Differentiation of ADB-PINACA Isomers using Gas Chromatography/Mass Spectrometry

Inge Corbin, James Kollar, Shabrel Simmons, DFSC, Forest Park, GA 30297

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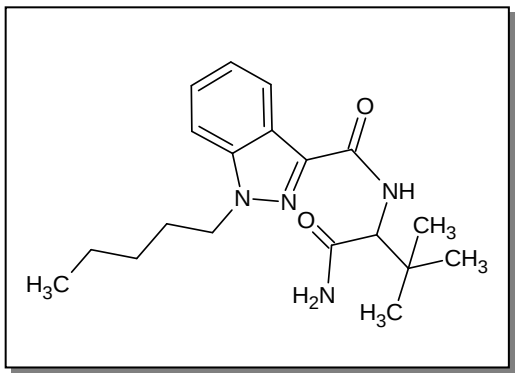
Compound Information



Name: ADB-PINACA

Synonyms: *N*-(1-Amino-3,3-dimethyl-1-oxobutan-2-yl)-1-pentyl-1*H*-indazole-3-carboxamide

CAS#: 1633766-73-0

Molecular Formula: C19H28N4O2

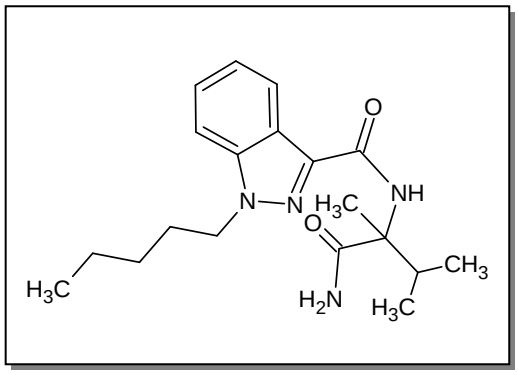
Nominal Mass: 344 Da

Monoisotopic Mass: 344.2212 Da

SMILES: O=C(NC(C(N)=O)C(C)(C)C)C1=NN(CCCCC)C2=C1C=CC=C2

InChl Key: FWTARAXQGJRQKN-UHFFFAOYSA-N

InChl: 1S/C19H28N4O2/c1-5-6-9-12-23-14-11-8-7-10-13(14)15(22-23)18(25)21-16(17(20)24)19(2,3)4/h7-8,10-11,16H,5-6,9,12H2,1-4H3,(H2,20,24)(H,21,25)



Name: Isomer 1

Synonyms: N-(1-amino-2,3-dimethyl-1-oxobutan-2-yl)-1-pentyl-1H-indazole-3-carboxamide

CAS#: N/A

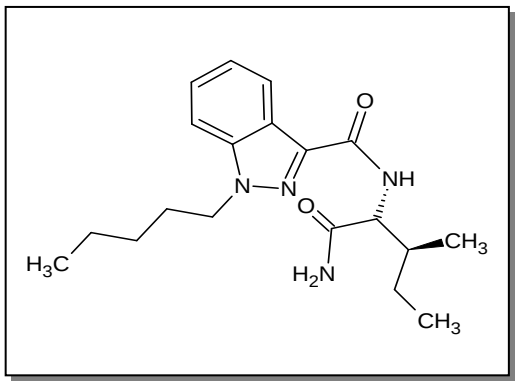
Nominal Mass: 344 Da

Monoisotopic Mass: 344.2212 Da

SMILES: O=C(NC(C(N)=O)(C)C(C)(C)C1=NN(CCCCC)C2=C1C=CC=C2

InChl Key: WLFSZTSBEOZUTQ-UHFFFAOYSA-N

InChl: 1S/C19H28N4O2/c1-5-6-9-12-23-15-11-8-7-10-14(15)16(22-23)17(24)21-19(4,13(2)3)18(20)25/h7-8,10-11,13H,5-6,9,12H2,1-4H3,(H2,20,25)(H,21,24)



Name: Isomer 2

Synonyms: N-((2S,3S)-1-amino-3-methyl-1-oxopentan-2-yl)-1-pentyl-1H-indazole-3-carboxamide

CAS#: N/A

Molecular Formula: C19H28N4O2

Nominal Mass: 344 Da

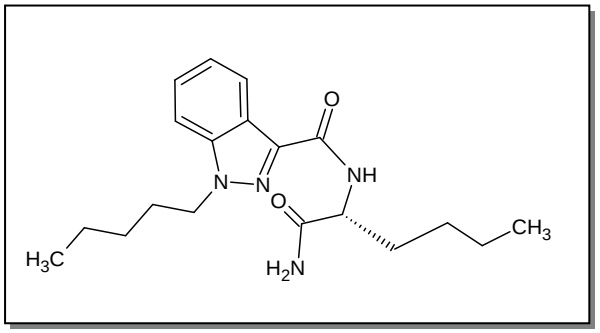
Monoisotopic Mass: 344.2212 Da

SMILES: O=C(N[C@H](C(N)=O)[C@@H](C)CC)C1=NN(CCCCC)C2=C1C=CC=C2

InChl Key: QFGOKLQWEVQXAP-BBRMVZONSA-N

InChl: 1S/C19H28N4O2/c1-4-6-9-12-23-15-11-8-7-10-14(15)17(22-23)19(25)21-16(18(20)24)13(3)5-2/h7-8,10-11,13,16H,4-6,9,12H2,1-3H3,(H2,20,24)(H,21,25)/t13-,16-/m0/s1

Name: Isomer 3



Synonyms: (S)-N-(1-amino-1-oxohexan-2-yl)-1-pentyl-1H-indazole-3-carboxamide

CAS#: N/A

Molecular Formula: C19H28N4O2

Nominal Mass: 344 Da

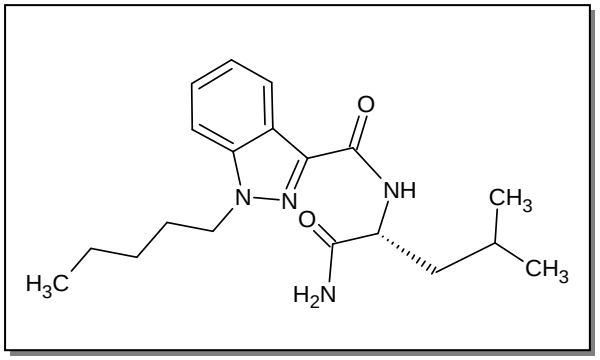
Monoisotopic Mass: 344.2212 Da

SMILES:
O=C(N[C@H](C(N)=O)CCCC)C1=NN(CCCCC)C2=C1C=CC=C2

InChl Key: BIAATZFCIKCULE-HNNXBMFYSA-N

InChl: 1S/C19H28N4O2/c1-3-5-9-13-23-16-12-8-7-10-14(16)17(22-23)19(25)21-15(18(20)24)11-6-4-2/h7-8,10,12,15H,3-6,9,11,13H2,1-2H3,(H2,20,24)(H,21,25)/t15-/m0/s1

