

Triterpenoid saponins from *Anagallis monelli* ssp. *linifolia* (L.) Maire and their chemotaxonomic significance

Chouaib Aouane^{a,b}, Ahmed Kabouche^a, Laurence Voutquenne-Nazabadioko^{b*}, Charlotte Sayagh^b, Agathe Martinez^b, Abdulmagid Alabdul Magid^b, Zahia Kabouche^a

^a*Université des frères Mentouri-Constantine 1, Département de chimie, Laboratoire d'Obtention des Substances Thérapeutiques (LOST), Campus Chaabet-Ersas, 25000 Constantine, Algeria*

^b*Université de Reims Champagne Ardenne, CNRS, ICMR UMR 7312, 51097 Reims, France*

Abstract

Thirteen undescribed triterpenoid saponins named monellosides A-M, were isolated from the aerial parts of *Anagallis monelli* ssp. *linifolia* (L.) Maire, together with ten known oleanane-type glycosides. Their structures were elucidated by 1D and 2D-NMR spectroscopy (COSY, TOCSY, HSQC, HMBC and ROESY) as well as high resolution mass spectrometry (HR-ESI-MS) and acid hydrolysis. Monellosides A-M have a carbohydrate chain linked on the C-3 of the aglycone with a common β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-arabinopyranosyl sequence which was further glycosylated by a glucose and/or a xylose. The sequence β -D-xylopyranosyl-(1 \rightarrow 2)- β -D-glucopyranosyl-(1 \rightarrow 4)-[β -D-glucopyranosyl-(1 \rightarrow 2)-] α -L-arabinopyranosyl was common to all the 13,28-epoxy-oleanane core skeleton except one compound. In order to discuss the reclassification of *Anagallis* in Primulaceae, we compared saponins from species of Myrsinaceae and Primulaceae families and showed that these species were characterized by a pentacyclic triterpenoid saponin with a 13,28-epoxy bridge skeleton. Our phytochemical results increase the knowledge of saponins of the genus *Anagallis*, their chemotaxonomy and stimulate the evaluation of the biological activities of these saponins.

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Fig S103. The structures of compounds **14–23** isolated from *Anagallis monelli ssp linifolia*

Compound 1

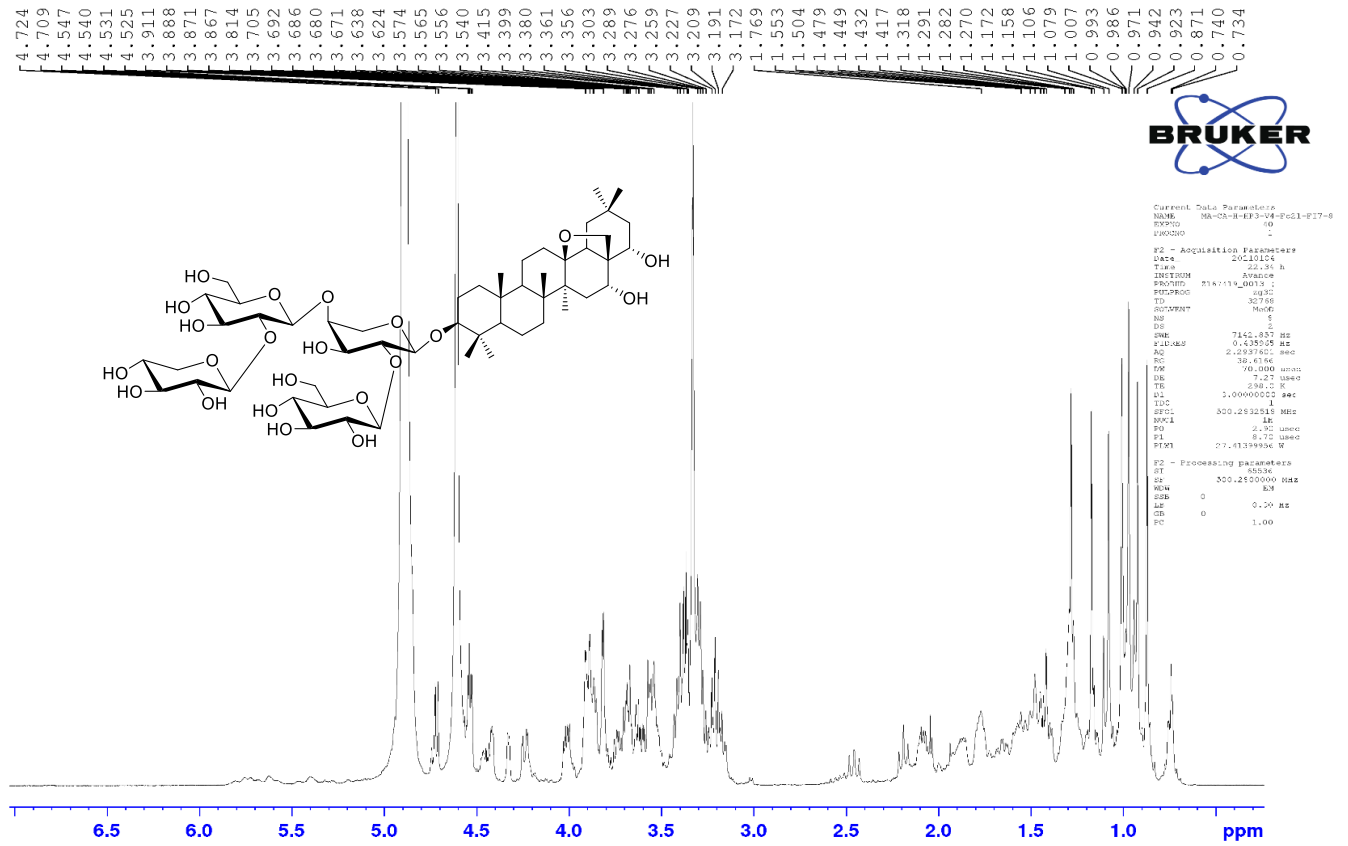


Fig. S1. ¹H NMR Spectrum (500 MHz, MeOH-d₄) of compound 1

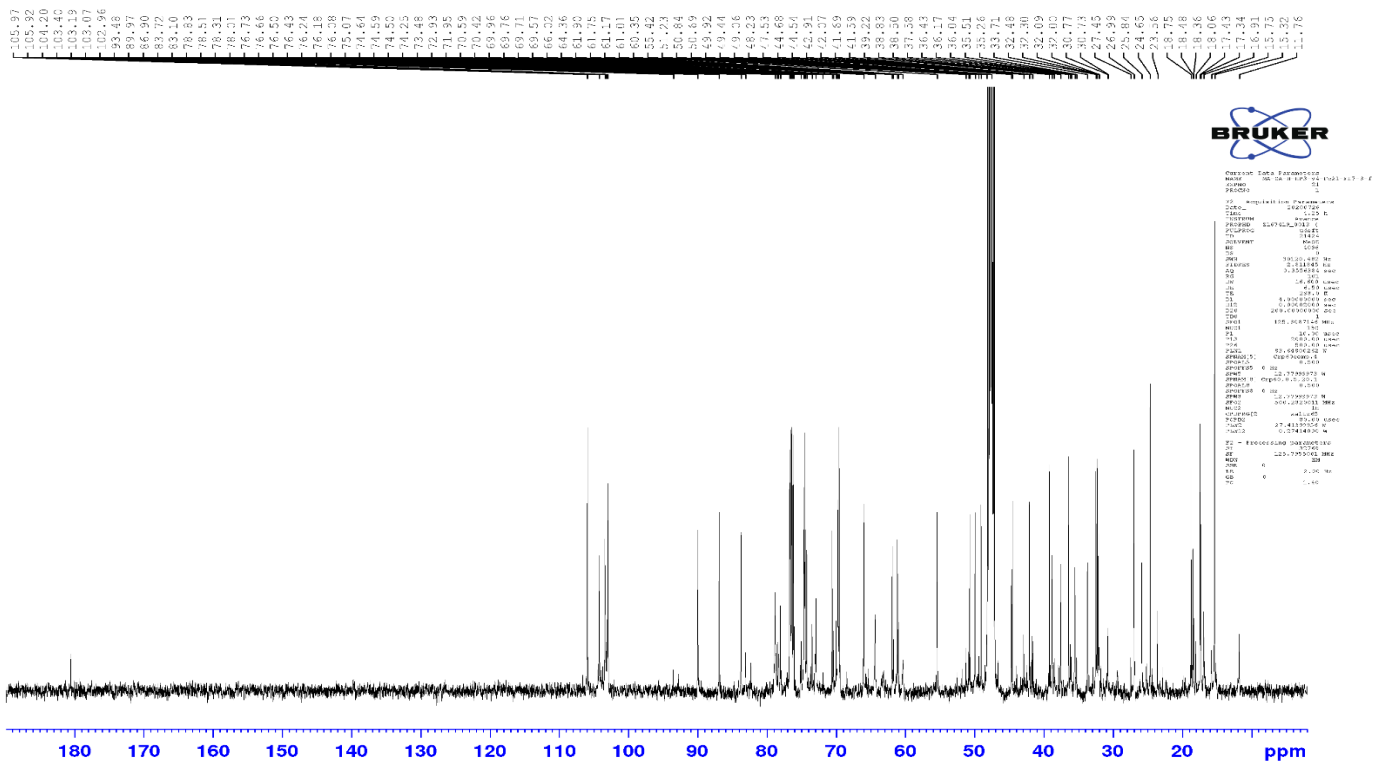


Fig. S2. ¹³C NMR Spectrum (125 MHz, MeOH-d₄) of compound 1

compound 1
CA-HP3-V4-fc21-FI 7-8-f3

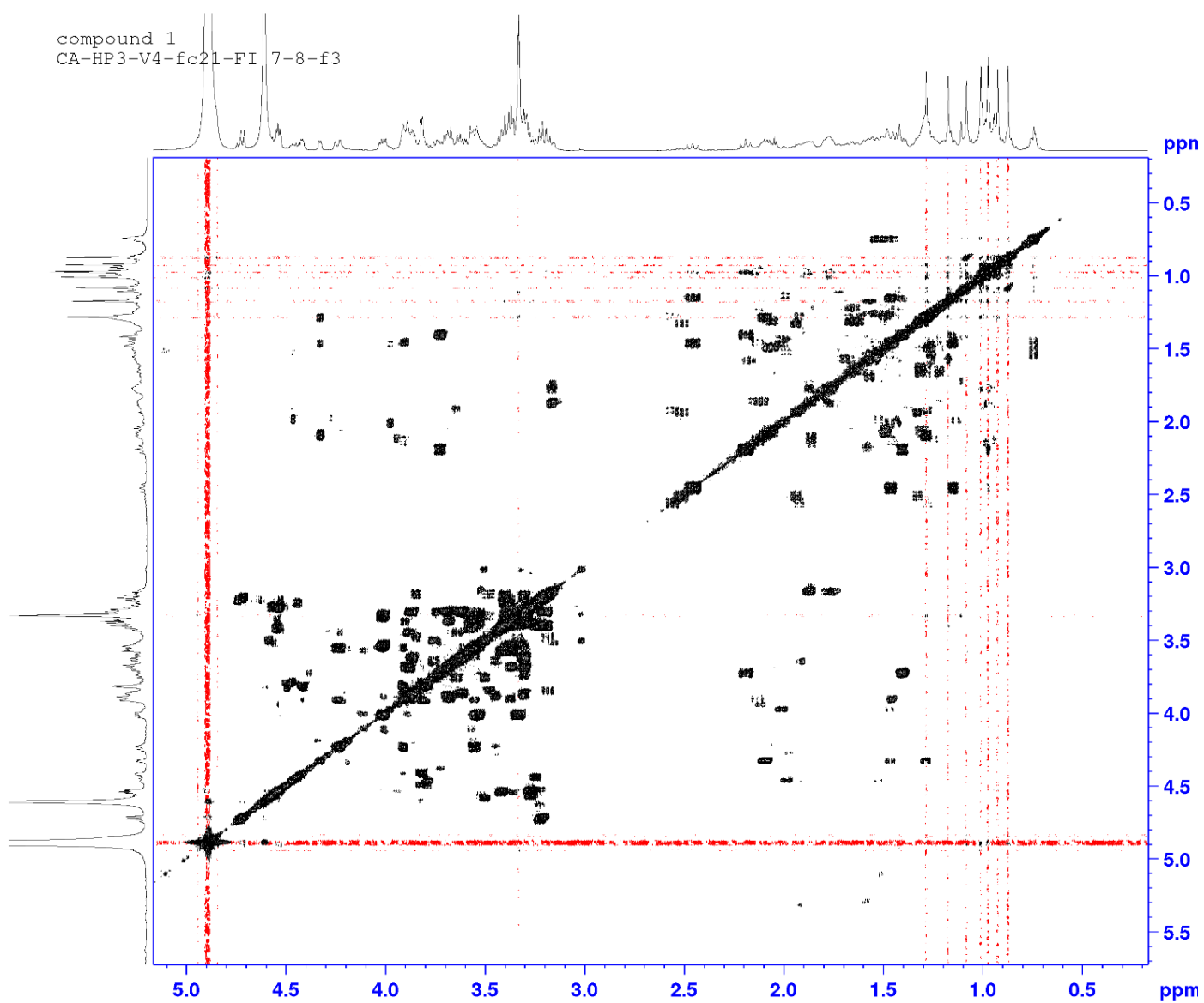


Fig. S3. COSY Spectrum of compound 1

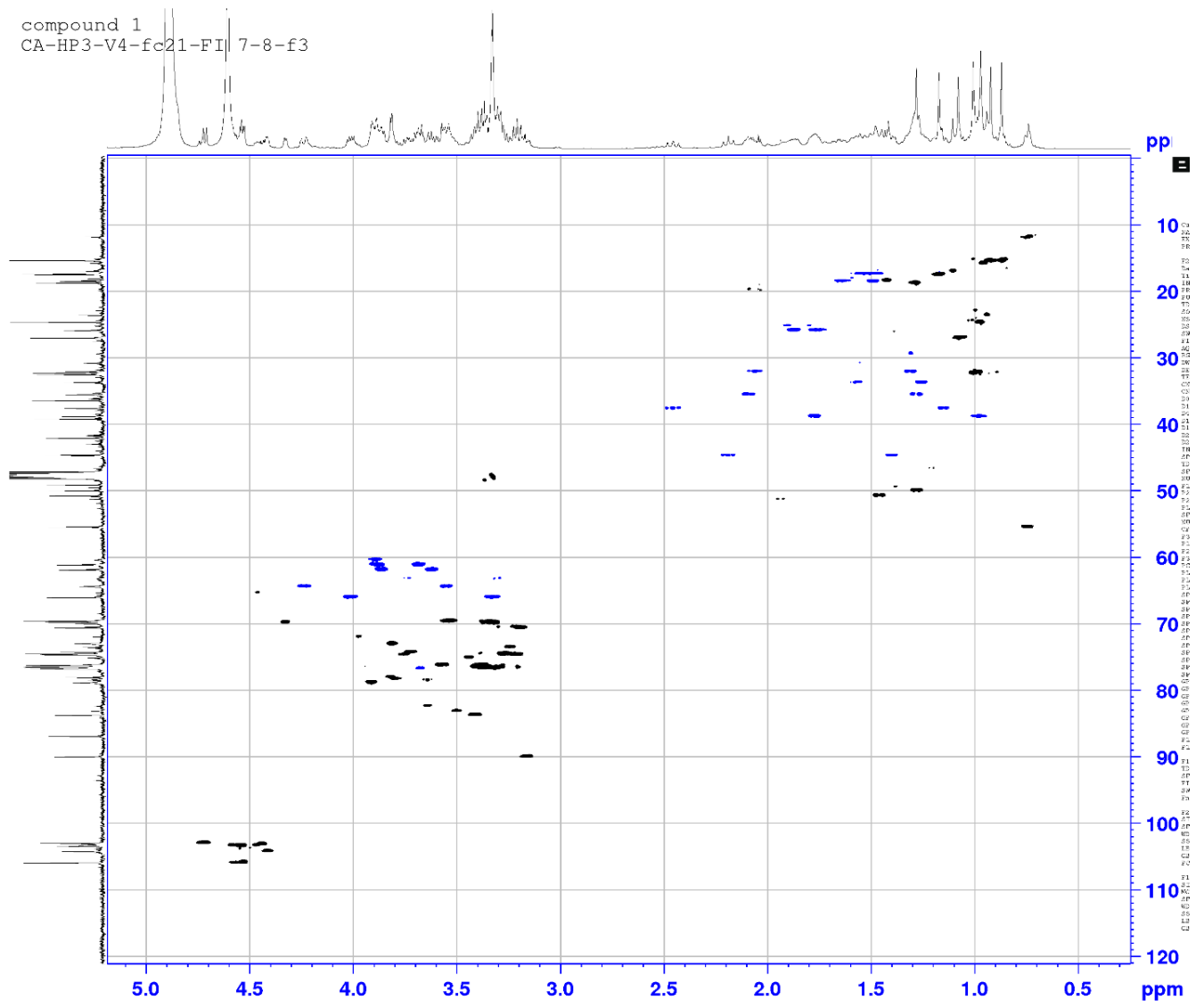


Fig. S4. HSQC spectrum of compound **1**

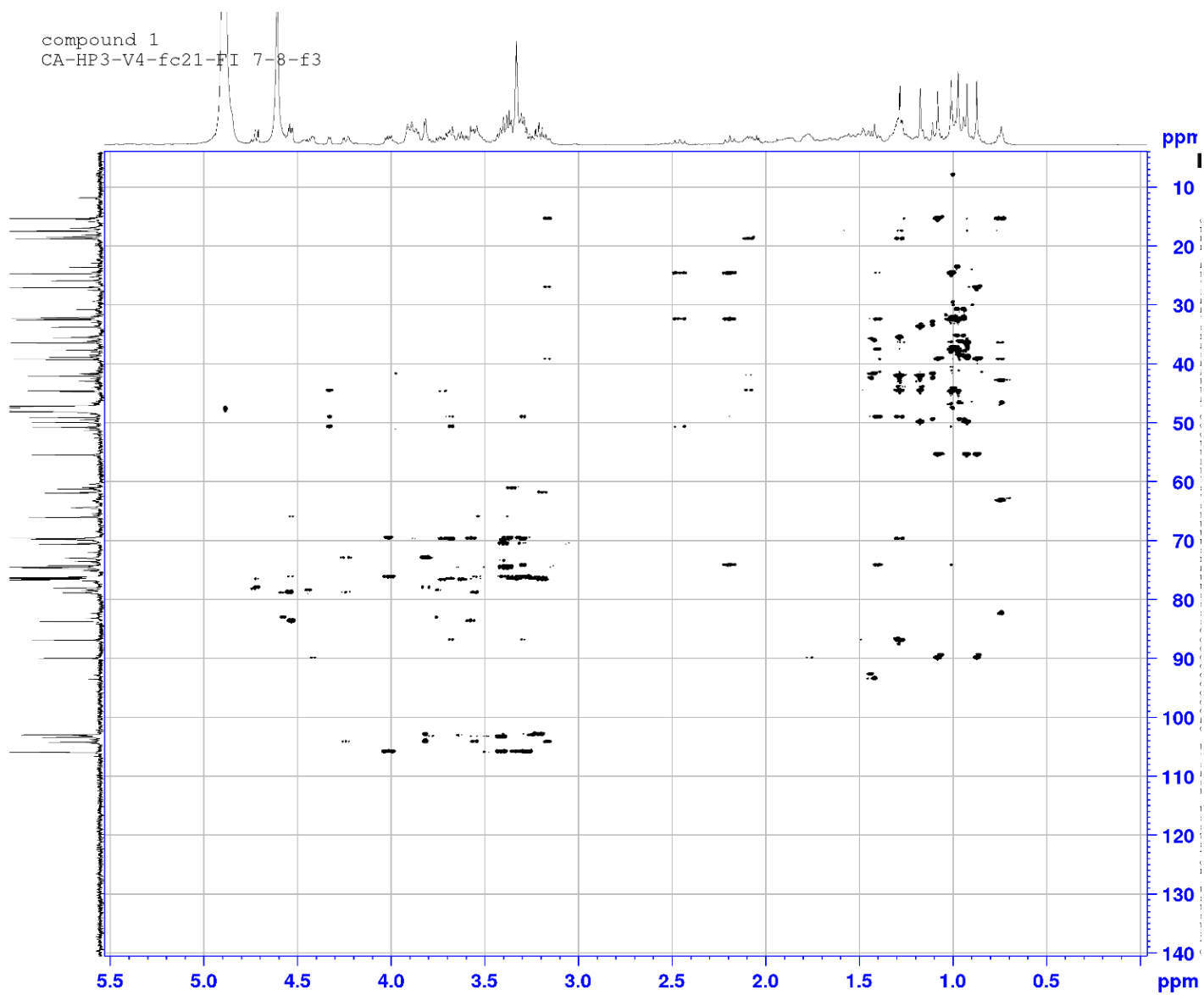


Fig. S5. HMBC spectrum of compound 1

compound 1
CA-HP3-V4-fc21-Fl 7-8-f3

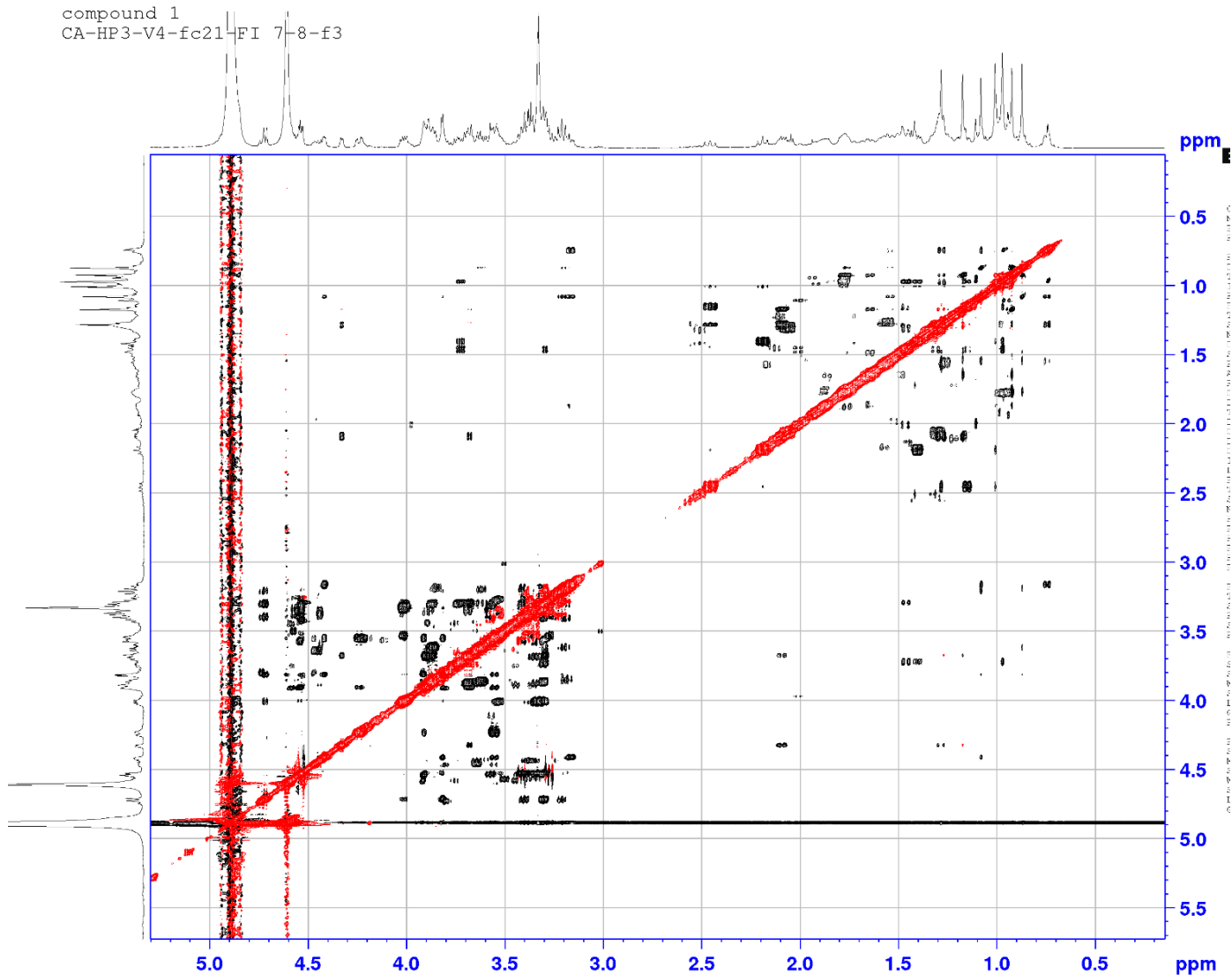


Fig. S6. ROESY spectrum of compound 1

Elemental Composition Report

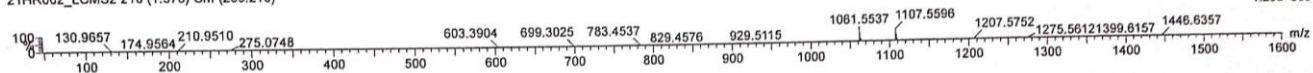
Single Mass Analysis

Tolerance = 5.0 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
119 formula(e) evaluated with 1 results within limits (up to 15 closest results for each mass)

Elements Used:
C: 0-60 H: 0-100 O: 0-30
HP3_V4_Fc21_FL7_8_F3
21HR002_LCMS2 210 (1.578) Cm (209:210)

1: TOF MS ES-
1.29e+008



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1061.5537	1061.5532	0.5	0.5	10.5	796.5	n/a	n/a	C52 H85 O22

Fig. S7. HR-MS spectrum of compound 1

Compound 2

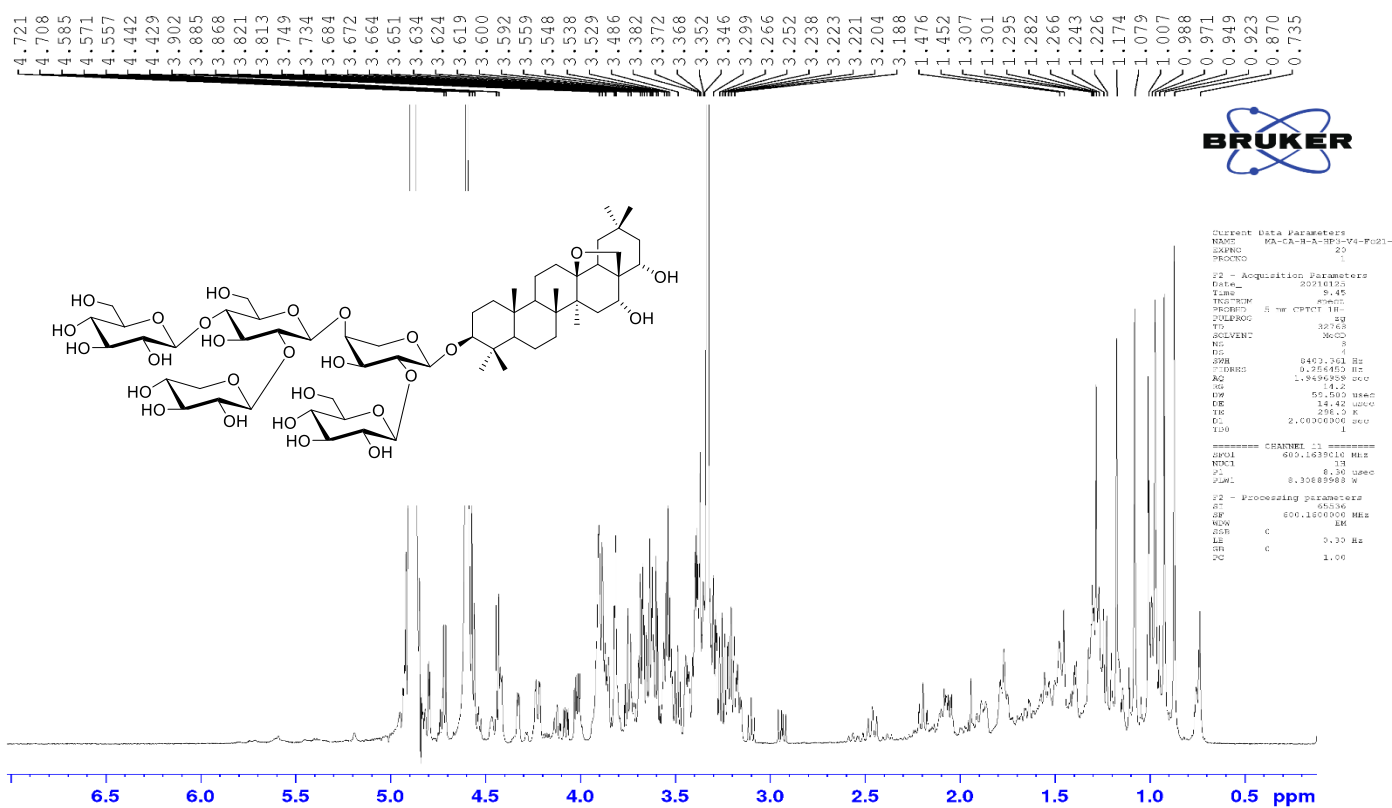


Fig. S8. ¹H NMR Spectrum (600 MHz, MeOH-d₄) of compound 2

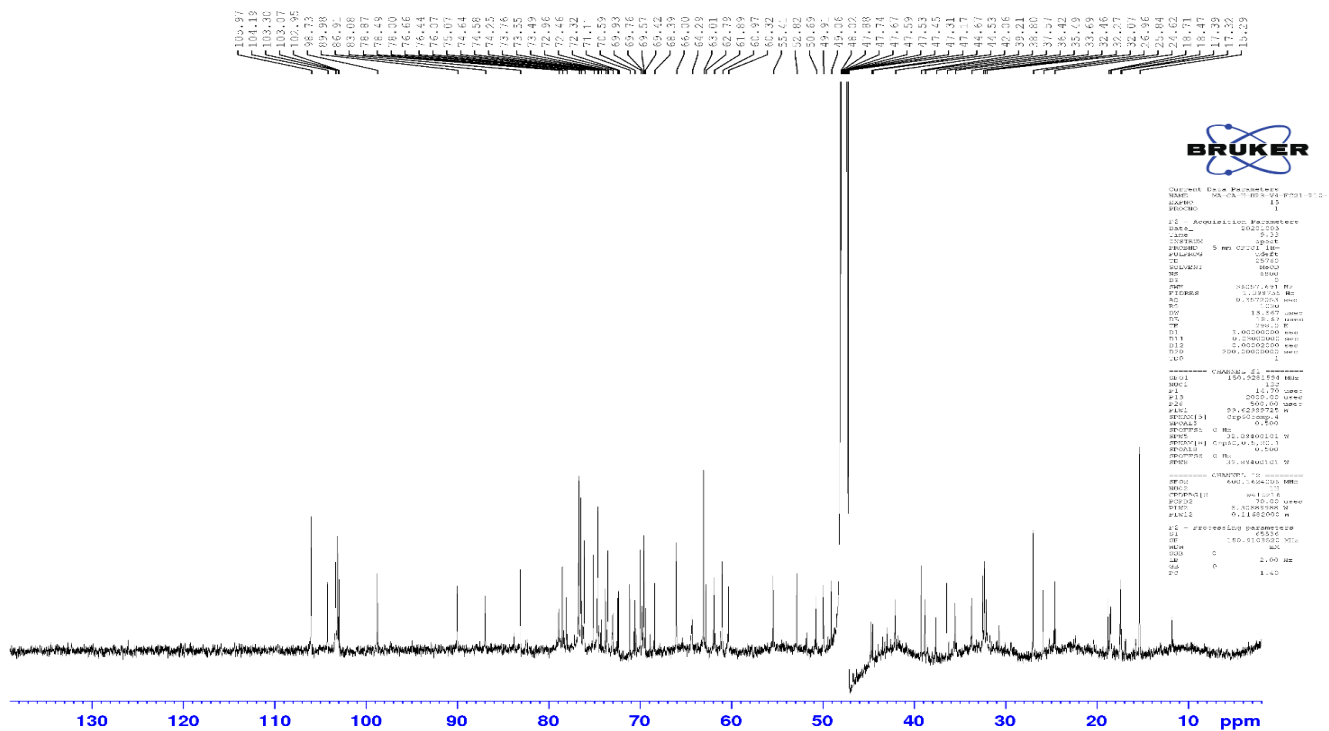


Fig. S9. ¹³C NMR Spectrum (150 MHz, MeOH-d₄) of compound 2

compound 2
CA-H-A-HP3-V4-FC21-P10-11-F13

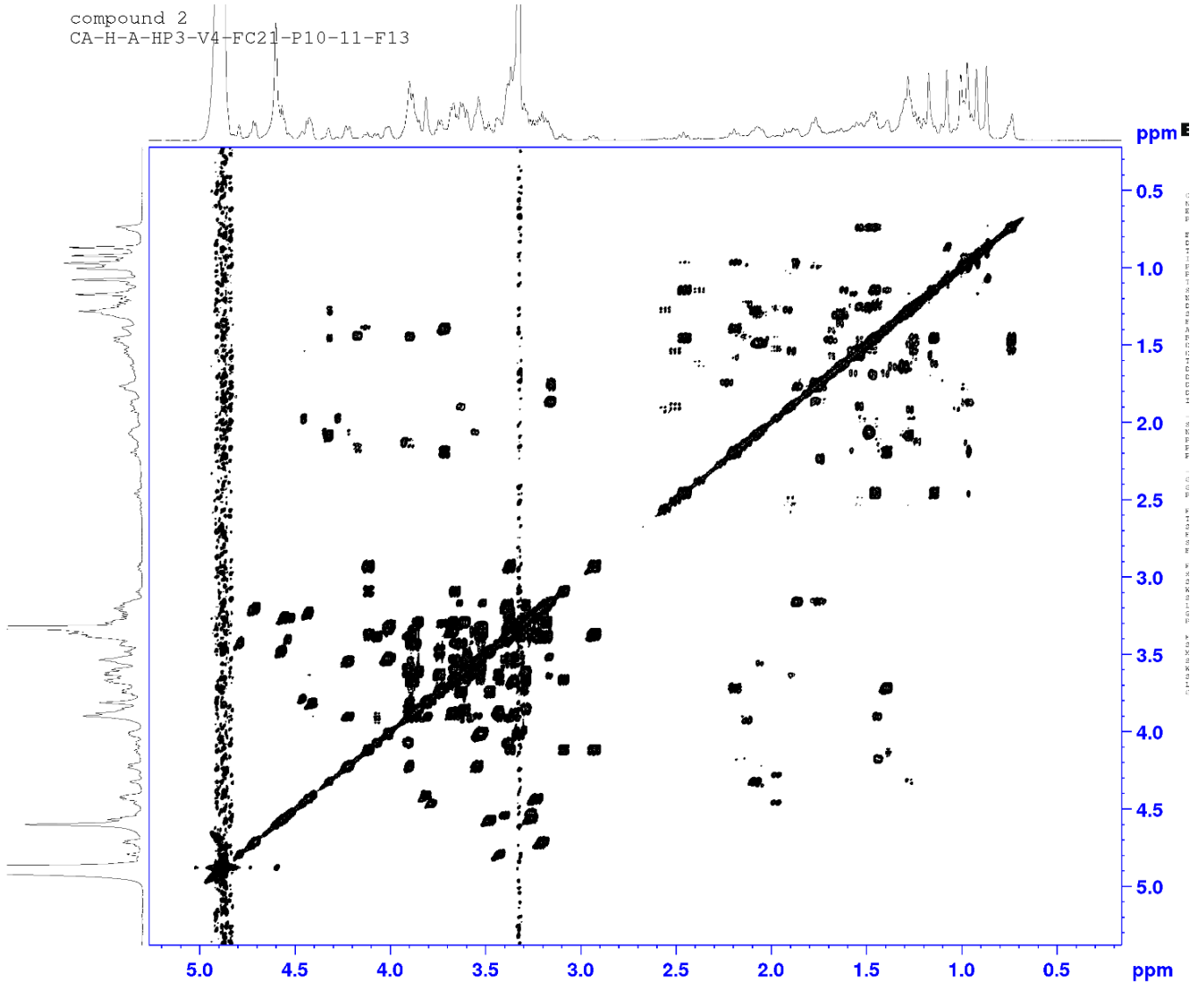


Fig. S10. COSY spectrum of compound 2

compound 2
CA-H-A-HP3-V4-FC21-P10-11-F13

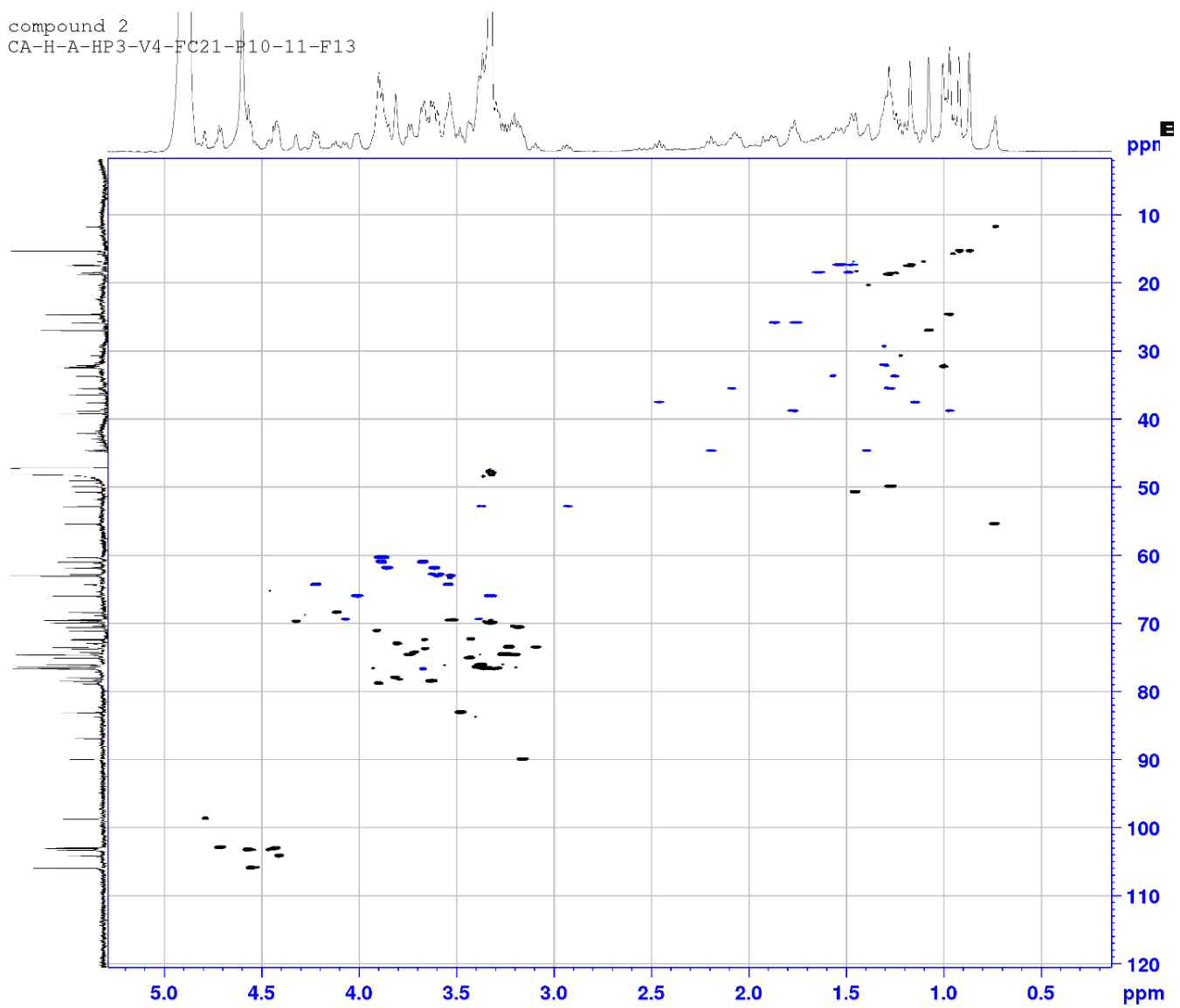


Fig. S11. HSQC spectrum of compound 2

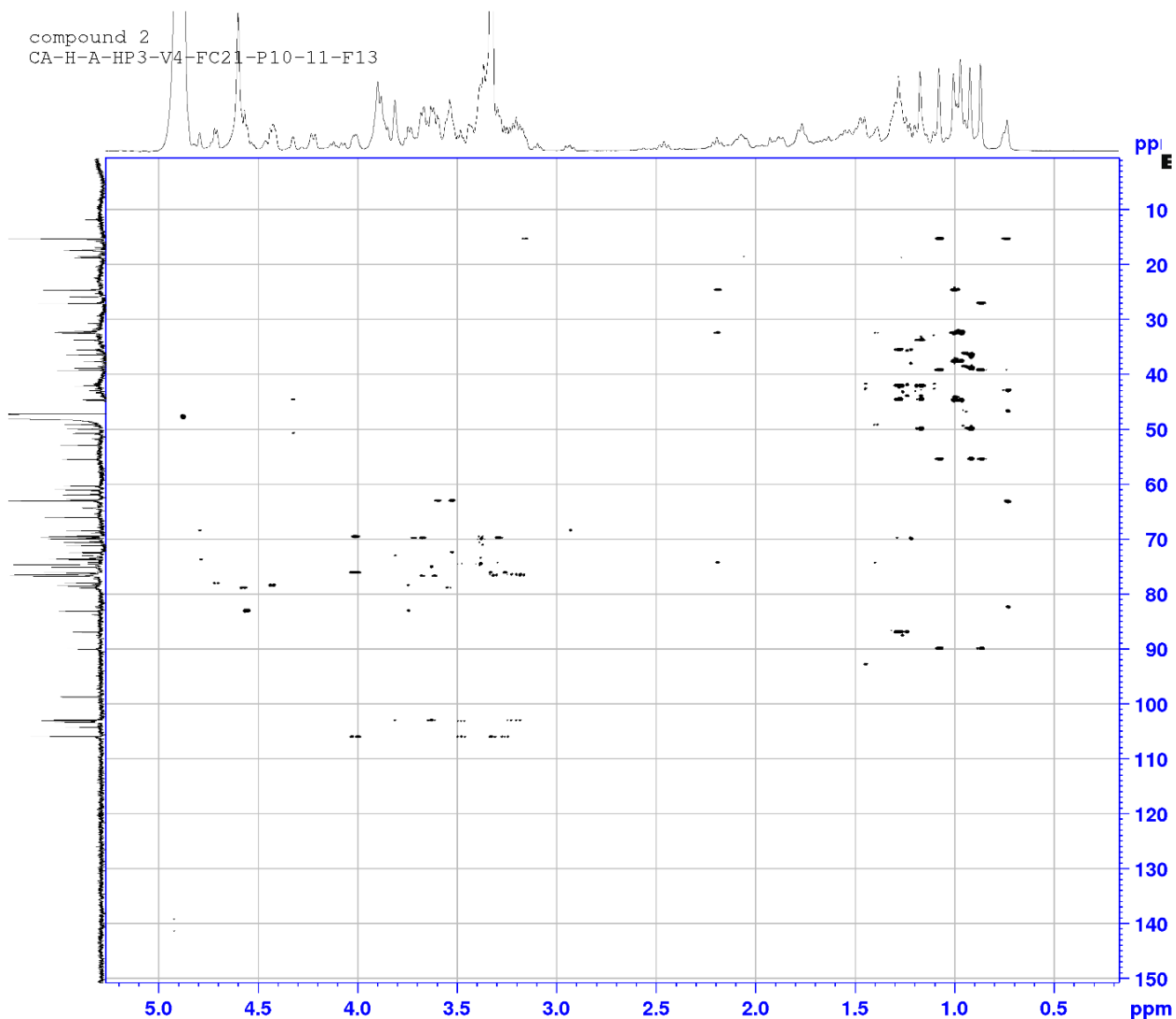


Fig. S12. HMBC spectrum of compound 2

compound 2
CA-H-A-HP3-V4-FC21-P10-11-F13

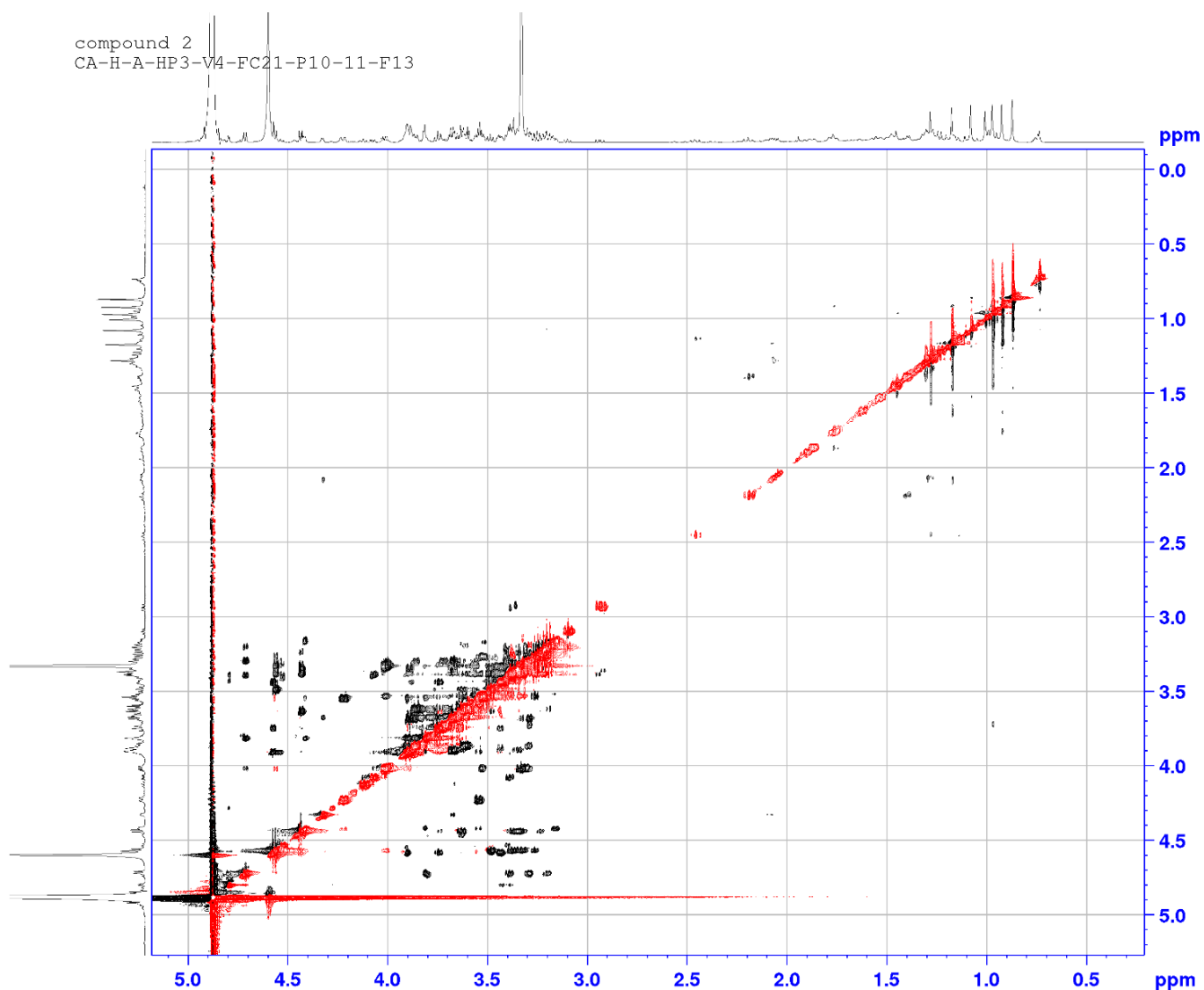


Fig. S13. ROESY spectrum of compound 2

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = 1.0, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

