Supporting Information

Regioselective manipulation of GlcNAc provides allosamine, lividosamine, and related compounds

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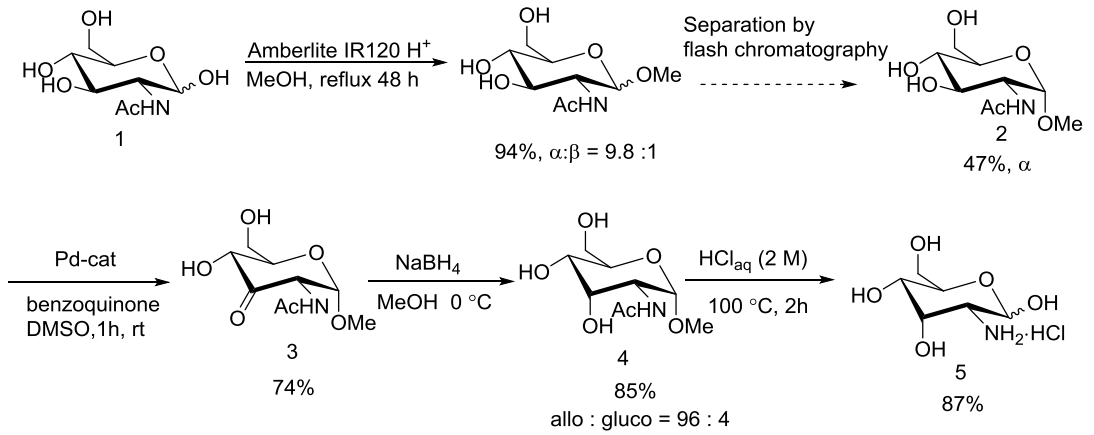
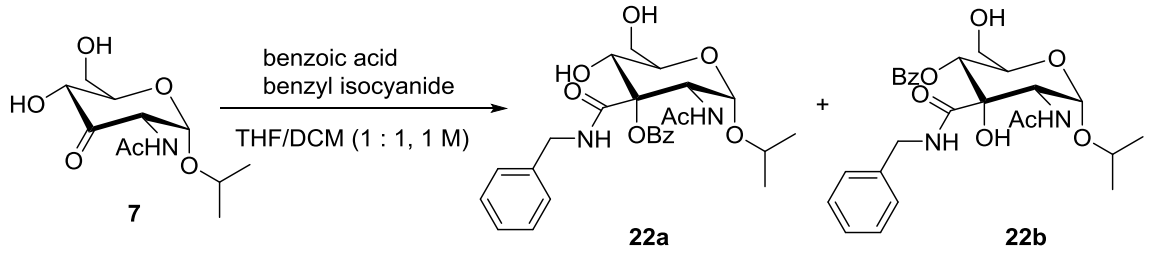
Prof. Dr. Martin Witte – m.d.witte@rug.nl.

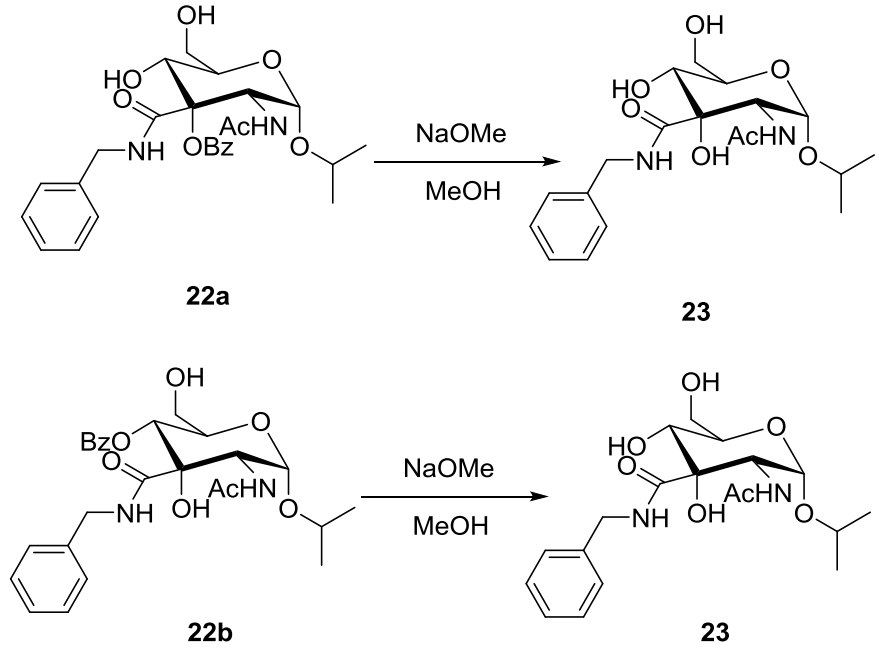


Scheme S1. Initial study to prepare D-allosamine starting from methyl-α-GlucNAc

4-(benzylcarbamoyl)-4-hydroxy-2-(hydroxymethyl)-6-isopropoxytetrahydro-2*H*-pyran-3-yl benzoate (22a and 22b)

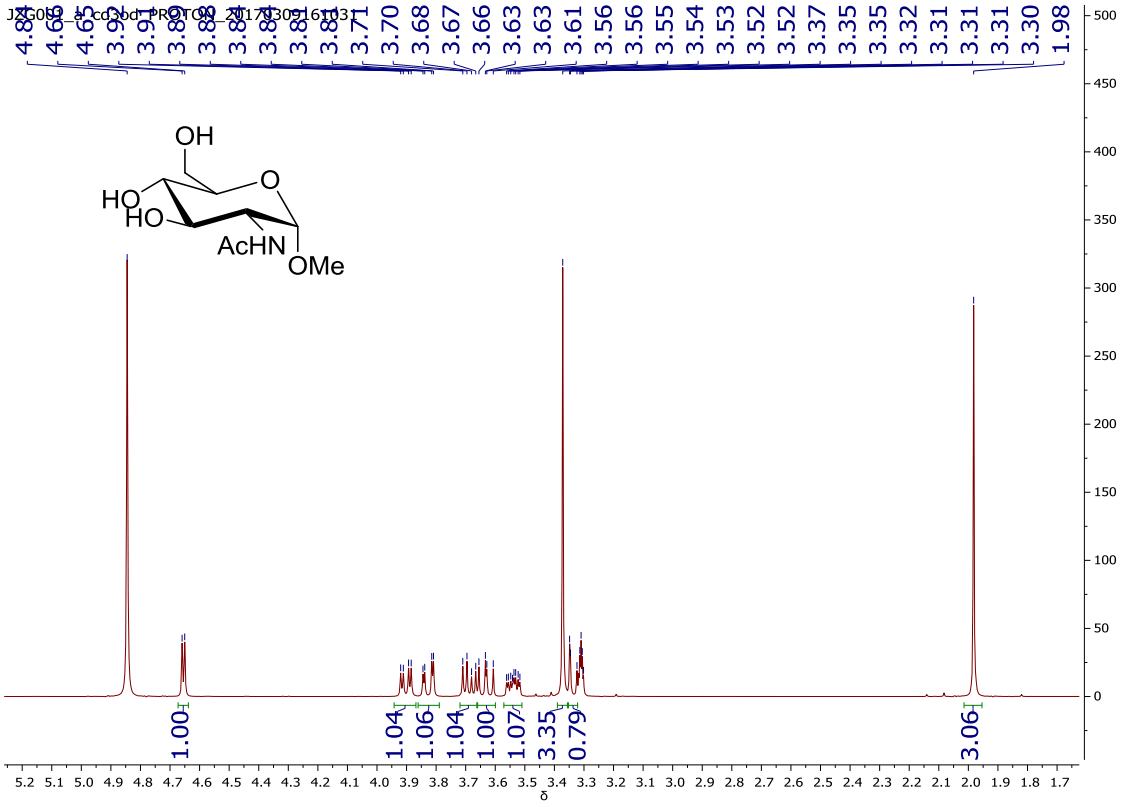


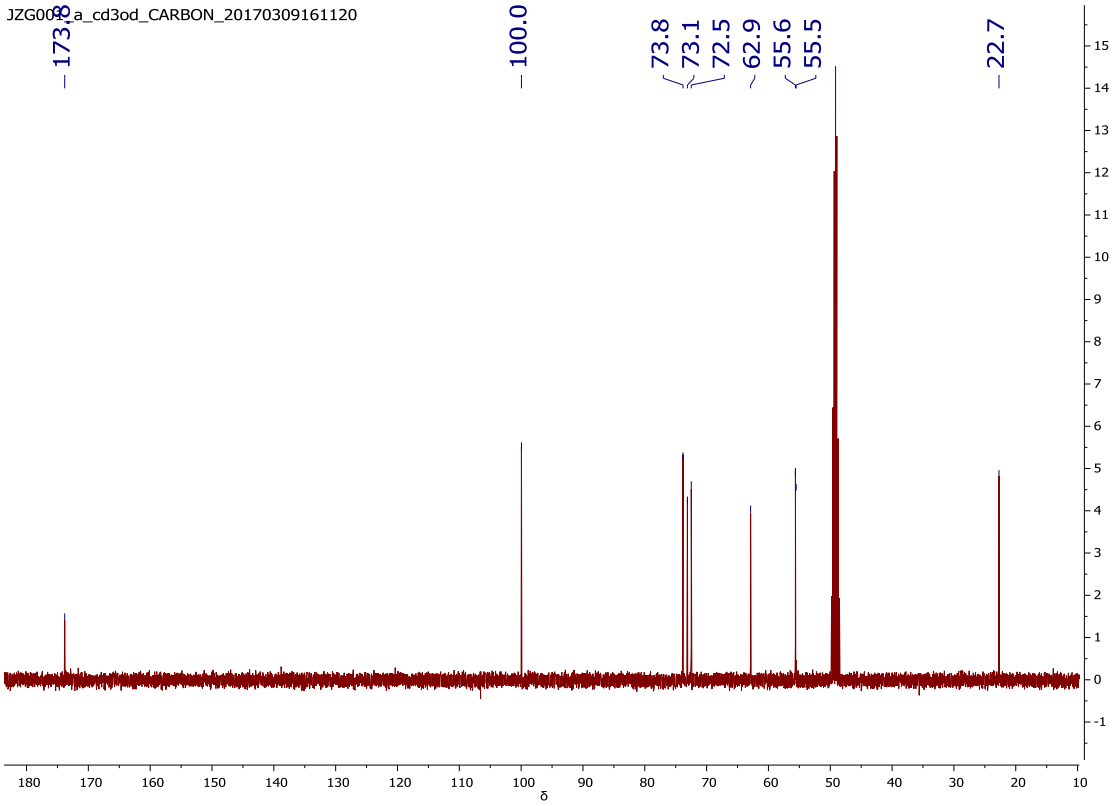
(2*S*,3*R*,4*S*,5*R*,6*R*)-3-acetamido-*N*-benzyl-4,5-dihydroxy-6-(hydroxymethyl)-2-isopropoxytetrahydro-2*H*-pyran-4-carboxamide (23)



Spectroscopic data

Methyl 2-acetamido-2-deoxy-α-D-glucopyranoside (2)

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173.8
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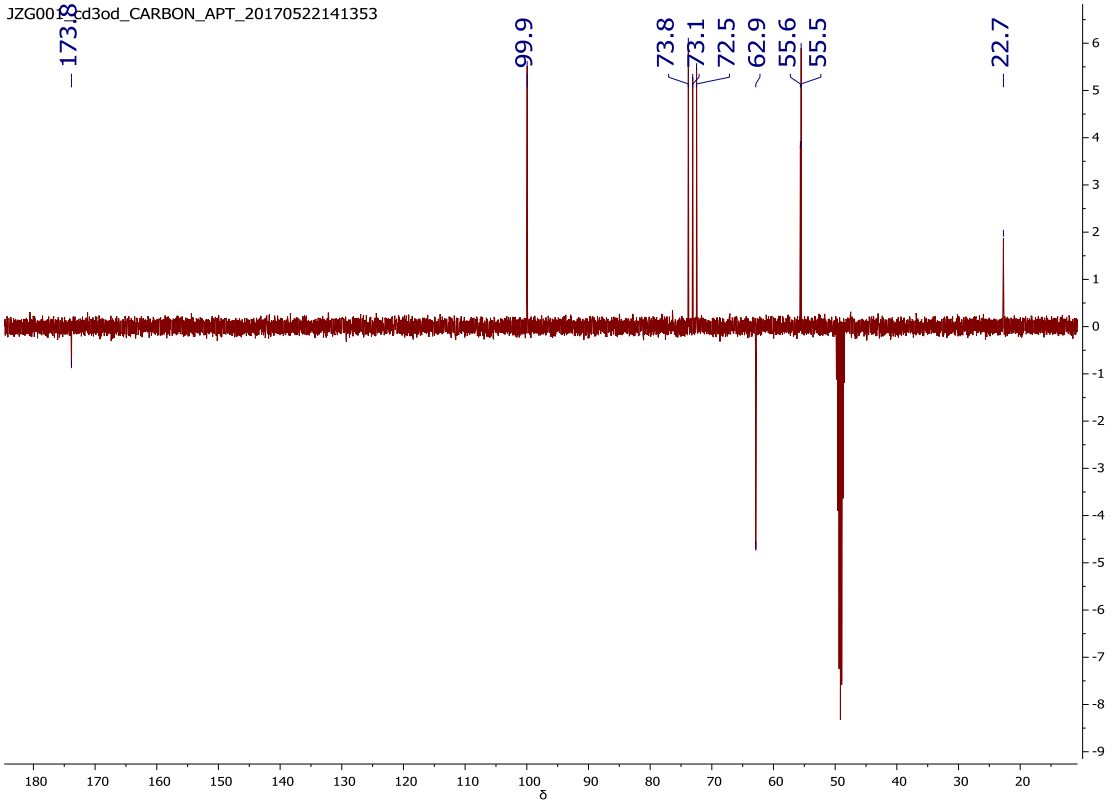
73.8
73.1
72.5
62.9
55.6
55.5
22.7
δ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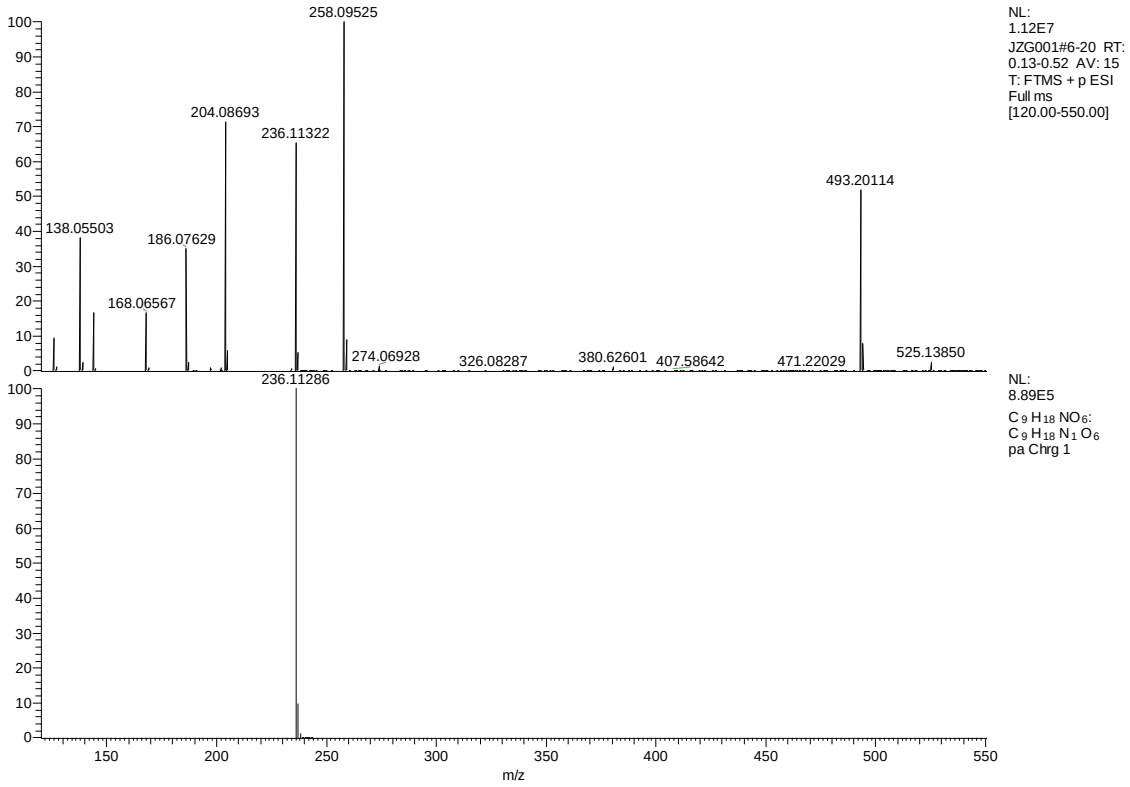
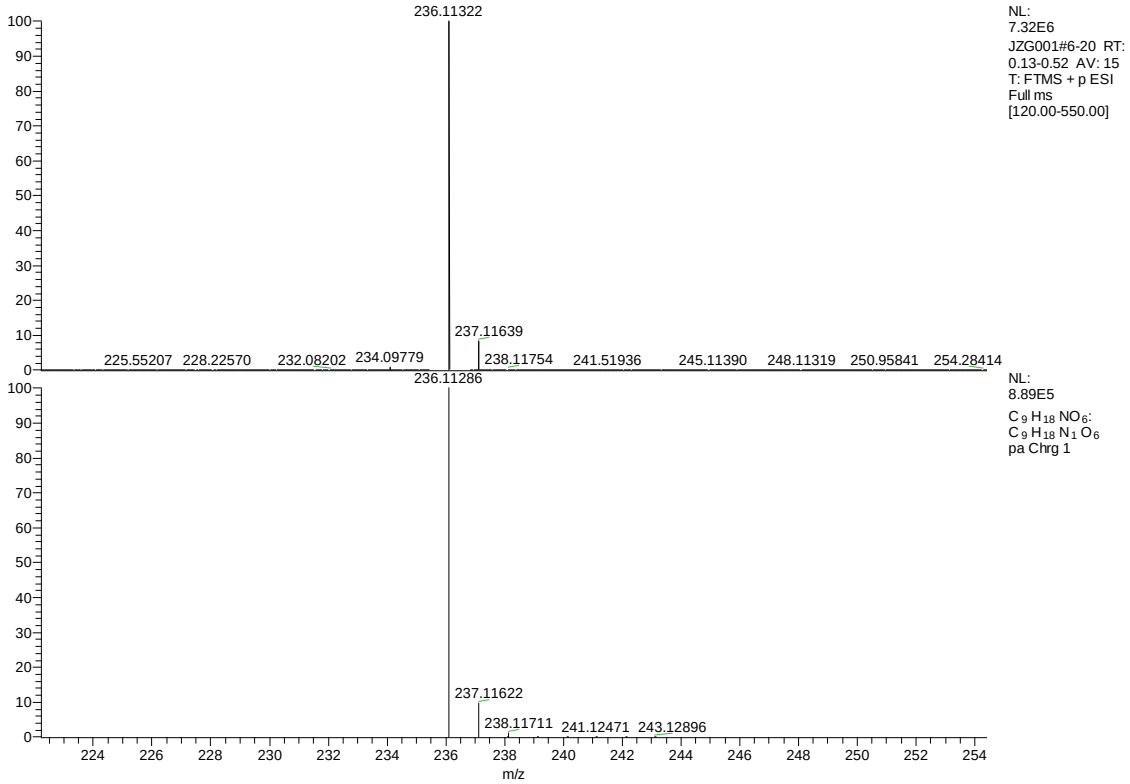
173.8
99.9
73.8
73.1
72.5
62.9
55.6
55.5
22.7
δ


258.09525
204.08693
236.11322
493.20114
138.05503
186.07629
168.06567
274.06928
326.08287
380.62601
407.58642
471.22029
525.13850
NL:
1.12E7
JZG001#6-20 RT:
0.13-0.52 AV: 15
T: FTMS + p ESI
Full ms
[120.00-550.00]
236.11286
NL:
8.89E5
C 9 H 18 NO 6:
C 9 H 18 N 1 O 6
pa Chrg 1
m/z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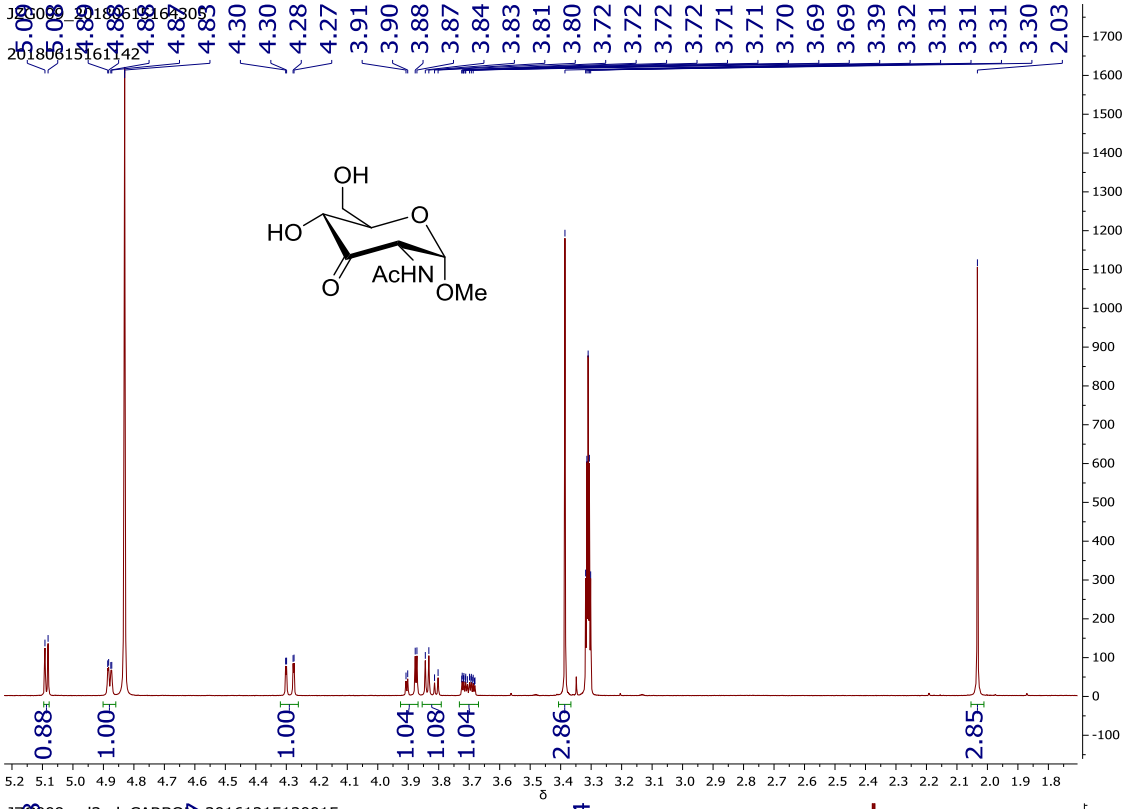
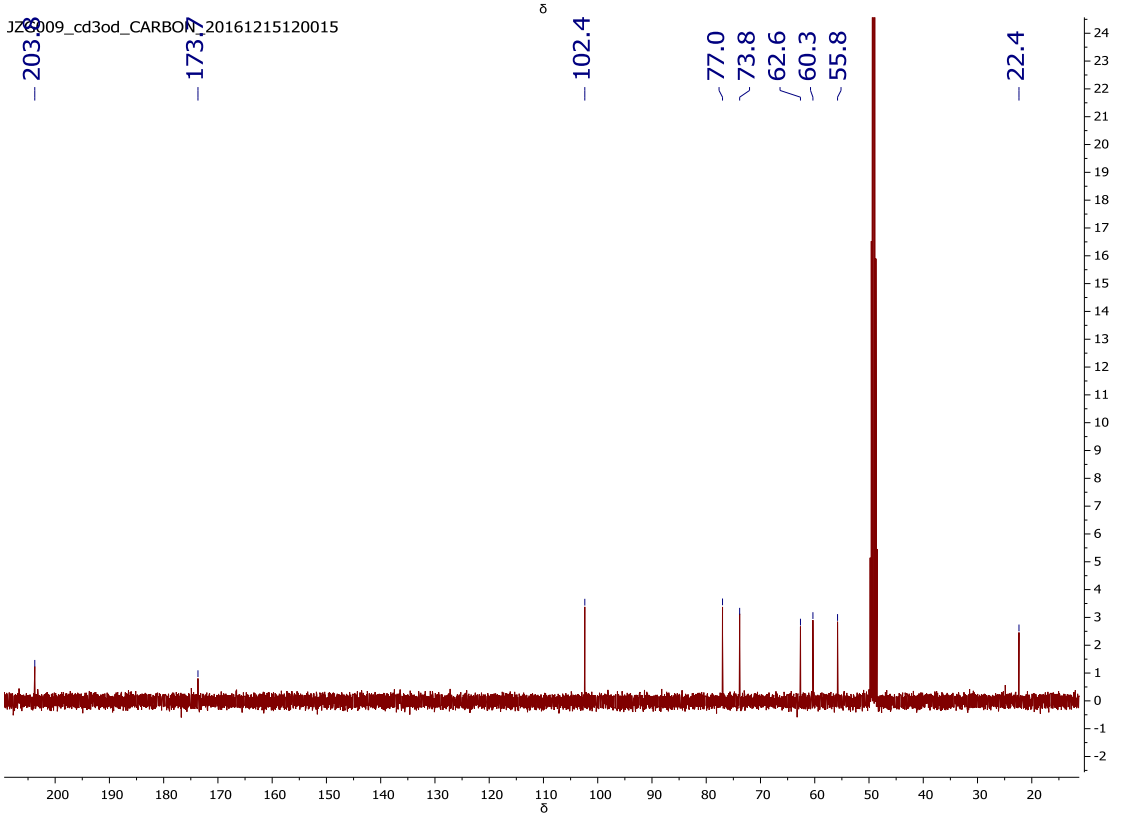
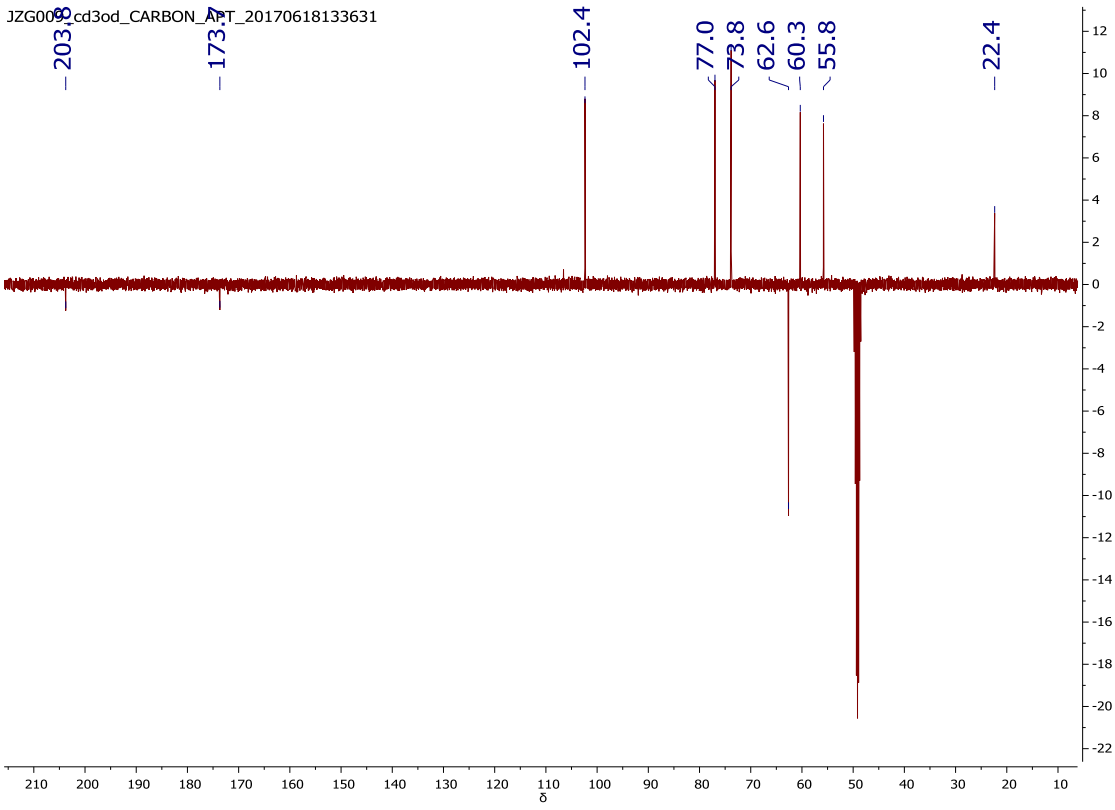
237.11639
225.55207
228.22570
232.08202
234.09779
238.11754
241.51936
245.11390
248.11319
250.95841
254.28414
NL:
7.32E6
JZG001#6-20 RT:
0.13-0.52 AV: 15
T: FTMS + p ESI
Full ms
[120.00-550.00]
236.11286
237.11622
238.11711
241.12471
243.12896
NL:
8.89E5
C 9 H 18 NO 6:
C 9 H 18 N 1 O 6
pa Chrg 1
m/z

Methyl 2-acetamido-2-deoxy-α-D-glucopyran-3-ulose (3)



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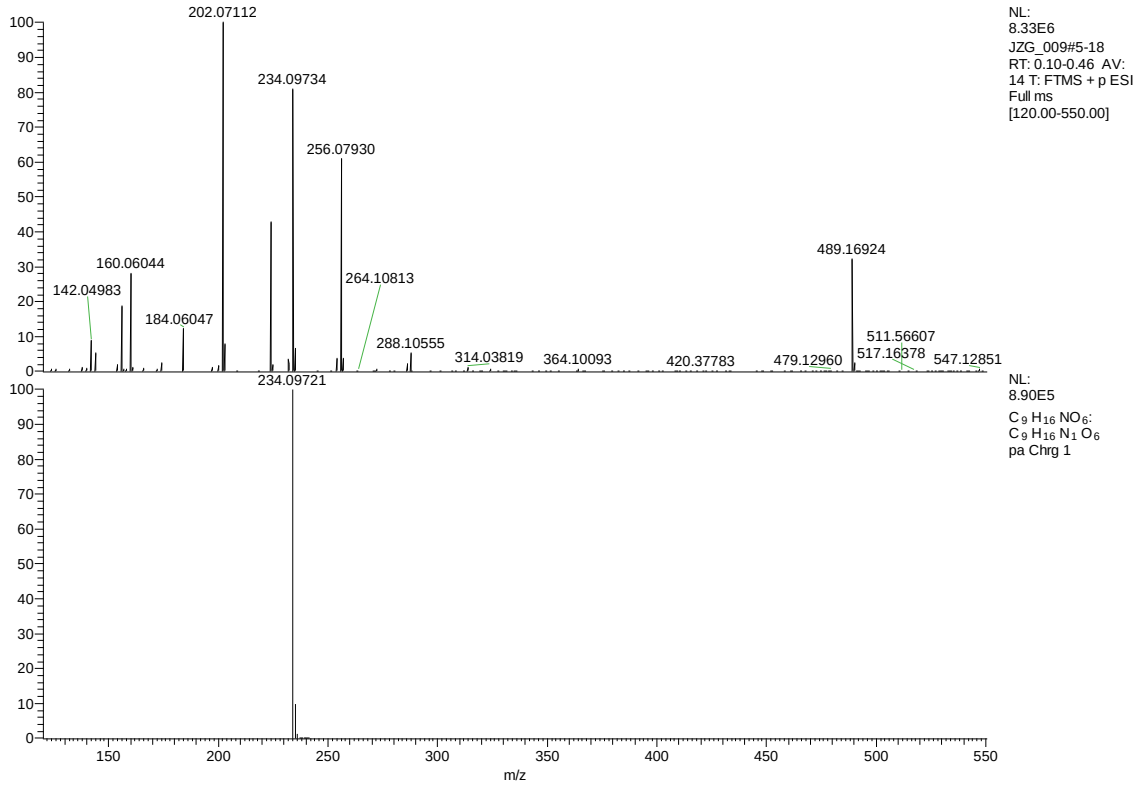
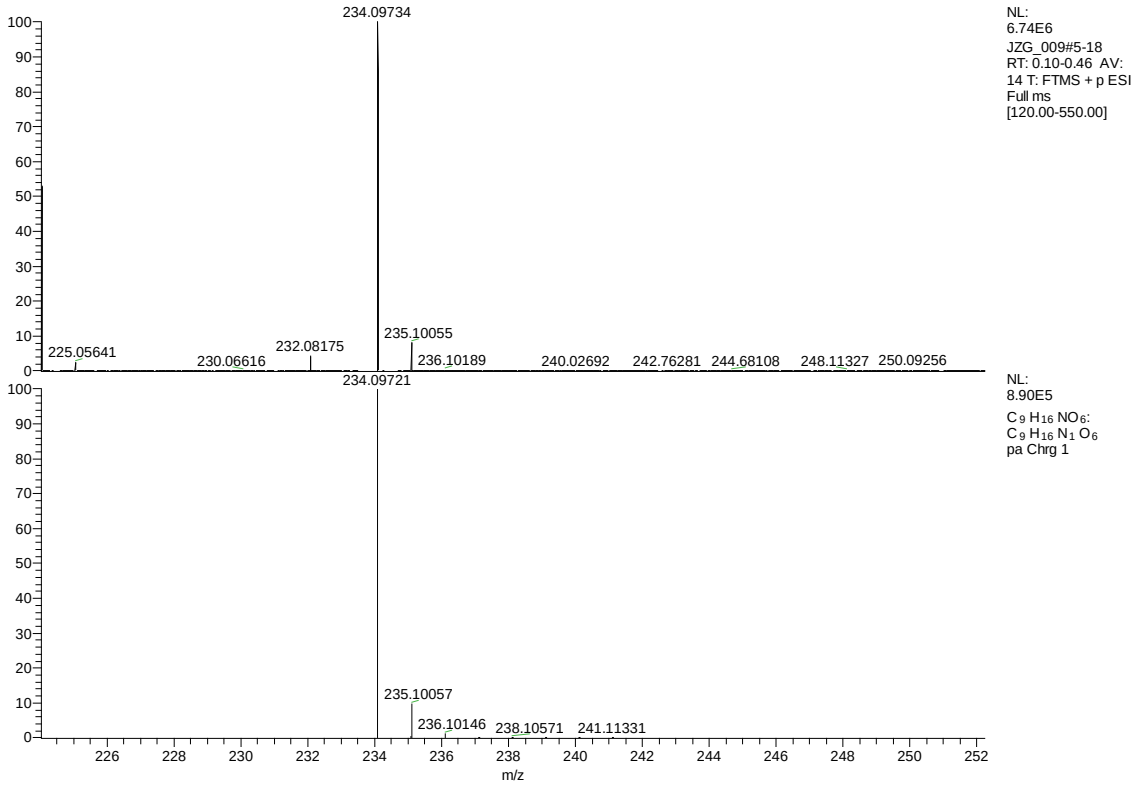
173.7
102.4
77.0
73.8
62.6
60.3
55.8
22.4
δ


202.07112
234.09734
256.07930
160.06044
142.04983
184.06047
264.10813
288.10555
314.03819
364.10093
420.37783
479.12960
489.16924
511.56607
517.16378
547.12851
234.09721
NL:
8.33E6
JZG_009#5-18
RT: 0.10-0.46 AV:
14 T: FTMS + p ESI
Full ms
[120.00-550.00]
NL:
8.90E5
C9 H16 NO6:
C9 H16 N1 O6
pa Chrg 1
m/z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NL:
6.74E6
JZG_009#5-18
RT: 0.10-0.46 AV:
14 T: FTMS + p ESI
Full ms
[120.00-550.00]
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230.06616
232.08175
235.10055
236.10189
240.02692
242.76281
244.68108
248.11327
250.09256
234.09721
NL:
8.90E5
C9 H16 NO6:
C9 H16 N1 O6
pa Chrg 1
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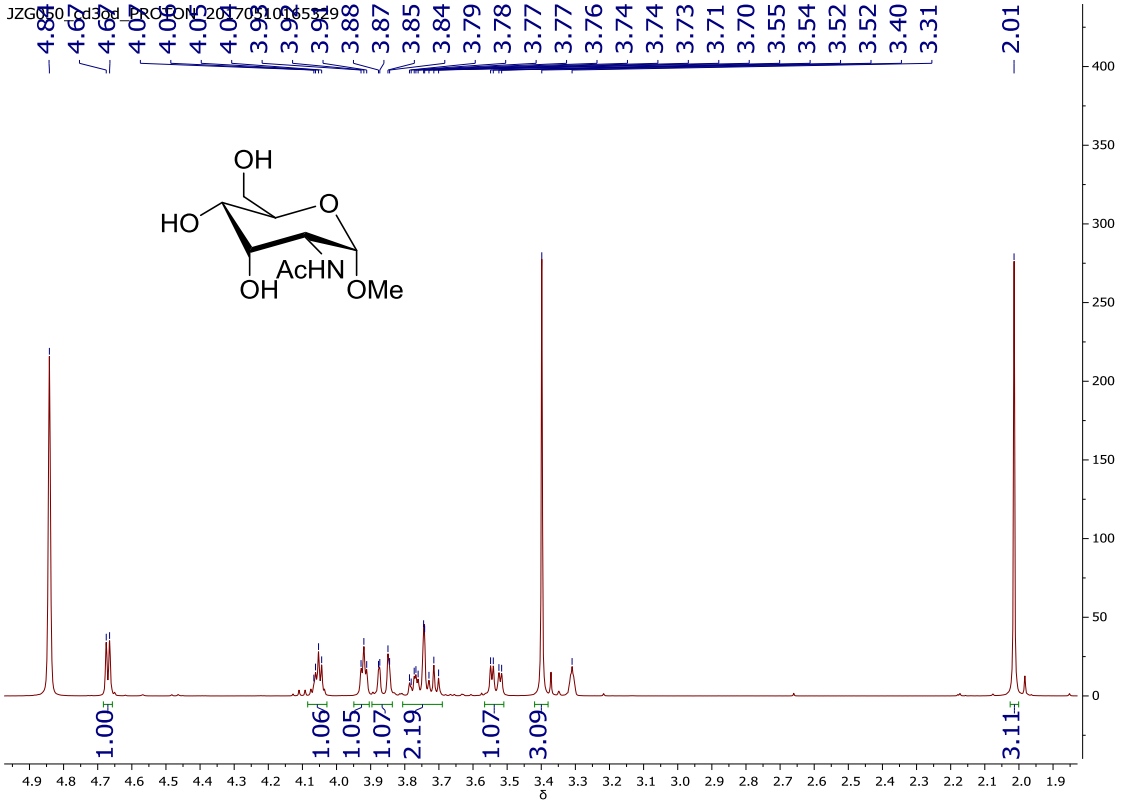
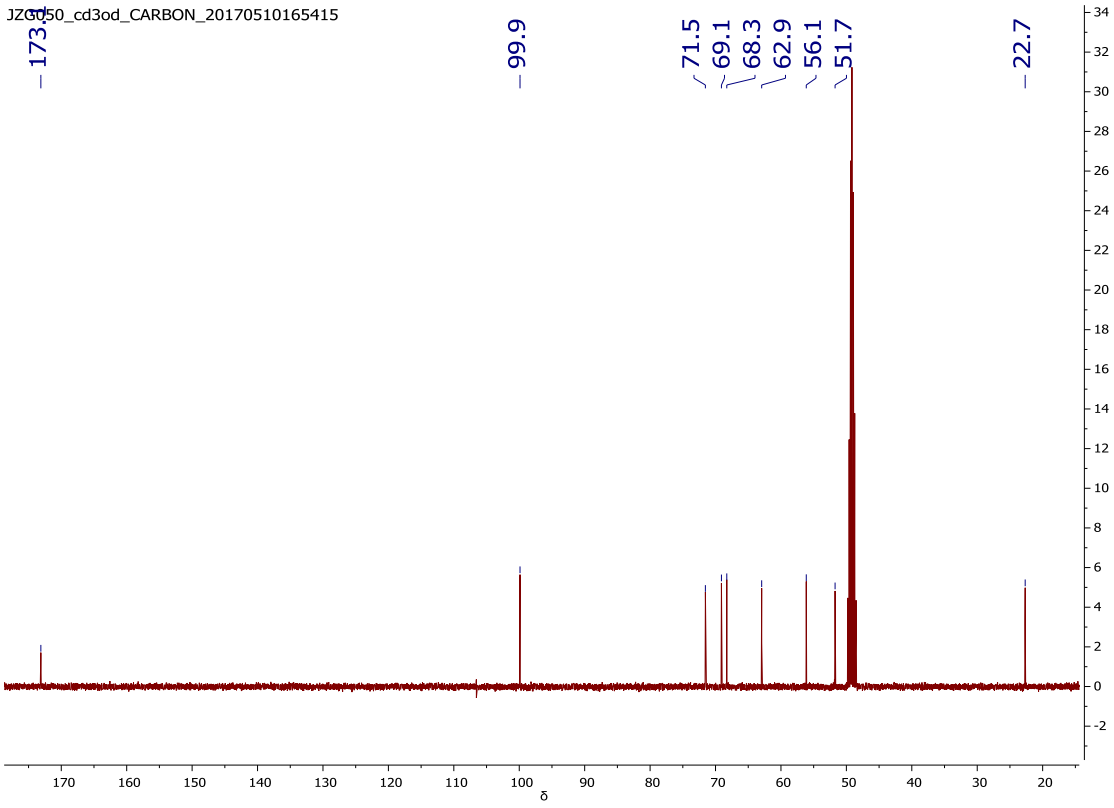
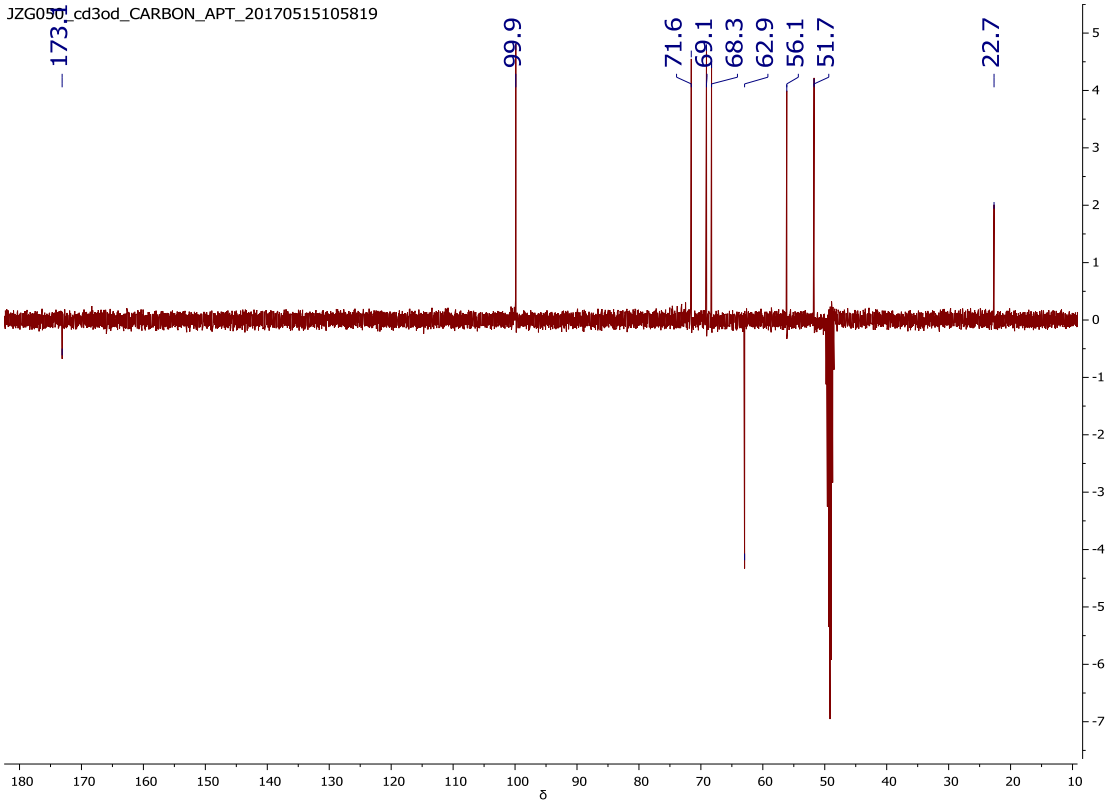
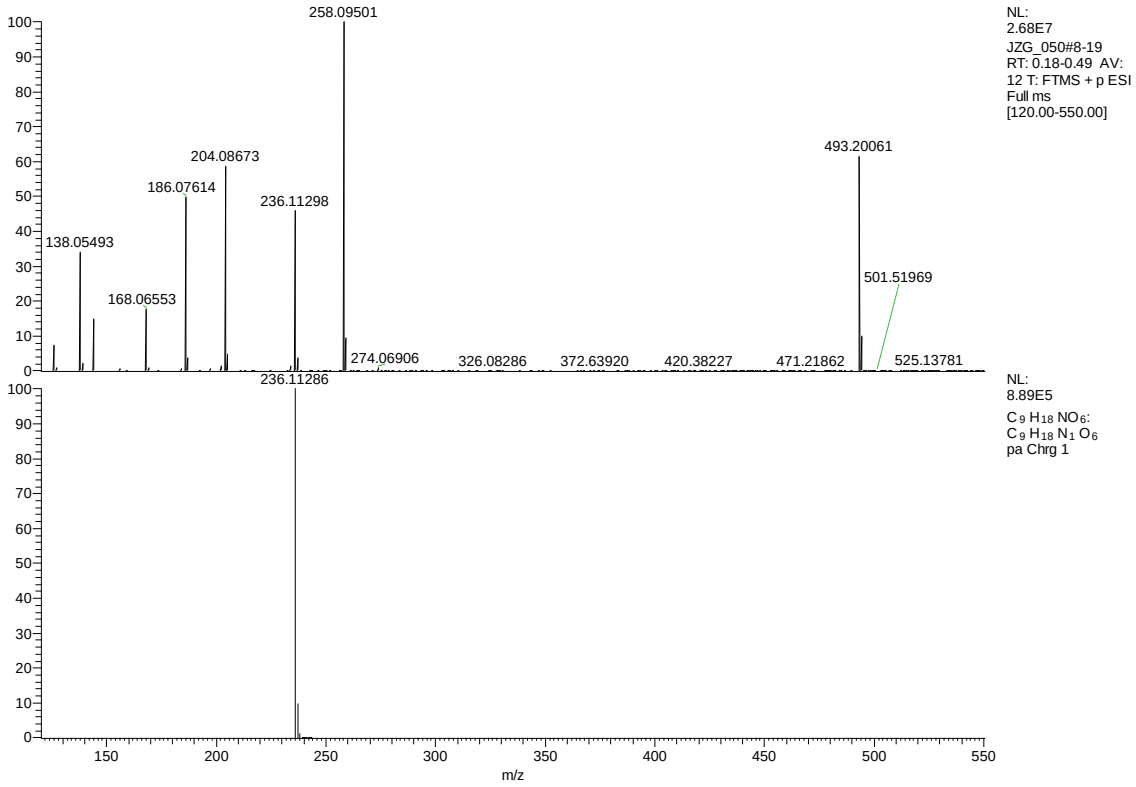
236.10146
238.10571
241.11331
m/z

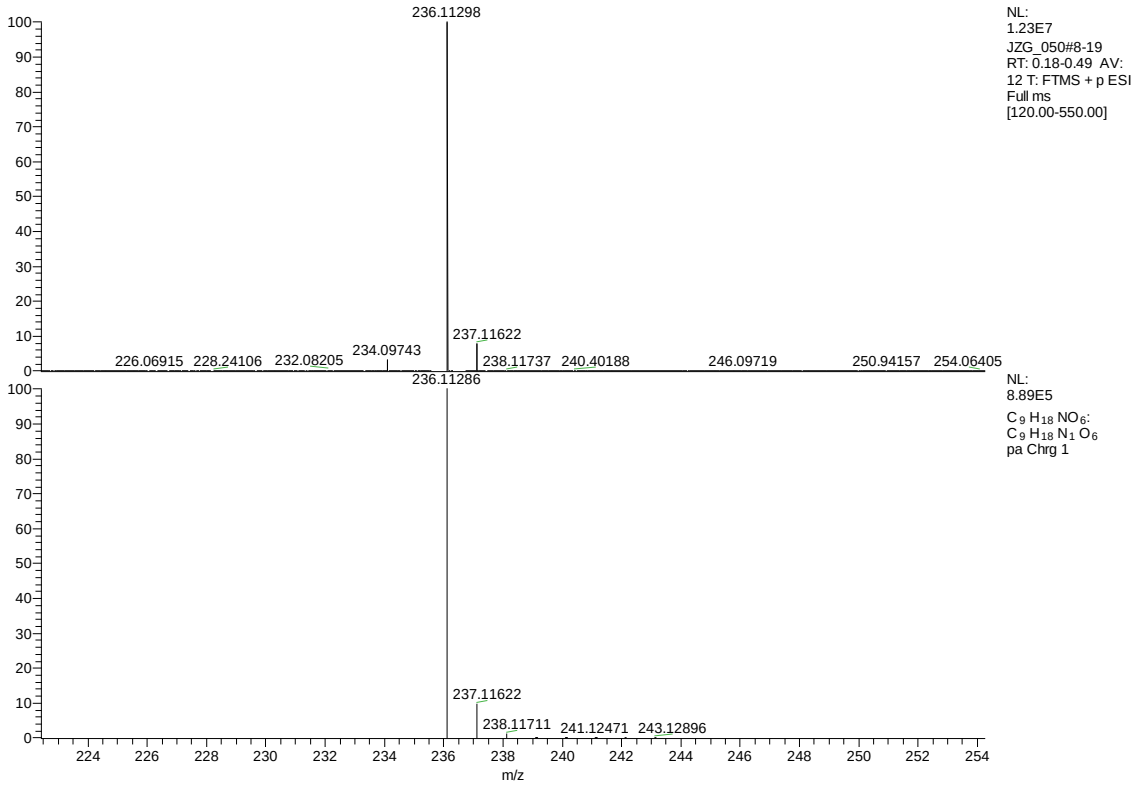
Methyl 2-acetamido-2-deoxy-α-D-allopyranoside (4)




JZG050_cd3od_CARBON_20170510165415
173.4
99.9
71.5
69.1
68.3
62.9
56.1
51.7
22.7
δ


JZG050_cd3od_CARBON_APT_20170515105819
173.4
99.9
71.6
69.1
68.3
62.9
56.1
51.7
22.7
δ


258.09501
493.20061
204.08673
186.07614
236.11298
138.05493
501.51969
168.06553
274.06906
326.08286
372.63920
420.38227
471.21862
525.13781
NL:
2.68E7
JZG_050#8-19
RT: 0.18-0.49 AV:
12 T: FTMS + p ESI
Full ms
[120.00-550.00]
236.11286
NL:
8.89E5
C9 H18 NO6:
C9 H18 N1 O6
pa Chrg 1
m/z


236.11298
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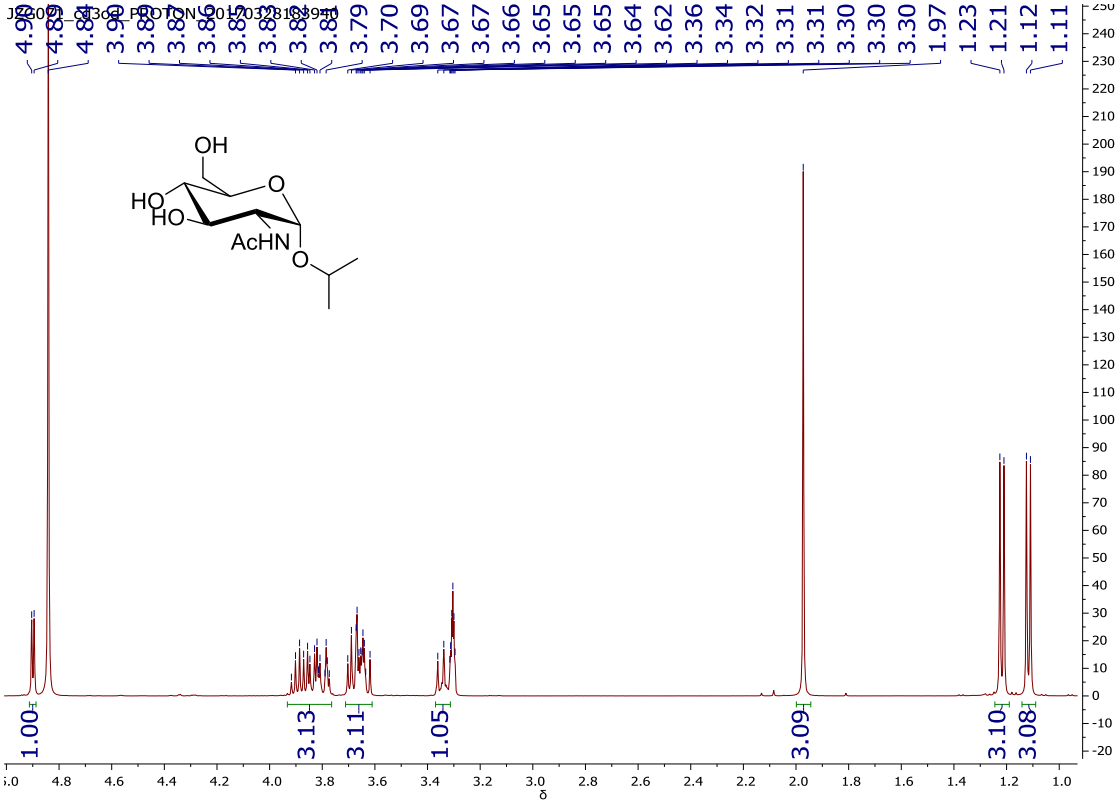
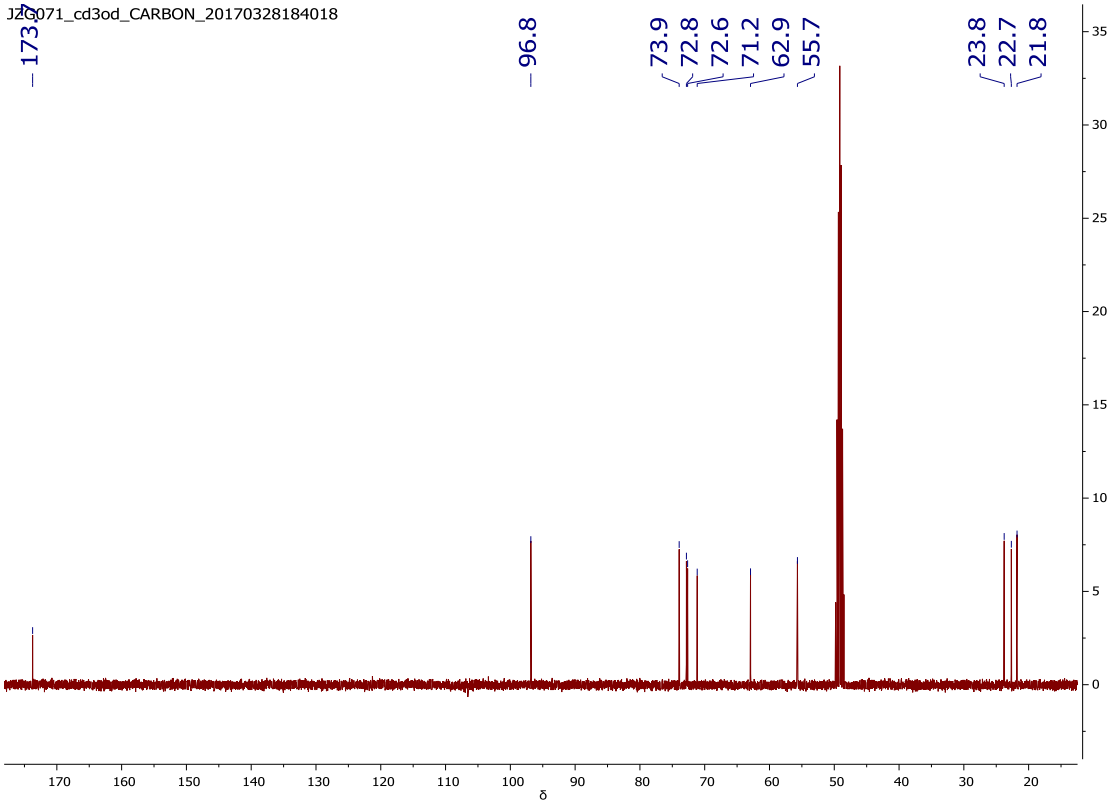
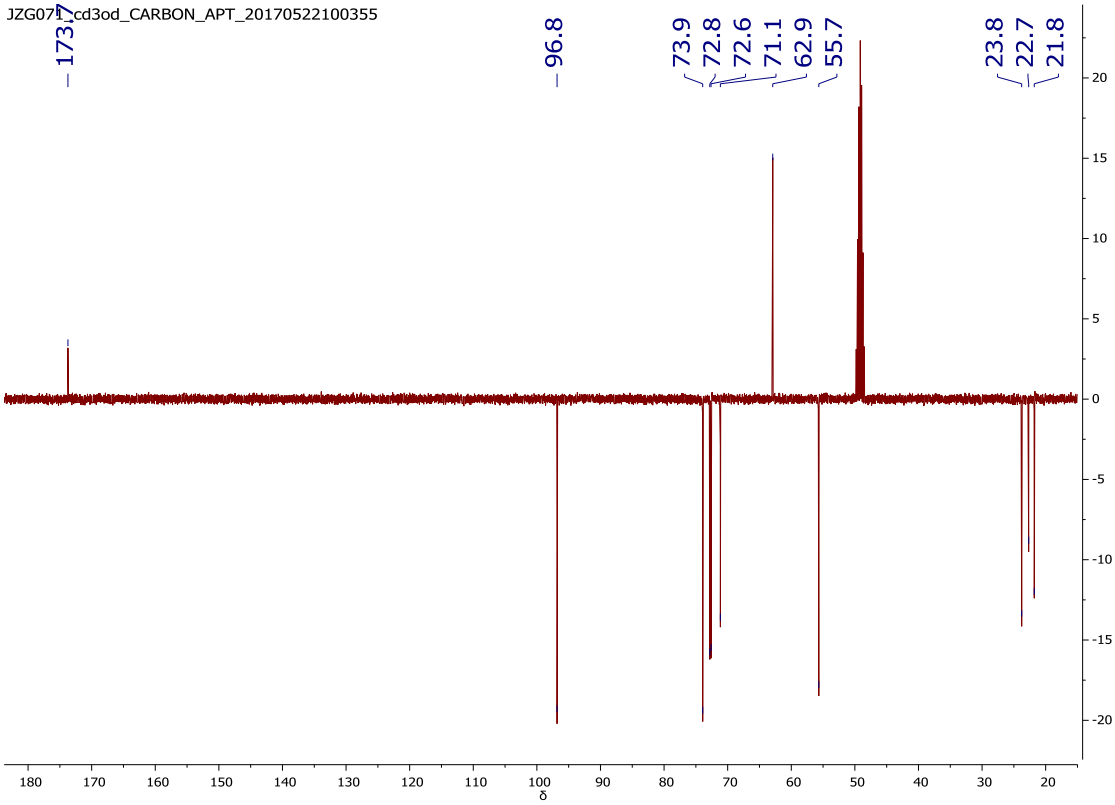
228.24106
232.08205
234.09743
238.11737
240.40188
246.09719
250.94157
254.06405
NL:
1.23E7
JZG_050#8-19
RT: 0.18-0.49 AV:
12 T: FTMS + p ESI
Full ms
[120.00-550.00]
236.11286
NL:
8.89E5
C9 H18 NO6:
C9 H18 N1 O6
pa Chrg 1
237.11622
238.11711
241.12471
243.12896
m/z

