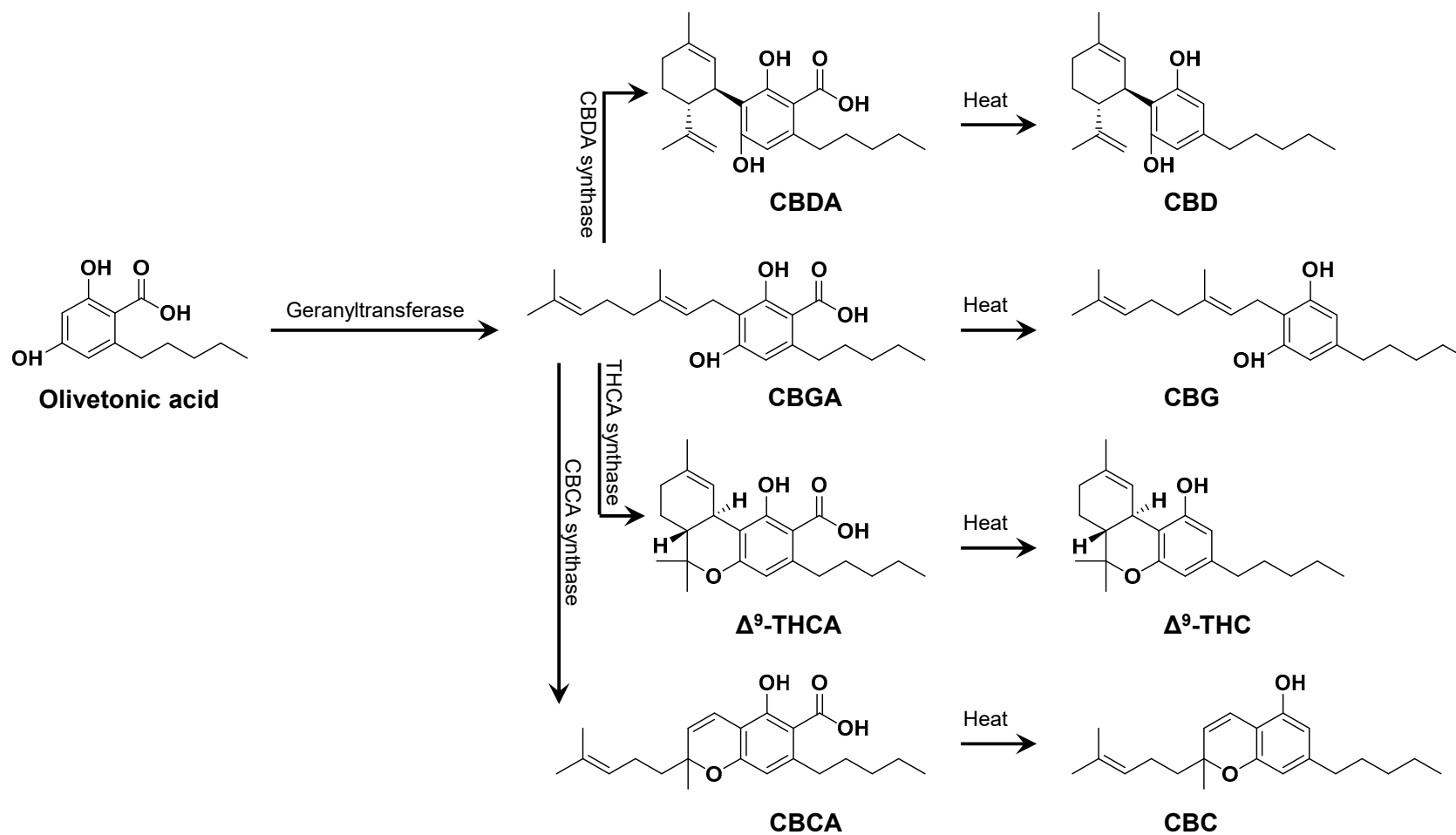
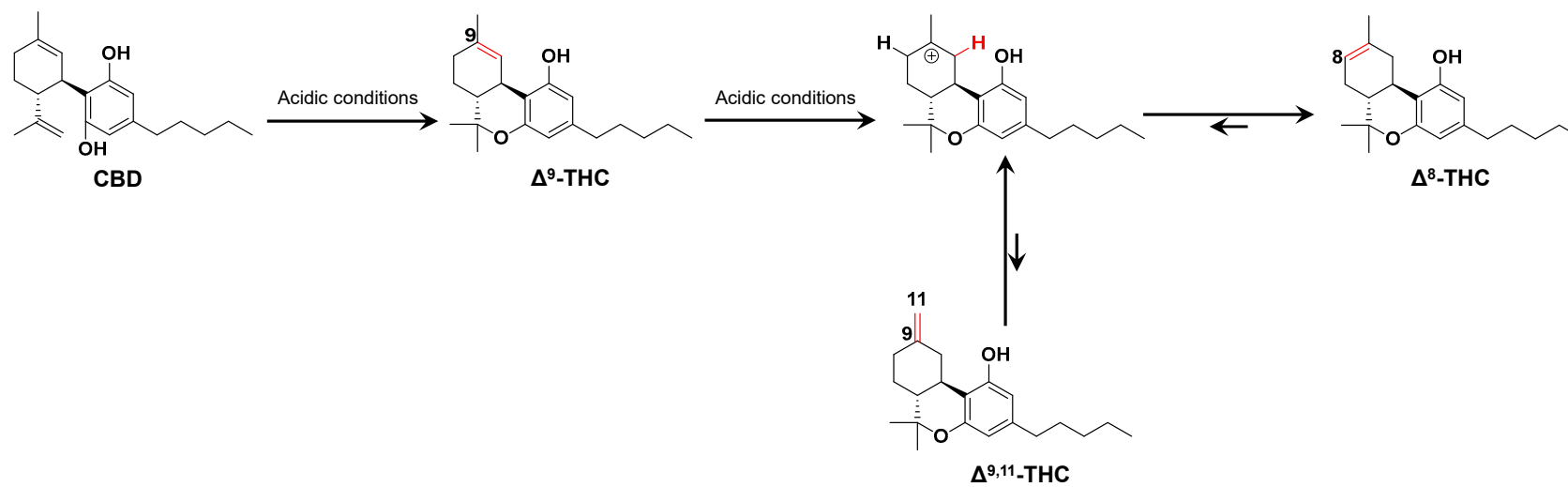


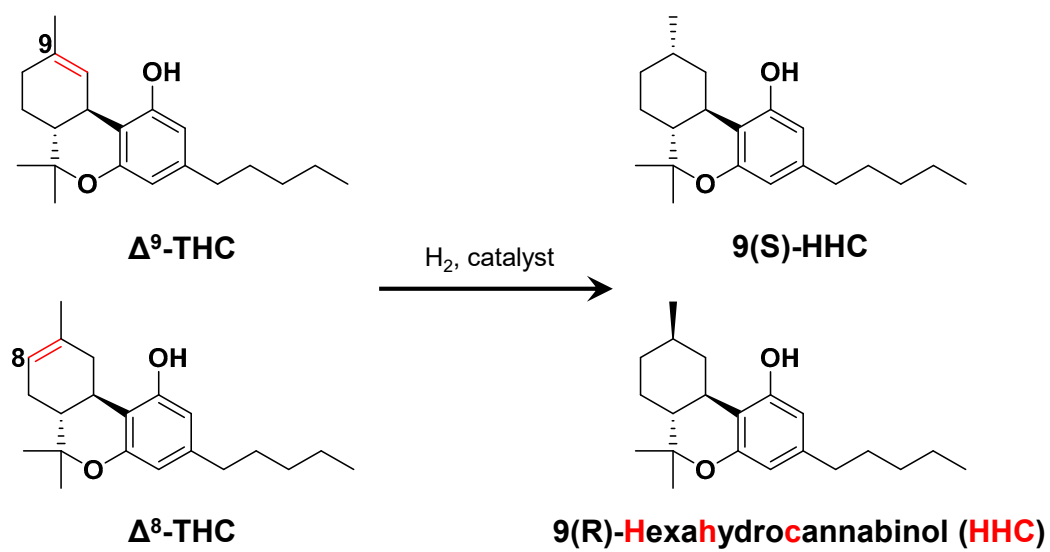
Supplementary Figure S1. Biosynthetic pathways of natural cannabinoids.



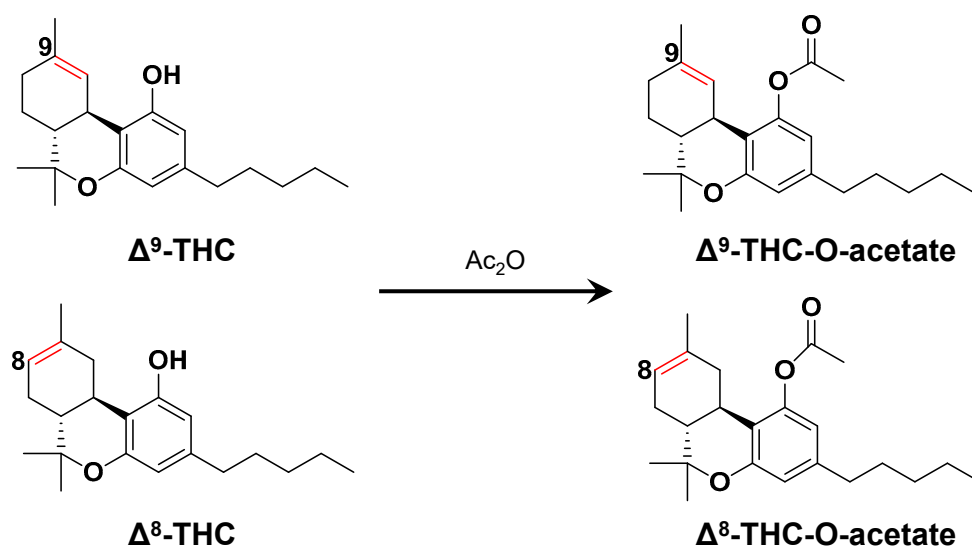
Supplementary Figure S2. Synthetic pathways of THC isomers: Δ^9 -/ Δ^8 -/ $\Delta^{9,11}$ -THC.



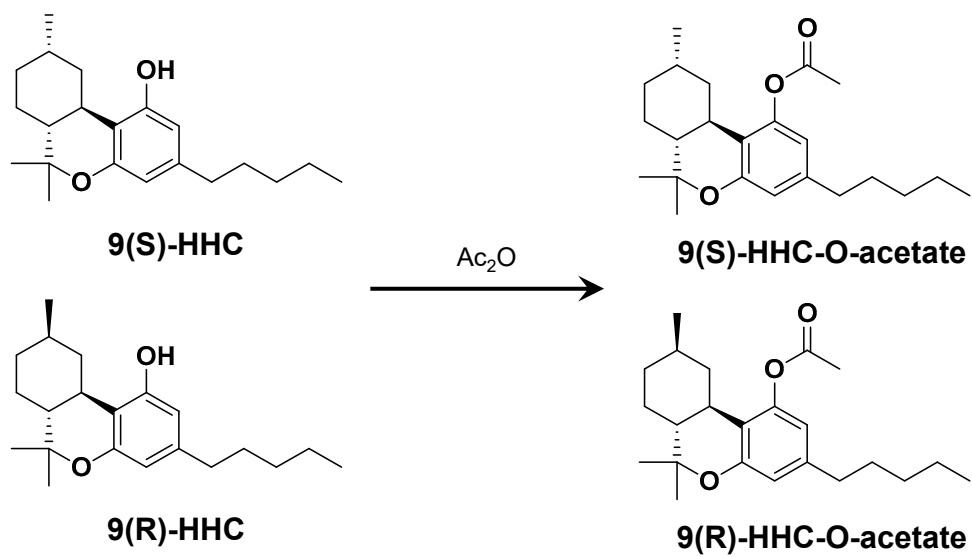
Supplementary Figure S3. Synthetic pathways of THC analogs: 9(S)/9(R)-HHC.



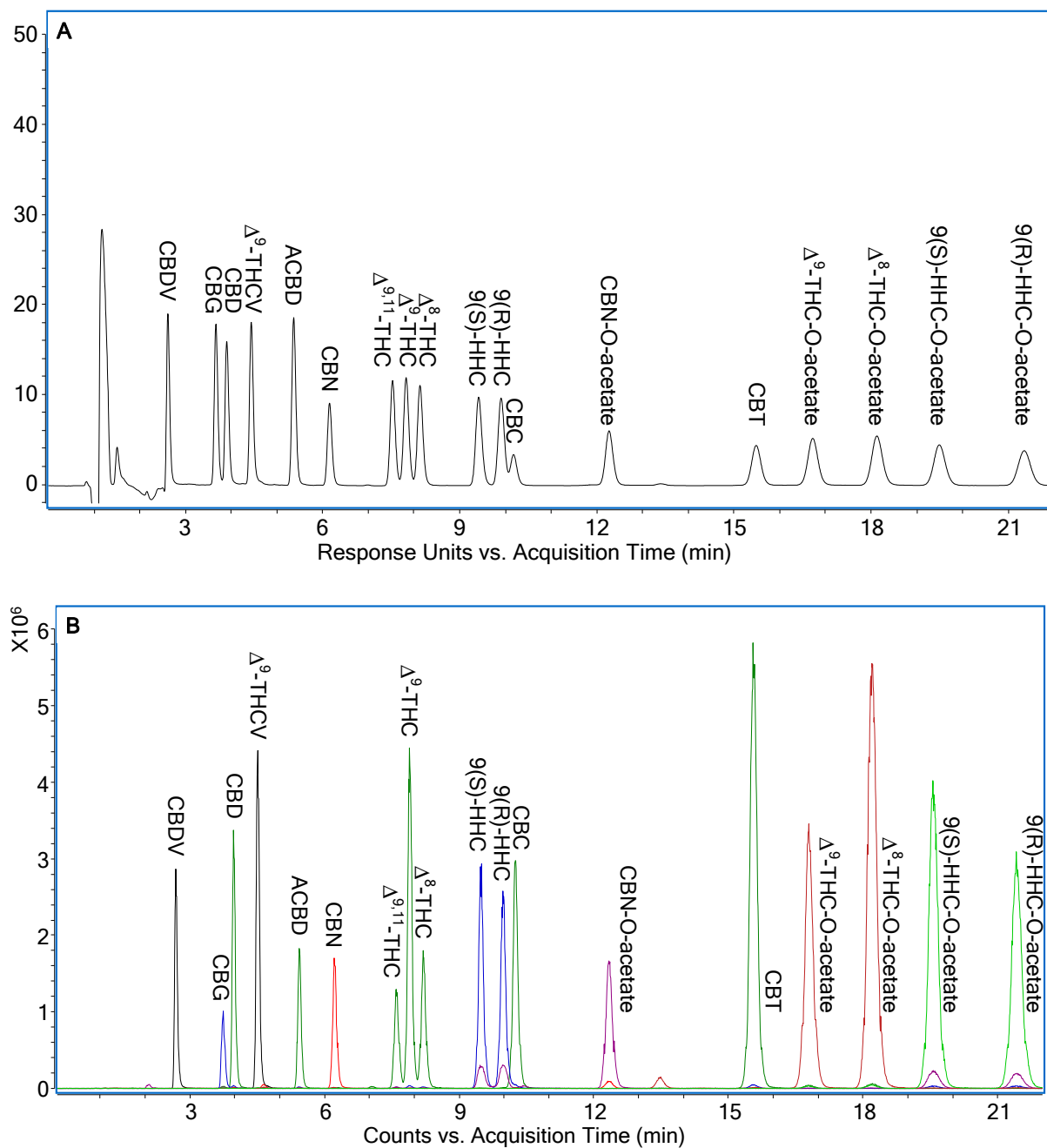
Supplementary Figure S4. Synthetic pathways of THC analogs: Δ^9 -/ Δ^8 -THC-O-acetate.



