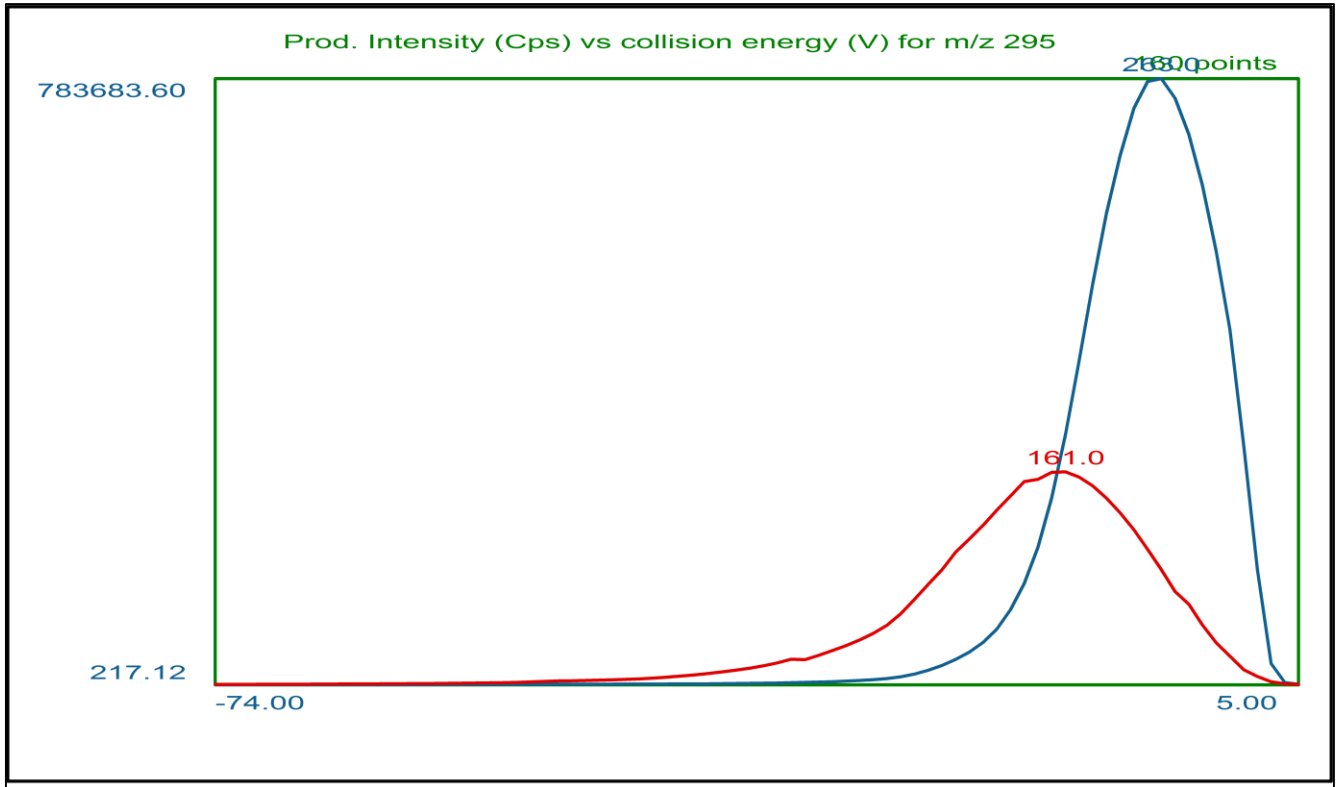
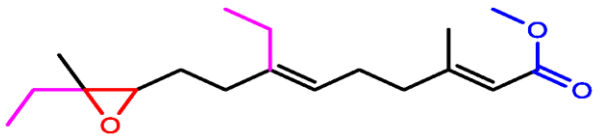
Supplemental Figure 1. Optimization of multiple reaction monitoring (MRM) detection on the Bruker EvoQ LC-TQ Elite Triple Quadrupole Mass Spectrometer and confirmation experiments using the Bruker Solarix 7T Fourier-transform ion cyclotron resonance (FT-ICR) ultra high-resolution mass spectrometer (UHRMS).

A) Optimization of MRM collision-induced dissociation (CID). The most abundant MRM transitions were selected for LC-MS/MS quantitative analysis, while the second highest were selected for confirmation. In order to add an additional differentiation feature between the isomers JHB_3 and $JHSB_3$, an exception for this rule was in which the third most abundant MRM transition for JHB_3 (m/z 283→251) was used instead of the second most abundant (m/z 283→119) which was common between them.
B) Comparison of UHRMS signals for protonated pseudomolecular ions ($[M+H]^+$) with theoretical (according to molecular formulas). Internal calibration was used. Very low mass errors (<0.2 ppm) were observed for all compounds.
C) Fragmentation spectra (CID, MS/MS) obtained by direct infusion of individual standards using the FT-ICR UHRMS.
D) Accurate masses of protonated pseudomolecular ion ($[M+H]^+$) and MS/MS fragments, with mass errors according to proposed structures.
E) Proposed fragmentation pathways for JHs and MF based on collision-induced dissociation (CID) MS/MS experiments using UHRMS.

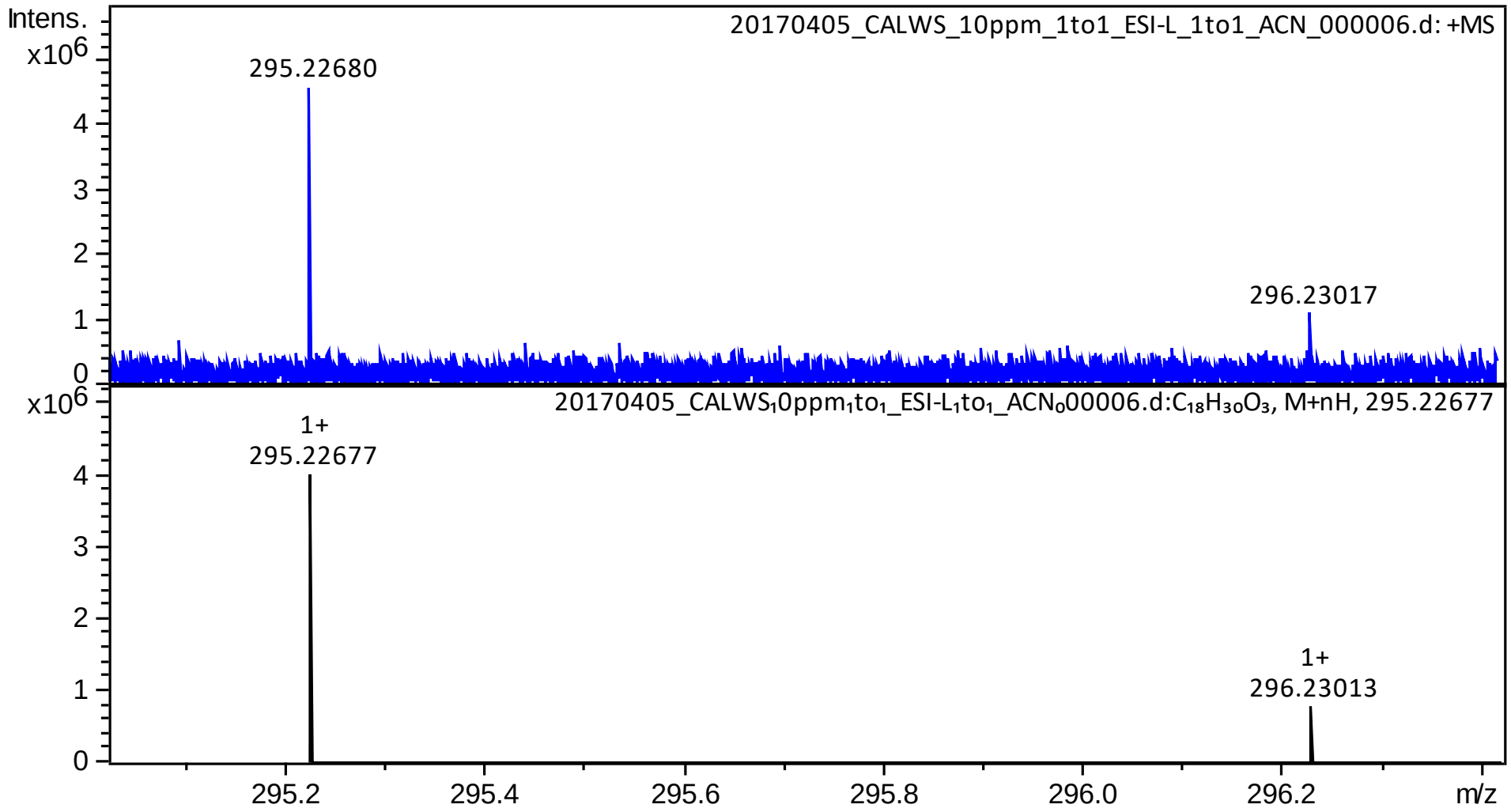
A: JH I



Instrument:	EVOQ LC-TQ Elite		
Date:	10 Jan 2018 14:09:42		
Compound: JH I			
Charge State: 1			
Precursor: 295.0 m/z			
CID pressure : 1.5 mTorr			
Prod	CE(V)	Intens.	Ratio(%)
263.00	-5.0	7.84e5	100.00
161.00	-12.0	2.75e5	35.15



B: JH I



Ultra high resolution mass spectra of the standard obtained by direct infusion using the Solarix 7T FT-ICR MS .

C: JH I

Fourier-transformation cyclotron resonance (FT-ICR) ultra high-resolution MS/MS.

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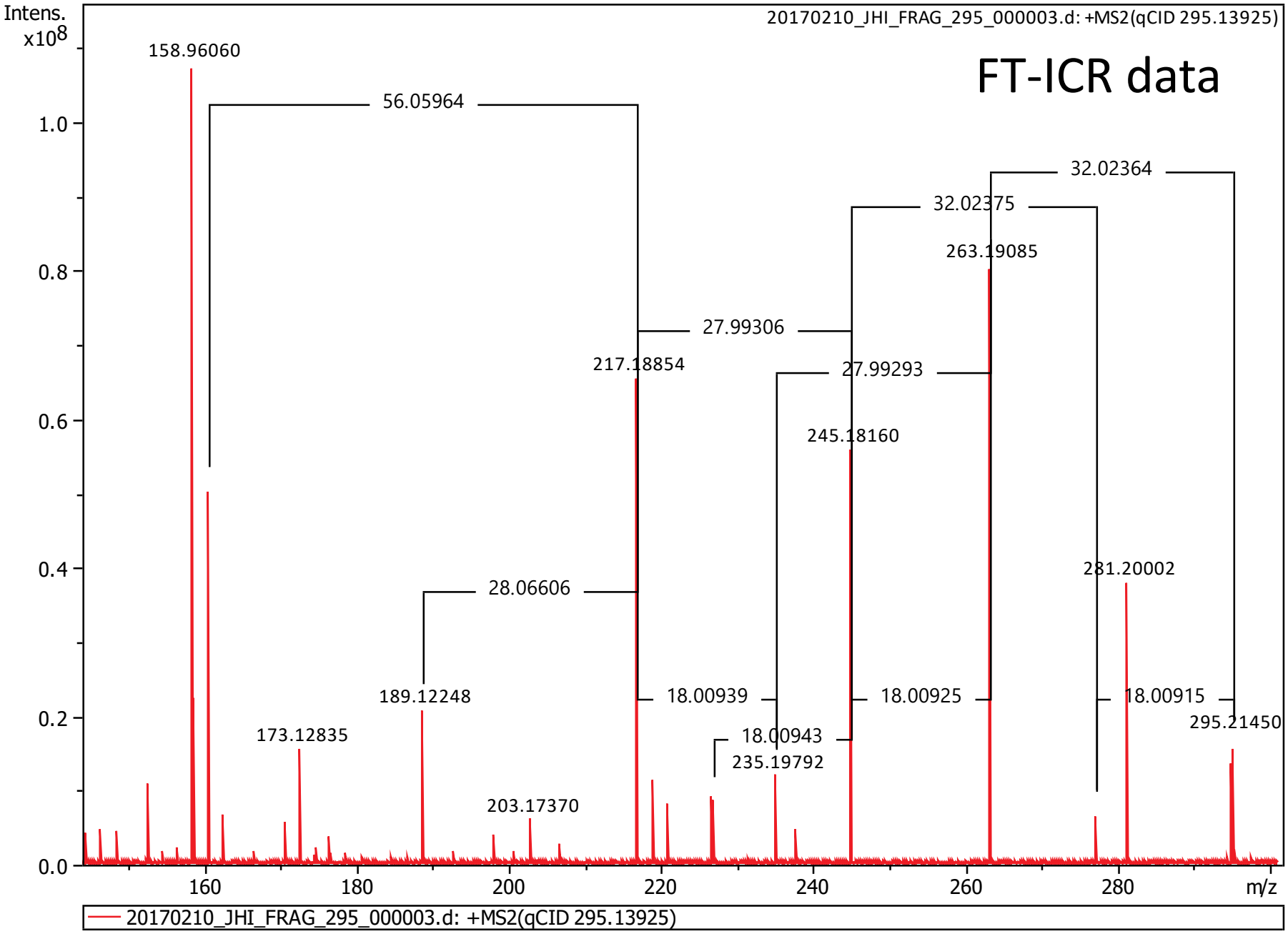


