Supporting information

Osirisynes G-I, New Long-chain Highly Oxygenated Polyacetylenes from the Mayotte Marine Sponge *Haliclona* sp.

Pierre-Eric Campos[1], Gaëtan Herbette[2], Christophe Chendo[2], Patricia Clerc[1], Florent Tintillier[1], Nicole J. de Voogd[3,4], Eleni-Dimitra Papanagnou[5], Ioannis P. Trougakos[5], Moran Jerabek [6], Jérôme Bignon[7], Géraldine Le Goff[7], Jamal Ouazzani[7] and Anne Gauvin-Bialecki[1]*

[1] Laboratoire de chimie et de biotechnologie des produits naturels, Faculté des Sciences et Technologies, Université de La Réunion, 15 Avenue René Cassin, CS 92003, 97744 Saint-Denis Cedex 9, La Réunion, France
[2] Aix-Marseille Univ, CNRS, Centrale Marseille, FSCM, Spectropole, Campus de St Jérôme-Service 511, 13397 Marseille, France
[3] Naturalis Biodiversity Center, Darwinweg 2, 2333 CR Leiden, Netherlands
[4] Institute of Environmental Sciences, Leiden University, Einsteinweg 2, 2333 CC Leiden, Netherlands
[5] Department of Cell Biology and Biophysics, Faculty of Biology, National and Kapodistrian University of Athens, Athens, 15784, Greece
[6] Crelux GmbH, Am Klopferspitz 19a, 82152 Planegg-Martinsried, Germany
[7] Institut de Chimie des Substances Naturelles, CNRS UPR 2301, Univ. Paris-Sud, Université Paris-Saclay, 1, av. de la Terrasse, 91198 Gif-sur-Yvette, France

Figure S1: HRESIMS spectrum for osirisyne G (**1**) 4
Figure S2: ^{1}H NMR (600 MHz, CD_3OD) spectrum for osirisyne G (**1**) 5
Figure S3: ^{1}H-^{1}H COSY NMR (600 MHz) spectrum for osirisyne G (**1**) 6
Figure S4: ^{1}H-^{13}C HSQC NMR (600 MHz) spectrum for osirisyne G (**1**) 7
Figure S5: ^{1}H-^{13}C HMBC NMR (600 MHz) spectrum for osirisyne G (**1**) 8
Figure S6: HRESIMS spectrum for osirisyne H (**2**) 9
Figure S7: ESI^+-MS/MS (S7.a.) and ESI^--MS/MS (S7.b.) spectra of osirisyne H (**2**) with outlines of dissociation of the precursor ion 10
Figure S8*:* Dissociation mechanisms of the fragmentation of osirisyne H (**2**) in ESI^+-MS/MS with the mass *m/z* of the different fragments. 12
Figure S9: ^{1}H NMR (600 MHz, CD_3OD) spectrum for osirisyne H (**2**) 14
Figure S10: ^{1}H-^{1}H COSY NMR (600 MHz) spectrum for osirisyne H (**2**) 15
Figure S11: ^{1}H-^{13}C HSQC NMR (600 MHz) spectrum for osirisyne H (**2**) 16
Figure S12: ^{1}H-^{13}C HMBC NMR (600 MHz) spectrum for osirisyne H (**2**) 17
Figure S13: ^{1}H-^{13}C HSQC-TOCSY NMR (600 MHz) spectrum for osirisyne H (**2**) 18
Figure S14: HRESIMS spectrum for osirisyne I (**3**) 19
Figure S15*:* ESI^+-MS/MS (S13.a.) and ESI^--MS/MS (S13.b.) spectra of osirisyne I (**3**) with outlines of dissociation of the precursor ion 20
Figure S16*:* Dissociation mechanisms of the fragmentation of osirisyne I (**3**) in ESI^+-MS/MS (14.a.) and ESI^--MS/MS (14.b.) with the mass *m/z* of the different fragments. 22
Figure S17: IRTF spectrum for osirisyne I (**3**) 25
Figure S18: ^{1}H NMR (600 MHz, CD_3OD) spectrum for osirisyne I (**3**) 26
Figure S19: ^{13}C NMR (600 MHz, CD_3OD) spectrum for osirisyne I (**3**) 27
Figure S20: ^{1}H-^{1}H COSY NMR (600 MHz) spectrum for osirisyne I (**3**) 28
Figure S21: ^{1}H-^{13}C HSQC NMR (600 MHz) spectrum for osirisyne I (**3**) 29
Figure S22: ^{1}H-^{13}C HMBC NMR (600 MHz) spectrum for osirisyne I (**3**) 30
Figure S23: ^{1}H-^{1}H NOESY NMR (600 MHz) spectrum for osirisyne I (**3**) 31
Figure S24: ^{1}H-^{13}C TOCSY-HSQC NMR (600 MHz) spectrum for osirisyne I (**3**) 32
Figure S25: HRESIMS spectrum for osirisyne A (**4**) 33
Figure S26*:* ESI^+-MS/MS (S22.a.) and ESI^--MS/MS (S22.b.) spectra of osirisyne A (**4**) with outlines of dissociation of the precursor ion 34
Figure S27: ^{1}H NMR (600 MHz, CD_3OD) spectrum for osirisyne A (**4**) 36
Figure S28: ^{13}C NMR (600 MHz, CD_3OD) spectrum for osirisyne A (**4**) 37
Figure S29: HRESIMS spectrum for osirisyne B (**4**) 38
Figure S30*:* ESI^+-MS/MS (S25.a.) and ESI^--MS/MS (S25.b.) spectra of osirisyne B (**5**) with outlines of dissociation of the precursor ion 39
Figure S31: ^{1}H NMR (600 MHz, CD_3OD) spectrum for osirisyne B (**5**) 41
Figure S32: ^{13}C NMR (600 MHz, CD_3OD) spectrum for osirisyne B (**5**) 42
Figure S33: ^{1}H-^{1}H TOCSY NMR (600 MHz) spectrum for osirisyne B (**5**) 43
Figure S34: HRESIMS spectrum for osirisyne E (**6**) 44
Figure S35*:* ESI^+-MS/MS (S28.a.) and ESI^--MS/MS (S28.b.) spectra of osirisyne E (**6**) with outlines of dissociation of the precursor ion 45
Figure S36: ^{1}H NMR (600 MHz, CD_3OD) spectrum for osirisyne E (**6**) 47
Figure S37: ^{13}C NMR (600 MHz, CD_3OD) spectrum for osirisyne E (**6**) 48

In situ Haliclona sp. photo

S0. Observed data for known compounds.

Osirisyne A (**4**): amorphous solid, ^{1}H and ^{13}C NMR data see **Supporting Information**; HRESIMS *m/z* 811.4996 $[M - H]^-$ (calcd for $C_{47}H_{71}O_{11}^-$, 811.5002).

Osirisyne B (**5**): amorphous solid, ^{1}H and ^{13}C NMR data see **Supporting Information**; HRESIMS *m/z* 795.5049 $[M - H]^-$ *(*calcd for $C_{47}H_{71}O_{10}^-$, 795.5053).

Osirisyne E (**6**): amorphous solid, ^{1}H and ^{13}C data see **Supporting Information**; HRESIMS *m/z* 795.5059 $[M - H]^-$ *(*calcd for $C_{47}H_{71}O_{10}^-$, 795.5053).

Figure S1: HRESIMS spectrum for osirisyne G (**1**)

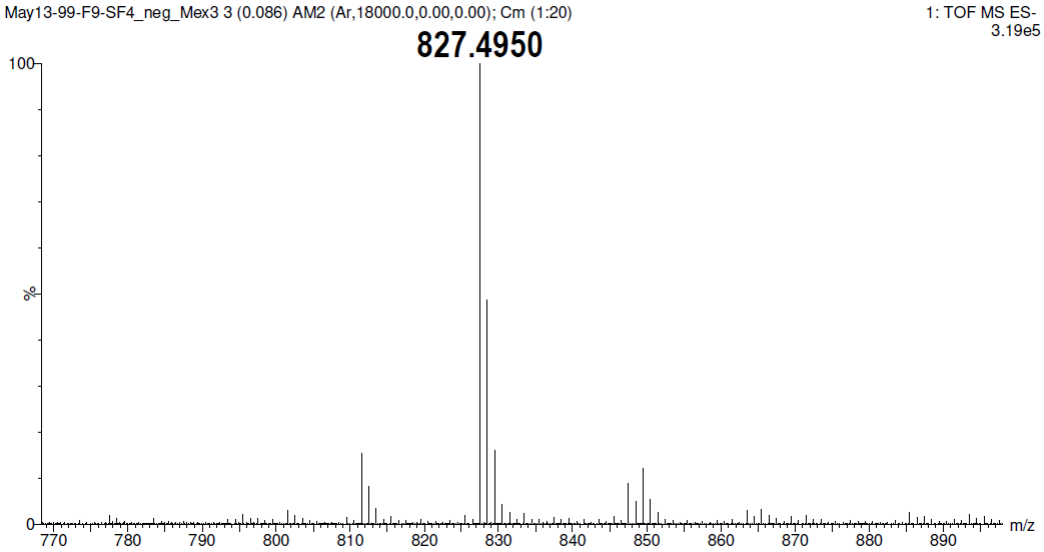


Figure S2: ^{1}H NMR (600 MHz, CD_3OD) spectrum for osirisyne G (**1**)

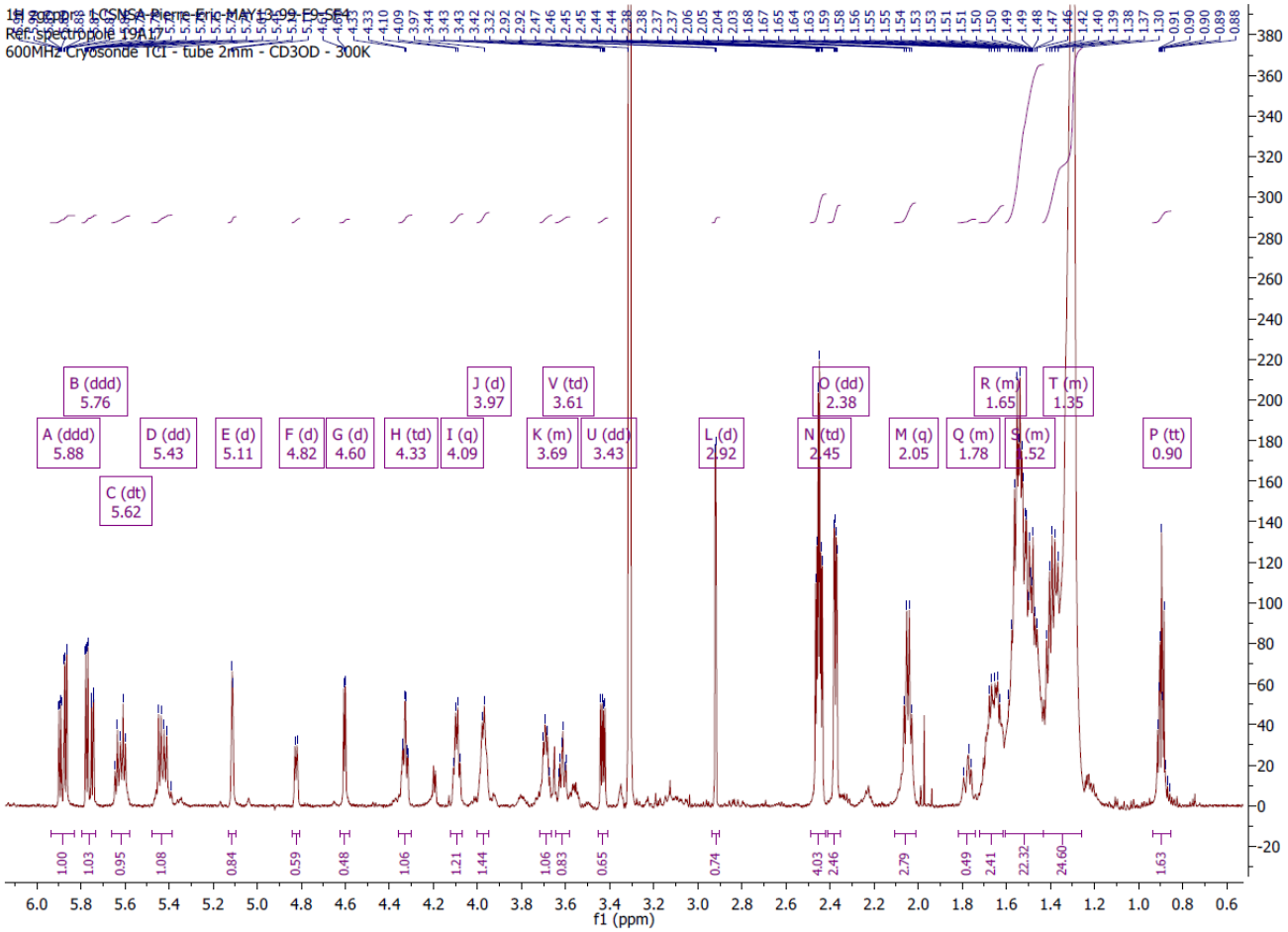


Figure S3: ^{1}H-^{1}H COSY NMR (600 MHz) spectrum for osirisyne G (**1**)

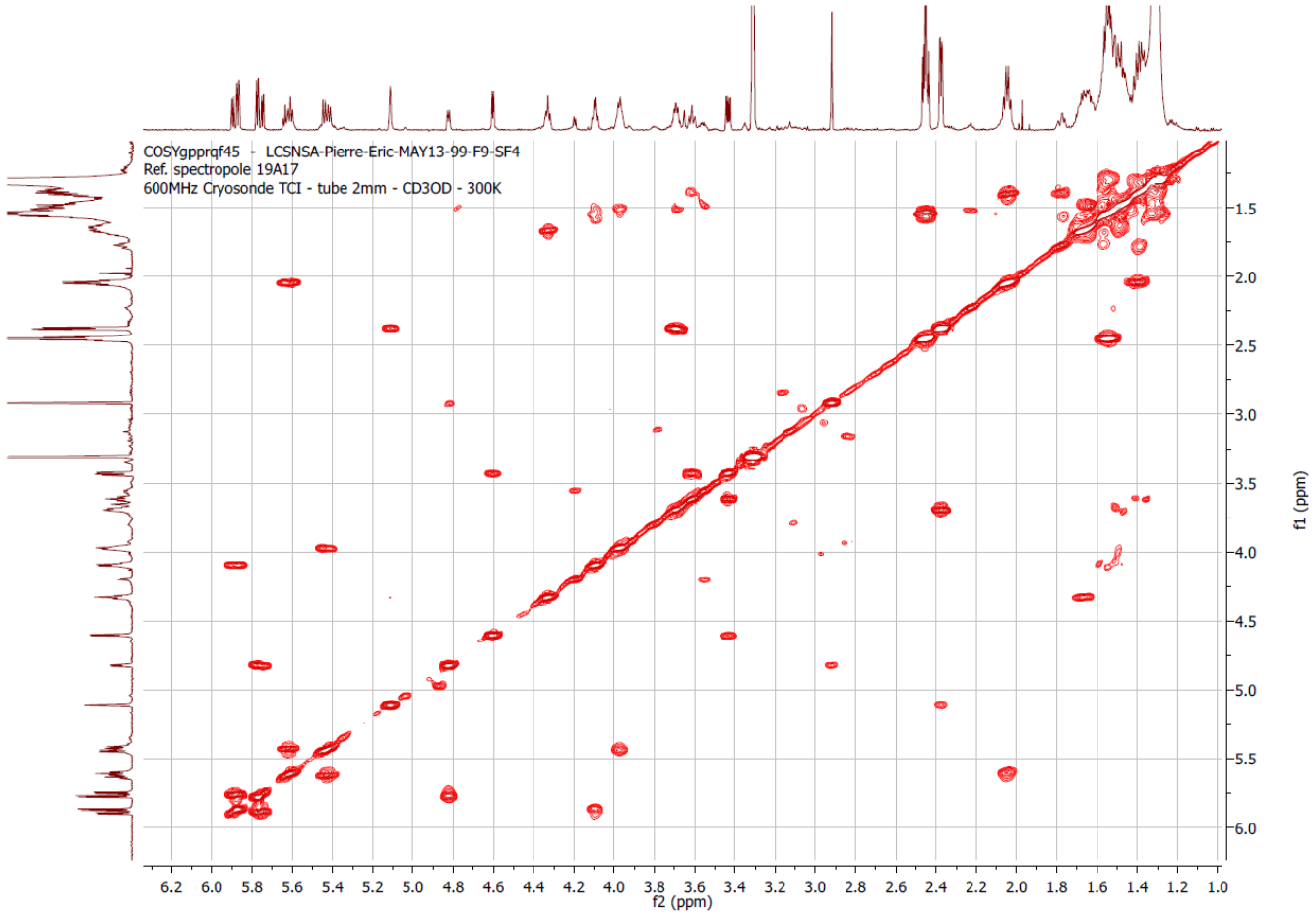


Figure S4: ^{1}H-^{13}C HSQC NMR (600 MHz) spectrum for osirisyne G (**1**)

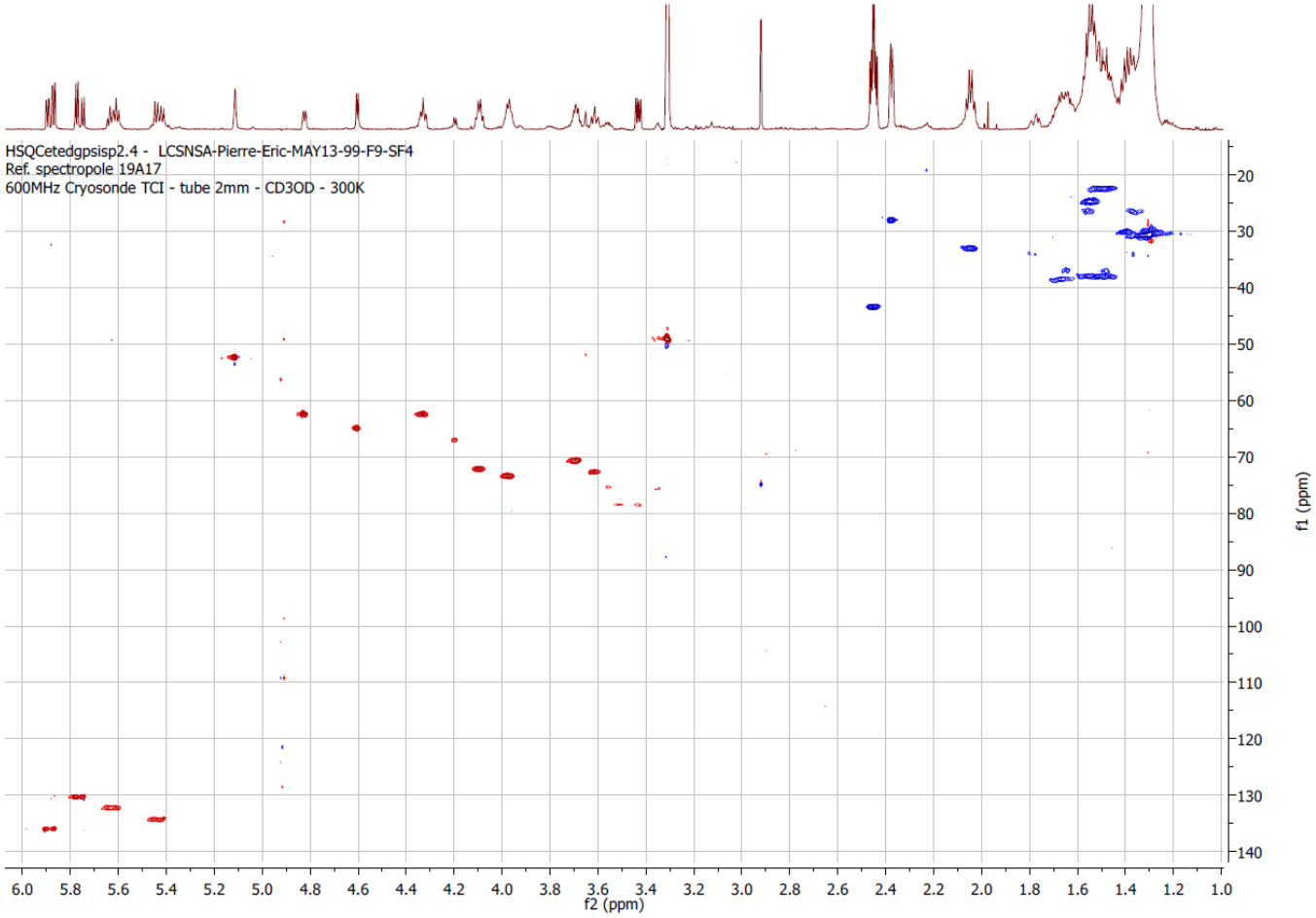


Figure S5: ^{1}H-^{13}C HMBC NMR (600 MHz) spectrum for osirisyne G (**1**)

