Supporting Information

Ultrafast, Selective and Highly Sensitive Non-Chromatographic Analysis of Fourteen Cannabinoids in Cannabis Extracts, Δ8-Tetrahydrocannabinol Synthetic Mixtures and Edibles by Cyclic Ion Mobility Spectrometry-Mass Spectrometry

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Table S1. Preparation of acid-treated CBD mixtures.

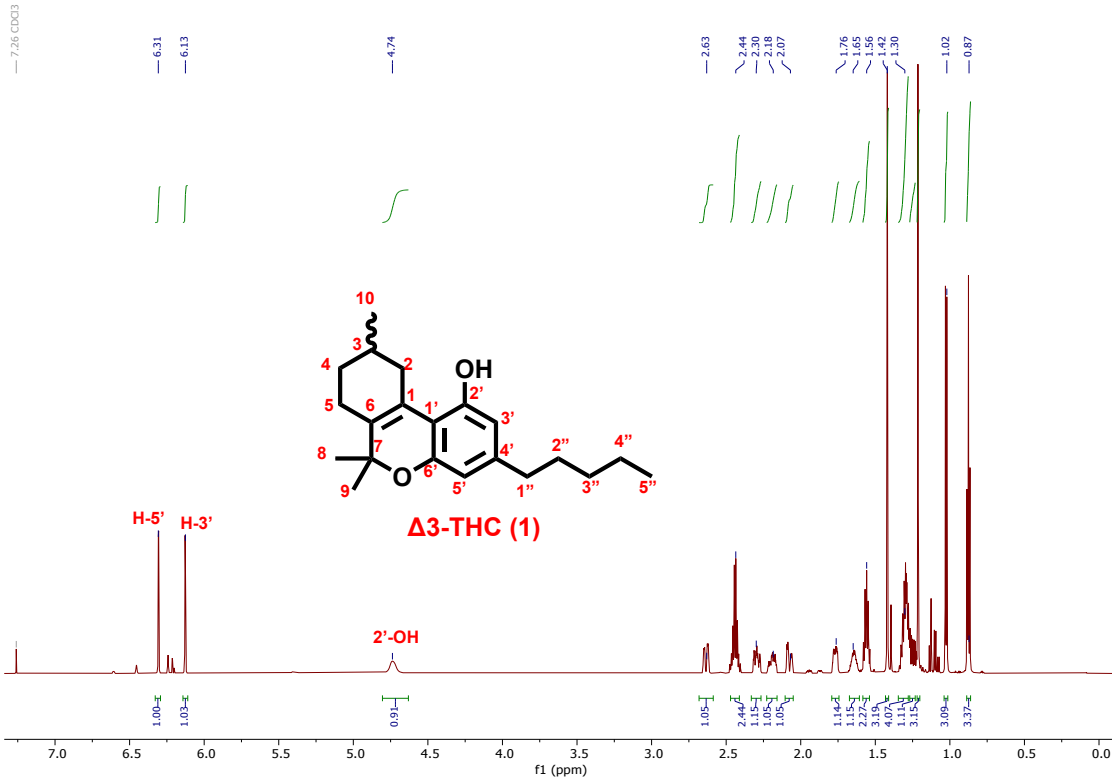
#	Acid	Solvent	Temperature (°C)	Time (h)
1	pTSA 10% (mole ratio of acid/CBD=0.1)	Toluene	Room temperature	39
2	pTSA 200% (mole ratio of acid/CBD=2)	Toluene	Room temperature	39
3	pTSA 200% (mole ratio of acid/CBD=1)	DCM	Room temperature	43
4	pTSA 200% (mole ratio of acid/CBD=1)	Hexane	Room temperature	43
5	$BF_3 \cdot OEt_2$ (mole ratio of acid/CBD=1)	ACN	−10	6
6	H_2SO_4 (mole ratio of acid/CBD=1)	EtOH	70	39
7	acetic acid (mole ratio of acid/CBD=1)	EtOH	70	39
8	HCl (mole ratio of acid/CBD=1)	EtOH	70	39

Data are from our previous paper.[1]

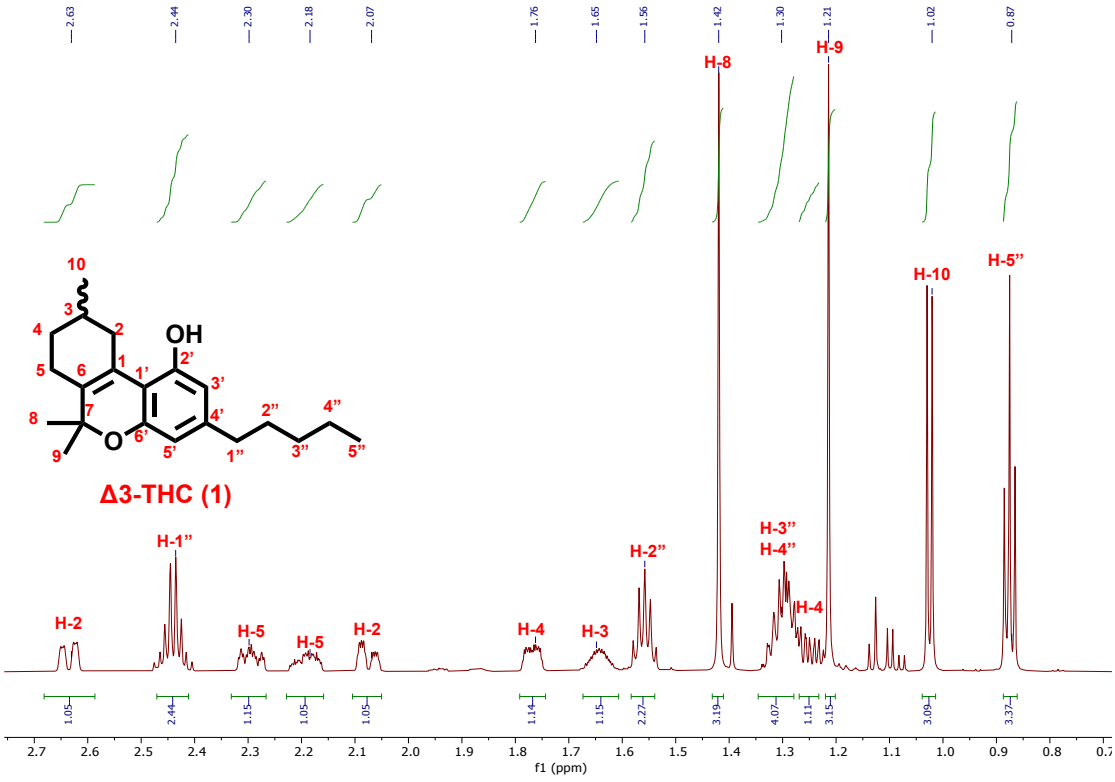
Table S2. Cannabinoid composition information of Cannabis and Δ8-THC gummies provided by merchants.

Products	Cannabinoid composition information
C#1	Not available
C#2	THC 24.55%, CBD 7.72%; CBG 1.46%; THCA 6.17%; CBDA 2.43%; CBC 0.33%; THCV 2.31%; CBN 0.57%; CBL 0.
C#3	THC 1.05%; CBD 0; CBG 1.19%; THCA 19.31%; CBDA 0.02%; CBC 0.11%; THCV 0.63%; CBN 0.09%; CBL 0.
G#1	Δ8-THC 1 g; Δ9-THC<0.3%; CBD<0.3%
G#2	Δ8-THC 1.25%; Δ9-THC<0.3%

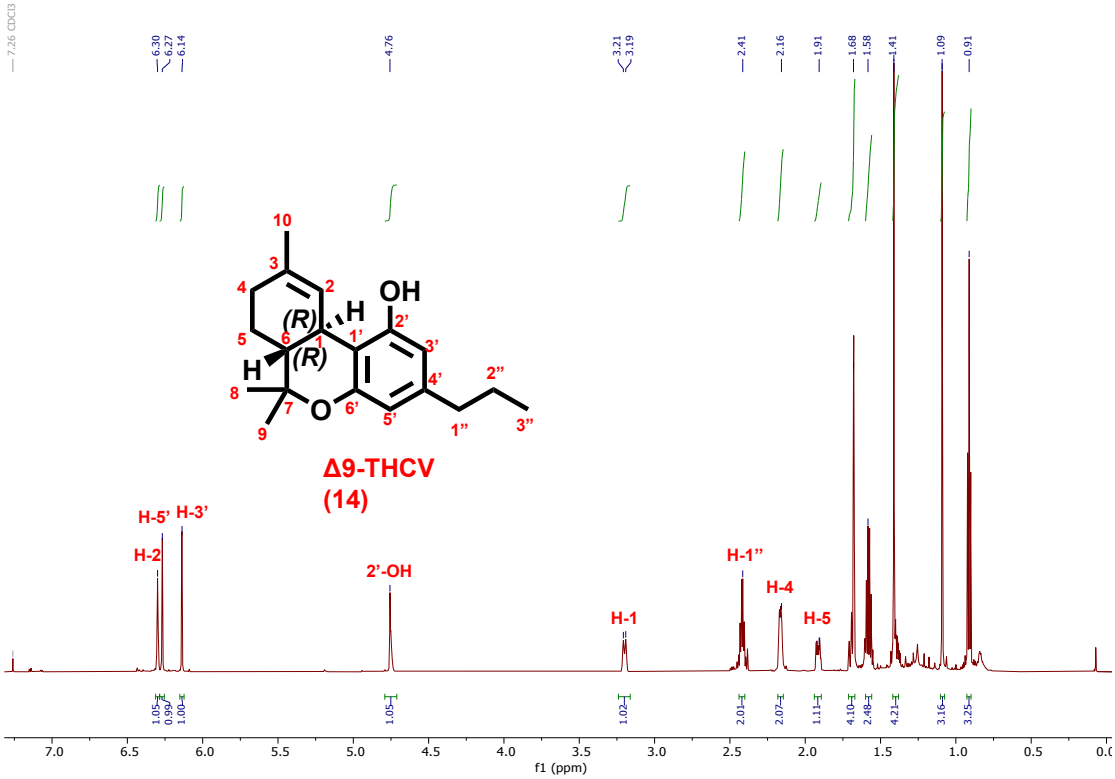
a)


7.26 CDCl3
6.31
6.13
4.74
2.63
2.44
2.30
2.18
2.07
1.76
1.65
1.56
1.42
1.30
1.02
0.87
10
3
4
2
OH
5
6
1
1'
2'
3'
8
7
4'
2"
4"
9
O
6'
5'
1"
3"
5"
H-5'
H-3'
Δ3-THC (1)
2'-OH
f1 (ppm)

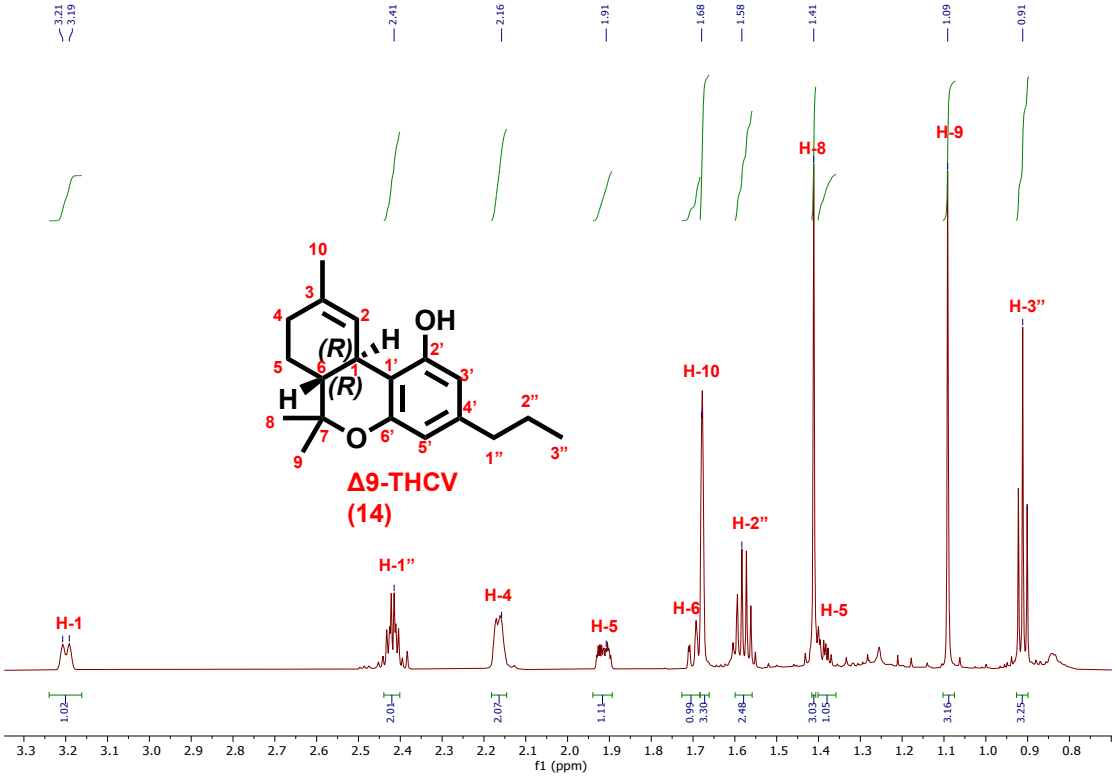
Zoom in


2.63
2.44
2.30
2.18
2.07
1.76
1.65
1.56
1.42
1.30
1.21
1.02
0.87
H-8
H-9
H-10
H-5"
10
3
4
2
OH
5
6
1
1'
2'
3'
8
7
4'
2"
4"
9
O
6'
5'
1"
3"
5"
Δ3-THC (1)
H-1"
H-2
H-5
H-5
H-2
H-4
H-3
H-2"
H-3"
H-4"
H-4
f1 (ppm)

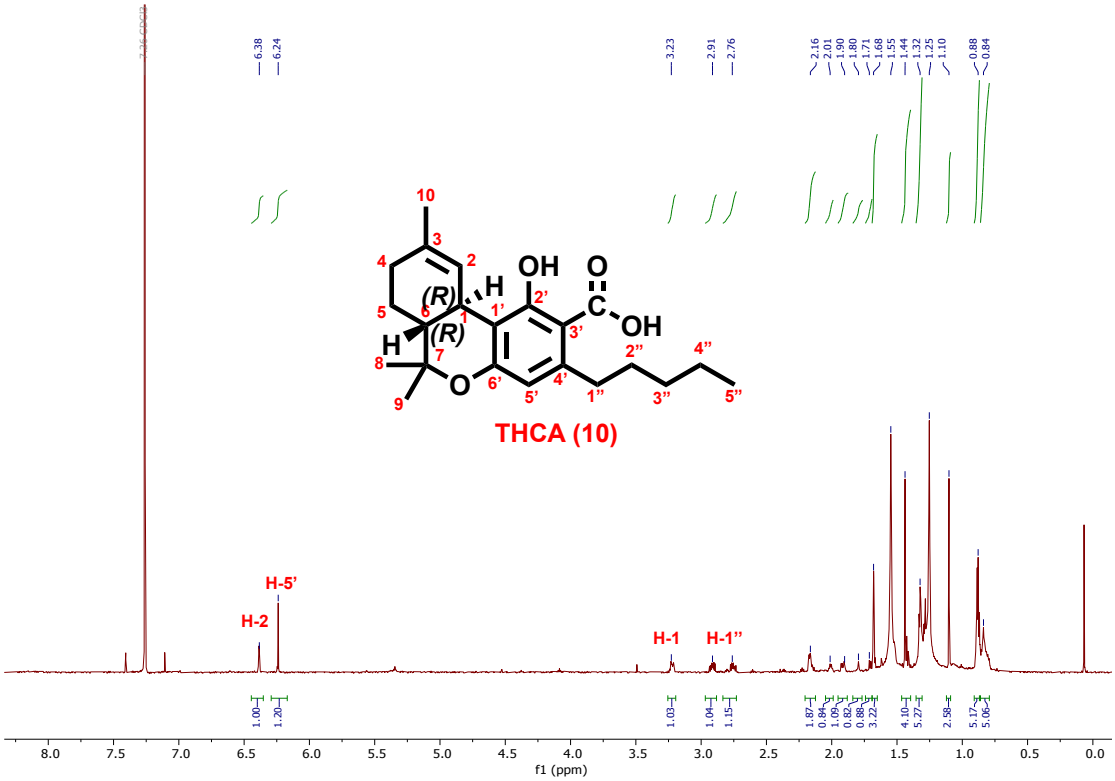
b)


Δ9-THCV
(14)
H-5'
H-3'
H-2
2'-OH
H-1
H-1"
H-4
H-5
f1 (ppm)

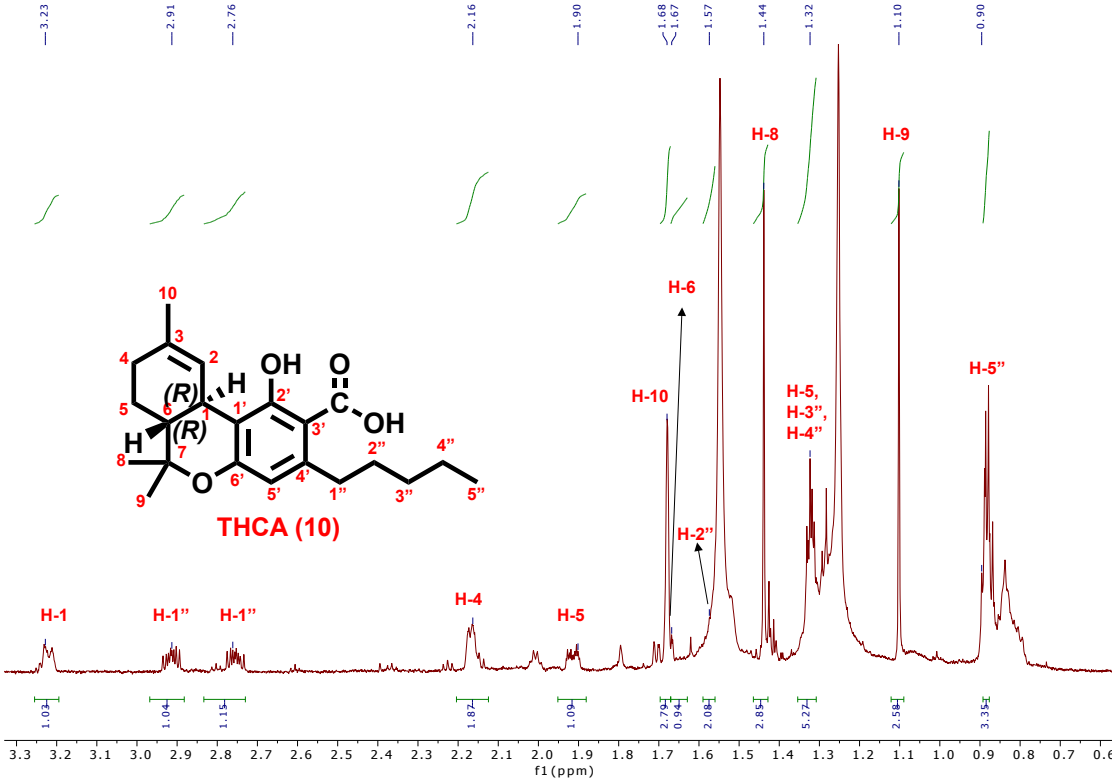
Zoom in


Δ9-THCV
(14)
H-1
H-1"
H-4
H-5
H-6
H-10
H-2"
H-8
H-9
H-3"
f1 (ppm)

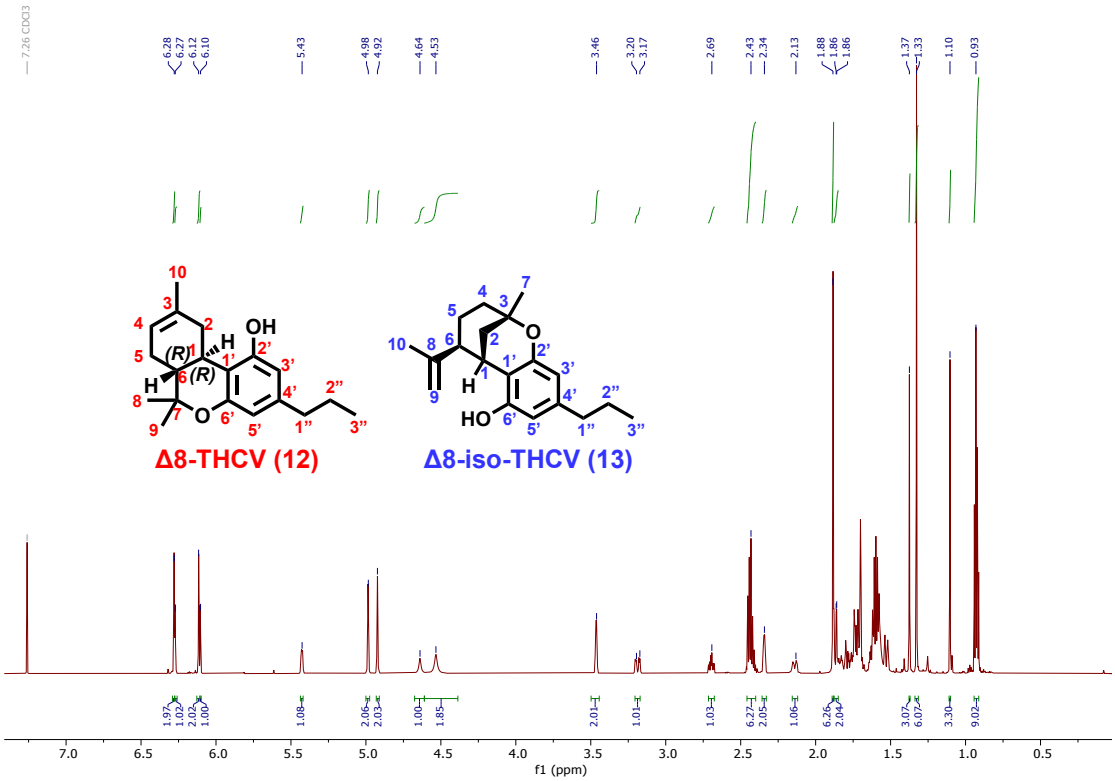
c)


THCA (10)
H-5'
H-2
H-1
H-1"
f1 (ppm)

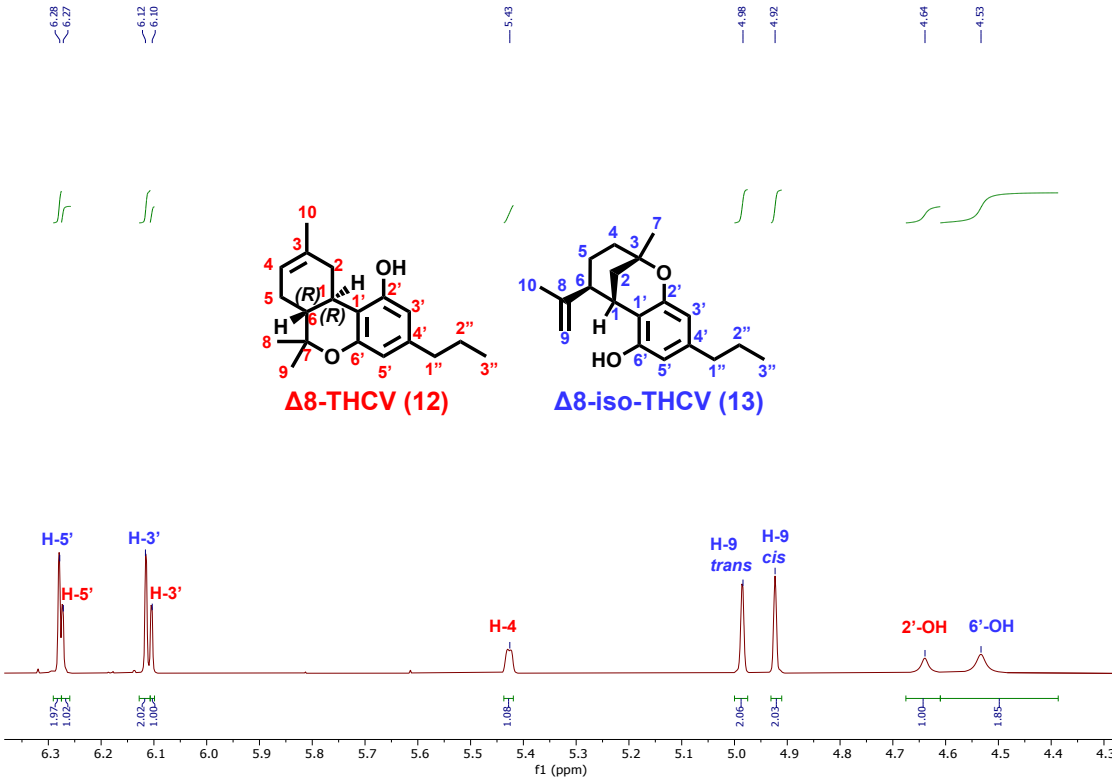
Zoom in


THCA (10)
H-1
H-1"
H-1"
H-4
H-5
H-10
H-6
H-2"
H-8
H-9
H-5,
H-3",
H-4"
H-5"
f1 (ppm)

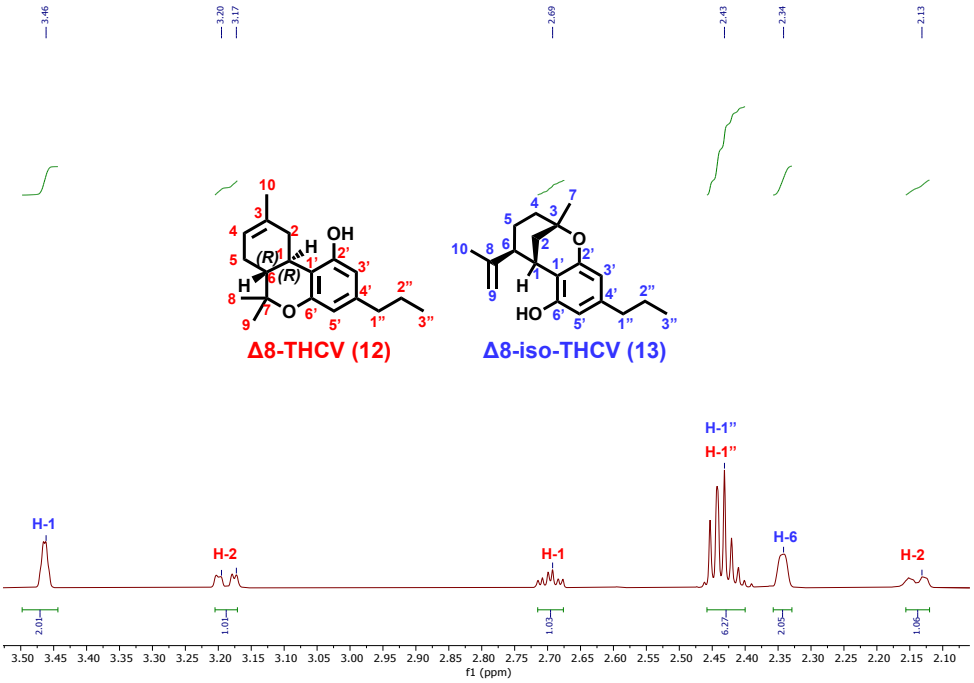
d)



Zoom in



Zoom in



Zoom in

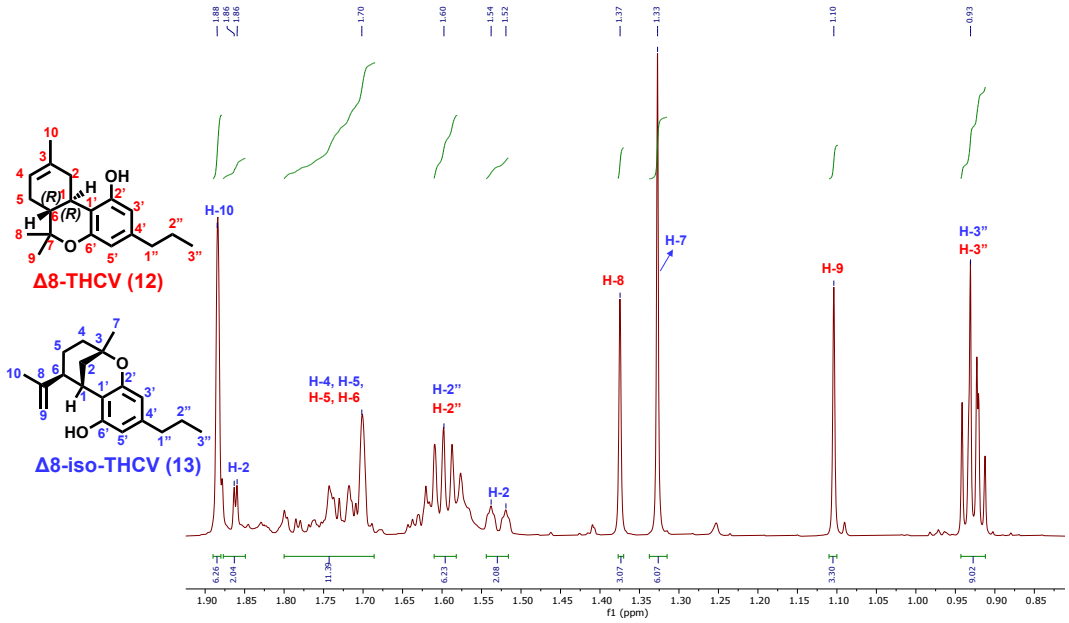


Figure S1. ^{1}H NMR spectra of a) Δ3-THC, b) Δ9-THCV, c) THCA, and d) a mixture of Δ8-THCV and Δ8-iso-THCV.

5 mg of Δ3-THC (**1**), Δ9-THCV (**14**), THCA (**10**), or a mixture of Δ8-THCV and Δ8-iso-THCV (**12, 13**) were dissolved in $CDCl_3$, and ^{1}H NMR spectra were recorded on a Bruker Avance 700 MHz spectrometer at 298 K. The assignments are based on data by Cheng et al.,[2] Srebnik et al.,[3] Dadiotis et al.,[4] Radwan et al.[5]

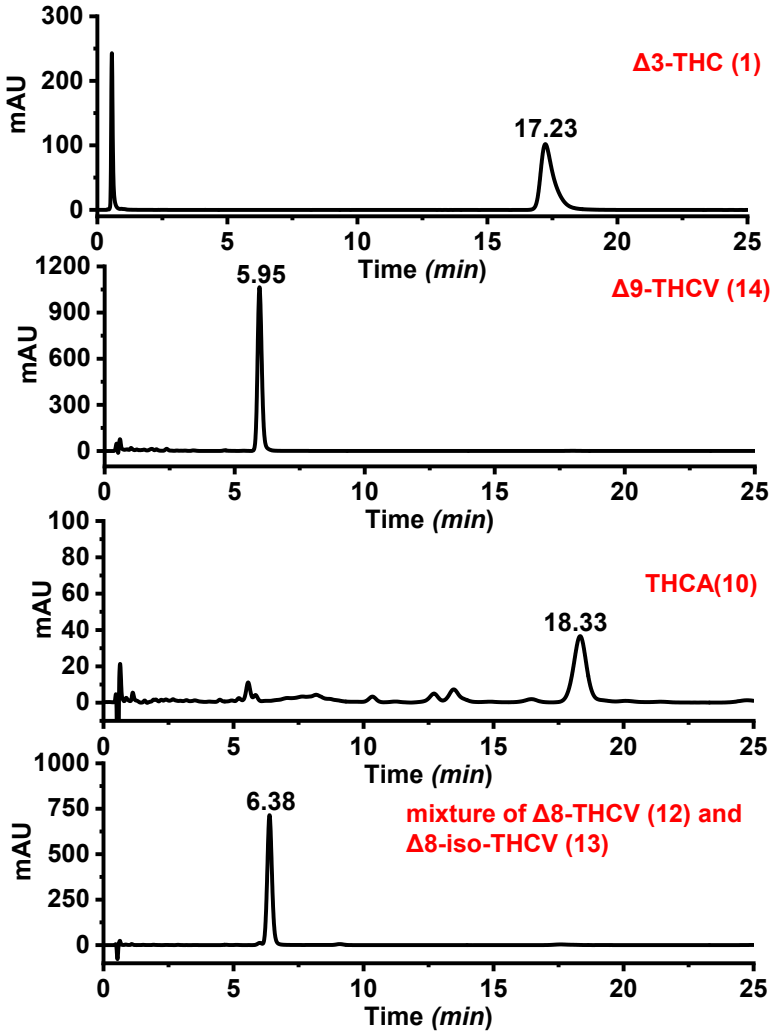
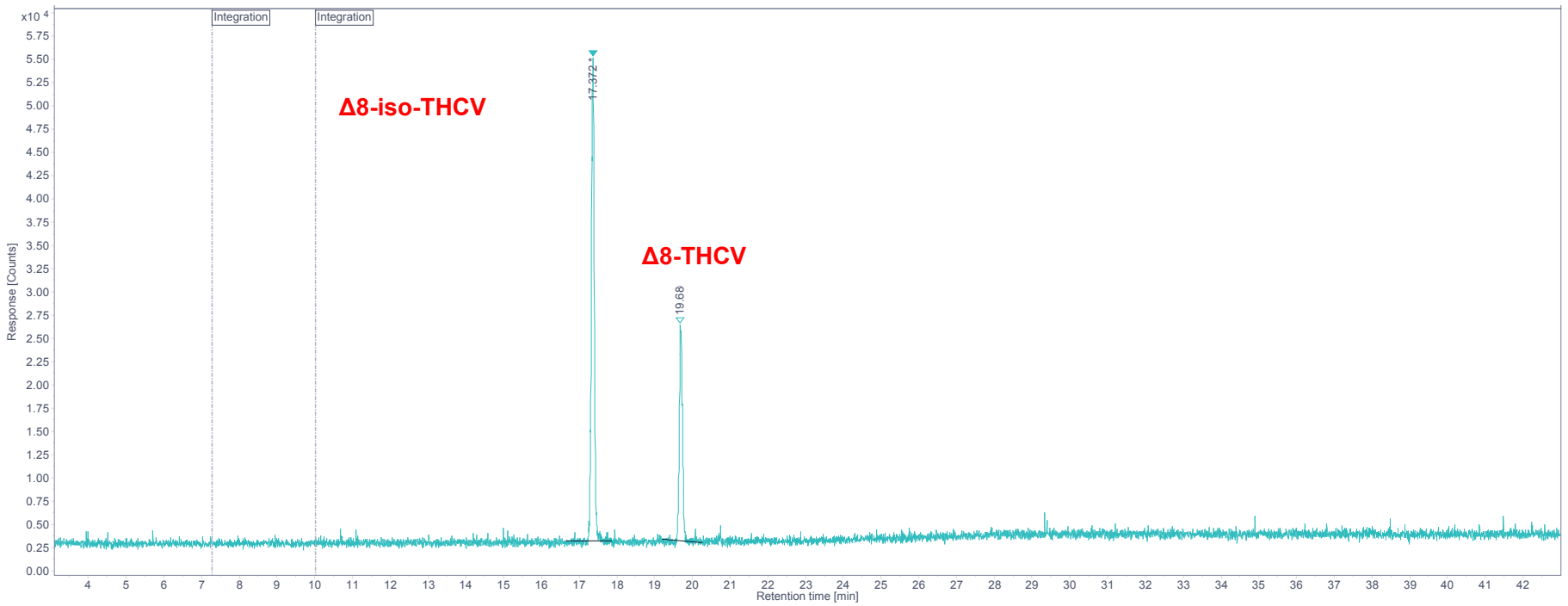
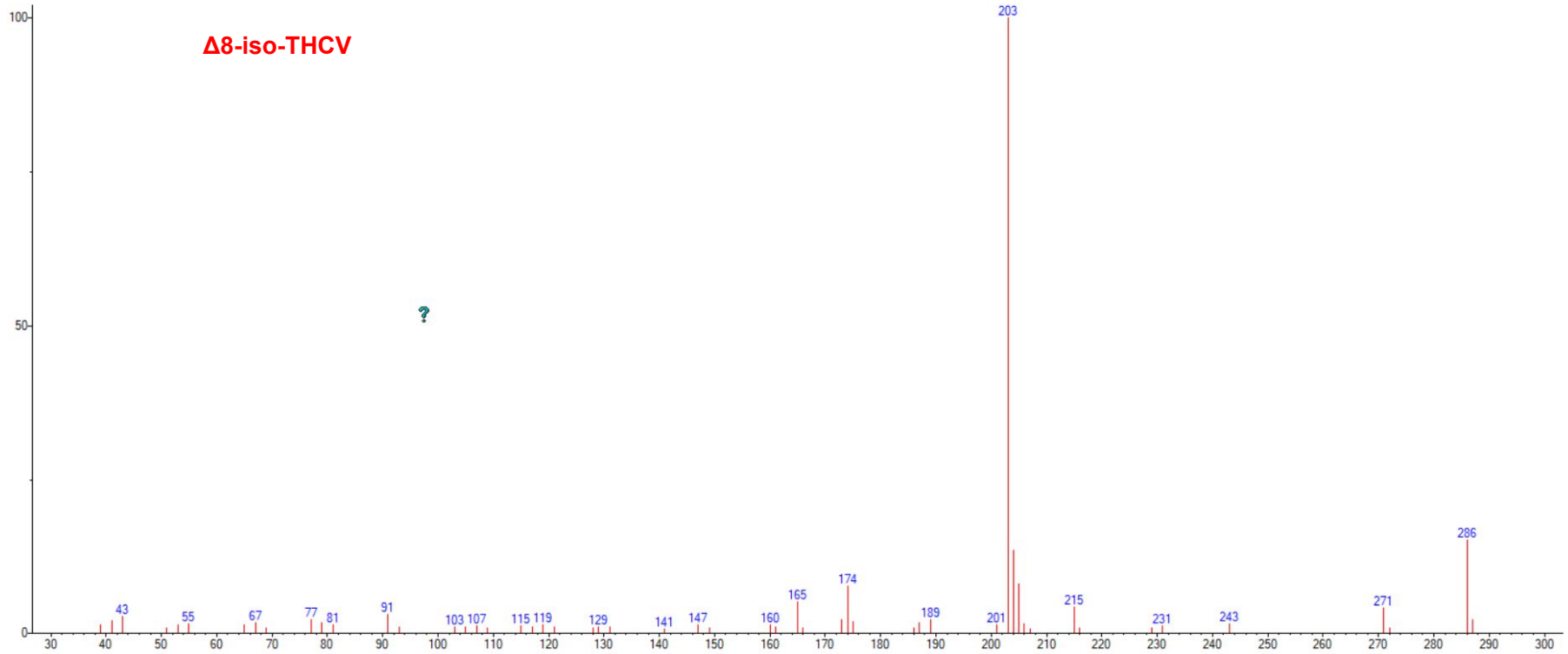


Figure S2. RP-UHPLC-UV (215nm) chromatograms of Δ3-THC, Δ9-THCV, THCA, and mixture of Δ8-THCV and Δ8-iso-THCV.

A Zorbax Eclipse Plus C18 chromatographic column (2.1 mm × 100 mm, particle size: 1.8 μm; Agilent Technologies, Santa Clara, CA, USA) was integrated with a 1290 Infinity ultra-performance liquid chromatography (UHPLC) system (Agilent Technologies, Santa Clara, United States) employing Diode Array Detection (DAD) as the detection method. The mobile phase employed was a solution comprising 5 mM formic acid in water (mobile phase A) and acetonitrile (mobile phase B). Isocratic elution was achieved by maintaining a constant ratio of 58% mobile phase B at a flow rate of 0.50 mL·min^{-1}. An aliquot of purified Δ3-THC (**1**), Δ9-THCV (**14**), THCA (**10**), and a mixture of Δ8-THCV (**12**) and Δ8-iso-THCV (**13**) was sampled with the tip of a spatula and dissolved in MeOH. Subsequently, 8 μL of each sample was injected for the analysis.


x10 4
Integration
Integration
Δ8-iso-THCV
17.372
Δ8-THCV
19.68
Response [Counts]
Retention time [min]


Δ8-iso-THCV
?
100
50
0
203
286
43
55
67
77
81
91
103
107
115
119
129
141
147
160
165
174
189
201
215
231
243
271
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
260
270
280
290
300

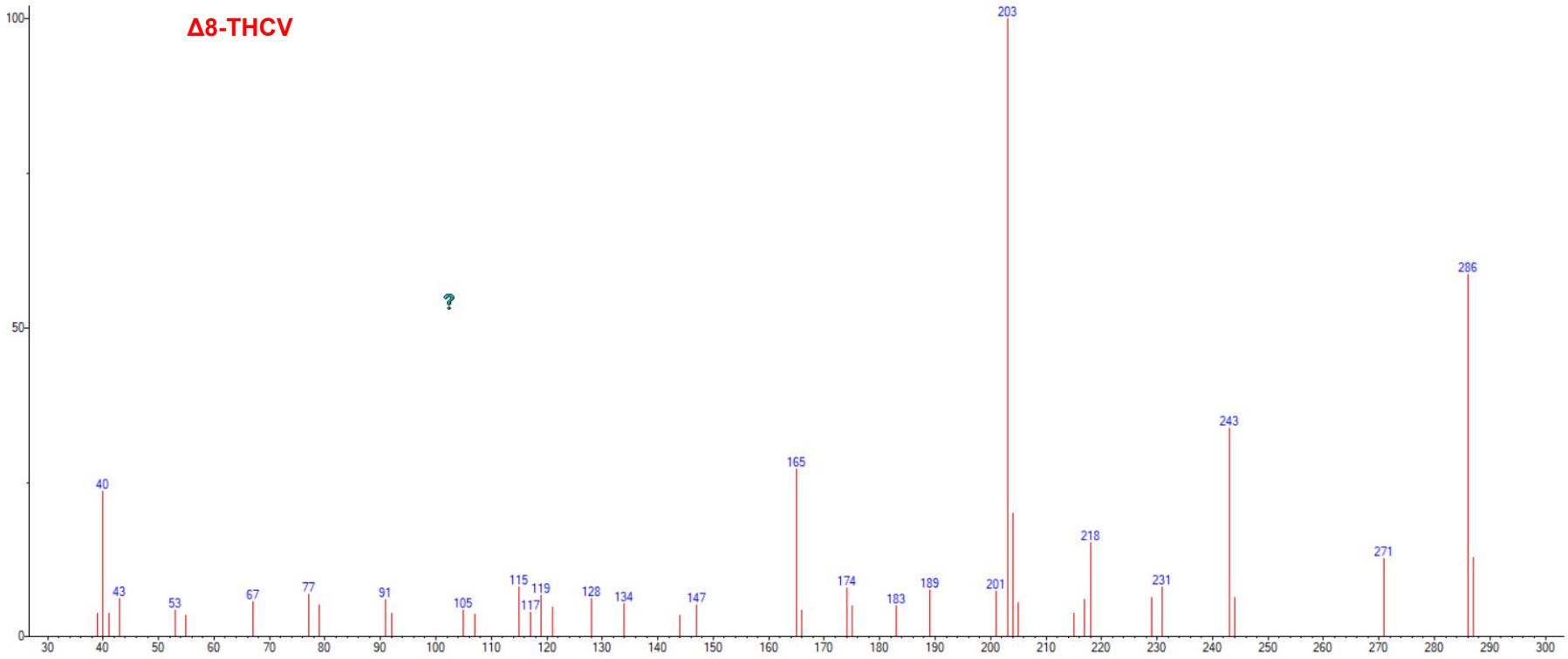


Figure S3. GC-FID profile of the mixture of Δ8-THCV and Δ8-iso-THCV, and EI-MS spectra of Δ8-THCV and Δ8-iso-THCV.

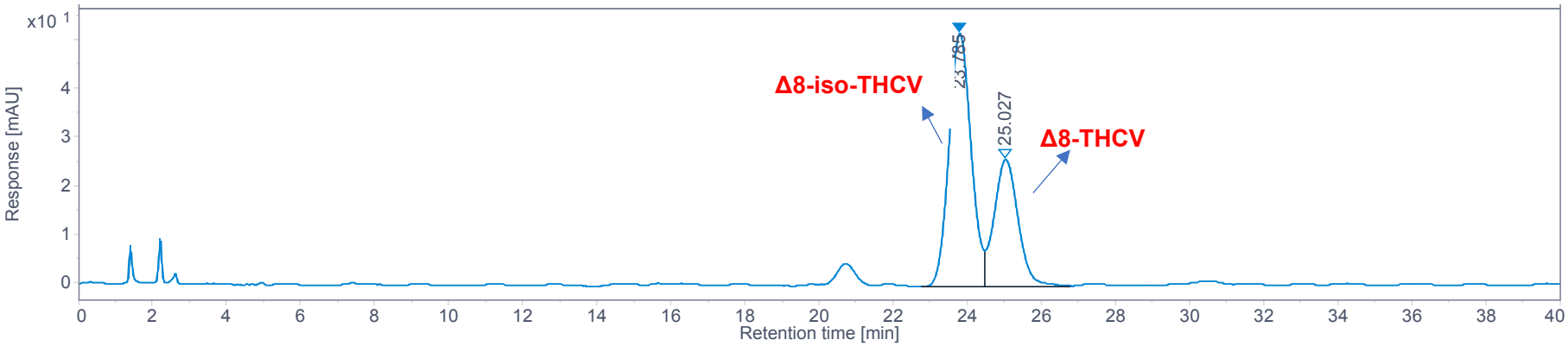


Figure S4. Silica-Ag(Ⅰ) HPLC-DAD (215 nm) profile of the mixture Δ8-THCV and Δ8-iso-THCV.

Table S3. Calibrants used for multi-pass CCS calibrations.