Isopropyl 2-acetamido-2-deoxy-α-D-glucopyranoside (6)



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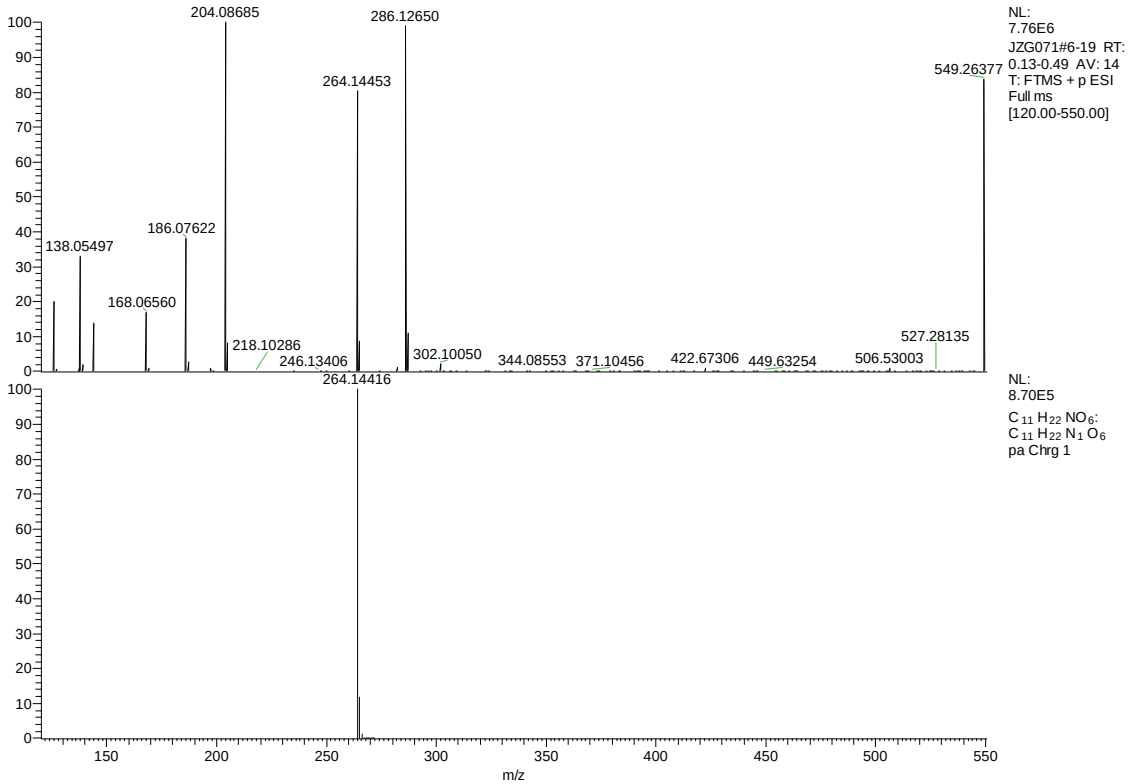
96.8
73.9
72.8
72.6
71.1
62.9
55.7
23.8
22.7
21.8
δ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264.14453
549.26377
186.07622
138.05497
168.06560
218.10286
246.13406
264.14416
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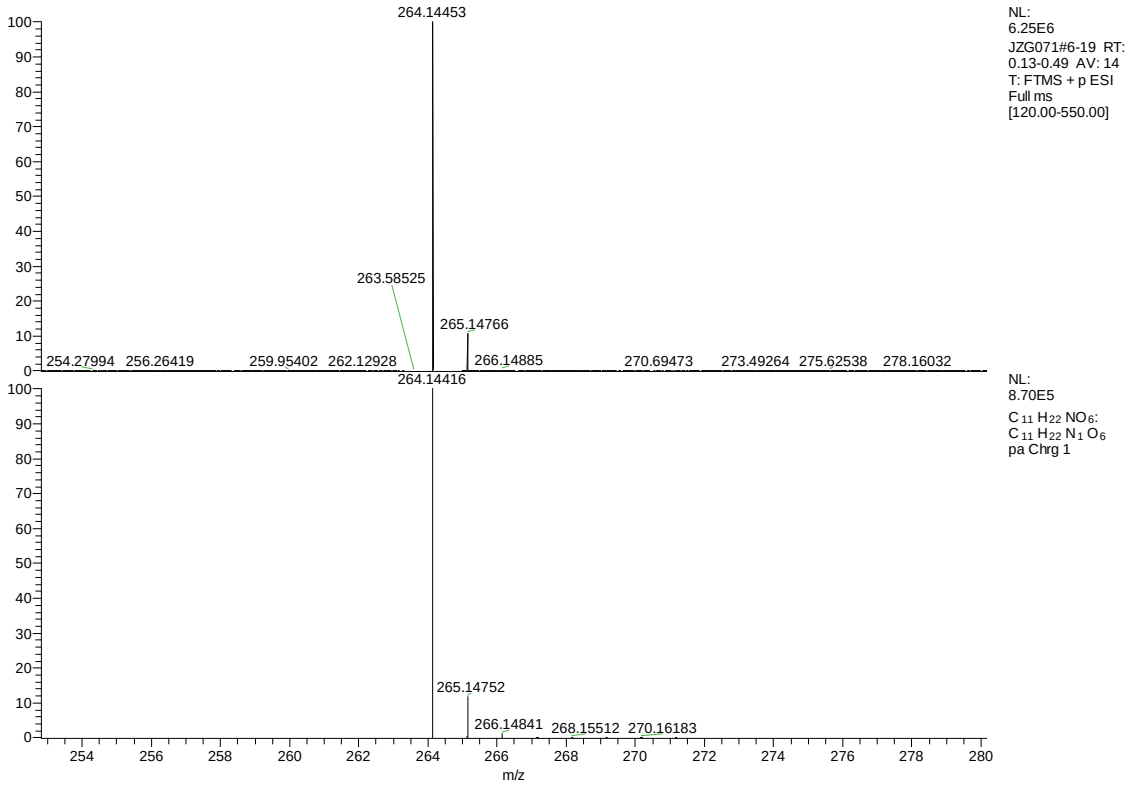
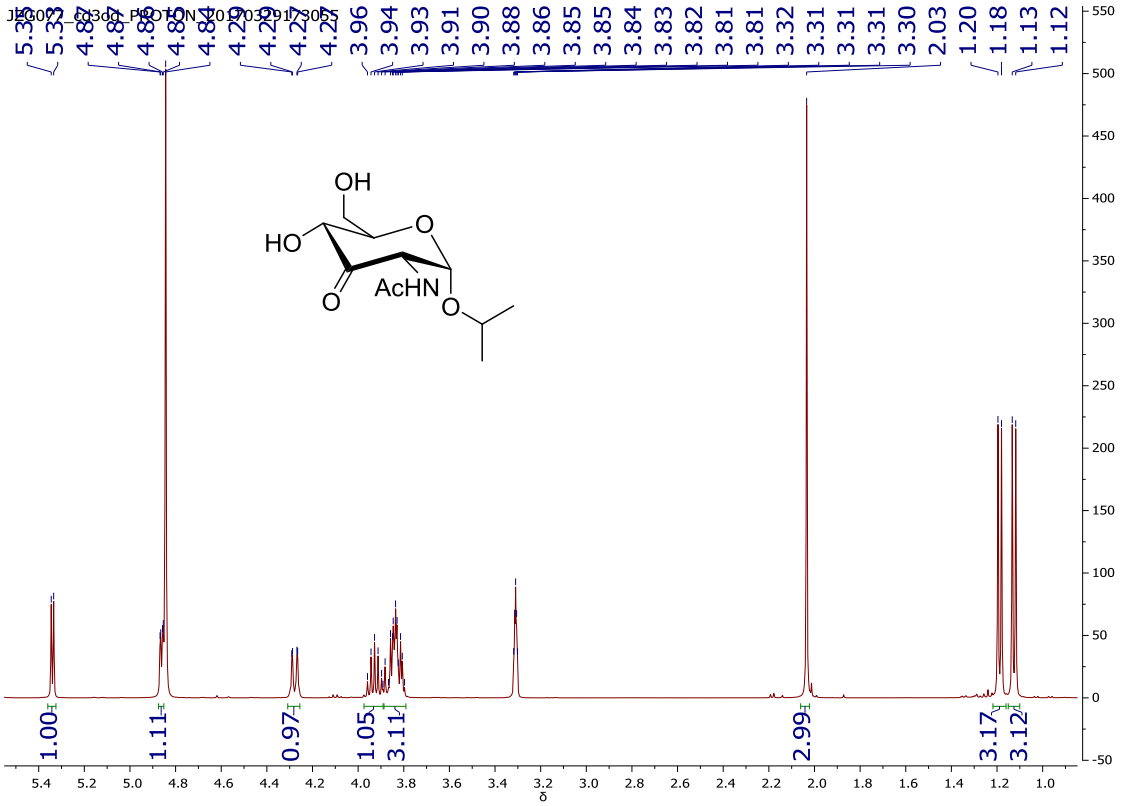
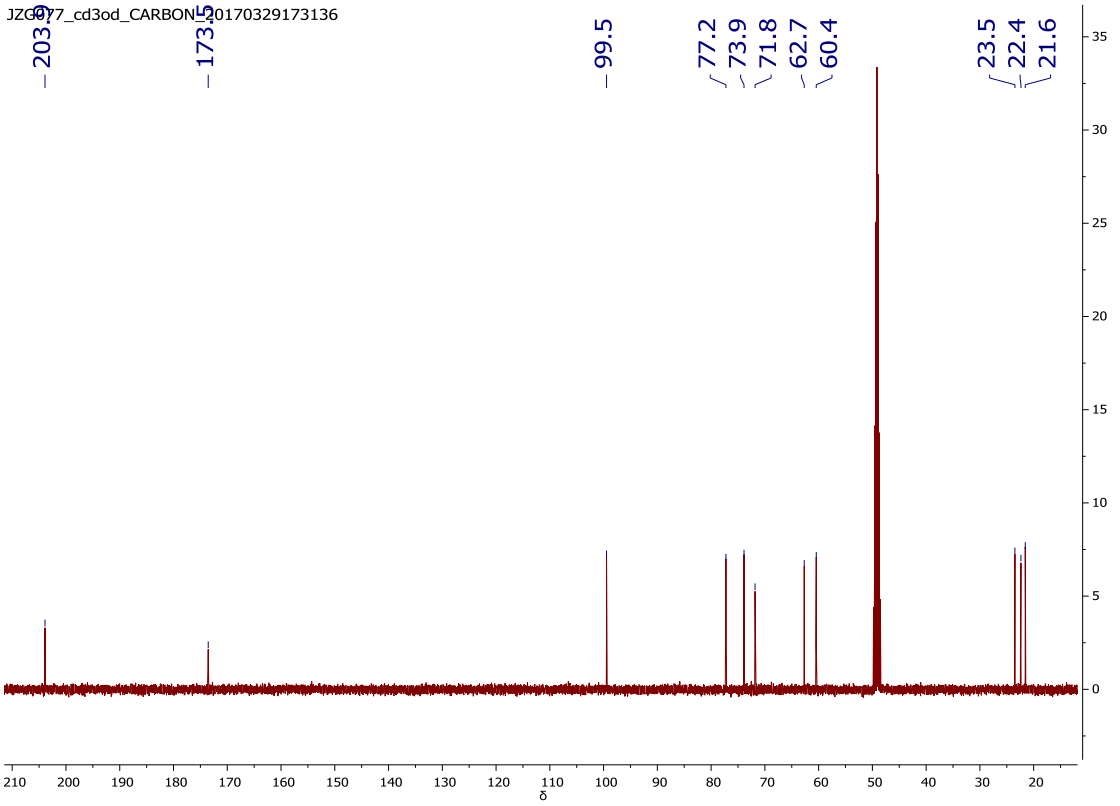
344.08553
371.10456
422.67306
449.63254
506.53003
527.28135
NL:
7.76E6
JZG071#6-19 RT:
0.13-0.49 AV: 14
T: FTMS + p ESI
Full ms
[120.00-550.00]
NL:
8.70E5
C11H22NO6:
C11H22N1O6
pa Chrg 1
m/z



Isopropyl 2-acetamido-2-deoxy-α-D-glucopyran-3-uloside (7)

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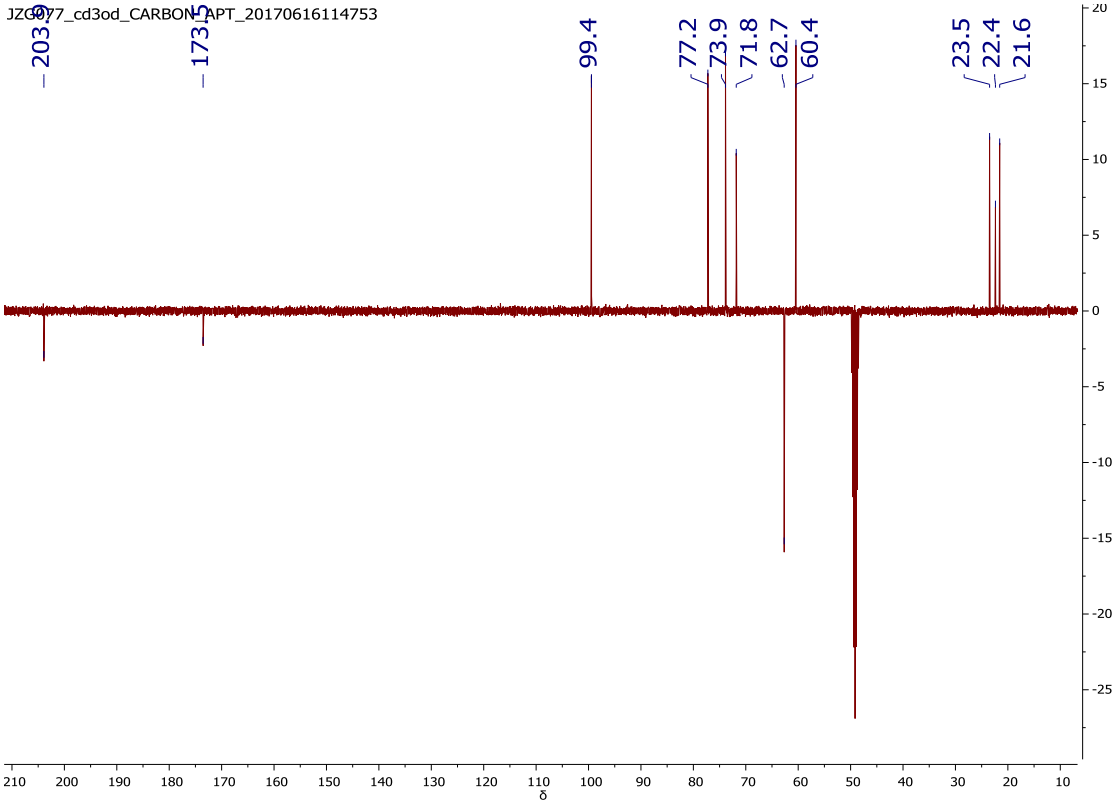
99.5
77.2
73.9
71.8
62.7
60.4
23.5
22.4
21.6
δ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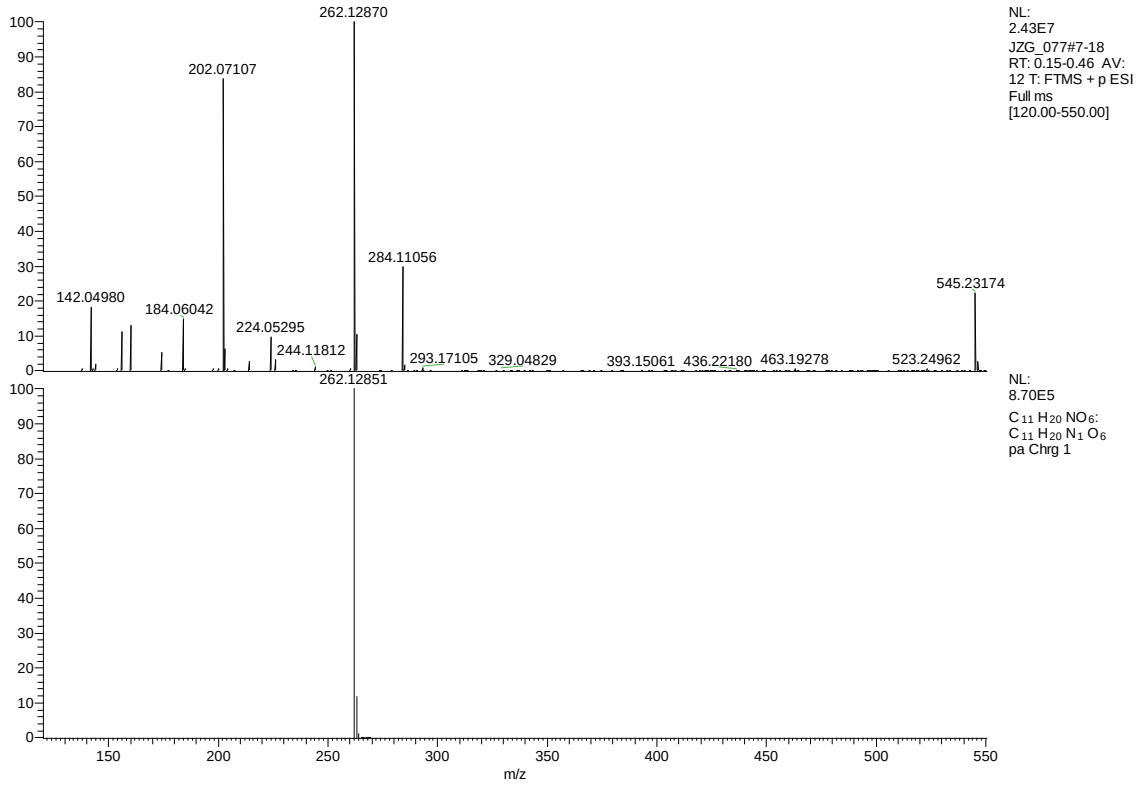
77.2
73.9
71.8
62.7
60.4
23.5
22.4
21.6
δ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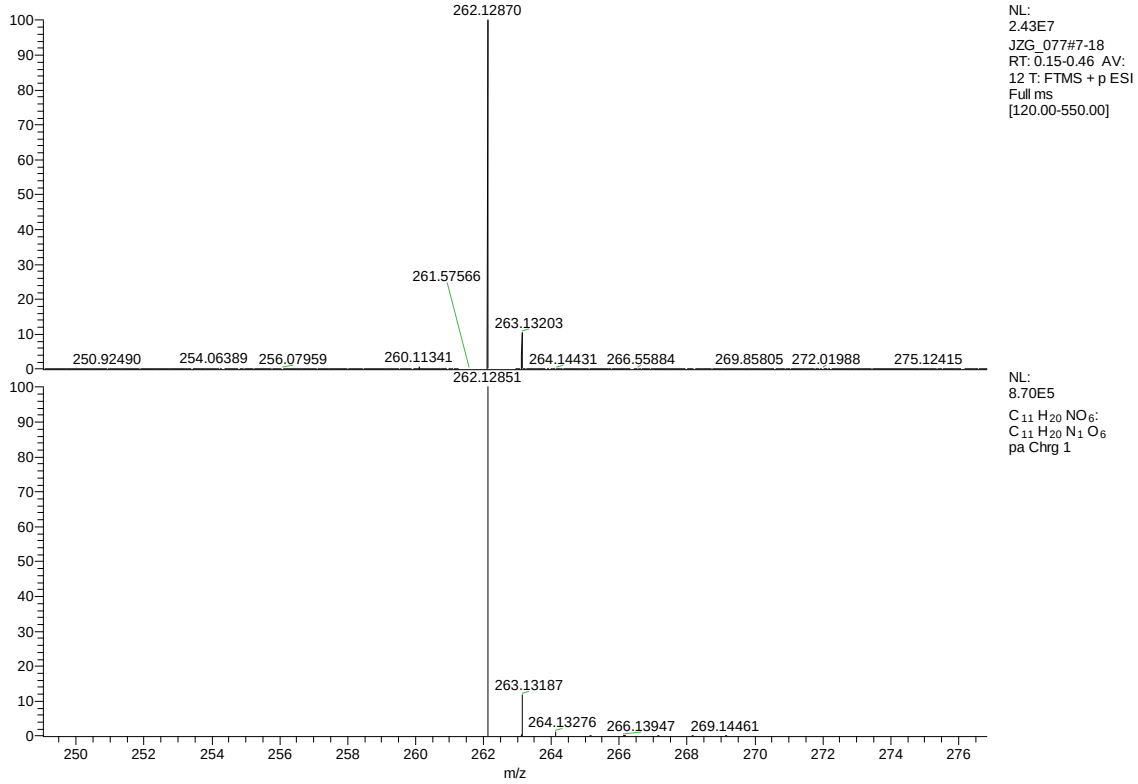
202.07107
284.11056
142.04980
184.06042
224.05295
244.11812
293.17105
329.04829
393.15061
436.22180
463.19278
523.24962
545.23174
NL:
2.43E7
JZG_077#7-18
RT: 0.15-0.46 AV:
12 T: FTMS + p ESI
Full ms
[120.00-550.00]
262.12851
NL:
8.70E5
C11 H20 NO6:
C11 H20 N1 O6
pa Chrg 1
m/z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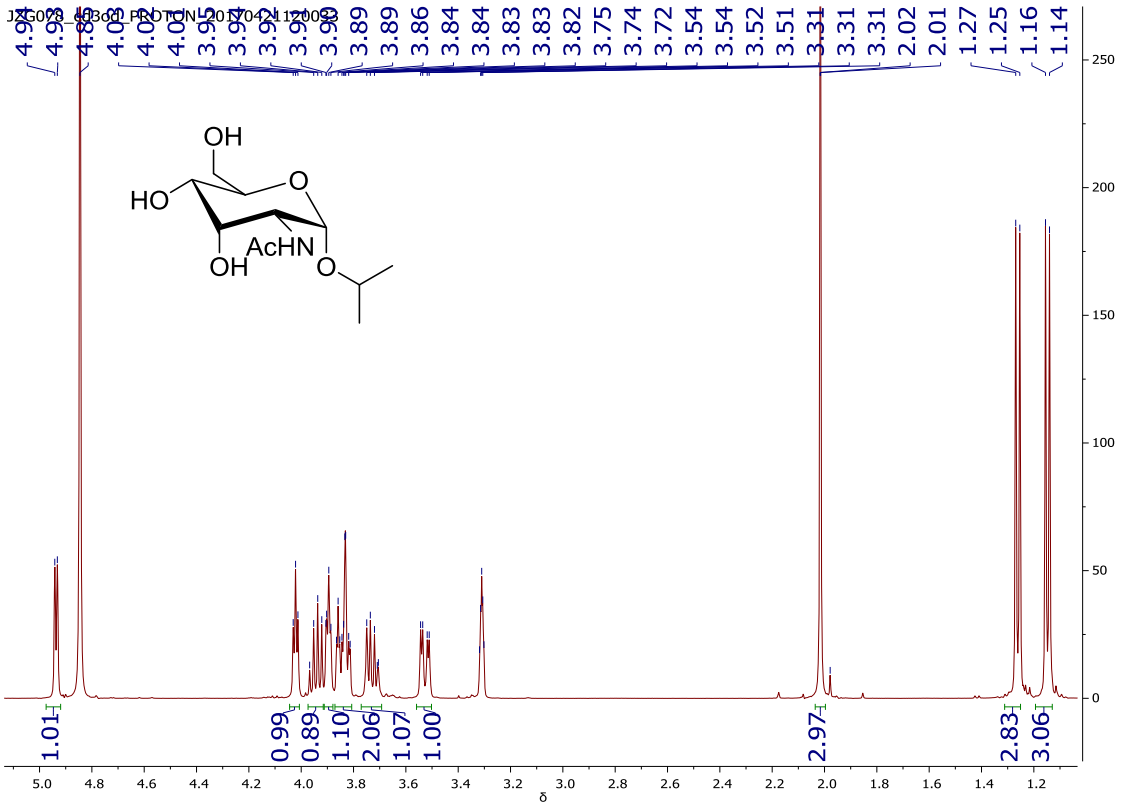
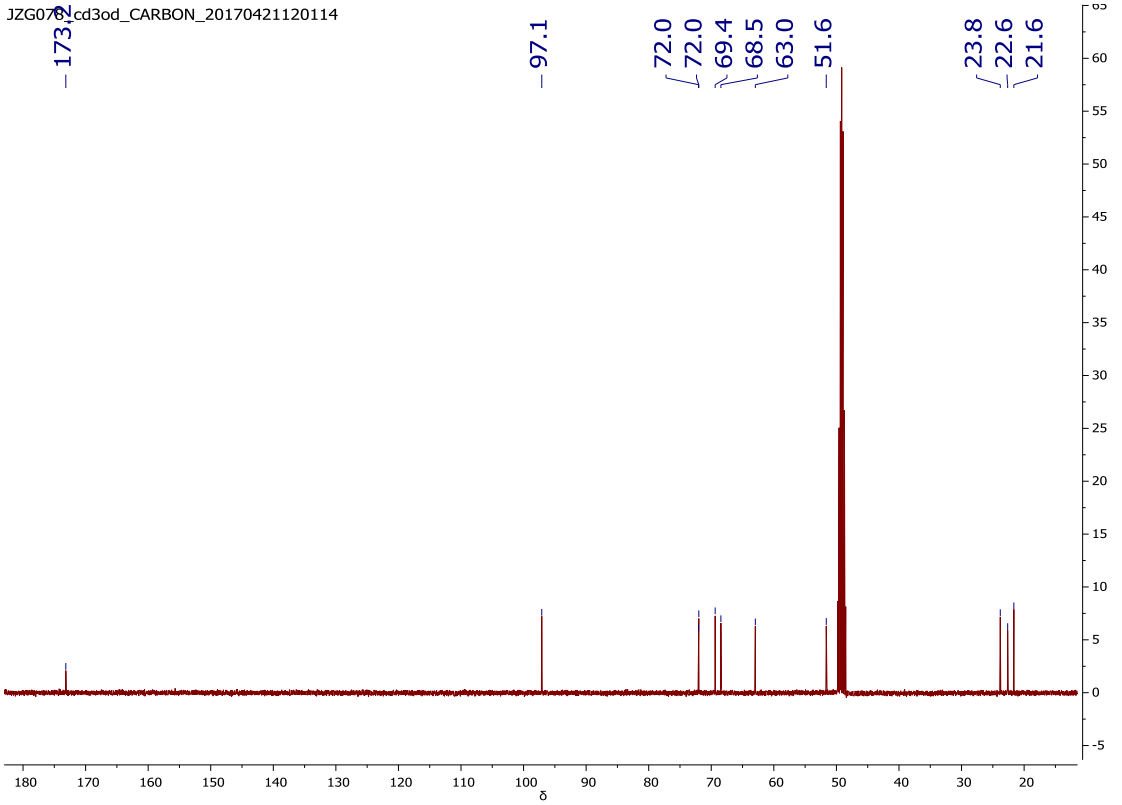
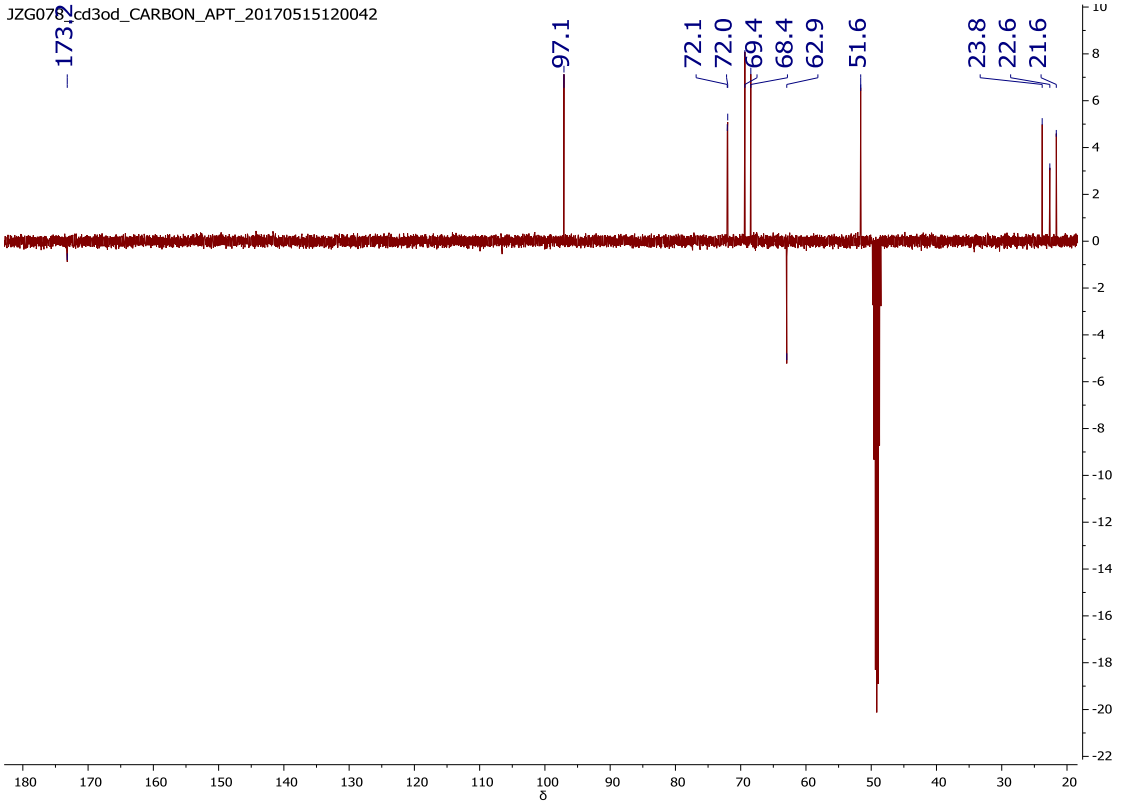
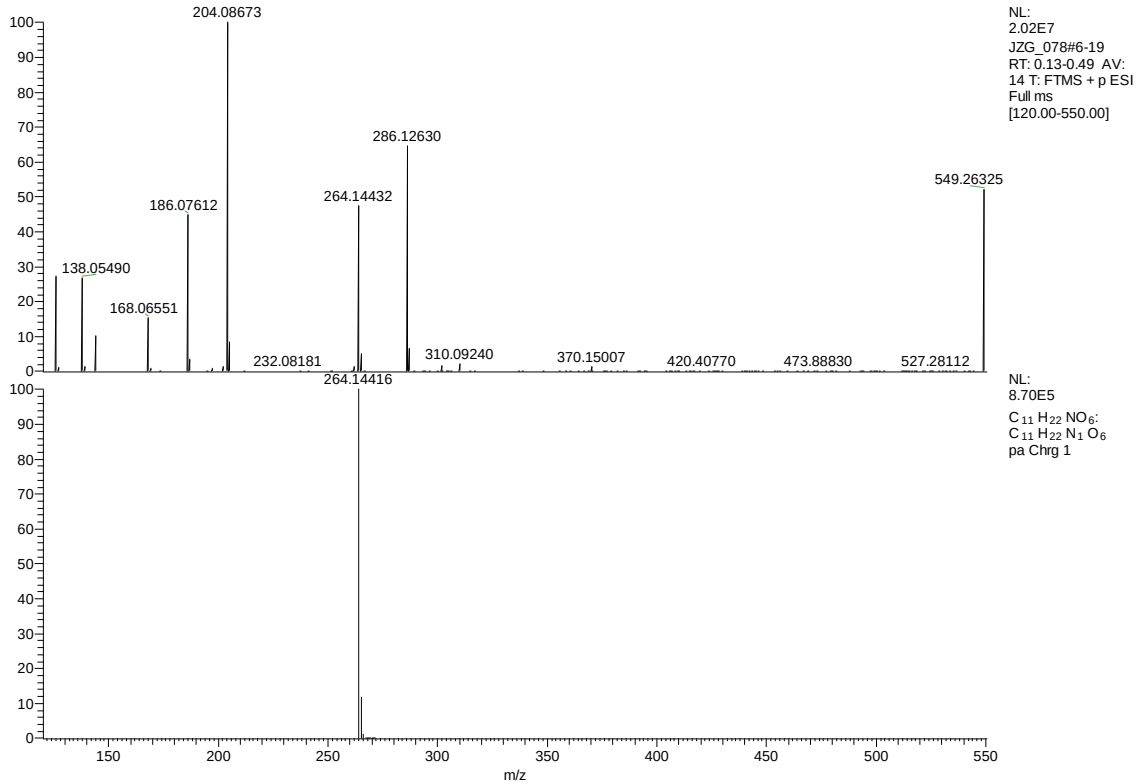
263.13203
250.92490
254.06389
256.07959
260.11341
264.14431
266.55884
269.85805
272.01988
275.12415
262.12851
NL:
2.43E7
JZG_077#7-18
RT: 0.15-0.46 AV:
12 T: FTMS + p ESI
Full ms
[120.00-550.00]
263.13187
264.13276
266.13947
269.14461
NL:
8.70E5
C11 H20 NO6:
C11 H20 N1 O6
pa Chrg 1
m/z

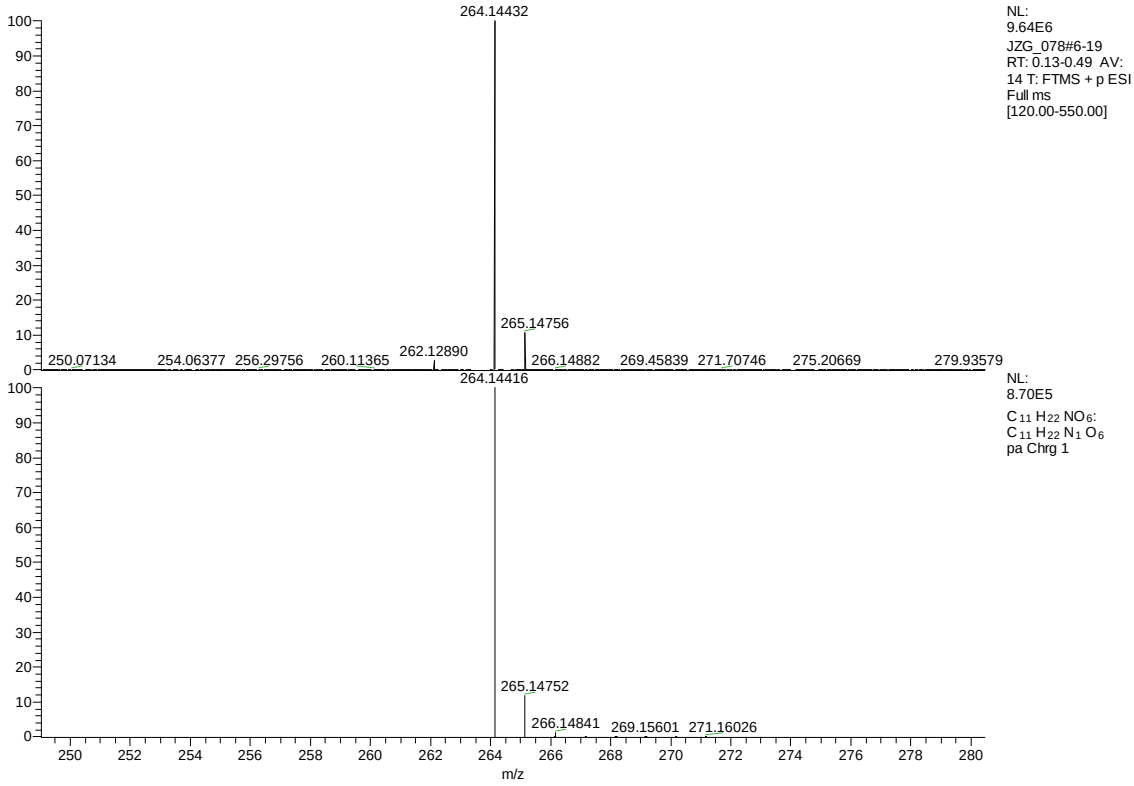
Isopropyl 2-acetamido-2-deoxy-α-D-allopyranoside (8)



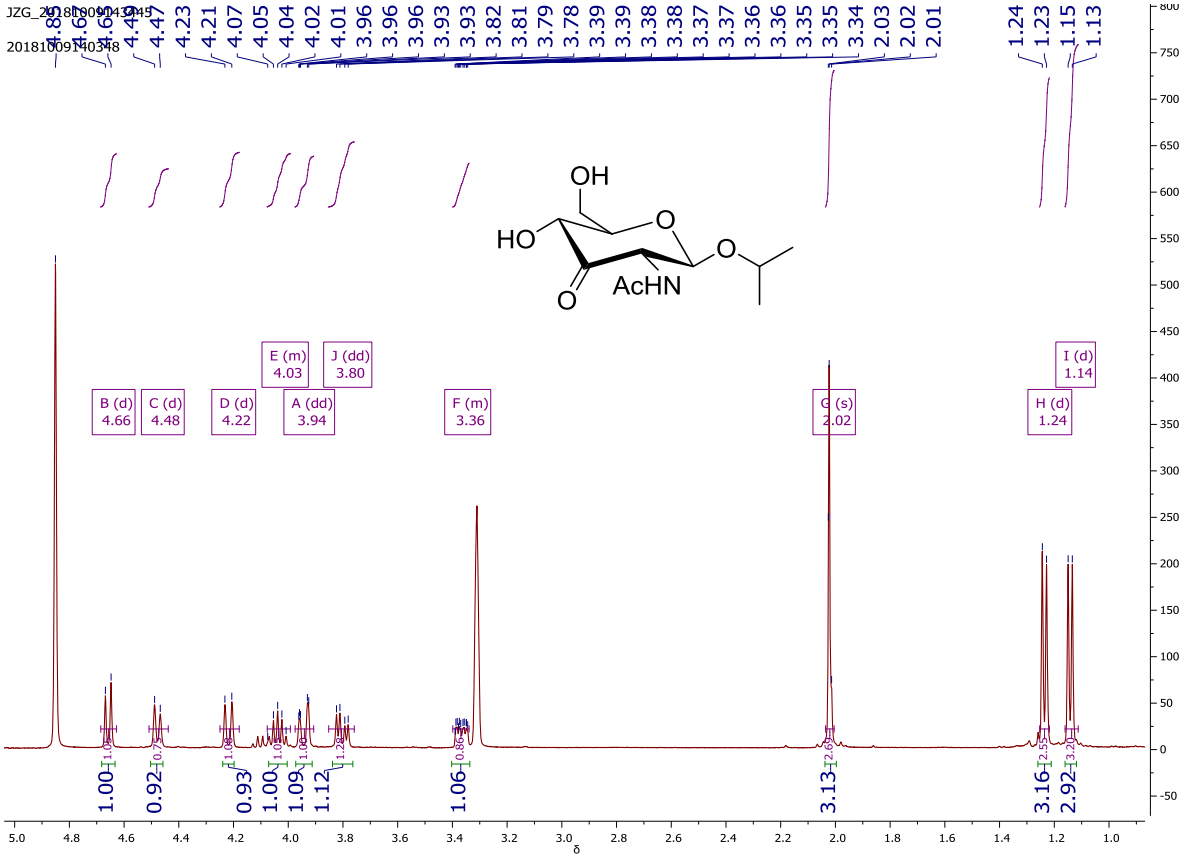


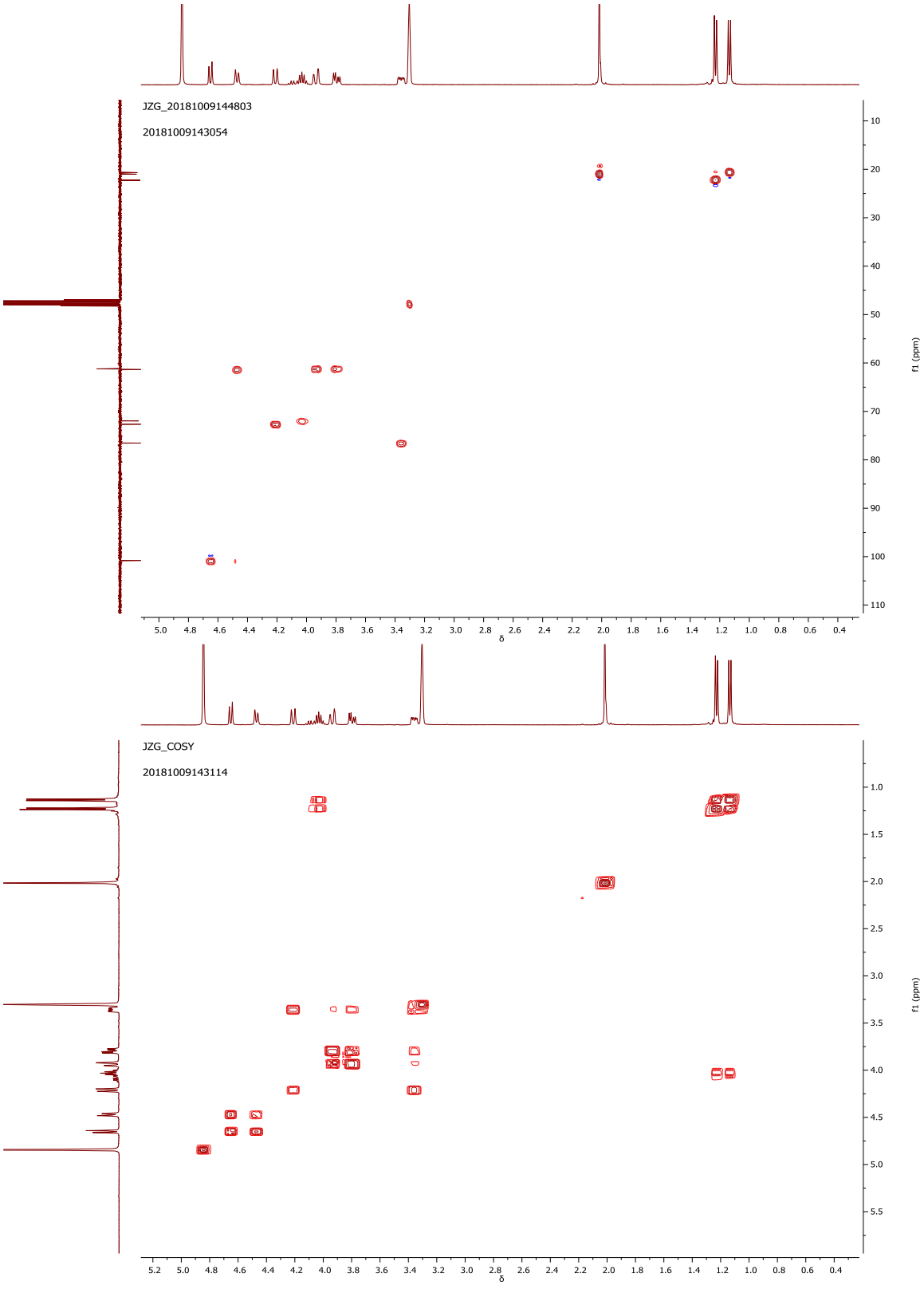

JZG078_cd3od_CARBON_APT_20170515120042
173.2
97.1
72.1
72.0
69.4
68.4
62.9
51.6
23.8
22.6
21.6
δ

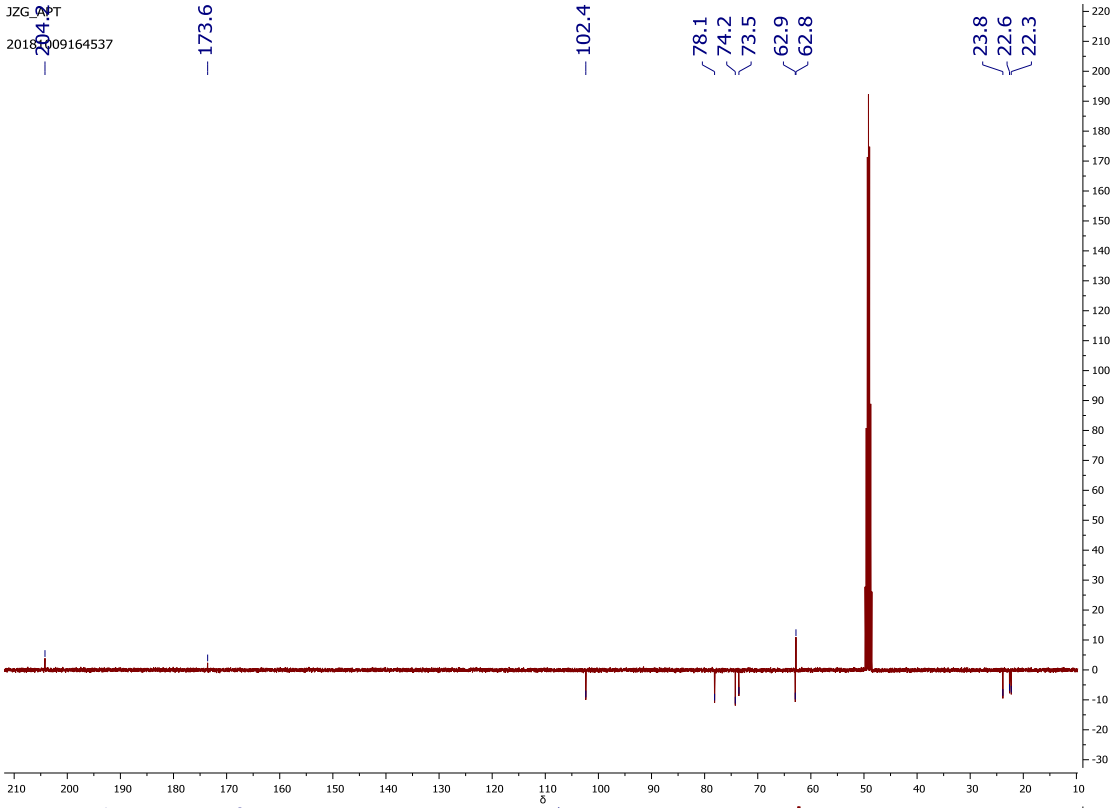

204.08673
286.12630
549.26325
186.07612
264.14432
138.05490
168.06551
232.08181
310.09240
370.15007
420.40770
473.88830
527.28112
NL:
2.02E7
JZG_078#6-19
RT: 0.13-0.49 AV:
14 T: FTMS + p ESI
Full ms
[120.00-550.00]
264.14416
NL:
8.70E5
C11 H22 NO6:
C11 H22 N1 O6
pa Chrg 1
m/z

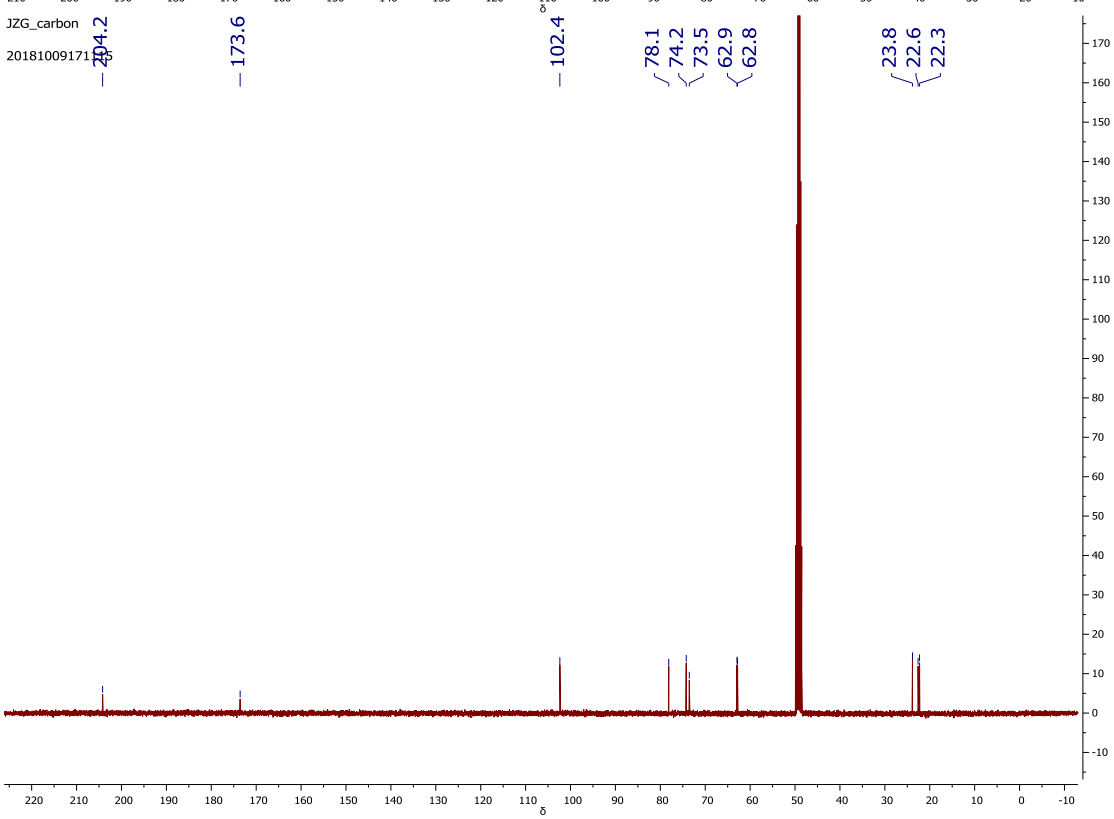

264.14432
NL:
9.64E6
JZG_078#6-19
RT: 0.13-0.49 AV:
14 T: FTMS + p ESI
Full ms
[120.00-550.00]
265.14756
250.07134
254.06377
256.29756
260.11365
262.12890
266.14882
269.45839
271.70746
275.20669
279.93579
264.14416
NL:
8.70E5
C11 H22 NO6:
C11 H22 N1 O6
pa Chrg 1
265.14752
266.14841
269.15601
271.16026
m/z

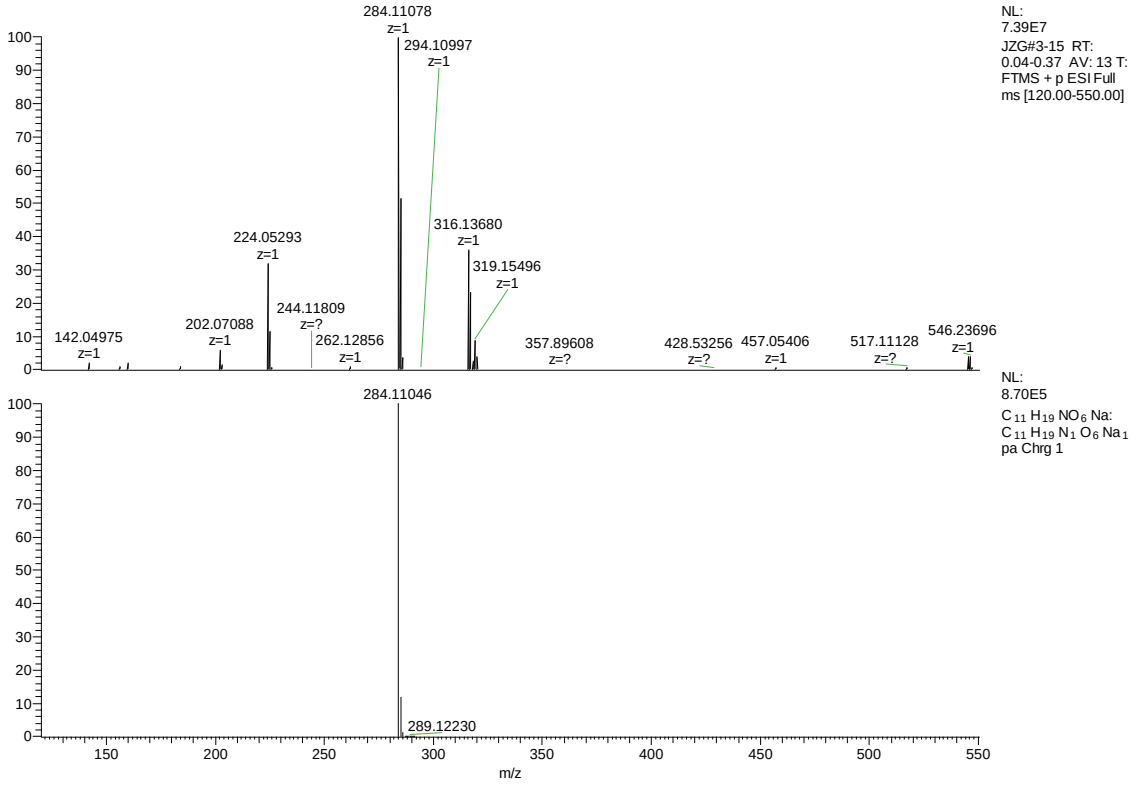
Isopropyl 2-acetamido-2-deoxy-β-D-glucopyran-3-uloside (25).