D: JH I

Table showing the MS/MS fragments of the hormone using the Solarix 7T FT-ICR MS.

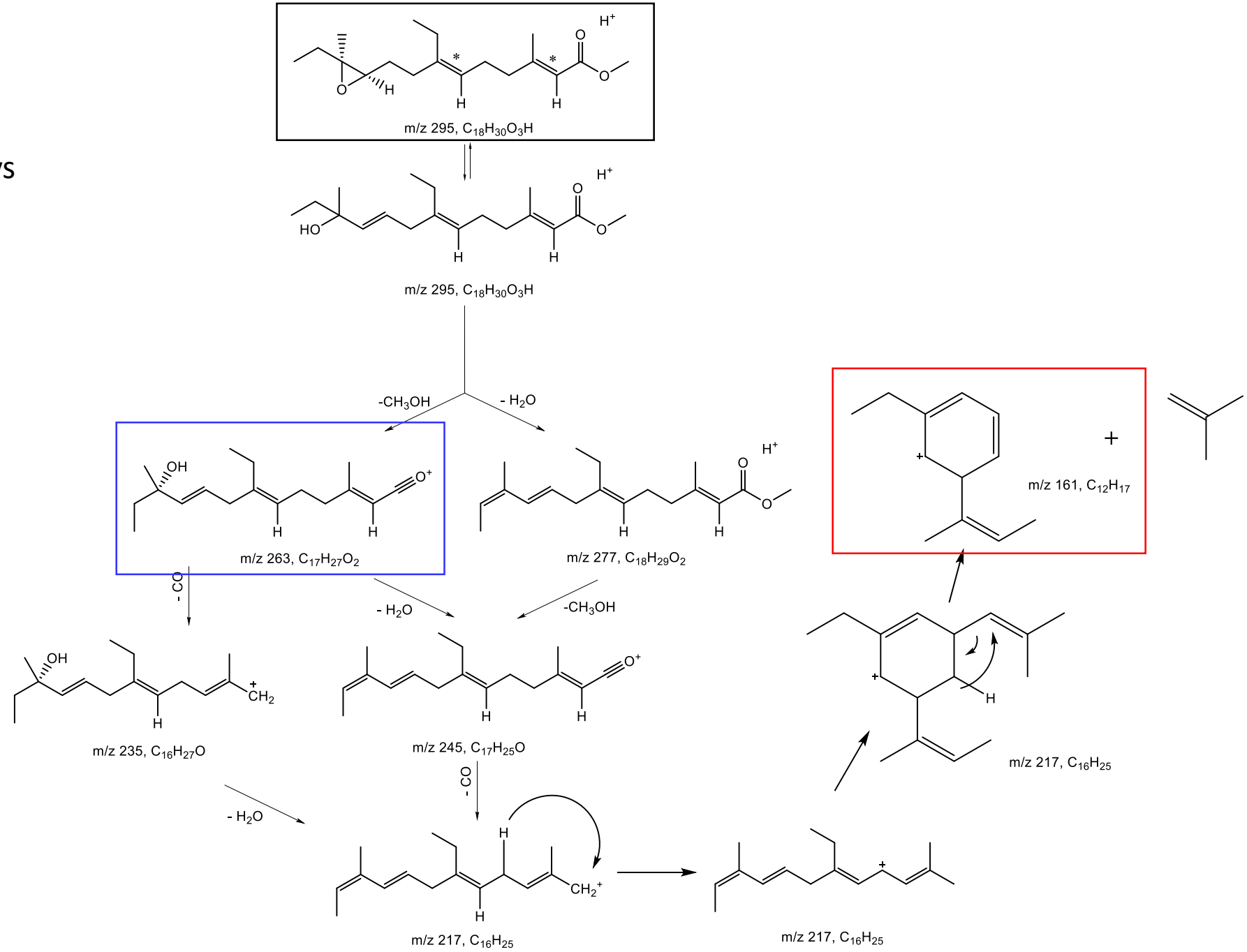
UHRMS data	m/z	Formula	Δm/z (ppm)
FT-ICR MS	295.22680	$[C18H30O3+H]^+$	0.098
FT-ICR MS^2 (CID on 295.2268)	277.21593	$[C18H29O2+H]^+$	-0.999
	263.20045	$C17H27O2^+$	-0.407
	245.18993	$C17H25O^+$	-0.253
	235.20559	$C16H27O^+$	-0.221
	217.19508	$C16H25^+$	0.014
	161.13249	$C12H17^+$	0.081

E: JH I

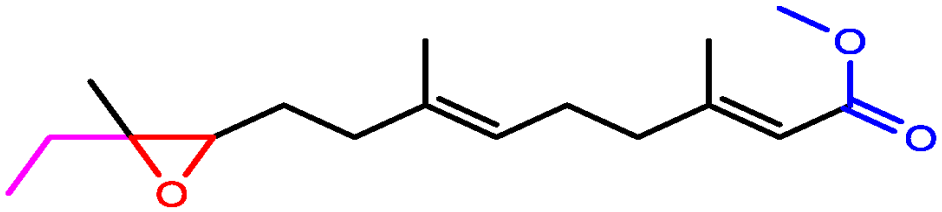
Proposed fragmentation pathways according to the FT-ICR results.

Black box: parent ion
Blue box: primary transition
Red box: secondary transition

.

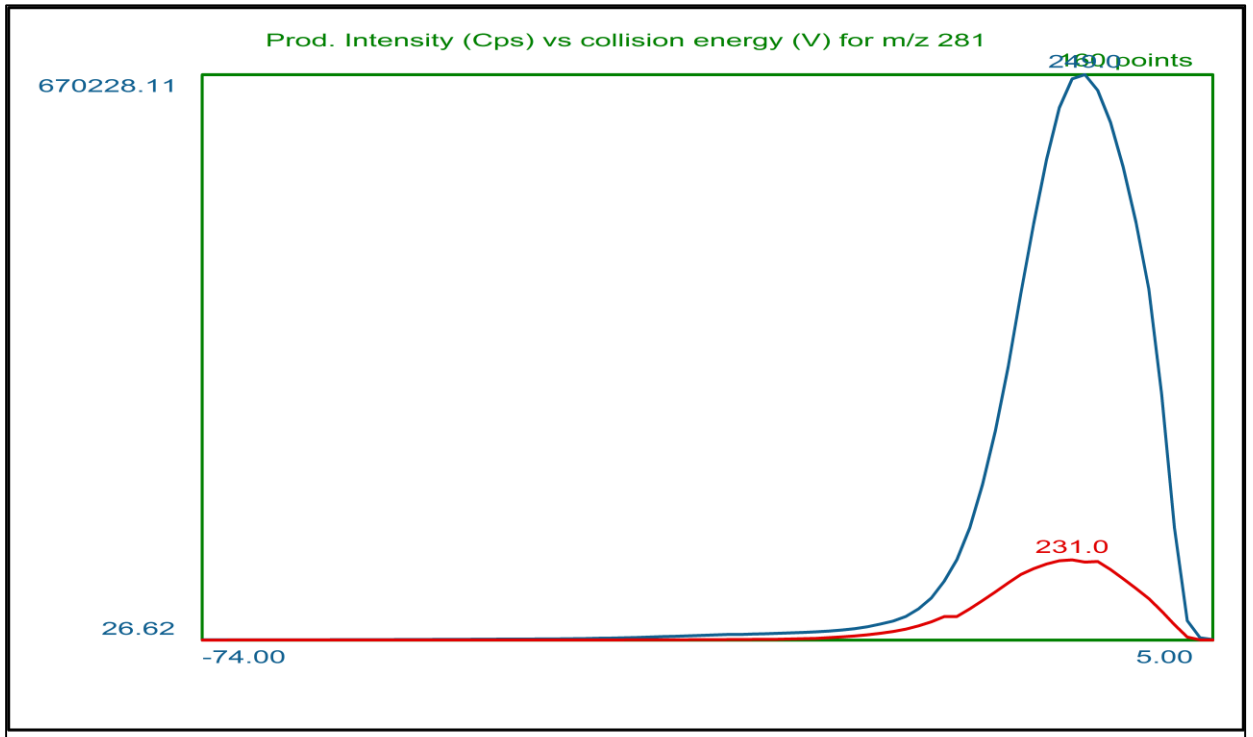


A: JH II



Multiple reaction monitoring (MRM) optimization output using the Bruker EvoQ LC-TQ Elite Triple Quadrupole Mass Spectrometer.

