Supplemental Material

Electrospray ionisation mass spectrometric studies of *N*-substituted 10-(aminosulfonyl)bornyl acrylate derivatives

Lulama P. Mciteka,[a,b] Kevin A. Lobb,[a] Marietjie A. Stander,[c] and Perry T. Kaye[a]*

[a]Department of Chemistry, Rhodes University, Makhanda, South Africa
[b]Department of Chemistry, University of the Western Cape, Bellville, Cape Town
[c]Central Analytical Facilities, Stellenbosch University, Stellenbosch, South Africa
Email: P.Kaye@ru.ac.za

Table of Contents

I Mass Spectrometry (MS) Methodology

Direct injection MS analysis

1 mg of each sample was dissolved in 1 ml methanol (Romil), followed by a further 10-fold dilution into methanol. 2 µL of sample was injected into a stream of methanol flowing at 0.3 ml/min, using a Waters ultra pressure liquid chromatograph (UPLC) (Waters, Midford, USA) which conveyed the sample to a Waters Synapt G2 quadrupole time-of-flight (QTOF) mass spectrometer used for high-resolution accurate mass analysis.

Data was acquired in resolution mode, the mass spectrometer was optimized for best sensitivity, a cone voltage of 15 V, desolvation gas was nitrogen at 650 L/hr and desolvation temperature 275 ºC. The instrument was operated with an electrospray ionization probe in the positive mode. Sodium formate was used for calibration and leucine encephalin was infused in the background as lock mass for accurate mass determinations.

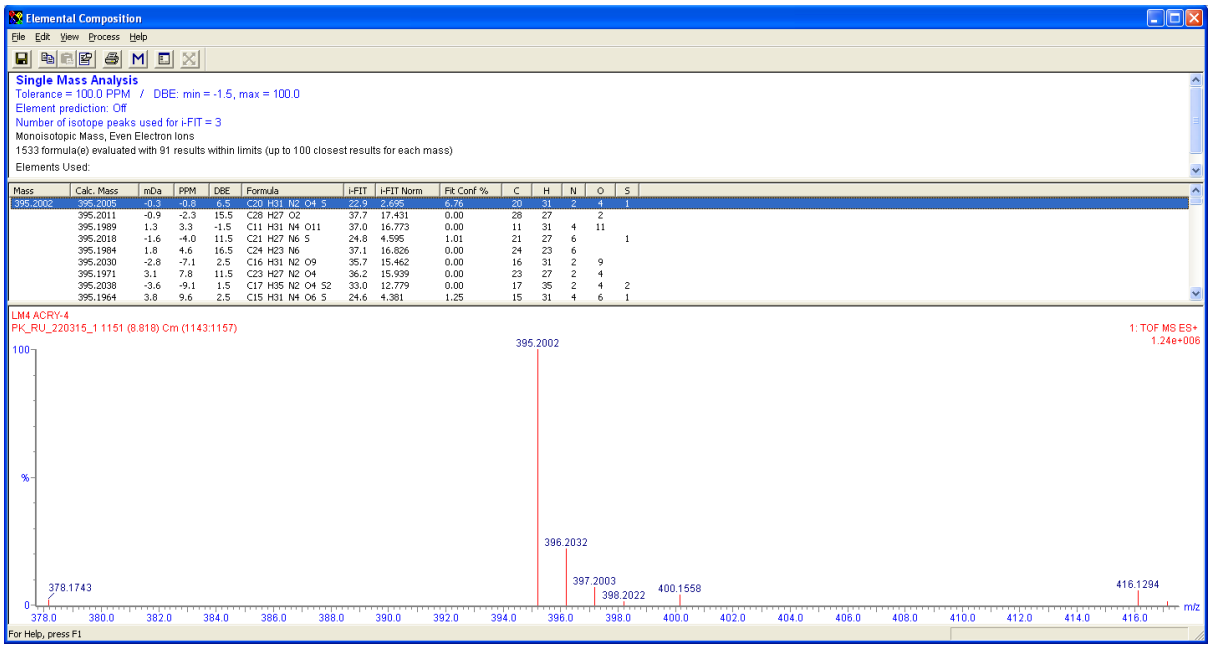
LC-MS/MS analysis

The MS/MS experiments were conducted with liquid chromatographic separation using a Waters BEH C18, 2.1 x 100 mm, 1.7 µm particle size column kept at 50 ºC and the same instrument as above, A generic gradient starting at 100% mobile phase A (0.1% formic acid in MilliQ water) to 100% mobile phase B (acetonitrile with 0.1% formic acid) over 12 minutes using a flow rate of 0.4 mL/min.

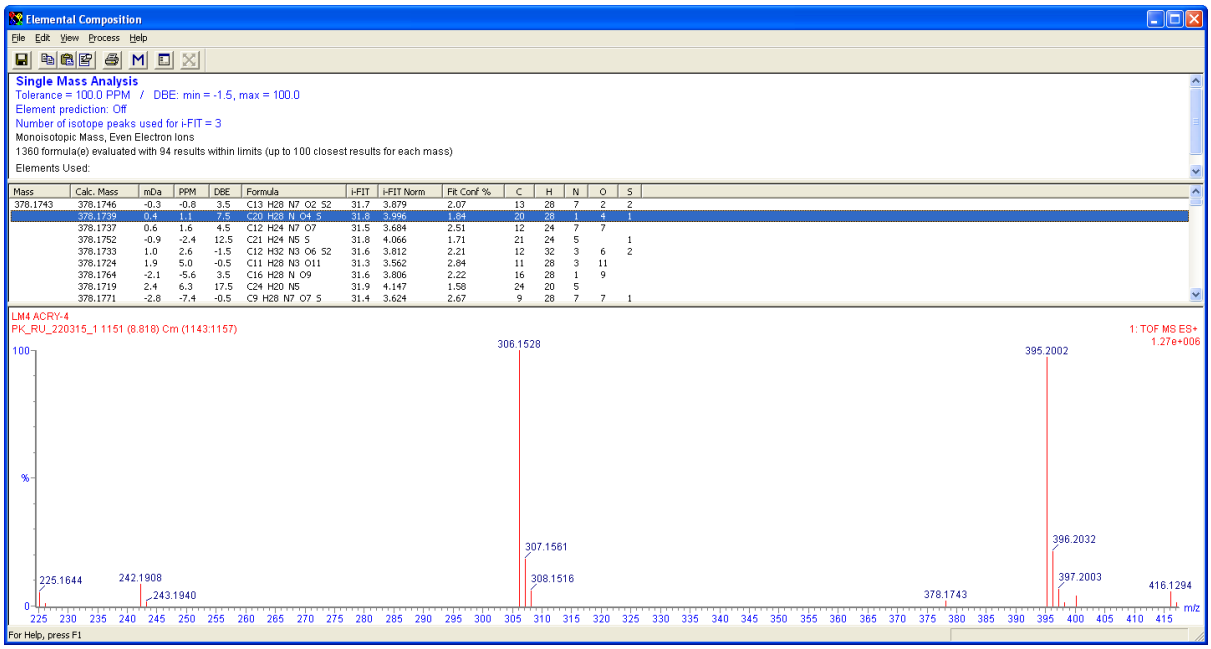
The MS/MS experiments were conducted by collision-induced dissociation of selected parent ions by accelerating these ions to high kinetic energy using an electrical potential followed by collision with argon gas molecules in the Trap collision cell at a collision energy of 30 V.