Major mix calibrant	Positive ionization mode	
	m/z	CCS (Å²)
Sulphaguanidine	215.5970	146.8
Sulfadimethoxine	311.0809	168.4
Val-Tyr-Val	380.2180	191.7
Verapamil	455.2904	208.8
Terfenadine	472.3210	228.7
Reserpine	609.2807	252.3

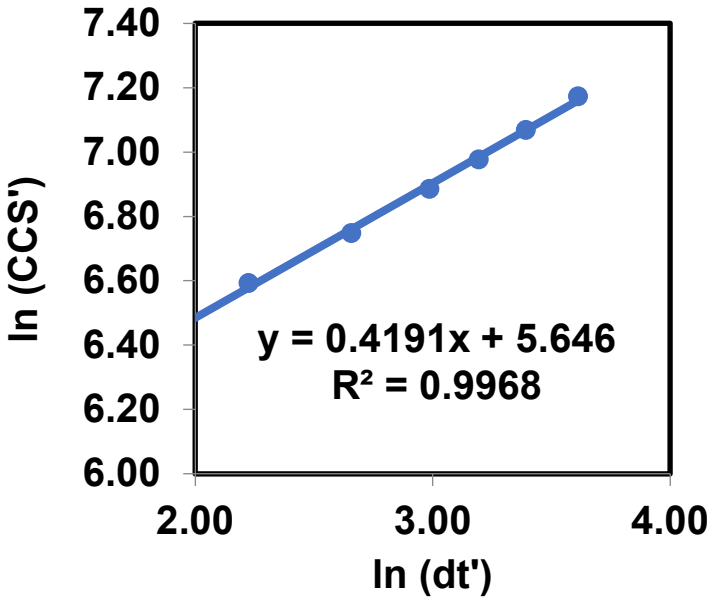


Figure S5. The logarithmic fit calibration curve between drift time and CCS values.

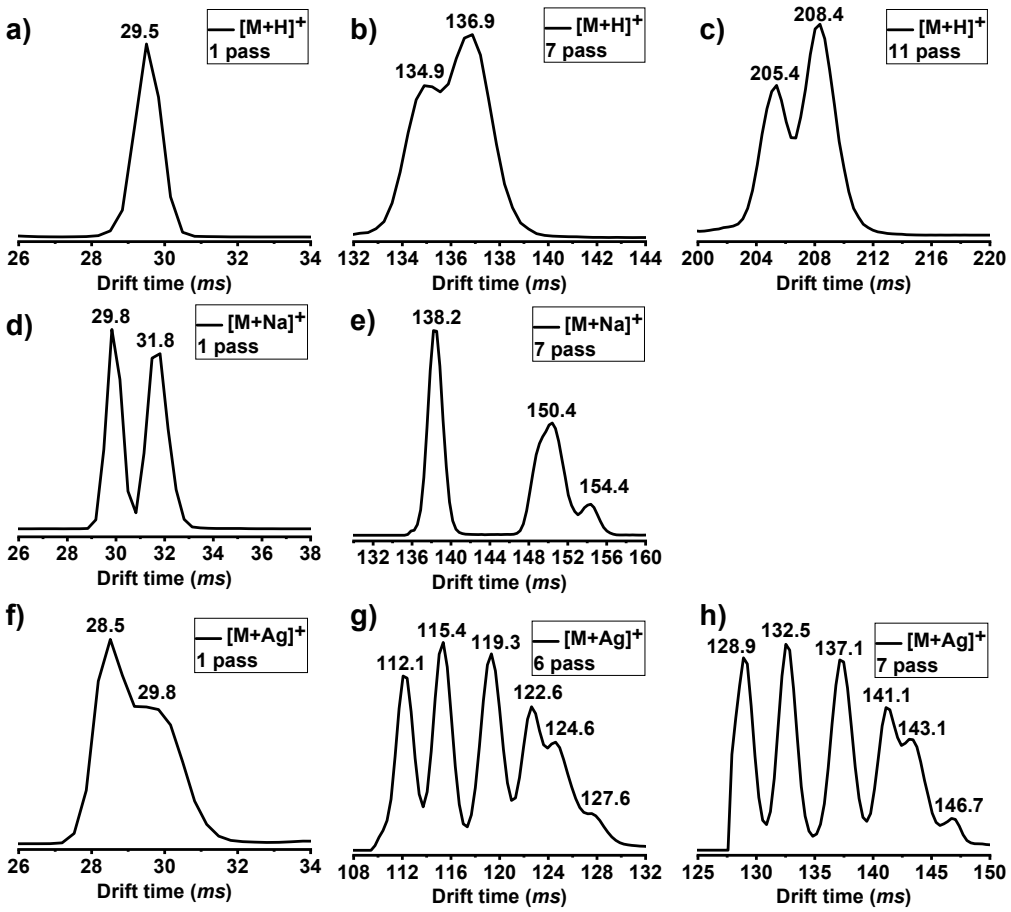
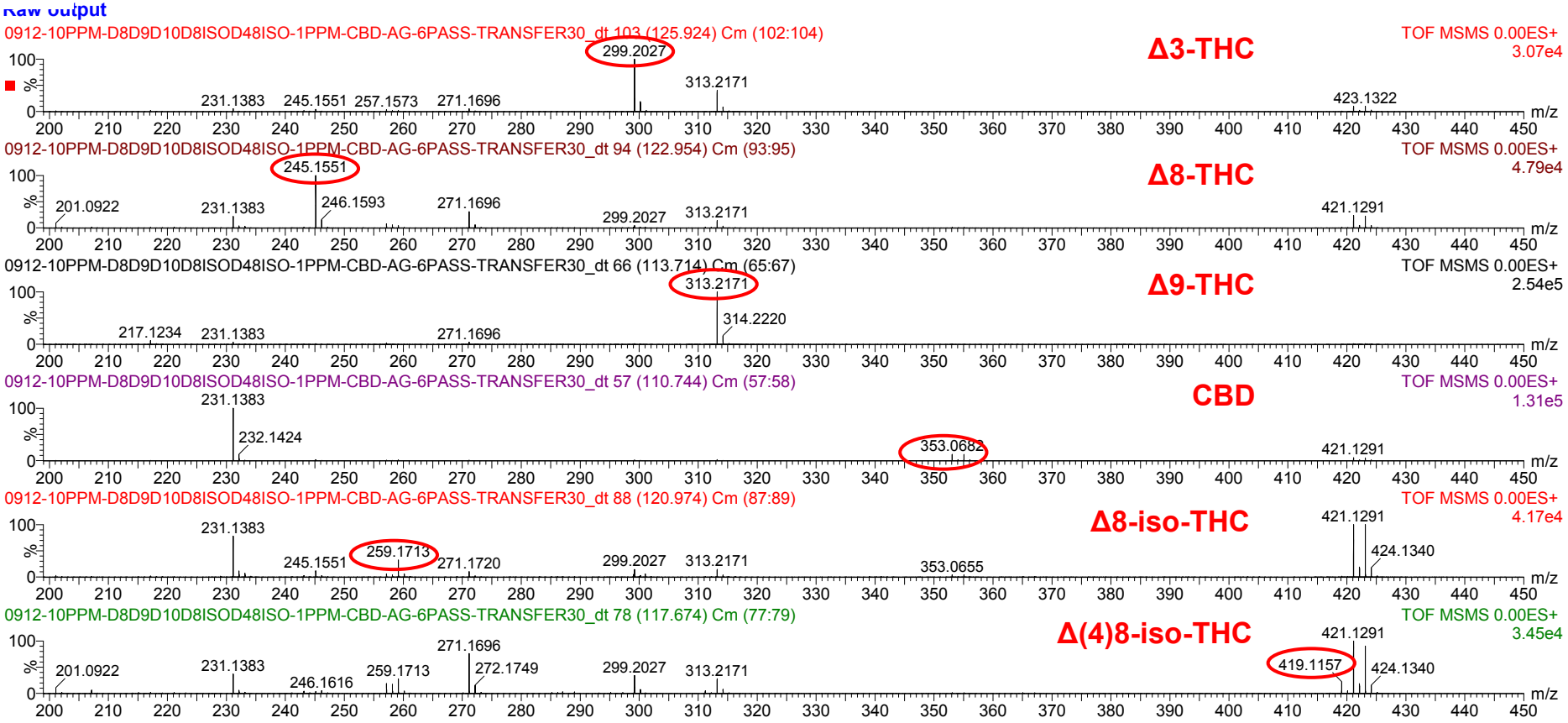
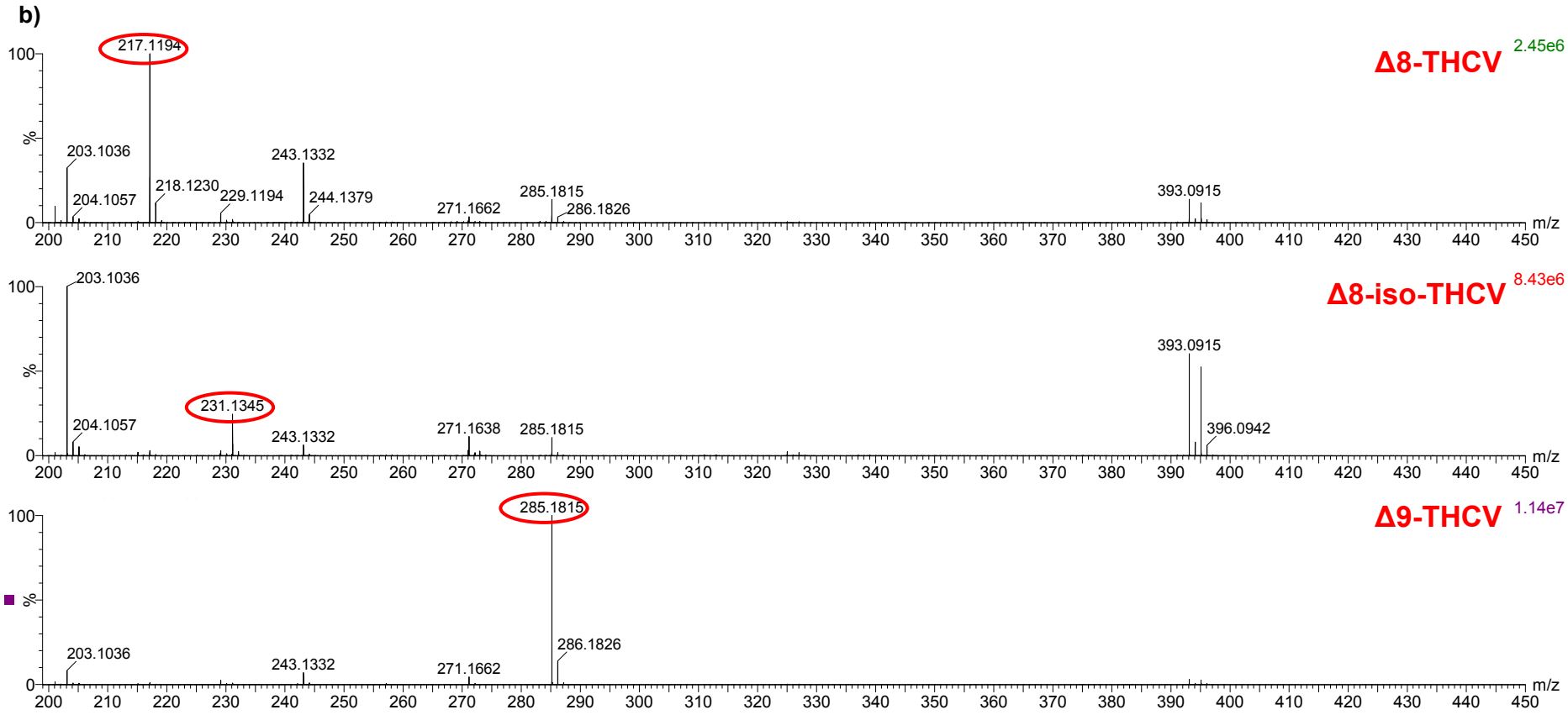
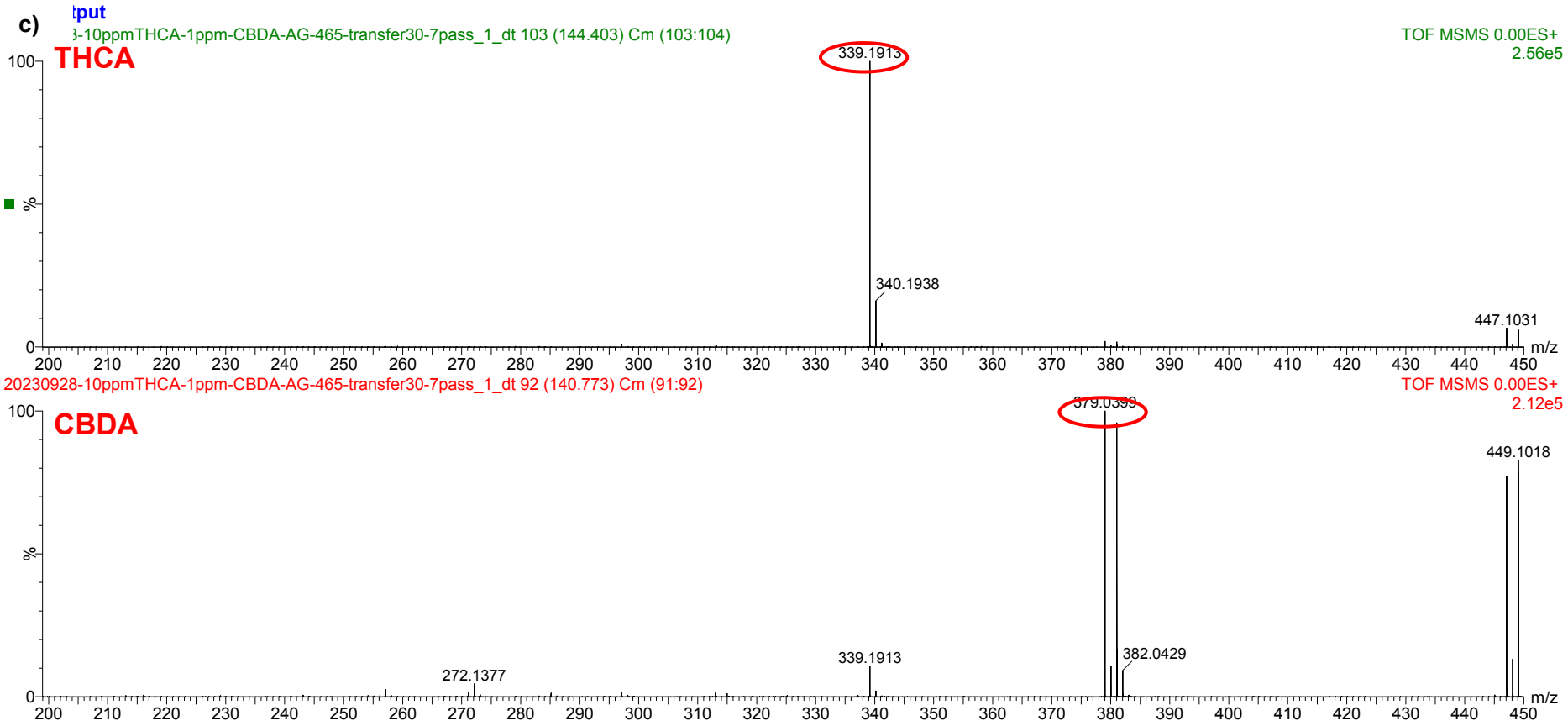


Figure S6. Mobiligrams of charged adducts of the mixture of Δ3-THC, Δ8-THC, Δ9-THC, CBD, Δ8-iso-THC and Δ(4)8-iso-THC. Protonated species (extracting $[M+H]^+$ signal at *m/z* 315) after a) 1 pass, b) 7 passes and c) 11 passes. Sodiated species (extracting $[M+Na]^+$ signal at *m/z* 337) after d) 1 pass and e) 7 passes. Argentated species (extracting $[M+Ag]^+$ signal at *m/z* 421) after f) 1 pass, g) 6 passes and h) 7 passes.

a)


Raw output
0912-10PPM-D8D9D10D8ISOD48ISO-1PPM-CBD-AG-6PASS-TRANSFER30_dt 103 (125.924) Cm (102:104)
TOF MSMS 0.00ES+
3.07e4
Δ3-THC
299.2027
313.2171
231.1383
245.1551
257.1573
271.1696
423.1322
0912-10PPM-D8D9D10D8ISOD48ISO-1PPM-CBD-AG-6PASS-TRANSFER30_dt 94 (122.954) Cm (93:95)
TOF MSMS 0.00ES+
4.79e4
Δ8-THC
245.1551
201.0922
231.1383
246.1593
271.1696
299.2027
313.2171
421.1291
0912-10PPM-D8D9D10D8ISOD48ISO-1PPM-CBD-AG-6PASS-TRANSFER30_dt 66 (113.714) Cm (65:67)
TOF MSMS 0.00ES+
2.54e5
Δ9-THC
313.2171
314.2220
217.1234
231.1383
271.1696
0912-10PPM-D8D9D10D8ISOD48ISO-1PPM-CBD-AG-6PASS-TRANSFER30_dt 57 (110.744) Cm (57:58)
TOF MSMS 0.00ES+
1.31e5
CBD
231.1383
232.1424
353.0682
421.1291
0912-10PPM-D8D9D10D8ISOD48ISO-1PPM-CBD-AG-6PASS-TRANSFER30_dt 88 (120.974) Cm (87:89)
TOF MSMS 0.00ES+
4.17e4
Δ8-iso-THC
231.1383
259.1713
245.1551
271.1720
299.2027
313.2171
353.0655
421.1291
424.1340
0912-10PPM-D8D9D10D8ISOD48ISO-1PPM-CBD-AG-6PASS-TRANSFER30_dt 78 (117.674) Cm (77:79)
TOF MSMS 0.00ES+
3.45e4
Δ(4)8-iso-THC
271.1696
201.0922
231.1383
246.1616
259.1713
272.1749
299.2027
313.2171
421.1291
419.1157
424.1340
m/z


b)
Δ8-THCV
2.45e6
217.1194
203.1036
243.1332
218.1230
229.1194
204.1057
244.1379
271.1662
285.1815
286.1826
393.0915
Δ8-iso-THCV
8.43e6
203.1036
393.0915
231.1345
204.1057
243.1332
271.1638
285.1815
396.0942
Δ9-THCV
1.14e7
285.1815
203.1036
243.1332
271.1662
286.1826
100
%
0
m/z
200
210
220
230
240
250
260
270
280
290
300
310
320
330
340
350
360
370
380
390
400
410
420
430
440
450


c)
tput
-10ppmTHCA-1ppm-CBDA-AG-465-transfer30-7pass_1_dt 103 (144.403) Cm (103:104)
TOF MSMS 0.00ES+
2.56e5
THCA
339.1913
340.1938
447.1031
100
%
0
m/z
200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450
20230928-10ppmTHCA-1ppm-CBDA-AG-465-transfer30-7pass_1_dt 92 (140.773) Cm (91:92)
TOF MSMS 0.00ES+
2.12e5
CBDA
379.0399
449.1018
339.1913
382.0429
272.1377
100
%
0
m/z
200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450

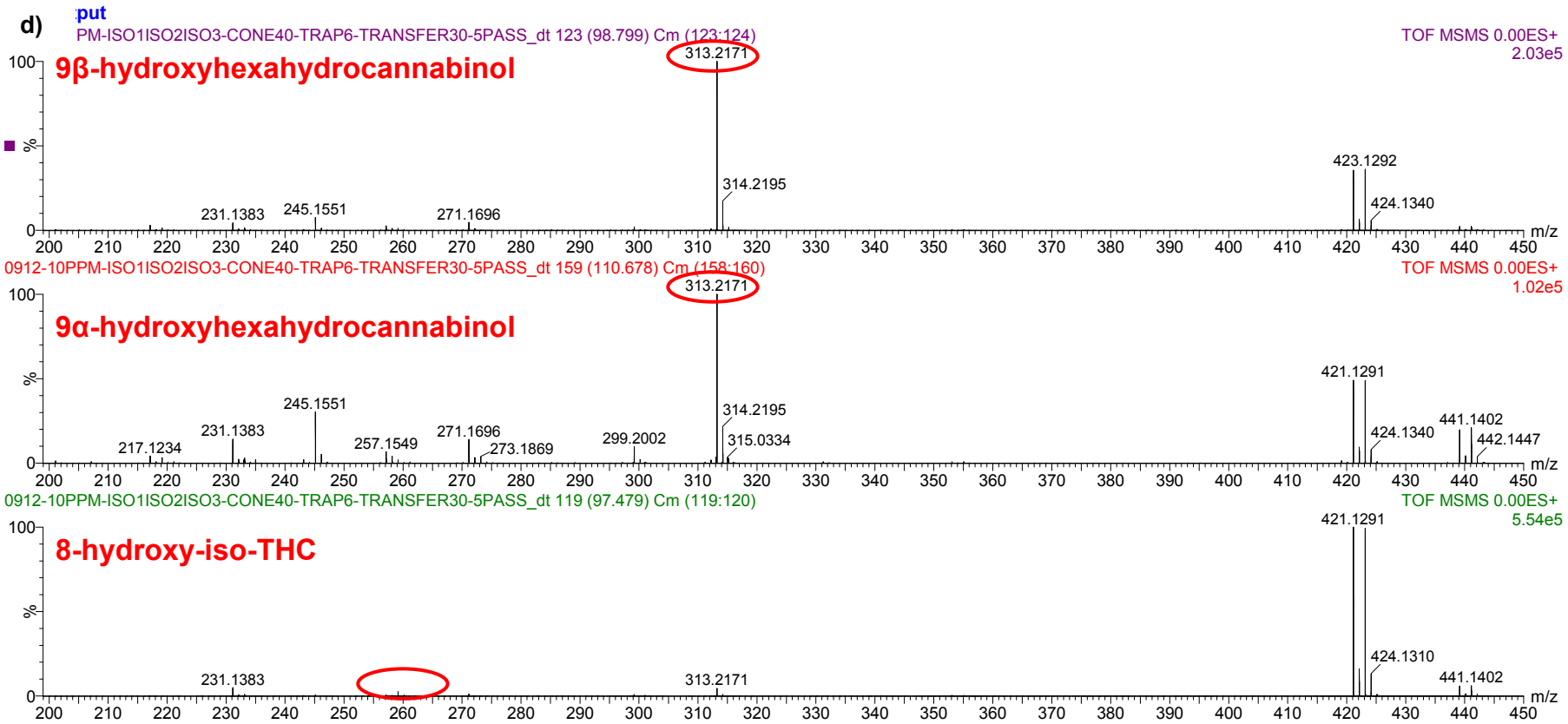


Figure S7. Characteristic fragments of a) Δ8-THC, Δ9-THC, Δ3-THC, CBD, Δ8-iso-THC and Δ(4)8-iso-THC; b) Δ8-THCV, Δ8-iso-THCV and Δ9-THCV; c) THCA and CBDA; d) 9α-hydroxyhexahydrocannabinol, 9β-hydroxyhexahydrocannabinol and 8-hydroxy-iso-THC in the presence of Ag(I) at trap energy of 30 V.

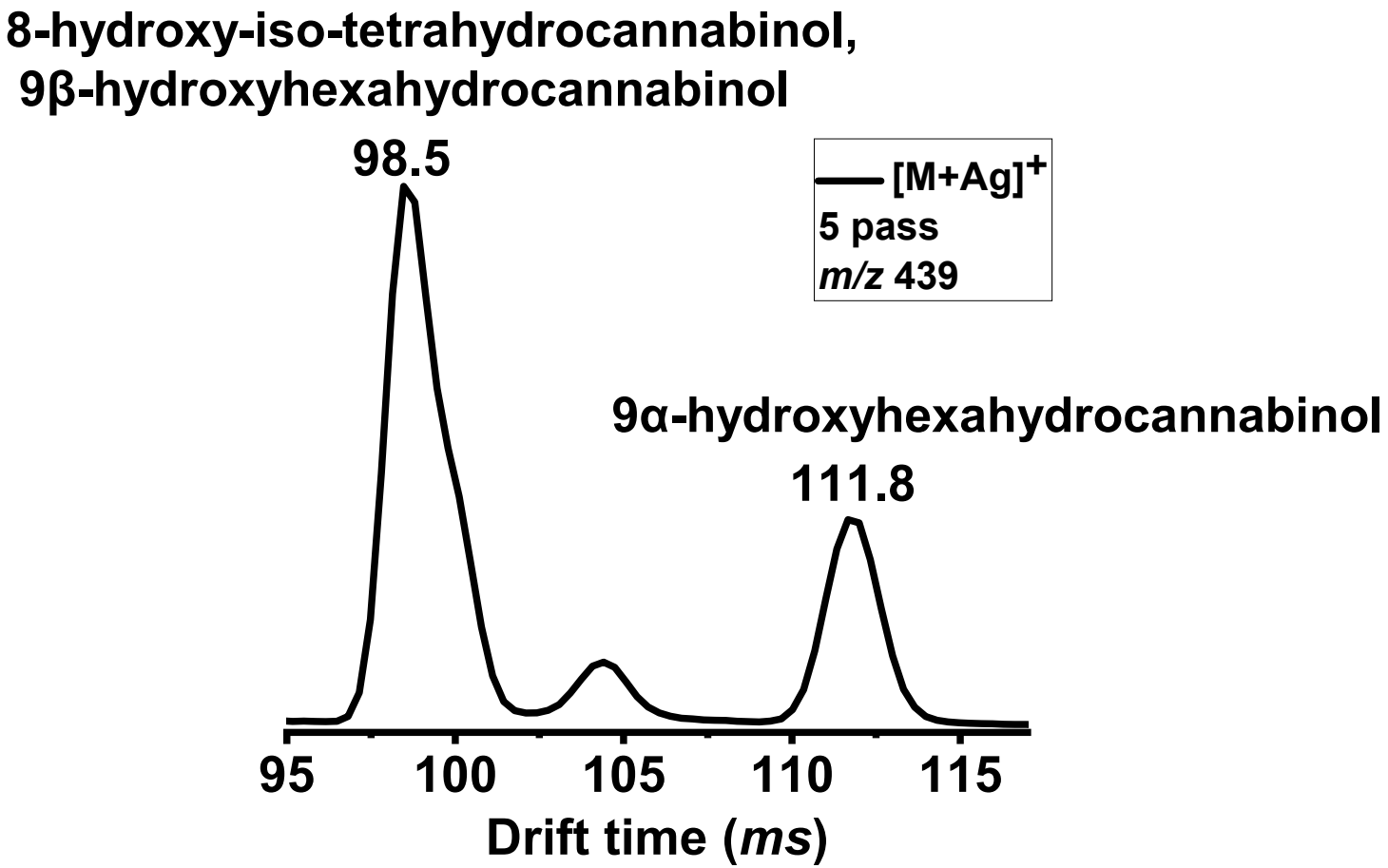


Figure S8. Mobiligram of the mixture consisting of 8-hydroxy-iso-THC, 9α-hydroxyhexahydrocannabinol, and 9β-hydroxyhexahydrocannabinol in the form of Ag(I) species.

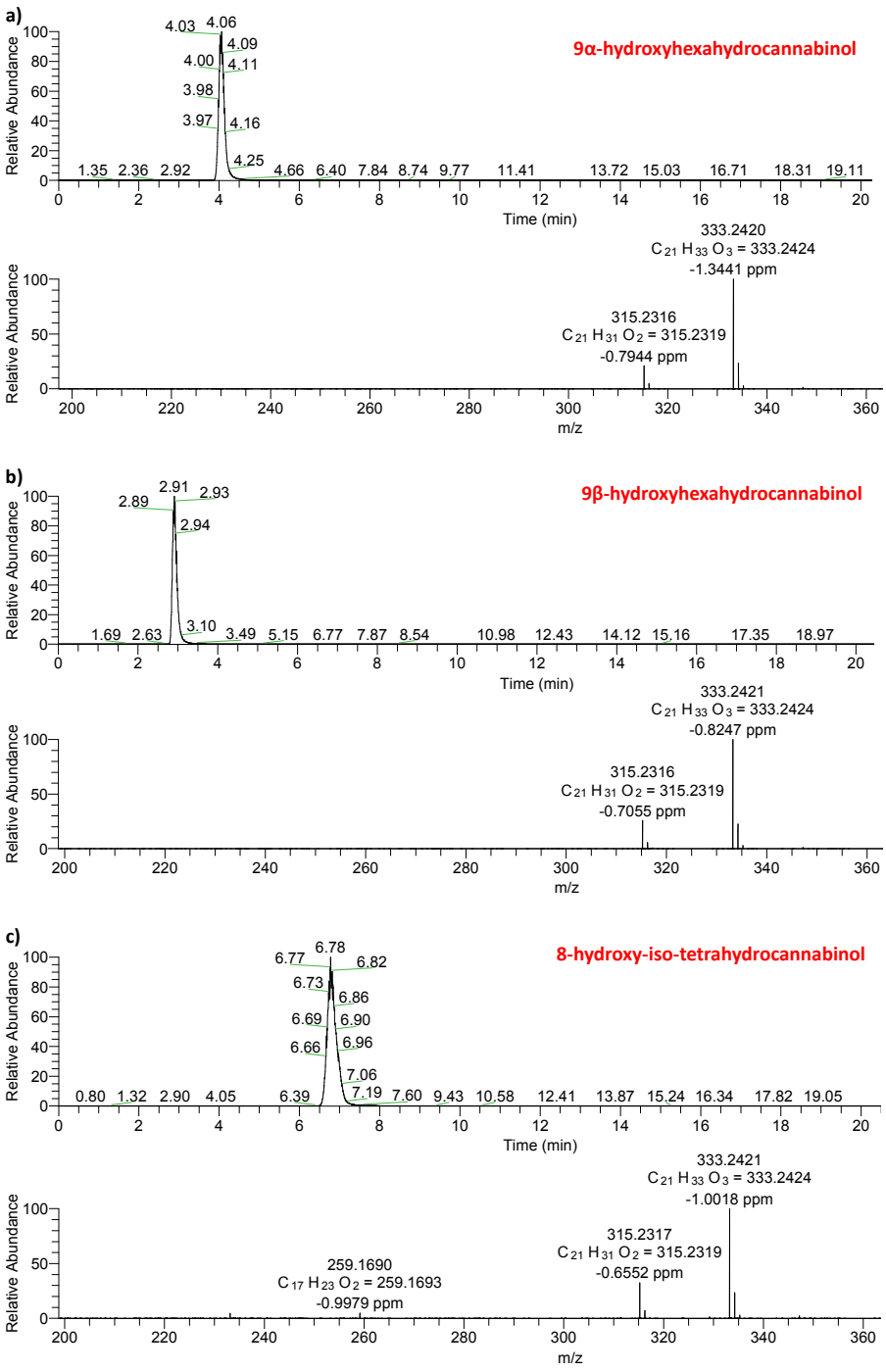


Figure S9. Reversed-phase UHPLC-ESI-Orbitrap mass spectra of a) 9α-hydroxyhexahydrocannabinol, b) 9β-hydroxyhexahydrocannabinol, and c) 8-hydroxy-iso-THC.

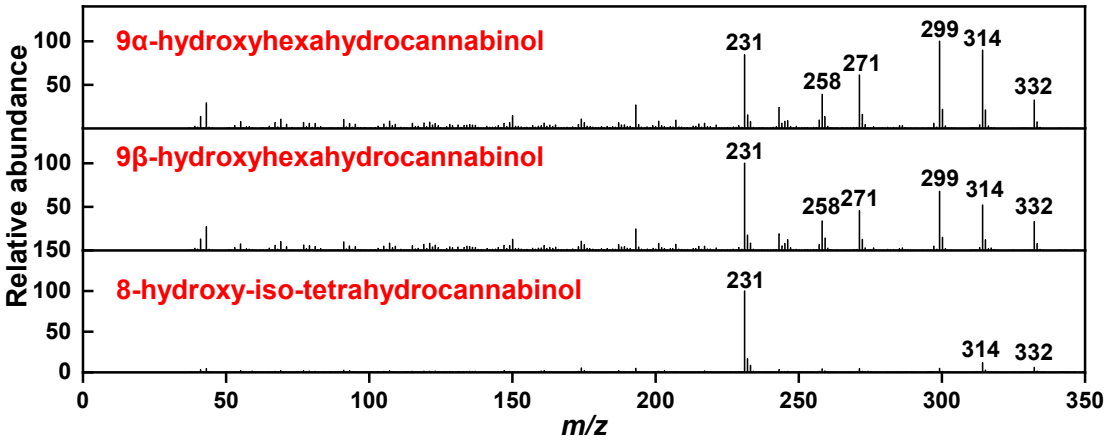
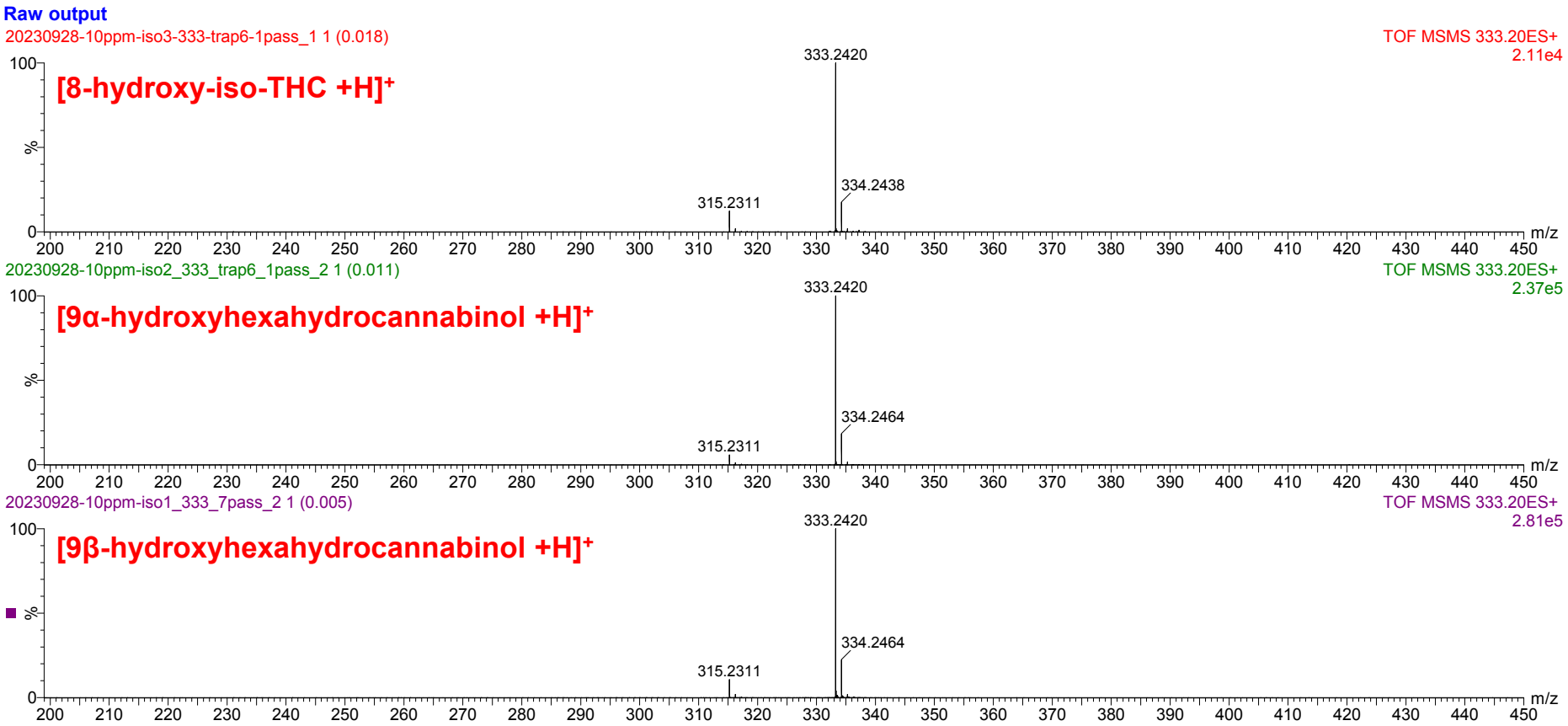
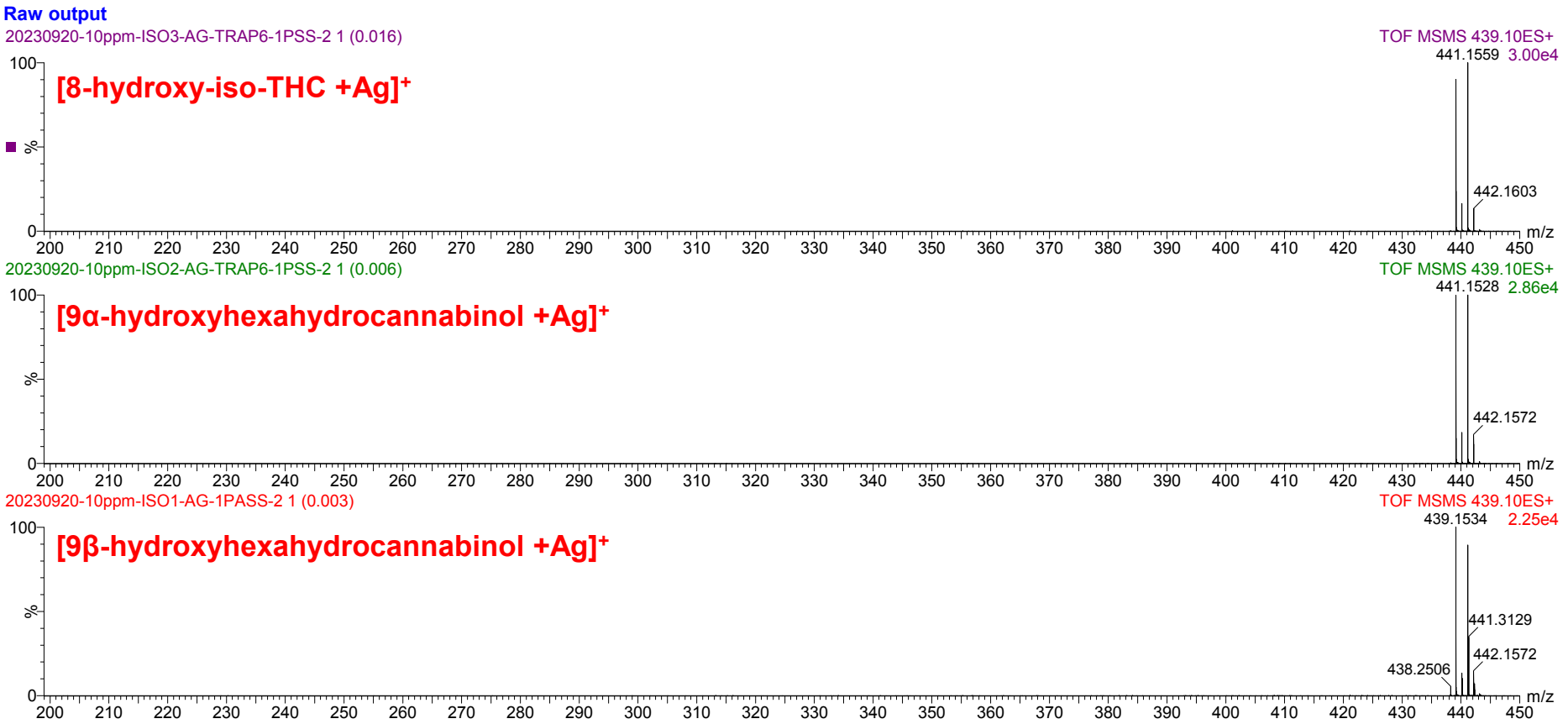


Figure S10. EI-MS spectra obtained after GC separation of 9α-hydroxyhexahydrocannabinol, 9β-hydroxyhexahydrocannabinol, and 8-hydroxy-iso-THC.

a)


Raw output
20230928-10ppm-iso3-333-trap6-1pass_1 1 (0.018)
TOF MSMS 333.20ES+
2.11e4
[8-hydroxy-iso-THC +H]+
333.2420
334.2438
315.2311
20230928-10ppm-iso2_333_trap6_1pass_2 1 (0.011)
TOF MSMS 333.20ES+
2.37e5
[9α-hydroxyhexahydrocannabinol +H]+
333.2420
334.2464
315.2311
20230928-10ppm-iso1_333_7pass_2 1 (0.005)
TOF MSMS 333.20ES+
2.81e5
[9β-hydroxyhexahydrocannabinol +H]+
333.2420
334.2464
315.2311
%
m/z

b)


Raw output
20230920-10ppm-ISO3-AG-TRAP6-1PSS-2 1 (0.016)
TOF MSMS 439.10ES+
441.1559 3.00e4
[8-hydroxy-iso-THC +Ag]+
442.1603
20230920-10ppm-ISO2-AG-TRAP6-1PSS-2 1 (0.006)
TOF MSMS 439.10ES+
441.1528 2.86e4
[9α-hydroxyhexahydrocannabinol +Ag]+
442.1572
20230920-10ppm-ISO1-AG-1PASS-2 1 (0.003)
TOF MSMS 439.10ES+
439.1534 2.25e4
[9β-hydroxyhexahydrocannabinol +Ag]+
441.3129
442.1572
438.2506
%
m/z
100
0
200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450

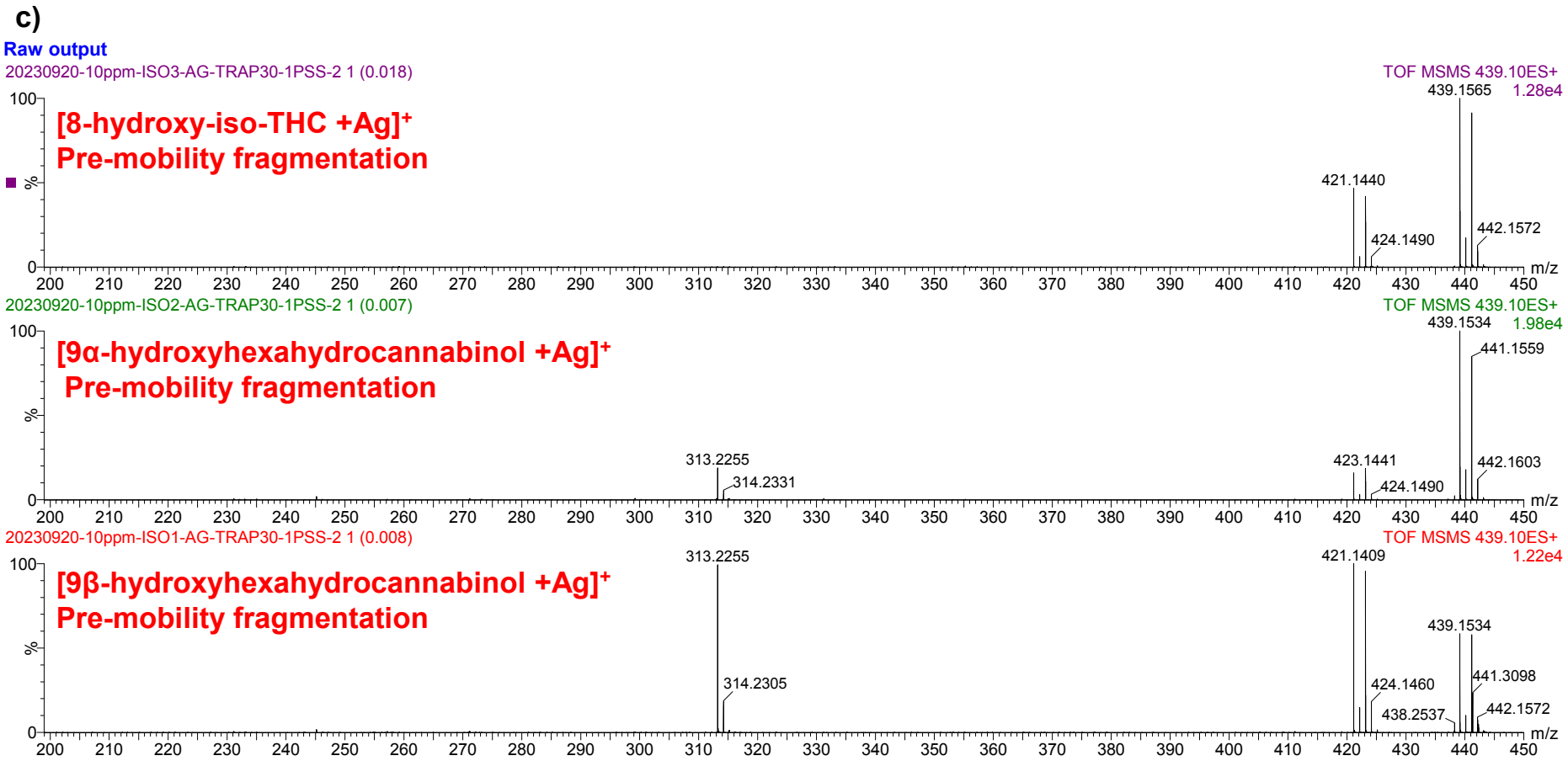


Figure S11. Mass spectra of a) protonated 8-hydroxy-iso-tetrahydrocannabinol, 9α-hydroxyhexahydrocannabinol, and 9β-hydroxyhexahydrocannabinol b) Ag(I) species of 8-hydroxy-iso-THC, 9α-hydroxyhexahydrocannabinol, and 9β-hydroxyhexahydrocannabinol, c) pre-mobility fragmentation of 8-hydroxy-iso-THC, 9α-hydroxyhexahydrocannabinol, and 9β-hydroxyhexahydrocannabinol in the presence of Ag(I) with trap energy of 30 V.