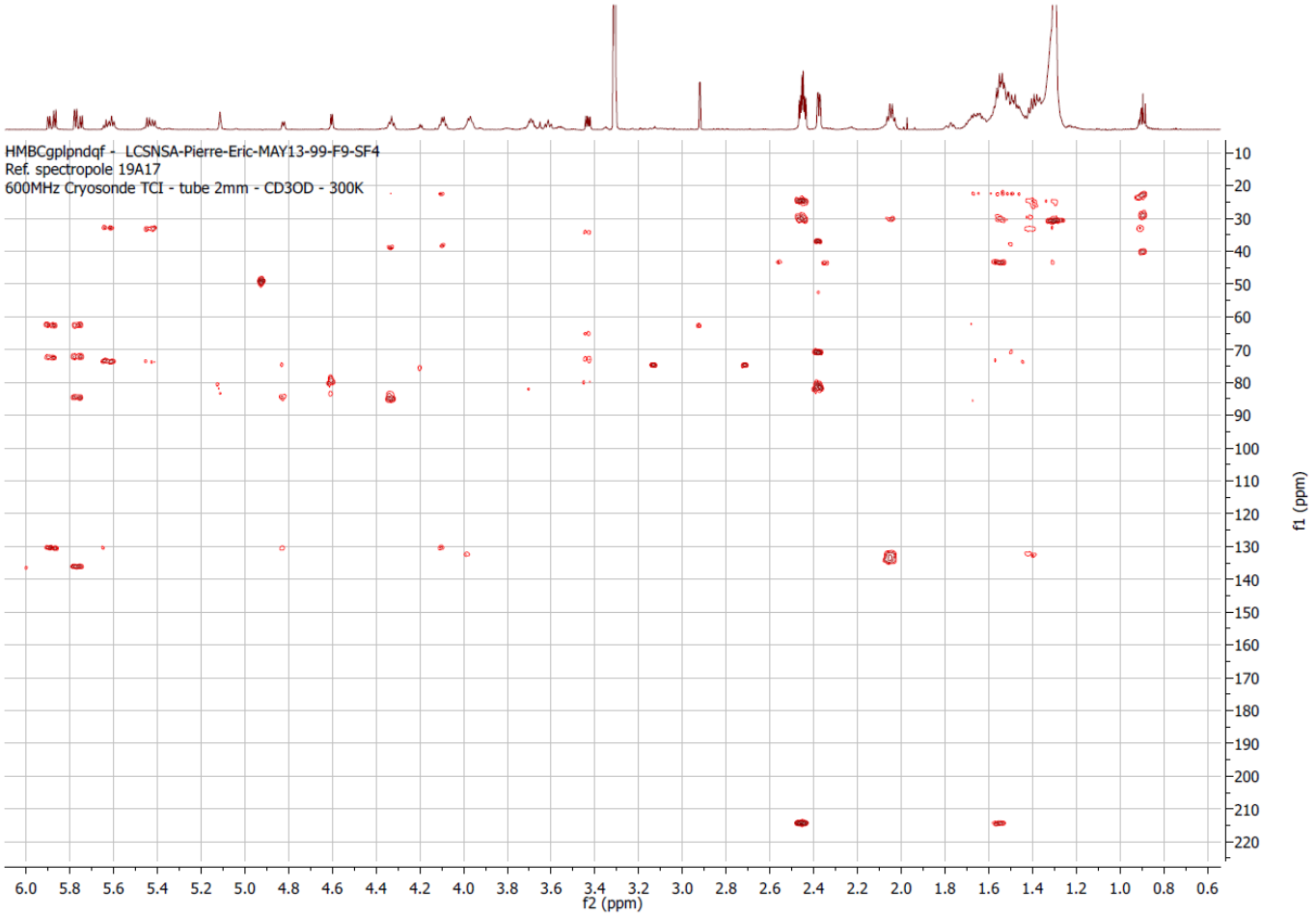


Figure S6: HRESIMS spectrum for osirisyne H (**2**)

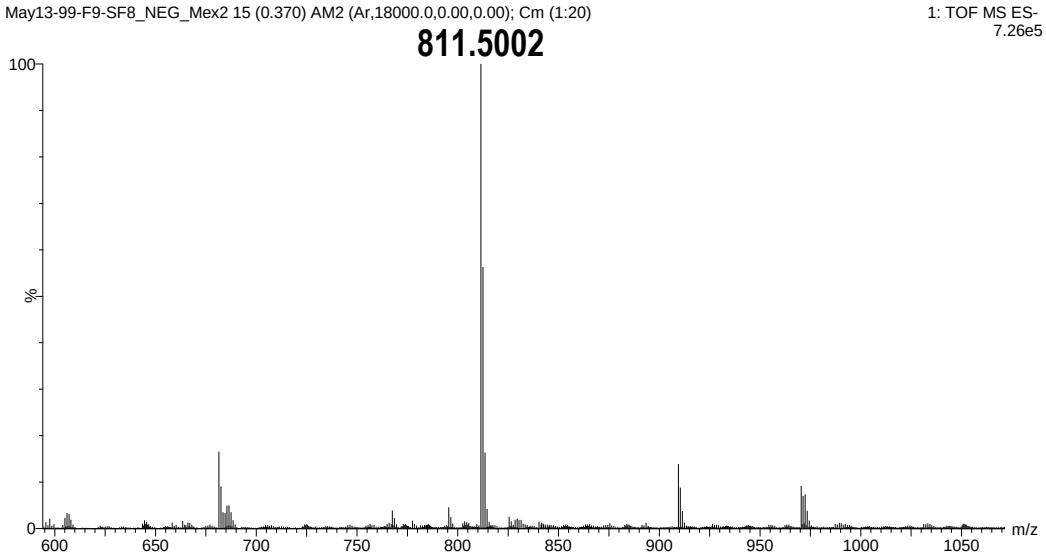
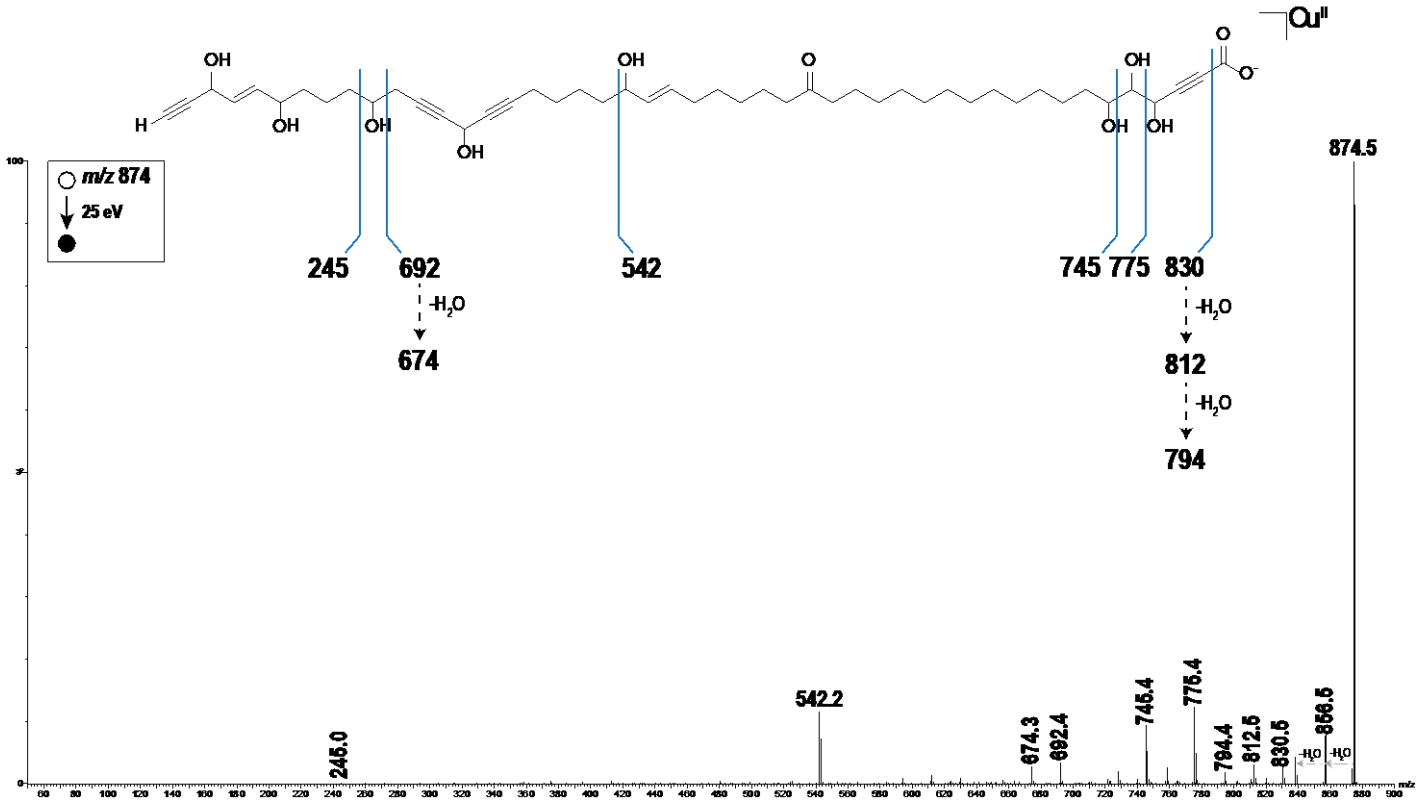


Figure S7: ESI$^+$-MS/MS (S7.a.) and ESI$^-$-MS/MS (S7.b.) spectra of osirisyne H (**2**) with outlines of dissociation of the precursor ion.

S7.a



S7.b.

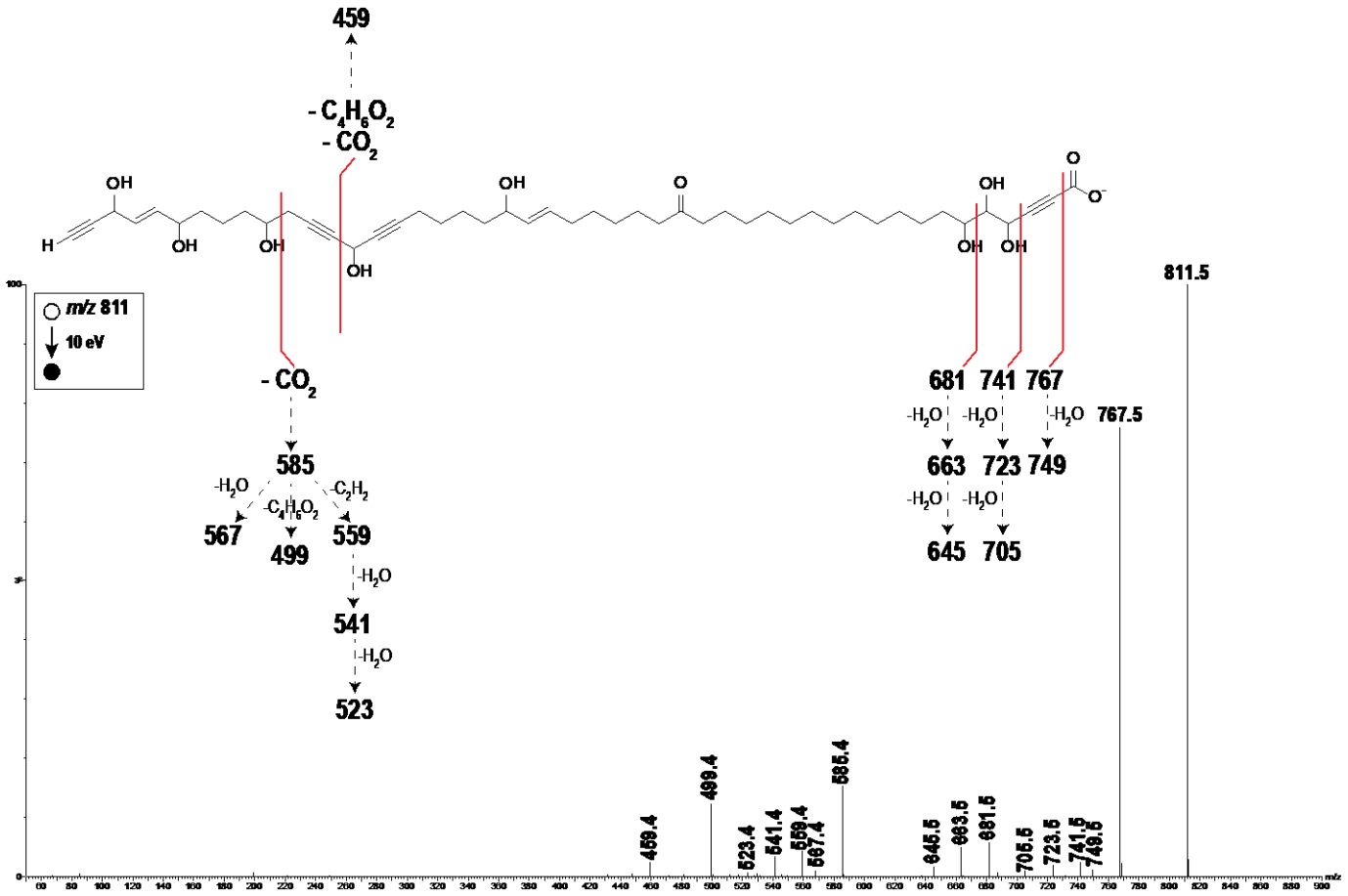
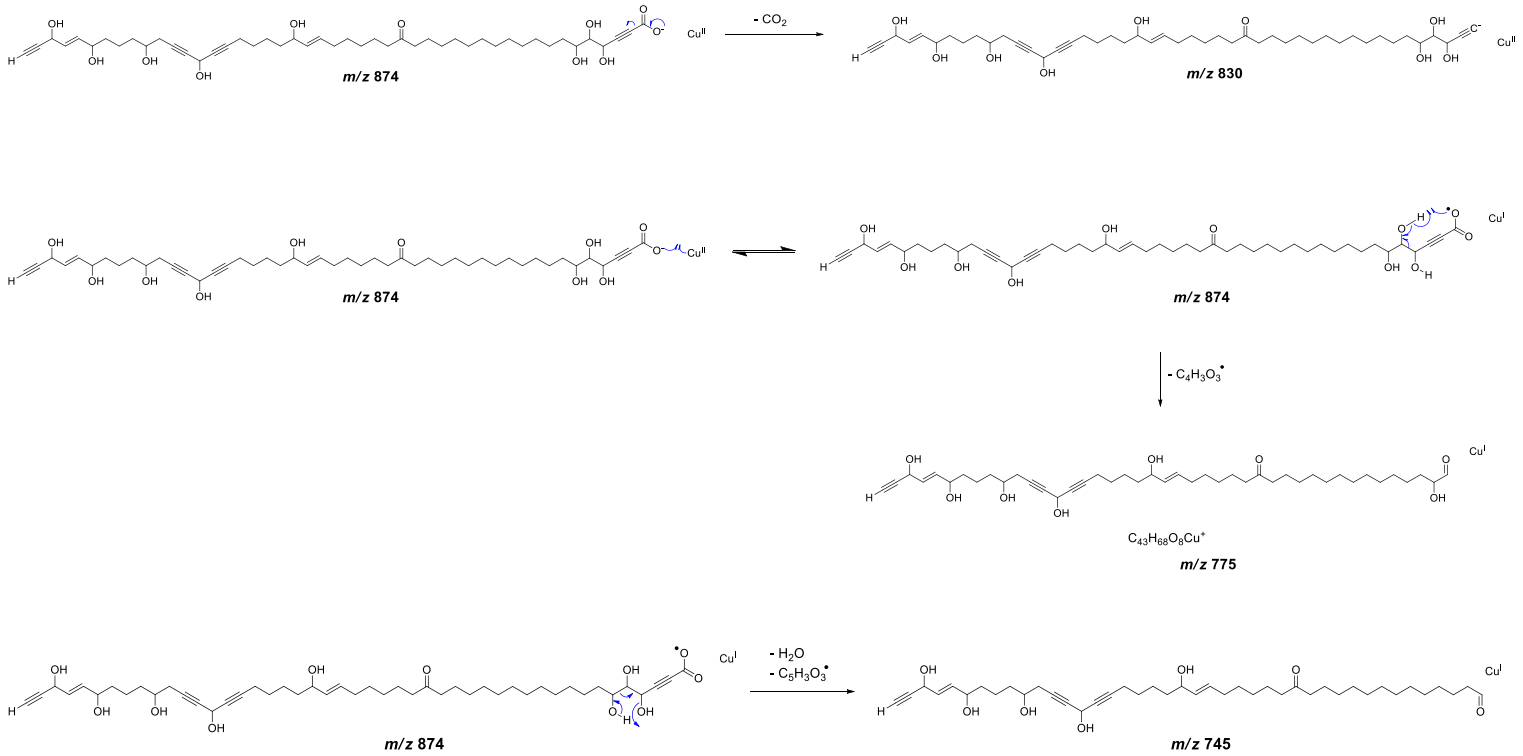

459
- C4H6O2
- CO2
OH
OH
OH
OH
OH
OH
OH
O
O
O-
H
m/z 811
10 eV
- CO2
585
-H2O
-C2H2
-C4H6O2
567
499
559
-H2O
541
-H2O
523
681 741 767
-H2O
-H2O
-H2O
767.5
663 723 749
-H2O
-H2O
645 705
811.5
468.4
499.4
523.4
541.4
559.4
567.4
585.4
645.5
663.5
681.5
706.5
723.5
741.5
749.5

Figure S8*:* Dissociation mechanisms of the fragmentation of osirisyne H (**2**) in ESI$^+$-MS/MS with the mass *m/z* of the different fragments.



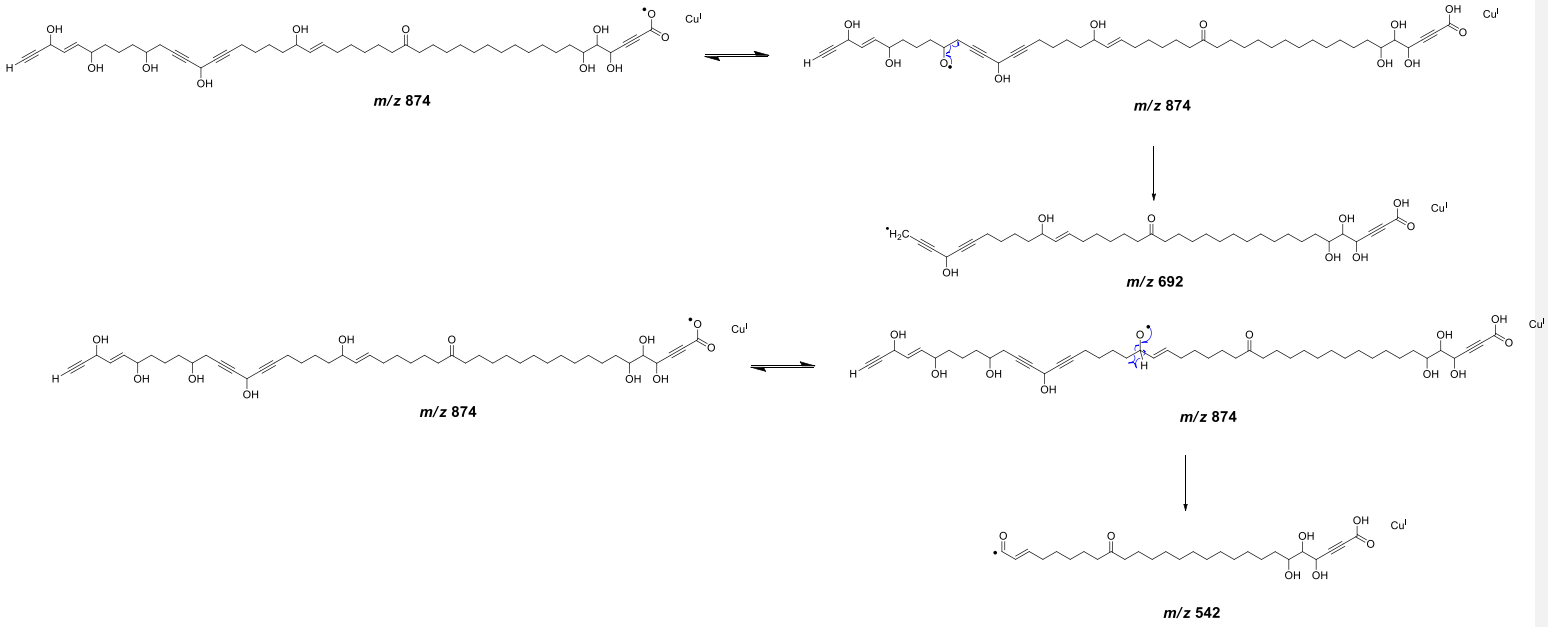

m/z 874
m/z 874
m/z 692
m/z 874
m/z 874
m/z 542

Figure S9: ^{1}H NMR (600 MHz, CD_3OD) spectrum for osirisyne H (**2**)

