
Supplementary Information (SI)

- S1: Absorbance vs photolysis time measurements & Higher Collision-Induced Dissociation (HCD) of THC
 - S2: Absorbance vs photolysis time measurements for CBD
 - S3: ESI-MS & Higher Collision-Induced Dissociation (HCD) of CBD
 - S4: Absorbance vs photolysis time measurements & ESI-MS of THC-COOH
 - S5: Higher Collision-Induced Dissociation (HCD) of THC-COOH
 - S6: Absorbance vs photolysis time measurements & ESI-MS of THC-OH
 - S7: Higher Collision-Induced Dissociation (HCD) of THC-OH
 - S8: Absorbance vs photolysis time measurements, TRMPS, and HCD of CBDA
 - S9: Absorbance vs photolysis time measurements, TRMPS, and HCD of THCA
 - S10: UV-Vis absorption spectra for photolysis of JWH-018 & MDMB-FUBINACA
 - S11: Absorbance vs photolysis time measurements for JWH-018 & MDMB-FUBINACA
 - S12: ESI-MS of JWH-018 & MDMB-FUBINACA
 - S13: Table of proposed structure of photolysis fragments
 - S13A: Proposed Photochemical Reaction Pathways
 - S14: Quartz syringe photolysis apparatus
 - S15: Experimental setup used for UV photolysis
 - S16: UV-Vis Absorbance vs Wavelength spectra at 0 min. for all cannabinoids
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S1: Absorbance vs photolysis time measurements for THC & Higher Collision-Induced Dissociation (HCD) of [THC-H]-

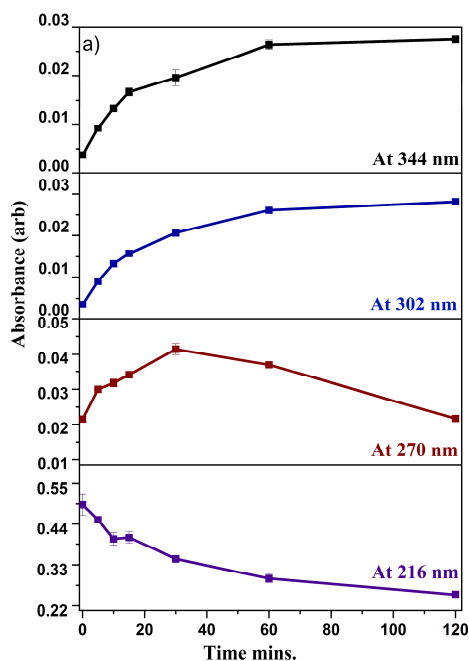


Figure S1: Absorbance versus time plots obtained for solutions of THC irradiated at 280 nm, obtained from the UV-Vis absorption spectra at a selection of wavelengths (216, 270, 302, and 344 nm)

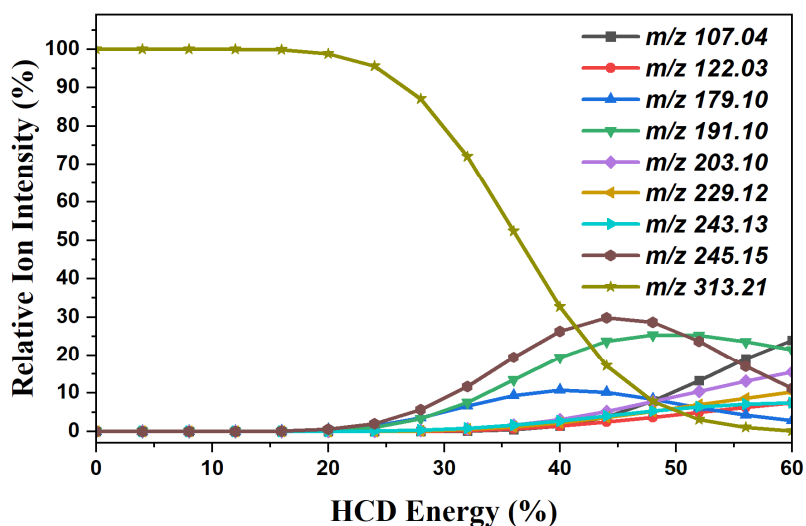


Figure S2: Precursor ion dissociation curve along with fragment ion production curves for [THC-H]⁻ (m/z 313) displayed as a function of HCD energy. The solid lines are a three-point adjacent average of the data points.

S2: Absorbance vs photolysis time measurements for CBD

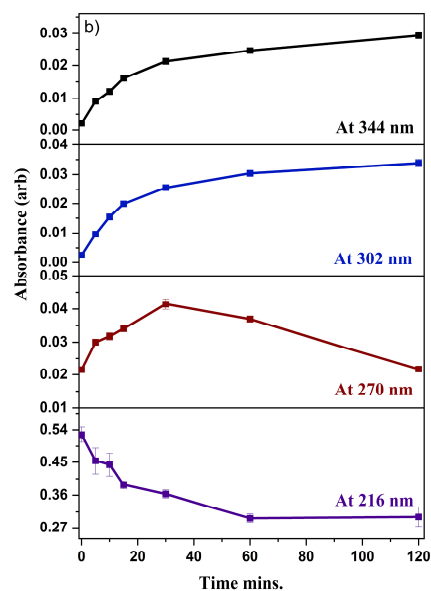


Figure S3: Absorbance versus time plots obtained for solutions of CBD irradiated at 280 nm, obtained from the UV-Vis absorption spectra at a selection of wavelengths (216, 270, 302, and 344 nm).

S3: ESI-MS & Higher Collision-Induced Dissociation (HCD) of CBD

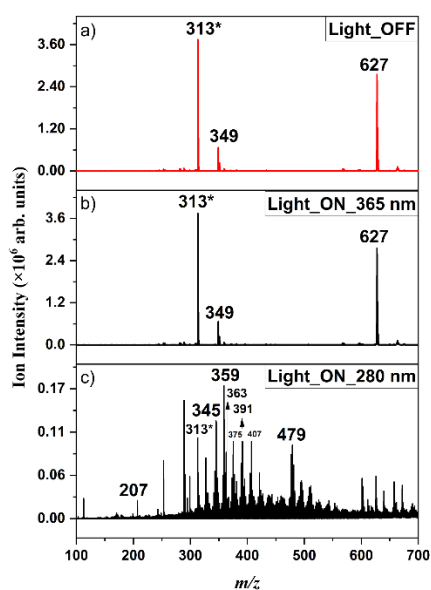


Figure S4: (a) Photolysis OFF and (b-c) photolysis ON ESI MS of CBD obtained in negative ion mode. (b) and (c) displays the ESI-MS obtained with 365 and 280 nm photolysis, respectively. The [CBD-H]⁻ precursor ion is visible at m/z 313.

