Supporting Information

for

Synthesis of 1,2-*cis*-2-*C*-branched aryl-*C*-glucosides via desulfurization of carbohydrate based hemithioacetals

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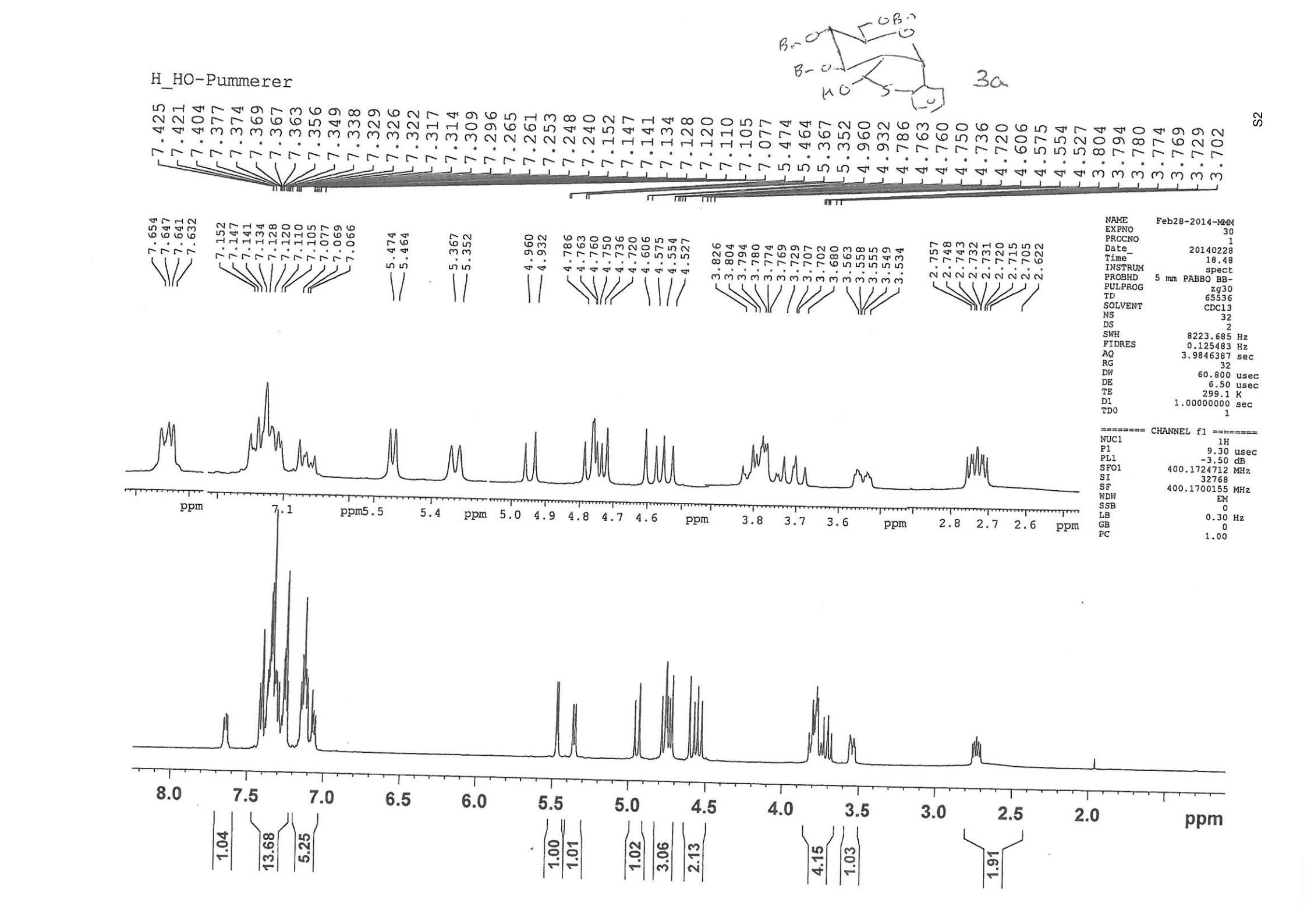
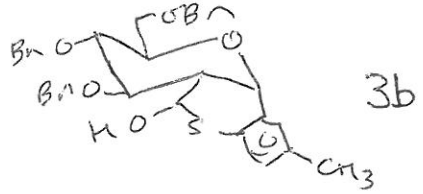
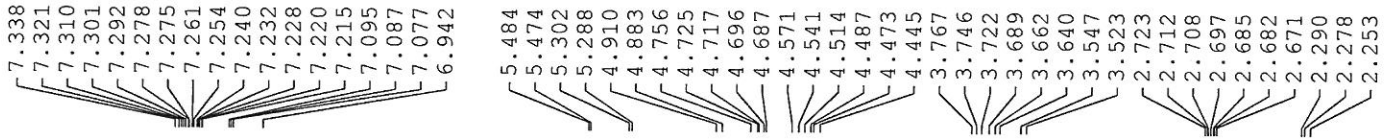
^{1}H and ^{13}C NMR spectra

