Supplementary materials

Myricetin Inhibits Photodegradation of Profenofos in Water: Pathways and Mechanisms

Nan Zhang [1], Yawei Yang [1], Xin Wang [1], Taozhong Shi [1], Pei Lv [1], Qing X. Li [2] and Rimao Hua [1,*]

[1] Key Laboratory of Agri-Food Safety of Anhui Province, School of Resource & Environment,
Anhui Agricultural University, Hefei 230036, China;
zhangnan@stu.ahau.edu.cn (N.Z.);
yaweiyang@stu.ahau.edu.cn (Y.Y.); wx225@stu.ahau.edu.cn (X.W.);
tzs@ahau.edu.cn (T.S.); lvpei@ahau.edu.cn (P.L.)

[2] Department of Molecular Biosciences and Bioengineering, University of Hawaii at Manoa,
Honolulu, HI 96822, USA; qingl@hawaii.edu

* Correspondence: rimaohua@ahau.edu.cn; Tel.: +86-551-65786320; Fax: +86-551-65786296

Table of Contents

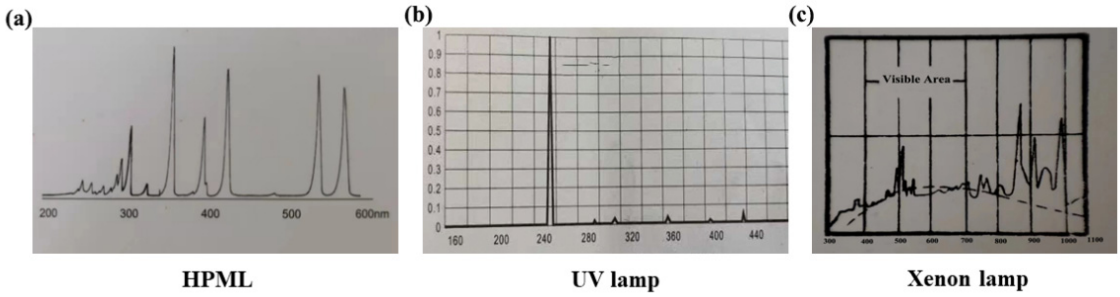


Figure S1. Spectral maps of the three artificial light sources.

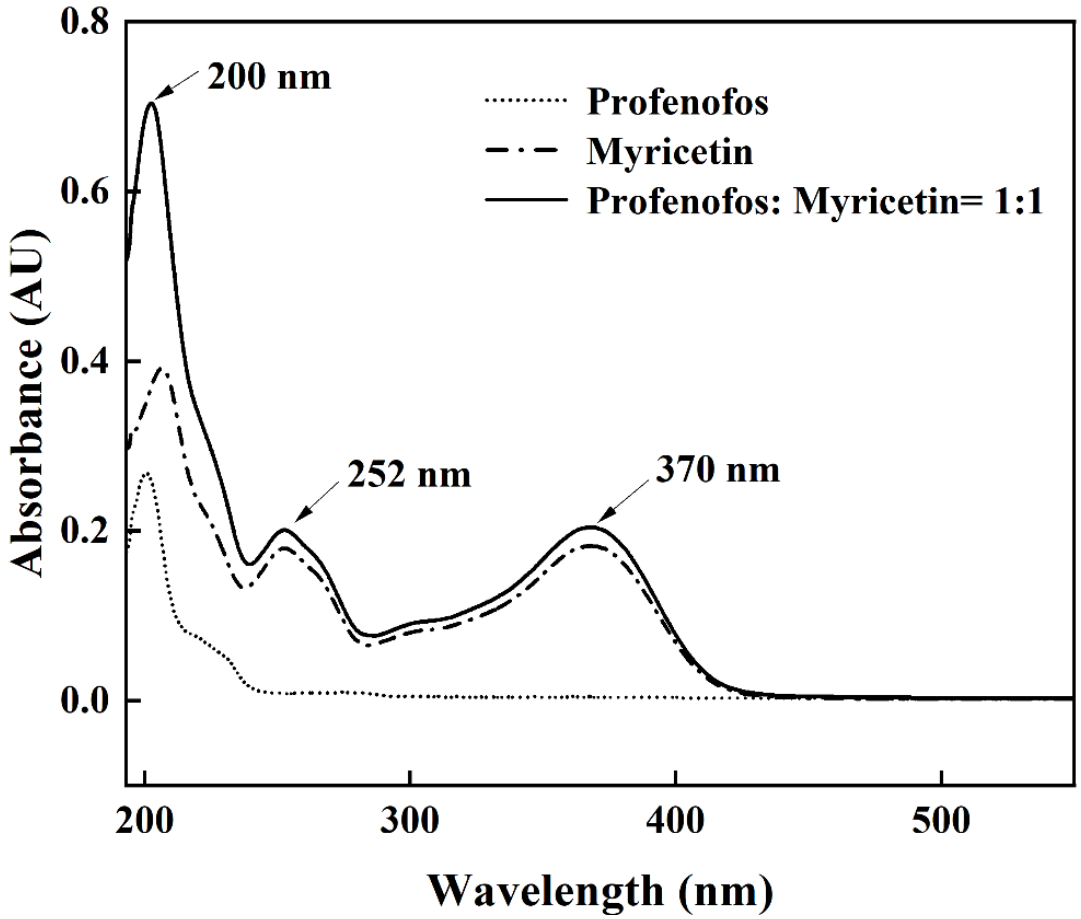


Figure S2. Absorption spectra of profenofos, myricetin and profenofos with myricetin (1:1 mol ratio) in water at 5 μmol (with a 1 cm optical path).

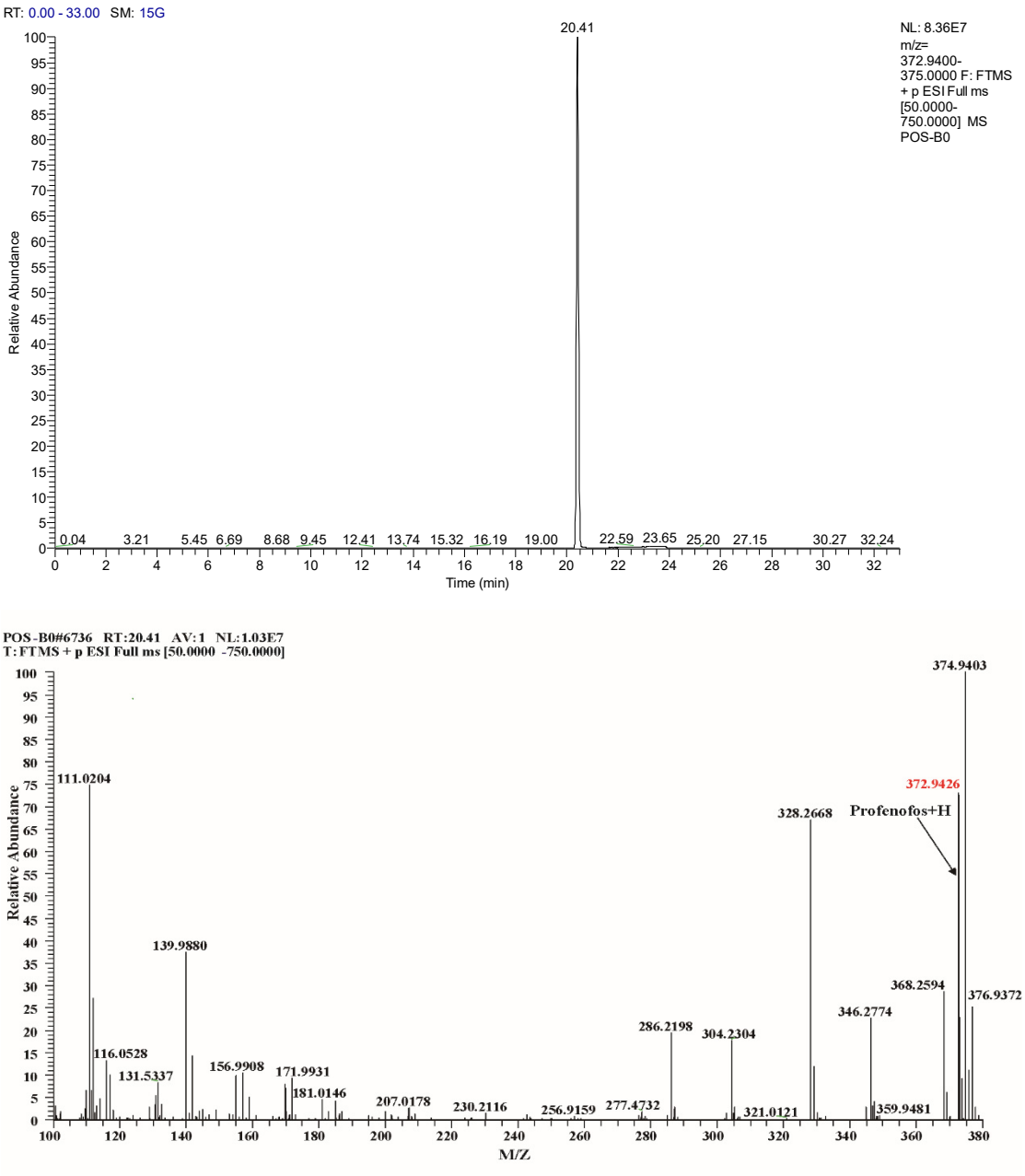


Figure S3. Extract ion chromatogram and secondary fragment ion of profenofos.

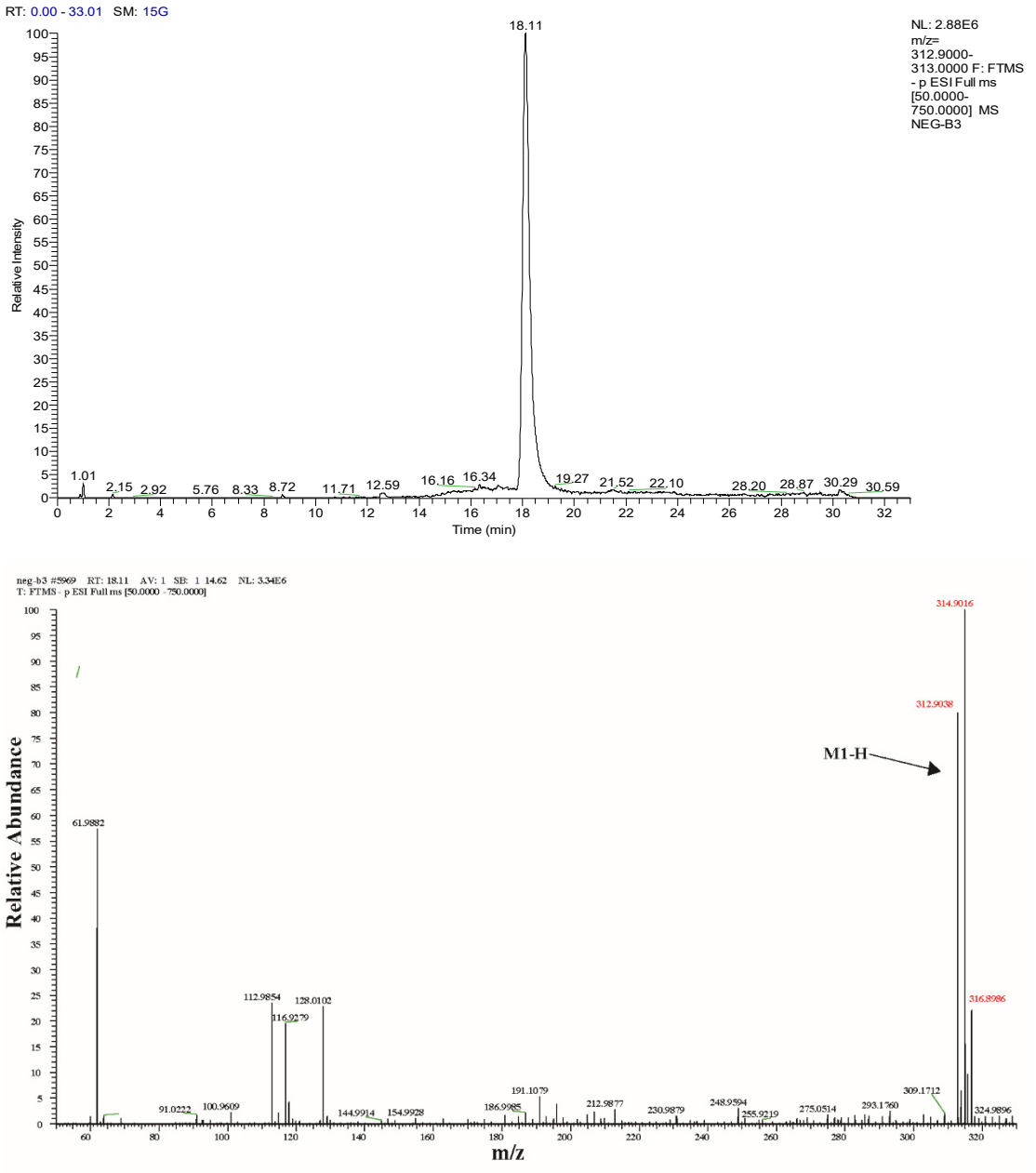


Figure S4. Extract ion chromatogram and secondary fragment ion of M1.