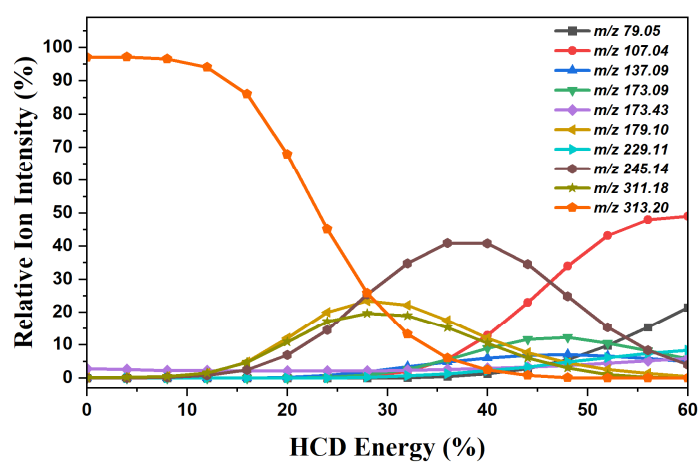


Figure S5: Precursor ion dissociation curve along with fragment ion production curves for [CBD-H]⁺ (m/z 313) displayed as a function of HCD energy. The solid lines are a three-point adjacent average of the data points.

S4: Absorbance vs photolysis time measurements & ESI-MS of THC-COOH

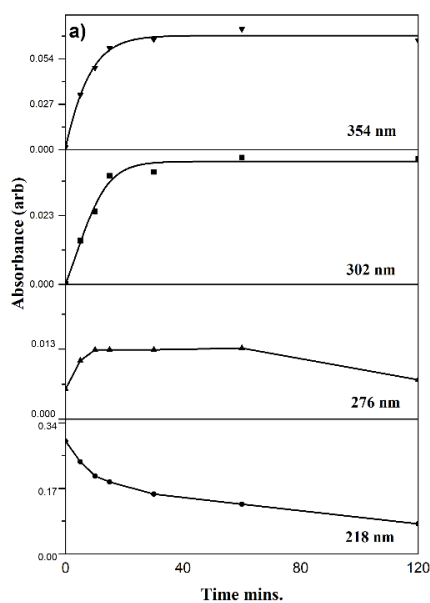


Figure S6: Absorbance versus time plots obtained for solutions of THC-COOH irradiated at 280 nm, obtained from the UV-Vis absorption spectra at a selection of wavelengths (218, 276, 302, and 354 nm).

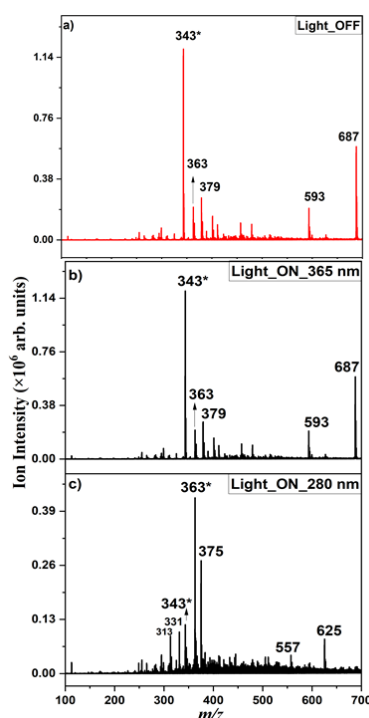


Figure S7: (a) Photolysis OFF and (b-c) photolysis ON ESI mass spectra of THC-COOH obtained in negative ion mode. (b) and (c) displays the ESI-MS obtained with 365 and 280 nm photolysis, respectively. The $[\text{THC-COOH-H}]^-$ precursor ion is visible at m/z 343.

S5: Higher Collision-Induced Dissociation (HCD) of THC-COOH

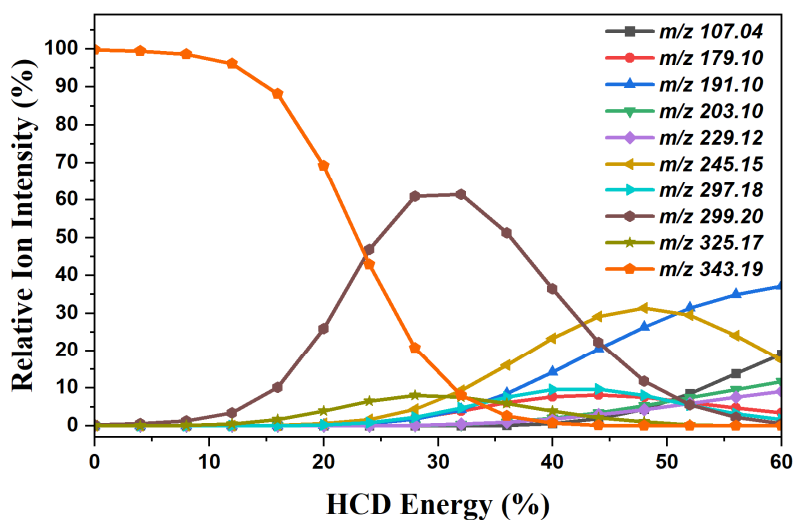


Figure S8: Precursor ion dissociation curve along with fragment ion production curves for $[\text{THC-COOH-H}]^-$ (m/z 343) displayed as a function of HCD energy. The solid lines are a three-point adjacent average of the data points.

Table S1: Comparison of observed m/z fragments from THC-COOH photolysis observed in negative ESI mode under three conditions: no light (OFF), 280 nm UV light (30 min), and 365 nm UV light (30 min).

<i>m/z</i>	THC-COOH_No Photolysis	THC-COOH_280 nm	THC-COOH_365 nm
191	✓ ^a	X	✓ ^a
245	✓ ^a	X	✓ ^a
297	✓ ^a	X	✓ ^a
299	✓ ^a	X	✓ ^a
313	X	✓ (s)	X
315	X	✓ (s)	X
325	✓ ^a	X	✓ ^a
331	X	✓ (v.s)	X
343*	✓ (v.s)	✓ (v.w)	✓ (v.s)
363	✓ (s)	✓ (v.s)	X
364	X	✓ (s)	X
375	X	✓ (v.v.s)	X
376	X	✓ (s)	X
383	X	✓ (s)	X
445	X	✓ (w)	X
479	X	✓ (w)	X
511	X	✓ (w)	X
525	X	✓ (w)	X
557	X	✓ (s)	X
599	✓	X	✓
625	X	✓ (s)	X
687**	✓ (v.s)	X	✓ (v.s)

^a Present as a strong fragment at 20 % HCD (Figure S8)

-Very strong (v.s.), Very very strong (v.v.s.), strong (s), Very weak (v.w) and weak (w).