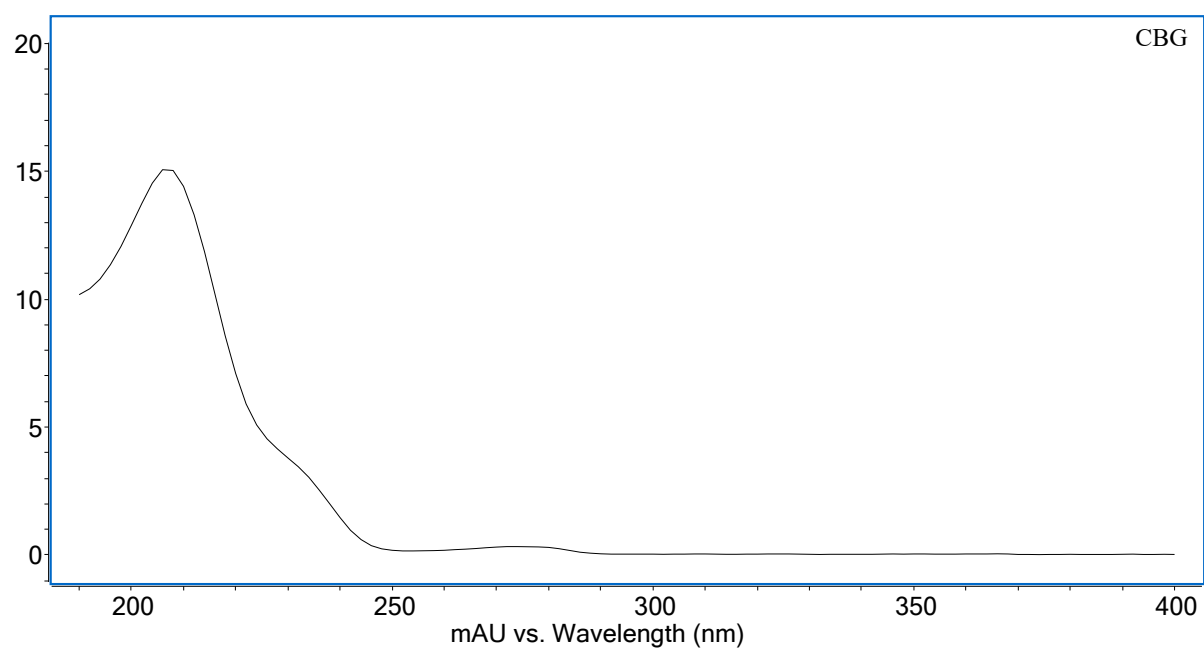
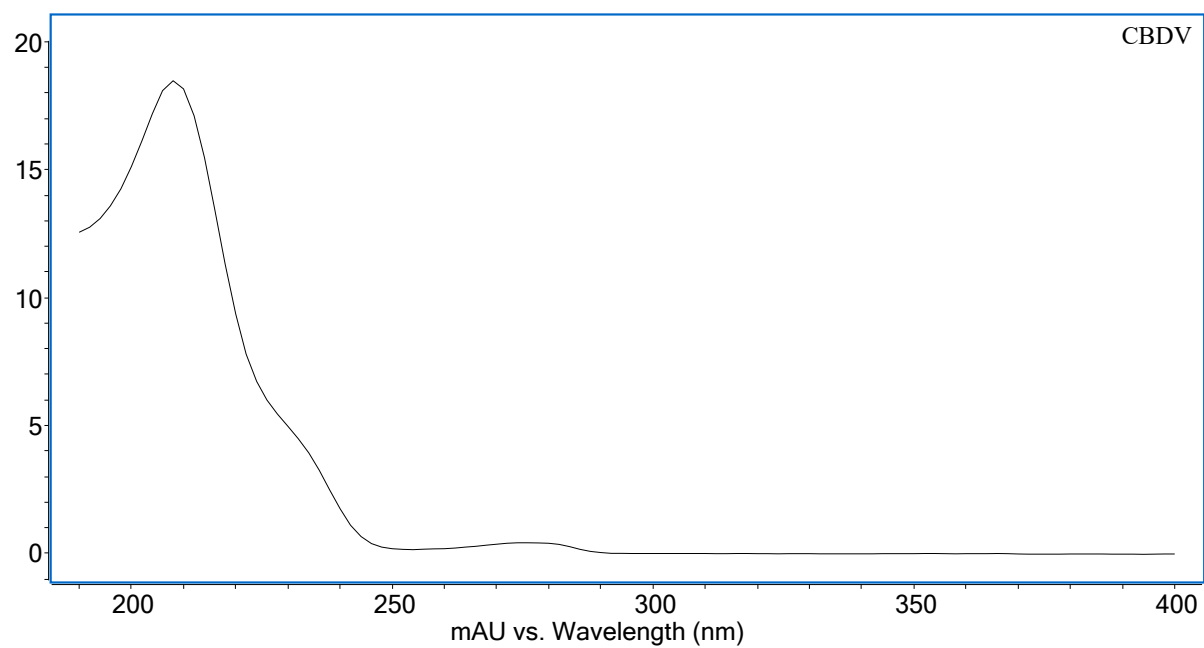
Supplementary Figure S5. Synthetic pathways of THC analogs: 9(S)/9(R)-HHC-O-acetate.

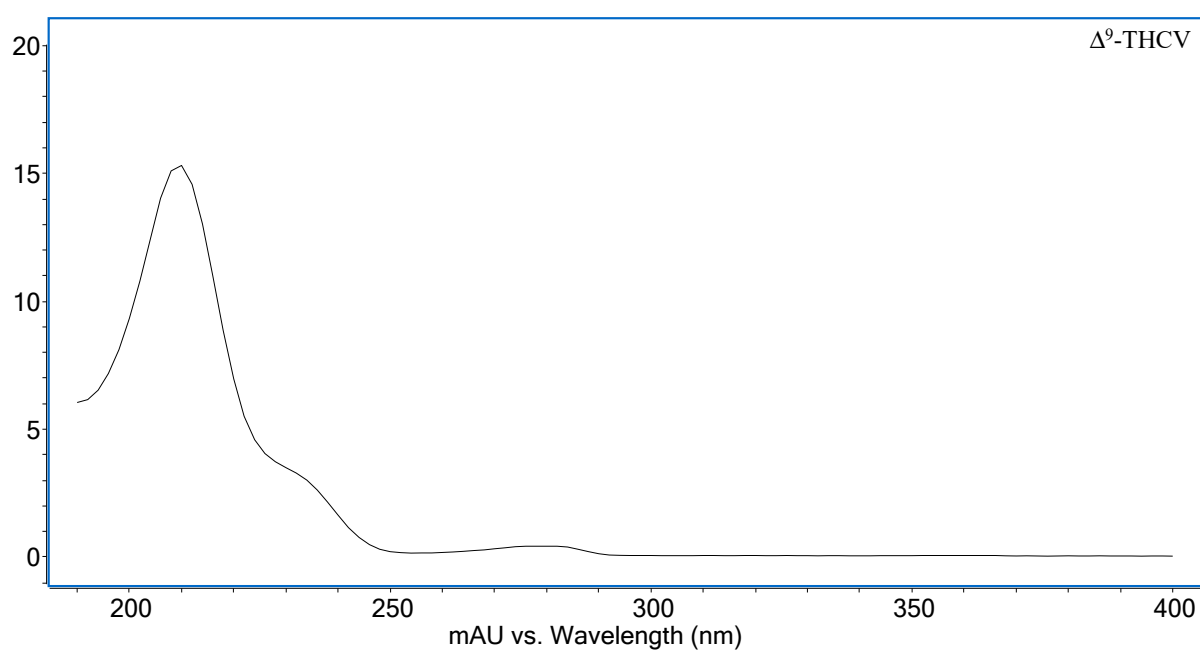
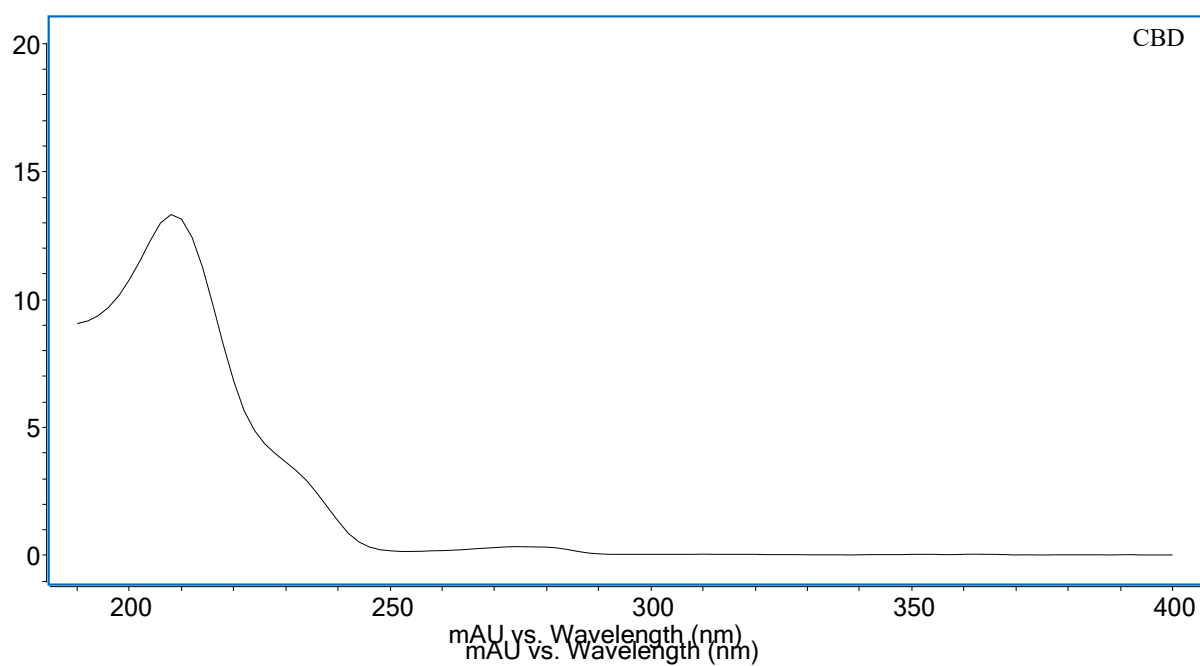


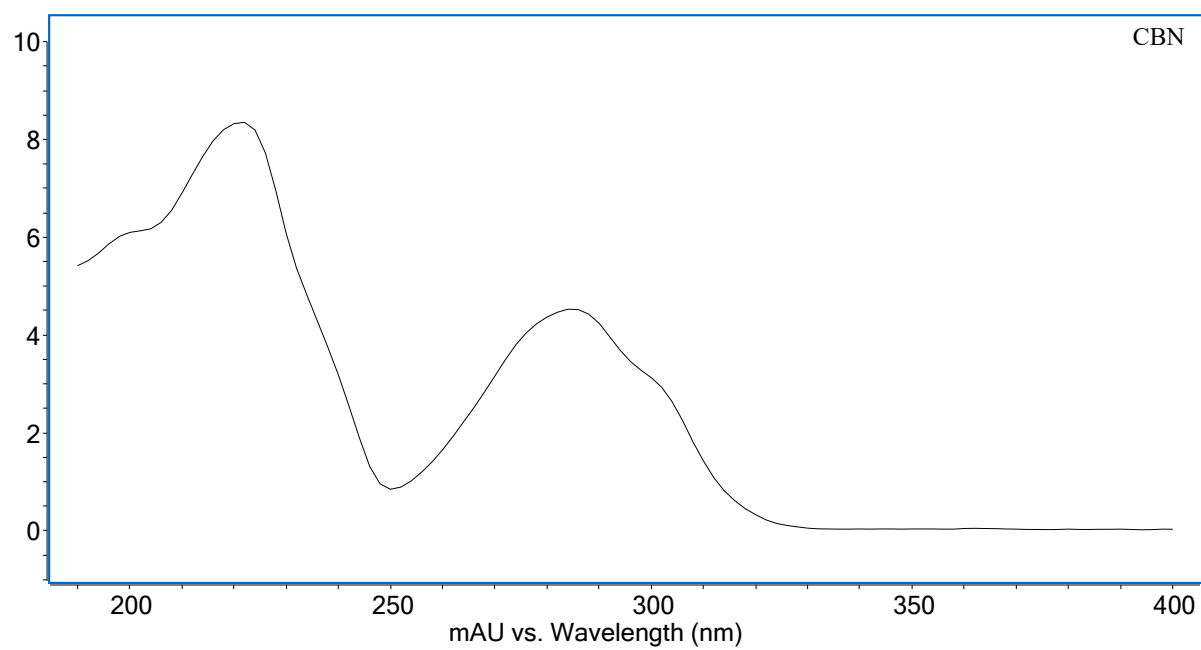
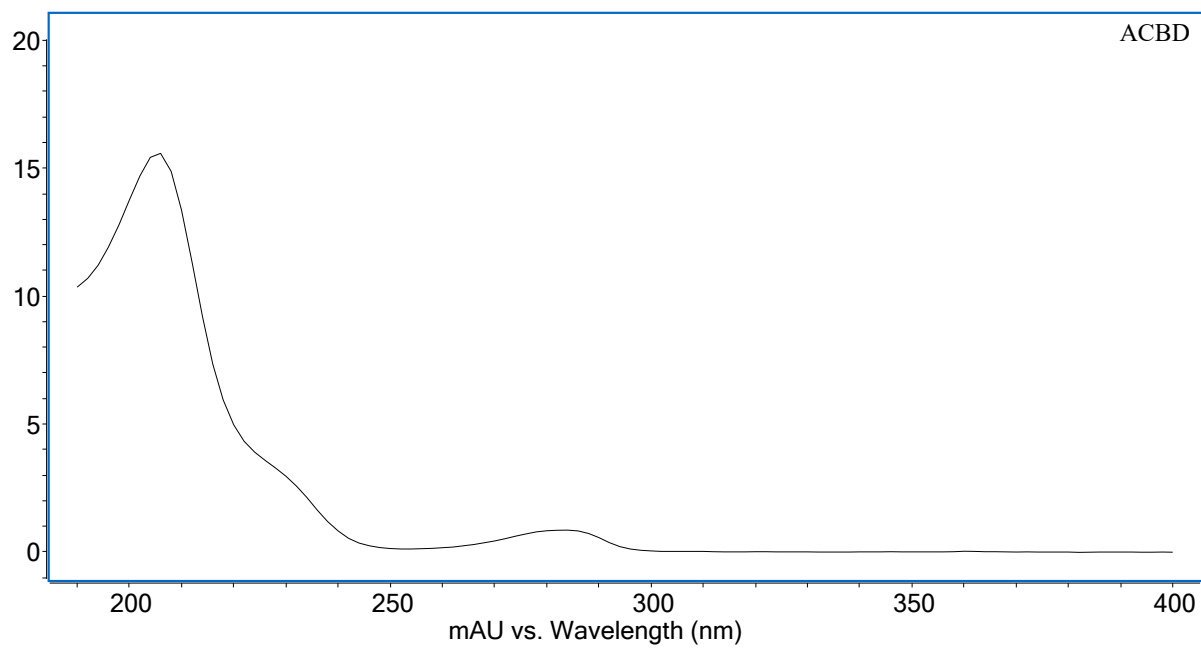
Supplementary Figure S6. LC separation of the eighteen cannabinoids using an Agilent Poroshell 120 EC-C18 column (150 mm × 2.1 mm, 2.7 μm): (A) LC-UV chromatogram at 208 nm; (B) Corresponding LC-ESI/TOFMS EICs of the eighteen cannabinoids in **Supplementary Figure S6A** using their $[M+H]^+$ ions with ± 20 ppm.. The A solvent was 0.02% (v/v) formic acid. The B solvent was acetonitrile. The mobile phase contained 75.0% (v/v) B. The flow rate was 0.3 mL/min. The eighteen cannabinoids were at 1 μg/mL individual concentration.