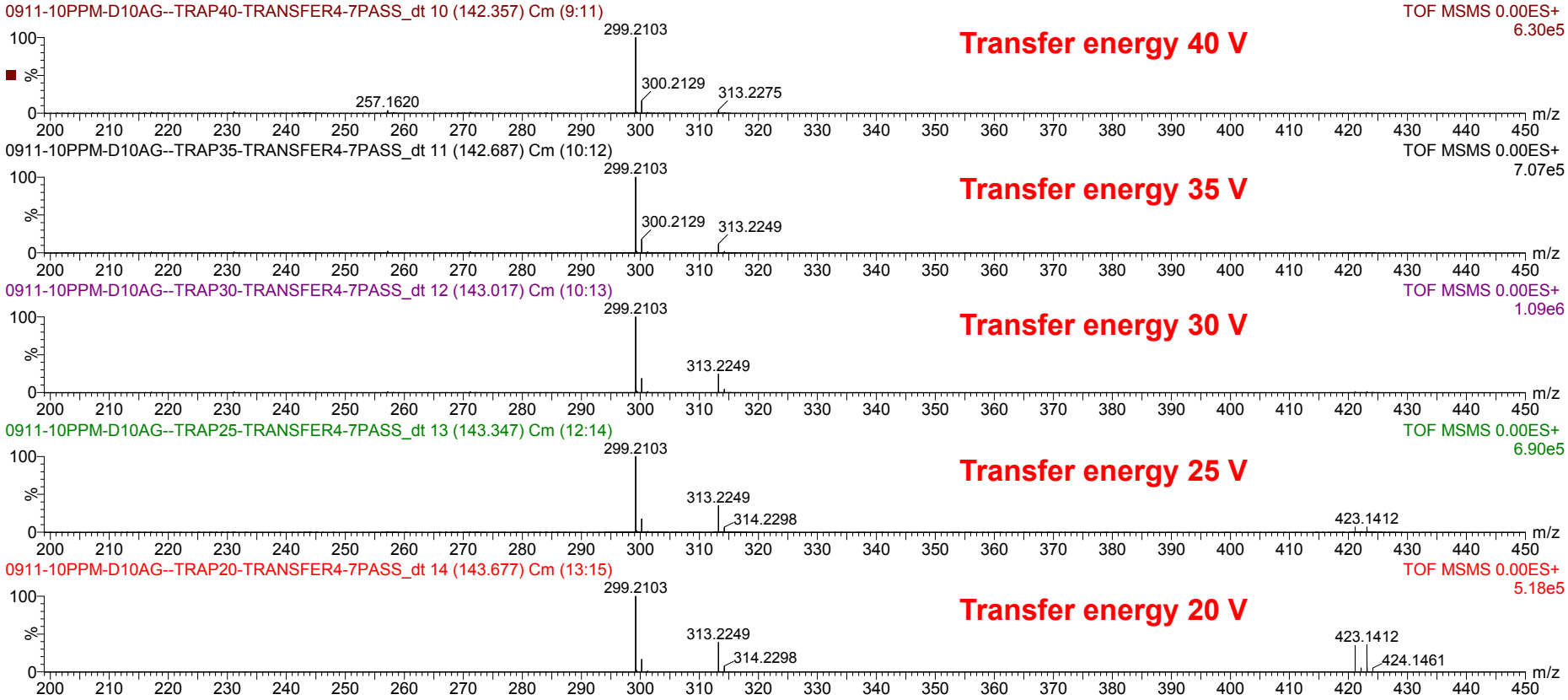
Table S4. Comparison of predicted CCS values by AllCCS, CCS values from literature and experimental CCS values obtained by cIMS of cannabinoids as protonated species and sodiated species.

Compounds	**$[M+H]^+$ (*m/z* 315) (Å²)**				**$[M+Na]^+$ (*m/z* 337) (Å²)**	
	Experimental $^{TW}CCS_{N2}$	Predicted CCS	Literature[6] $^{DT}CCS_{N2}$	Literature[7] $^{TI}CCS_{N2}$	Experimental $^{TW}CCS_{N2}$	Predicted CCS
Δ3-THC	188.4±0.01	186.5 (−1.0%)			197.9±0.03	203.5 (2.8%)
Δ8-THC	187.8±0.05	187.5 (−0.2%)			196.4±0.04	203.4 (3.6%)
Δ9-THC	187.8±0.03	187.5 (−0.2%)	187.4 (−0.2%)	183.9 (−2.1%)	194.8±0.01	203.5 (4.5%)
CBD	187.8±0.01	183.8 (−2.1%)	185.3 (−1.3%)	183.9 (−2.1%)	188.5±0.02	198.3 (5.2%)
Δ8-iso-THC	186.5±0.03	183.3 (−1.7%)			195.7±0.01	198.8 (1.6%)
Δ(4)8-iso-THC	186.6±0.04	185.1 (−0.8%)			195.8±0.01	202.3 (3.3%)
9α-hydroxyhexahydrocannabinol	191.2±0.02	190.7 (−0.3%)			201.7±0.02	205.8 (2.0%)
9β-hydroxyhexahydrocannabinol	191.6±0.2	190.6 (−0.5%)			193.0±0.01	205.6 (6.5%)
8-hydroxy-iso-THC	187.9±0.01	183.7 (−2.2%)			200.8±0.02	196.9 (−1.9%)
THCA	194.0±0.2	196.8 (1.4%)			212.2±0.01	210.8 (−0.7%)
CBDA	193.6±0.03	195.0 (0.7%)			206.7±0.01	208.3 (0.8%)
Δ8-THCV	174.9±0.01	172.5 (−1.4%)			188.0±0.02	191.5 (1.9%)
Δ8-iso-THCV	173.5±0.01	174.9 (0.8%)			183.8±0.01	194.4 (5.8%)
Δ9-THCV	174.7±0.01	175.0 (0.2%)			185.9±0.01	194.4 (4.6%)

*Values in brackets represent relative deviations from experimental CCS value

a) Δ3-THC

Raw output

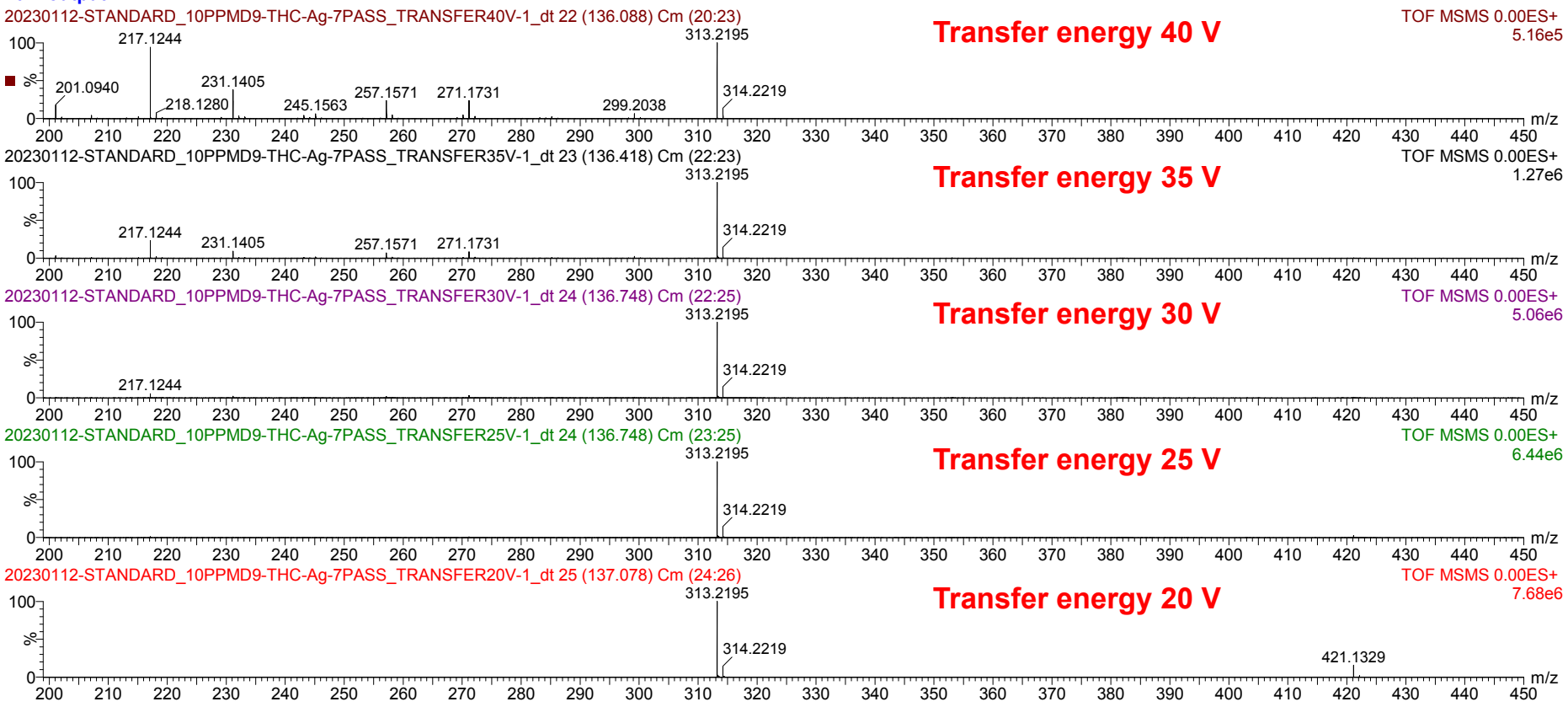


b) Δ8-THC

Raw output

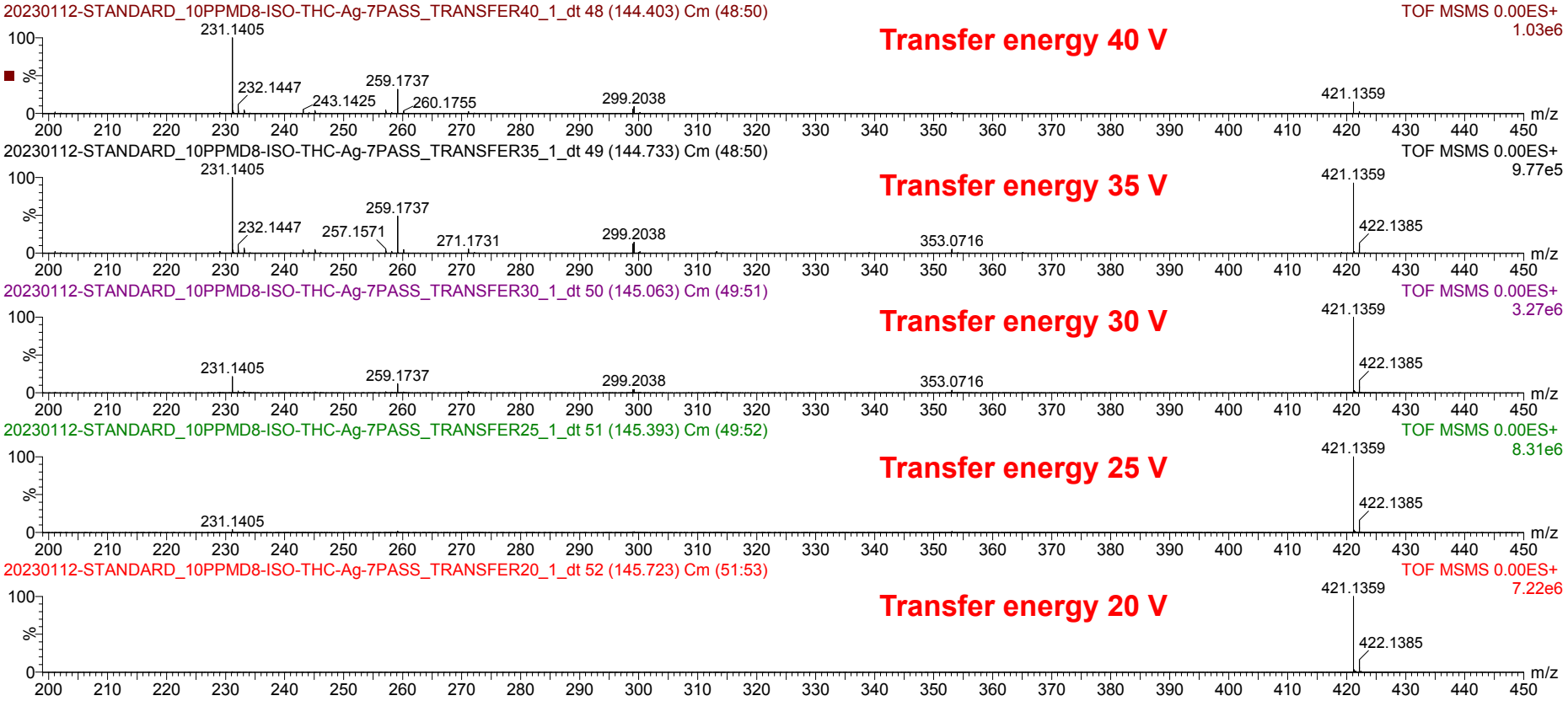
c) Δ9-THC

Raw output



d) Δ8-iso-THC

Raw output



e) Δ(4)8-iso-THC

Raw output

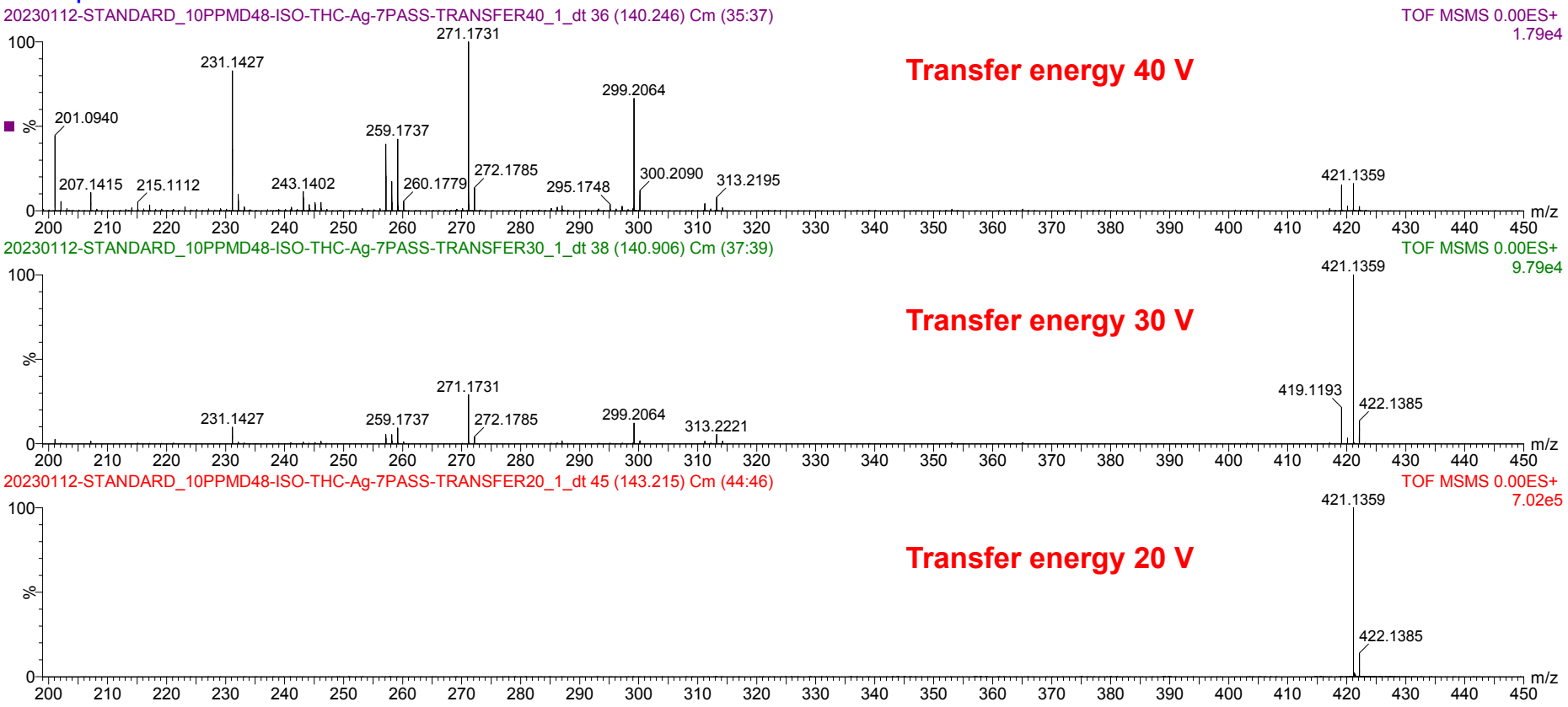
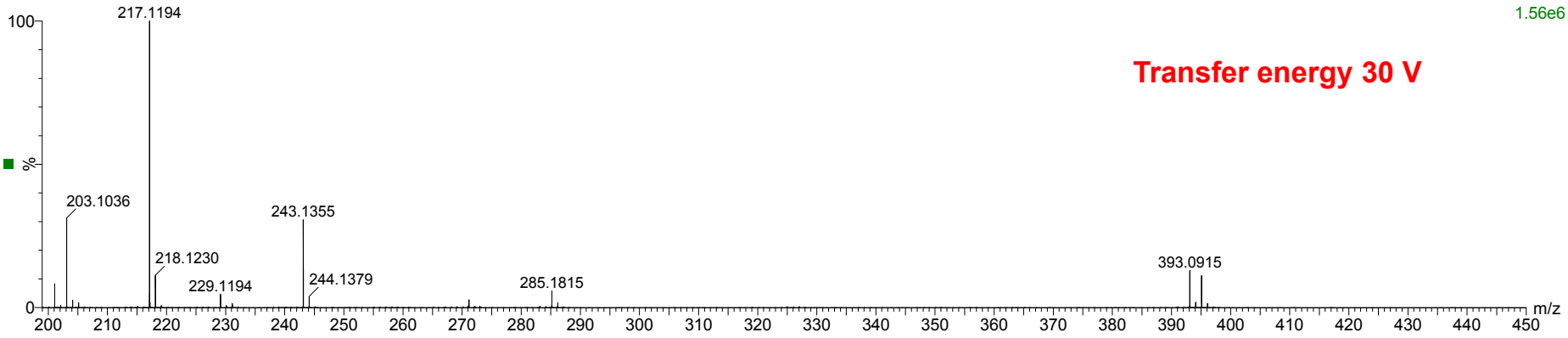
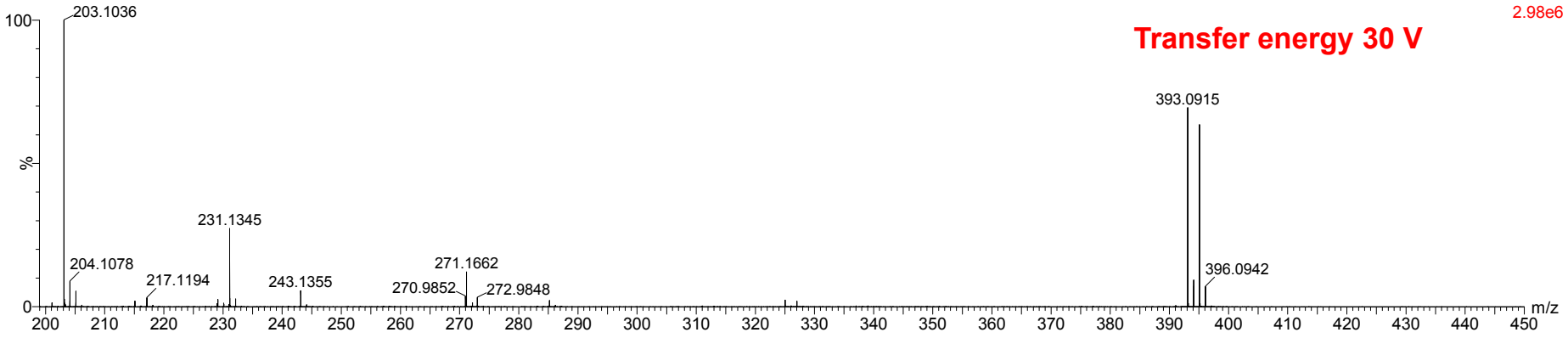


Figure S12-1. Post-mobility fragmentation of a) Δ3-THC (10 μg·mL^{-1}), b) Δ8-THC (10 μg·mL^{-1}), c) Δ9-THC (10 μg·mL^{-1}), d) Δ8-iso-THC (10 μg·mL^{-1}), e) Δ(4)8-iso-THC (10 μg·mL^{-1}), and f) CBD (1.0 μg·mL^{-1}), in the presence of Ag(I) after 7-pass separation under different transfer energies. (selecting $[M+Ag]^+$ precursor at *m/z* 421 for cIMS separation, followed by fragmentation).

a) Δ8-THCV



b) Δ8-iso-THCV



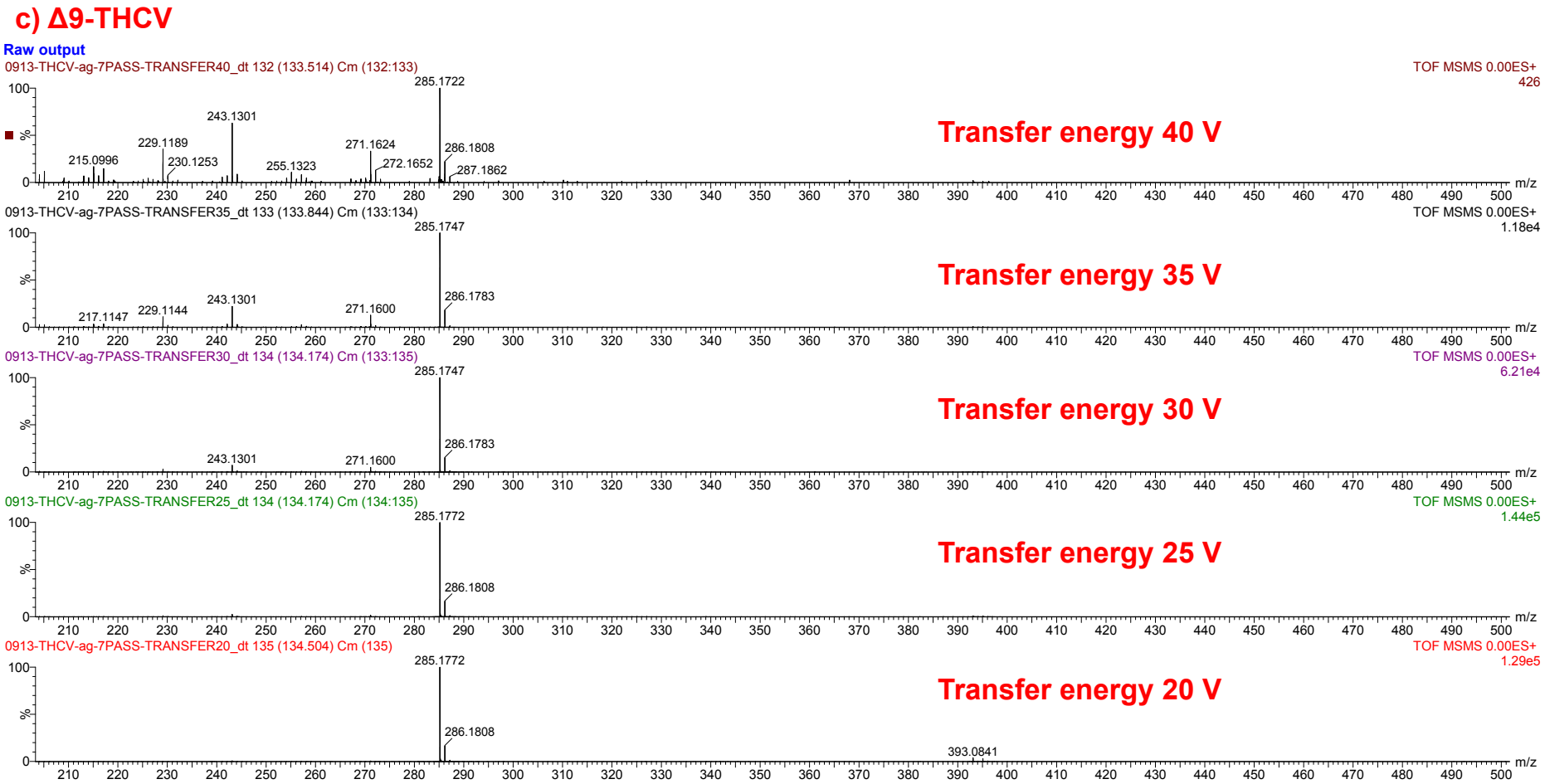


Figure S12-2. Post-mobility fragmentation of a) Δ8-THCV (1.0 μg·mL^{-1}), b) Δ8-iso-THCV (1.0 μg·mL^{-1}) and c) Δ9-THCV (10 μg·mL^{-1}) in the presence of Ag(I) after 7-pass separation under different transfer energies (selecting $[M+Ag]^+$ precursor at *m/z* 393 for cIMS separation, followed by fragmentation).

a) THCA

Raw output

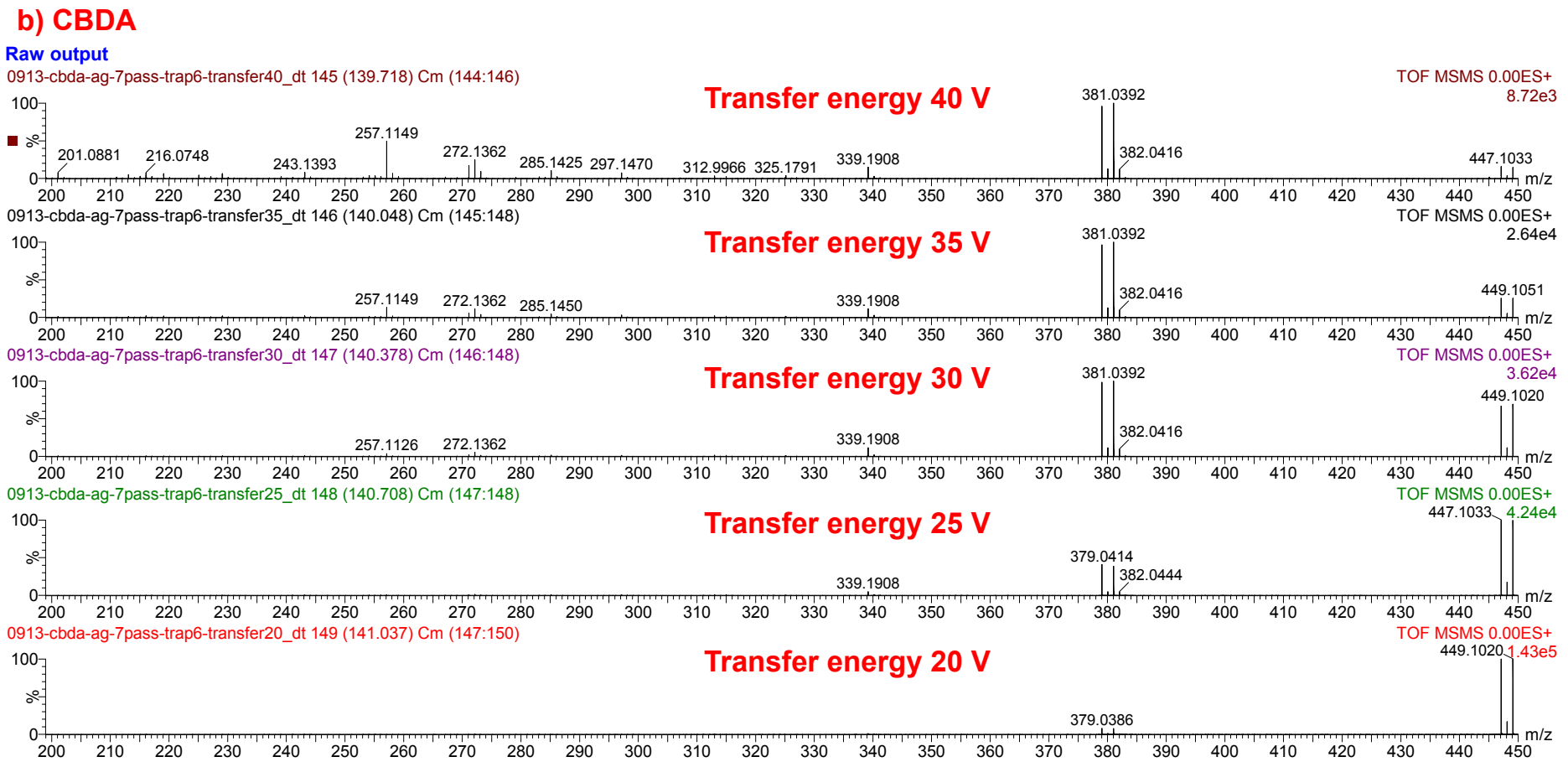
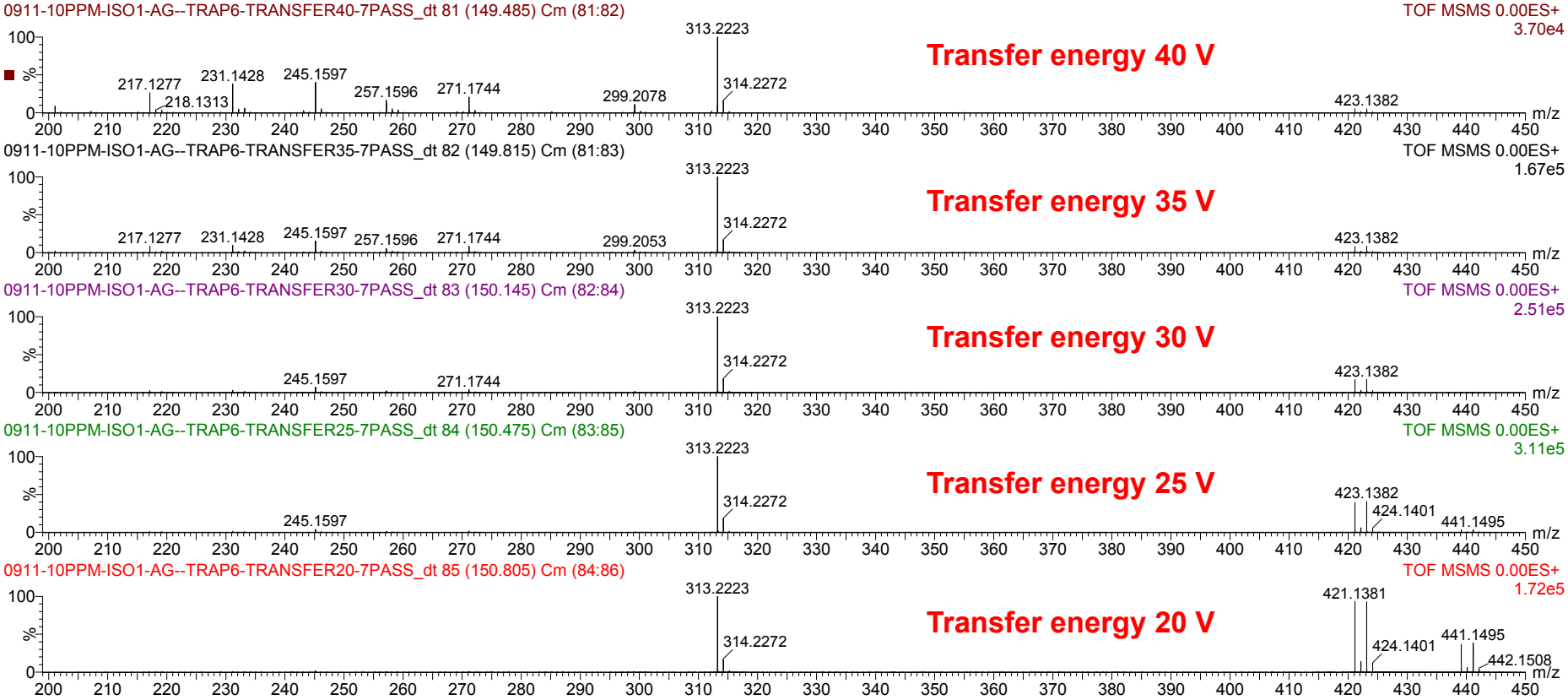


Figure S12-3. Post-mobility fragmentation of a) THCA (10 μg·mL^{-1}) and b) CBDA (10 μg·mL^{-1}) in the presence of Ag(I) after 7-pass separation under different transfer energies (selecting $[M+Ag]^+$ precursor at *m/z* 465 for cIMS separation, followed by fragmentation).

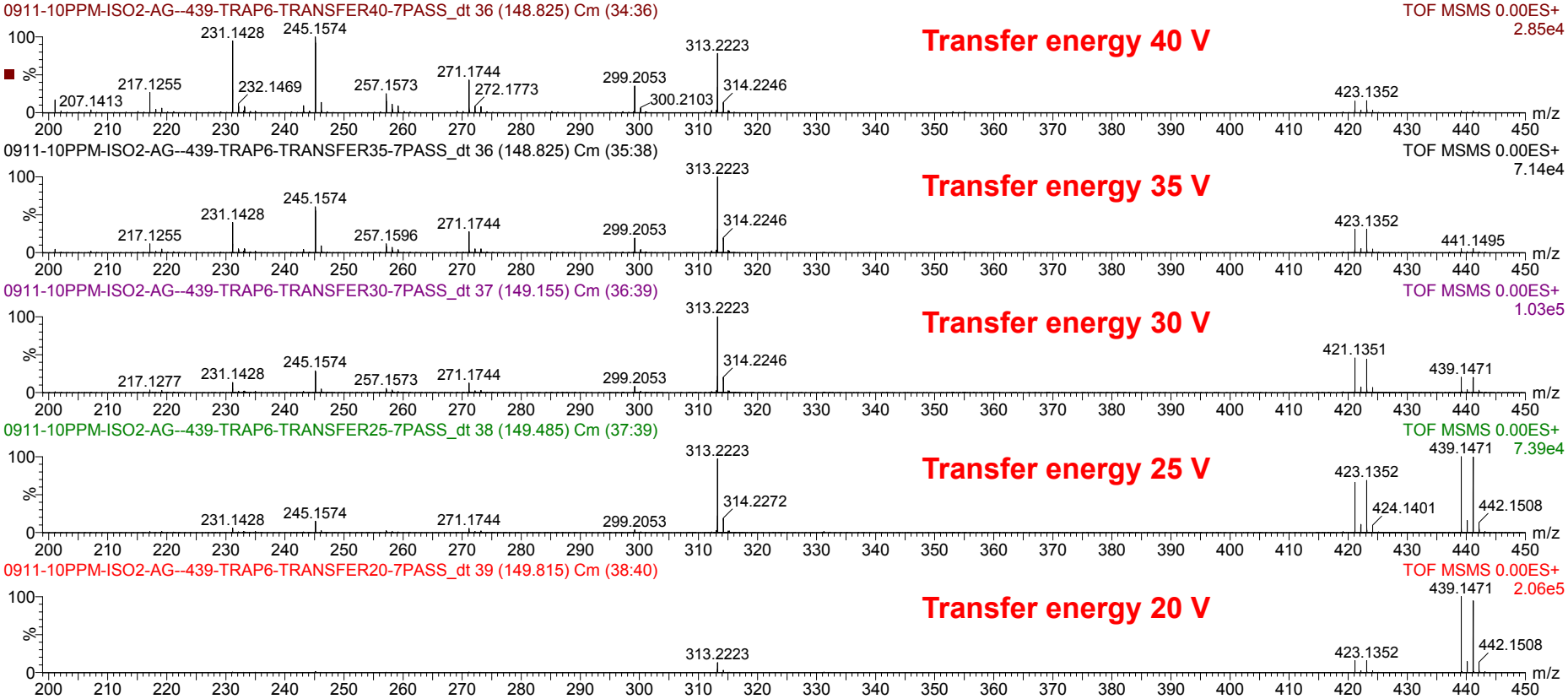
a) 9β-hydroxyhexahydrocannabinol

Raw output



b) 9α-hydroxyhexahydrocannabinol

Raw output



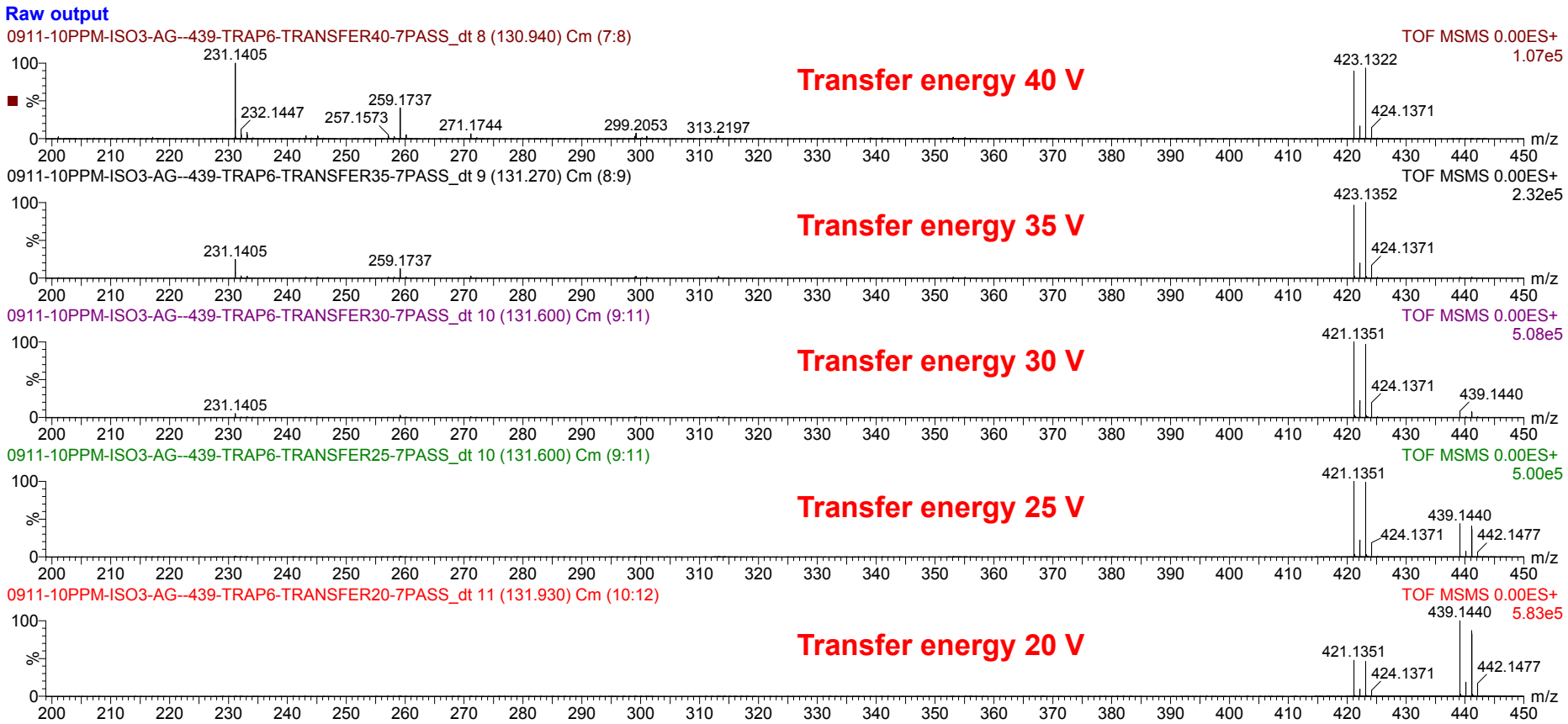
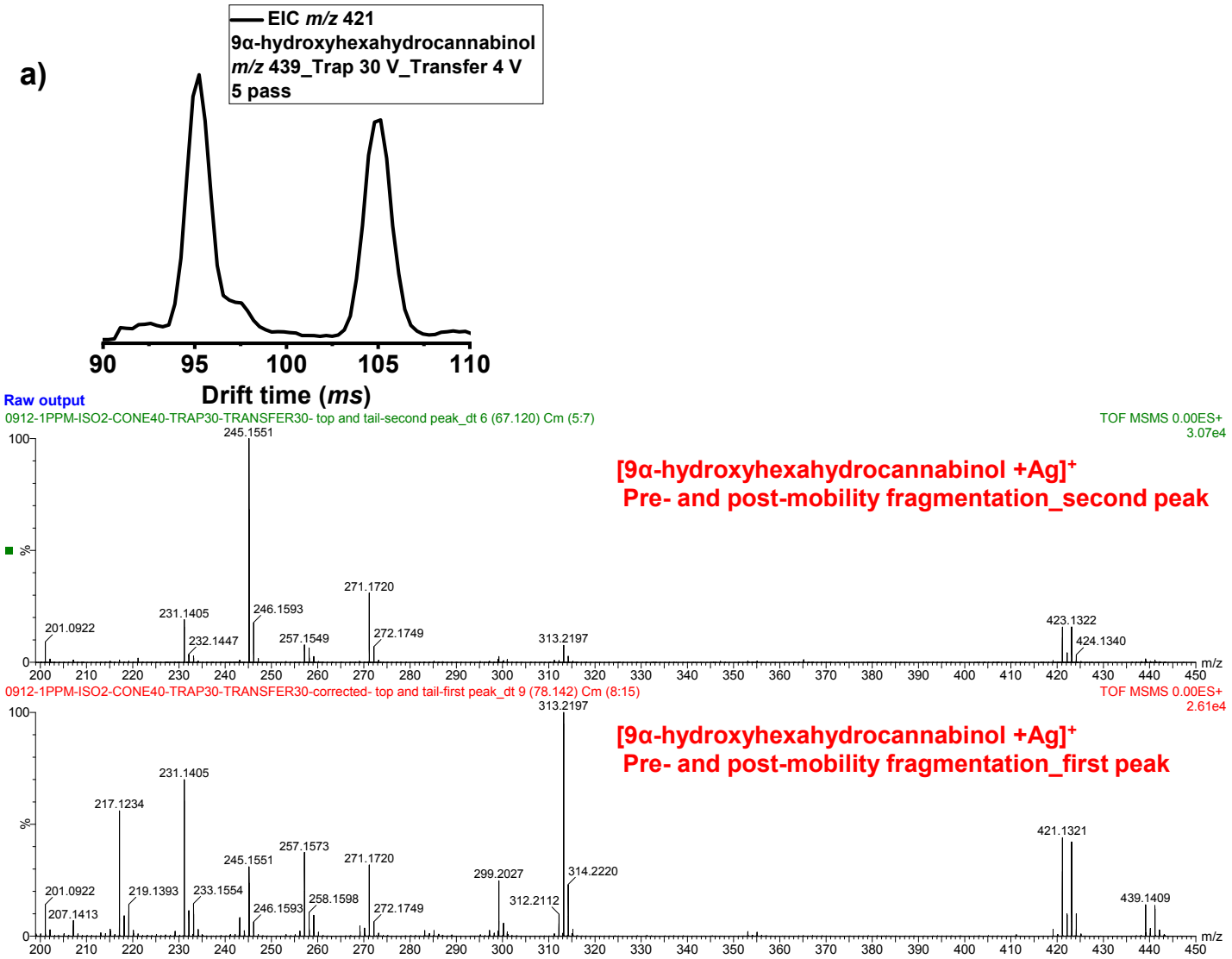
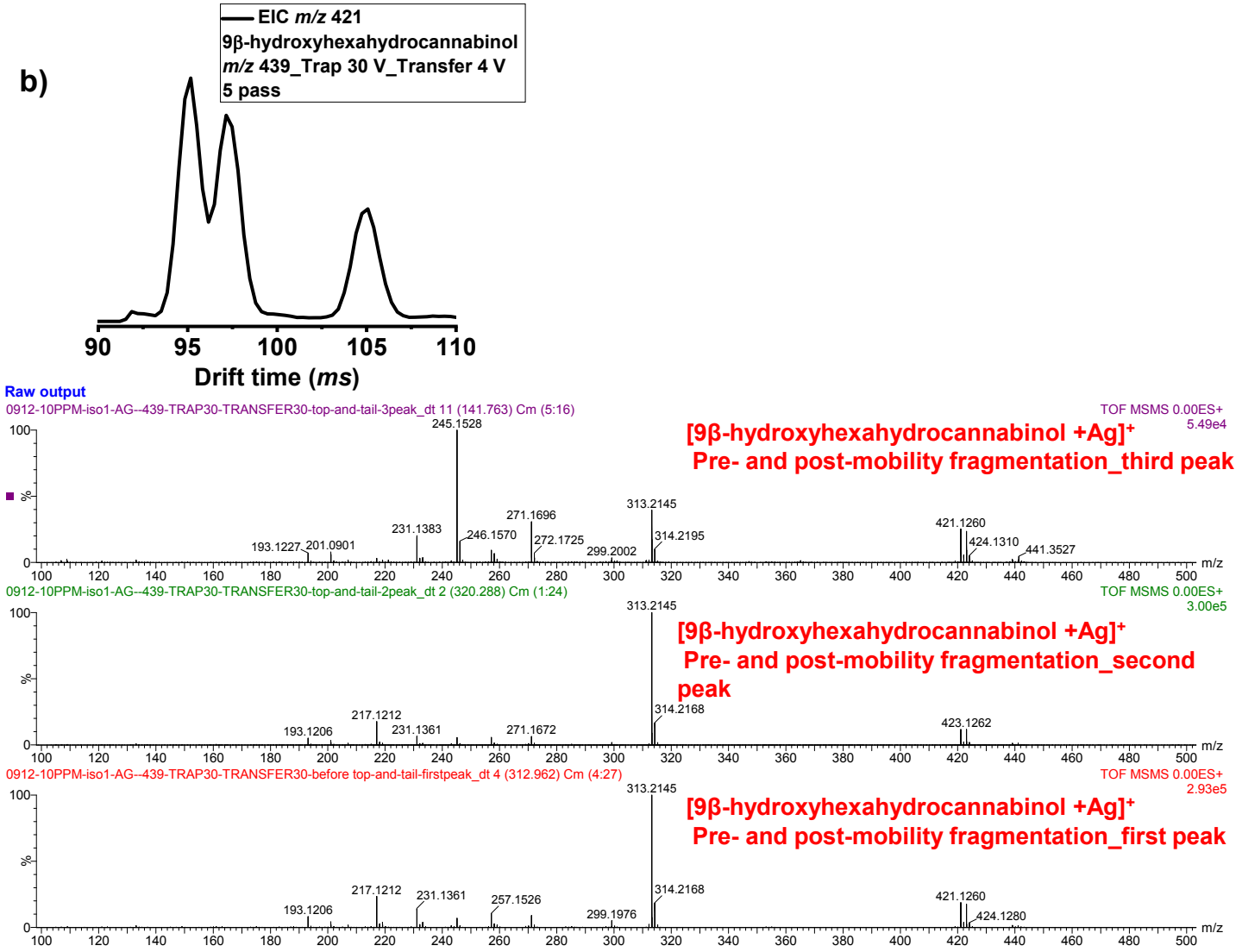


Figure S12-4. Post-mobility fragmentation of a) 9β-hydroxyhexahydrocannabinol (10 μg·mL^{-1}), b) 9α-hydroxyhexahydrocannabinol (10 μg·mL^{-1}) and c) 8-hydroxy-iso-tetrahydrocannabinol (10 μg·mL^{-1}) in the presence of Ag(I) after 7-pass separation under different transfer energies (selecting $[M+Ag]^+$ precursor at *m/z* 439 for cIMS separation, followed by fragmentation).


a)
EIC m/z 421
9α-hydroxyhexahydrocannabinol
m/z 439_Trap 30 V_Transfer 4 V
5 pass
90
95
100
105
110
Drift time (ms)
Raw output
0912-1PPM-ISO2-CONE40-TRAP30-TRANSFER30- top and tail-second peak_dt 6 (67.120) Cm (5:7)
TOF MSMS 0.00ES+
3.07e4
[9α-hydroxyhexahydrocannabinol +Ag]+
Pre- and post-mobility fragmentation_second peak
0912-1PPM-ISO2-CONE40-TRAP30-TRANSFER30-corrected- top and tail-first peak_dt 9 (78.142) Cm (8:15)
TOF MSMS 0.00ES+
2.61e4
[9α-hydroxyhexahydrocannabinol +Ag]+
Pre- and post-mobility fragmentation_first peak
m/z


b)
EIC m/z 421
9β-hydroxyhexahydrocannabinol
m/z 439_Trap 30 V_Transfer 4 V
5 pass
90
95
100
105
110
Drift time (ms)
Raw output
0912-10PPM-iso1-AG--439-TRAP30-TRANSFER30-top-and-tail-3peak_dt 11 (141.763) Cm (5:16)
TOF MSMS 0.00ES+
5.49e4
[9β-hydroxyhexahydrocannabinol +Ag]+
Pre- and post-mobility fragmentation_third peak
245.1528
313.2145
271.1696
231.1383
246.1570
272.1725
314.2195
421.1260
193.1227
201.0901
299.2002
424.1310
441.3527
0912-10PPM-iso1-AG--439-TRAP30-TRANSFER30-top-and-tail-2peak_dt 2 (320.288) Cm (1:24)
TOF MSMS 0.00ES+
3.00e5
[9β-hydroxyhexahydrocannabinol +Ag]+
Pre- and post-mobility fragmentation_second peak
313.2145
217.1212
314.2168
193.1206
231.1361
271.1672
423.1262
0912-10PPM-iso1-AG--439-TRAP30-TRANSFER30-before top-and-tail-firstpeak_dt 4 (312.962) Cm (4:27)
TOF MSMS 0.00ES+
2.93e5
[9β-hydroxyhexahydrocannabinol +Ag]+
Pre- and post-mobility fragmentation_first peak
313.2145
217.1212
231.1361
257.1526
314.2168
193.1206
299.1976
421.1260
424.1280
%
m/z

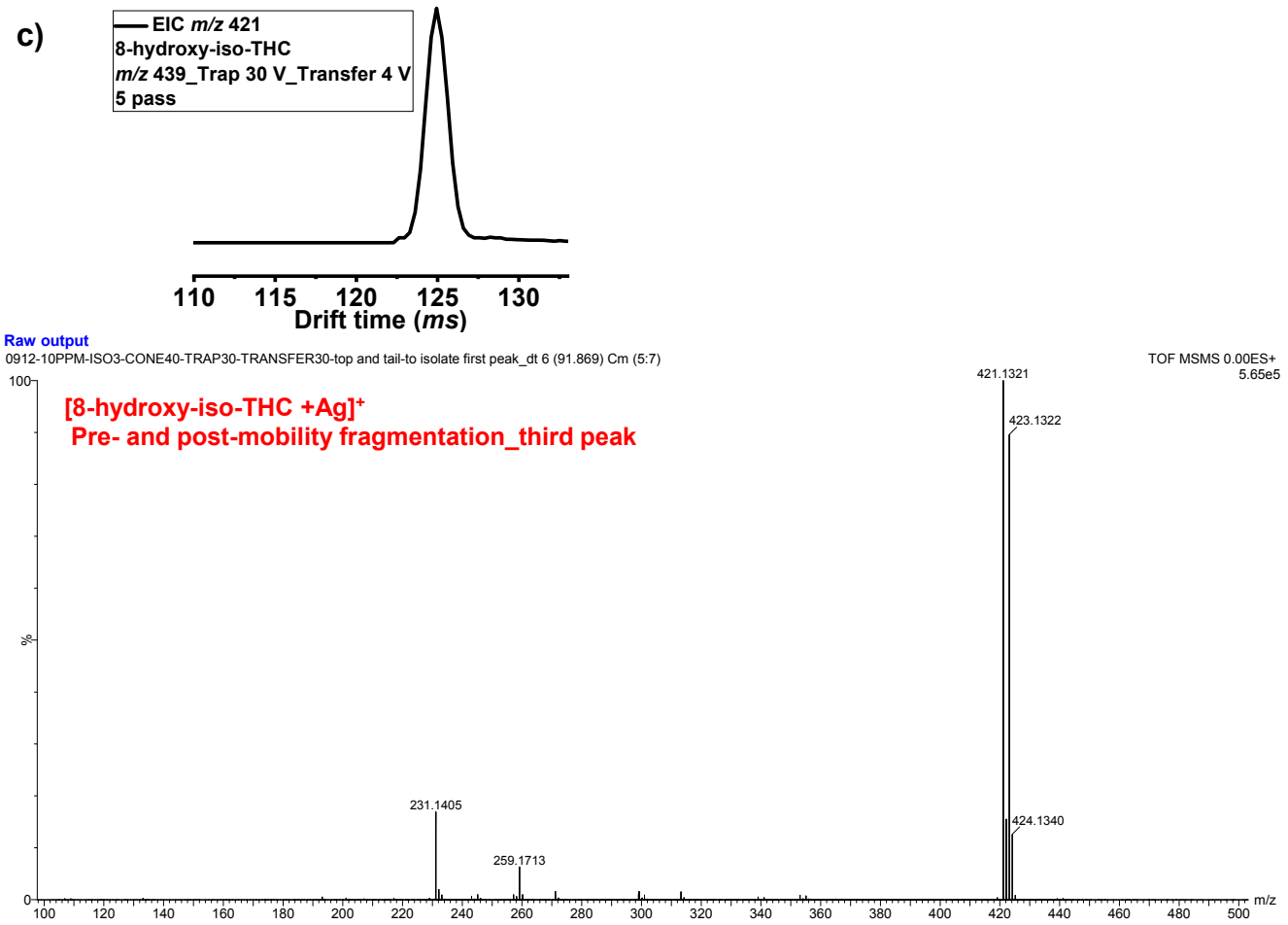


Figure S13. Pre- and post-mobility fragmentation of a) 9α-hydroxyhexahydrocannabinol, b) 9β-hydroxyhexahydrocannabinol, and c) 8-hydroxy-iso-THC in the presence of Ag(I) with trap energy of 30 V and transfer energy of 30 V.