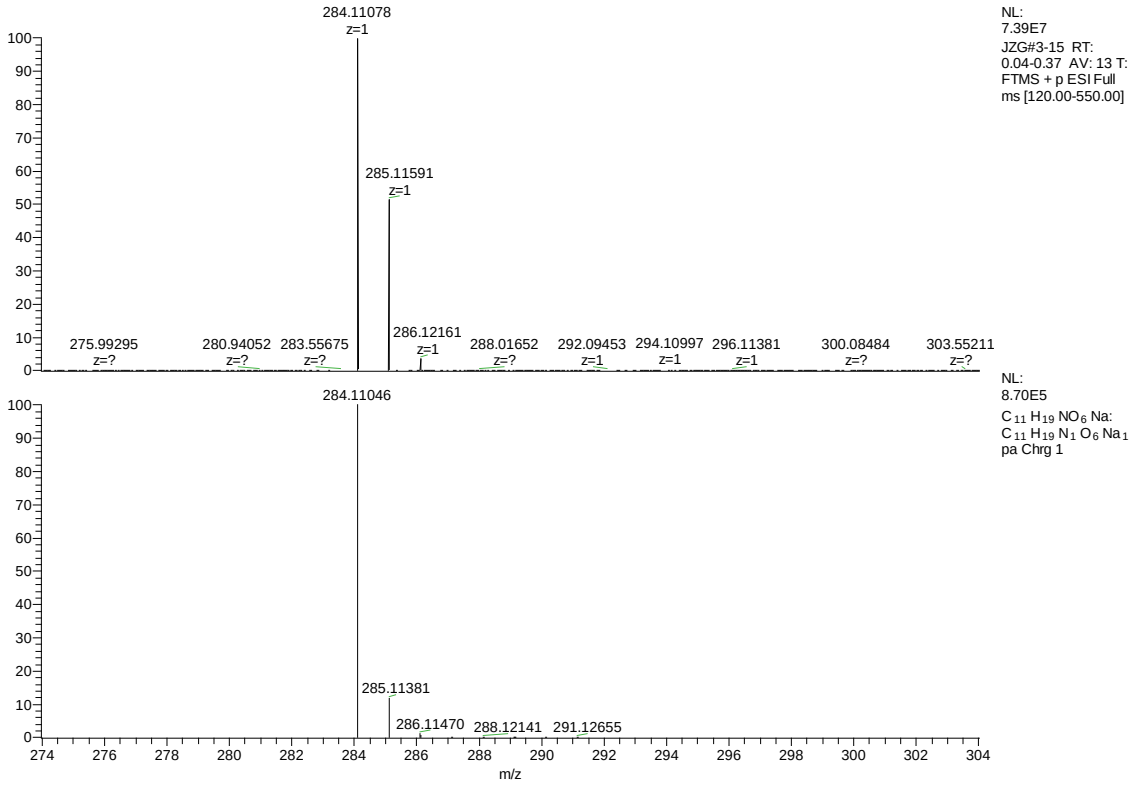



JZG_20181009144803
20181009143054
f1 (ppm)
δ
JZG_COSY
20181009143114
f1 (ppm)
δ

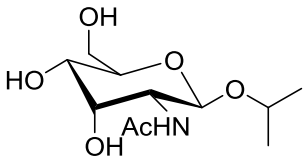

JZG_DEPT
204.3
173.6
102.4
78.1
74.2
73.5
62.9
62.8
23.8
22.6
22.3
δ


JZG_carbon
204.2
173.6
102.4
78.1
74.2
73.5
62.9
62.8
23.8
22.6
22.3
δ

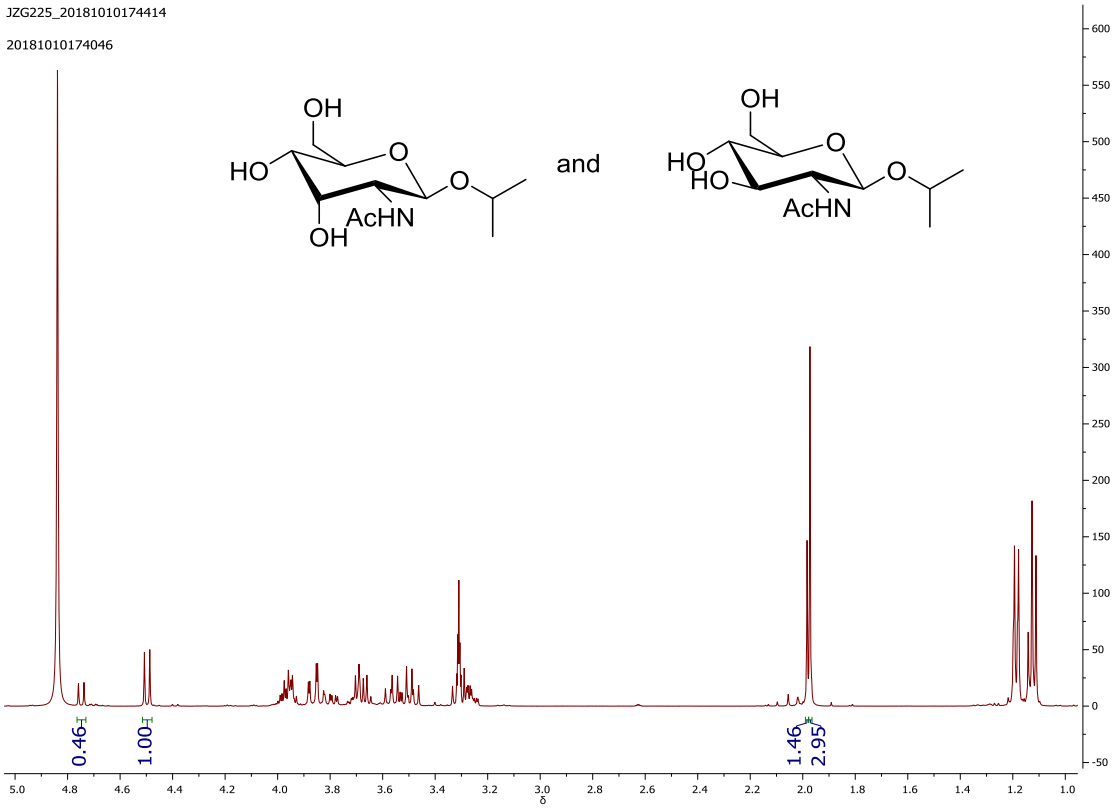

284.11078
z=1
294.10997
z=1
316.13680
z=1
319.15496
z=1
224.05293
z=1
244.11809
z=?
202.07088
z=1
262.12856
z=1
142.04975
z=1
357.89608
z=?
428.53256
z=?
457.05406
z=1
517.11128
z=?
546.23696
z=1
NL:
7.39E7
JZG#3-15 RT:
0.04-0.37 AV: 13 T:
FTMS + p ESI Full
ms [120.00-550.00]
284.11046
289.12230
NL:
8.70E5
C11 H19 NO6 Na:
C11 H19 N1 O6 Na1
pa Chrg 1
m/z

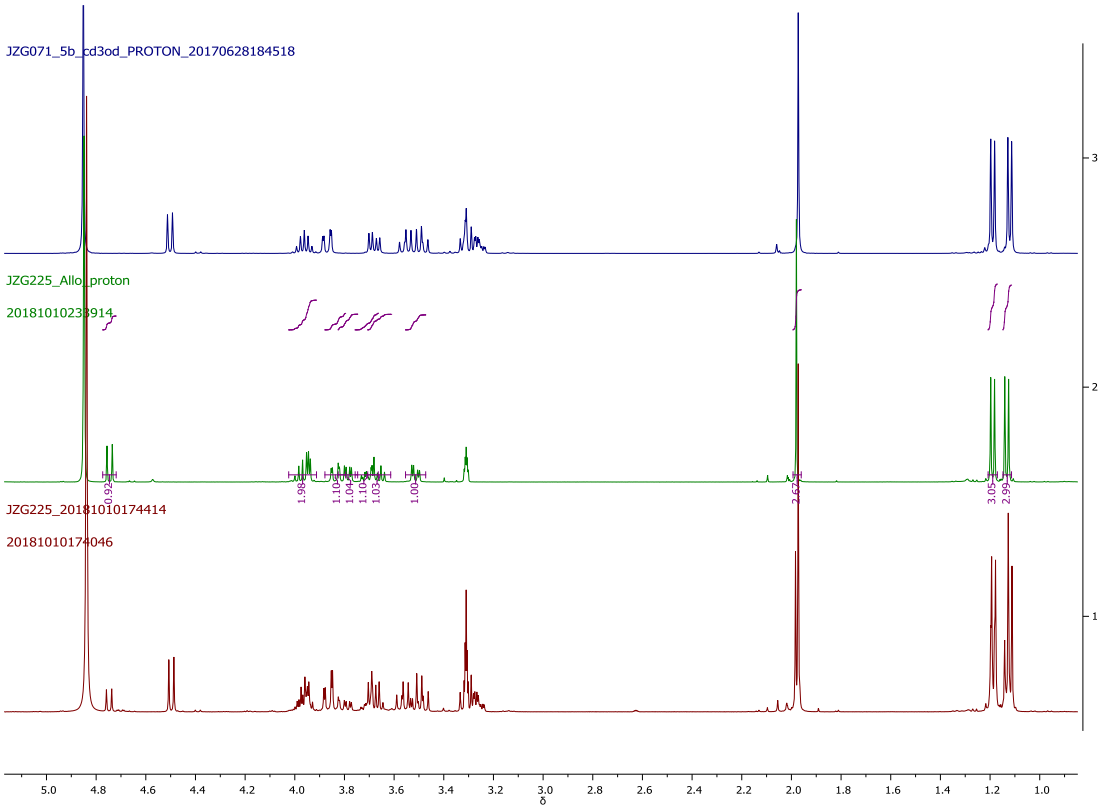

284.11078
z=1
285.11591
z=1
286.12161
z=1
275.99295
z=?
280.94052
z=?
283.55675
z=?
288.01652
z=?
292.09453
z=1
294.10997
z=1
296.11381
z=1
300.08484
z=?
303.55211
z=?
NL:
7.39E7
JZG#3-15 RT:
0.04-0.37 AV: 13 T:
FTMS + p ESI Full
ms [120.00-550.00]
284.11046
285.11381
286.11470
288.12141
291.12655
NL:
8.70E5
C11 H19 NO6 Na:
C11 H19 N1 O6 Na1
pa Chrg 1
m/z

Isopropyl 2-acetamido-2-deoxy-β-D-allopyranoside (**26**).

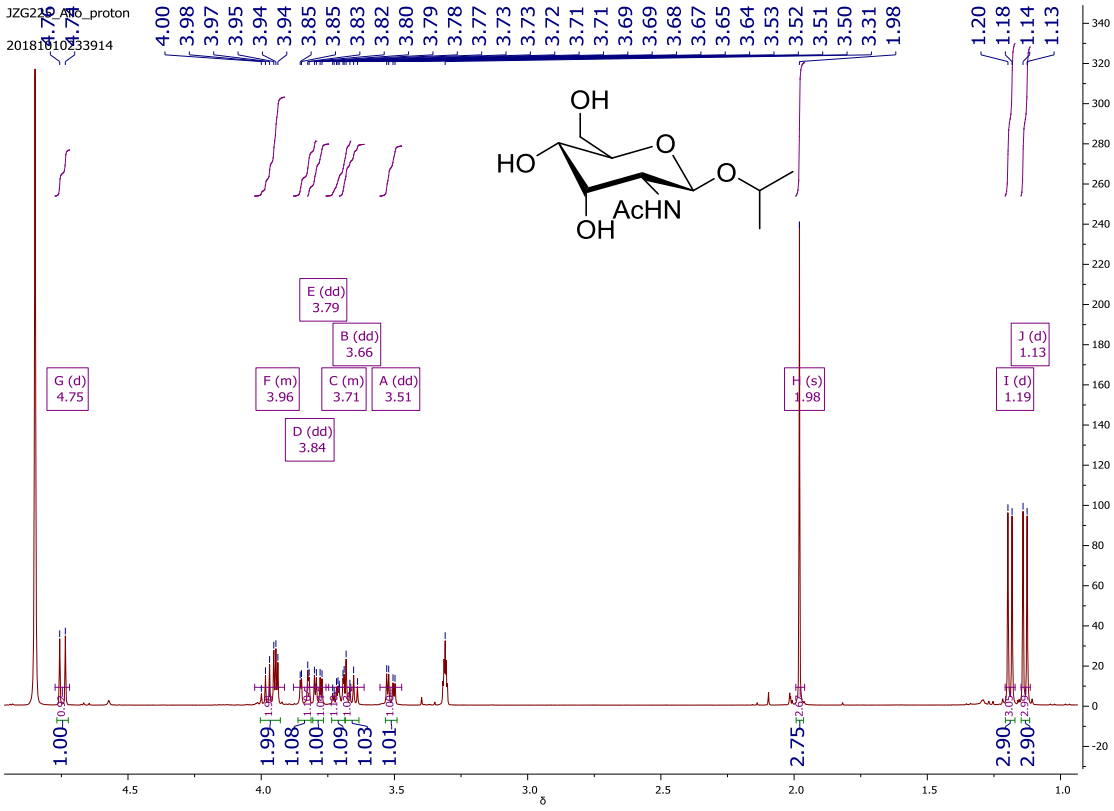


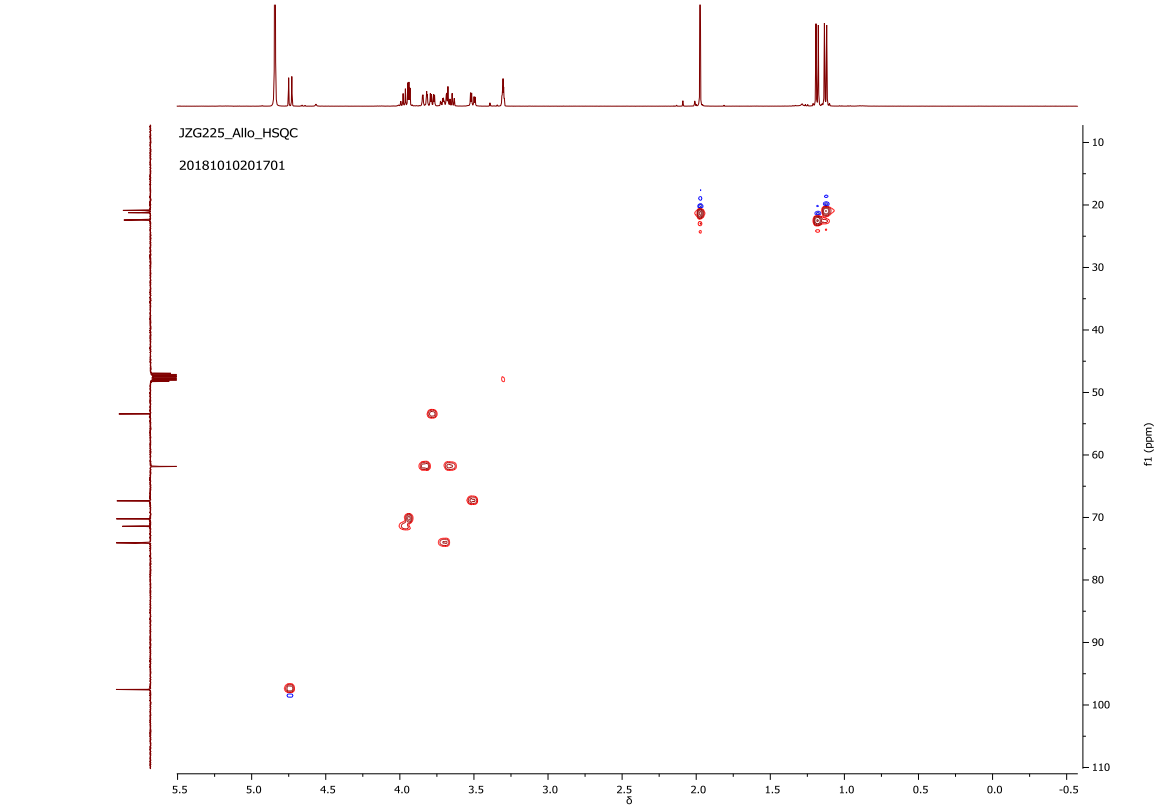
A mixture of Gluco and allo-configured products after reduction with $NaBH_4$.

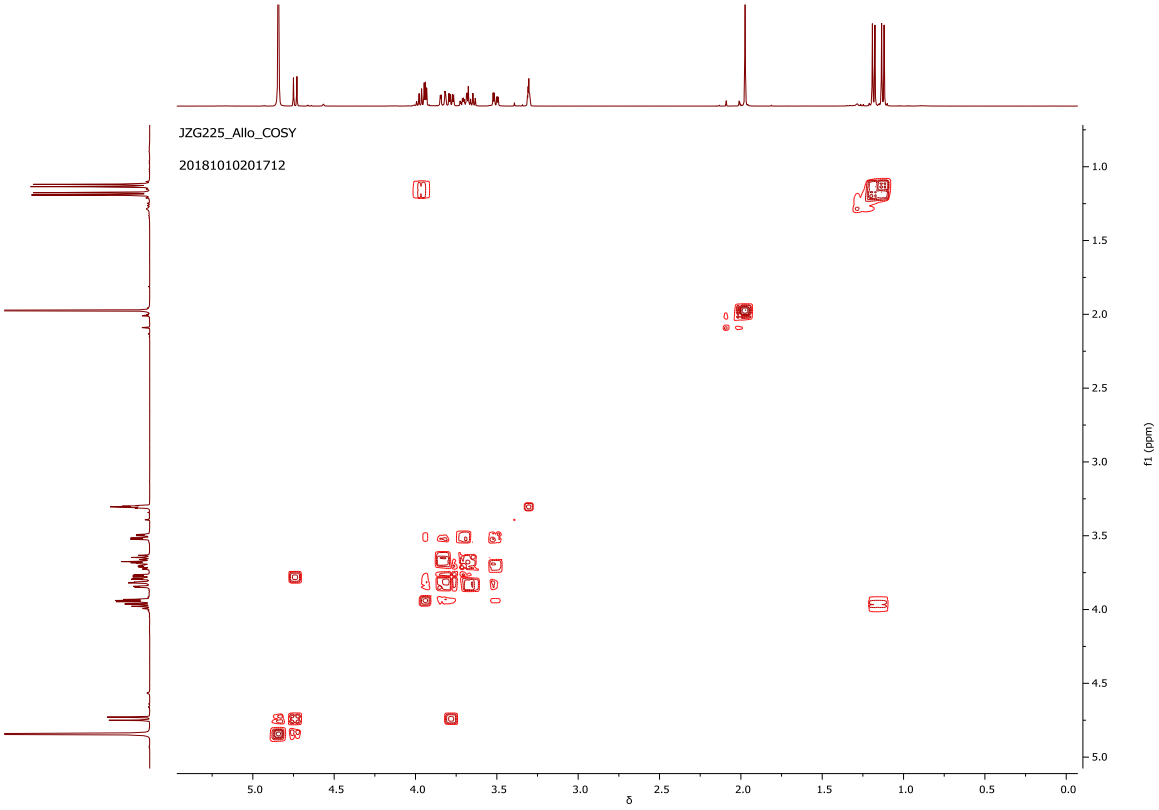


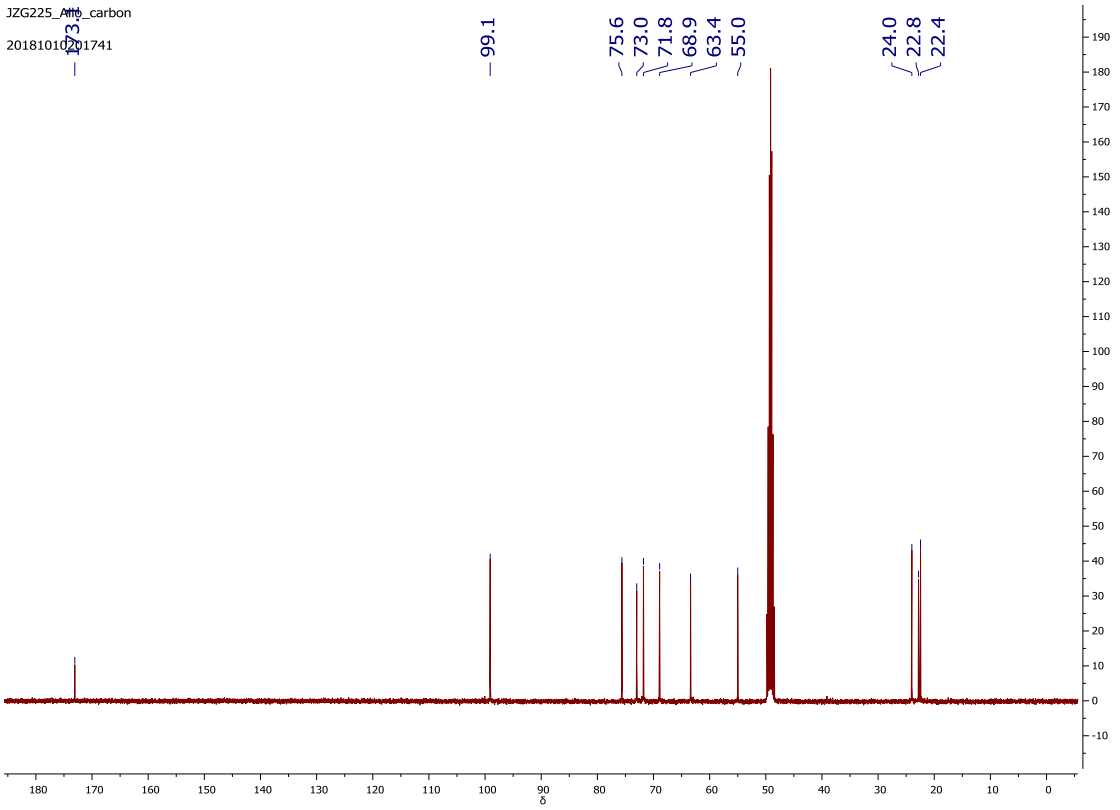


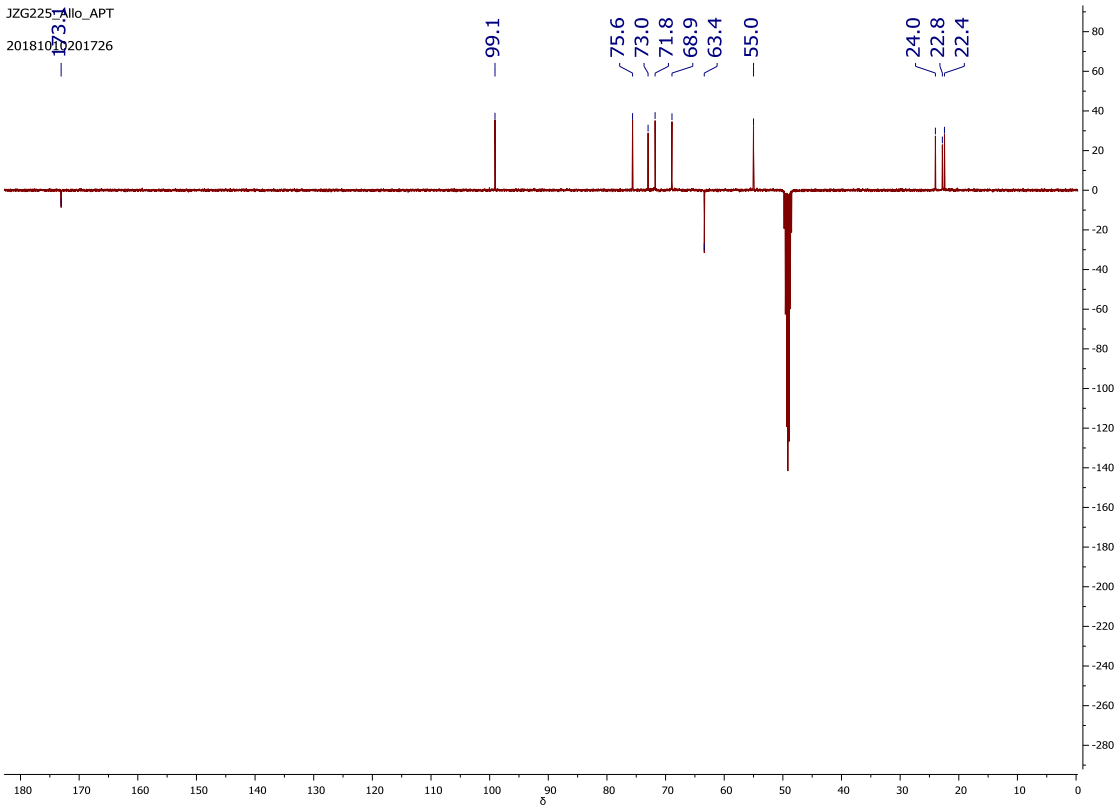
Isopropyl 2-acetamido-2-deoxy-β-D-allopyranoside

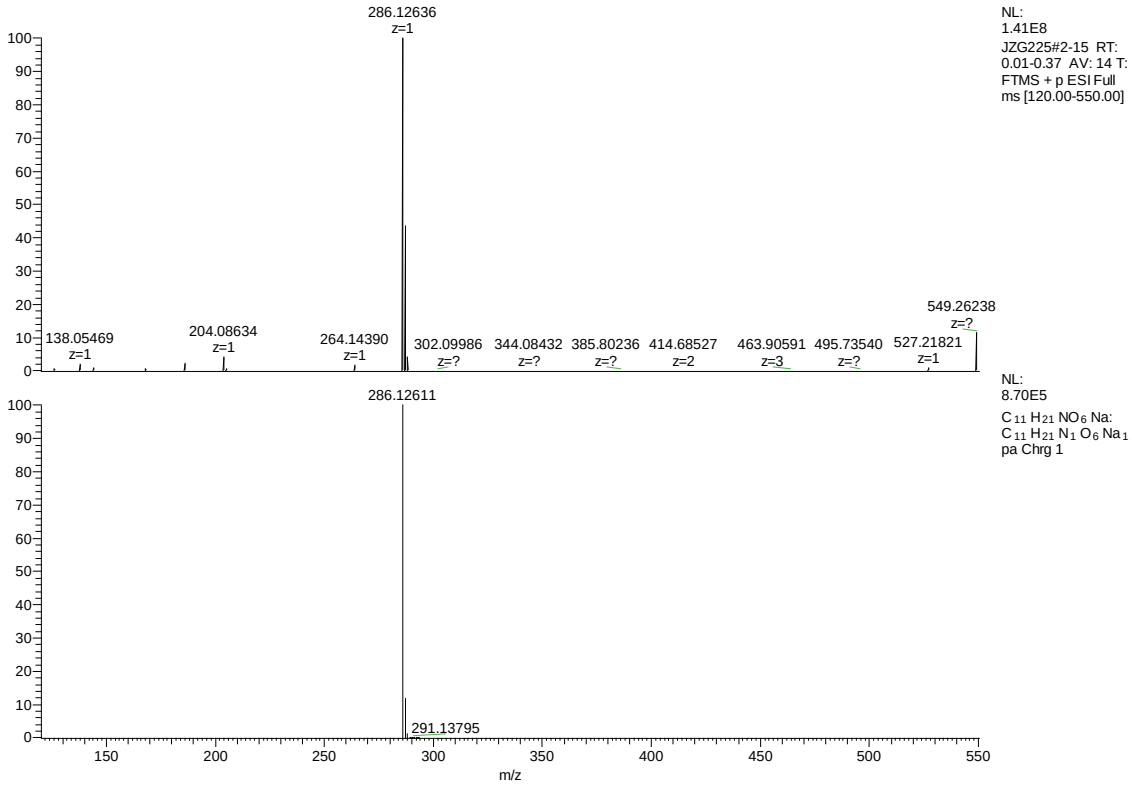


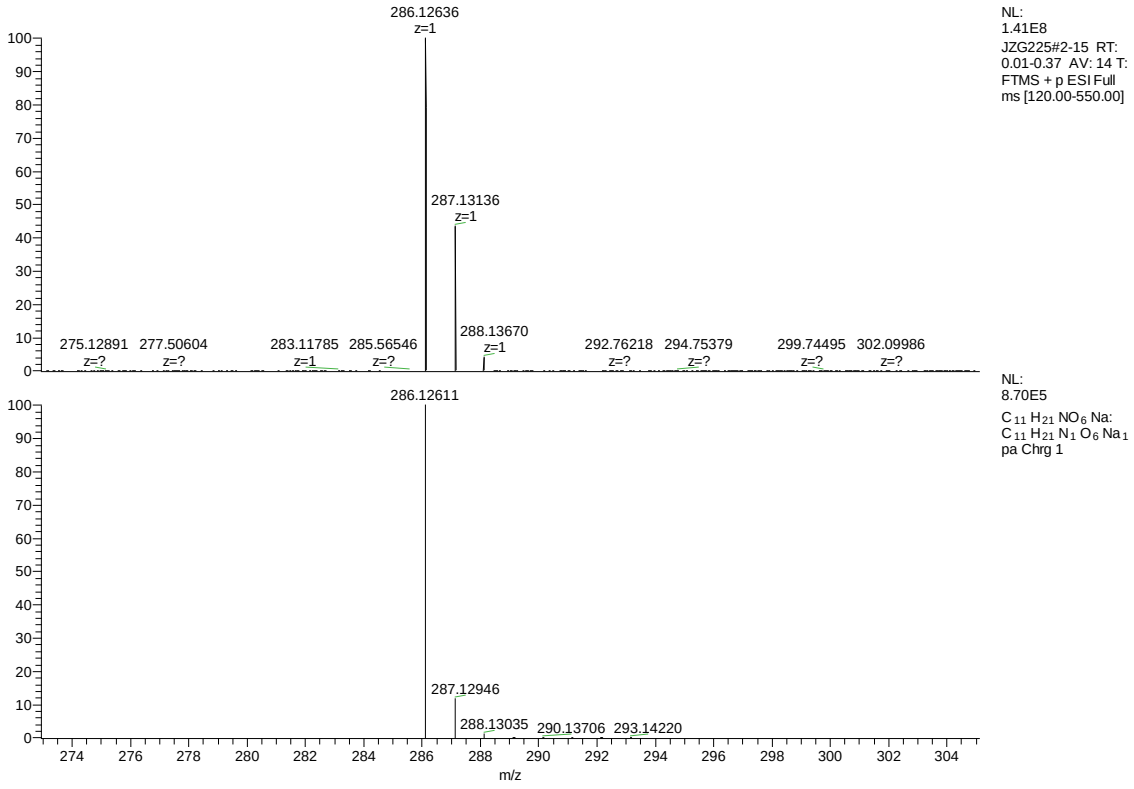

JZG225_Allo_HSQC
20181010201701
f1 (ppm)
δ


JZG225_Allo_COSY
20181010201712
f1 (ppm)
δ

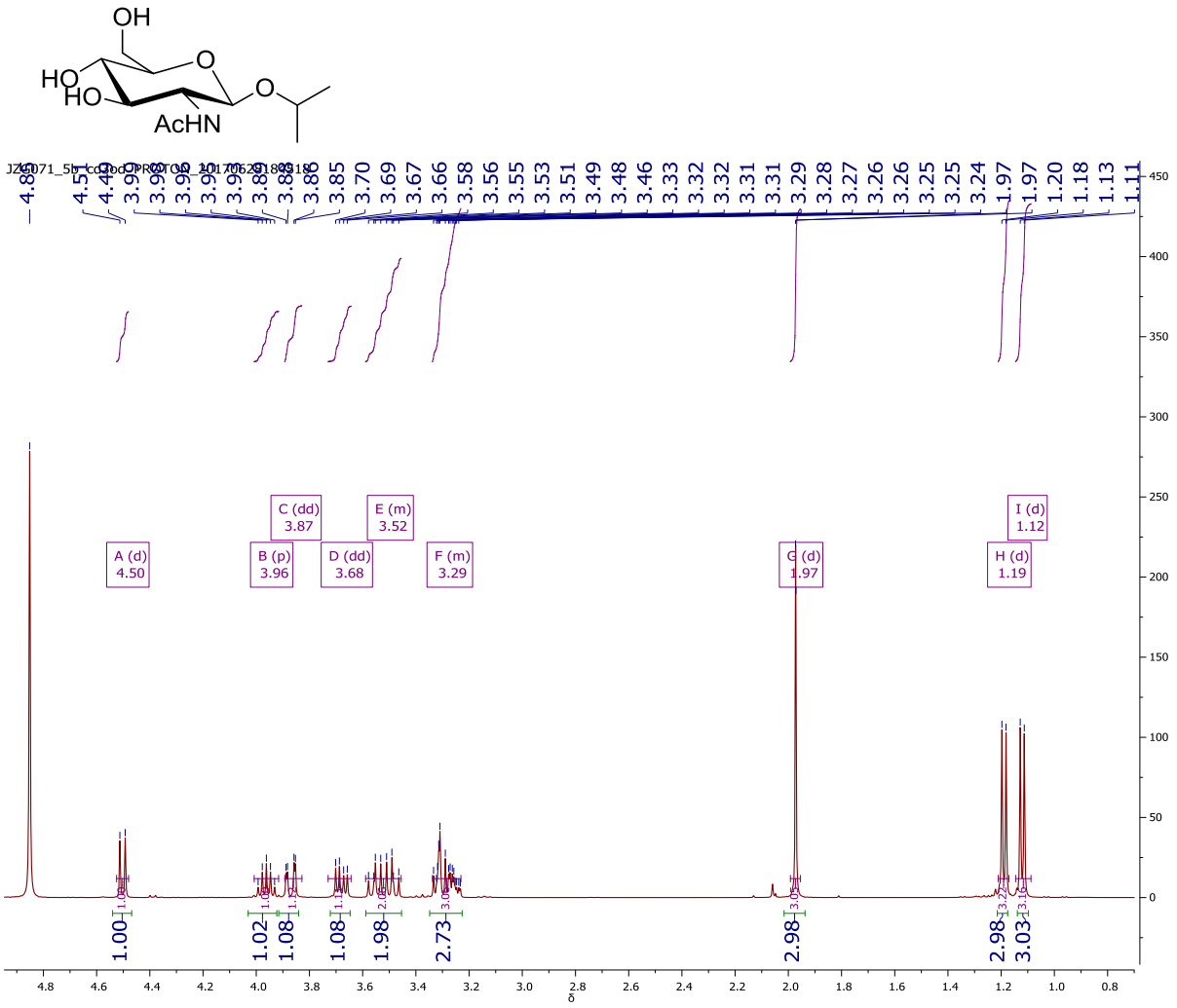

JZG225_Allo_carbon
20181012201741
173.1
99.1
75.6
73.0
71.8
68.9
63.4
55.0
24.0
22.8
22.4
δ

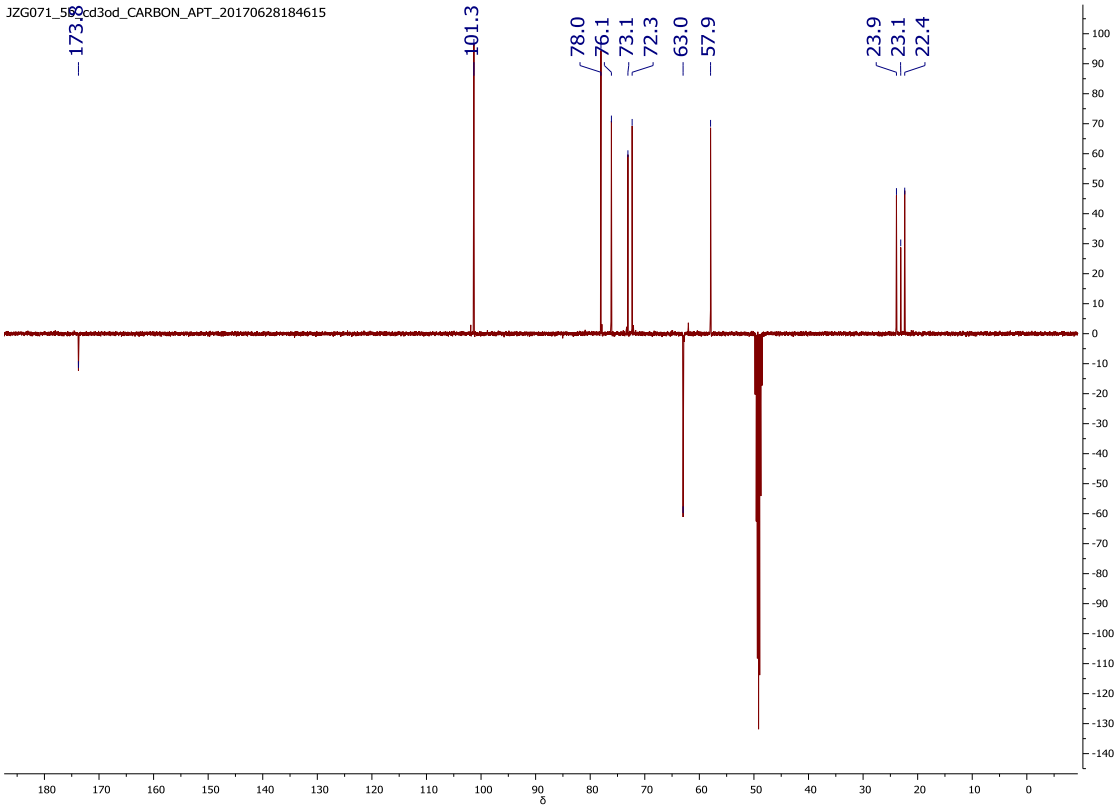

JZG225_Allo_APT
20181012201726
173.1
99.1
75.6
73.0
71.8
68.9
63.4
55.0
24.0
22.8
22.4
δ

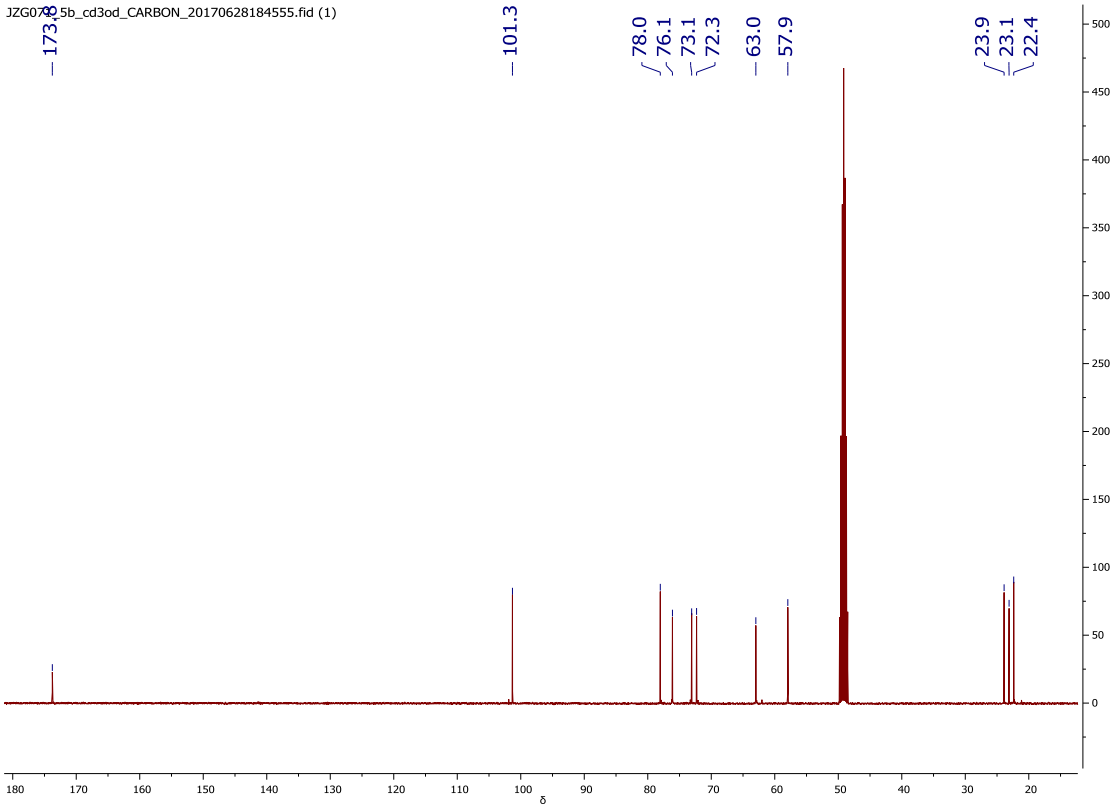

286.12636
z=1
NL:
1.41E8
JZG225#2-15 RT:
0.01-0.37 AV: 14 T:
FTMS + p ESI Full
ms [120.00-550.00]
138.05469
z=1
204.08634
z=1
264.14390
z=1
302.09986
z=?
344.08432
z=?
385.80236
z=?
414.68527
z=2
463.90591
z=3
495.73540
z=?
527.21821
z=1
549.26238
z=?
286.12611
NL:
8.70E5
C 11 H 21 NO 6 Na:
C 11 H 21 N 1 O 6 Na 1
pa Chrg 1
291.13795
m/z


286.12636
z=1
NL:
1.41E8
JZG225#2-15 RT:
0.01-0.37 AV: 14 T:
FTMS + p ESI Full
ms [120.00-550.00]
287.13136
z=1
275.12891
z=?
277.50604
z=?
283.11785
z=1
285.56546
z=?
288.13670
z=1
292.76218
z=?
294.75379
z=?
299.74495
z=?
302.09986
z=?
286.12611
NL:
8.70E5
C 11 H 21 NO 6 Na:
C 11 H 21 N 1 O 6 Na 1
pa Chrg 1
287.12946
288.13035
290.13706
293.14220
m/z

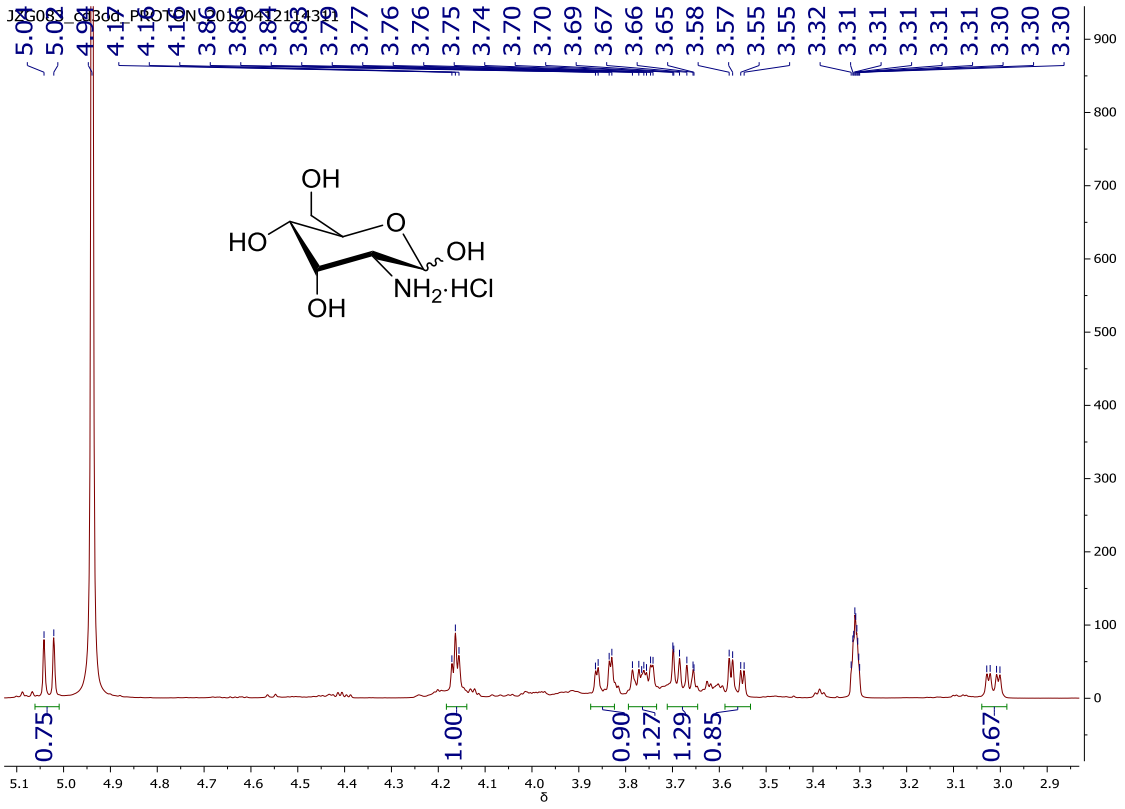
Isopropyl 2-acetamido-2-deoxy-β-D-glucopyranoside

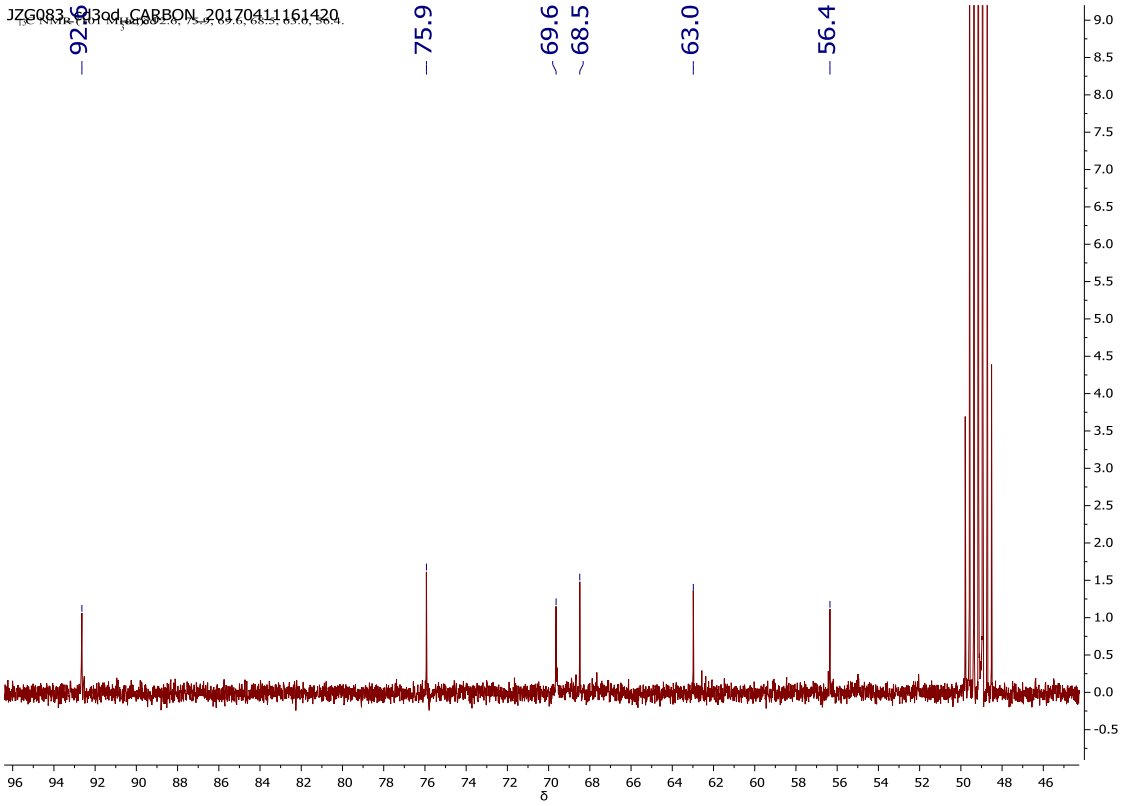


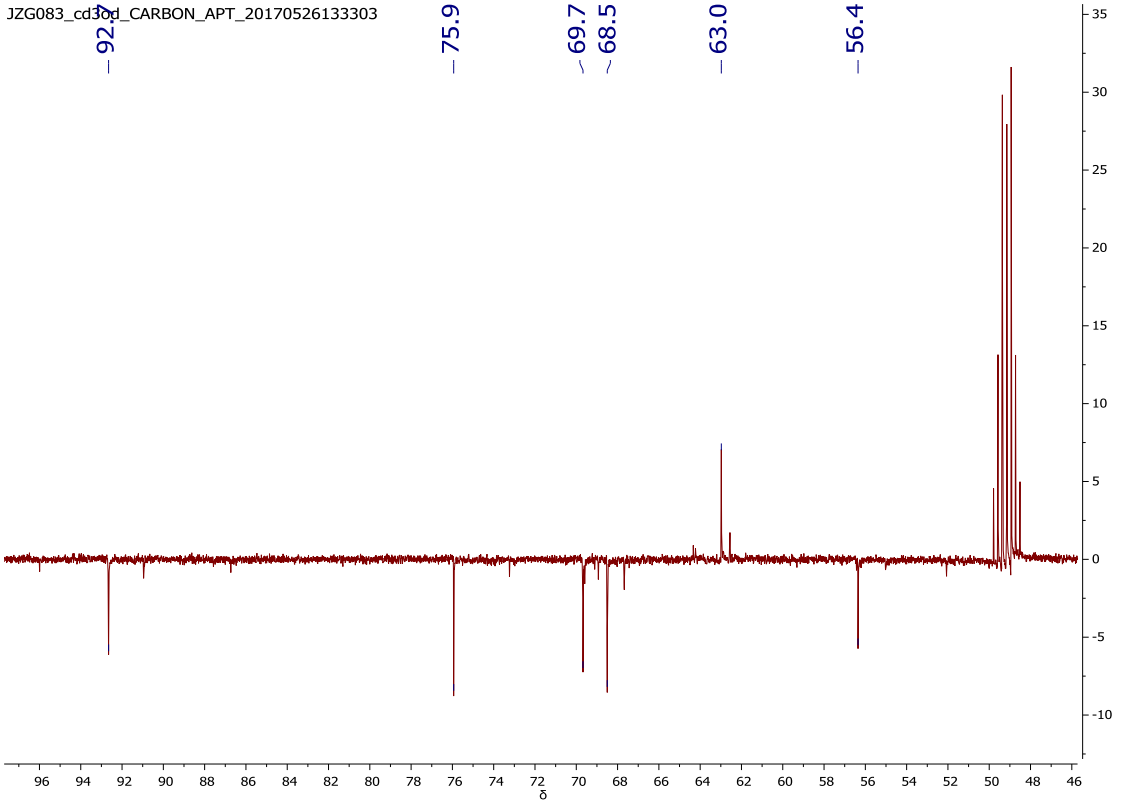

JZG071_5b_cd3od_CARBON_APT_20170628184615
173.4
101.3
78.0
76.1
73.1
72.3
63.0
57.9
23.9
23.1
22.4
δ

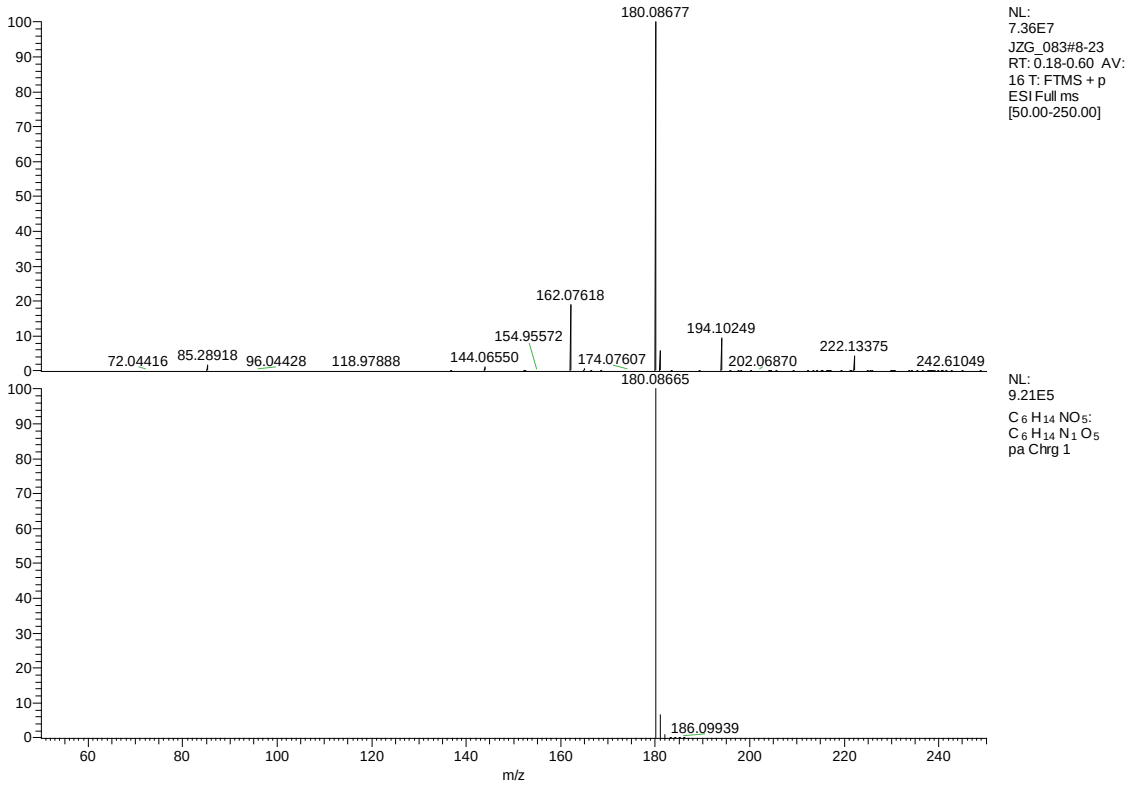

JZG071_5b_cd3od_CARBON_20170628184555.fid (1)
173.4
101.3
78.0
76.1
73.1
72.3
63.0
57.9
23.9
23.1
22.4
δ

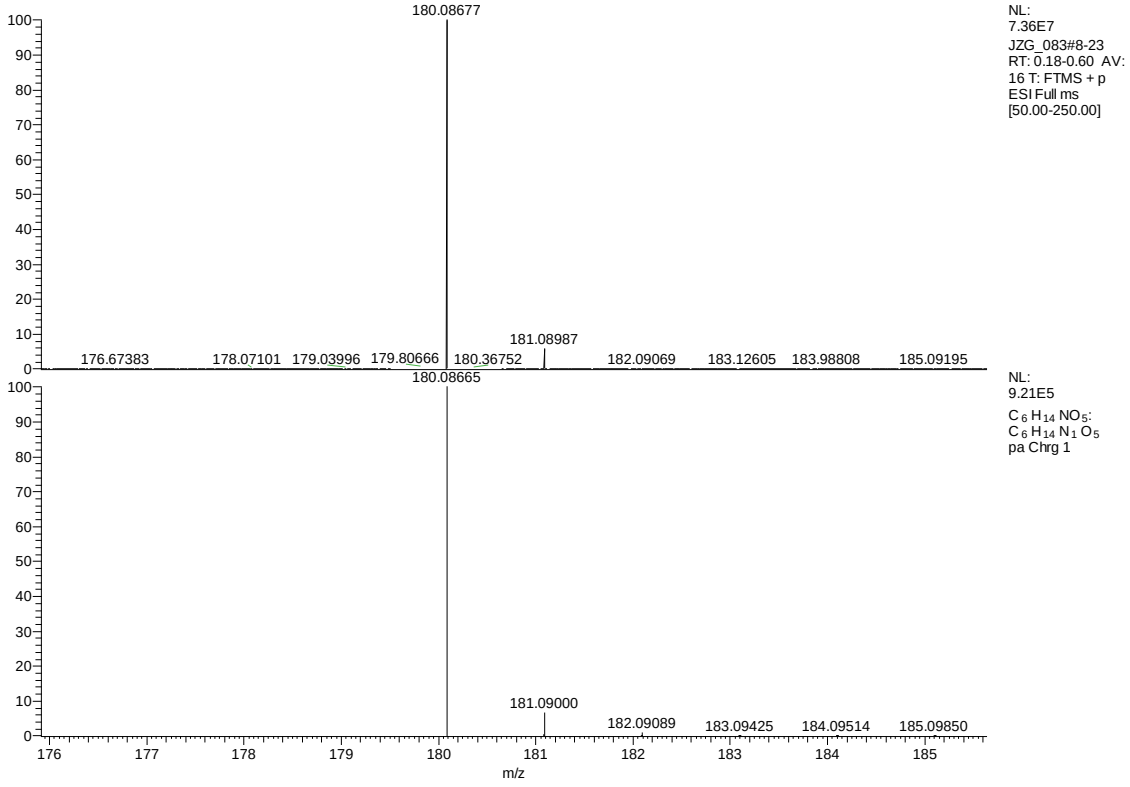
D-Allosamine (5)