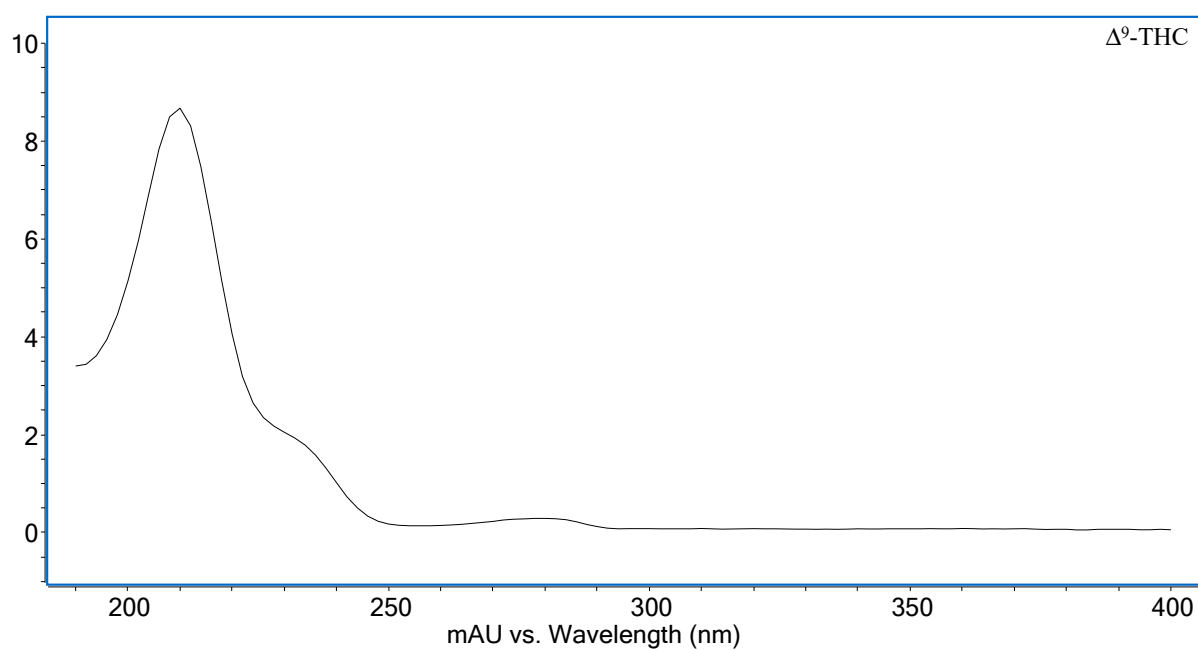
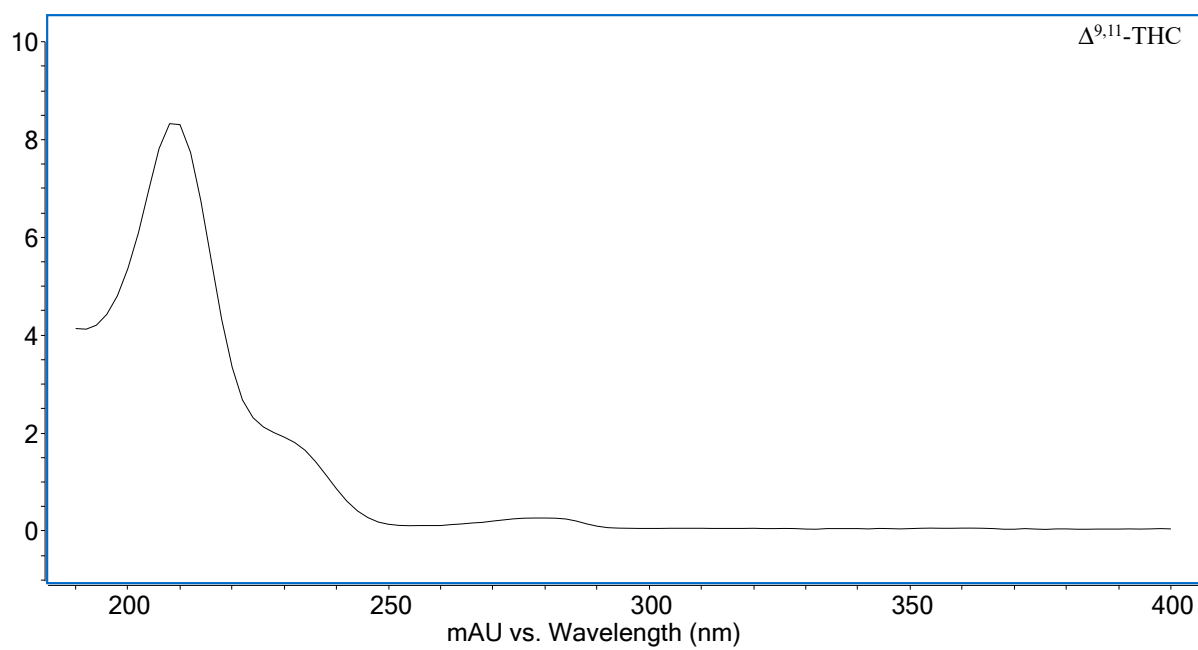


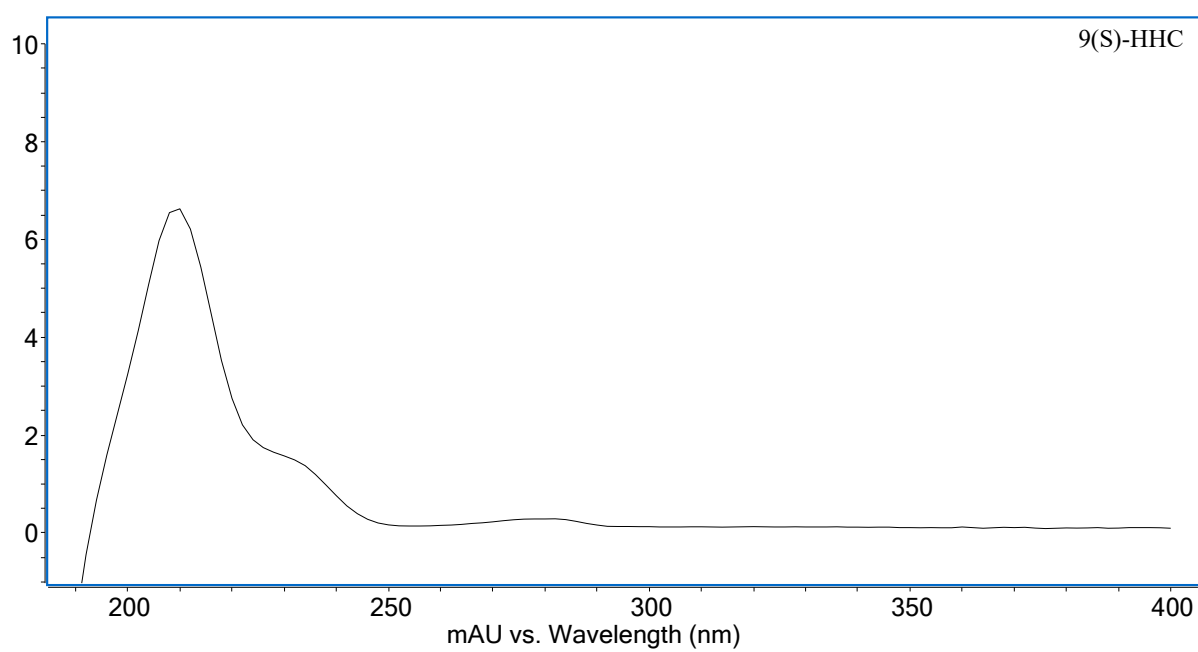
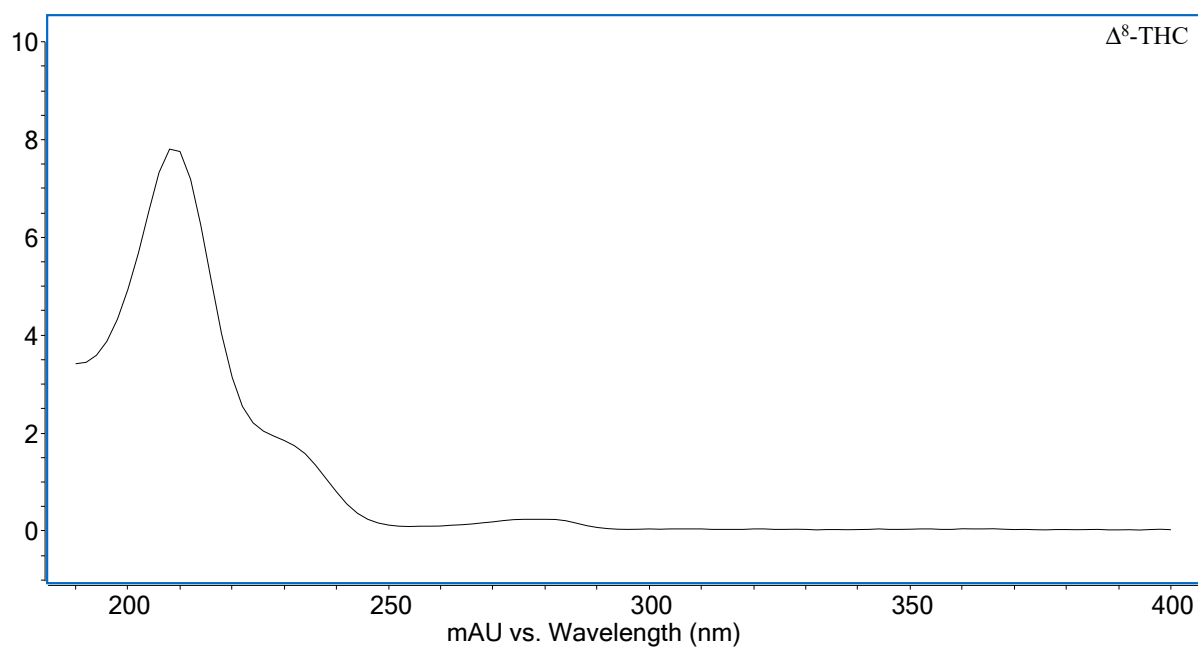
Supplementary Figure S7. UV absorption spectra of the eighteen cannabinoids that were extracted from **Figure 2A**.