46 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

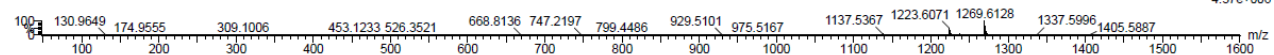
Elements Used:

C: 0-60 H: 0-100 O: 0-30

V4_FC21_F110_11_f13

21HR322_NEG 279 (2.090) Cm (279:286)

1: TOF MS ES-
4.37e+006



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1223.6071	1223.6061	1.0	0.8	11.5	820.6	n/a	n/a	C58 H95 O27

Fig. S14. HR-MS spectrum of compound 2

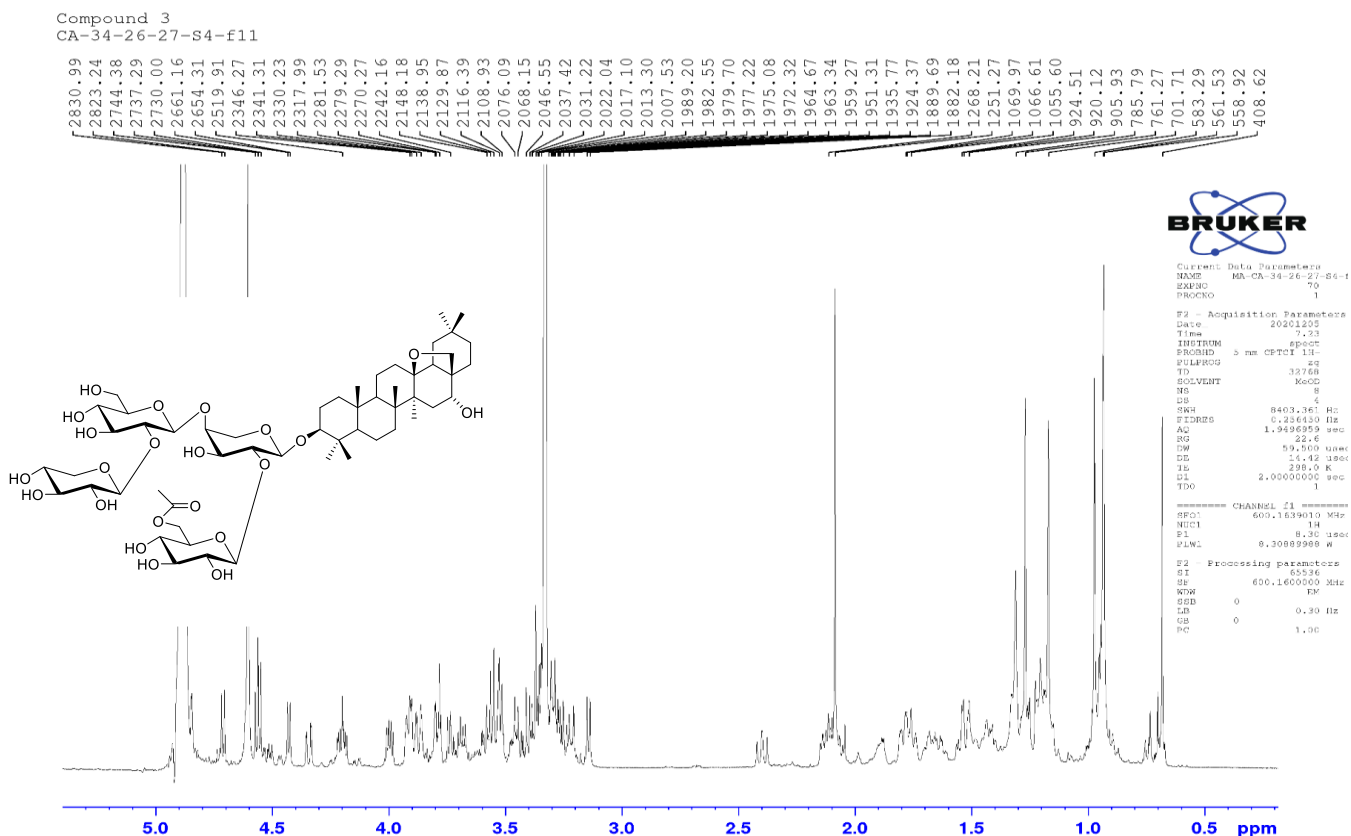


Fig. S15. ^1H NMR Spectrum (600 MHz, $\text{MeOH-}d_4$) of compound 3

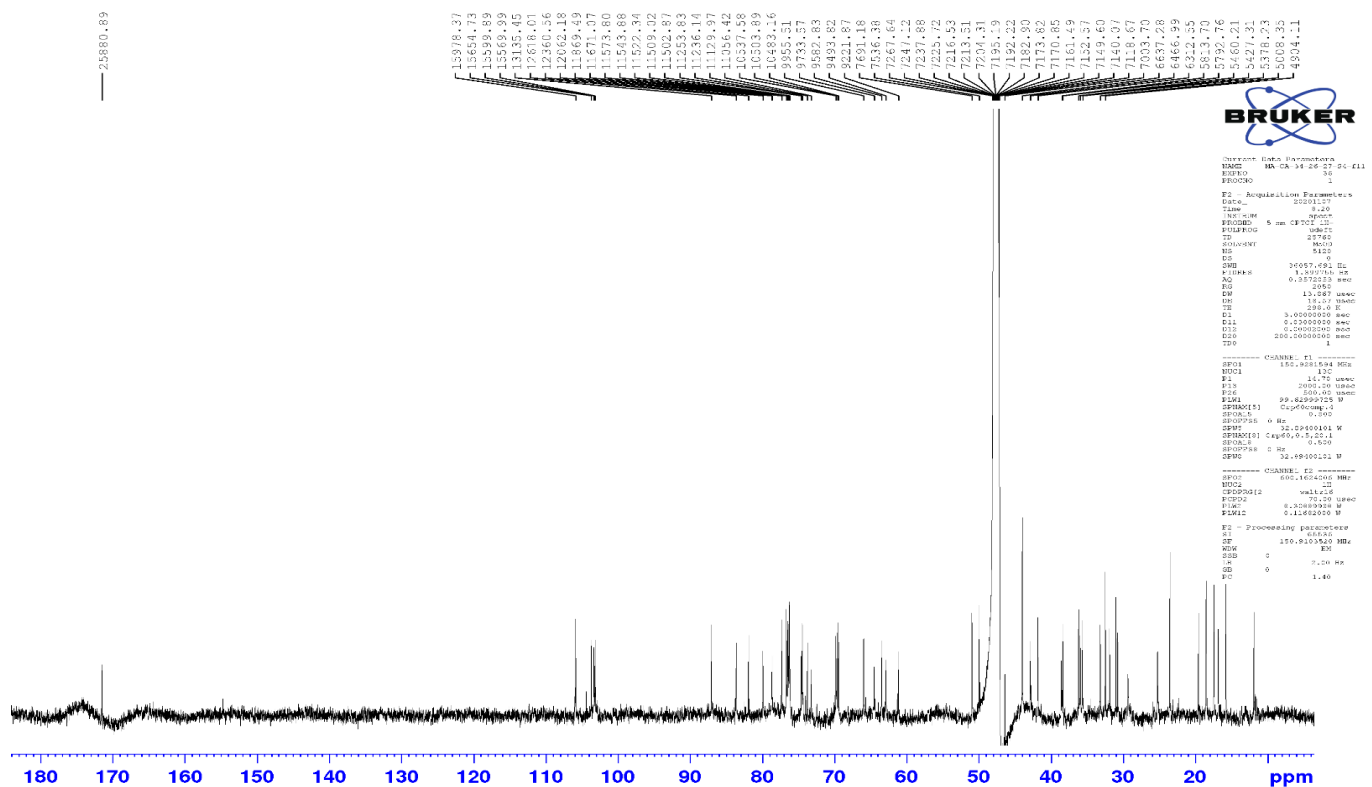


Fig. S16. ^{13}C NMR Spectrum (150 MHz, $\text{MeOH-}d_4$) of compound 3

compound 3
CA-34-26-27-S4-F11

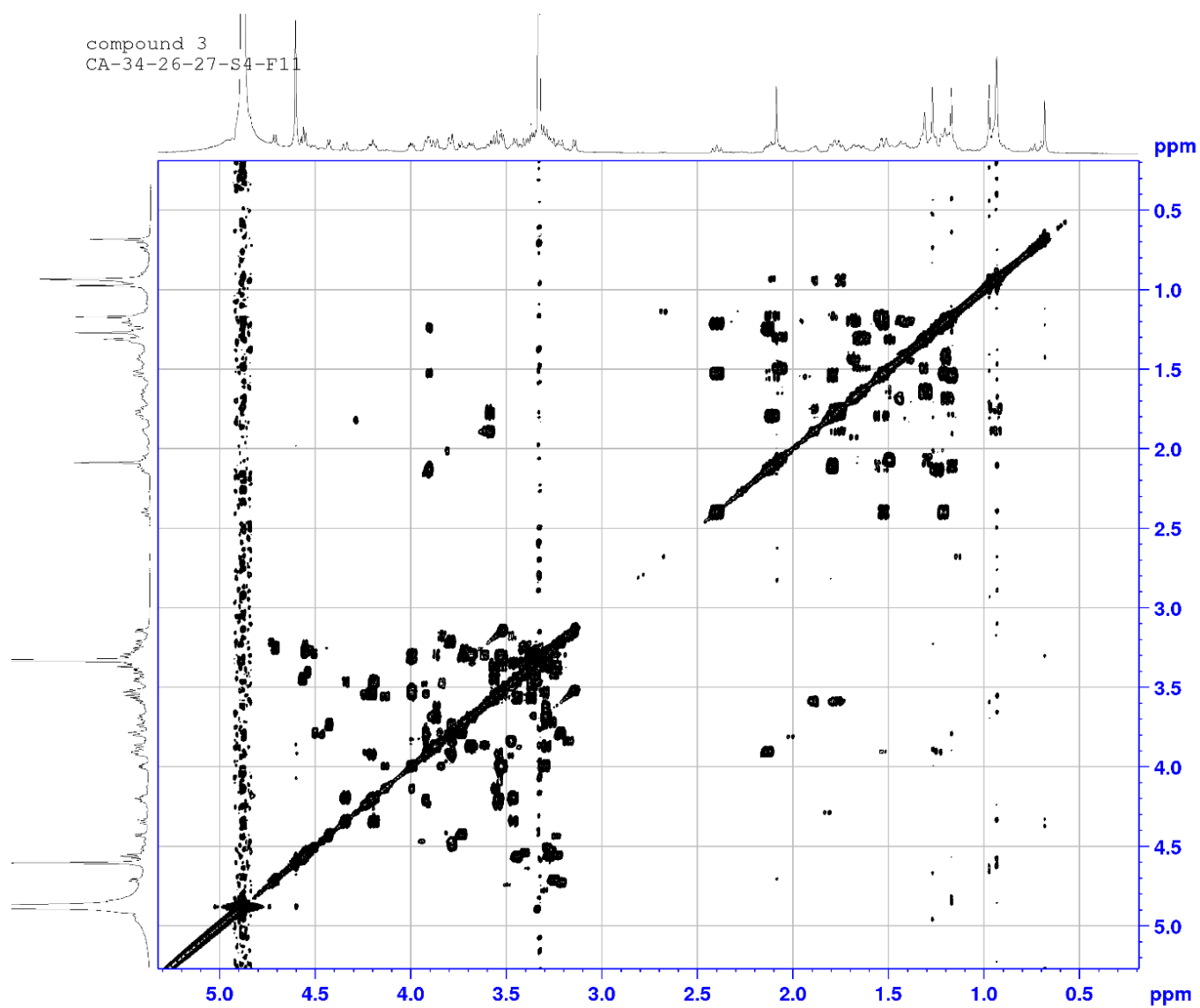


Fig. S17. COSY spectrum of compound 3

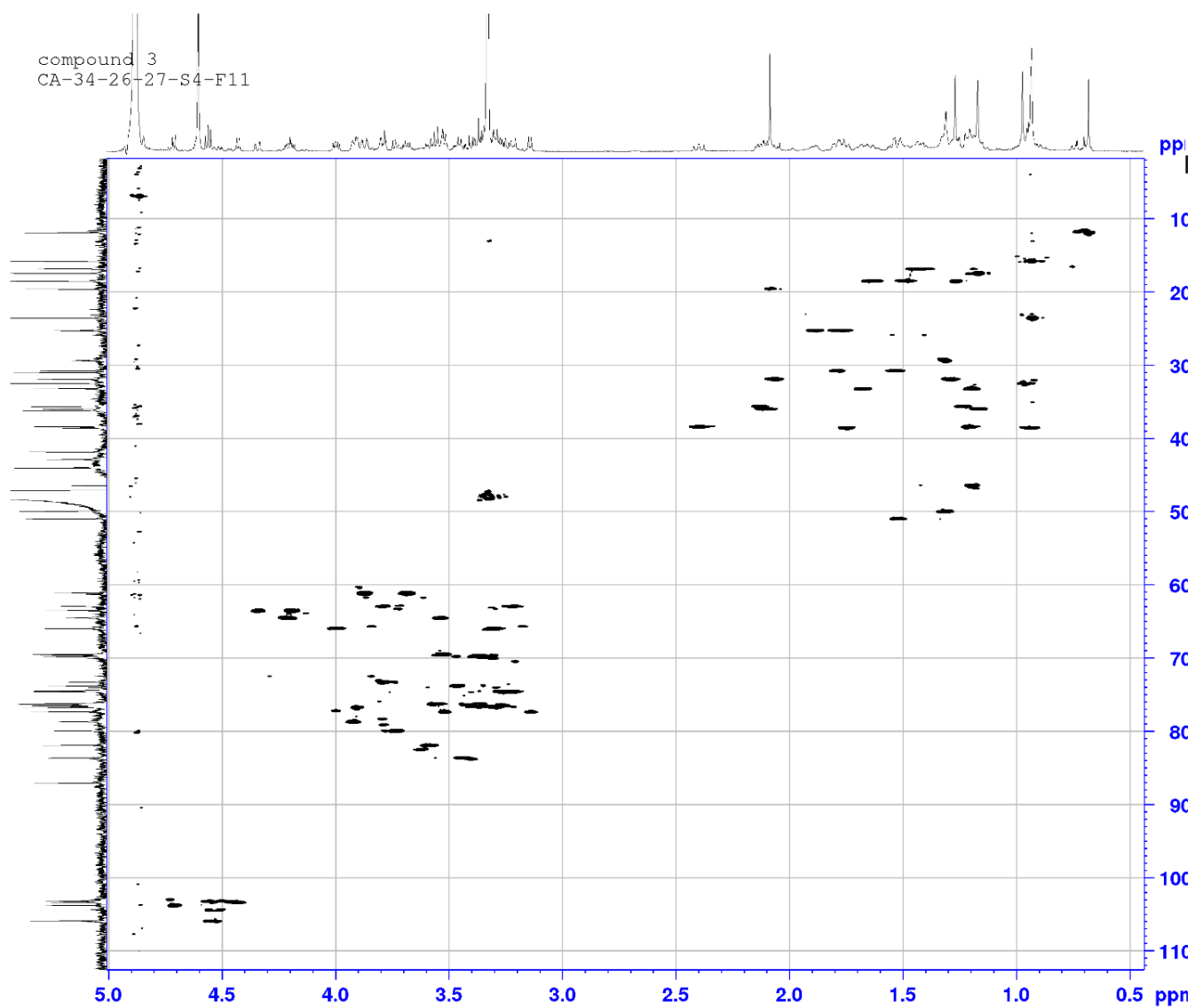


Fig. S18. HSQC spectrum of compound **3**

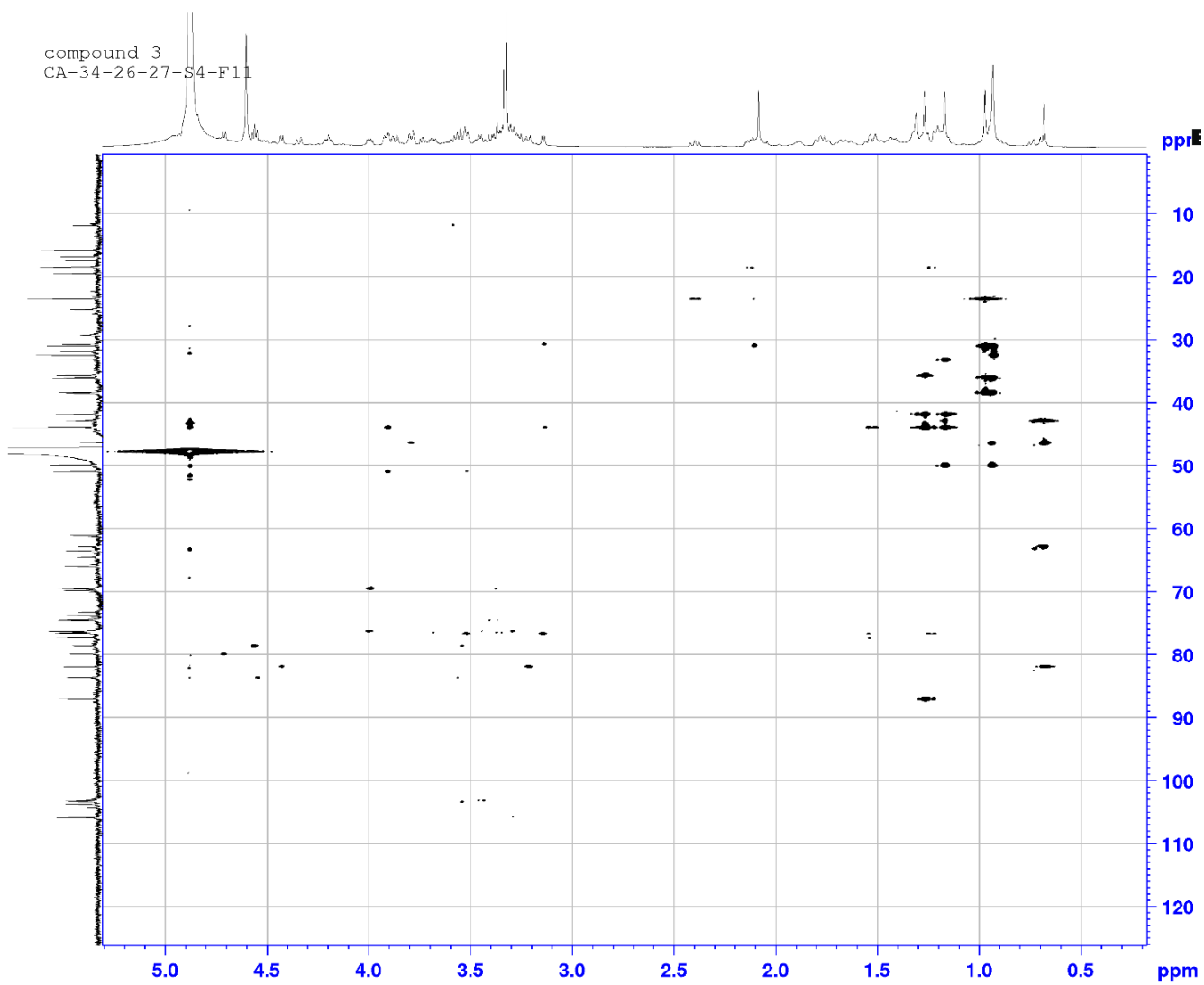


Fig. S19. HMBC spectrum of compound 3

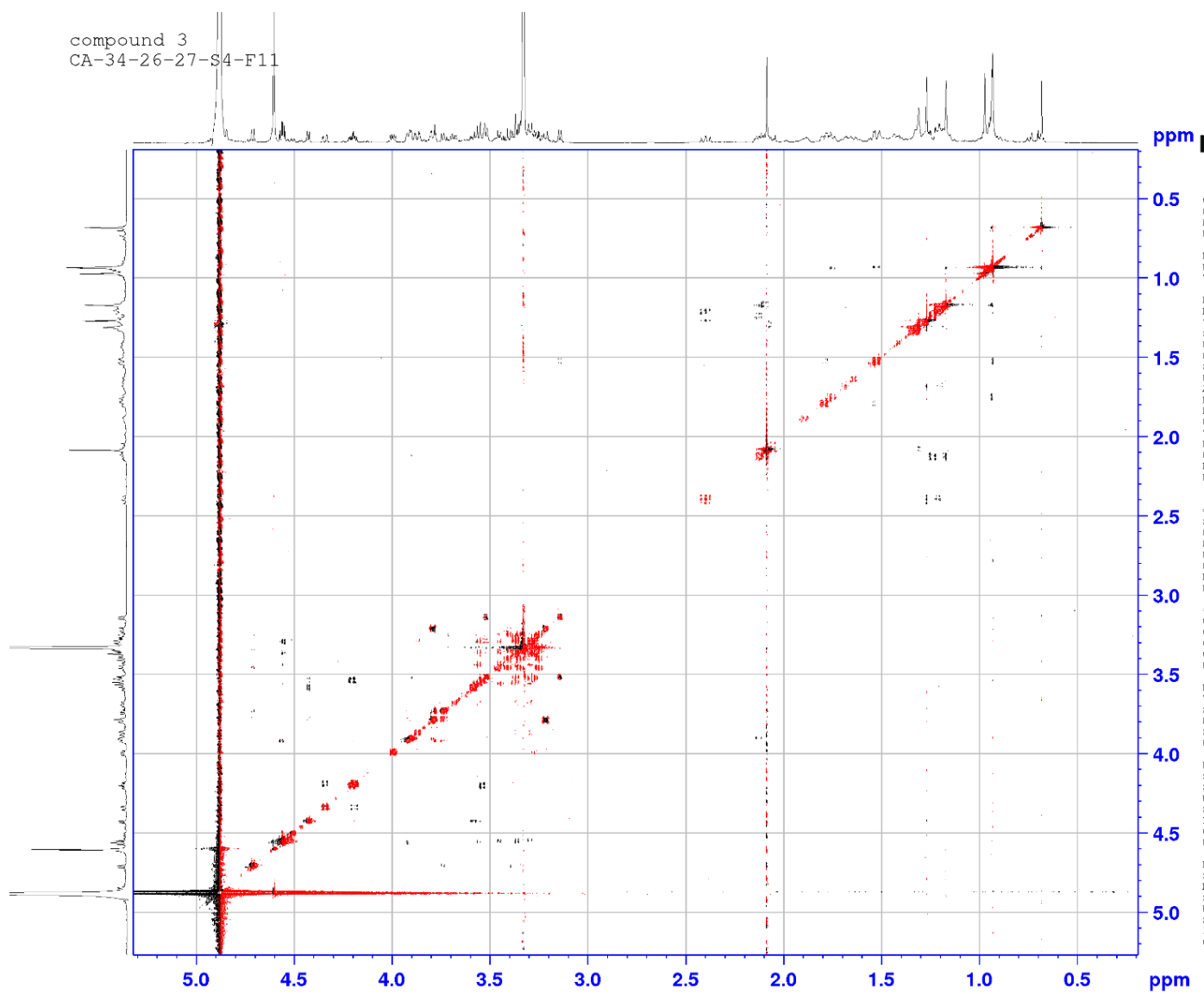


Fig. S20. ROESY spectrum of compound 3

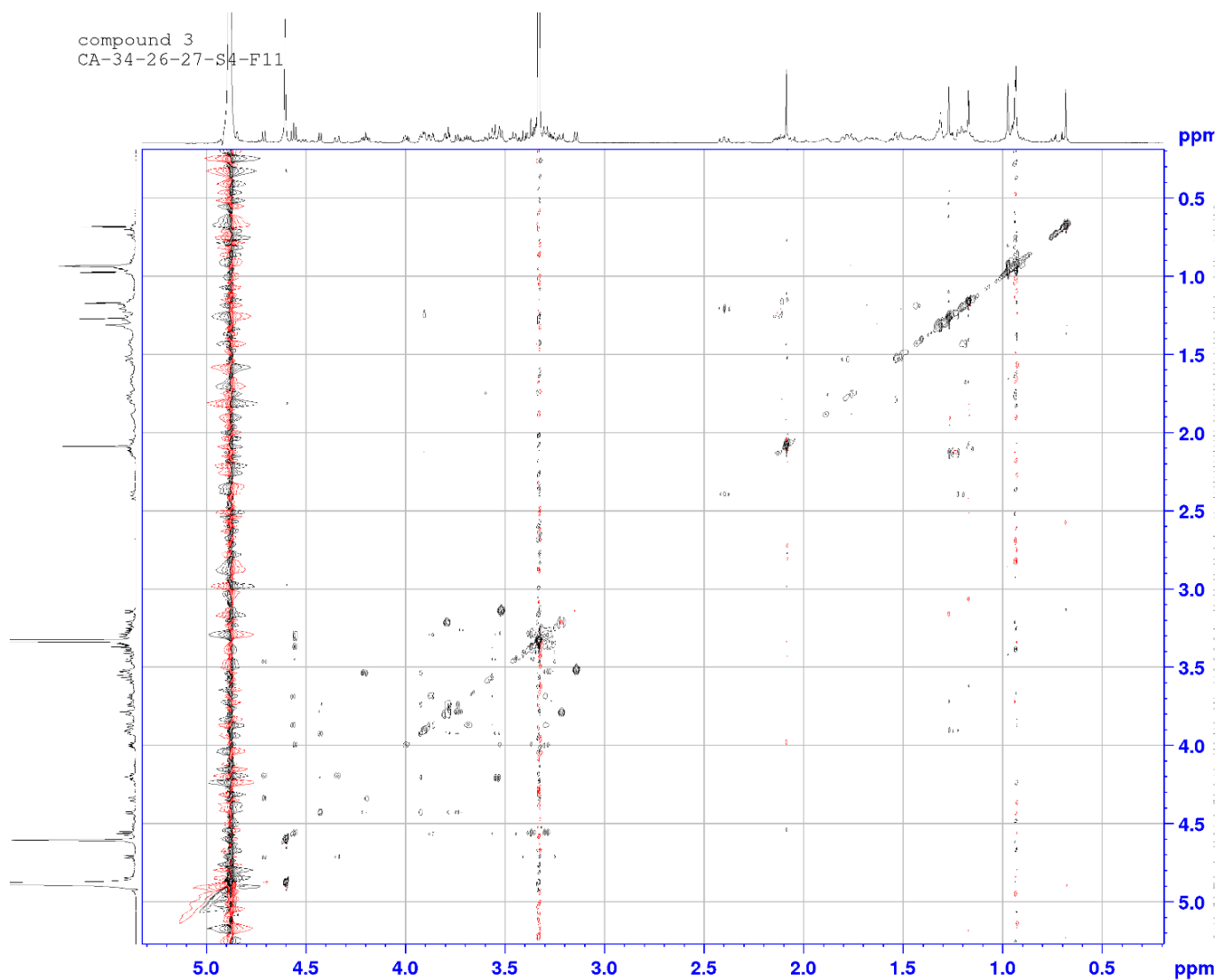


Fig. S21. TOCSY spectrum of compound 3

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 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

159 formula(e) evaluated with 2 results within limits (up to 15 closest results for each mass)

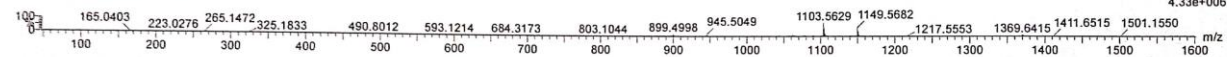
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HP3_V4_F26_27_S4_F11

20HR675 34 (0.269) Cm (27:36)

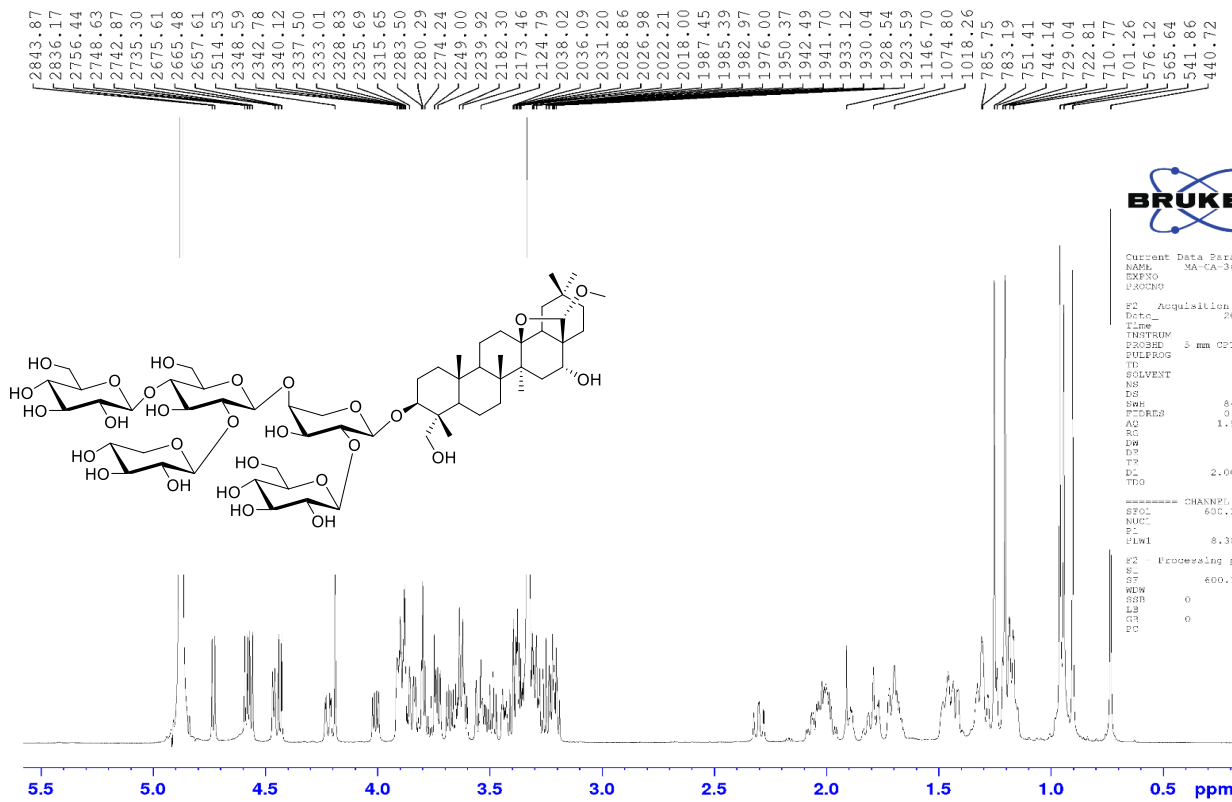
1: TOF MS ES-
4.33e+006



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1103.5629	1103.5638	-0.9	-0.8	11.5	938.0	0.003	99.73	C54 H87 O23
	1103.5579	5.0	4.5	20.5	943.9	5.933	0.27	C61 H83 O18

Fig. S22. HR-MS spectrum of compound 3

Compound 4
CA-36-P14-F32



BRUKER

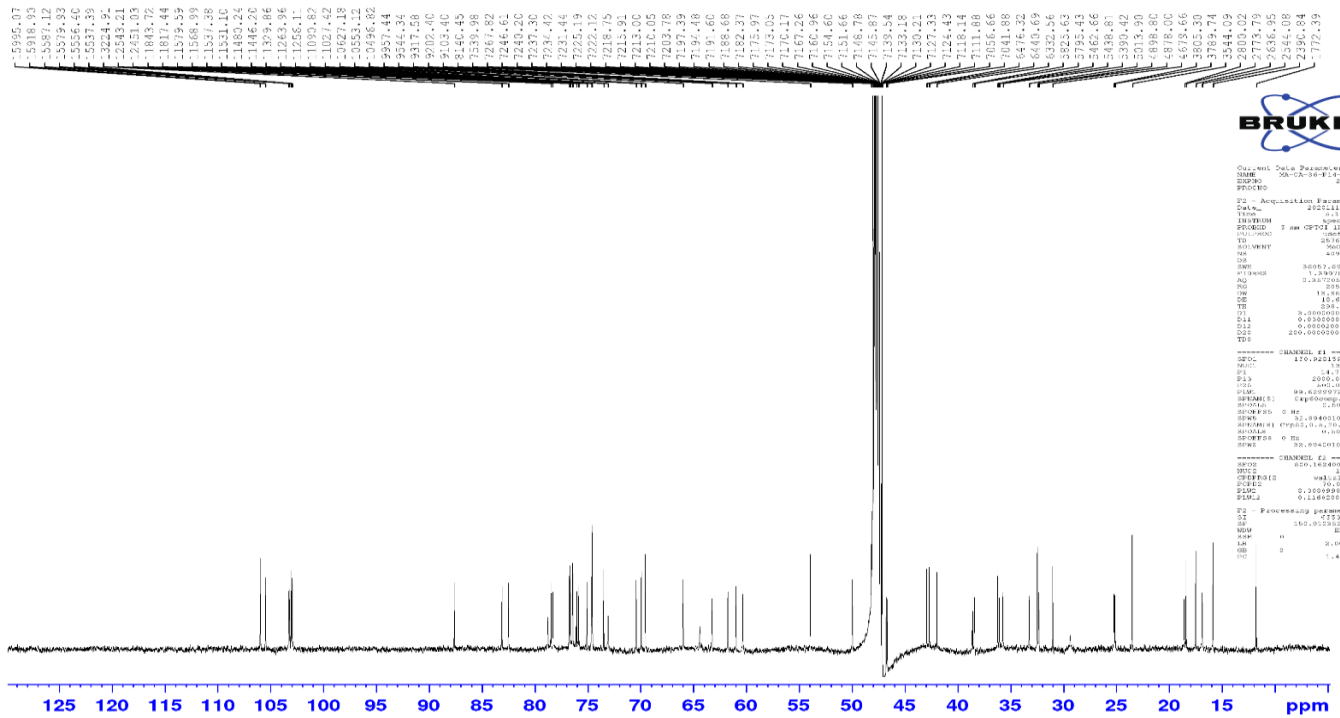
Current Data Parameters
NAME MA-CA-36-P14-F32
EXPNO 32
PROCNO 1

F2 Acquisition Parameters
Date_ 20201129
Time 9.46
INSTRUM spect
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PULPROG zgpg30
TD 32768
SOLVENT MeOH
NS 8
DS 4
SWH 8403.361 Hz
FIDRES 0.256400 Hz
AQ 1.9496359 sec
RG 261.5
DQ 59.500 usec
SFO 600.140000 MHz
PC 298.2 K
TD 2,000,000 usec

----- CHANNEL f1 -----
SFO1 600.140000 MHz
NUC1 13
P1 8.20 usec
PLW1 8.30889988 W

F2 Processing parameters
SI 65536
SF 600.140000 MHz
EX
LB 0.30 Hz
GB 0
PC 1.00

Fig. S23. ¹H NMR Spectrum (600 MHz, MeOH-d₄) of compound 4



BRUKER

Current Data Parameters
NAME MA-CA-36-P14-F32
EXPNO 32
PROCNO 1

F2 Acquisition Parameters
Date_ 20201129
Time 9.46
INSTRUM spect
PROBHD 5 mm CCP131H
PULPROG zgpg30
TD 32768
SOLVENT MeOH
NS 8
DS 4
SWH 30967.090 Hz
FIDRES 1.5272639 Hz
AQ 1.9496359 sec
RG 261.5
DQ 59.500 usec
SFO 100.626159 MHz
NUC1 13
P1 8.20 usec
PLW1 8.30889988 W

----- CHANNEL f1 -----
SFO1 100.626159 MHz
NUC1 13
P1 8.20 usec
PLW1 8.30889988 W

----- CHANNEL f2 -----
SFO2 200.626159 MHz
NUC2 13
P2 8.20 usec
PLW2 8.30889988 W