II HRMS ESI MS Spectra

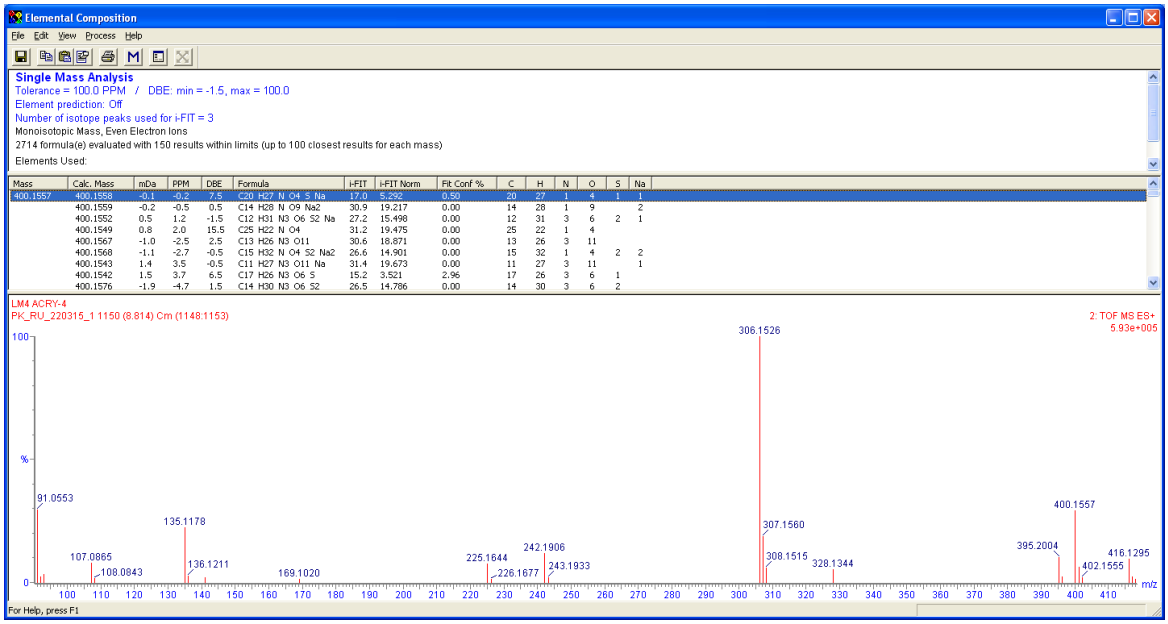
Elemental composition fit of 4a-NH_4^+ (*m/z* 395 ion) with its HRMS ESI Mass Spectrum :



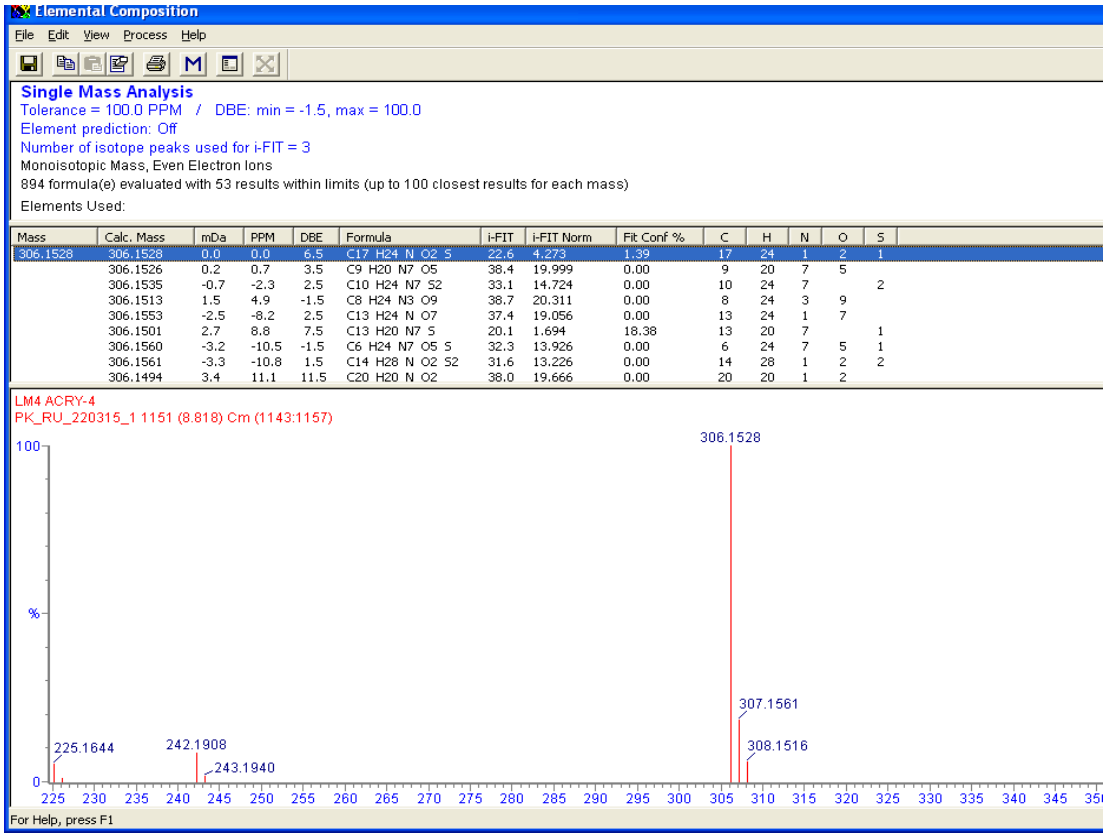
Elemental composition fit of 4a-H^+ (*m/z* 378 ion) with its HRMS ESI Mass Spectrum:



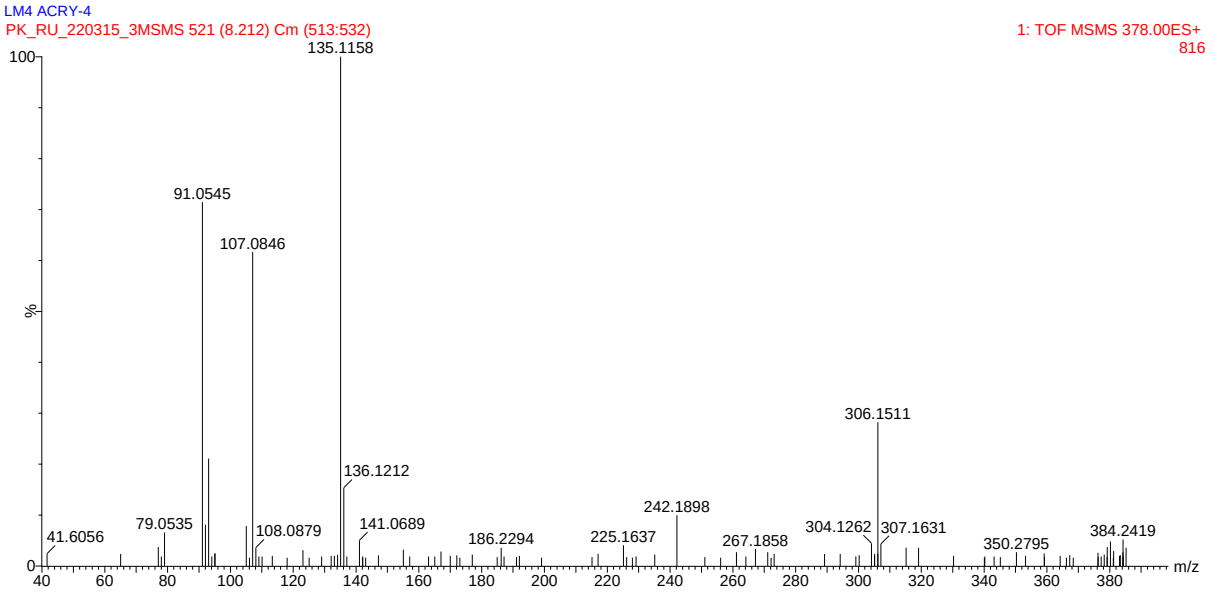
Elemental composition fit of 4a-Na$^+$ (*m/z* 400 ion) with the HRMS ESI Mass Spectrum



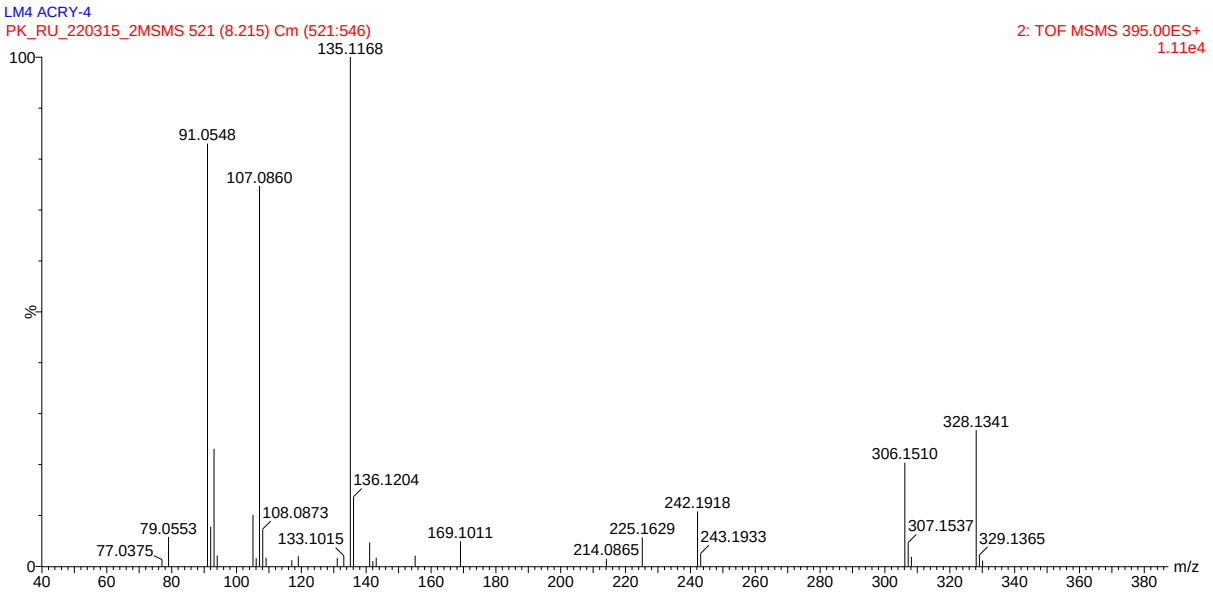
Elemental composition fit of 4ai (*m/z* 306 ion) with the HRMS ESI Mass Spectrum:



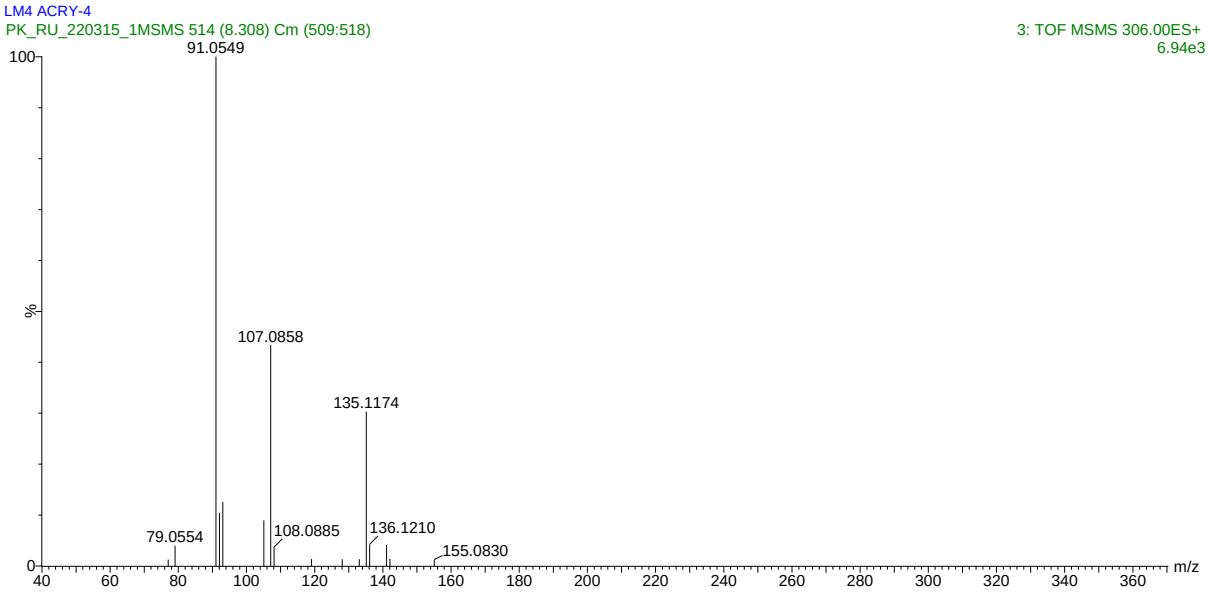
ESI MS/MS Spectrum of 4a-H^+ (*m/z* 378)



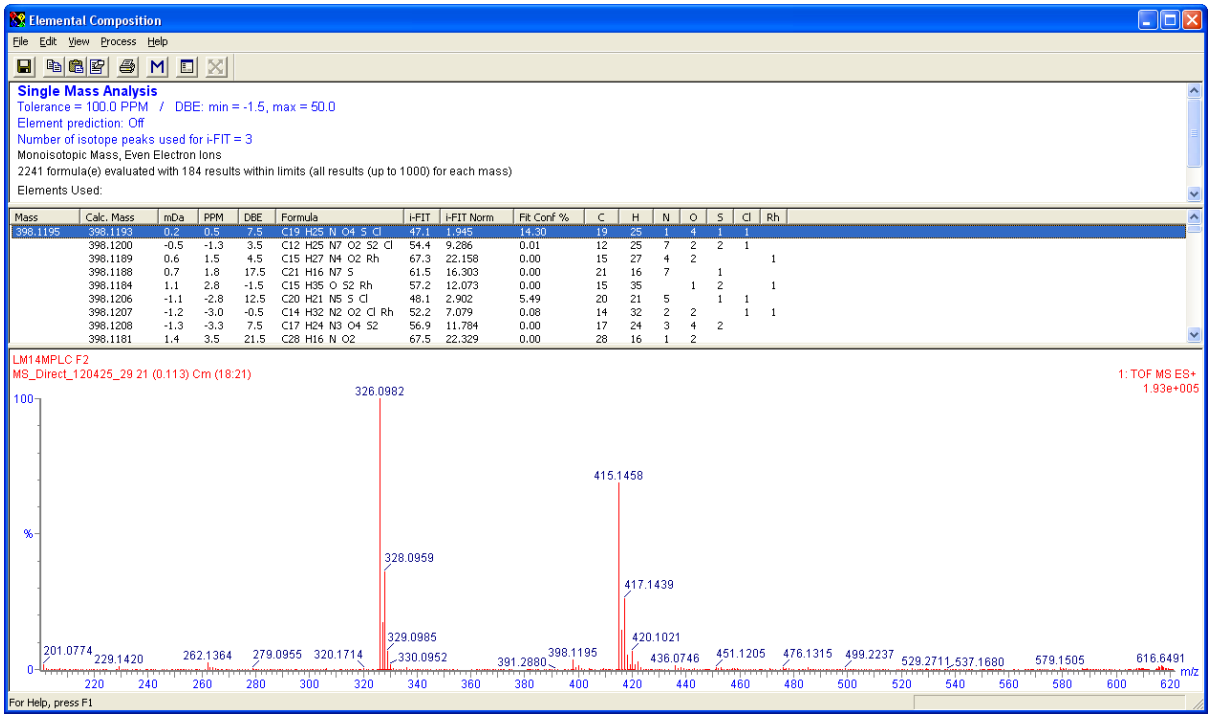
ESI MS/MS Spectrum of 4a-NH_4^+ (*m/z* 395)



