Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Bioactive compounds from the seeds of *Amomum tsaoko* Crevost et Lemaire, a Chinese spice as inhibitors of sphingosine kinases, SPHK1/2

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Supporting Information Contents:

Figure S1. HR-ESIMS data of **1**

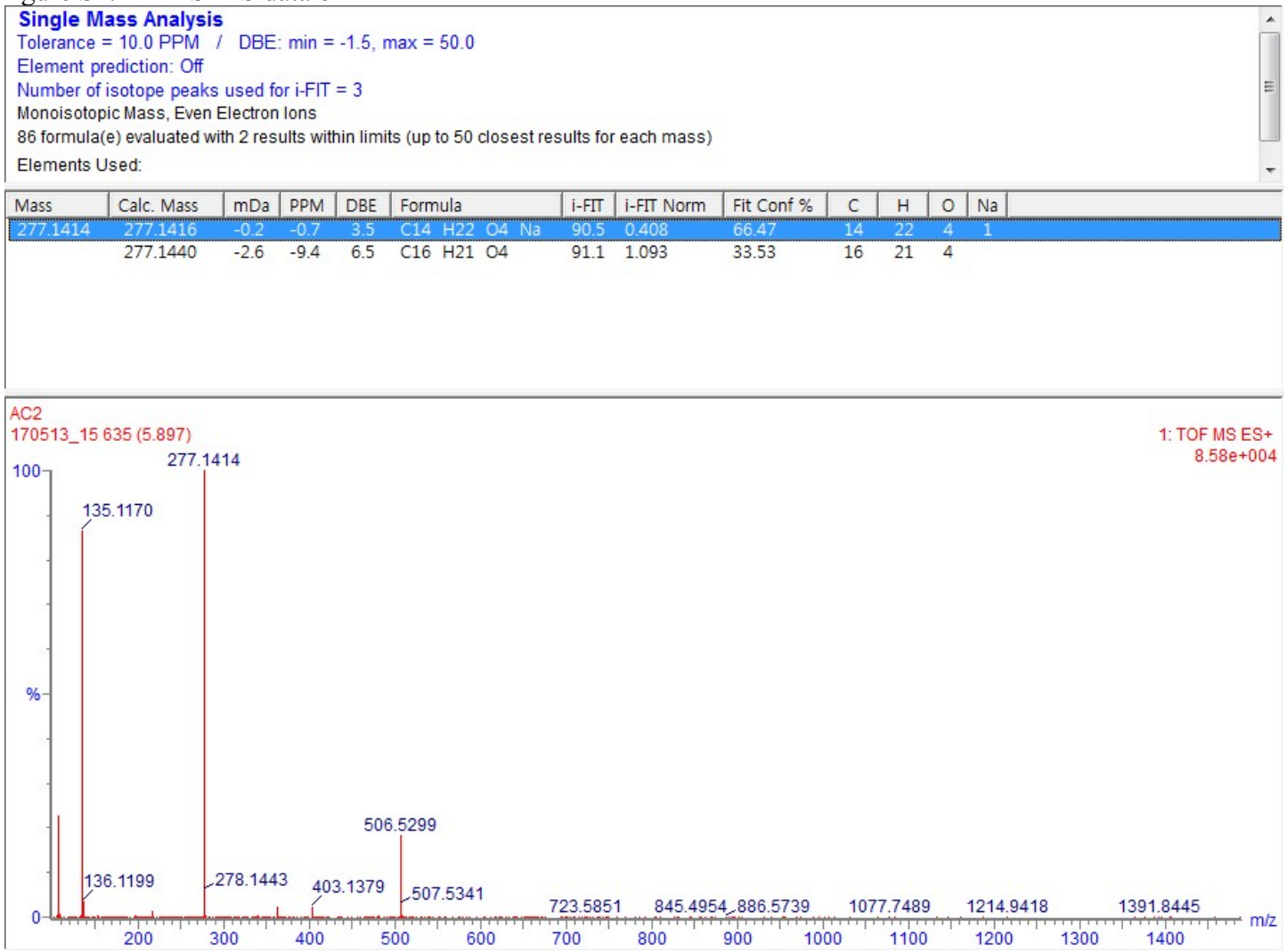


Figure S2. ^{1}H NMR spectrum of **1** ($CDCl_3$, 700 MHz)

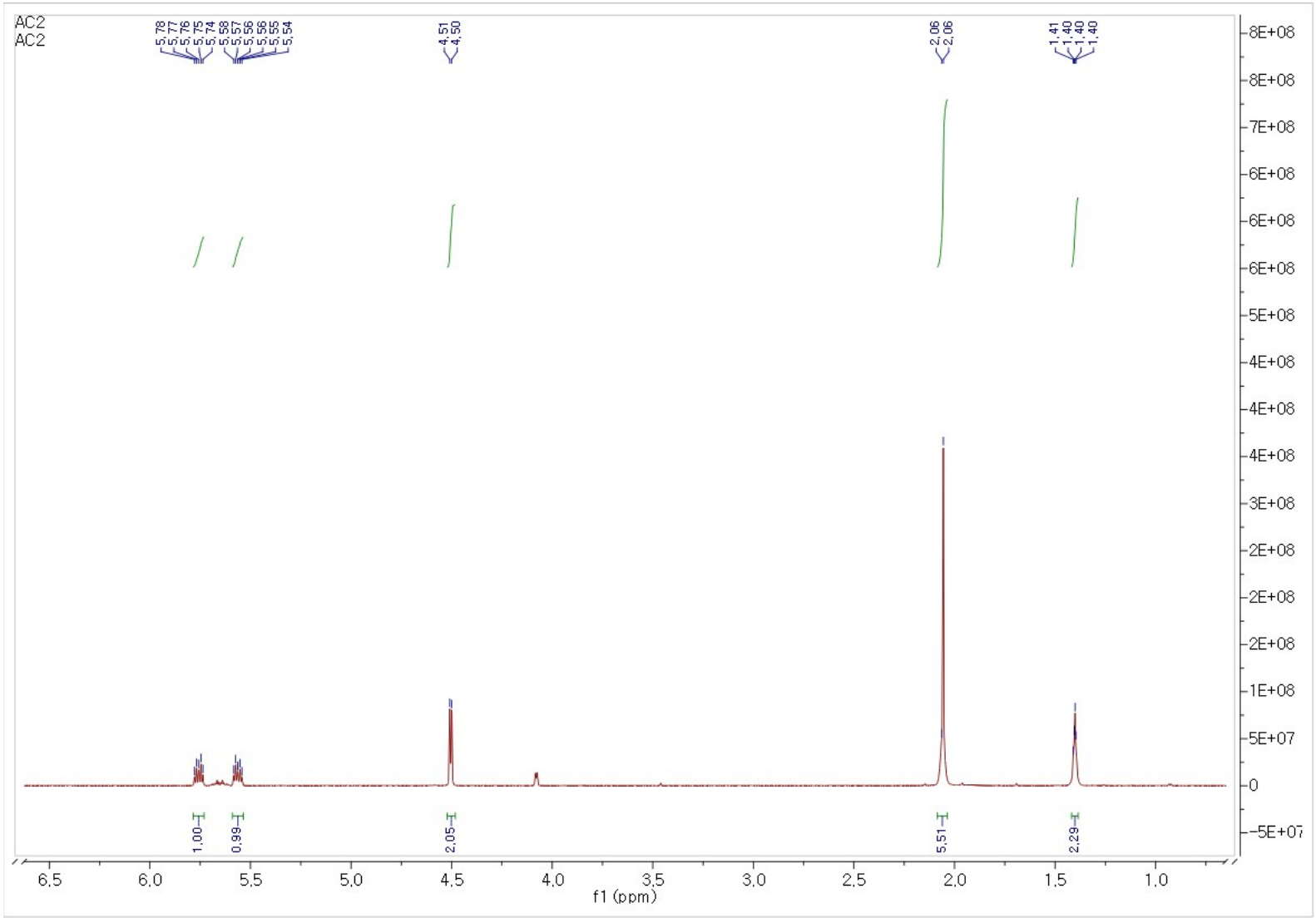


Figure S3. ^{13}C NMR spectrum of **1** ($CDCl_3$, 175 Hz)

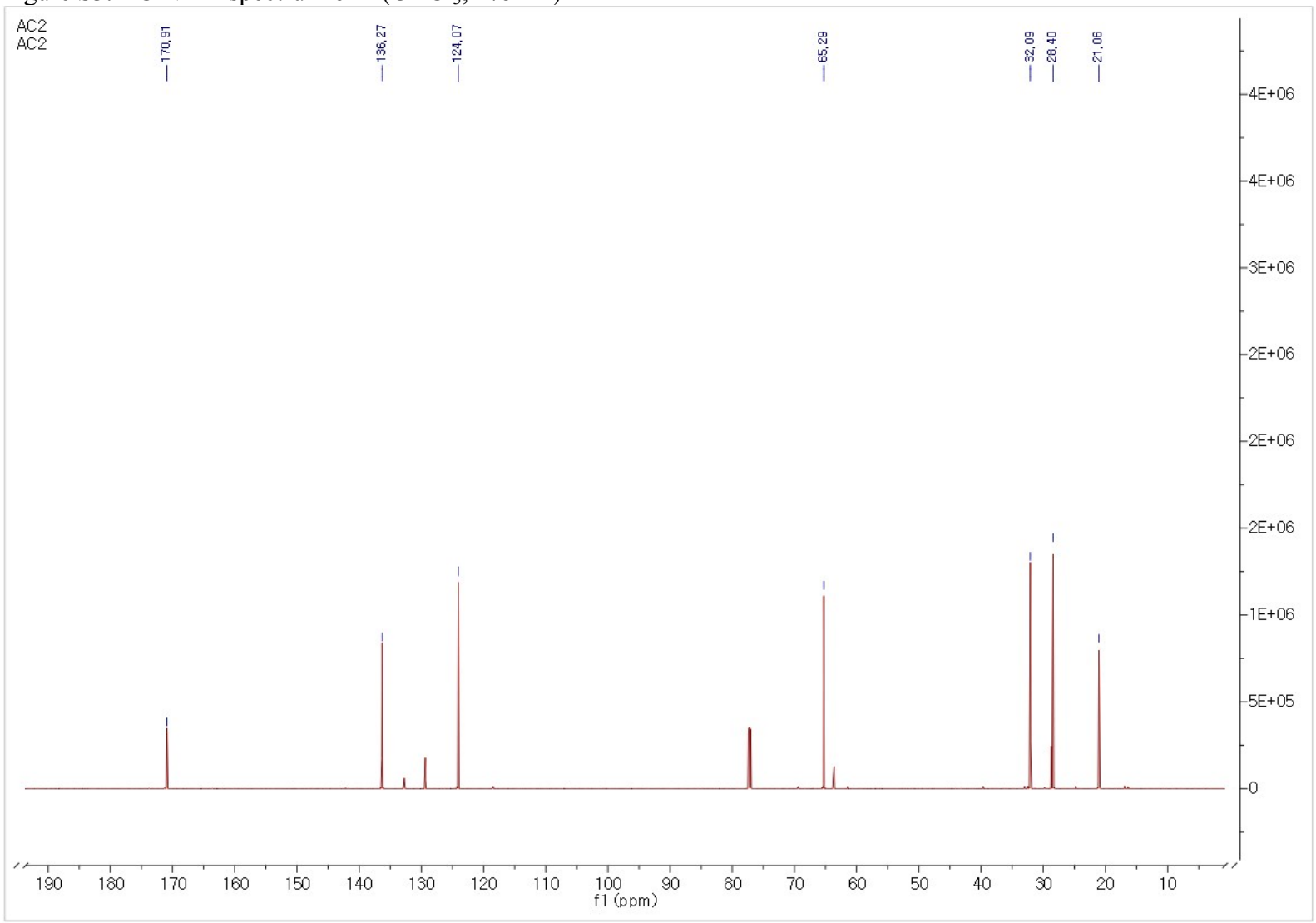


Figure S4. ^{1}H-^{1}H COSY spectrum of **1** ($CDCl_3$)

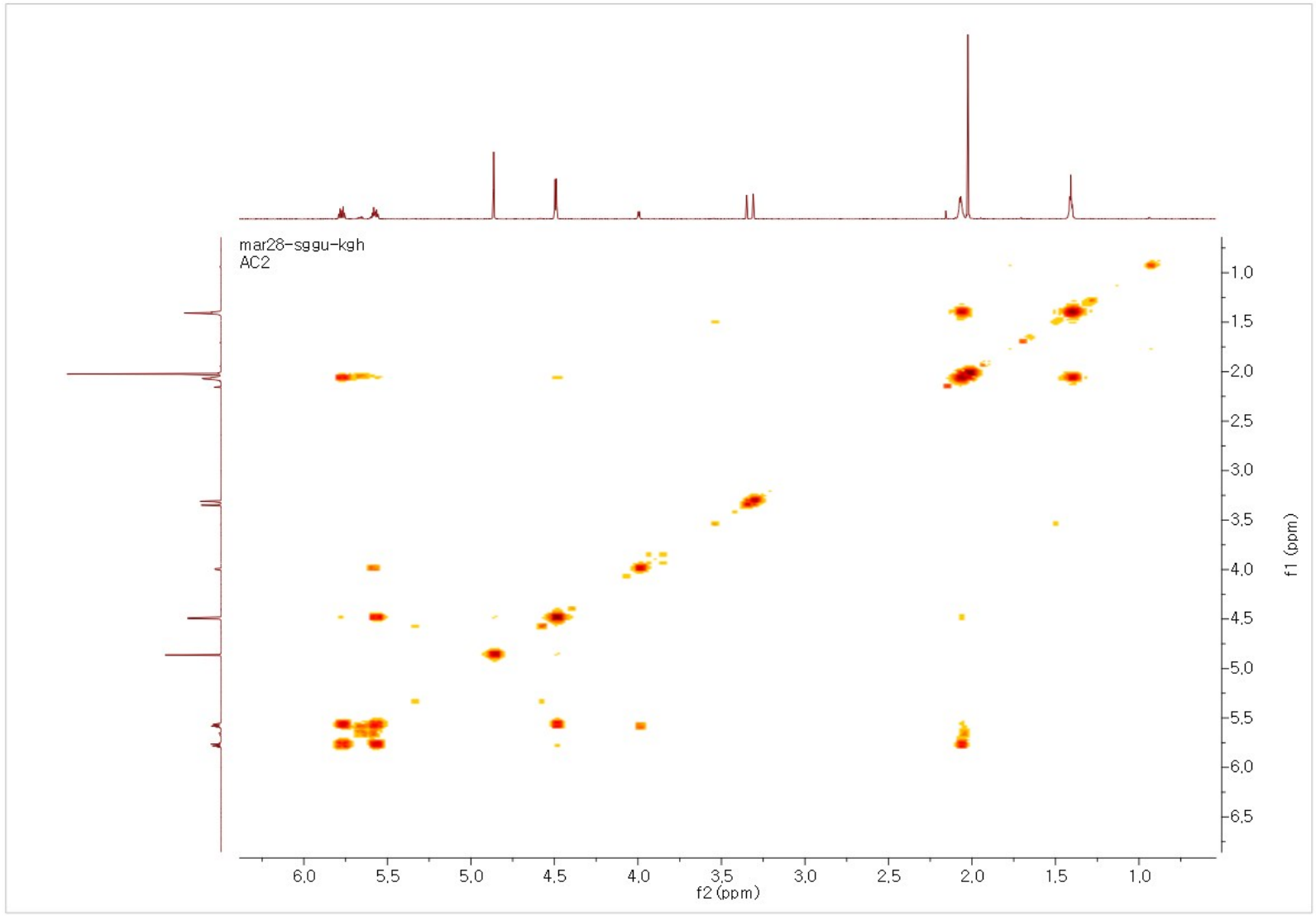


Figure S5. HSQC spectrum of **1** ($CDCl_3$)