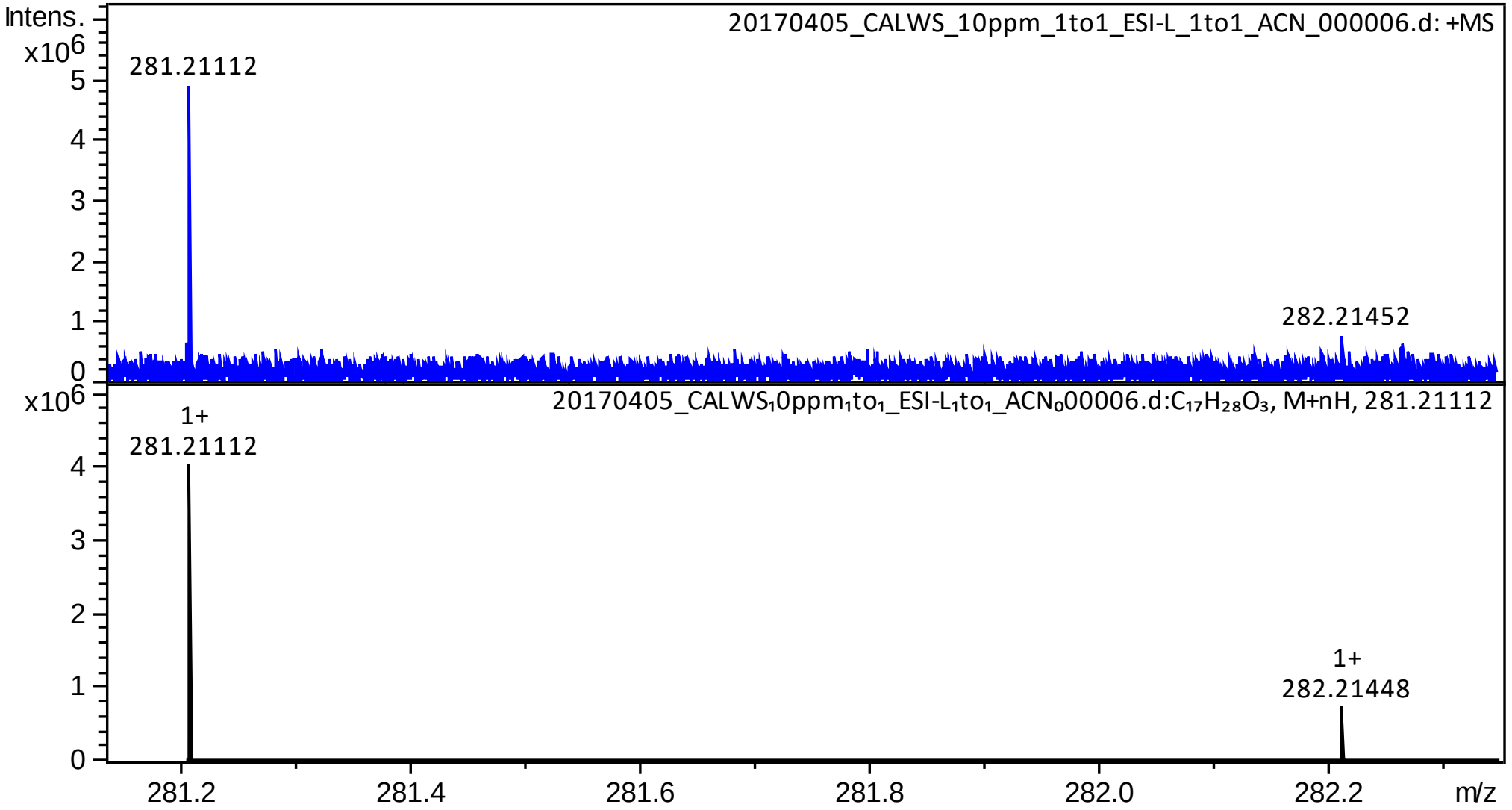
Bruker LC-TQ MRM optimization output



Instrument: EVOQ LC-TQ Elite
Date: 10 Jan 2018 14:09:16
Compound: JH II
Charge State: 1
Precursor: 281.0 m/z
CID pressure : 1.5 mTorr

Prod	CE(V)	Intens.	Ratio(%)
249.00	-5.0	6.70e5	100.00
231.00	-6.0	9.51e4	14.19

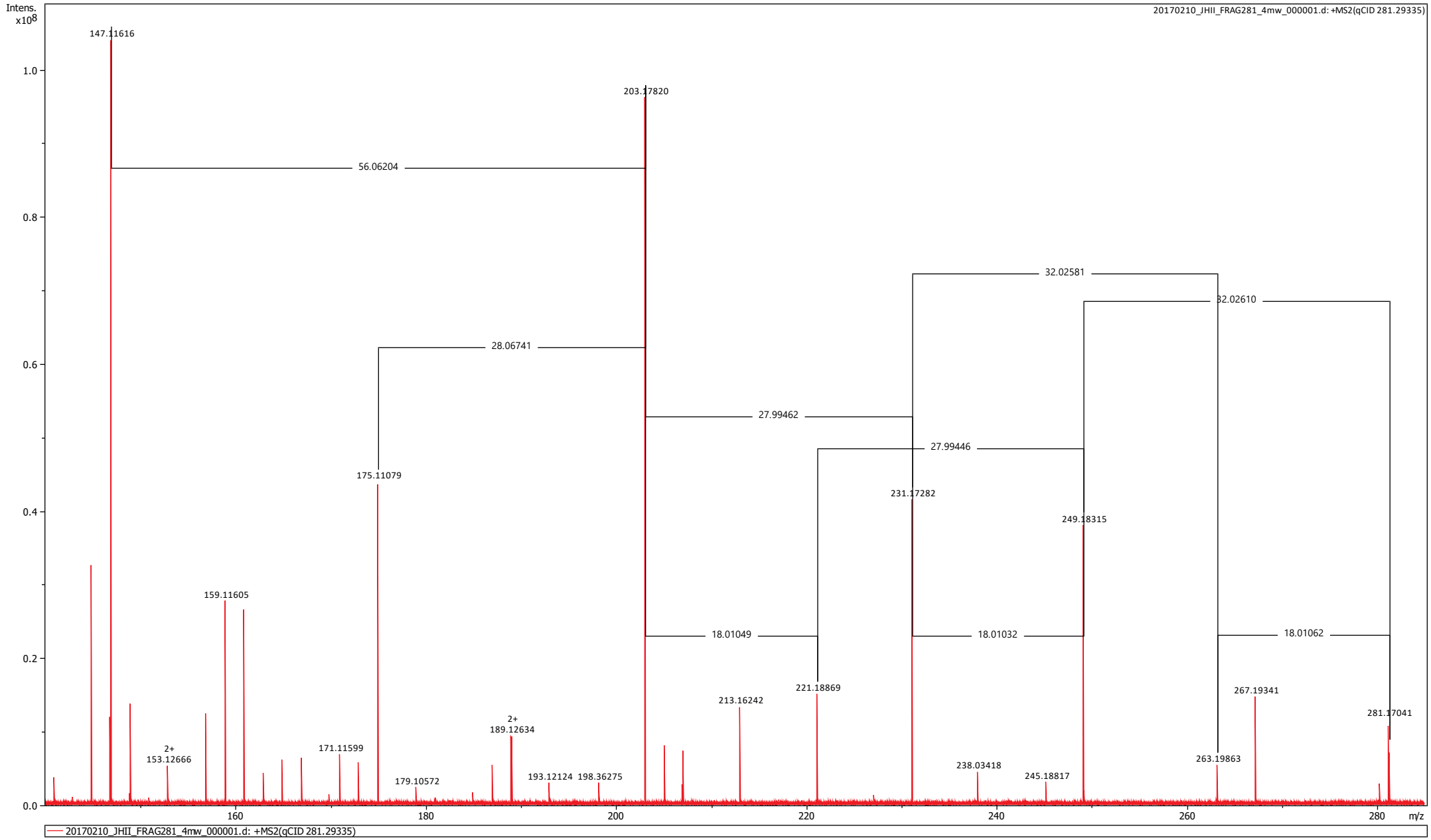
B: JH II



Ultra high resolution mass spectra of the standard obtained by direct infusion using the Solarix 7T FT-ICR MS .

C: JH II

Fourier-transformation cyclotron resonance (FT-ICR) ultra high-resolution MS/MS.



D: JH II

Table showing the MS/MS fragments of the hormone using the Solarix 7T FT-ICR MS.

UHRMS data	m/z	Formula	Δm/z (ppm)
FT-ICR MS	281.21112	$[C17H28O3+H]^+$	<0.001
FT-ICR MS^2 (CID on 281.21112)	263.200557	$[C17H26O2+H]^+$	0.581
	249.184906	$C_{16}H_{25}O_2^+$	0.337
	231.174342	$C_{16}H_{23}O^+$	0.294
	221.189992	$C_{15}H_{25}O^+$	0.669
	203.179427	$C_{15}H_{23}^+$	0.015
	263.200557	$C_{11}H_{15}^+$	0.581

E: JH II

Proposed fragmentation pathways according to the FT-ICR results.

