Synthesis of vicinal dideoxy-difluorinated galactoses

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Supporting information

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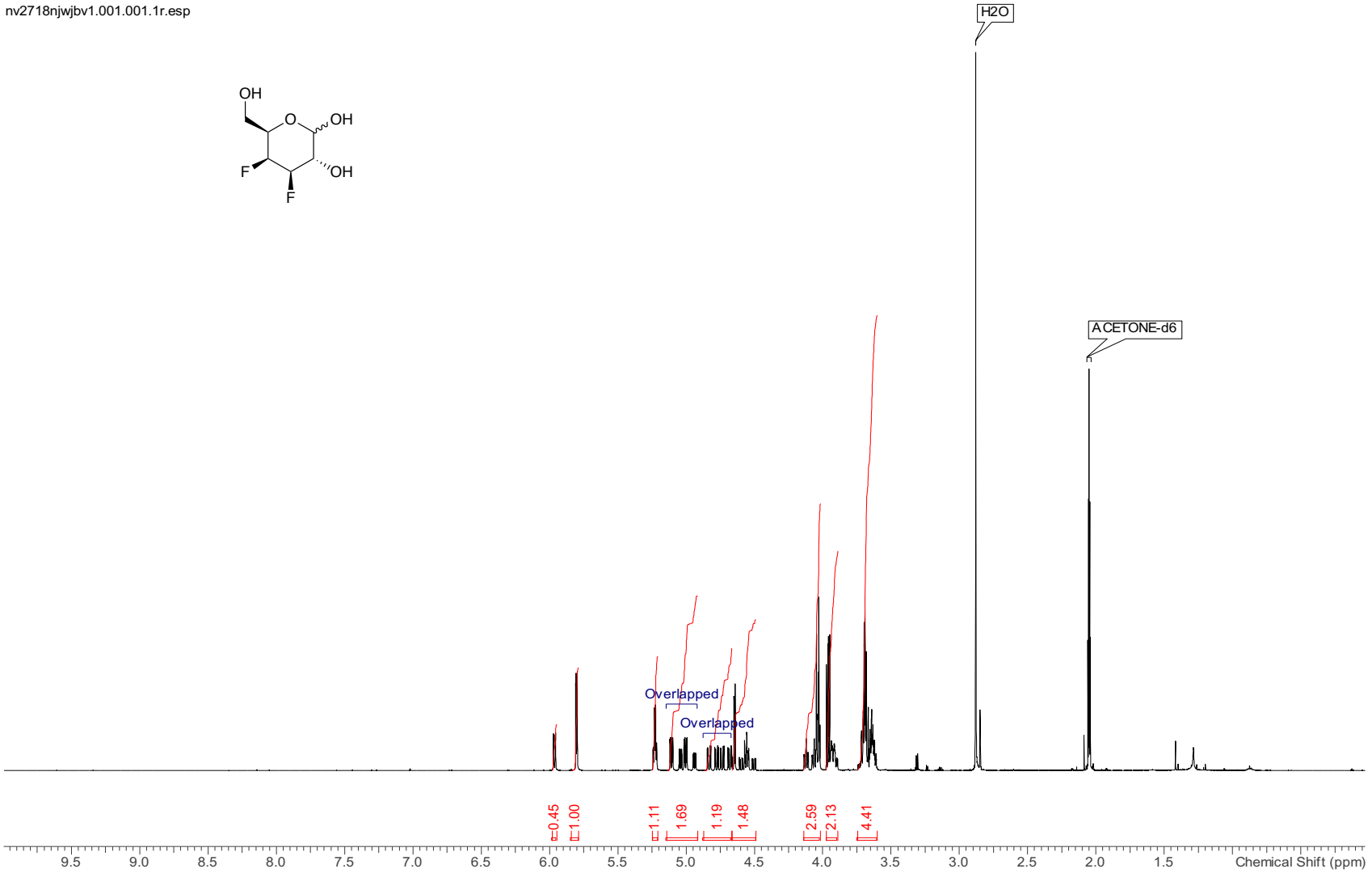
1.1.1 ^{1}H NMR (500 MHz, acetone-d_6) (compound 15a)



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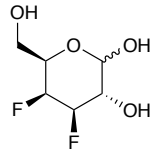
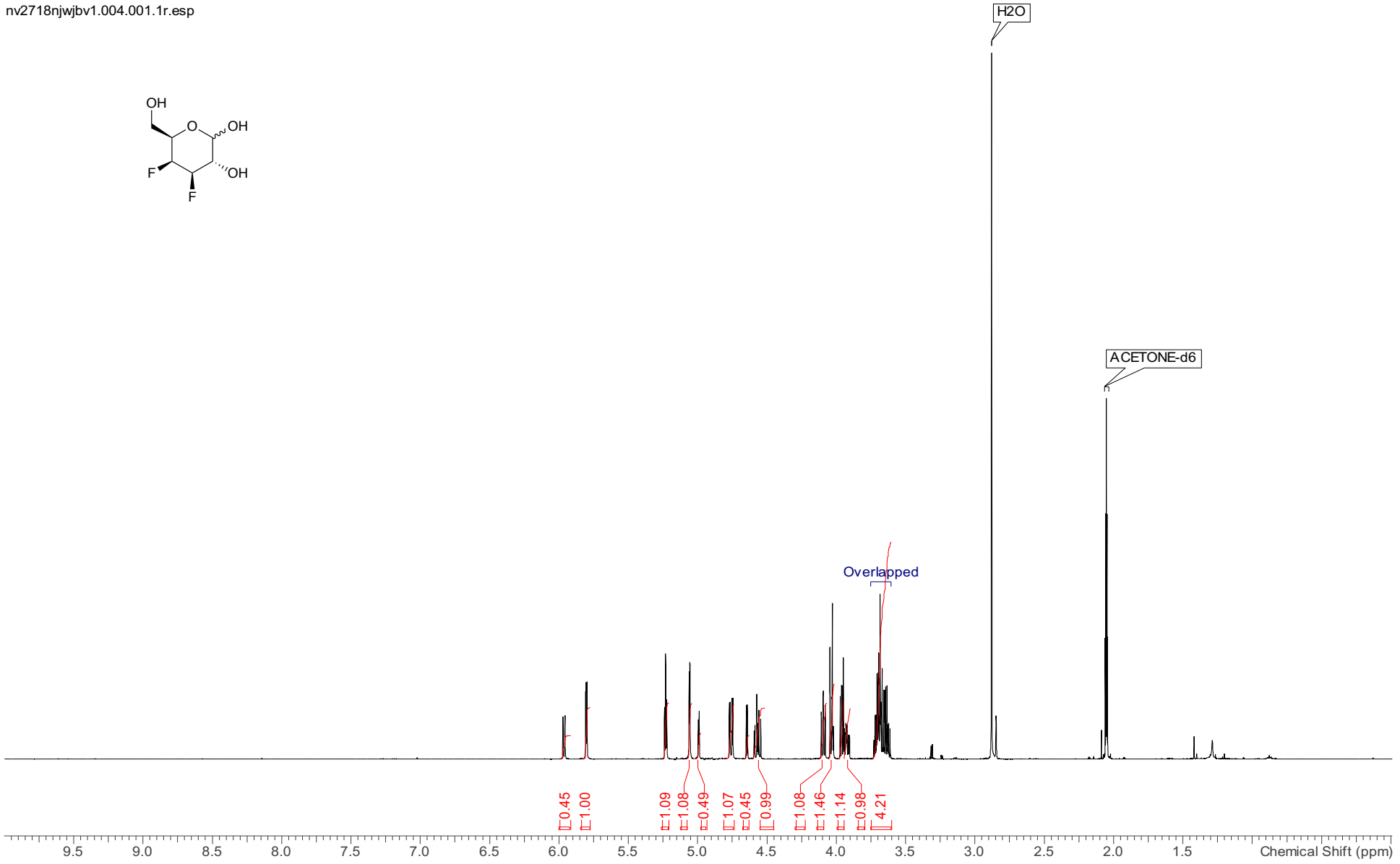


1.1.2 $^{1}H\{^{19}F\}$ NMR (500 MHz, acetone-d_6) (compound 15a)



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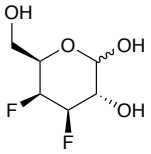
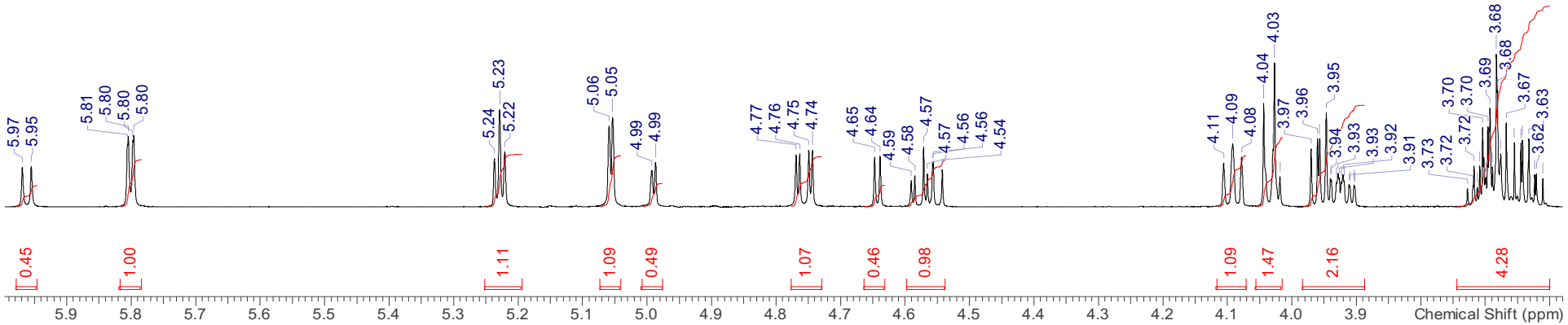
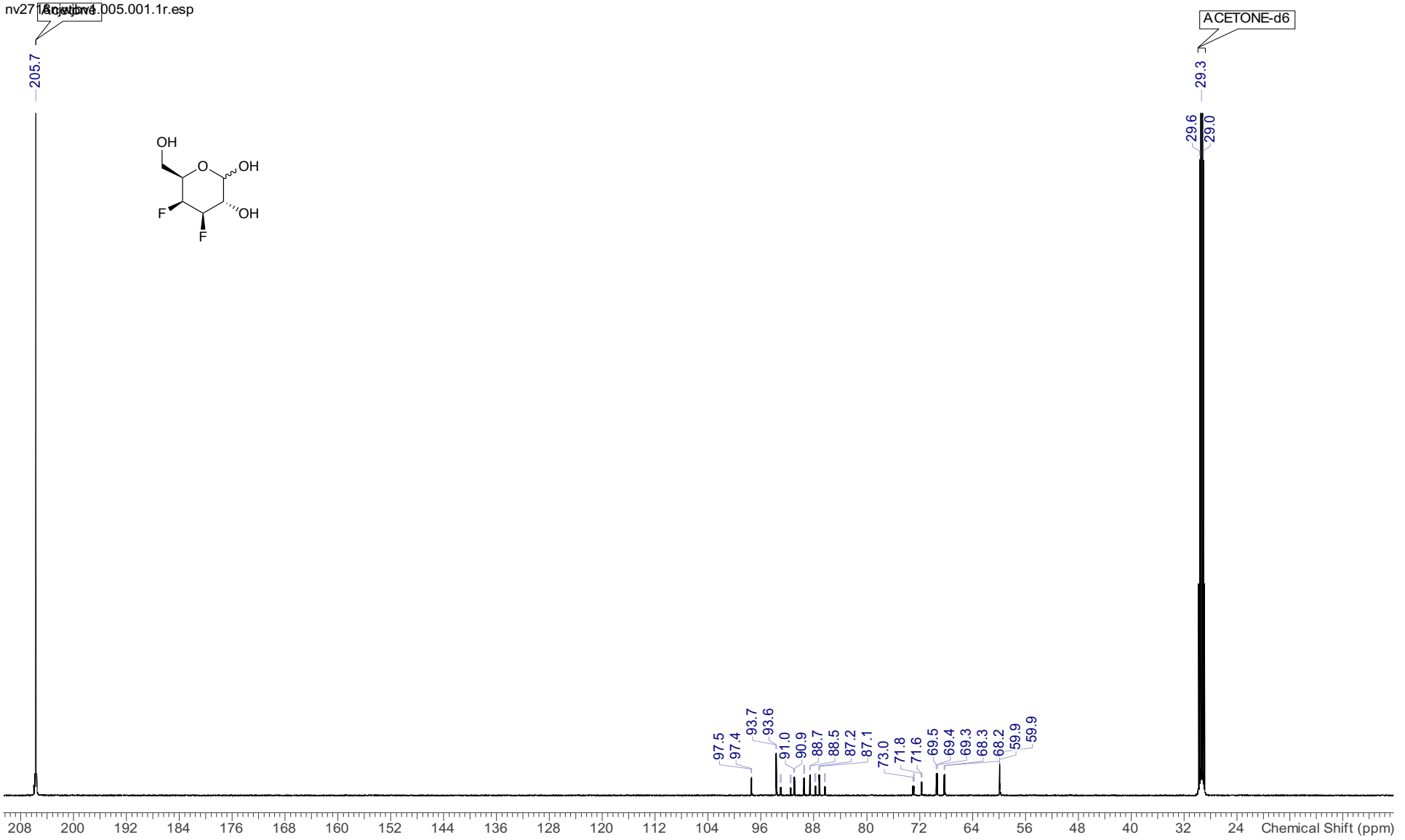
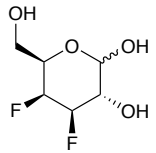




1.1.3 ^{13}C NMR (126 MHz, acetone-d_6) (compound 15a)

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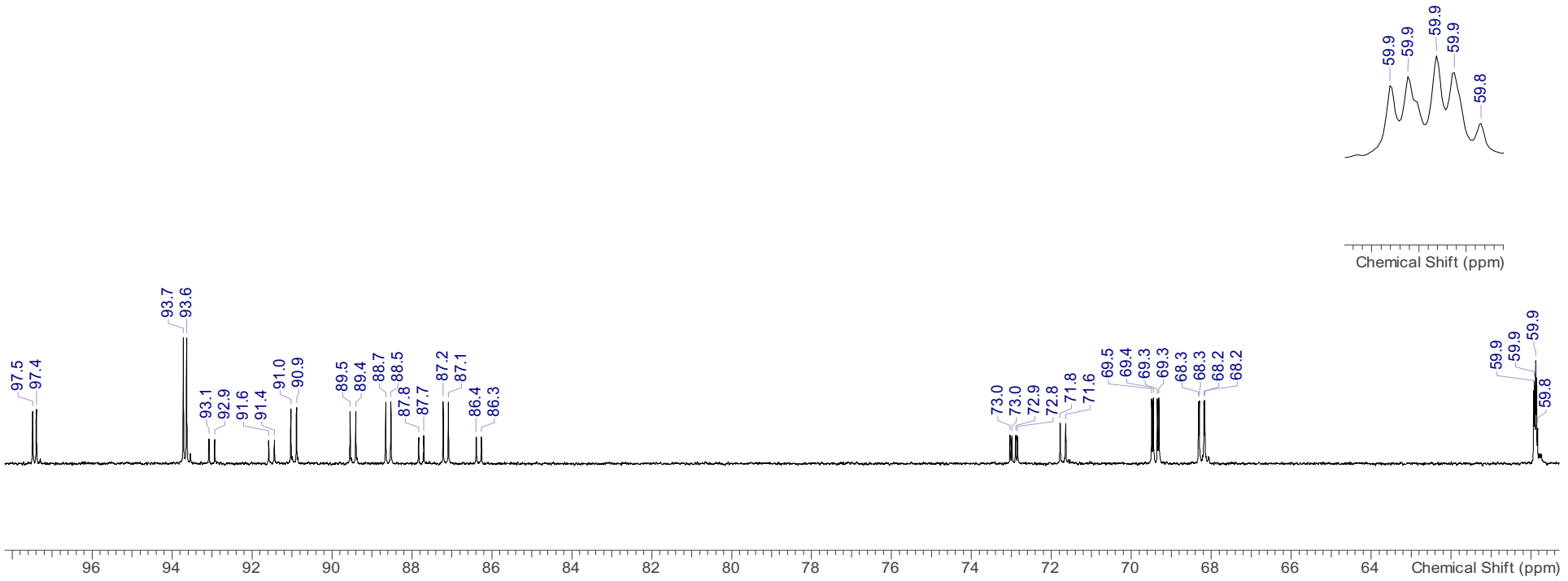
OH
F
OH
F


59.9
59.9
59.9
59.9
59.8
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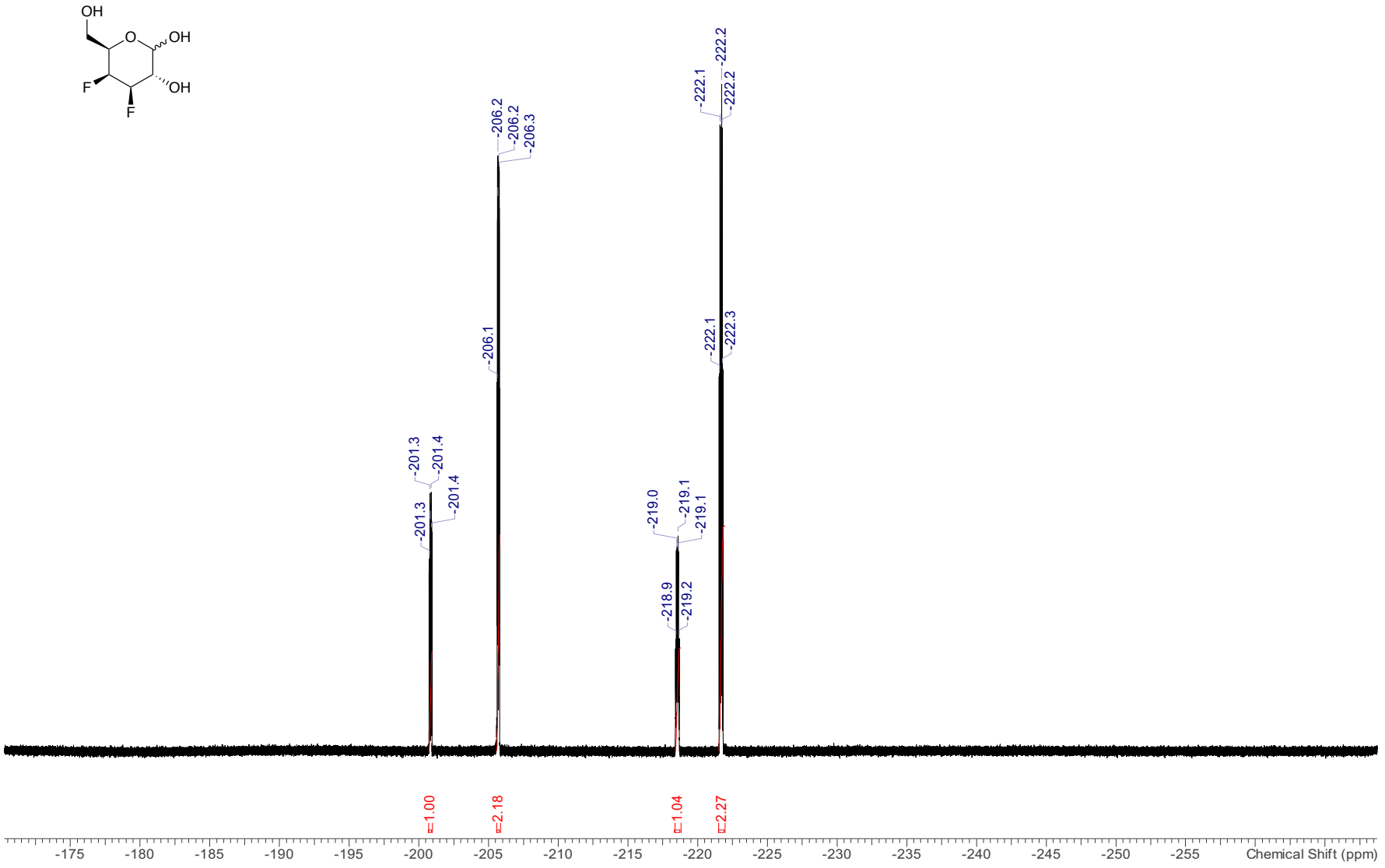
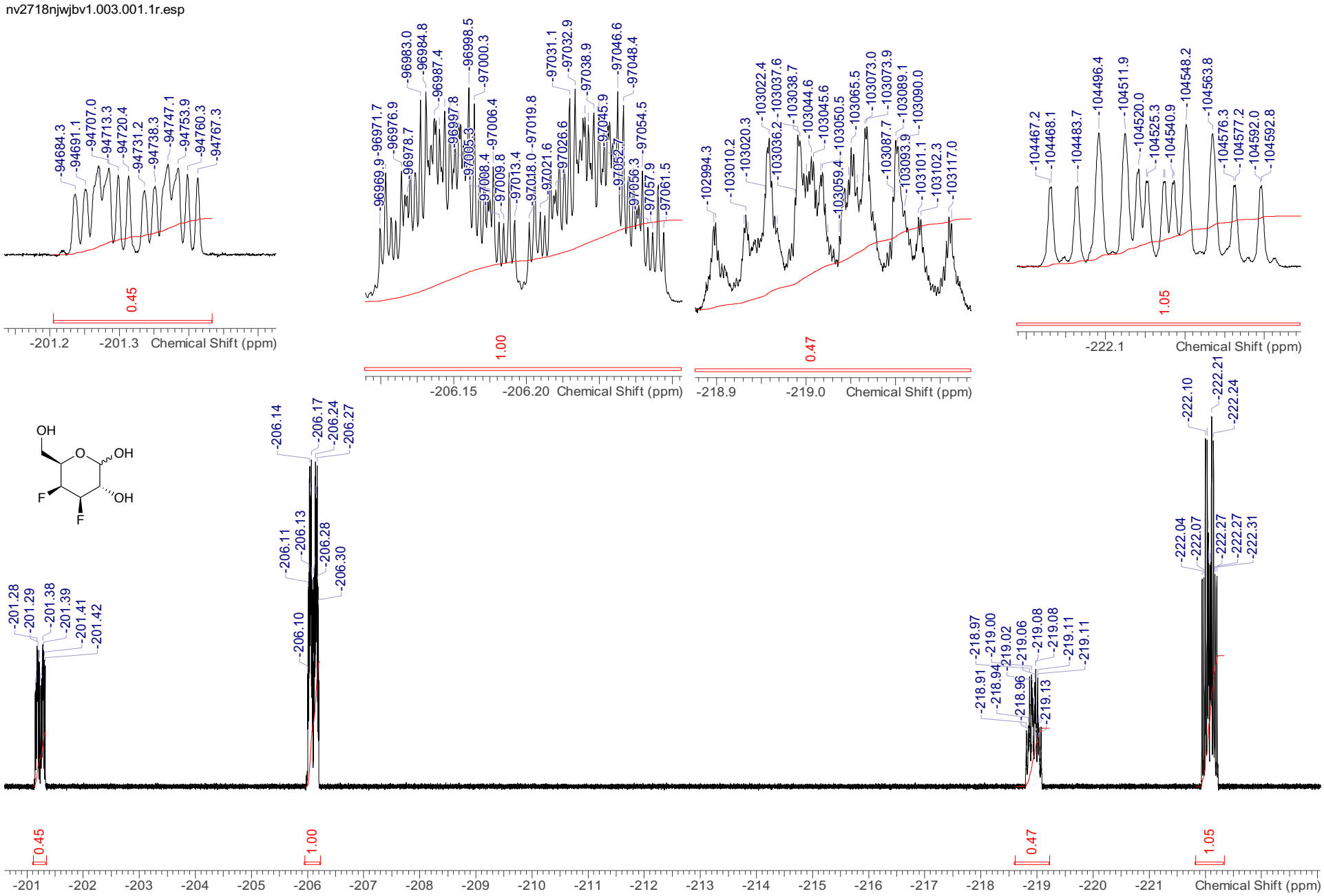
97.4
93.7
93.6
93.1
92.9
91.6
91.4
91.0
90.9
89.5
89.4
88.7
88.5
87.8
87.7
87.2
87.1
86.4
86.3
73.0
73.0
72.9
72.8
71.8
71.6
69.5
69.4
69.3
69.3
68.3
68.3
68.2
68.2
59.9
59.9
59.9
59.8
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
Chemical Shift (ppm)

1.1.4 ^{19}F NMR (471 MHz, acetone-d_6) (compound 15a)

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-94713.3
-94720.4
-94731.2
-94738.3
-94747.1
-94753.9
-94760.3
-94767.3
0.45
-201.2
-201.3
Chemical Shift (ppm)
-96969.9
-96971.7
-96976.9
-96978.7
-96983.0
-96984.8
-96987.4
-96997.8
-96998.5
-97000.3
-97005.3
-97006.4
-97008.4
-97009.8
-97013.4
-97018.0
-97019.8
-97021.6
-97026.6
-97031.1
-97032.9
-97038.9
-97045.9
-97046.6
-97048.4
-97052.7
-97054.5
-97056.3
-97057.9
-97061.5
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-206.20
Chemical Shift (ppm)
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-103010.2
-103020.3
-103022.4
-103036.2
-103037.6
-103038.7
-103044.6
-103045.6
-103050.5
-103059.4
-103065.5
-103073.0
-103073.9
-103087.7
-103089.1
-103090.0
-103093.9
-103101.1
-103102.3
-103117.0
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-218.9
-219.0
Chemical Shift (ppm)
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-104468.1
-104483.7
-104496.4
-104511.9
-104520.0
-104525.3
-104540.9
-104548.2
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-104576.3
-104577.2
-104592.0
-104592.8
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-222.1
Chemical Shift (ppm)
OH
O
OH
F
OH
F
-201.28
-201.29
-201.38
-201.39
-201.41
-201.42
-206.10
-206.11
-206.13
-206.14
-206.17
-206.24
-206.27
-206.28
-206.30
-218.91
-218.94
-218.96
-218.97
-219.00
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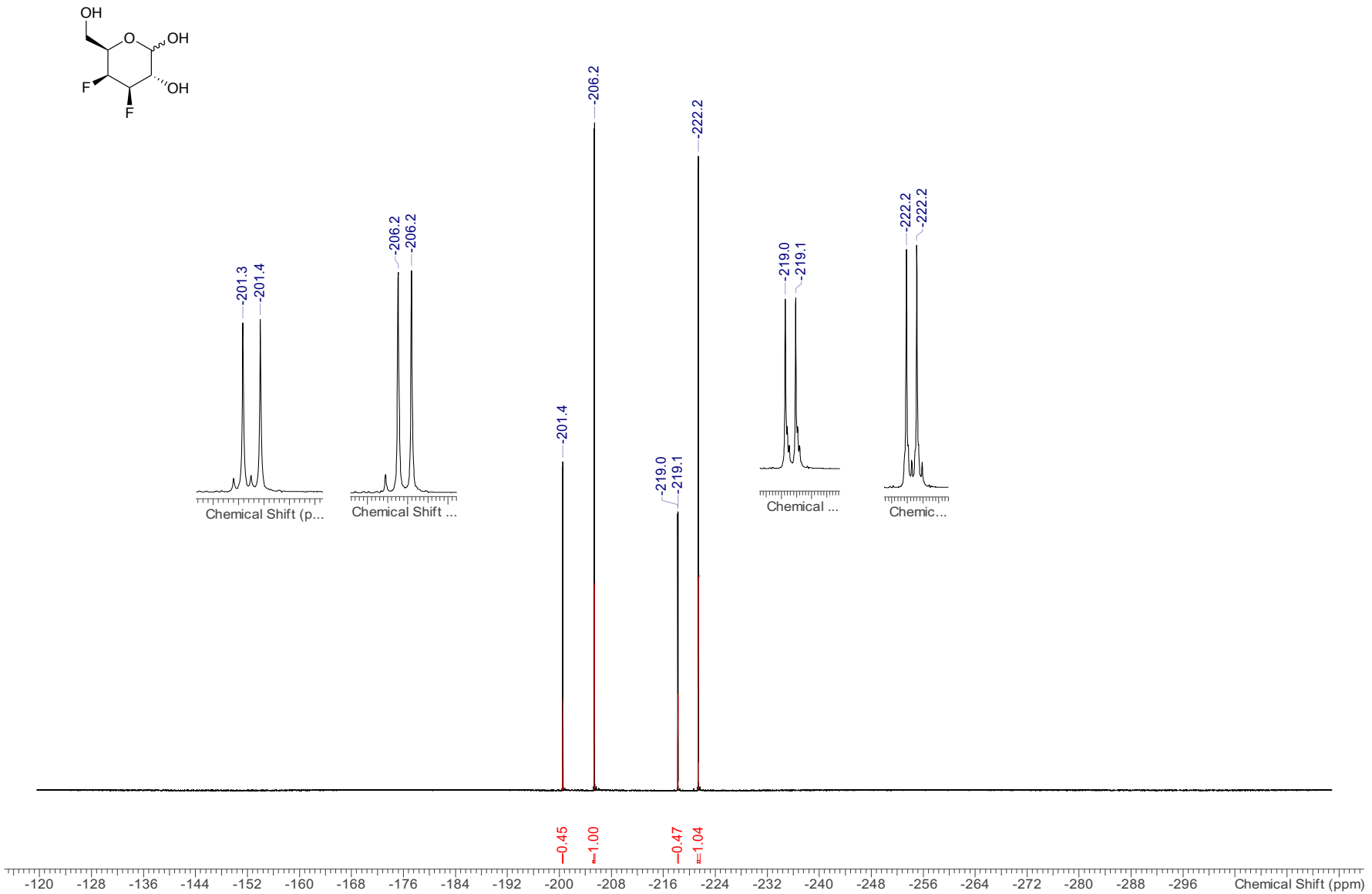
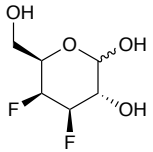
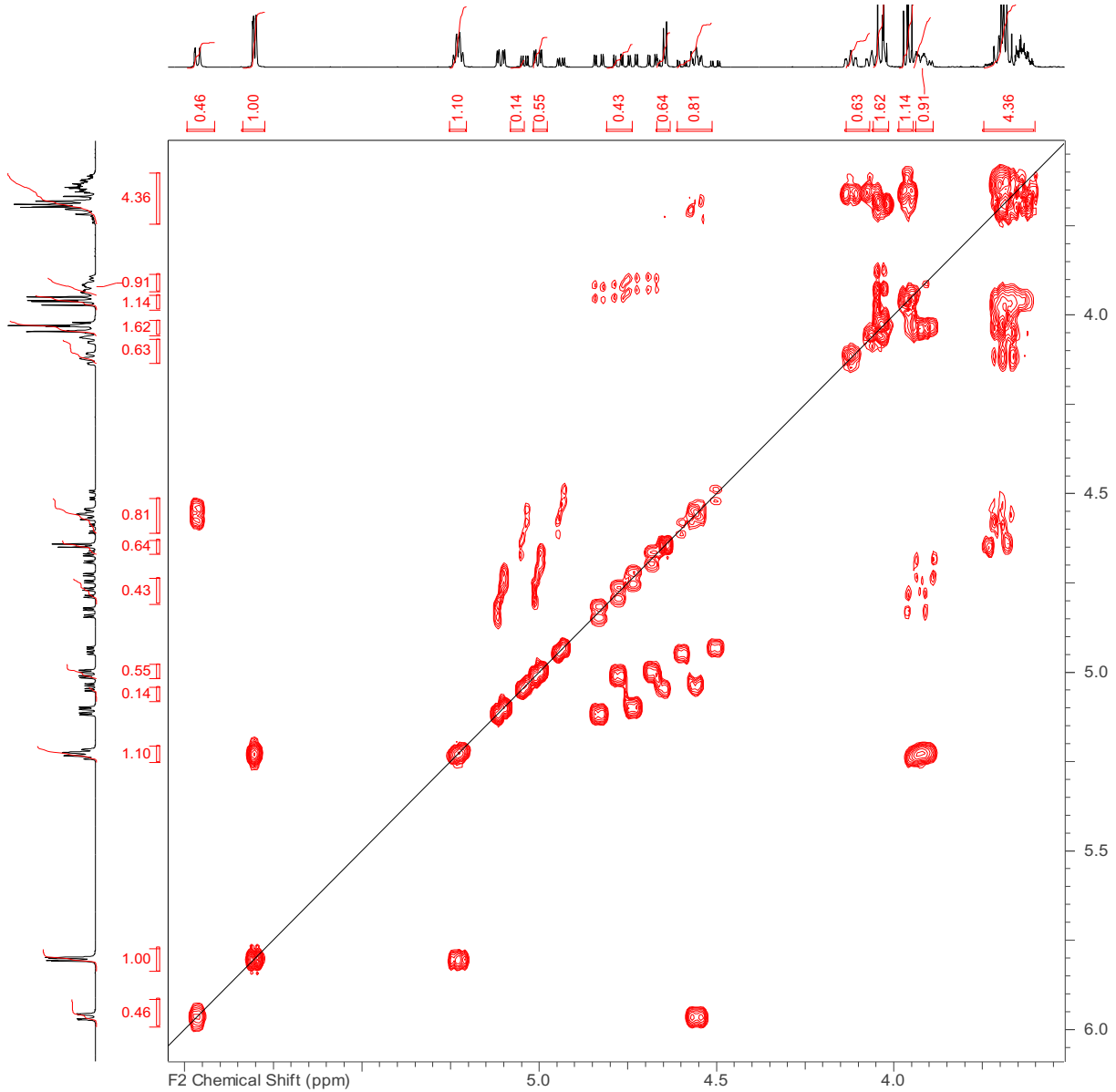
-222.04
-222.07
-222.10
-222.21
-222.24
-222.27
-222.27
-222.31
0.45
1.00
0.47
1.05
-201
-202
-203
-204
-205
-206
-207
-208
-209
-210
-211
-212
-213
-214
-215
-216
-217
-218
-219
-220
-221
Chemical Shift (ppm)

1.1.5 $^{19}F\{^{1}H\}$ NMR (471 MHz, acetone-d_6) (compound 15a)

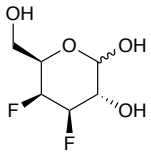


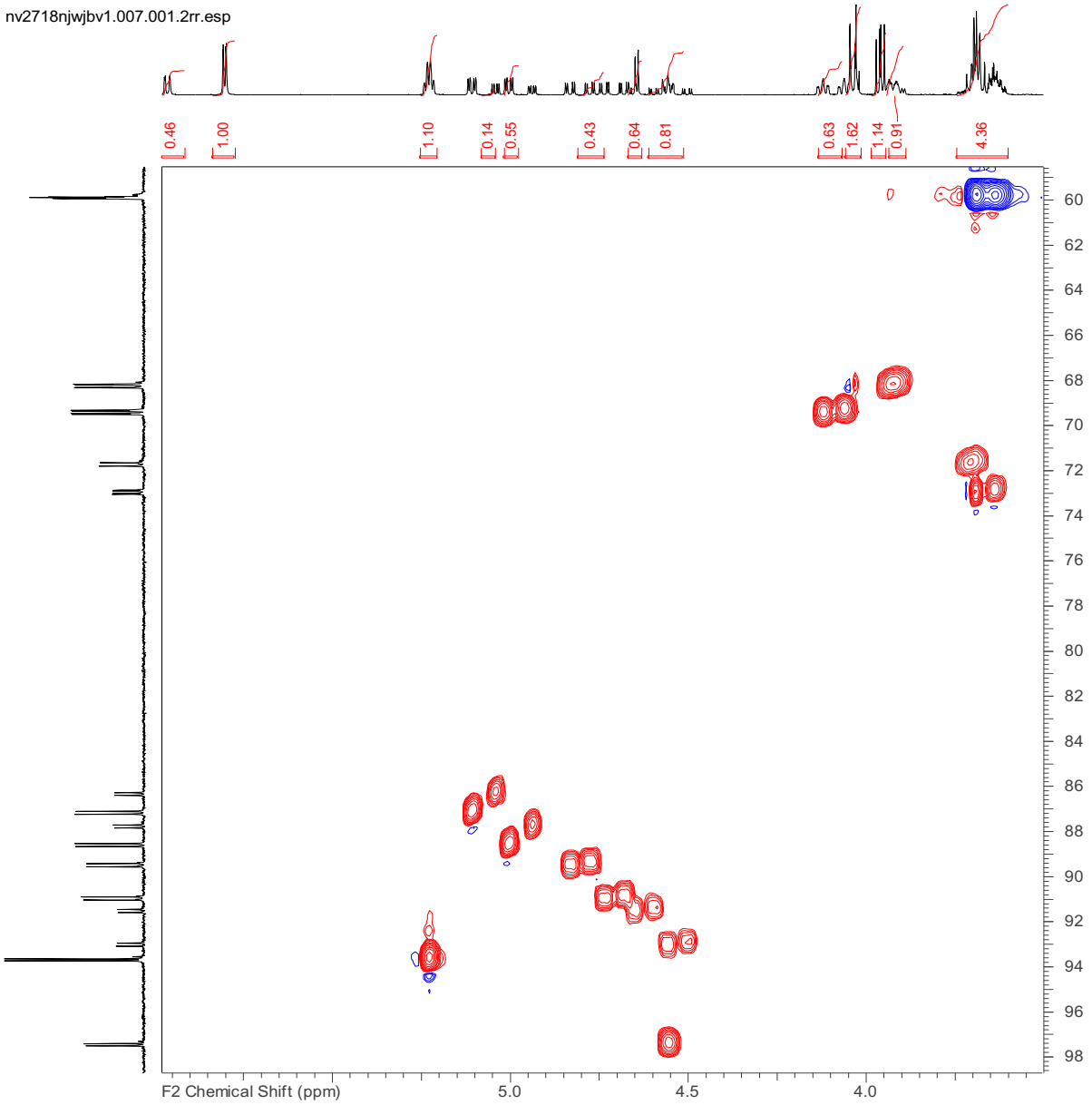
1.1.6 COSY ^{1}H-^{1}H (500 MHz, acetone-d_6) (compound 15a)



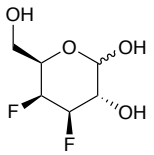


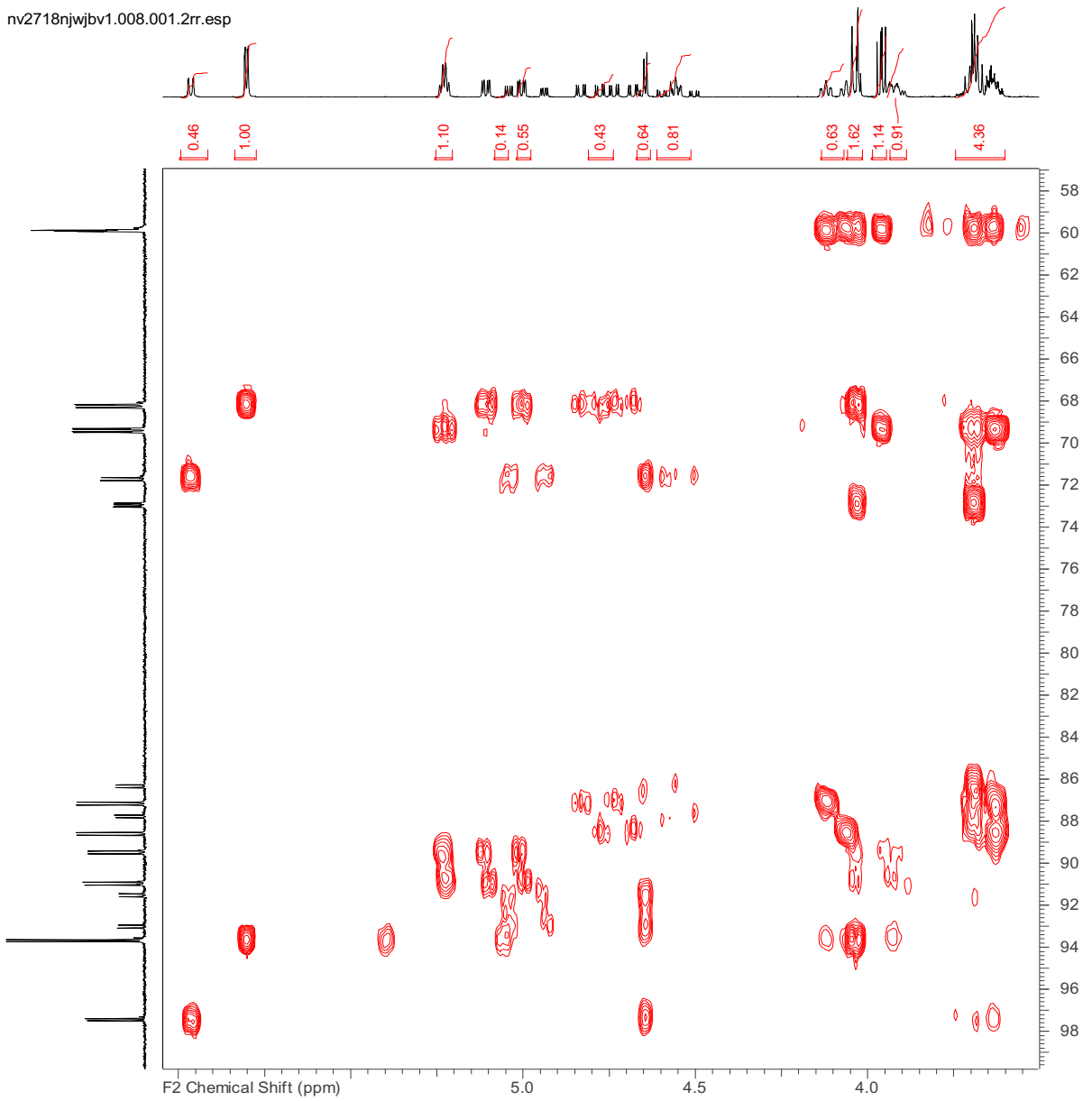
1.1.7 HSQC (500 MHz, acetone-d_6) (compound 15a)





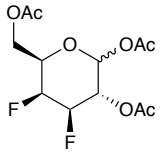
1.1.8 HMBC (500 MHz, acetone-d_6) (compound 15a)

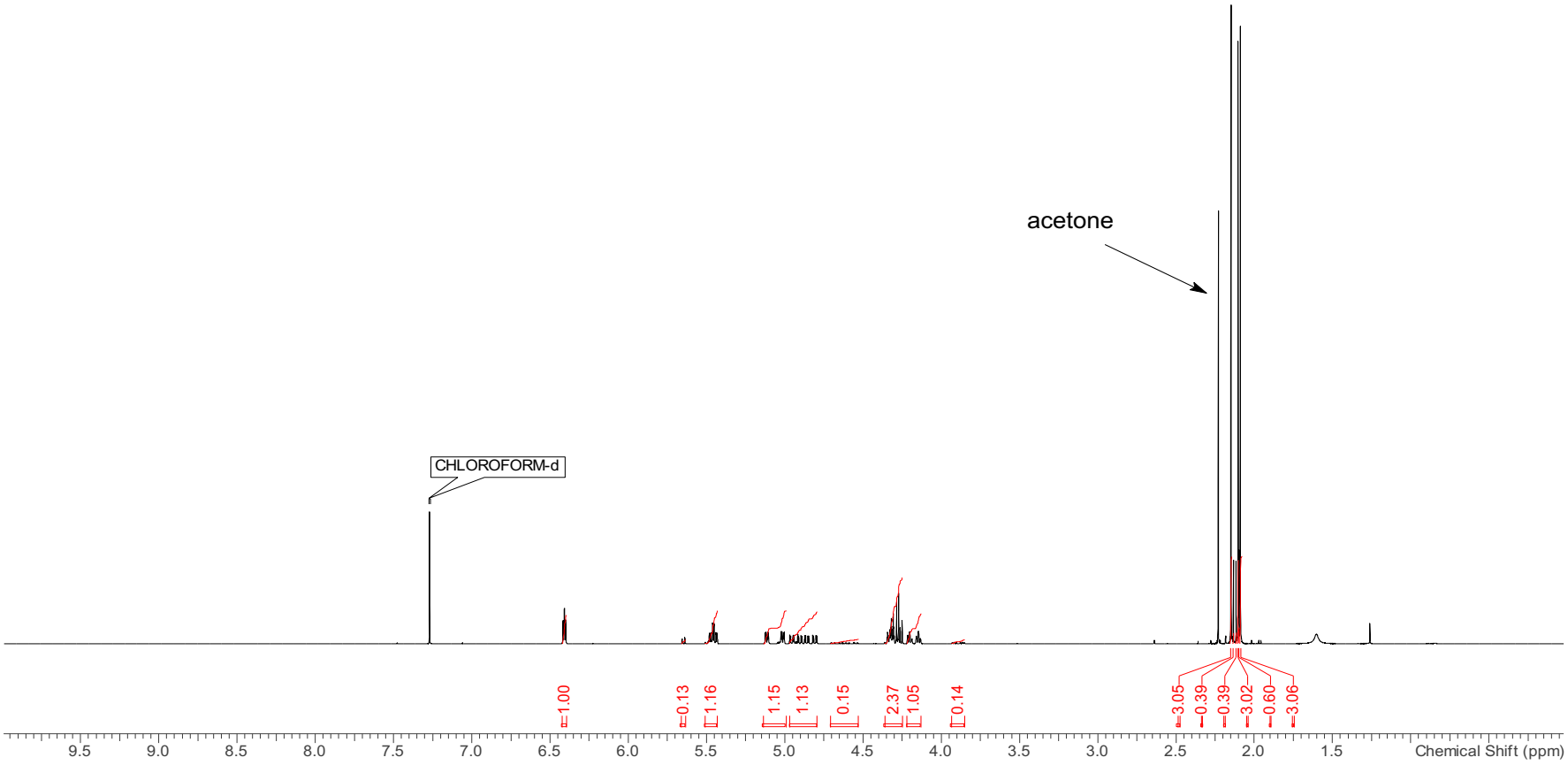


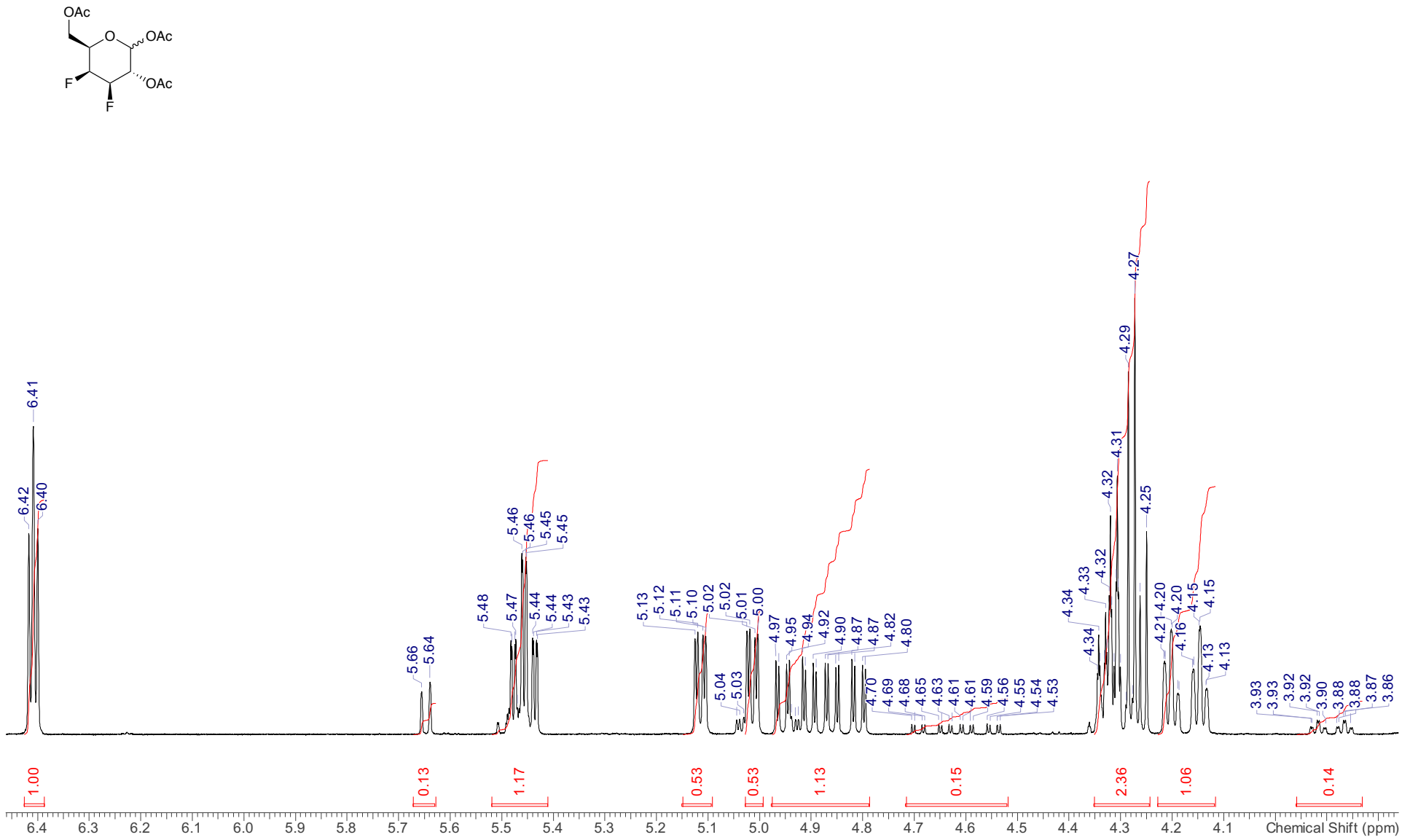


1.2 1,2,6-Tri-*O*-acetyl-3,4-dideoxy-3,4-difluoro-D-galactopyranose 15b.