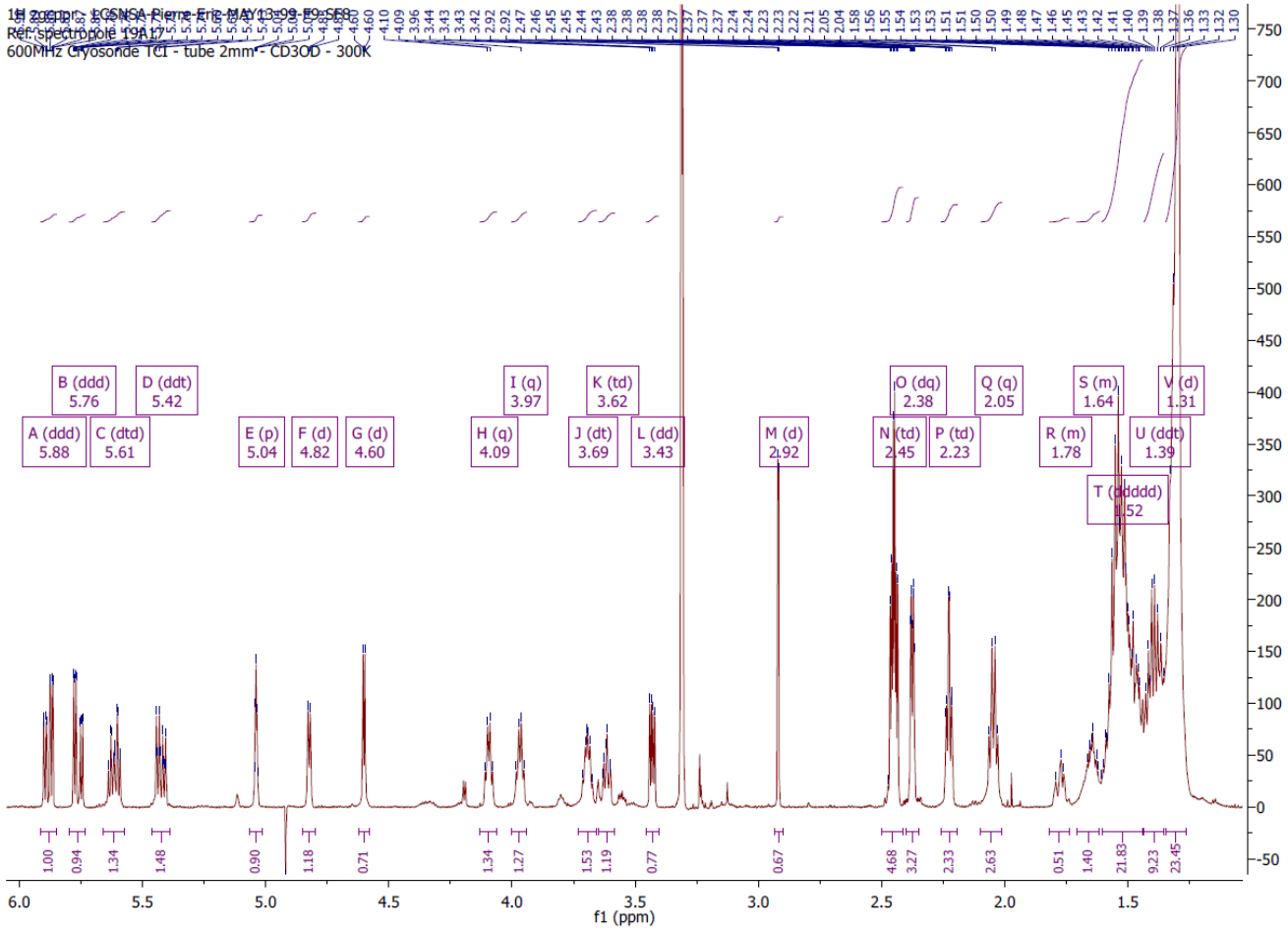


Figure S10: ^{1}H-^{1}H COSY NMR (600 MHz) spectrum for osirisyne H (**2**)

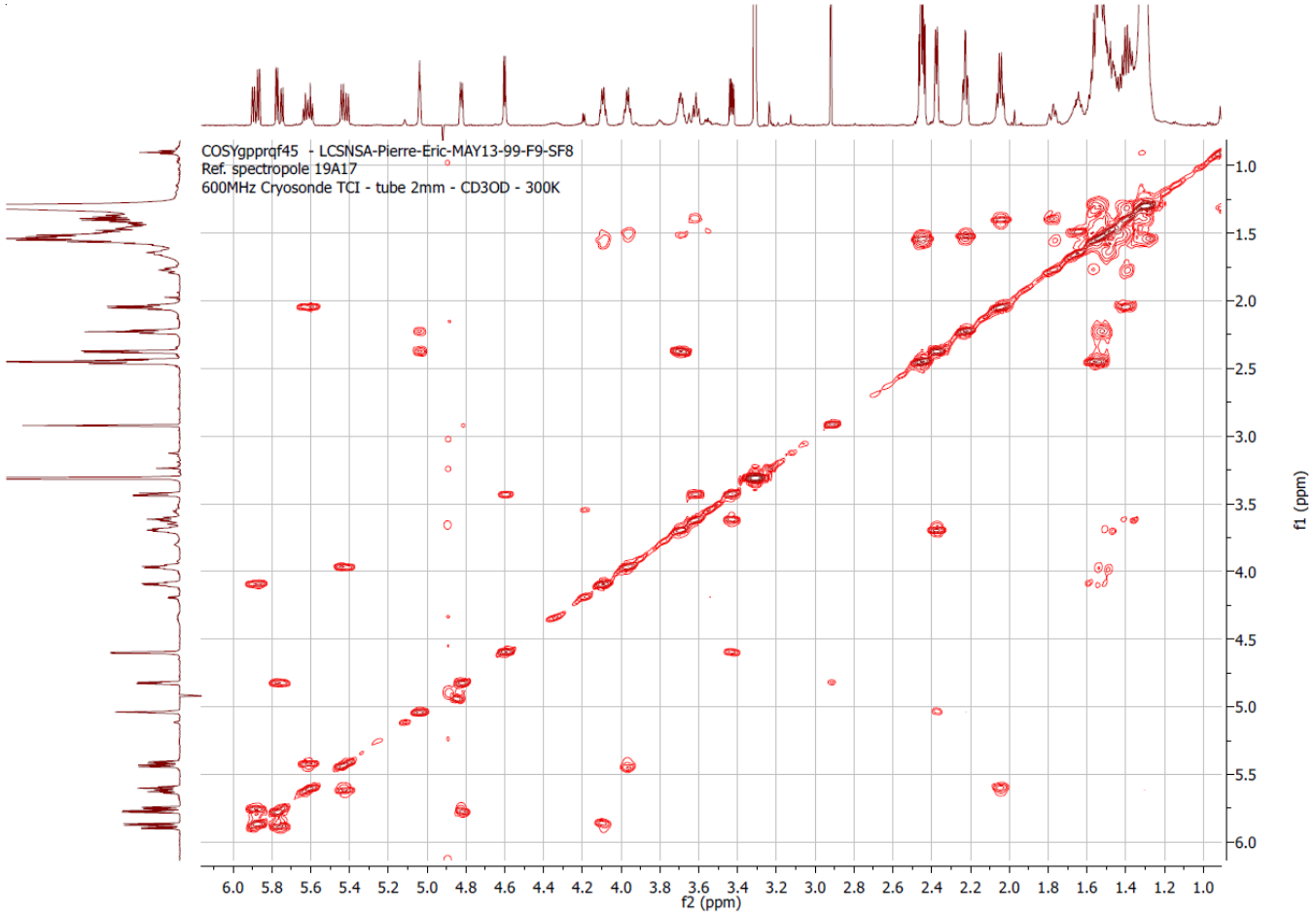


Figure S11: ^{1}H-^{13}C HSQC NMR (600 MHz) spectrum for osirisyne H (**2**)

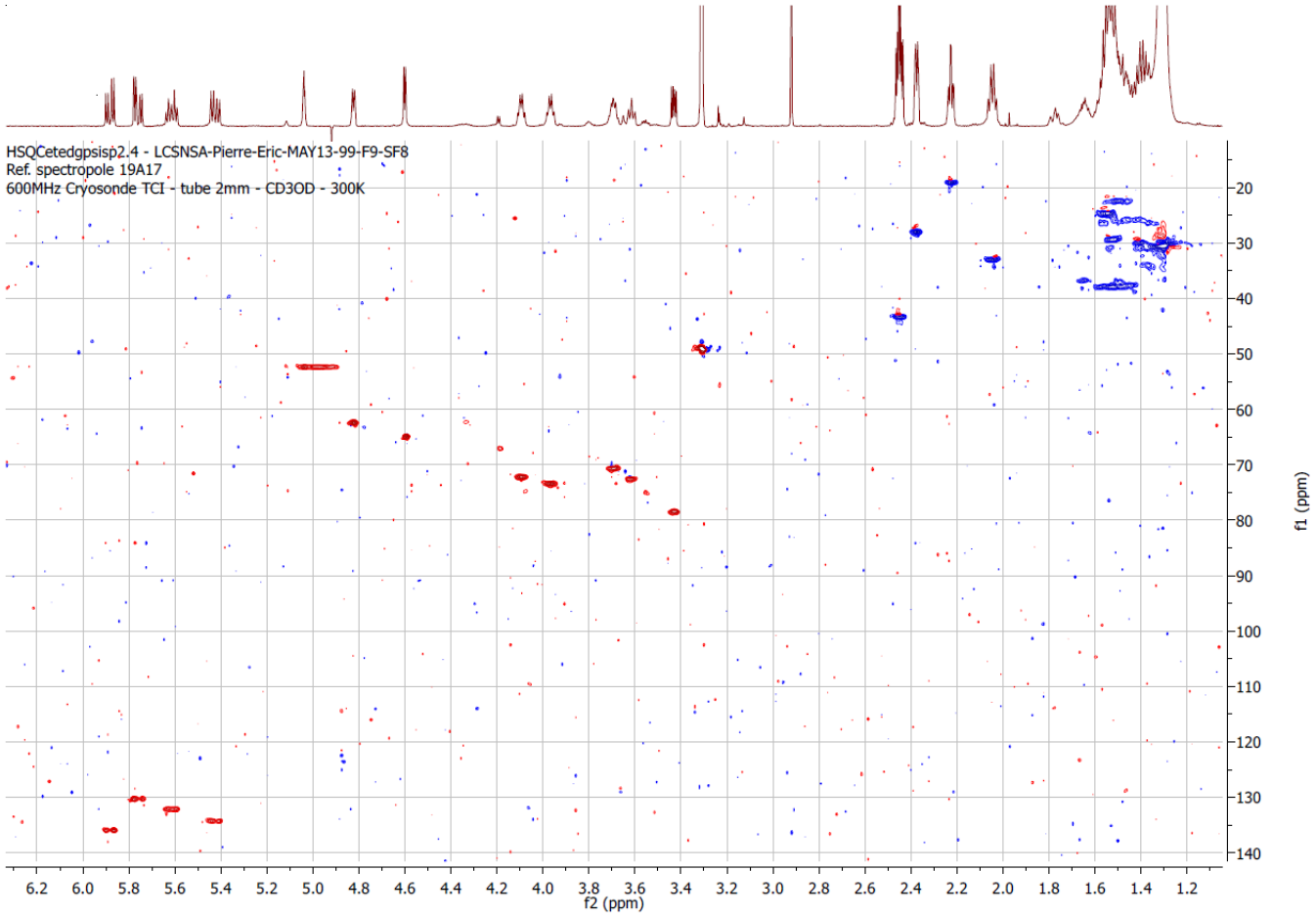


Figure S12: ^{1}H-^{13}C HMBC NMR (600 MHz) spectrum for osirisyne H (**2**)

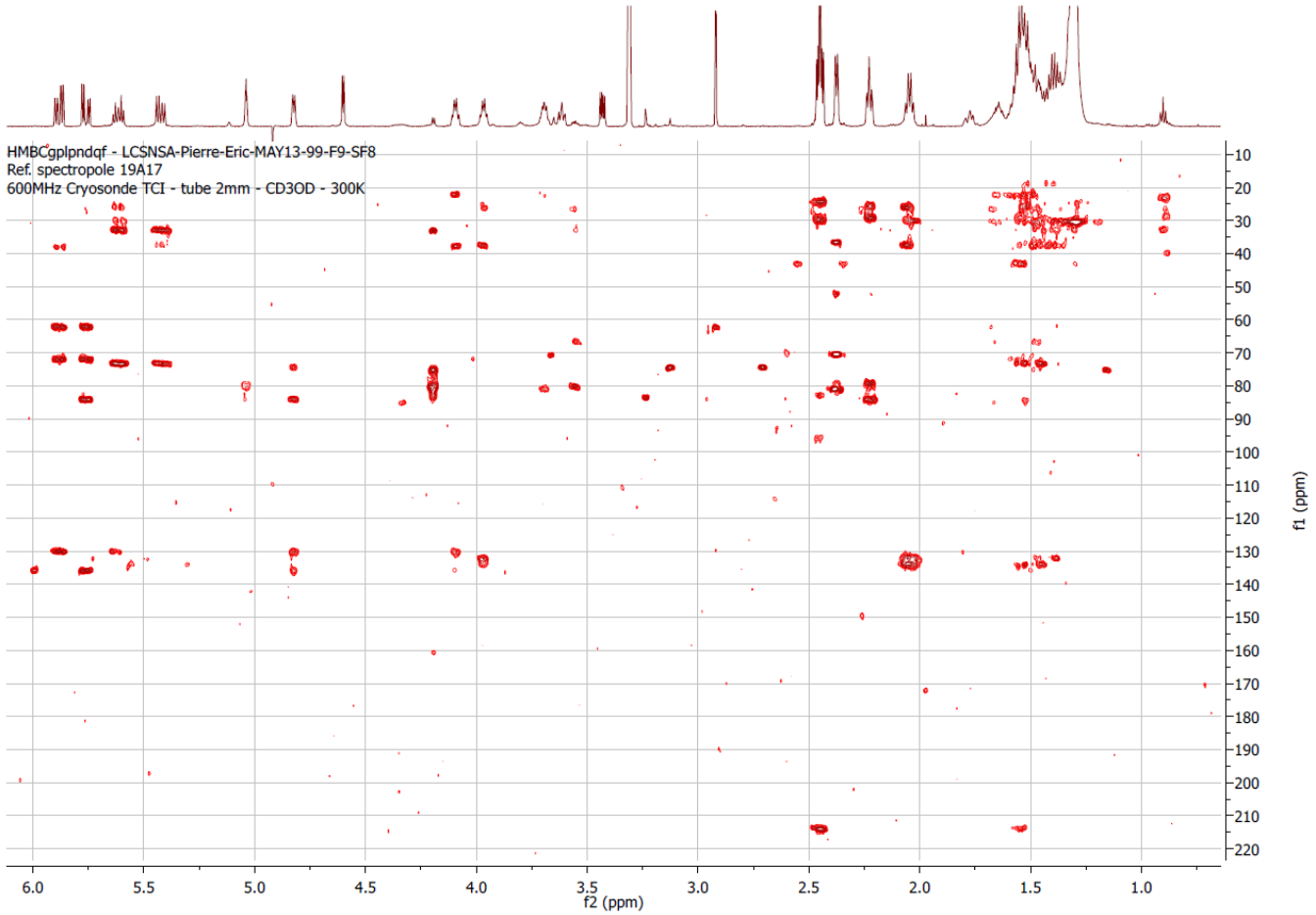


Figure S13: ^{1}H-^{13}C HSQC-TOCSY NMR (600 MHz) spectrum for osirisyne H (**2**)

Figure S14: HRESIMS spectrum for osirisyne I (**3**)

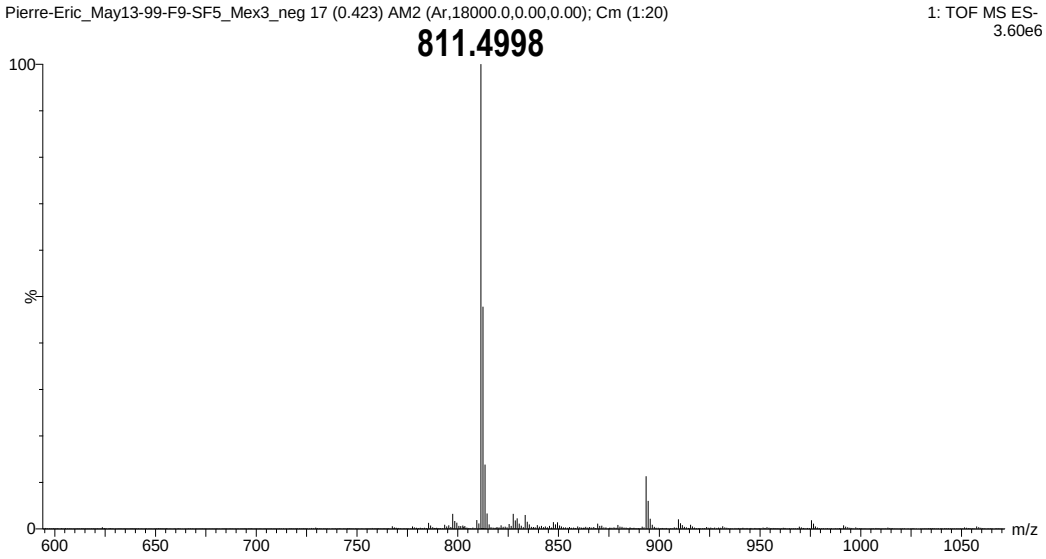
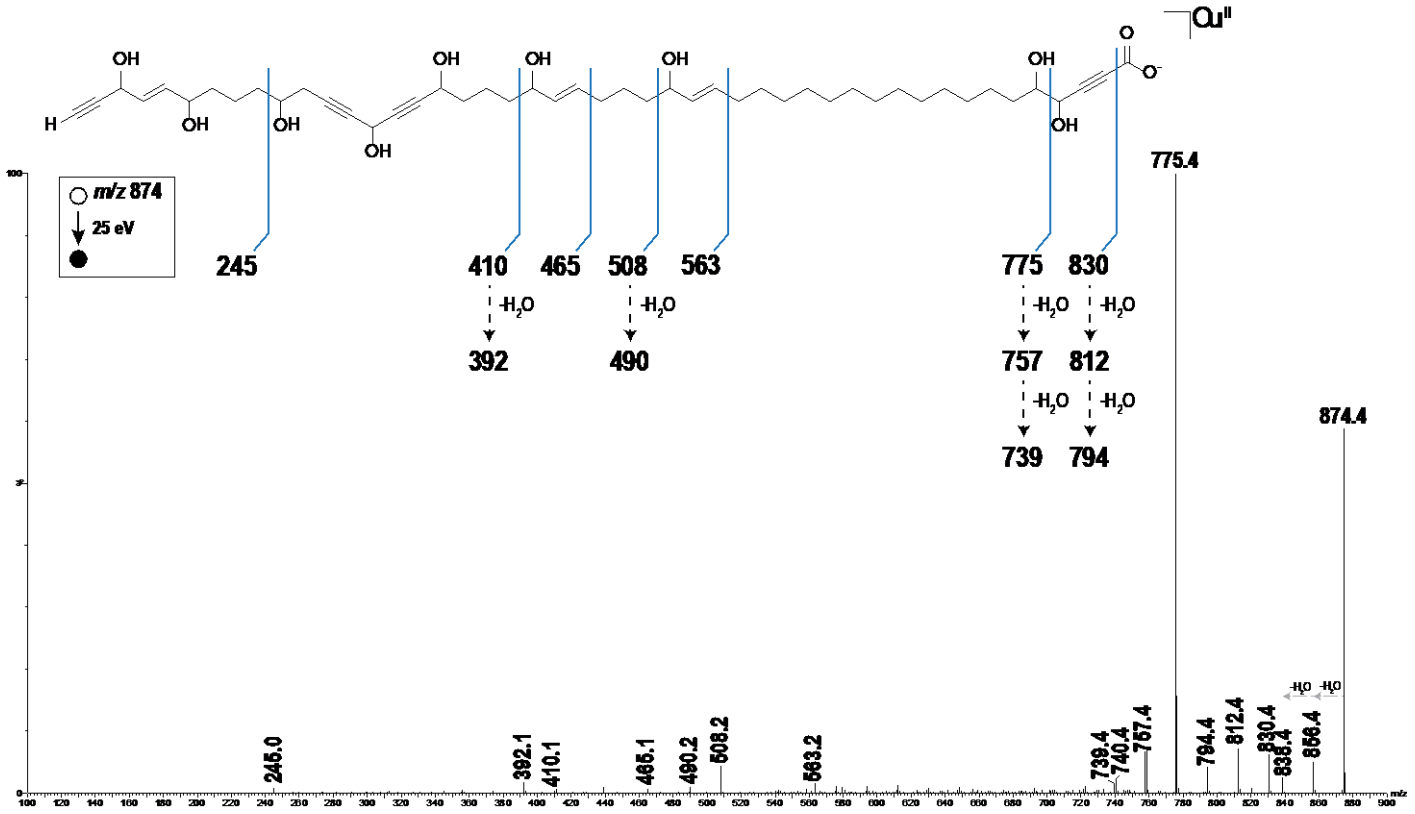


Figure S15: ESI$^+$-MS/MS (S13.a.) and ESI$^-$-MS/MS (S13.b.) spectra of osirisyne I (**3**) with outlines of dissociation of the precursor ion.

