

## Supplementary Information

### Integrative Approach Based on Leaf Spray Mass Spectrometry, HPLC-DAD-MS/MS, and NMR for Comprehensive Characterization of Isoquinoline-Derived Alkaloids in Leaves of *Onychopetalum amazonicum* R. E. Fr.

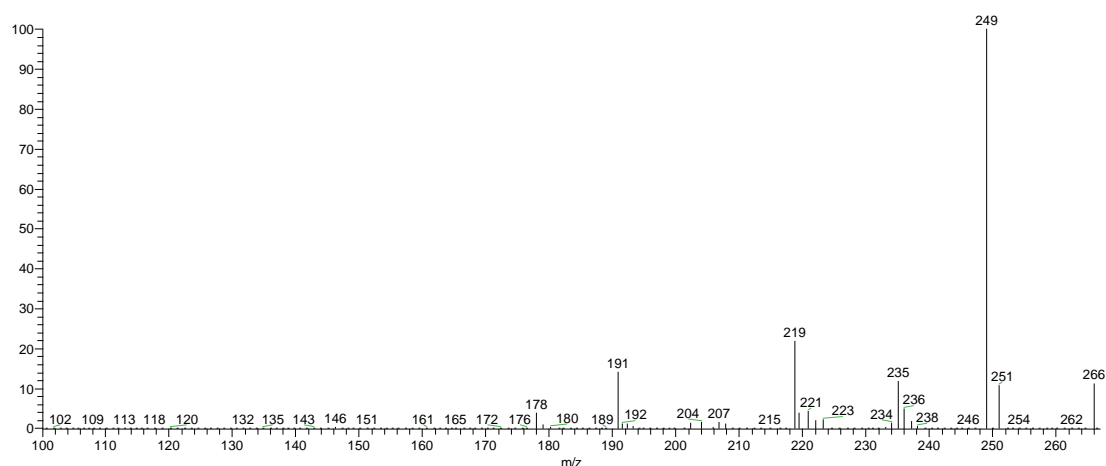
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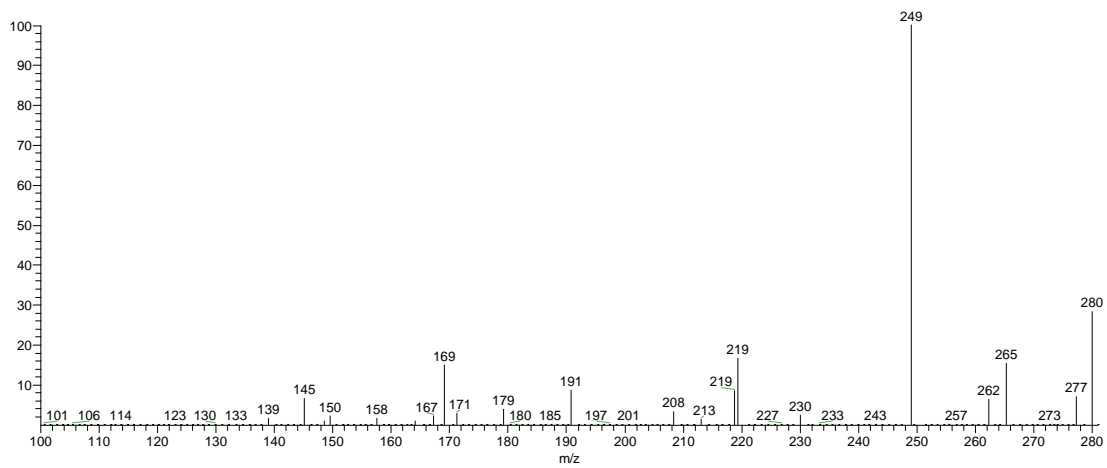
<sup>b</sup>Departamento de Química, Universidade Federal do Amazonas (UFAM), 69077-000 Manaus-AM, Brazil

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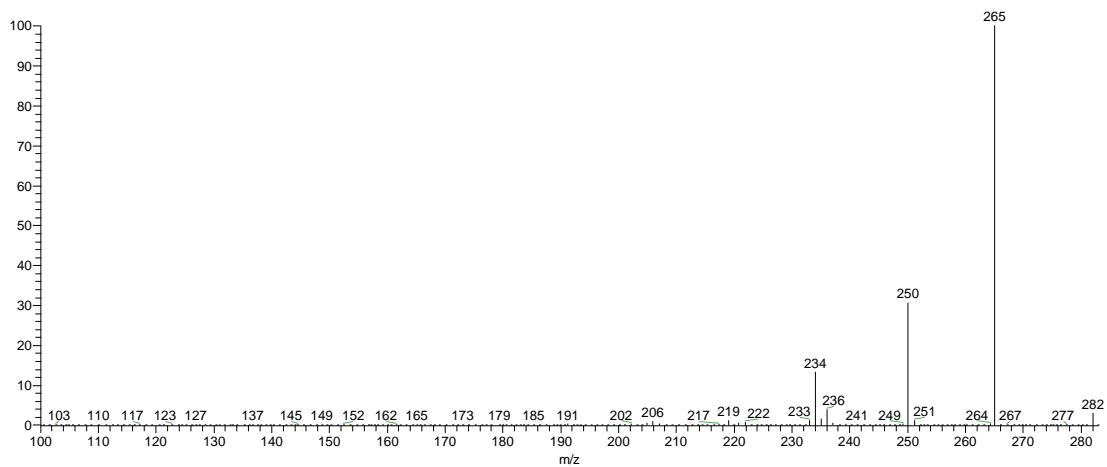
<sup>d</sup>Grupo de Pesquisa em Metabolômica e Espectrometria de Massas, Universidade do Estado do Amazonas (UEA), 69050-010 Manaus-AM, Brazil



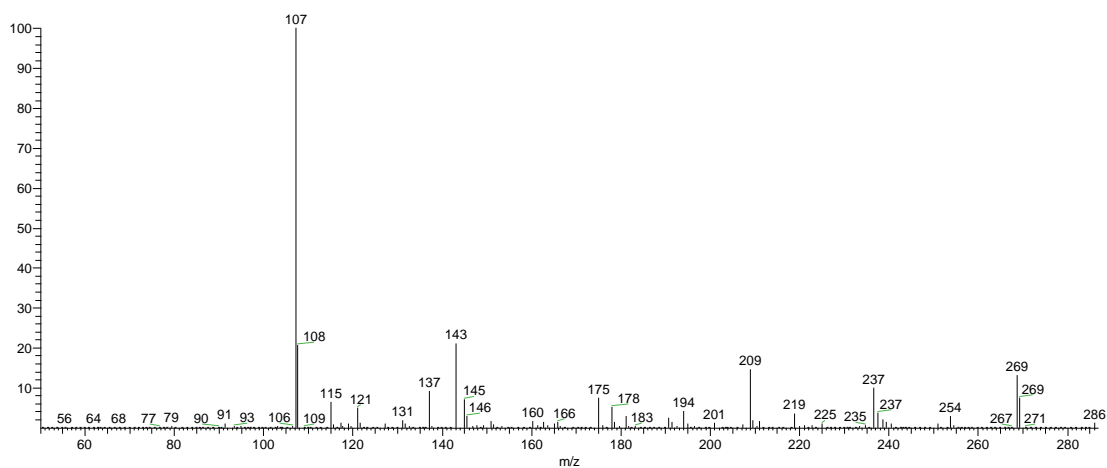
**Figure S1.** LS-MS<sup>2</sup> spectrum of the ion at  $m/z$  266 present in the leaves of *O. amazonicum*.



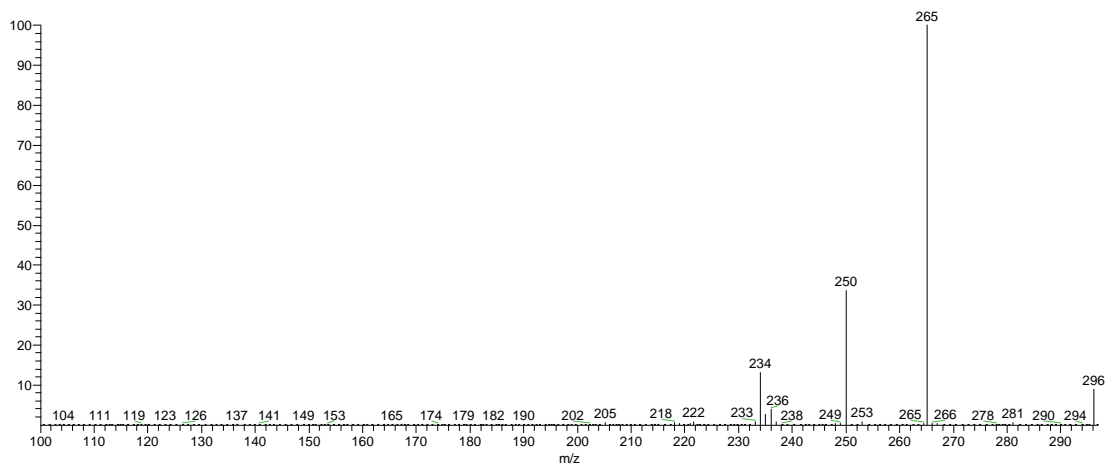
**Figure S2.** LS-MS<sup>2</sup> spectrum of the ion at  $m/z$  280 present in the leaves of *O. amazonicum*.



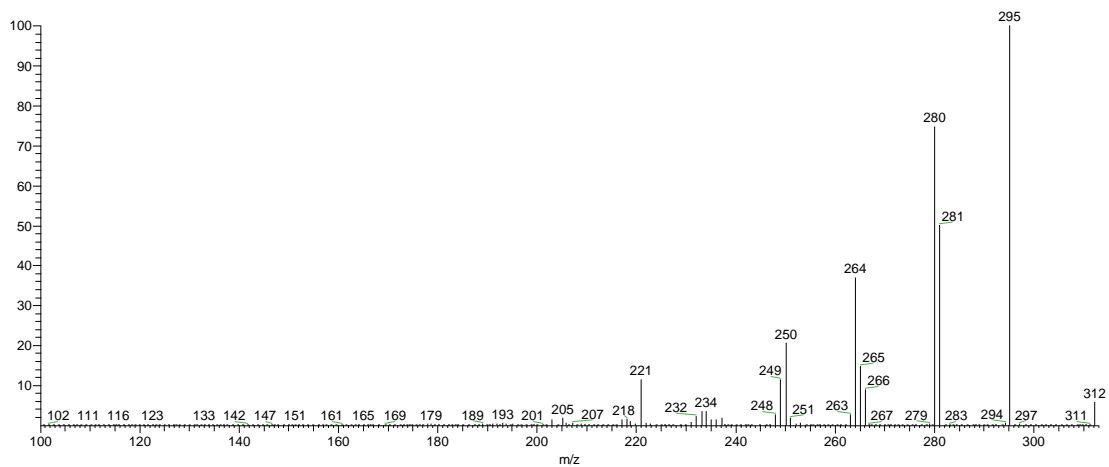
**Figure S3.** LS-MS<sup>2</sup> spectrum of the ion at  $m/z$  282 present in the leaves of *O. amazonicum*.



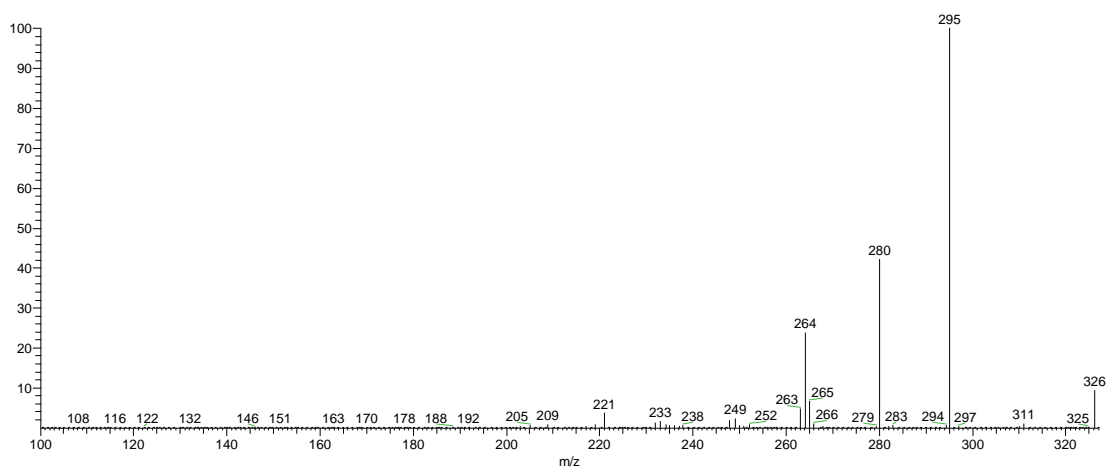
**Figure S4.** LS-MS<sup>2</sup> spectrum of the ion at  $m/z$  286 present in the leaves of *O. amazonicum*.



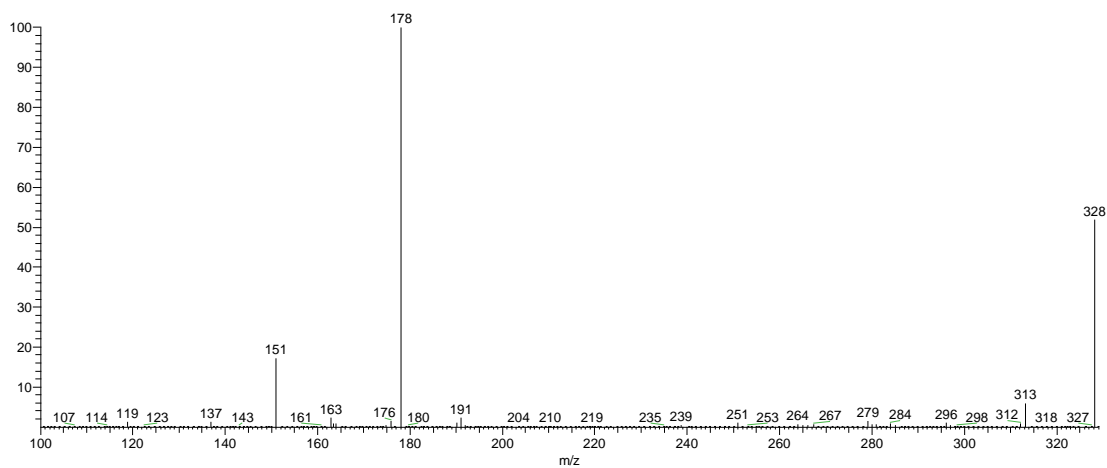
**Figure S5.** LS-MS<sup>2</sup> spectrum of the ion at  $m/z$  296 present in the leaves of *O. amazonicum*.



