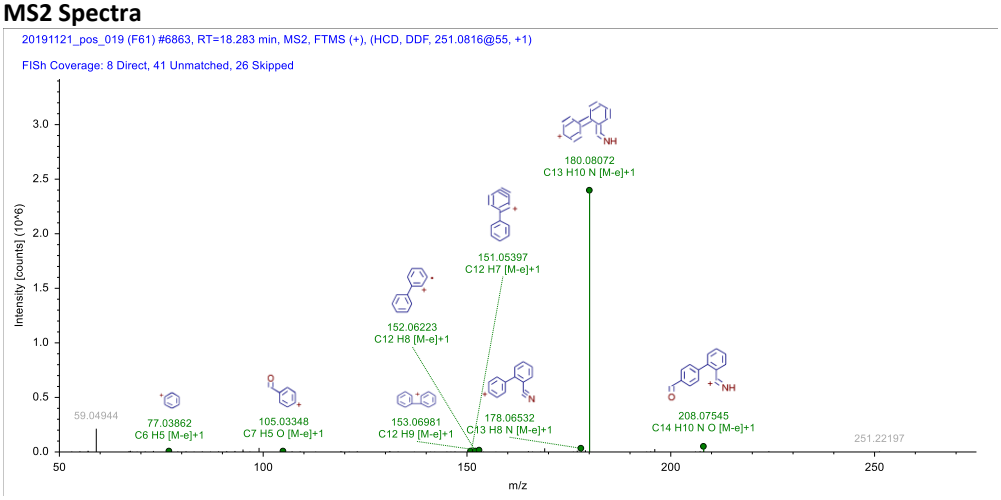
a: 150310: 0.56(++) a: 171121: 0.46(++) 180905: 0.72(+++) 170420: 0.32(+)
b: 150414: 0.56(++) b: 180418: 0.74(+++)
c: 181017: 0.19(-)

MS2 spectra match sufficient: y

MS Spectra

Pos 251.0924 [m+H]+

MS2 Spectra



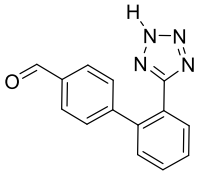
Formula

C14H10ON4

Atomic modification

Multiple parent substances

Proposed Structure



Confidence Level

Level 3

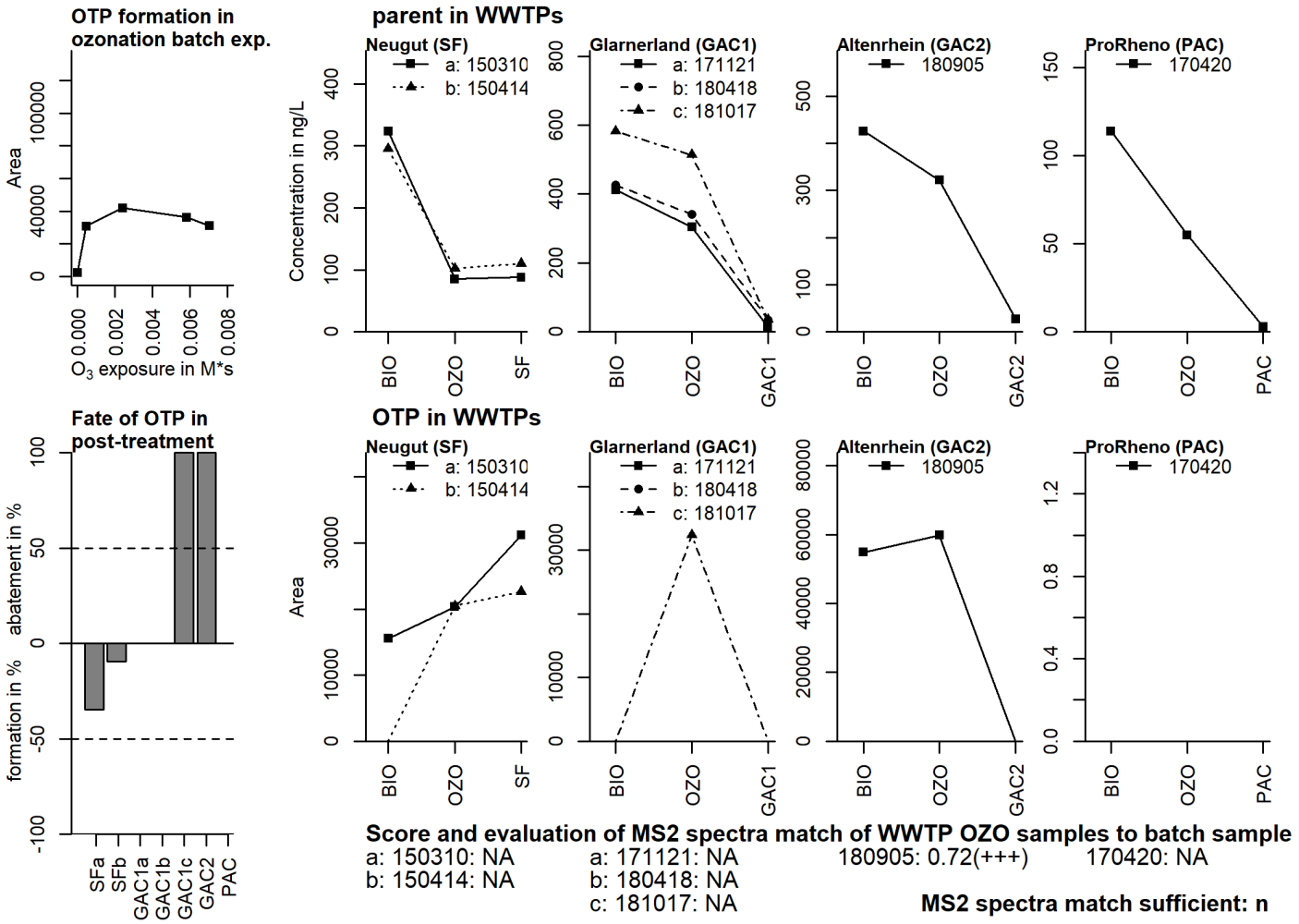
Massbank ID

ET403601

Additional Evidence for Structure Interpretation

The chemical formula for this TP is C14H10ON4 and fits to the tetrazolebiphenylmethyl moiety, which is common for all sartans and to which an oxygen atom was added. Diehle et al. (2019) suggested this OTP as a probable OTP for valsartan (Level 2b). The observed evidence from our MS spectrum and the MS^2 spectrum match the one from Diehle et al. (2019).

Name SIT_n_405.0789_18.6



Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

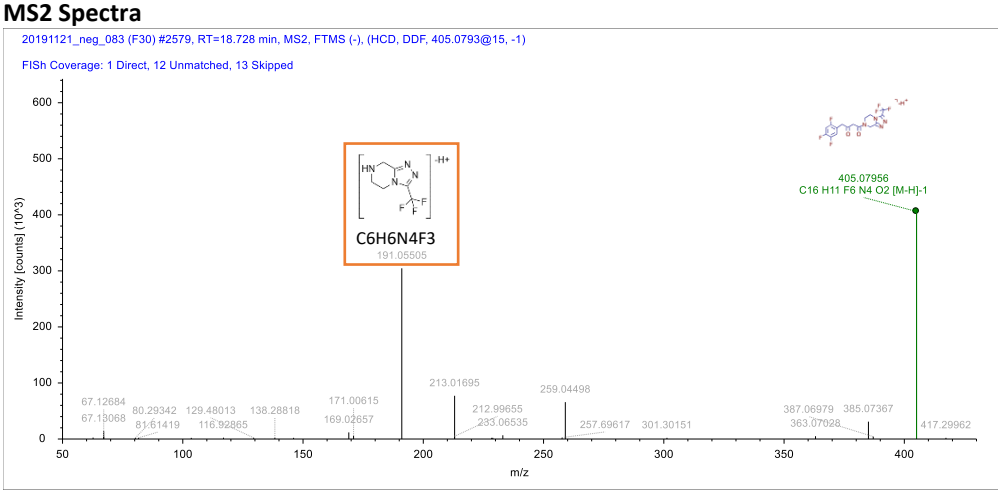
a: 150310: NA
b: 150414: NA
a: 171121: NA
b: 180418: NA
c: 181017: NA
180905: 0.72(+++)
170420: NA

MS2 spectra match sufficient: n

MS Spectra

Neg 405.0789 [m-H]-

MS2 Spectra



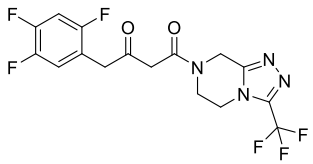
Formula

C16H12O2N4F6

Atomic modification

-NH3 +O

Proposed Structure



Additional Evidence for Structure Interpretation

The MS^2 fragment at the nominal mass 191 was also observed for the parent compound. It indicates that the drawn structure of the MS^2 fragment 191 is a substructure of this OTP and that the modification likely did not take place at the aromatic moiety.
The atomic modification from the elemental formula of the parent compound to this OTP fits to the cleavage of the primary amine moiety and the formation of a carbonyl moiety.
The drawn structure was confirmed (level 1) by Hermes et al. (2020) as OTP of sitagliptin and the evidence from our MS and MS^2 spectrum match the one from Hermes et al. (2020).

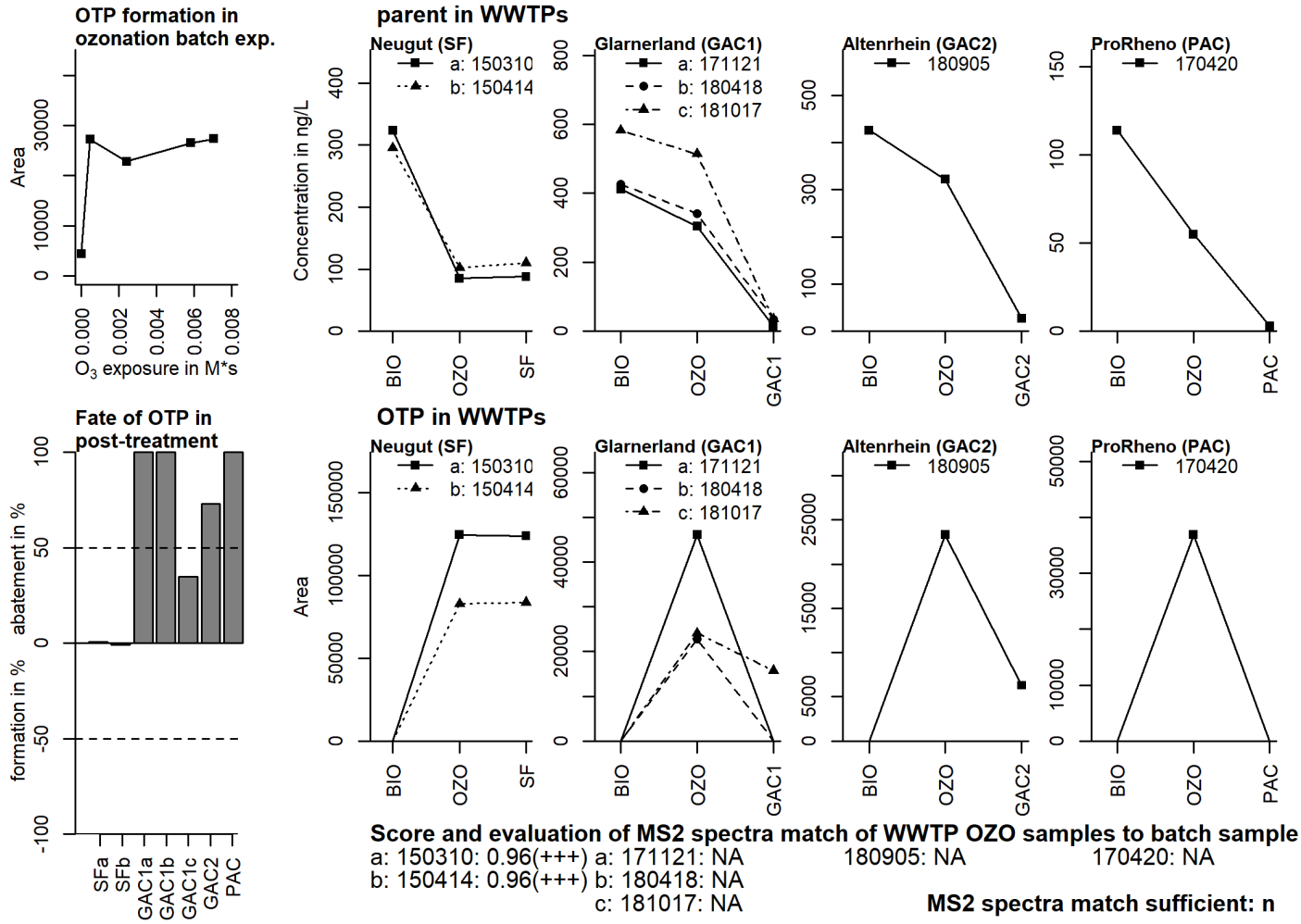
Confidence Level

Level 2a

Massbank ID

ET407401

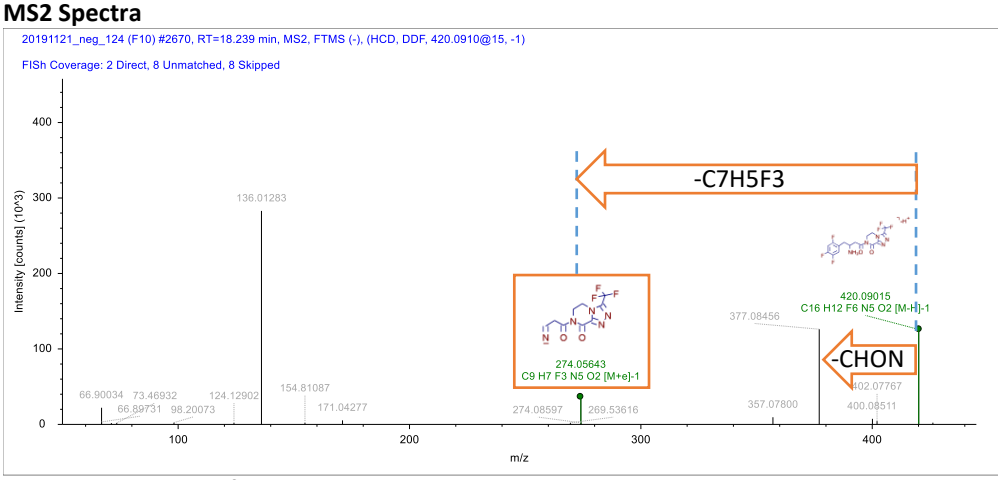
Name SIT_n_420.0899_18.2



MS Spectra

Neg	420.0889	[m-H]-
Neg	466.0952	m+FA-H
Pos	422.1045	[m+H]+

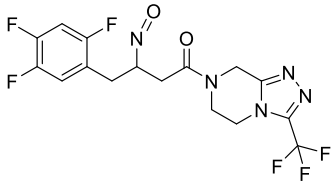
MS2 Spectra



Formula
C16H13O2N5F6

Atomic modification
-H2 +O

Proposed Structure

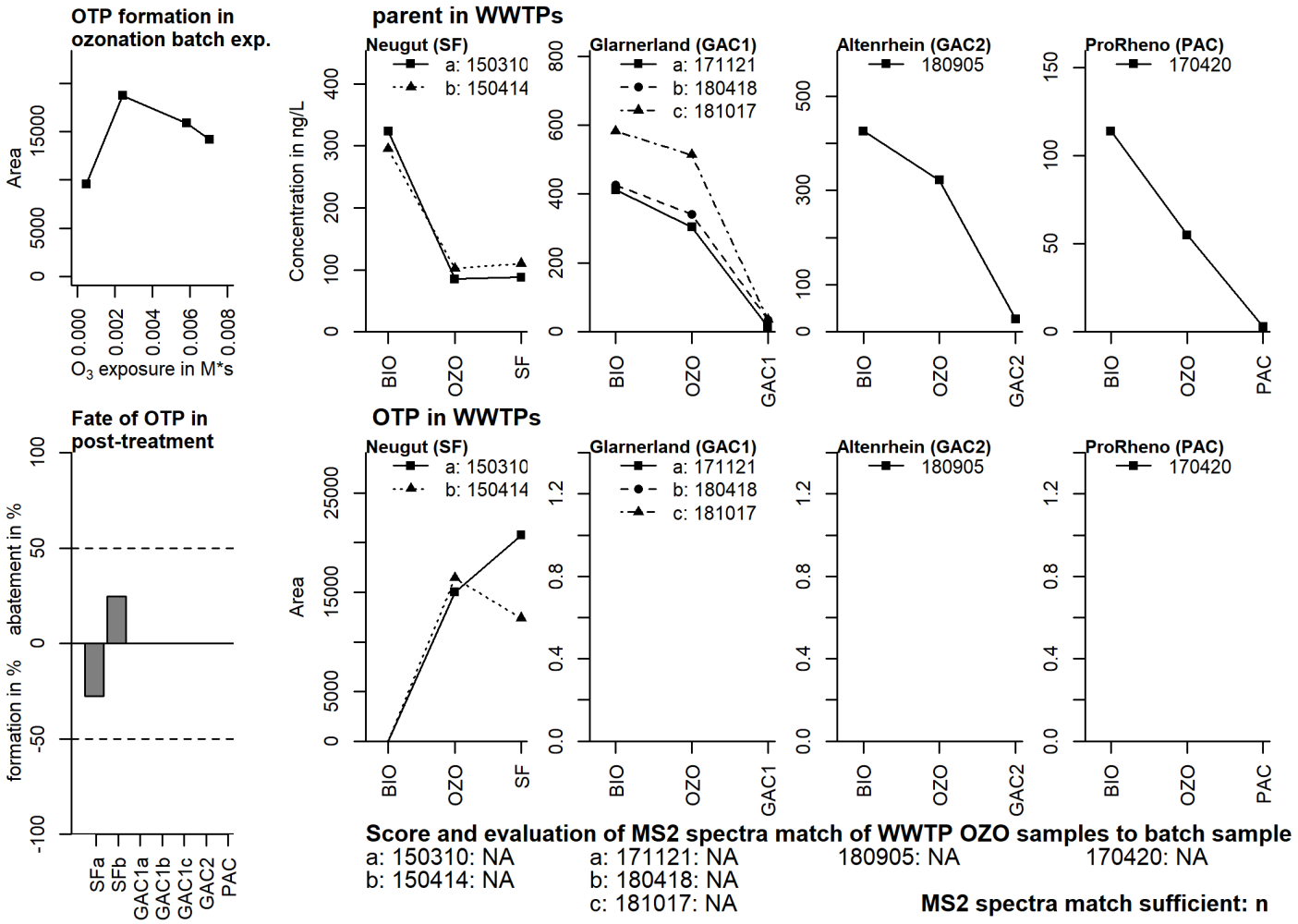


Additional Evidence for Structure Interpretation
The atomic modification from the elemental formula of the parent compound to this OTP is –H2 +O. The neutral loss of C7H5F3 between the molecular ion and fragment 274 indicates that the modification did not take place at the methyltrifluorophenyl moiety.
This atomic modification fits to the formation the nitroso group, a reaction that is known to happen during ozonation (Lim et al. 2019). Hermes et al. (2020) detected three OTPs of sitagliption with this exact same mass and also suggested the formation of nitroso-sitagliptin, which tautomerizes with the oxime form.