S13.a.



S13.b.

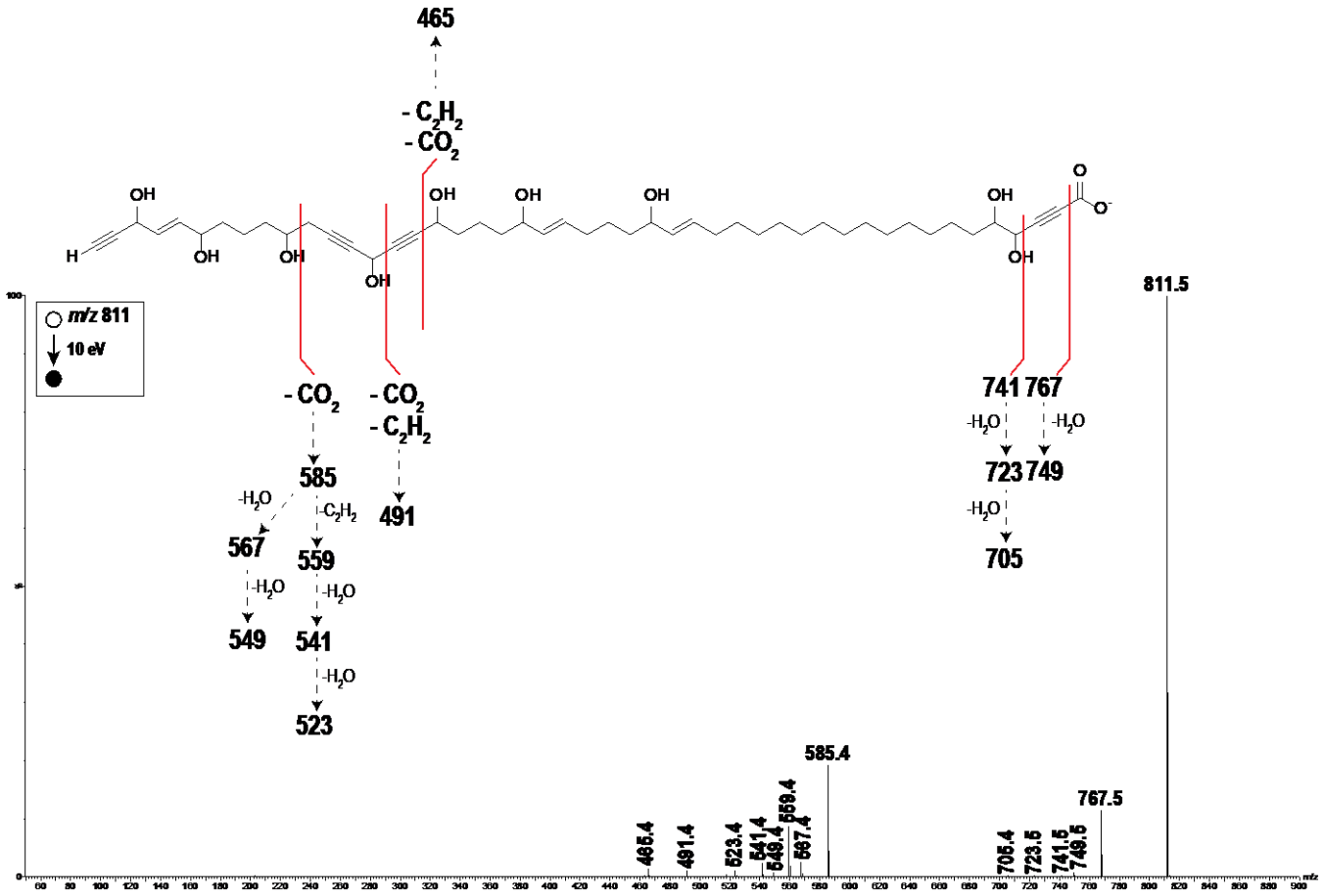
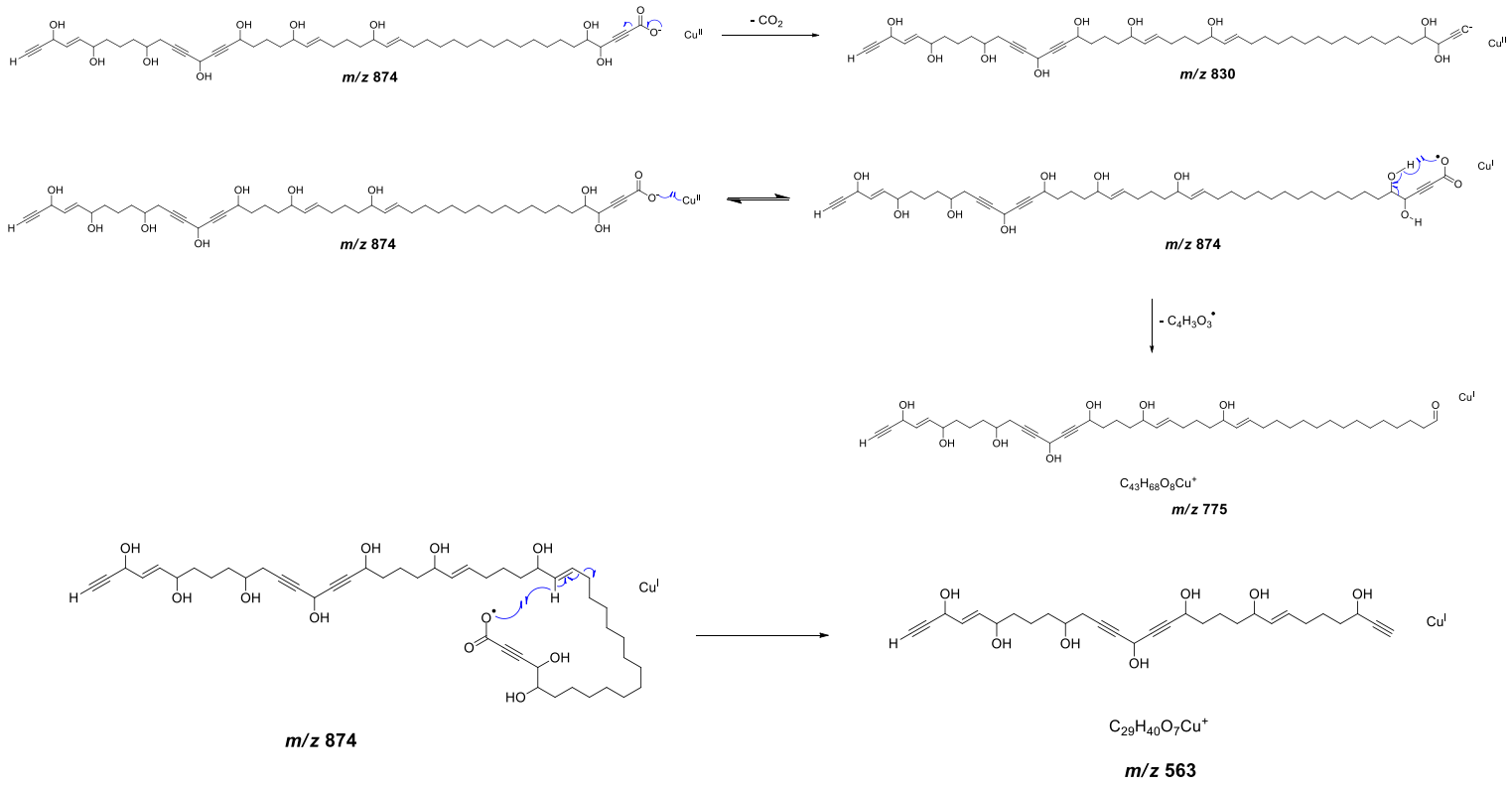
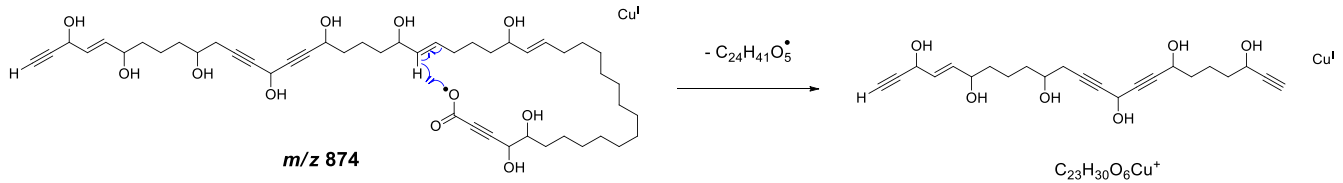

465
- C2H2
- CO2
OH
H
O
O-
m/z 811
10 eV
- CO2
- CO2
- C2H2
585
491
-H2O
-C2H2
567
559
549
541
523
741 767
723 749
705
811.5
585.4
767.5
465.4
491.4
523.4
541.4
549.4
559.4
567.4
706.4
723.5
741.5
749.5

Figure S16*:* Dissociation mechanisms of the fragmentation of osirisyne I (**3**) in ESI$^+$-MS/MS (14.a.) and ESI$^-$-MS/MS (14.b.) with the mass *m/z* of the different fragments.

14.a.

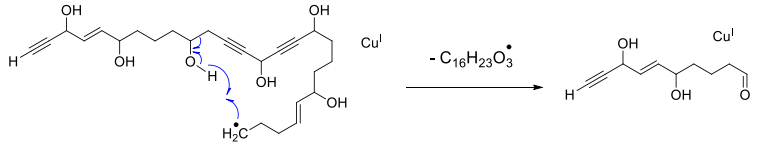




***m/z* 874**

$C_{23}H_{30}O_6Cu^+$

***m/z* 465**

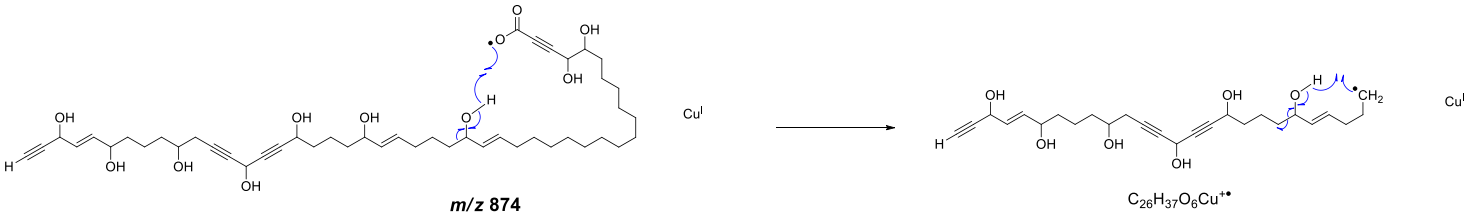


$C_{26}H_{37}O_6Cu^+$

***m/z* 508**

$C_{10}H_{14}O_3Cu^+$

***m/z* 245**

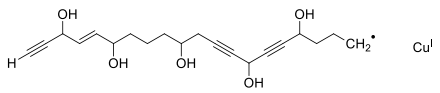


***m/z* 874**

$C_{26}H_{37}O_6Cu^{+\bullet}$

***m/z* 508**

- $C_6H_{10}O$



$C_{20}H_{27}O_5Cu^{+\bullet}$

***m/z* 410**

14.b.

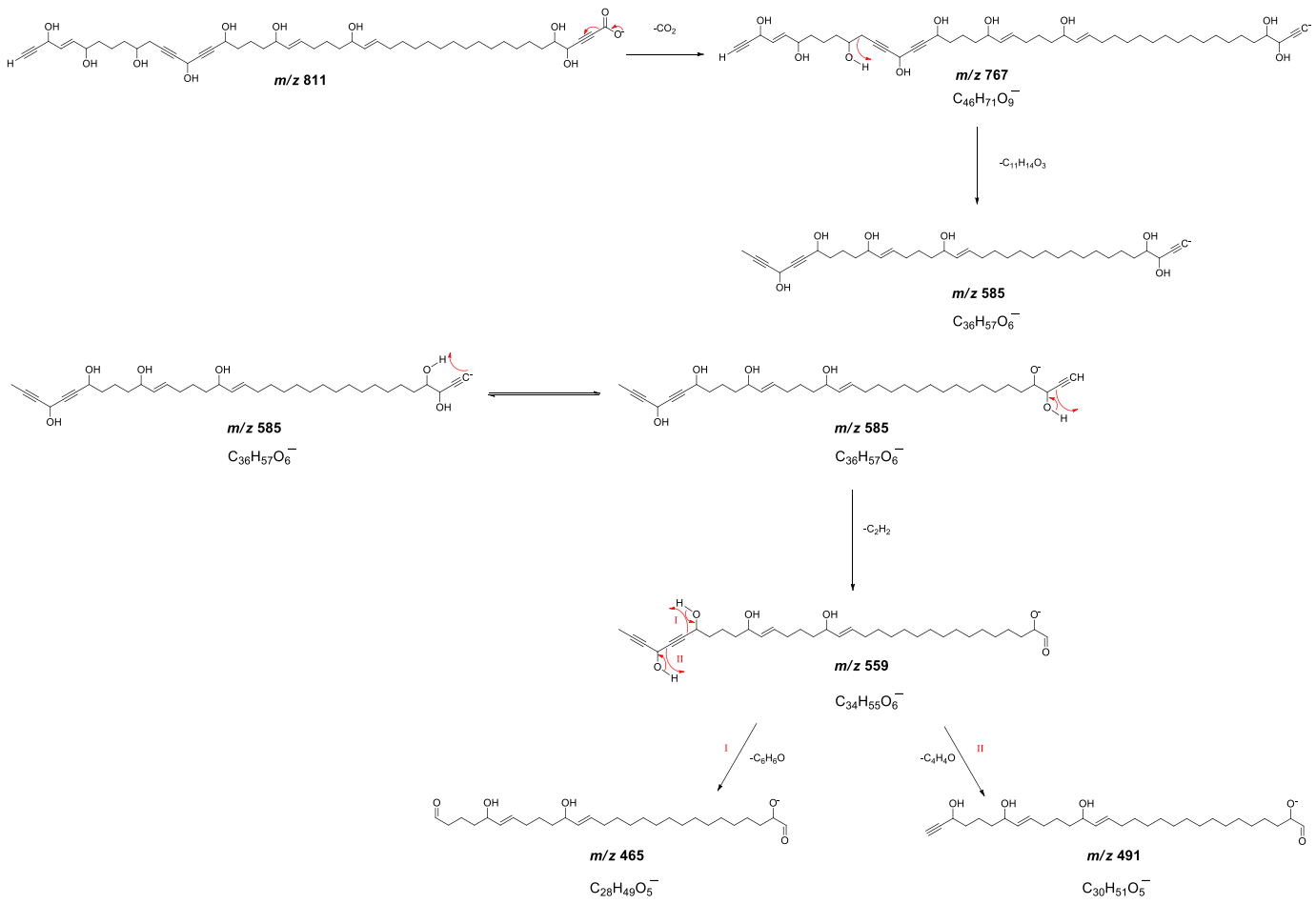

-CO2
m/z 811
m/z 767
C46H71O9−
-C11H14O3
m/z 585
C36H57O6−
m/z 585
C36H57O6−
m/z 585
C36H57O6−
-C2H2
m/z 559
C34H55O6−
I
-C6H6O
II
-C4H4O
m/z 465
C28H49O5−
m/z 491
C30H51O5−

Figure S17: IRTF spectrum for osirisyne I (**3**)

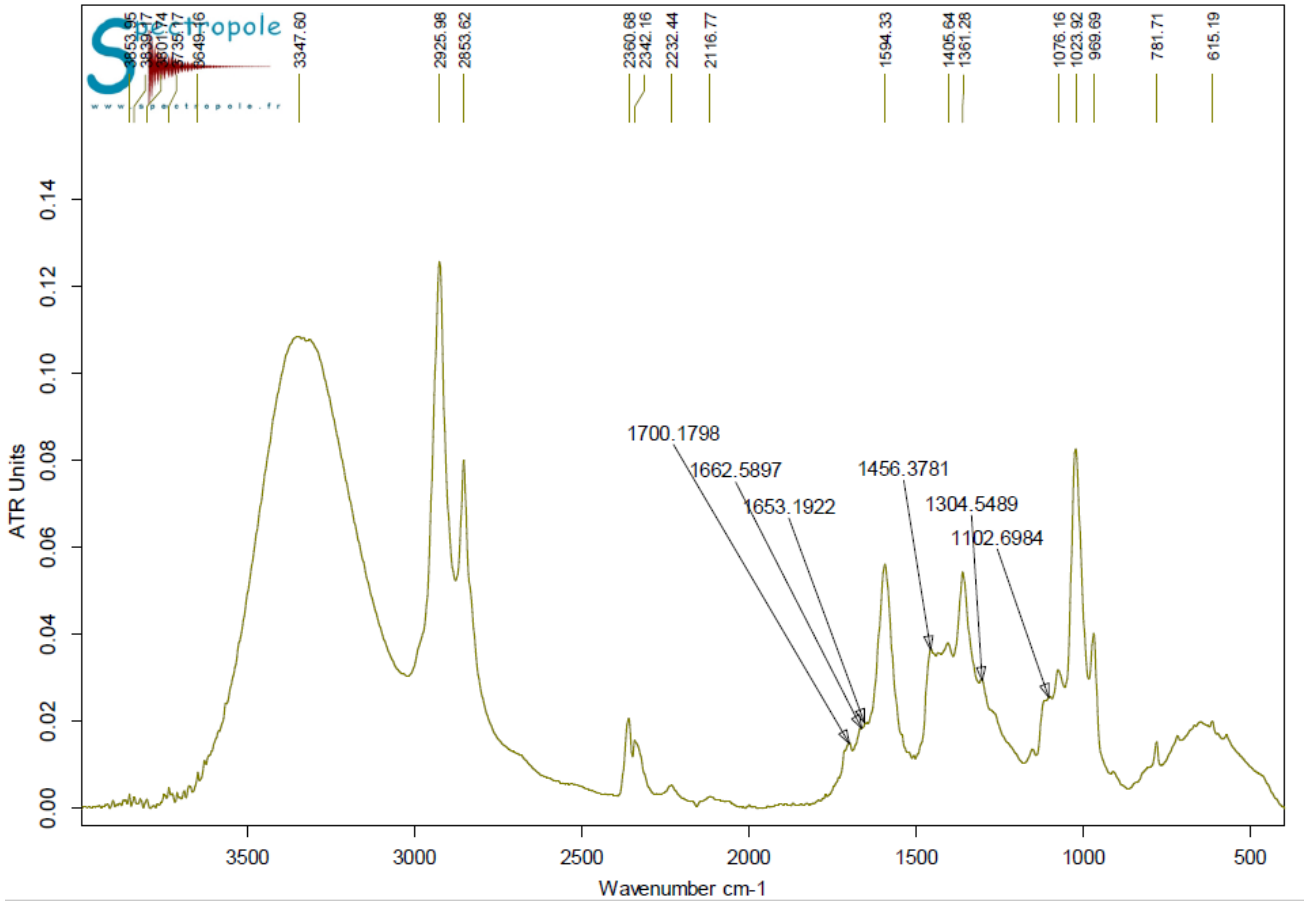


Figure S18: ^{1}H NMR (600 MHz, CD_3OD) spectrum for osirisyne I (**3**)