Table S5. CCS of 9α-hydroxyhexahydrocannabinol, 9β-hydroxyhexahydrocannabinol, and 8-hydroxy-iso-THC as well as their dehydrated species in the presence of Ag(I).

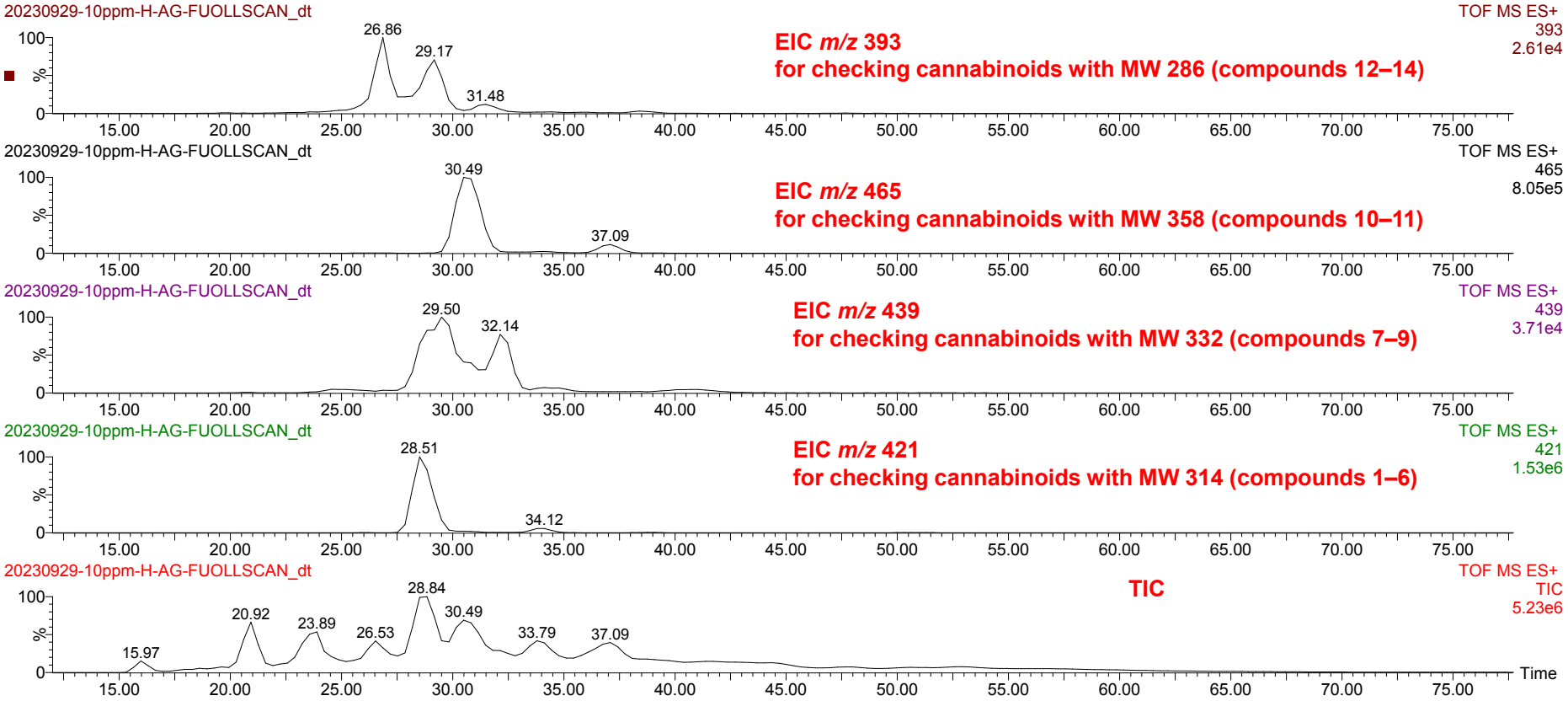
	$[M+Ag]^+$ $^{TW}CCS_{N2}(Å^2)$
9α-hydroxyhexahydrocannabinol	195.6±0.01
Dehydrated 9α-hydroxyhexahydrocannabinol	182.0±0.01 190.6±0.02 (−0.2% to Δ8-THC)
9β-hydroxyhexahydrocannabinol	185.9±0.01
Dehydrated 9β-hydroxyhexahydrocannabinol	181.9±0.01 183.9±0.01 190.6±0.01 (−0.2% to Δ8-THC)
8-hydroxy-iso-THC	184.6±0.02
Dehydrated 8-hydroxy-iso-THC	179.7±0.01

Table S6. Intra-day, inter-day, and inter-pass relative standard deviation of $[\Delta 8\text{-THC+Ag}]^+$ CCS.

Measured date and separation passes	$[\Delta 8\text{-THC+Ag}]^+$ eCCS	Intra-day RSD (%)	Inter-day RSD (%)	Inter-pass RSD (%)
11 th November 2022_7 passes	190.7 190.7 190.7	0		
12 th January 2023_7 passes	190.9 190.9 190.8	0.03		
			0.04	
20 th September 2023_7 passes	190.7 190.7 190.7	0		
				0.3
28 th September 2023_7 passes	190.7 190.7 190.7	0		
12 th January 2023_1 pass	190.3 190.3 190.2	0.03		
			0.2	
20 th September 2023_1 pass	189.3 189.6 189.7	0.1		

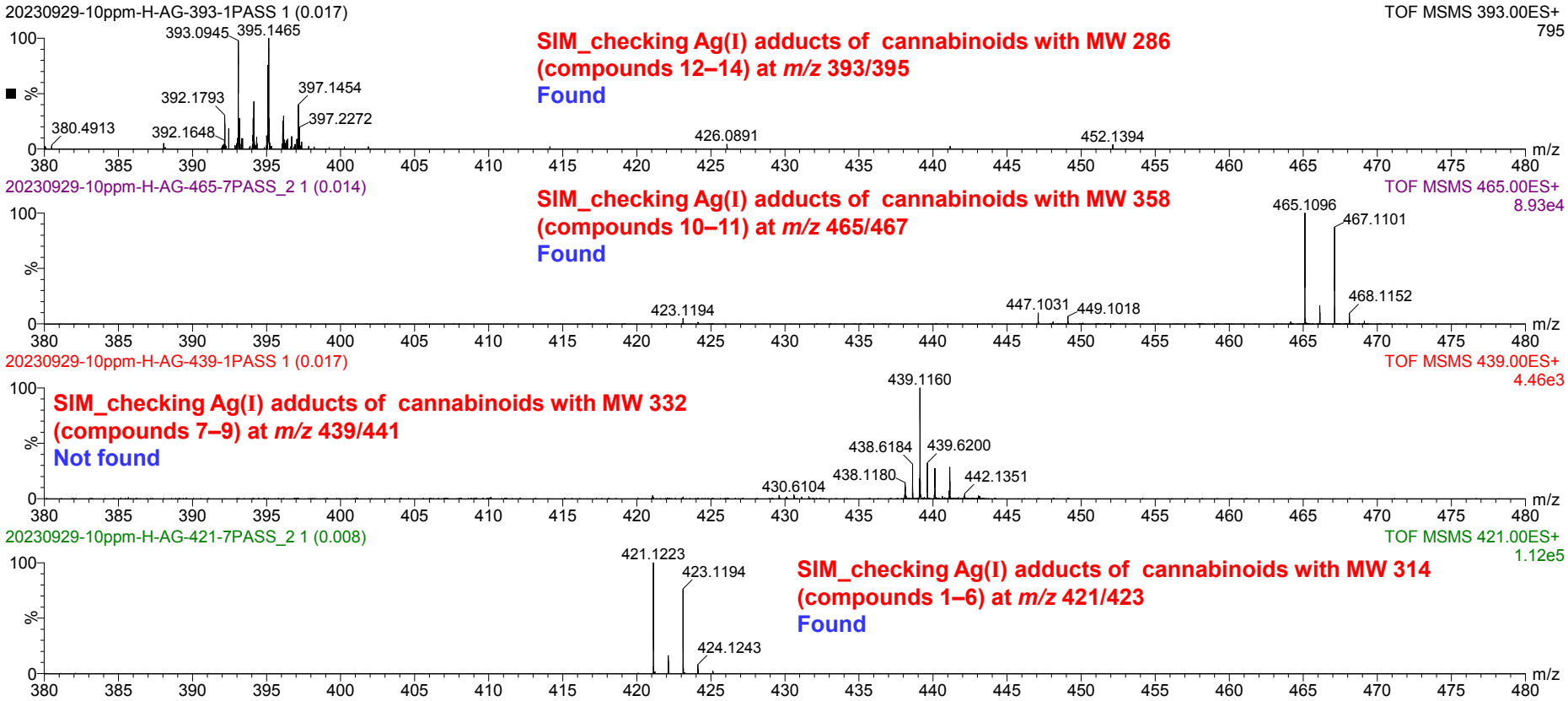
C#1 _full scan_for checking Ag(I) adducts

Raw output



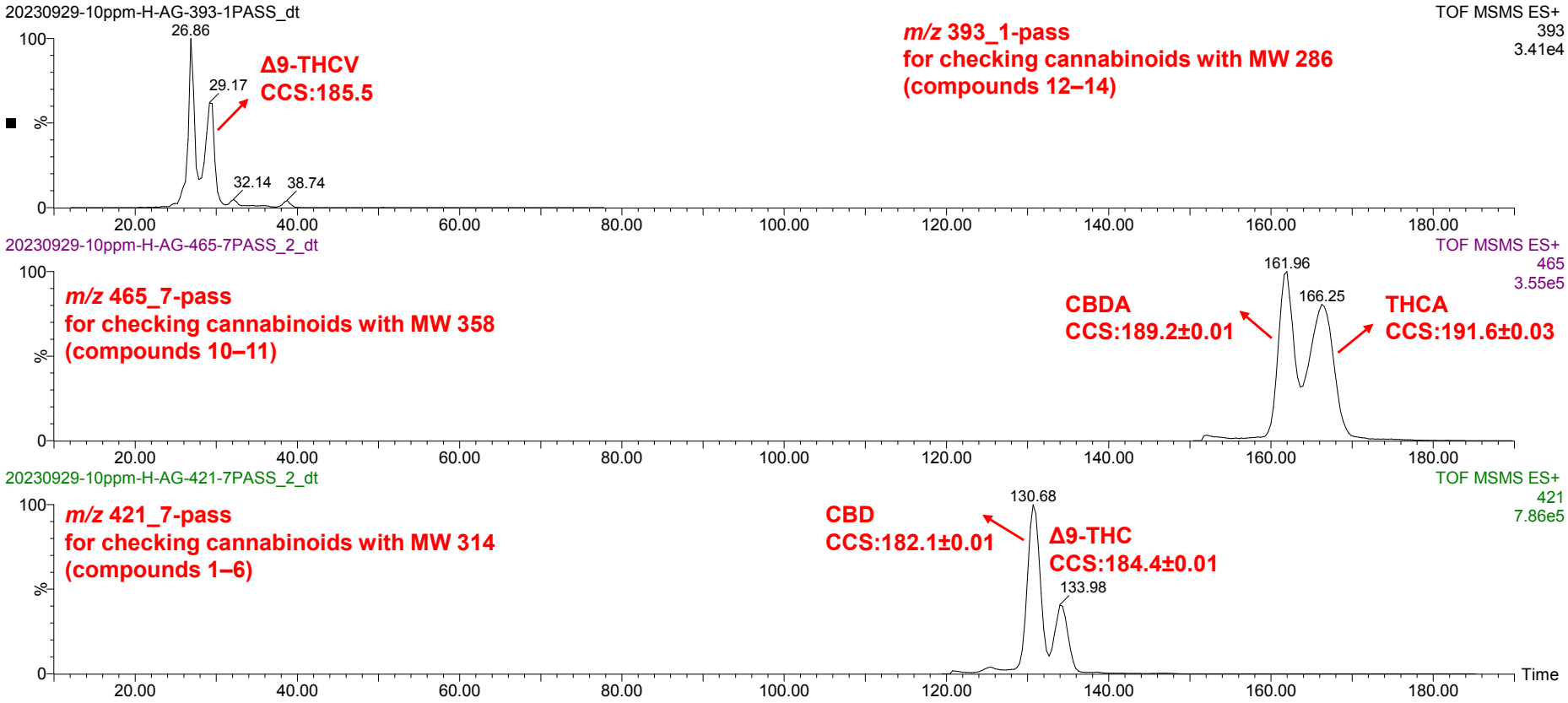
C#1 _SIM_for checking Ag(I) adducts

Raw output

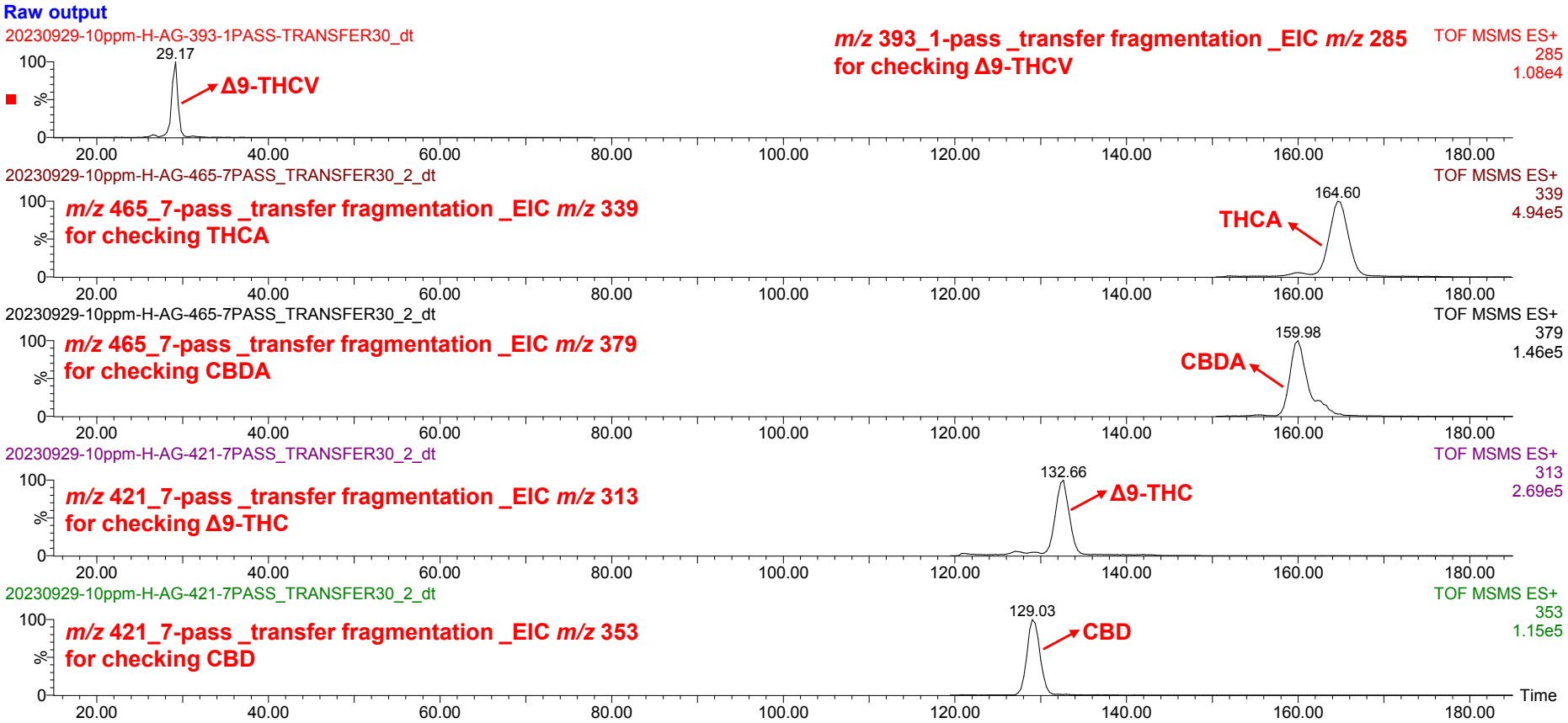


C#1 _mobility separation_for checking CCS

Raw output



C#1_mobility separation+transfer fragmentation_for checking fragments



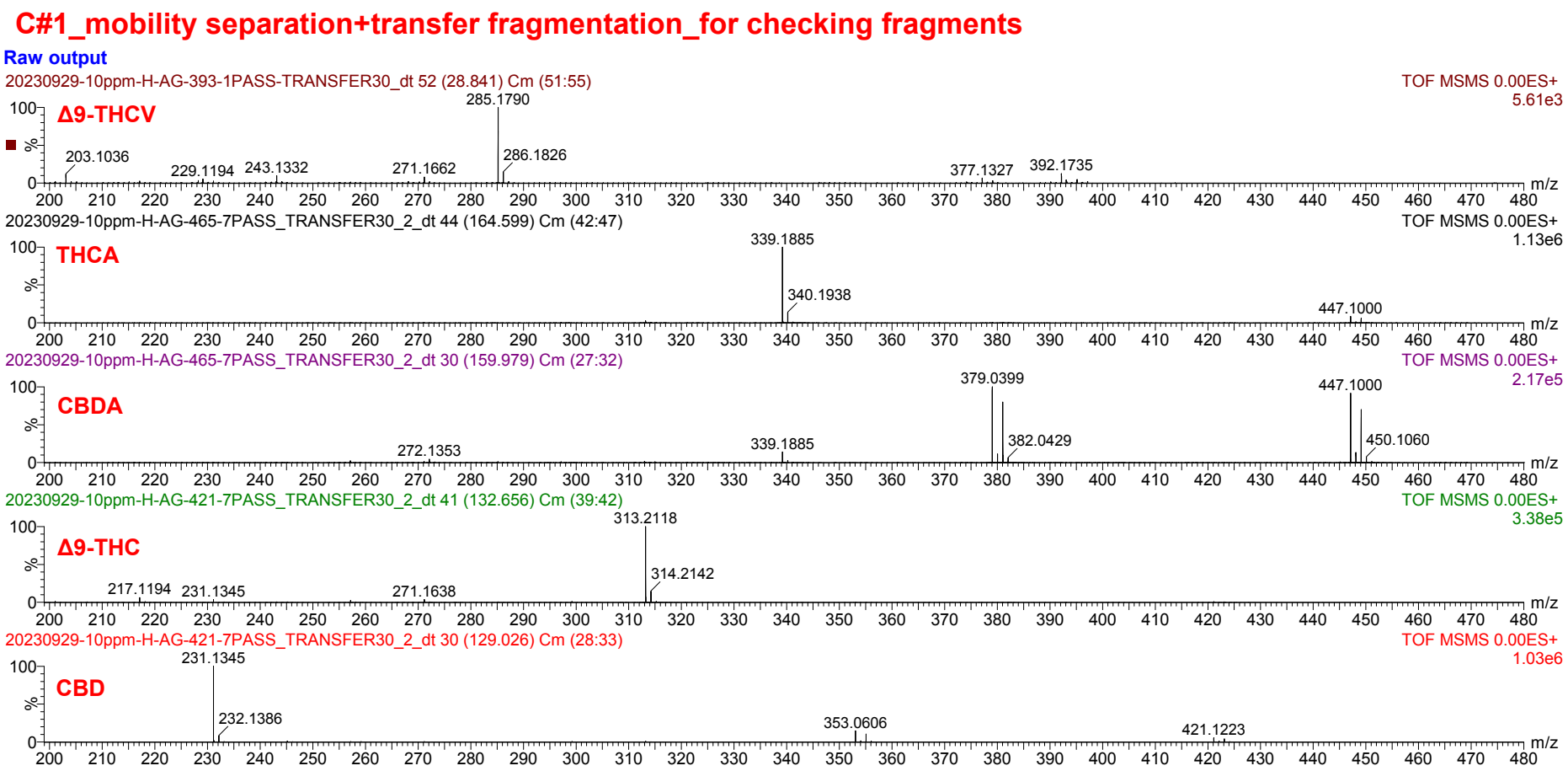
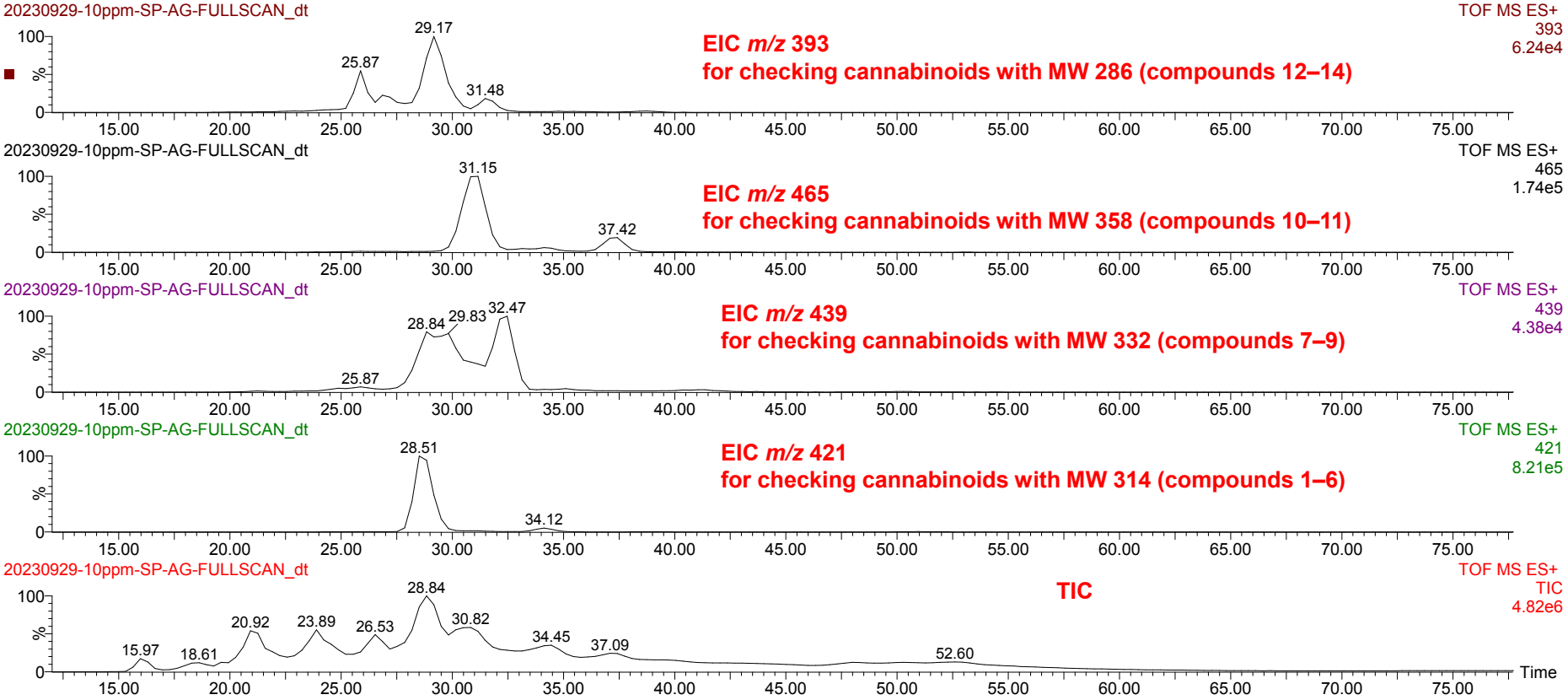


Figure S14-1. Mobiligram and mass spectra of cannabinoids in sample C#1.

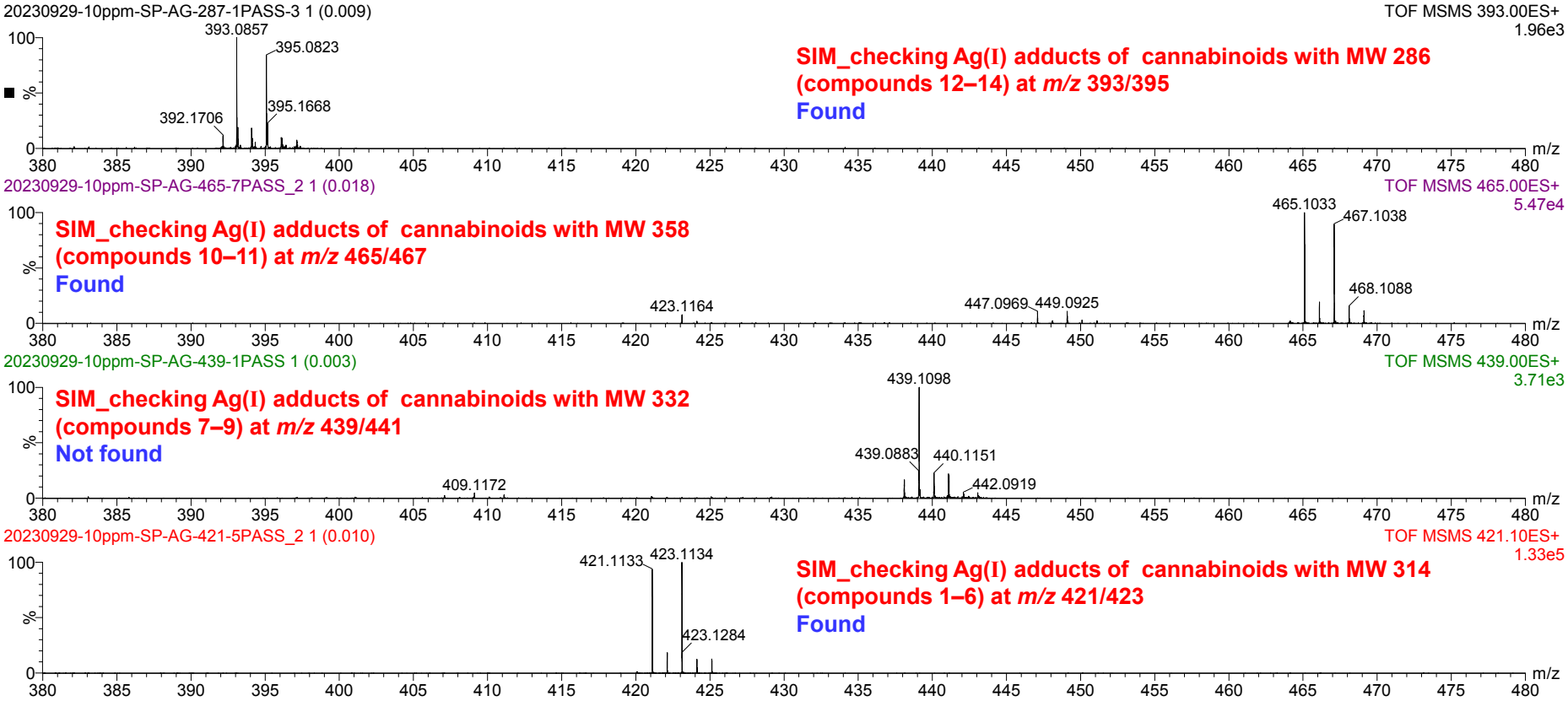
C#2 _full scan_for checking Ag(I) adducts

Raw output



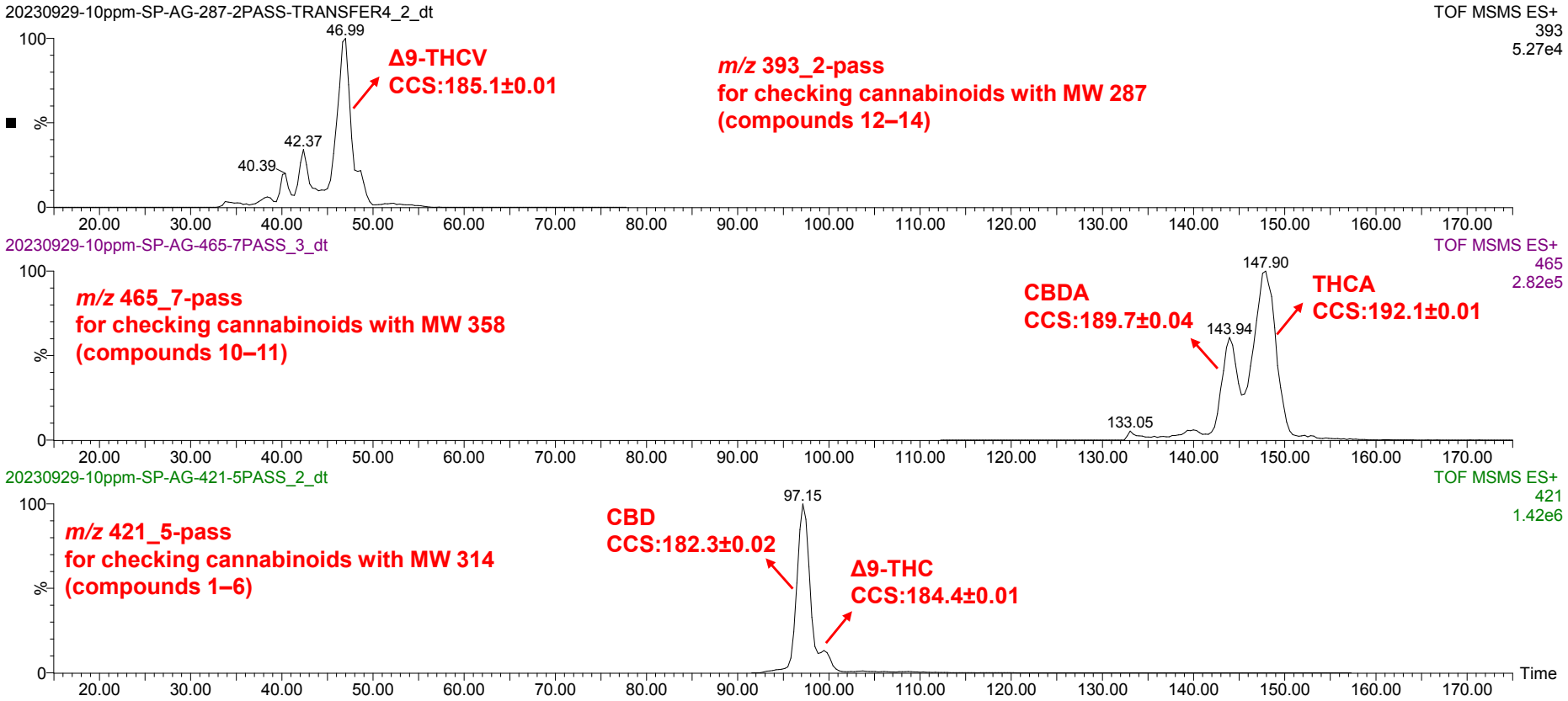
C#2 _SIM_for checking Ag(I) adducts

Raw output



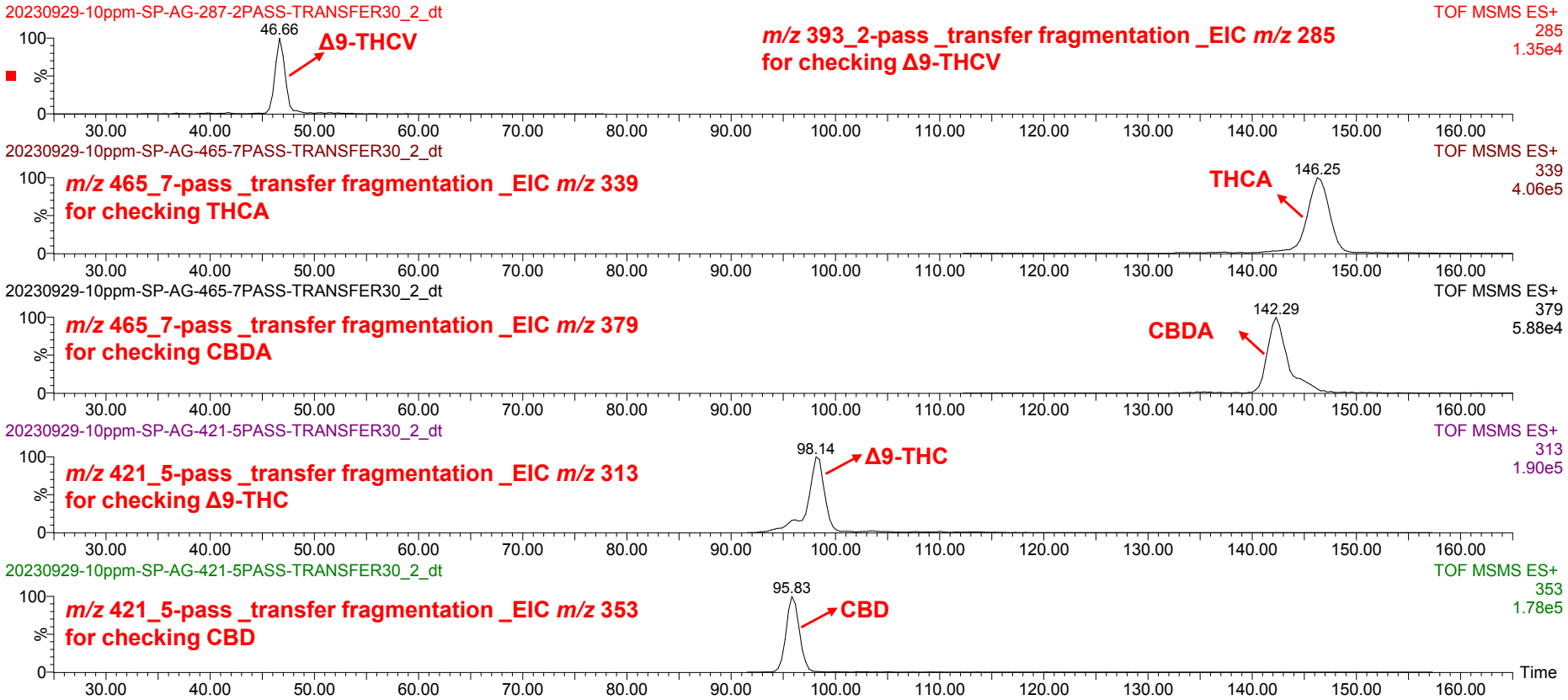
C#2 _mobility separation_for checking CCS

Raw output



C#2_mobility separation+transfer fragmentation_for checking fragments

Raw output



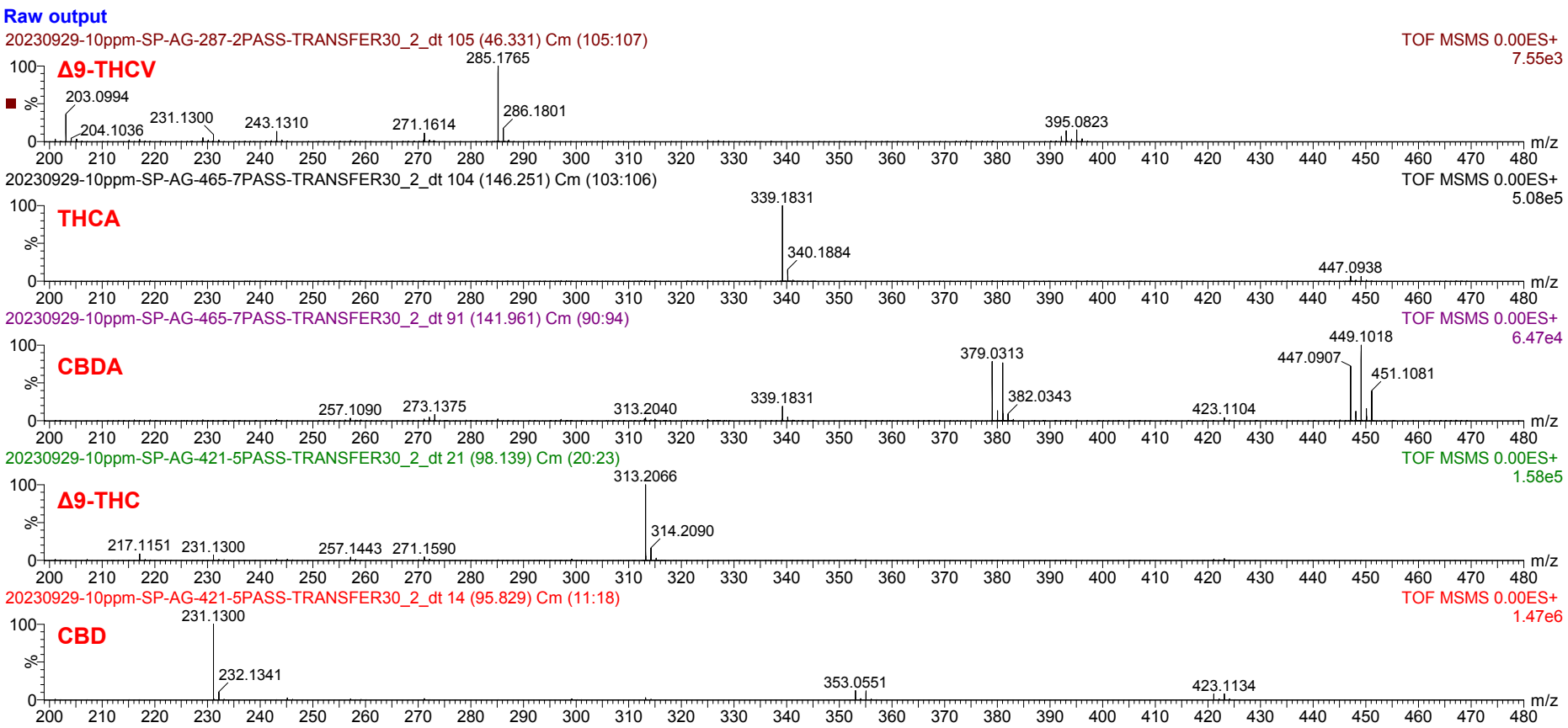
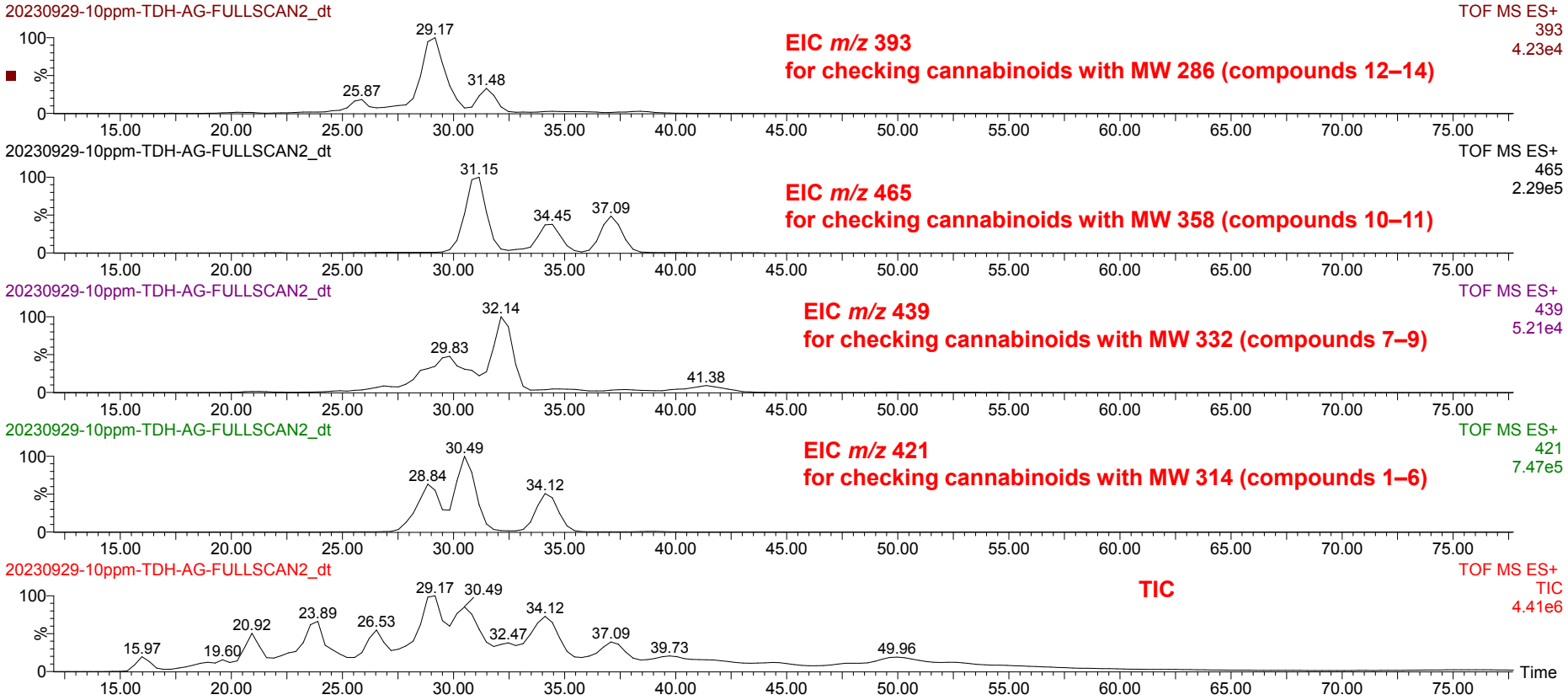


Figure S14-2. Mobiligram and mass spectra of cannabinoids in sample C#2.