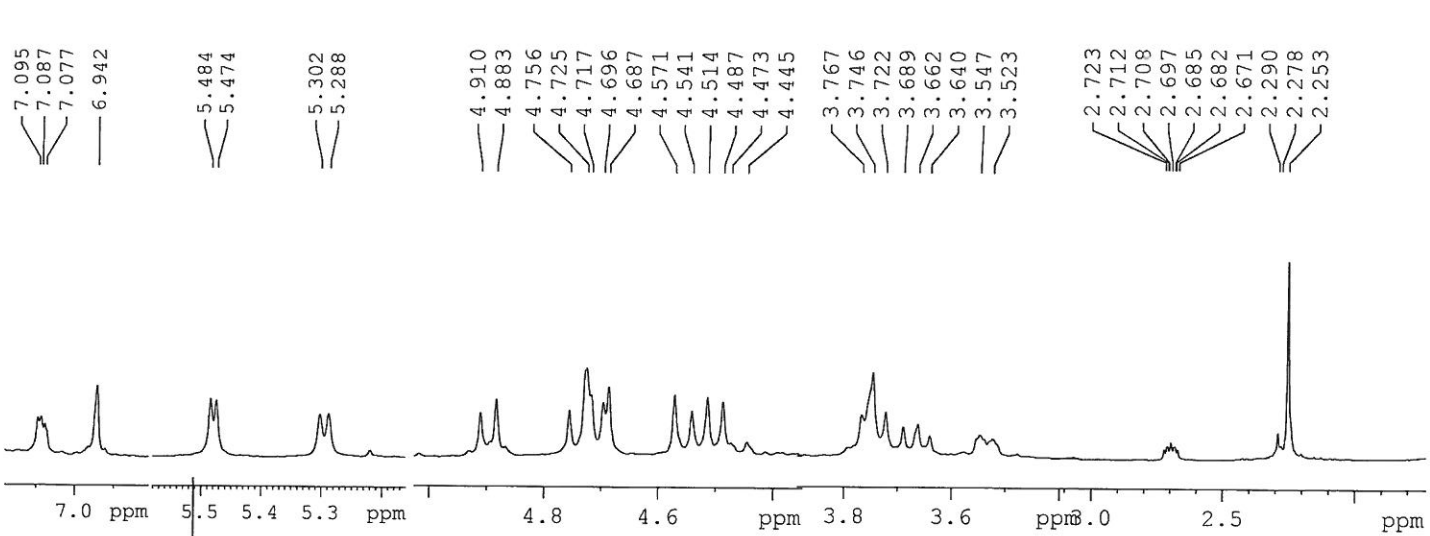

H_HO-Pummerer
3a
7.425 7.421 7.404 7.377 7.374 7.369 7.367 7.363 7.356 7.349 7.338 7.329 7.326 7.322 7.317 7.314 7.309 7.296 7.265 7.261 7.253 7.248 7.240 7.152 7.147 7.141 7.134 7.128 7.120 7.110 7.105 7.077 5.474 5.464 5.367 5.352 4.960 4.932 4.786 4.763 4.760 4.750 4.736 4.720 4.606 4.575 4.554 4.527 3.804 3.794 3.780 3.769 3.729 3.702
7.654 7.647 7.641 7.632
7.152 7.147 7.141 7.134 7.128 7.120 7.110 7.105 7.077 7.069 7.066
5.474 5.464
5.367 5.352
4.960 4.932
4.786 4.763 4.760 4.750 4.736 4.720 4.606 4.575 4.554 4.527
3.826 3.804 3.794 3.780 3.774 3.769 3.729 3.707 3.702 3.680 3.563 3.558 3.555 3.549 3.534
2.757 2.748 2.743 2.732 2.731 2.720 2.715 2.705 2.622
NAME Feb28-2014-MMM
EXPNO 30
PROCNO 1
Date_ 20140228
Time 18.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 299.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.30 usec
PL1 -3.50 dB
SFO1 400.1724712 MHz
SI 32768
SF 400.1700155 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm
1.04 13.68 5.25 1.00 1.01 1.02 3.06 2.13 4.15 1.03 1.91

4-Me_HO-Pummerer



3b





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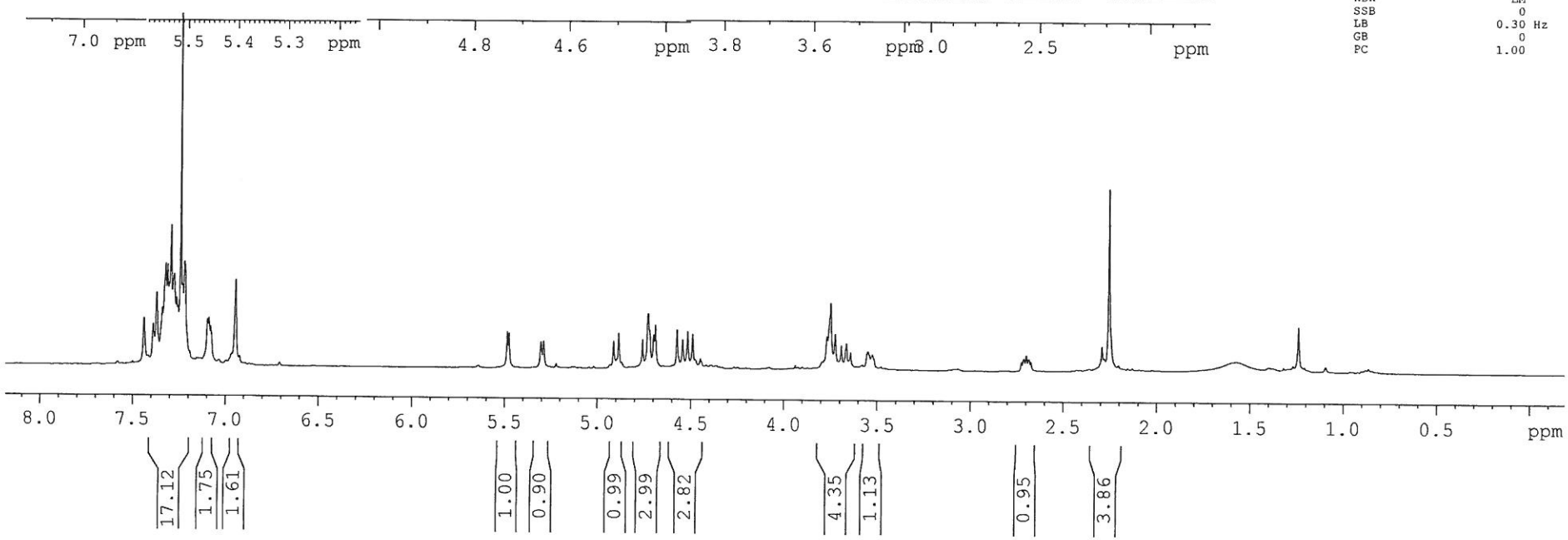
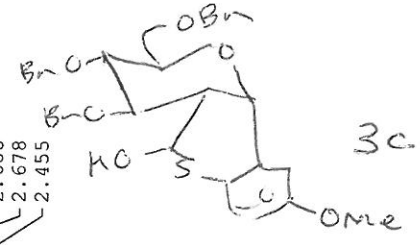
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	114
DW	60.800 usec
DE	6.50 usec
TE	297.4 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	9.30 usec
PL1	-3.50 dB
SFO1	400.1724712 MHz
SI	32768
SF	400.1700158 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