F2 Processing parameters
SI 65536
SF 100.626159 MHz
EX
LB 0.30 Hz
GB 0
PC 1.00

Fig. S24. ¹³C NMR Spectrum (150 MHz, MeOH-d₄) of compound 4

compound 4
CA-36-P14-F31

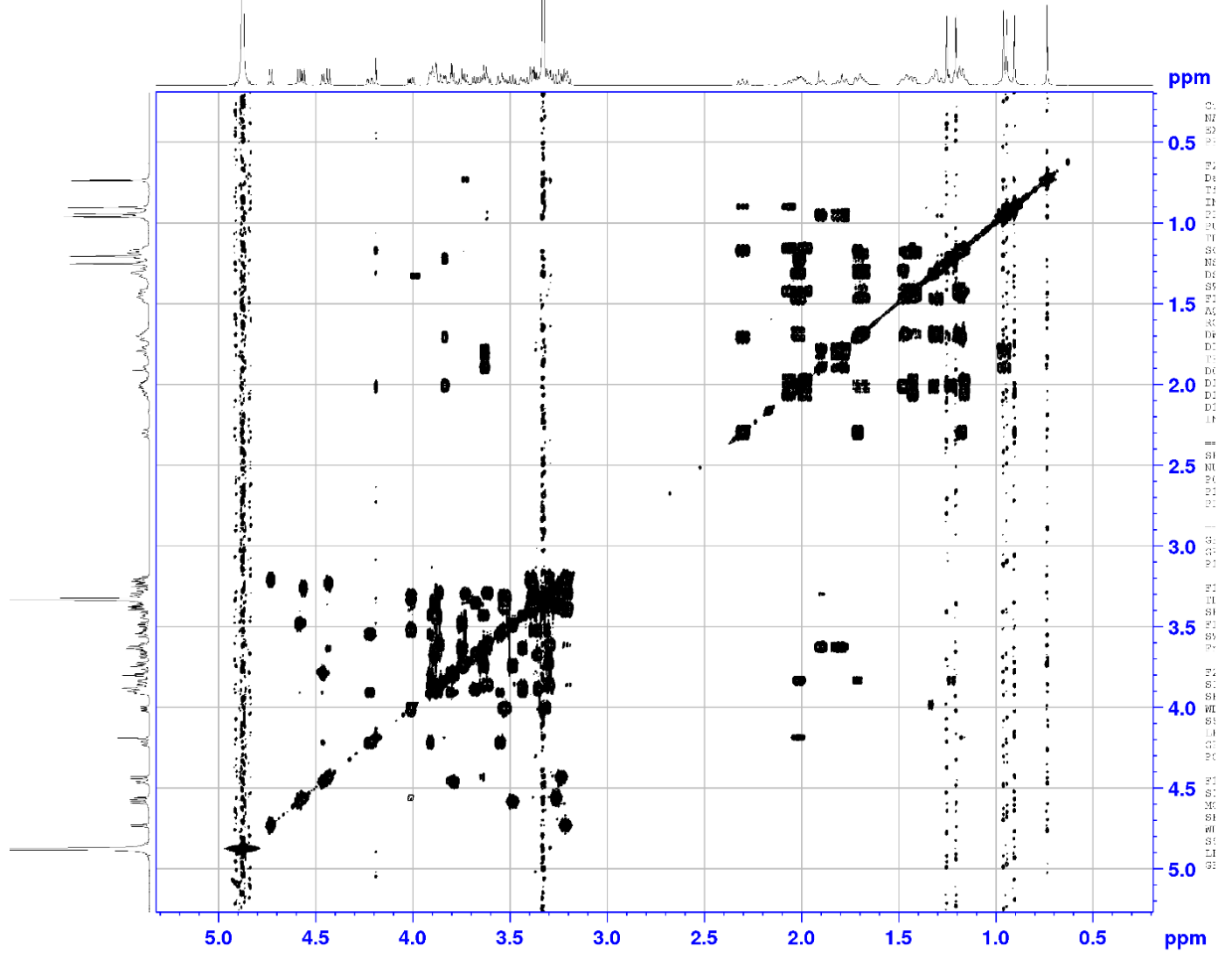


Fig. S25. COSY spectrum of compound 4

compound 4
CA-36-P14-F31

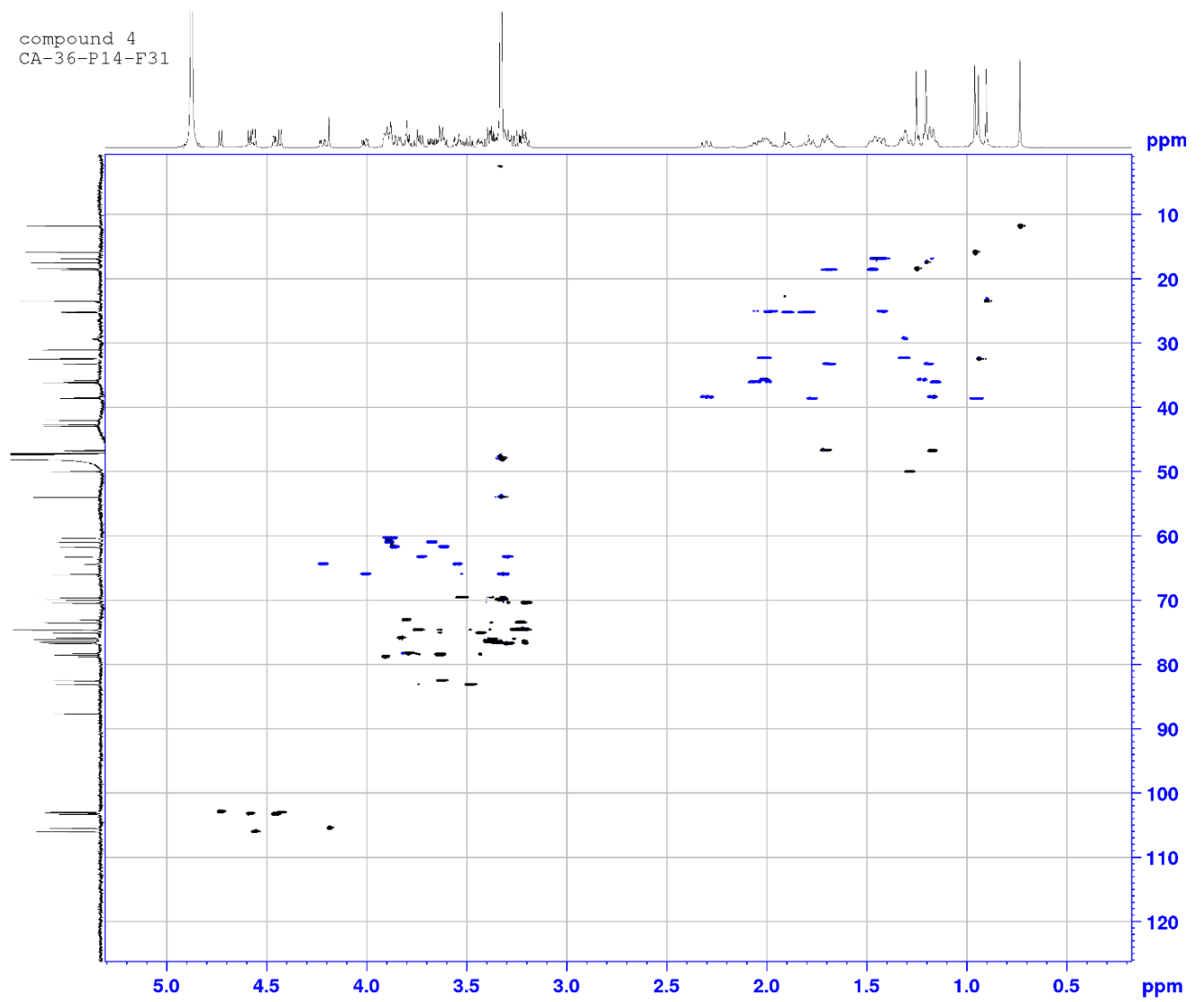


Fig. S26. HSQC spectrum of compound **4**

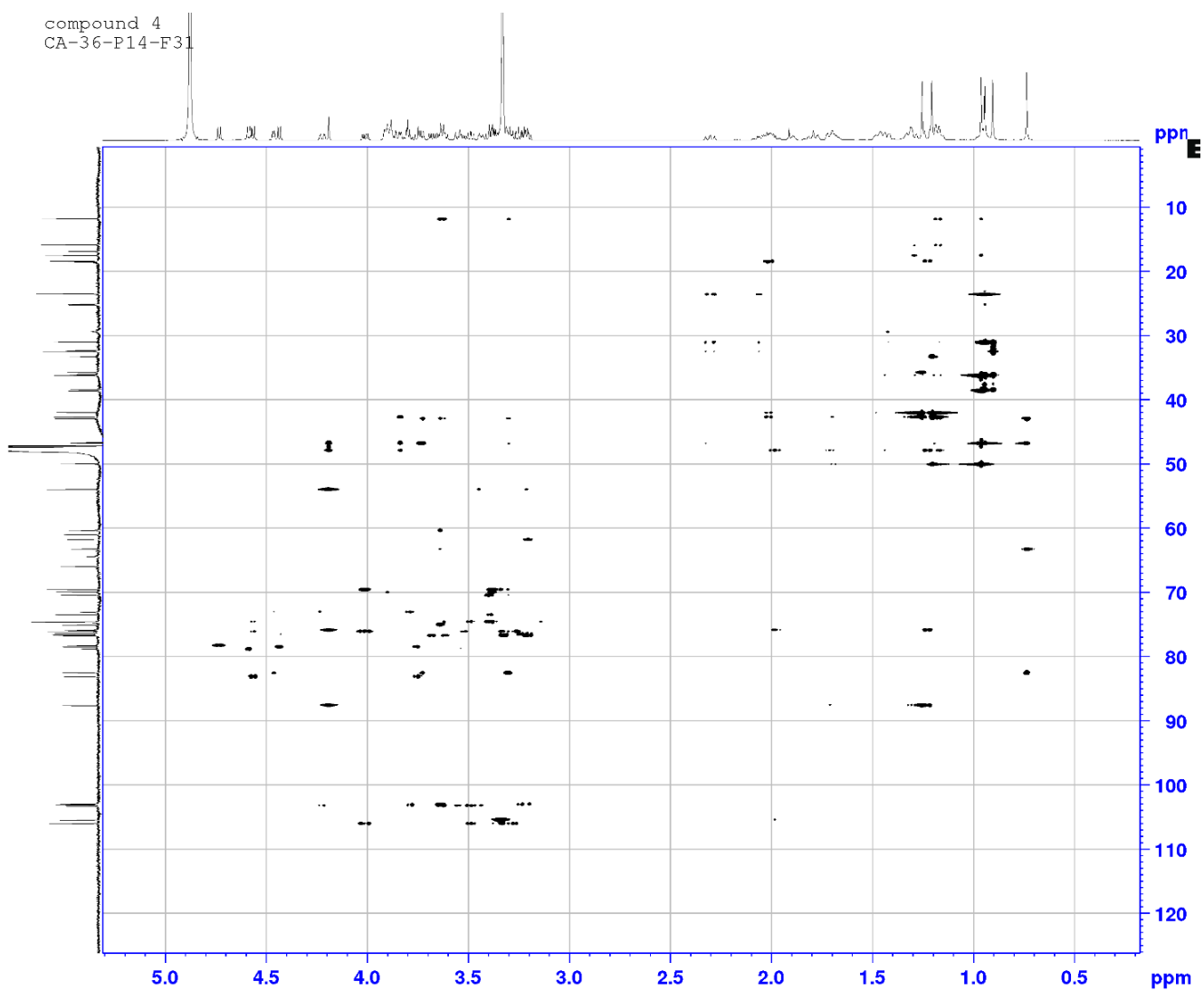


Fig. S27. HMBC spectrum of compound 4

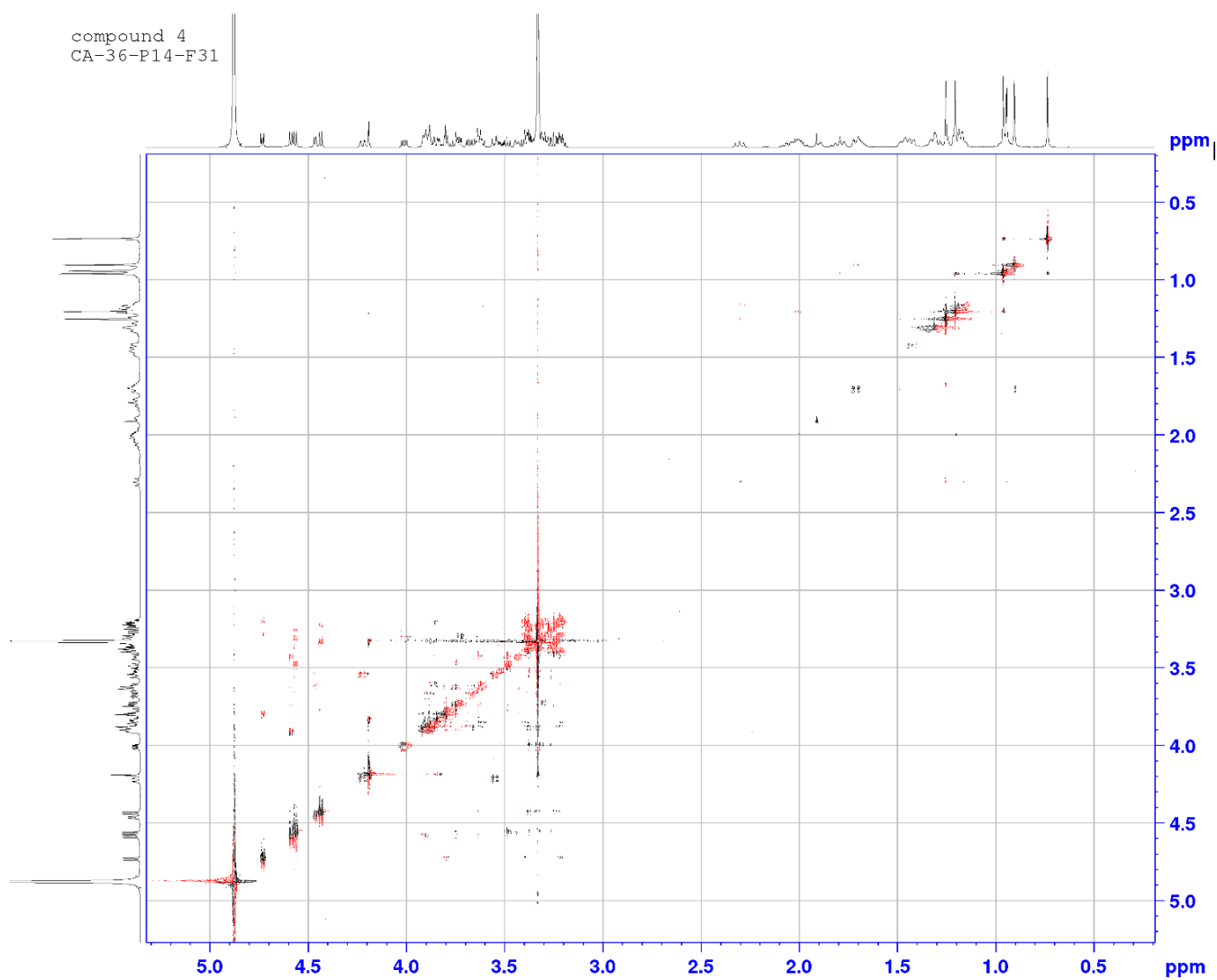


Fig. S28. ROESY spectrum of compound 4

compound 4
CA-36-P14-F31

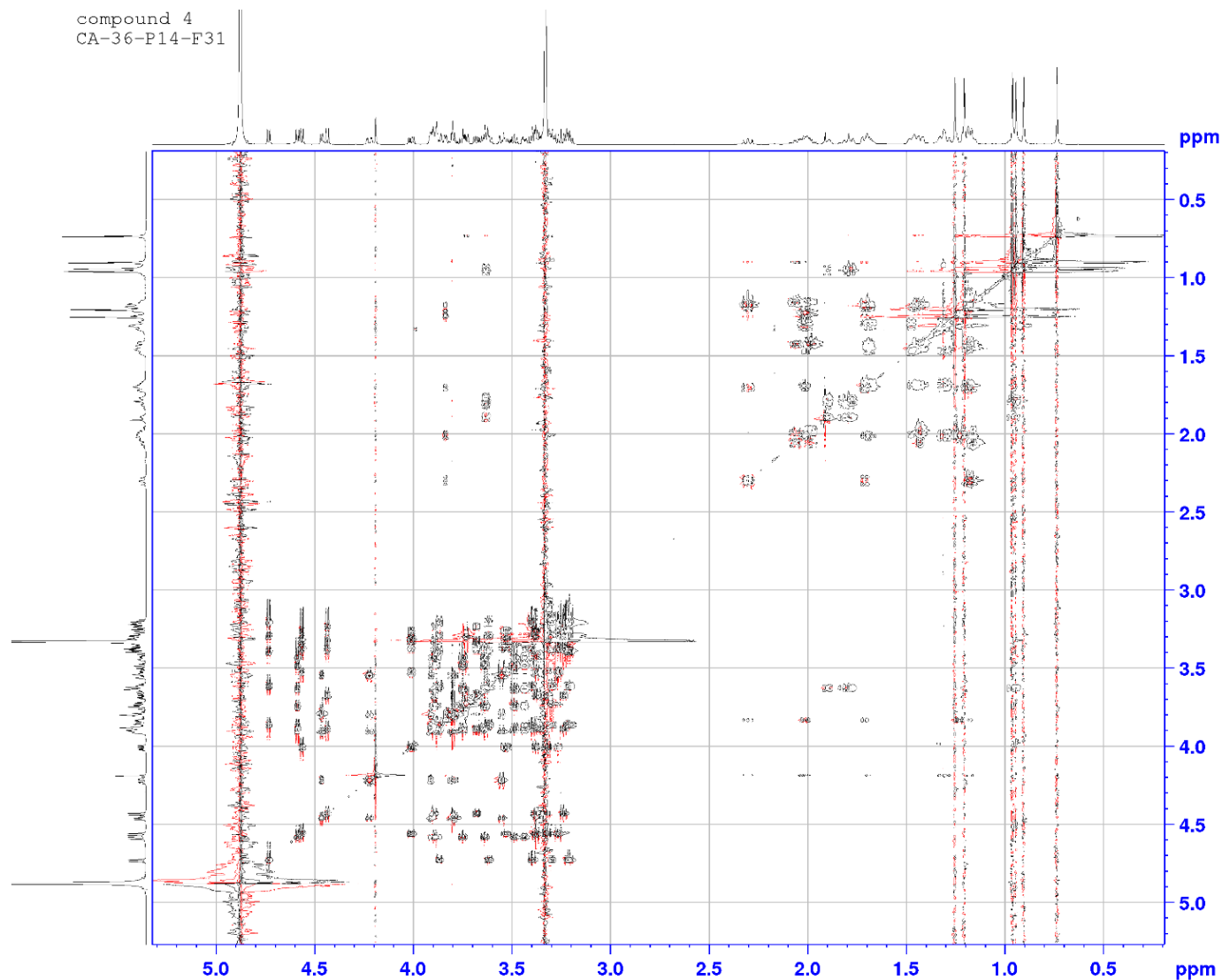


Fig. S29: TOCSY spectrum of compound 4

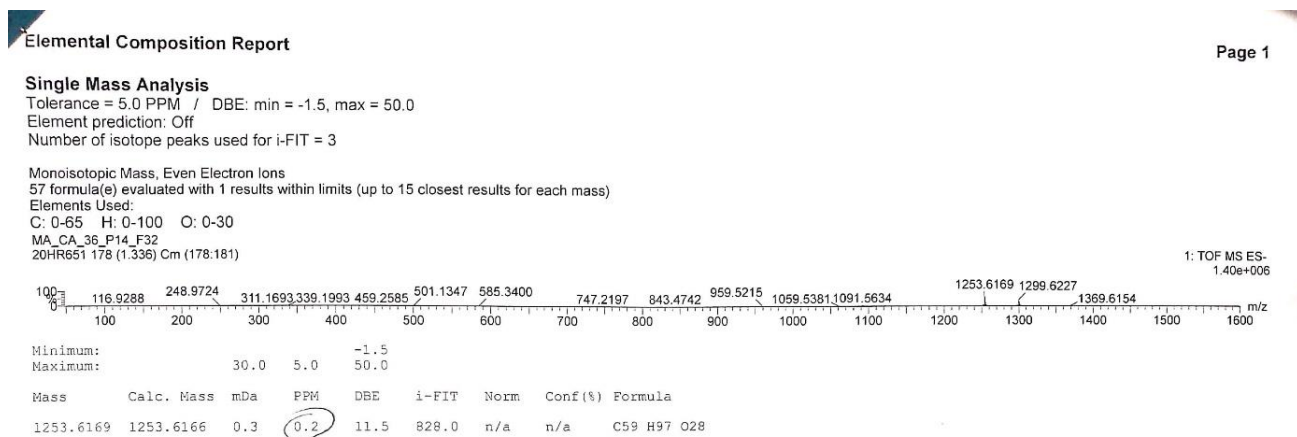


Fig. S30. HR-MS spectrum of compound 4

Compound 5
CA-H-HP3-V4-FC21-F7-8-S4-F3

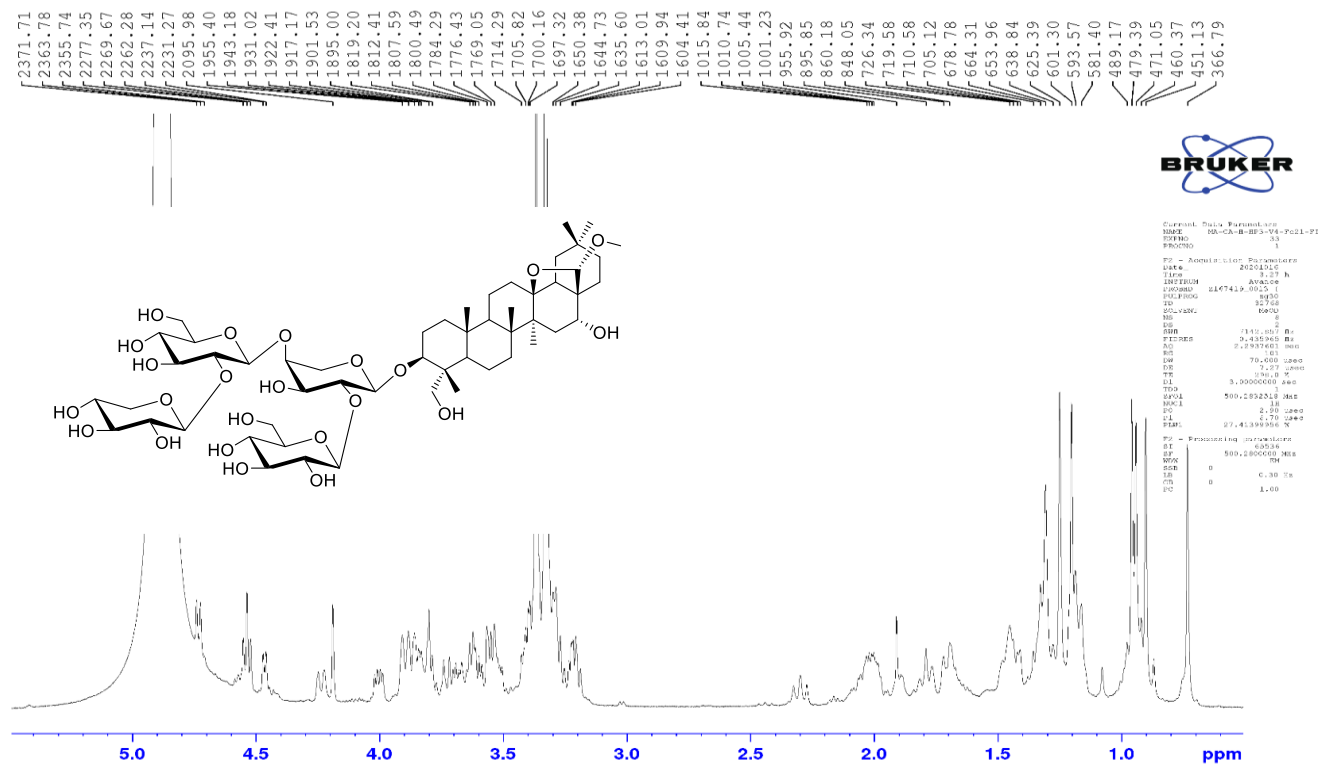


Fig. S31. ¹H NMR Spectrum (500 MHz, MeOH-d₄) of compound 5

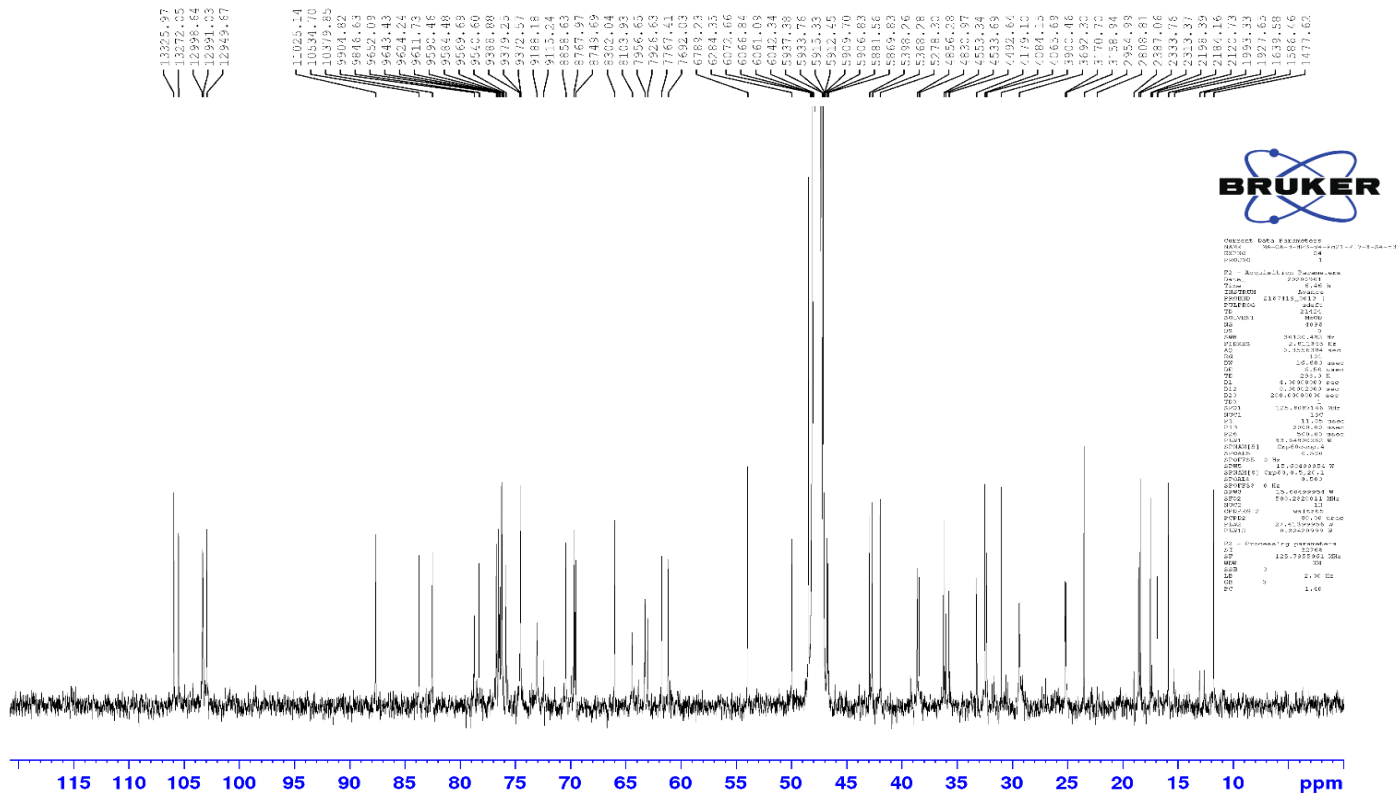


Fig. S32. ¹³C NMR Spectrum (125 MHz, MeOH-d₄) of compound 5

compound 5
CA-H-HP3-V4-FC21-FI7-8-S4-F2

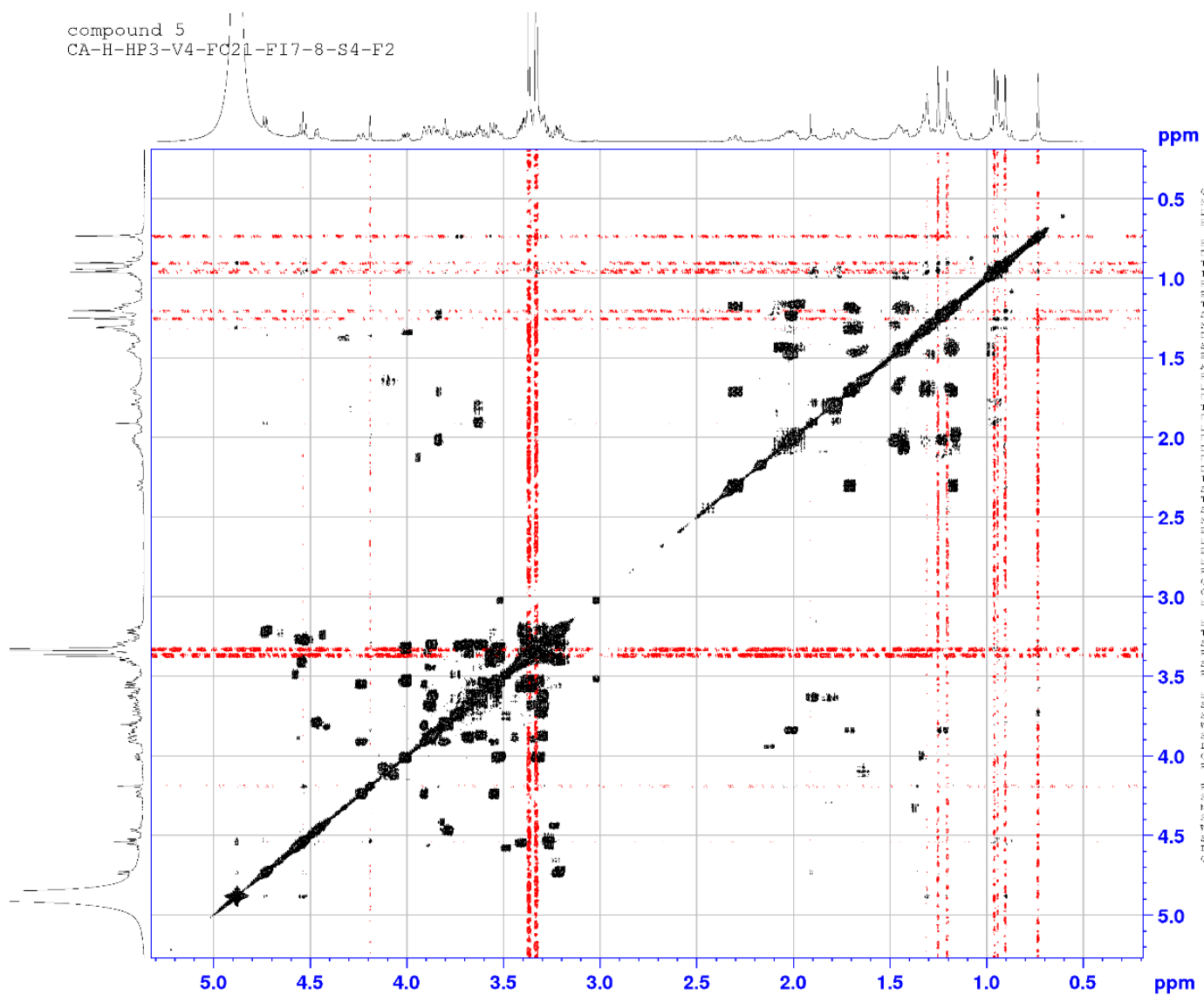


Fig. S33. COSY NMR spectrum of compound 5

compound 5
CA-H-HP3-V4-FC21-FI7-8-S4-F2

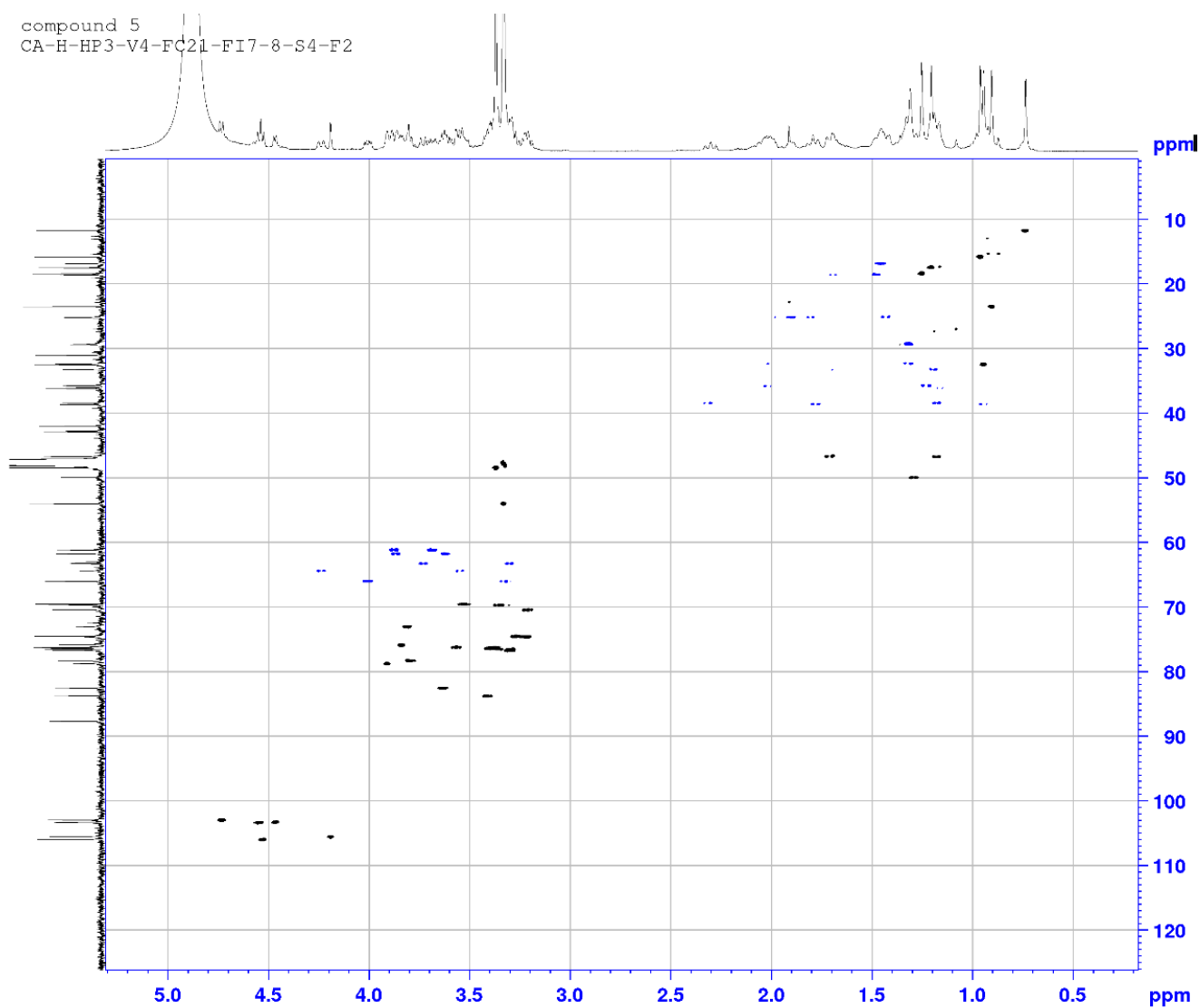


Fig. S34. HSQC spectrum of compound 5

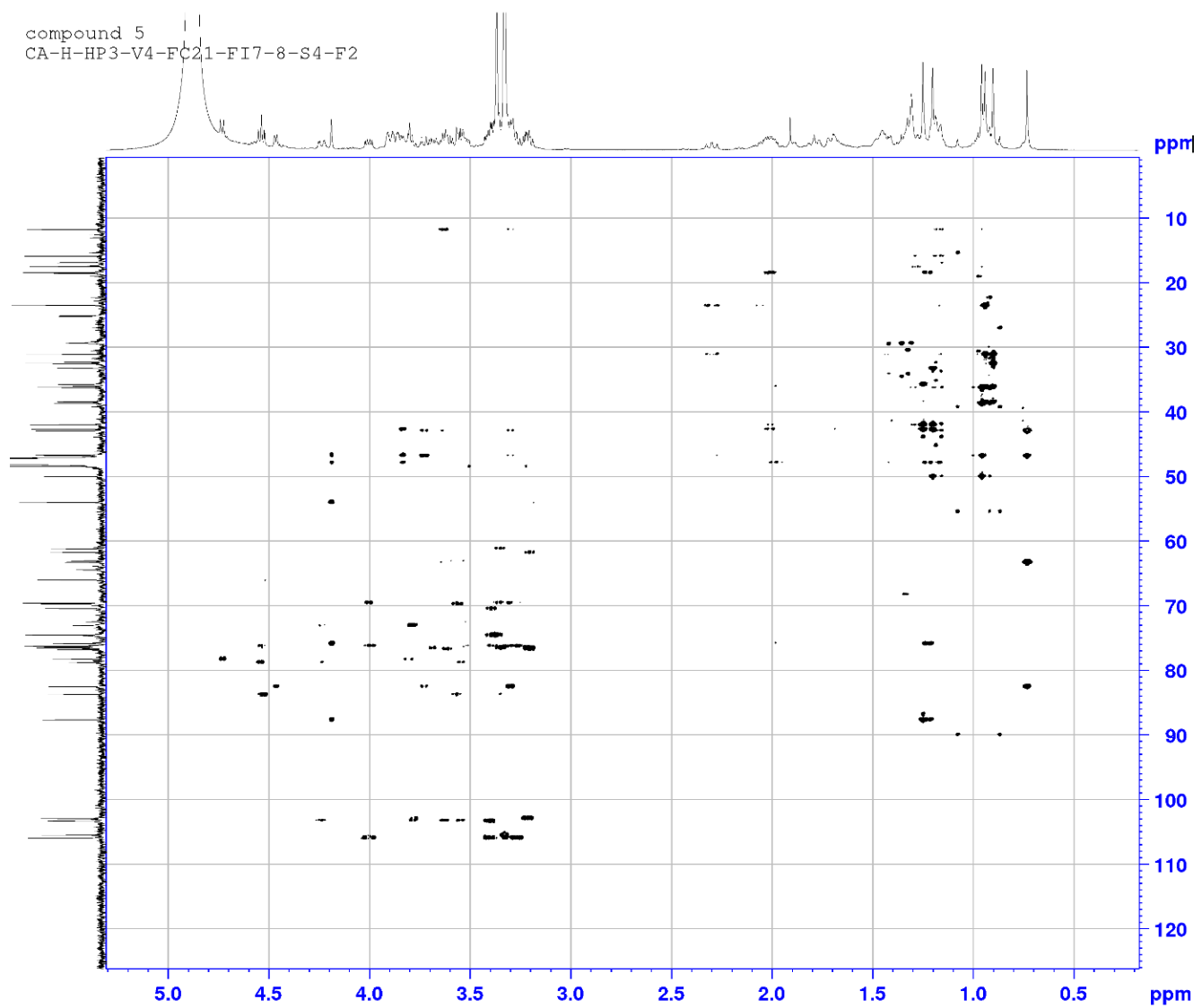


Fig. S35. HMBC spectrum of compound **5**

compound 5
CA-H-HP3-V4-FC21-FI7-8-S4-F2

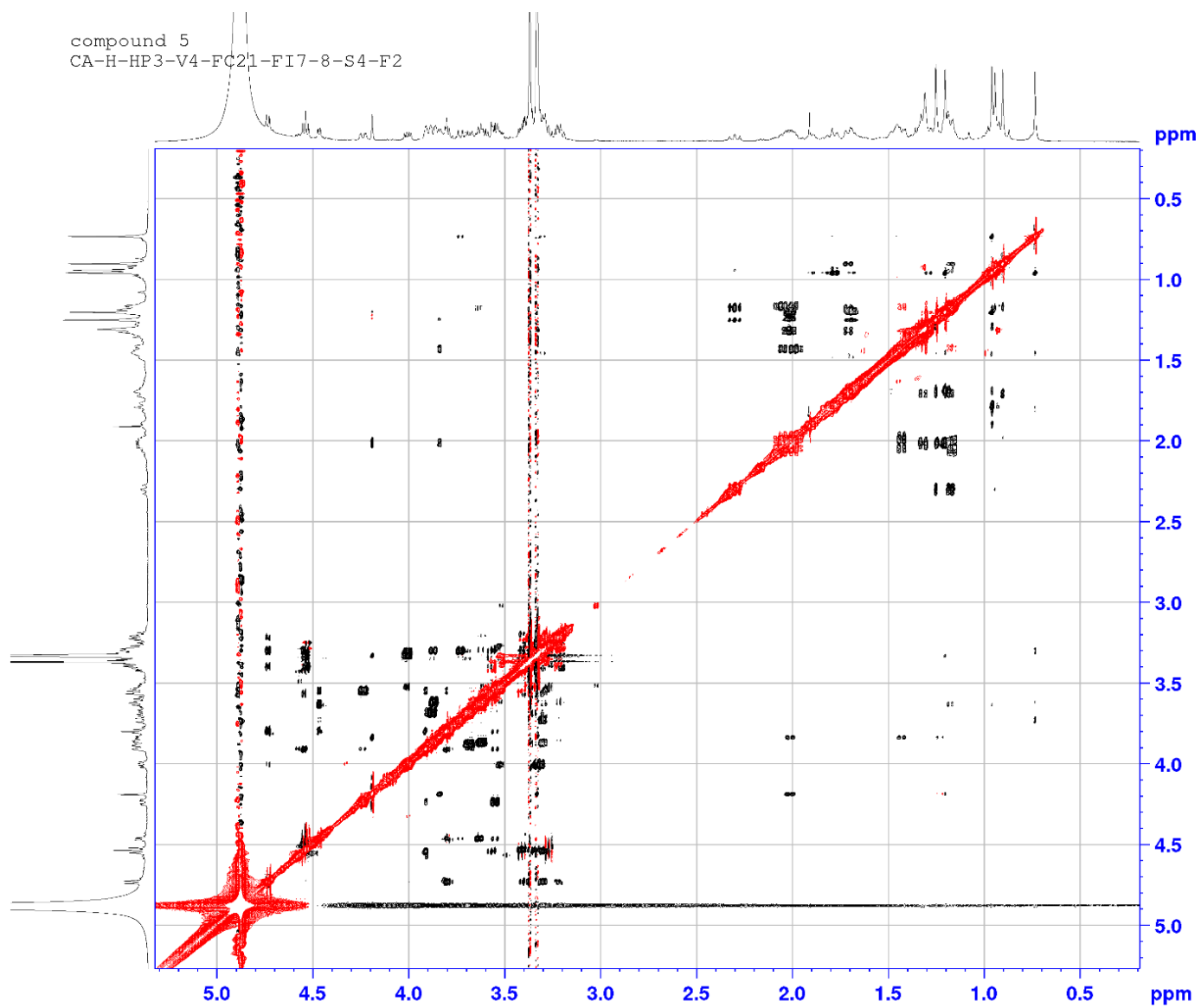


Fig. S36. ROESY spectrum of compound 5

compound 5
CA-H-HP3-V4-FC21-FI7-8-S4-F2

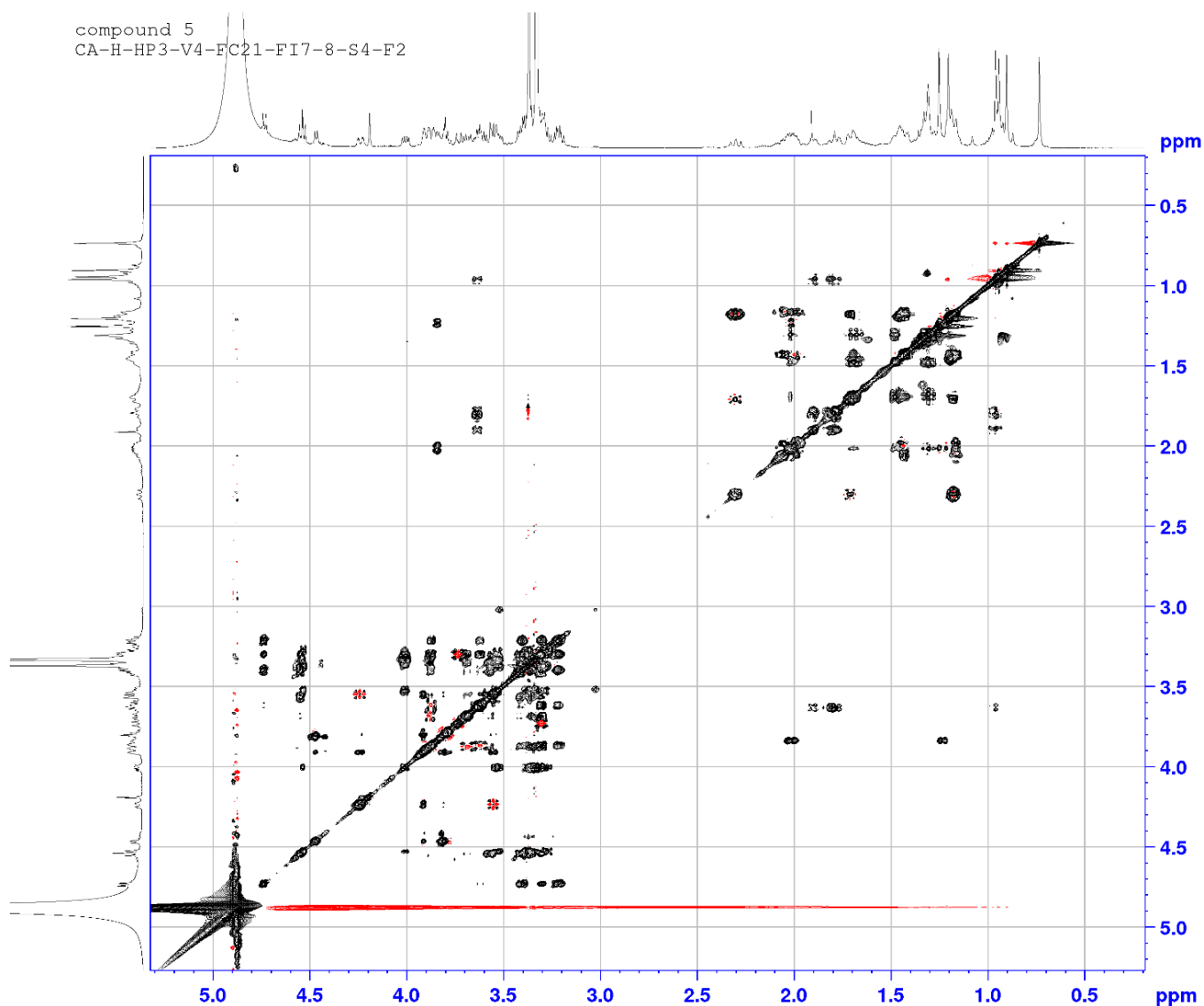


Fig. S37. TOCSY spectrum of compound 5

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 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

137 formula(e) evaluated with 2 results within limits (up to 15 closest results for each mass)

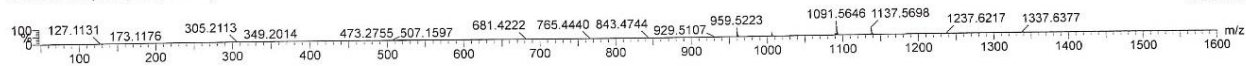
Elements Used:

C: 0-65 H: 0-100 O: 0-30

MA_CA_HP3_V4_Fc21_Fi7_8_S4_F3

20HR646 184 (1.385) Cm (184:186)

1: TOF MS ES-
2.05e+006



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1091.5646	1091.5638	0.8	0.7	10.5	898.5	0.094	91.05	C53 H87 O23
	1091.5697	-5.1	-4.7	1.5	900.8	2.414	8.95	C46 H91 O28