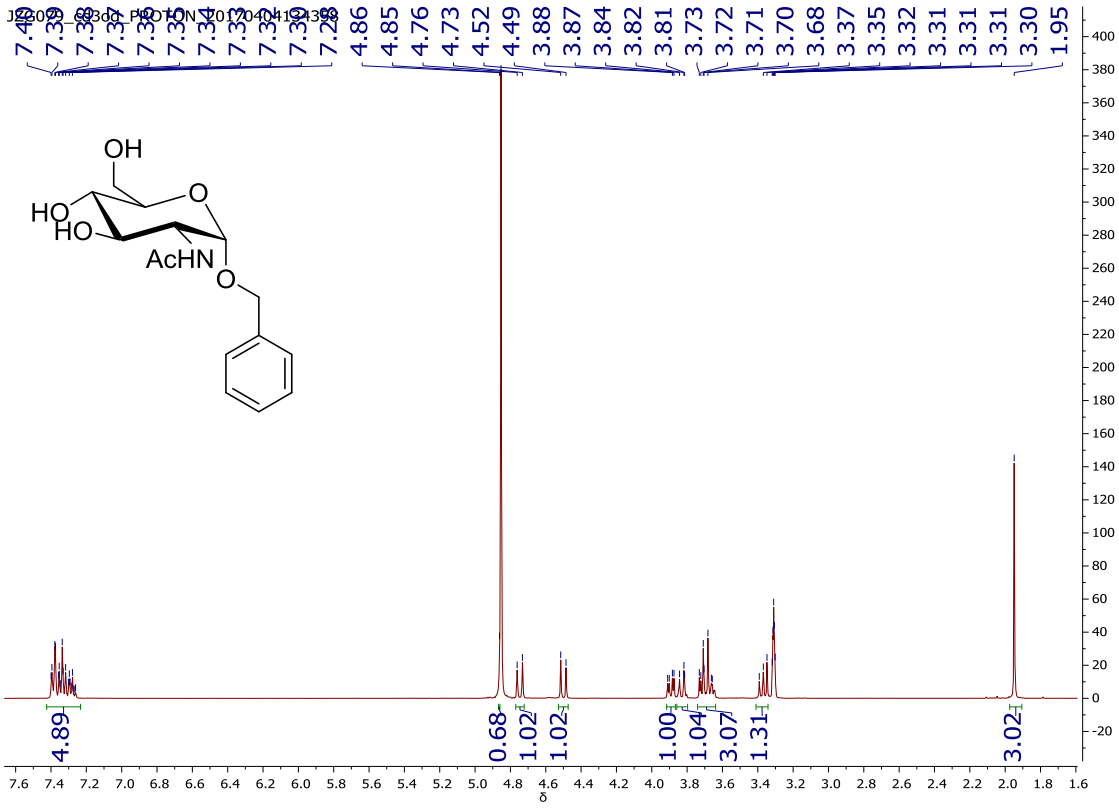

JZG083_cd3od_CARBON_20170411161420
92.6
75.9
69.6
68.5
63.0
56.4
δ

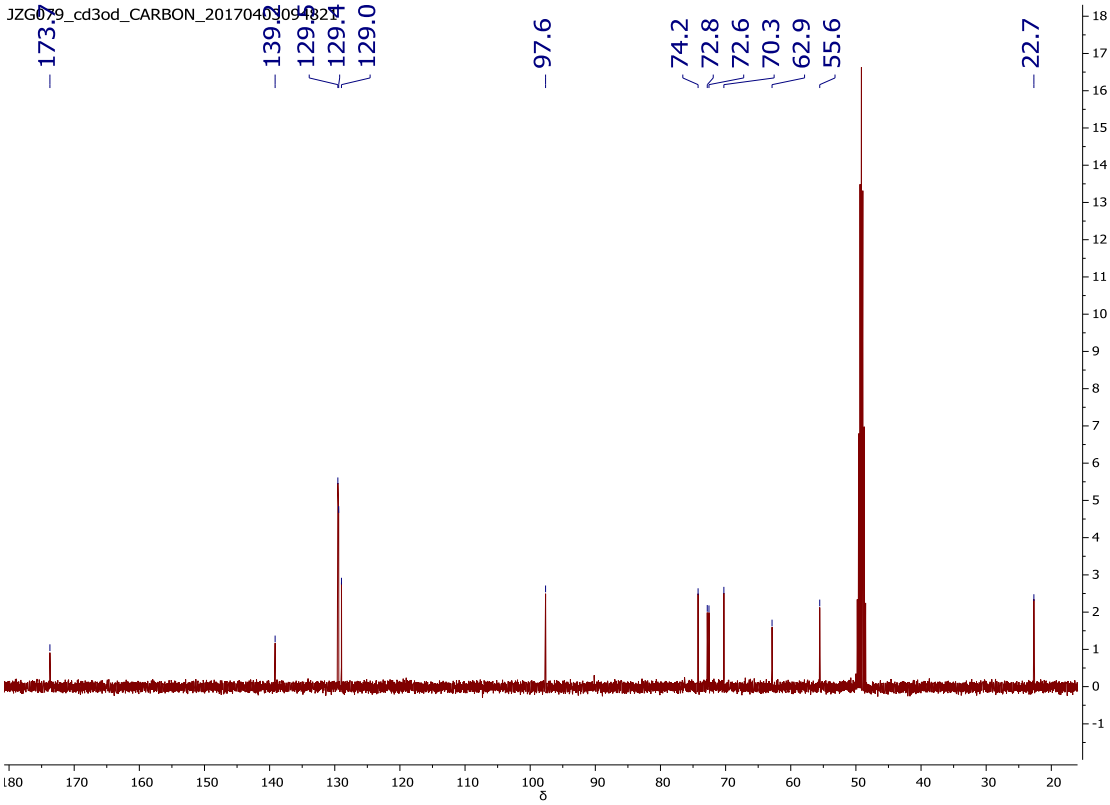

JZG083_cd3od_CARBON_APT_20170526133303
92.6
75.9
69.7
68.5
63.0
56.4
δ

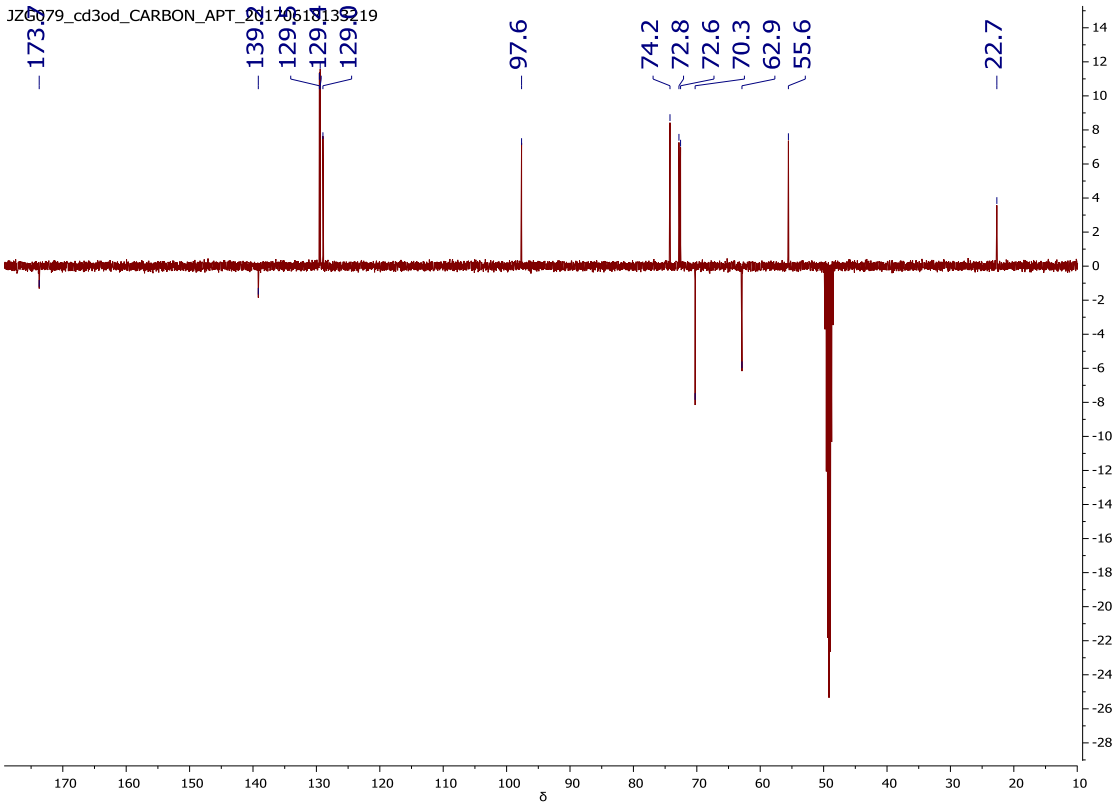

180.08677
NL:
7.36E7
JZG_083#8-23
RT: 0.18-0.60 AV:
16 T: FTMS + p
ESI Full ms
[50.00-250.00]
162.07618
154.95572
194.10249
222.13375
72.04416
85.28918
96.04428
118.97888
144.06550
174.07607
202.06870
242.61049
180.08665
NL:
9.21E5
C6 H14 NO5:
C6 H14 N1 O5
pa Chrg 1
186.09939
m/z

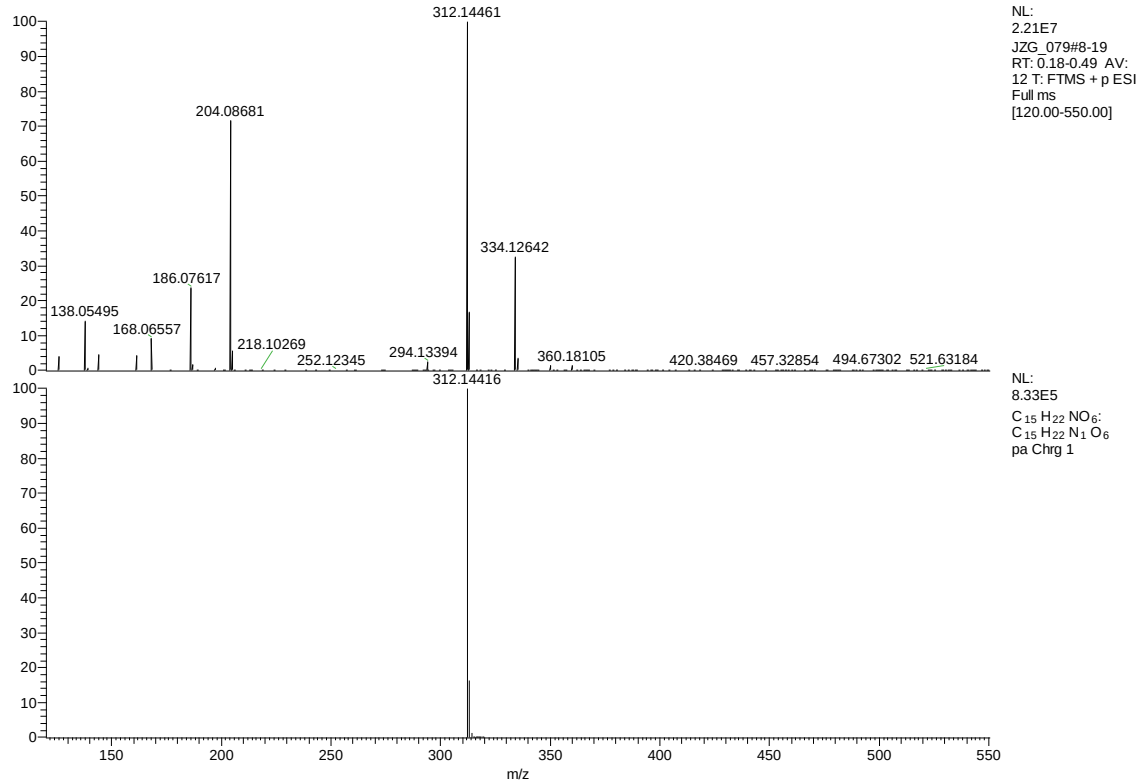

180.08677
NL:
7.36E7
JZG_083#8-23
RT: 0.18-0.60 AV:
16 T: FTMS + p
ESI Full ms
[50.00-250.00]
181.08987
176.67383
178.07101
179.03996
179.80666
180.36752
182.09069
183.12605
183.98808
185.09195
180.08665
NL:
9.21E5
C6 H14 NO5:
C6 H14 N1 O5
pa Chrg 1
181.09000
182.09089
183.09425
184.09514
185.09850
m/z

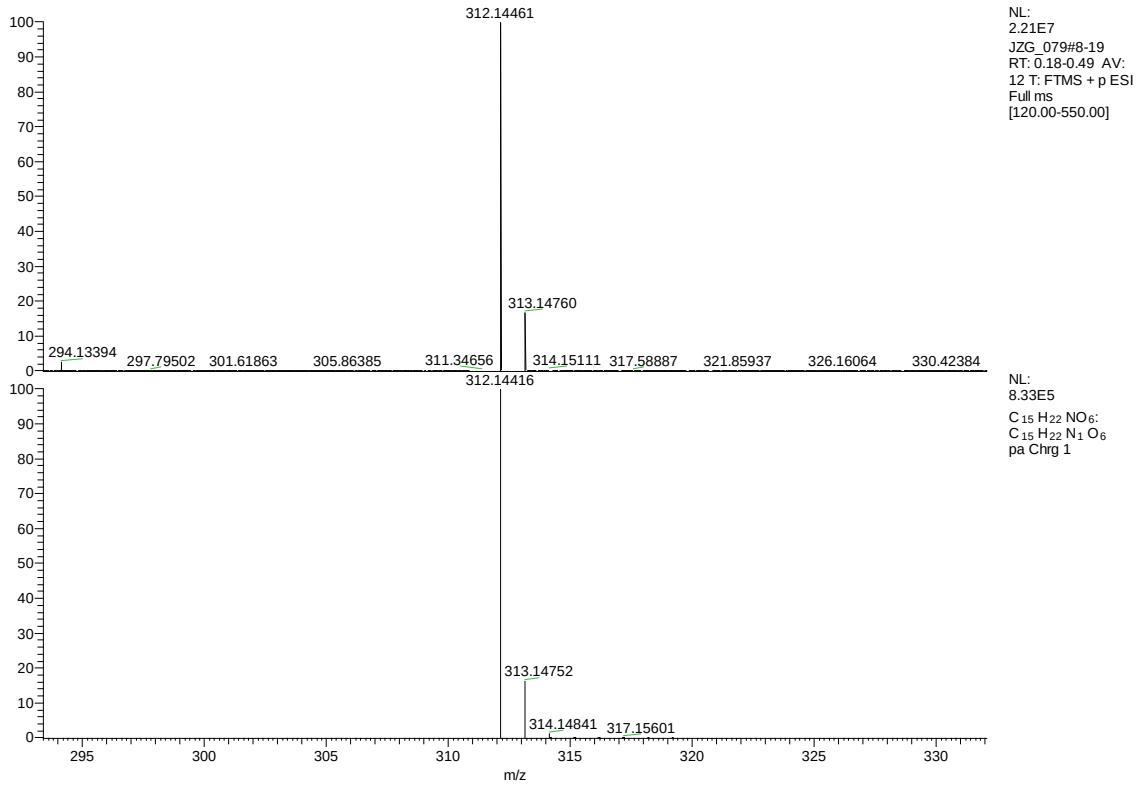
Benzyl 2-acetamido-2-deoxy-α-D-glucopyranoside (9)



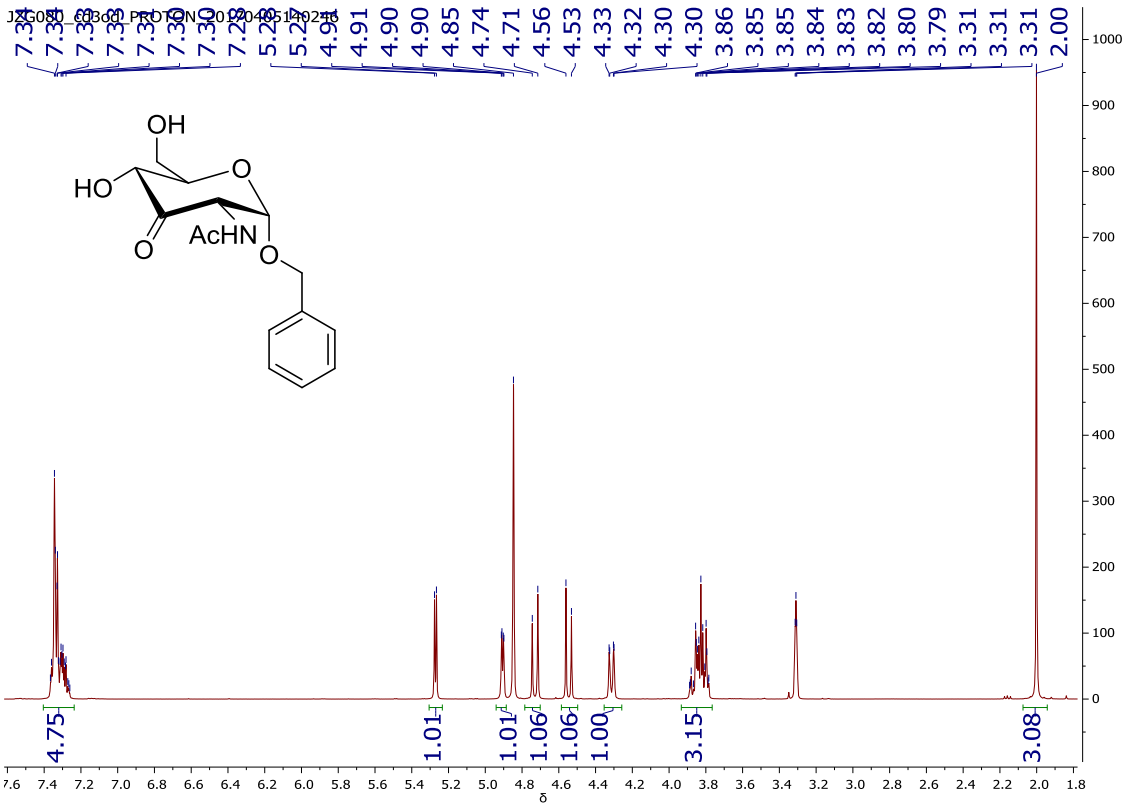


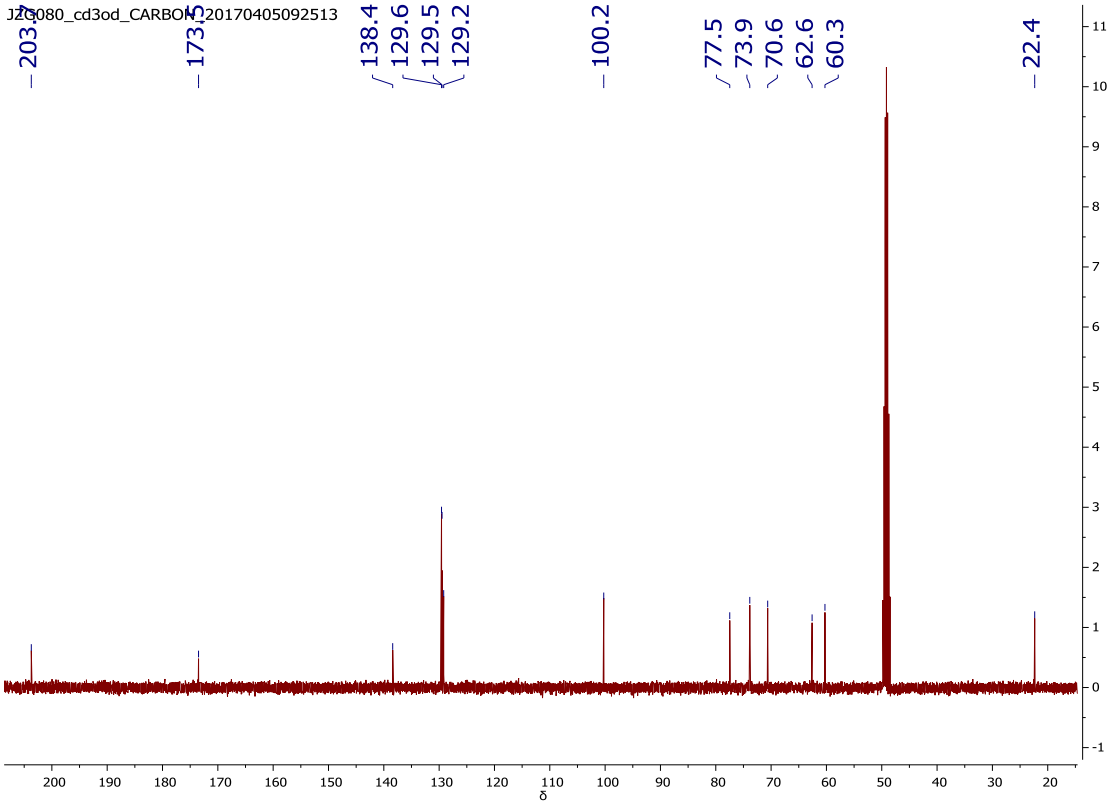

JZG079_cd3od_CARBON_APT_20170518_132219
173.2
139.2
129.4
129.1
129.2
97.6
74.2
72.8
72.6
70.3
62.9
55.6
22.7
δ

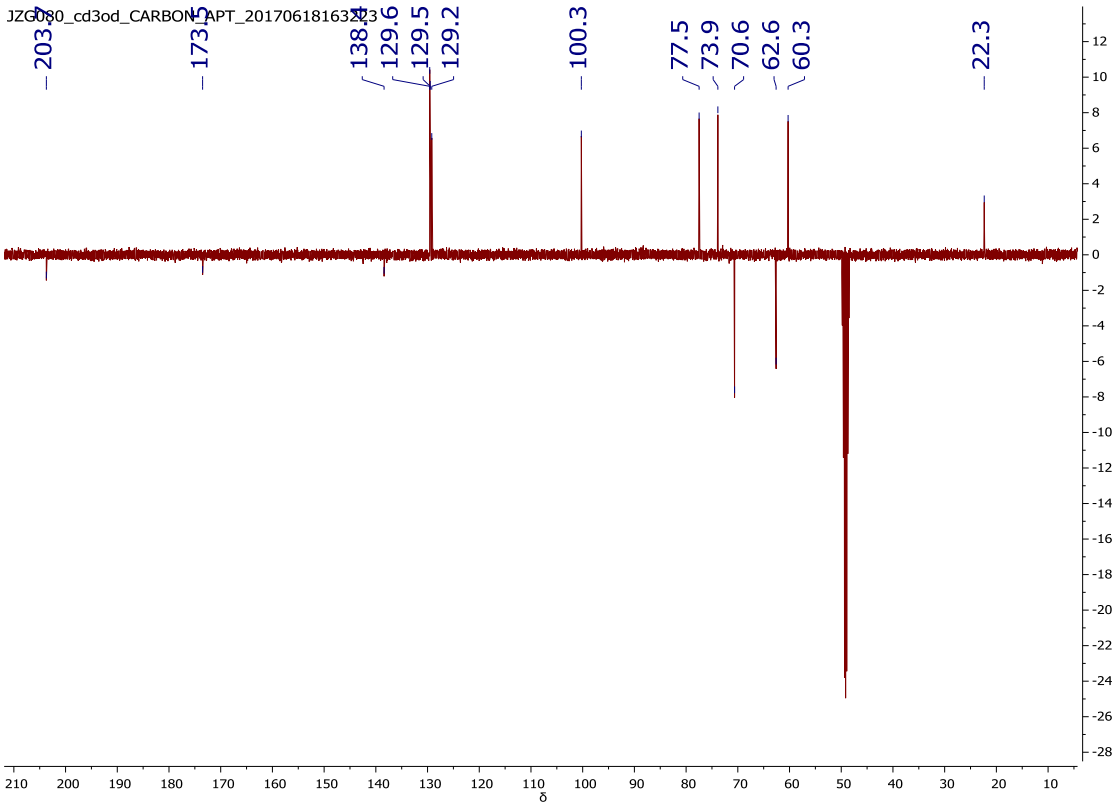

312.14461
204.08681
334.12642
186.07617
138.05495
168.06557
218.10269
252.12345
294.13394
360.18105
420.38469
457.32854
494.67302
521.63184
NL:
2.21E7
JZG_079#8-19
RT: 0.18-0.49 AV:
12 T: FTMS + p ESI
Full ms
[120.00-550.00]
312.14416
NL:
8.33E5
C15 H22 NO6:
C15 H22 N1 O6
pa Chrg 1
m/z

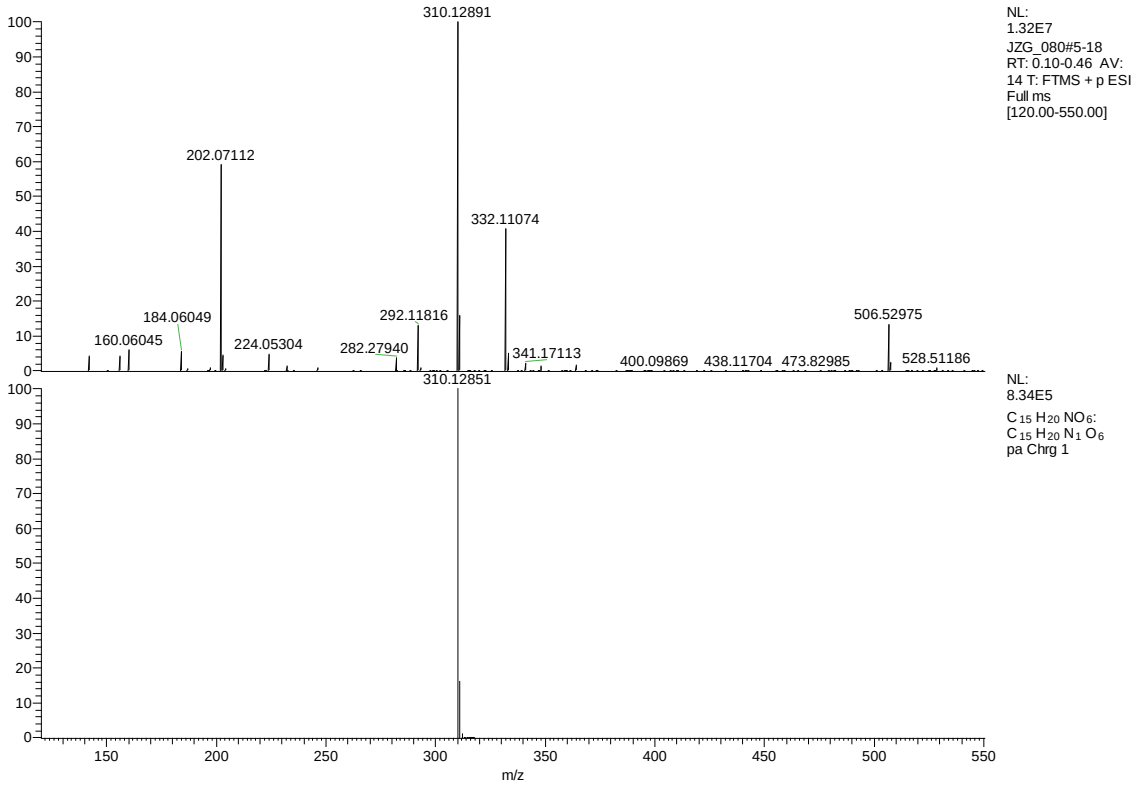


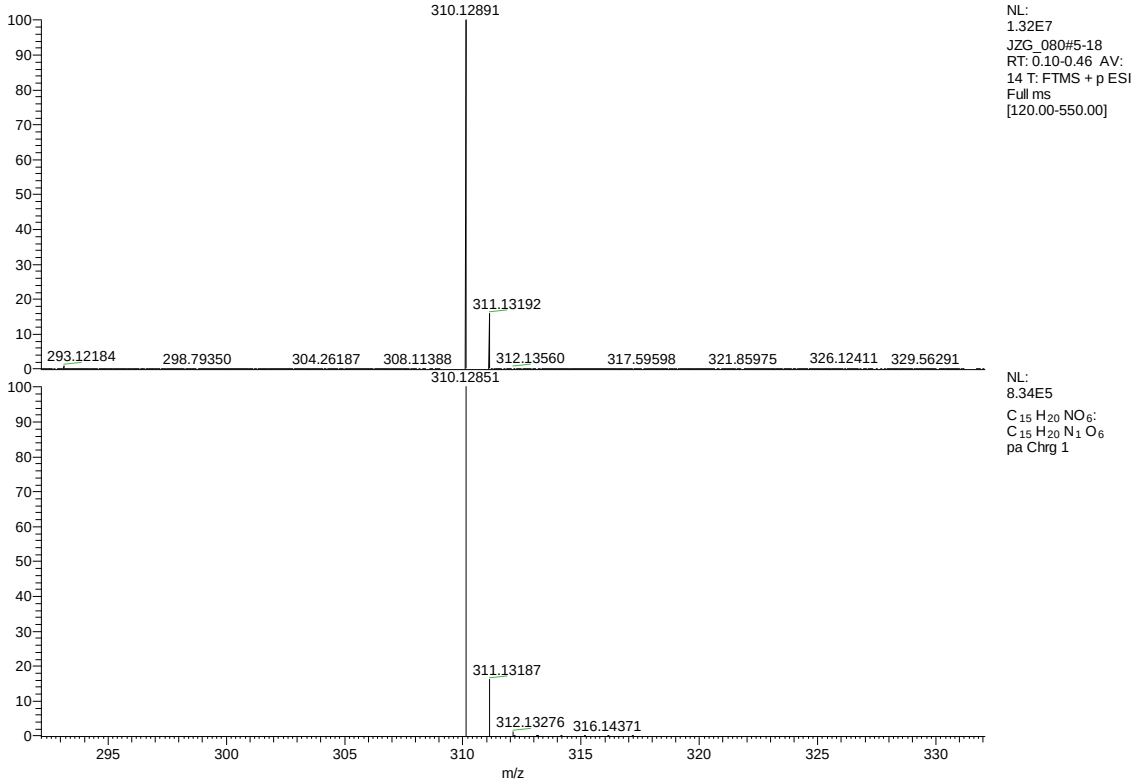
Benzyl 2-acetamido-2-deoxy-α-D-glucopyran-3-uloside (10)



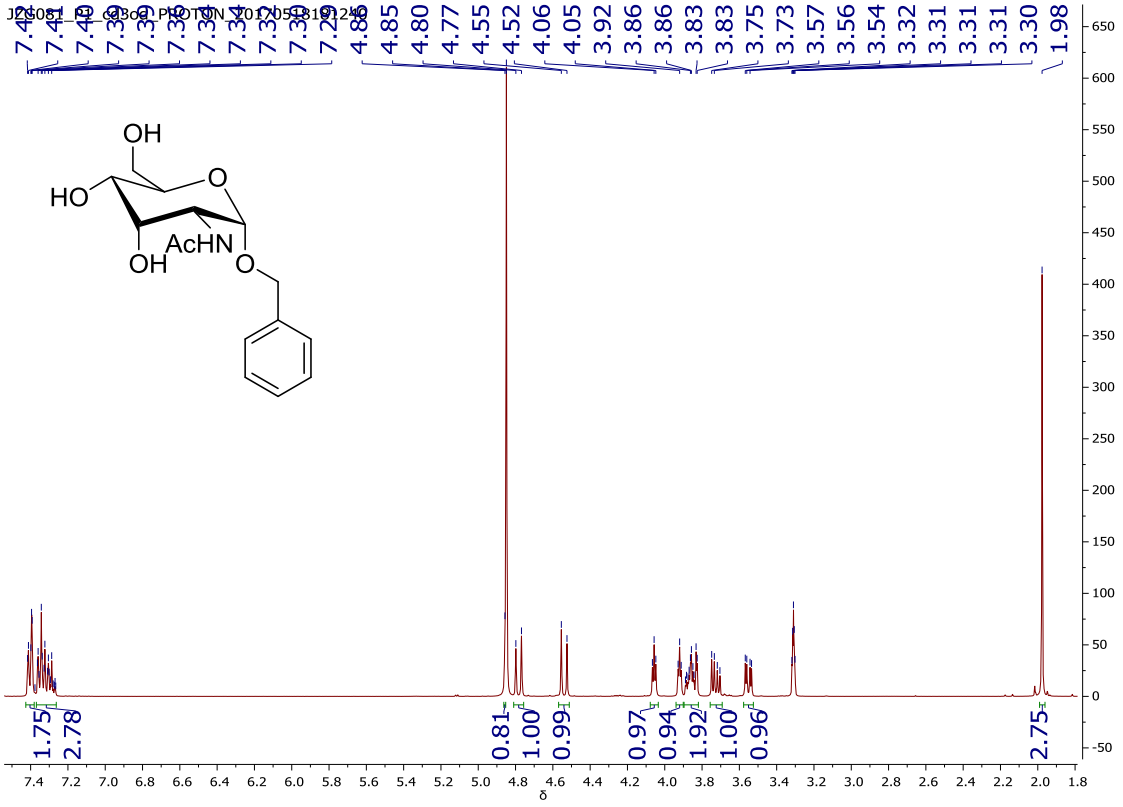

JZG080_cd3od_CARBON_20170405092513
203.1
173.5
138.4
129.6
129.5
129.2
100.2
77.5
73.9
70.6
62.6
60.3
22.4
δ

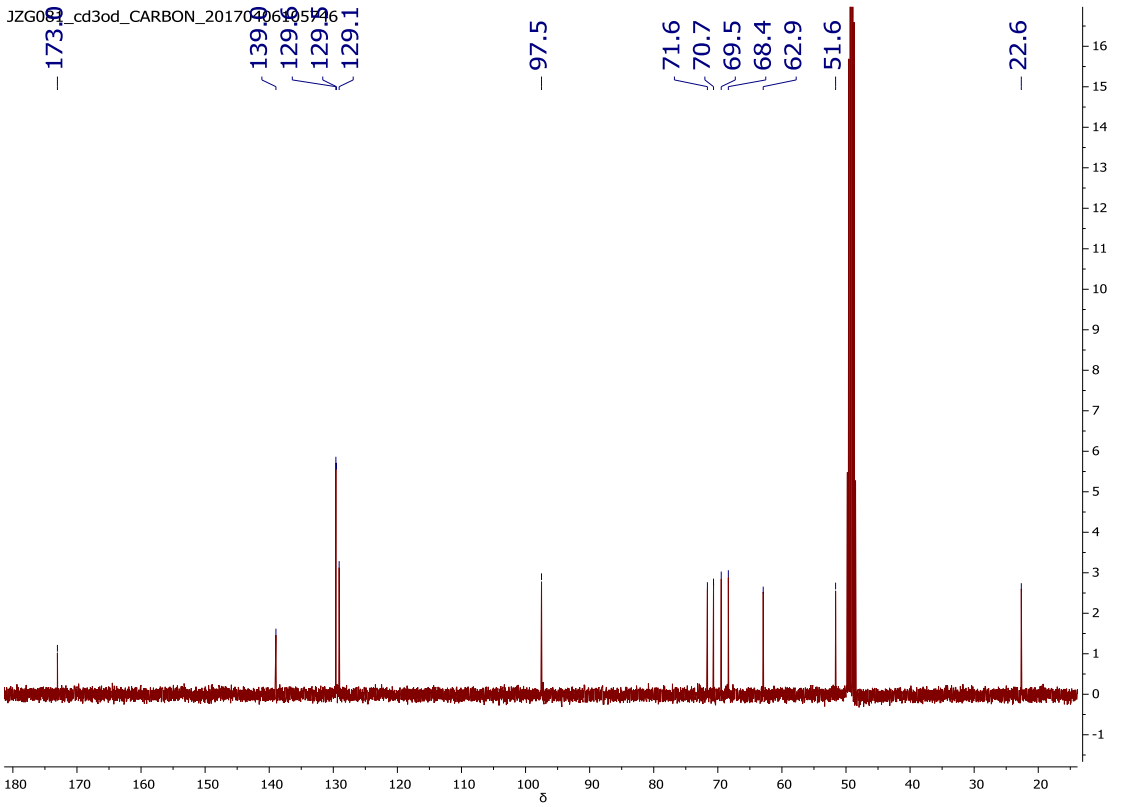

JZG080_cd3od_CARBON_APT_20170618163223
203.1
173.5
138.4
129.6
129.5
129.2
100.3
77.5
73.9
70.6
62.6
60.3
22.3
δ

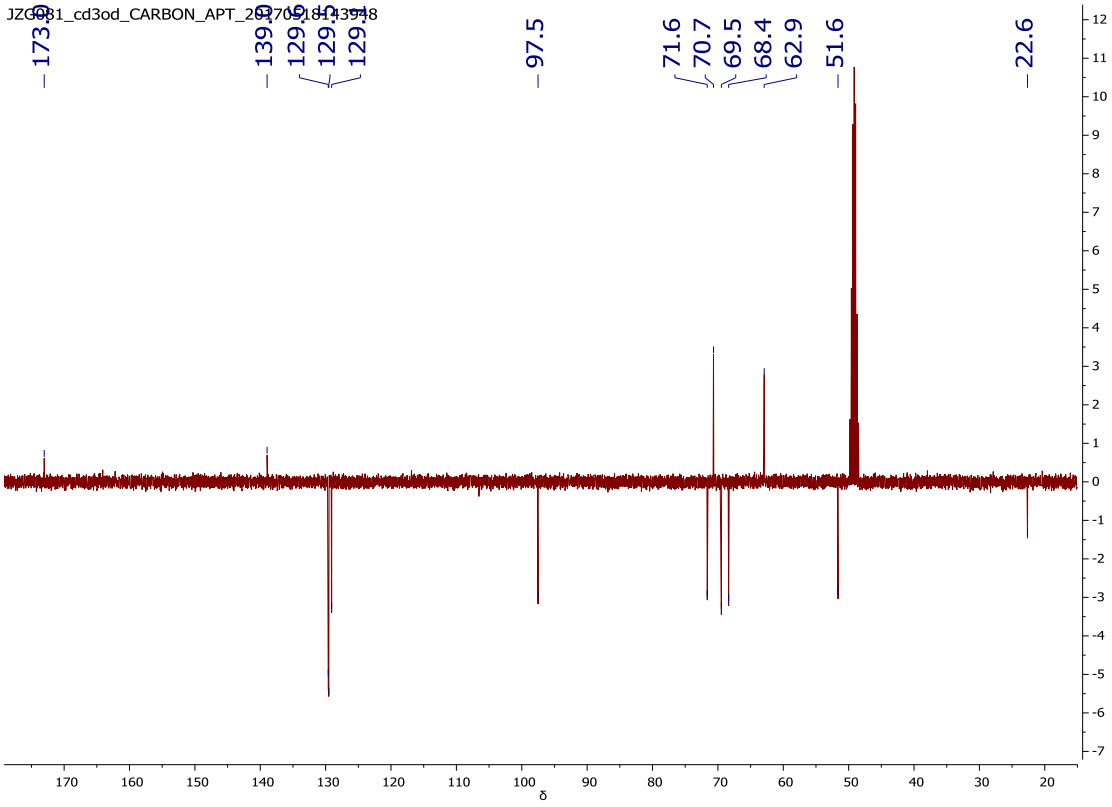

310.12891
202.07112
332.11074
184.06049
160.06045
224.05304
292.11816
282.27940
341.17113
400.09869
438.11704
473.82985
506.52975
528.51186
NL:
1.32E7
JZG_080#5-18
RT: 0.10-0.46 AV:
14 T: FTMS + p ESI
Full ms
[120.00-550.00]
310.12851
NL:
8.34E5
C15 H20 NO6:
C15 H20 N1 O6
pa Chrg 1
m/z

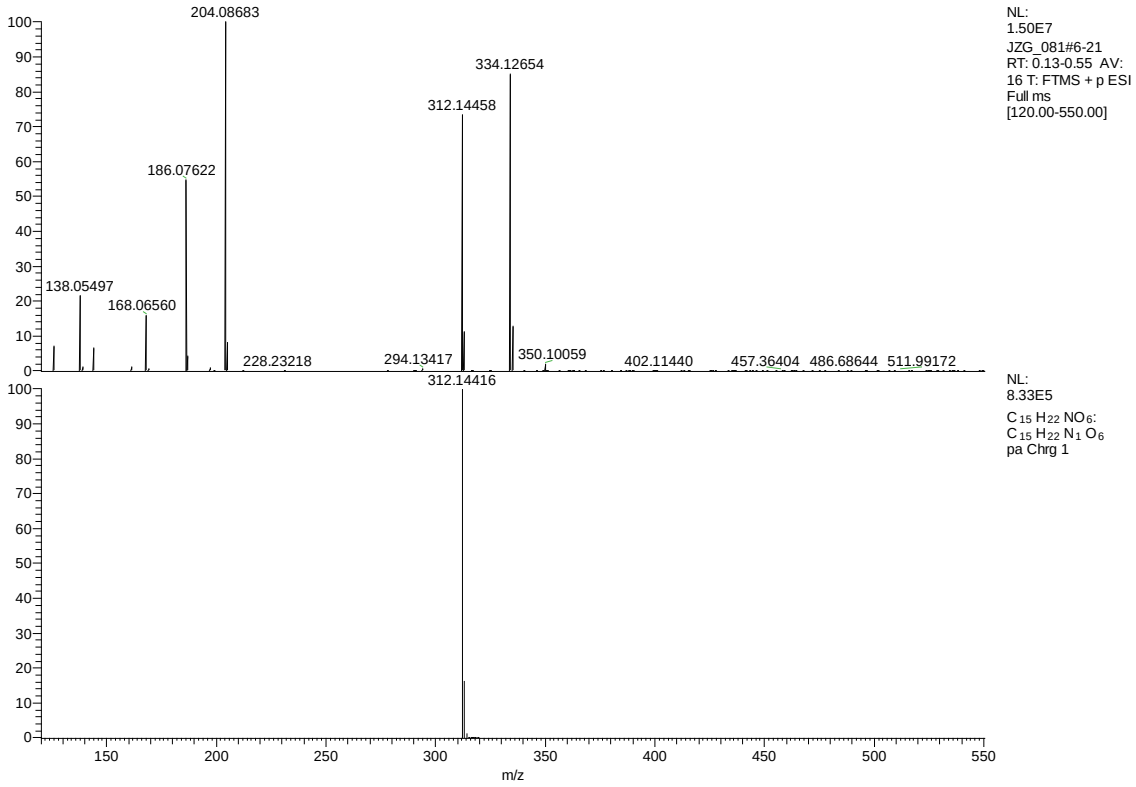

310.12891
311.13192
293.12184
298.79350
304.26187
308.11388
312.13560
317.59598
321.85975
326.12411
329.56291
NL:
1.32E7
JZG_080#5-18
RT: 0.10-0.46 AV:
14 T: FTMS + p ESI
Full ms
[120.00-550.00]
310.12851
311.13187
312.13276
316.14371
NL:
8.34E5
C15 H20 NO6:
C15 H20 N1 O6
pa Chrg 1
m/z

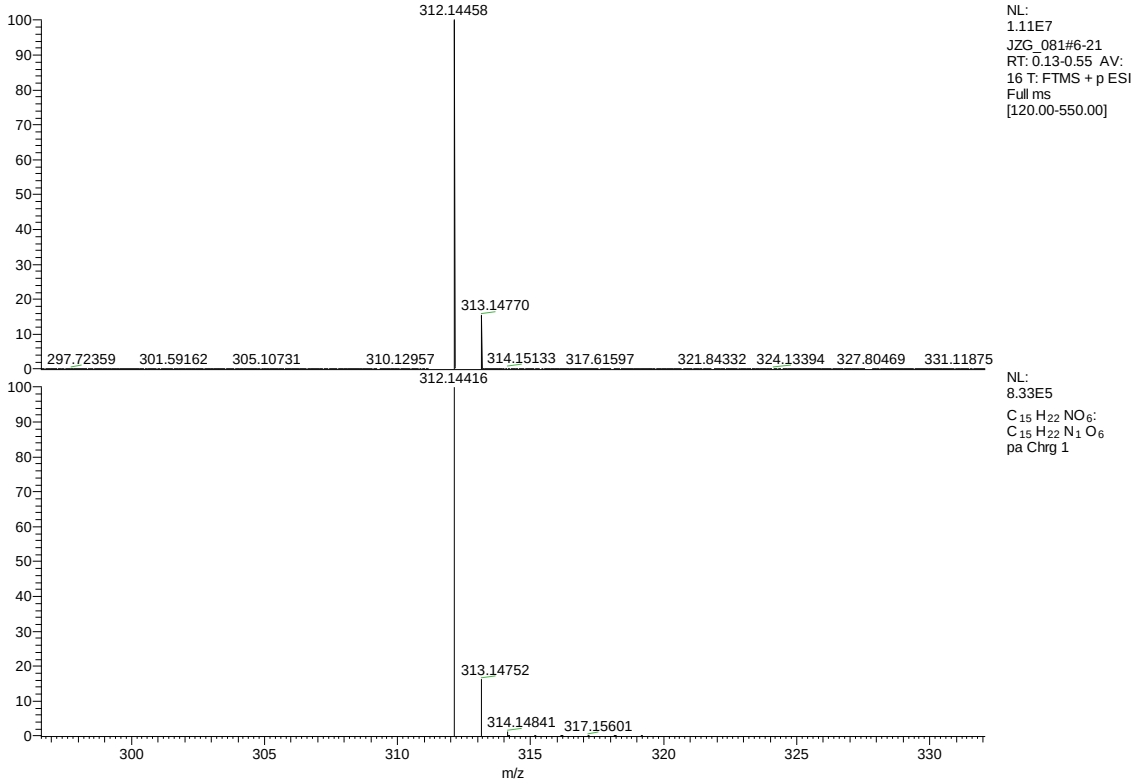
Benzyl 2-acetamido-2-deoxy-α-D-allopyranoside (11)



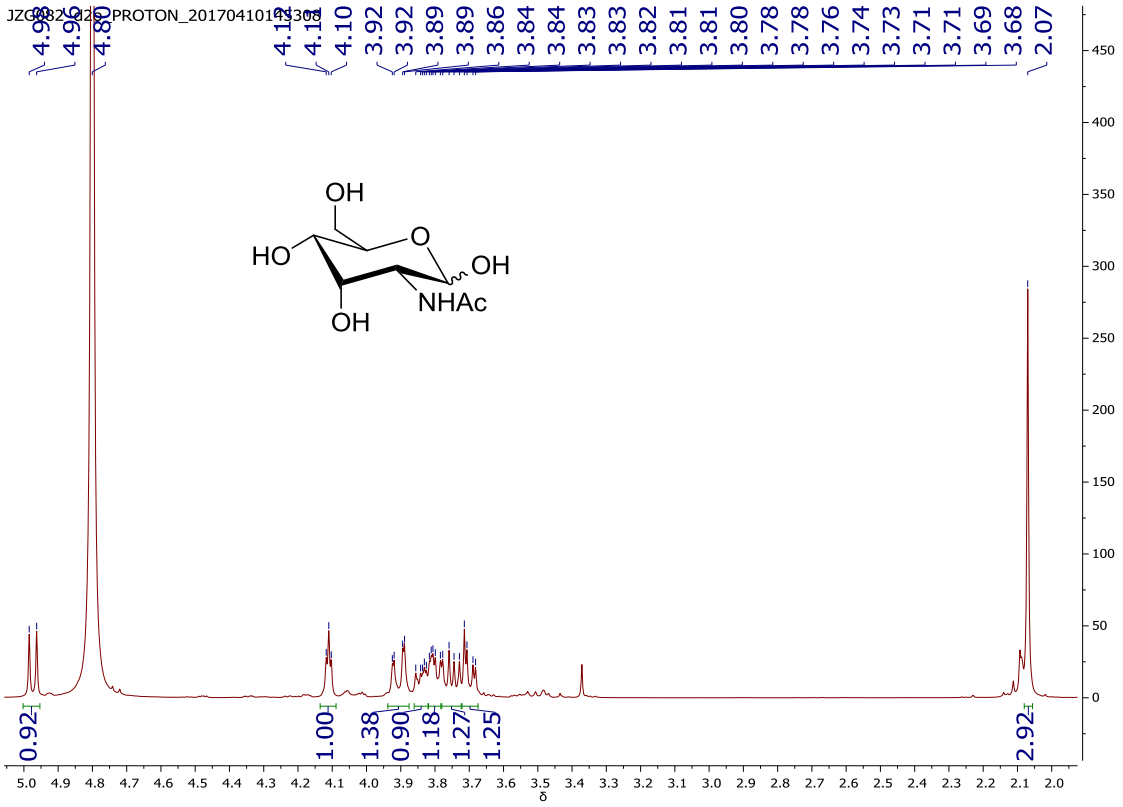


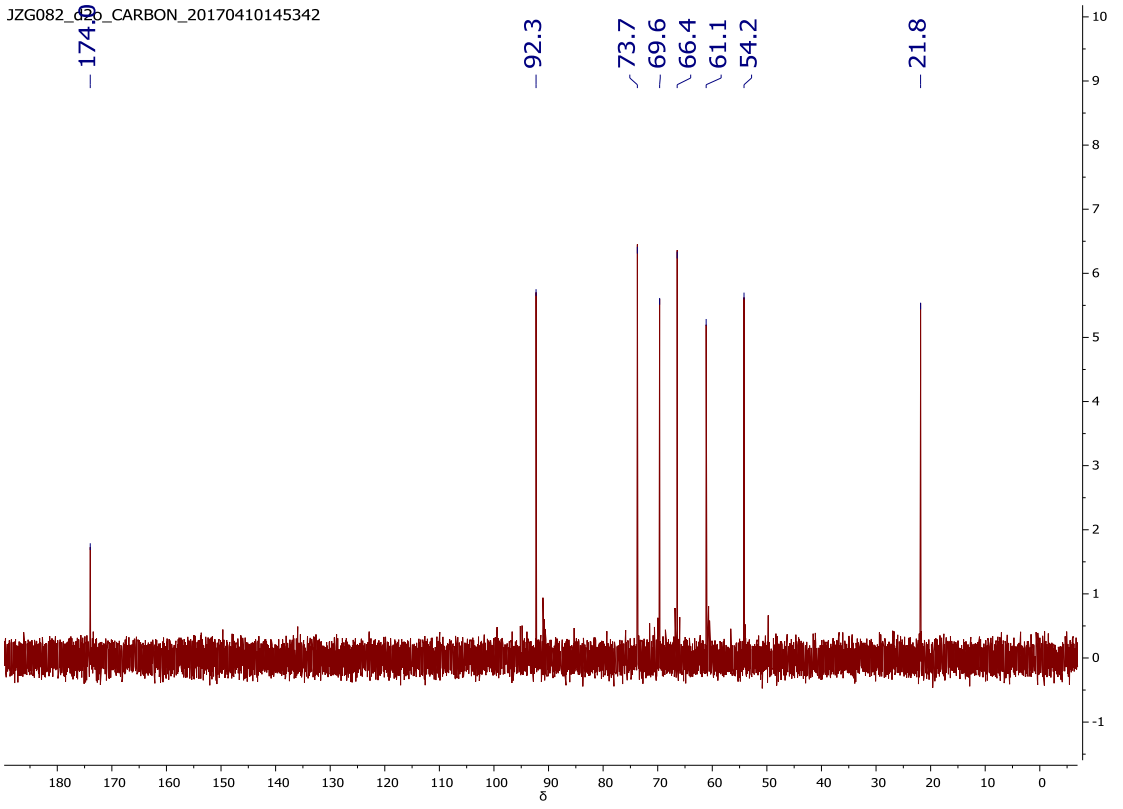

JZG081_cd3od_CARBON_APT_20170518143948
173.3
139.1
129.8
129.4
129.1
97.5
71.6
70.7
69.5
68.4
62.9
51.6
22.6
δ

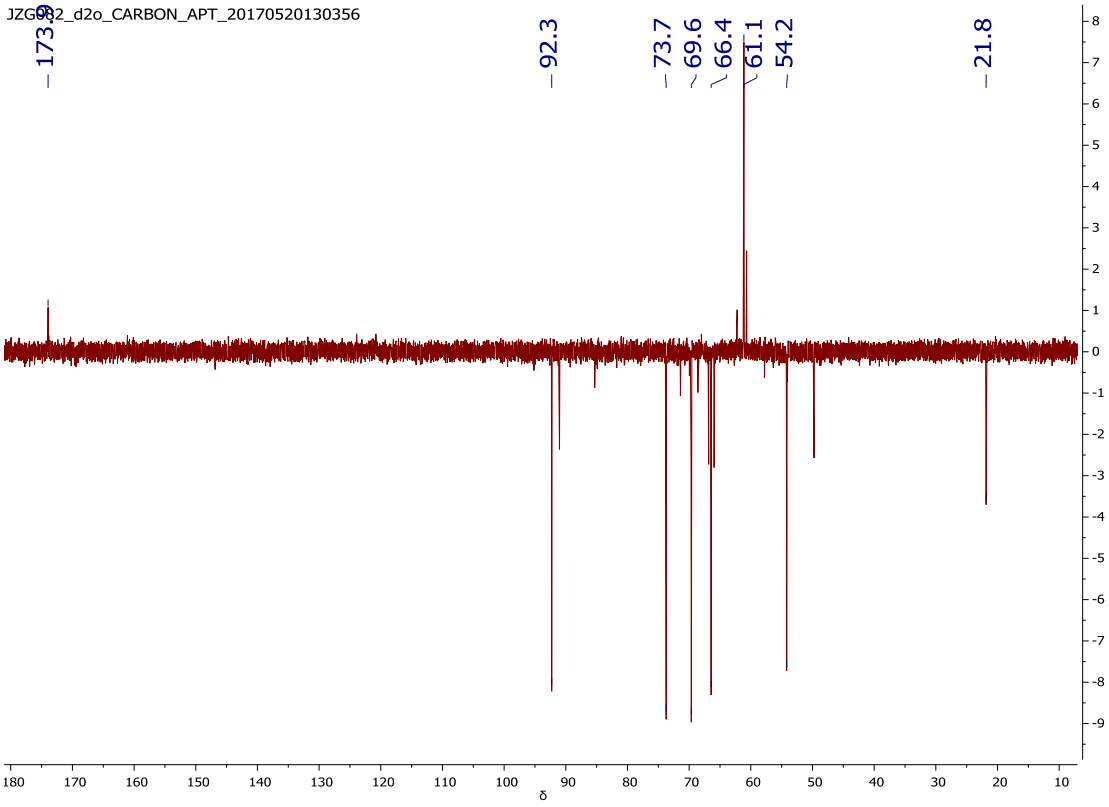

204.08683
334.12654
312.14458
186.07622
138.05497
168.06560
228.23218
294.13417
350.10059
402.11440
457.36404
486.68644
511.99172
312.14416
NL:
1.50E7
JZG_081#6-21
RT: 0.13-0.55 AV:
16 T: FTMS + p ESI
Full ms
[120.00-550.00]
NL:
8.33E5
C15 H22 NO6:
C15 H22 N1 O6
pa Chrg 1
m/z

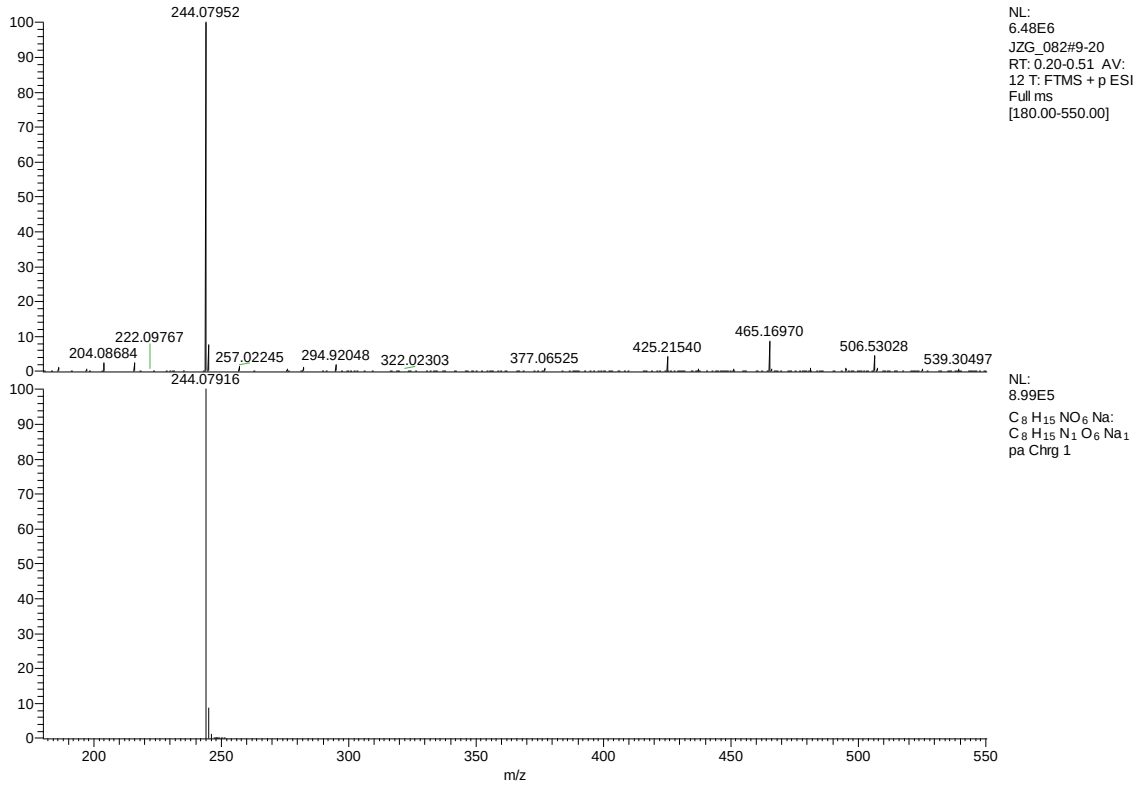

312.14458
313.14770
297.72359
301.59162
305.10731
310.12957
314.15133
317.61597
321.84332
324.13394
327.80469
331.11875
312.14416
313.14752
314.14841
317.15601
NL:
1.11E7
JZG_081#6-21
RT: 0.13-0.55 AV:
16 T: FTMS + p ESI
Full ms
[120.00-550.00]
NL:
8.33E5
C15 H22 NO6:
C15 H22 N1 O6
pa Chrg 1
m/z

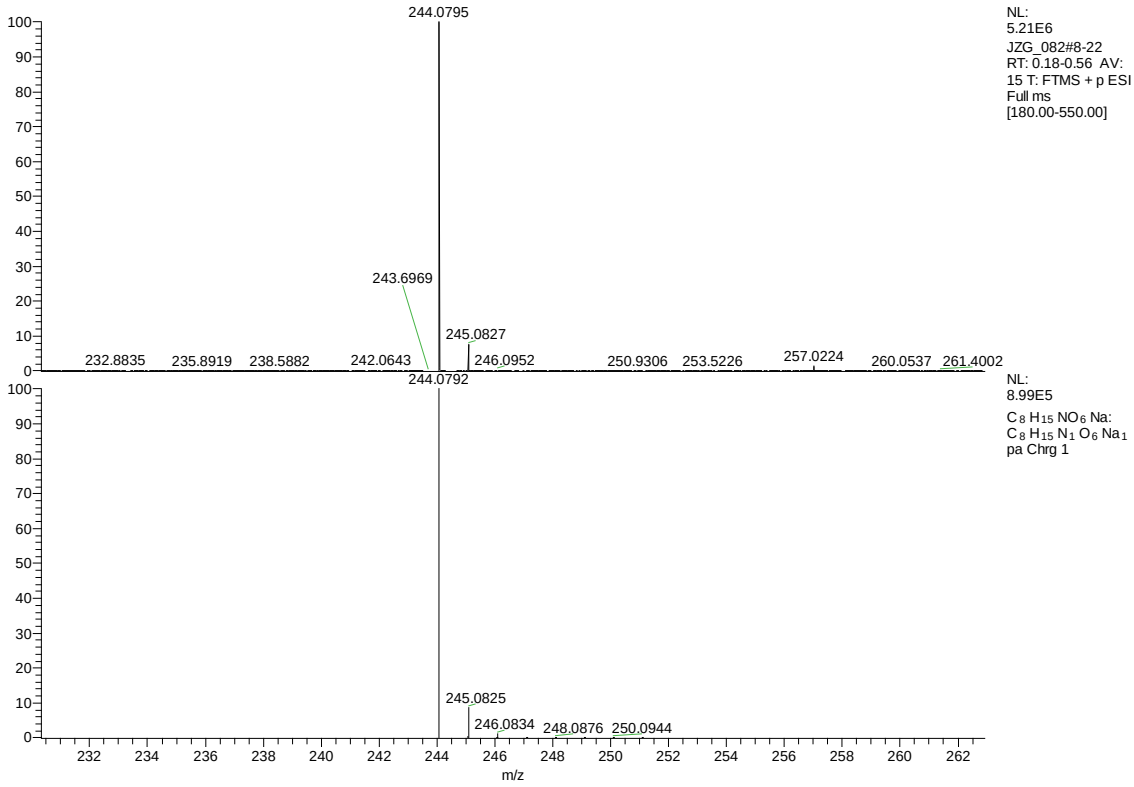
N-acetyl D-allosamine (12)