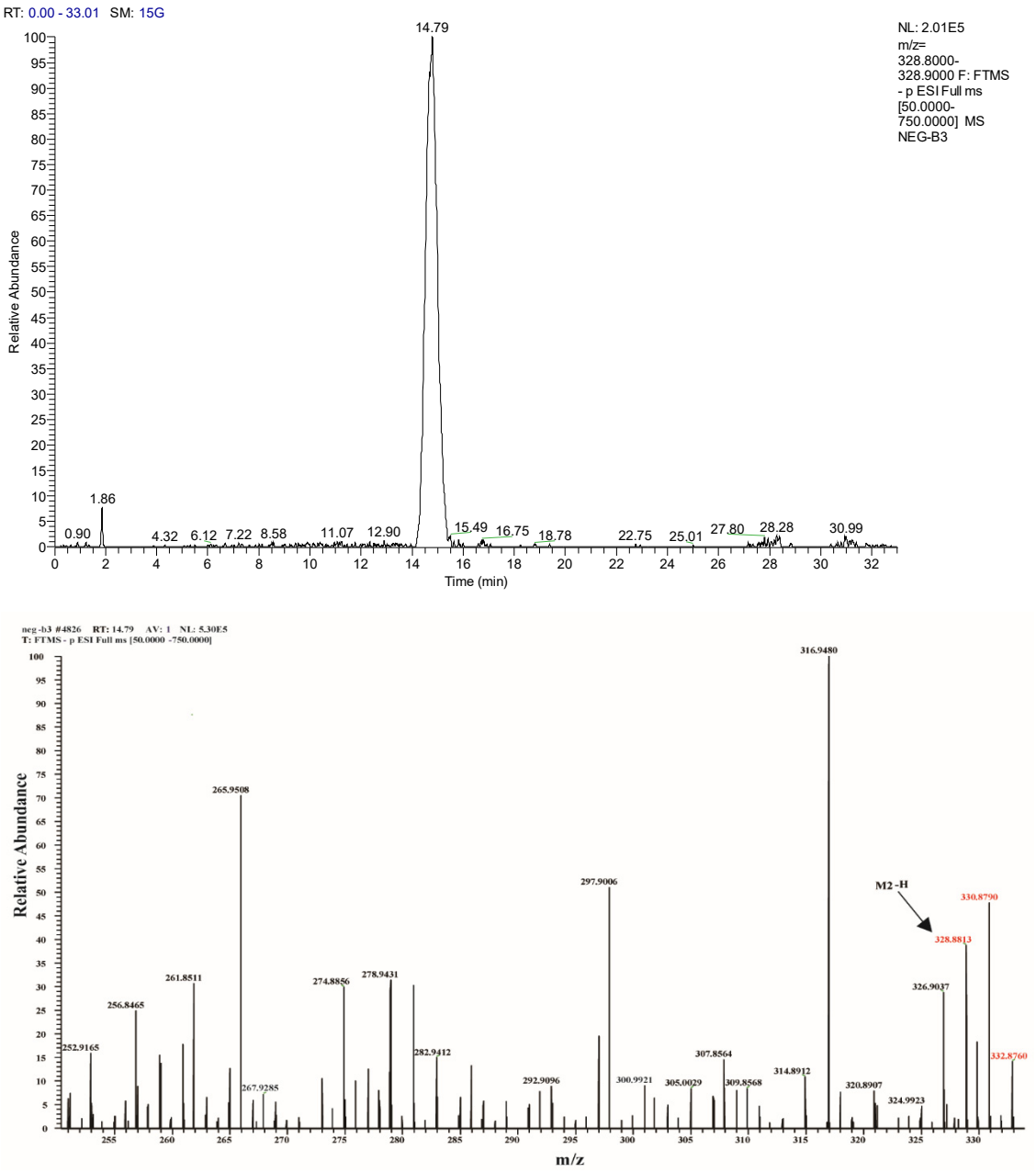


Figure S5. Extract ion chromatogram and secondary fragment ion of M2.

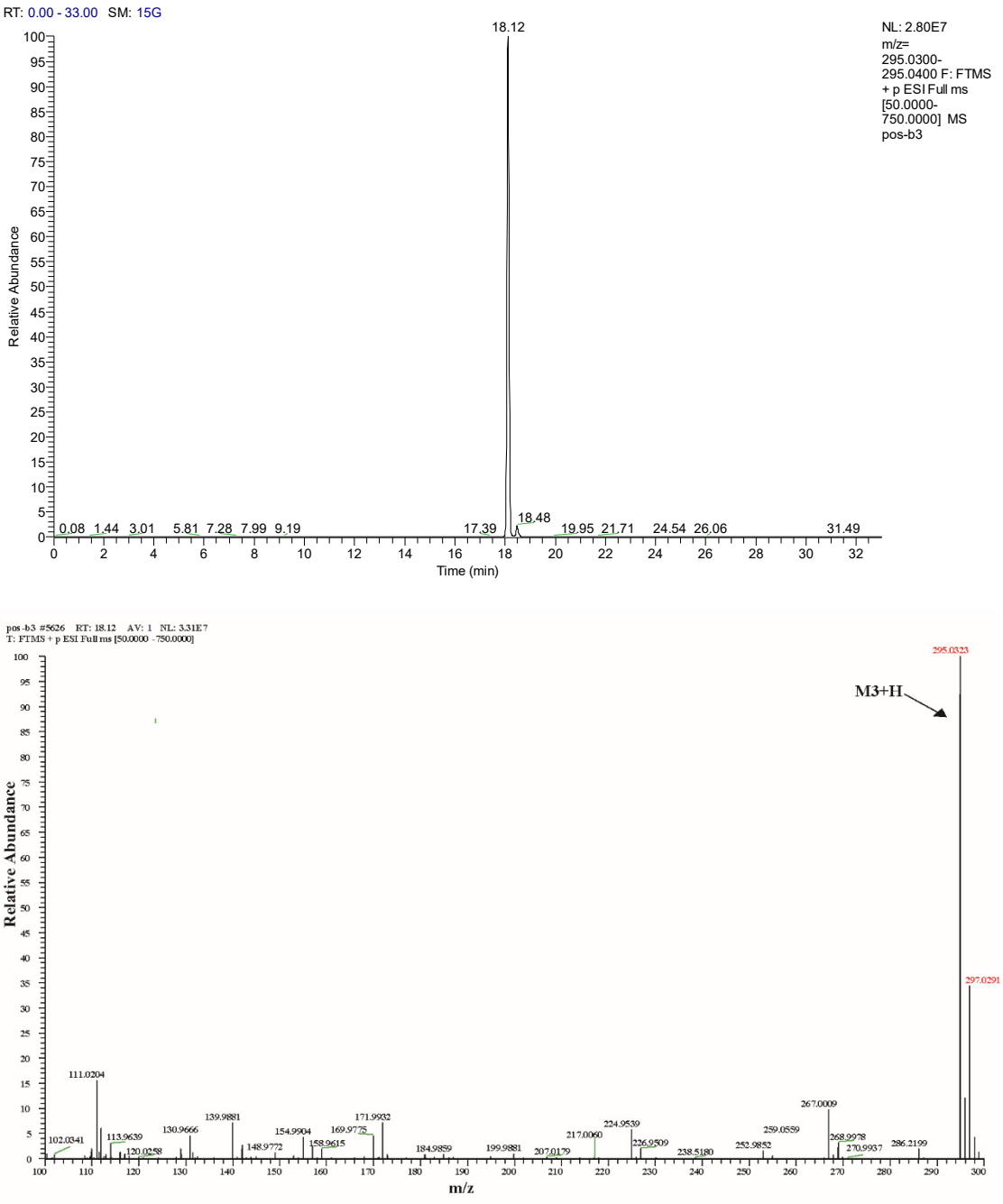


Figure S6. Extract ion chromatogram and secondary fragment ion of M3.

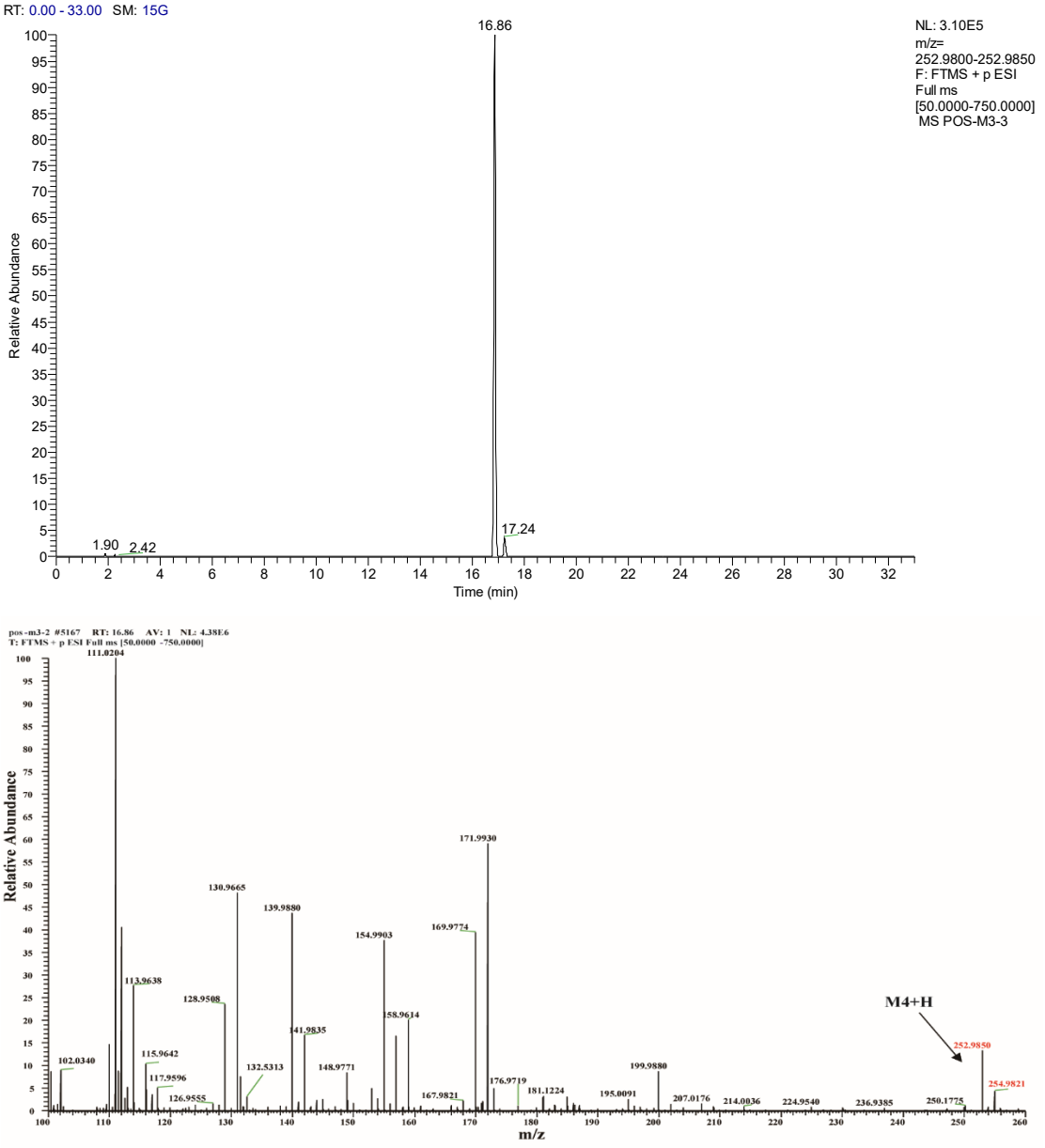


Figure S7. Extract ion chromatogram and secondary fragment ion of M4.