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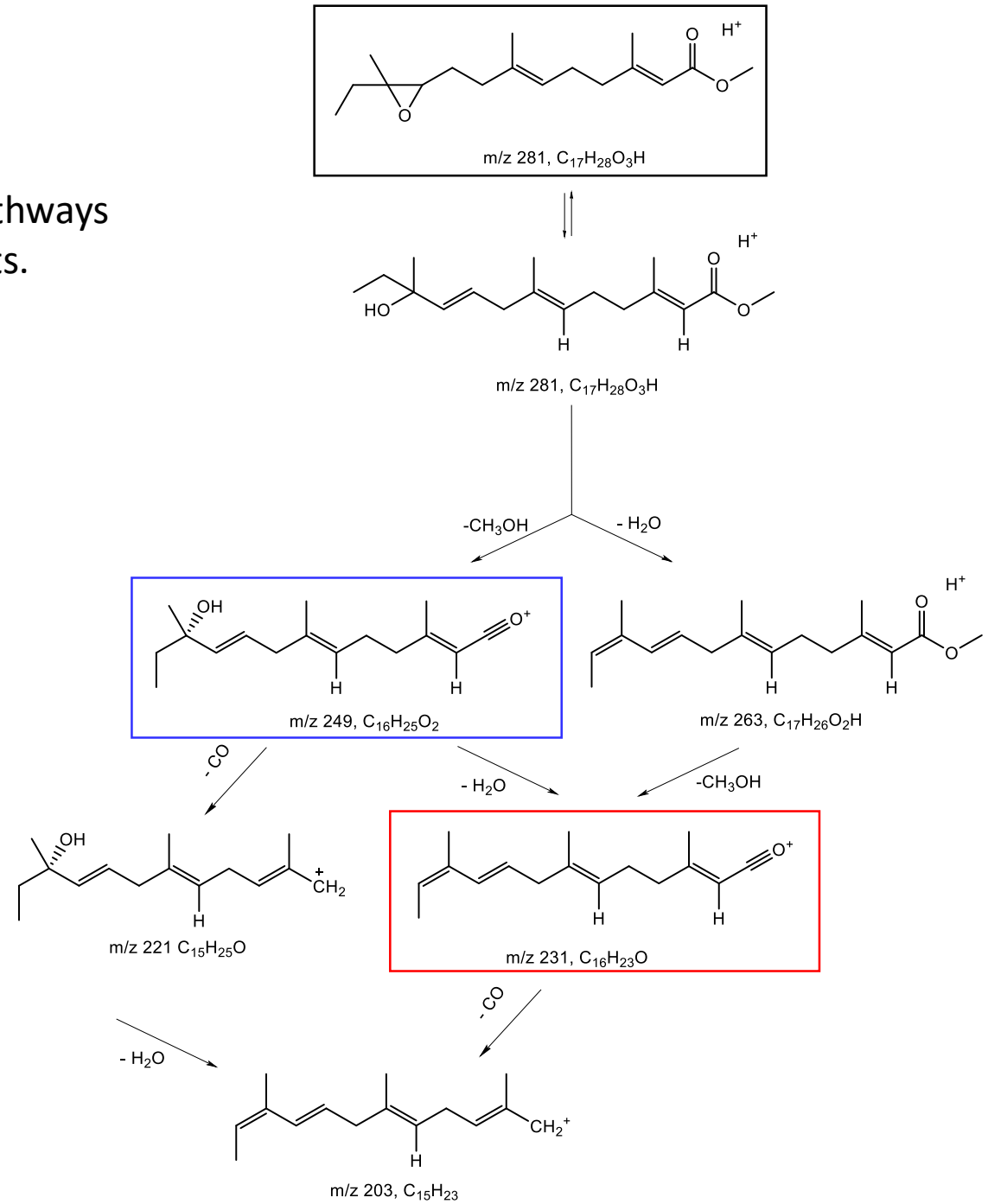
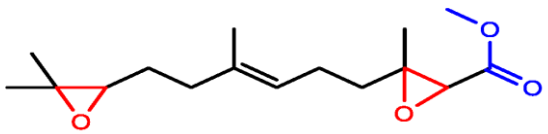
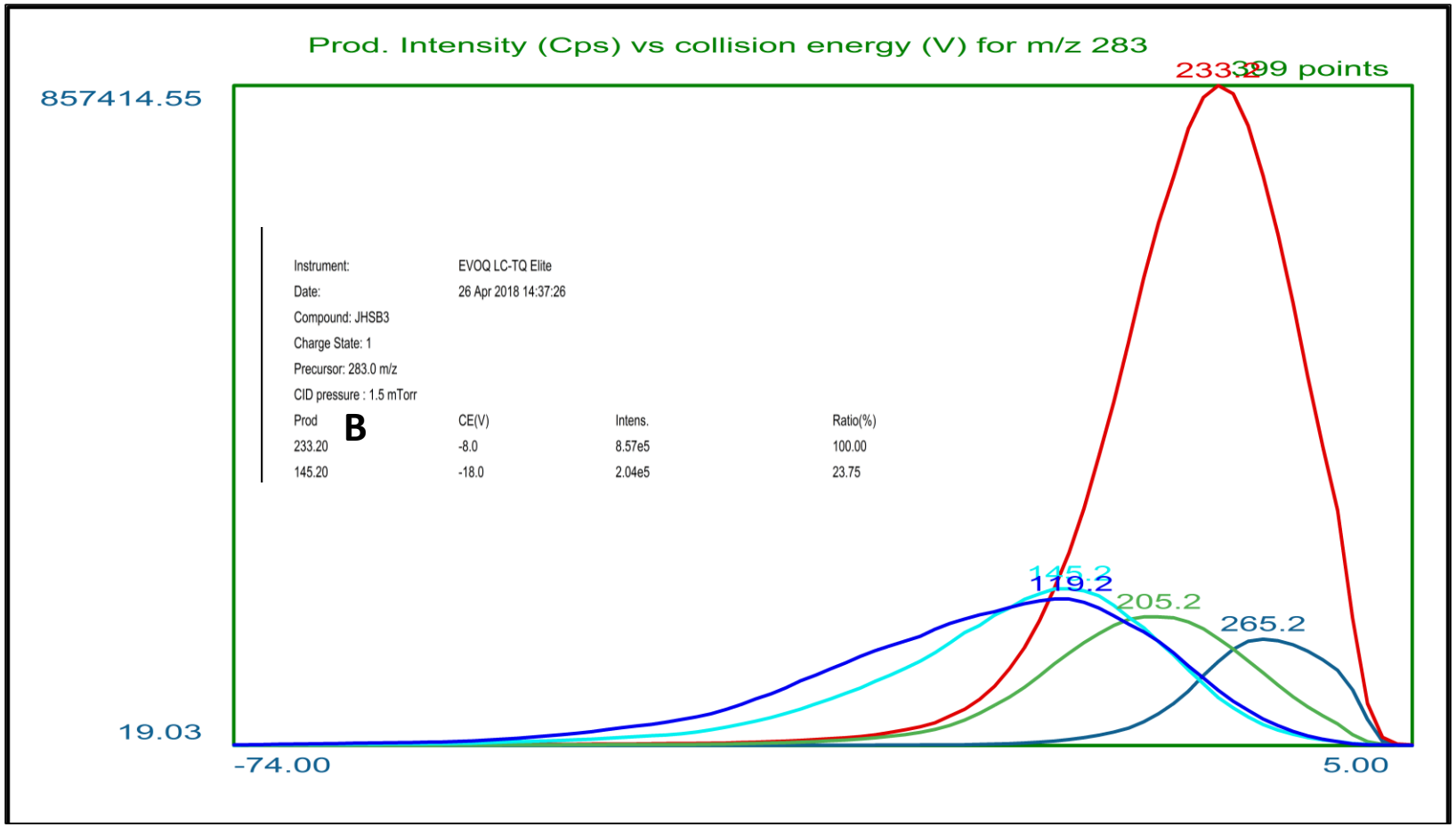


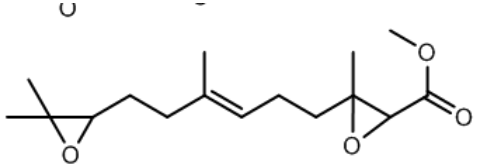
A: JHSB3



Multiple reaction monitoring (MRM) optimization output using the Bruker EvoQ LC-TQ Elite Triple Quadrupole Mass Spectrometer.

Bruker LC-TQ MRM optimization output



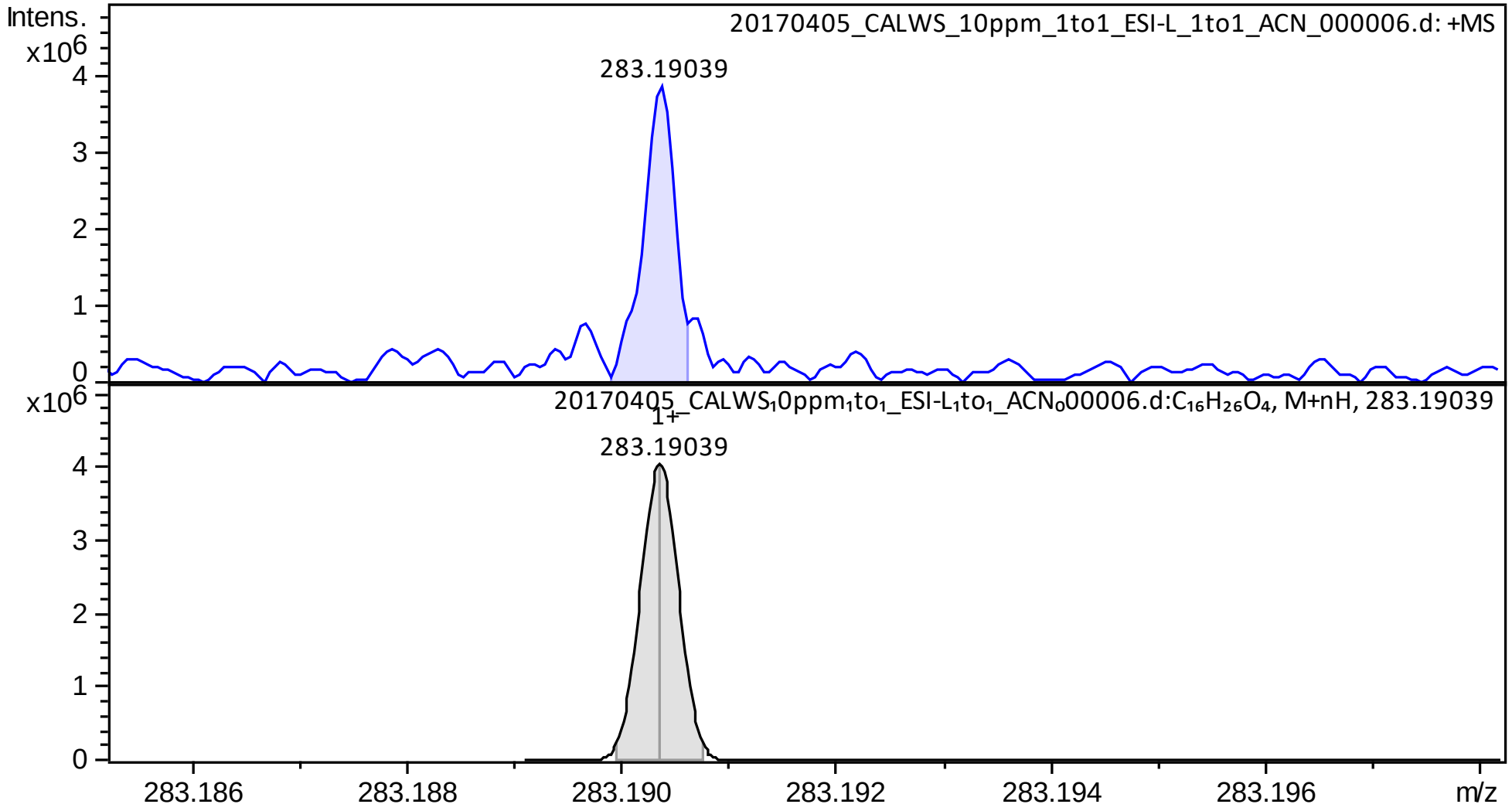


$JHSB_3$

283.3→233.2 ; 8.0
283.3→145.2 ; 18.0

8.8

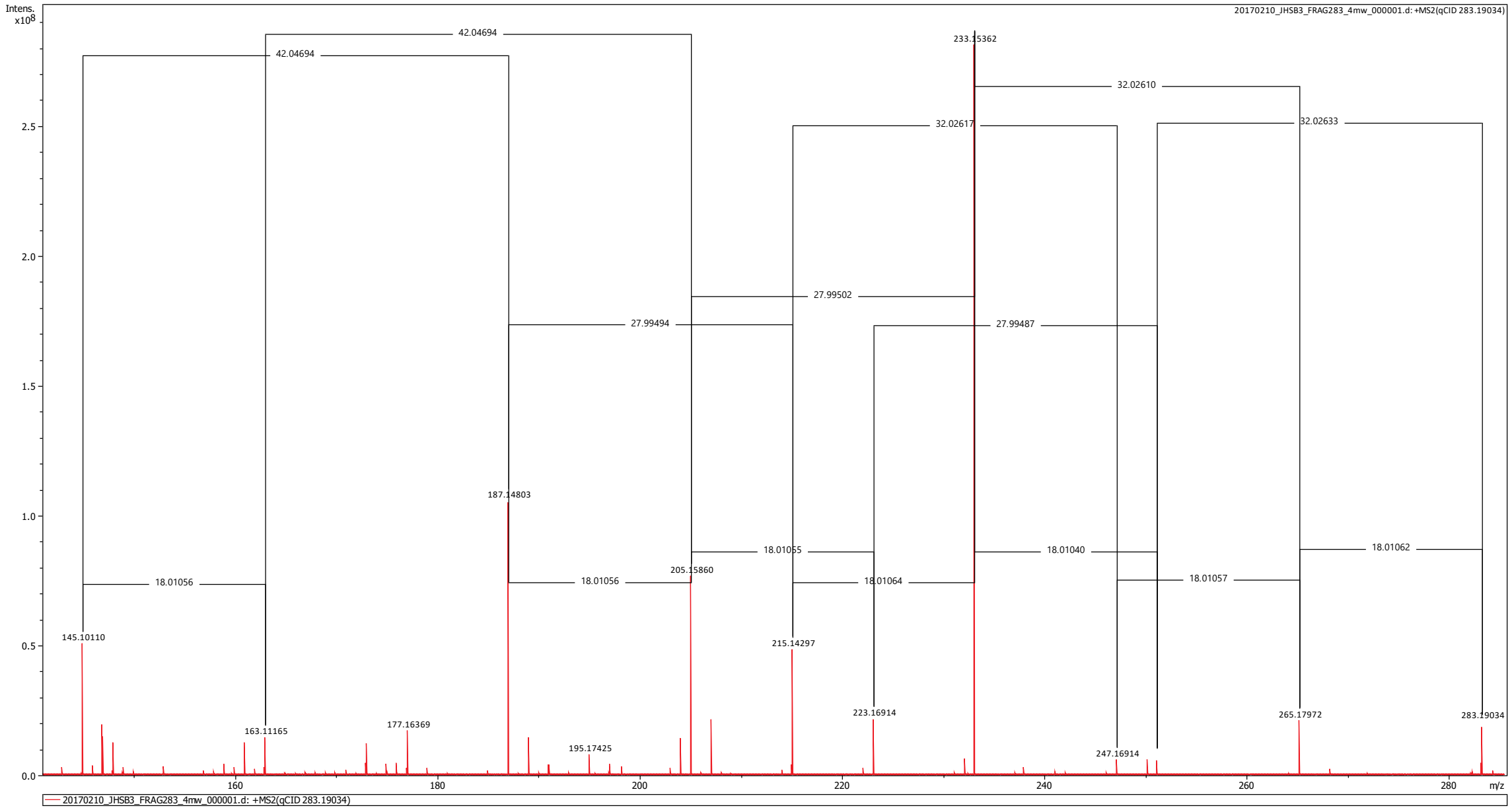
B: JHSB3



Ultra high resolution mass spectra of the standard obtained by direct infusion using the Solarix 7T FT-ICR MS .