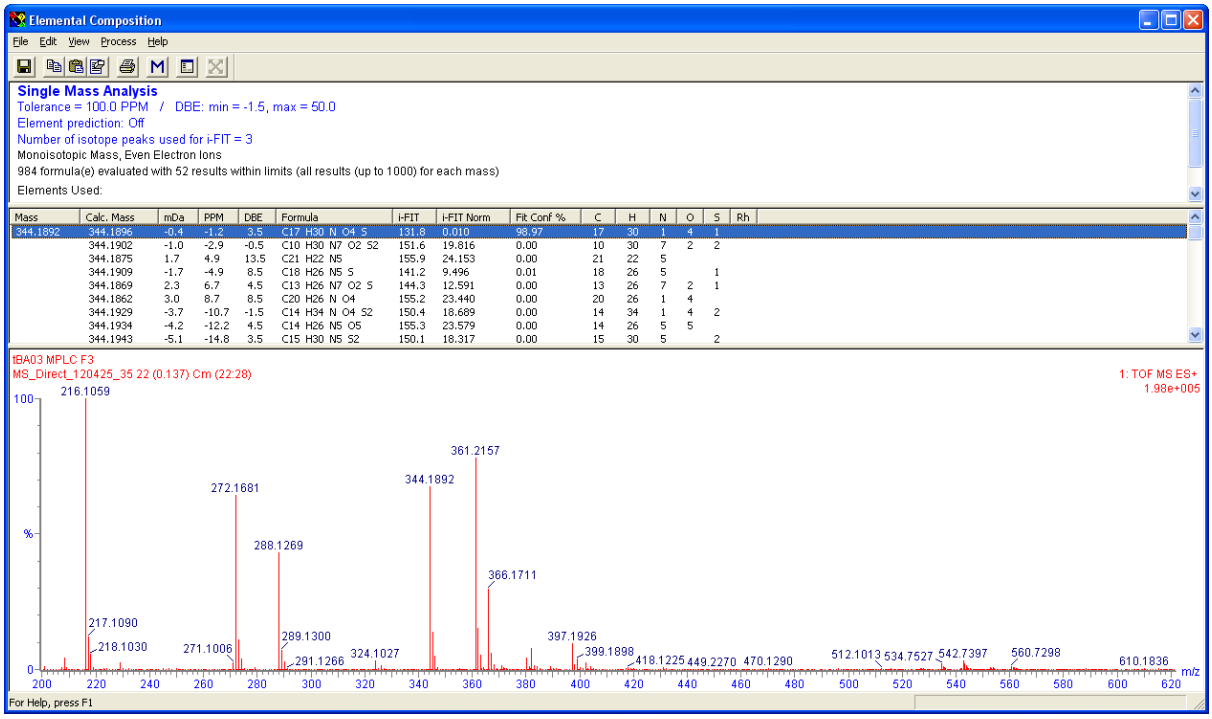
MS-MS ESI Mass Spectrum of fragment 4aI (*m/z* 306: "base peak") in spectra of 4aI-H^+ (*m/z* 378) and 4a-NH_4^+ (*m/z* 395)



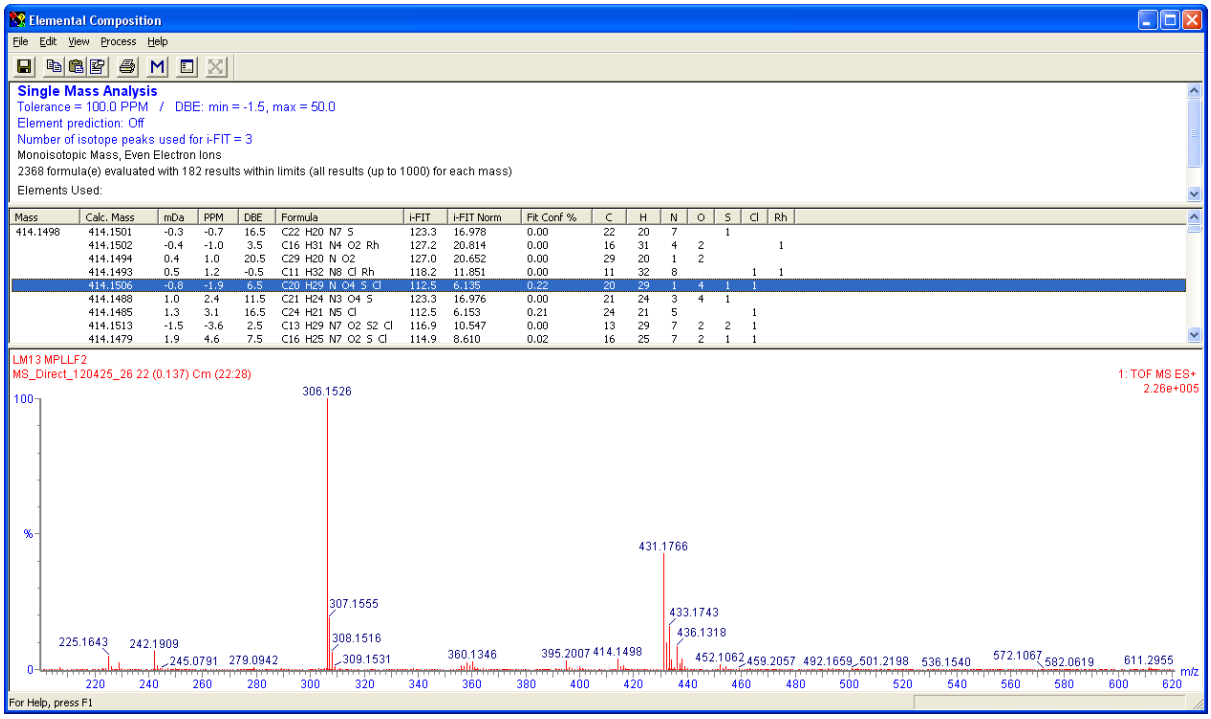
Elemental composition fit of 4b (*m/z* 398 ion) with the HRMS ESI Mass Spectrum