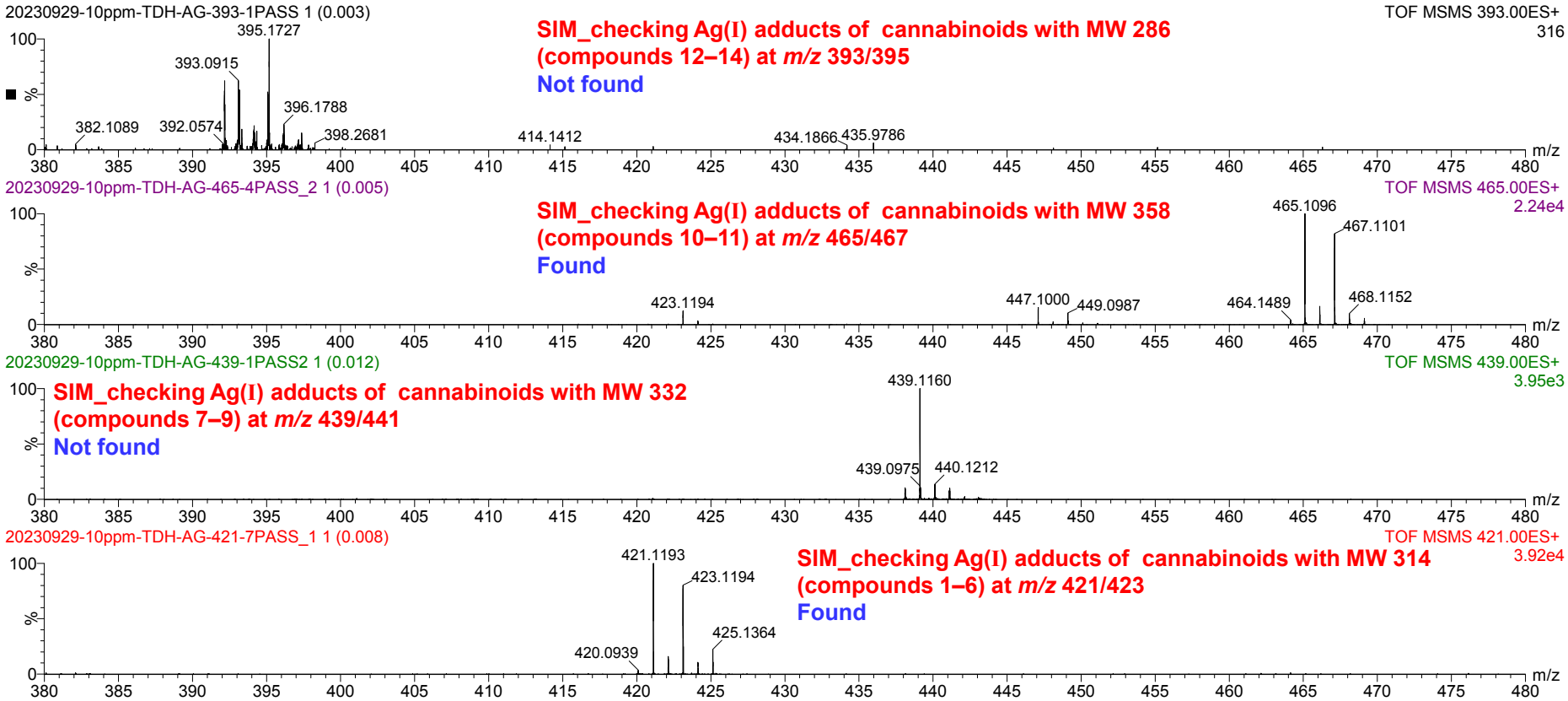
C#3 _full scan_for checking Ag(I) adducts

Raw output



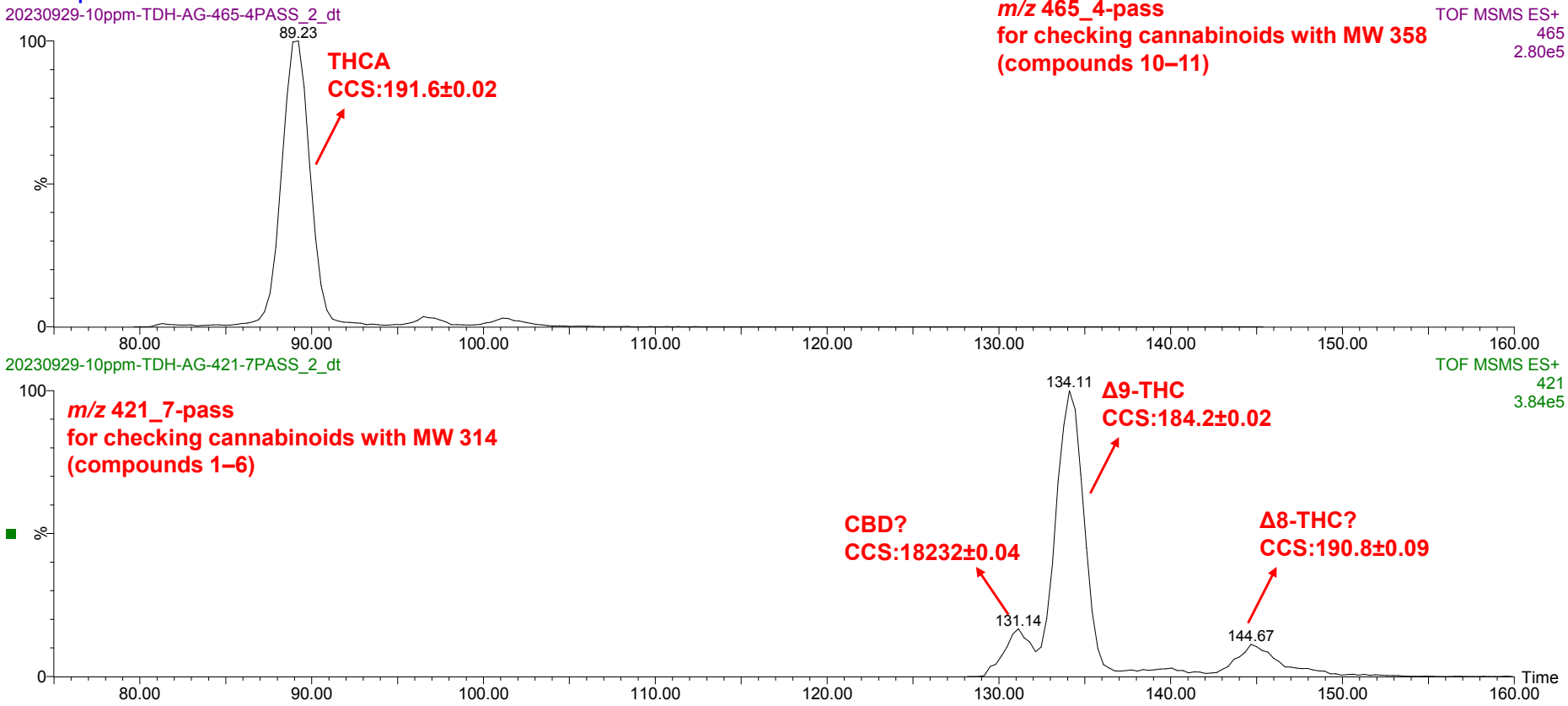
C#3 _SIM_for checking Ag(I) adducts

Raw output



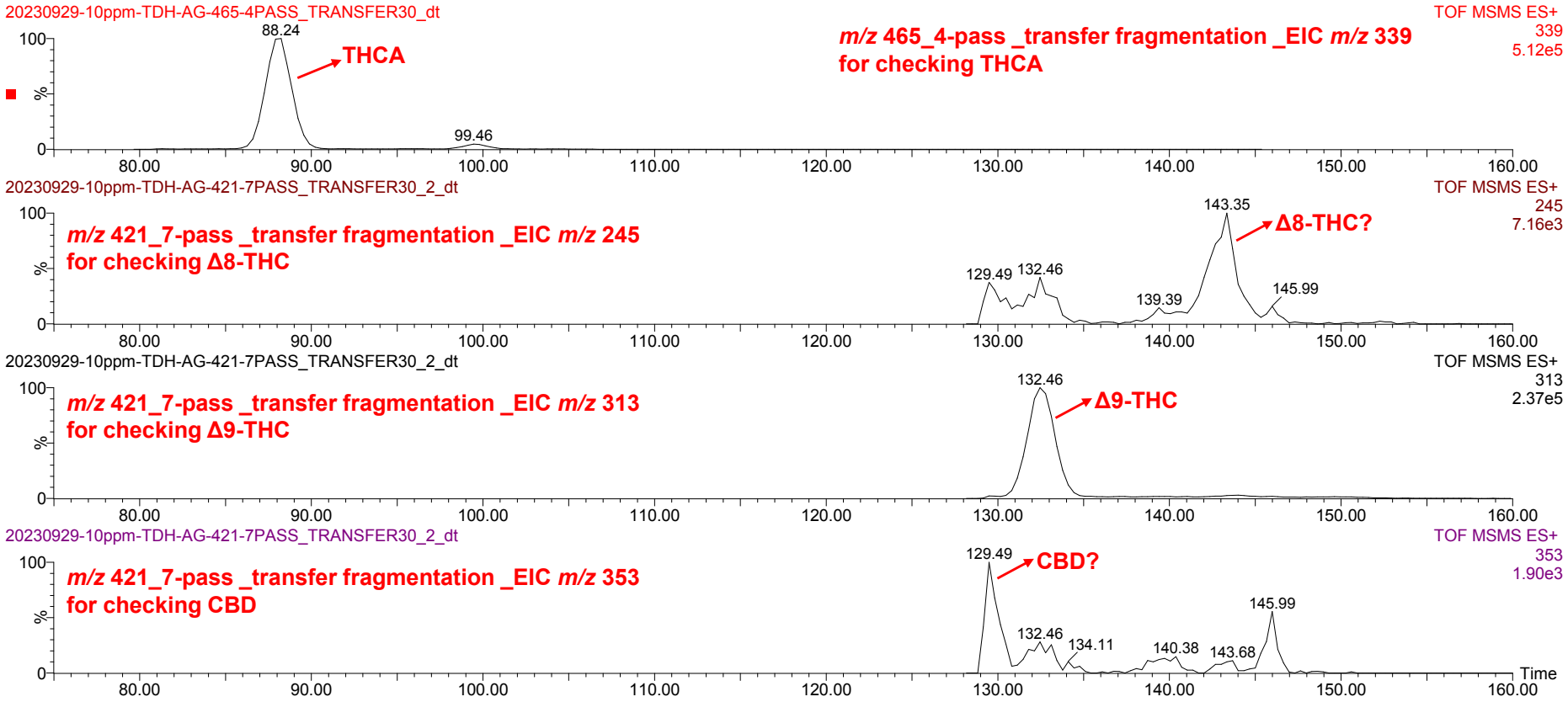
C#3 _mobility separation_for checking CCS

Raw output



C#3_mobility separation+transfer fragmentation_for checking fragments

Raw output



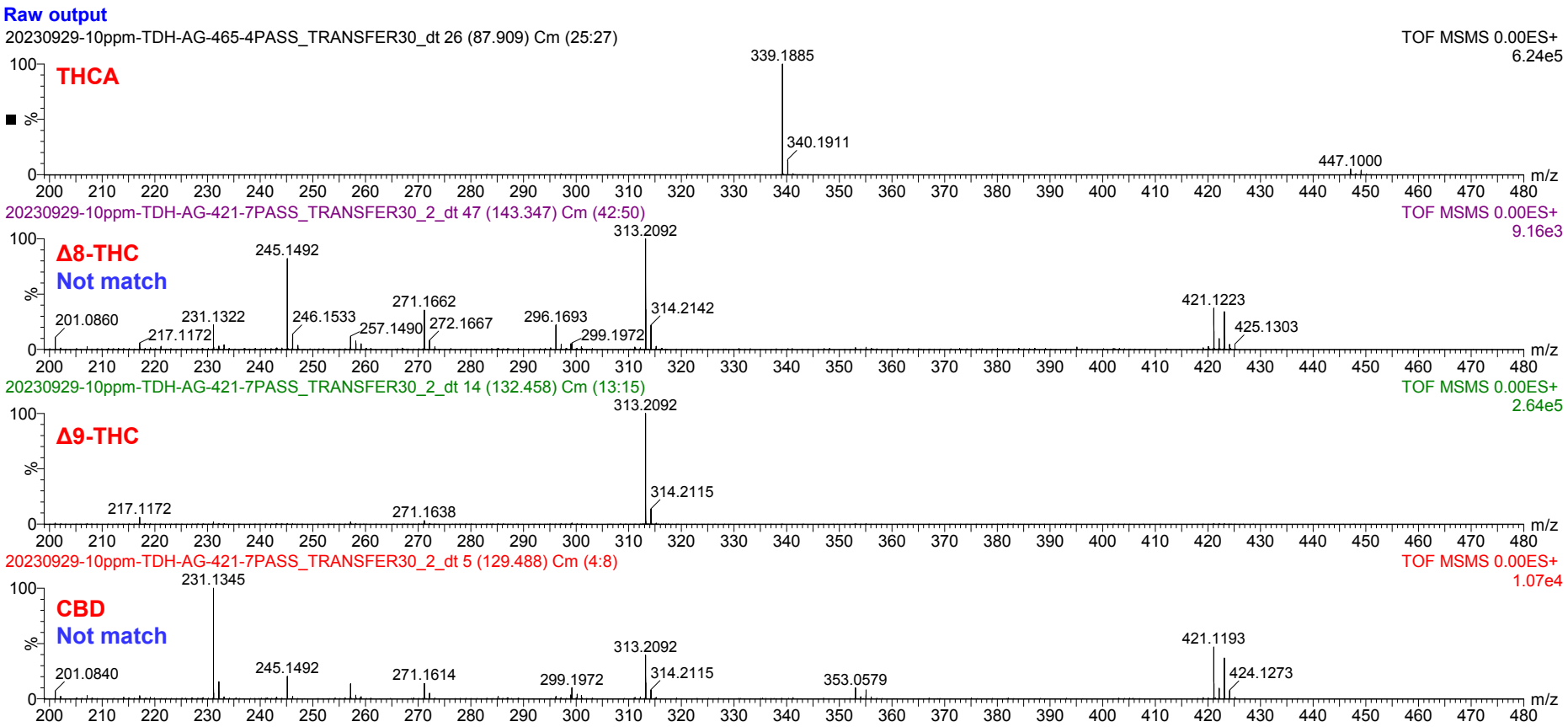
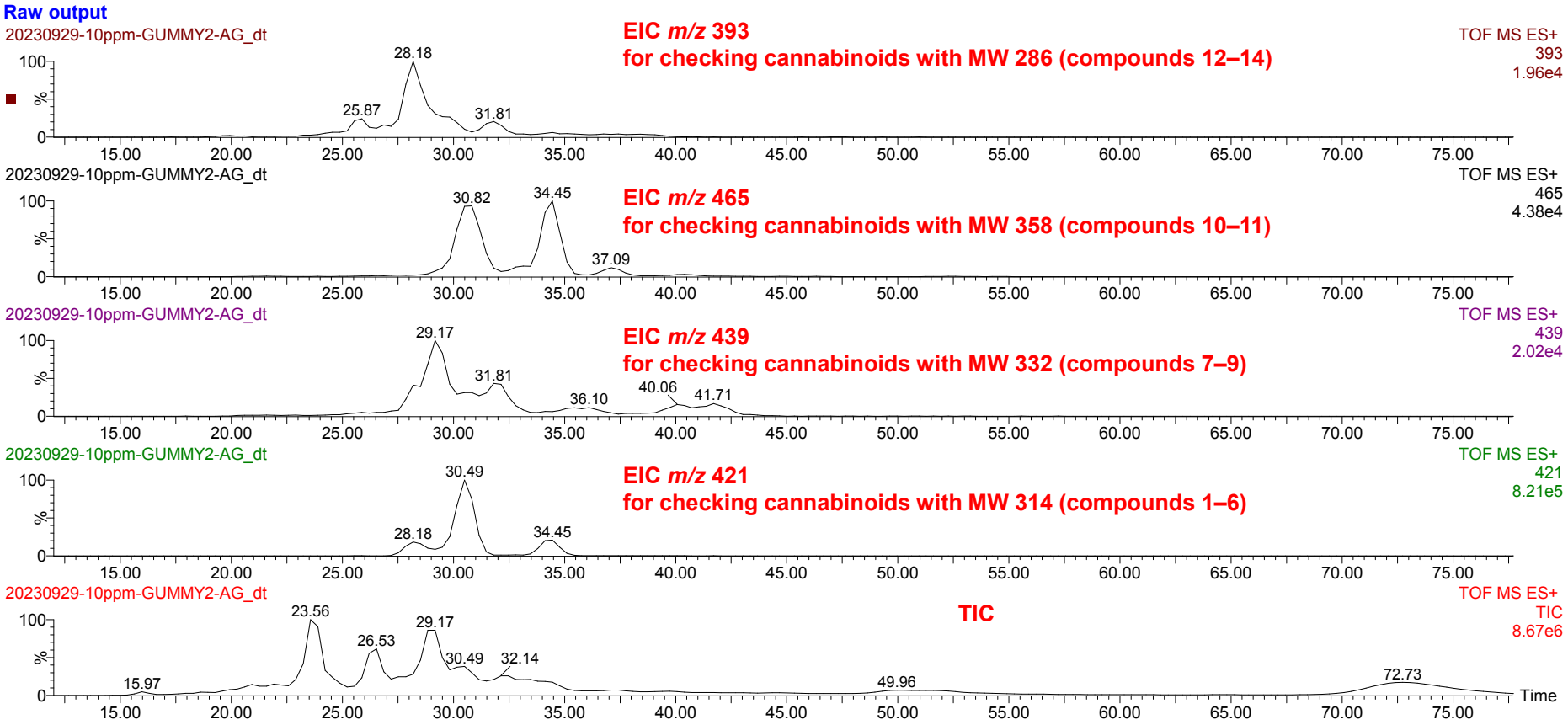


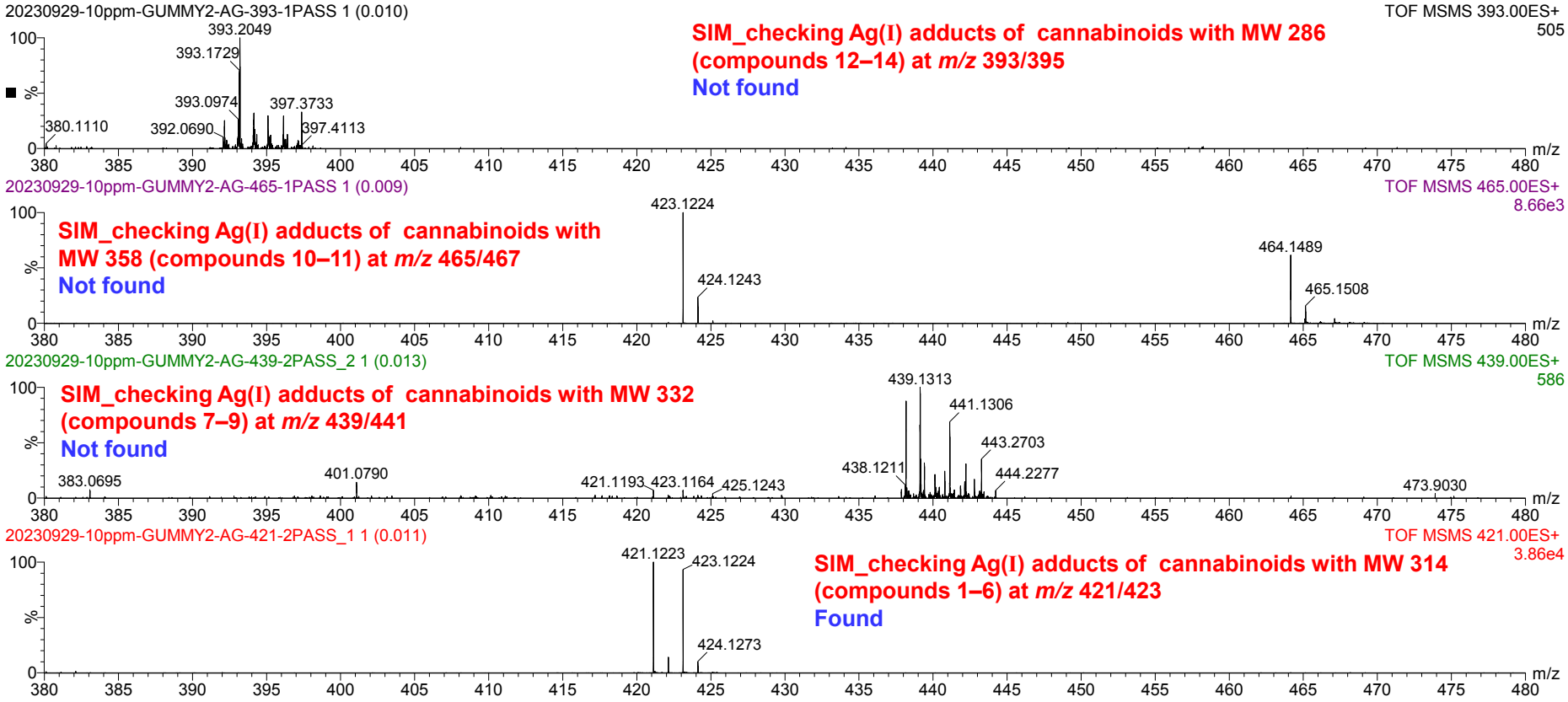
Figure S14-3. Mobiligram and mass spectra of cannabinoids in sample C#3.

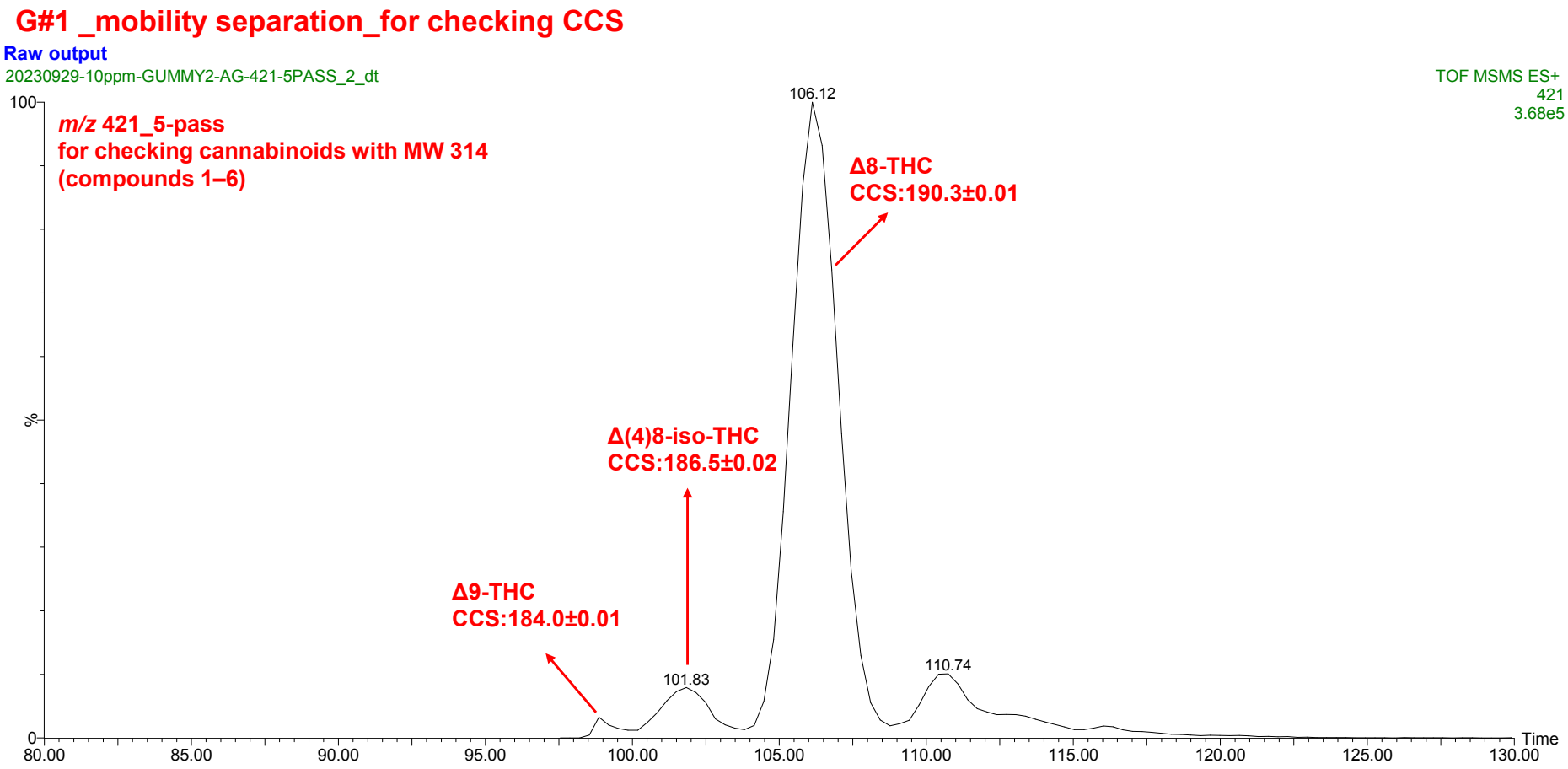
G#1 _full scan_for checking Ag(I) adducts



G#1 _SIM_for checking Ag(I) adducts

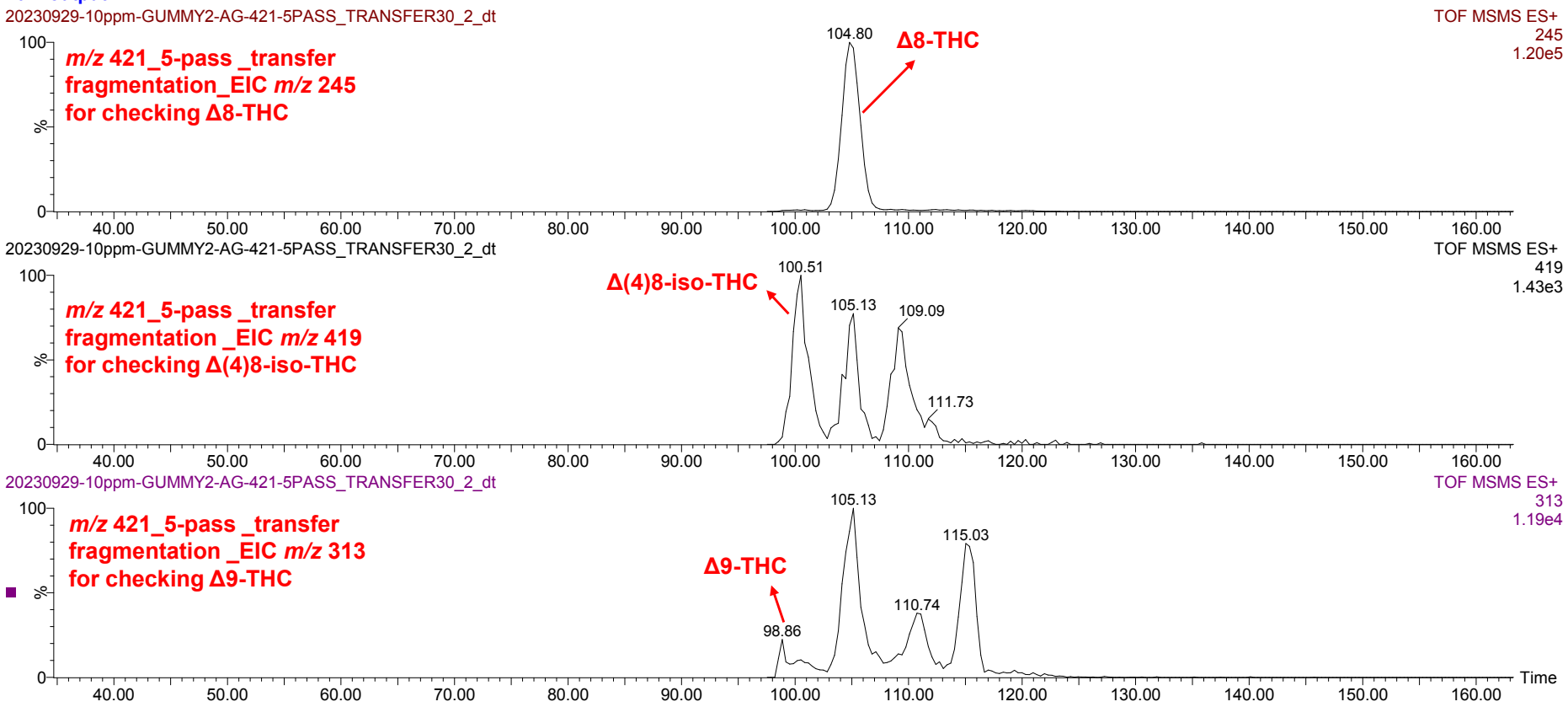
Raw output




G#1 _mobility separation_for checking CCS
Raw output
20230929-10ppm-GUMMY2-AG-421-5PASS_2_dt
TOF MSMS ES+
421
3.68e5
m/z 421_5-pass
for checking cannabinoids with MW 314
(compounds 1–6)
Δ8-THC
CCS:190.3±0.01
Δ(4)8-iso-THC
CCS:186.5±0.02
Δ9-THC
CCS:184.0±0.01
106.12
101.83
110.74
100
%
0
Time
80.00
85.00
90.00
95.00
100.00
105.00
110.00
115.00
120.00
125.00
130.00

G#1_mobility separation+transfer fragmentation_for checking fragments

Raw output



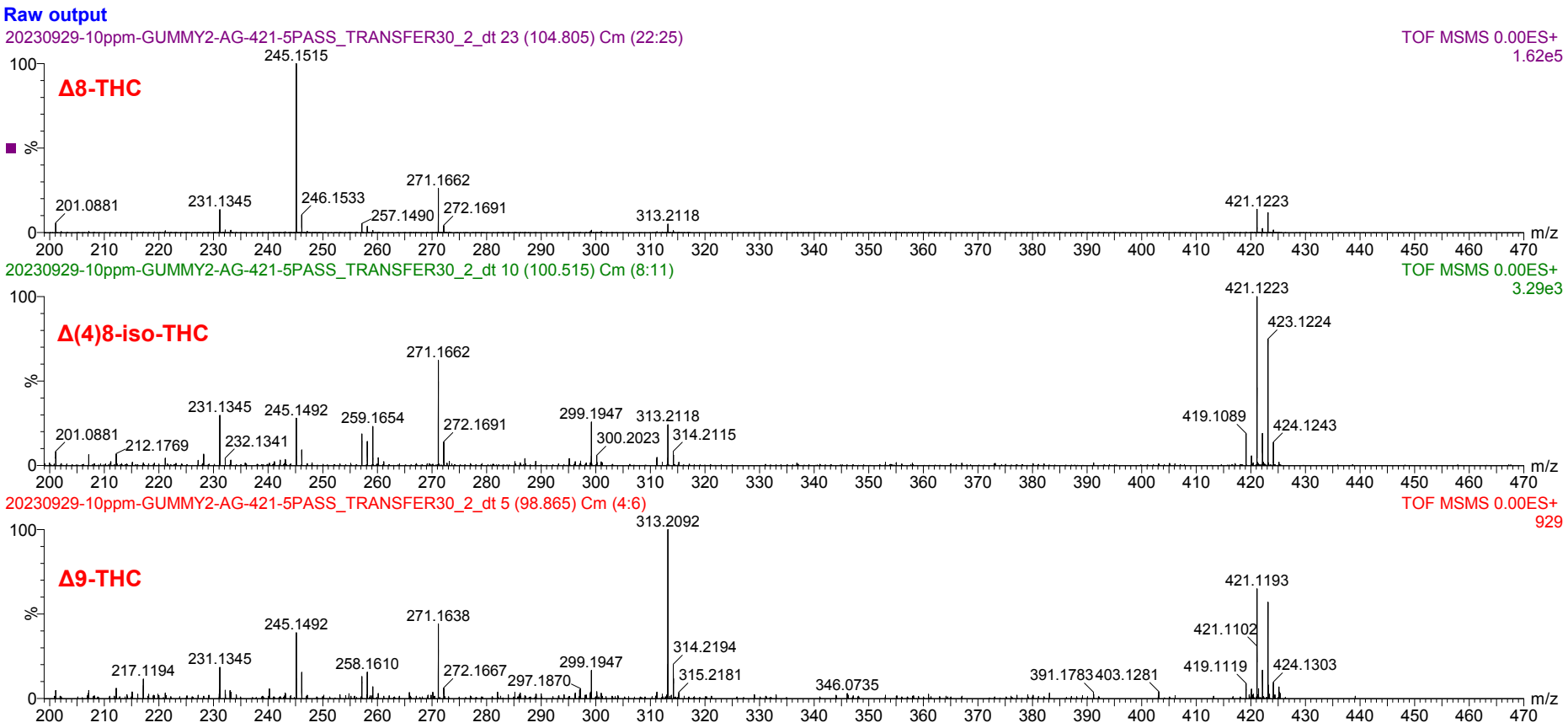
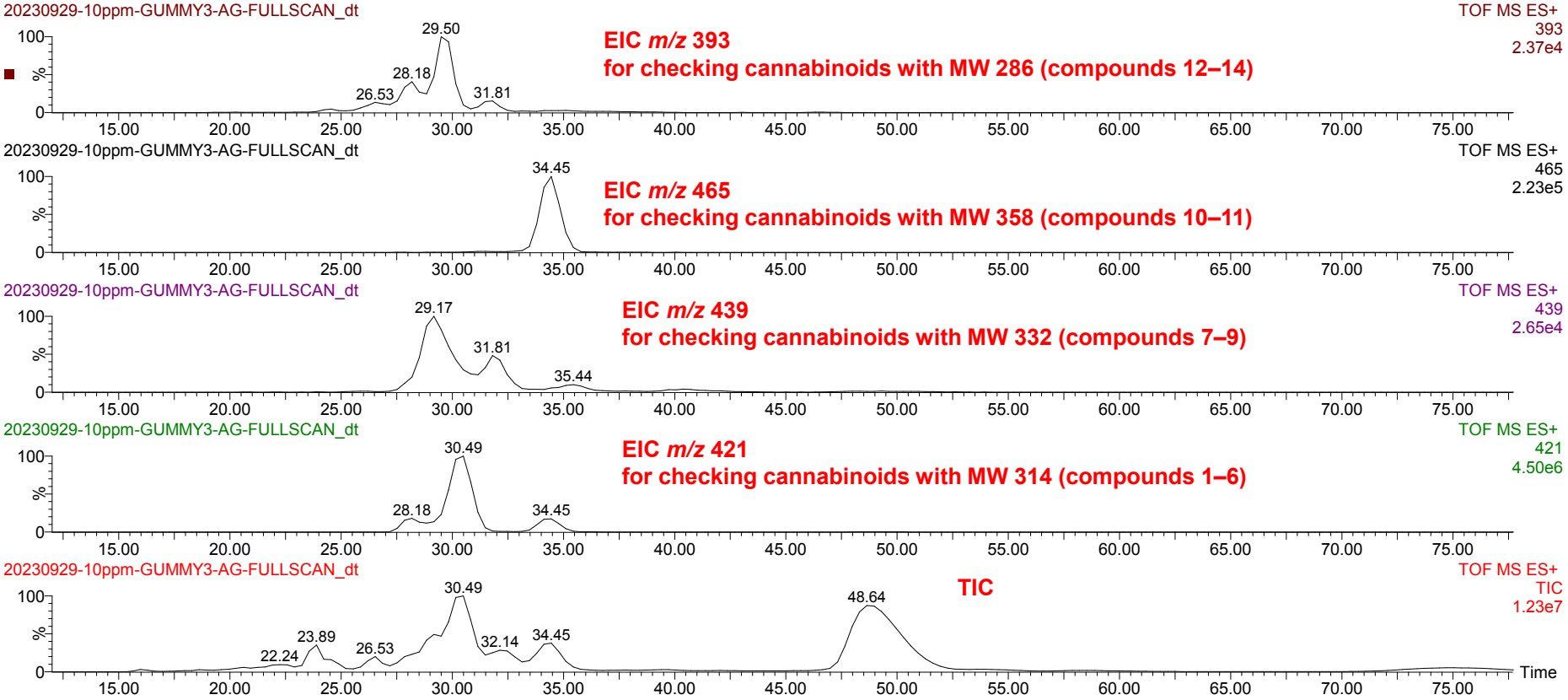


Figure S14-4. Mobiligram and mass spectra of cannabinoids in sample G#1.

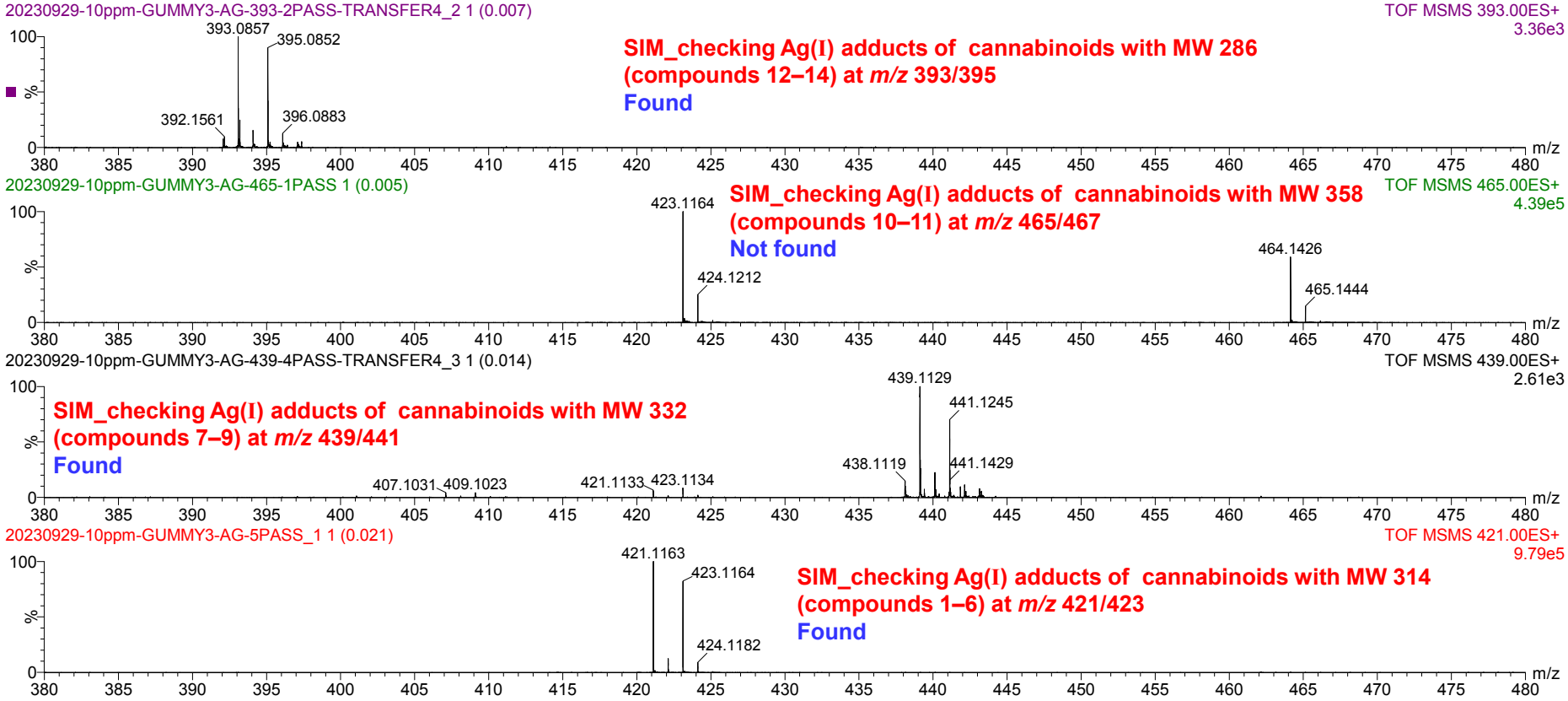
G#2 _full scan_for checking Ag(I) adducts

Raw output



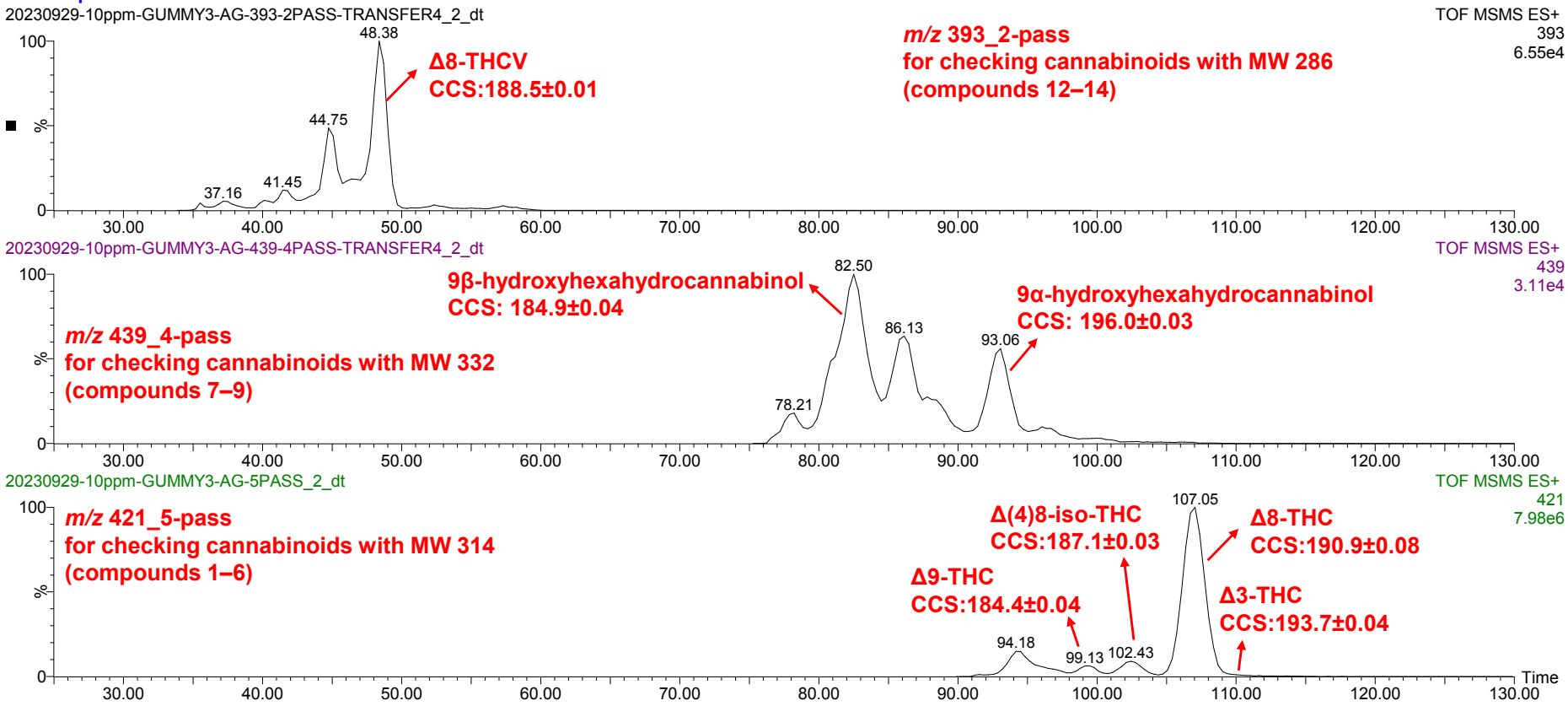
G#2 _SIM_for checking Ag(I) adducts

Raw output



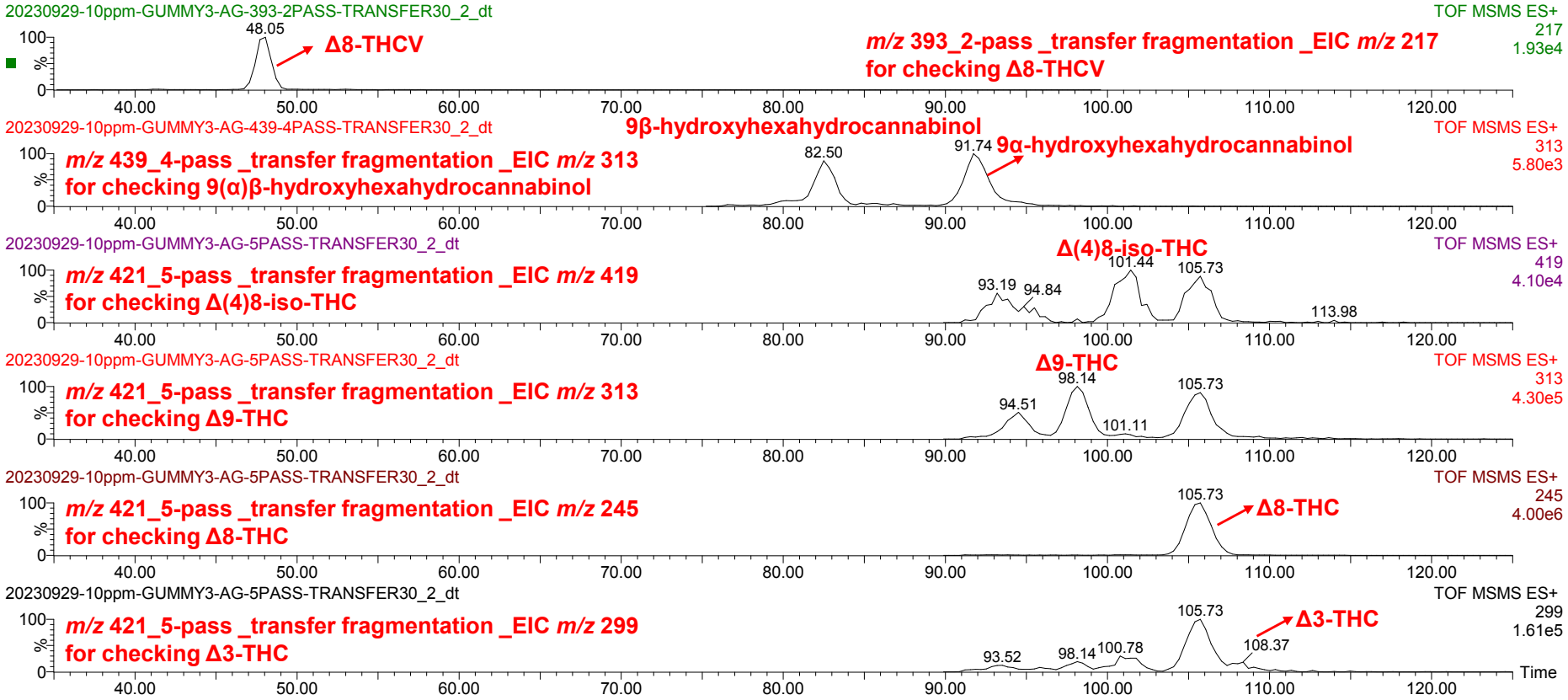
G#2 _mobility separation_for checking CCS