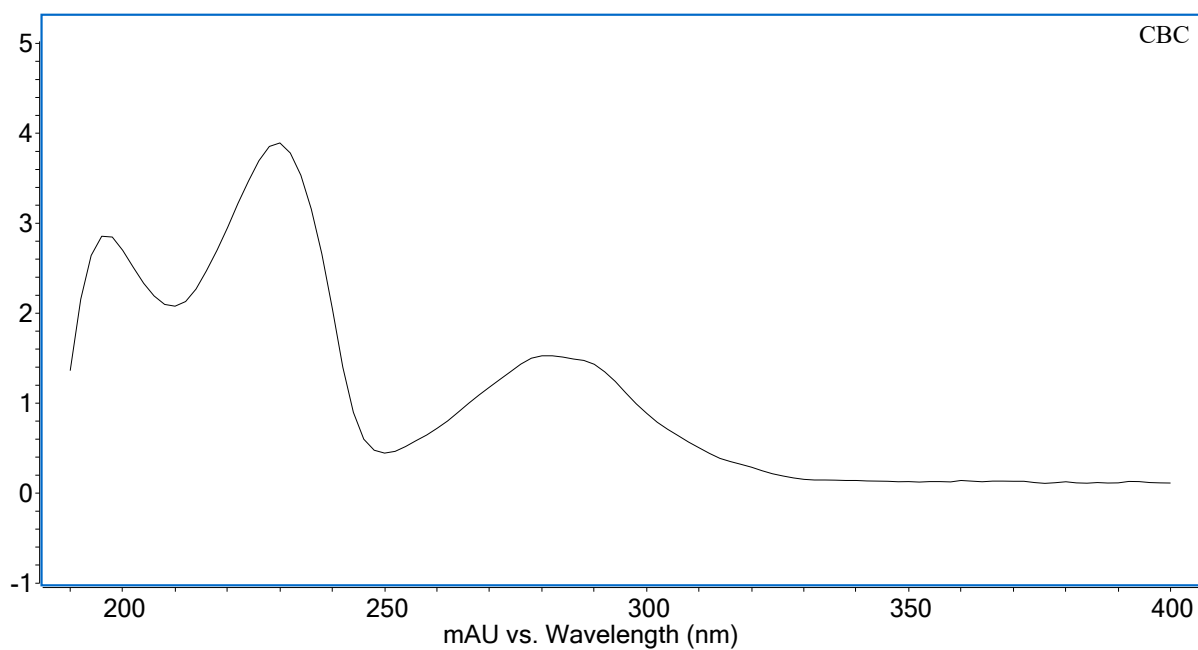
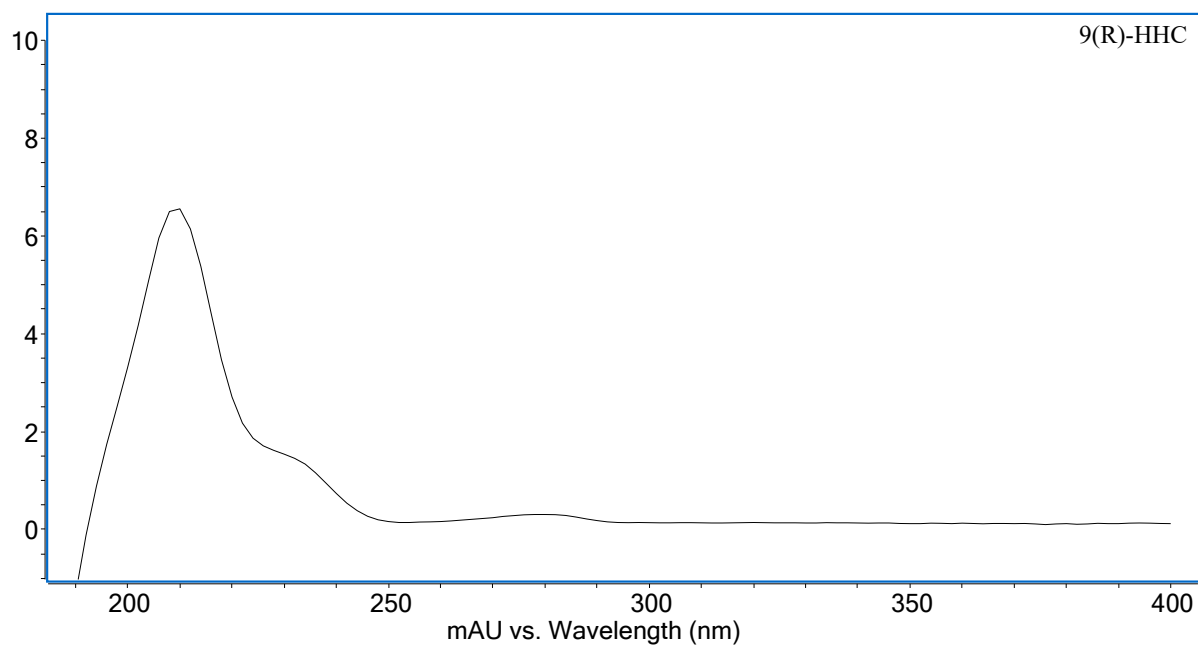


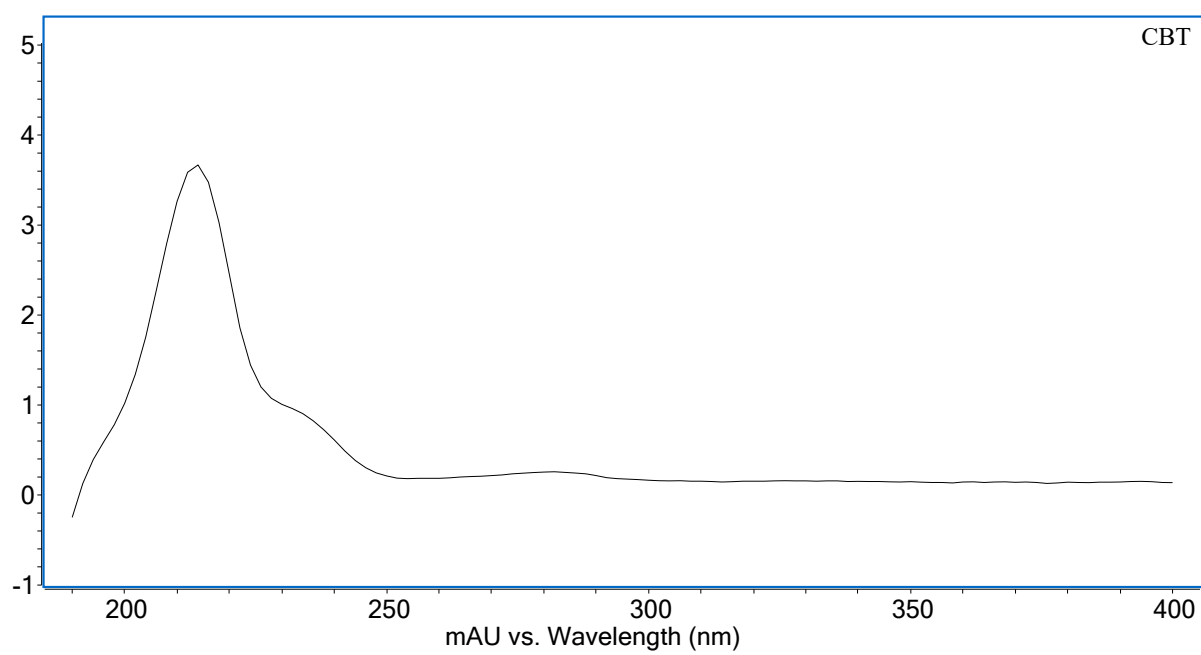
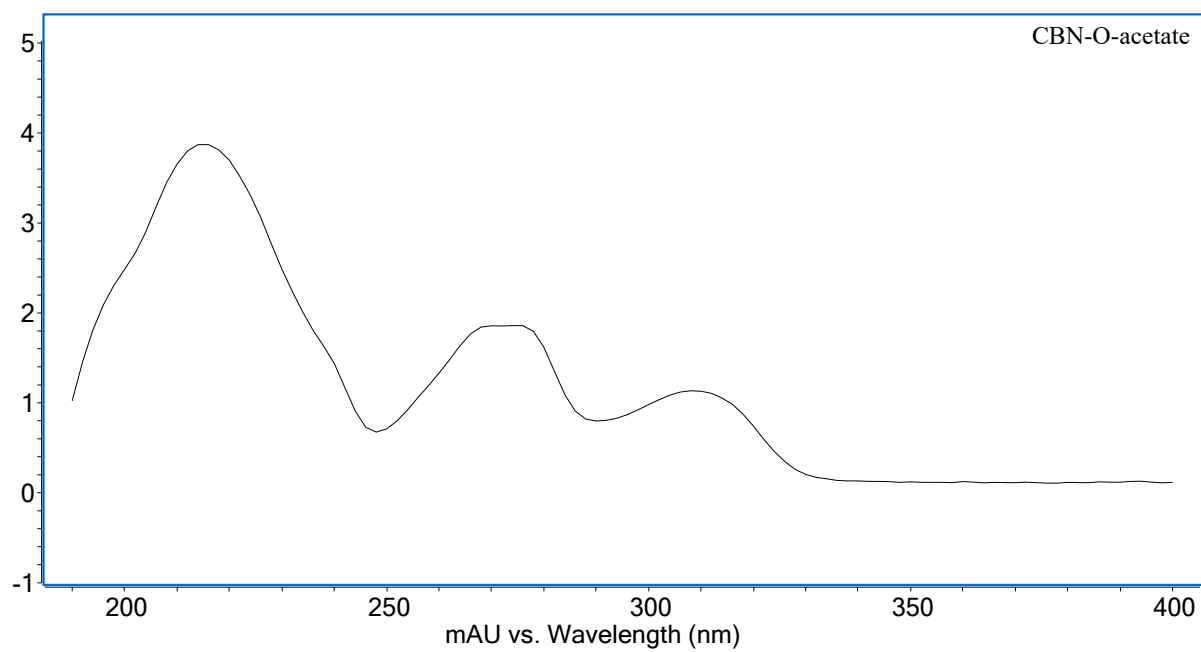


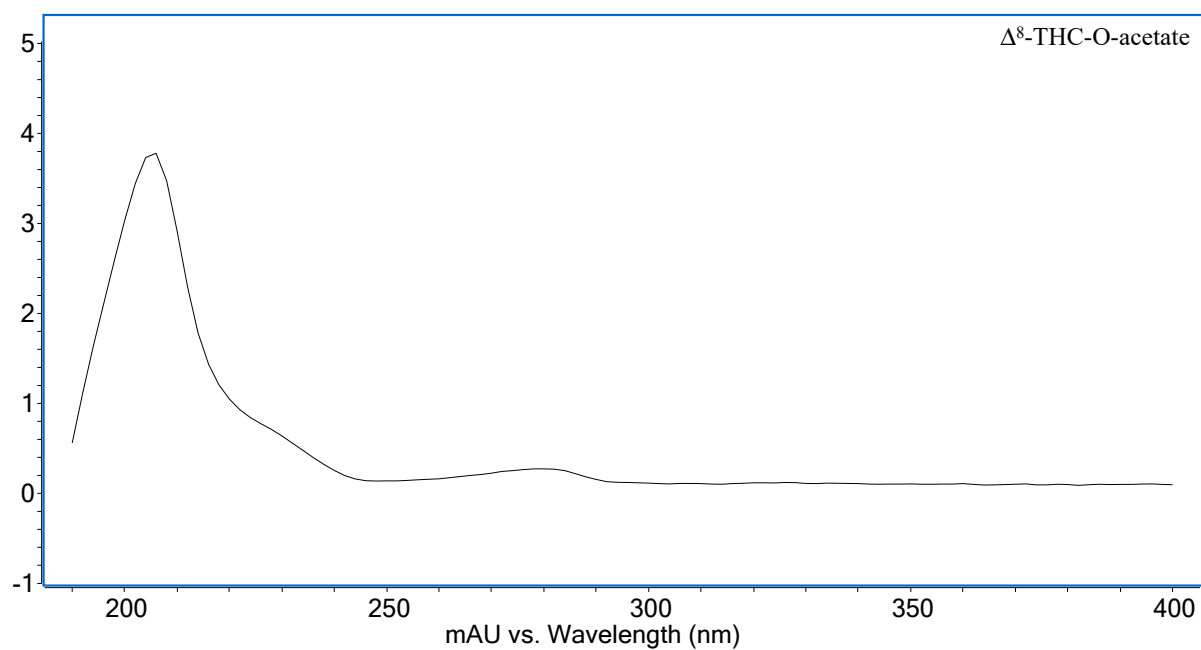
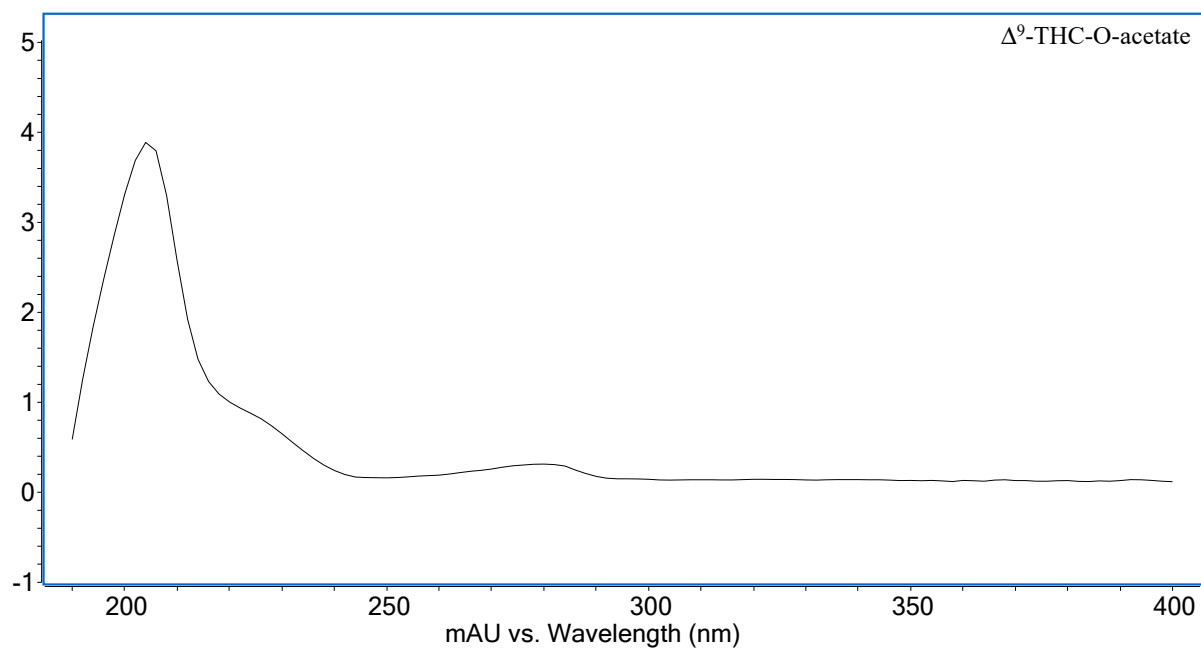