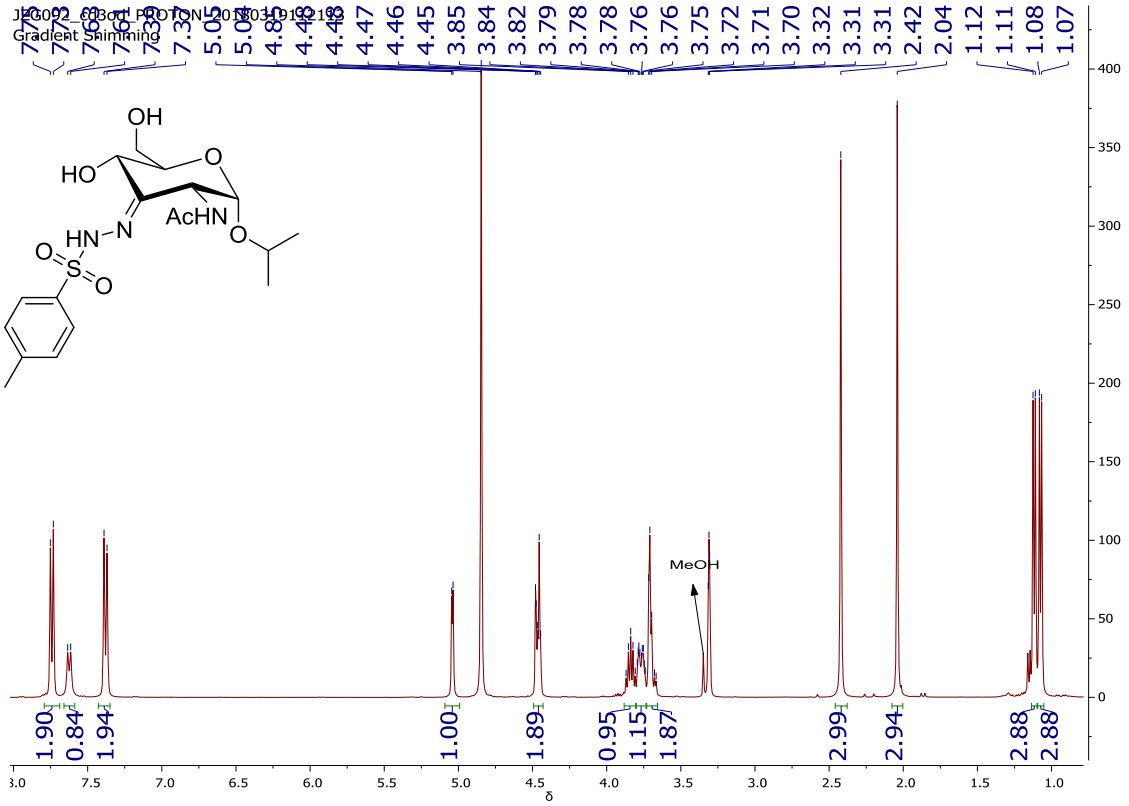


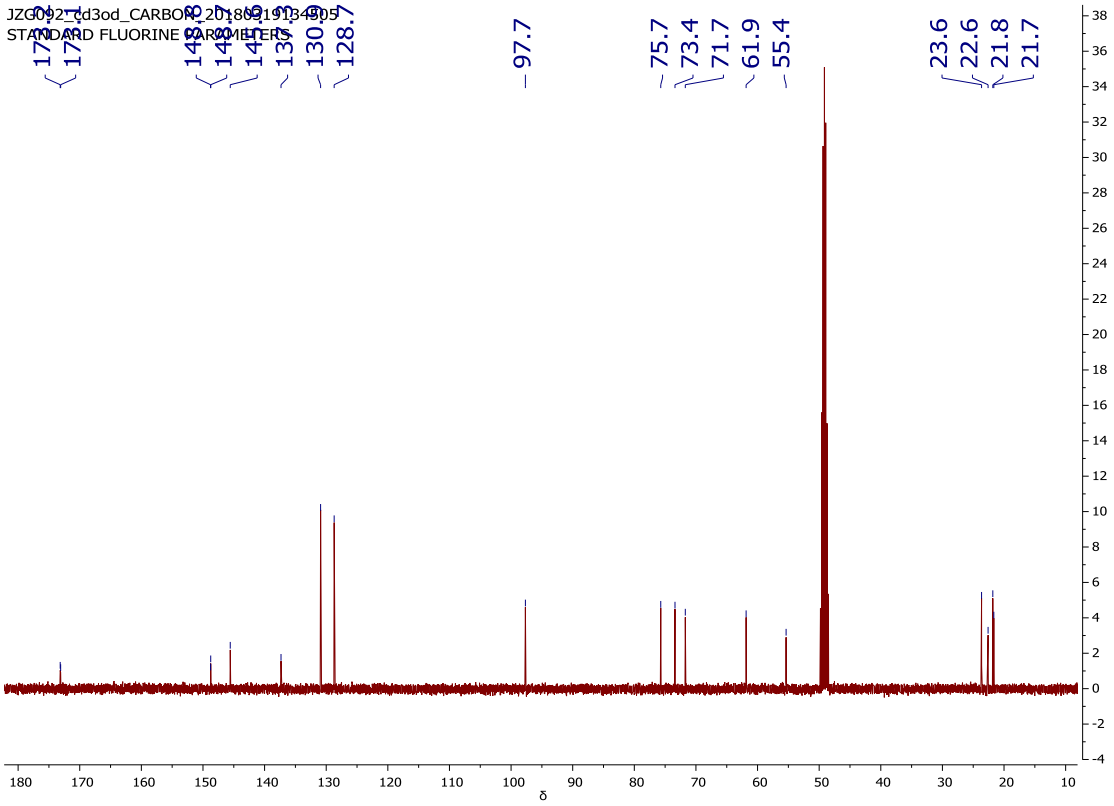

JZG082_d2o_CARBON_APT_20170520130356
173.9
92.3
73.7
69.6
66.4
61.1
54.2
21.8
δ

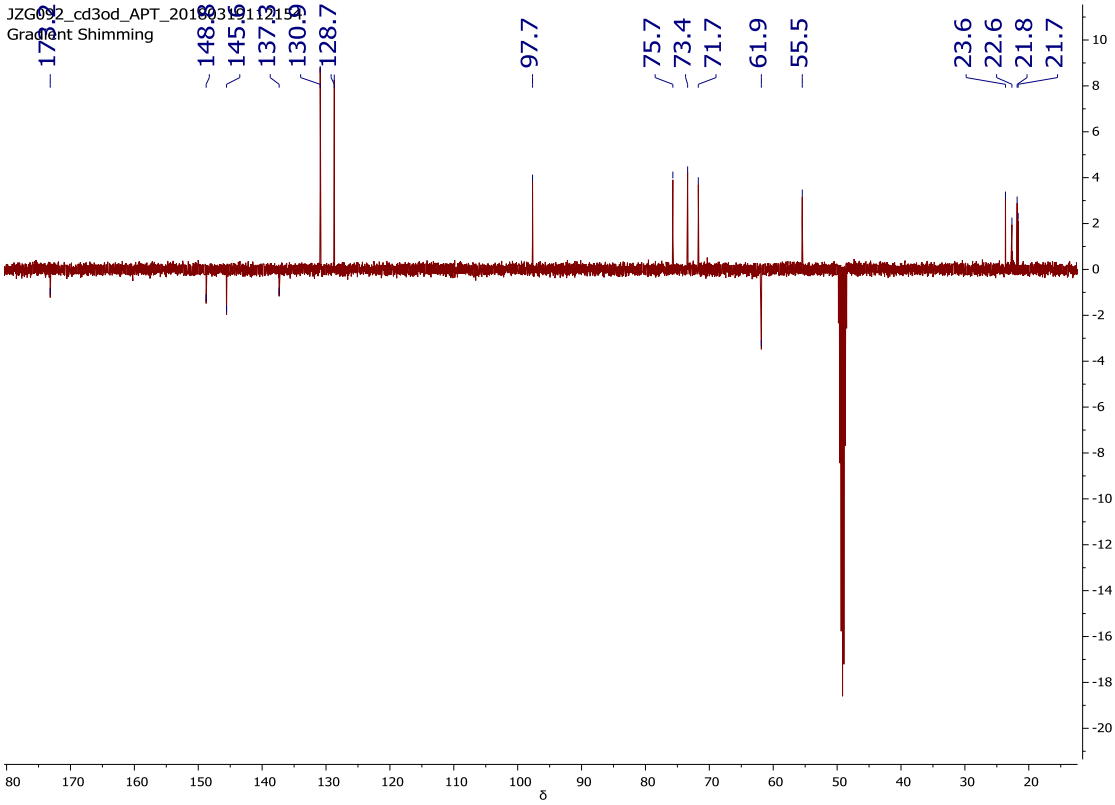

244.07952
222.09767
204.08684
257.02245
294.92048
322.02303
377.06525
425.21540
465.16970
506.53028
539.30497
NL:
6.48E6
JZG_082#9-20
RT: 0.20-0.51 AV:
12 T: FTMS + p ESI
Full ms
[180.00-550.00]
244.07916
NL:
8.99E5
C8 H15 NO6 Na:
C8 H15 N1 O6 Na1
pa Chrg 1
m/z

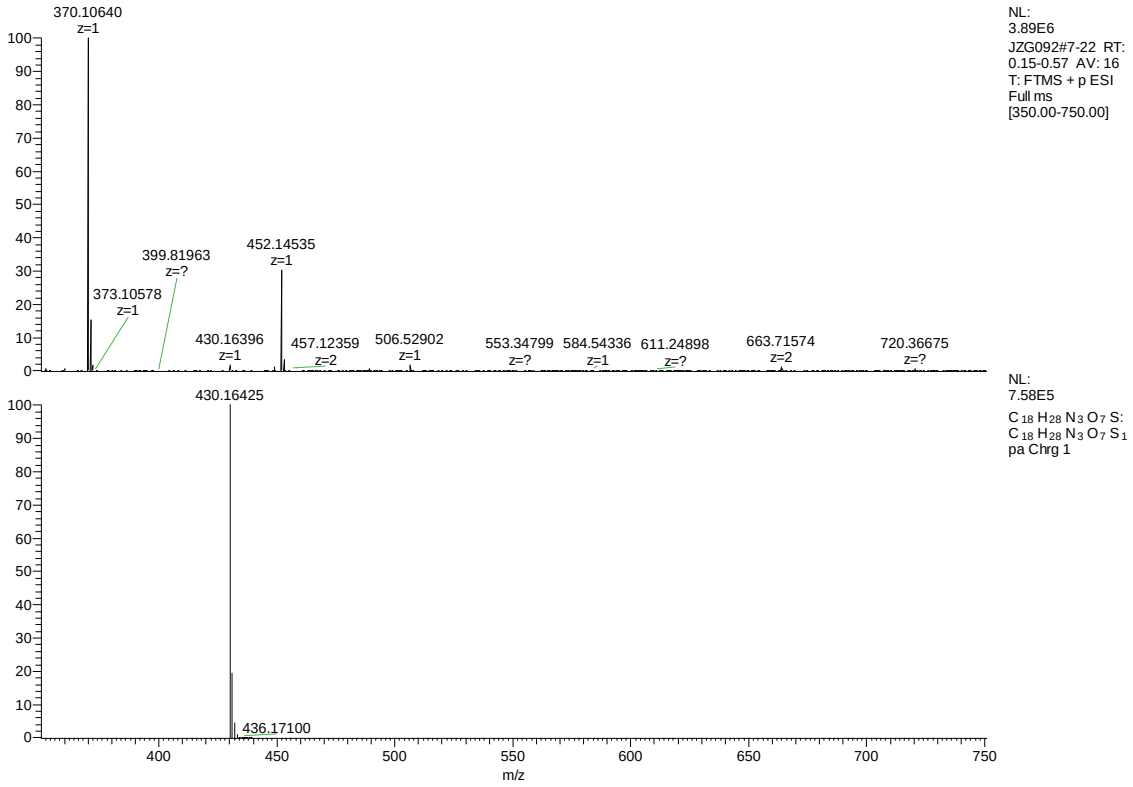


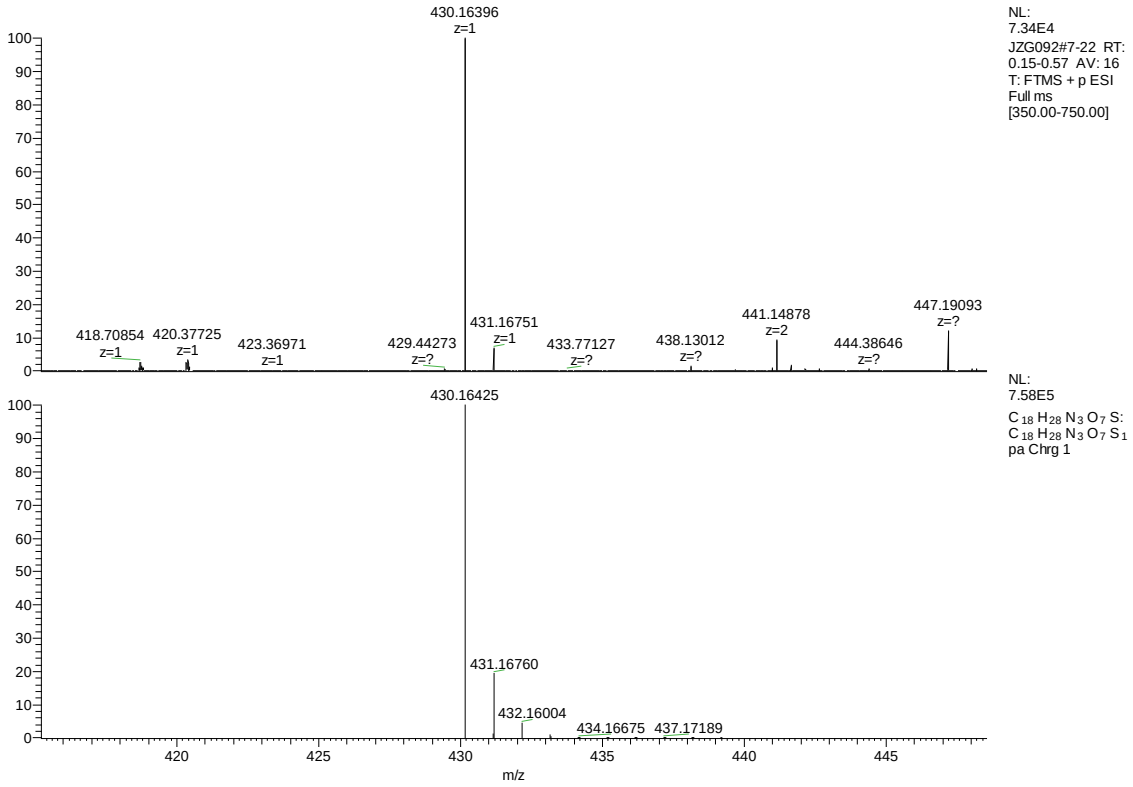
_N_-((2_S_,3_R_,5_S_,6_R_,_Z_)-5-hydroxy-6-(hydroxymethyl)-2-isopropoxy-4-(2-tosylhydrazono)tetrahydro-2_H_-pyran-3-yl)acetamide (13)

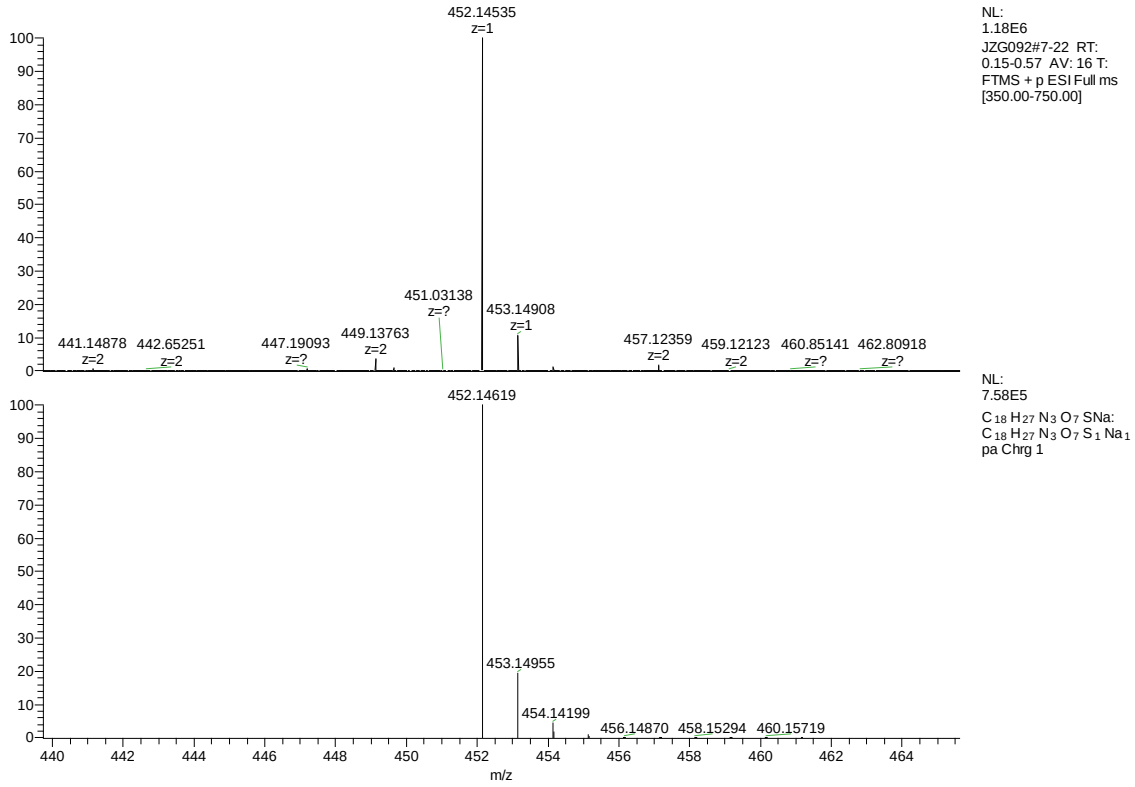



JZG092_cd3od_CARBON_20180919134505
STANDARD FLUORINE PARAMETERS
97.7
75.7
73.4
71.7
61.9
55.4
23.6
22.6
21.8
21.7
128.7
δ

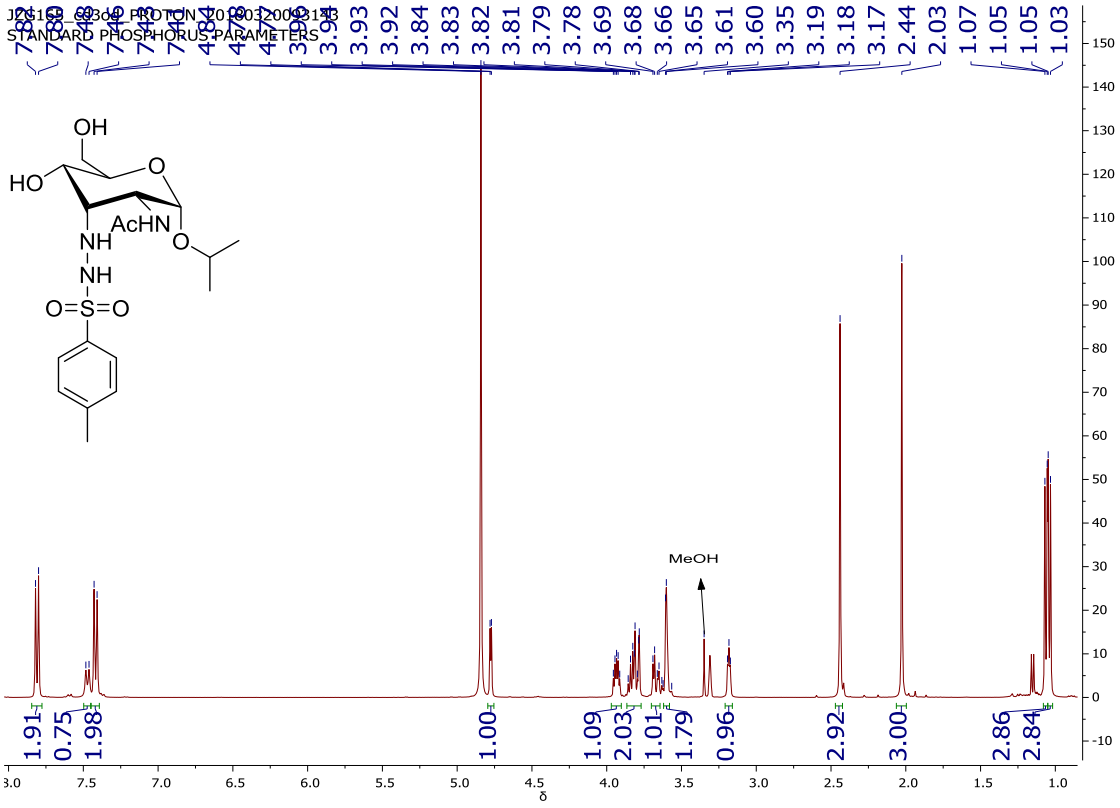

JZG092_cd3od_APT_20180319112154
Gradient Shimming
97.7
75.7
73.4
71.7
61.9
55.5
23.6
22.6
21.8
21.7
130.9
128.7
δ

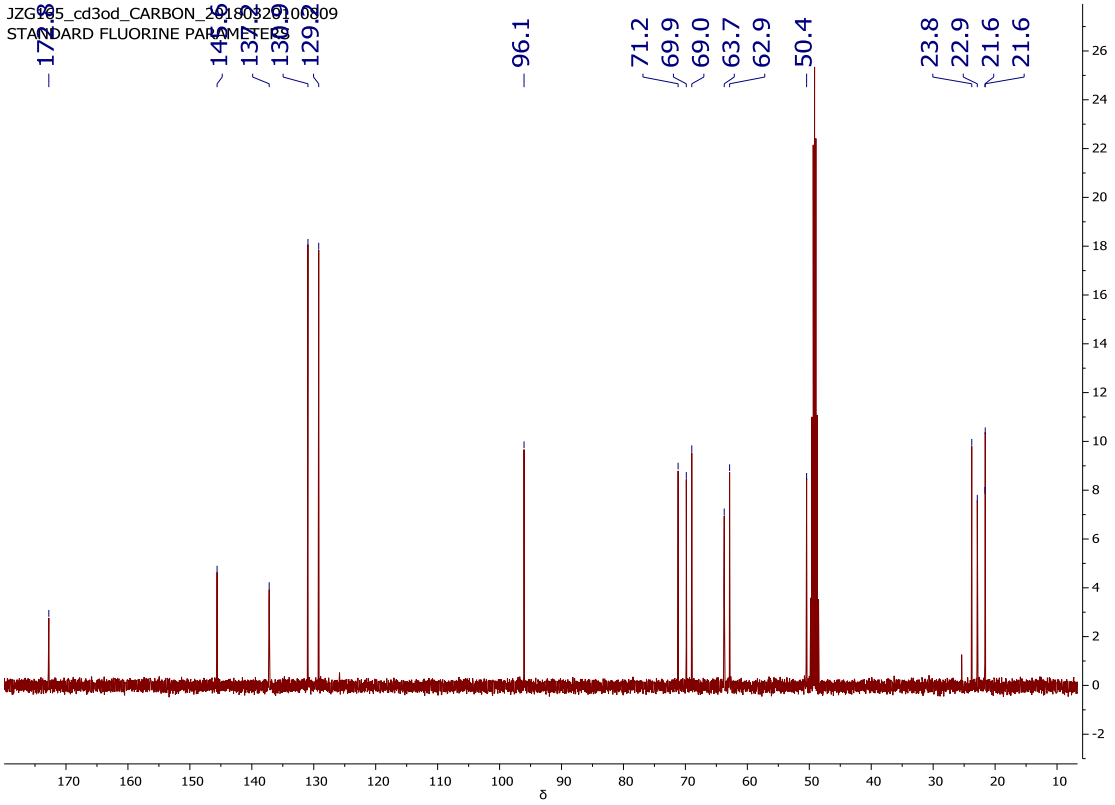

370.10640
z=1
399.81963
z=?
373.10578
z=1
452.14535
z=1
430.16396
z=1
457.12359
z=2
506.52902
z=1
553.34799
z=?
584.54336
z=1
611.24898
z=?
663.71574
z=2
720.36675
z=?
NL:
3.89E6
JZG092#7-22 RT:
0.15-0.57 AV: 16
T: FTMS + p ESI
Full ms
[350.00-750.00]
430.16425
436.17100
NL:
7.58E5
C 18 H 28 N 3 O 7 S:
C 18 H 28 N 3 O 7 S 1
pa Chrg 1
m/z

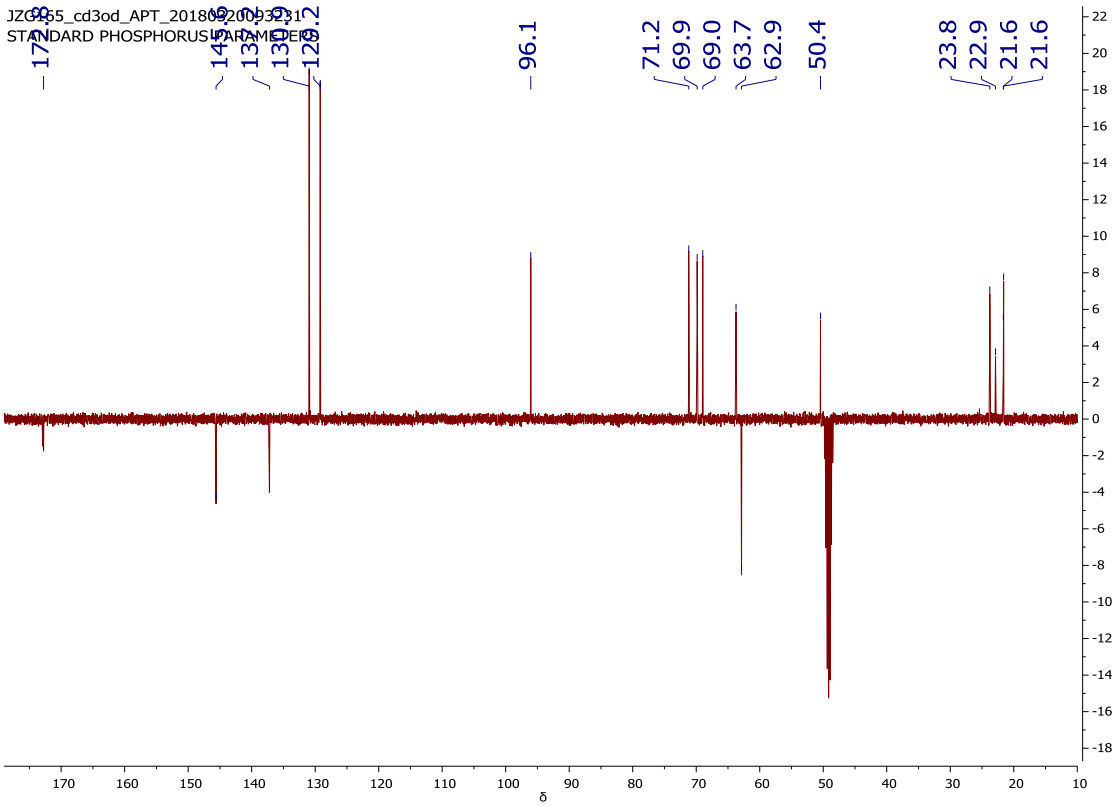

430.16396
z=1
418.70854
z=1
420.37725
z=1
423.36971
z=1
429.44273
z=?
431.16751
z=1
433.77127
z=?
438.13012
z=?
441.14878
z=2
444.38646
z=?
447.19093
z=?
NL:
7.34E4
JZG092#7-22 RT:
0.15-0.57 AV: 16
T: FTMS + p ESI
Full ms
[350.00-750.00]
430.16425
431.16760
432.16004
434.16675
437.17189
NL:
7.58E5
C 18 H 28 N 3 O 7 S:
C 18 H 28 N 3 O 7 S 1
pa Chrg 1
m/z

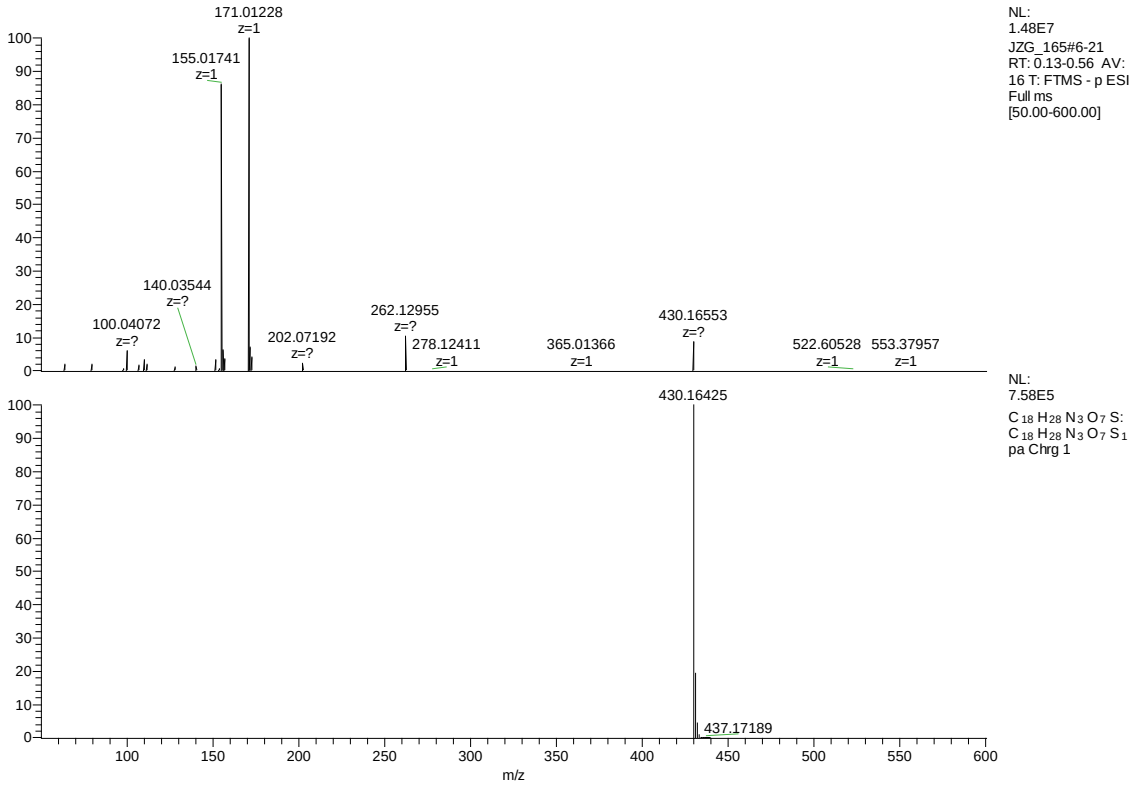


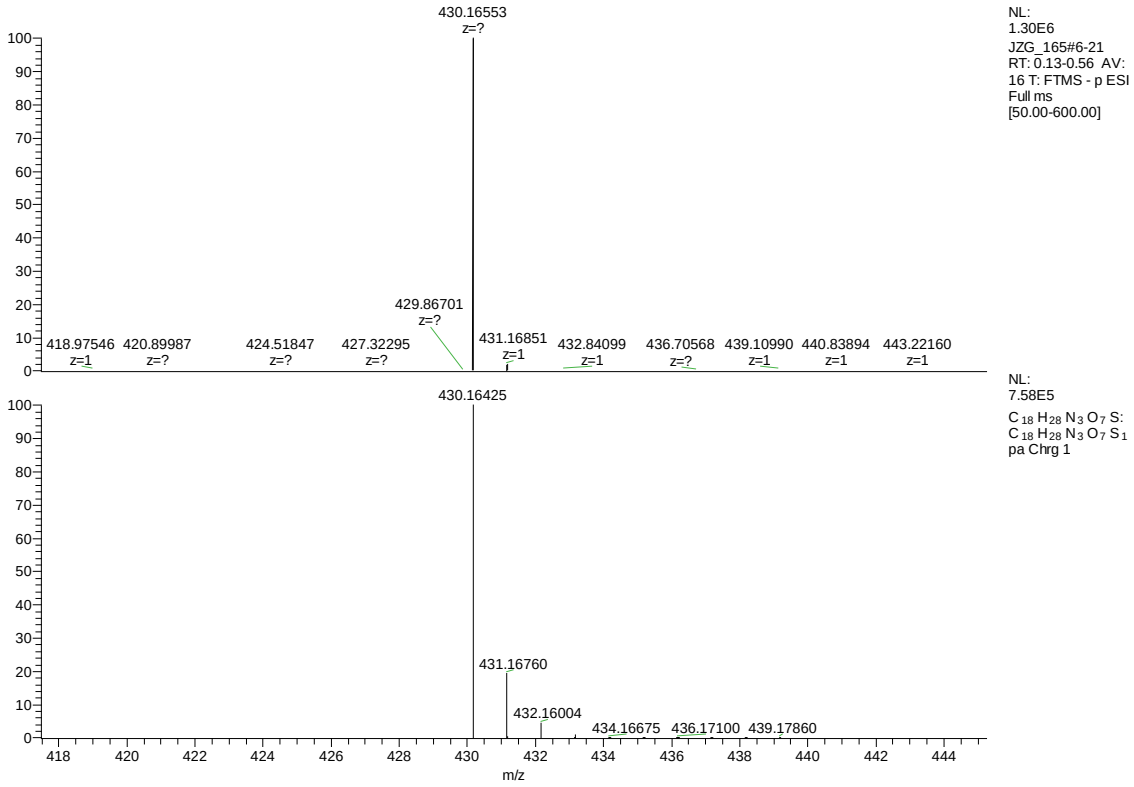
_N_-((2_S_,3_R_,4_S_,5_S_,6_R_)-5-hydroxy-6-(hydroxymethyl)-2-isopropoxy-4-(2-tosylhydrazinyl)tetrahydro-2_H_-pyran-3-yl)acetamide (14)



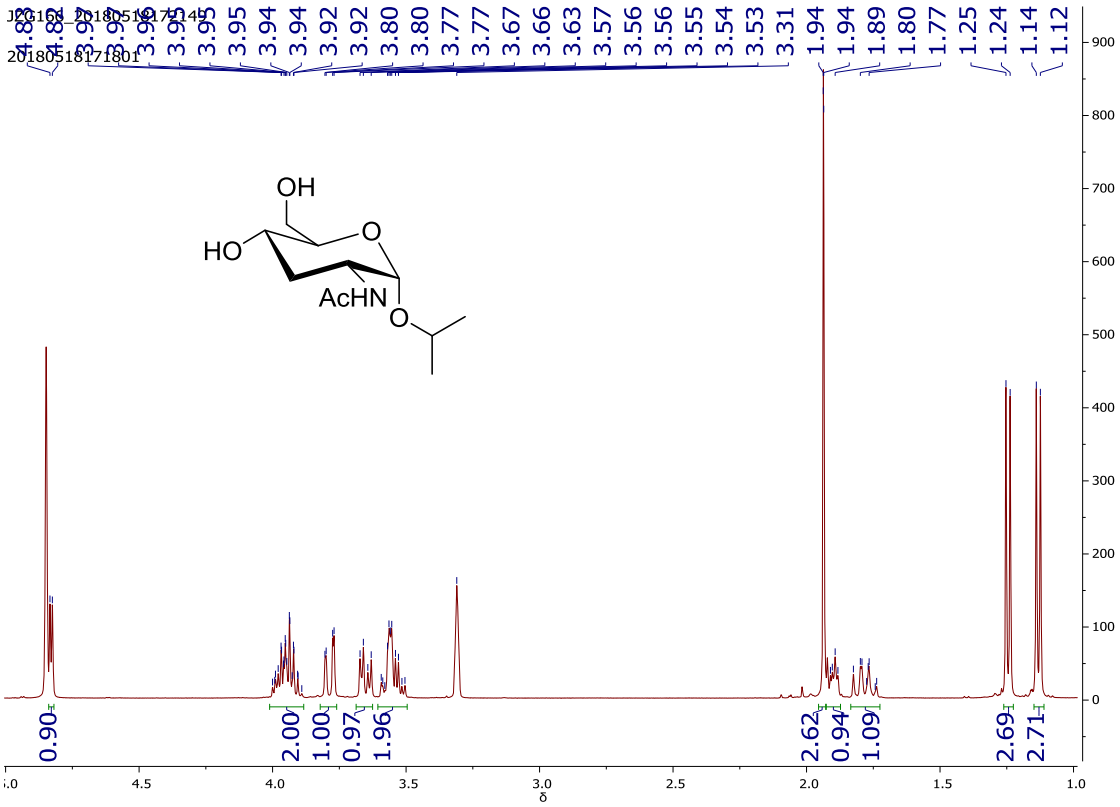

JZG165_cd3od_CARBON_20180220100809
STANDARD FLUORINE PARAMETERS
96.1
71.2
69.9
69.0
63.7
62.9
50.4
23.8
22.9
21.6
21.6
δ

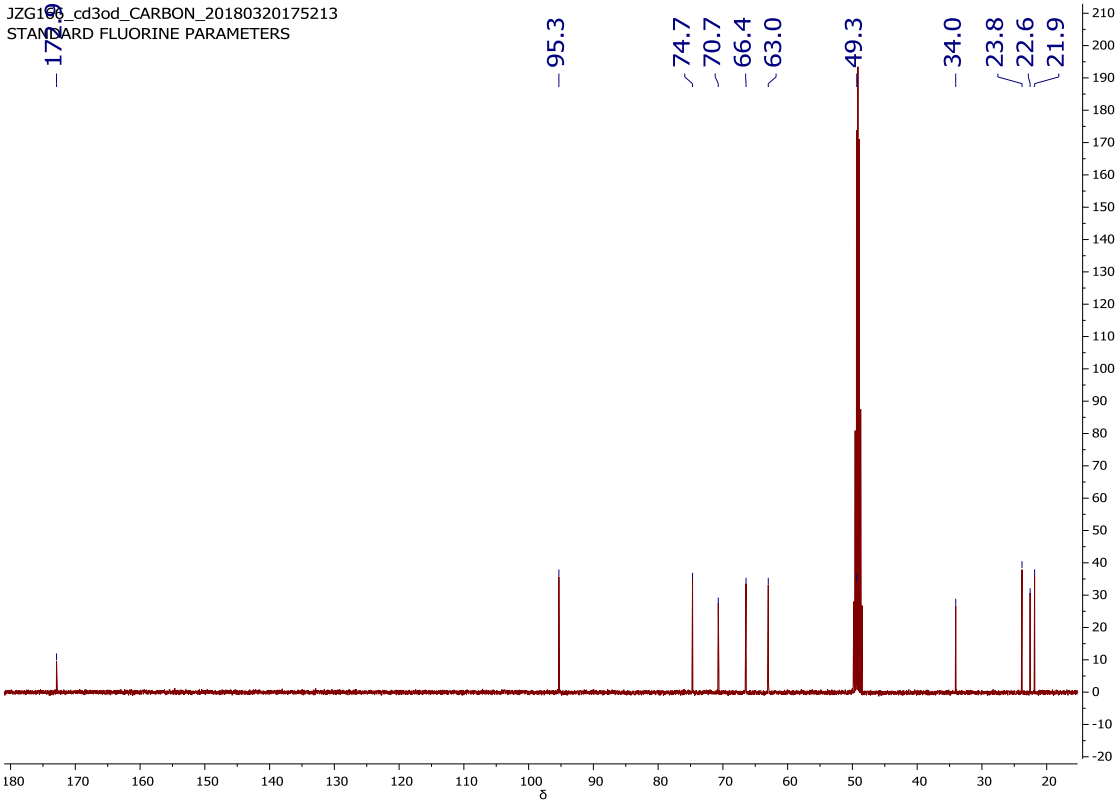

JZG165_cd3od_APT_20180220093231
STANDARD PHOSPHORUS PARAMETERS
96.1
71.2
69.9
69.0
63.7
62.9
50.4
23.8
22.9
21.6
21.6
δ

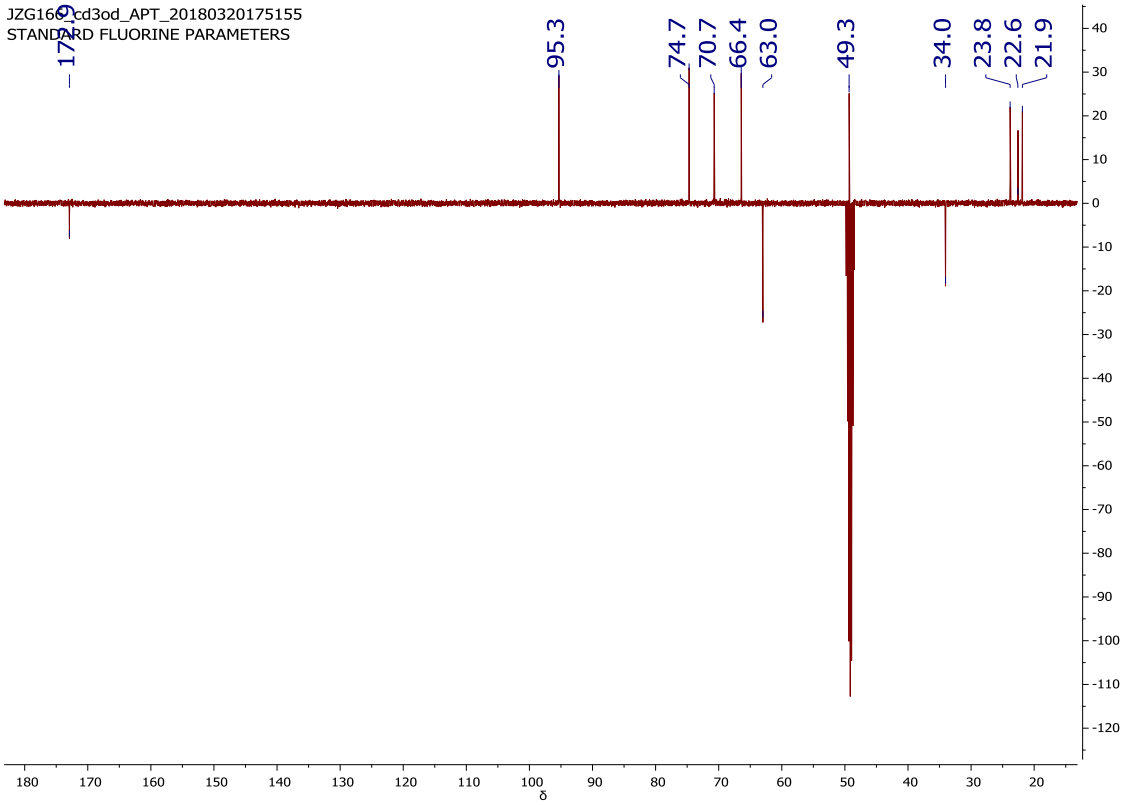

171.01228
z=1
155.01741
z=1
140.03544
z=?
100.04072
z=?
202.07192
z=?
262.12955
z=?
278.12411
z=1
365.01366
z=1
430.16553
z=?
522.60528
z=1
553.37957
z=1
NL:
1.48E7
JZG_165#6-21
RT: 0.13-0.56 AV:
16 T: FTMS - p ESI
Full ms
[50.00-600.00]
430.16425
437.17189
NL:
7.58E5
C 18 H 28 N 3 O 7 S:
C 18 H 28 N 3 O 7 S 1
pa Chrg 1
m/z

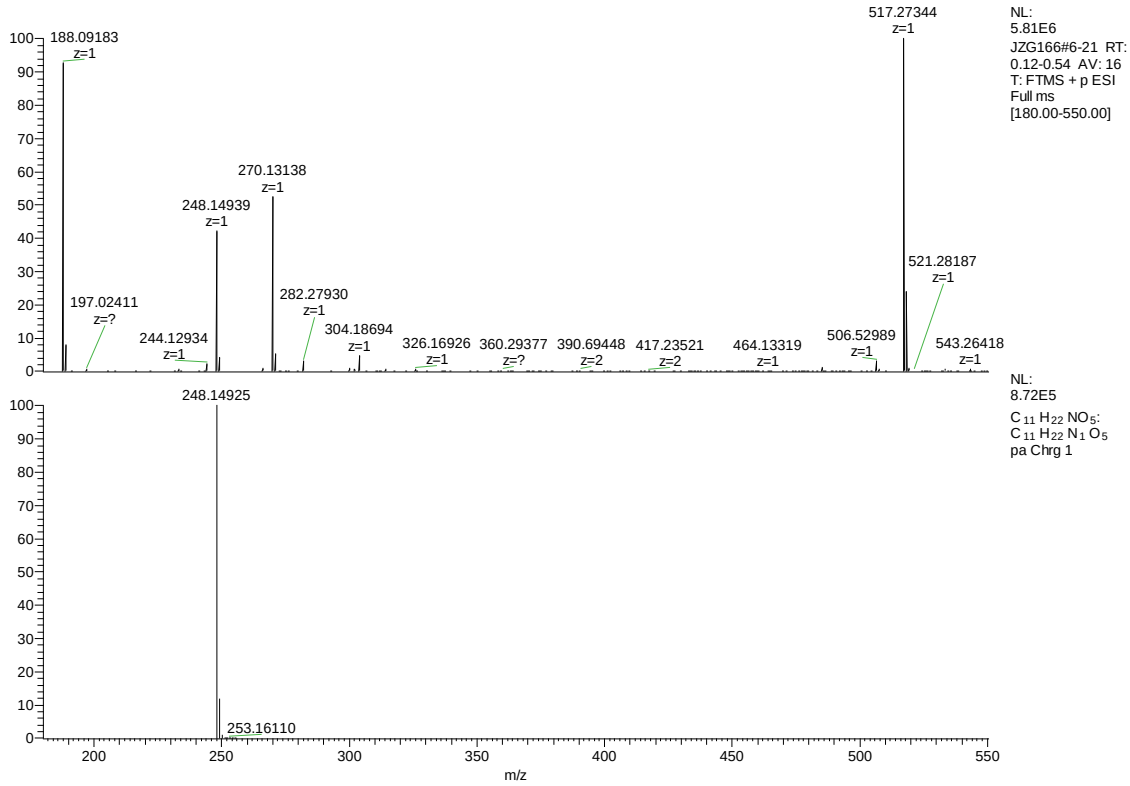

430.16553
z=?
429.86701
z=?
418.97546
z=1
420.89987
z=?
424.51847
z=?
427.32295
z=?
431.16851
z=1
432.84099
z=1
436.70568
z=?
439.10990
z=1
440.83894
z=1
443.22160
z=1
NL:
1.30E6
JZG_165#6-21
RT: 0.13-0.56 AV:
16 T: FTMS - p ESI
Full ms
[50.00-600.00]
430.16425
431.16760
432.16004
434.16675
436.17100
439.17860
NL:
7.58E5
C 18 H 28 N 3 O 7 S:
C 18 H 28 N 3 O 7 S 1
pa Chrg 1
m/z

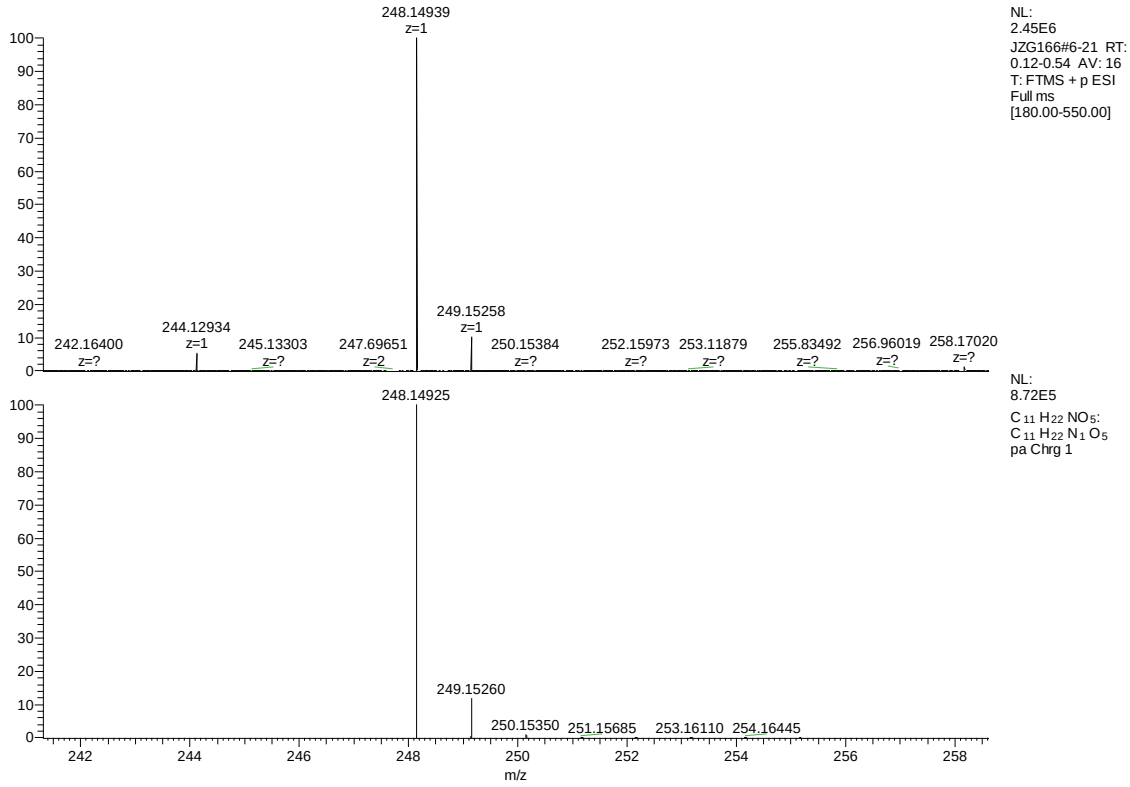
Isopropyl 2-acetamido-2,3-dideoxy-α-D-ribo-hexopyranoside (15)



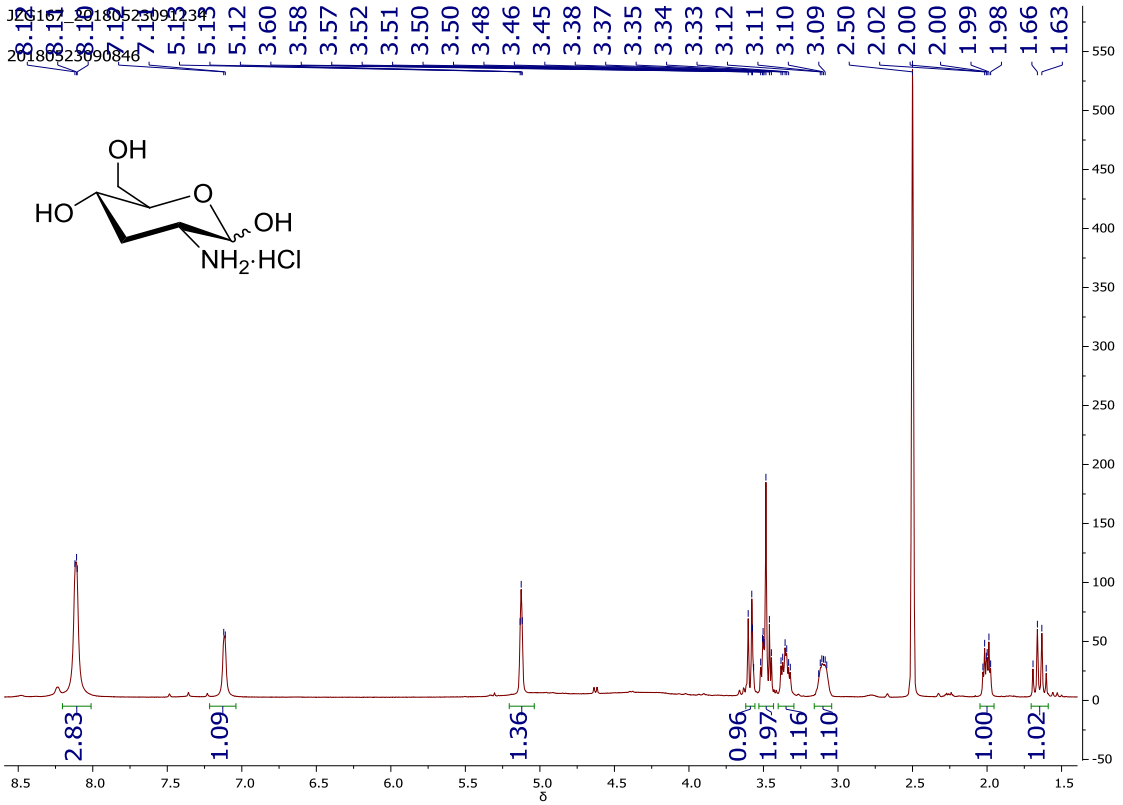


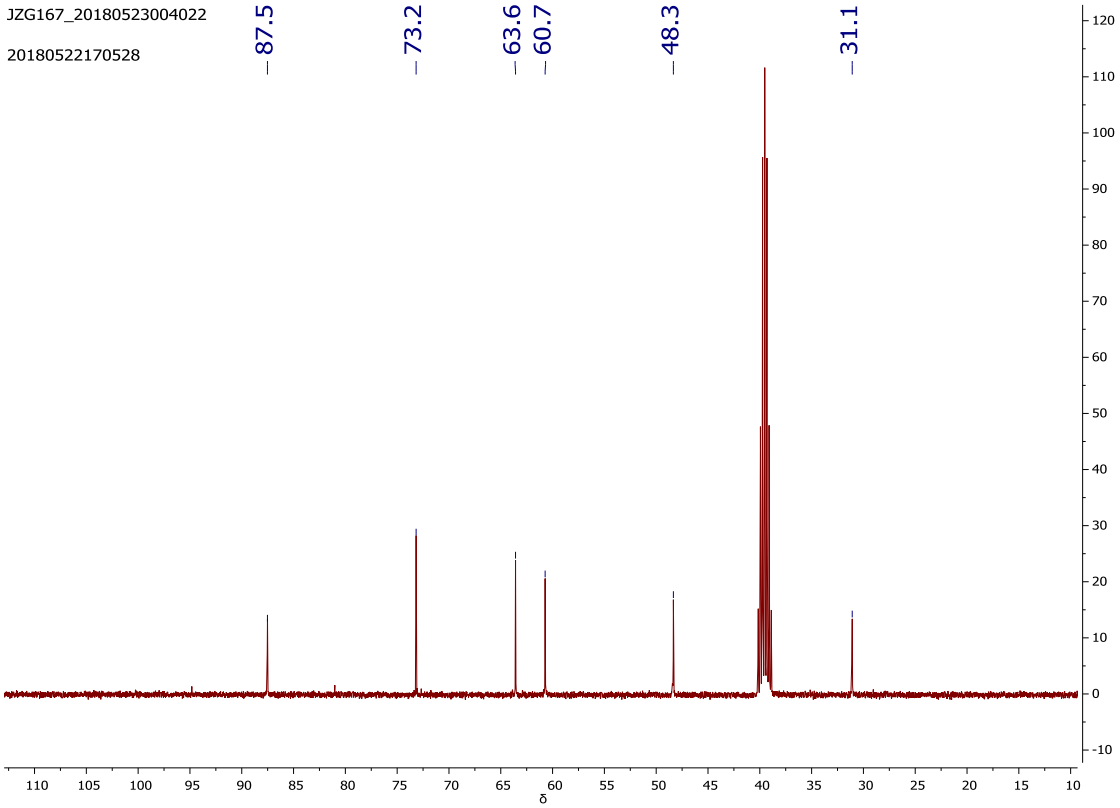

JZG166_cd3od_APT_20180320175155
STANDARD FLUORINE PARAMETERS
95.3
74.7
70.7
66.4
63.0
49.3
34.0
23.8
22.6
21.9
δ

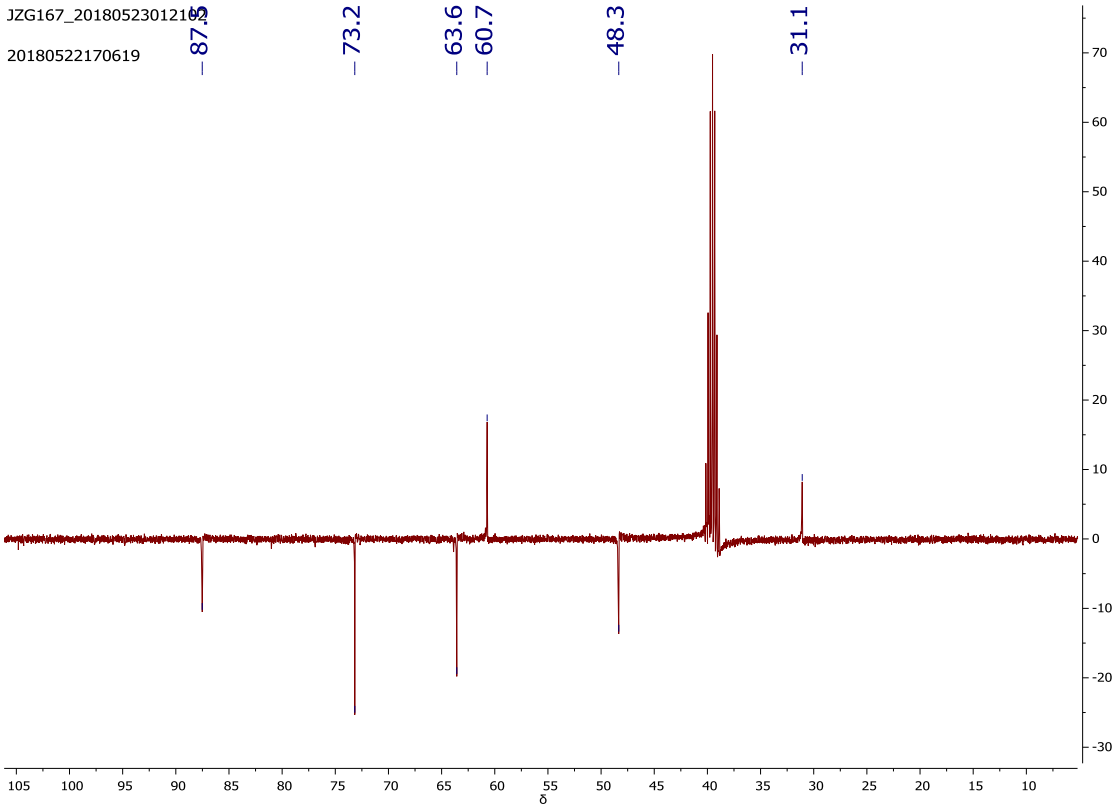

188.09183
z=1
517.27344
z=1
NL:
5.81E6
JZG166#6-21 RT:
0.12-0.54 AV: 16
T: FTMS + p ESI
Full ms
[180.00-550.00]
270.13138
z=1
248.14939
z=1
521.28187
z=1
197.02411
z=?
282.27930
z=1
304.18694
z=1
244.12934
z=1
326.16926
z=1
360.29377
z=?
390.69448
z=2
417.23521
z=2
464.13319
z=1
506.52989
z=1
543.26418
z=1
NL:
8.72E5
C 11 H 22 NO 5:
C 11 H 22 N 1 O 5
pa Chrg 1
248.14925
253.16110
m/z