Raw output



G#2_mobility separation+transfer fragmentation_for checking fragments

Raw output



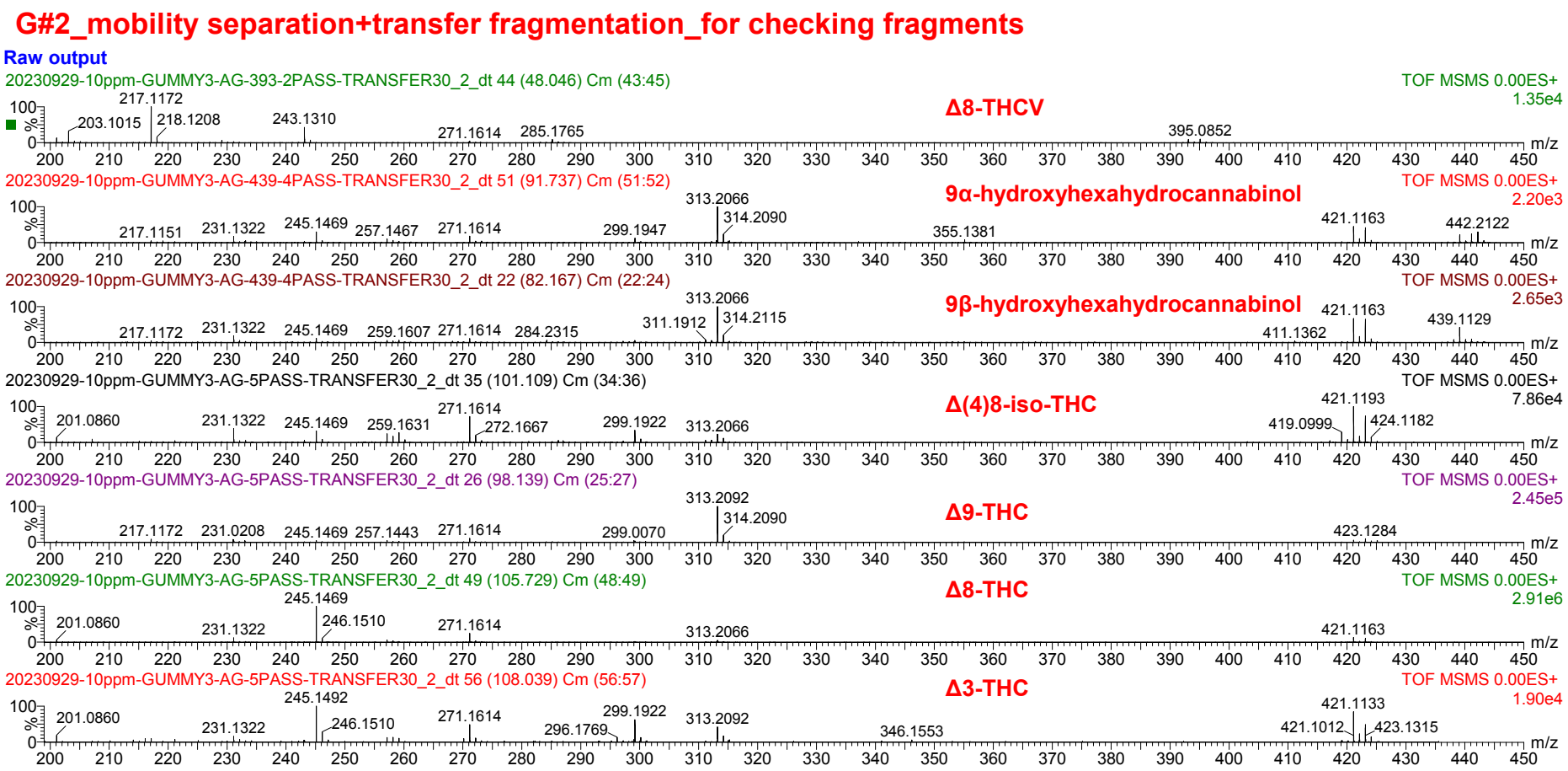


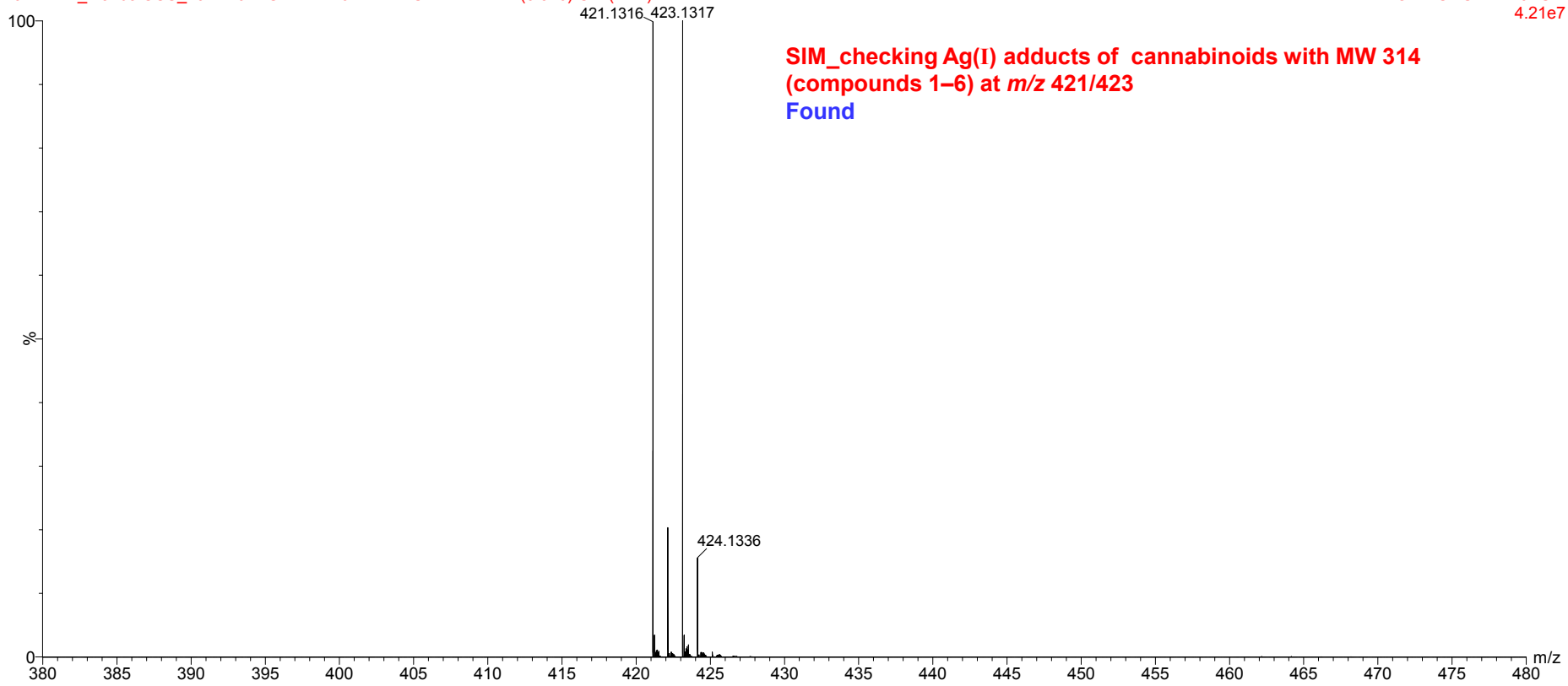
Figure S14-5. Mobiligram and mass spectra of cannabinoids in sample G#2.

R#1 _SIM_for checking Ag(I) adducts

Raw output

20221114_manualCCS_10PP10PTSA-TRAP6V-TRANSFER4-7P 17 (0.376) Cm (2:42)

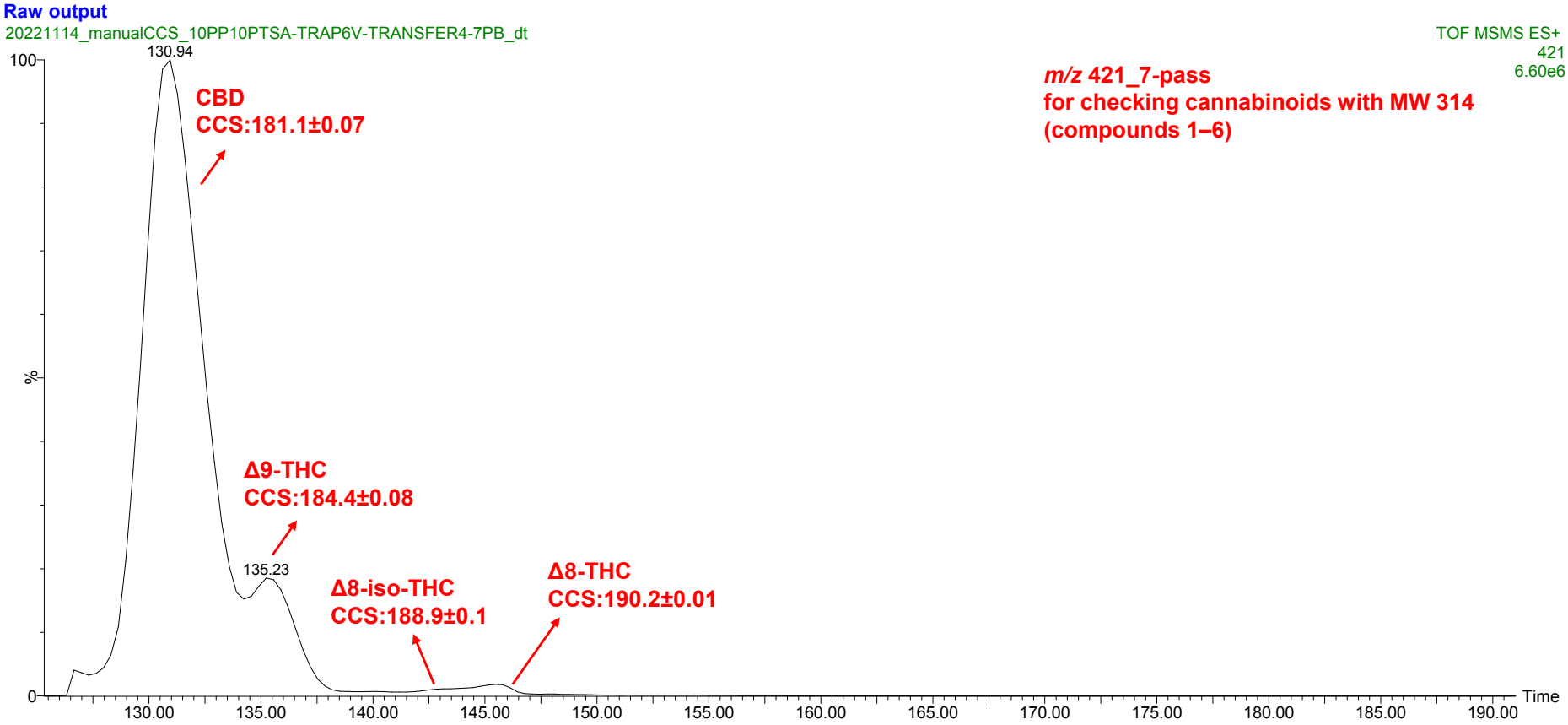
TOF MSMS 421.10ES+
4.21e7



SIM_checking Ag(I) adducts of cannabinoids with MW 314 (compounds 1–6) at *m/z* 421/423

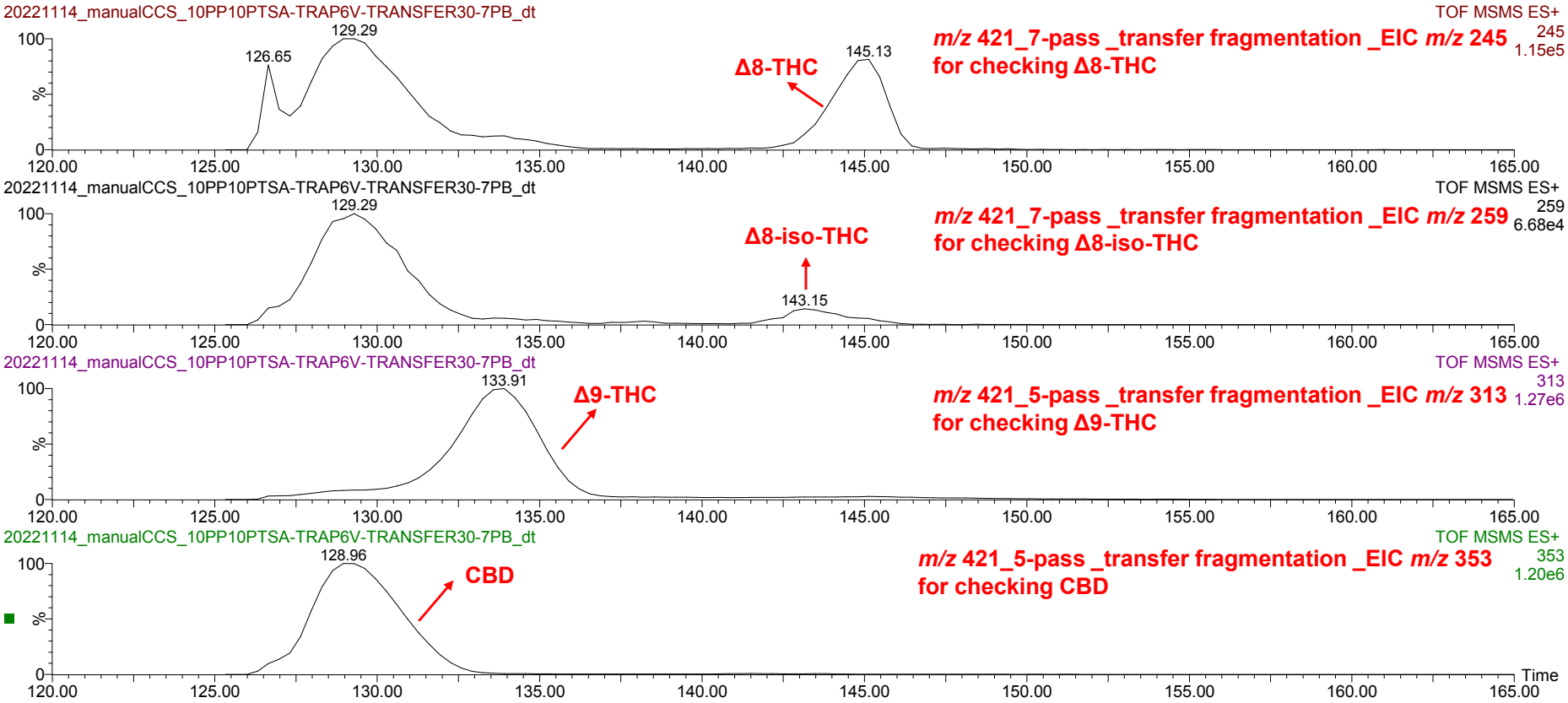
Found

R#1 _mobility separation_for checking CCS



R#1_mobility separation+transfer fragmentation_for checking fragments

Raw output



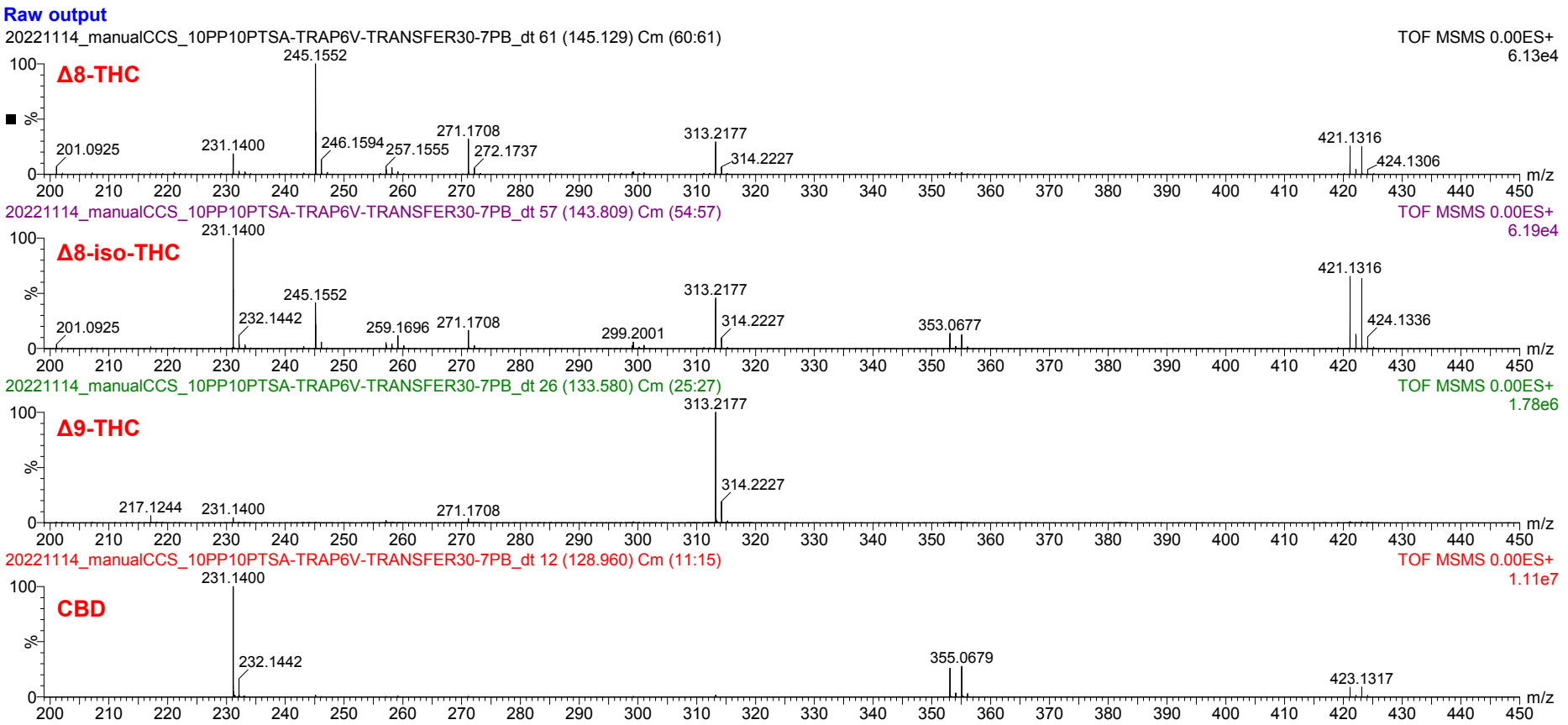


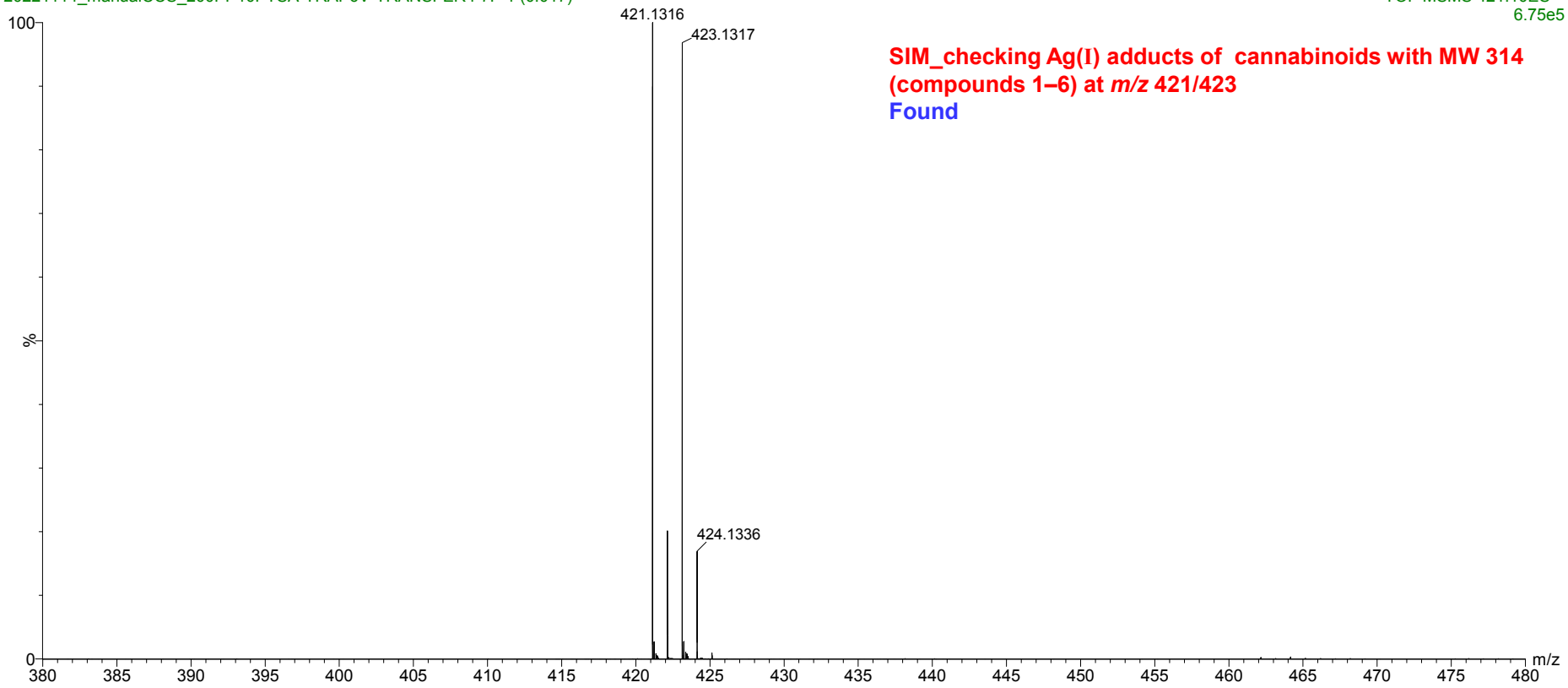
Figure S14-6. Mobiligram and mass spectra of cannabinoids in sample R#1.

R#2 _SIM_for checking Ag(I) isotope pattern

ADC129.25-5PPB-SEP119.25

20221114_manualCCS_200PP10PTSA-TRAP6V-TRANSFER4-7P 1 (0.017)

TOF MSMS 421.10ES+
6.75e5

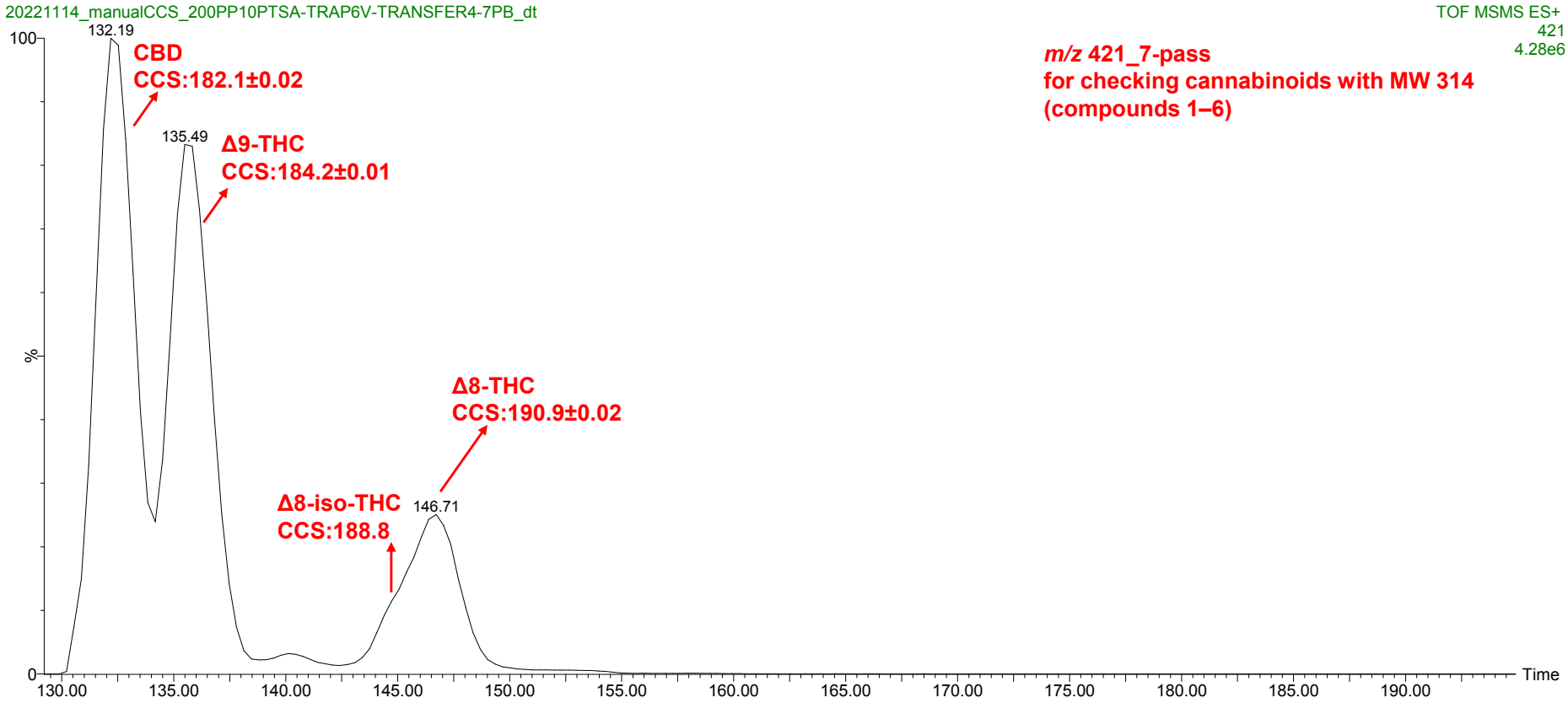


SIM_checking Ag(I) adducts of cannabinoids with MW 314 (compounds 1–6) at *m/z* 421/423

Found

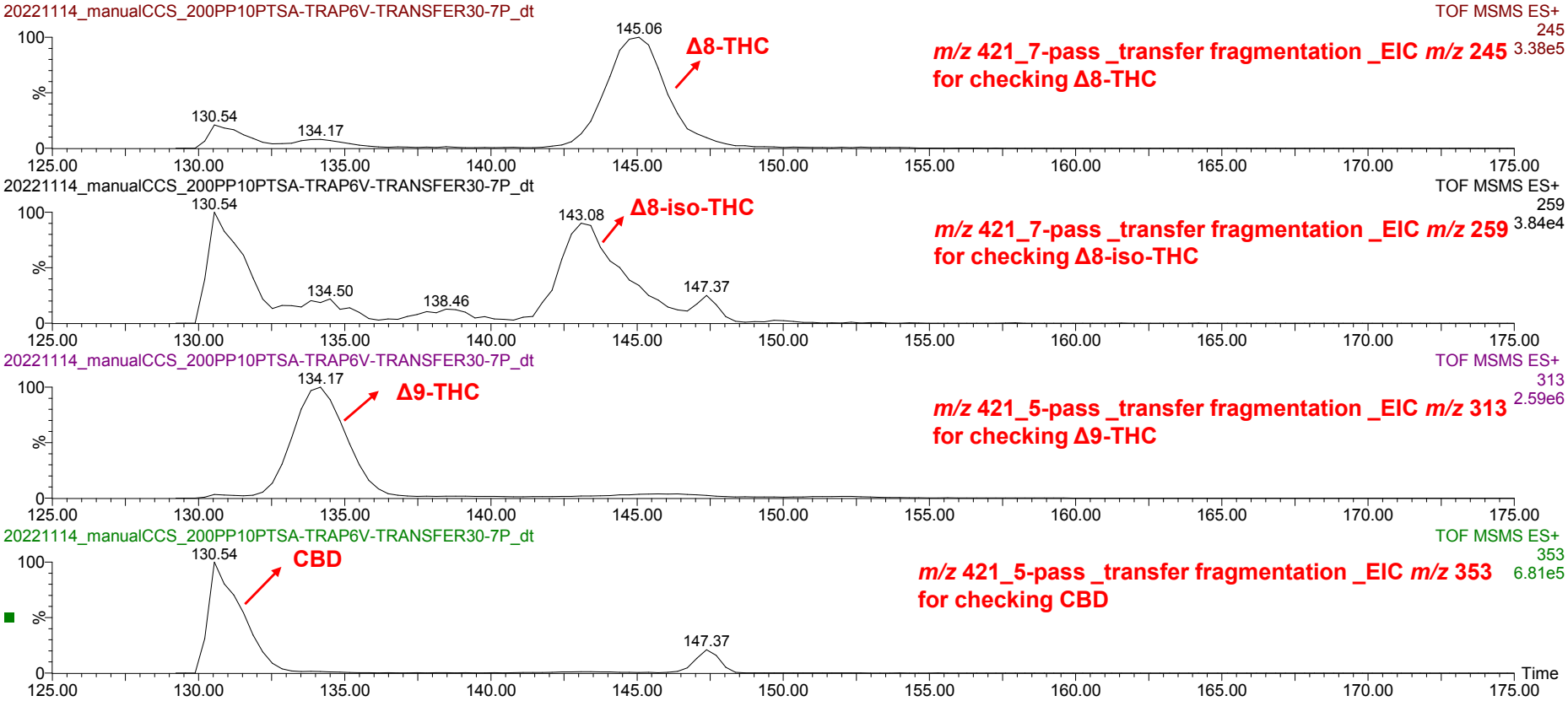
R#2 _mobility separation_for checking CCS

Raw output



R#2_mobility separation+transfer fragmentation_for checking fragments

Raw output



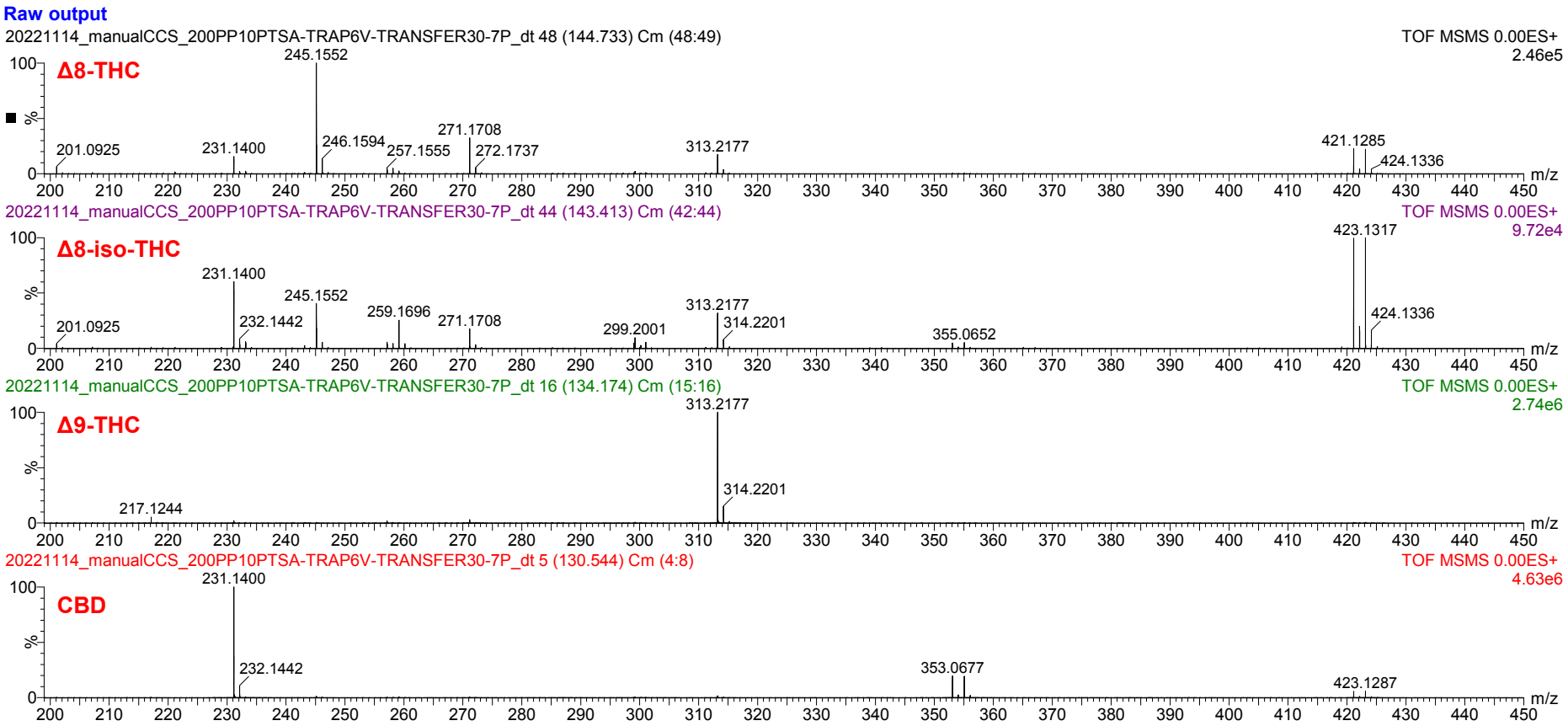


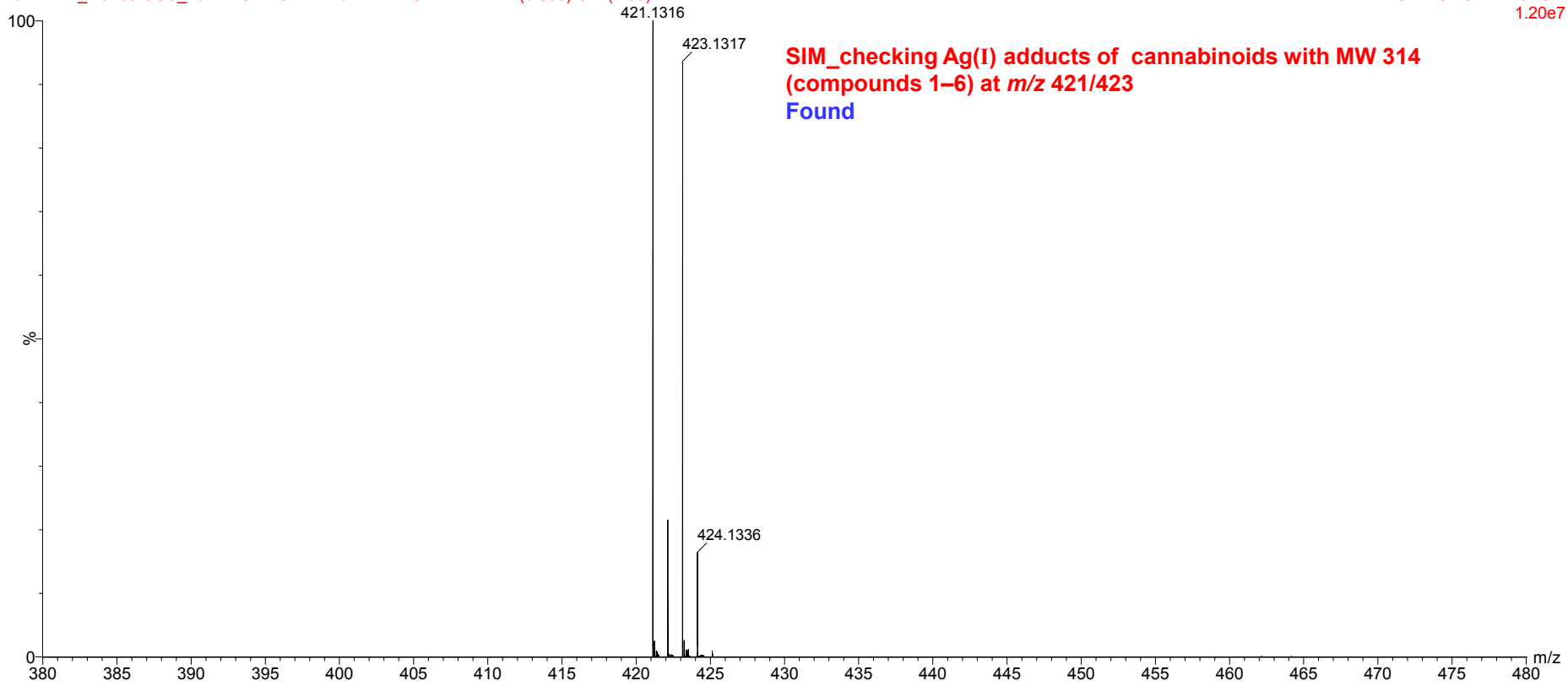
Figure S14-7. Mobiligram and mass spectra of cannabinoids in sample R#2.

R#3 _SIM_for checking Ag(I) adducts

ADC12-5PPB-SEP2

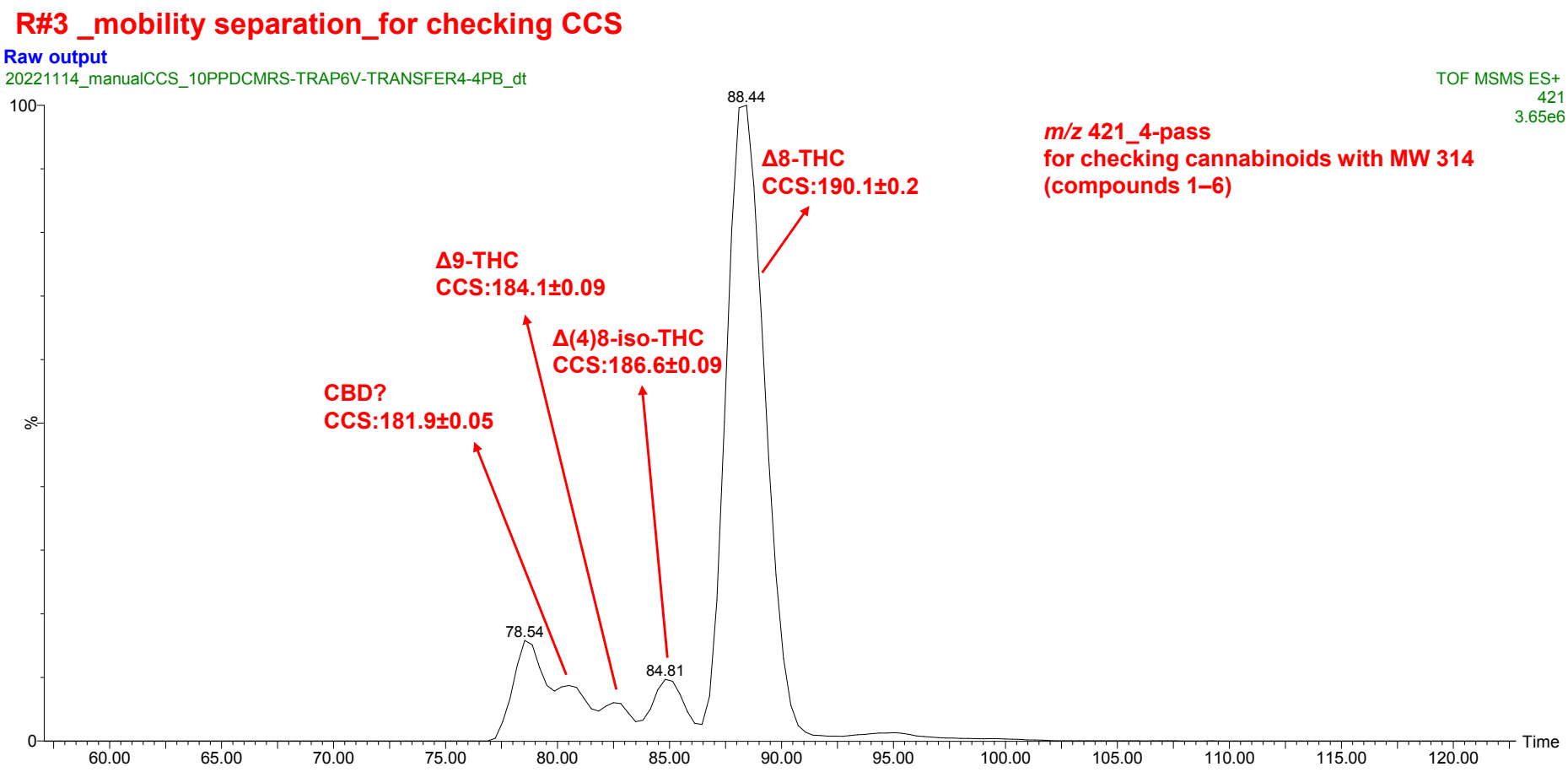
20221114_manualCCS_10PPDCMRS-TRAP6V-TRANSFER4-1P 47 (0.856) Cm (2:53)

TOF MSMS 421.10ES+
1.20e7



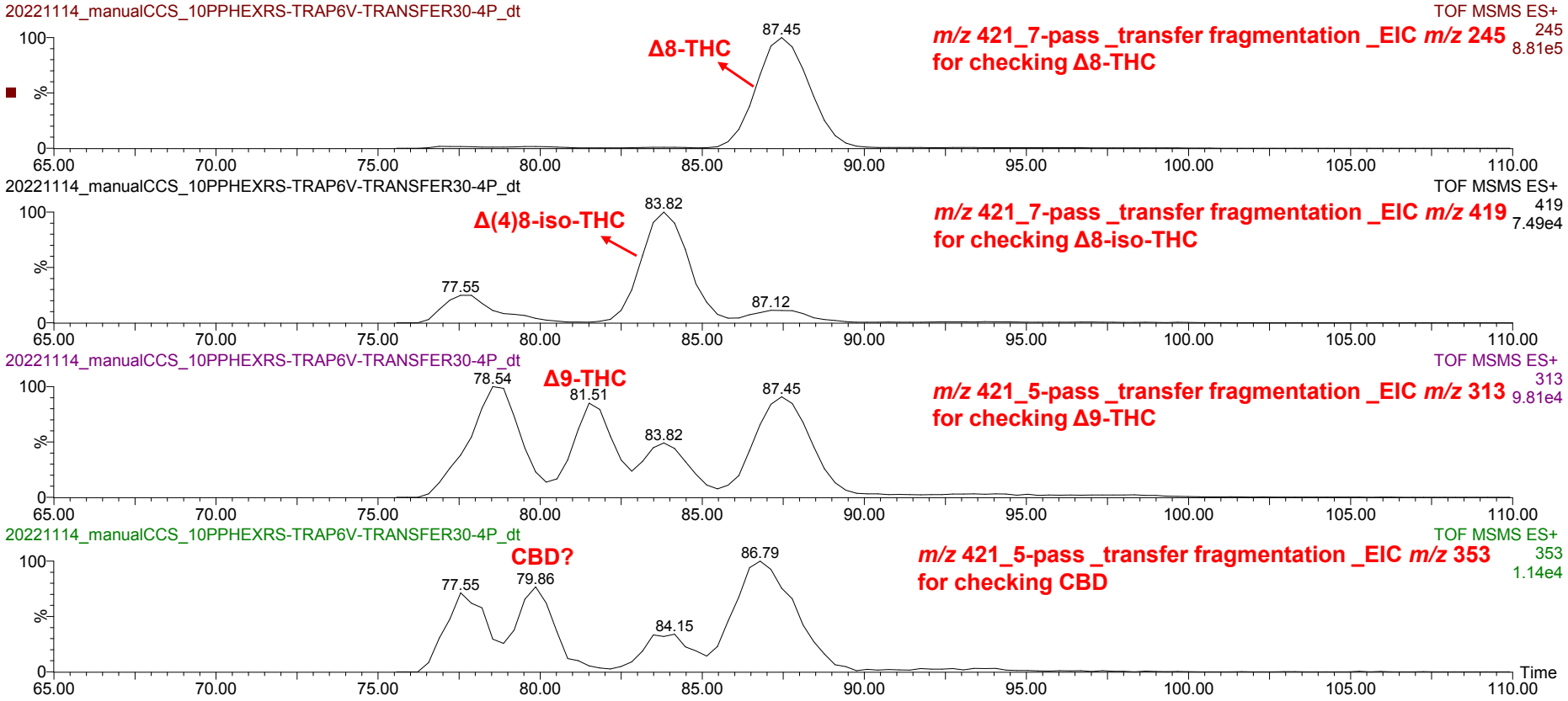
SIM_checking Ag(I) adducts of cannabinoids with MW 314 (compounds 1–6) at *m/z* 421/423