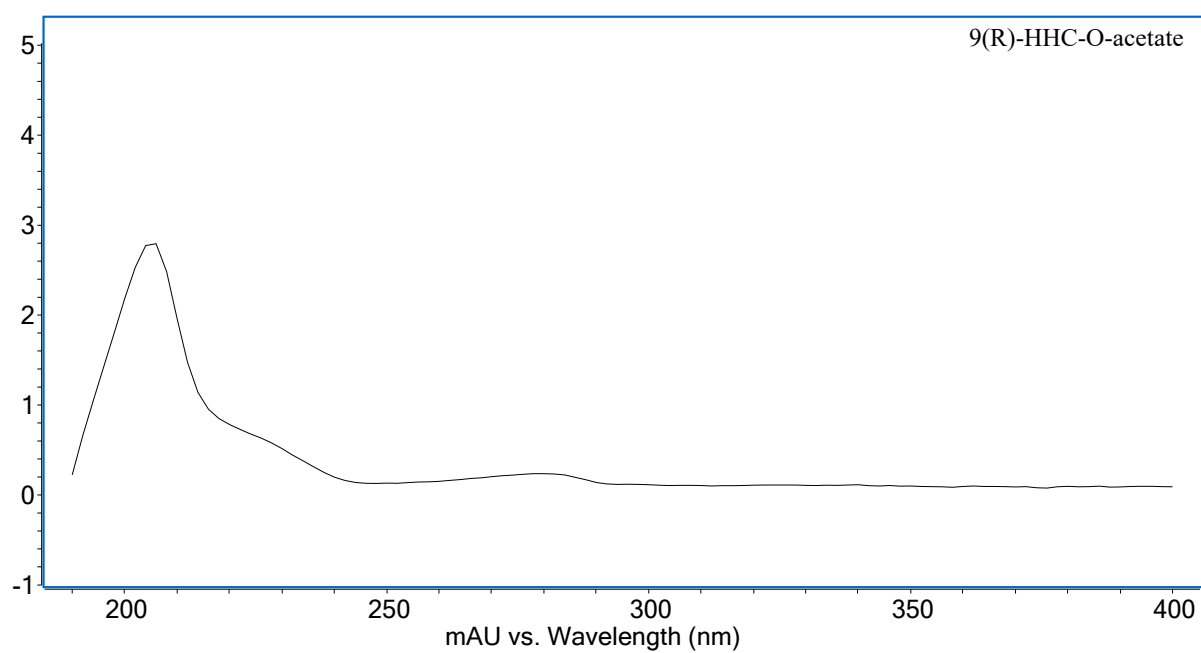
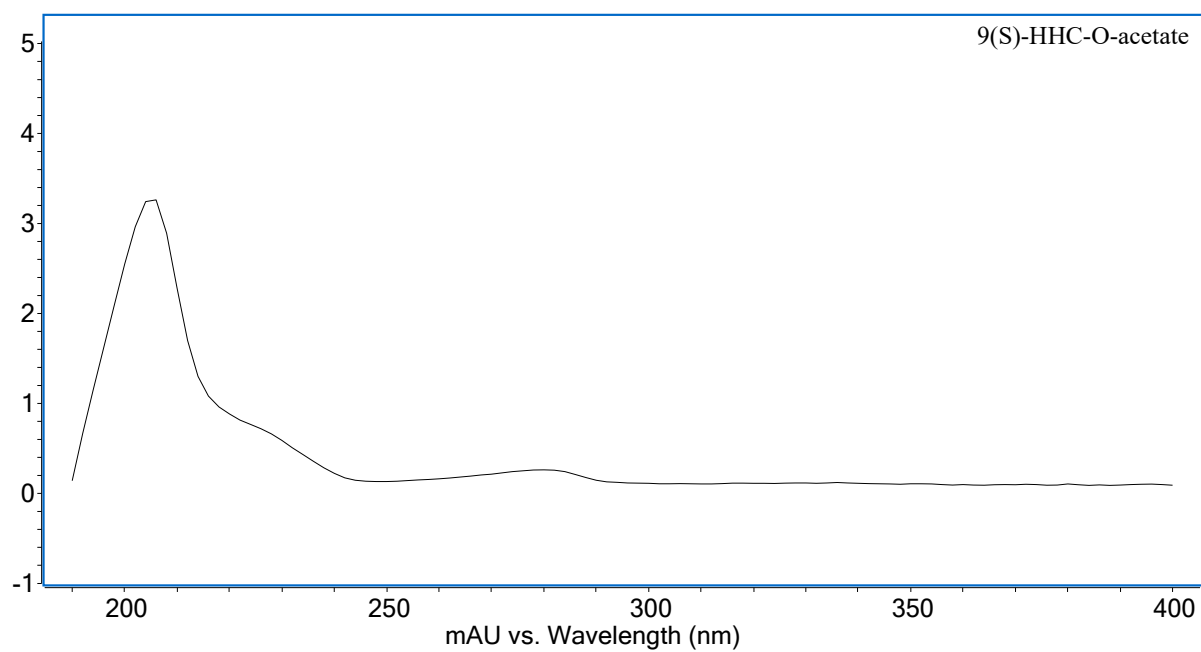




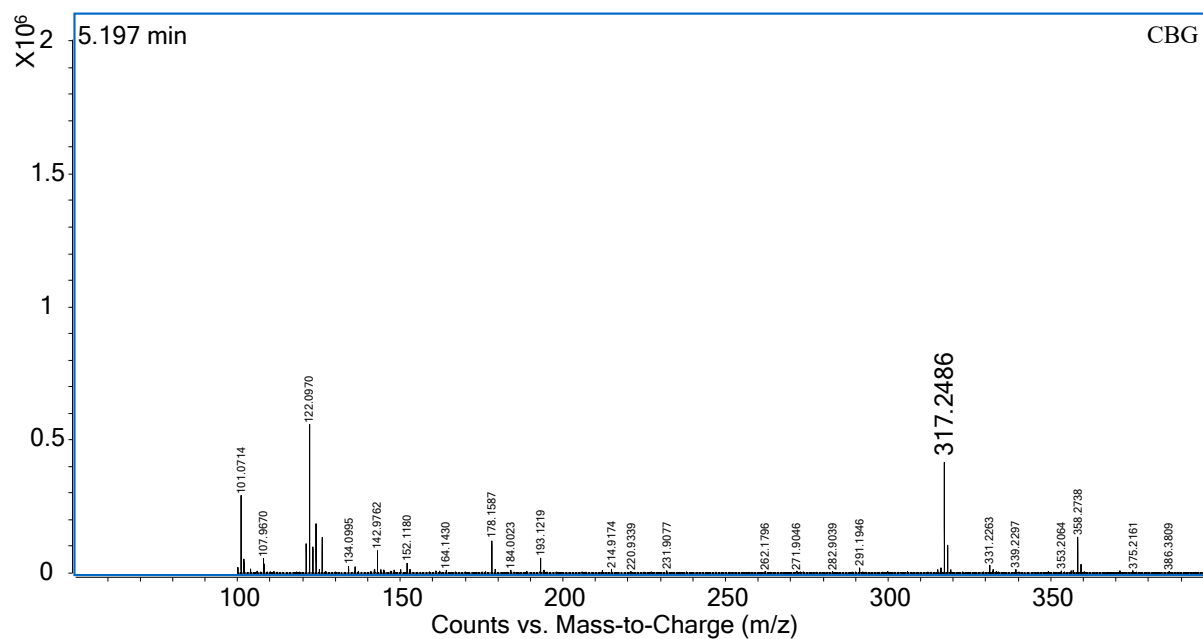
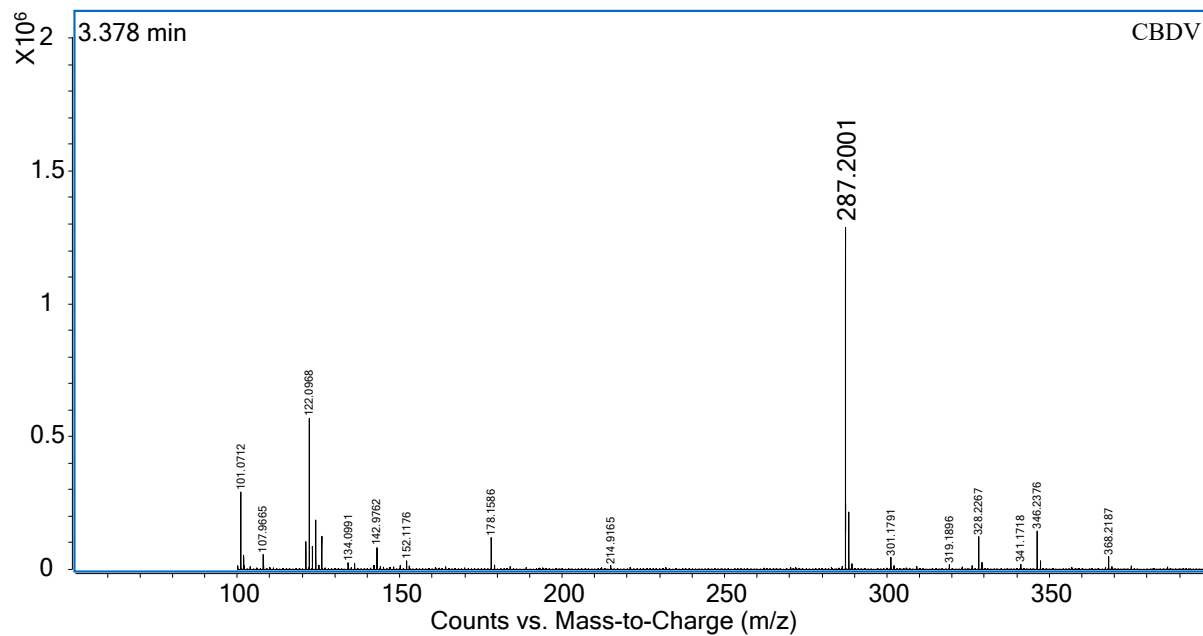


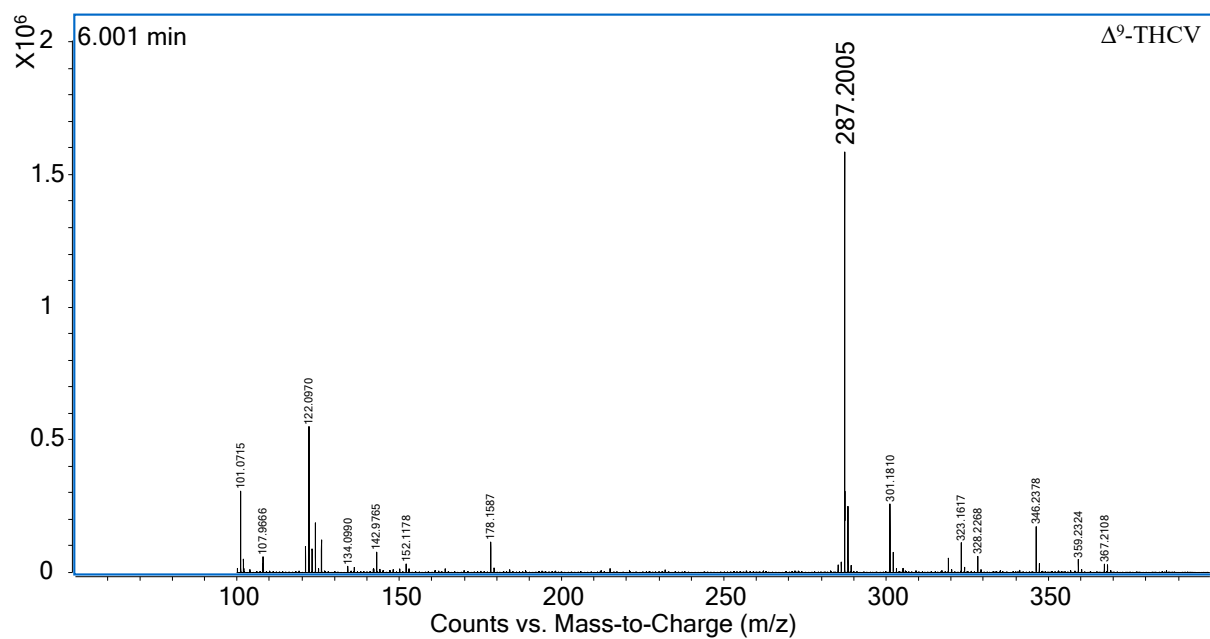
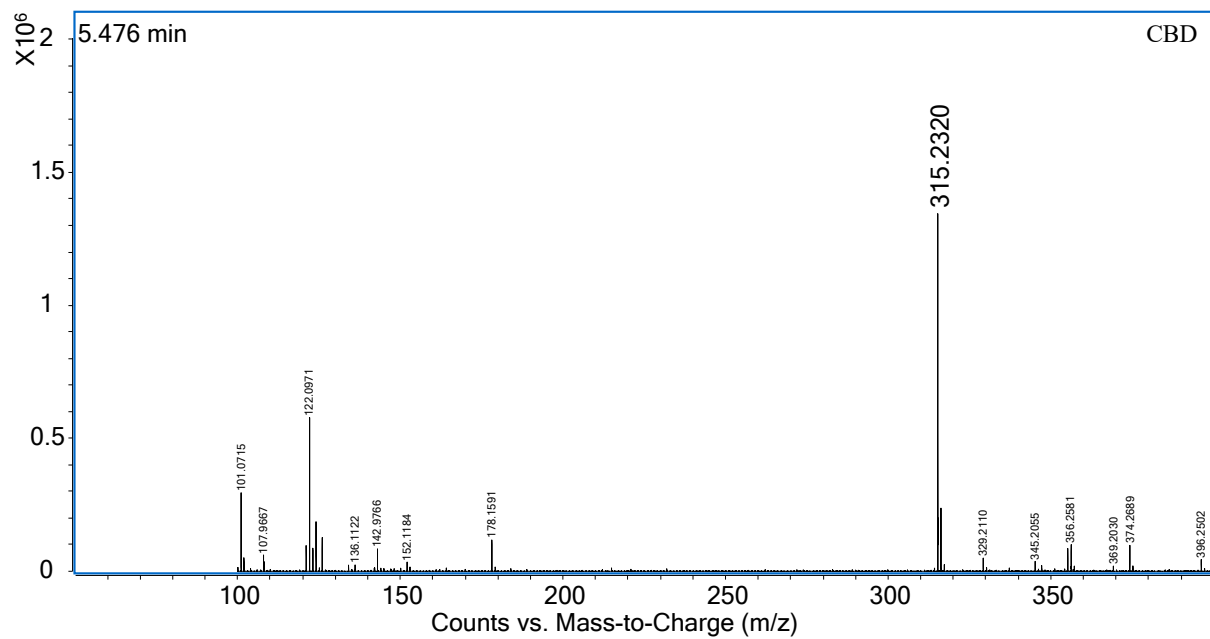