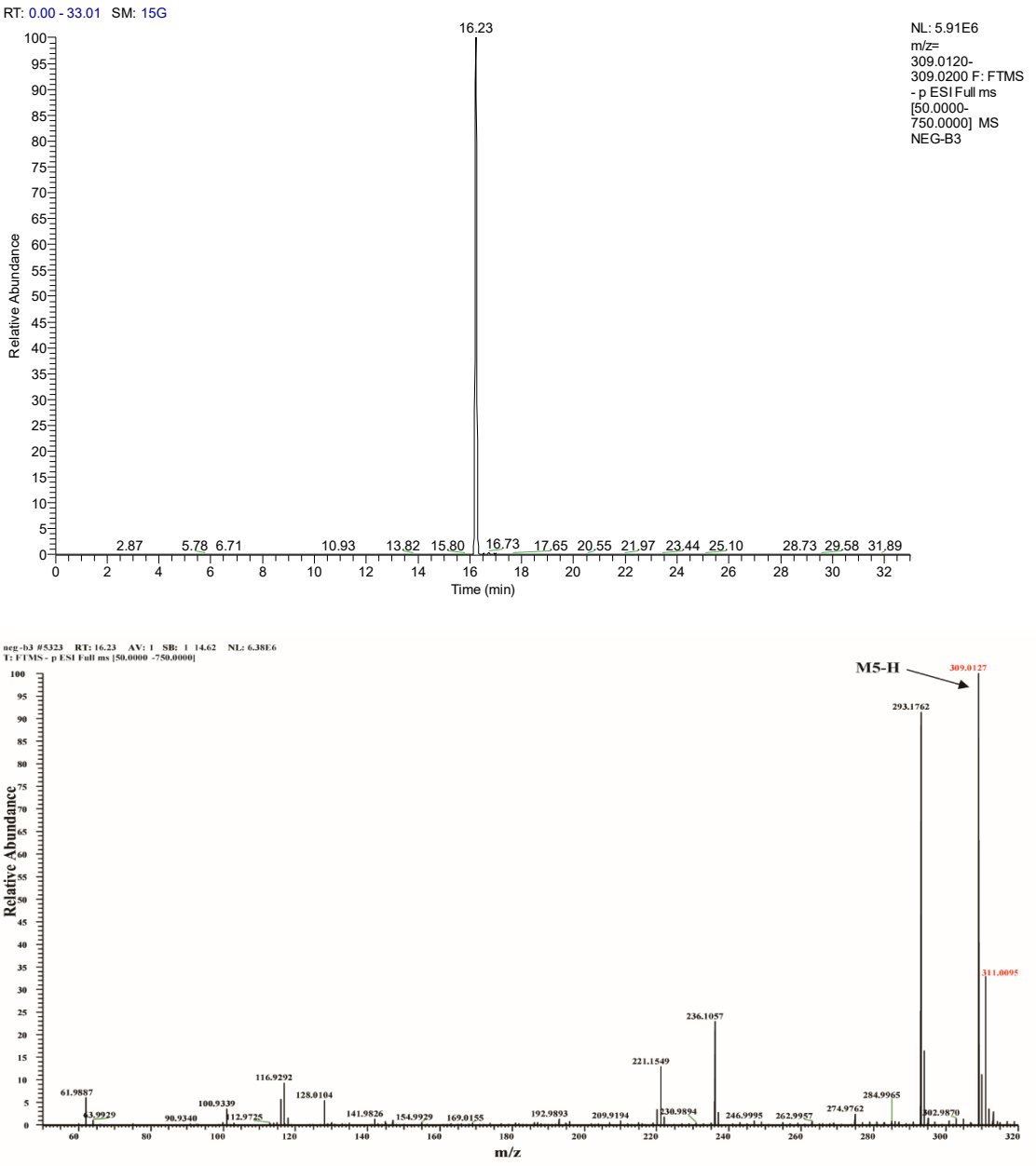


Figure S8. Extract ion chromatogram and secondary fragment ion of M5.

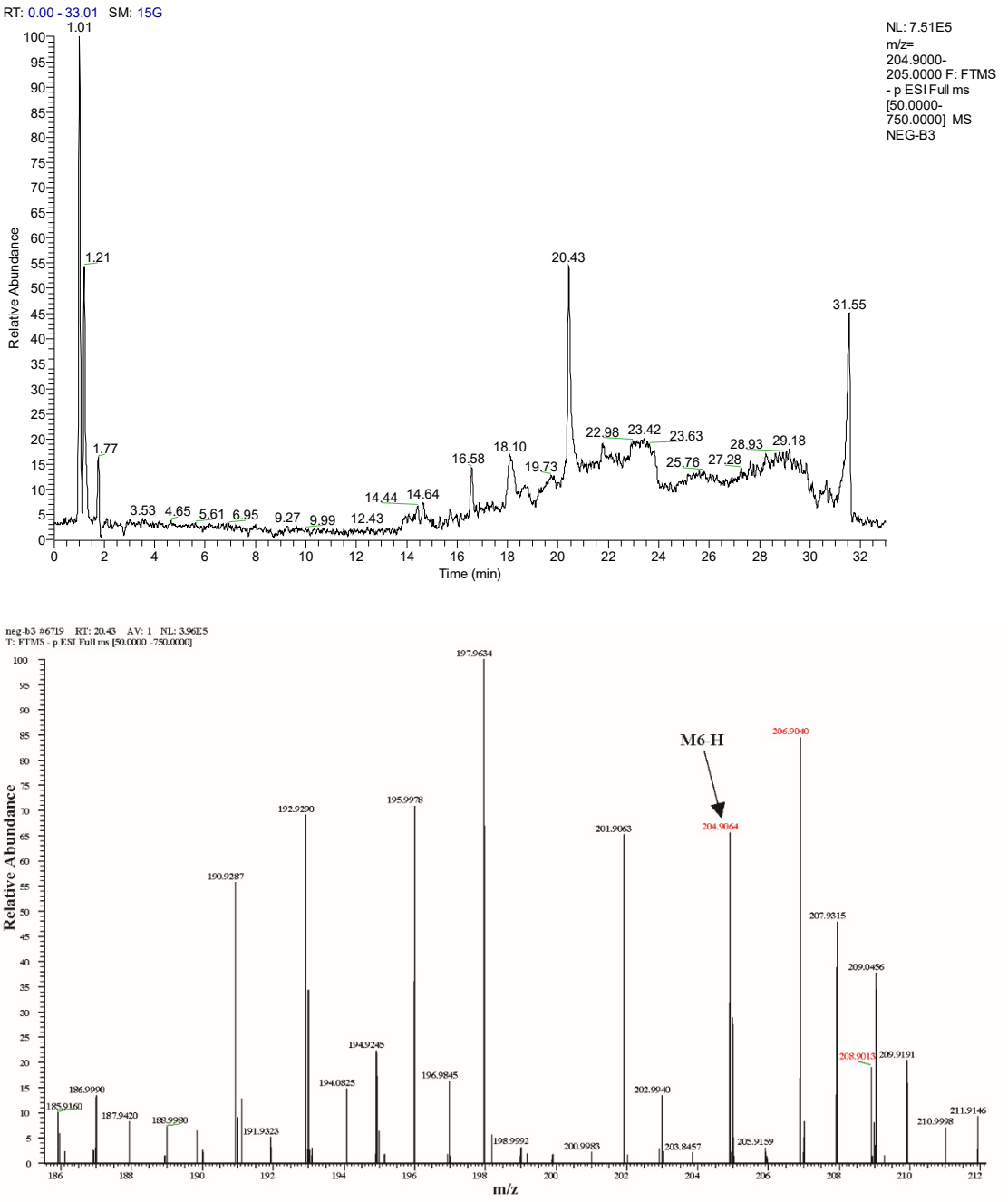


Figure S9. Extract ion chromatogram and secondary fragment ion of M6.

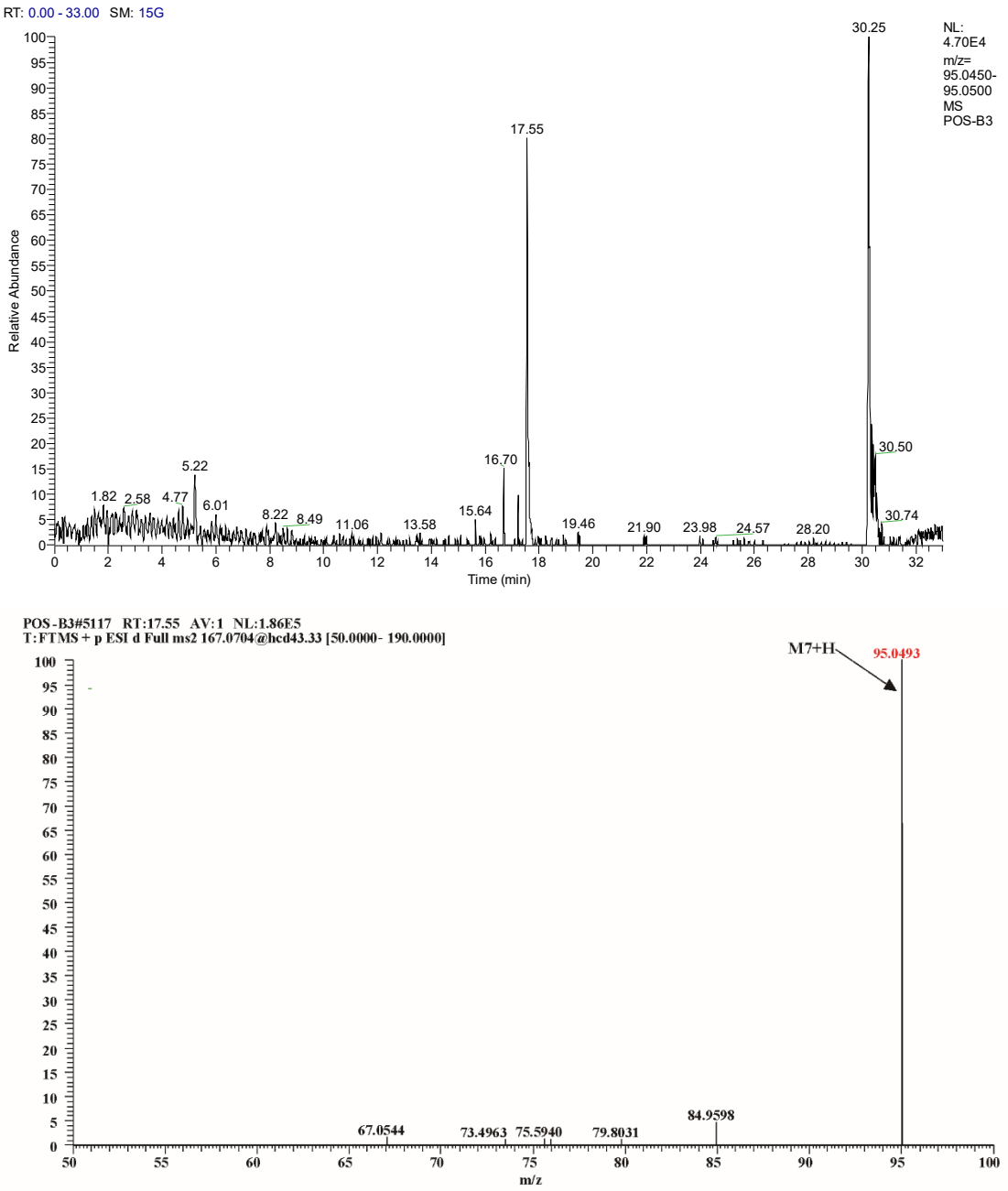


Figure S10. Extract ion chromatogram and secondary fragment ion of M7.