4-MeO-HO-Pum



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PROCNO	1
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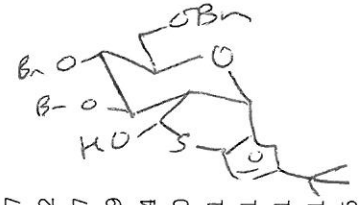
Time	18.40
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	50.8
DW	60.800 usec
DE	6.50 usec
TE	294.6 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.30 usec
PL1	-3.50 dB
SFO1	400.1724712 MHz
SI	32768
SF	400.1700157 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

tert-Butyl_HO-Pum



3d

NAME	Apr26-2014-MMM
EXPNO	20
PROCNO	1
Date_	20140426
Time	11.58
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	101
DW	60.800 usec
DE	6.50 usec
TE	288.6 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	9.30 usec
PL1	-3.50 dB
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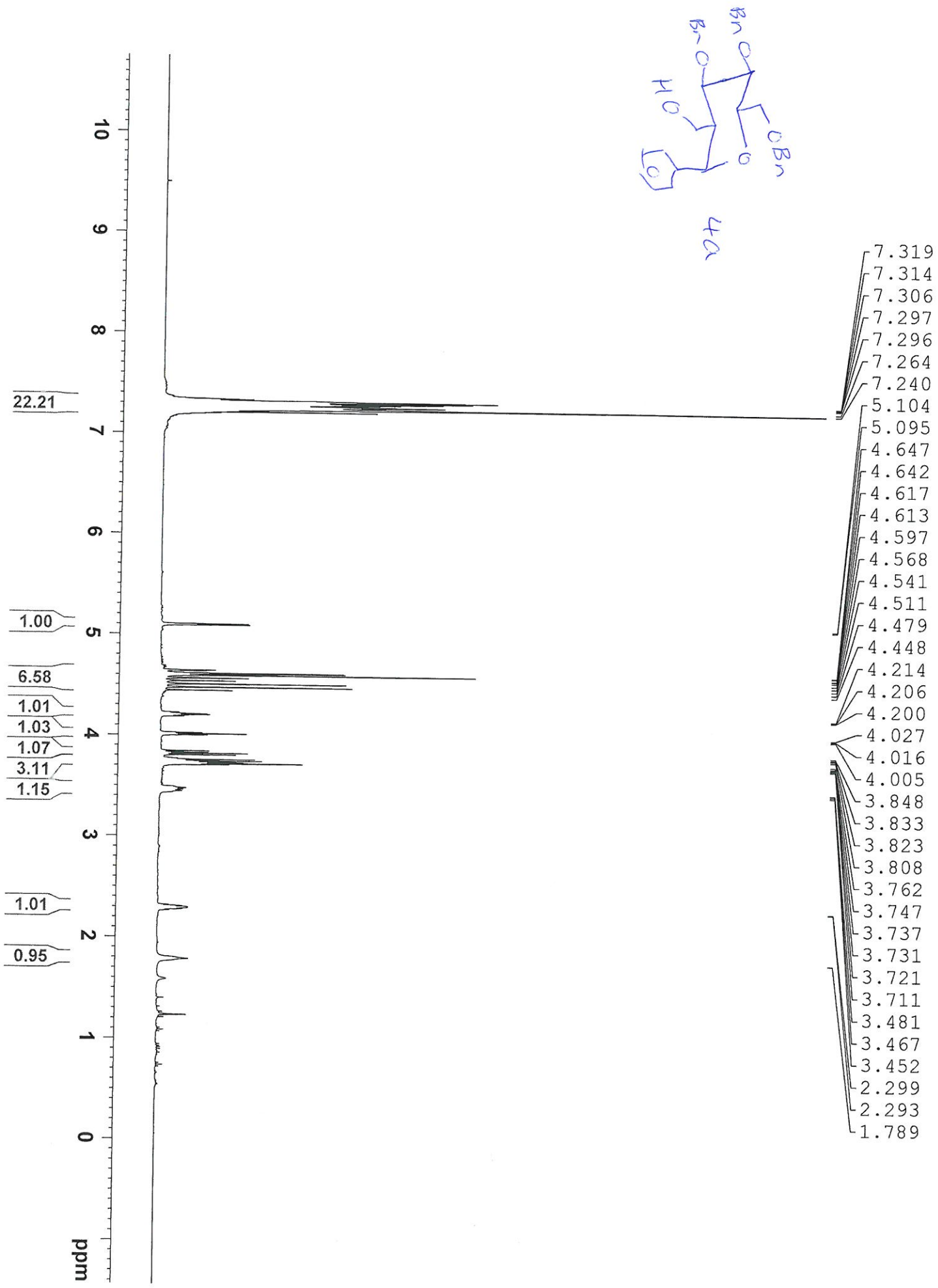
SI	32768
SF	400.1700160 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00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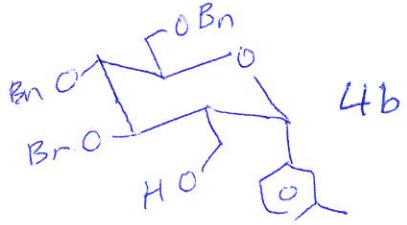
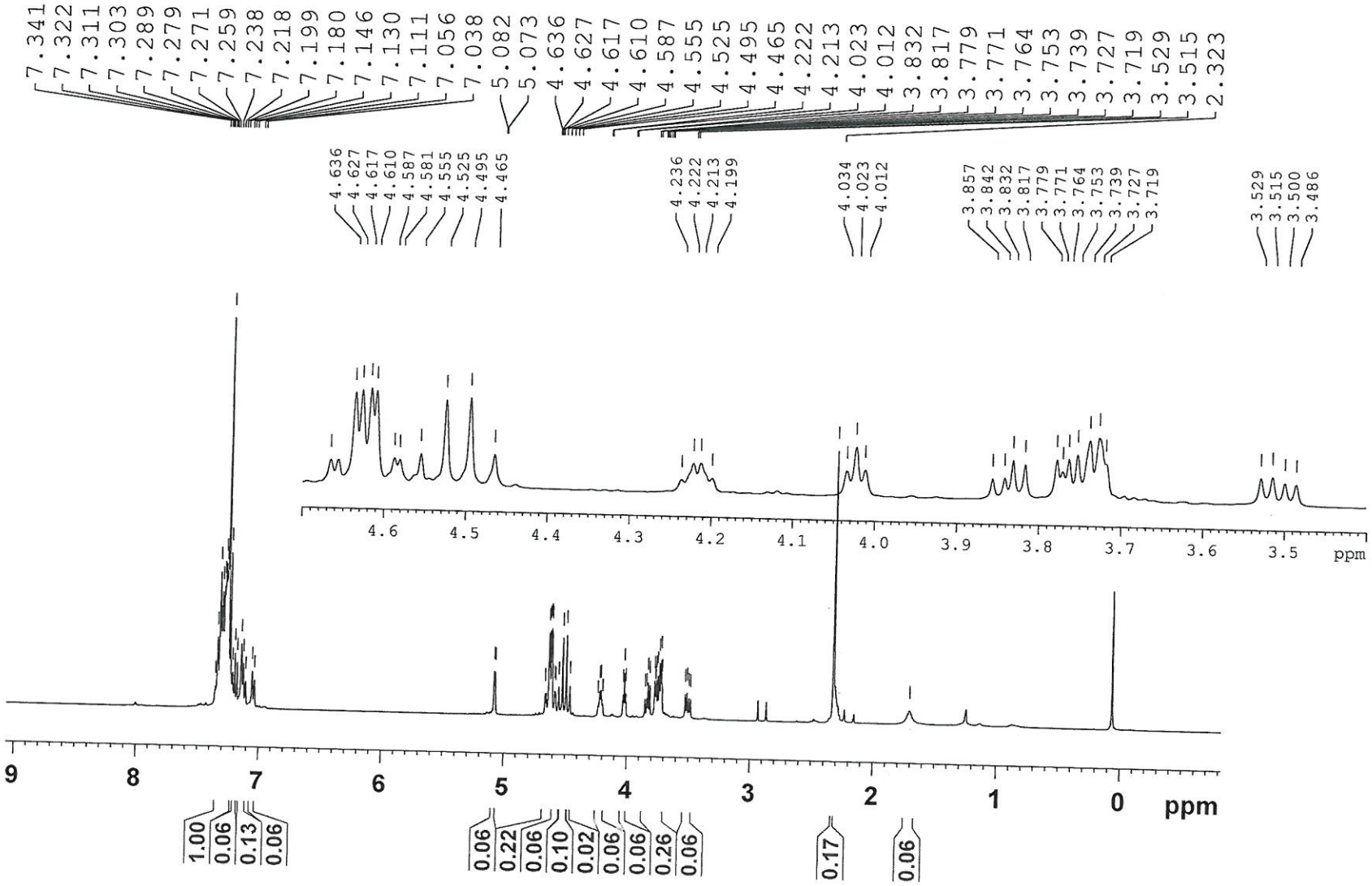
7.296
7.264
7.240
5.104
5.095
4.647
4.642
4.617
4.613
4.597
4.568
4.541
4.511
4.479
4.448
4.214
4.206
4.200
4.027
4.016
4.005
3.848
3.833
3.823
3.808
3.762
3.747
3.737
3.731
3.721
3.711
3.481
3.467
3.452
2.299
2.293
1.789
22.21
1.00
6.58
1.01
1.03
1.07
3.11
1.15
1.01
0.95
ppm
4a