Elemental composition fit of 4c (*m/z* 344 ion) with the HRMS ESI Mass Spectrum

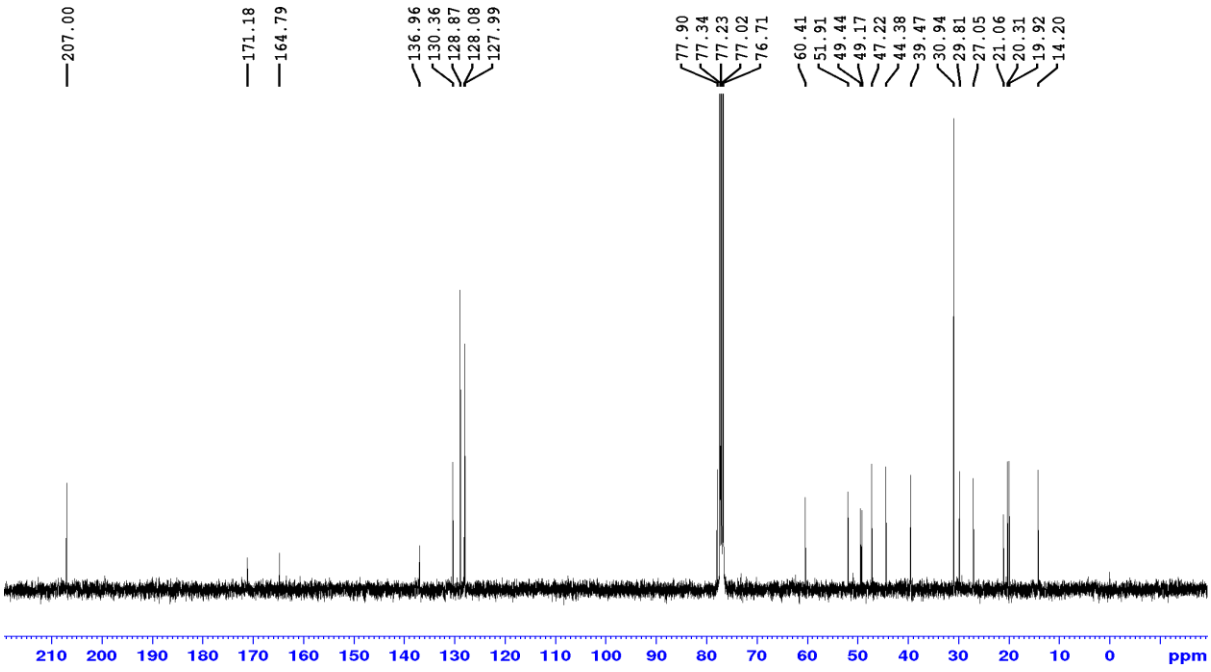


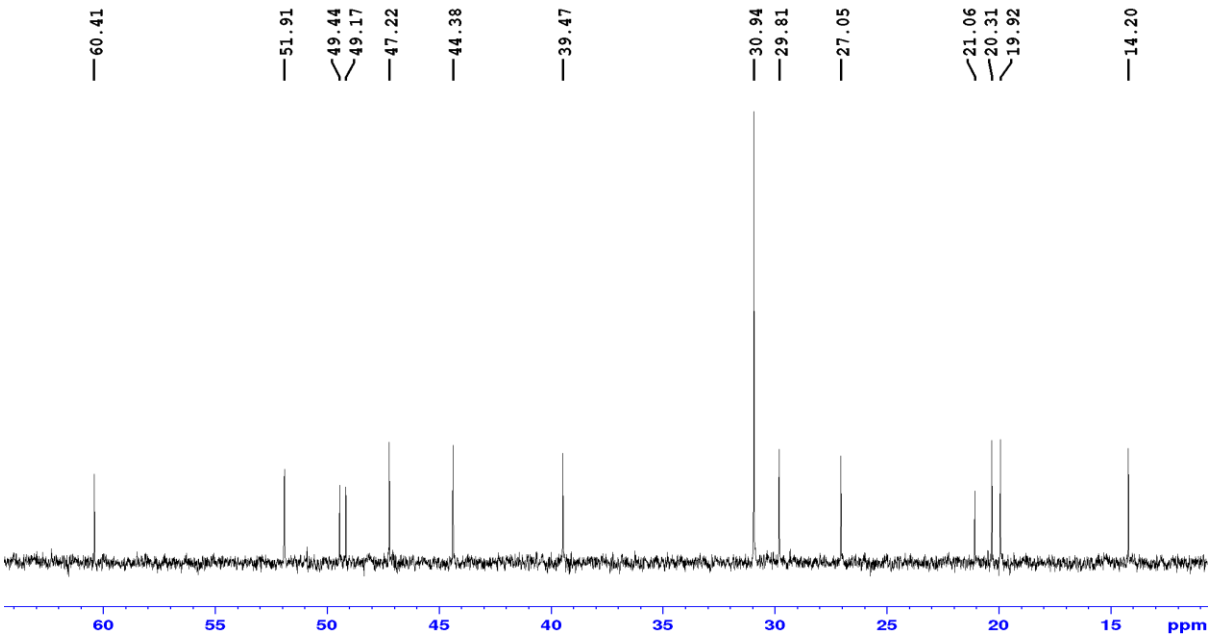
Elemental composition fit of 5a (*m/z* 414 ion) with the HRMS ESI Mass Spectrum