C: JHSB3

Fourier-transformation cyclotron resonance (FT-ICR) ultra high-resolution MS/MS.



D: JHSB3

Table showing the MS/MS fragments of the hormone using the Solarix 7T FT-ICR MS.

UHRMS data	m/z	Ion	Formula	Δm/z (ppm)
FT-ICR MS	283.19039	$[M+H]^+$	$[C16H26O4+H]^+$	0.014
FT-ICR MS^2 (CID on 283.19039)	265.17972	$[M+H]^+ - H_2O$	$[C16H24O3+H]^+$	-0.381
	251.16407	$[M+H]^+ - CH_3OH$	$C15H23O3^+$	-0.402
	247.16914	$[M+H]^+ - H_2O - H_2O$	$[C16H22O2+H]^+$	-0.469
	233.15362	$[M+H]^+ - H_2O - CH_3OH$ $[M+H]^+ - CH_3OH - H_2O$	$C15H21O2^+$	0.060
	223.16914		$C14H23O2^+$	-0.520
	215.14297	$[M+H]^+ - H_2O - CH_3OH- CO$	$C15H19O^+$	-0.335
	205.15860	$[M+H]^+ - H_2O - CH_3OH- CO$	$C14H21O^+$	-0.445
	187.14803		$C14H19^+$	-0.518
	145.10110		$C11H13^+$	-0.530

E: JHSB3

Proposed fragmentation pathways according to the FT-ICR results.

Black box: parent ion
Blue box: primary transition
Red box: secondary transition

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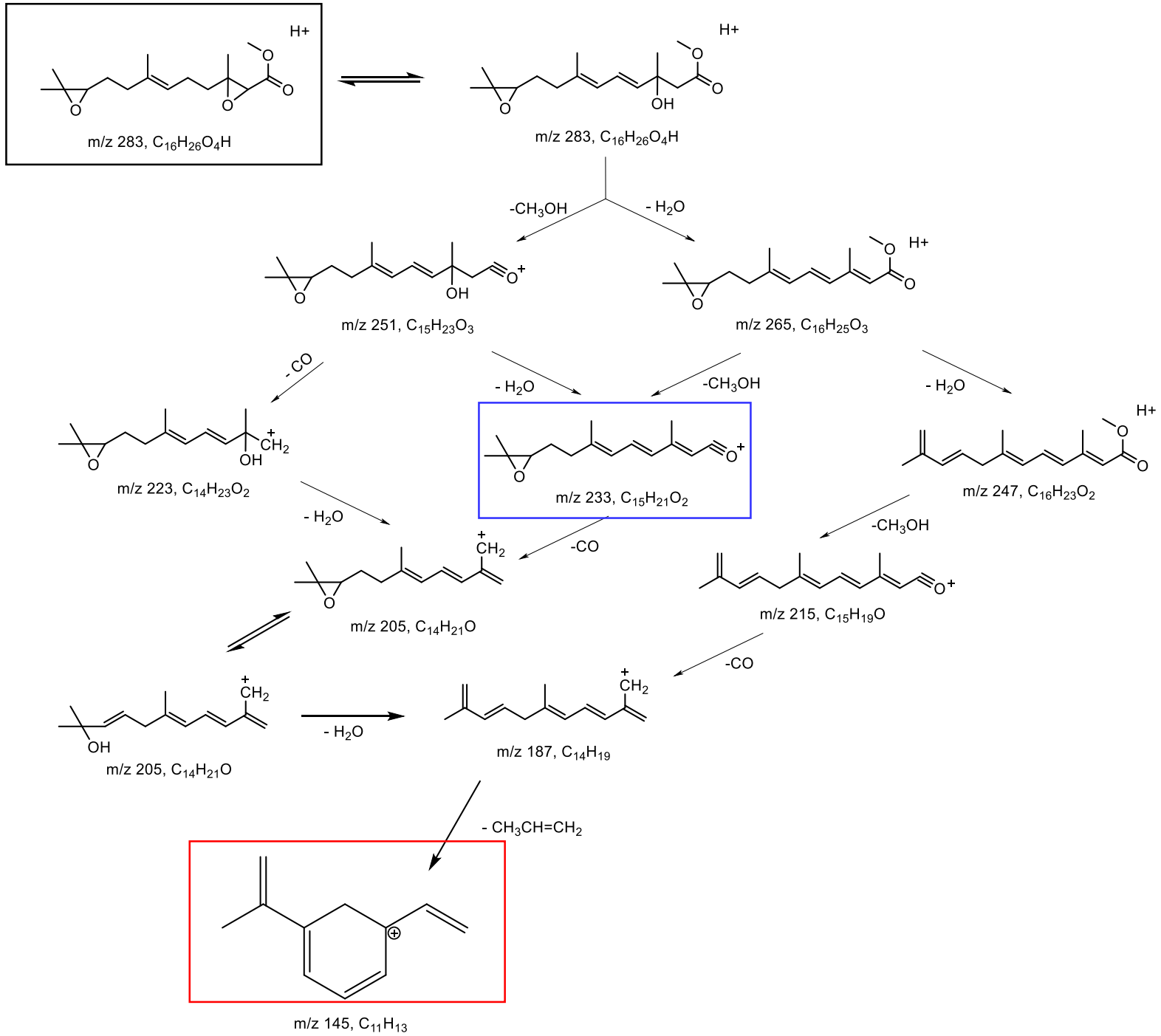
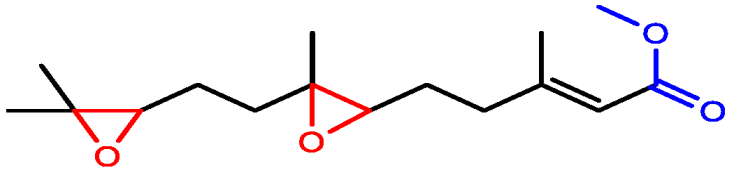
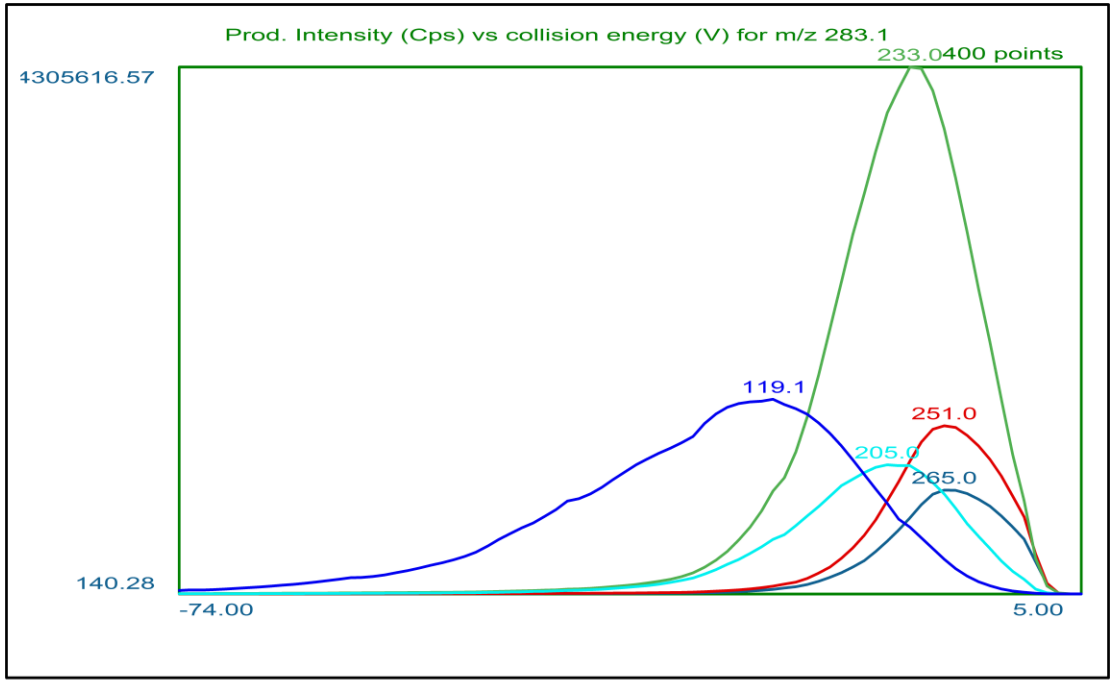


A: JHB3



Multiple reaction monitoring (MRM) optimization output using the Bruker EvoQ LC-TQ Elite Triple Quadrupole Mass Spectrometer.

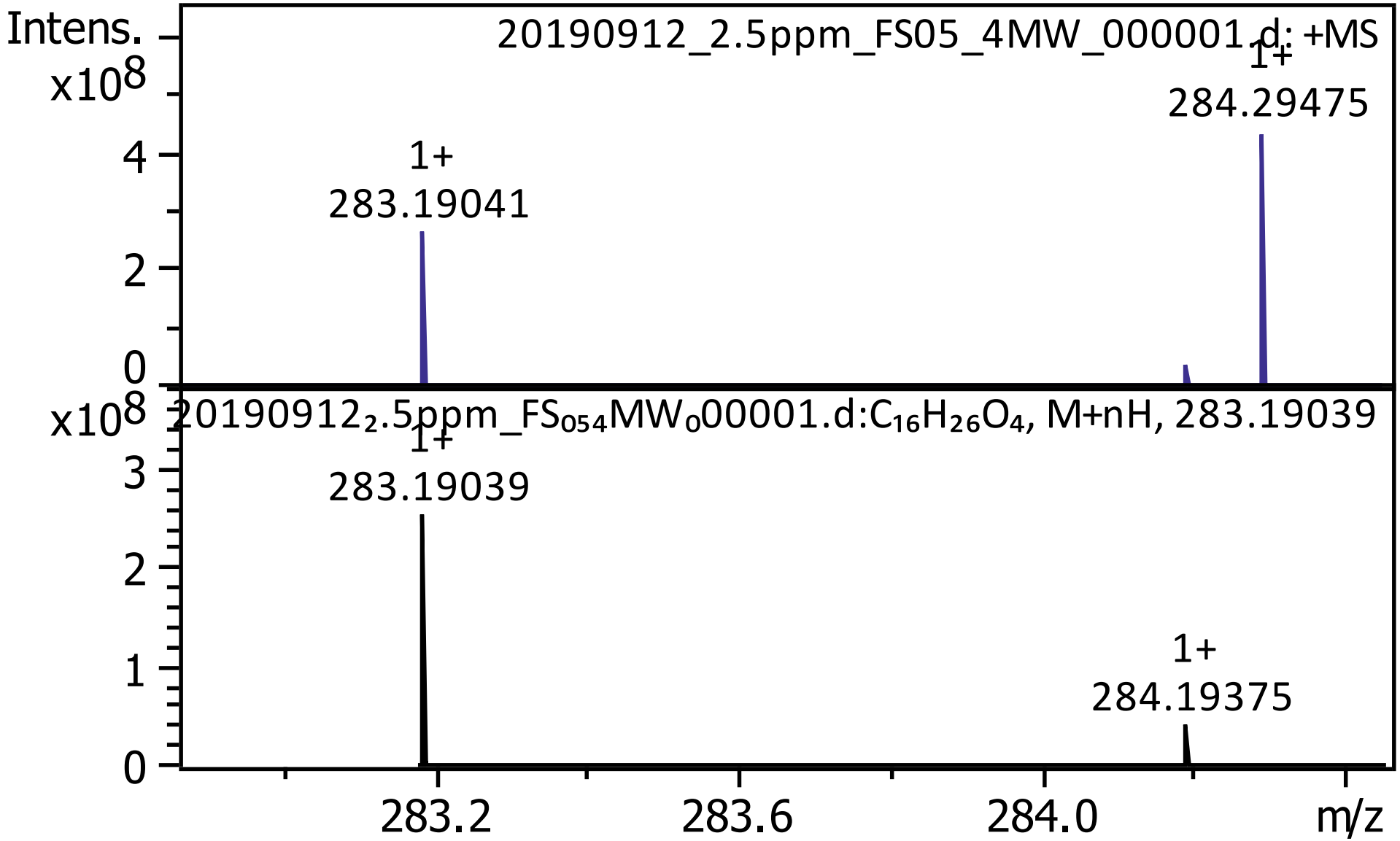


m/z 251 was selected as secondary (instead of m/z 119) because it is not abundant for JHSB3