4M_OH


OBn
BnO
O
BnO
HO
O
4b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7.322
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7.303
7.289
7.279
7.271
7.259
7.238
7.218
7.199
7.180
7.146
7.130
7.111
7.056
7.038
5.082
5.073
4.636
4.627
4.617
4.610
4.587
4.555
4.525
4.495
4.465
4.222
4.213
4.023
4.012
3.832
3.817
3.779
3.771
3.764
3.753
3.739
3.727
3.719
3.529
3.515
2.323
4.636
4.627
4.617
4.610
4.587
4.581
4.555
4.525
4.495
4.465
4.236
4.222
4.213
4.199
4.034
4.023
4.012
3.857
3.842
3.832
3.817
3.779
3.771
3.764
3.753
3.739
3.727
3.719
3.529
3.515
3.500
3.486
ppm
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.06
0.13
0.06
0.06
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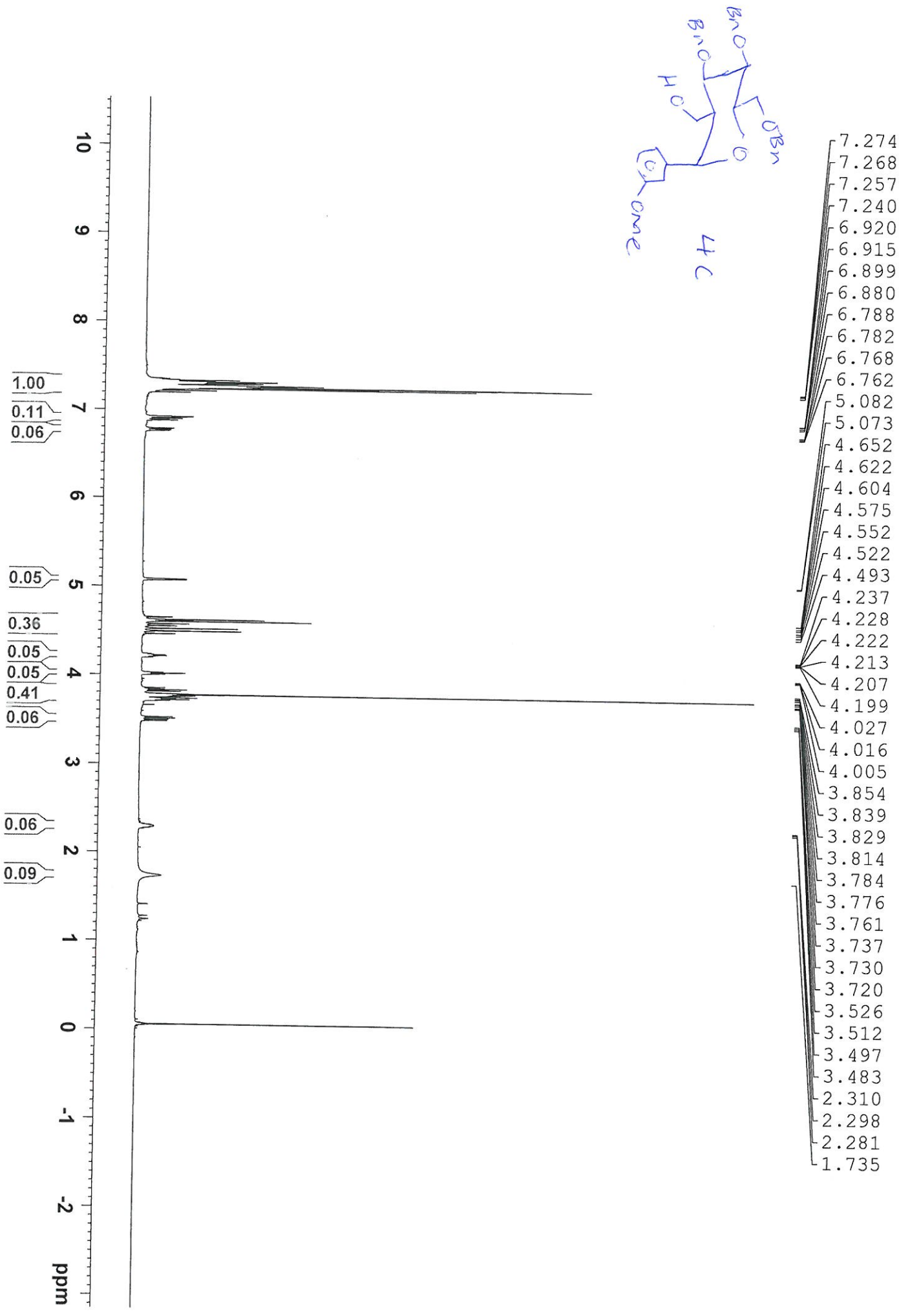
0.06
0.10
0.02
0.06
0.06
0.26
0.06
0.17
0.06