Fig. S38. HR-MS spectrum of compound 5

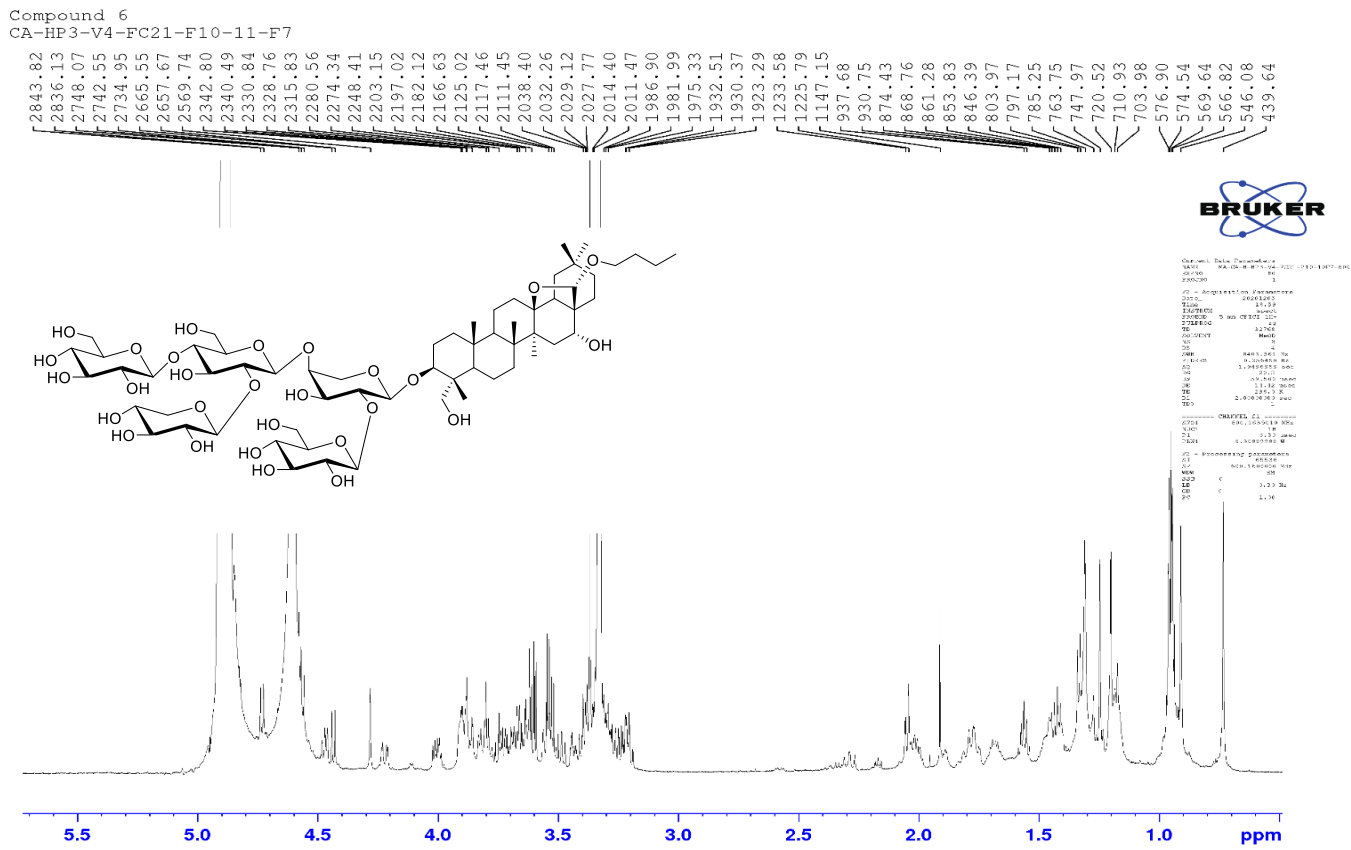


Fig. S39. ¹H NMR Spectrum (600 MHz, MeOH-*d*₄) of compound **6**

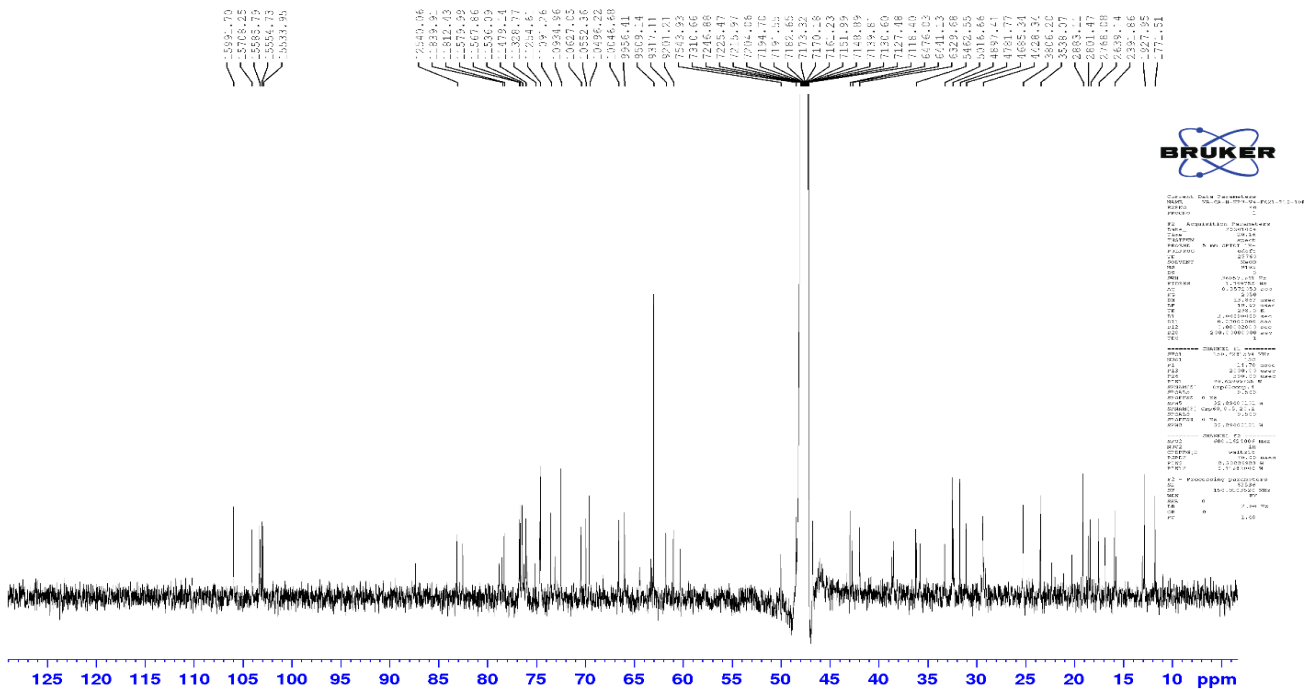


Fig. S40. ¹³C NMR Spectrum (150 MHz, MeOH-*d*₄) of compound **6**

compound 6
CA-H-HP3-V4-FC21-P10-10-F7

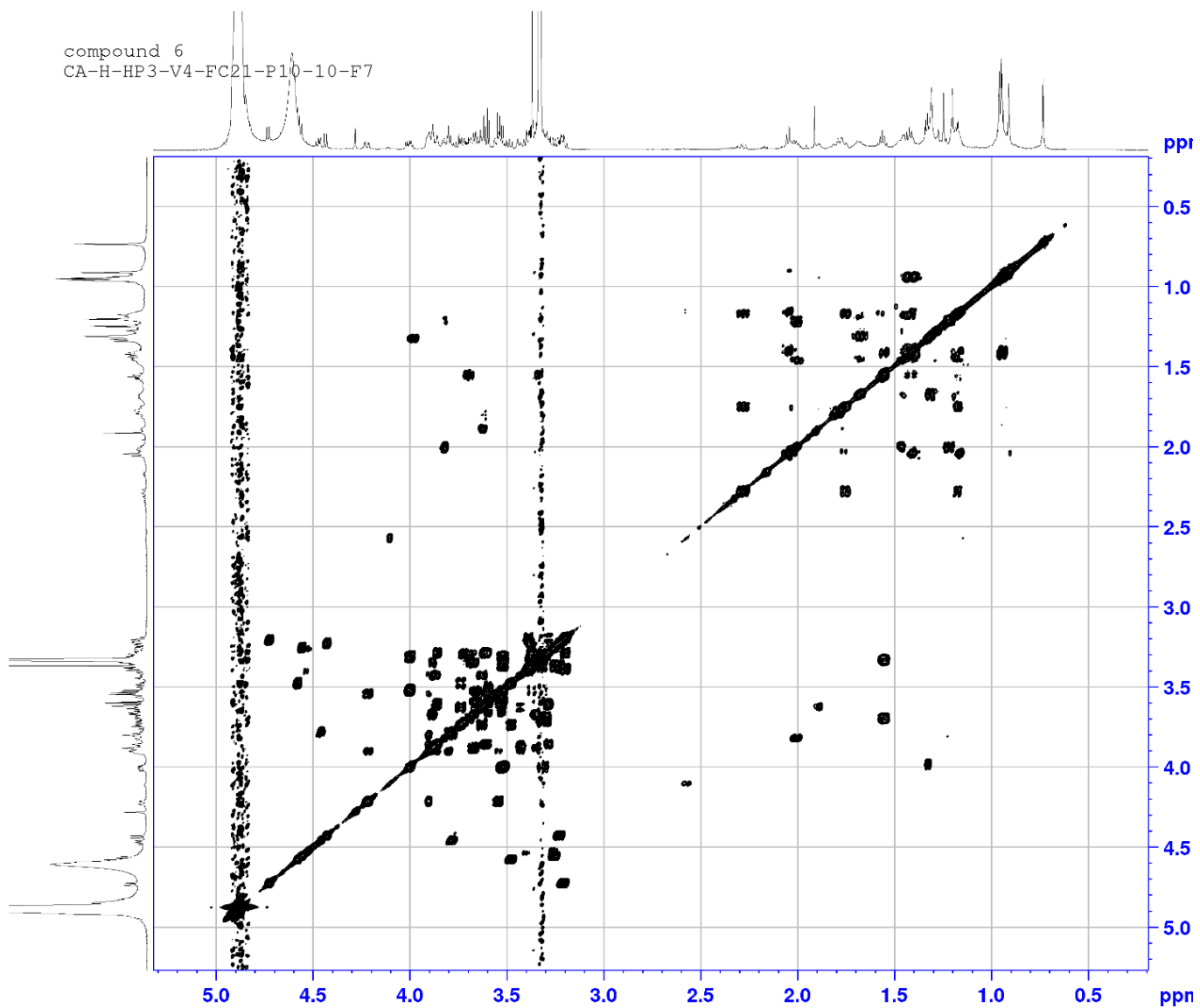


Fig. S41. COSY spectrum of compound 6

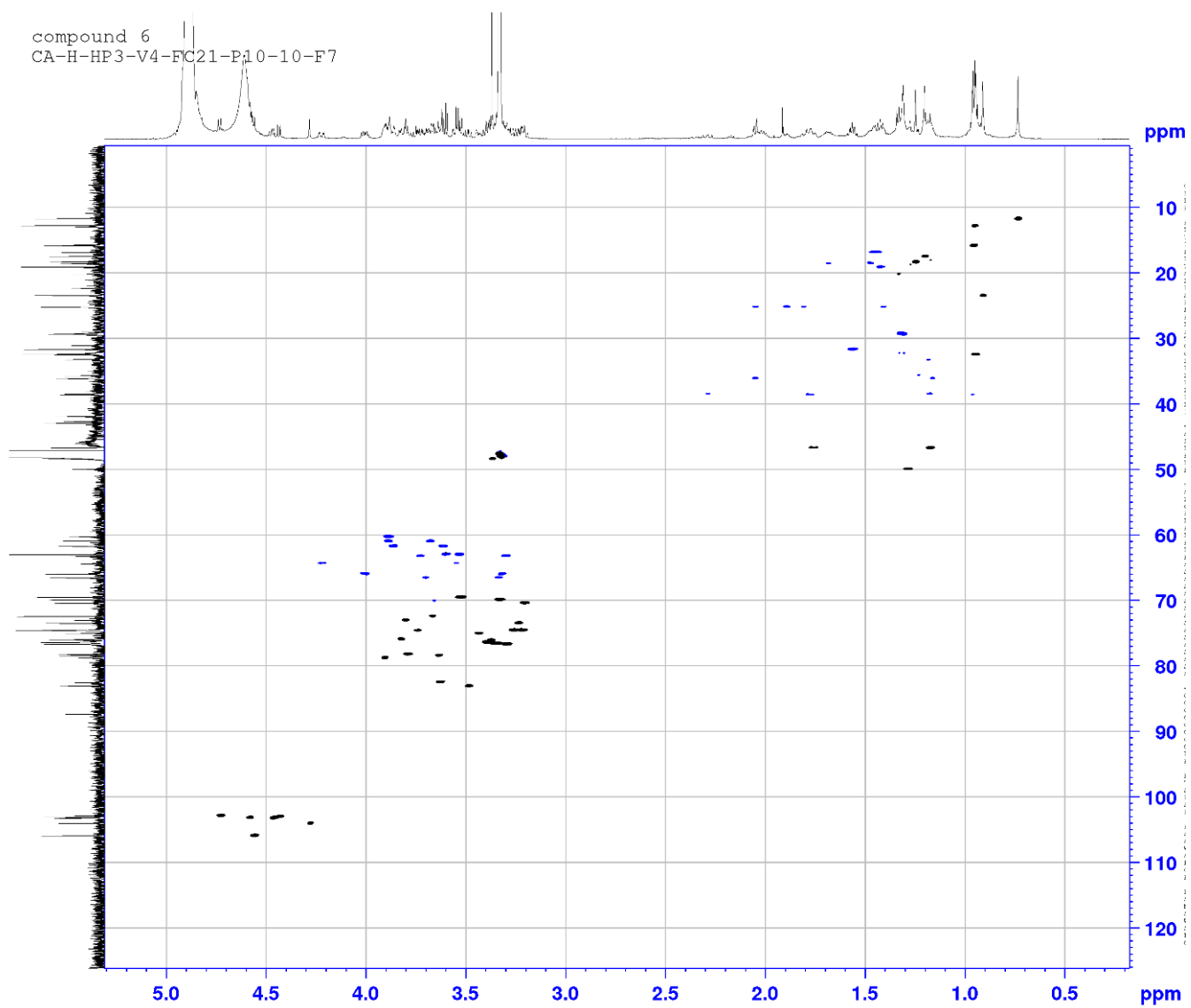


Fig. S42. HSQC spectrum of compound **6**

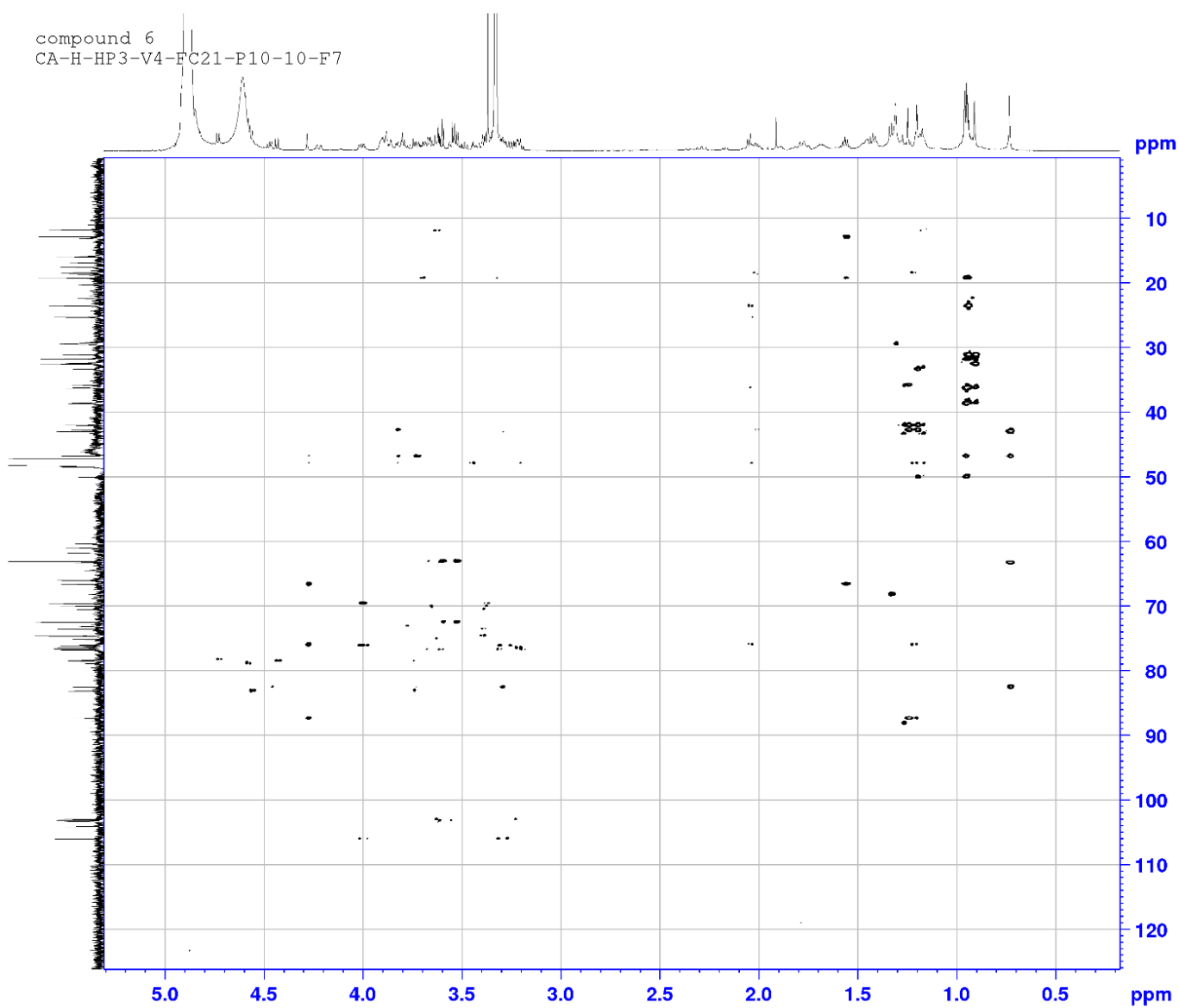


Fig. S43. HMBC spectrum of compound **6**

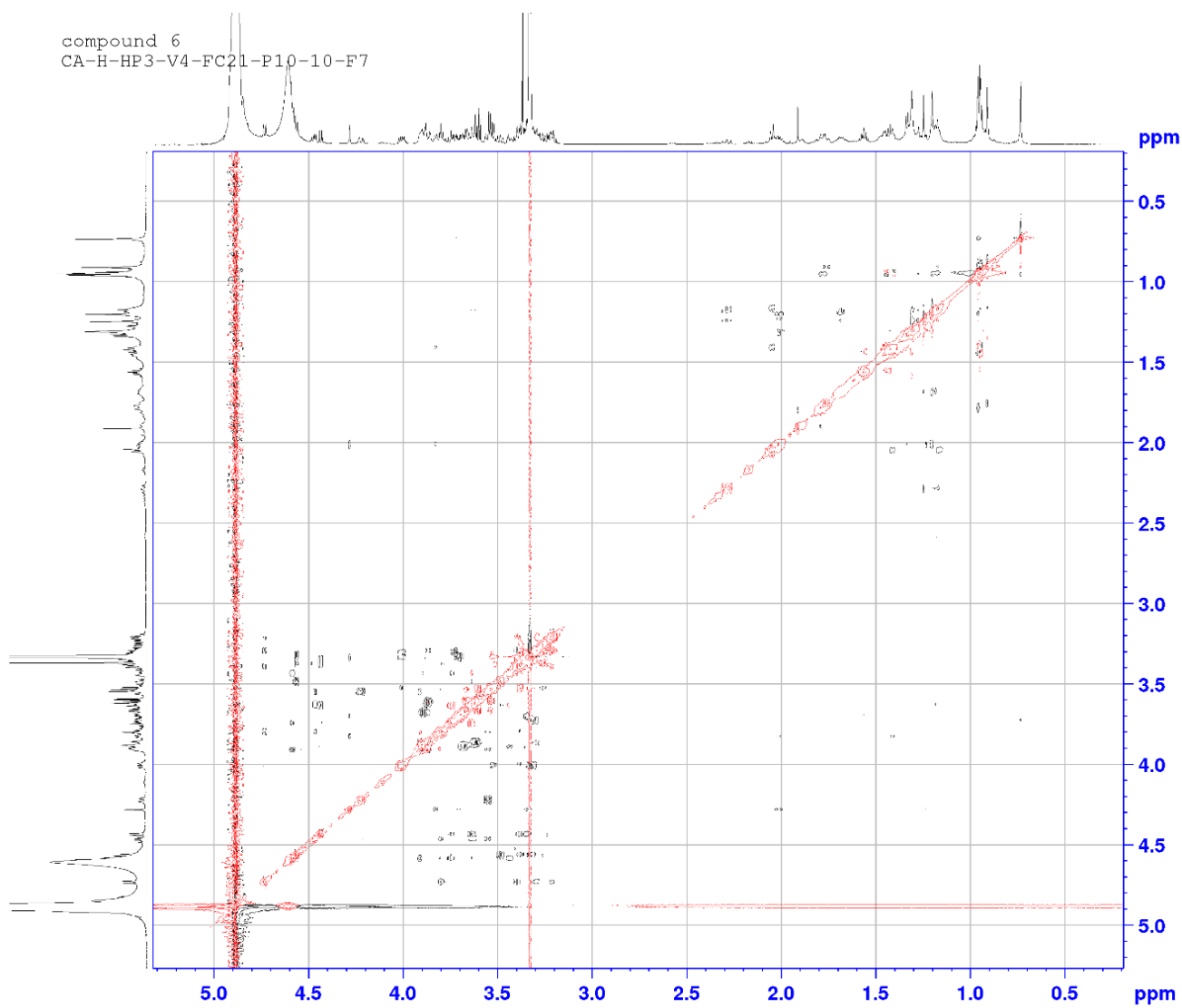


Fig. S44. ROESY spectrum of compound **6**

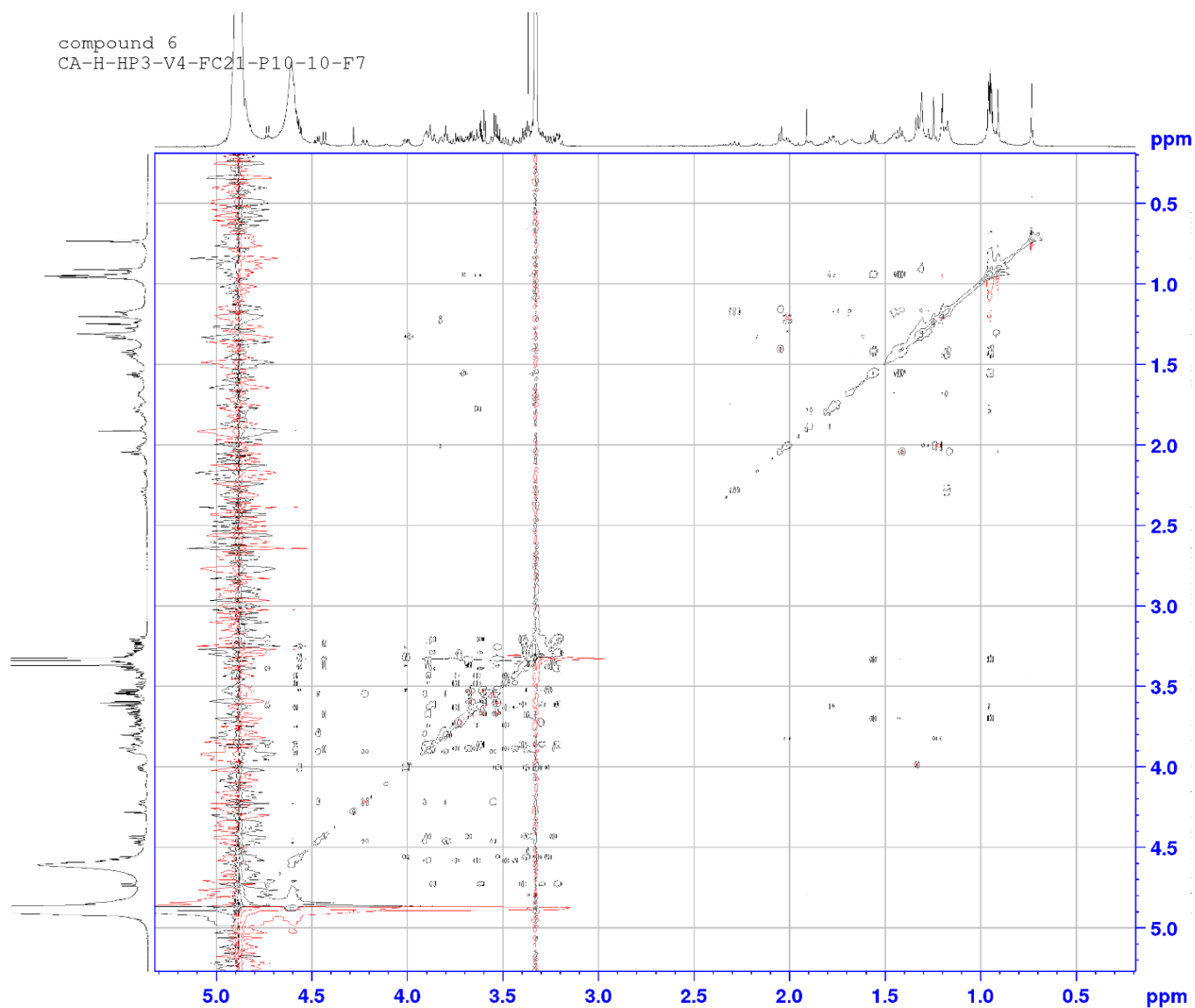


Fig. S45. TOCSY spectrum of compound 6

Elemental Composition Report

Pa6

Single Mass Analysis

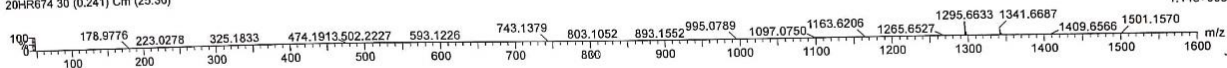
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
57 formula(e) evaluated with 1 results within limits (up to 15 closest results for each mass)

Elements Used:
C: 0-65 H: 0-1020 O: 0-30

HP3_V4_FC21_P10_11_F7
20HR674_30 (0.241) Cm (25:30)

1: TOF MS ES-
1.14e+006



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1295.6633	1295.6636	-0.3	-0.2	11.5	777.1	n/a	n/a	C62 H103 O28