S6: Absorbance vs photolysis time measurements & ESI-MS of THC-OH

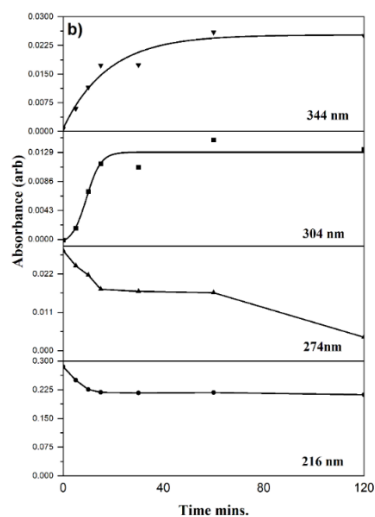


Figure S9: Absorbance versus time plots obtained for solutions of THC-OH irradiated at 280 nm, obtained from the UV-Vis absorption spectra at a selection of wavelengths (216, 274, 304, and 344 nm).

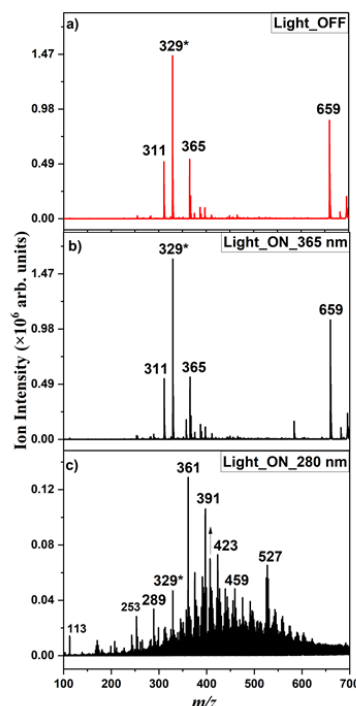


Figure S10: (a) Photolysis OFF and (b-c) photolysis ON ESI mass spectra of THC-OH obtained in negative ion mode. (b) and (c) displays the ESI-MS obtained with 365 and 280 nm photolysis, respectively. The [THC-OH-H]⁻ precursor ion is visible at m/z 329.

S7: Higher Collision-Induced Dissociation (HCD) of THC-OH

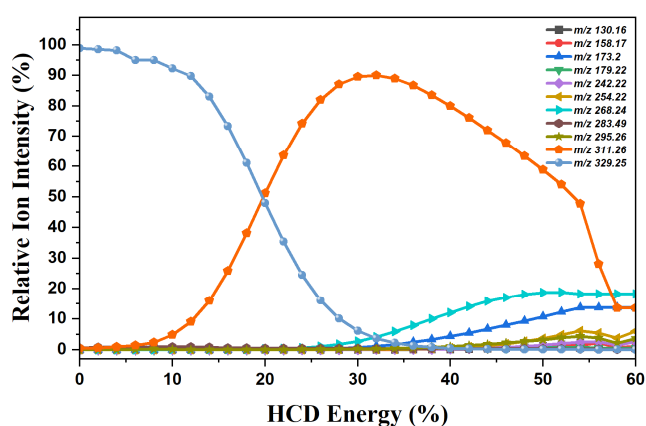


Figure S11. Precursor ion dissociation curve along with fragment ion production curves for [THC-OH-H]⁻ (m/z 329) displayed as a function of HCD energy. The solid lines are a three-point adjacent average of the data points.

Table S2: Comparison of observed m/z fragments from THC-OH photolysis observed in negative ESI mode under three conditions: no light (OFF), 280 nm UV light (30 min), and 365 nm UV light (30 min).

m/z	THC-OH_No Photolysis	THC-OH_280 nm	THC-OH_365 nm
242	✓ ^a	✗	✓ ^a
283	✓ ^a	✗	✓ ^a
295	✓ ^a	✗	✓ ^a
311	✓ ^a	✗	✓ ^a
329*	✓ (v.s)	✓ (v.w)	✓ (v.s)
361	✗	✓ (v.s)	✓
391	✗	✓ (s)	✓
407	✗	✓ (s)	✓
409	✗	✓ (s)	✓
423	✗	✓ (s)	✓
439	✗	✓ (s)	✓
459	✗	✓ (s)	✓
525	✗	✓ (s)	✓
527	✗	✓ (s)	✓
529	✗	✓ (s)	✓
659**	✓ (v.s)	✗	✓ (v.s)

^a Present as a strong fragment at 20 % HCD (Figure S11)

-Very strong (vs.), and strong (s).

S8: Absorbance vs photolysis time measurements, TRMPS, and HCD of CBDA

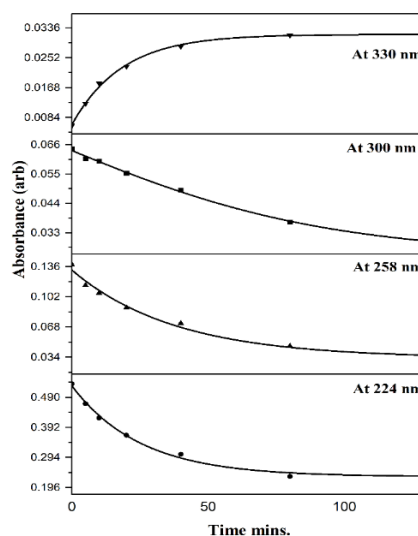


Figure S12: Absorbance versus time plots obtained for solutions of CBDA irradiated at 280 nm, obtained from the UV-Vis absorption spectra at a selection of wavelengths (224, 258, 300, and 330 nm).

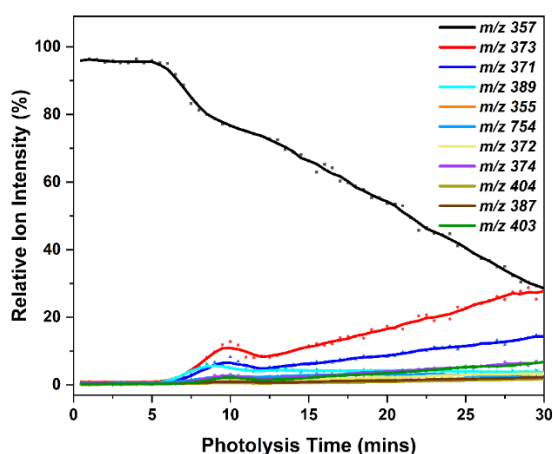


Figure S13: ESI-MS ion intensities (negative ion mode) for 365 nm photolysis of solution-phase CBDA displayed as a function of time, showing the decrease of the precursor ion, [CBDA-H]⁻ (m/z 357) and increase in the 10 most intense photoproduct ions. Photolysis is initiated at $t = 3$ min and there is a 1 min lead time for the solution to reach the MS.