BnO
BnO
HO
OBn
O
OMe
4C
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7.268
7.257
7.240
6.920
6.915
6.899
6.880
6.788
6.782
6.768
6.762
5.082
5.073
4.652
4.622
4.604
4.575
4.552
4.522
4.493
4.237
4.228
4.222
4.213
4.207
4.199
4.027
4.016
4.005
3.854
3.839
3.829
3.814
3.784
3.776
3.761
3.737
3.730
3.720
3.526
3.512
3.497
3.483
2.310
2.298
2.281
1.735
1.00
0.11
0.06
0.05
0.36
0.05
0.05
0.41
0.06
0.06
0.09
10
9
8
7
6
5
4
3
2
1
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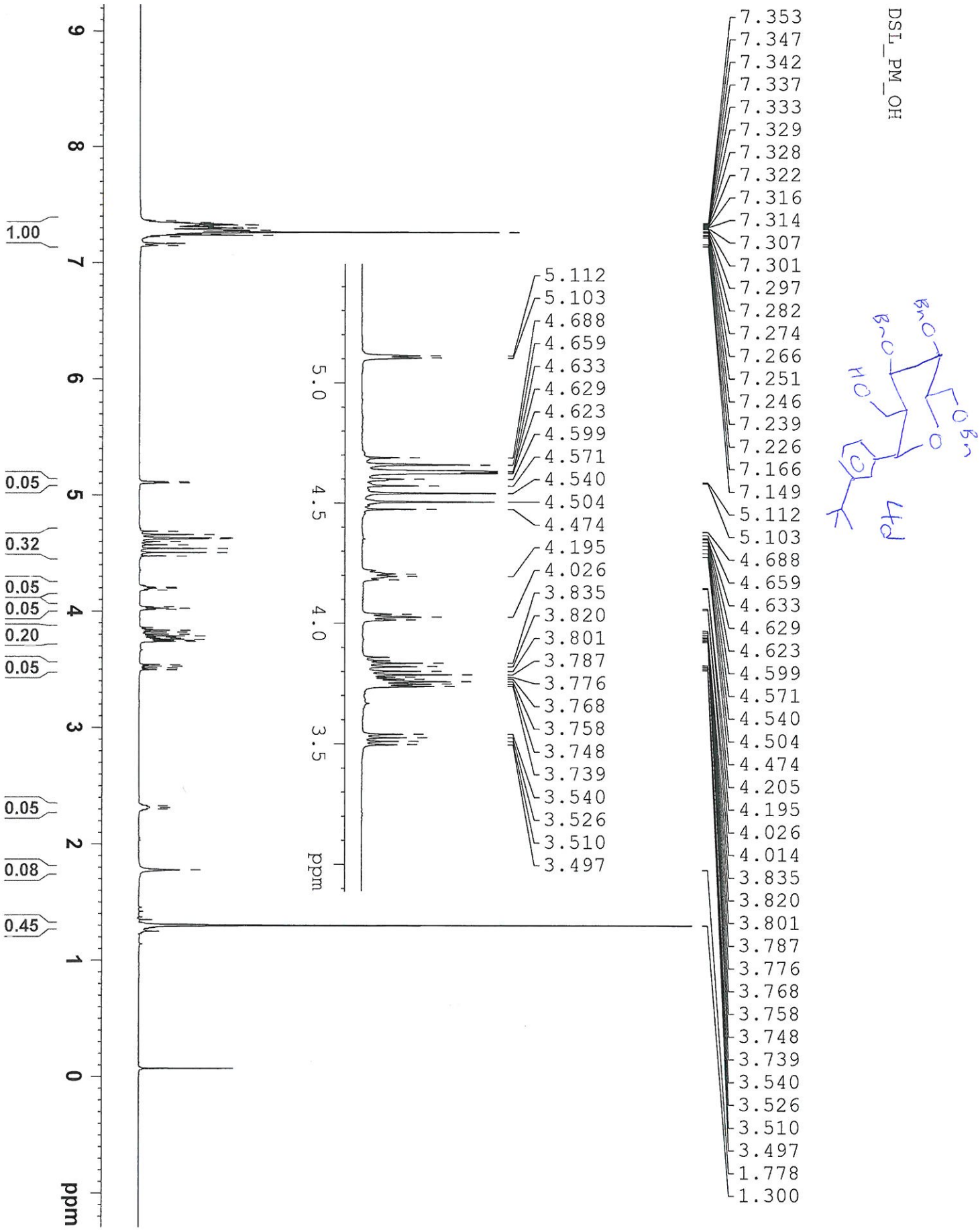
-1
-2
ppm