Instrument:	EVOQ LC-TQ Elite
Date:	27 Aug 2019 9:02:16
Compound: JHB3	
Charge State: 1	
Precursor: 283.1 m/z	
CID pressure : 1.5 mTorr	

Prod	CE(V)	Intens.	Ratio(%)
233.00	-10.0	4.31e6	100.00
119.10	-22.0	1.59e6	36.96
251.00	-7.0	1.37e6	31.93
205.00	-12.0	1.06e6	24.51
265.00	-7.0	8.49e5	19.72

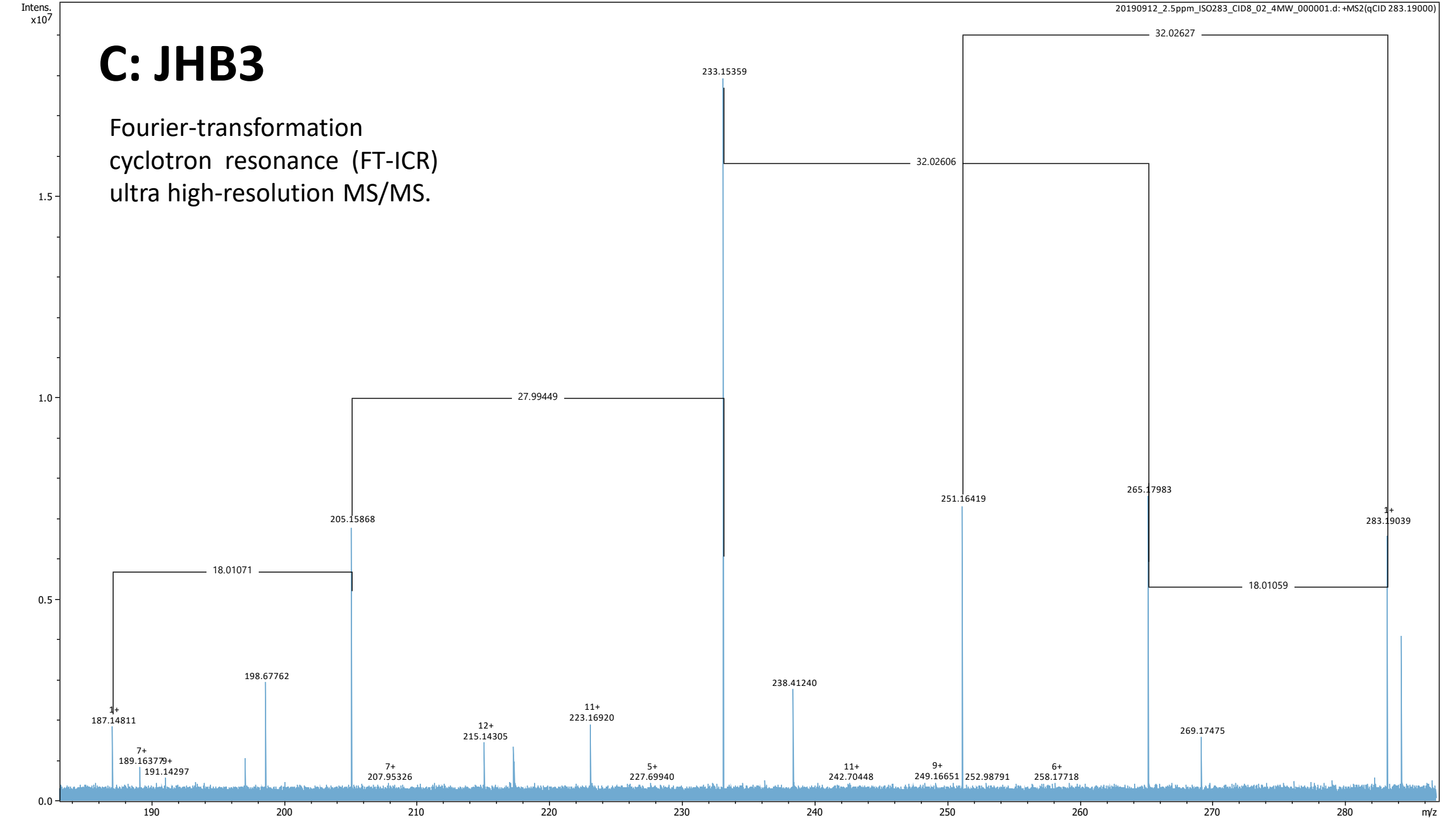
B: JHB3



Ultra high resolution mass spectra of the standard obtained by direct infusion using the Solarix 7T FT-ICR MS .

C: JHB3

Fourier-transformation cyclotron resonance (FT-ICR) ultra high-resolution MS/MS.



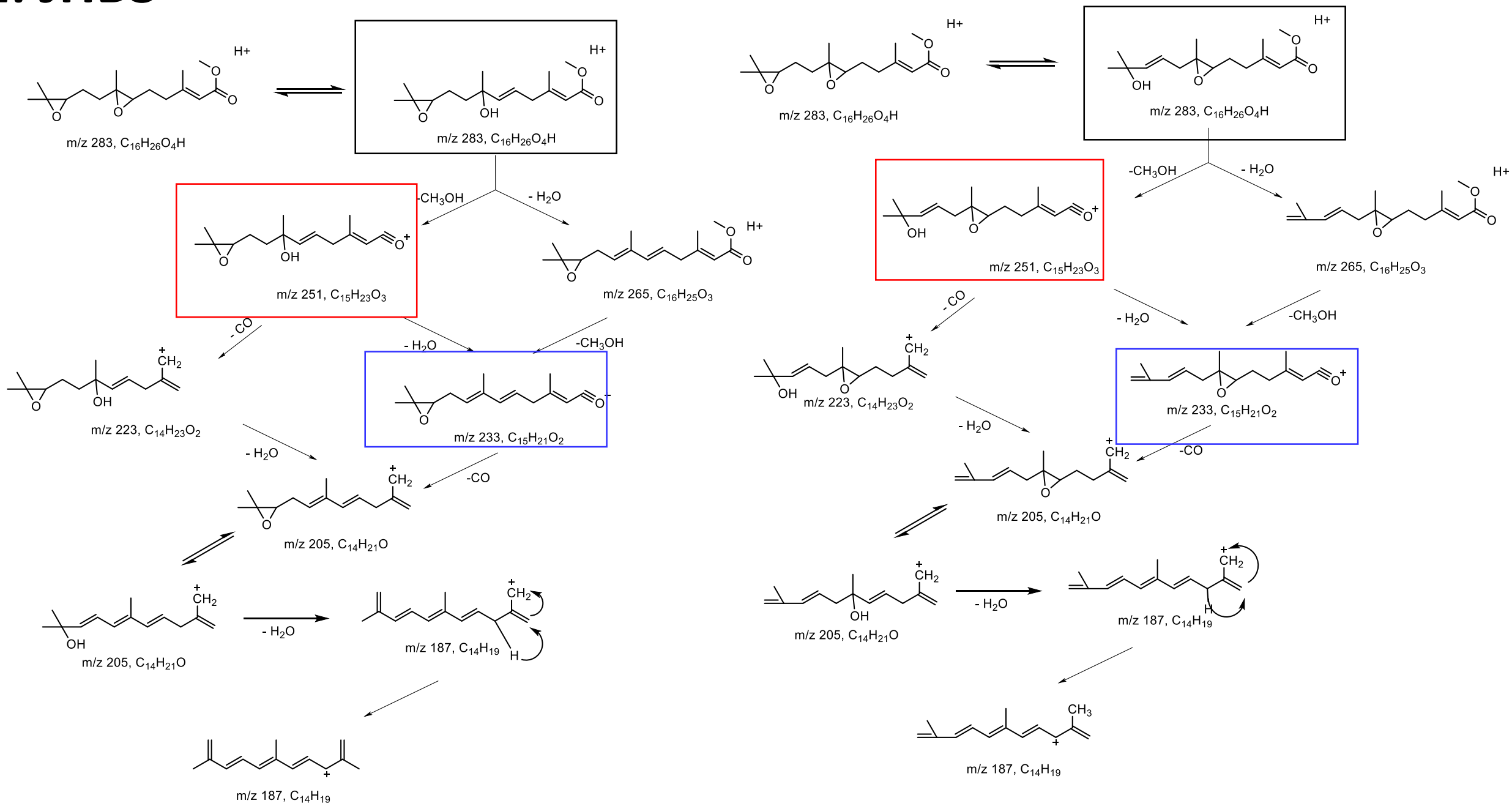
C: JHB3

Table showing the MS/MS fragments of the hormone using the Solarix 7T FT-ICR MS.

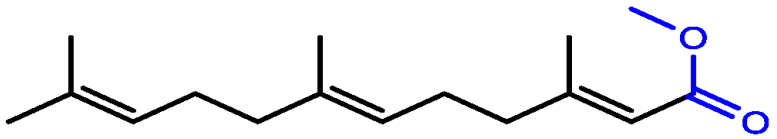
UHRMS data	m/z	Ion	Formula	Δm/z (ppm)
FT-ICR MS	283.19041	$[M+H]^+$	$[C16H26O4+H]^+$	0.085
FT-ICR MS^2 (CID on 283.19039)	265.17983	$[M+H]^+ - H_2O$	$[C16H24O3+H]^+$	0.034
	251.16419	$[M+H]^+ - CH_3OH$	$C15H23O3^+$	0.076
	233.15359	$[M+H]^+ - H_2O - CH_3OH$ $[M+H]^+ - CH_3OH - H_2O$	$C15H21O2^+$	-0.069
	223.1692		$C14H23O2^+$	-0.251
	215.14305	$[M+H]^+ - H_2O - CH_3OH - CO$	$C15H19O^+$	0.037
	205.15868	$[M+H]^+ - H_2O - CH_3OH - CO$	$C14H21O^+$	-0.058
	187.14811		$C14H19^+$	-0.091

E: JHB3

Proposed fragmentation pathways according to the FT-ICR results.