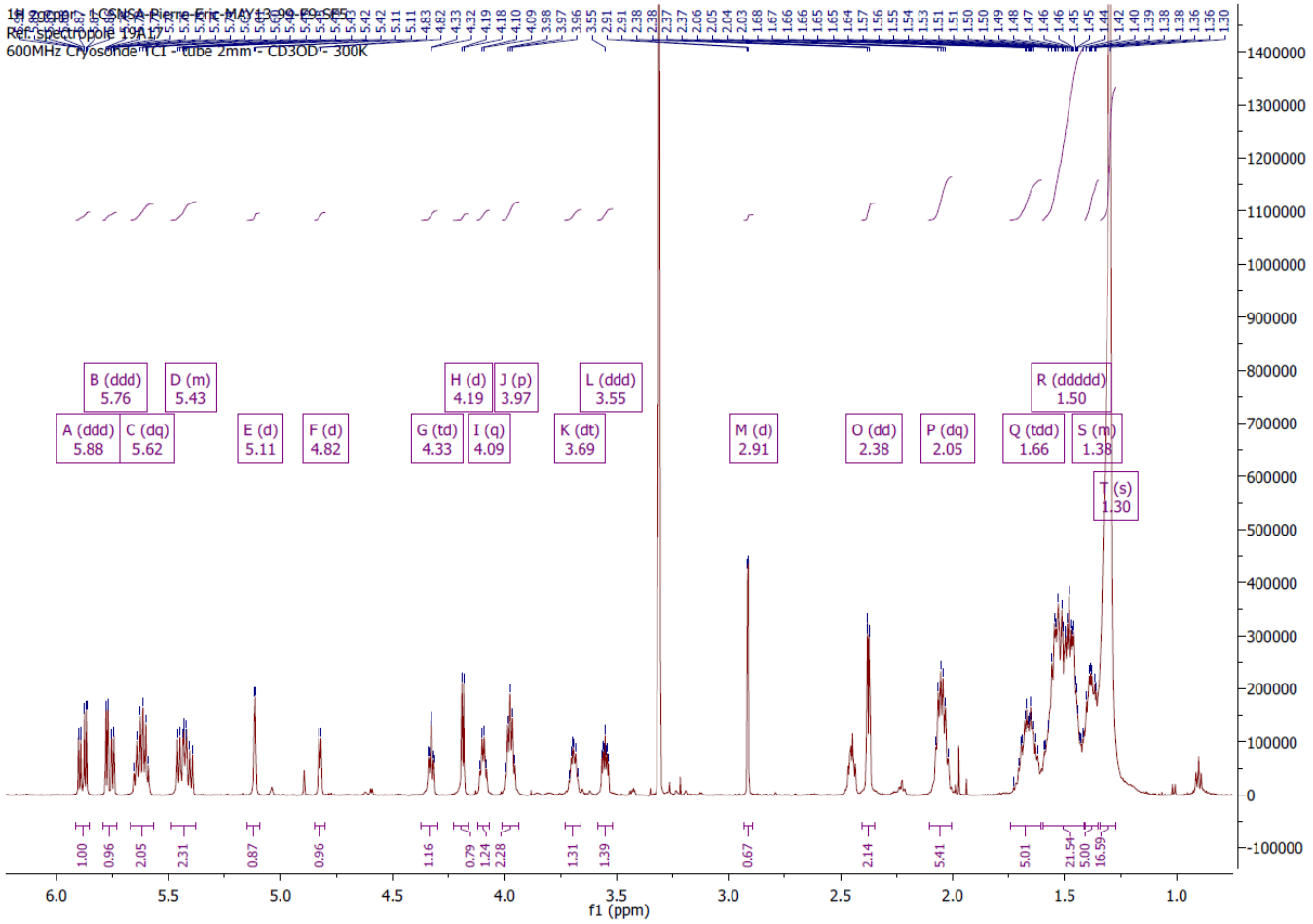


Figure S19: ^{13}C NMR (600 MHz, CD_3OD) spectrum for osirisyne I (**3**)

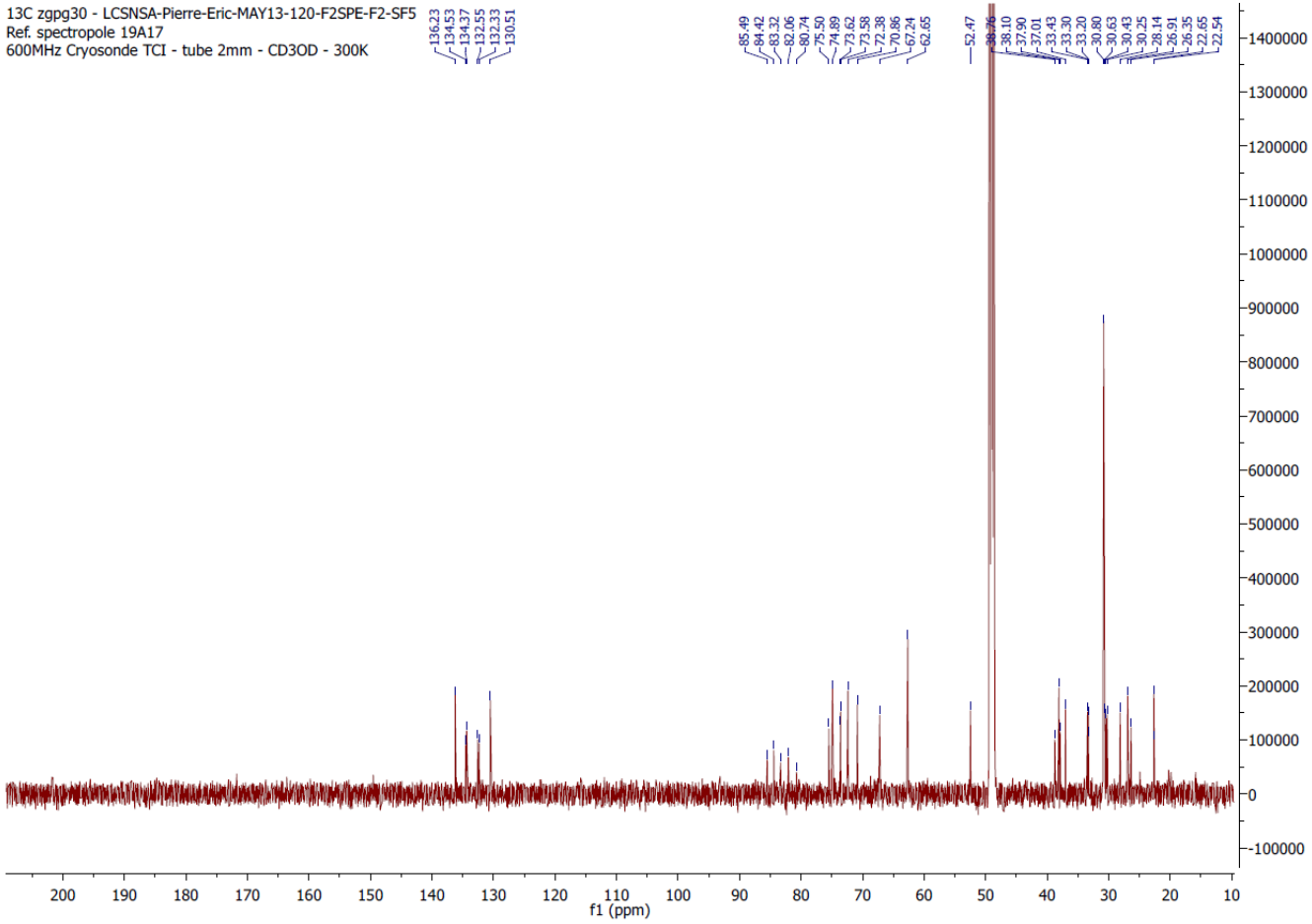


Figure S20: ^{1}H-^{1}H COSY NMR (600 MHz) spectrum for osirisyne I (**3**)

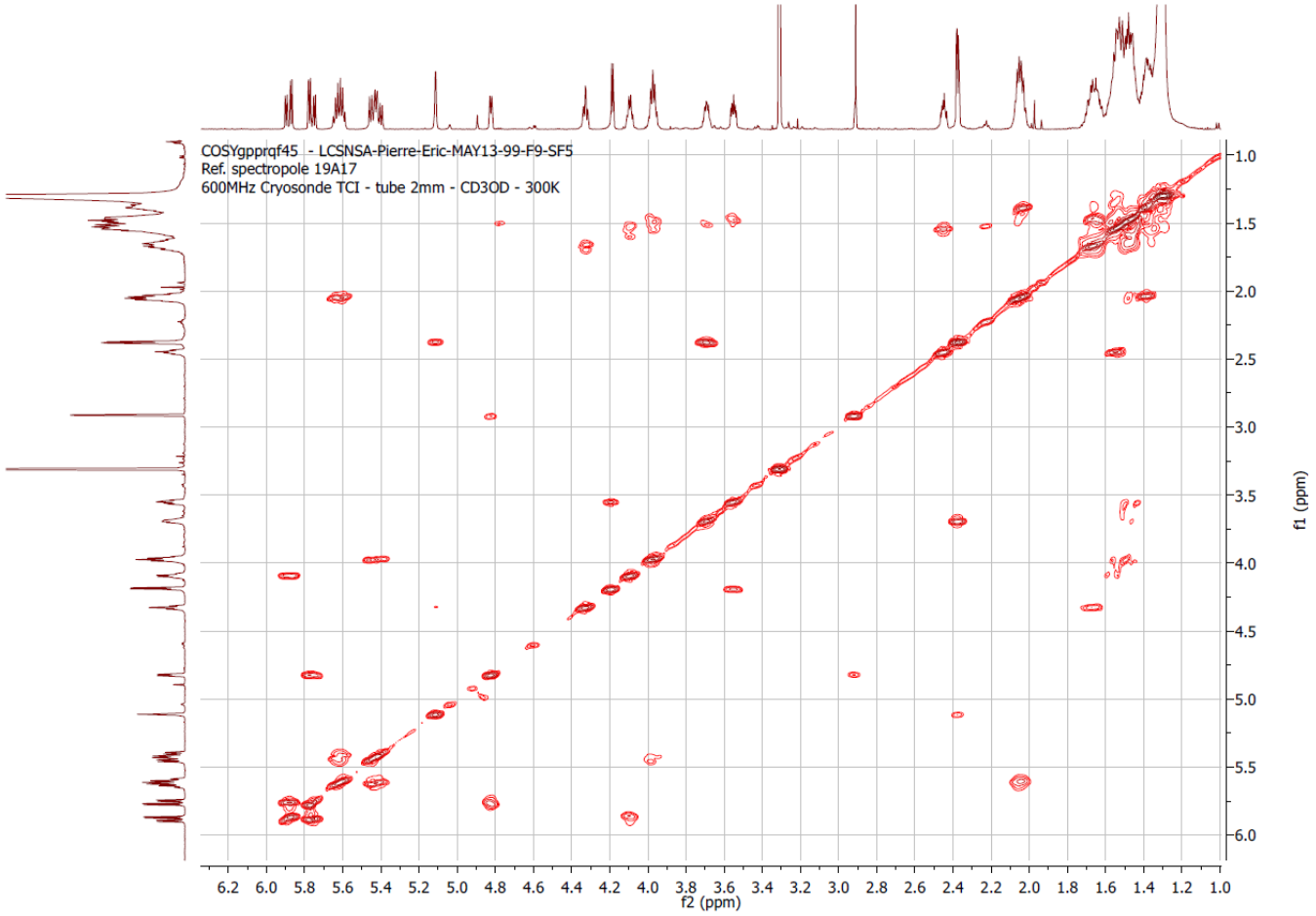


Figure S21: ^{1}H-^{13}C HSQC NMR (600 MHz) spectrum for osirisyne I (**3**)

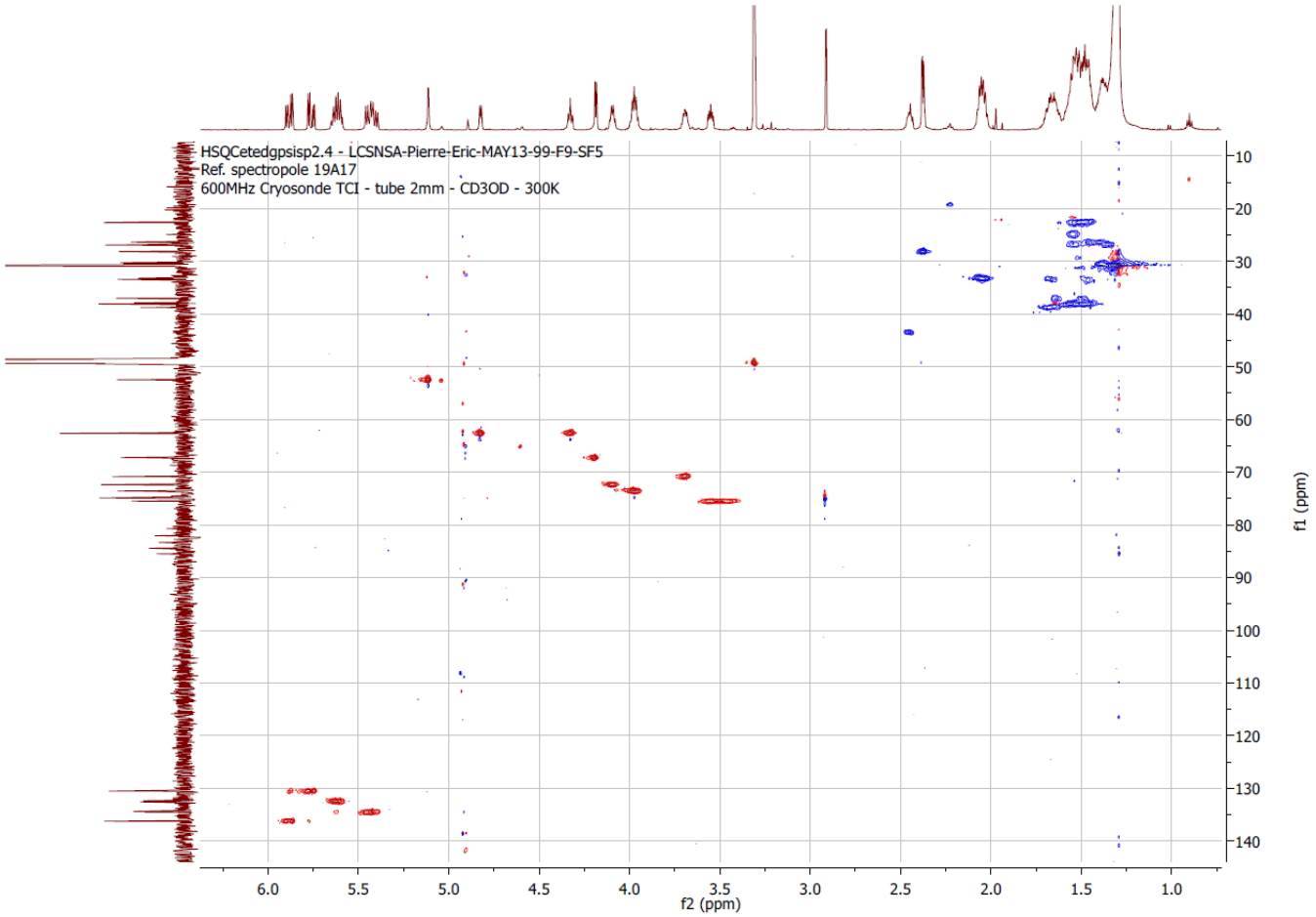


Figure S22: ^{1}H-^{13}C HMBC NMR (600 MHz) spectrum for osirisyne I (**3**)

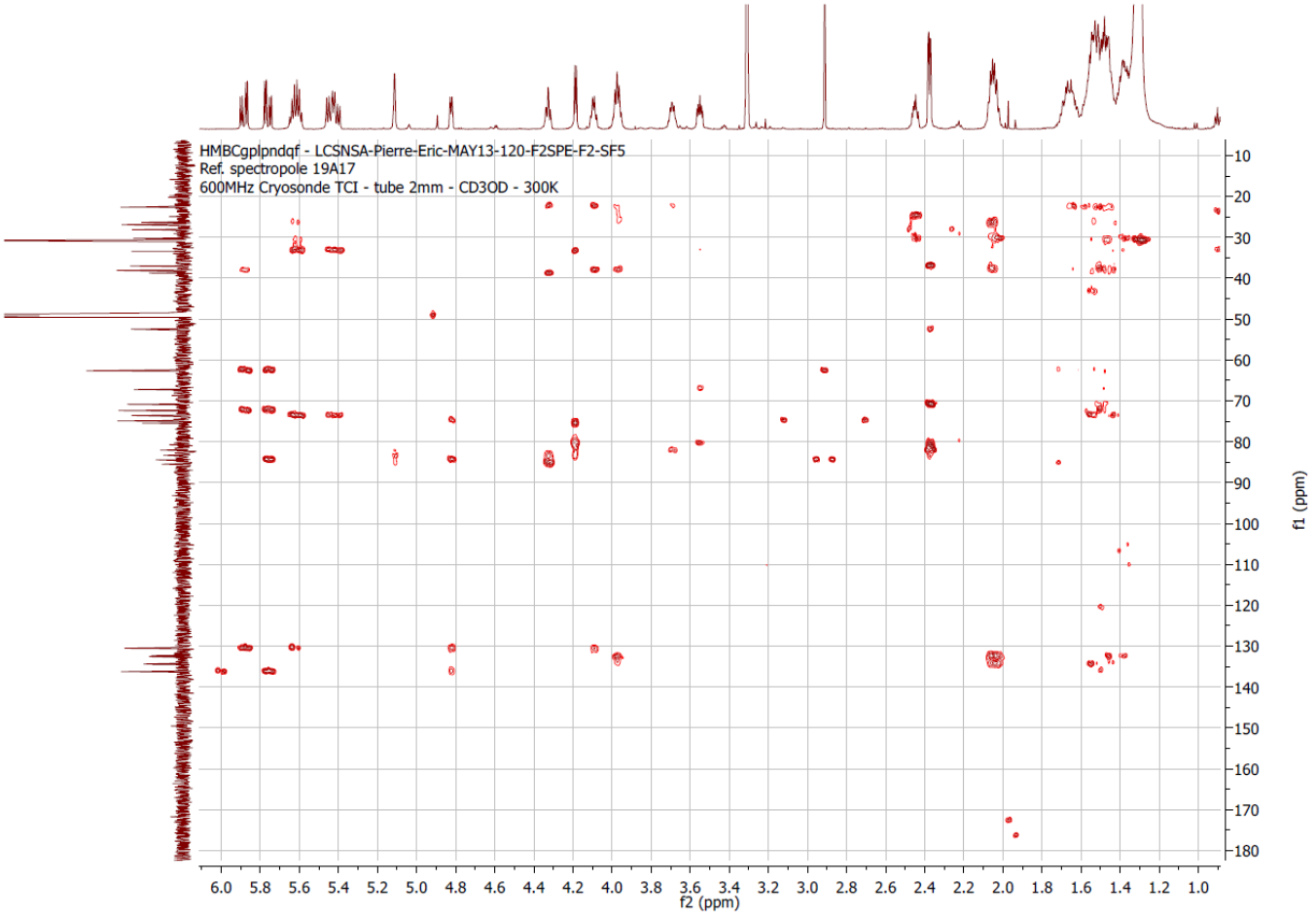


Figure S23: ^{1}H-^{1}H NOESY NMR (600 MHz) spectrum for osirisyne I (**3**)

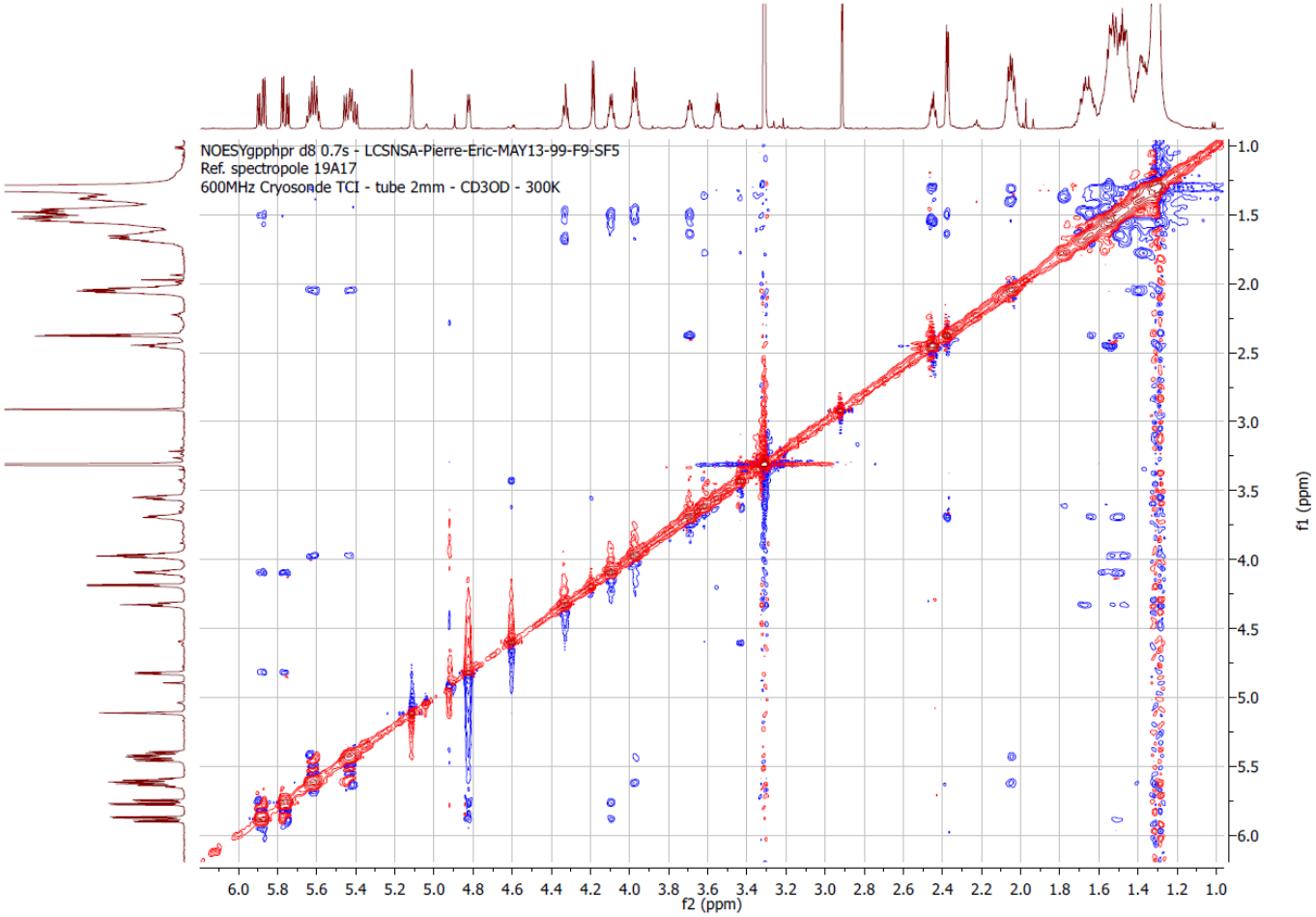


Figure S24: ^{1}H-^{13}C TOCSY-HSQC NMR (600 MHz) spectrum for osirisyne I (**3**)