Found


R#3 _mobility separation_for checking CCS
Raw output
20221114_manualCCS_10PPDCMRS-TRAP6V-TRANSFER4-4PB_dt
TOF MSMS ES+
421
3.65e6
m/z 421_4-pass
for checking cannabinoids with MW 314
(compounds 1–6)
Δ8-THC
CCS:190.1±0.2
Δ9-THC
CCS:184.1±0.09
Δ(4)8-iso-THC
CCS:186.6±0.09
CBD?
CCS:181.9±0.05
88.44
78.54
84.81
100
%
0
Time
60.00
65.00
70.00
75.00
80.00
85.00
90.00
95.00
100.00
105.00
110.00
115.00
120.00

R#3_mobility separation+transfer fragmentation_for checking fragments

Raw output



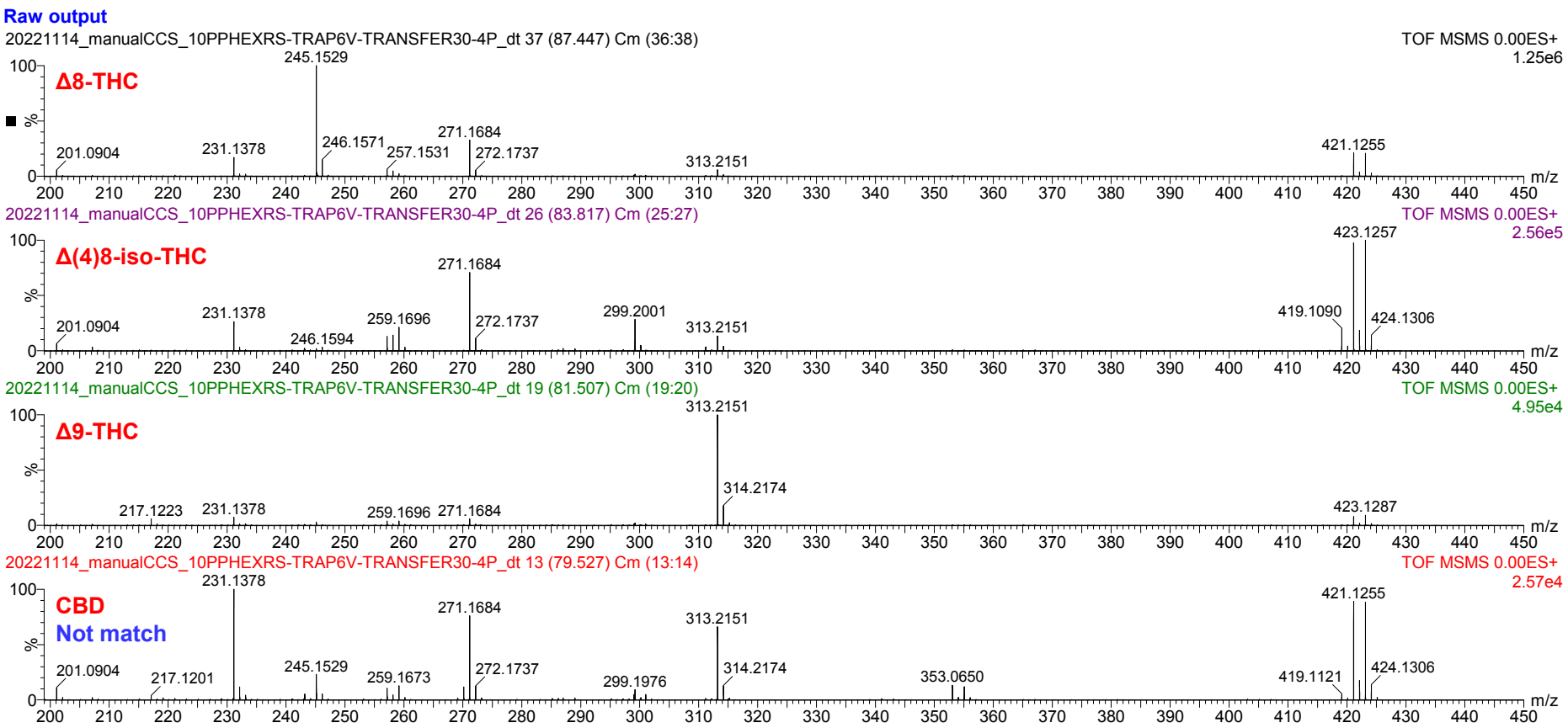


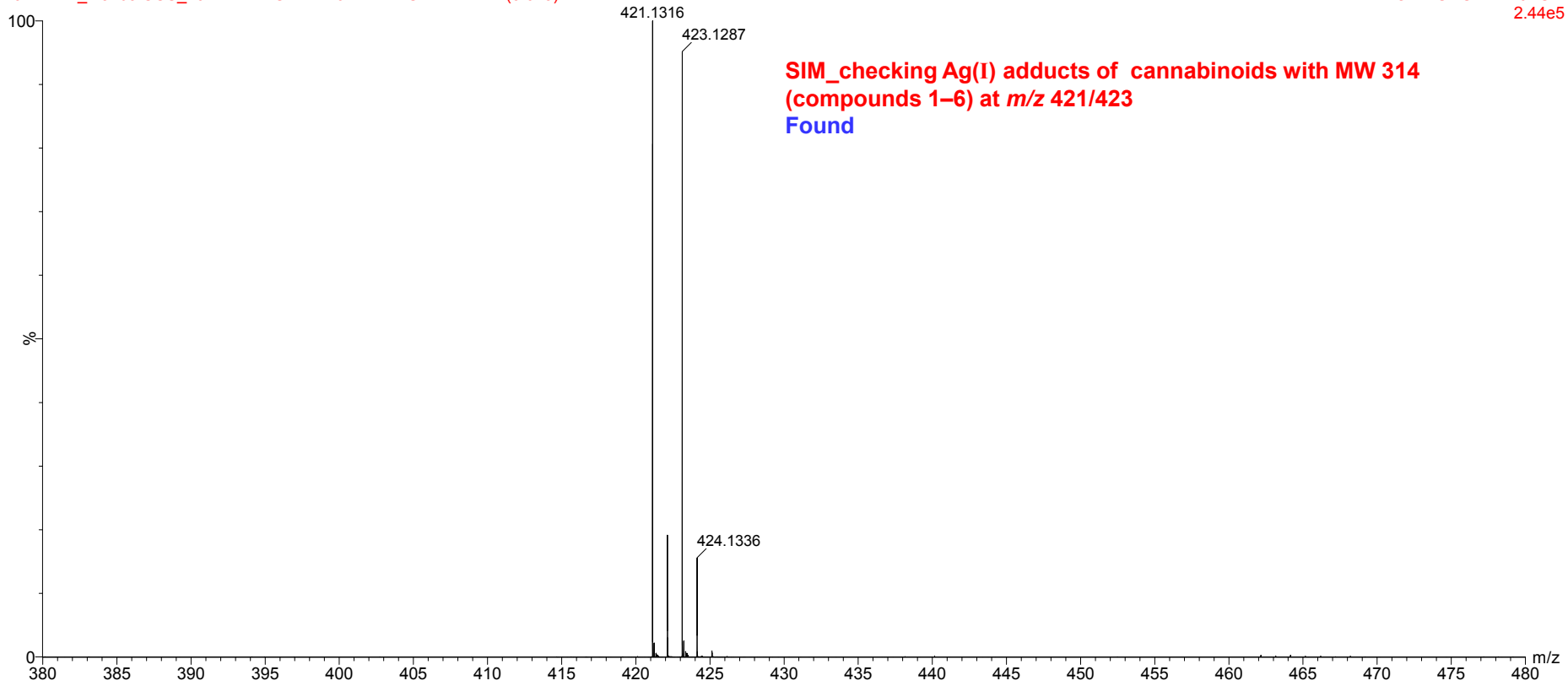
Figure S14-8. Mobiligram and mass spectra of cannabinoids in sample R#3.

R#4 _SIM_for checking Ag(I) adducts

ADC75.57-5PPB-SEP65.57

20221114_manualCCS_10PPHEXRS-TRAP6V-TRANSFER4-4P 1 (0.015)

TOF MSMS 421.10ES+
2.44e5

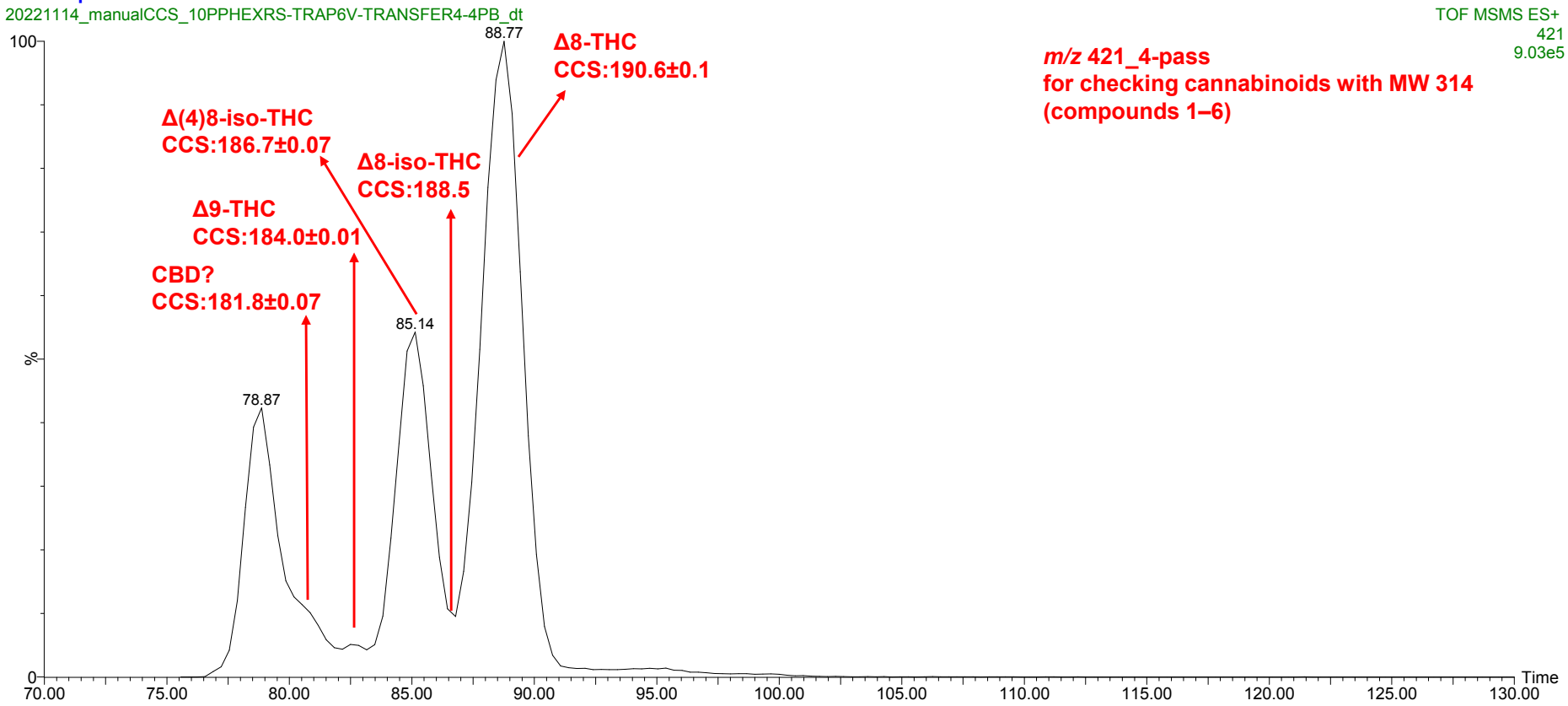


SIM_checking Ag(I) adducts of cannabinoids with MW 314 (compounds 1–6) at *m/z* 421/423

Found

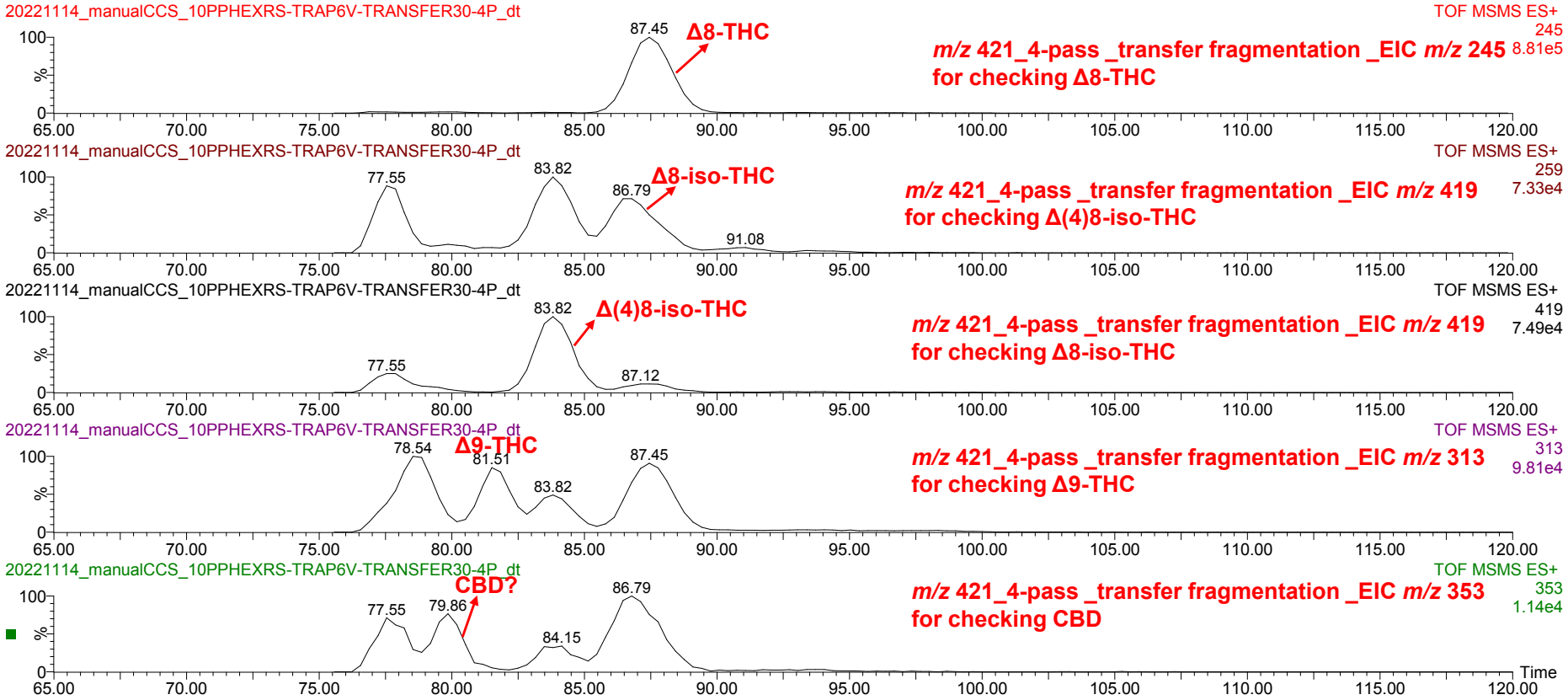
R#4 _mobility separation_for checking CCS

Raw output



R#4_mobility separation+transfer fragmentation_for checking fragments

Raw output



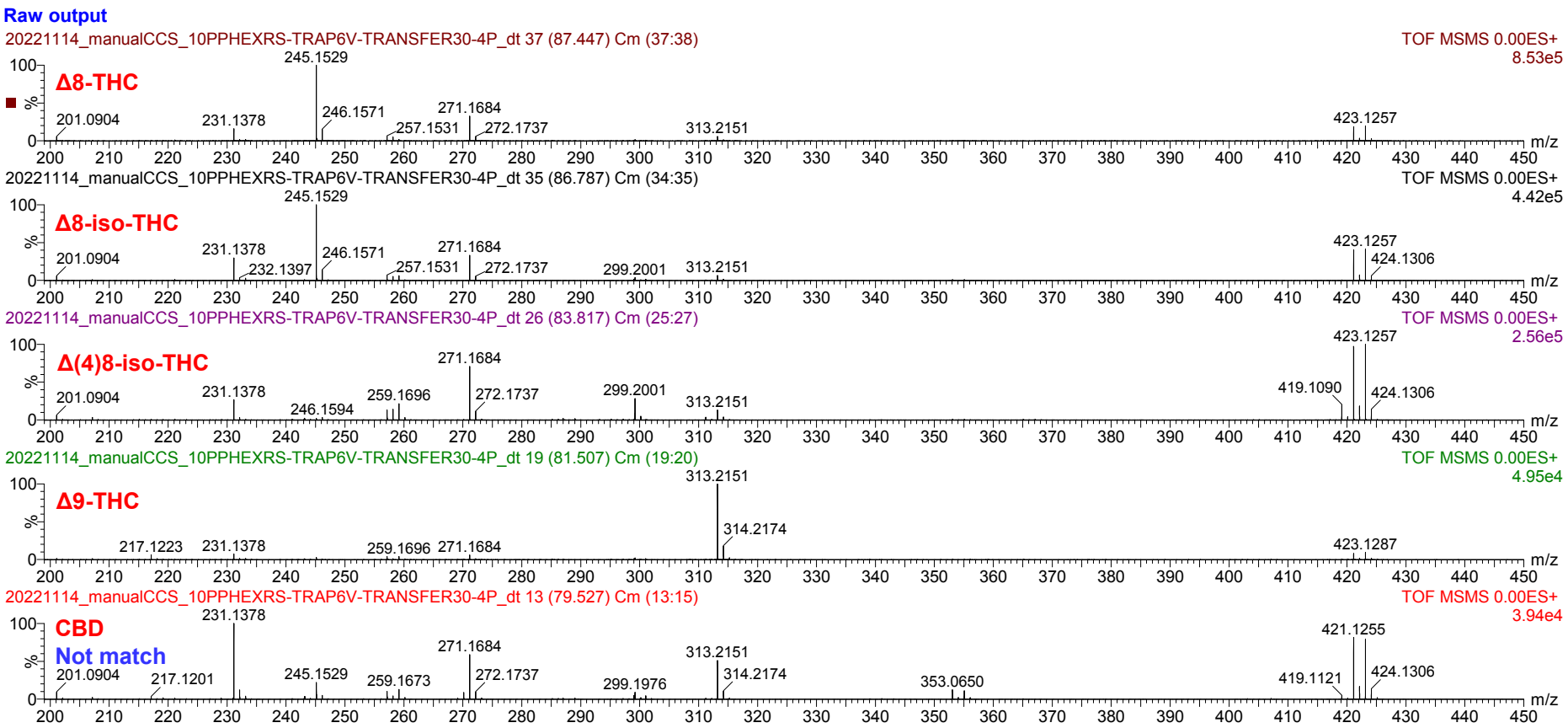


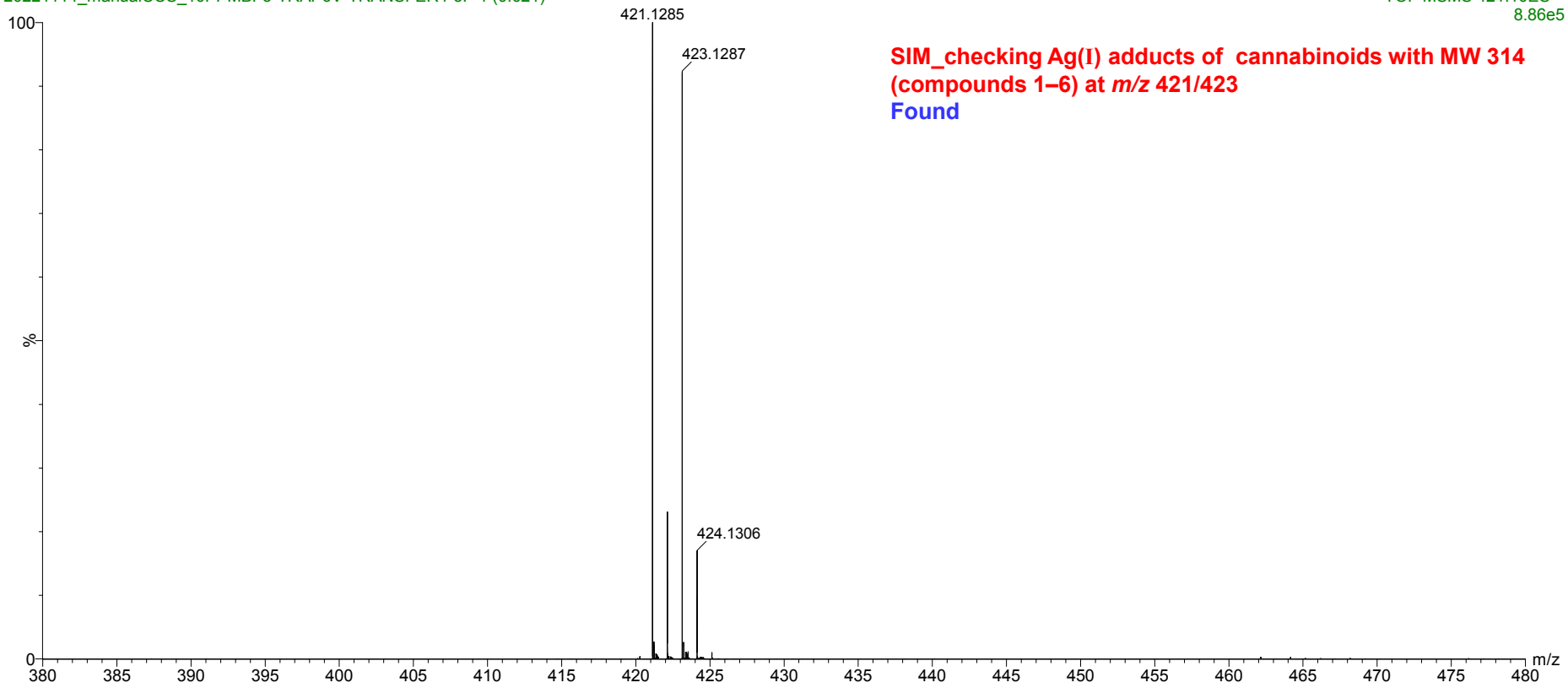
Figure S14-9. Mobiligram and mass spectra of cannabinoids in sample R#4.

R#5 _SIM_for checking Ag(I) adducts

ADC92.96-5PPB-SEP82.96

20221114_manualCCS_10PPMBF3-TRAP6V-TRANSFER4-5P 1 (0.021)

TOF MSMS 421.10ES+
8.86e5



SIM_checking Ag(I) adducts of cannabinoids with MW 314 (compounds 1–6) at *m/z* 421/423

Found

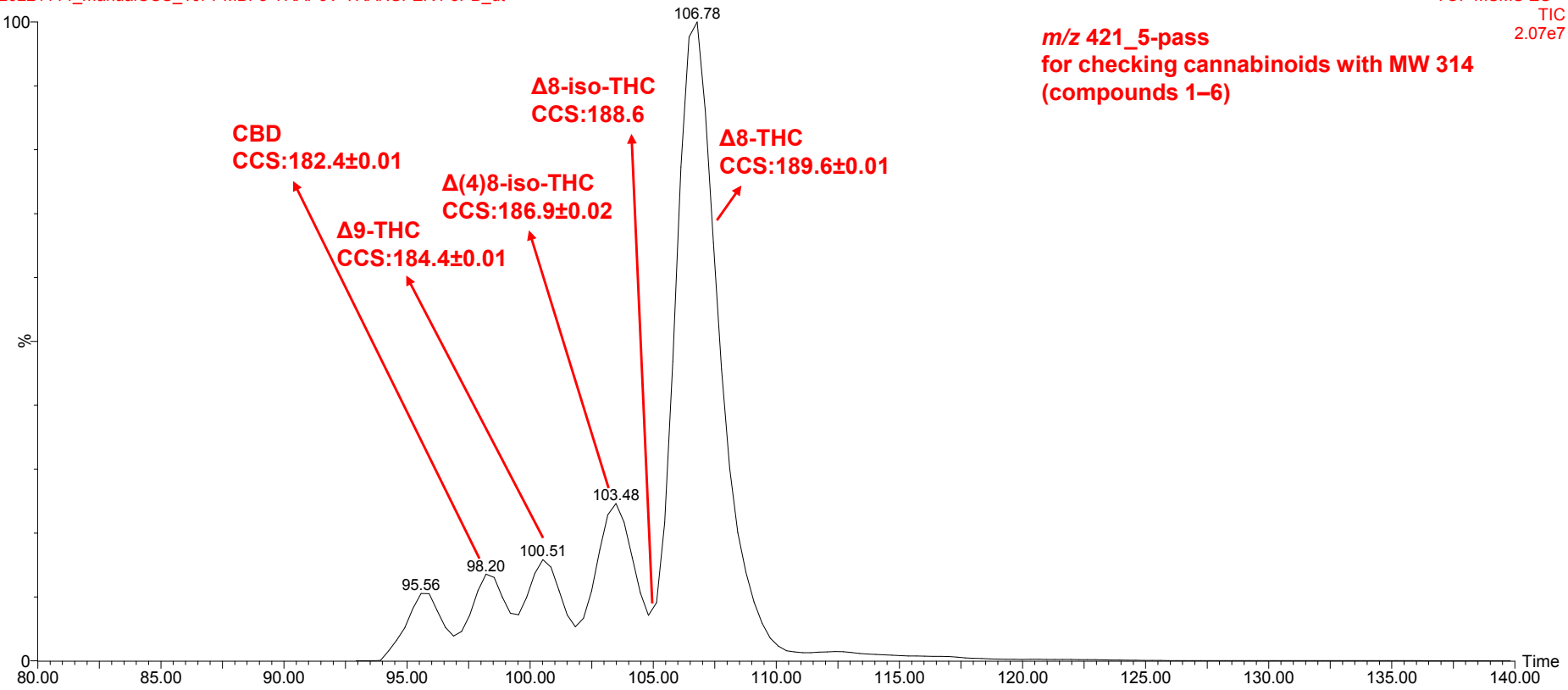
R#5 _mobility separation_for checking CCS

Raw output

20221114_manualCCS_10PPMBF3-TRAP6V-TRANSFER4-5PB_dt

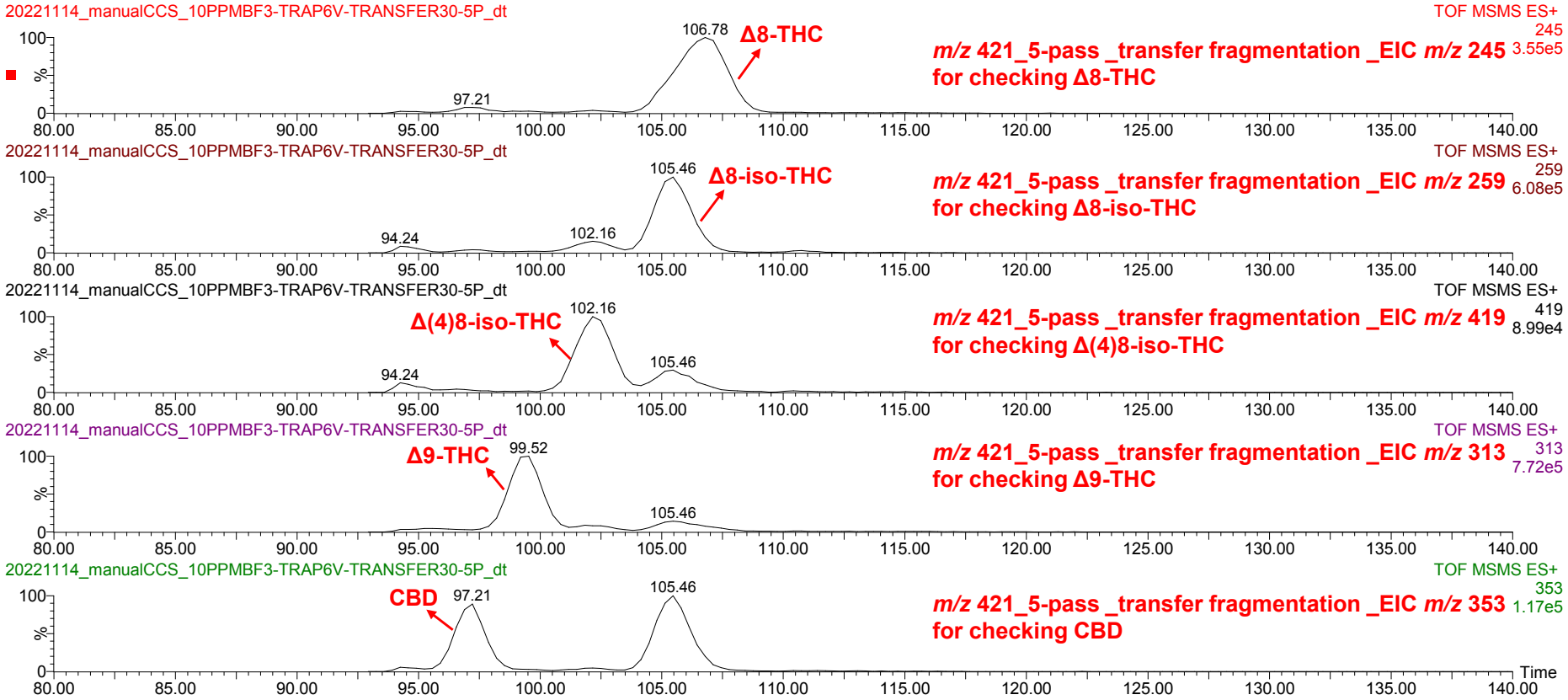
TOF MSMS ES+
TIC
2.07e7

***m/z* 421_5-pass**
for checking cannabinoids with MW 314
(compounds 1–6)



R#5_mobility separation+transfer fragmentation_for checking fragments

Raw output



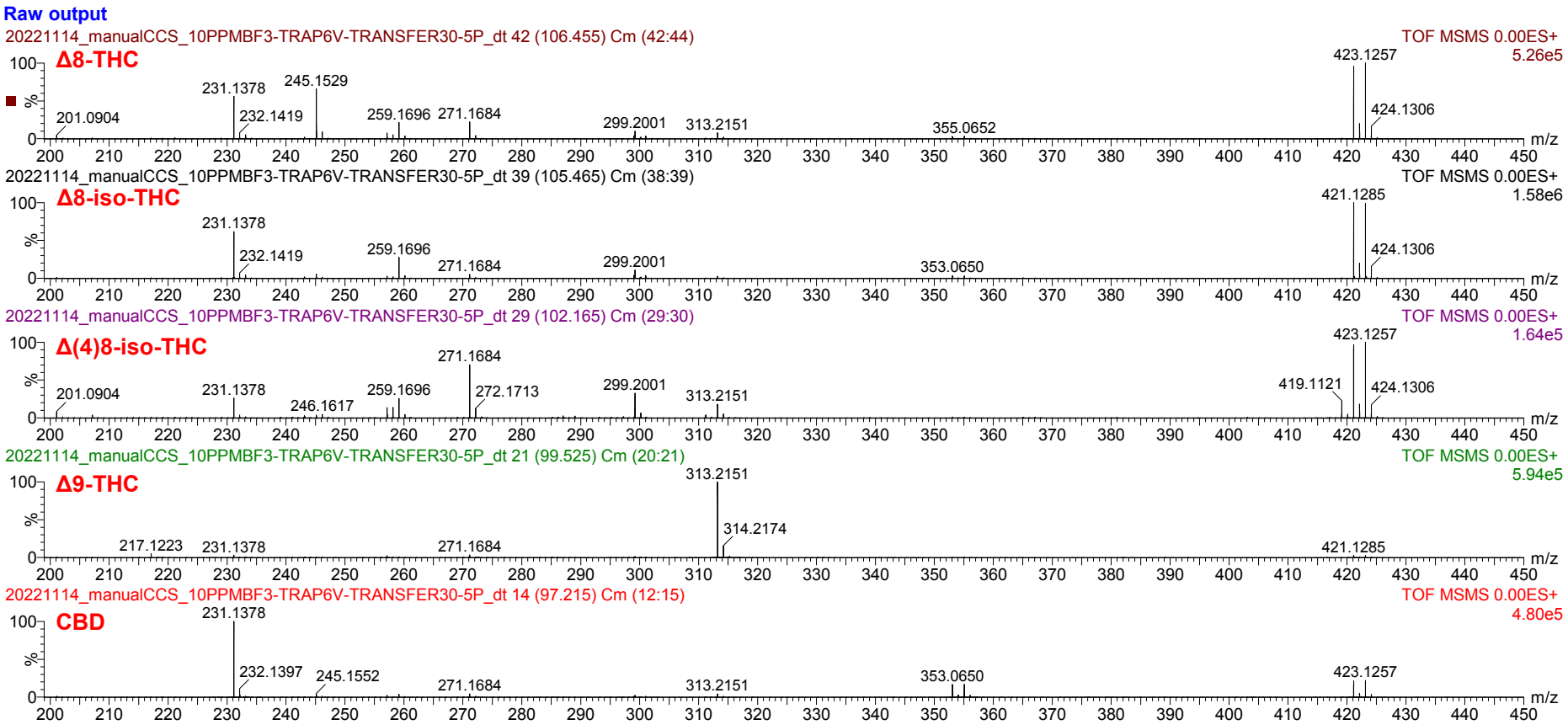


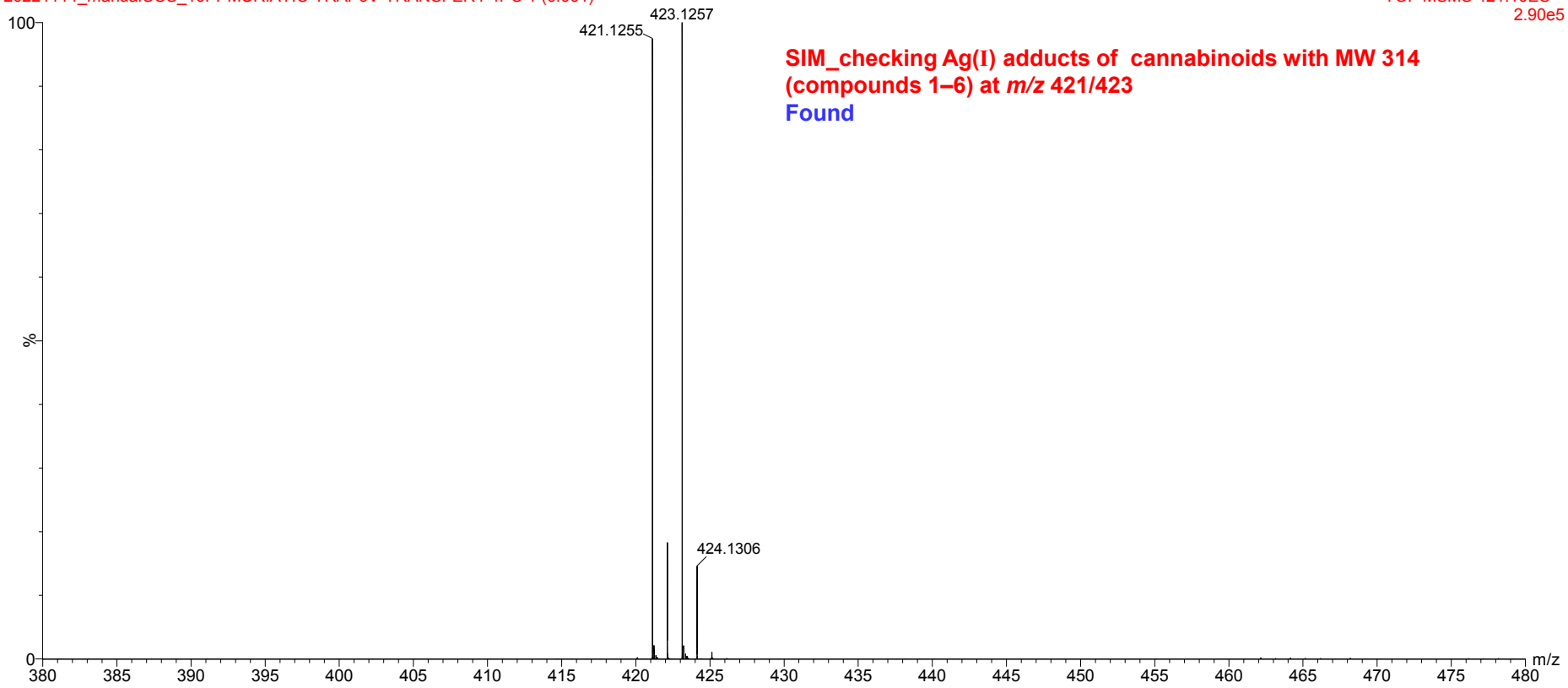
Figure S14-10. Mobiligram and mass spectra of cannabinoids in sample R#5.

R#6 _SIM_for checking Ag(I) adducts

Raw output

20221114_manualCCS_10PPMURIATIC-TRAP6V-TRANSFER4-4PC 1 (0.001)

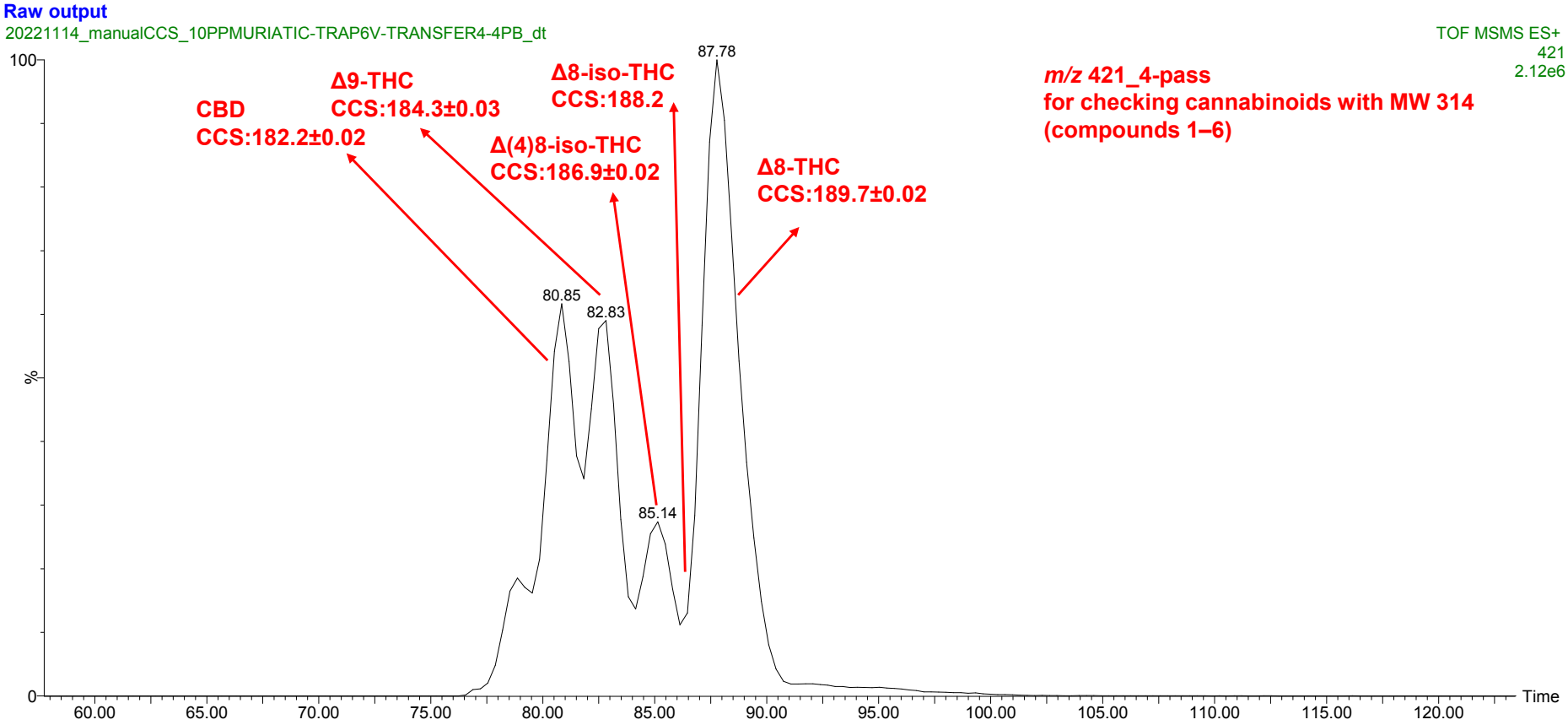
TOF MSMS 421.10ES+
2.90e5



SIM_checking Ag(I) adducts of cannabinoids with MW 314 (compounds 1–6) at *m/z* 421/423

Found

R#6 _mobility separation_for checking CCS



R#6_mobility separation+transfer fragmentation_for checking fragments

Raw output

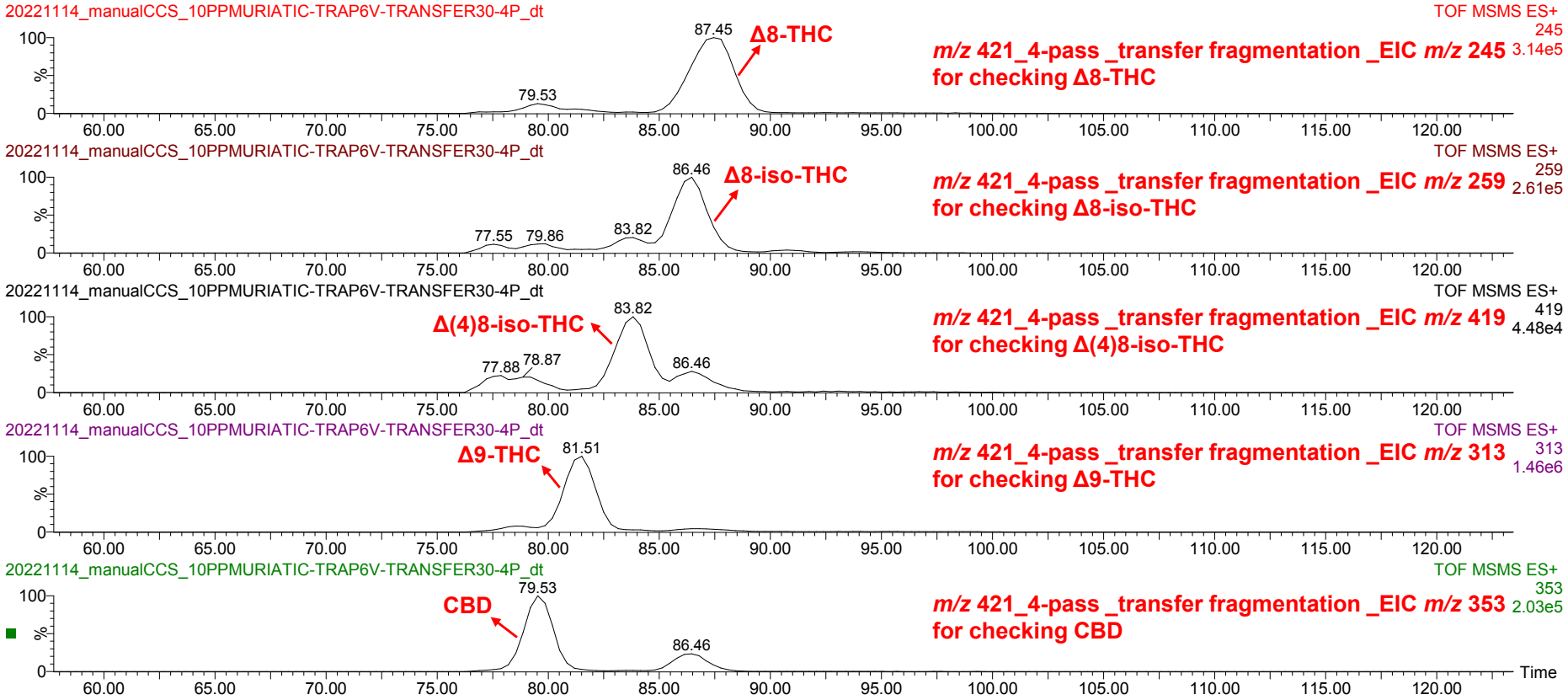


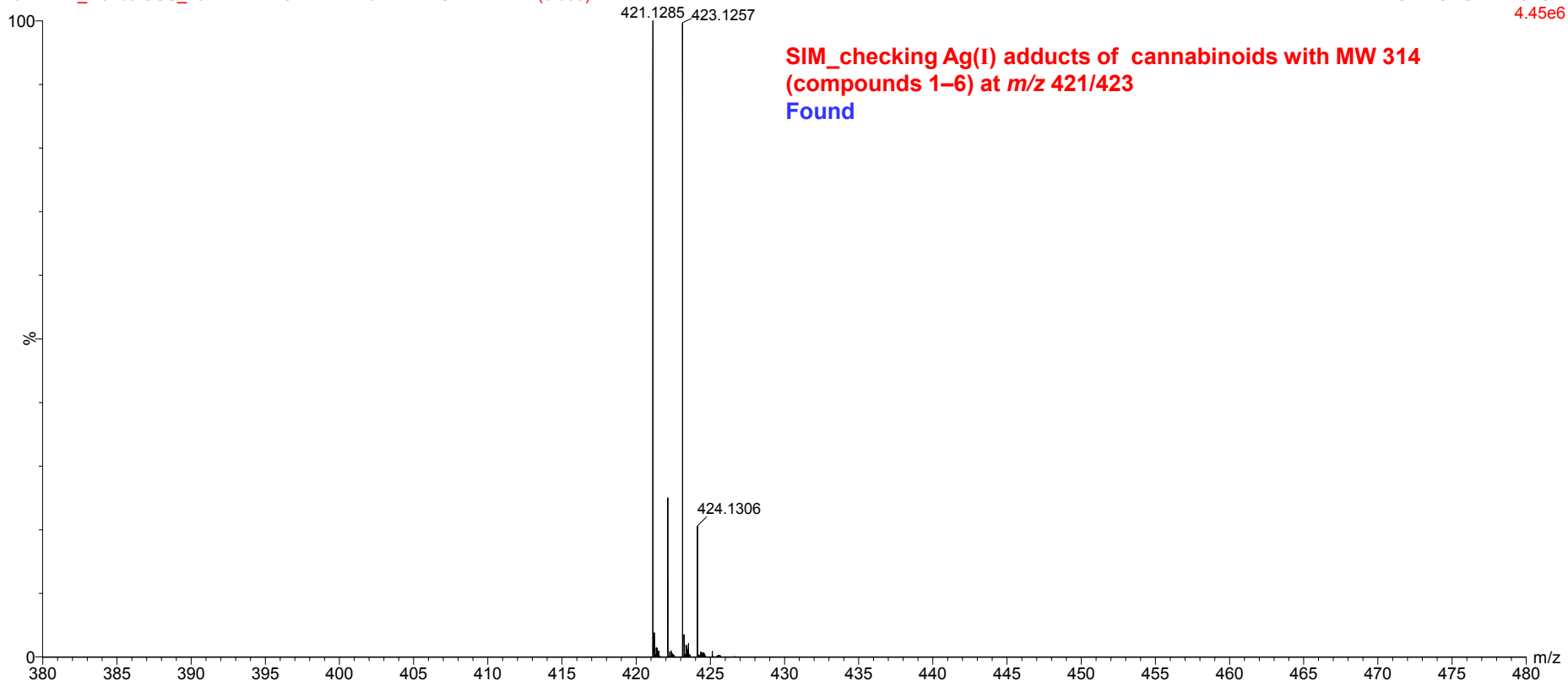
Figure S14-11. Mobiligram and mass spectra of cannabinoids in sample R#6.