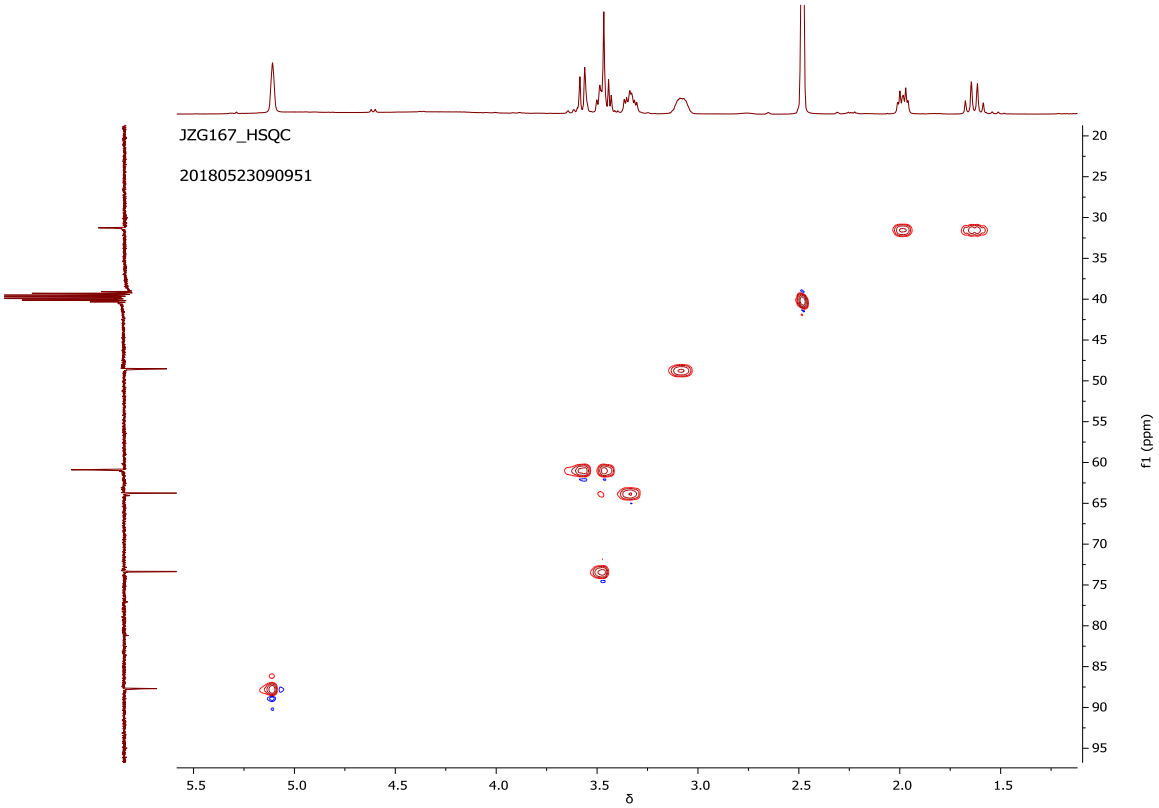


D-lividosamin (16)

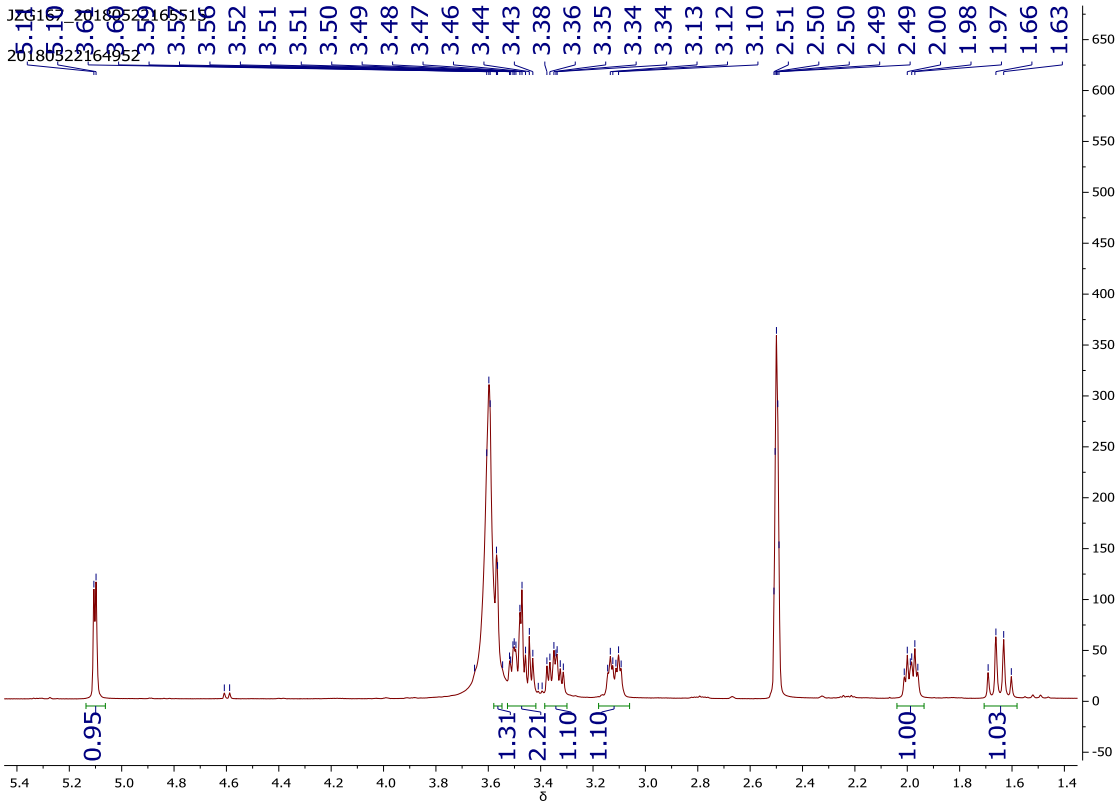


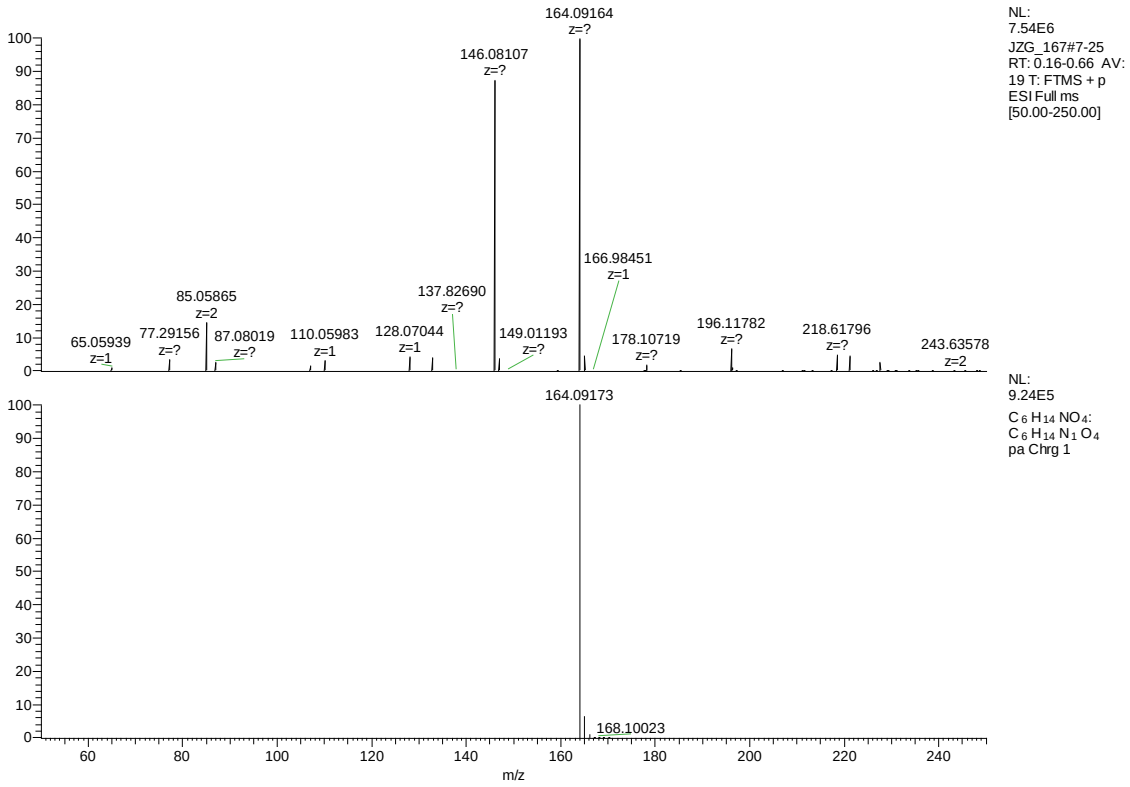

JZG167_20180523004022
20180522170528
87.5
73.2
63.6
60.7
48.3
31.1
δ

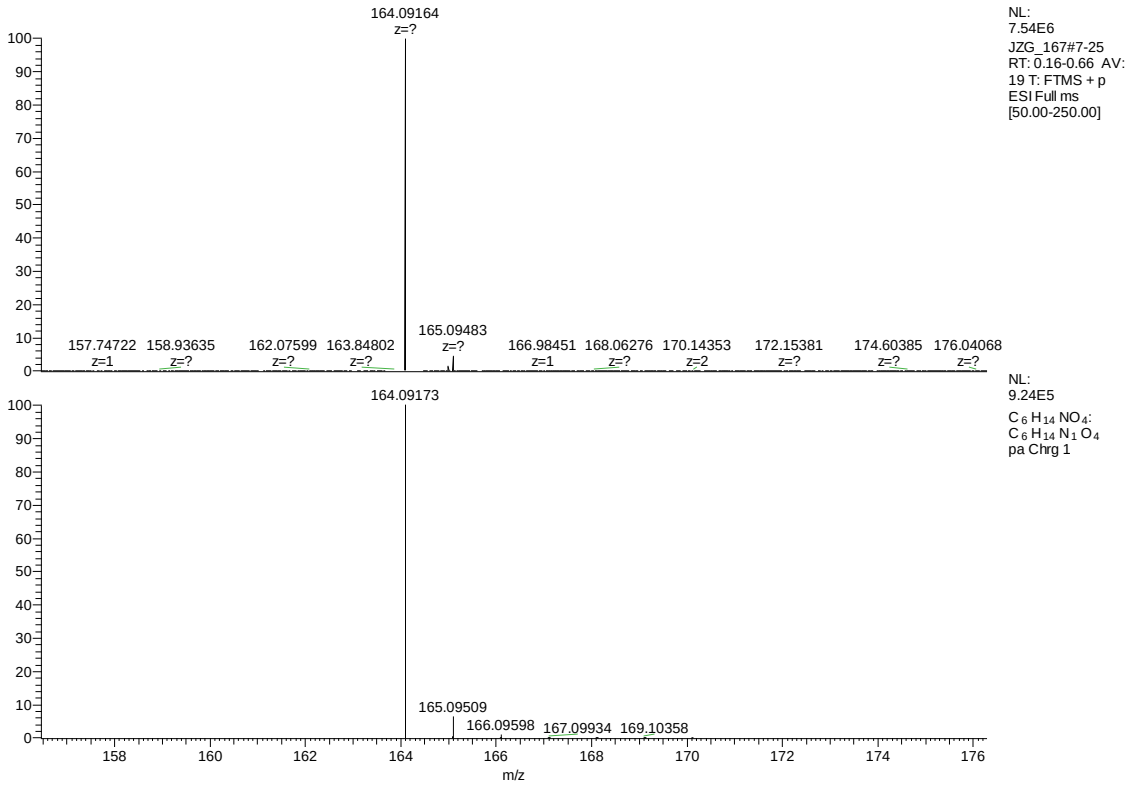

JZG167_20180523012102
20180522170619
87.5
73.2
63.6
60.7
48.3
31.1
δ



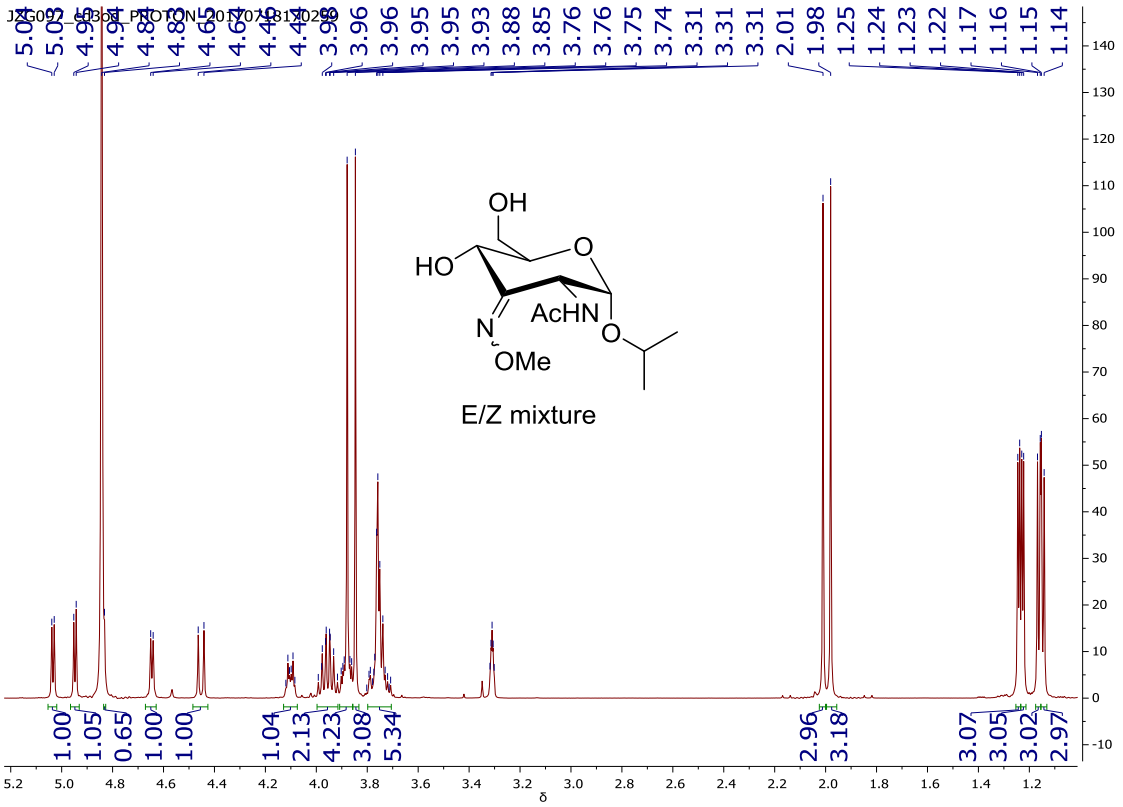
^{1}H NMR of D-lividosamine hydrochloride after D_2O

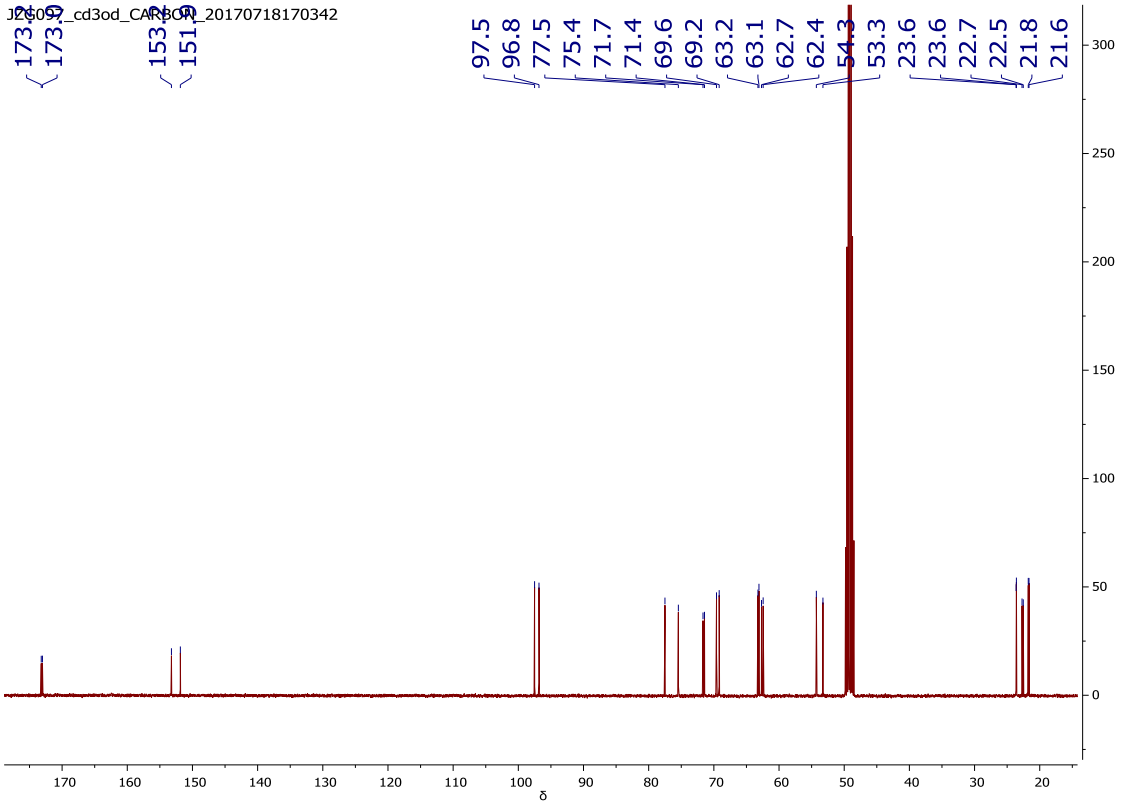


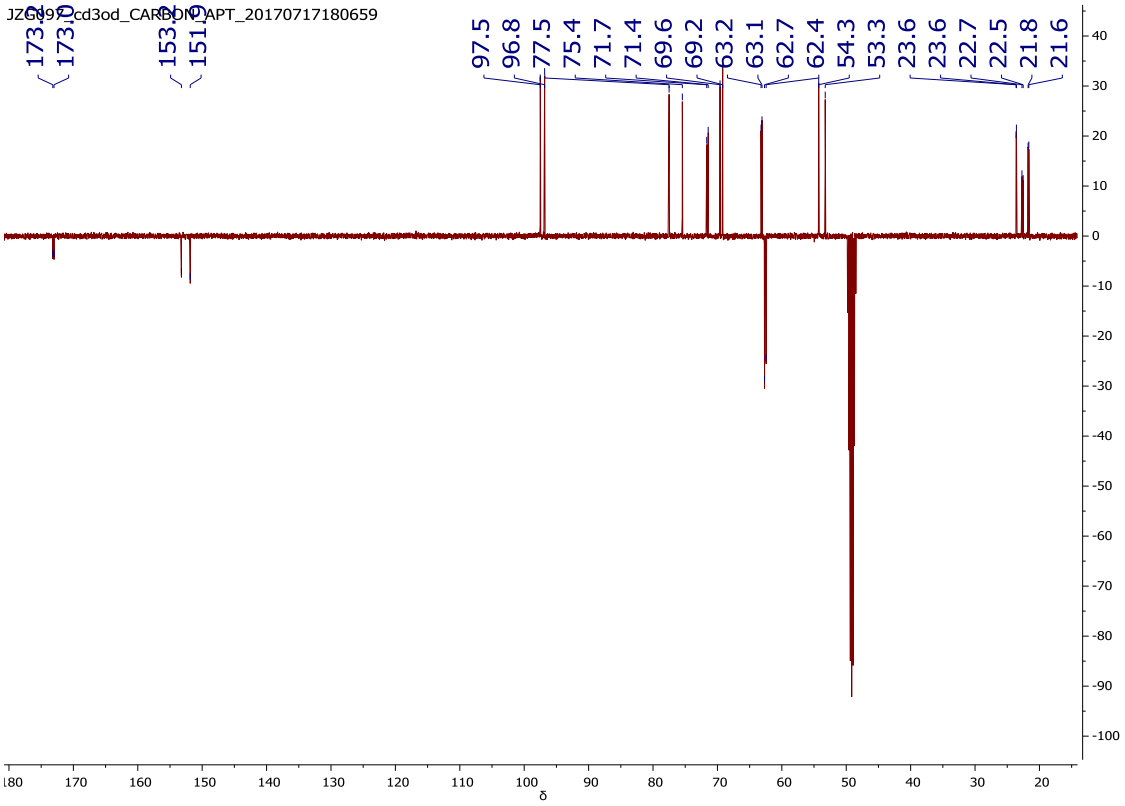

164.09164
z=?
146.08107
z=?
166.98451
z=1
85.05865
z=2
137.82690
z=?
65.05939
z=1
77.29156
z=?
87.08019
z=?
110.05983
z=1
128.07044
z=1
149.01193
z=?
178.10719
z=?
196.11782
z=?
218.61796
z=?
243.63578
z=2
NL:
7.54E6
JZG_167#7-25
RT: 0.16-0.66 AV:
19 T: FTMS + p
ESI Full ms
[50.00-250.00]
164.09173
168.10023
NL:
9.24E5
C6 H14 NO4:
C6 H14 N1 O4
pa Chrg 1
m/z

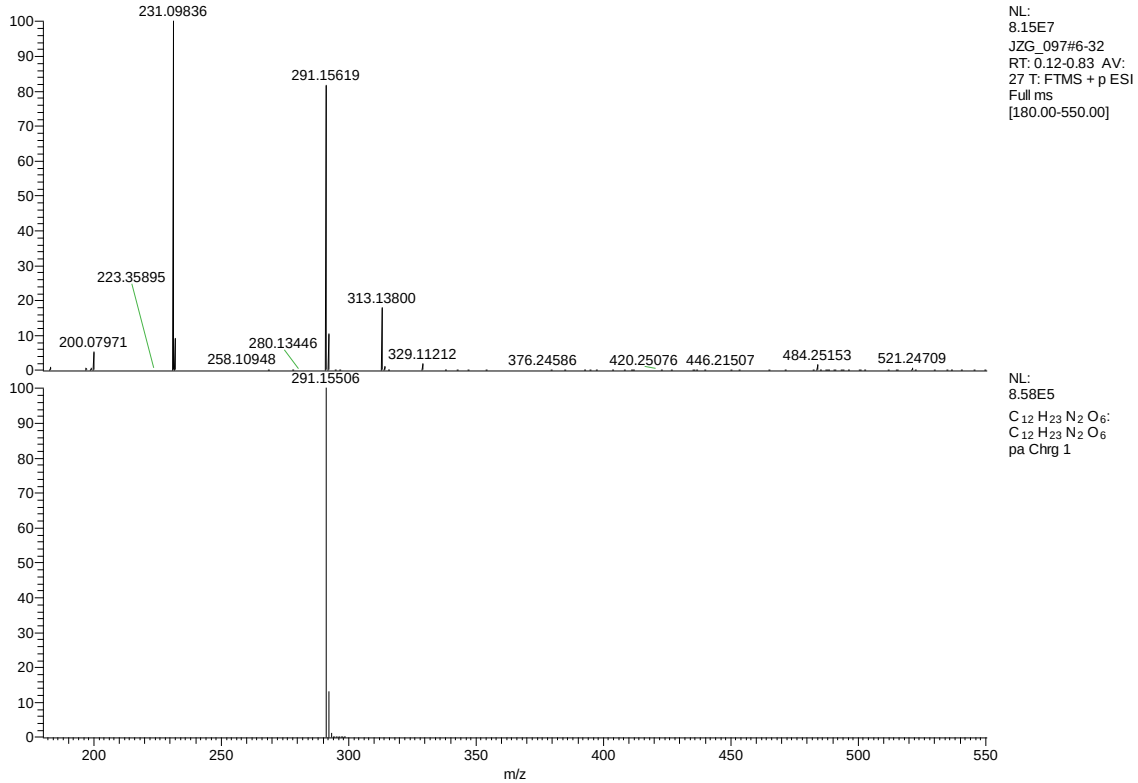

164.09164
z=?
157.74722
z=1
158.93635
z=?
162.07599
z=?
163.84802
z=?
165.09483
z=?
166.98451
z=1
168.06276
z=?
170.14353
z=2
172.15381
z=?
174.60385
z=?
176.04068
z=?
NL:
7.54E6
JZG_167#7-25
RT: 0.16-0.66 AV:
19 T: FTMS + p
ESI Full ms
[50.00-250.00]
164.09173
165.09509
166.09598
167.09934
169.10358
NL:
9.24E5
C6 H14 NO4:
C6 H14 N1 O4
pa Chrg 1
m/z

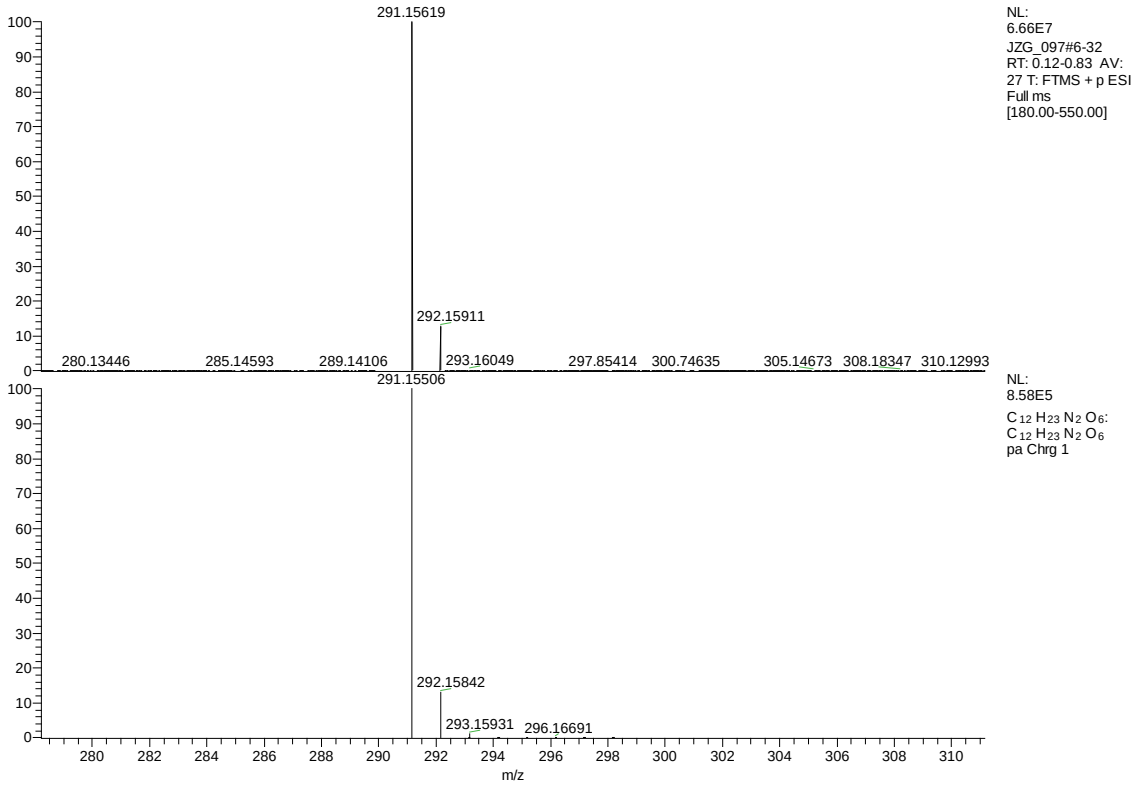
_E/Z_-Isopropyl 2-acetamido-2-deoxy-3-_O_-methyloxime-α-D-ribo-hexapyranoside (17)

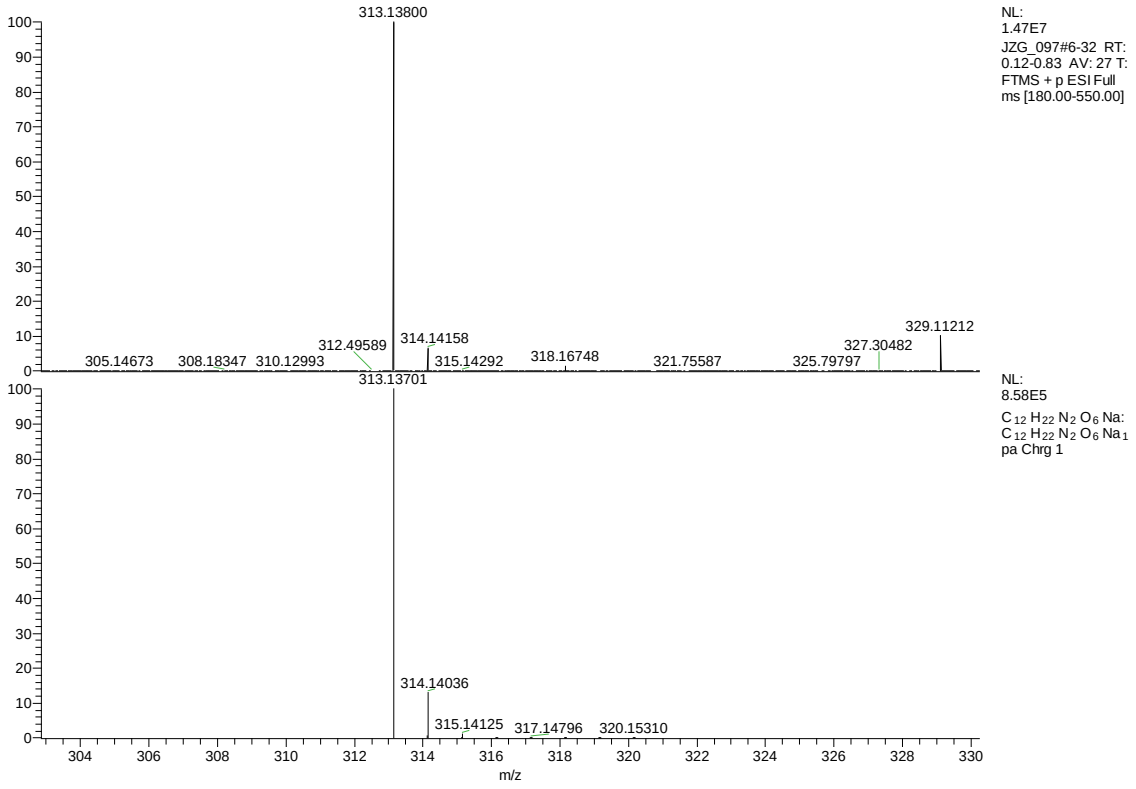




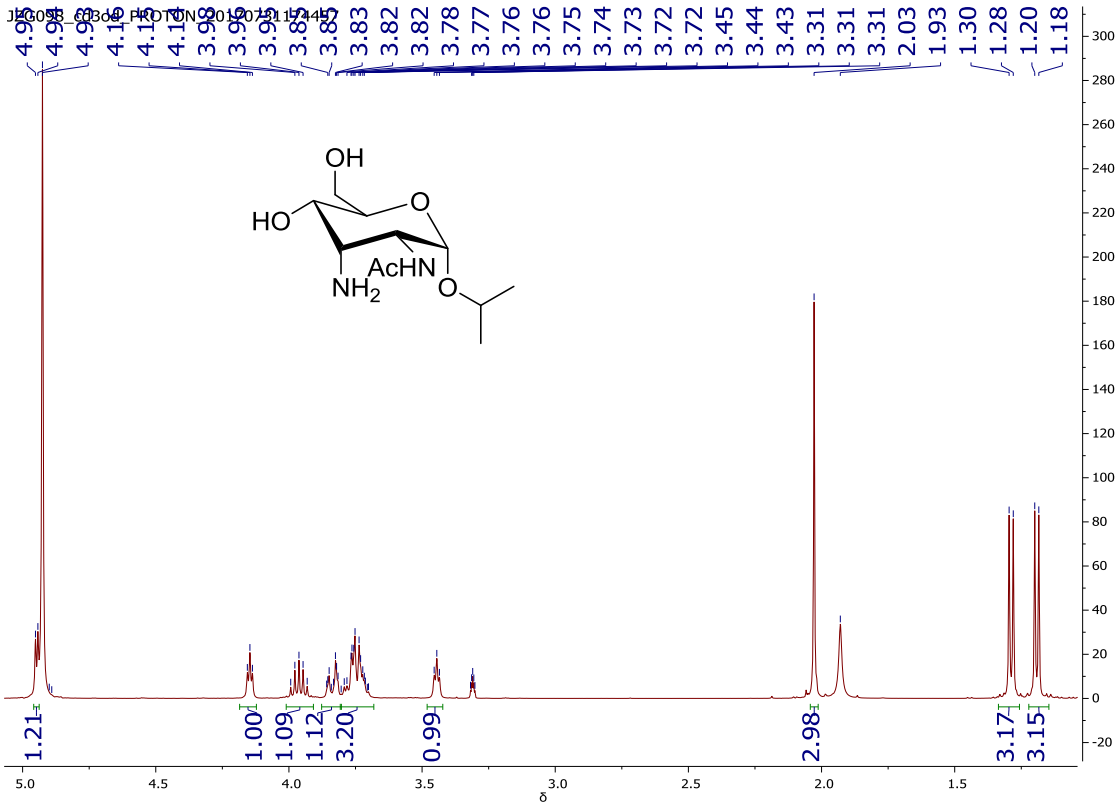

JZG097_cd3od_CARBON_APT_20170717180659
173.2
173.0
153.1
151.9
97.5
96.8
77.5
75.4
71.7
71.4
69.6
69.2
63.2
63.1
62.7
62.4
54.3
53.3
23.6
23.6
22.7
22.5
21.8
21.6
δ

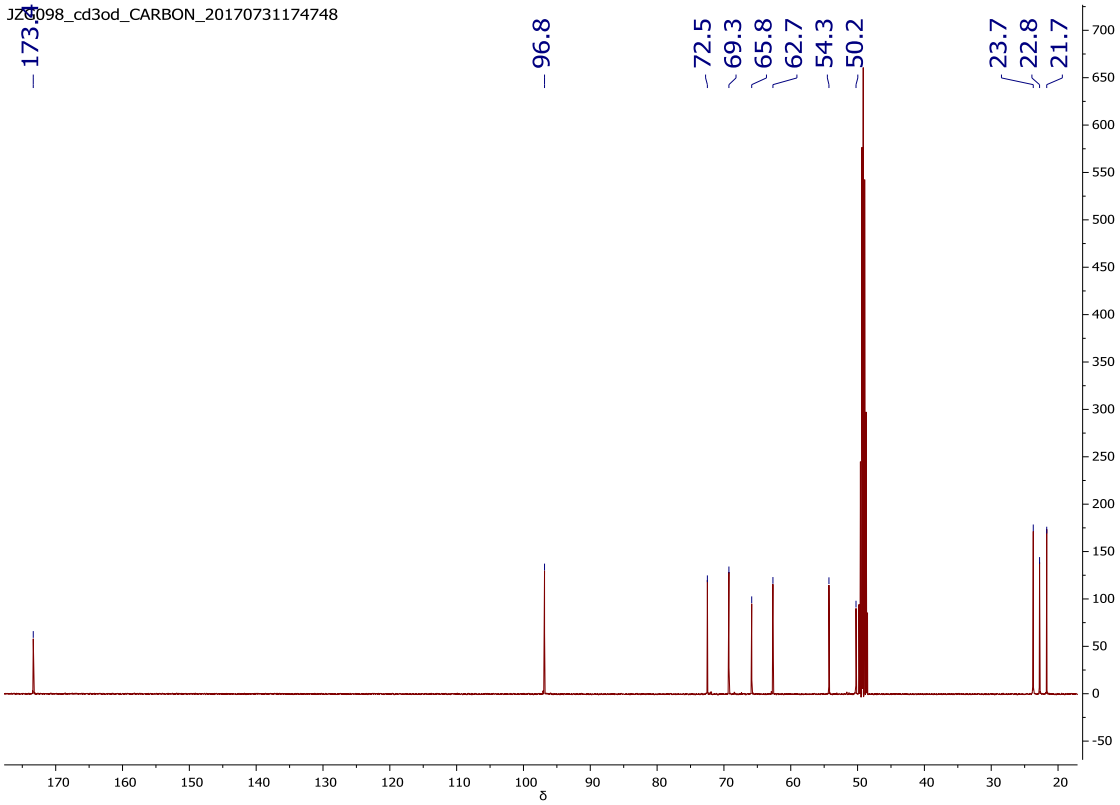

231.09836
291.15619
223.35895
313.13800
200.07971
280.13446
258.10948
329.11212
376.24586
420.25076
446.21507
484.25153
521.24709
NL:
8.15E7
JZG_097#6-32
RT: 0.12-0.83 AV:
27 T: FTMS + p ESI
Full ms
[180.00-550.00]
291.15506
NL:
8.58E5
C12H23N2O6:
C12H23N2O6
pa Chrg 1
m/z

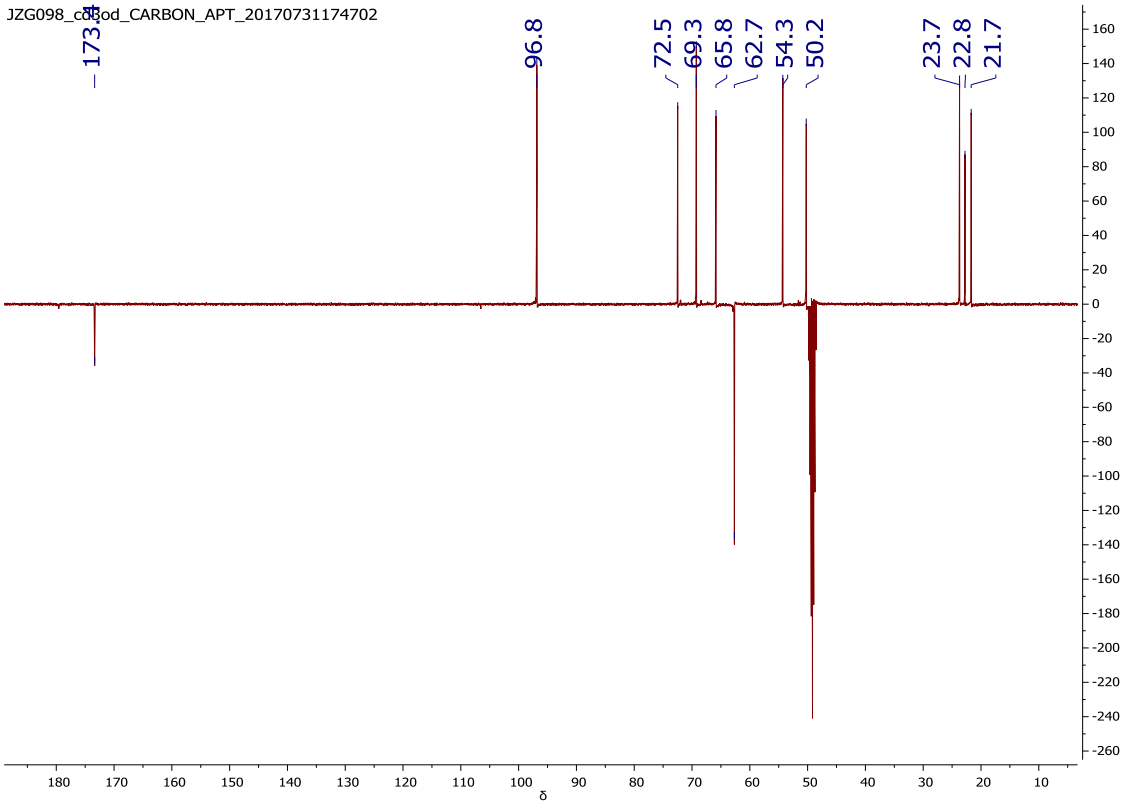

291.15619
292.15911
280.13446
285.14593
289.14106
293.16049
297.85414
300.74635
305.14673
308.18347
310.12993
NL:
6.66E7
JZG_097#6-32
RT: 0.12-0.83 AV:
27 T: FTMS + p ESI
Full ms
[180.00-550.00]
291.15506
292.15842
293.15931
296.16691
NL:
8.58E5
C12 H23 N2 O6:
C12 H23 N2 O6
pa Chrg 1
m/z

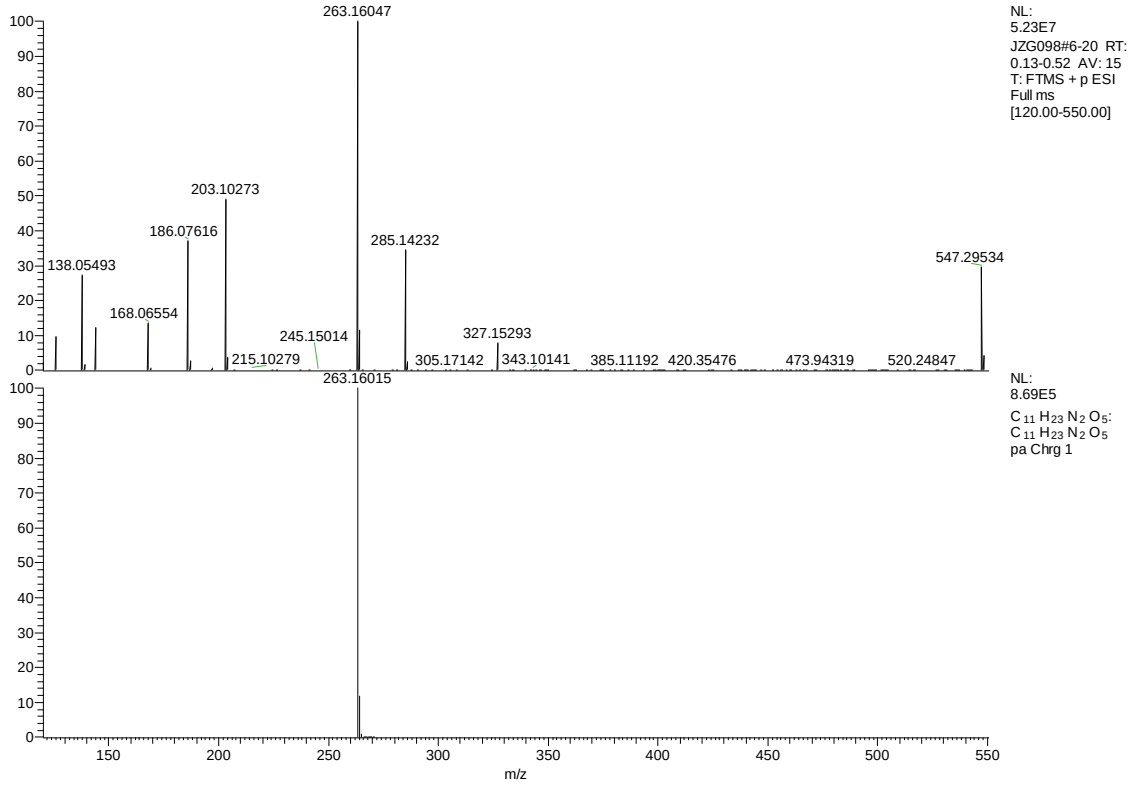

313.13800
329.11212
312.49589
314.14158
327.30482
305.14673
308.18347
310.12993
315.14292
318.16748
321.75587
325.79797
NL:
1.47E7
JZG_097#6-32 RT:
0.12-0.83 AV: 27 T:
FTMS + p ESI Full
ms [180.00-550.00]
313.13701
314.14036
315.14125
317.14796
320.15310
NL:
8.58E5
C12 H22 N2 O6 Na:
C12 H22 N2 O6 Na1
pa Chrg 1
m/z

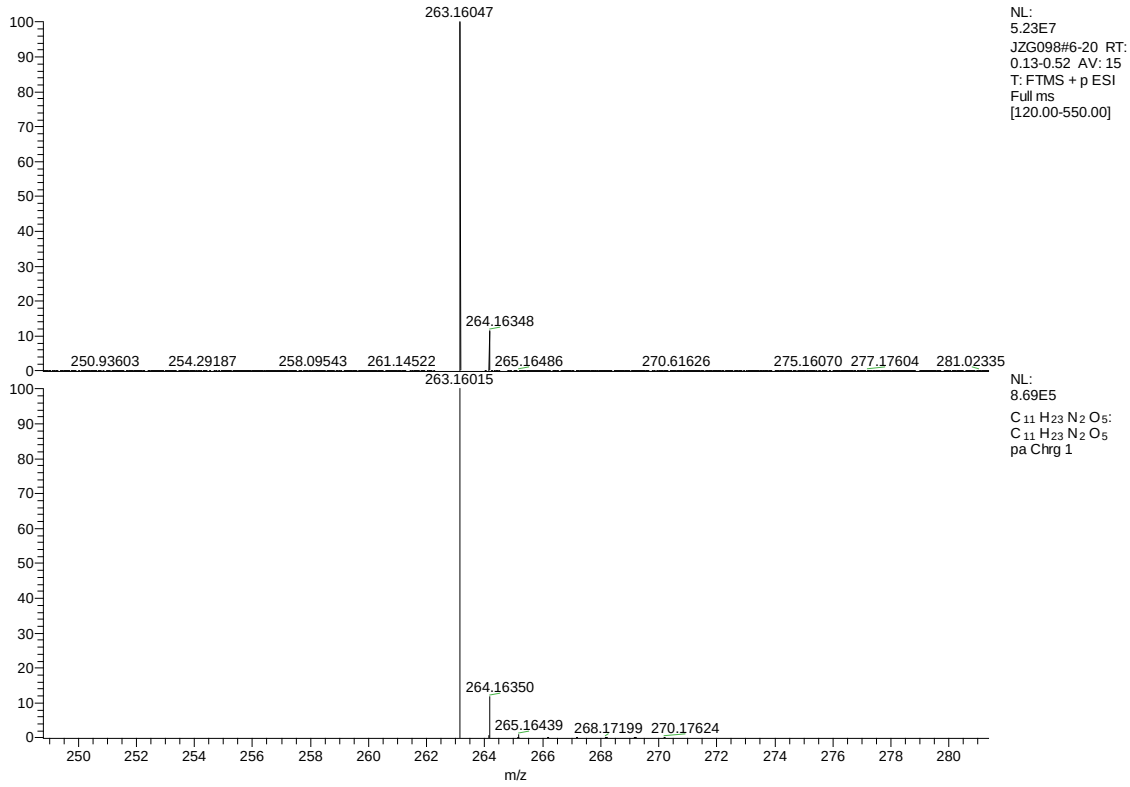
Isopropyl 2-acetamido-3-amino-2,3-dideoxy-α-D-allopyranoside (18)



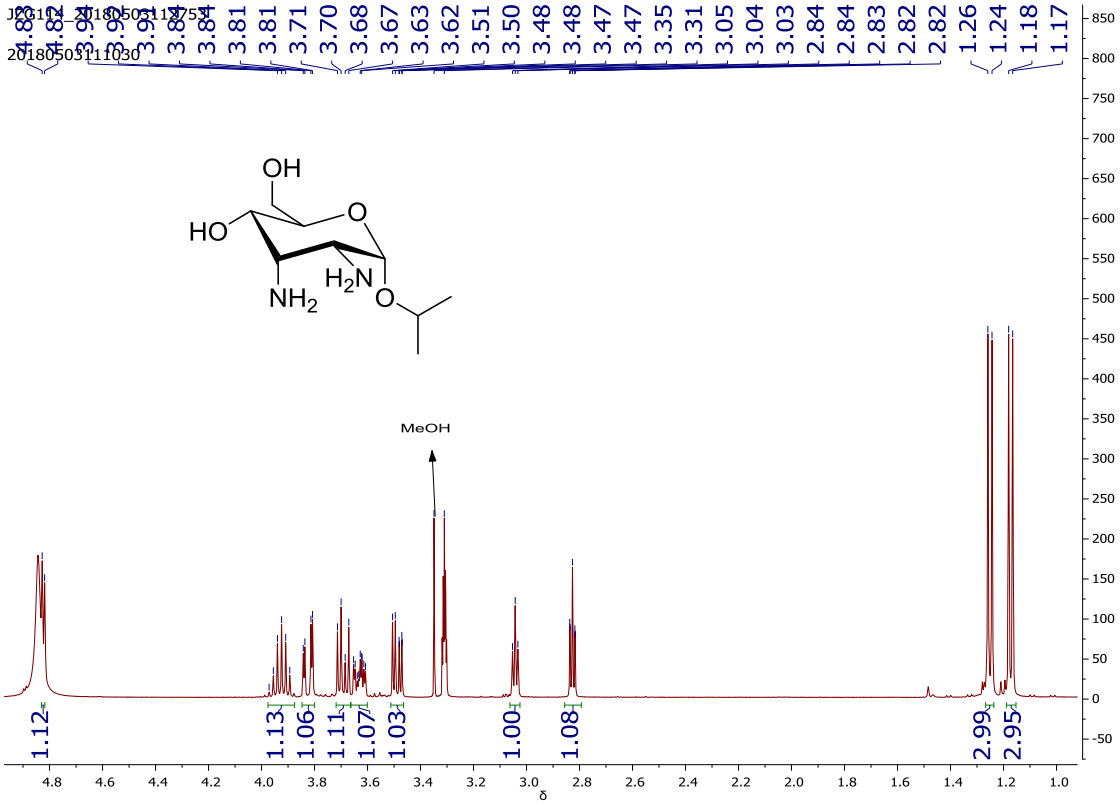


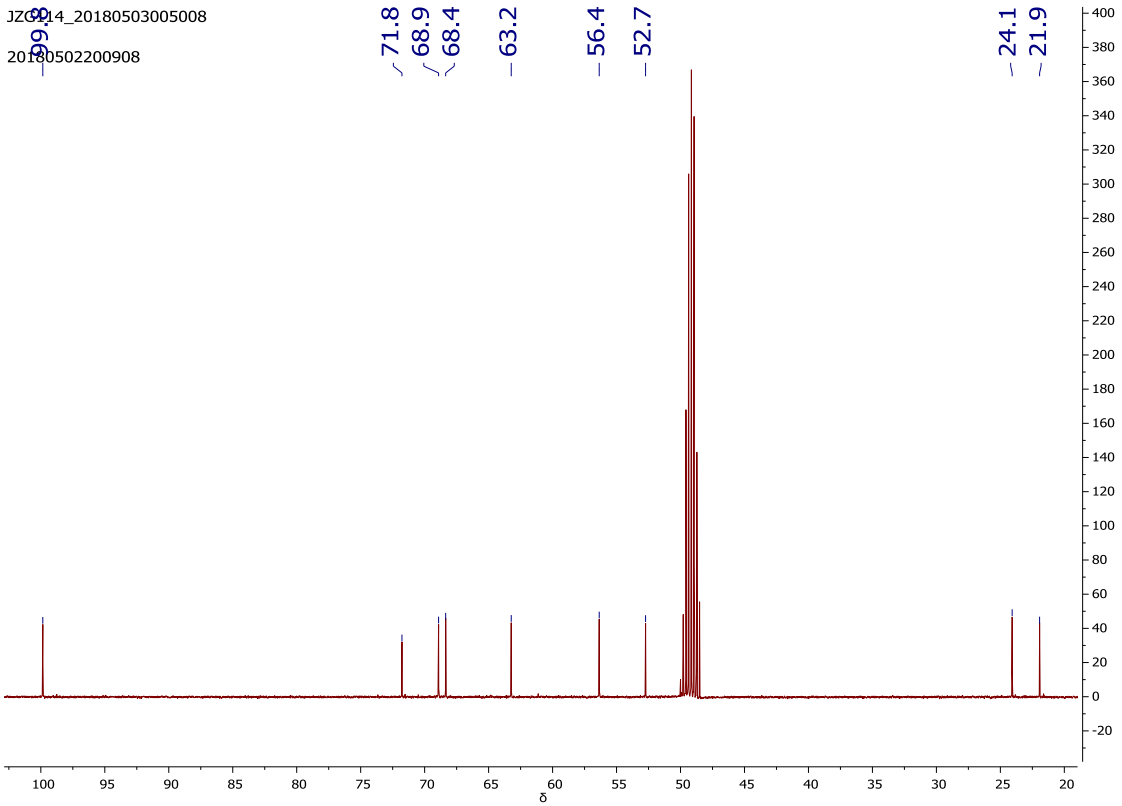

JZG098_cd3od_CARBON_APT_20170731174702
173.4
96.8
72.5
69.3
65.8
62.7
54.3
50.2
23.7
22.8
21.7
δ