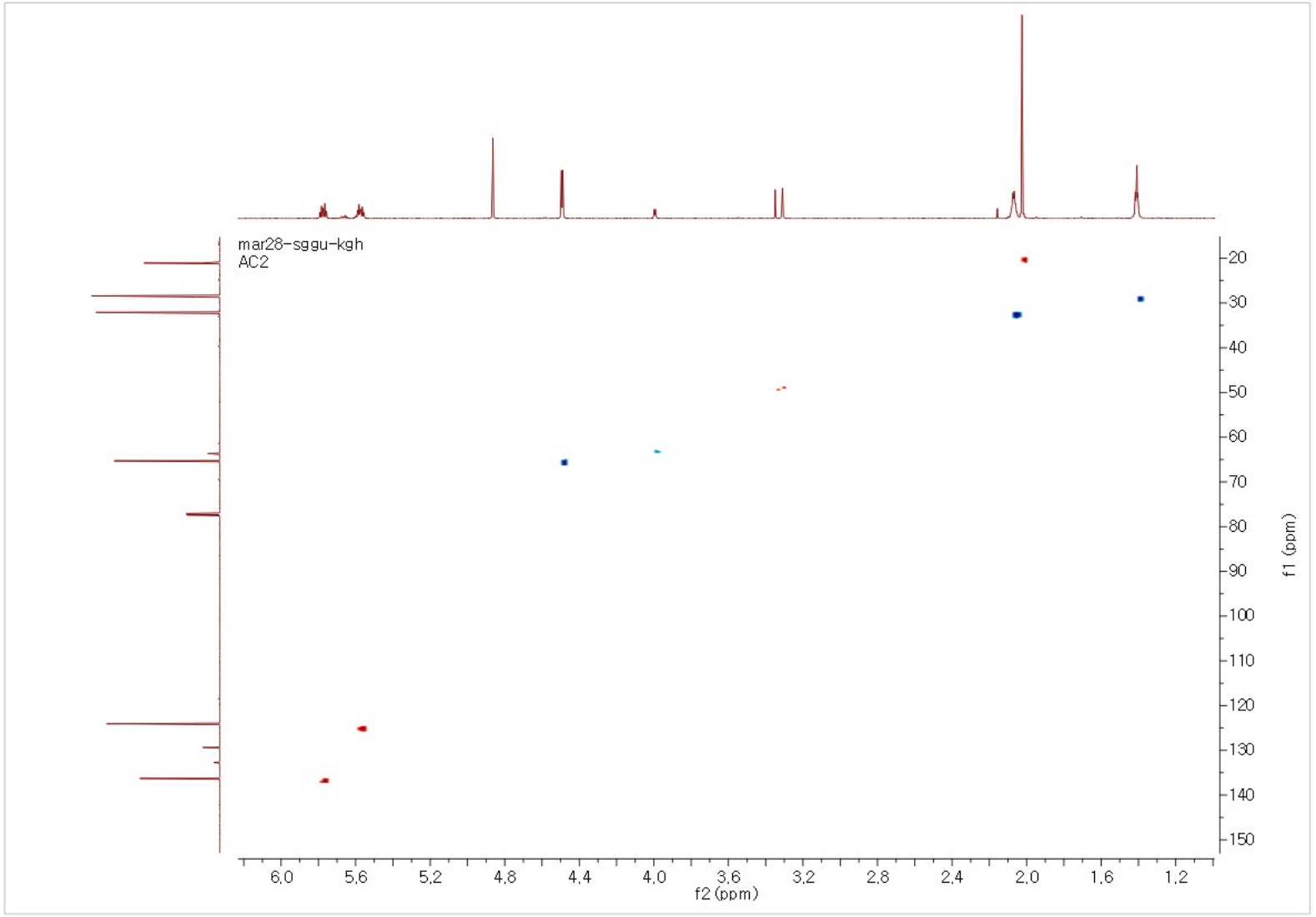


Figure S6. HMBC spectrum of **1** ($CDCl_3$)

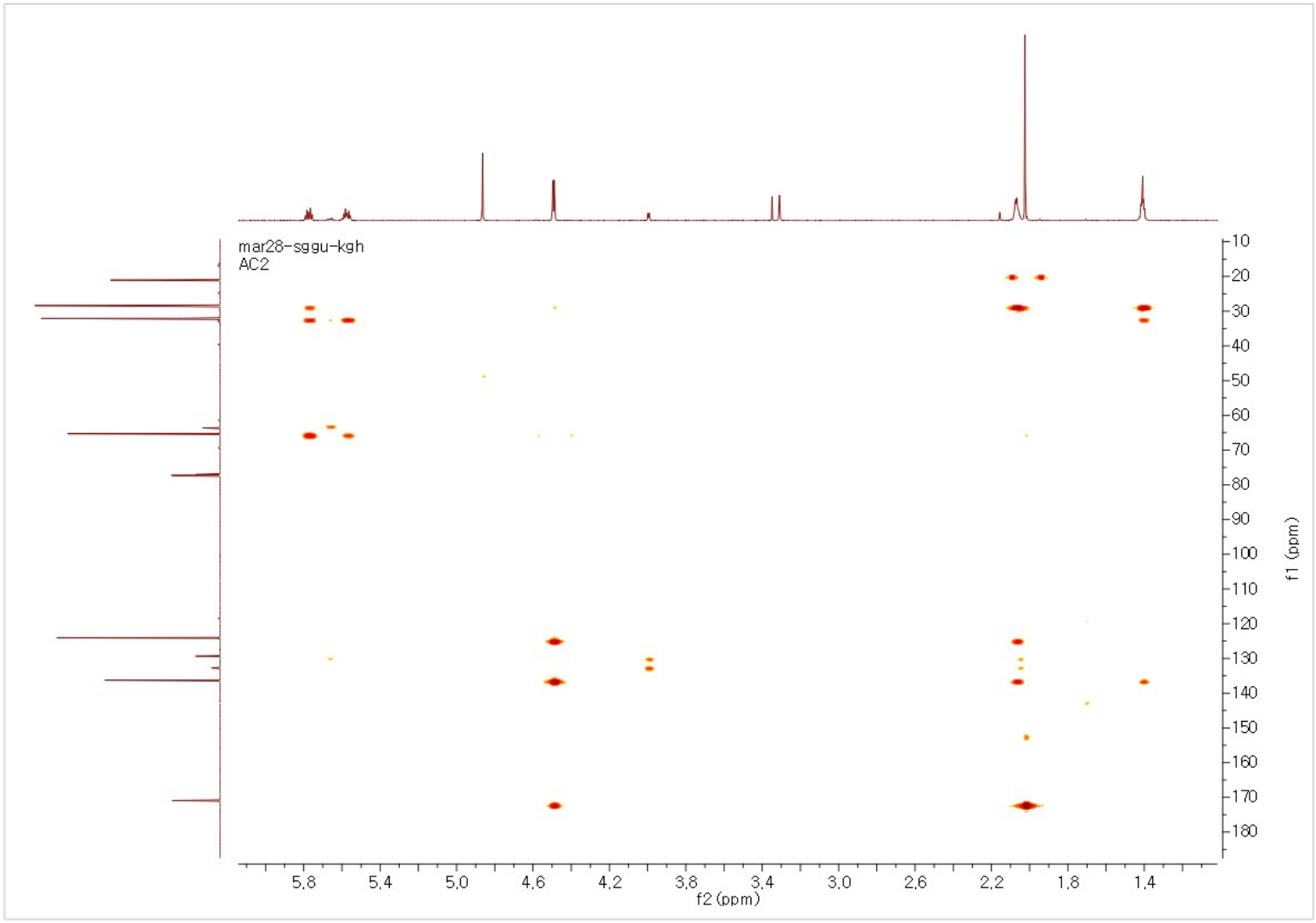


Figure S7. HR-ESIMS data of **2**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
70 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	Na
235.1310	235.1310	0.0	0.0	2.5	C12 H20 O3 Na	35.9	n/a	n/a	12	20	3	1

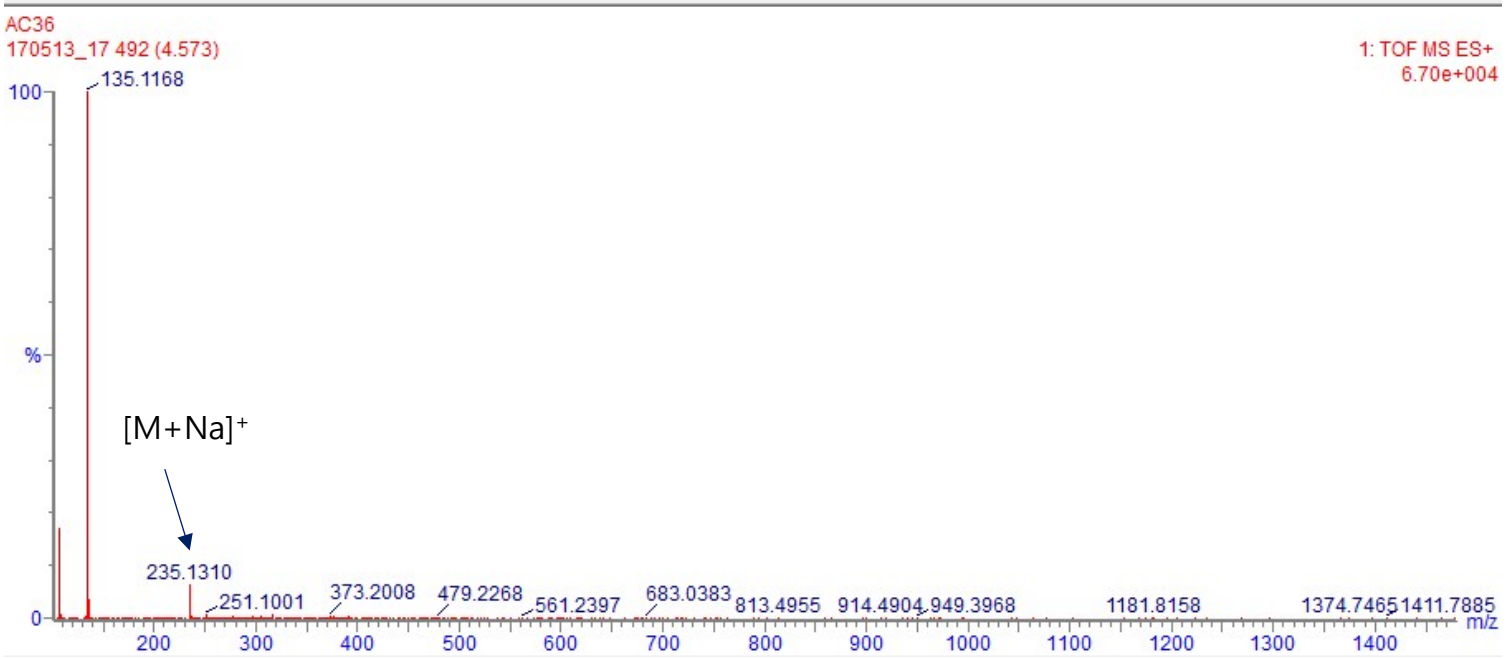


Figure S8. ^{1}H NMR spectrum of **2** ($CDCl_3$, 700 MHz)

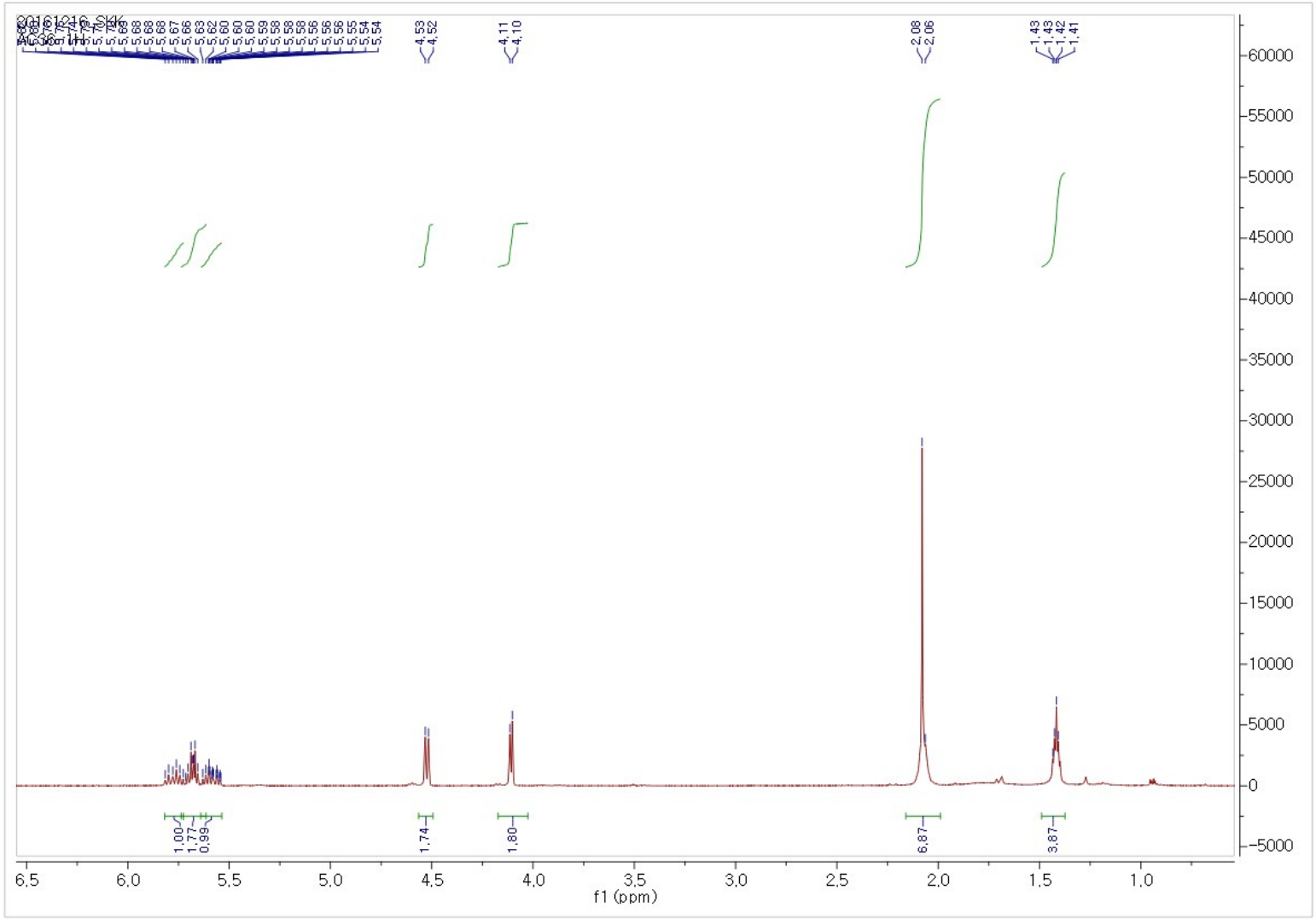


Figure S9. ^{13}C NMR spectrum of **2** ($CDCl_3$, 175 MHz)