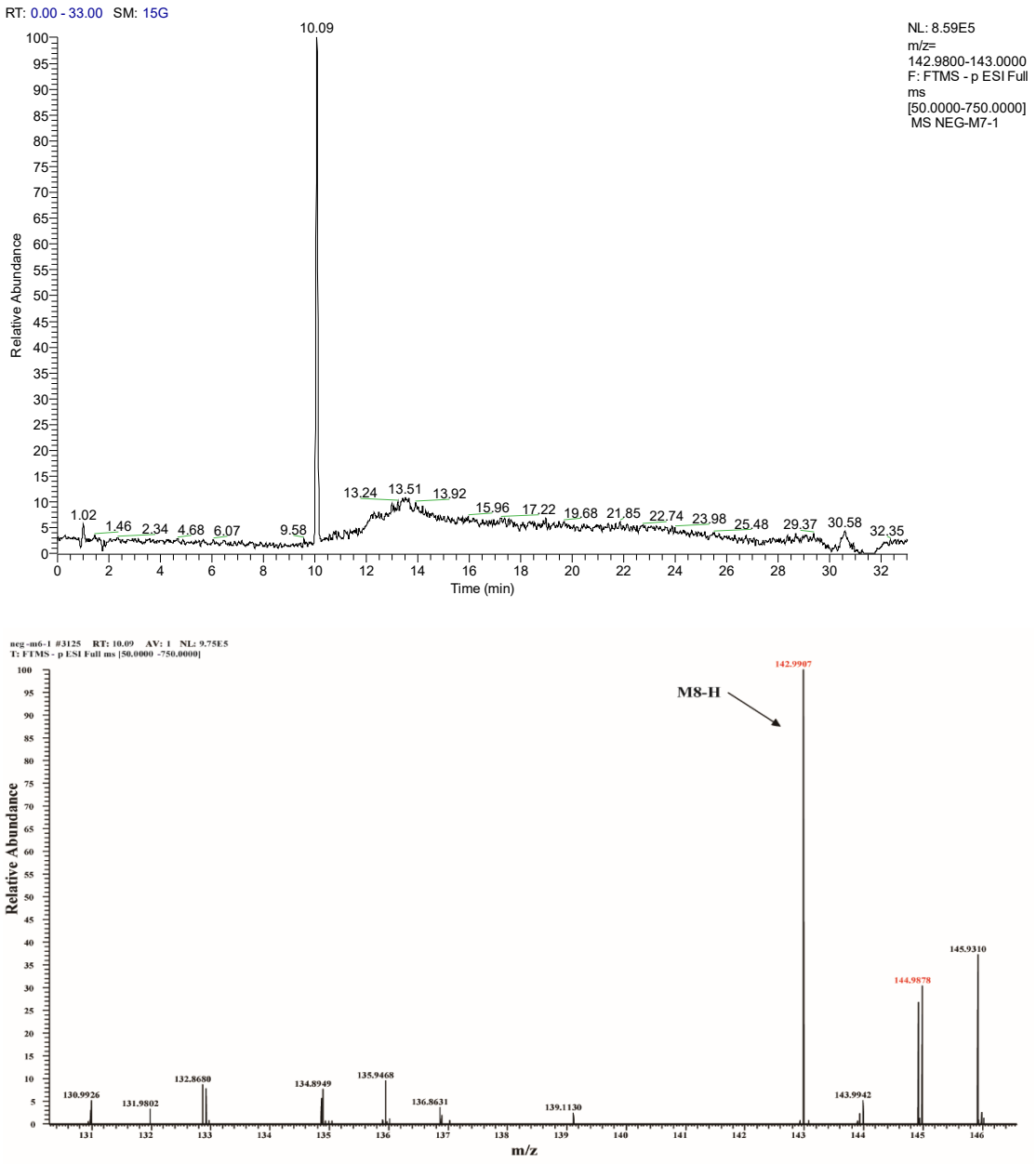


Figure S11. Extract ion chromatogram and secondary fragment ion of M8.

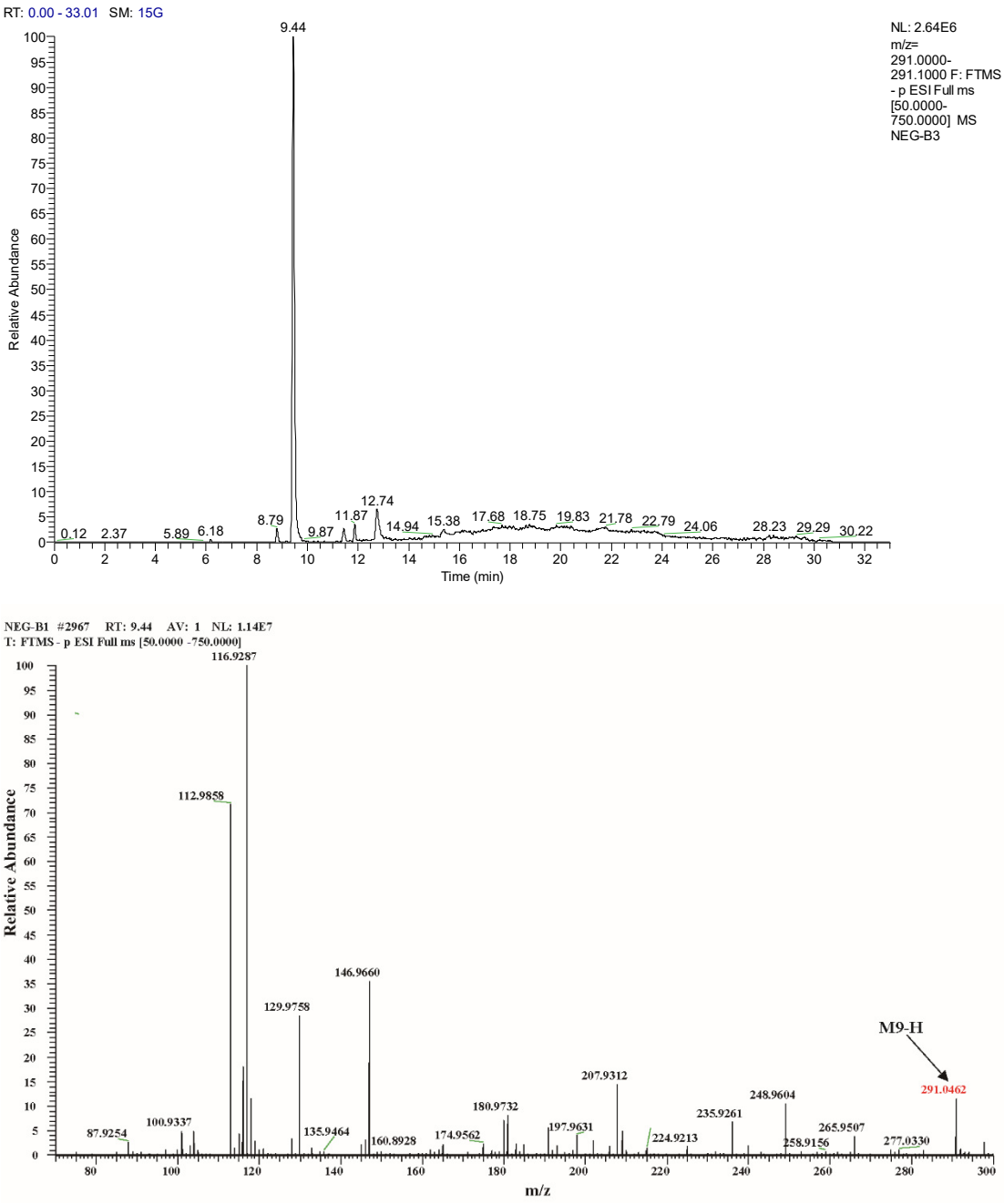


Figure S12. Extract ion chromatogram and secondary fragment ion of M9.

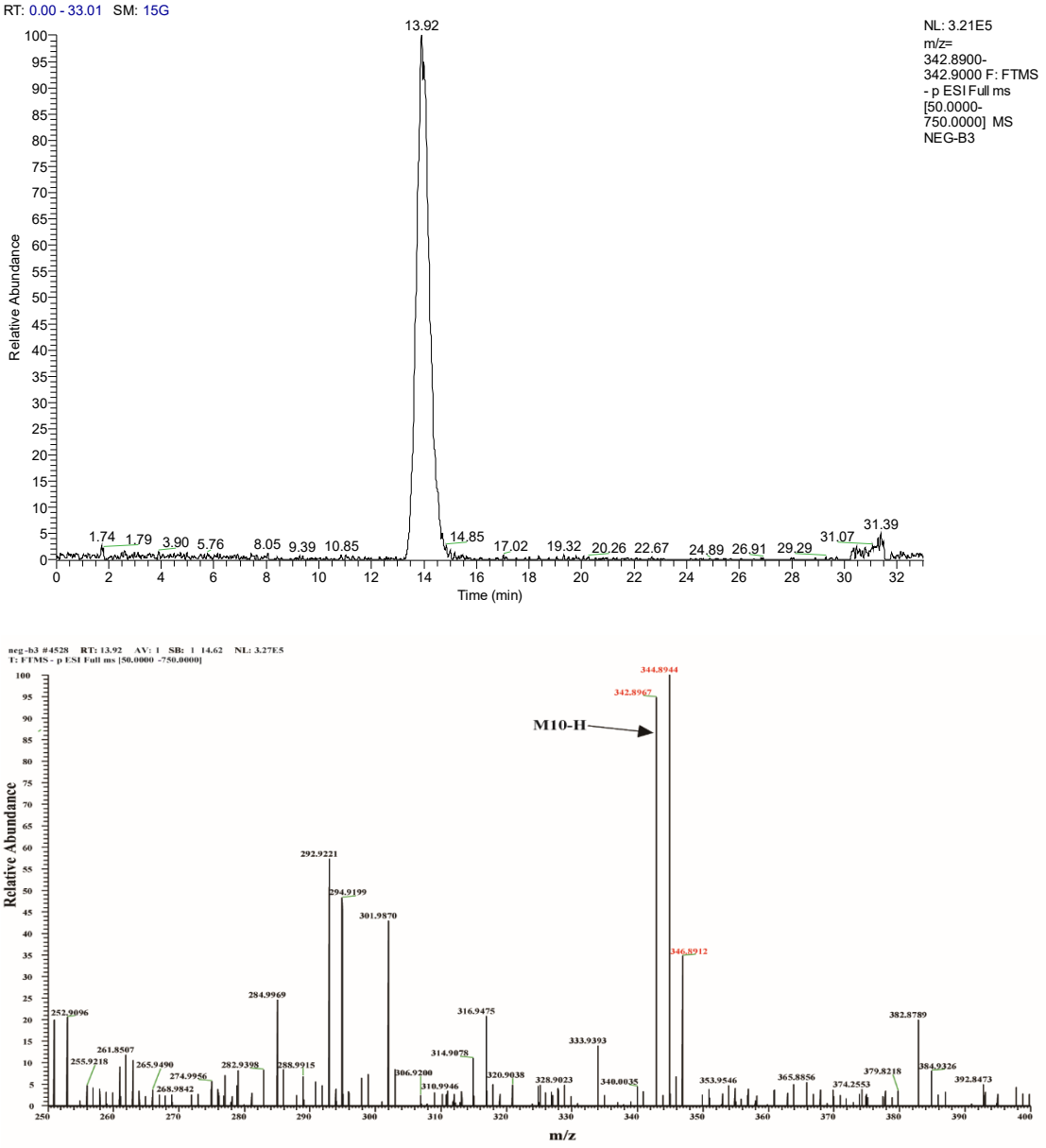


Figure S13. Extract ion chromatogram and secondary fragment ion of M10.

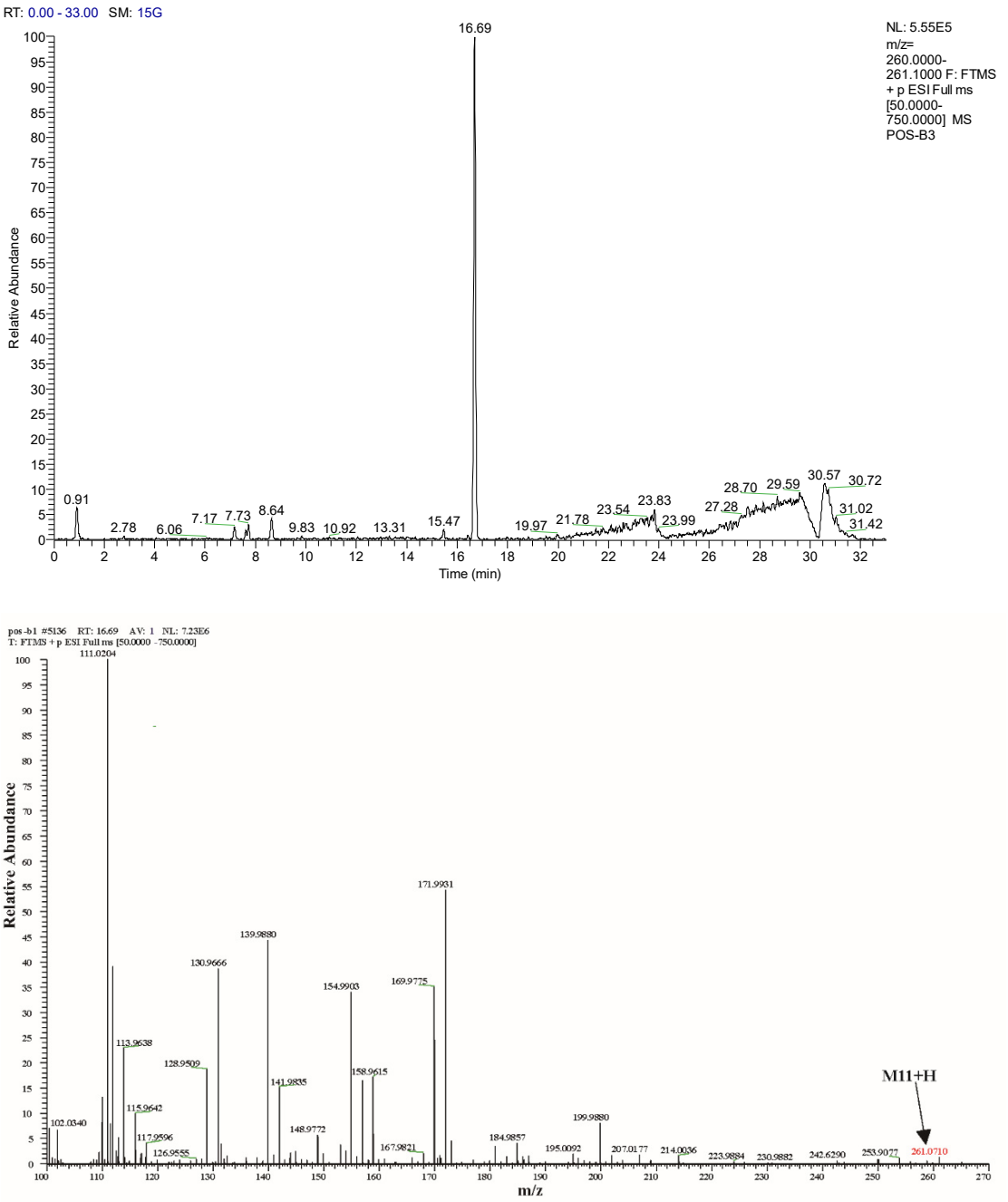


Figure S14. Extract ion chromatogram and secondary fragment ion of M11.