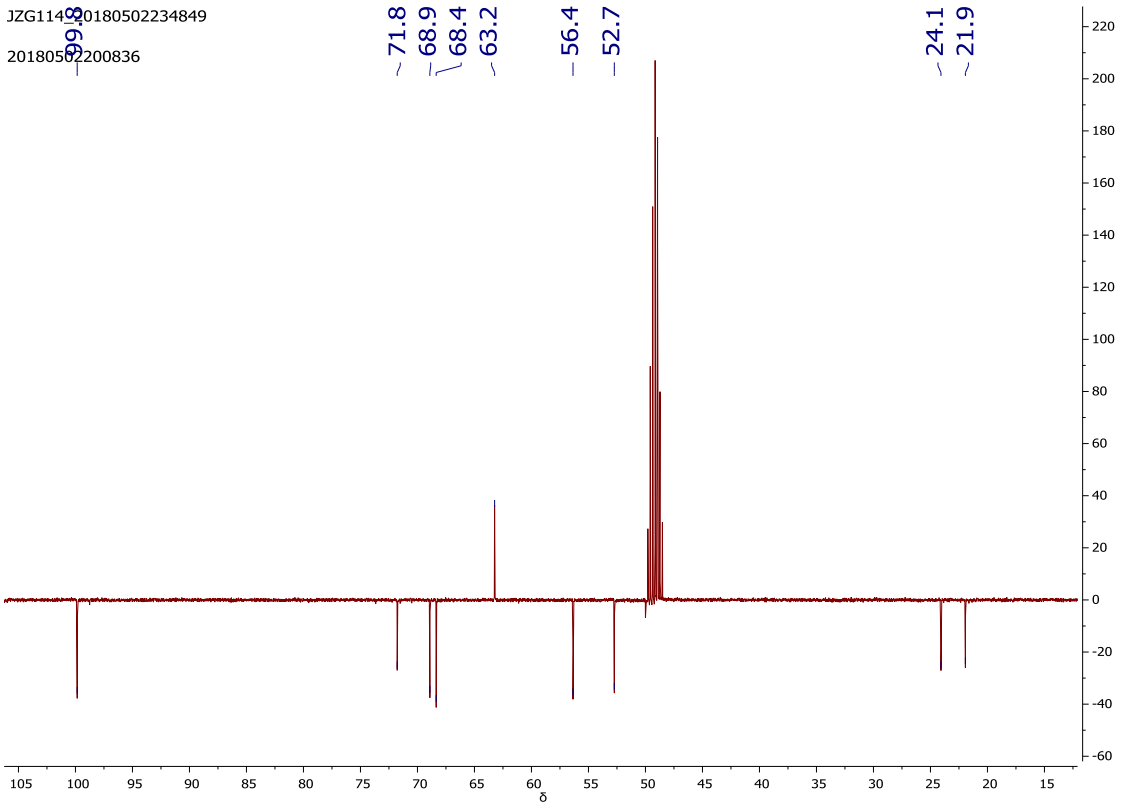

263.16047
203.10273
186.07616
285.14232
138.05493
547.29534
168.06554
245.15014
327.15293
215.10279
305.17142
343.10141
385.11192
420.35476
473.94319
520.24847
263.16015
NL:
5.23E7
JZG098#6-20 RT:
0.13-0.52 AV: 15
T: FTMS + p ESI
Full ms
[120.00-550.00]
NL:
8.69E5
C 11 H 23 N 2 O 5:
C 11 H 23 N 2 O 5
pa Chrg 1
m/z

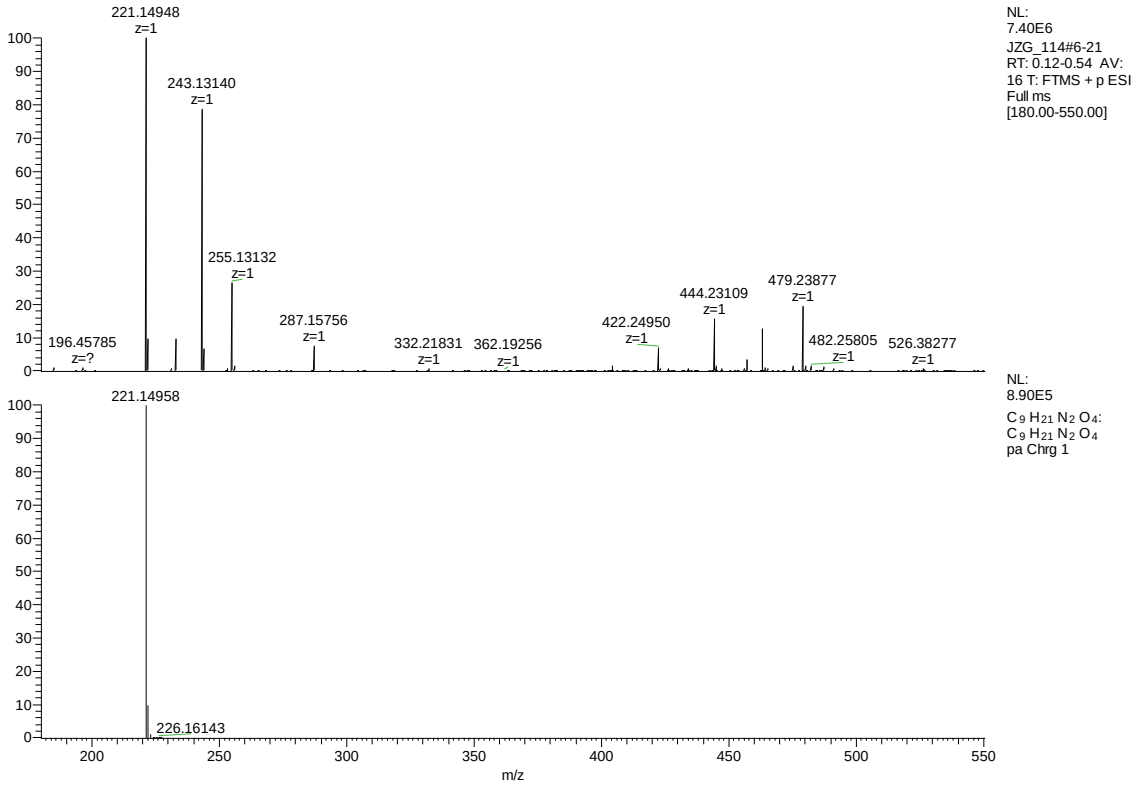


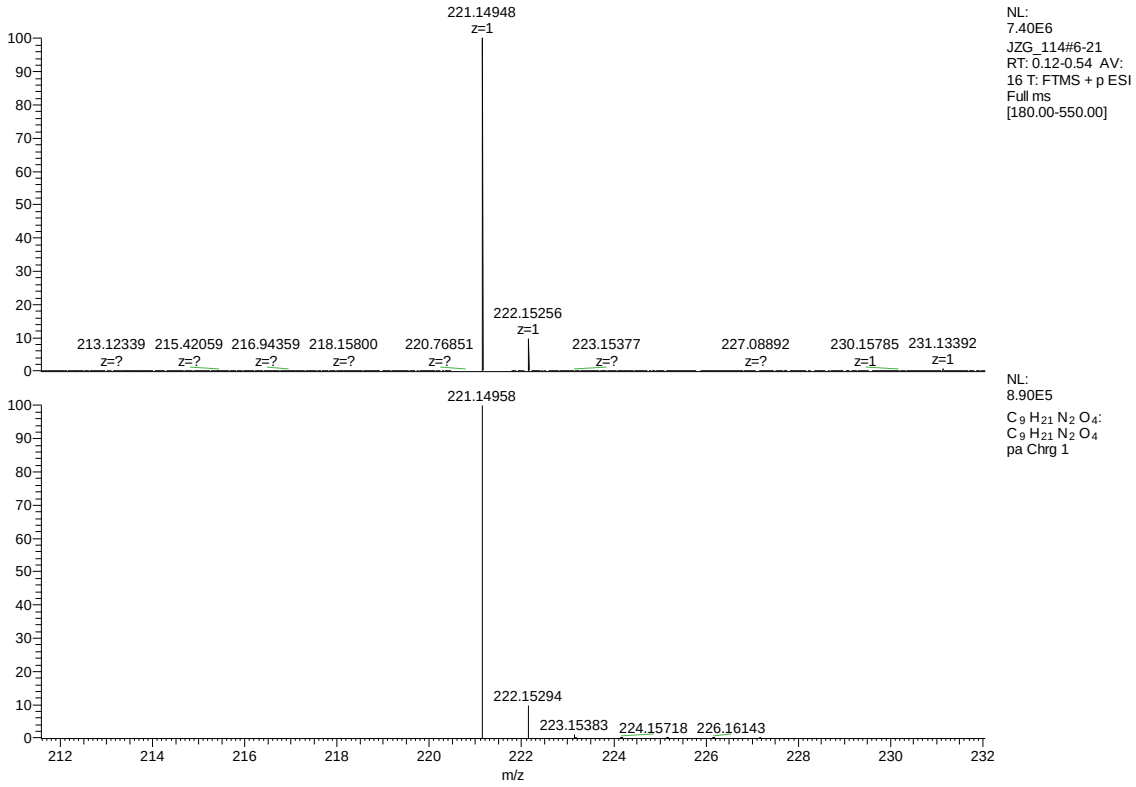
Isopropyl 2,3-diamino-2,3-dideoxy-α-D-allopyranoside (19)



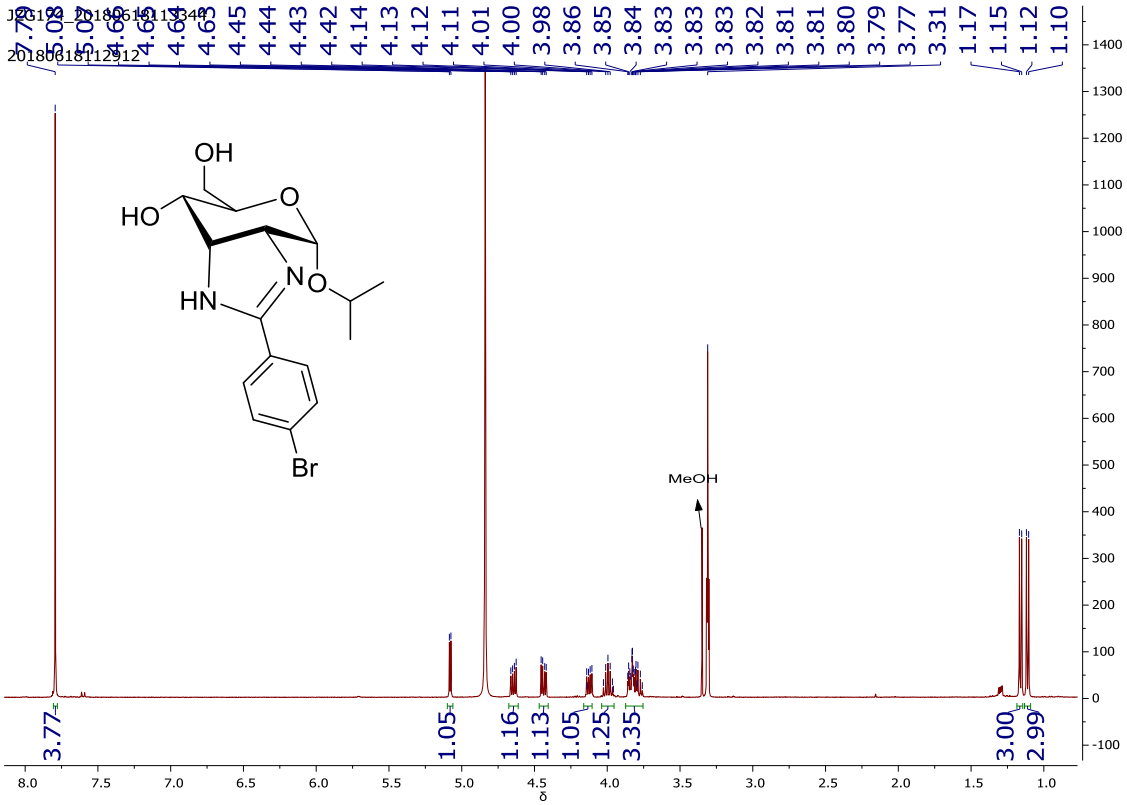

JZG114_20180503005008
20180502200908
99.8
71.8
68.9
68.4
63.2
56.4
52.7
24.1
21.9
δ

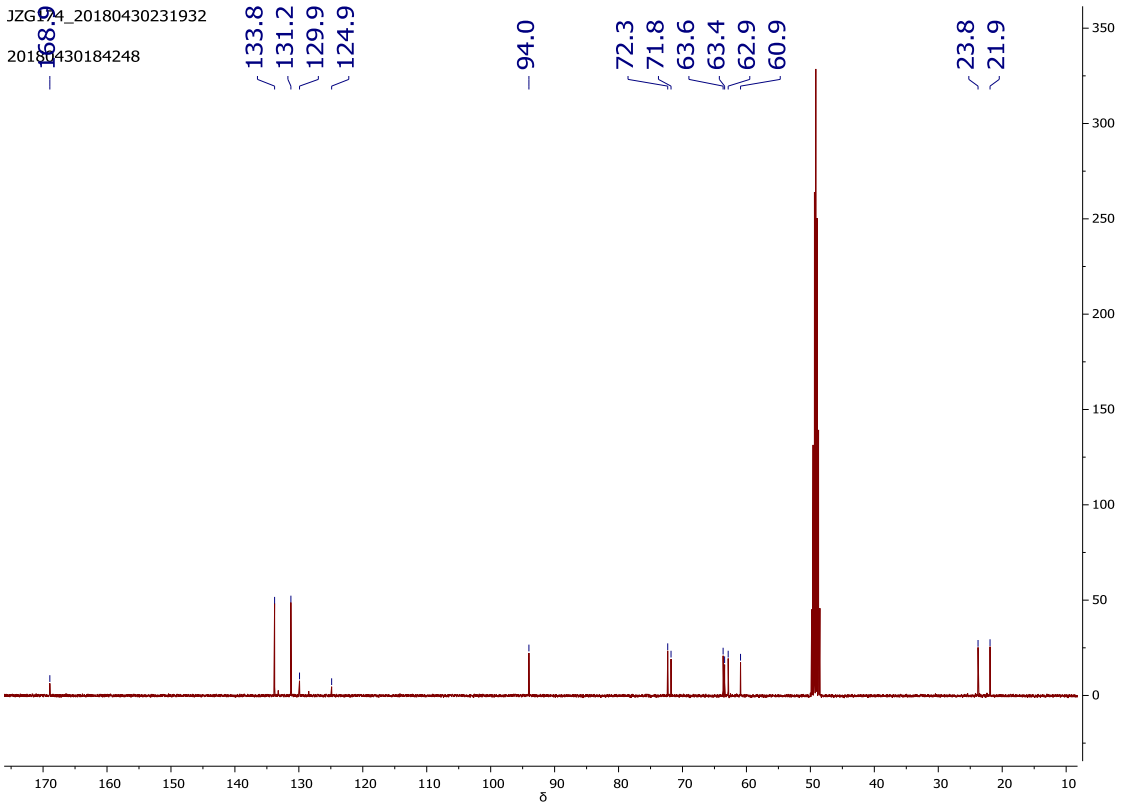

JZG114_20180502234849
20180502200836
99.8
71.8
68.9
68.4
63.2
56.4
52.7
24.1
21.9
δ

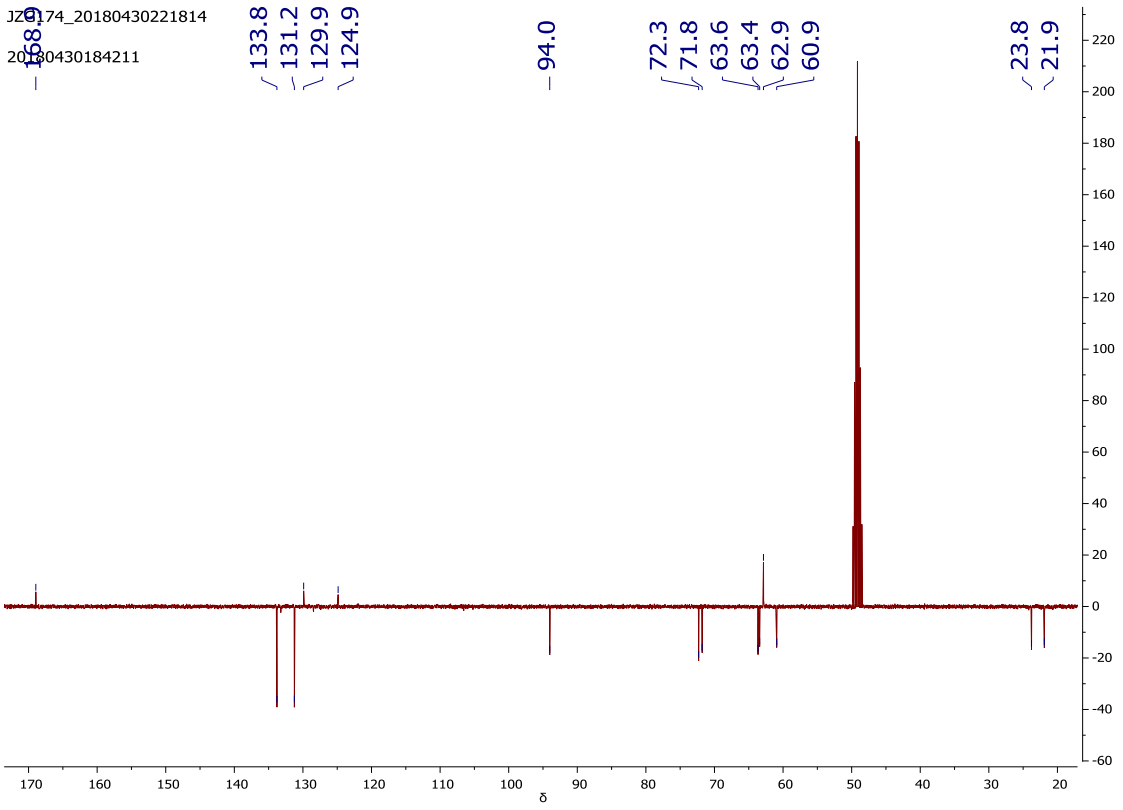

221.14948
z=1
243.13140
z=1
255.13132
z=1
287.15756
z=1
196.45785
z=?
332.21831
z=1
362.19256
z=1
422.24950
z=1
444.23109
z=1
479.23877
z=1
482.25805
z=1
526.38277
z=1
NL:
7.40E6
JZG_114#6-21
RT: 0.12-0.54 AV:
16 T: FTMS + p ESI
Full ms
[180.00-550.00]
221.14958
226.16143
NL:
8.90E5
C9 H21 N2 O4:
C9 H21 N2 O4
pa Chrg 1
m/z

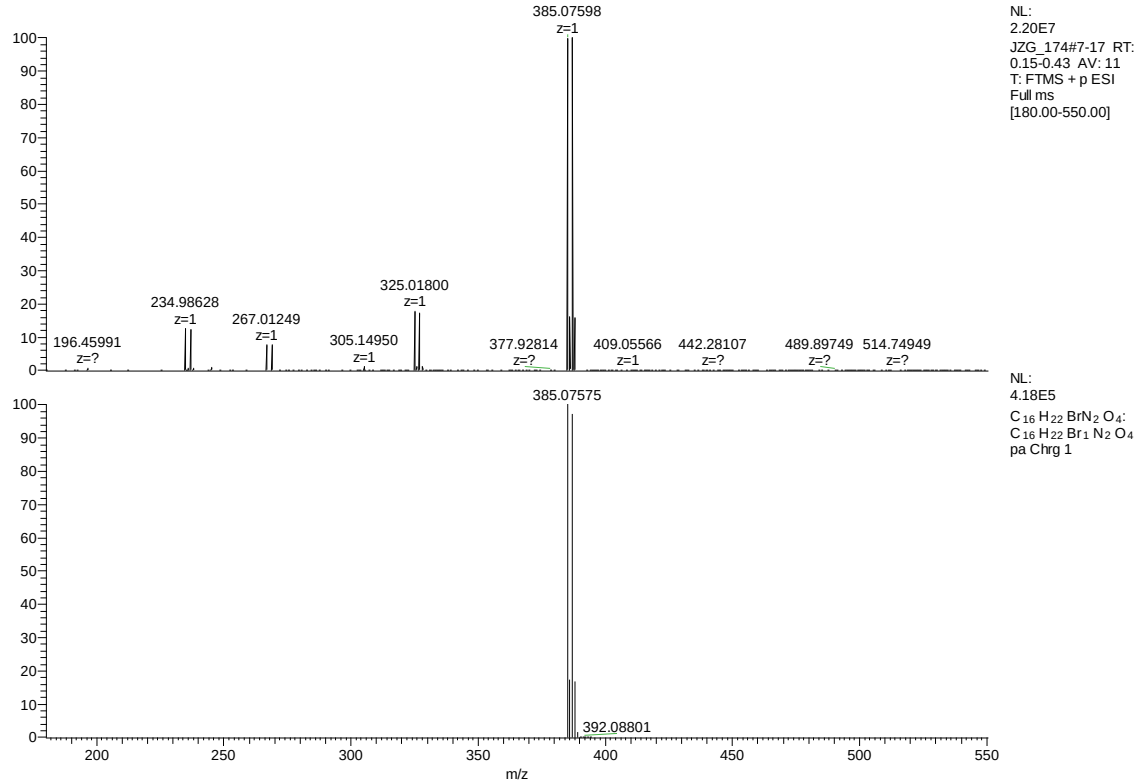

221.14948
z=1
213.12339
z=?
215.42059
z=?
216.94359
z=?
218.15800
z=?
220.76851
z=?
222.15256
z=1
223.15377
z=?
227.08892
z=?
230.15785
z=1
231.13392
z=1
NL:
7.40E6
JZG_114#6-21
RT: 0.12-0.54 AV:
16 T: FTMS + p ESI
Full ms
[180.00-550.00]
221.14958
222.15294
223.15383
224.15718
226.16143
NL:
8.90E5
C9 H21 N2 O4:
C9 H21 N2 O4
pa Chrg 1
m/z

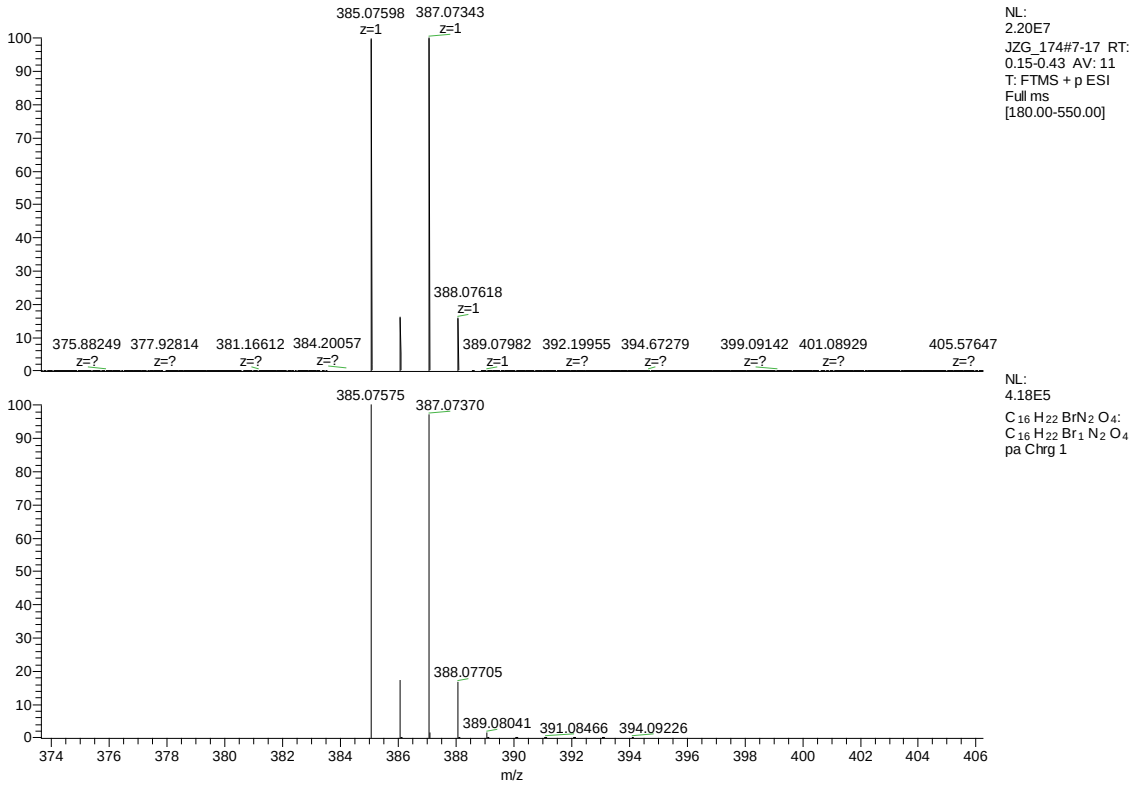
(3a*R*,4*S*,6*R*,7*S*,7a*S*)-2-(4-bromophenyl)-6-(hydroxymethyl)-4-isopropoxy-3,3a,4,6,7,7a-hexahydropyrano[3,4-d]imidazol-7-ol (20)



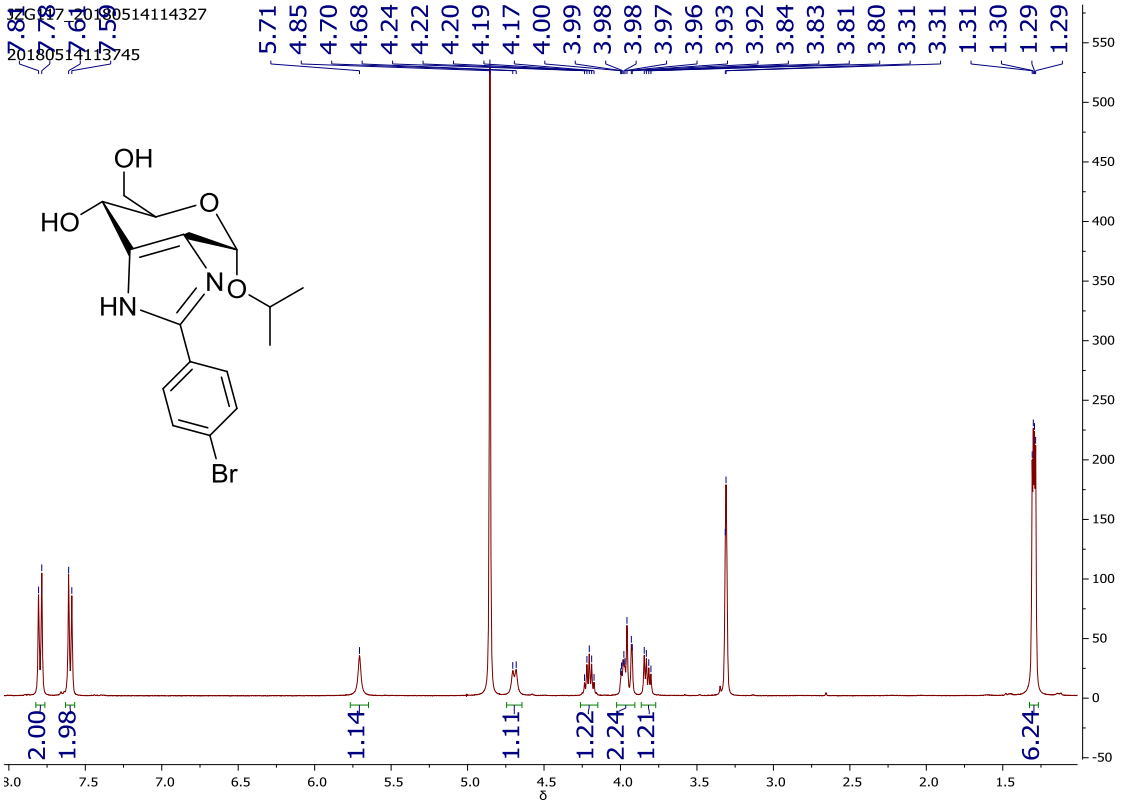


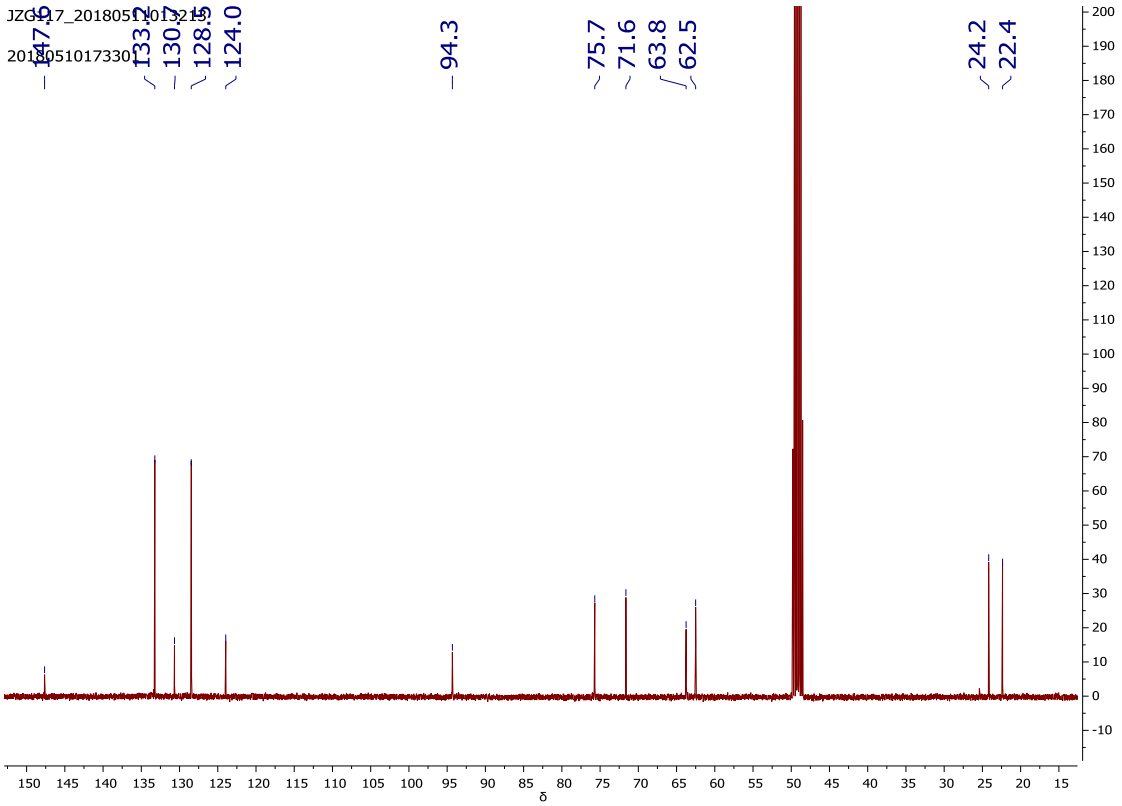

JZG174_20180430221814
20180430184211
168.9
133.8
131.2
129.9
124.9
94.0
72.3
71.8
63.6
63.4
62.9
60.9
23.8
21.9
δ

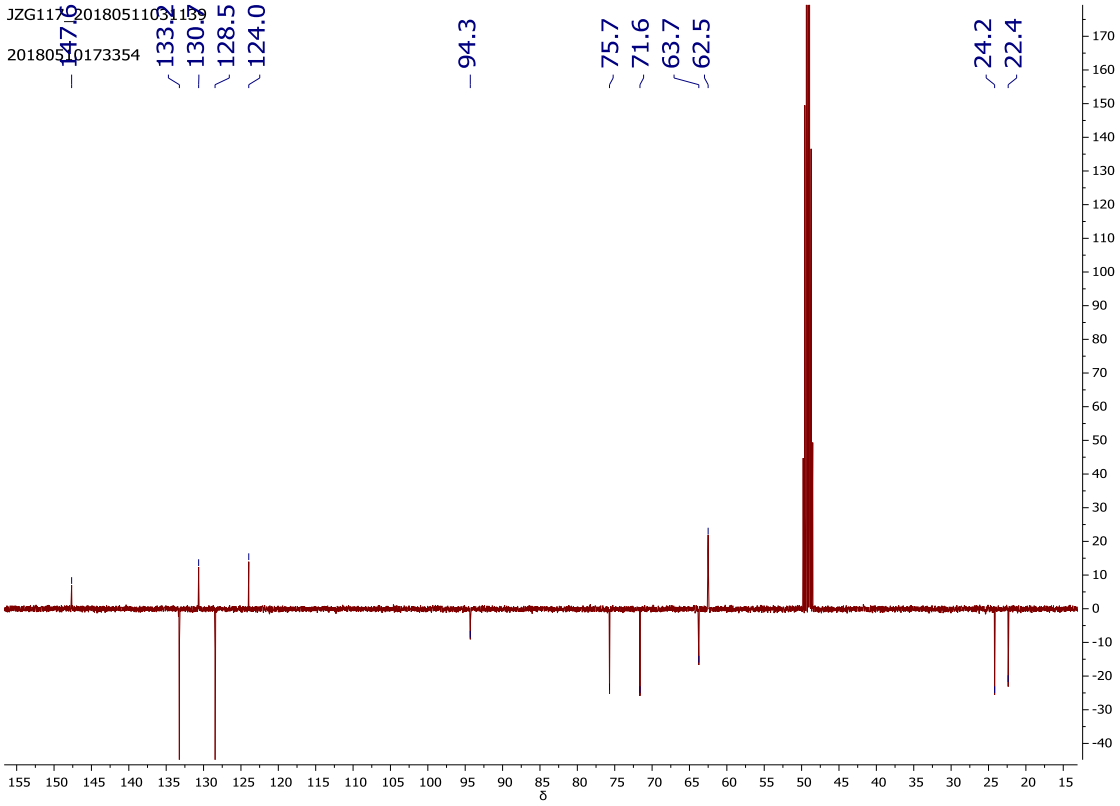

385.07598
z=1
NL:
2.20E7
JZG_174#7-17 RT:
0.15-0.43 AV: 11
T: FTMS + p ESI
Full ms
[180.00-550.00]
196.45991
z=?
234.98628
z=1
267.01249
z=1
305.14950
z=1
325.01800
z=1
377.92814
z=?
409.05566
z=1
442.28107
z=?
489.89749
z=?
514.74949
z=?
385.07575
NL:
4.18E5
C16 H22 BrN2 O4:
C16 H22 Br1 N2 O4
pa Chrg 1
392.08801
m/z

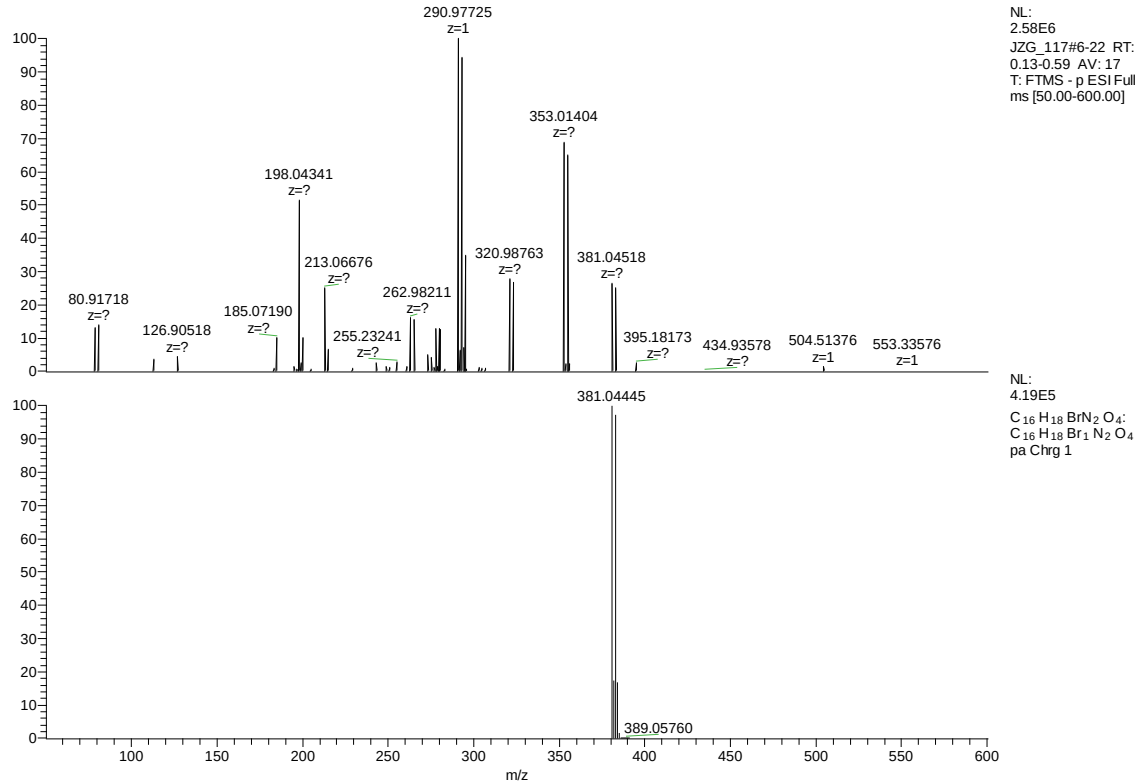

385.07598
z=1
387.07343
z=1
388.07618
z=1
375.88249
z=?
377.92814
z=?
381.16612
z=?
384.20057
z=?
389.07982
z=1
392.19955
z=?
394.67279
z=?
399.09142
z=?
401.08929
z=?
405.57647
z=?
NL:
2.20E7
JZG_174#7-17 RT:
0.15-0.43 AV: 11
T: FTMS + p ESI
Full ms
[180.00-550.00]
385.07575
387.07370
388.07705
389.08041
391.08466
394.09226
NL:
4.18E5
C16 H22 BrN2 O4:
C16 H22 Br1 N2 O4
pa Chrg 1
m/z

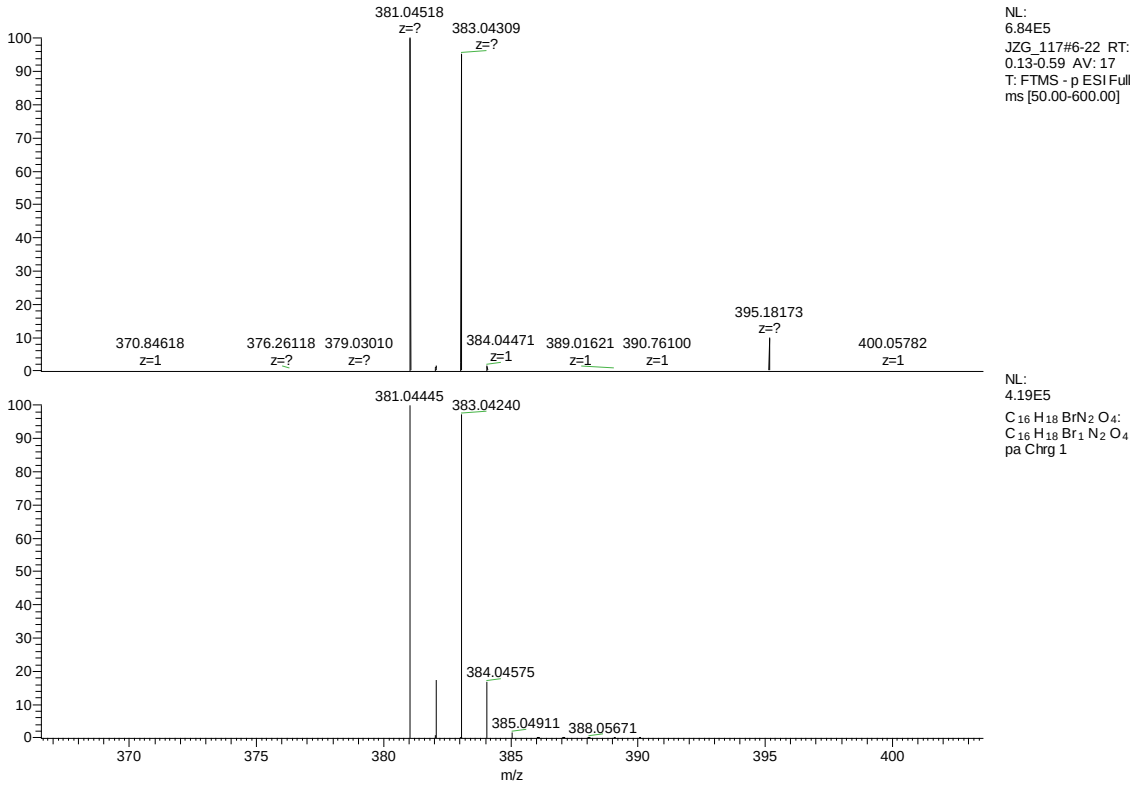
(4*S*,6*R*,7*S*)-2-(4-bromophenyl)-6-(hydroxymethyl)-4-isopropoxy-3,4,6,7-tetrahydropyrano [3, 4-d] imidazol-7-ol (21)



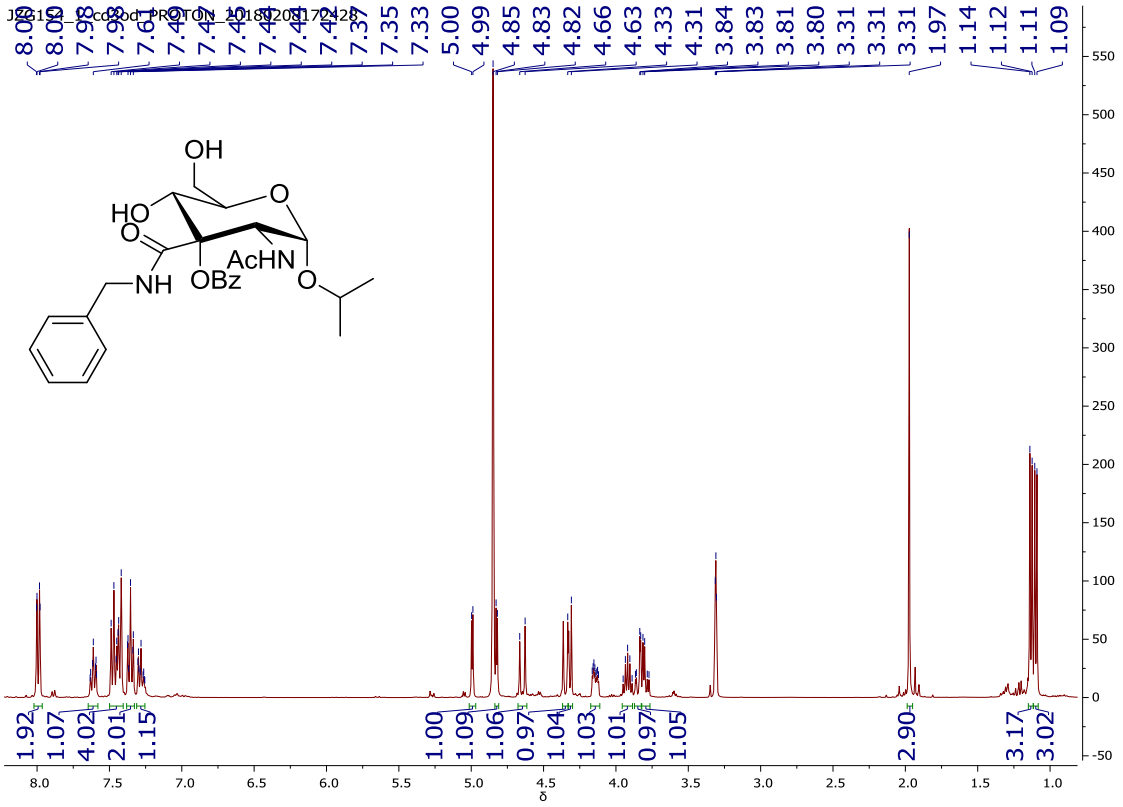


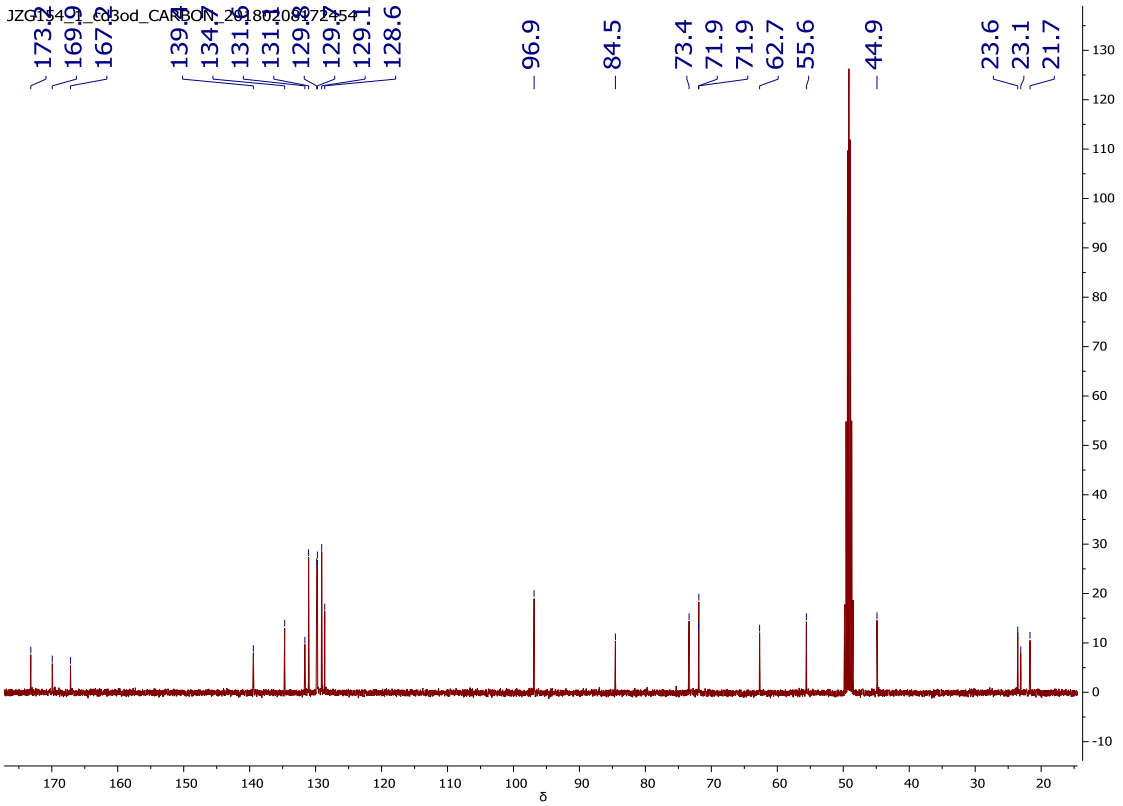

JZG117-20180511031139
20180510173354
147.5
133.2
130.4
128.5
124.0
94.3
75.7
71.6
63.7
62.5
24.2
22.4
δ

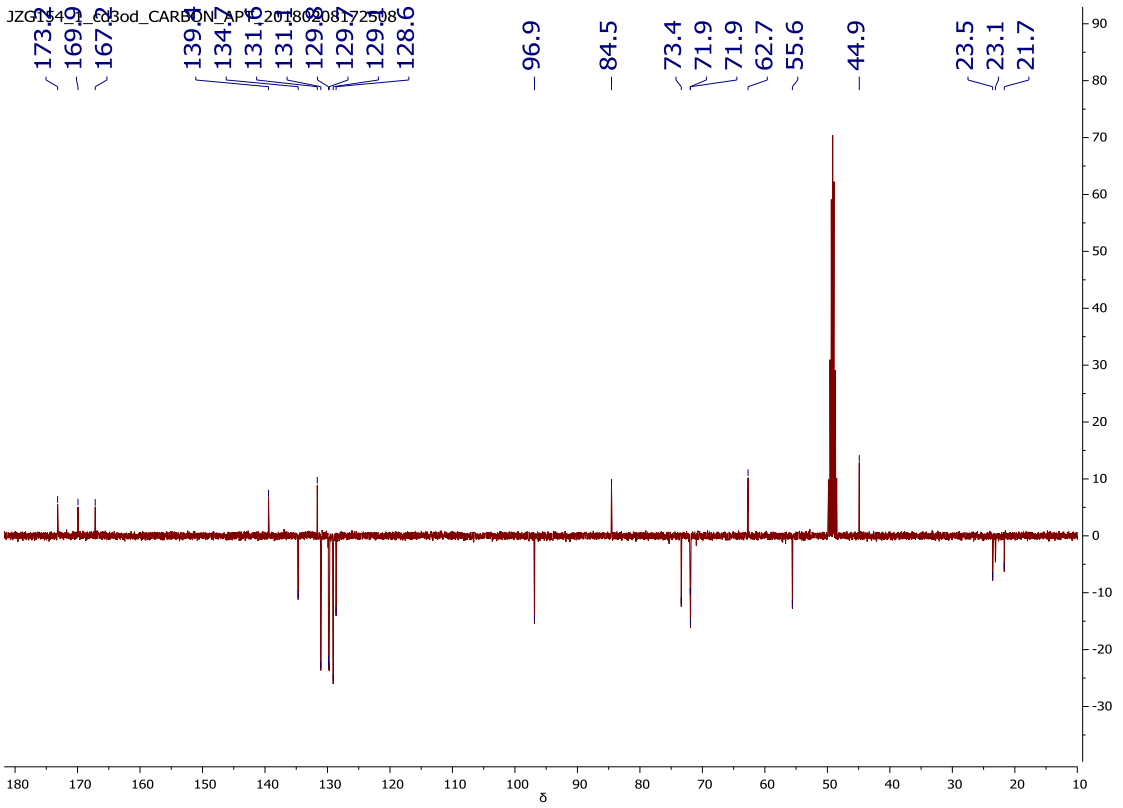

290.97725
z=1
353.01404
z=?
198.04341
z=?
213.06676
z=?
320.98763
z=?
381.04518
z=?
262.98211
z=?
80.91718
z=?
185.07190
z=?
126.90518
z=?
255.23241
z=?
395.18173
z=?
434.93578
z=?
504.51376
z=1
553.33576
z=1
NL:
2.58E6
JZG_117#6-22 RT:
0.13-0.59 AV: 17
T: FTMS - p ESI Full
ms [50.00-600.00]
381.04445
389.05760
NL:
4.19E5
C16 H18 BrN2 O4:
C16 H18 Br1 N2 O4
pa Chrg 1
m/z

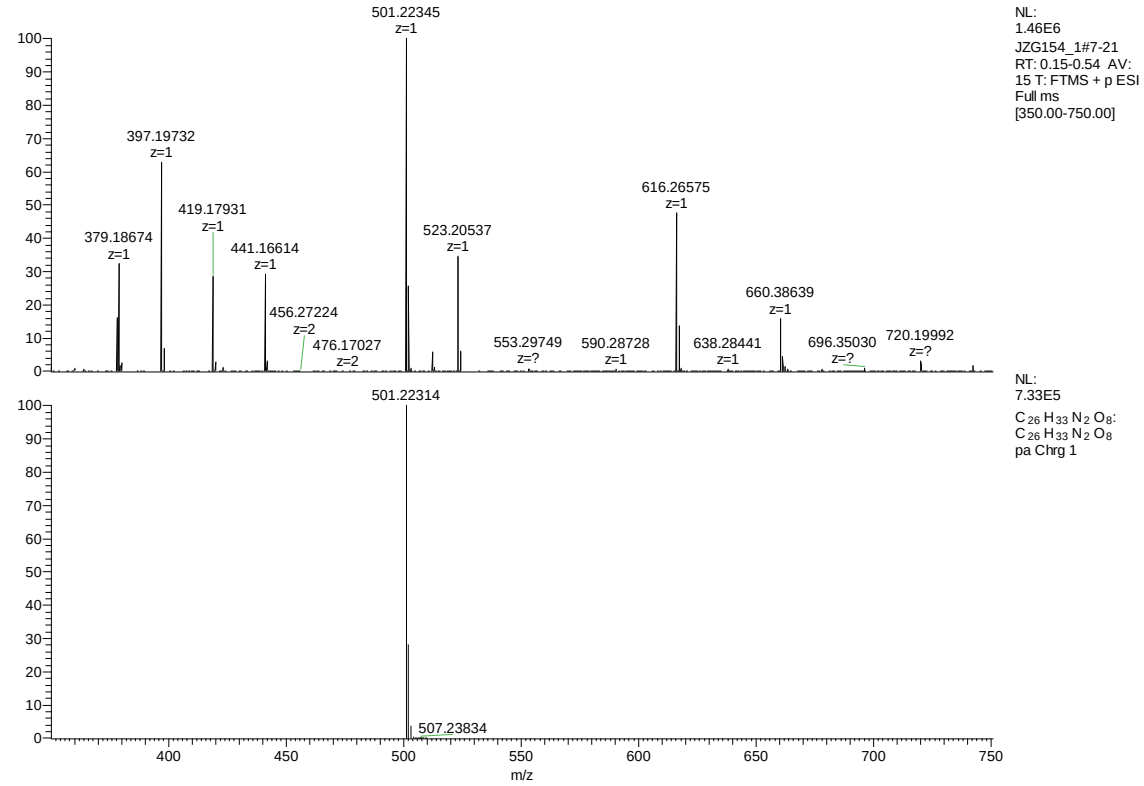

381.04518
z=?
383.04309
z=?
370.84618
z=1
376.26118
z=?
379.03010
z=?
384.04471
z=1
389.01621
z=1
390.76100
z=1
395.18173
z=?
400.05782
z=1
NL:
6.84E5
JZG_117#6-22 RT:
0.13-0.59 AV: 17
T: FTMS - p ESI Full
ms [50.00-600.00]
381.04445
383.04240
384.04575
385.04911
388.05671
NL:
4.19E5
C16 H18 BrN2 O4:
C16 H18 Br1 N2 O4
pa Chrg 1
m/z

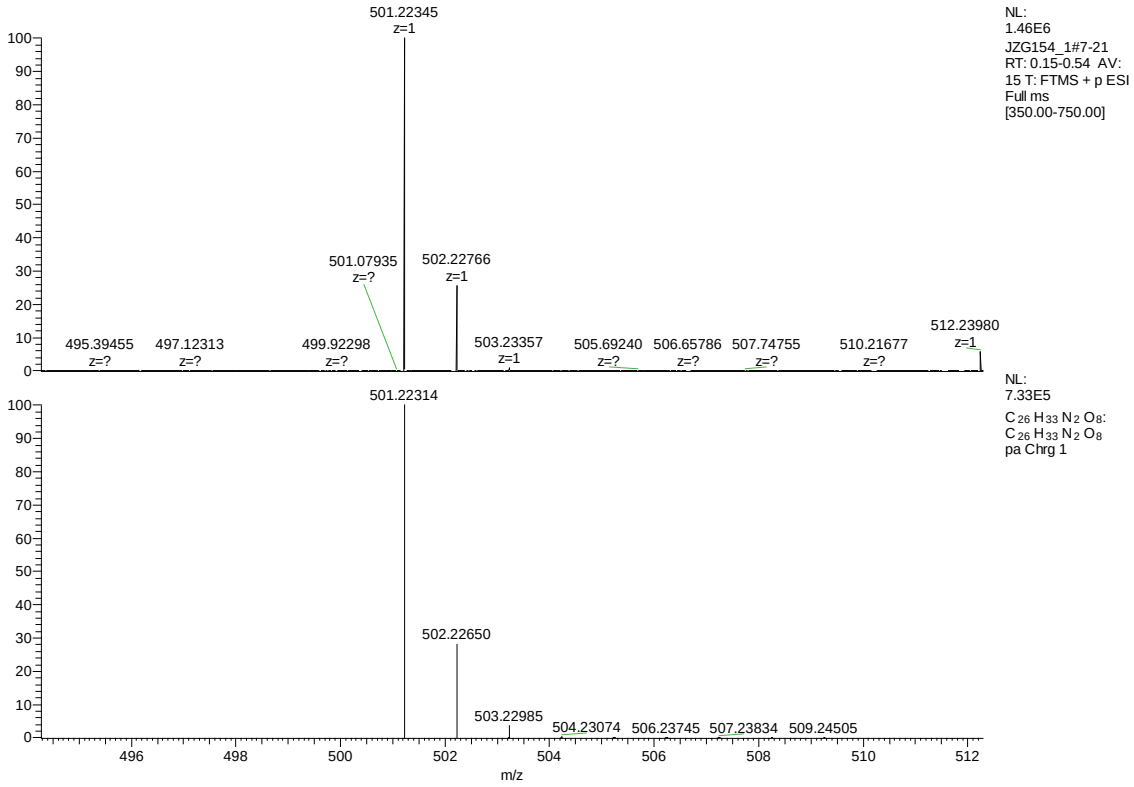
(2*S*,3*R*,4*S*,5*R*,6*R*)-3-acetamido-4-(benzylcarbamoyl)-5-hydroxy-6-(hydroxymethyl)-2-isopropoxytetrahydro-2*H*-pyran-4-yl benzoate (22a)