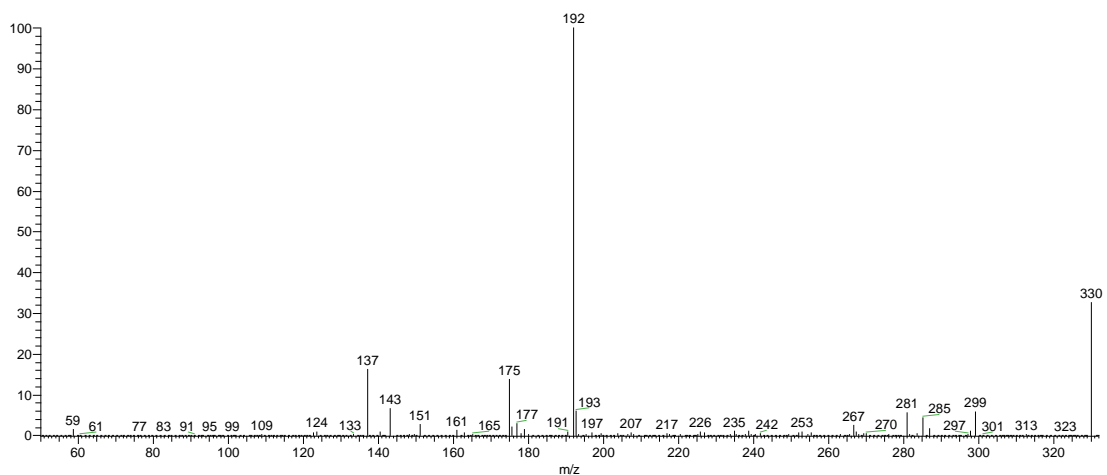
**Figure S6.** LS-MS<sup>2</sup> spectrum of the ion at  $m/z$  312 present in the leaves of *O. amazonicum*.



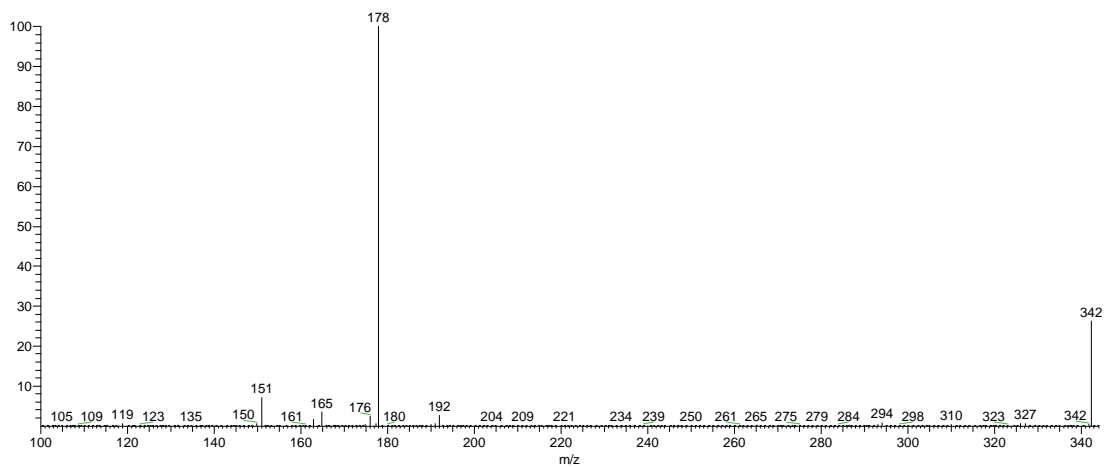
**Figure S7.** LS-MS<sup>2</sup> spectrum of the ion at  $m/z$  326 present in the leaves of *O. amazonicum*.



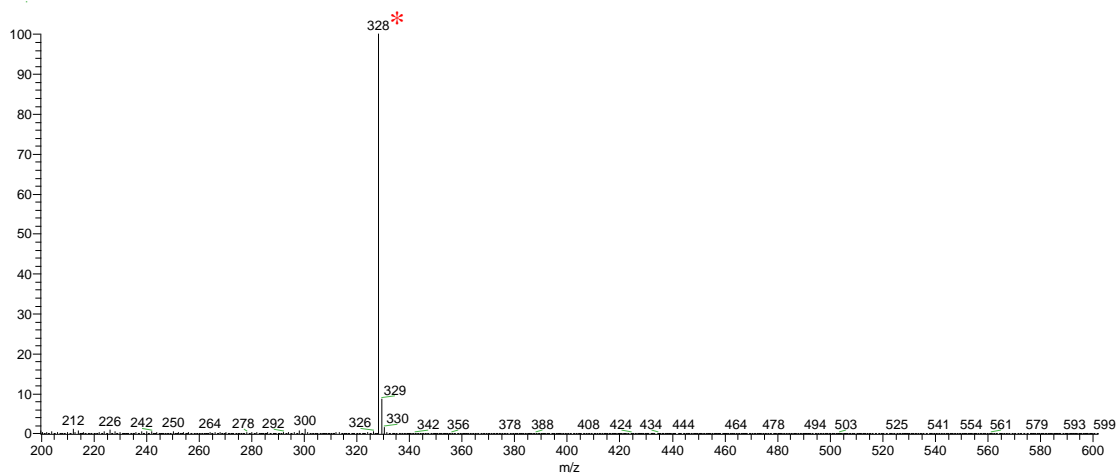
**Figure S8.** LS-MS<sup>2</sup> spectrum of the ion at  $m/z$  328 present in the leaves of *O. amazonicum*.



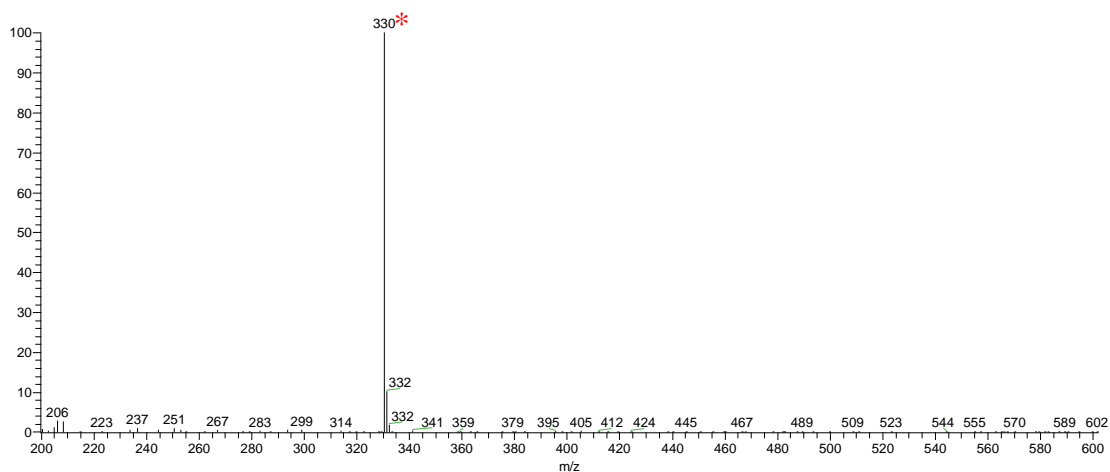
**Figure S9.** LS-MS<sup>2</sup> spectrum of the ion at  $m/z$  330 present in the leaves of *O. amazonicum*.



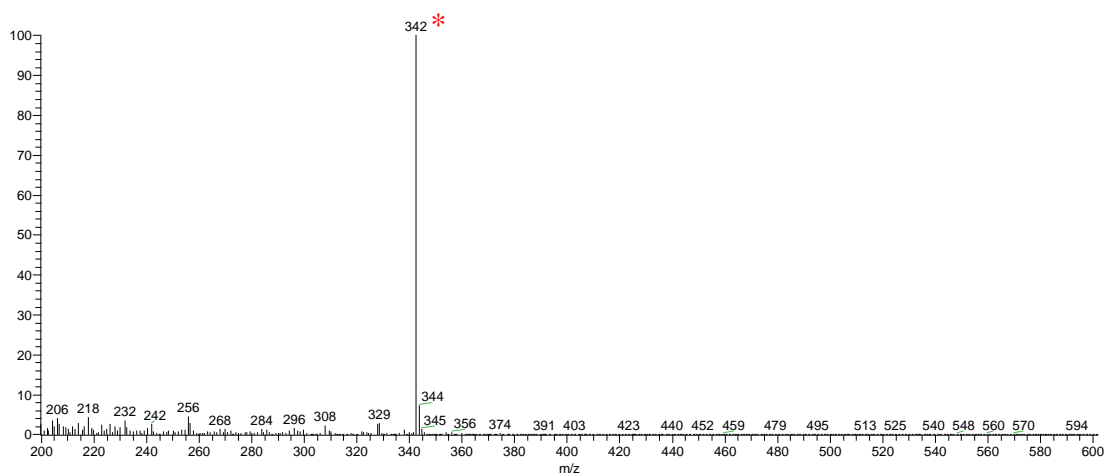
**Figure S10.** LS-MS<sup>2</sup> spectrum of the ion at  $m/z$  342 present in the leaves of *O. amazonicum*.



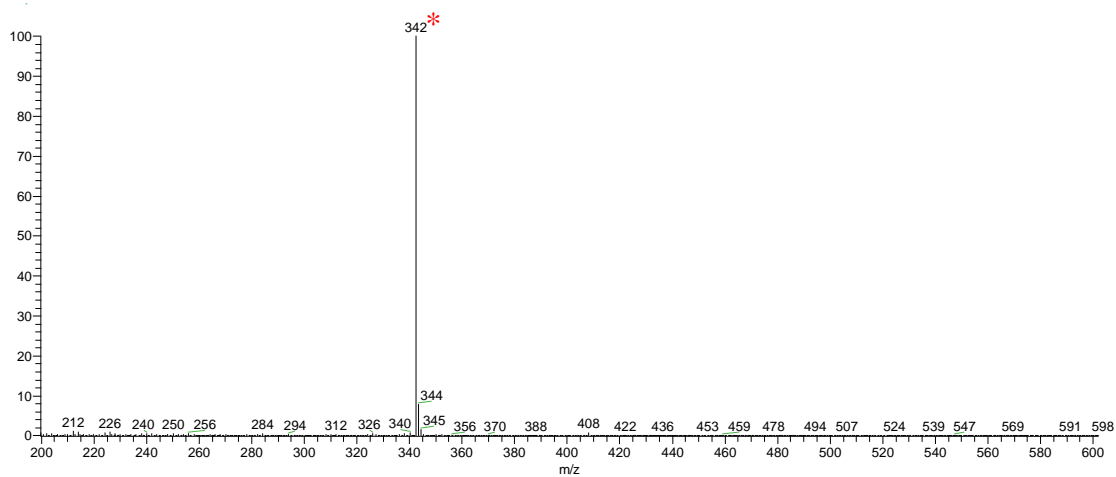
**Figure S11.** Mass spectrum of the peak I. The \* denotes the ion subjected to fragmentation.



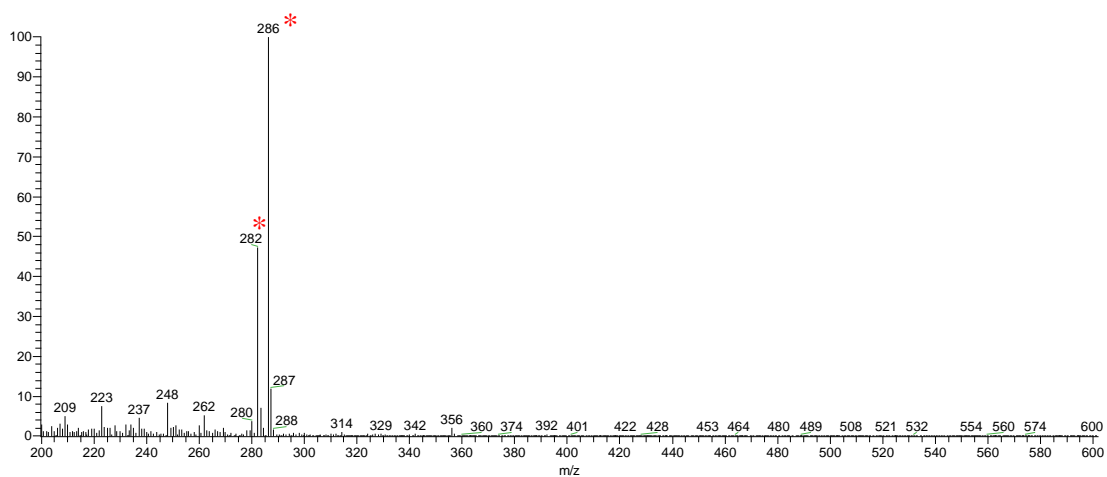
**Figure S12.** Mass spectrum of the peak II. The \* denotes the ion subjected to fragmentation.