Fig. S46. HR-MS spectrum of compound 6

Compound 7
CA-HP3-V4-FC21-F7-8-S4-F4

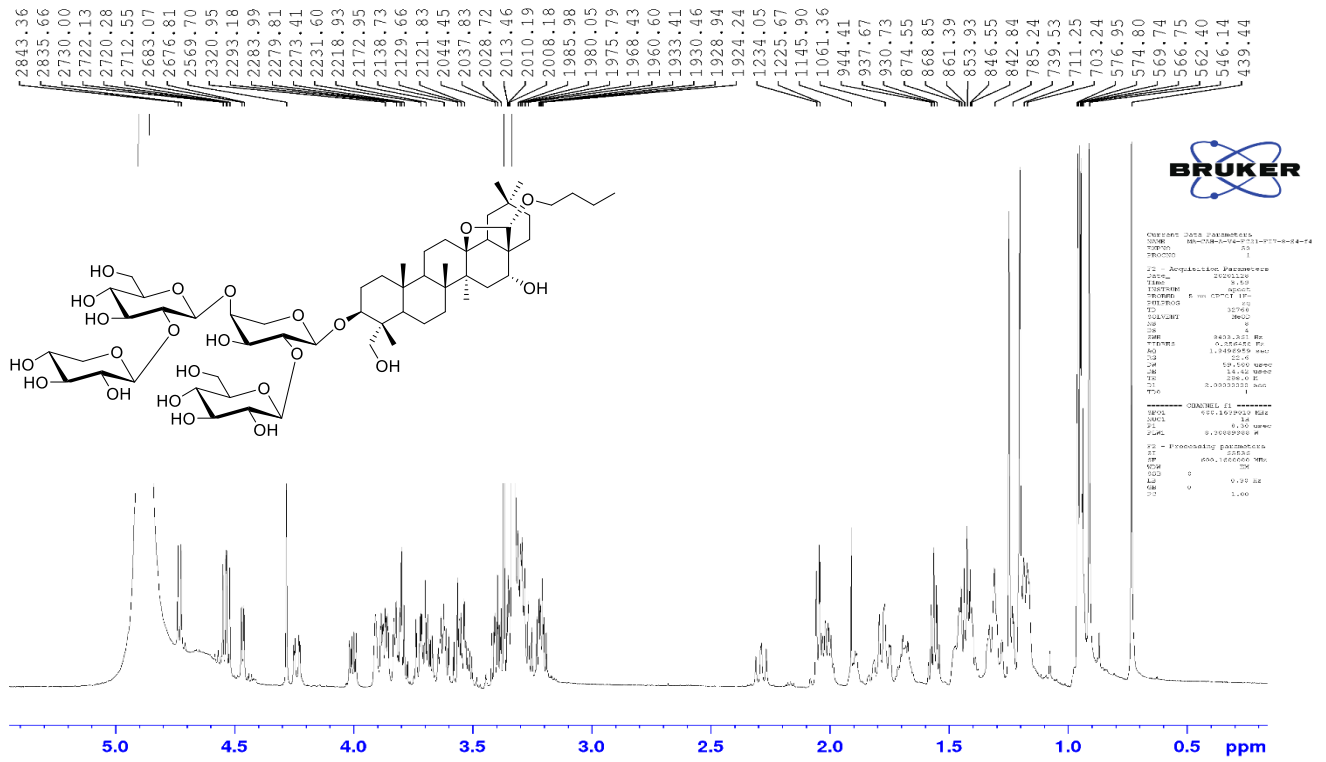


Fig. S47. ^1H NMR Spectrum (600 MHz, $\text{MeOH-}d_4$) of compound 7

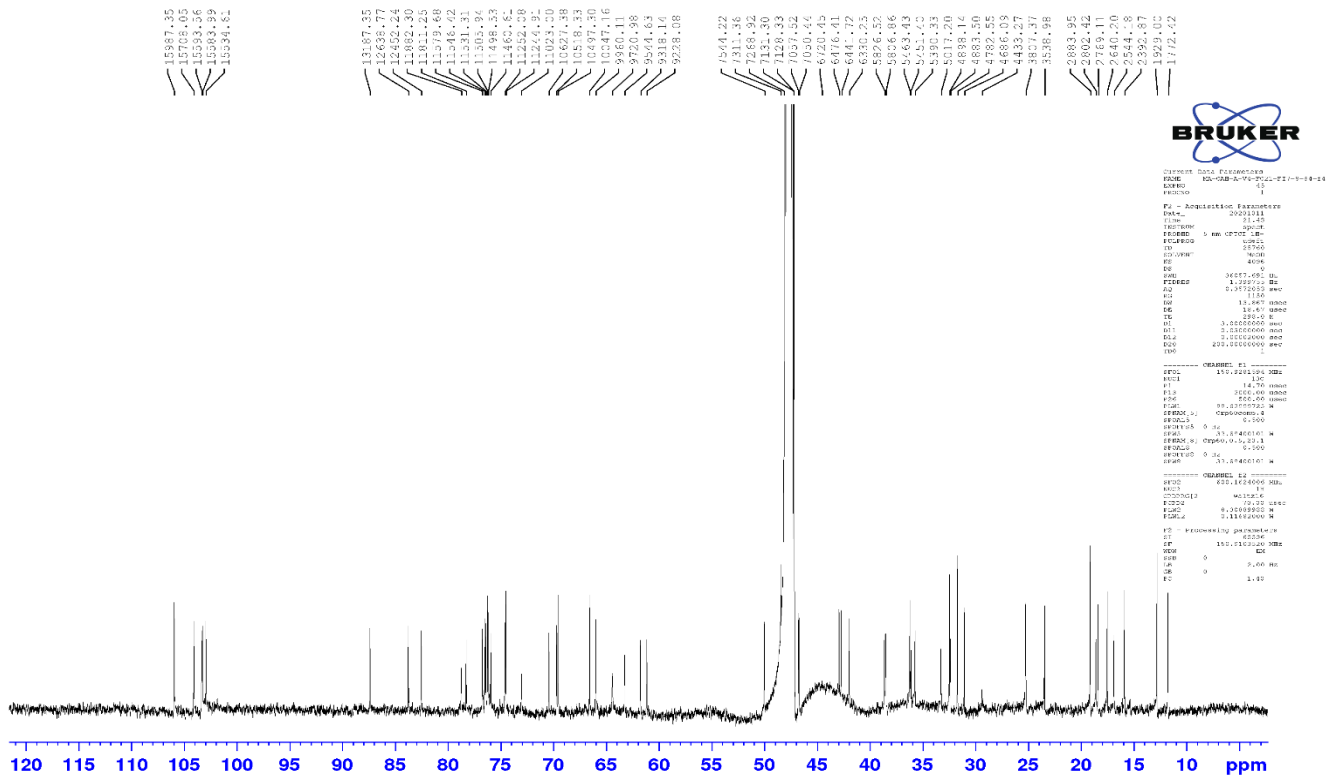


Fig. S48. ^{13}C NMR Spectrum (150 MHz, $\text{MeOH-}d_4$) of compound 7

compound 7
CA-H-HP3-V4-FC21-FI7-8-S4-F4

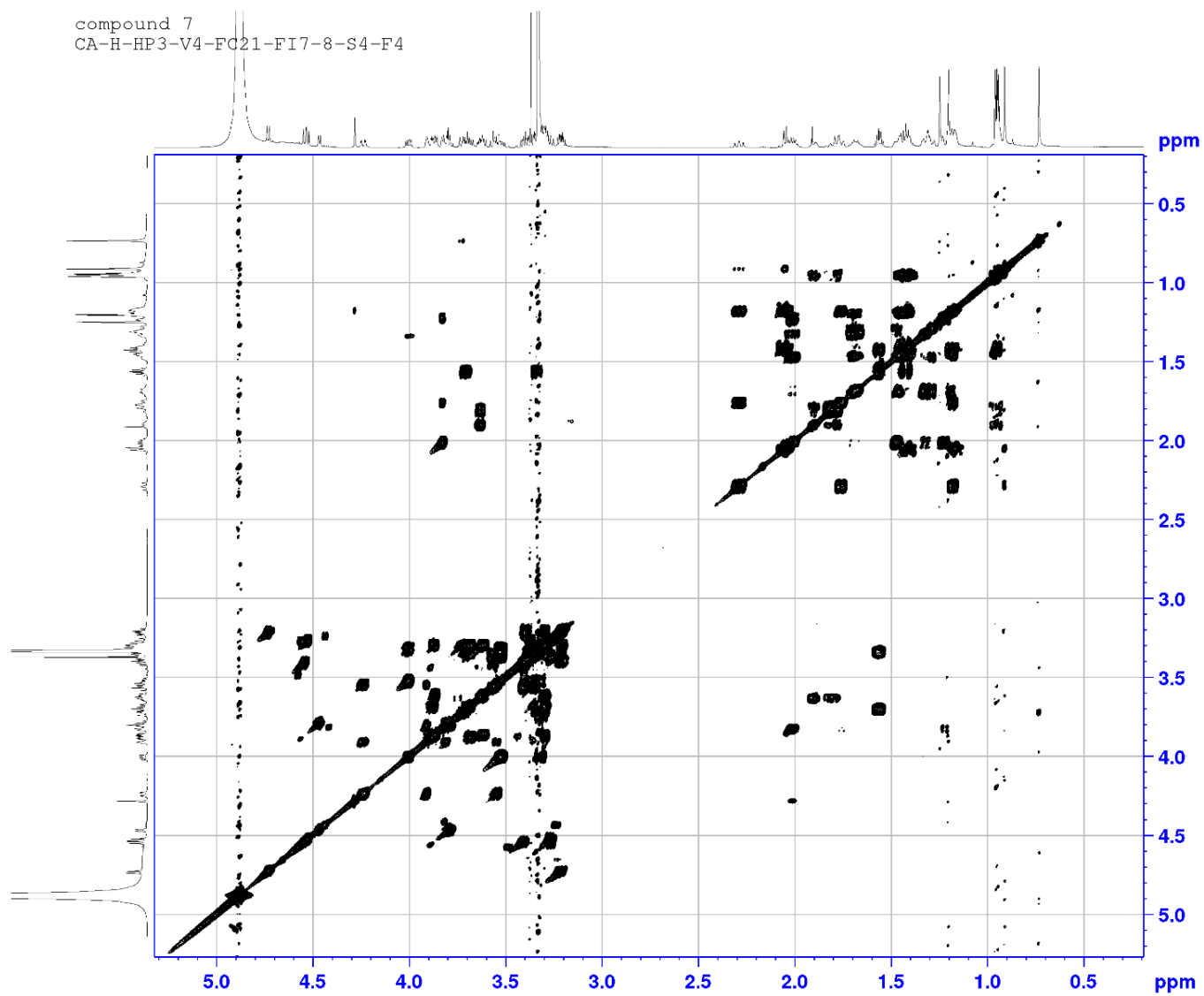


Fig. S49. COSY spectrum of compound 7

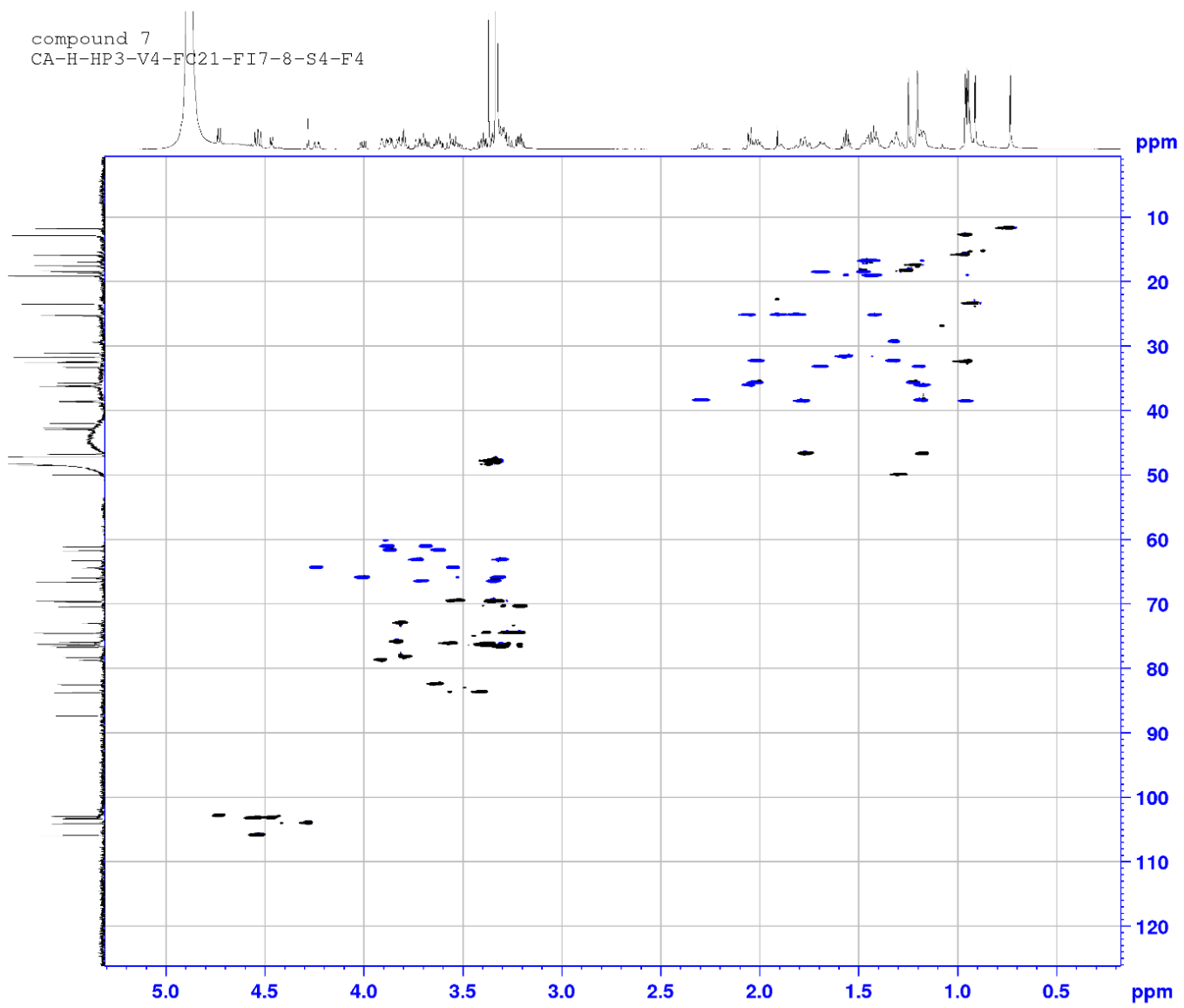


Fig. S50. HSQC spectrum of compound 7

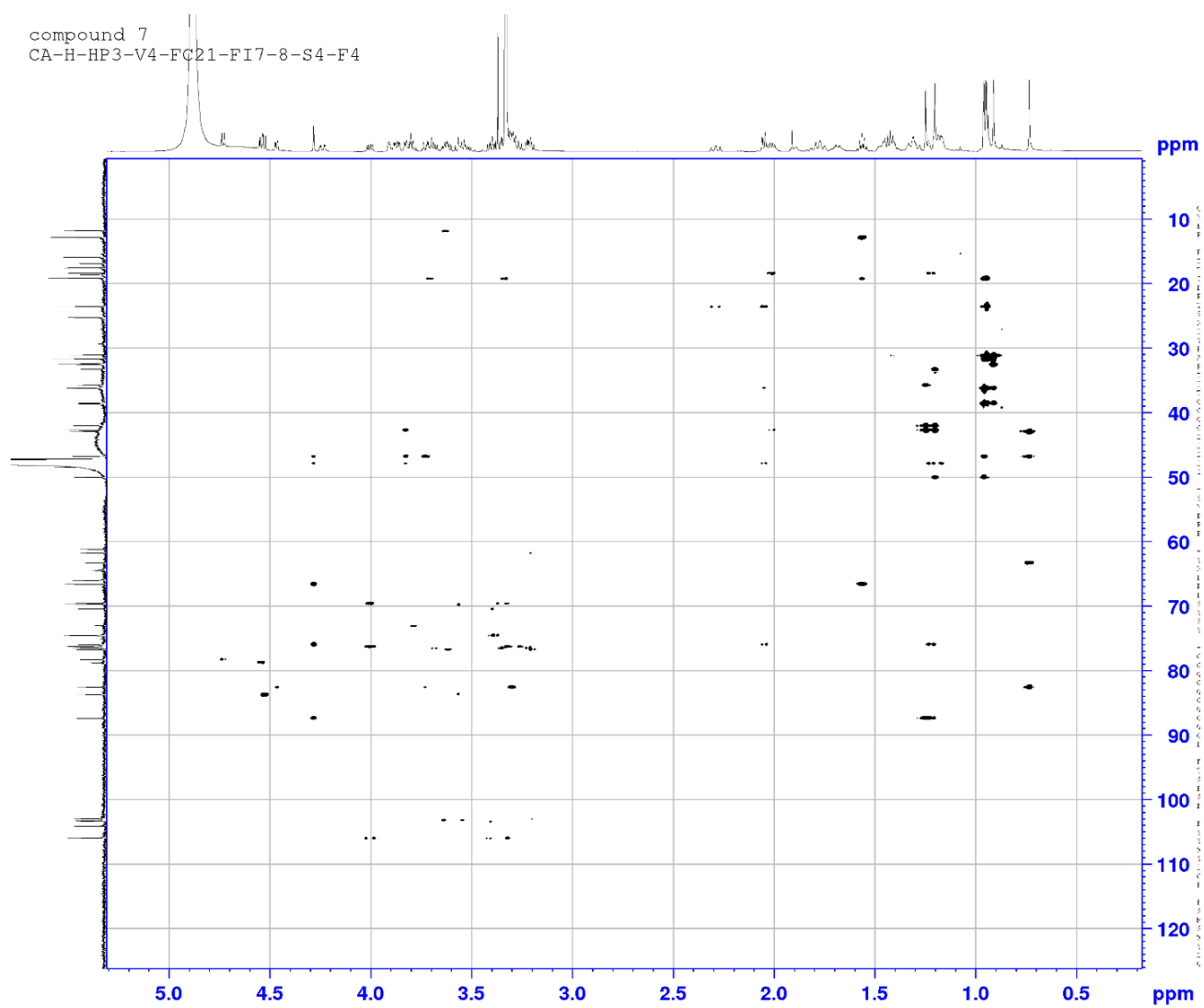


Fig. S51. HMBC spectrum of compound 7

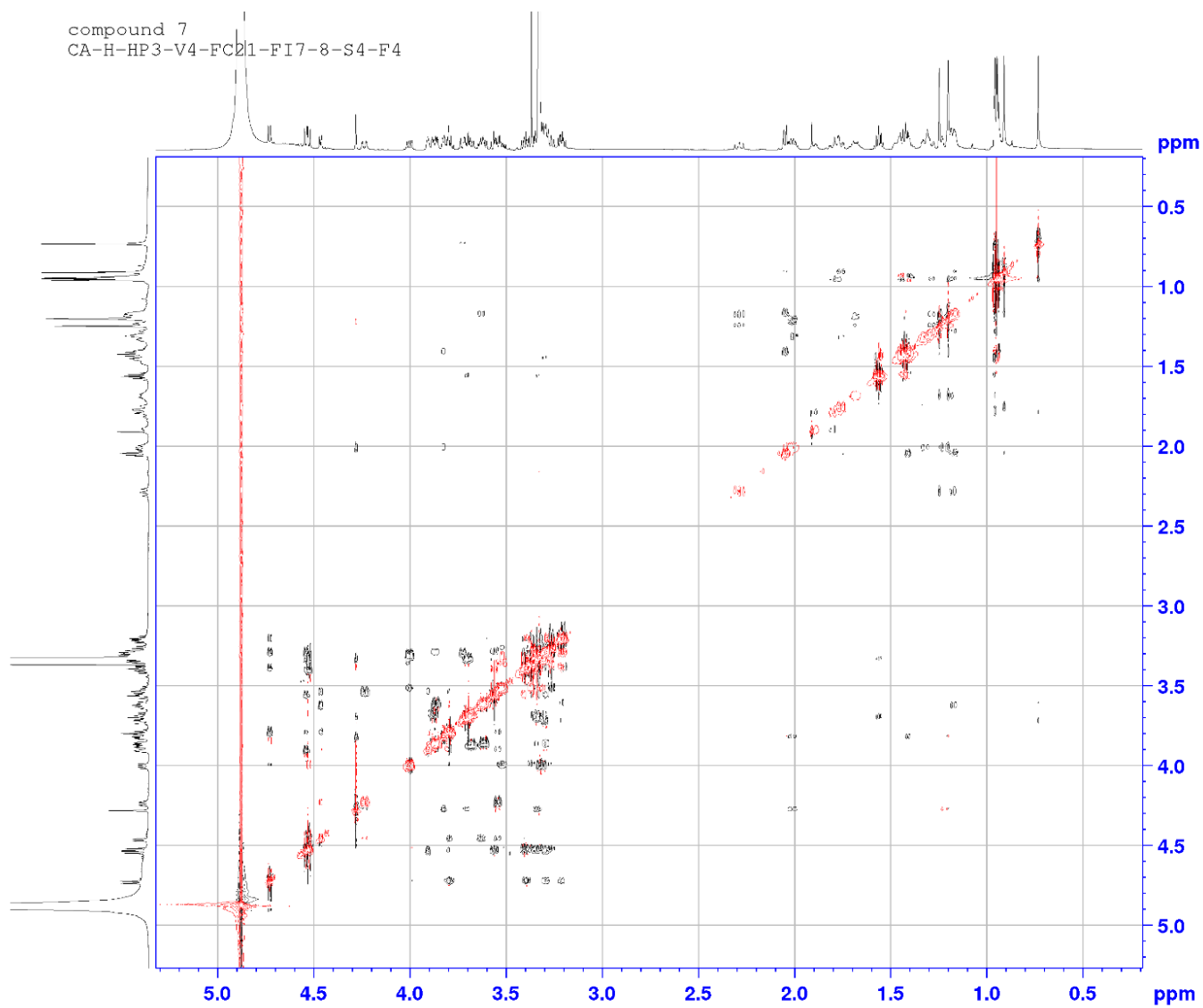


Fig. S52. ROESY spectrum of compound 7

compound 7
 CA-H-HP3-V4-FC21-FI7-8-S4-F4

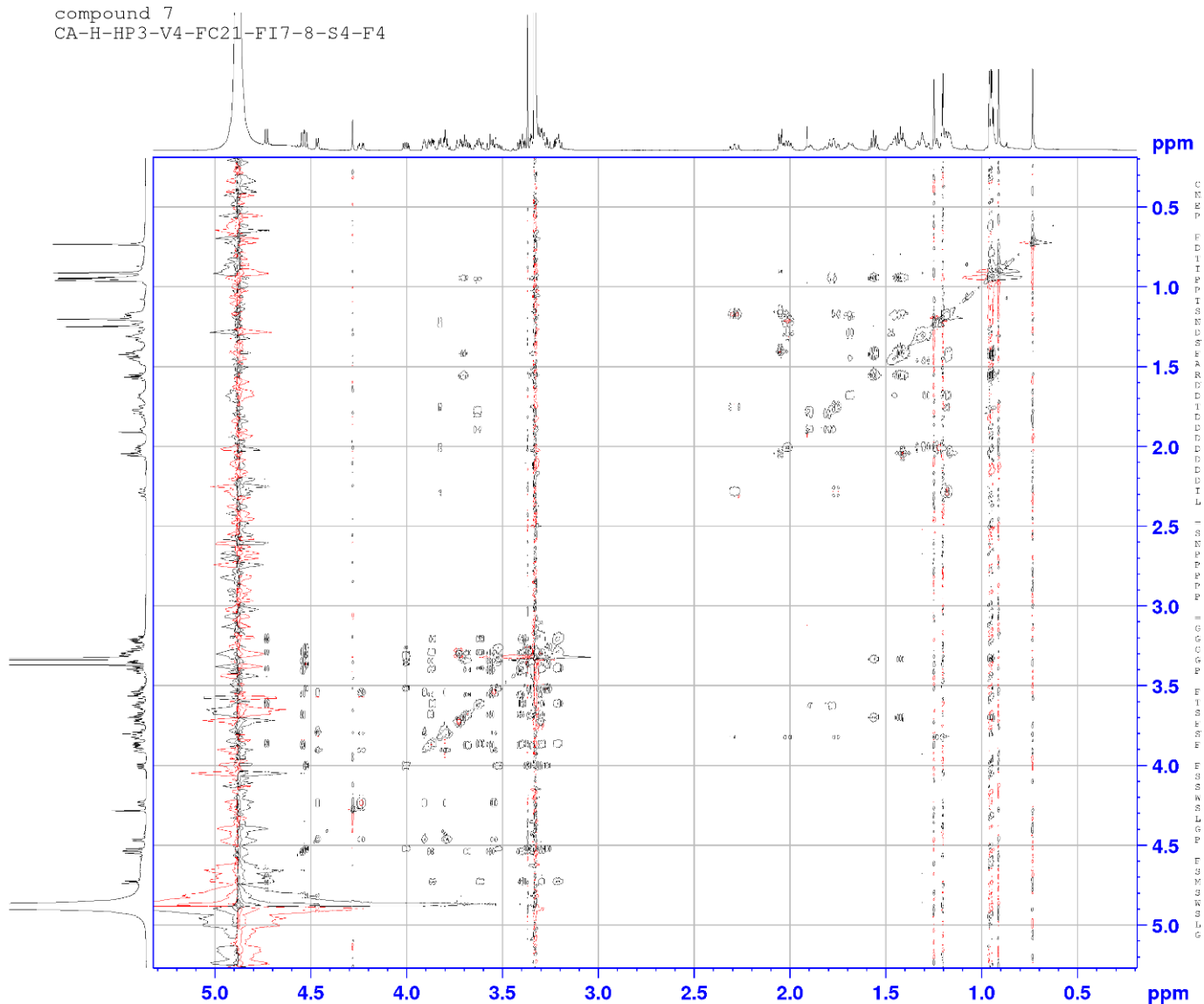


Fig. S53. TOCSY spectrum of compound 7

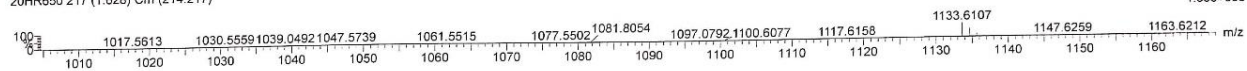
Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 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
 113 formula(e) evaluated with 1 results within limits (up to 15 closest results for each mass)
 Elements Used:
 C: 0-65 H: 0-100 O: 0-30
 MA_CA_HP3_V4_Fc11_Fi7_8_S4_F4
 20HR650 217 (1.628) Cm (214:217)

1: TOF MS ES-
 1.35e+006



Mass	Calc. Mass	mDa	PEM	DBE	i-FIT	Norm	Conf (%)	Formula
1133.6107	1133.6108	-0.1	0.1	10.5	843.1	n/a	n/a	C56 H93 O23

Fig. S54. HR-MS spectrum of compound 7

Compound 8
CA-HP3-V4-FC22-24P5-6F20

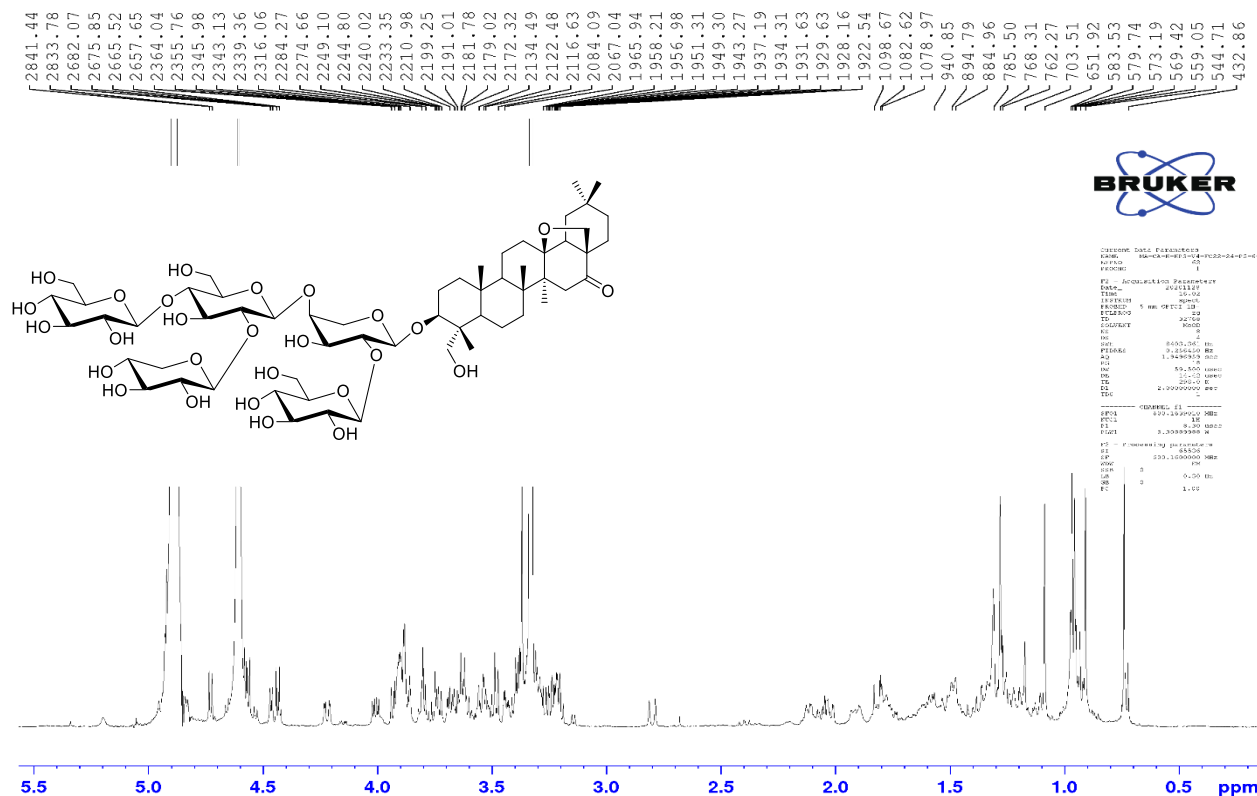


Fig. S55. ¹H NMR Spectrum (600 MHz, MeOH-*d*₄) of compound 8

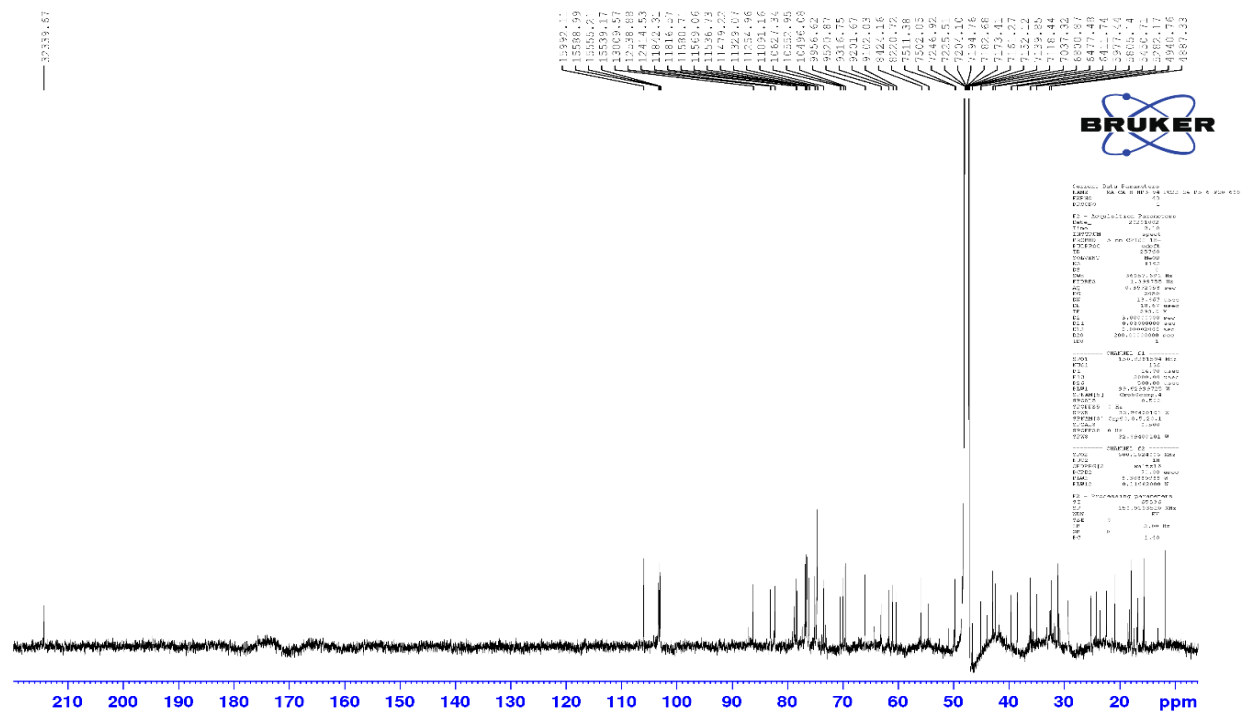


Fig. S56. ¹³C NMR Spectrum (150 MHz, MeOH-*d*₄) of compound 8

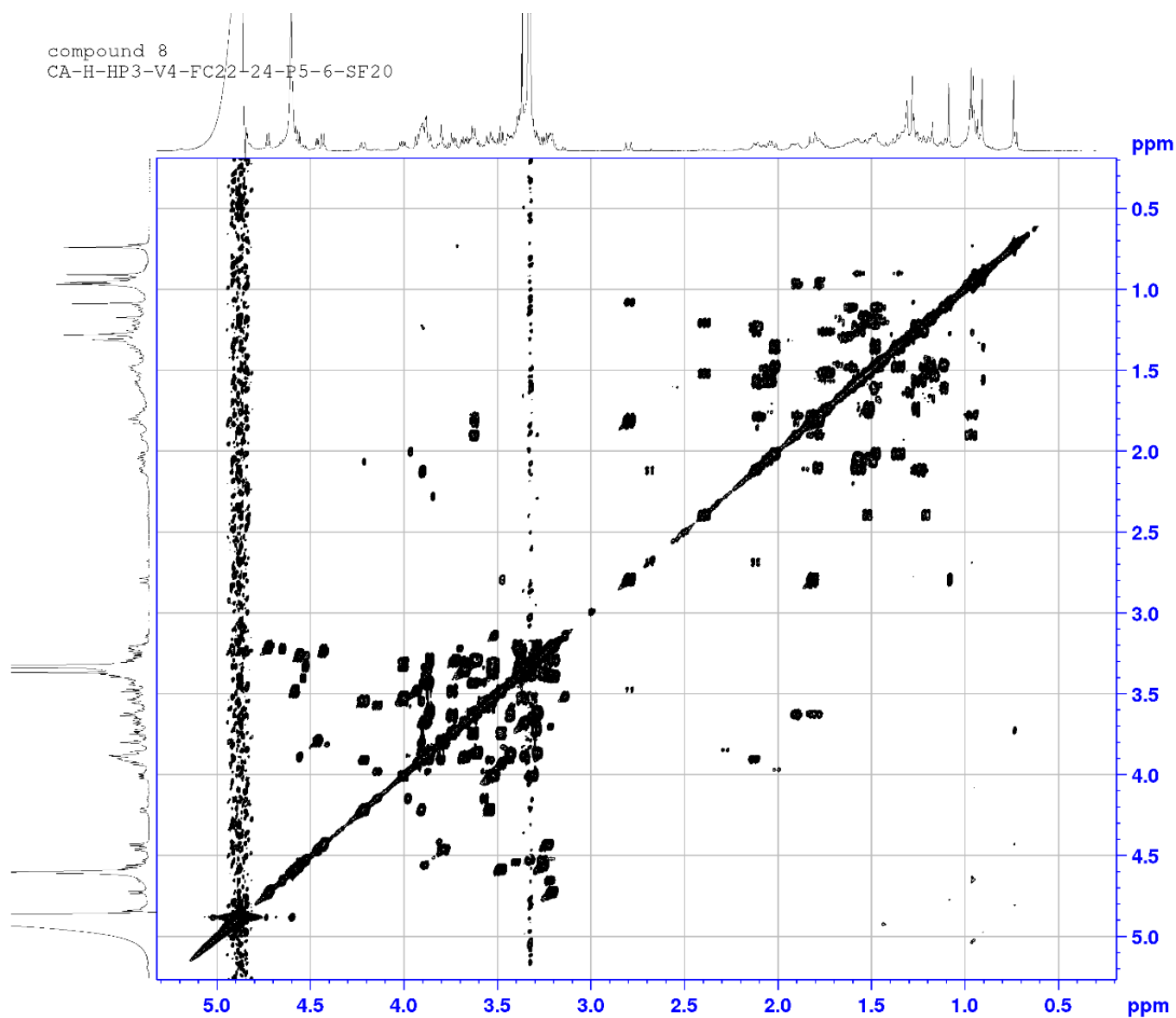


Fig. S57. COSY spectrum of compound 8

compound 8
CA-H-HP3-V4-FC22-24-P5-6-SF20

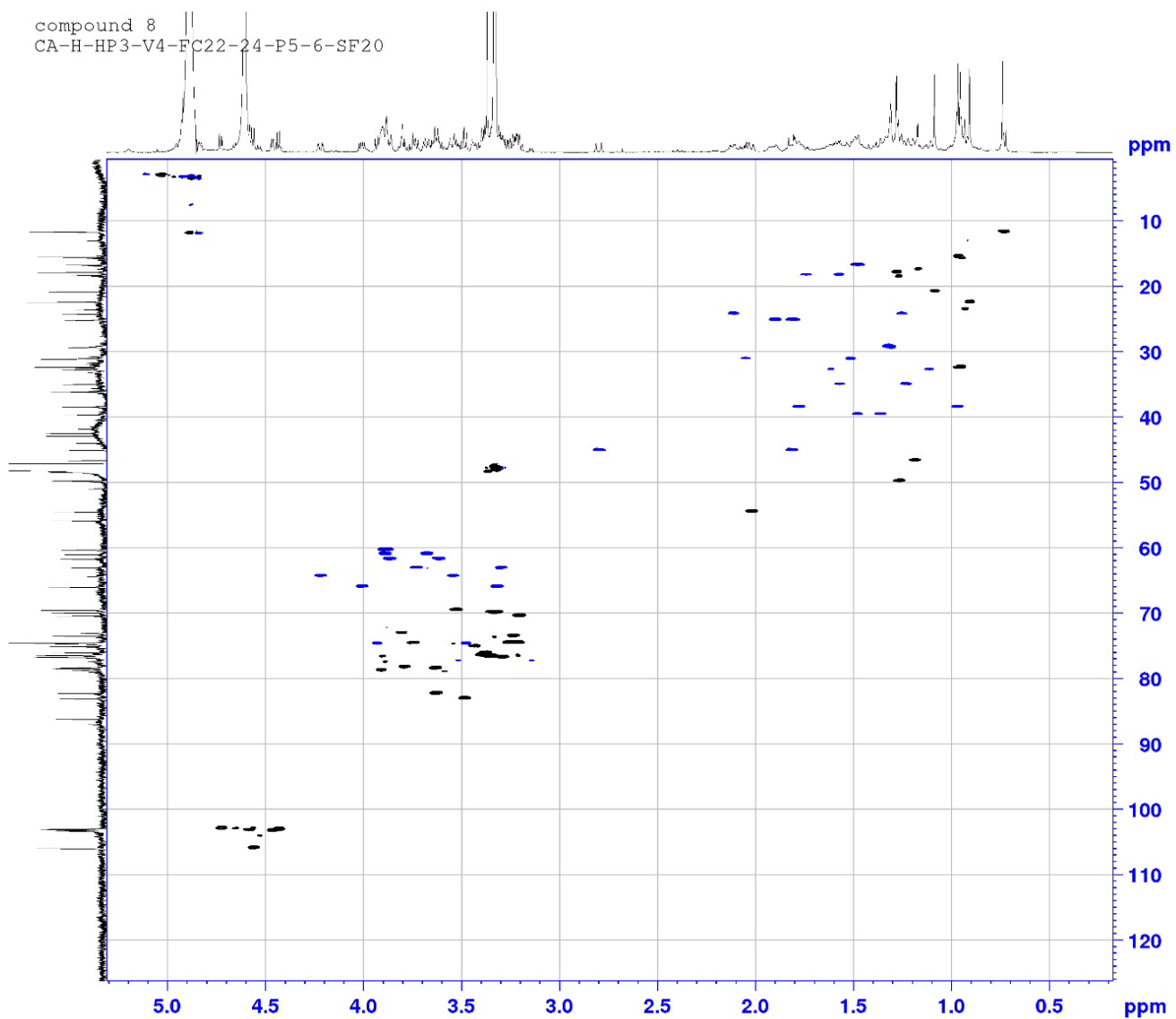


Fig. S58. HSQC spectrum of compound **8**

compound 8
CA-H-HP3-V4-FC22-24-P5-6-SF20

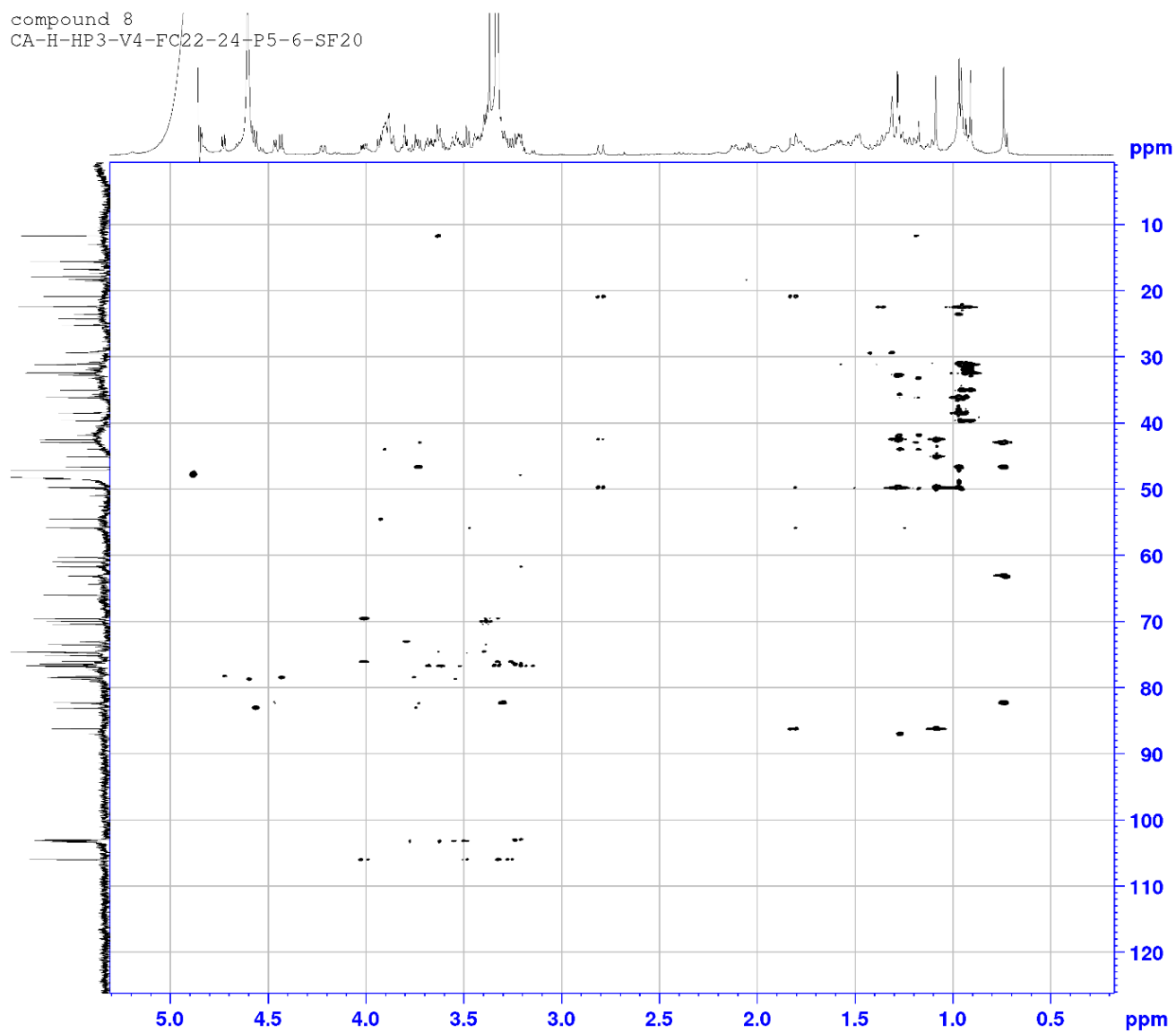


Fig. S59. HMBC spectrum of compound 8

compound 8
CA-H-HP3-V4-FC22-24-P5-6-SF20

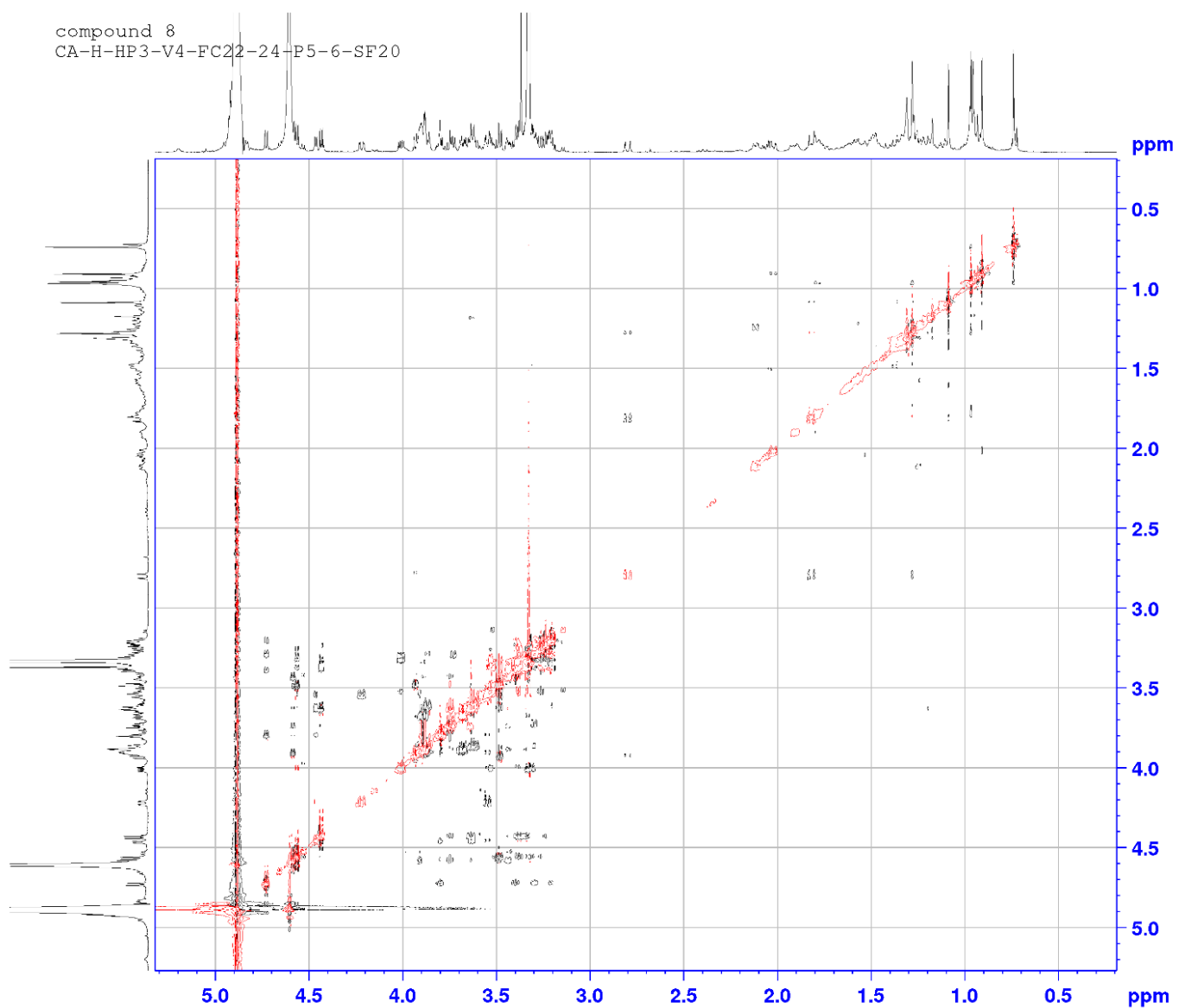


Fig. S60. ROESY spectrum of compound **8**

compound 8
 CA-H-HP3-V4-FC22-24-P5-6-SF20

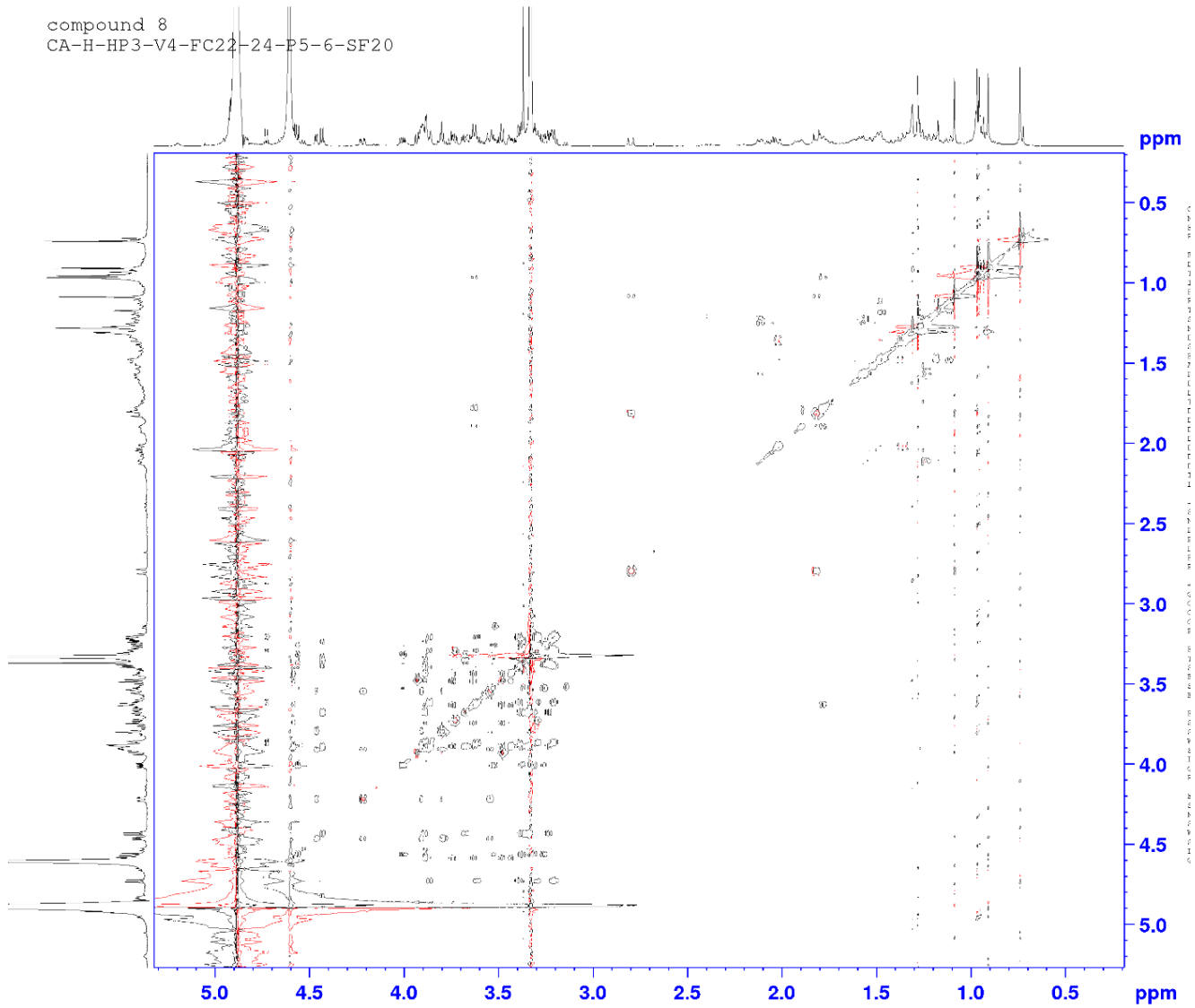


Fig. S61. TOCSY spectrum of compound 8

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 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
 158 formula(e) evaluated with 2 results within limits (up to 15 closest results for each mass)
 Elements Used:
 C: 0-65 H: 0-100 O: 0-30 Na: 0-1
 MA_CA_HP3_V4_FC22_24_85_6_F20
 20HR669 60 (0.461) Cm (60:64)

1: TOF MS ES-
 2.55e+005

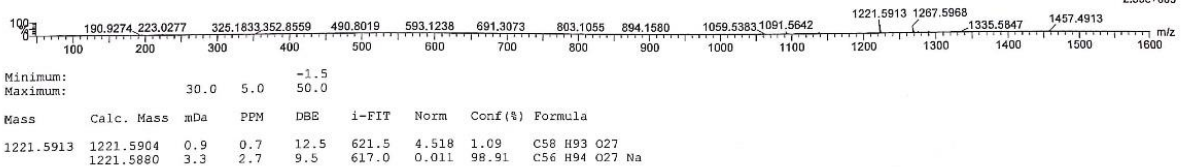


Fig. S62. HR-MS spectrum of compound 8

Compound 9
CA-34-27-S4-f8

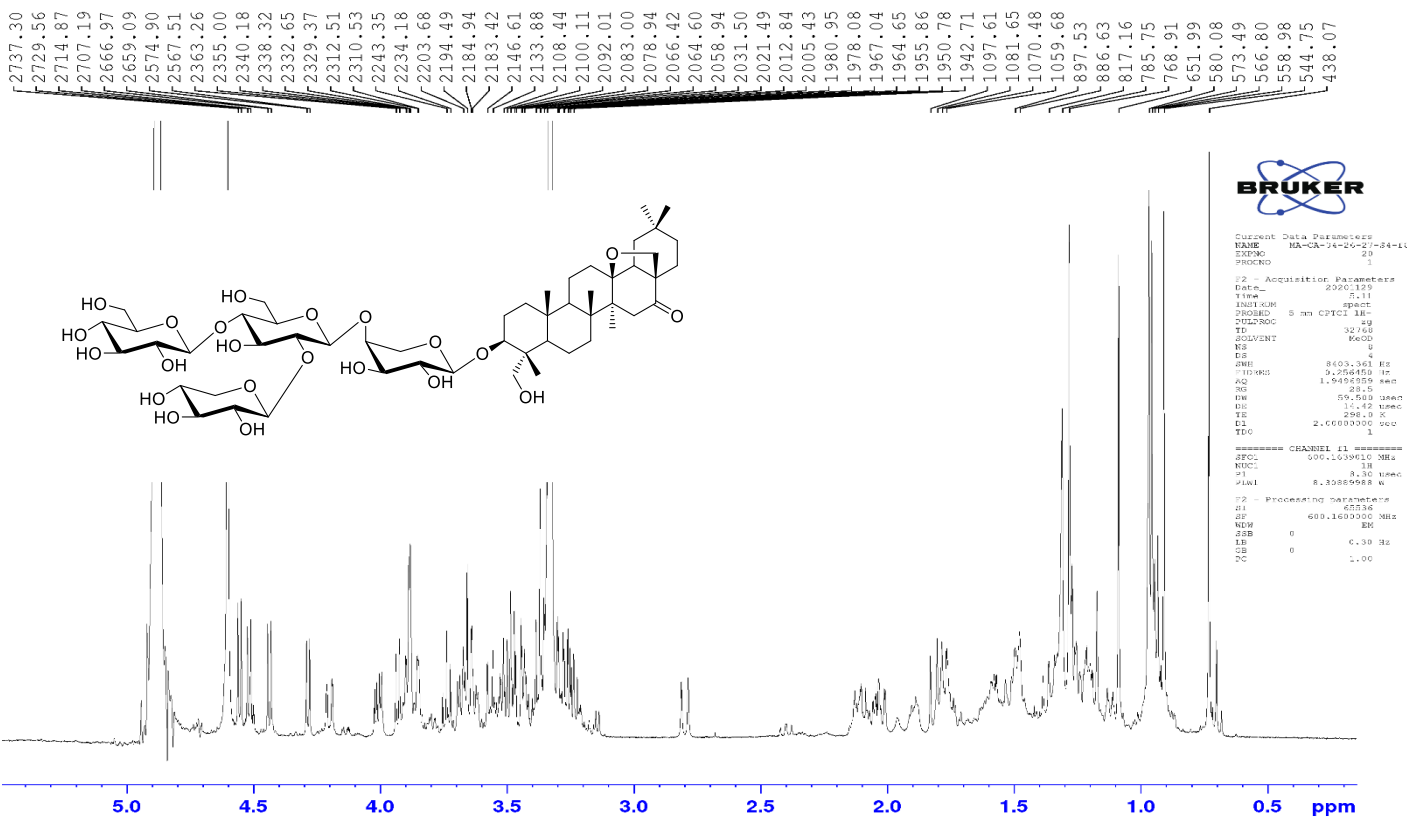


Fig. S63. ¹H NMR Spectrum (600 MHz, MeOH-*d*₄) of compound 9

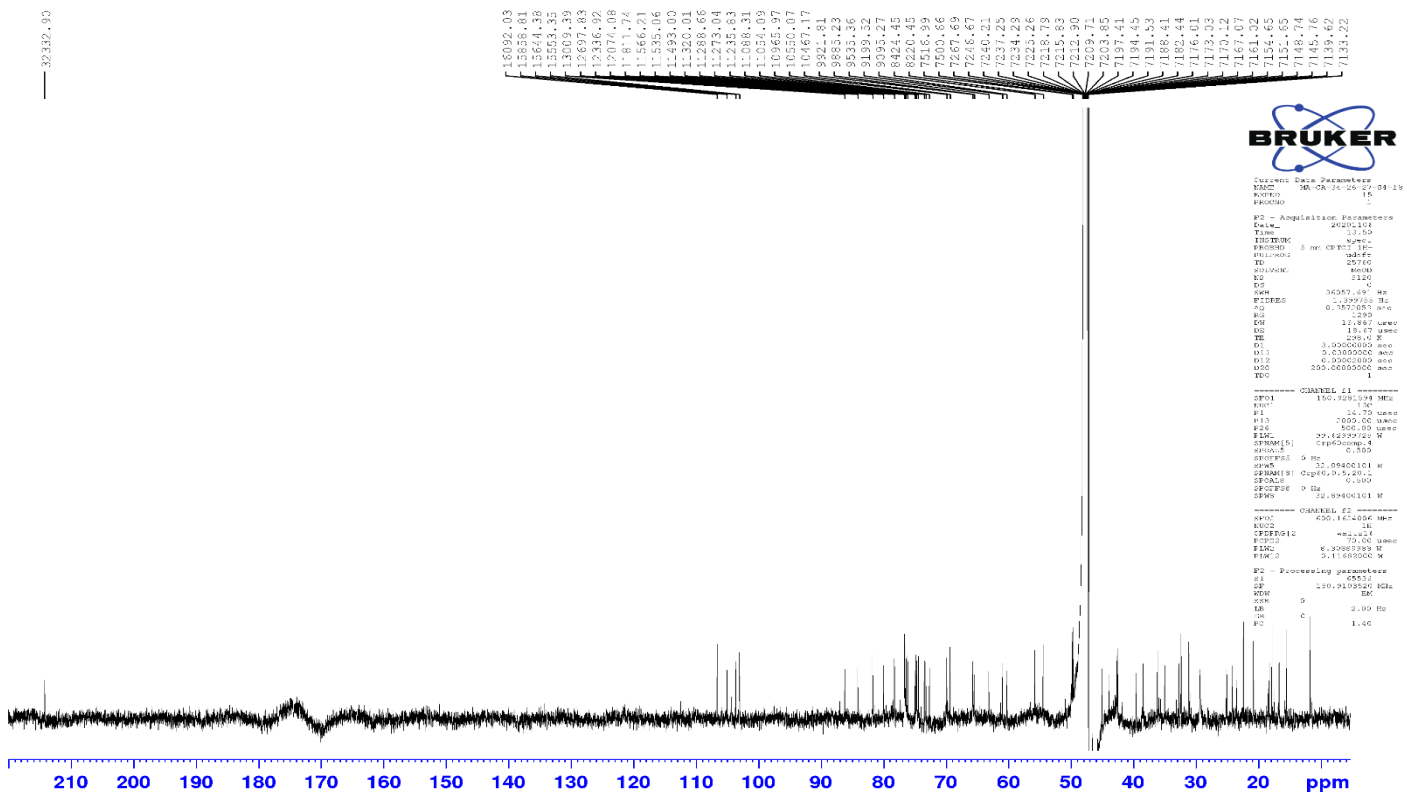


Fig. S64. ¹³C NMR Spectrum (150 MHz, MeOH-*d*₄) of compound 9

compound 9
CA-34-26-27-S4-F8

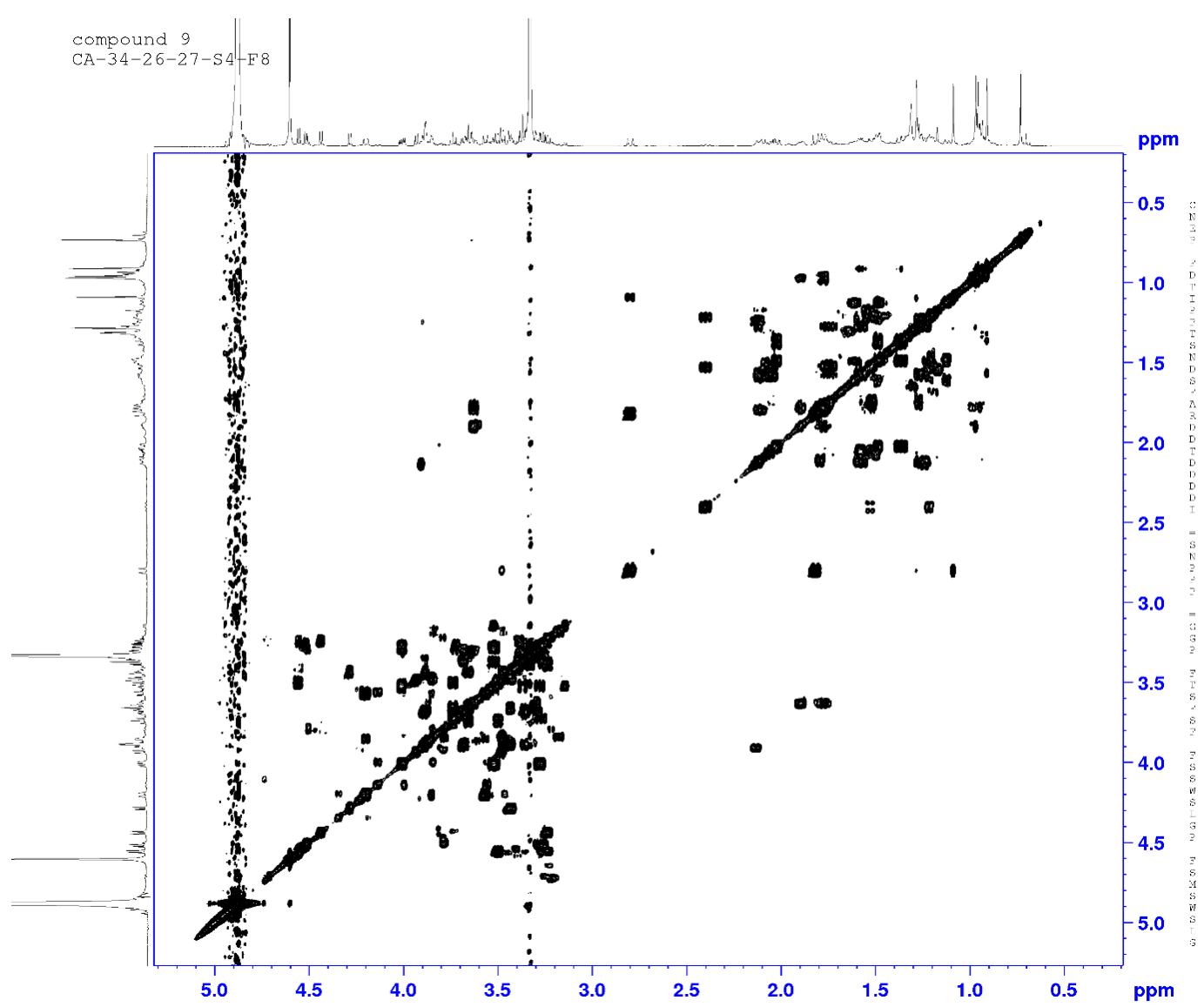


Fig. S65. COSY spectrum of compound 9

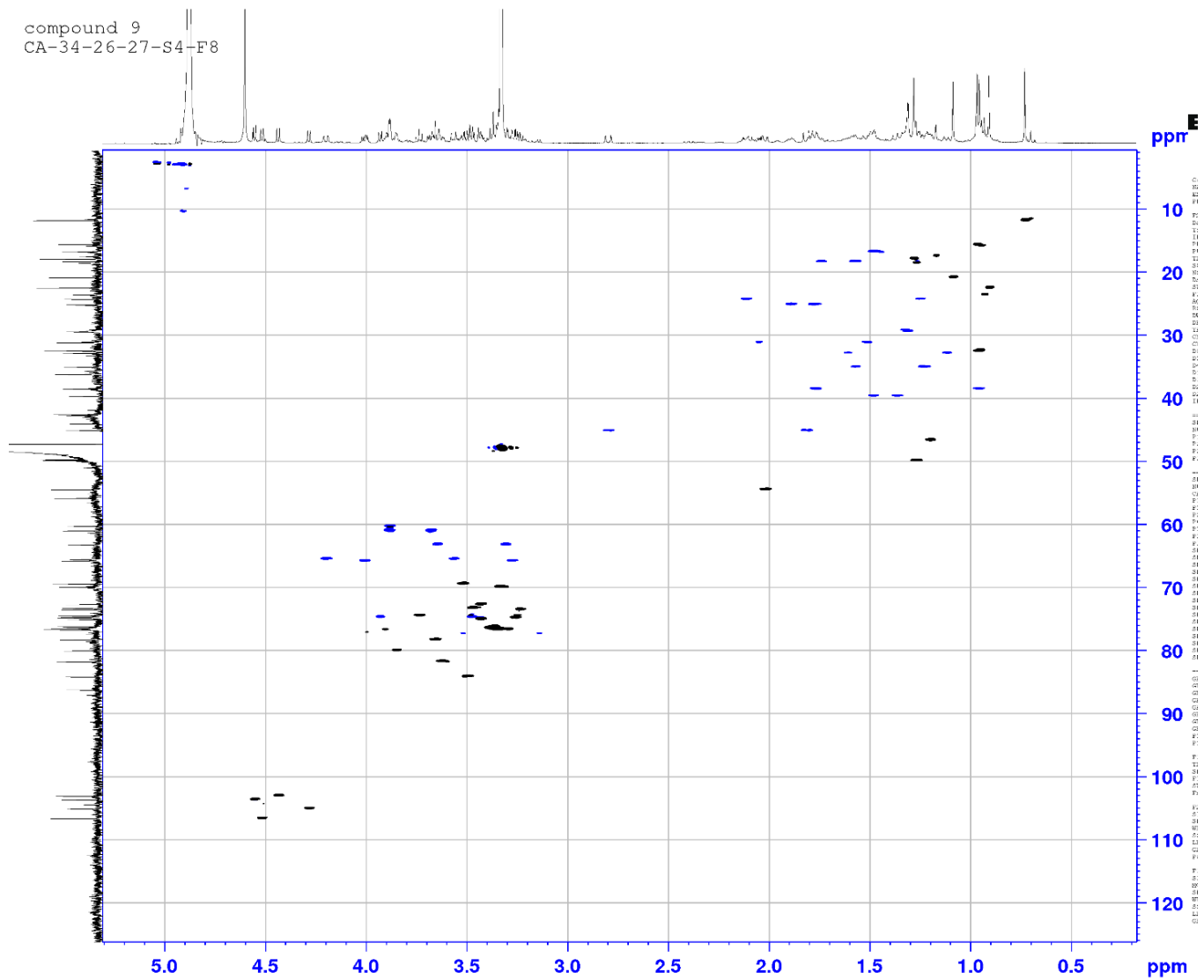


Fig. S66. HSQC spectrum of compound **9**

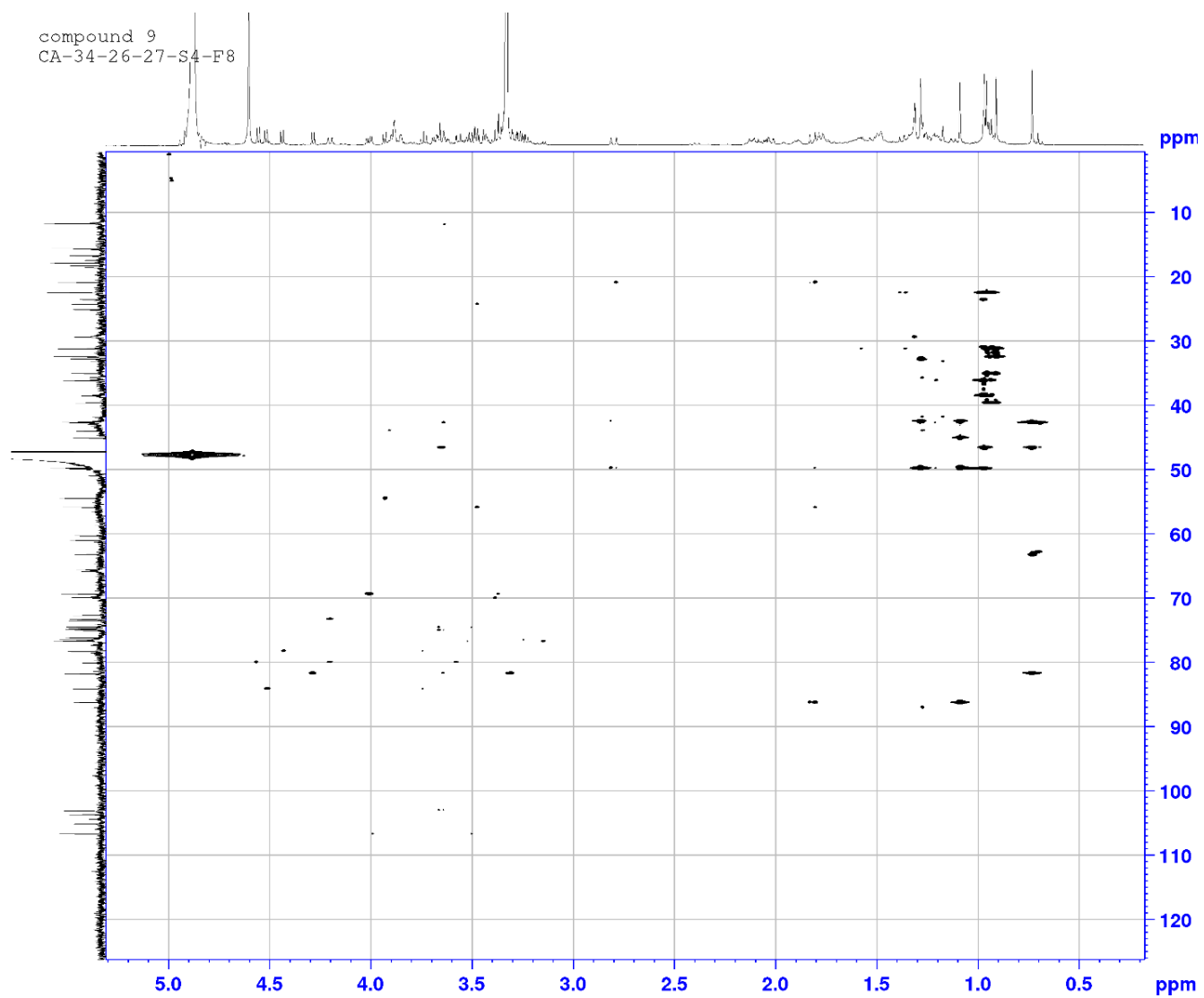


Fig. S67. HMBC spectrum of compound **9**

compound 9
CA-34-26-27-S4-F8

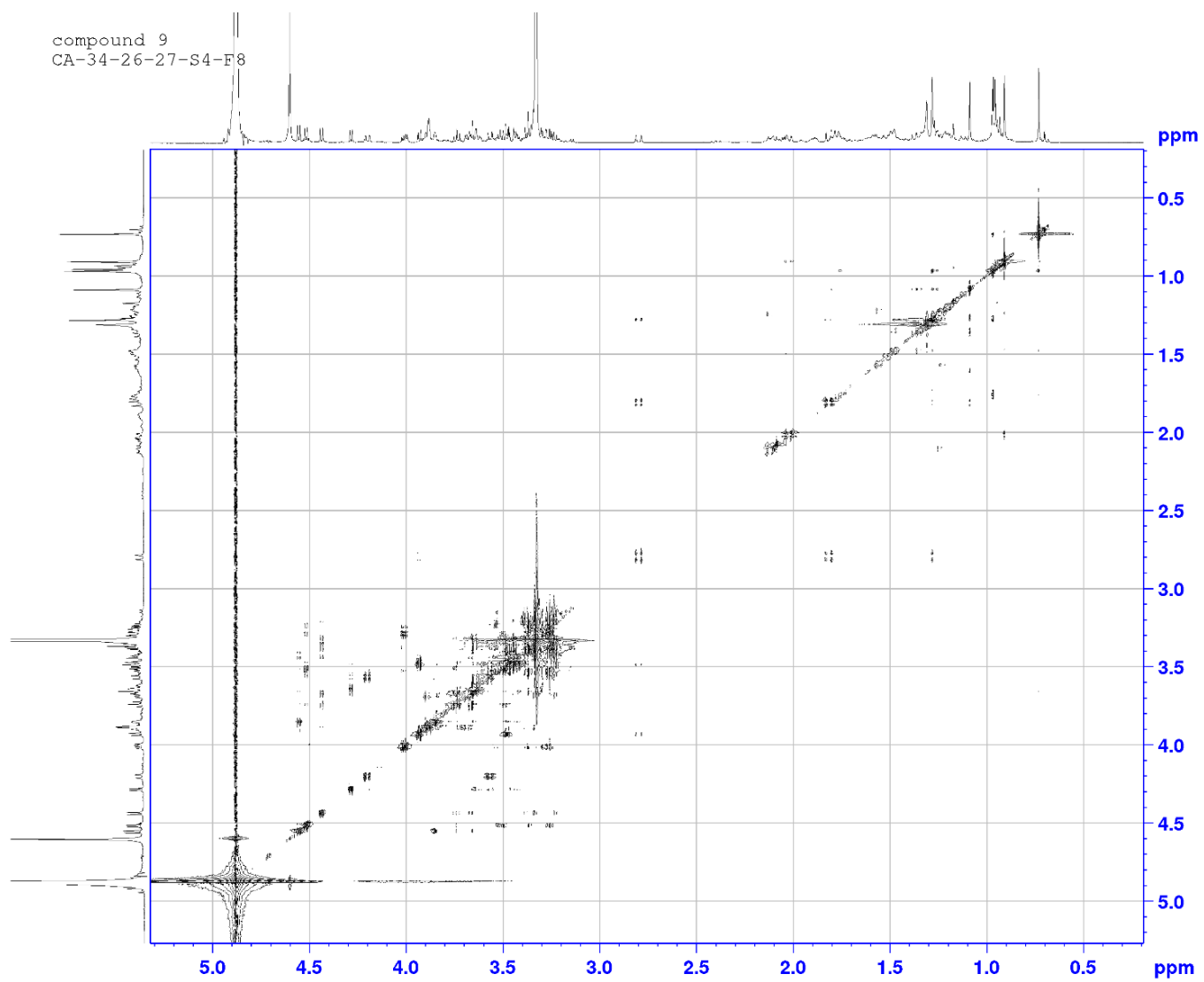


Fig. S68. ROESY spectrum of compound **9**

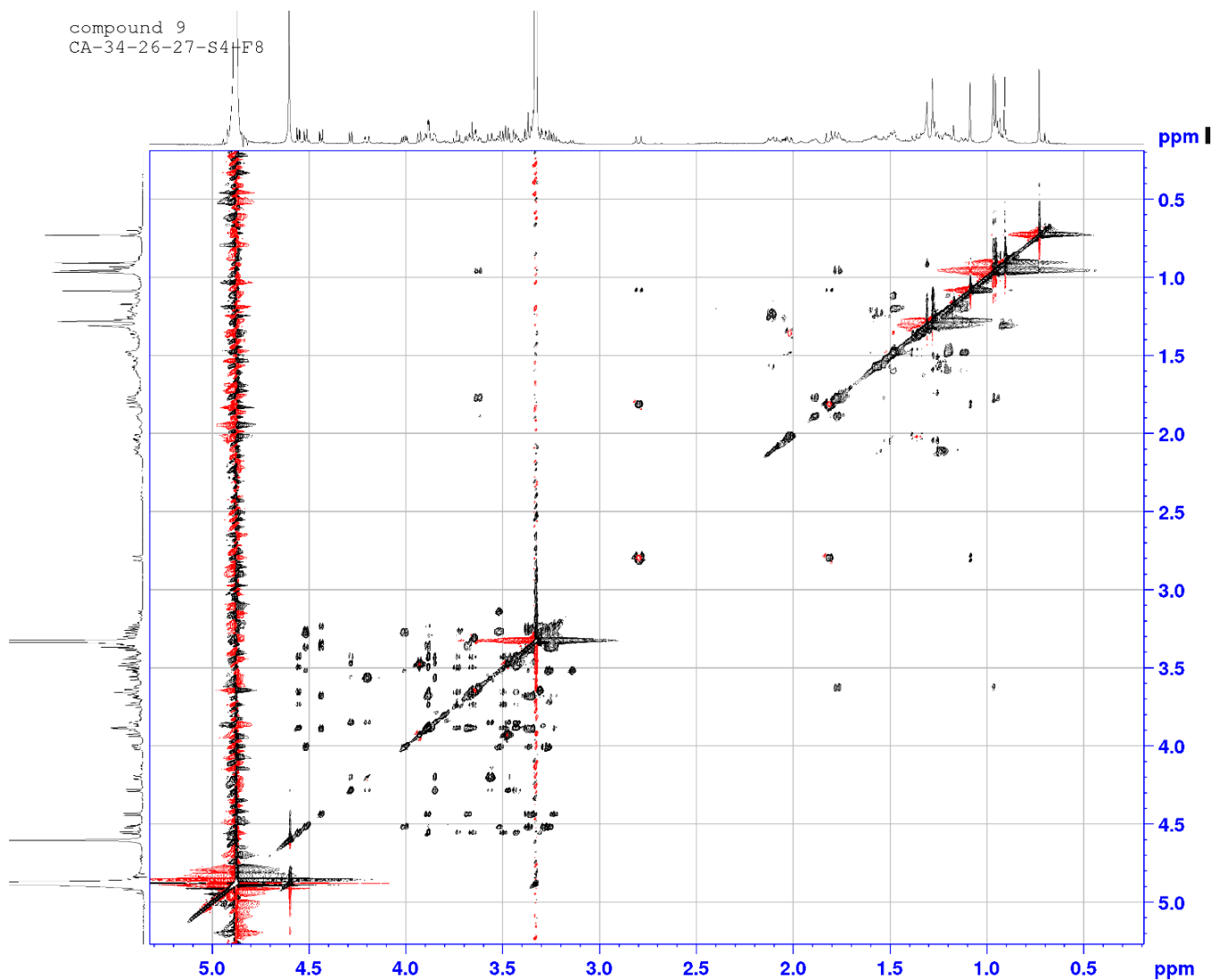


Fig. S69. TOCSY spectrum of compound 9

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 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

151 formula(e) evaluated with 2 results within limits (up to 15 closest results for each mass)

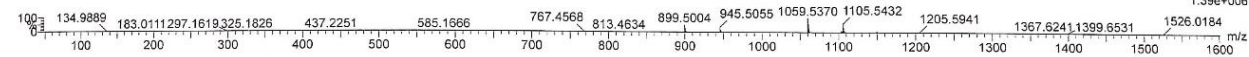
Elements Used:

C: 0-65 H: 0-100 O: 0-30

MA_CA_HP3_V4_F26_27_S4_F8

20HR644 181 (1.366) Cm (181)

1: TOF MS ES-
1.39e+006



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1059.5370	1059.5376	-0.6	-0.6	11.5	842.2	0.000	99.99	C52 H63 O22
	1059.5317	5.3	5.0	20.5	851.3	9.055	0.01	C59 H79 O17

Fig. S70. HR-MS spectrum of compound 9

Compound 10
A-HP3-V6-S16-f1

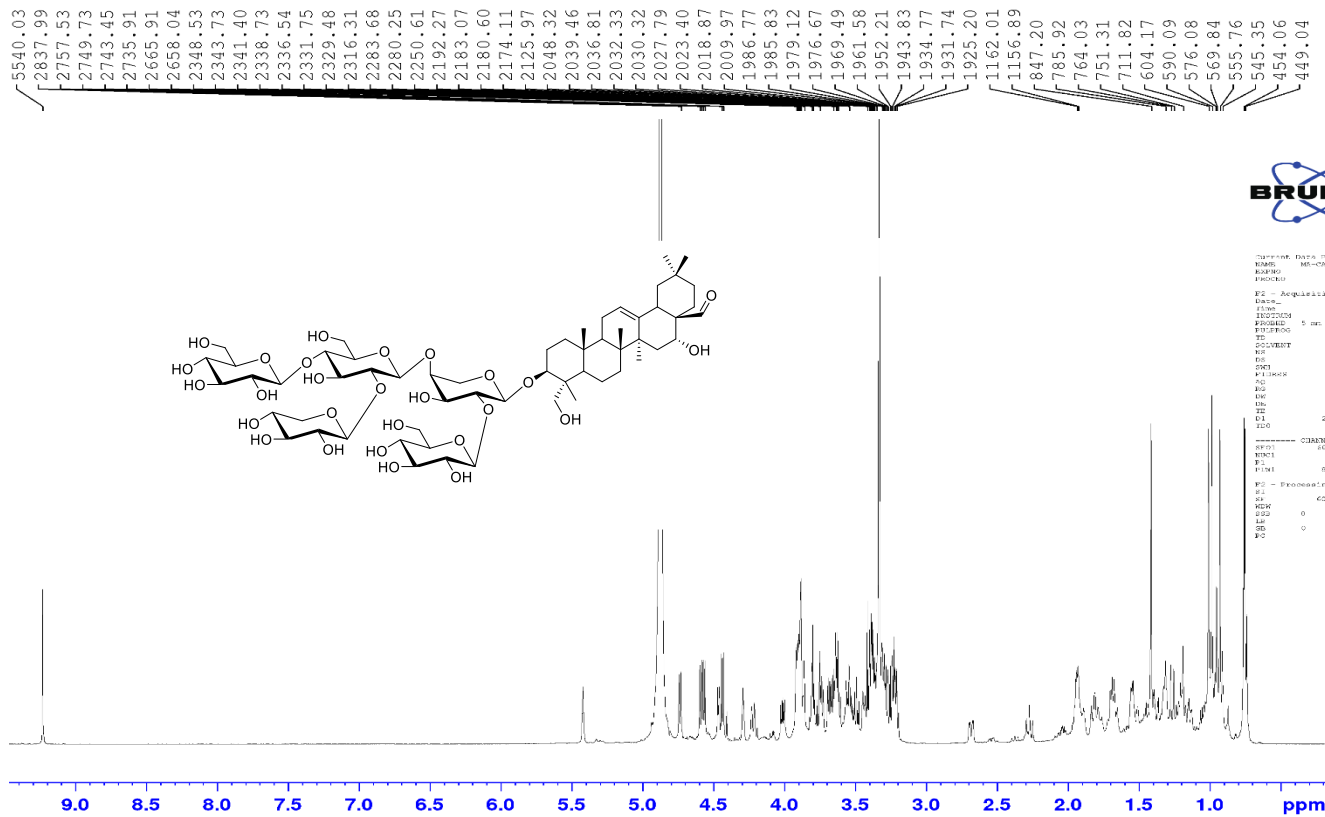


Fig. S71. ¹H NMR Spectrum (600 MHz, MeOH-d₄) of compound 10

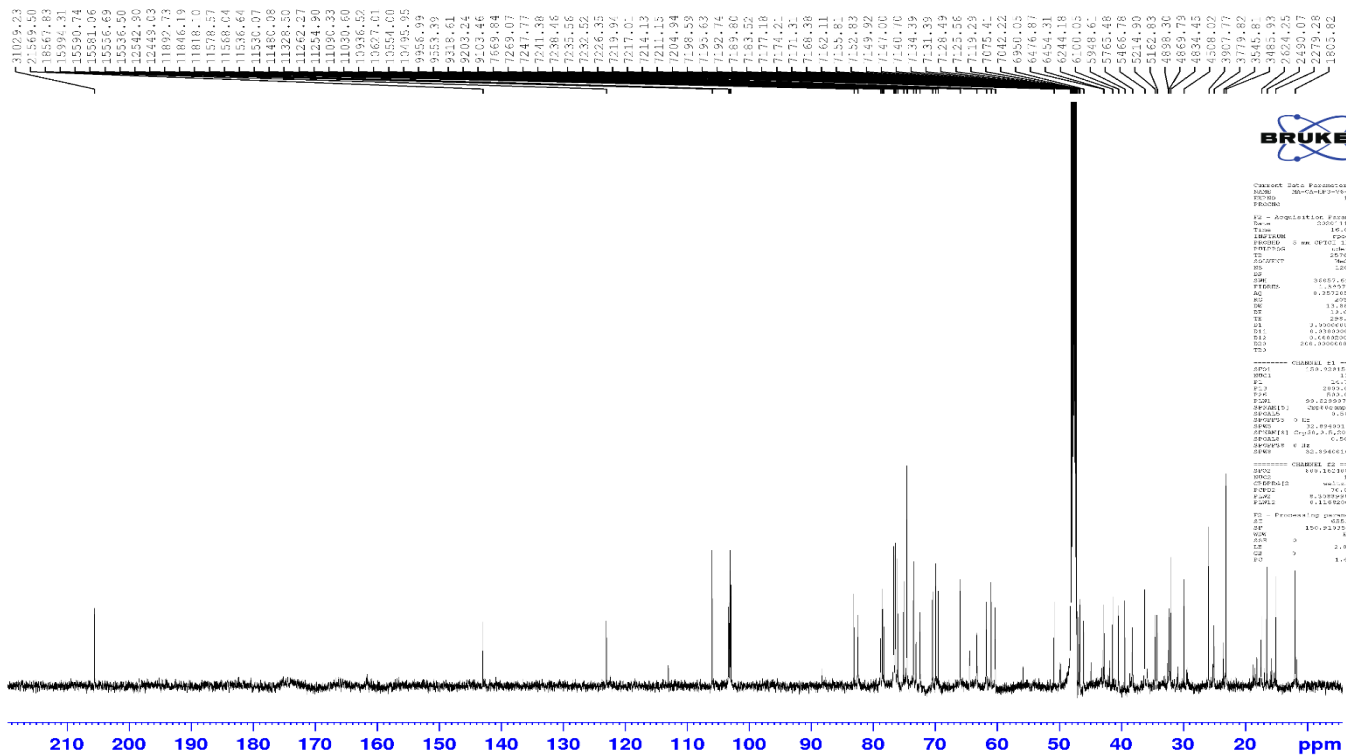


Fig. S72. ¹³C NMR Spectrum (150 MHz, MeOH-d₄) of compound 10

compound 10
CA-HP3-V6-S16-F1

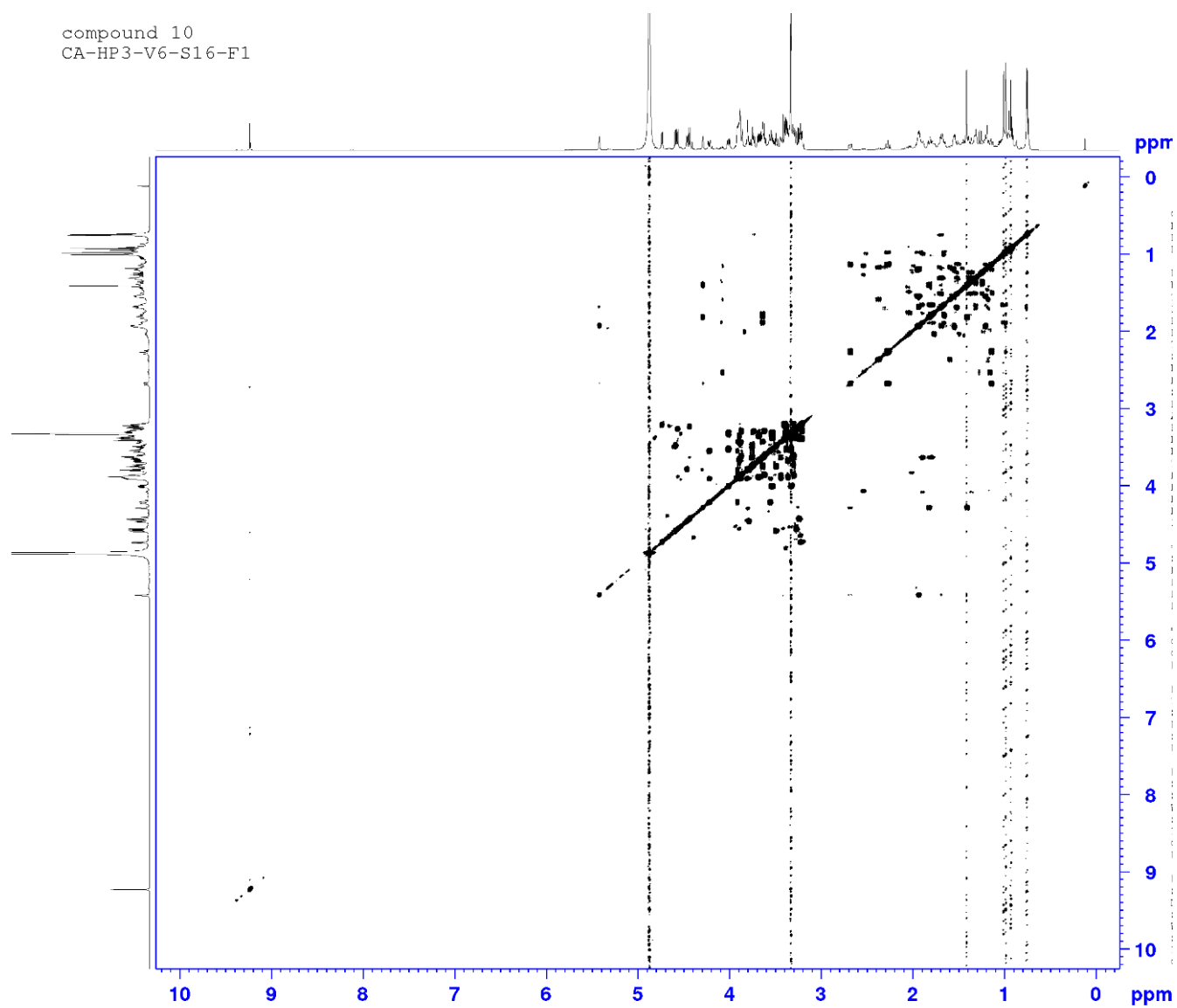


Fig. S73. COSY spectrum of compound **10**

compound 10
CA-HP3-V6-S16-F1

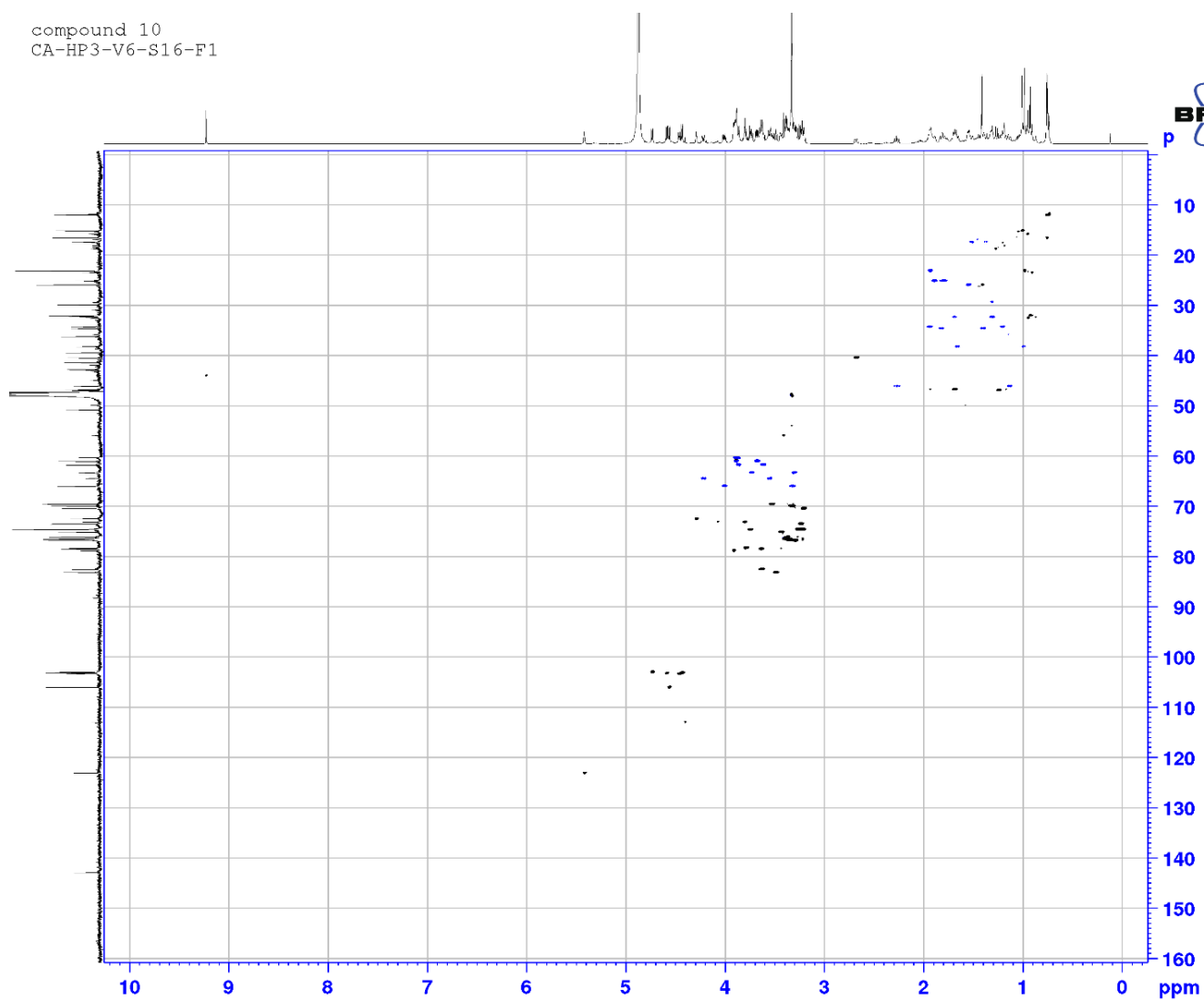


Fig. S74. HSQC spectrum of compound 10

compound 10
CA-HP3-V6-S16-F1

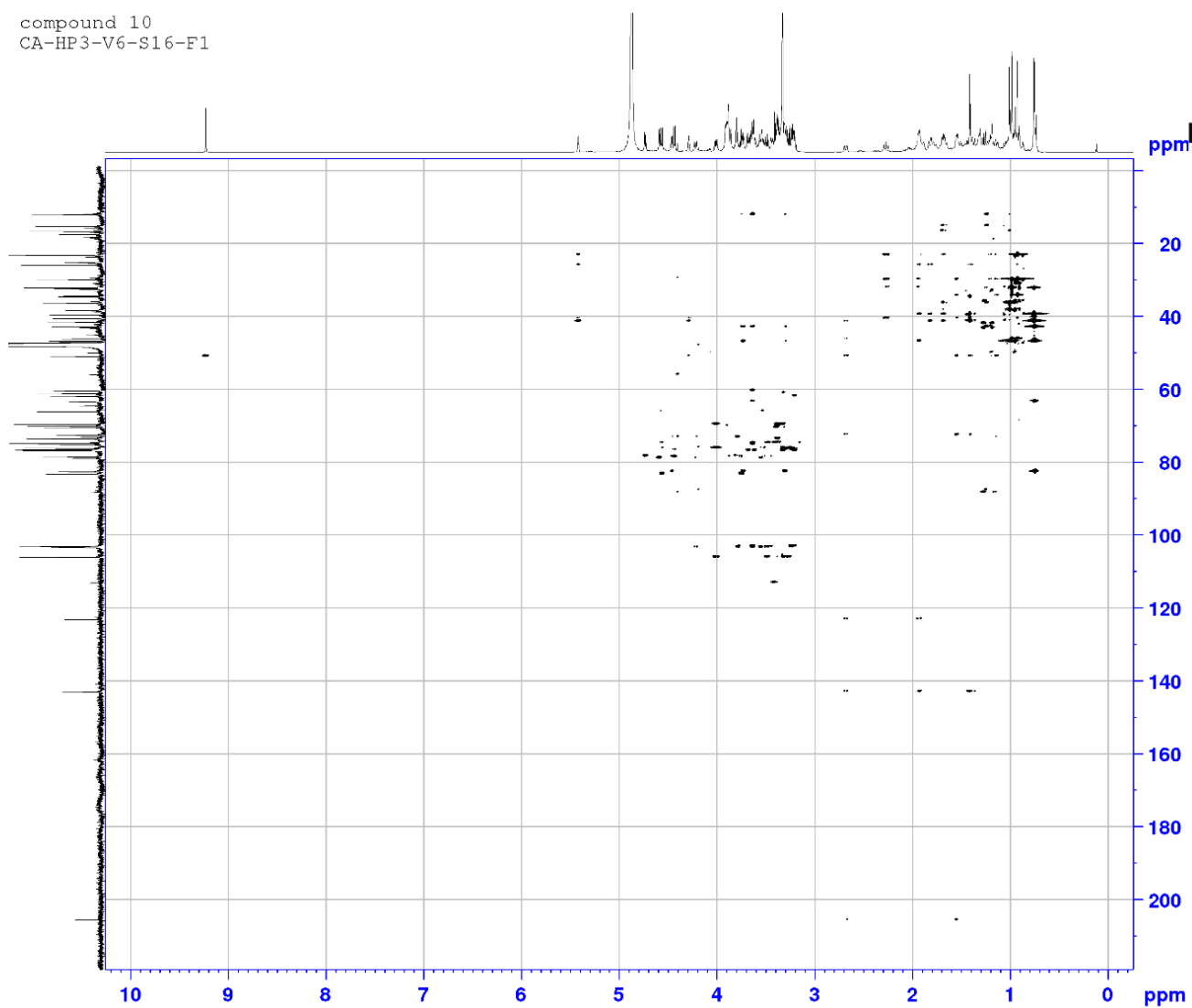


Fig. S75. HMBC spectrum of compound **10**

compound 10
CA-HP3-V6-S16-F1

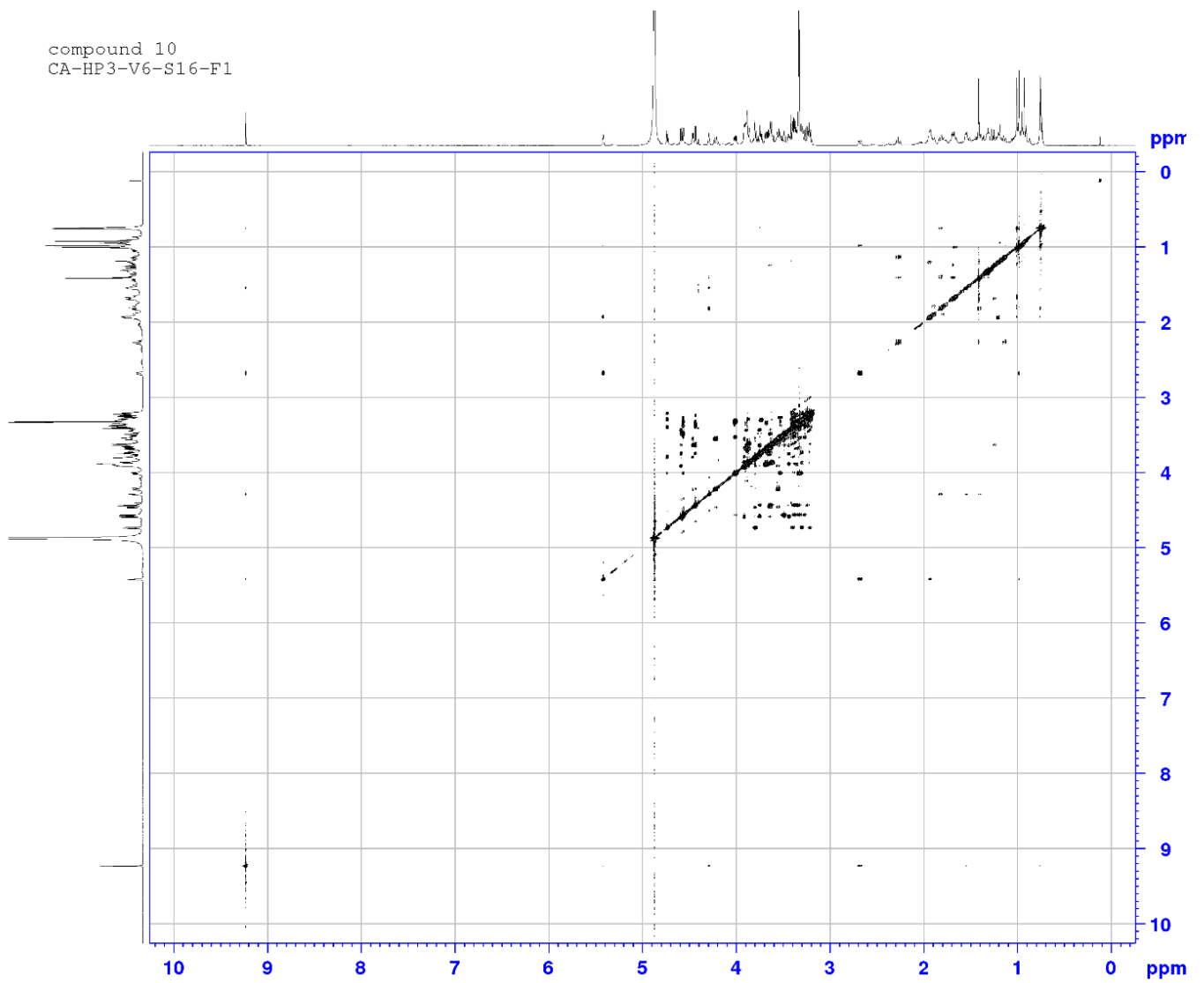


Fig. S76. ROESY spectrum of compound **10**

compound 9
CA-HP3-V6-S16-F1

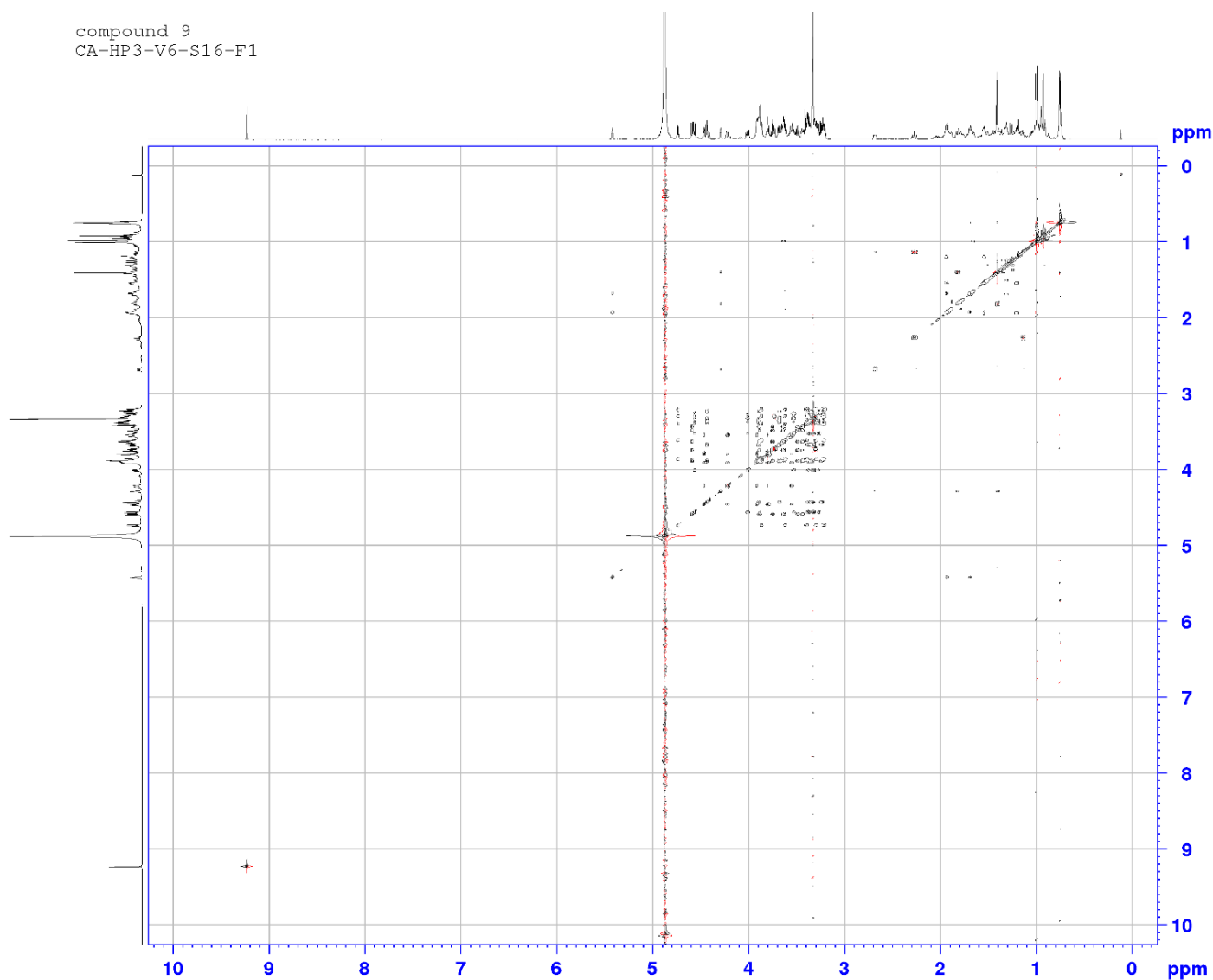


Fig. S77. TOCSY spectrum of compound 10

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 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 1 results within limits (up to 15 closest results for each mass)

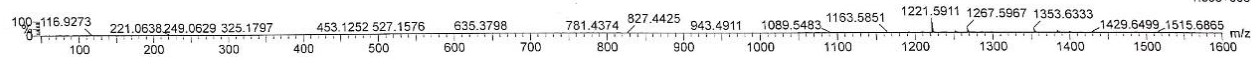
Elements Used:

C: 0-65 H: 0-100 O: 0-30

MA: CA_HP3_V6_S16_F1

20HR645 165 (1.272) Cm (168:169)

1: TOF MS ES-
1.89e+006



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1221.5911	1221.5904	0.7	0.6	12.5	833.7	n/a	n/a	C58 H93 O27

Fig. S78. HR-MS spectrum of compound 10

Compound 11
CA-HP3-V4-fc21-FI 7-8-S4-f2

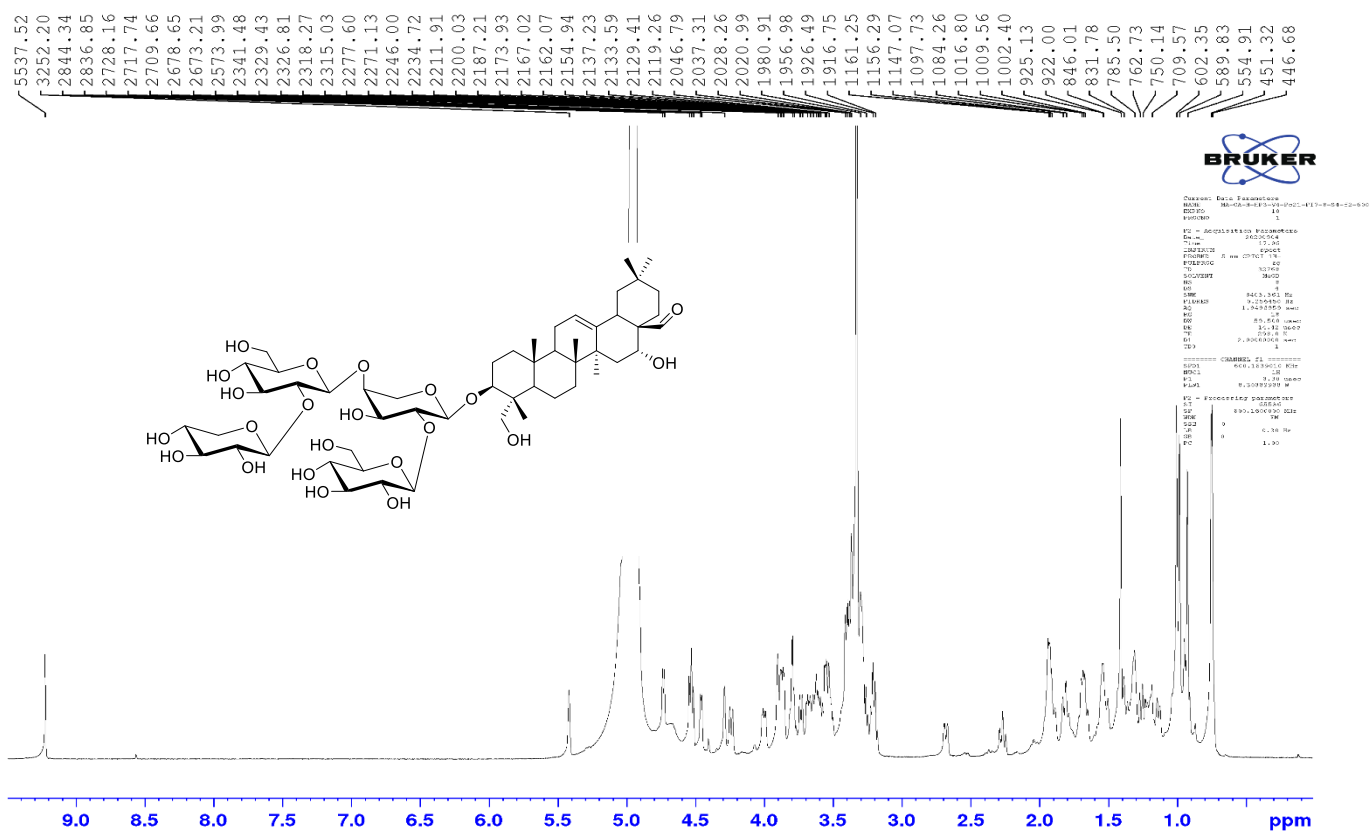


Fig. S79. ¹H NMR Spectrum (600 MHz, MeOH-d₄) of compound 11

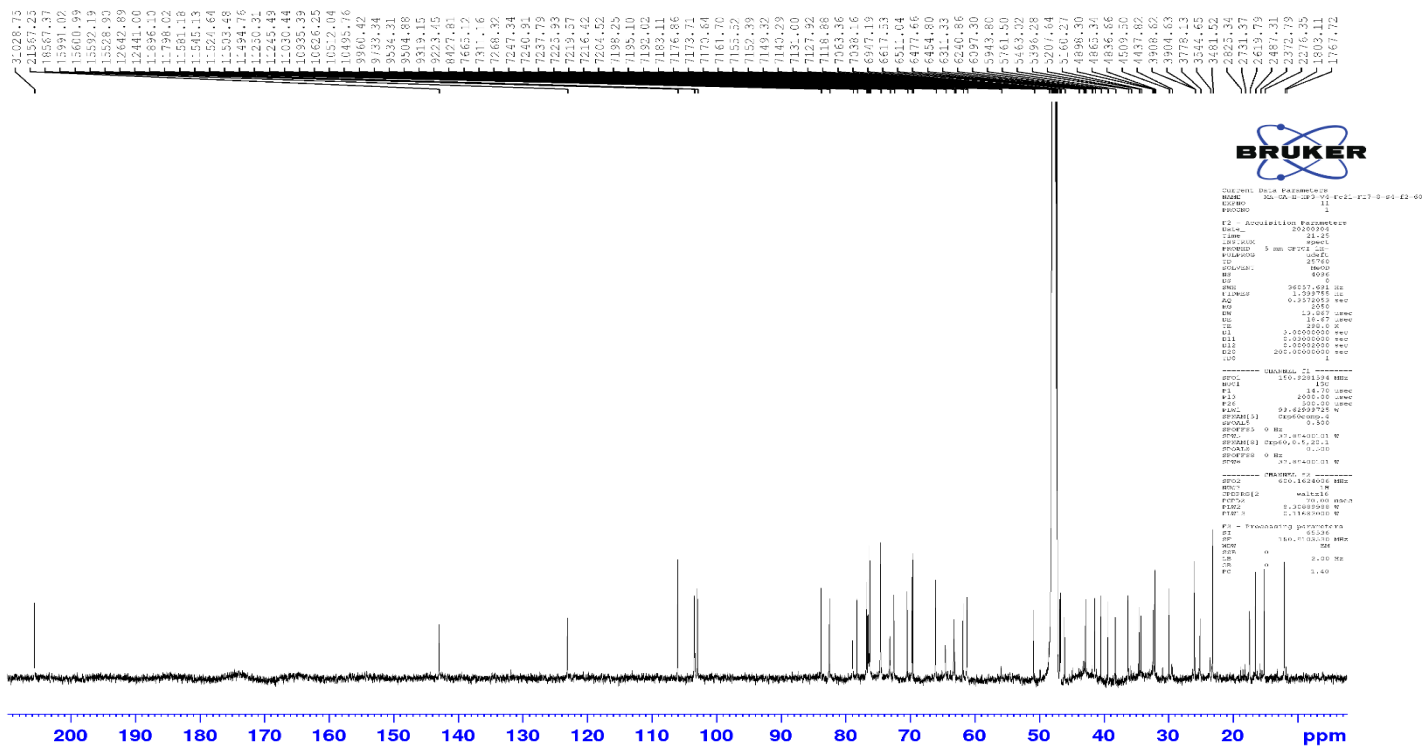


Fig. S80. ¹³C NMR Spectrum (150 MHz, MeOH-d₄) of compound 11

compound 11
CA-HH-HP3-V4-FB21-FI7-8-S4-F2

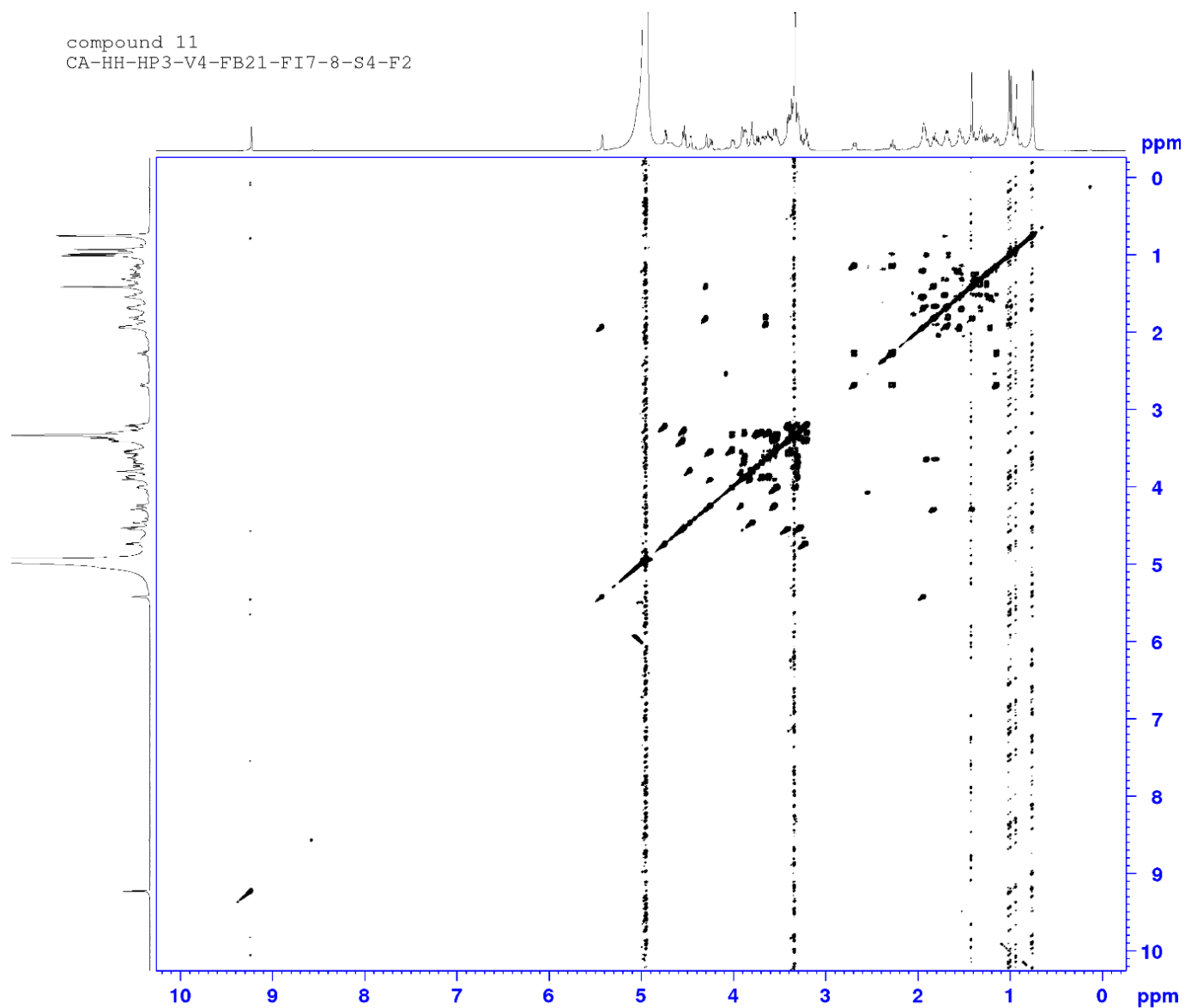


Fig. S81. COSY spectrum of compound 11

compound 11
CA-HH-HP3-V4-FB21-FI7-8-S4-F2

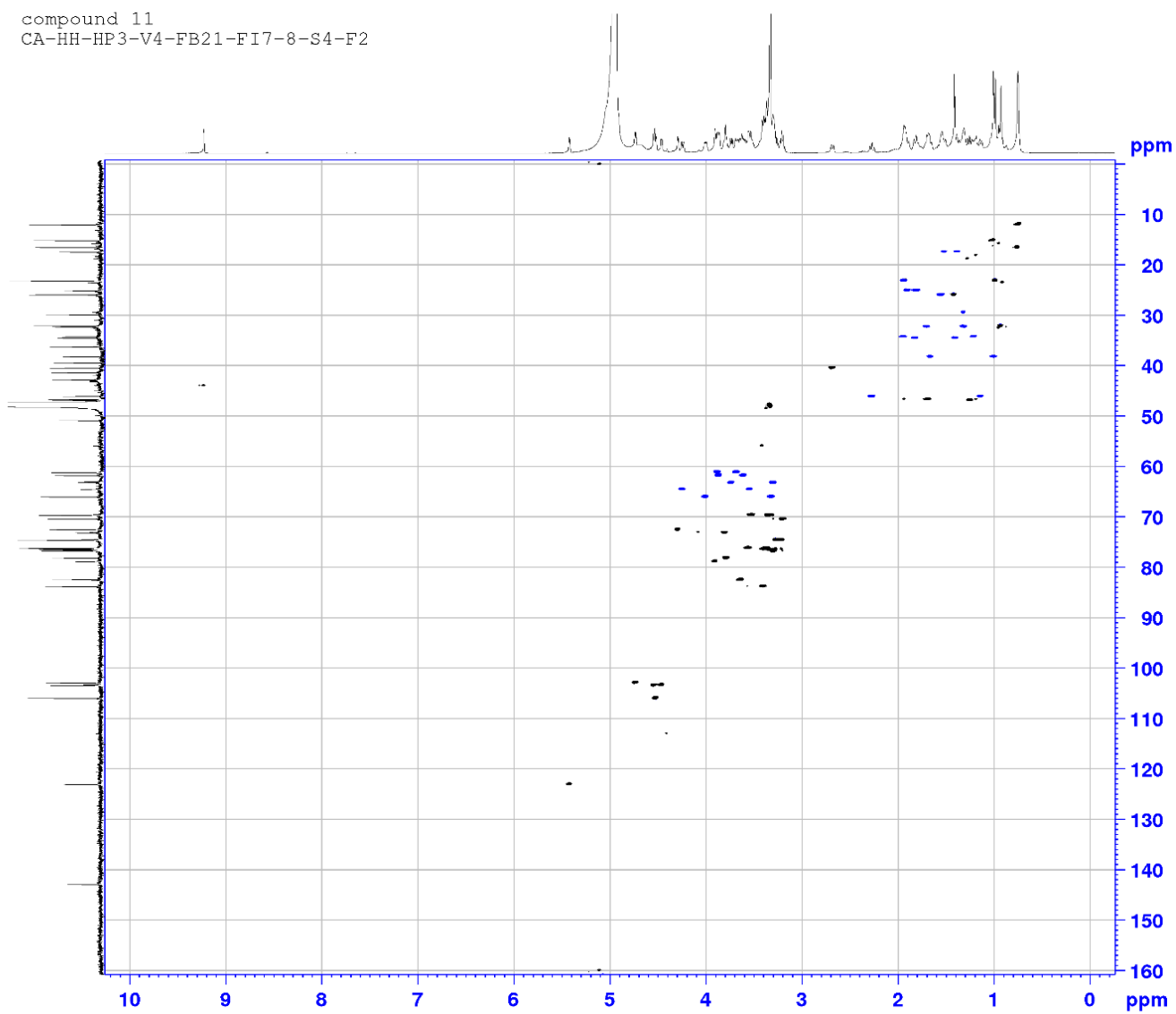


Fig. S82. HSQC spectrum of compound **11**

compound 11
CA-HH-HP3-V4-FB21-FI7-8-S4-F2

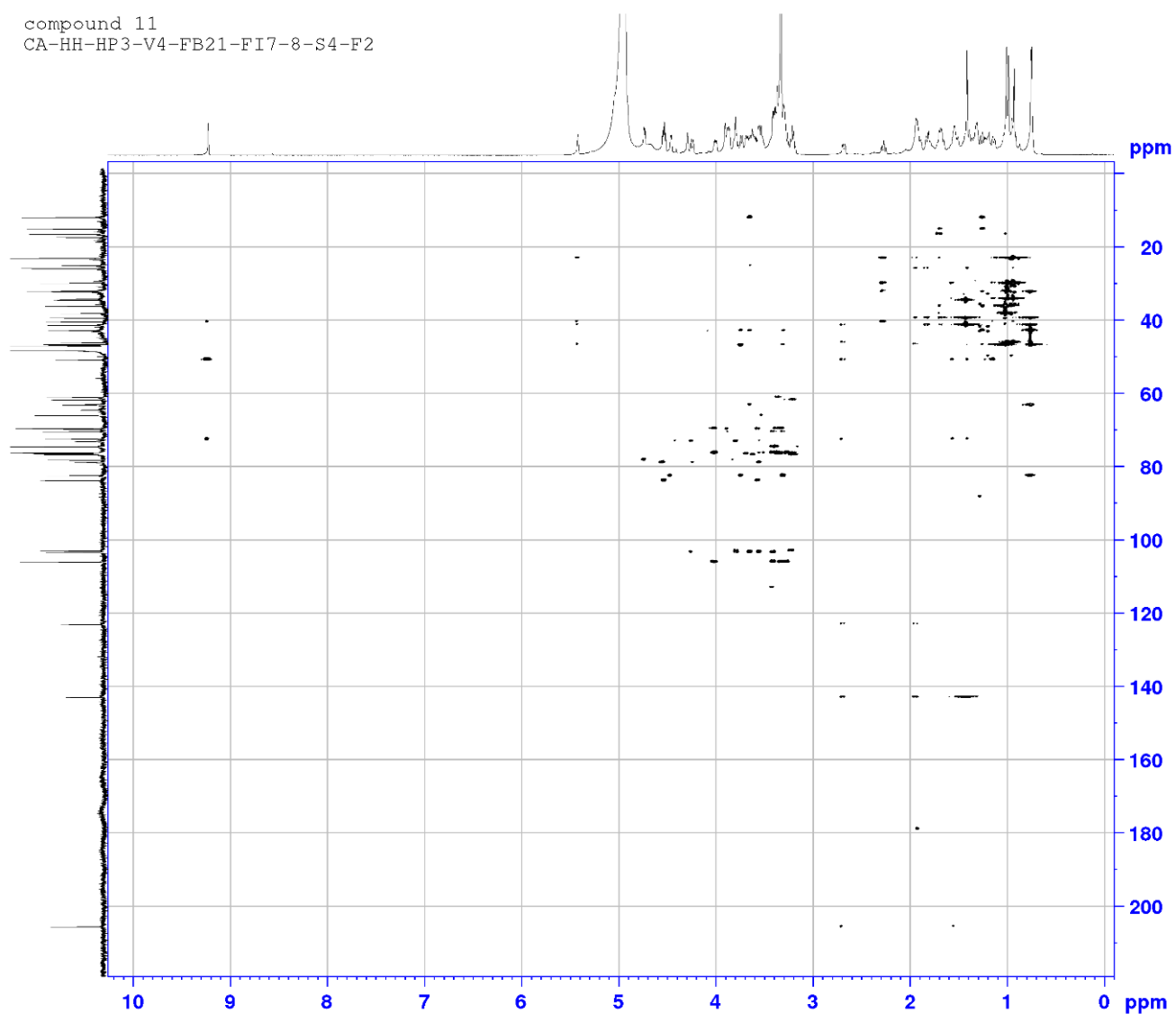


Fig. S83. HMBC spectrum of compound **11**

compound 11
CA-HH-HP3-V4-FB21-FI7-8-S4-F2

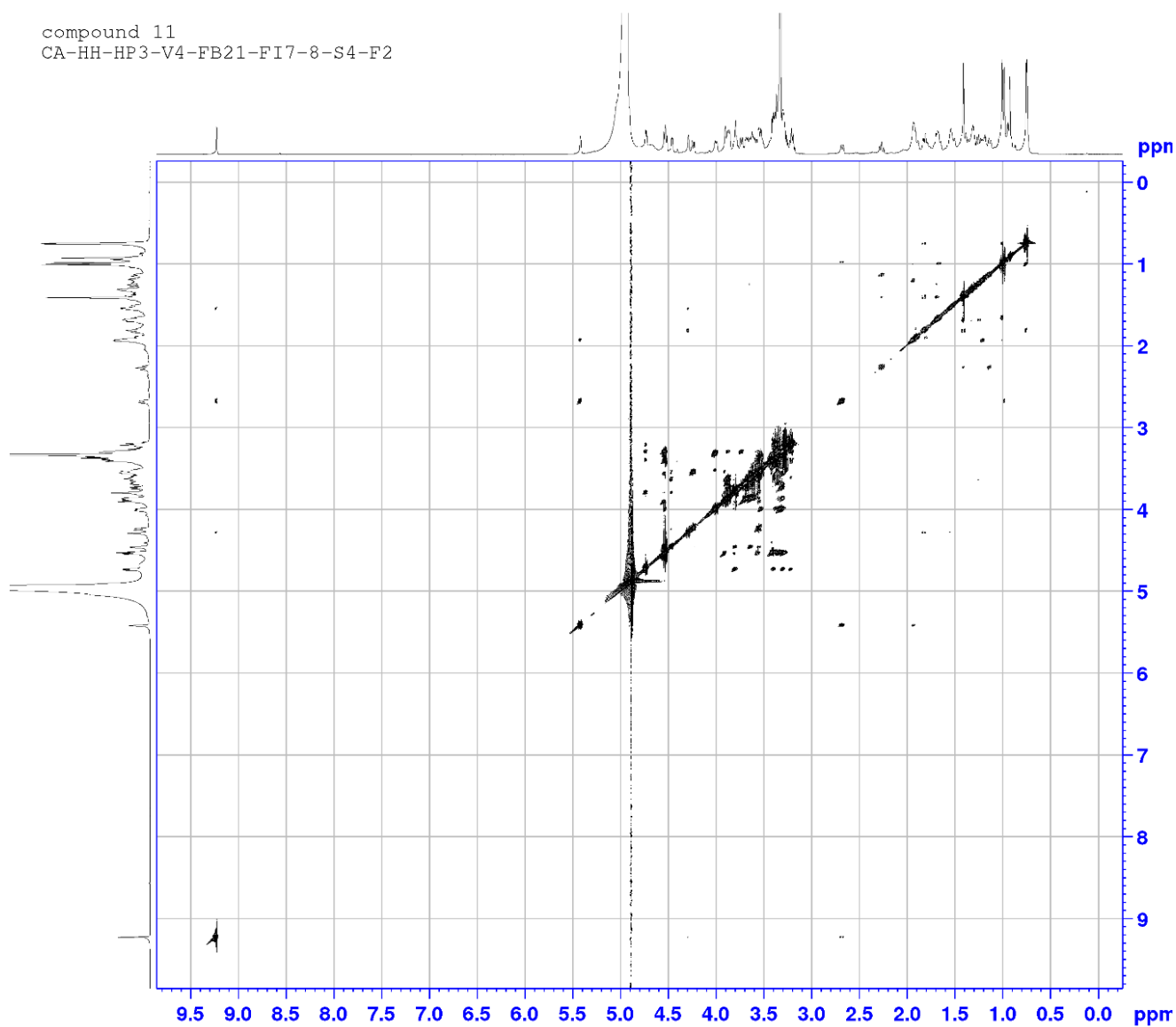


Fig. S84. ROESY spectrum of compound **11**

compound 11
 CA-HH-HP3-V4-FB21-FI7-8-S4-F2

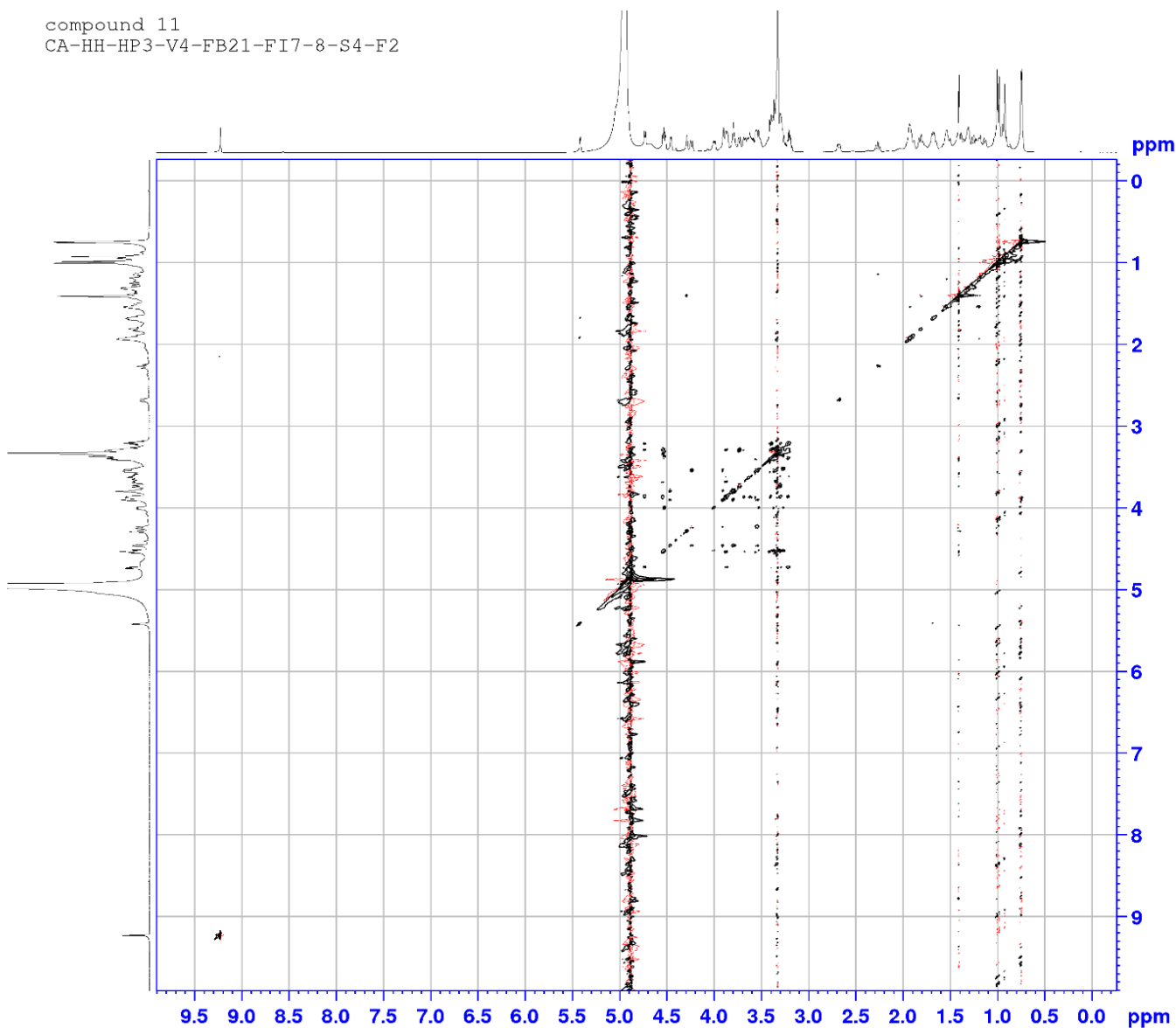


Fig. S85. TOCSY spectrum of compound 11

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 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

151 formula(e) evaluated with 2 results within limits (up to 15 closest results for each mass)

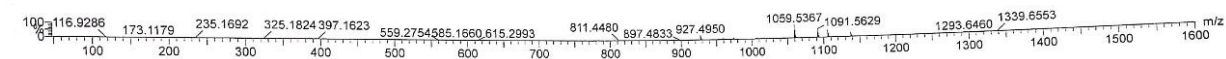
Elements Used:

C: 0-65 H: 0-100 O: 0-30

MA_CA_HP3_V4_Fc11_FI7_8_S4_F2

20HR649 180 (1.351) Cm (180:182)

1: TOF MS ES-
1.58e+006



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
1059.5367	1059.5376	-0.9	-0.5	11.5	667.2	0.000	99.97	C52 H83 O22
	1059.5317	5.0	4.7	20.5	875.4	8.234	0.03	C59 H79 O17