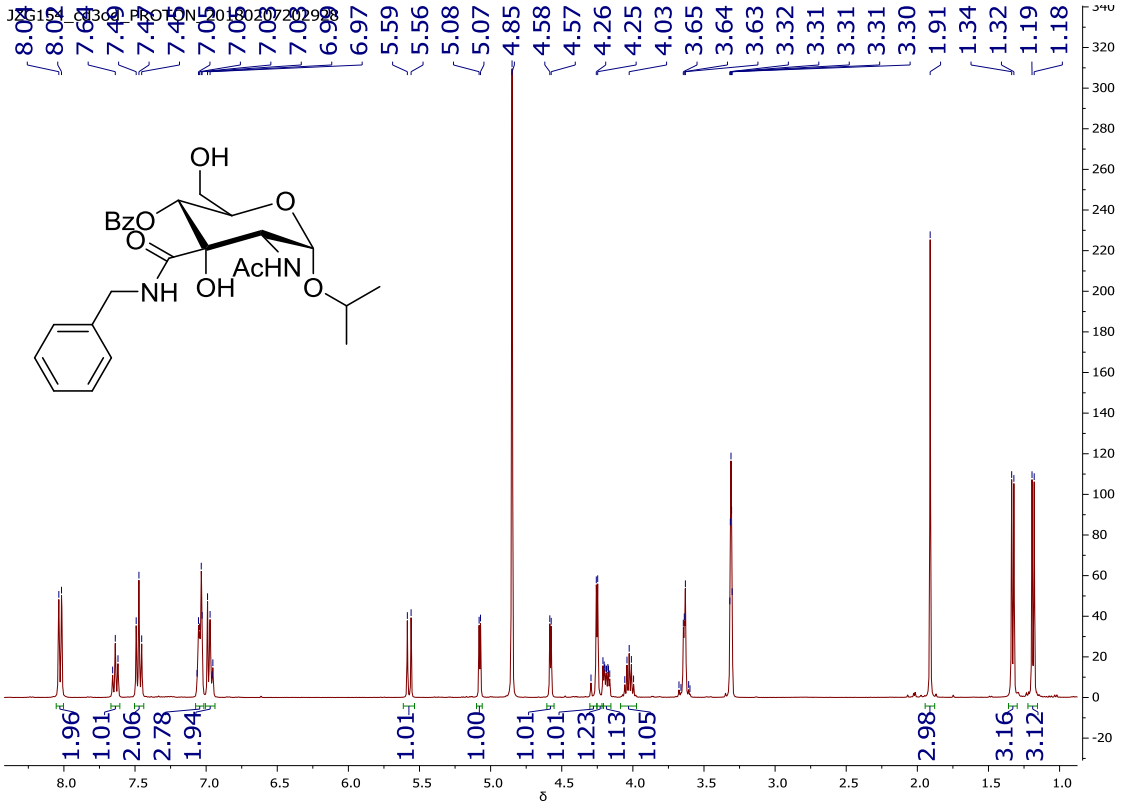


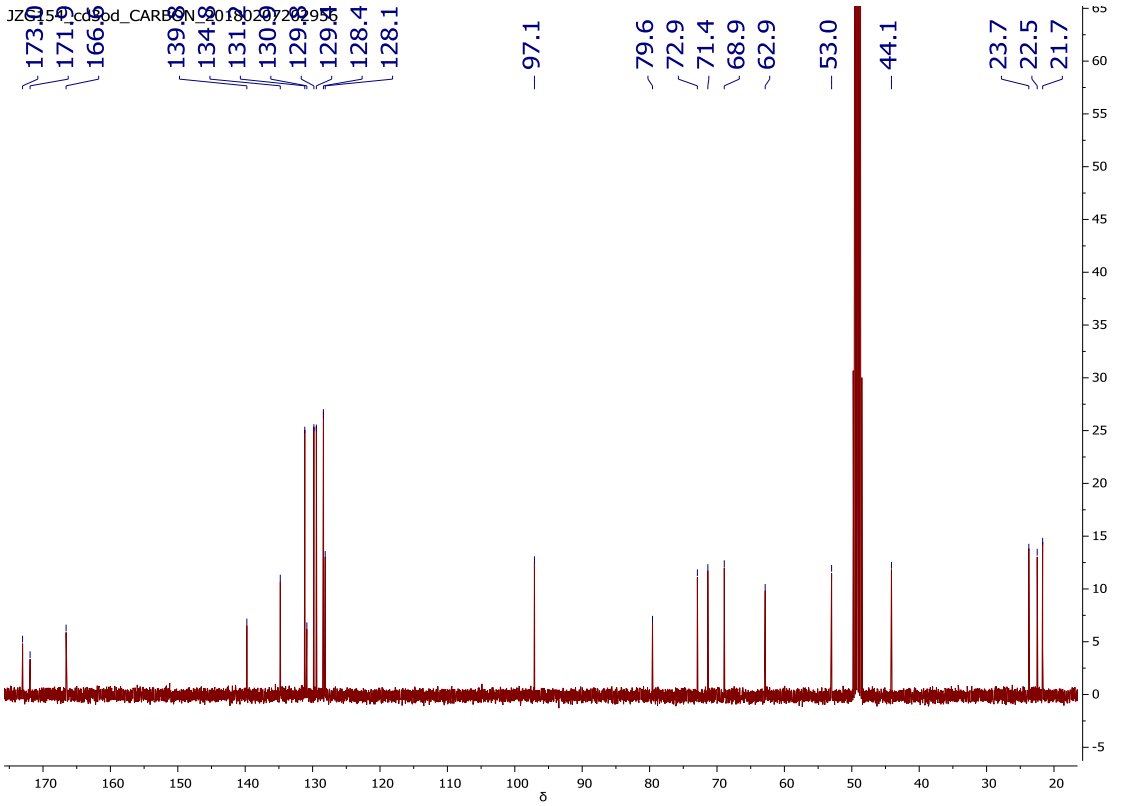

JZG154_1_60sod_CARBON_APT_20180208172508
173.4
169.9
167.8
139.4
134.7
131.6
131.2
129.8
129.7
129.1
128.6
96.9
84.5
73.4
71.9
71.9
62.7
55.6
44.9
23.5
23.1
21.7
δ

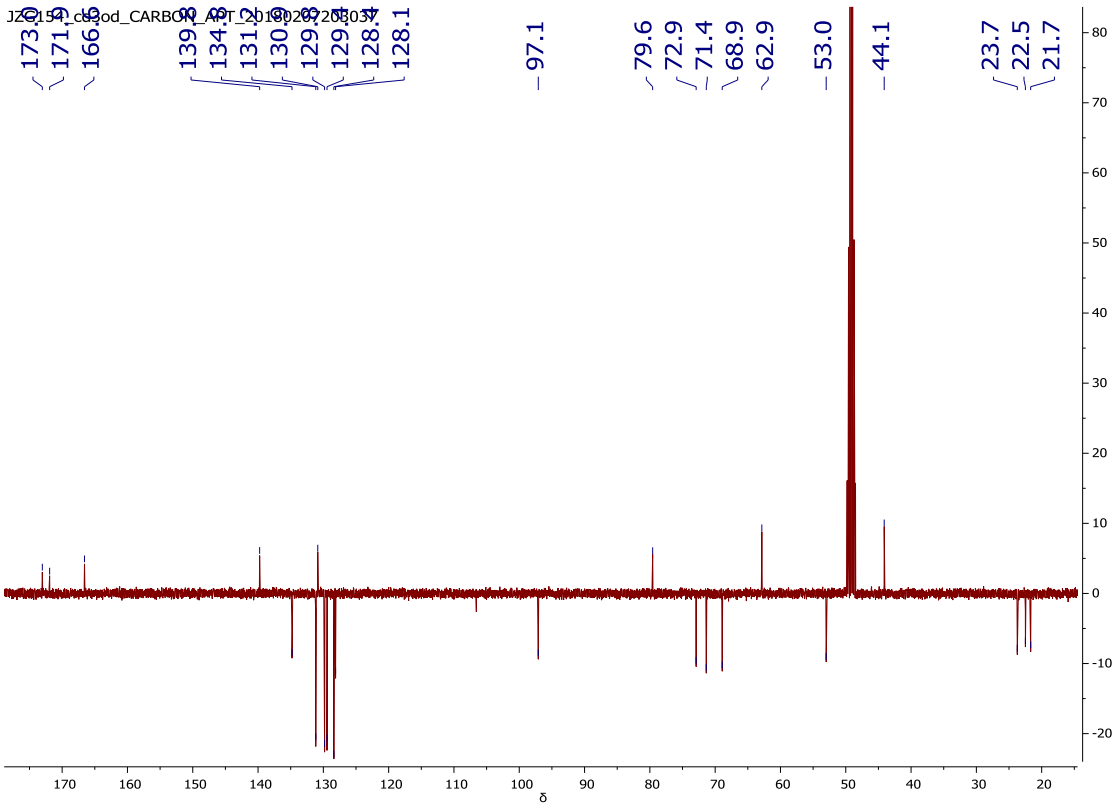

501.22345
z=1
397.19732
z=1
419.17931
z=1
379.18674
z=1
441.16614
z=1
456.27224
z=2
476.17027
z=2
523.20537
z=1
553.29749
z=?
590.28728
z=1
616.26575
z=1
638.28441
z=1
660.38639
z=1
696.35030
z=?
720.19992
z=?
NL:
1.46E6
JZG154_1#7-21
RT: 0.15-0.54 AV:
15 T: FTMS + p ESI
Full ms
[350.00-750.00]
501.22314
507.23834
NL:
7.33E5
C26 H33 N2 O8:
C26 H33 N2 O8
pa Chrg 1
m/z

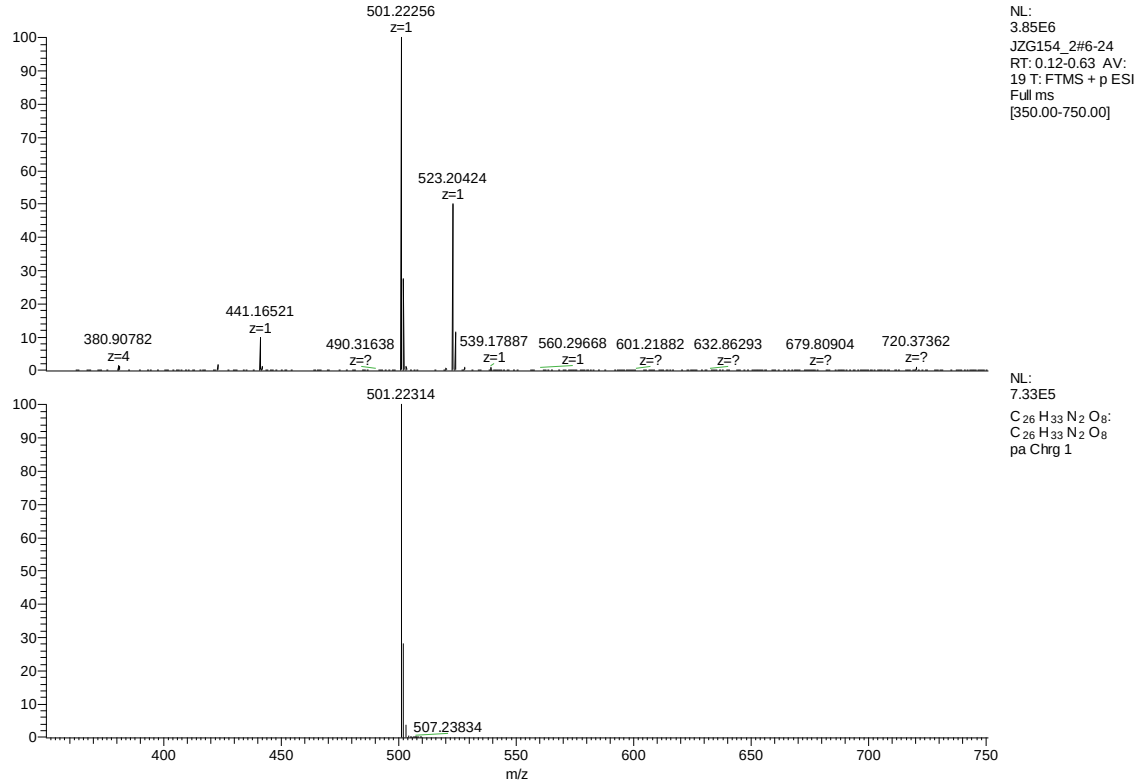

501.22345
z=1
NL:
1.46E6
JZG154_1#7-21
RT: 0.15-0.54 AV:
15 T: FTMS + p ESI
Full ms
[350.00-750.00]
501.07935
z=?
502.22766
z=1
495.39455
z=?
497.12313
z=?
499.92298
z=?
503.23357
z=1
505.69240
z=?
506.65786
z=?
507.74755
z=?
510.21677
z=?
512.23980
z=1
NL:
7.33E5
C26 H33 N2 O8:
C26 H33 N2 O8
pa Chrg 1
501.22314
502.22650
503.22985
504.23074
506.23745
507.23834
509.24505
m/z

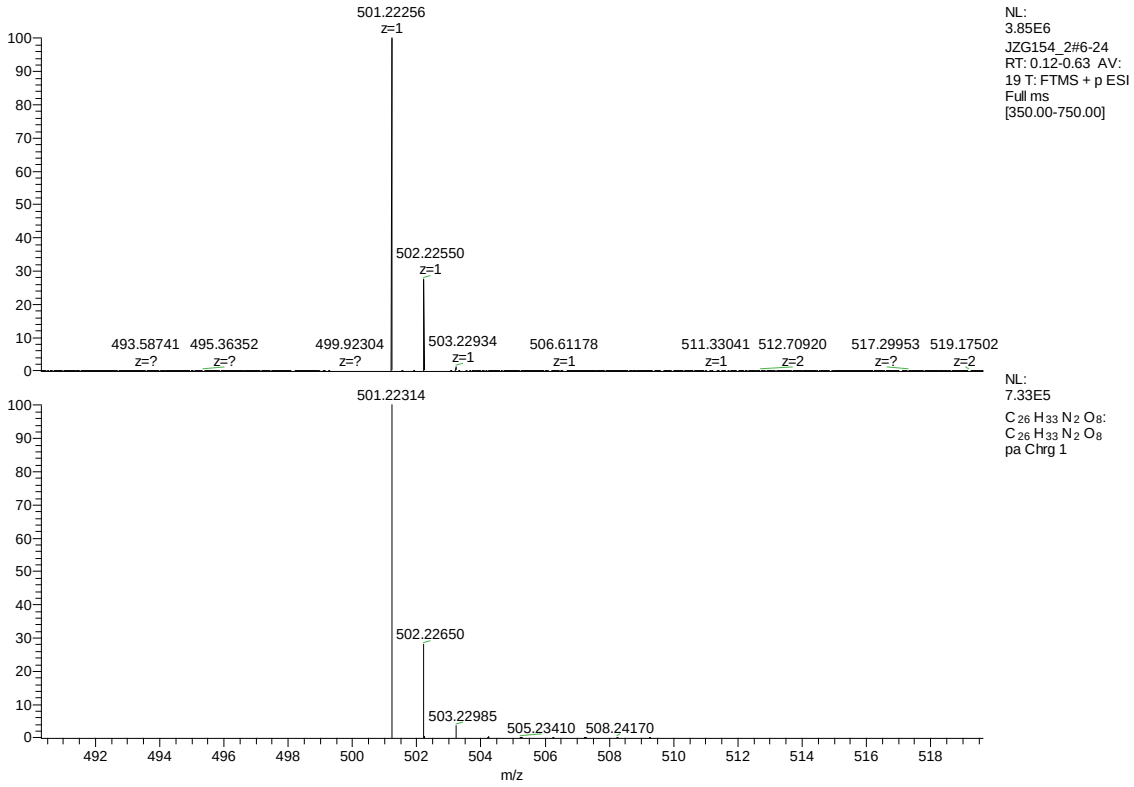
(2*R*,3*R*,4*S*,5*R*,6*S*)-5-acetamido-4-(benzylcarbamoyl)-4-hydroxy-2-(hydroxymethyl)-6-isopropoxytetrahydro-2*H*-pyran-3-yl benzoate (22b)



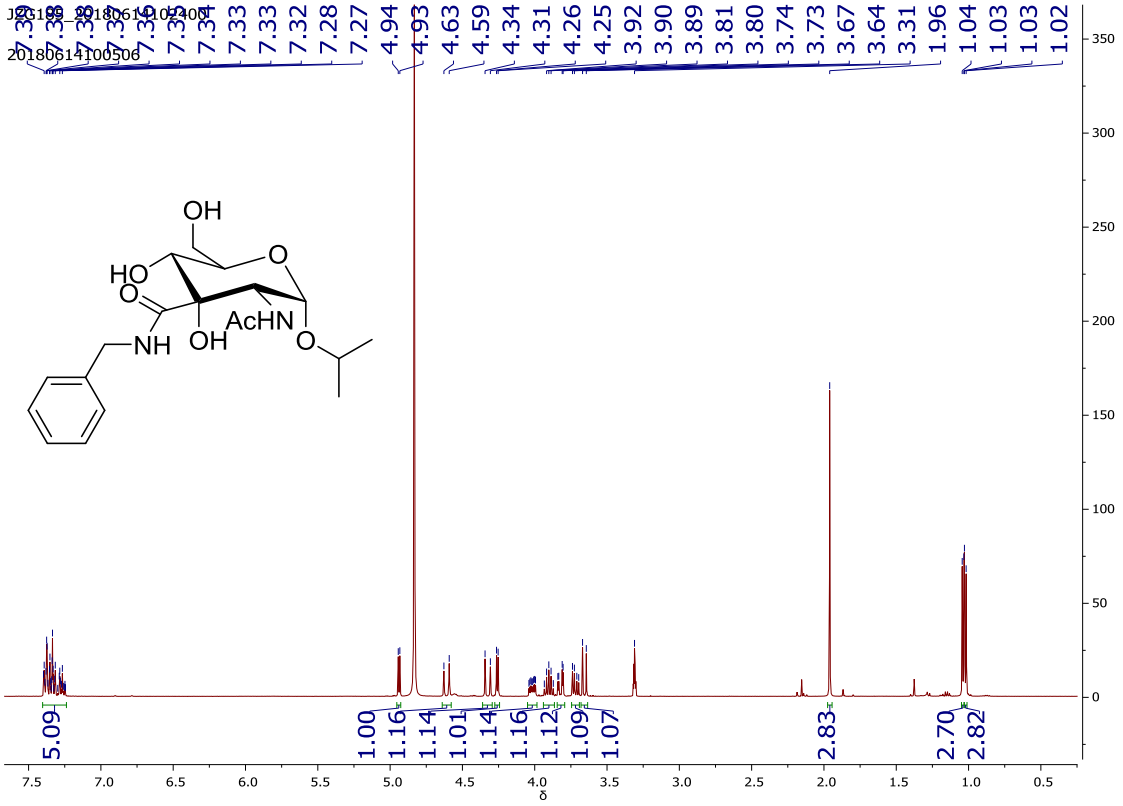


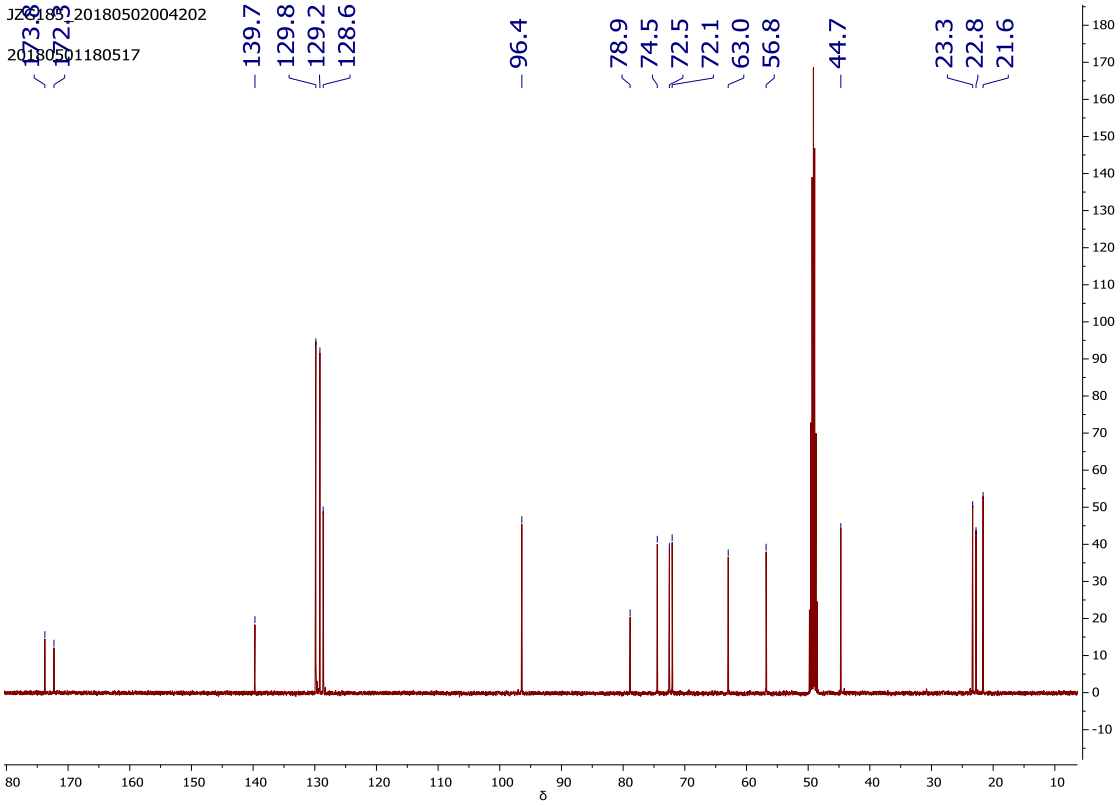

JZG154_cd3od_CARBON_APT_20180207203037
173.9
171.9
166.6
139.8
134.2
131.8
130.8
129.2
129.1
128.7
128.1
97.1
79.6
72.9
71.4
68.9
62.9
53.0
44.1
23.7
22.5
21.7
δ


501.22256
z=1
523.20424
z=1
441.16521
z=1
380.90782
z=4
490.31638
z=?
539.17887
z=1
560.29668
z=1
601.21882
z=?
632.86293
z=?
679.80904
z=?
720.37362
z=?
NL:
3.85E6
JZG154_2#6-24
RT: 0.12-0.63 AV:
19 T: FTMS + p ESI
Full ms
[350.00-750.00]
501.22314
507.23834
NL:
7.33E5
C26 H33 N2 O8:
C26 H33 N2 O8
pa Chrg 1
m/z


501.22256
z=1
NL:
3.85E6
JZG154_2#6-24
RT: 0.12-0.63 AV:
19 T: FTMS + p ESI
Full ms
[350.00-750.00]
502.22550
z=1
493.58741
z=?
495.36352
z=?
499.92304
z=?
503.22934
z=1
506.61178
z=1
511.33041
z=1
512.70920
z=2
517.29953
z=?
519.17502
z=2
NL:
7.33E5
C26 H33 N2 O8:
C26 H33 N2 O8
pa Chrg 1
501.22314
502.22650
503.22985
505.23410
508.24170
m/z

(2*S*,3*R*,4*S*,5*R*,6*R*)-3-acetamido-*N*-benzyl-4,5-dihydroxy-6-(hydroxymethyl)-2-isopropoxytetrahydro-2*H*-pyran-4-carboxamide (23)

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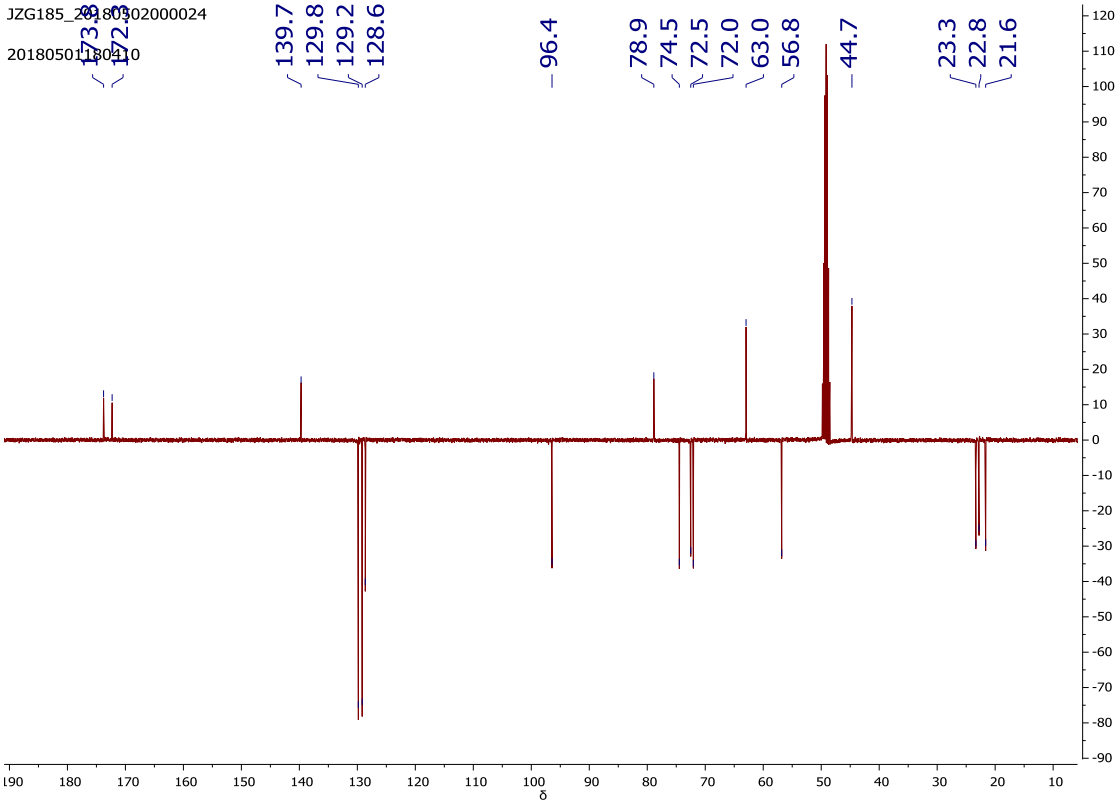
173.3
172.3
139.7
129.8
129.2
128.6
96.4
78.9
74.5
72.5
72.1
63.0
56.8
44.7
23.3
22.8
21.6
δ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173.3
172.3
139.7
129.8
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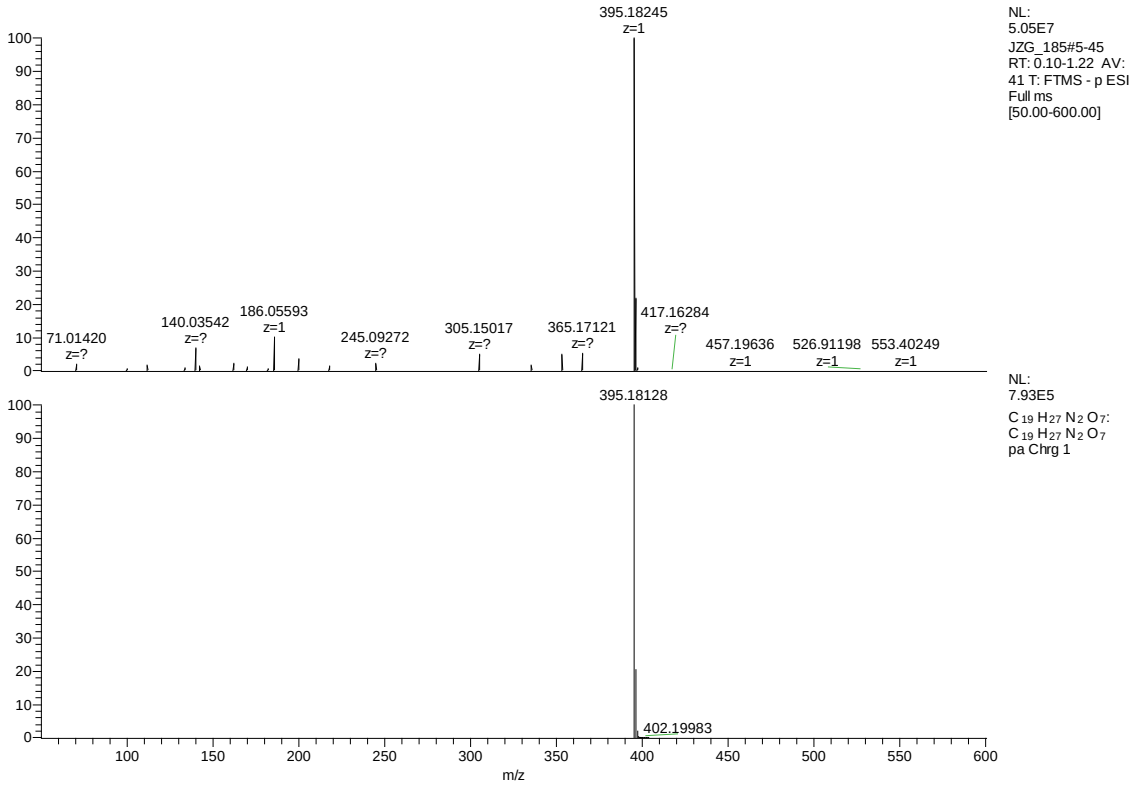
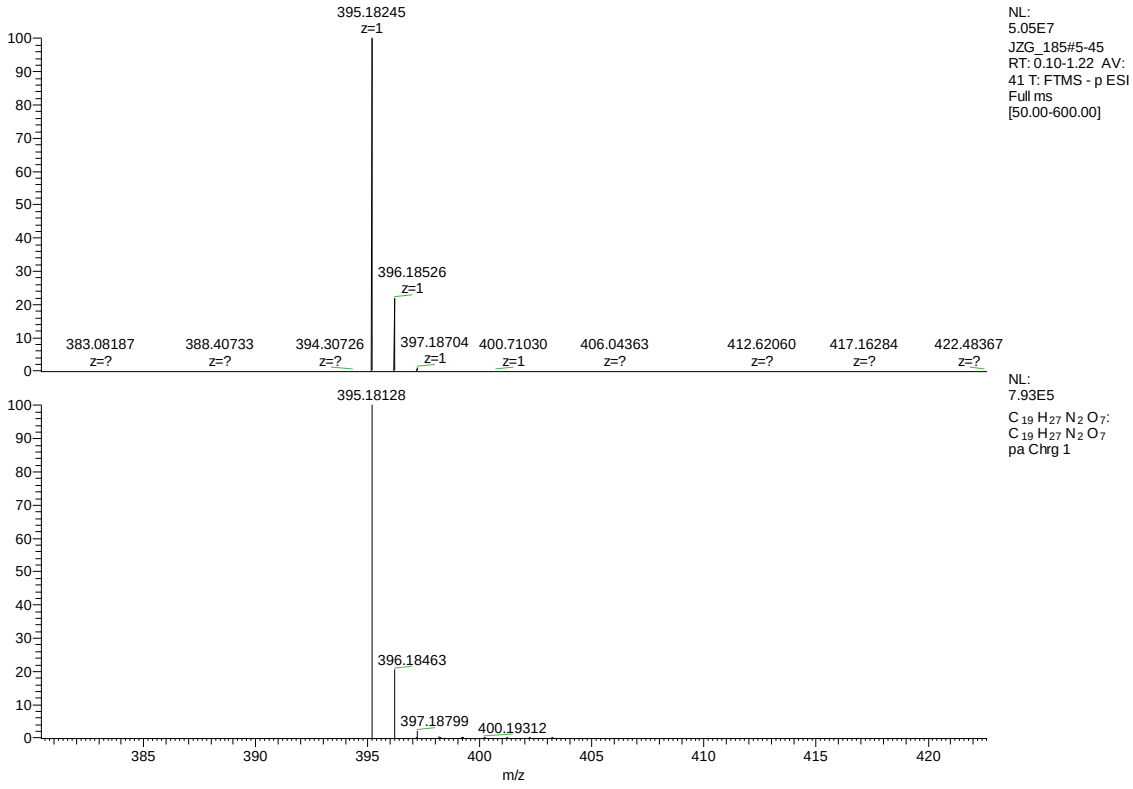
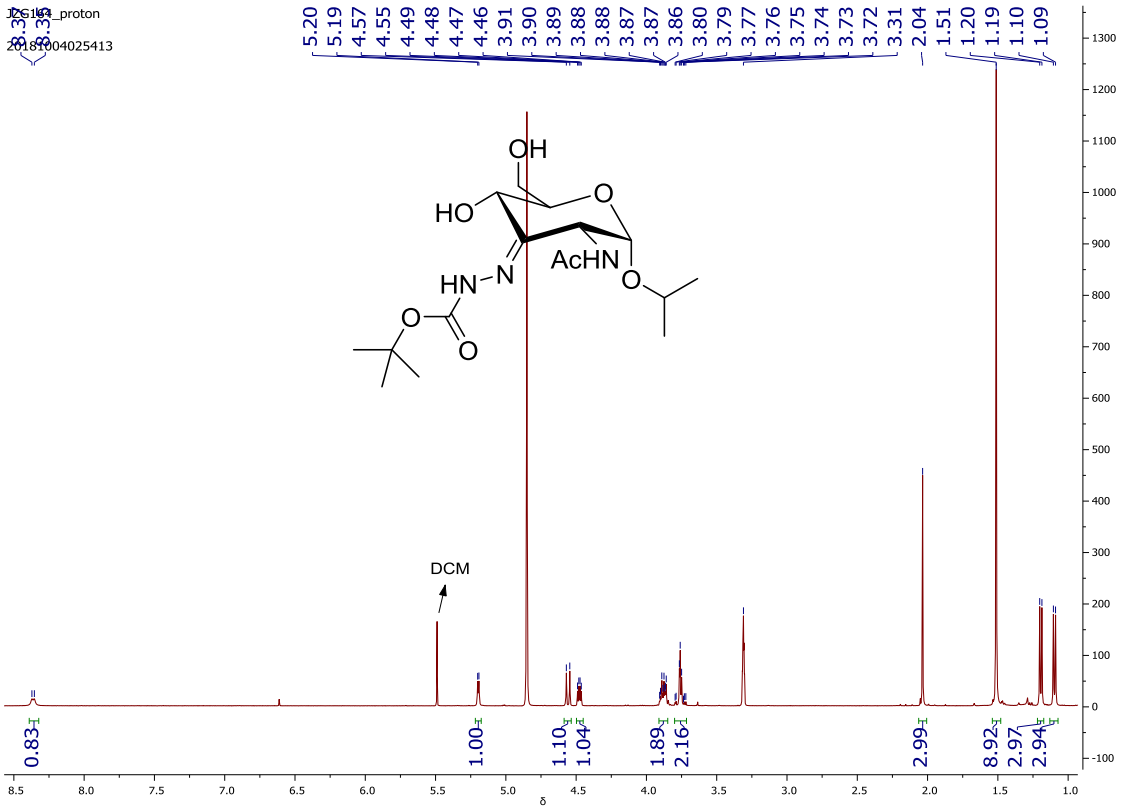
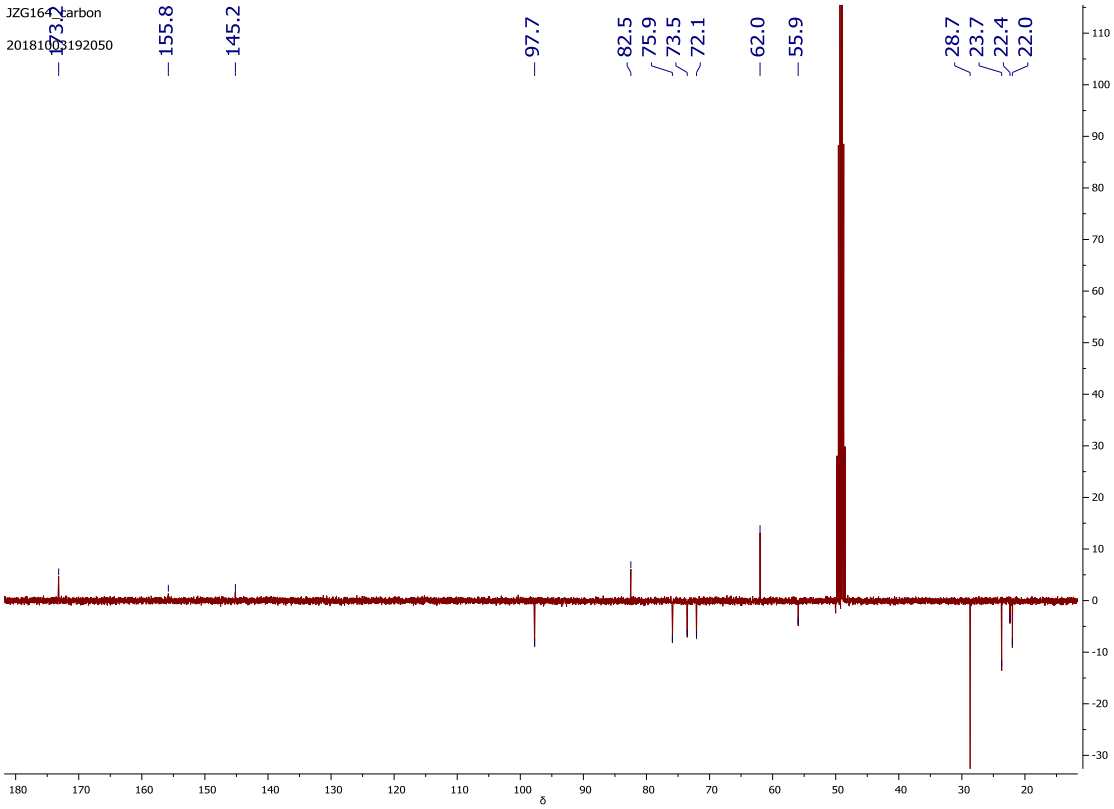
74.5
72.5
72.0
63.0
56.8
44.7
23.3
22.8
21.6
δ


395.18245
z=1
NL:
5.05E7
JZG_185#5-45
RT: 0.10-1.22 AV:
41 T: FTMS - p ESI
Full ms
[50.00-600.00]
71.01420
z=?
140.03542
z=?
186.05593
z=1
245.09272
z=?
305.15017
z=?
365.17121
z=?
417.16284
z=?
457.19636
z=1
526.91198
z=1
553.40249
z=1
395.18128
NL:
7.93E5
C 19 H 27 N 2 O 7:
C 19 H 27 N 2 O 7
pa Chrg 1
402.19983
m/z


395.18245
z=1
NL:
5.05E7
JZG_185#5-45
RT: 0.10-1.22 AV:
41 T: FTMS - p ESI
Full ms
[50.00-600.00]
396.18526
z=1
383.08187
z=?
388.40733
z=?
394.30726
z=?
397.18704
z=1
400.71030
z=1
406.04363
z=?
412.62060
z=?
417.16284
z=?
422.48367
z=?
395.18128
NL:
7.93E5
C 19 H 27 N 2 O 7:
C 19 H 27 N 2 O 7
pa Chrg 1
396.18463
397.18799
400.19312
m/z

Tert-butyl (*Z*)-2-((2*S*,3*R*,5*S*,6*R*)-3-acetamido-5-hydroxy-6-(hydroxymethyl)-2-isopropoxytetrahydro-4*H*-pyran-4-ylidene)hydrazine-1-carboxylate (24)

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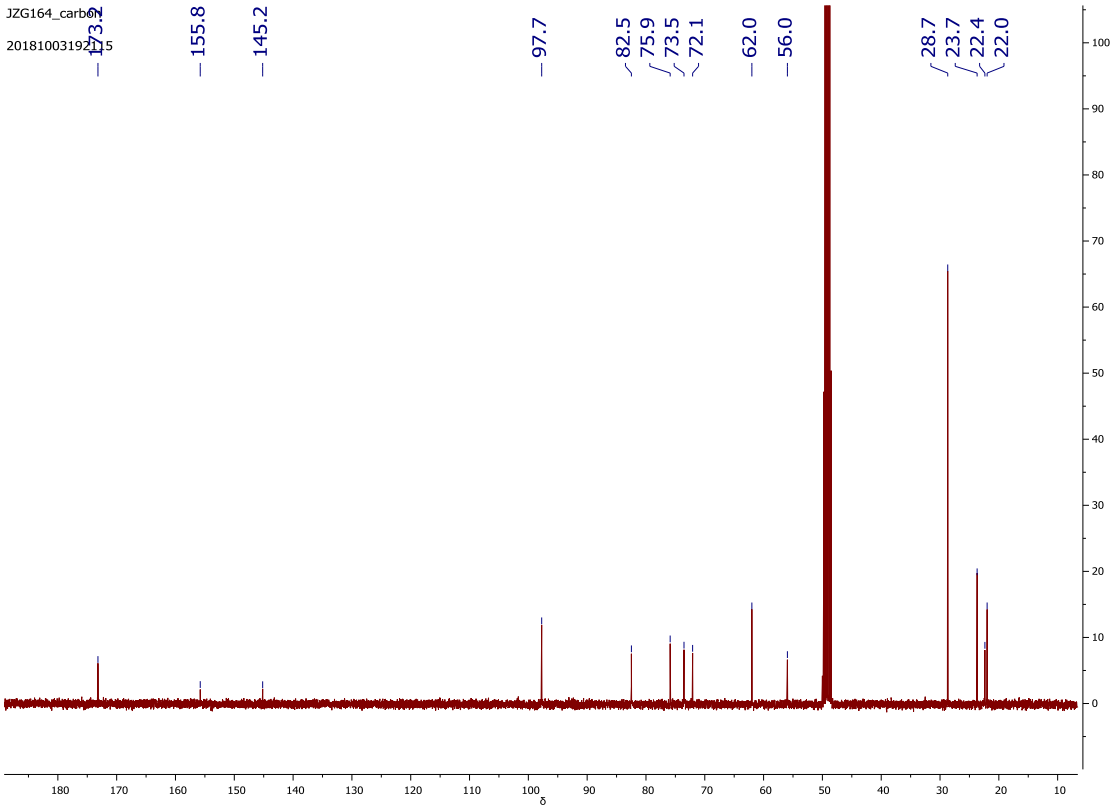
155.8
145.2
97.7
82.5
75.9
73.5
72.1
62.0
55.9
28.7
23.7
22.4
22.0
δ


JZG164_carbon
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145.2
97.7
82.5
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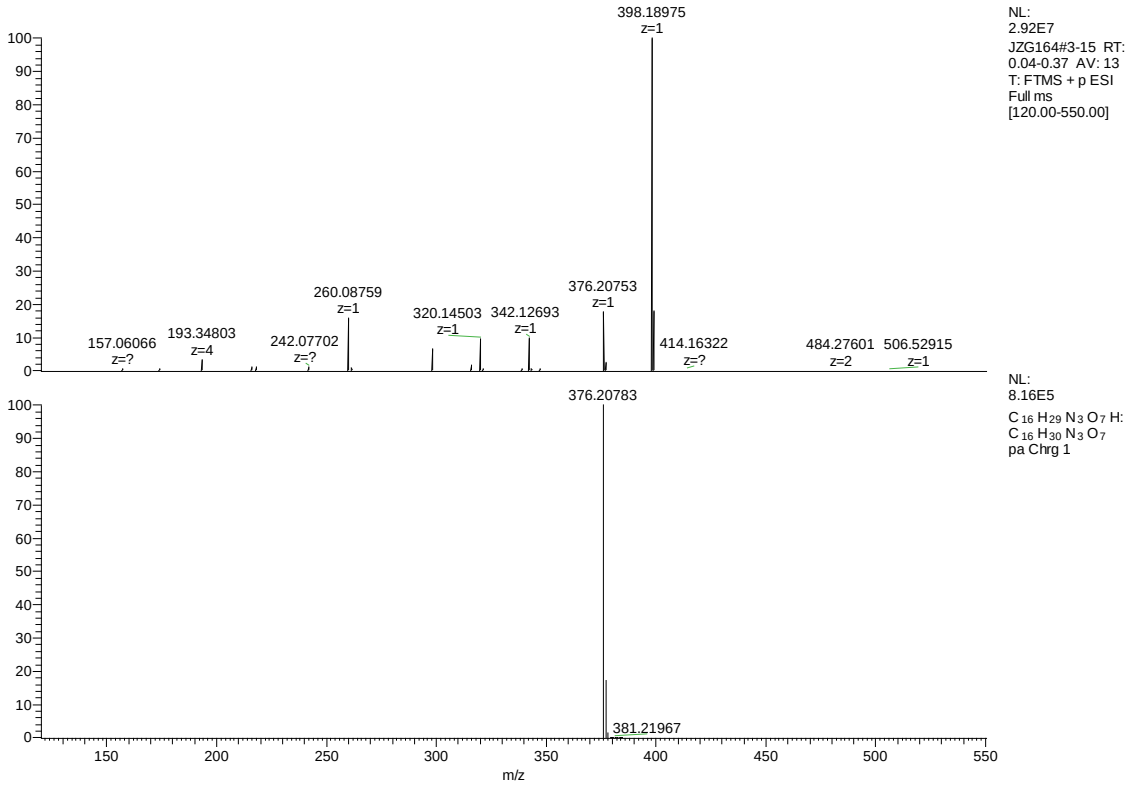
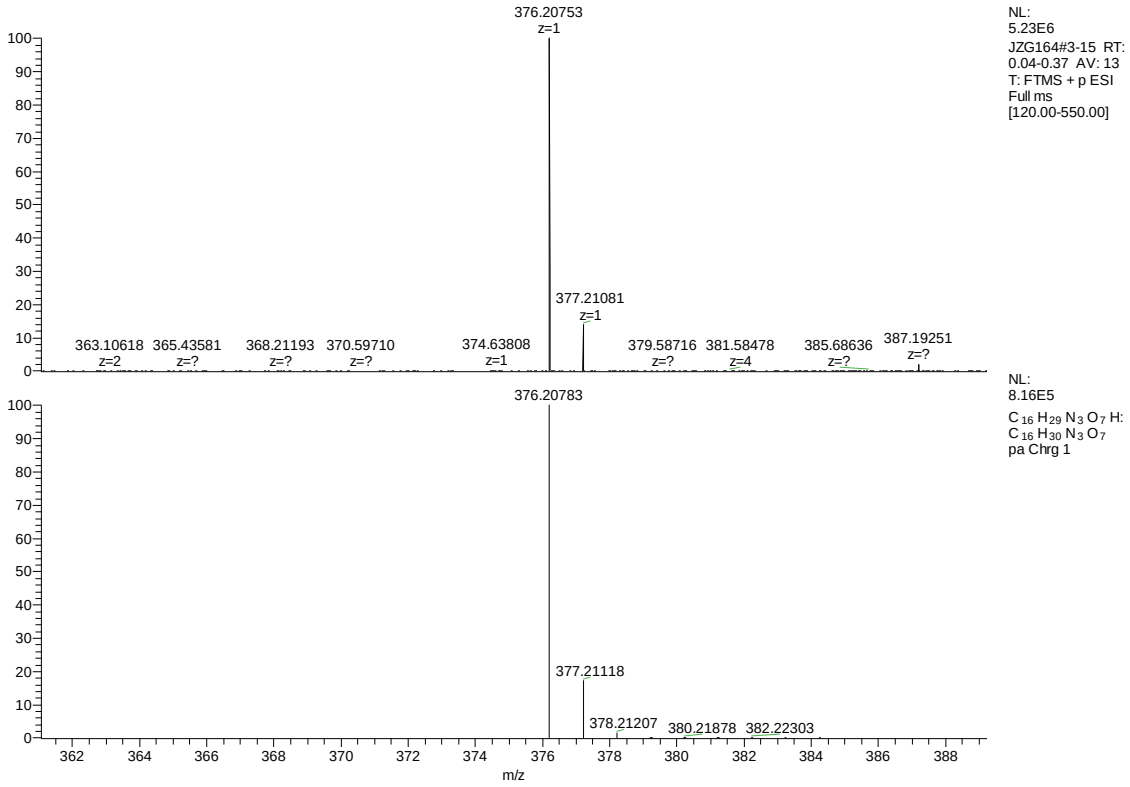
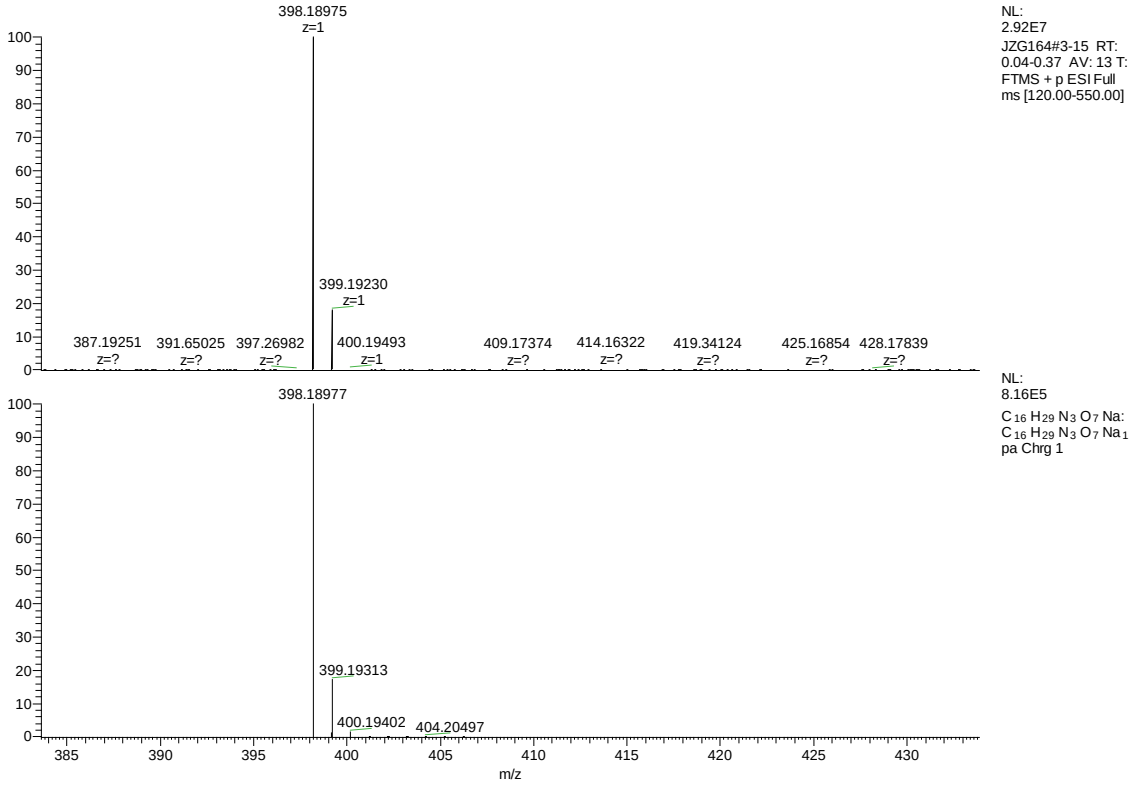
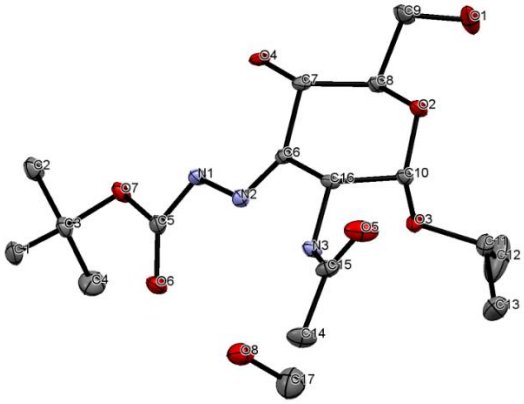
73.5
72.1
62.0
56.0
28.7
23.7
22.4
22.0
δ

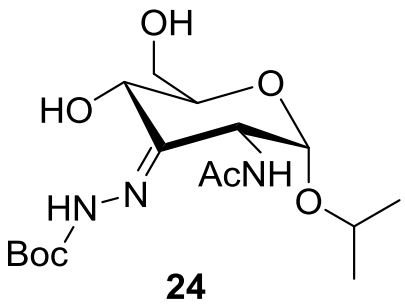

398.18975
z=1
NL:
2.92E7
JZG164#3-15 RT:
0.04-0.37 AV: 13
T: FTMS + p ESI
Full ms
[120.00-550.00]
260.08759
z=1
376.20753
z=1
320.14503
z=1
342.12693
z=1
157.06066
z=?
193.34803
z=4
242.07702
z=?
414.16322
z=?
484.27601
z=2
506.52915
z=1
NL:
8.16E5
376.20783
C 16 H 29 N 3 O 7 H:
C 16 H 30 N 3 O 7
pa Chrg 1
381.21967
m/z


376.20753
z=1
NL:
5.23E6
JZG164#3-15 RT:
0.04-0.37 AV: 13
T: FTMS + p ESI
Full ms
[120.00-550.00]
377.21081
z=1
363.10618
z=2
365.43581
z=?
368.21193
z=?
370.59710
z=?
374.63808
z=1
379.58716
z=?
381.58478
z=4
385.68636
z=?
387.19251
z=?
NL:
8.16E5
376.20783
C 16 H 29 N 3 O 7 H:
C 16 H 30 N 3 O 7
pa Chrg 1
377.21118
378.21207
380.21878
382.22303
m/z


398.18975
z=1
NL:
2.92E7
JZG164#3-15 RT:
0.04-0.37 AV: 13 T:
FTMS + p ESI Full
ms [120.00-550.00]
399.19230
z=1
387.19251
z=?
391.65025
z=?
397.26982
z=?
400.19493
z=1
409.17374
z=?
414.16322
z=?
419.34124
z=?
425.16854
z=?
428.17839
z=?
NL:
8.16E5
C16 H29 N3 O7 Na:
C16 H29 N3 O7 Na1
pa Chrg 1
398.18977
399.19313
400.19402
404.20497
m/z

X-ray crystallography:





24

Figure S1. Molecular structure of compound **24**•CH_3OH, showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

A single crystal of compound **24** was mounted on top of a cryoloop and transferred into the cold nitrogen stream (100 K) of a Bruker-AXS D8 Venture diffractometer. Data collection and reduction was done using the Bruker software suite APEX3.[1] The final unit cell was obtained from the xyz centroids of 9994 reflections after integration. A multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*). The structures were solved by direct methods using *SHELXT*[3] and refinement of the structure was performed using *SHLELXL*.[4] The hydrogen atoms were generated by geometrical considerations, constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Crystal data and details on data collection and refinement are presented in Table S1

Table S1. Crystallographic data for **24**

chem formula	C17 H33 N3 O8
M_r	407.46
cryst syst	Monoclinic
color, habit	Colourless, block
size (mm)	0.52 x 0.27 x 0.15
space group	P 21
a (Å)	10.2358(7)
b (Å)	8.6625(6)
c (Å)	12.4764(10)
α, deg	90
β, deg	90.477(2)

γ, deg	90
V (Å^3)	1106.21(14)
Z	2
ρ_{calc}, g.cm^{-3}	1.450
μ(Mo K$\overline{\alpha}$), cm^{-1}	0.097
F(000)	440
temp (K)	100(2)
θ range (deg)	3.081 – 28.329
data collected (h,k,l)	-13:13, -11:11, -16:16
no. of rflns collected	39951
no. of indpndt reflns	5506
observed reflns	4867 ($F_o \geq 2\ \sigma(F_o)$)
R(F) (%)	3.92
wR(F^2) (%)	9.08
GooF	1.042
Weighting a,b	0.0422, 0.3097
params refined	266
restraints	1
min, max resid dens	-0.248, 0.409

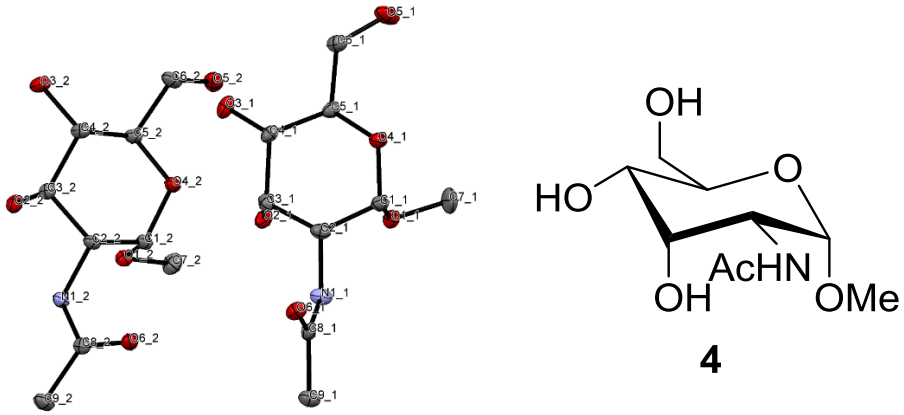


Figure S2. Molecular structure of **4** with two molecules per unit cell, showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

A single crystal of compound **4** was mounted on top of a cryoloop and transferred into the cold nitrogen stream (100 K) of a Bruker-AXS D8 Venture diffractometer. Data collection and reduction was done using the Bruker software suite APEX3.[2] The final unit cell was obtained from the xyz centroids of 9804 reflections after integration. A

multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*). The structures were solved using *SHELXT*[3] and refinement of the structure was performed using *SHELXL*.[4] The hydrogen atoms were generated by geometrical considerations, constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. The absolute configuration of the model was chosen based on anomalous dispersion effects, and refinement of Flack's parameter converged to 0.03(3). Crystal data and details on data collection and refinement are presented in Table S2

Table S2. Crystallographic data for **4**

chem formula	C9 H17 N O6
M_r	235.23
cryst syst	orthorhombic
color, habit	colorless, block
size (mm)	0.40 x 0.25 x 0.12
space group	P 21 21 21
a (Å)	9.6845(2)
b (Å)	11.1866(2)
c (Å)	20.2699(5)
V (Å^3)	2195.97(8)
Z	8
ρ_{calc}, g.cm^{-3}	1.423
μ(Mo K$\overline{\alpha}$), cm^{-1}	1.026
F(000)	1008
temp (K)	100(2)
θ range (deg)	4.362 – 74.583
data collected (h,k,l)	-12:11, -13:13, -25:25
no. of rflns collected	30369
no. of indpndt reflns	4453
observed reflns	4365 ($F_o \geq 2\ \sigma(F_o)$)
R(F) (%)	2.34
wR(F^2) (%)	6.04
GooF	1.089
Weighting a,b	0.0359, 0.3176
params refined	305
restraints	0
min, max resid dens	-0.171, 0.204
Flack x	0.03(3)

Literature

(1) Bruker, (2016). *APEX3* (v2012.4-3), *SAINT* (Version 8.18C) and *SADABS* (Version 2012/1). Bruker AXS Inc., Madison, Wisconsin, USA.
(2) Bruker, (2016). *APEX3* (v2016.1-0), *SAINT* (Version 8.37A) and *SADABS* (Version 2014/5). Bruker AXS Inc., Madison, Wisconsin, USA.
(3) Sheldrick, G. M. SHELXT– Integrated space-group and crystal-structure determination. *Acta Crystallographica Section A* **2015,** 71, 3-8.
(4) Sheldrick, G. M. A short history of SHELX. *Acta Crystallographica Section A* **2008,** 64, 112-122.