DSL_PM_OH
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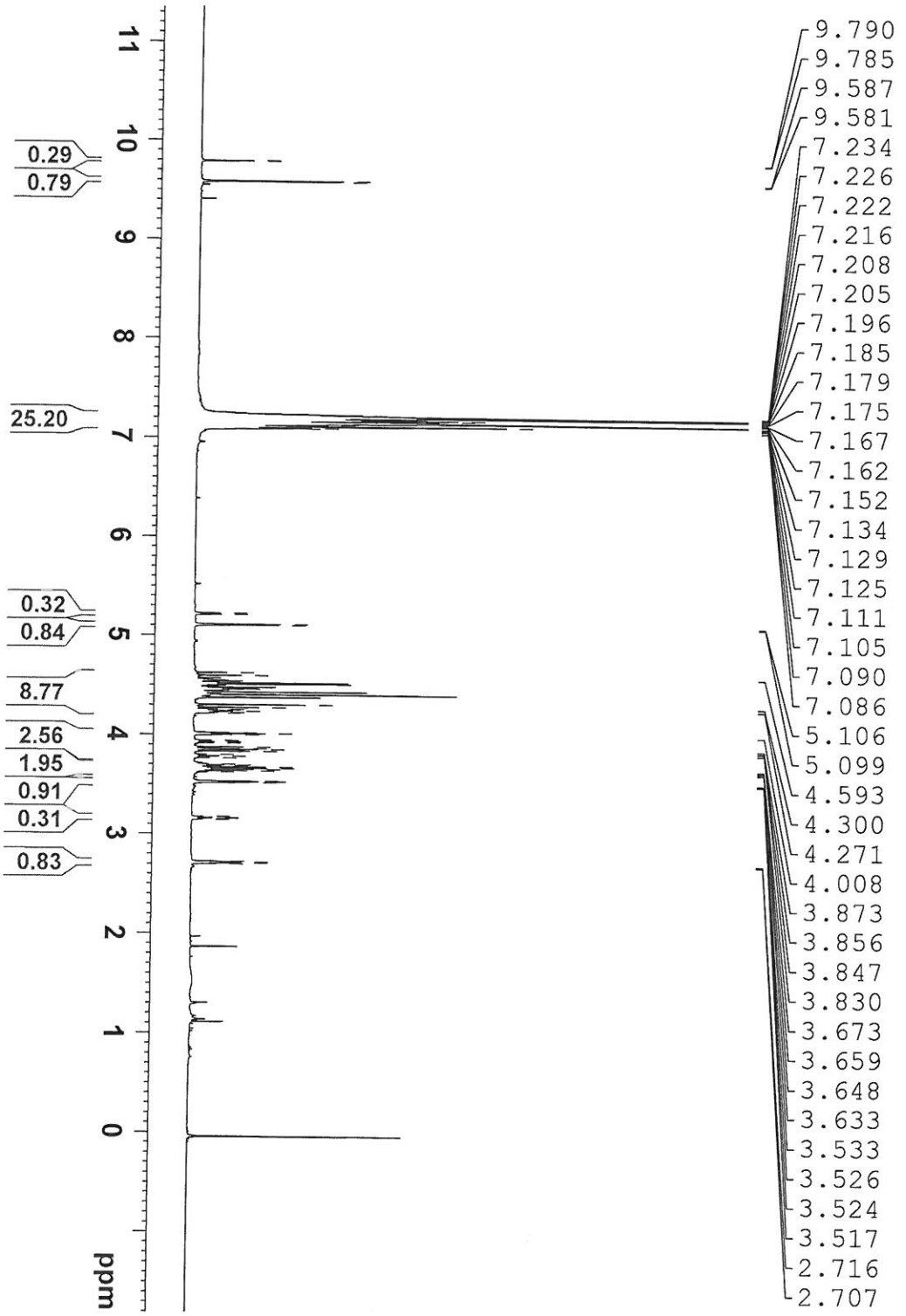
7.337
7.333
7.329
7.328
7.322
7.316
7.314
7.307
7.301
7.297
7.282
7.274
7.266
7.251
7.246
7.239
7.226
7.166
7.149
5.112
5.103
4.688
4.659
4.633
4.629
4.623
4.599
4.571
4.540
4.504
4.474
4.205
4.195
4.026
4.014
3.835
3.820
3.801
3.787
3.776
3.768
3.758
3.748
3.739
3.540
3.526
3.510
3.497
1.778
1.300
BnO
BnO
HO
OBn
4d
1.00
0.05
0.32
0.05
0.05
0.20
0.05
0.05
0.08
0.45
ppm
5.0
4.5
4.0
3.5
ppm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0.79
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0.84