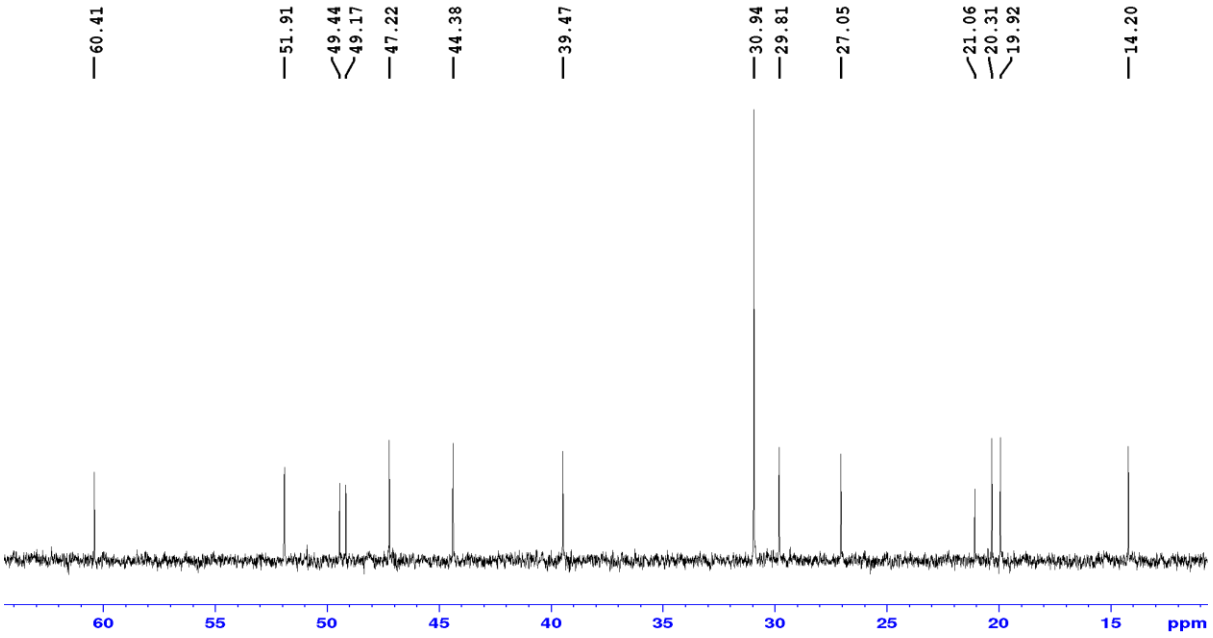


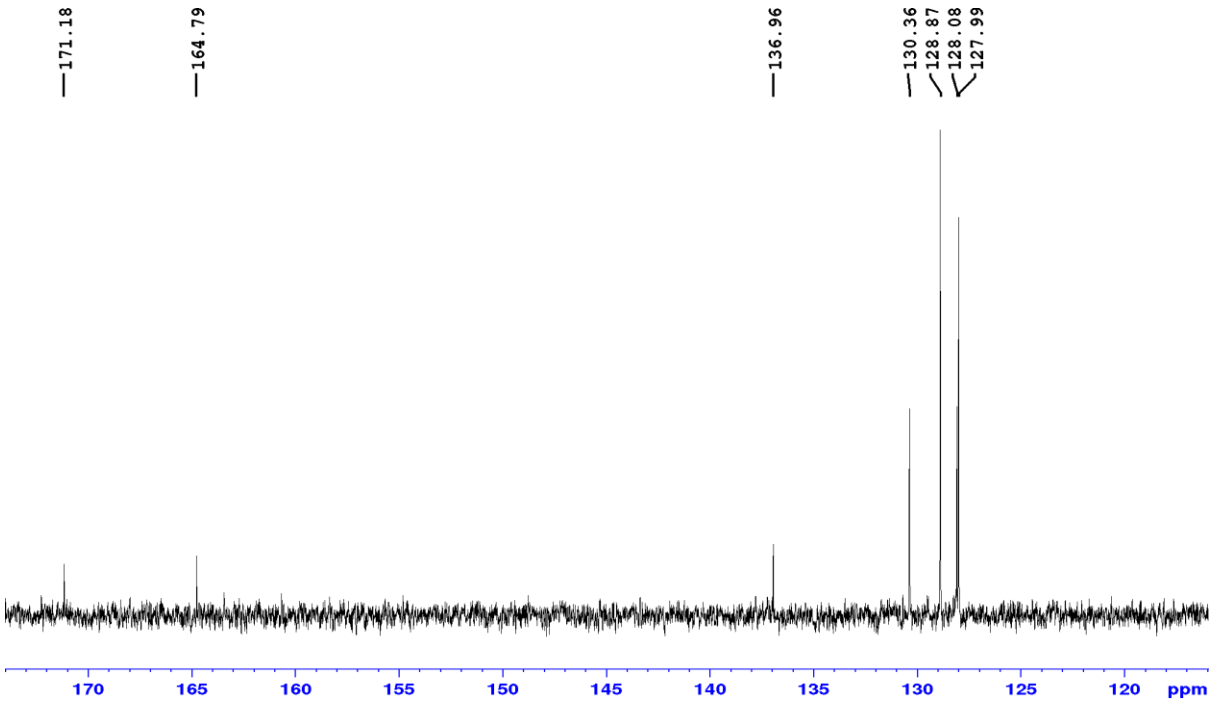
II NMR Spectra for compound 4a

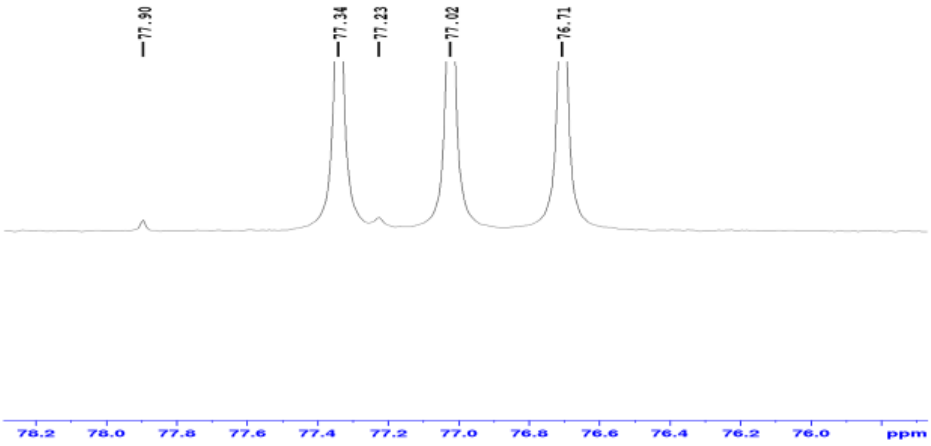
Note: Extraneous signals at *ca*. 1.26, 2.05 and 4.12 ppm in the ^{1}H NMR spectra and at *ca*. 14.2, 21.0, 60.5 and 171.4 ppm in the ^{13}C NMR spectra are attributed to the presence of residual ethyl acetate.