1.2.1 ^{1}H NMR (500 MHz, $CDCl_3$) (compound 15b)



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OAc
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OAc
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5.46
5.45
5.45
5.44
5.44
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5.43
5.13
5.12
5.11
5.10
5.04
5.03
5.02
5.02
5.01
5.00
4.97
4.95
4.94
4.92
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4.63
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4.61
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4.55
4.54
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4.34
4.33
4.32
4.32
4.31
4.29
4.27
4.25
4.21
4.20
4.20
4.16
4.15
4.15
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3.92
3.92
3.90
3.88
3.88
3.87
3.86
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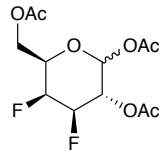
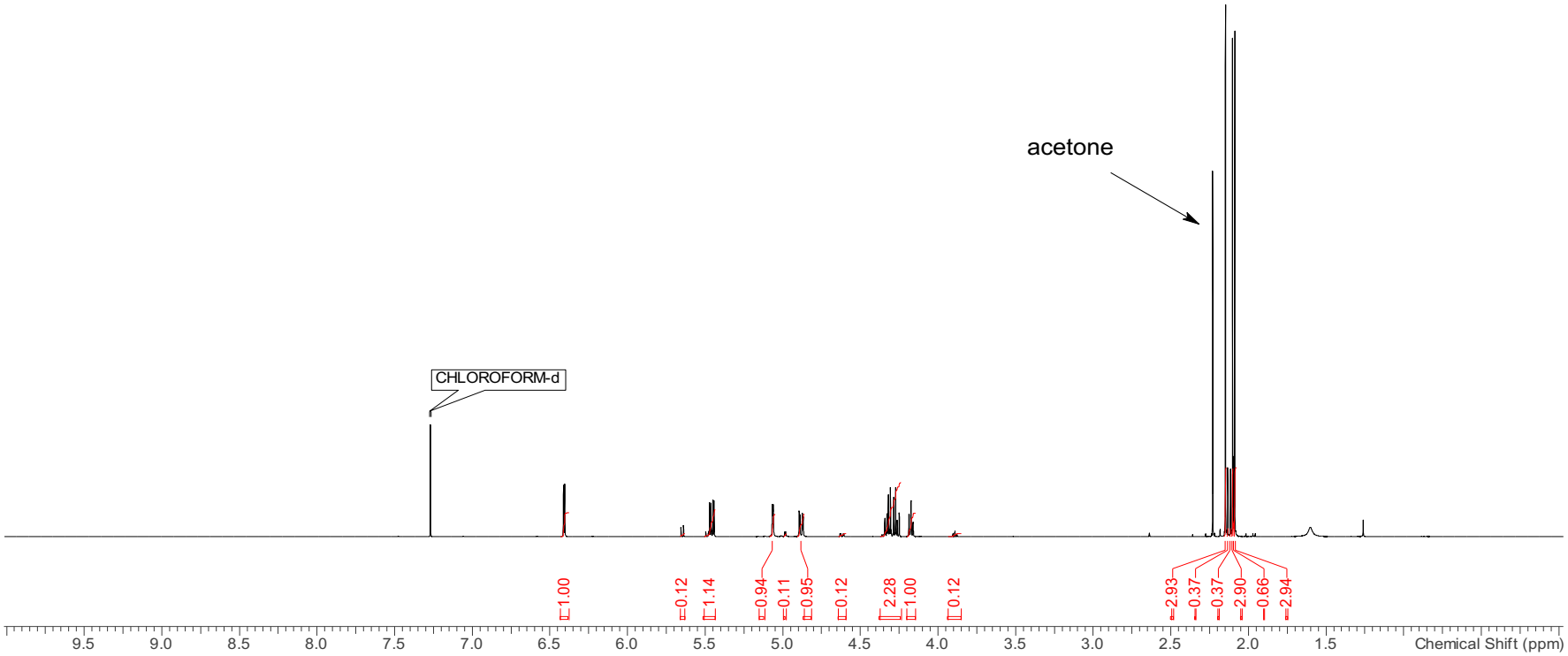
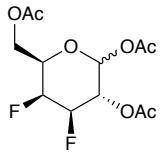
1.17
0.53
0.53
1.13
0.15
2.36
1.06
0.14
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
Chemical Shift (ppm)

1.2.2 $^{1}H\{^{19}F\}$ NMR (500 MHz, $CDCl_3$) (compound 15b)



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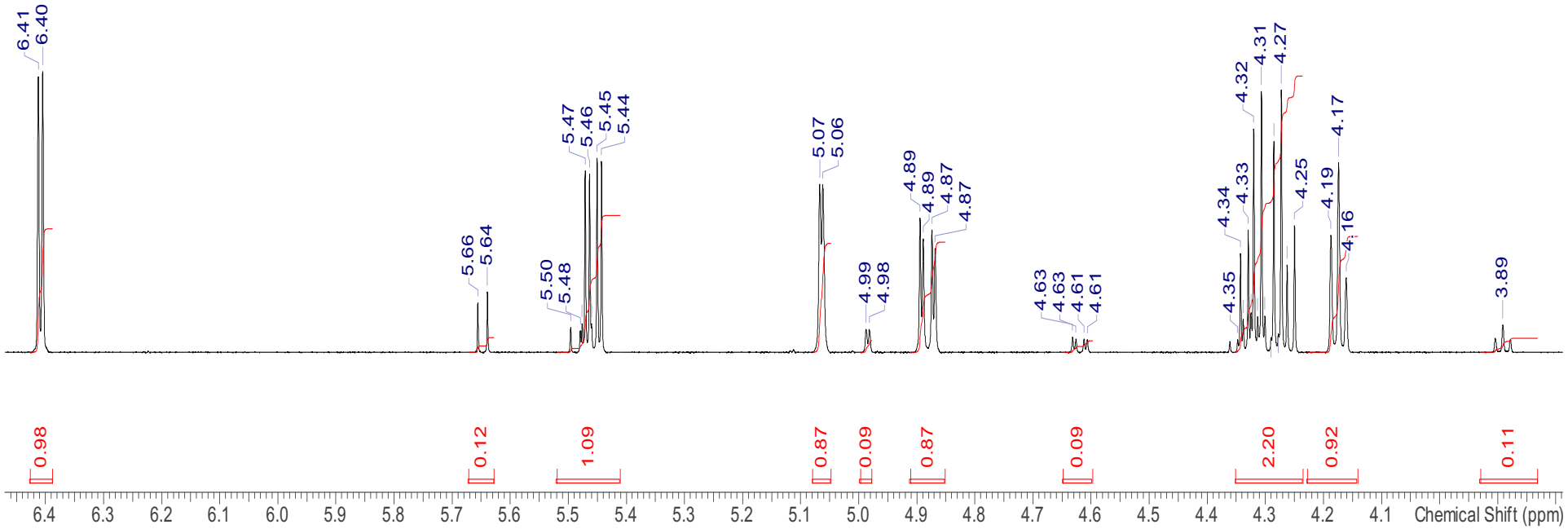
OAc
F
OAc
F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5.06
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4.98
4.89
4.89
4.87
4.87
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4.63
4.61
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4.33
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4.31
4.27
4.25
4.19
4.17
4.16
3.89
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0.12
1.09
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0.09
0.87
0.09
2.20
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0.11
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
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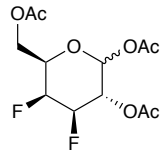
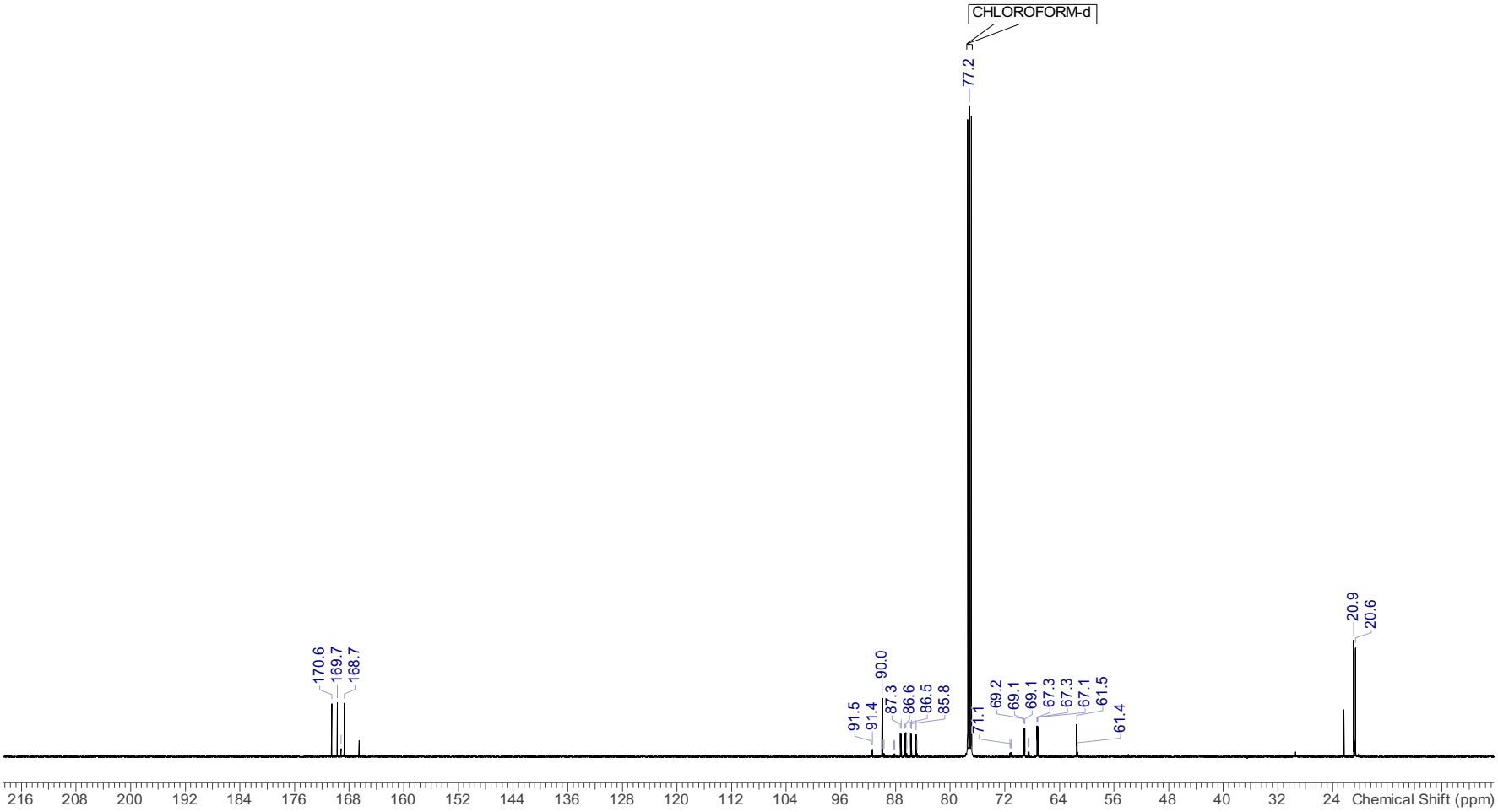
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
Chemical Shift (ppm)

1.2.3 ^{13}C NMR (126 MHz, $CDCl_3$) (compound 15b)





1.2.4 ^{19}F NMR (471 MHz, $CDCl_3$) (compound 15b)

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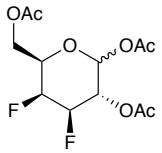

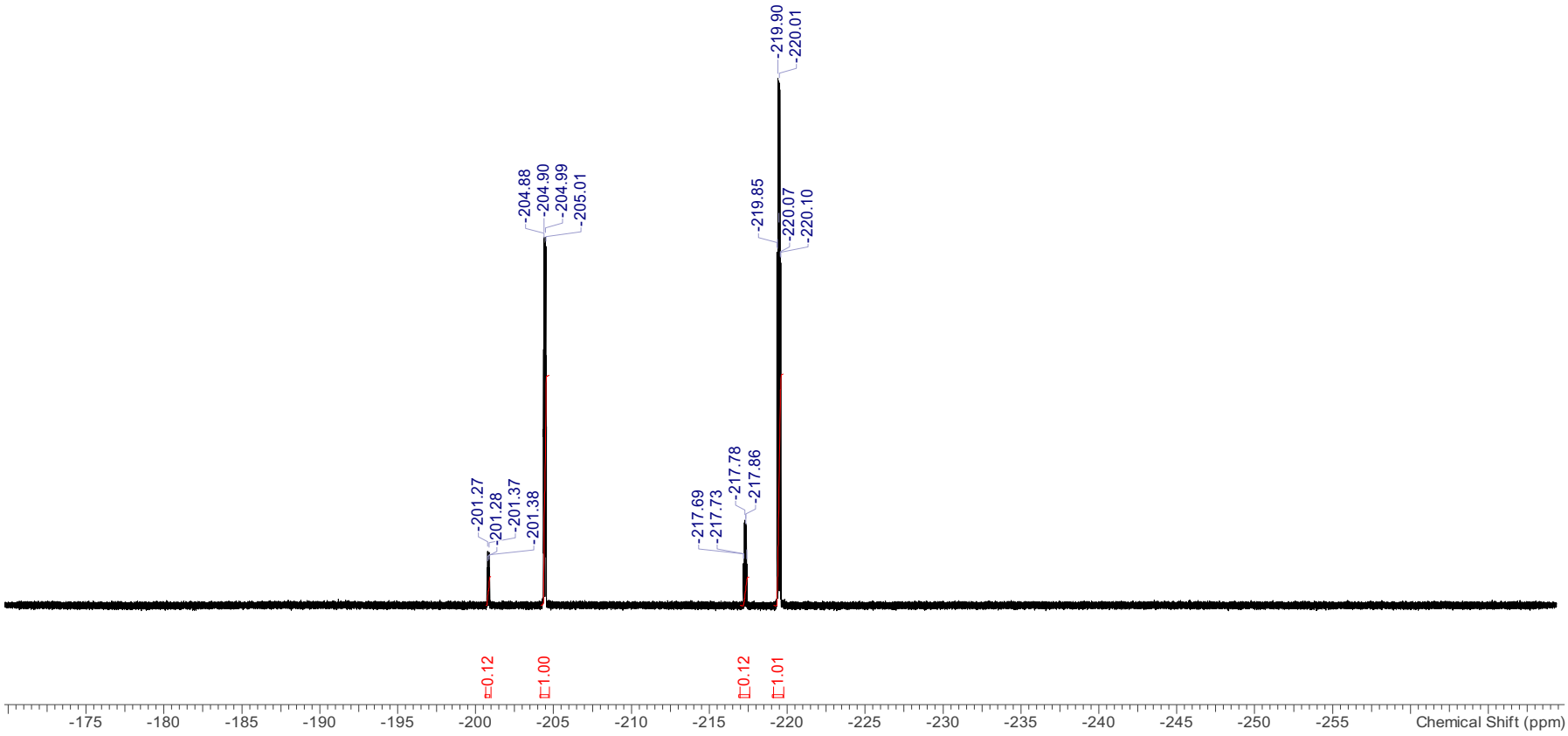

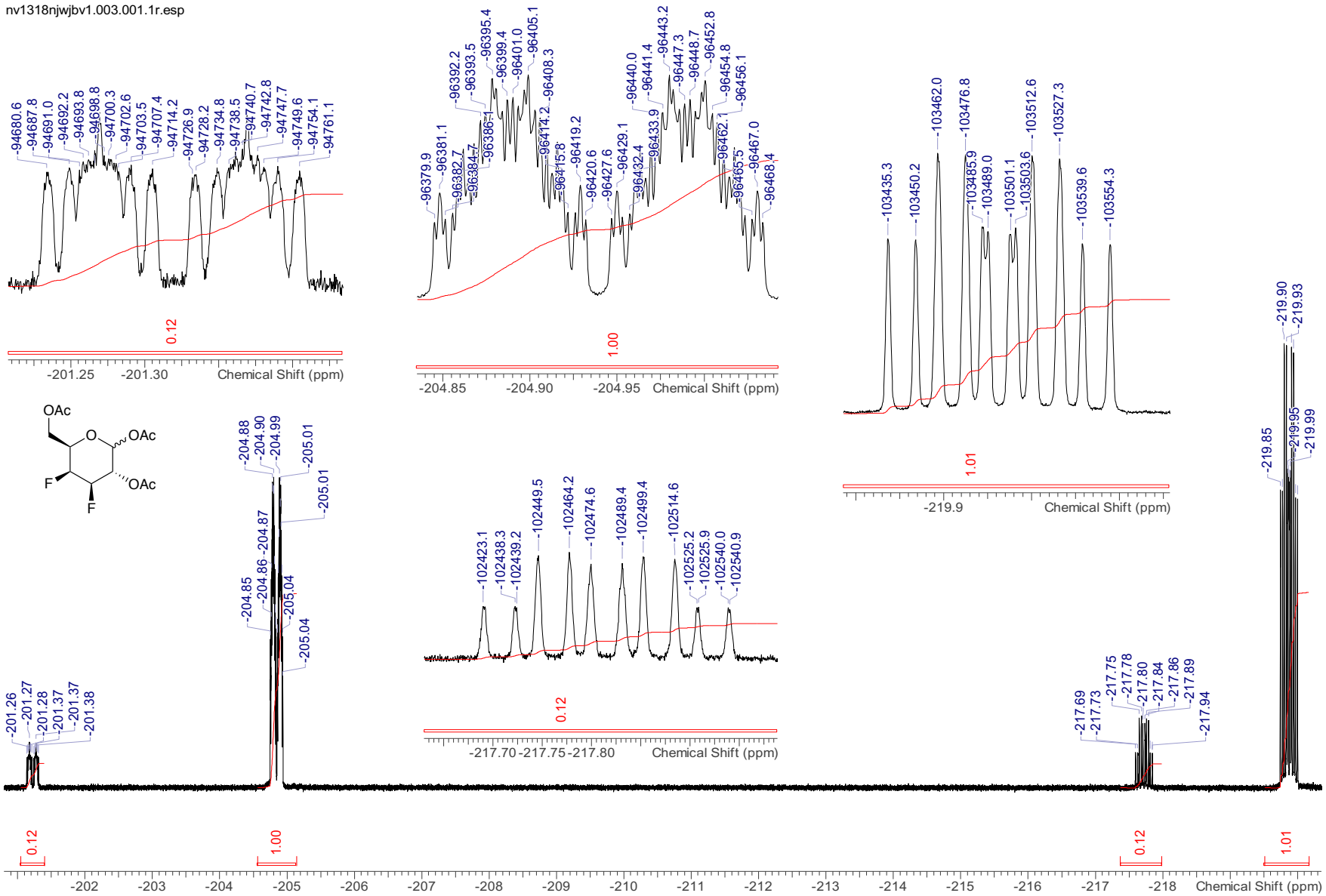
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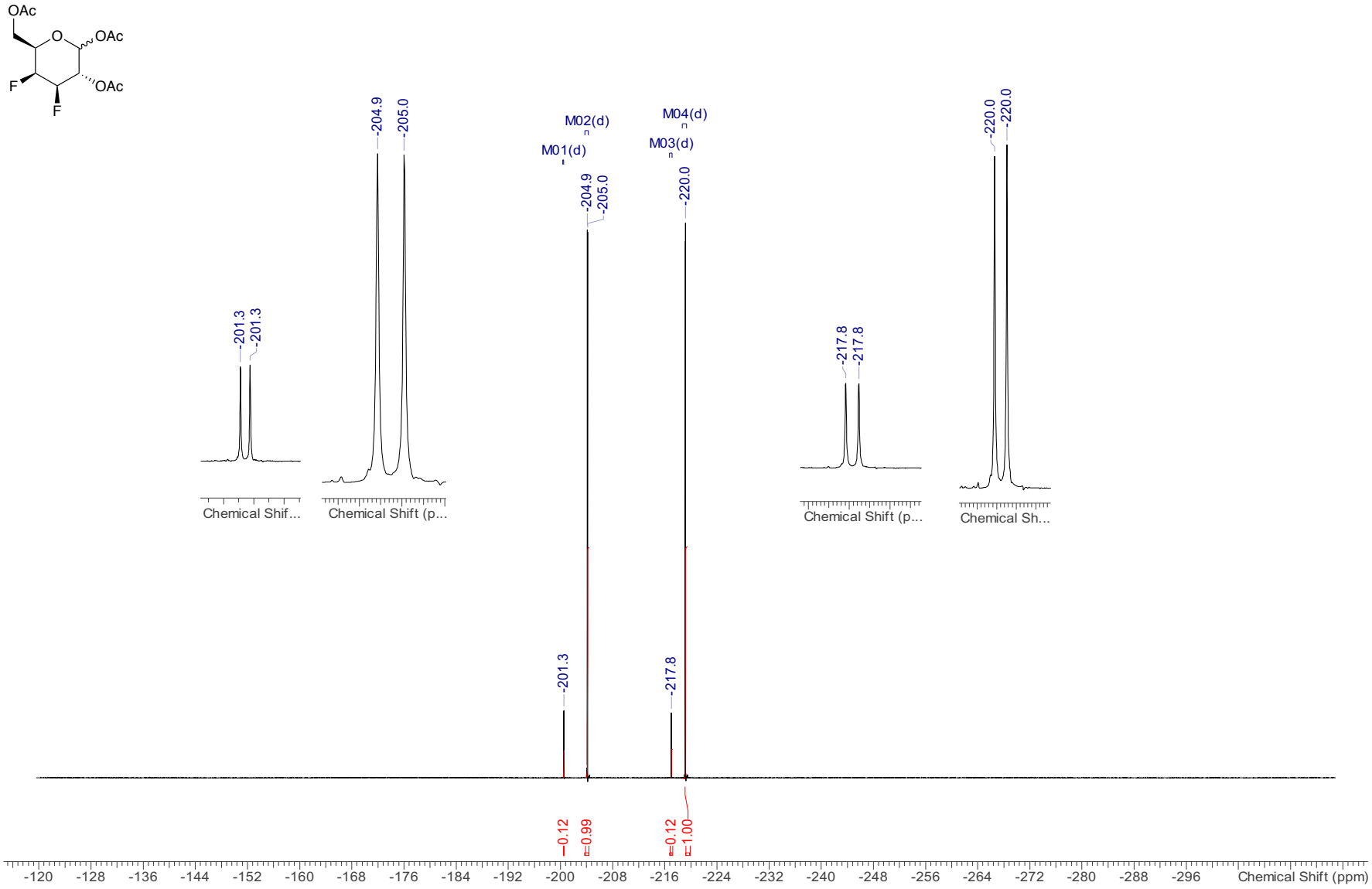
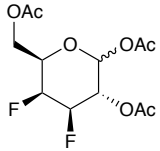
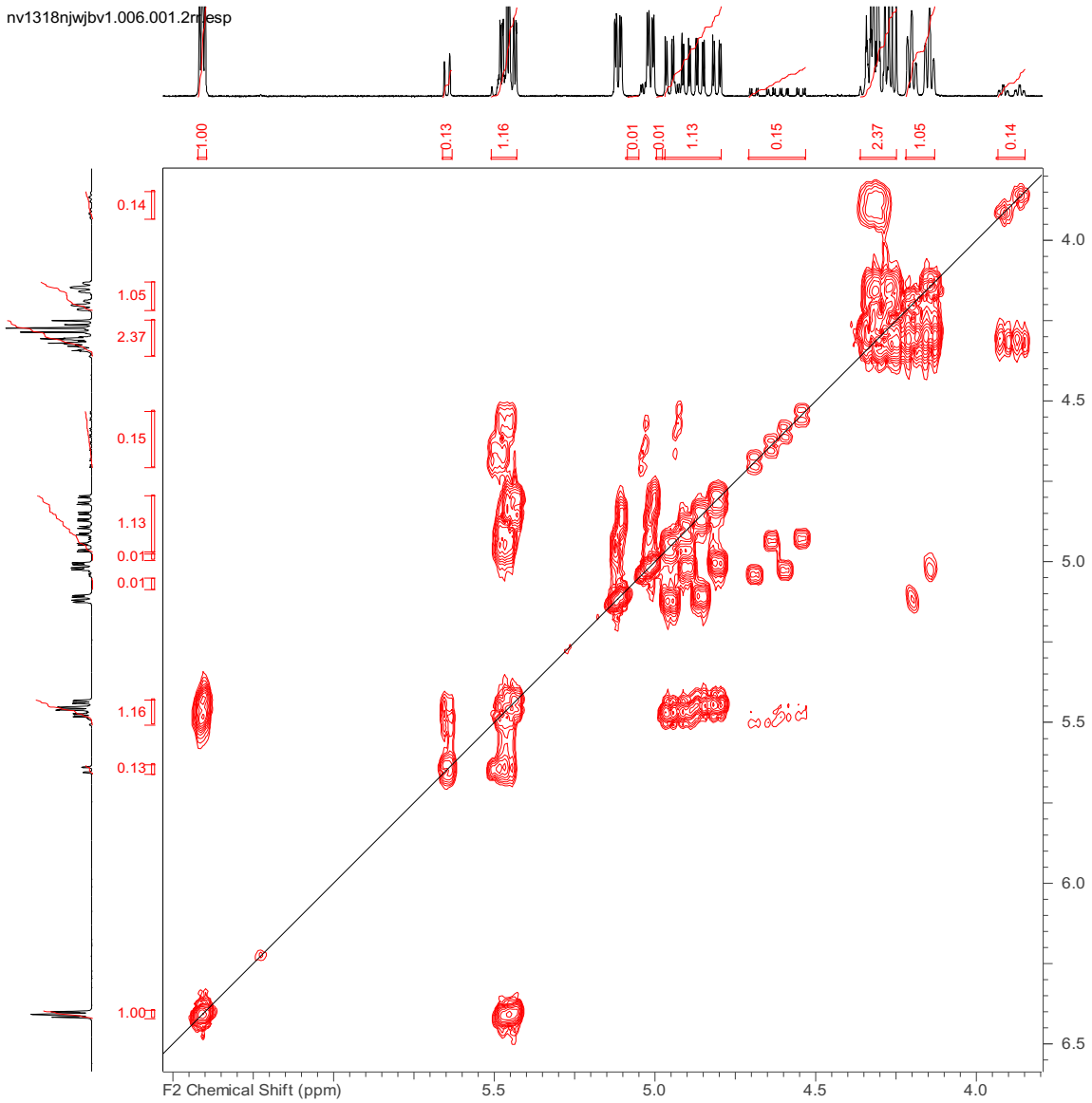
OAc
OAc
OAc
F
F
O
Chemical Shift (ppm)

1.2.5 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) (compound 15b)

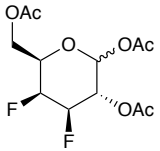


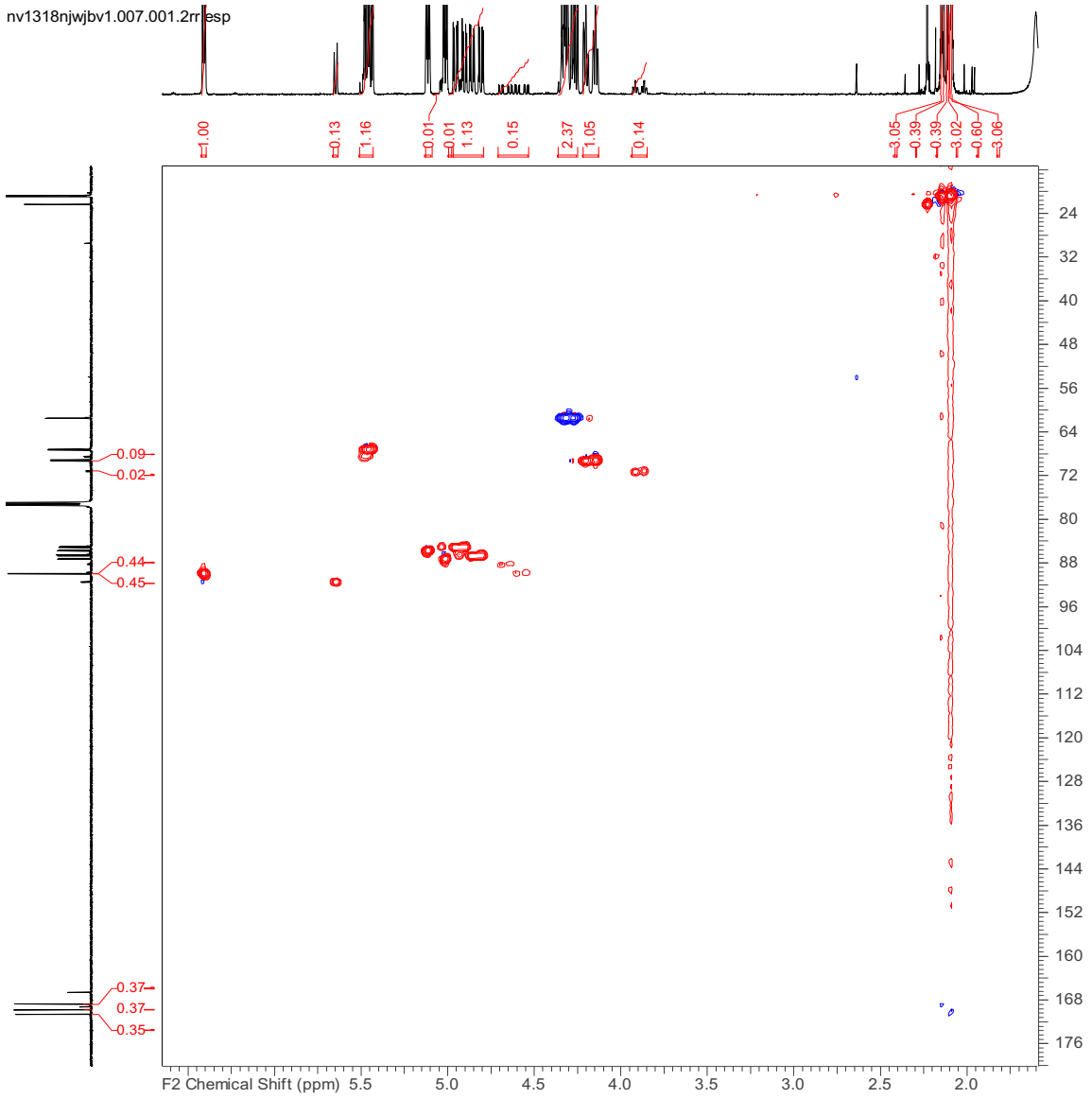
1.2.6 COSY ^{1}H-^{1}H (500 MHz, $CDCl_3$) (compound 15b)



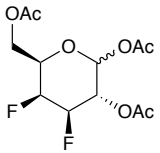


1.2.7 HSQC (500 MHz, $CDCl_3$) (compound 15b)





Expansion: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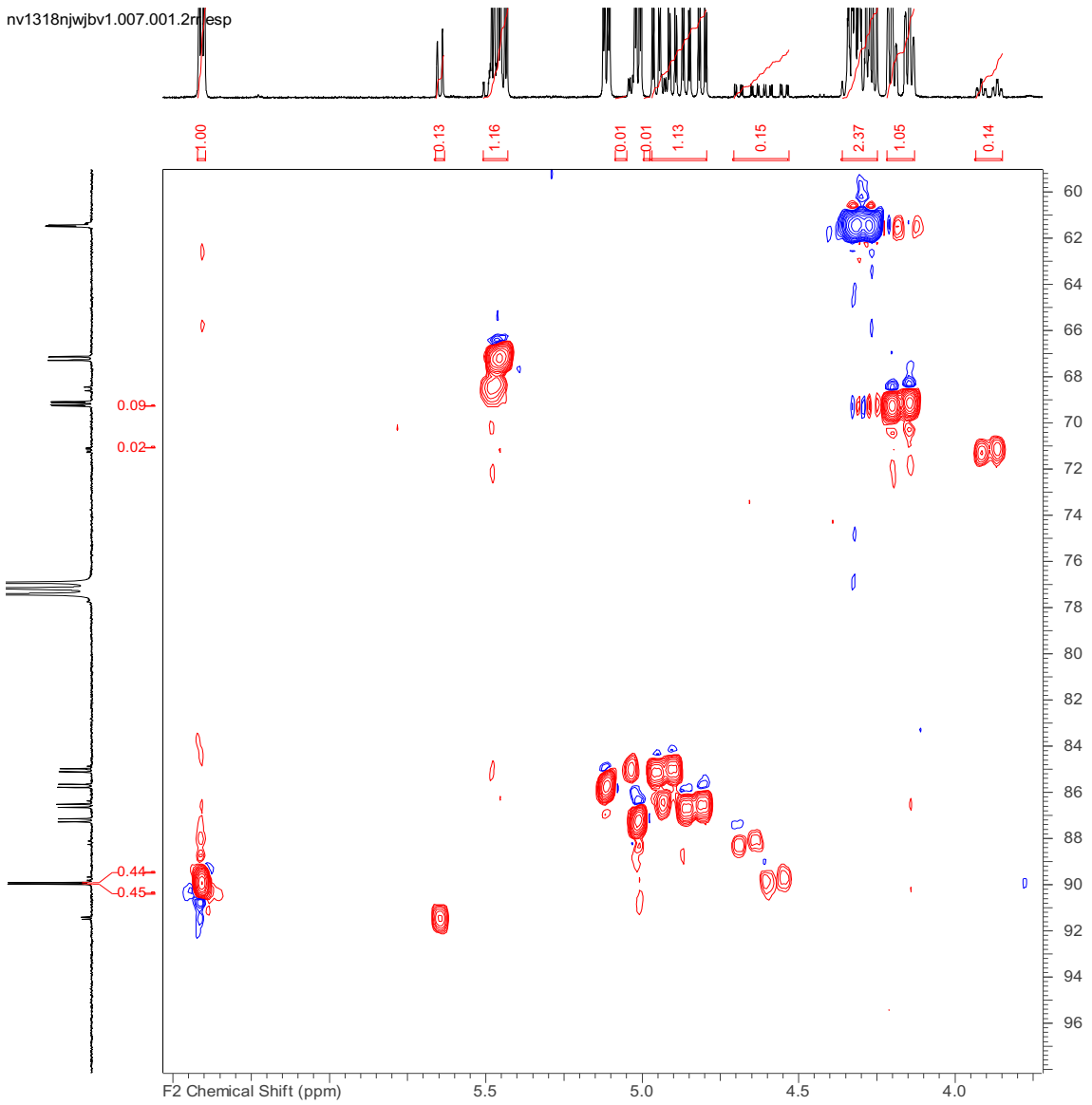
OAc
F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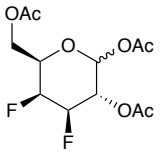
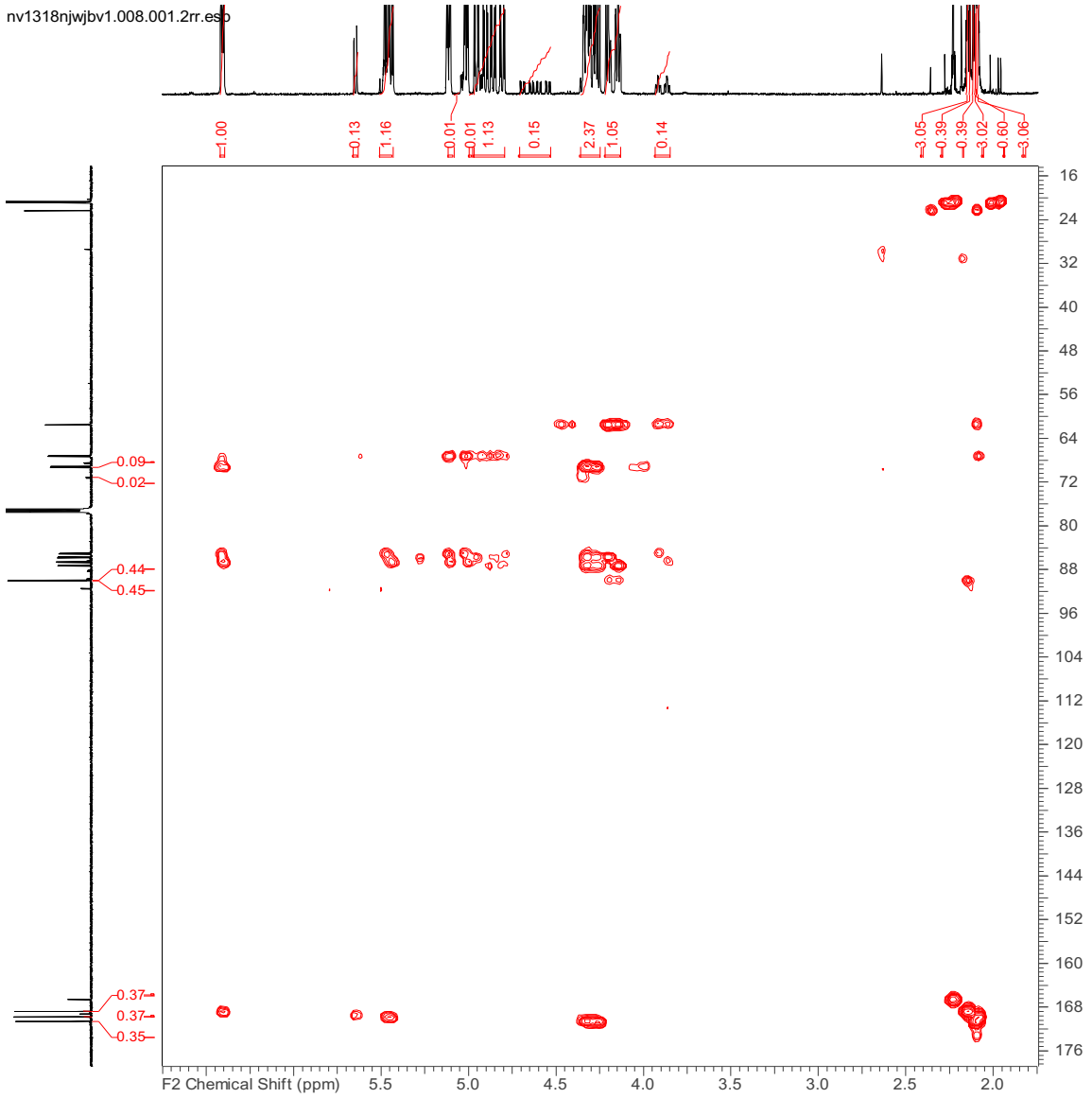
60
62
64
66
68
70
72
74
76
78
80
82
84
86
88
90
92
94
96
F2 Chemical Shift (ppm)
5.5
5.0
4.5
4.0

1.2.8 HMBC (500 MHz, $CDCl_3$) (compound 15b)

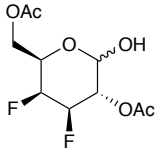




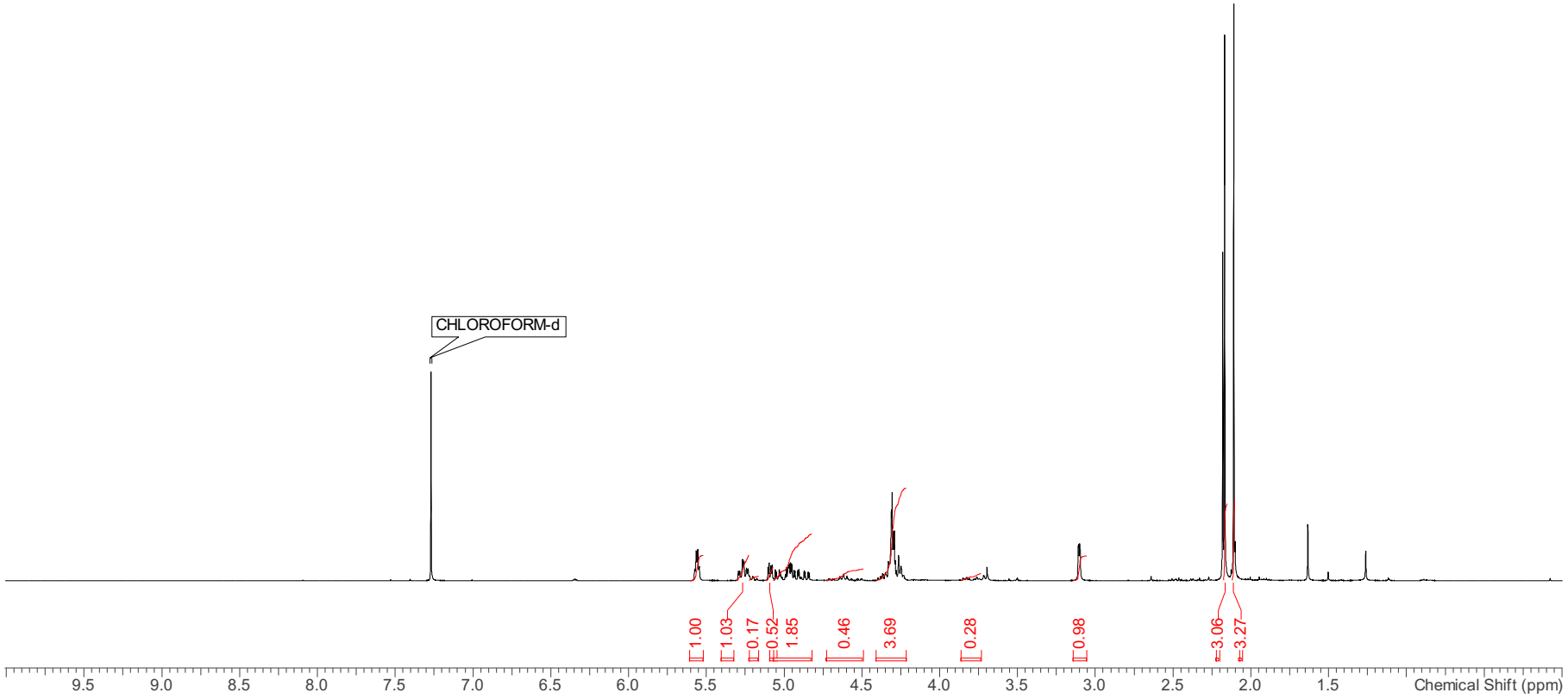
1.3 2,6-Di-*O*-acetyl-3,4-dideoxy-3,4-difluoro-D-galactopyranose 15c

1.3.1 ^{1}H NMR (400 MHz, $CDCl_3$) (compound 15c)

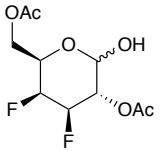
dc1118jbv6.010.001.1r.esp



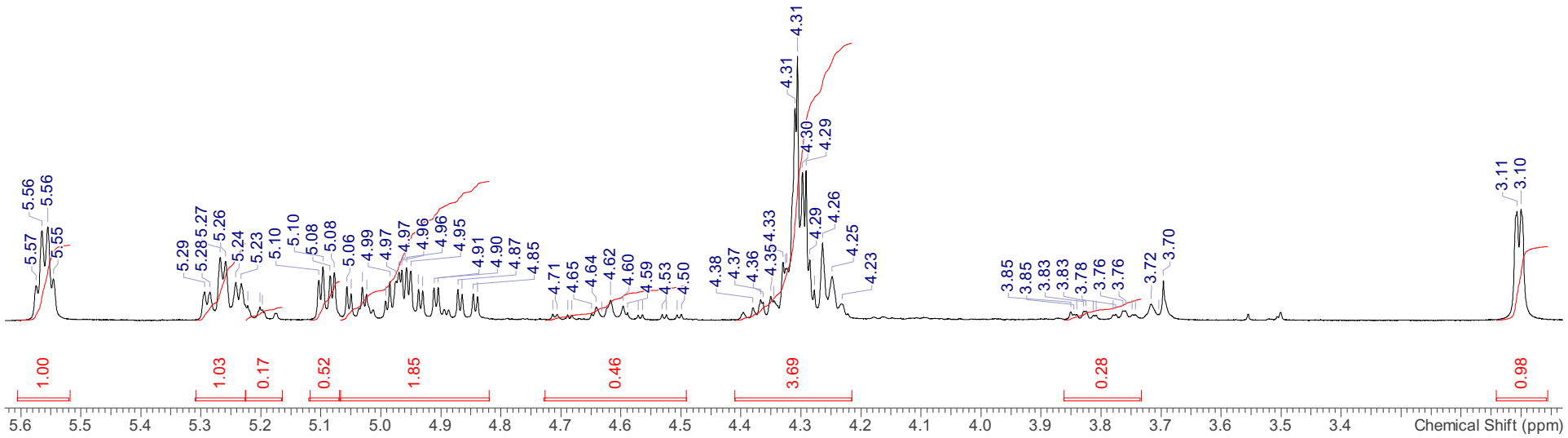
15c



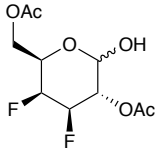
dc1118jbv6.010.001.1r.esp



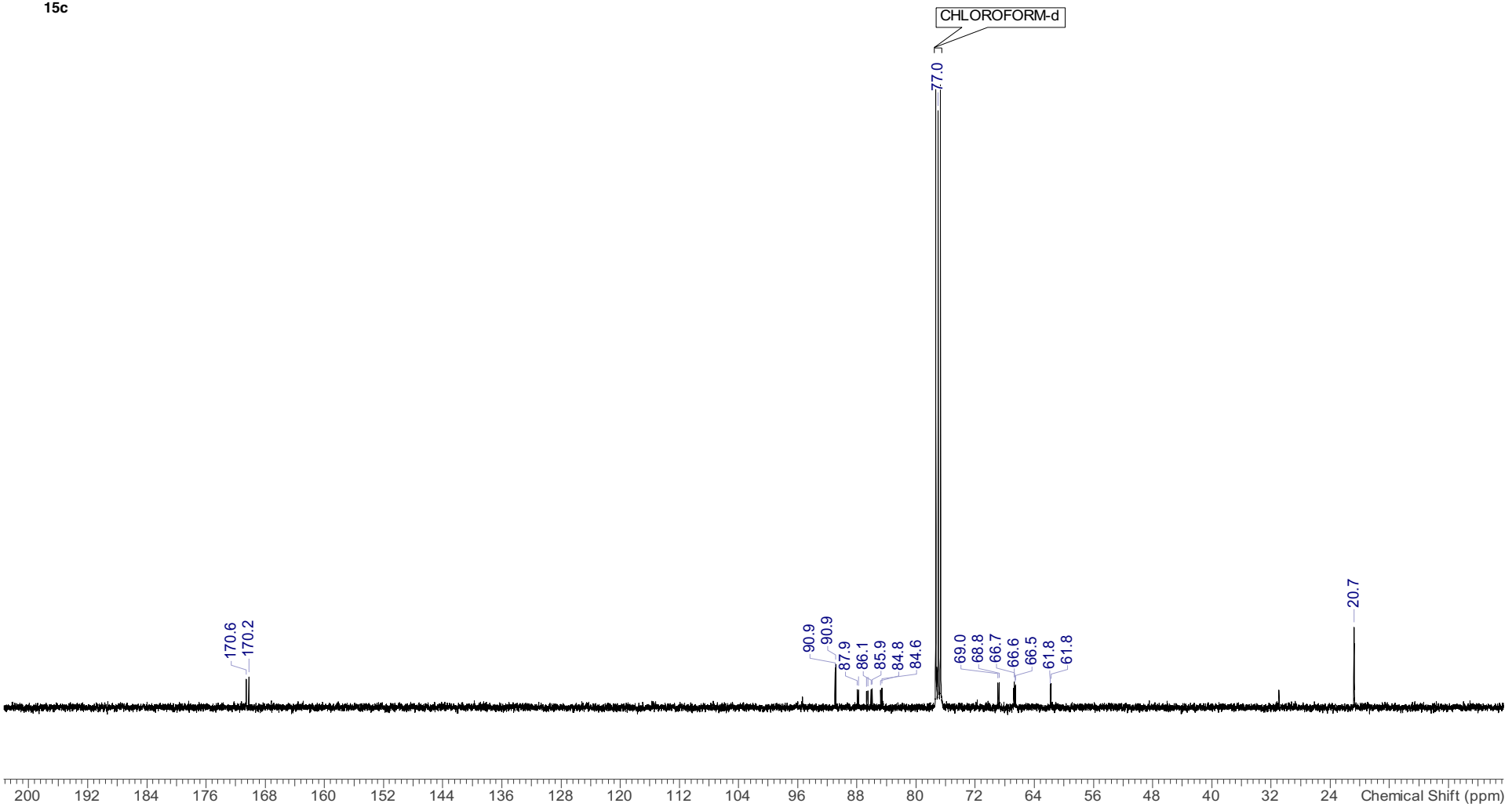
15c

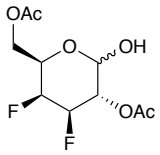


1.3.2 ^{13}C NMR (101 MHz, $CDCl_3$) (compound 15c)

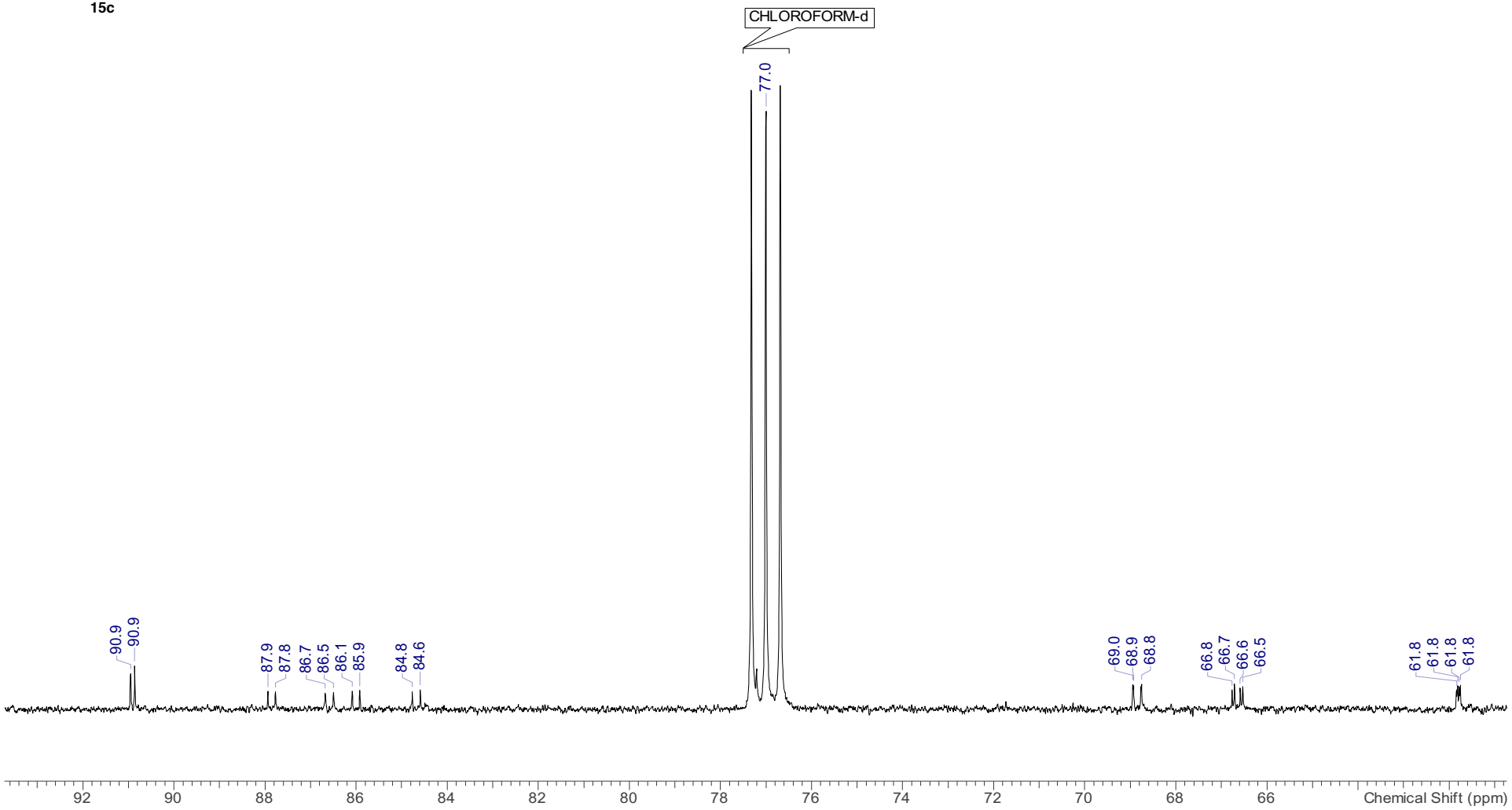


15c

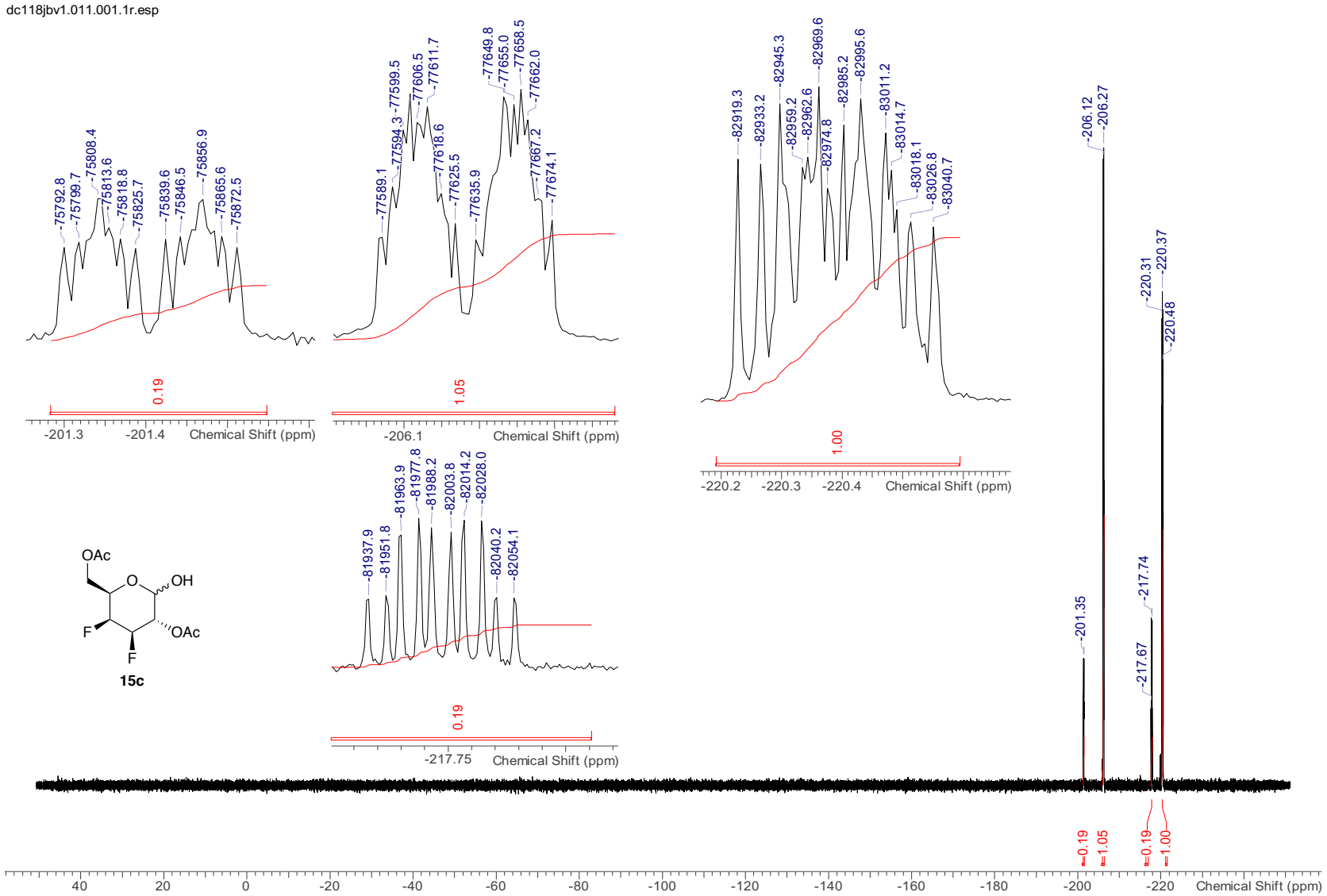



OAc
O
OH
F
OAc
F

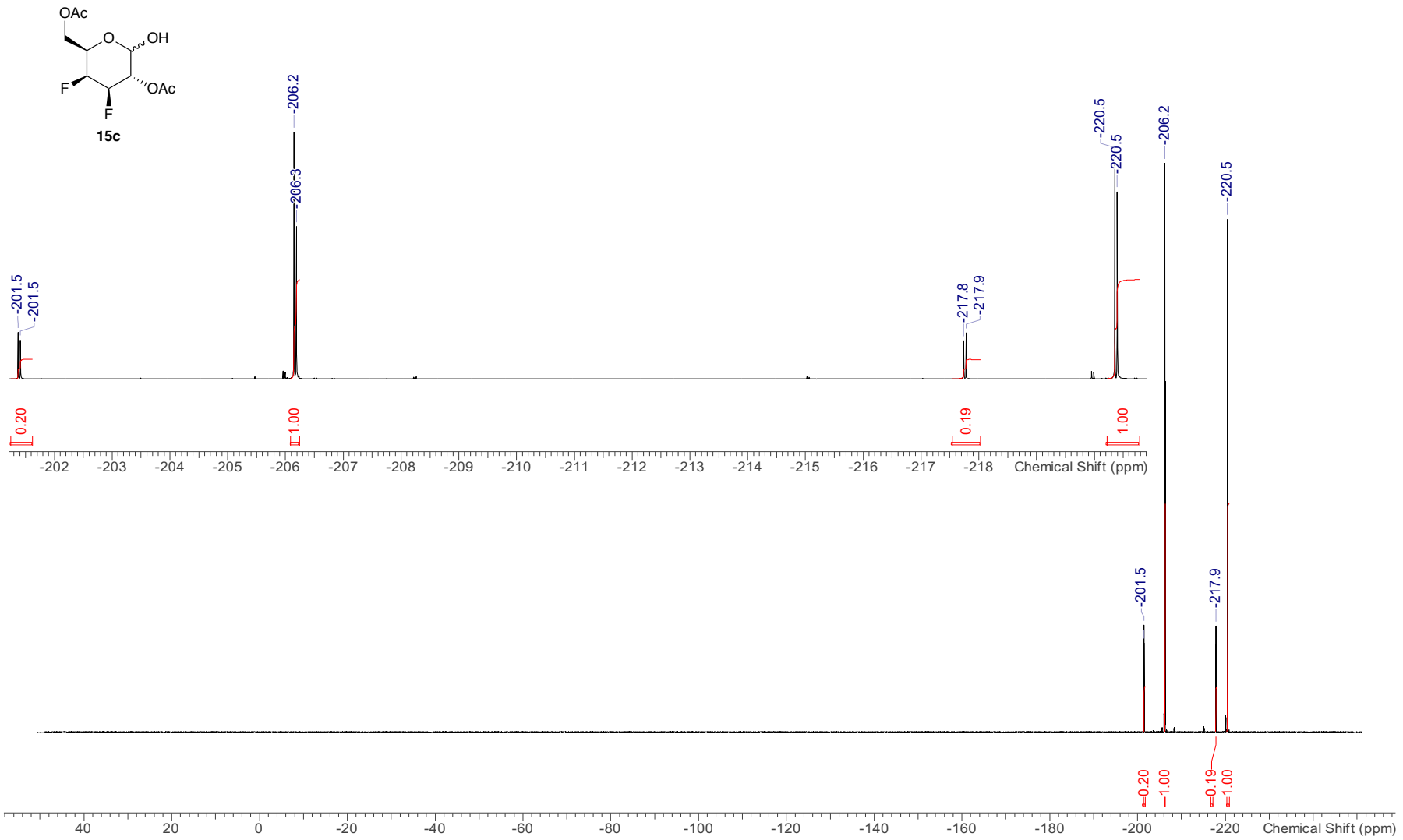
15c


CHLOROFORM-d
77.0
90.9
90.9
87.9
87.8
86.7
86.5
86.1
85.9
84.8
84.6
69.0
68.9
68.8
66.8
66.7
66.6
66.5
61.8
61.8
61.8
61.8
92
90
88
86
84
82
80
78
76
74
72
70
68
66
Chemical Shift (ppm)

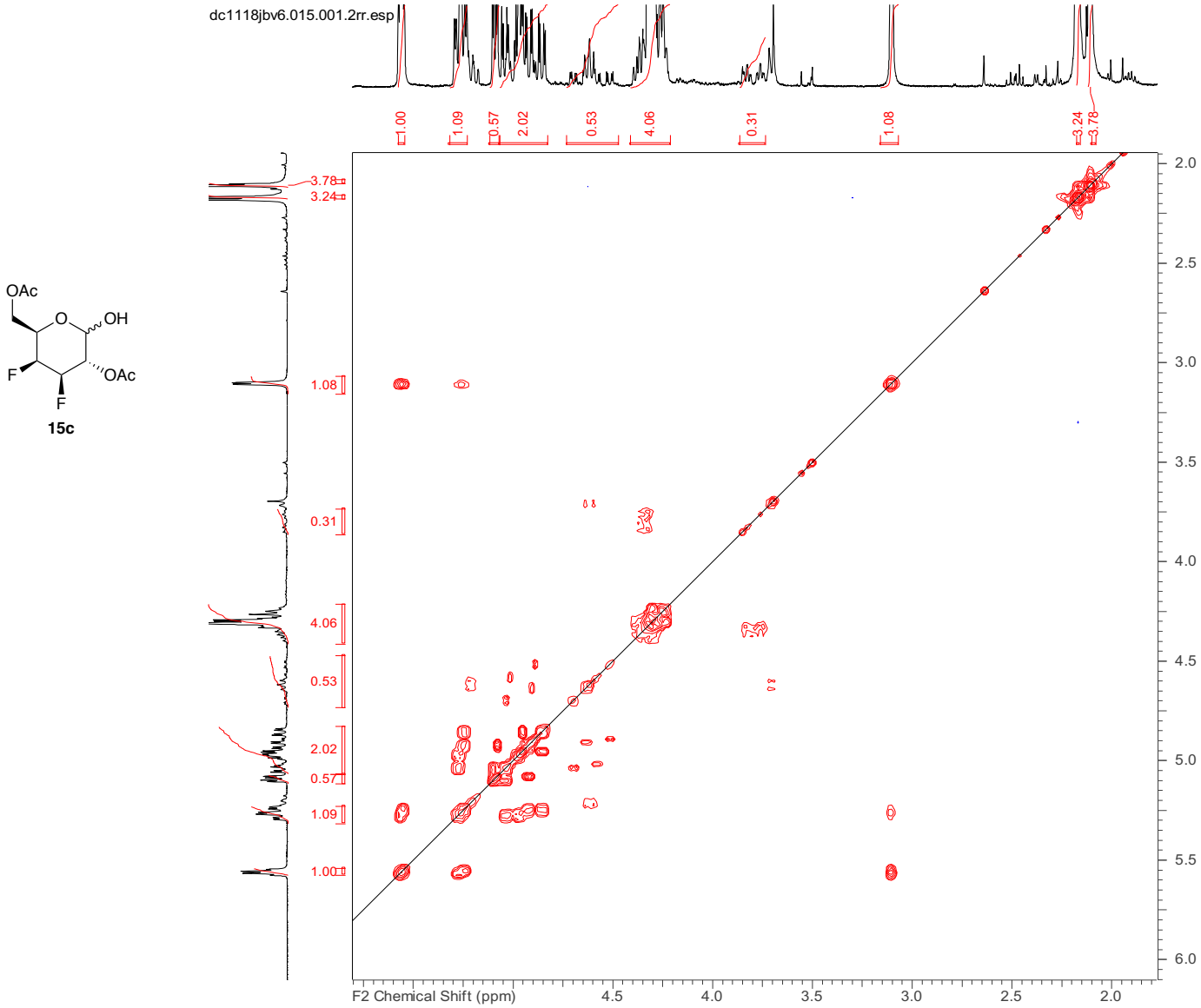
1.3.3 ^{19}F NMR (376 MHz, $CDCl_3$) (compound 15c)



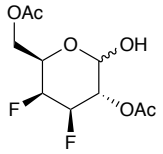
1.3.4 $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) (compound 15c)



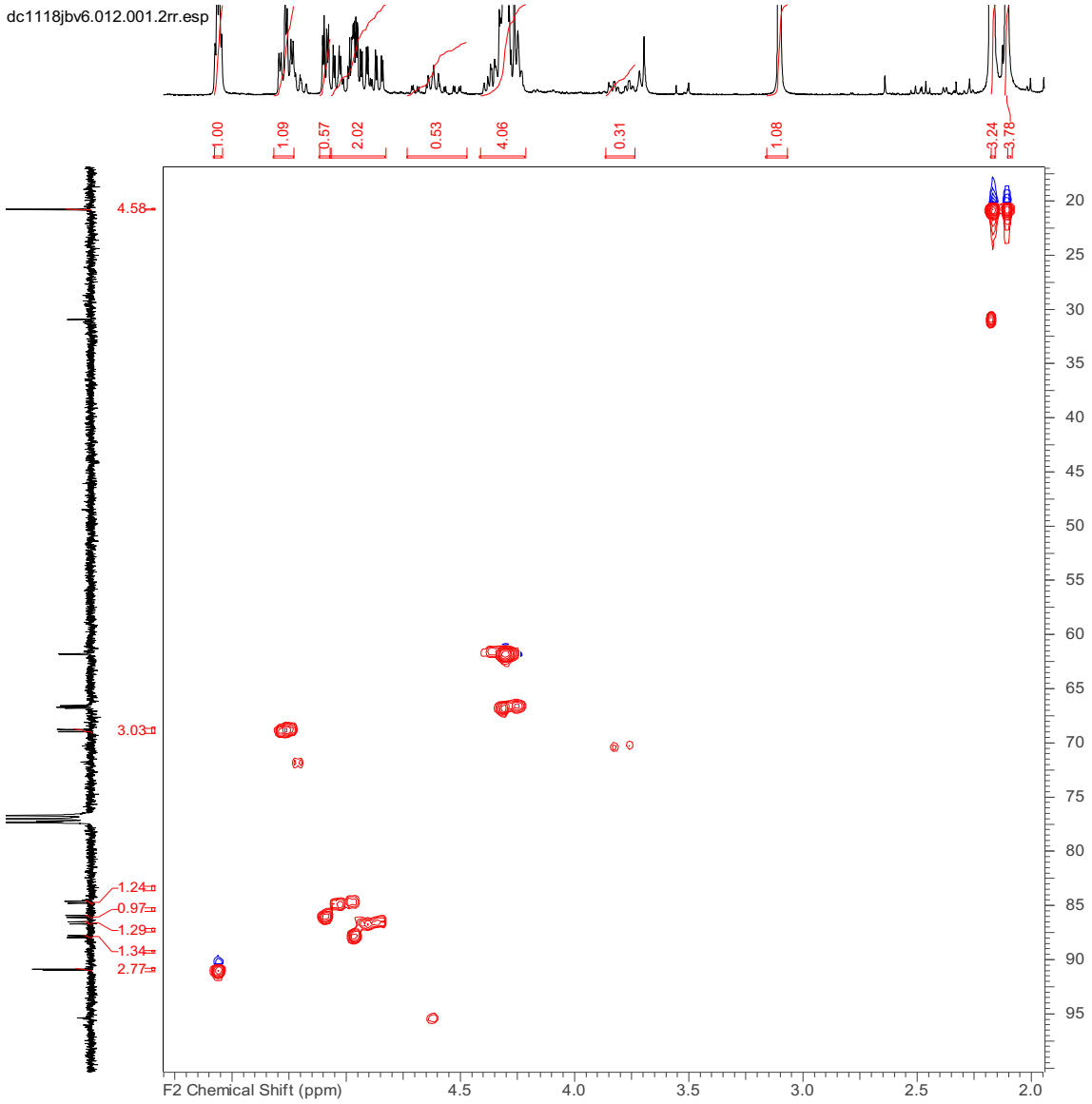
1.3.5 COSY ^{1}H-^{1}H (400 MHz, $CDCl_3$) (compound 15c)



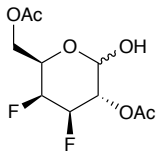
1.3.6 HSQC (400 MHz, $CDCl_3$) (compound 15c)



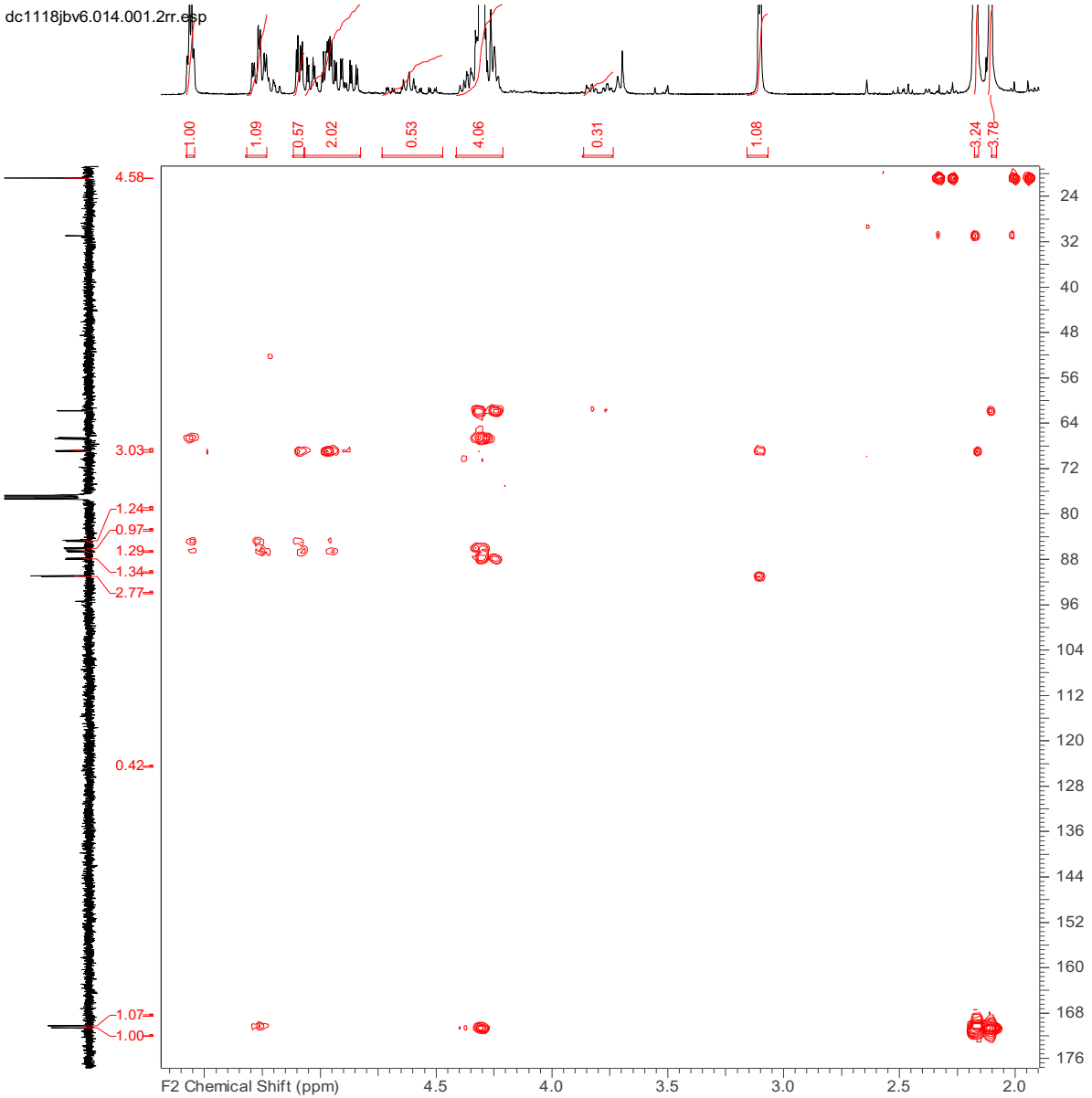
15c



1.3.7 HMBC (400 MHz, $CDCl_3$) (compound 15c)

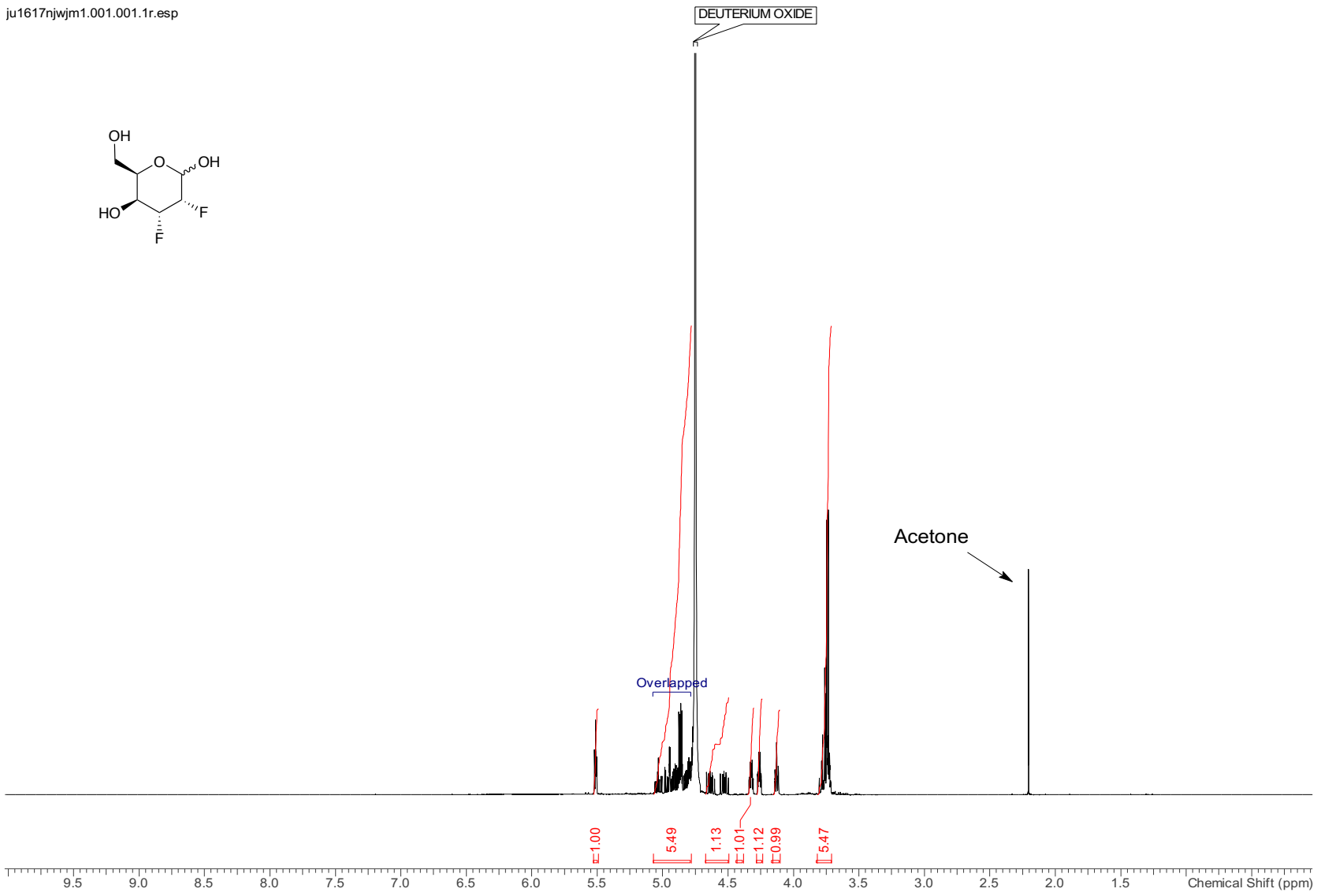


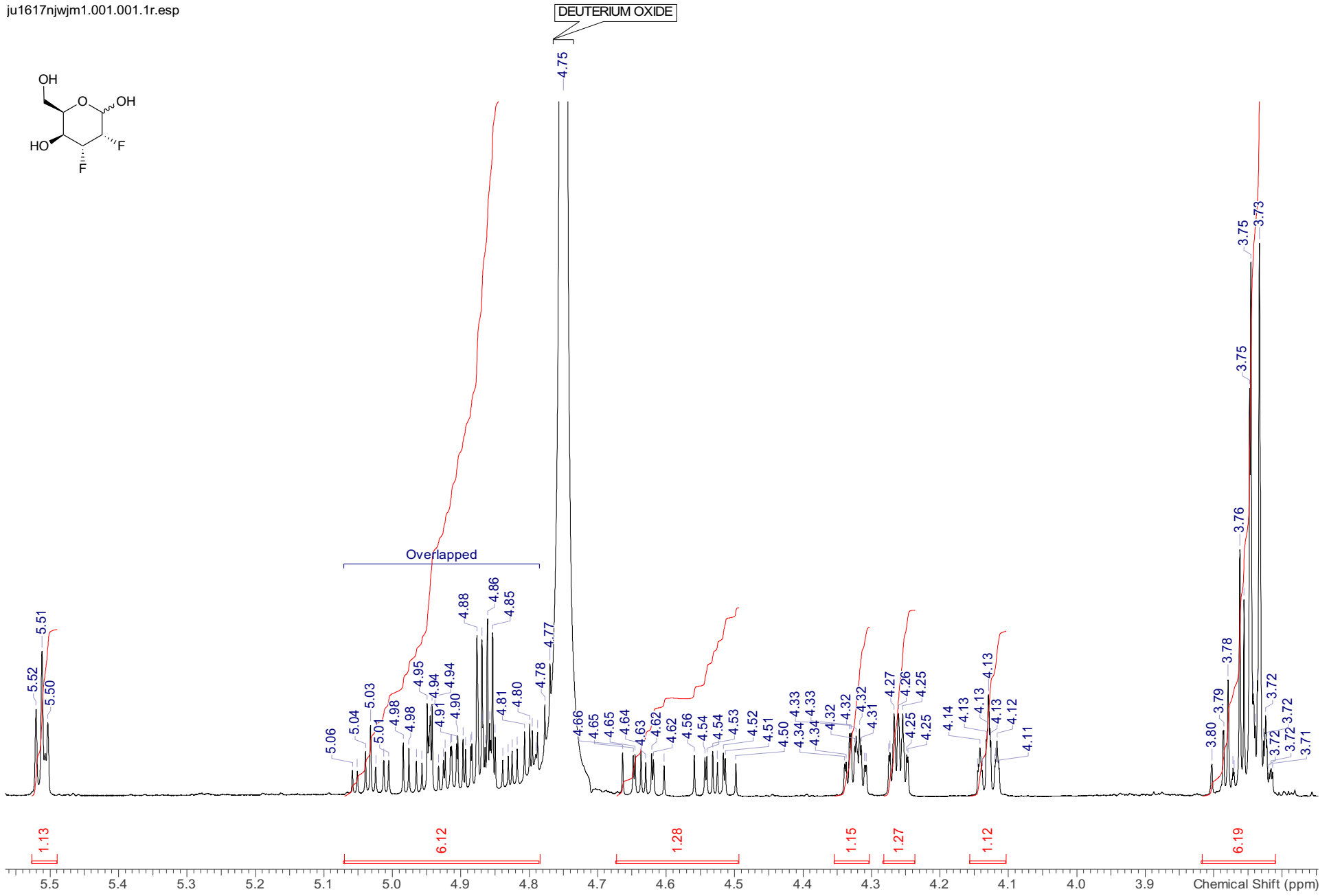
15c



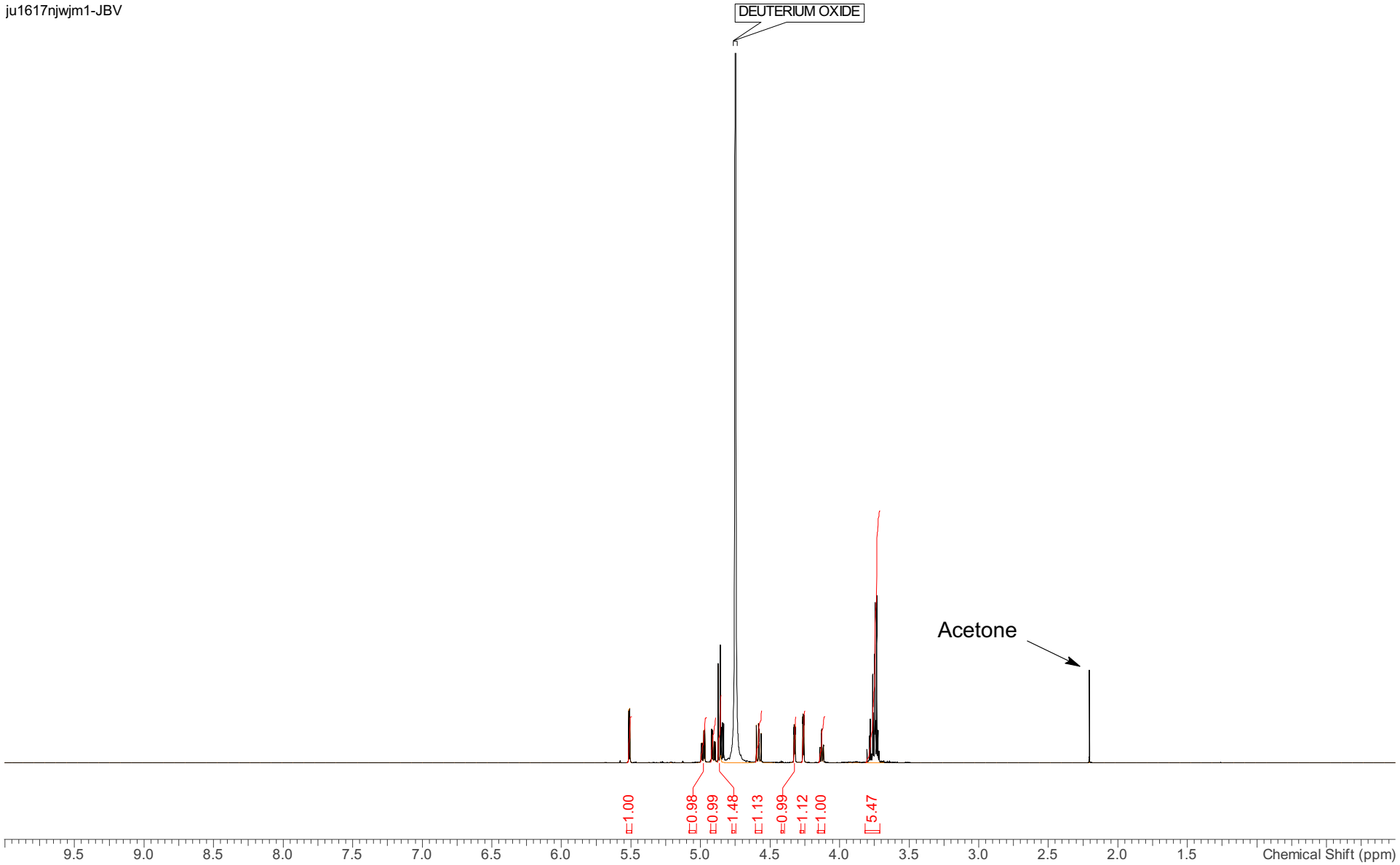
1.4 2,3-Dideoxy-2,3-difluorogalactose 16a

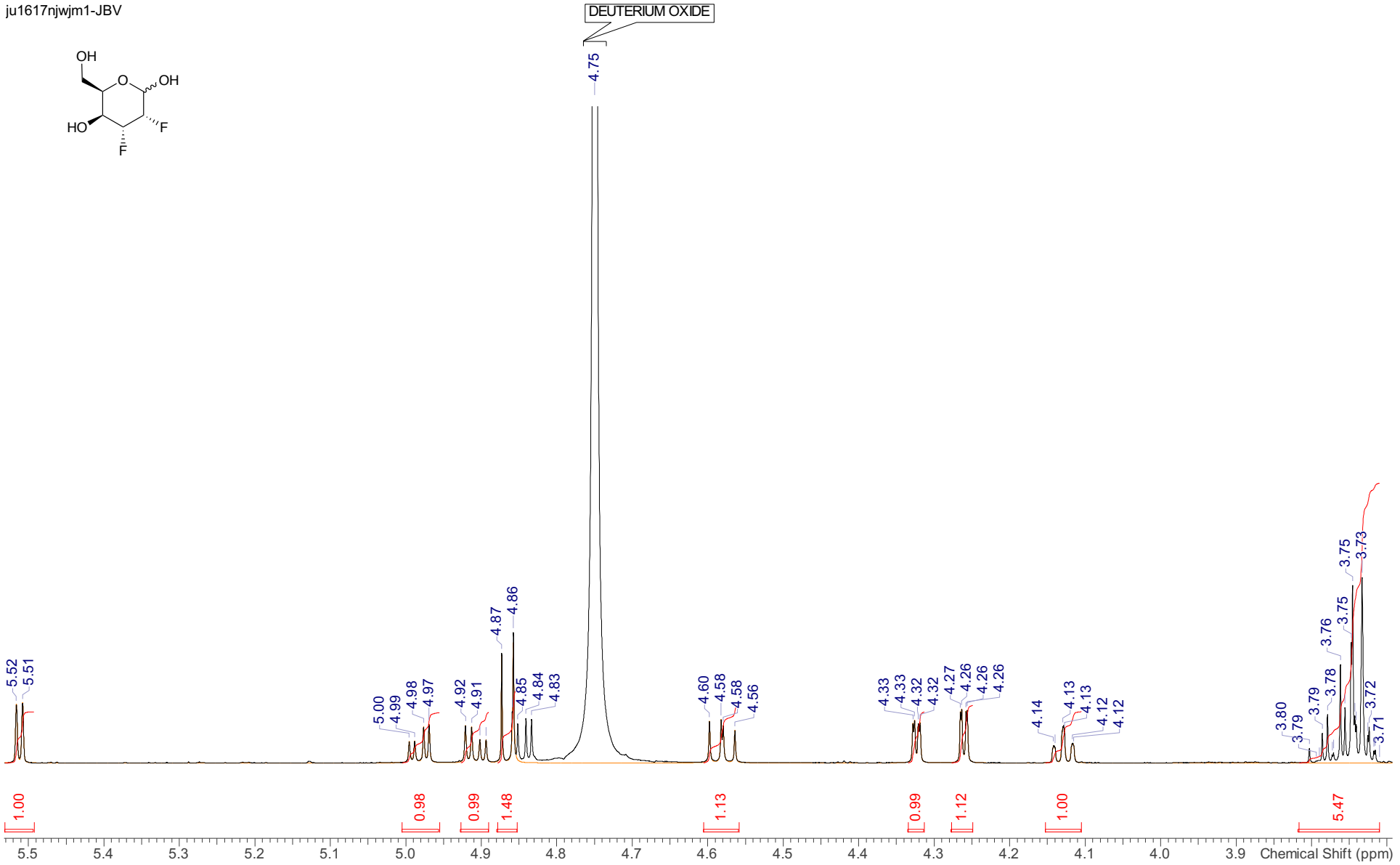
1.4.1 ^{1}H NMR (500 MHz, D_2O) (compound 16a)



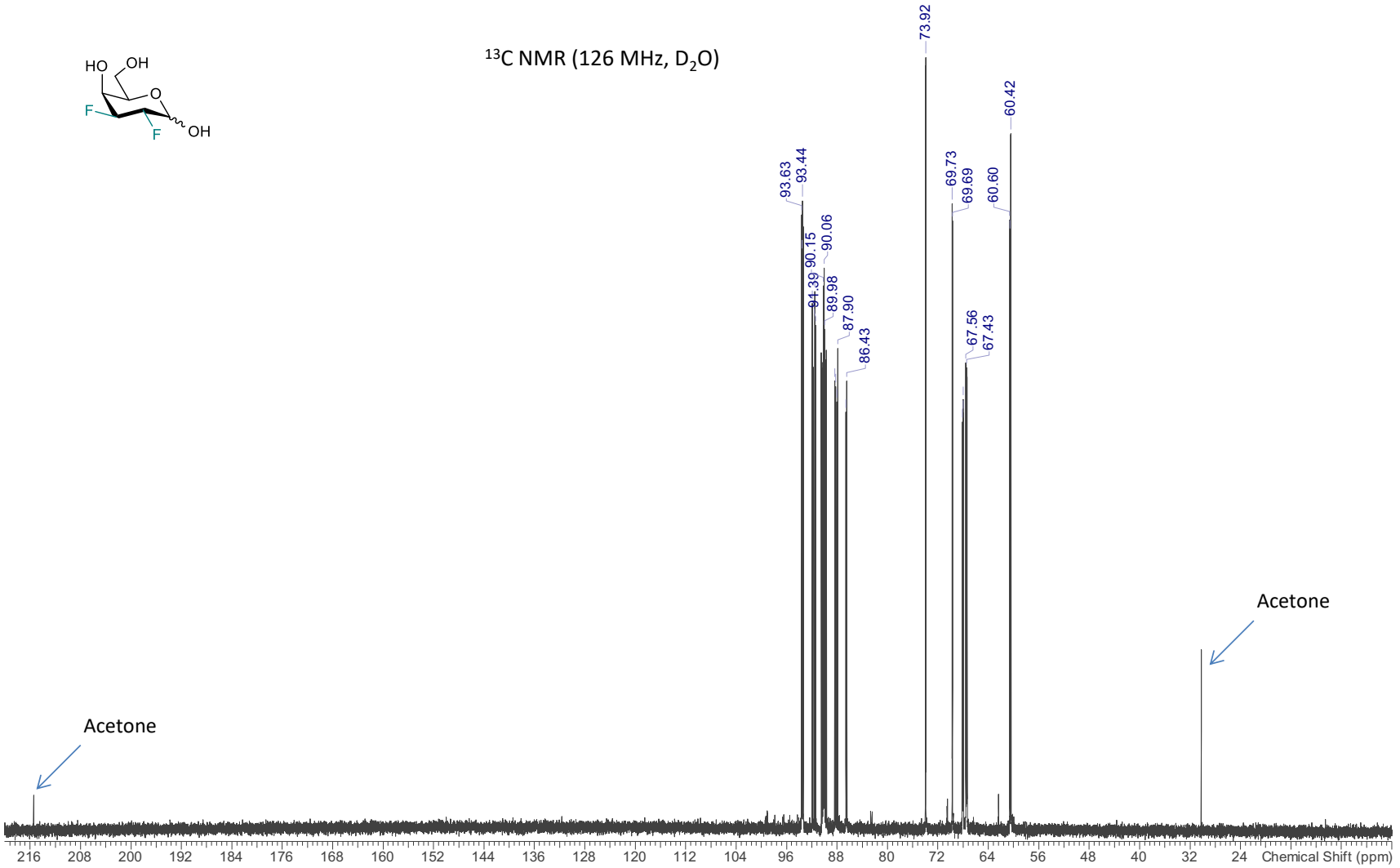

ju1617njwjm1.001.001.1r.esp
DEUTERIUM OXIDE
4.75
OH
O
OH
HO
F
F
Overlapped
5.52
5.51
5.50
5.06
5.04
5.03
5.01
4.98
4.98
4.95
4.94
4.94
4.91
4.90
4.88
4.86
4.85
4.81
4.80
4.78
4.77
4.66
4.65
4.65
4.64
4.63
4.62
4.62
4.56
4.54
4.54
4.53
4.52
4.51
4.50
4.34
4.33
4.34
4.33
4.32
4.32
4.32
4.31
4.27
4.26
4.25
4.25
4.25
4.14
4.13
4.13
4.13
4.12
4.11
3.80
3.79
3.78
3.76
3.75
3.75
3.73
3.72
3.72
3.72
3.71
1.13
6.12
1.28
1.15
1.27
1.12
6.19
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
Chemical Shift (ppm)

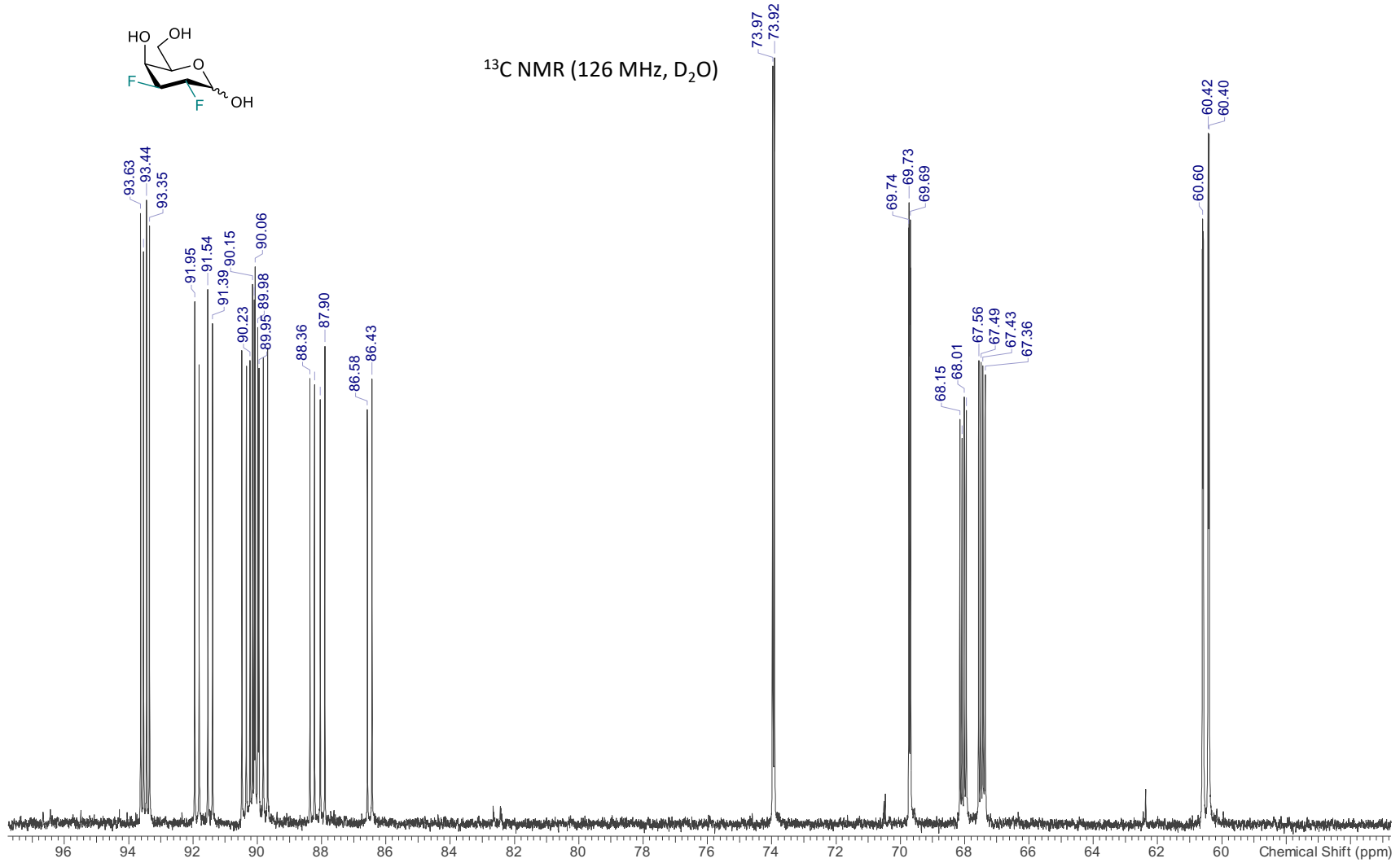
1.4.2 $^{1}H\{^{19}F\}$ NMR (500 MHz, D_2O) (compound 16a)



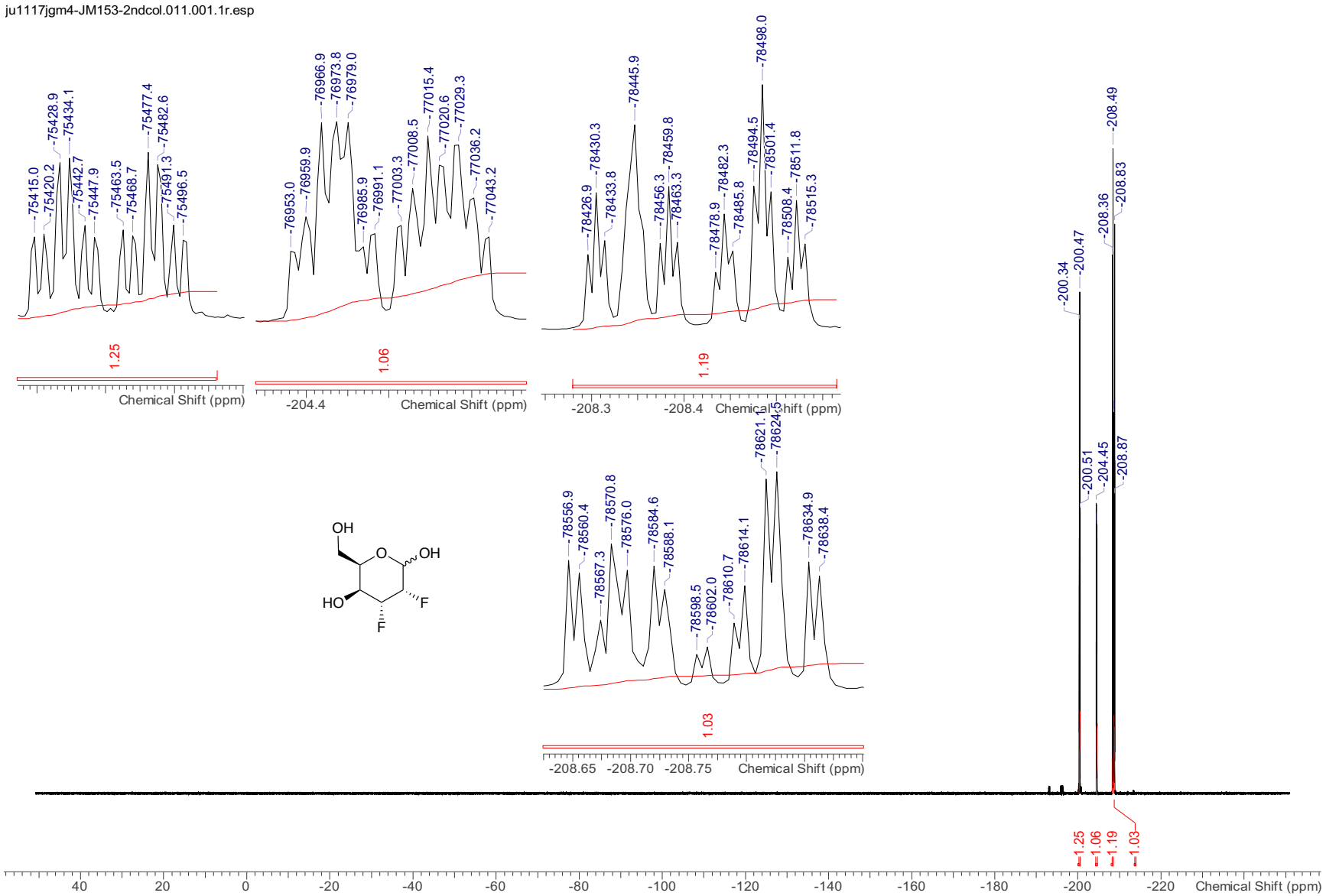

ju1617njwjm1-JBV
DEUTERIUM OXIDE
4.75
5.52
5.51
5.00
4.99
4.98
4.97
4.92
4.91
4.87
4.86
4.85
4.84
4.83
4.60
4.58
4.58
4.56
4.33
4.33
4.32
4.32
4.27
4.26
4.26
4.26
4.14
4.13
4.13
4.12
4.12
3.80
3.79
3.79
3.78
3.76
3.75
3.75
3.73
3.72
3.71
1.00
0.98
0.99
1.48
1.13
0.99
1.12
1.00
5.47
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
Chemical Shift (ppm)

1.4.3 ^{13}C NMR (126 MHz, D_2O) (compound 16a)

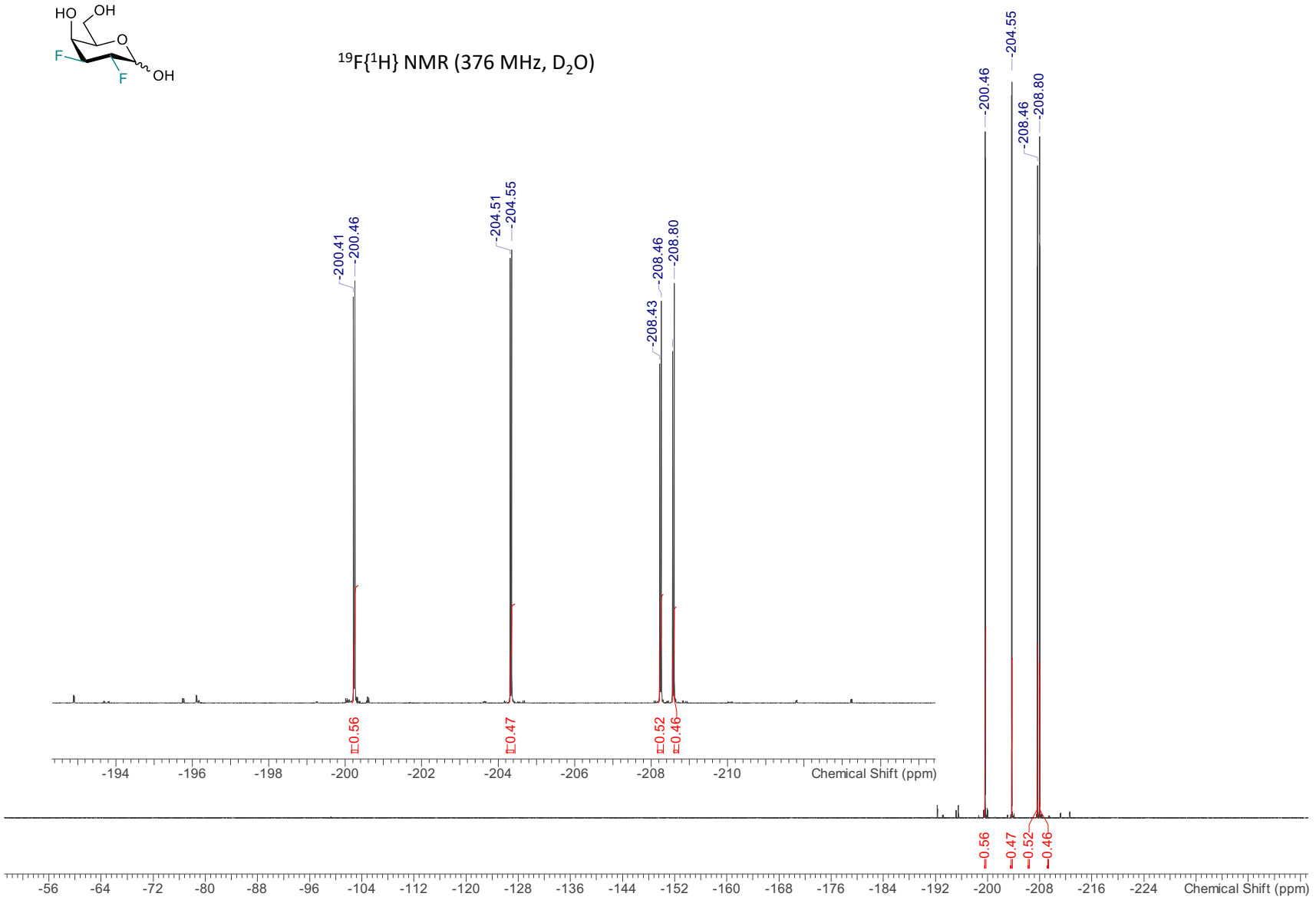



HO
OH
O
F
F
OH
^{13}C NMR (126 MHz, D_2O)
93.63
93.44
93.35
91.95
91.54
91.39
90.15
90.06
90.23
89.98
89.95
88.36
87.90
86.58
86.43
73.97
73.92
69.74
69.73
69.69
68.15
68.01
67.56
67.49
67.43
67.36
60.60
60.42
60.40
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
Chemical Shift (ppm)

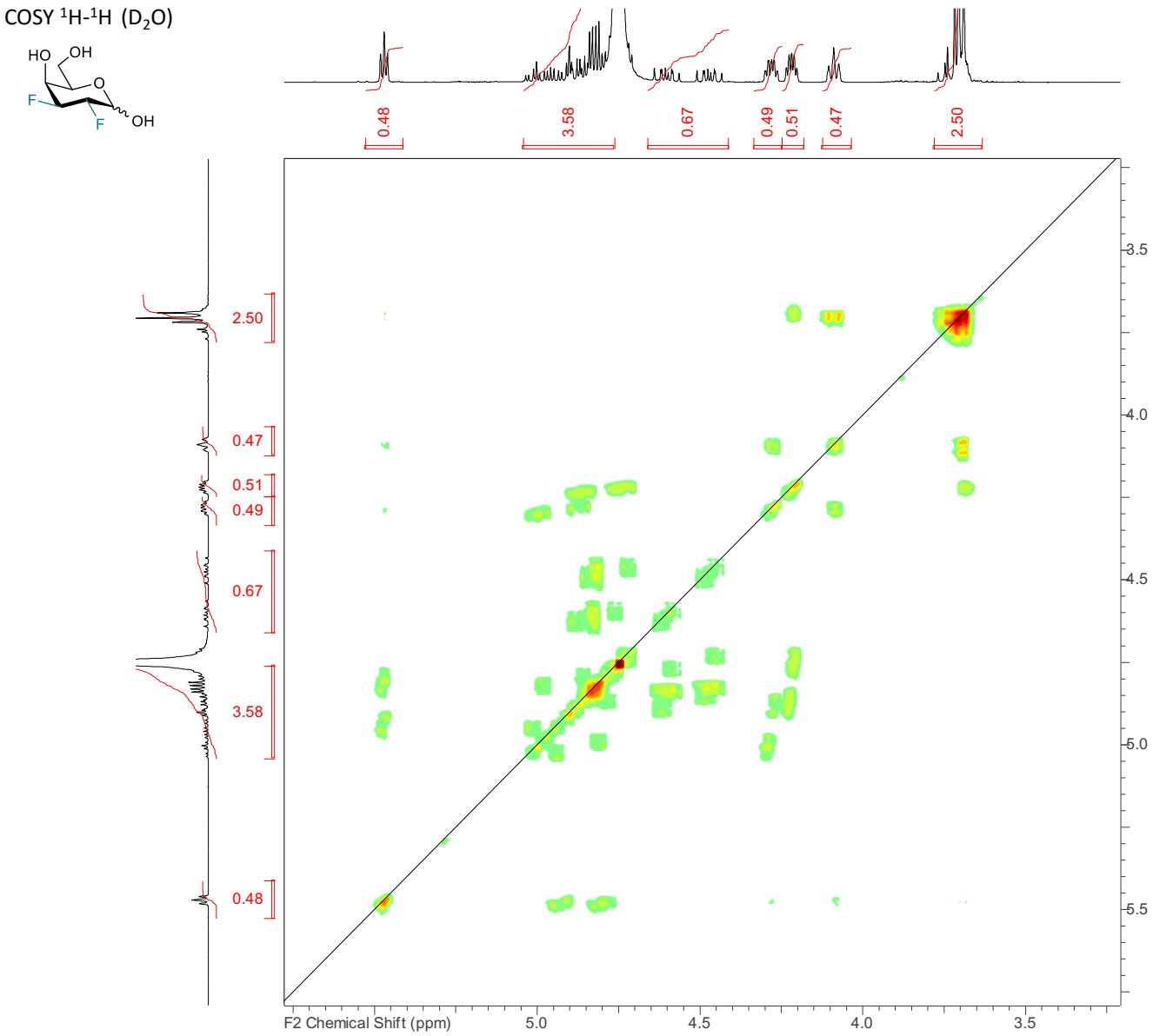
1.4.4 ^{19}F NMR (376 MHz, D_2O) (compound 16a)



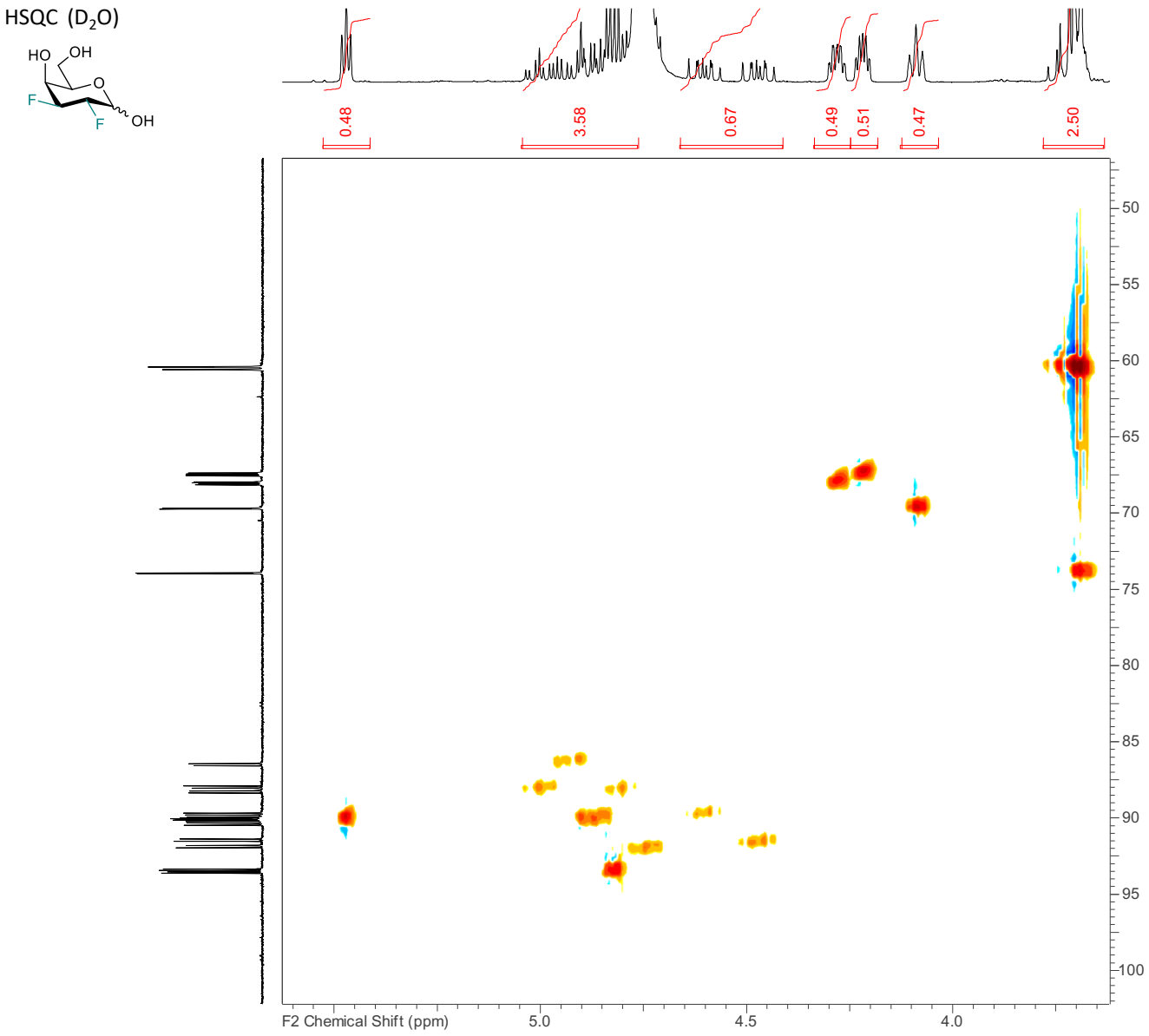
1.4.5 $^{19}F\{^{1}H\}$ NMR (376 MHz, D_2O) (compound 16a)



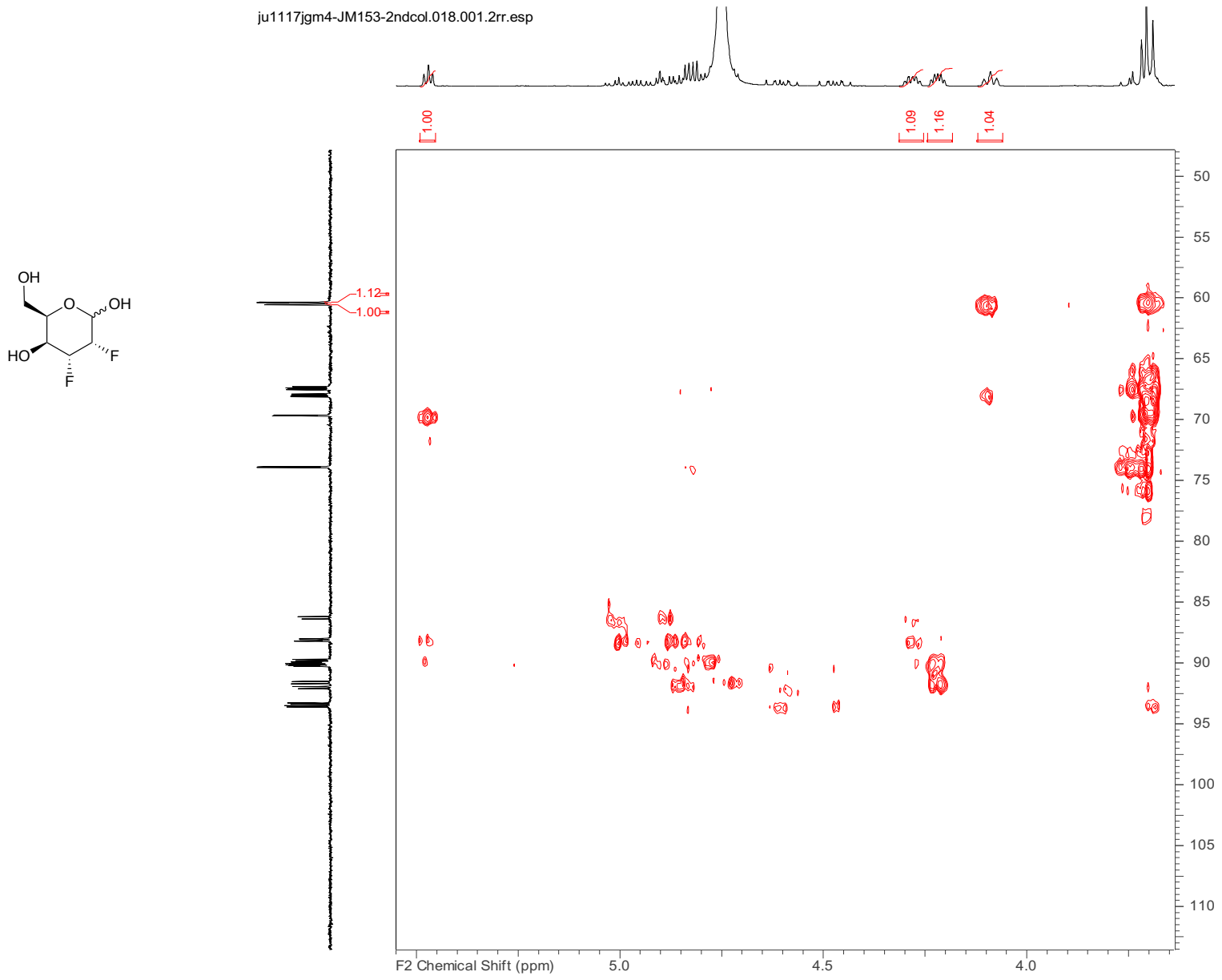
1.4.6 COSY ^{1}H-^{1}H (400 MHz, D_2O) (compound 16a)



1.4.7 HSQC (400 MHz, D_2O)

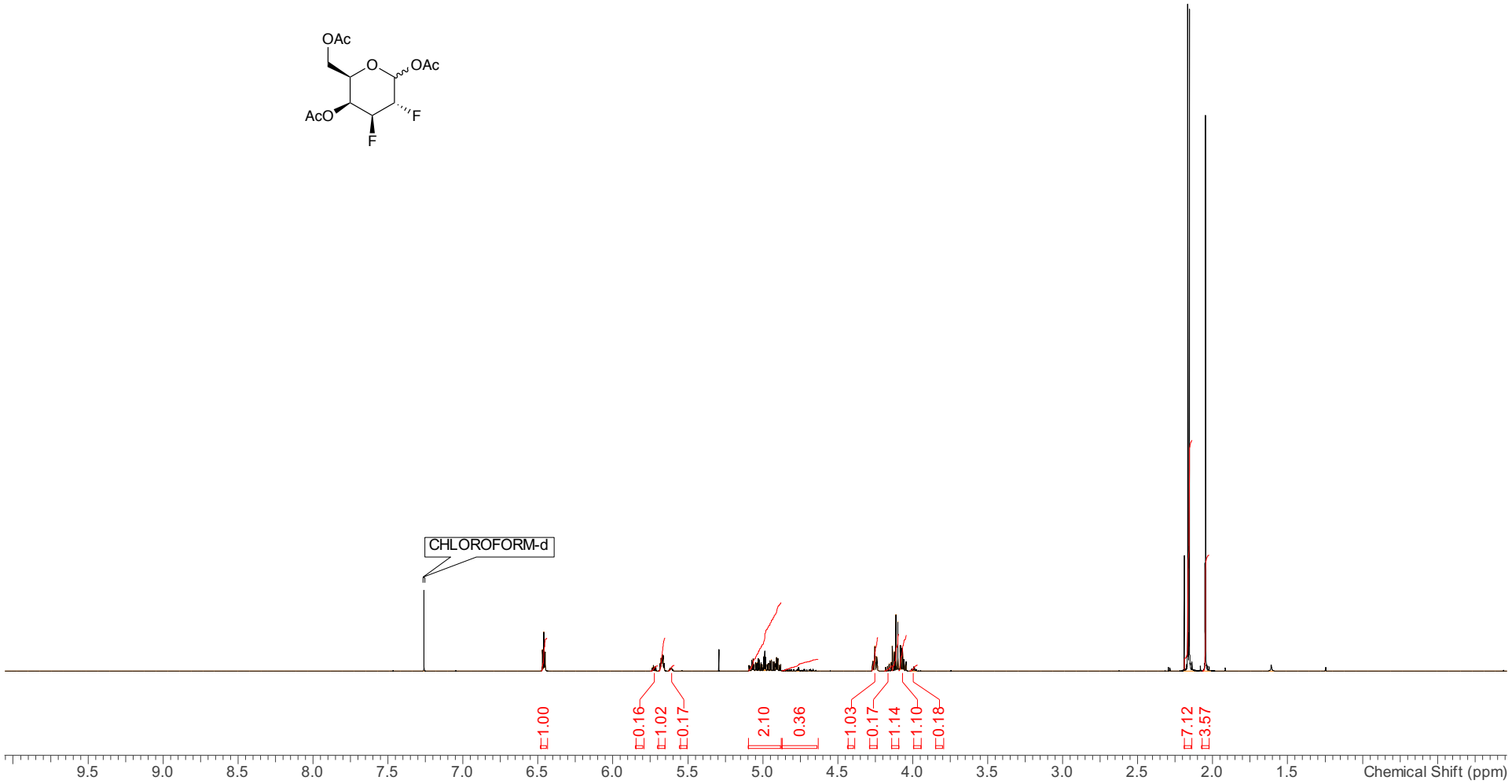


1.4.8 HMBC (400 MHz, D_2O)

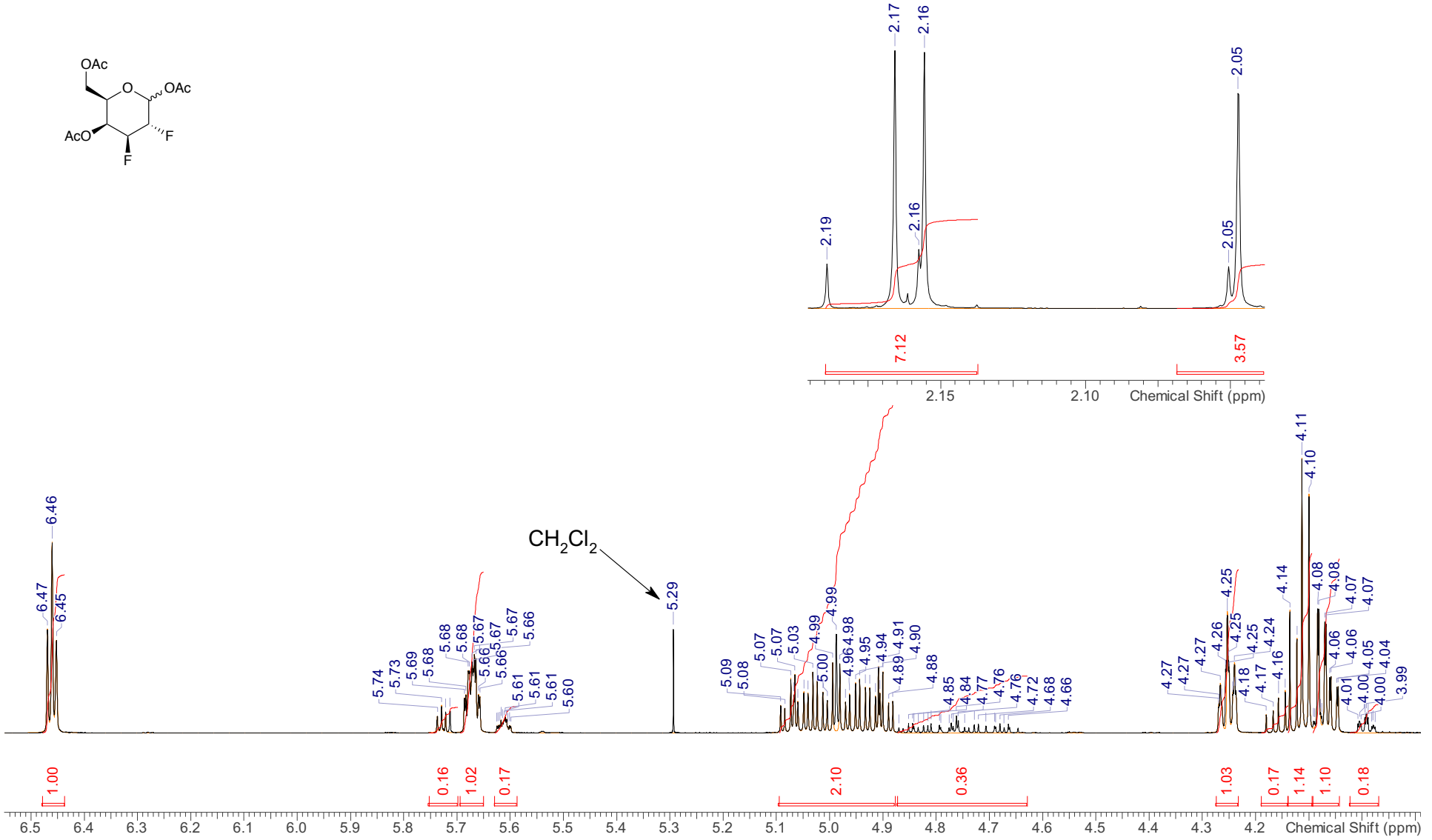


1.5 1,4,6-Tri-*O*-acetyl-2,3-dideoxy-2,3-difluorogalactose 16b

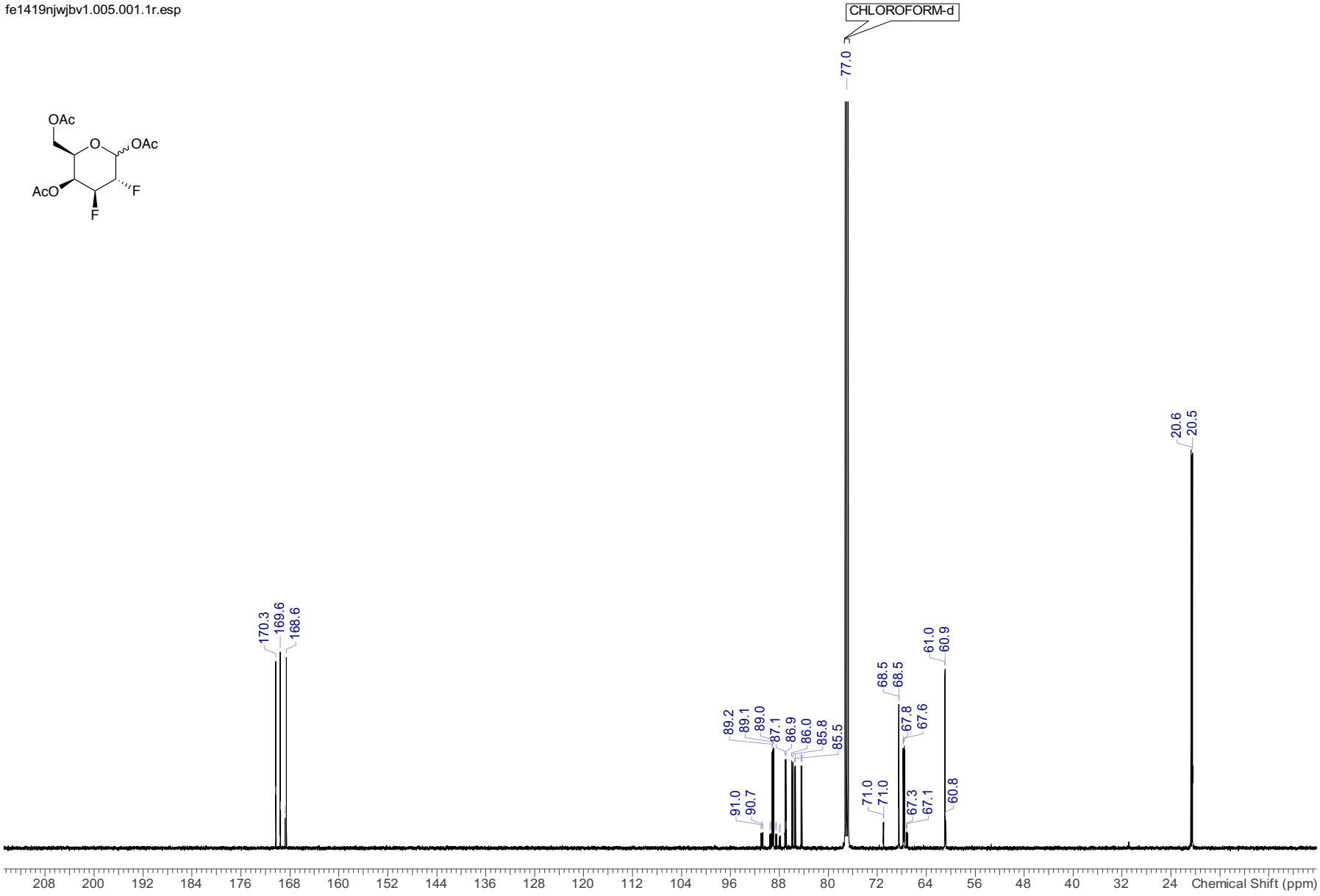
1.5.1 ^{1}H NMR (500 MHz, $CDCl_3$) (compound 16b)

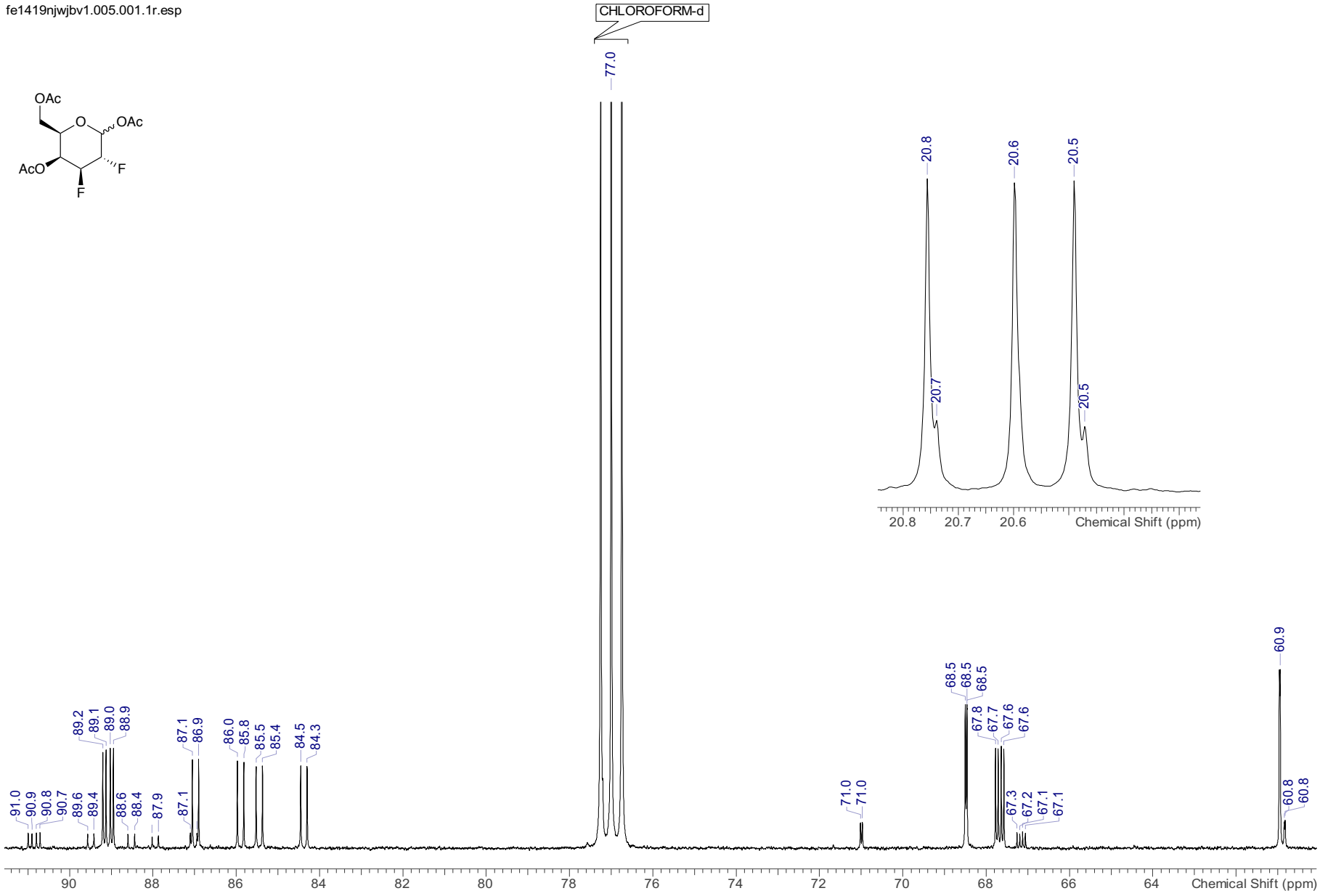


fe1419njwjbv1.001.001.1r.esp

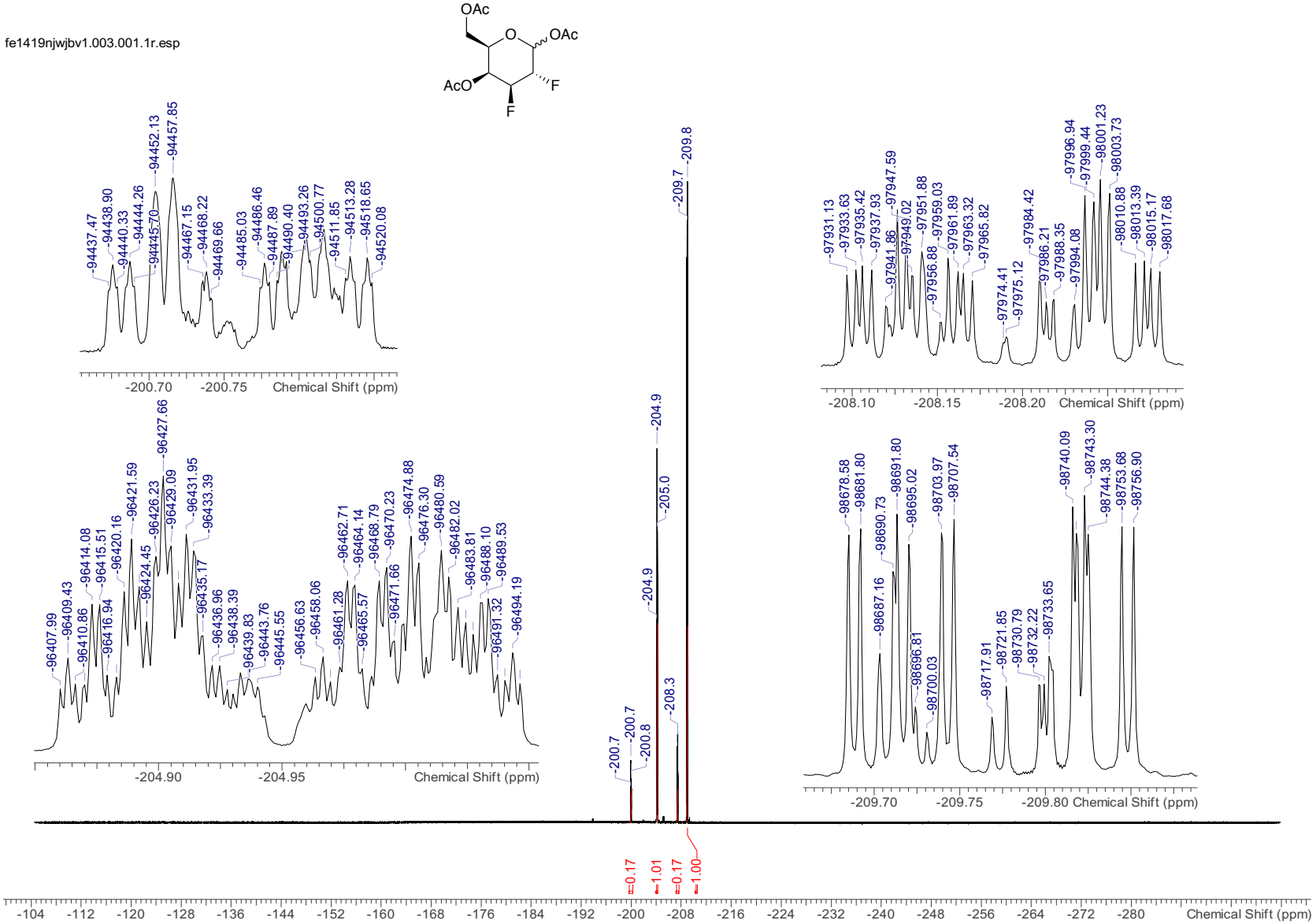


1.5.2 ^{13}C NMR (126 MHz, $CDCl_3$) (compound 16b)

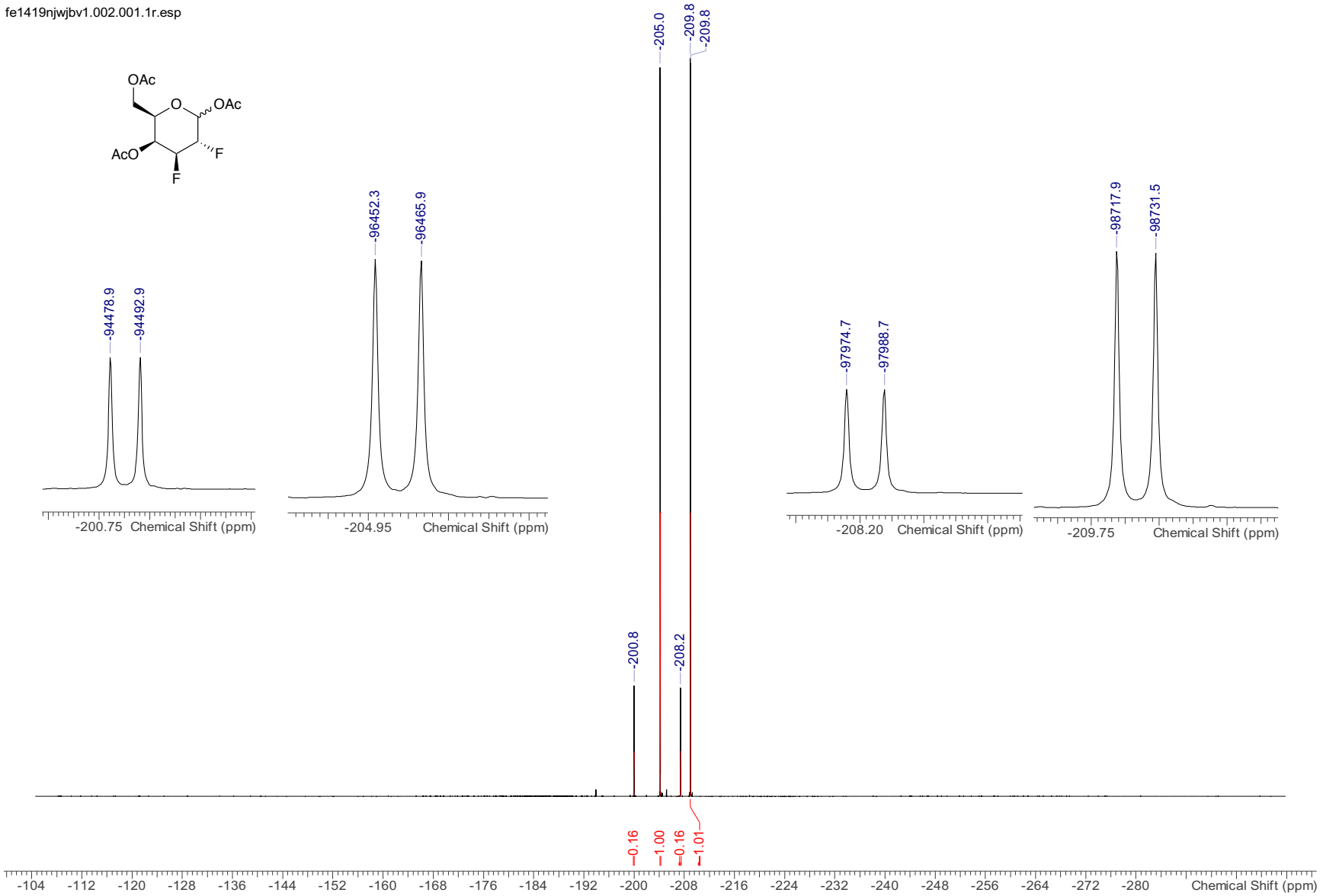



fe1419njwjbv1.005.001.1r.esp
CHLOROFORM-d
77.0
OAc
O
OAc
AcO
F
F
20.8
20.6
20.5
20.7
20.5
20.8 20.7 20.6 Chemical Shift (ppm)
91.0 90.9 90.8 90.7 89.6 89.4 89.2 89.1 89.0 88.9 88.6 88.4 87.9 87.1 87.1 86.9 86.0 85.8 85.5 85.4 84.5 84.3
71.0 71.0
68.5 68.5 68.5 67.8 67.7 67.6 67.6 67.3 67.2 67.1 67.1
60.9 60.8 60.8
90 88 86 84 82 80 78 76 74 72 70 68 66 64 Chemical Shift (ppm)

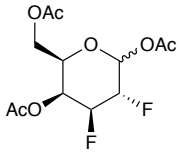
1.5.3 ^{19}F NMR (471 MHz, $CDCl_3$) (compound 16b)

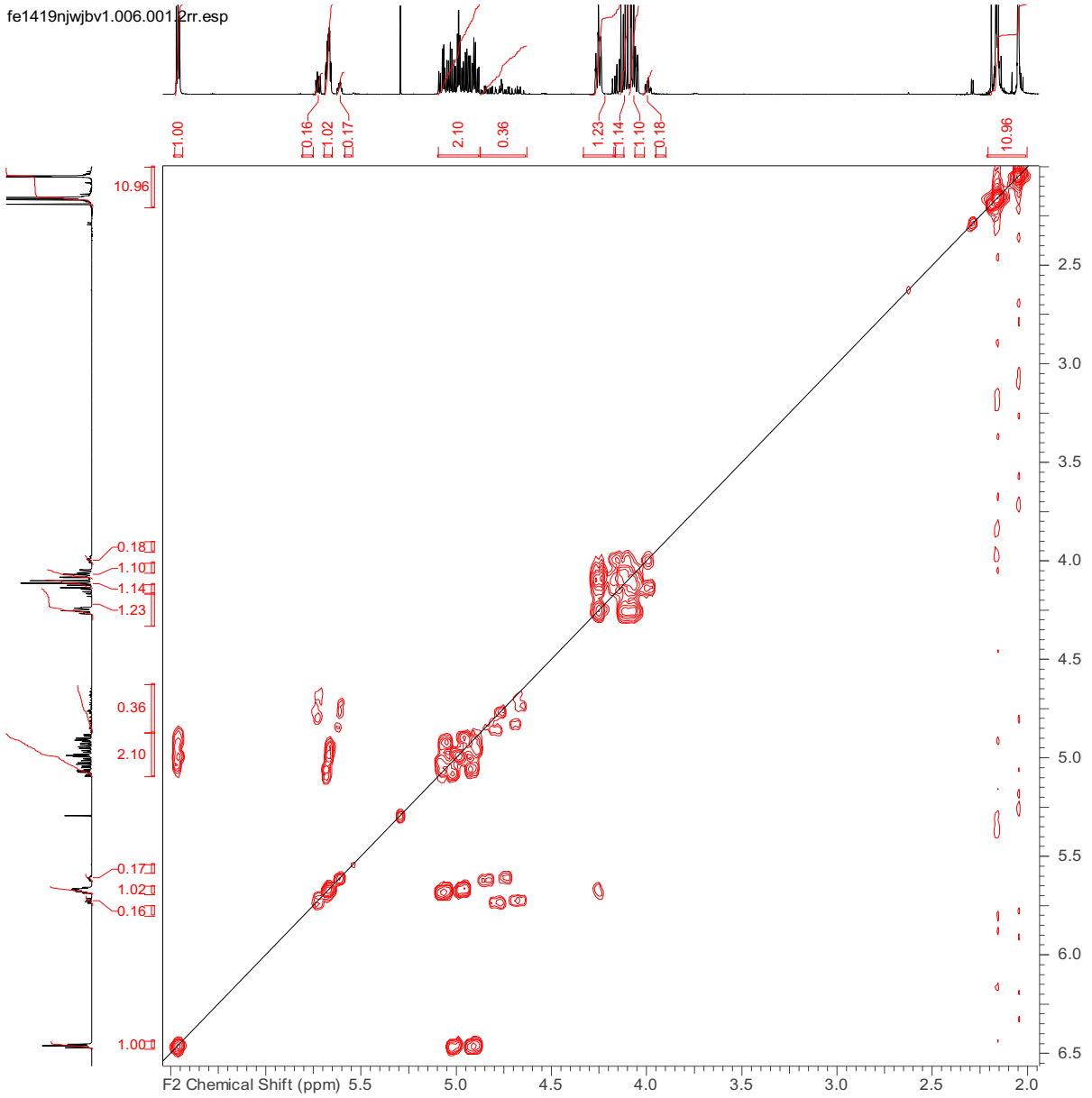


1.5.4 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) (compound 16b)

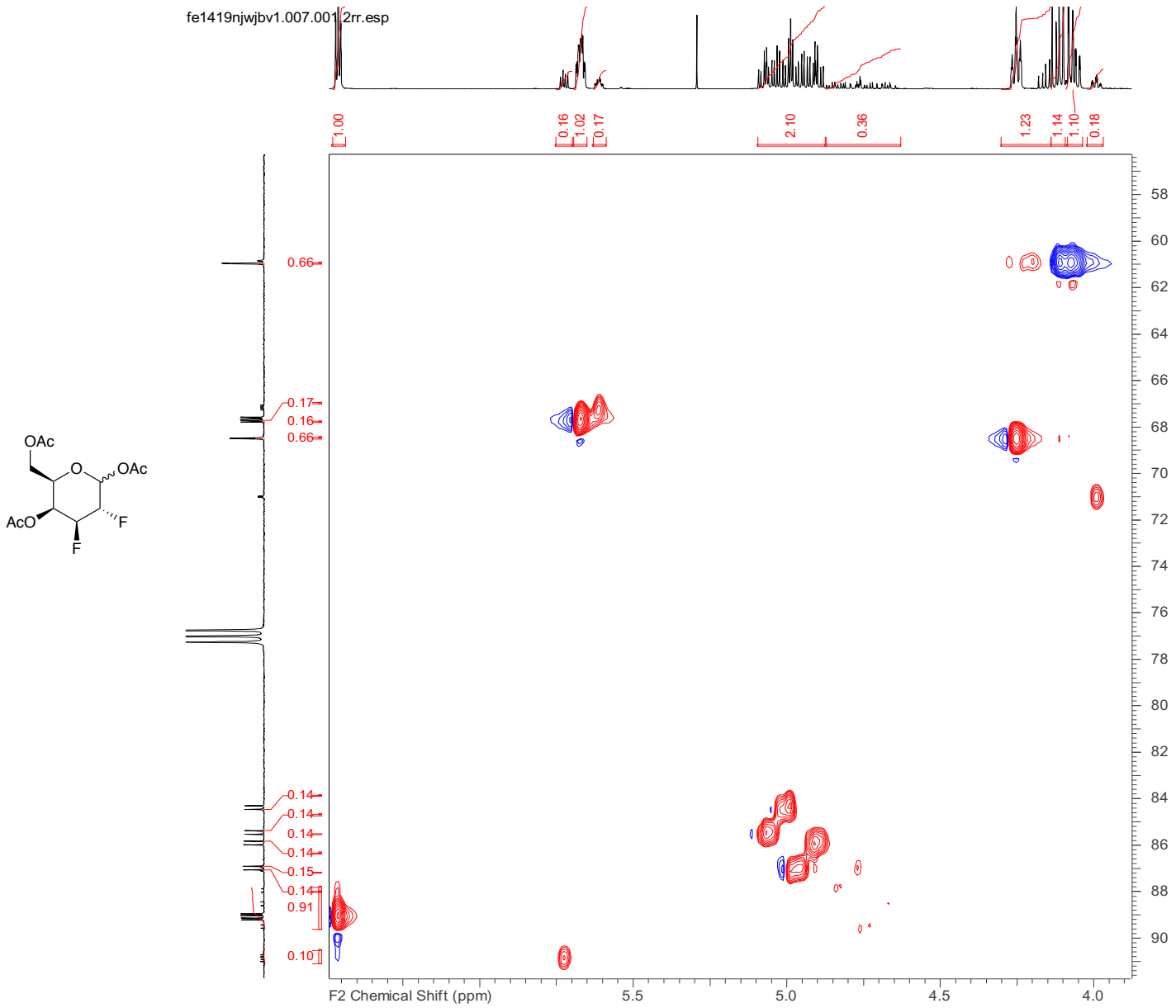


1.5.5 COSY (500 MHz, $CDCl_3$) (compound 16b)

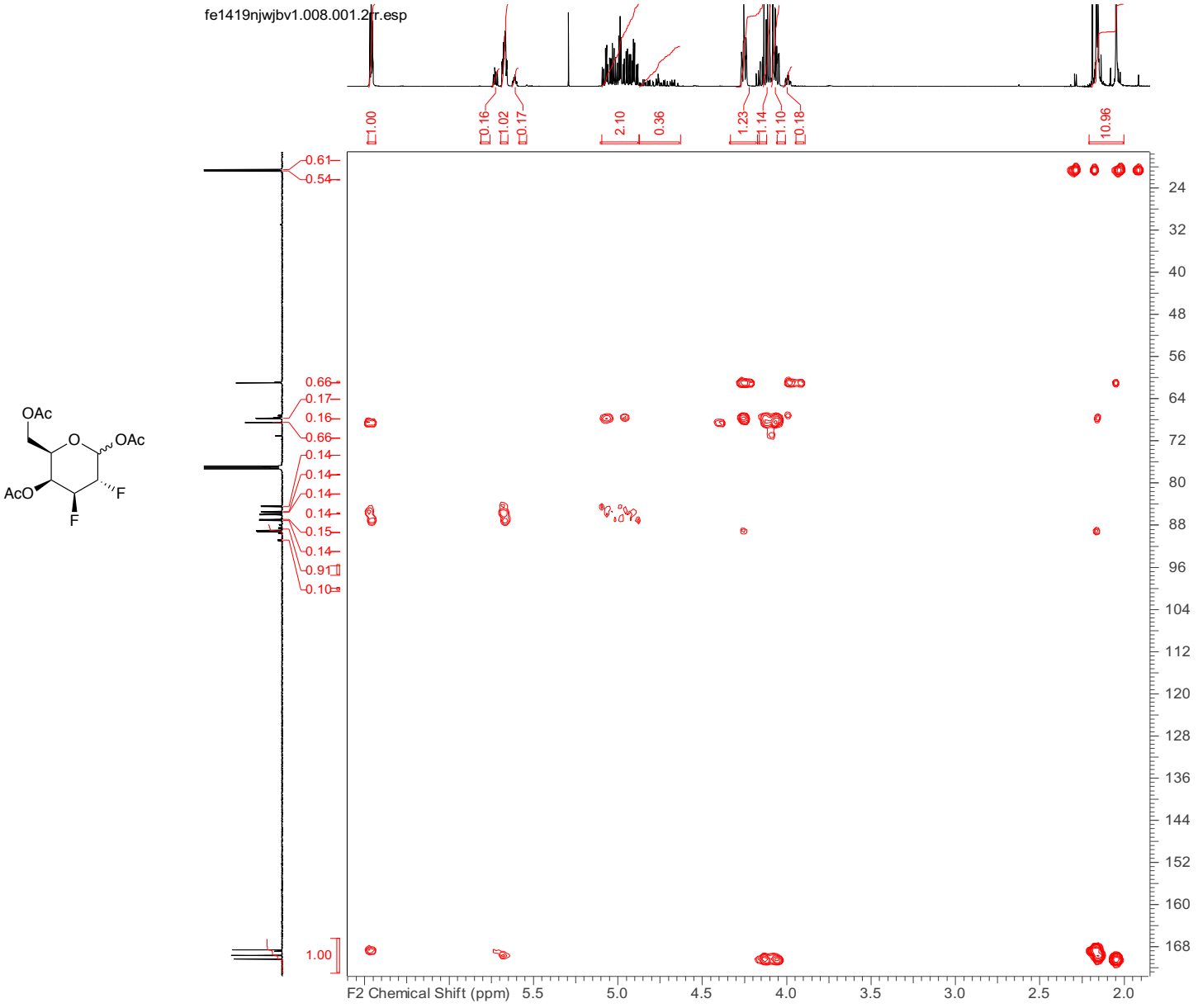




1.5.6 HSQC (500 MHz, $CDCl_3$) (compound 16b)

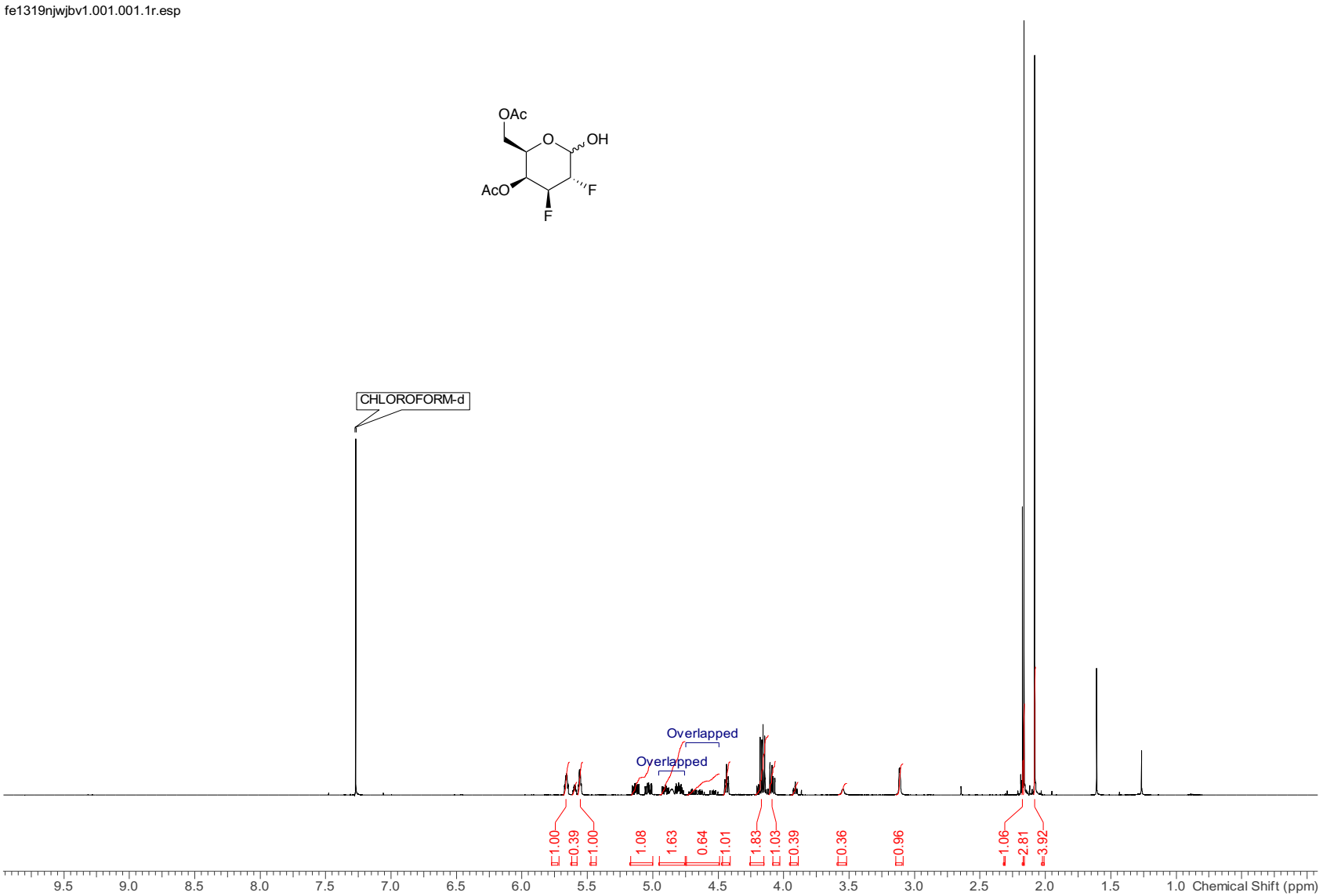


1.5.7 HMBC (500 MHz, $CDCl_3$) (compound 16b)

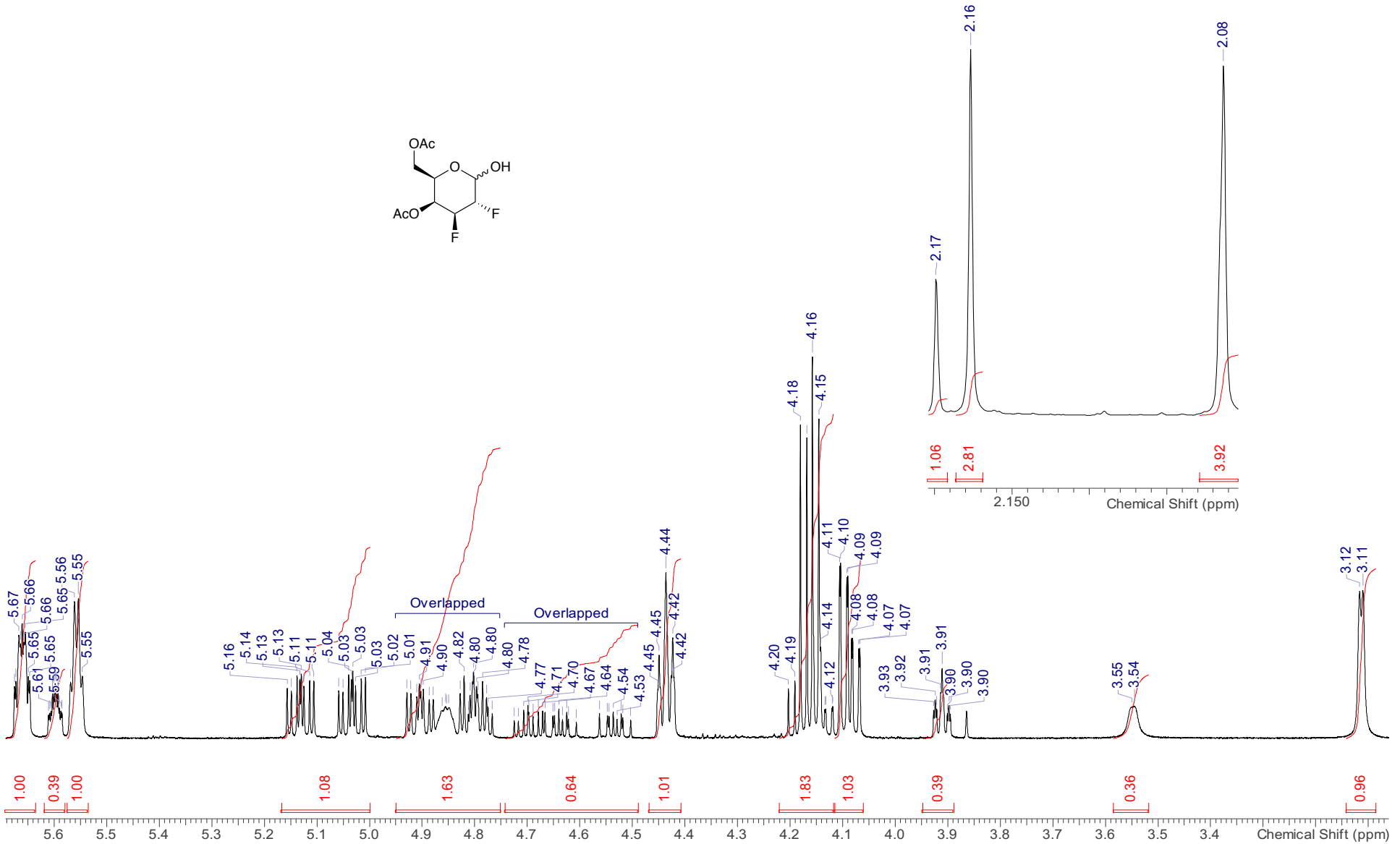


1.6 4,6-Di-*O*-Acetyl-2,3-dideoxy-2,3-difluorogalactose 16c

1.6.1 ^{1}H NMR (500 MHz, $CDCl_3$) (compound 16c)

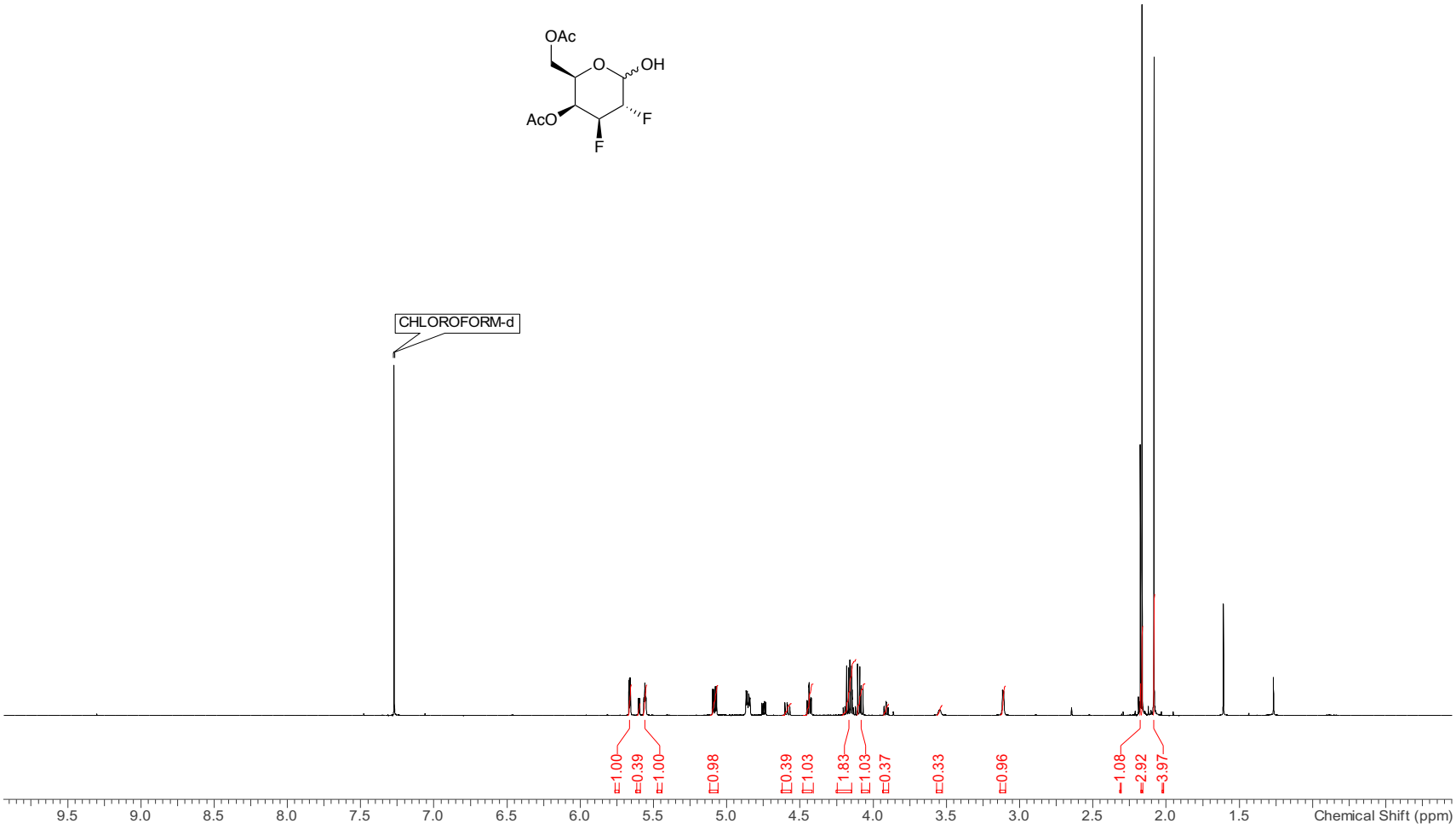


fe1319njwjbv1.001.001.1r.esp

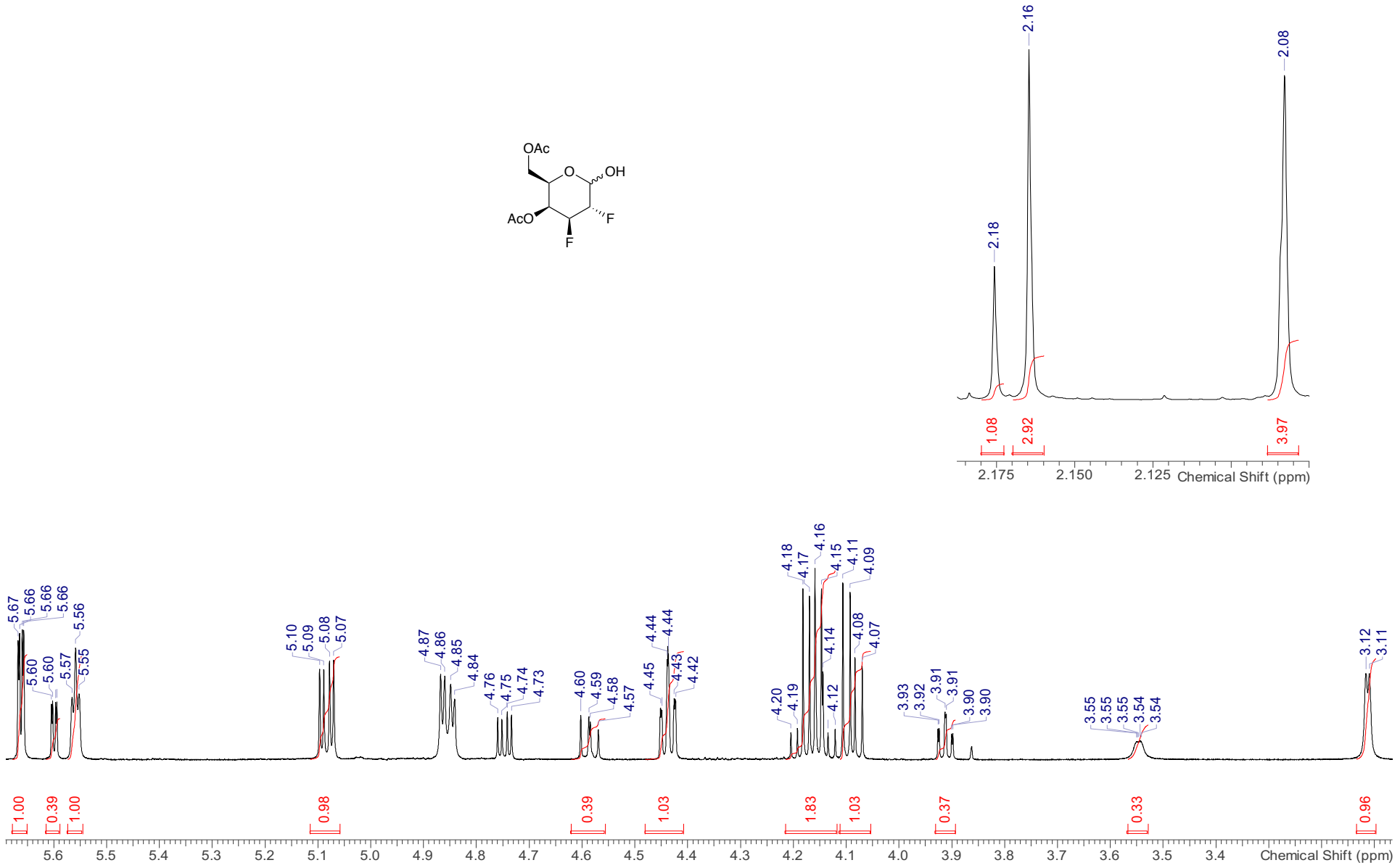


1.6.2 $^{1}H\{^{19}F\}$ NMR (500 MHz, $CDCl_3$) (compound 16c)

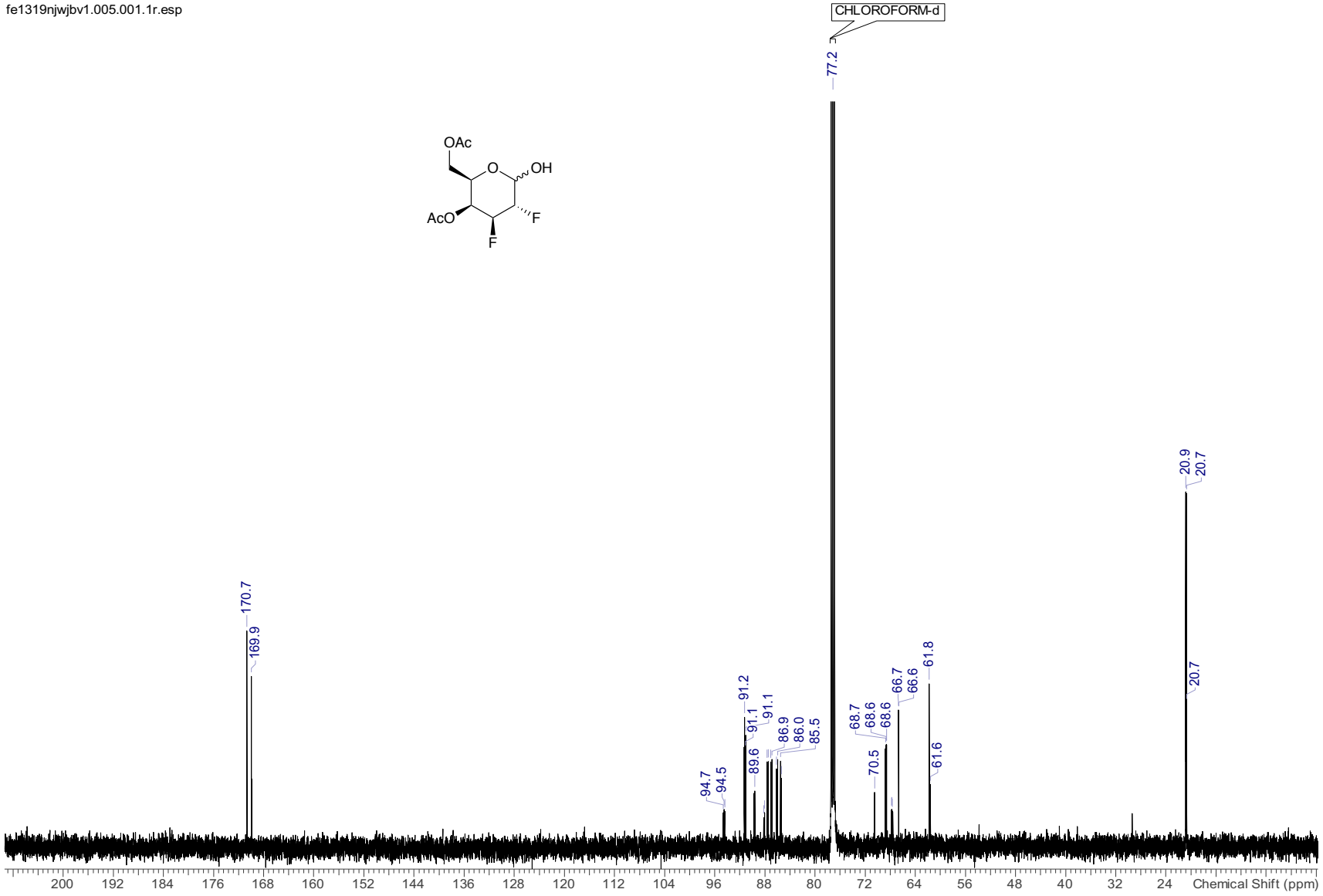
fe1319njwjbv1.004.001.1r.esp

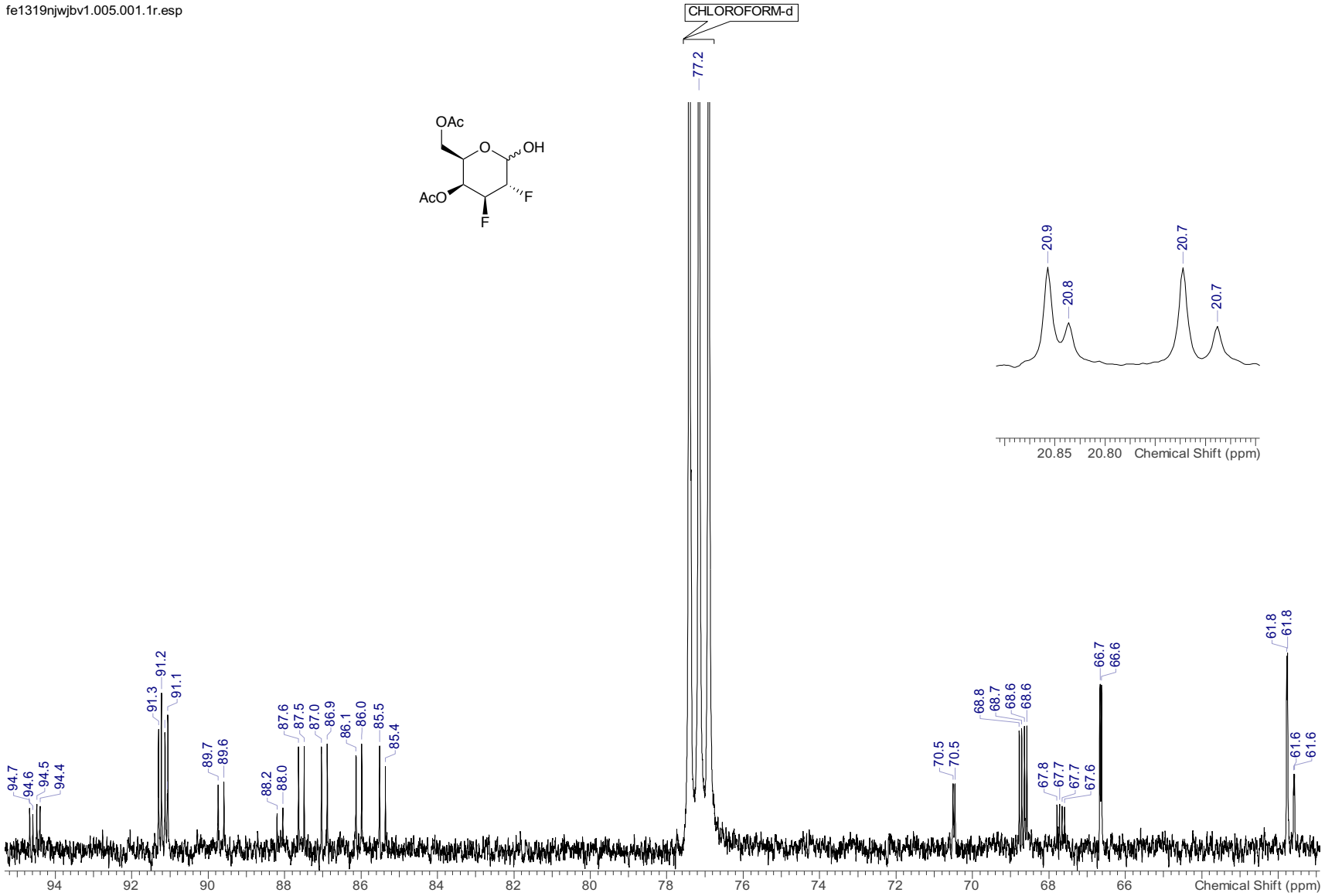


fe1319njwjbv1.004.001.1r.esp

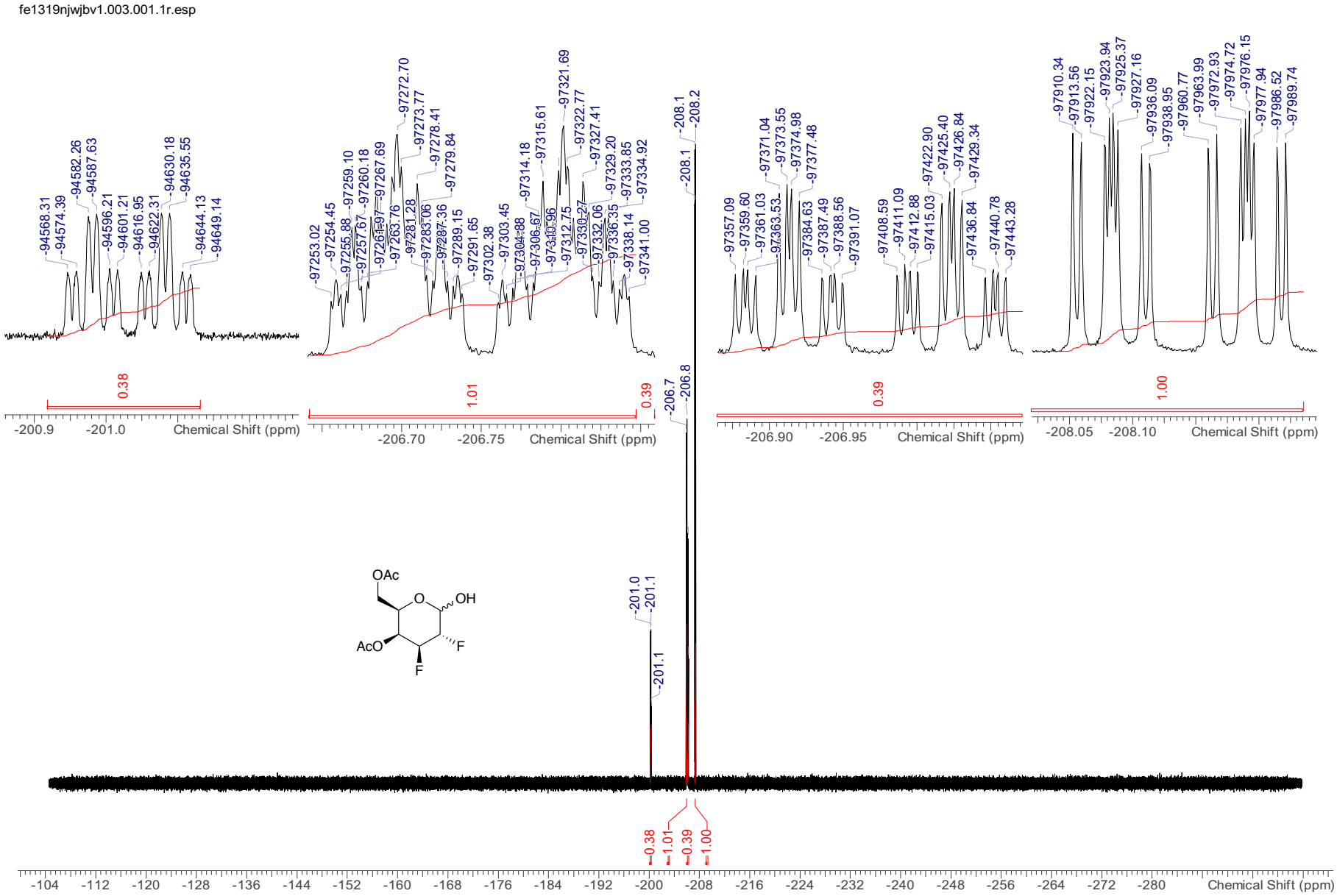


1.6.3 ^{13}C NMR (126 MHz, $CDCl_3$) (compound 16c)




fe1319njwjbv1.005.001.1r.esp
CHLOROFORM-d
77.2
OAc
O
OH
AcO
F
F
20.9
20.8
20.7
20.7
20.85
20.80
Chemical Shift (ppm)
94.7
94.6
94.5
94.4
91.3
91.2
91.1
89.7
89.6
88.2
88.0
87.6
87.5
87.0
86.9
86.1
86.0
85.5
85.4
70.5
70.5
68.8
68.7
68.6
68.6
67.8
67.7
67.7
67.6
66.7
66.6
61.8
61.8
61.6
61.6
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
Chemical Shift (ppm)

1.6.4 ^{19}F NMR (471 MHz, $CDCl_3$) (compound 16c)



1.6.5 ^{19}F NMR (471 MHz, $CDCl_3$) (compound 16c)

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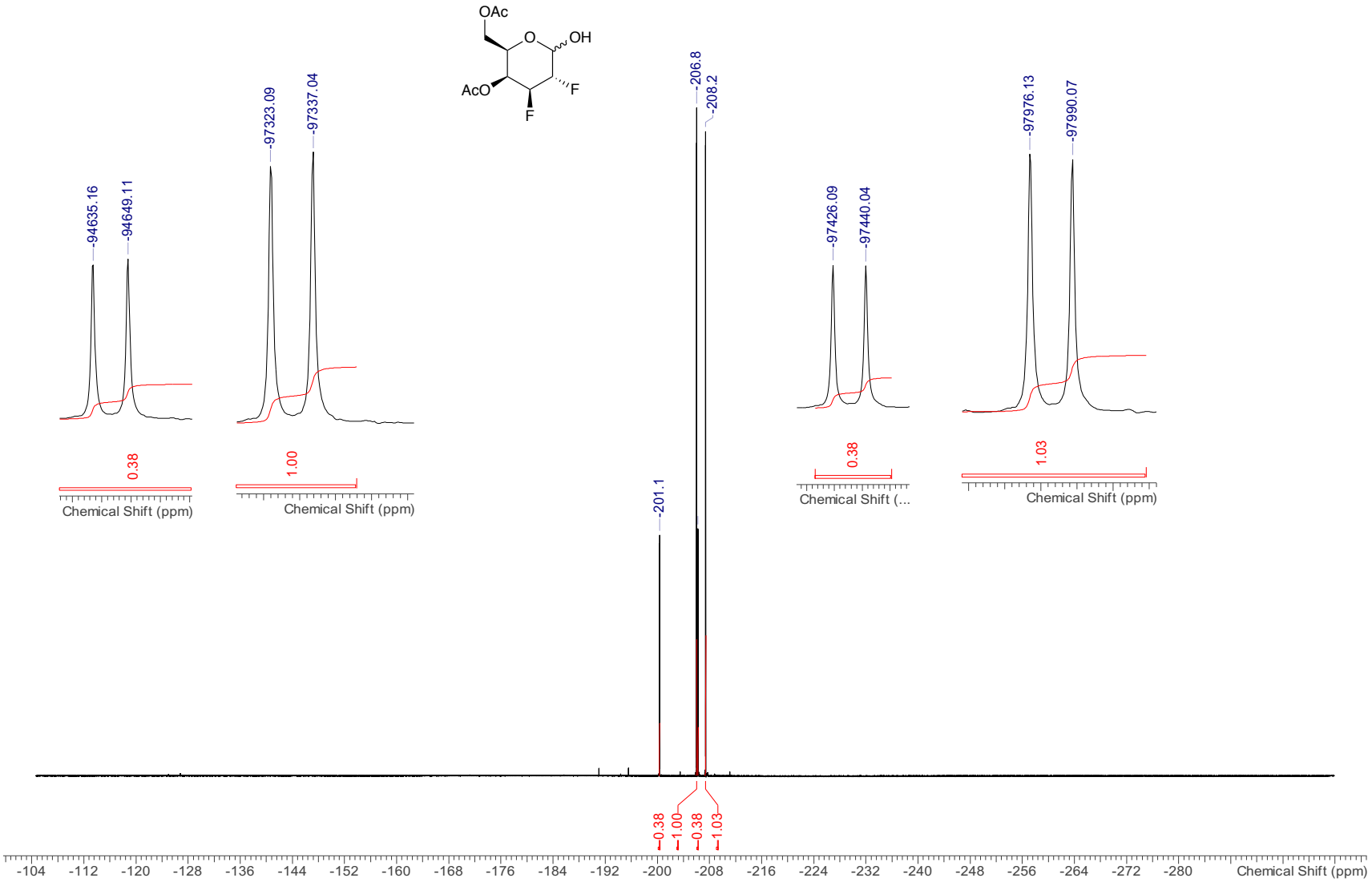
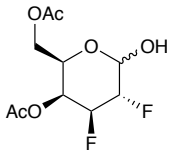
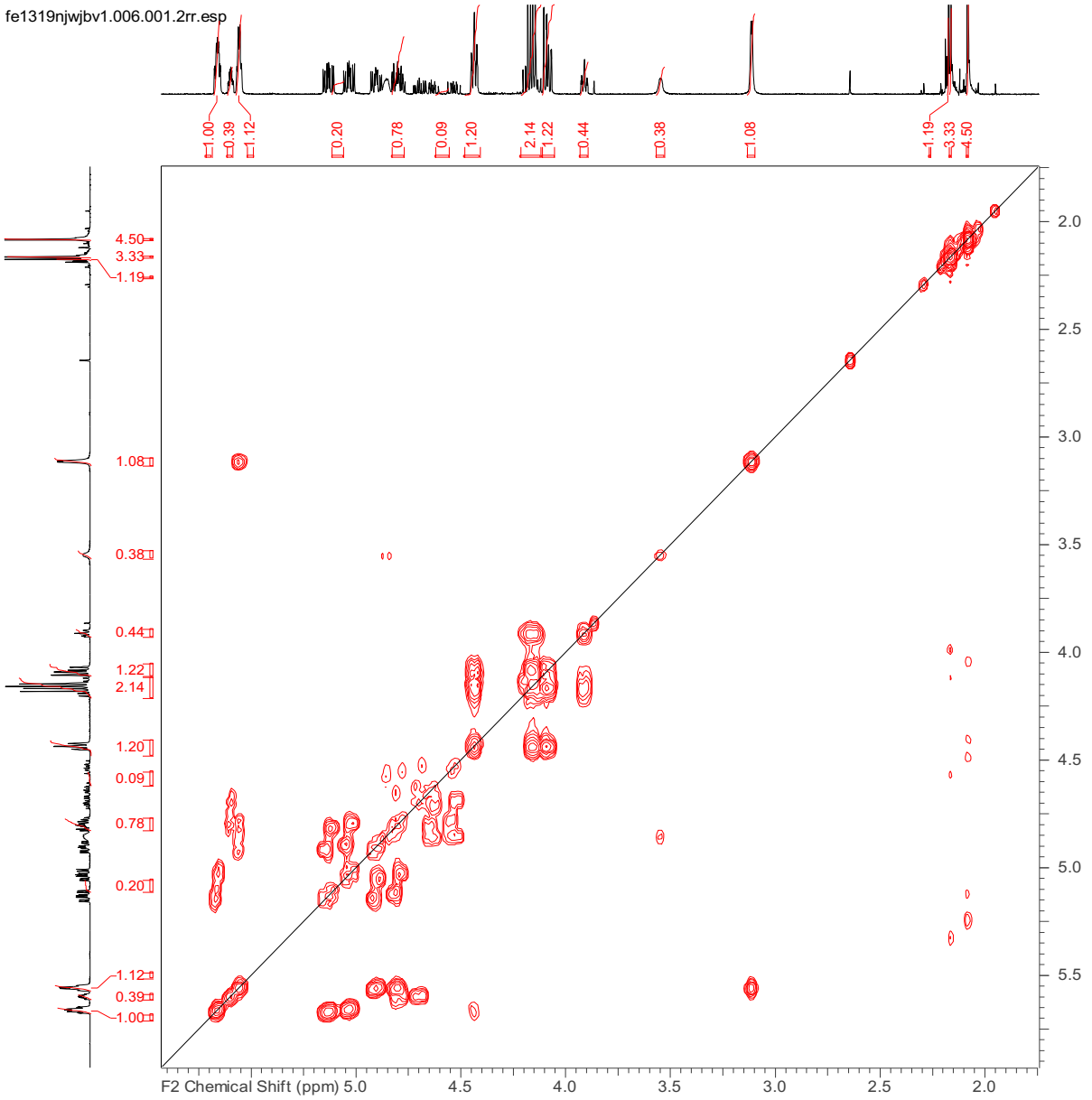
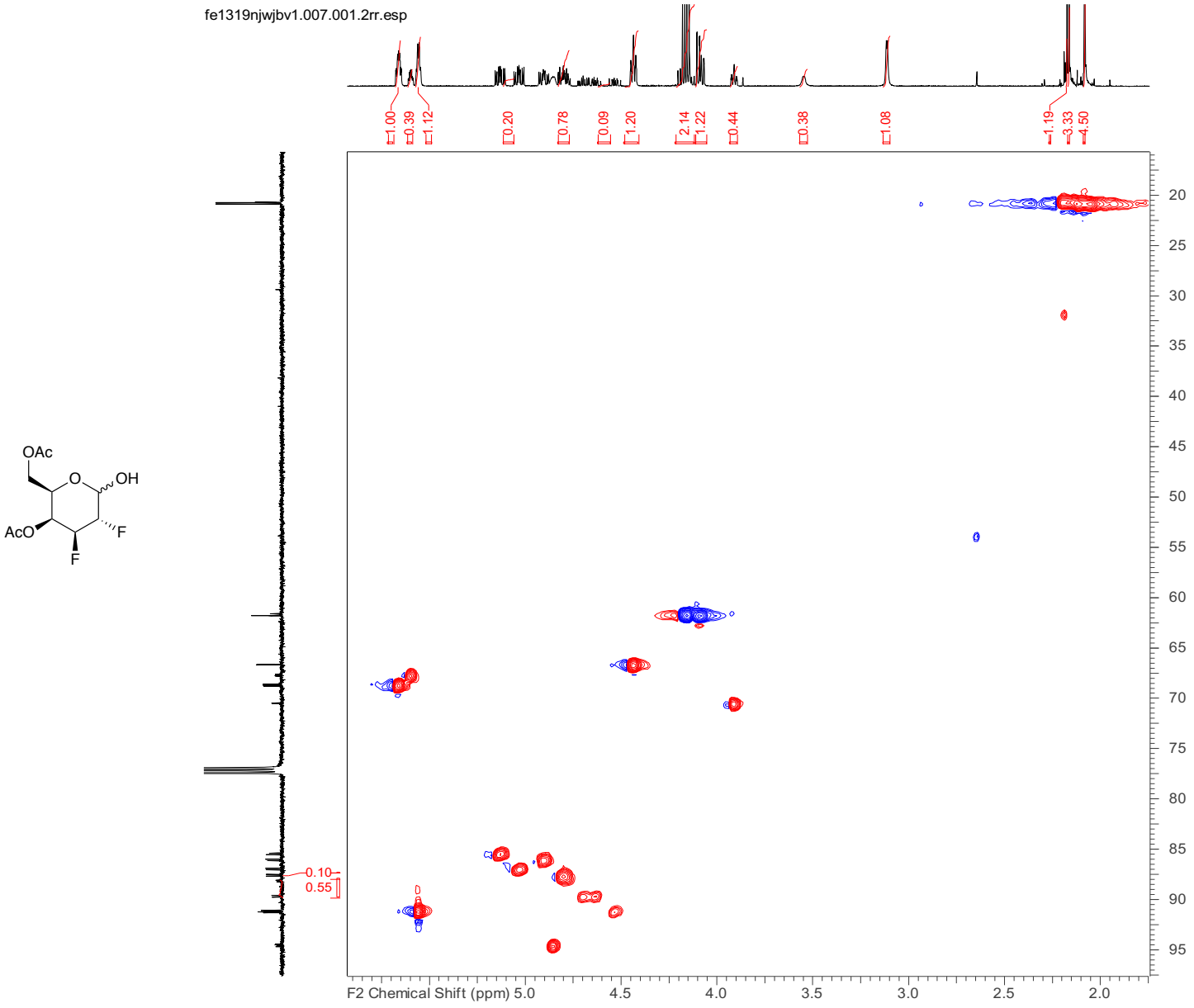


1.6.6 COSY ^{1}H-^{1}H (500 MHz, $CDCl_3$) (compound 16c)

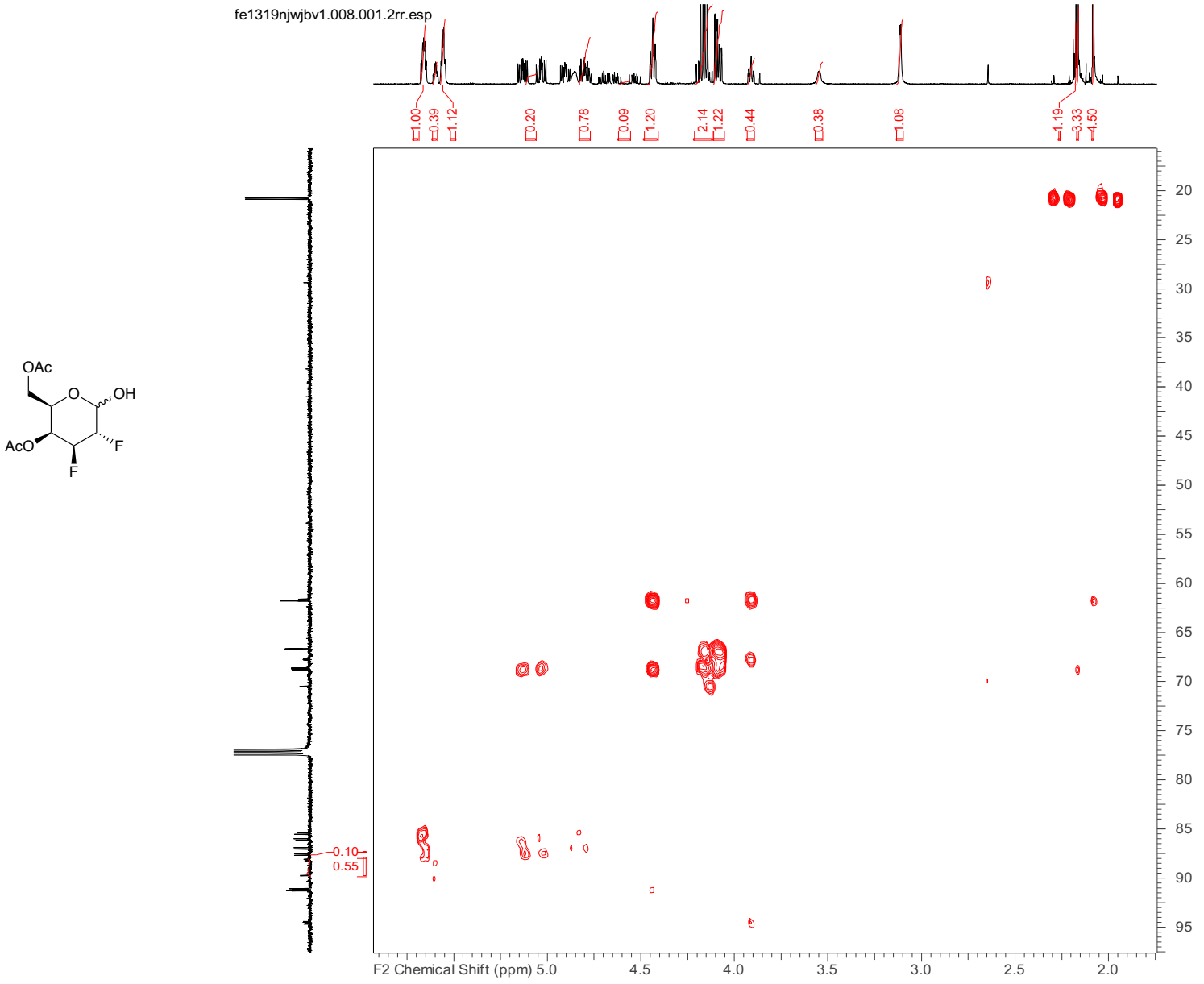




1.6.7 HSQC (500 MHz, $CDCl_3$) (compound 16c)



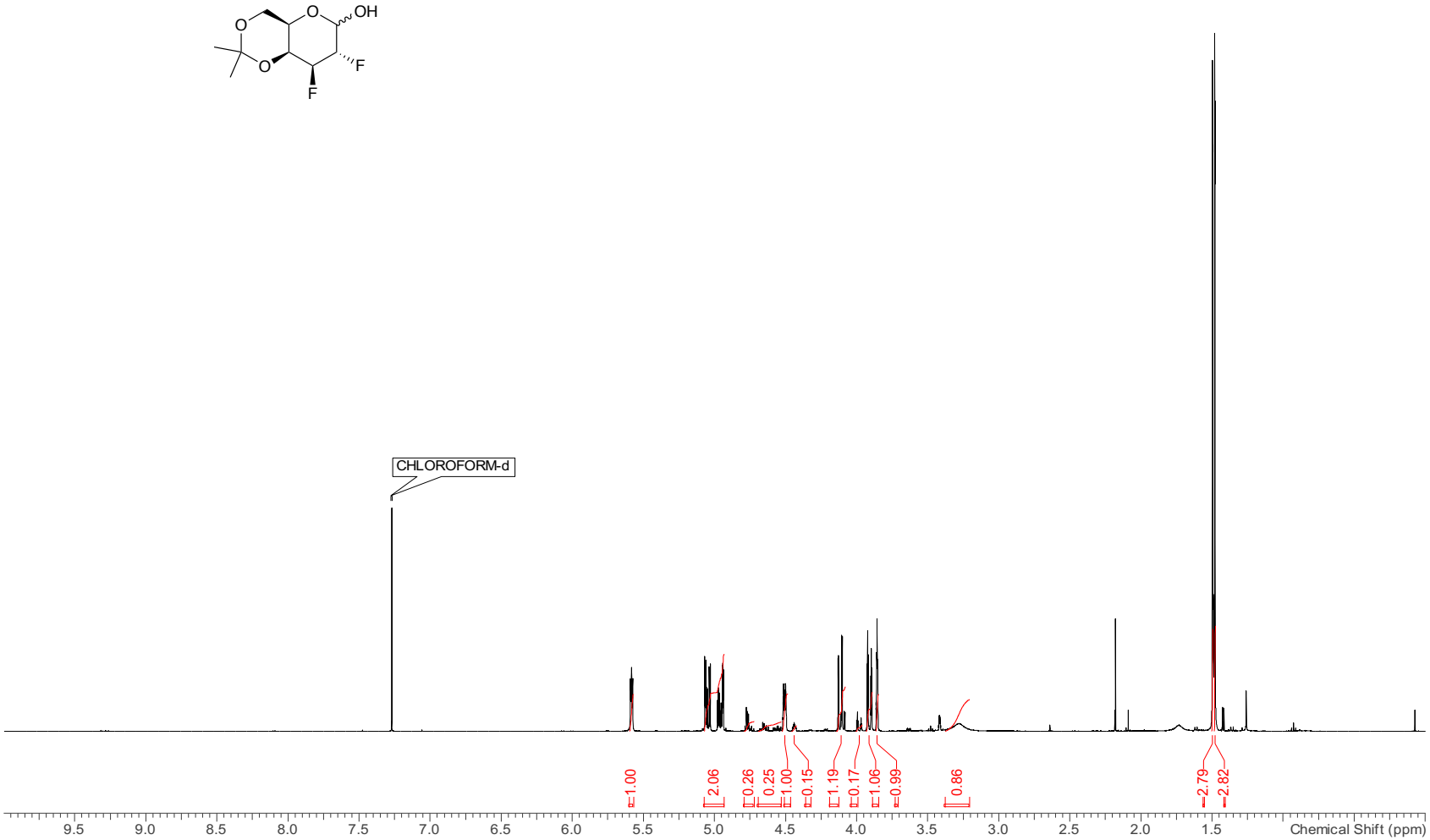
1.6.8 HMBC (500 MHz, $CDCl_3$) (compound 16c)



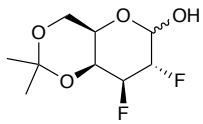
1.7 4,6-Di-*O*-isopropylidene-2,3-dideoxy-2,3-difluoro-D-galactopyranose 16d

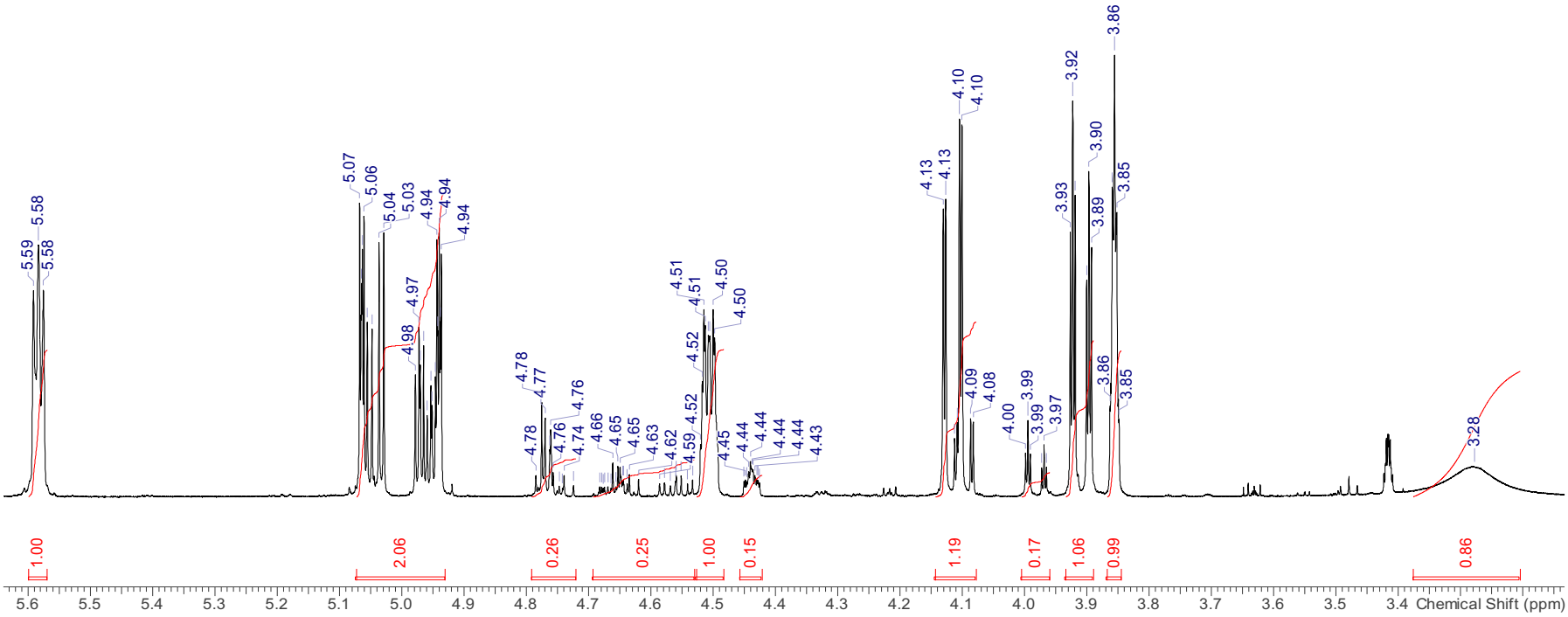
1.7.1 ^{1}H NMR (500 MHz, $CDCl_3$) (compound 16d)

fe1916njwjm1.001.001.1r.esp



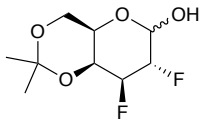
fe1916njwjm1.001.001.1r.esp

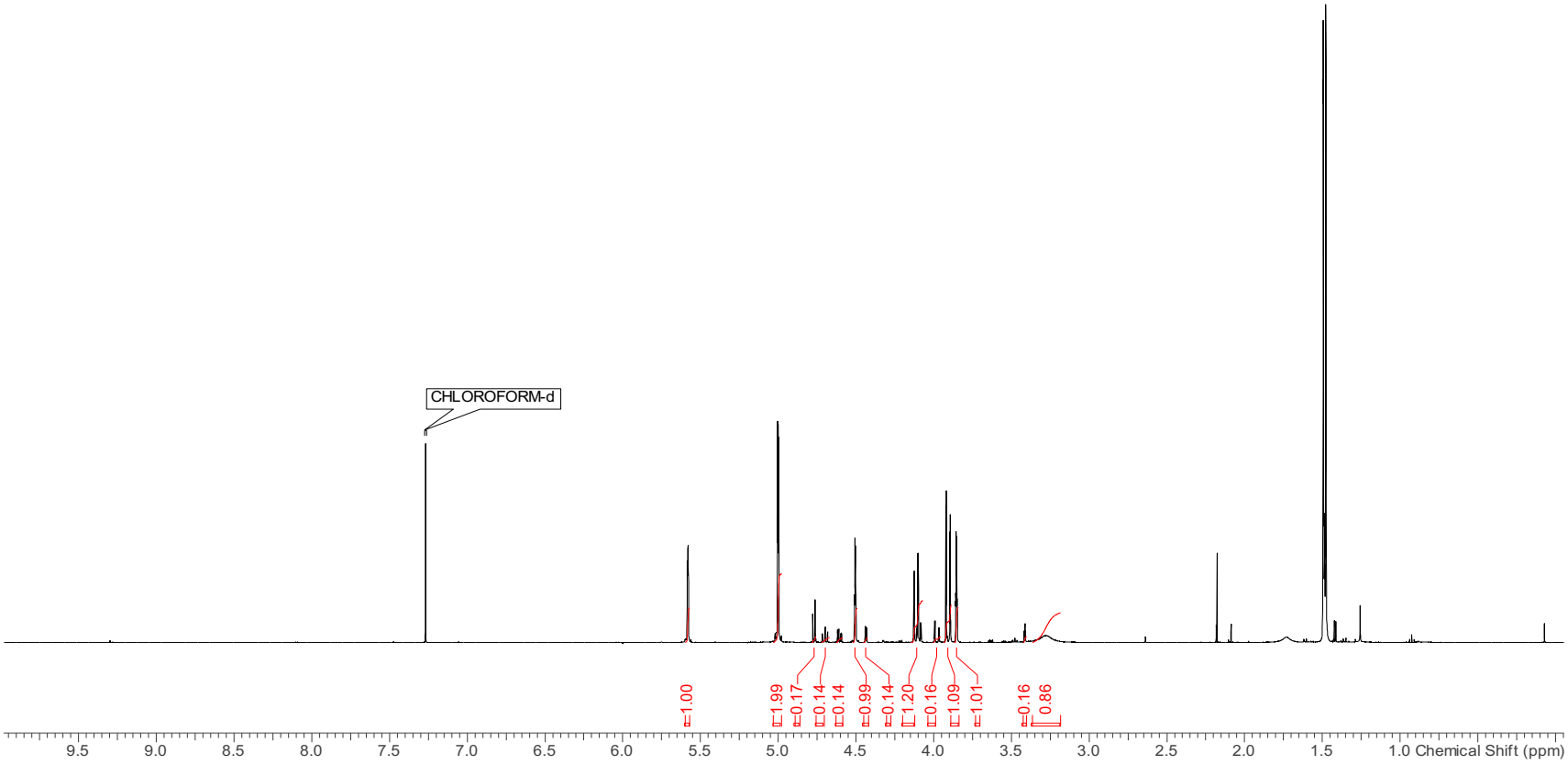




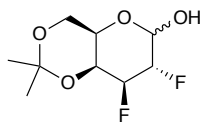
1.7.2 $^{1}H\{^{19}F\}$ NMR (500 MHz, $CDCl_3$) (compound 16d)

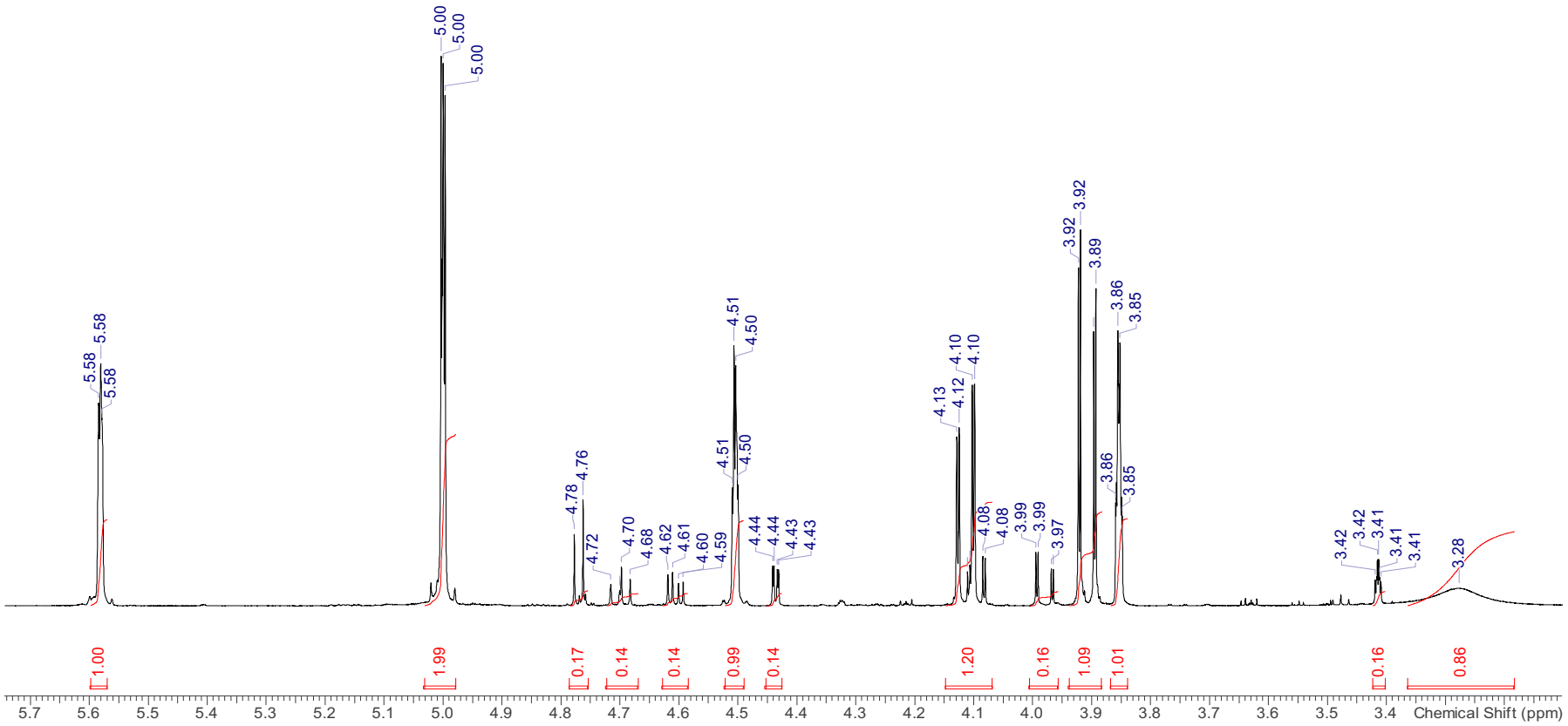
fe1916njwjm1.003.001.1r.esp





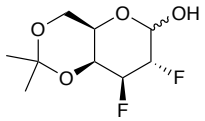
fe1916njwjm1.003.001.1r.esp

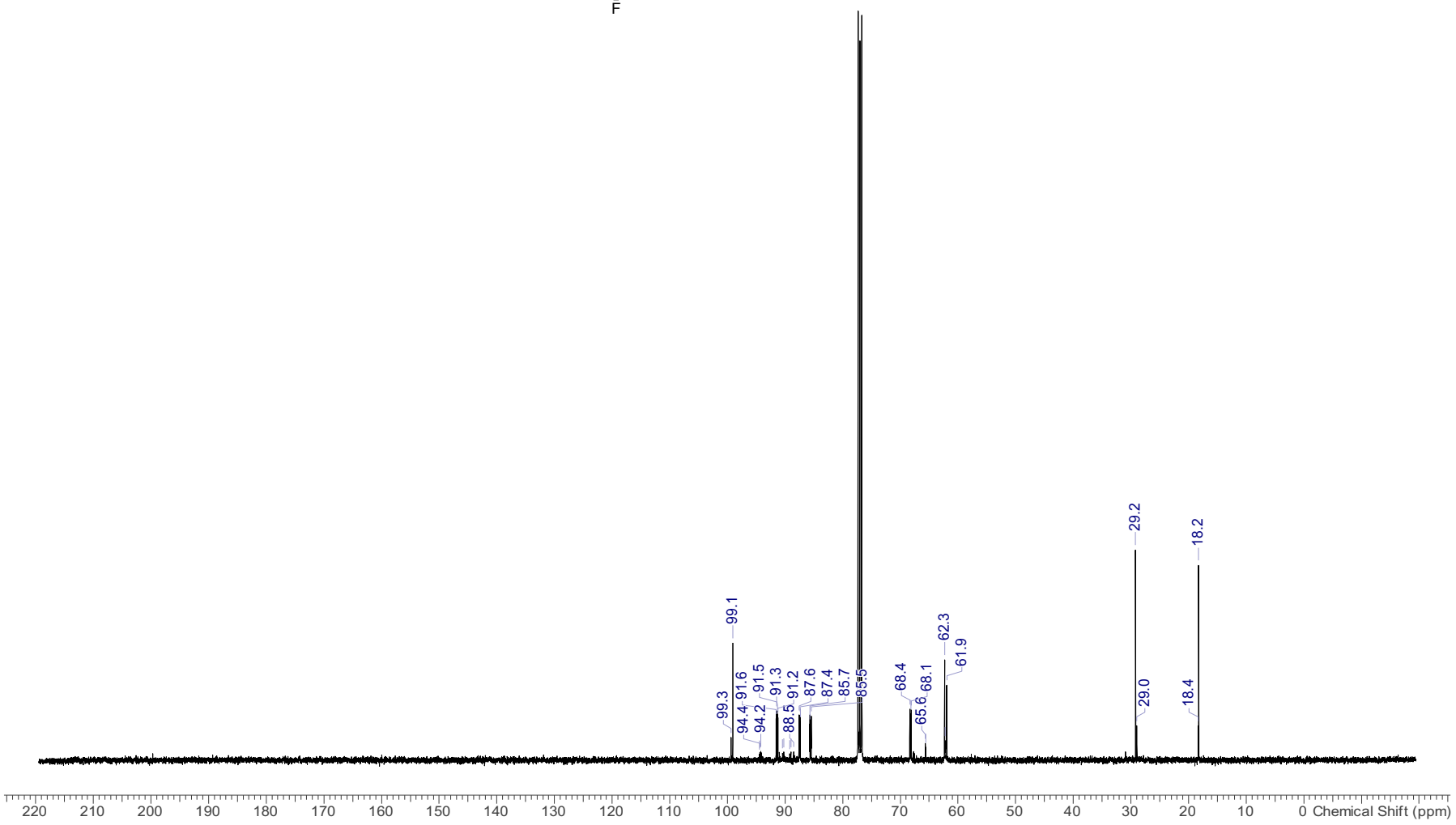


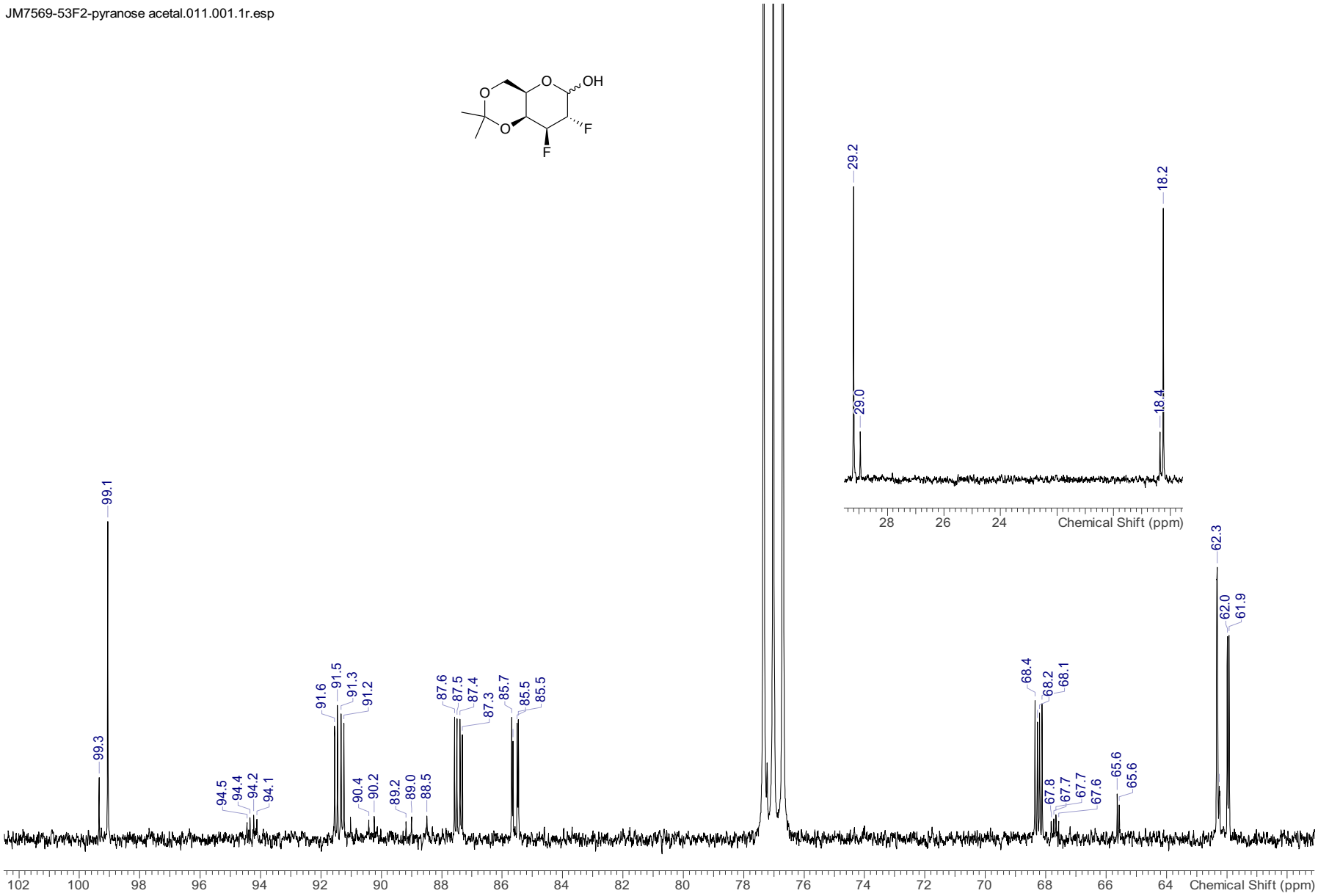


1.7.3 ^{13}C NMR (100 MHz, $CDCl_3$) (compound 16d)

JM7569-53F2-pyranose acetal.011.001.1r.esp






JM7569-53F2-pyranose acetal.011.001.1r.esp
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O
OH
F
F
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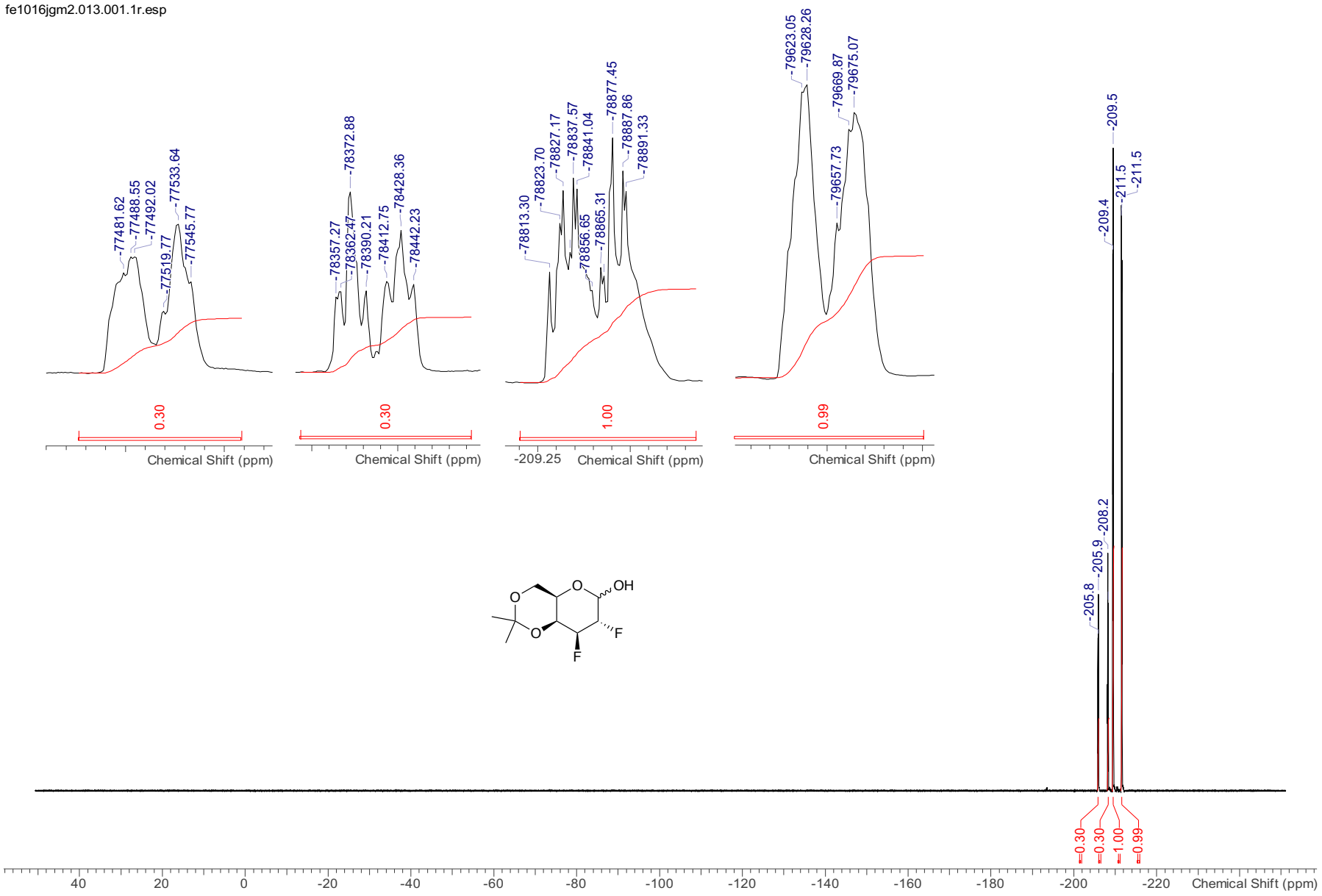
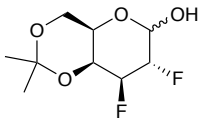
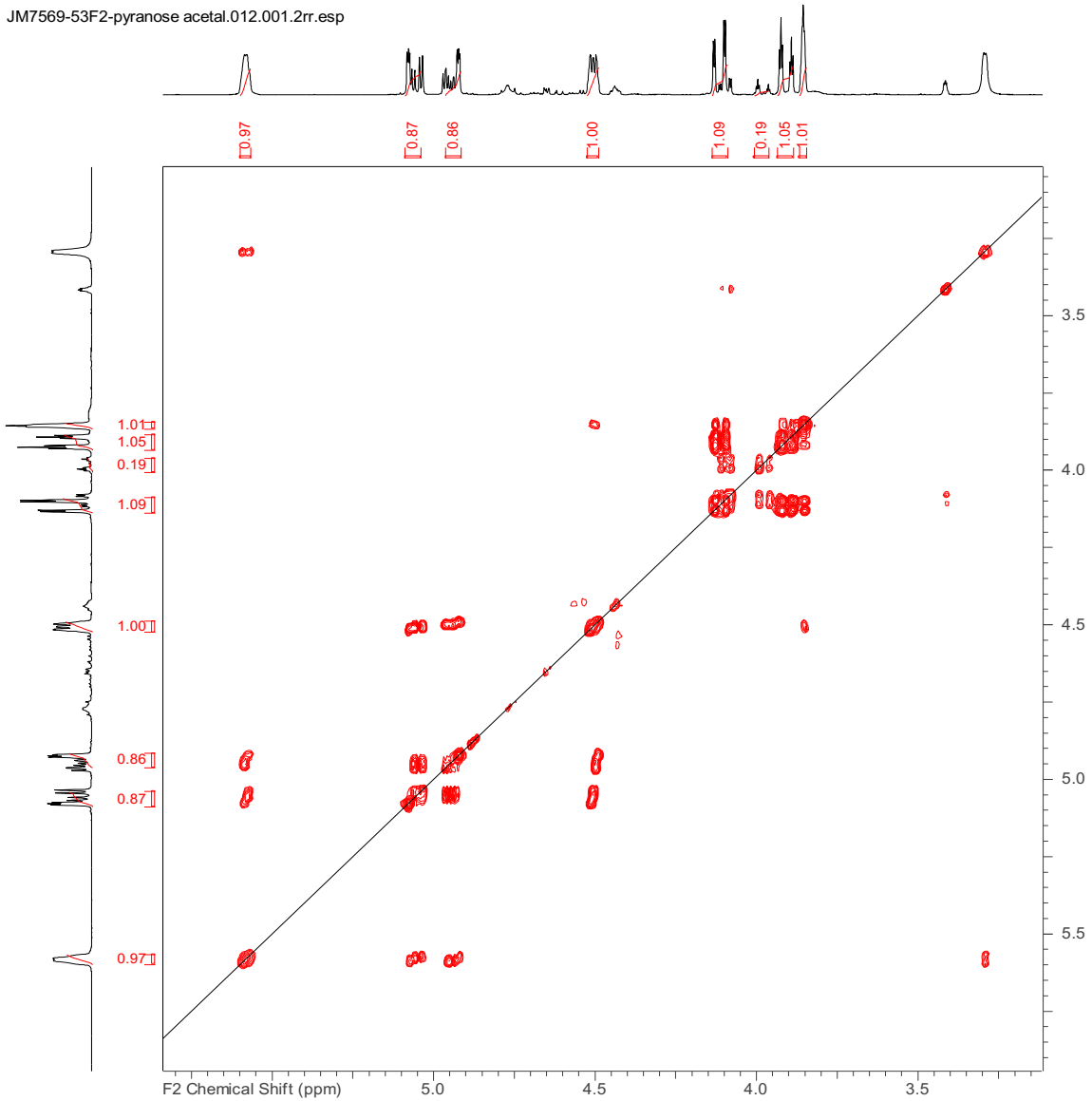
18.2
18.4
28
26
24
Chemical Shift (ppm)
99.1
99.3
94.5
94.4
94.2
94.1
91.6
91.5
91.3
91.2
90.4
90.2
89.2
89.0
88.5
87.6
87.5
87.4
87.3
85.7
85.5
85.5
68.4
68.2
68.1
67.8
67.7
67.7
67.6
65.6
65.6
62.3
62.0
61.9
102
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
Chemical Shift (ppm)

1.7.4 ^{19}F NMR (376 MHz, $CDCl_3$) (compound 16d)

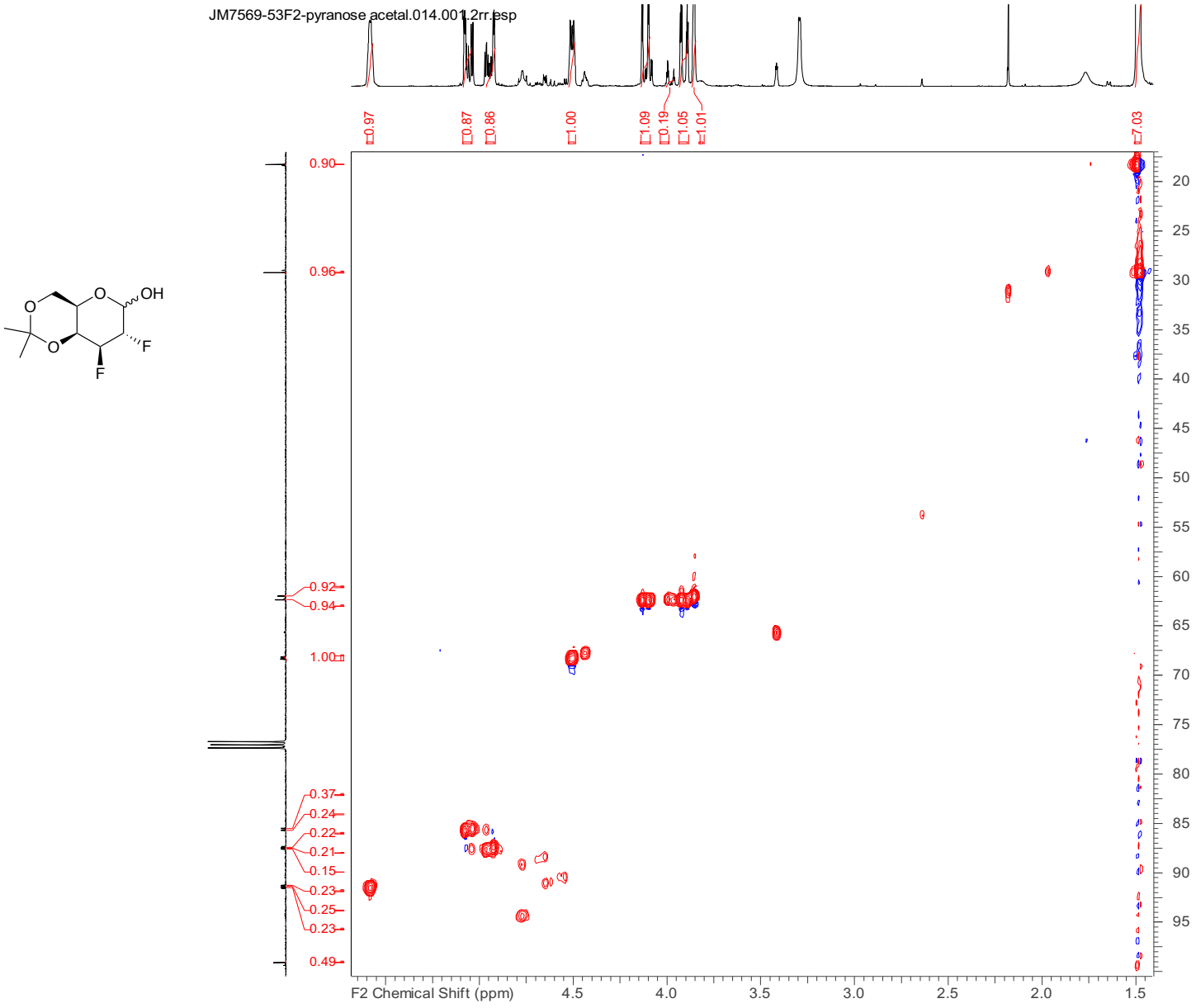


1.7.5 COSY ^{1}H-^{1}H (400 MHz, $CDCl_3$) (compound 16d)

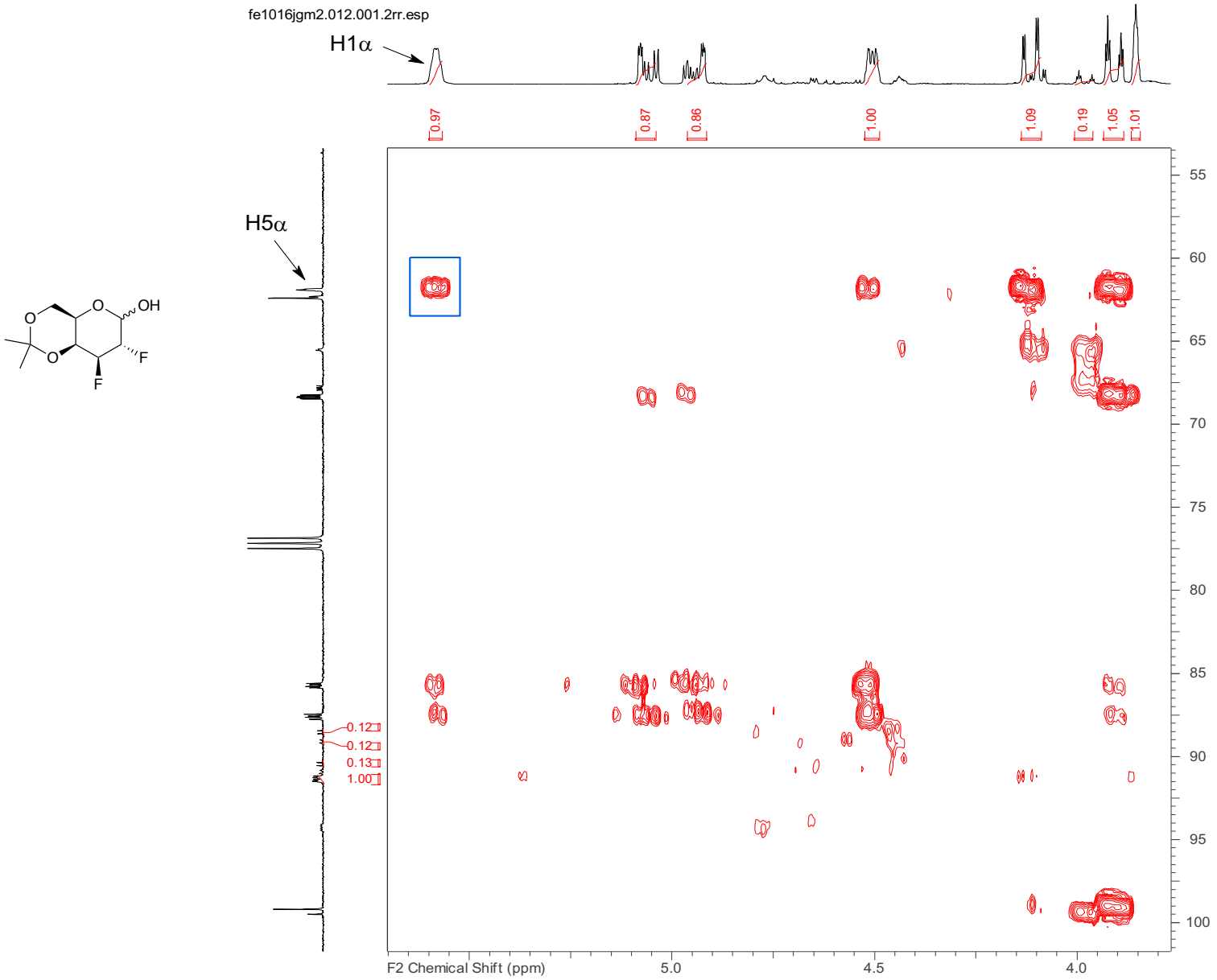




1.7.6 HSQC (400 MHz, $CDCl_3$) (compound 16d)

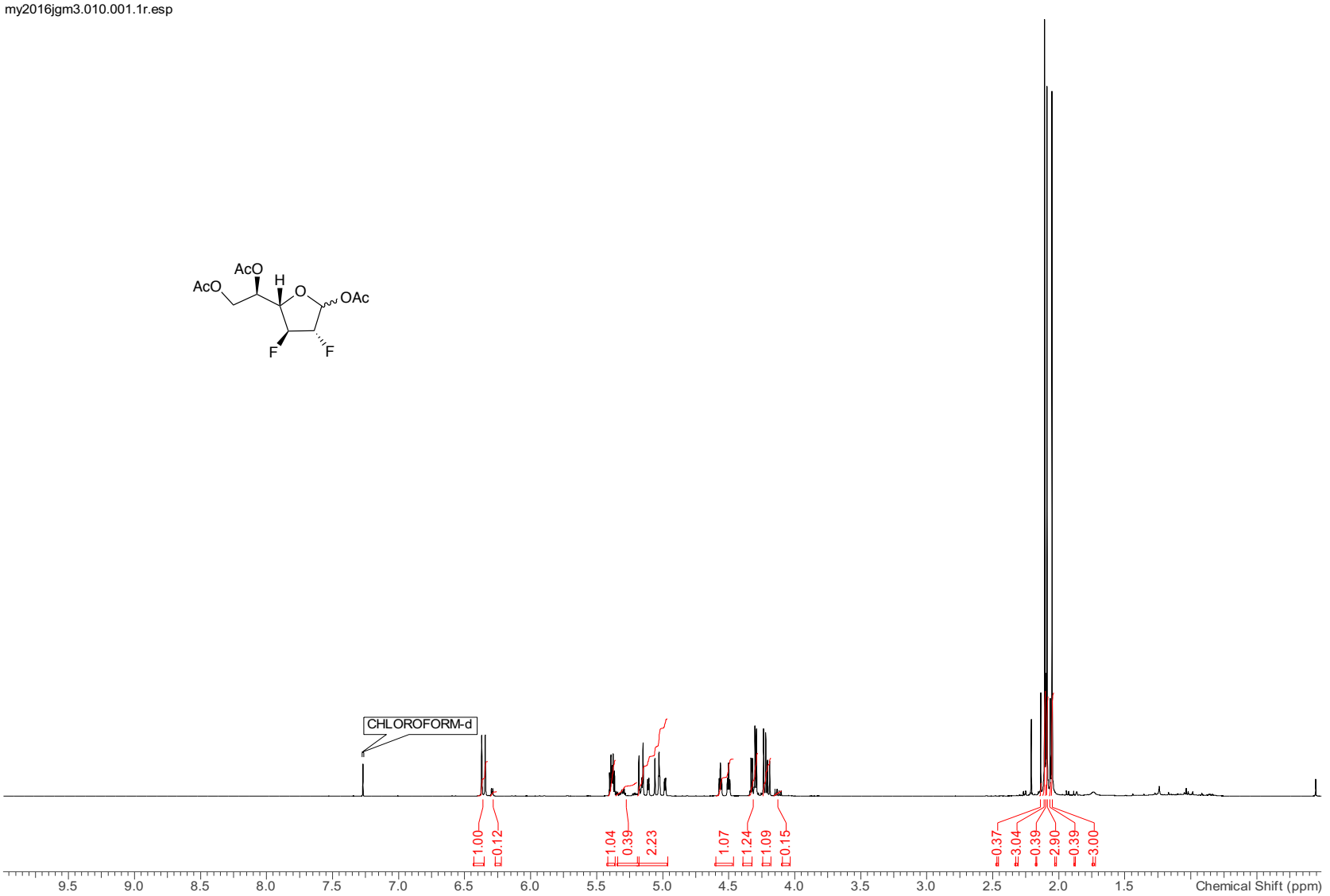


1.7.7 HMBC (400 MHz, $CDCl_3$) (compound 16d)



1.8 1,5,6-Tri-*O*-acetyl-2,3-dideoxy-2,3-difluoro-D-galactofuranose 17b

1.8.1 ^{1}H NMR (400 MHz, $CDCl_3$) (compound 17b)



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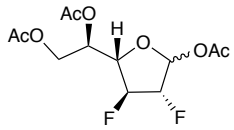
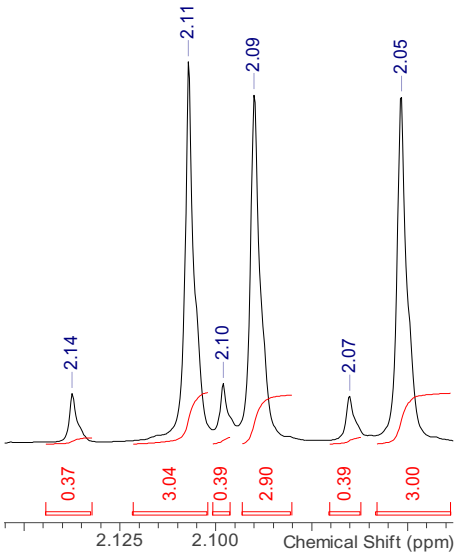
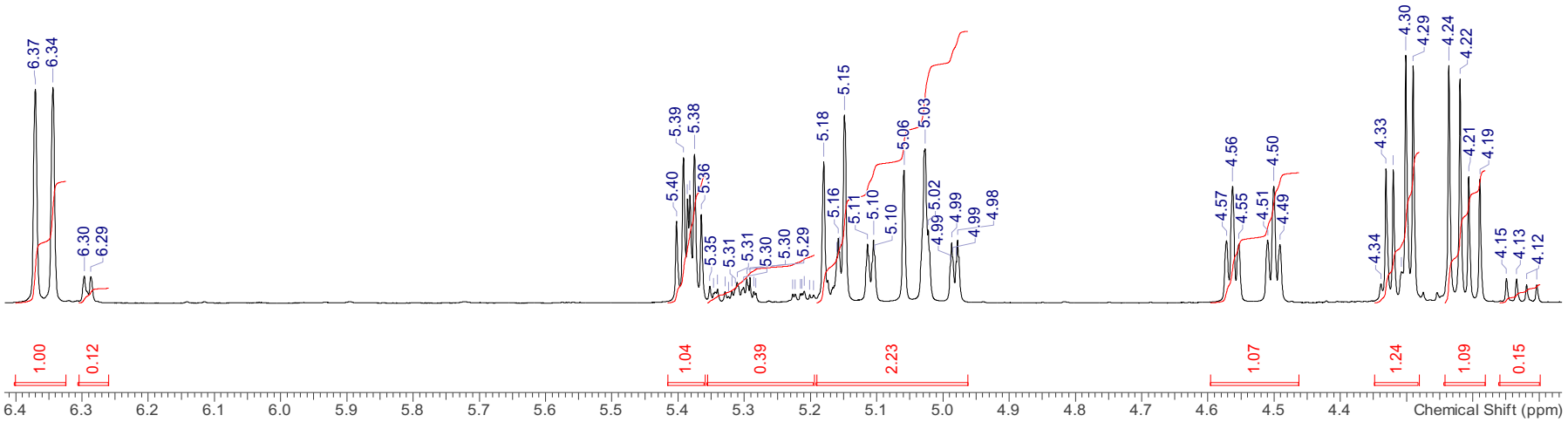
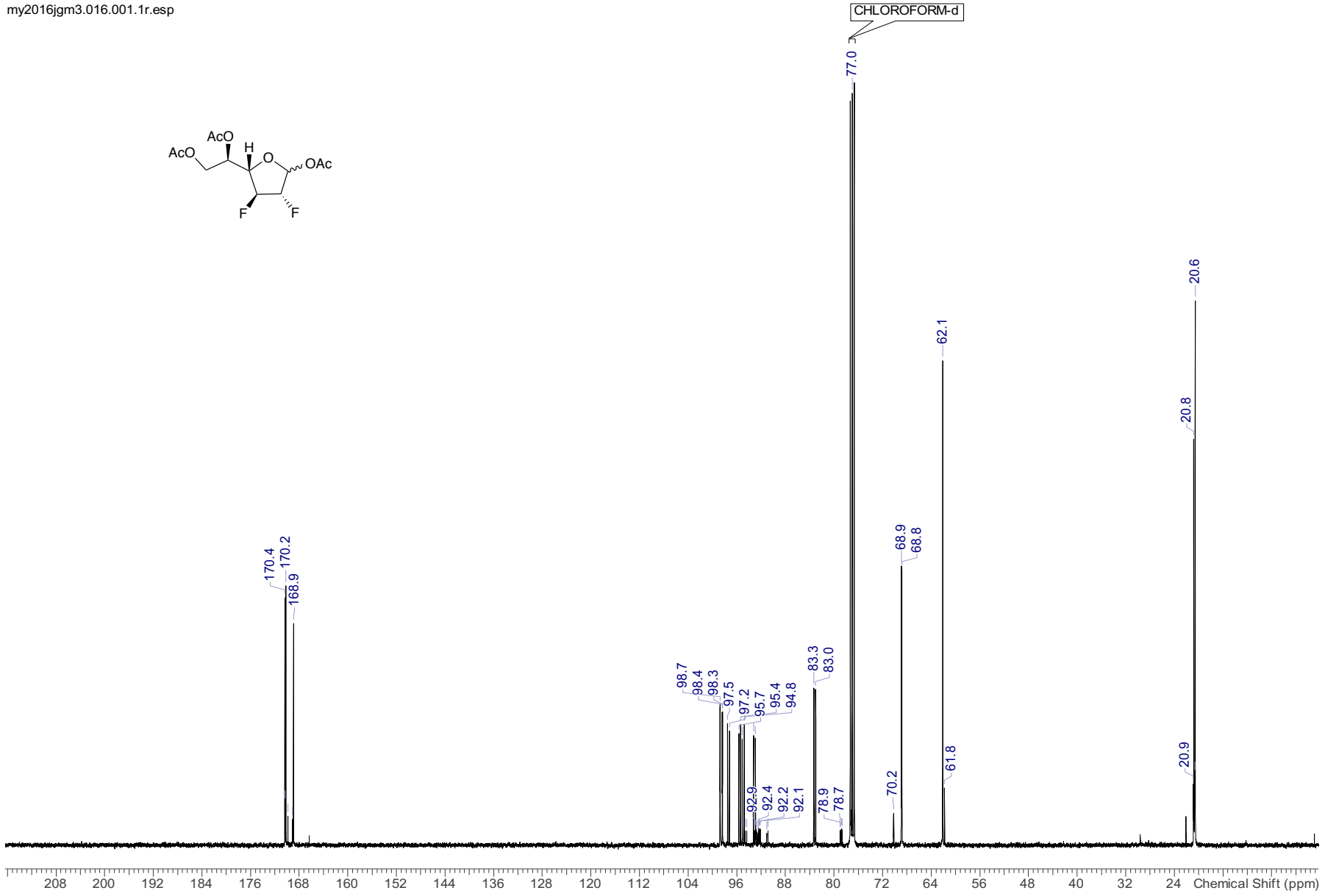


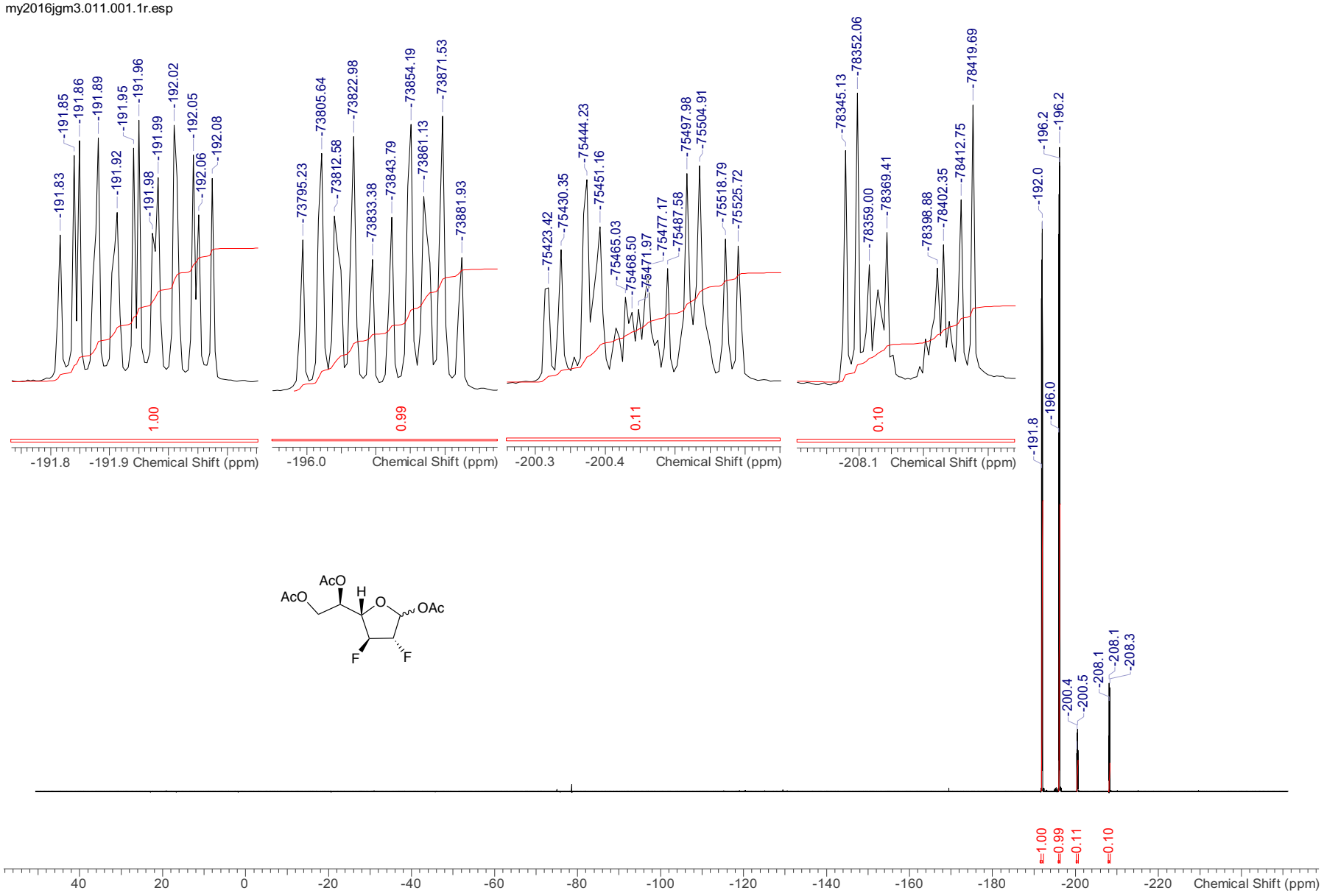




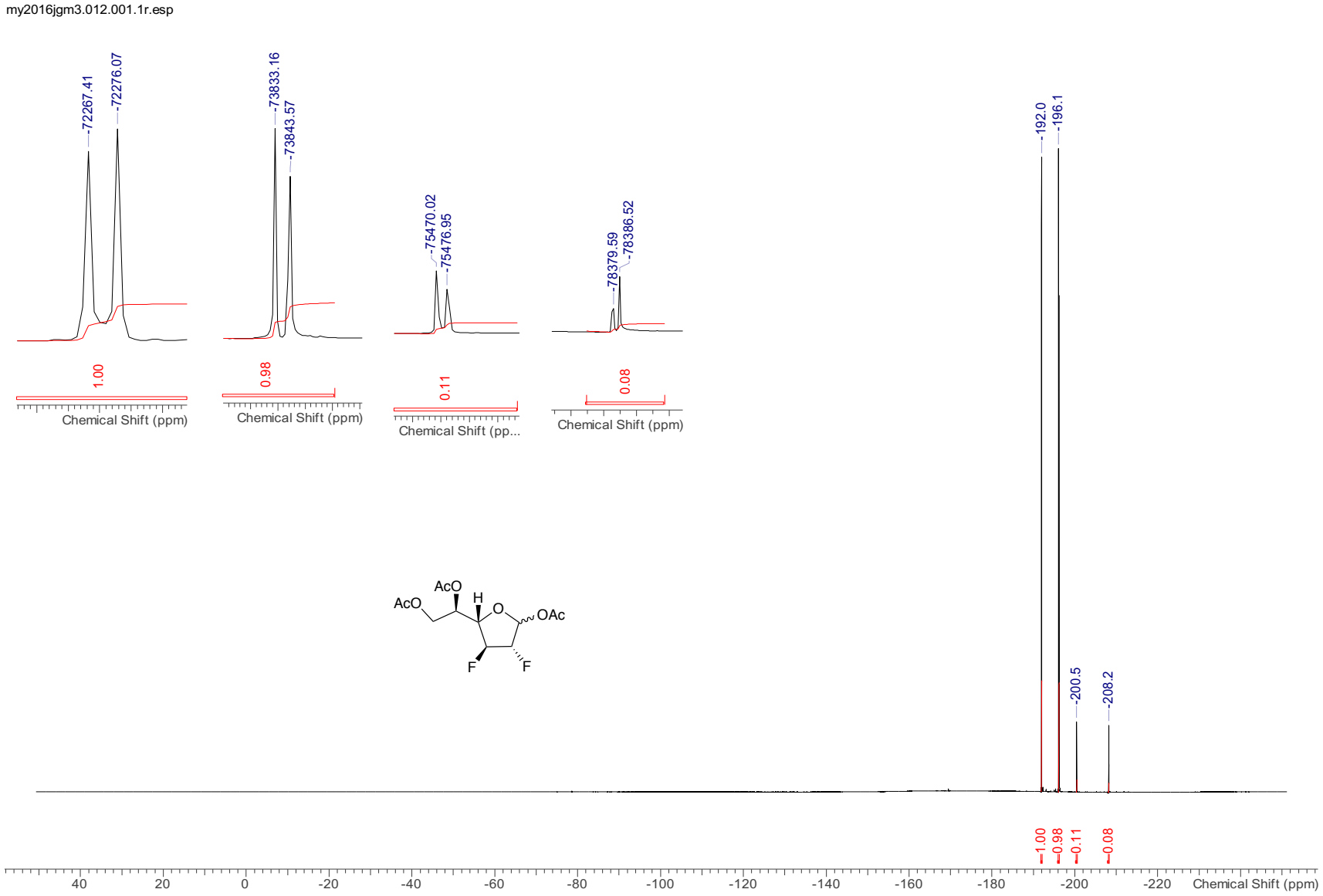
1.8.2 ^{13}C NMR (100 MHz, $CDCl_3$) (compound 17b)



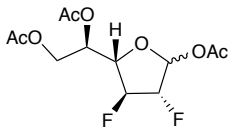
1.8.3 ^{19}F NMR (376 MHz, $CDCl_3$) (compound 17b)

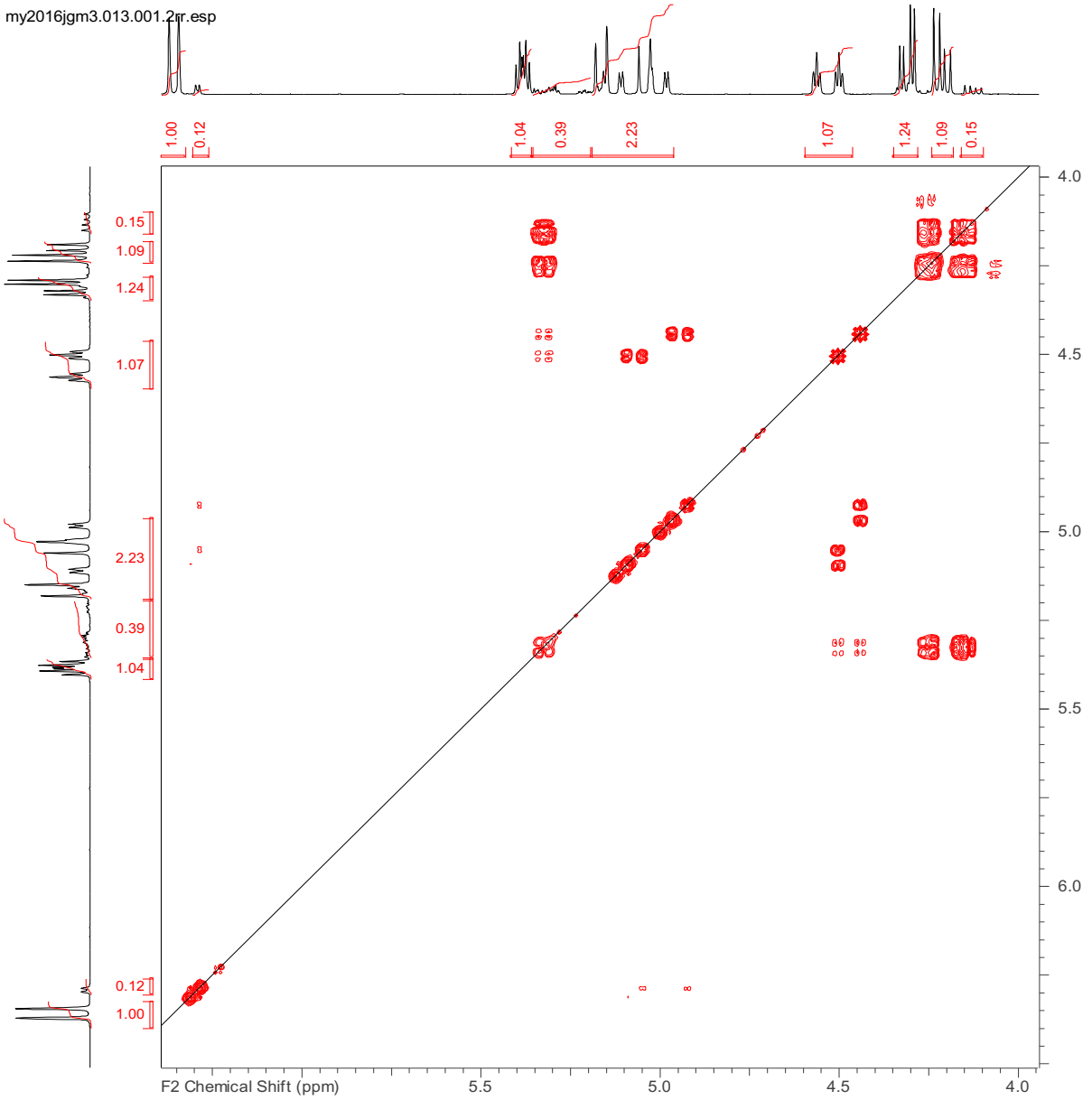


1.8.4 $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) (compound 17b)

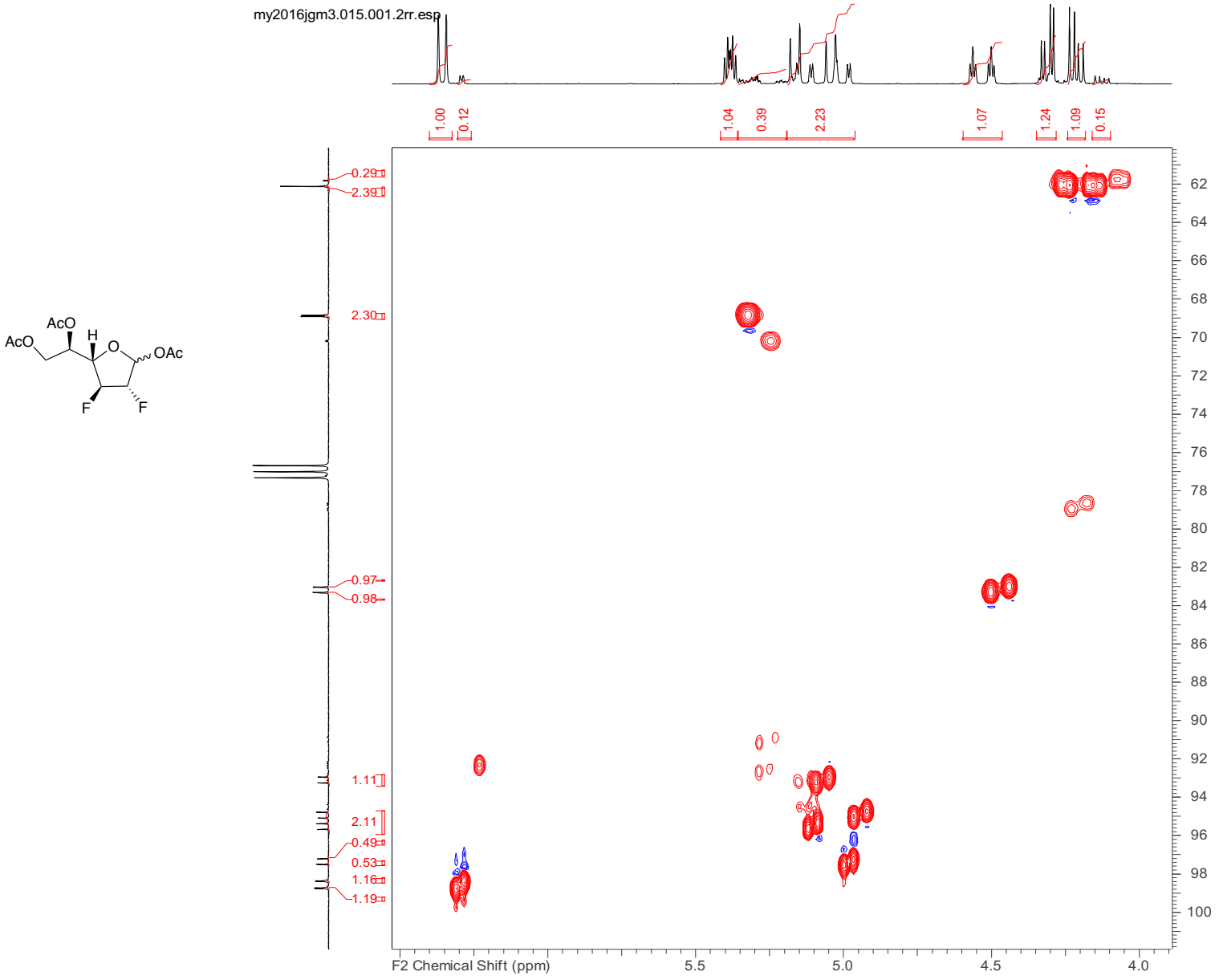


1.8.5 COSY ^{1}H-^{1}H (400 MHz, $CDCl_3$) (compound 17b)

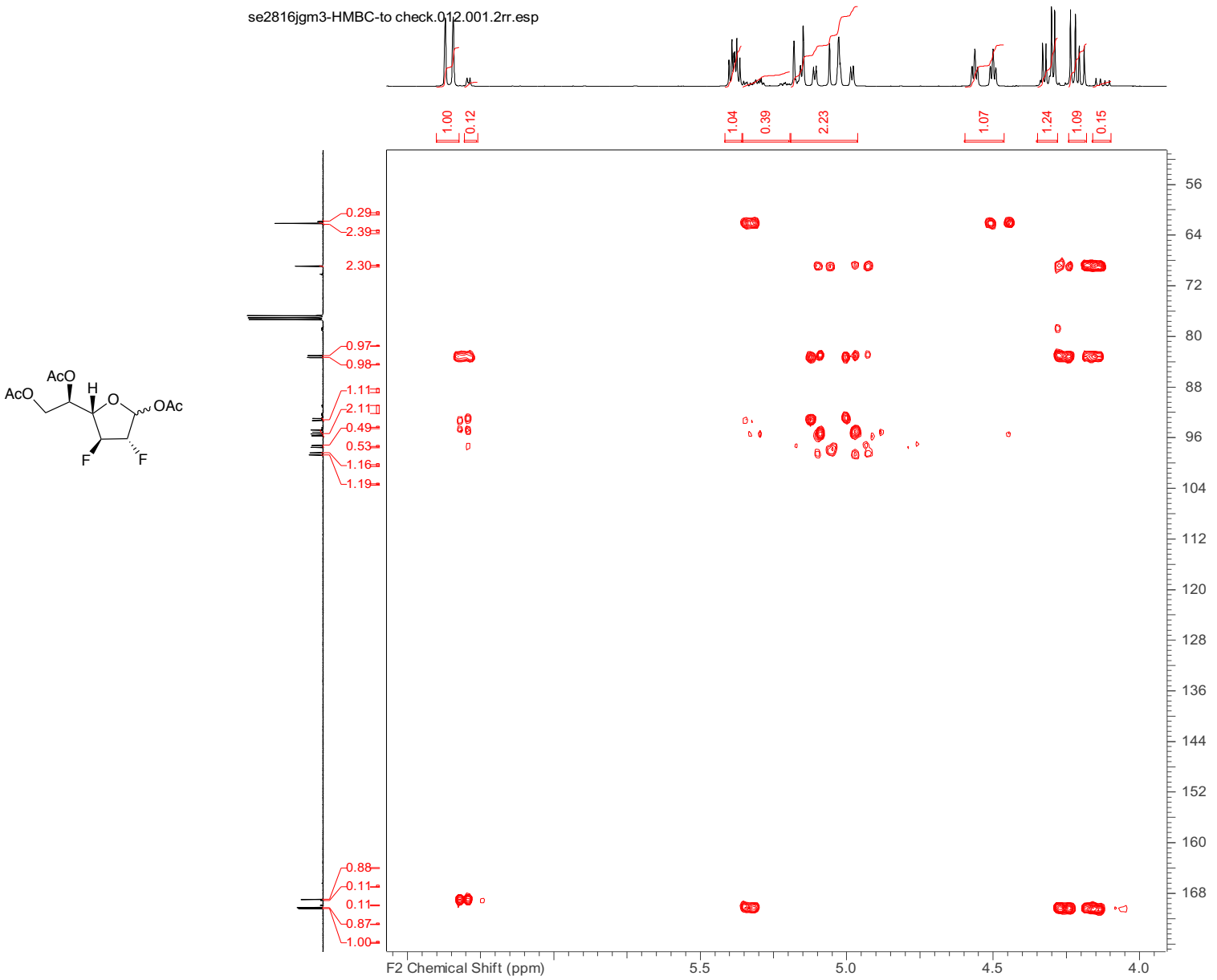




1.8.6 HSQC (400 MHz, $CDCl_3$) (compound 17b)



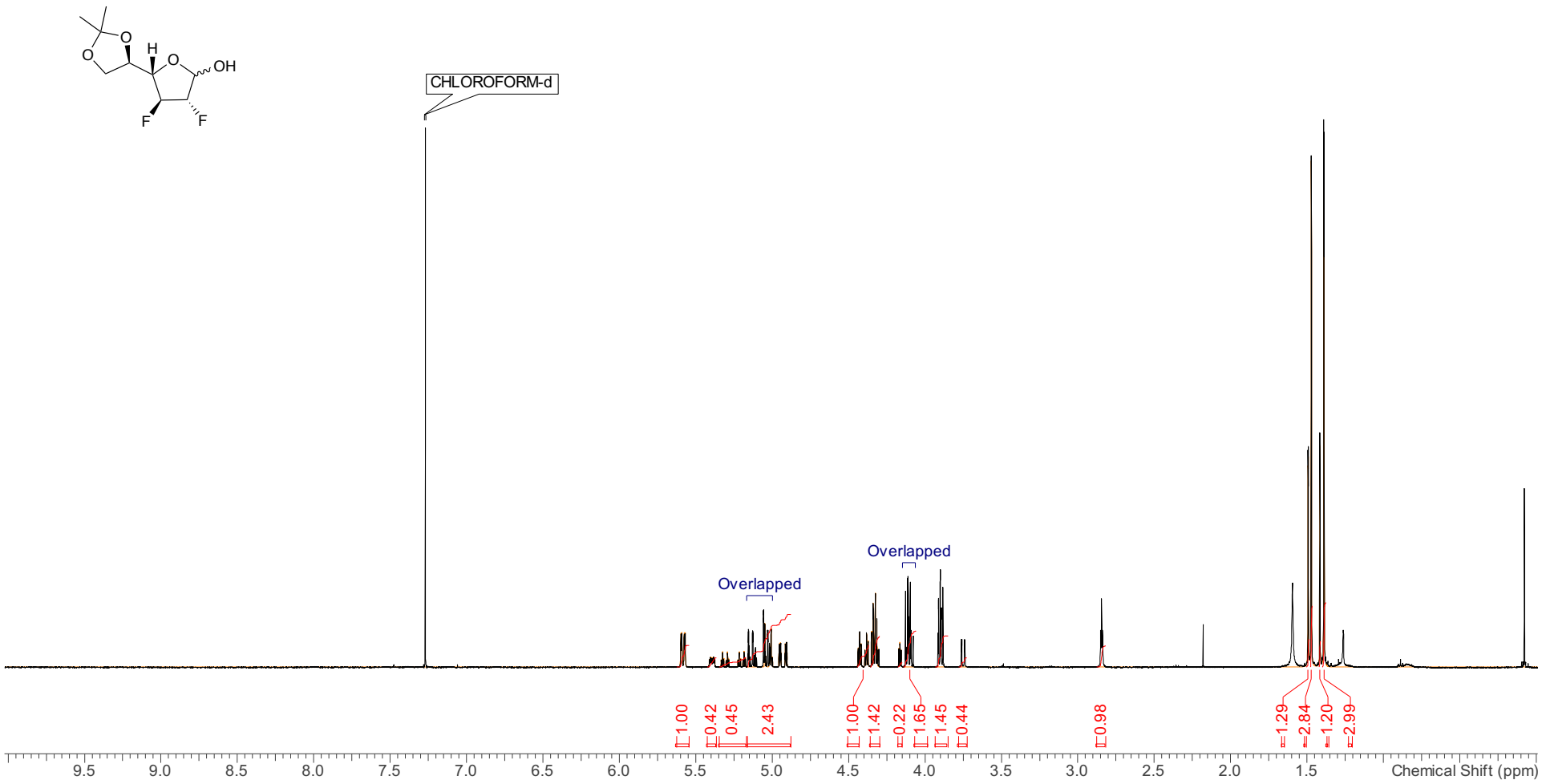
1.8.7 HMBC (400 MHz, $CDCl_3$) (compound 17b)



1.9 5,6-Di-*O*-isopropylidene-2,3-dideoxy-2,3-difluoro-D-galactofuranose 17c

1.9.1 ^{1}H NMR (500 MHz, $CDCl_3$) (compound 17c)

fe1616njwjm1.001.001.1r.esp



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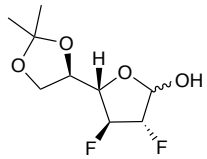
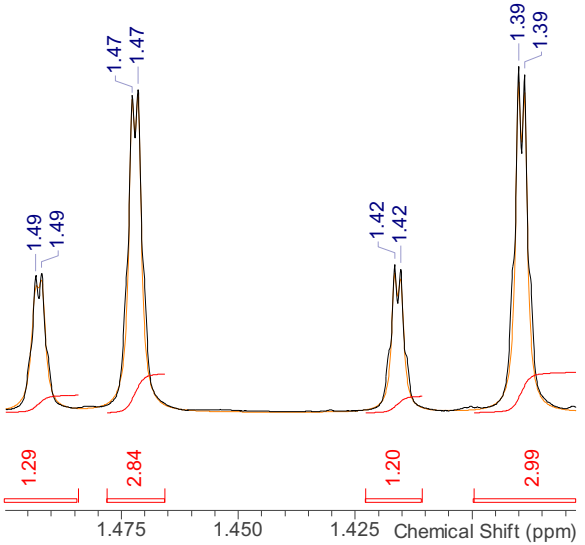
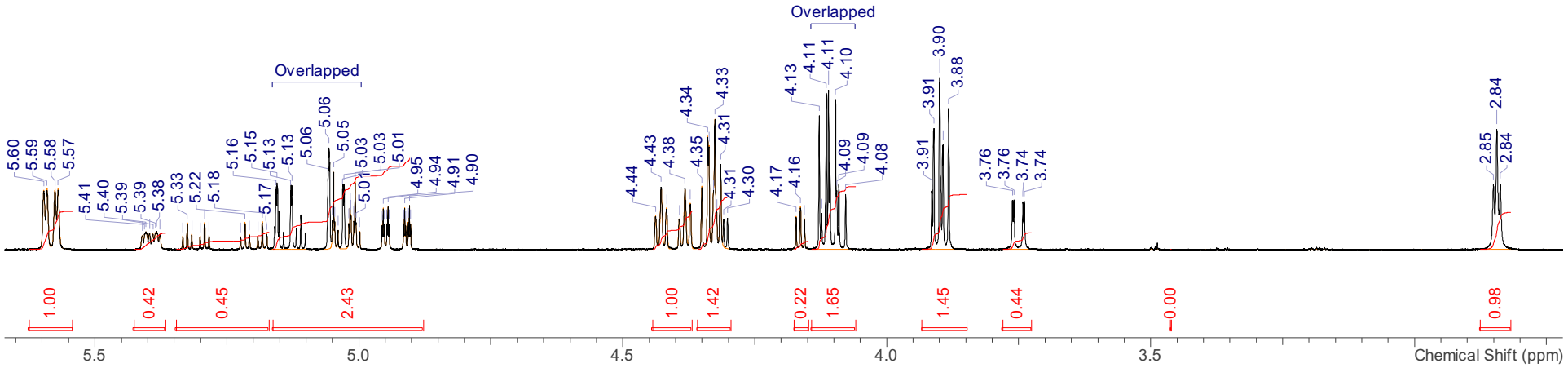
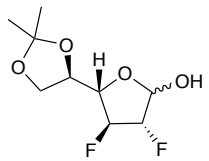
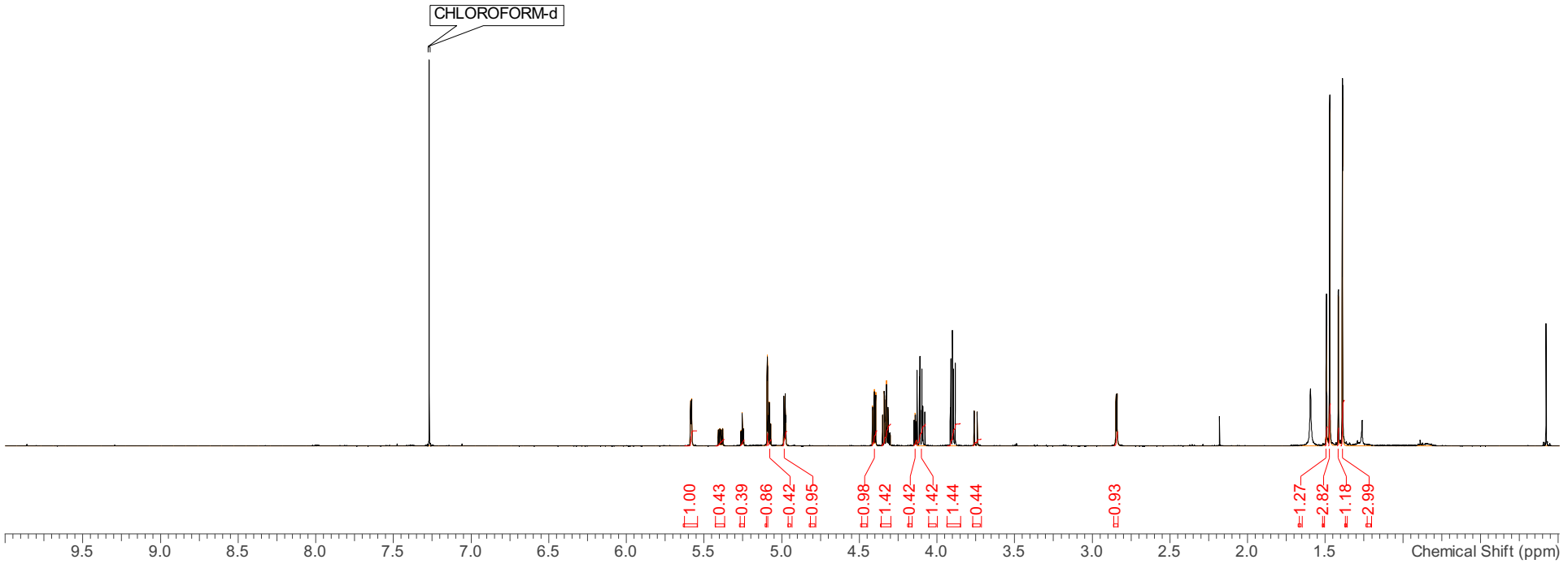






1.9.2 $^{1}H\{^{19}F\}$ NMR (500 MHz, $CDCl_3$) (compound 17c)





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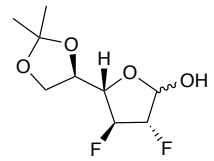
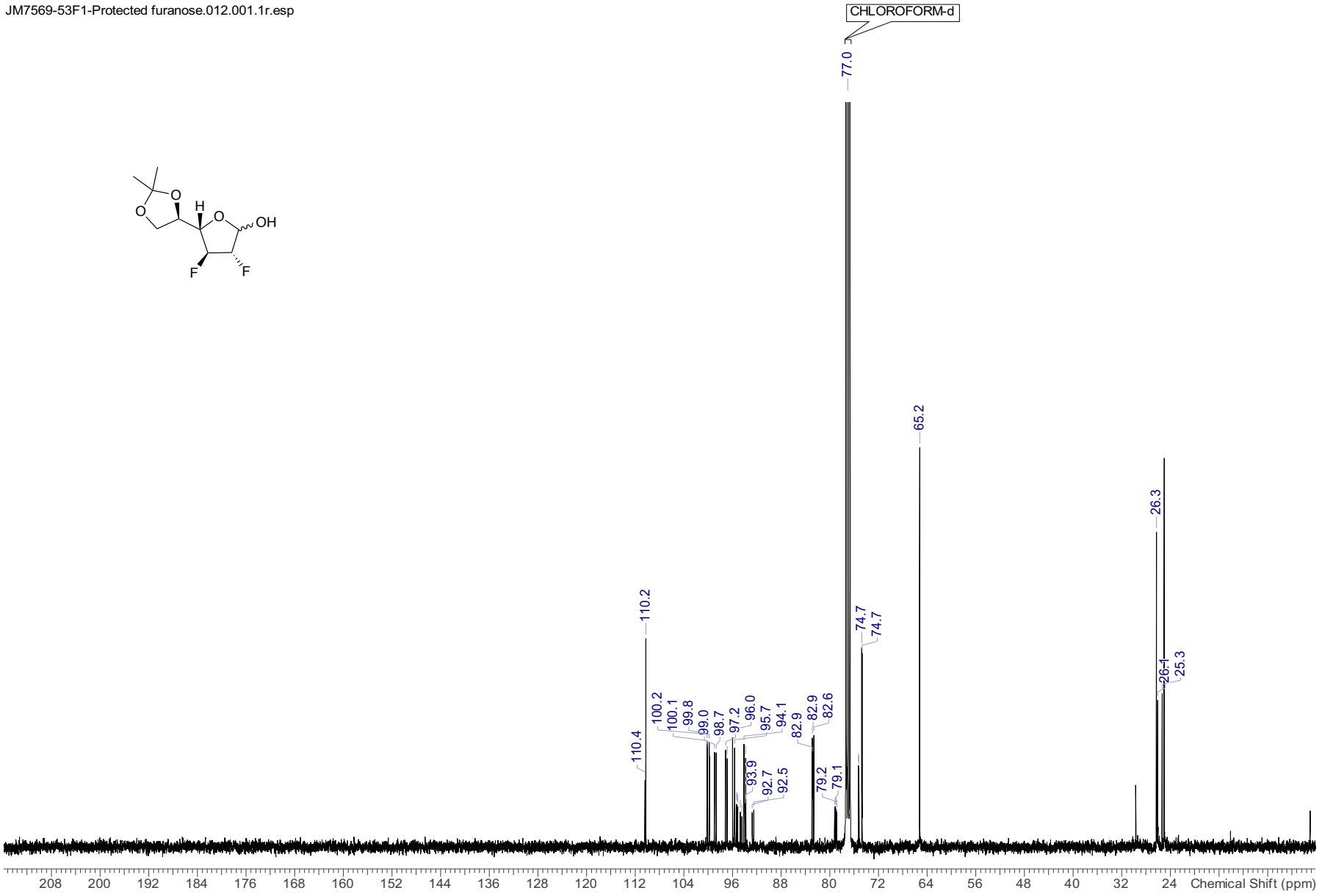
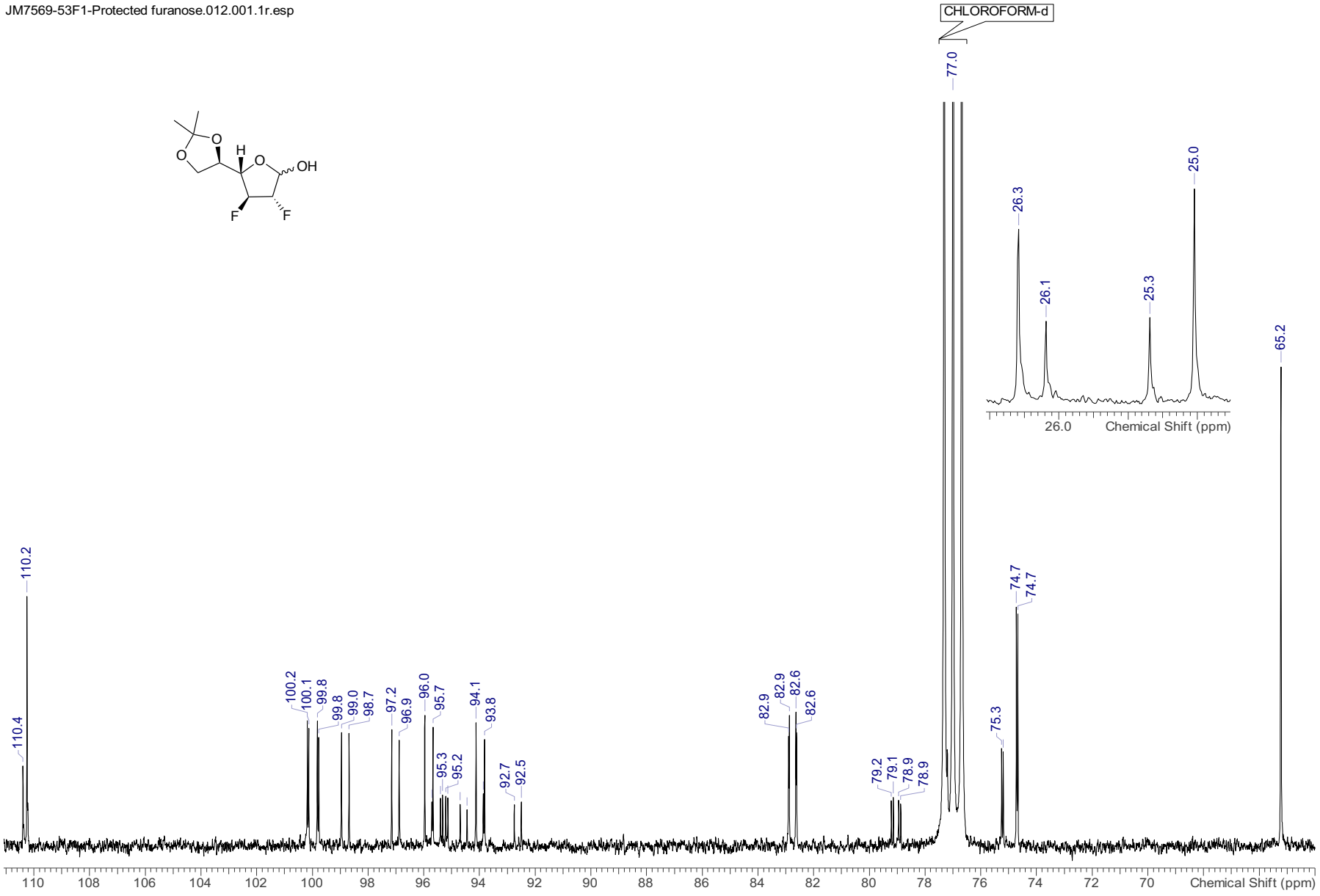


1.9.3 ^{13}C NMR (100 MHz, $CDCl_3$) (compound 17c)




JM7569-53F1-Protected furanose.012.001.1r.esp
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25.3
25.0
26.0
Chemical Shift (ppm)
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110.2
110.4
100.2
100.1
99.8
99.8
99.0
98.7
97.2
96.9
96.0
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95.3
95.2
94.1
93.8
92.7
92.5
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82.6
82.6
79.2
79.1
78.9
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75.3
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110
108
106
104
102
100
98
96
94
92
90
88
86
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82
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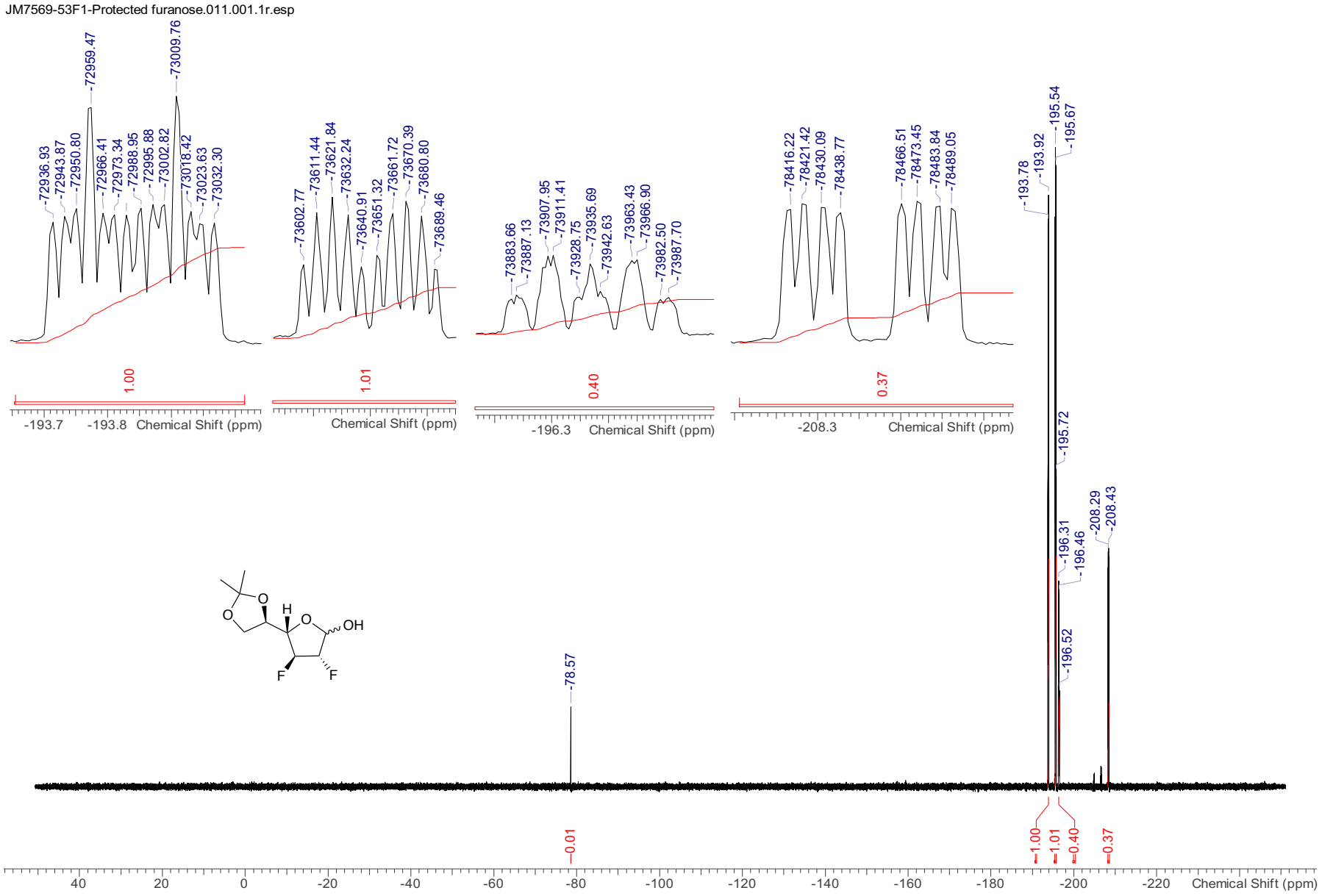
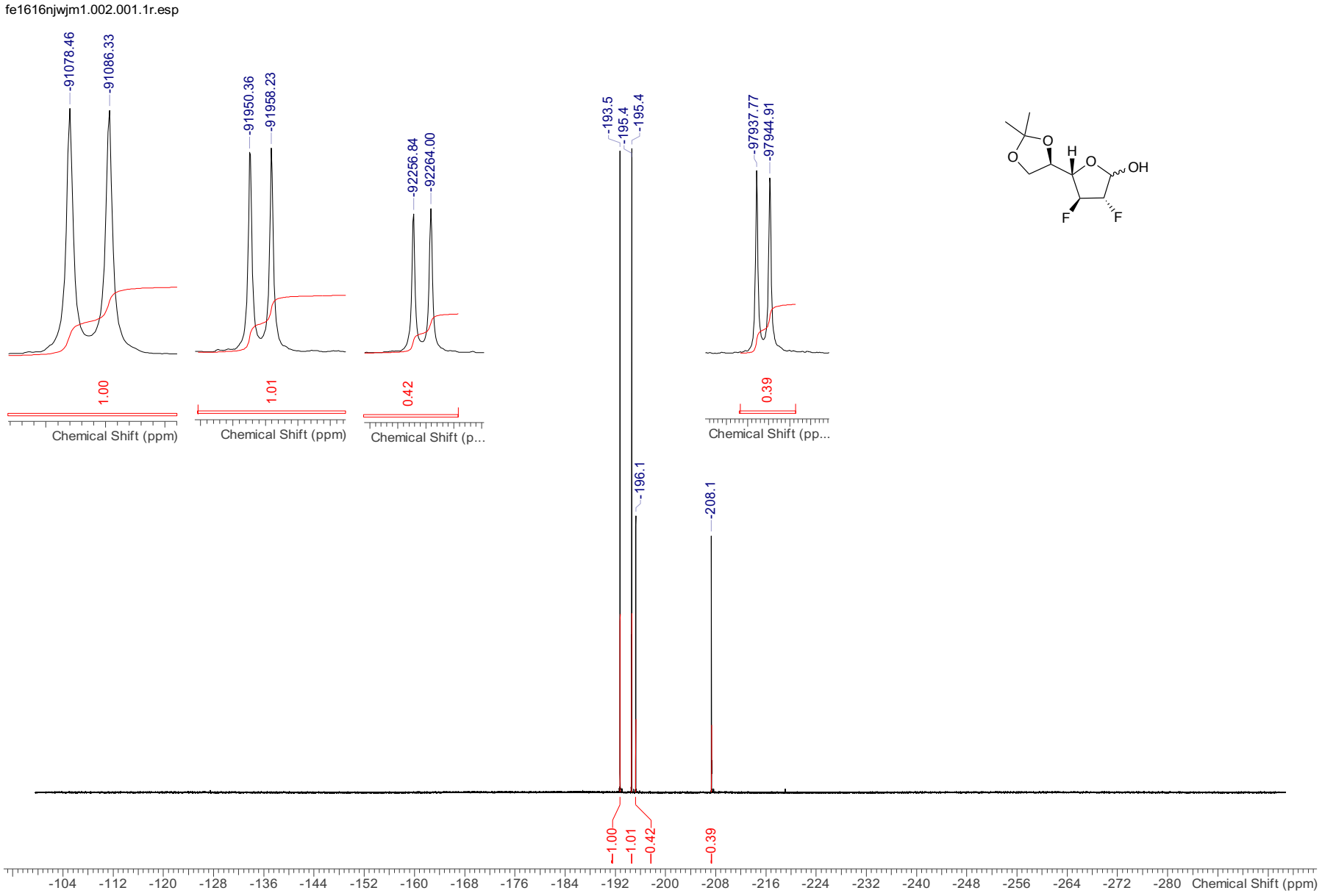
76
74
72
70
Chemical Shift (ppm)

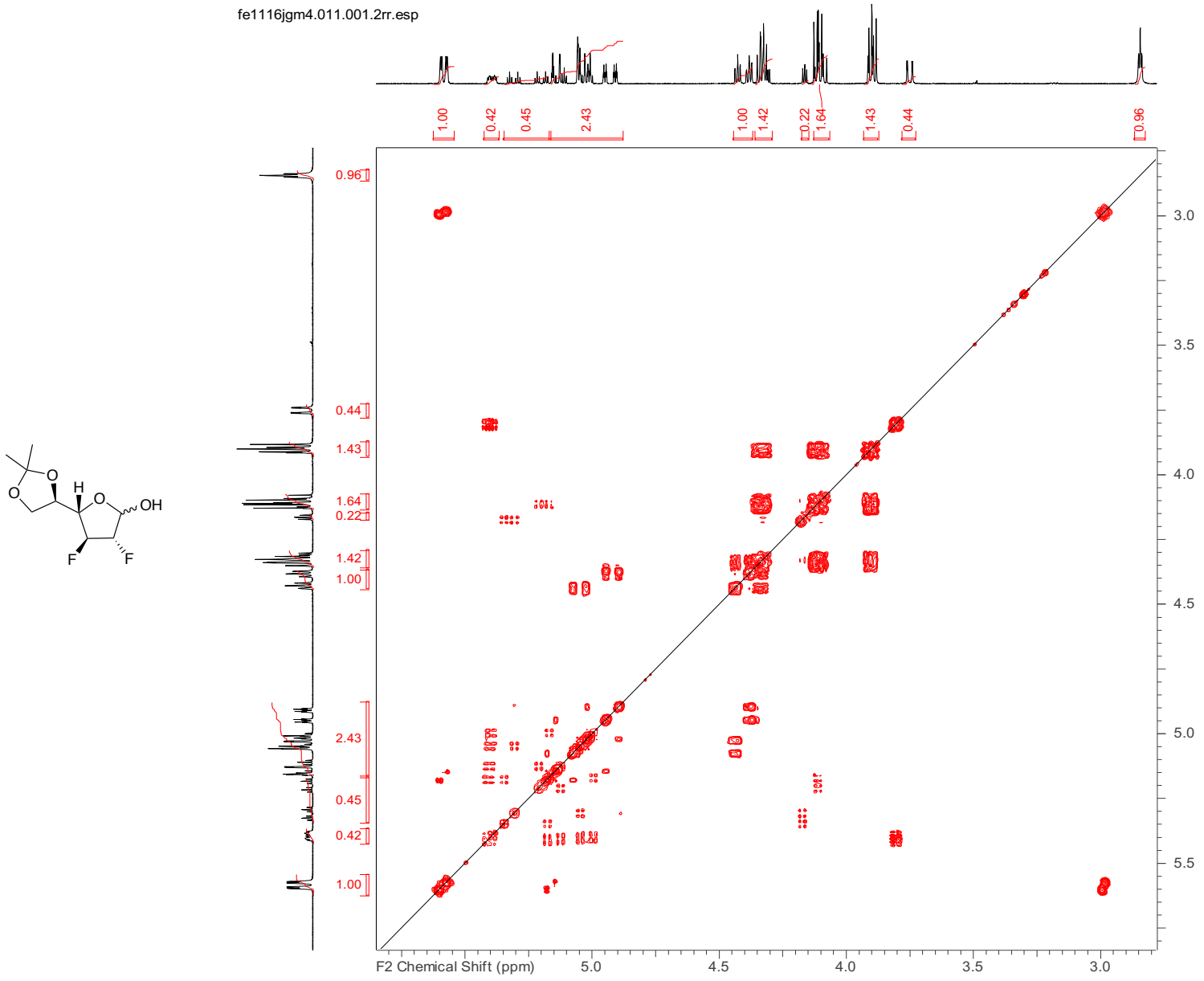
1.9.4 ^{19}F NMR (376 MHz, $CDCl_3$) (compound 17c)



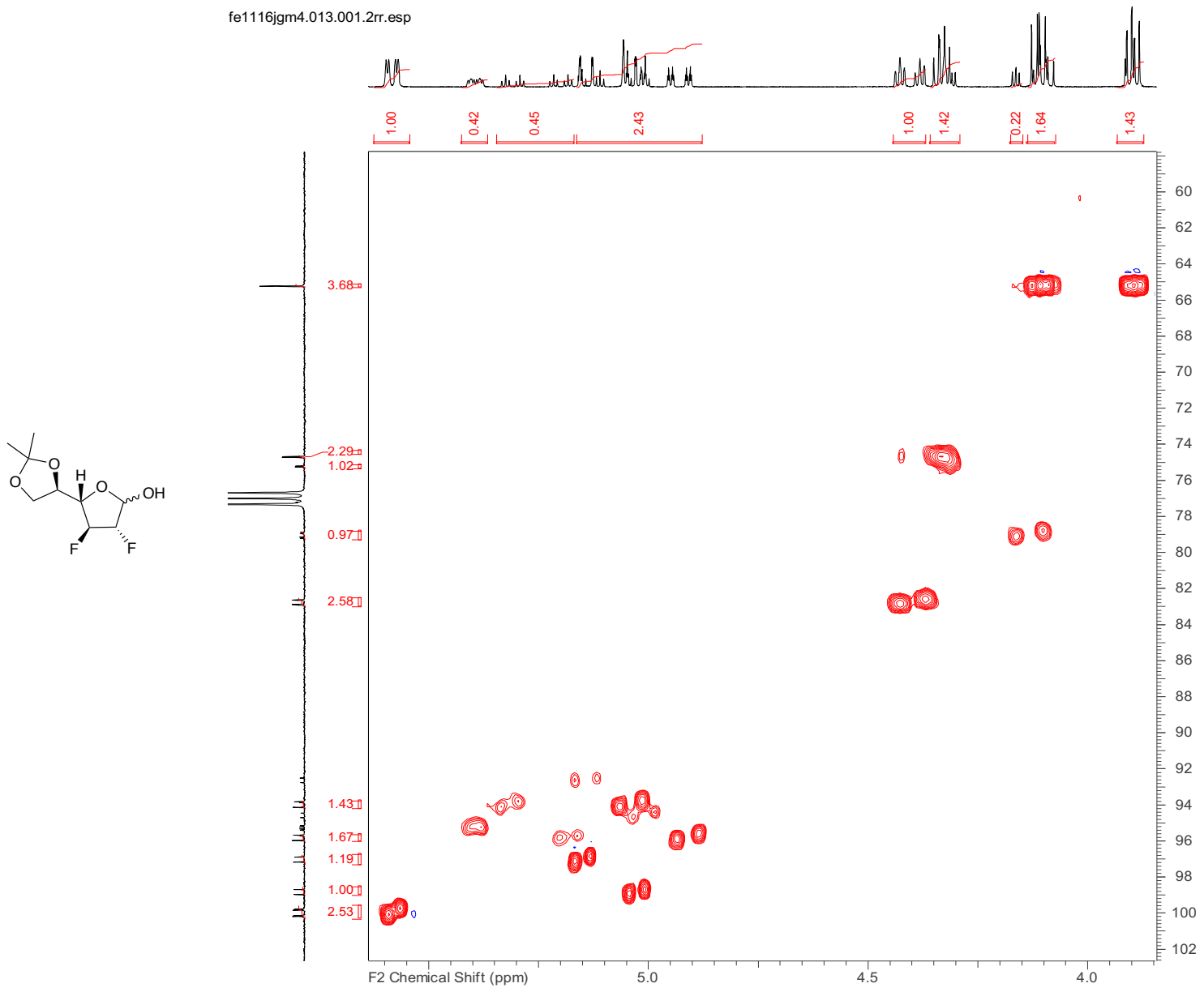
1.9.5 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) (compound 17c)



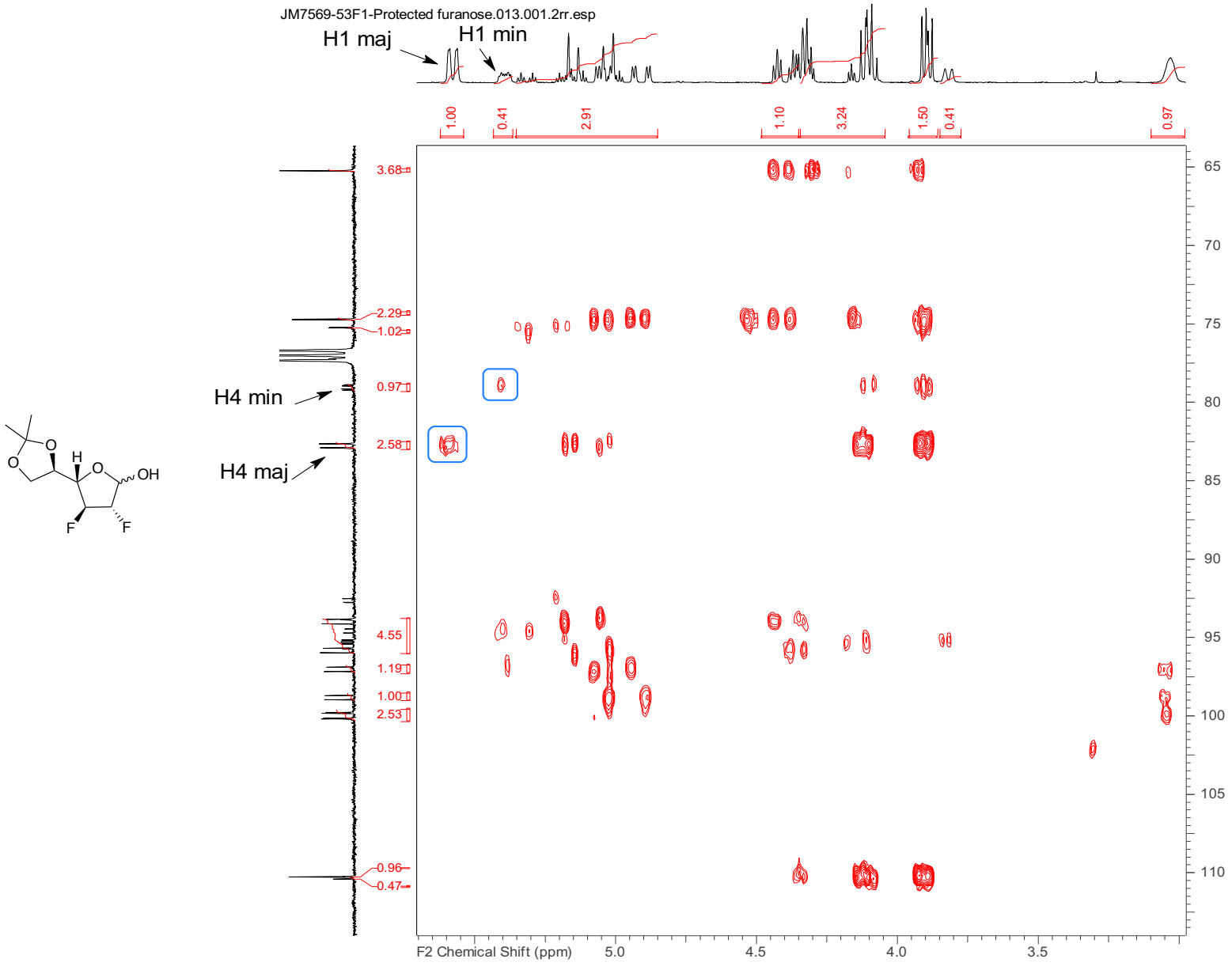
1.9.6 COSY ^{1}H-^{1}H (400 MHz, $CDCl_3$) (compound 17c)



1.9.7 HSQC (400 MHz, $CDCl_3$) (compound 17c)



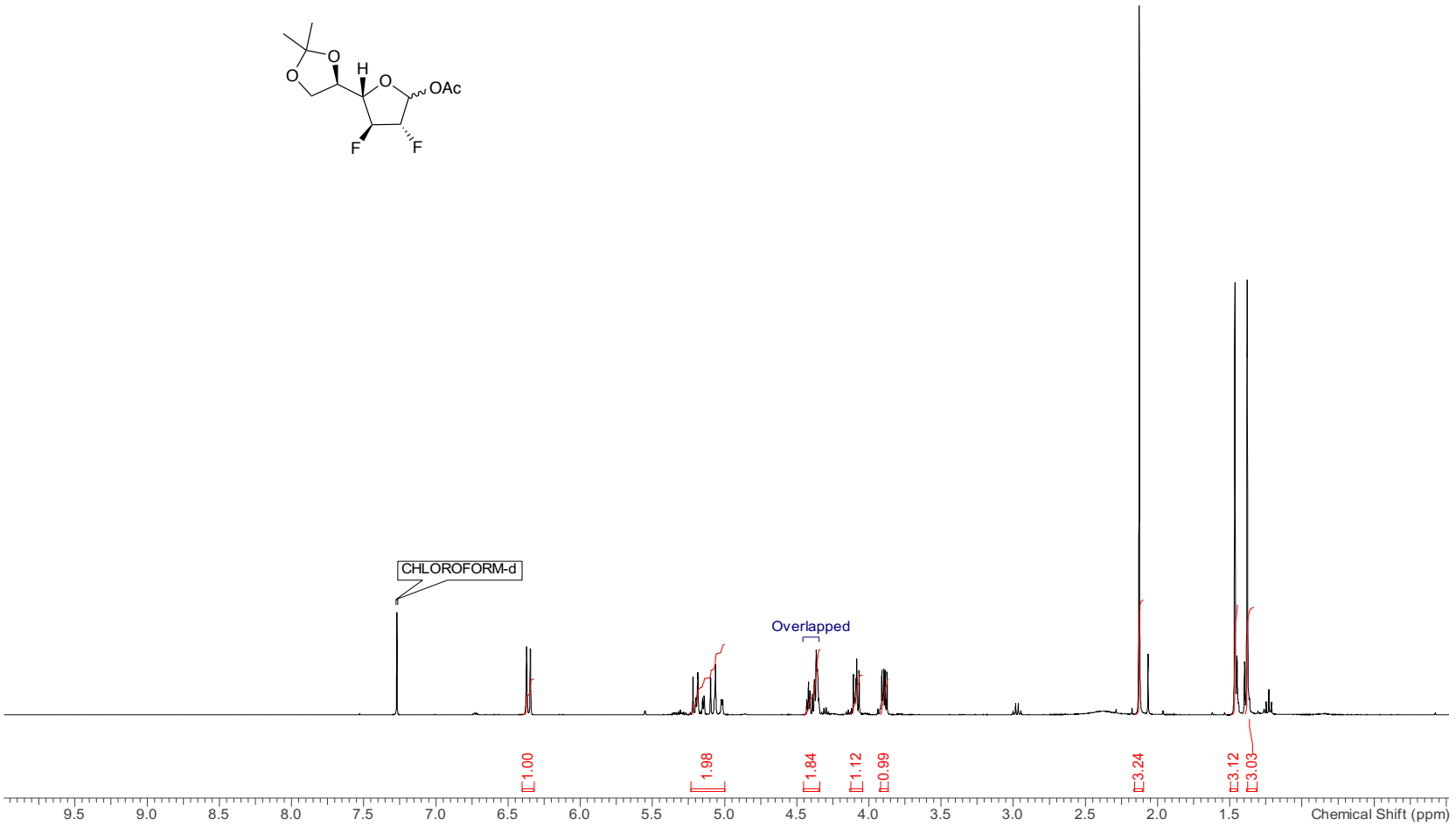
1.9.8 HMBC (400 MHz, $CDCl_3$) (compound 17c)



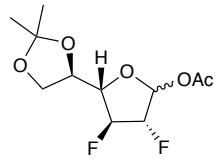
1.10 1-*O*-Acetyl-5,6-di-*O*-isopropylidene-2,3-dideoxy-2,3-difluoro-D-galactofuranose 17d

1.10.1 ^{1}H NMR (400 MHz, $CDCl_3$) (compound 17d)

my1716jgm7.010.001.1r.esp

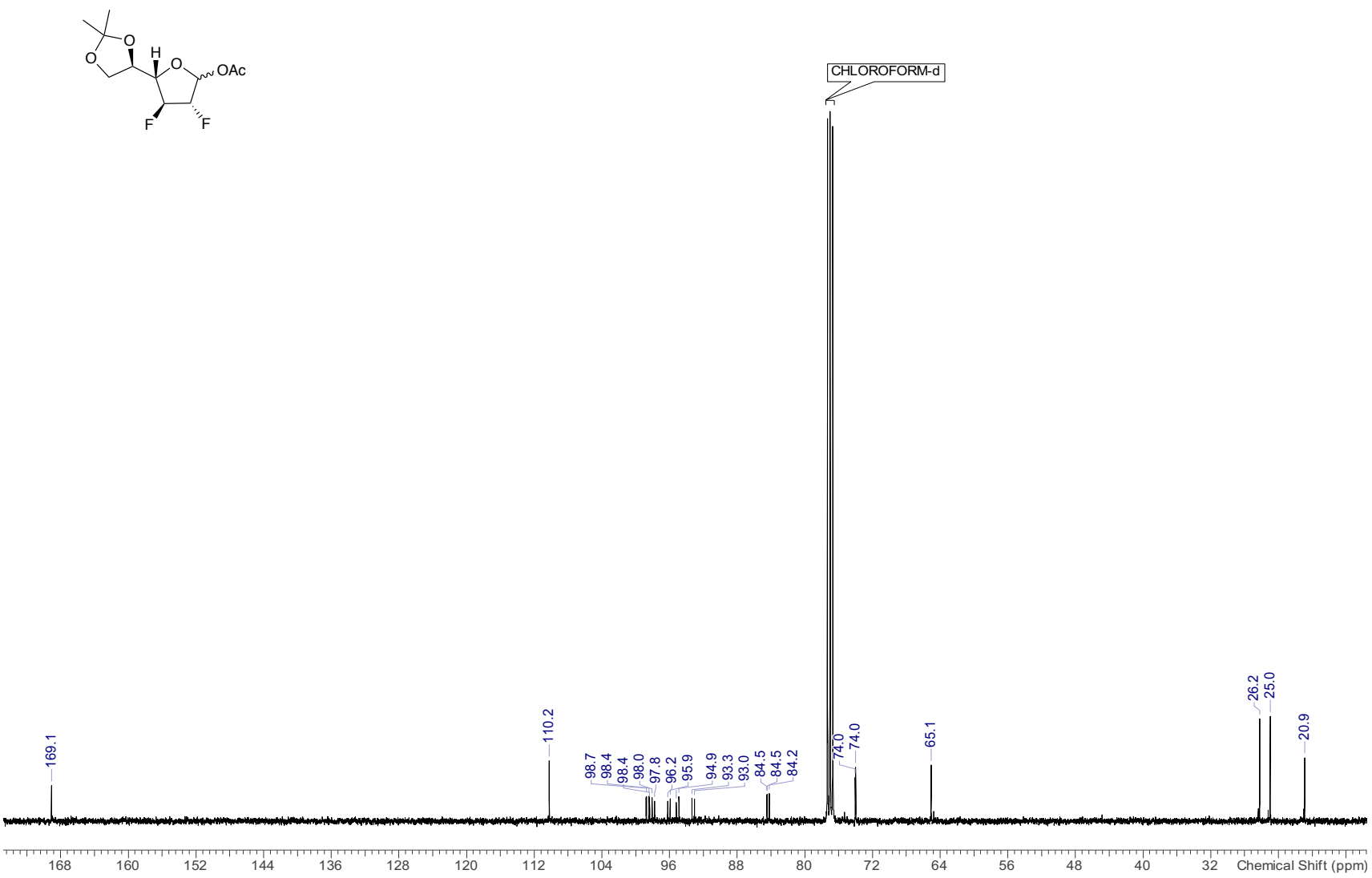


my1716jgm7.010.001.1r.esp



1.10.2 ^{13}C NMR (100 MHz, $CDCl_3$) (compound 17d)

my1716jgm7.016.001.1r.esp



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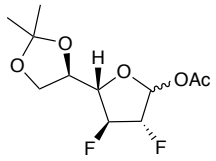
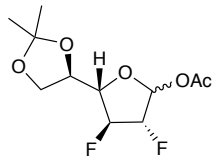
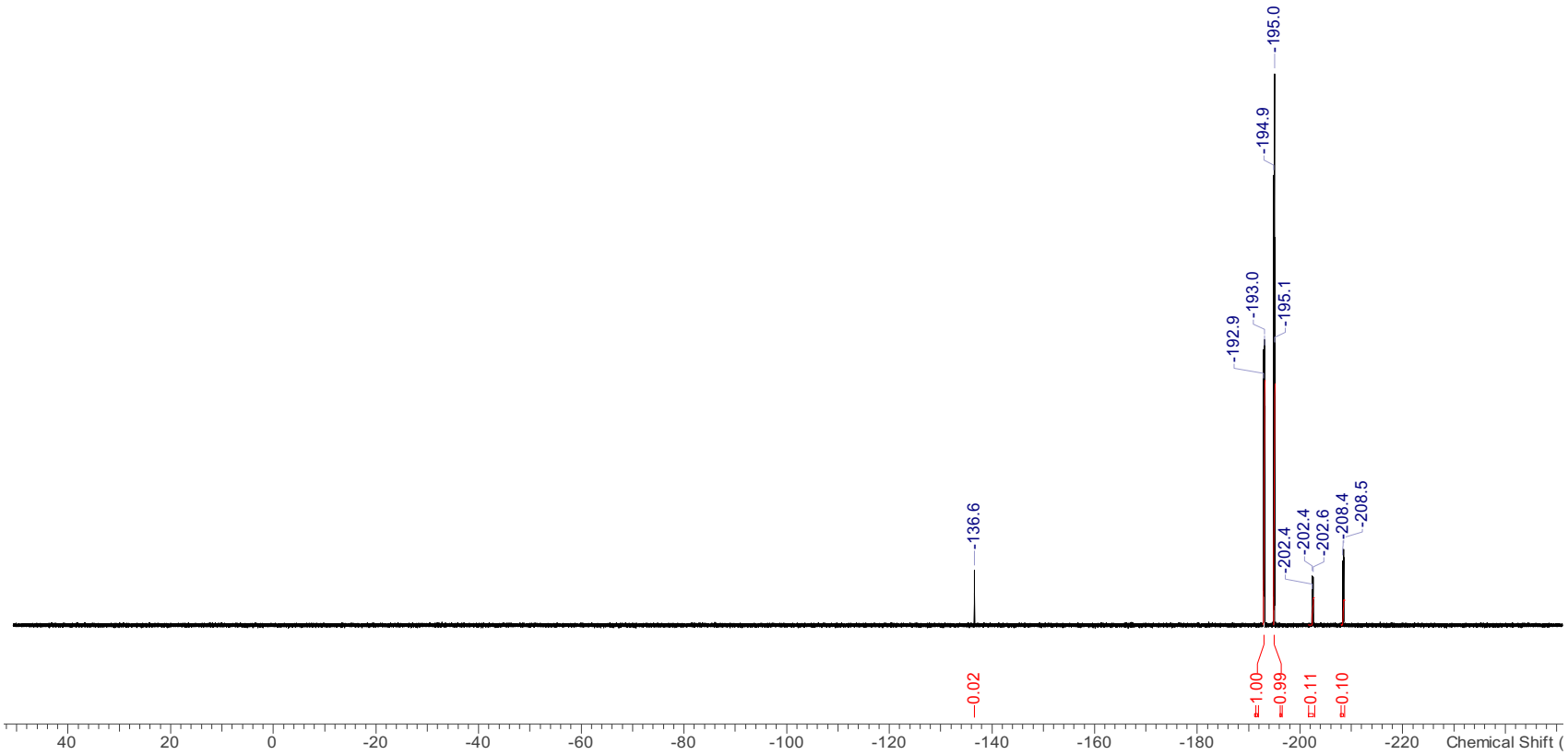


1.10.3 ^{19}F NMR (376 MHz, $CDCl_3$) (compound 17d)





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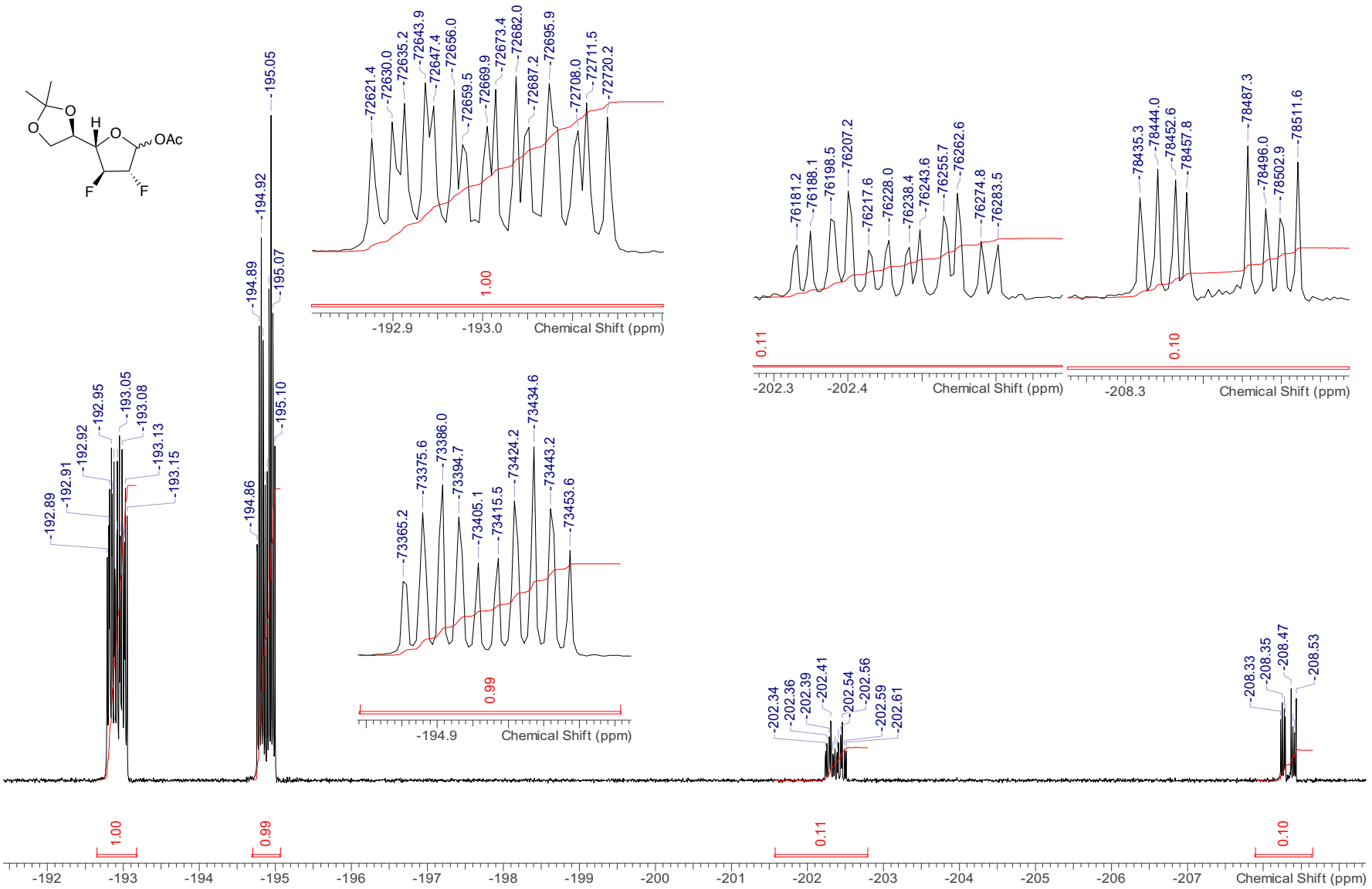
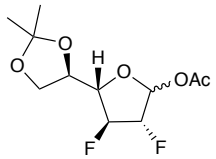
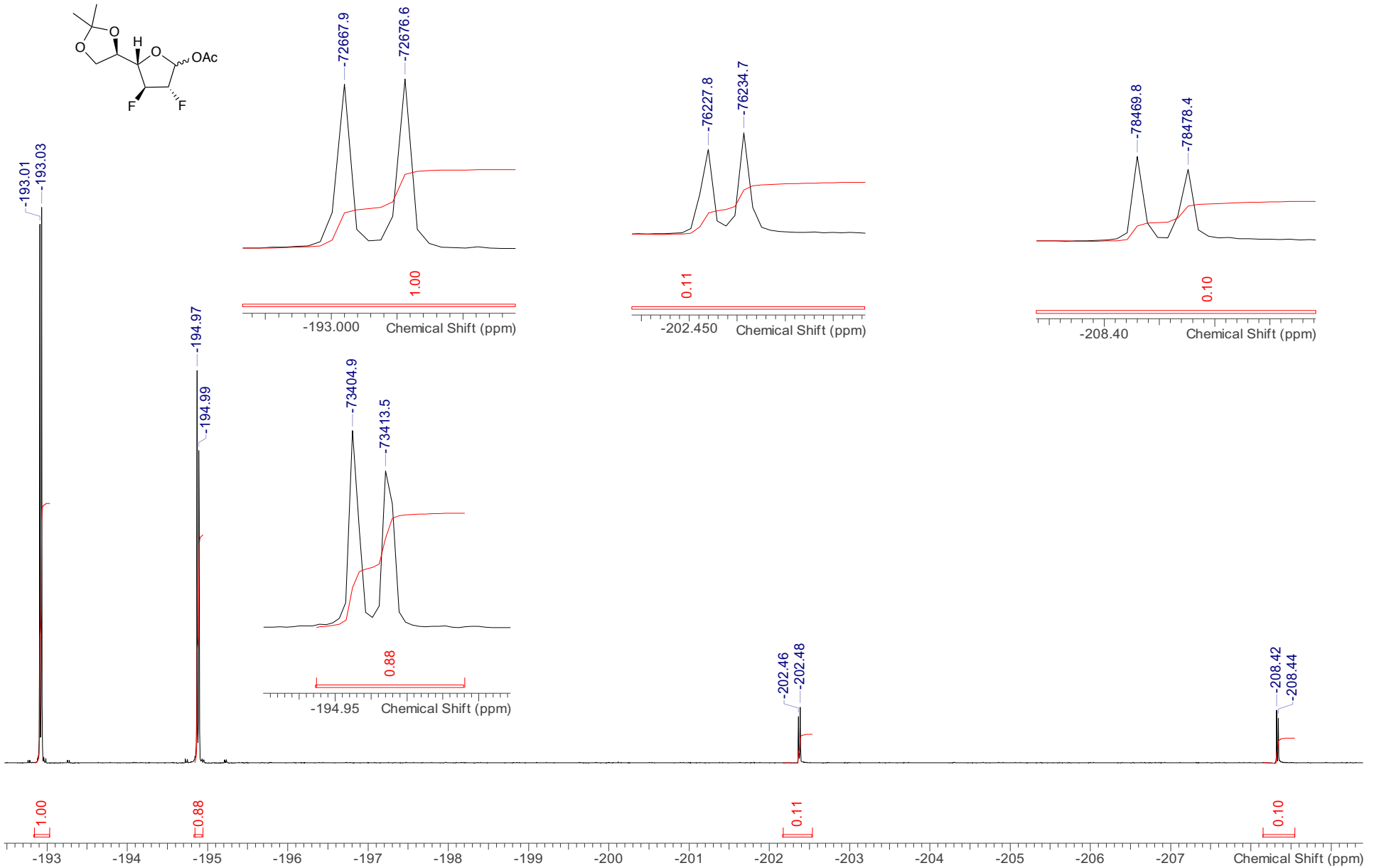


1.10.4 $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) (compound 17d)

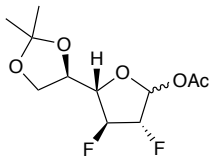
my1716jgm7.012.001.1r.esp

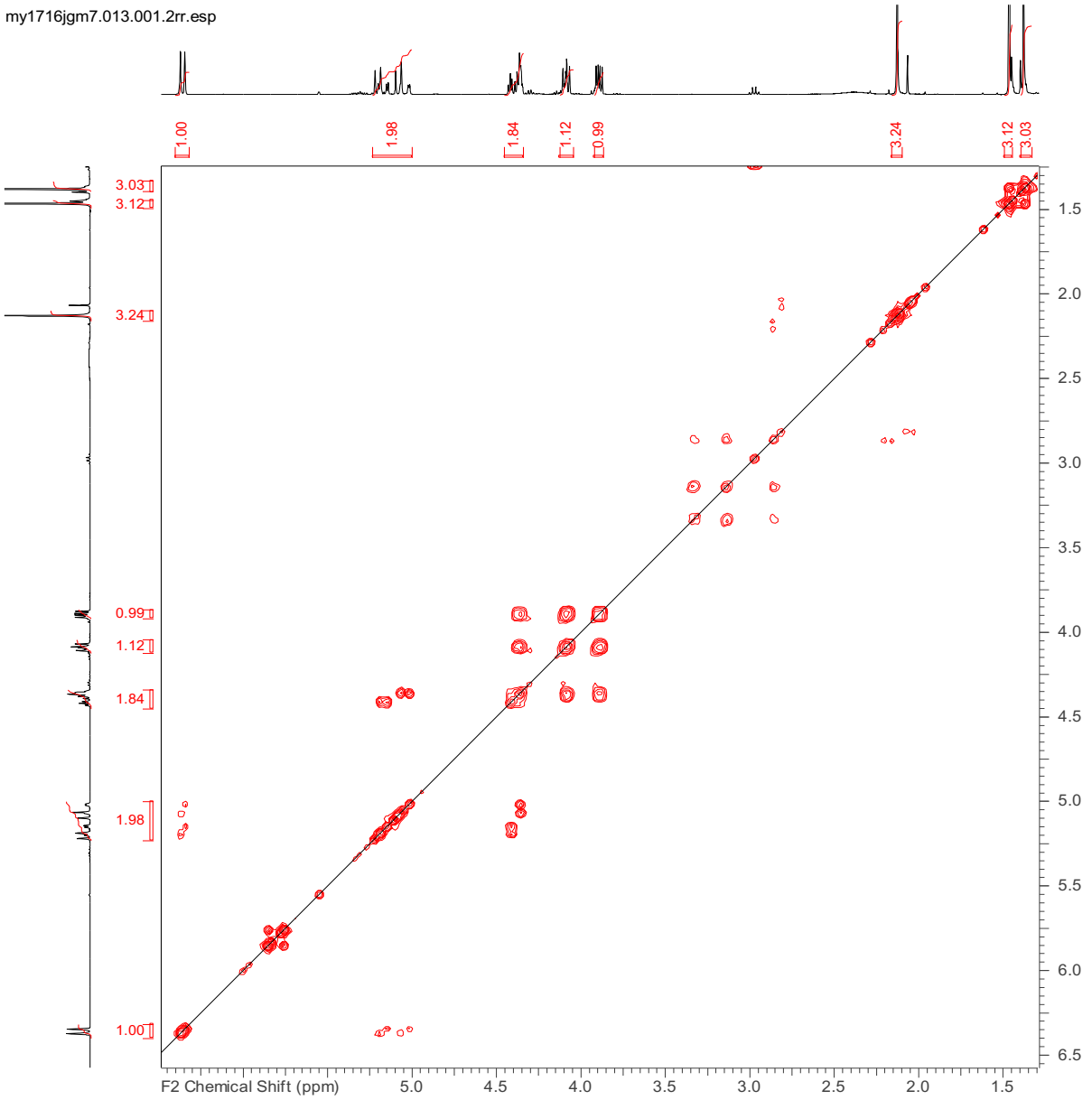


my1716jgm7.012.001.1r.esp

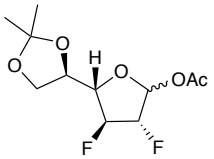


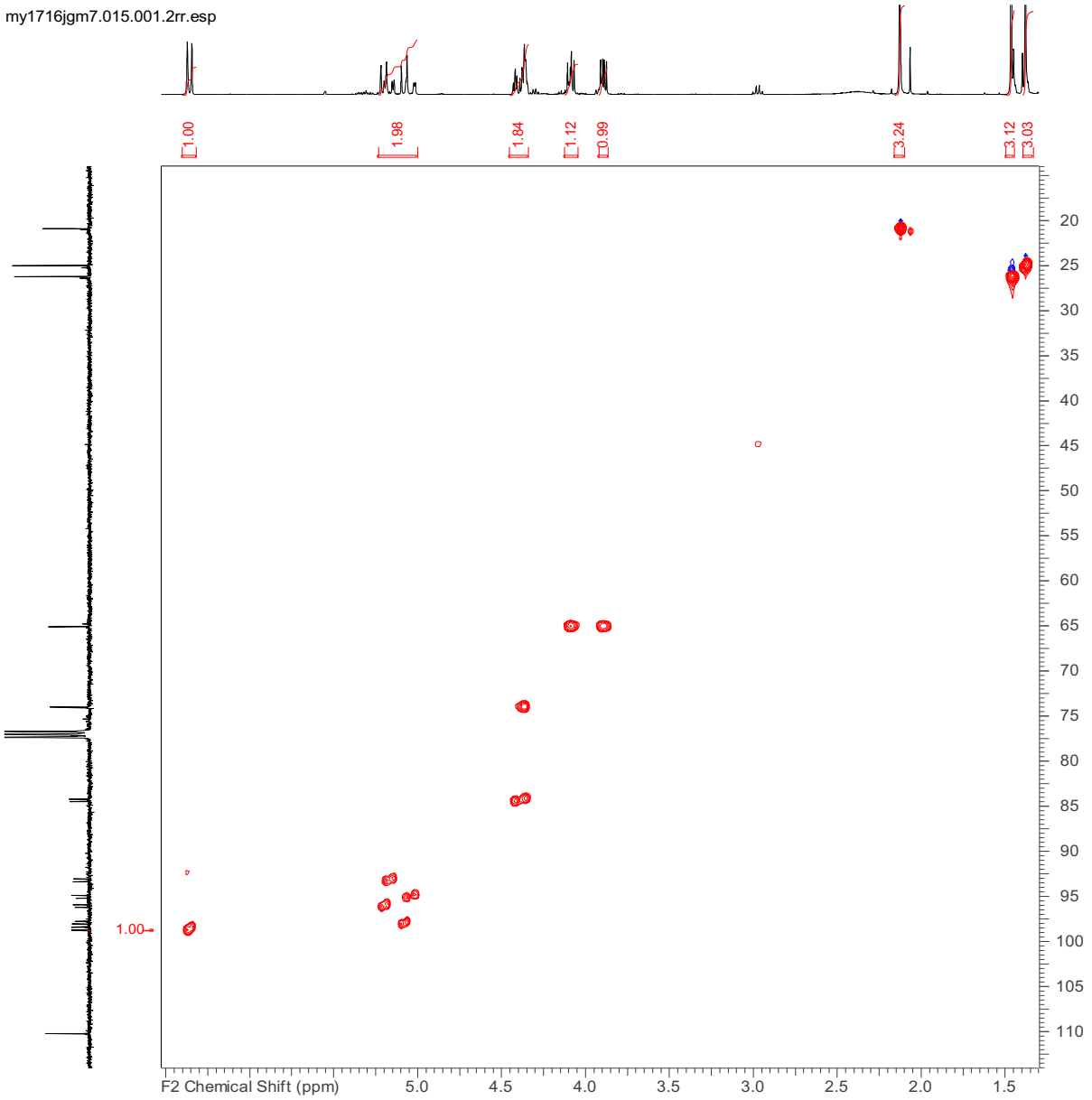
1.10.5 COSY 1H-1H (400 MHz, $CDCl_3$) (compound 17d)





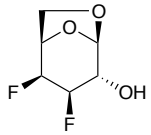
1.10.6 HSQC (400 MHz, $CDCl_3$) (compound 17d)

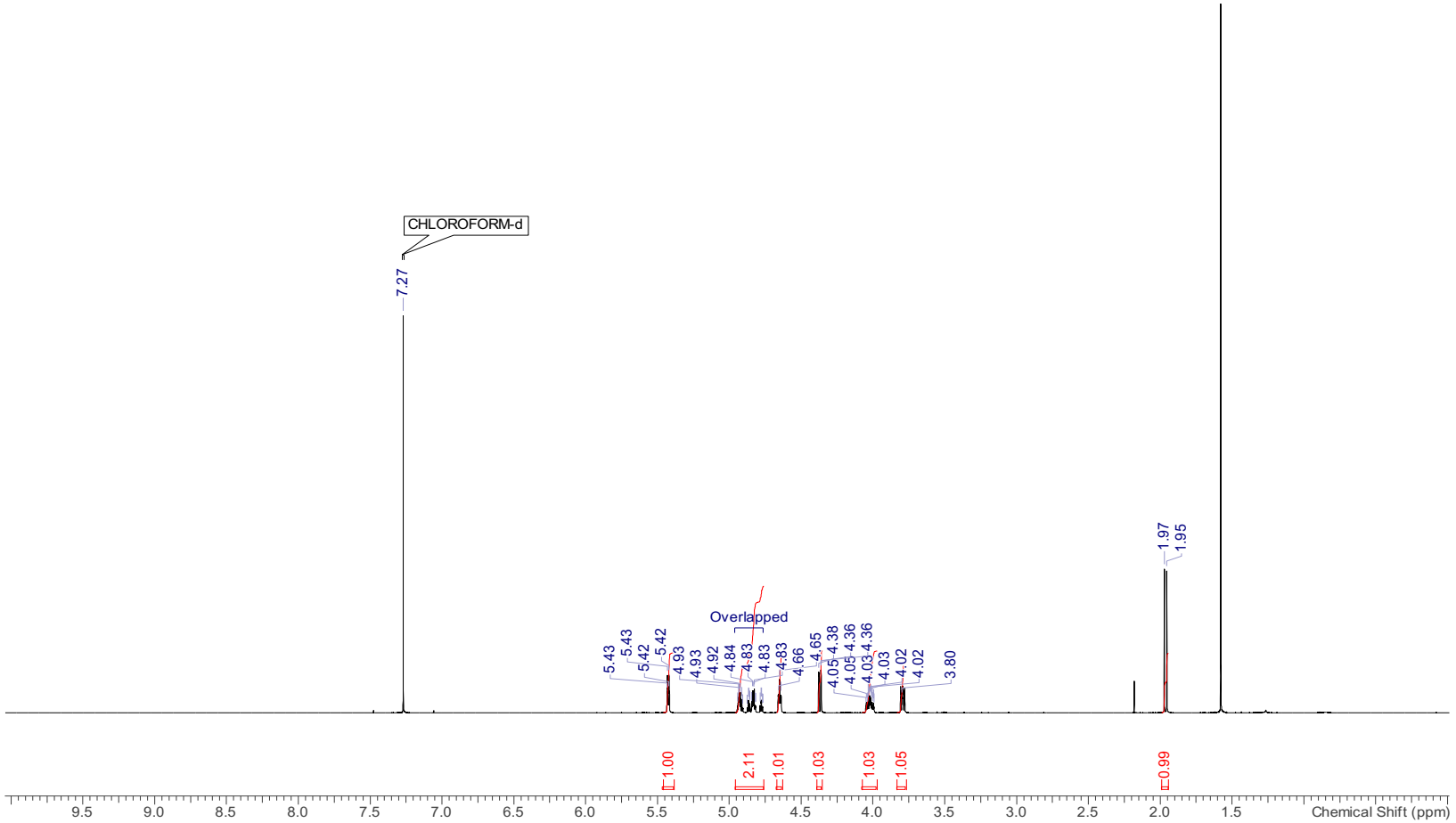


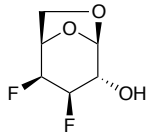


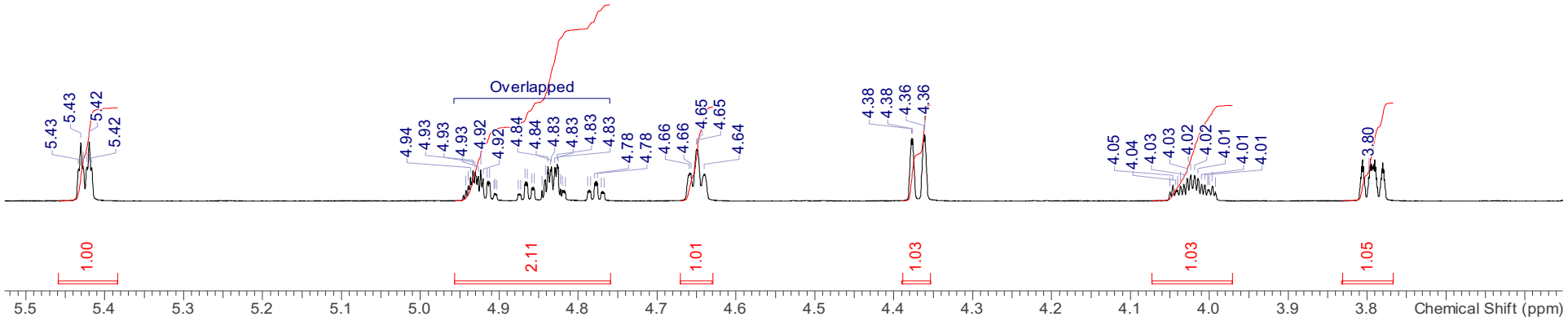
1.11 1,6-Anhydro-3,4-dideoxy-3,4-difluoro-β-D-galactopyranose 19

1.11.1 ^{1}H NMR (500 MHz, $CDCl_3$) (compound 19)






O
O
F
OH
F


5.43
5.43
5.42
5.42
Overlapped
4.94
4.93
4.93
4.93
4.92
4.92
4.84
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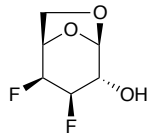
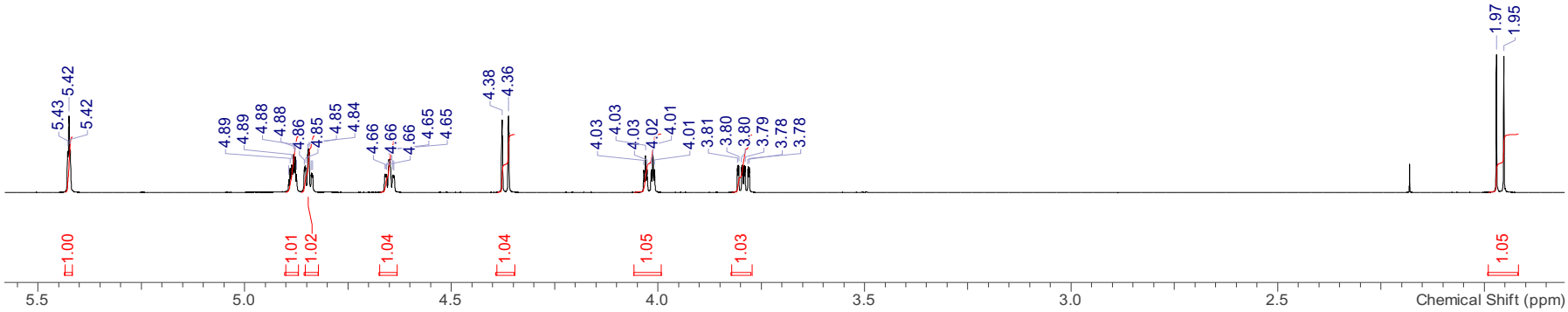
4.04
4.03
4.03
4.02
4.02
4.01
4.01
4.01
3.80
1.00
2.11
1.01
1.03
1.03
1.05
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
Chemical Shift (ppm)

1.11.2 $^{1}H\{^{19}F\}$ NMR (500 MHz, $CDCl_3$) (compound 19)

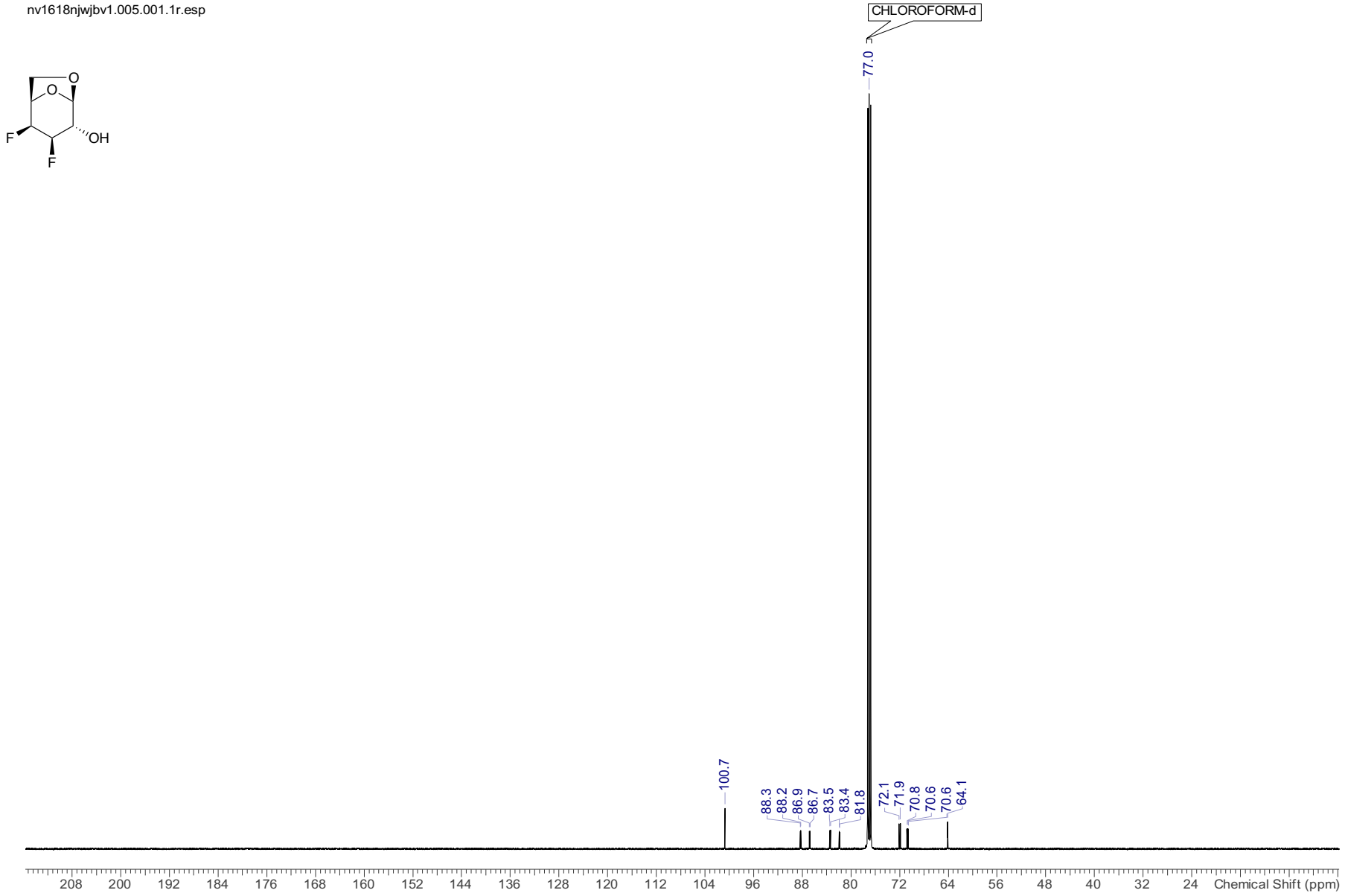
nv1618njwjbv1.004.001.1r.esp

nv1618njwjbv1.004.001.1r.esp

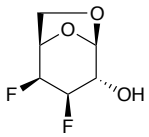




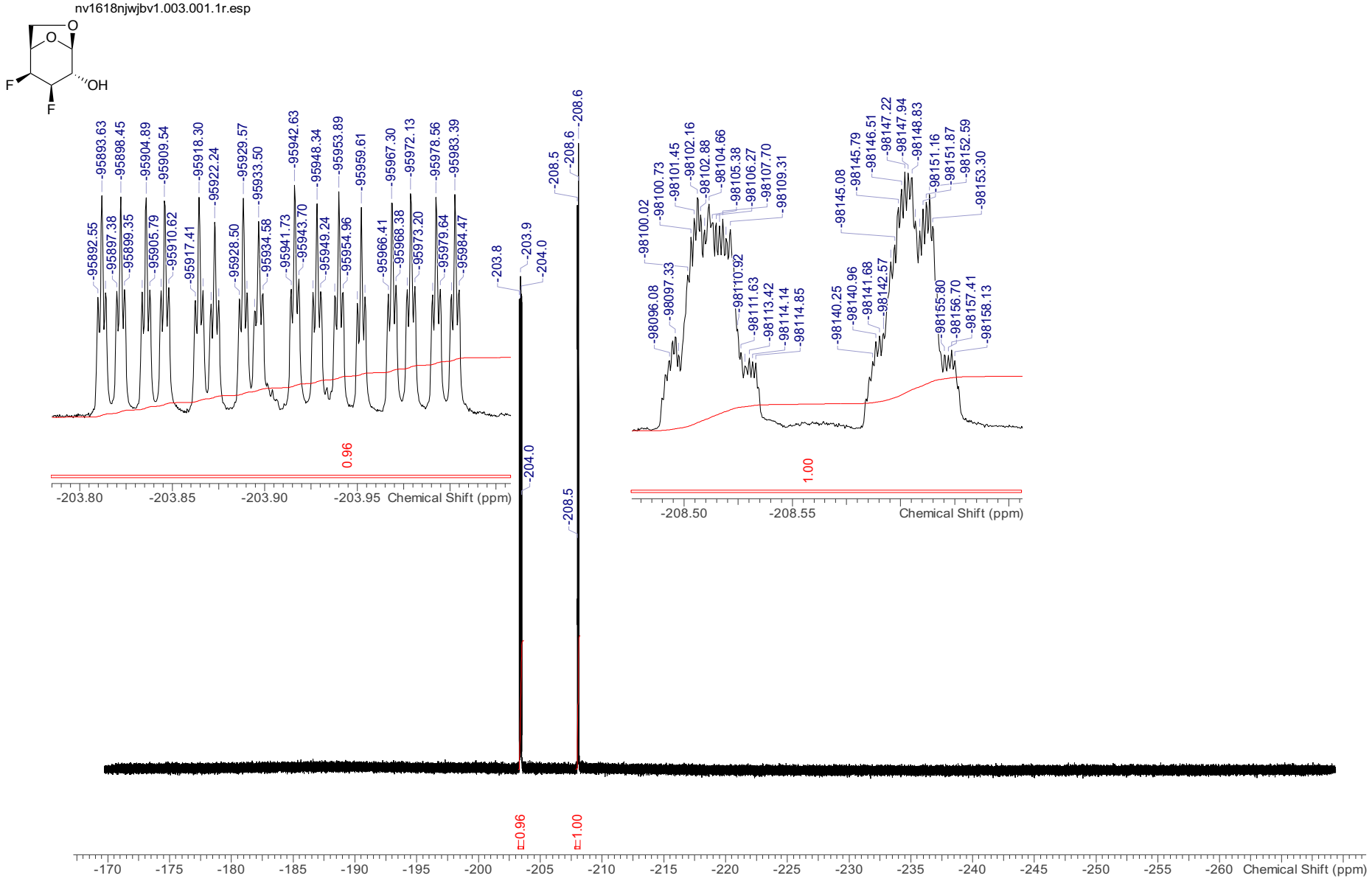
1.11.3 ^{13}C NMR (126 MHz, $CDCl_3$) (compound 19)



nv1618njwjbv1.005.001.1r.esp

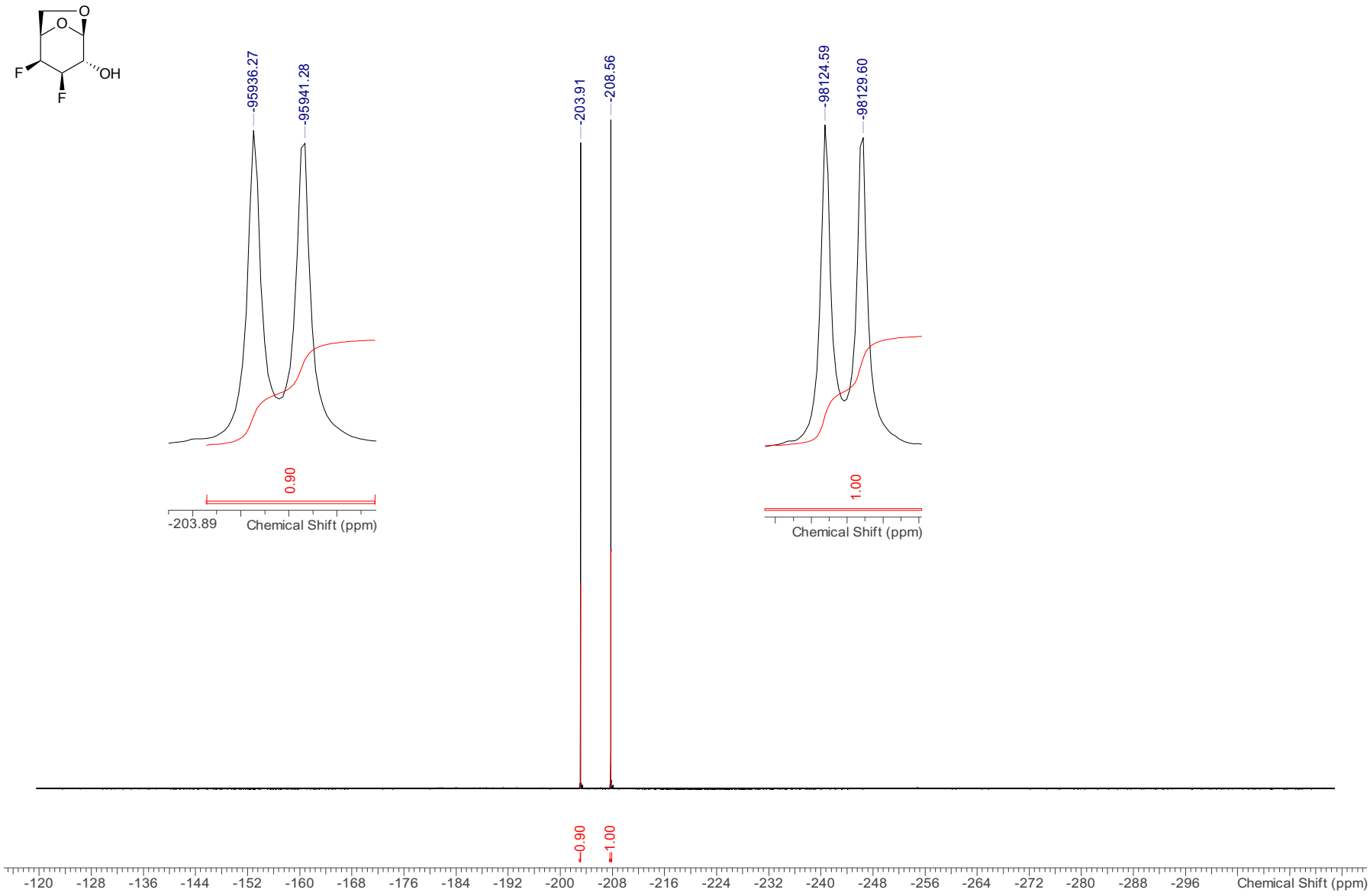


1.11.4 ^{19}F NMR (471 MHz, $CDCl_3$) (compound 19)

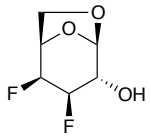


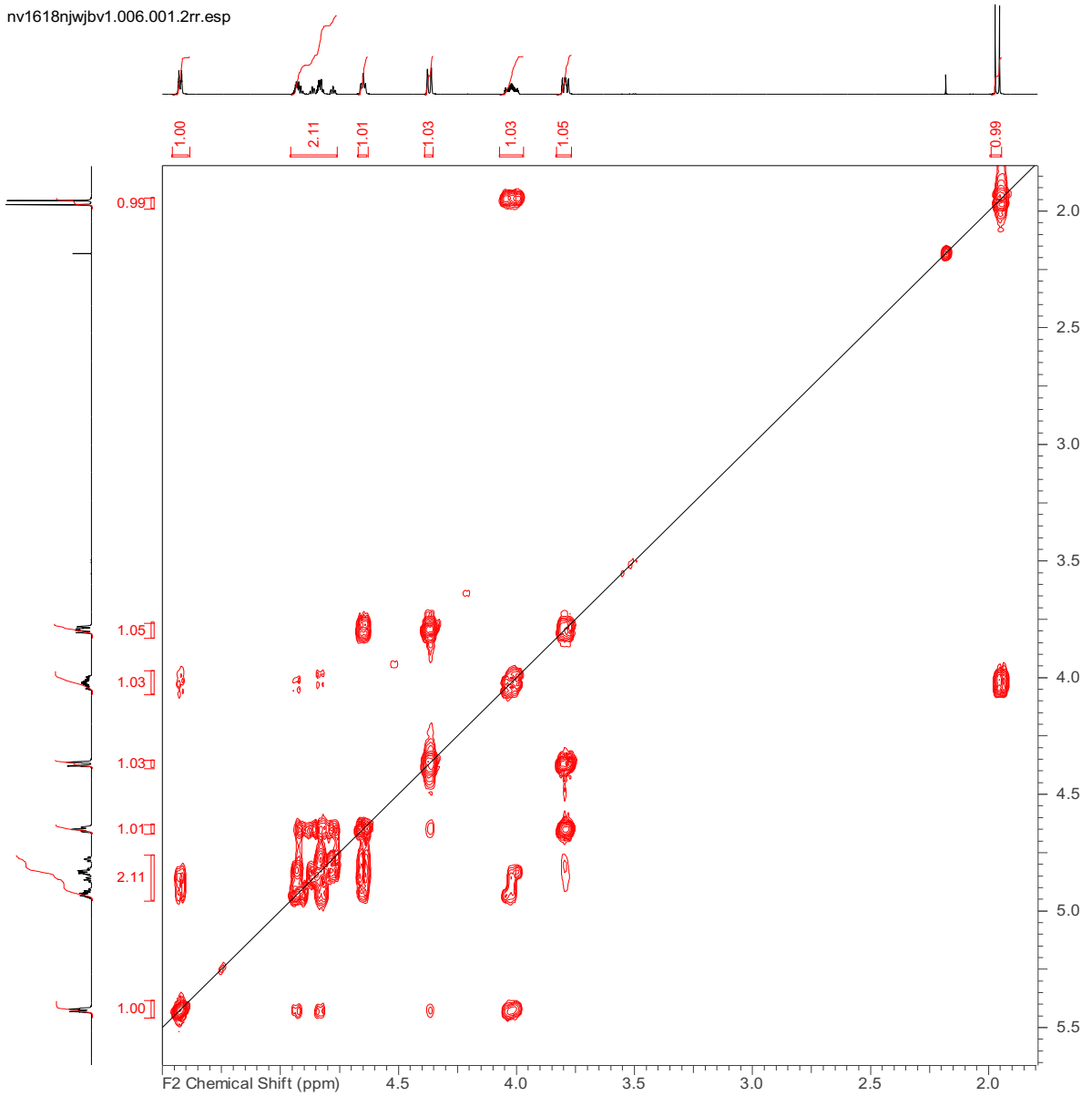
1.11.5 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) (compound 19)

nv1618njwjbv1.002.001.1r.esp

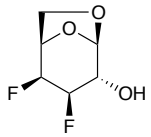


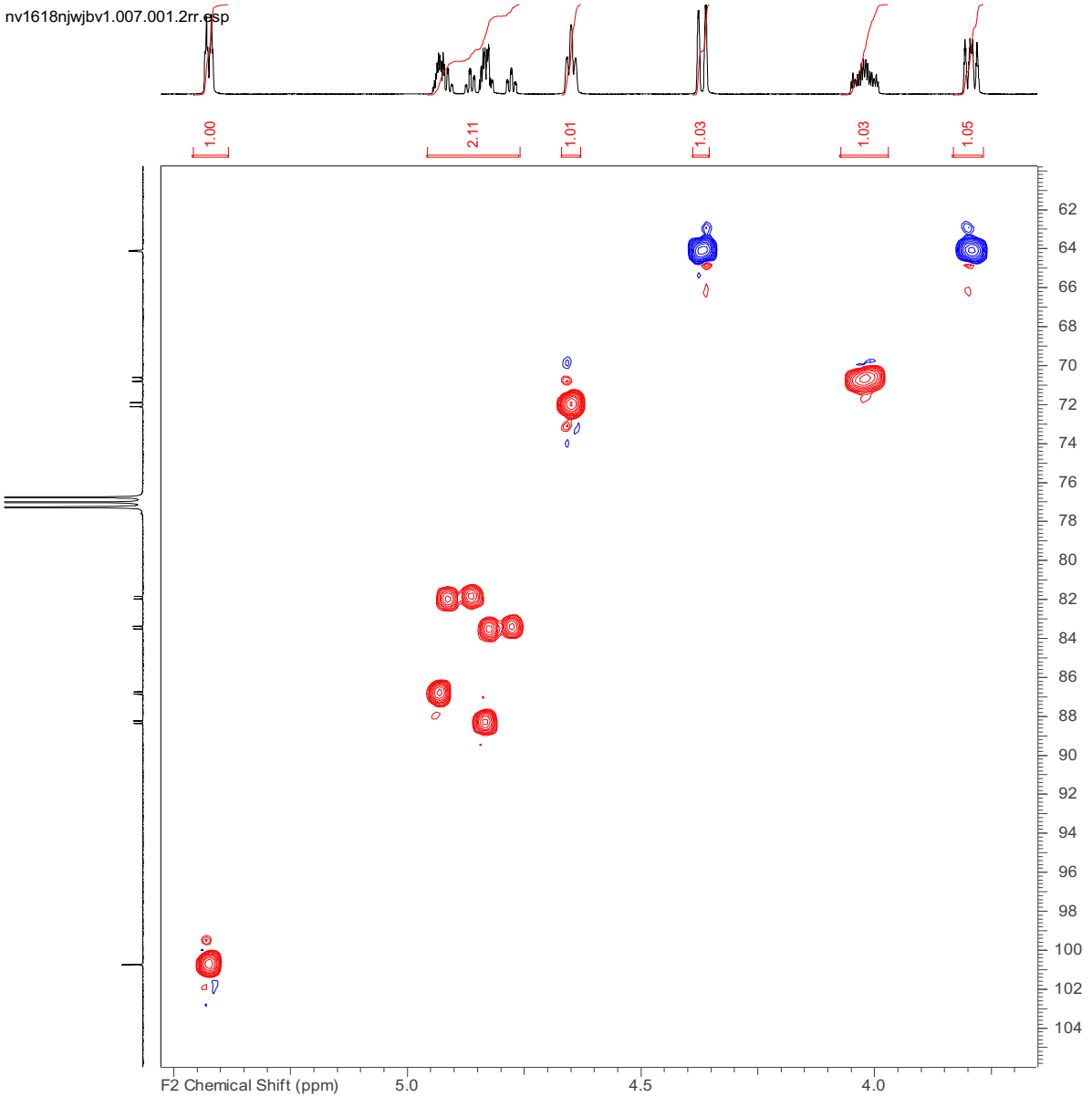
1.11.6 COSY ^{1}H-^{1}H (500 MHz, $CDCl_3$) (compound 19)



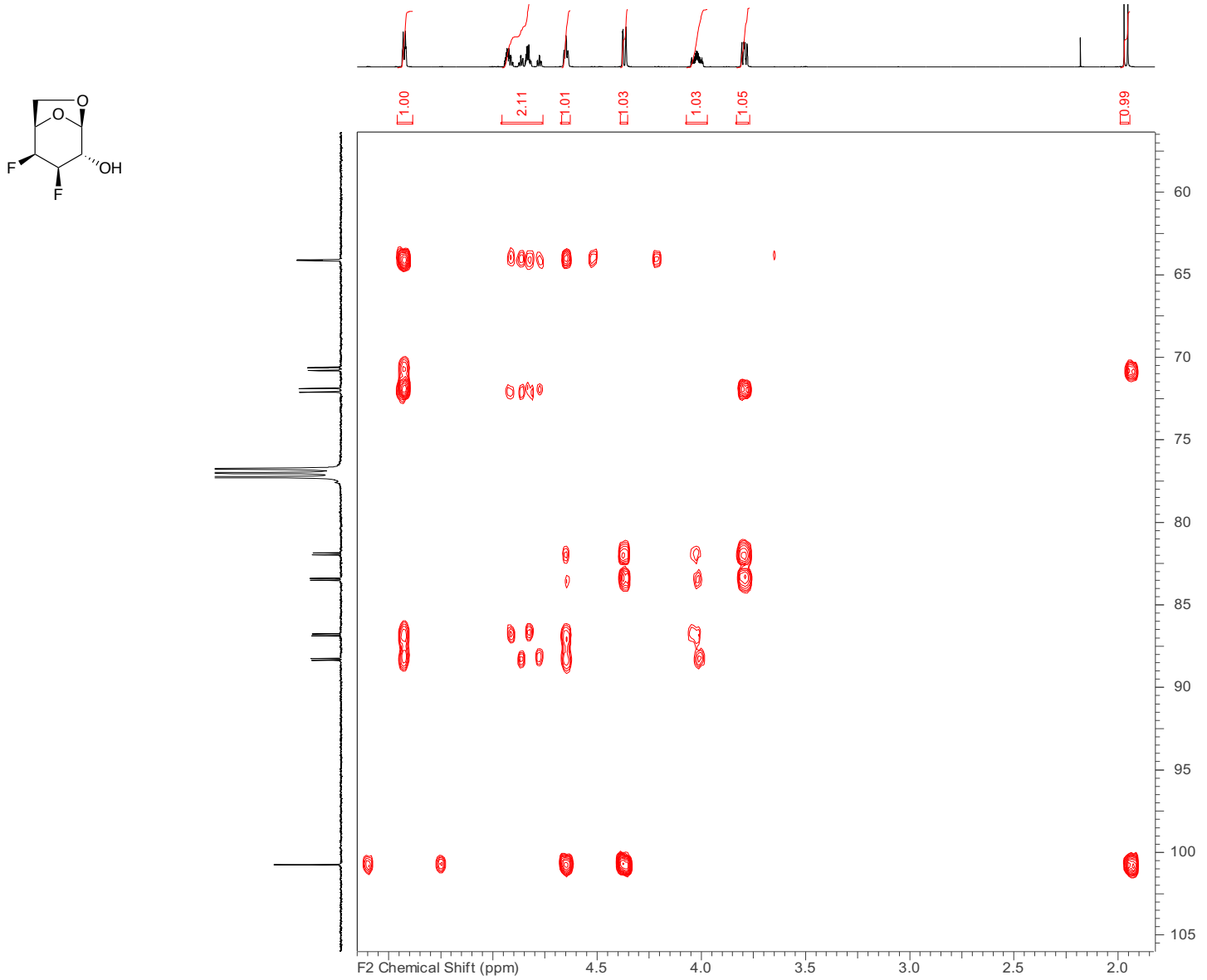


1.11.7 HSQC (500 MHz, $CDCl_3$) (compound 19)





1.11.8 HMBC (500 MHz, $CDCl_3$) (compound 19)

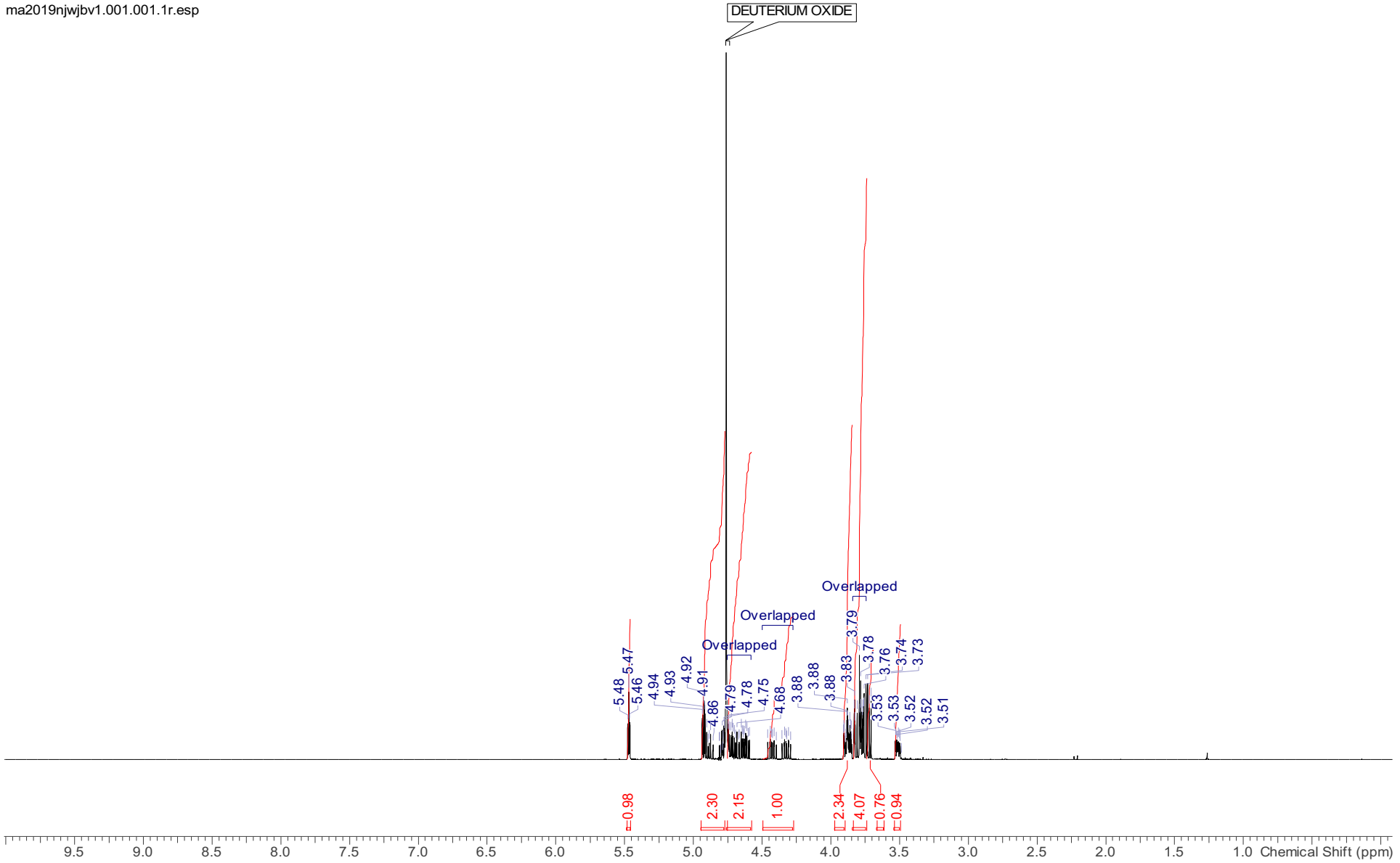


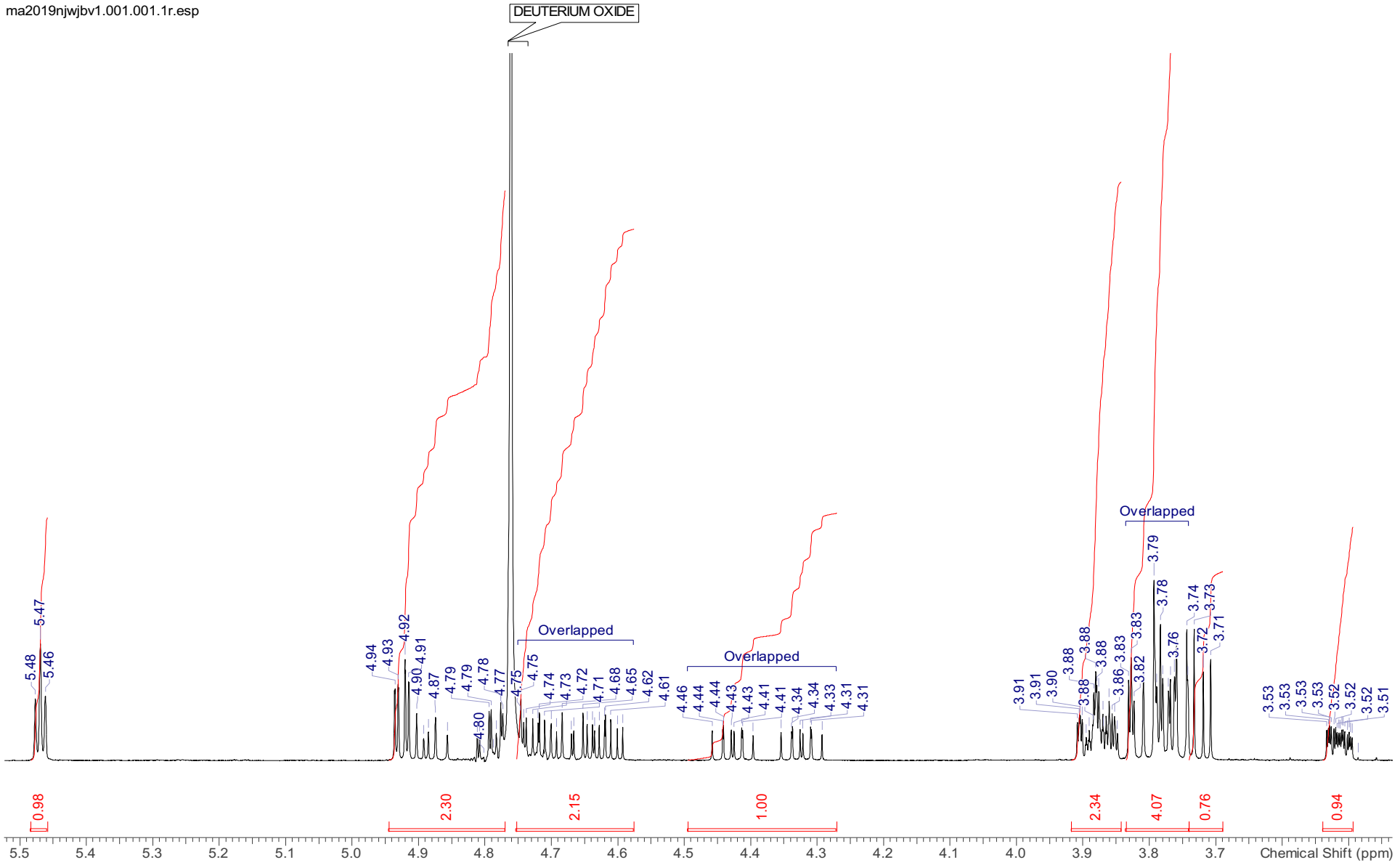
2 1H NMR data of 2,3-dideoxy-2,3-difluorogalactcose (13) in D_2O

2.1 Characterisation data

^{1}H NMR (500 MHz, D_2O): (ratio α:β 1:1) δ 5.47 (1H, t, *J* 3.8 Hz, H-1α), 4.93 (1H, ddd, *J* 7.7, 2.5, 0.5 Hz, H-1β), 4.83 (1H, ddt, *J* 54.6, 14.2, 8.9, 8.9 Hz, H-3α), 4.72 (1H, ddt, *J* 53.3, 16.1, 8.7, 8.7 Hz, H-3β), 4.67 (1H, dddd, *J* 49.9, 13.7, 9.0, 4.0 Hz, H-2α), 4.38 (1H, dddd, *J* 51.8, 14.3, 8.6, 7.9 Hz, H-2β), 3.92 – 3.84 (2H, m, H-5α + H-6α), 3.83 – 3.74 (4H, m, H-4α + H-4β + H-6β + H-6'β), 3.73 (1H, dd, *J* 12.5, 5.5 Hz, H-6'α), 3.51 (1H, dddd, *J* 10.1, 5.5, 2.3, 1.3 Hz, H-5β) ppm; **^{1}H{^{19}F} NMR** (500 MHz, D_2O): (ratio α:β 1:1) δ 5.46 (1H, d, *J* 3.8 Hz, H-1α), 4.92 (1H, d, *J* 7.9 Hz, H-1β), 4.83 (1H, br t, *J* 8.8 Hz, H-3α), 4.71 (1H, t, *J* 8.7 Hz, H-3β), 4.66 (1H, dd, *J* 8.8, 4.1 Hz, H-2α), 4.37 (1H, dd, *J* 8.6, 7.9 Hz, H-2β), 3.88 (1H, dd, *J* 12.6, 2.3 Hz, H-6α) 3.87 (1H, dddd, *J* 10.3, 4.7, 2.3, 0.6 Hz, H-5α), 3.83 (1H, dd, *J* 12.4, 2.3 Hz, H-6β), 3.80 – 3.74 (3H, m, H-4α + H-4β + H-6'β), 3.72 (1H, dd, *J* 12.4, 5.6 Hz, H-6'α), 3.51 (1H, ddd, *J* 10.0, 5.6, 2.3 Hz, H-5β) ppm.

2.2 ^{1}H NMR (500 MHz, D_2O) (compound 13)




ma2019njwjbv1.001.001.1r.esp
DEUTERIUM OXIDE
Overlapped
Overlapped
Overlapped
5.48
5.47
5.46
4.94
4.93
4.92
4.91
4.90
4.87
4.80
4.79
4.79
4.78
4.77
4.75
4.75
4.74
4.73
4.72
4.71
4.68
4.65
4.62
4.61
4.46
4.44
4.44
4.43
4.43
4.41
4.41
4.34
4.34
4.33
4.31
4.31
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3.91
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3.88
3.86
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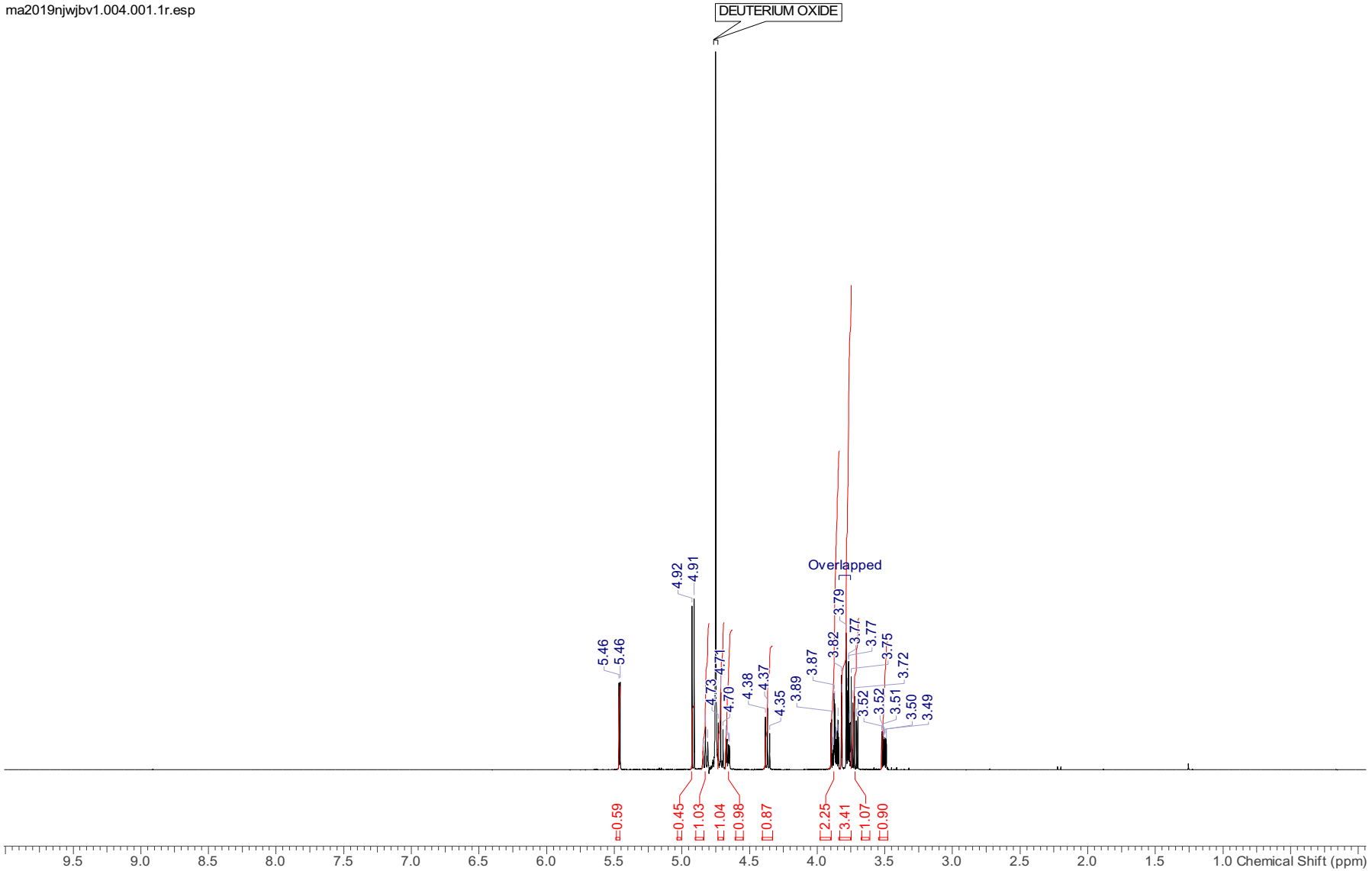
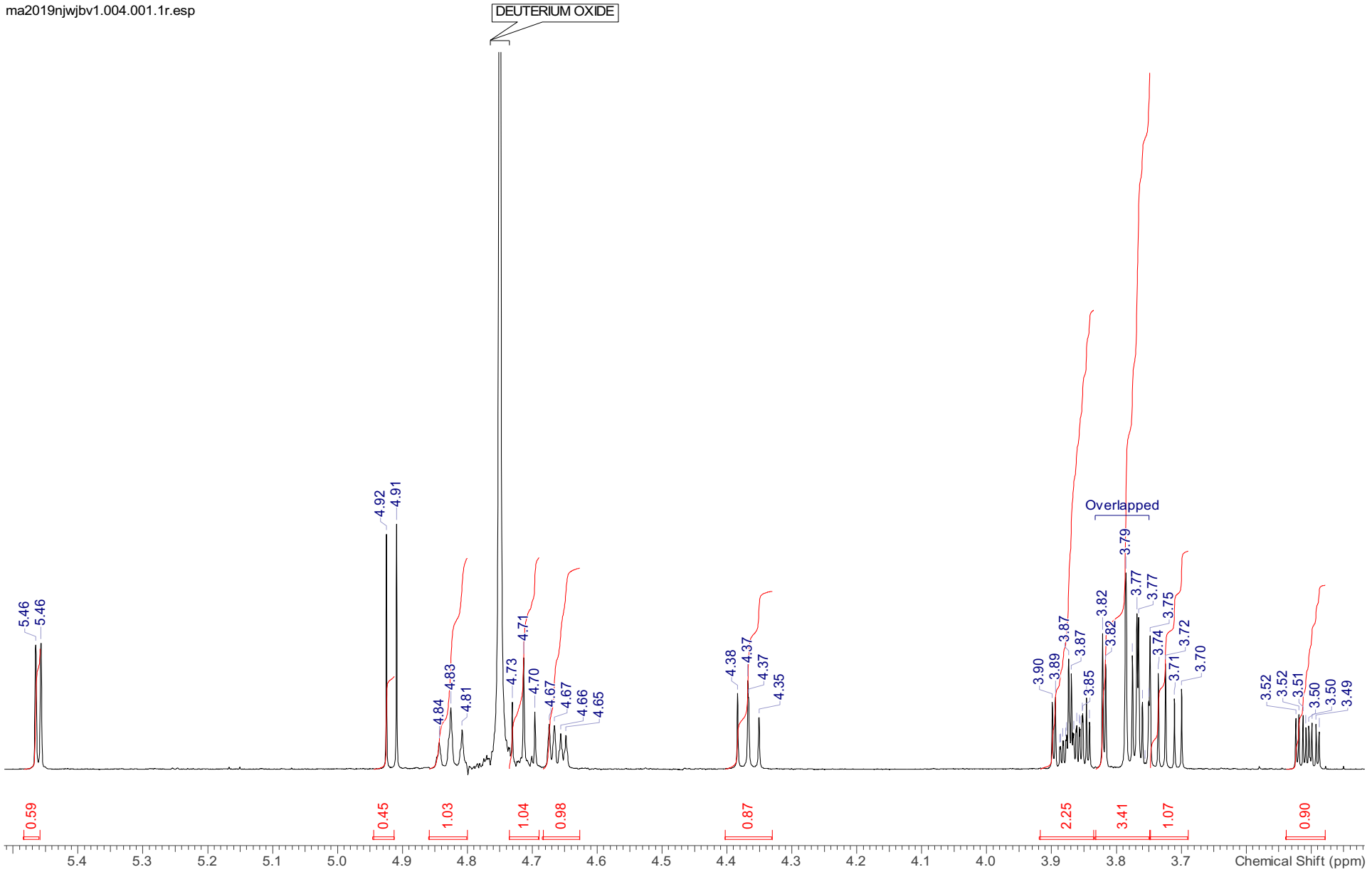
3.76
3.74
3.73
3.72
3.71
3.53
3.53
3.53
3.53
3.52
3.52
3.51
0.98
2.30
2.15
1.00
2.34
4.07
0.76
0.94
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
Chemical Shift (ppm)

2.3 $^{1}H\{^{19}F\}$ NMR (500 MHz, D_2O) (compound 13)




ma2019njwjbv1.004.001.1r.esp
DEUTERIUM OXIDE
Overlapped
5.46
5.46
4.92
4.91
4.84
4.83
4.81
4.73
4.71
4.70
4.67
4.67
4.66
4.65
4.38
4.37
4.37
4.35
3.90
3.89
3.87
3.87
3.85
3.82
3.82
3.79
3.77
3.77
3.75
3.74
3.72
3.71
3.70
3.52
3.52
3.51
3.50
3.50
3.49
0.59
0.45
1.03
1.04
0.98
0.87
2.25
3.41
1.07
0.90
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
Chemical Shift (ppm)

3 Crystallographic data

3.1 3,4-dideoxy-3,4-difluorogalactose 15a

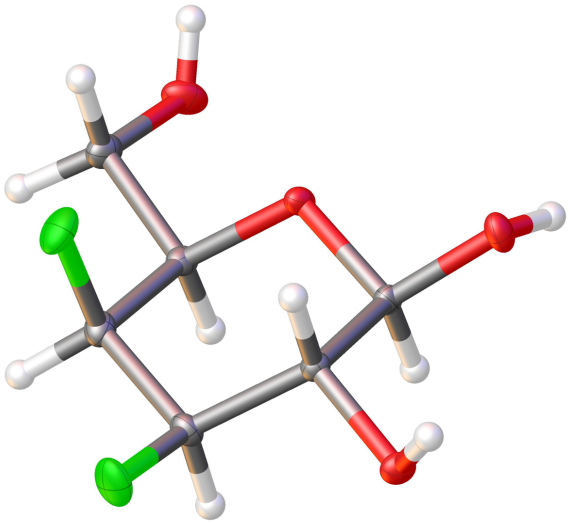


Figure 1: Thermal ellipsoids drawn at the 50% probability level.

Experimental. Single clear colourless prism-shaped crystals of **JBVLNS42tube7-24** were recrystallised from methanol by slow evaporation. A suitable crystal 0.28×0.09×0.07 mm^3 was selected and mounted on a MITIGEN holder silicon oil on an Rigaku AFC12 FRE-VHF diffractometer. The crystal was kept at a steady T = 100(2) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2016/6 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_6H_{10}F_2O_4$, M_r = 184.14, orthorhombic, $P2_12_12_1$ (No. 19), a = 8.3866(2) Å, b = 8.4182(2) Å, c = 10.2320(2) Å, $\alpha = \beta = \gamma = 90^\circ$, V = 722.38(3) Å^3, T = 100(2) K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.171, 16292 reflections measured, 1816 unique (R_{int} = 0.0207) which were used in all calculations. The final wR_2 was 0.0609 (all data) and R_1 was 0.0218 (I > 2(I)).

3.2 1,6-Anhydro-3,4-dideoxy-3,4-difluoro-β-D-galactopyranose 19

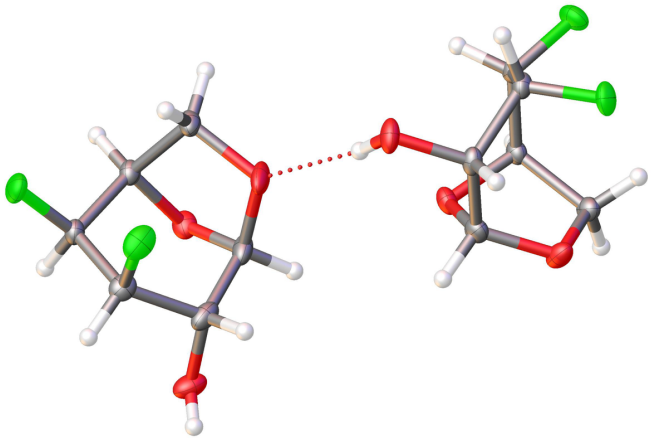


Figure 2: Thermal ellipsoids drawn at the 50% probability level.

Experimental. Single clear colourless prism-shaped crystals of **MB-7922-053** were recrystallised from EtOAc by slow evaporation. A suitable crystal 0.23×0.12×0.06 mm^3 was selected and mounted on a MITIGEN holder silicon oil on an Rigaku AFC12 FRE-VHF diffractometer. The crystal was kept at a steady T = 100(2) K during data collection. The structure was solved with the ShelXT 2014/5 (Sheldrick, 2014) structure solution program using the direct phasing methods solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2016/6 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_6H_8F_2O_3$, M_r = 166.12, orthorhombic, $P2_12_12_1$ (No. 19), a = 5.6134(2) Å, b = 10.6394(3) Å, c = 21.7983(5) Å, $\alpha = \beta = \gamma = 90^\circ$, V = 1301.86(7) Å^3, T = 100(2) K, Z = 8, Z' = 2, μ(MoK$_\alpha$) = 0.169, 17978 reflections measured, 4125 unique (R_{int} = 0.0346) which were used in all calculations. The final wR_2 was 0.0761 (all data) and R_1 was 0.0307 (I > 2(I)).

3.3 4,6-Di-*O*-Acetyl-2,3-dideoxy-2,3-difluoro-α-D-galactopyranose α-16d

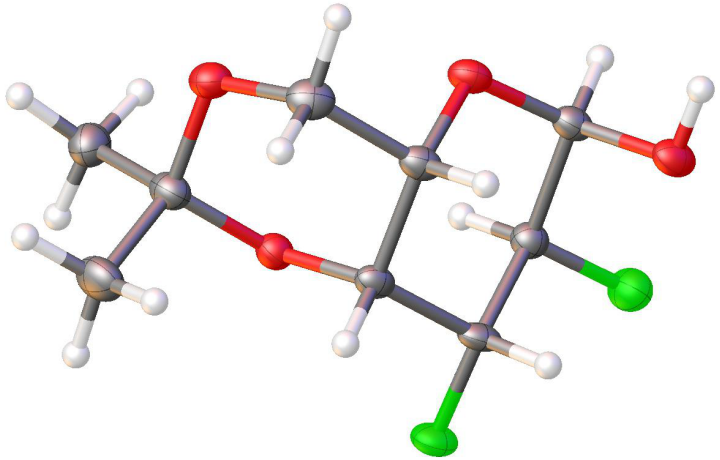


Figure 3: Thermal ellipsoids drawn at the 50% probability level.

Experimental. Single clear colourless block-shaped crystals of (**2016sot0008-K-100K**) were recrystallised from pentane and Et_2O by slow evaporation. A suitable crystal (0.31×0.24×0.04) was selected and mounted on a MITIGEN holder in perfluoroether oil on a Rigaku AFC12 FRE-HF diffractometer. The crystal was kept at T = 100(2) K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Direct Methods solution method. The model was refined with ShelXL (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_9H_{14}F_2O_4$, M_r = 224.20, monoclinic, $P2_1$ (No. 4), a = 10.9535(5) Å, b = 7.9162(3) Å, c = 11.9942(5) Å, β = 98.836(4)°, $\alpha = \gamma = 90°$, V = 1027.67(7) Å^3, T = 100(2) K, Z = 4, Z' = 2, μ(MoK_α) = 0.134, 9660 reflections measured, 5263 unique (R_{int} = 0.0220) which were used in all calculations. The final wR_2 was 0.0943 (all data) and R_1 was 0.0404 (I > 2(I)).