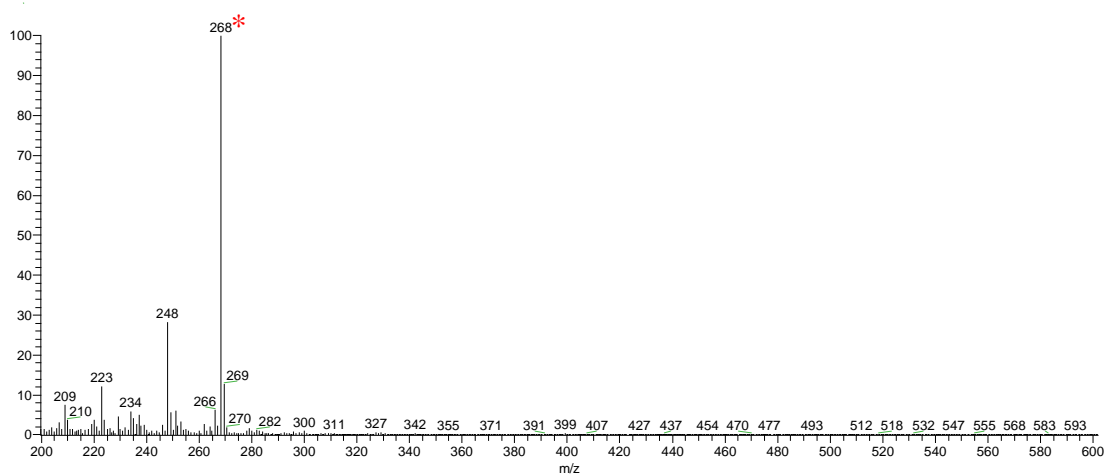
**Figure S13.** Mass spectrum of the peak III. The \* denotes the ion subjected to fragmentation.



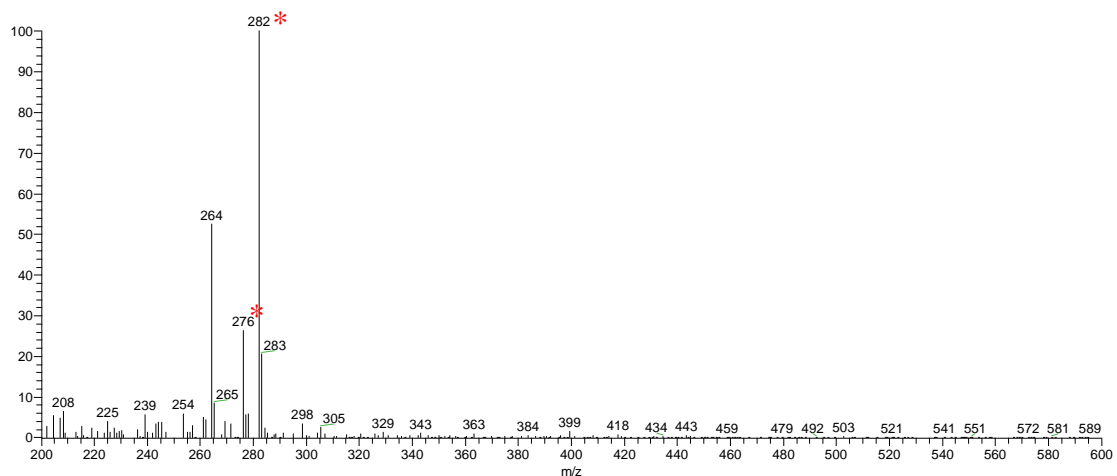
**Figure S14.** Mass spectrum of the peak IV. The \* denotes the ion subjected to fragmentation.



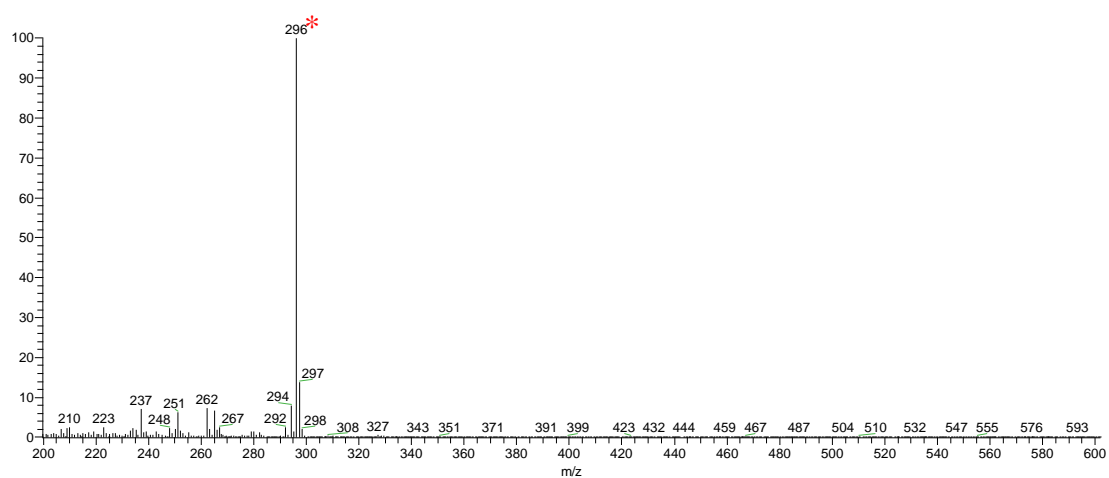
**Figure S15.** Mass spectrum of the peak V. The \* denotes the ion subjected to fragmentation.



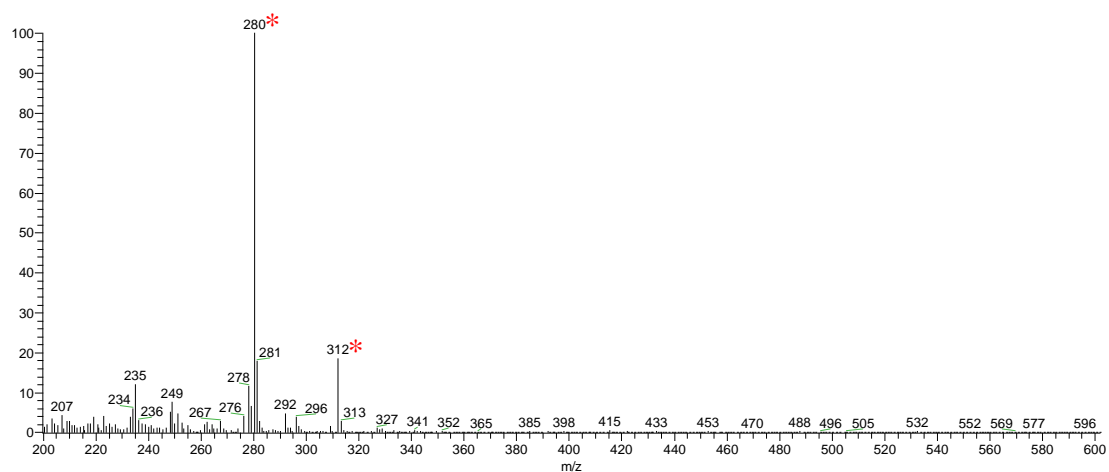
**Figure S16.** Mass spectrum of the peak VI. The \* denotes the ion subjected to fragmentation.



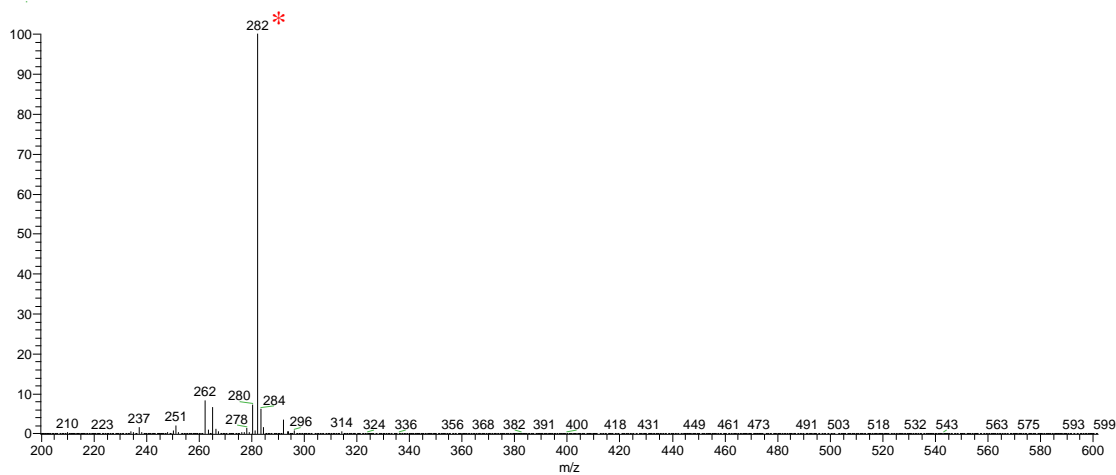
**Figure S17.** Mass spectrum of the peak VII. The \* denotes the ion subjected to fragmentation.



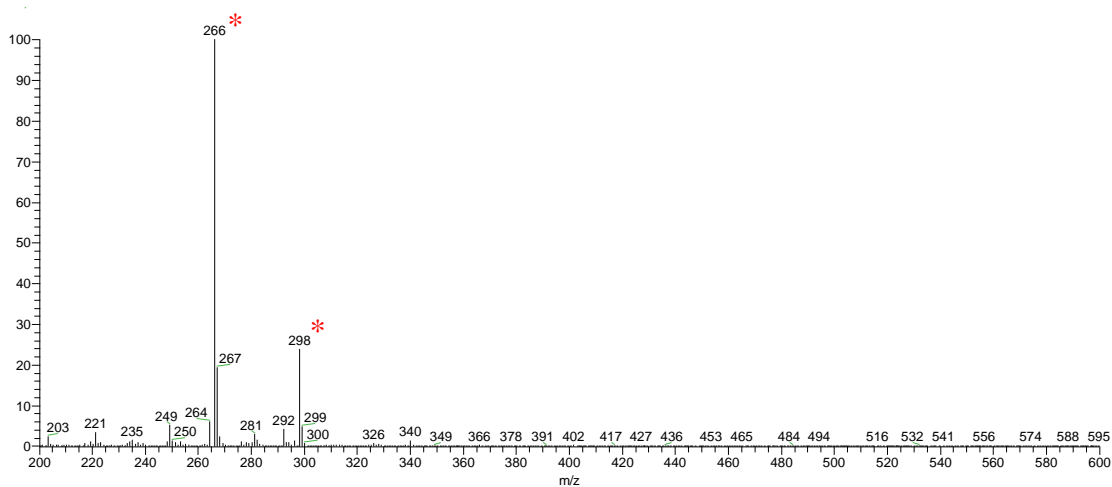
**Figure S18.** Mass spectrum of the peak VIII. The \* denotes the ion subjected to fragmentation.



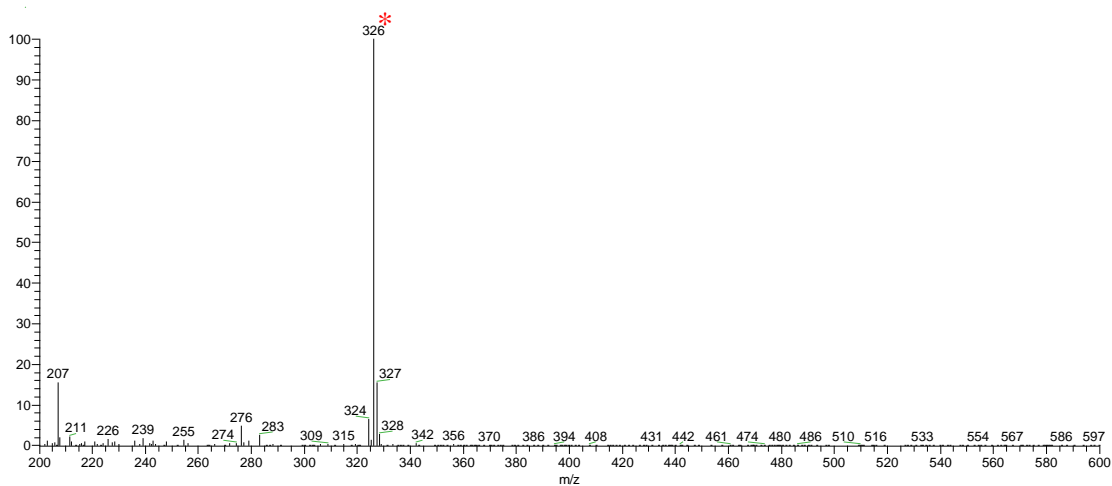
**Figure S19.** Mass spectrum of the peak IX. The \* denotes the ion subjected to fragmentation.