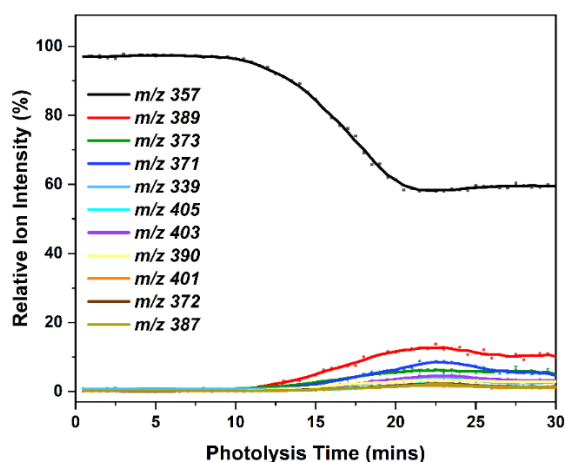


Figure S14: ESI-MS ion intensities (negative ion mode) for 280 nm photolysis of solution-phase CBDA displayed as a function of time, showing the decrease of the precursor ion, [CBDA-H]⁻ (m/z 357) and increase in the 10 most intense photoproduct ions. Photolysis is initiated at $t = 3$ min and there is a 1 min lead time for the solution to reach the MS.

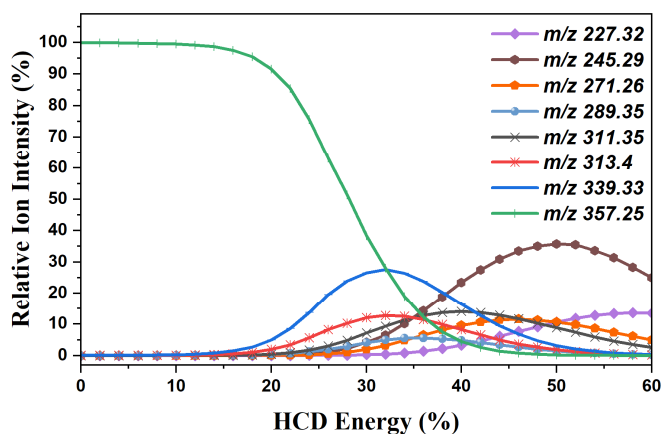


Figure S15: Precursor ion dissociation curve along with fragment ion production curves for [CBDA-H]⁻ (m/z 357) displayed as a function of HCD energy. The solid lines are a three-point adjacent average of the data points.

Table S3: Comparison of observed m/z fragments from CBDA photolysis observed in negative ESI mode under three conditions: no light (OFF), 280 nm UV light (30 min), and 365 nm UV light (30 min).

m/z	CBDA_No Photolysis	CBDA_280 nm	CBDA_365 nm
227	✓ ^a	✗	✗
245	✓ ^a	✗	✗
271	✓ ^a	✗	✗
289	✓ ^a	✗	✗
311	✓ ^a	✗	✗
313	✓ ^a	✗	✗
339	✓ ^a	✓ ^a	✗
355	✗	✗	✓ (w)
357**	✓ (v.s)	✓ (s)	✓ (s)
389	✗	✓ (s)	✓ (s)
371	✗	✓ (s)	✓ (v.s)
372	✗	✓ (w)	✓ (w)
373	✗	✓ (s)	✓ (v.s)
374	✗	✓ (w)	✓ (w)
403	✗	✓ (s)	✓ (s)
390	✗	✓ (w)	✗
387	✗	✓ (w)	✓ (w)
401	✗	✓ (w)	✗
403	✗	✓ (w)	✓ (w)
404	✗	✗	✓ (w)
405	✗	✓ (w)	✗
715**	✓ (s)	✓ (w)	✓ (w)
754	✗	✗	✓ (w)

^a Present as a strong fragment at 20 % HCD (Figure S15)

-Very strong (v.s.), strong (s), and weak (w).

S9: Absorbance vs photolysis time measurements, TRMPS, and HCD of THCA

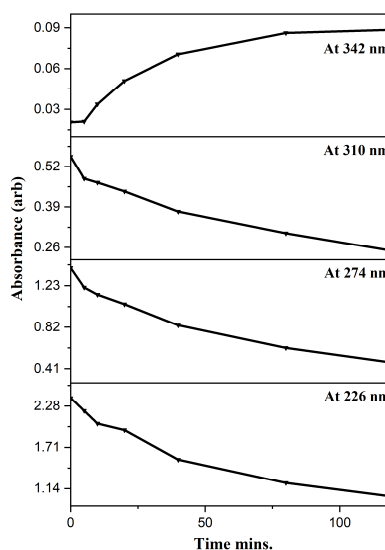


Figure S16: Absorbance versus time plots obtained for solutions of THCA irradiated at 280 nm, obtained from the UV-Vis absorption spectra at a selection of wavelengths (226, 274, 310, and 342 nm).

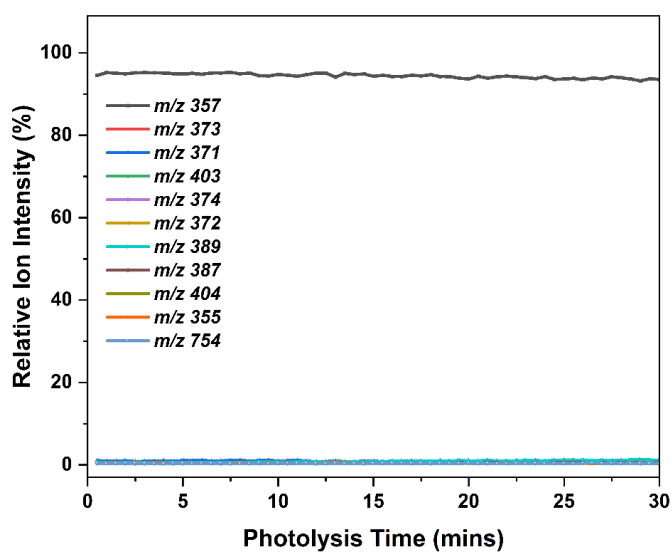


Figure S17: ESI-MS ion intensities (negative ion mode) for 365 nm photolysis of solution-phase THCA displayed as a function of time, showing the decrease of the precursor ion, [THCA-H]⁻ (m/z 357) and increase in the 10 most intense photoproduct ions. Photolysis is initiated at $t = 3$ min and there is a 1 min lead time for the solution to reach the MS.