Confidence Level
Level 3

Massbank ID
ET407501

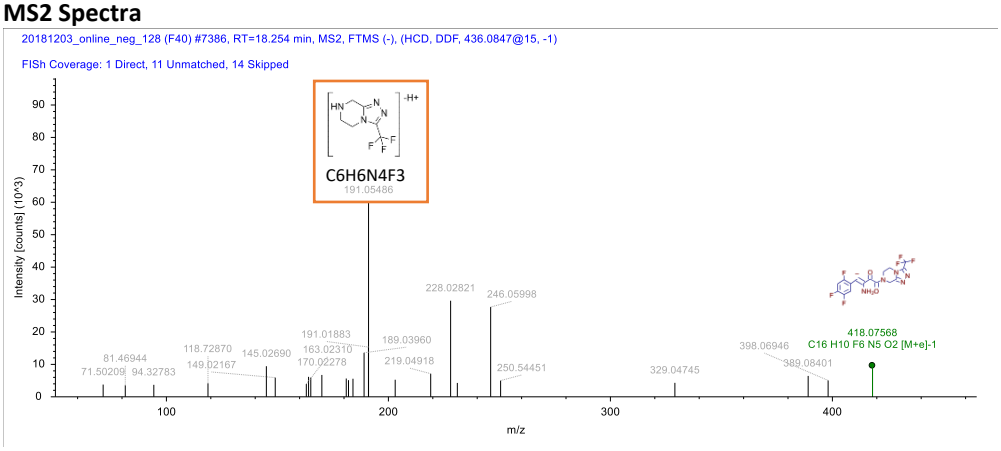
Name SIT_n_436.0847_18.3



MS Spectra

Neg	436.0847	[m-H]-
Neg	482.0847	[m+FA-H]-
Pos	438.0995	[m+H+]

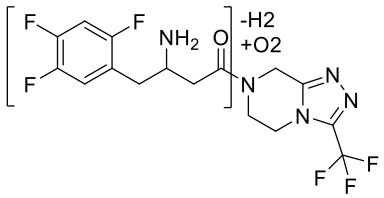
MS2 Spectra



Formula
C16H13O3N5F6

Atomic modification
-H2 +O2

Proposed Structure



Confidence Level
Level 3

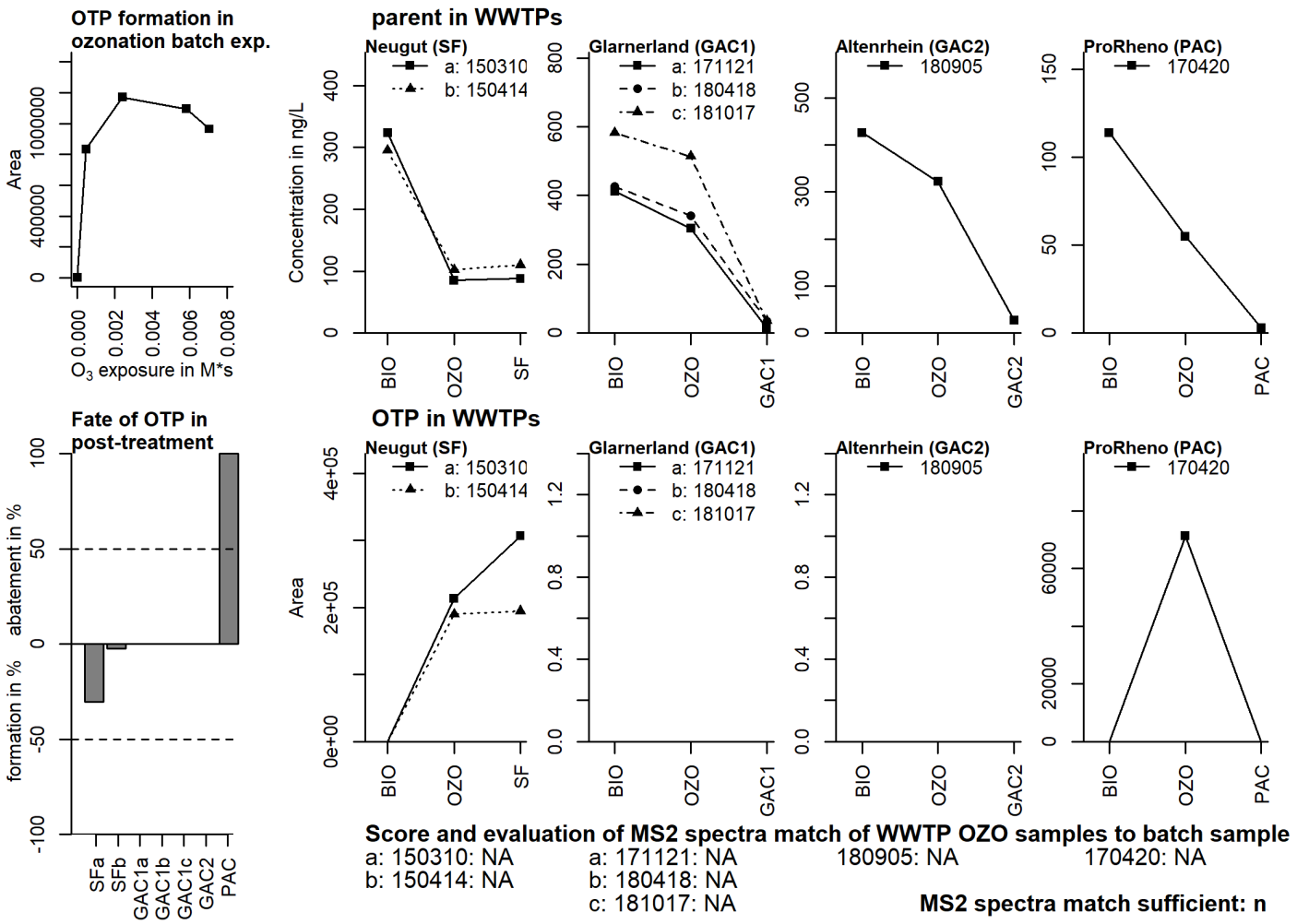
Massbank ID
ET407601

Additional Evidence for Structure Interpretation

For the parent compound sitagliptin two OTPs (SIT_n_436.0847_18.3 and SIT_n_436.0847_19.2) with the exact mass of 436.0847 were observed at different retention times (18.3 and 19.2 min). The MS^2 spectra of these OTPs are very similar. The atomic modification from the elemental formula of the parent compound to this OTP is –H2 +O2. The MS^2 fragment at the nominal mass 191 was also observed for the parent compound and corresponds to the trifluromethyltriazolopyrazine moiety, which indicates that no modification occurred at this moiety.

This atomic modification fits to the formation of e.g. a nitro group at the primary amine, a carbonyl group and the addition of an OH group or the formation of a hydroxylamine and a carbonyl moiety. The exact type and location of the modification(s) remain unknown. The structures of the MS^2 fragments are drawn exemplarily. Hermes et al. (2020) suggested the nitro structure as OTP of sitagliptin.

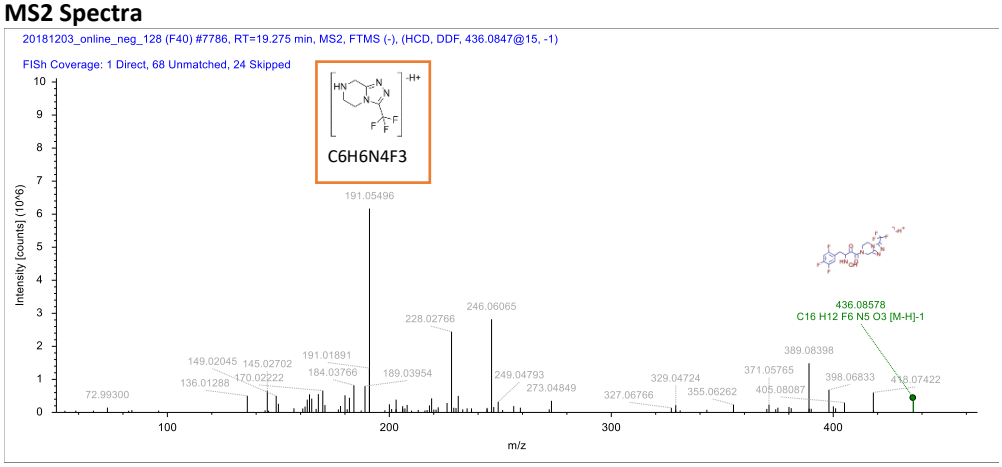
Name SIT_n_436.0847_19.2



MS Spectra

Neg 436.0847 [m-H]-

MS2 Spectra



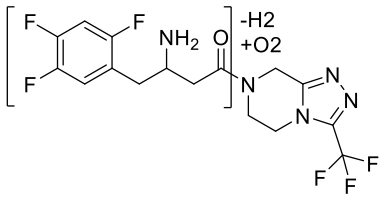
Formula

C16H13O3N5F6

Atomic modification

-H2 +O2

Proposed Structure



Confidence Level

Level 3

Massbank ID

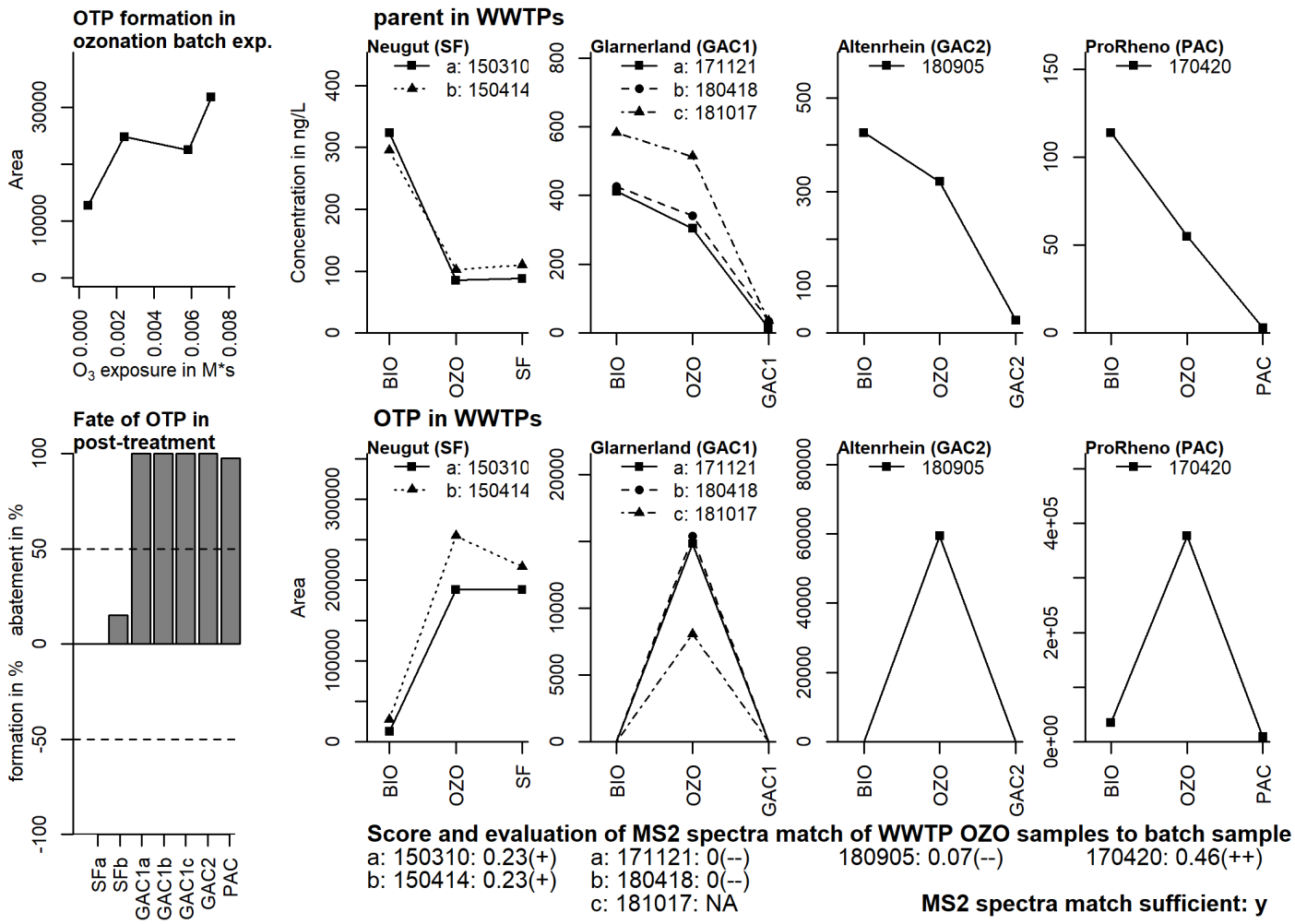
ET407701

Additional Evidence for Structure Interpretation

For the parent compound sitagliptin two OTPs (SIT_n_436.0847_18.3 and SIT_n_436.0847_19.2) with the exact mass of 436.0847 were observed at different retention times (18.3 and 19.2 min). The MS^2 spectra of these OTPs are very similar. The atomic modification from the elemental formula of the parent compound to this OTP is –H2 +O2. The MS^2 fragment at the nominal mass 191 was also observed for the parent compound and corresponds to the trifluromethyltriazolopyrazine moiety, which indicates that no modification occured at this moiety.

This atomic modification fits to the formation of e.g. a nitro group at the primary amine, a carbonyl group and the addition of an OH group or the formation of a hydroxylamine and a carbonyl moiety. The exact type and location of the modification(s) remain unknown. The structures of the MS^2 fragments are drawn exemplarily. Hermes et al. (2020) suggested the nitro structure as OTP of sitagliptin.

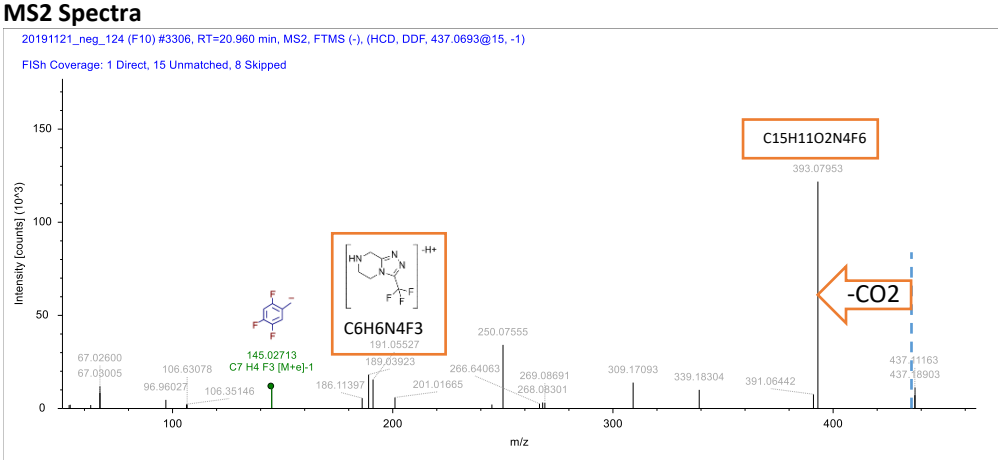
Name SIT_n_437.0687_20.7



MS Spectra

Neg 437.0687 [m-H]-

MS2 Spectra



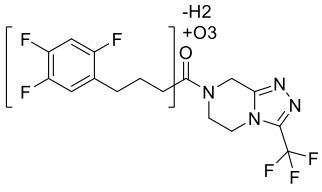
Formula

C16H12O4N4F6

Atomic modification

-NH3 +O3

Proposed Structure



Confidence Level

Level 3

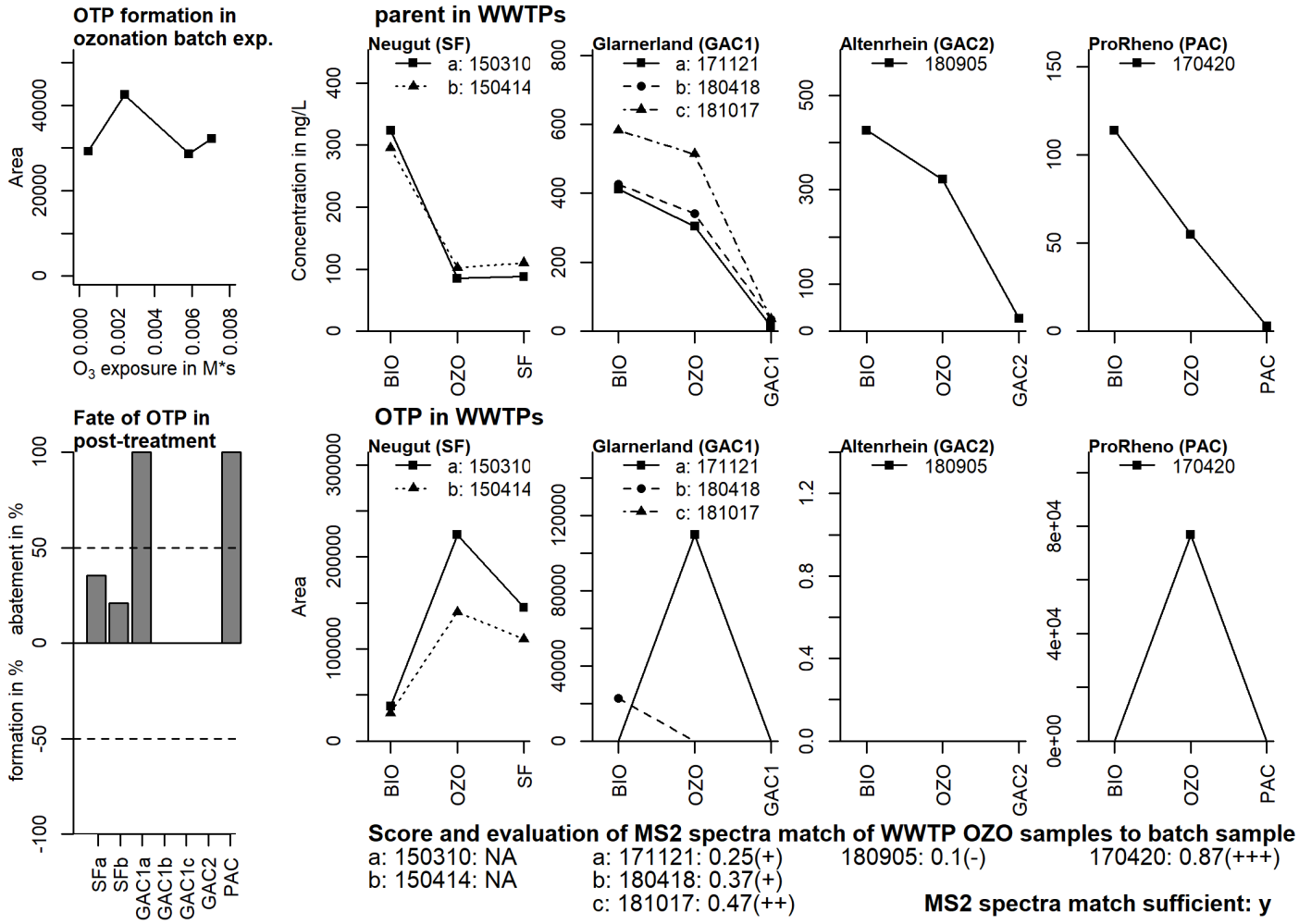
Massbank ID

ET407801

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is -NH3 +O3. The MS^2 fragment at the nominal mass 191 was also observed for the parent compound and corresponds to the trifluromethyltriazolopyrazine moiety, which indicates that no modification occurred at this moiety. The neutral loss of CO2 (-44) between the parent fragment and fragment 393 indicates the formation of a carboxylic acid moiety. The exact type and location of the modification(s) remain unknown. Hermes et al. (2020) detected an OTP of sitagliptin with the same exact mass but did not provide any structure suggestion. Our MS^2 matches the one of Hermes et al. (2020).

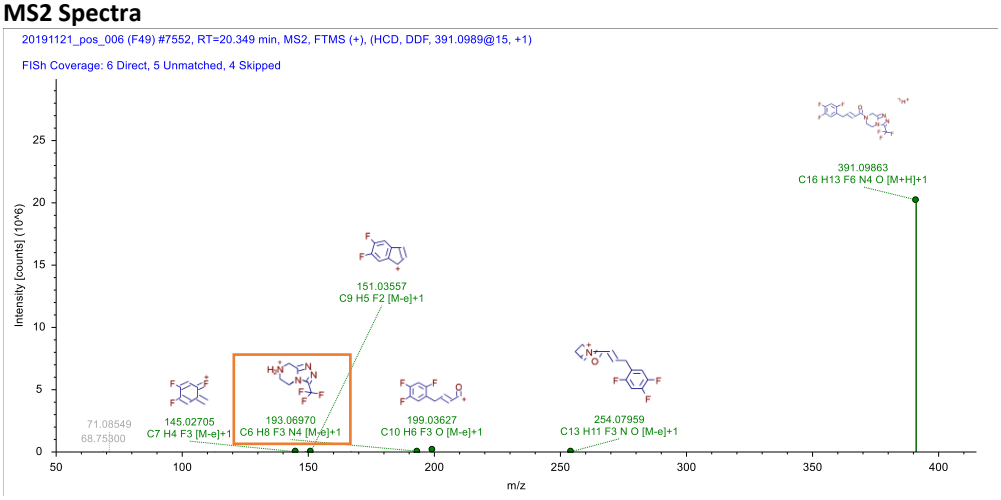
Name SIT_p_391.0988_19.8



MS Spectra

Pos	391.0988	[m+H]+
Neg	389.0841	[m-H]-
Neg	435.0896	m+FA-H

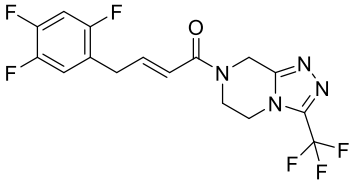
MS2 Spectra



Formula
C16H12ON4F6

Atomic modification
-NH3

Proposed Structure



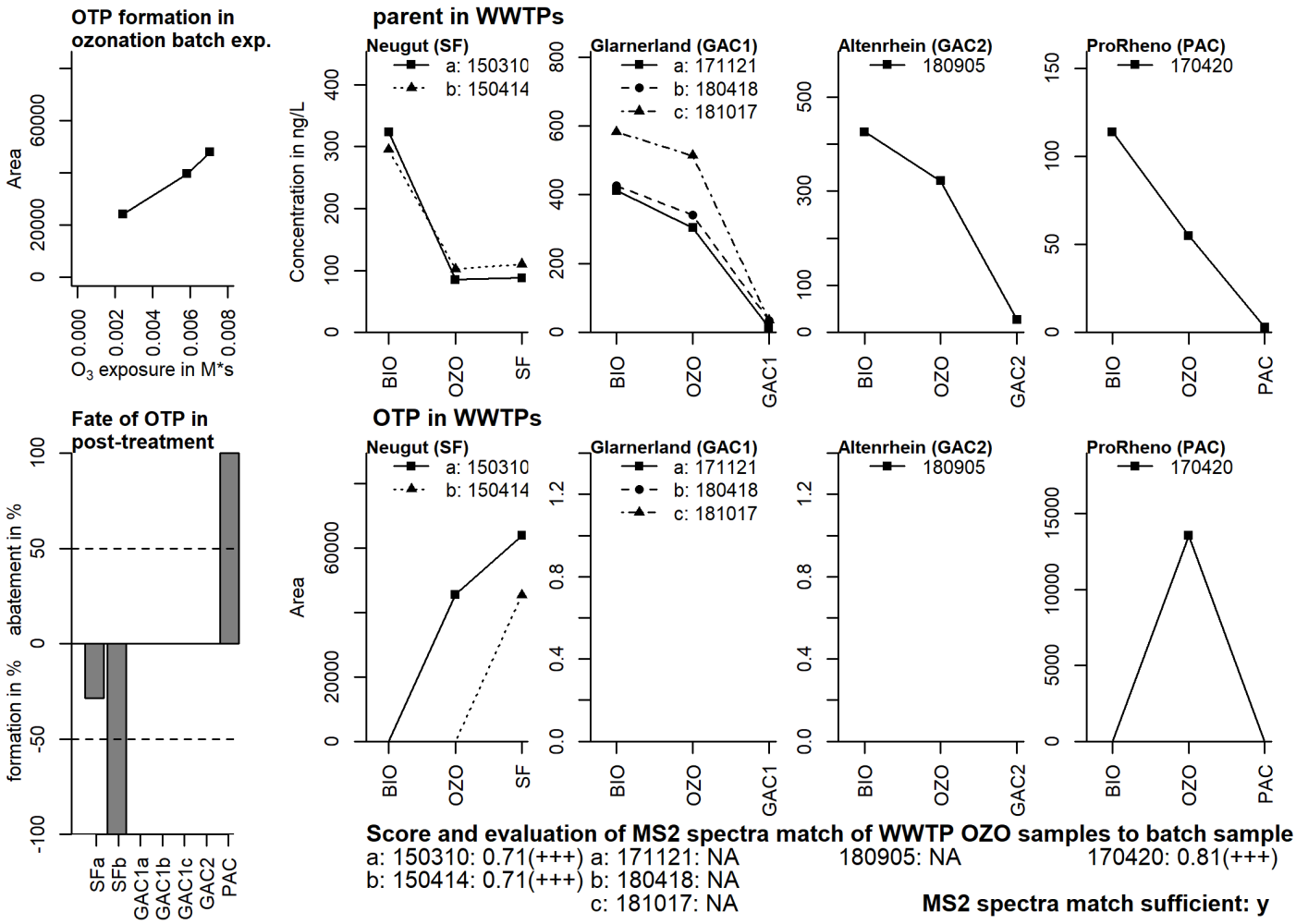
Confidence Level
Level 3

Massbank ID
ET403701

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is –NH3. Fragment 193, which was also observed for the parent compound, indicates that the trifluoromethyltriazolopyrazin moiety is retained in the OTP. Therefore, the atomic modification fits to the cleavage of the primary amine moiety and the abstraction of two additional hydrogen atoms. The exact location of the modification remains unknown. The structures of the MS^2 fragments are drawn exemplarily. The drawn structure was suggested by Hermes et al. (2020) as OTP of sitaglitptin and the evidence from our MS and MS^2 spectra match the one of Hermes et al. (2020). They suggested the formation of a C-C double bond at the location of the cleavage, although this is not reaction typically observed during ozonation. This remains unclear.

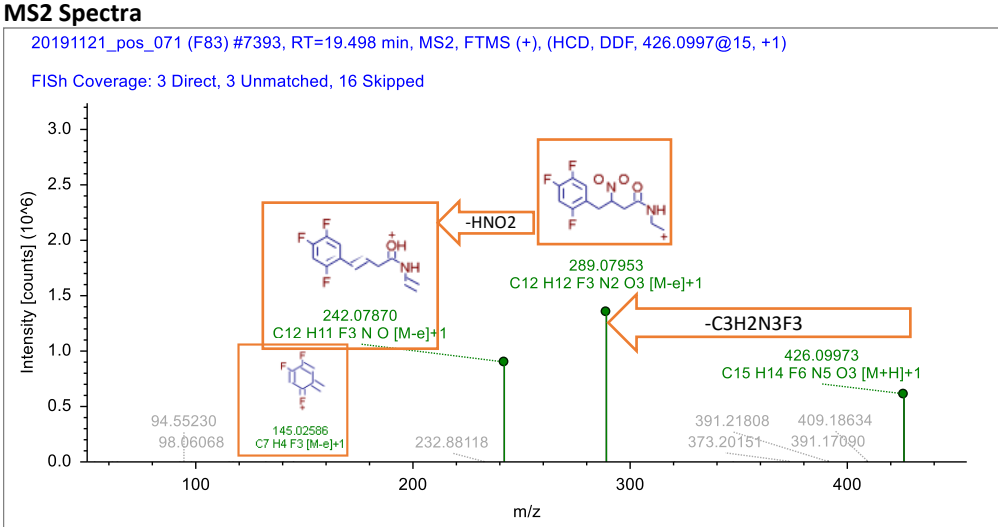
Name SIT_p_426.0996_19.1



MS Spectra

Pos 426.0996 [m+H]+

MS2 Spectra



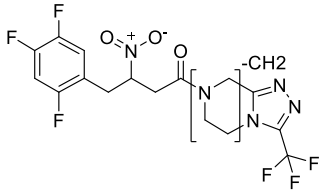
Formula

C15H13O3N5F6

Atomic modification

-CH2 +O2

Proposed Structure



Confidence Level

Level 3

Massbank ID

ET403801

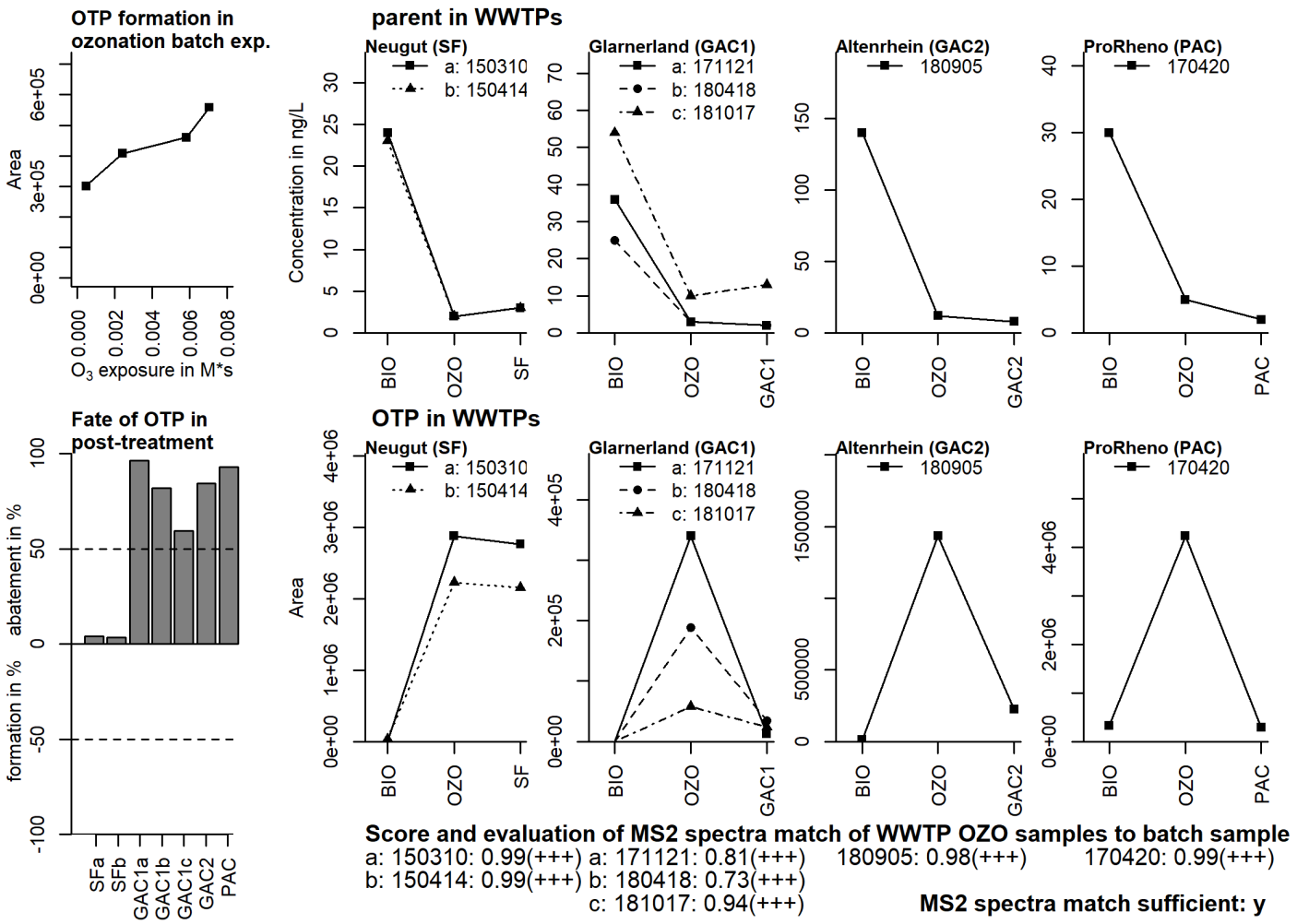
Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is –CH2 +O2. The neutral loss of C3H2N3F3 between the precursor and fragment 289 corresponds to the trifluromethyltriazole moiety and indicates that the modification did not take place at this moiety. Fragment 145 corresponds to the trifluoromethylphenyl moiety and indicates that the modification did not take place at this moiety. Fragment 289 indicates that the carbon atom was abstracted from the diazinane moiety. The exact location remains unknown.

Primary amines are known to react with ozone to form nitro moieties. The neutral loss of HNO2 between fragment 289 and fragment 242 suggests the presence of a nitro group. Therefore, the formation of the nitro moiety is likely (Lim et al. 2019).

Hermes et al. (2020) detected an OTP of sitagliptin with the same exact mass but did not provide any structure suggestion. Our MS^2 matches the one of Hermes et al. (2020).

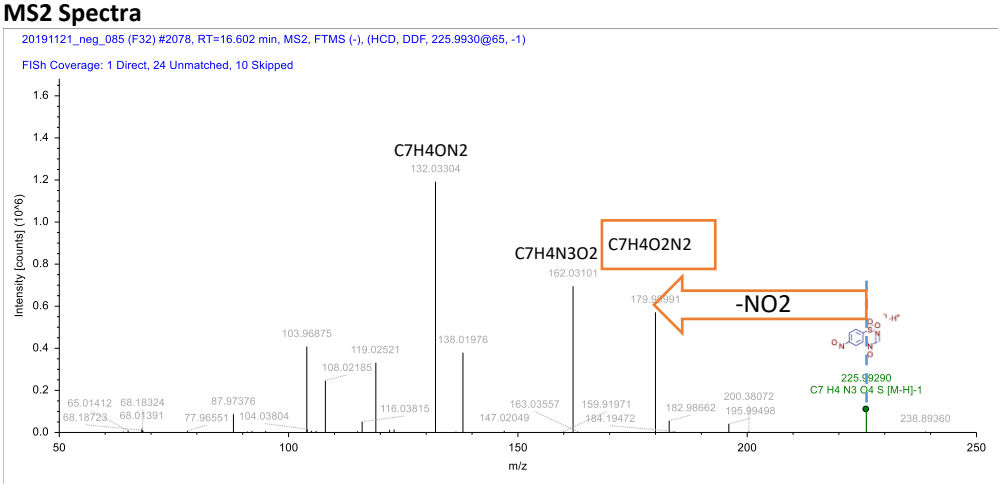
Name SMX_n_225.9926_16.4



MS Spectra

Neg 225.9926 [m-H]-

MS2 Spectra



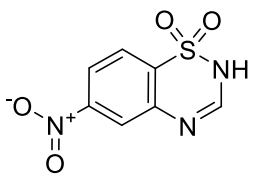
Formula

C7H5O4N3S

Atomic modification

-C3H6 +O

Proposed Structure



Confidence Level

Level 3

Massbank ID

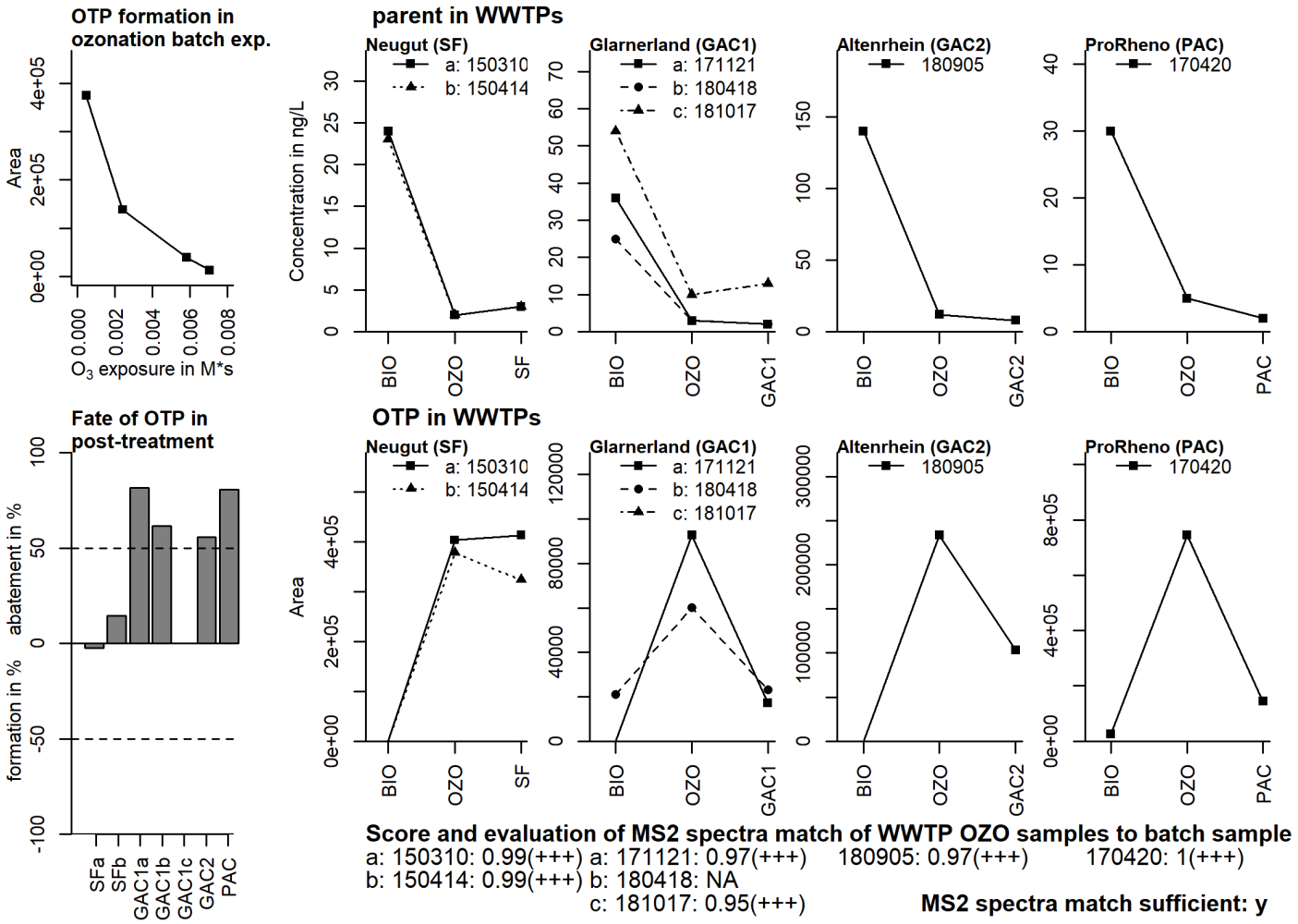
ET408101

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is -C3H6 +O, which fits to the formation of a nitro group and a cleavage within the methylisoxazol moiety. Aniline like moieties are known to react to nitro groups during ozonation (von Sonntag & von Gunten 2012). The neutral loss of NO2 between the molecular ion and fragment 179 indicates the presence of a nitro group.

Willach et al. (2017) detected an OTP of sulfomethoxazole with a similar mass but did not provide a structure suggestion. However, Martin De Vidales et al. (2012) detected an electrochemical oxidation product of sulfamethoxazole with exact an m/z of 225.9932 [m-H]- and suggested the proposed structure. The evidence from our MS and MS^2 spectra match the one from Martin De Vidales et al. (2012).

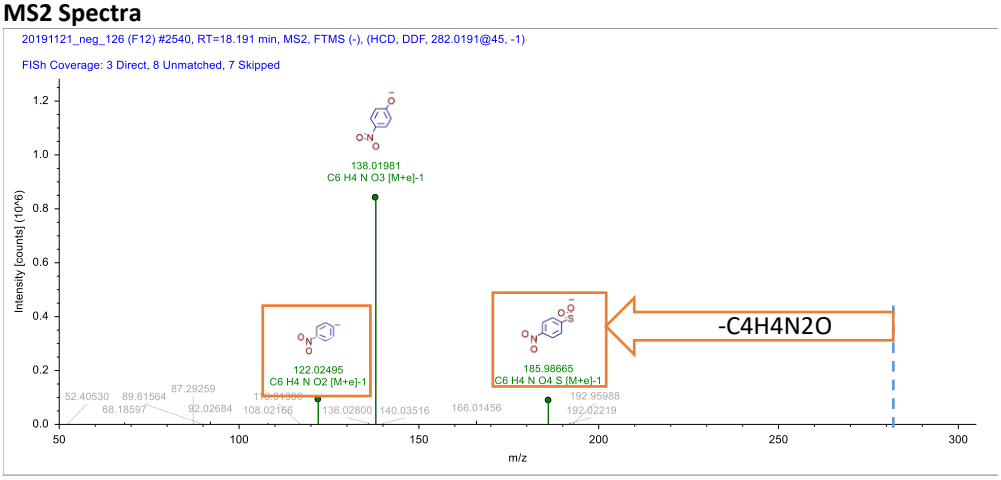
Name SMX_n_282.0188_18.0



MS Spectra

Neg 282.0188 [m-H]-

MS2 Spectra



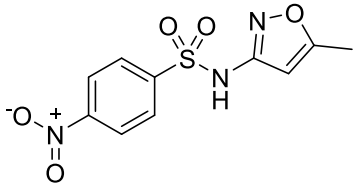
Formula

C10H9O5N3S

Atomic modification

-H2 +O2

Proposed Structure



Additional Evidence for Structure Interpretation

The neutral loss of C4H4N2O fits to the cleavage of the *N*-methyloxazol moiety. Fragment 122 indicates that the modification occurred at the aniline moiety. Aniline-like moieties are known to form nitro groups during ozonation (von Sonntag & von Gunten 2012). It is therefore likely that a nitro group was formed here. Nitro-sulfamethoxazole was proposed as ozonation transformation product in several studies (Abellan et al. 2008, Rodayan et al. 2010, Gomez-Ramos et al. 2011, Gao et al. 2014, Willach et al. 2017).

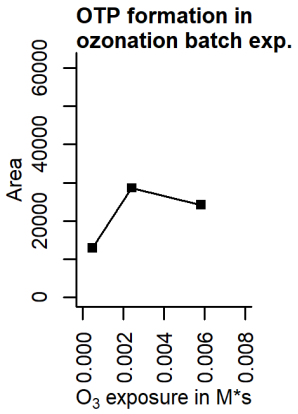
Confidence Level

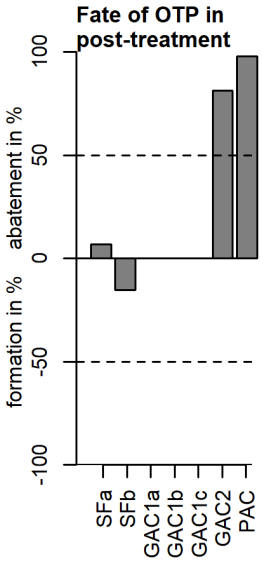
Level 3

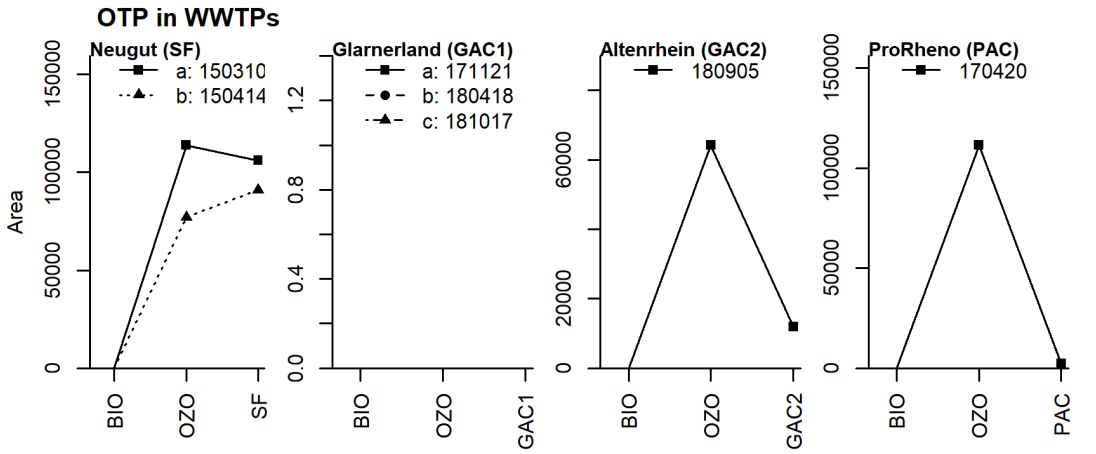
Massbank ID

ET408201

Name SMX/SMZ_n_200.9972_14.1







Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

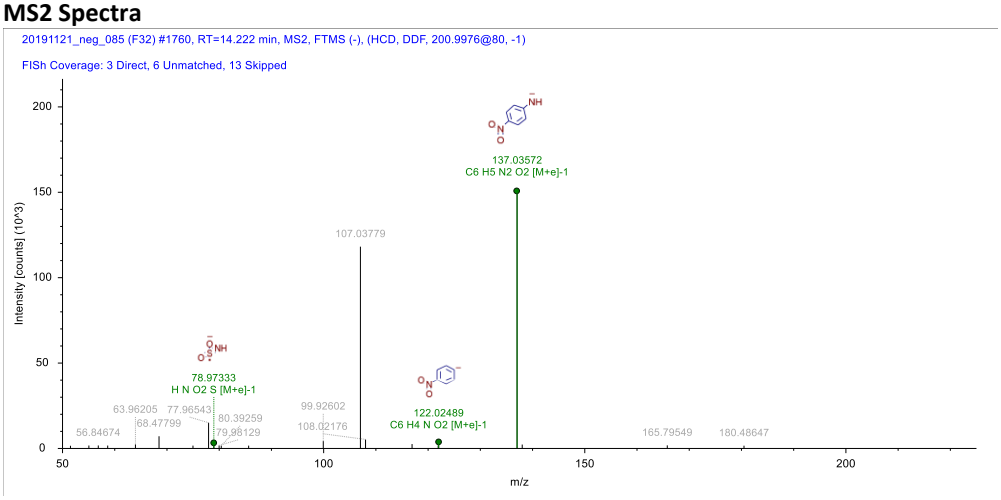
a: 150310: 0.74(+++) a: 171121: NA 180905: 0.69(+++) 170420: 0.74(+++)
b: 150414: 0.74(+++) b: 180418: NA
c: 181017: NA

MS2 spectra match sufficient: y

MS Spectra

Neg 200.9972 [m-H]-

MS2 Spectra



Formula

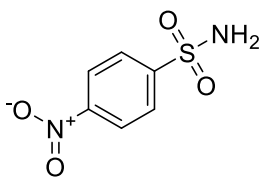
C6H6O4N2S

Atomic modification

SMX: -C4H5N +O

SMZ: -C6H8N2 +O2

Proposed Structure



Confidence Level

Level 3

Massbank ID

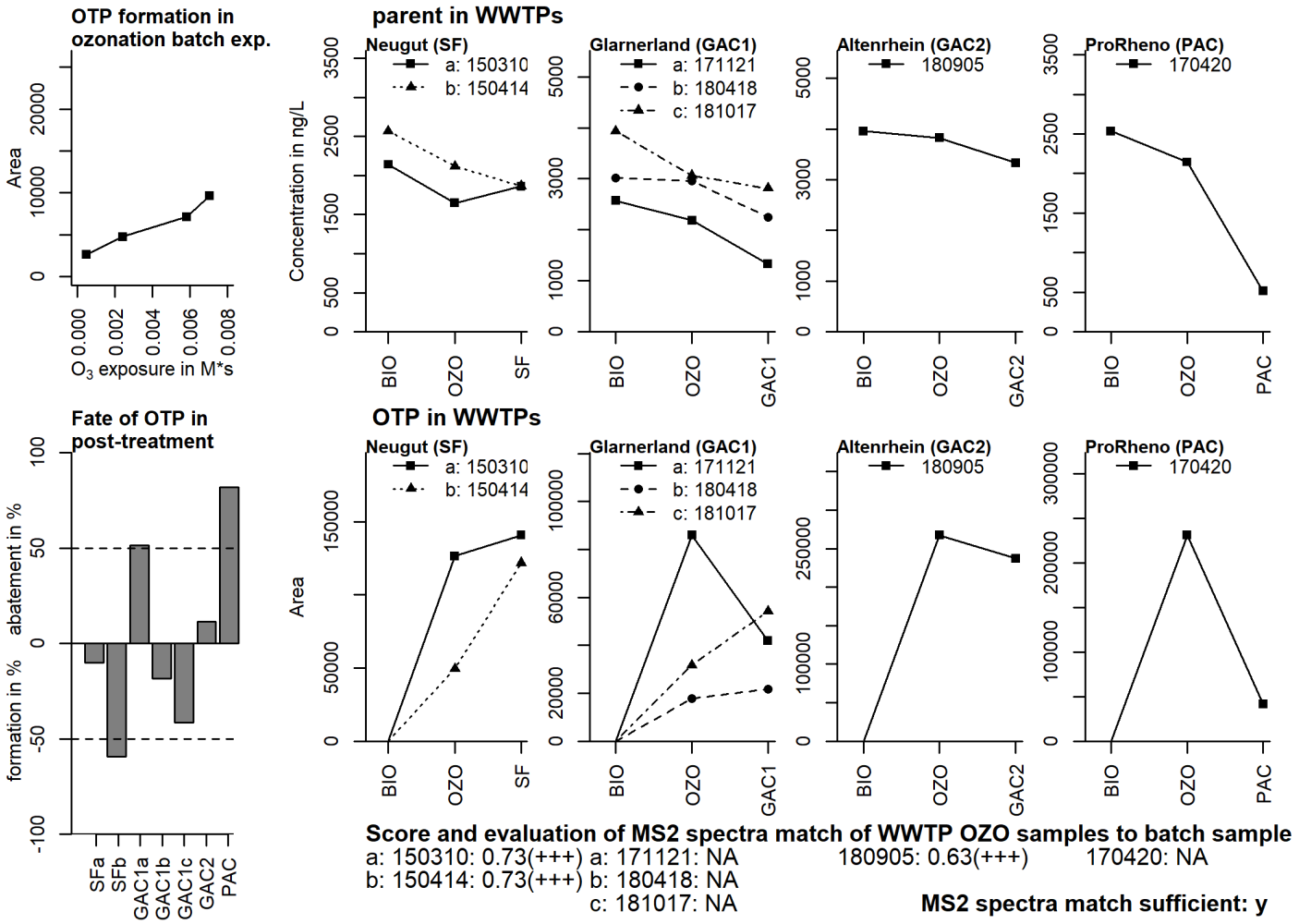
ET408001

Additional Evidence for Structure Interpretation

For sulfamethazine the loss of C6H8N2 fits to the cleavage of the dimethylpyrimidine moiety and for sulfamethoxazole the loss of C4H5N fits to the cleavage of the methyloxazole moiety. 2 oxygen atoms were added on the remaining benzenesulfonamide moiety.

Aniline-like moiety are known to form nitro groups during ozonation (von Sonntag & von Gunten 2012). It is therefore likely that this was the case here. Nitro-sulfamethoxazole was proposed as ozonation transformation product in several studies (Abellan et al. 2008, Rodayan et al. 2010, Gomez-Ramos et al. 2011, Gao et al. 2014, Willach et al. 2017), as well as methyloxazole (Gomez-Ramos et al. 2011, Gao et al. 2014). Therefore, the proposed structure is likely to be formed.

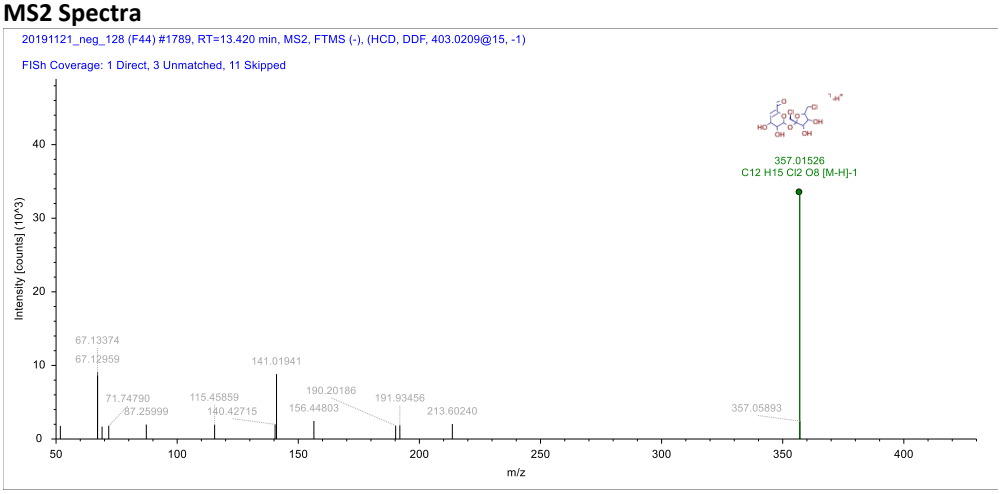
Name SUC_n_403.0202_13.3



MS Spectra

Neg 403.0202 [m+FA-H]-

MS2 Spectra



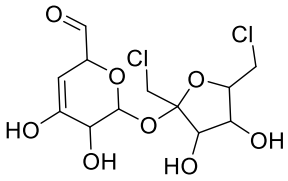
Formula

C12H16O8Cl2

Atomic modification

-H3Cl

Proposed Structure



Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is –H3Cl. This modification fits to a cleavage of a chlorine atom and the oxidation of a C-O bond. Hu et al. (2017) also detected an OTP of sucralose with a m/z of 403 and suggested the structure drawn for fragment 357 based on the MS^2 spectra.

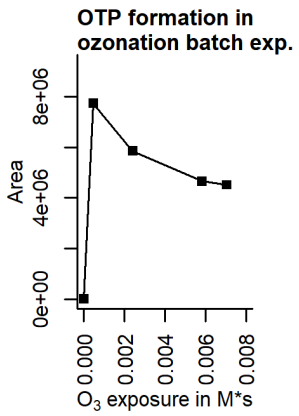
Confidence Level

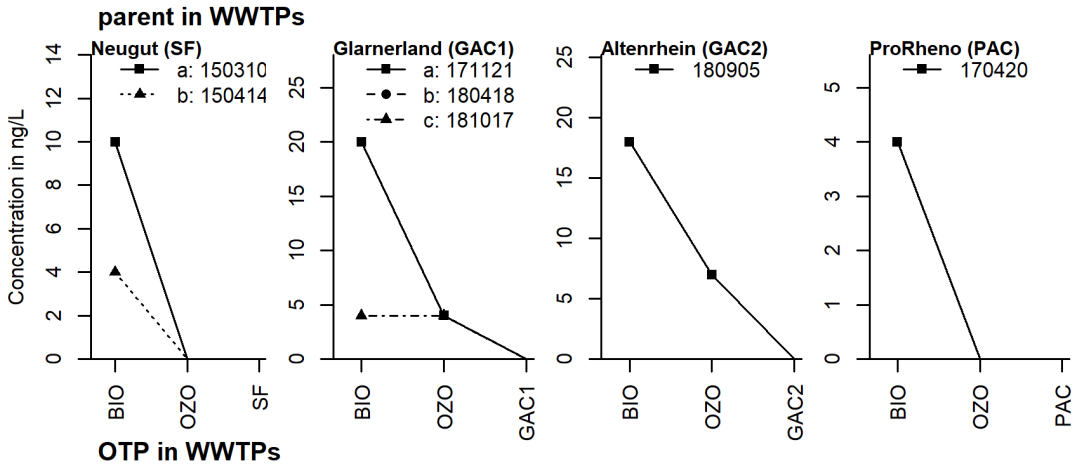
Level 3

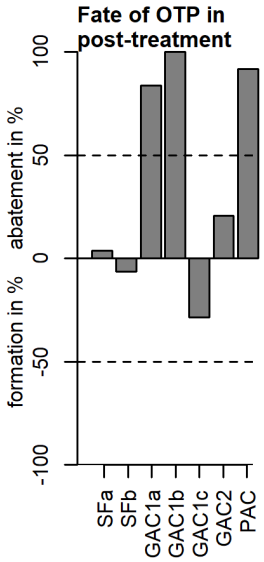
Massbank ID

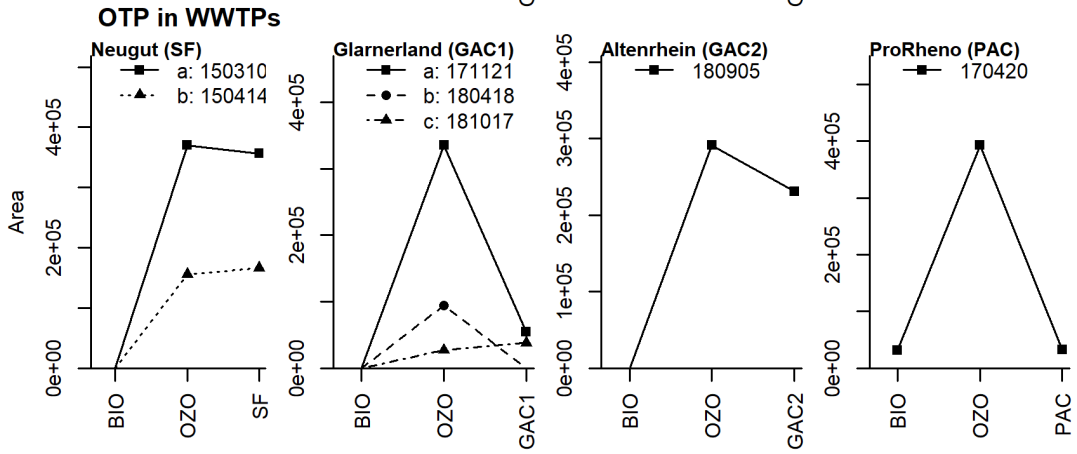
ET408367

Name SUL_p_358.1432_10.5









Score and evaluation of MS2 spectra match of WWTP OZO samples to batch sample

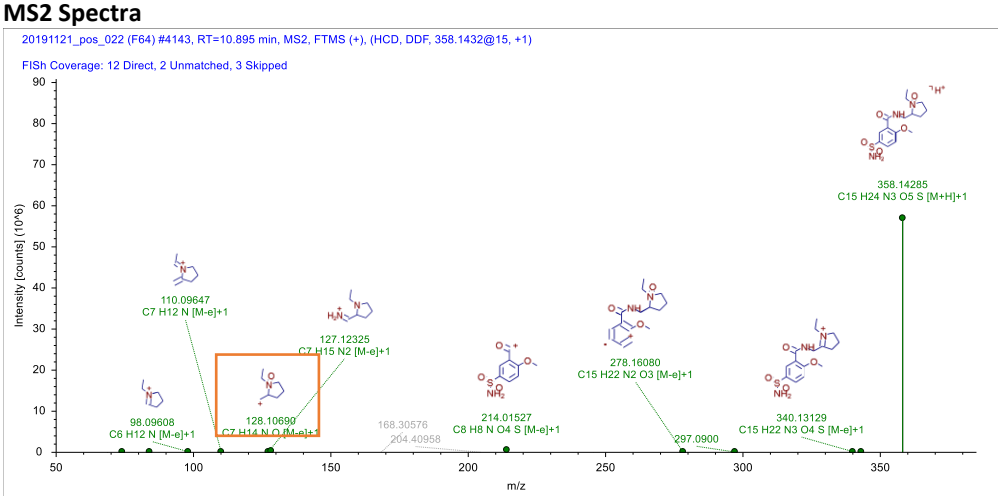
a: 150310: 0.96(+++) a: 171121: 0.98(+++) 180905: 0.99(+++) 170420: 1(+++)
b: 150414: 0.96(+++) b: 180418: 0.81(+++)
c: 181017: 1(+++)

MS2 spectra match sufficient: y

MS Spectra

Pos	358.1432	[m+H]+
Neg	356.1283	[m-H]-
Neg	402.1337	m+FA-H

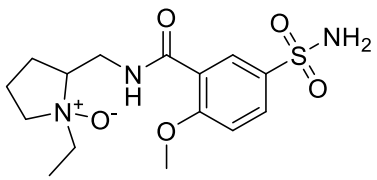
MS2 Spectra



Formula
C15H23O5N3S

Atomic modification
+O

Proposed Structure



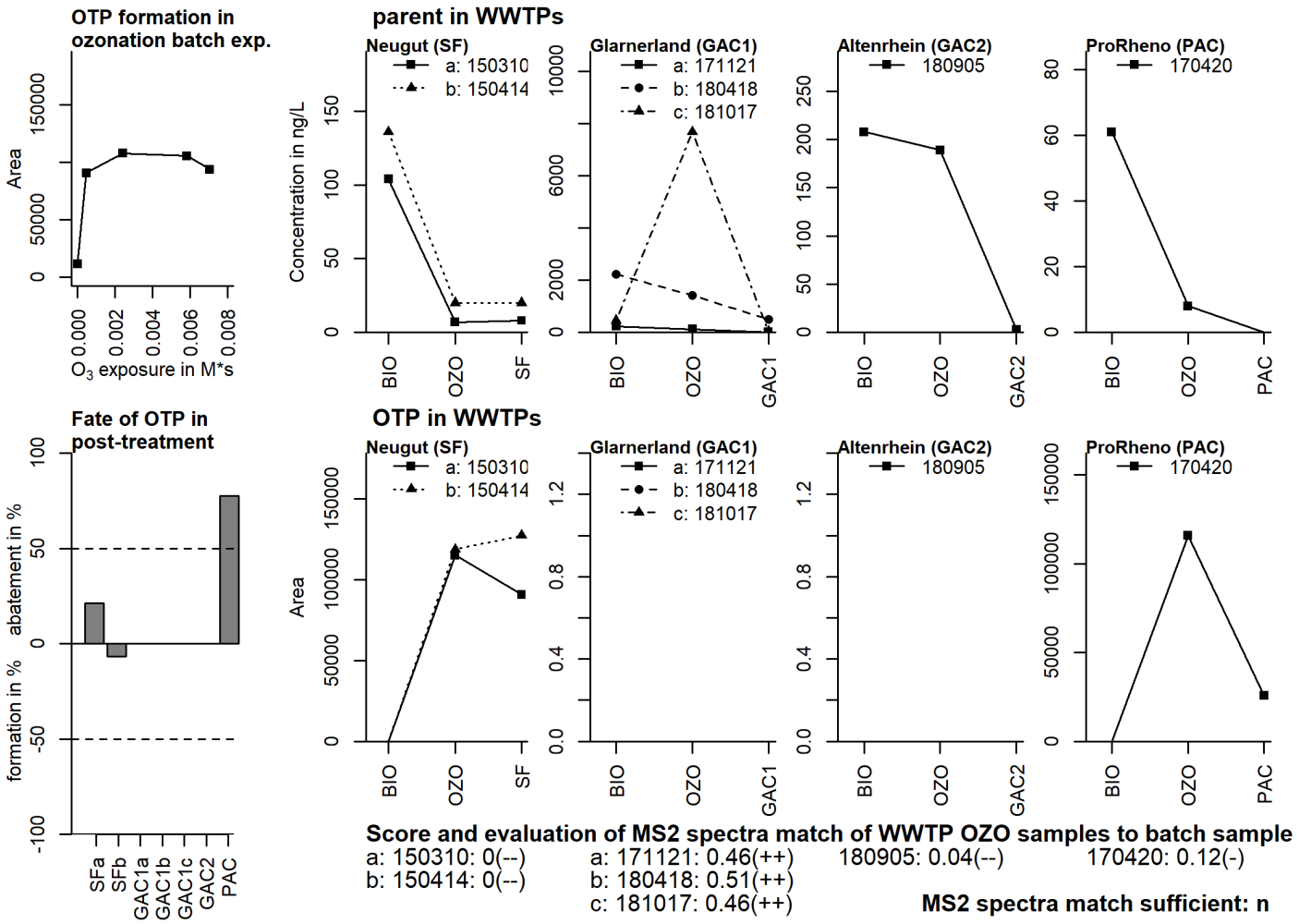
Confidence Level
Level 1

Massbank ID
ET403901

Additional Evidence for Structure Interpretation

A MS^2 fragment at the nominal mass of 112 was observed for the parent compound and corresponds to the ethylpyrrolidine moiety. The MS^2 fragment 128 here corresponds to the fragment 112 of the parent with an addition of an oxygen atom. Tertiary amines are very reactive to form *N*-oxides during ozonation (von Sonntag & von Gunten 2012). Therefore, the formation of a *N*-oxide at the ethylpyrrolidine is very likely.
Sulpiride *N*-oxide has been suggested as major OTP of Sulpiride by Bollmann et al. (2016) and Merel et al. (2017).

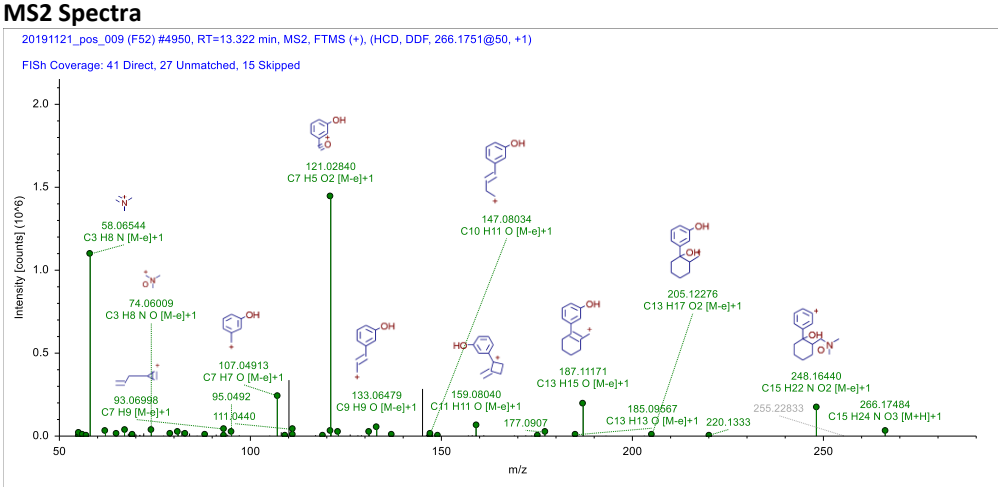
Name TRA_p_266.1749_12.8



MS Spectra

Pos 266.1749 [m+H]+

MS2 Spectra



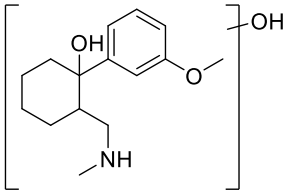
Formula

C15H23O3N

Atomic modification

-CH2 +O

Proposed Structure



Confidence Level

Level 3

Massbank ID

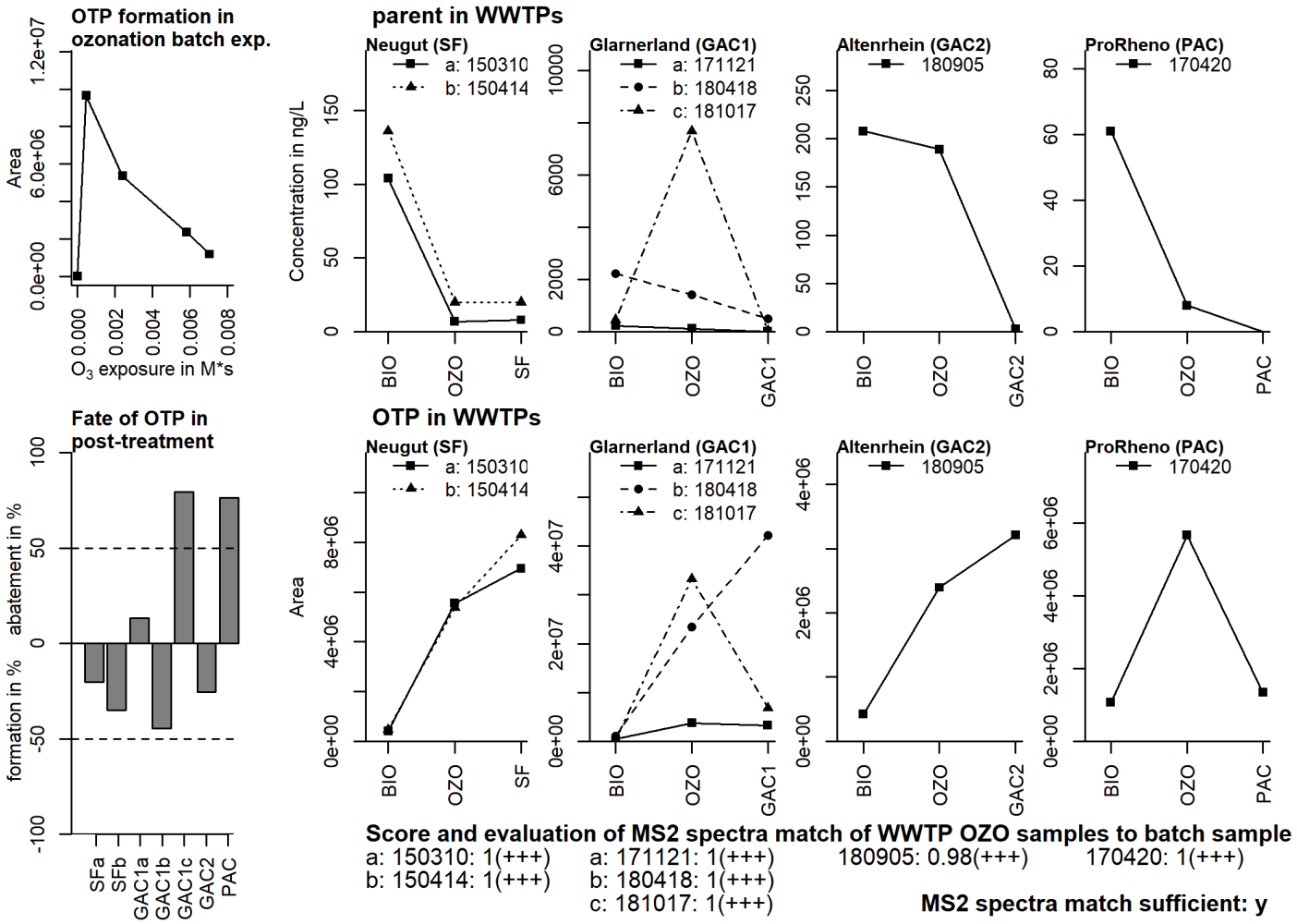
ET404001

Additional Evidence for Structure Interpretation

Fragment 121 was also observed for TRA_p_250.1801_13.5, which was identified as *N*-desmethyltramadol. The atomic modification from the elemental formula of the parent compound to this OTP is –CH2 +O. It is likely that *N*-demethylation occurred for this OTP as well at the dimethylamine moiety.

The oxygen atom was likely added by hydroxylation via a hydroxyl radical, most likely at an aliphatic C-atom, because once formed, phenol moieties quickly react further during ozonation.

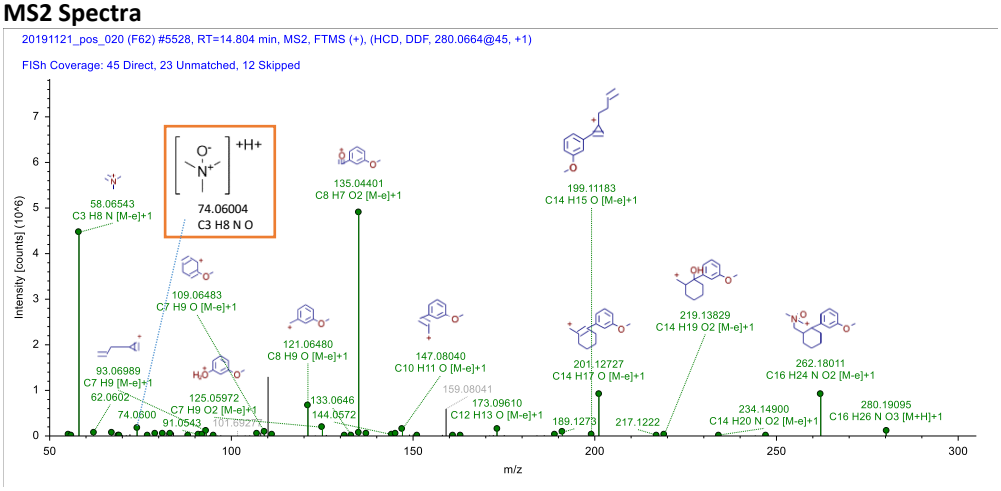
Name TRA_p_280.1905_14.4



MS Spectra

Pos 280.1905 [m+H]+

MS2 Spectra



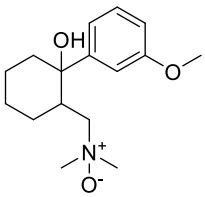
Formula

C16H25O3N

Atomic modification

+O

Proposed Structure



Confidence Level

Level 1

Massbank ID

ET404101

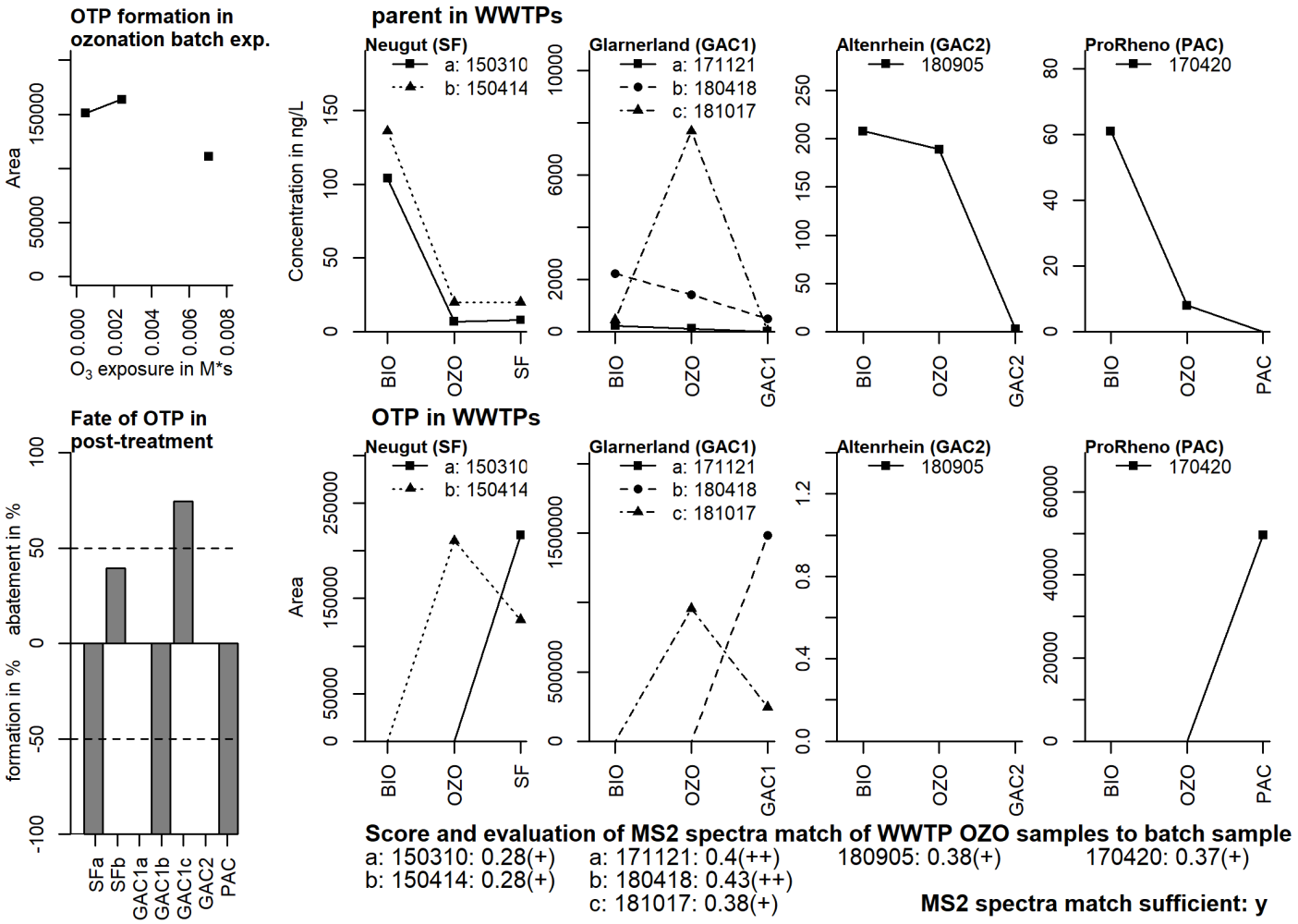
Additional Evidence for Structure Interpretation

A MS^2 fragment at the nominal mass of 58 was observed for the parent compound and corresponds to the trimethylamine moiety. The MS^2 fragment 74 corresponds to the fragment 58 of the parent with an addition of an oxygen atom.

Tertiary amines are very reactive to form *N*-oxides during ozonation (von Sonntag & von Gunten 2012). Therefore, the formation of a *N*-oxide at the trimethylamine moiety is very likely. Fragment 74 indicates the formation of the *N*-oxide.

Tramadol *N*-oxide has been confirmed as major OTP of tramadol by Zimmermann et al. (2012) and Merel et al. (2017). The observed evidence from our MS spectrum and the MS^2 spectrum match with the previous studies. The MS^2 spectrum also matches the reference spectrum we recorded for tramadol *N*-oxide.

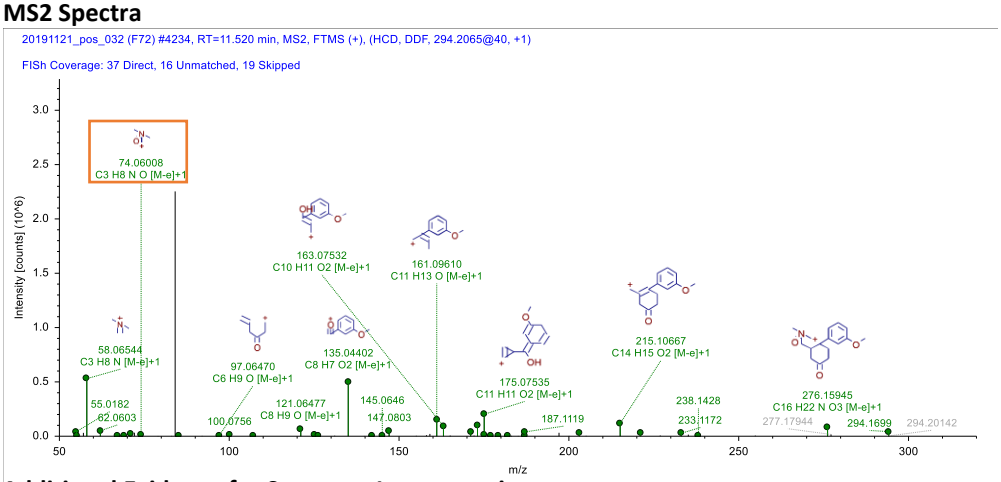
Name TRA_p_294.1699_11.0



MS Spectra

Pos 294.1699 [m+H]+

MS2 Spectra



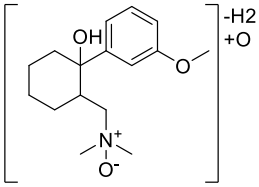
Formula

C16H23NO4

Atomic modification

-H2 +O2

Proposed Structure



Confidence Level

Level 3

Massbank ID

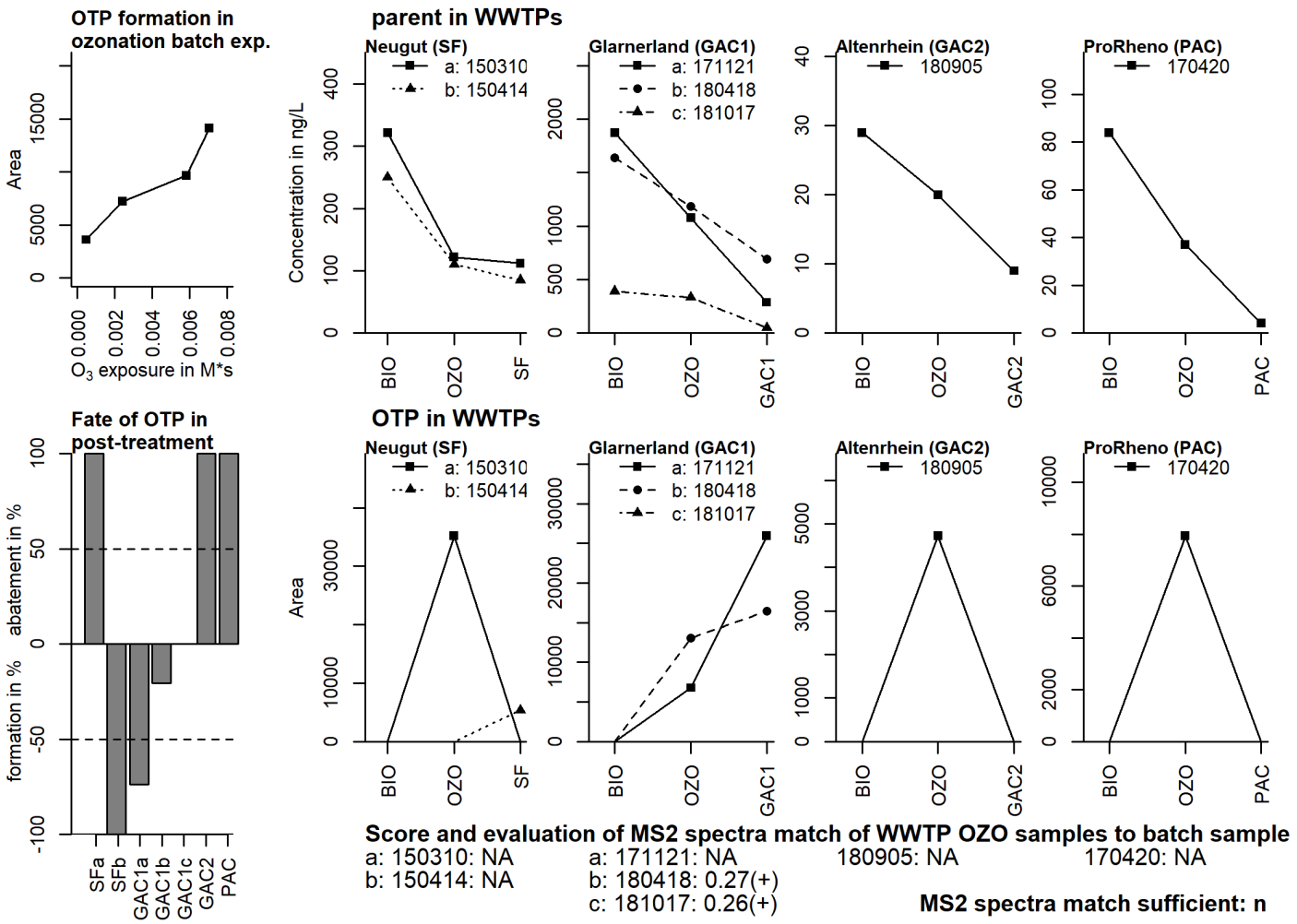
ET404201

Additional Evidence for Structure Interpretation

The atomic modification from the elemental formula of the parent compound to this OTP is –H2 +O2. Fragment 74, which was also found in the MS^2 spectrum of TRA_p_280.1905_14.4, identified as tramadol *N*-oxide, indicates that the *N*-oxide was formed in this OTP as well.

The atomic modification –H2 +O fits to the formation of a carbonyl moiety. There is no further evidence for the exact type and location of the modification. The structures of the MS^2 fragments are drawn exemplarily.

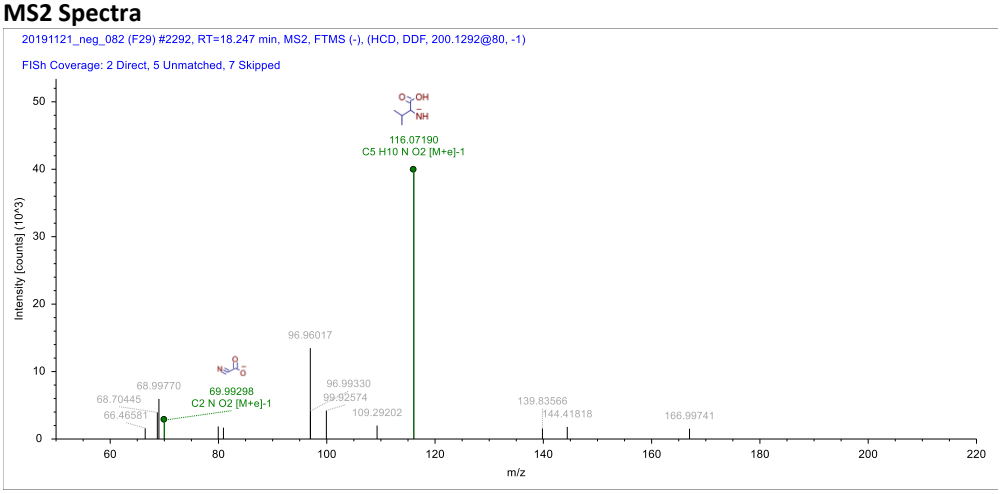
Name VAL_n_200.1289_18.1



MS Spectra

Neg 200.1289 [m-H]-

MS2 Spectra



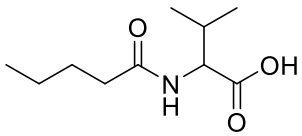
Formula

C10H19O3N

Atomic modification

-C14H10N4

Proposed Structure



Additional Evidence for Structure Interpretation

A fragment with mass 200 was observed for the parent compound and corresponds to the molecular ion of this OTP. The atomic modification from the parent structure to this OTP fits to a cleavage of the moiety, which is common for all sartans (tetrazolebiphenylmethyl moiety).

Diehle et al. (2019) suggested the formation of this structure and our MS^2 spectra matches with the previous observations.

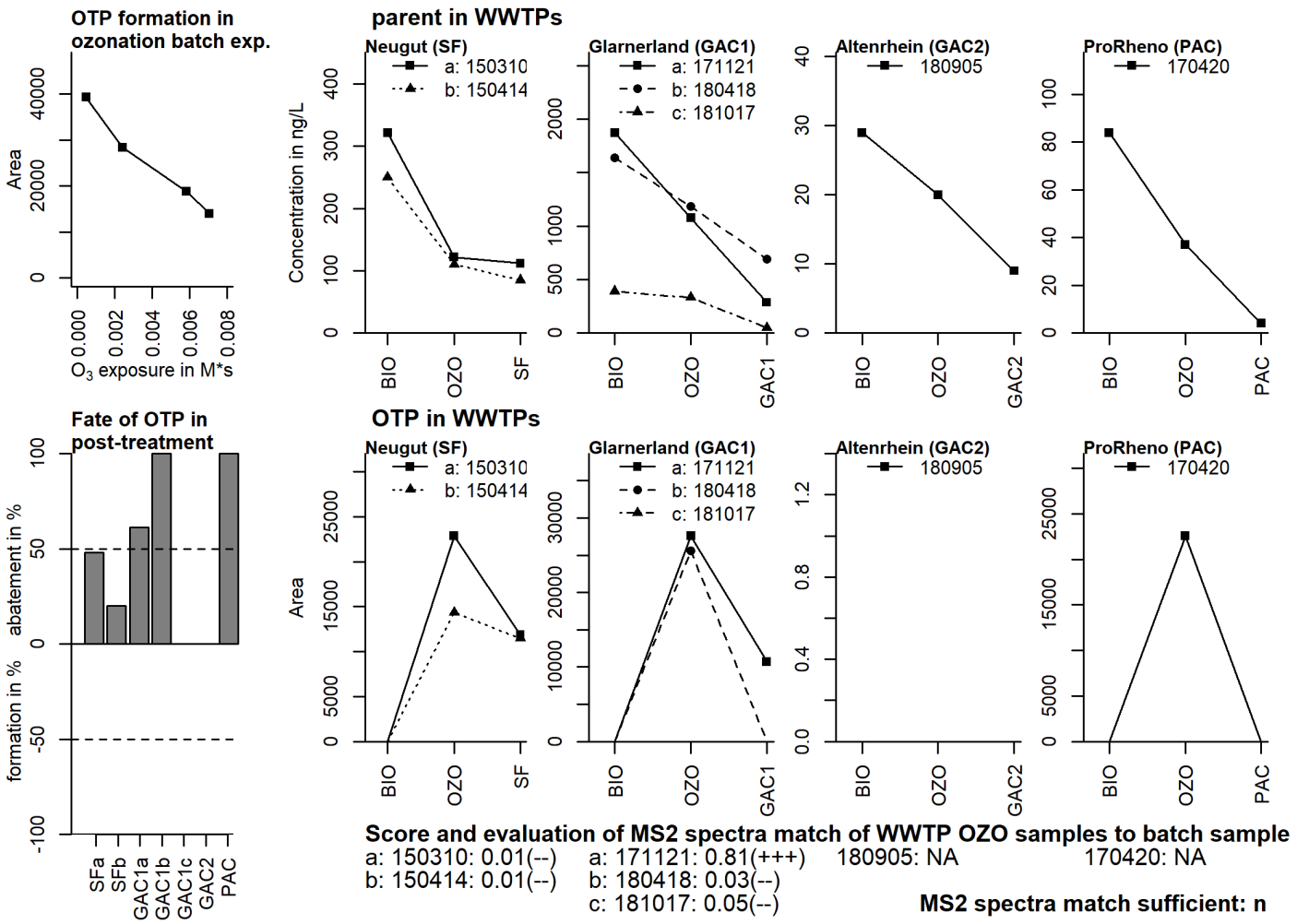
Confidence Level

Level 3

Massbank ID

ET408401

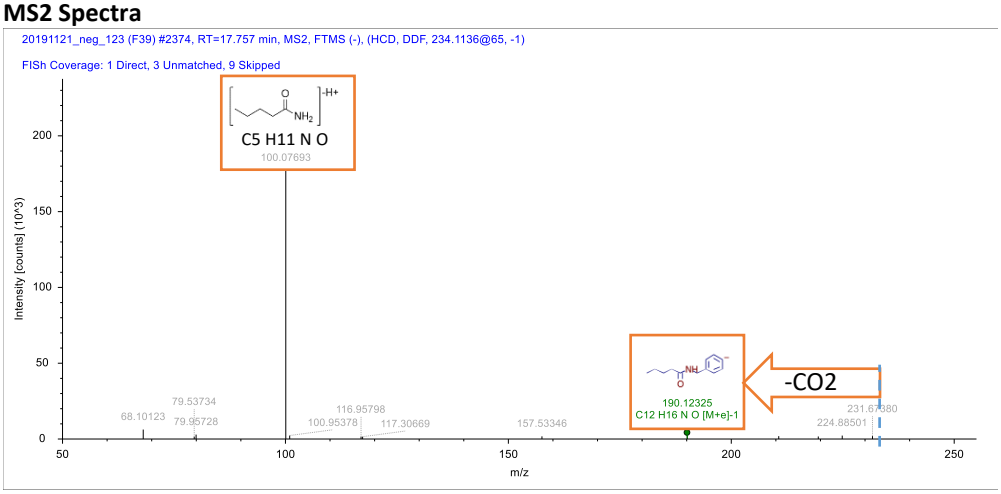
Name VAL_n_234.1133_17.8



MS Spectra

Neg 234.1133 [m-H]-

MS2 Spectra



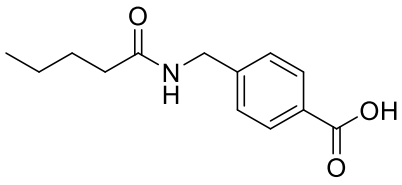
Formula

C13H17O3N

Atomic modification

-C11H12N4

Proposed Structure



Confidence Level

Level 3

Massbank ID

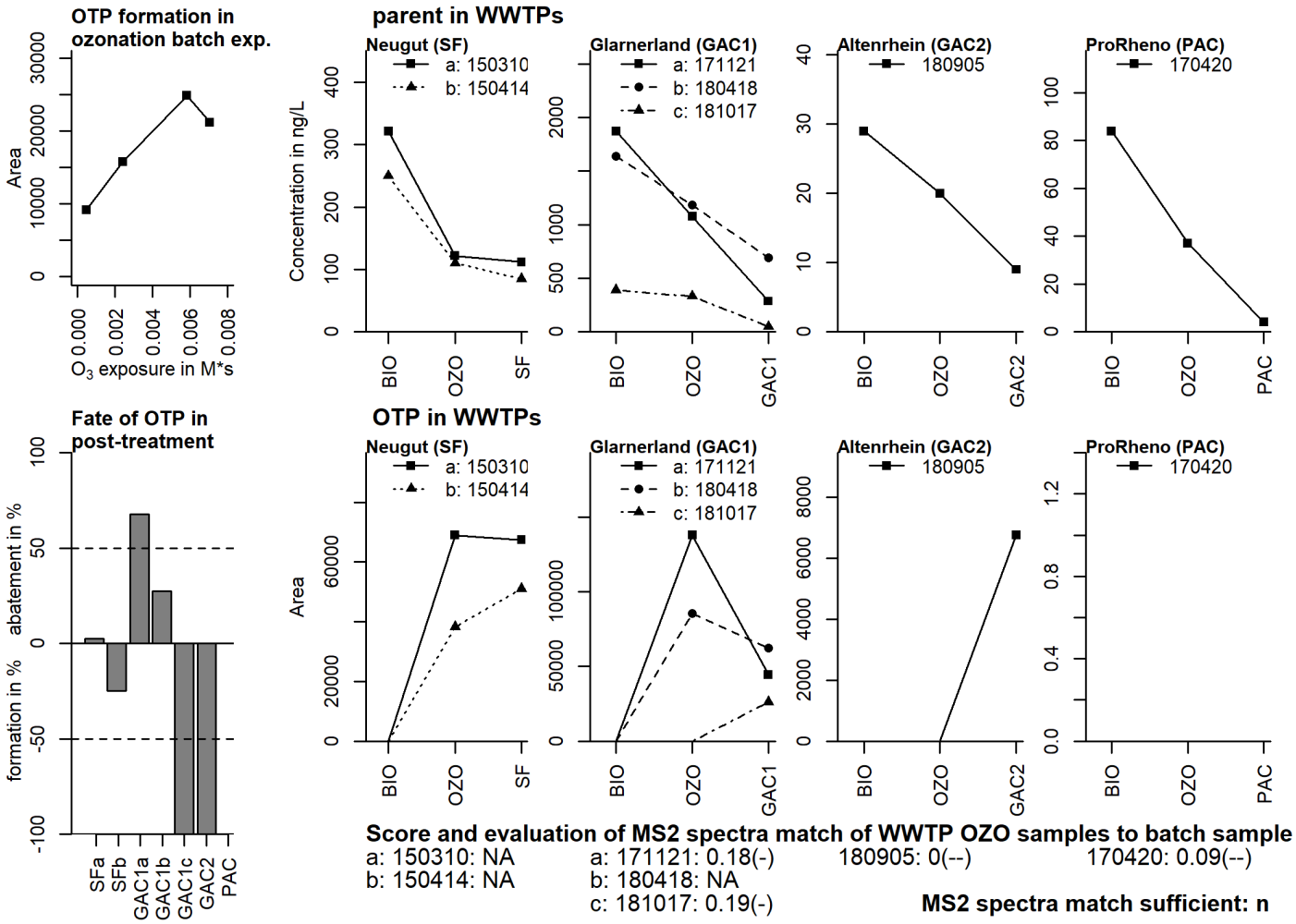
ET408501

Additional Evidence for Structure Interpretation

The atomic modification for the elemental formula of the parent compound to this OTP is --C11H12N4. This fits to a cleavage within the benzene moiety of the tetrazolebiphenylmethyl part, which is common for all sartans, the cleavage of the methylbutanoic acid moiety and the addition of 2 oxygen atoms. Fragment 100 fits to the pentanamide moiety of the parent compound. The neutral loss of CO2 between the molecular ion and fragment 190 indicates formation of a carboxylic acid moiety. Aromatic compounds are known to form cis,cis-Muconic acid like structures (von Sonntag & von Gunten 2012). Therefore, the formation of this kind of structure, followed by a C-C bond cleavage, resulting in a p-benzoic acid moiety, is probable.

Diehle et al. (2019) suggested the formation of this structure and our MS^2 spectra matches with these previous observations.

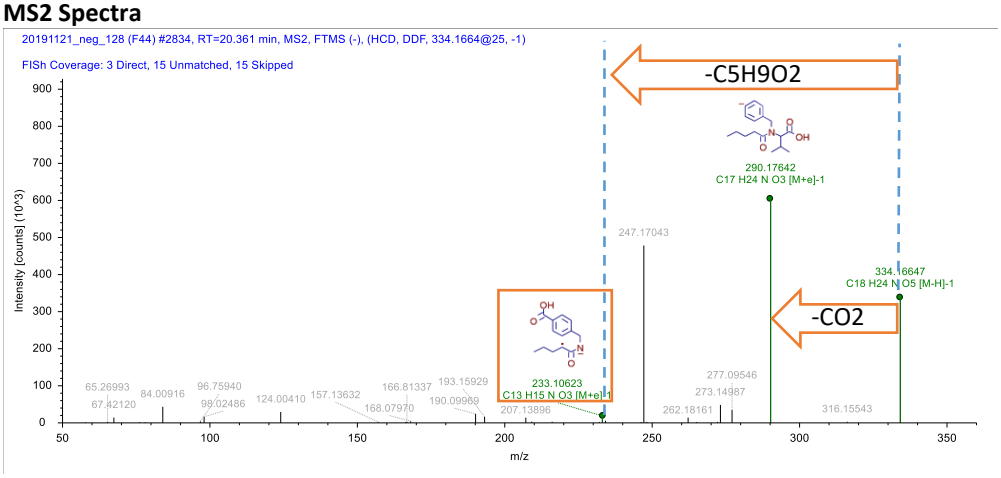
Name VAL_n_334.1657_20.4



MS Spectra

Neg 334.1657 [m-H]-

MS2 Spectra



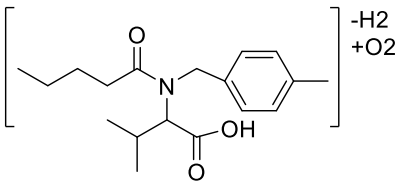
Formula

C18H25O5N

Atomic modification

-C6H4N4 +O2

Proposed Structure



Confidence Level

Level 3

Massbank ID

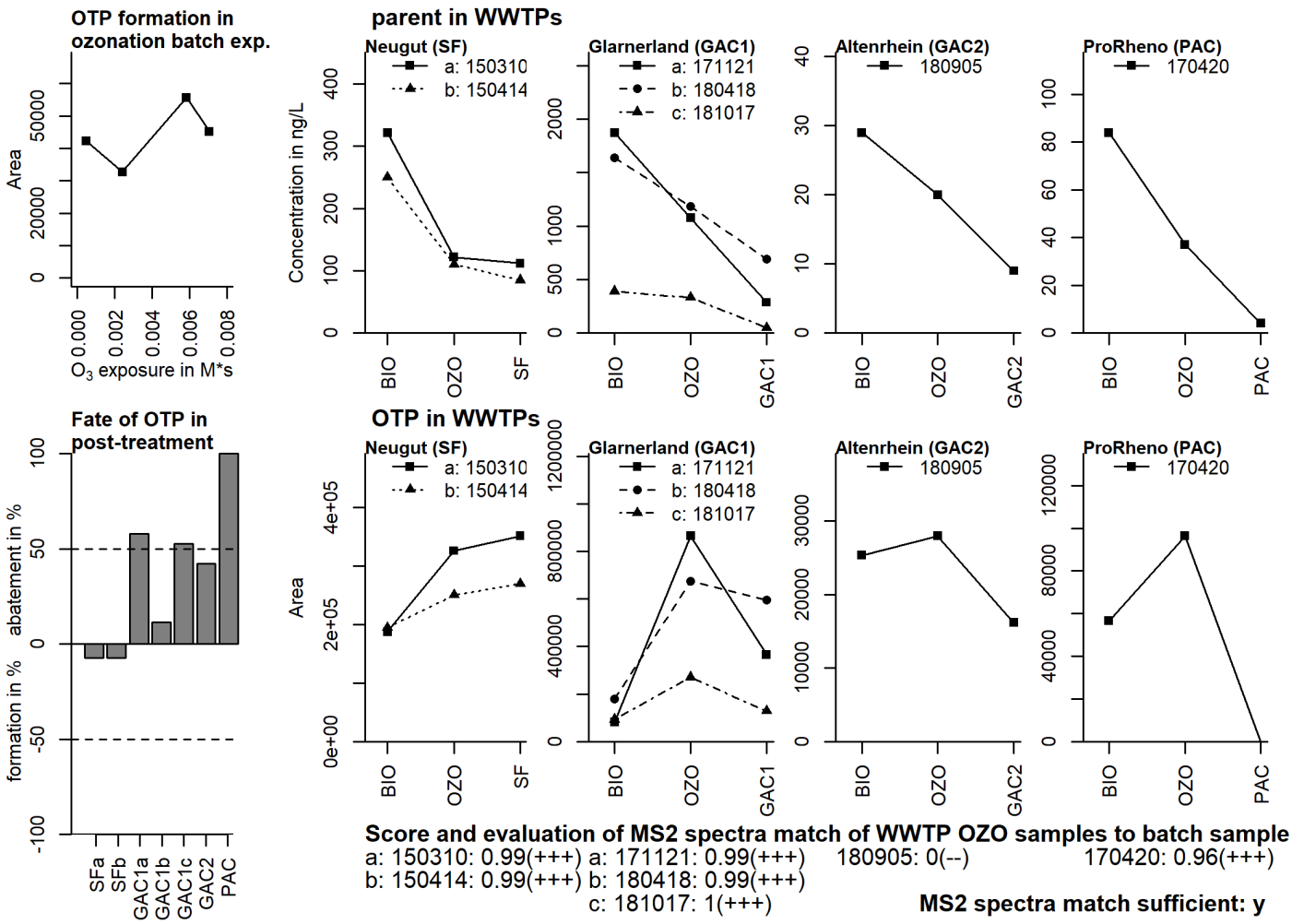
ET408601

Additional Evidence for Structure Interpretation

The atomic modification for the elemental formula of the parent compound to this OTP is -C6H4N4 +O2. This fits to a cleavage within the benzene moiety of the tetrazolebiphenylmethyl part, which is common for all sartans, and the addition of 2 oxygen atoms. The neutral loss of C5H9O2 between the precursor and fragment 207 indicates that the 2 oxygens are connected to the p-methylbenzyl or the pentanamide moiety. The exact type and position remain unknown. Aromatic compounds are known to form cis,cis-Muconic acid like structures (von Sonntag & von Gunten 2012). Therefore, the formation of this kind of structure, followed by a C-C bond cleavage, resulting in a p-benzoic acid moiety, is probable. There is however no further evidence. The structures of the MS^2 fragments are drawn exemplarily.

Diehle et al. (2019) detected an OTP of valsartan with the exact same mass and suggested the same structure.

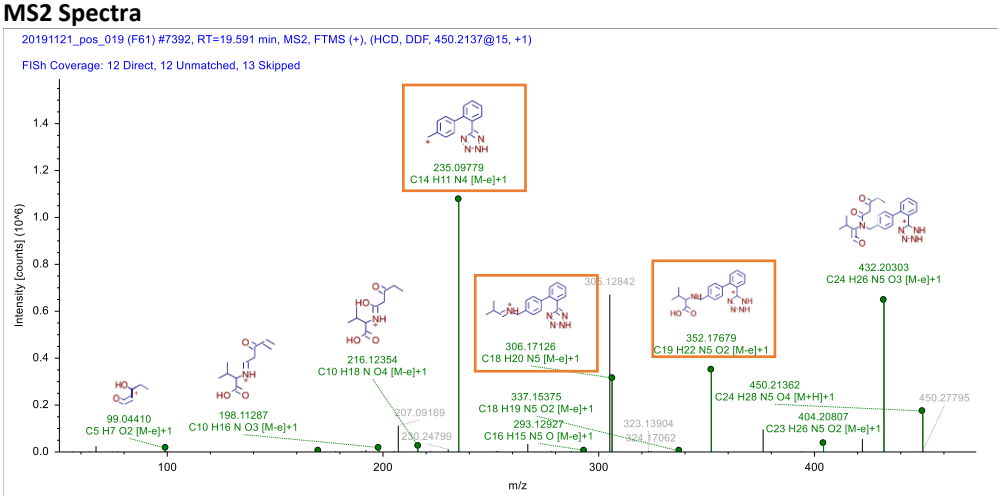
Name VAL_p_450.2132_19.2



MS Spectra

Pos	450.2132	[m+H]+
Neg	448.1988	[m-H]-

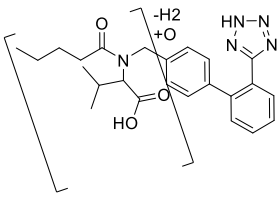
MS2 Spectra



Formula
C24H27N5O4

Atomic modification
-H2 +O

Proposed Structure



Confidence Level
Level 3

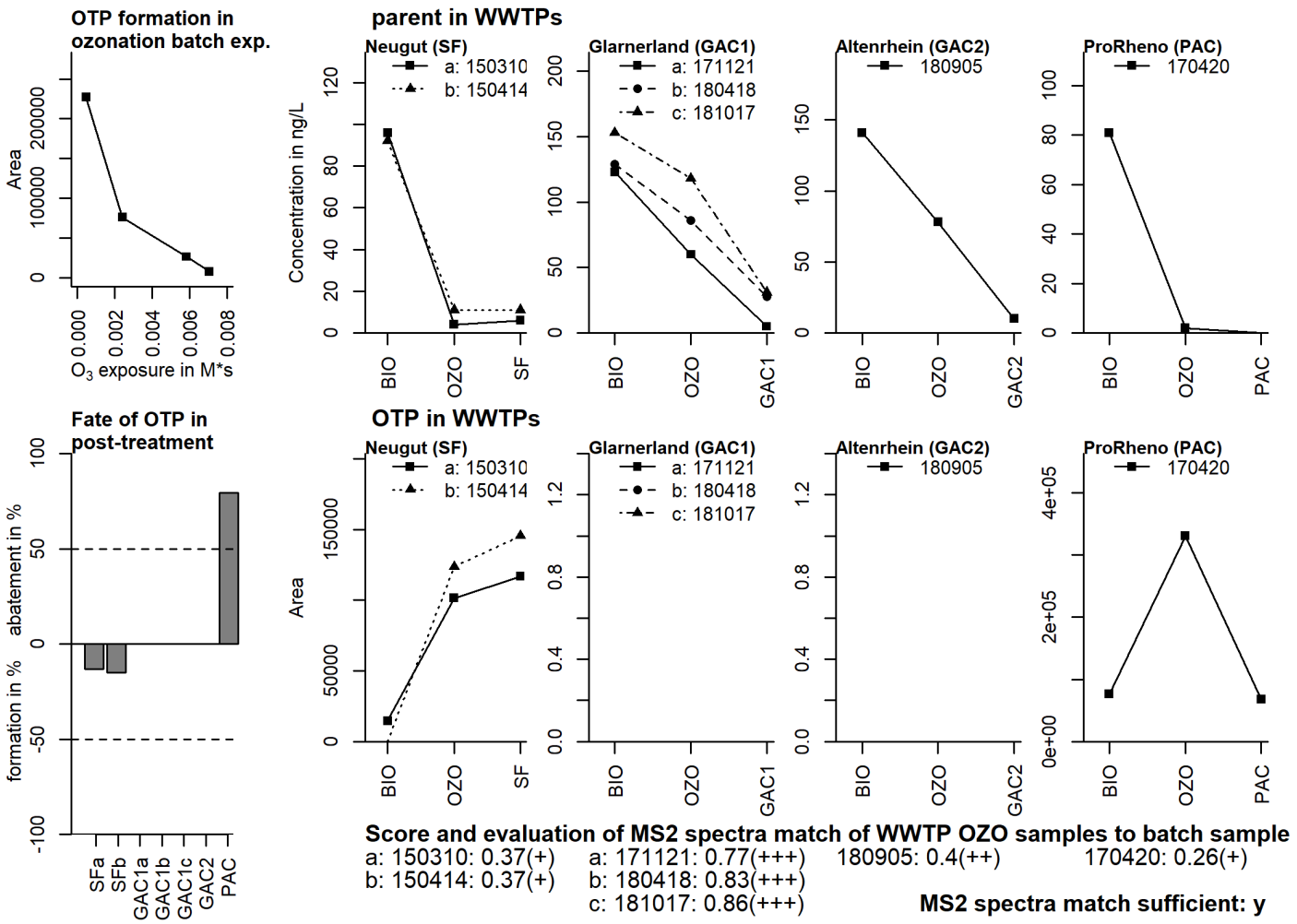
Massbank ID
ET404301

Additional Evidence for Structure Interpretation

The MS^2 fragments at the nominal masses 352, 306 and 235 were also observed for the parent compound. They indicate that the structure drawn for the fragment 352 is the substructure of this OTP.

Fragment 235 indicates the modification(s) did not take place at the methylbiphenyltetrazole moiety. The modification –H2 +O fits to the formation of a carbonyl group or an oxidation to a double bond with addition of an OH group, as suggested by Diehle et al. (2019). Diehle et al. (2019) detected two OTPs of valsartan with the same exact mass of 449. The exact type and location of the modification(s) remain unknown. The structures of the MS^2 fragments are drawn exemplarily.

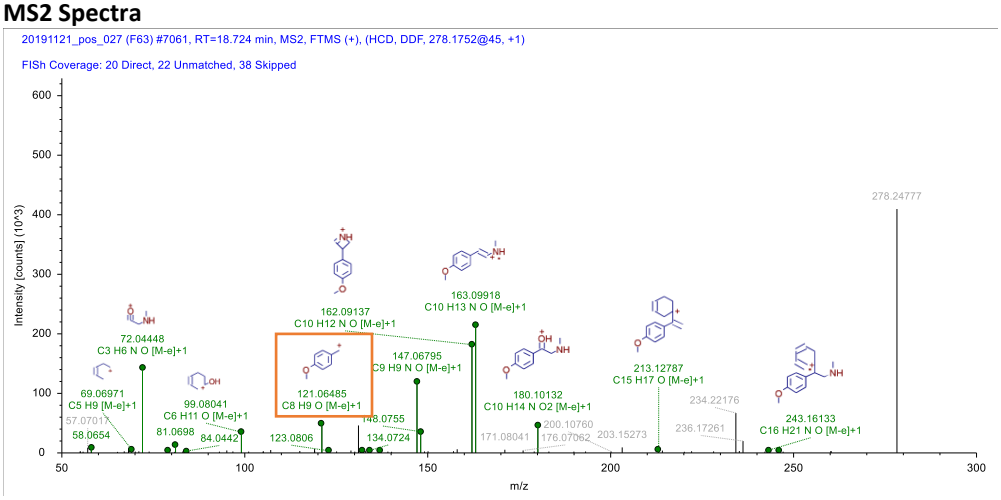
Name VEN_p_278.1749_19.4



MS Spectra

Pos 278.1749 [m+H]+

MS2 Spectra



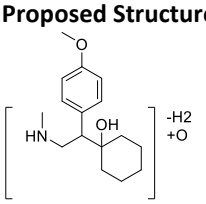
Formula

C16H23NO3

Atomic modification

+O –CH4

Proposed Structure



Confidence Level

Level 3

Massbank ID

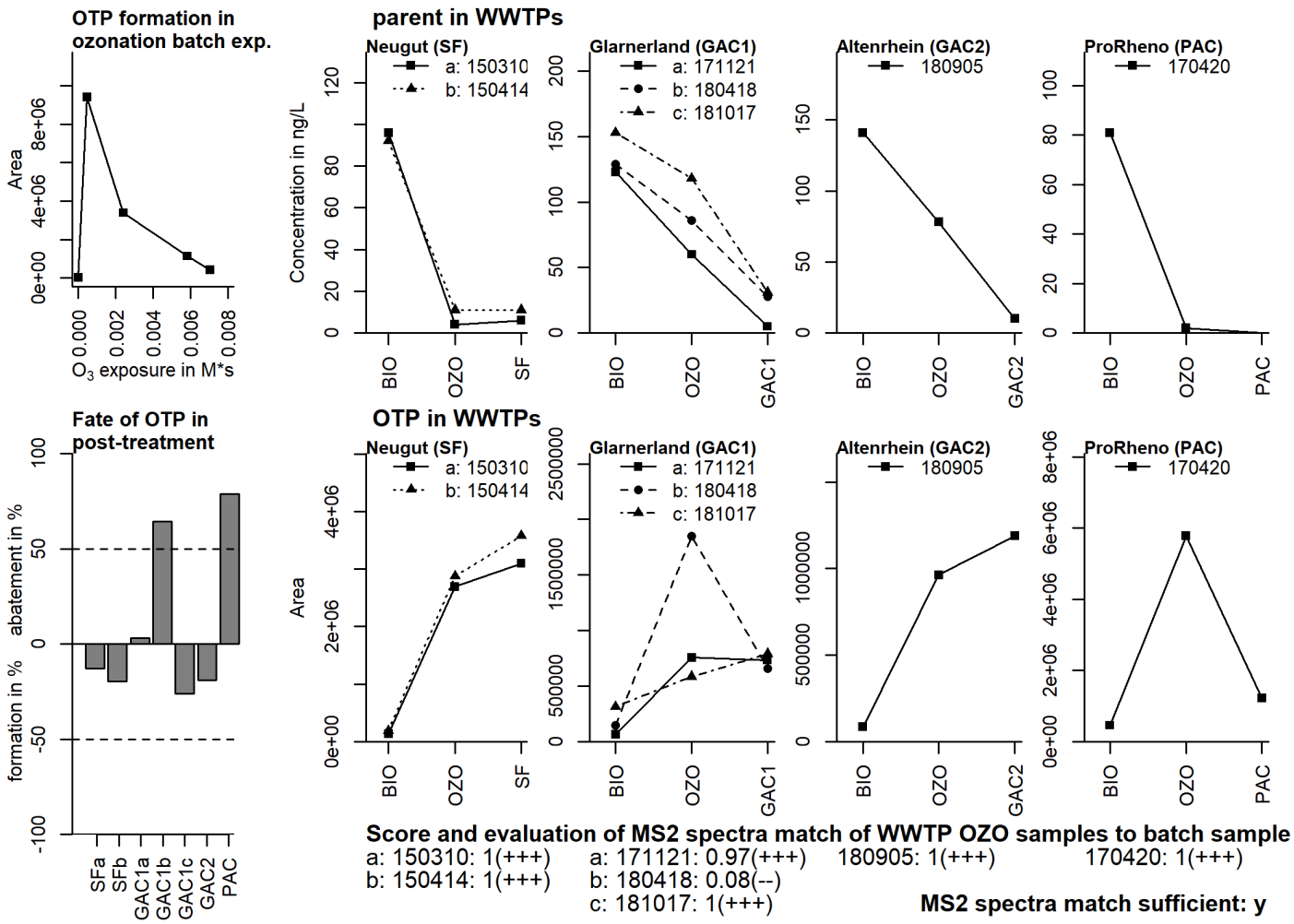
ET404401

Additional Evidence for Structure Interpretation

The MS^2 fragments at the nominal mass 121 was also observed for the parent compound. It indicates that the structure drawn for the fragment 121 is a substructure of this OTP and that the methyl group of the methoxy moiety is conserved.

N-desmethyl venlafexine was identified as minor OTP of venlafaxine by Zucker et al. (2018). Therefore, is it likely that one methyl group was cleaved at the tertiary amine moiety. The remaining modification of –H2 + O fits to the formation of a carbonyl moiety. Fragment 121 indicates the modification occurred at the methylaminomethylcyclohexanol moiety. However, there is no further indication for the exact type and location of the modification(s). The structures of the MS^2 fragments are drawn exemplarily.

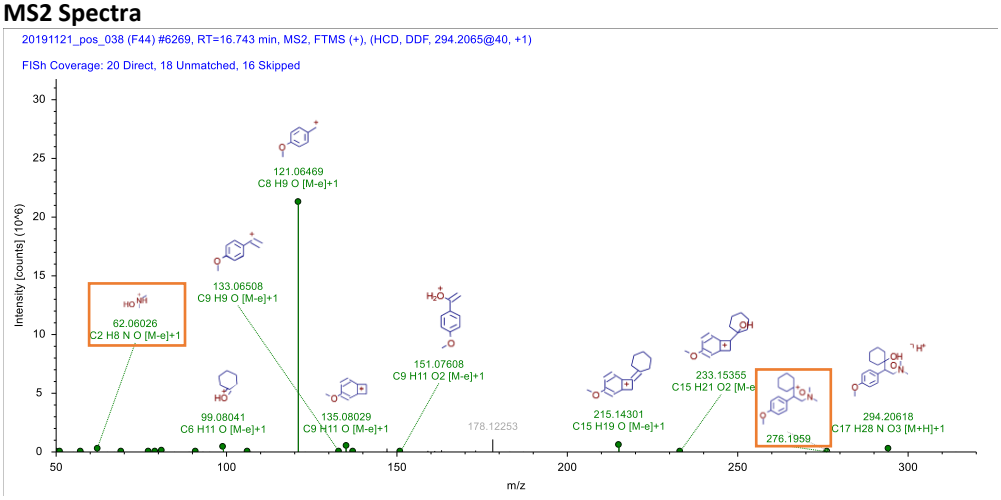
Name VEN_p_294.2064_16.1



MS Spectra

Pos 294.2064 [m+H]+

MS2 Spectra



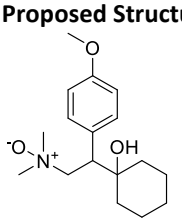
Formula

C17H27NO3

Atomic modification

+O

Proposed Structure



Confidence Level

Level 1

Massbank ID

ET404501

Additional Evidence for Structure Interpretation

The MS^2 fragments at the nominal masses 215, 135 and 121 were also observed for the parent compound. The MS^2 fragment 276 corresponds to the fragment 260 of the parent with an addition of an oxygen atom.

Tertiary amines are very reactive to form *N*-oxides during ozonation (von Sonntag & von Gunten 2012). Therefore, the formation of a *N*-oxide at the trimethylamine moiety is very likely. Fragment 62 indicates the formation of the *N*-oxide.

Venlaflaxin *N*-oxide has been identified as major OTP of venlaflaxin in different studies (Merel et al. 2017, Zucker et al. 2018, Lester et al. 2013, Lajeunesse et al. 2013). The MS^2 spectrum here matches the reference spectrum we recorded for venlaflaxin *N*-oxide.