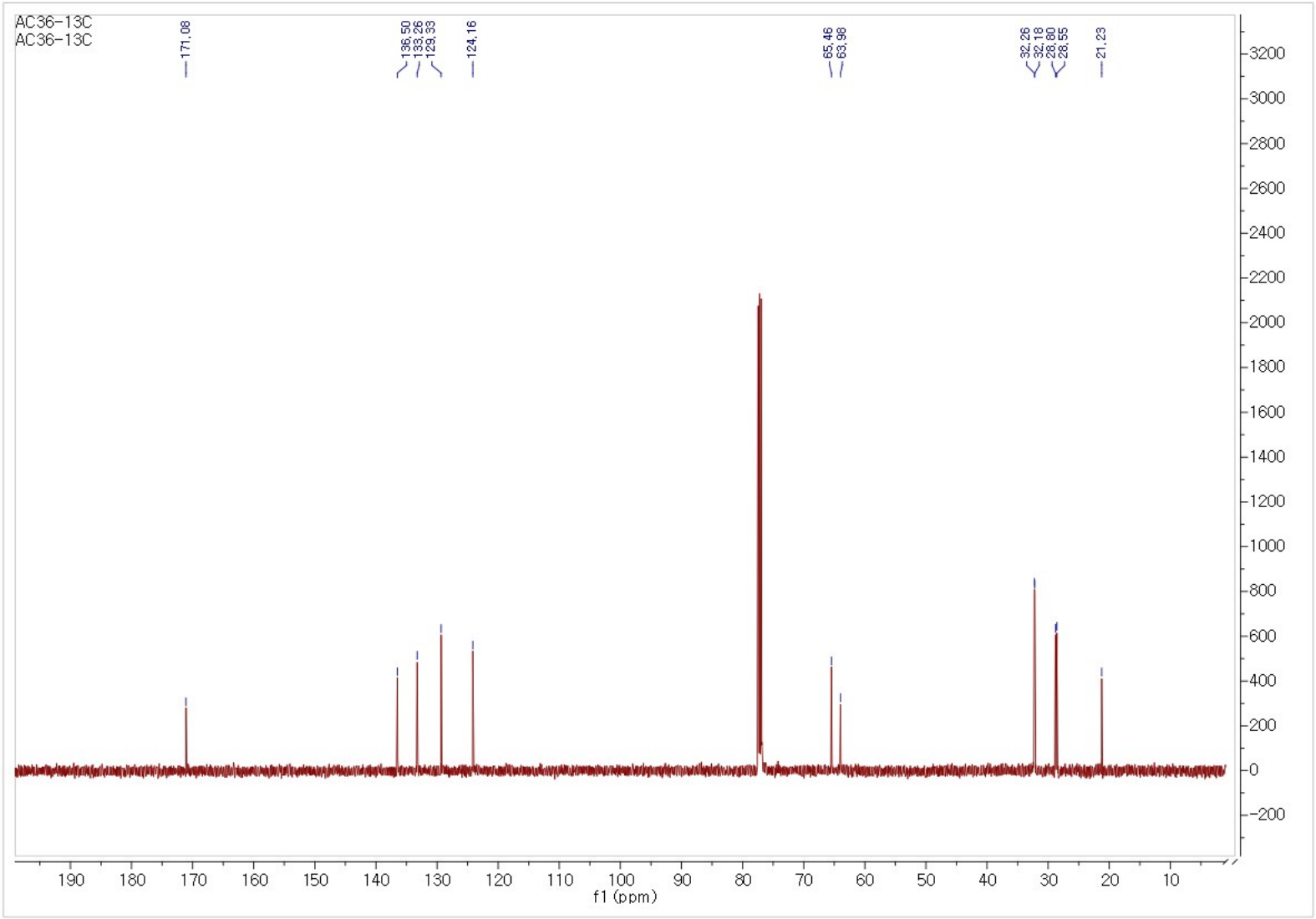


Figure S10. TOCSY spectrum of **2** ($CDCl_3$)

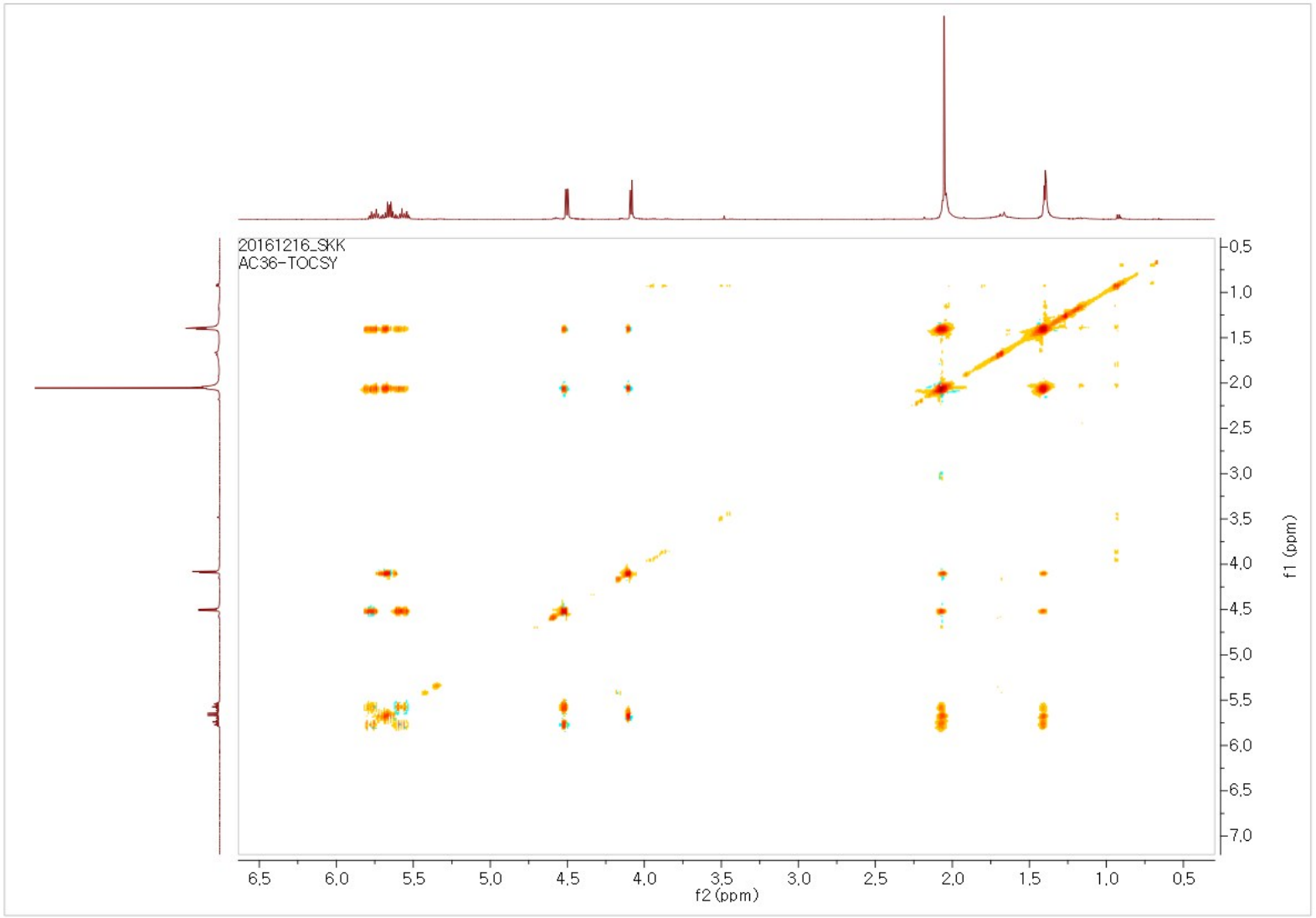


Figure S11. HSQC spectrum of **2** ($CDCl_3$)

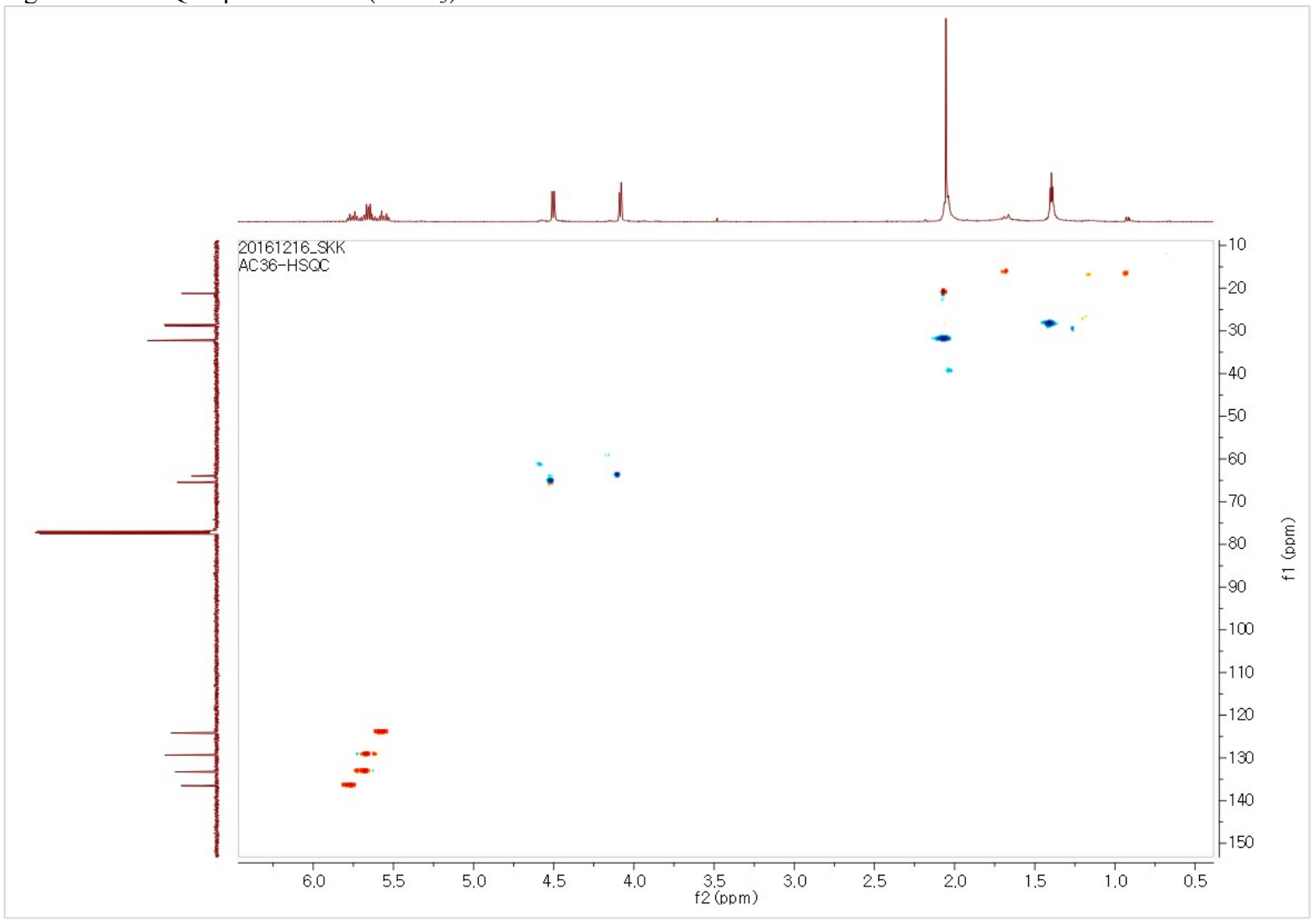


Figure S12. HMBC spectrum of **2** ($CDCl_3$)