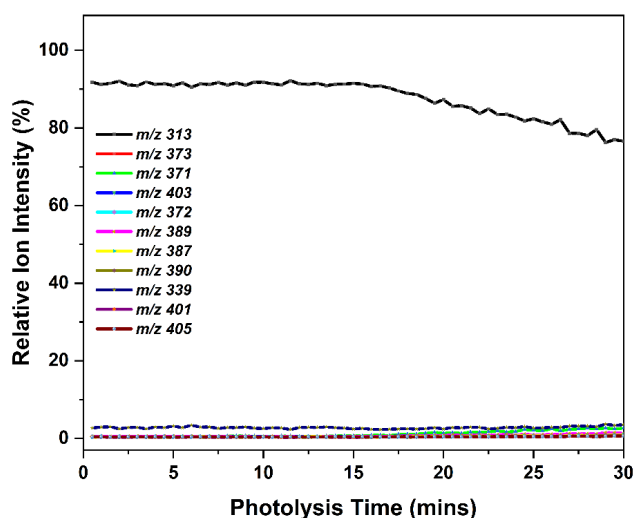


Figure S18: ESI-MS ion intensities (negative ion mode) for 280 nm photolysis of solution-phase THCA displayed as a function of time, showing the decrease of the precursor ion, [THCA-H]⁻ (m/z 357) and increase in the 10 most intense photoproduct ions. Photolysis is initiated at $t = 3$ min and there is a 1 min lead time for the solution to reach the MS.

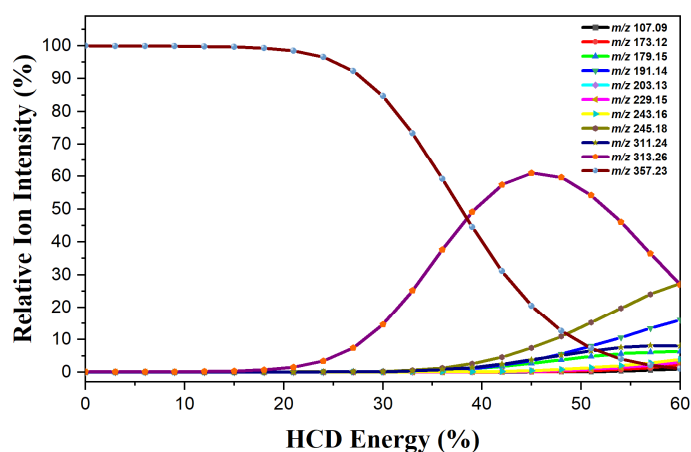


Figure S19: Precursor ion dissociation curve along with fragment ion production curves for [THCA-H]⁻ (m/z 357) displayed as a function of HCD energy. The solid lines are a three-point adjacent average of the data points.

Table S4. Comparison of observed m/z fragments from THCA photolysis observed in negative ESI mode under three conditions: no light (OFF), 280 nm UV light (30 min), and 365 nm UV light (30 min).

m/z	THCA_No Photolysis	THCA_280 nm	THCA_365 nm
179	✓ ^a	✗	✗
191	✓ ^a	✗	✗
203	✓ ^a	✗	✗
229	✓ ^a	✗	✓ ^a
243	✓ ^a	✗	✓ ^a
245	✓ ^a	✗	✓ ^a

311	✓ ^a	X	✓ ^a
313	✓ ^a	X	✓ ^a
357**	✓ (v.s)	✓ (s)	✓ (s)
339	X	✓ (w)	X
355	X	X	✓ (w)
371	X	✓ (s)	✓ (s)
372	X	✓ (w)	✓ (w)
373	X	✓ (w)	✓ (w)
389	X	✓ (s)	✓ (s)
387	X	✓ (w)	✓ (w)
390	X	✓ (w)	X
374	X	X	✓ (w)
401	X	✓ (w)	X
403	X	✓ (s)	X
404	X	X	✓ (w)
405	X	✓ (w)	X
455	X	X	✓ (s)
684	X	✓ (s)	✓ (w)
715**	✓ (s)	✓ (w)	✓ (s)

^a Present as a strong fragment at 20 % HCD (Figure S19)

-Very strong (v.s.), strong (s), and weak (w).

S10: UV-Vis absorption spectra for photolysis of JWH-018 & MDMB-FUBINACA

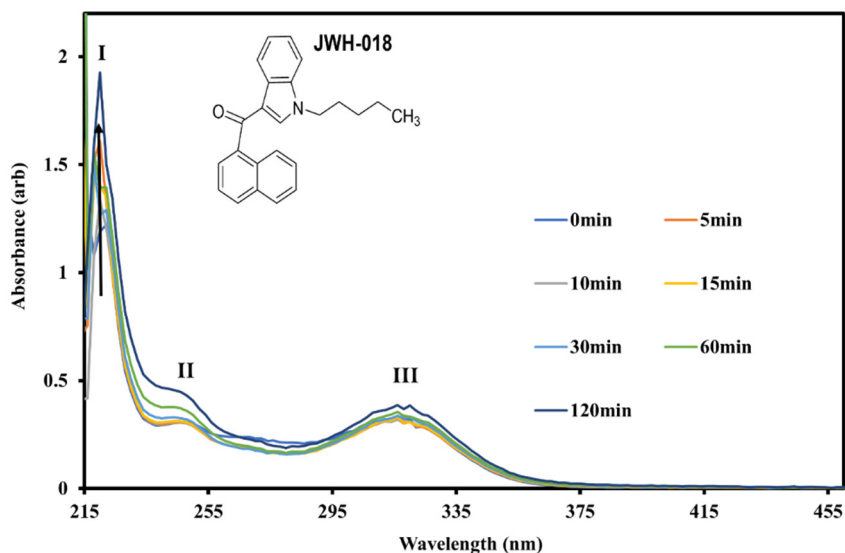


Figure S20: Solution-phase UV-Vis absorption spectra of JWH-018 in MeOH obtained following irradiation at 280 nm over 0–120 mins.

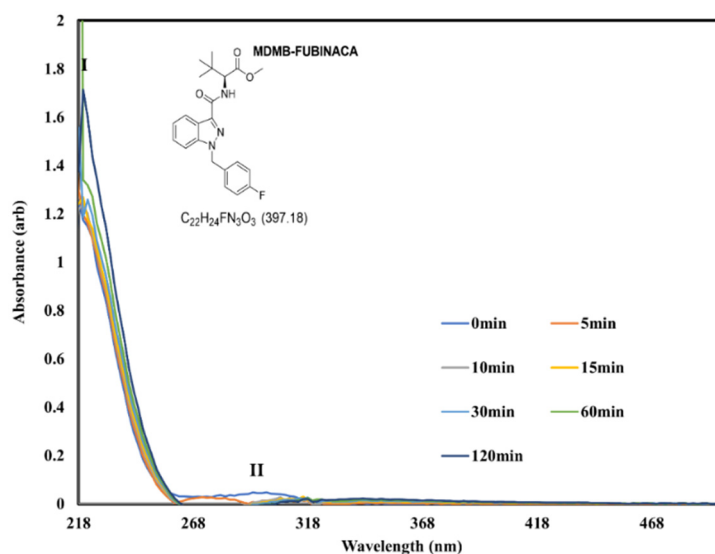


Figure S21: Solution-phase UV-Vis absorption spectra of MDMB-FUBINACA in ACN obtained following irradiation at 280 nm over 0–120 mins.

S11: Absorbance vs photolysis time measurements for JWH-018 & MDMB-FUBINACA

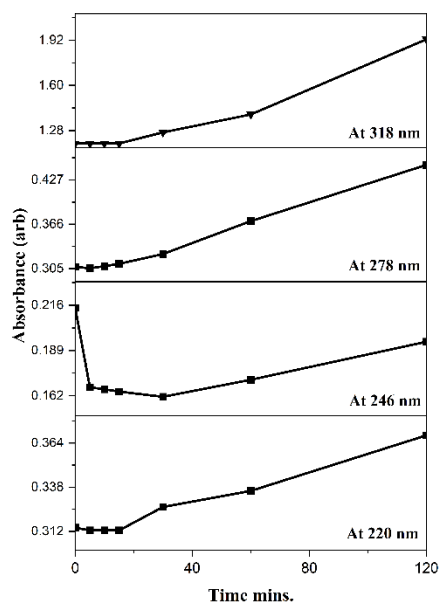


Figure S22: Absorbance versus time plots obtained for solutions of JWH-018 irradiated at 280 nm, obtained from the UV-Vis absorption spectra at a selection of wavelengths (220, 246, 278, and 318 nm).

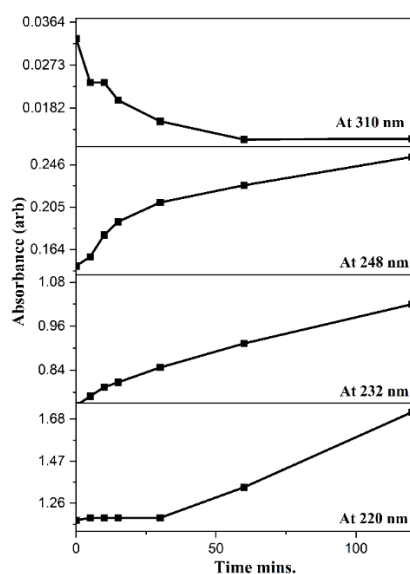


Figure S23: Absorbance versus time plots obtained for solutions of MDMB-FUBINACA irradiated at 280 nm, obtained from the UV-Vis absorption spectra at a selection of wavelengths (220, 232, 248, and 310 nm).

S12: ESI-MS of JWH-018 & MDMB-FUBINACA

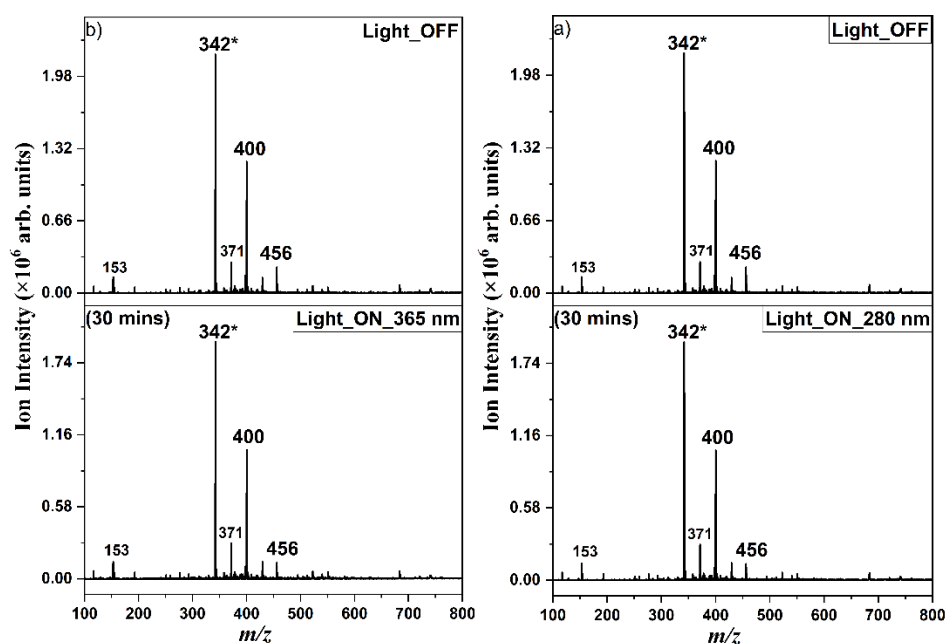


Figure S24: (a) Photolysis OFF and (b) photolysis ON ESI mass spectra of JWH-018 obtained in positive ion mode. (b) (LHS) and (b) (RHS) displays the ESI-MS obtained with 365 and 280 nm photolysis, respectively. The $[JWH-018+H]^+$ precursor ion is visible at m/z 342.

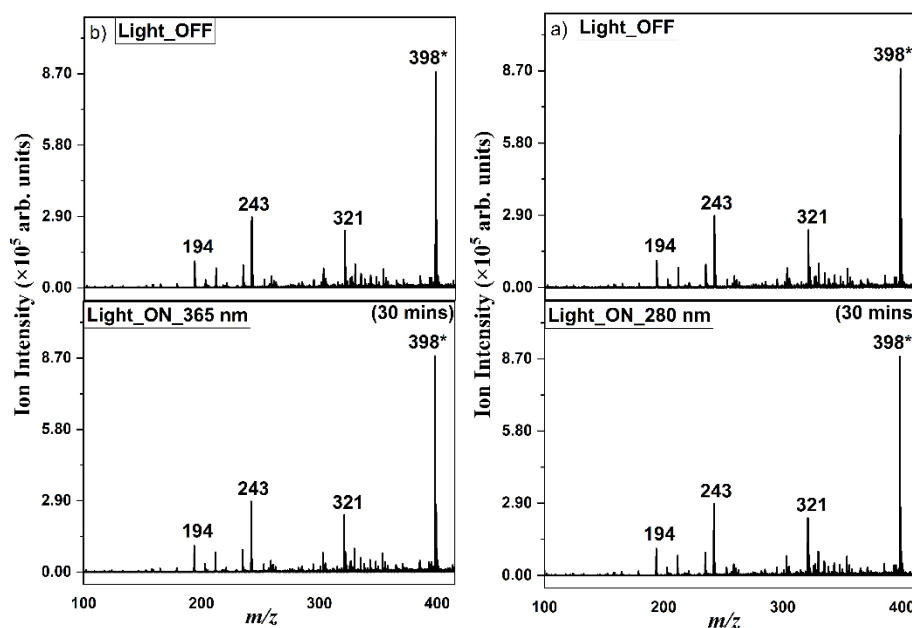
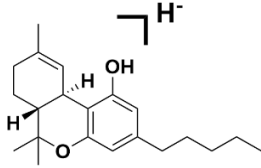
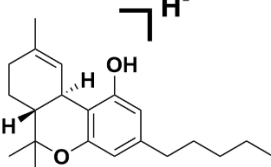
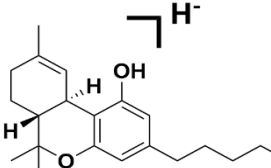
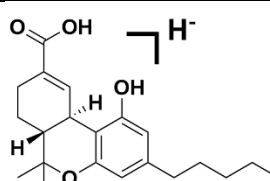
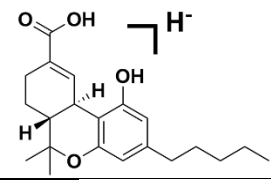
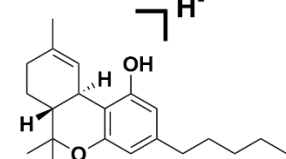
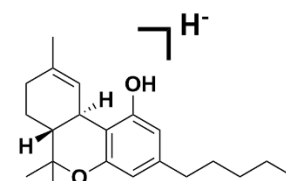
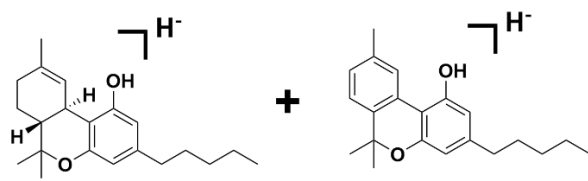
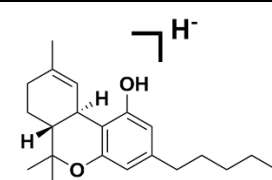
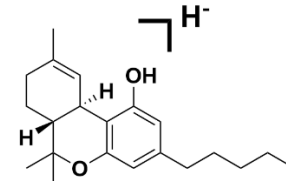
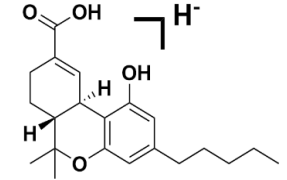
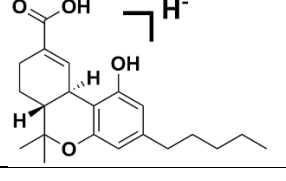


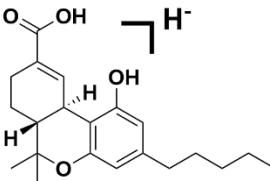
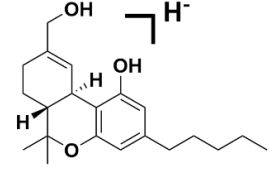
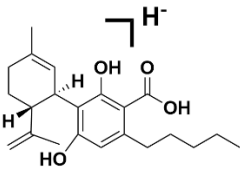
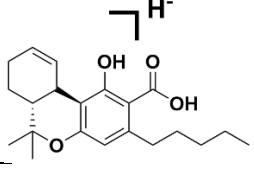
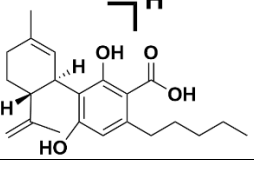
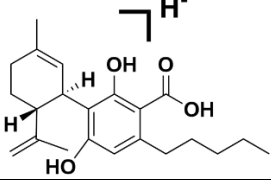
Figure S25: (a) Photolysis OFF and (b) photolysis ON ESI mass spectra of MDMB-FUBINACA obtained in positive ion mode. (b) (LHS) and (b) (RHS) displays the ESI-MS obtained with 365 and 280 nm photolysis, respectively. The [MDMB-FUBINACA+H]⁺ precursor ion is visible at m/z 398.

S13: Table of proposed structure of photolysis fragments

Table S5: Tentative structural assignments of negative-ion photoproducts observed during photolysis of THC, CBD, THC-COOH, THC-OH, CBDA, and THCA based on observed m/z values and plausible secondary photochemical processes.

[THC-H] ⁻ & [CBD-H] ⁻	
m/z	Proposed Structure
345	 H^- + CH ₃ OH or O ₂
359	 H^- + CH ₃ OH or O ₂ + O - 2H
363	 H^- + CH ₃ OH or O ₂ + H ₂ O

375	 $+ \text{CH}_3\text{OH} \text{ or } \text{O}_2$
389	 $+ \text{CH}_3\text{OH} \text{ or } \text{O}_2 + \text{O} - 2\text{H}$
477	 $+ \text{C}_6\text{H}_4(\text{OH})\text{C}_4\text{H}_9$
381	 $+ \text{CH}_2=\text{C}(\text{CH}_3)_2 - 2\text{H}$
511	 $- m/z 111$
[THC-COOH-H]⁻	
313	
315	 $+ 2\text{H}$
331	 $- \text{CH}_2 + 2\text{H}$
363	 $+ \text{O} + 4\text{H}$

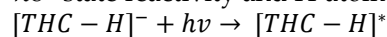
375	 $+ \text{CH}_3\text{OH}$
[THC-OH-H]⁻	
361	 $+ \begin{matrix} \text{CH}_3\text{OH} \\ \text{or} \\ \text{O}_2 \end{matrix}$
[CBDA-H]⁻ & [THCA-H]⁻	
373	 $+ \text{O}$
371	 $+ \text{O} - 2\text{H}$
389	 $+ \begin{matrix} \text{CH}_3\text{OH} \\ \text{or} \\ \text{O}_2 \end{matrix}$
403	 $+ \begin{matrix} \text{CH}_3\text{OH} \\ \text{or} \\ \text{O}_2 \end{matrix} + \text{O} - 2\text{H}$

S13A: Proposed Photochemical Reaction Pathways

The following mechanistic schemes are proposed to rationalise the principal photoproduct ions observed during online LED irradiation (280 and 365 nm). Assignments are based on observed mass shifts, growth/decay behaviour, and the tentative structural proposals in Table S6. The pathways reflect established features of aromatic and terpene photochemistry, including excited-state reactivity, radical formation, oxygen trapping, oxidative functionalisation, and rearrangement processes.