**Figure S20.** Mass spectrum of the peak X. The \* denotes the ion subjected to fragmentation.

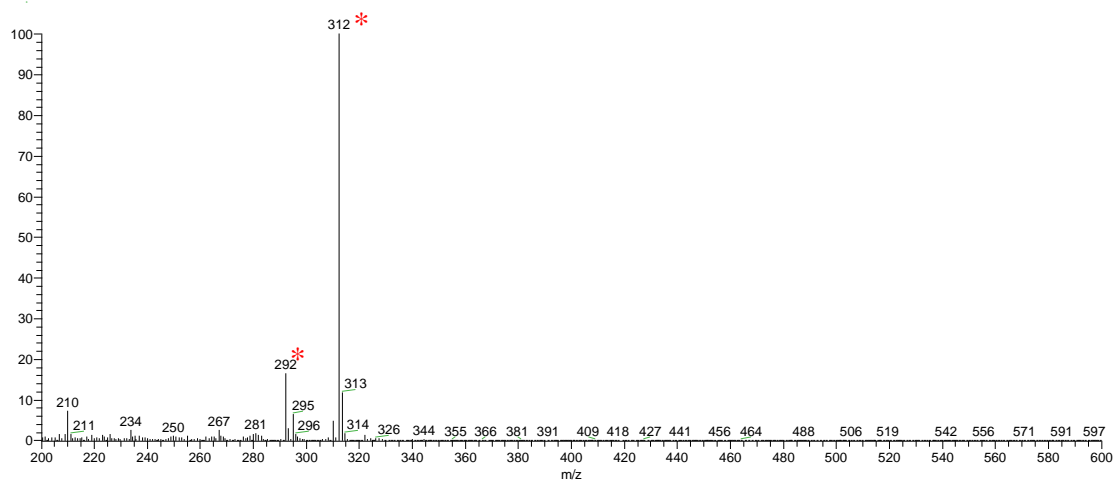


**Figure S21.** Mass spectrum of the peak XI. The \* denotes the ion subjected to fragmentation.

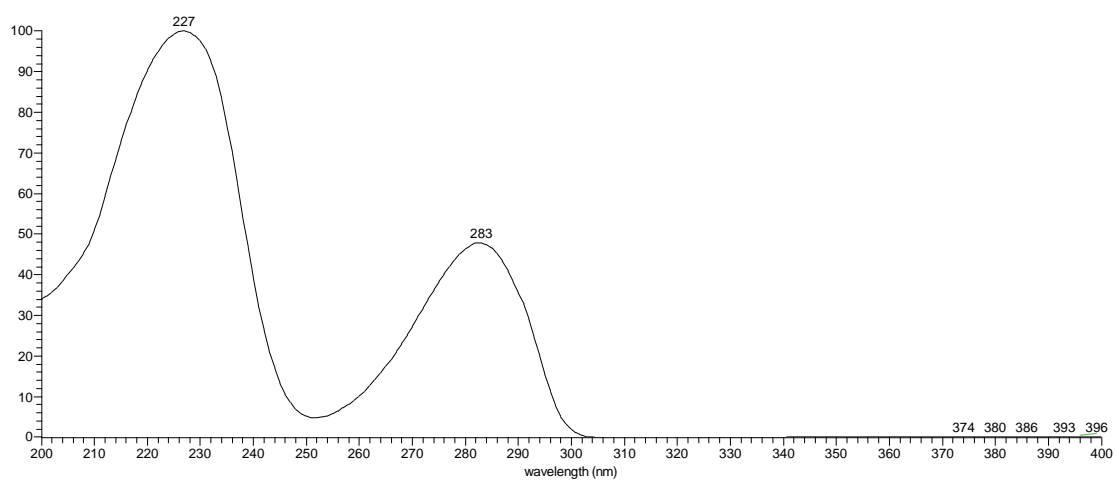


**Figure S22.** Mass spectrum of the peak XII. The \* denotes the ion subjected to fragmentation.

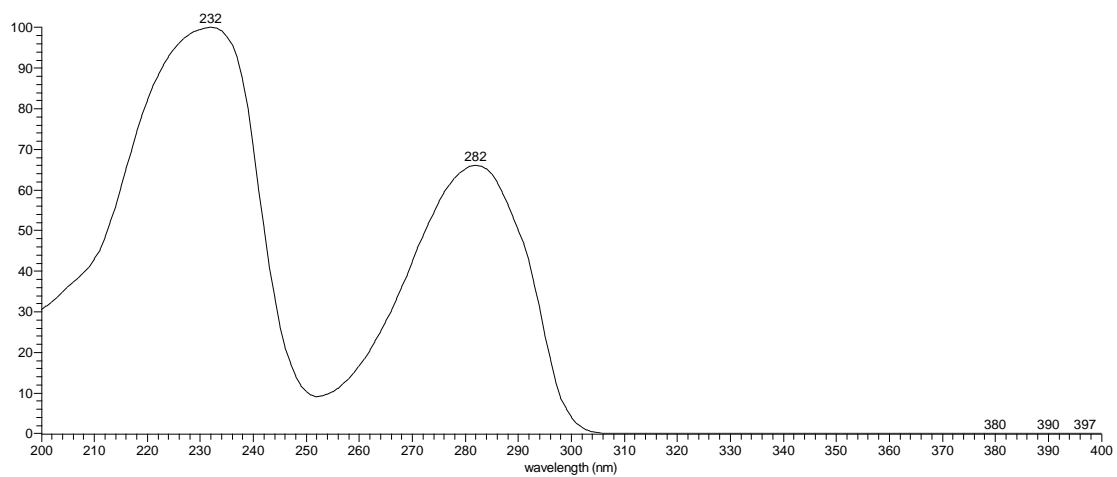




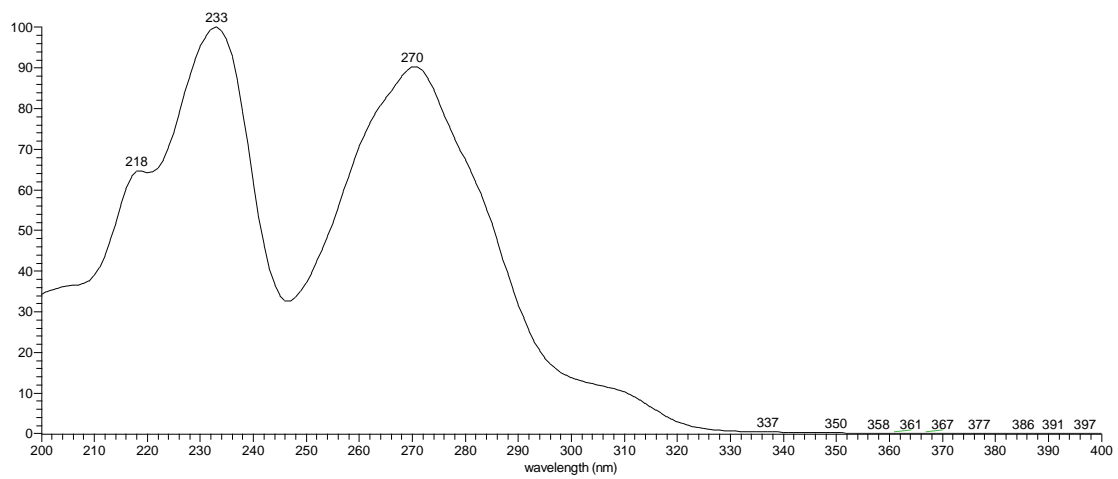
**Figure S23.** Mass spectrum of the peak XIII. The \* denotes the ion subjected to fragmentation.



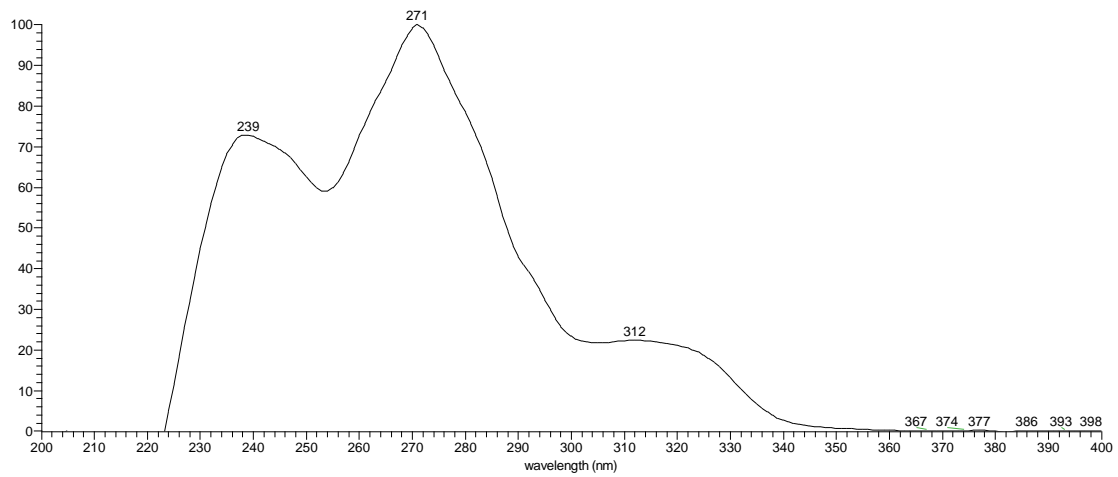
**Figure S24.** DAD spectra to the peak I.



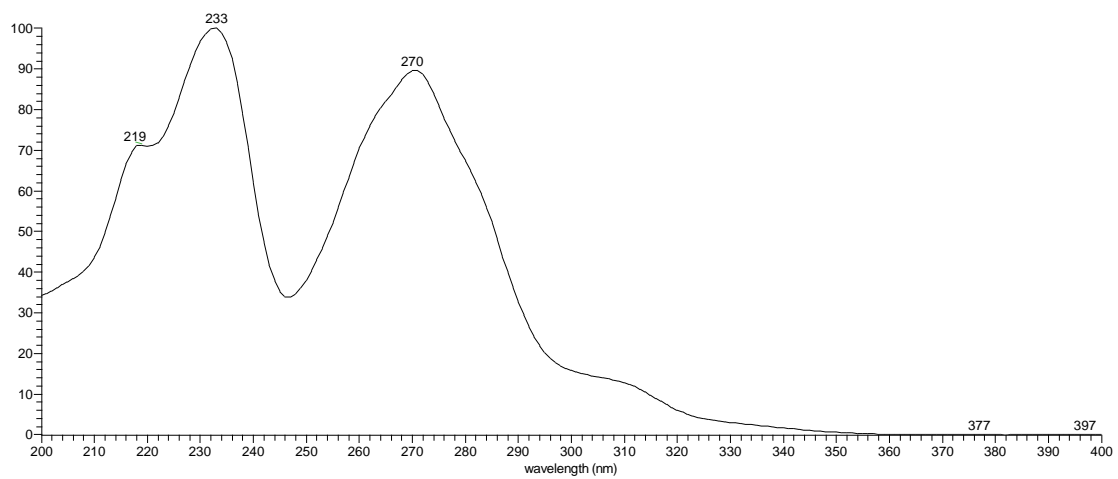
**Figure S25.** DAD spectra to the peak IV.



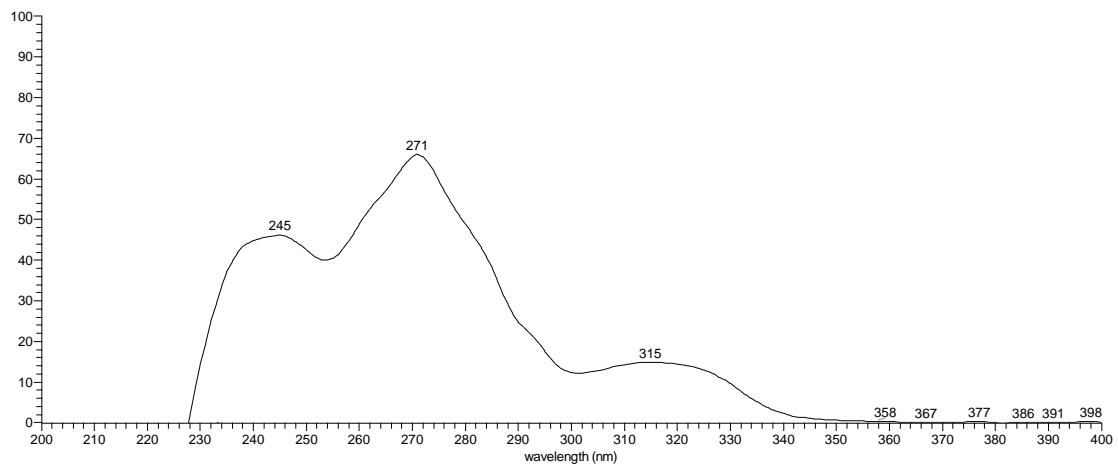
**Figure S26.** DAD spectra to the peak VIII.



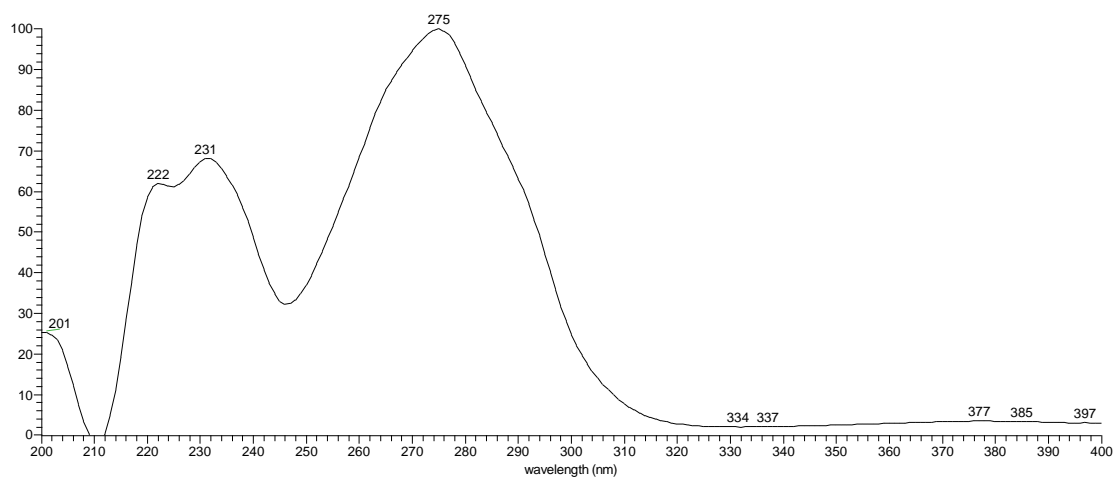
**Figure S27.** DAD spectra to the peak IX.



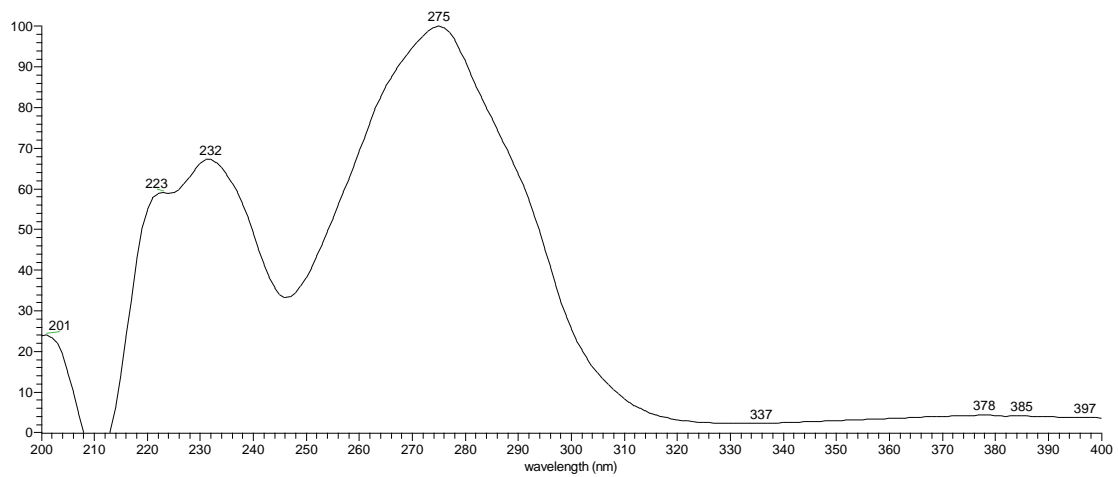
**Figure S28.** DAD spectra to the peak X.