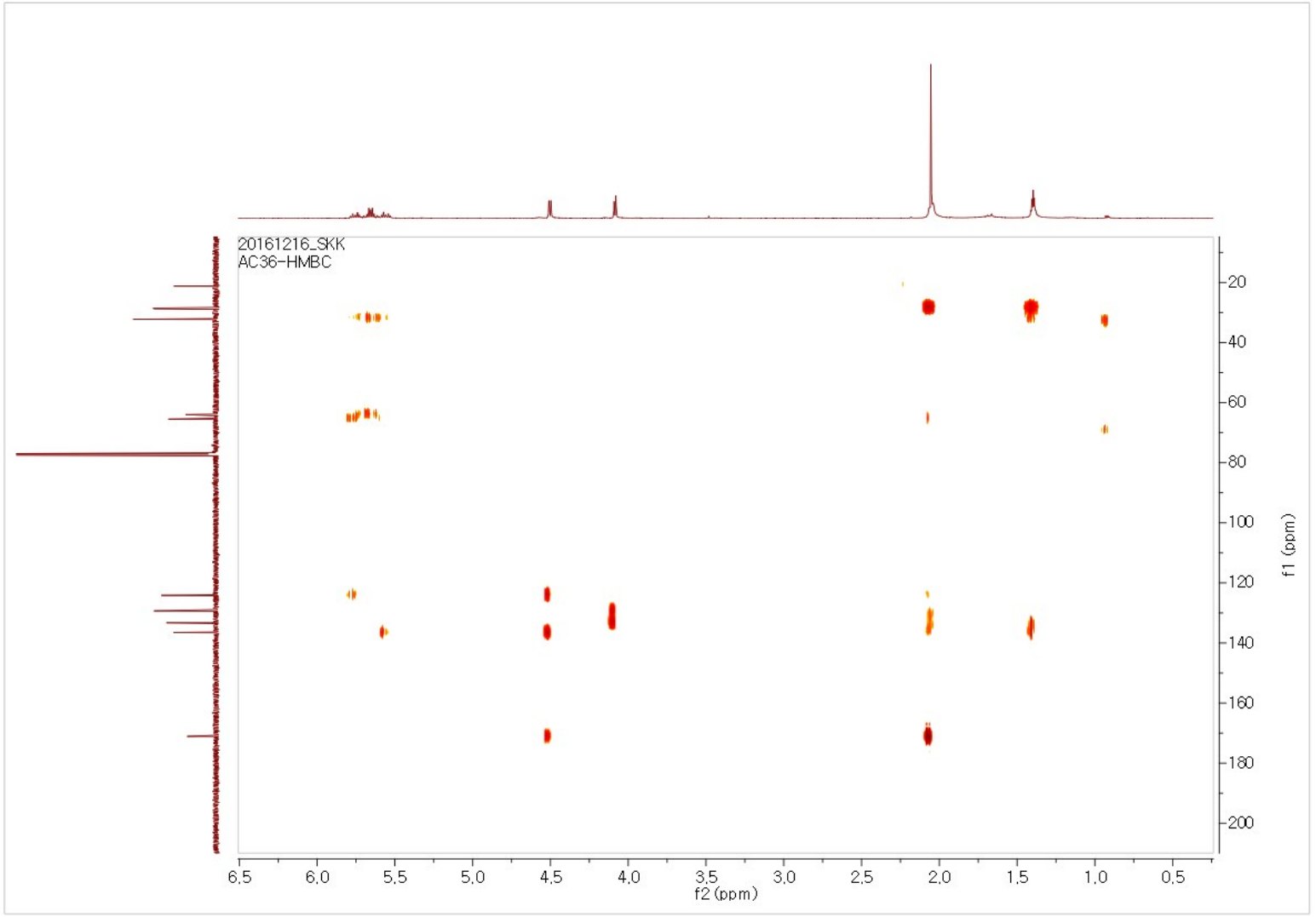


Figure S13. HR-ESIMS data of **5**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
80 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	Na
265.1795	265.1804	-0.9	-3.4	4.5	C16 H25 O3	354.4	0.022	97.81	16	25	3	
	265.1780	1.5	5.7	1.5	C14 H26 O3 Na	358.2	3.823	2.19	14	26	3	1

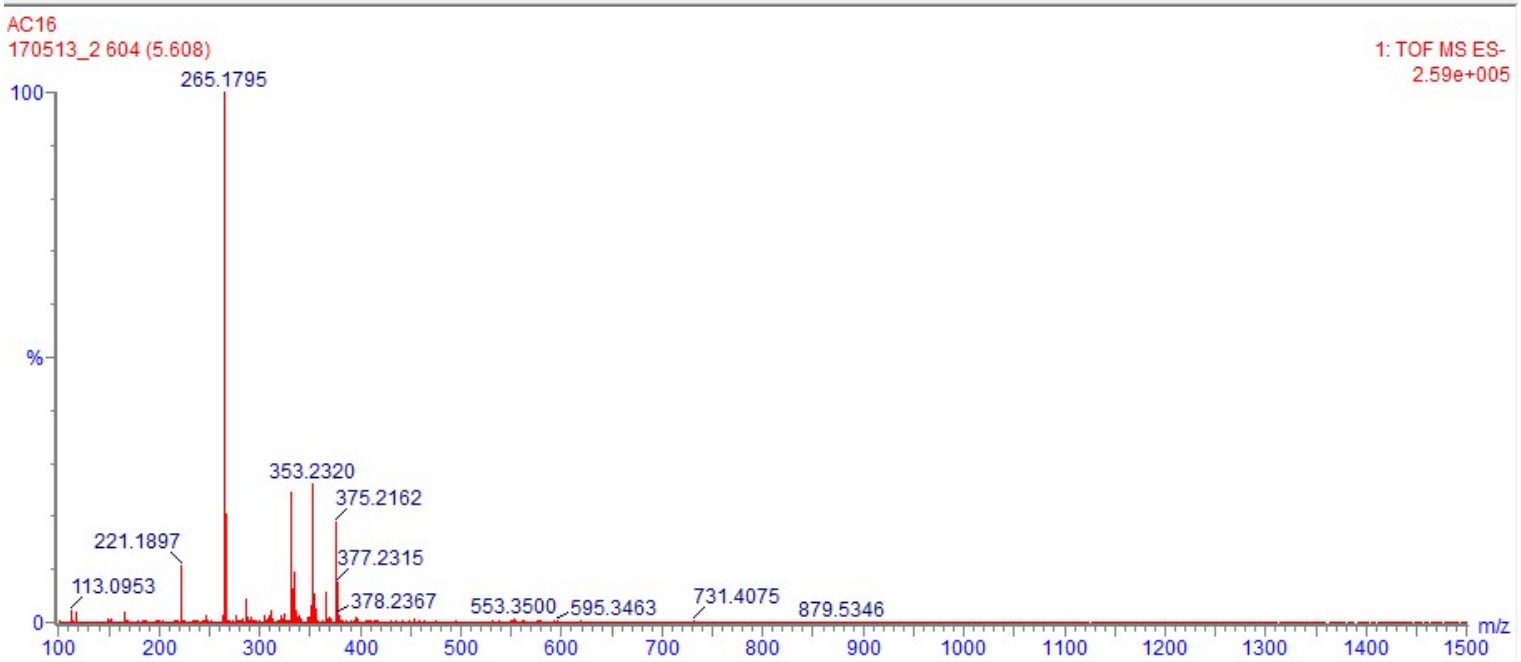


Figure S14. ^{1}H NMR spectrum of **5** ($CDCl_3$, 600 MHz)

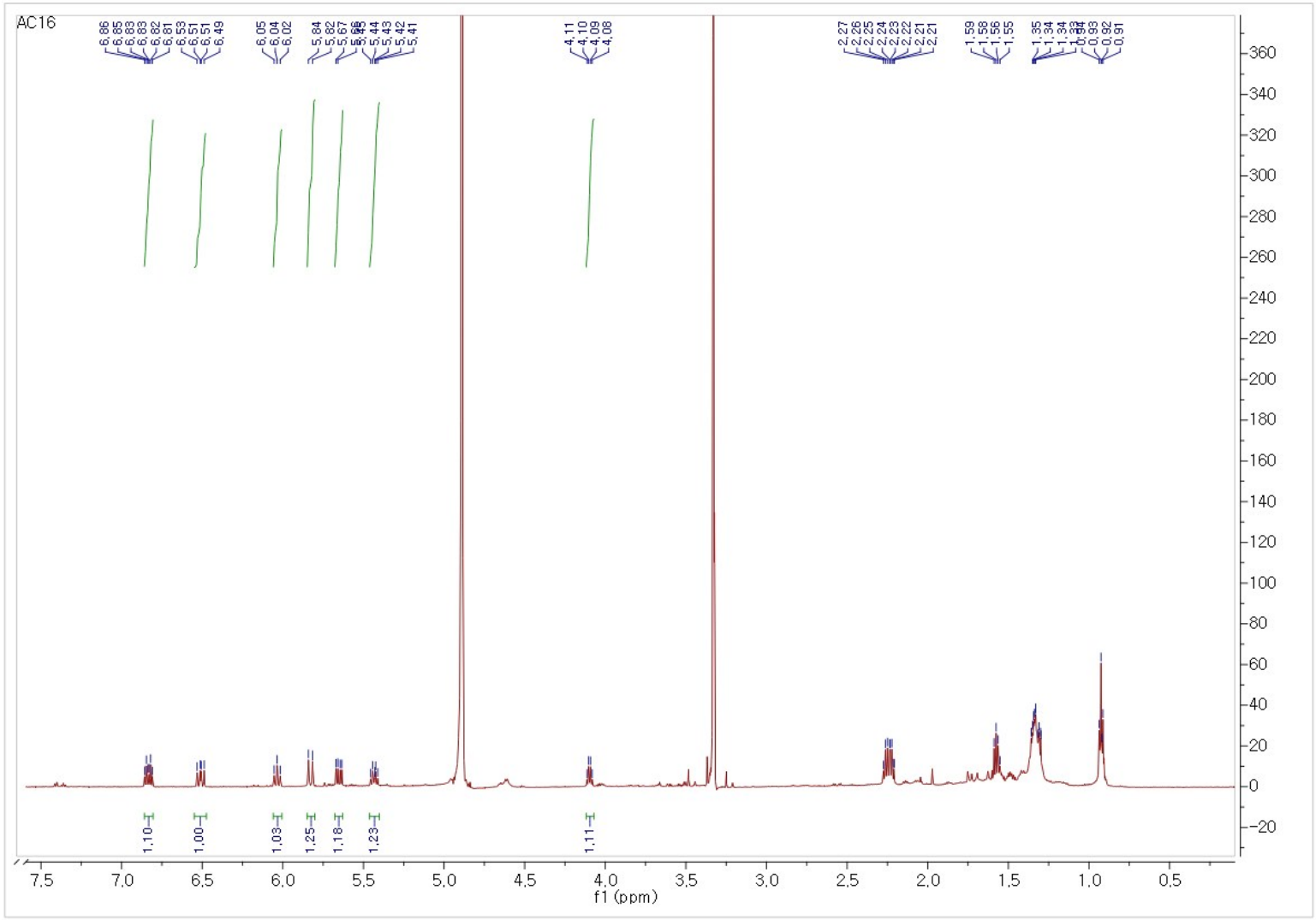


Figure S15. ^{13}C NMR spectrum of **5** ($CDCl_3$, 150 MHz)

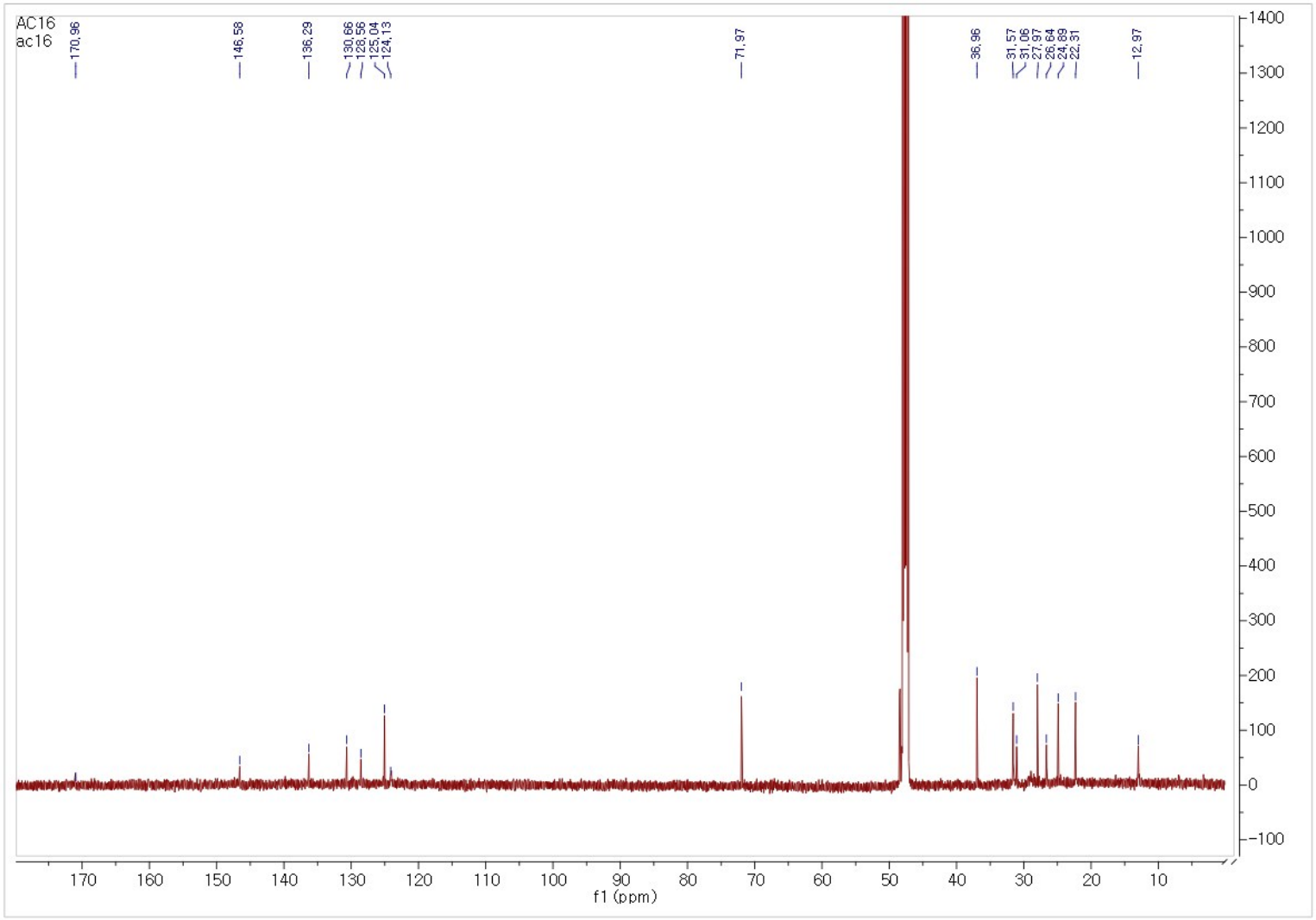


Figure S16. ^{1}H-^{1}H COSY spectrum of **5** ($CDCl_3$)