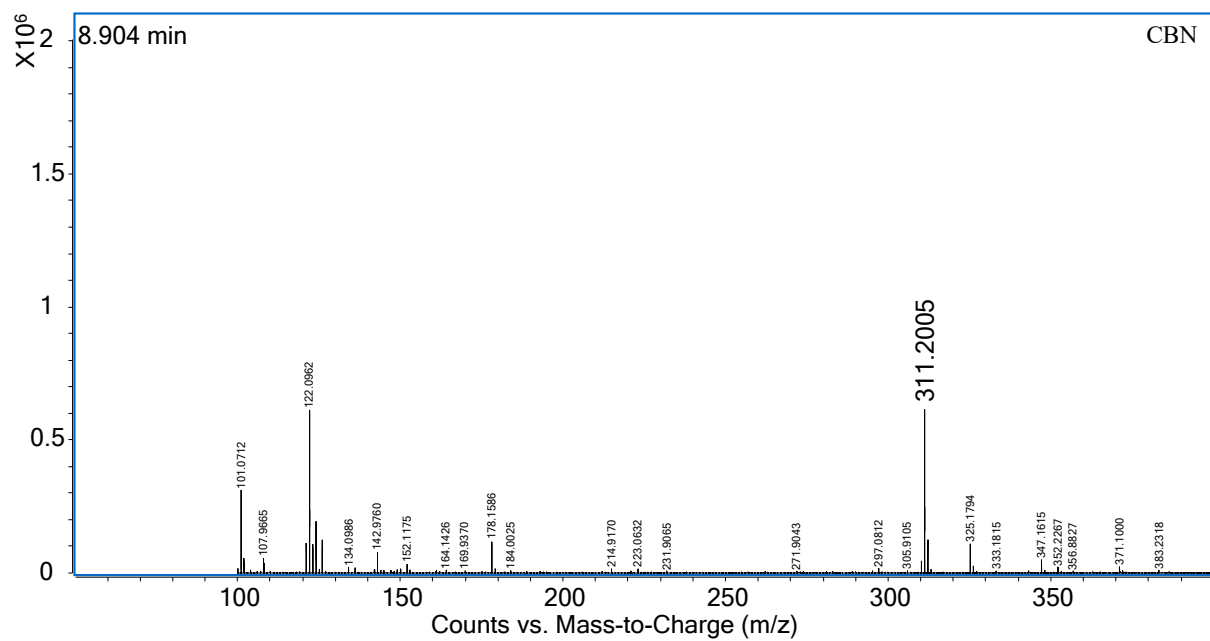
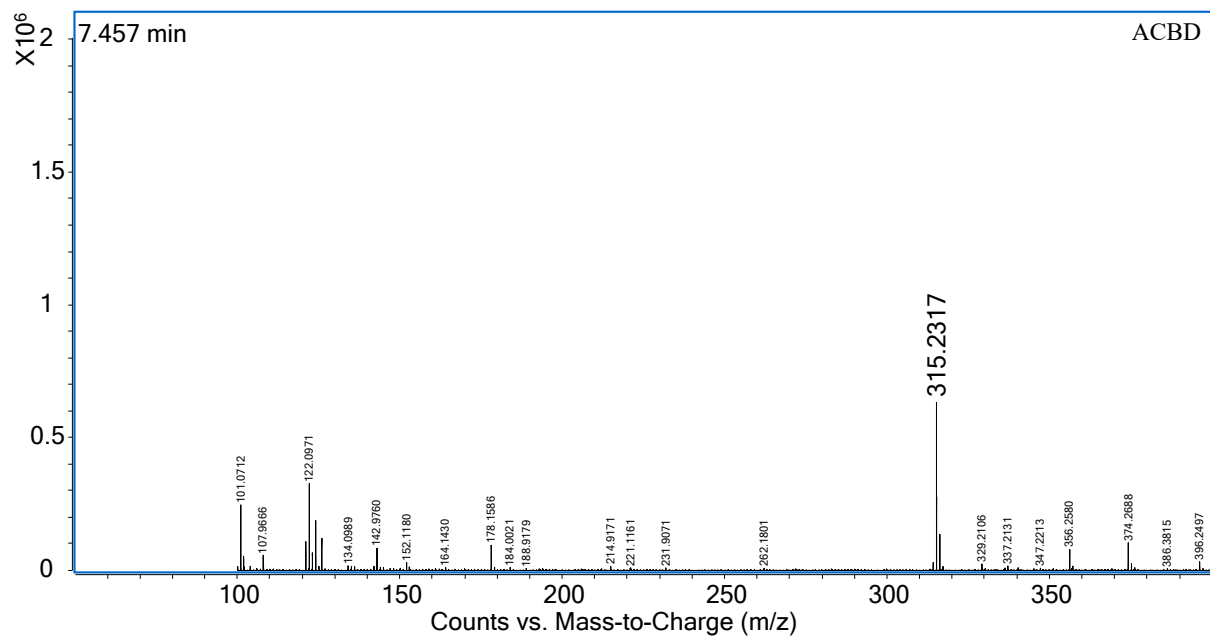


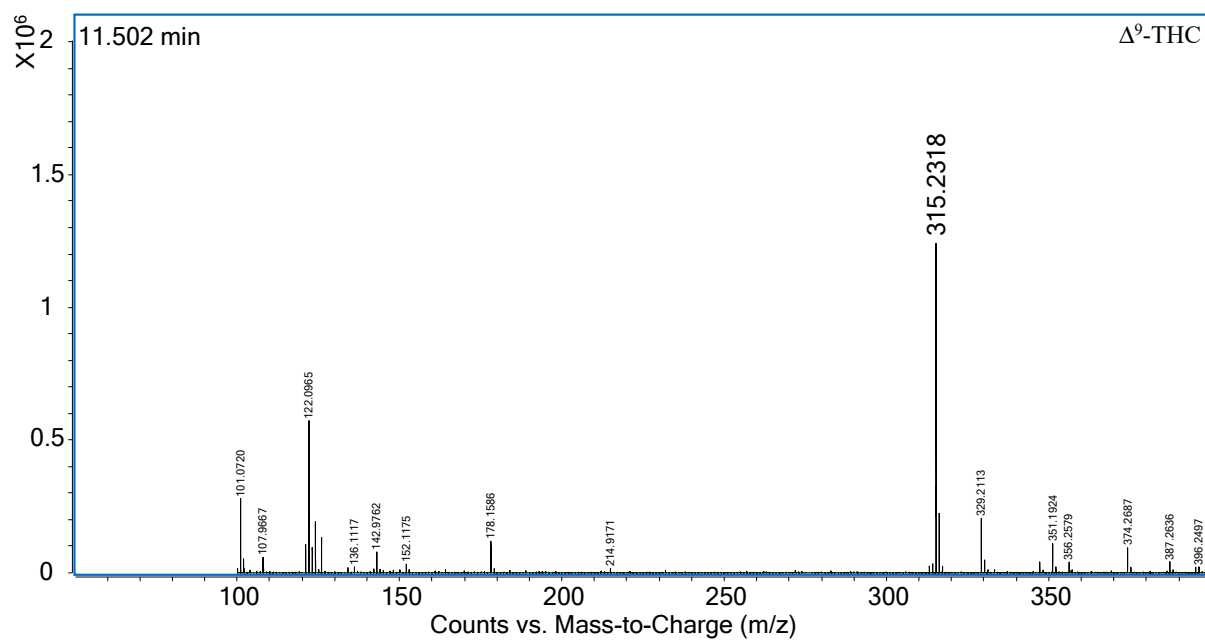
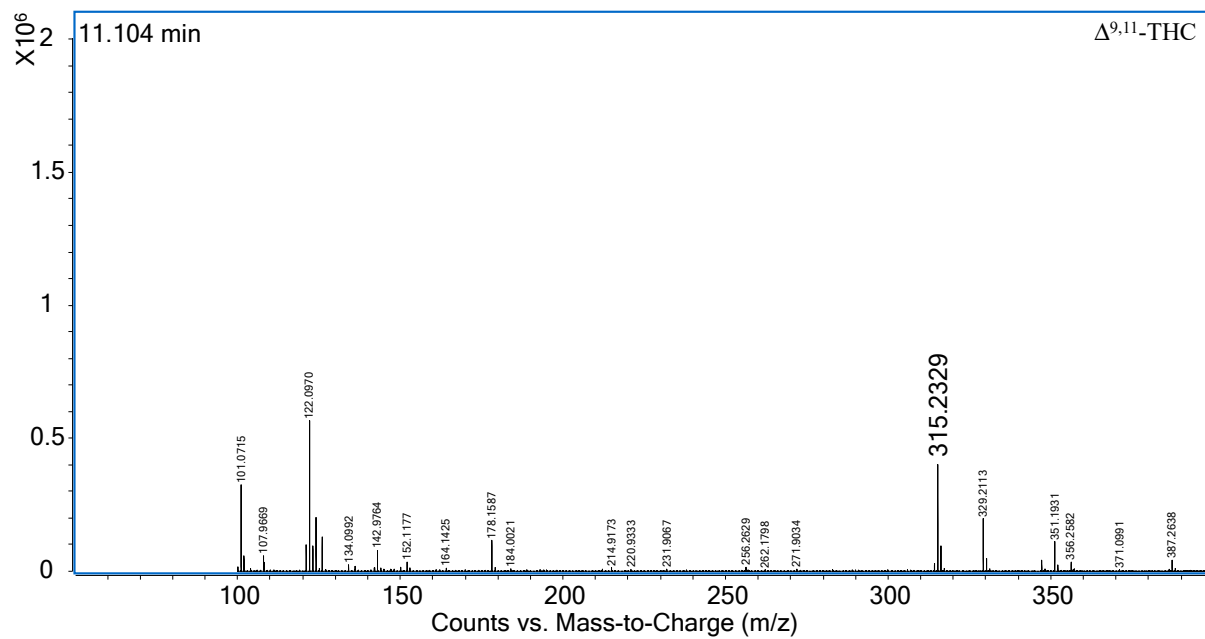


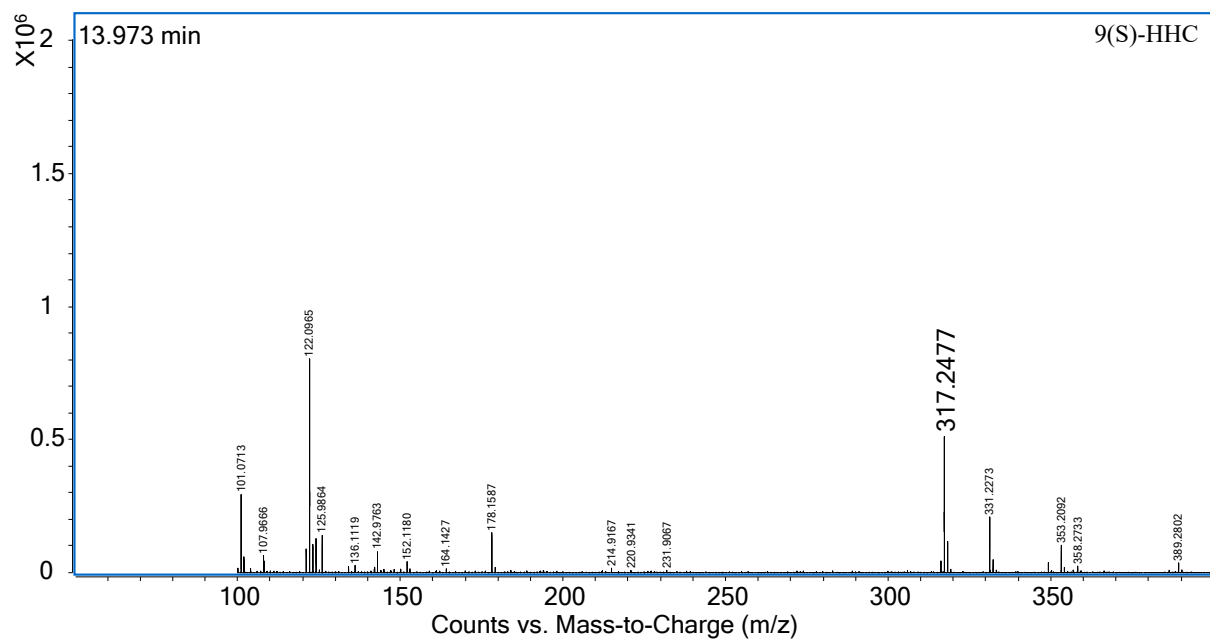
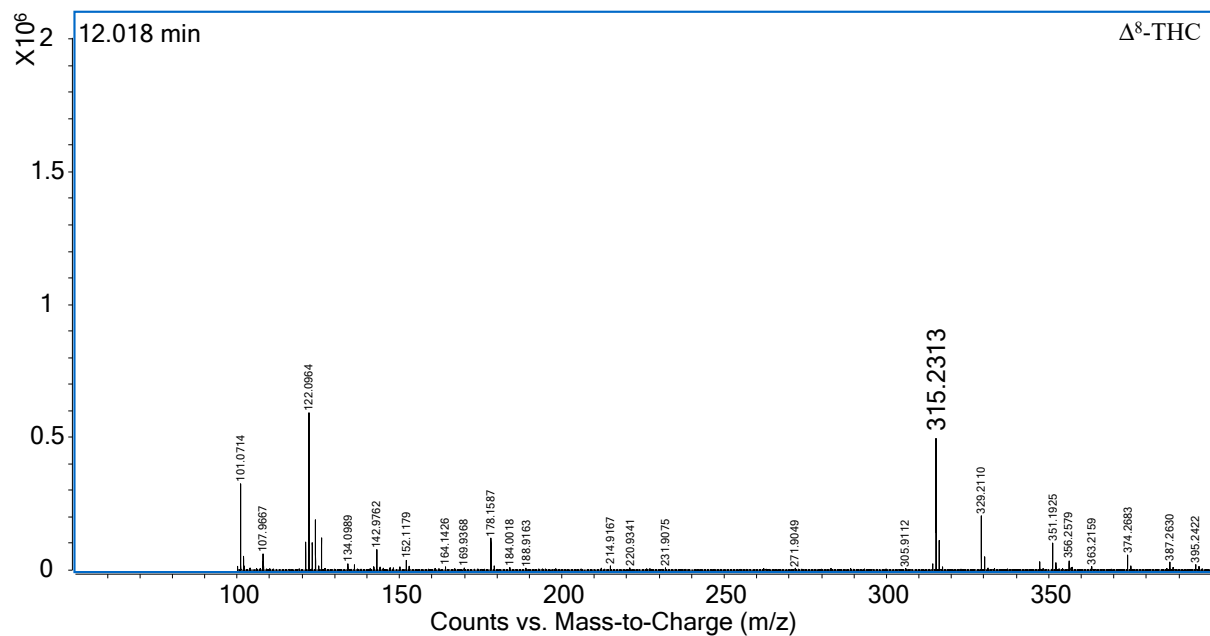
Supplementary Figure S8. ESI/TOFMS spectra of the eighteen cannabinoids that were extracted from **Figure 2A**.