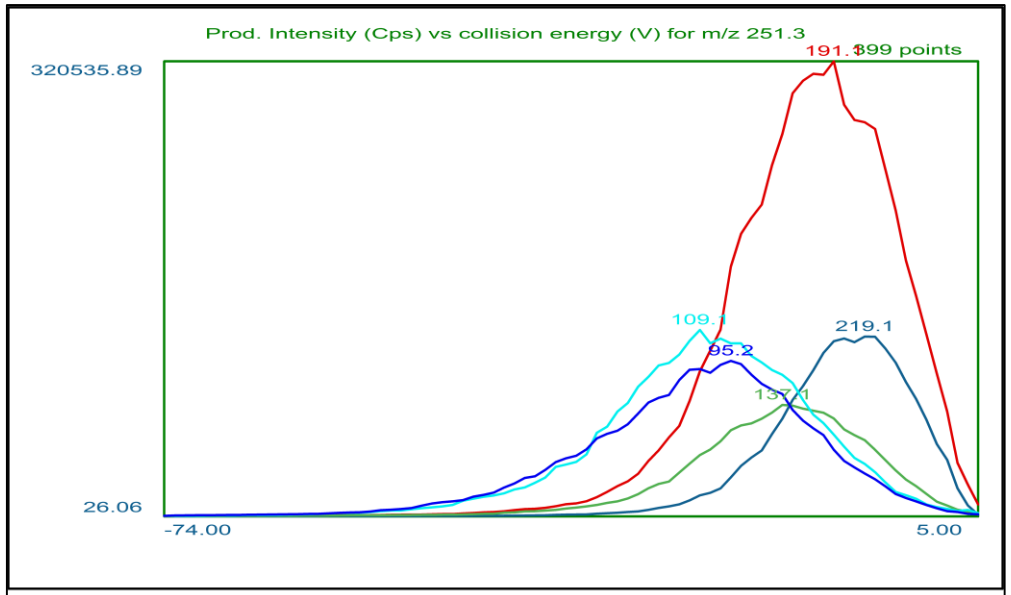


A: MF



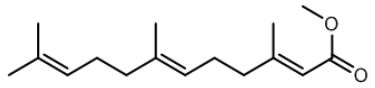
Multiple reaction monitoring (MRM) optimization output using the Bruker EvoQ LC-TQ Elite Triple Quadrupole Mass Spectrometer.

Bruker LC-TQ MRM OPT



Instrument:	EVOQ LC-TQ Elite
Date:	14 Jun 2018 16:50:13
Compound: Methyl Farnesoate	
Charge State: 1	
Precursor: 251.3 m/z	
CID pressure : 1.5 mTorr	

Prod	CE(V)	Intens.	Ratio(%)
191.10	-9.0	3.21e5	100.00
109.10	-22.0	1.31e5	40.95
219.10	-6.0	1.27e5	39.53
95.20	-19.0	1.10e5	34.17
137.10	-14.0	7.85e4	24.50

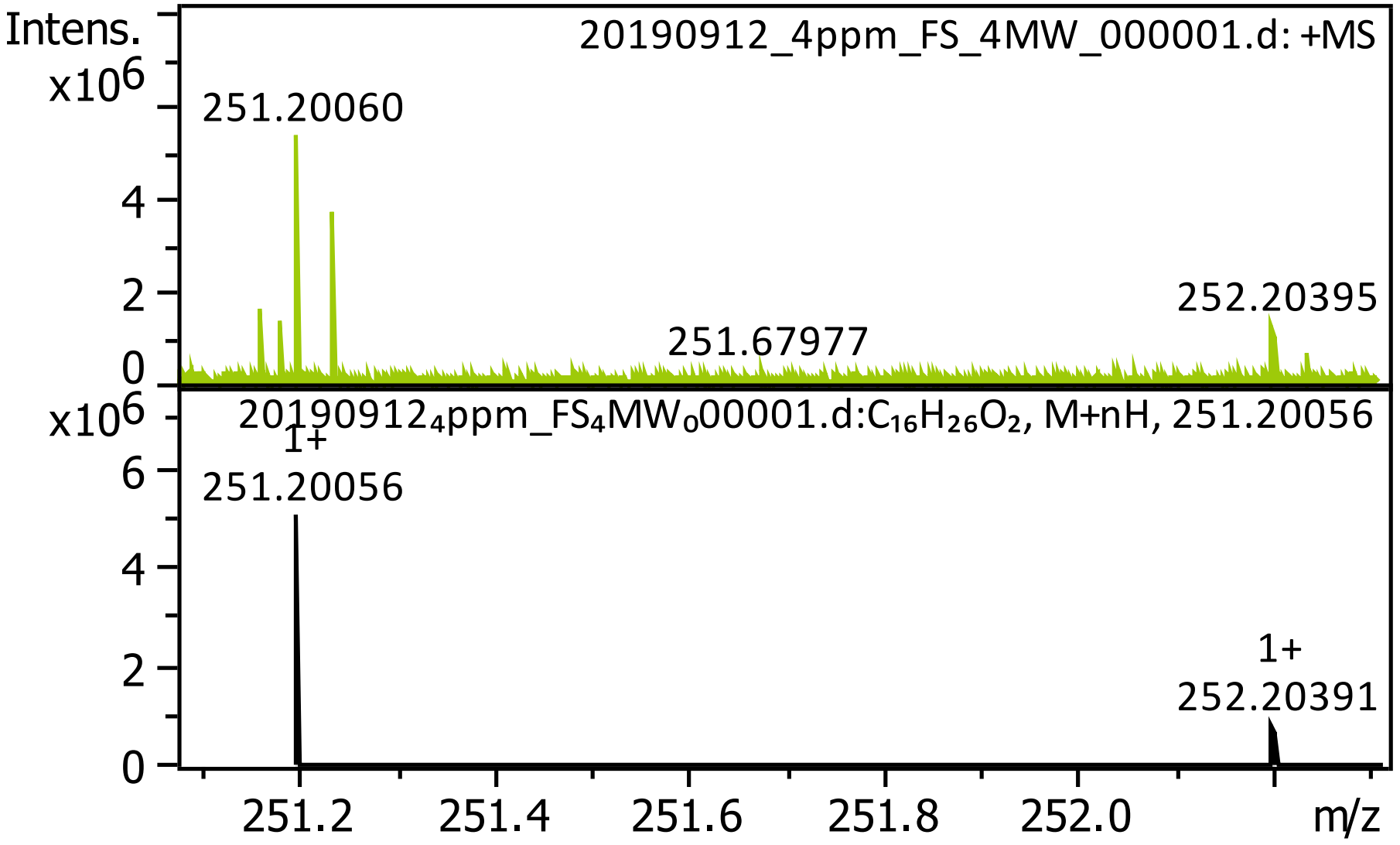


MF

251.3→191.2 ; 9.0
295.2→219.2 ; 6.0

10.0

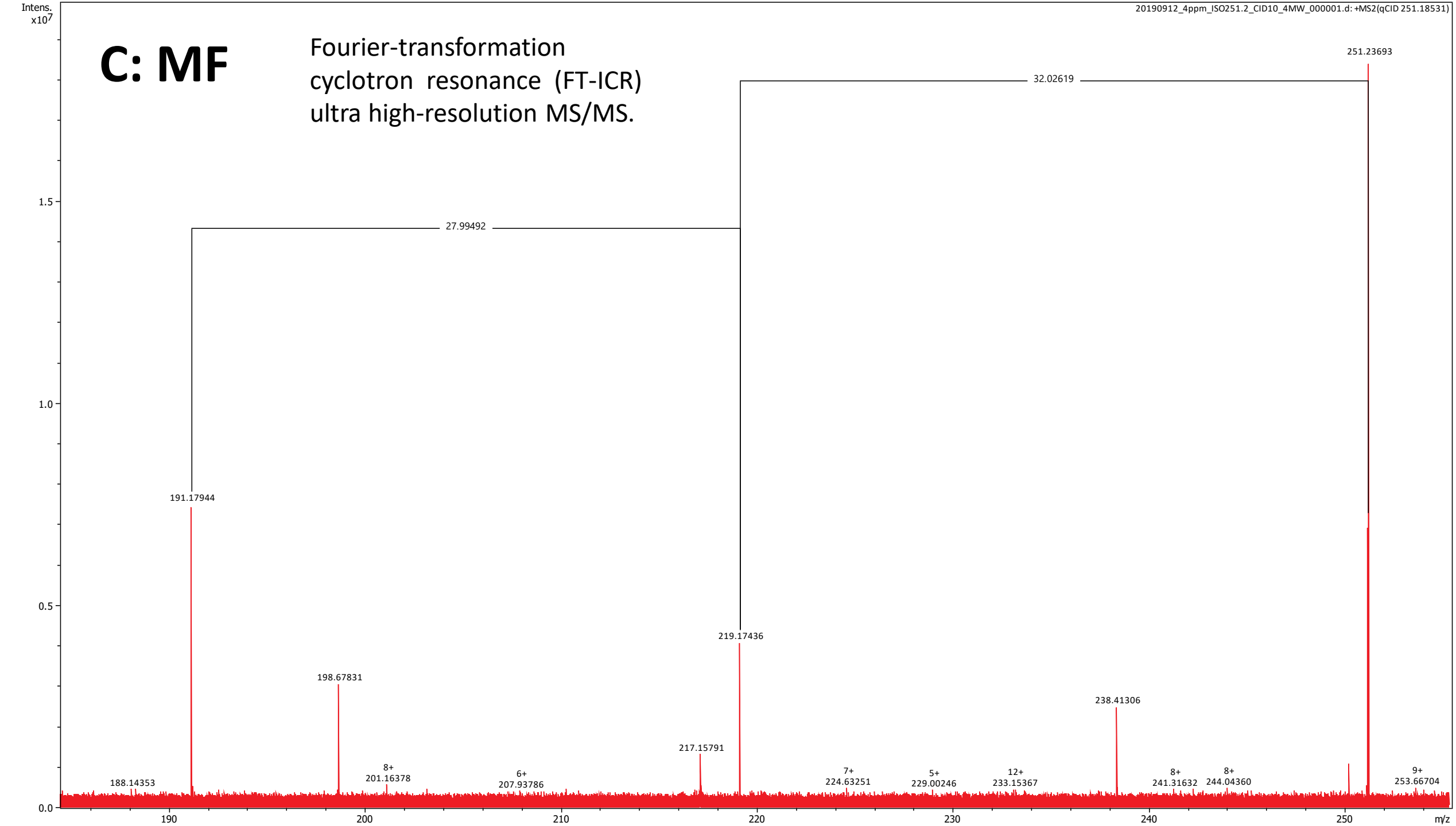
B: MF



Ultra high resolution mass spectra of the standard obtained by direct infusion using the Solarix 7T FT-ICR MS .

C: MF

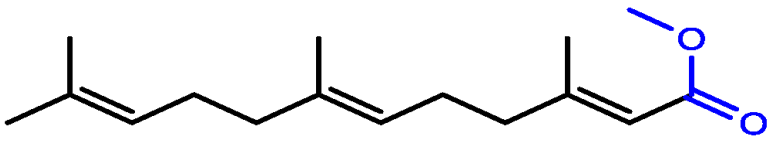
Fourier-transformation cyclotron resonance (FT-ICR) ultra high-resolution MS/MS.



C: MF

Table showing the MS/MS fragments of the hormone using the Solarix 7T FT-ICR MS.