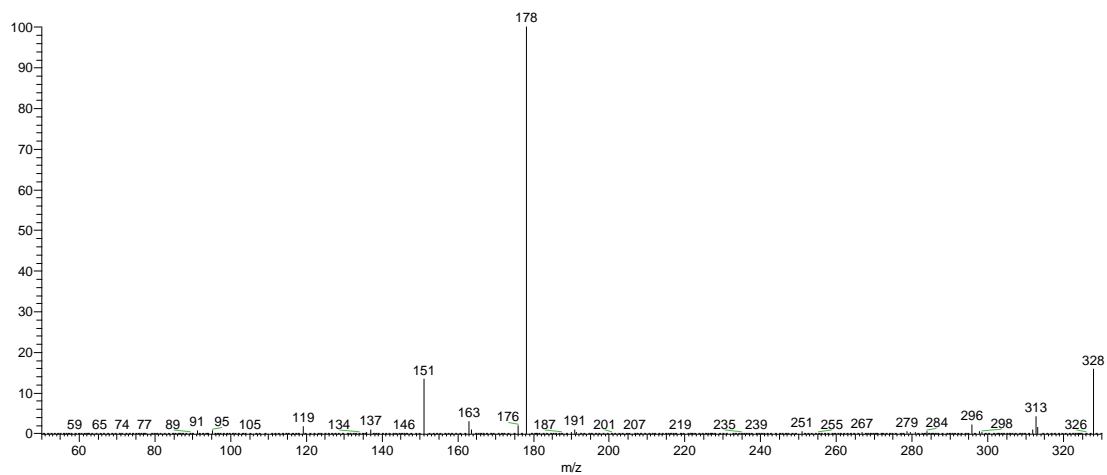
**Figure S29.** DAD spectra to the peak XI.



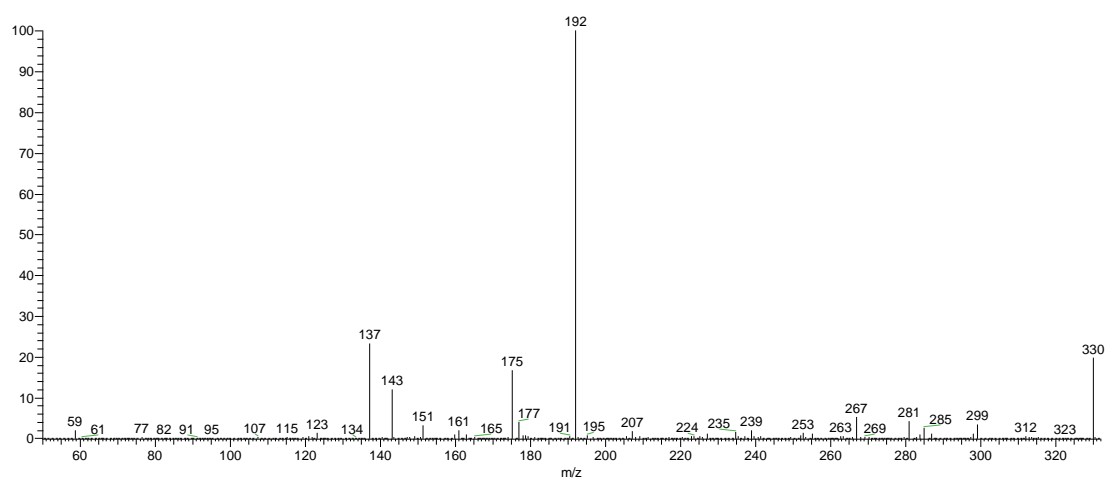
**Figure S30.** DAD spectra to the peak XII.



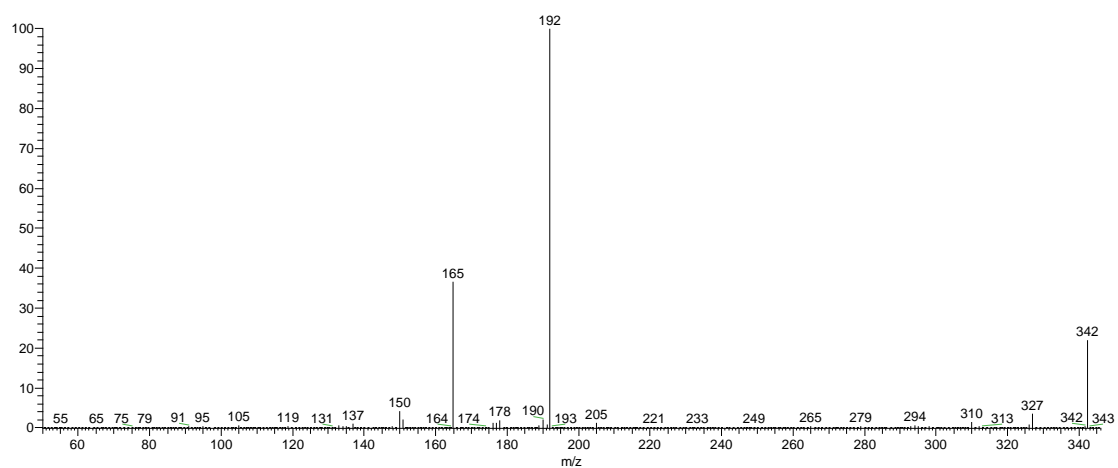
**Figure S31.** DAD spectra to the peak XIII.



**Figure S32.** MS<sup>2</sup> spectrum of the ion at  $m/z$  328 present in the peak I.



**Figure S33.** MS<sup>2</sup> spectrum of the ion at  $m/z$  330 present in the peak II.



**Figure S34.** MS<sup>2</sup> spectrum of the ion at  $m/z$  342 present in the peak III.

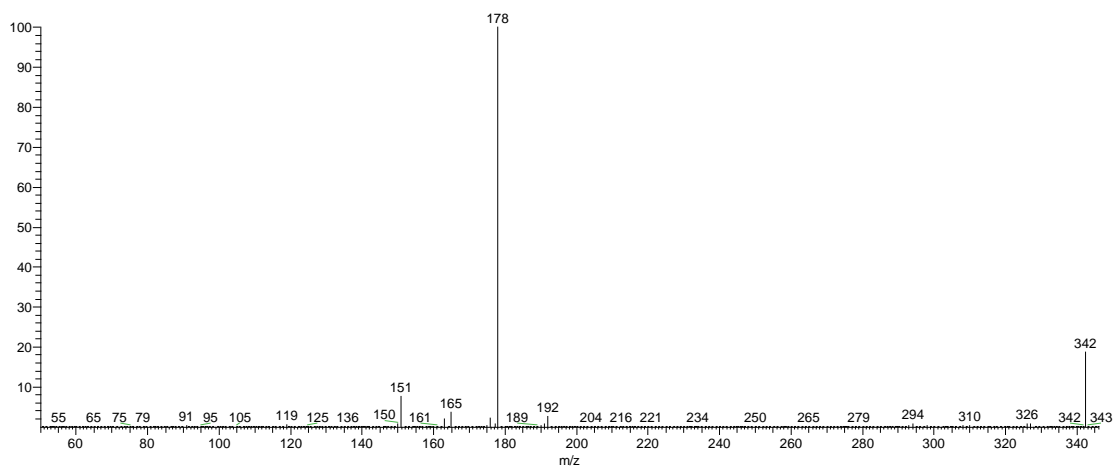


Figure S35. MS<sup>2</sup> spectrum of the ion at  $m/z$  342 present in the peak IV.

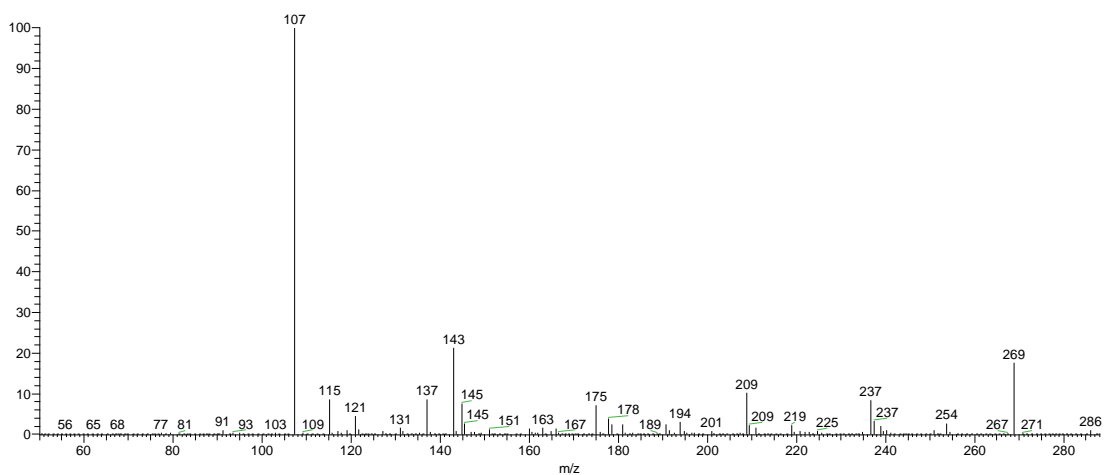


Figure S36. MS<sup>2</sup> spectrum of the ion at  $m/z$  286 present in the peak V.

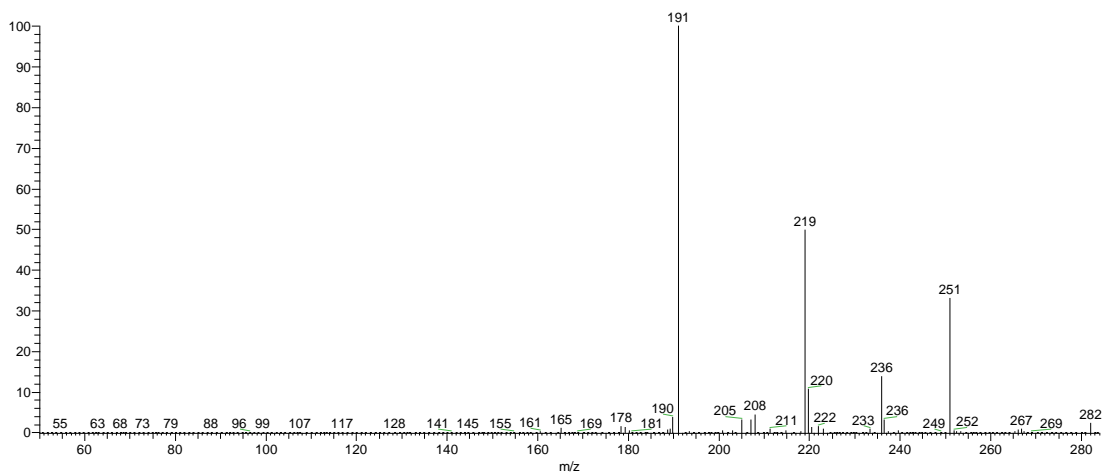


Figure S37. MS<sup>2</sup> spectrum of the ion at  $m/z$  282 present in the peak V.

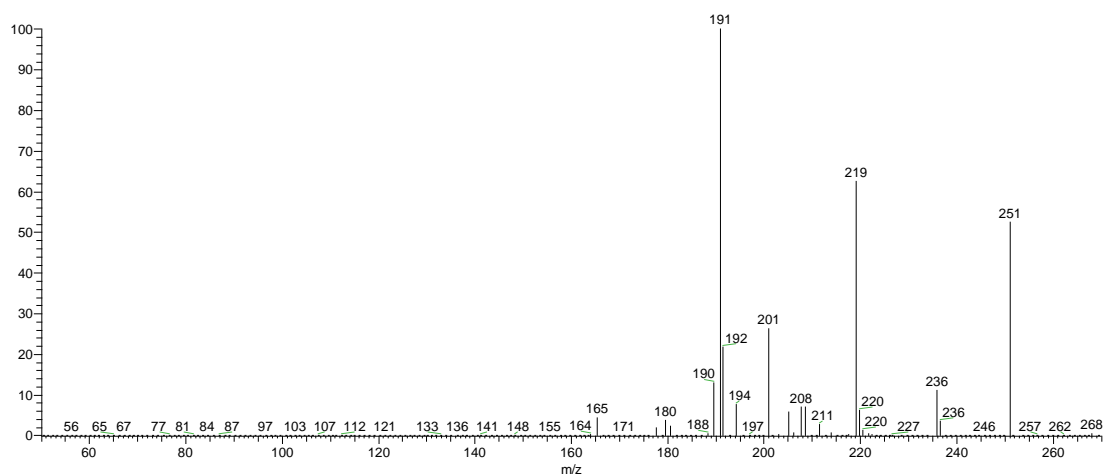


Figure S38. MS<sup>2</sup> spectrum of the ion at  $m/z$  268 present in the peak VI.

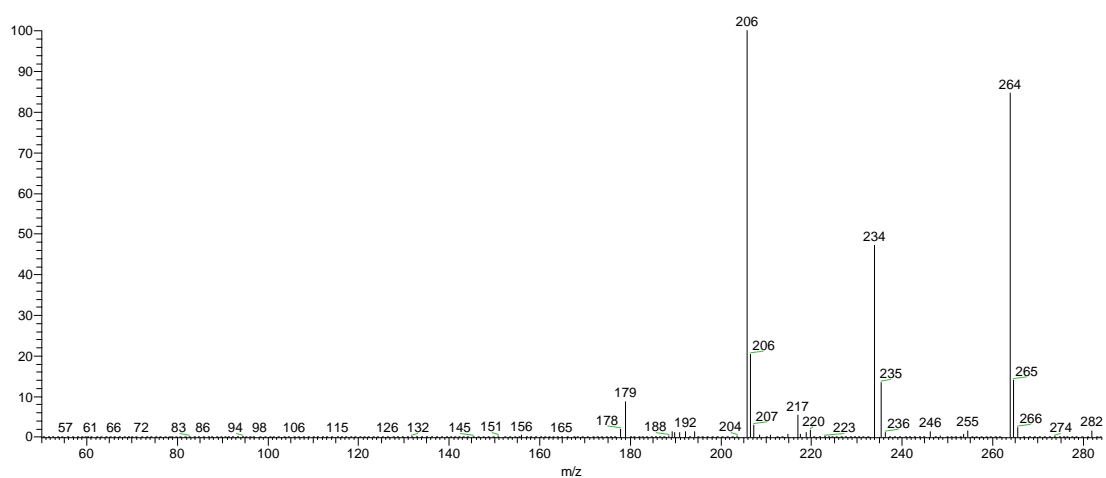


Figure S39. MS<sup>2</sup> spectrum of the ion at  $m/z$  282 present in the peak VII.

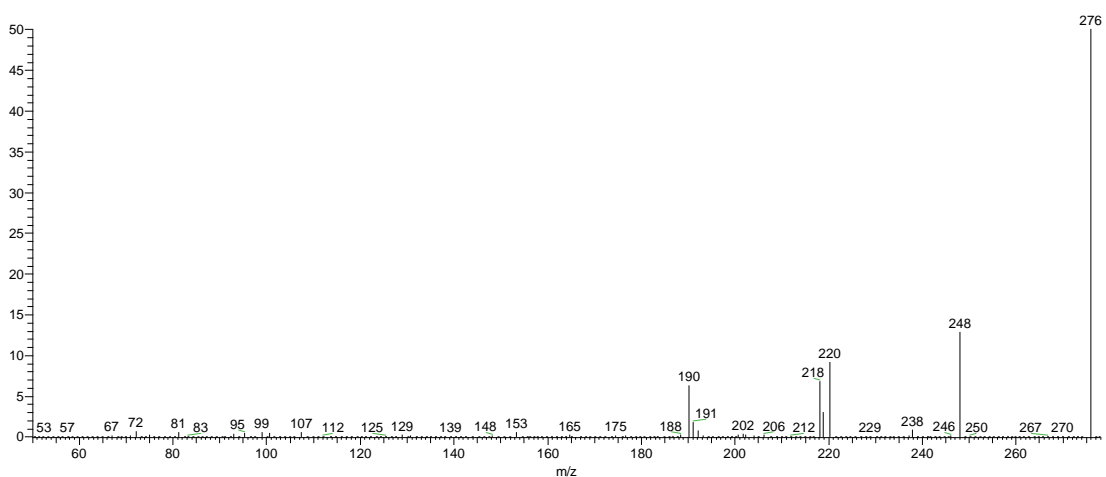


Figure S40. MS<sup>2</sup> spectrum of the ion at  $m/z$  276 present in the peak VII.

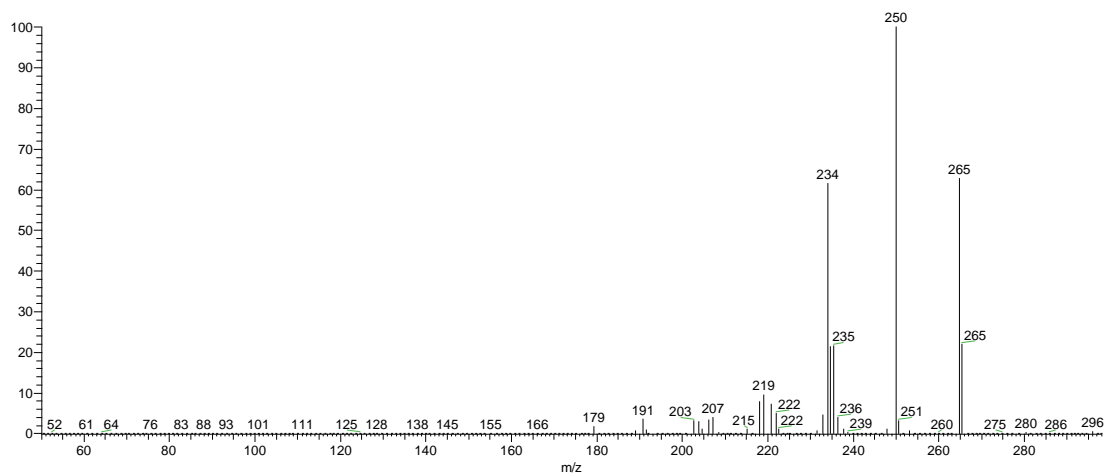


Figure S41. MS<sup>2</sup> spectrum of the ion at  $m/z$  296 present in the peak VIII.

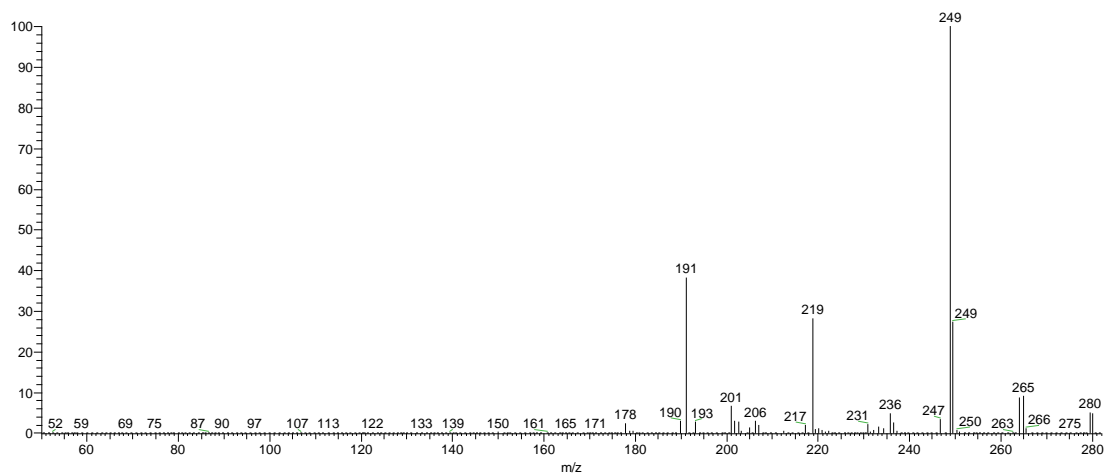


Figure S42. MS<sup>2</sup> spectrum of the ion at  $m/z$  280 present in the peak IX.

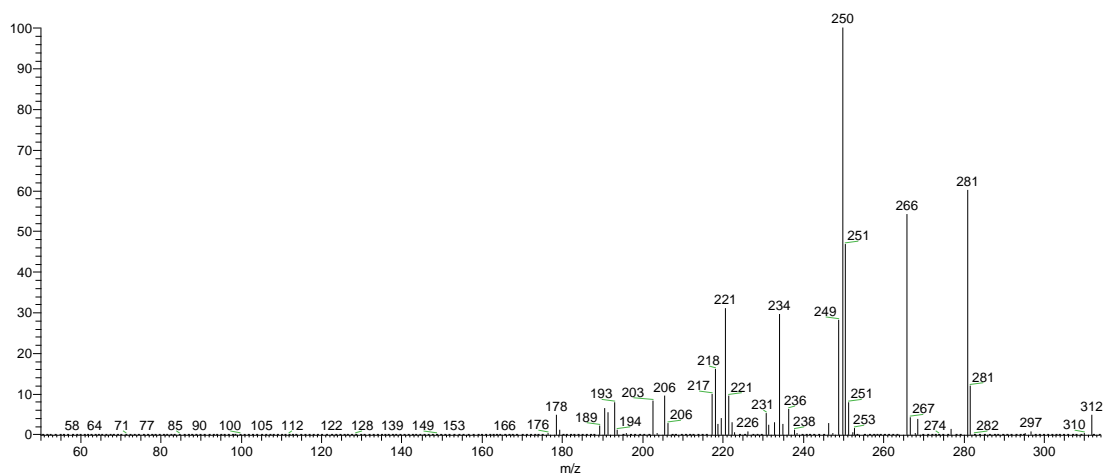


Figure S43. MS<sup>2</sup> spectrum of the ion at  $m/z$  312 present in the peak IX.

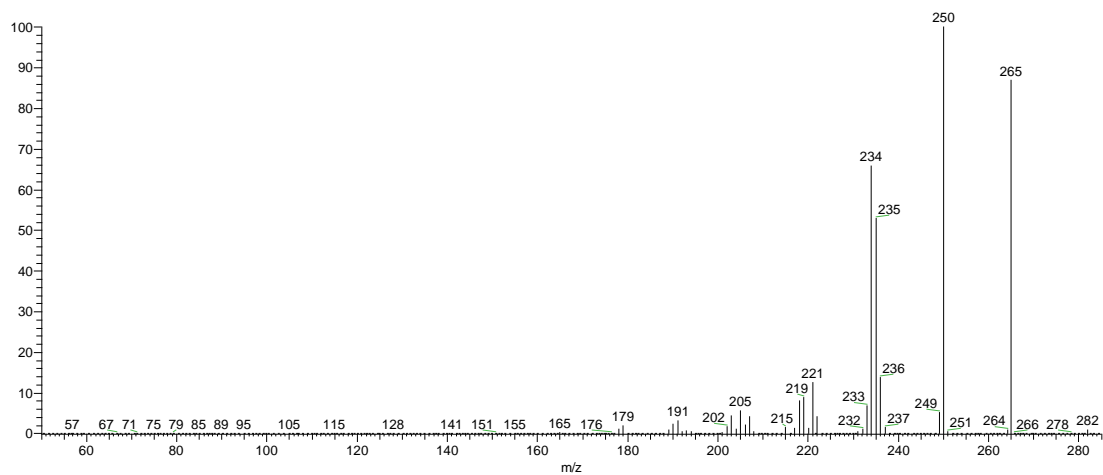


Figure S44. MS<sup>2</sup> spectrum of the ion at  $m/z$  282 present in the peak X.

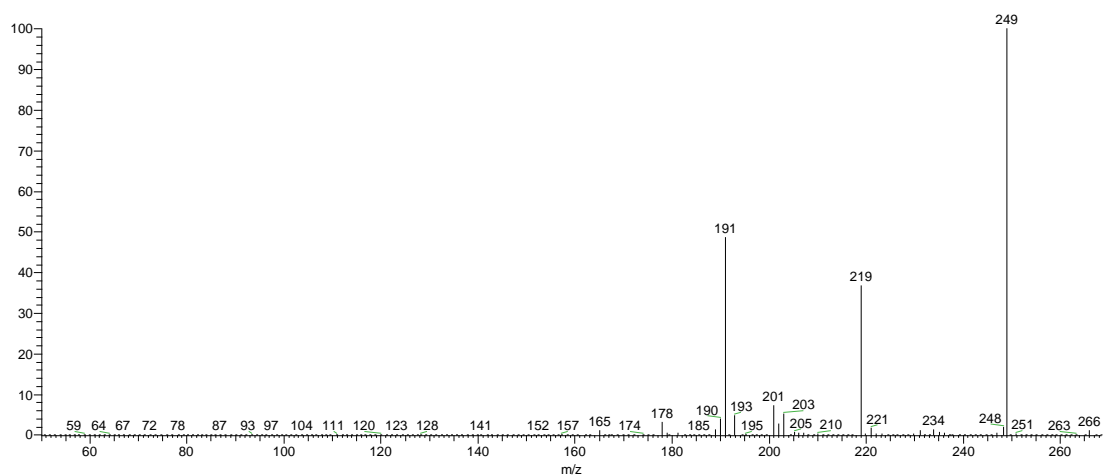


Figure S45. MS<sup>2</sup> spectrum of the ion at  $m/z$  266 present in the peak XI.

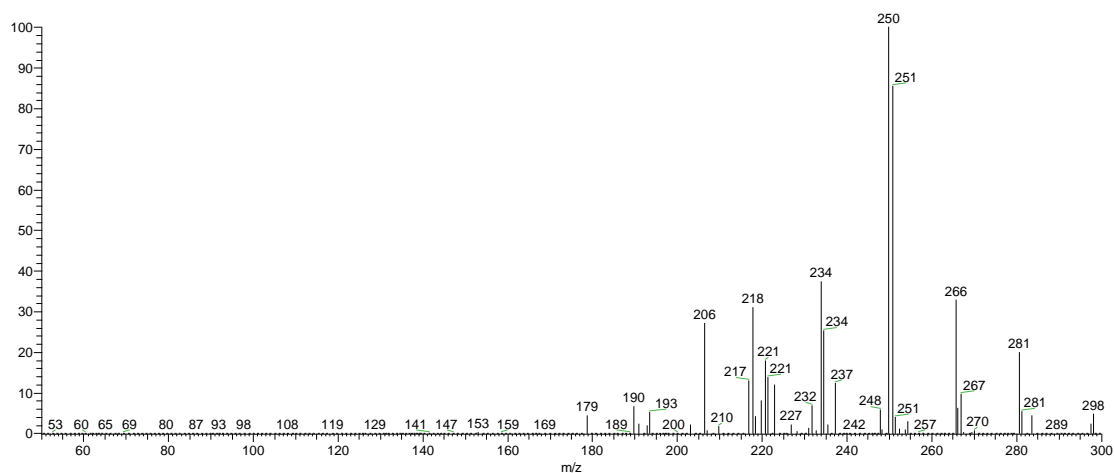
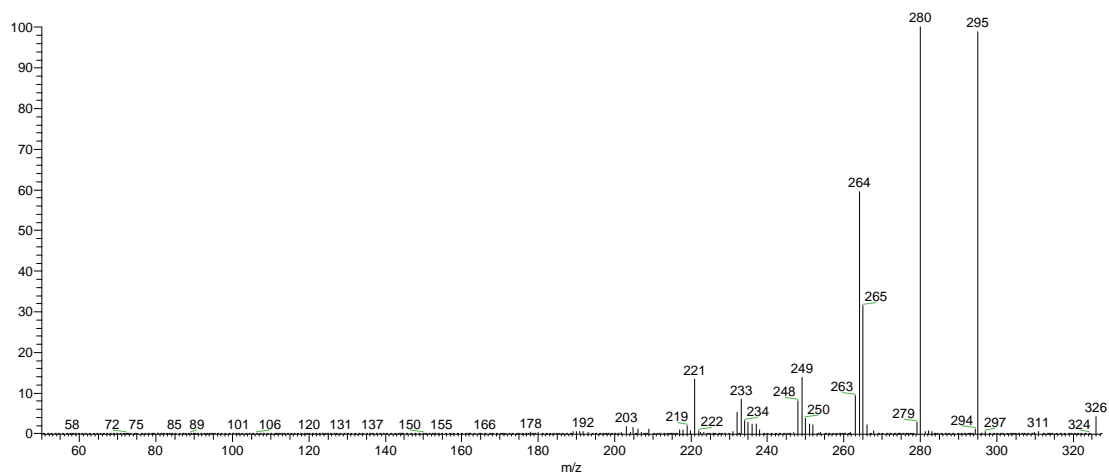
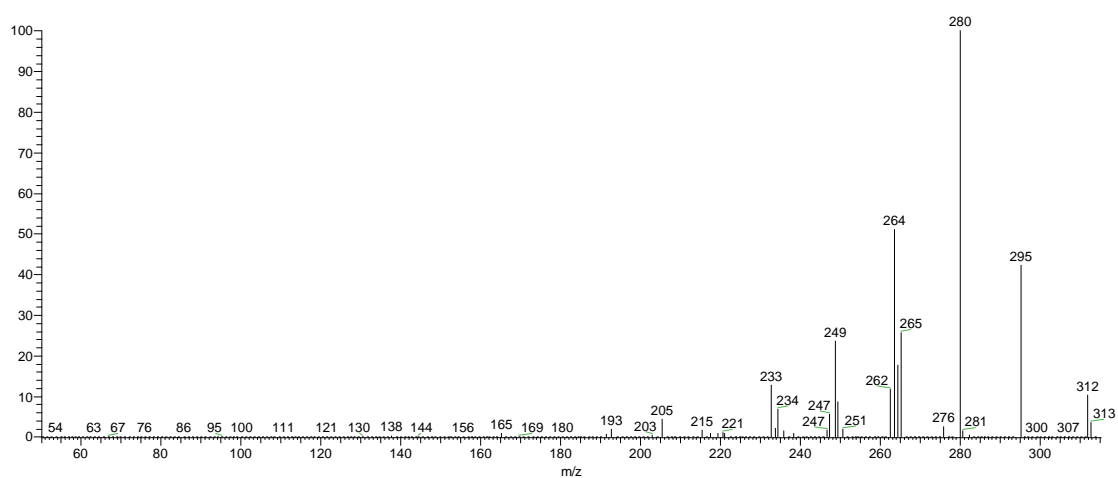


Figure S46. MS<sup>2</sup> spectrum of the ion at  $m/z$  298 present in the peak XI.

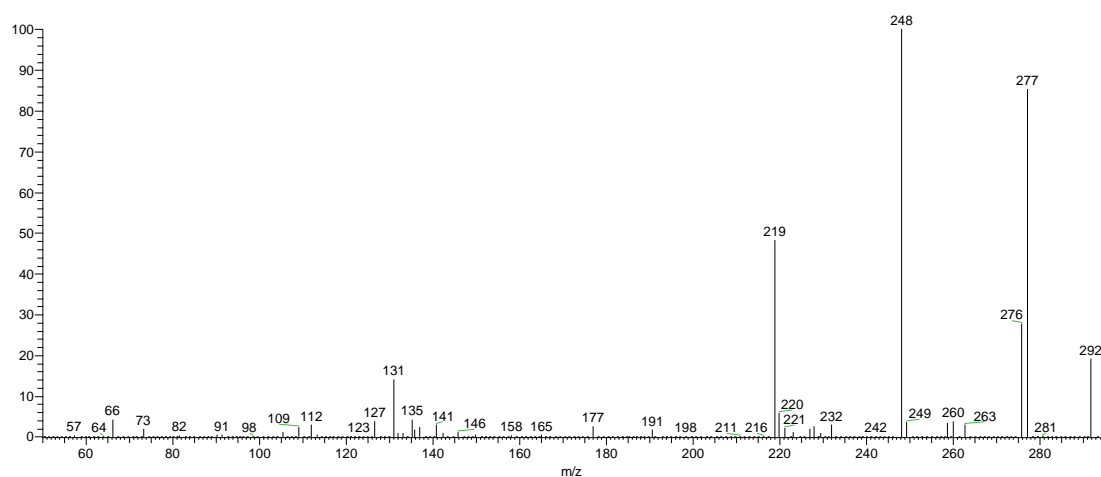




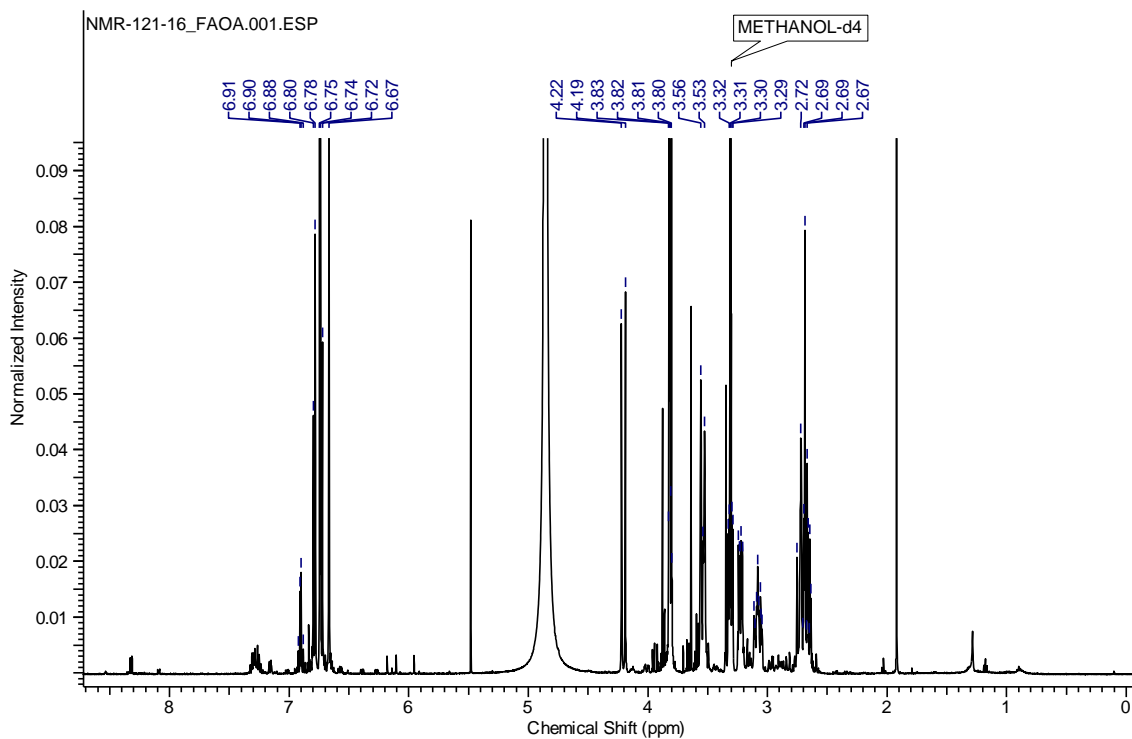
**Figure S47.** MS<sup>2</sup> spectrum of the ion at  $m/z$  326 present in the peak XII.



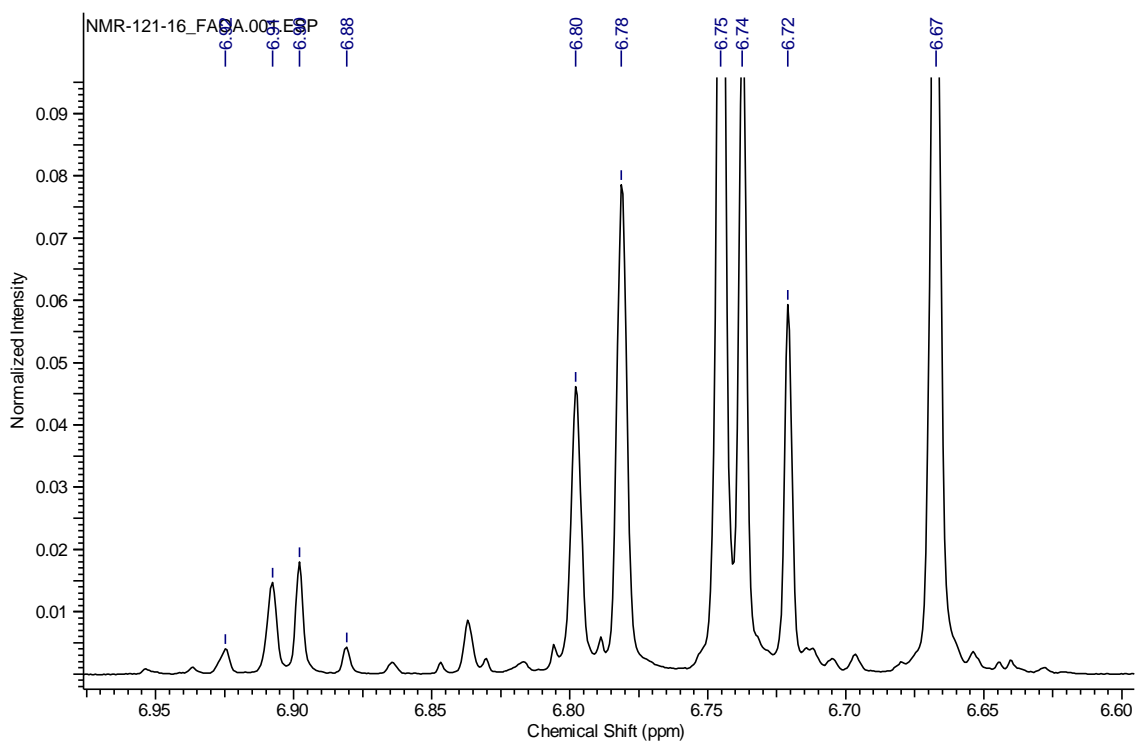
**Figure S48.** MS<sup>2</sup> spectrum of the ion at  $m/z$  312 present in the peak XIII.



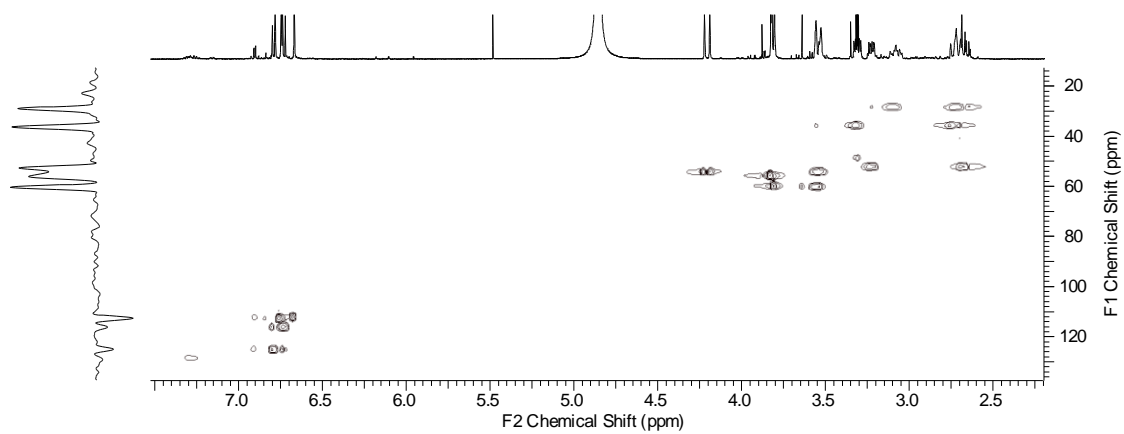
**Figure S49.** MS<sup>2</sup> spectrum of the ion at  $m/z$  292 present in the peak XIII.



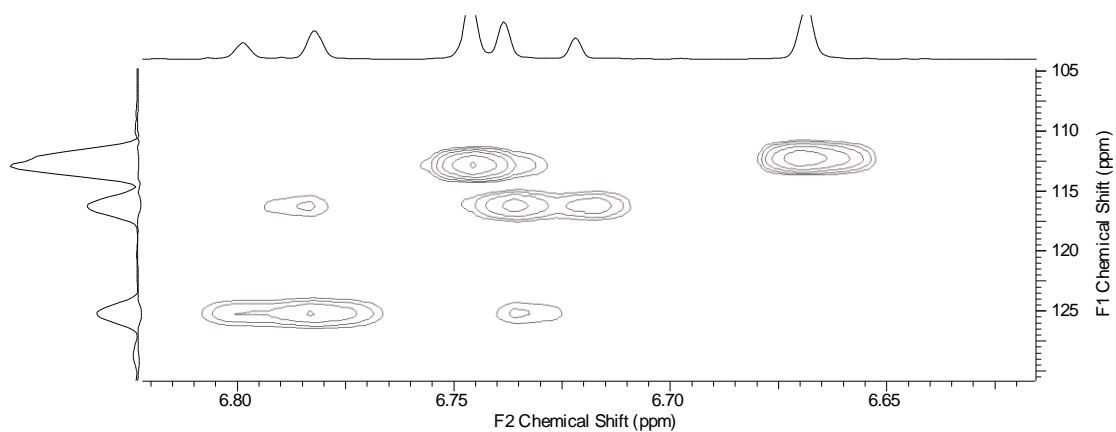
**Figure S50.**  $^1\text{H}$  NMR spectrum (500.13 MHz,  $\text{CD}_3\text{OD}$ ) for the alkaloid fraction.



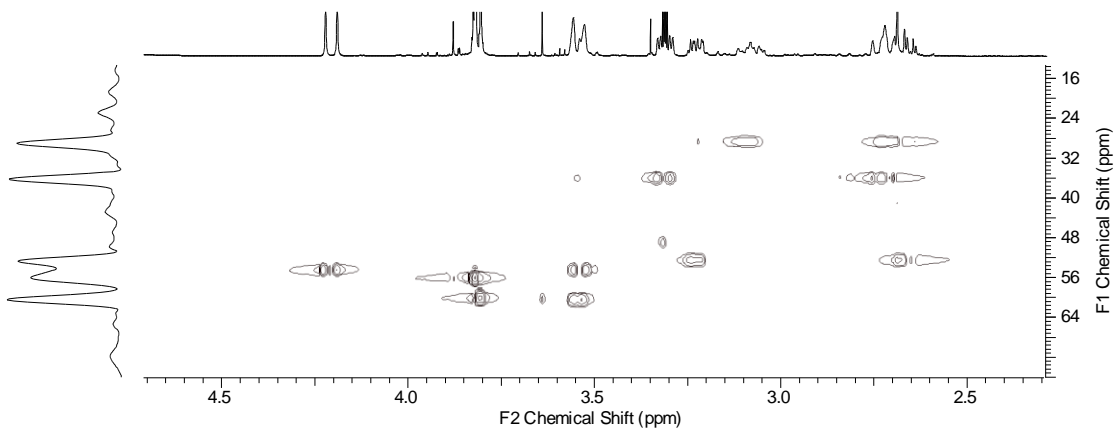
**Figure S51.**  $^1\text{H}$  NMR spectrum (500.13 MHz,  $\text{CD}_3\text{OD}$ ) for the alkaloid fraction.



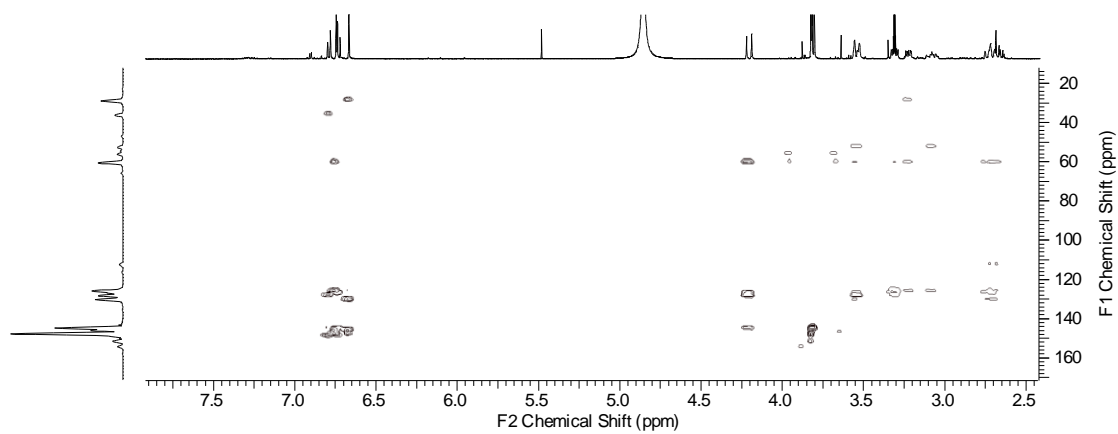
**Figure S52.**  $^1\text{H}$ - $^{13}\text{C}$  correlations observed by HSQC for the alkaloid fraction.



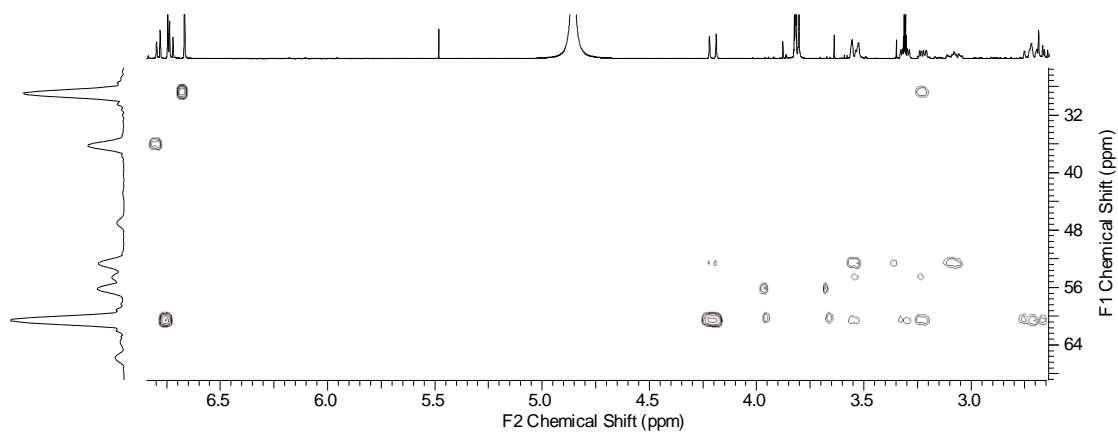
**Figure S53.**  $^1\text{H}$ - $^{13}\text{C}$  correlations observed by HSQC for the alkaloid fraction.



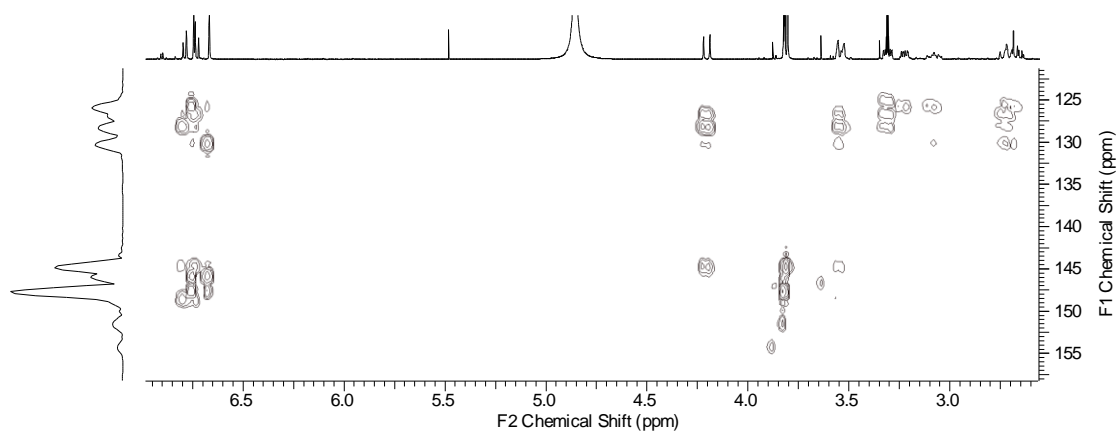
**Figure S54.**  $^1\text{H}$ - $^{13}\text{C}$  correlations observed by HSQC for the alkaloid fraction.



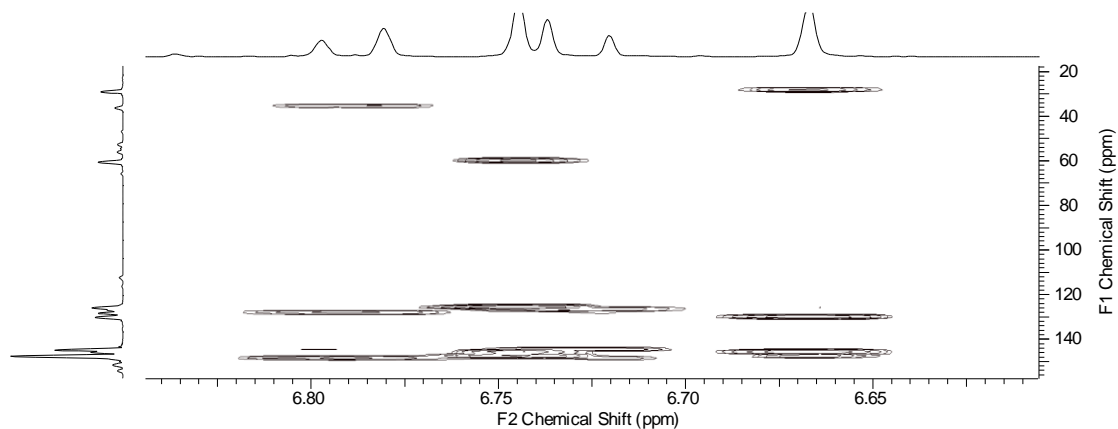
**Figure S55.**  $^1\text{H}$ - $^{13}\text{C}$  correlations observed by HMBC for the alkaloid fraction.



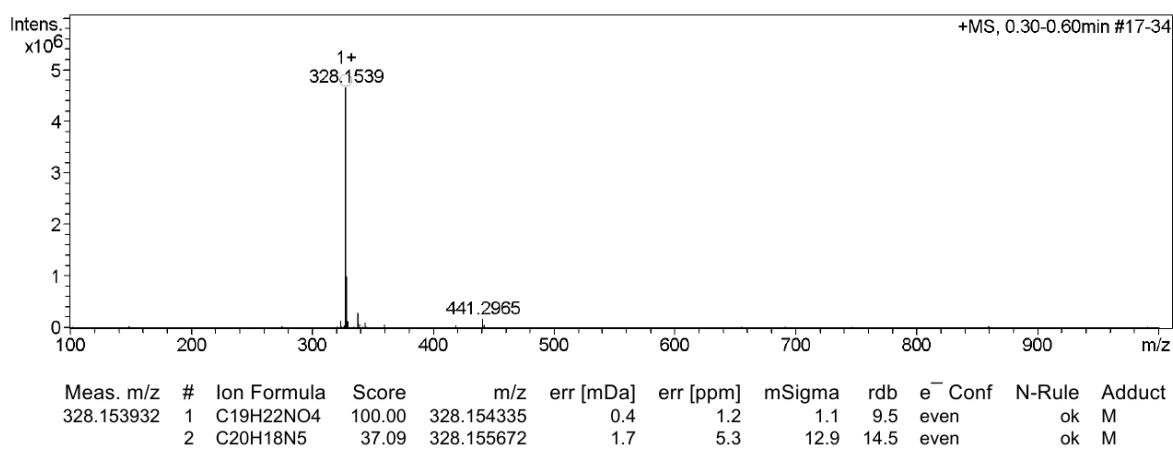
**Figure S56.**  $^1\text{H}$ - $^{13}\text{C}$  correlations observed by HMBC for the alkaloid fraction.



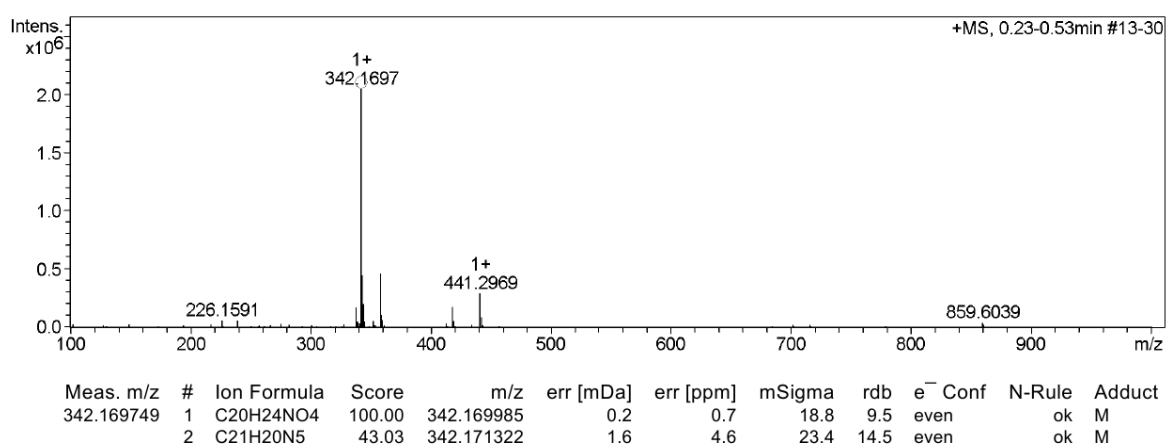
**Figure S57.**  $^1\text{H}$ - $^{13}\text{C}$  correlations observed by HMBC for the alkaloid fraction.



**Figure S58.**  $^1\text{H}$ - $^{13}\text{C}$  correlations observed by HMBC for the alkaloid fraction.



**Figure S59.** High resolution mass spectrum of the ion at  $m/z$  328 present in the peak I (Figure 2b).



**Figure S60.** High resolution mass spectrum of the ion at  $m/z$  342 present in the peak IV (Figure 2b).

**Table S1.** Assignment of  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of the compound **16**

Stepholidine			
Position	$^1\text{H}$ $\delta$ (mult., $J$ in Hz) <sup>a</sup>	$^{13}\text{C}$ <sup>b</sup>	$^{13}\text{C}$ <sup>c</sup>
1	6.67(s)	112.9	112.0
2		145.9	144.6
3		147.9	146.3
4	6.75 (s)	112.3	111.4
4a		125.9	125.5
5	2.72 (m) and 3.08 (m)	28.9	28.7
6	2.67 (m) and 3.22 (m)	52.7	52.0
8	3.53 (m) and 4.19 (d, $J$ 15.9)	54.6	54.1
8a		121.5	127.9
9		144.8	143.4
10		148.7	147.5
11	6.73 (d, $J$ 8.5)	116.3	115.4
12	6.79 (d, $J$ 8.5)	125.2	124.7
12a		126.7	126.4
13	2.74 (m) and 3.30 (m)	36.2	35.8
13a	3.80 (m)	60.5	59.6
13b		130.2	129.9
3-OCH <sub>3</sub>	3.82 (s)	56.3	56.0
9-OCH <sub>3</sub>	3.80 (s)	60.2	60.2

<sup>a</sup>Acquired in CD<sub>3</sub>OD, 500.13 MHz; <sup>b</sup>protonated carbons assigned using an HSQC experiment and quaternary carbons assigned using the HMBC experiment. <sup>c</sup>reference 1.

## Reference

1. Costa, E. V.; Sampaio, M. F. C.; Salvador, M. J.; Nepel, A.; Barison, A.; *Quim. Nova* **2015**, *38*, 769.