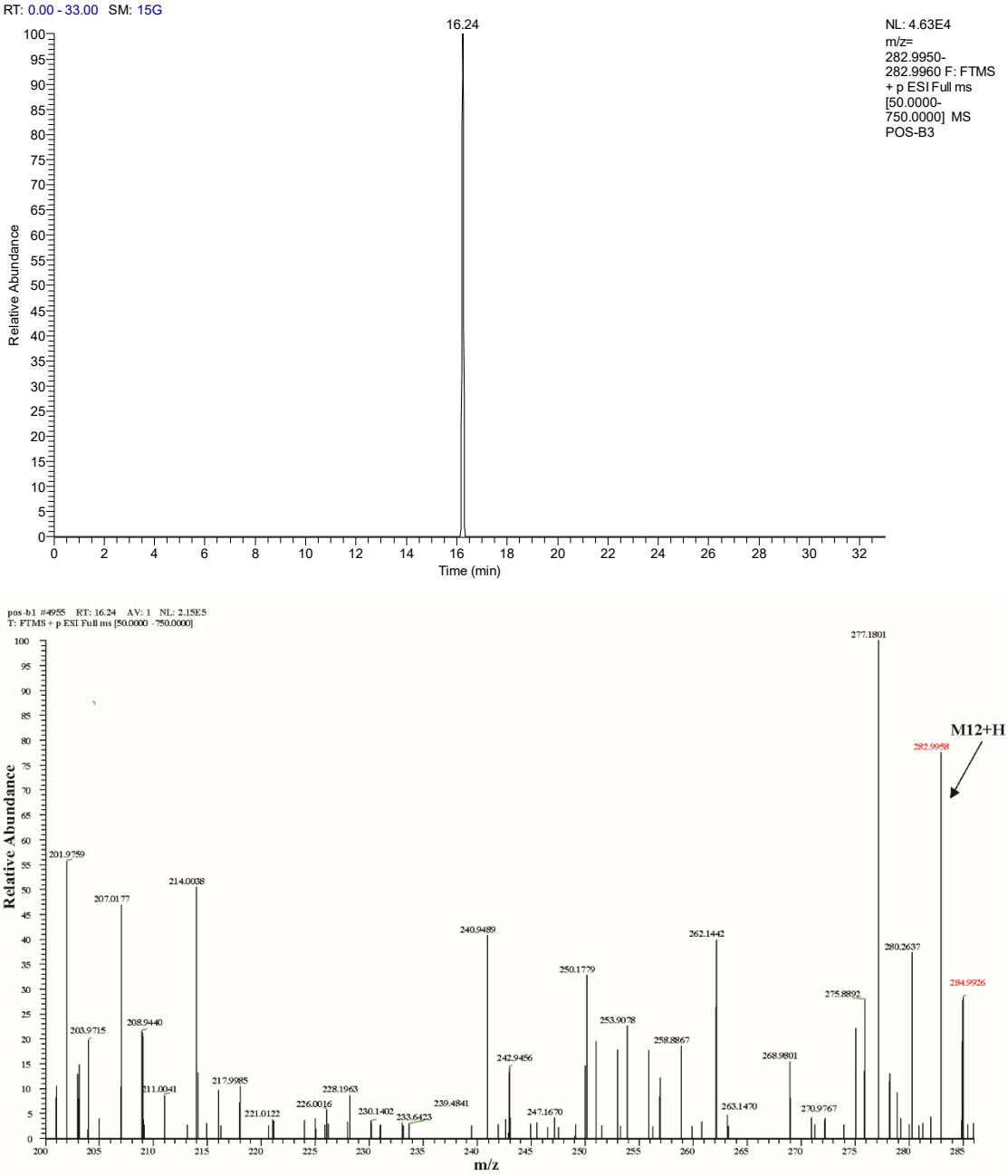


Figure S15. Extract ion chromatogram and secondary fragment ion of M12.

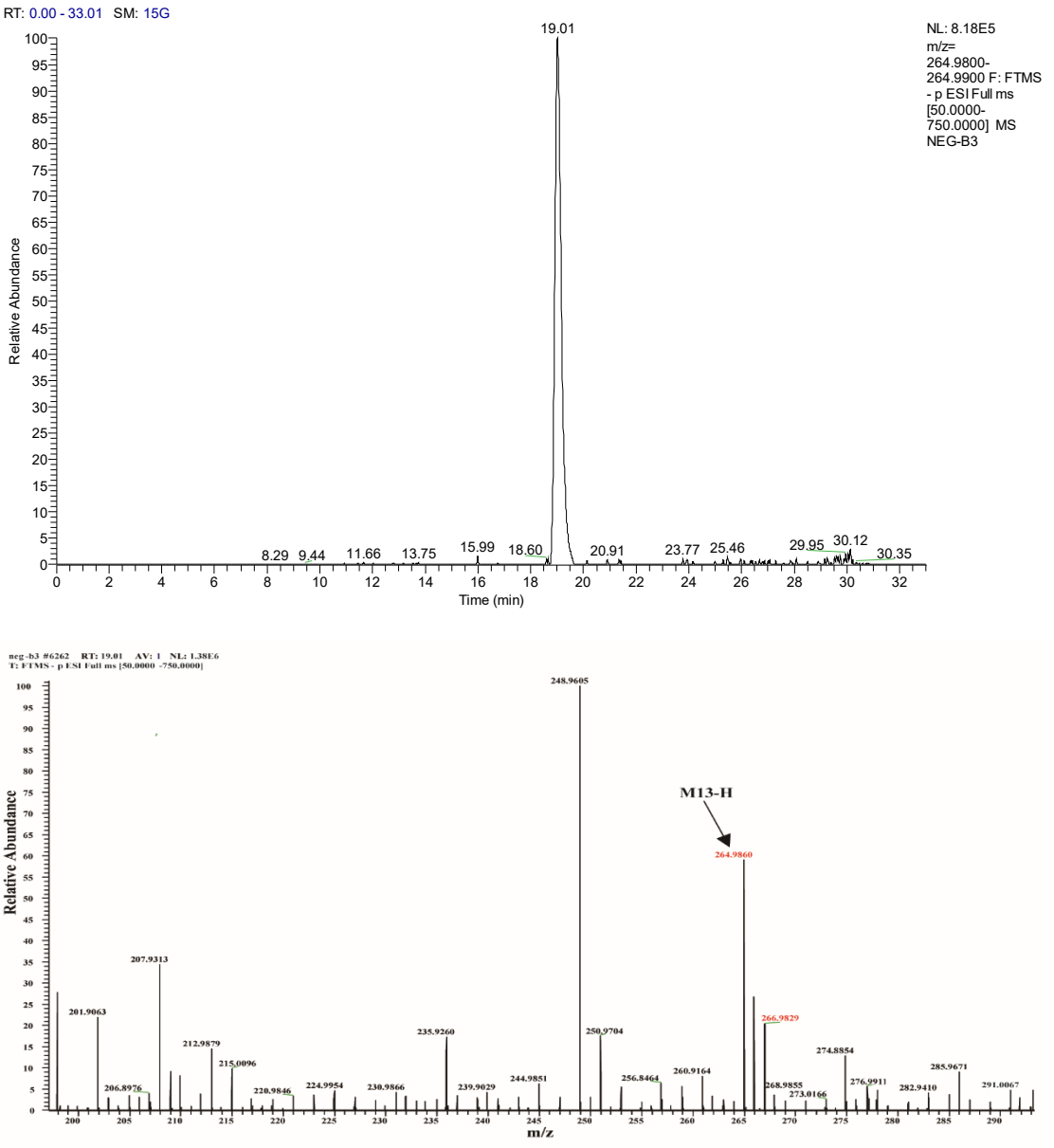


Figure S16. Extract ion chromatogram and secondary fragment ion of M13.

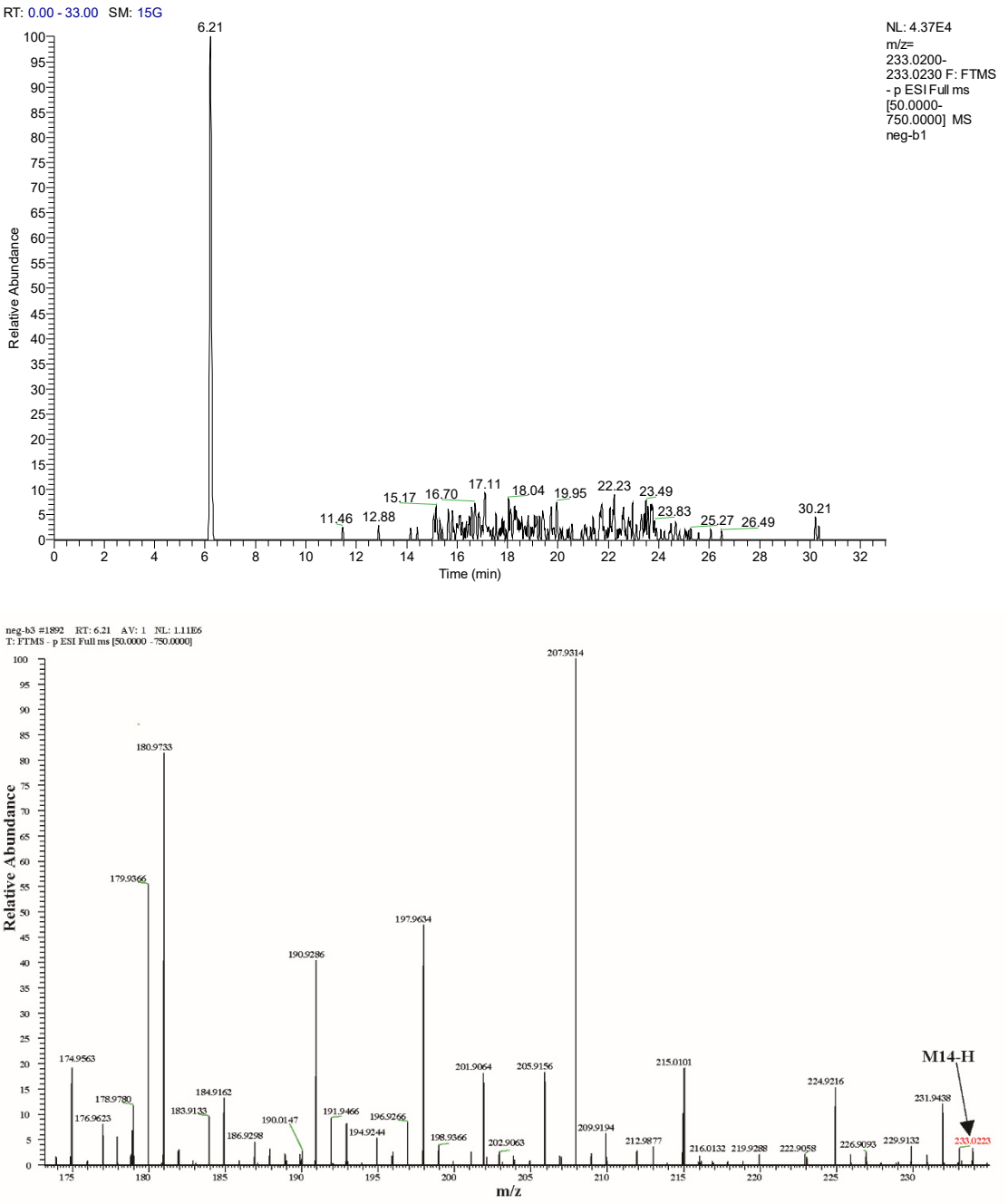


Figure S17. Extract ion chromatogram and secondary fragment ion of M14.

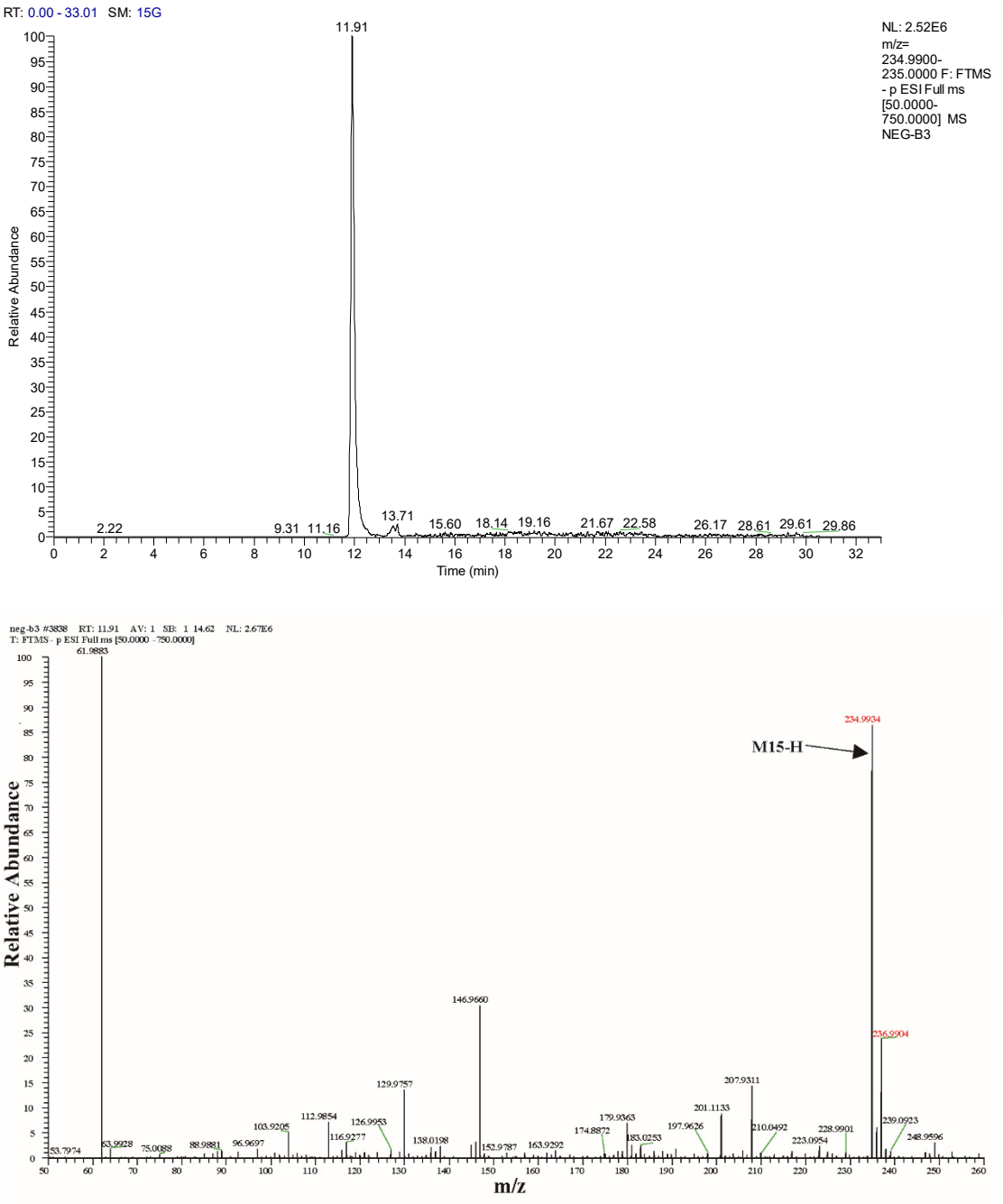


Figure S18. Extract ion chromatogram and secondary fragment ion of M15.

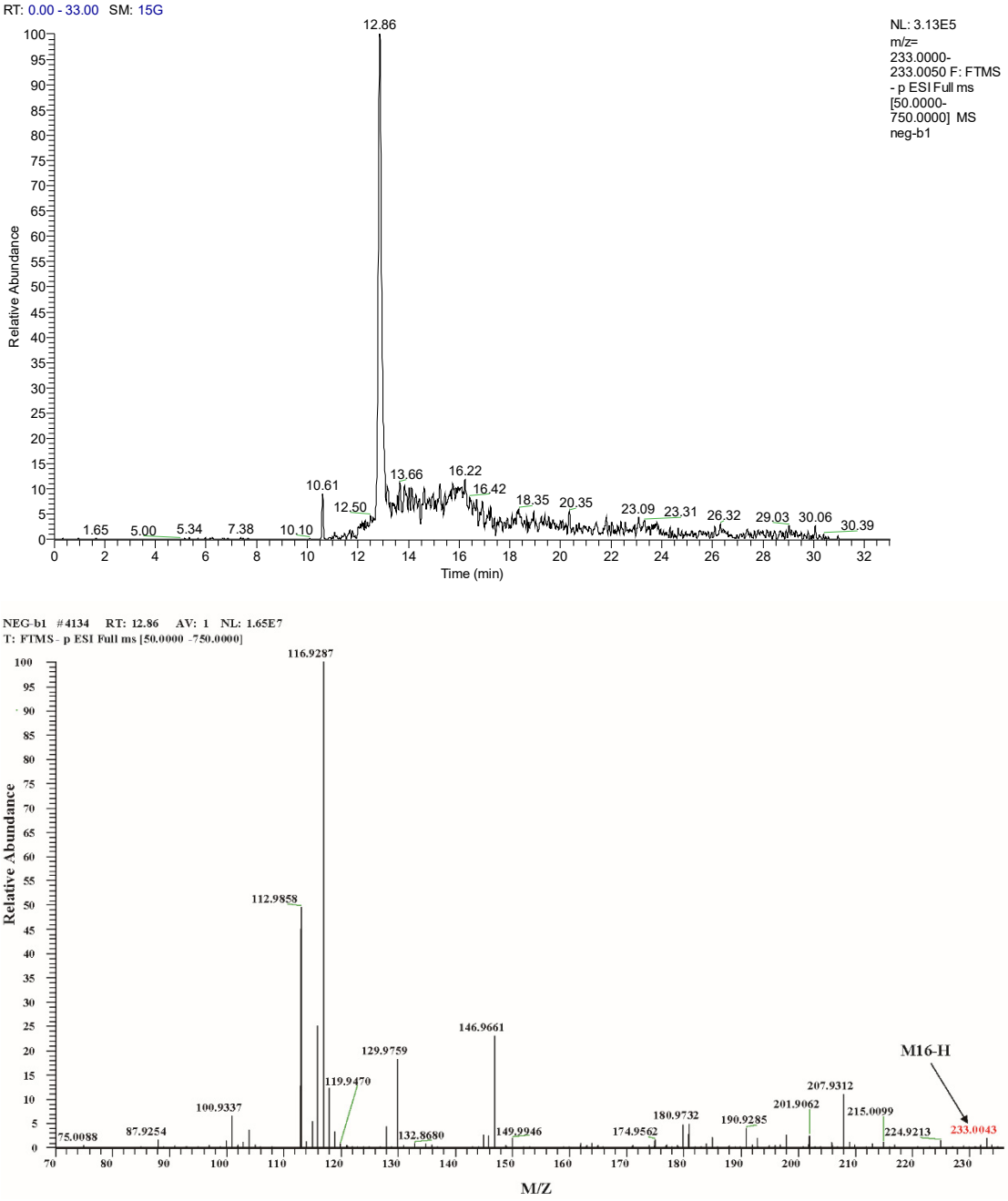


Figure S19. Extract ion chromatogram and secondary fragment ion of M16.

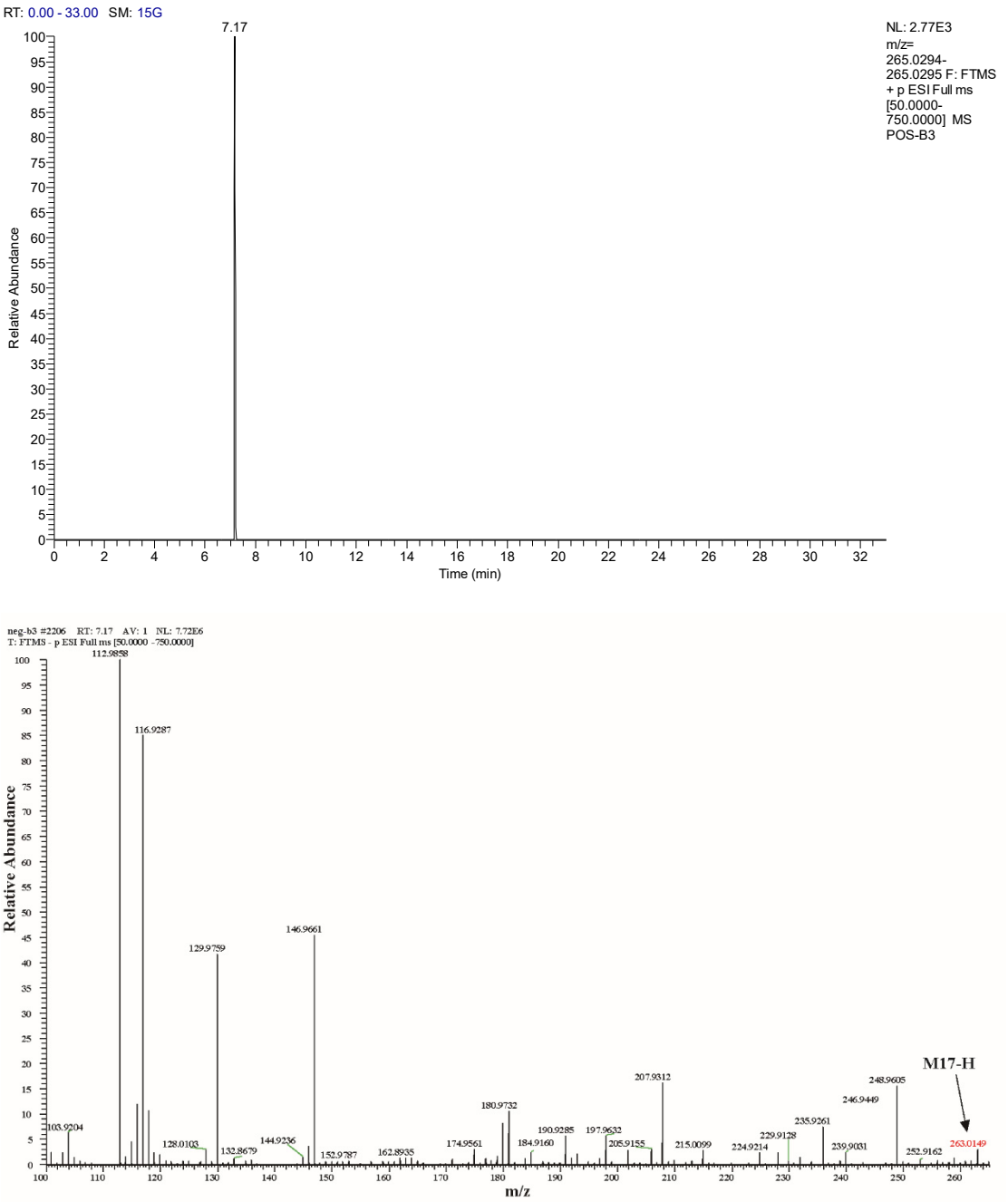


Figure S20. Extract ion chromatogram and secondary fragment ion of M17.