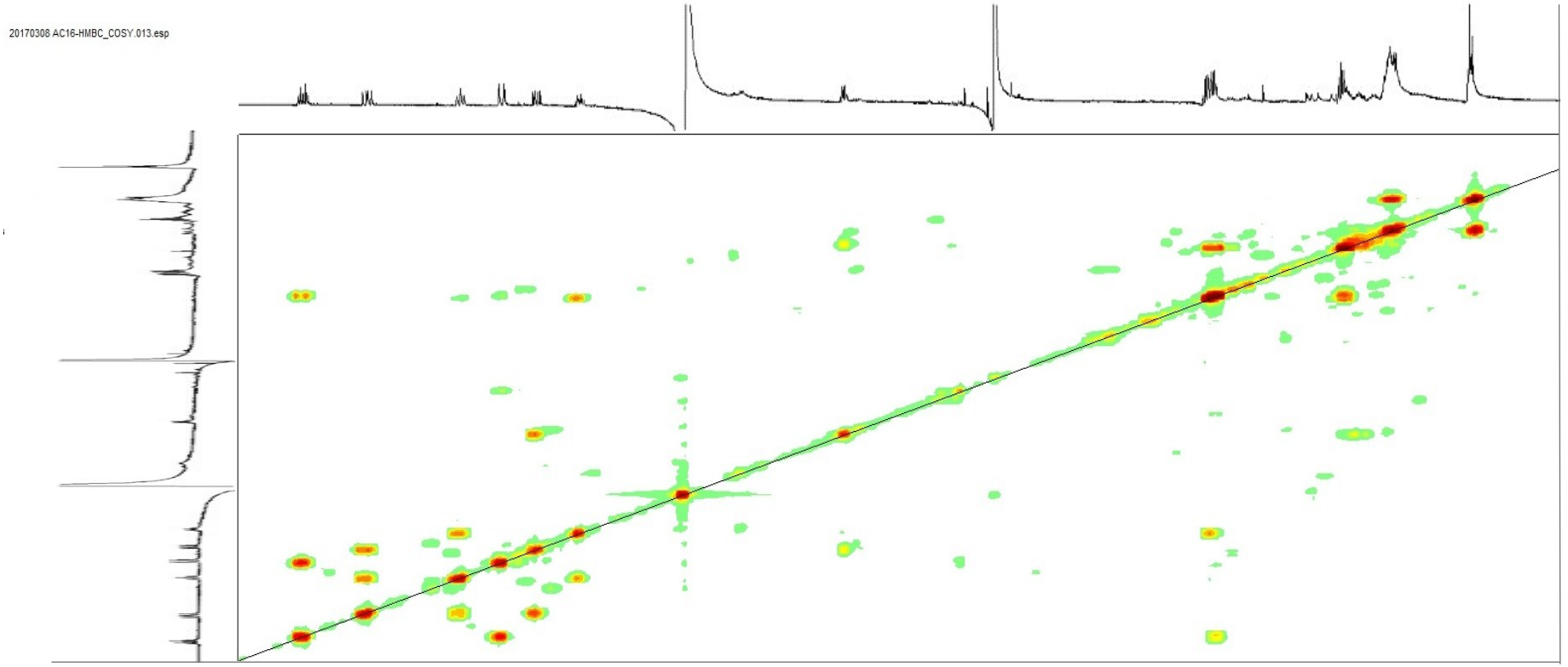


Figure S17. HSQC spectrum of **5** ($CDCl_3$)

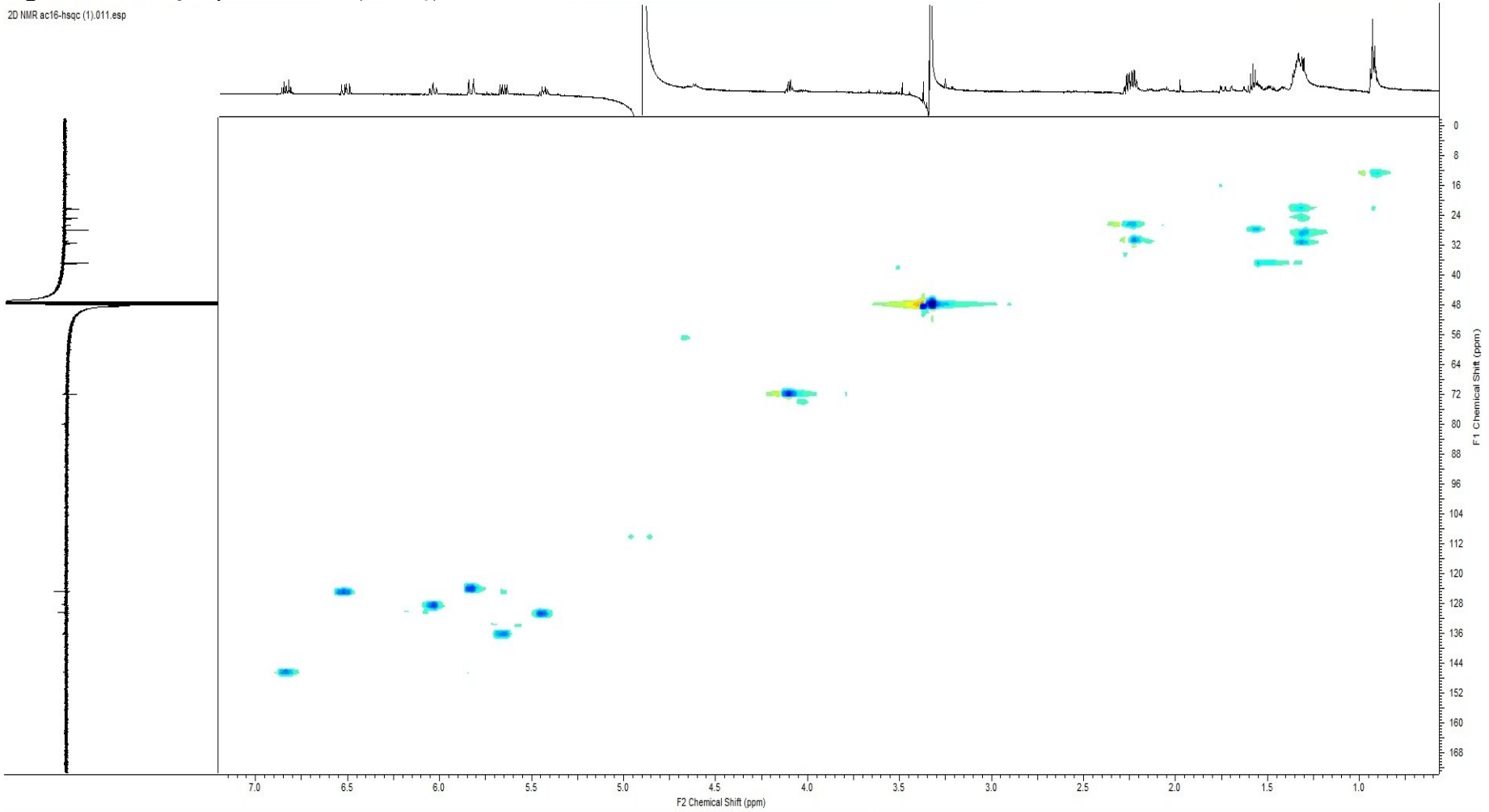


Figure S18. HMBC spectrum of **5** ($CDCl_3$)

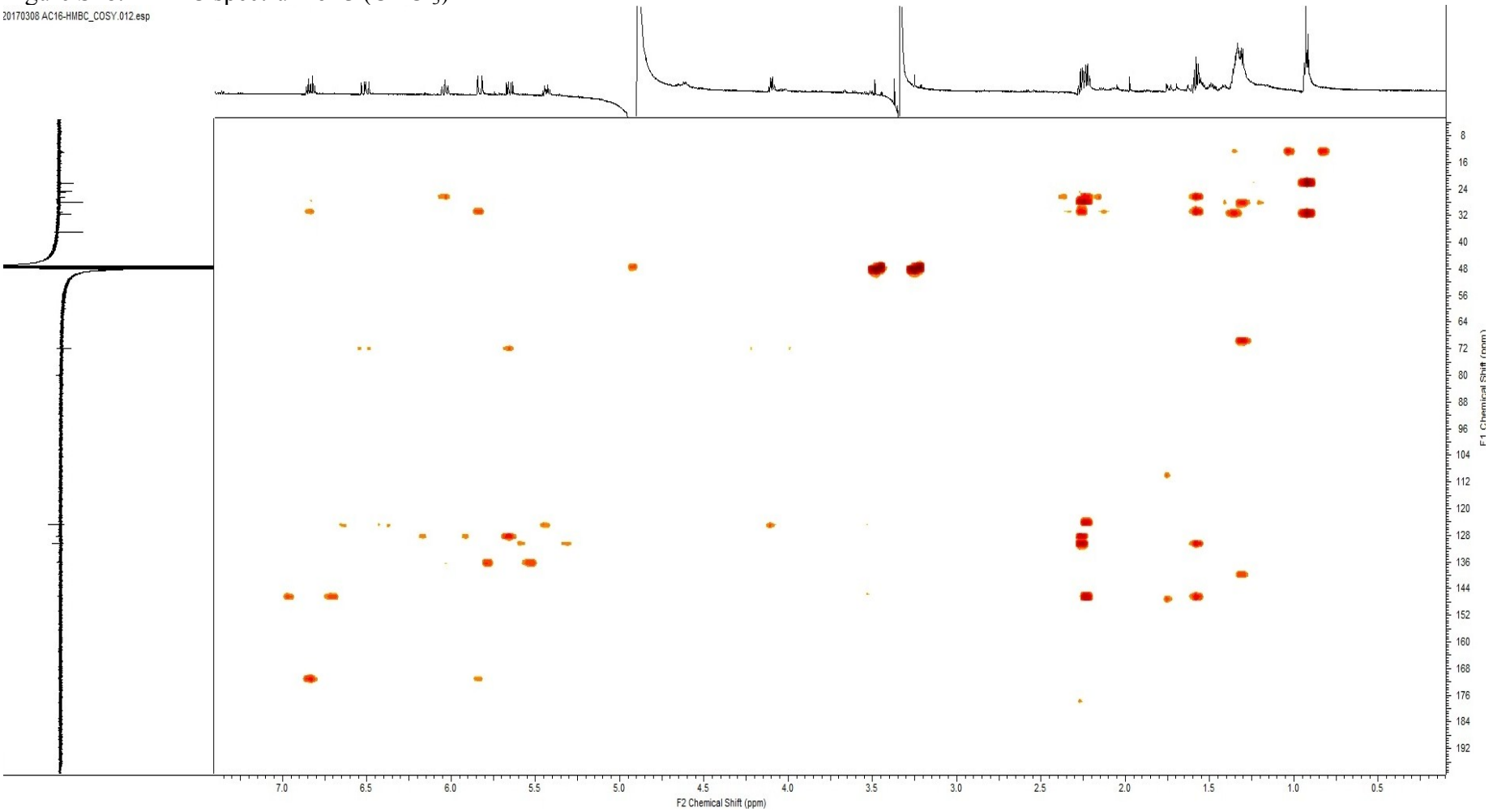


Figure S19. MS/MS analysis of **5** (MS^2 265 → full-scan)

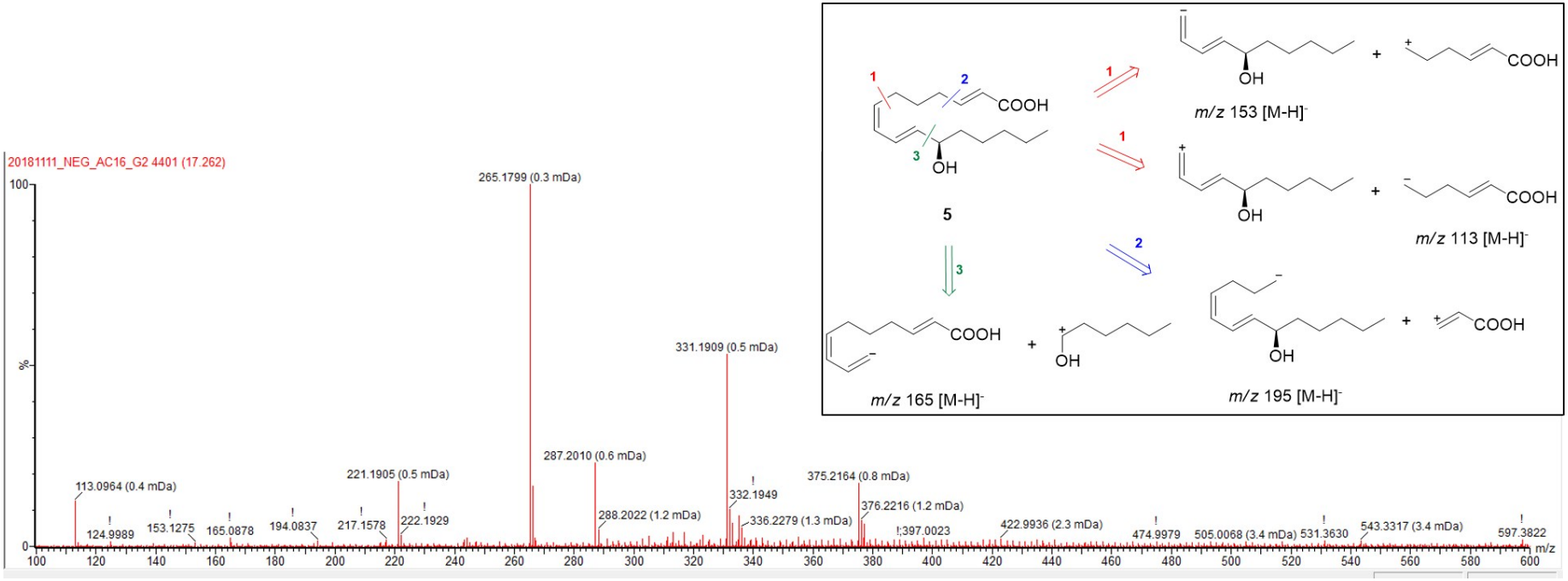
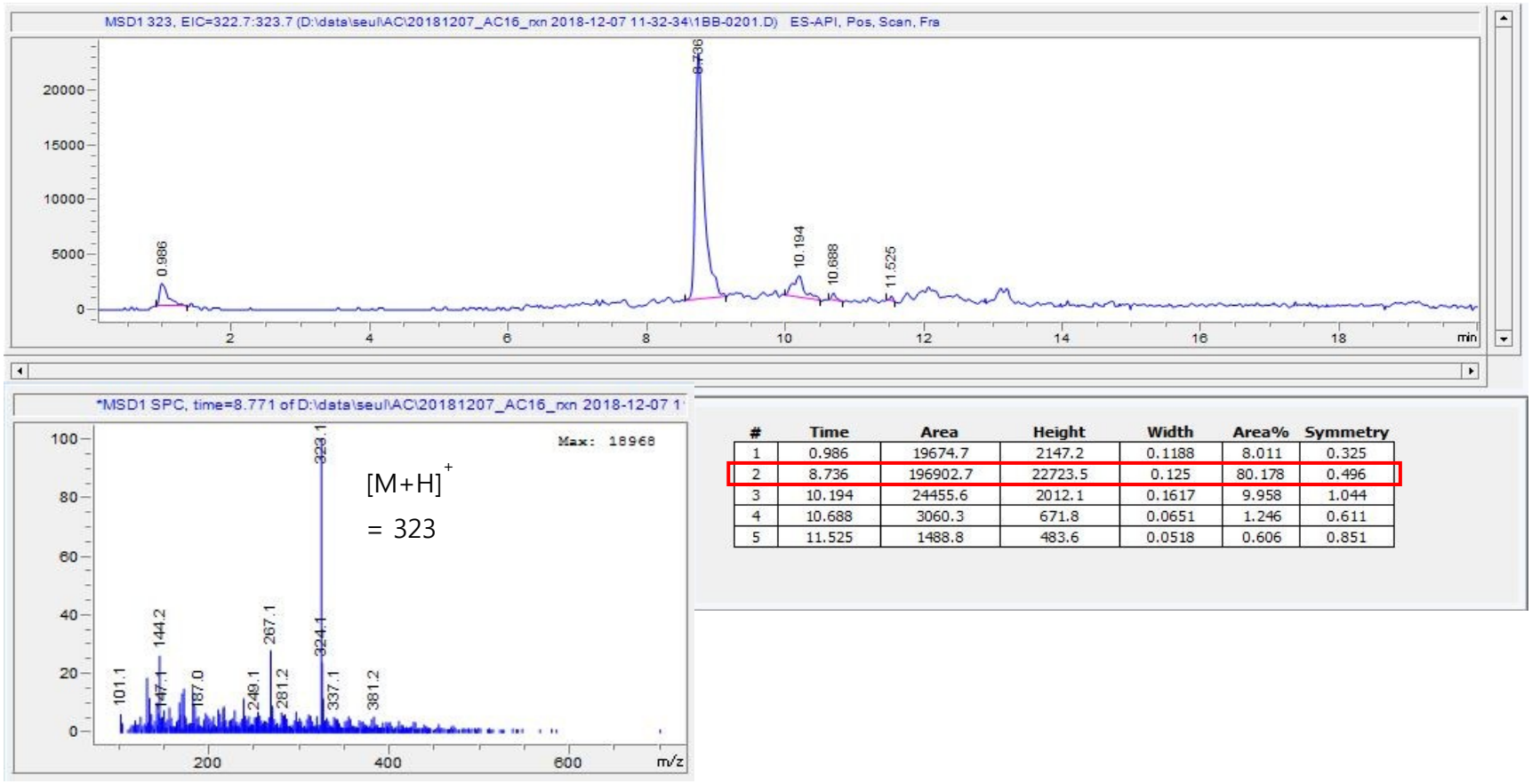


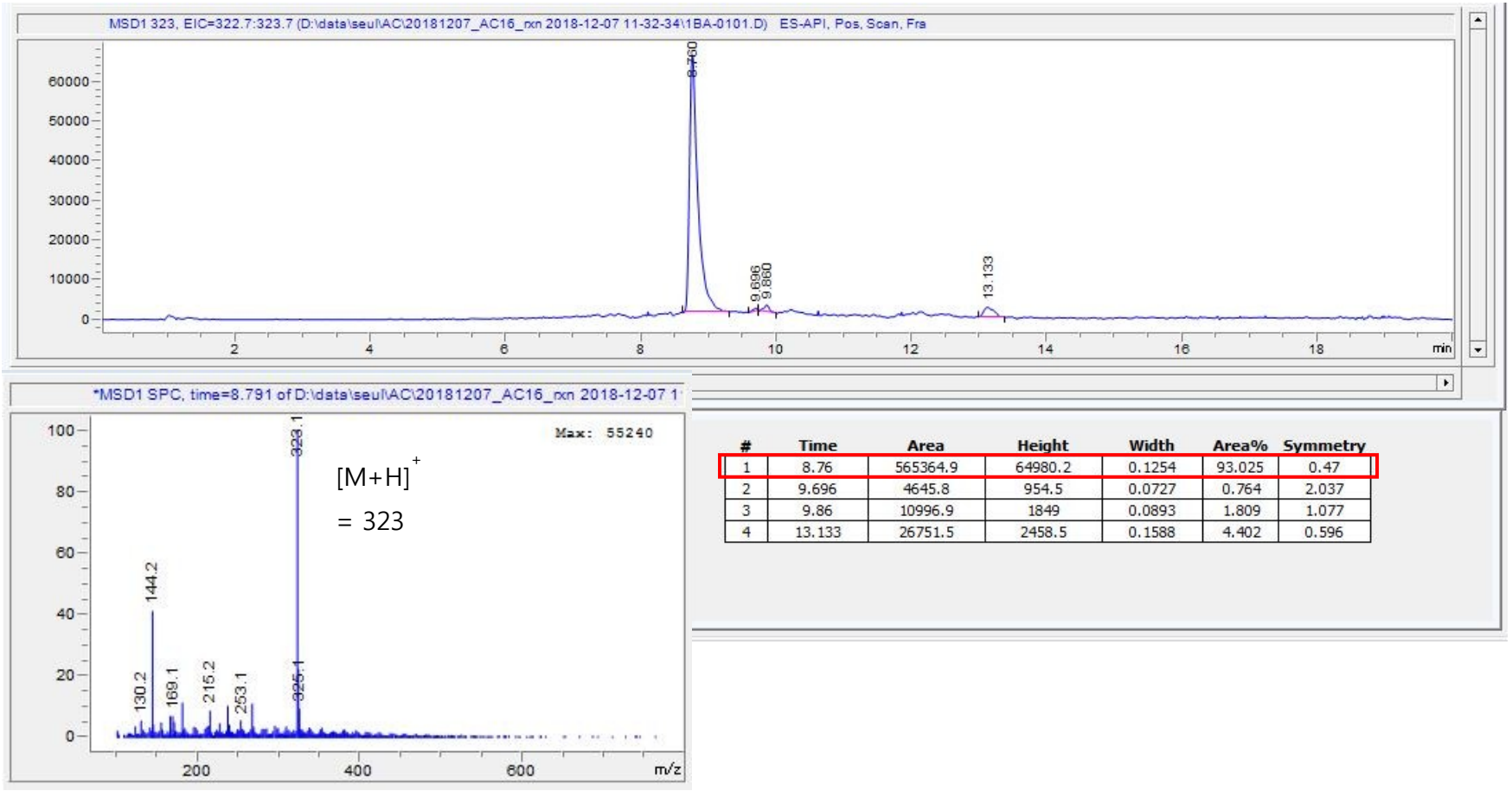
Figure S20. LC/MS data of acylated derivative from CEA reaction of **5**: (a) An acylated derivative of compound **5** in *R*-HBTM catalyzed acylation reaction at 10 min; (b) An acylated derivative of compound **5** in *S*-HBTM catalyzed acylation reaction at 10 min

a) An acylated derivative of compound **5** in *R*-HBTM catalyzed acylation reaction at 10 min



#	Time	Area	Height	Width	Area%	Symmetry
1	0.986	19674.7	2147.2	0.1188	8.011	0.325
2	8.736	196902.7	22723.5	0.125	80.178	0.496
3	10.194	24455.6	2012.1	0.1617	9.958	1.044
4	10.688	3060.3	671.8	0.0651	1.246	0.611
5	11.525	1488.8	483.6	0.0518	0.606	0.851

b) An acylated derivative of compound **5** in *S*-HBTM catalyzed acylation reaction at 10 min



#	Time	Area	Height	Width	Area%	Symmetry
1	8.76	565364.9	64980.2	0.1254	93.025	0.47
2	9.696	4645.8	954.5	0.0727	0.764	2.037
3	9.86	10996.9	1849	0.0893	1.809	1.077
4	13.133	26751.5	2458.5	0.1588	4.402	0.596

Figure S21. HR-ESIMS data of **10**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
58 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	Na
211.0962	211.0970	-0.8	-3.8	4.5	C11 H15 O4	100.2	0.710	49.15	11	15	4	
	211.0946	1.6	7.6	1.5	C9 H16 O4 Na	100.2	0.676	50.85	9	16	4	1

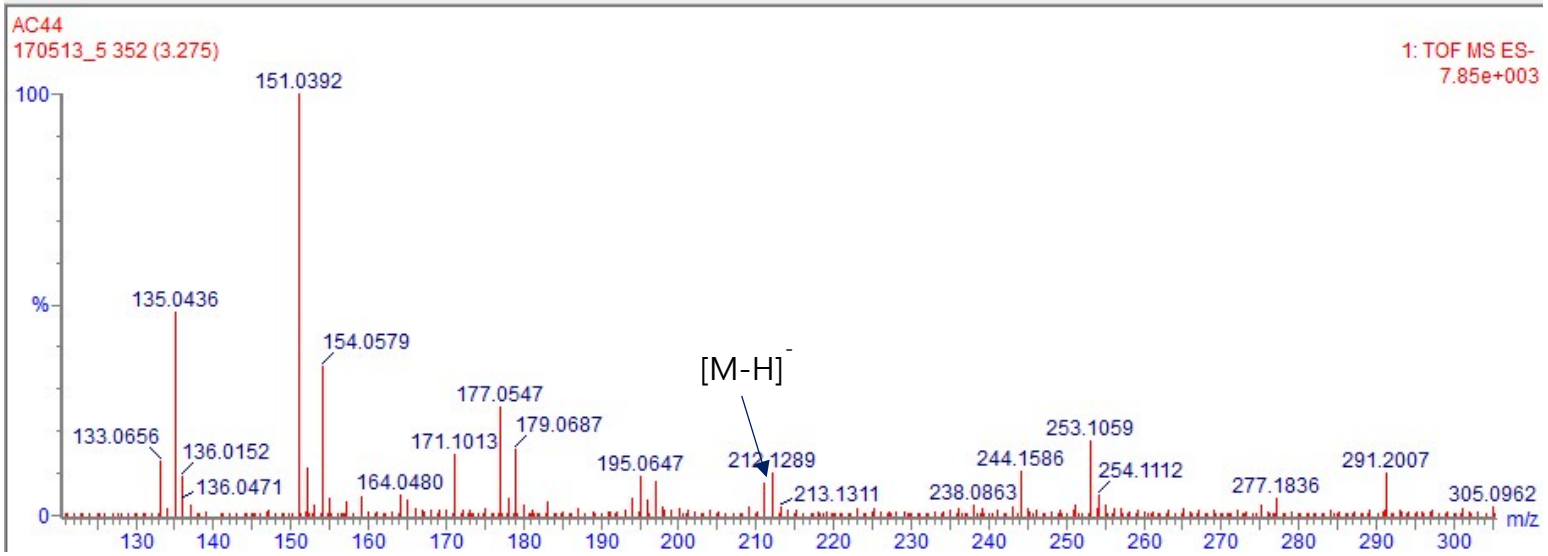


Figure S22. ^{1}H NMR spectrum of **10** (CD_3OD, 850 MHz)

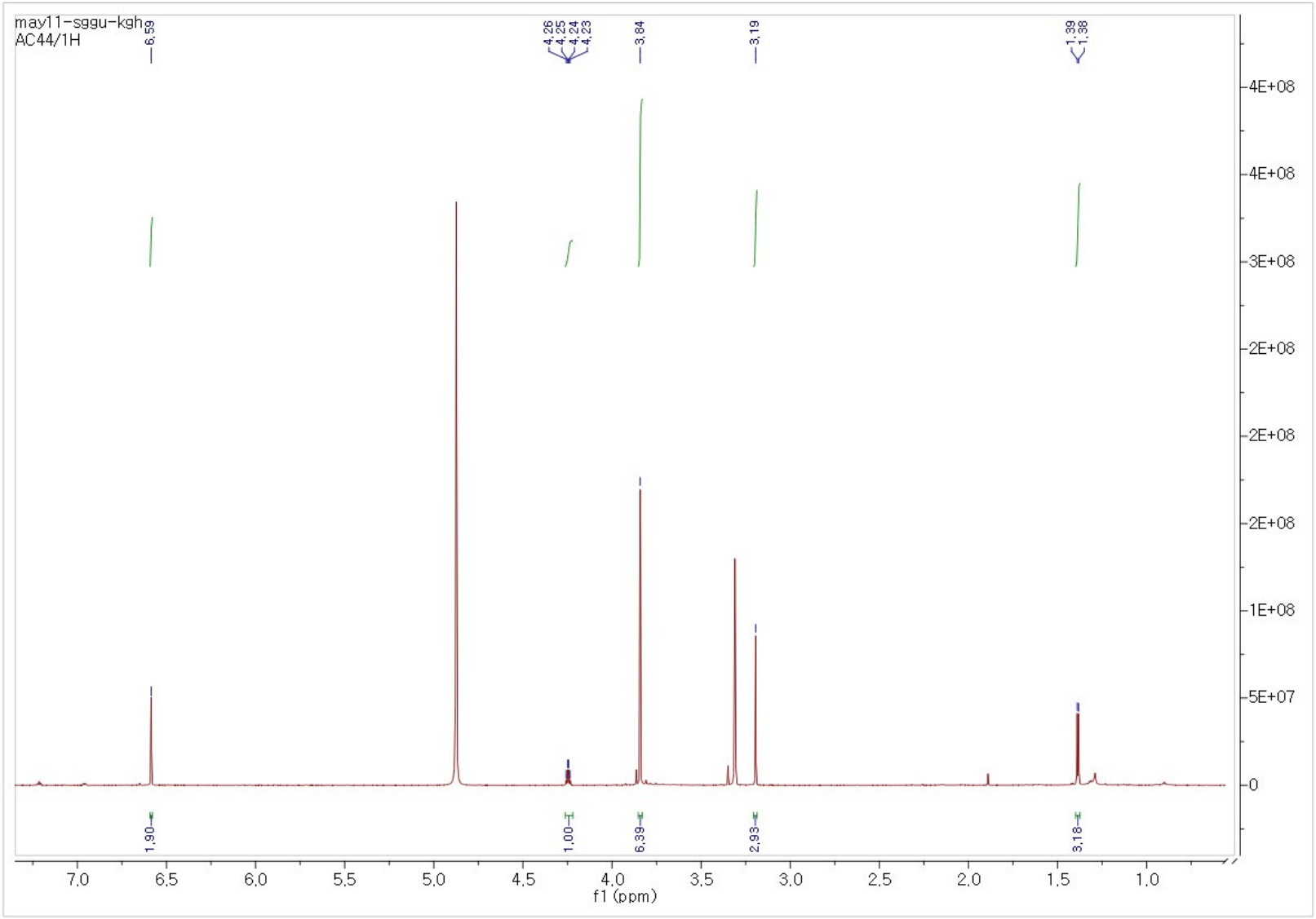


Figure S23. ^{1}H-^{1}H COSY spectrum of **10** (CD_3OD)

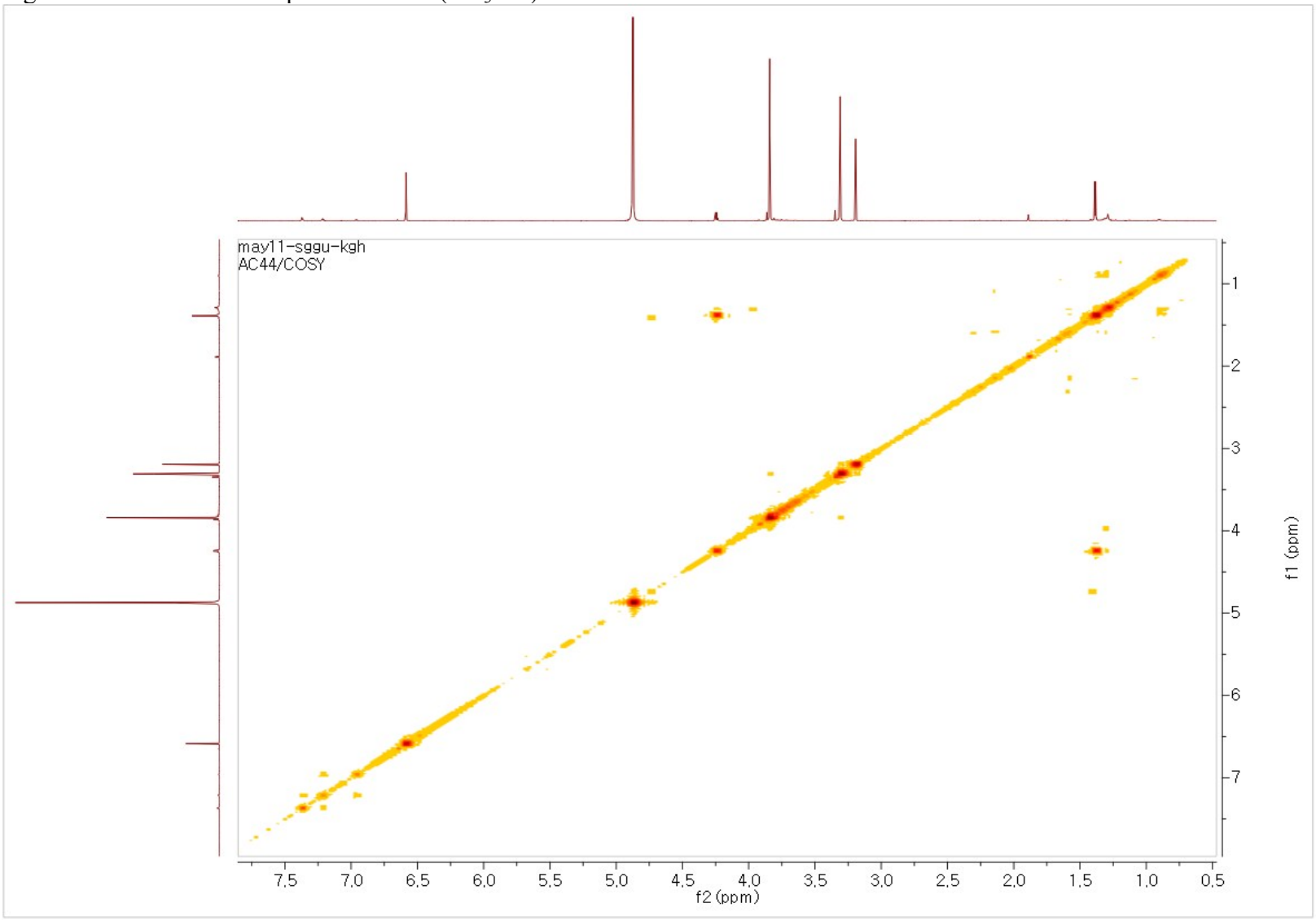


Figure S24. HSQC spectrum of **10** (CD_3OD)

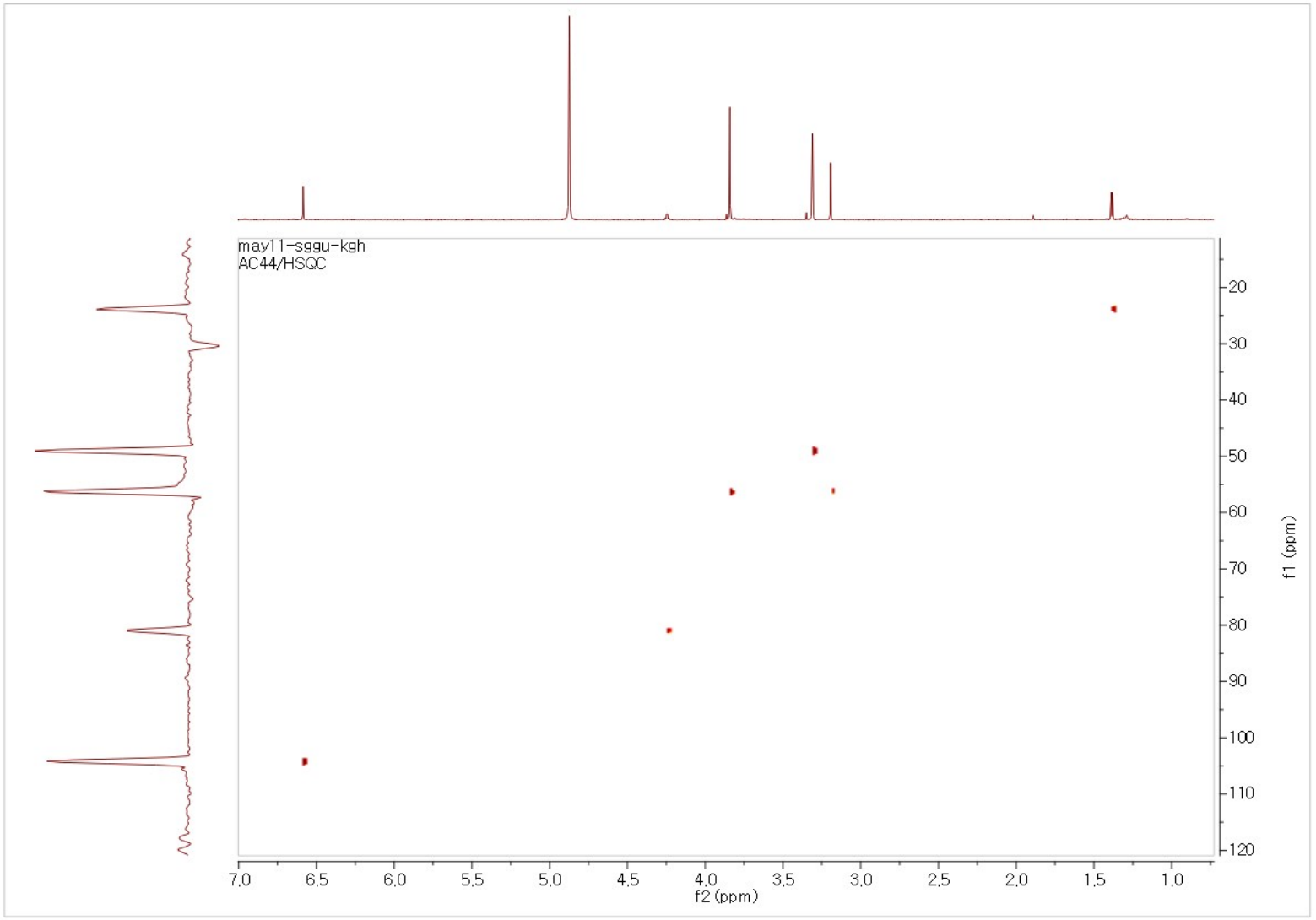


Figure S25. HMBC spectrum of **10** (CD_3OD)

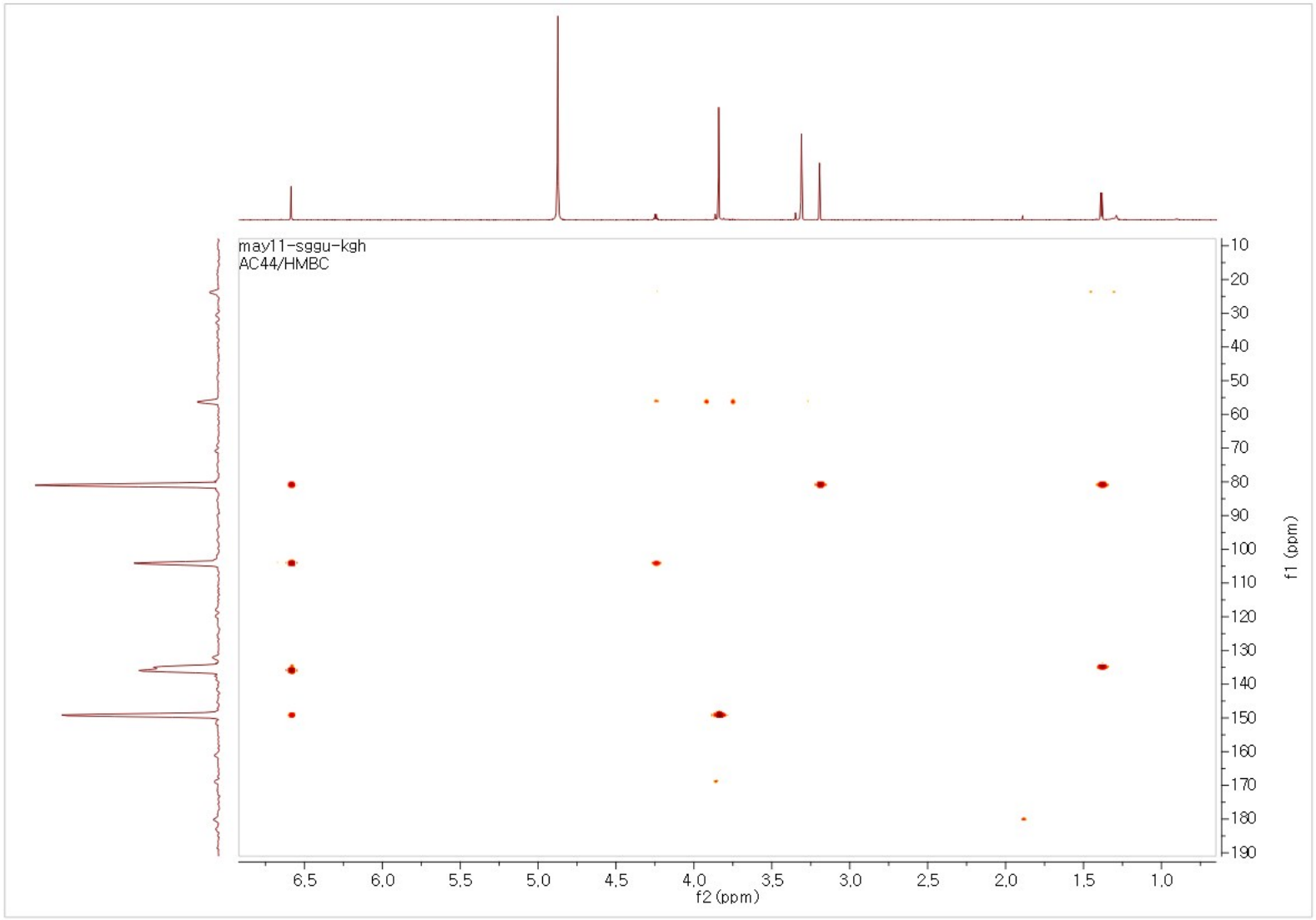


Figure S26. HR-ESIMS data of **11**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
72 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	Na
249.1102	249.1103	-0.1	-0.4	3.5	C12 H18 O4 Na	64.2	0.496	60.91	12	18	4	1
	249.1127	-2.5	-10.0	6.5	C14 H17 O4	64.6	0.939	39.09	14	17	4	

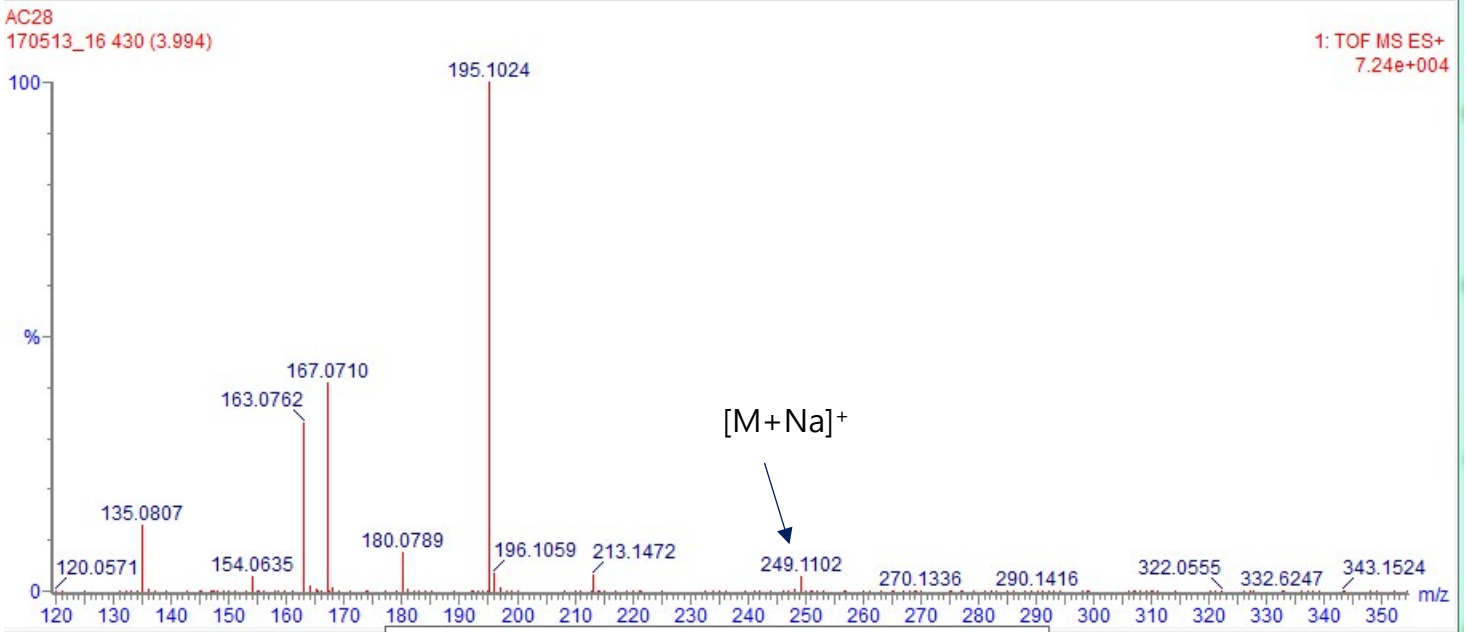


Figure S27. ^{1}H NMR spectrum of **11** (CD_3OD, 800 MHz)

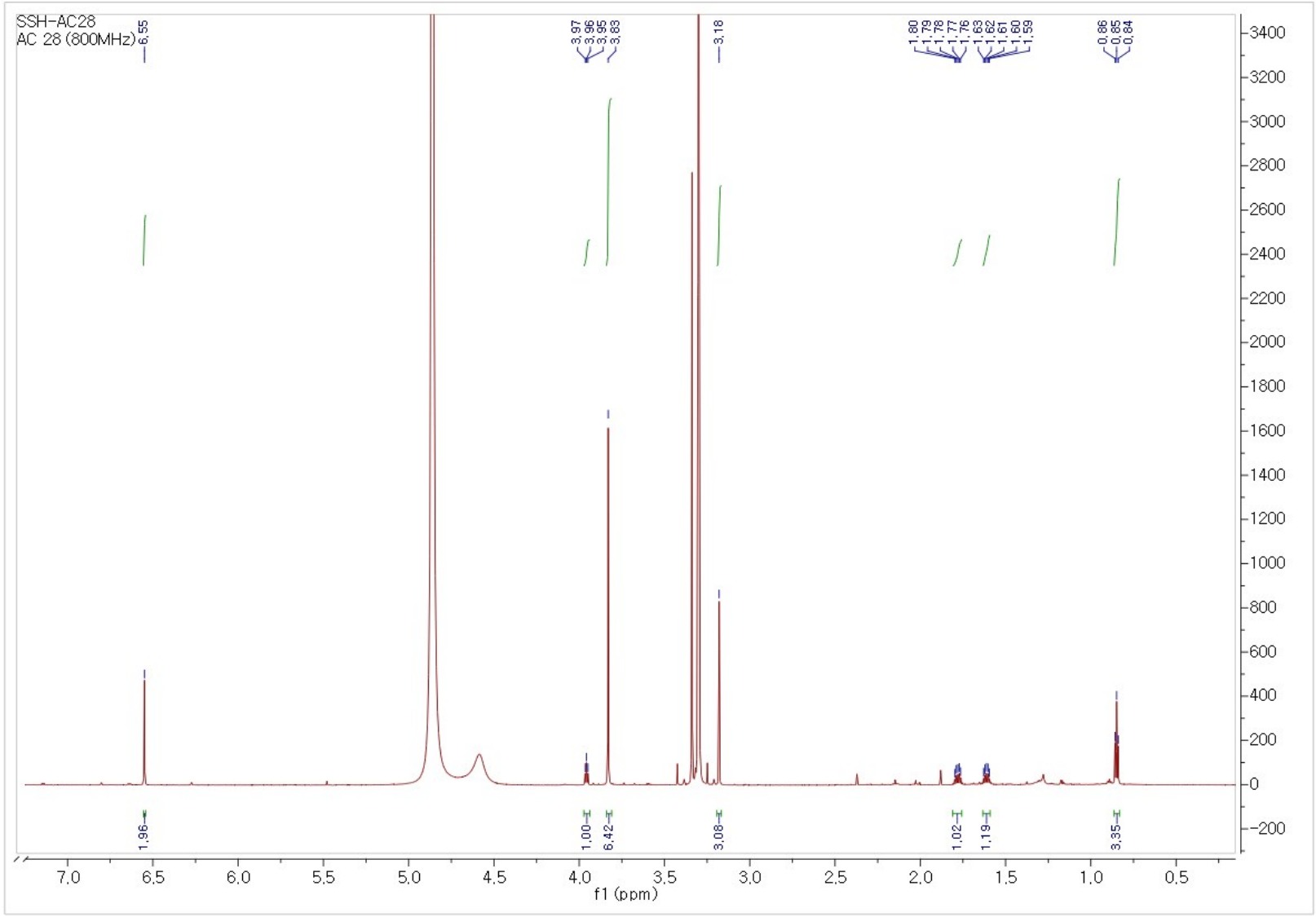


Figure S28. ^{1}H-^{1}H COSY spectrum of **11** (CD_3OD)

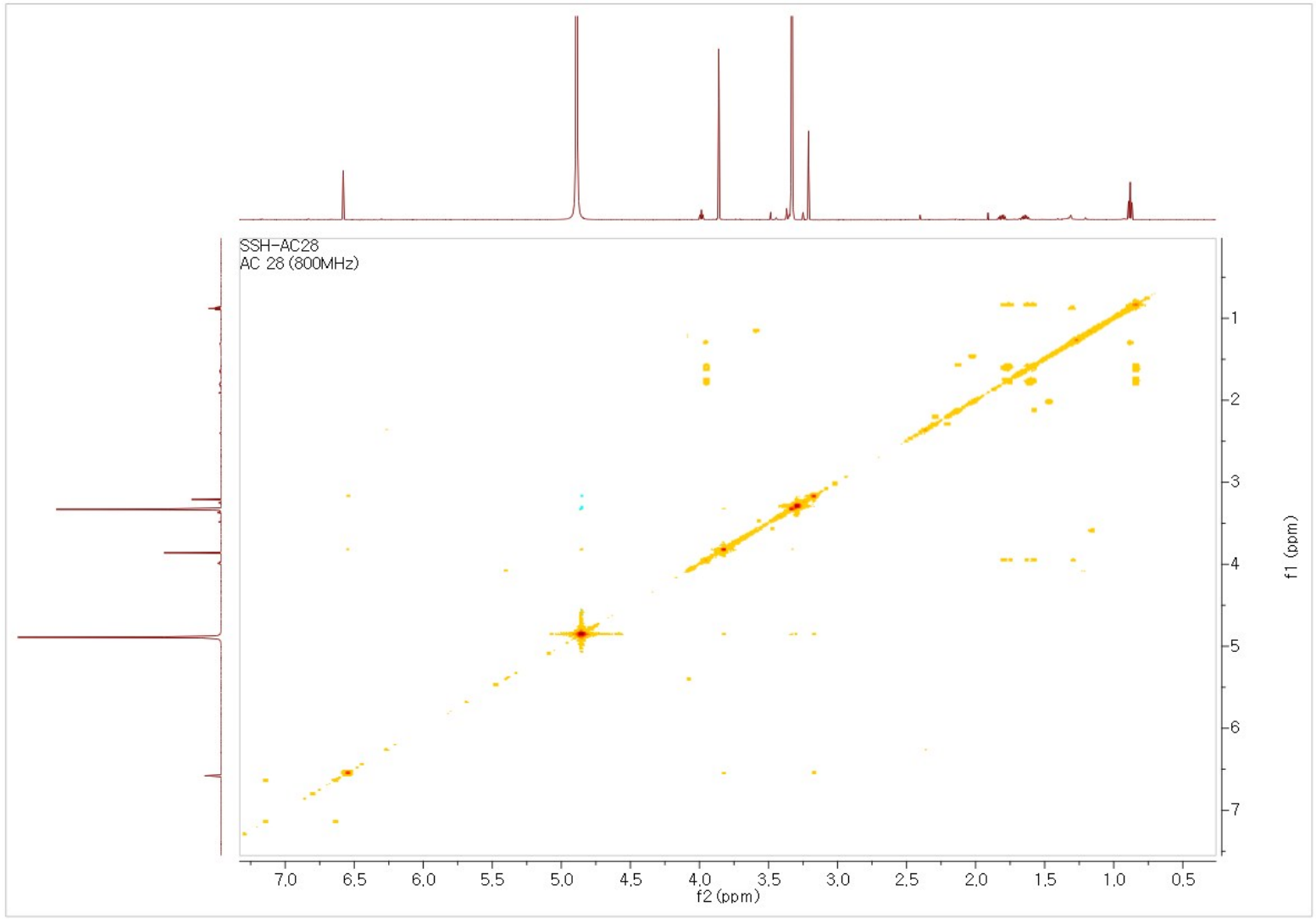


Figure S29. HSQC spectrum of **11** (CD_3OD)

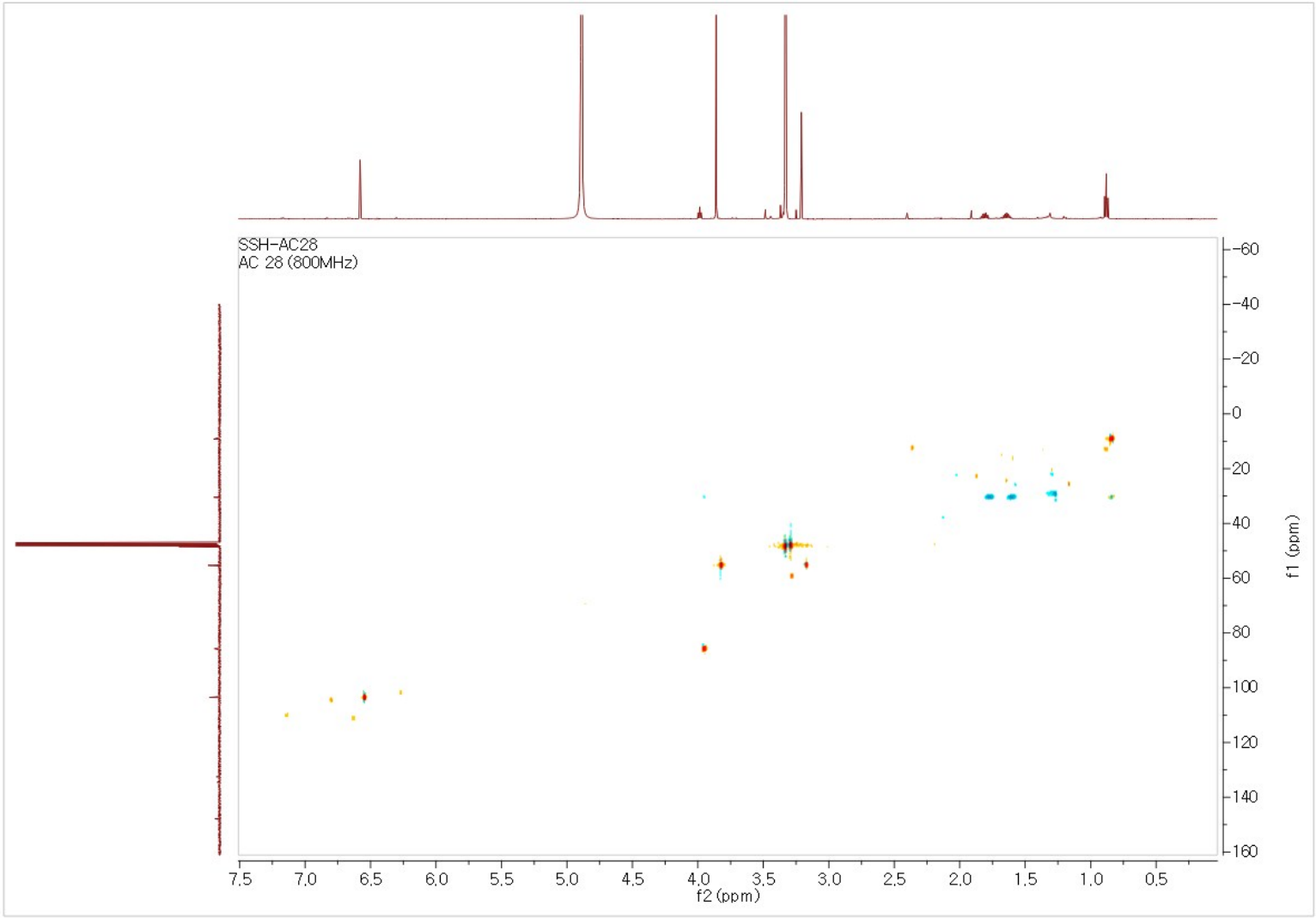


Figure S30. HMBC spectrum of **11** (CD_3OD)

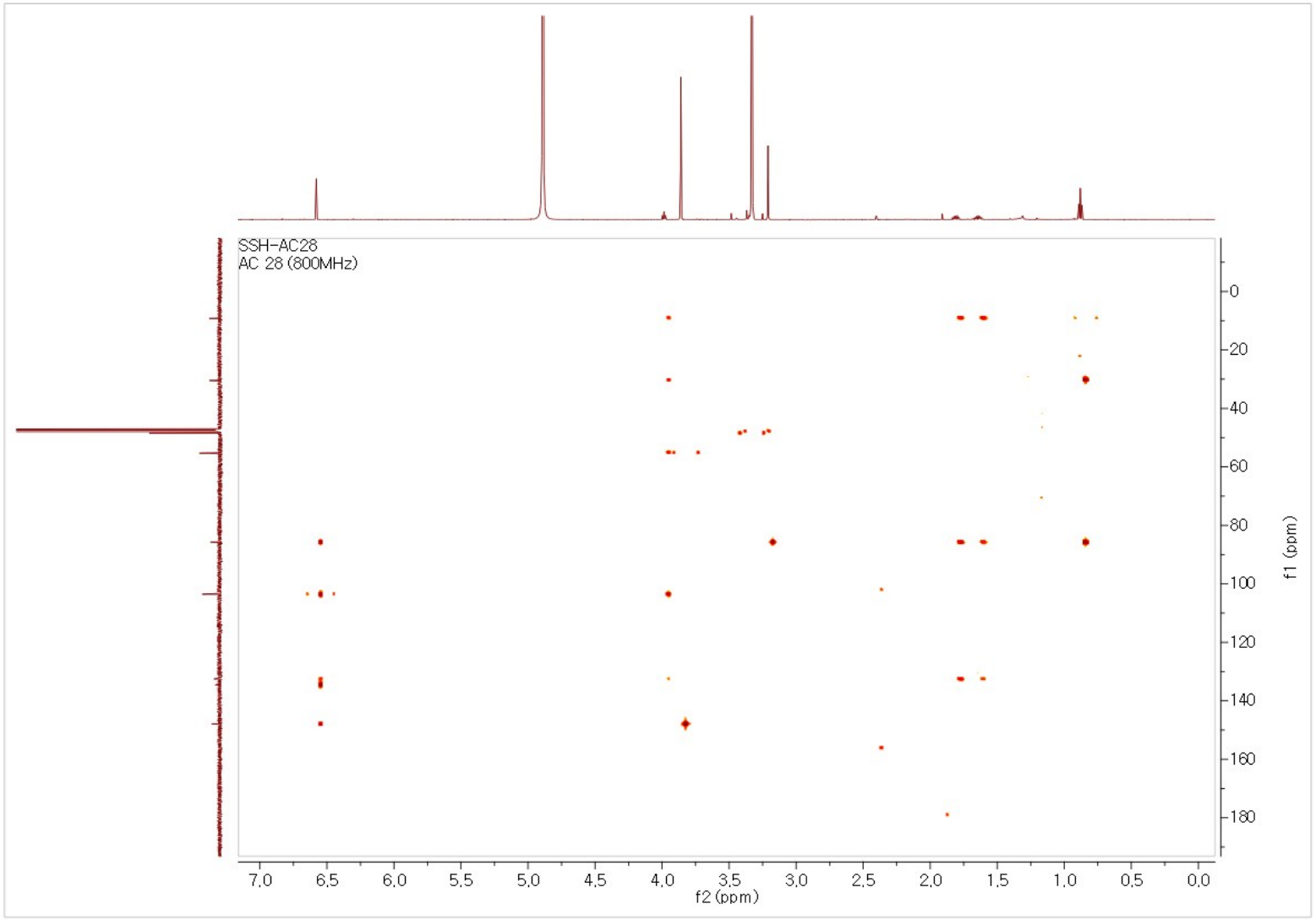


Figure S31. Amino acid sequence alignment of human SPHK1(PDB id : 3VZD) and human SPHK2 using the homology modeling module embedded in the Schrodinger Maestro 11.6 software.