R#7 _SIM_for checking Ag(I) adducts

ADC120.83-5PPB-110.83

20221114_manualCCS_10PPMVINEGAR-TRAP6V-TRANSFER4-7P 1 (0.003)

TOF MSMS 421.10ES+
4.45e6



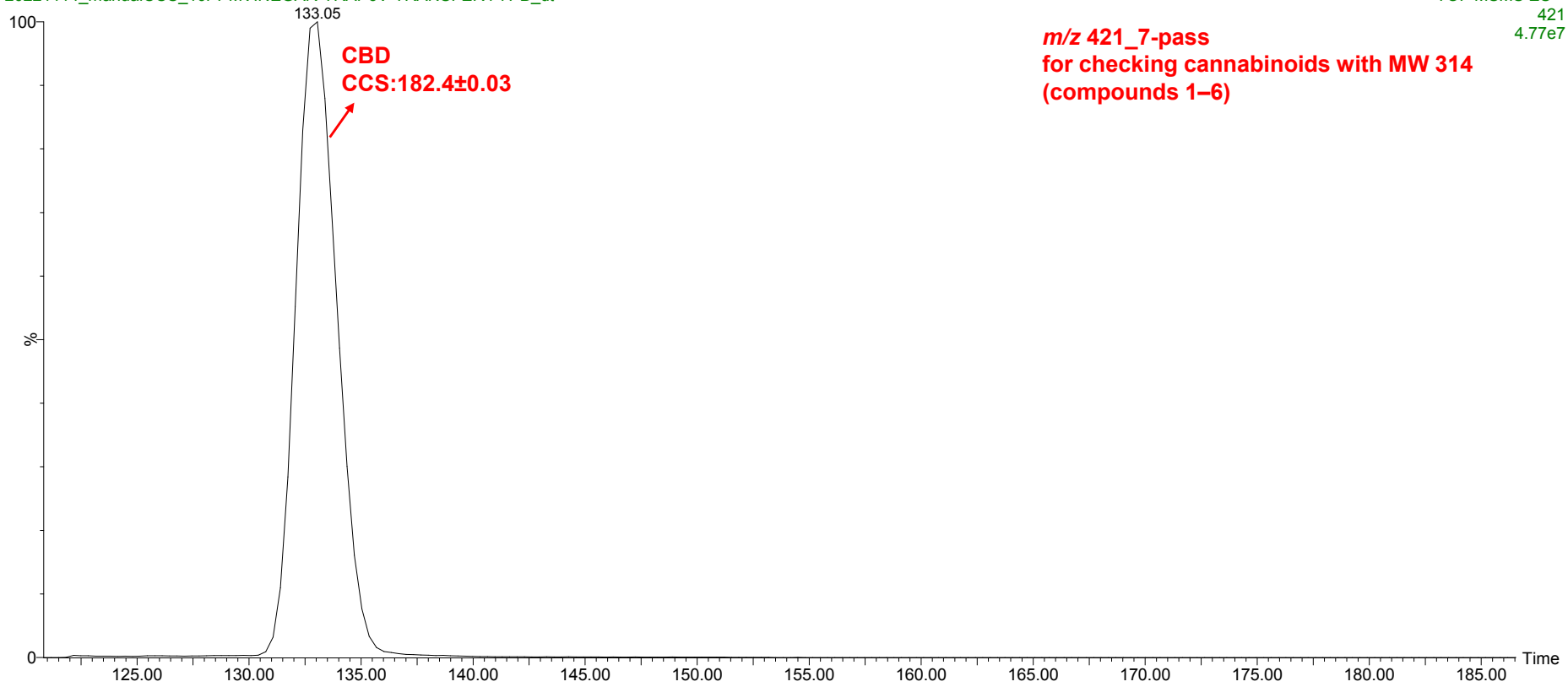
SIM_checking Ag(I) adducts of cannabinoids with MW 314 (compounds 1–6) at *m/z* 421/423

Found

R#7 _mobility separation_for checking CCS

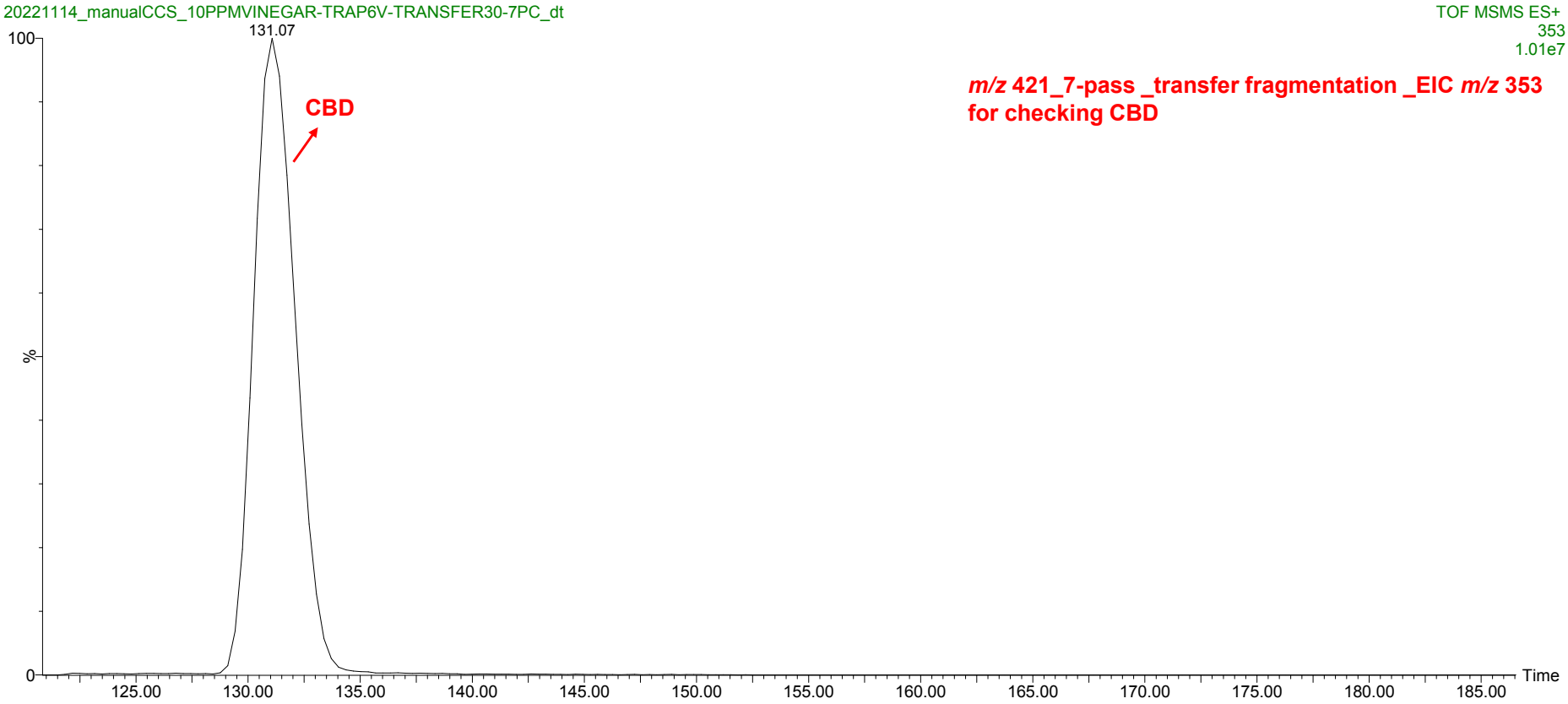
Raw output

20221114_manualCCS_10PPMVINEGAR-TRAP6V-TRANSFER4-7PB_dt



R#7_mobility separation+transfer fragmentation_for checking fragments

Raw output



***m/z* 421_7-pass _transfer fragmentation _EIC *m/z* 353 for checking CBD**

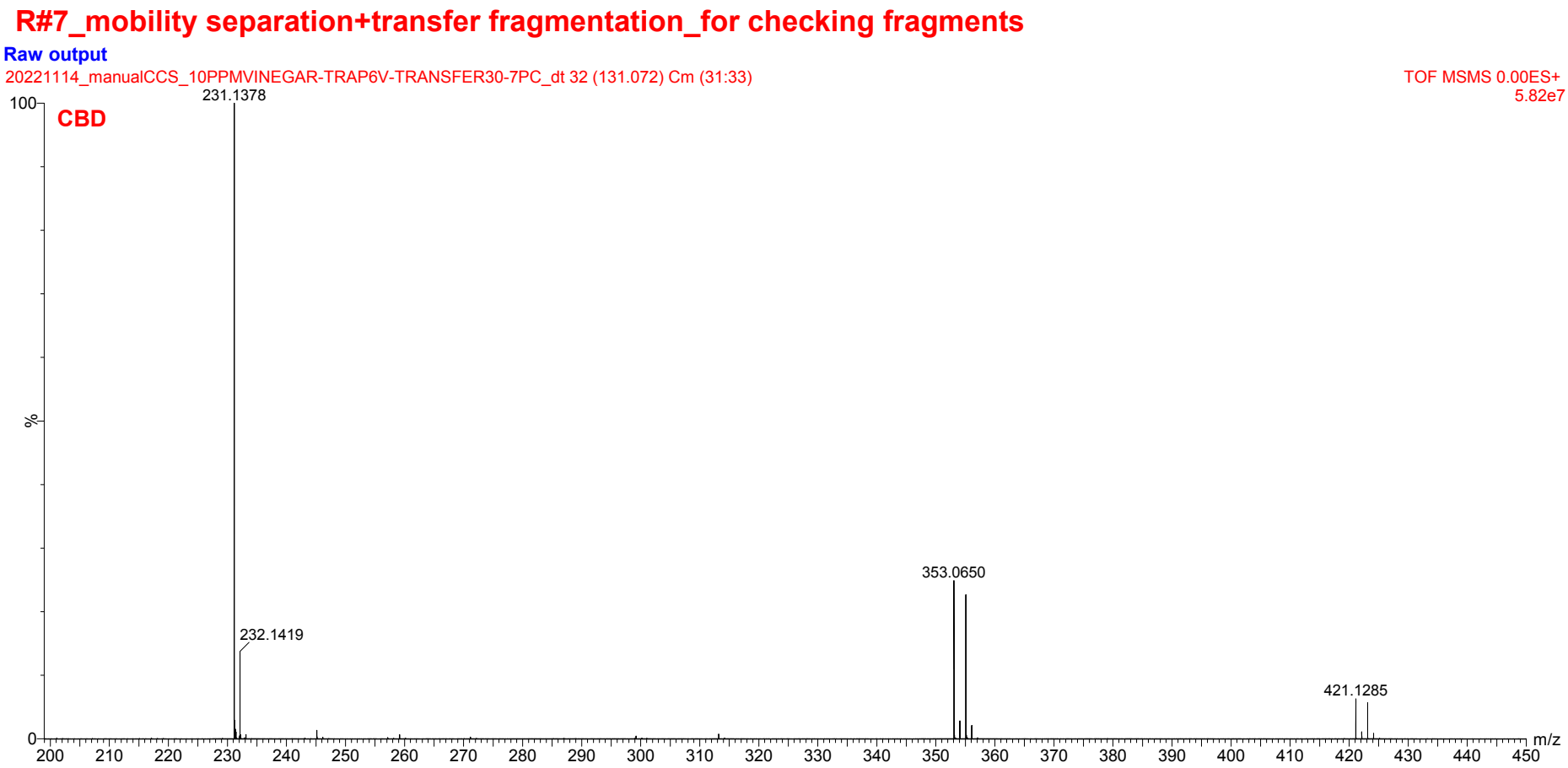


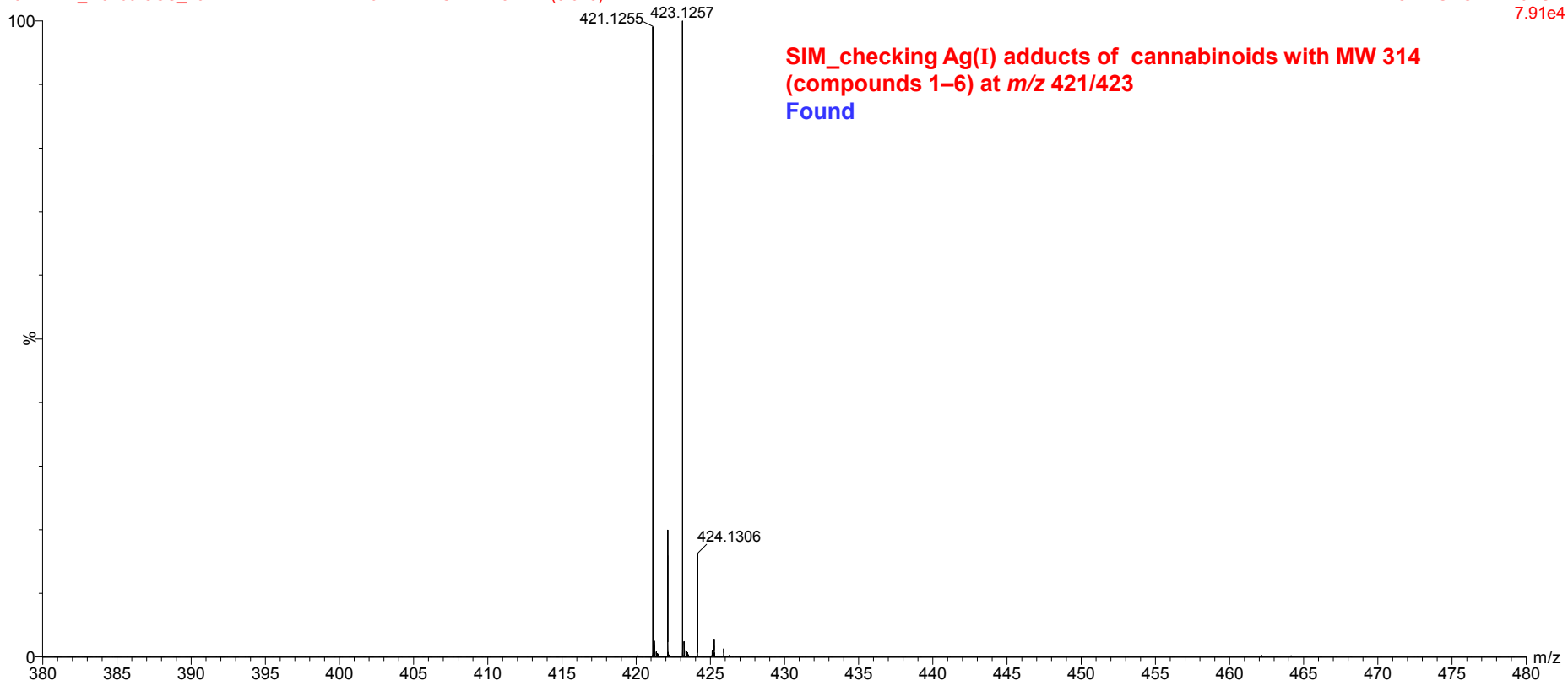
Figure S14-12. Mobiligram and mass spectra of cannabinoids in sample R#7.

R#8 _SIM_for checking Ag(I) adducts

Raw output

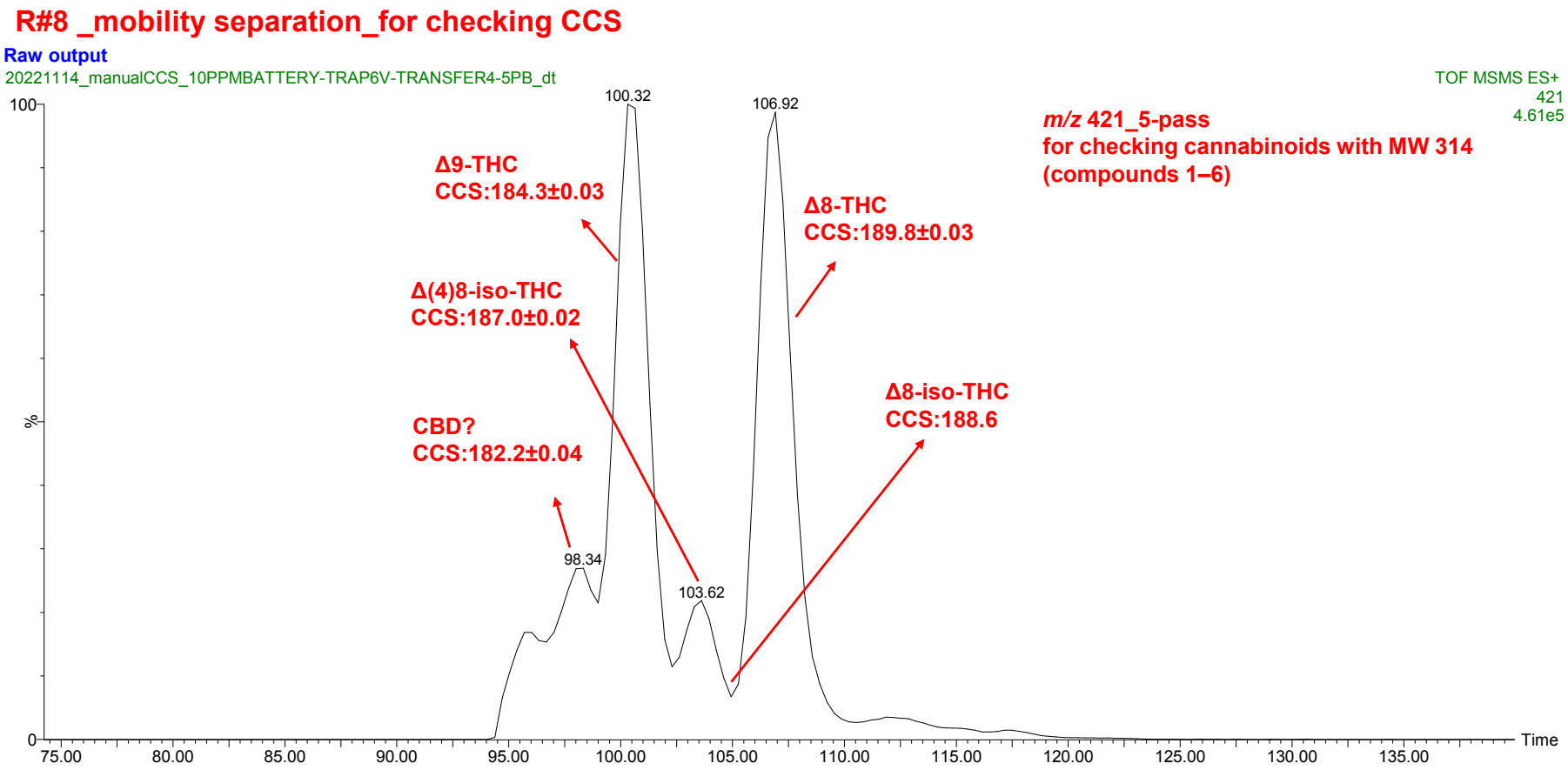
20221114_manualCCS_10PPMBATTERY-TRAP6V-TRANSFER4-5PB 1 (0.018)

TOF MSMS 421.10ES+
7.91e4



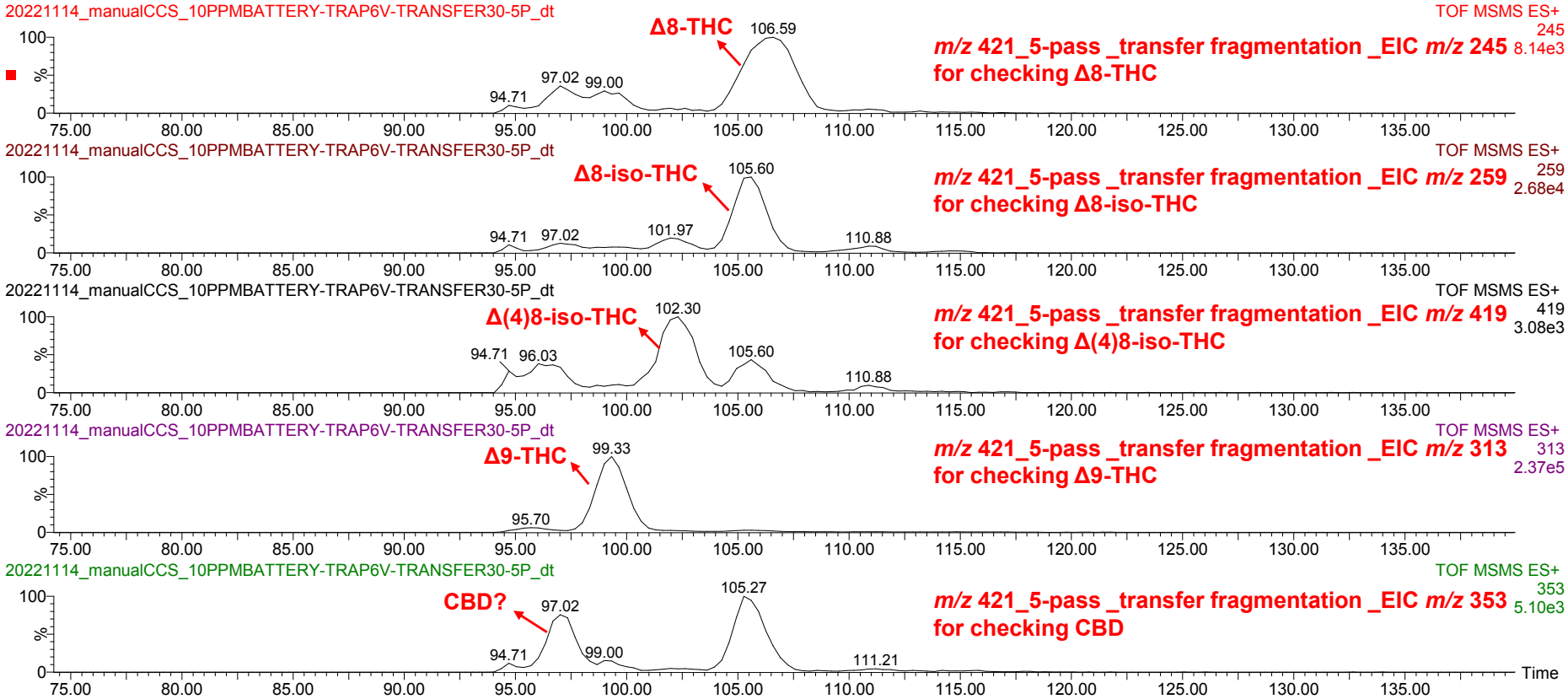
SIM_checking Ag(I) adducts of cannabinoids with MW 314 (compounds 1–6) at *m/z* 421/423

Found


R#8 _mobility separation_for checking CCS
Raw output
20221114_manualCCS_10PPMBATTERY-TRAP6V-TRANSFER4-5PB_dt
TOF MSMS ES+
421
4.61e5
m/z 421_5-pass
for checking cannabinoids with MW 314
(compounds 1–6)
Δ9-THC
CCS:184.3±0.03
Δ8-THC
CCS:189.8±0.03
Δ(4)8-iso-THC
CCS:187.0±0.02
Δ8-iso-THC
CCS:188.6
CBD?
CCS:182.2±0.04
100.32
106.92
98.34
103.62
100
%
0
Time
75.00
80.00
85.00
90.00
95.00
100.00
105.00
110.00
115.00
120.00
125.00
130.00
135.00

R#8_mobility separation+transfer fragmentation_for checking fragments

Raw output



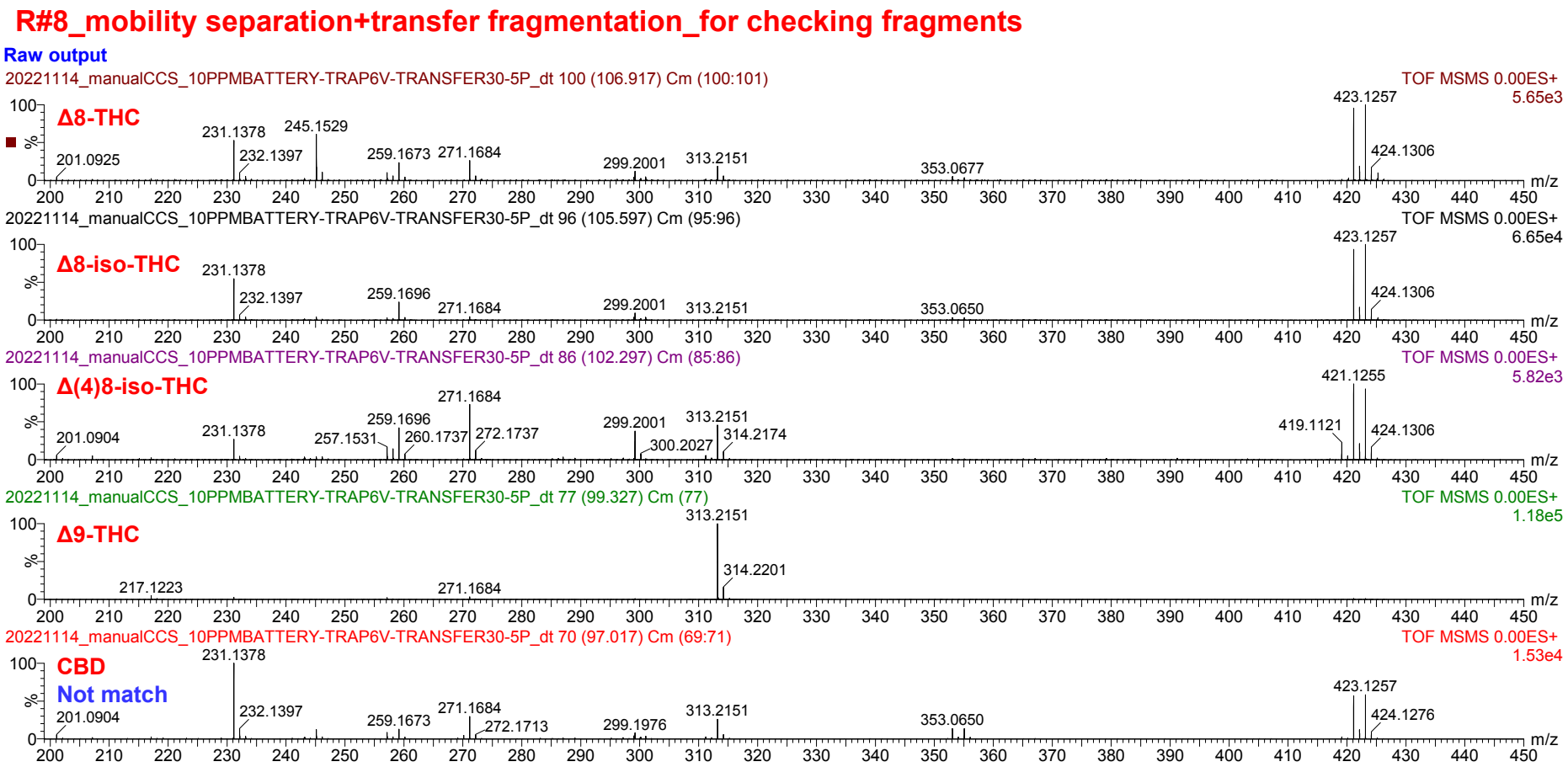


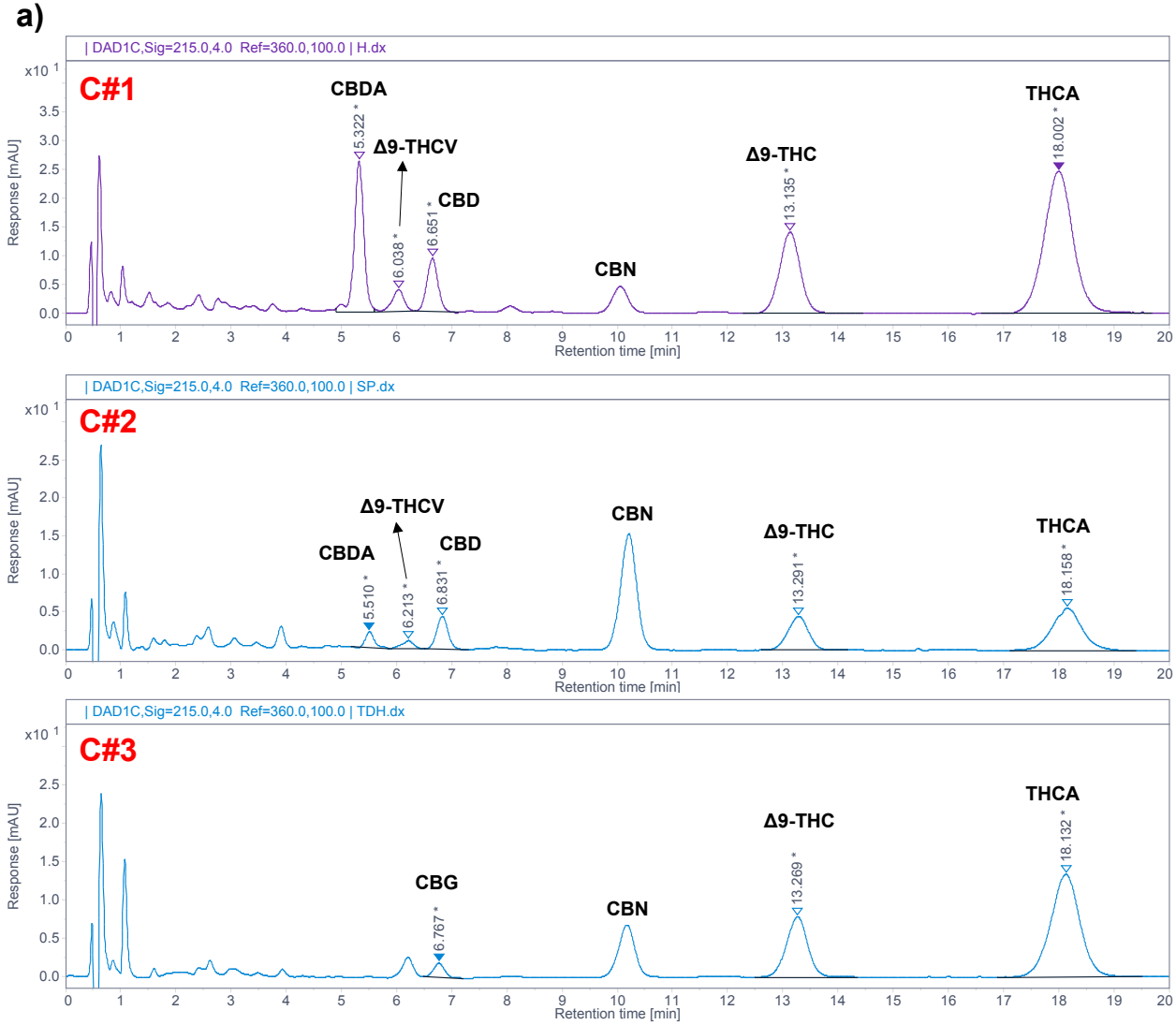
Figure S14-13. Mobiligram and mass spectra of cannabinoids in sample R#8.

Table S7. CCS values of detected cannabinoids in samples.

Sample	Δ8-THC	Δ9-THC	Δ3-THC	CBD	Δ8-iso-THC	Δ(4)8-iso-THC	THCA	CBDA	Δ8-THCV and Δ8-iso-THCV	Δ9-THCV	9α-hydroxyhexahydrocannabinol	9β-hydroxyhexahydrocannabinol	8-hydroxy-iso-THC
C#1	/	184.2±0.01 (0.2%)	/	182.1±0.01 (0.2%)	/	/	191.6±0.03 (0.4%)	189.2±0.01 (0.3%)	/	185.5 (0.3%)	/	/	/
C#2	/	184.4±0.01 (0.3%)	/	182.3±0.02 (0.3%)	/	/	192.1±0.01 (0.6%)	189.7±0.04 (0.6%)	/	185.1±0.01 (0.1%)	/	/	/
C#3	/	184.2±0.02 (0.2%)	/	/	/	/	191.6±0.02 (0.4%)	/	/	/	/	/	/
G#1	190.3±0.01 (−0.3%)	184.0±0.01 (0.05%)	/	/	/	186.5±0.02 (−0.3%)	/	/	/	/	/	/	/
G#2	190.9±0.08 (0)	184.4±0.04 (0.3%)	193.7±0.04 (0.4%)	/	/	187.1±0.03 (0)	/	/	/	/	196.0±0.03 (0.2%)	184.9±0.04 (−0.5%)	/
R#1	190.2±0.01 (−0.4%)	184.0±0.08 (0.05%)	/	181.1±0.07 (−0.4%)	188.9±0.1 (−0.3%)	/	NA	NA	NA	NA	NA	NA	NA
R#2	190.9±0.02 (0)	184.2±0.01 (0.2%)	/	182.1±0.02 (0.2%)	188.8* (−0.4%)	/	NA	NA	NA	NA	NA	NA	NA
R#3	190.1±0.2 (−0.4%)	184.1±0.09 (0.1%)	/	/	/	186.6±0.09 (−0.3%)	NA	NA	NA	NA	NA	NA	NA
R#4	190.6±0.1 (−0.2%)	184.0±0.01 (0.05%)	/	/	188.5* (−0.5%)	186.7±0.07 (−0.2%)	NA	NA	NA	NA	NA	NA	NA
R#5	189.6±0.01 (−0.7%)	184.4±0.01 (0.3%)	/	182.4±0.01 (0.3%)	188.6* (−0.5%)	186.9±0.02 (−0.1%)	NA	NA	NA	NA	NA	NA	NA
R#6	189.7±0.02 (−0.6%)	184.3±0.03 (0.2%)	/	182.2±0.02 (0.2%)	188.2* (−0.7%)	186.9±0.02 (−0.1%)	NA	NA	NA	N	NA	NA	NA
R#7	/	/	/	182.4±0.03 (0.3%)	/	/	NA	NA	NA	NA	NA	NA	NA
R#8	189.8±0.03 (−0.6%)	184.3±0.03 (0.2%)	/	/	188.6* (−0.5%)	187.0±0.02 (−0.05%)	NA	NA	NA	NA	NA	NA	NA

Values in brackets represent the relative deviation compared to the CCS values ($^{TW}CCS_{N2}$ (Å^2)) from standards; ± SD (n=3); NA represents “not analyzed”; * represents the drift time decided by characteristic fragment due to the overlap of precursor ions.

a)


| DAD1C,Sig=215.0,4.0 Ref=360.0,100.0 | H.dx
C#1
CBDA
5.322 *
Δ9-THCV
6.038 *
CBD
6.651 *
CBN
Δ9-THC
13.135 *
THCA
18.002 *
Response [mAU]
Retention time [min]
| DAD1C,Sig=215.0,4.0 Ref=360.0,100.0 | SP.dx
C#2
CBDA
5.510 *
Δ9-THCV
6.213 *
CBD
6.831 *
CBN
Δ9-THC
13.291 *
THCA
18.158 *
Response [mAU]
Retention time [min]
| DAD1C,Sig=215.0,4.0 Ref=360.0,100.0 | TDH.dx
C#3
CBG
6.767 *
CBN
Δ9-THC
13.269 *
THCA
18.132 *
Response [mAU]
Retention time [min]

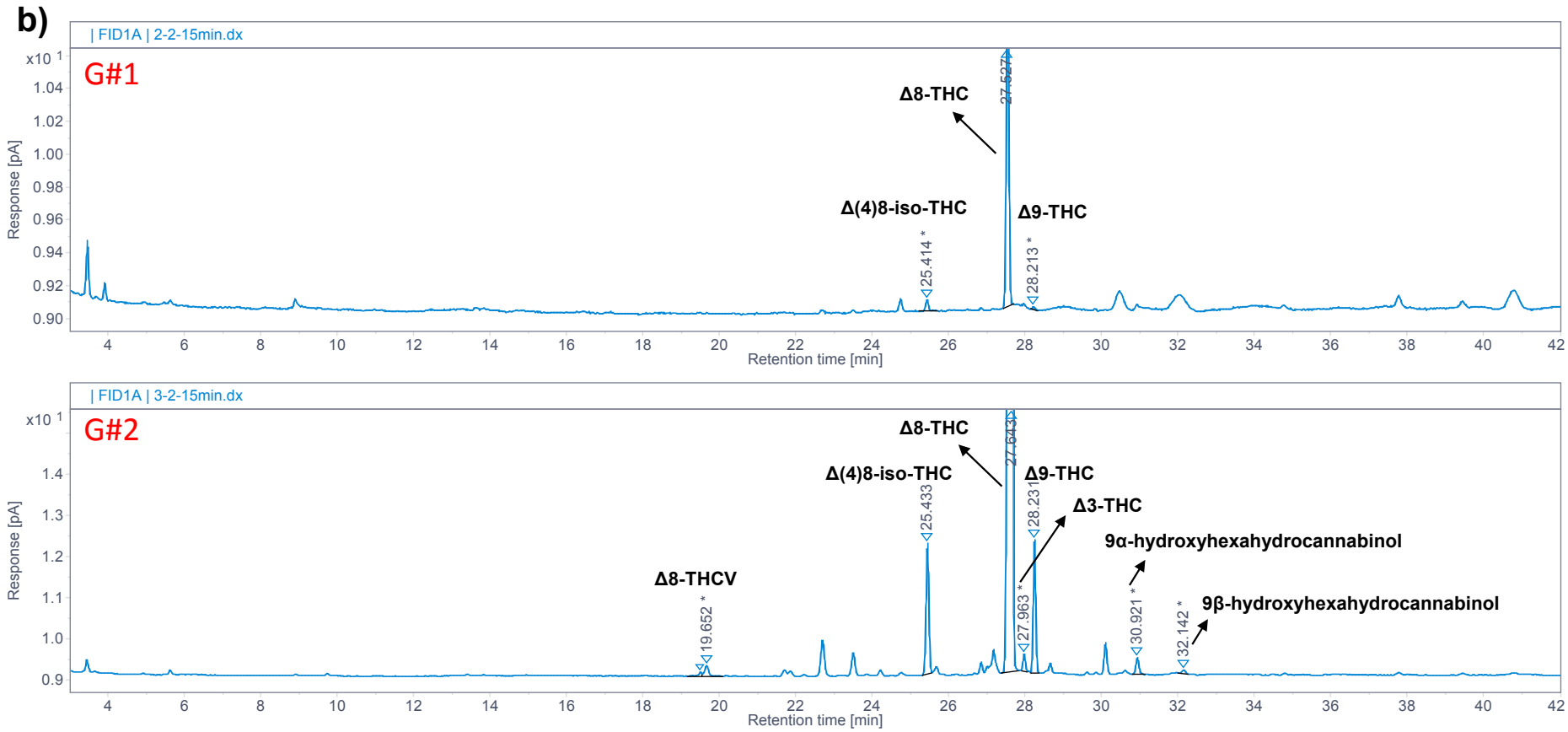


Figure S15. a) Reversed-phase UHPLC-UV (215 nm) profile of samples C#1, C#2, and C#3; b) GC-FID profile of samples G#1 and G#2.

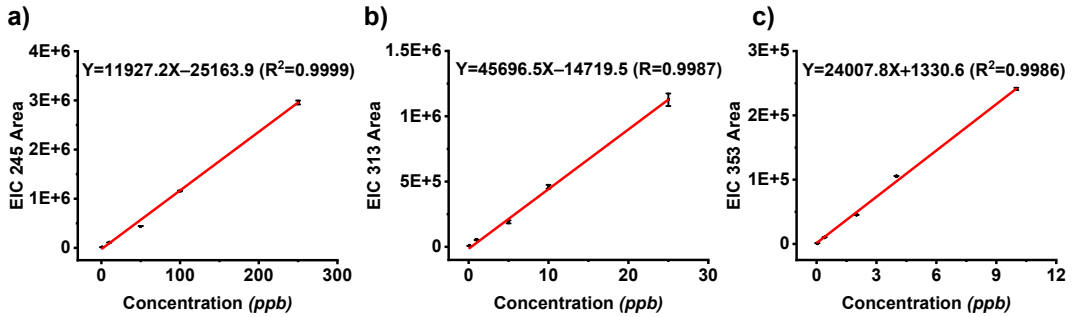


Figure S16. Calibration curves between the extracted ion chromatogram peak area of characteristic fragments and concentrations of a) Δ8-THC, b) Δ9-THC, and c) CBD. Error bars represent the standard deviation (n=3).

Table S8. Absolute weight percentages (w/w%, after solvent evaporation) of Δ8-THC, Δ9-THC, and CBD in acid-treated CBD mixtures by cIMS and GC-FID.

	Δ8-THC			Δ9-THC			CBD		
Sample	GC-FID	cIMS	Deviation	GC-FID	cIMS	Deviation	GC-FID	cIMS	Deviation
R#1	11 (2.6%)	15 (0.4%)	36%	49 (0.3%)	70 (0.4%)	43%	26 (2.0%)	36 (0.2%)	39%
R#2	26 (4.0%)	30 (3.2%)	15%	48 (0.1%)	61 (3.2%)	27%	6.9 (0.4%)	6.6 (3.1%)	−4%
R#3	78 (2.1%)	115 (0.9%)	47%	1.6 (1.1%)	2.4 (0.3%)	50%	ND[b]	ND[b]	/
R#4	70 (1.8%)	96 (1.3%)	37%	1.1 (5.6%)	2.9 (1.1%)	164%	ND[b]	ND[b]	/
R#5	14 (3.7%)	23 (1.1%)	64%	6.3 (5.2%)	11 (0.9%)	75%	ND	0.6 (2.2%)	/
R#6	8.1 (0.5%)	13 (0.7%)	61%	8.9 (1.2%)	14 (1.2%)	57%	4.2 (0.2%)	1.2 (1.8%)	−71%
R#7	ND	ND	/	ND	ND	/	48 (0.7%)	59 (0.5%)	23%
R#8	1.4 (1.1%)	3.1 (1.3%)	121%	5.0 (2.5%)	6.7 (1.0%)	34%	ND	ND	/

All values are average of triplicate experiments; ND: Not detected (<LOD).

Table S9. Ratio of Δ9-THC/Δ8-THC in acid-treated CBD mixtures analyzed by cIMS and GC-FID.

Sample	Δ8-THC		Δ9-THC		Δ9-THC/Δ8-THC ratio	
	GC-FID	cIMS	GC-FID	cIMS	GC-FID	cIMS
R #1	11 (2.6%)	15 (0.4%)	49 (0.3%)	70 (0.4%)	4.5	4.7
R #2	26 (4.0%)	30 (3.2%)	48 (0.1%)	61 (3.2%)	1.8	2.0
R #3	78 (2.1%)	115 (0.9%)	1.6 (1.1%)	2.4 (0.3%)	0.02	0.02
R #4	70 (1.8%)	96 (1.3%)	1.1 (5.6%)	2.9 (1.1%)	0.02	0.03
R #5	14 (3.7%)	23 (1.1%)	6.3 (5.2%)	11 (0.9%)	0.45	0.48
R #6	8.1 (0.5%)	13 (0.7%)	8.9 (1.2%)	14 (1.2%)	1.1	1.1
R #7	ND	ND	ND	ND	/	/
R #8	1.4 (1.1%)	3.1 (1.3%)	5.0 (2.5%)	6.7 (1.0%)	3.6	2.2

All values are average of triplicate experiments; ND: Not detected (<LOD).

Table S10. Comparison of LODs between the cIMS method and GC-FID method[1]

	cIMS	GC-FID
Injection volume	5 µL	1 µL
split ratios	NA	Split ratio for injector 1:10, split ratio for detector 1:1.
LOD expressed as concentration	0.2 $ng \cdot ml^{-1}$ for Δ8-THC, 0.04 $ng \cdot ml^{-1}$ for Δ9-THC, and 0.008 $ng \cdot ml^{-1}$ for CBD.	0.3 $\mu g \cdot ml^{-1}$ for Δ8-THC, 0.3 $\mu g \cdot ml^{-1}$ for Δ9-THC, and 1.3 $\mu g \cdot ml^{-1}$ for CBD.
LOD expressed as absolute mass	1 pg for Δ8-THC, 0.2 pg for Δ9-THC, and 0.04 pg for CBD.	15 pg for Δ8-THC, 15 pg for Δ9-THC, and 65 pg for CBD.

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