Fig. S86. HR-MS spectrum of compound 11

Compound 12
CA-HP3-V6-S16-f2

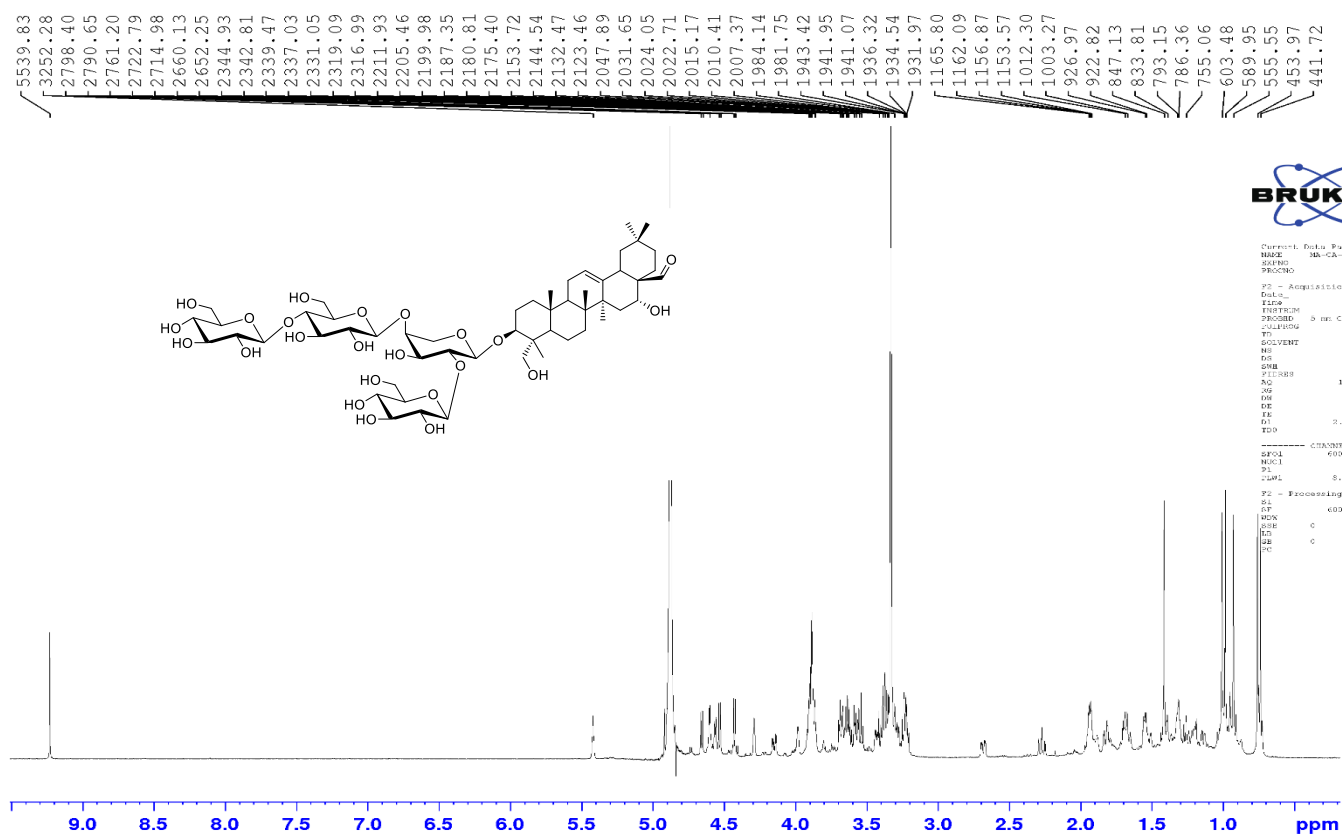


Fig. S87. ¹H NMR Spectrum (600 MHz, MeOH-d₄) of compound 12

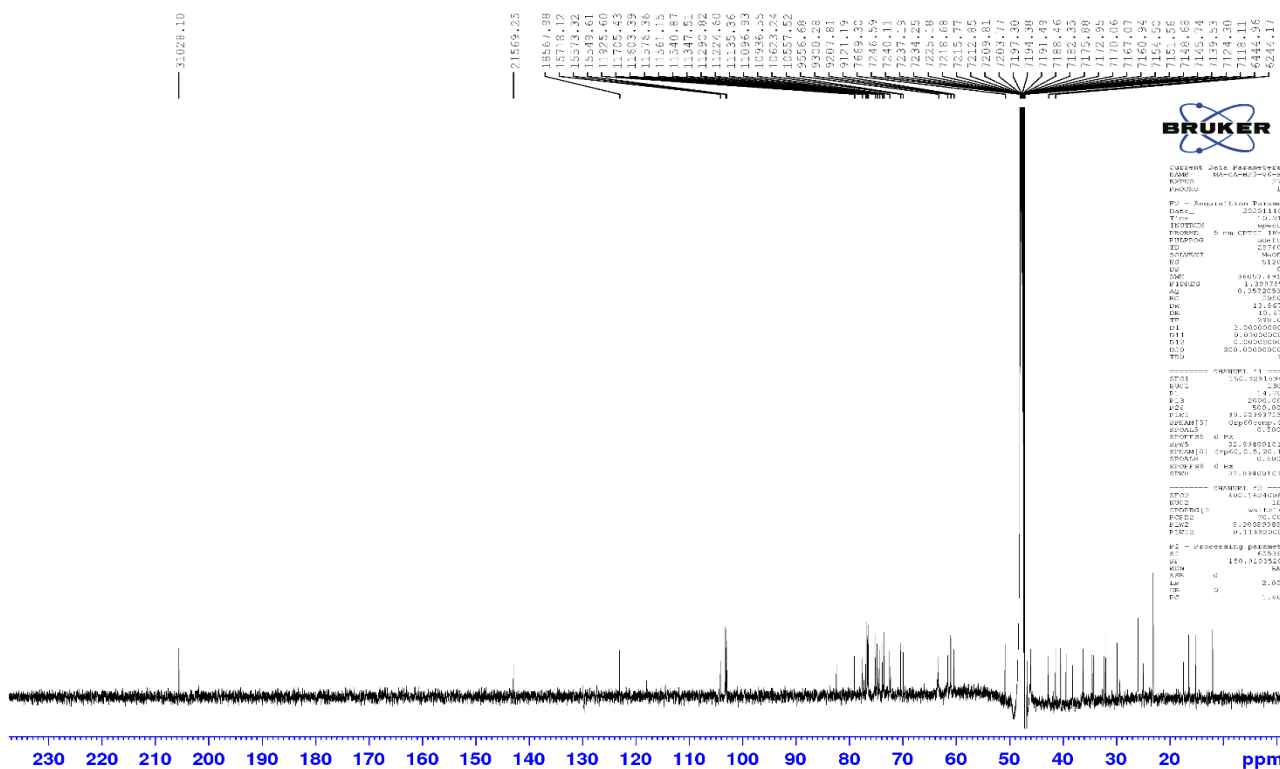


Fig. S88. ¹³C NMR Spectrum (150 MHz, MeOH-d₄) of compound 12

compound 12
CA-HH-HP3-V6-S16-F2

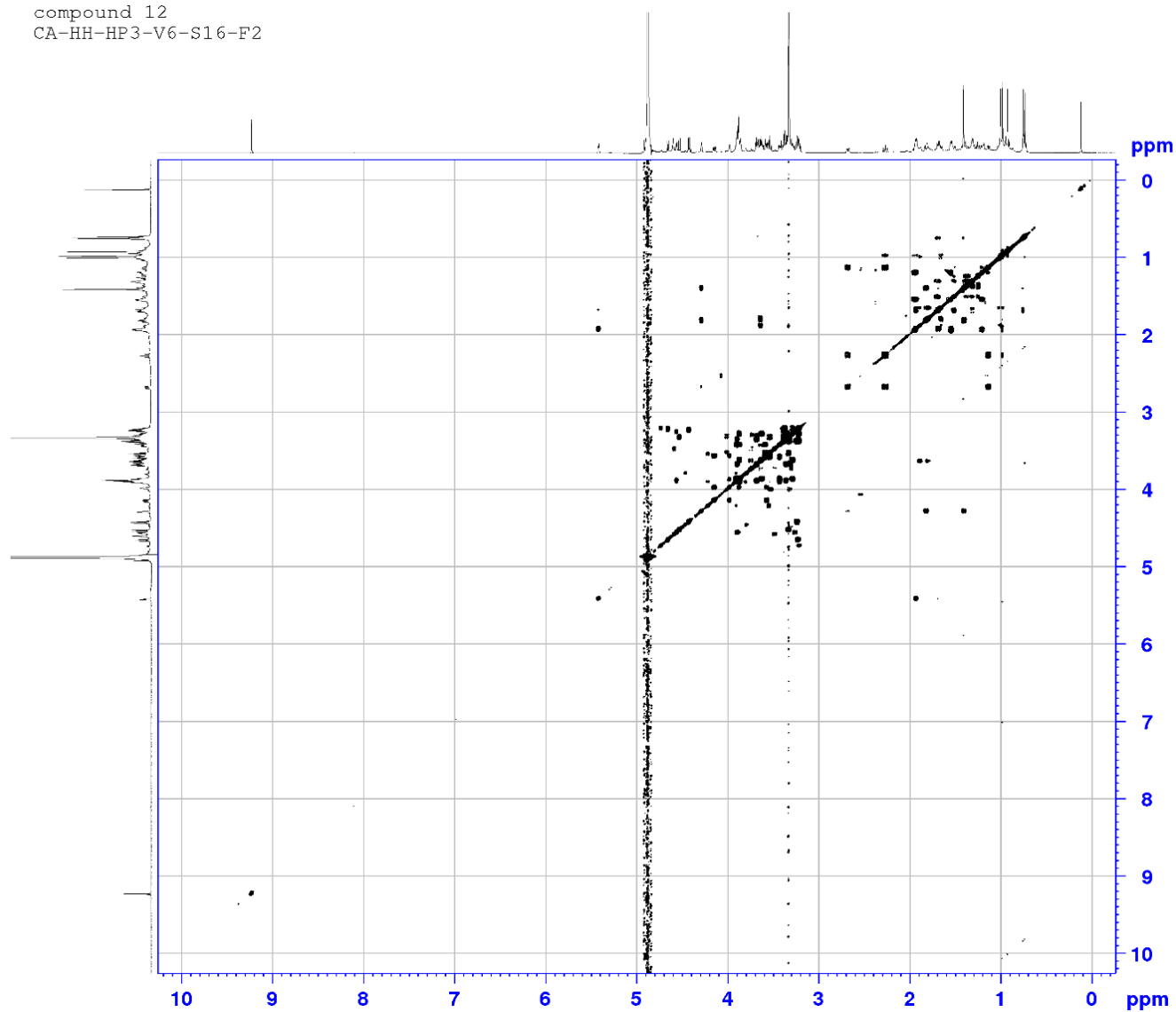


Fig. S89. COSY spectrum of compound 12

compound 12
CA-HH-HP3-V6-S16-F2

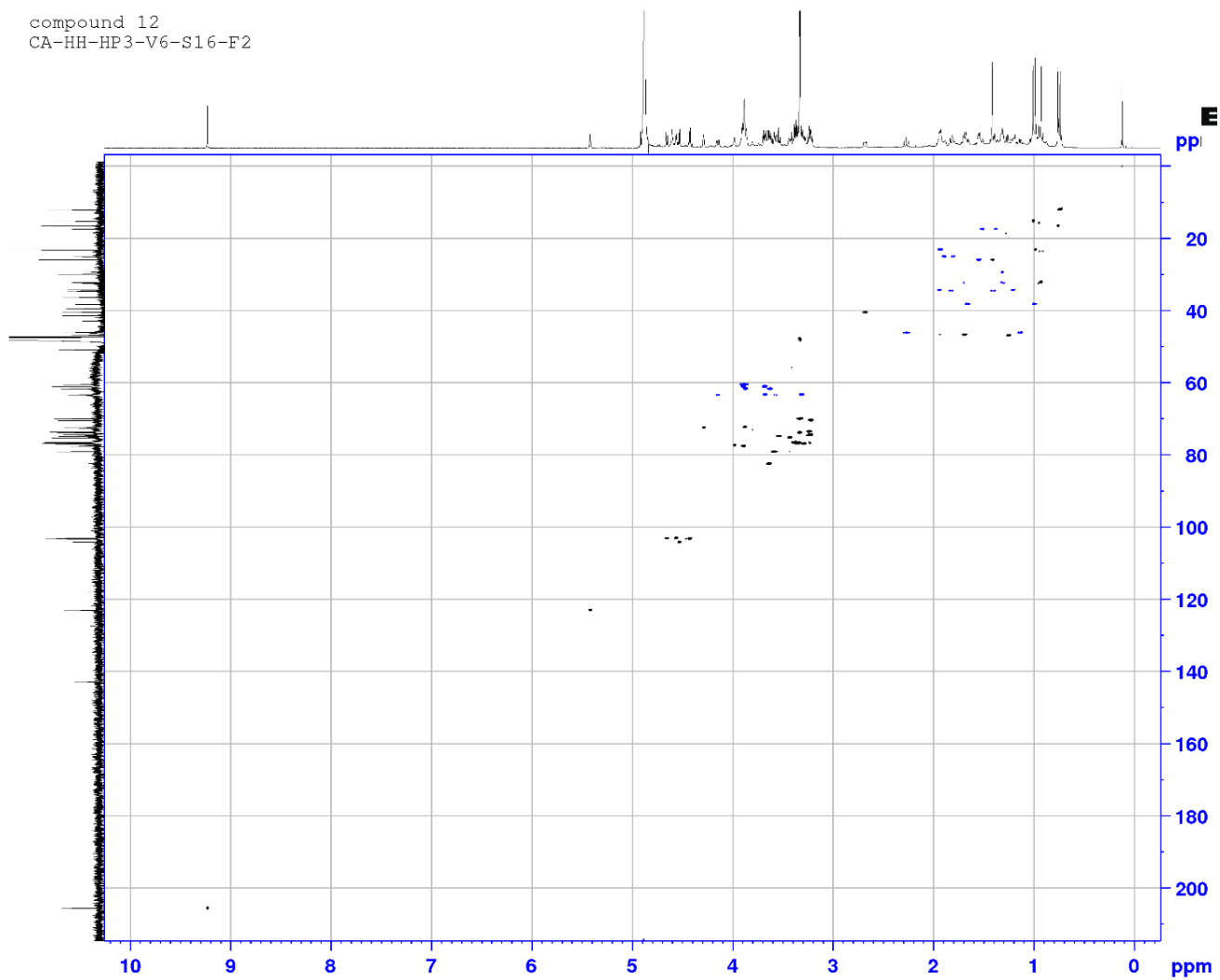


Fig. S90. HSQC spectrum of compound 12

compound 12
CA-HH-HP3-V6-S16-F2

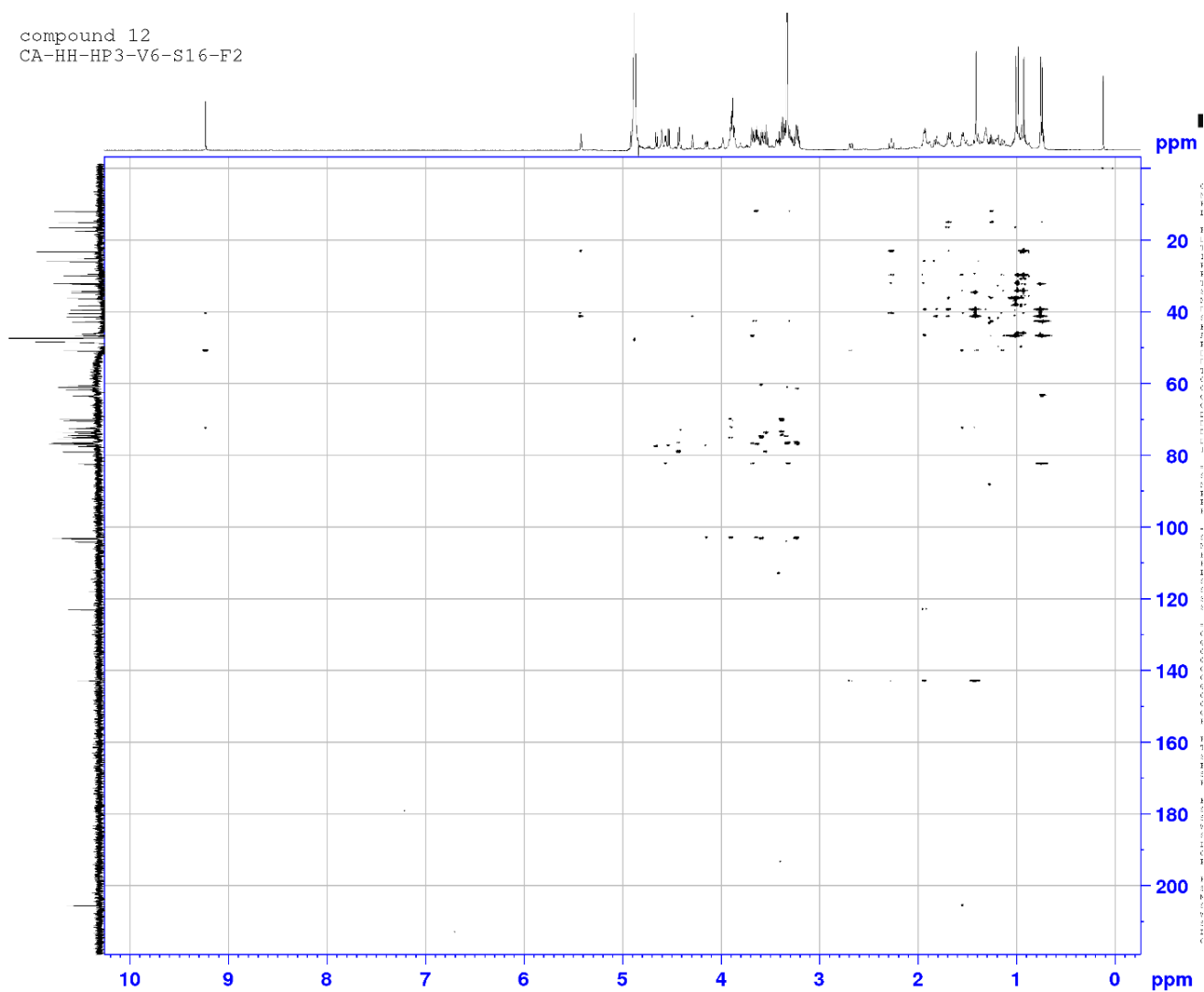


Fig. S91. HMBC spectrum of compound 12

compound 12
CA-HH-HP3-V6-S16-F2

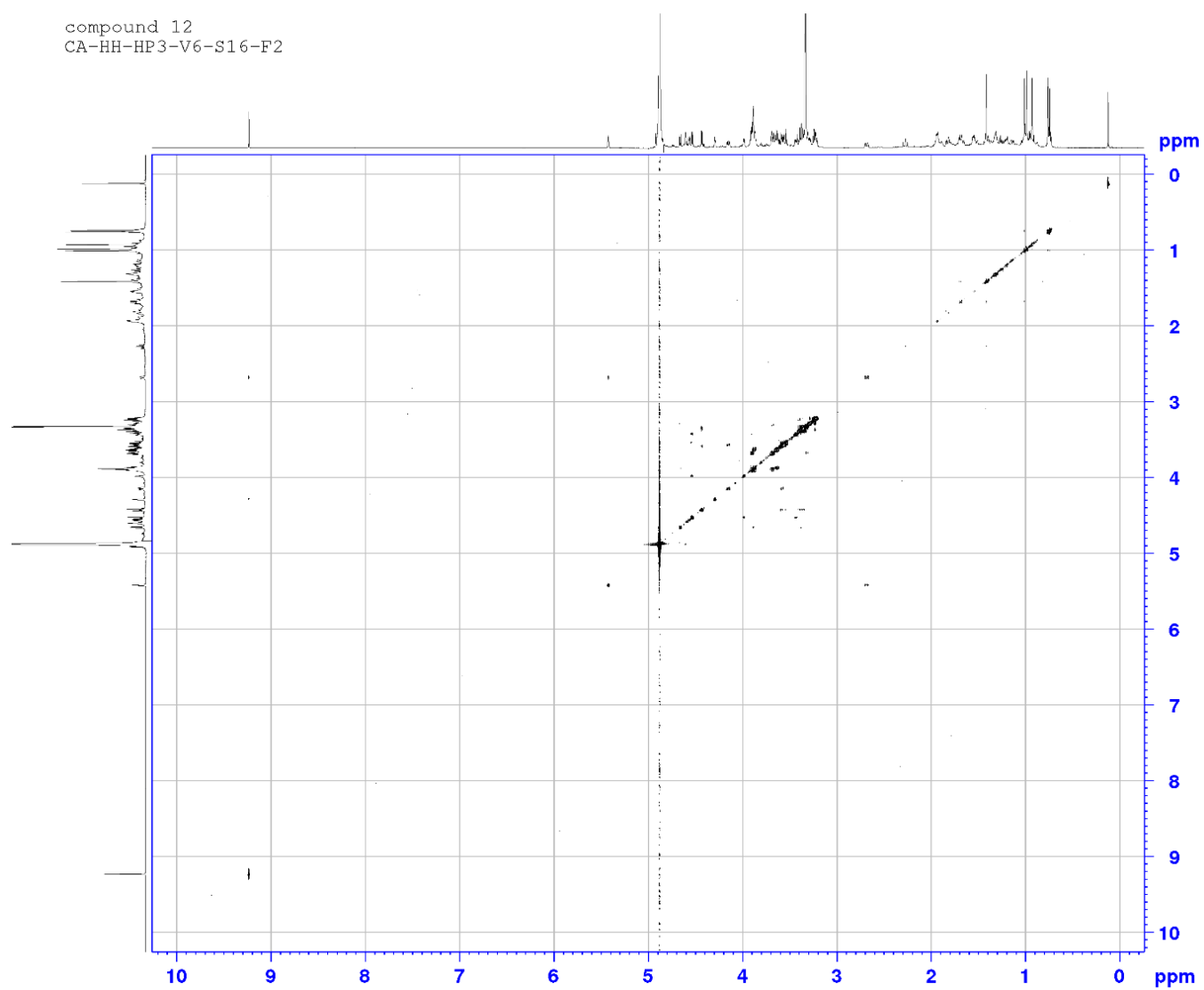


Fig. S92. ROESY spectrum of compound 12

compound 12
CA-HH-HP3-V6-S16-F2

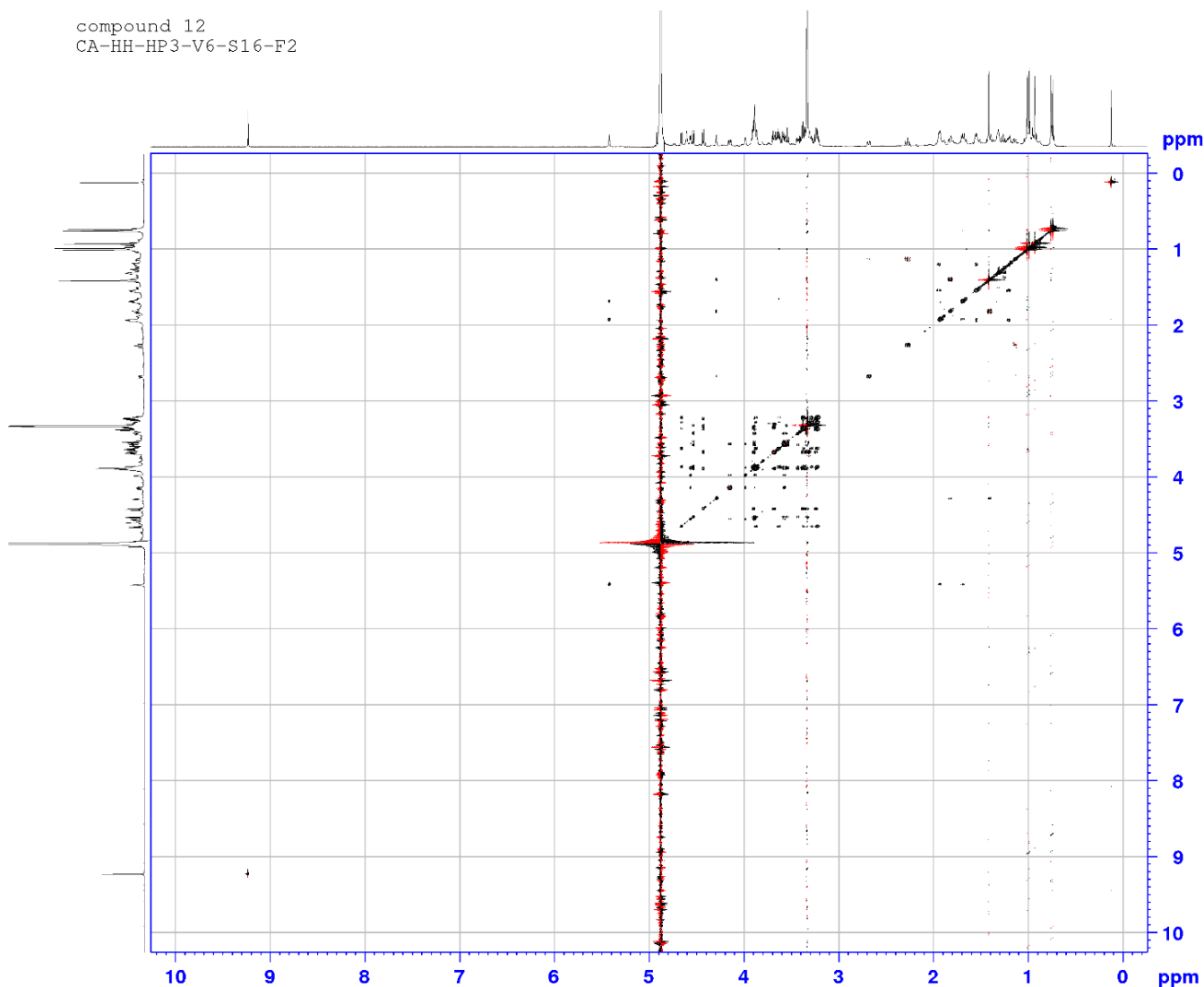


Fig. S93. TOCSY spectrum of compound 12

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 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

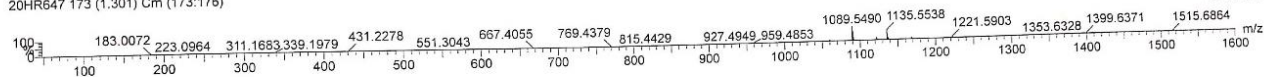
133 formula(e) evaluated with 2 results within limits (up to 15 closest results for each mass)

Elements Used:

C: 0-65 H: 0-100 O: 0-30

MA_CA_HP3_V6_S16_F2

20HR647 173 (1.301) Cm (173:176)



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1089.5490	1089.5482	0.8	0.7	11.5	975.8	0.000	99.98	C53 H85 O23
	1089.5540	-5.0	-4.6	2.5	984.2	8.453	0.02	C46 H89 O28

Fig. S94. HR-MS spectrum of compound 12

Compound 13
CA-HP3-V6-S16-f6

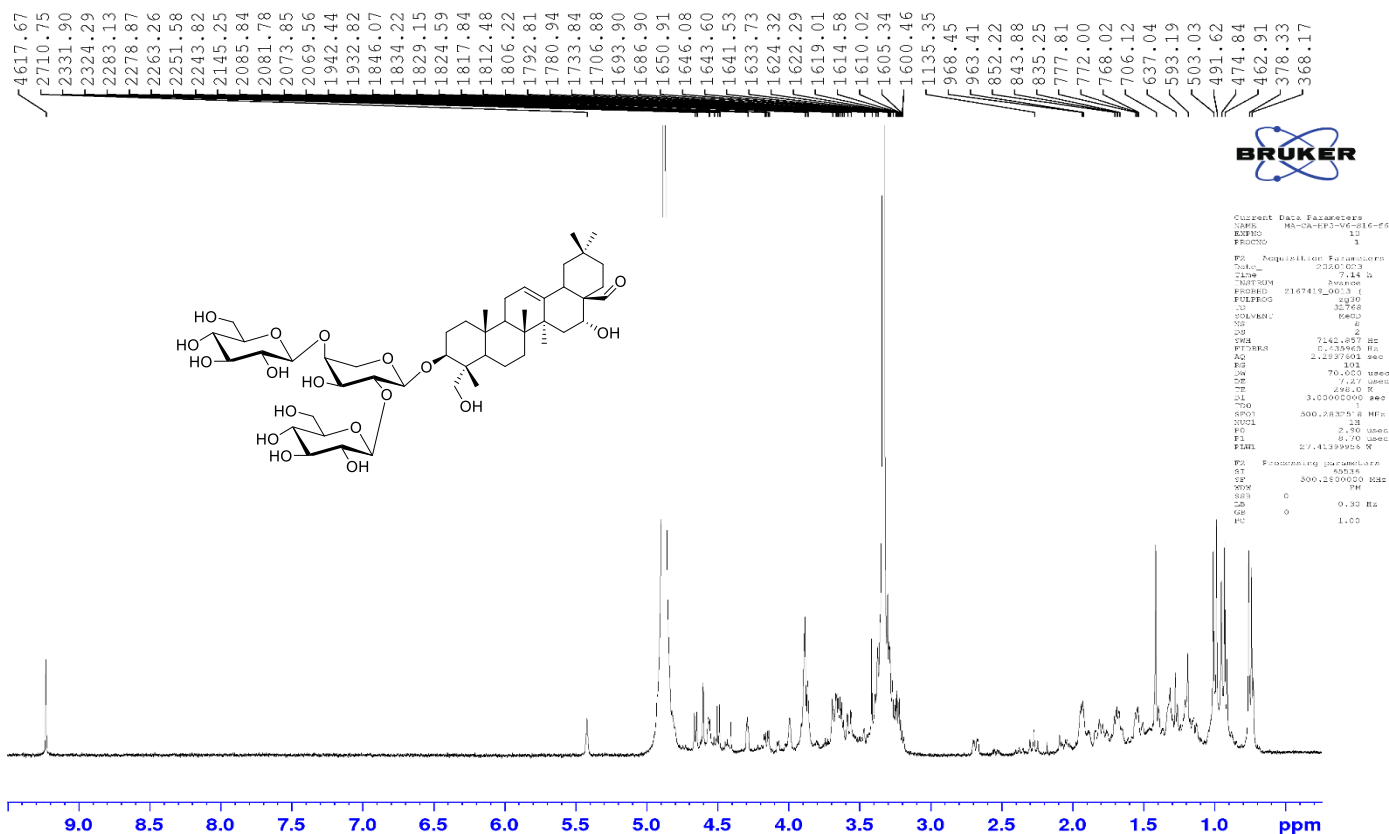


Fig. S95. ¹H NMR Spectrum (500 MHz, MeOH-*d*₄) of compound 13

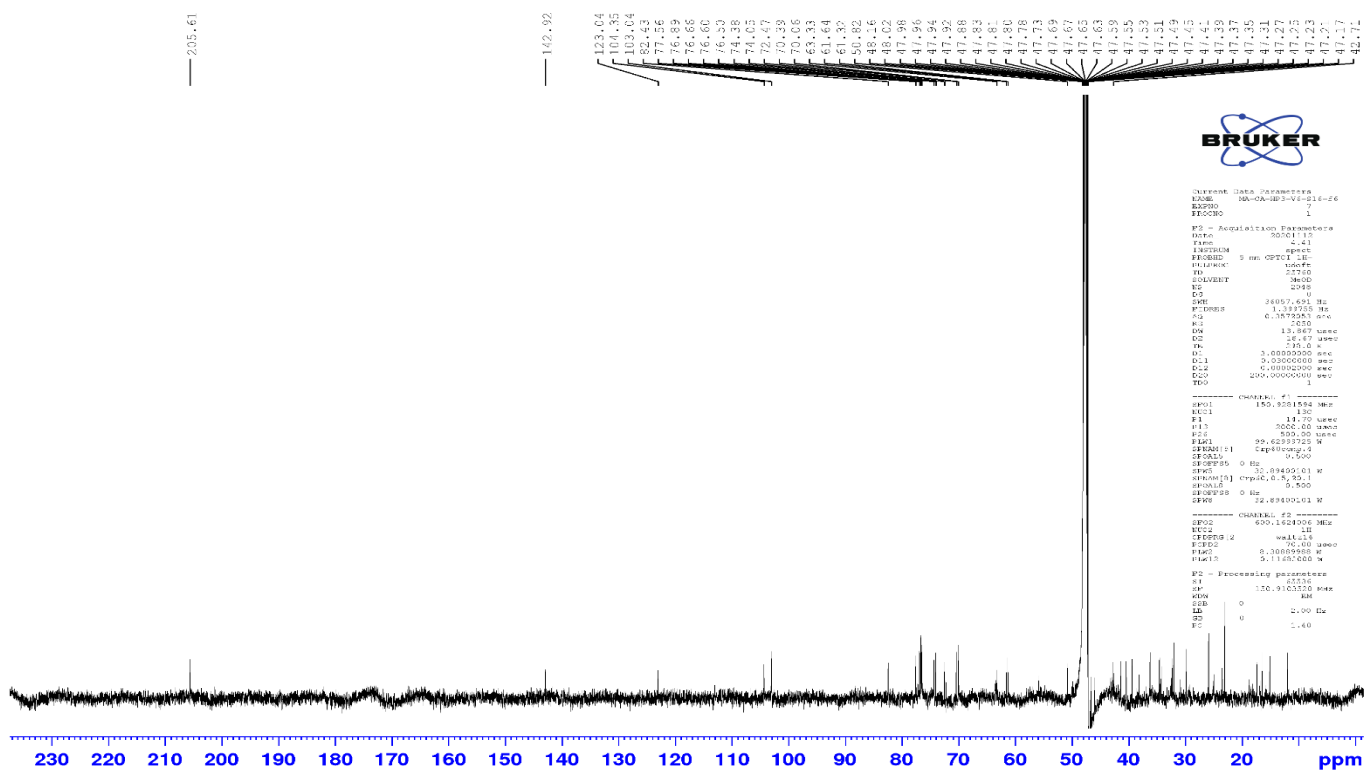


Fig. S96. ¹³C NMR Spectrum (150 MHz, MeOH-*d*₄) of compound 13

compound 13
CA-HH-HP3-V6-S16-F6

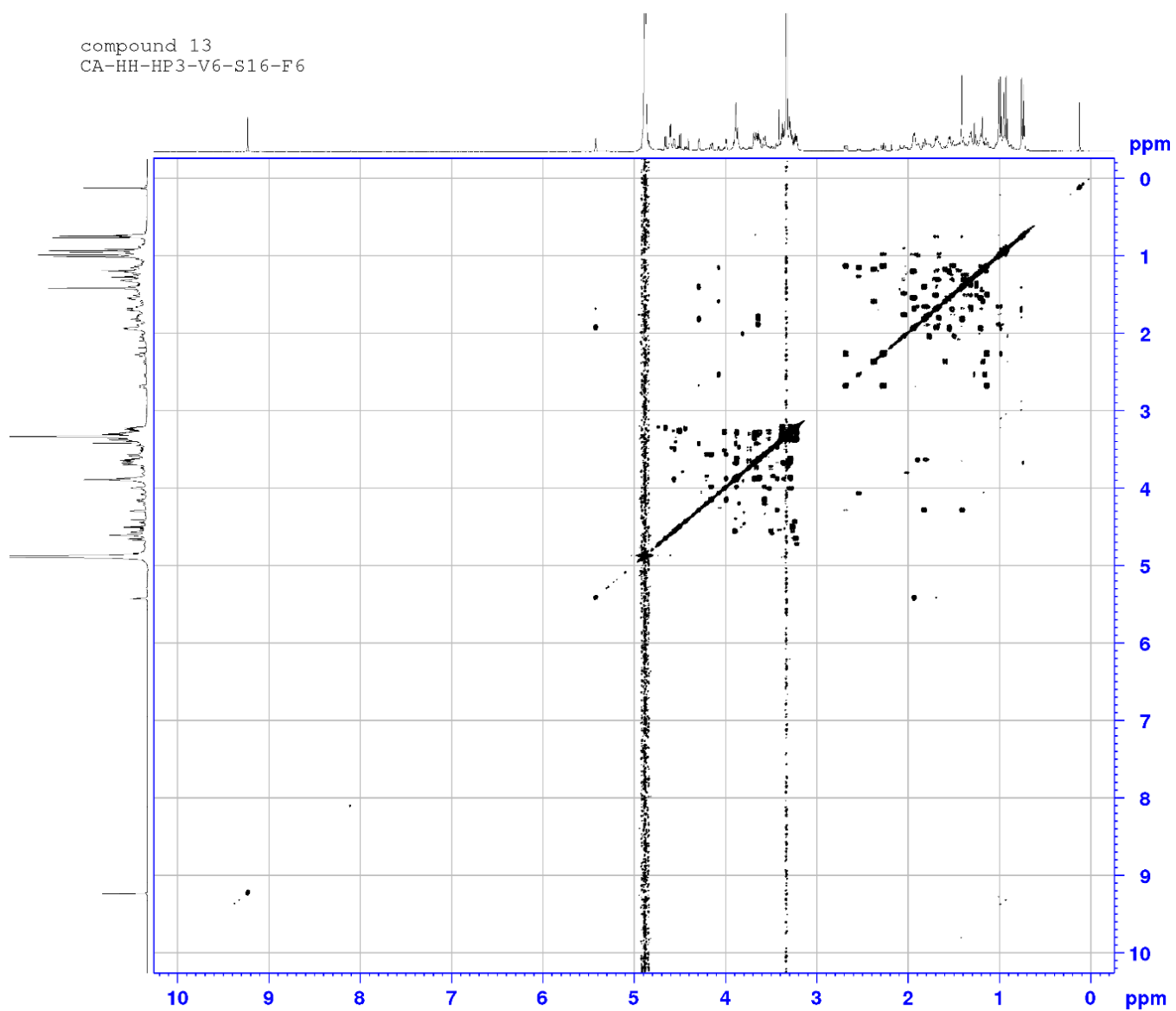


Fig. S97. COSY spectrum of compound 13

compound 13
CA-HH-HP3-V6-S16-F6

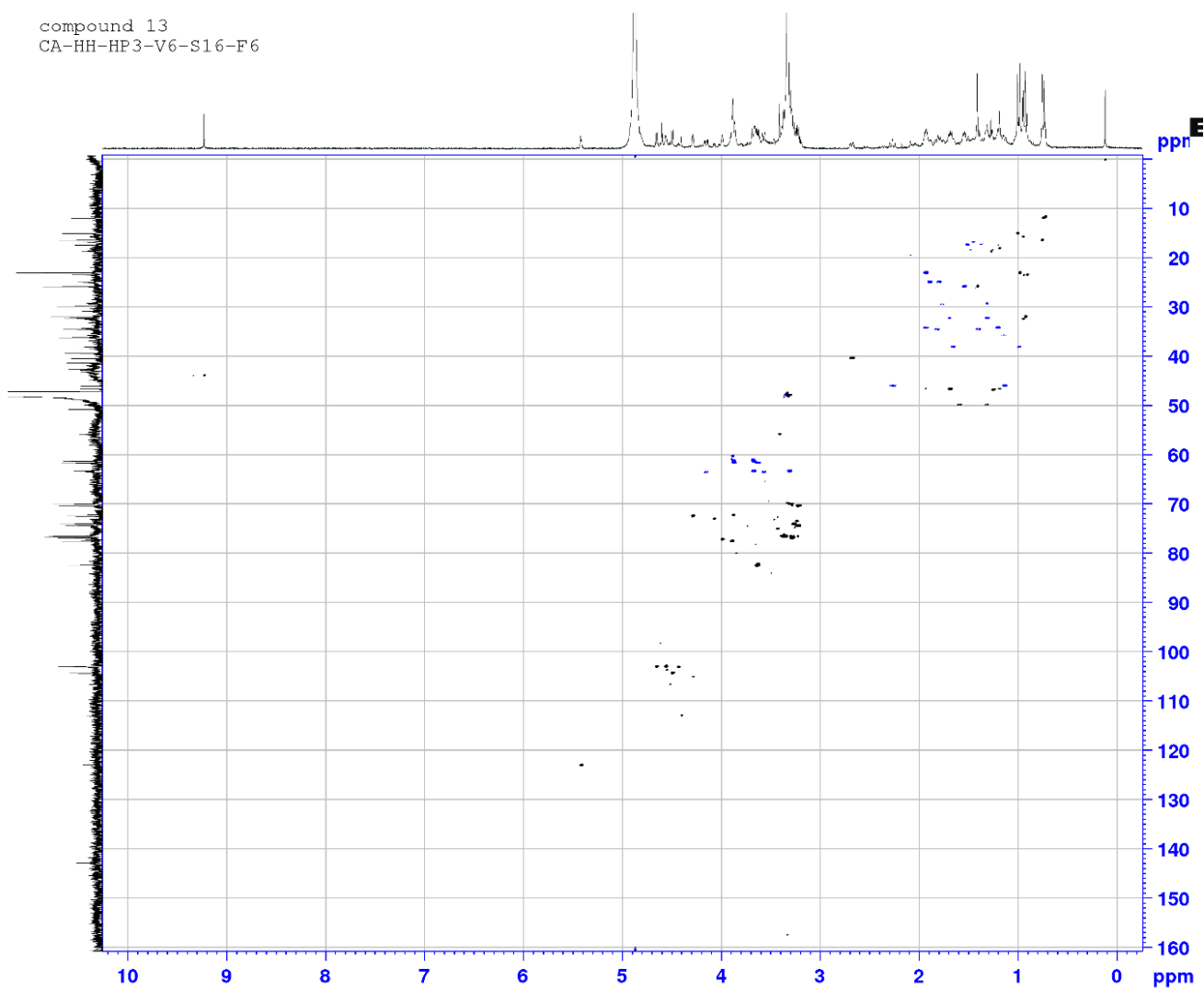


Fig. S98. HSQC spectrum of compound **13**

compound 13
CA-HH-HP3-V6-S16-F6

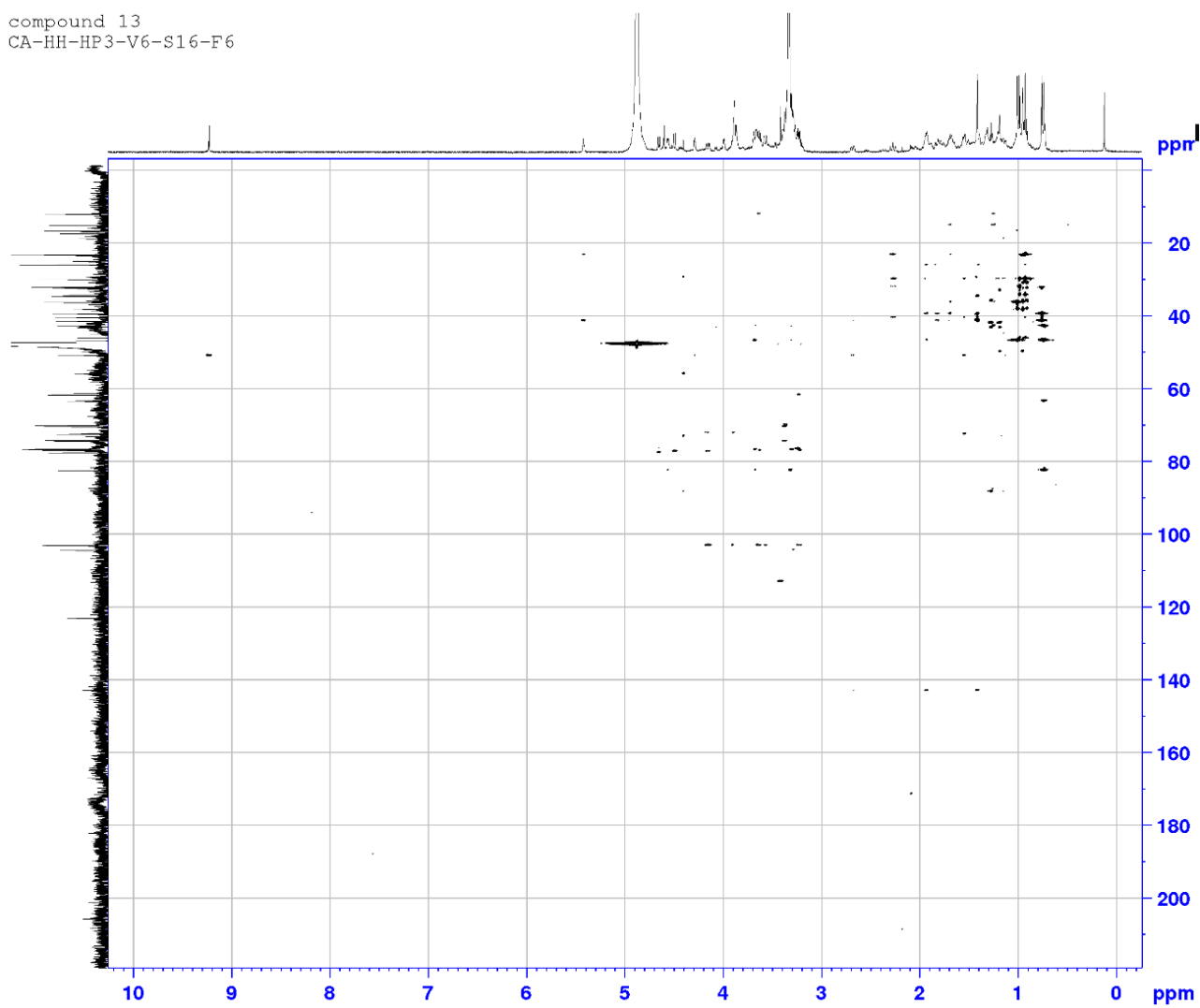


Fig. S99. HMBC spectrum of compound **13**

compound 13
CA-HH-HP3-V6-S16-F6

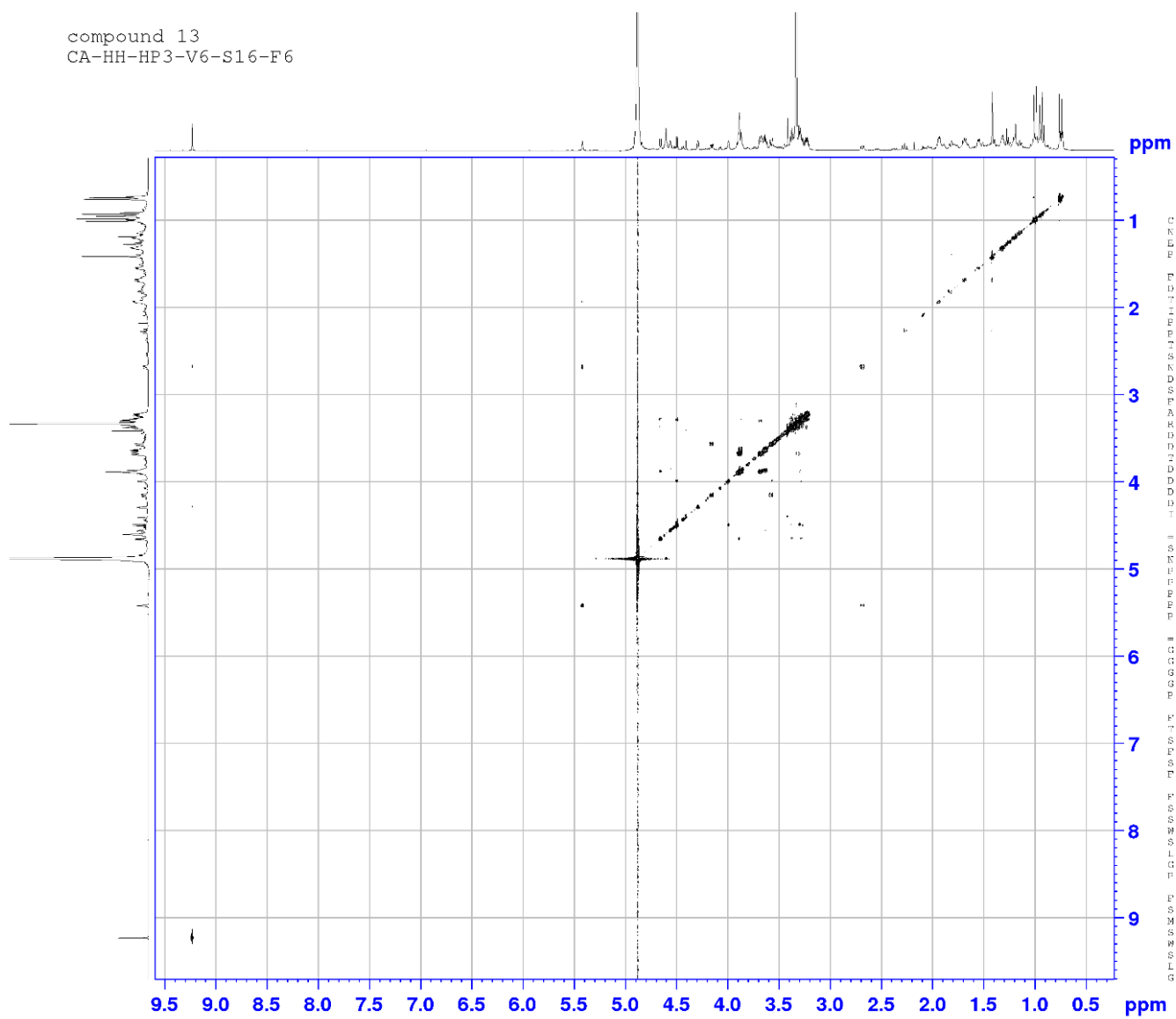


Fig. S100. ROESY spectrum of compound **13**

compound 13
CA-HH-HP3-V6-S16-F6

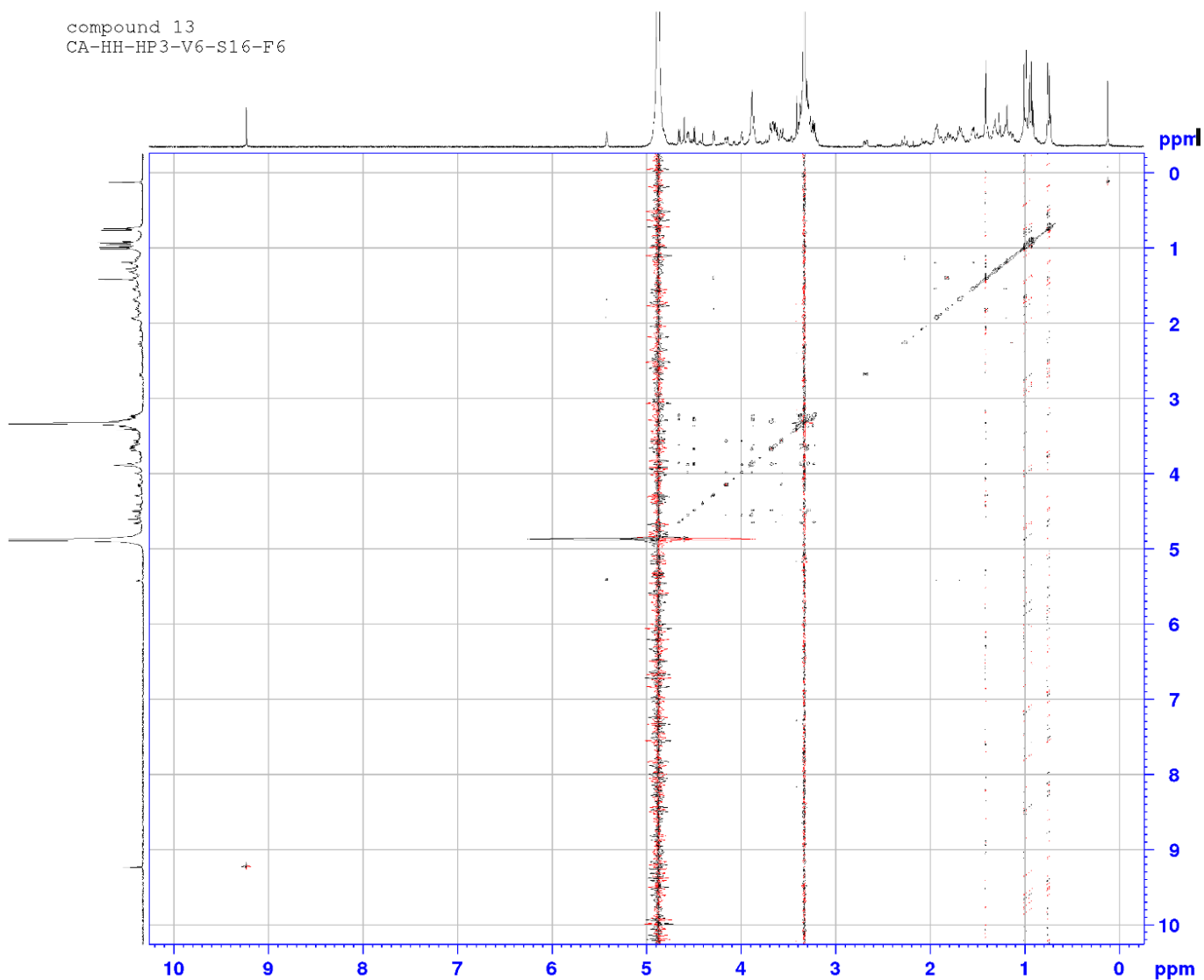


Fig. S101. TOCSY spectrum of compound 13

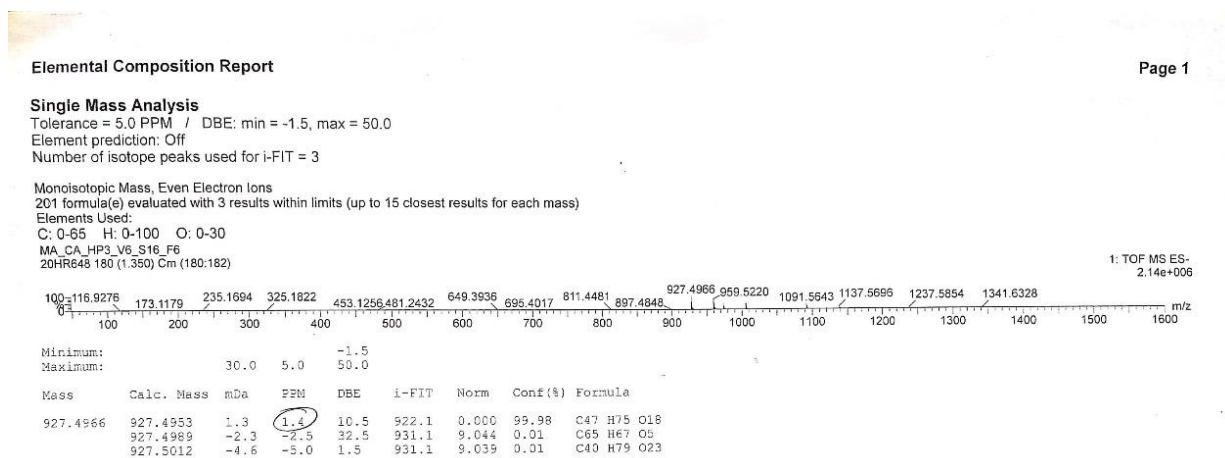
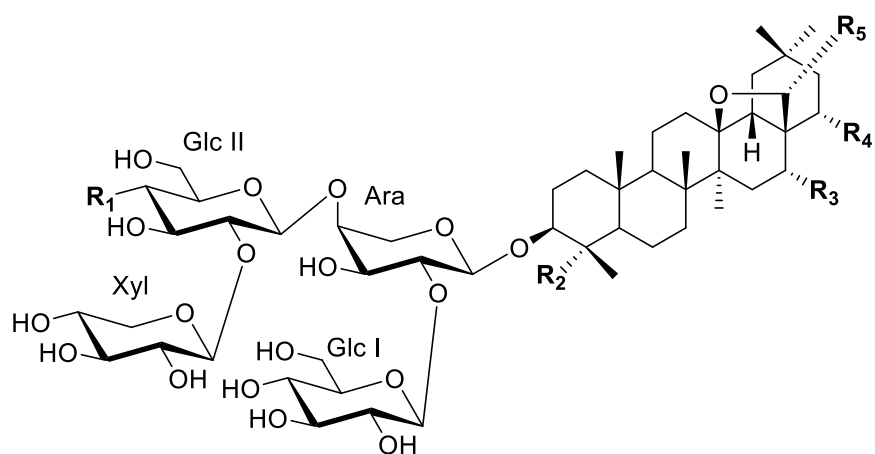


Fig. S102. HR-MS spectrum of compound 13



	R ₁	R ₂	R ₃	R ₄	R ₅
14	Glc	CH ₃	OH	H	H
15	H	CH ₃	OH	H	H
16	H	CH ₃	OH	OH	OH
17	Glc	CH ₃	OH	OH	OH
18	Glc	CH ₃	OH	OAc	H
19	Glc	CH ₂ OH	OH	H	H
20	H	CH ₂ OH	OH	H	H
21	Glc	CH ₂ OH	OH	OAc	H
22	H	CH ₂ OH	=O	H	H

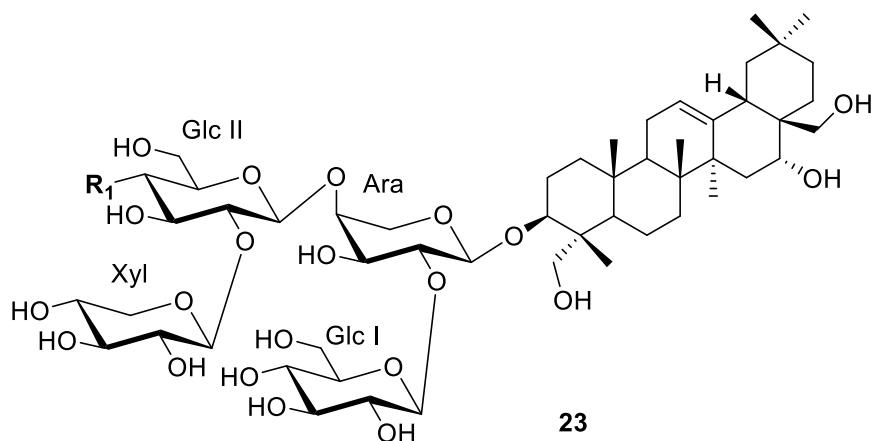


Fig S103. The structures of compounds **14–23** isolated from *Anagallis monelli ssp linifolia*