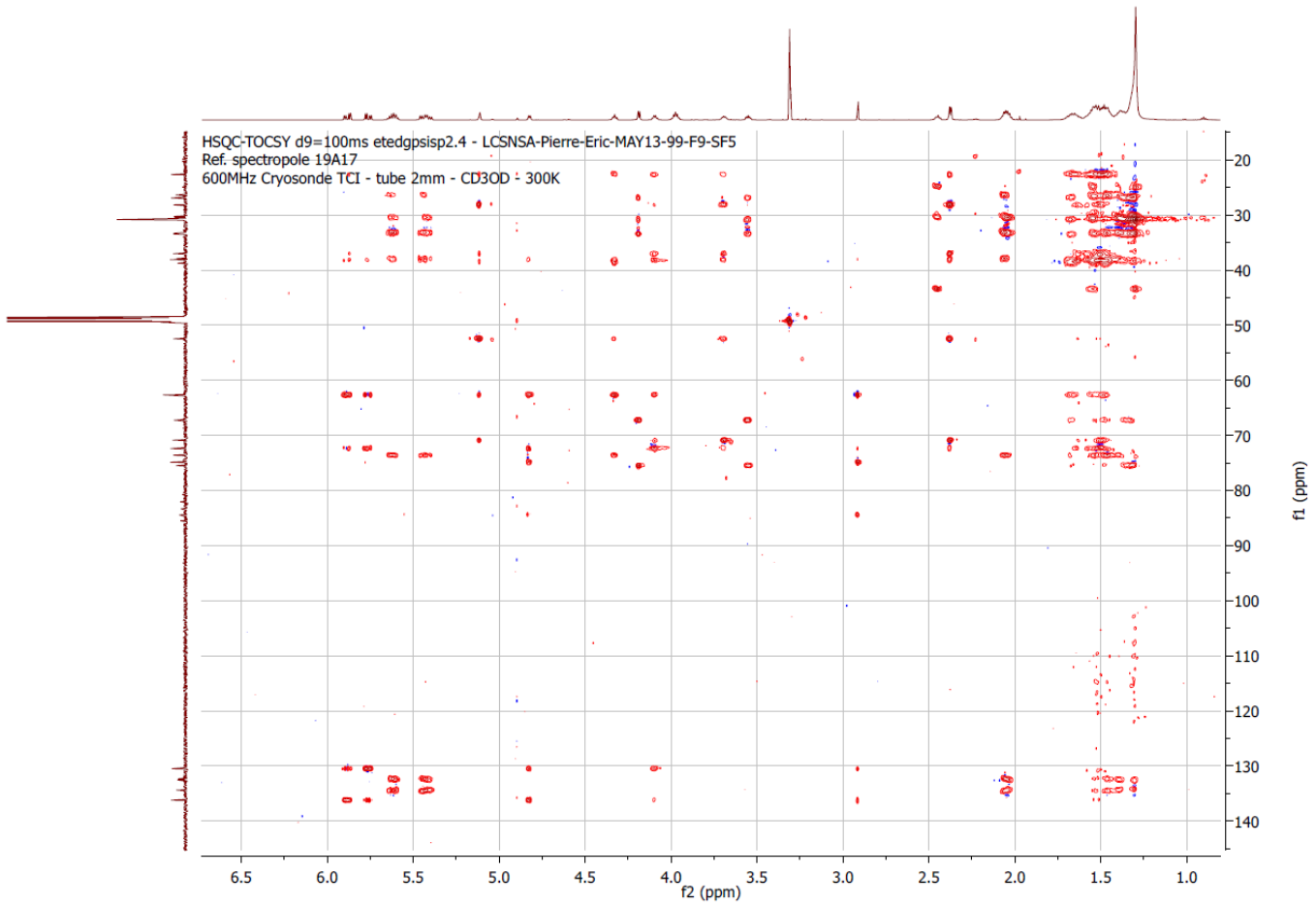


Figure S25: HRESIMS spectrum for osirisyne A (**4**)

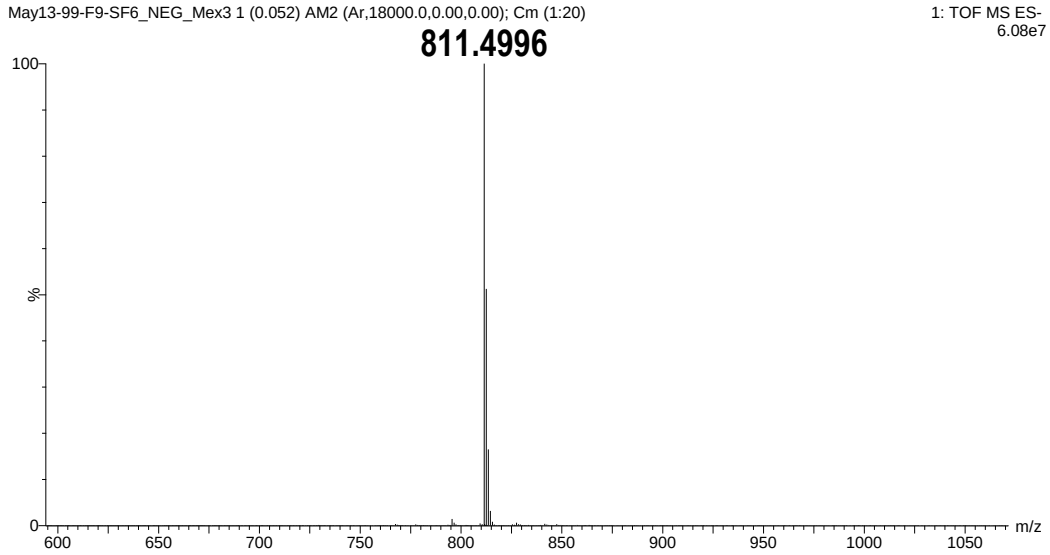
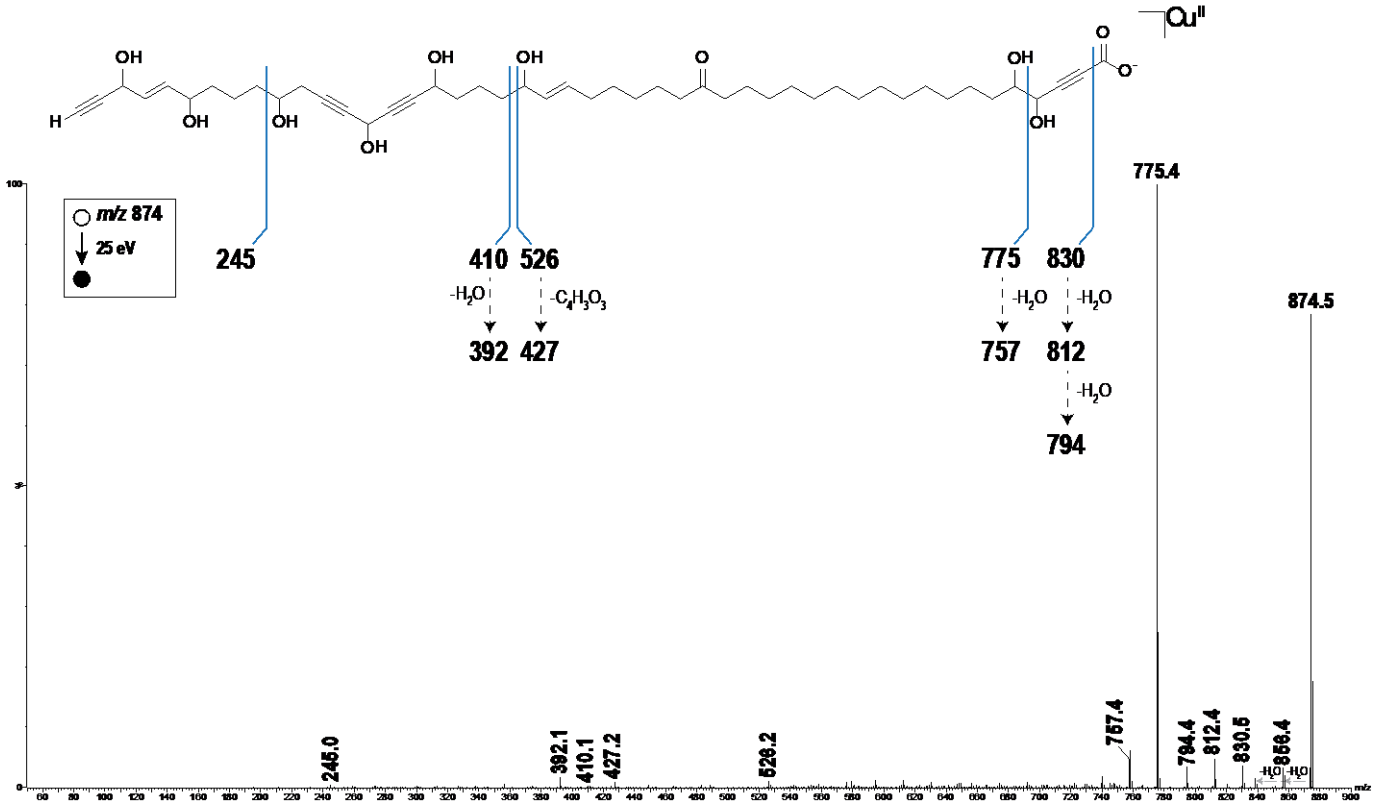


Figure S26: ESI$^+$-MS/MS (S22.a.) and ESI$^-$-MS/MS (S22.b.) spectra of osirisyne A (**4**) with outlines of dissociation of the precursor ion.

S22.a.



S22.b.

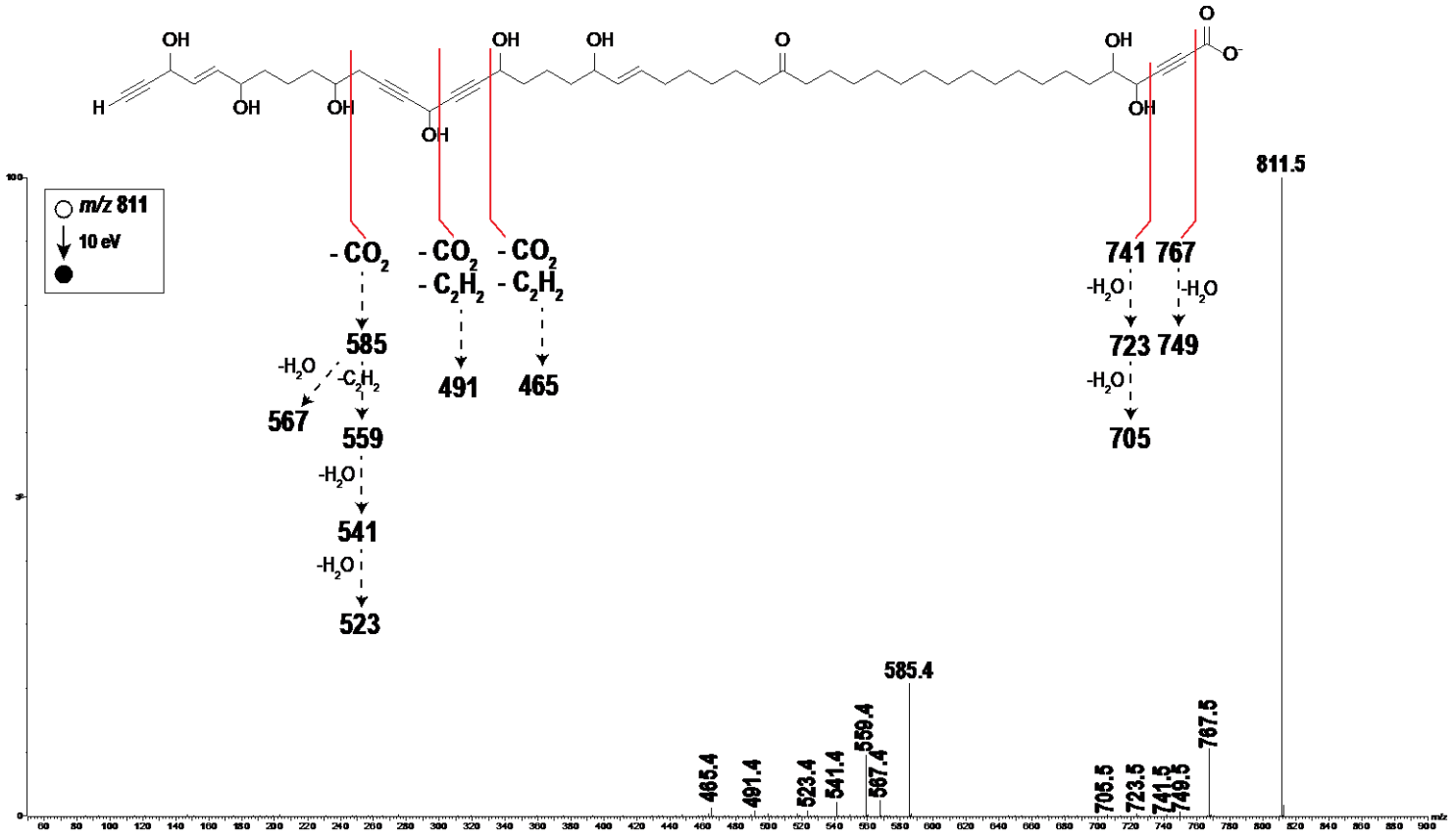

m/z 811
10 eV
- CO2
- CO2
- C2H2
- CO2
- C2H2
585
491
465
567
559
541
523
-H2O
-C2H2
741 767
723 749
705
811.5
585.4
559.4
567.4
541.4
523.4
491.4
465.4
767.5
705.5
723.5
741.5
749.5

Figure S27: ^{1}H NMR (600 MHz, CD_3OD) spectrum for osirisyne A (**4**)

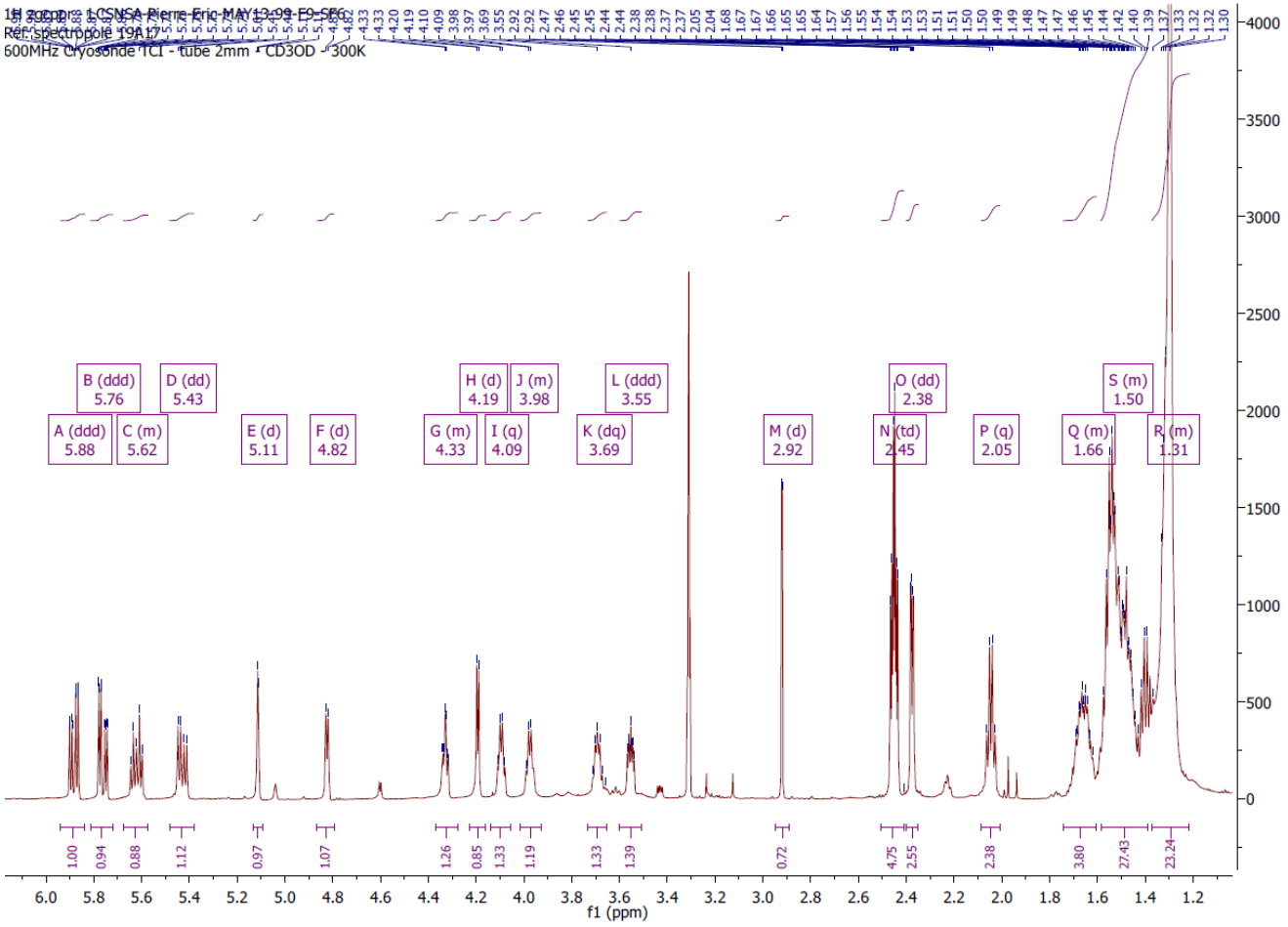
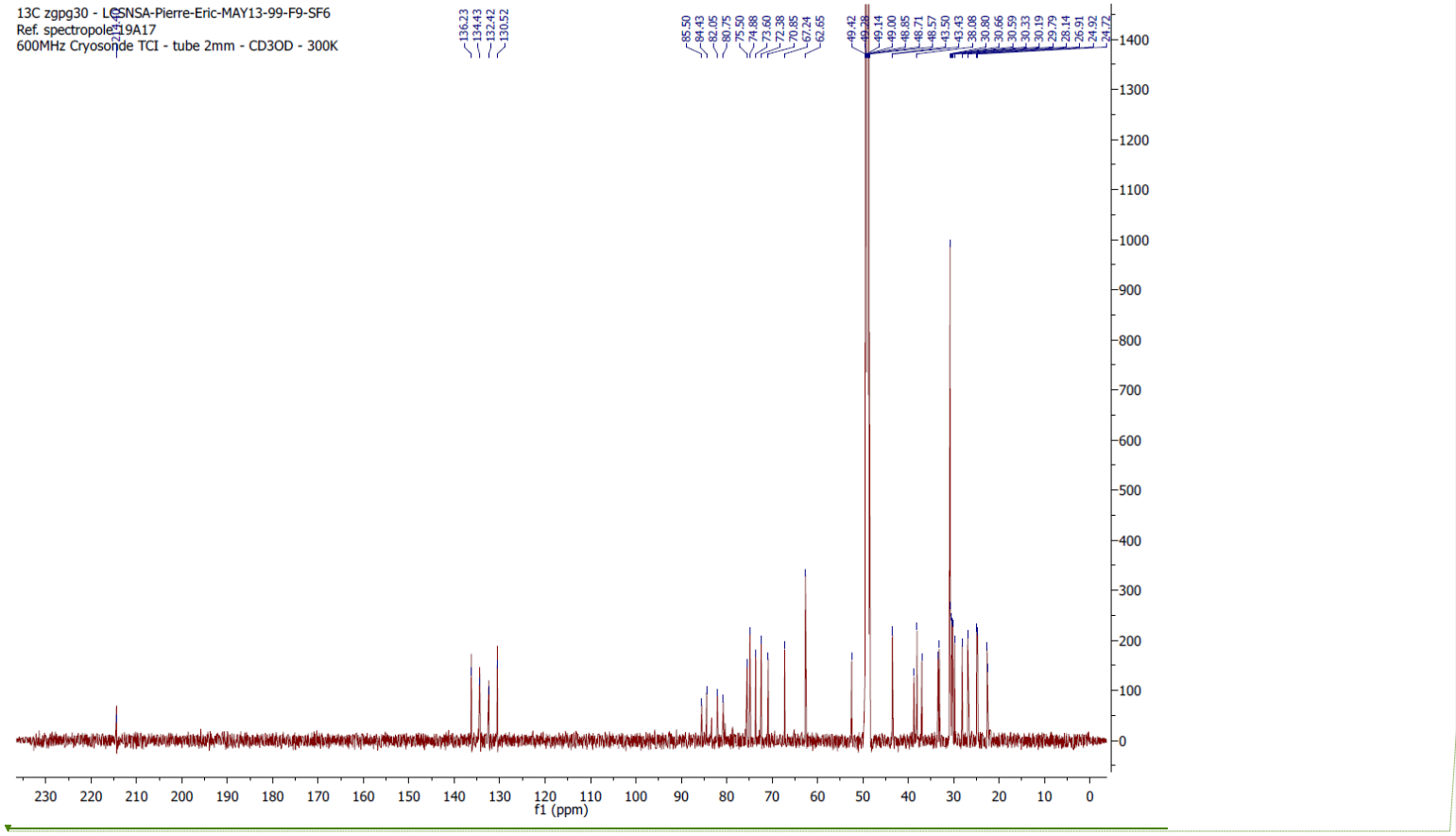