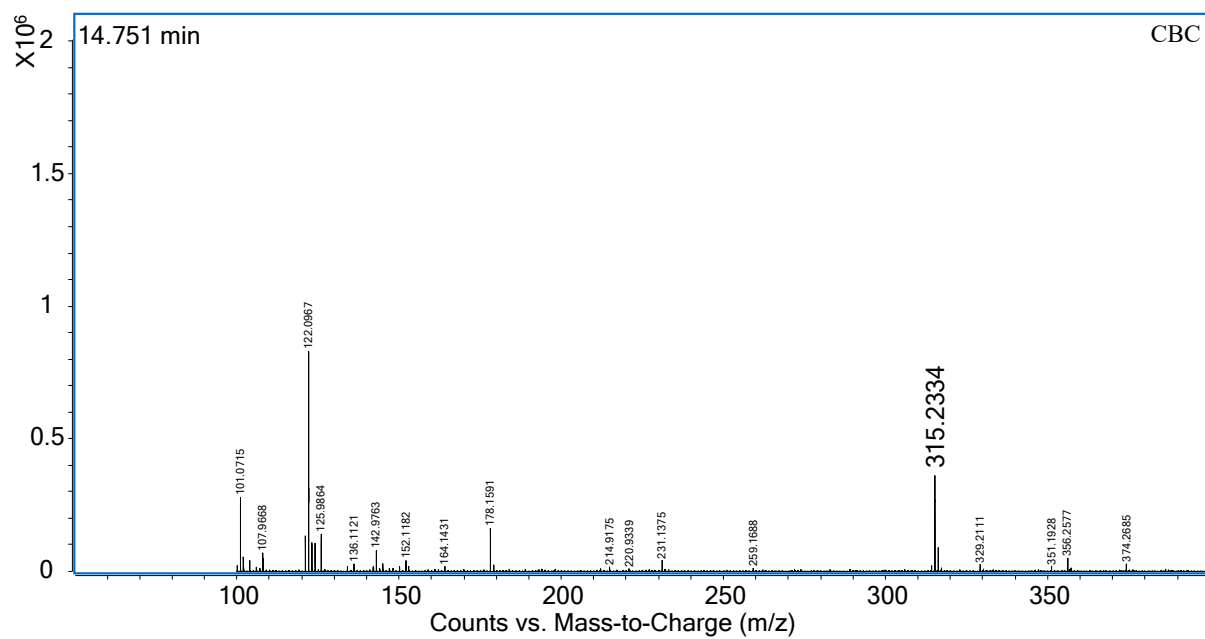
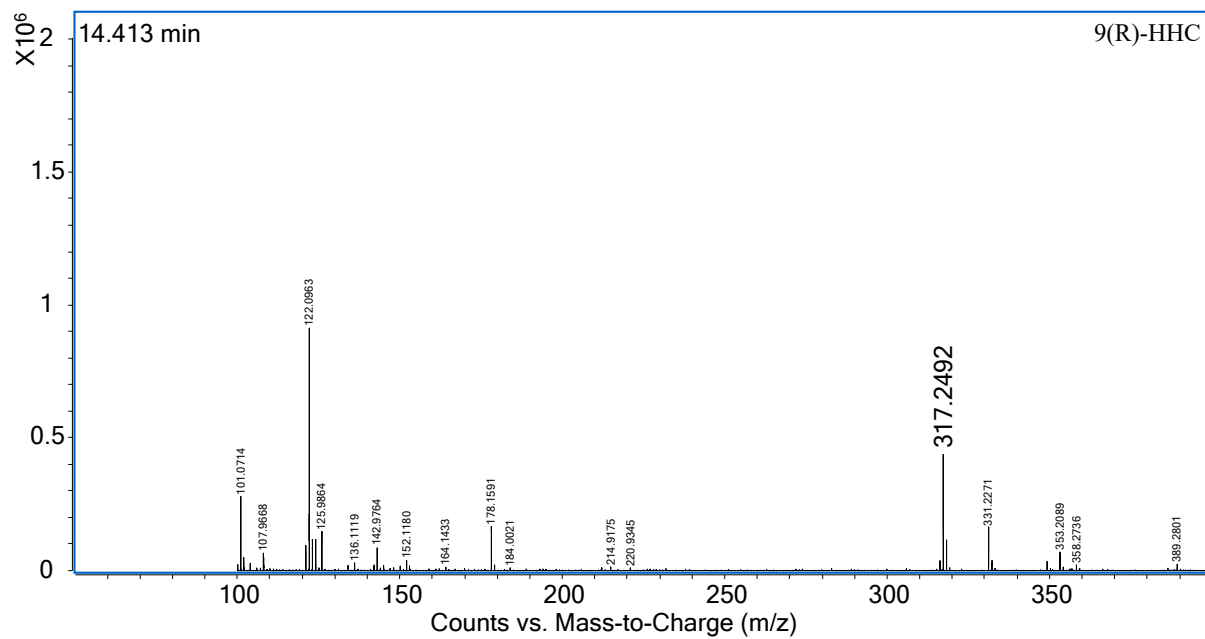


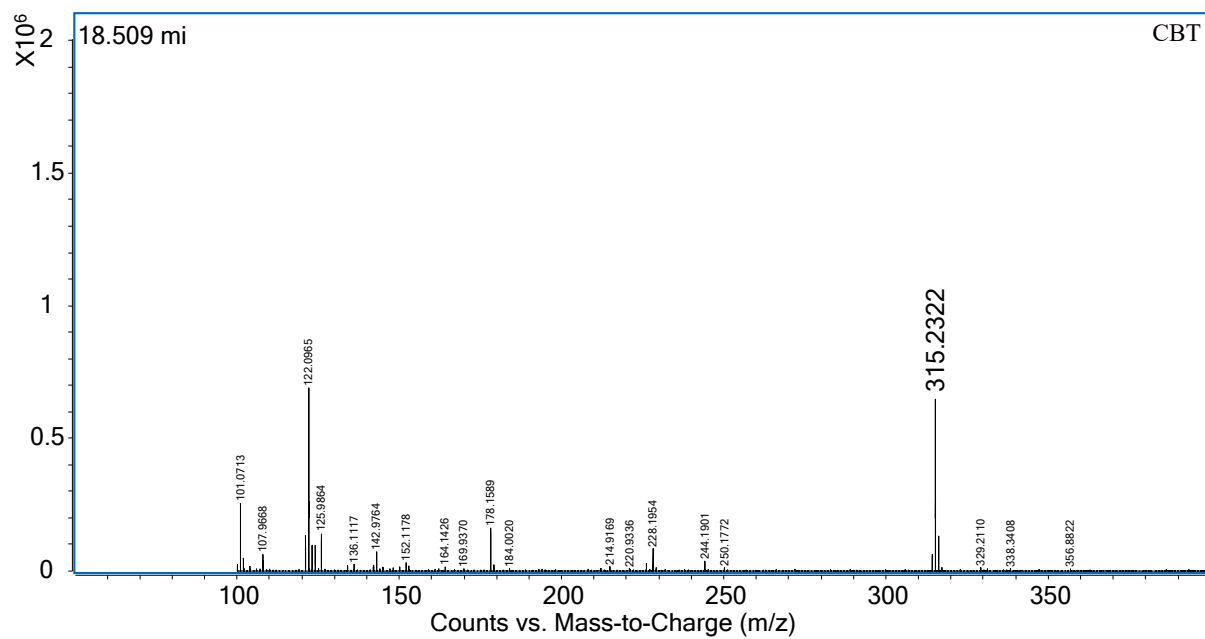
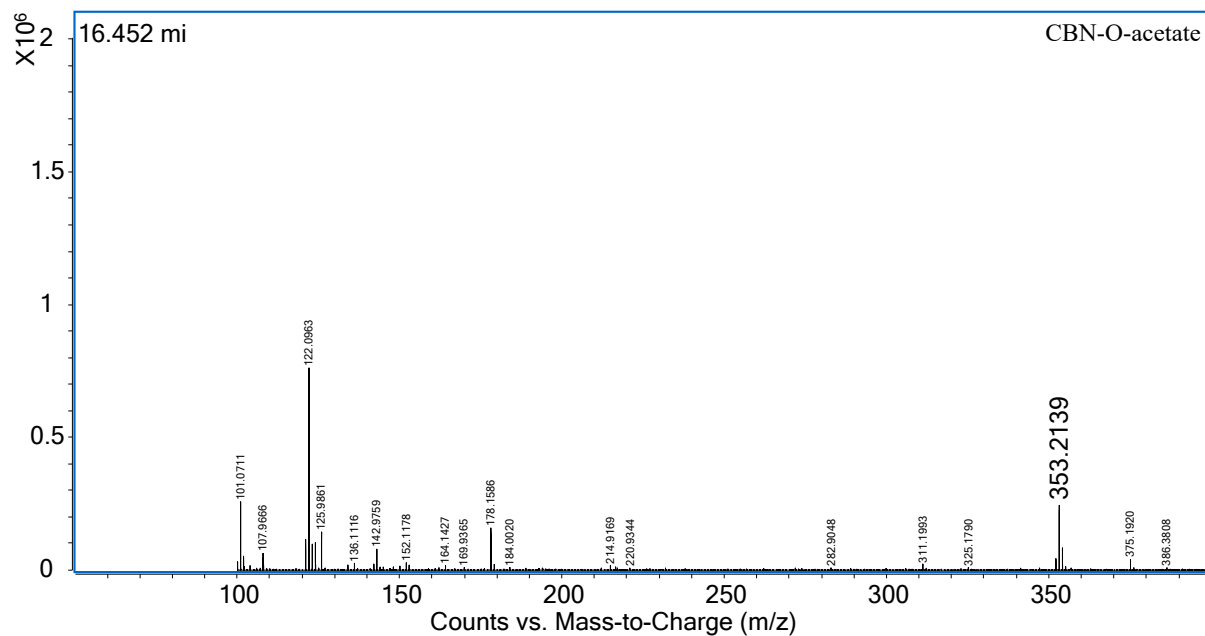


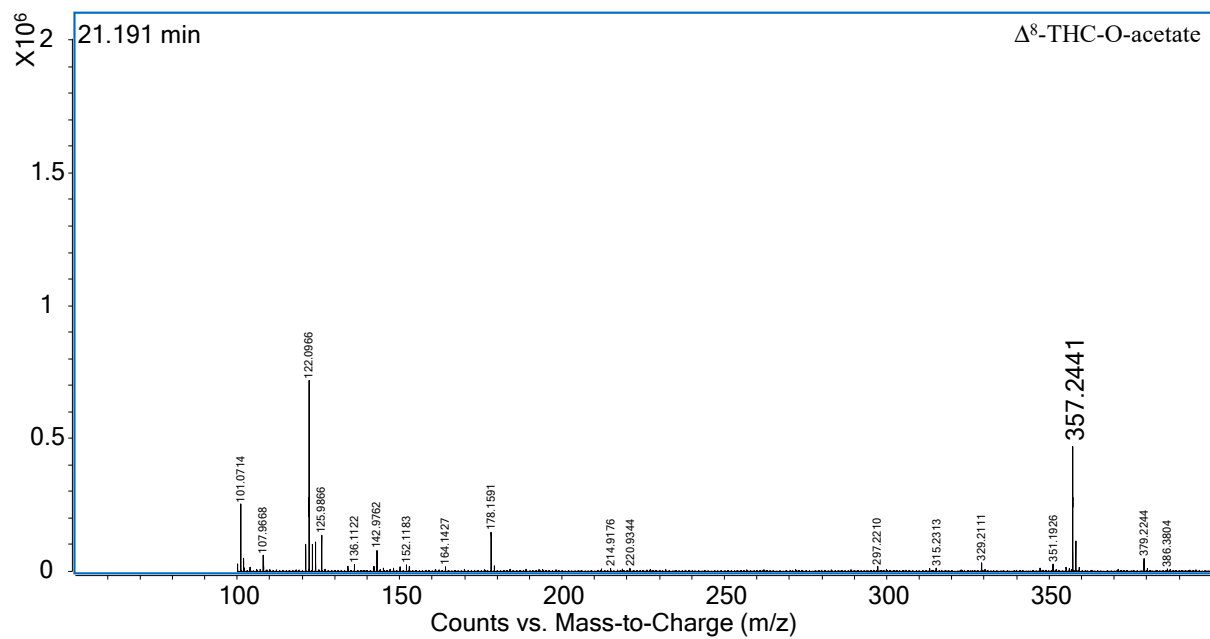
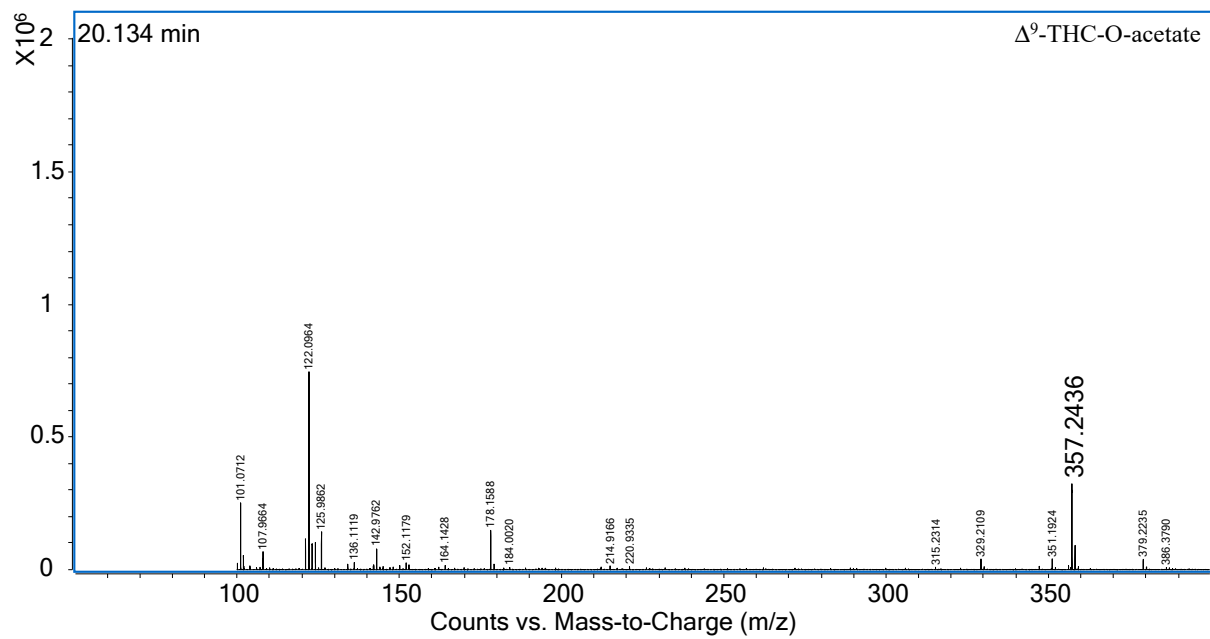