Name: Isomer 4



Synonyms: (S)-N-(1-amino-4-methyl-1-oxopentan-2-yl)-1-pentyl-1H-indazole-3-carboxamide

CAS#: N/A

Molecular Formula: C19H28N4O2

Nominal Mass: 344 Da

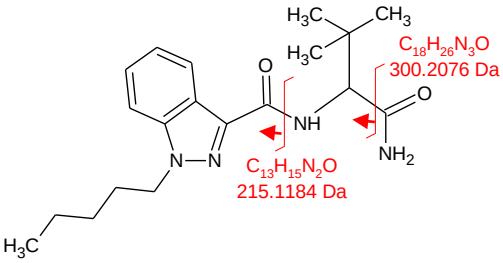
Monoisotopic Mass: 344.2212 Da

SMILES:
O=C(N[C@H](C(N)=O)CC(C)C)C1=NN(CCCCC)C2=C1C=CC=C2

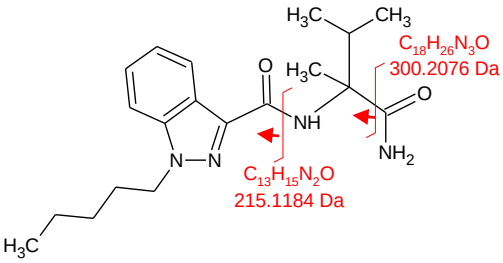
InChl Key: DHGROCCLLLHPHU-HNNXBMFYSA-N

InChl: 1S/C19H28N4O2/c1-4-5-8-11-23-16-10-7-6-9-14(16)17(22-23)19(25)21-15(18(20)24)12-13(2)3/h6-7,9-10,13,15H,4-5,8,11-12H2,1-3H3,(H2,20,24)(H,21,25)/t15-/m0/s1

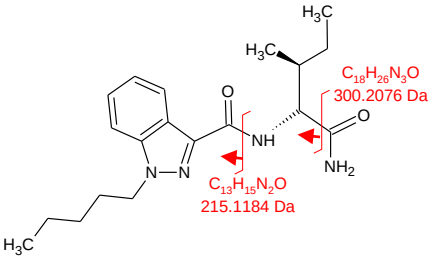
Background: Four positional isomers of ADB-PINACA which were predicted to have similar mass spectra to that of ADB-PINACA were synthesized by Cayman Chemical Company. These compounds were analyzed by gas chromatography/low resolution electron impact mass spectrometry. The major peaks in the mass spectra of all of these compounds are 300, 215, and 145. It was noted that ADB-PINACA can be differentiated from these positional isomers by mass spectrometry alone, based on the presence of a 271 peak in the mass spectrum of ADB-PINACA, which is absent or relatively minor in the positional isomers.



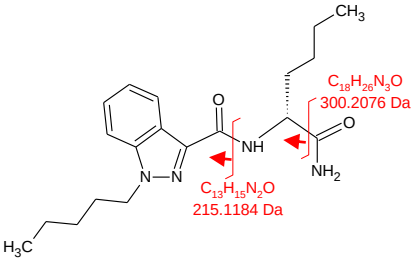
ADB-PINACA



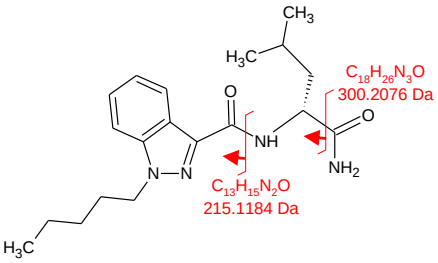
Isomer 1



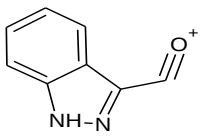
Isomer 2



Isomer 3



Isomer 4



145 m/z ion

Gas chromatography / Mass spectrometry:

Sample Preparation: ~1mg/mL in methanol

Instrument Agilent 7890A GC/ 5975C MS

GC Parameter:

Column: HP-5MS 30m x 250 μm x .25 μm

Carrier Gas: He

Oven Program: 240°C hold for 1 min. Ramp 30°C/min to 300 hold for 11 minutes

Injection parameter: **Injector Volume:** 1 uL **Split ratio:** 100:1

MS Parameters: **Injector** 250°C

MSD transfer line: 290°C

MS Source: 230°C

MS Quad: 150°C

Mass Scan Range: 34-550 amu

Threshold: 150

Tune File: atune.u

Figure 1: ADB-PINACA GC-MS

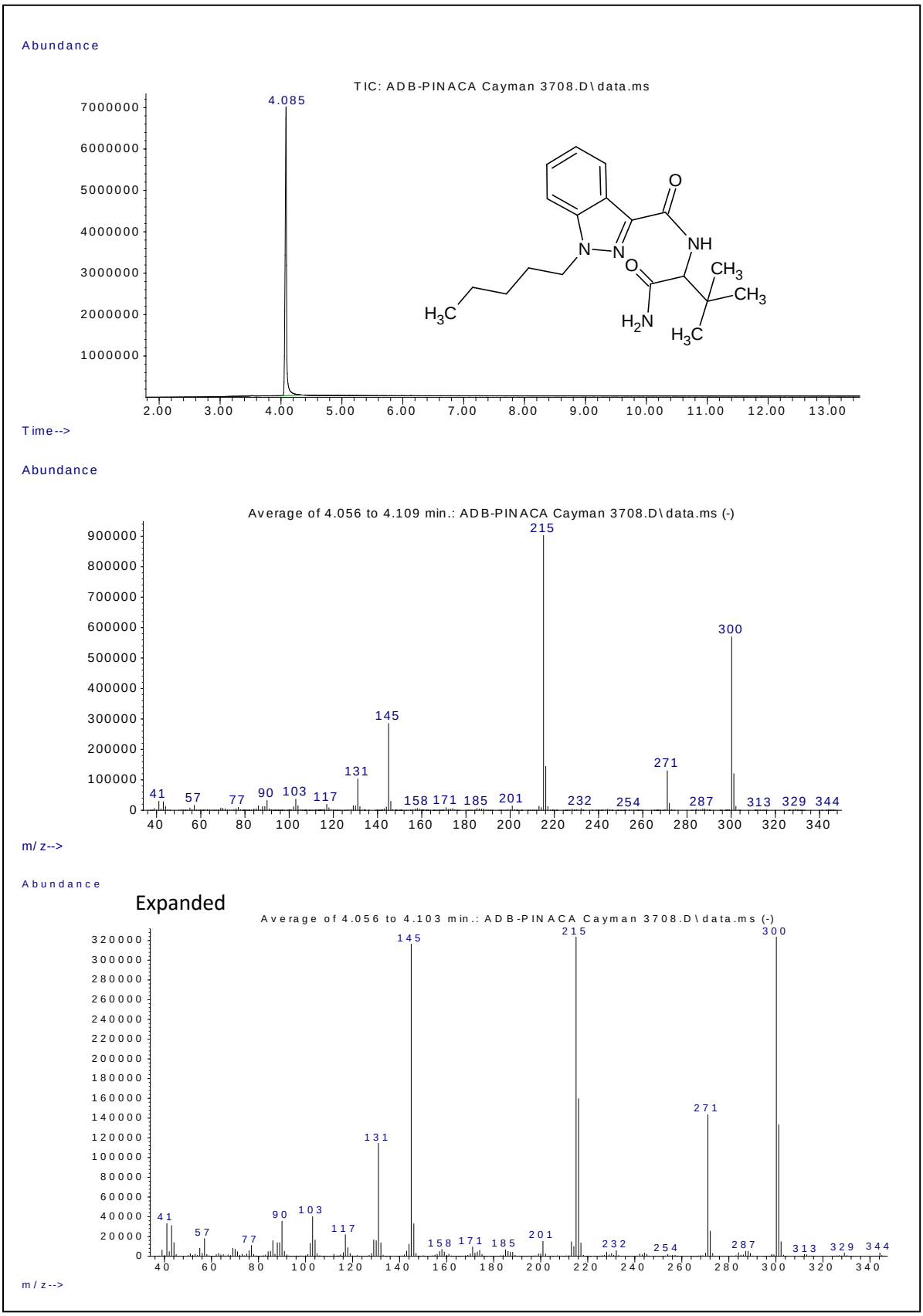


Figure 2: Isomer 1 GC-MS

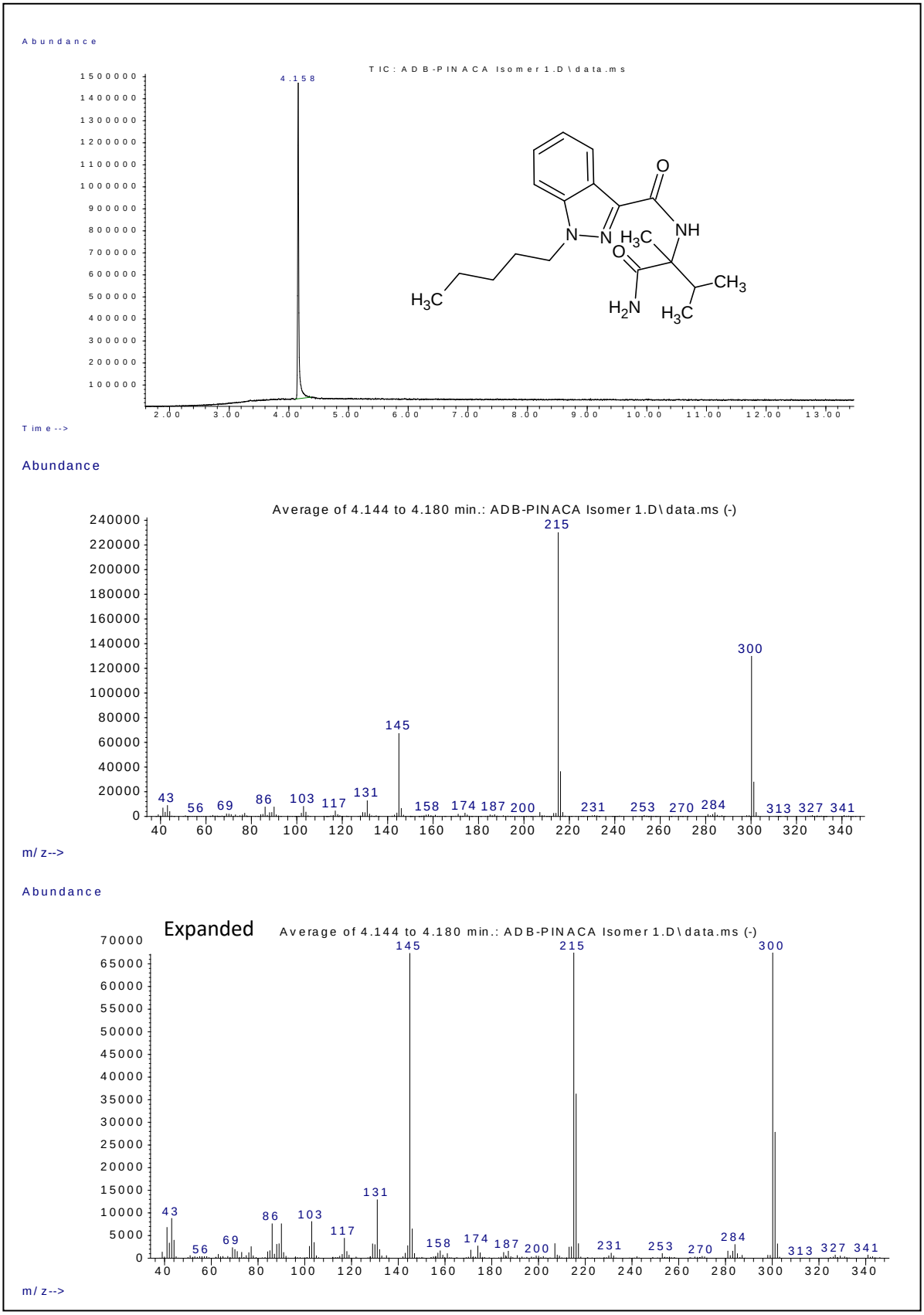