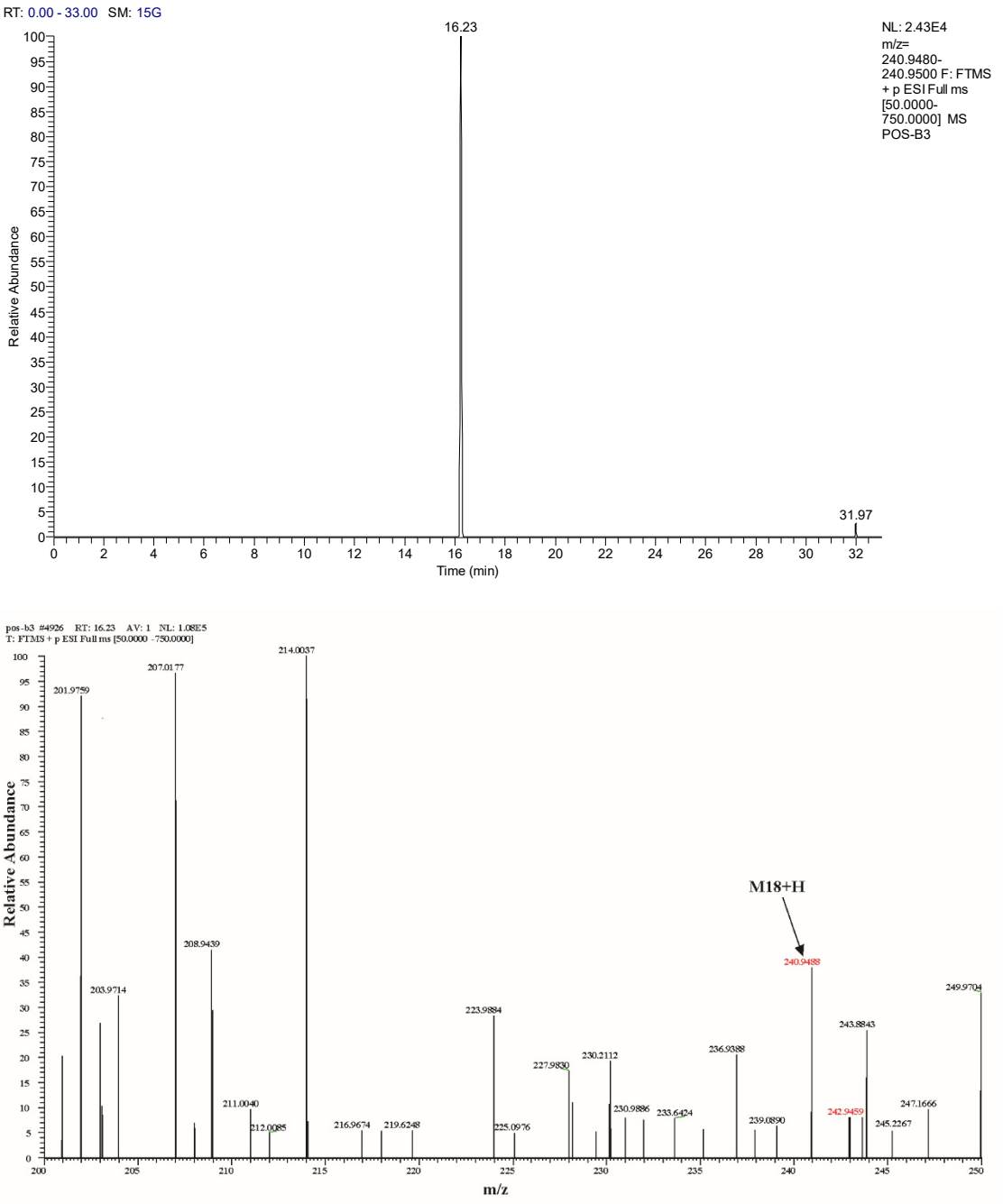


Figure S21. Extract ion chromatogram and secondary fragment ion of M18.

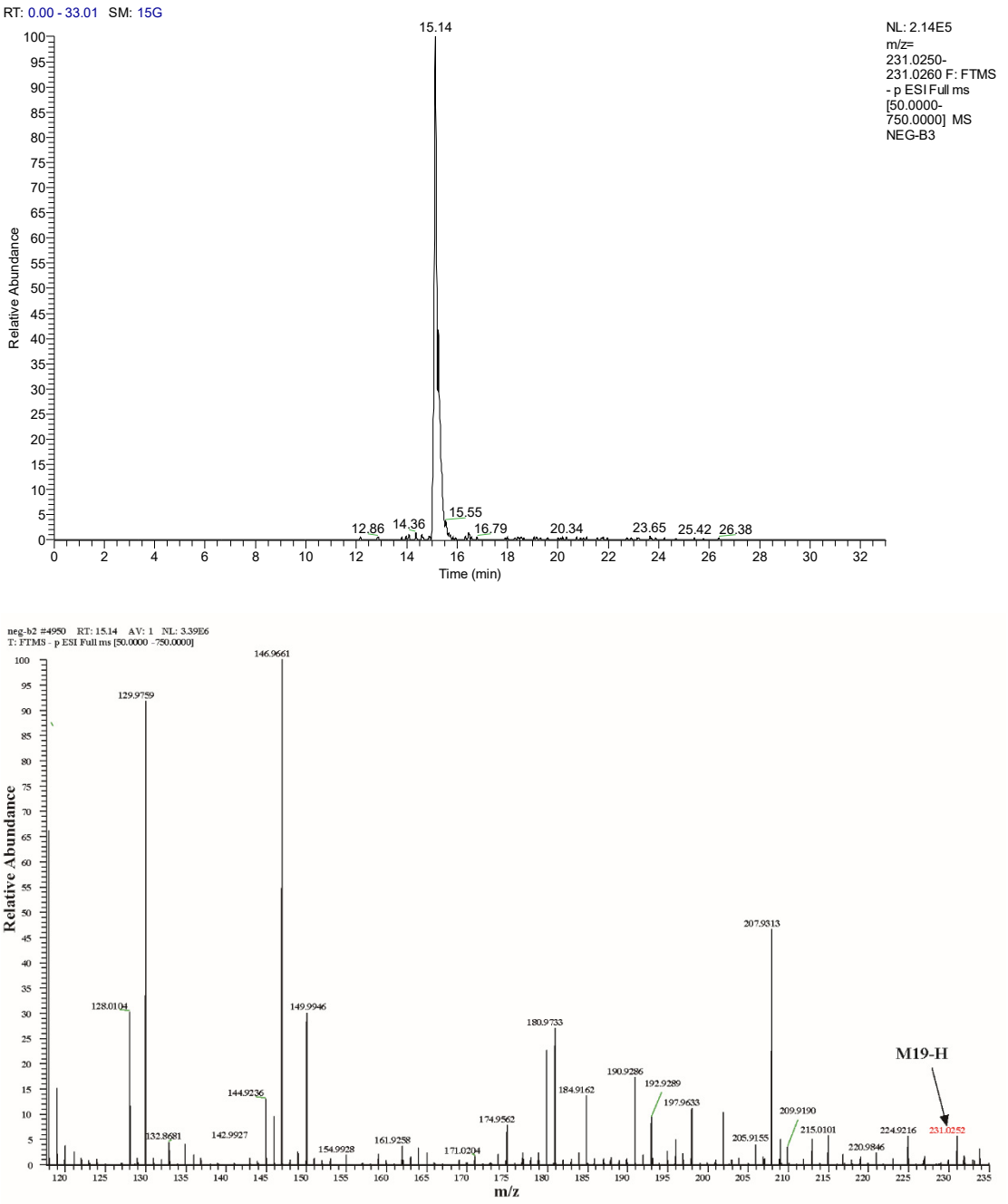


Figure S22. Extract ion chromatogram and secondary fragment ion of M19.

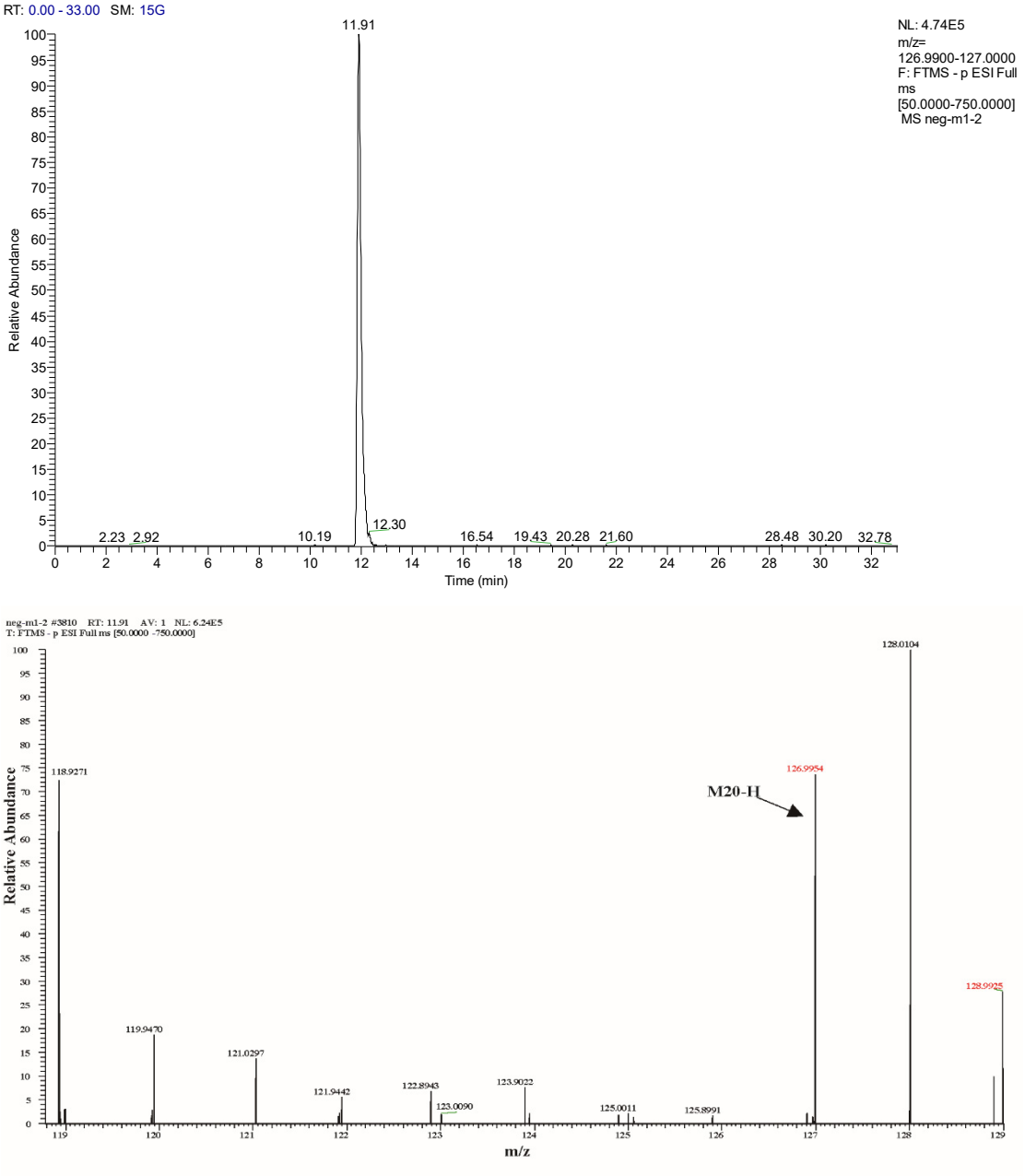


Figure S23. Extract ion chromatogram and secondary fragment ion of M20.

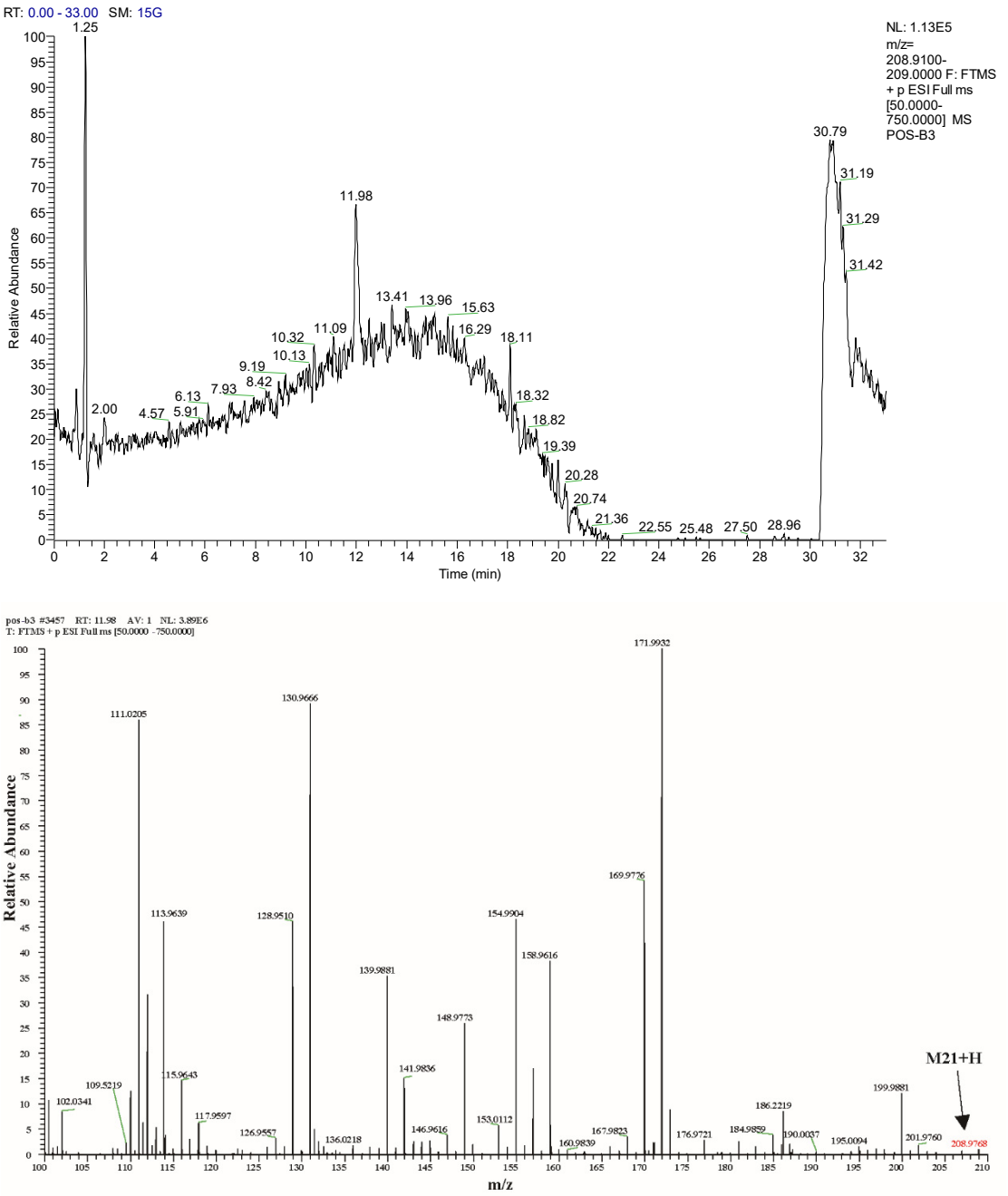


Figure S24. Extract ion chromatogram and secondary fragment ion of M21.

Table S1. Mobile phase of Thermofisher QE focus mass spectrometer (a) and Waters UPLC-Xevo TQ-S MS (b).

(a)

Retention (min)	Flow ($mL \cdot min^{-1}$)	0.075% FA + Water (%)	Acetonitrile (%)
0.00	0.20	95.00	5.00
0.25	0.20	95.00	5.00
25.00	0.20	5.00	95.00
27.00	0.20	5.00	95.00
28.00	0.20	95.00	5.00
33.00	0.20	95.00	5.00

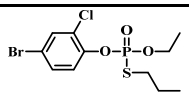
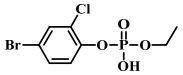
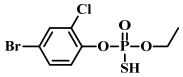
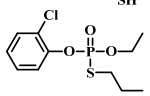
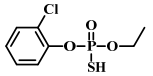
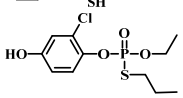
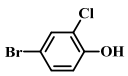
(b)

Retention (min)	Flow ($mL \cdot min^{-1}$)	0.075% FA + Water (%)	Acetonitrile (%)
0.00	0.30	90.00	10.00
0.25	0.30	90.00	10.00
10.00	0.30	10.00	90.00
10.10	0.30	90.00	10.00
12.00	0.30	90.00	10.00

Table S2. The parent ions, daughter ion fragments and ion scanning mass spectrometry conditions of profenofos and photoproducts.

Compound name	Retention time (min)	Parent ion (m/z)	Fragmetor (eV)	Daughter (m/z)	CE (eV)
Profenofos	9.11	372.9 (M+H)	25	302.6 / 127.9	40 / 20
M1	4.41	312.94 (M-H)	26	204.9 / 78.85	22 / 44
M2	5.73	328.92 (M-H)	24	168.91 / 78.85	26 / 36
M3	7.97	295.05 (M+H)	24	224.98 / 128.92	16 / 30
M4	4.20	251.01 (M-H)	18	142.97 / 126.96	14 / 18
M5	6.57	309.05 (M-H)	28	141.98 / 75.01	20 / 20
M6	4.49	204.94 (M-H)	46	78.86 / 34.98	20 / 16

Table S3. Scanning mass spectrometry conditions for profenofos and its photoproducts.

Types	Compound name	Molecular formula	Retention time (min)	Parent ion (m/z)	△ppm	Chemical Structure
Profenofos	*O*-(4-bromo-2-chlorophenyl) *O*-ethyl *S*-propyl phosphorothioate	C11H15BrClO3PS	20.41	372.9424 (M-H)	0.54	
M1	*O*-(4-bromo-2-chlorophenyl)-*O*-ethyl phosphate	C8H9BrClO4P	18.11	312.9038 (M-H)	/	
M2	O-(4-bromo-2-chlorophenyl) O-ethyl *S*-hydrogen phosphorothioate	C8H9BrClO3PS	14.79	328.8809 (M-H)	1.22	
M3	*O*-(2-chlorophenyl) *O*-ethyl *S*-propyl phosphorothioate	C11H16ClO3PS	18.12	295.0319 (M+H)	1.36	
M4	*O*-(2-chlorophenyl) *O*-ethyl *S*-hydrogen phosphorothioate	C8H10ClO3PS	18.86	252.9850 (M+H)	/	
M5	*O*-(2-chloro-4-hydroxyphenyl) *O*-ethyl S-propyl phosphorothioate	C11H16ClO4PS	16.23	309.0123 (M-H)	1.29	
M6	4-bromo-2-chlorophenol	C6H4BrClO	20.43	204.9061 (M-H)	1.47	
M7	phenol	C6H6O	17.55	95.0491 (M+H)	2.11	

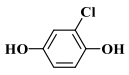
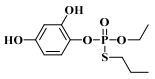
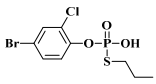
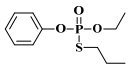
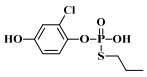
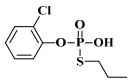
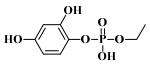
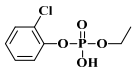
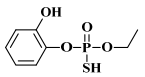
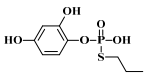
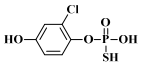
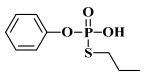
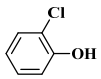
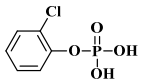
M8	2-chlorobenzene-1,4-diol	C6H5ClO2	10.09	142.9905 (M-H)	1.41	
M9	*O*-(2,4-dihydroxyphenyl) *O*-ethyl S-propyl phosphorothioate	C11H17O5PS	9.44	291.0462 (M-H)	/	
M10	*O*-(4-bromo-2-chlorophenyl) *S*-propyl *O*-hydrogen phosphorothioate	C9H11BrClO3PS	13.92	342.8966 (M-H)	0.29	
M11	*O*-ethyl *O*-phenyl *S*-propyl phosphorothioate	C11H17O3PS	16.69	261.0709 (M+H)	0.38	
M12	*O*-(2-chloro-4-hydroxyphenyl) *S*-propyl O-hydrogen phosphorothioate	C9H12ClO4PS	16.24	282.9955 (M+H)	1.06	
M13	*O*-(2-chlorophenyl) *S*-propyl *O*-hydrogen phosphorothioate	C9H12ClO3PS	19.01	264.9861 (M-H)	-0.38	
M14	2,4-dihydroxyphenyl ethyl hydrogen phosphate	C8H11O6P	6.21	233.0220 (M-H)	1.29	
M15	2-chlorophenyl ethyl hydrogen phosphate	C8H10ClO4P	11.91	234.9932 (M-H)	0.85	
M16	*O*-ethyl *O*-(2-hydroxyphenyl) *S*-hydrogen phosphorothioate	C8H11O4PS	12.86	233.0043 (M-H)	/	
M17	*O*-(2,4-dihydroxyphenyl) *S*-propyl *O*-hydrogen phosphorothioate	C9H13O5PS	7.17	263.0149 (M-H)	/	
M18	*O*-(2-chloro-4-hydroxyphenyl) *O*, *S*-dihydrogen phosphorothioate	C6H6ClO4PS	16.23	240.9486 (M+H)	0.83	
M19	O-phenyl S-propyl O-hydrogen phosphorothioate	C9H13O3PS	15.14	231.0250 (M-H)	0.87	
M20	2-chlorophenol	C6H5ClO	11.91	126.9956 (M-H)	-1.59	
M21	2-chlorophenyl dihydrogen phosphate	C6H6ClO4P	11.98	208.9765 (M+H)	1.44	

Table S4. Precision and accuracy of the analytical method.

name	Spiked level ($mg \cdot kg^{-1}$)	Average recovery (%)	RSD (%)	LOD ($\mu g \cdot kg^{-1}$)	LOQ ($\mu g \cdot kg^{-1}$)
Profenofos	0.01	95.2	2.1	1	3
	0.1	85.2	4.5		
	1	100.6	3.2		
M1	0.01	91.2	4.6	0.0017	0.0056
	0.1	96.1	3.2		
	1	85.2	2.5		
M2	0.01	109.7	6.7	0.00088	0.0029
	0.1	104.9	9.6		
	1	96.3	4.2		
M3	0.01	103.2	4.2	0.000065	0.00022
	0.1	91.2	5.1		
	1	96.8	5.0		
M4	0.01	92.5	5.2	0.00049	0.0016
	0.1	97.4	3.6		
	1	88.2	2.8		
M5	0.01	101.3	4.8	0.0012	0.0039
	0.1	95.3	2.7		
	1	102.5	3.6		
M6	0.01	85.6	5.1	0.005	0.017
	0.1	99.4	6.5		
	1	98.6	2.5		
Myricetin	0.01	93.5	3.2	0.011	0.037
	0.1	97.4	1.3		
	1	102.8	4.1		

Table S5. Photoproducts toxicity prediction by ECOSAR.

Compounds	Acute toxicity ($mg \cdot L^{-1}$)			Chronic toxicity ($mg \cdot L^{-1}$)		
	Fish (96 h LC_{50})	Daphnid (48 h LC_{50})	Green algae (96 h EC_{50})	Fish (96 h LC_{50})	Daphnid (48 h LC_{50})	Green algae (96 h EC_{50})
Profenofos	0.836	0.0013	3.12	0.0076	/	3.28
M1	24.8	15.6	17.9	2.74	2.04	5.94
M2	2.55	0.0043	187	0.011	/	24.8
M3	1.35	0.0022	28.5	0.0079	/	9
M4	3.98	0.0071	1650	0.011	/	65.6
M5	2.1	0.0035	113	0.0096	/	18.6
M6	5.38	3.74	0.493 ↑	0.593	0.492	1.34 ↑
M7	27.7	9.64	2.4 ↑	2.61	0.969	4.53
M8	0.156 ↑	0.173	0.289 ↑	0.0098	0.142	0.462 ↑
M9	4.89	0.0088	2340	0.013	/	84.3
M10	338	185	119	31.7	28.8	16.4
M11	2.01	0.0034	148	0.0084	/	19.6
M12	9.27	6.03	0.845 ↑	1.01	0.772	2.22 ↑
M13	12.6	8.15	10.3	1.44	1.13	3.57
M14	80.9	1090	14.1	54.8	442	1.55 ↑
M15	117	68	55.6	11.7	7.06	15.3
M16	9.14	0.0018	33700	0.014	/	293
M17	284	5300	30.5	218	2260	2.95 ↑
M18	88.9	29	7.64	8.26	2.84	14
M19	41.7	25.4	25	4.42	2.99	7.62
M20	0.095 ↑	0.738	0.047 ↑	0.0091	4.87	0.011
M21	13.7	6.35	1.21 ↑	1.37	0.715	2.67 ↑

Note: Toxicity categories: highly toxic (< 1 $mg \cdot L^{-1}$, red); moderately toxic (1−10 $mg \cdot L^{-1}$, Yellow); slightly toxic (10−100 $mg \cdot L^{-1}$, pale green); non-toxic (> 100 $mg \cdot L^{-1}$, green).

Table S6. Effect of myricetin on the decrease in photodegradation of four pesticides.

Name	Ratio	degradation rate (%)	Degradation rate with myricetin (%)
Methyl parathion	1:5	32.6	27.9
Malathion	1:5	29.5	25.3
Cyhalofop-butyl	1:5	65.6	38.1
Imidacloprid	1:5	82.7	50.1

Note: (1) Light intensity: HPML, 7.2×10^6–9.5×10^6 lx, 25±1℃; (2) Reaction time: 10 min; (3) Three parallel samples per group.

Table S7. Properties of paddy, farm ditch, and pond water.

Surface water	Paddy water	farm ditch water	Pond water
Dissolved oxygen ($mg \cdot L^{-1}$)	6.0	5.4	3.6
turbidity NTU	3.1	1.6	46.8
conductivity ($us \cdot cm^{-1}$)	162	344	302
pH	7.4	7.2	7.3
hardness ($mg \cdot L^{-1}$)	62	110	96
COD ($mg \cdot L^{-1}$)	4	5	13
BOD ($mg \cdot L^{-1}$)	1.0	1.4	3.5
Cu^{2+} ($mg \cdot L^{-1}$)	<0.006	<0.006	<0.006
Fe^{3+} ($mg \cdot L^{-1}$)	0.21	<0.02	<0.02
Cl^{-} ($mg \cdot L^{-1}$)	1.00	1.95	12.2
SO_4^{2-} ($mg \cdot L^{-1}$)	2.86	<0.018	18.9
NO_3^{-} ($mg \cdot L^{-1}$)	1.37	2.87	1.09
phenols ($mg \cdot L^{-1}$)	<0.0003	<0.0003	<0.0003