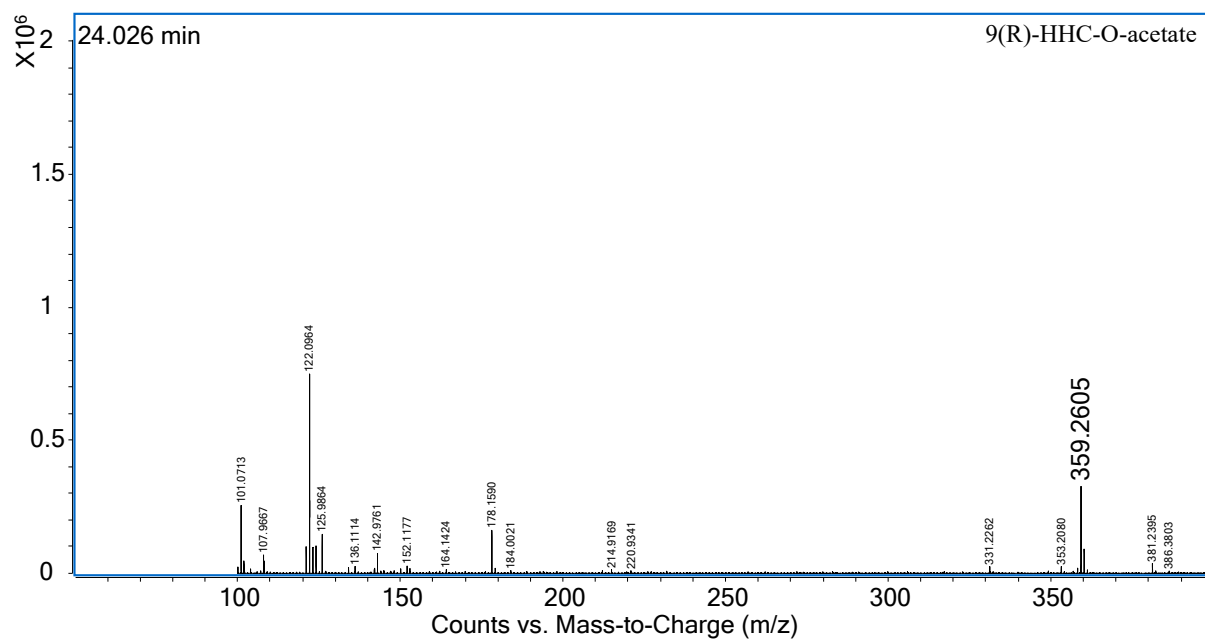
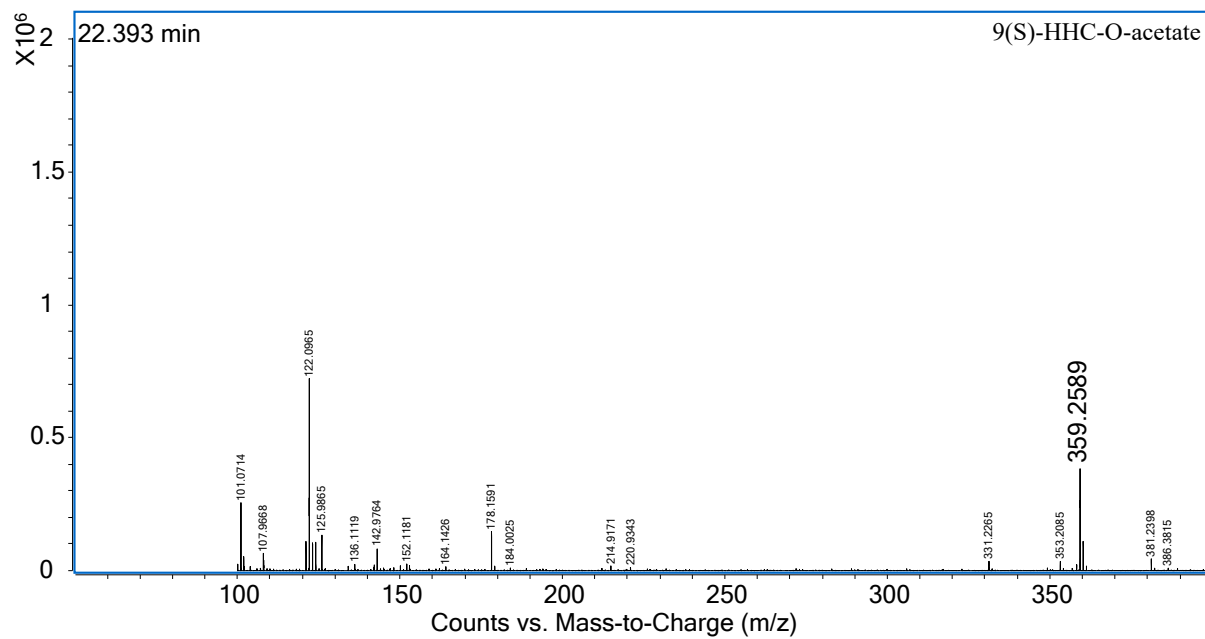












Supplementary Table S1. Summary of calibration curves (cannabinoid-O-acetate abbreviated as x-O-, where x = any cannabinoid).

Validation parameters		CBDV	CBG	CBD	Δ^9 -THCV	CBN	$\Delta^{9,11}$ -THC	Δ^9 -THC	Δ^8 -THC	
R ²	Day 1	0.9956	0.9949	0.9921	0.9954	0.9961	0.9947	0.9962	0.9966	
	Day 2	0.9936	0.9936	0.9927	0.9928	0.9922	0.9932	0.9957	0.9922	
	Day 3	0.9933	0.9951	0.9939	0.9922	0.9928	0.9974	0.9953	0.9945	
LLOQ	Day 1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
	Day 2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
	Day 3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
ULOQ	Day 1	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	
	Day 2	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	
	Day 3	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	
Validation parameters		9(S)-HHC	9(R)-HHC	CBC	CBN-O-	CBT	Δ^9 -THC-O-	Δ^8 -THC-O-	9(S)-HHC-O-	9(R)-HHC-O-
R ²	Day 1	0.9941	0.9968	0.9970	0.9956	0.9948	0.9952	0.9955	0.9961	0.9946
	Day 2	0.9914	0.9933	0.9949	0.9932	0.9924	0.9928	0.9934	0.9942	0.9887
	Day 3	0.9930	0.9946	0.9944	0.9928	0.9923	0.9931	0.9923	0.9941	0.9897
LLOQ	Day 1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Day 2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Day 3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
ULOQ	Day 1	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
	Day 2	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
	Day 3	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0

Supplementary Table S2. Accuracy (%) of the QC samples: triplicate measurements for both intraday and interday.

Conc.	Accuracy	CBDV	CBG	CBD	D ⁹ -THCV	CBN	D ^{9,11} -THC	D ⁹ -THC	D ⁸ -THC	
0.1	Day 1	101.2	99.3	99.2	101.7	102.1	102.9	103.0	105.4	
	Day 2	100.5	99.6	99.7	100.5	102.3	96.6	100.2	104.2	
	Day 3	102.0	99.3	99.0	101.3	102.6	103.2	96.6	102.6	
	Interday	101.2	99.4	99.3	101.2	102.3	100.9	99.9	104.1	
1.0	Day 1	97.9	100.2	99.7	98.2	97.2	98.8	98.7	101.6	
	Day 2	97.5	100.3	100.1	98.4	98.6	96.9	98.1	98.7	
	Day 3	98.2	100.7	99.4	98.4	99.4	98.9	98.3	98.8	
	Interday	97.9	100.4	99.7	98.3	98.4	98.2	98.4	99.7	
50.0	Day 1	104.0	106.0	105.8	105.7	105.6	105.4	102.8	101.7	
	Day 2	104.0	106.2	101.1	107.7	105.9	105.5	103.8	105.4	
	Day 3	103.6	106.2	102.2	107.5	105.8	103.6	102.9	105.4	
	Interday	103.9	106.1	103.1	107.0	105.8	104.8	103.2	104.2	
Conc.	Accuracy	9(S)-HHC	9(R)-HHC	CBC	CBN-O-	CBT	Δ^9 -THC-O-	Δ^8 -THC-O-	9(S)-HHC-O-	9(R)-HHC-O-
0.1	Day 1	99.9	103.3	102.0	103.4	97.8	98.2	100.8	114.6	103.9
	Day 2	98.2	103.9	100.8	100.6	94.2	100.1	106.3	108.4	102.0
	Day 3	97.9	103.5	101.9	103.7	98.4	103.0	102.5	110.8	98.1
	Interday	98.6	103.5	101.6	102.6	96.8	100.4	103.2	111.3	101.3
1.0	Day 1	97.3	98.9	100.0	97.1	97.0	97.0	99.2	96.3	95.6
	Day 2	100.5	100.5	100.4	96.2	96.7	97.2	98.4	98.1	100.1
	Day 3	104.2	101.2	100.1	97.5	97.6	98.4	98.1	97.4	97.3
	Interday	100.7	100.2	100.2	97.0	97.1	97.5	98.6	97.3	97.7
50.0	Day 1	107.7	104.8	103.3	104.7	106.2	103.7	104.8	103.0	104.2
	Day 2	110.7	105.8	103.7	104.5	105.8	104.1	104.8	102.5	104.3
	Day 3	110.1	108.1	103.1	104.6	106.1	104.3	105.1	102.9	104.1
	Interday	109.5	106.2	103.4	104.6	106.1	104.0	104.9	102.8	104.2

Supplementary Table S3. Precision of the QC samples: triplicate measurements for both intraday and interday.

Conc.	RSD (%)	CBDV	CBG	CBD	Δ ⁹ -THCV	CBN	Δ ^{9,11} -THC	Δ ⁹ -THC	Δ ⁸ -THC	
0.1	Day 1	1.0	0.1	3.1	1.1	1.0	2.2	1.6	2.4	
	Day 2	0.3	0.1	2.7	1.2	0.8	0.4	4.3	3.3	
	Day 3	2.5	0.4	2.2	0.2	1.1	4.8	2.2	2.9	
	Interday	0.7	0.2	0.4	0.6	0.2	3.7	3.2	1.4	
1.0	Day 1	0.1	0.1	0.4	0.3	0.4	0.2	0.5	1.1	
	Day 2	0.9	0.2	1.0	0.2	1.2	4.7	1.1	0.7	
	Day 3	0.3	0.4	0.4	0.4	0.2	0.6	0.4	0.2	
	Interday	0.4	0.3	0.3	0.1	1.1	1.2	0.3	1.7	
50.0	Day 1	0.1	0.1	0.2	0.2	0.1	0.1	0.7	3.2	
	Day 2	0.1	0.2	1.0	0.6	0.3	0.2	0.2	0.2	
	Day 3	0.2	0.2	1.9	0.7	0.1	3.1	0.5	0.3	
	Interday	0.2	0.1	2.4	1.0	0.1	1.0	0.5	2.0	
Conc.	RSD (%)	9(S)-HHC	9(R)-HHC	CBC	CBN-O-	CBT	Δ ⁹ -THC-O-	Δ ⁸ -THC-O-	9(S)-HHC-O-	9(R)-HHC-O-
0.1	Day 1	4.1	1.3	3.0	1.8	11.5	3.1	2.4	0.8	4.2
	Day 2	3.1	4.1	1.2	3.5	0.5	4.2	1.5	4.6	11.3
	Day 3	2.3	2.4	0.5	2.5	6.8	2.4	6.5	0.5	10.6
	Interday	1.1	0.3	0.7	1.7	2.4	2.4	2.7	2.8	2.9
1.0	Day 1	1.4	0.3	0.2	0.4	0.3	0.2	2.5	0.4	0.7
	Day 2	2.4	1.0	0.9	1.2	0.6	1.6	0.6	0.7	3.1
	Day 3	2.4	0.7	2.8	0.9	0.1	2.0	2.0	1.0	1.6
	Interday	3.4	1.2	0.2	0.7	0.5	0.8	0.6	0.9	2.3
50.0	Day 1	0.3	0.1	0.1	0.1	0.3	0.7	0.1	0.1	0.1
	Day 2	1.4	0.3	1.4	0.5	0.1	0.2	0.2	0.4	0.1
	Day 3	1.9	3.7	0.7	0.4	0.2	0.5	0.3	0.4	0.5
	Interday	1.4	1.6	0.3	0.1	0.2	0.3	0.1	0.2	0.1

Supplementary Table S4. Uncertainty estimates for cannabinoid quantification.

Conc.	CBDV	CBG	CBD	Δ^9 -THCV	CBN	$\Delta^{9,11}$ -THC	Δ^9 -THC	Δ^8 -THC	
0.1	0.006	0.001	0.009	0.003	0.004	0.013	0.012	0.010	
1.0	0.02	0.01	0.02	0.01	0.03	0.10	0.03	0.04	
50.0	0.3	0.3	3.2	1.4	0.4	3.3	1.0	3.8	
Conc.	9(S)-HHC	9(R)-HHC	CBC	CBN-O-	CBT	Δ^9 -THC-O-	Δ^8 -THC-O-	9(S)-HHC-O-	9(R)-HHC-O-
0.1	0.011	0.010	0.007	0.010	0.027	0.012	0.015	0.011	0.033
1.0	0.10	0.03	0.06	0.03	0.02	0.05	0.07	0.03	0.09
50.0	2.8	4.0	1.6	0.6	0.5	0.9	0.4	0.6	0.6

Note:

Expanded uncertainty values (U) were calculated for each analyte using both intraday and interday precision data from QC samples, as reported in Supplementary Table S3. The combined standard uncertainty (μ_c) was obtained by pooling the standard deviations from multiple intraday replicates and combining them with the interday standard deviation using the formula:

$$\mu_c = \sqrt{SD_{intra}^2 + SD_{inter}^2}$$

Expanded uncertainty was then calculated as:

$$U = k \times \mu_c$$

with a coverage factor k=2, corresponding to an approximate 95% confidence interval. These values provide an estimate of method variability due to repeatability and intermediate precision, in line with ISO 17025 guidelines. Other sources of uncertainty such as calibration or extraction recovery were not included in this estimate but may be addressed in future full validation efforts.