Supporting information

Aethiopinolones A-E, new pregnenolone type steroids from the East African basidiomycete *Fomitiporia aethiopica*

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[†] These authors contributed equally to this work.

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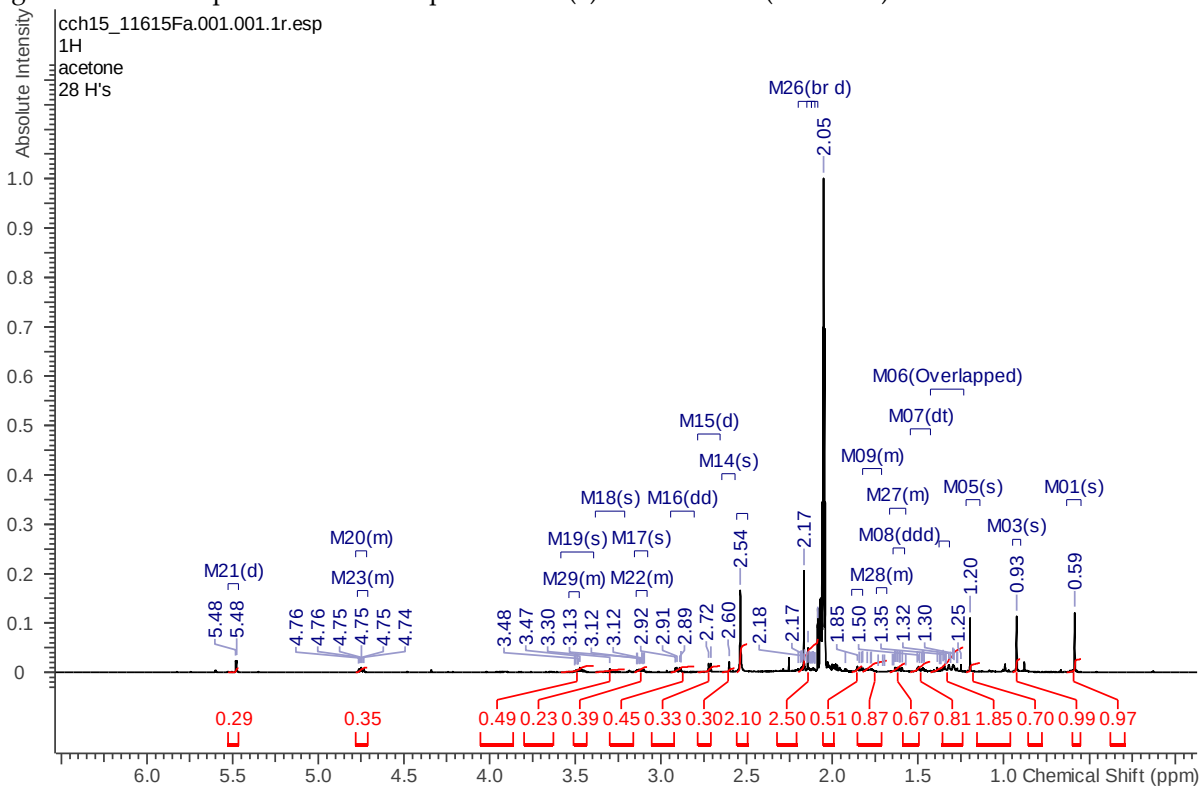

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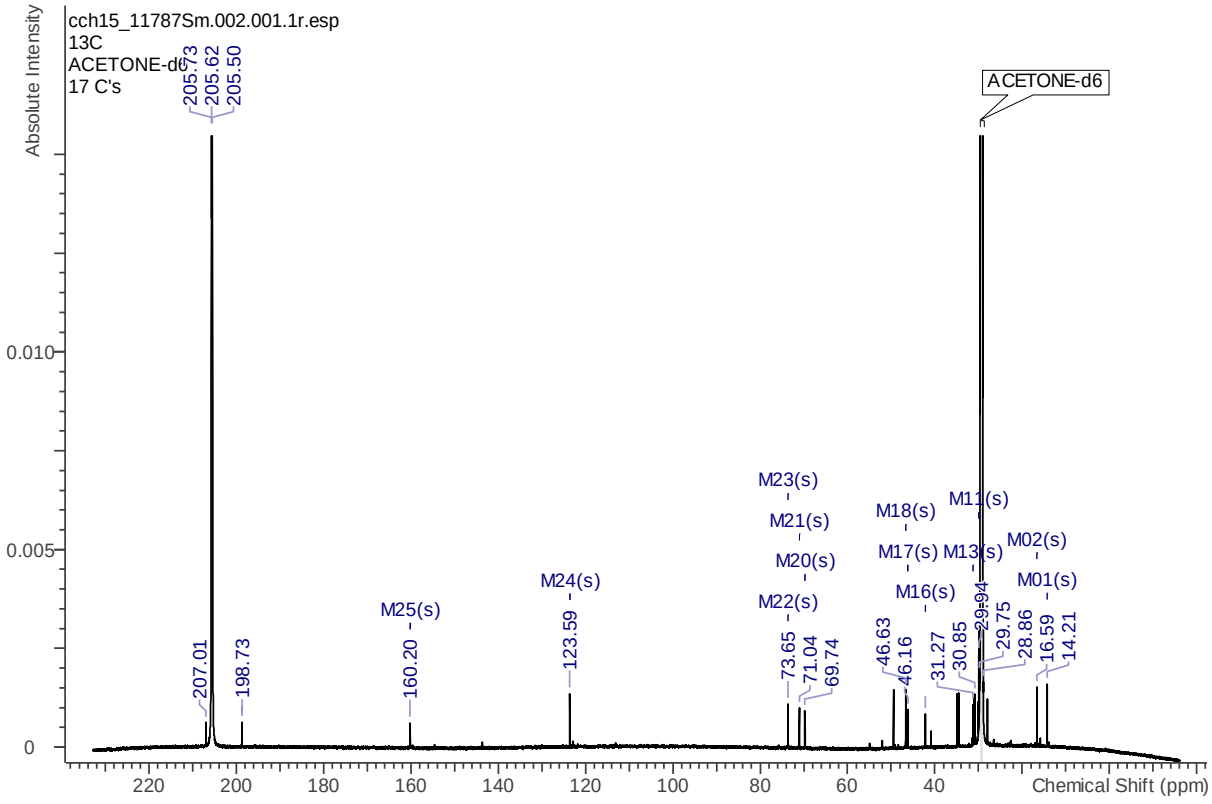
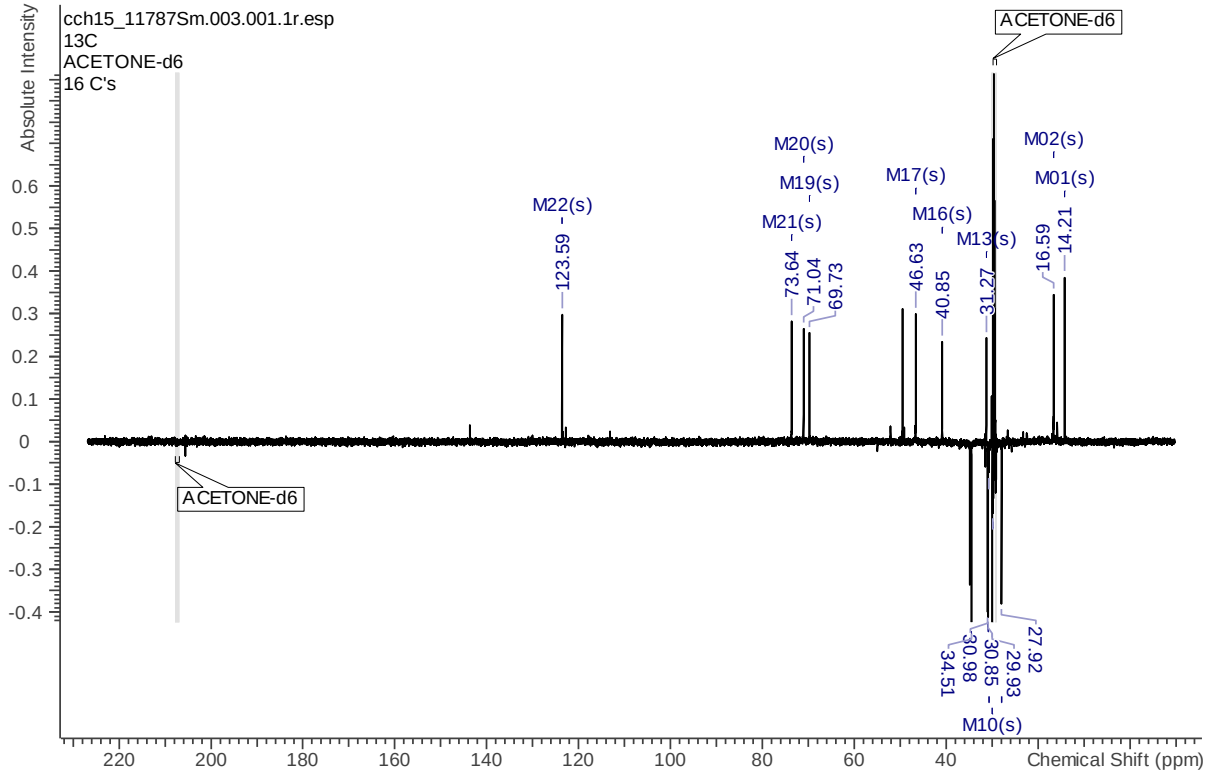


Figure 3:DEPT spectrum of Aethiopinolone A (**1**) in acetone-d_6 (175 MHz)



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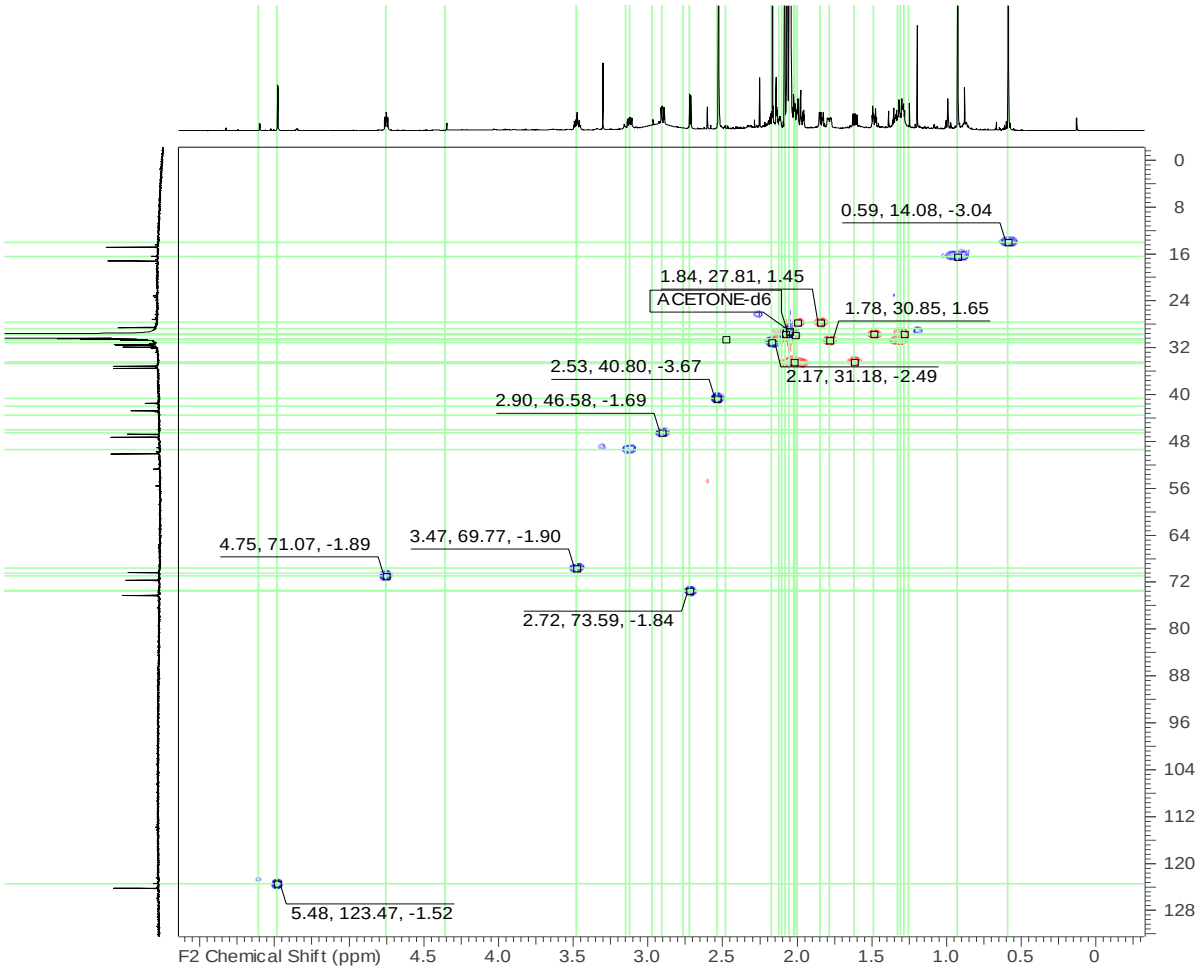

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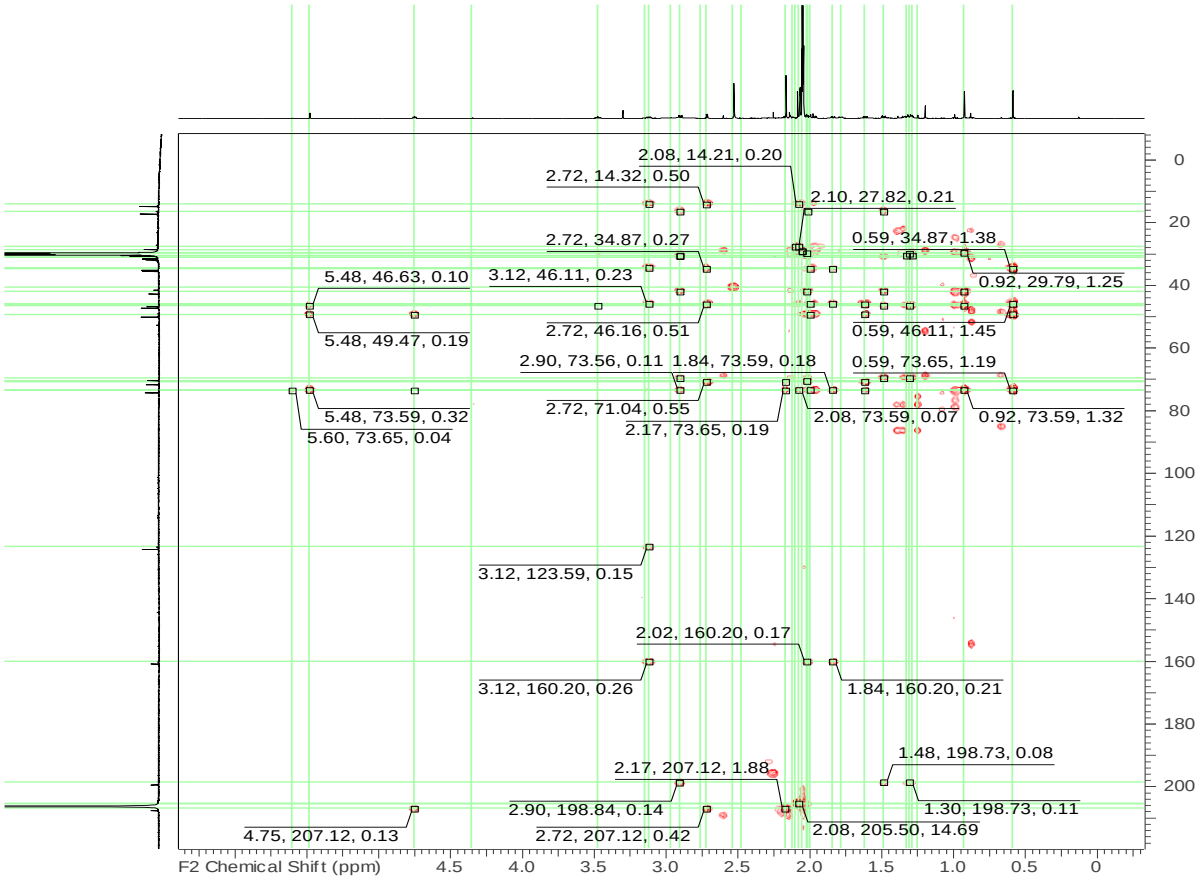

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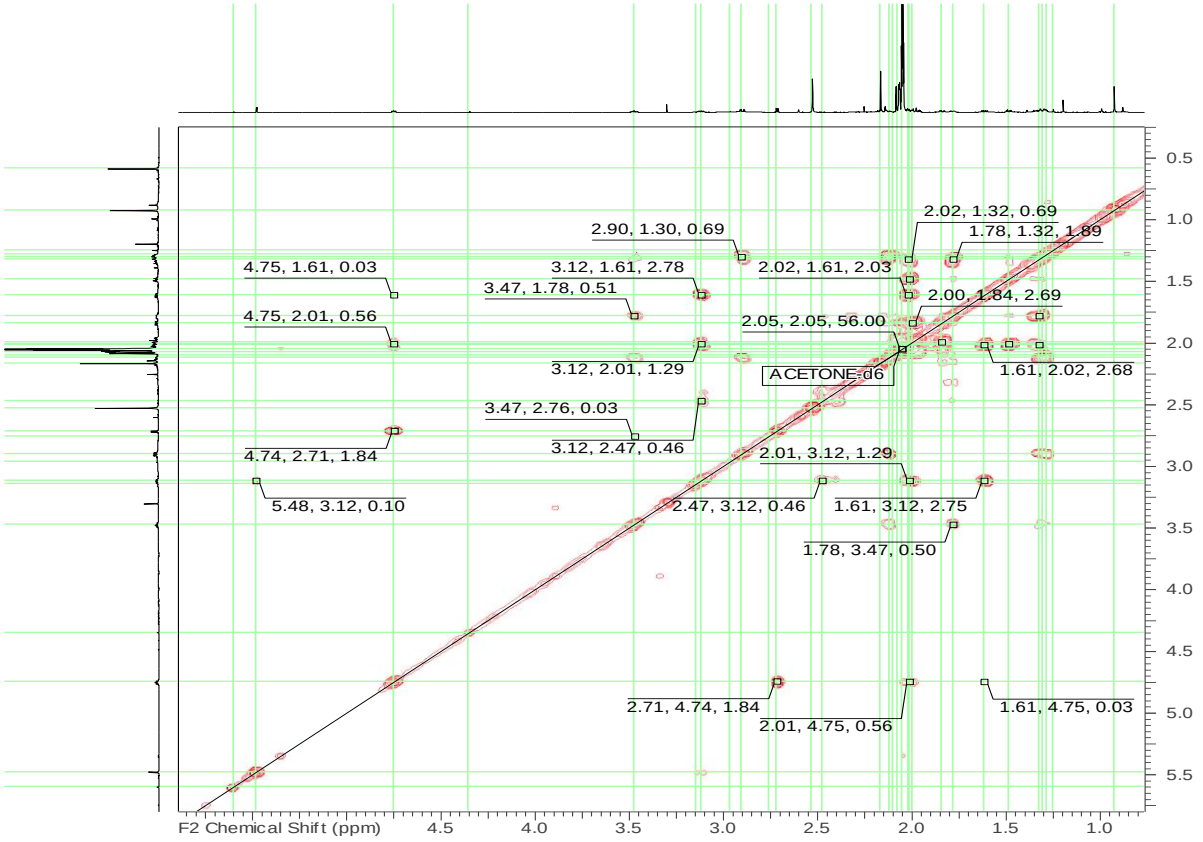
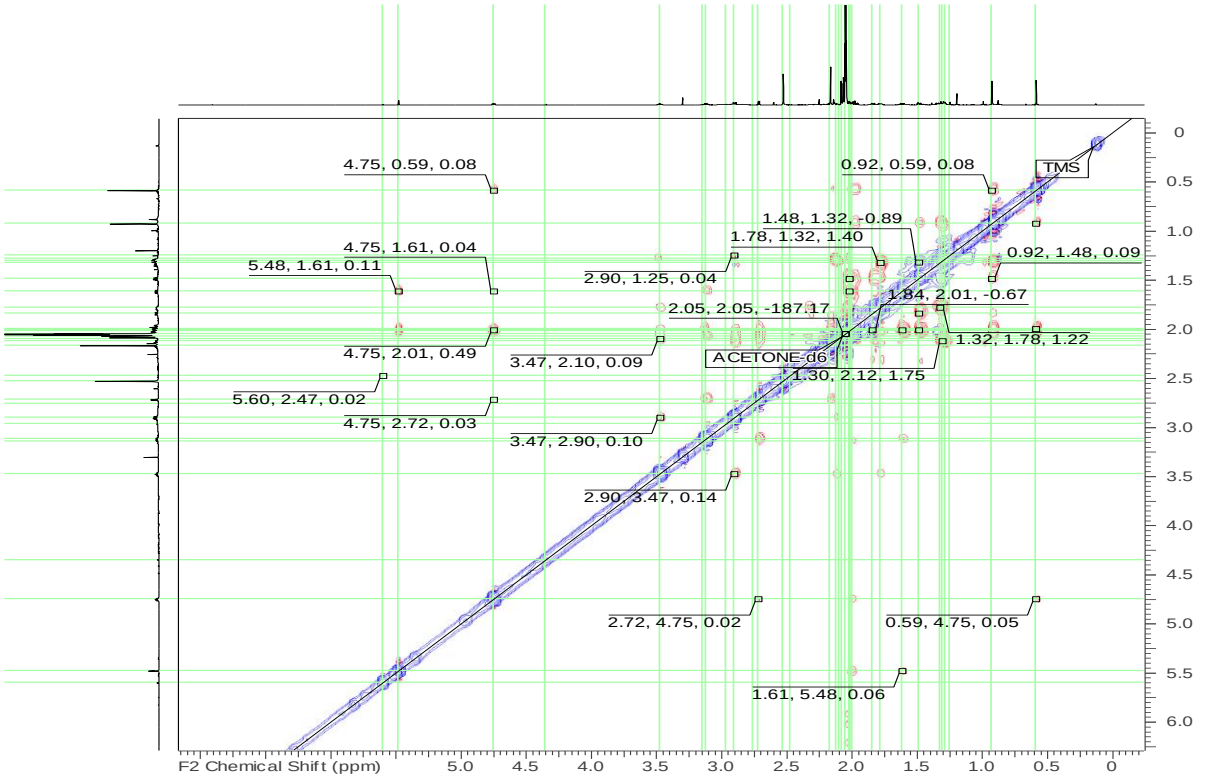


Figure 7:^{1}H, ^{1}H ROESY spectrum of Aethiopinolone A (**1**) in acetone-d_6 (500 MHz)



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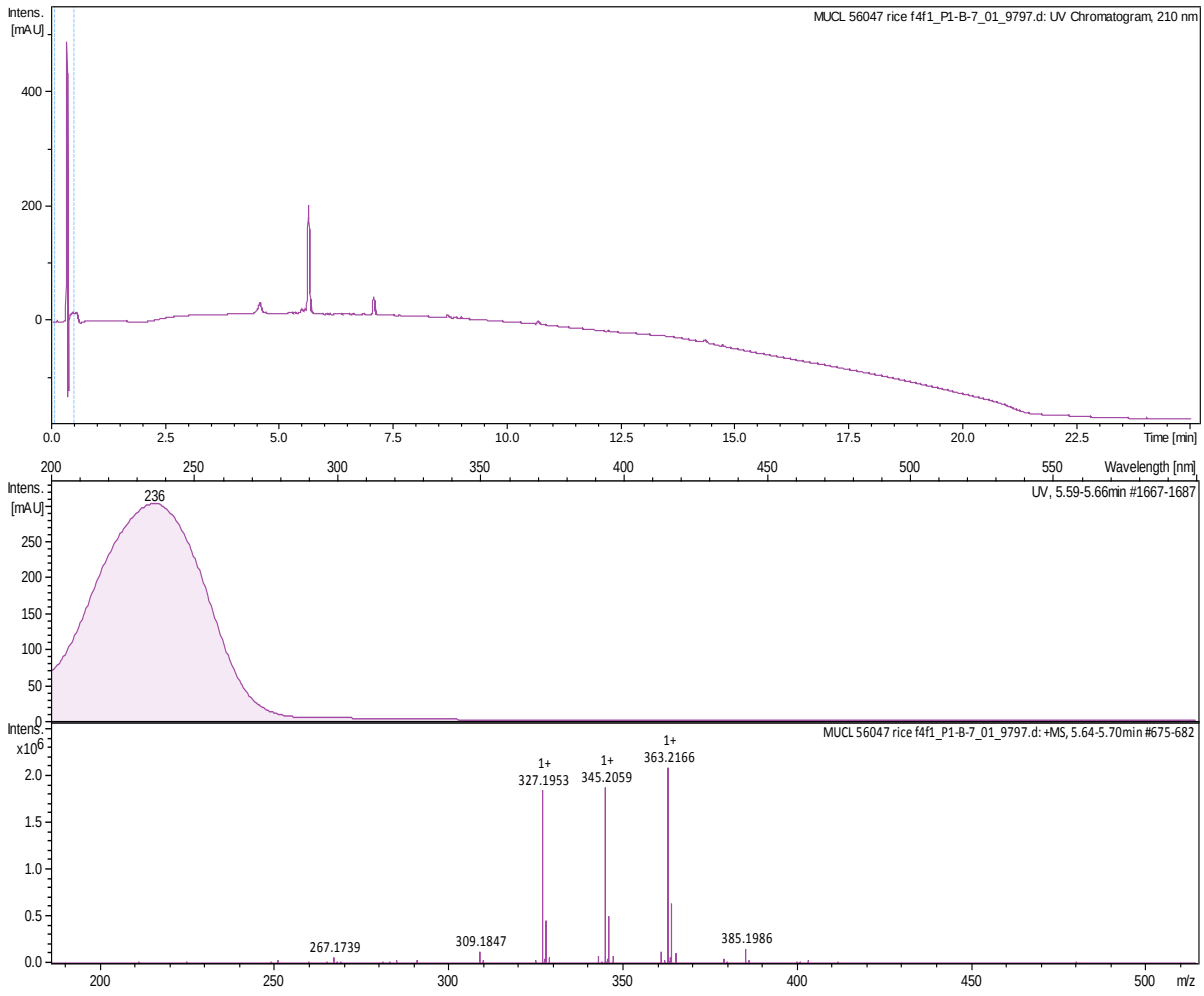

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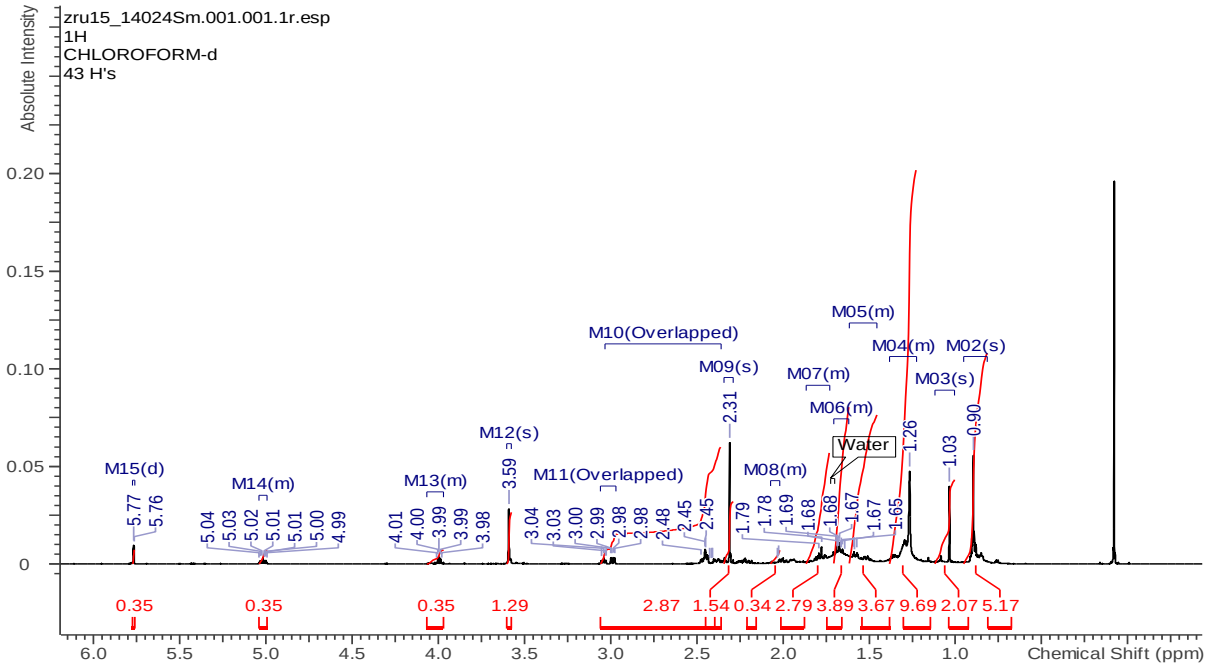
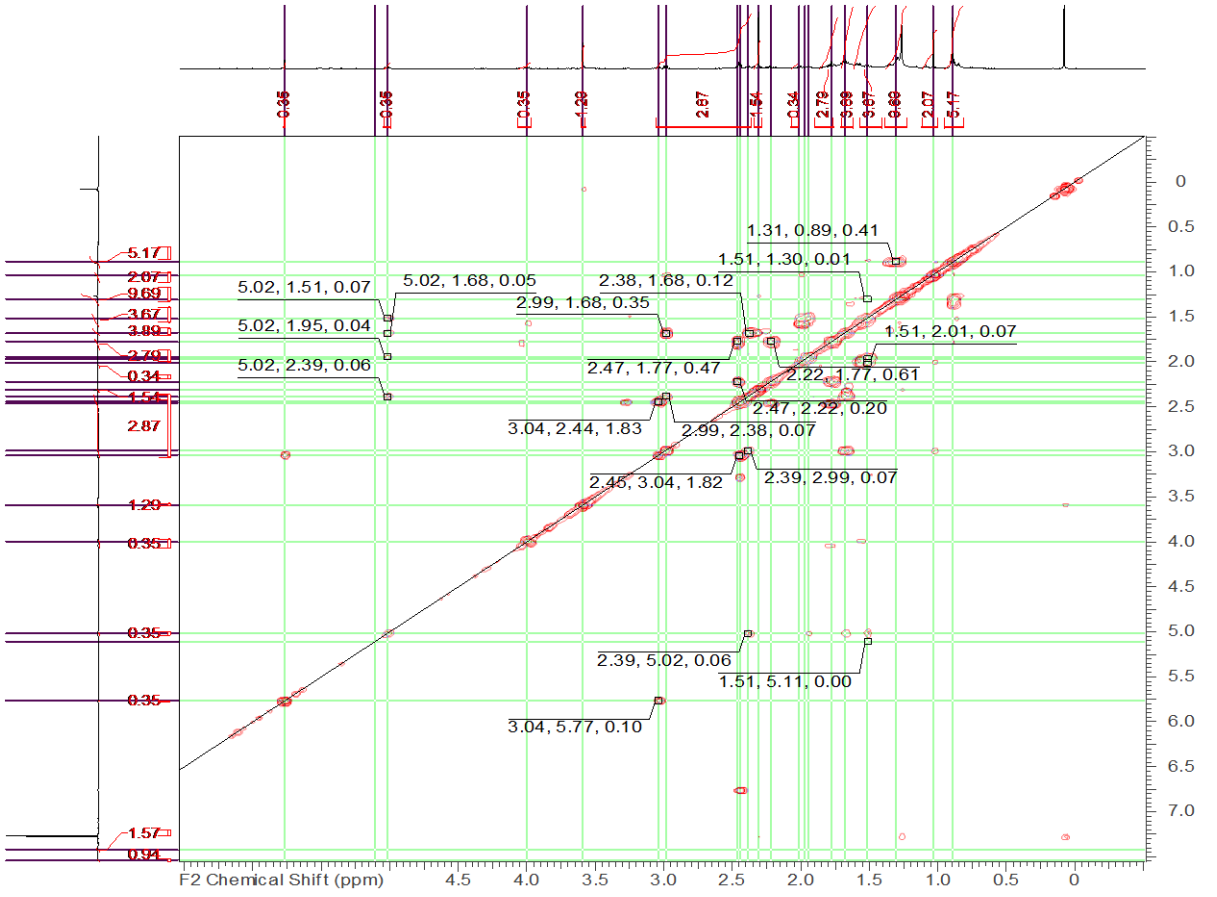


Figure 10: ^{1}H,^{1}H COSY NMR spectrum of Aethiopinolone A (**1**) (*S*)- MTPA ester in chloroform –d (700 MHz)



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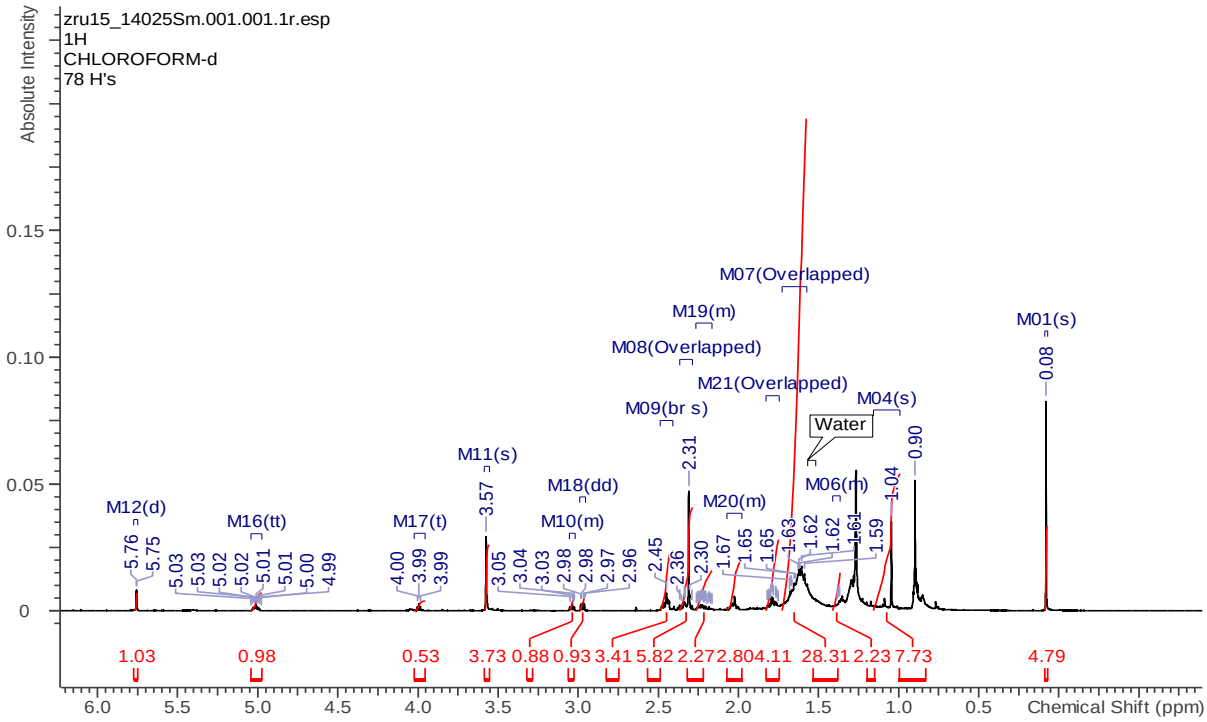

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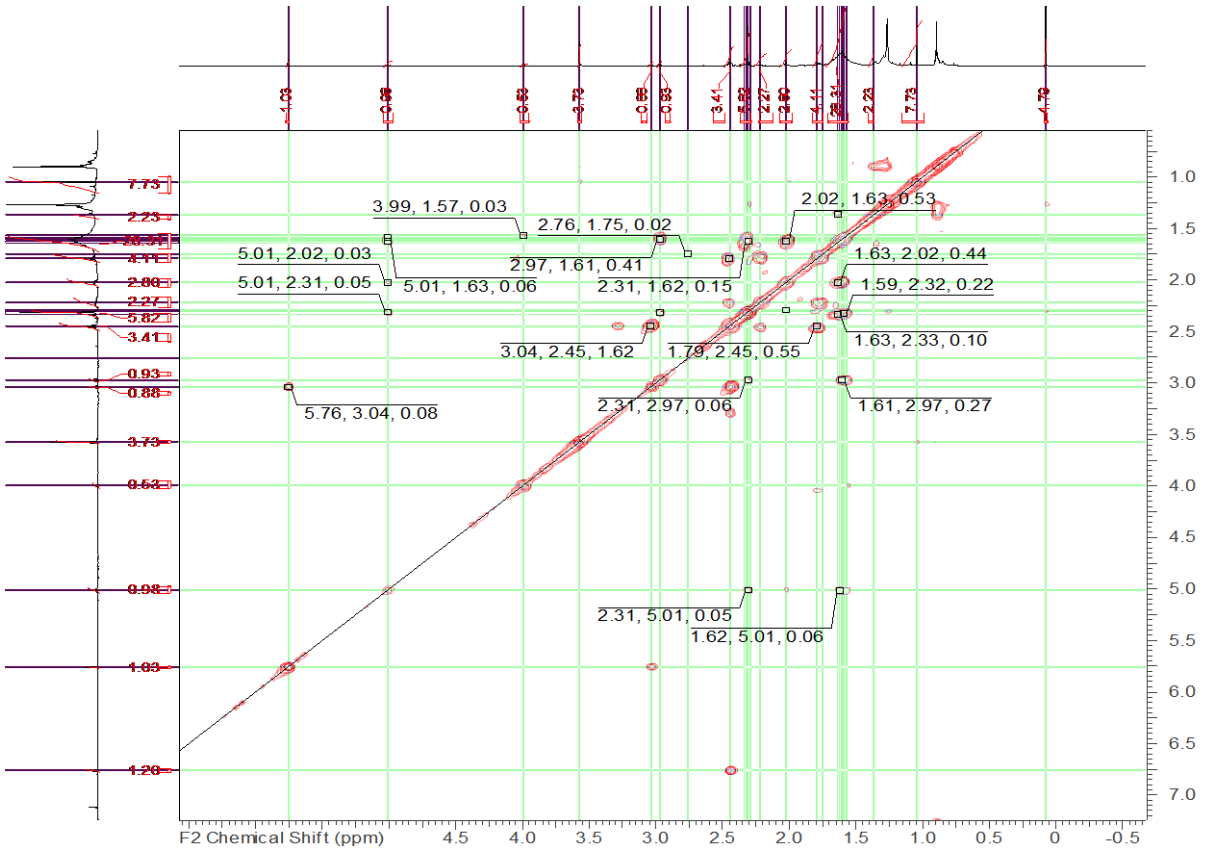


1 and 2D NMR data for Aethiopinolone B (2)

Figure 13: ^{1}H NMR spectrum of Aethiopinolone B (**2**) in DMSO-d$_6$ (500 MHz)

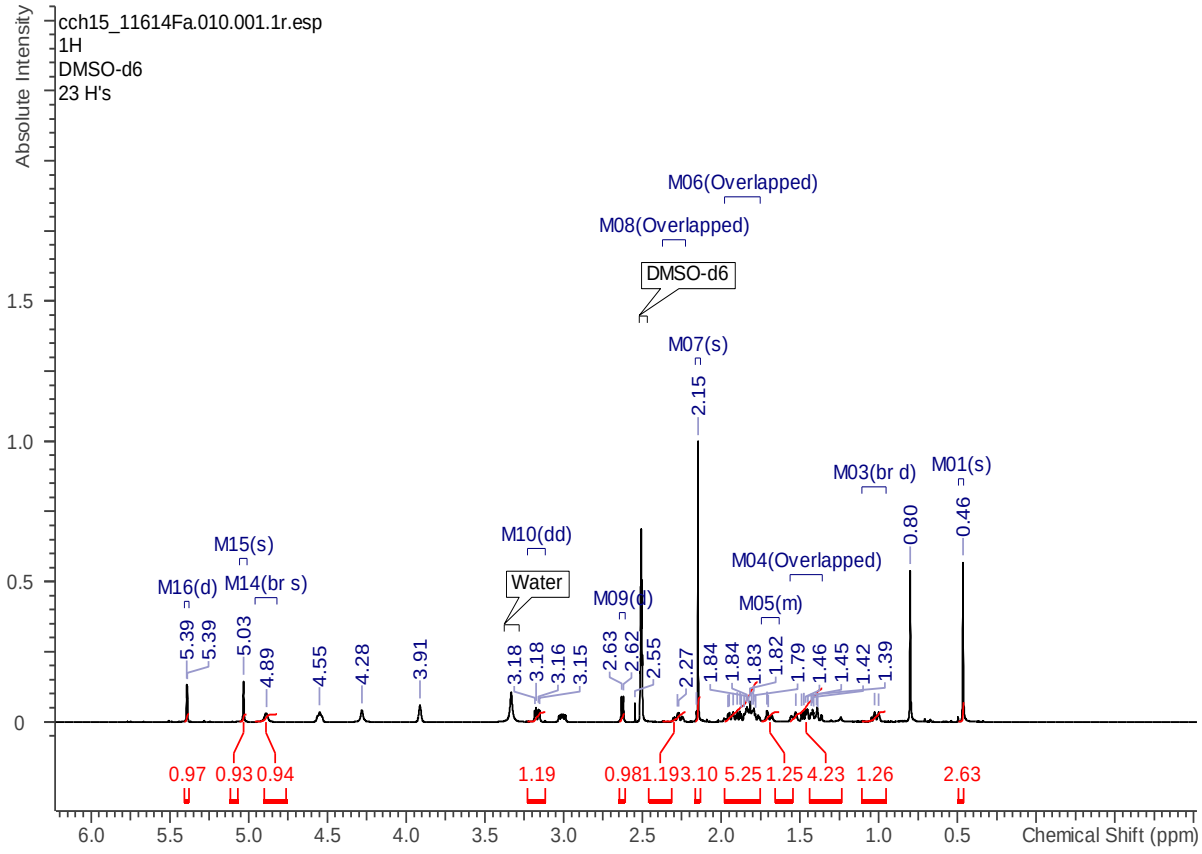
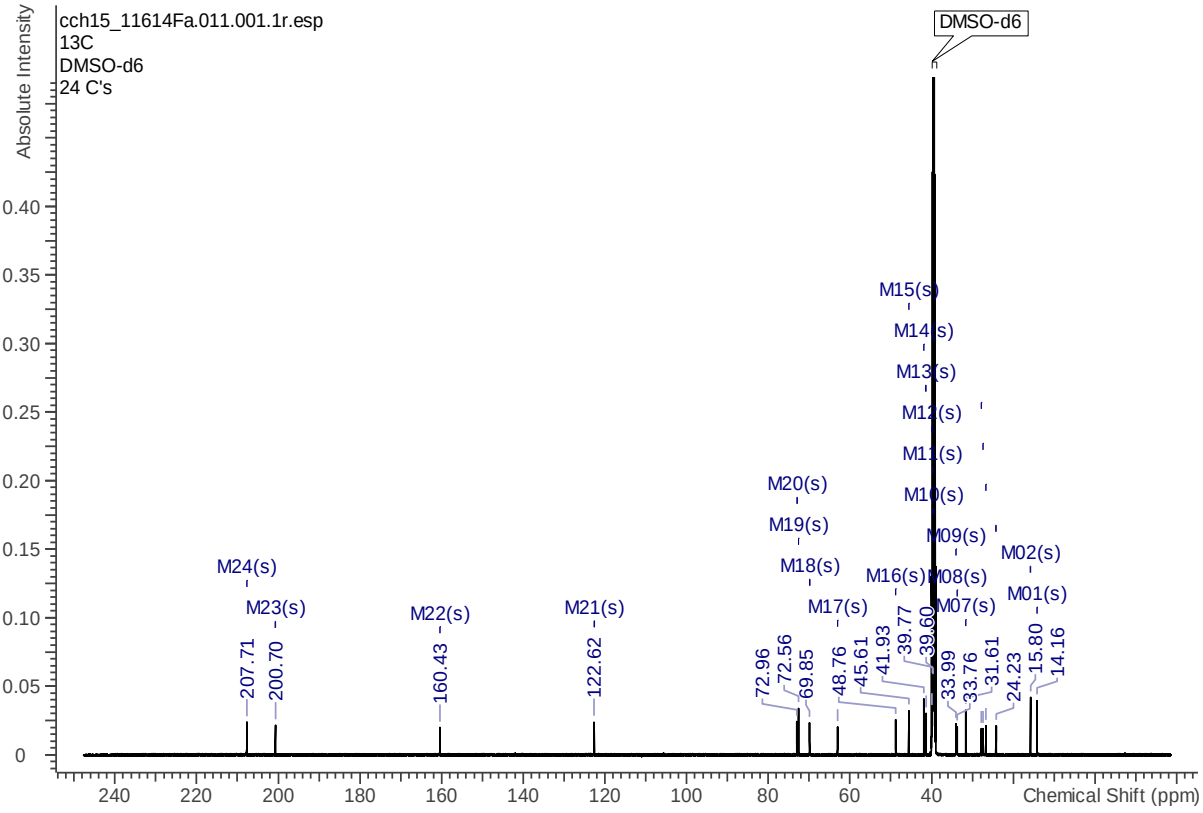


Figure 14: ^{13}C NMR spectrum of Aethiopinolone B (**2**) in in DMSO-d$_6$ (125 MHz)



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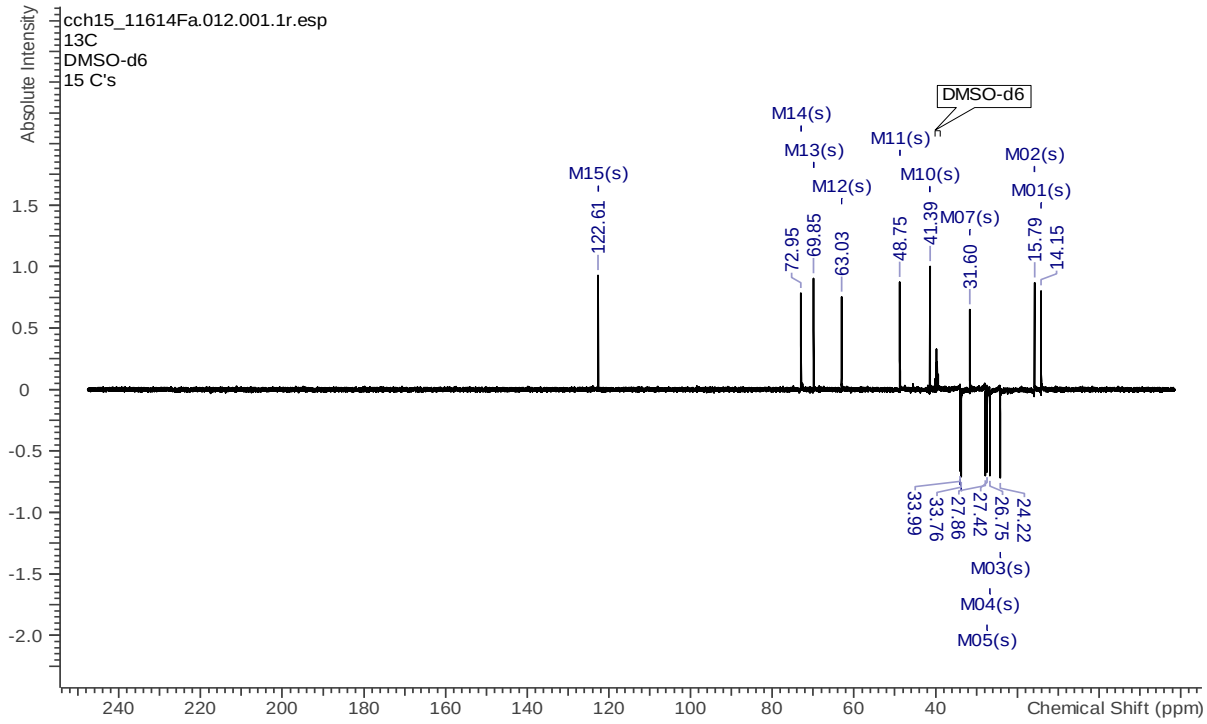
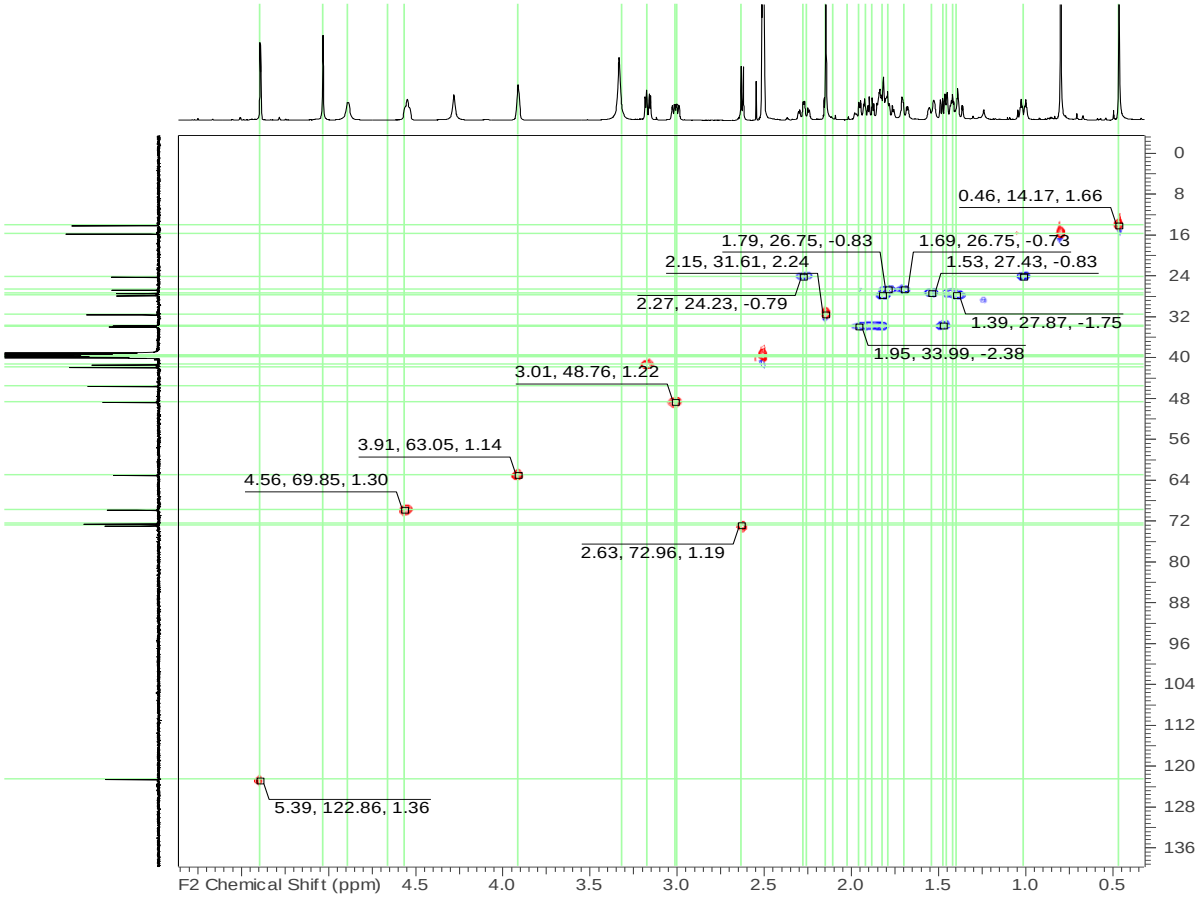


Figure 16: ^{1}H, ^{13}C HSQC spectrum of Aethiopinolone B (**2**) in in DMSO-d_6 (500 MHz, 125 MHz)



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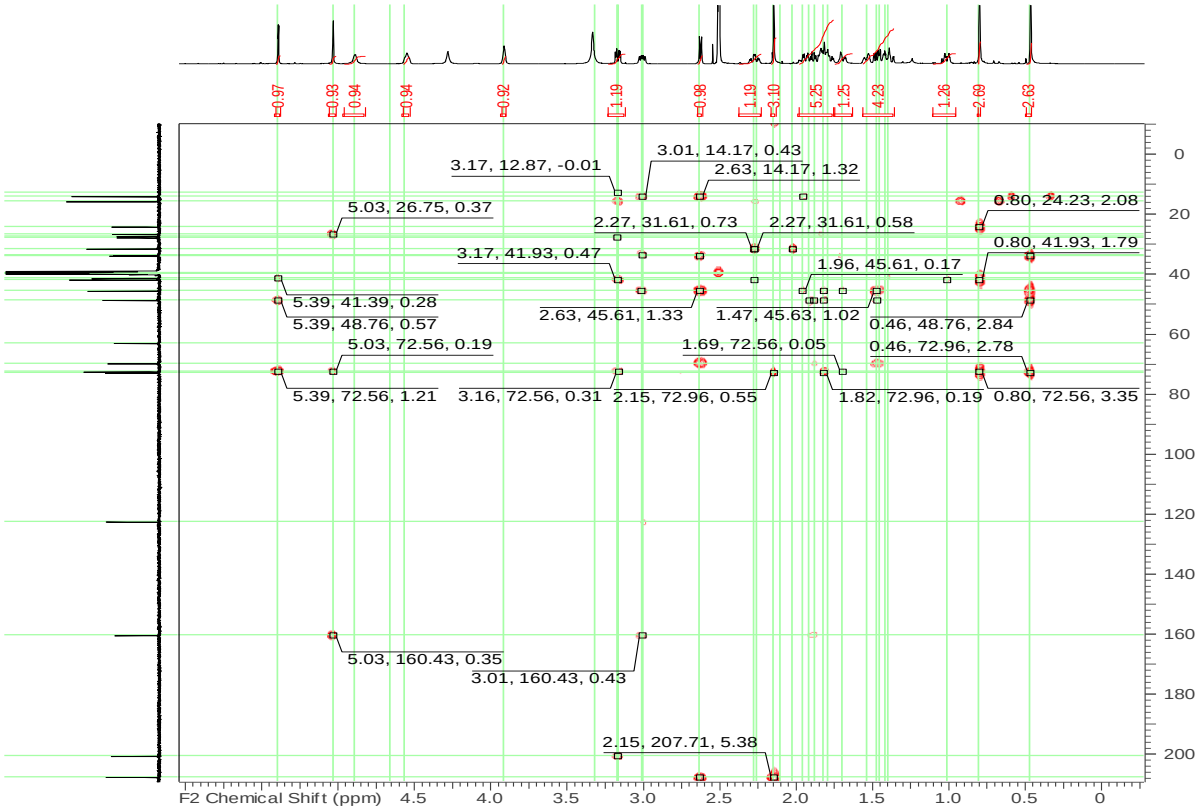

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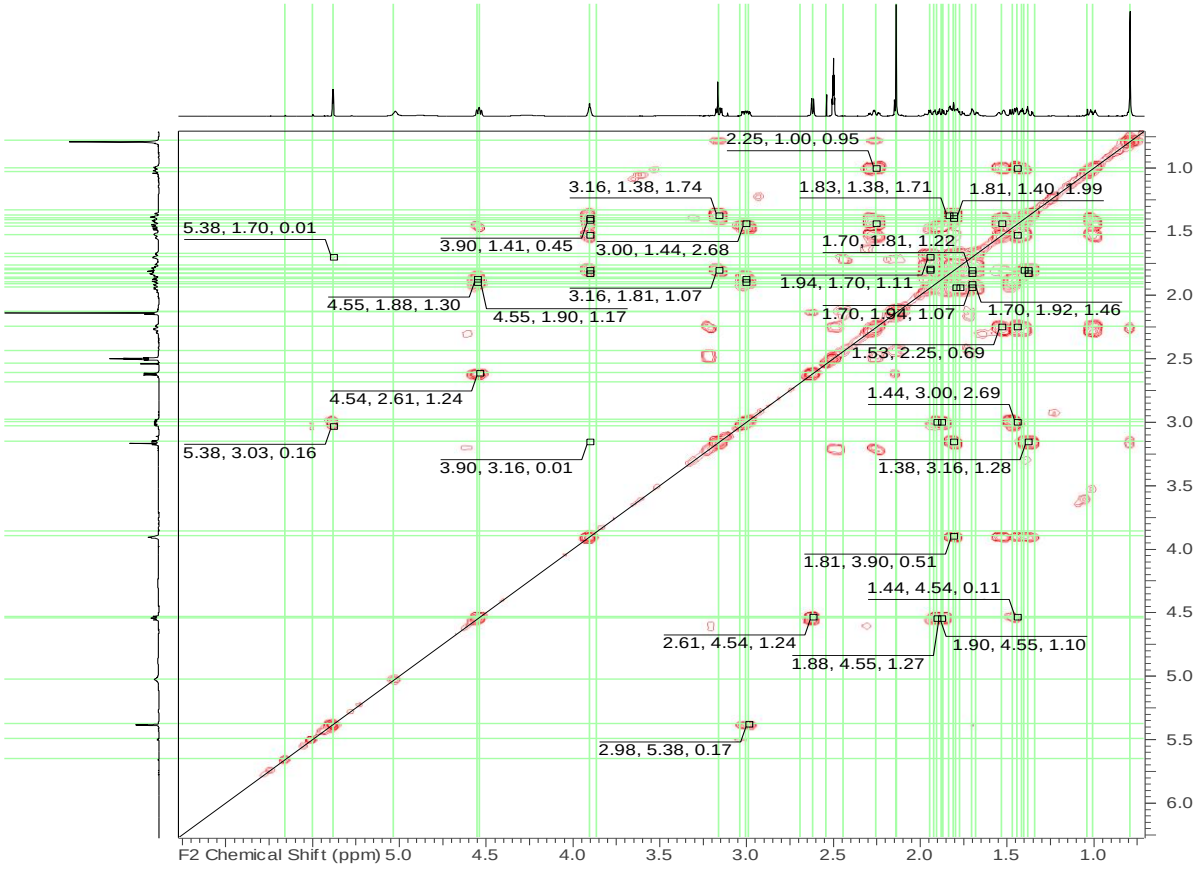

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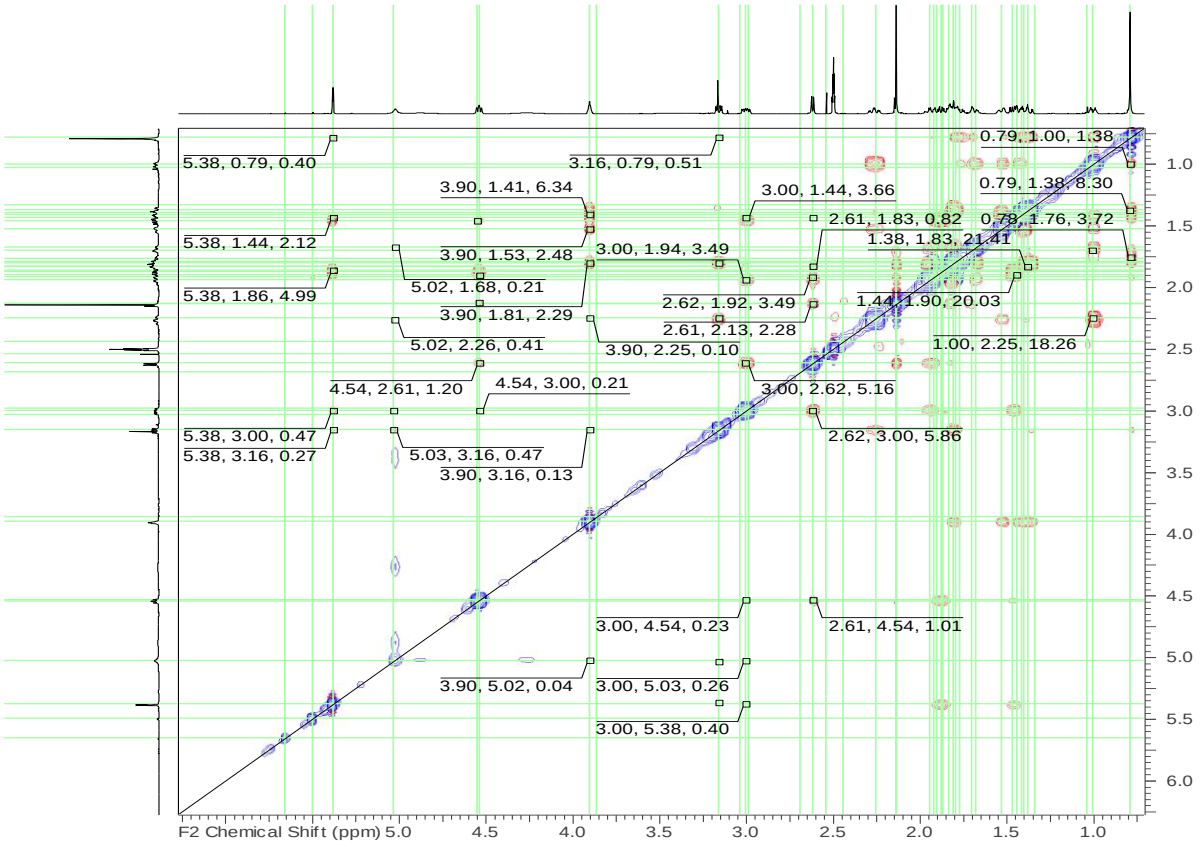
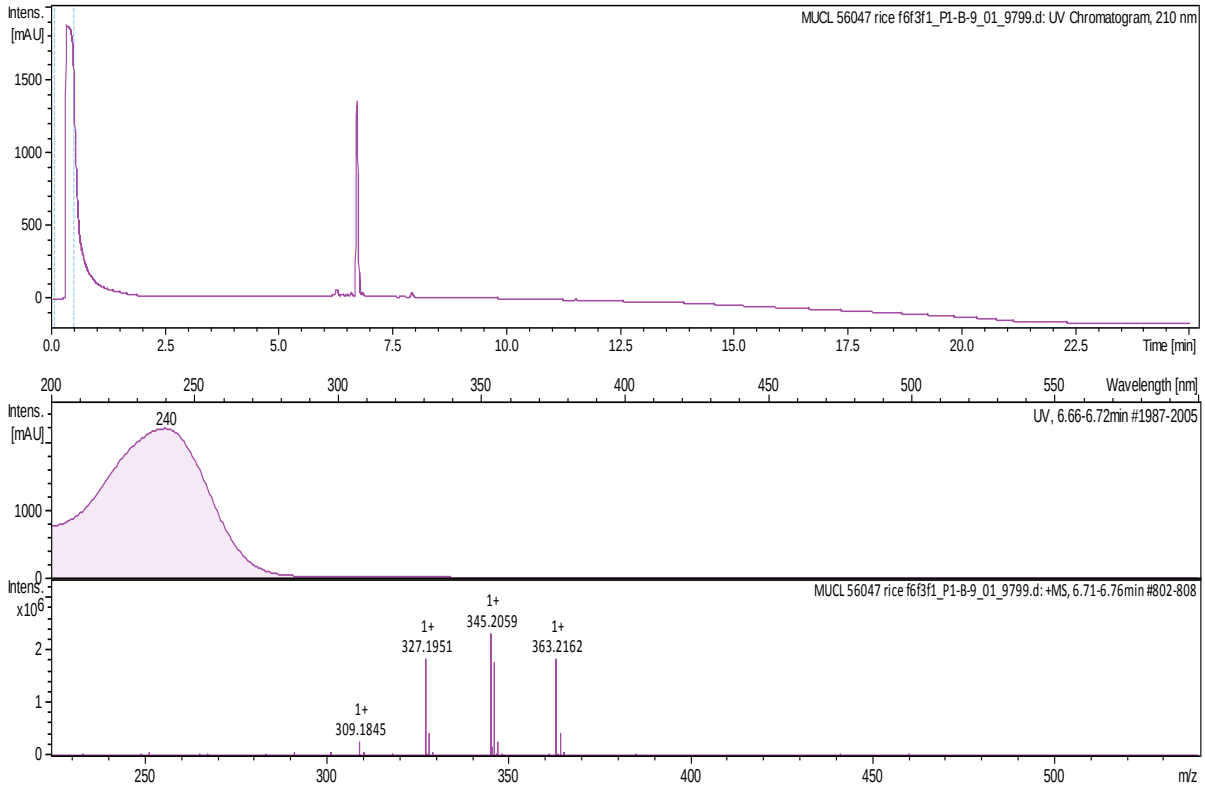
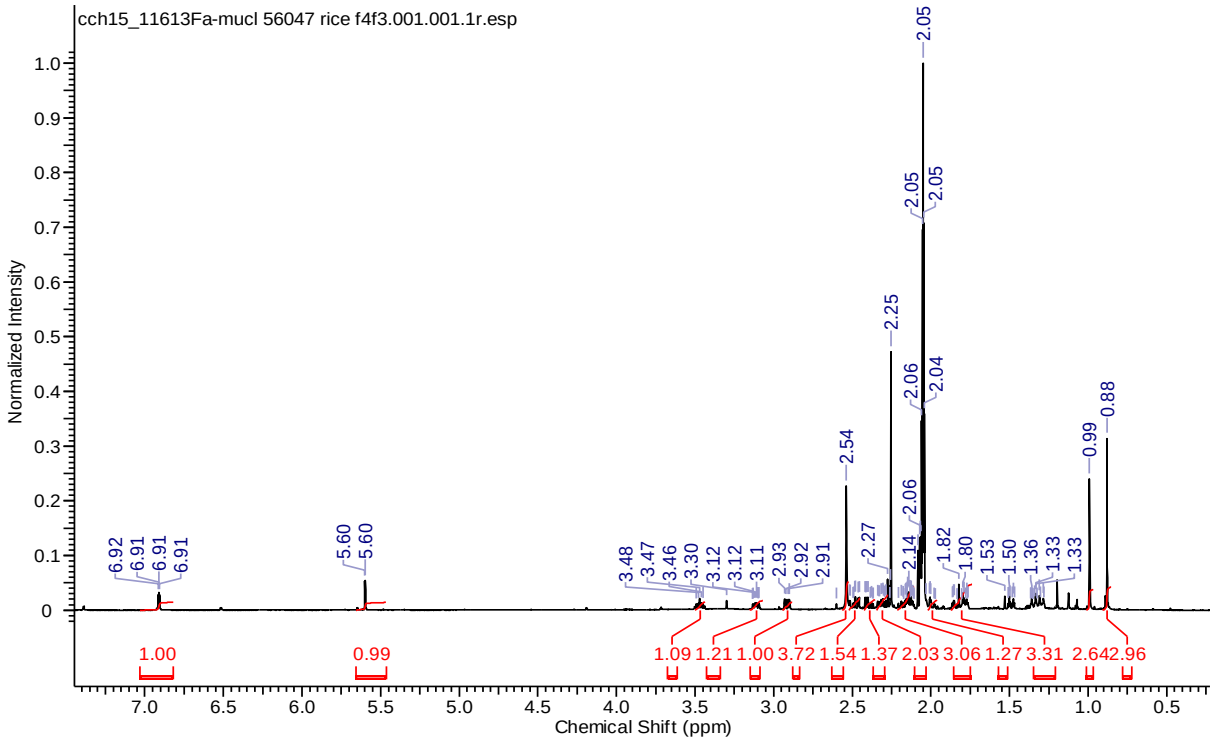


Figure 20: HRMS spectrum of Aethiopinolone B (**2**)



1 and 2D NMR data for Aethiopinolone C (3)

Figure 21: ^{1}H NMR spectrum of Aethiopinolone C (**3**) in acetone-d$_6$ (500 MHz)



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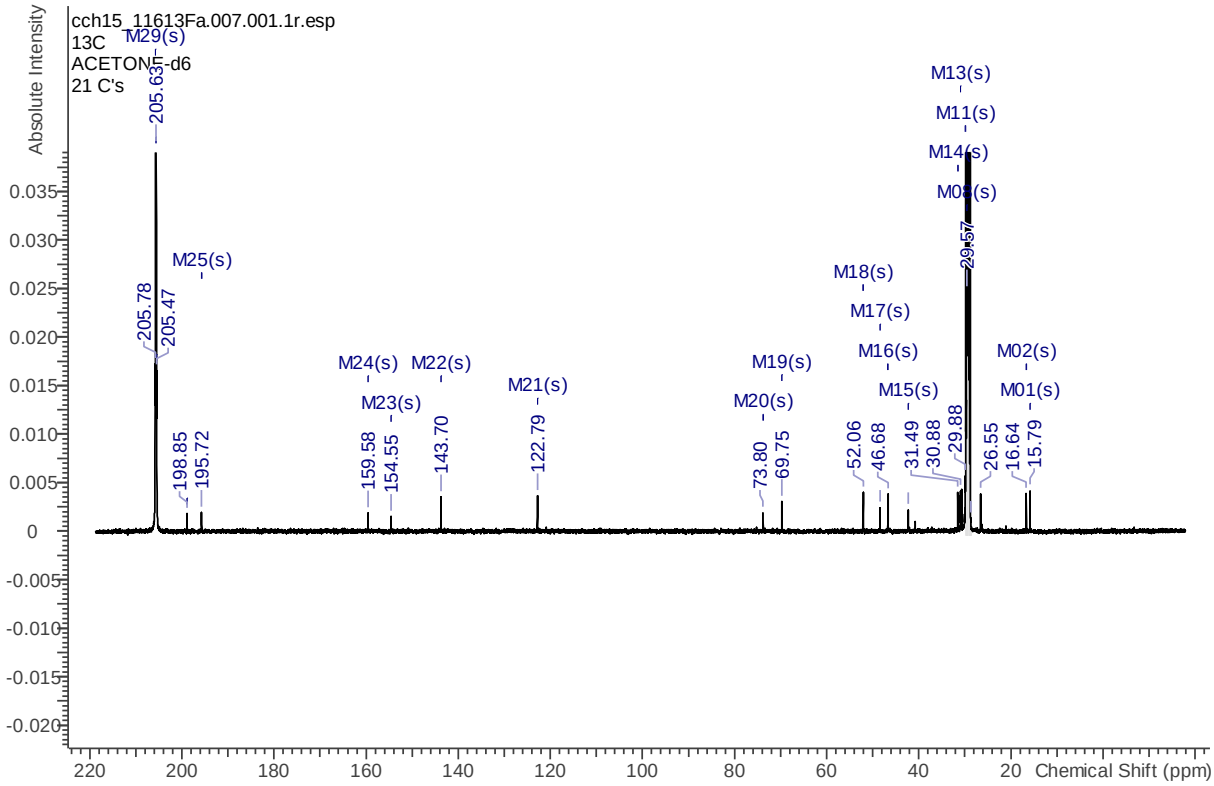


Figure 23: DEPT NMR spectrum of Aethiopinolone C (**3**) in acetone-d_6 (125 MHz)

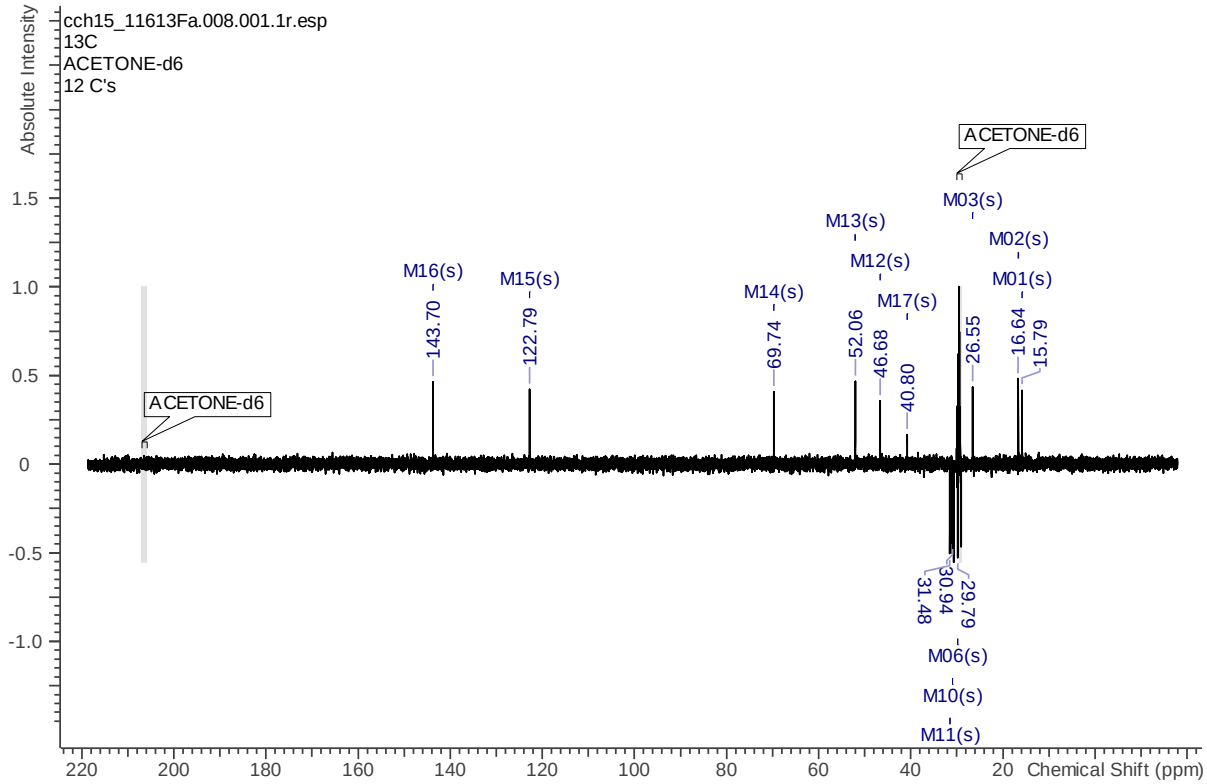
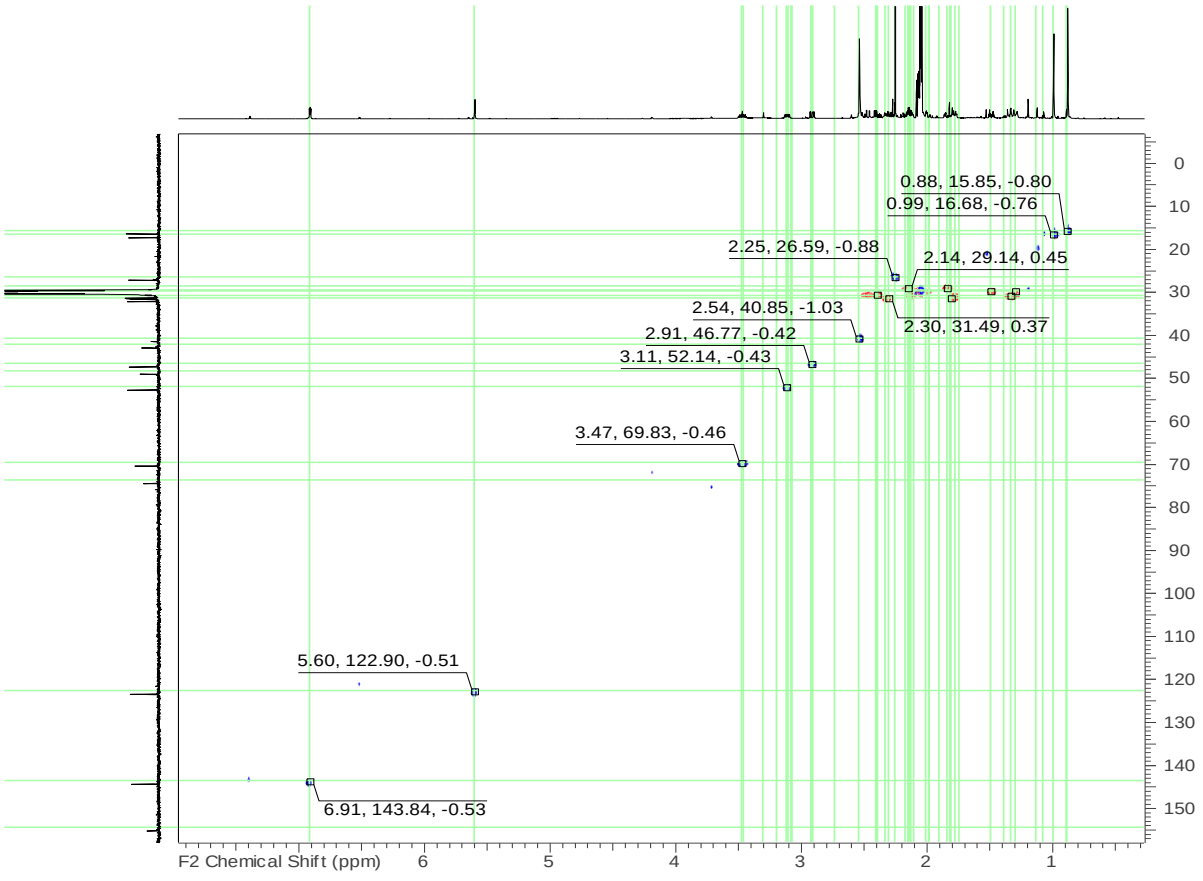


Figure 24:^{1}H, ^{13}C HSQC spectrum of Aethiopinolone C (**3**) in acetone-d_6 (500MHz, 125 MHz)



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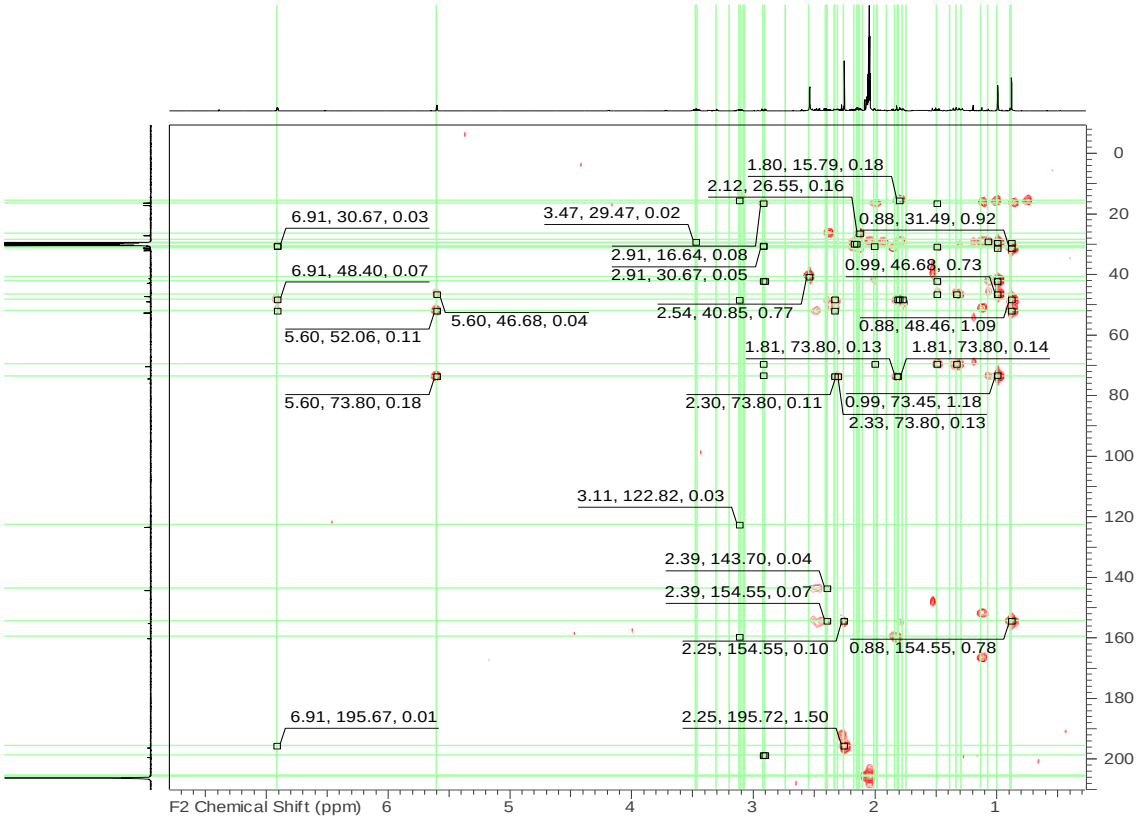


Figure 26: ^{1}H,^{1}H COSY spectrum of Aethiopinolone C (**3**) in acetone-d_6 (500MHz)

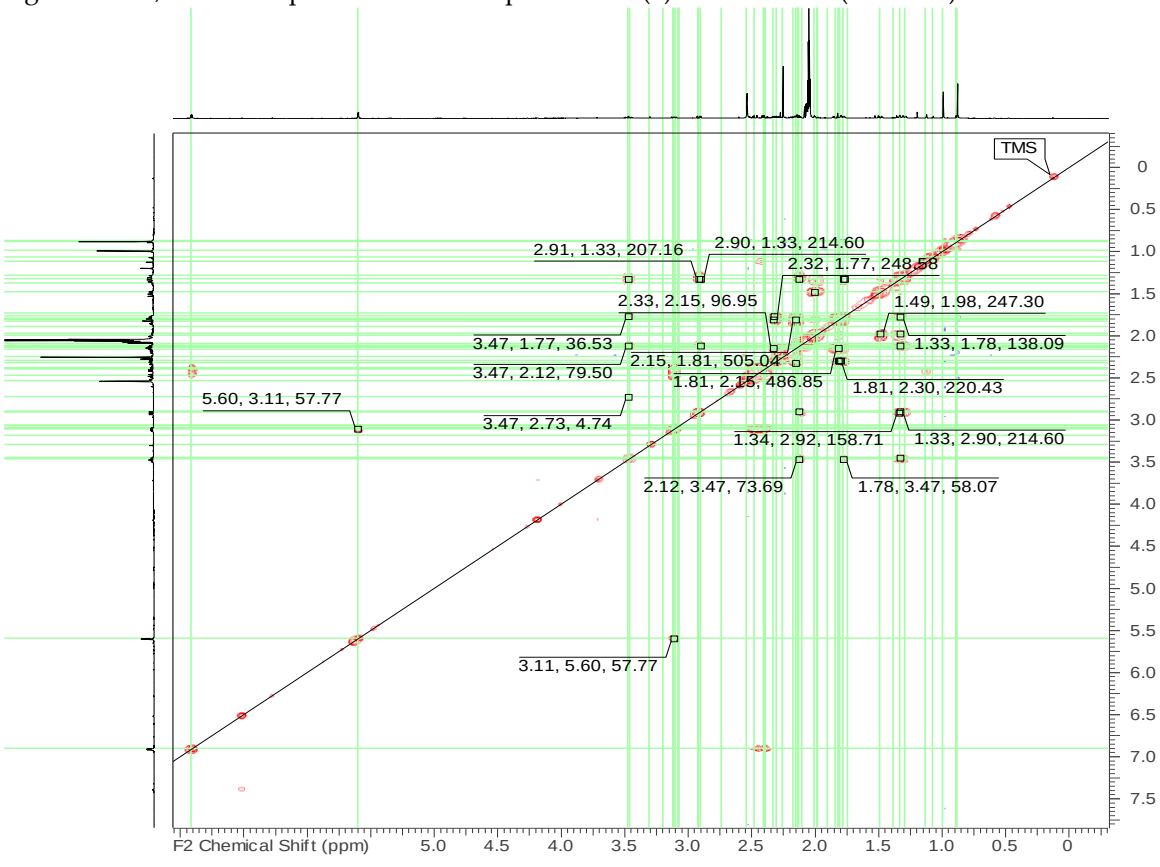


Figure 27: ^{1}H, ^{1}H ROESY spectrum of Aethiopinolone C (**3**) in acetone-d_6 (500MHz)

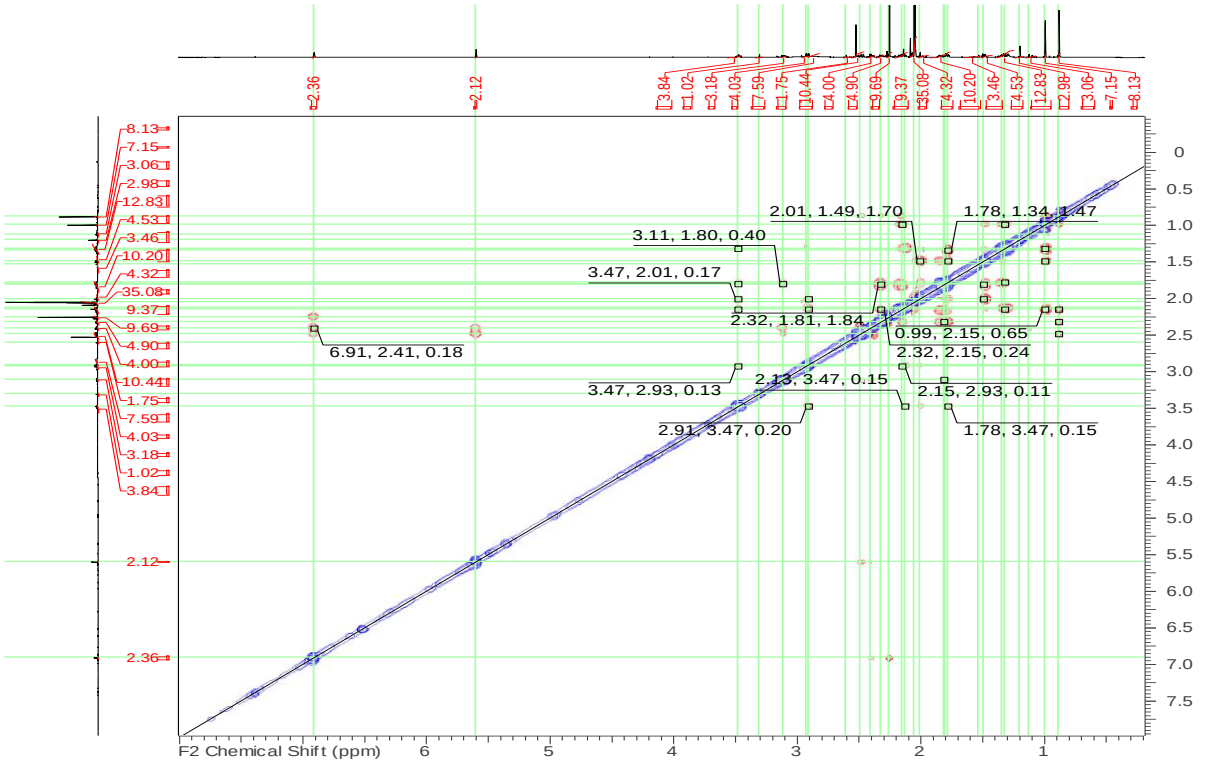


Figure 28: HRMS data for Aethiopinolone C (**3**)

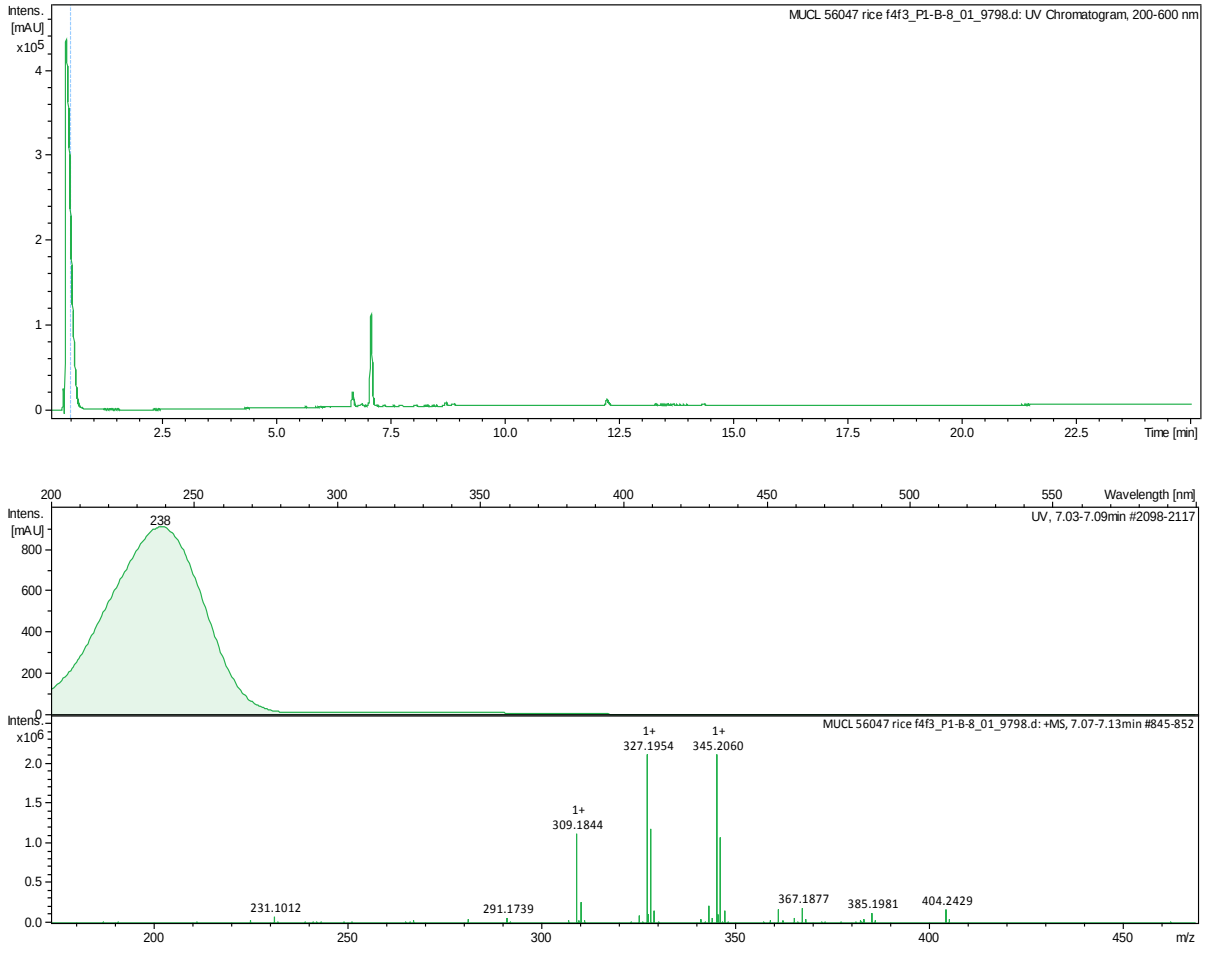


Figure 29:^{1}H NMR spectrum of Aethiopinolone C (**3**) (*S*)- MTPA ester in pyridine –d_5 (700 MHz)

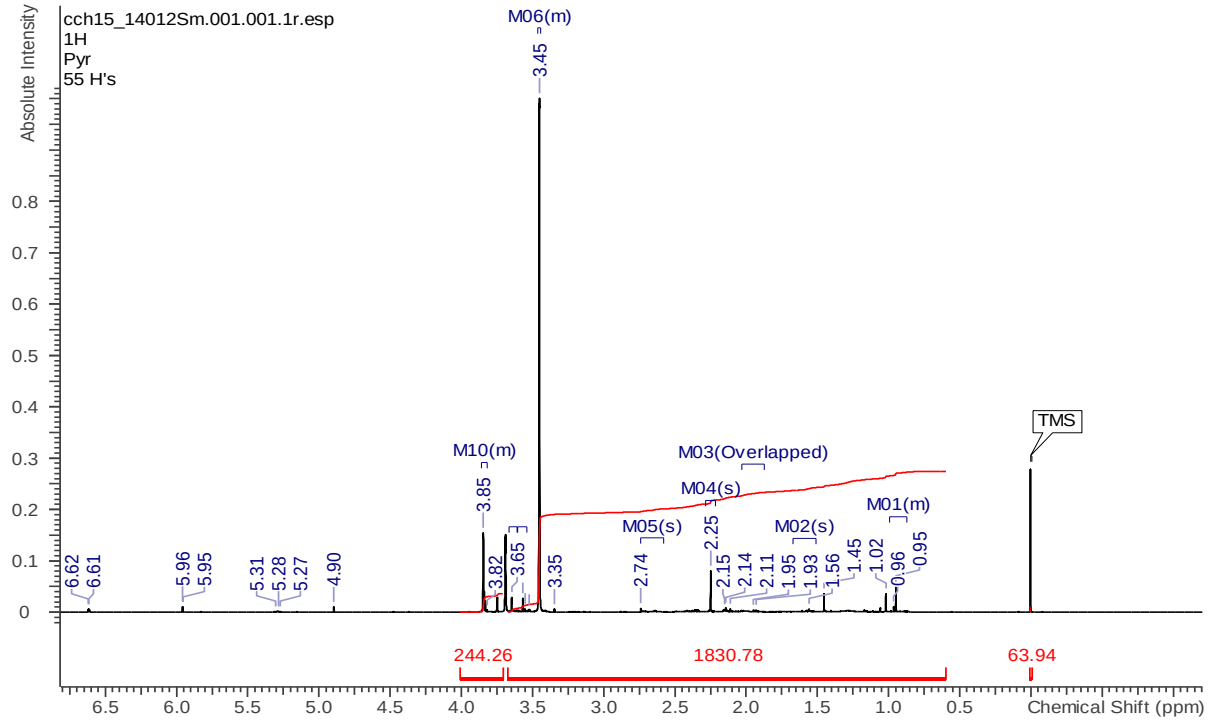


Figure 30:^{1}H, ^{1}HCOSY spectrum of Aethiopinolone C (**3**) (S)- MTPA ester in pyridine –d_5 (700 MHz)

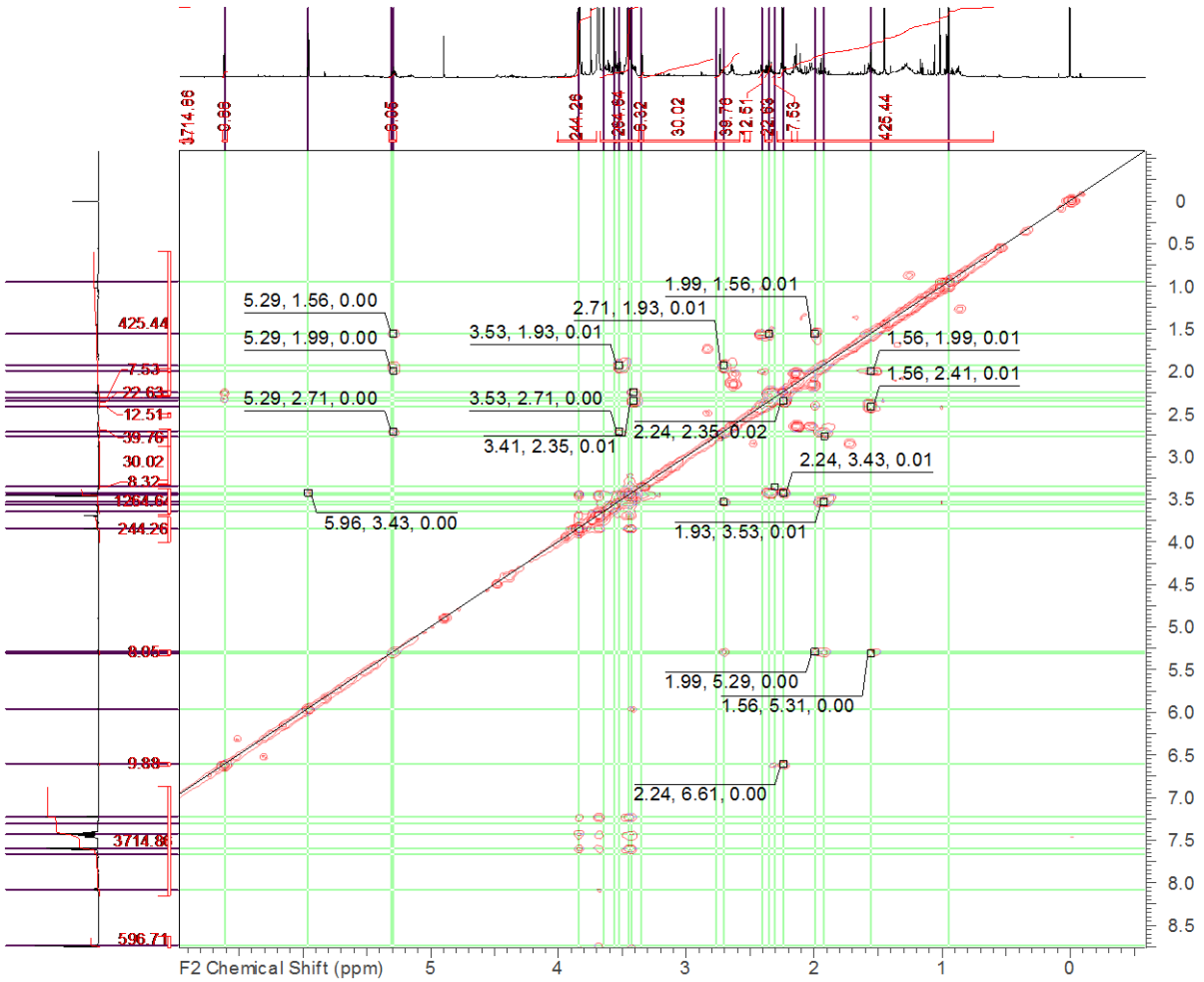
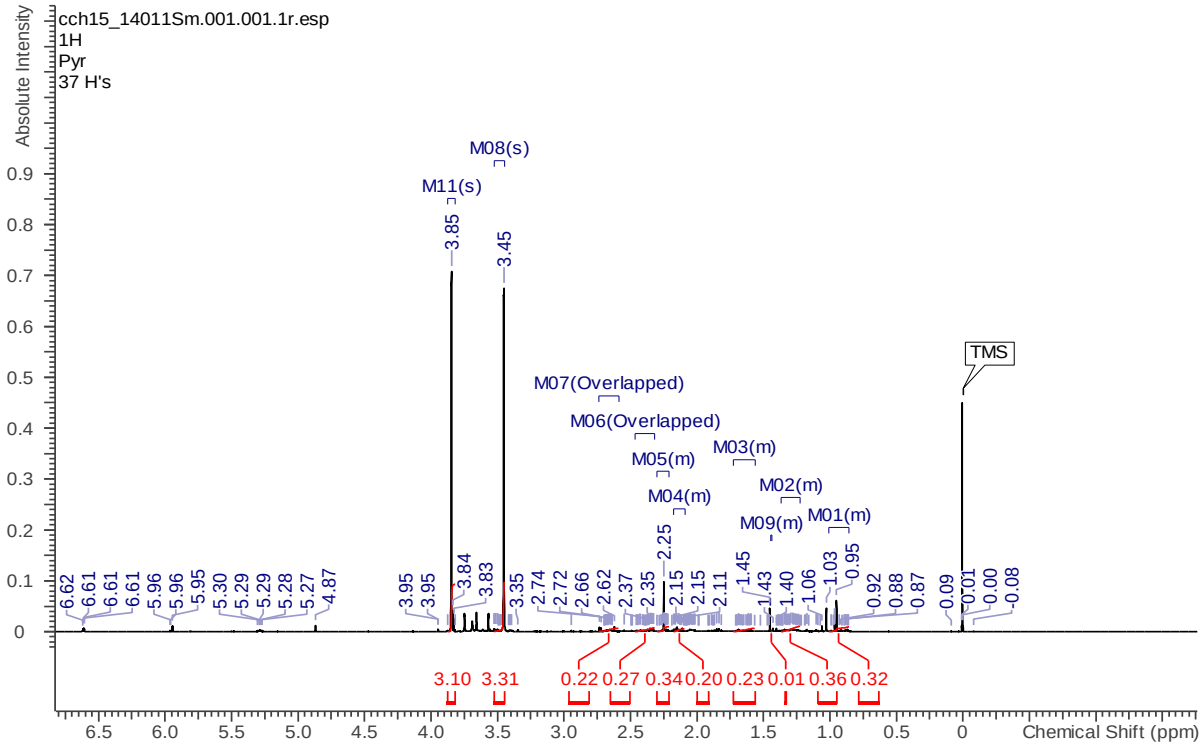


Figure 31:[1]H NMR spectrum of Aethiopinolone C (**3**) (*R*)- MTPA ester in pyridine –d_5 (700 MHz)



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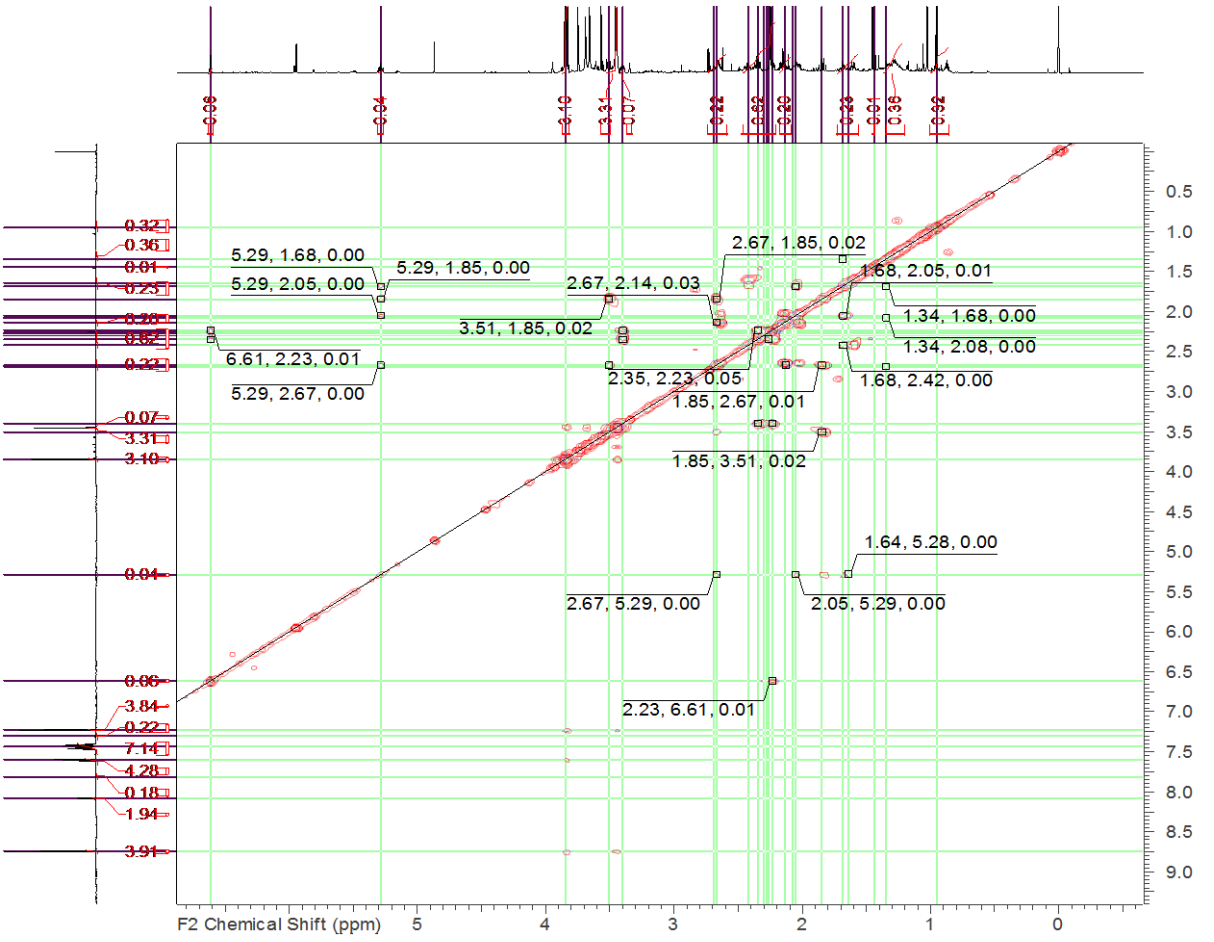


1 and 2D NMR data for Aethiopinolone D (4)

Figure 33:[1]H NMR spectrum for Aethiopinolone D (**4**) in acetone-d_6 (175 MHz)

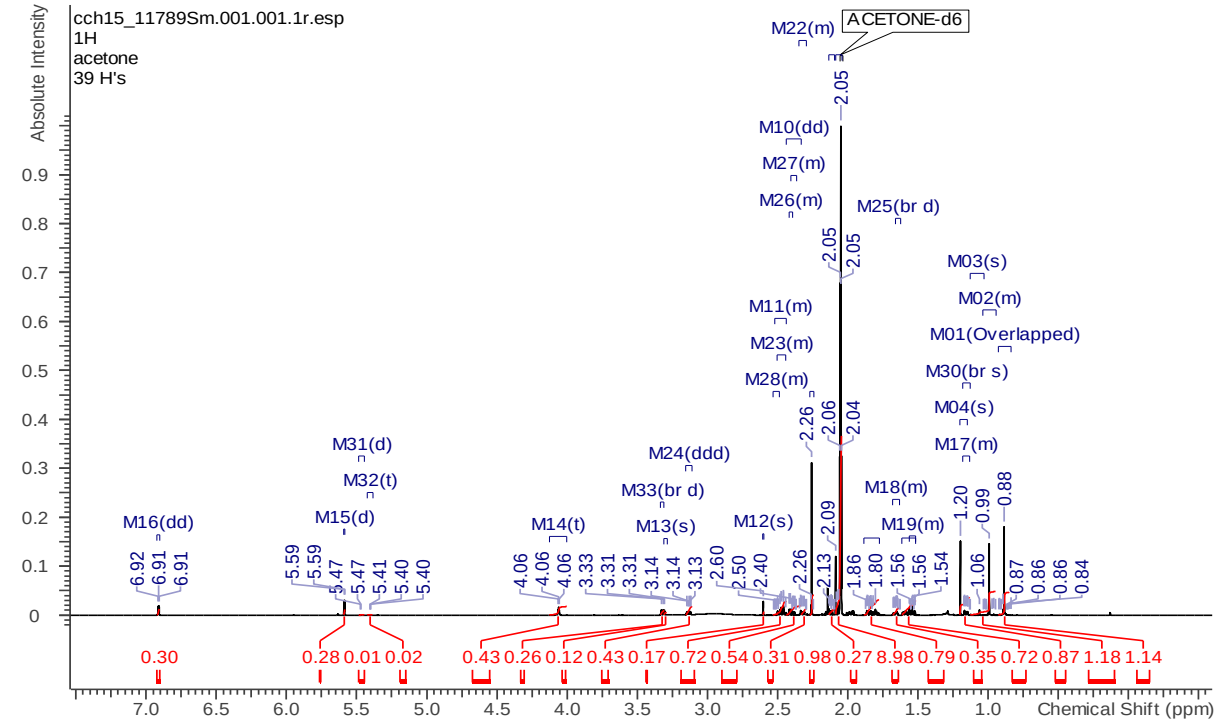
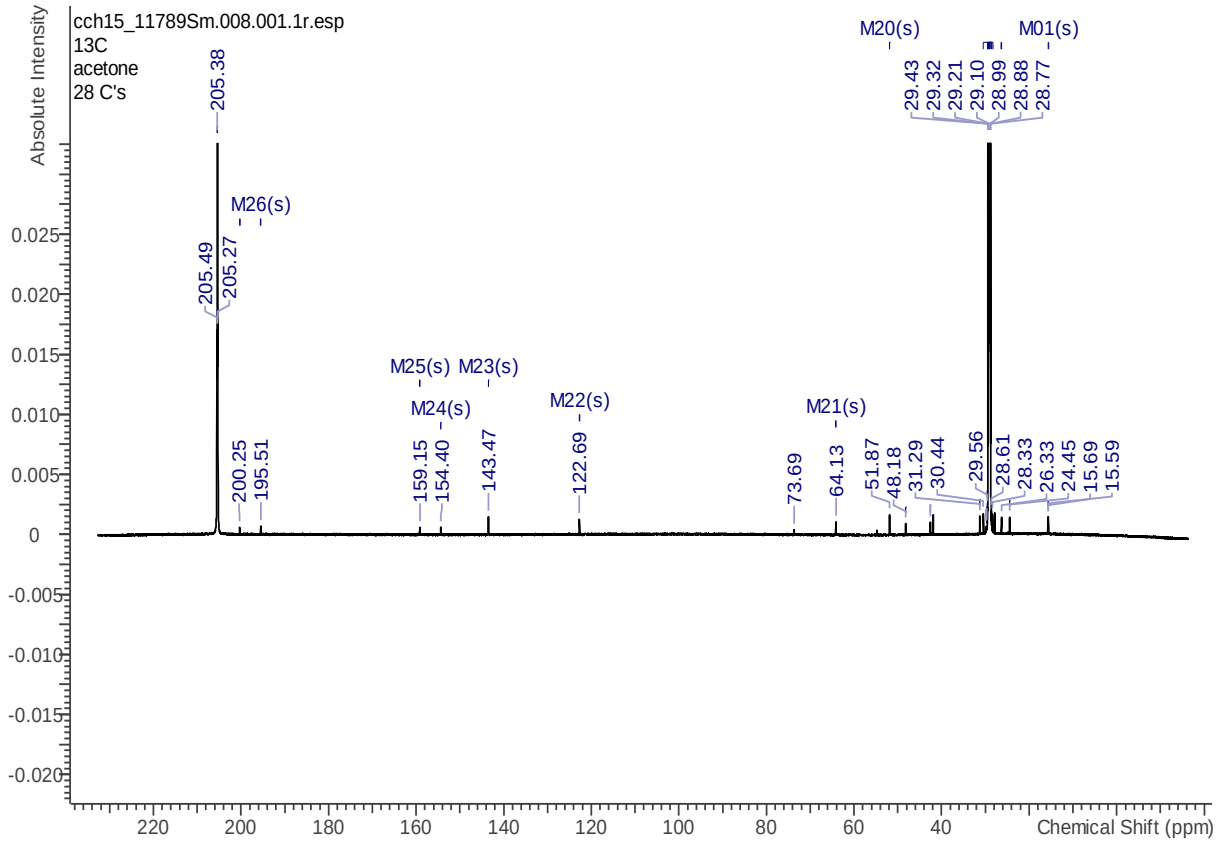


Figure 34: [13]C NMR spectrum of Aethiopinolone D (**4**) in acetone-d_6 (175 MHz)



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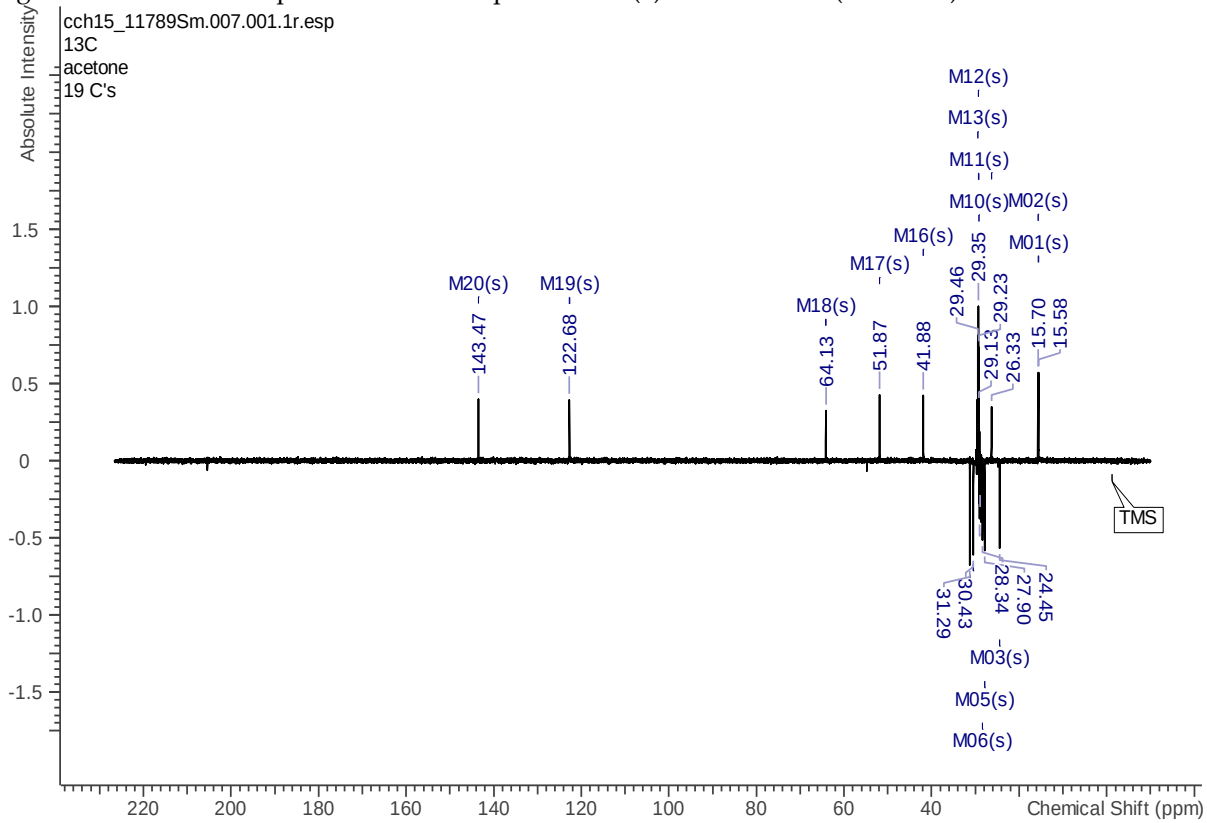


Figure 36:^{1}H, ^{13}C HSQC spectrum of Aethiopinolone D (**4**) in acetone-d$_6$ (700 MHz, 175 MHz)

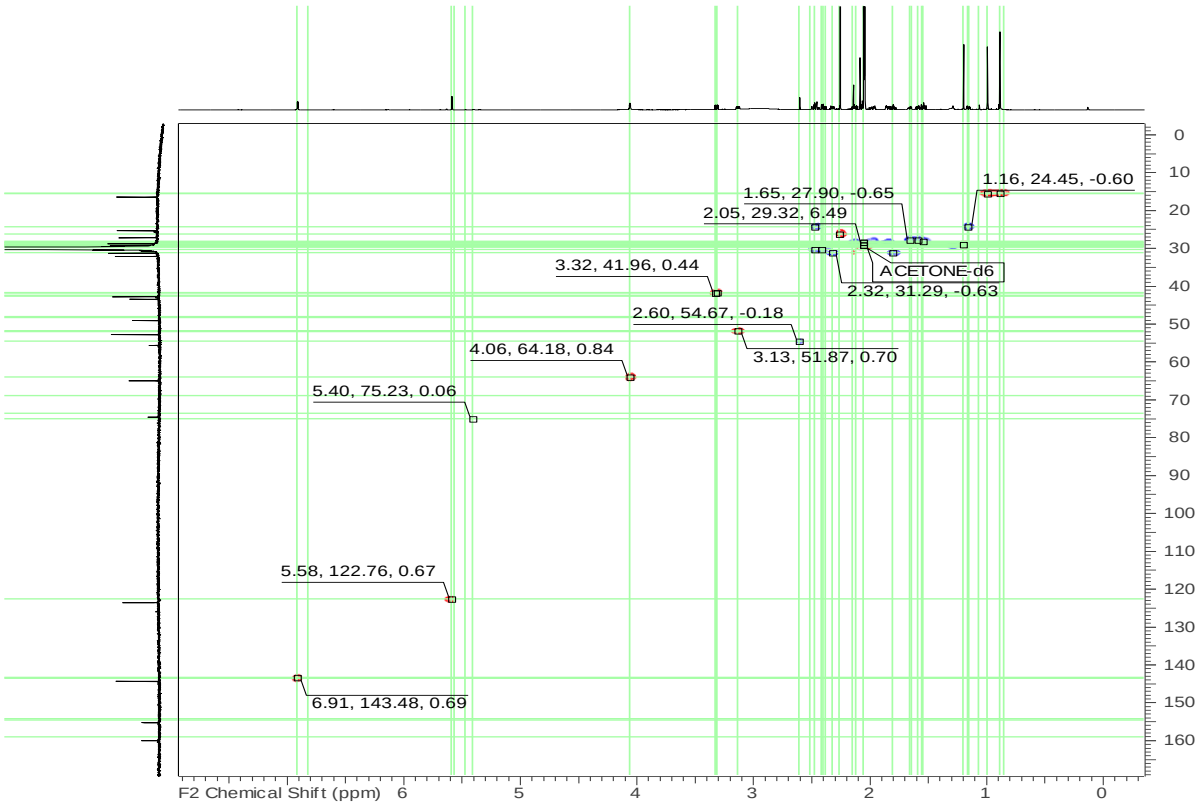


Figure 37:$^{1}H,^{13}C$ HMBC spectrum of Aethiopinolone D (**4**) in acetone-d_6 (700 MHz, 175 MHz)

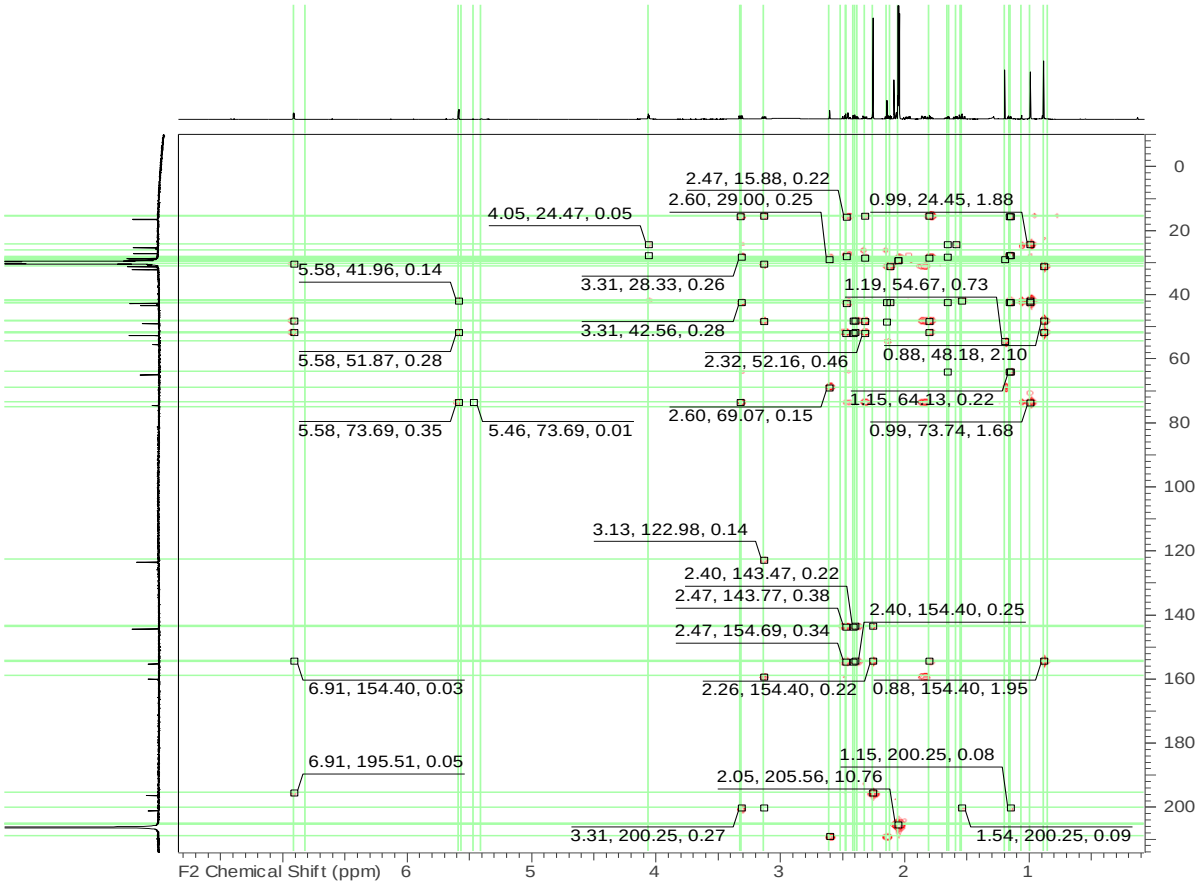


Figure 38:^{1}H, ^{1}H COSY spectrum of Aethiopinolone D (**4**) in acetone-d_6 (700 MHz)

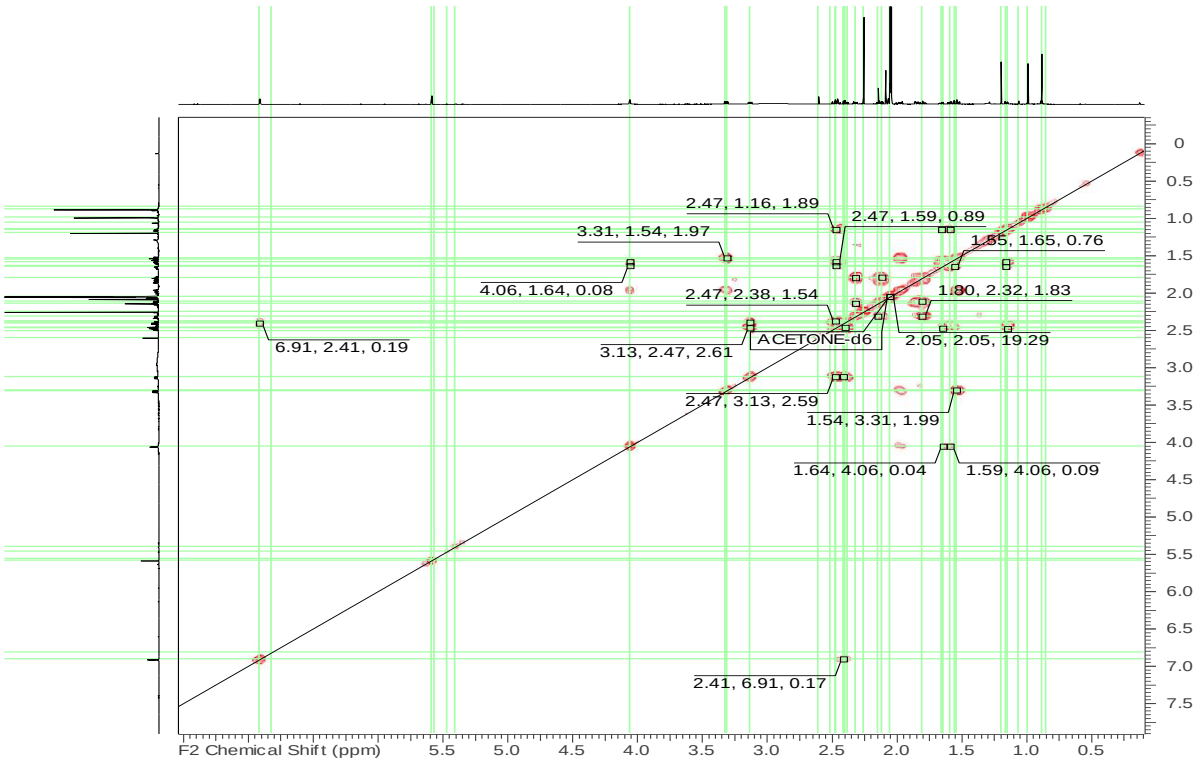


Figure 39: ^{1}H, ^{1}H ROESY spectrum of Aethiopinolone D (**4**) in acetone-d_6 (700 MHz)

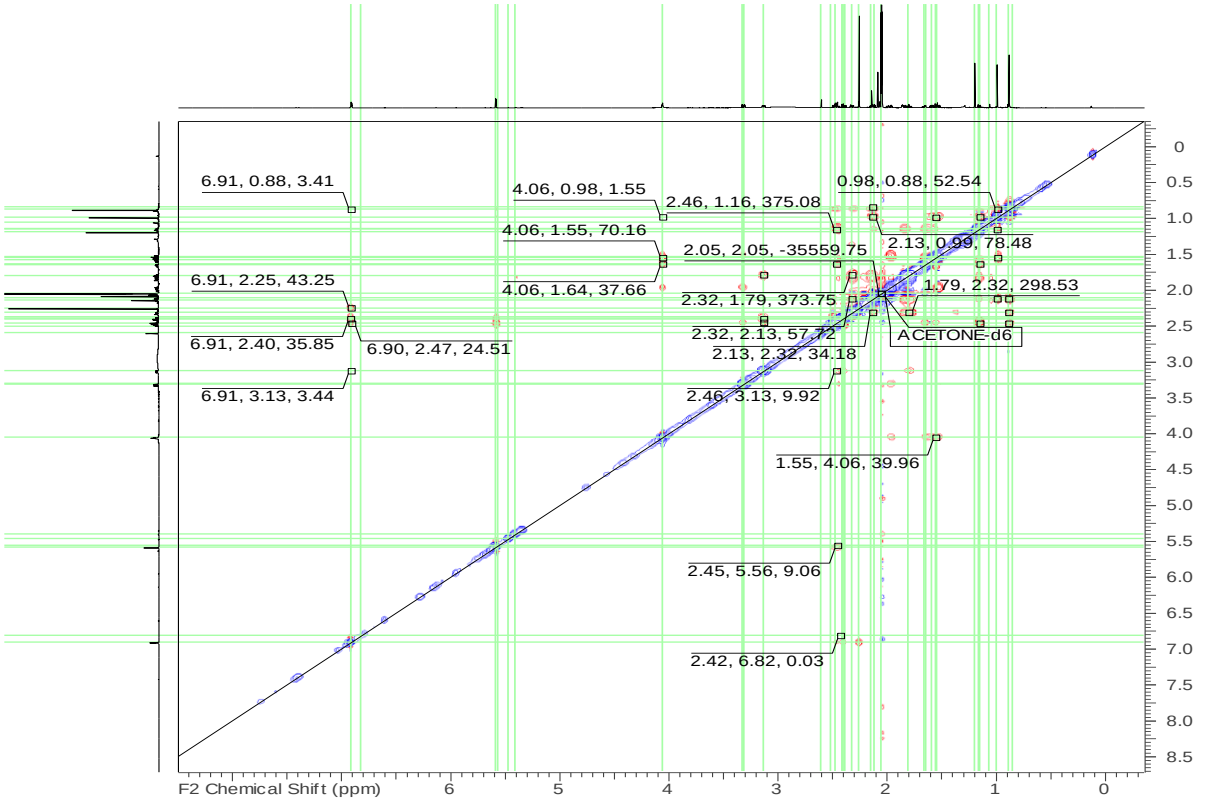


Figure 40: HRMS spectrum for Aethiopinolone D (**4**)

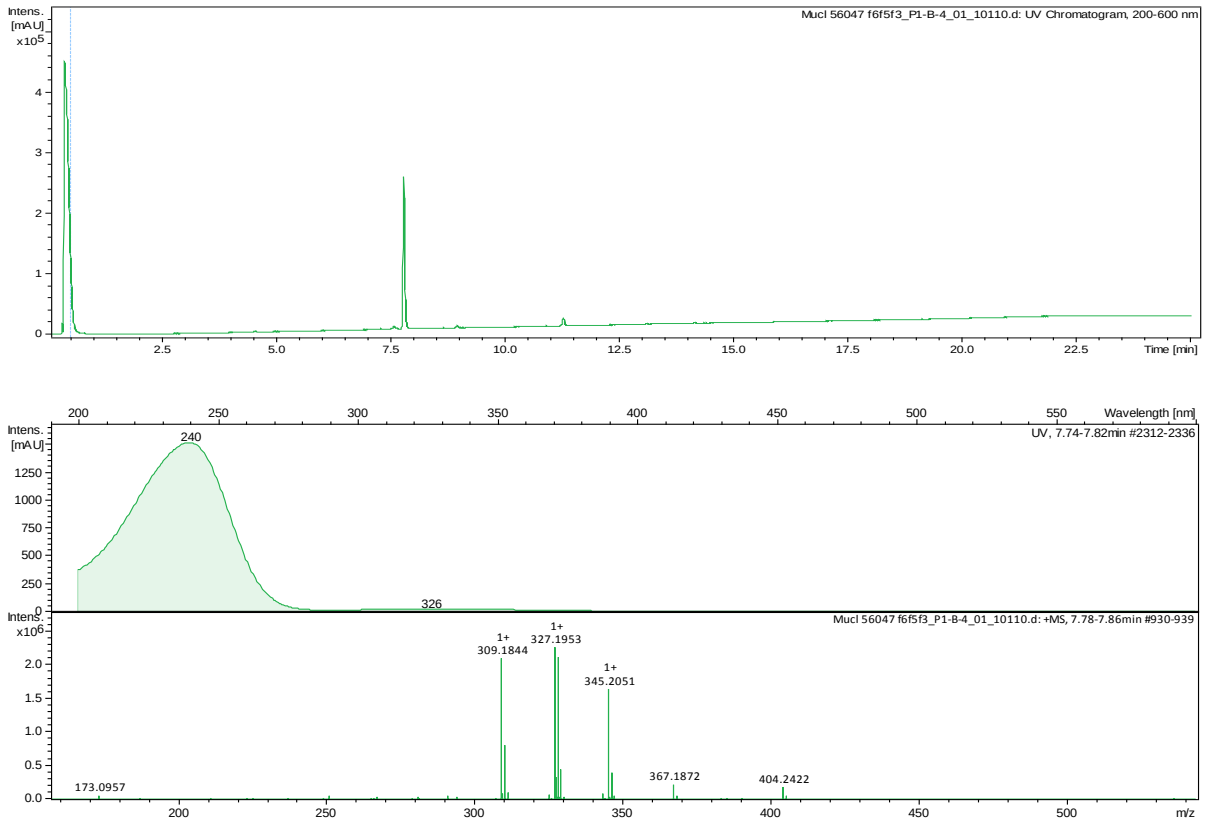


Figure 41:^{1}H NMR spectrum of Aethiopinolone D (**4**) (*S*)- MTPA ester in pyridine –d_5 (700 MHz)

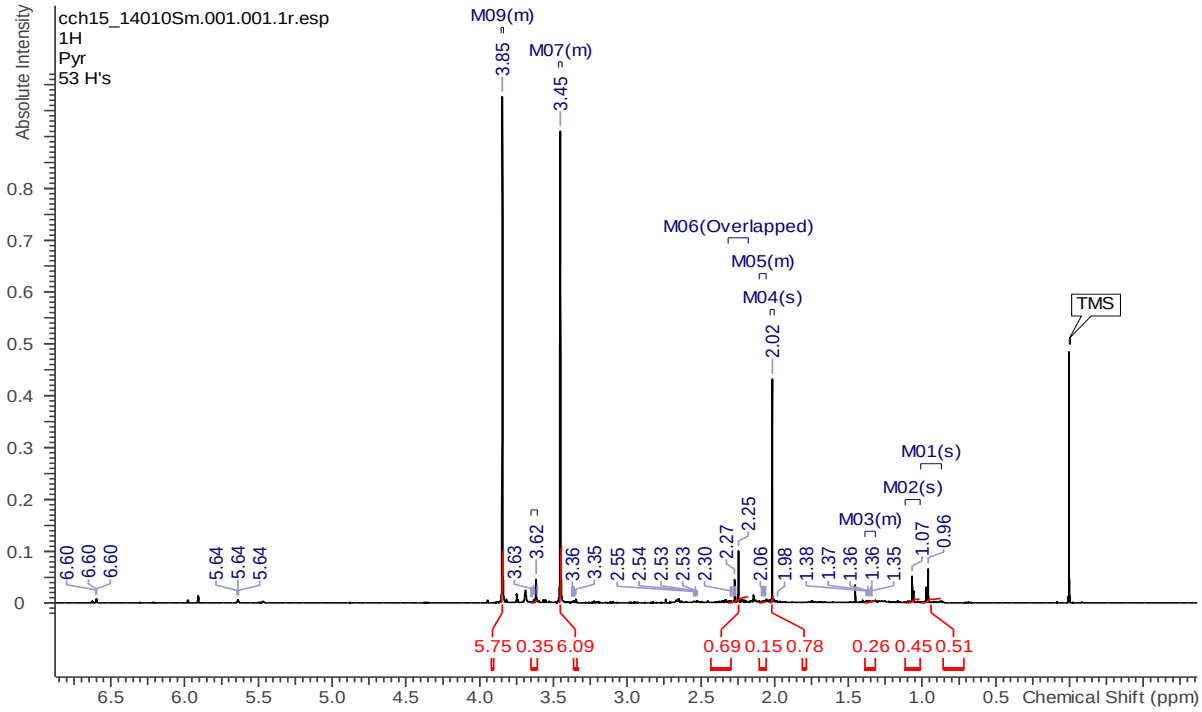


Figure 42:^{1}H, ^{1}H COSY spectrum of Aethiopinolone D (**4**) (*S*)- MTPA ester in pyridine –d_5 (700 MHz)

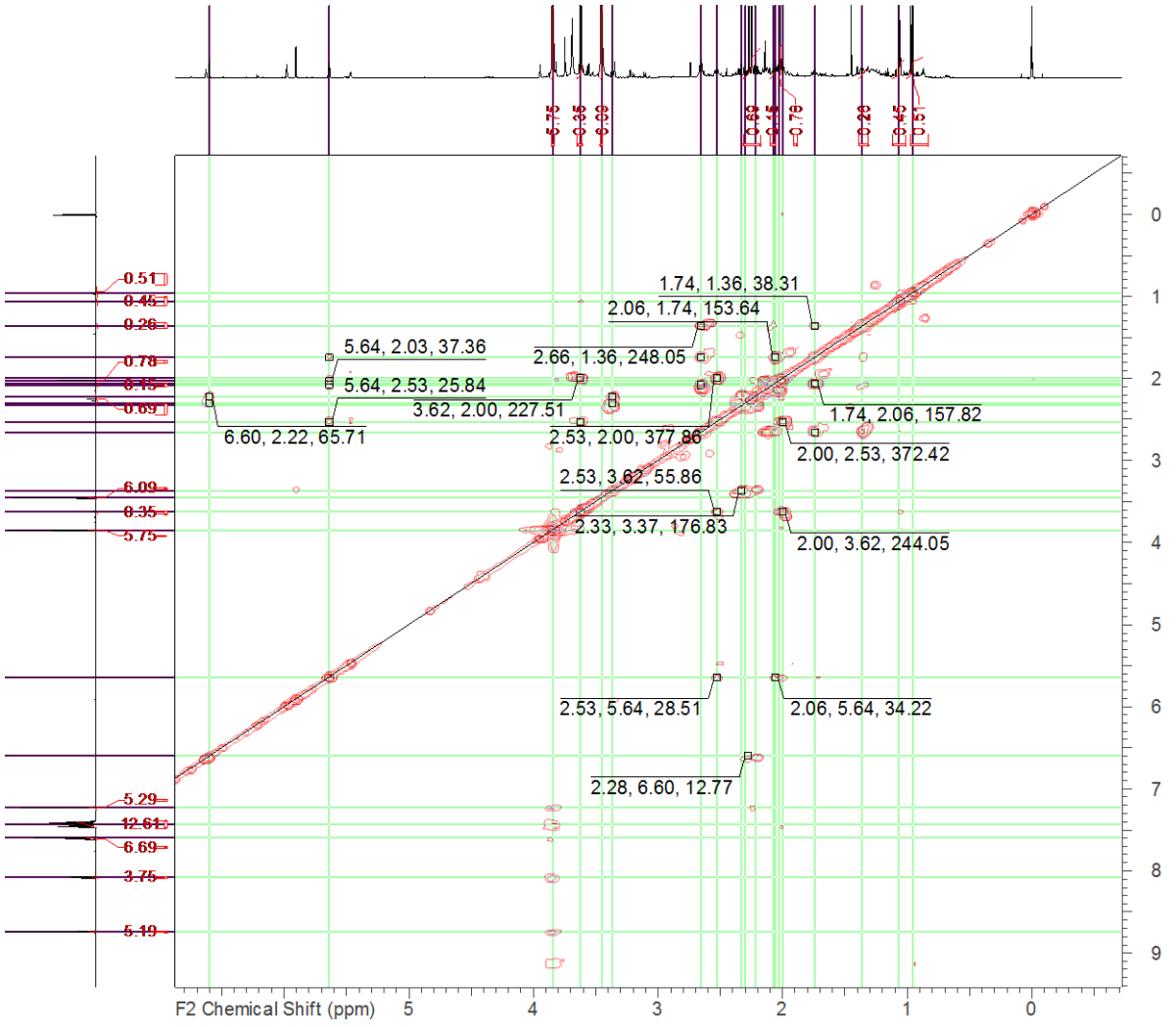


Figure 43:^{1}H NMR spectrum of Aethiopinolone D (**4**) (R)- MTPA ester in pyridine –d_5 (700 MHz)

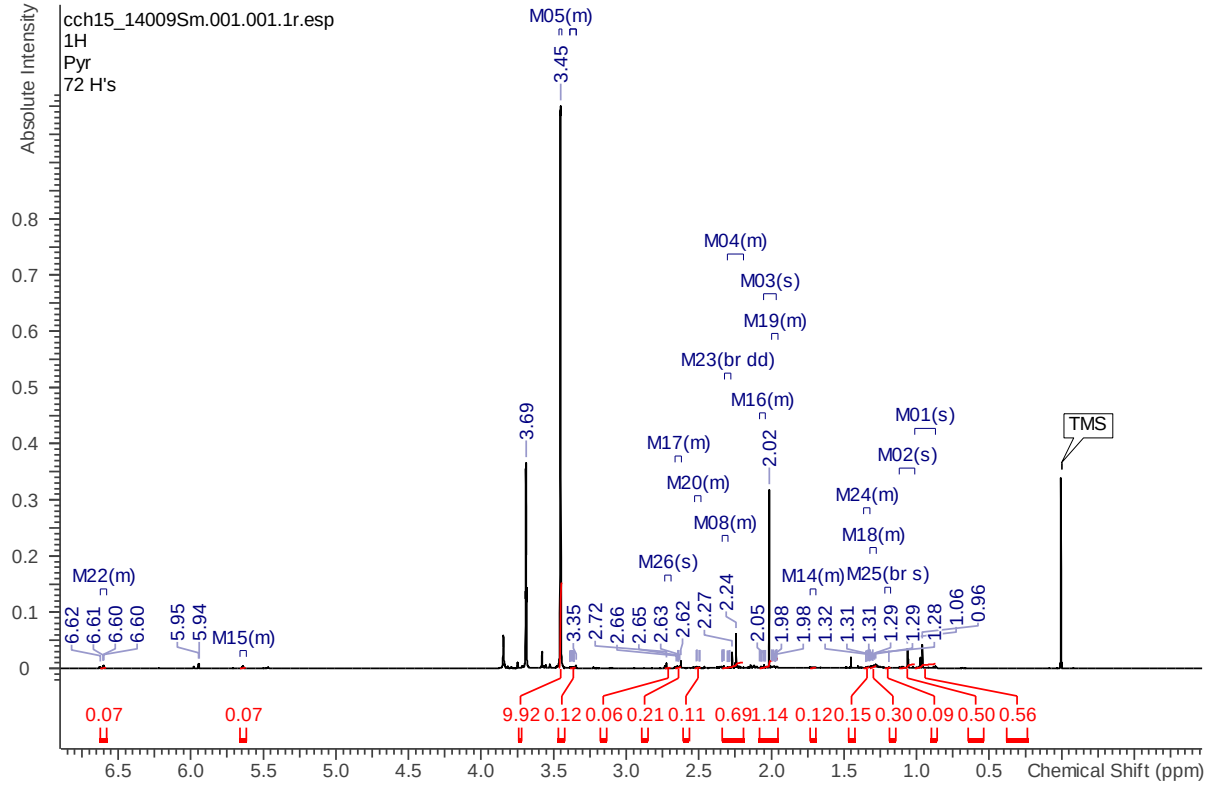
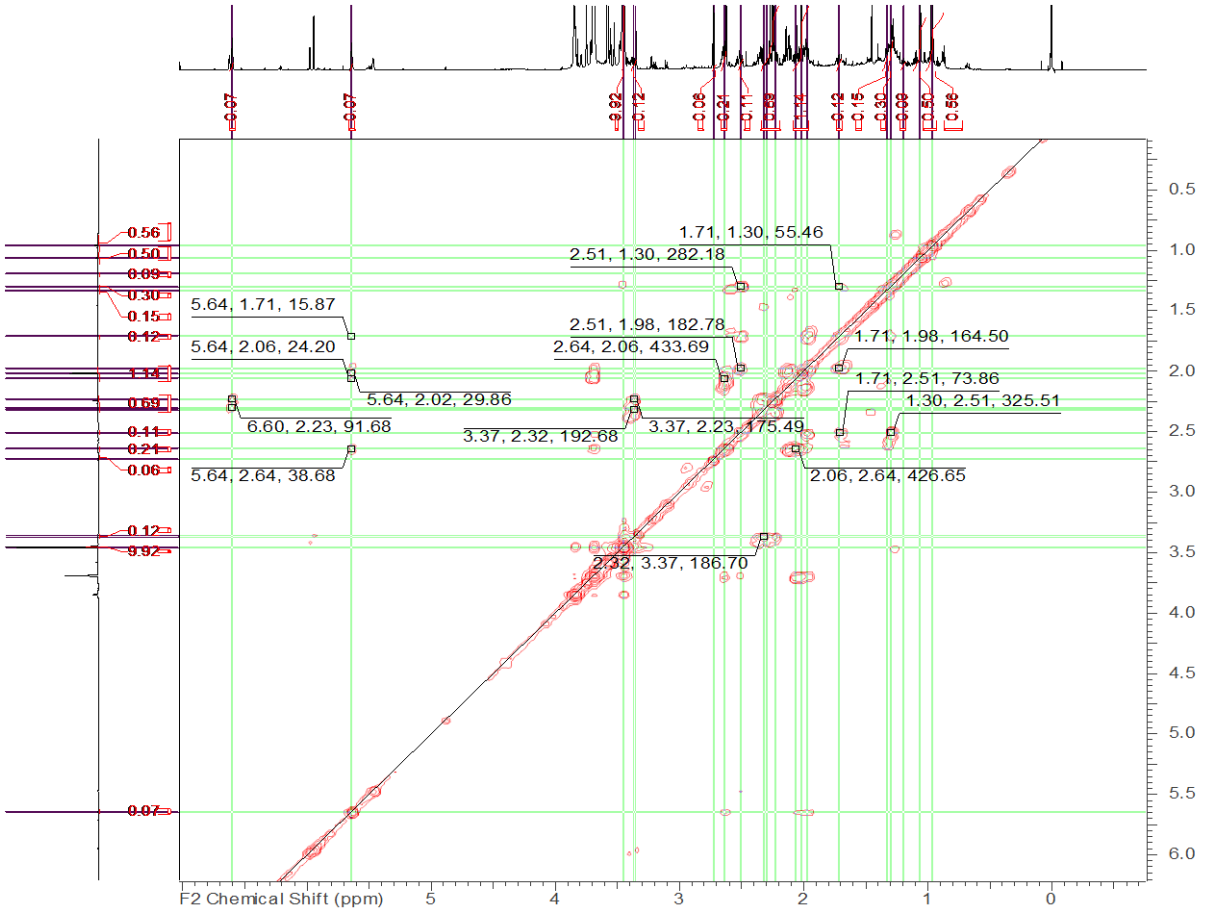


Figure 44:^{1}H, ^{1}H COSY spectrum of Aethiopinolone D (**4**) (*R*)- MTPA ester in pyridine –d_5 (700 MHz)



1 and 2D NMR data for Aethiopinolone E (5)

Figure 45:[1]H NMR spectrum of Aethiopinolone E (**5**) in acetone-d_6 (700 MHz)

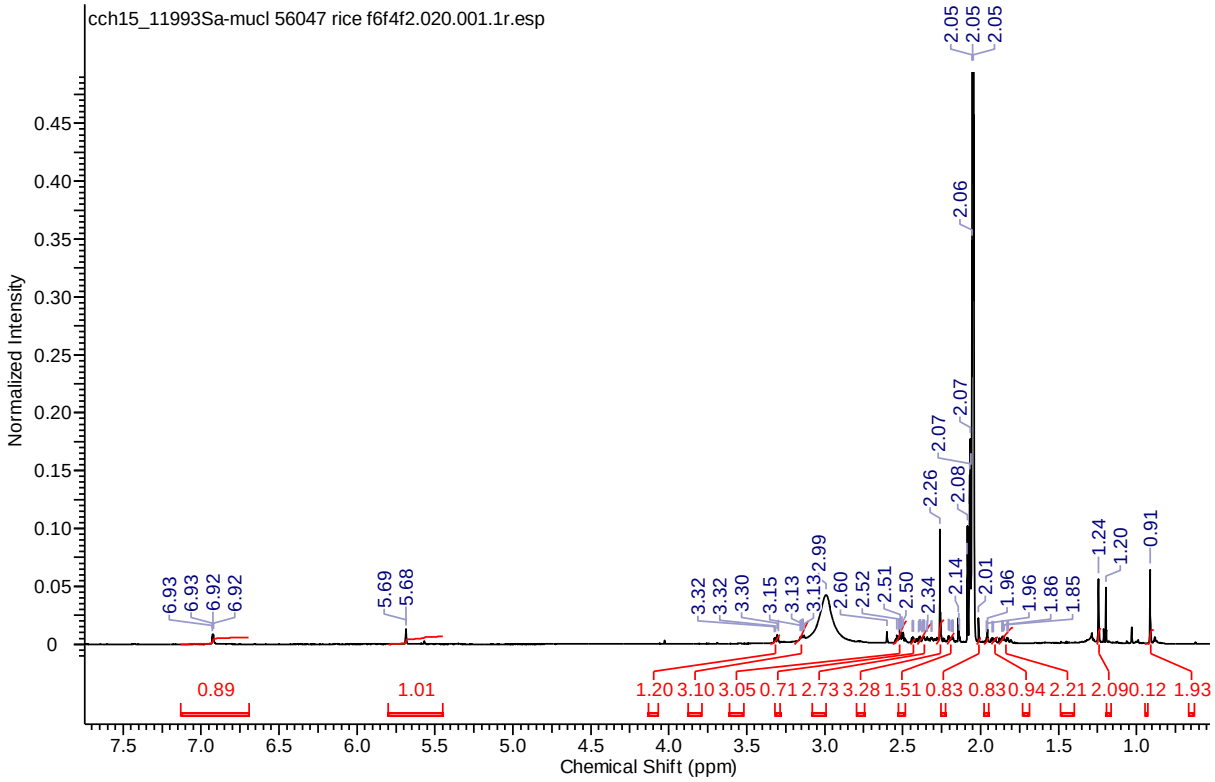


Figure 46:[13]C NMR spectrum of Aethiopinolone E (**5**) in acetone-d_6 (175 MHz)

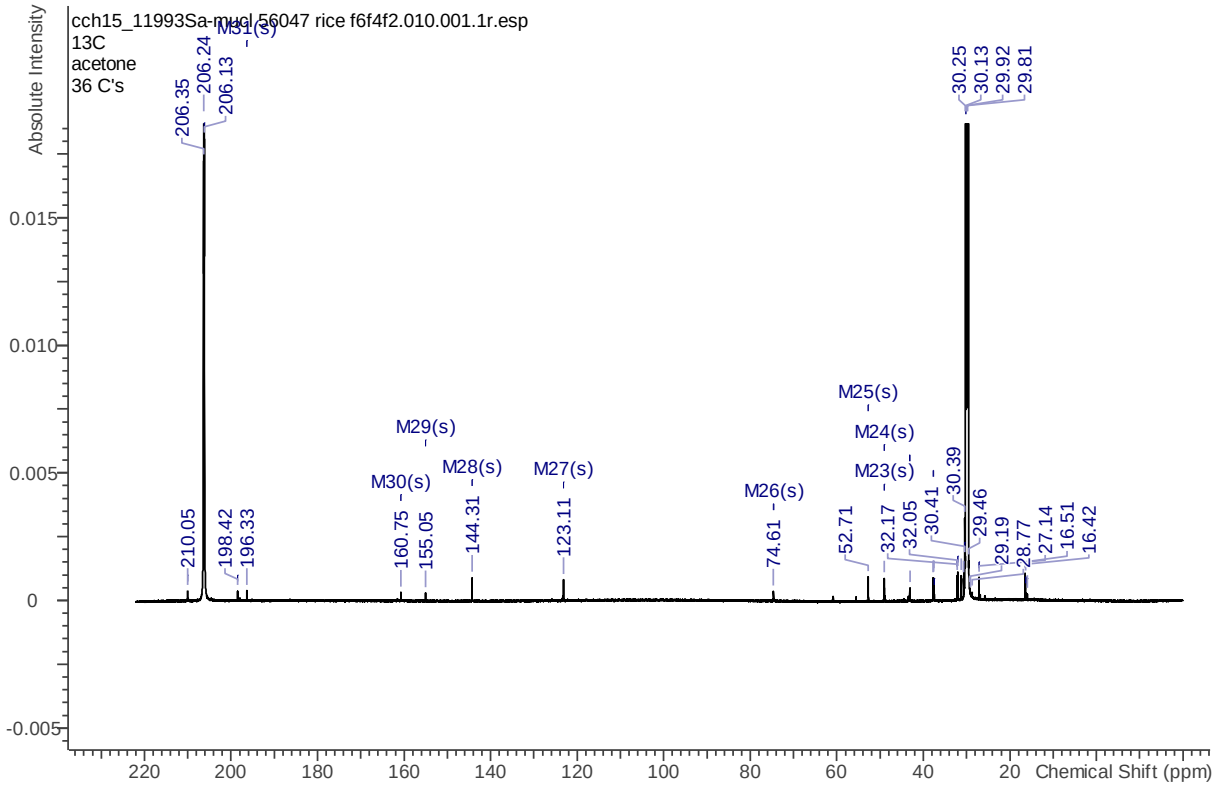


Figure 47: DEPT NMR spectrum of Aethiopinolone E (**5**) in acetone-d_6 (175 MHz)

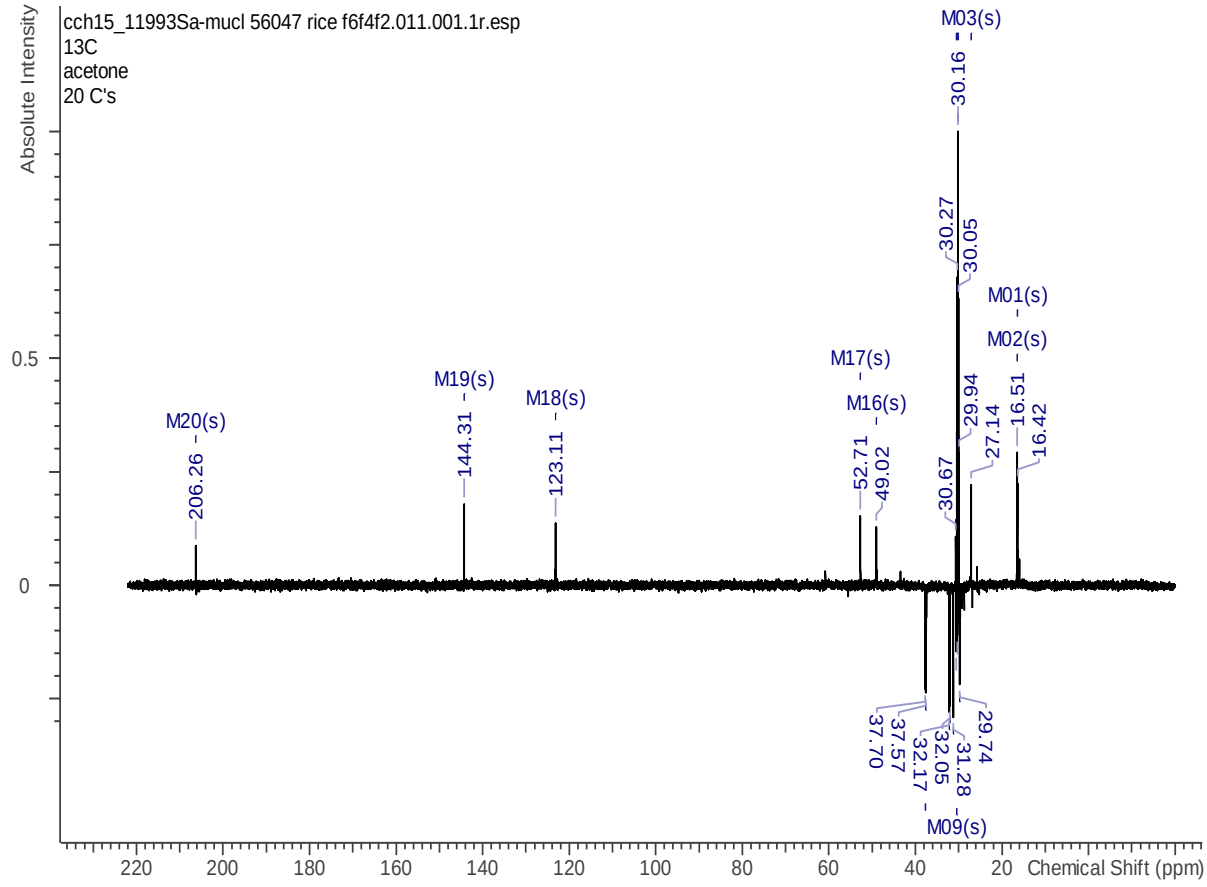


Figure 48:^{1}H, ^{13}C HSQC NMR spectrum of Aethiopinolone E (**5**) in acetone-d_6 (700 MHz, 175 MHz)

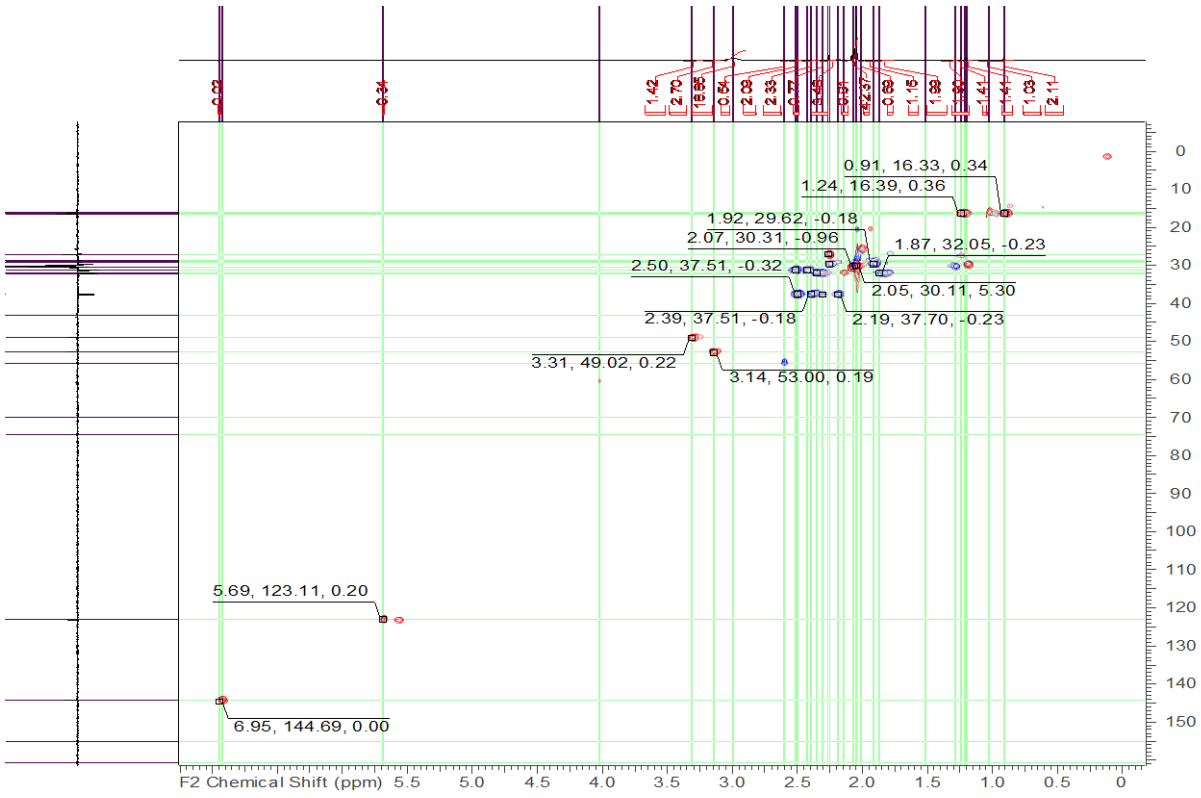


Figure 49:^{1}H, ^{13}C HMBC NMR spectrum of Aethiopinolone E (5) in acetone-d$_6$ (700 MHz, 175 MHz)

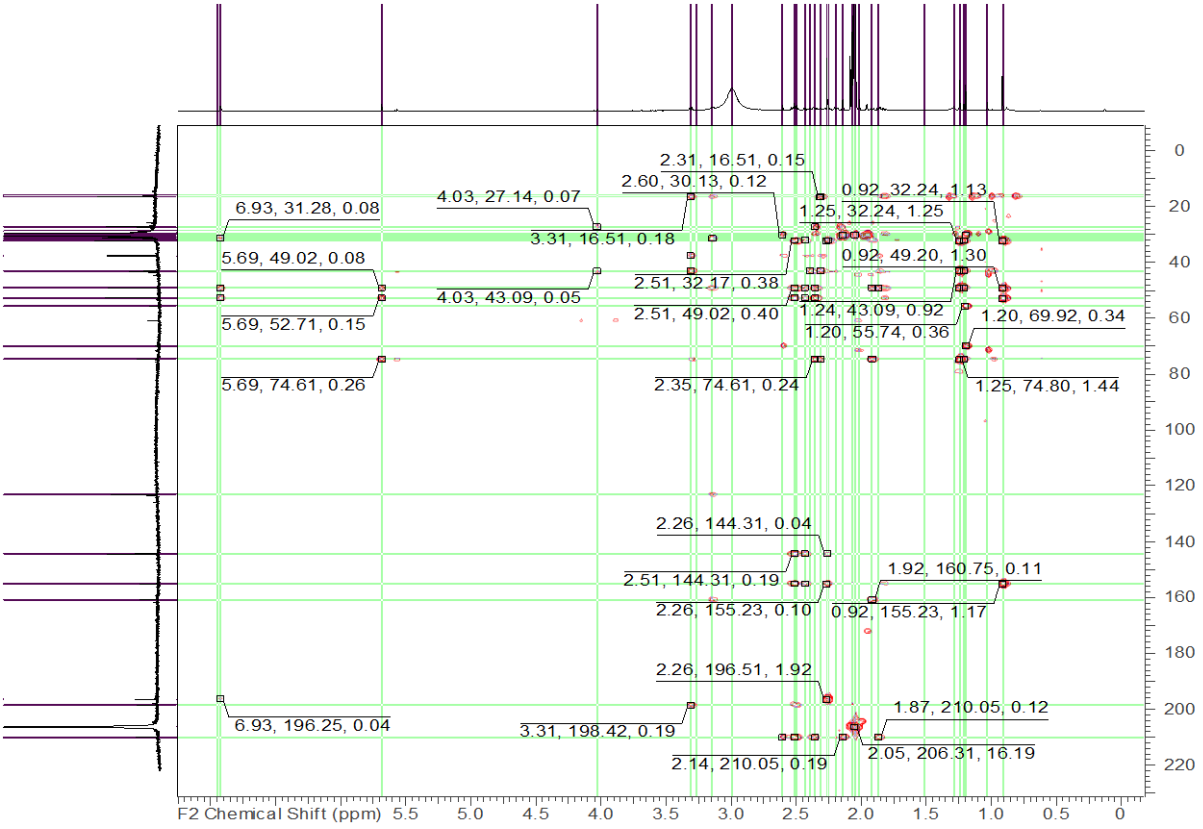


Figure 50:^{1}H, ^{1}H COSY NMR spectrum of Aethiopinolone E (**5**) in acetone-d$_6$ (700 MHz)

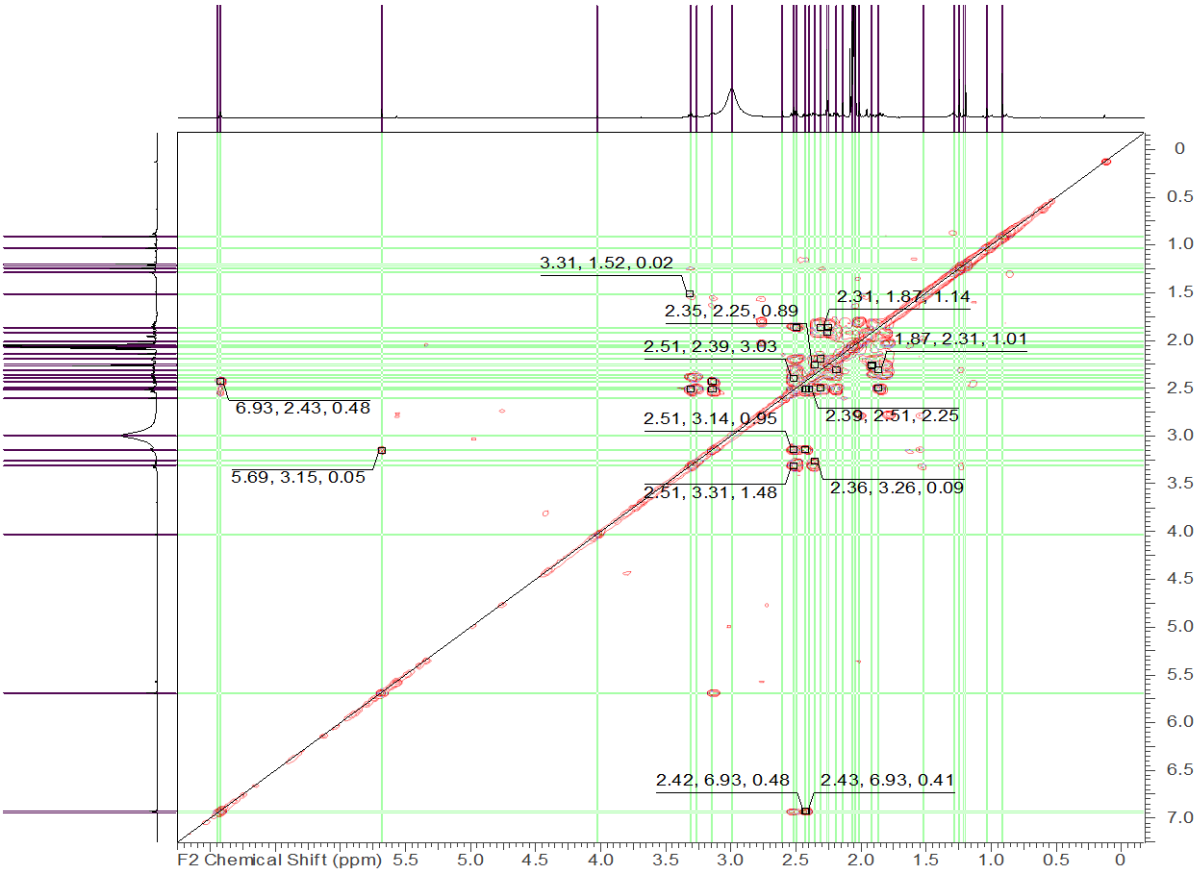


Figure 51:^{1}H, ^{1}H ROESY NMR spectrum of Aethiopinolone E (**5**) in acetone-d_6 (700 MHz)

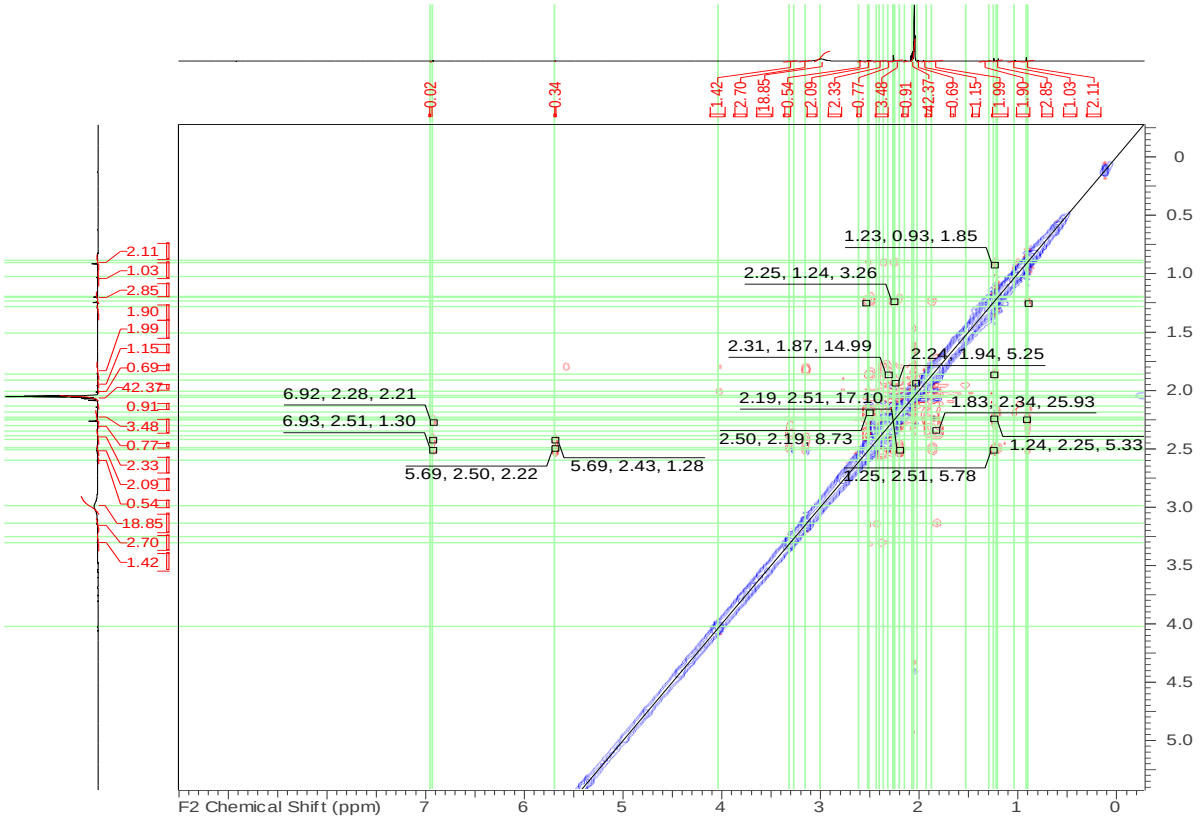


Figure 52: HRMS spectrum for Aethiopinolone **E** (**5**)

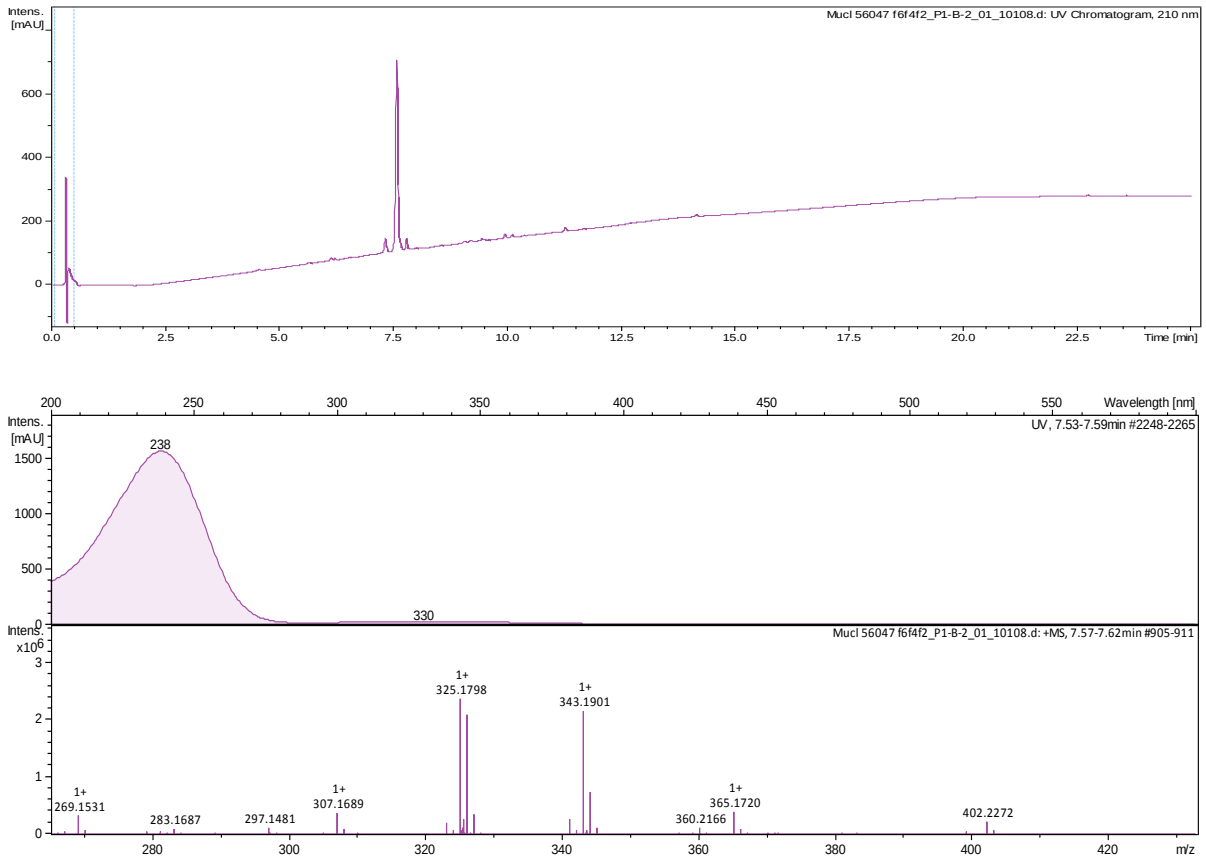


Table 1.

Table 1: *S*-MTPA ester and *R*-MTPA ester chemical shifts analysis for Aethiopinolone A (**1**)

	S	R	S-R
4α	2.388	2.309	+0.079
4β	1.631	1.590	+0.041
5	2.985	2.970	+0.015
7	5.766	5.757	+0.009
14	3.040	3.038	+0.002
17	2.470	2.468	+0.002
3	5.016	5.012	+0.004
2α	1.945	2.023	-0.078
2β	1.515	1.625	-0.110
1α	2.011	2.334	-0.016
1β	1.303	1.364	-0.061
19	1.034	1.045	-0.011
18	0.896	0.0897	-0.001

Table 2: *S*-MTPA ester and *R*-MTPA ester chemical shifts analysis for Aethiopinolone C (**3**)

	S	R	S-R
4β	1.926	1.846	+0.080
4α	2.711	2.669	+0.042
5	3.528	3.506	+0.022
3	5.290	5.287	+0.003
2β	1.556	1.685	-0.129
2α	1.983	2.049	-0.066
1α	2.397	2.418	-0.021
19	1.019	1.027	-0.008
18	0.948	0.950	-0.002

Table 3: *S*-MTPA ester and *R*-MTPA ester chemical shifts analysis for Aethiopinolone D (**4**)

	S	R	S-R
4β	1.999	2.011	-0.012
4α	2.530	2.640	-0.11
5	3.619	3.715	-0.096
3	5.639	5.640	-0.001
2β	2.078	1.976	+0.102
2α	1.741	1.713	+0.028
1α	2.657	2.507	+0.15
1 β	1.361	1.298	+0.063
19	1.067	1.062	+0.005
18	0.971	0.959	+0.012

ITS sequences of the producing organism

TTGAGGCAAGGGTCAAAAATGGTTTAAGGTAACAGAGTACCTGTCTGACACATAGGCAGACT
ATTGGAAGCAGACAGTCTAAGTAAGCACTGGTGAATATAGATAGAAAACTATTACACCAAAC
AATGCGAACTACAGTCCAGCTAATGCATTTGAGAGGAGCCGATACAGACAGTACCAGCATAC
ATATTGCCTCCAAGTCCAAGCCCCTTCTTCAATTAAGAAAAAGAGGATTGAGAATTACATGAC
ACTCAAACAGGCATGCCCCTCGGAATACCAAGGGGCGCAAGGTGCGTTCAAAGATTCGATGA
TTCACTGAATTCTGCAATTCACATTACTTATCGCATTTCGCTGCGTTCTTCATCGATGCGAGAG
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AGGAACAAGAAAATGTTTGTATAGGTAAAAGTCAAAGTGTTCATAGTAAGTAAAGCCAAGAT
CATTACTACTGCCAGAAGGGGTACCC

Pictures of the herbarium and the culture of *Fomitiporia aethiopica*