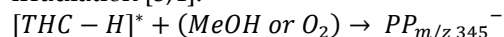
A) THC ([THC-H]⁻, *m/z* 313)

Photoexcitation of THC generates an electronically excited state capable of homolytic bond weakening at the allylic/phenolic region, consistent with established UV-induced $\pi\sigma^*$ state reactivity and H-atom elimination in aromatic systems [1,2].

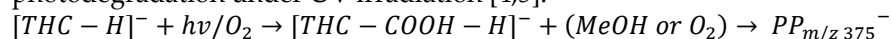


Subsequent radical trapping by dissolved O_2 or solvent (MeOH) affords the *m/z* 345 product (net +32 Da addition), consistent with oxygen-mediated and solvent-assisted

phototransformation pathways reported previously for cannabinoids under UV irradiation [3,4].

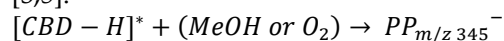


Further oxidative transformation via an oxidised intermediate consistent with a THC-COOH-type species (m/z 343) leads to formation of m/z 375, in agreement with stepwise oxygen incorporation processes reported previously for cannabinoid photodegradation under UV irradiation [4,5].

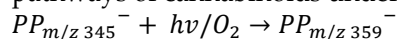


B) CBD ([CBD-H]⁻, m/z 313)

CBD undergoes analogous photoexcitation and radical formation consistent with established UV-induced phenolic excited-state reactivity [1,2]. Subsequent trapping by dissolved oxygen or solvent yields the m/z 345 product, in agreement with reported oxygen-mediated photo transformation pathways for cannabinoids under UV irradiation [3,5].

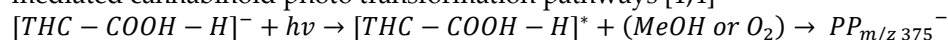


Secondary oxidative dehydrogenation of the intermediate produce's m/z 359 (consistent with net +O -2H), in agreement with reported oxidative transformation pathways of cannabinoids under UV irradiation [3].

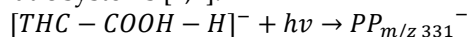


C) THC-COOH ([THC-COOH-H]⁻, m/z 343)

Excited-state activation enables solvent or O₂ addition to yield m/z 375, consistent with established UV-induced excited-state reactivity of phenolic systems and oxygen-mediated cannabinoid photo transformation pathways [1,4]

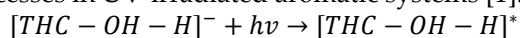


Formation of m/z 331 is attributed to photoinduced bond cleavage within the terpene framework followed by intramolecular hydrogen transfer, consistent with established excited-state bond weakening and H-atom rearrangement processes in UV-irradiated aromatic systems [1,2].

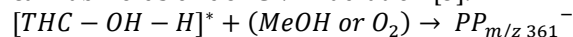


D) THC-OH ([THC-OH-H]⁻, m/z 329)

UV excitation promotes radical formation at the hydroxylated terpene region, consistent with established excited-state bond weakening and H-atom elimination processes in UV-irradiated aromatic systems [1].

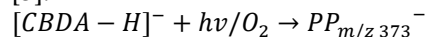


Subsequent trapping by dissolved O₂ or solvent affords m/z 361 (net +32 Da), consistent with oxygen-mediated photo transformation pathways reported for cannabinoids under UV irradiation [3].



E) CBDA ([CBDA-H]⁻, m/z 357)

Photooxidation results in oxygen incorporation to form m/z 373 (net +O), consistent with reported oxidative transformation pathways of cannabinoids under UV irradiation [3].

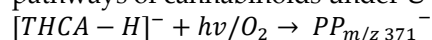


Radical trapping or solvent addition yields m/z 389 (net +32 Da), consistent with oxygen-mediated photo transformation pathways reported for cannabinoids under UV irradiation [3].



F) THCA ([THCA-H]⁻, m/z 357)

Oxidative functionalization accompanied by dehydrogenation yields m/z 371 (consistent with net $+O - 2H$), in agreement with reported oxidative photo transformation pathways of cannabinoids under UV irradiation [3].



Overall, cannabinoid photolysis under monochromatic UV irradiation proceeds predominantly via excited-state radical chemistry followed by oxygen-mediated functionalization, solvent trapping, oxidative dehydrogenation, and structural rearrangement processes, consistent with established photochemical behavior of phenolic systems and reported UV-induced cannabinoid transformation pathways [1,3].

References

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- [3] Ahmed, R.; Zhou, Y.; Singh, P. Photodegradation of cannabidiol (CBD) and Δ^9 -THC in cannabis chemotypes. *Photochem. Photobiol. Sci.* **2024**, *23*, 1567–1578.
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S14: Quartz syringe photolysis apparatus

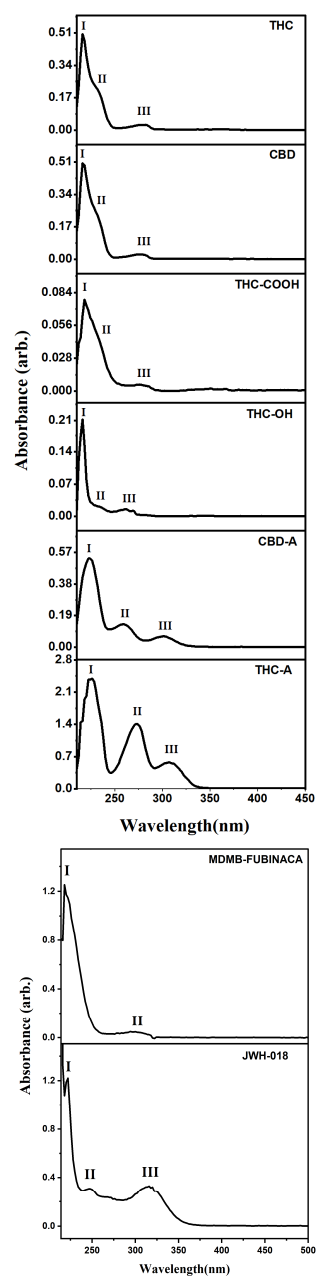


Figure S26: Picture of the Quartz syringe which is used in the current experiments.

S15: Experimental setup used for UV photolysis



Figure S27: Photo of the experimental setup used for UV photolysis. A UV LED shines on the ESI-syringe, allowing the sample to be exposed to light before entering the mass spectrometer.

S16: UV-Vis Absorbance vs Wavelength spectra at 0 min. for all cannabinoids**Figure S28.** Solution-phase UV-Vis absorption spectra of Cannabinoids at 0 min.