UHRMS data	m/z	Ion	Formula	Δm/z (ppm)
FT-ICR MS	251.2006	$[M+H]^+$	$[C16H26O4+H]^+$	0.171
FT-ICR MS^2 (CID on 251.2006)	219.17436	$[M+H]^+ - H_2O$	$[C16H22O2+H]^+$	0.082
	191.17944	$[M+H]^+ - CH_3OH$	$C15H23O3^+$	0.068

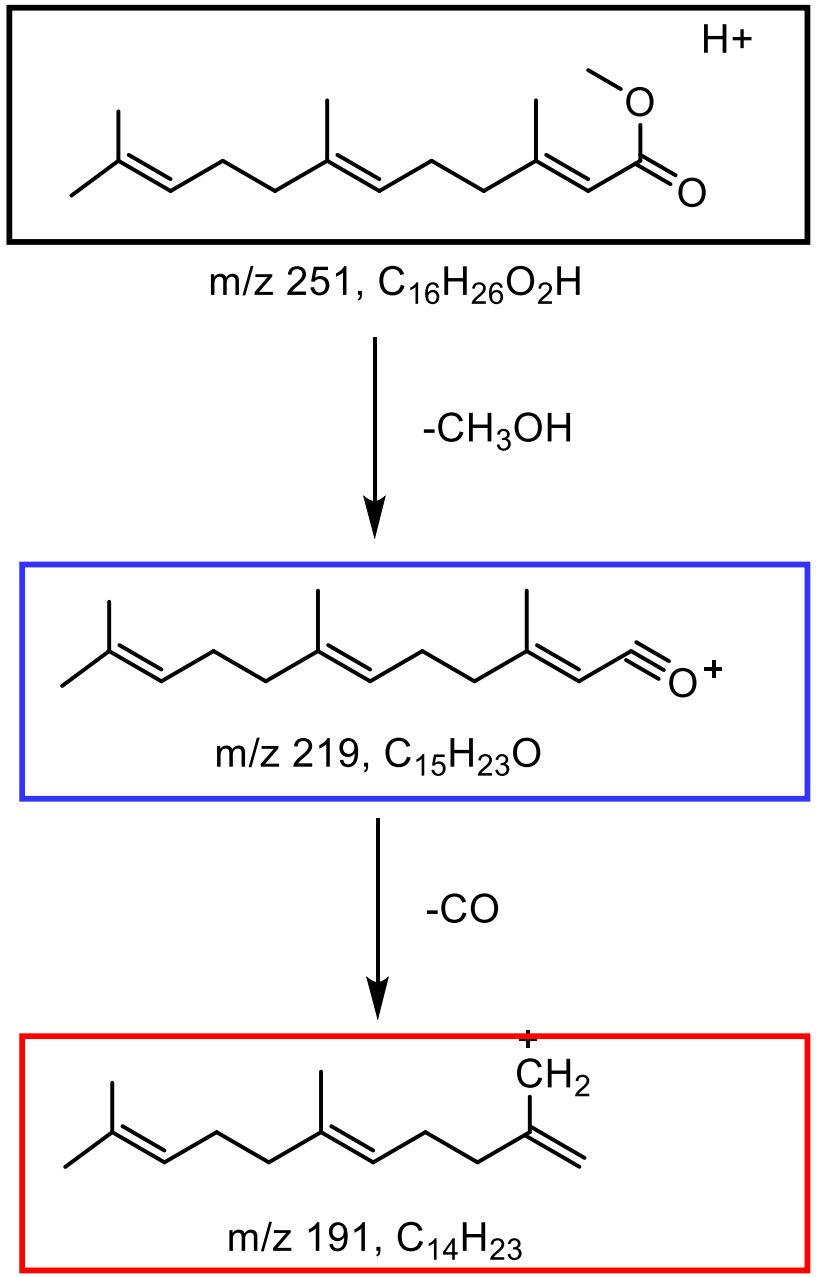


E: MF

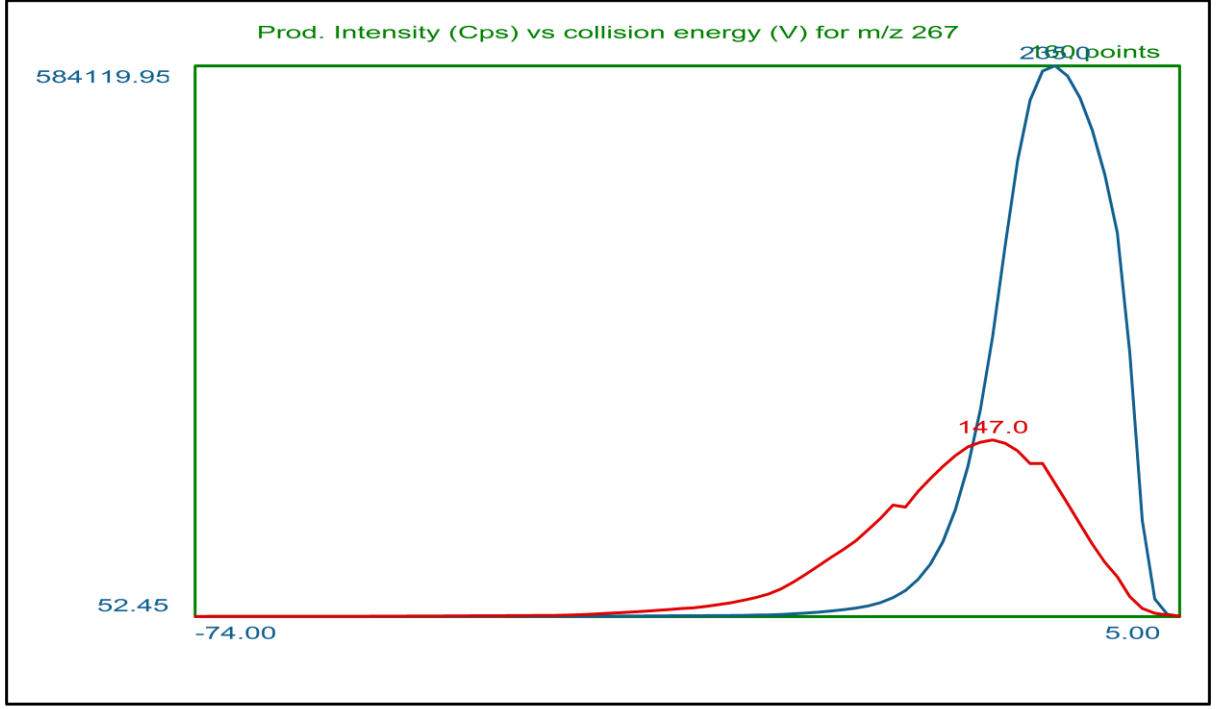
Proposed fragmentation pathways according to the FT-ICR results.

Black box: parent ion
Blue box: primary transition
Red box: secondary transition

.



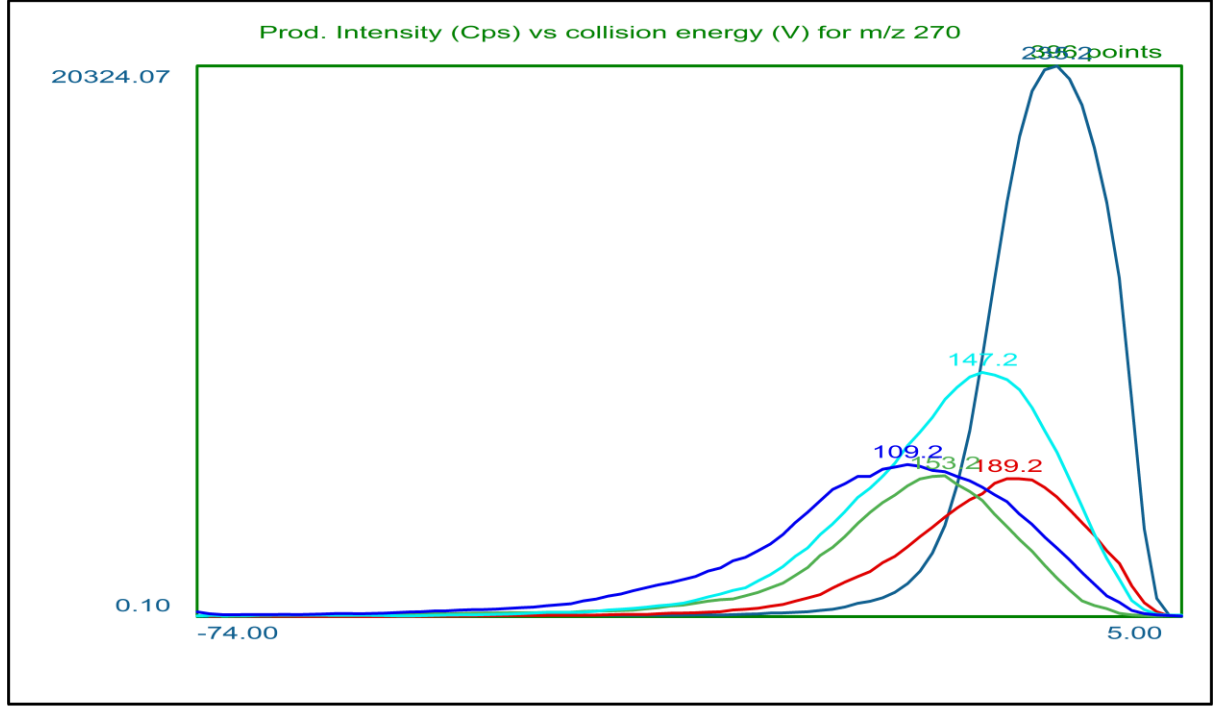
A: JH III



Instrument:	EVOQ LC-TQ Elite
Date:	10 Jan 2018 14:08:51
Compound: JH III	
Charge State: 1	
Precursor: 267.0 m/z	
CID pressure : 1.6 mTorr	

Prod	CE(V)	Intens.	Ratio(%)
235.00	-5.0	5.84e5	100.00
147.00	-10.0	1.87e5	32.08

A: JH III-D3

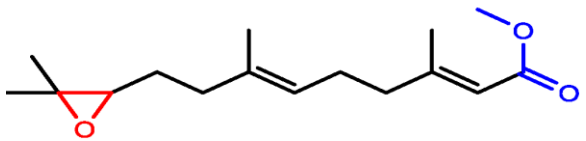


Instrument:	EVOQ LC-TQ Elite
Date:	23 Jan 2018 15:34:21
Compound: JH III-D3	
Charge State: 1	
Precursor: 270.0 m/z	
CID pressure : 1.5 mTorr	

Prod	CE(V)	Intens.	Ratio(%)
235.20	-5.0	2.03e4	100.00
147.20	-11.0	9.01e3	44.34
109.20	-17.0	5.61e3	27.61
153.20	-14.0	5.20e3	25.58
189.20	-9.0	5.09e3	25.05

Fragmentation of JH III (from Ramirez et al, 2016)

	Parent *m/z*	Fragment *m/z*
In-source MS/MS	267	249, 235, 217, 189, 147
	249	217, 189, 147
	235	217, 189, 147
	217	189, 147
	189	147
MS/MS^n	267 –> 235	217, 207, 189
	267 –> 249	217, 189, 147
	267 –> 217	189, 147
	267 –> 189	147
FT-ICR MS/MS	267.195461 $C_{16}H_{27}O_3$	249.18492 $C_{16}H_{25}O_2$
		235.169298 $C_{15}H_{23}O_2$
		217.158786 $C_{15}H_{21}O$
		207.174417 $C_{14}H_{23}O$
		189.163858 $C_{14}H_{21}$
		147.116827 $C_{11}H_{15}$



Fragmentation of JH III (from Ramirez et al, 2016)