Figure S28: ^{13}C NMR (600 MHz, CD_3OD) spectrum for osirisyne A (**4**)



13C zgpg30 - LCSNSA-Pierre-Eric-MAY13-99-F9-SF6
Ref. spectropole-19A17
600MHz Cryosonde TCI - tube 2mm - CD3OD - 300K

Deleted:

Figure S29: HRESIMS spectrum for osirisyne B (**4**)

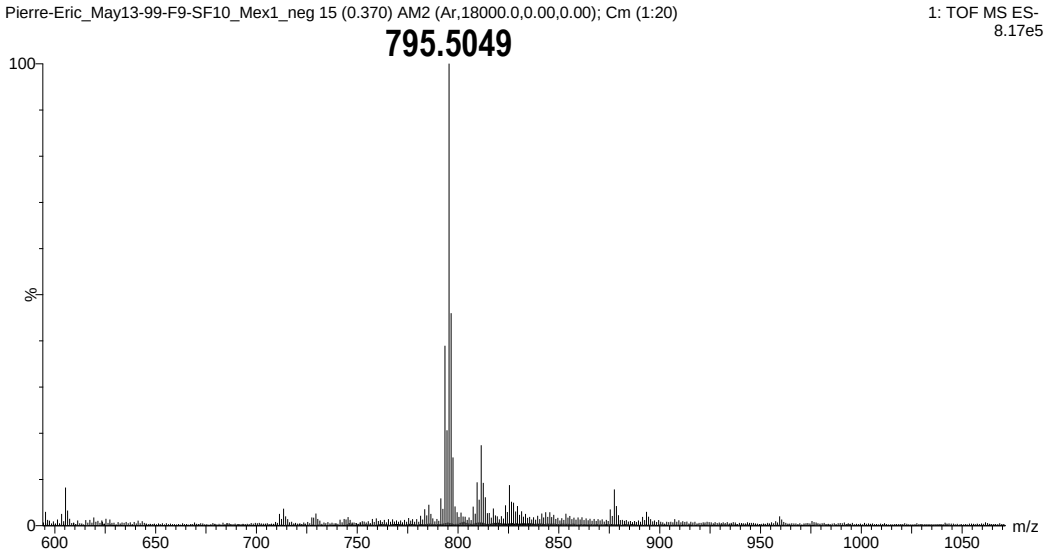
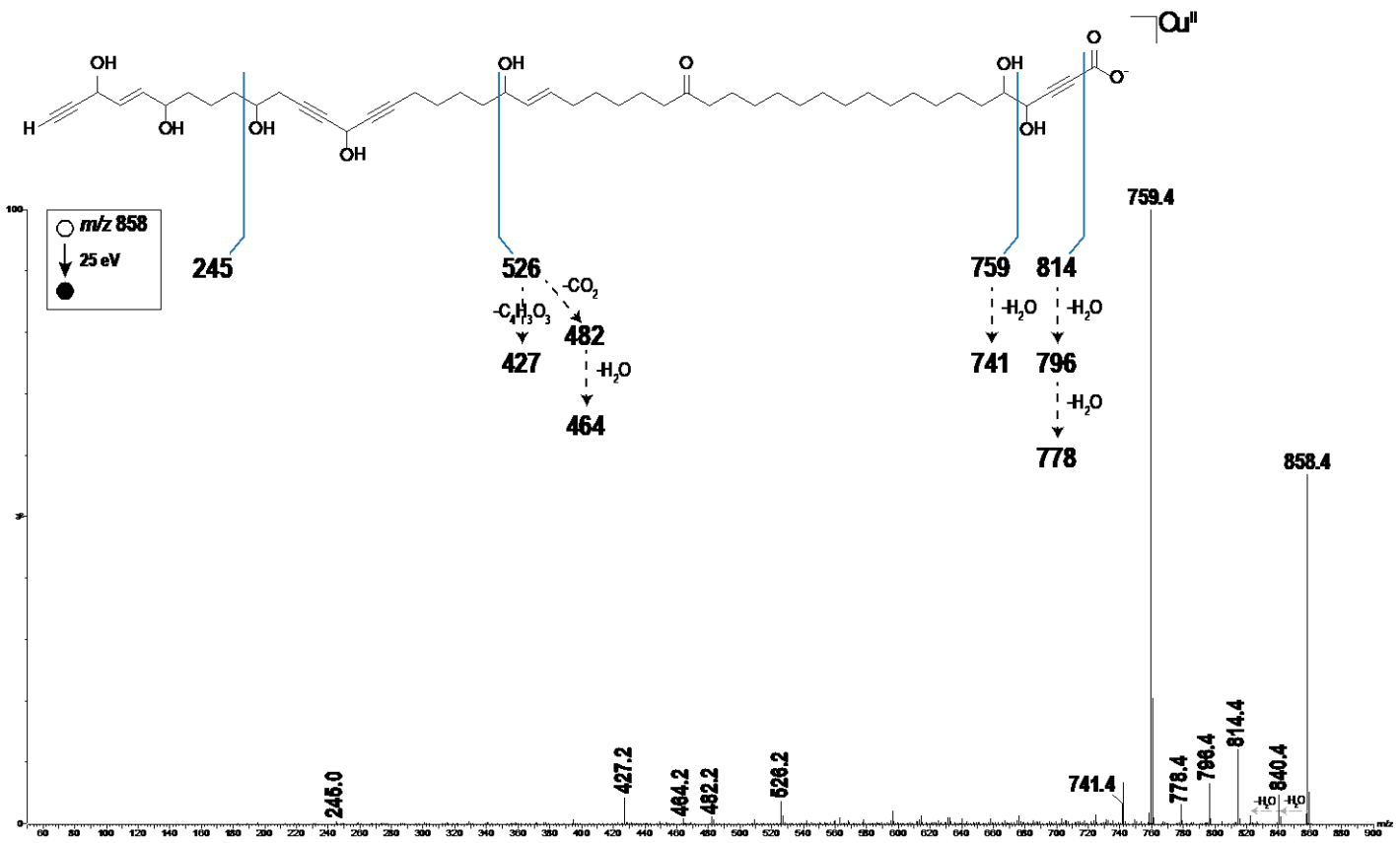


Figure S30: ESI$^+$-MS/MS (S25.a.) and ESI$^-$-MS/MS (S25.b.) spectra of osirisyne B (**5**) with outlines of dissociation of the precursor ion.

S25.a.



S25.b.

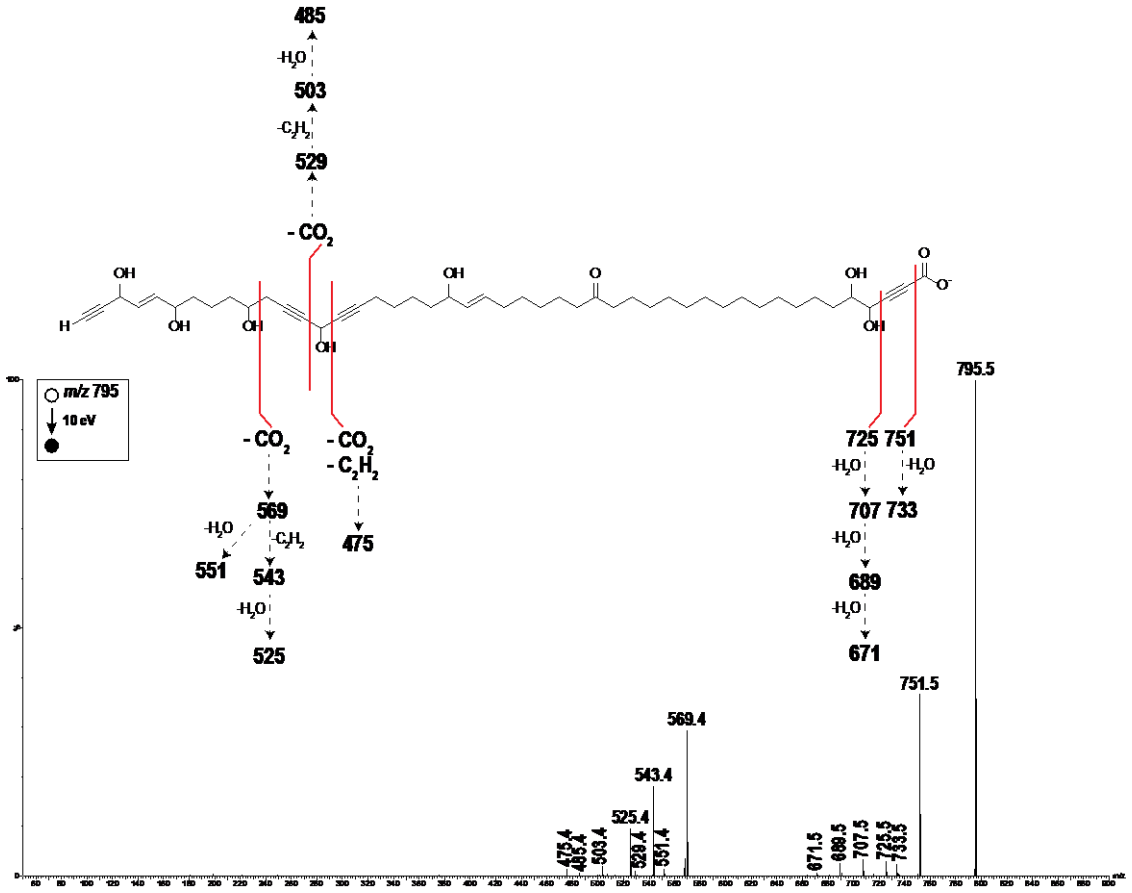

485
-H2O
503
-C2H2
529
-CO2
OH
OH
OH
OH
OH
OH
O
O
O-
H
m/z 795
10 eV
-CO2
-CO2
-C2H2
569
475
-H2O
-C2H2
551
543
-H2O
525
725 751
-H2O
-H2O
707 733
-H2O
689
-H2O
671
795.5
751.5
569.4
543.4
525.4
475.4
485.4
503.4
528.4
551.4
671.5
689.5
707.5
725.5
733.5

Figure S31: ^{1}H NMR (600 MHz, CD_3OD) spectrum for osirisyne B (**5**)

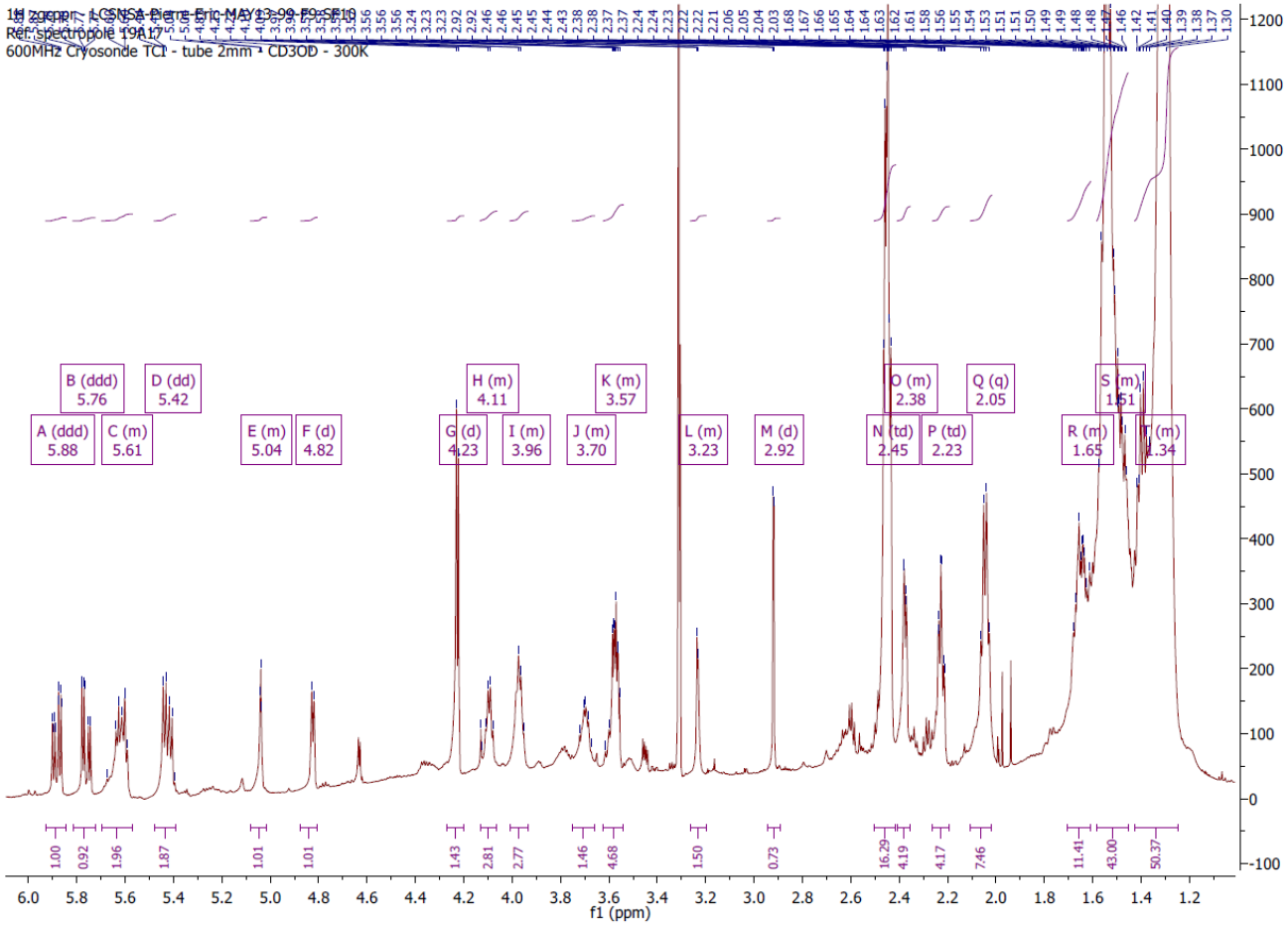
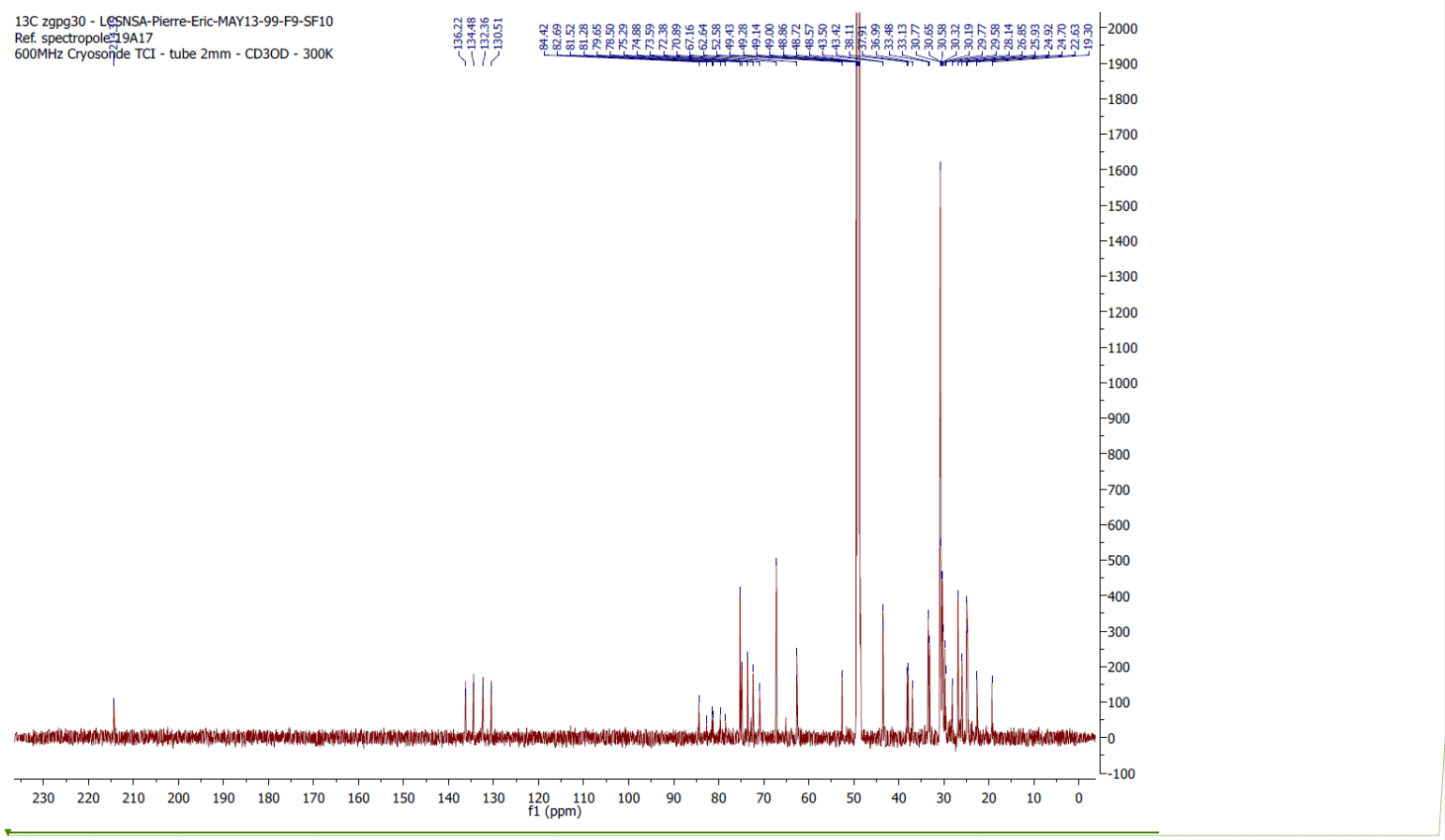


Figure S32: ^{13}C NMR (600 MHz, CD_3OD) spectrum for osirisyne B (**5**)



Deleted:

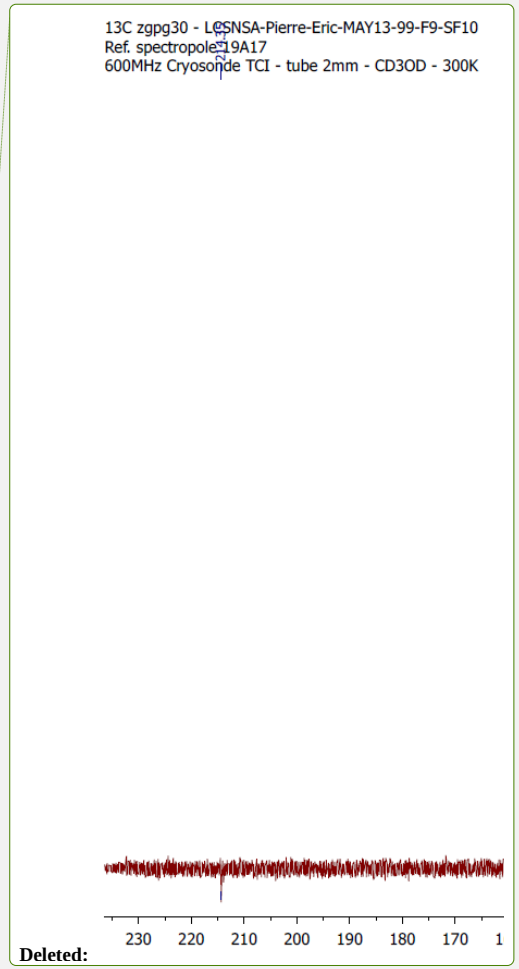
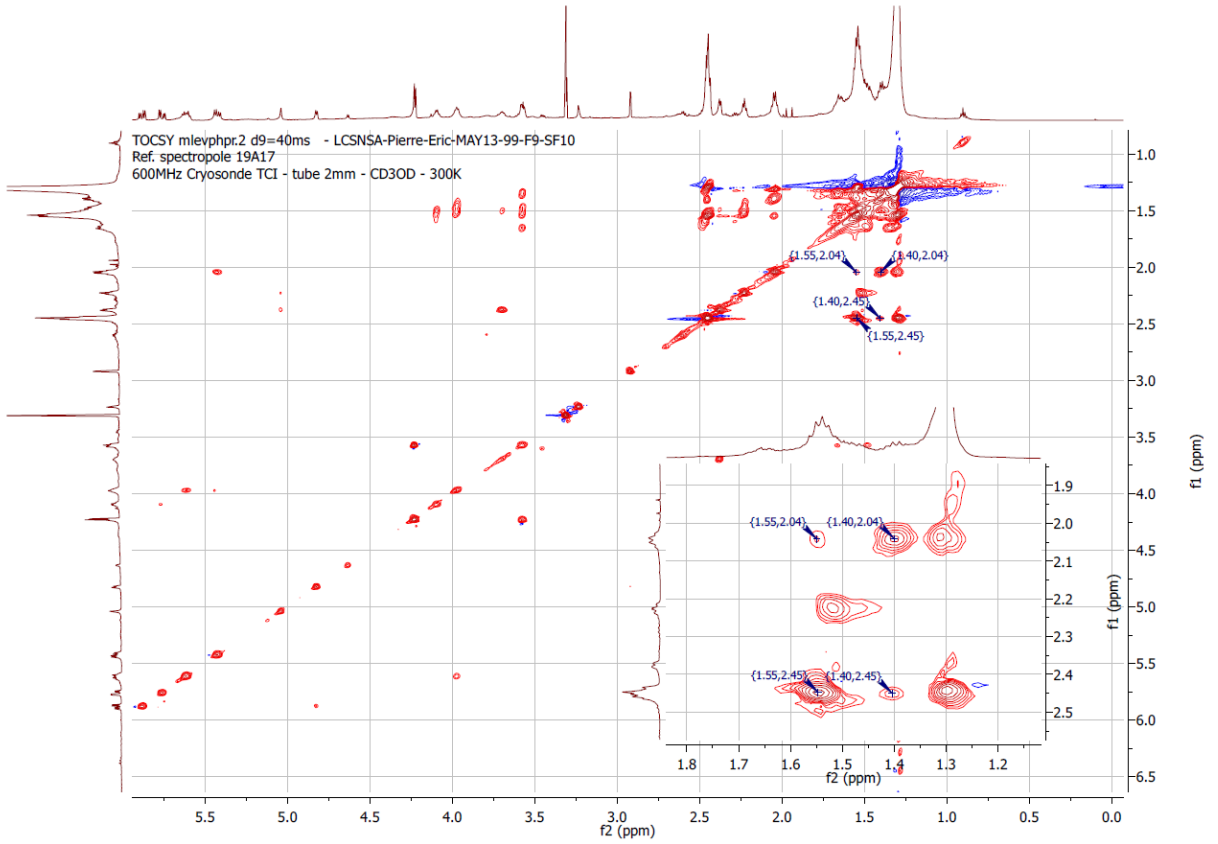