Figure 3: Isomer 2 GC-MS

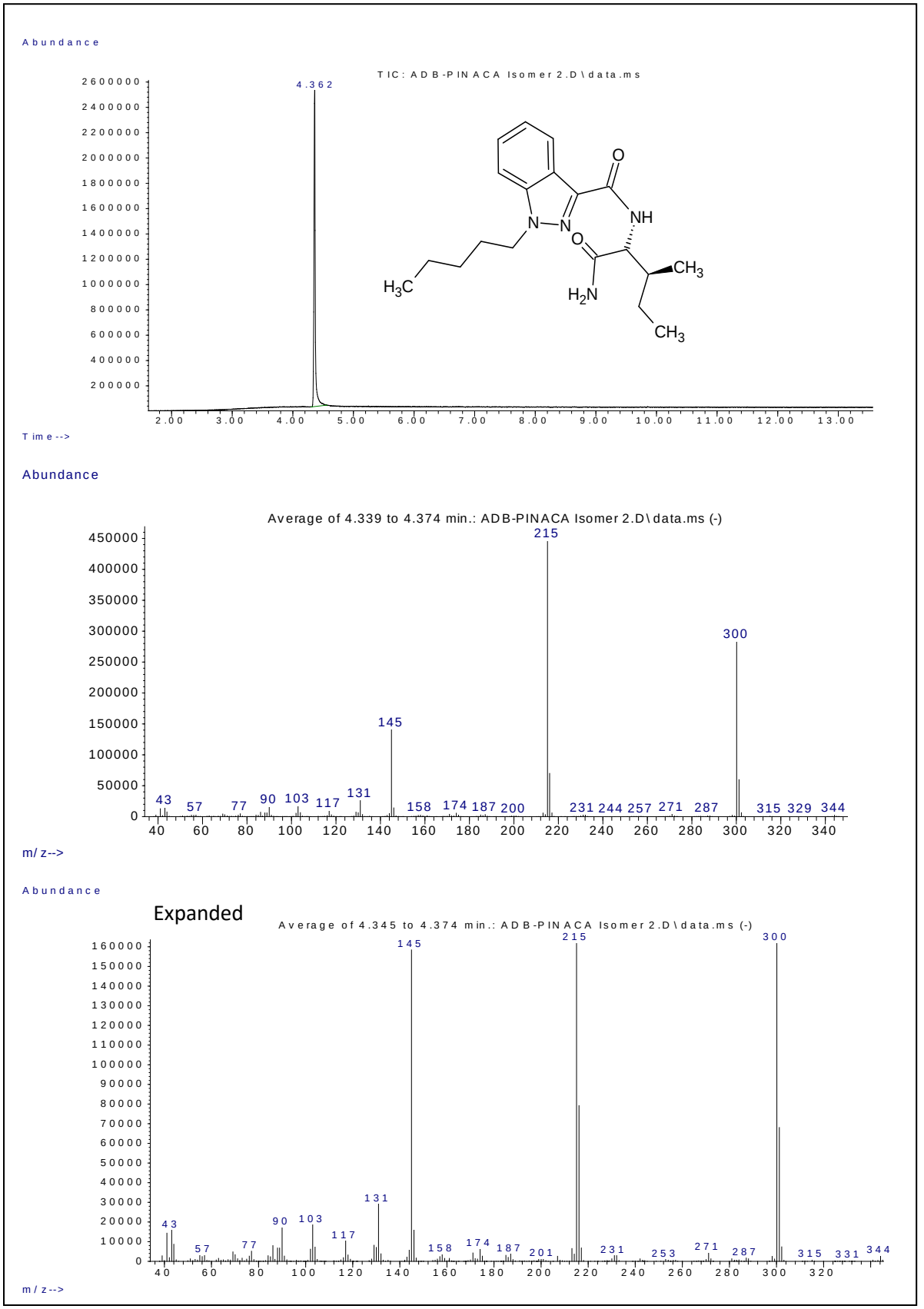


Figure 4: Isomer 3 GC-MS

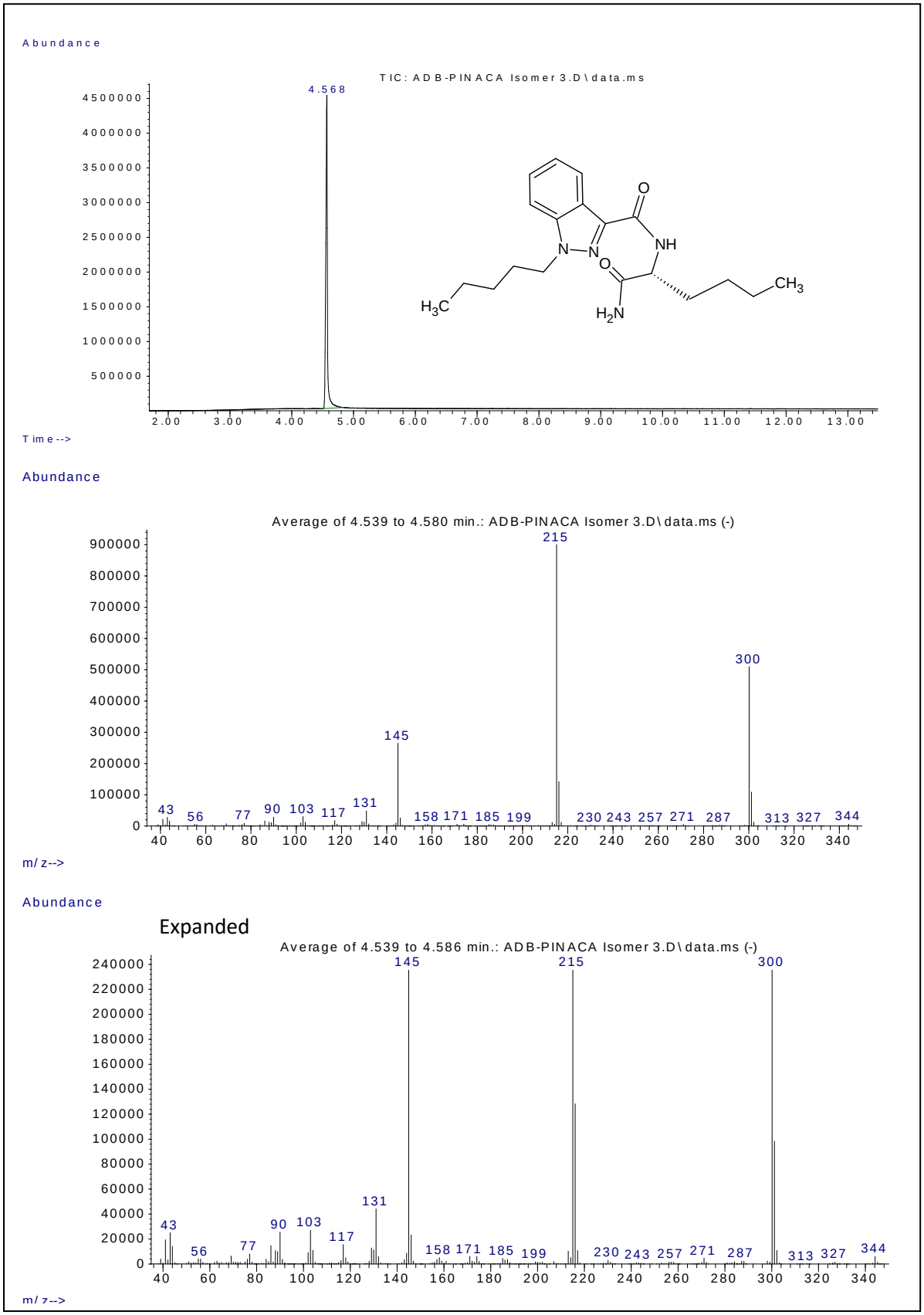


Figure 5: Isomer 4 GC-MS

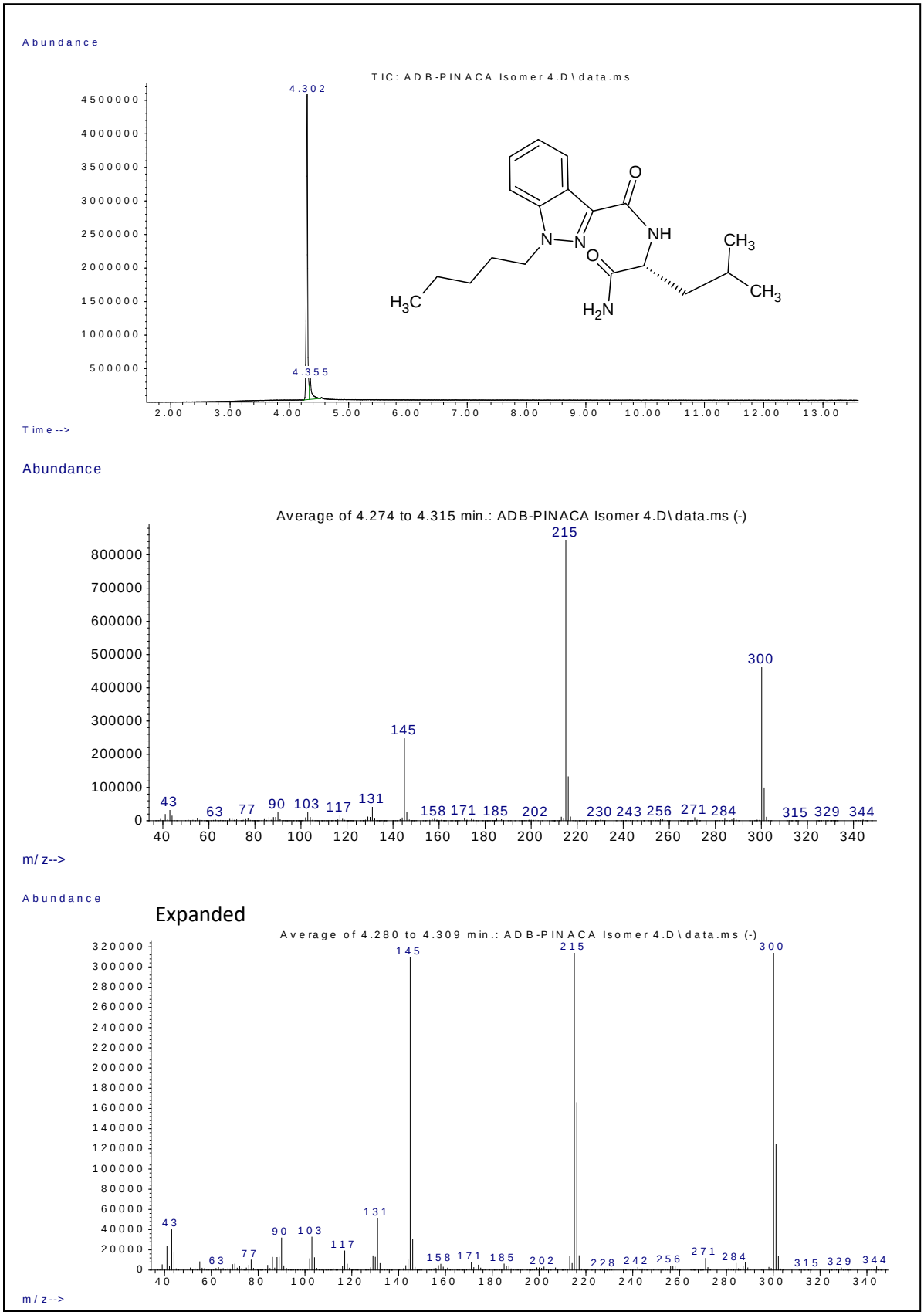
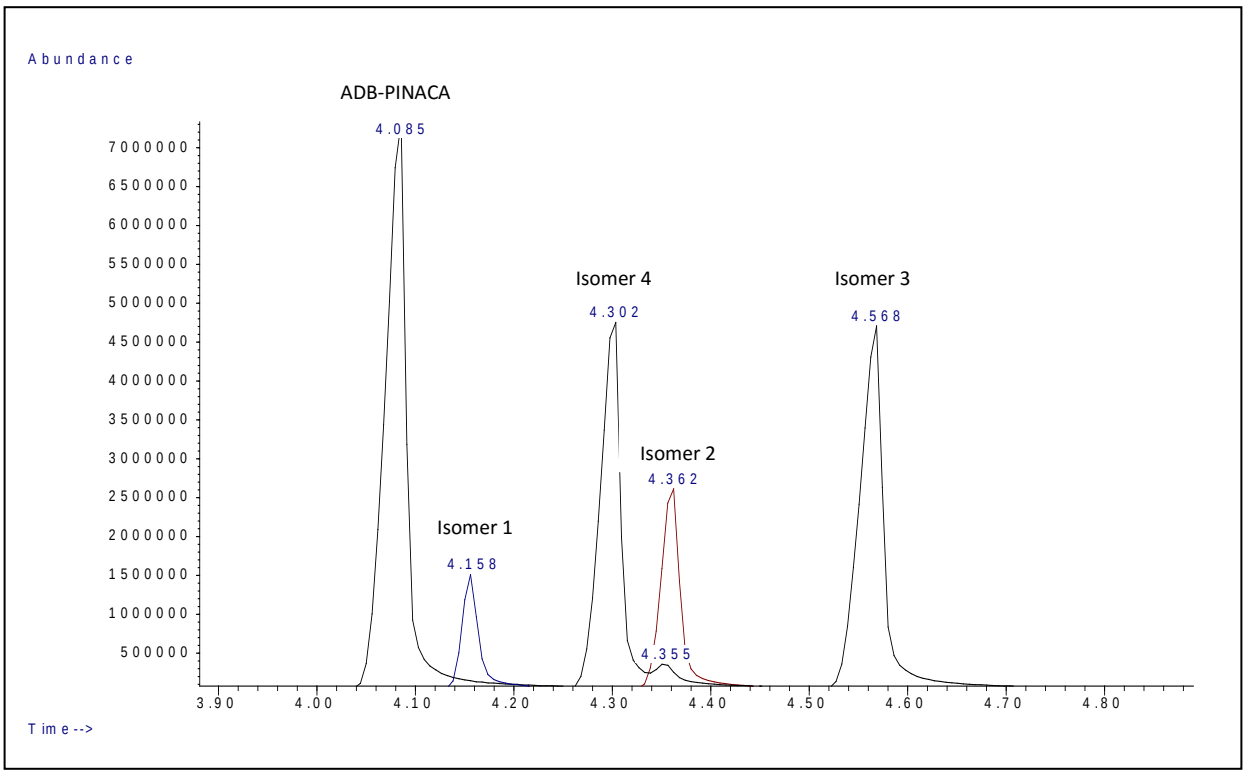


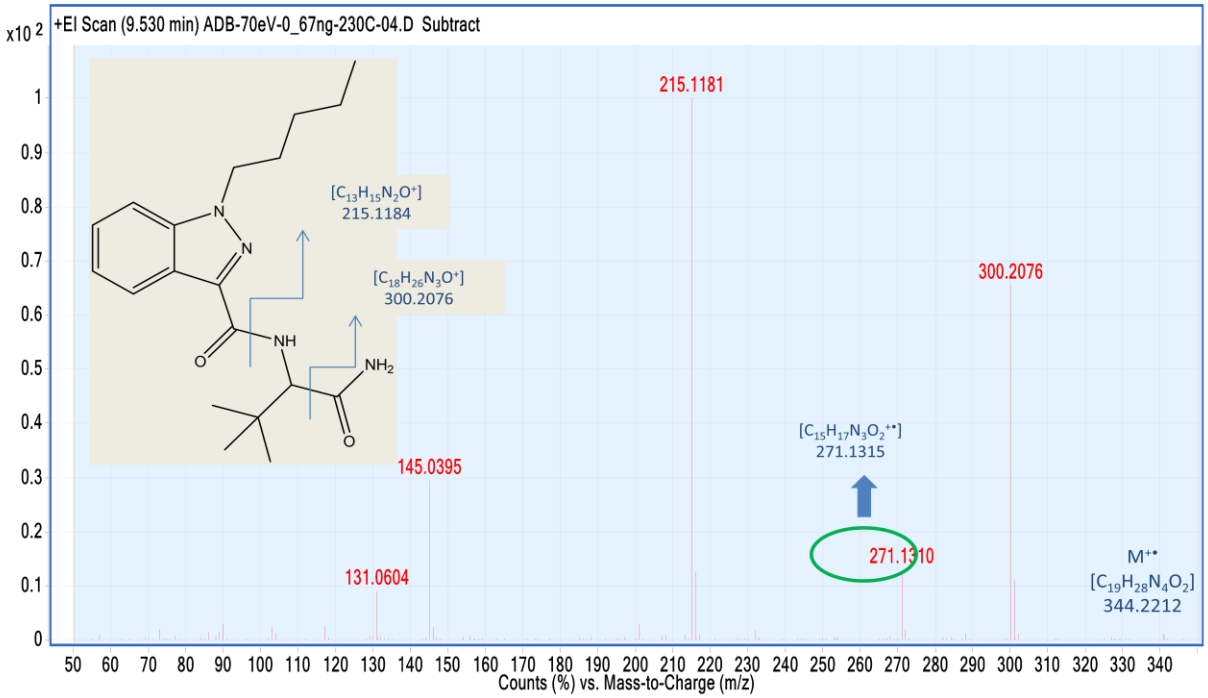
Figure 6: Overlay of ADB-PINACA and Isomers 1- 4



Compound	Retention Time	Relative Retention Time
ADB-PINACA	4.085	1.000
Isomer 1	4.158	1.018
Isomer 2	4.362	1.068
Isomer 3	4.568	1.118
Isomer 4	4.302	1.053

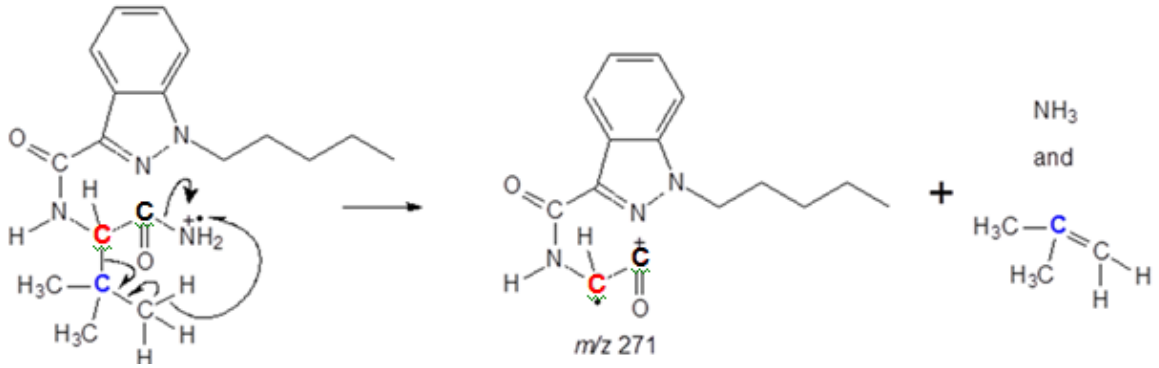
Discussion:

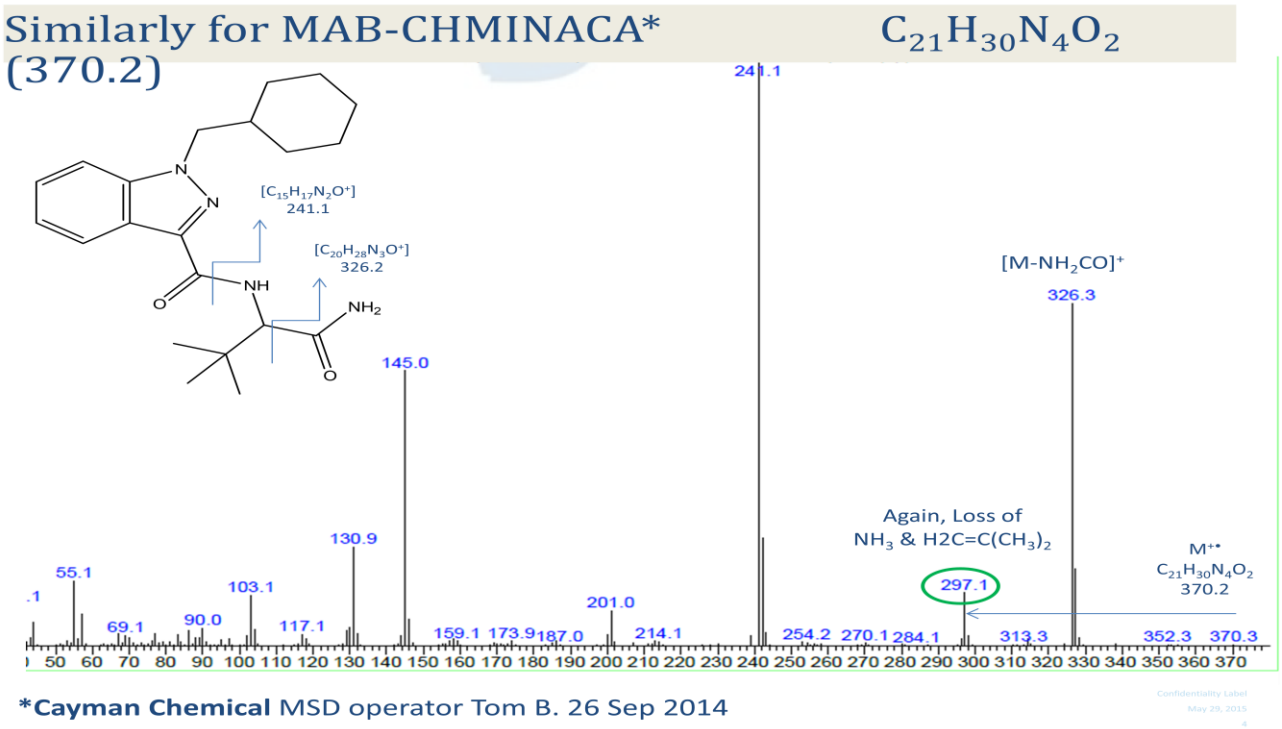
Structure and Spectrum of ADB-PINACA (7200 QTOF)



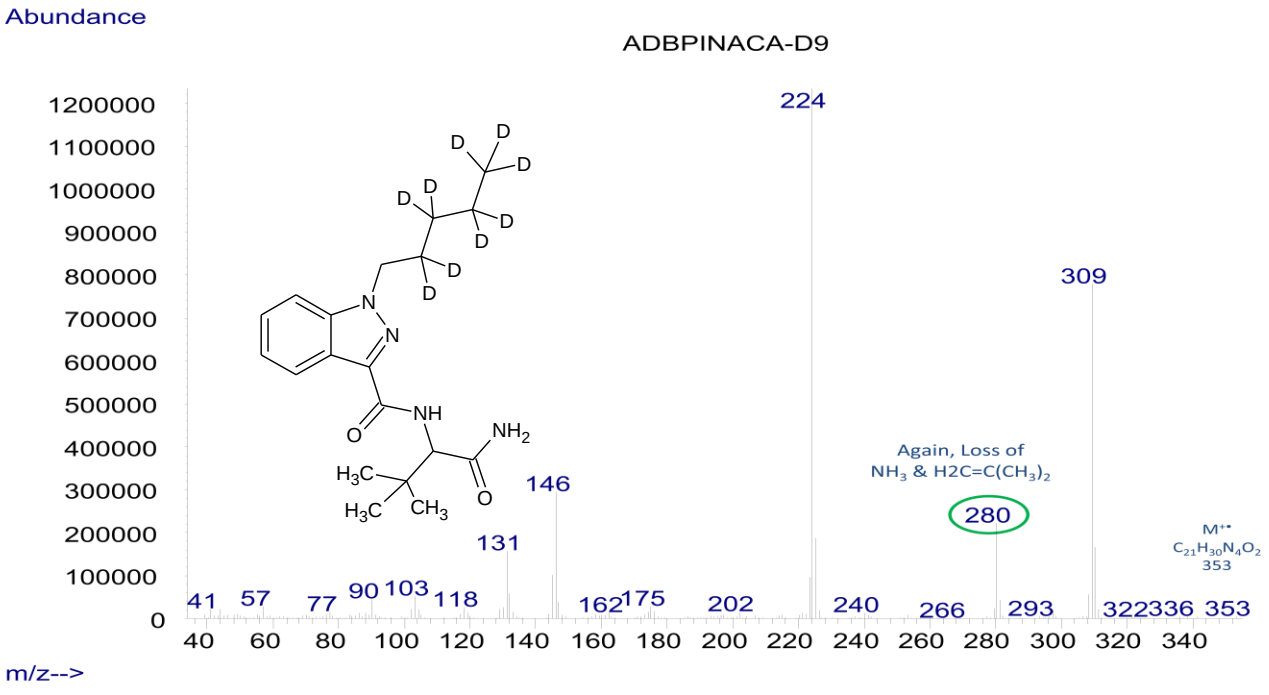
"ADB-PINACA" is a combination a 1-amino-3,3-dimethyl-1-oxobutan-2-yl (ADB) with a 1-pentyl-1H-indazole-3-carboxamide (PINACA)

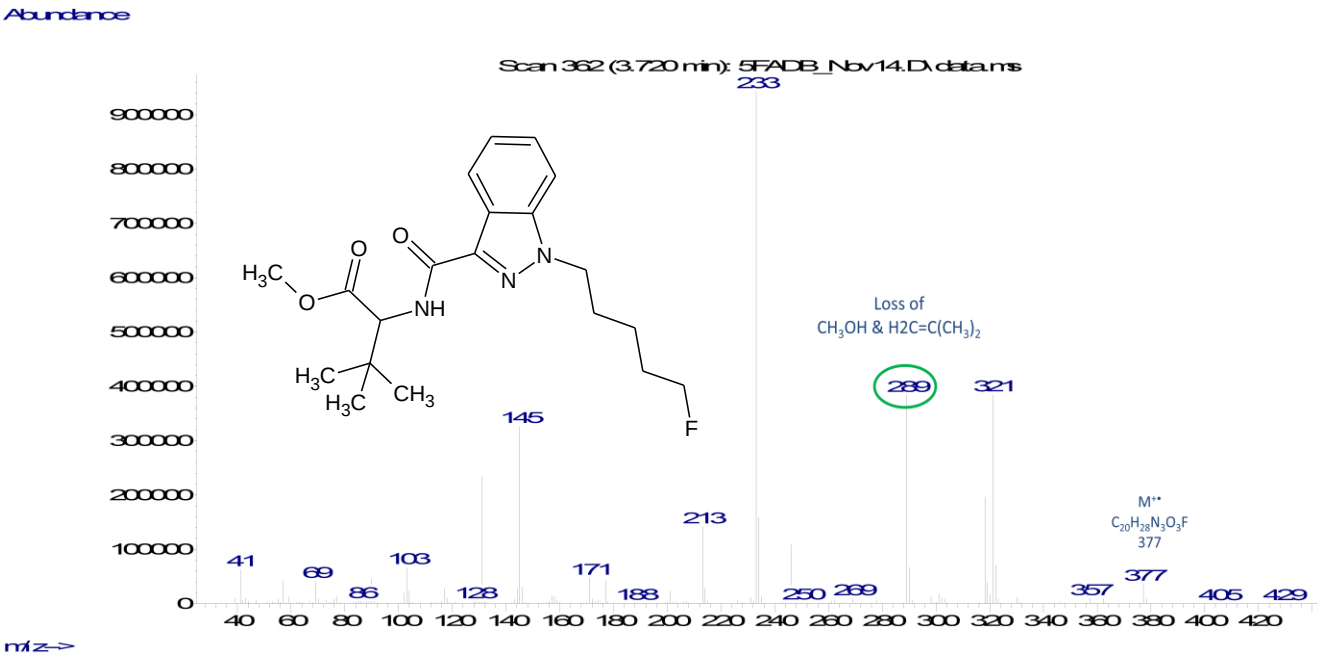
Suggested mechanism of formation of the *m/z* 271 fragment



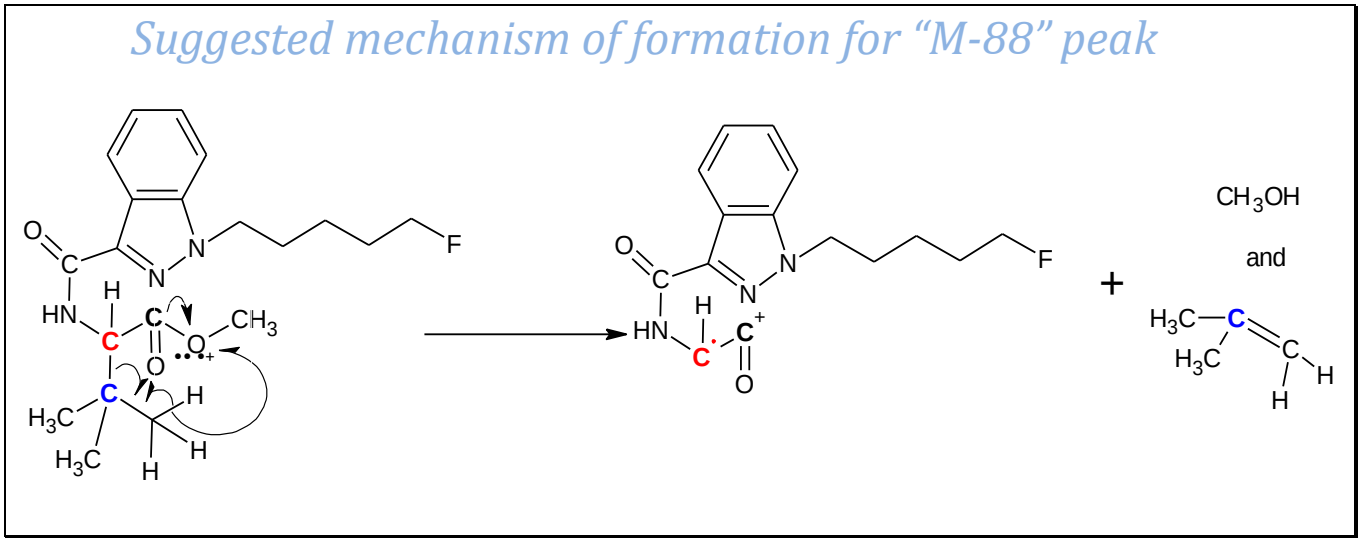


ADB-PINACA, which contains a tertiary butyl group, has an M-73 peak present in the mass spectrum. This peak is relatively minor or absent in the mass spectra of positional isomers that do not have the tertiary butyl group. Some support for the suggested mechanism of formation of the M-73 ion has been shown by analyzing an ADB-PINACA standard with a partially-deuterated pentyl chain. The M-73 peak is still present in the mass spectrum of this compound, suggesting that the leaving group is the t-butyl group and not the pentyl side chain.





A similar mechanism may occur in molecules that have a terminal methoxy group, as shown above in the mass spectrum of 5F-ADB. Rather than producing an M-73 peak as seen in molecules with a terminal amine, an M-88 peak is present.



Acknowledgements:

7200 QTOF spectra provided by Agilent Technologies

Proposed mechanism provided by Prof. O. David Sparkman, Dr. Harry Prest, and Dr. Kirk E. Lokits

References:

Namera A, Konuma K, Kawamura M, Saito T, Nakamoto A, Saito T, Nagao M, (2015) Comprehensive review of the detection methods for synthetic cannabinoids and cathinones. Forensic Toxicology 33:175–194

External Links:

Forendex

Wikipedia