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1.95
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0.31
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ppm
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9.785
9.587
9.581
7.234
7.226
7.222
7.216
7.208
7.205
7.196
7.185
7.179
7.175
7.167
7.162
7.152
7.134
7.129
7.125
7.111
7.105
7.090
7.086
5.106
5.099
4.593
4.300
4.271
4.008
3.873
3.856
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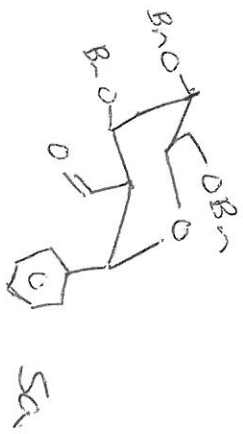
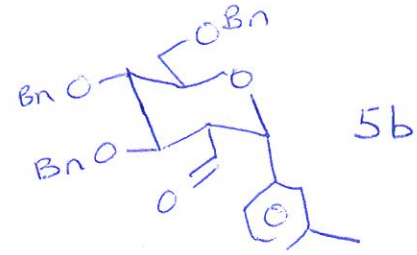
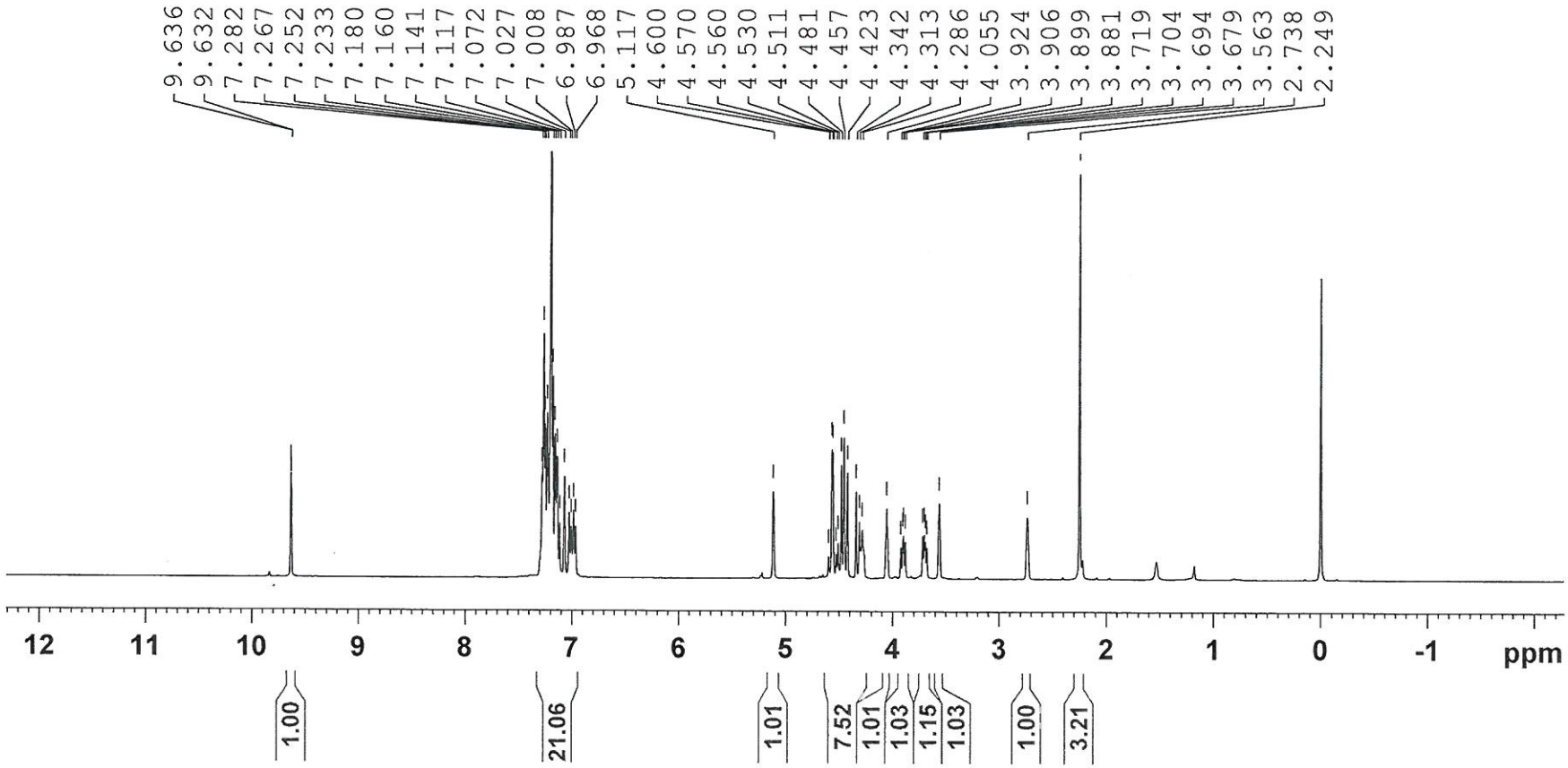
3.533
3.526
3.524
3.517
2.716
2.707