Figure S33: ^{1}H-^{1}H TOCSY NMR (600 MHz) spectrum for osirisyne B (**5**)



Formatted: Font: Bold

Figure S34: HRESIMS spectrum for osirisyne E (**6**)

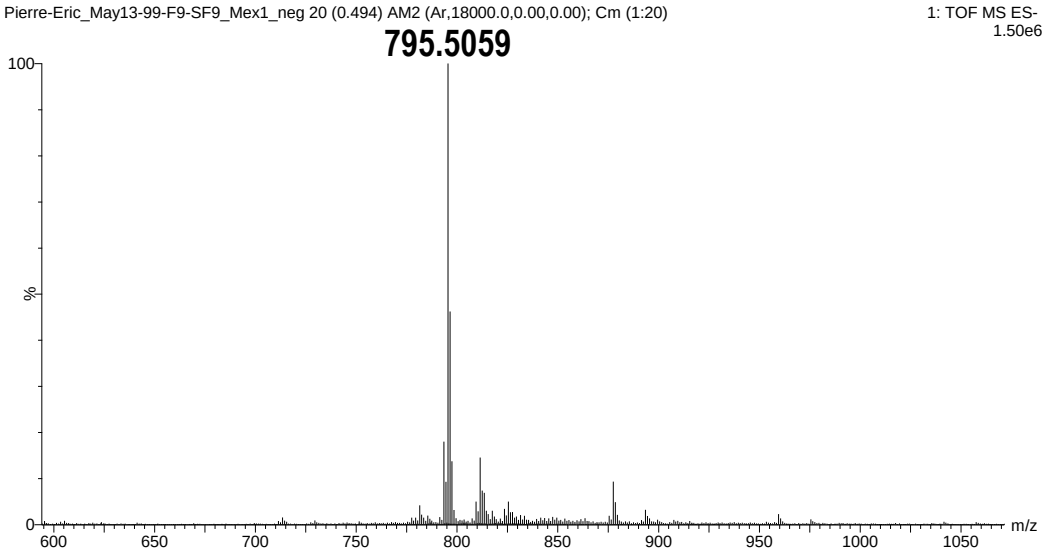
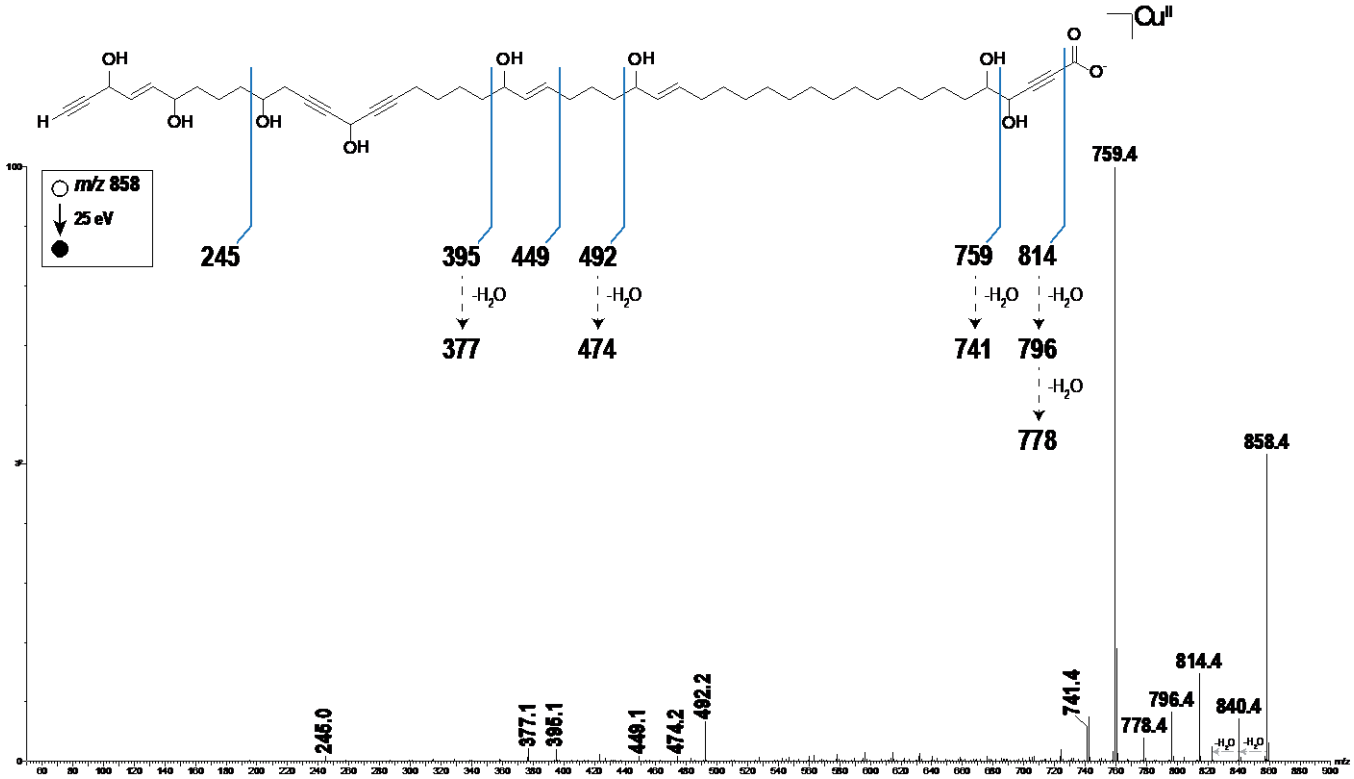


Figure S35: ESI$^+$-MS/MS (S28.a.) and ESI$^-$-MS/MS (S28.b.) spectra of osirisyne E (**6**) with outlines of dissociation of the precursor ion.

S28.a.



S28.b.

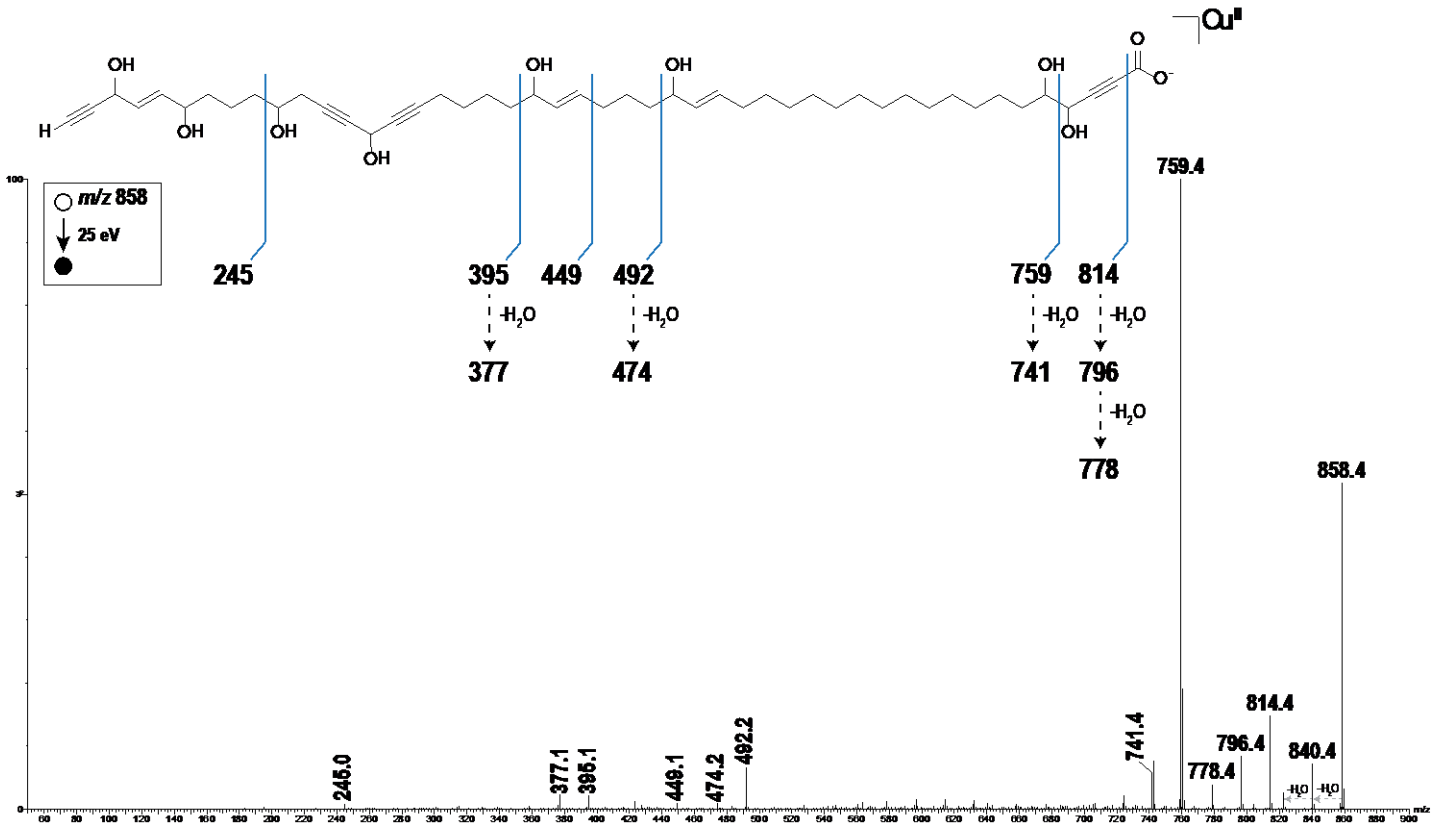

Cu
OH
H
O
O⁻
m/z 858
25 eV
245
395
449
492
759
814
-H2O
377
474
741
796
778
759.4
858.4
814.4
796.4
840.4
778.4
741.4
492.2
474.2
449.1
395.1
377.1
245.0

Figure S36: ^{1}H NMR (600 MHz, CD_3OD) spectrum for osirisyne E (**6**)

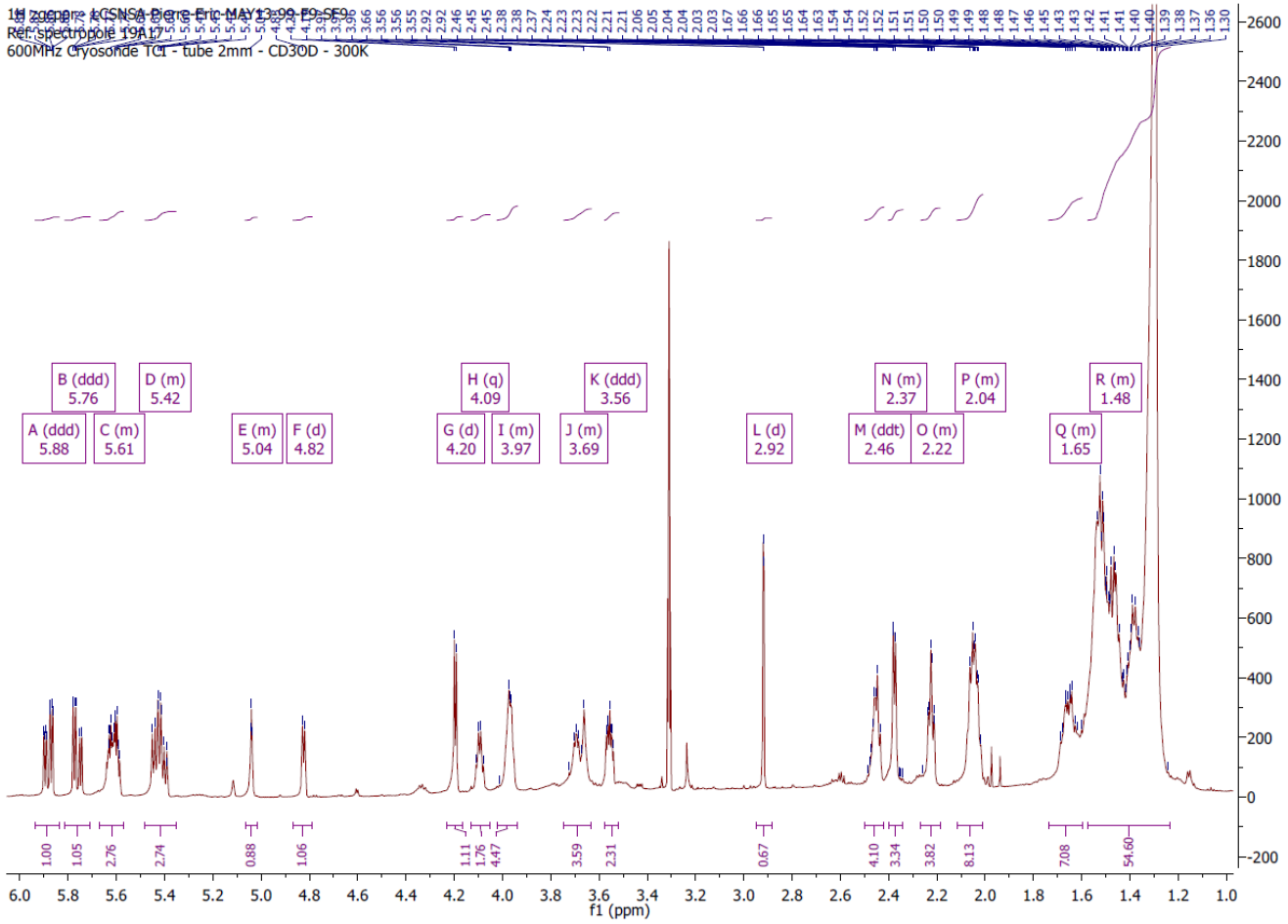
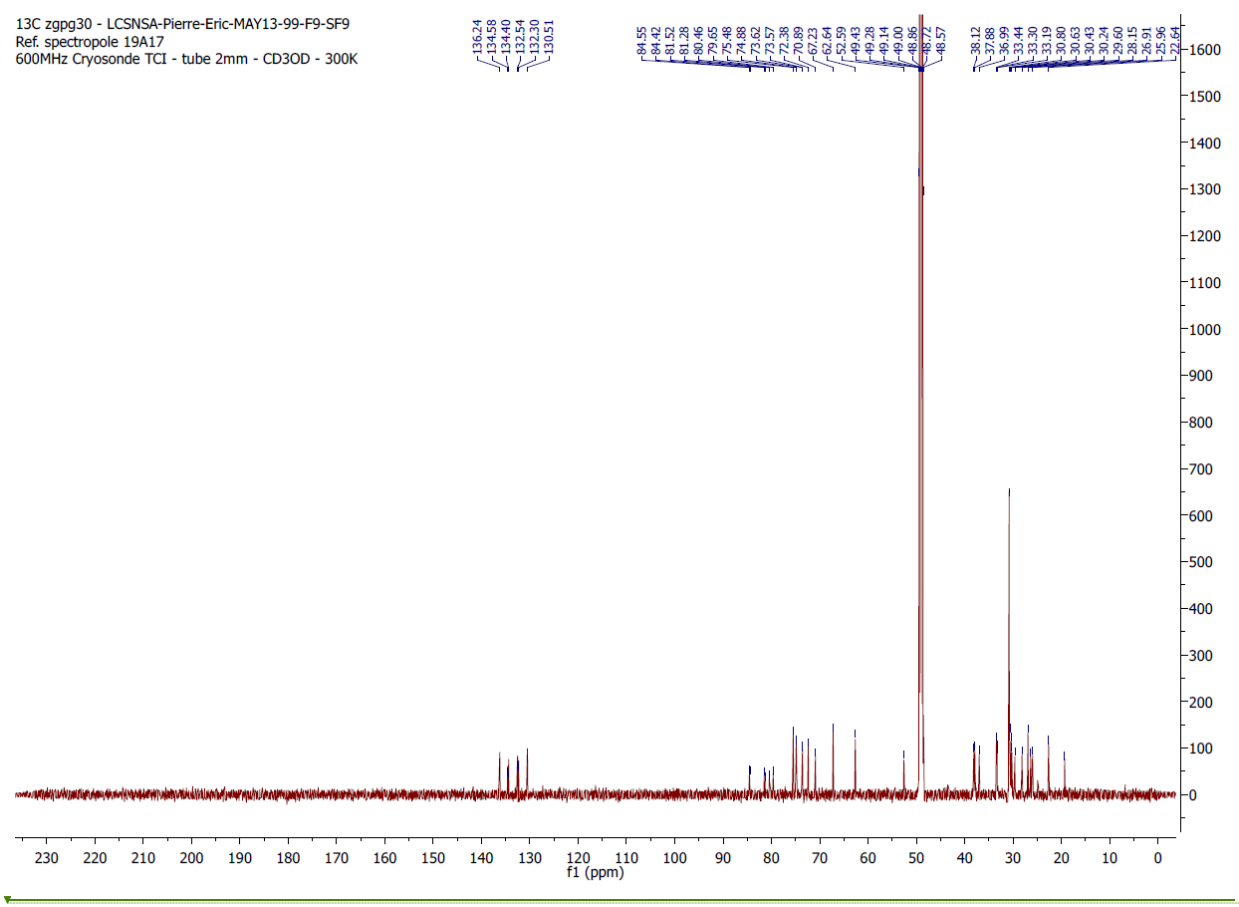
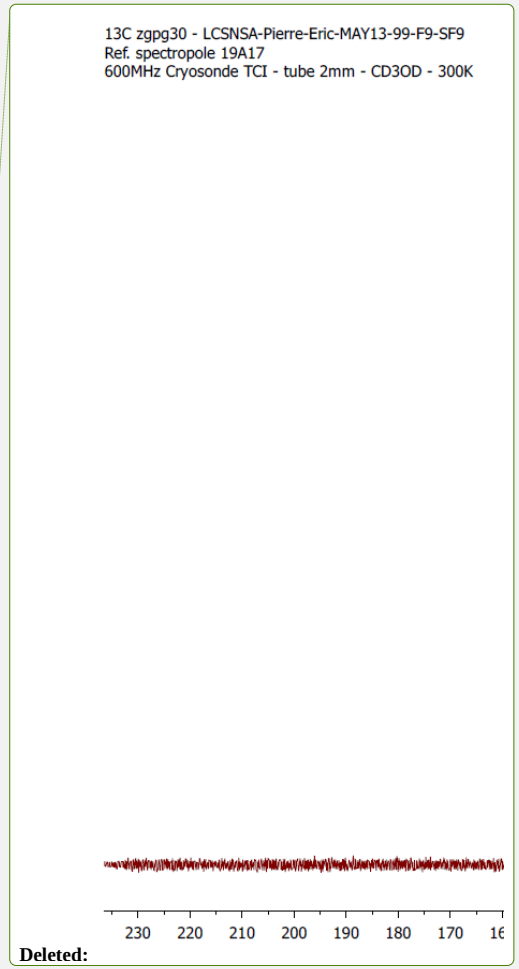


Figure S37: ^{13}C NMR (600 MHz, CD_3OD) spectrum for osirisyne E (**6**)





Deleted: