Content

Acid hydrolysis of compounds 1-7

Compounds **1-7** (each, 5.0 mg) were separately dissolved in 1.0 M HCl (dioxane–H_2O, 1:1, v/v, 1.0 mL) and heated to 80 °C in a water bath for 3 h. For each compound, the acidic solution was neutralized with silver carbonate, the precipitated silver chloride was removed, and the solution was concentrated thoroughly under a nitrogen atmosphere. The residue was re-dissolved in 1.0 mL of water and extracted with chloroform (three times, each 1 mL). The aqueous layer was concentrated to dryness using nitrogen gas and monosaccharides were purified by preparative TLC (pre-coated silica gel 60 F_{254}, MeCOEt–isoPrOH–Me_2CO–H_2O (20:10:7:6). The specific rotations $[\alpha]_D^{25}$ of sugars were determined after dissolving in H_2O.

For compound **1**: glucose (1.2 mg, R_f = 0.42, $[\alpha]_D^{25}$ +48.0), arabinose (0.8 mg, R_f = 0.48, $[\alpha]_D^{25}$ +42.0), rhamnose (0.8 mg, R_f = 0.65, $[\alpha]_D^{25}$ +18.0).

For compound **2**: glucose (1.3 mg, R_f = 0.42, $[\alpha]_D^{25}$ +47.0), arabinose (0.7 mg, R_f = 0.48, $[\alpha]_D^{25}$ +41.0), rhamnose (0.8 mg, R_f = 0.65, $[\alpha]_D^{25}$ +19.0).

For compound **3**: glucose (1.2 mg, R_f = 0.42, $[\alpha]_D^{25}$ +47.0), arabinose (0.8 mg, R_f = 0.48, $[\alpha]_D^{25}$ +41.5), rhamnose (0.9 mg, R_f = 0.65, $[\alpha]_D^{25}$ +19.0).

For compound **4**: glucose (1.2 mg, R_f = 0.42, $[\alpha]_D^{25}$ +48.5), arabinose (0.8 mg, R_f = 0.48, $[\alpha]_D^{25}$ +41.5), rhamnose (0.8 mg, R_f = 0.65, $[\alpha]_D^{25}$ +18.0).

For compound **5**: glucose (1.2 mg, R_f = 0.42, $[\alpha]_D^{25}$ +48.0), arabinose (0.8 mg, R_f = 0.48, $[\alpha]_D^{25}$ +42.0), rhamnose (0.8 mg, R_f = 0.65, $[\alpha]_D^{25}$ +18.0).

For compound **6**: glucose (1.3 mg, R_f = 0.42, $[\alpha]_D^{25}$ +48.0), arabinose (0.8 mg, R_f = 0.48, $[\alpha]_D^{25}$ +41.0), rhamnose (0.9 mg, R_f = 0.65, $[\alpha]_D^{25}$ +18.0).

For compound **7**: glucose (1.3 mg, R_f = 0.42, $[\alpha]_D^{25}$ +48.0), arabinose (0.9 mg, R_f = 0.48, $[\alpha]_D^{25}$ +41.0).

α-Glucosidase inhibitory assay

The *α*-glucosidase (G0660, Sigma-Aldrich, St. Louis, MO) enzyme inhibition assay was performed according to the previously described method. In brief, 20 µL of sample solution and 40 µL of *α*-glucosidase solution were well mixed with 100 µL of 0.1 M phosphate buffer (pH 7.0) in a 96-well plate. After 5 min pre-incubation at 37 ^{o}C, the substrate, *p*-nitrophenyl-*α*-D-glucopyranoside solution (40 µL) was added, and the reaction mixture was incubated at 37 ^{o}C for 30 min. The absorbance of was then measured at 405 nm by using an ELISA Bio-Rad microplate reader. Reaction mixture containing acarbose solution instead of sample solution was used as positive control. And reaction mixture containing buffer solution instead of sample solution was used as negative control.

α-Amylase inhibitory assay

The *α*-amylase (A3176, Sigma-Aldrich, St. Louis, MO) enzyme inhibitory activity was measured using the reported method. Substrate was prepared by boiling 100 mg potato starch in 5 mL phosphate buffer (pH 7.0) for 5 min, then cooling to room temperature. The sample solution (20 µL) and substrate (30 µL) were mixed with 30 µL of 0.1 M phosphate buffer (pH 7.0). After 5 min pre-incubation, 20 µL of *α*-amylase solution was added and the reaction mixture was incubated at 37^{o}C for 15 min. The reaction was stopped by adding 50 µL HCl 1 M and then 50 µL iodine solution. The absorbances were then measured at 650 nm by a microplate reader. Reaction mixture containing acarbose solution instead of sample solution was used as positive control. And reaction mixture containing buffer solution instead of sample solution was used as negative control.

Table S1. The α-glucosidase and α-amylase inhibitory effects of the compounds **1**-**13** (200 μM)

Comp.	α-glucosidase inhibition (%)		α-amylase inhibition (%)	
	Mean	SD	Mean	SD
1	94.65	2.19	88.29	2.50
2	82.25	1.87	85.03	1.84
3	84.26	1.59	92.42	1.86
4	81.48	2.42	91.11	2.51
5	64.73	2.64	31.91	1.72
6	60.81	2.37	64.46	1.80
7	55.34	1.38	44.92	2.94
8	92.68	1.12	94.22	1.57
9	90.95	1.23	83.88	2.25
10	67.98	1.20	48.04	2.32
11	53.62	1.15	62.71	2.06
12	46.36	2.36	69.74	2.20
13	42.20	2.70	57.38	2.64
Acarbose*	84.05	2.58	61.23	2.15

[*]Acarbose was used as a positive control (at 100 μg/mL ~ 155 μM). Experiments were peformed in triplicate.

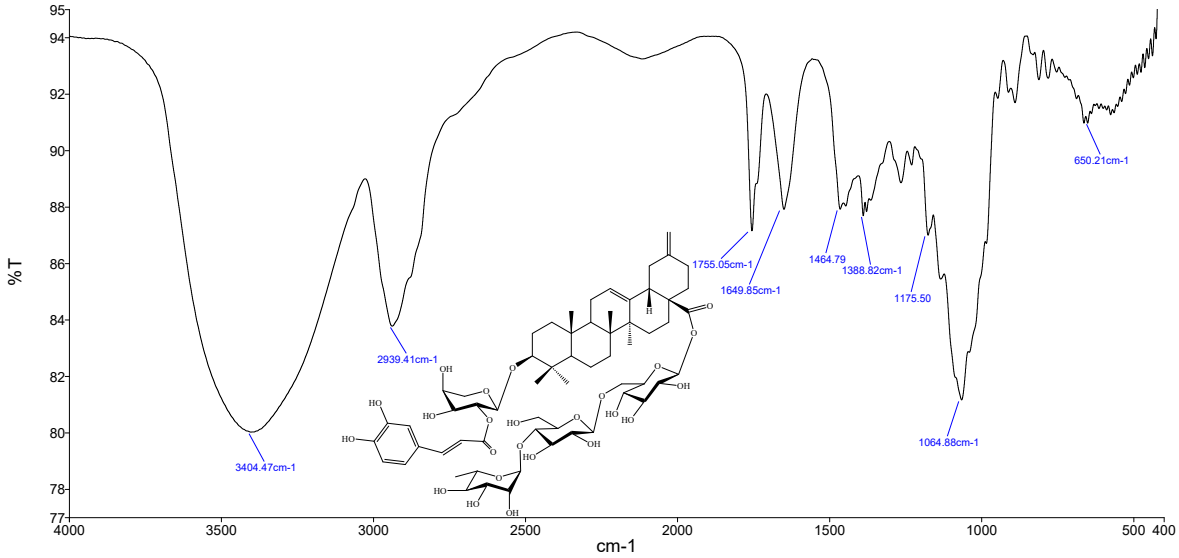
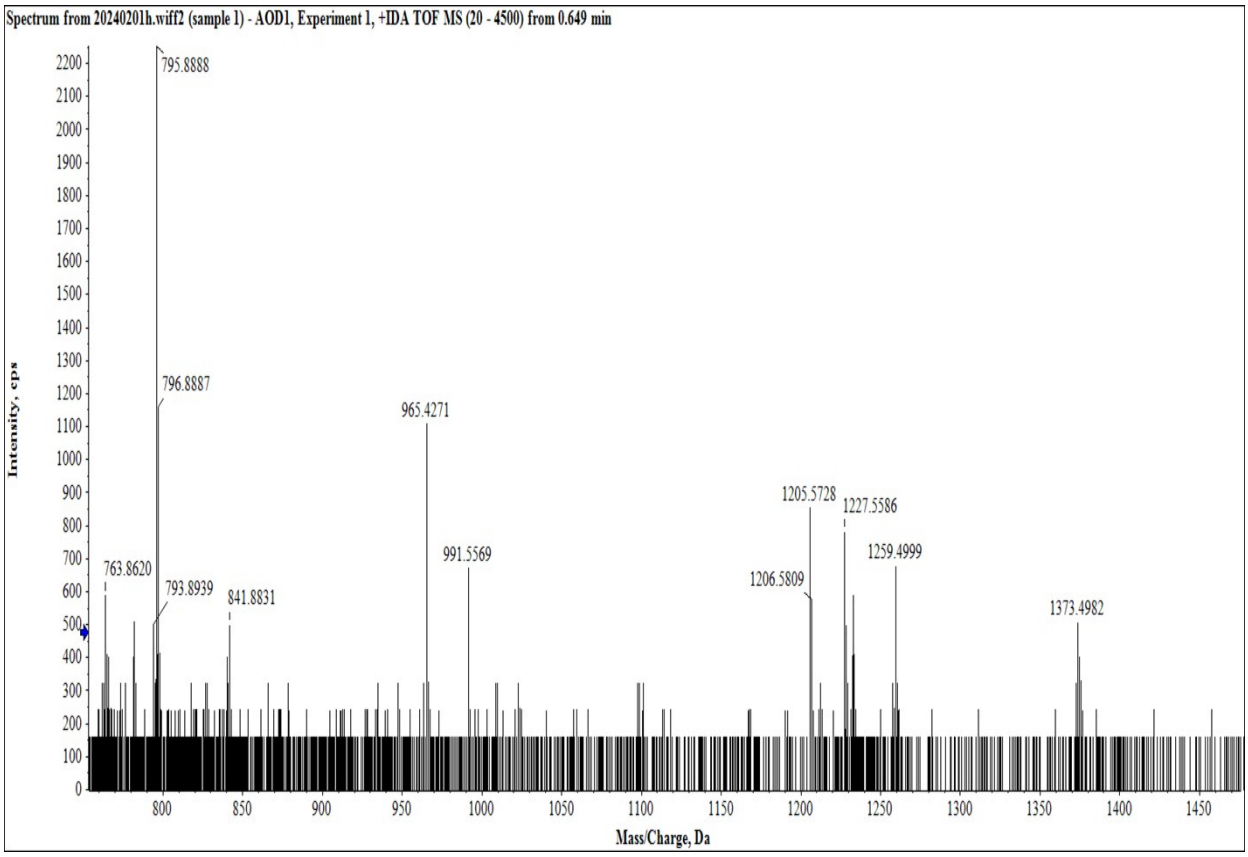


Figure S1. IR spectrum of compound **1**



HR-ESI-MS *m/z*: 1227.5586 $[M+Na]^+$, (calcd. for $[C_{61}H_{88}O_{24}Na]^+$, 1227.5558, Δ=+2.3 ppm); *m/z*: 1205.5728 $[M+H]^+$, (calcd. for $[C_{61}H_{89}O_{24}]^+$, 1205.5739, Δ=-0.9 ppm).

Figure S2. HR-ESI-MS of compound **1**

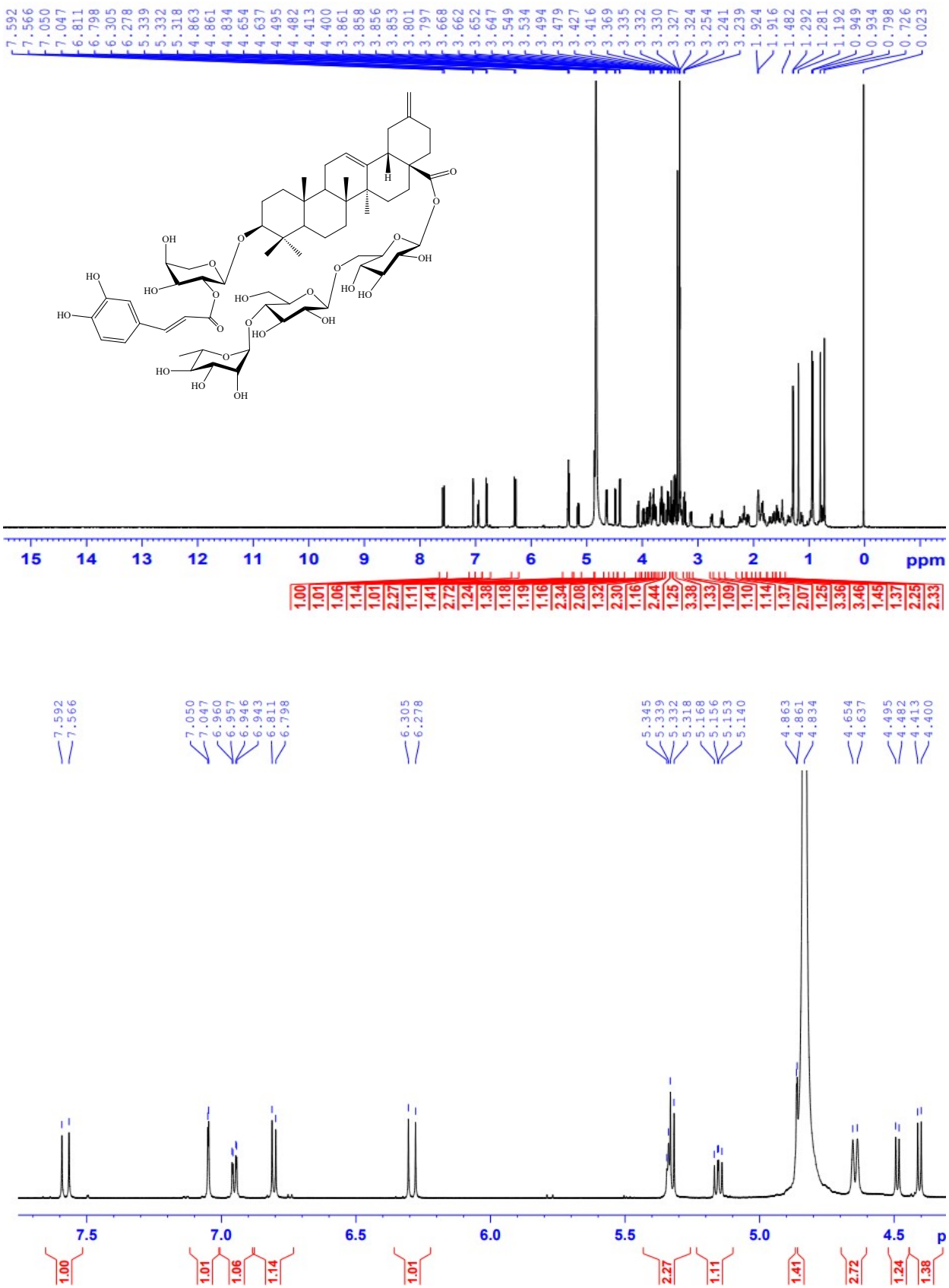


Figure S3. ^{1}H-NMR spectrum of compound **1** in CD_3OD

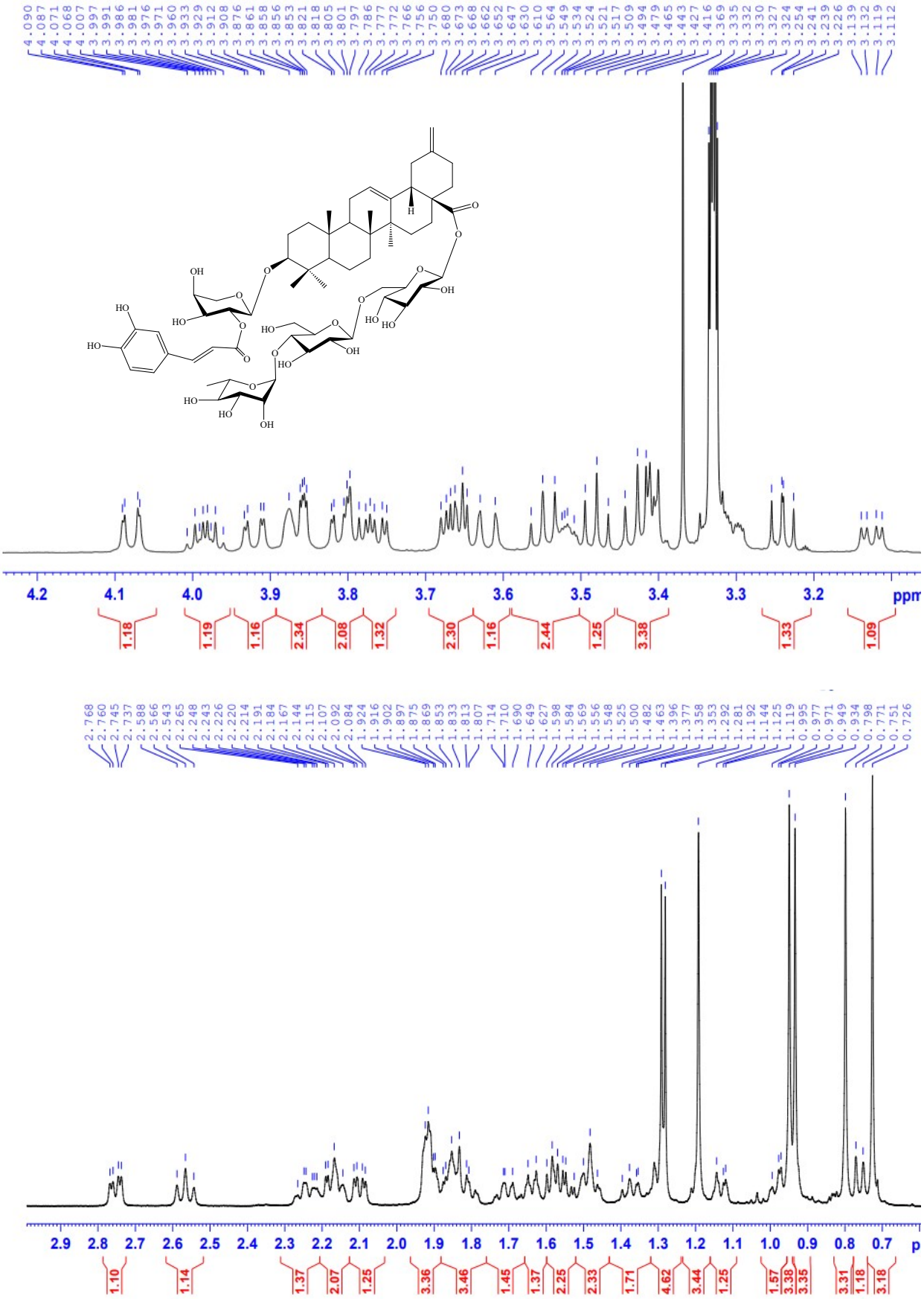


Figure S4. Extended ^{1}H-NMR spectrum of compound **1** in CD_3OD

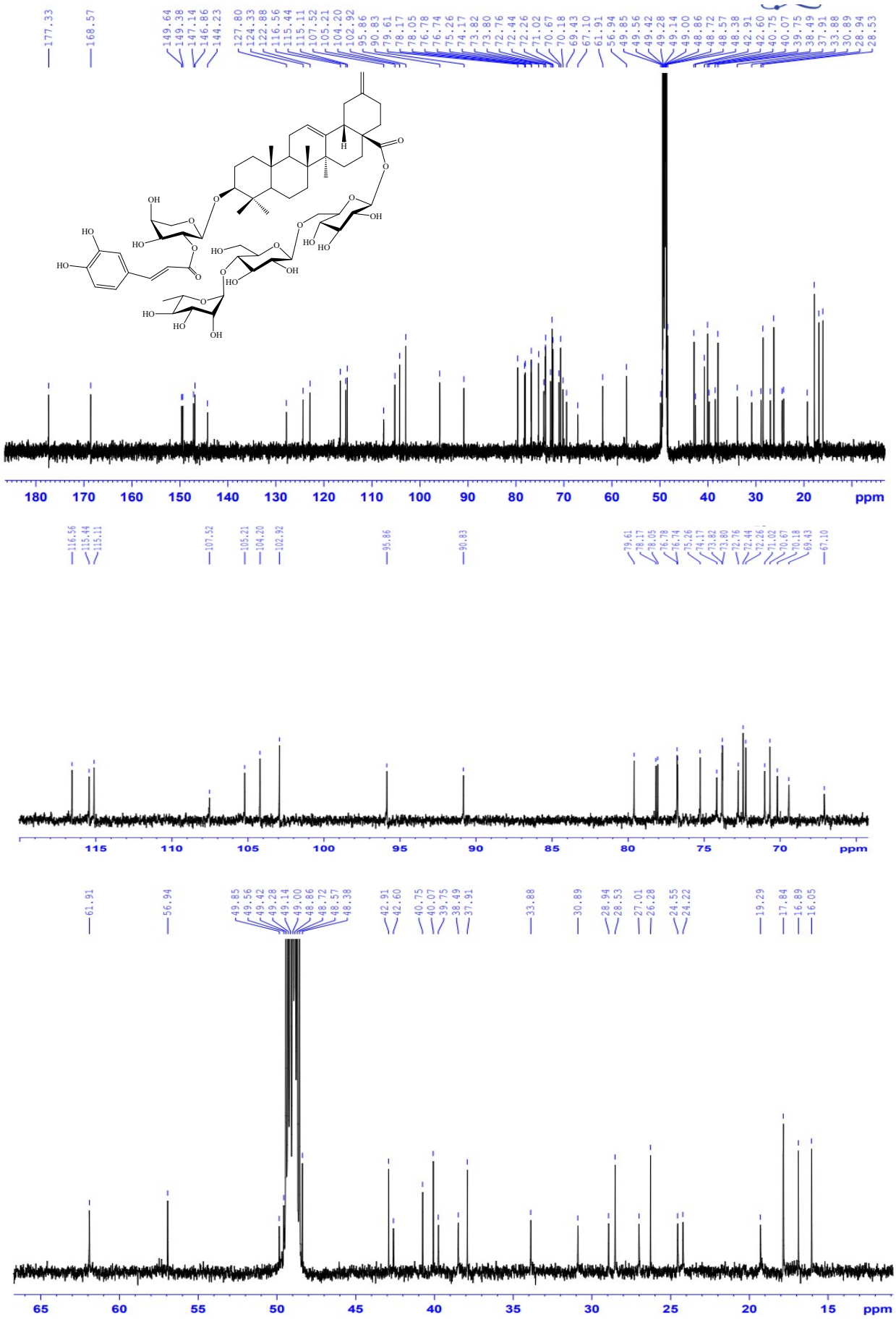


Figure S5. ^{13}C-NMR spectrum of compound **1** in CD_3OD

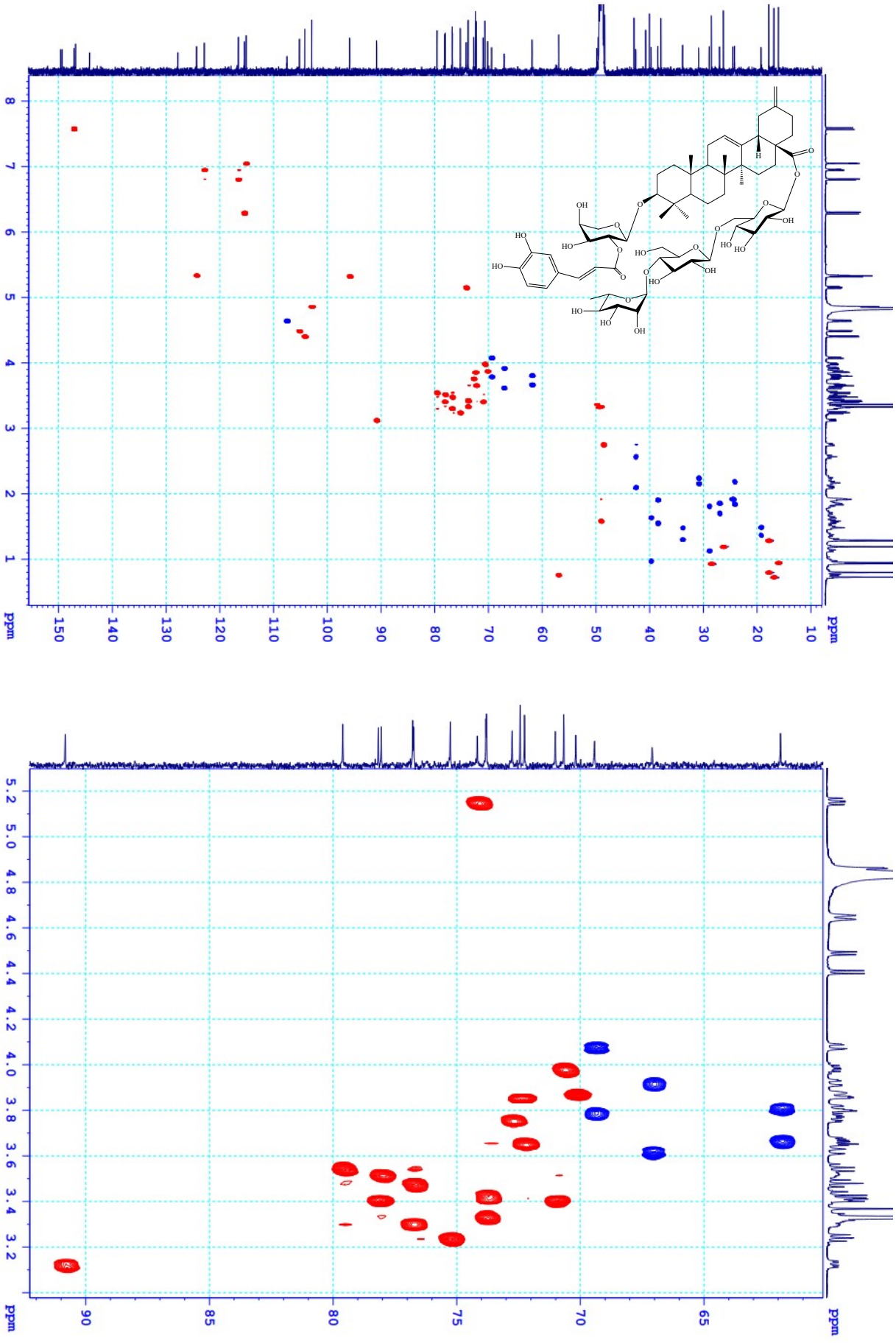
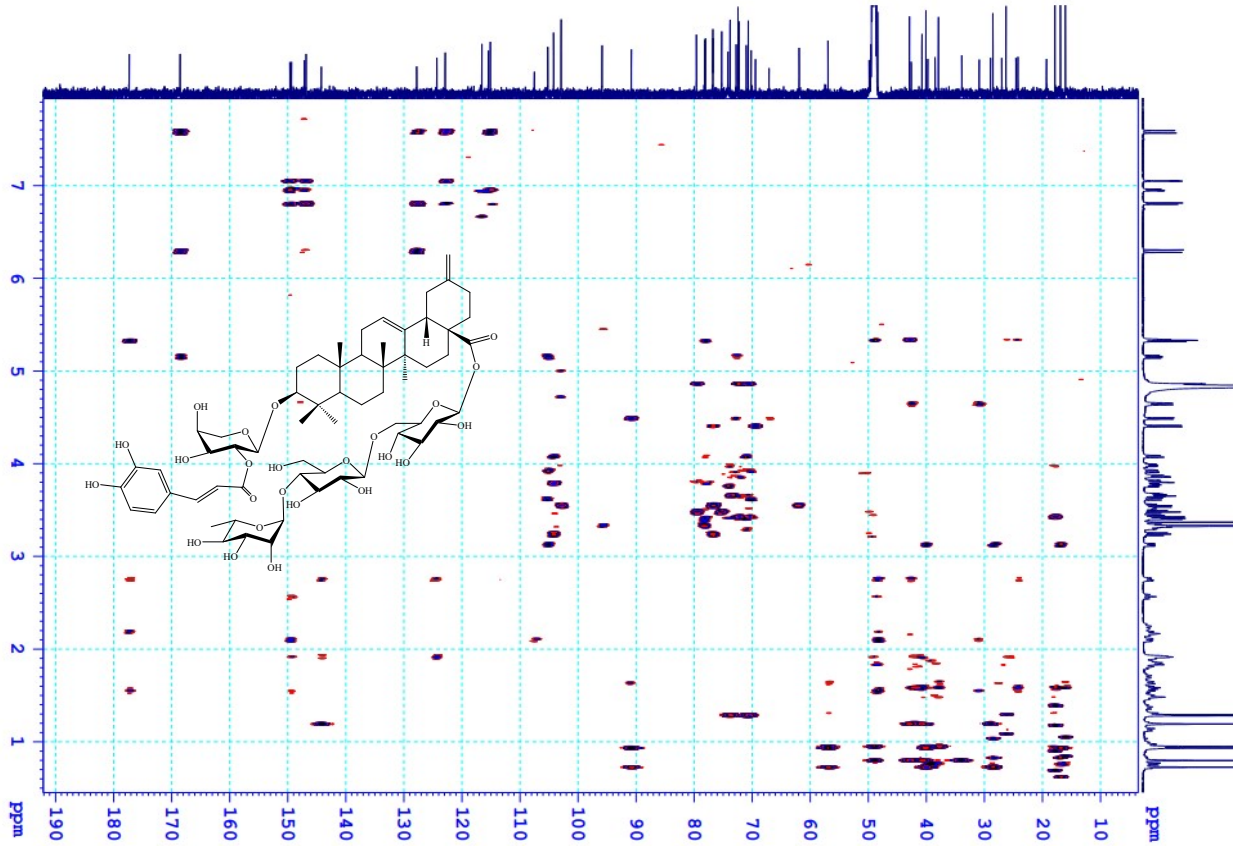


Figure S6. HSQC spectrum of compound **1** in CD_3OD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140
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50
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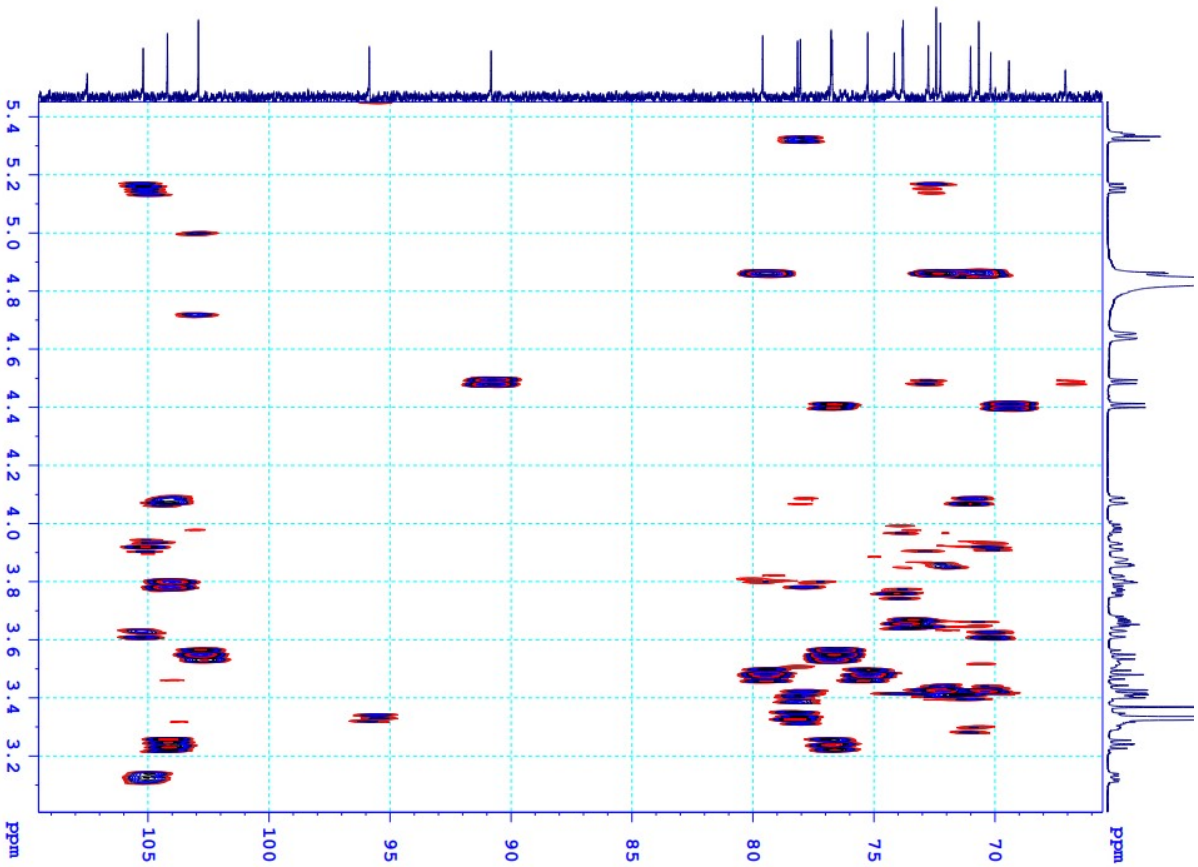
30
20
10
ppm
7
6
5
4
3
2
1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80
75
70
ppm
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5.0
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4.6
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4.2
4.0
3.8
3.6
3.4
3.2

Figure S7. HMBC spectrum of compound **1** in CD_3OD

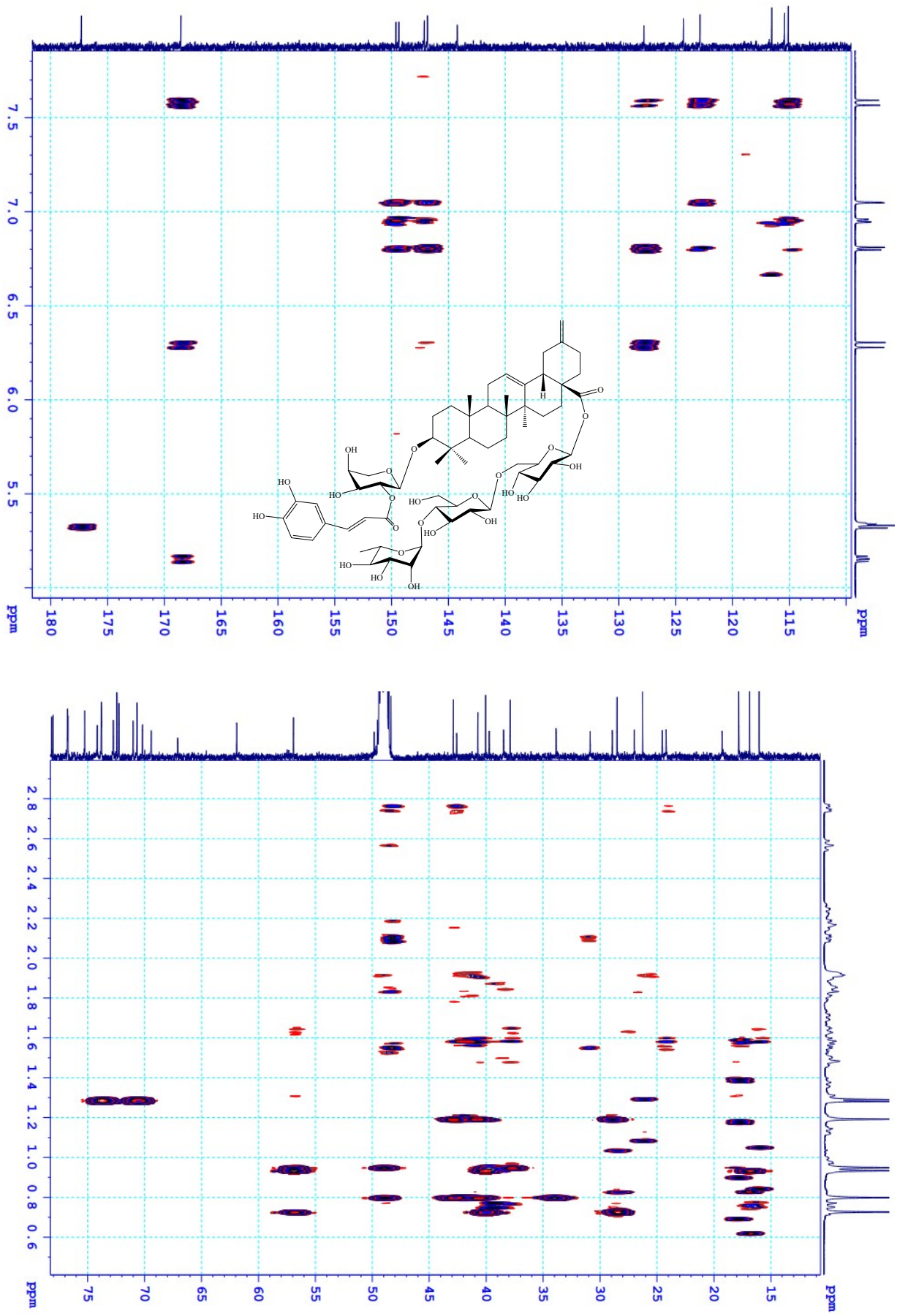


Figure S8. Expanded HMBC spectrum of compound **1** in CD_3OD

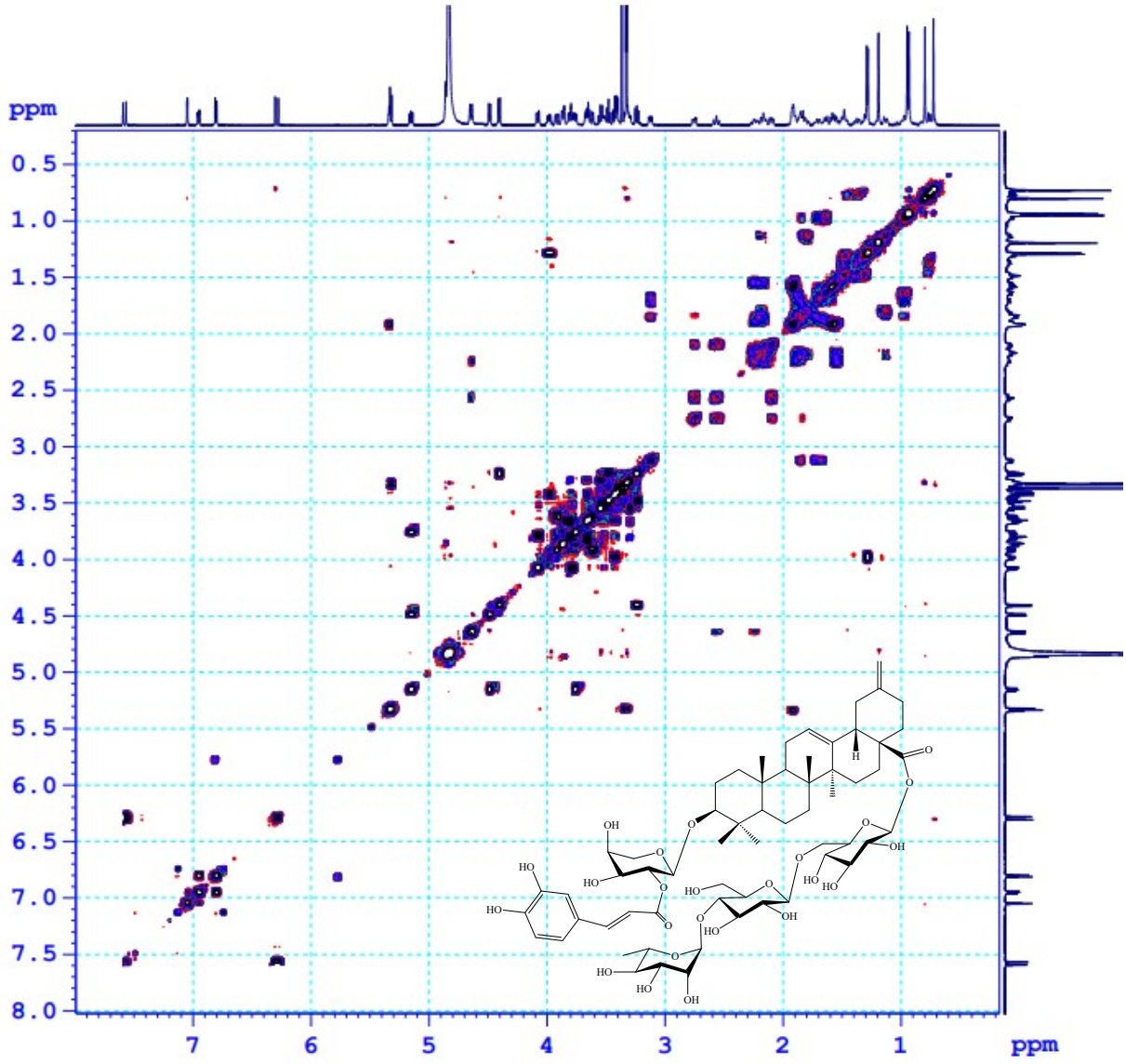


Figure S9. COSY spectrum of compound **1** in CD_3OD

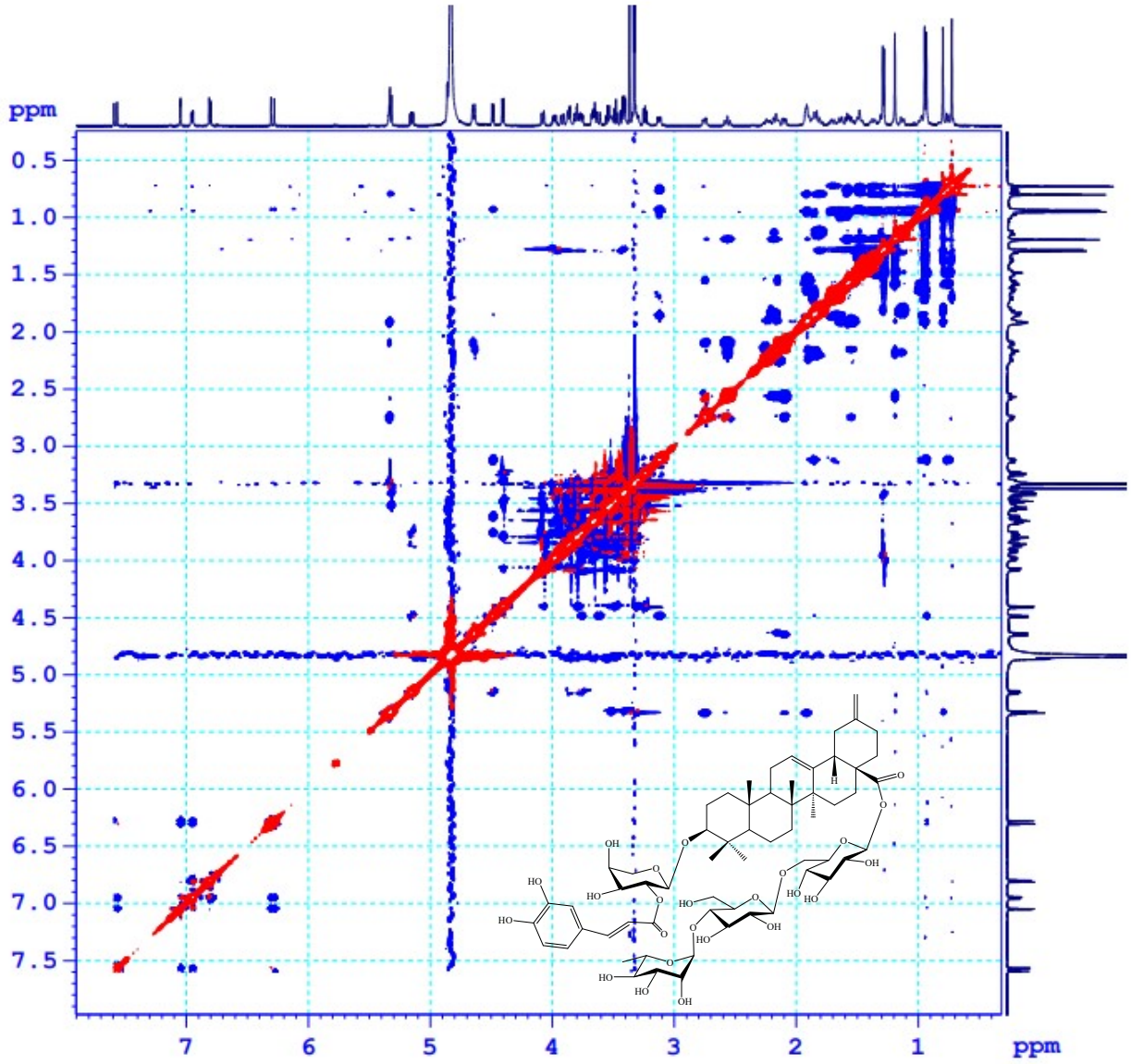


Figure S10. NOESY spectrum of compound **1** in CD_3OD

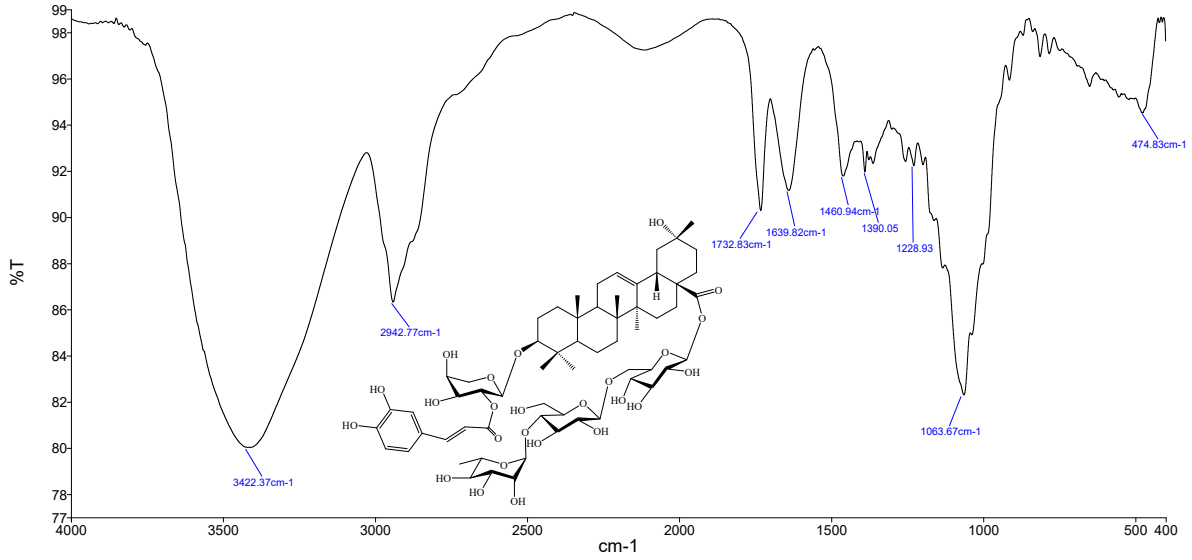


Figure S11. IR spectrum of compound **2**

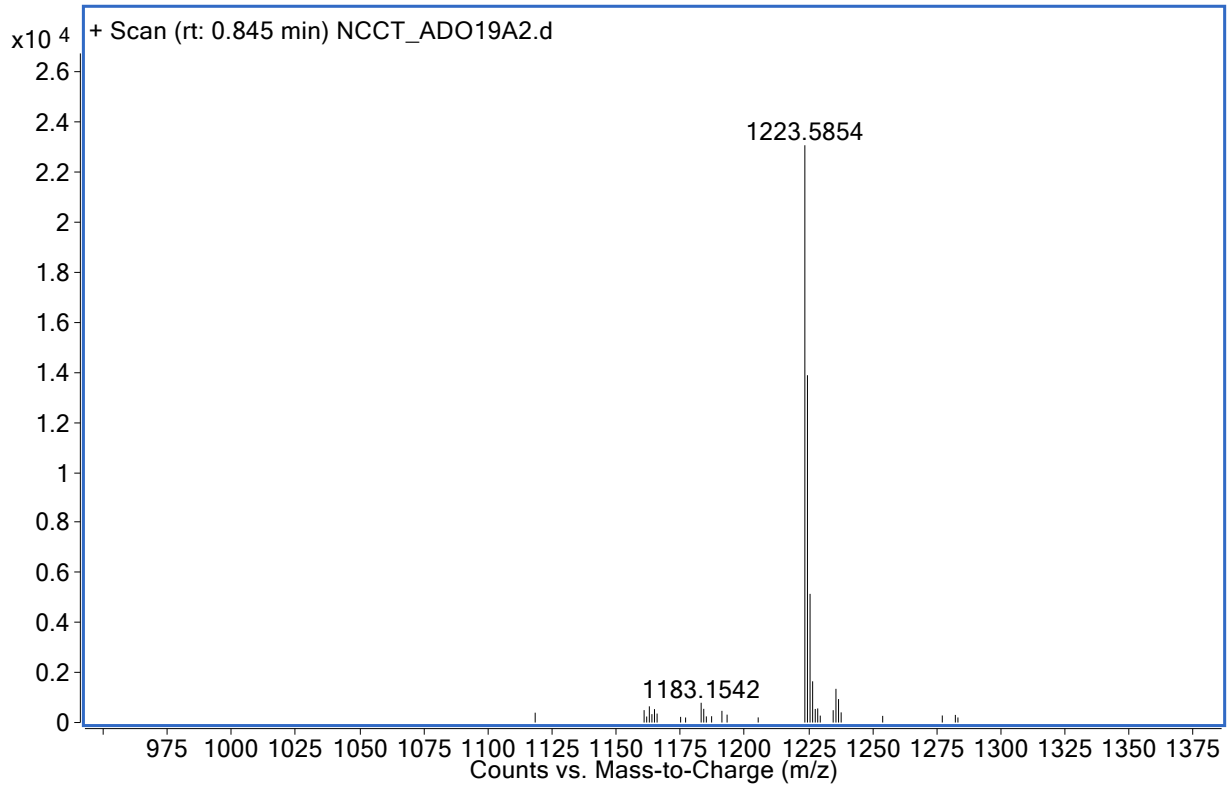


Figure S12. HR-ESI-MS of compound **2**

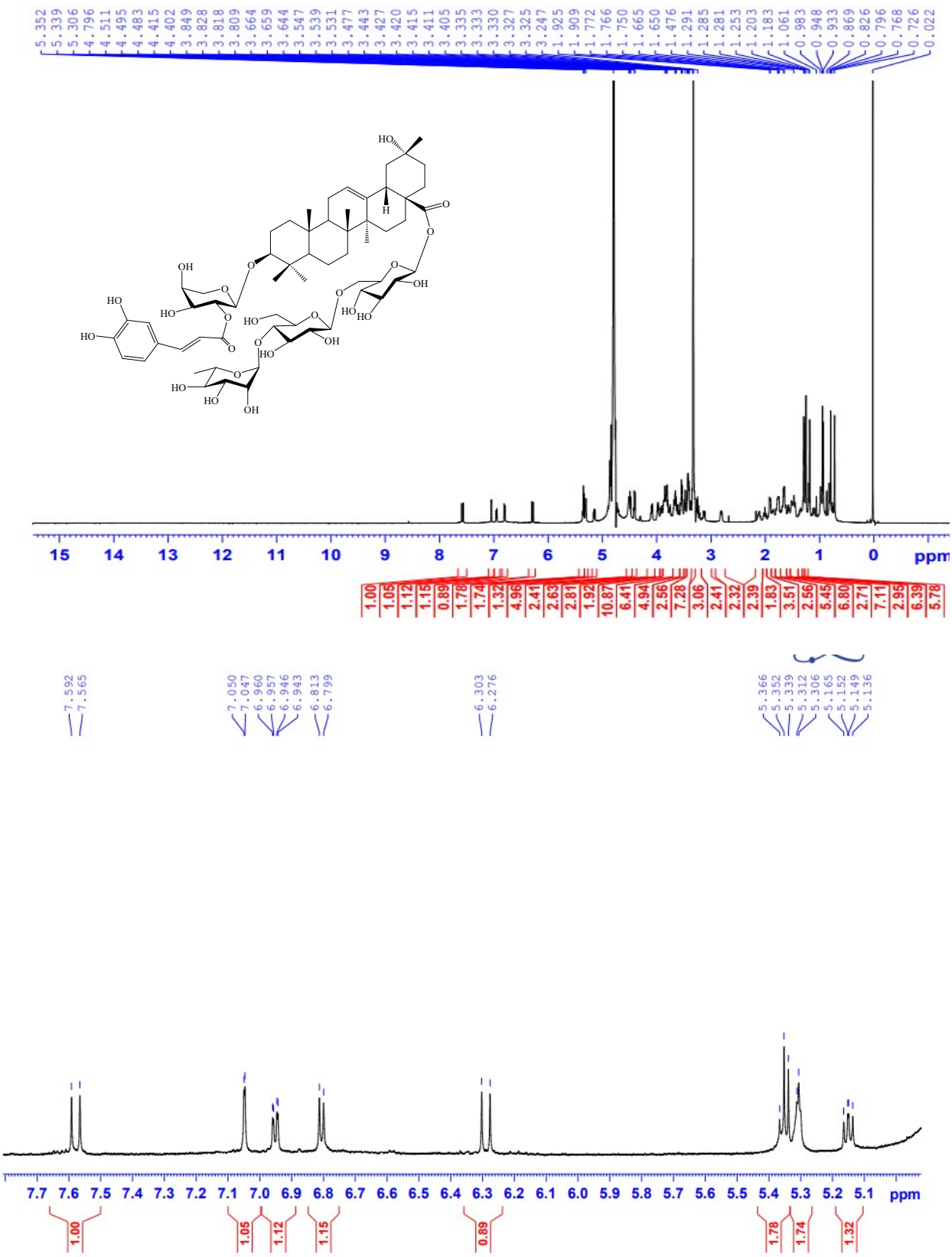


Figure S13. ^{1}H-NMR spectrum of compound **2** in CD_3OD

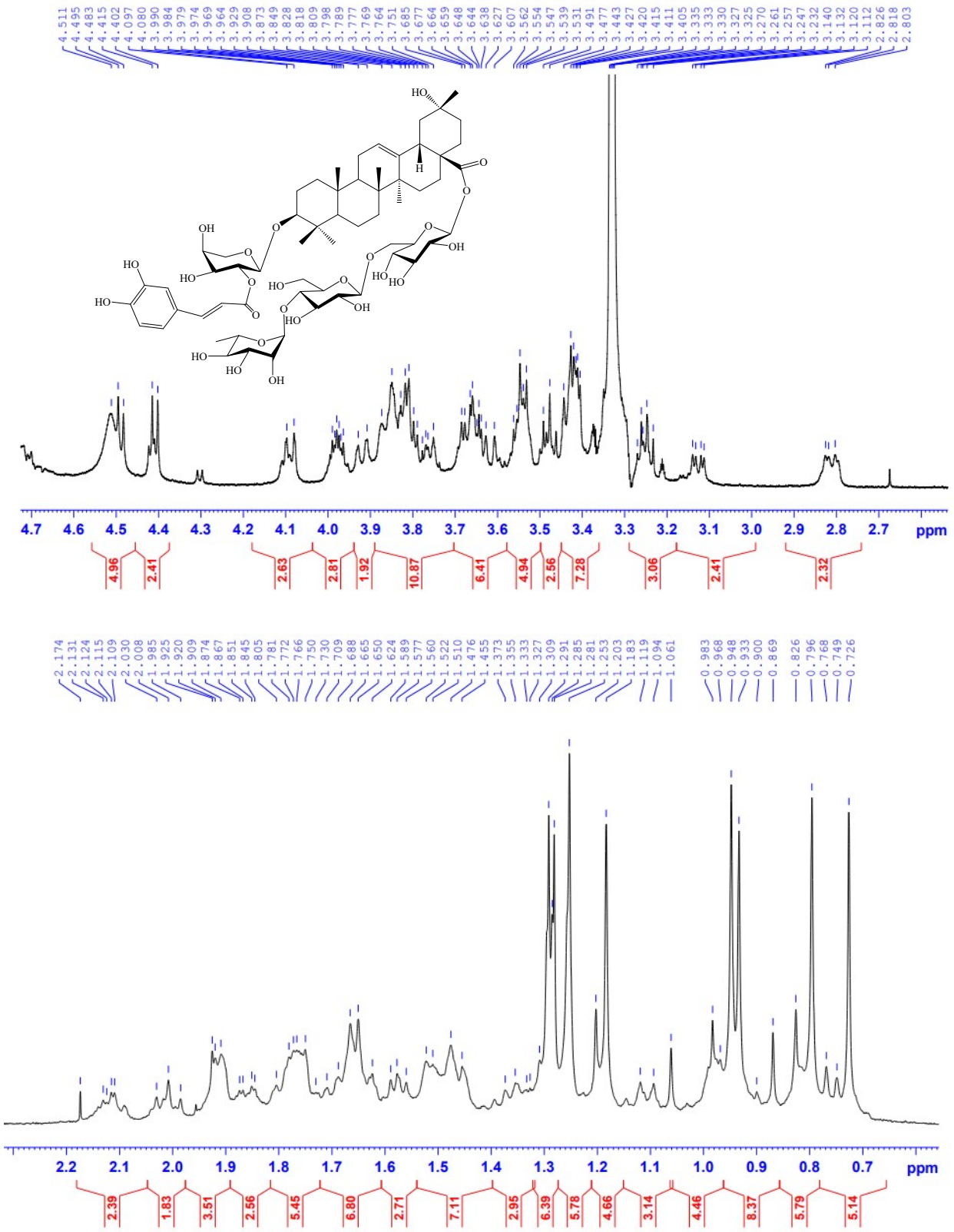
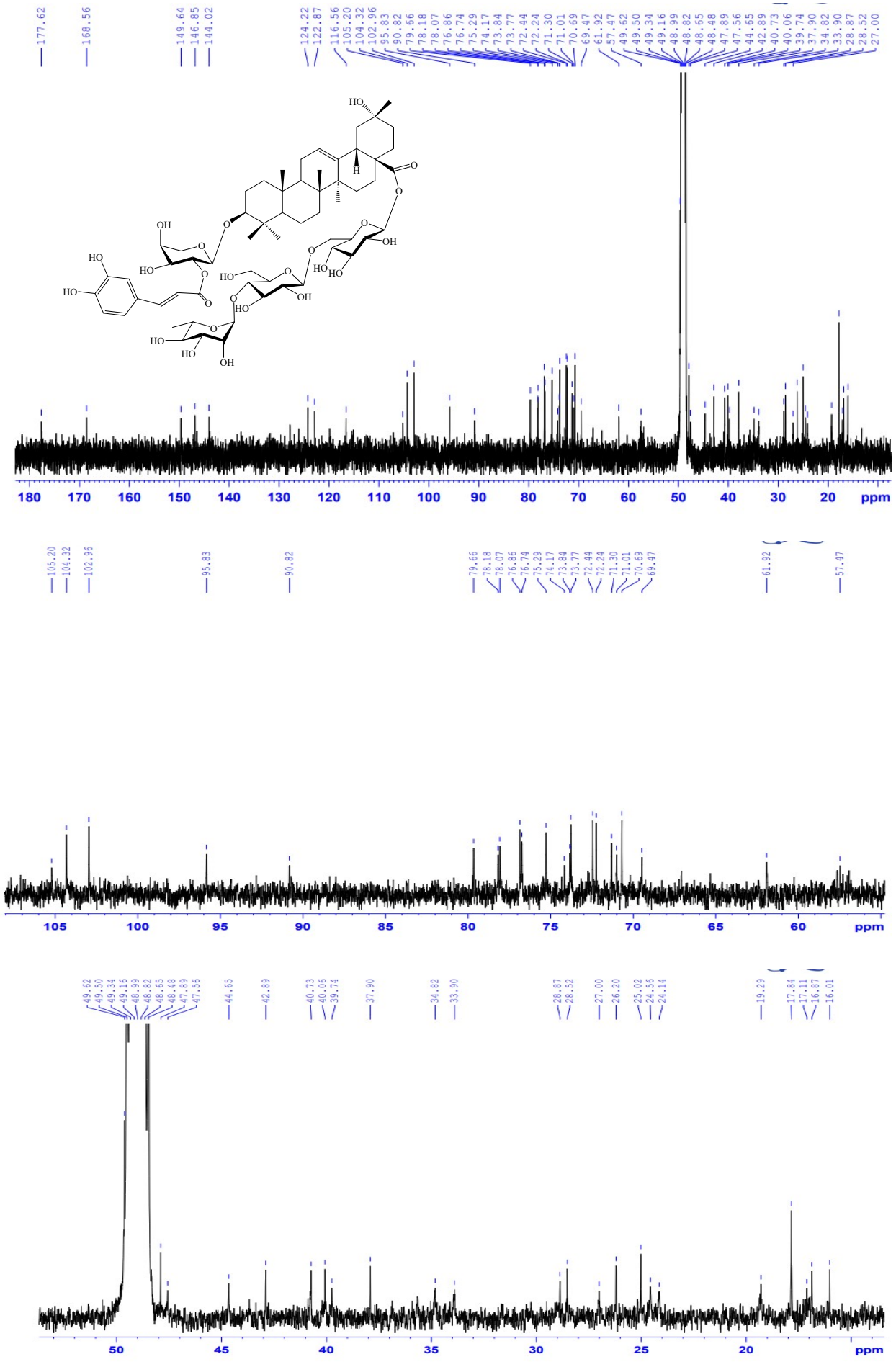


Figure S14. Extended ^{1}H-NMR spectrum of compound **2** in CD_3OD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90.82
79.66
78.18
78.07
76.86
76.74
75.29
74.17
73.84
73.77
72.44
72.24
71.30
71.01
70.69
69.47
61.92
57.47
49.62
49.50
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33.90
28.87
28.52
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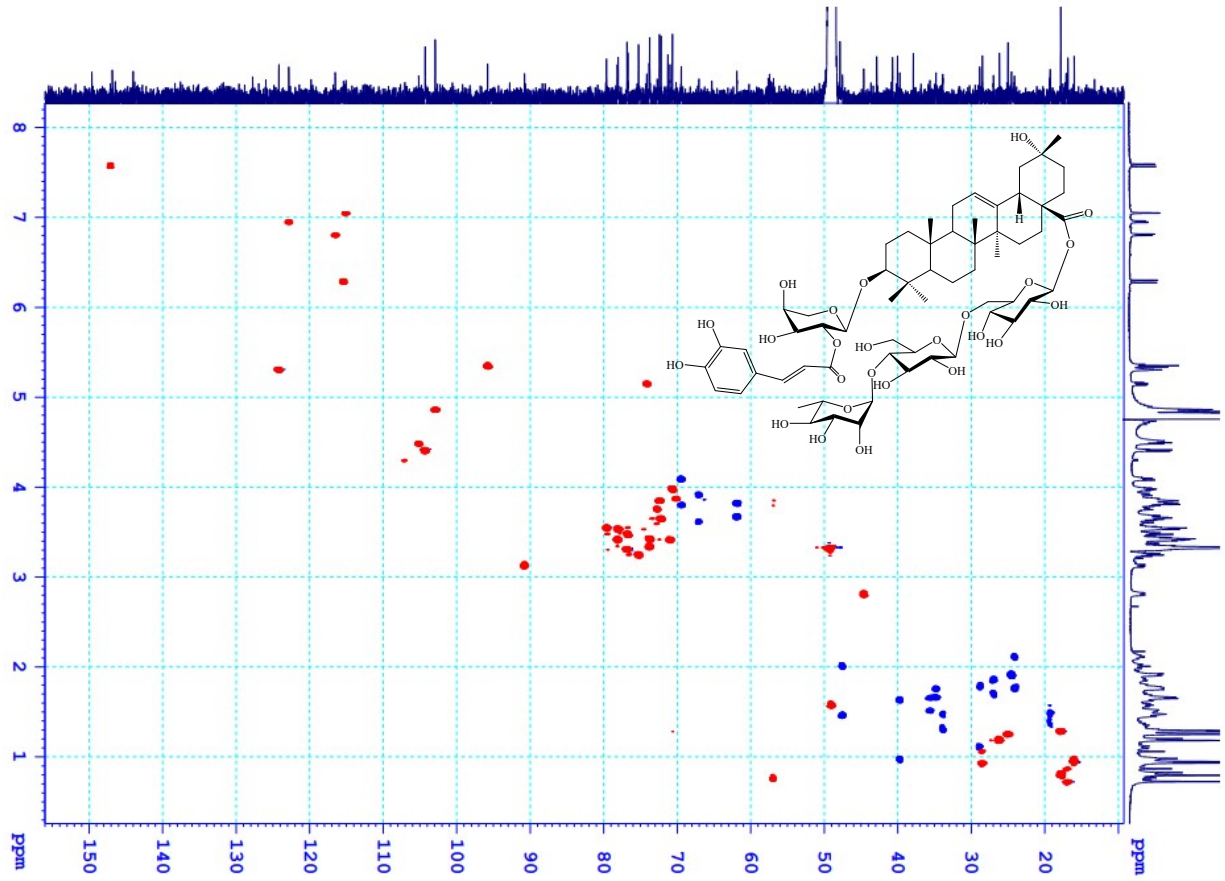
16.01
ppm

Figure S15. ^{13}C-NMR spectrum of compound **2** in CD_3OD



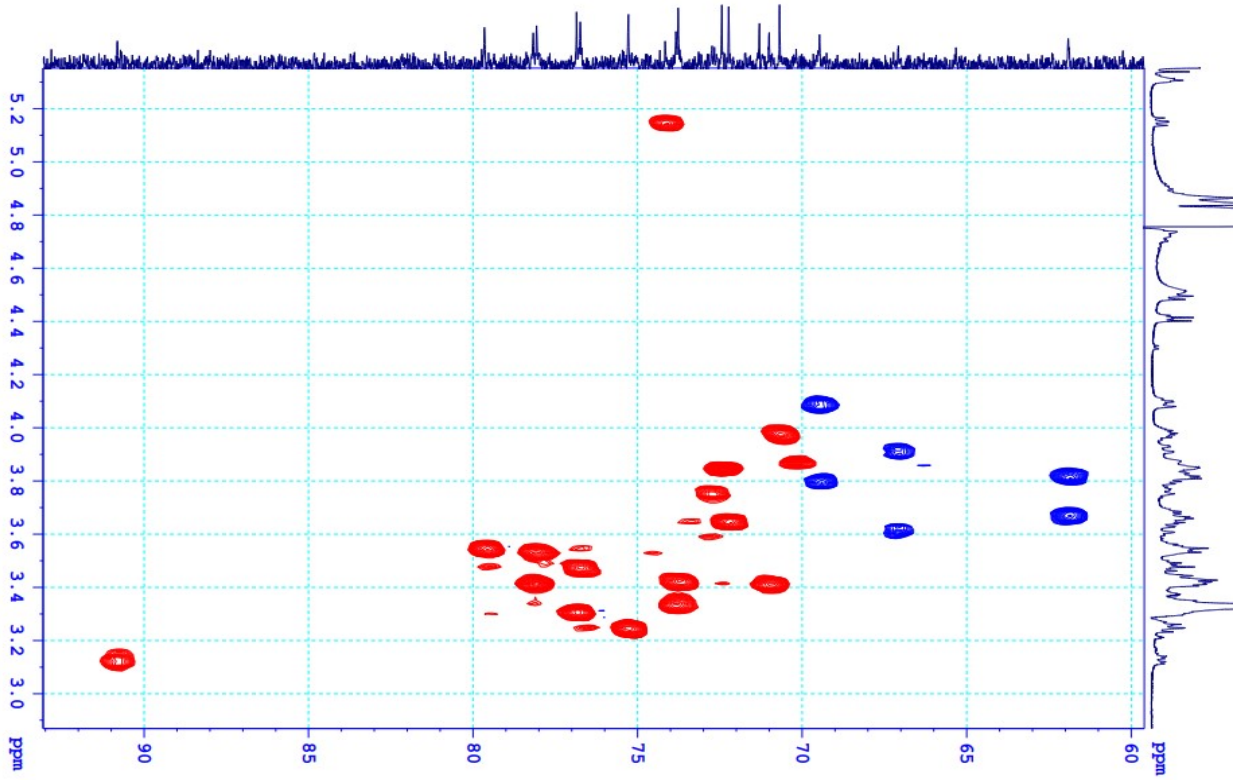
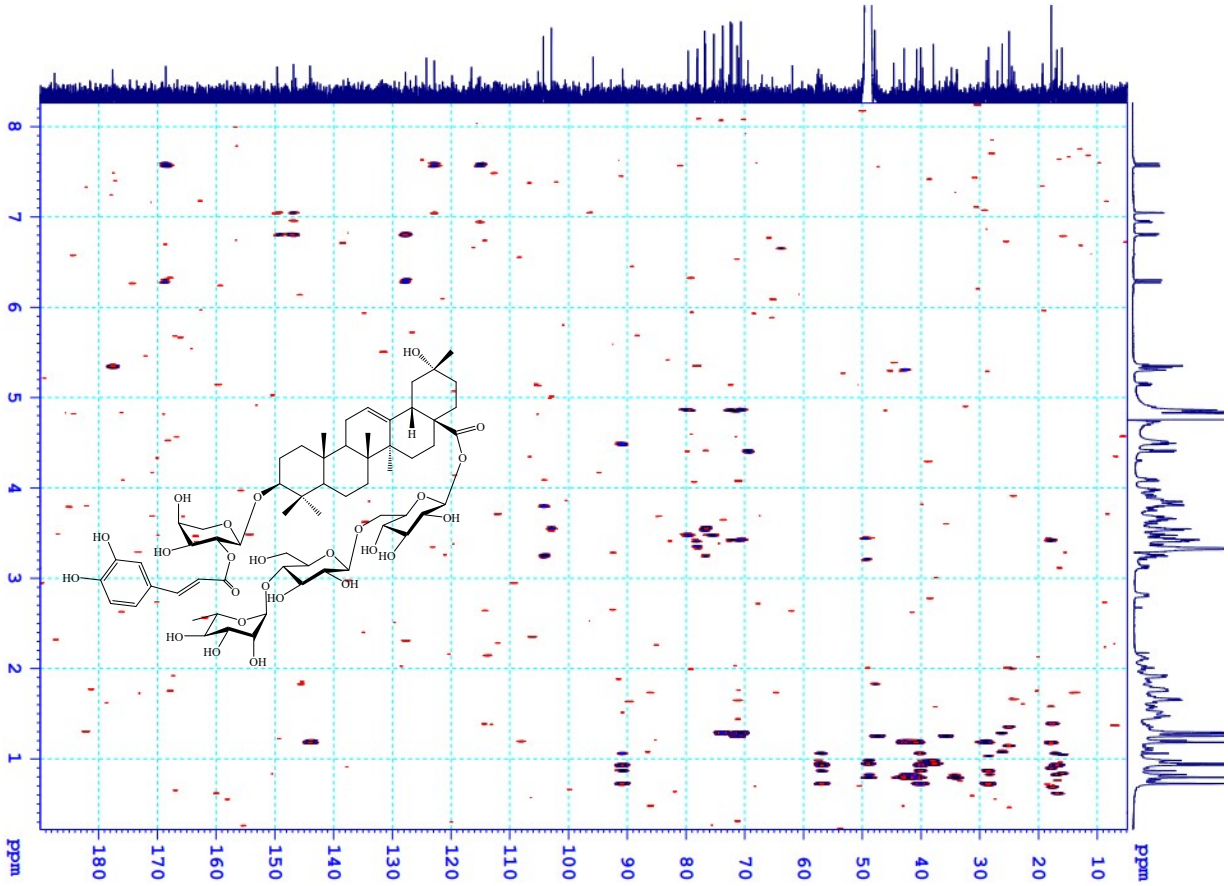


Figure S16. HSQC spectrum of compound **2** in CD_3OD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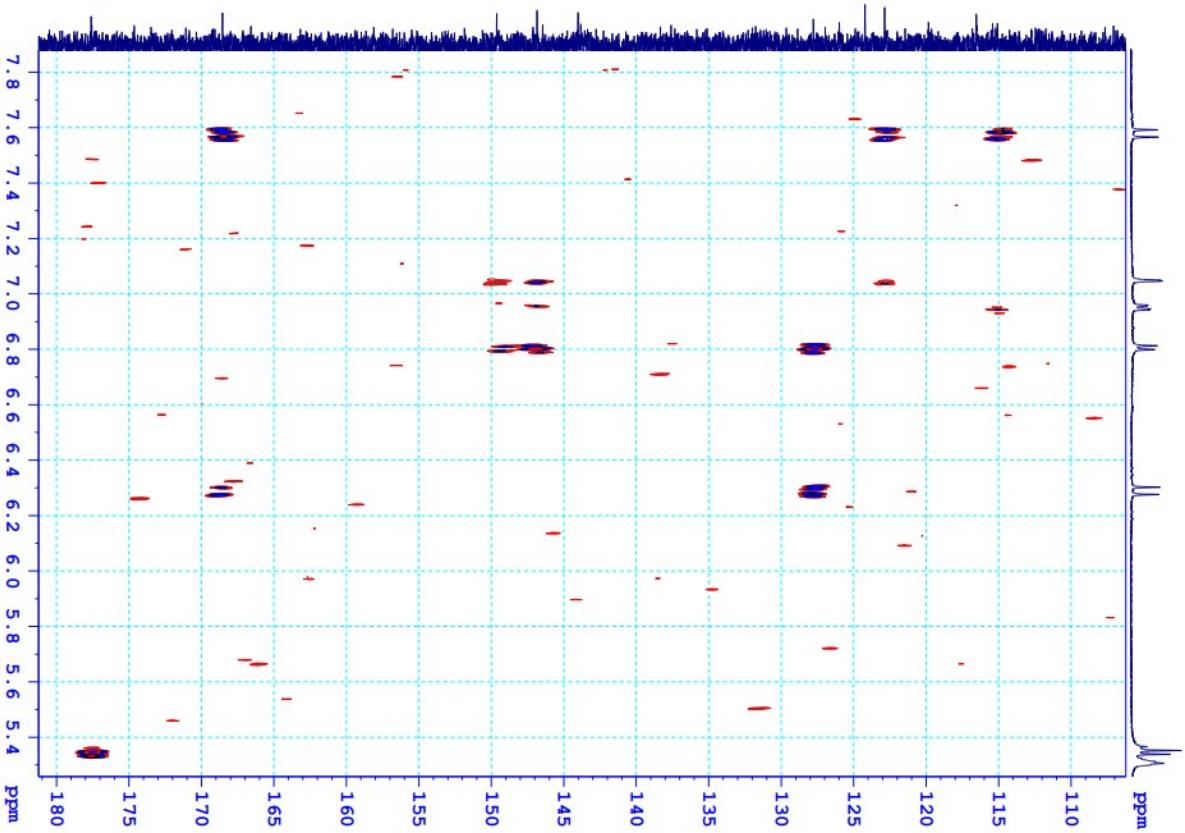
ppm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ppm

Figure S17. HMBC spectrum of compound **2** in CD_3OD

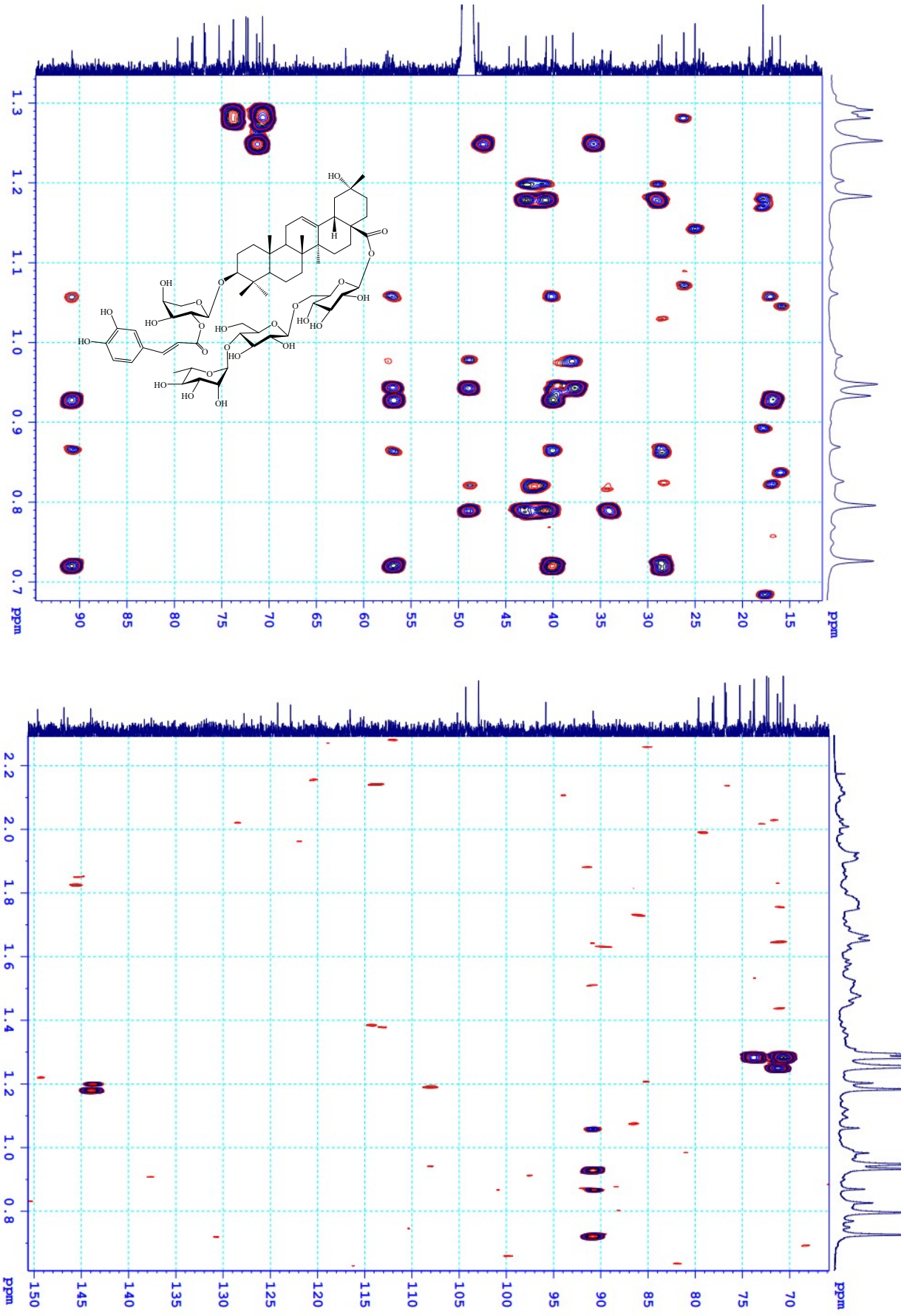
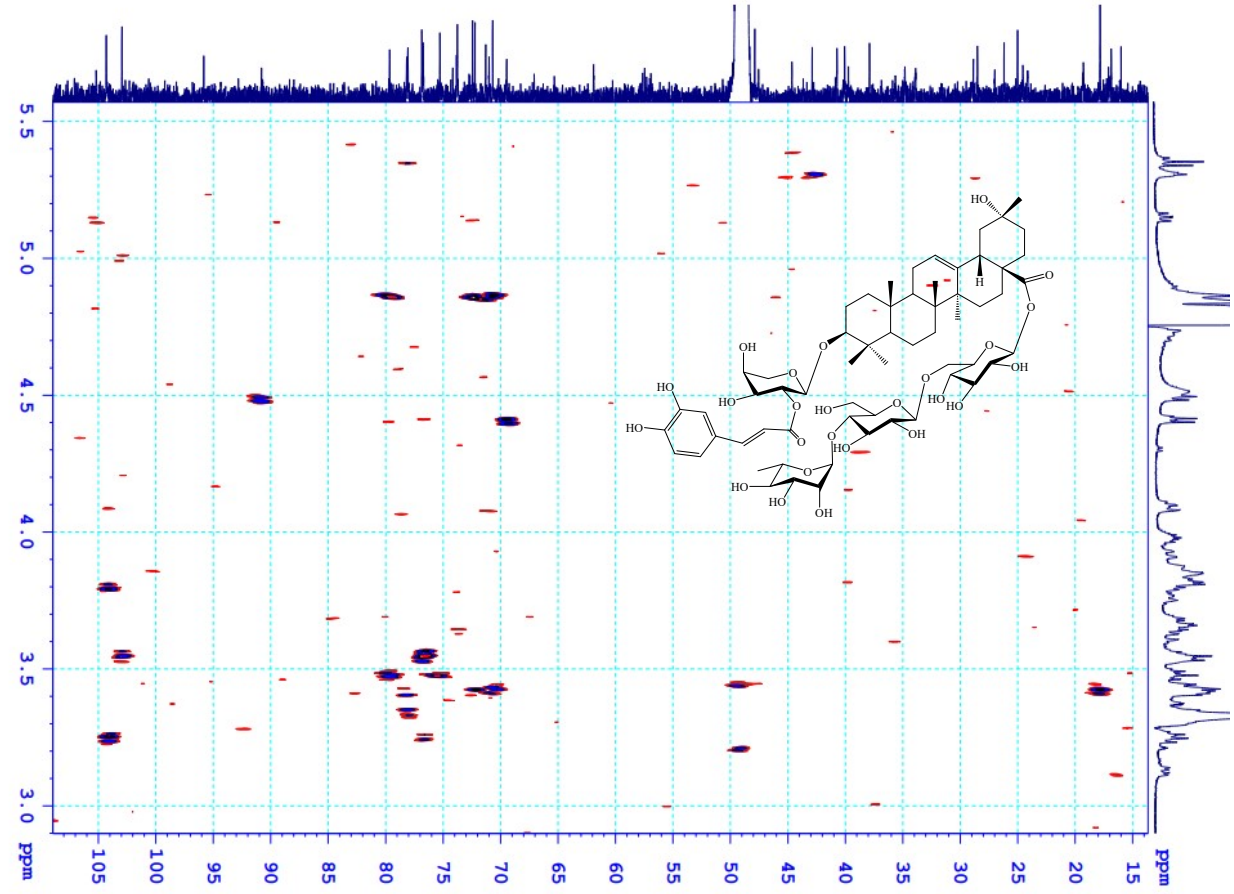


Figure S18. Extended HMBC spectrum of compound **2** in CD_3OD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ppm

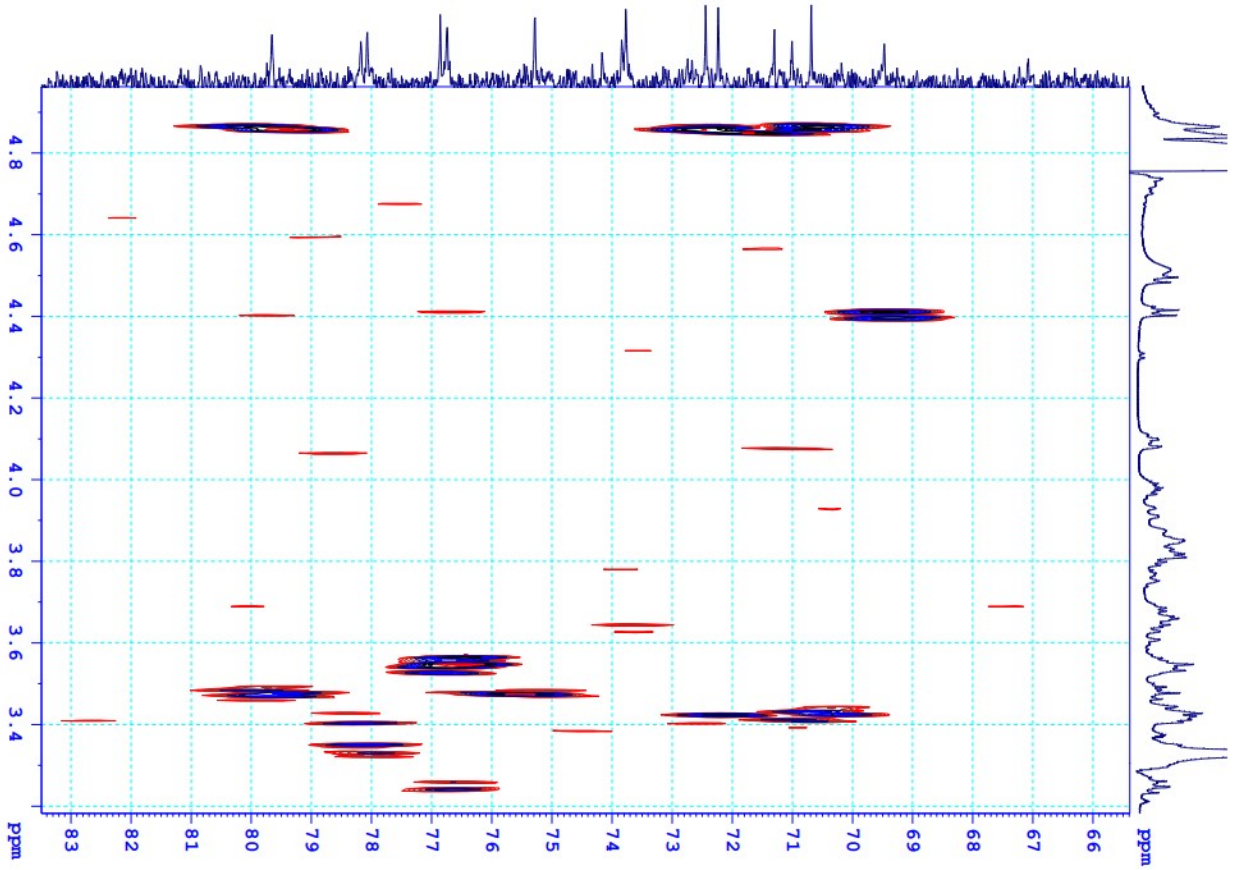

ppm
ppm

Figure S19. Extended HMBC spectrum of compound **2** in CD_3OD

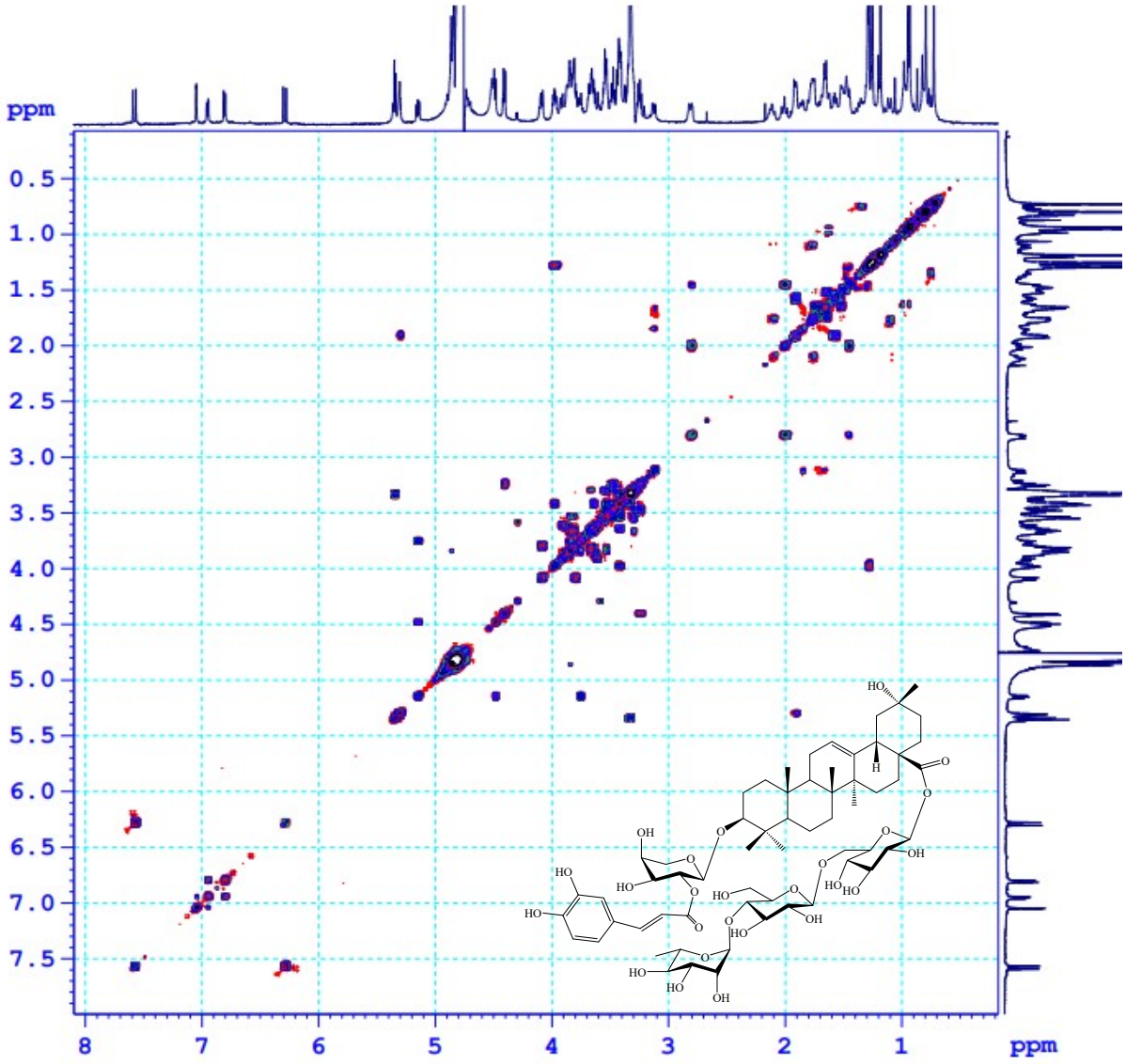


Figure S20. COSY spectrum of compound **2** in CD_3OD

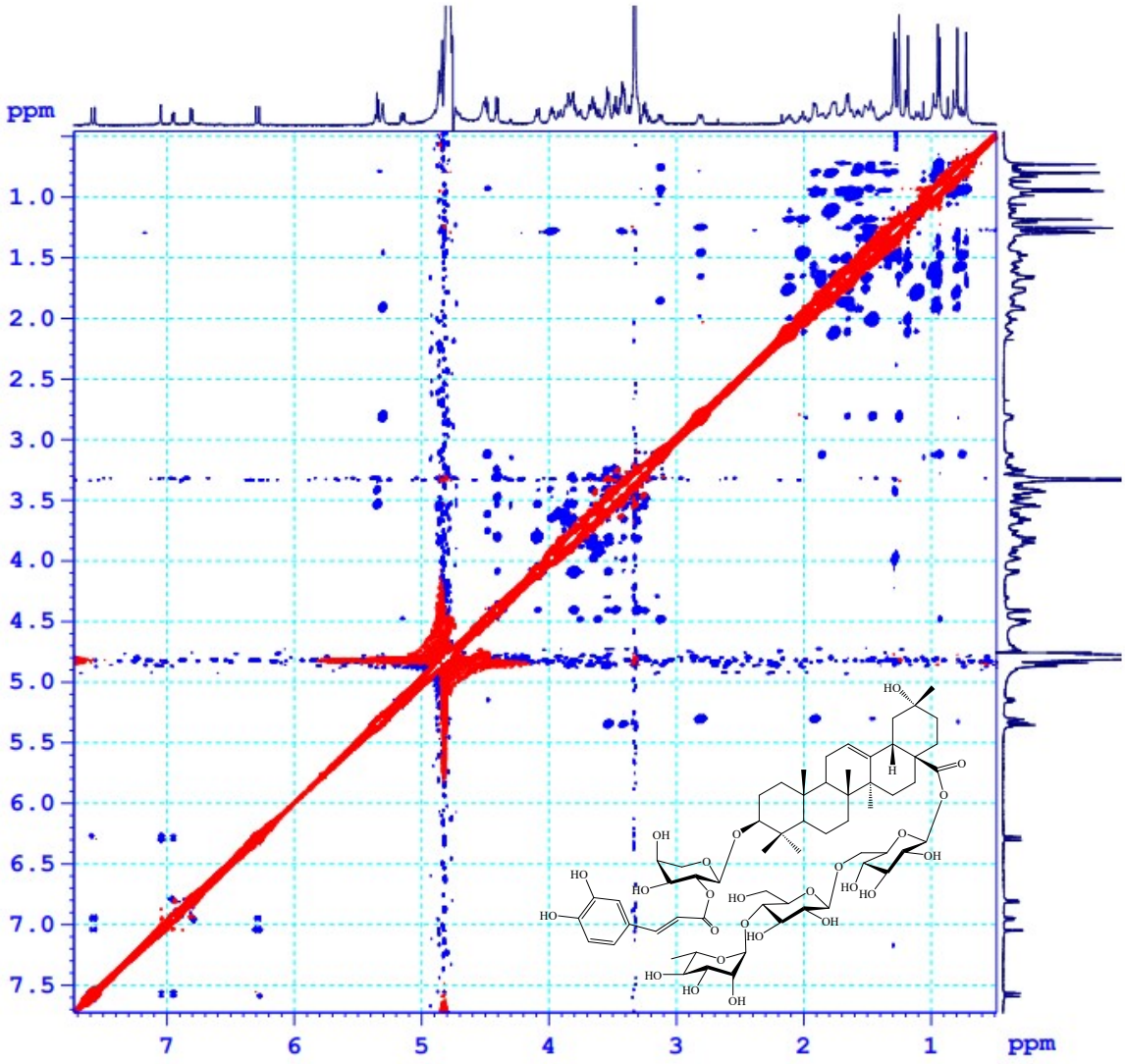


Figure S21. NOESY spectrum of compound **2** in CD_3OD

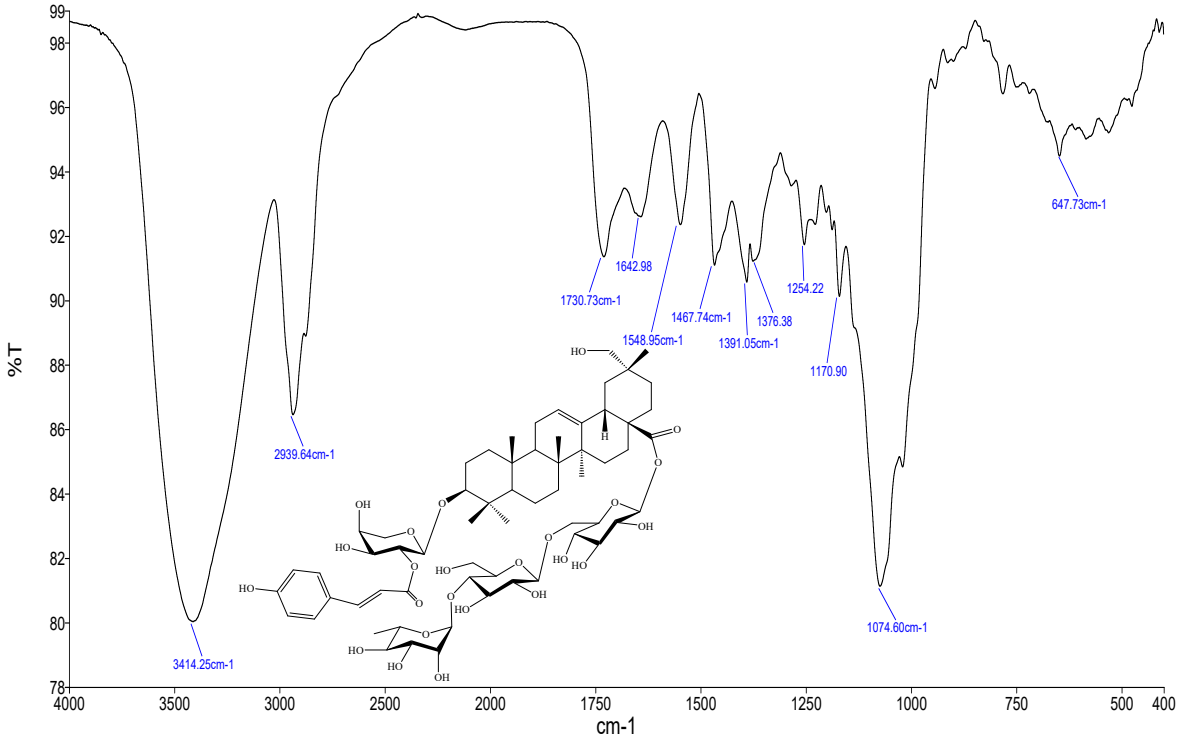


Figure S22. IR spectrum of compound **3**

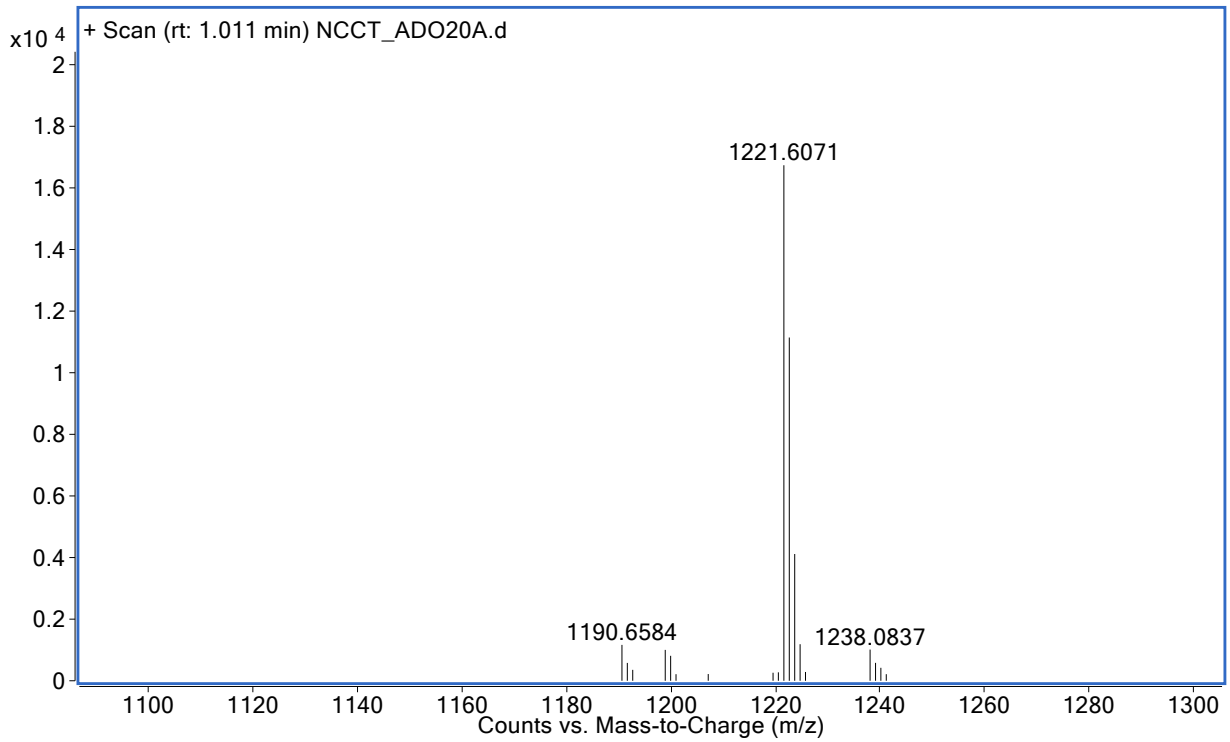


Figure S23. HR-ESI-MS spectrum of compound **3**

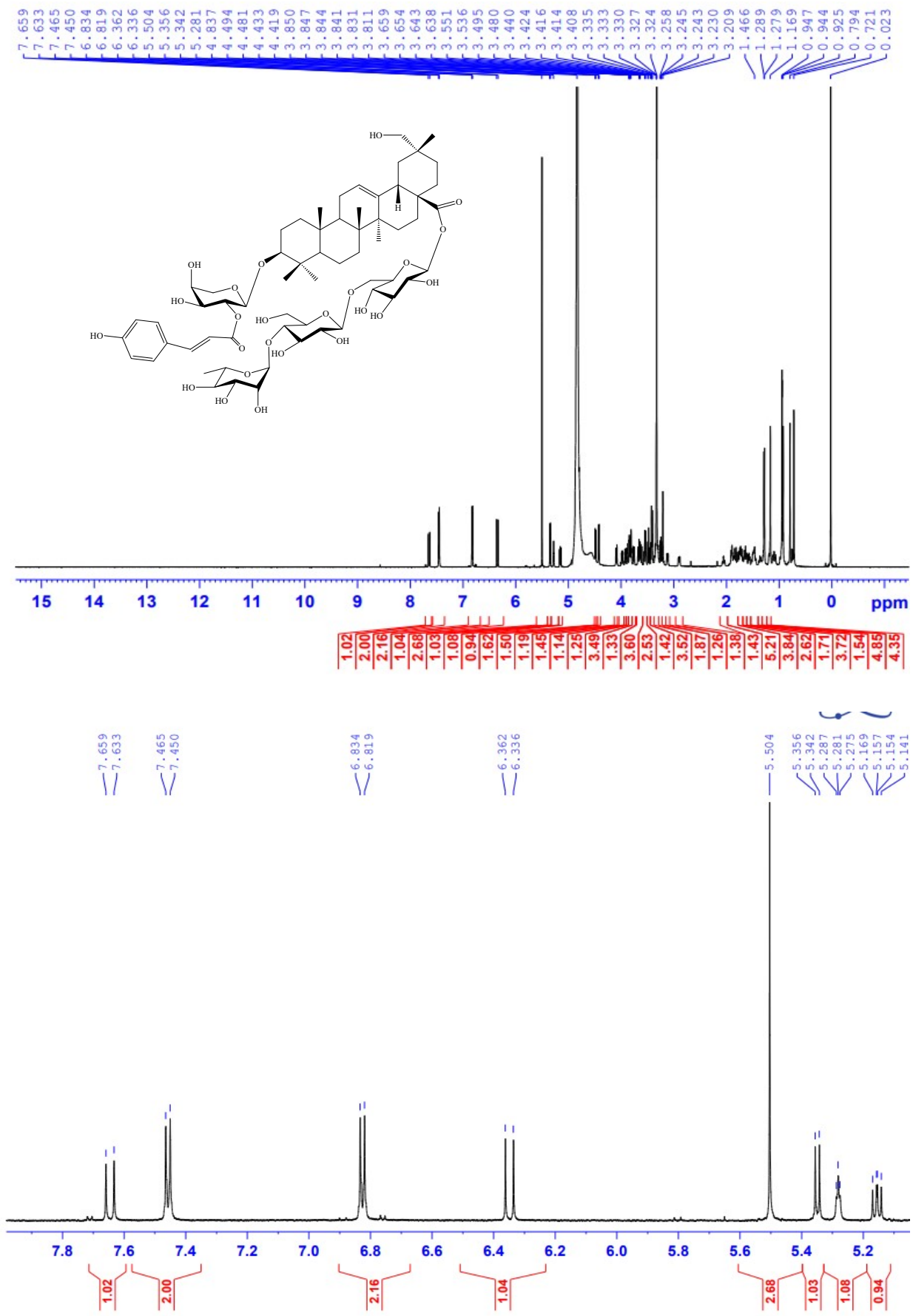


Figure S24. ^{1}H NMR spectrum of compound **3** in CD_3OD

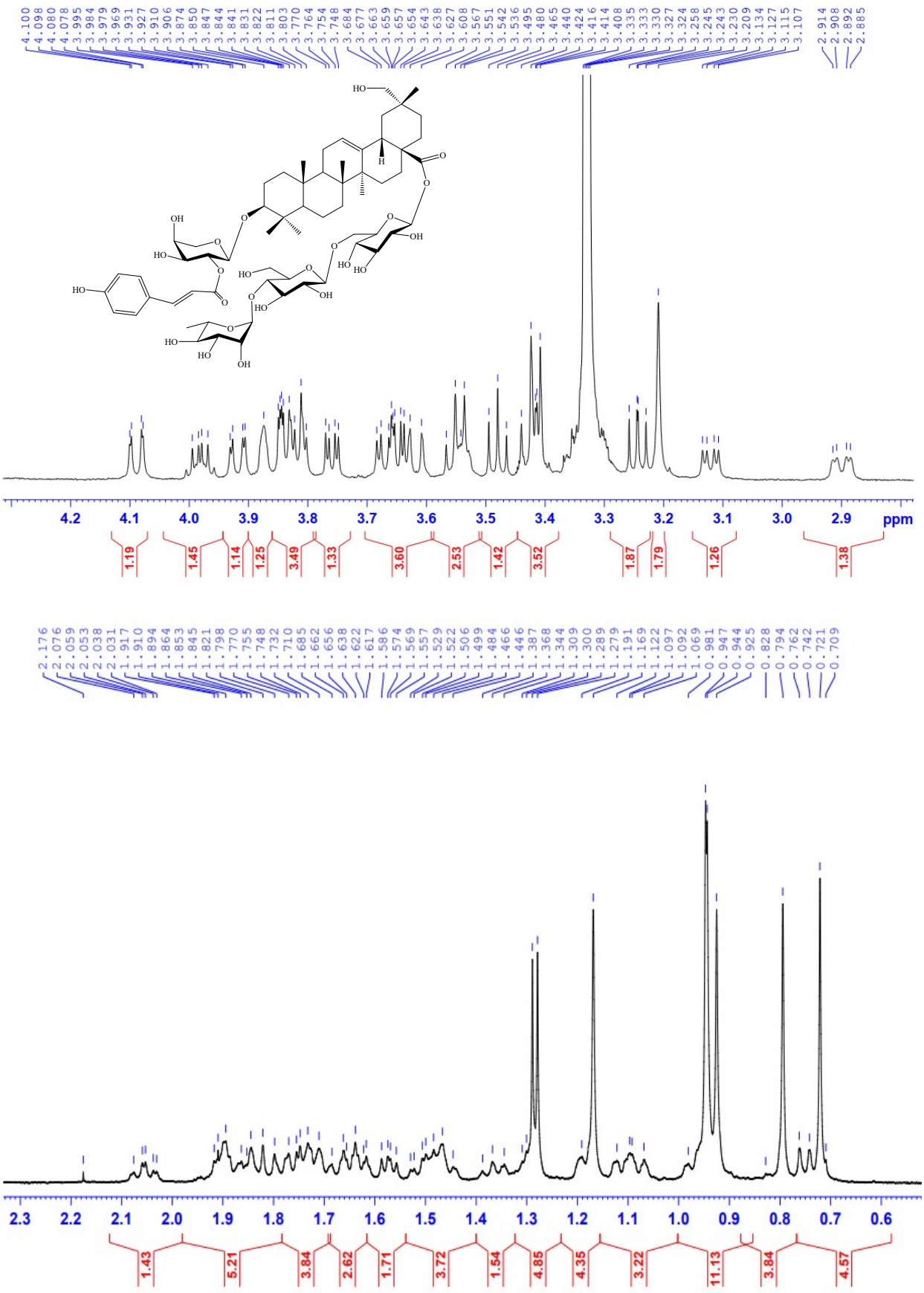
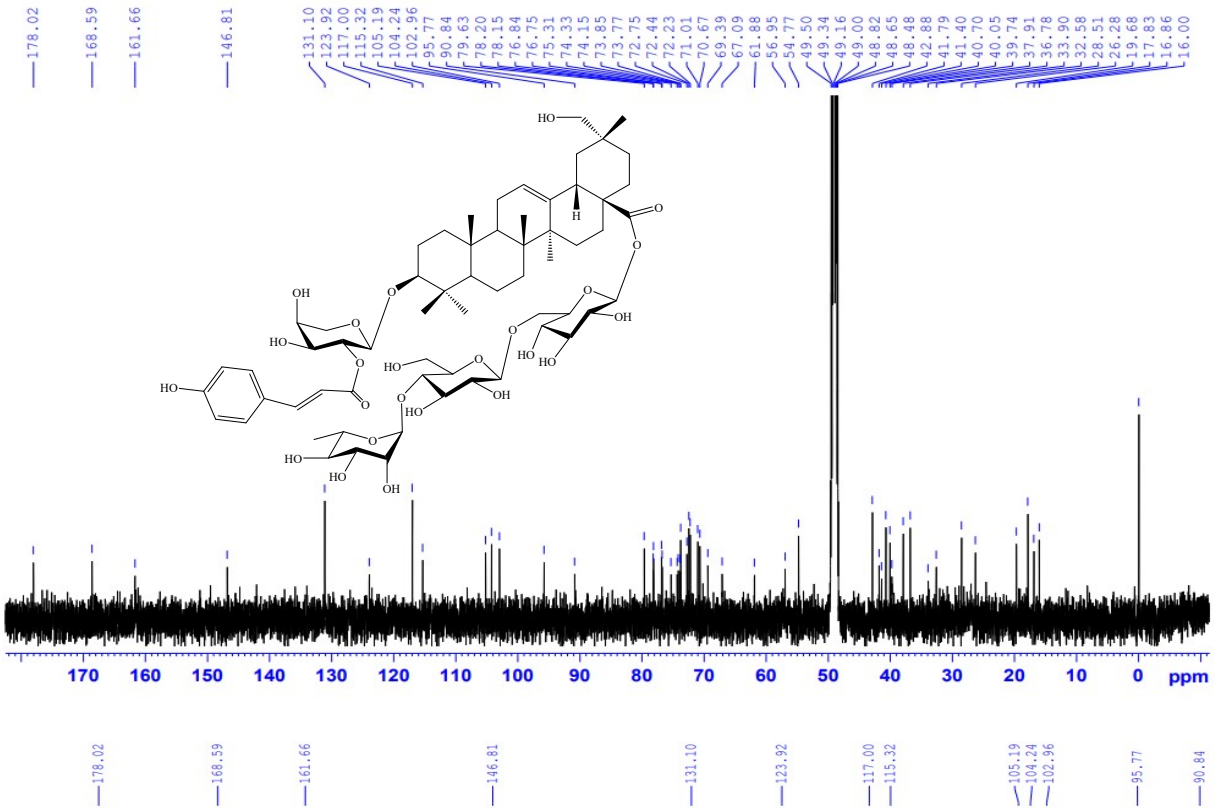


Figure S25. Extended ^{1}H NMR spectrum of compound **3** in CD_3OD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146.81
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16.00
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178.02
168.59
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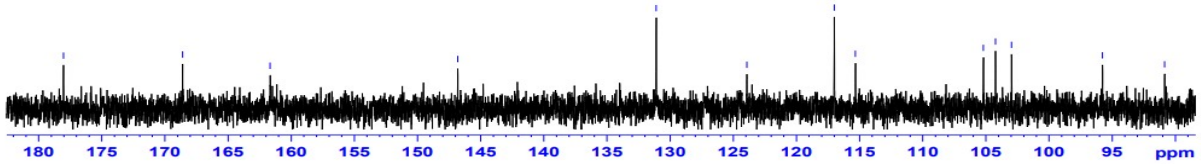
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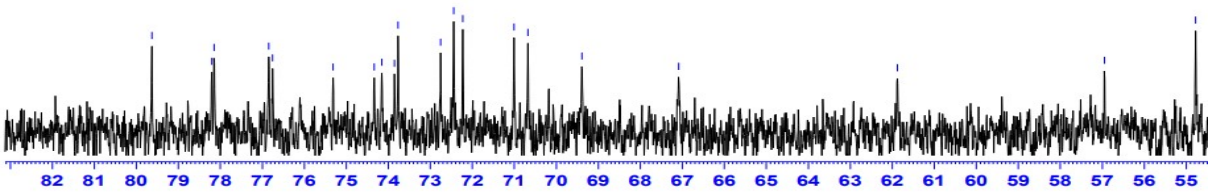
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Figure S26. ^{13}C NMR spectrum of compound **3** in CD_3OD

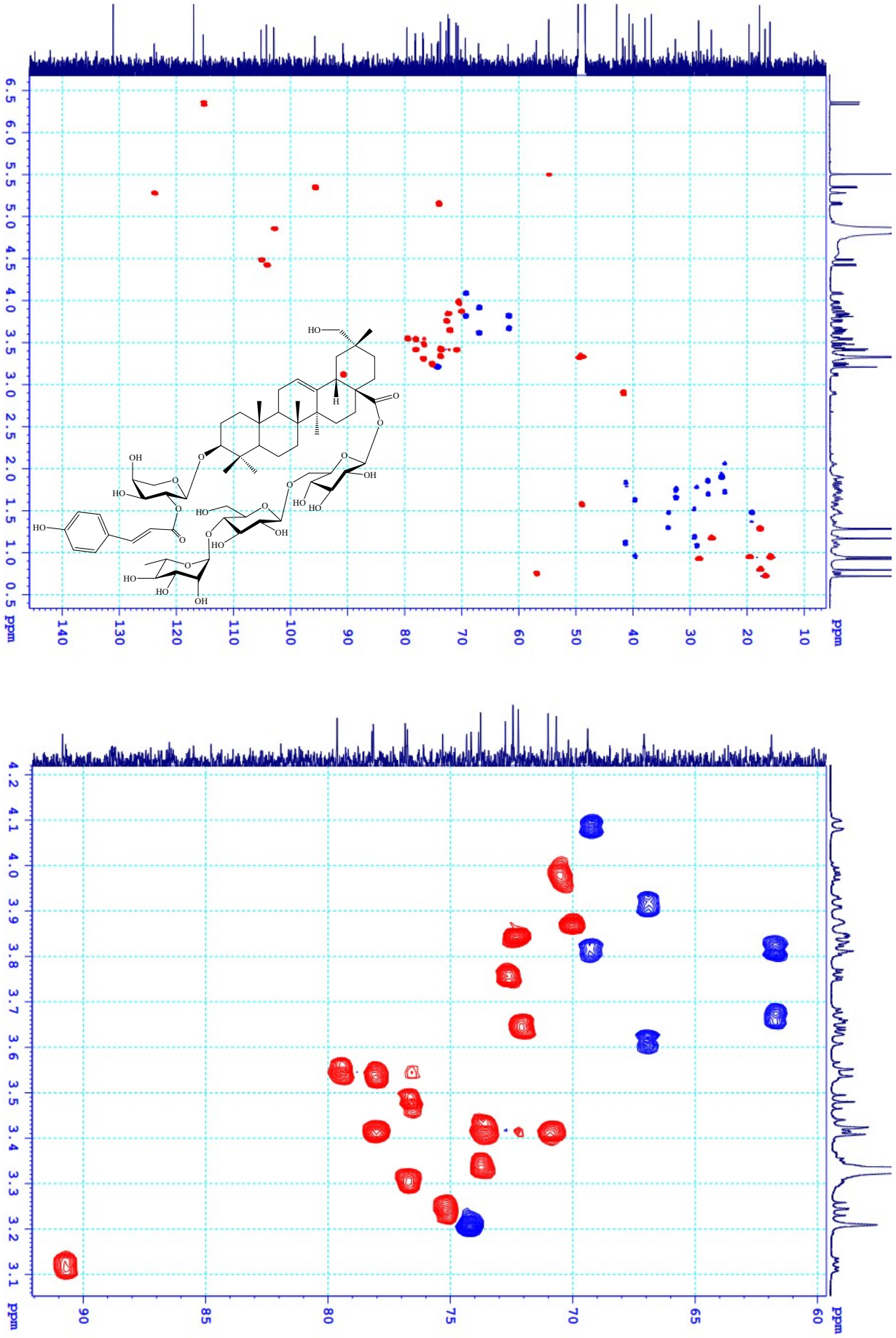
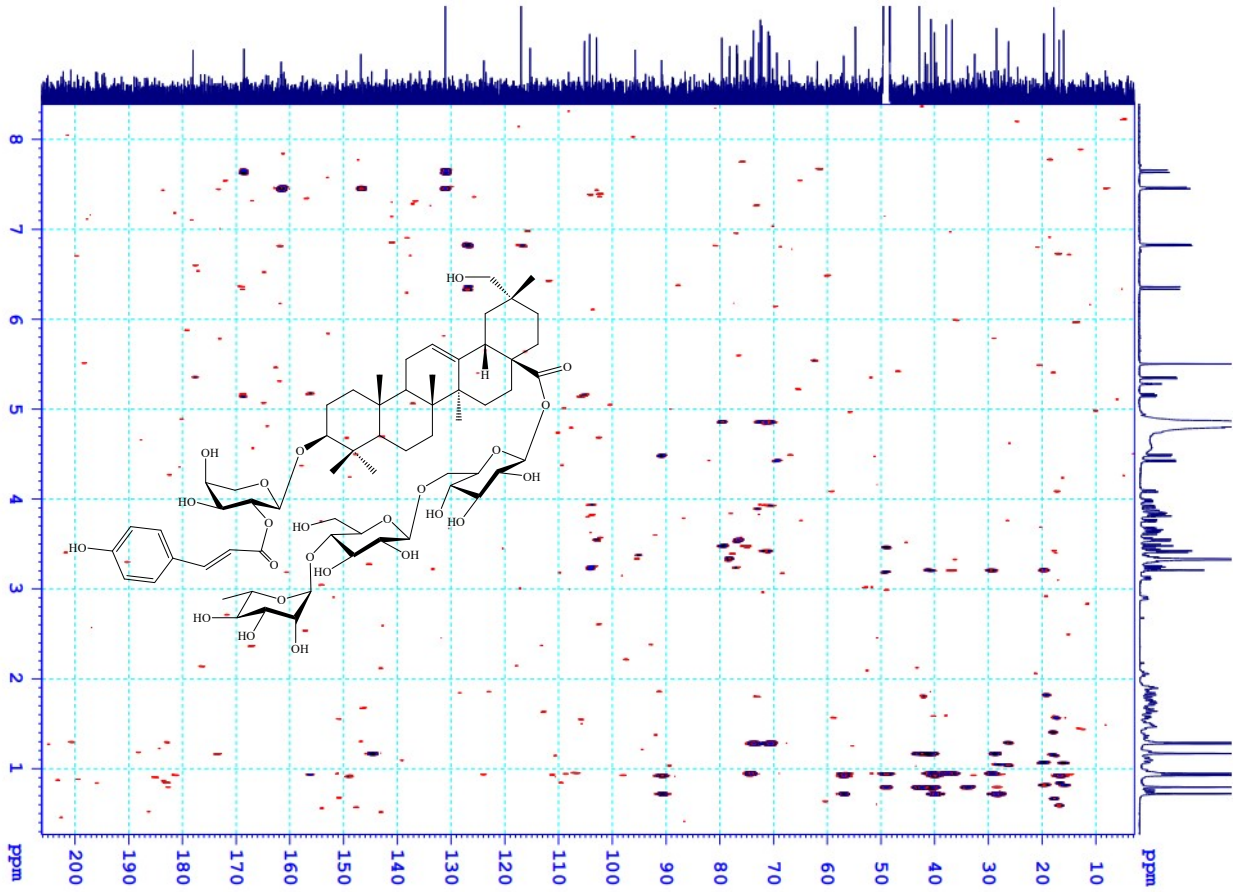


Figure S27. HSQC spectrum of compound **3** in CD_3OD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H

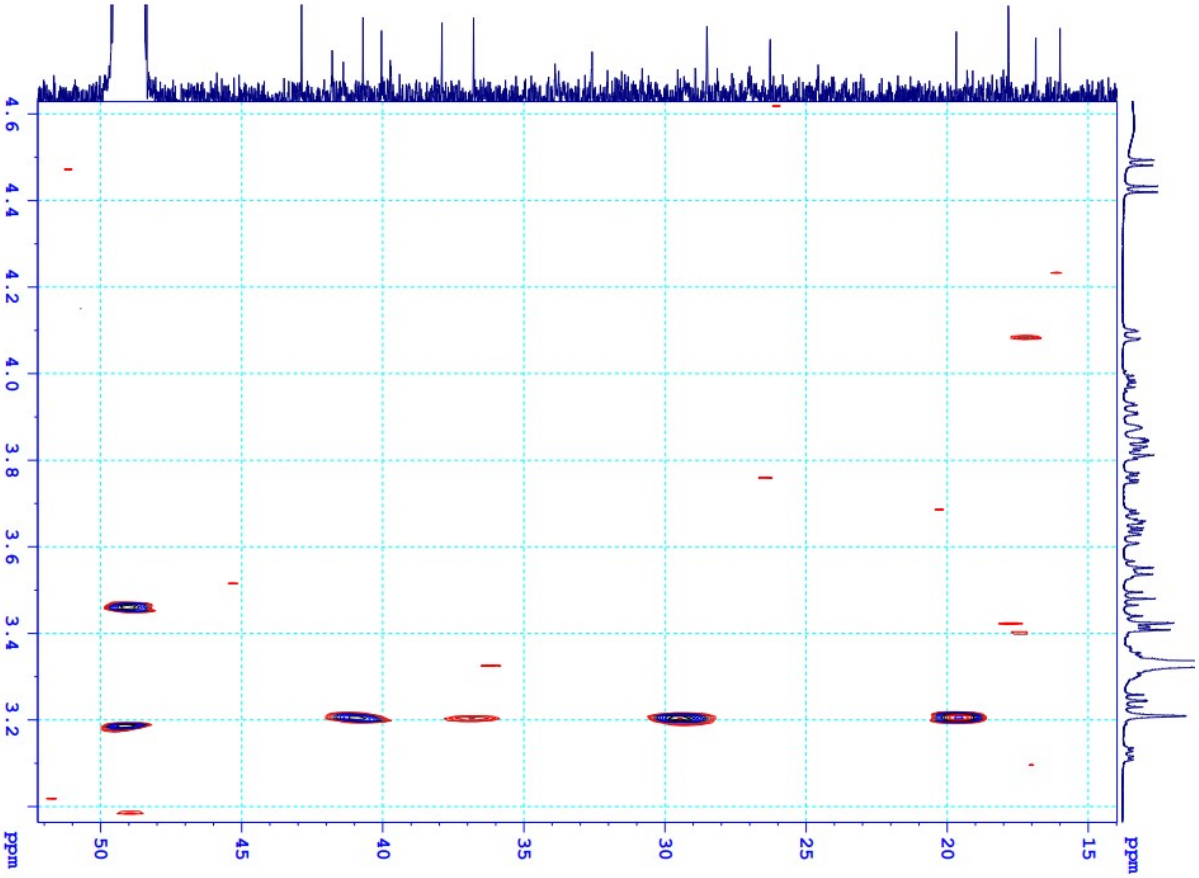


Figure S28. HMBC spectrum of compound **3** in CD_3OD

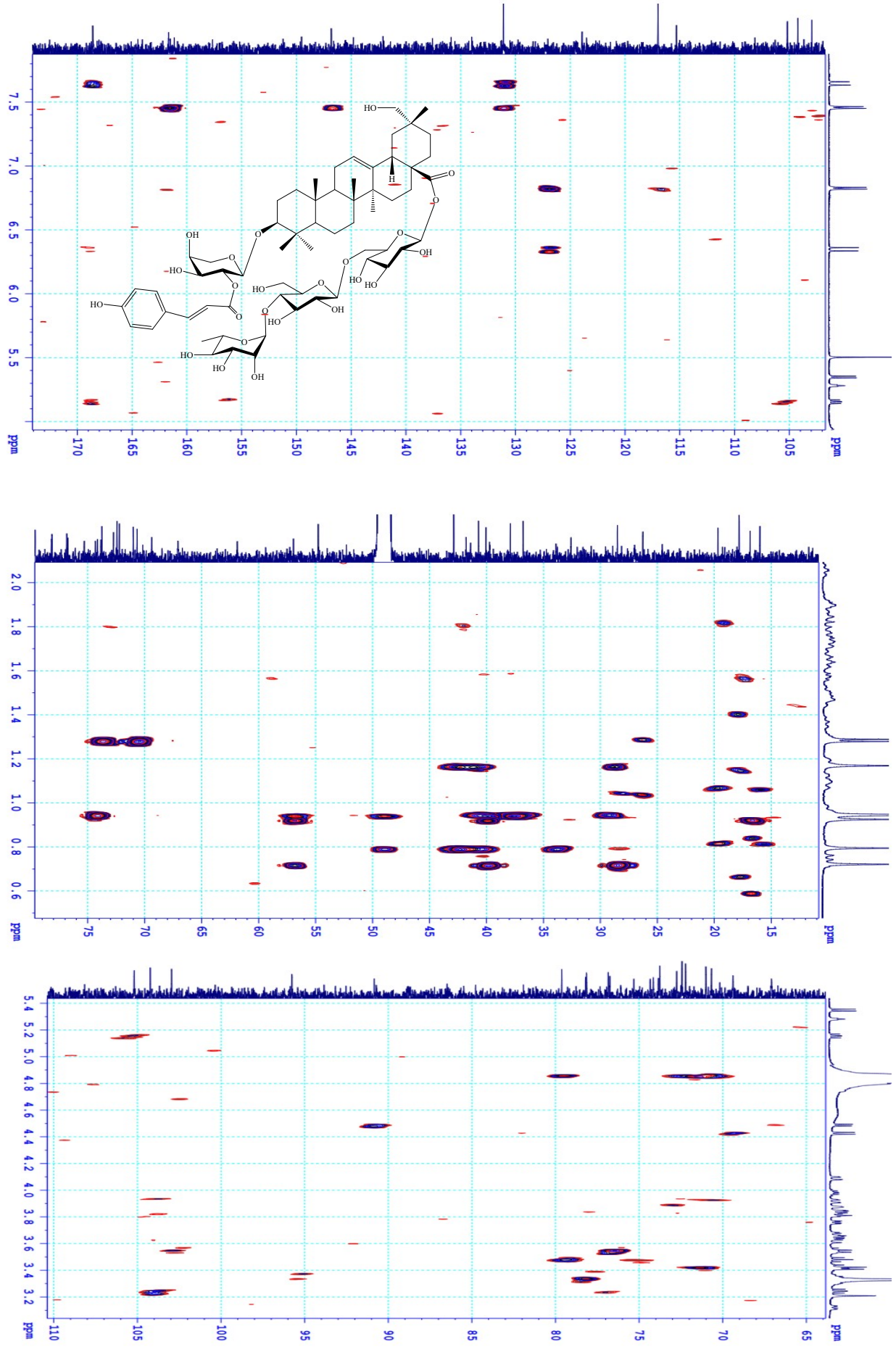


Figure S29. Extended HMBC spectrum of compound **3** in CD_3OD

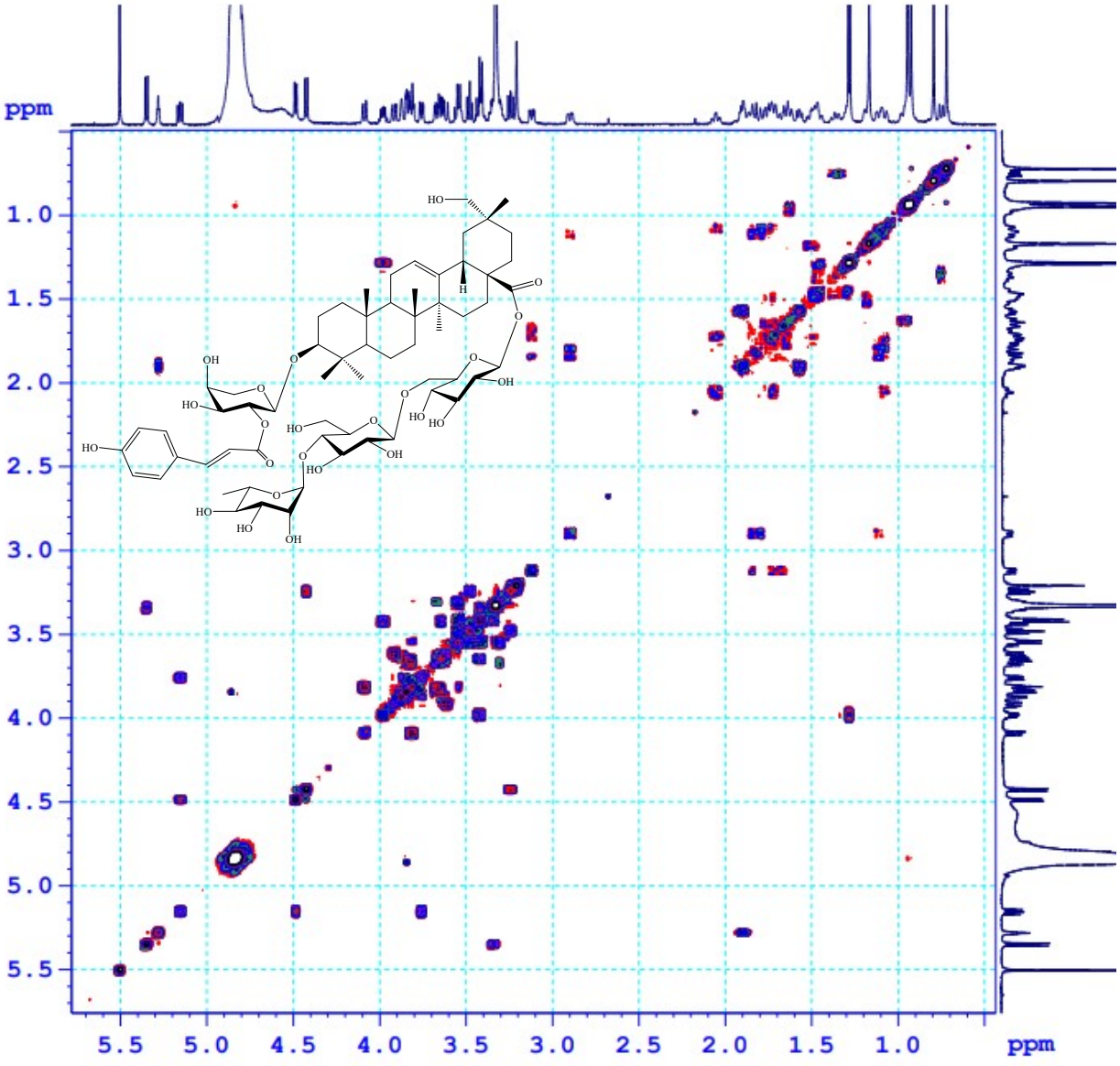


Figure S30. COSY spectrum of compound **3** in CD_3OD

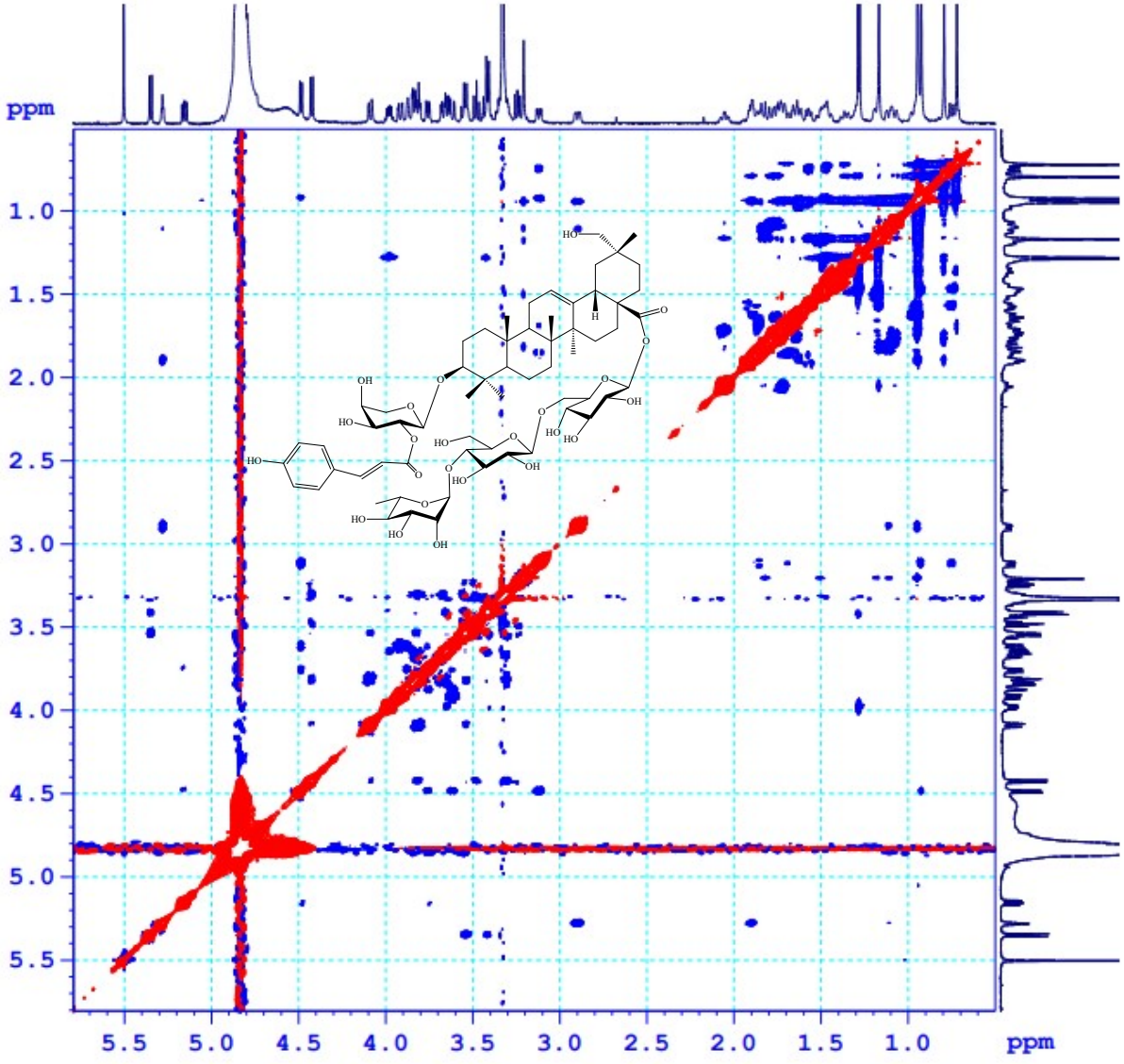


Figure S31. NOESY spectrum of compound **3** in CD_3OD

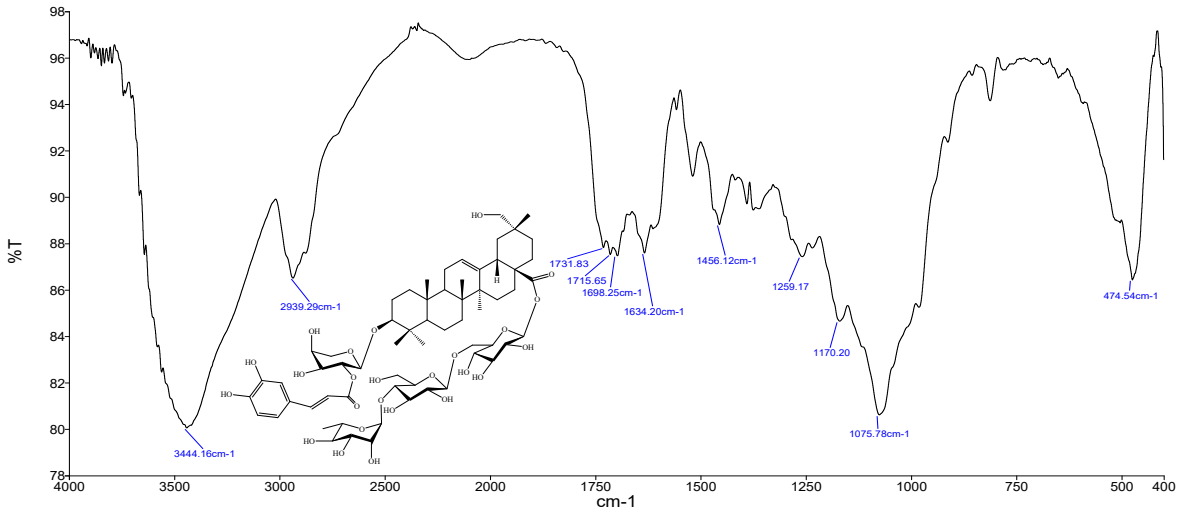
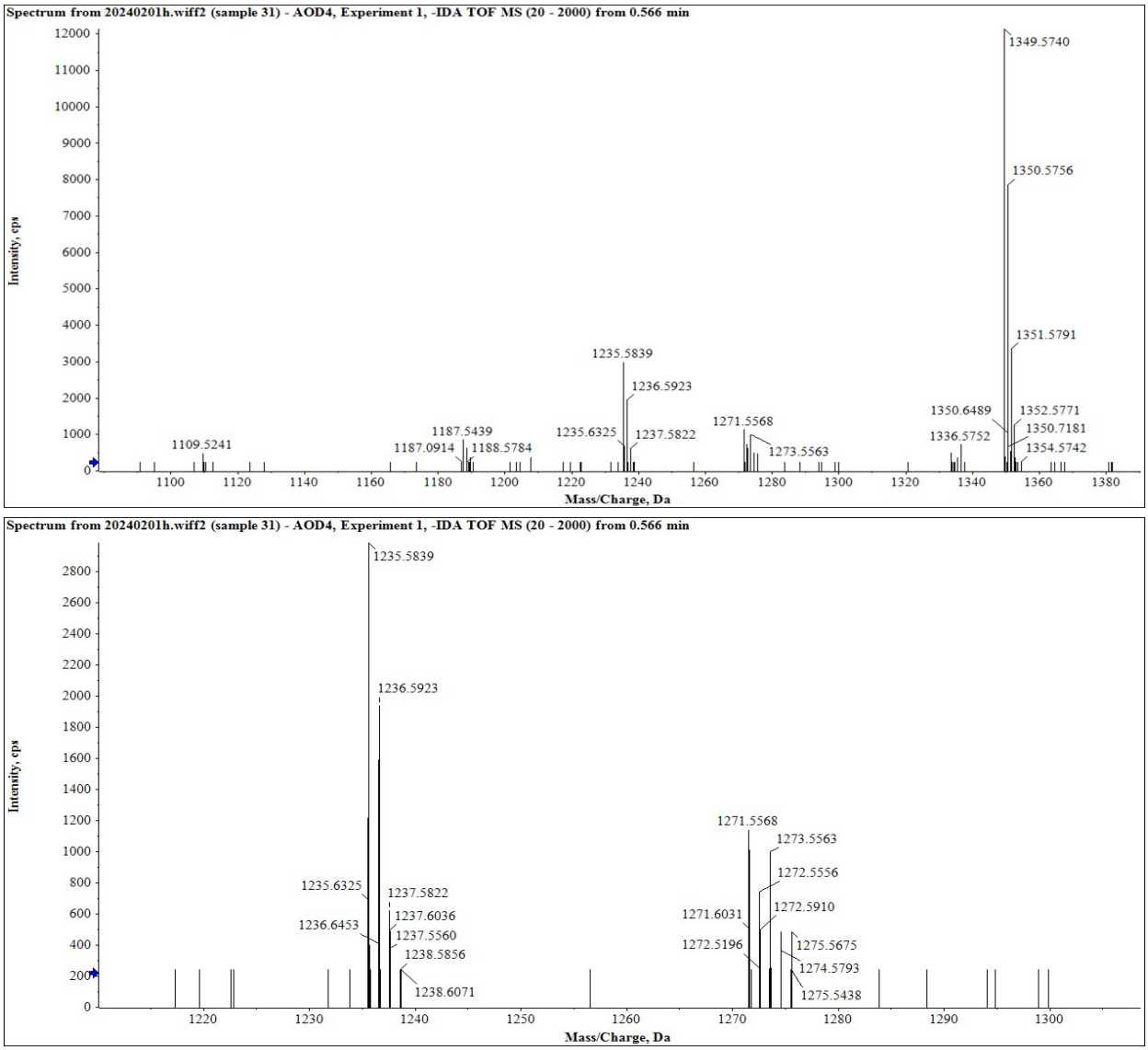


Figure S32. IR spectrum of compound **4**



HR-ESI-MS *m/z* 1235.5839 $[M-H]^-$, (calcd. for $[C_{62}H_{91}O_{25}]^-$, 1235.5855, Δ=-1.3 ppm), *m/z* 1271.5568 $[M+^{35}Cl]^-$, (calcd. for $[C_{62}H_{92}O_{25}{}^{35}Cl]^-$, 1271.5521, Δ=-4.2 ppm), *m/z* 1273.5563 $[M+^{37}Cl]^-$, (calcd. for $[C_{62}H_{92}O_{25}{}^{37}Cl]^-$, 1273.5592, Δ=-2.3 ppm)

Figure S33. HR-ESI-MS spectrum of compound **4**

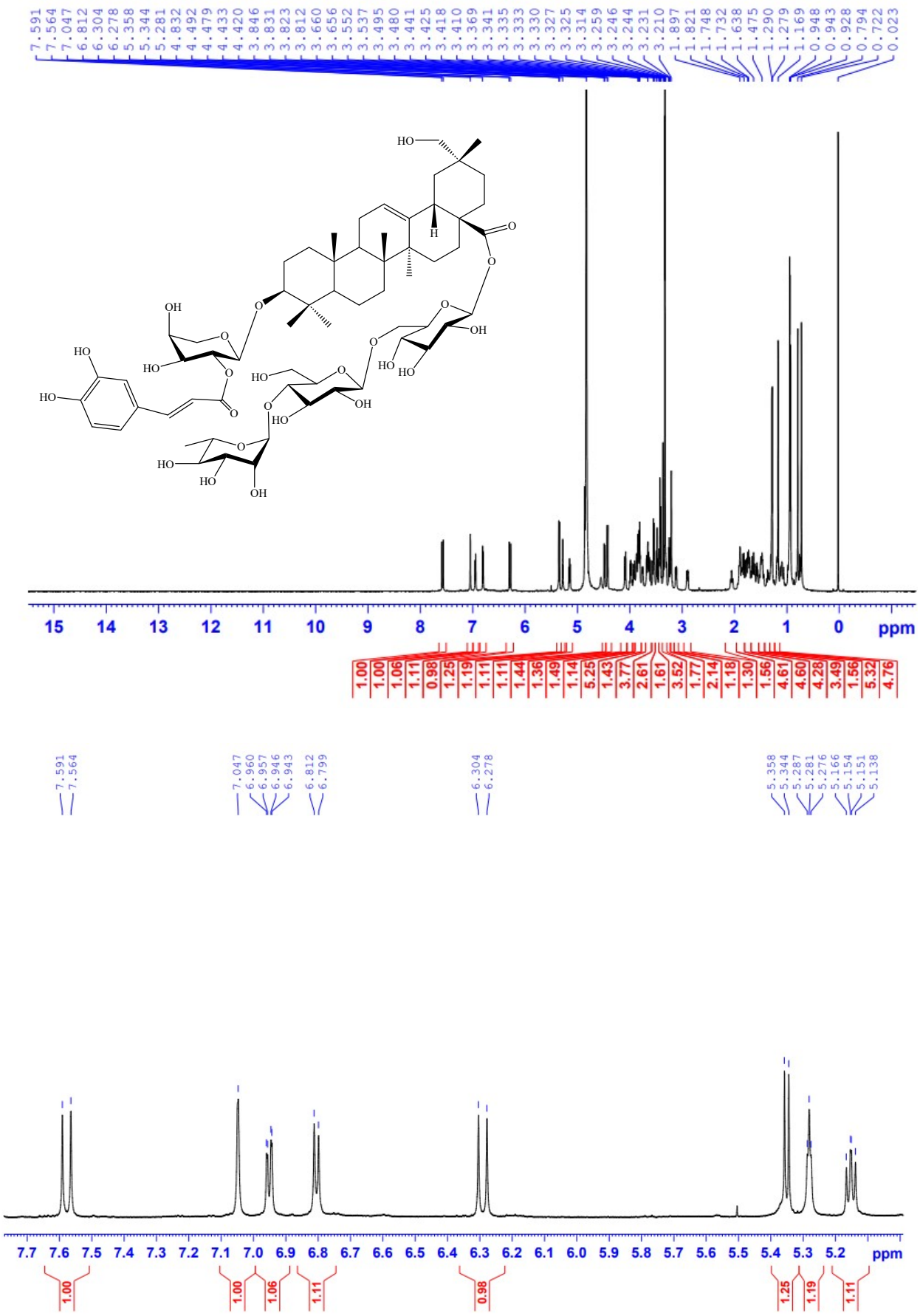


Figure S34. ^{1}H NMR spectrum of compound **4** in CD_3OD

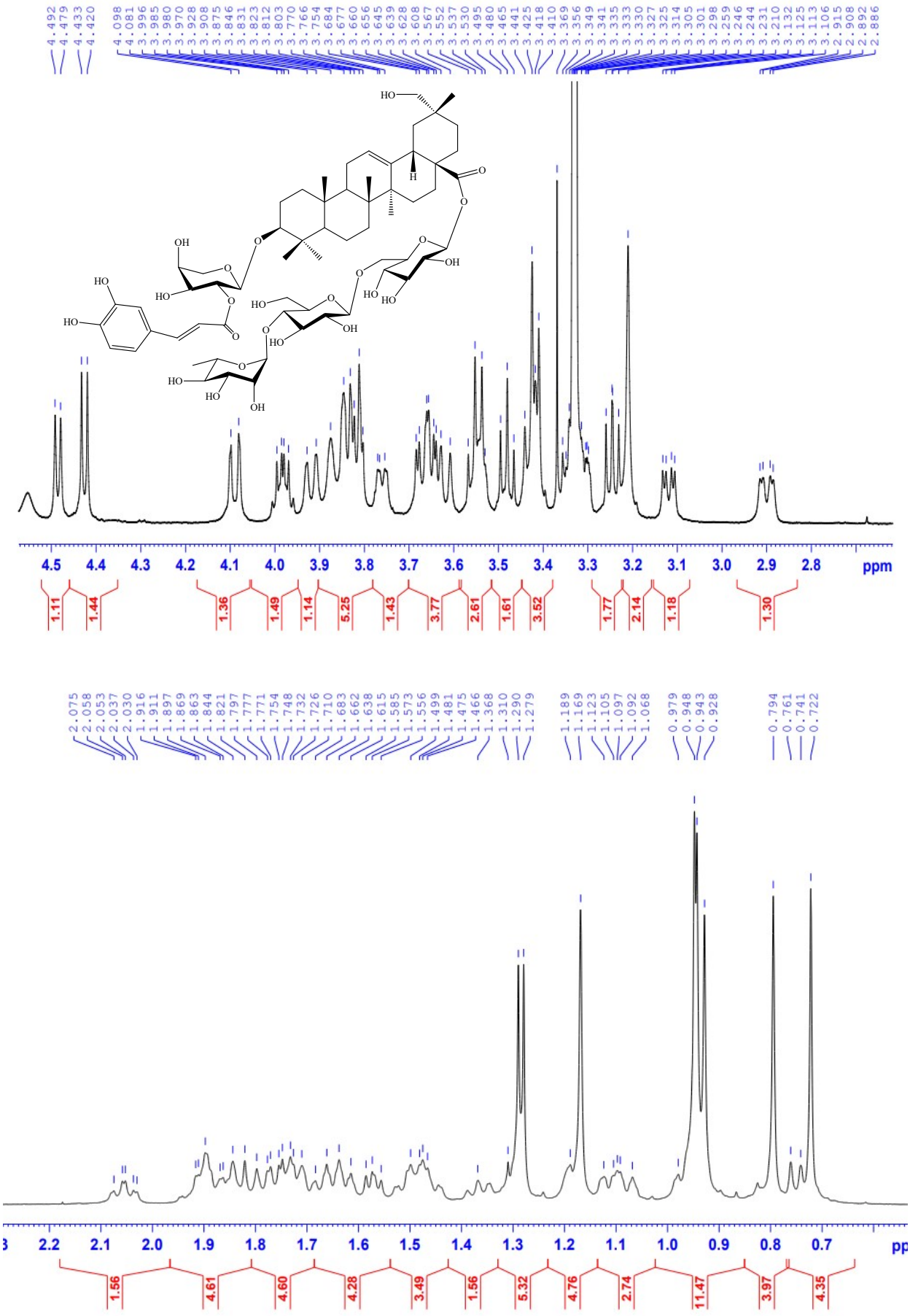


Figure S35. Extended ^{1}H NMR spectrum of compound **4** in CD_3OD

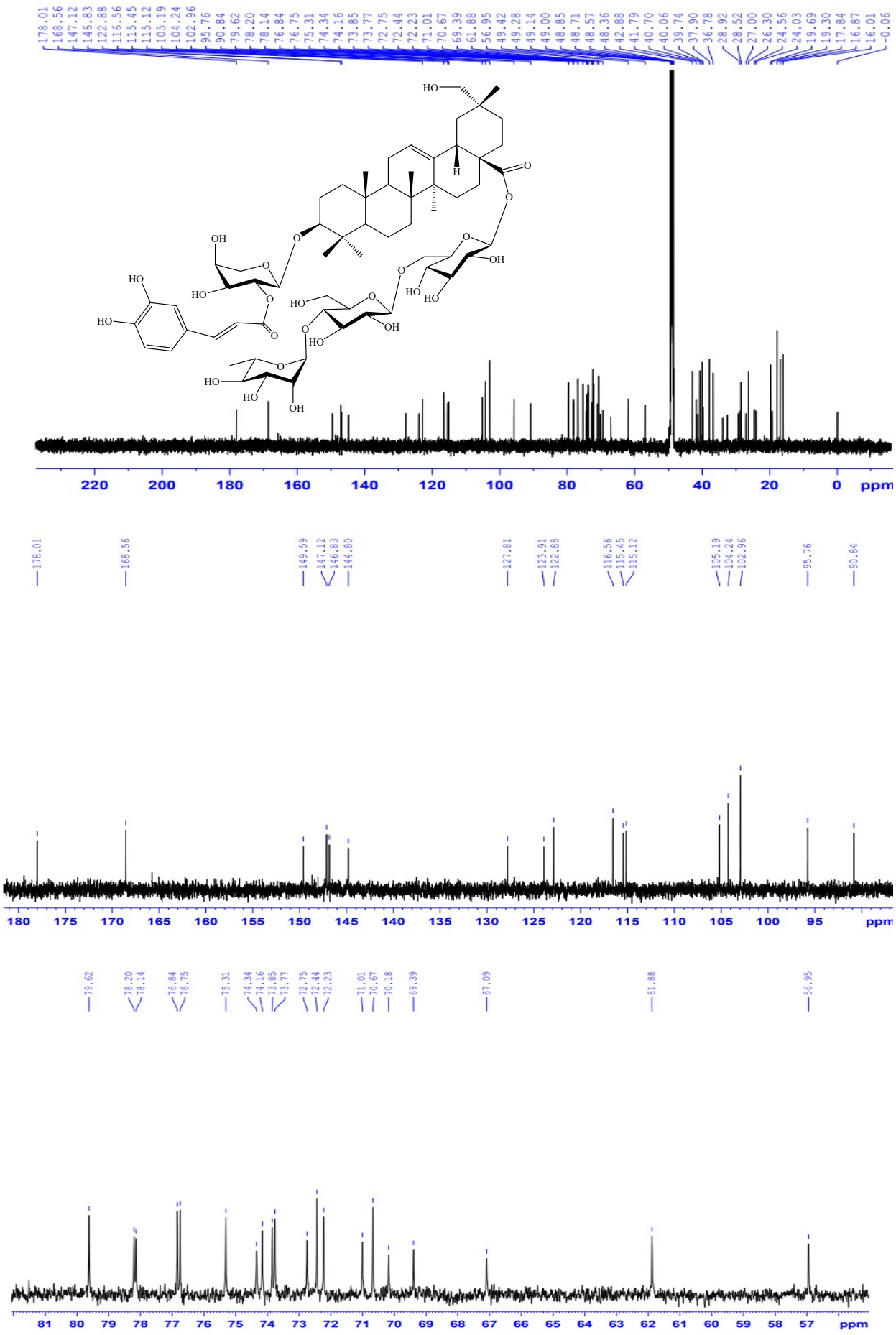


Figure S36. ^{13}C NMR spectrum of compound **4** in CD_3OD

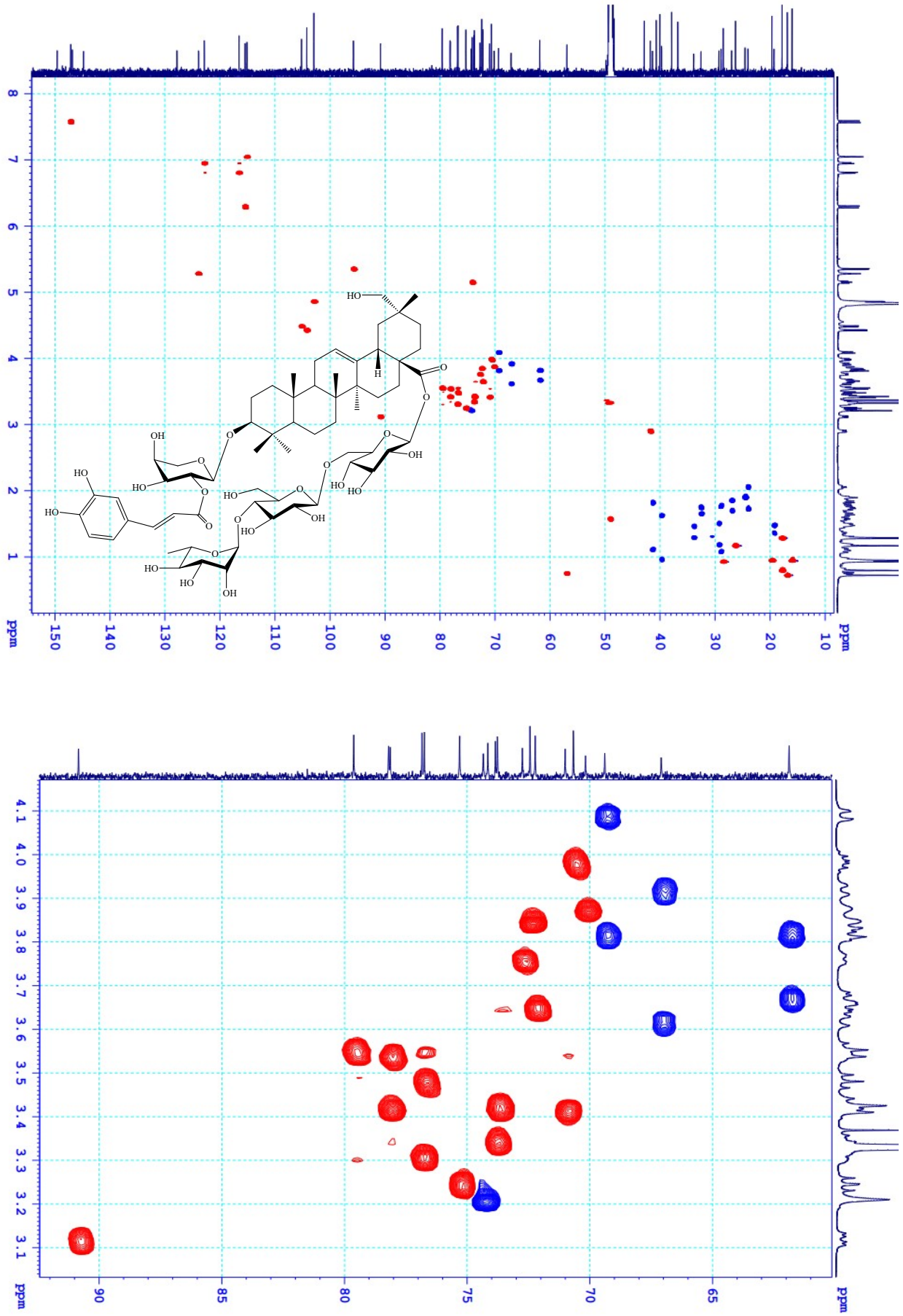


Figure S37. HSQC spectrum of compound **4** in CD_3OD

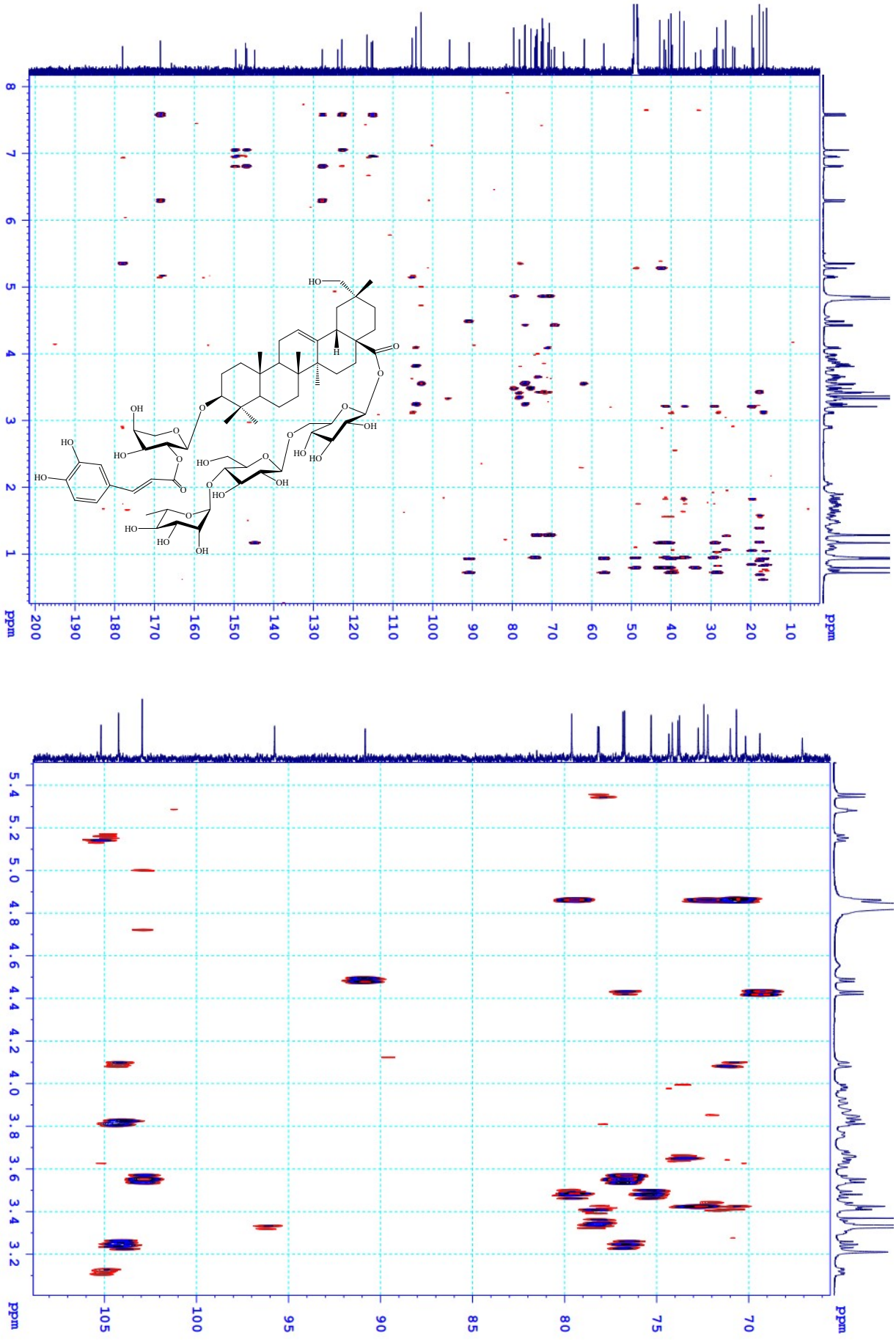


Figure S38. HMBC spectrum of compound **4** in CD_3OD

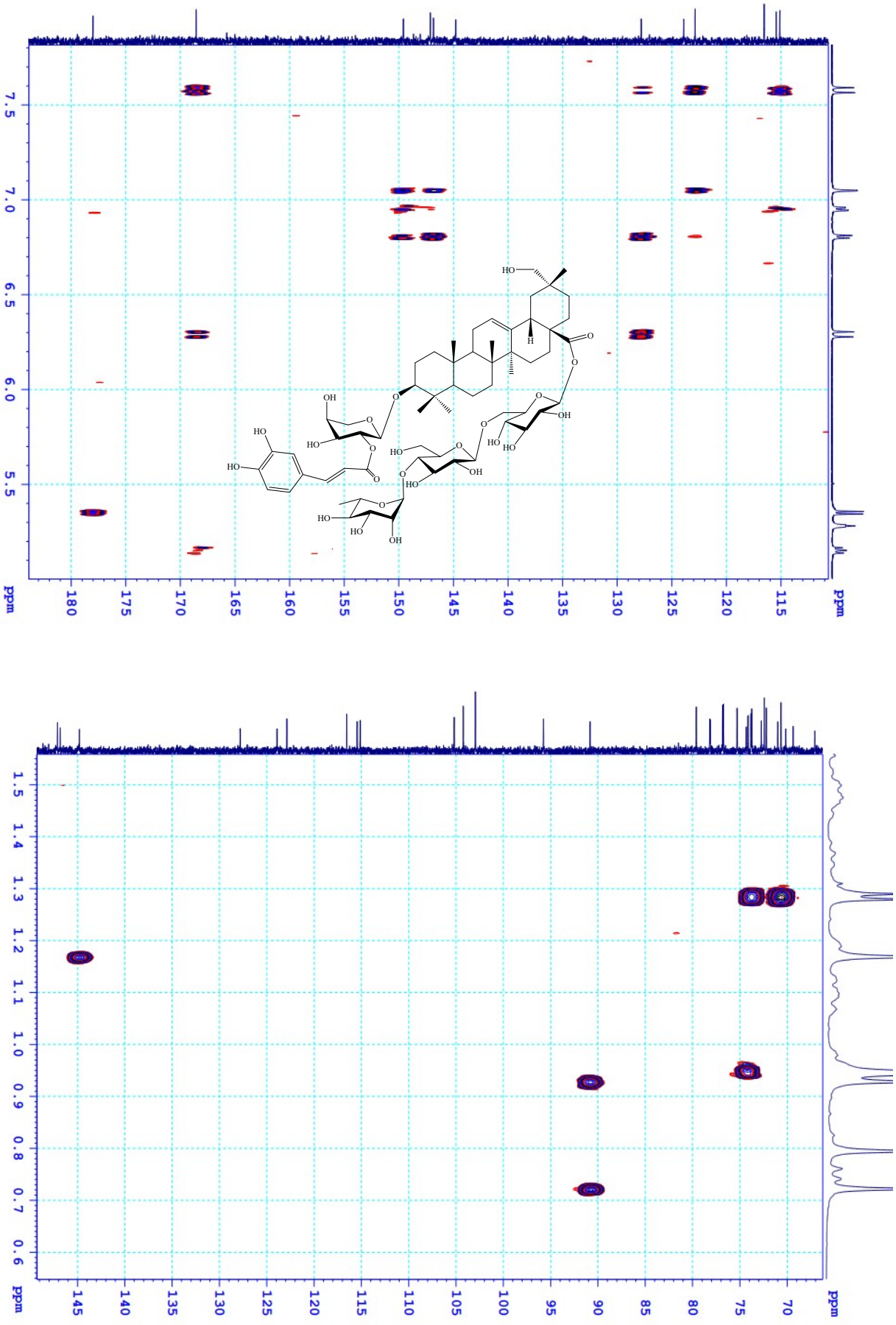


Figure S39. Extended HMBC spectrum of compound **4** in CD_3OD

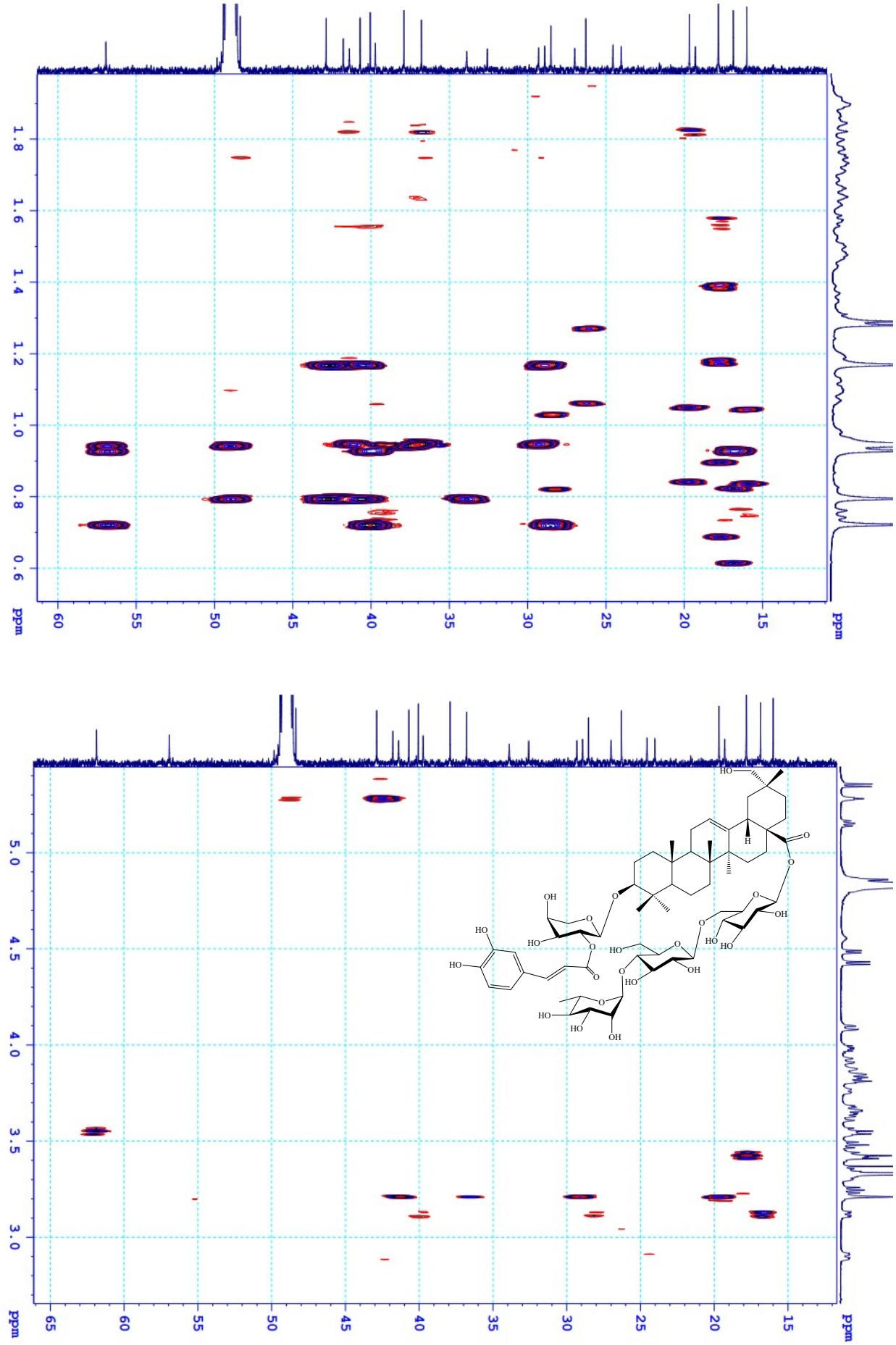


Figure S40. Extended HMBC spectrum of compound **4** in CD_3OD

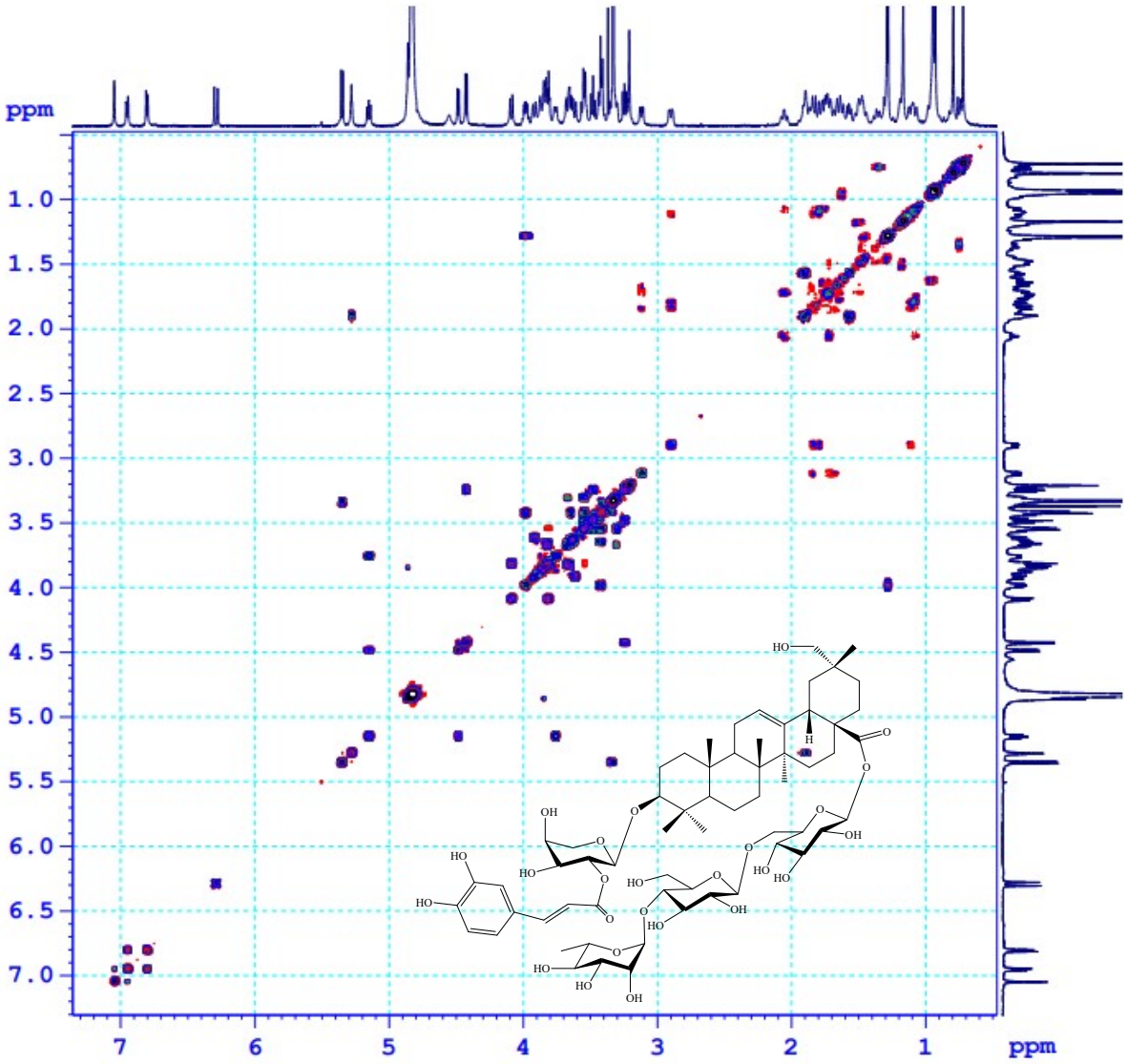


Figure S41. COSY spectrum of compound **4** in CD_3OD

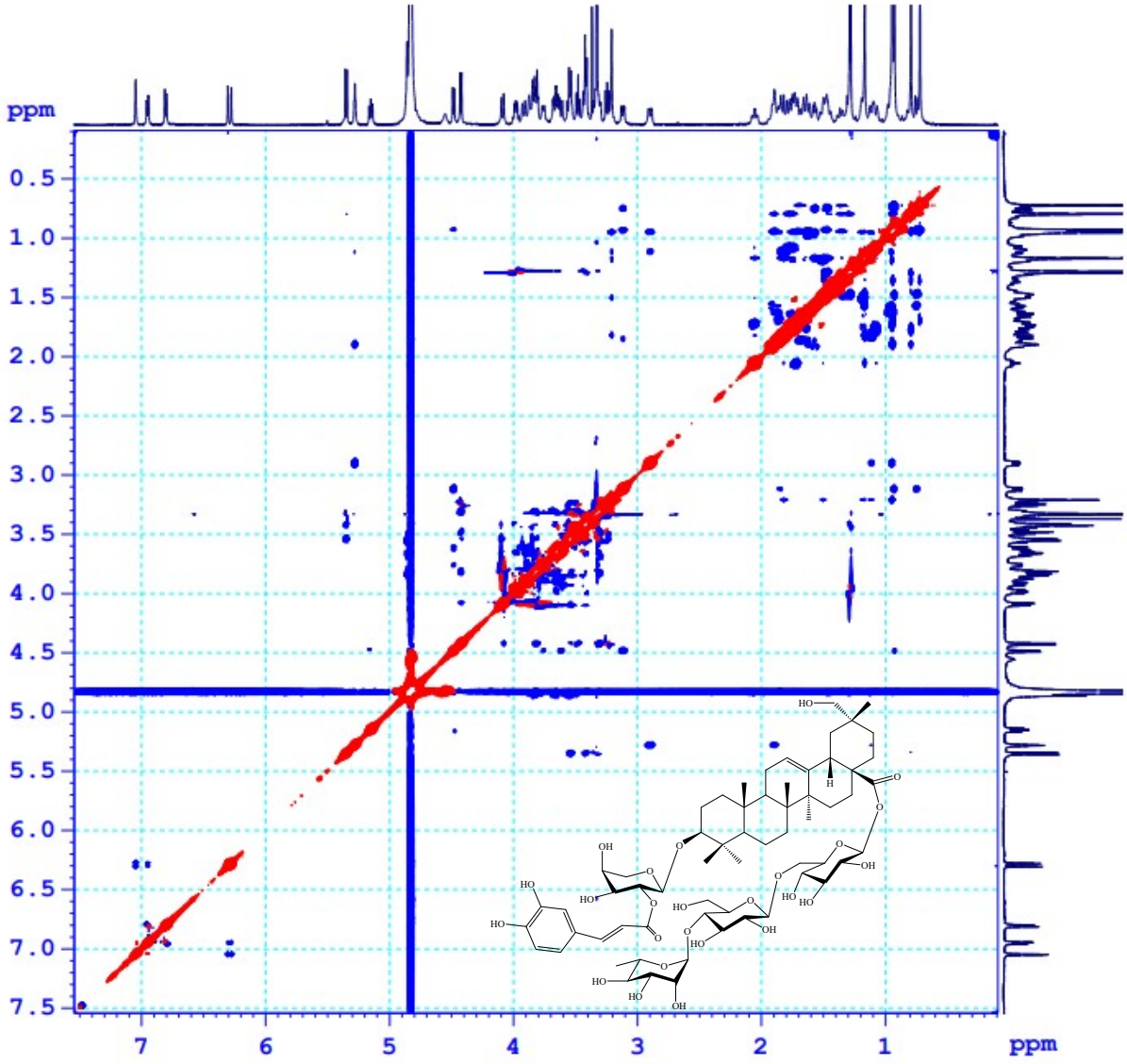


Figure S42. NOESY spectrum of compound **4** in CD_3OD

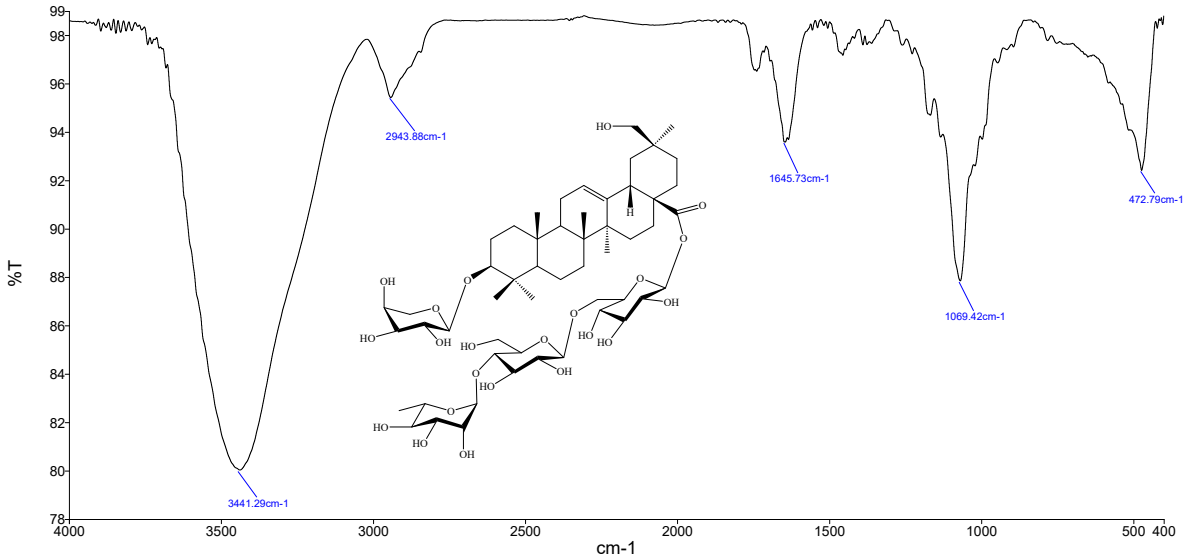
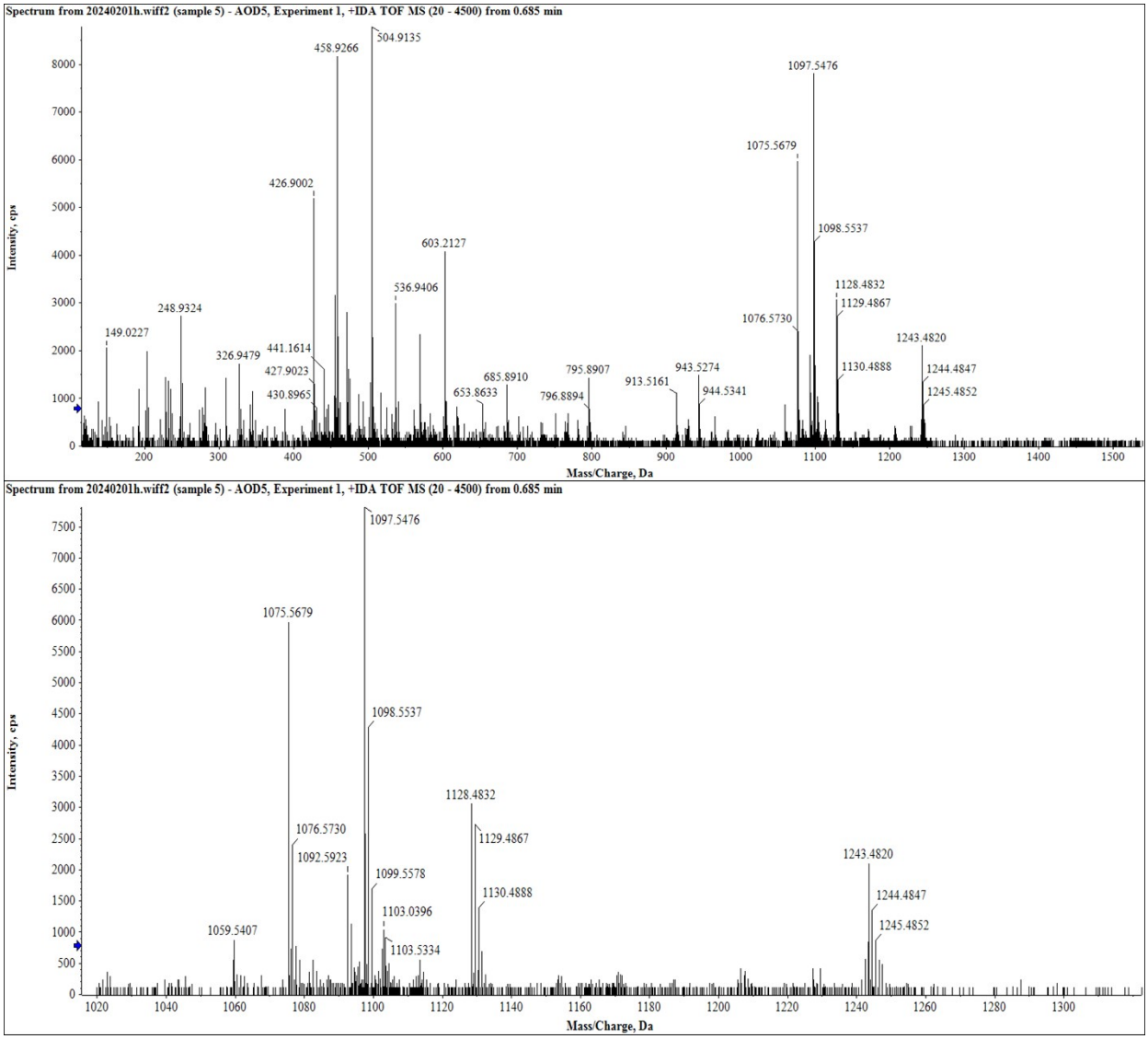


Figure S43. IR spectrum of compound **5**



HR-ESI-MS *m/z* 1075.5679 $[M+H]^+$, (calcd. for $[C_{53}H_{87}O_{22}]^+$, 1075.5684, Δ=-0.5 ppm), *m/z* 1097.5476 $[M+Na]^+$, (calcd. for $[C_{53}H_{86}O_{22}Na]^+$, 1097.5503, Δ=-2.5 ppm)

Figure S44. HR-ESI-MS spectrum of compound **5**

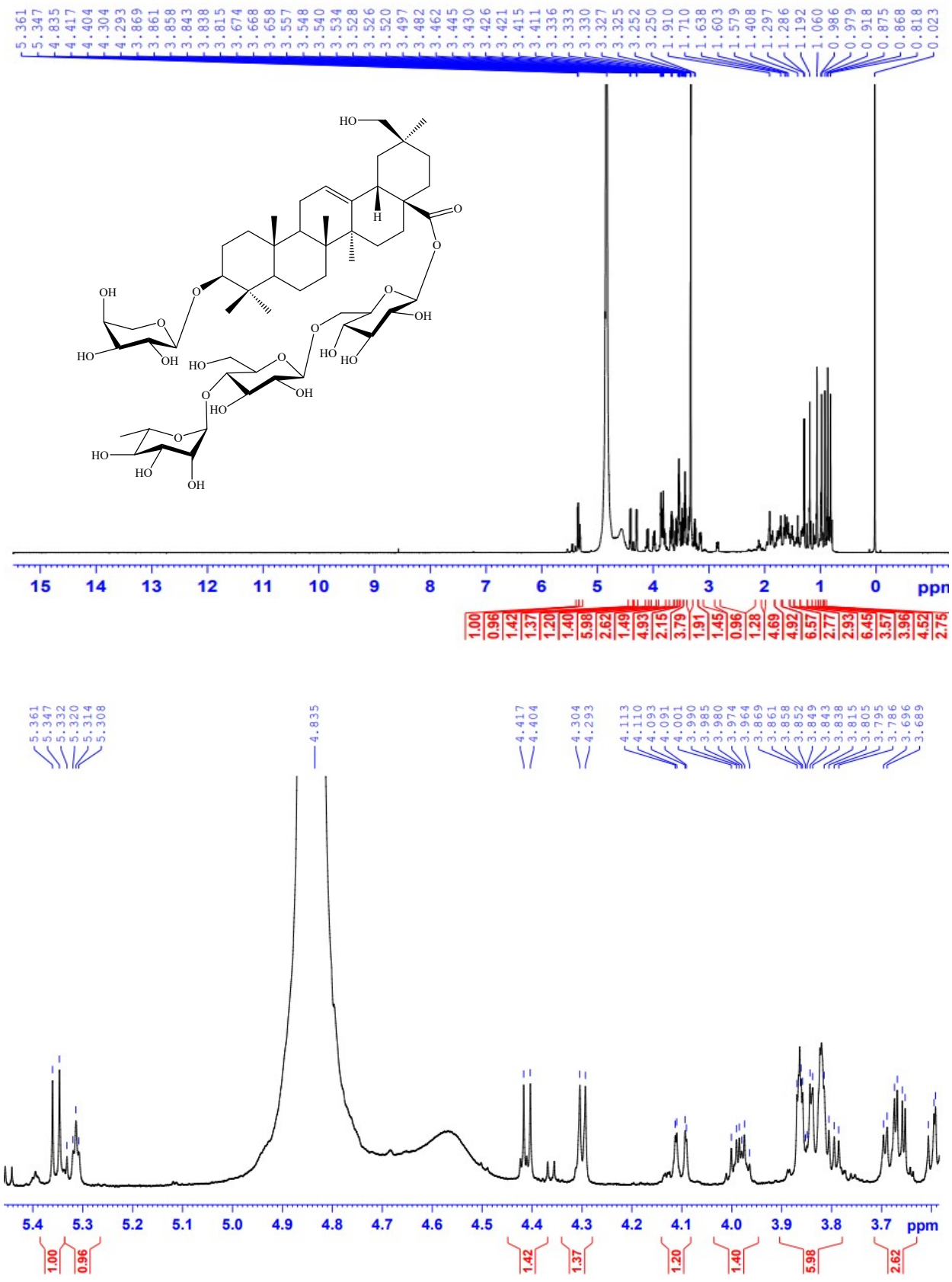


Figure S45. ^{1}H NMR spectrum of compound **5** in CD_3OD

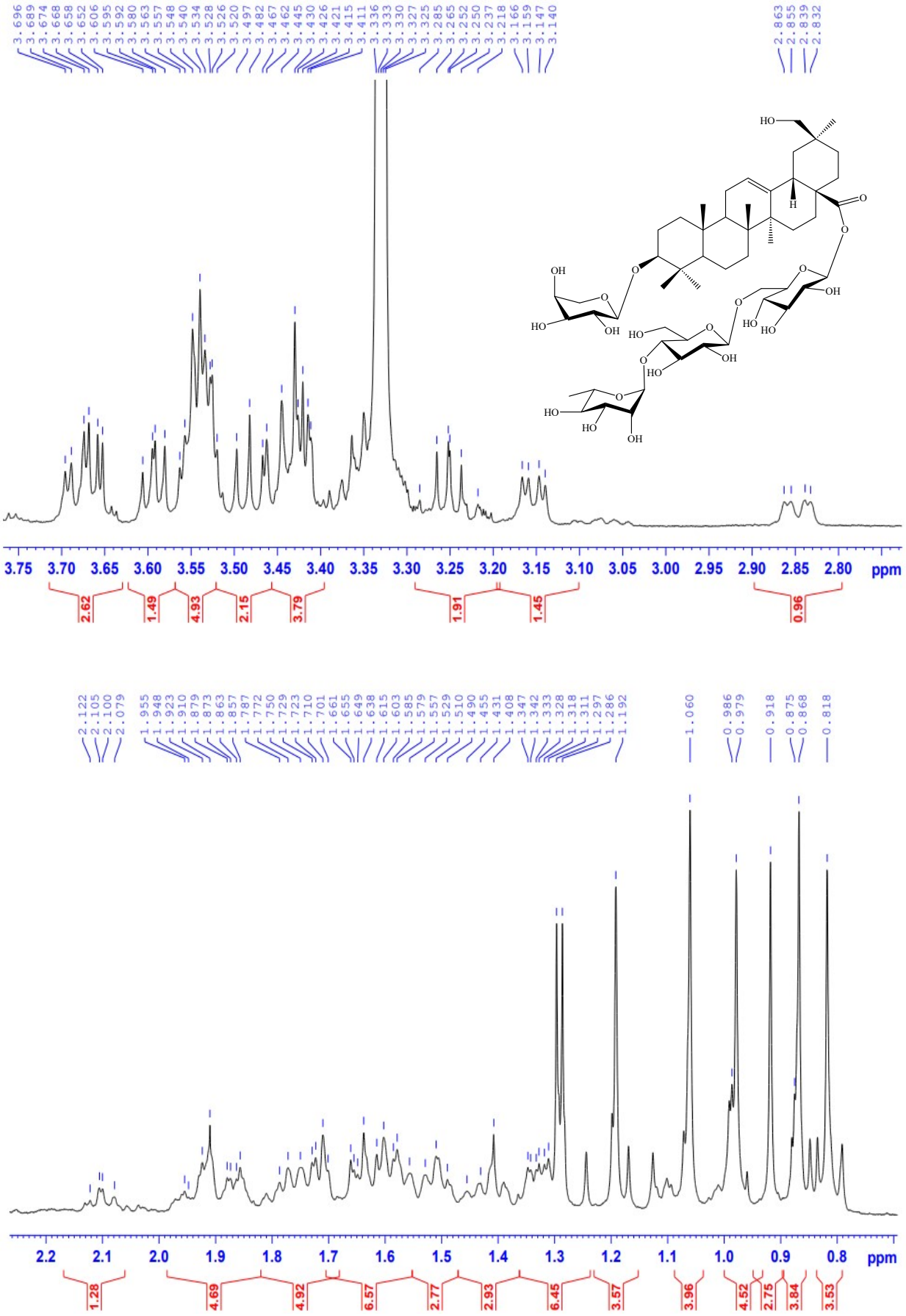


Figure S46. Extended ^{1}H NMR spectrum of compound **5** in CD_3OD

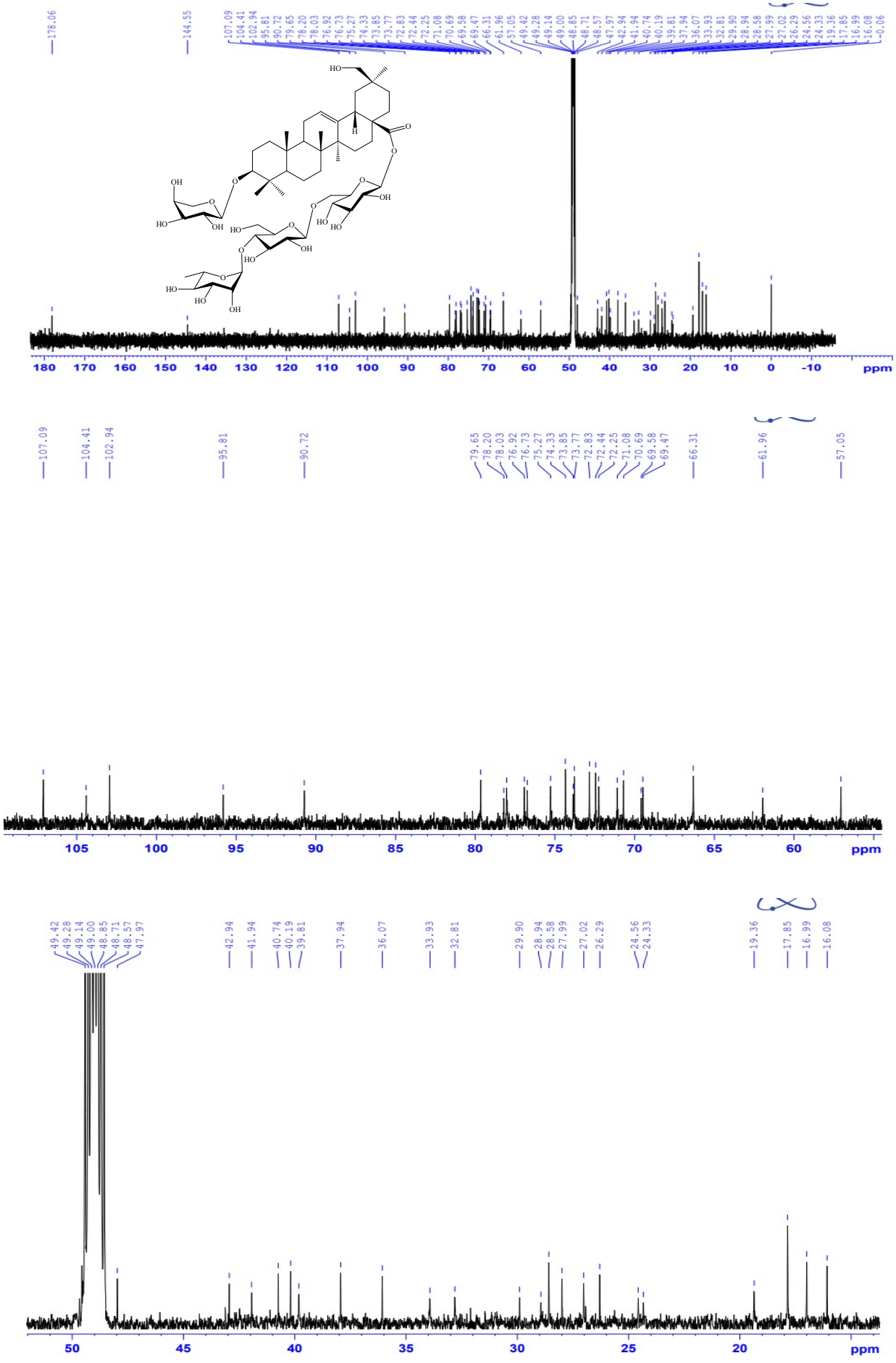
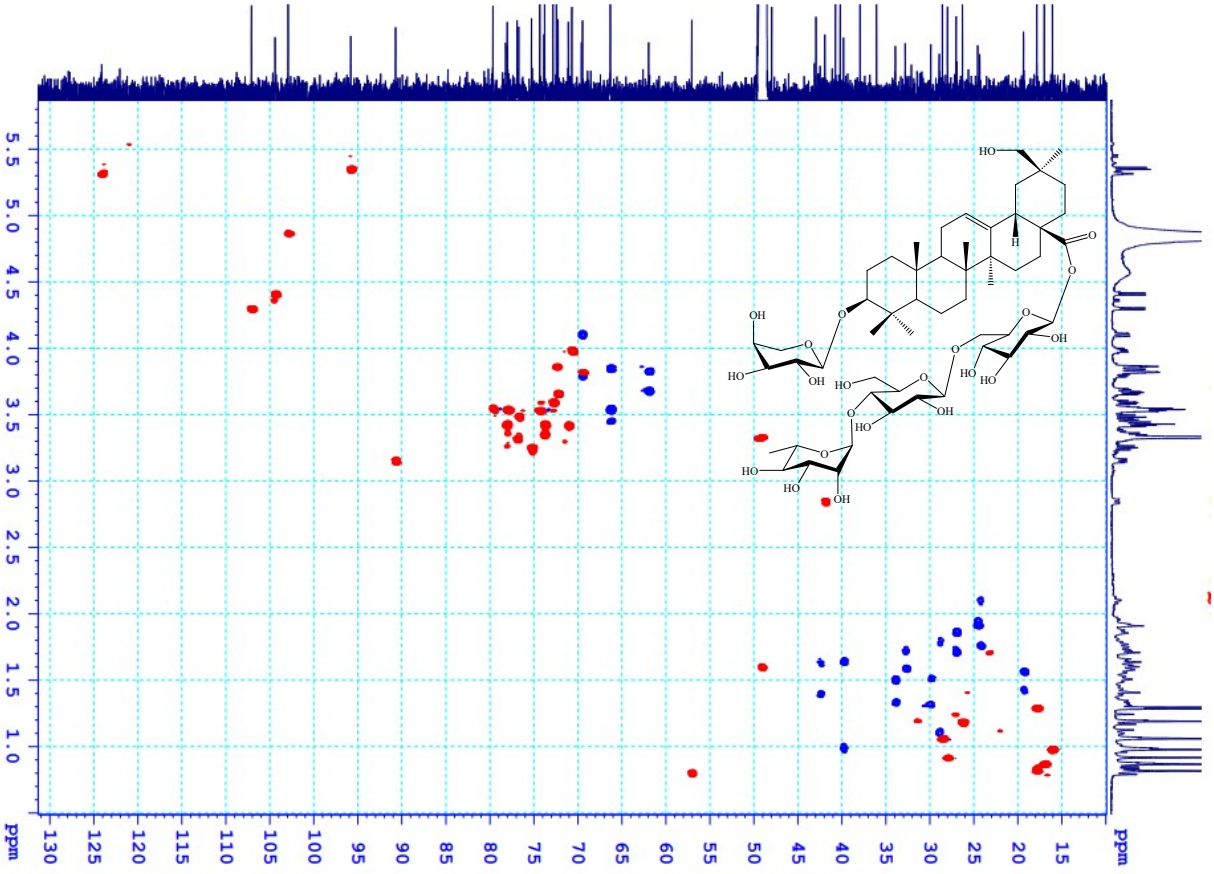


Figure S47. ^{13}C NMR spectrum of compound **5** in CD_3OD


5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm
130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
ppm
HO
H
O
OH
HO

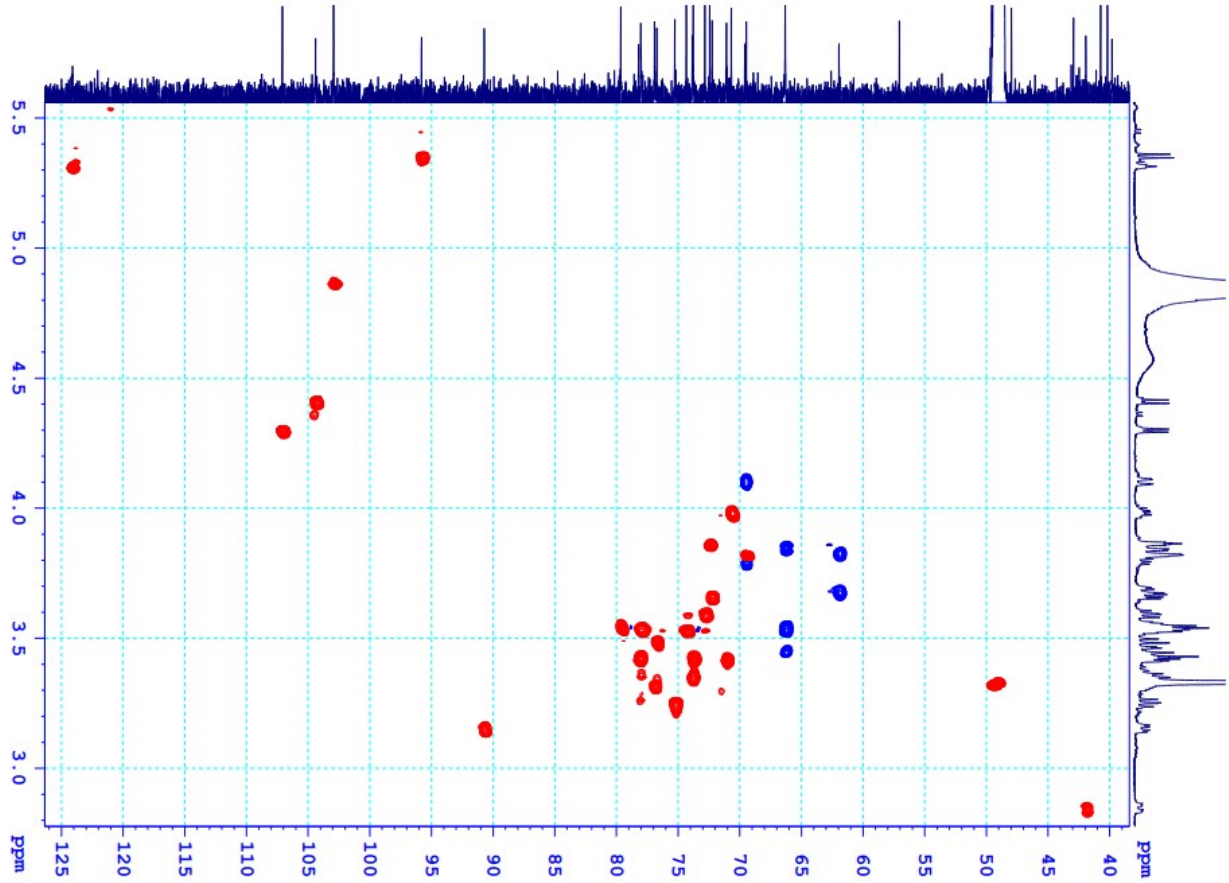


Figure S48. HSQC spectrum of compound **5** in CD_3OD

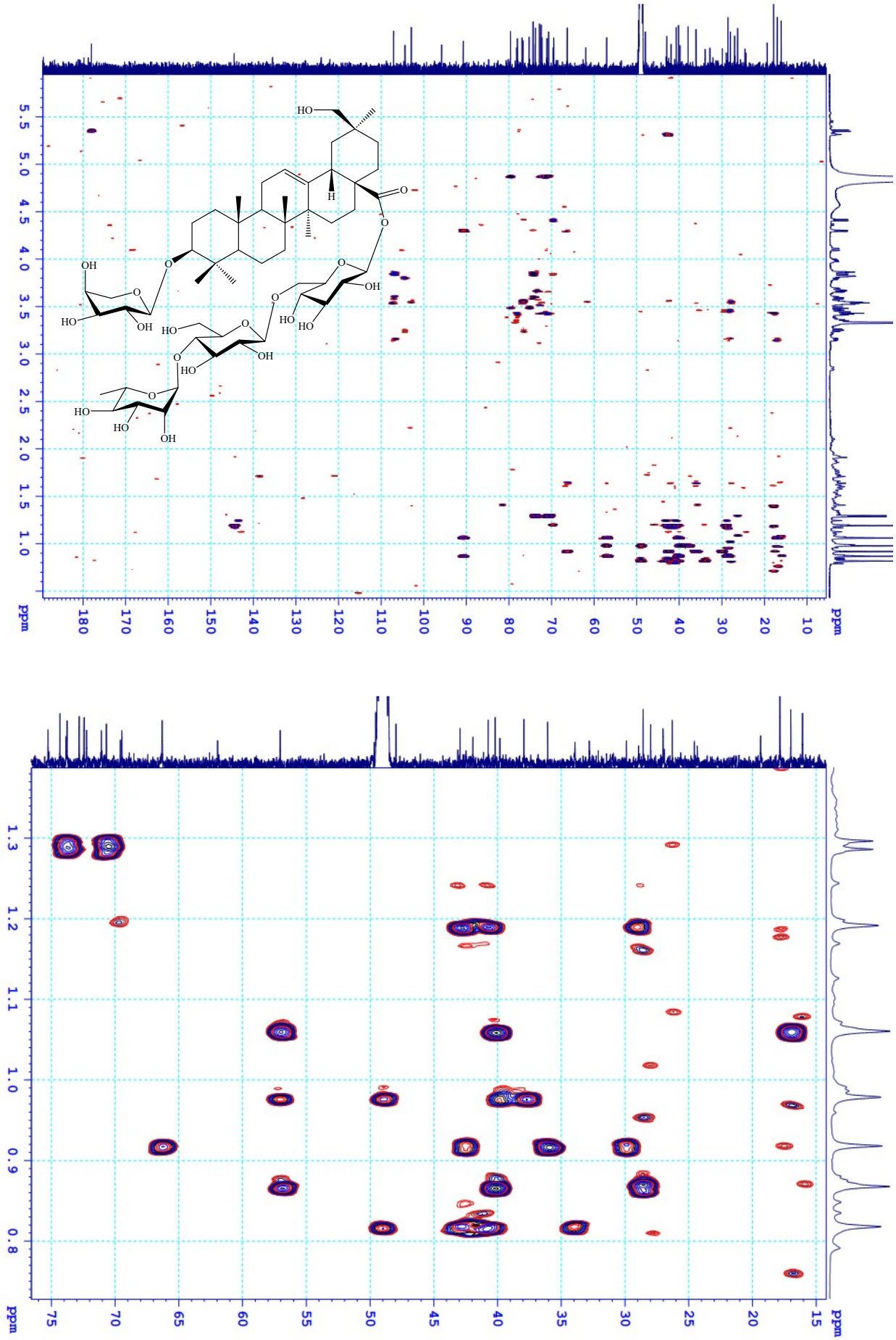


Figure S49. HMBC spectrum of compound **5** in CD_3OD

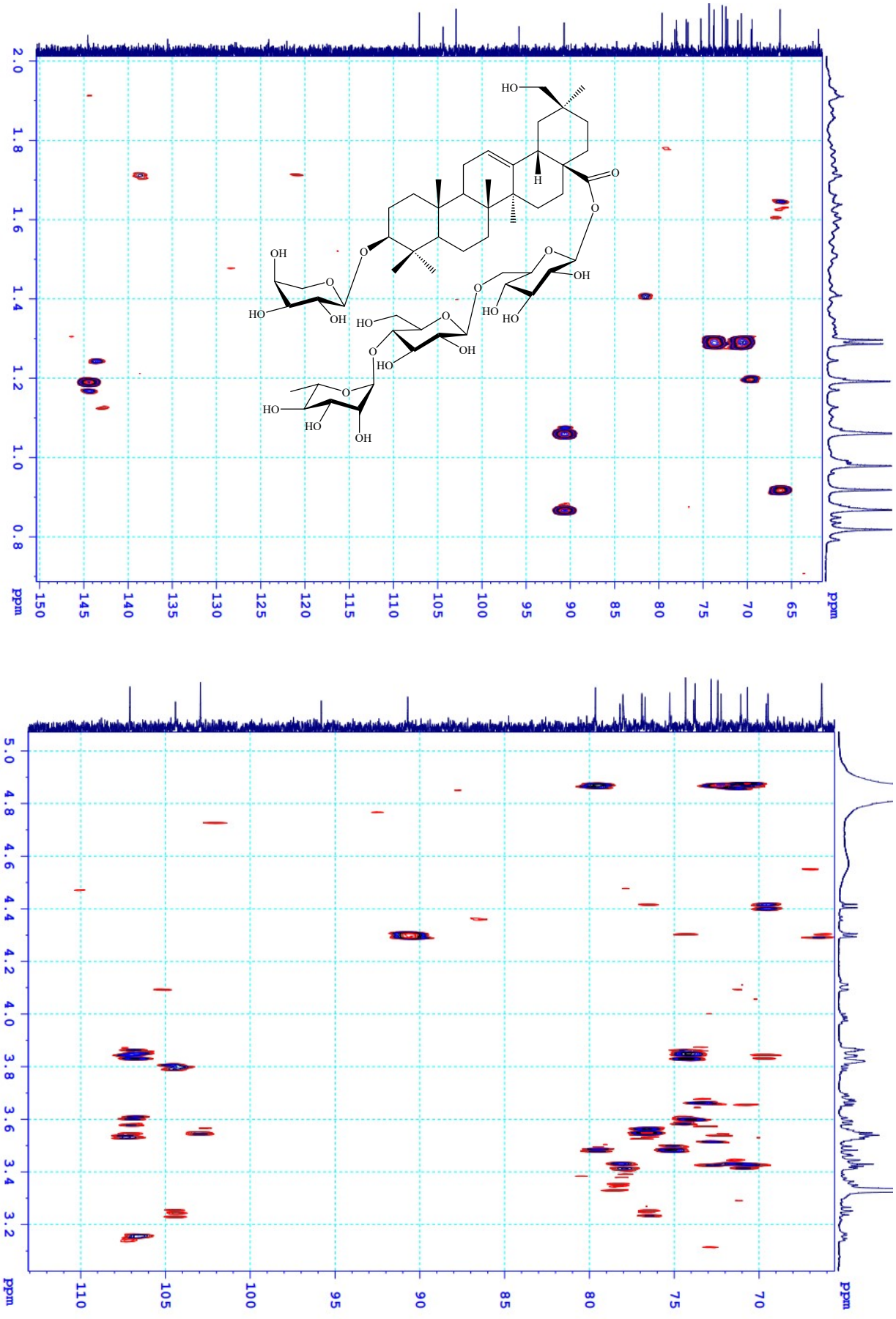


Figure S50. Extended HMBC spectrum of compound **5** in CD_3OD

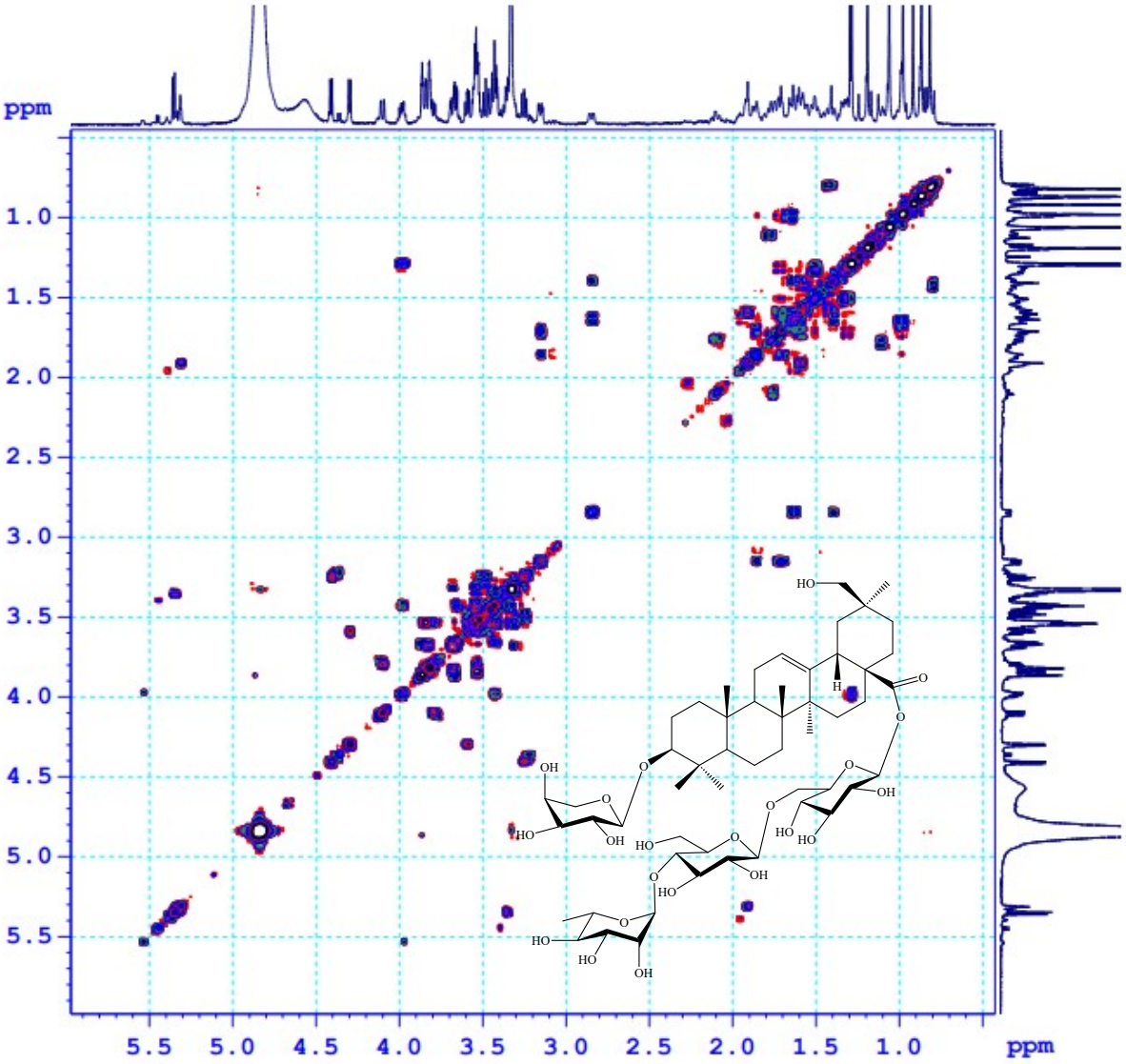


Figure S51. COSY spectrum of compound **5** in CD_3OD

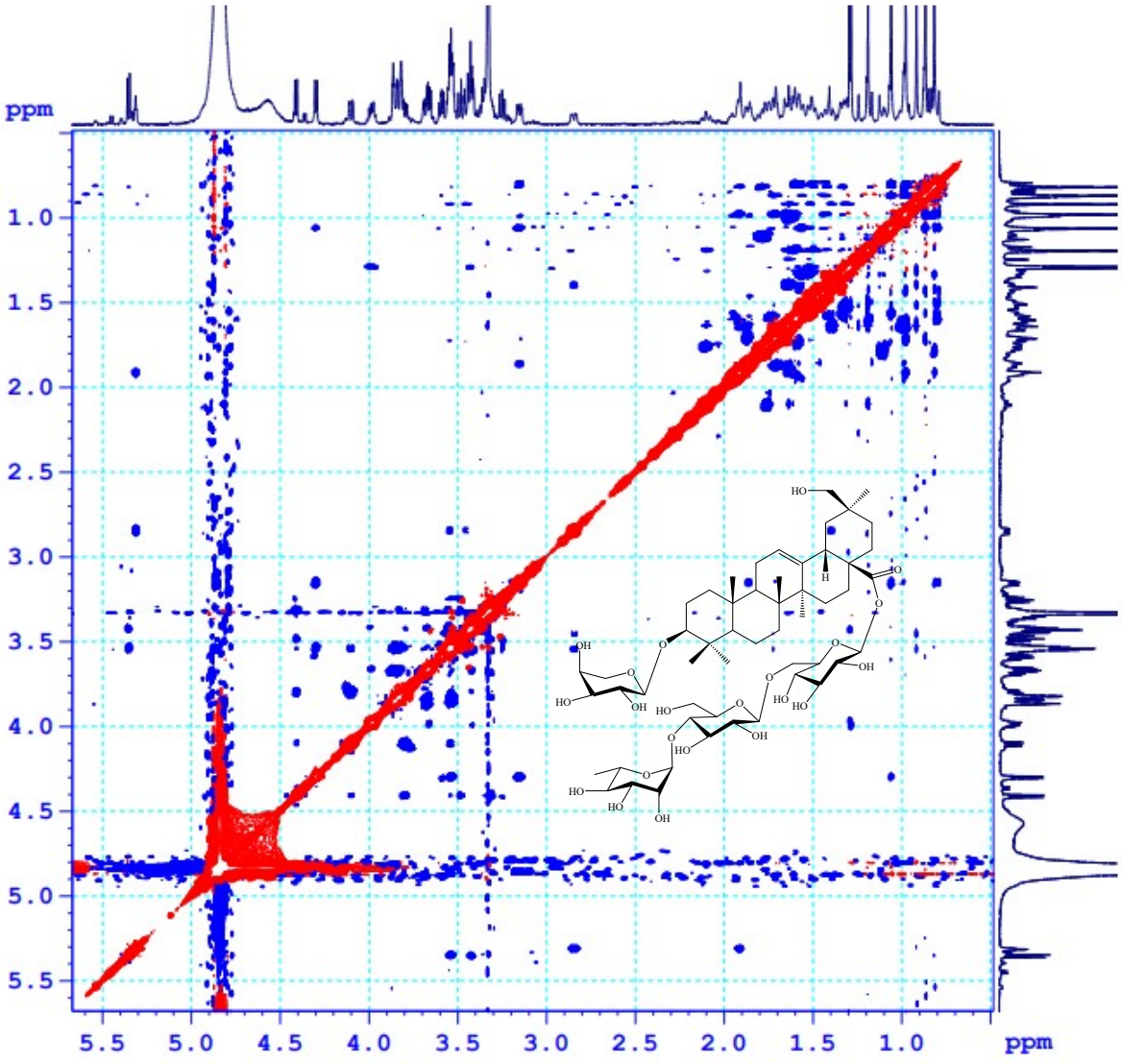


Figure S52. NOESY spectrum of compound **5** in CD_3OD

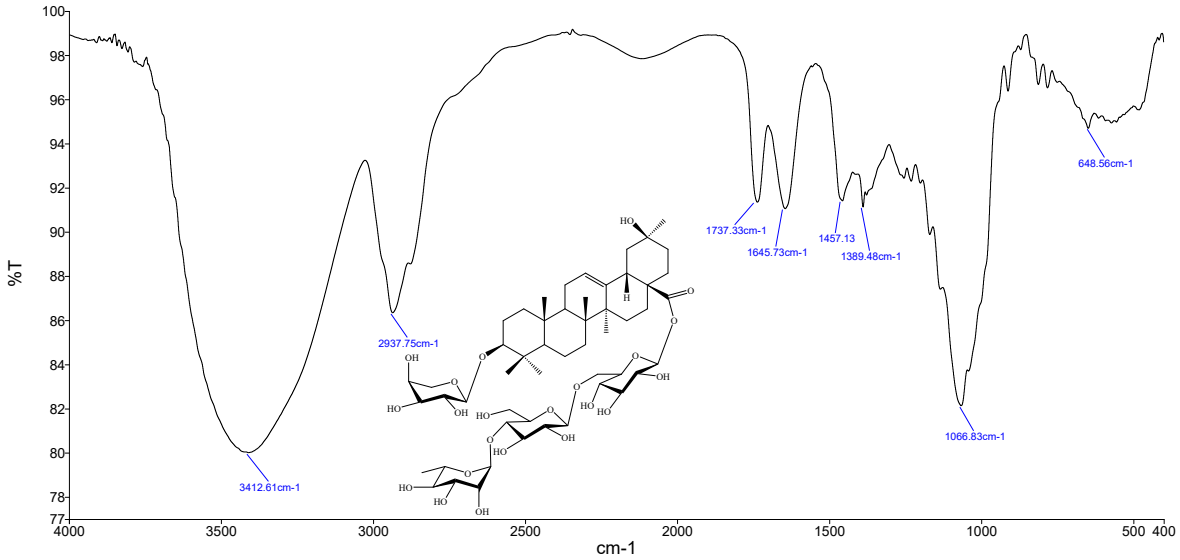
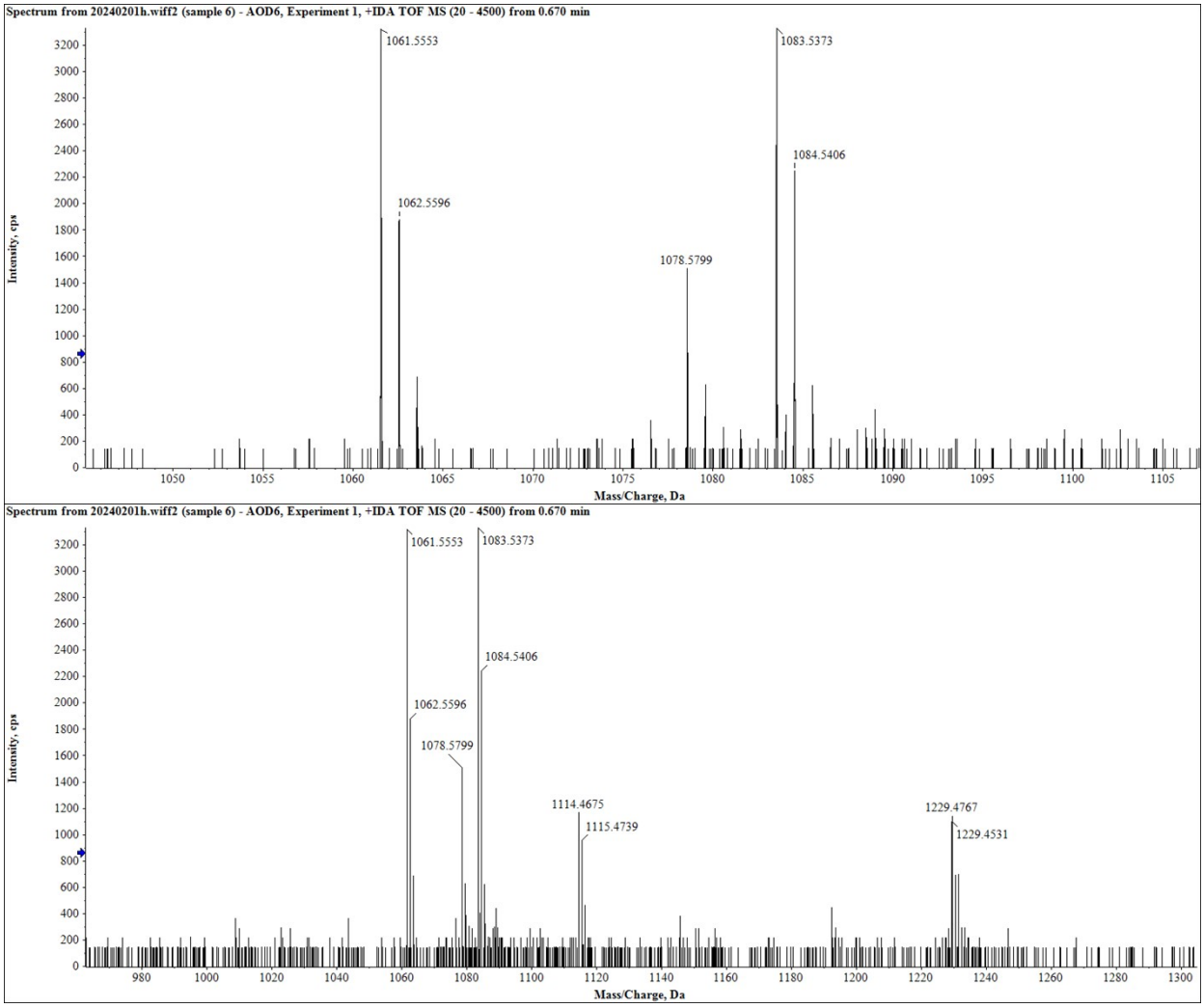


Figure S53. IR spectrum of compound **6**



HR-ESI-MS *m/z* 1061.5553 $[M+H]^+$, (calcd. for $[C_{52}H_{85}O_{22}]^+$, 1061.5527, Δ=+2.5 ppm), *m/z* 1083.5373 $[M+Na]^+$, (calcd. for $[C_{52}H_{84}O_{22}Na]^+$, 1083.5347, Δ=+2.4 ppm)

Figure S54. HR-ESI-MS spectrum of compound **6**

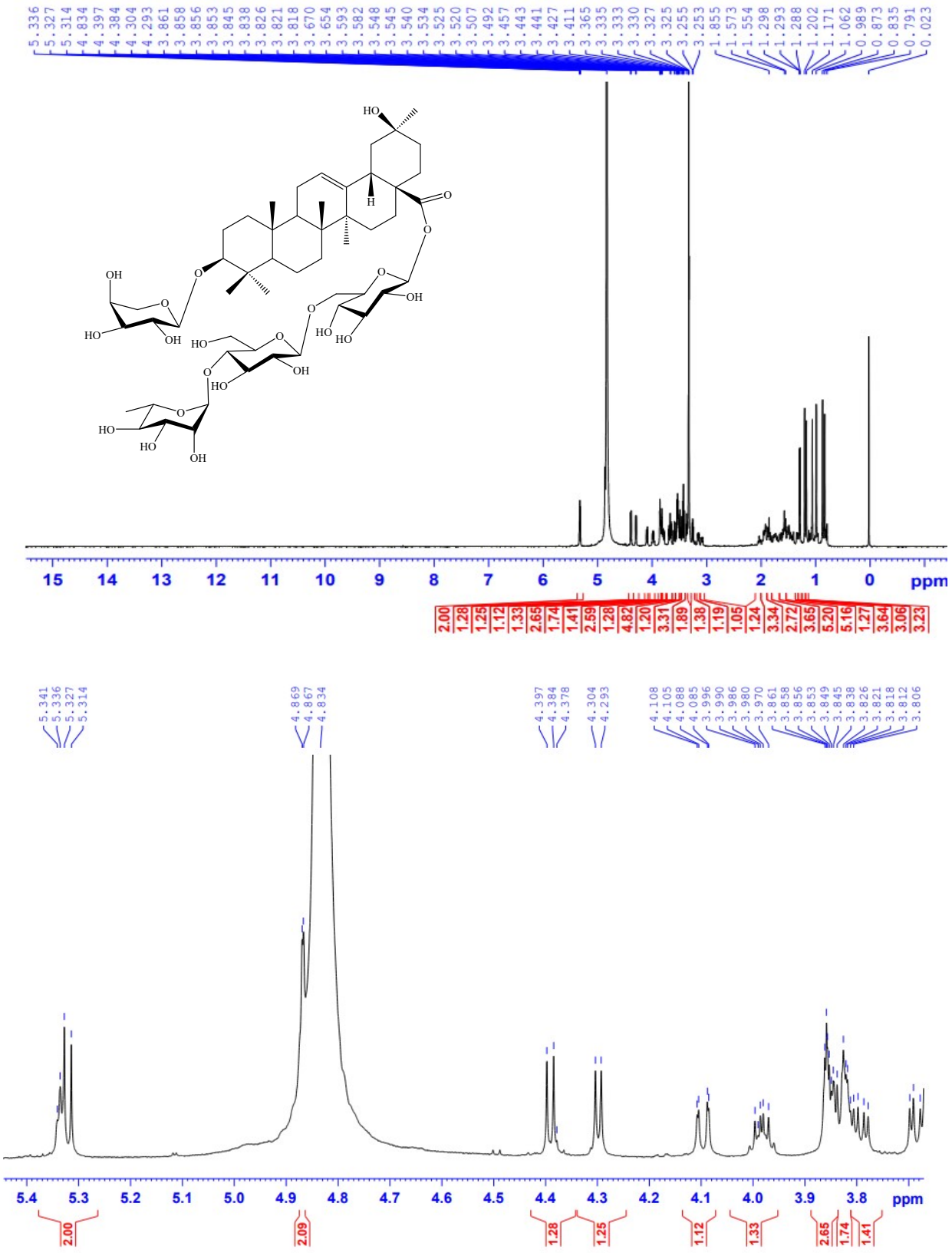


Figure S55. ^{1}H NMR spectrum of compound **6** in CD_3OD

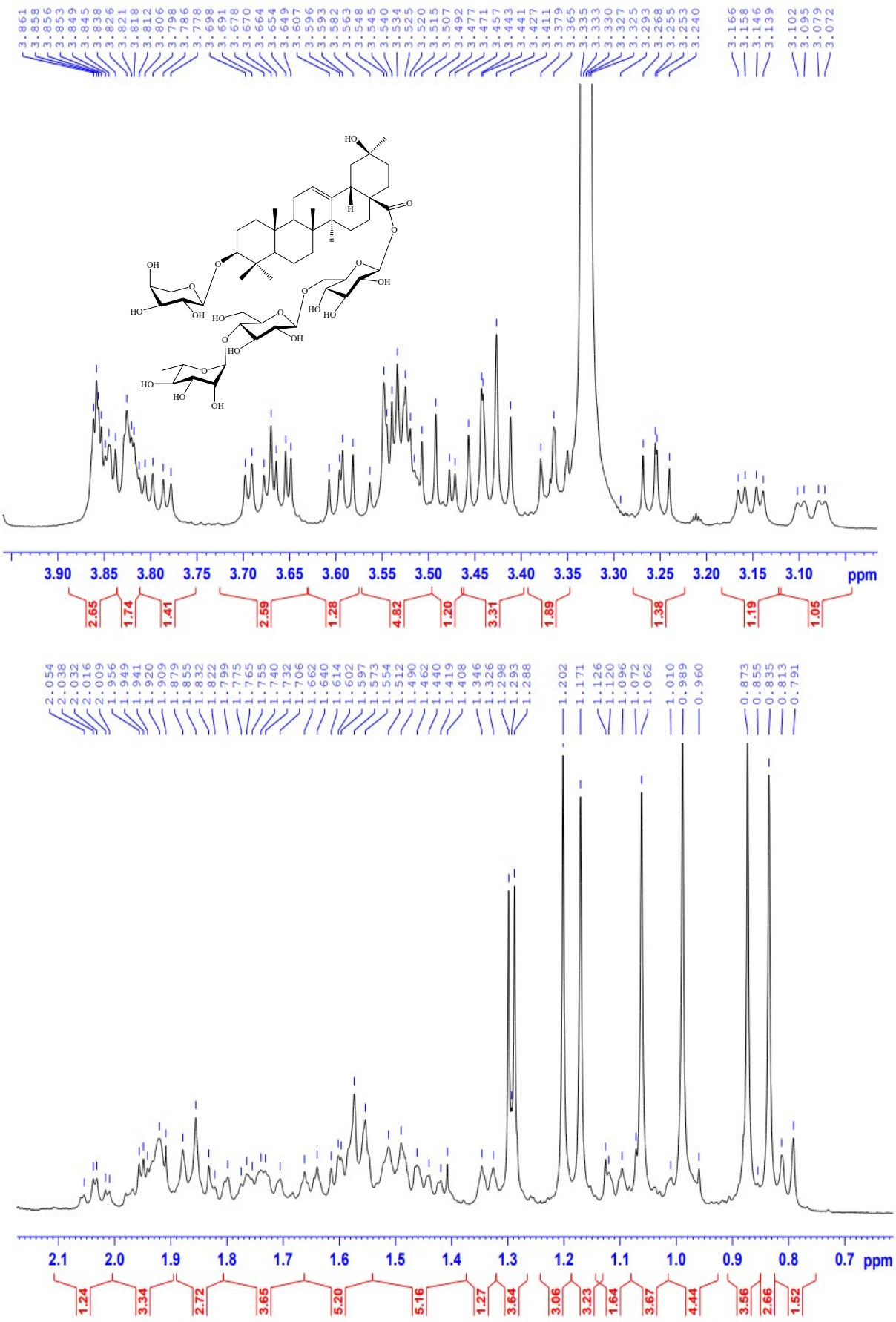
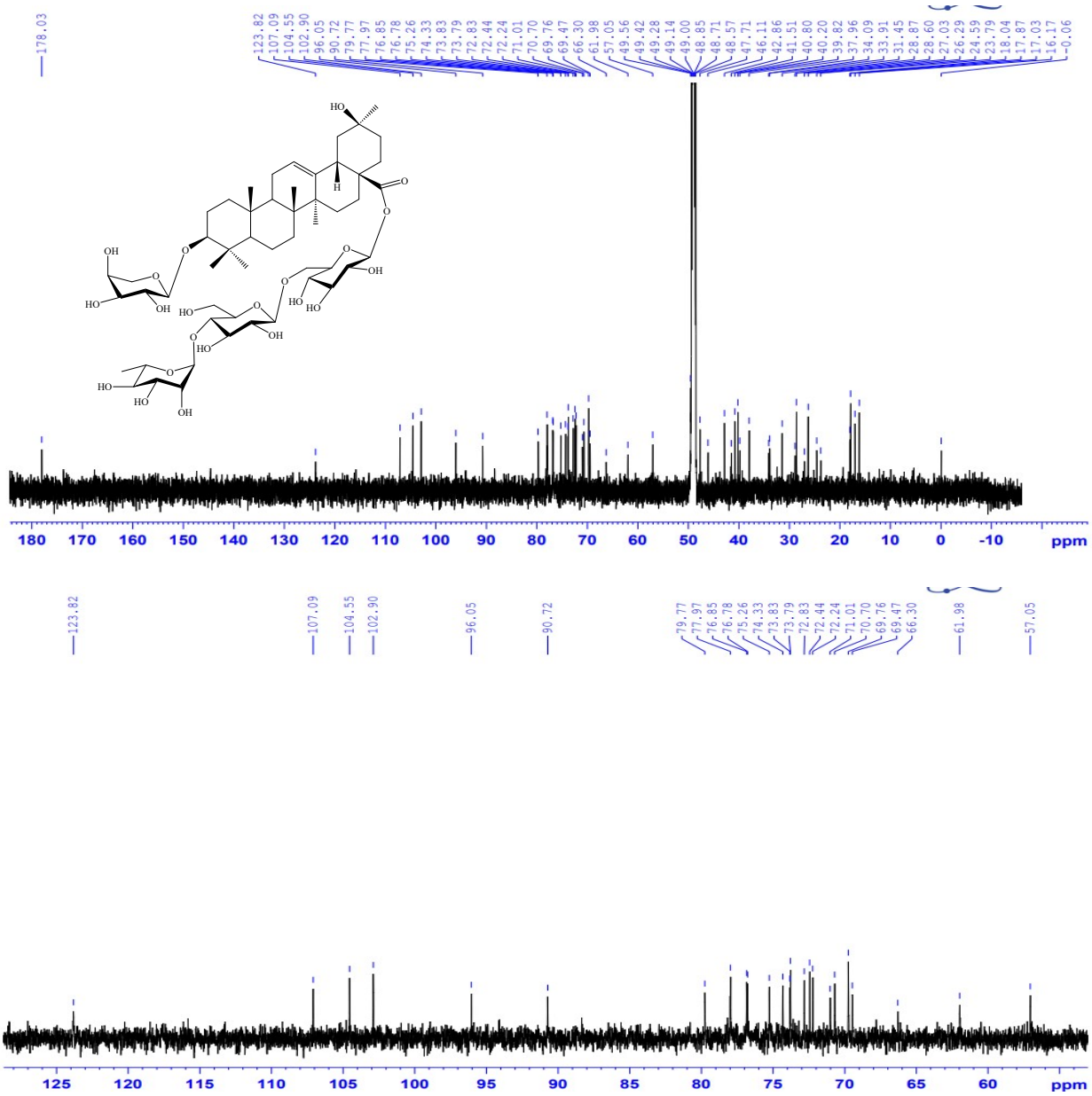


Figure S56. Extended ^{1}H NMR spectrum of compound **6** in CD_3OD


178.03
123.82
107.09
104.55
102.90
96.05
90.72
79.77
77.97
76.85
76.78
75.26
74.33
73.83
73.79
72.83
72.44
72.24
71.01
70.70
69.76
69.47
66.30
61.98
57.05
49.56
49.42
49.28
49.14
49.00
48.85
48.71
48.57
47.71
46.11
42.86
41.51
40.80
40.20
39.82
37.96
34.09
33.91
31.45
28.87
28.60
27.03
26.29
24.59
23.79
18.04
17.87
17.03
16.17
0.06
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

123.82
107.09
104.55
102.90
96.05
90.72
79.77
77.97
76.85
76.78
75.26
74.33
73.83
73.79
72.83
72.44
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69.76
69.47
66.30
61.98
57.05
125 120 115 110 105 100 95 90 85 80 75 70 65 60 ppm

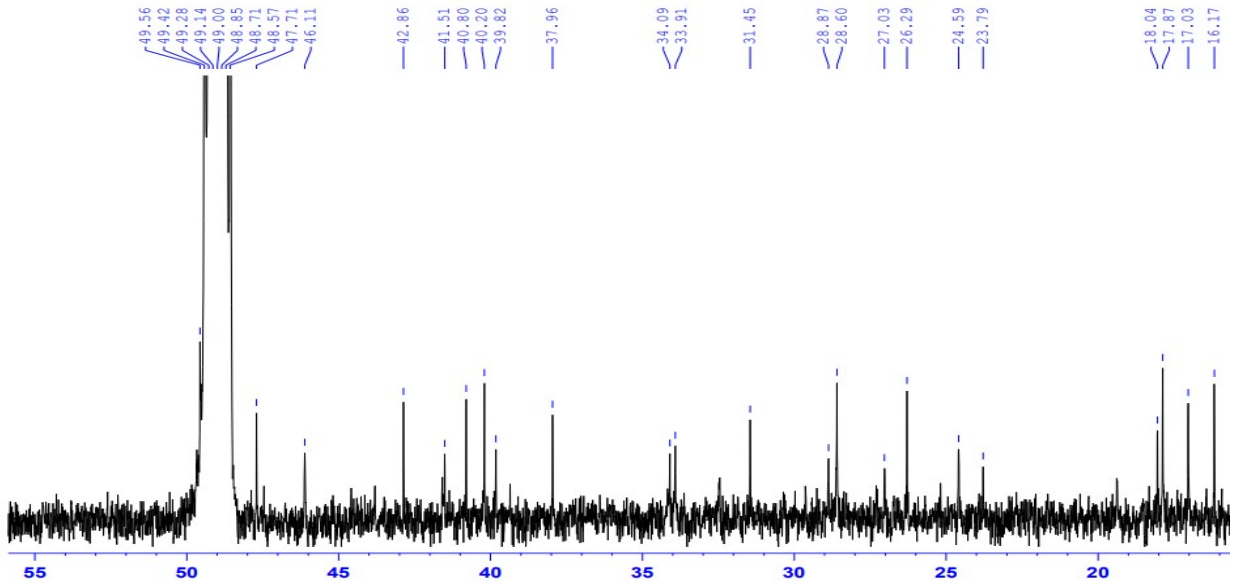
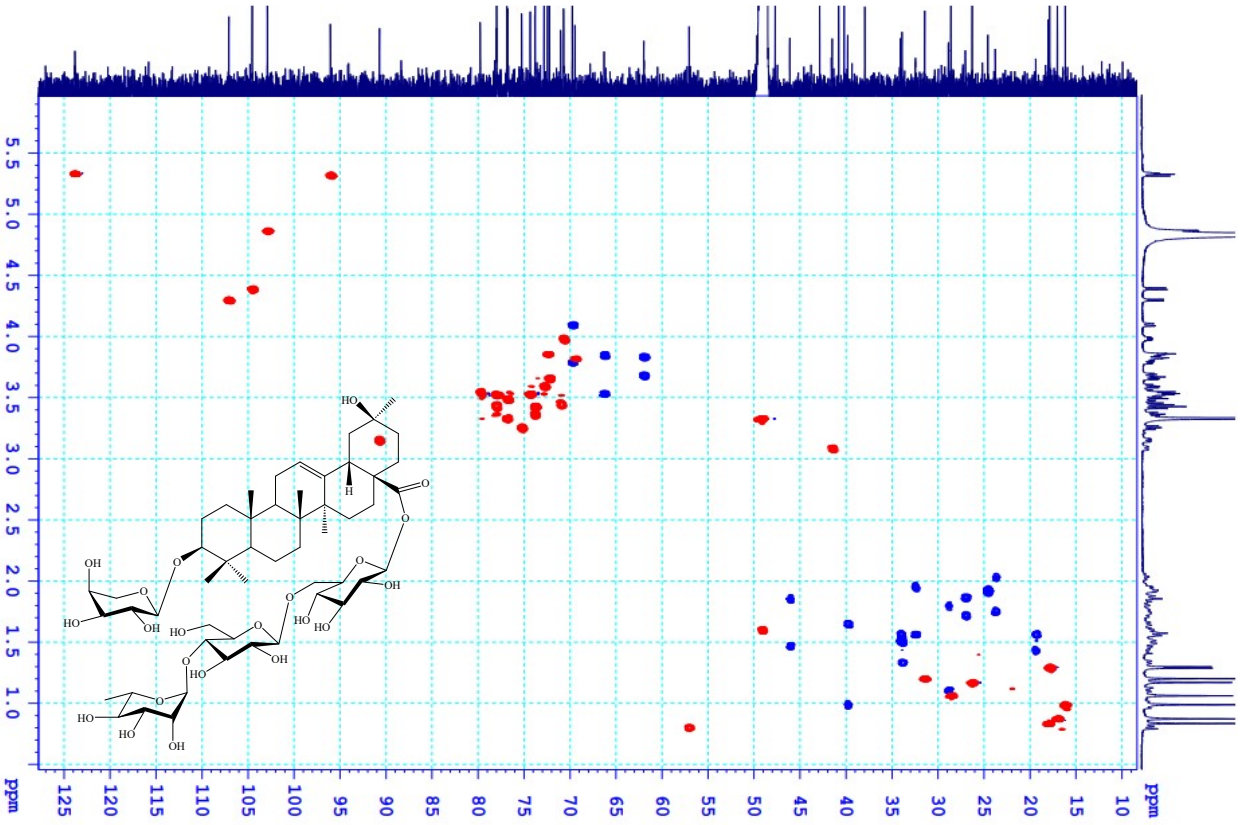


Figure S57. ^{13}C NMR spectrum of compound **6** in CD_3OD



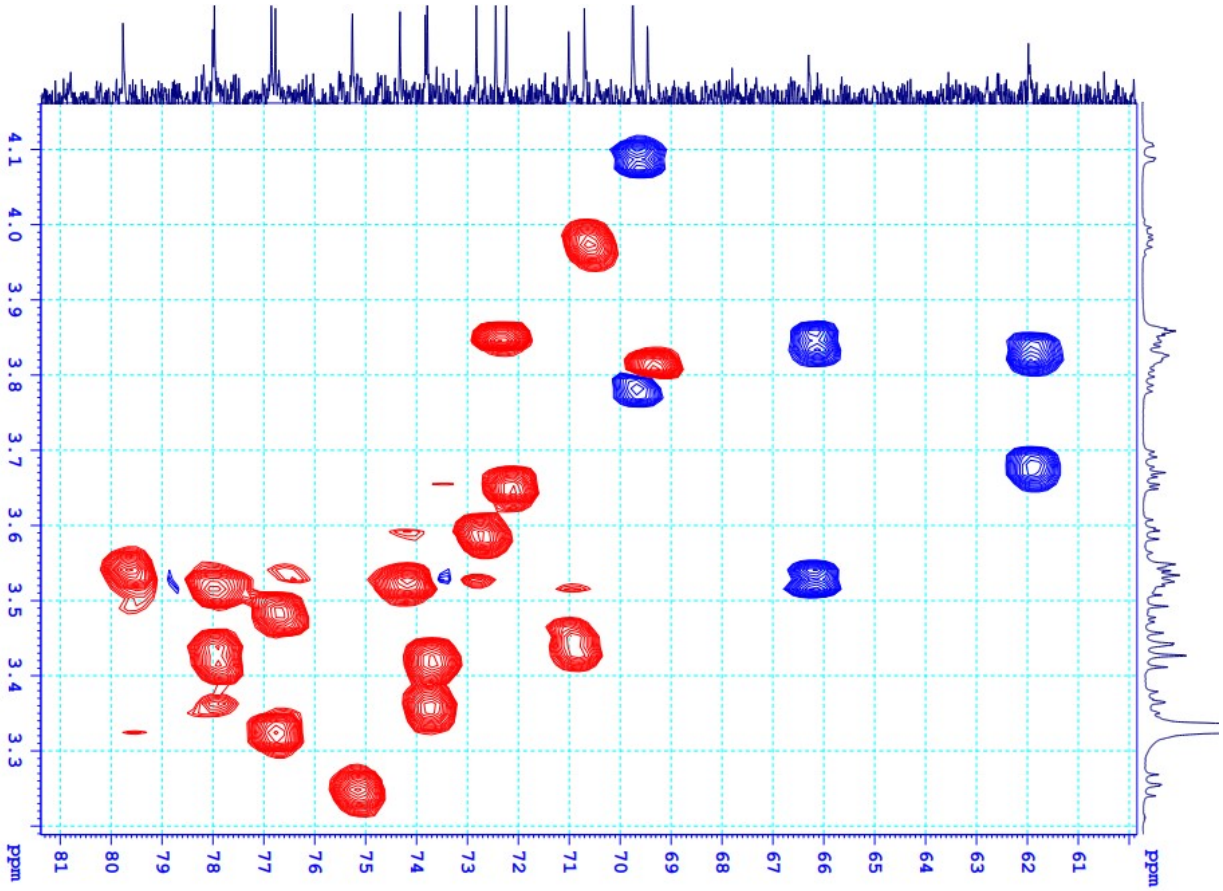


Figure S58. HSQC spectrum of compound **6** in CD_3OD

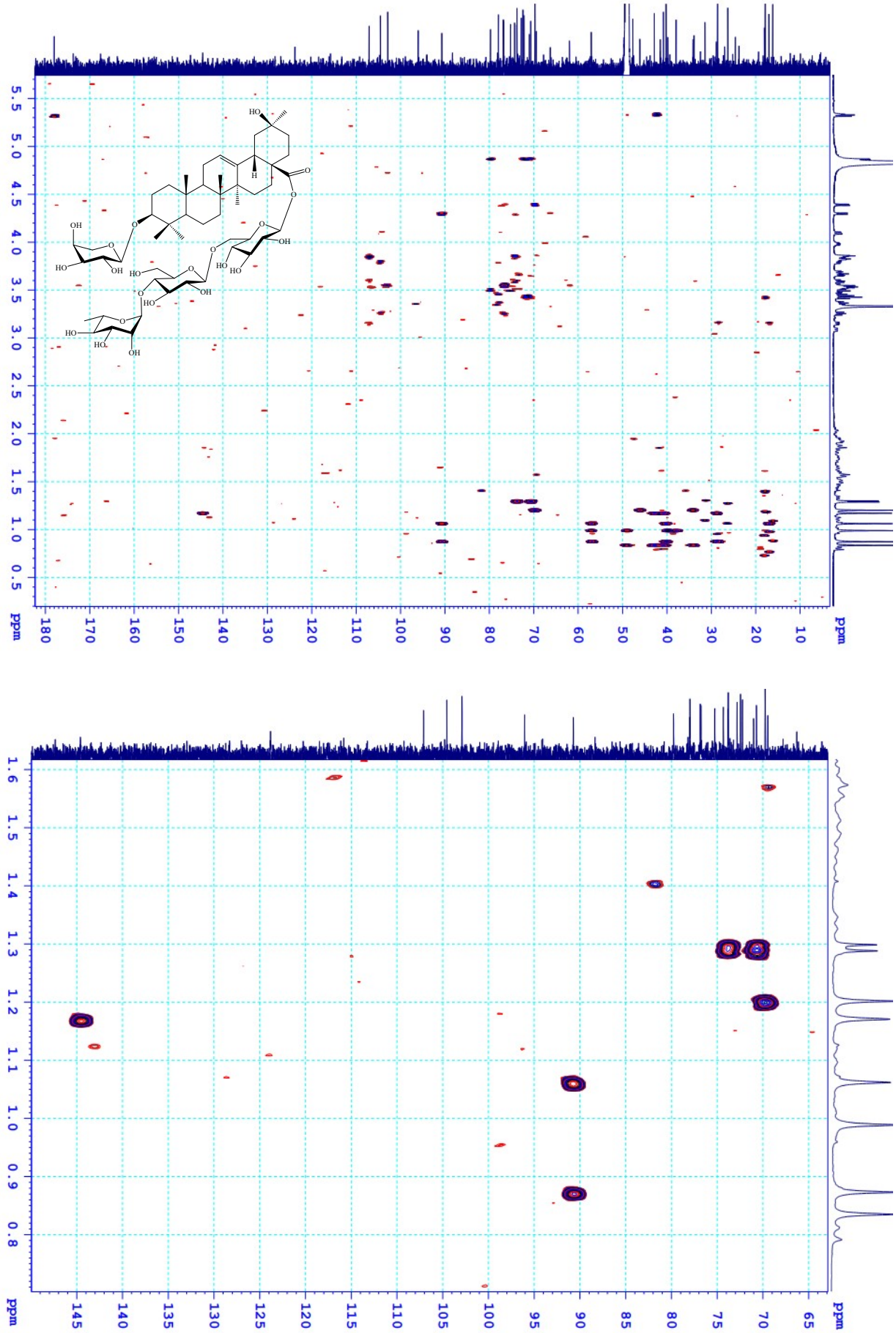
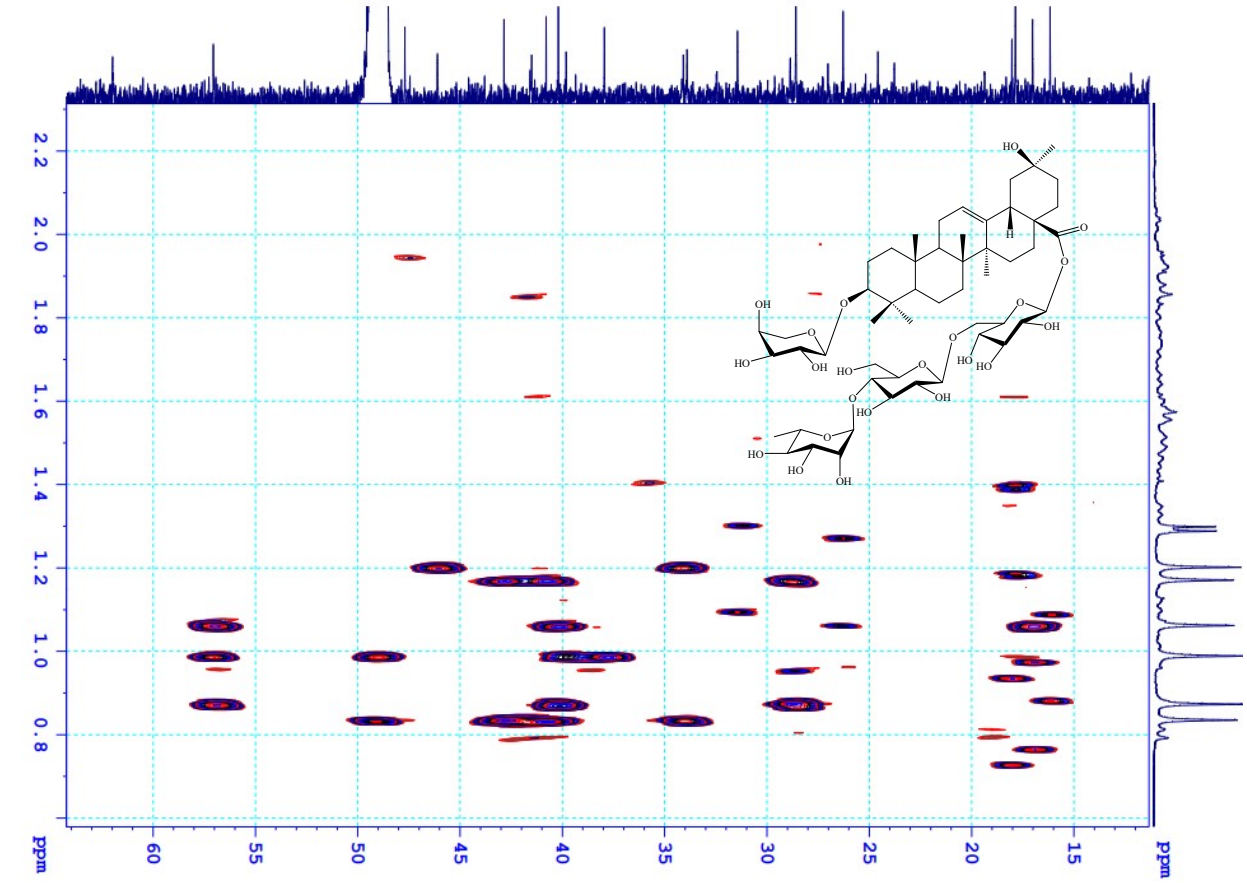


Figure S59. HMBC spectrum of compound **6** in CD_3OD


ppm
ppm

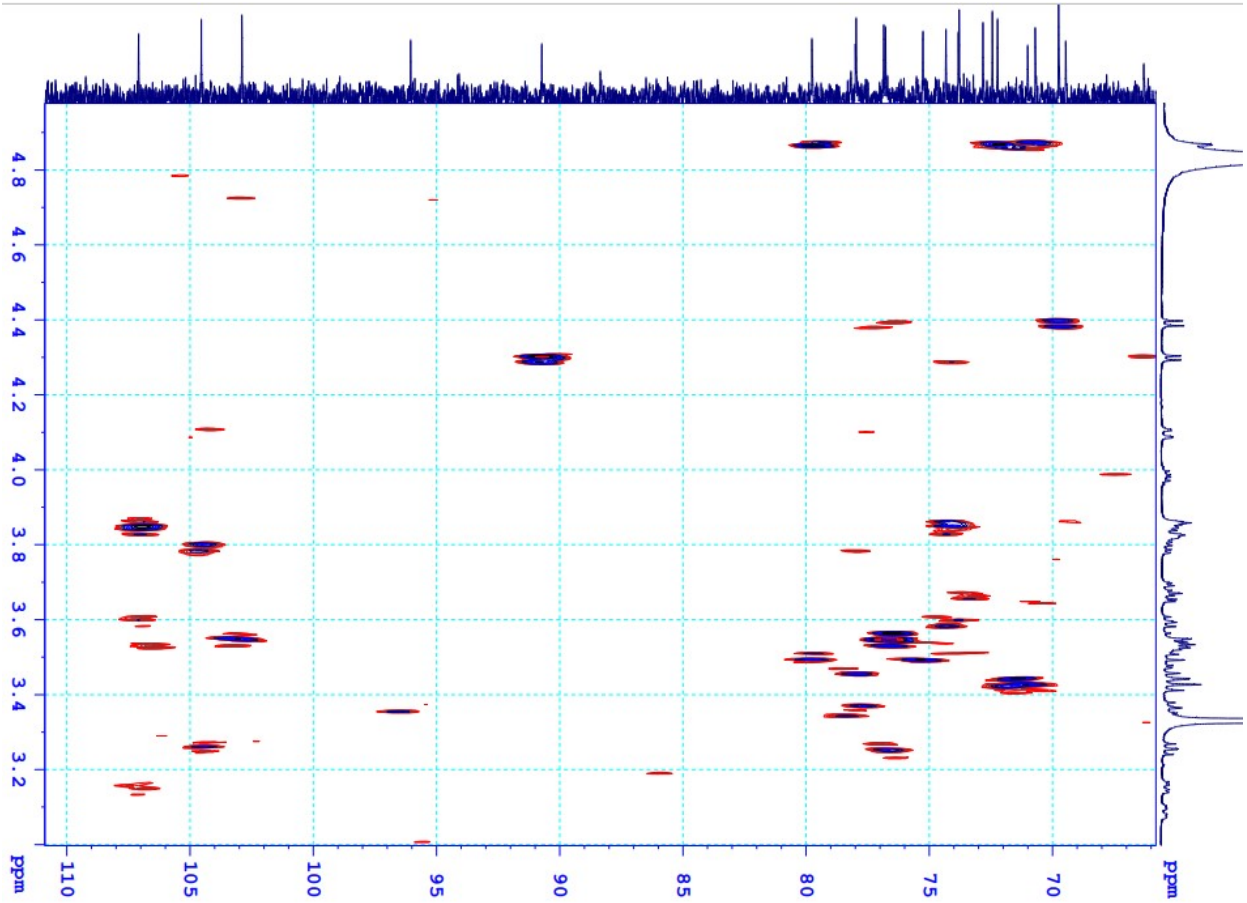

ppm
ppm

Figure S60. Extended HMBC spectrum of compound **6** in CD_3OD

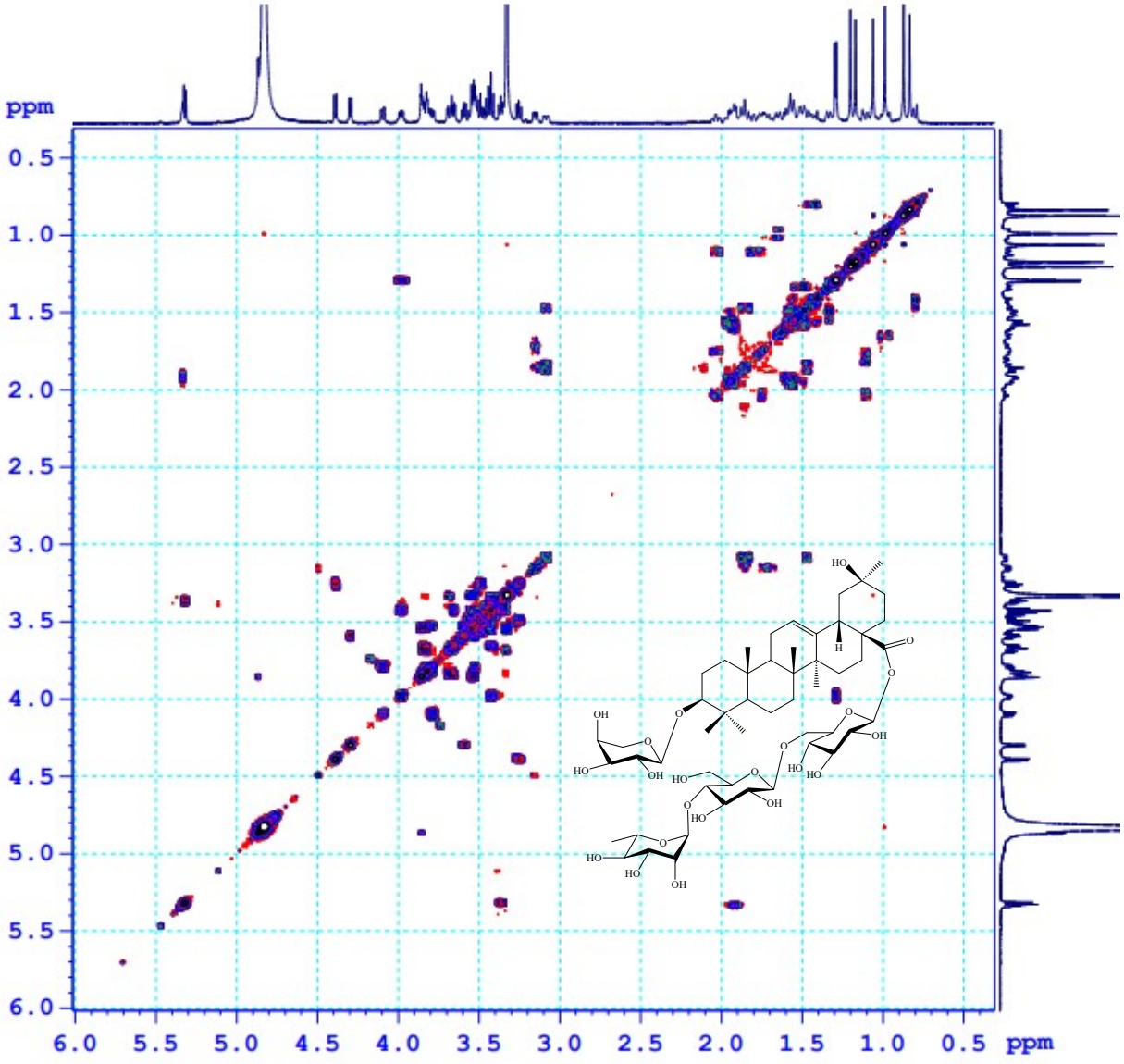


Figure S61. COSY spectrum of compound **6** in CD_3OD

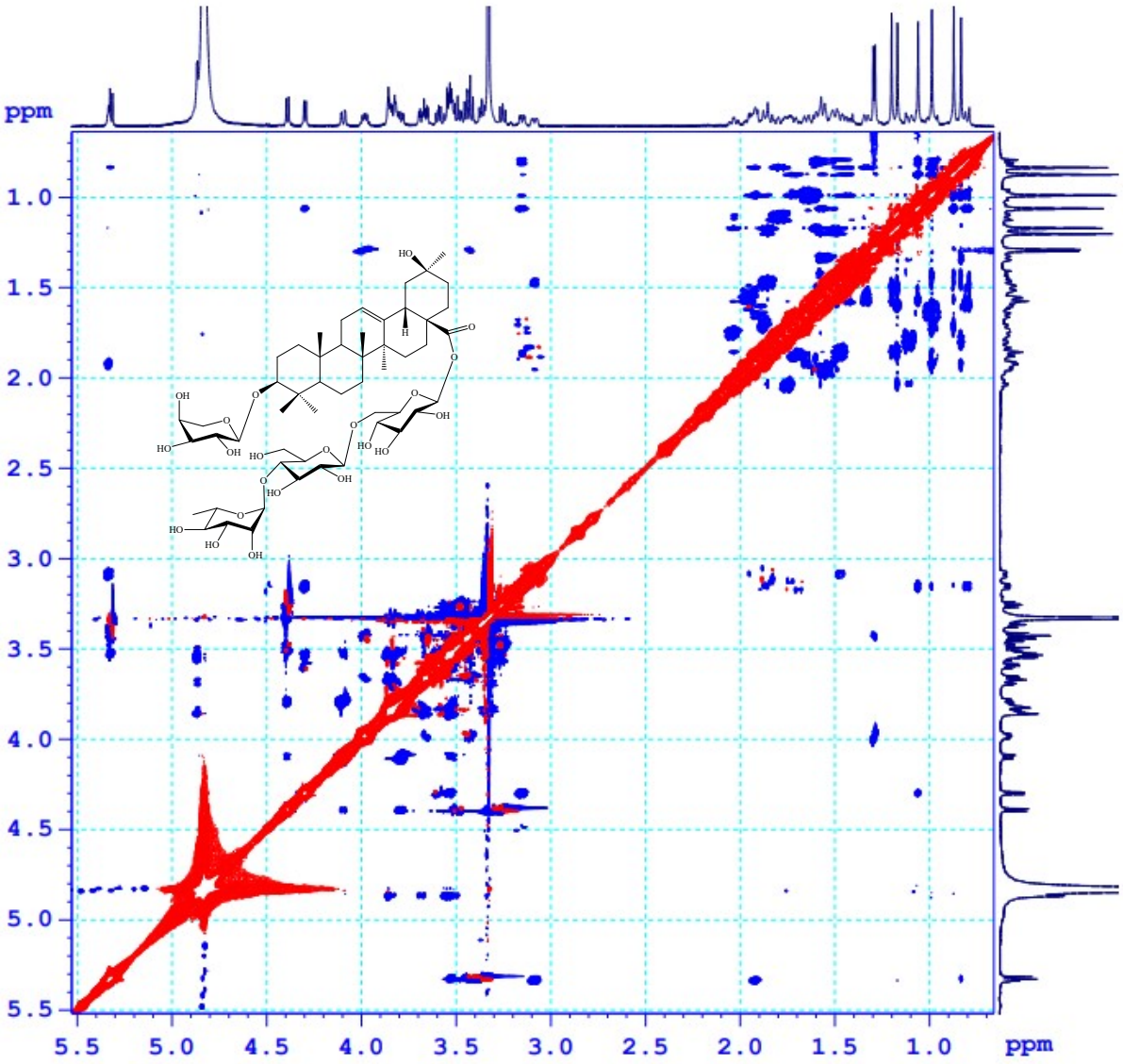


Figure S62. NOESY spectrum of compound **6** in CD_3OD

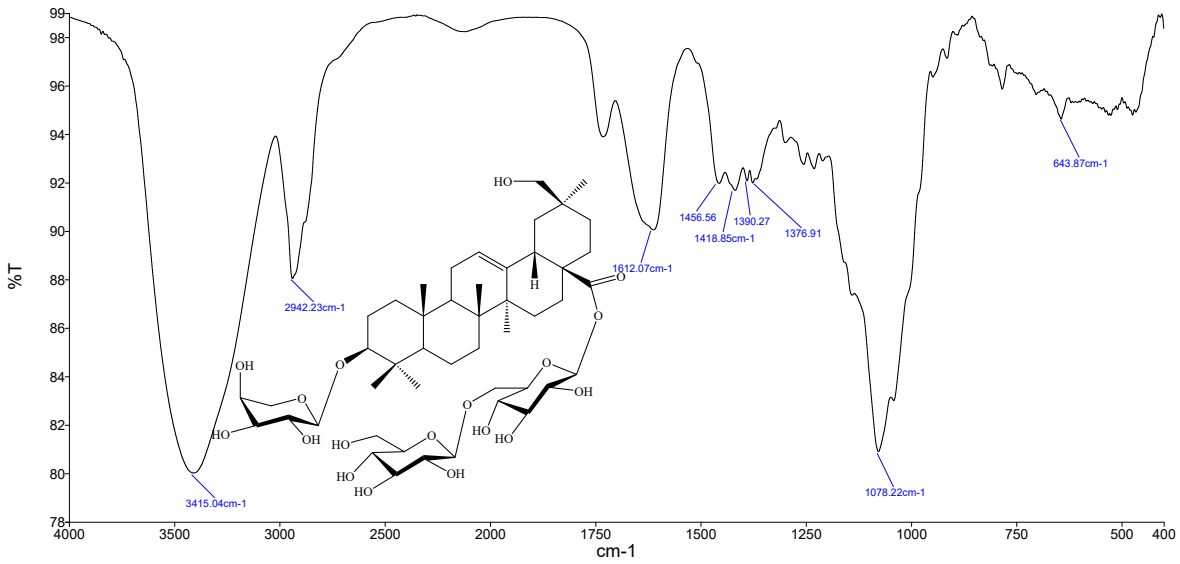
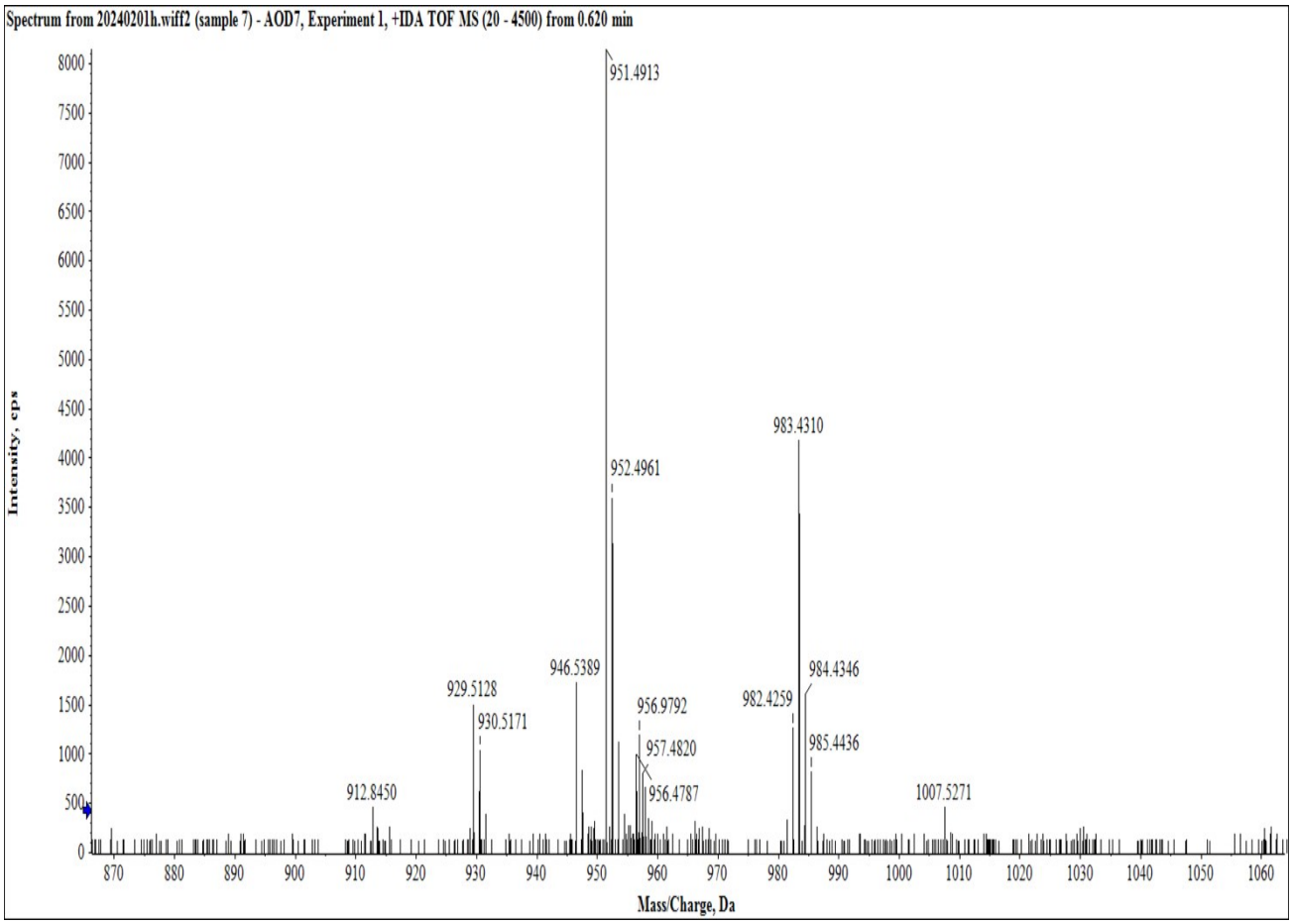


Figure S63. IR spectrum of compound **7**



HR-ESI-MS *m/z* 929.5128 $[M+H]^+$, (calcd. for $[C_{47}H_{77}O_{18}]^+$, 929.5105, Δ=+2.5 ppm), *m/z* 951.4913 $[M+Na]^+$, (calcd. for $[C_{47}H_{76}O_{18}Na]^+$, 951.4924, Δ=-1.7 ppm

Figure S64. HR-ESI-MS spectrum of compound **7**

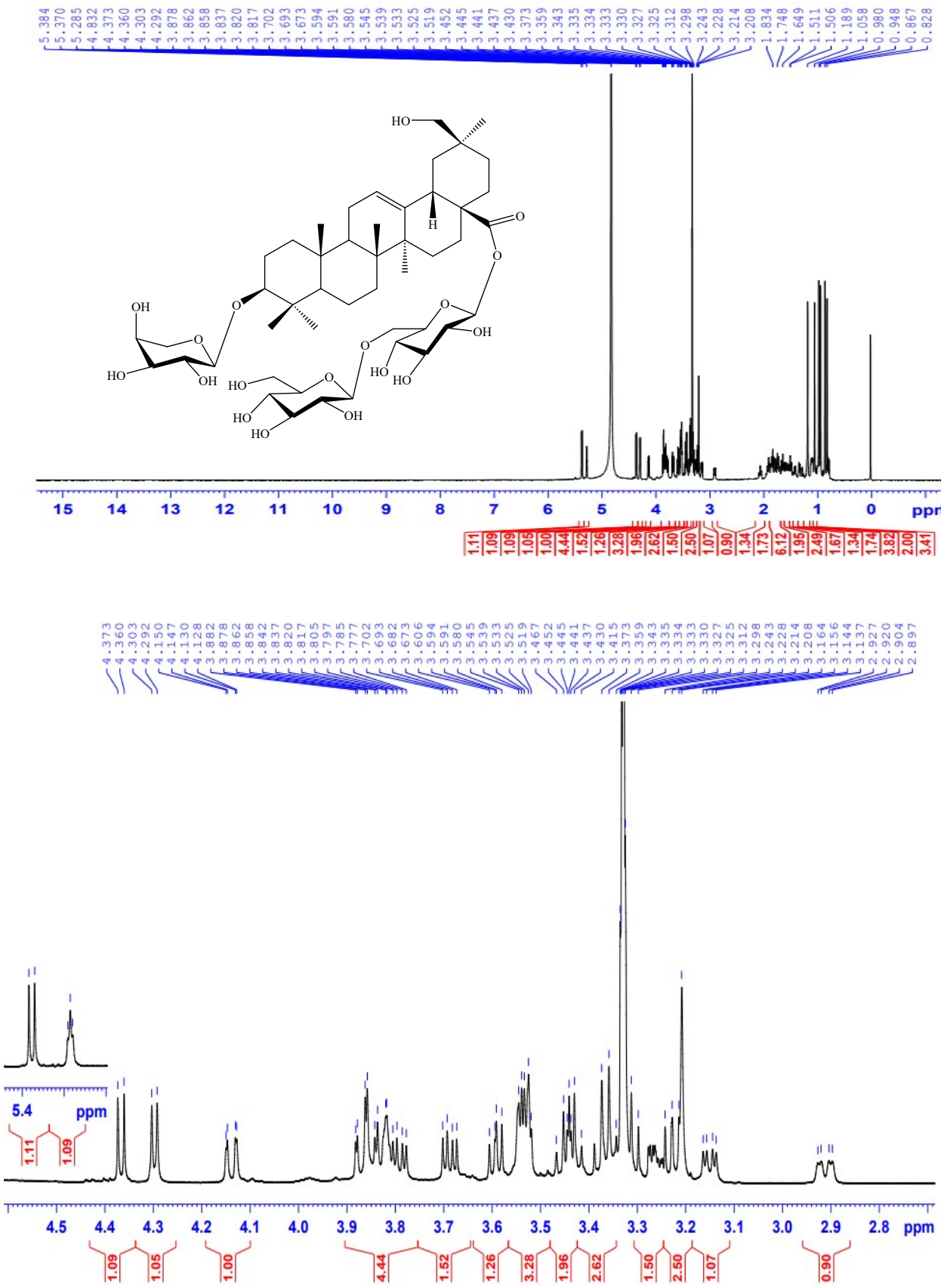


Figure S65. ^{1}H NMR spectrum of compound **7** in CD_3OD

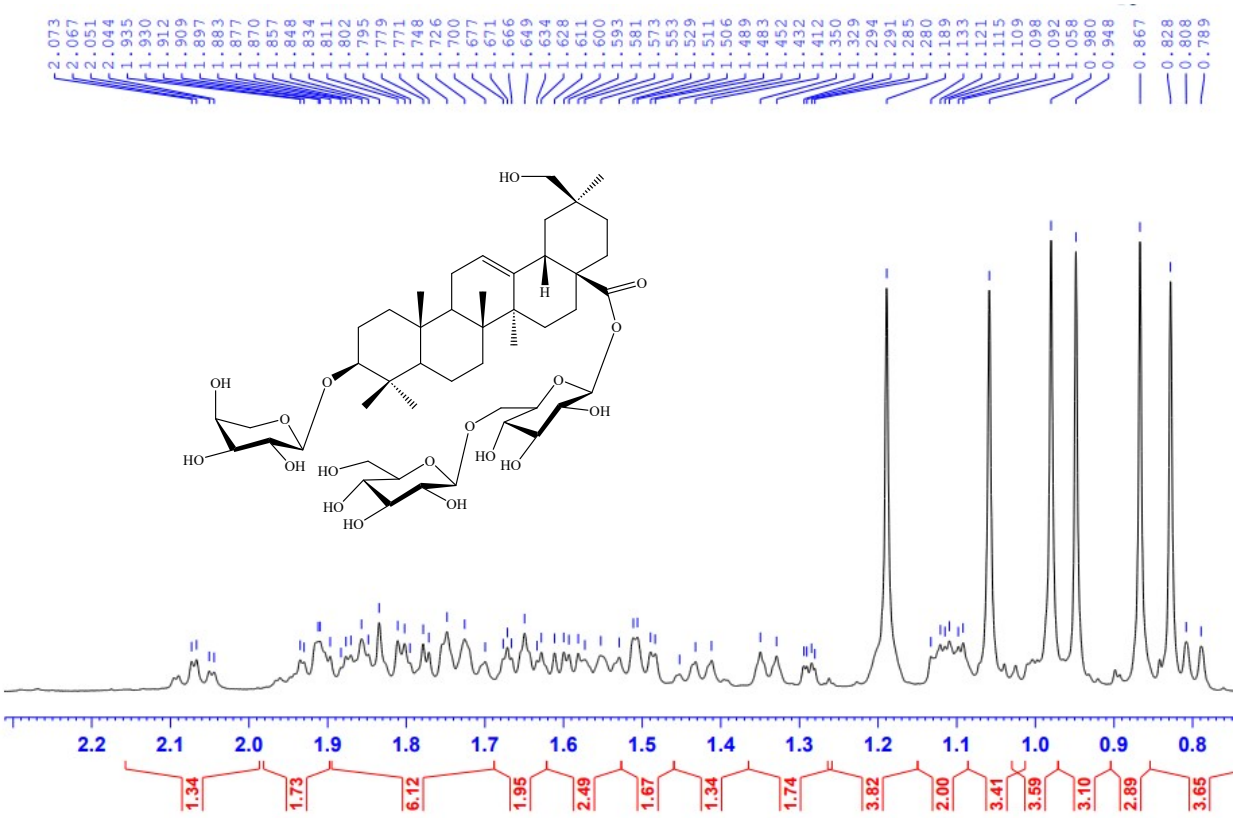


Figure S66. Extended ^{1}H NMR spectrum of compound **7** in CD_3OD

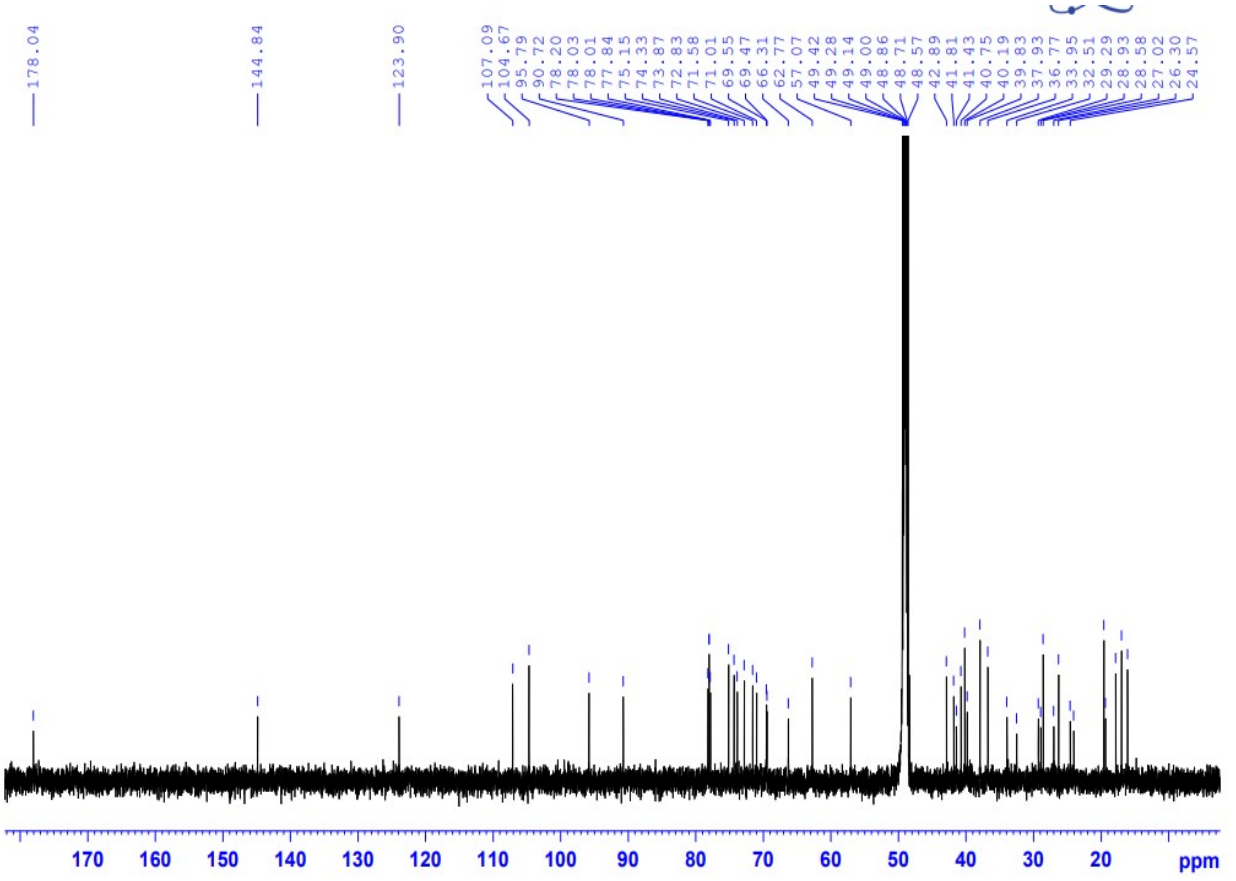


Figure S67. ^{13}C NMR spectrum of compound **7** in CD_3OD

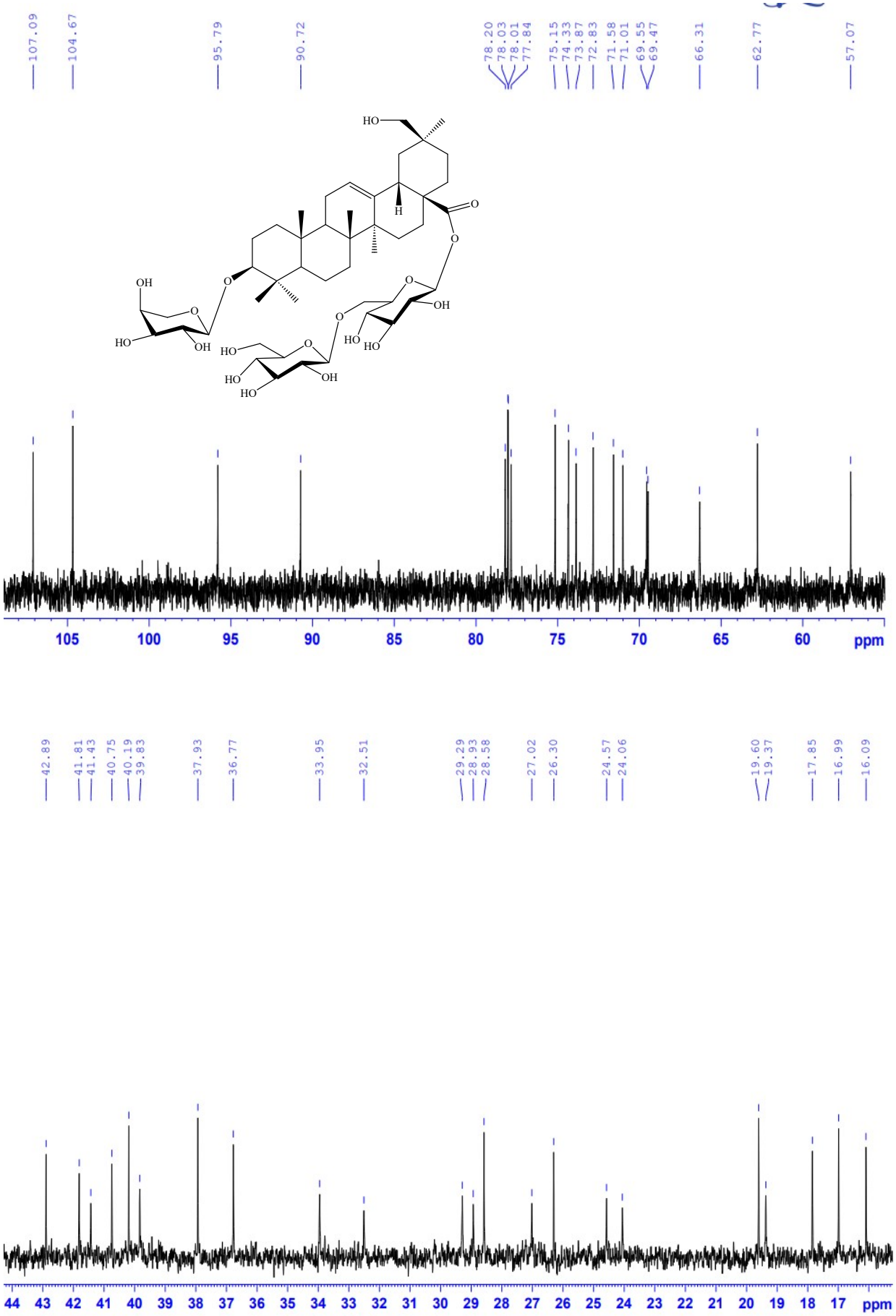
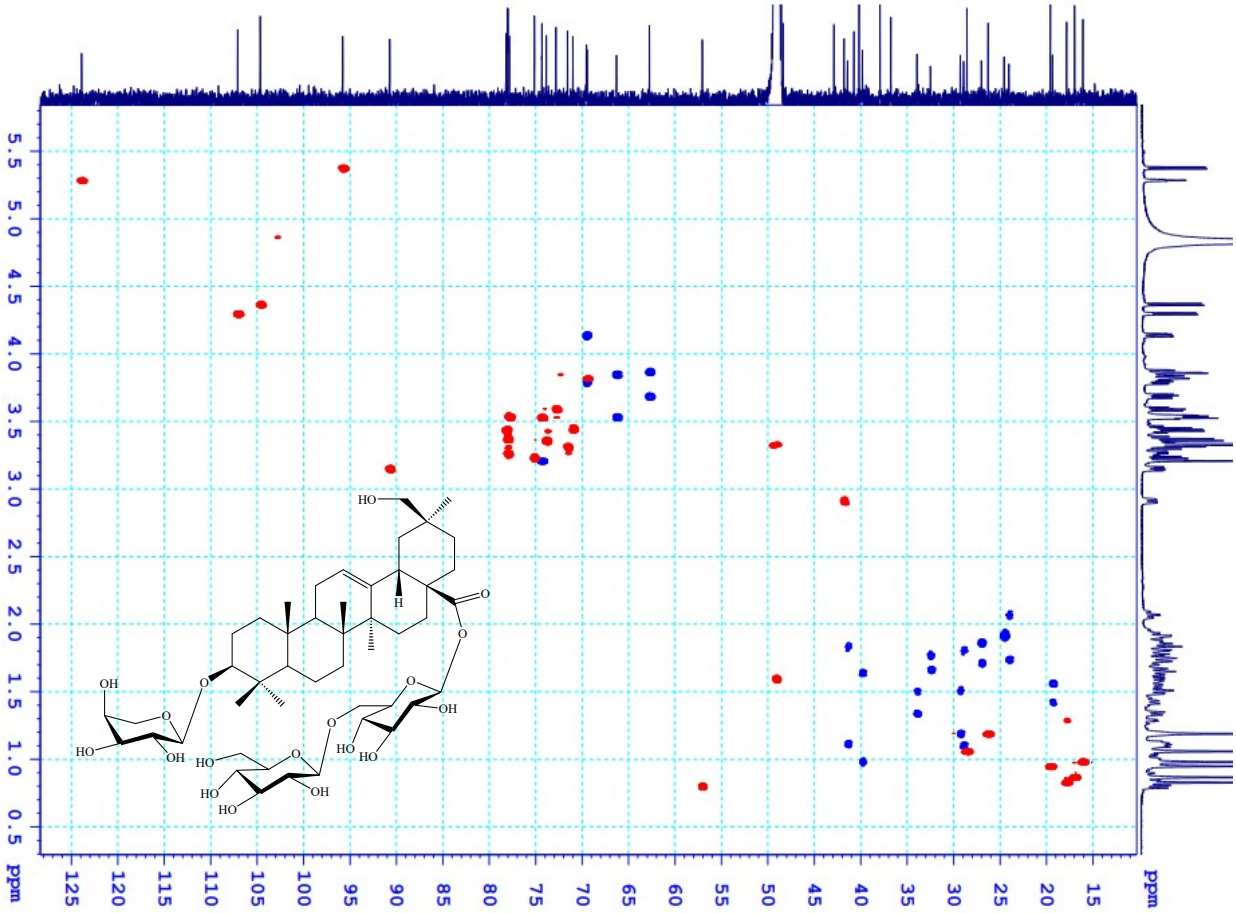


Figure S68. Extended ^{13}C NMR spectrum of compound **7** in CD_3OD


ppm
ppm

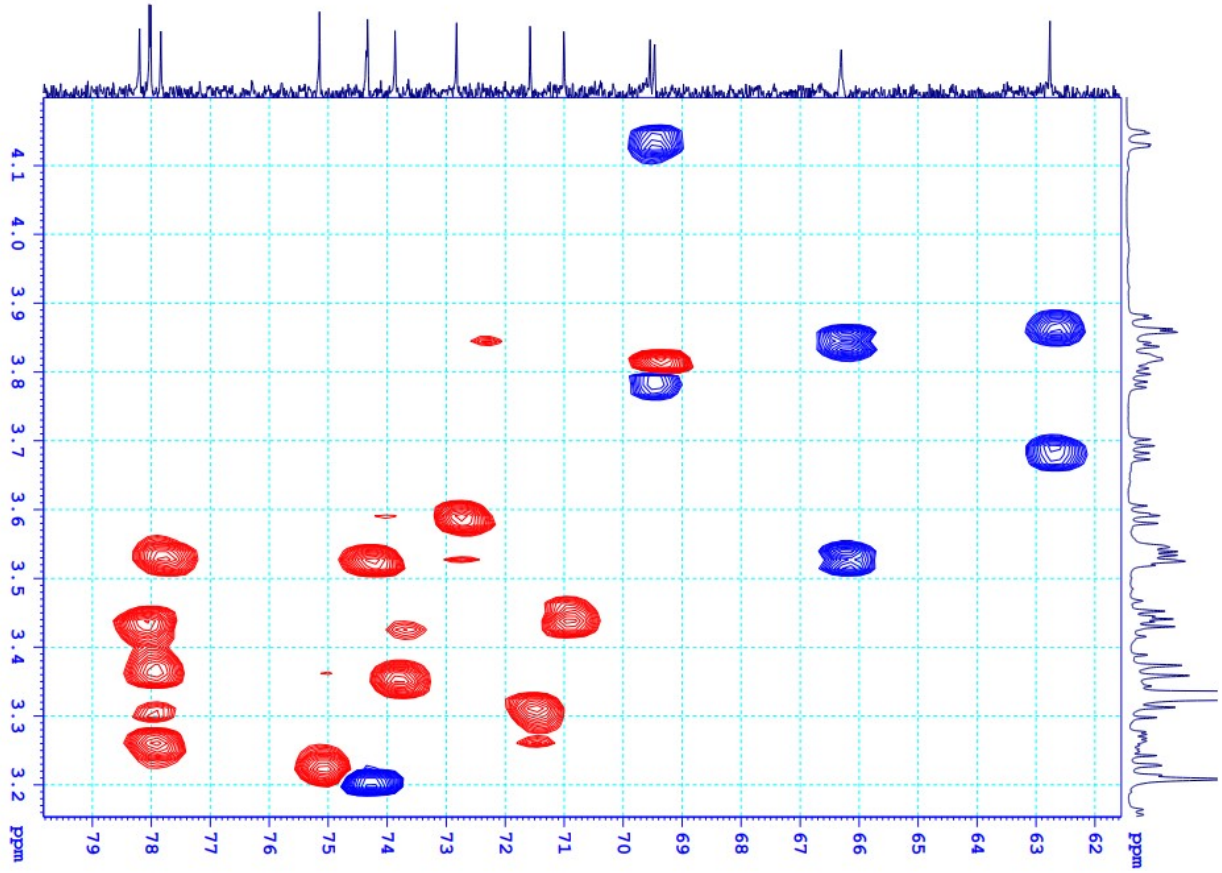

ppm
ppm

Figure S69. HSQC spectrum of compound **7** in CD_3OD

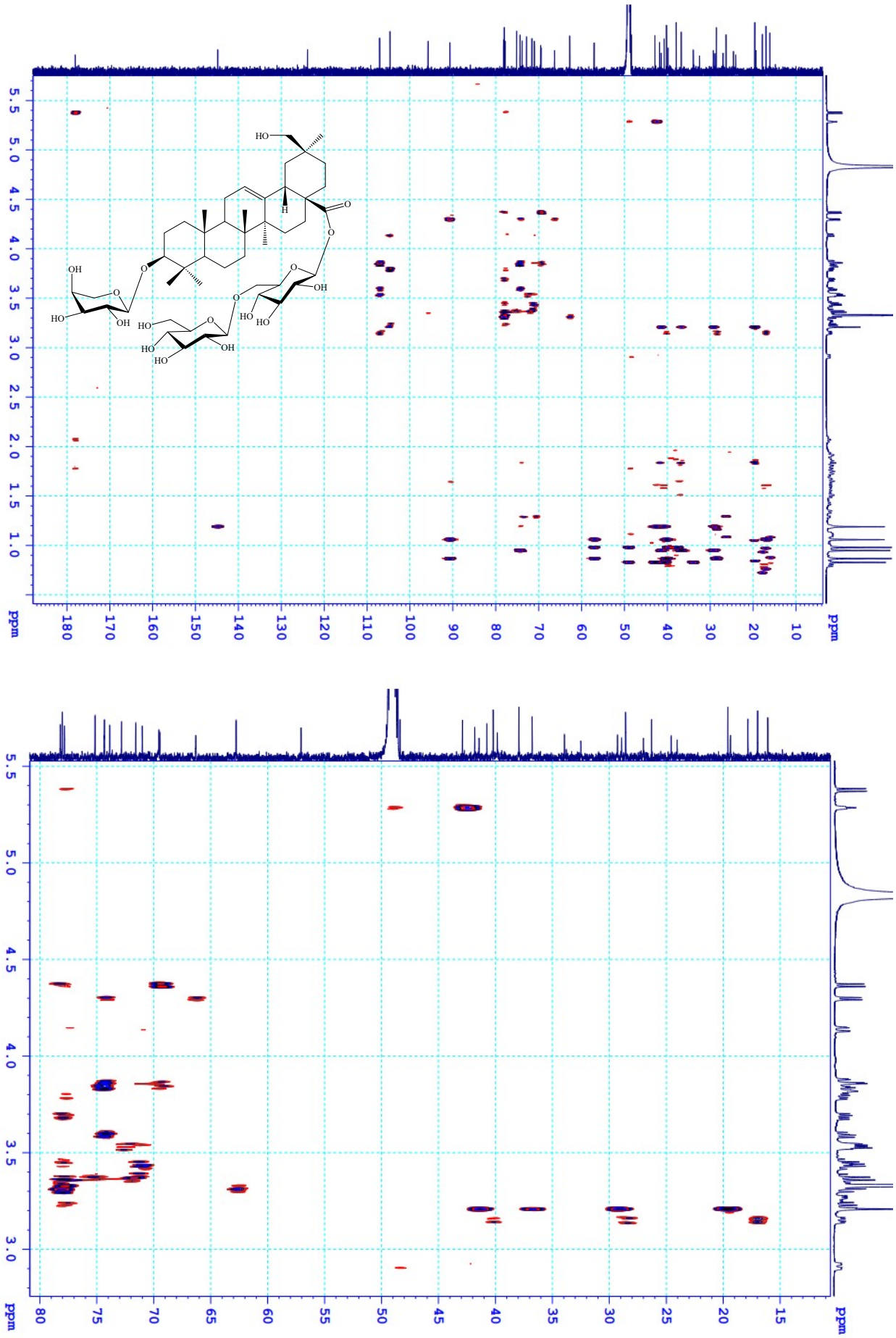
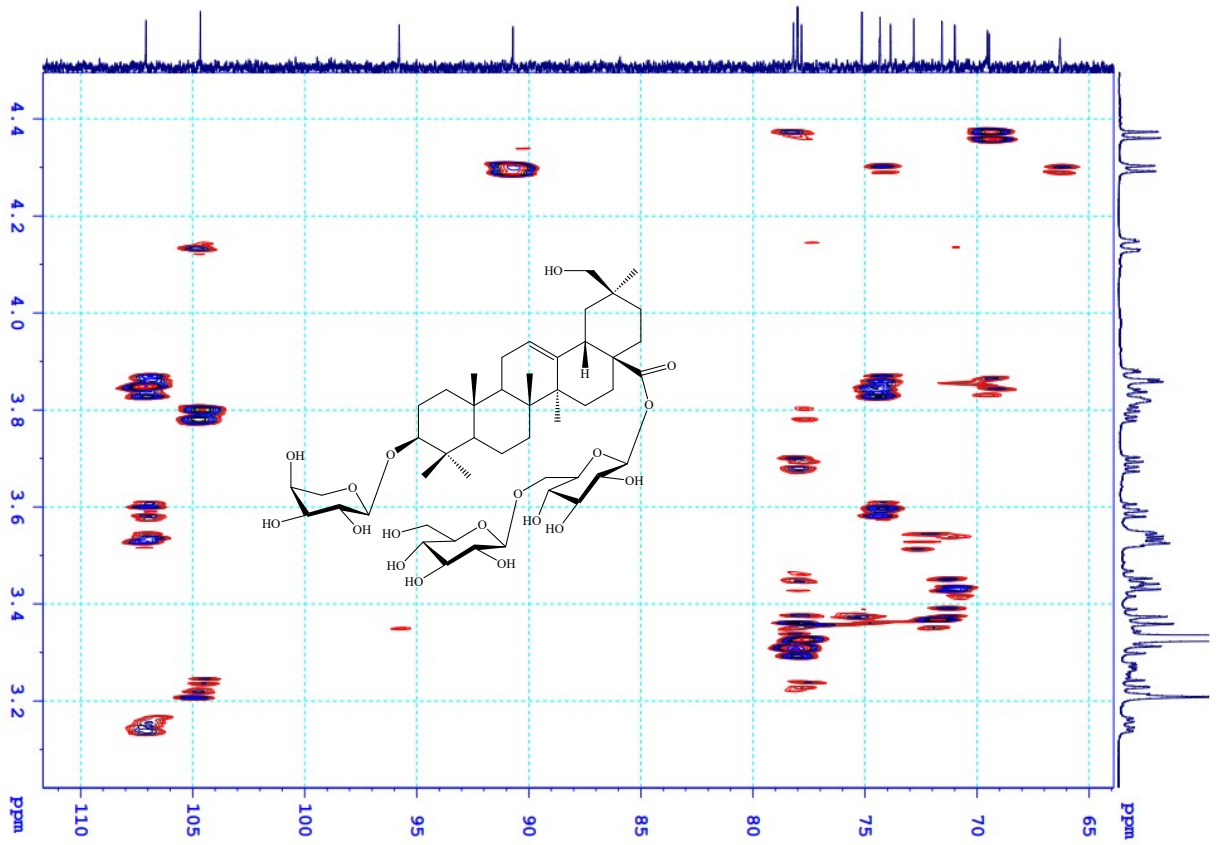


Figure S70. HMBC spectrum of compound **7** in CD_3OD



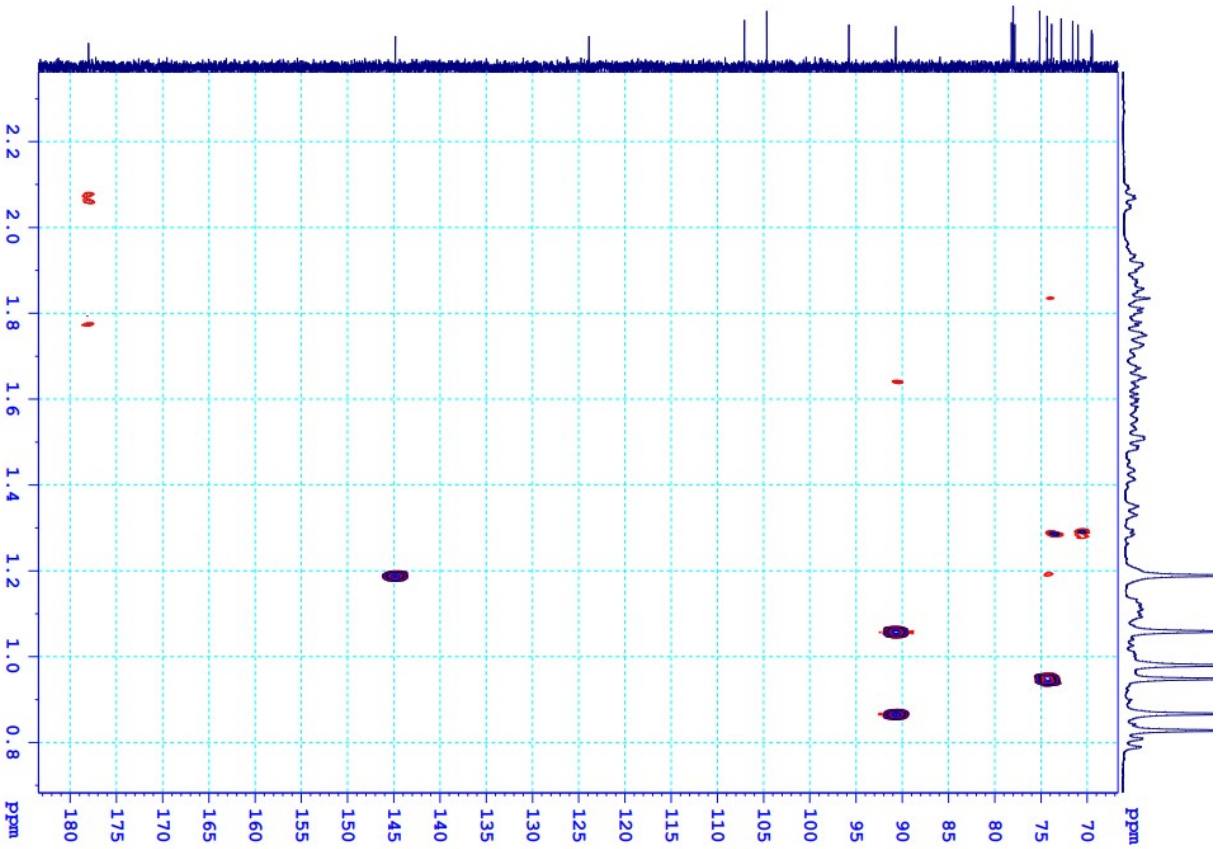


Figure S71. Extended HMBC spectrum of compound **7** in CD_3OD

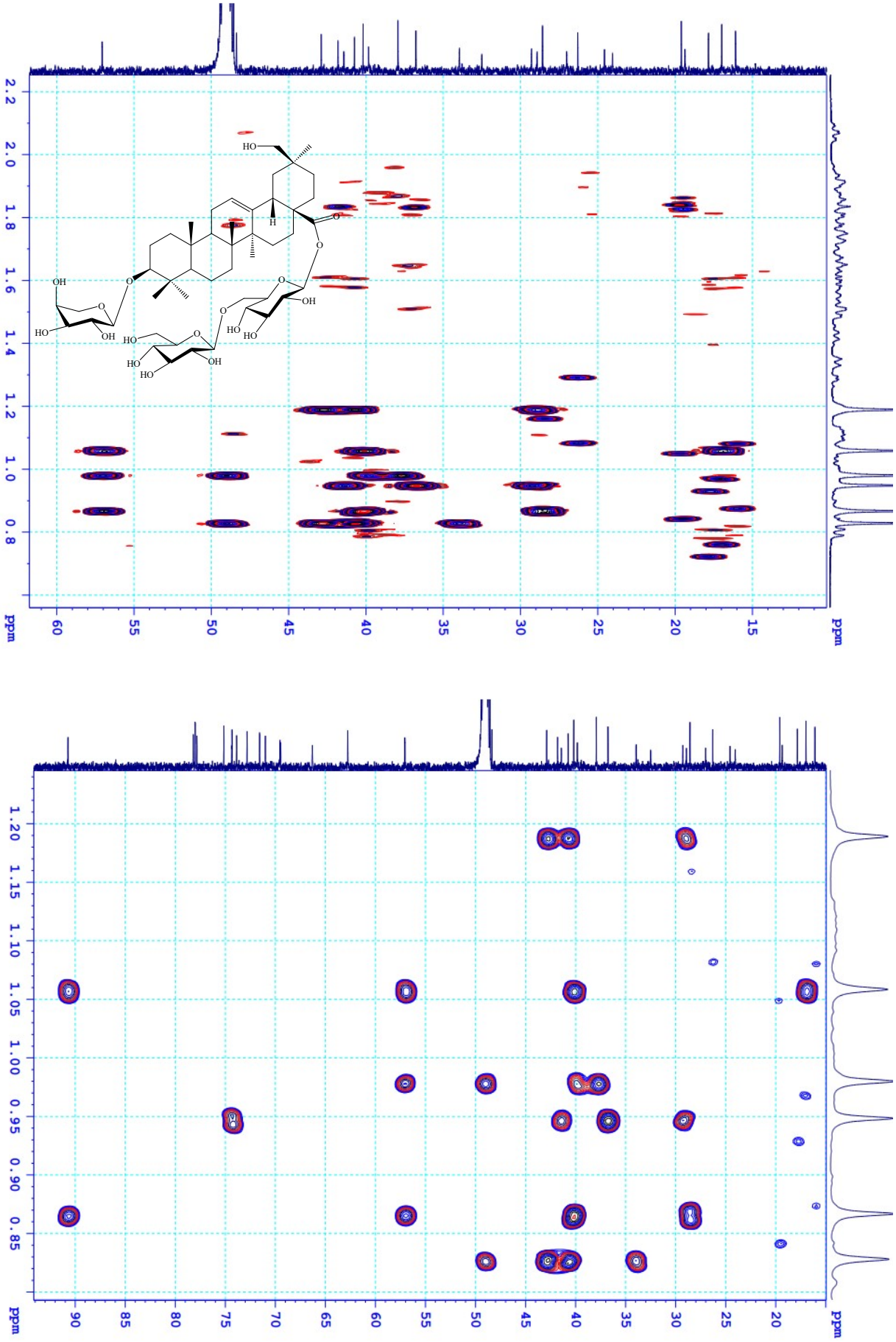


Figure S72. Extended HMBC spectrum of compound **7** in CD_3OD

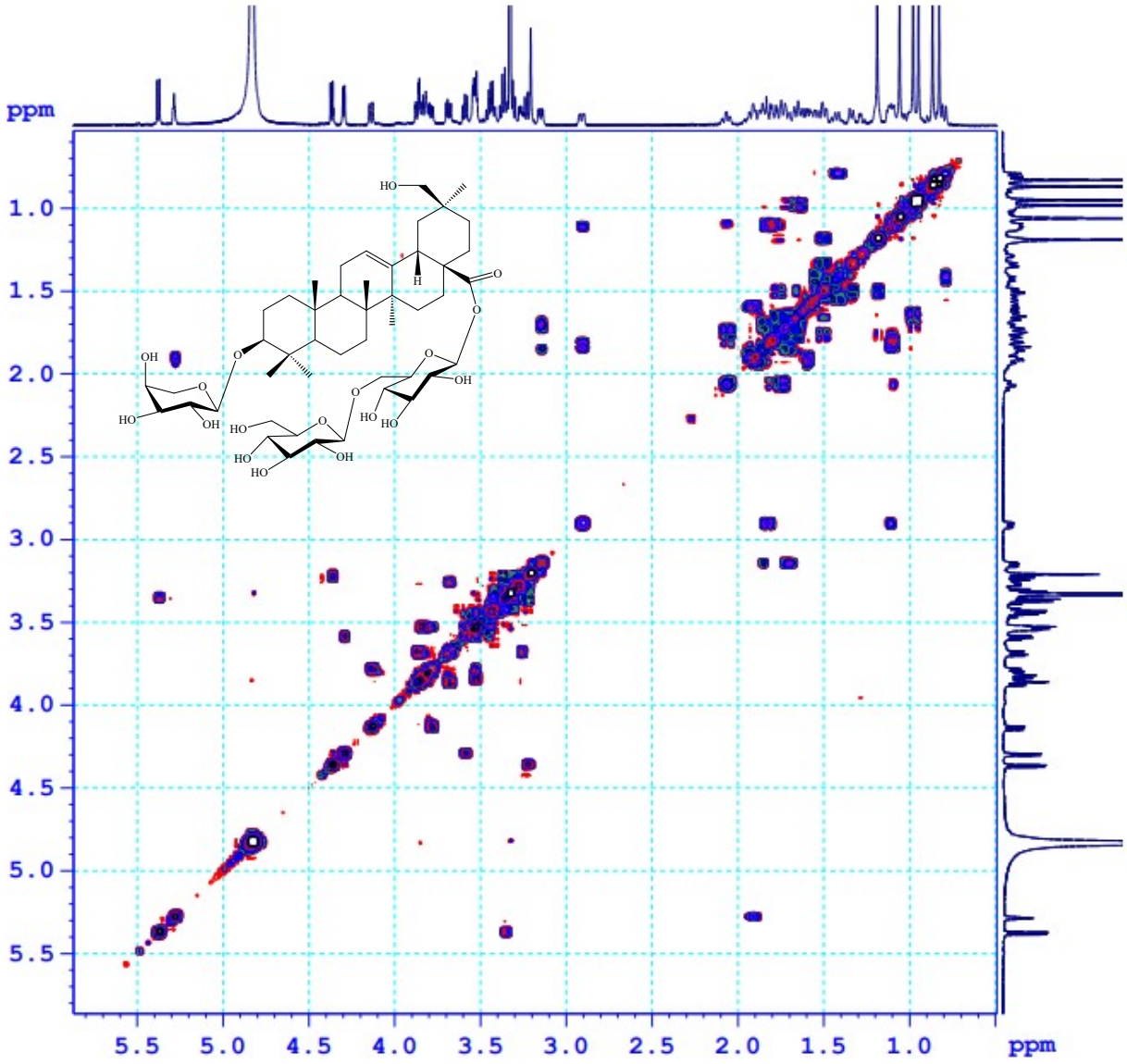


Figure S73. COSY spectrum of compound **7** in CD_3OD

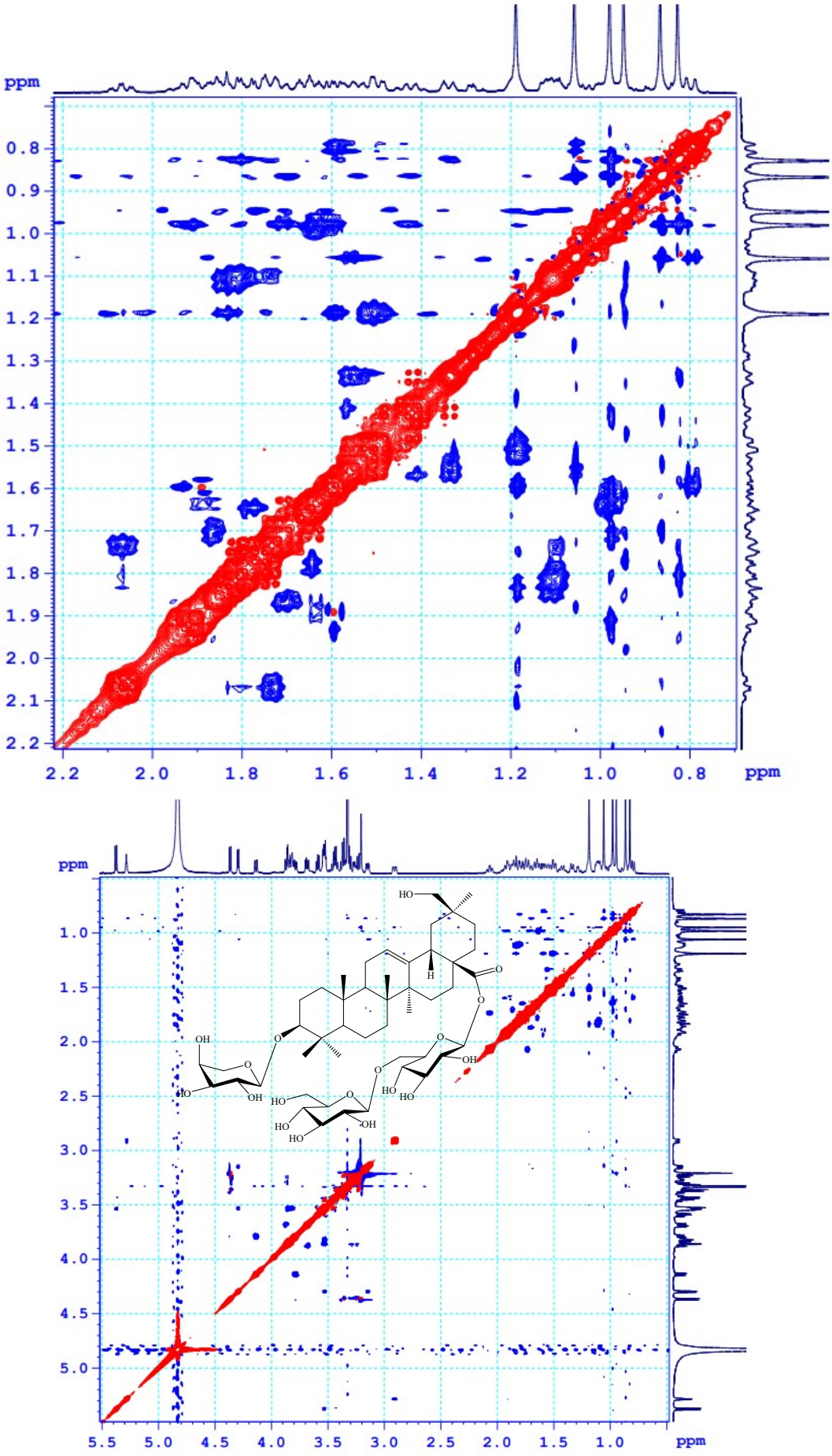


Figure S74. NOESY spectrum of compound **7** in CD_3OD

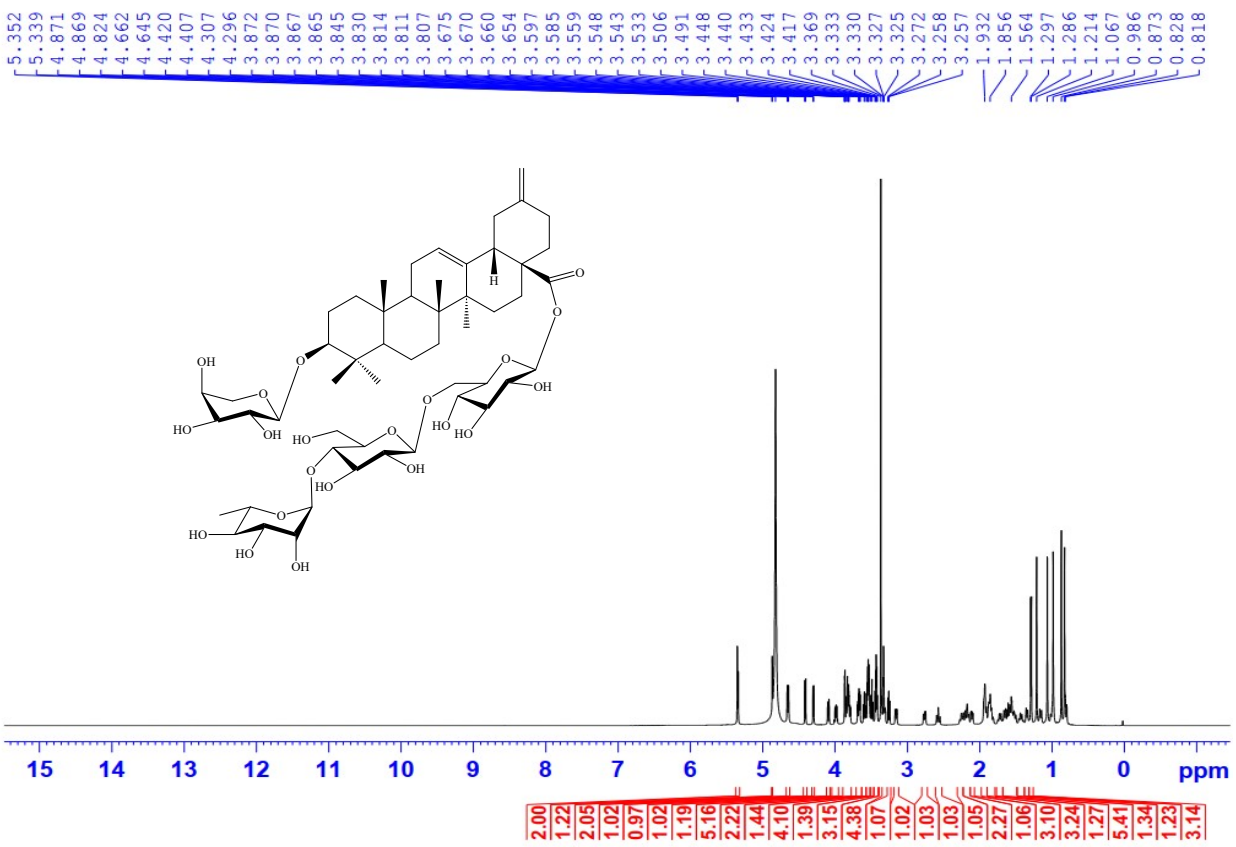


Figure S75. ^{1}H-NMR spectrum of compound **8** in CD_3OD

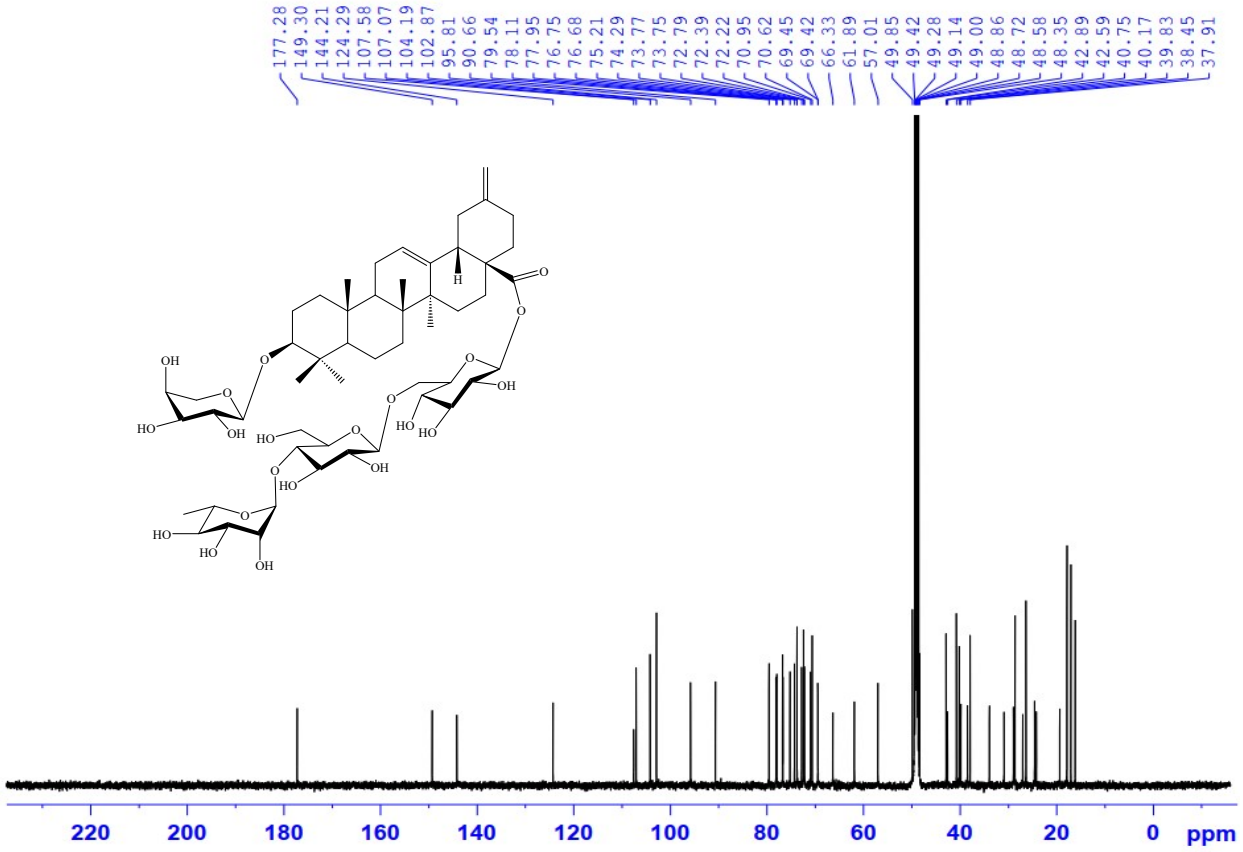


Figure S76. ^{13}C-NMR spectrum of compound **8** in CD_3OD

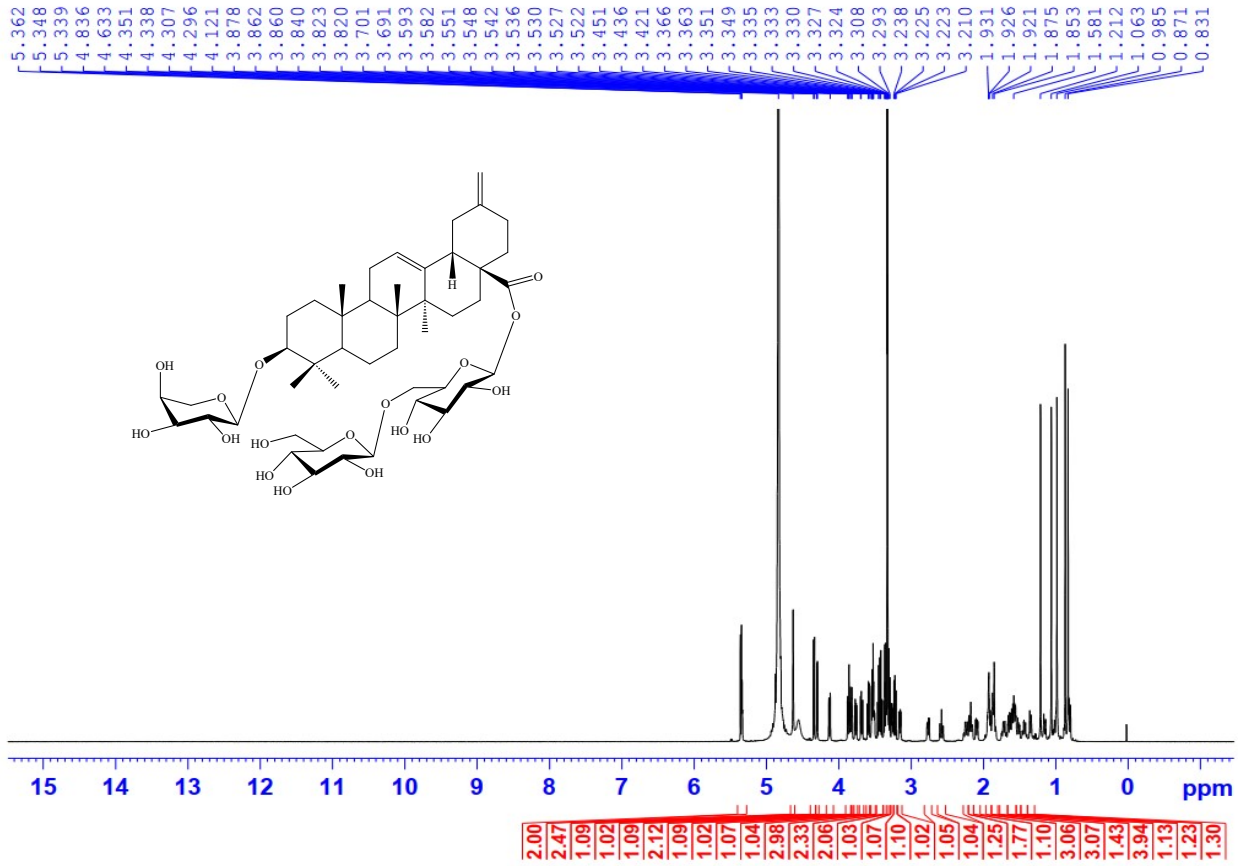


Figure S77. ^{1}H-NMR spectrum of compound **9** in CD_3OD

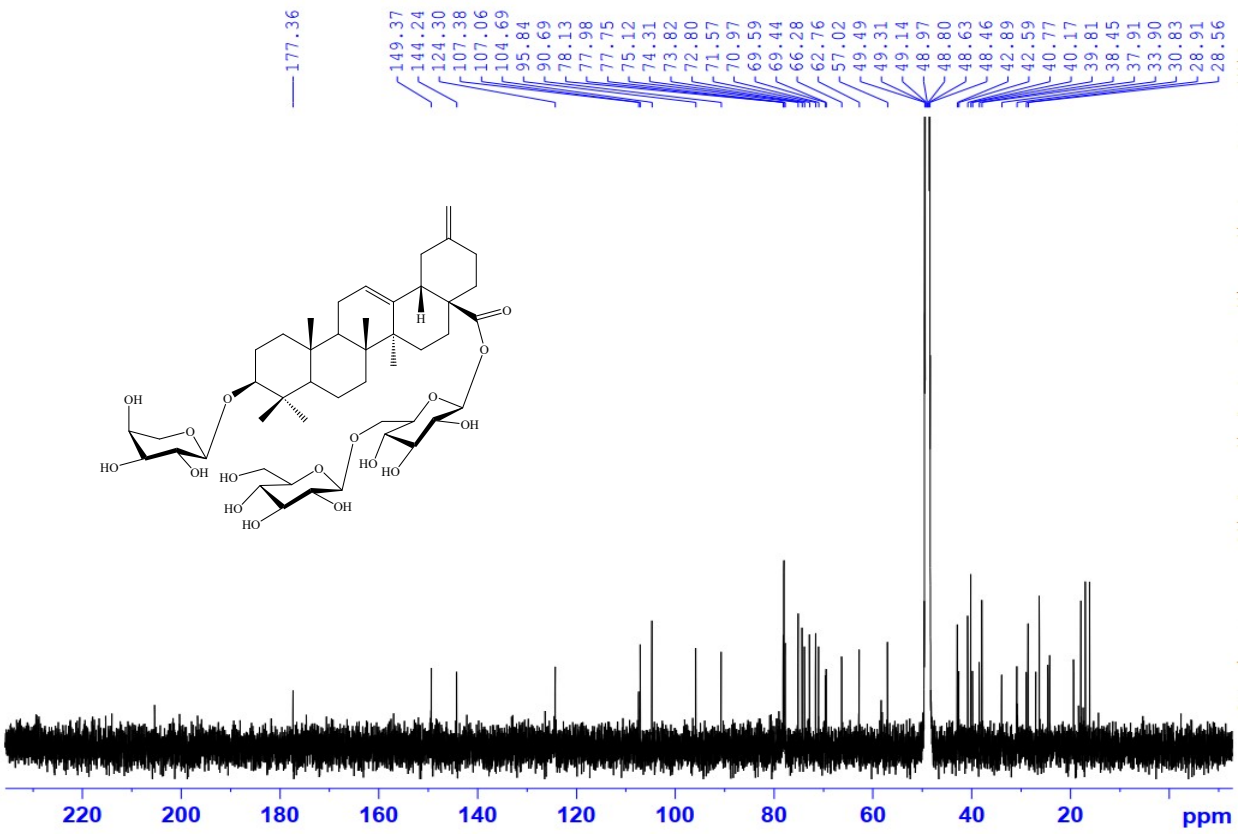


Figure S78. ^{13}C-NMR spectrum of compound **9** in CD_3OD

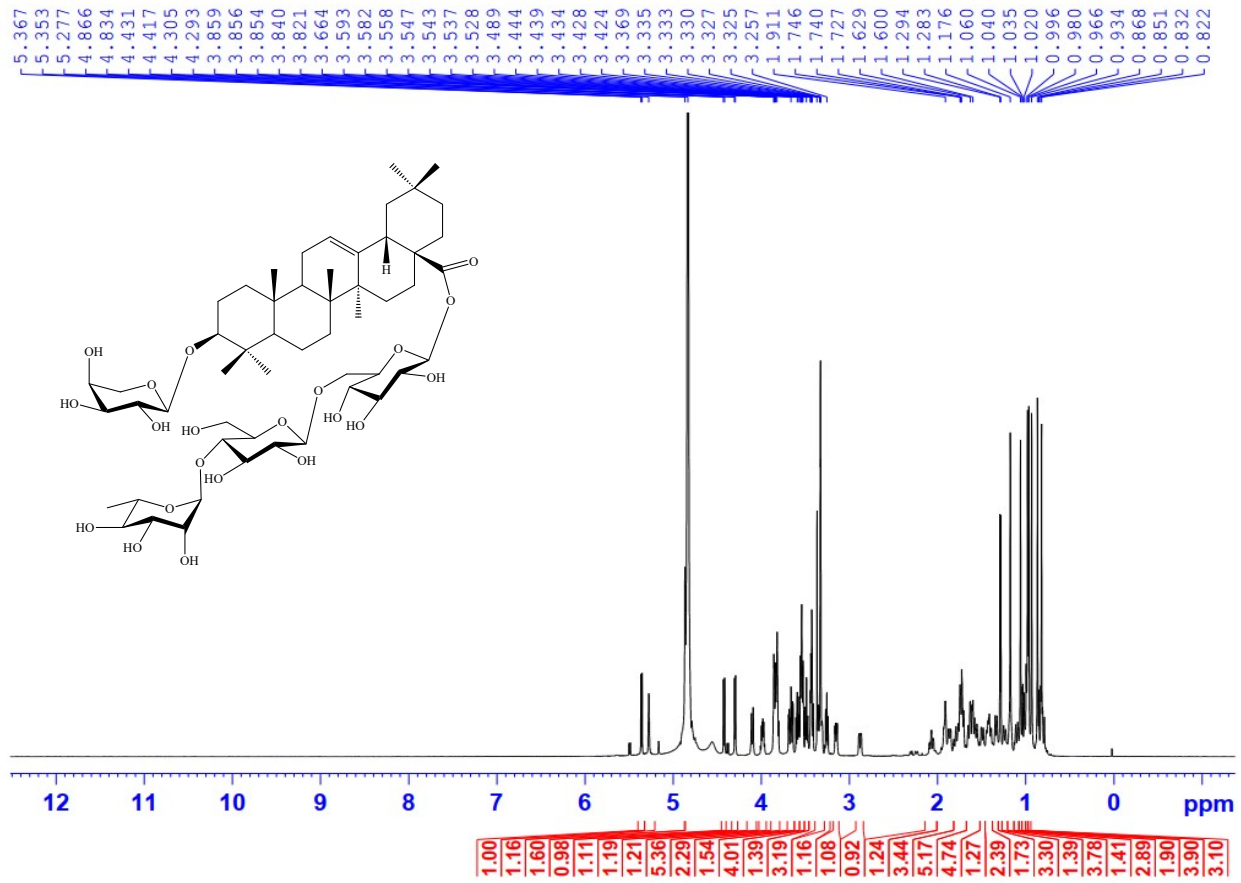


Figure S79. ^{1}H-NMR spectrum of compound **10** in CD_3OD

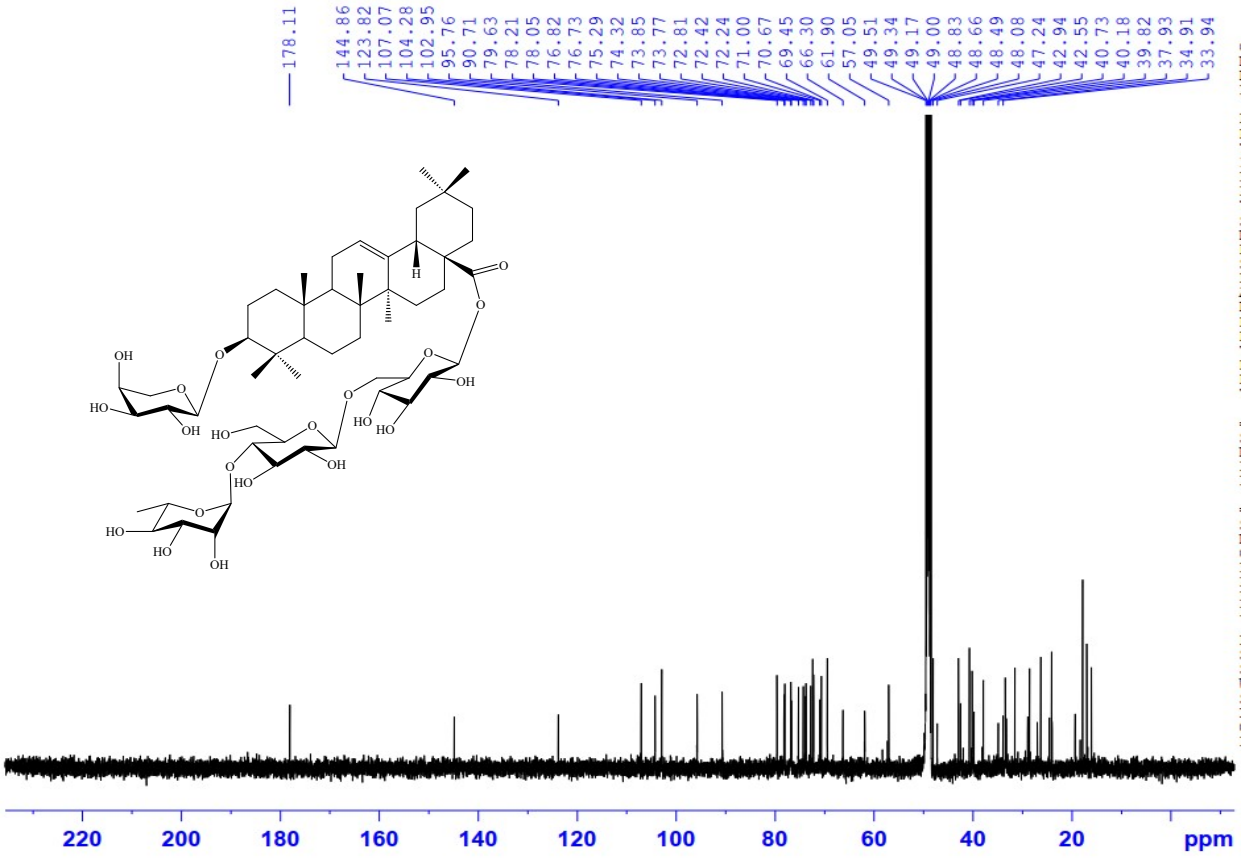


Figure S80. ^{13}C-NMR spectrum of compound **10** in CD_3OD

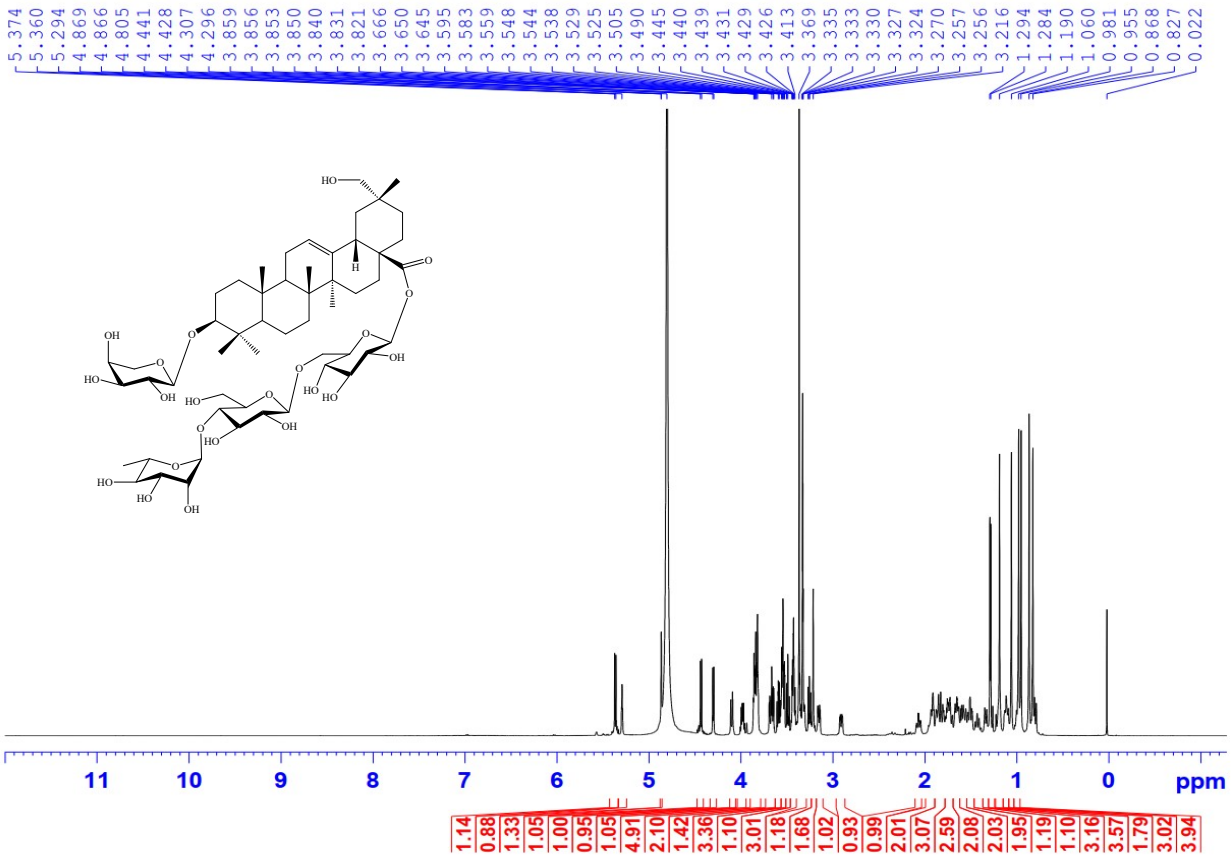


Figure S81. ^{1}H-NMR spectrum of compound **11** in CD_3OD

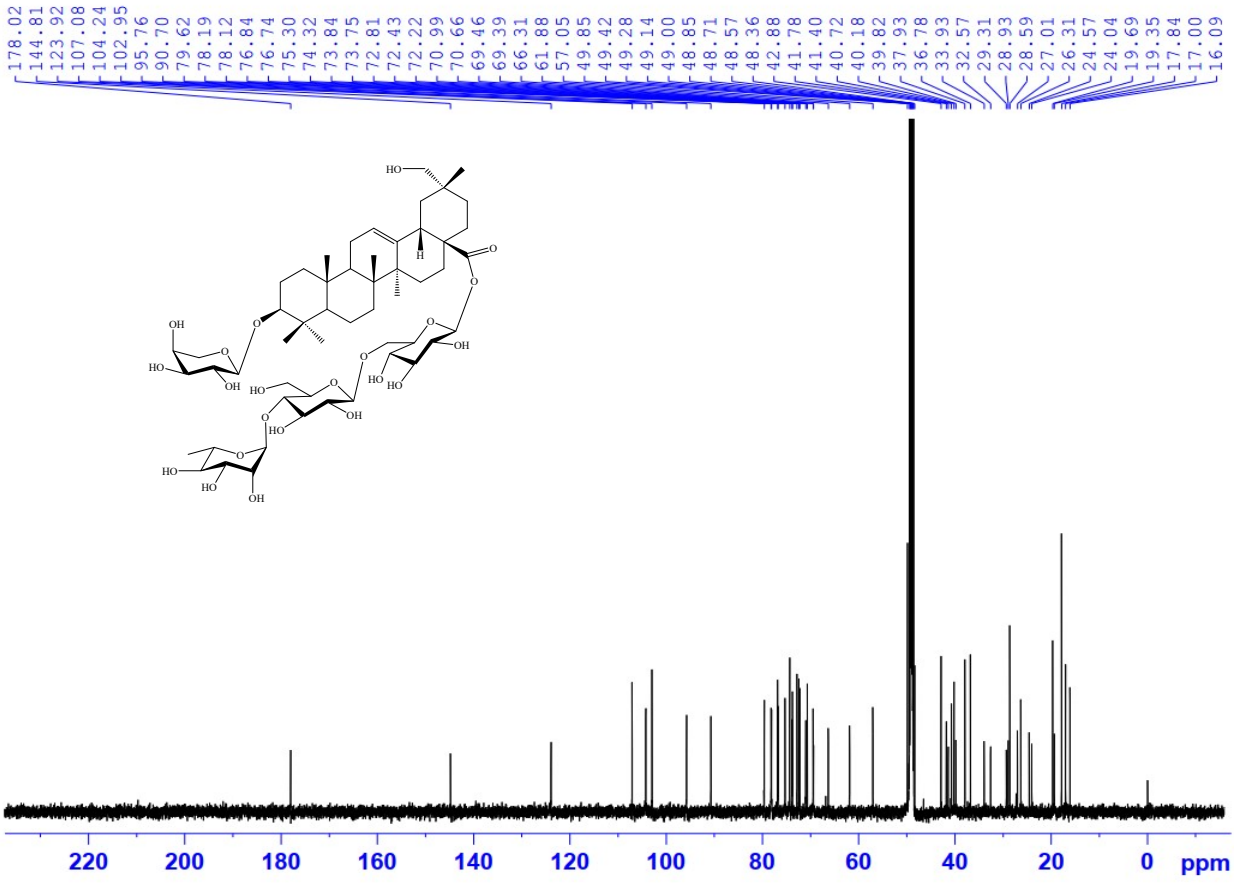


Figure S82. ^{13}C-NMR spectrum of compound **11** in CD_3OD

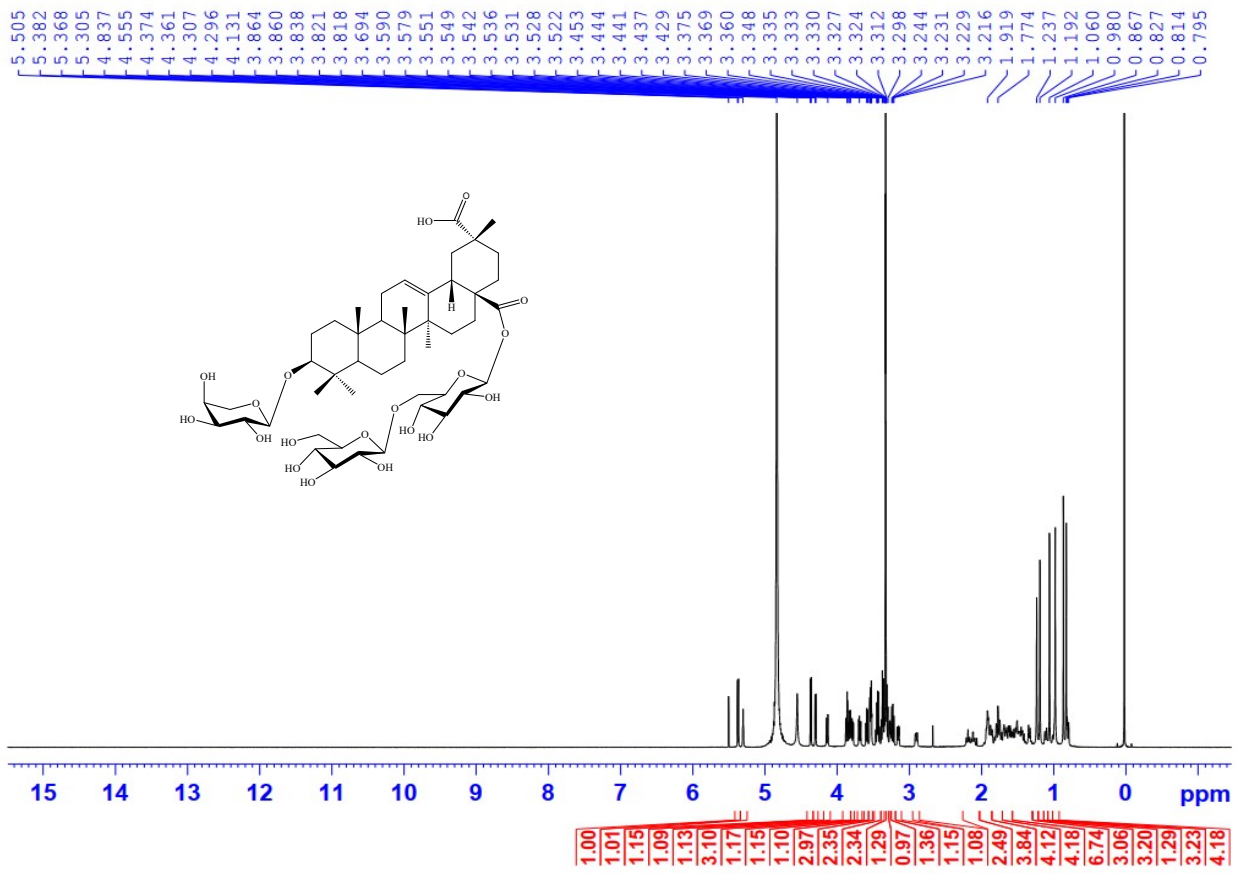


Figure S83. ^{1}H-NMR spectrum of compound **12** in CD_3OD

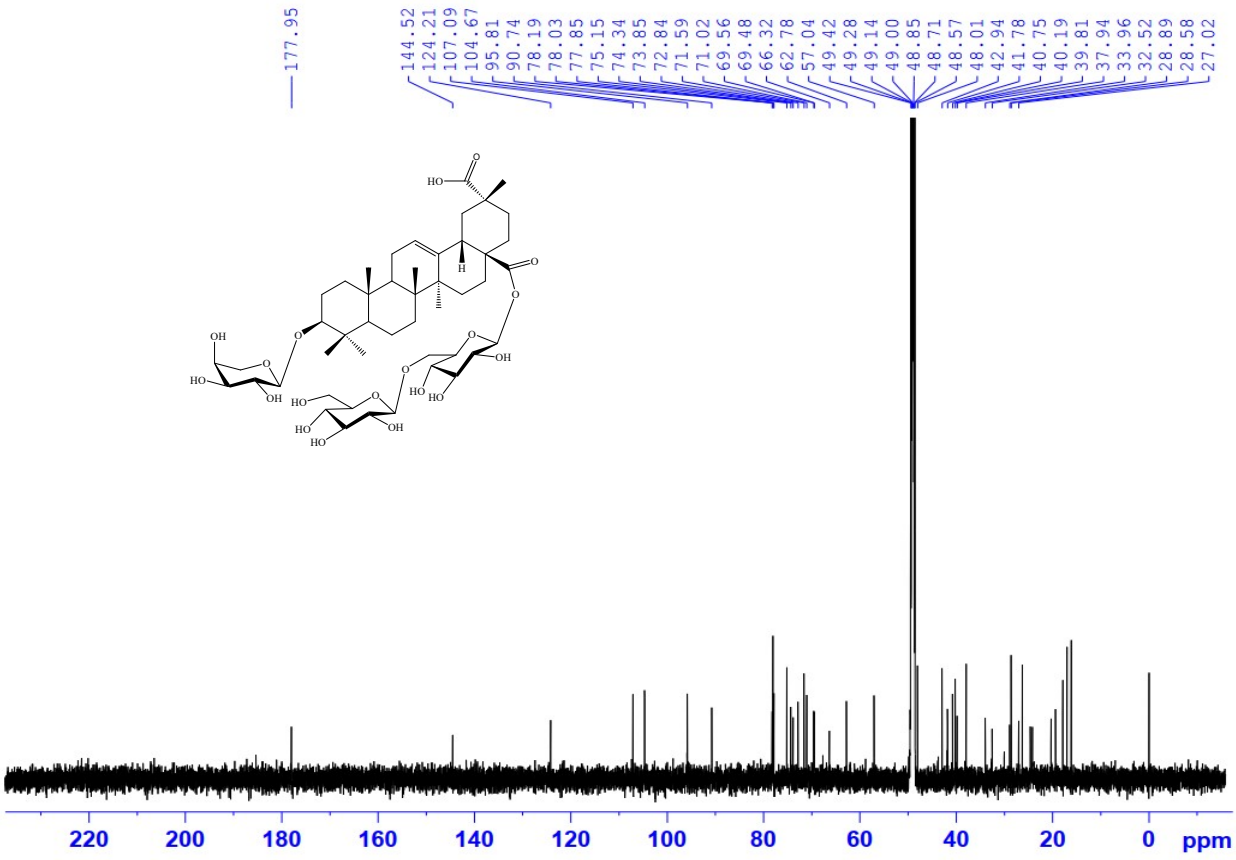


Figure S84. ^{13}C-NMR spectrum of compound **12** in CD_3OD

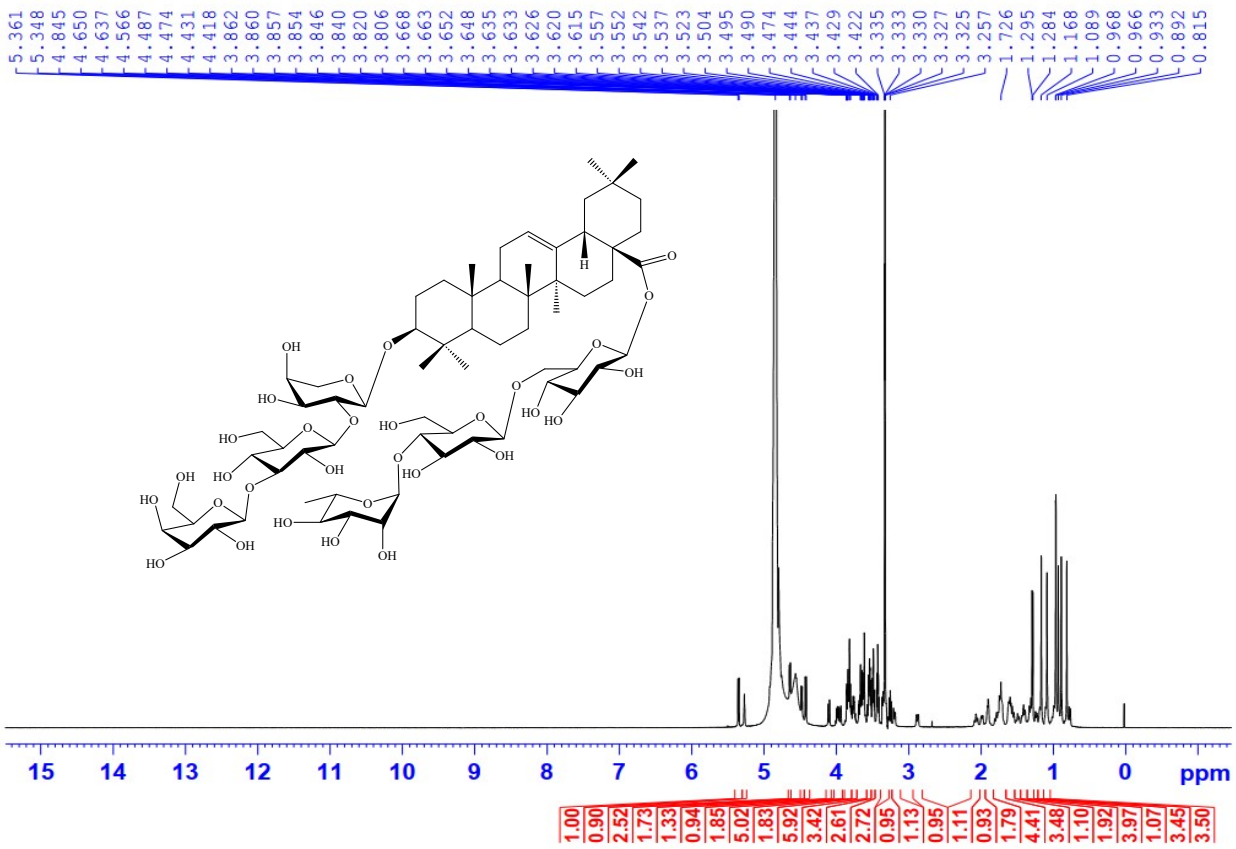


Figure S85. ^{1}H-NMR spectrum of compound **13** in CD_3OD

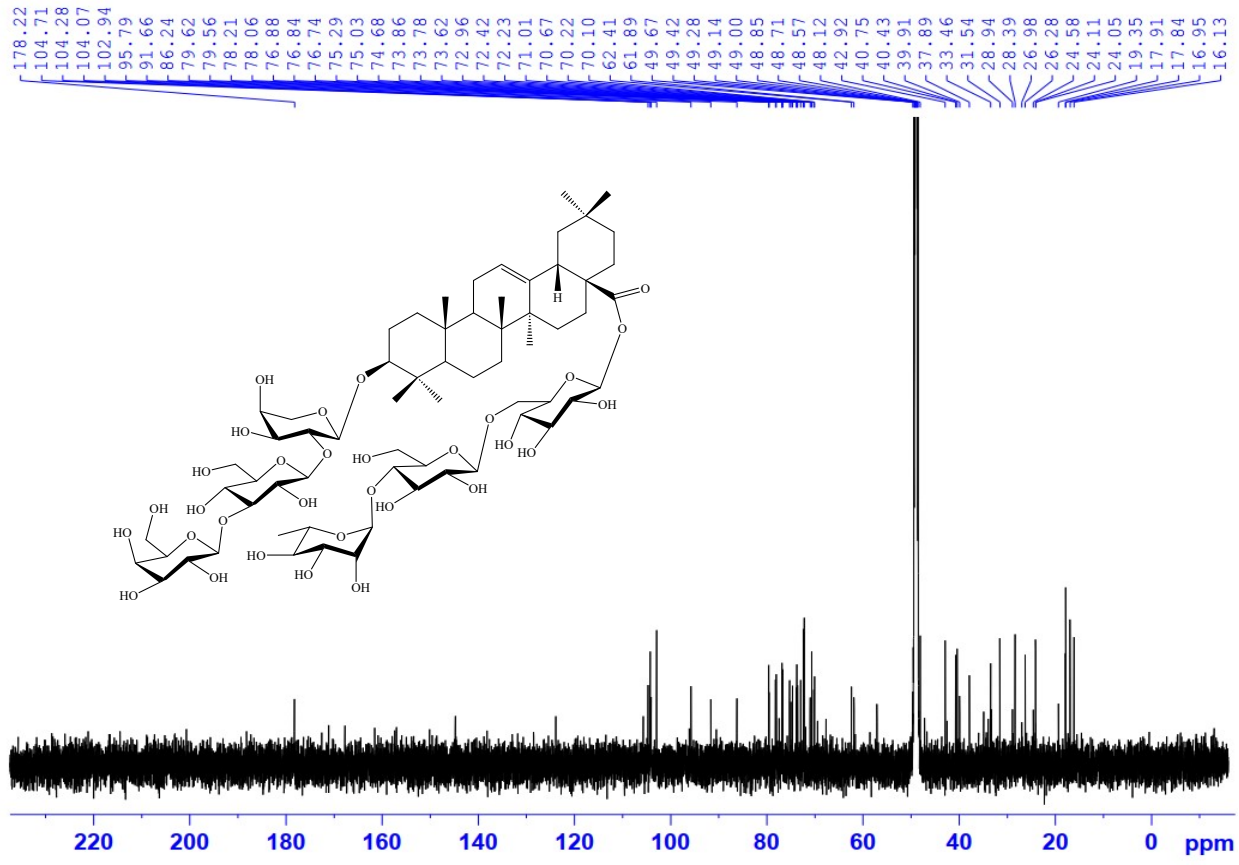


Figure S86. ^{13}C-NMR spectrum of compound **13** in CD_3OD