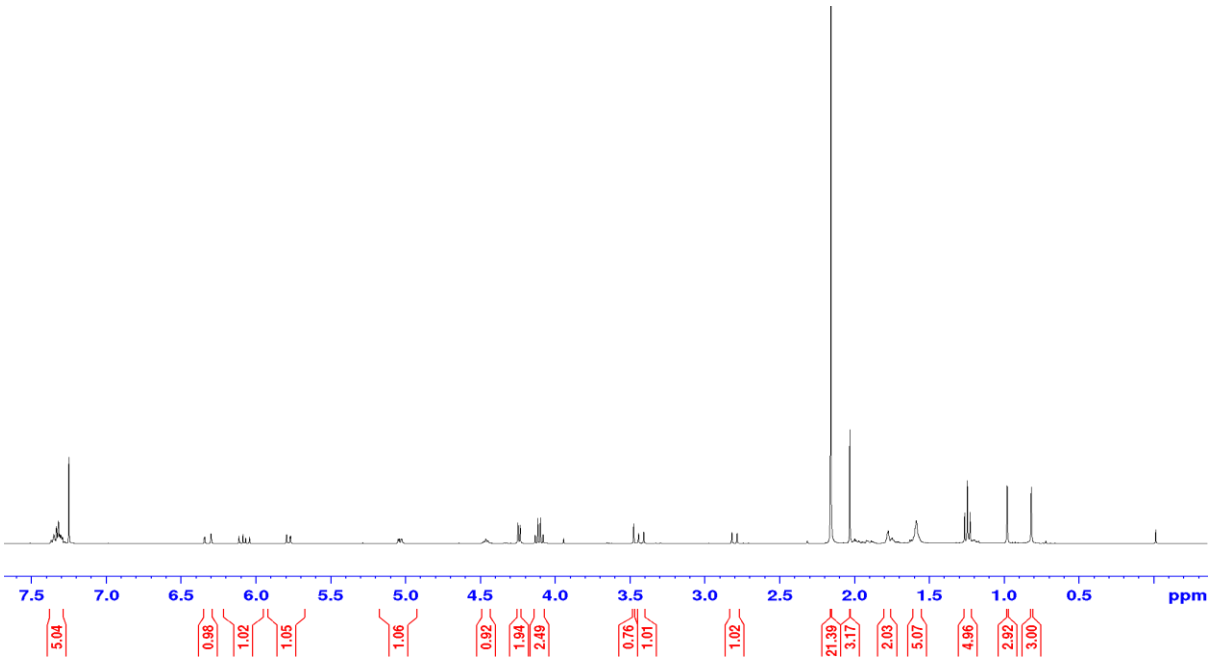


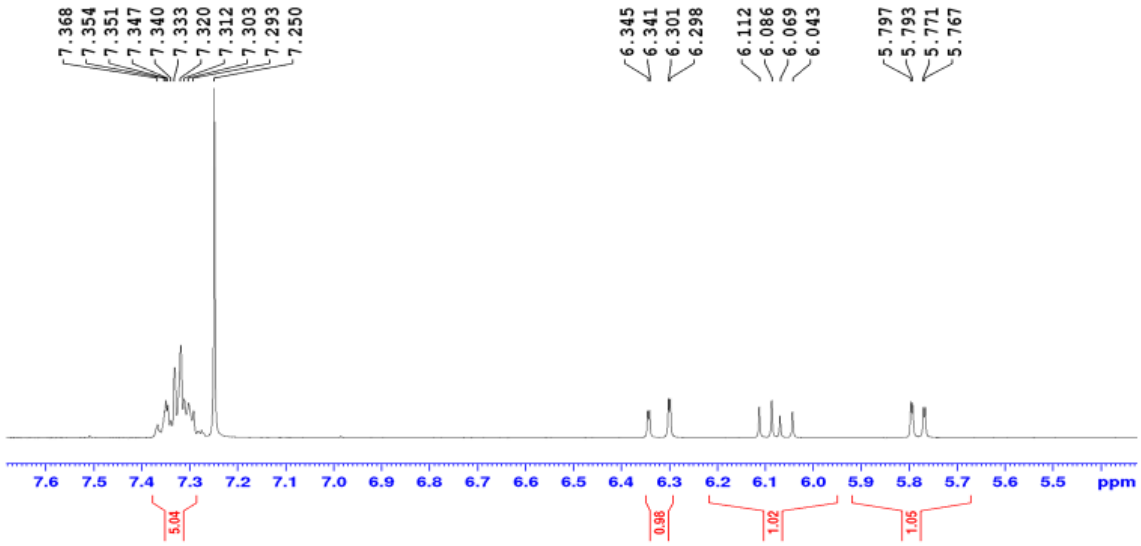

60.41
51.91
49.44
49.17
47.22
44.38
39.47
30.94
29.81
27.05
21.06
20.31
19.92
14.20
60
55
50
45
40
35
30
25
20
15
ppm


60.41
51.91
49.44
49.17
47.22
44.38
39.47
30.94
29.81
27.05
21.06
20.31
19.92
14.20
60
55
50
45
40
35
30
25
20
15
ppm


171.18
164.79
136.96
130.36
128.87
128.08
127.99
170
165
160
155
150
145
140
135
130
125
120
ppm


77.90
77.34
77.23
77.02
76.71
78.2
78.0
77.8
77.6
77.4
77.2
77.0
76.8
76.6
76.4
76.2
76.0
ppm


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
5.04
0.98
1.02
1.05
1.06
0.92
1.94
2.49
0.76
1.01
1.02
21.39
3.17
2.03
5.07
4.96
2.92
3.00


7.368
7.354
7.351
7.347
7.340
7.333
7.320
7.312
7.303
7.293
7.250
6.345
6.341
6.301
6.298
6.112
6.086
6.069
6.043
5.797
5.793
5.771
5.767
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
5.5
ppm
5.04
0.98
1.02
1.05

