

Supplementary Information

Disarming antibiotics with a flash of light: LED-illuminated NMR and MS analysis

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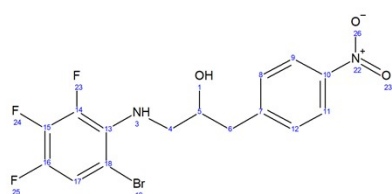
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1. NMR analysis of authentic compounds

1.1. Ethanolamine 3



Shift1 (ppm)	H's	Type	J (Hz)	Atom1	Multiplet1
2.81	1.000	dd	13.9, 7.0	6<">	M04
2.89	1.000	dd	13.9, 5.1	6<">	M05
3.13	1.000	ddd	13.2, 7.7, 1.5	4<">	M06
3.36	1.000	m	-	4<">	M07
3.92	1.000	m	-	5	M08
7.29	1.000	ddd	10.0, 7.8, 2.4	17	M03
7.41	2.000	d	8.8	8, 12	M02
8.09	2.000	d	8.4	9, 11	M01

¹H NMR (600 MHz, ACND₂O): δ = 2.81 (dd, *J* = 13.9, 7.0 Hz, 1 H, 6<">), 2.89 (dd, *J* = 13.9, 5.1 Hz, 1 H, 6<">), 3.13 (ddd, *J* = 13.2, 7.7, 1.5 Hz, 1 H, 4<">), 3.33 - 3.39 (m, 1 H, 4<">), 3.90 - 3.94 (m, 1 H, 5), 7.29 (ddd, *J* = 10.0, 7.8, 2.4 Hz, 1 H, 17), 7.41 (d, *J* = 8.8 Hz, 2 H, 8, 12), 8.09 (d, *J* = 8.4 Hz, 2 H, 9, 11) ppm

Solvent ACND₂O
Pulse Sequence zg30
Temperature (degree C) 24.900
Acquisition Time (sec) 1.3631
Number of Transients 128
Points Count 32768
Sweep Width (Hz) 12018.86
Spectrum Offset (Hz) 3726.1499

Original Points Count 16384
Nucleus 1H
Frequency (MHz) 600.1300

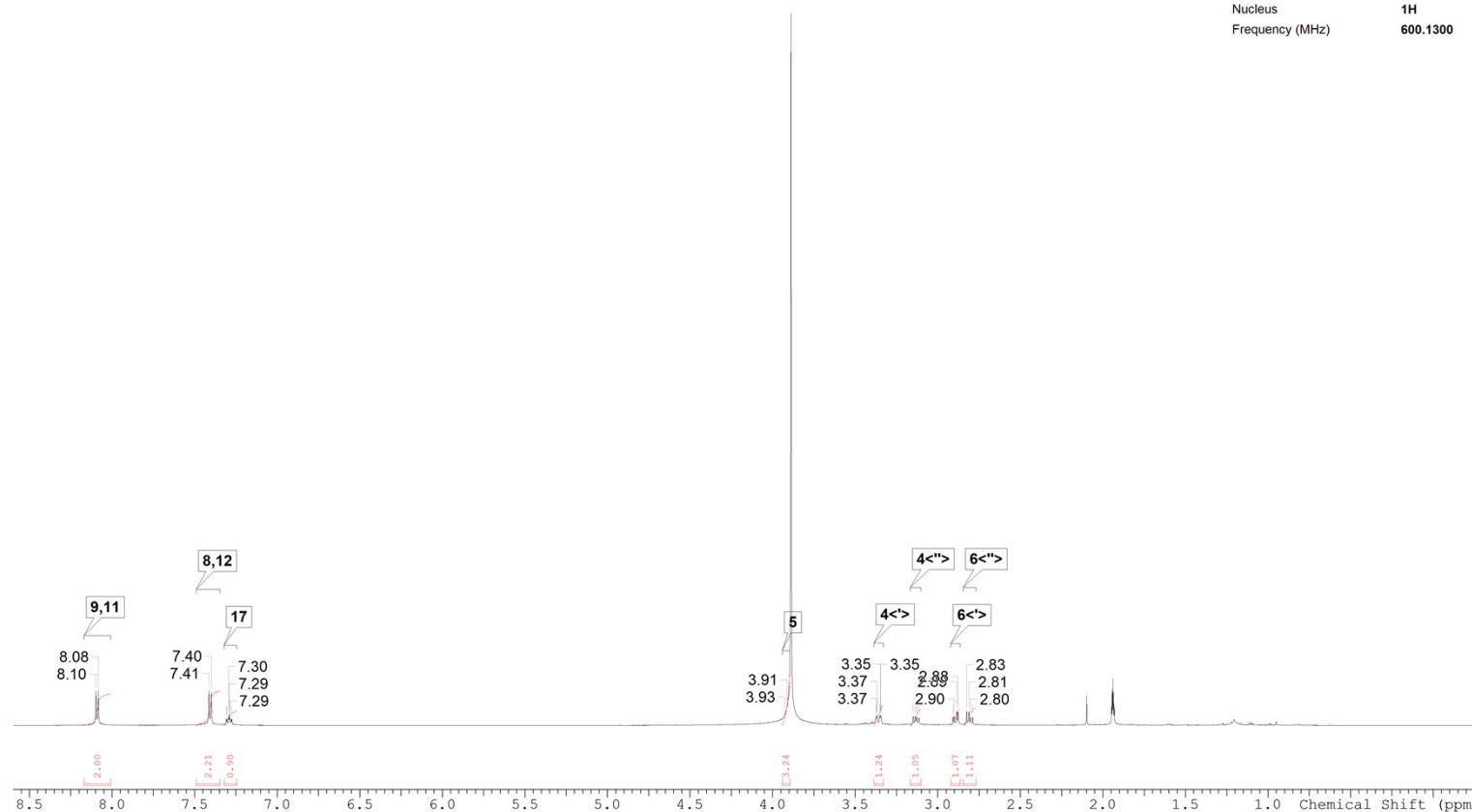


Fig. S1. ¹H spectrum, structure, numbering and full assignment of ethanolamine 3 in ACN:D₂O (7:3) at 25 °C.

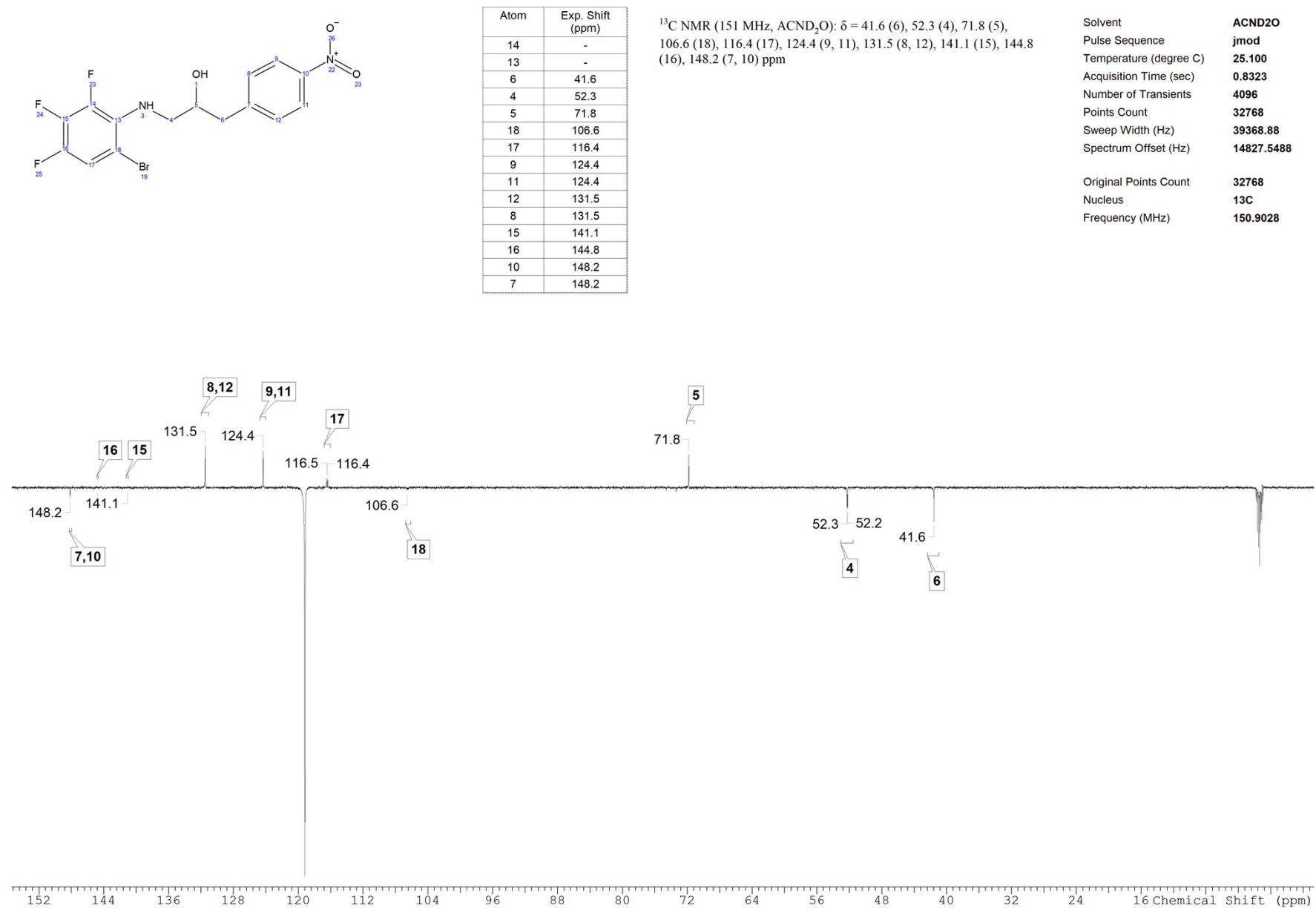


Fig. S2. ¹³C spectrum, structure, numbering and full assignment of ethanolamine **3** in ACN:D₂O (7:3) at 25 °C.

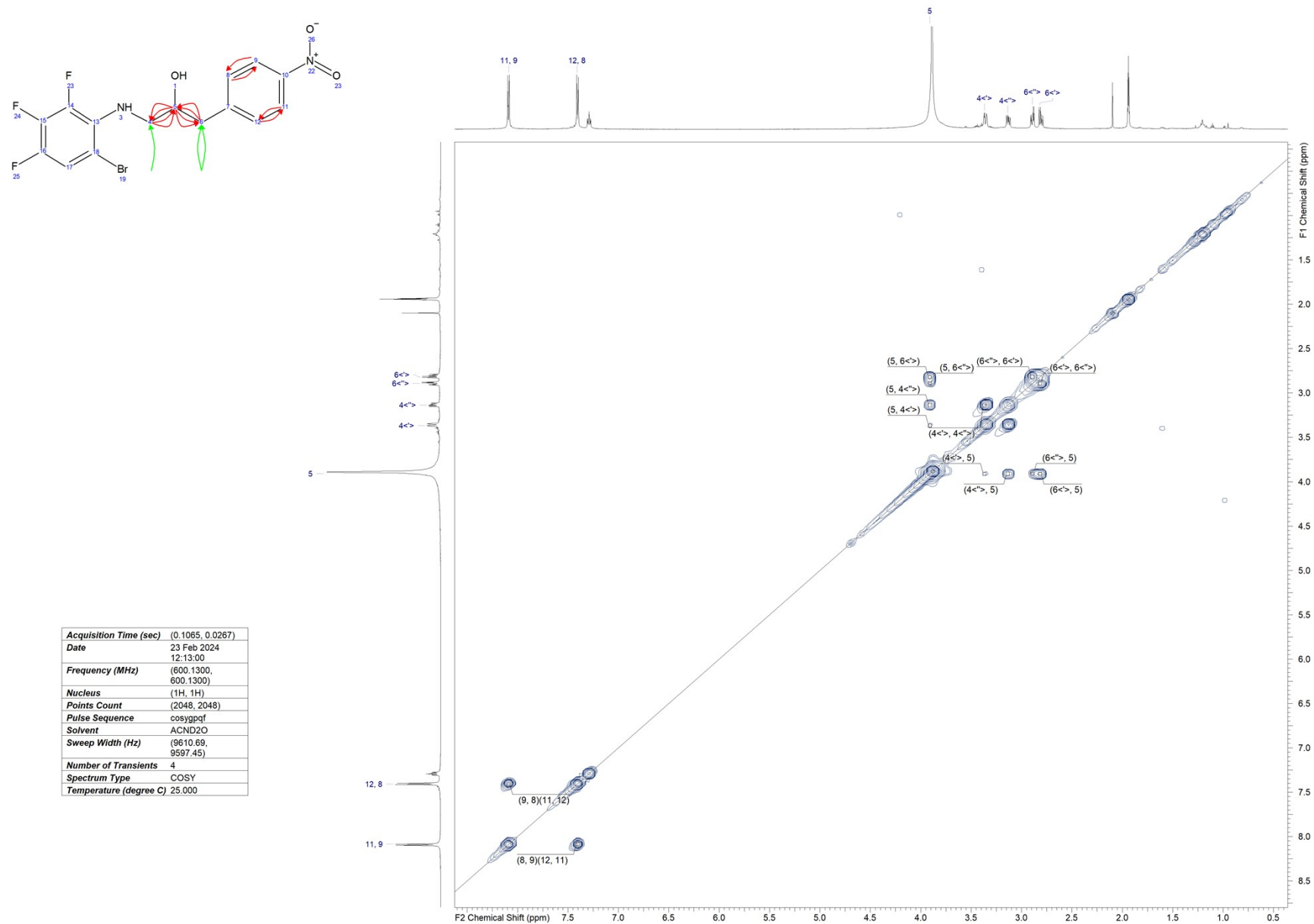


Fig. S3. Fully assigned ^1H - ^1H COSY spectrum of ethanolamine **3** in ACN:D₂O (7:3) at 25 °C.

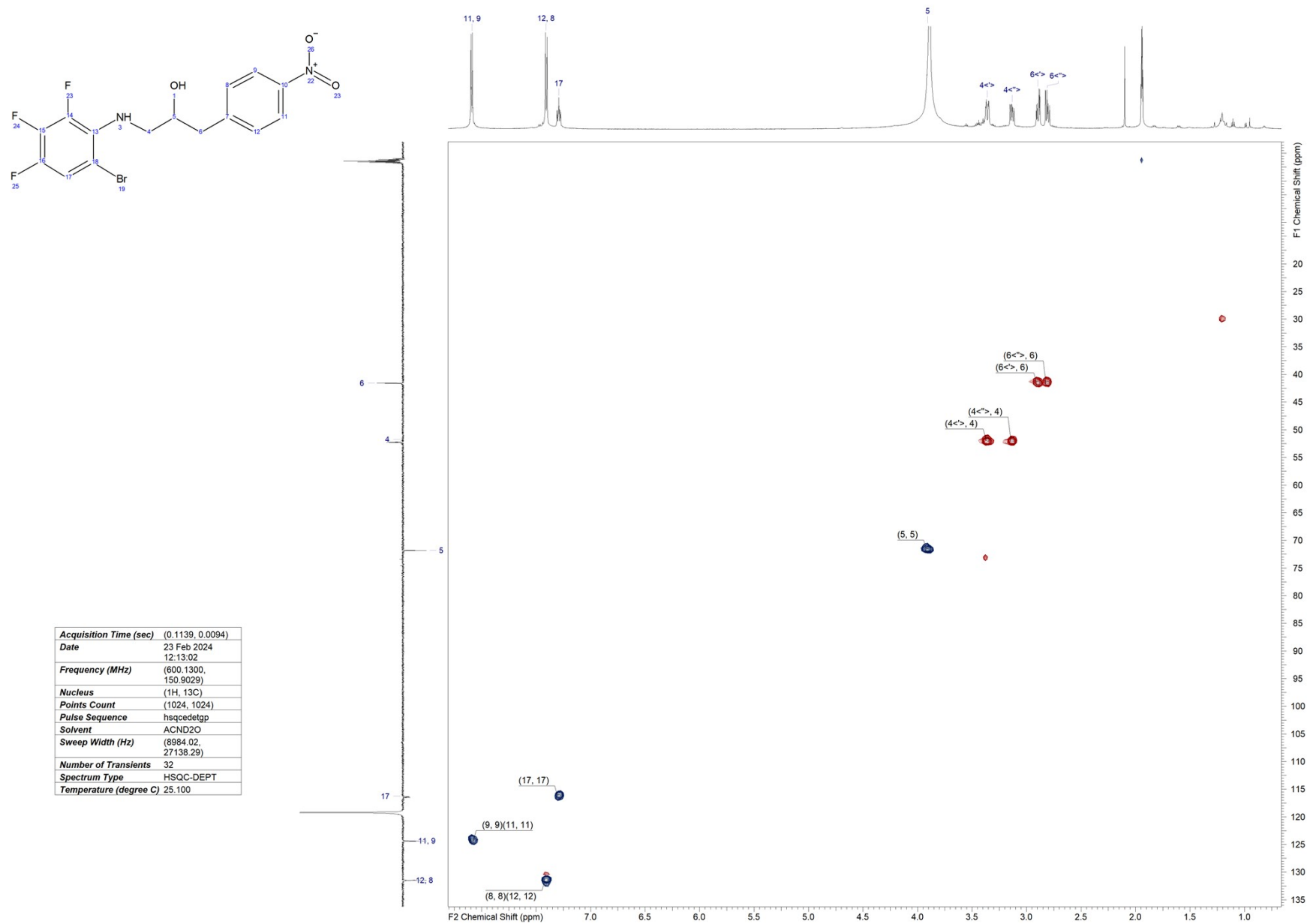


Fig. S4. Fully assigned ^1H - ^{13}C HSQC spectrum of ethanolamine **3** in $\text{ACN:D}_2\text{O}$ (7:3) at 25 °C.

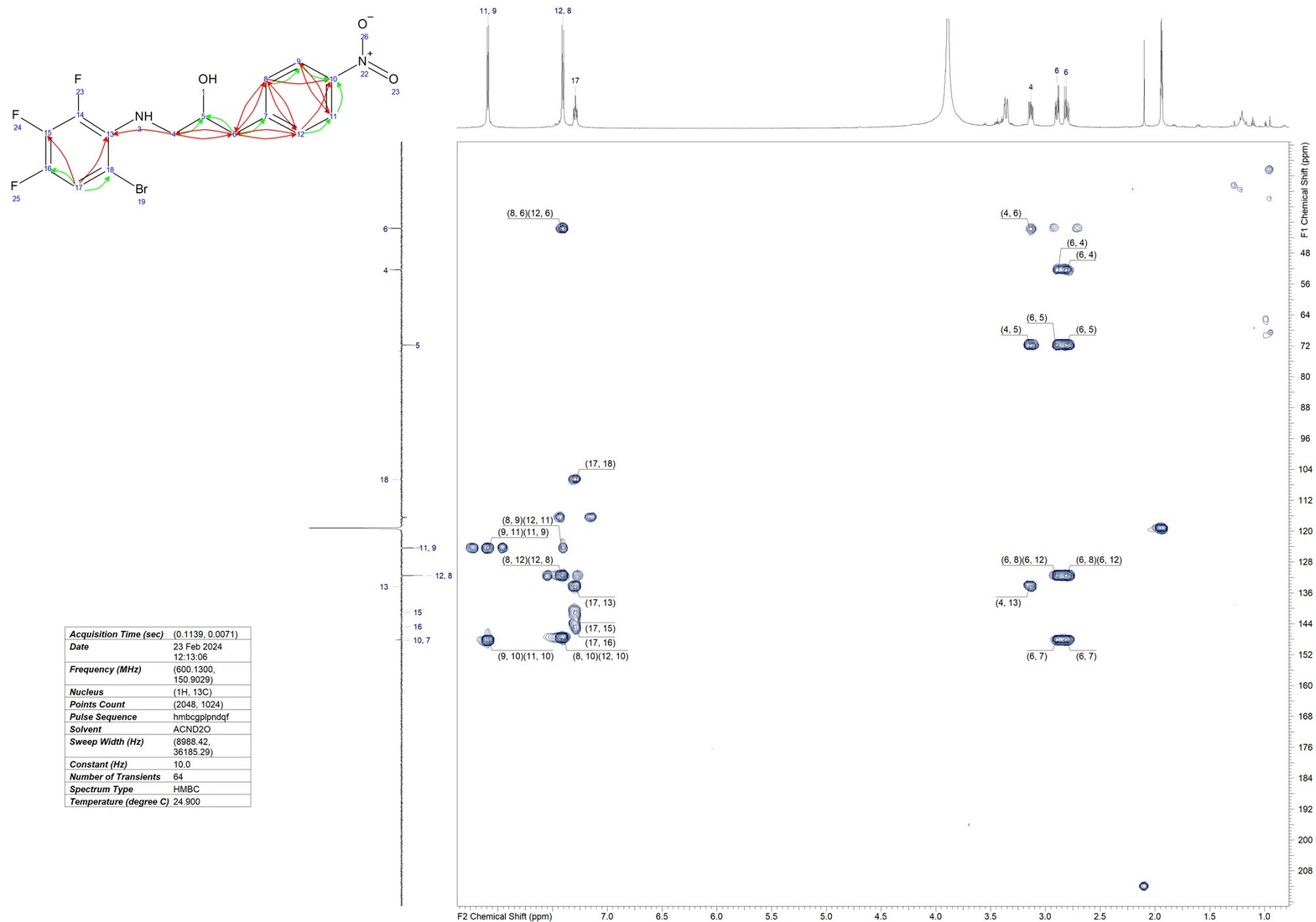


Fig. S5. Fully assigned ¹H-¹³C HMBC spectrum of ethanolamine **3** in ACN:D₂O (7:3) at 25 °C.

1.2. Oxazolidine 4

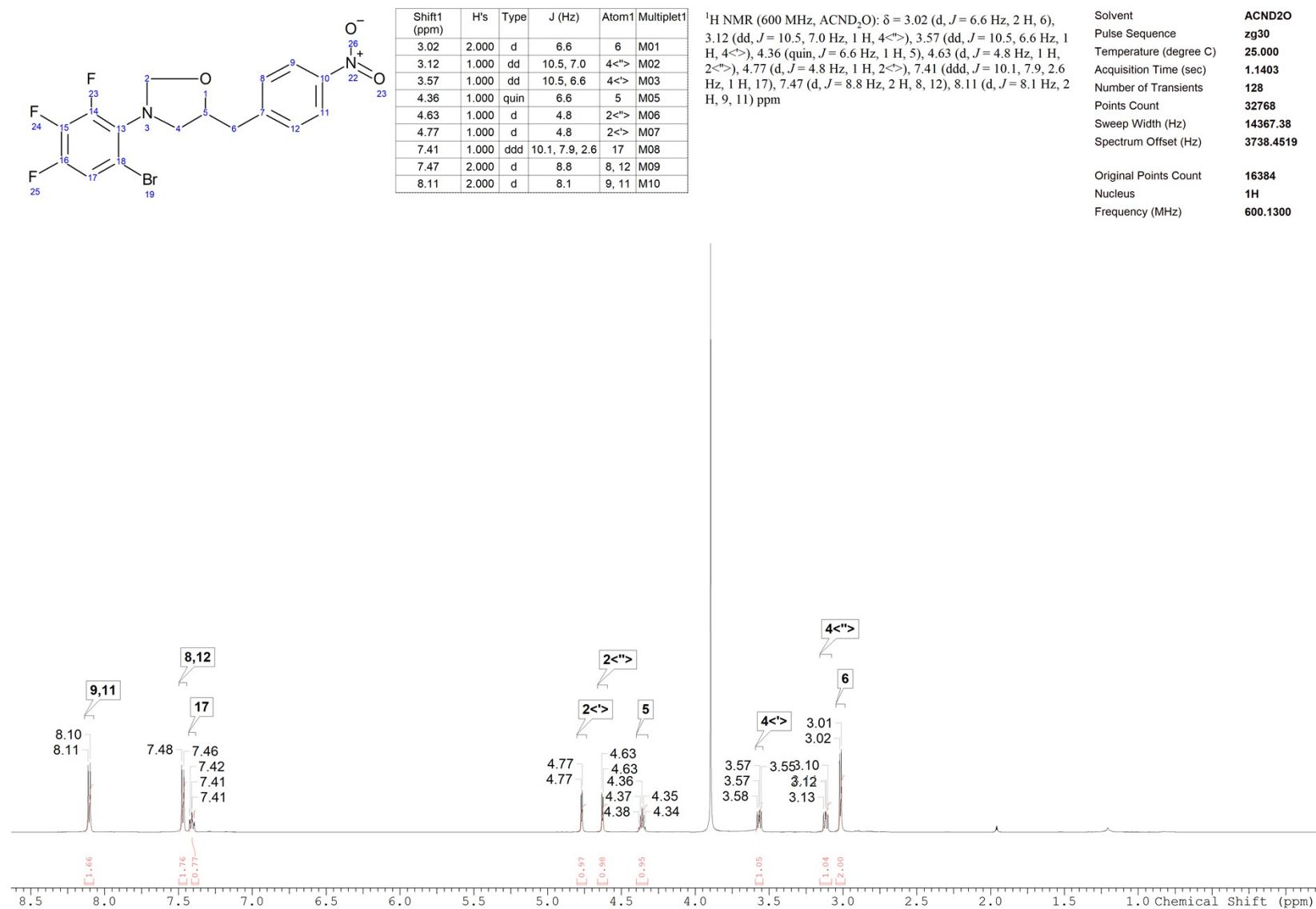
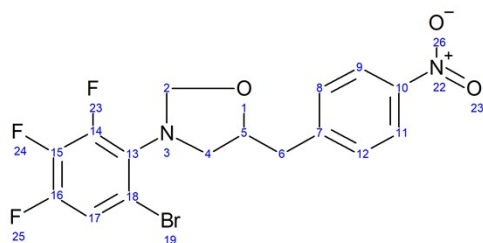


Fig. S6. ¹H spectrum, structure, numbering and full assignment of oxazolidine 4 in ACN:D₂O (7:3) at 25 °C.



Shift1 (ppm)	C's	Type	J (Hz)	Atom1	Multiplet1
38.49	1.000	s	-	6	M09
55.28	1.000	d	3.6	4	M10
76.85	1.000	s	-	5	M12
82.79	1.000	br d	6.0	2	M01
115.52	1.000	br d	20.4	17	M08
116.49	1.000	br s	-	18	M02
122.89	2.000	s	-	9, 11	M11
129.97	2.000	s	-	8, 12	M20
132.31	1.000	br d	9.6	13	M03
139.28	1.000	dt	251.4, 16.1	15	M04
146.08	1.000	s	-	7	M21
146.17	1.000	s	-	10	M05
147.18	1.000	dd	237.9, 3.6	14	M06
147.18	1.000	br dd	258.3, 2.4	16	M07

^{13}C NMR (151 MHz, ACND_2O): δ = 38.5 (6), 55.3 (4), 76.9 (5), 82.8 (2), 115.5 (17), 116.5 (18), 122.9 (9, 11), 130.0 (8, 12), 132.3 (13), 139.3 (15), 146.1 (7), 146.2 (10), 147.2 (16), 147.2 (14) ppm

Solvent **ACND2O**
Pulse Sequence **jmod**
Temperature (degree C) **25.000**
Acquisition Time (sec) **0.8323**
Points Count **32768**
Sweep Width (Hz) **39368.88**
Spectrum Offset (Hz) **14598.87**
Original Points Count **32768**
Nucleus **^{13}C**
Frequency (MHz) **150.9028**

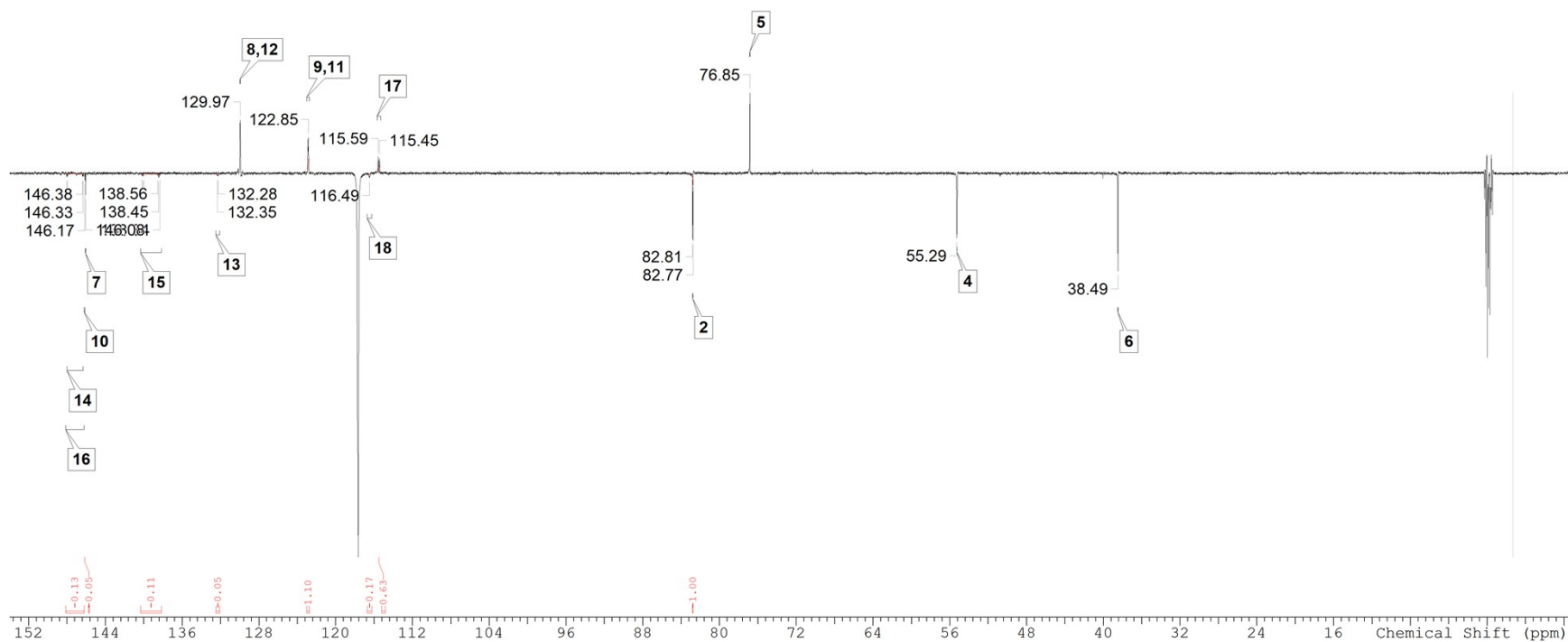


Fig. S7. ^{13}C spectrum, structure, numbering and full assignment of oxazolidine **4** in $\text{ACN}:\text{D}_2\text{O}$ (7:3) at 25 °C.

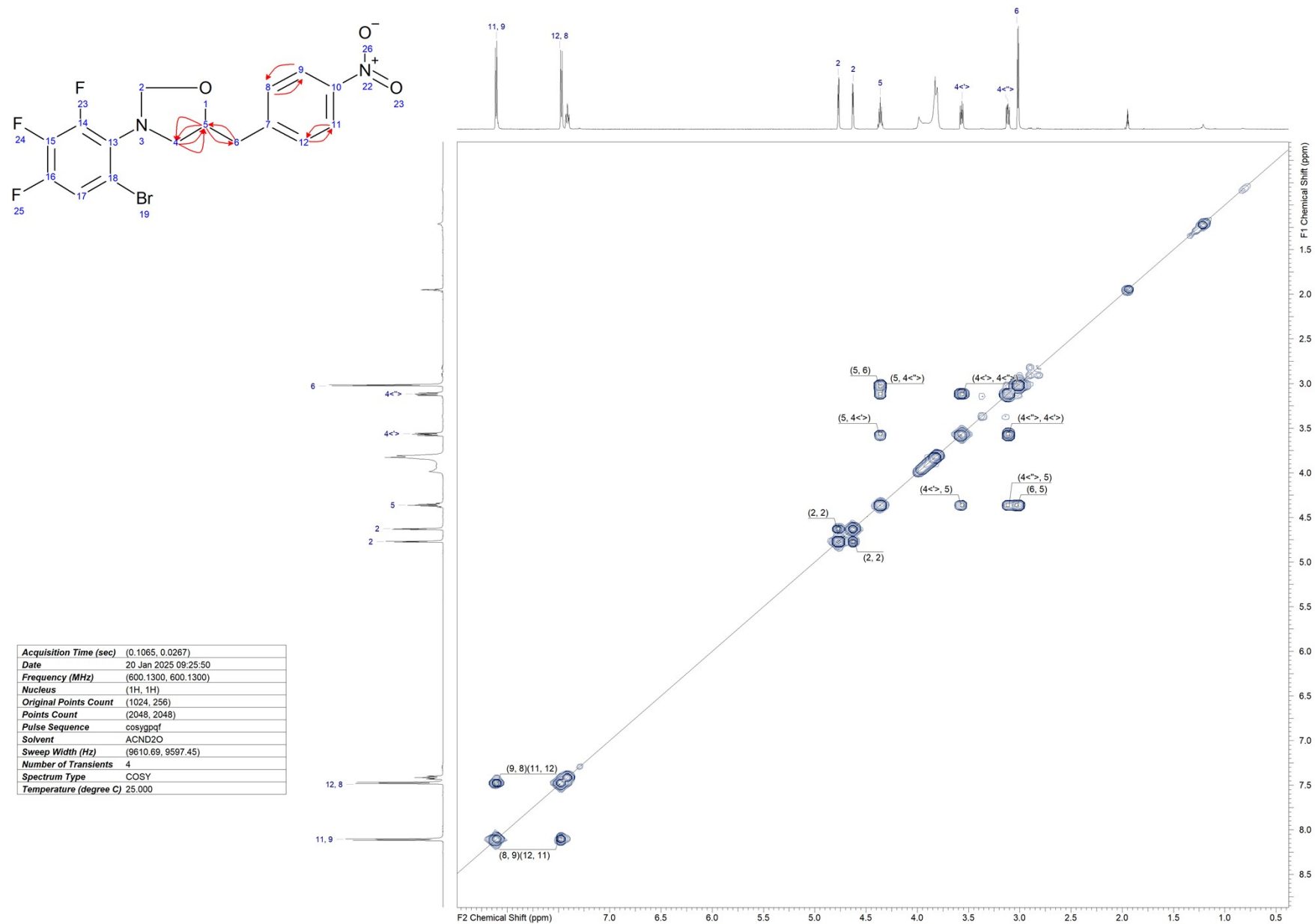


Fig. S8. Fully assigned ^1H - ^1H COSY spectrum of oxazolidine **4** in $\text{ACN:D}_2\text{O}$ (7:3) at 25 °C.

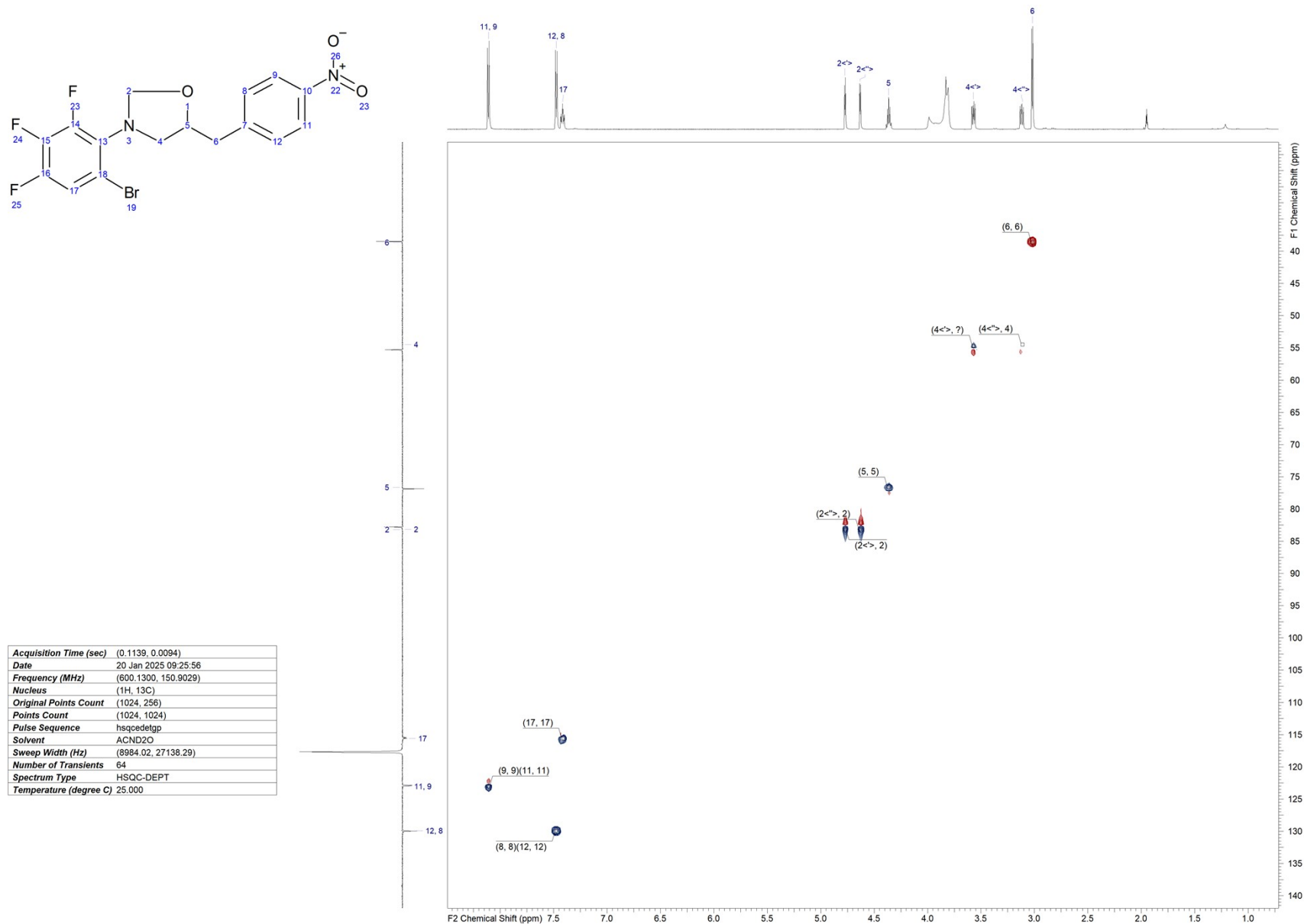


Fig. S9. Fully assigned ^1H - ^{13}C HSQC spectrum of oxazolidine **4** in $\text{ACN}:\text{D}_2\text{O}$ (7:3) at 25 °C.

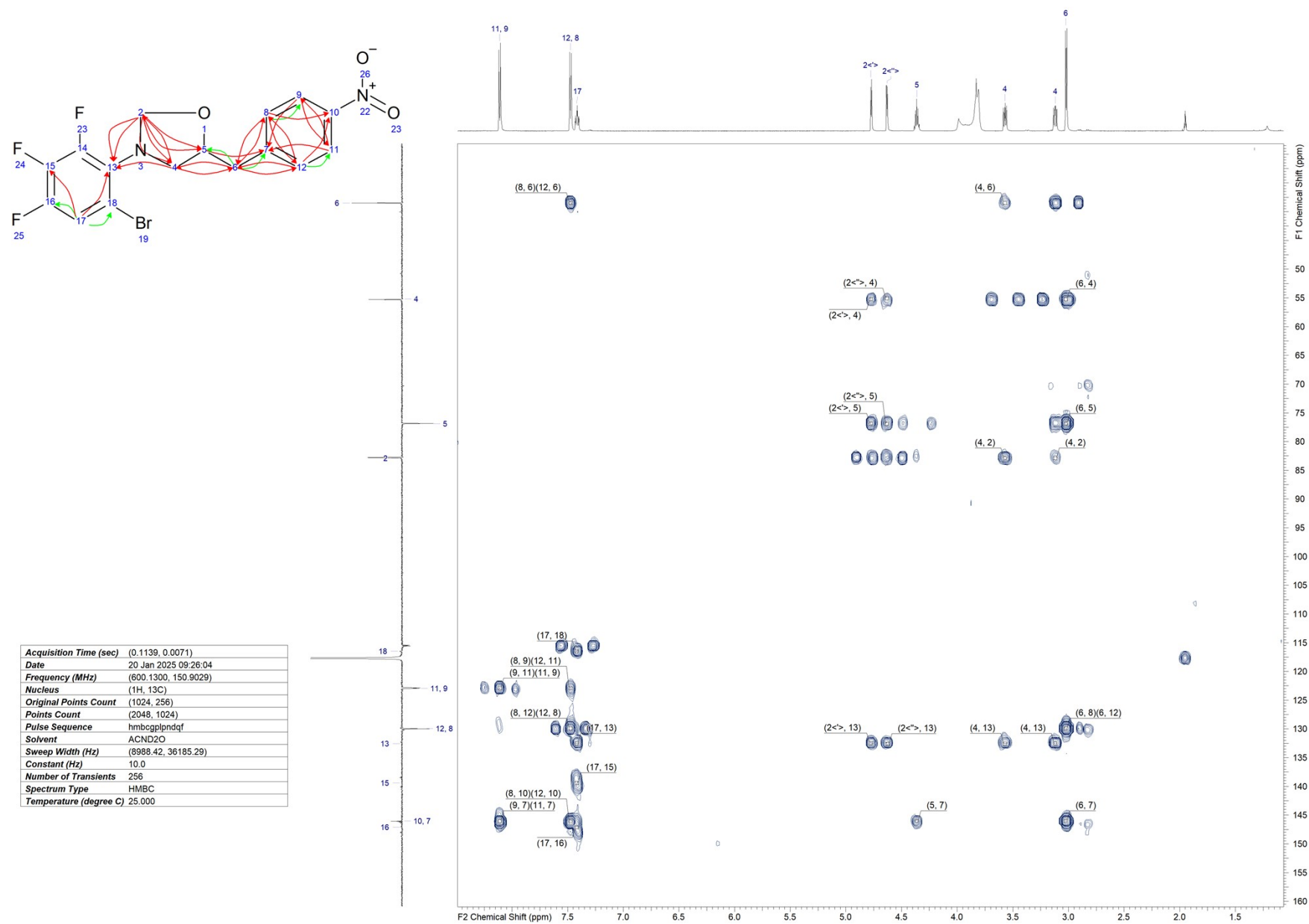


Fig. S10. Fully assigned ^1H - ^{13}C HMBC spectrum of oxazolidine **4** in $\text{ACN:D}_2\text{O}$ (7:3) at 25 °C.

1.3. Aniline **8**

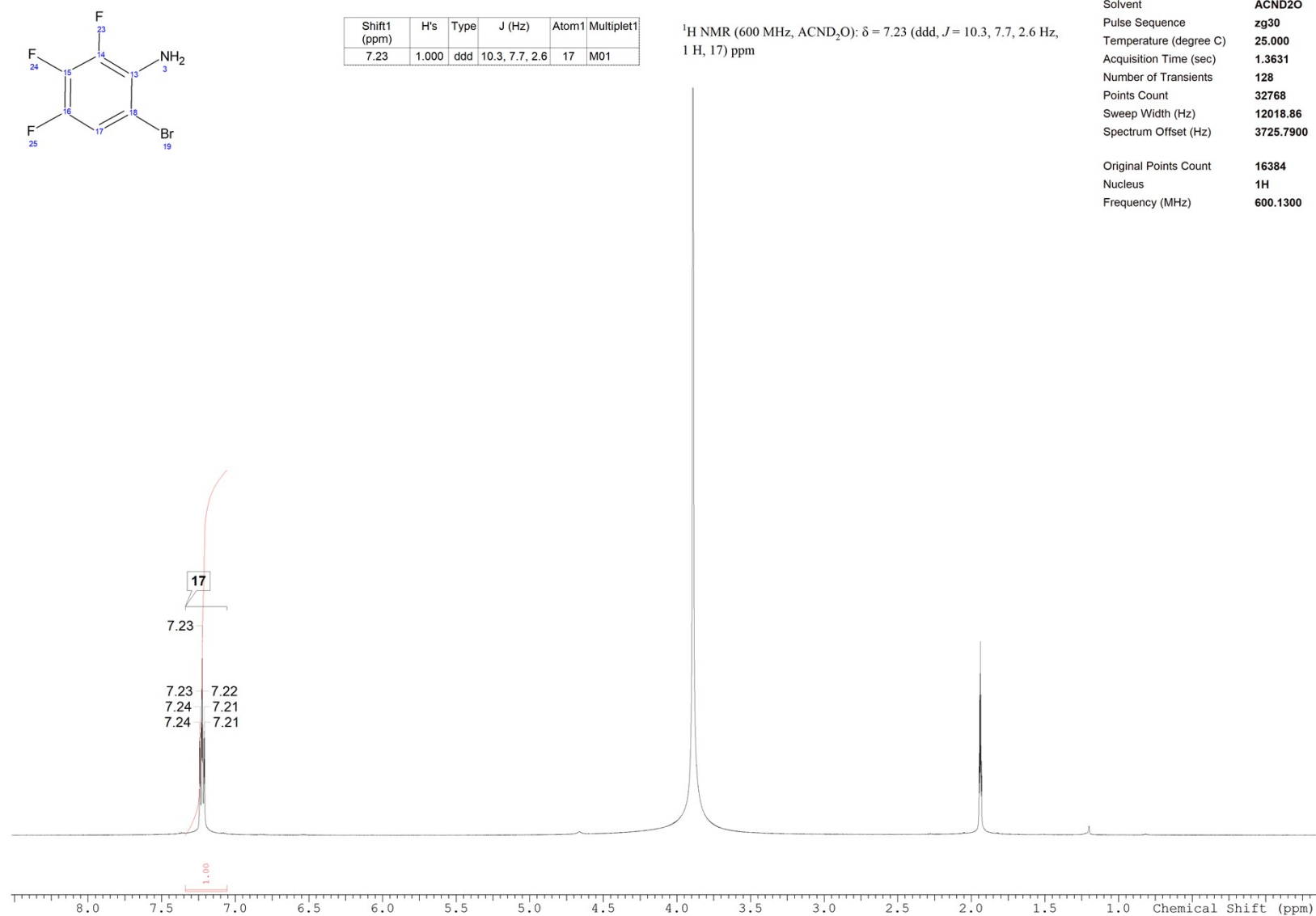
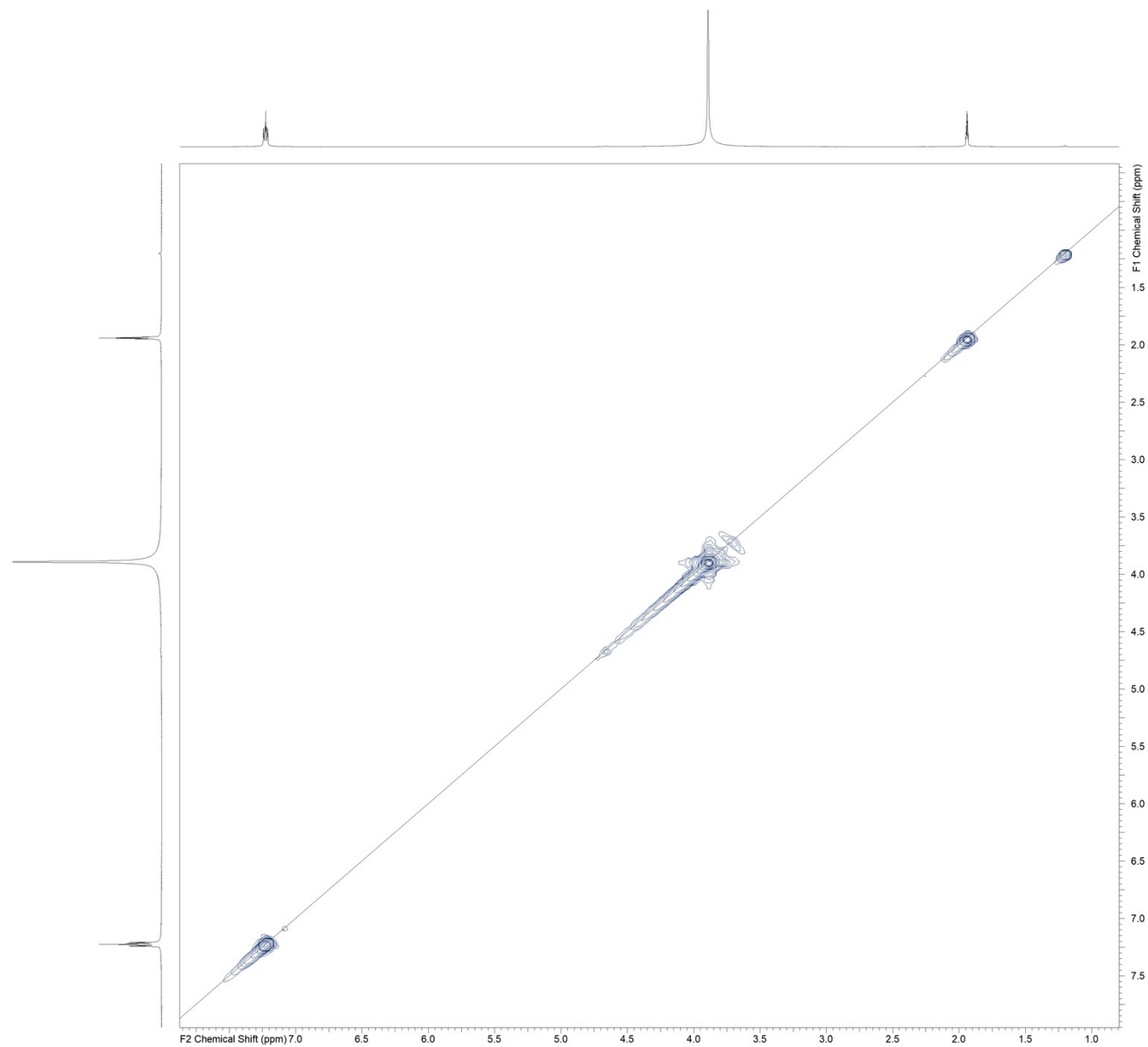
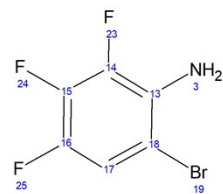
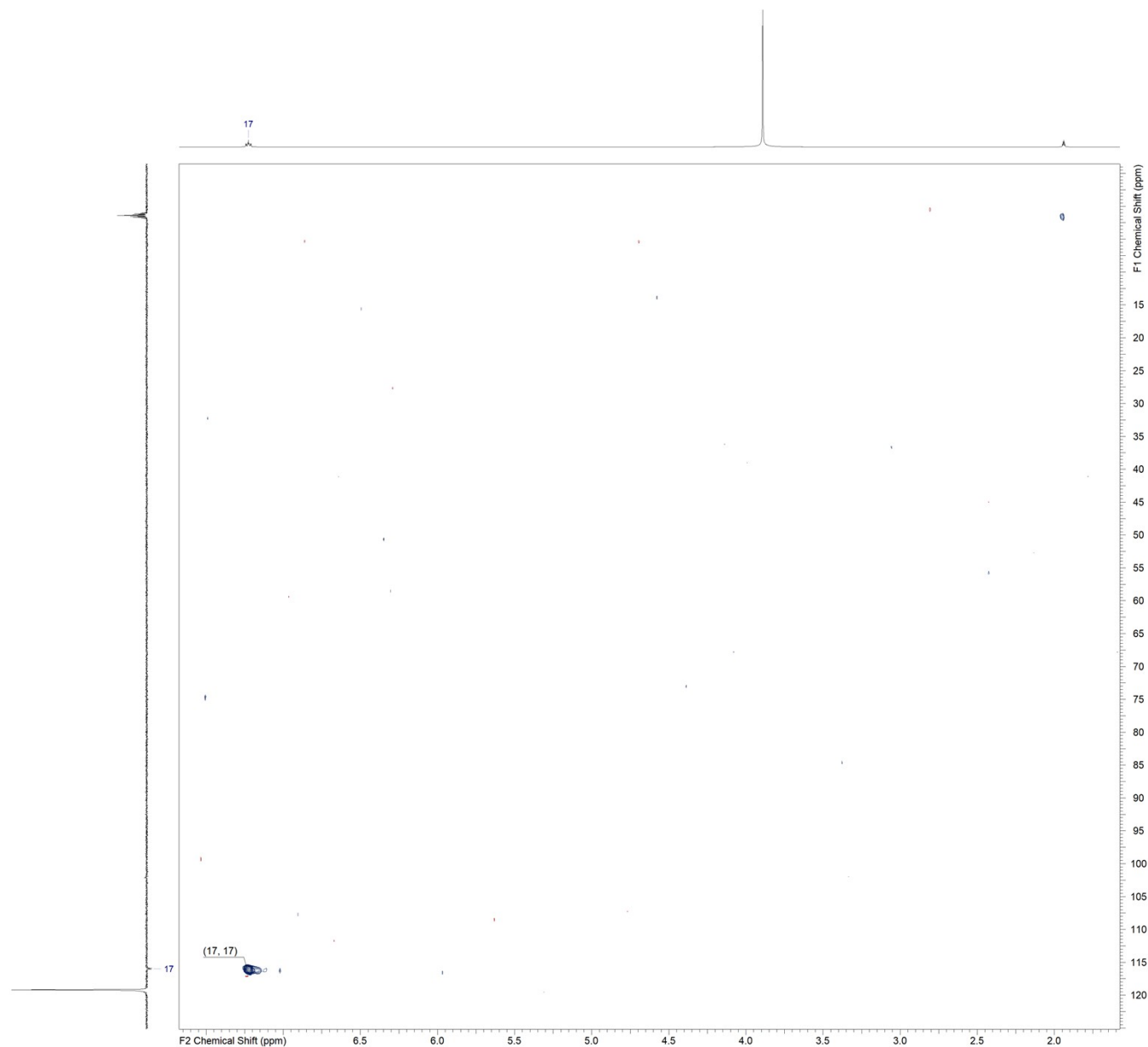
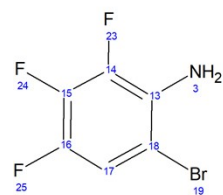


Fig. S11. ¹H spectrum, structure, numbering and full assignment of 6-bromo-2,3,4-trifluoroaniline **8** in ACN:D₂O (7:3) at 25 °C.



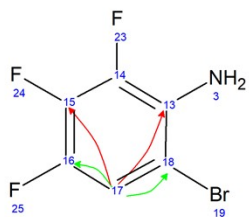
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Points Count	(2048, 2048)
Pulse Sequence	cosygpgf
Solvent	ACND2O
Sweep Width (Hz)	(9610.69, 9597.45)
Number of Transients	2
Spectrum Type	COSY
Temperature (degree C)	25.000

Fig. S12. ^1H - ^1H COSY spectrum of 6-bromo-2,3,4-trifluoroaniline **8** in $\text{ACN:D}_2\text{O}$ (7:3) at 25 °C.



Acquisition Time (sec)	(0.1139, 0.0094)
Date	23 Feb 2024 12:13:30
Frequency (MHz)	(600.1300, 150.9029)
Nucleus	(1H, 13C)
Points Count	(1024, 1024)
Pulse Sequence	hsqcetgcp
Solvent	ACND2O
Sweep Width (Hz)	(8984.02, 27138.29)
Number of Transients	16
Spectrum Type	HSQC-DEPT
Temperature (degree C)	25.200

Fig. S13. Fully assigned ^1H - ^{13}C HSQC spectrum of 6-bromo-2,3,4-trifluoroaniline **8** in $\text{ACN:D}_2\text{O}$ (7:3) at 25 °C.



Atom	Exp. Shift (ppm)
14	-
18	102.1
17	116.0
13	133.5
15	140.6
16	144.0

^{13}C NMR (151 MHz, ACND_2O): δ = 102.1 (18), 116.0 (17), 133.5 (13), 140.6 (15), 144.0 (16) ppm

Acquisition Time (sec)	(0.1139, 0.0071)
Date	23 Feb 2024 12:13:32
Frequency (MHz)	(600.1300, 150.9029)
Nucleus	(^1H , ^{13}C)
Points Count	(2048, 1024)
Pulse Sequence	hmbcpglndqf
Solvent	ACND ₂ O
Sweep Width (Hz)	(8988.42, 36185.29)
Constant (Hz)	10.0
Number of Transients	32
Spectrum Type	HMBC
Temperature (degree C)	24.900

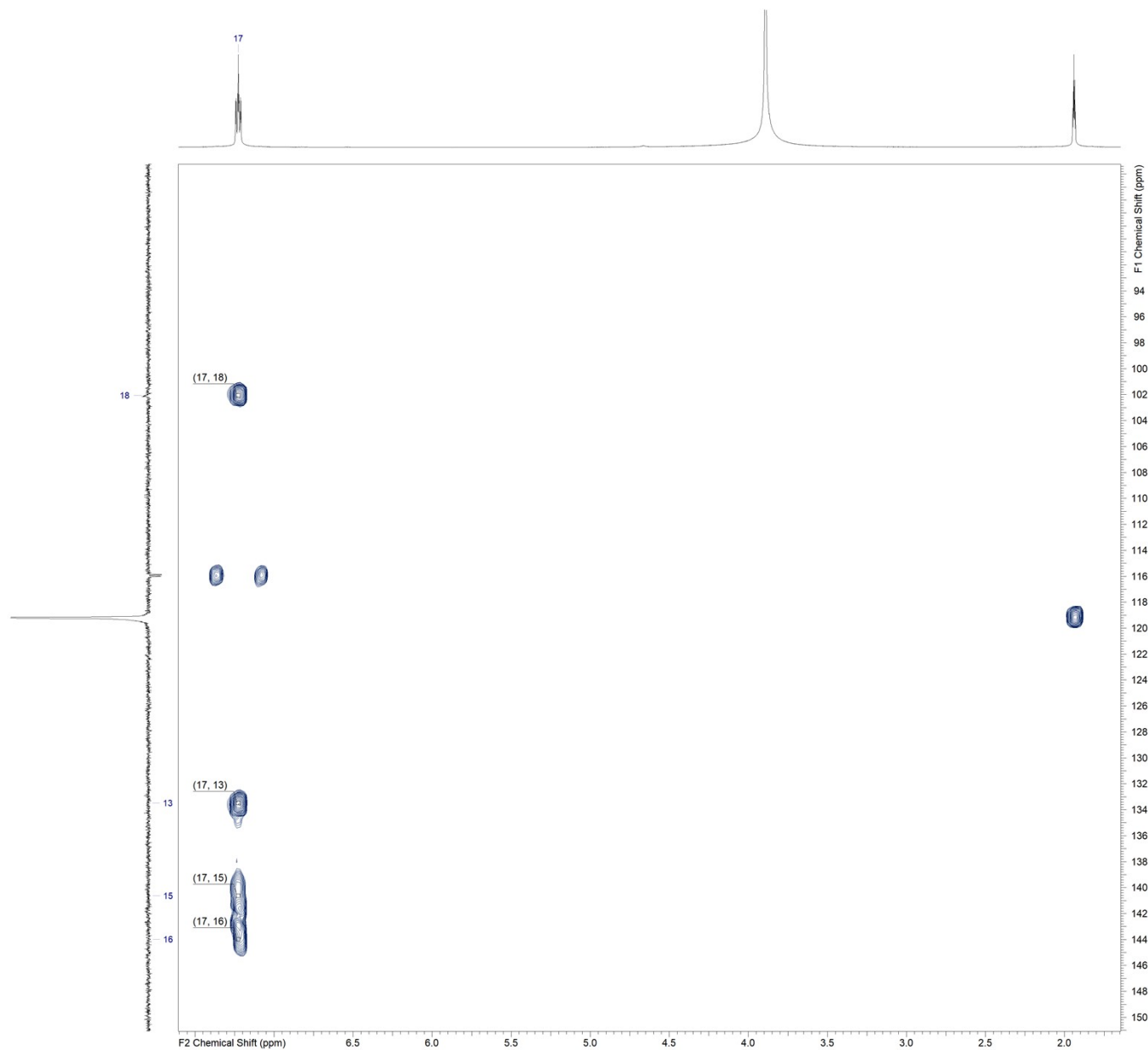


Fig. S14. Fully assigned ^1H - ^{13}C HMBC spectrum of 6-bromo-2,3,4-trifluoroaniline **8** in $\text{ACN}:\text{D}_2\text{O}$ (7:3) at 25 °C.

2. NMR analysis of mixtures

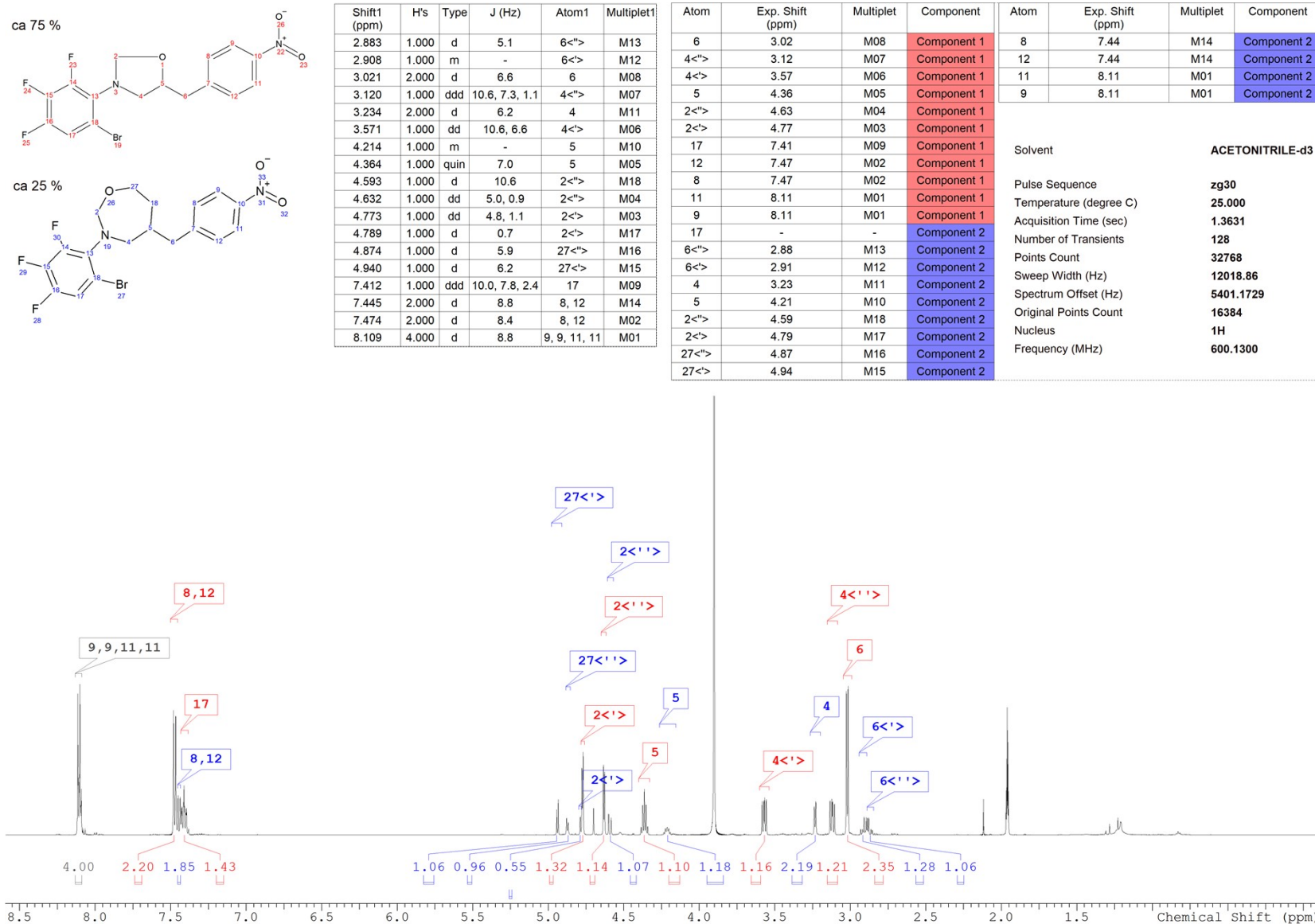


Fig. S15. ¹H spectrum, structure, numbering and full assignment of oxazolidine **4** and dioxazepine **5** mixture in ACN:D₂O (7:3) at 25 °C.

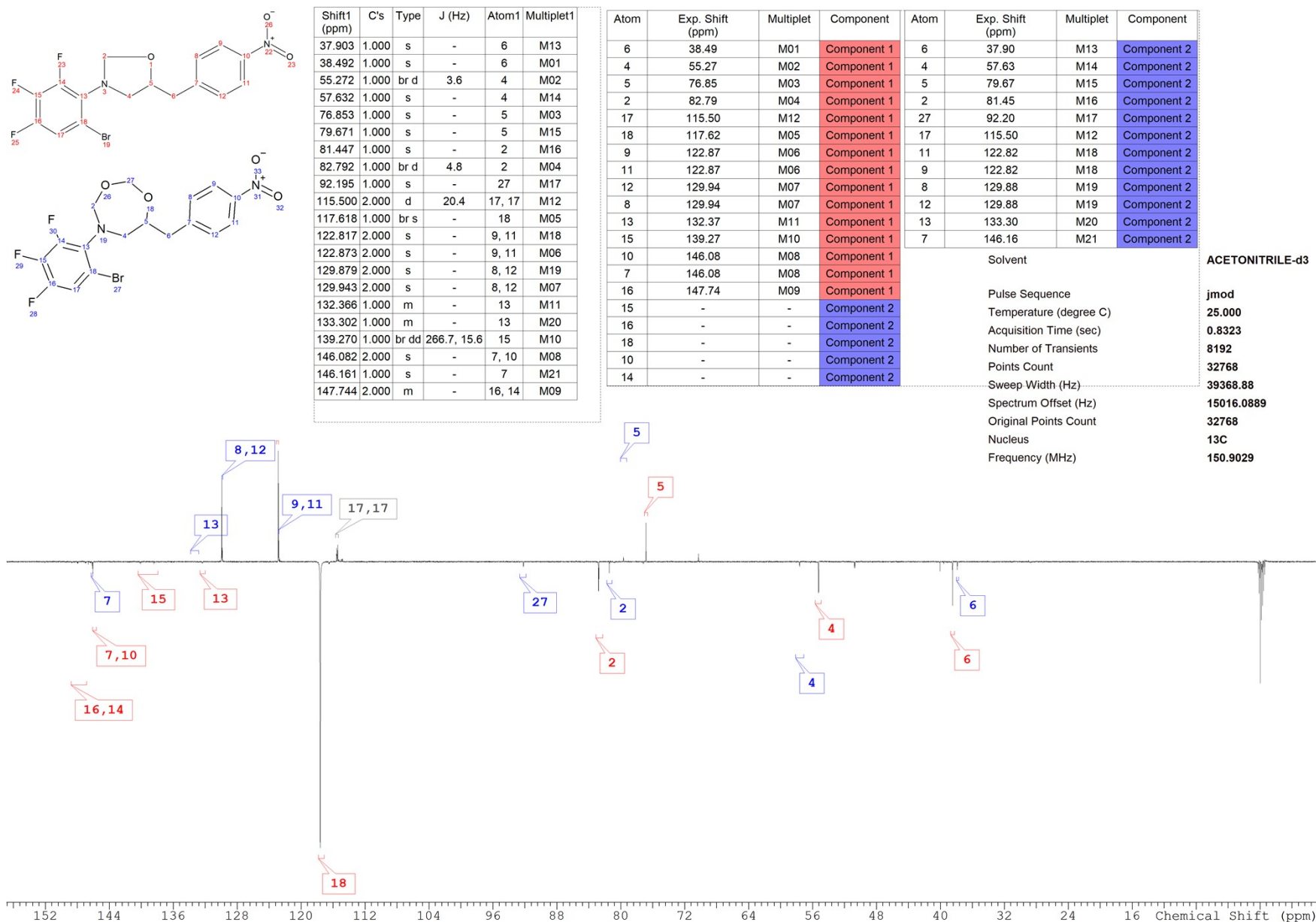


Fig. S16. ^{13}C spectrum, structure, numbering and full assignment of oxazolidine **4** and dioxazepine **5** mixture in ACN:D₂O (7:3) at 25 °C.

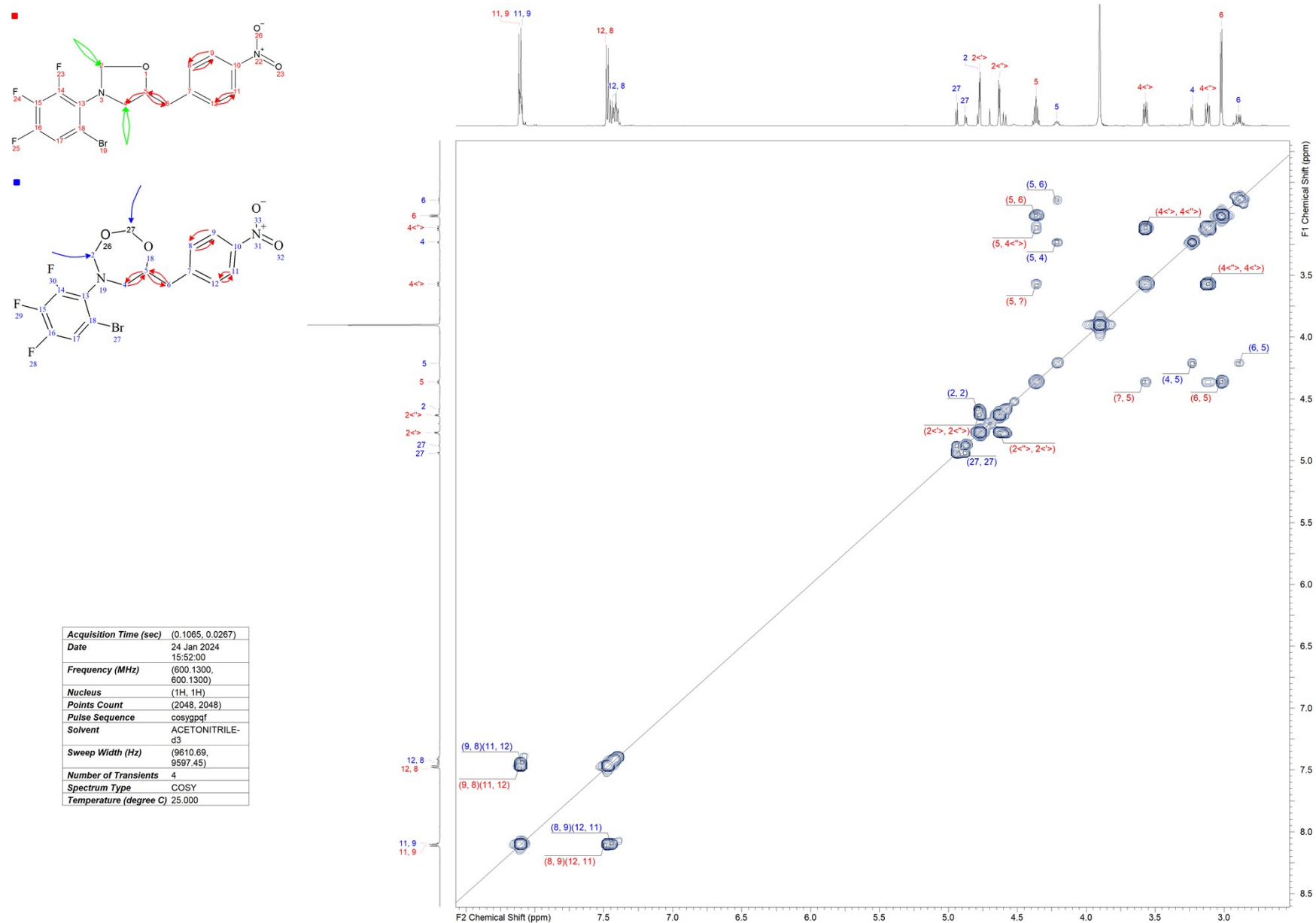
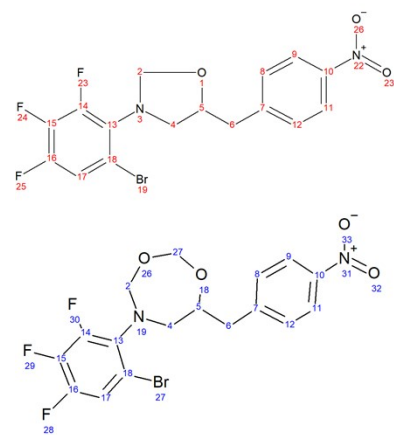


Fig. S17. Fully assigned ¹H-¹H COSY spectrum of oxazolidine **4** and dioxazepine **5** mixture in ACN:D₂O (7:3) at 25 °C.



Acquisition Time (sec)	(0.1139, 0.0094)
Date	24 Jan 2024
Frequency (MHz)	(600.1300, 150.9029)
Nucleus	(1H, 13C)
Points Count	(1024, 1024)
Pulse Sequence	hsqcetgcp
Solvent	ACETONITRILE-d3
Sweep Width (Hz)	(8984.02, 27138.29)
Number of Transients	96
Spectrum Type	HSQC-DEPT
Temperature (degree C)	25.100

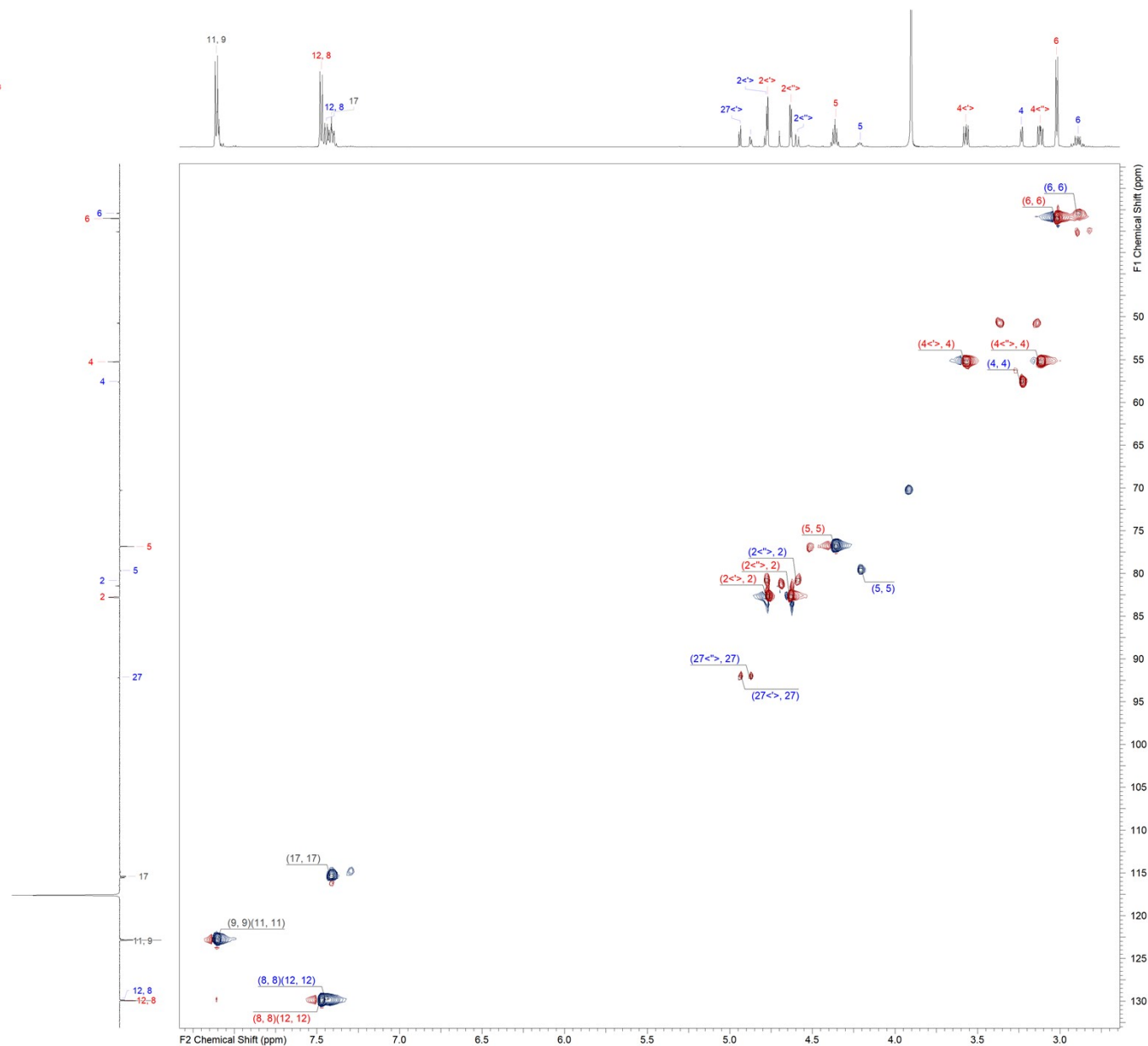


Fig. S18. Fully assigned ^1H - ^{13}C HSQC spectrum of oxazolidine **4** and dioxazepine **5** mixture in ACN:D₂O (7:3) at 25 °C.

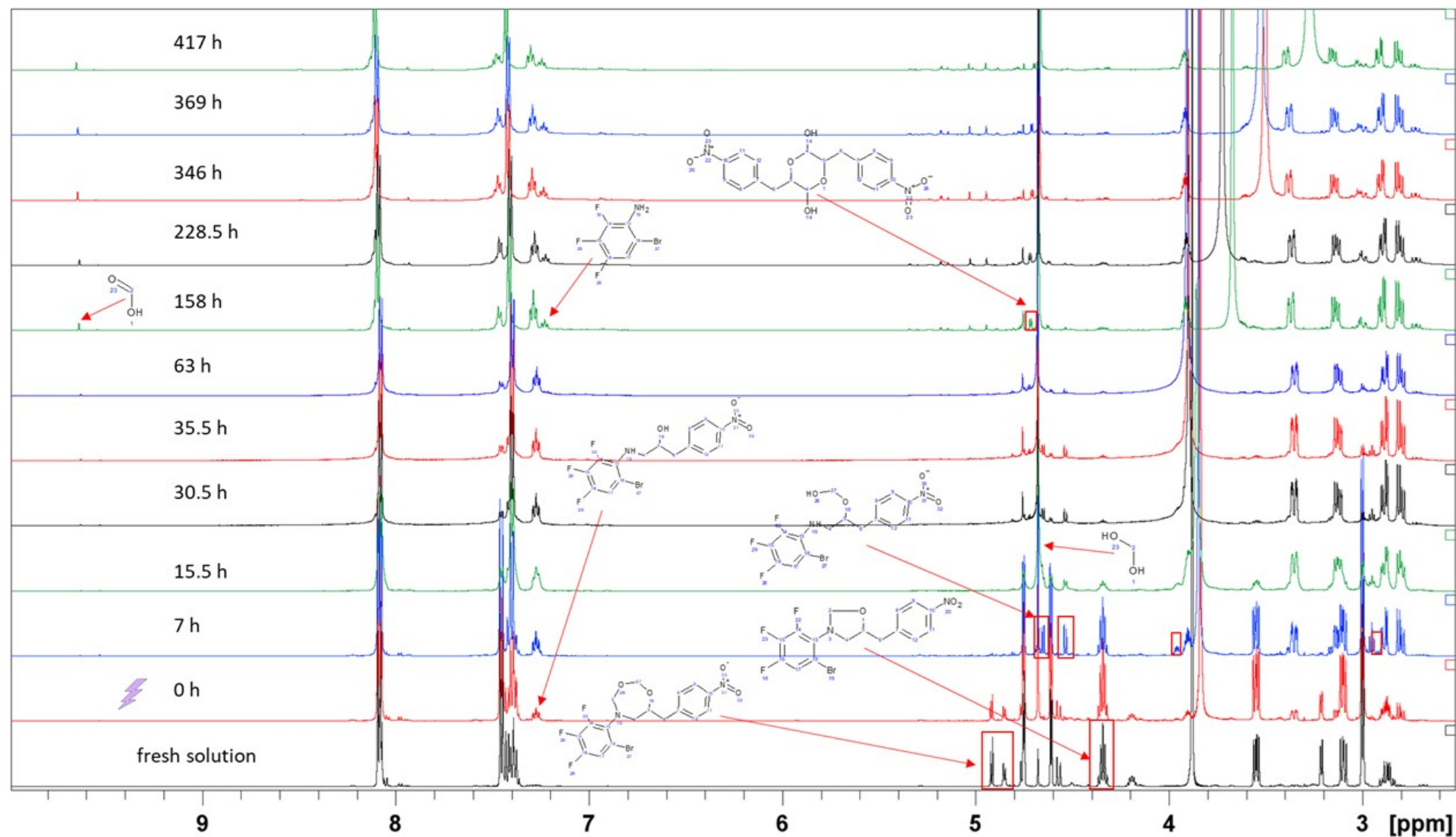
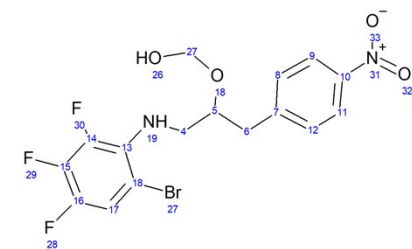


Fig. S20. Photodegradation of oxazolidine **4** and dioxazepine **5** mixture in ACN:D₂O (7:3) at room temperature using UV light ($\lambda = 310$ nm)



Shift1 (ppm)	H's	Type	J (Hz)	Atom1	Multiplet1
2.95	2.000	br t	6.8	6	M01
3.15	1.000	m	-	4<">	M03
3.37	1.000	m	-	4<">	M02
3.95	1.000	m	-	5	M04
4.53	1.000	s	-	27<">	M05
4.65	1.000	br d	7.0	27<">	M06
7.27	1.000	m	-	17	M09
7.40	2.000	d	8.8	8, 12	M08
8.08	2.000	m	-	9, 11	M07

^1H NMR (600 MHz, ACND_2O): δ = 2.95 (br t, J = 6.8 Hz, 2 H, 6), 3.14 - 3.21 (m, 1 H, 4<">), 3.36 - 3.40 (m, 1 H, 4<">), 3.93 - 4.00 (m, 1 H, 5), 4.53 (s, 1 H, 27<">), 4.65 (br d, J = 7.0 Hz, 1 H, 27<">), 7.24 - 7.29 (m, 1 H, 17), 7.40 (d, J = 8.8 Hz, 2 H, 8, 12), 8.03 - 8.13 (m, 2 H, 9, 11) ppm

Solvent	ACND2O
Pulse Sequence	zg30
Temperature (degree C)	25.100
Acquisition Time (sec)	1.1403
Number of Transients	128
Points Count	32768
Sweep Width (Hz)	14367.38
Spectrum Offset (Hz)	3725.3870
Original Points Count	16384
Nucleus	^1H
Frequency (MHz)	600.1317

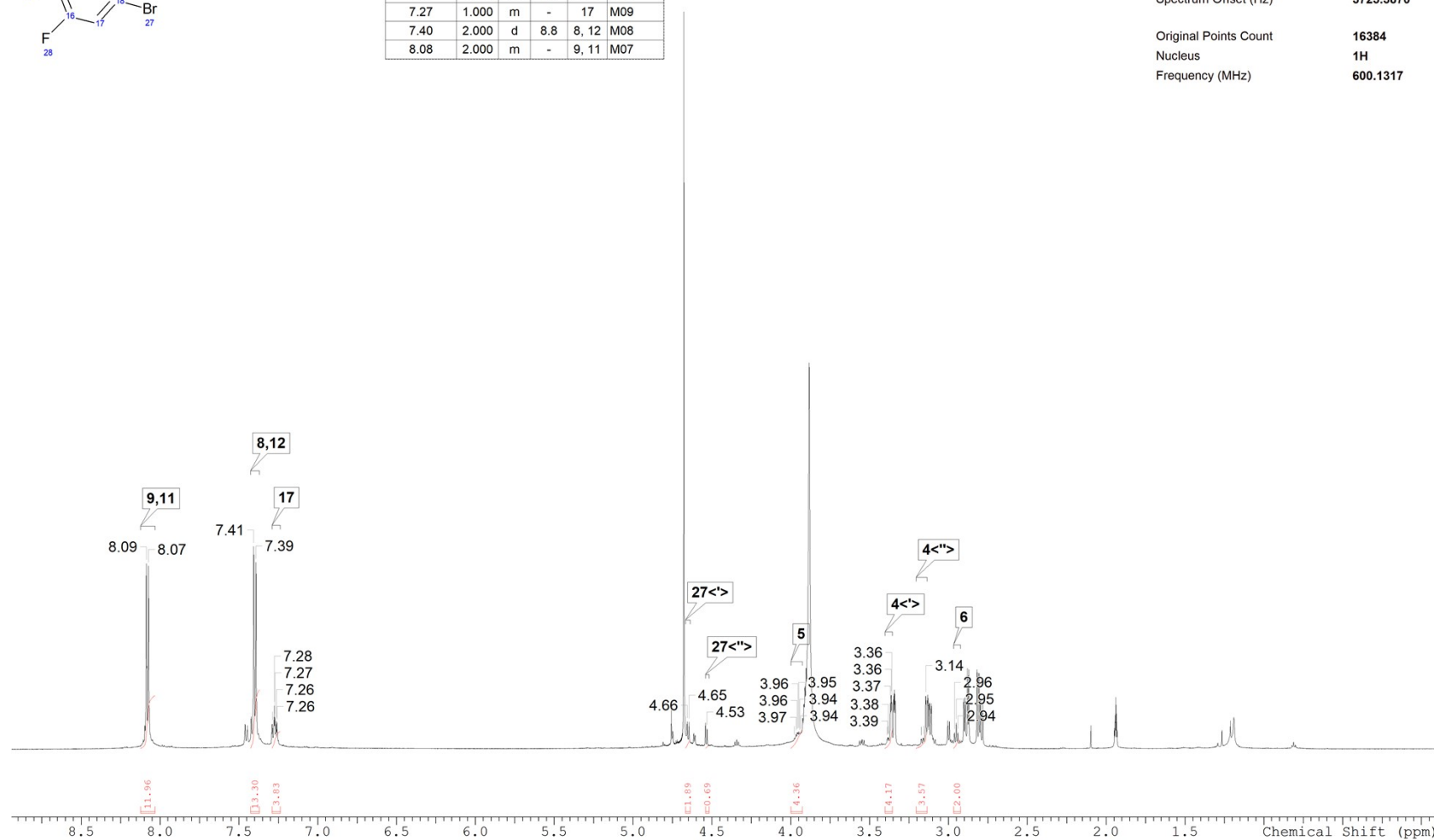
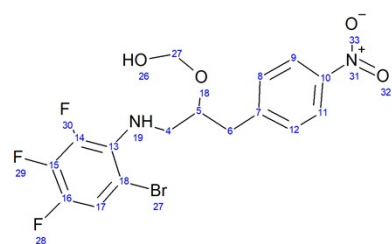


Fig. S21. ^1H spectrum, structure, numbering and full assignment of intermediate **6** in degradation mixture in $\text{ACN}:\text{D}_2\text{O}$ (7:3) at 25 °C after 19.5 hours of irradiation with UV light (λ = 310 nm).



Shift1 (ppm)	C's	Type	Atom1	Multiplet1
41.51	1.000	s	6	M01
51.91	1.000	s	4	M02
79.84	1.000	s	5	M03
90.83	1.000	s	27	M04
118.09	1.000	br s	17	M05
126.08	2.000	s	9, 11	M06
133.22	2.000	s	8, 12	M07
149.33	1.000	s	7	M08

^{13}C NMR (151 MHz, ACND_2O): δ = 41.5 (6), 51.9 (4), 79.8 (5), 90.8 (27), 118.1 (17), 126.1 (9, 11), 133.2 (8, 12), 149.3 (7) ppm

Solvent **ACND2O**
Pulse Sequence **jmod**
Temperature (degree C) **25.200**
Acquisition Time (sec) **0.8323**
Number of Transients **2048**
Points Count **32768**
Sweep Width (Hz) **39368.88**
Spectrum Offset (Hz) **15089.8027**

Original Points Count **32768**
Nucleus **^{13}C**
Frequency (MHz) **150.9028**

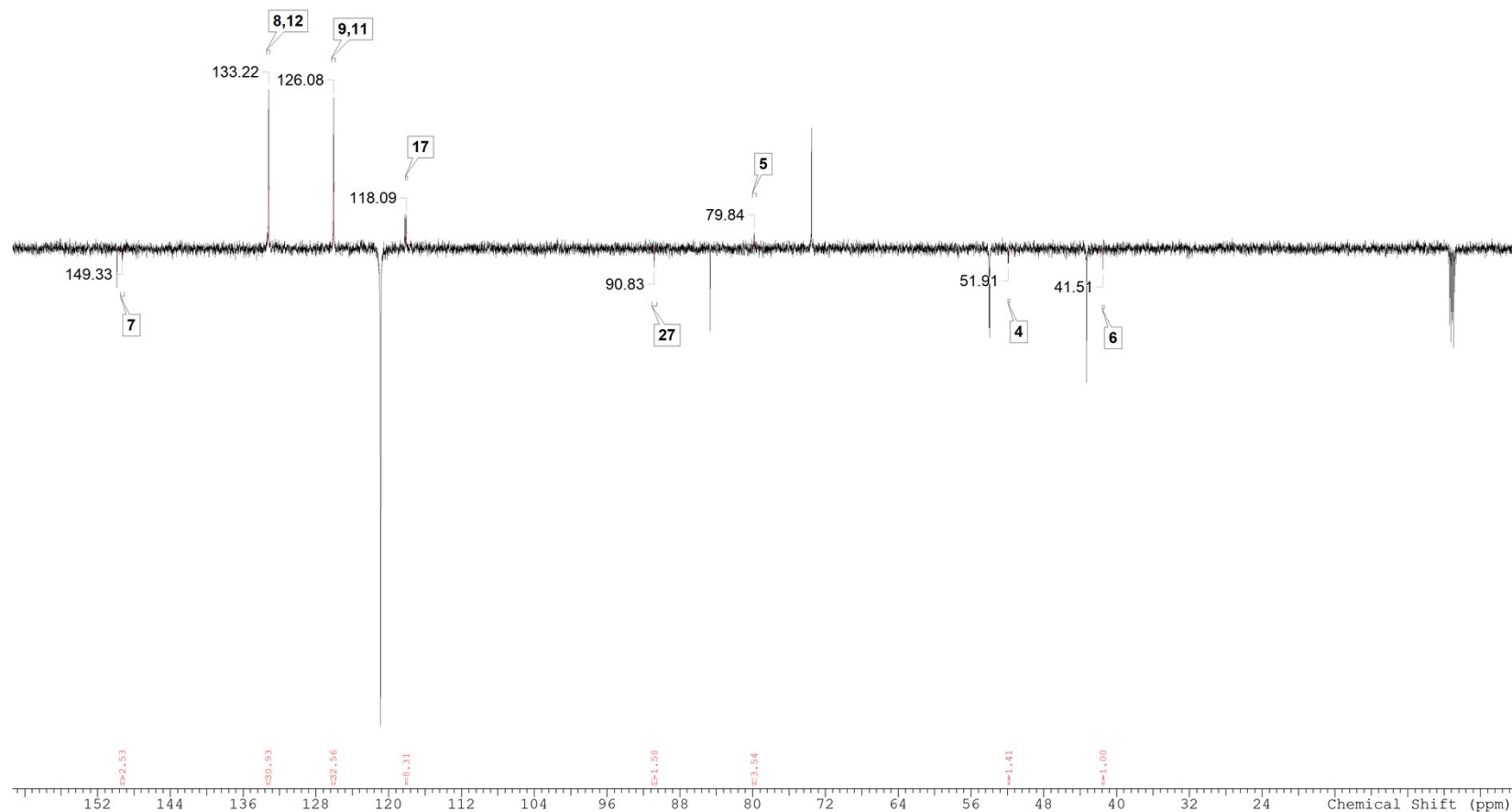


Fig. S22. ^{13}C spectrum, structure, numbering and full assignment of intermediate **6** in degradation mixture in $\text{ACN}:\text{D}_2\text{O}$ (7:3) at 25 °C after 19.5 hours of irradiation with UV light ($\lambda = 310$ nm).

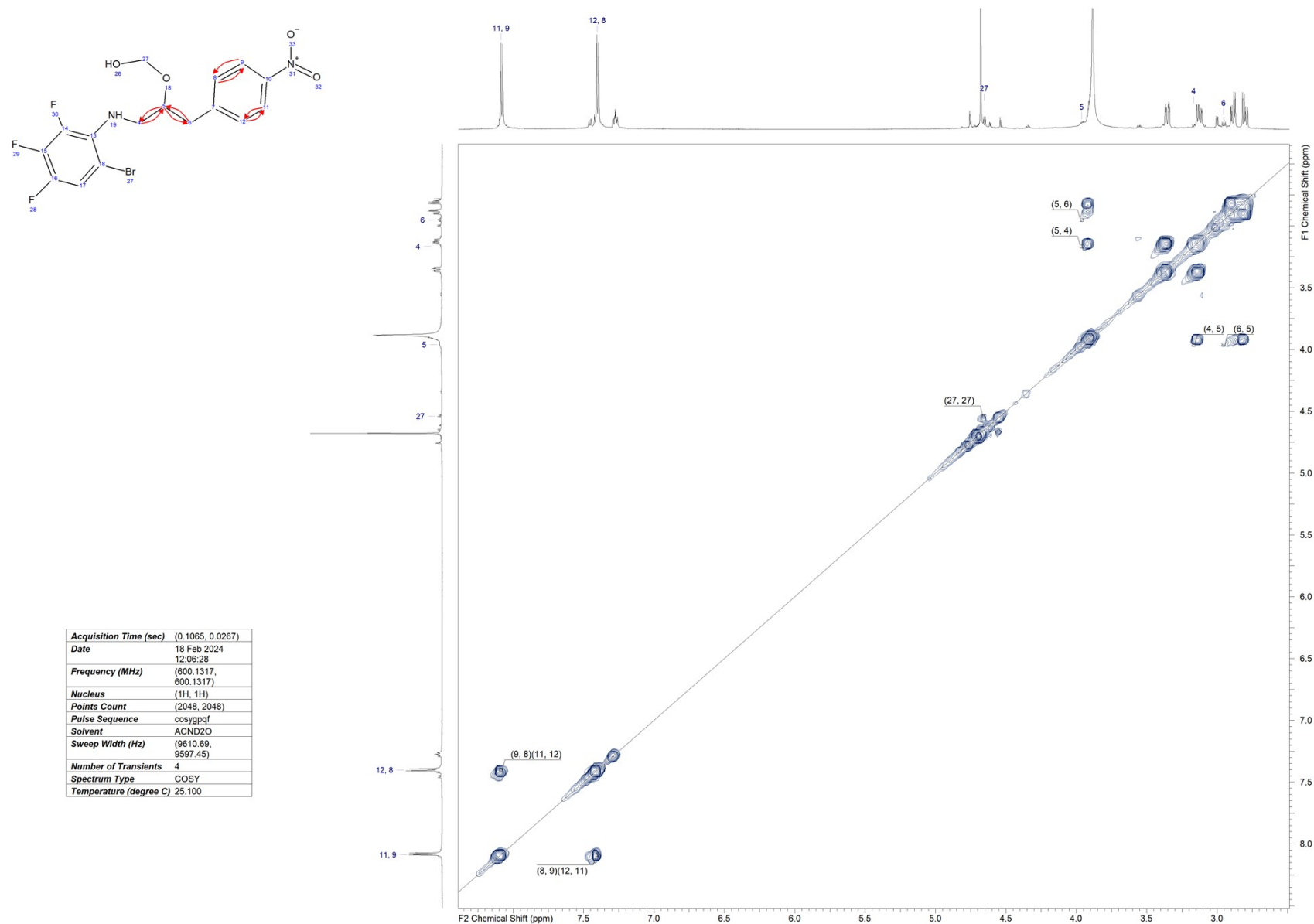


Fig. S23. Fully assigned ^1H - ^1H COSY spectrum of intermediate **6** in degradation mixture in ACN: D_2O (7:3) at 25 °C after 19.5 hours of irradiation with UV light ($\lambda = 310$ nm).

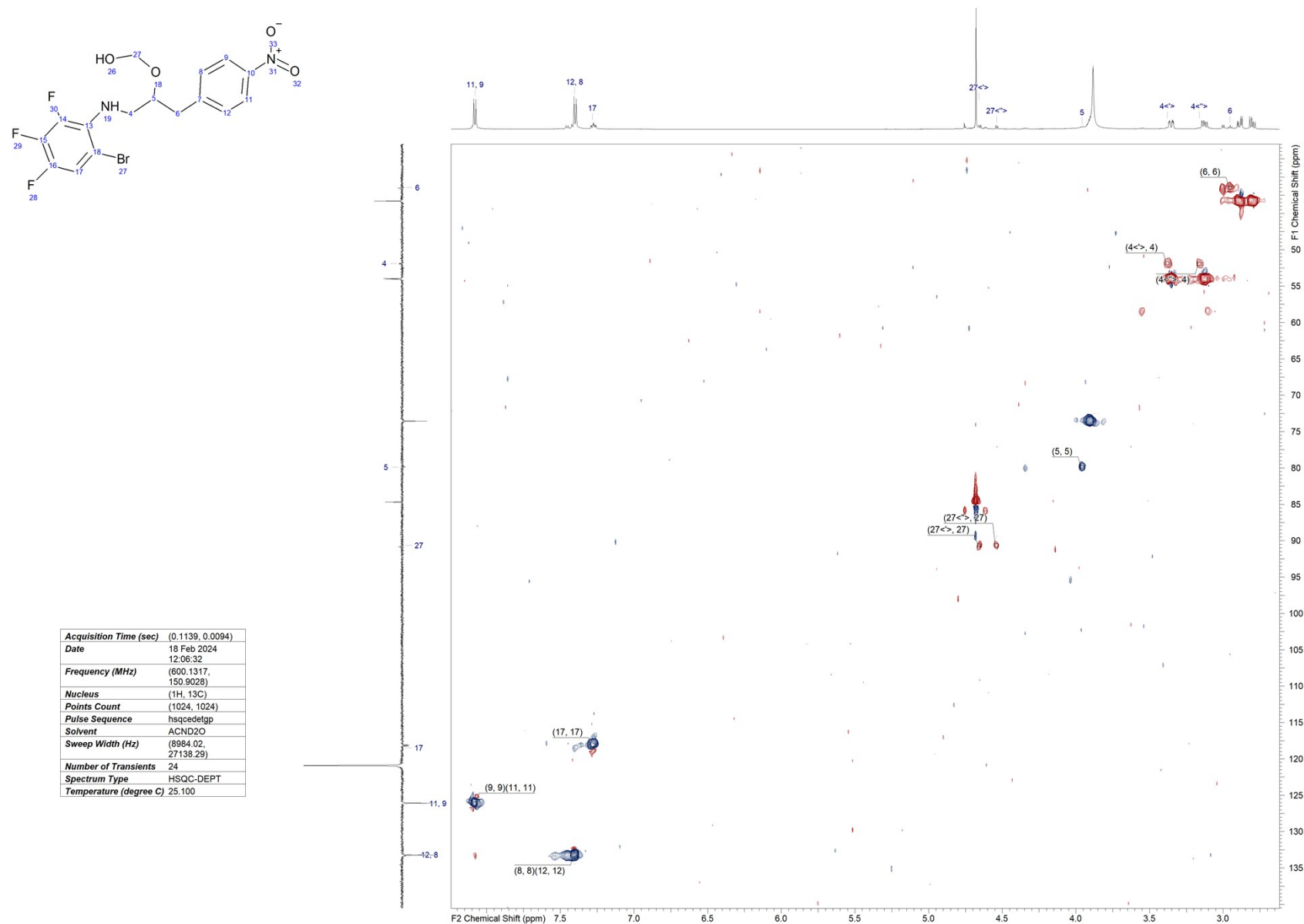


Fig. S24. Fully assigned ^1H - ^{13}C HSQC spectrum of intermediate **6** in degradation mixture in ACN:D₂O (7:3) at 25 °C after 19.5 hours of irradiation with UV light ($\lambda = 310$ nm).

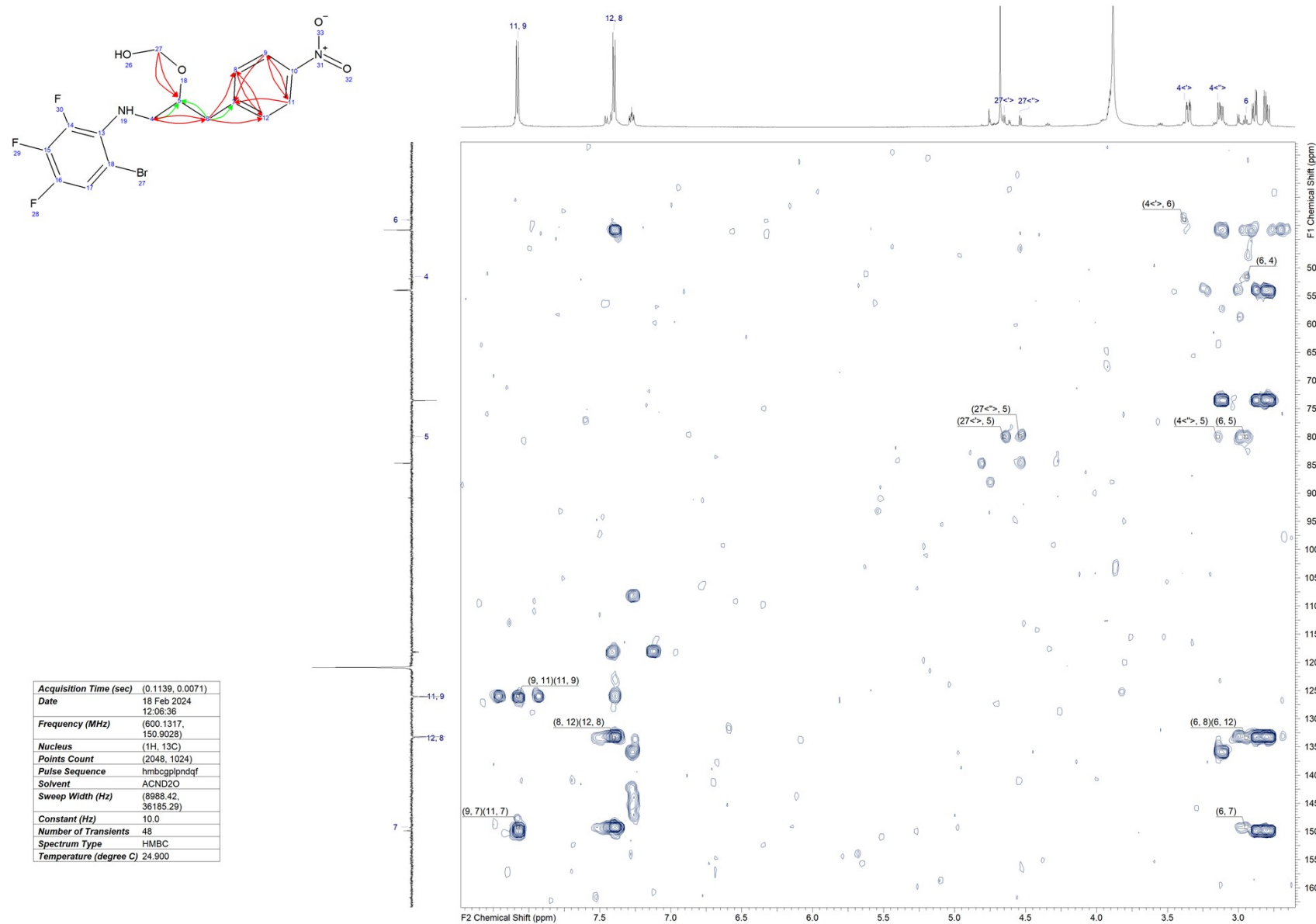
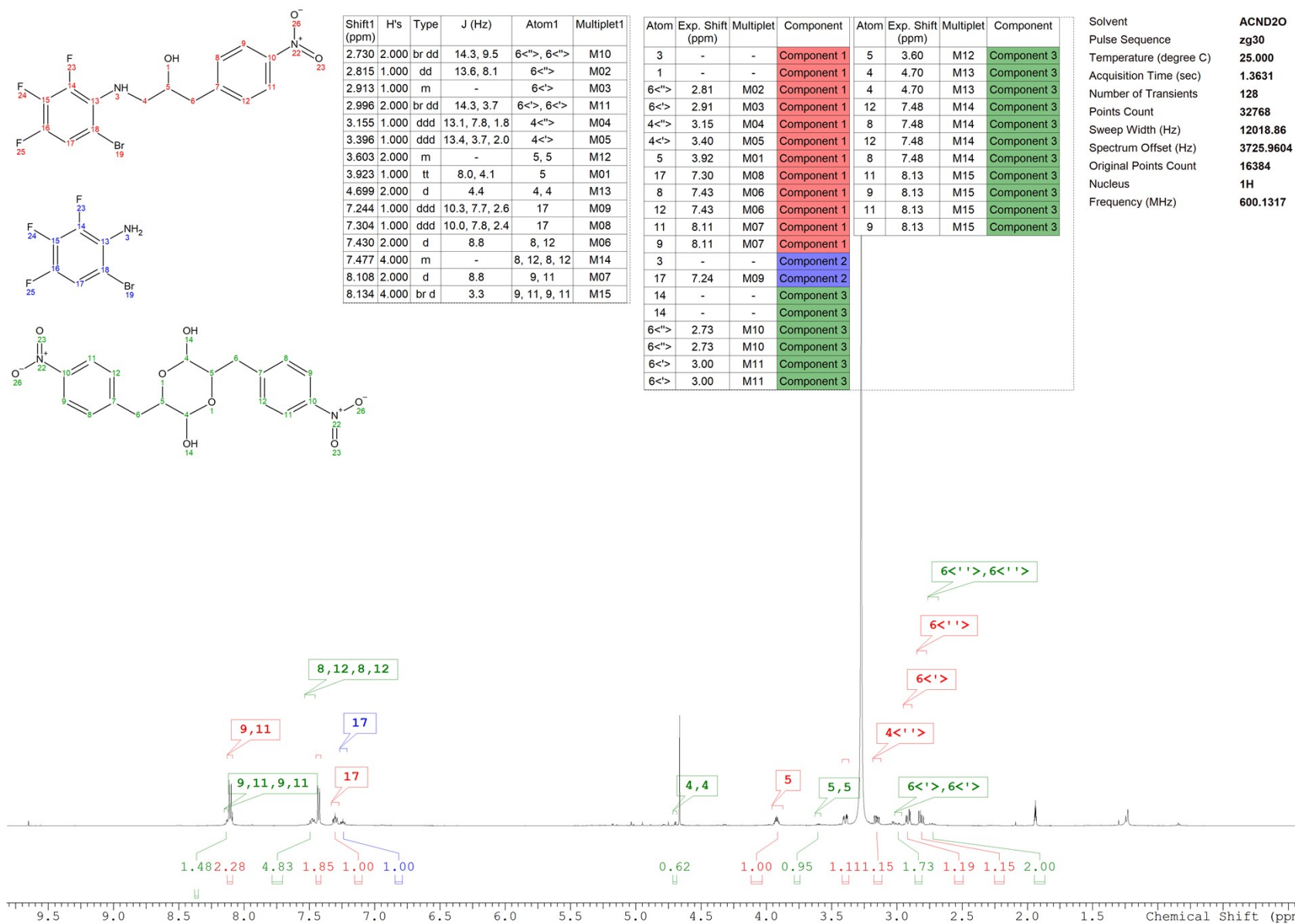


Fig. S25. Fully assigned ^1H - ^{13}C HMBC spectrum of intermediate **6** in degradation mixture in ACN:D₂O (7:3) at 25 °C after 19.5 hours of irradiation with UV light ($\lambda = 3$



Solvent: ACND2O
Pulse Sequence: zg30
Temperature (degree C): 25.000
Acquisition Time (sec): 1.3631
Number of Transients: 128
Points Count: 32768
Sweep Width (Hz): 12018.86
Spectrum Offset (Hz): 3725.9604
Original Points Count: 16384
Nucleus: 1H
Frequency (MHz): 600.1317

Fig. S26. ¹H spectrum, structures, numbering and full assignments of degradation mixture containing compounds ethanolamine **3** (red), 6-bromo-2,3,4-trifluoroaniline **8** (blue) and dimer **7** (green) in ACN:D₂O (7:3) at 25 °C.

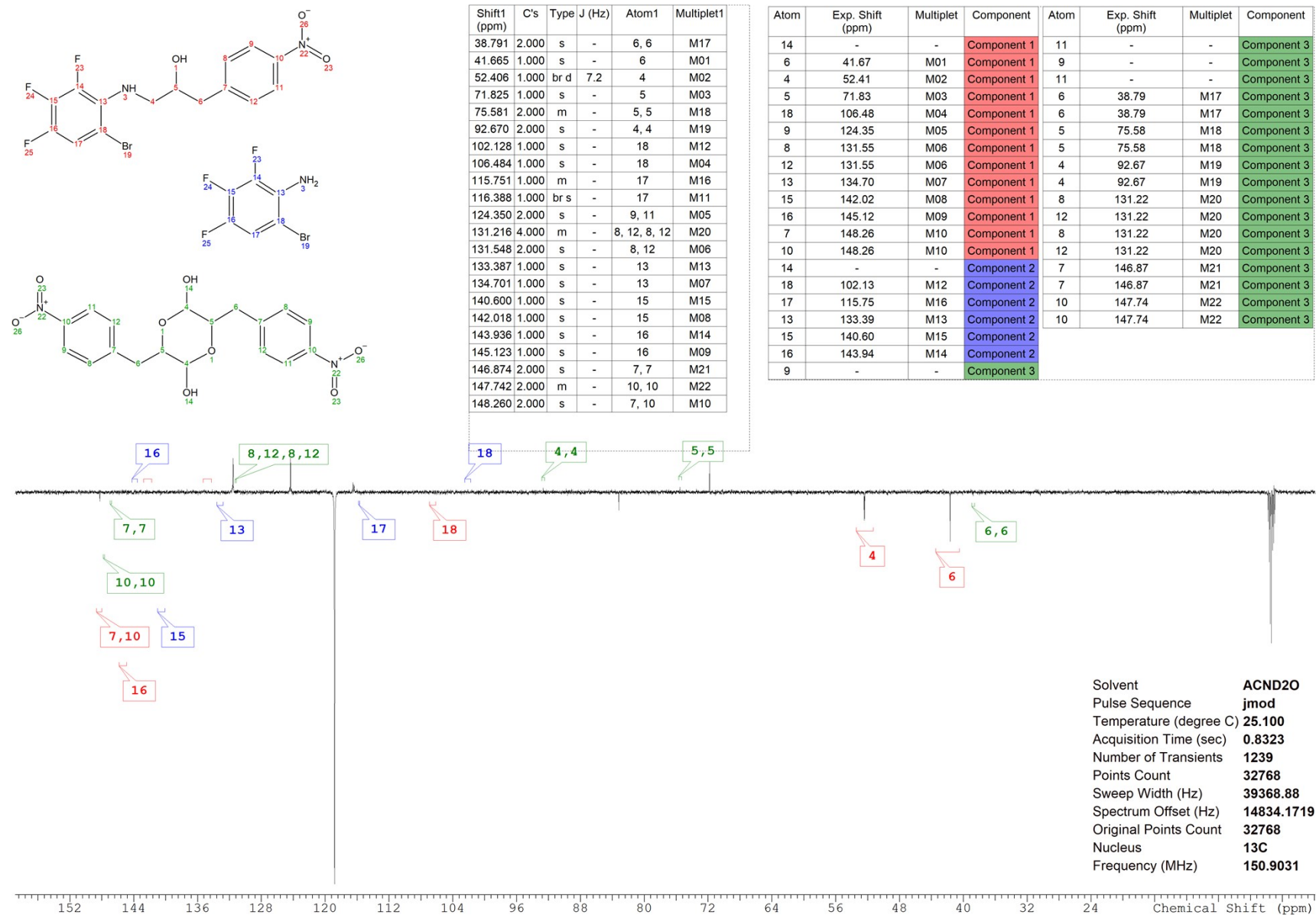


Fig. S27. ^{13}C spectrum, structures, numbering and full assignments of degradation mixture containing compounds ethanolamine **3** (red), 6-bromo-2,3,4-trifluoroaniline **8** (blue) and dimer **7** (green) in ACN:D₂O (7:3) at 25 °C.

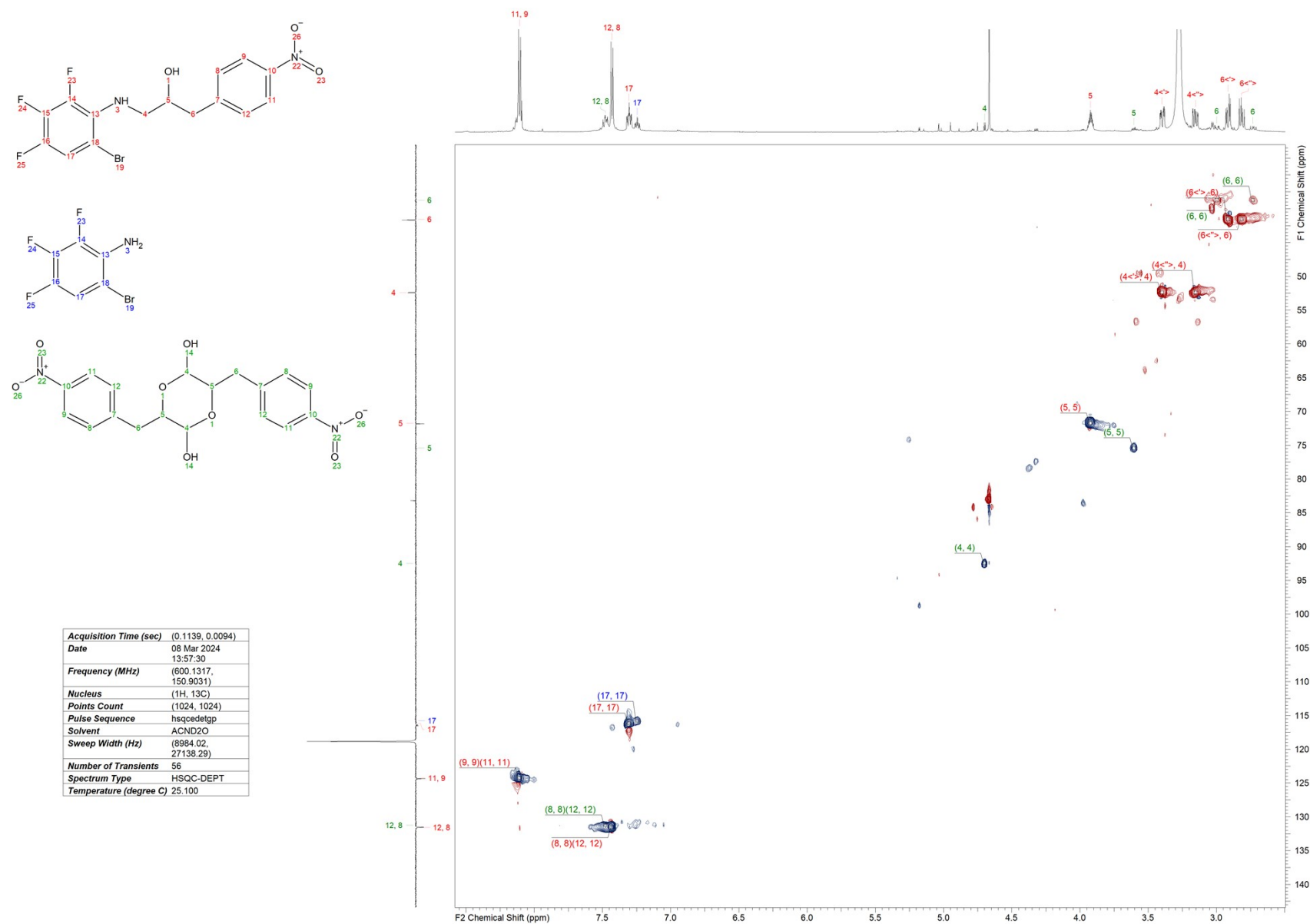


Fig. S29. Fully assigned ^1H - ^{13}C HSQC spectrum of degradation mixture containing compounds ethanolamine **3** (red), 6-bromo-2,3,4-trifluoroaniline **8** (blue) and dimer **7** (green) in $\text{ACN:D}_2\text{O}$ (7:3) at 25 °C.

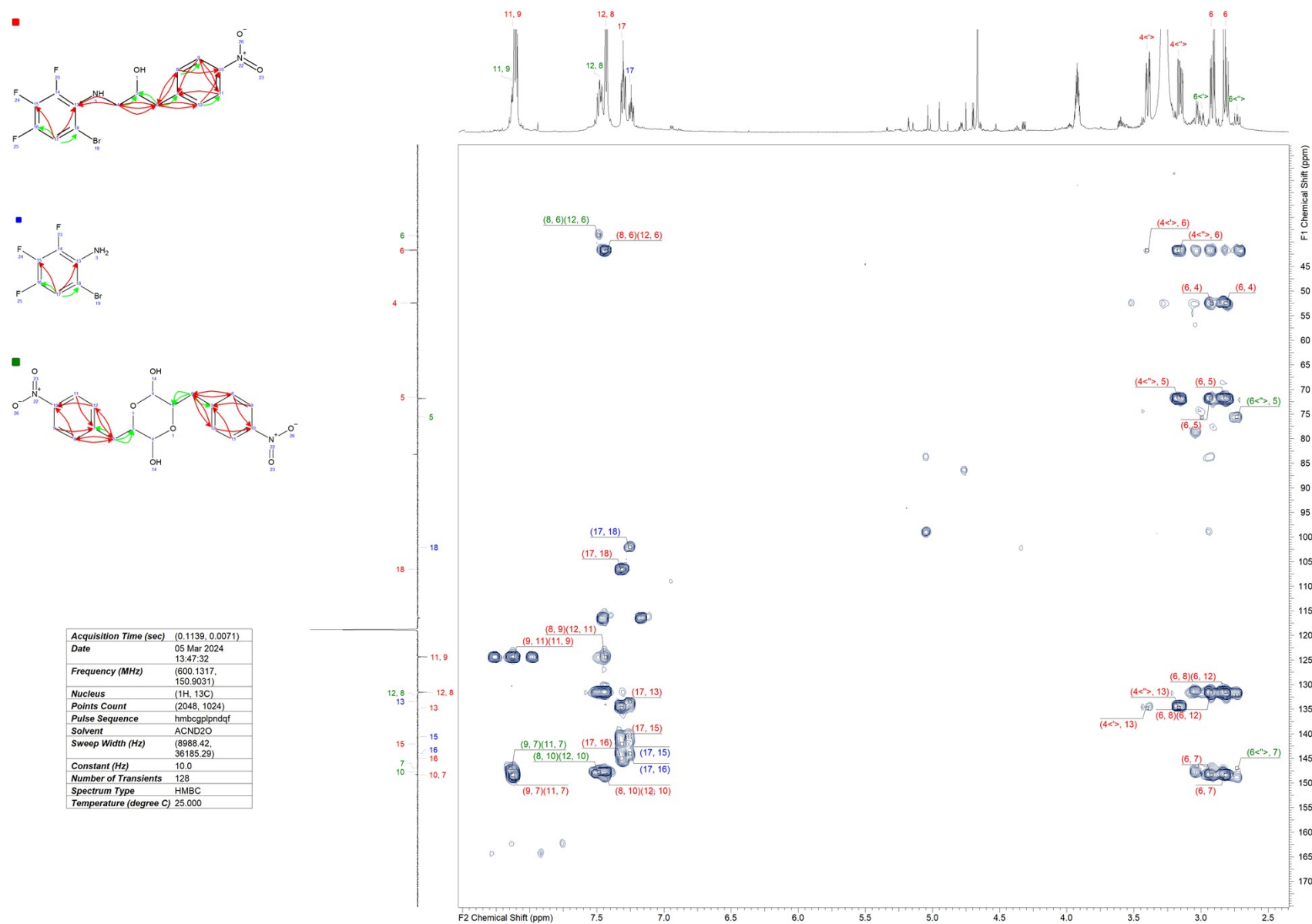


Fig. S30. Fully assigned ^1H - ^{13}C HMBC spectrum of degradation mixture containing compounds ethanolamine **3** (red), 6-bromo-2,3,4-trifluoroaniline **8** (blue) and dimer **7** (green) in $\text{ACN:D}_2\text{O}$ (7:3) at 25 °C.

3. MS analysis of authentic compounds

Table S1. Ion-source parameters for HRMS analyses in positive (ESI+) and negative (ESI–) mode of ionization.

Ion-source parameters	ESI+	ESI–
Drying gas flow (dm ³ /min)	200	200
Drying gas temperature (°C)	17	17
Nebulizer pressure (psi)	25	25
Sheath gas flow (dm ³ /min)	250	325
Sheath gas temperature (°C)	11	11
Capillary voltage (V)	3500	3500
Nozzle voltage (V)	0	1500
Fragmentor voltage (V)	175	175

3.1. Ethanolamine **3**

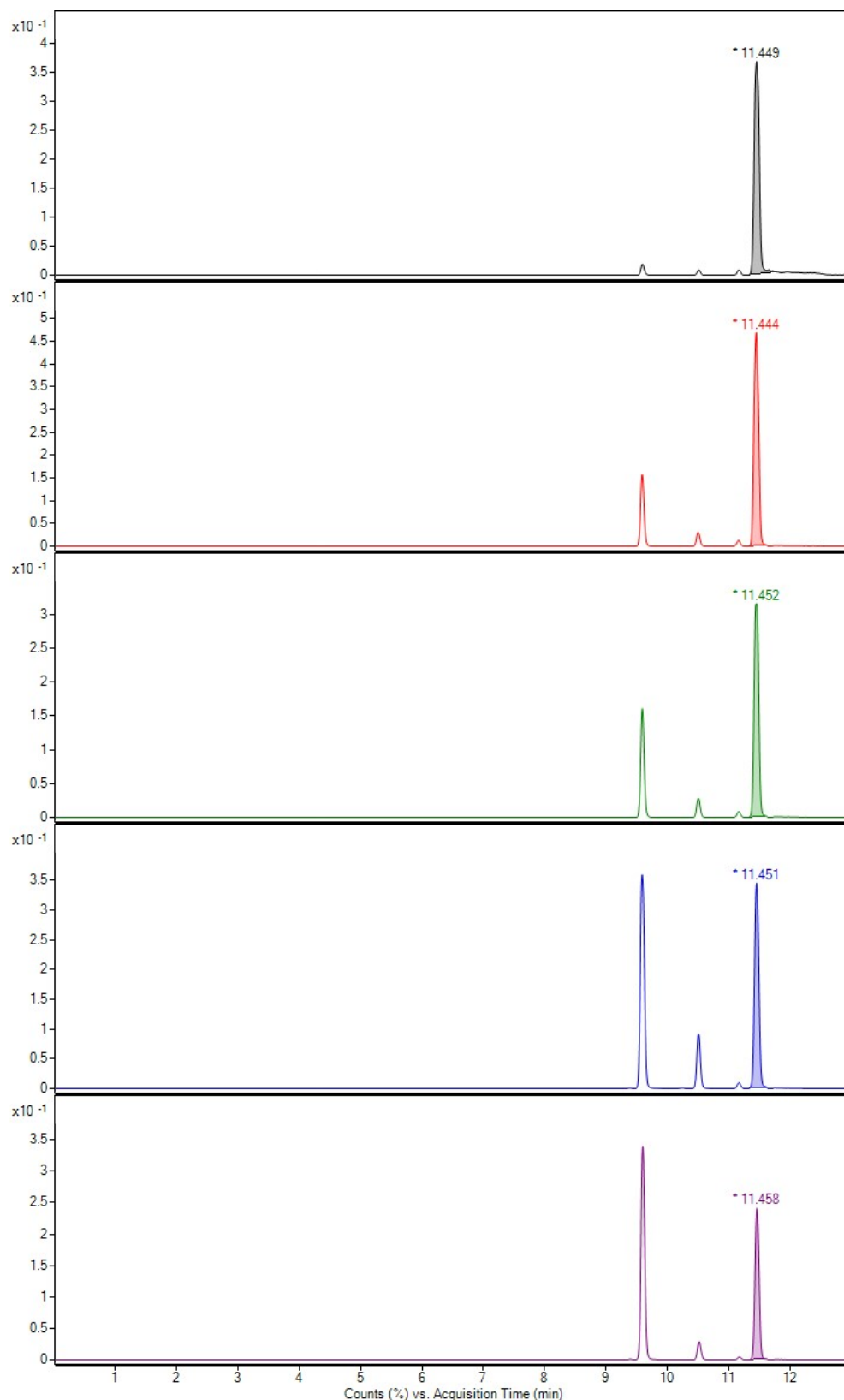


Fig. S31. EICs for m/z 402.9911 [M-H]⁻; 7 h, 25 h, 49 h, 122 h, and 195 h of irradiation.

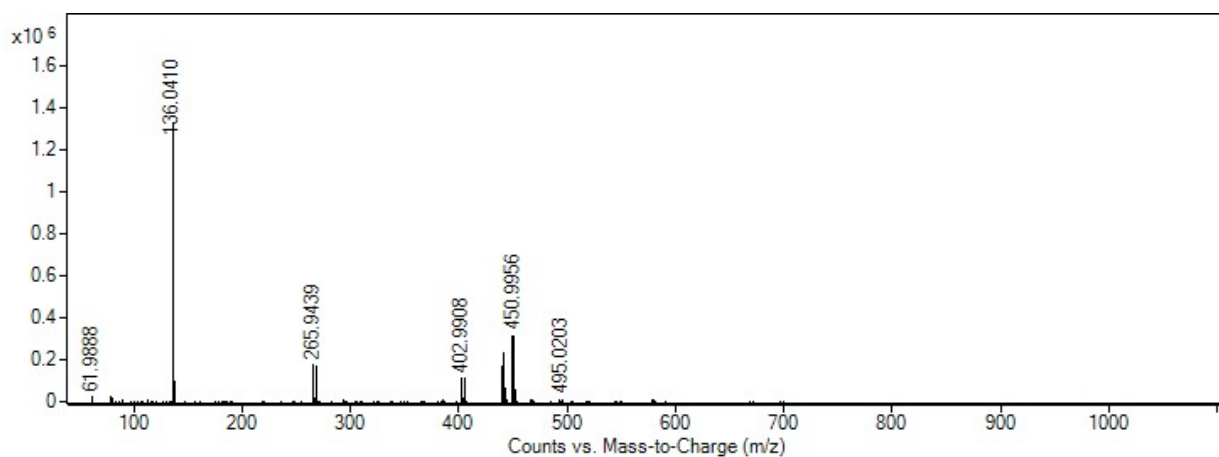


Fig. S32. HRMS spectrum of ethanolamine **3** at 11.45 min.

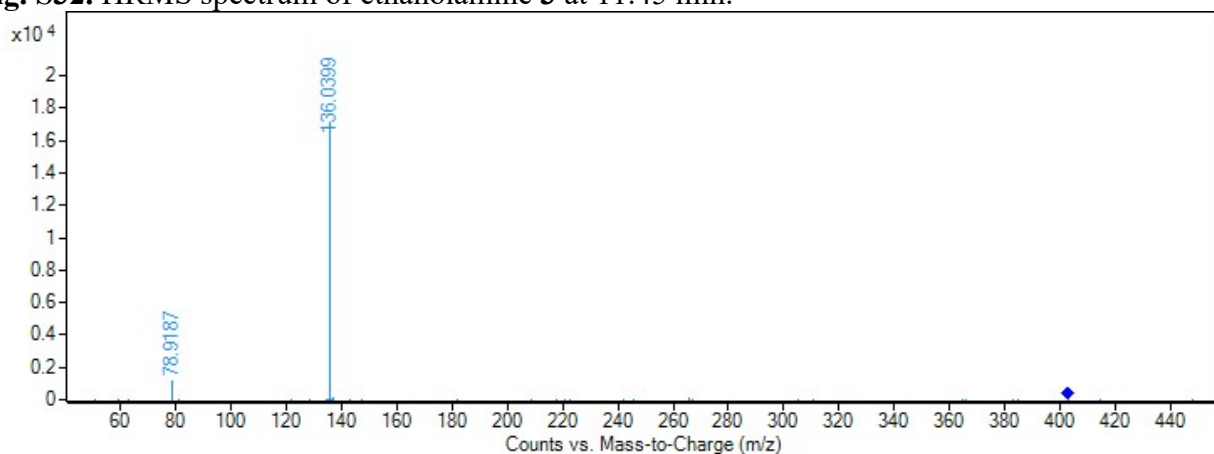


Fig. S33. MS/MS spectrum of $[M-H]^-$ (m/z 402.9908) at 10 V.

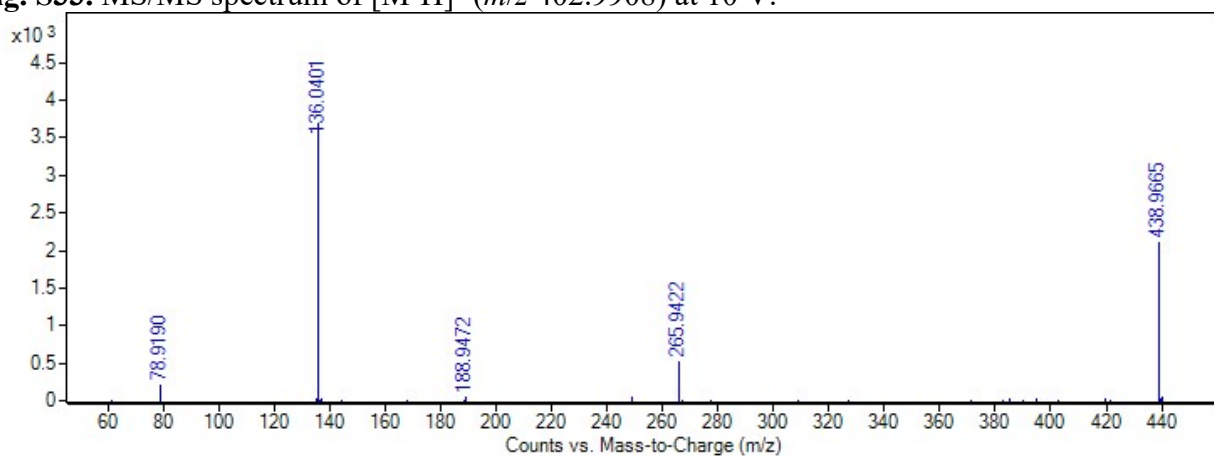


Fig. S34. MS/MS spectrum of $[M+Cl]^-$ (m/z 438.9690) at 10 V.

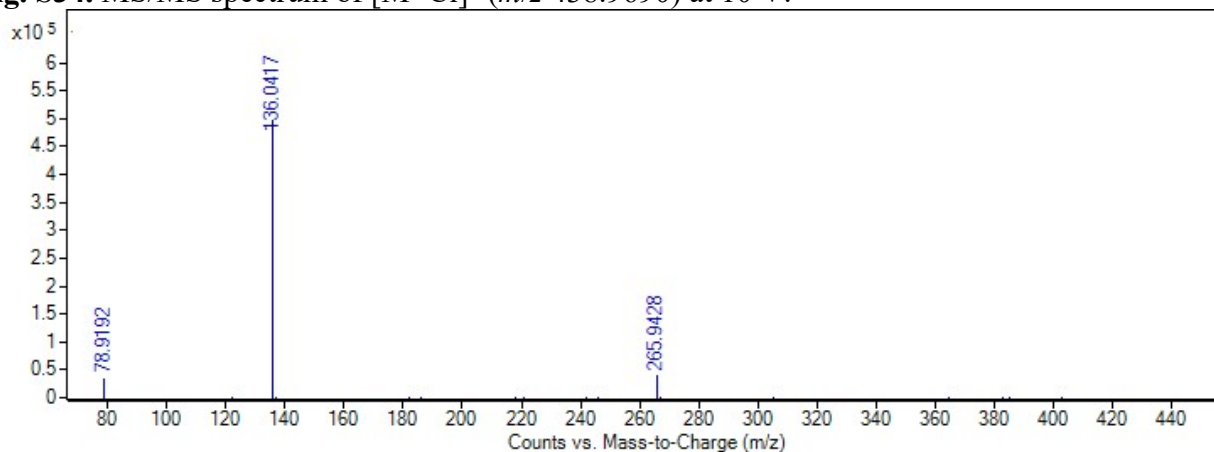


Fig. S35. MS/MS spectrum of $[M+HCOO]^-$ (m/z 448.9970) at 10 V.

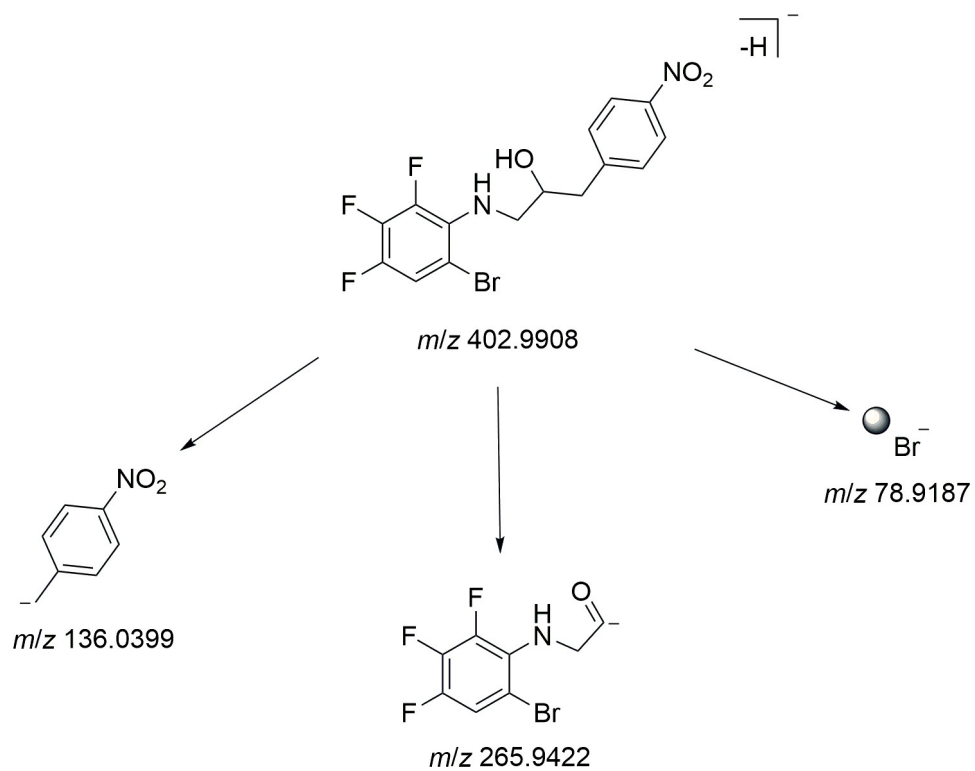


Fig. S36. Possible fragmentation pathway of ethanolamine 3 $[M-H]^-$ ion (m/z 402.9908).

4. MS analysis of degradation mixtures

The chromatographic peak of compound **3b** was noticed at a retention time of 6.03 min in the TIC of the sample irradiated for 7 h. Its presence was confirmed later in the TICs of samples irradiated for 25, 49, 122, and 195 hours (**Fig. S37**). The corresponding HRMS spectrum was characterized by the presence of the singly deprotonated ion at m/z value of 194.0460 (**Fig. S38**). Structure elucidation was possible after performing MS/MS analysis (**Fig. S39**) which revealed characteristic fragmentation where negatively charged 1-methyl-4-nitrobenzene ion (at m/z 136) was noticed (**Fig. S40**). This most characteristic fragment was observed in MS/MS spectra of all degradation products where the nitro group was not affected by photo-induced degradation.

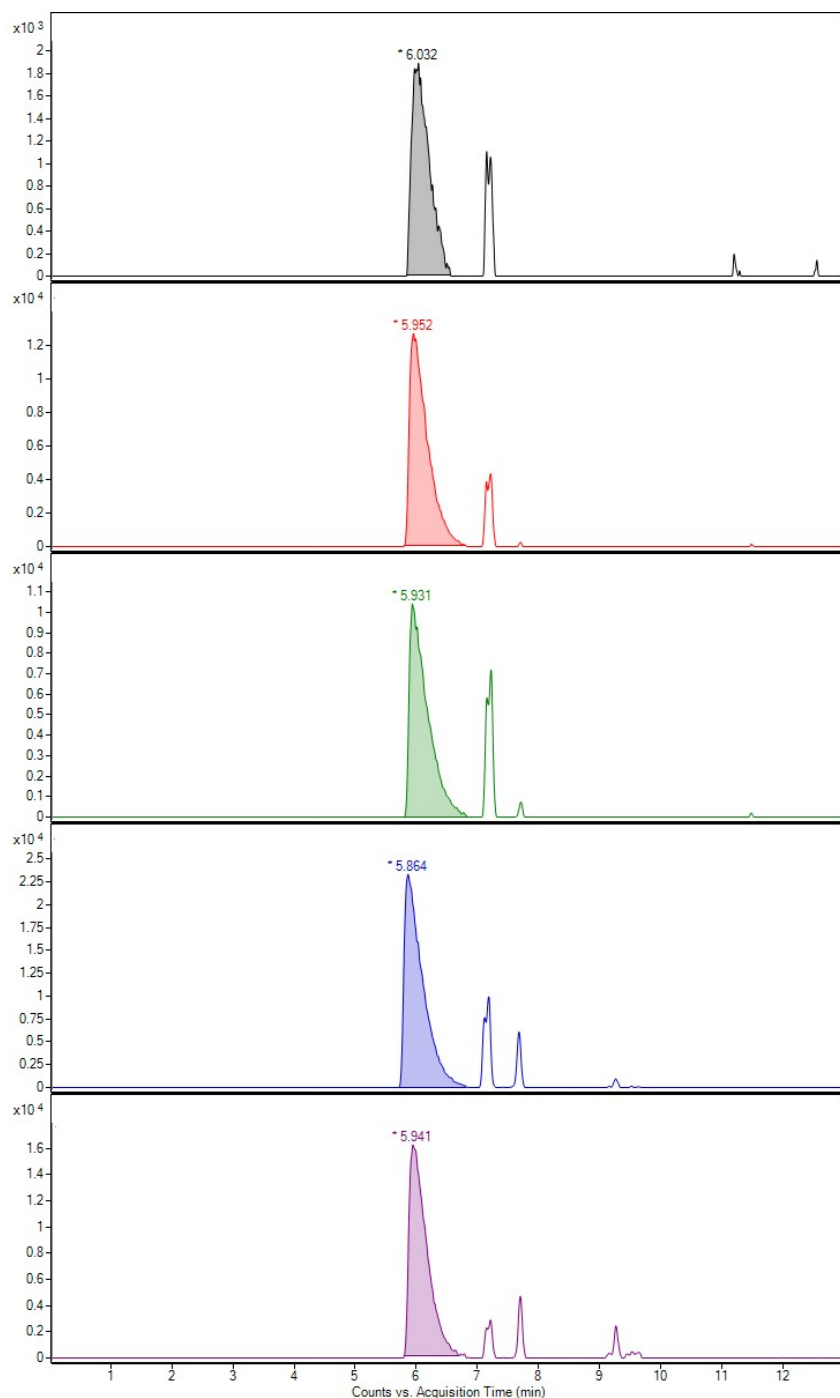


Fig. S37. EICs for m/z 194.0460 [M-H]⁻; 7 h, 25 h, 49 h, 122 h, and 195 h of irradiation.

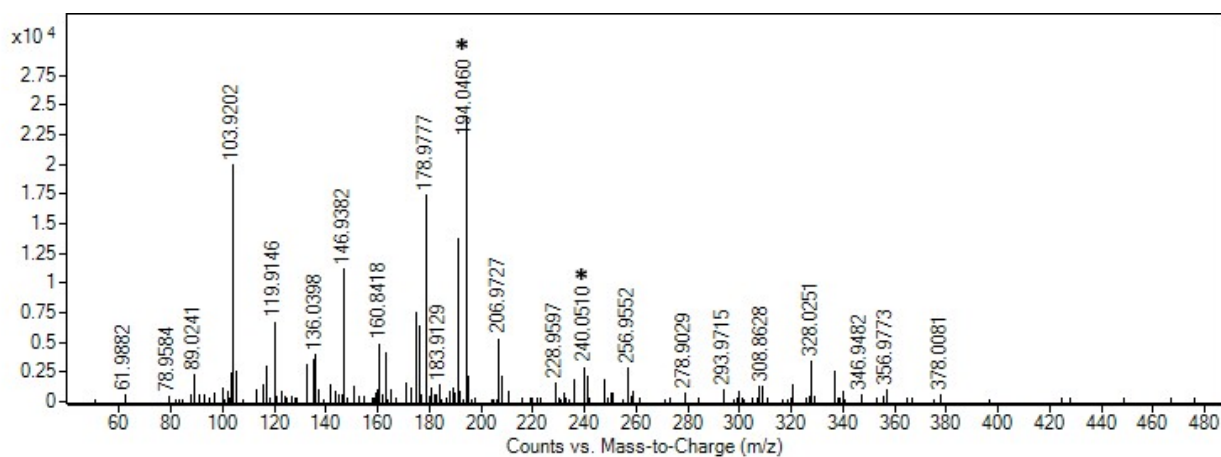


Fig. S38. HRMS spectrum of degradation product **3b** at 6.03 min.

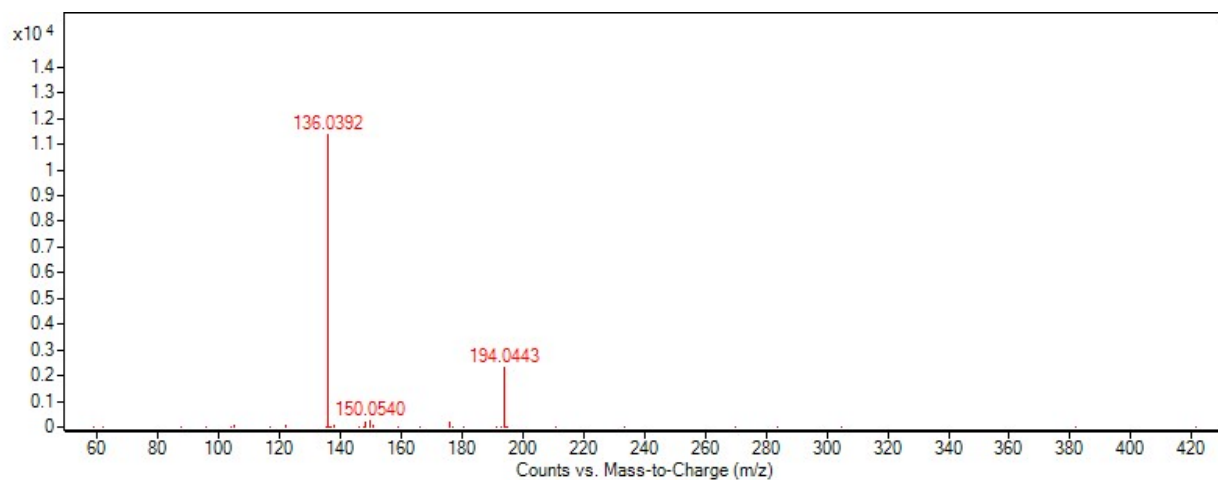


Fig. S39. MS/MS spectrum of of $[M-H]^-$ (m/z 194.0460) at 10 V.

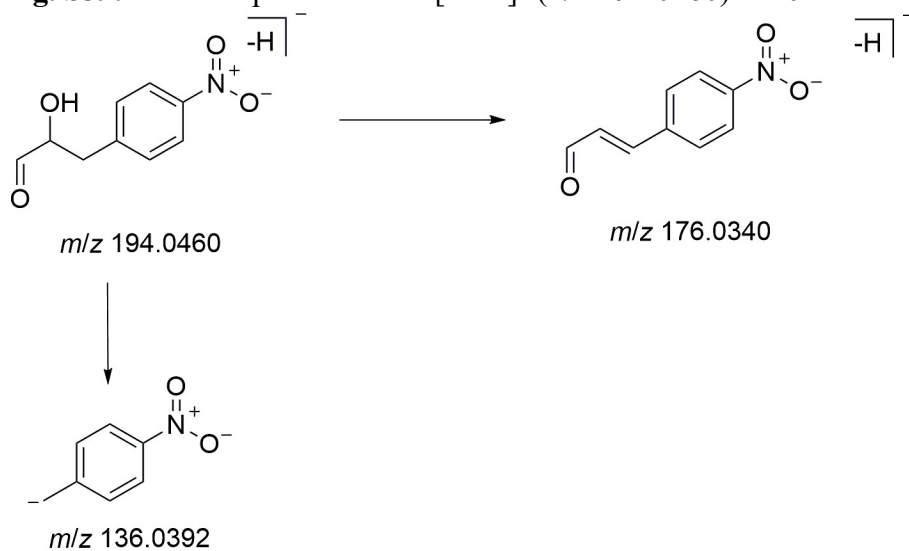


Fig. S40. Possible fragmentation pathway of **3b** $[M-H]^-$ ion (m/z 194.0460).

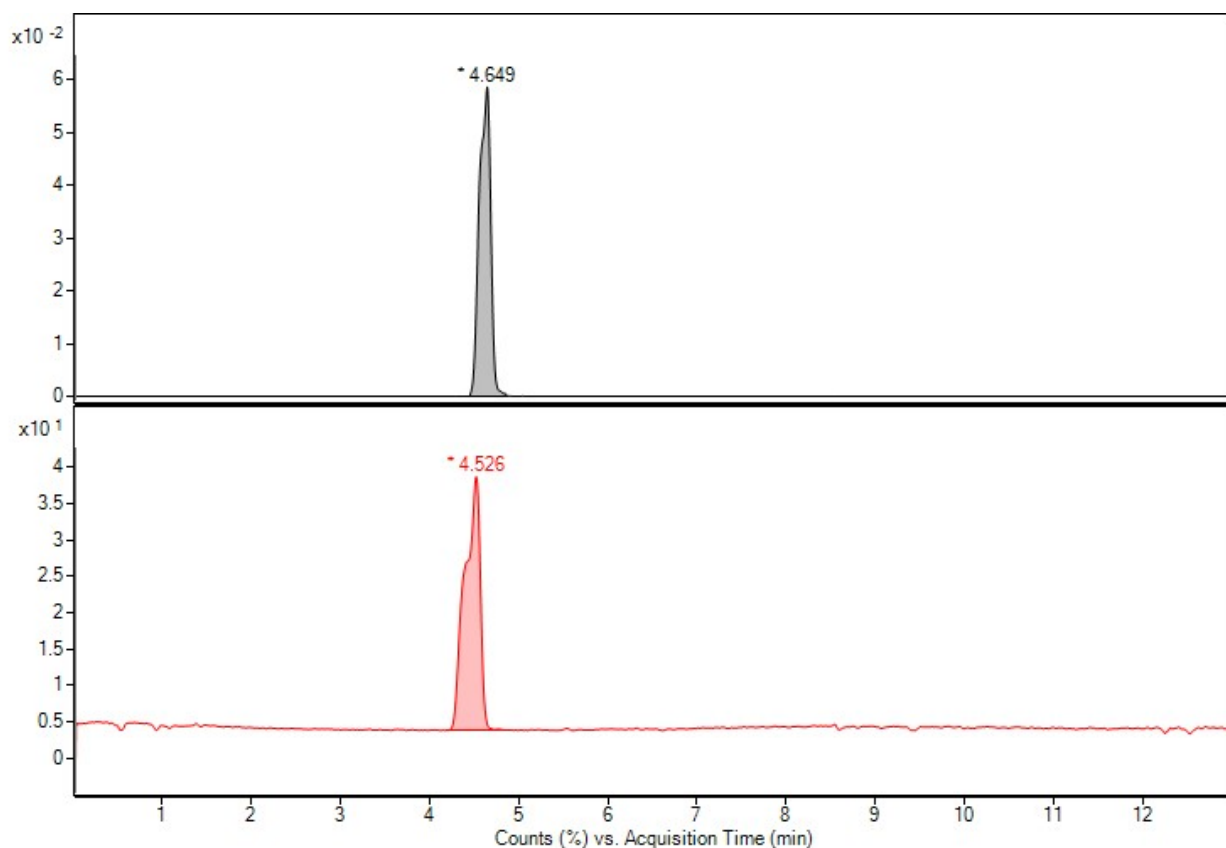


Fig. S41. Comparison of EIC for m/z 197.0912 with TIC of synthetic sample of ethanolamine **9**

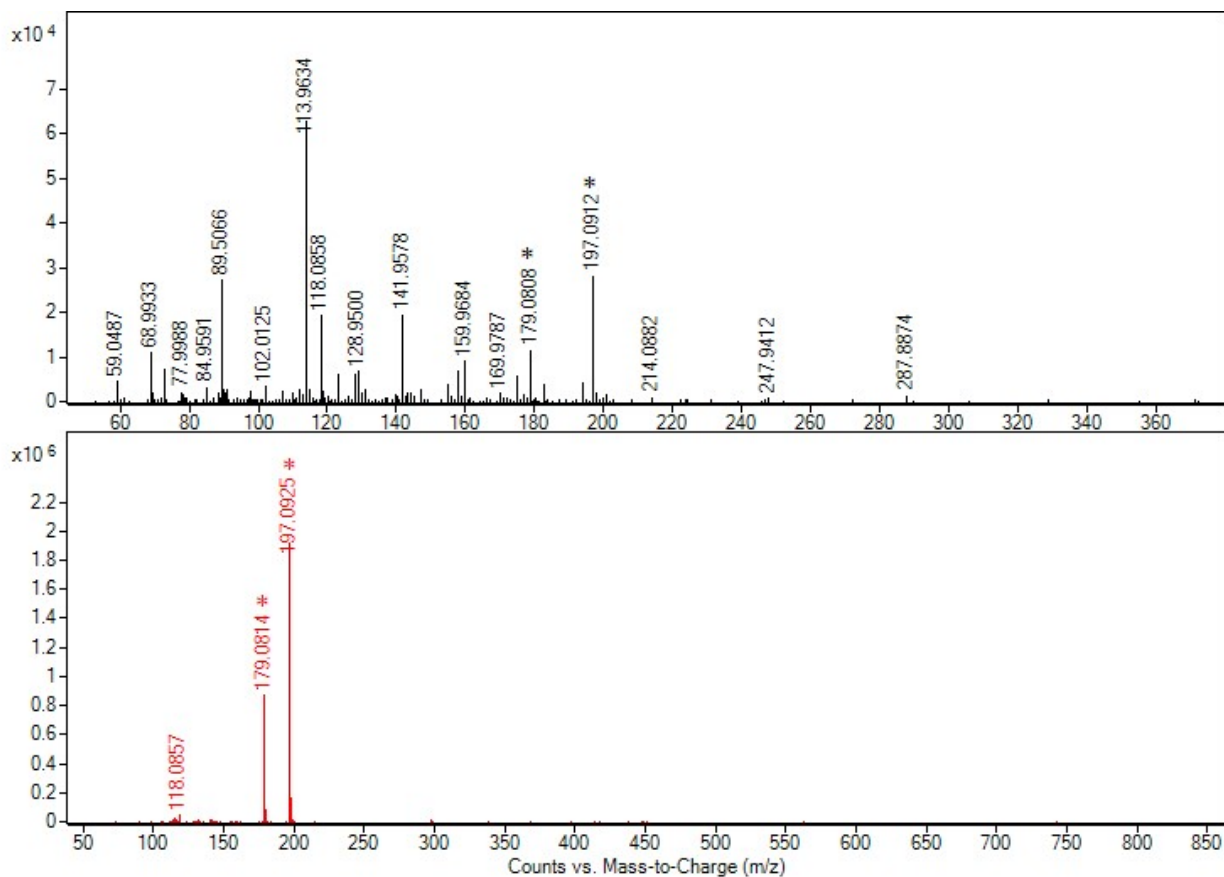


Fig. S42. Comparison of HRMS spectrum at 4.65 min from the TIC of degradation mixture after 195 h of irradiation with HRMS spectrum at 4.53 min from the TIC of synthetic sample of ethanolamine **9**

The chromatographic peak of compound **10** was noticed at a retention time of 7.15 min (**Fig. S43**). Peak splitting was observed possibly by the occurrence of two isomeric compounds. The corresponding HRMS spectrum was characterized by the signal at m/z of 257.0334 (**Fig. S44**) which was assigned to $[M+Cl]^-$ adduct according to its characteristic isotopic pattern. Additionally, the signal at m/z 194.0459 in the HRMS spectrum was assigned to in-source fragment after subjecting the mentioned $[M+Cl]^-$ adduct to CID experiments (**Fig. S45**).

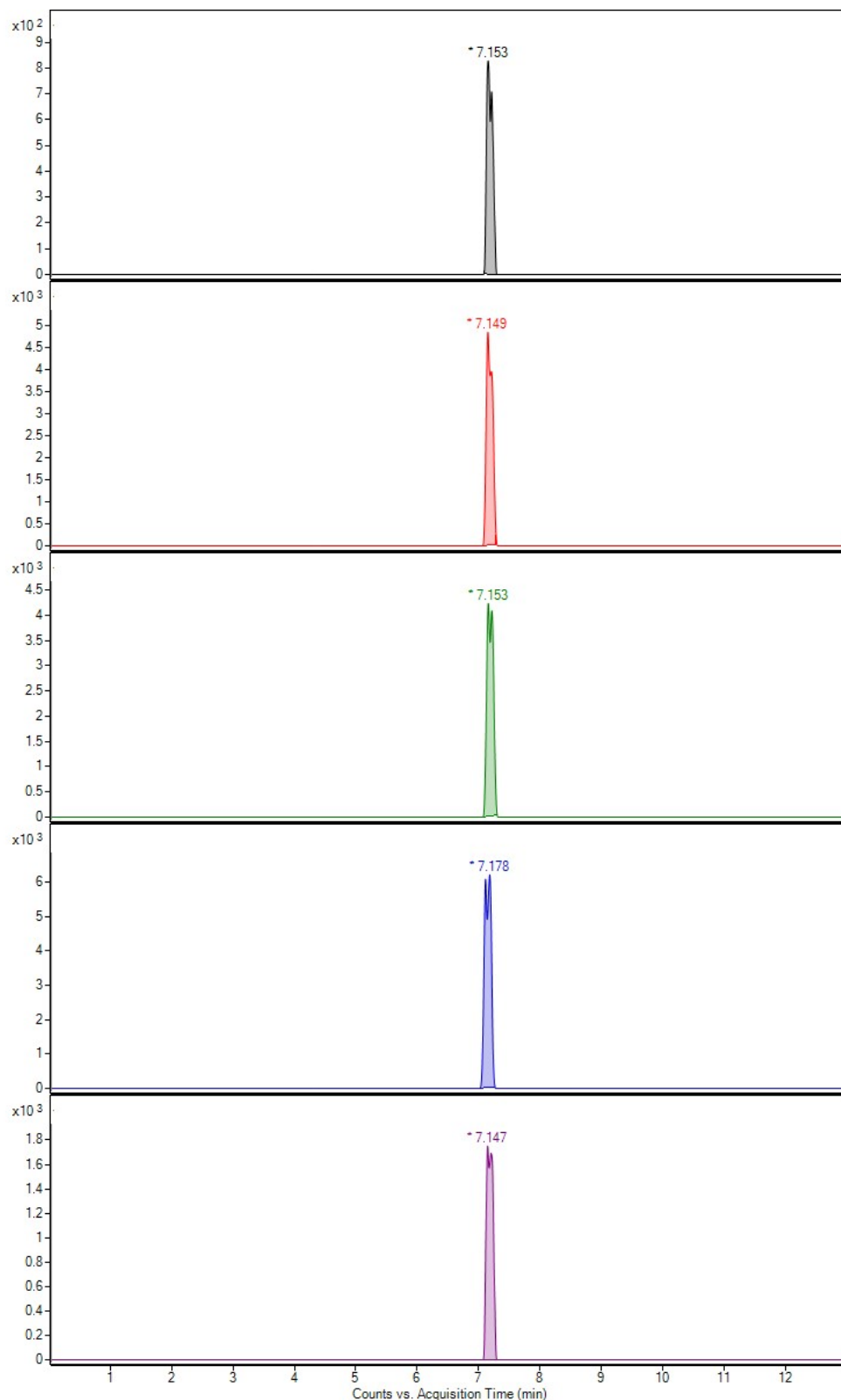


Fig. S43. EICs for m/z 257.0334 $[M+Cl]^-$; 7 h, 25 h, 49 h, 122 h, and 195 h of irradiation.

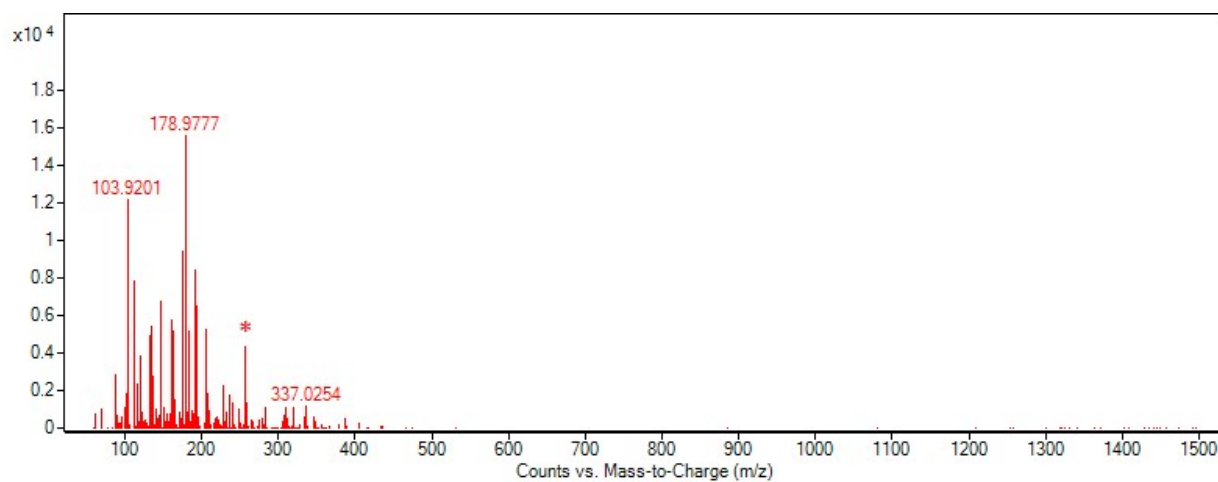


Fig. S44. HRMS spectrum of degradation product **10** at 7.15 min.

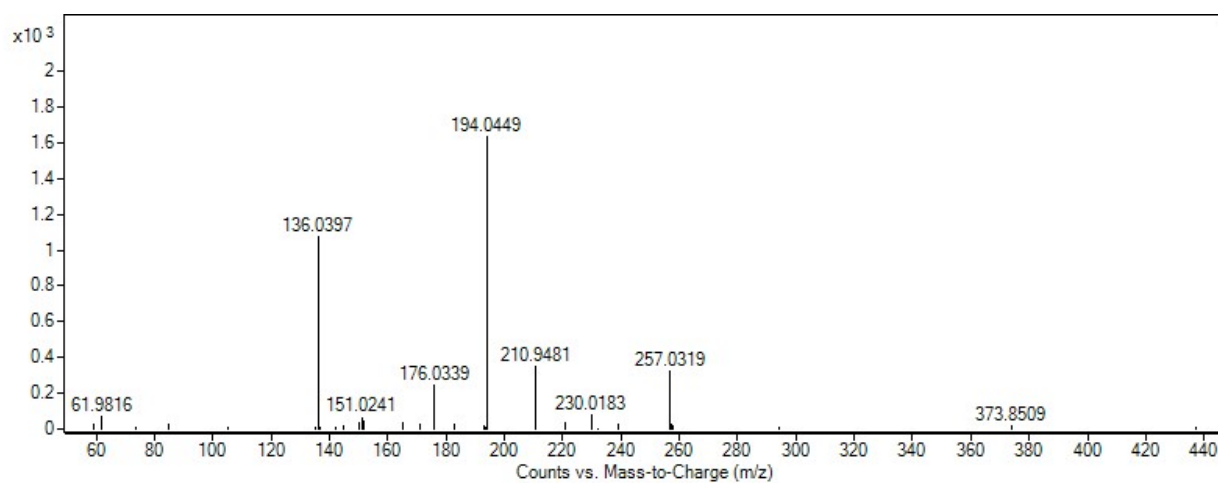


Fig. S45. MS/MS spectrum of of $[M+Cl]^-$ (m/z 257.0334) at 10 V.

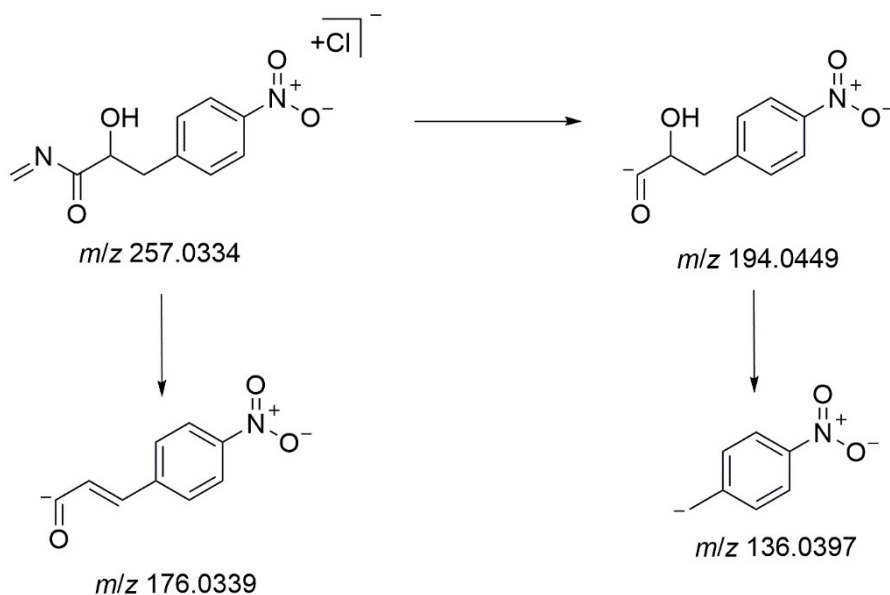


Fig. S46. Possible fragmentation pathway of **10** $[M+Cl]^-$ ion (m/z 257.0334).

Degradation products **11** and **12** were observed at retention times of 9.59 and 10.51 min, respectively (**Fig. S47**). HRMS spectra of these degradation products were almost identical with only one characteristic signal at m/z 400.9954 (or 400.9963 in the case of **12**) which was assigned to singly deprotonated molecular ion (**Fig. S48** and **Fig. S49**). Both these values m/z can only be assigned to compounds with a molecular formula of $C_{15}H_{13}BrF_2N_2O_4$ which corresponds to the substitution of one fluorine atom with hydroxyl group. However, CID experiments revealed completely different fragmentation patterns of these compounds (**Fig. S50** and **Fig. S52**). Unambiguous determination of substituted fluorine atom was not possible solely from MS/MS data (**Figs. Fig. S51** and **Fig. S53**).

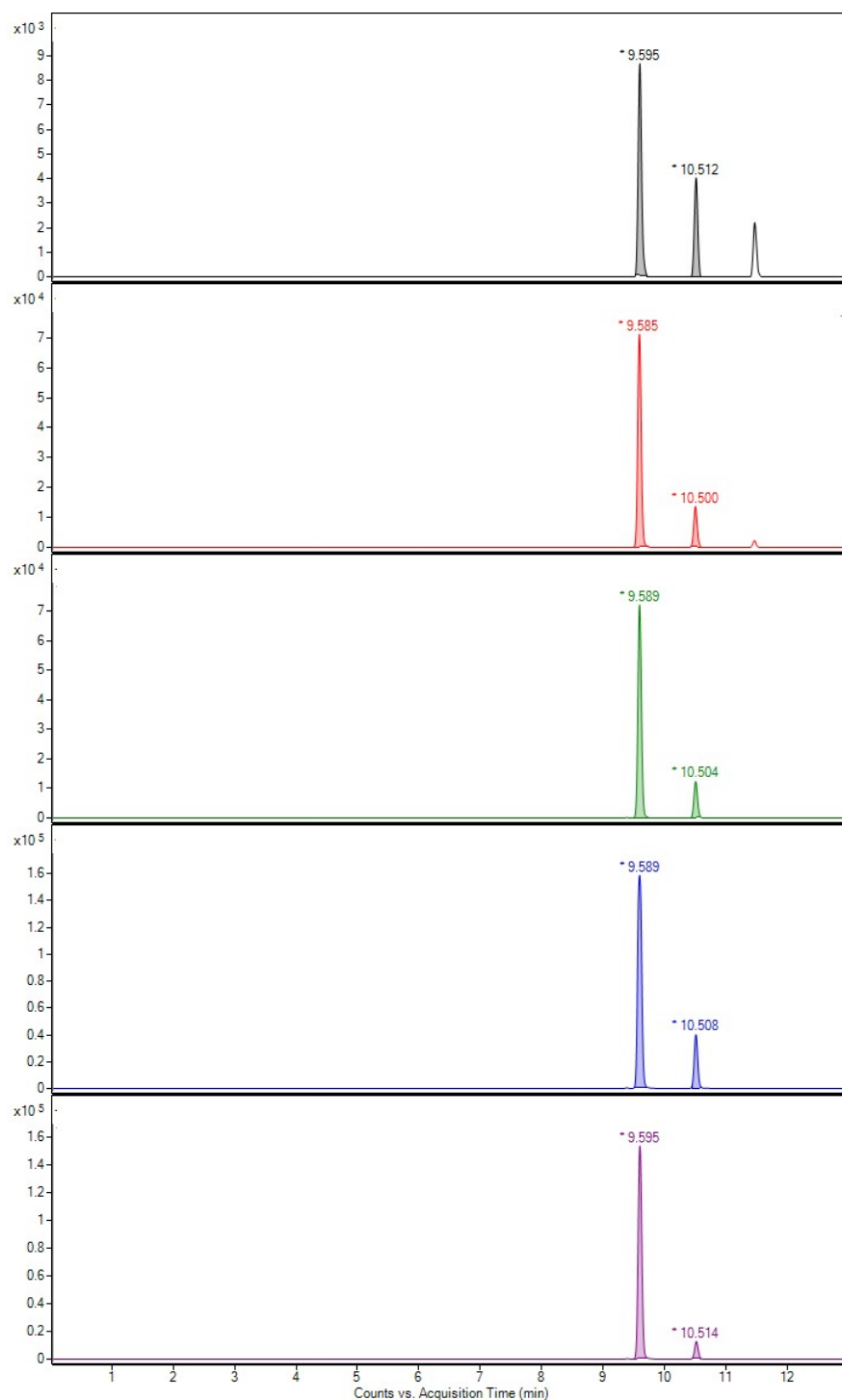


Fig. S47. EICs for m/z 400.9954 $[M-H]^-$ and 400.9963 $[M-H]^-$; 7 h, 25 h, 49 h, 122 h, and 195 h of irradiation.

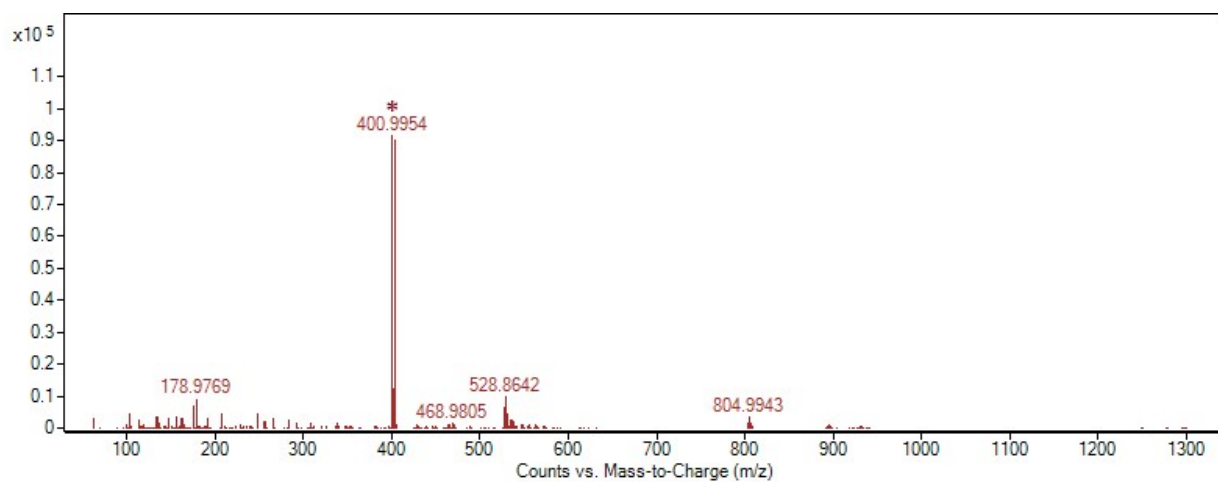


Fig. S48. HRMS spectrum of degradation product **11** at 9.59 min.

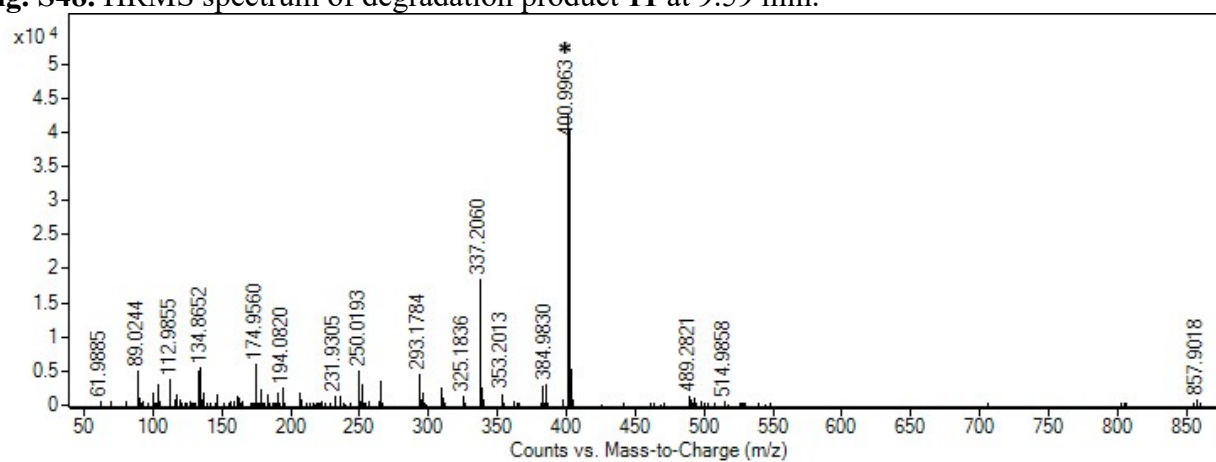


Fig. S49. HRMS spectrum of degradation product **12** at 10.51 min.

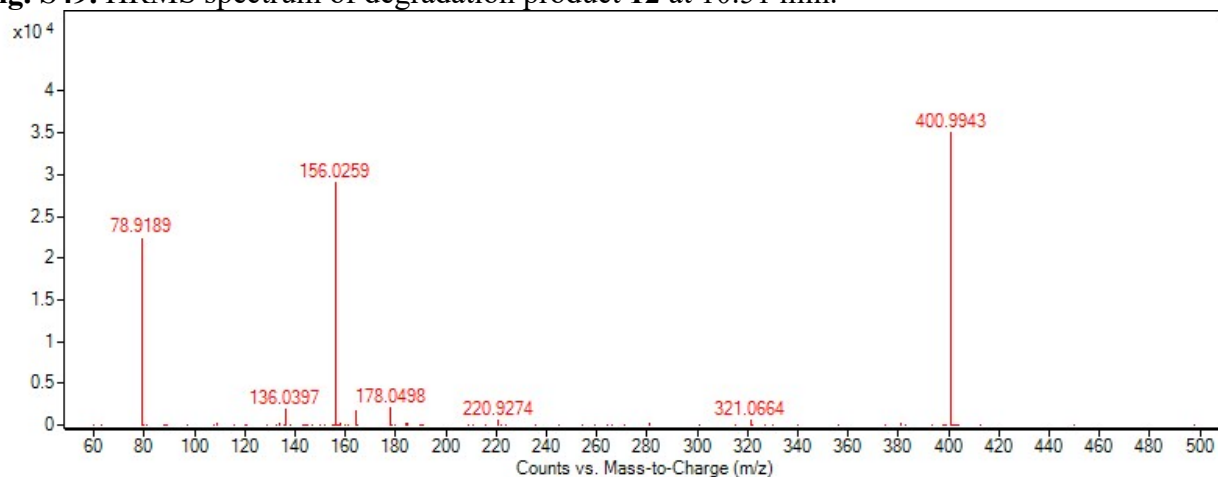


Fig. S50. MS/MS spectrum of $[M-H]^-$ (m/z 400.9954) at 10 V.

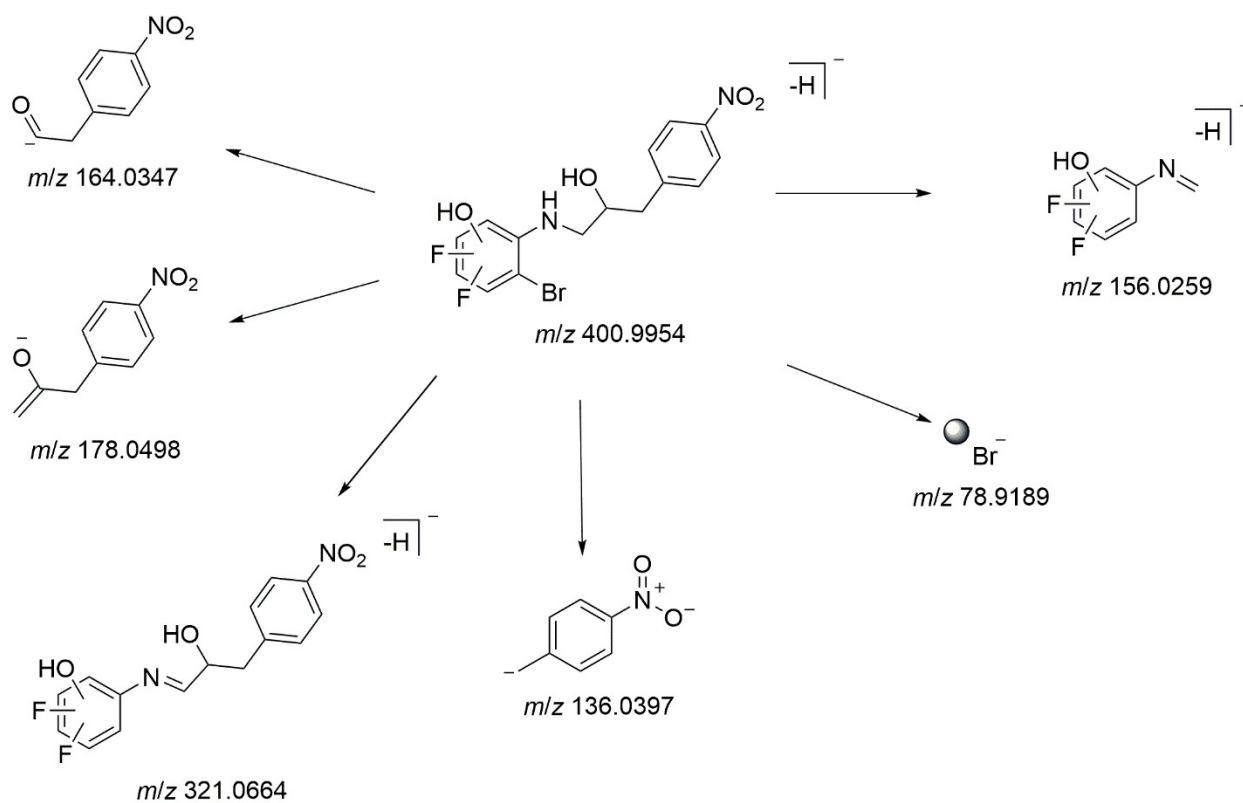


Fig. S51. Possible fragmentation pathway of **11** $[M-H]^-$ ion (m/z 400.9954).

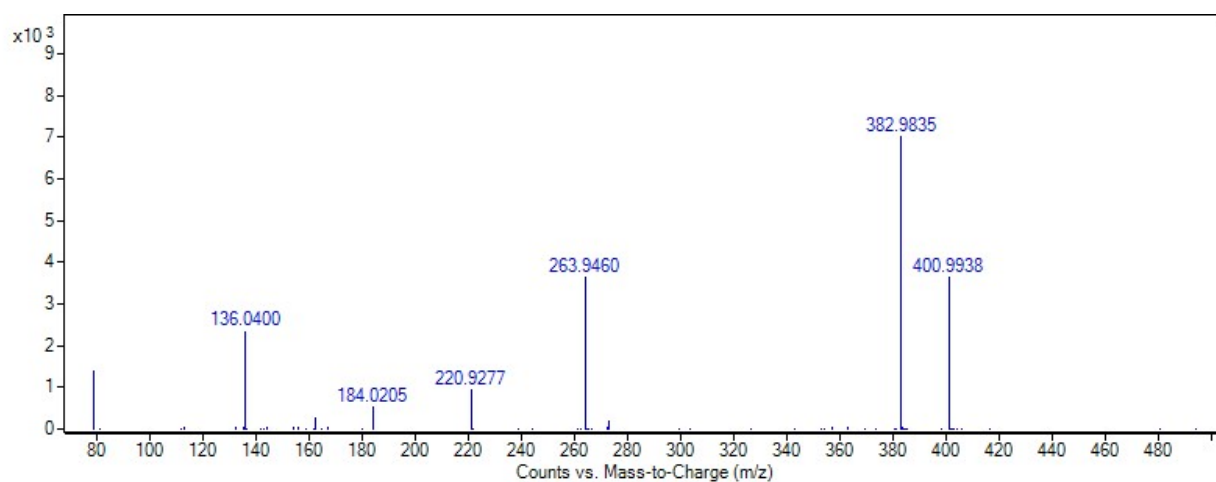


Fig. S52. MS/MS spectrum of of $[M-H]^-$ (m/z 400.9963) at 10 V.

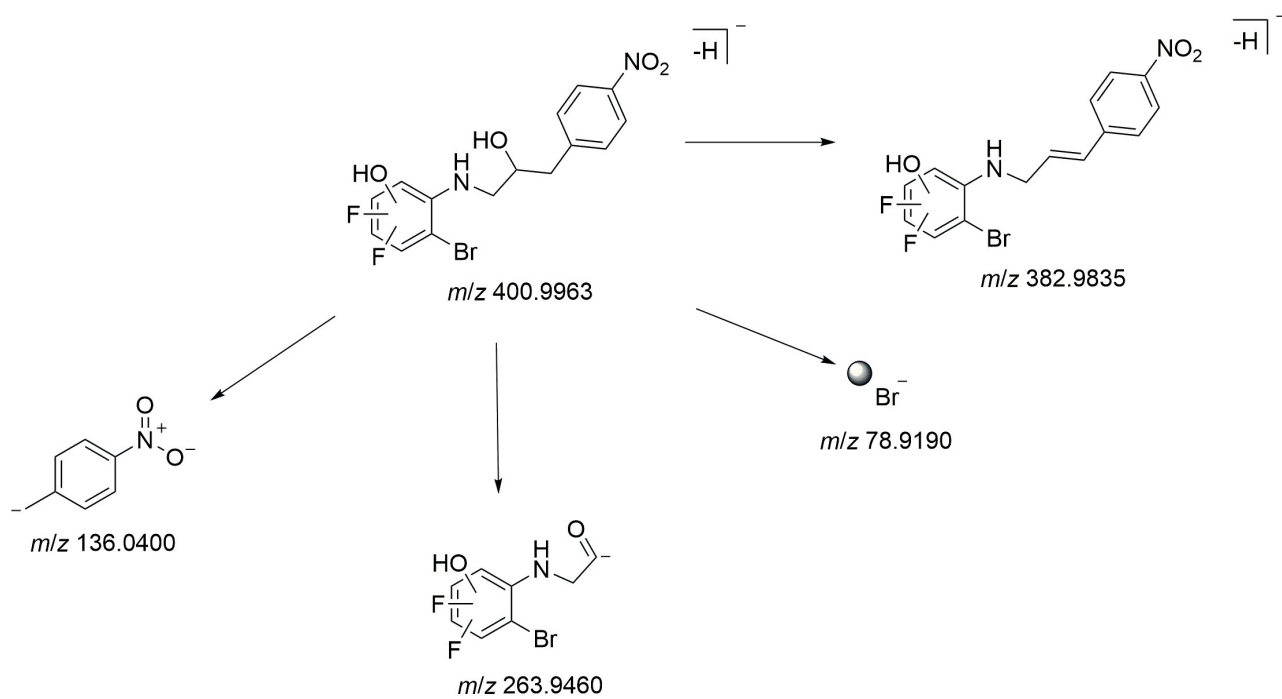


Fig. S53. Possible fragmentation pathway of **12** $[M-H]^-$ ion (m/z 400.9963).

Degradation product **13** was observed at the retention time of 9.86 min (**Fig. S54**). The corresponding HRMS spectrum was characterized by the signal at m/z of 341.0758 (**Fig. S55**) which was assigned to $[M-H]^-$ ion. Signal at m/z 323.0649 was assigned to the in-source fragment after performing MS/MS analysis (**Fig. S56**). The exact mass of this compound can only be assigned to the molecular formula of $C_{15}H_{13}F_3N_2O_4$, meaning that the bromine atom was substituted with one hydroxyl group. Careful examination of the isotope pattern of m/z 341.0758 (and m/z 323.0649) confirmed the absence of a bromine atom due to the lack of a characteristic $M+2$ Da signal.

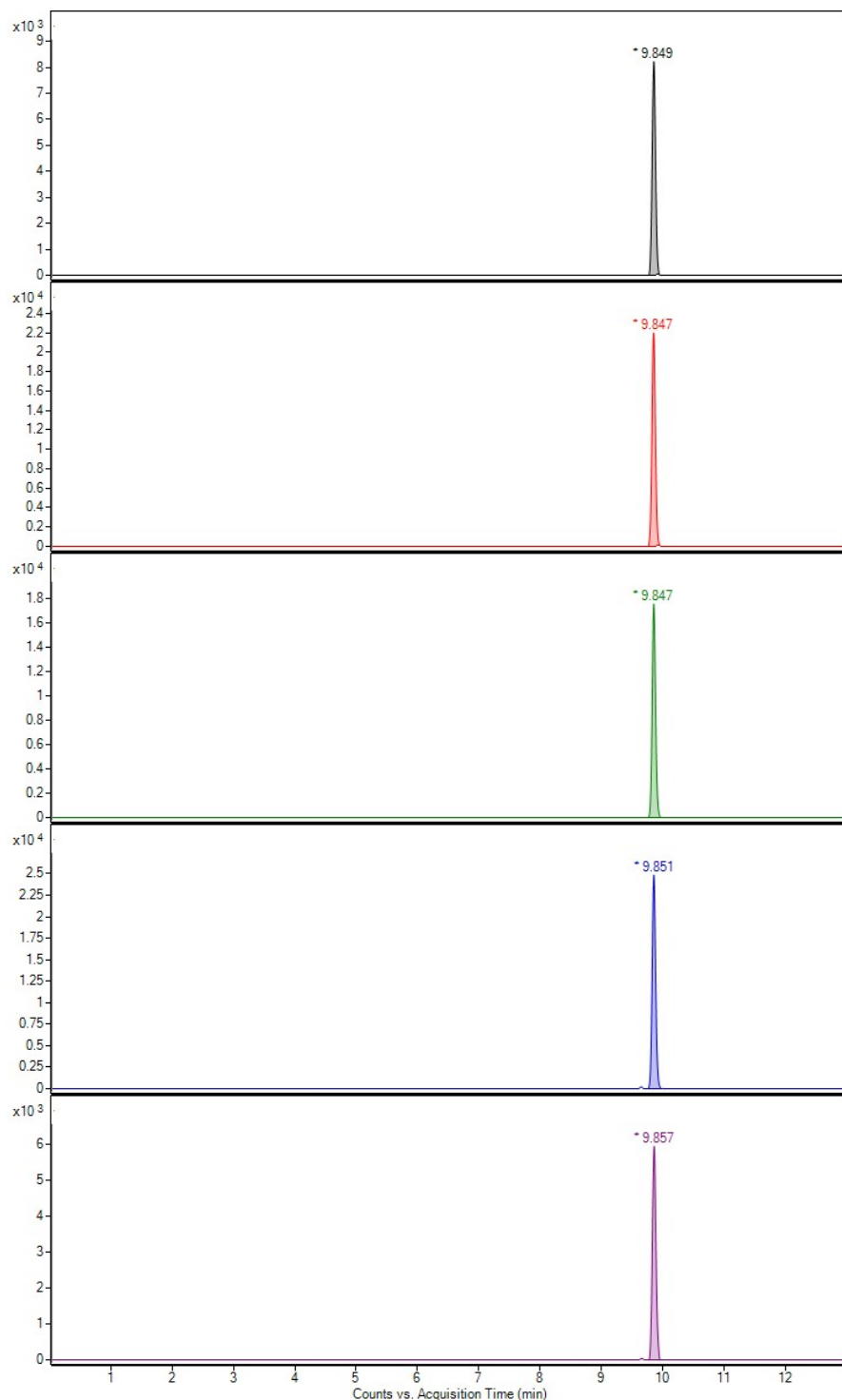


Fig. S54. EICs for m/z 341.0758 $[M-H]^-$; 7 h, 25 h, 49 h, 122 h, and 195 h of irradiation.

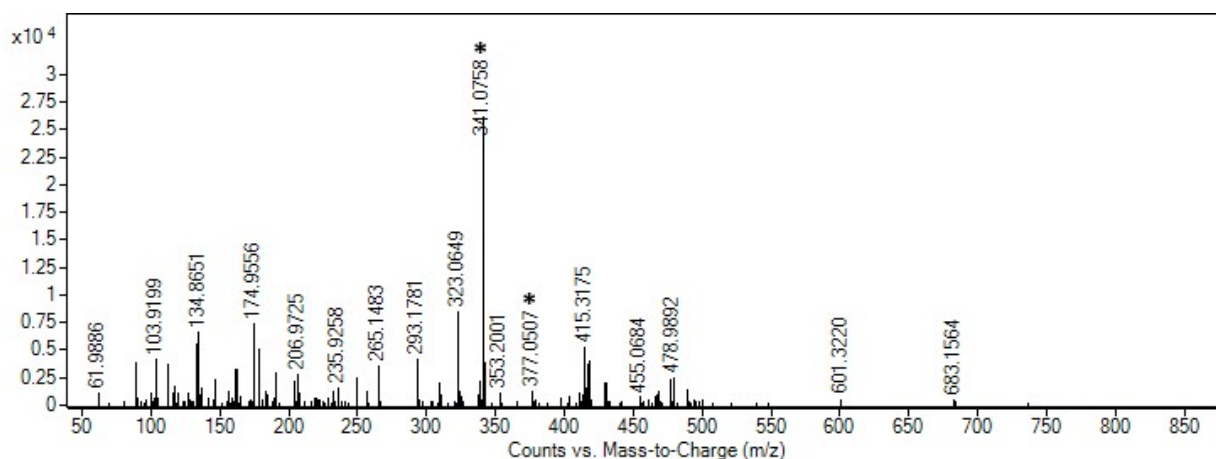


Fig. S55. HRMS spectrum of degradation product **13** at 9.86 min.

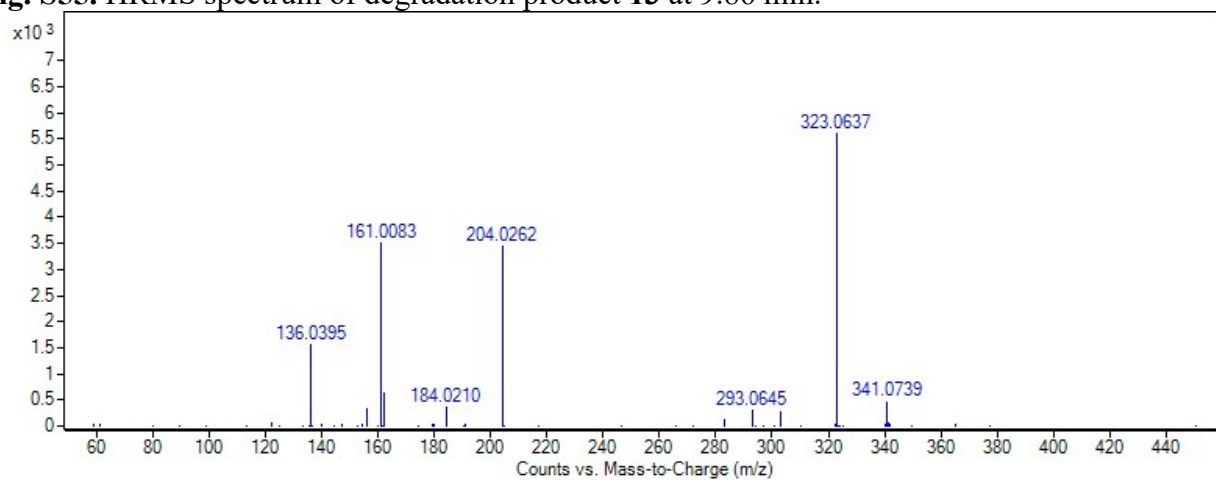


Fig. S56. MS/MS spectrum of of $[M-H]^-$ (m/z 341.0758) at 10 V.

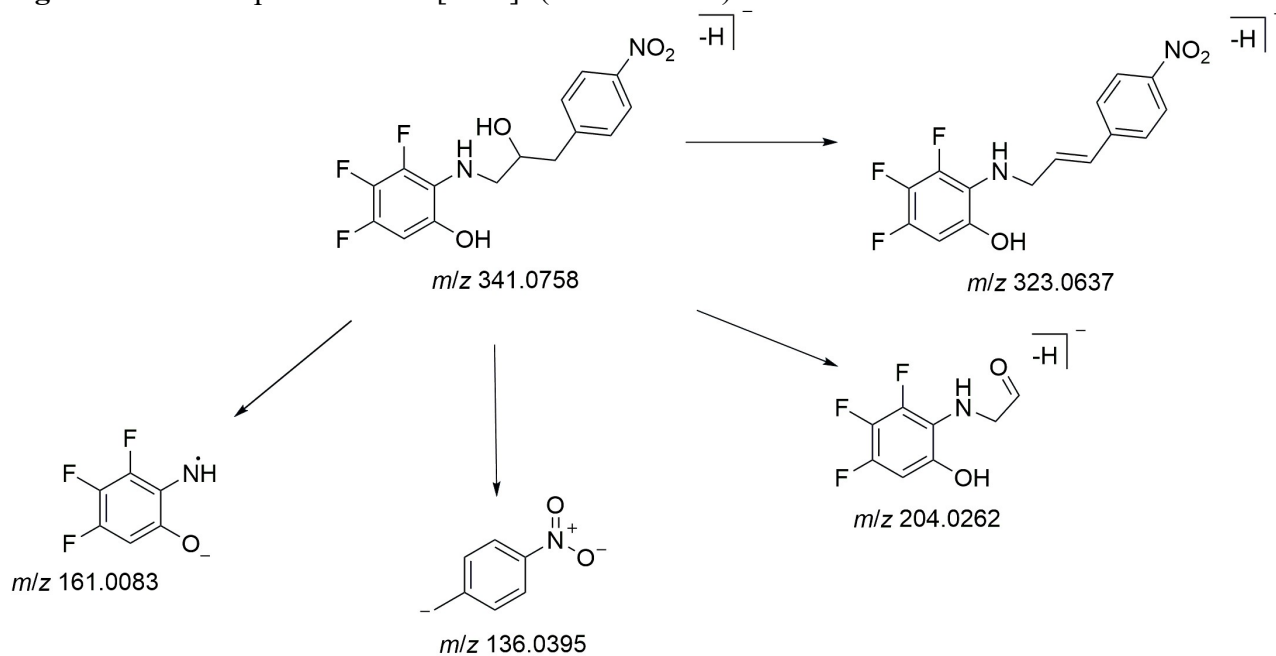


Fig. S57. Possible fragmentation pathway of **13** $[M-H]^-$ ion (m/z 341.0758).

Compound **14** was noticed at the retention time of 10.28 min in the samples irradiated for 25, 49, 122, and 195 hours (**Fig. S58**) while it was absent in the sample that was irradiated for 7 hours. Its HRMS spectrum (**Fig. S59**) was characterized by a signal at m/z 428.9908 assigned to $[M+HCOO]^-$ ion. Exact mass was assigned to the compound with a molecular formula of $C_{15}H_{11}BrF_3N_2O_3$ meaning that one fluorine atom was substituted by one hydroxyl group while the hydroxyl group from ethanolamine moiety from the compound **3** was lacking. MS/MS analysis (**Fig. S60**) revealed an interesting fragmentation pathway where loss of hydrogen bromide was observed (**Fig. S61**) which is relatively common for brominated aromatic compounds.

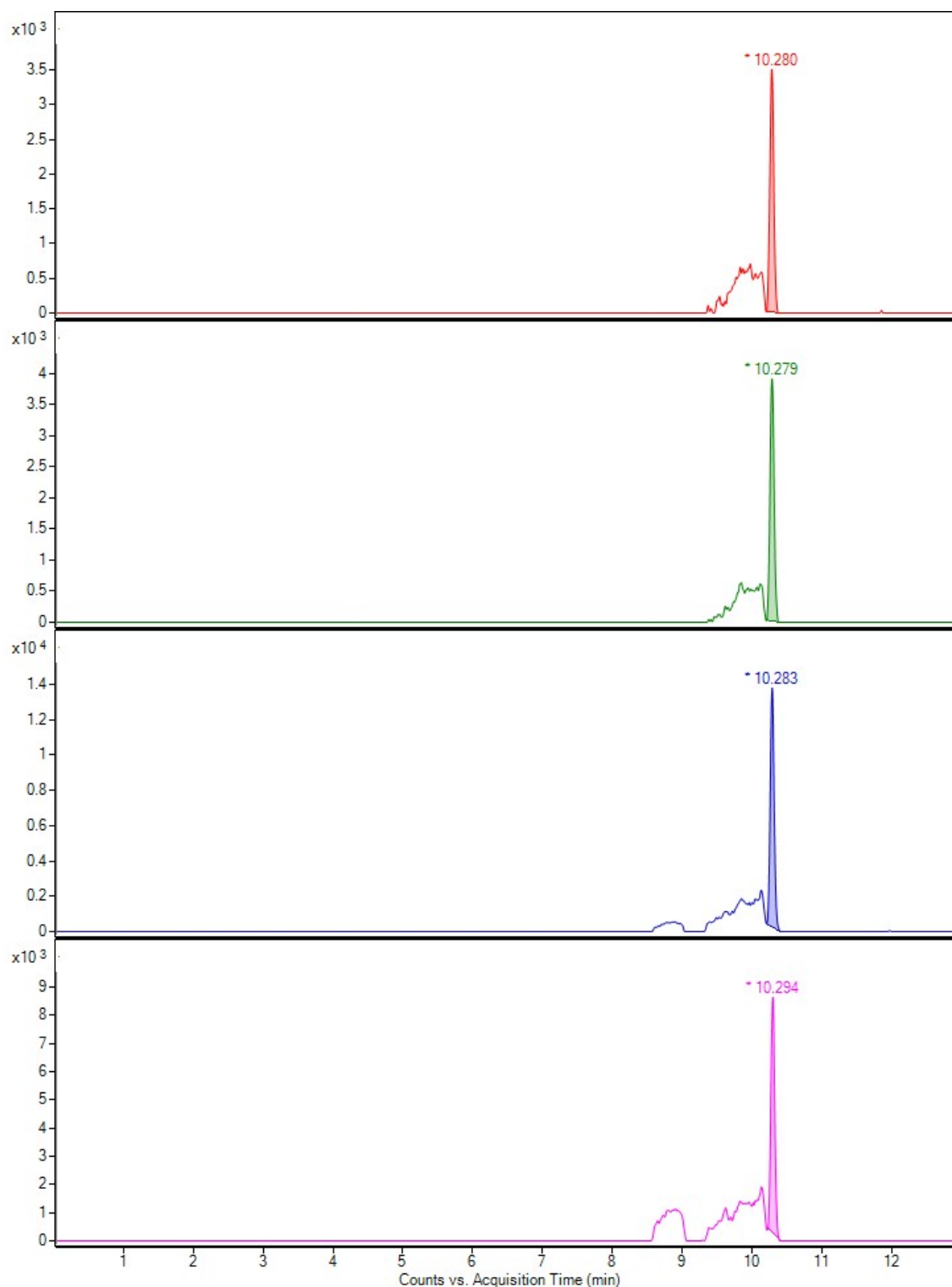


Fig. S58. EICs for m/z 428.9908 $[M+HCOO]^-$; 25 h, 49 h, 122 h, and 195 h of irradiation.

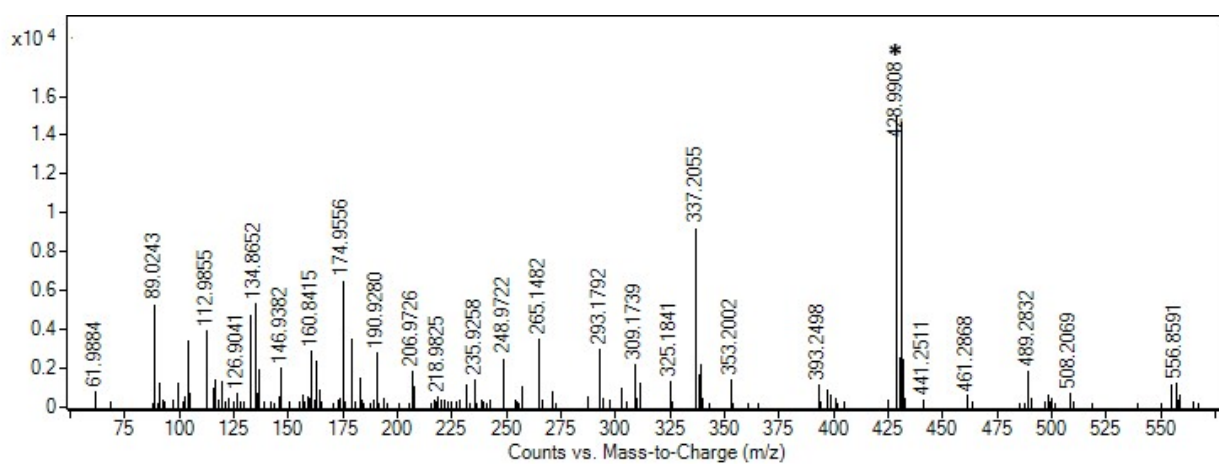


Fig. S59. HRMS spectrum of degradation product 14 at 10.28 min.

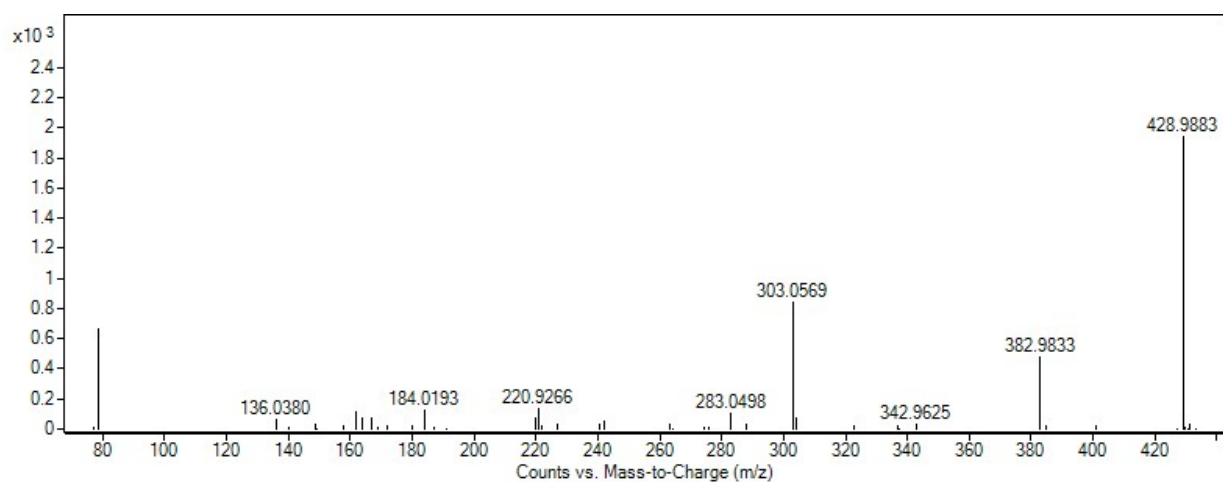


Fig. S60. MS/MS spectrum of $[M+HCOO]^-$ (m/z 428.9908) at 10 V.

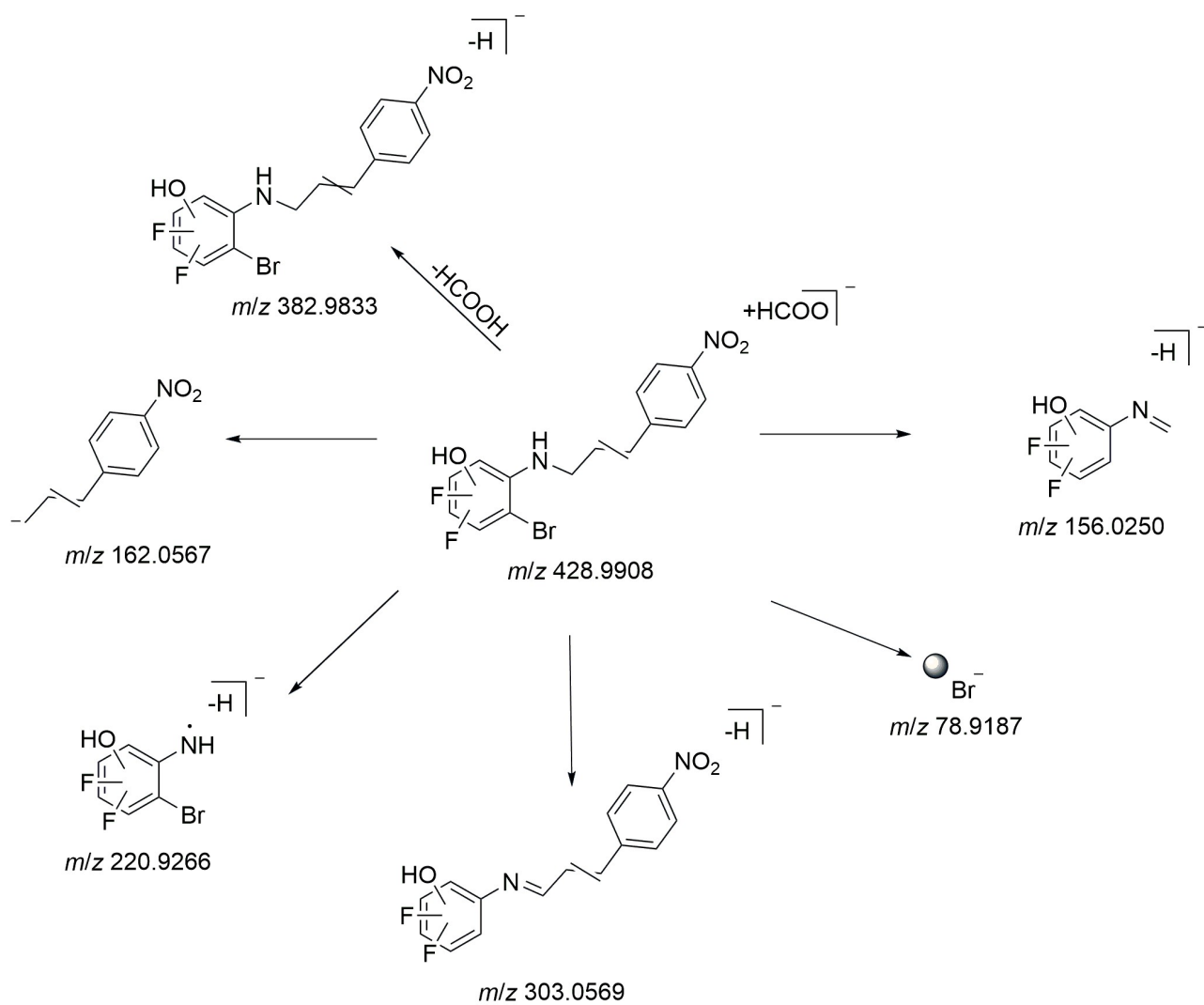


Fig. S61. Possible fragmentation pathway of **14** $[M+HCOO]^-$ ion (m/z 428.9908).

Degradation product **15** was noticed at the retention time of 11.57 min immediately after 7 hours of irradiation (**Fig. S62**). HRMS spectrum was characterized by signals at m/z 422.9729 and 433.0011 assigned to $[M+Cl]^-$ and $[M+HCOO]^-$ ions respectively (**Fig. S63**). After MS/MS analysis of $[M+HCOO]^-$ ion (**Fig. S64**) structure elucidation of **15** was possible. This analysis revealed the occurrence of the fragment with a m/z value of 120.0452 and complete absence of the characteristic 1-methyl-4-nitrobenzene fragment at m/z 136 meaning that the nitro group was reduced to the nitroso group.

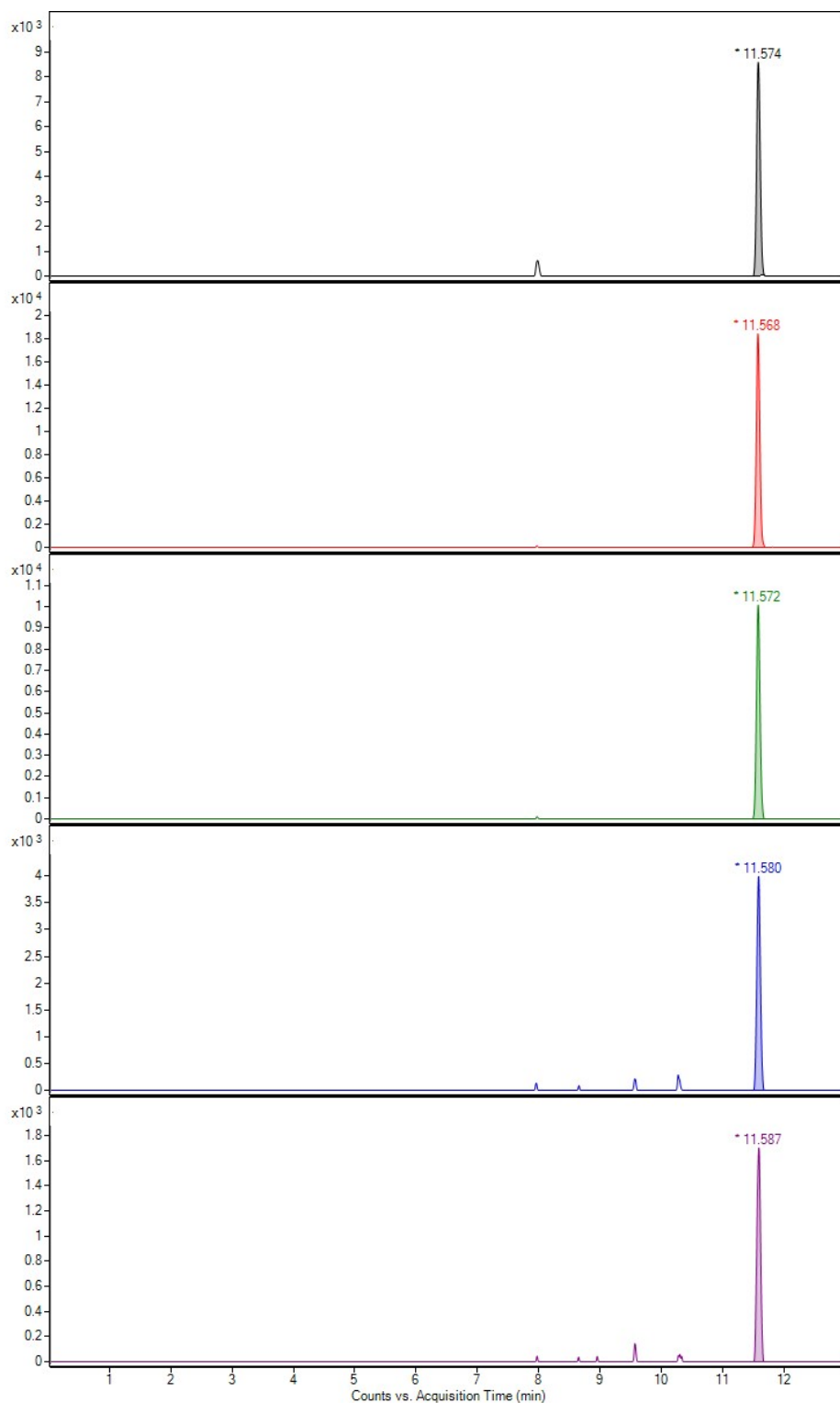


Fig. S62. EICs for m/z 433.0011 $[M+HCOO]^-$; 7 h, 25 h, 49 h, 122 h, and 195 h of irradiation.

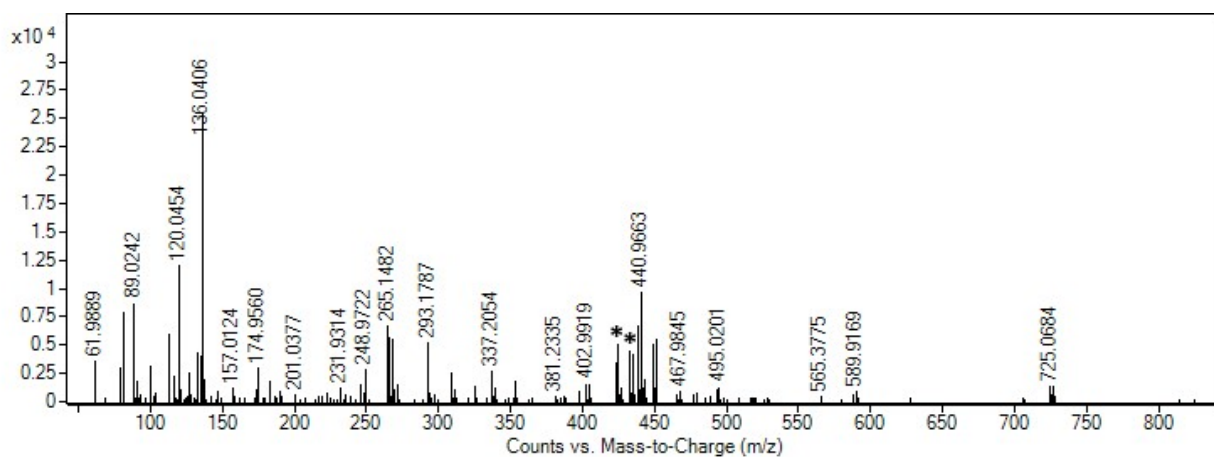


Fig. S63. HRMS spectrum of degradation product **15** at 11.57 min.

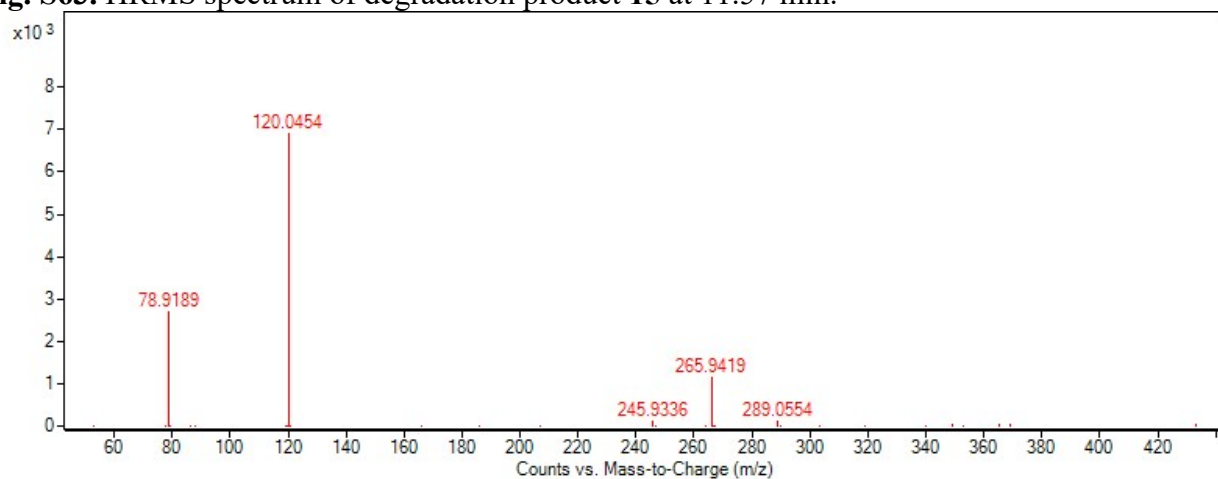


Fig. S64. MS/MS spectrum of of $[M+HCOO]^-$ (m/z 433.0011) at 10 V.

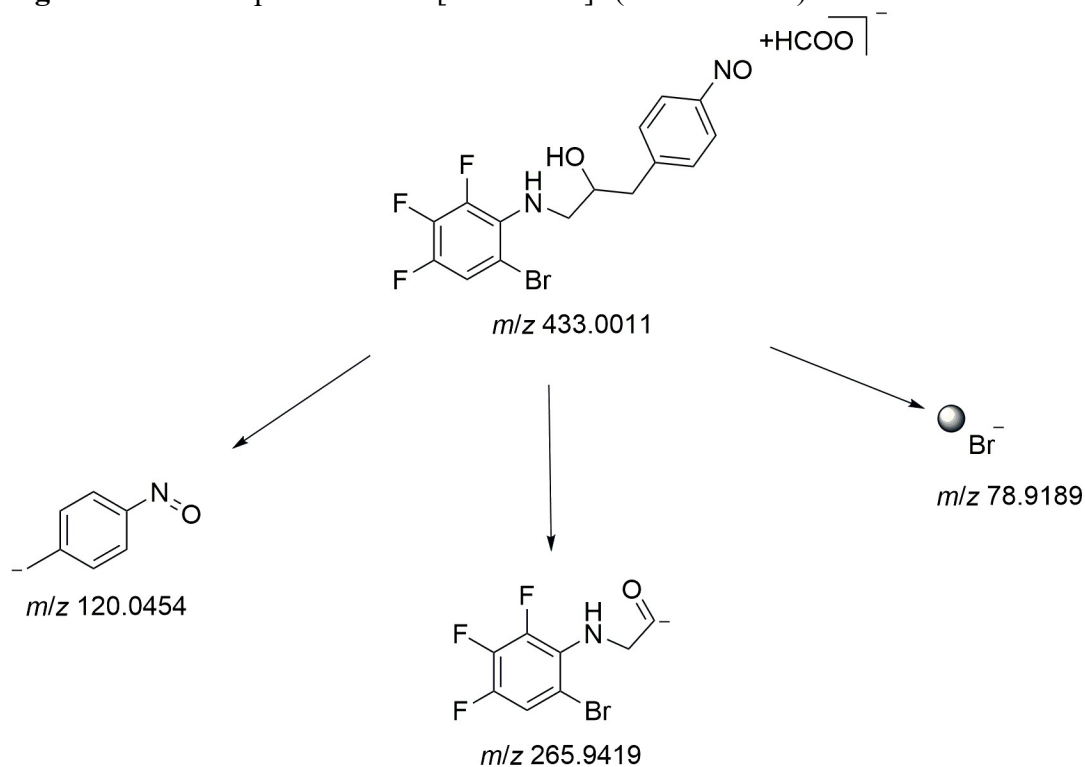


Fig. S65. Possible fragmentation pathway of **15** $[M+HCOO]^-$ ion (m/z 433.0011).

Degradation product **16** was noticed at the retention time of 11.86 (**Fig. S66**) with a complex HRMS spectrum which was characterized by signals at m/z 466.9630 and 476.9913 assigned to $[M+Cl]^-$ and $[M+HCOO]^-$ ions respectively (**Fig. S67**). After performing a thorough MS/MS analysis on $[M+HCOO]^-$ ion it was concluded that signals at m/z 364.9749 and 384.9812 from the native HRMS spectrum are in-source fragments. MS/MS analysis (**Fig. S68**) again revealed interesting fragmentation patterns accompanied by losses of hydrogen fluoride and/or hydrogen bromide (**Fig. S69**).

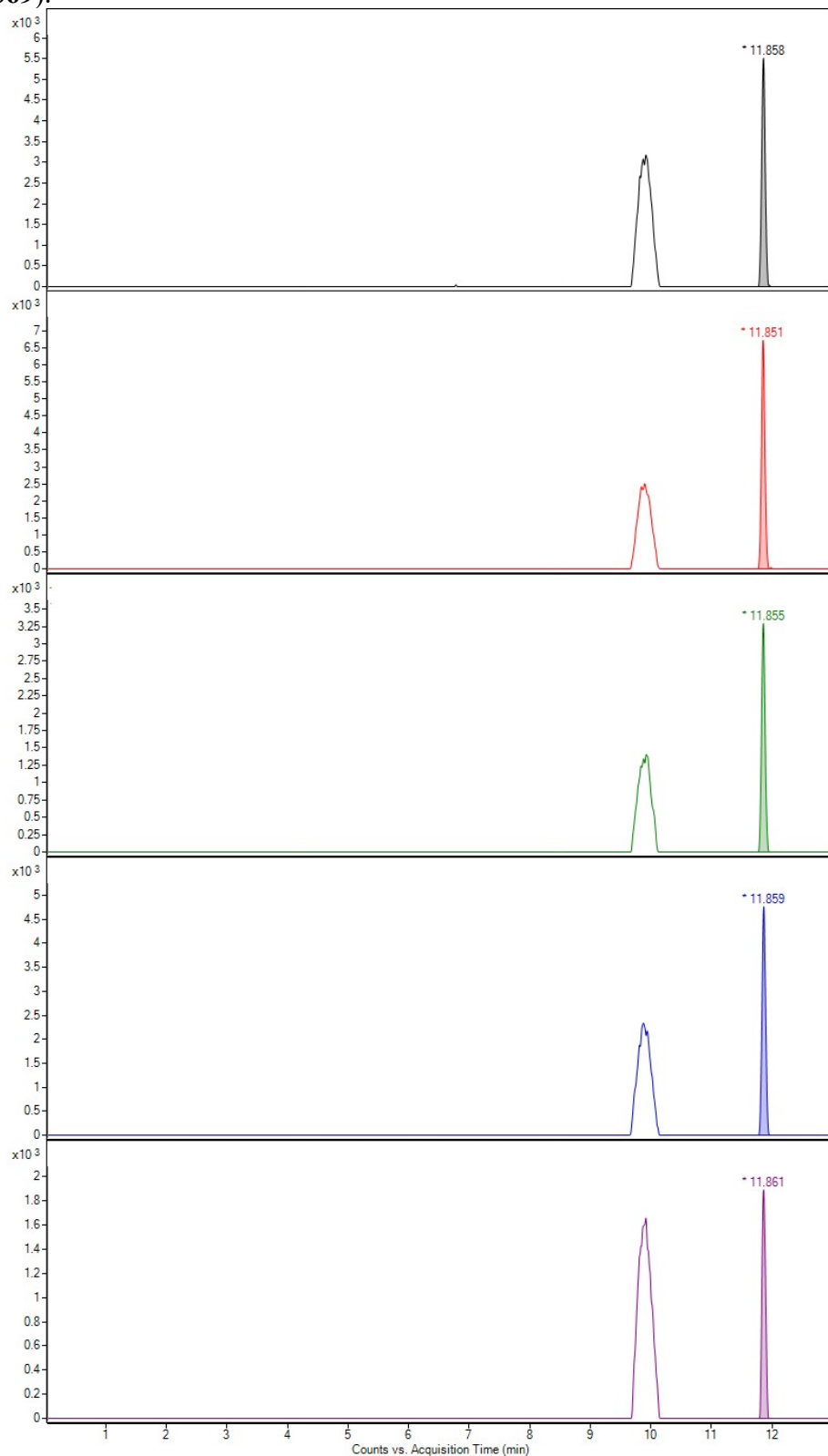


Fig. S66. EICs for m/z 476.9913 $[M+HCOO]^-$; 7 h, 25 h, 49 h, 122 h, and 195 h of irradiation.

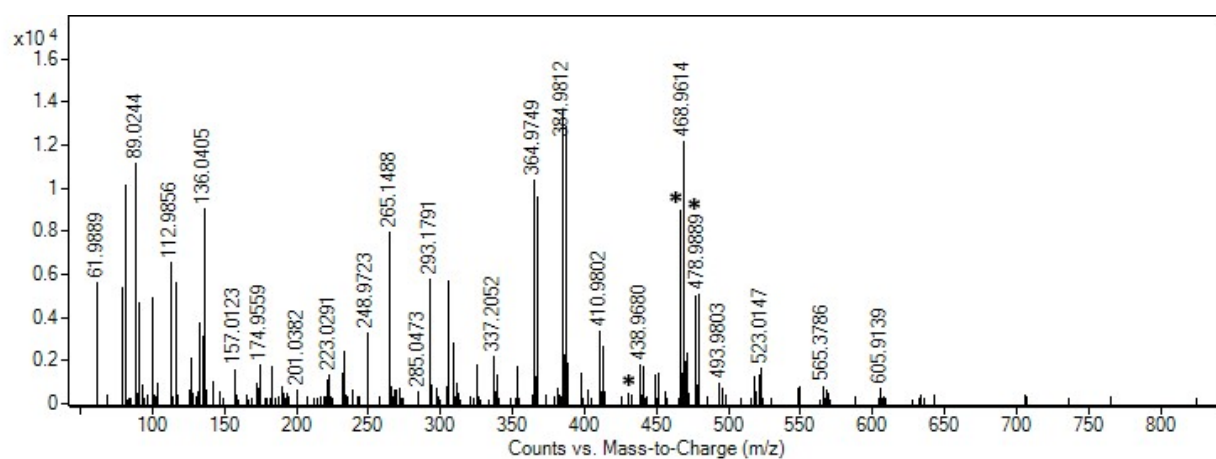


Fig. S67. HRMS spectrum of degradation product **16** at 11.86 min.

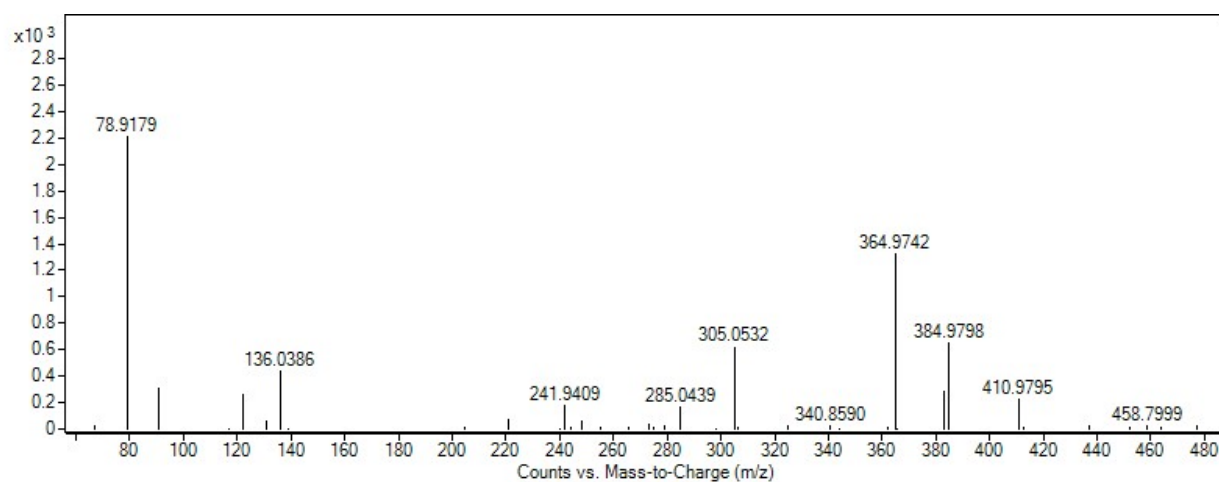


Fig. S68. MS/MS spectrum of $[M+HCOO]^-$ (m/z 476.9913) at 10 V.

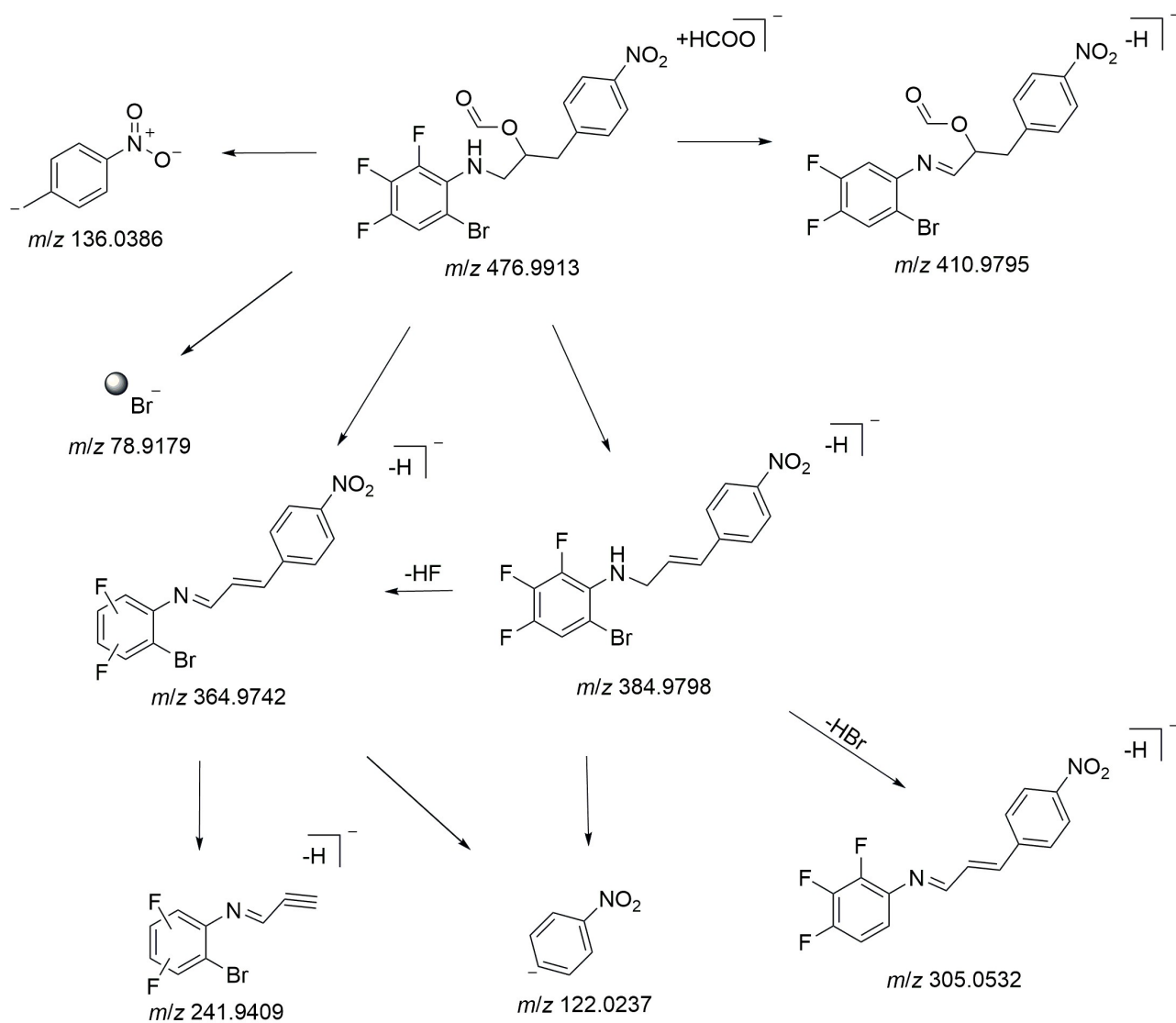


Fig. S69. Possible fragmentation pathway of **16** $[M+HCOO]^-$ ion (m/z 476.9913).

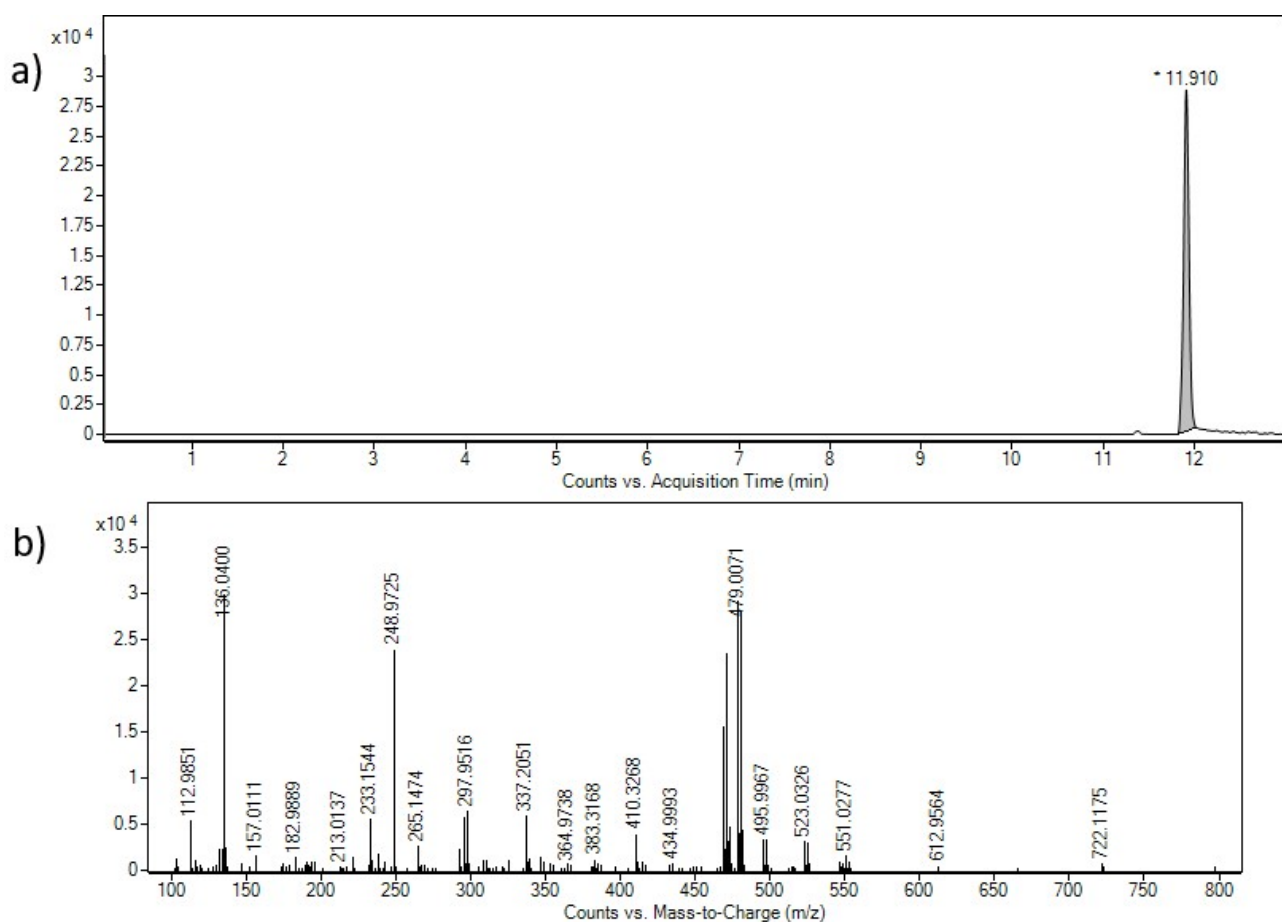


Fig. S70. a) EIC for m/z 479.0071 $[M+HCOO]^-$ and b) HRMS spectrum of intermediate **6** at 11.91 min.

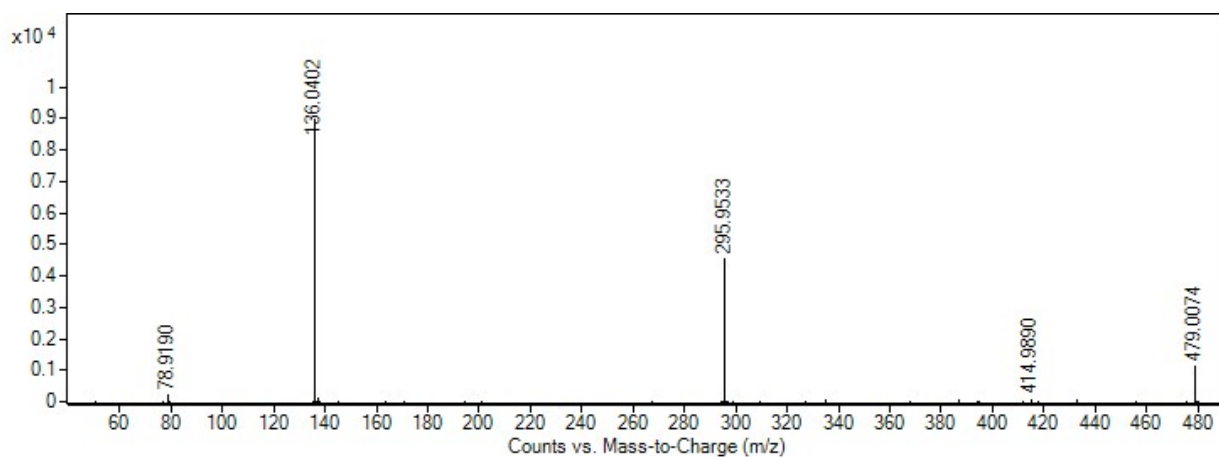


Fig. S71. MS/MS spectrum of $[M+HCOO]^-$ (m/z 479.0071) at 5 V.

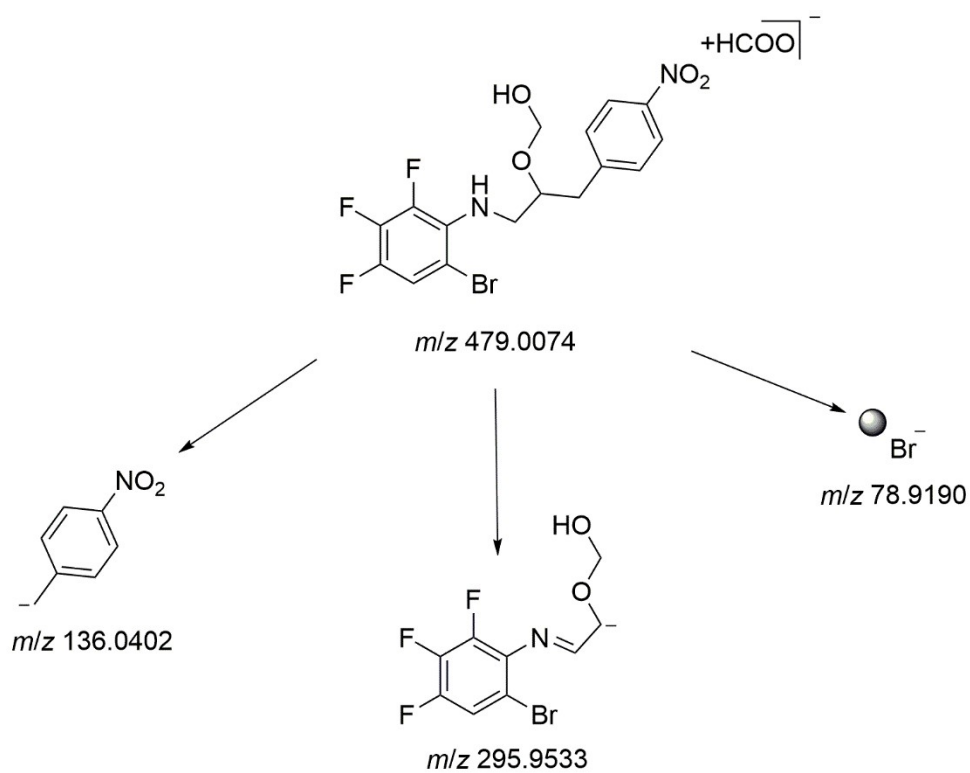


Fig. S72. Possible fragmentation pathway of intermediate **6** $[M+HCOO]^-$ ion (m/z 479.0071).

Comparison of the degradation products EICs at the first and last sampling

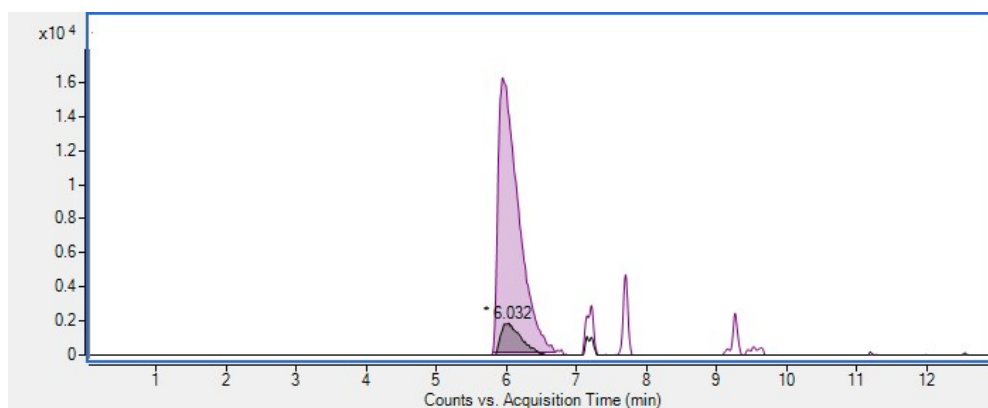


Fig. S73. EICs for compound **3b** m/z 194.0460 $[M-H]^-$; 7 h and 195 h of irradiation.

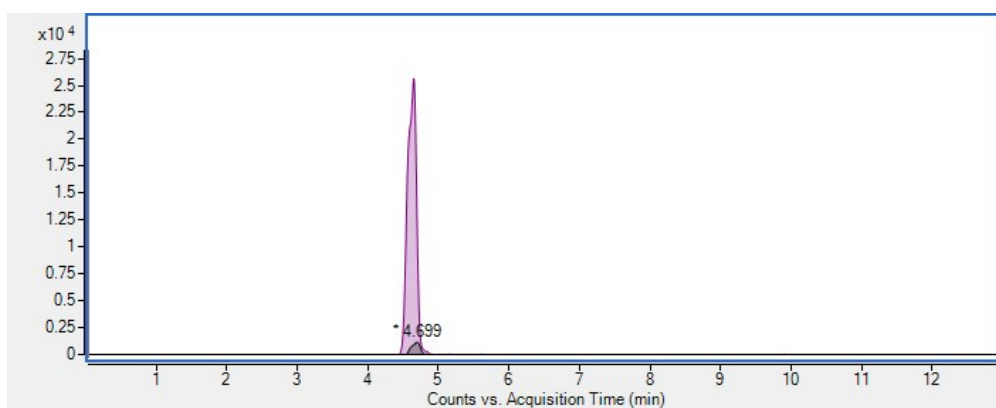


Fig. S74. EICs for compound **9** m/z 197.0912 $[M+H]^+$; 7 h and 195 h of irradiation.

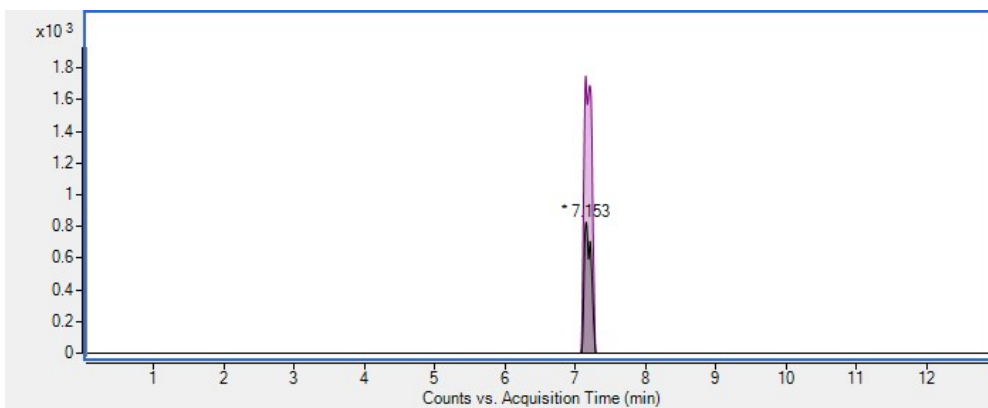


Fig. S75. EICs for compound **10** m/z 257.0334 $[M+Cl]^-$; 7 h and 195 h of irradiation.

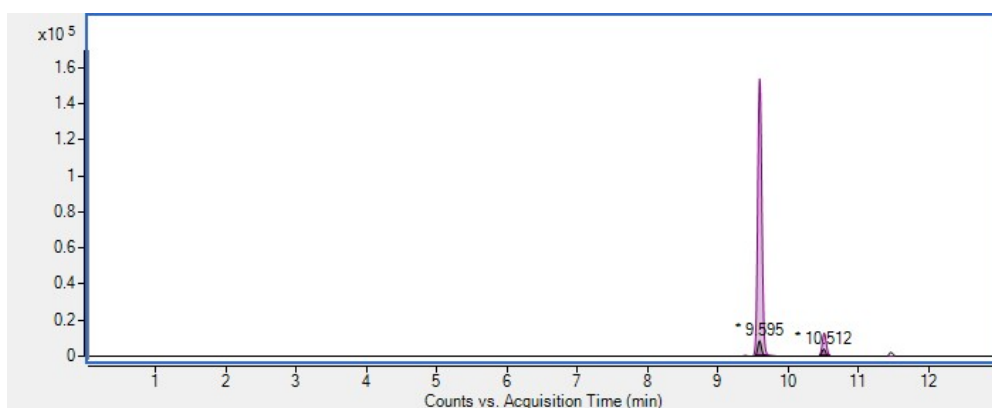


Fig. S76. EICs for compounds **11** and **12** m/z 400.9954 [M-H]⁻ and 400.9937 [M-H]⁻; 7 h and 195 h of irradiation.

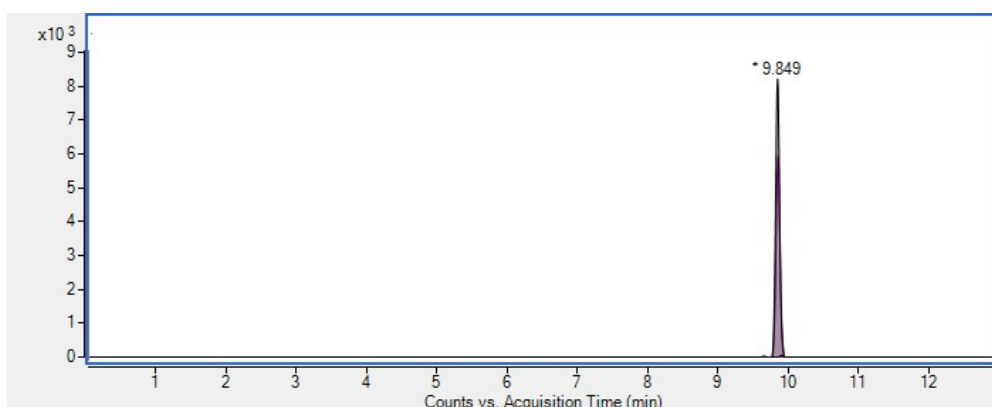


Fig. S77. EICs for compound **13** m/z 341.0758 [M-H]⁻; 7 h and 195 h of irradiation.

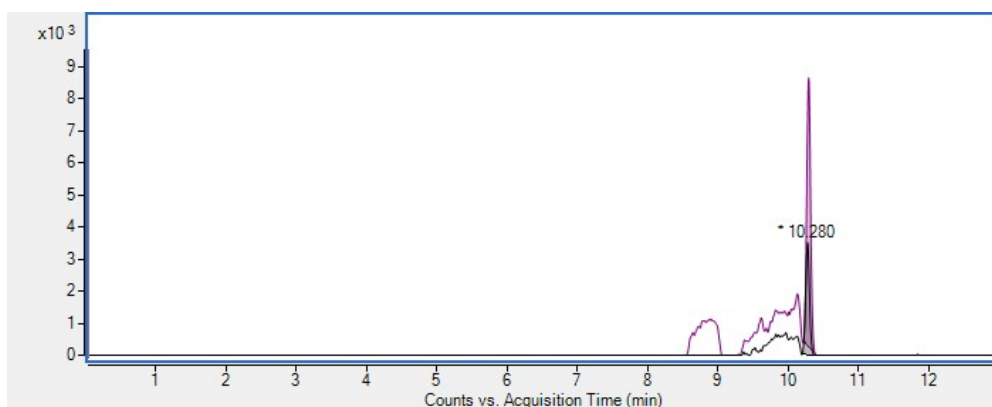


Fig. S78. EICs for compound **14** m/z 428.9908 [M+HCOO]⁻; 25 h and 195 h of irradiation.

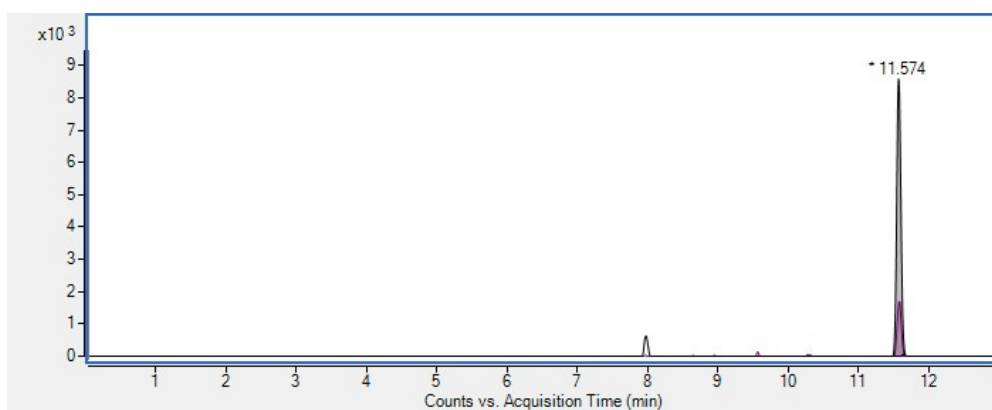


Fig. S79. EICs for compound **15** m/z 433.0011 [M+HCOO]⁻; 7 h and 195 h of irradiation.

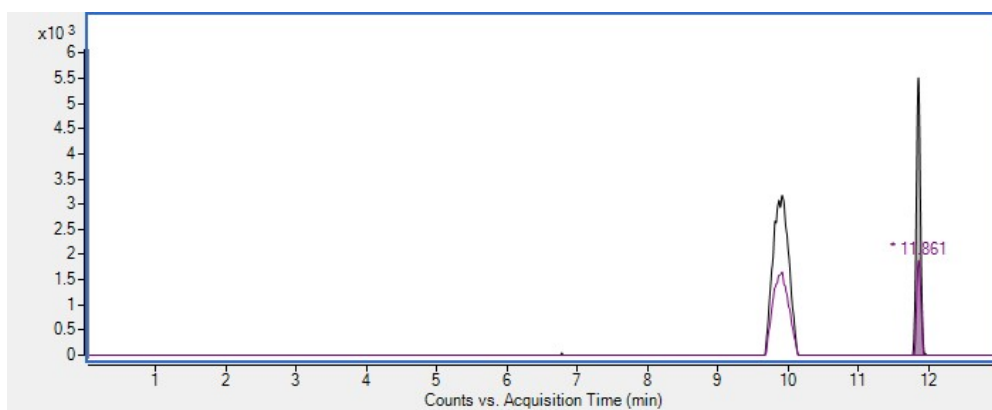


Fig. S80. EICs for compound **16** m/z 476.9913 $[M+HCOO]^-$; 7 h and 195 h of irradiation.

5. LC-UV-HRMS analysis of oxazolidine 4 and dioxazepine 5 mixture

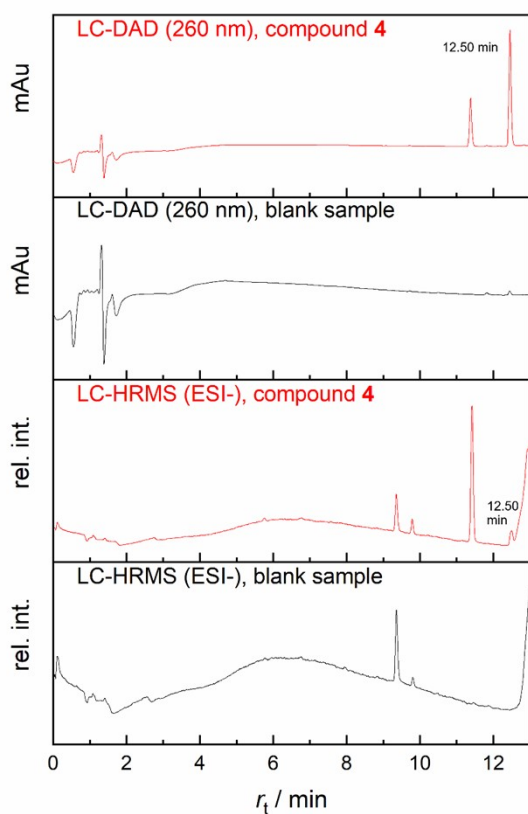


Fig. S81. Overlay of LC-DAD and LC-HRMS spectra of oxazolidine 4

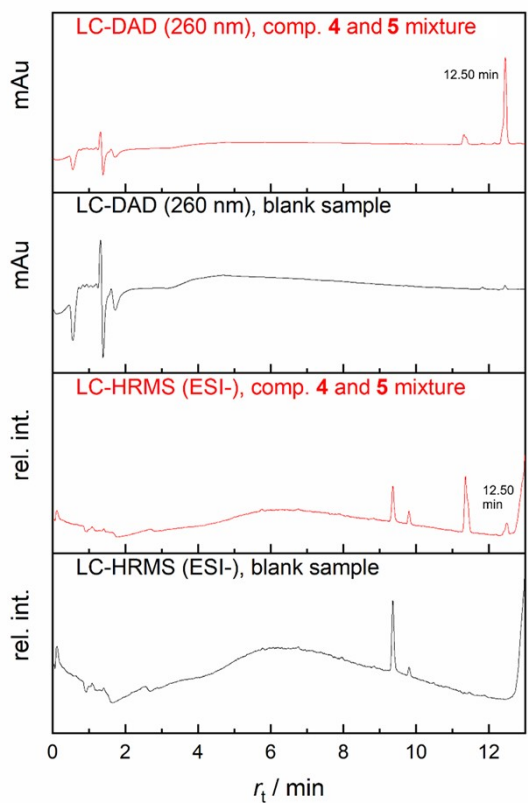


Fig. S82. Overlay of LC-DAD and LC-HRMS spectra of oxazolidine 4 and dioxazepine 5 mixture.

6. UV-Vis analysis of oxazolidine 4

LN-X71 F1

1 / 1

08-Mar-2024 01:53 AM

Instrument Serial #: 9A3Z183026

Method name: Fullspekter 190-900 nm (abs)

Instrument model: GENESYS 50

Method created: 13-Apr-2023 08:11 PM

Software Package Version: 2.6

Signature:

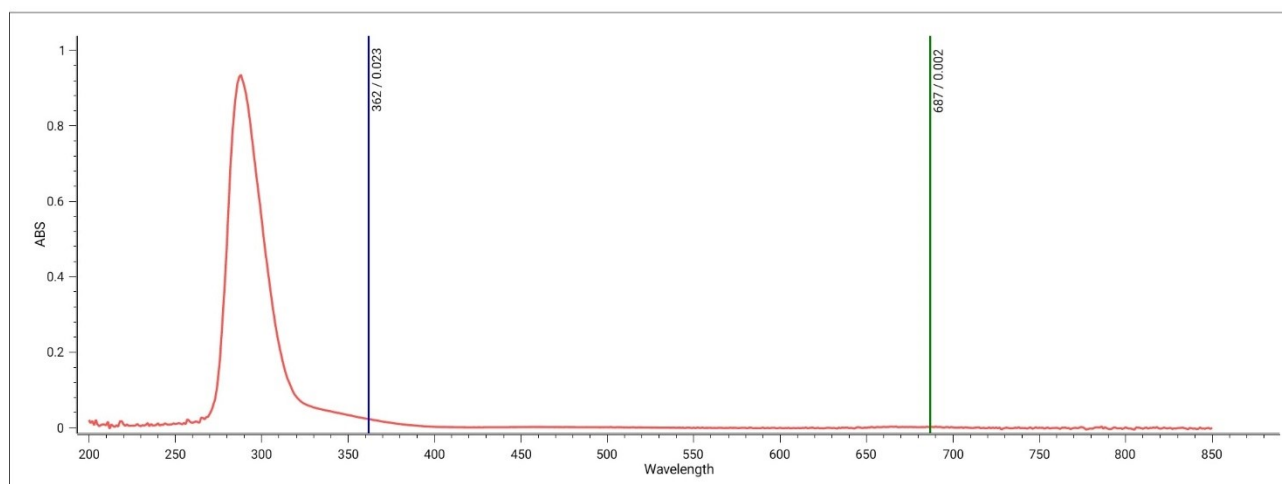
Method updated: 04-Oct-2023 10:21 PM

Scan: method parameters

Range **200 - 850 nm**

Interval **1.0 nm**

Speed **Medium**



Sample	ABS(363)	ABS(688)
Sample 3	0.023	0.002

Fig. S83. UV-Vis spectrum of oxazolidine 4.

7. Structural integrity of oxazolidine 4

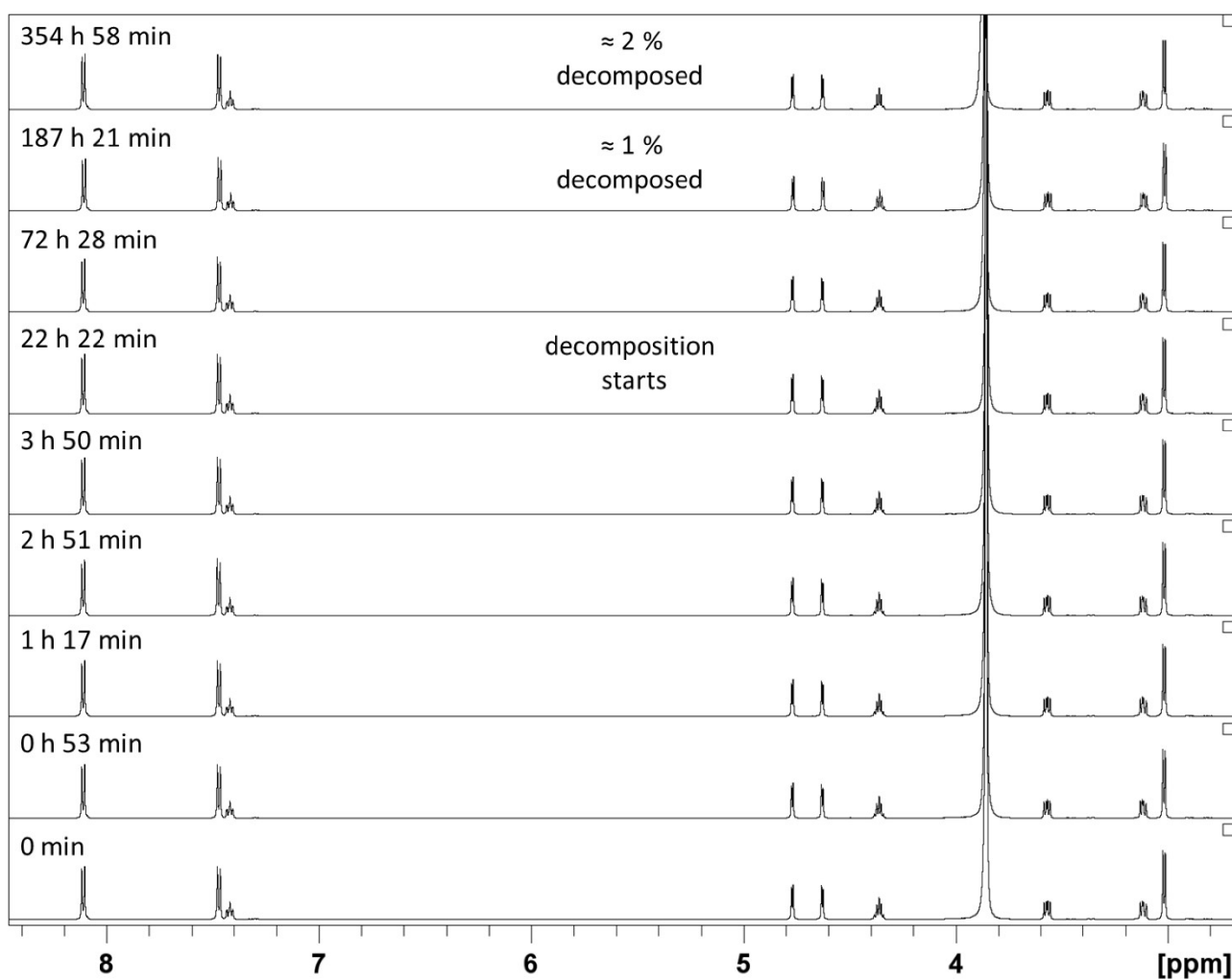


Fig. S84. Structural integrity of oxazolidine 4 in ACN-*d*₃:D₂O (7:3) during 14 days at room temperature shielded from light

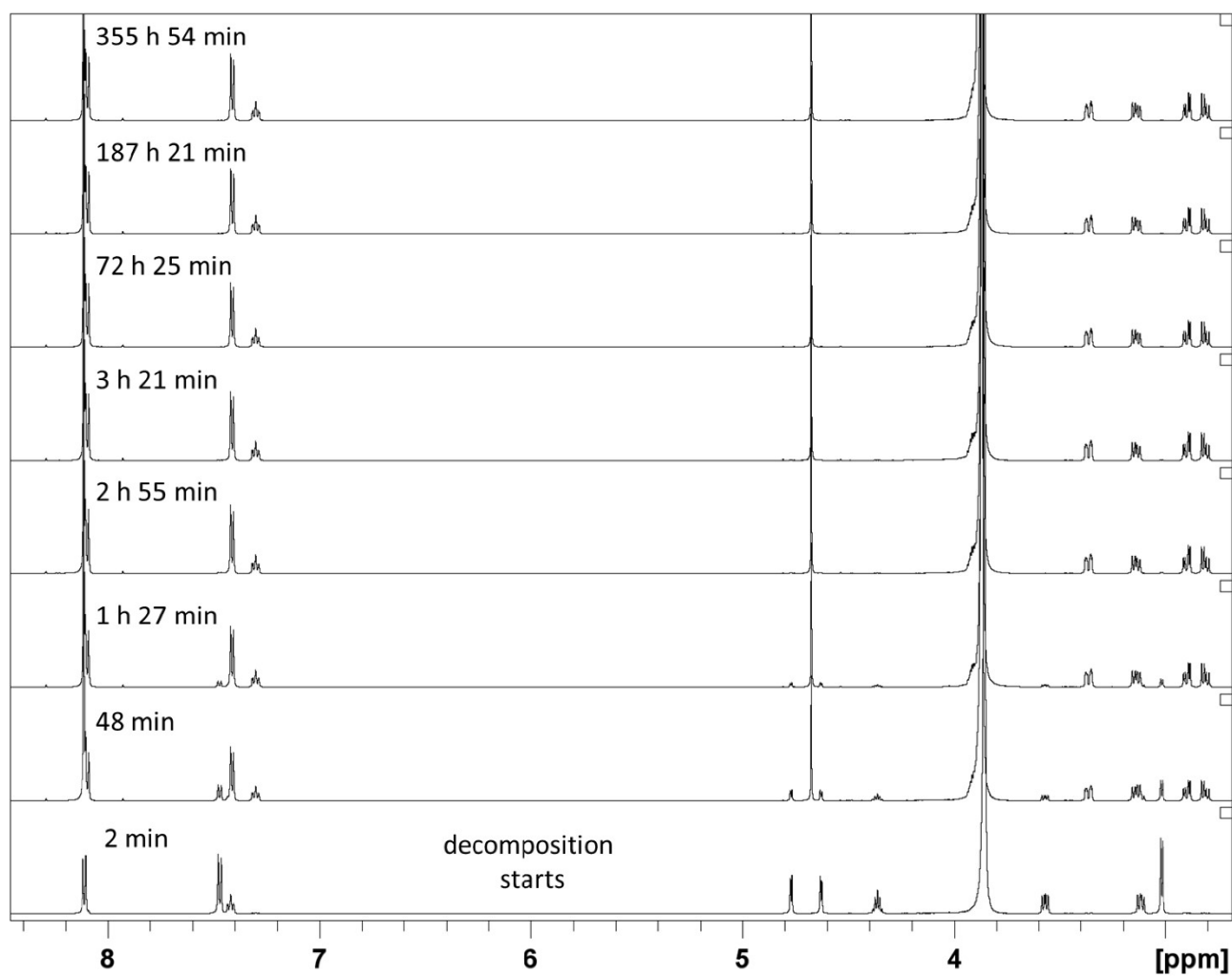


Fig. S85. Structural integrity of oxazolidine **4** in ACN-*d*₃:D₂O (7:3) during 14 days at room temperature with 0.1% formic acid in the dark

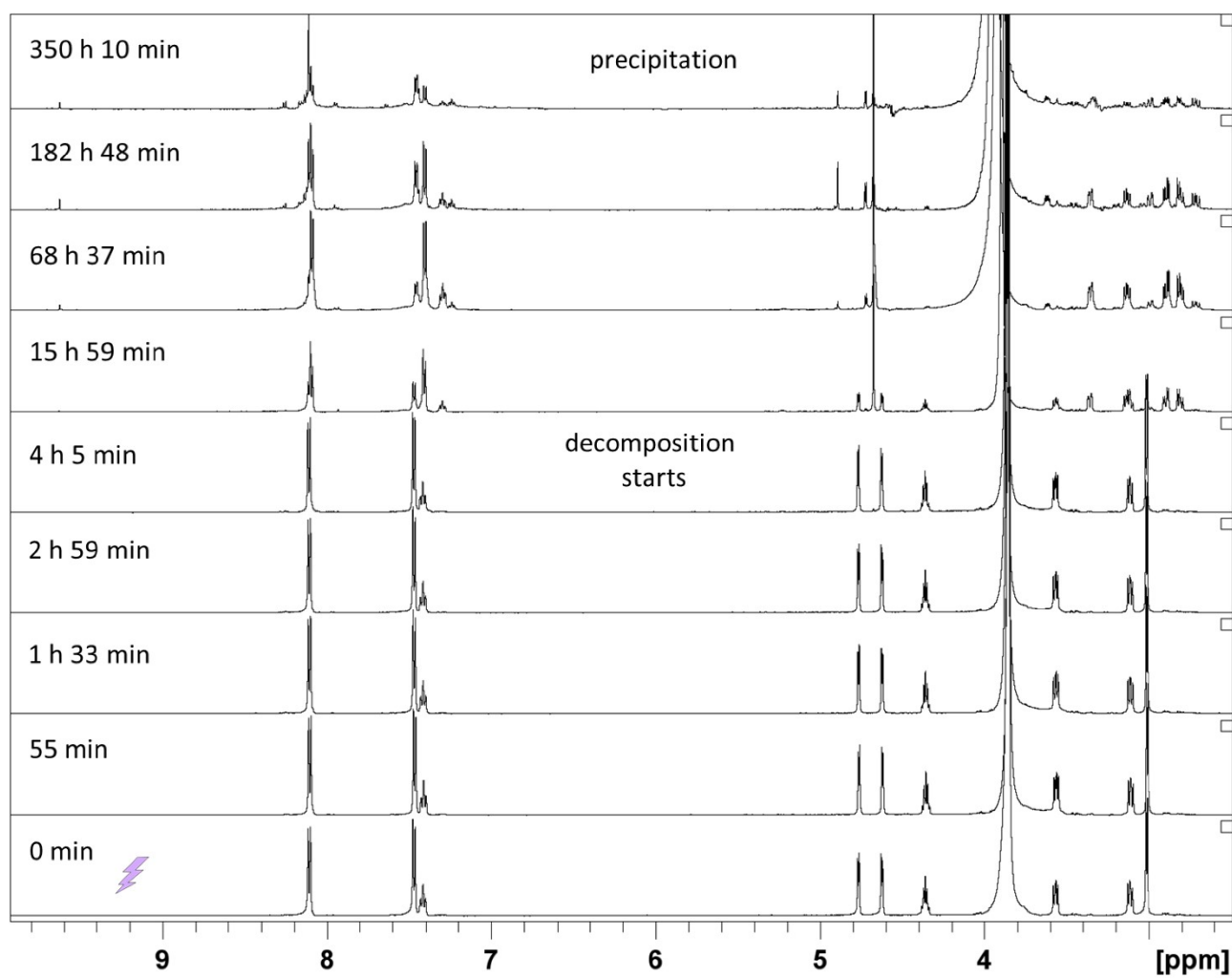


Fig. S86. Structural integrity of oxazolidine **4** in $\text{ACN-}d_3\text{:D}_2\text{O}$ (7:3) during 14 days at room temperature with UV light irradiation at 310 nm.