BnO
BnO
OBn
O
O
O

5g

4M_ALDEHYDE


OBn
BnO
BnO
O
O
5b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7.008
6.987
6.968
5.117
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4.560
4.530
4.511
4.481
4.457
4.423
4.342
4.313
4.286
4.055
3.924
3.906
3.899
3.881
3.719
3.704
3.694
3.679
3.563
2.738
2.249
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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1.01
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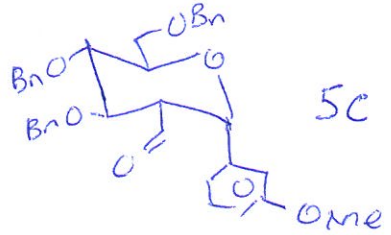
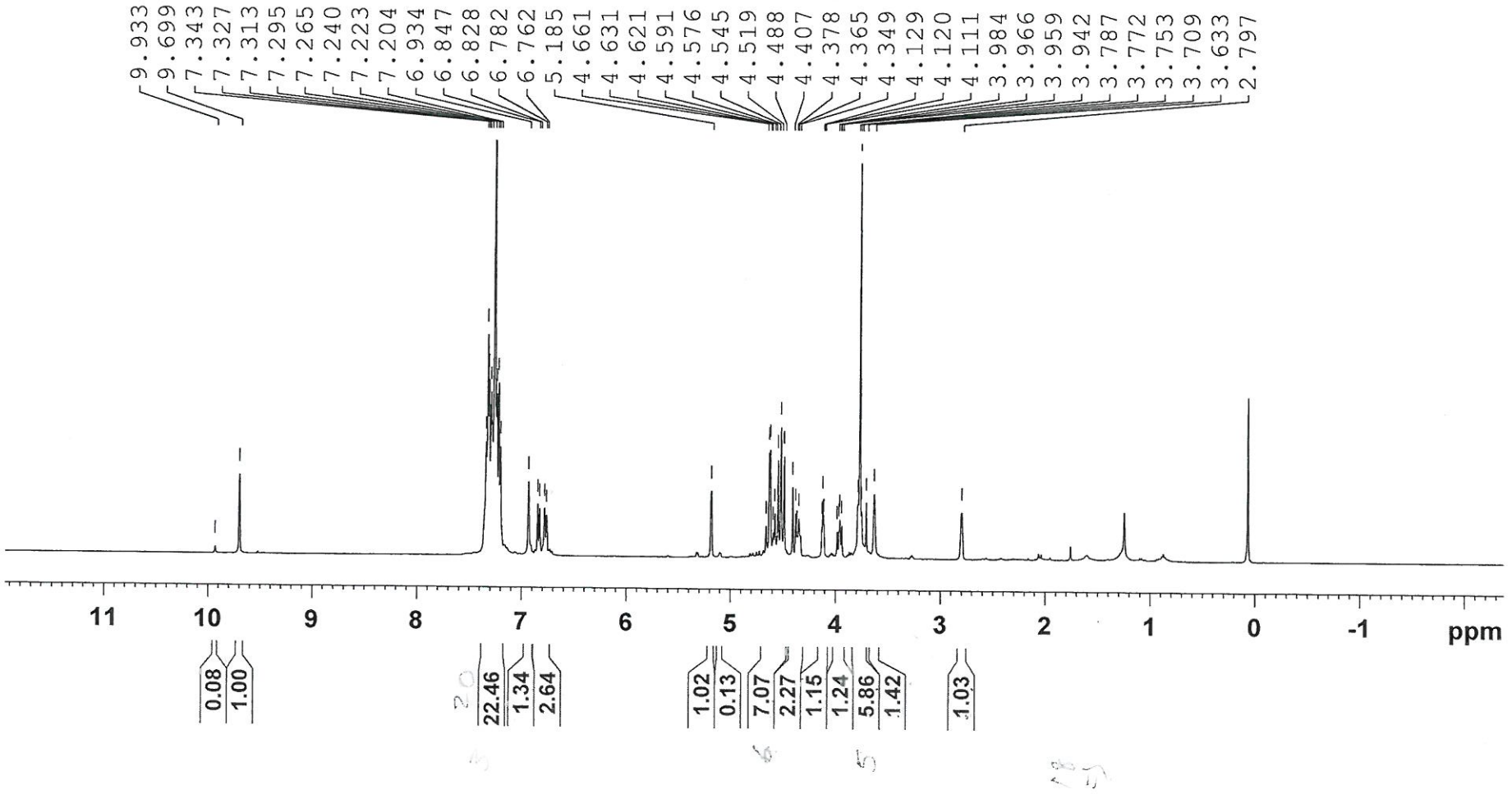
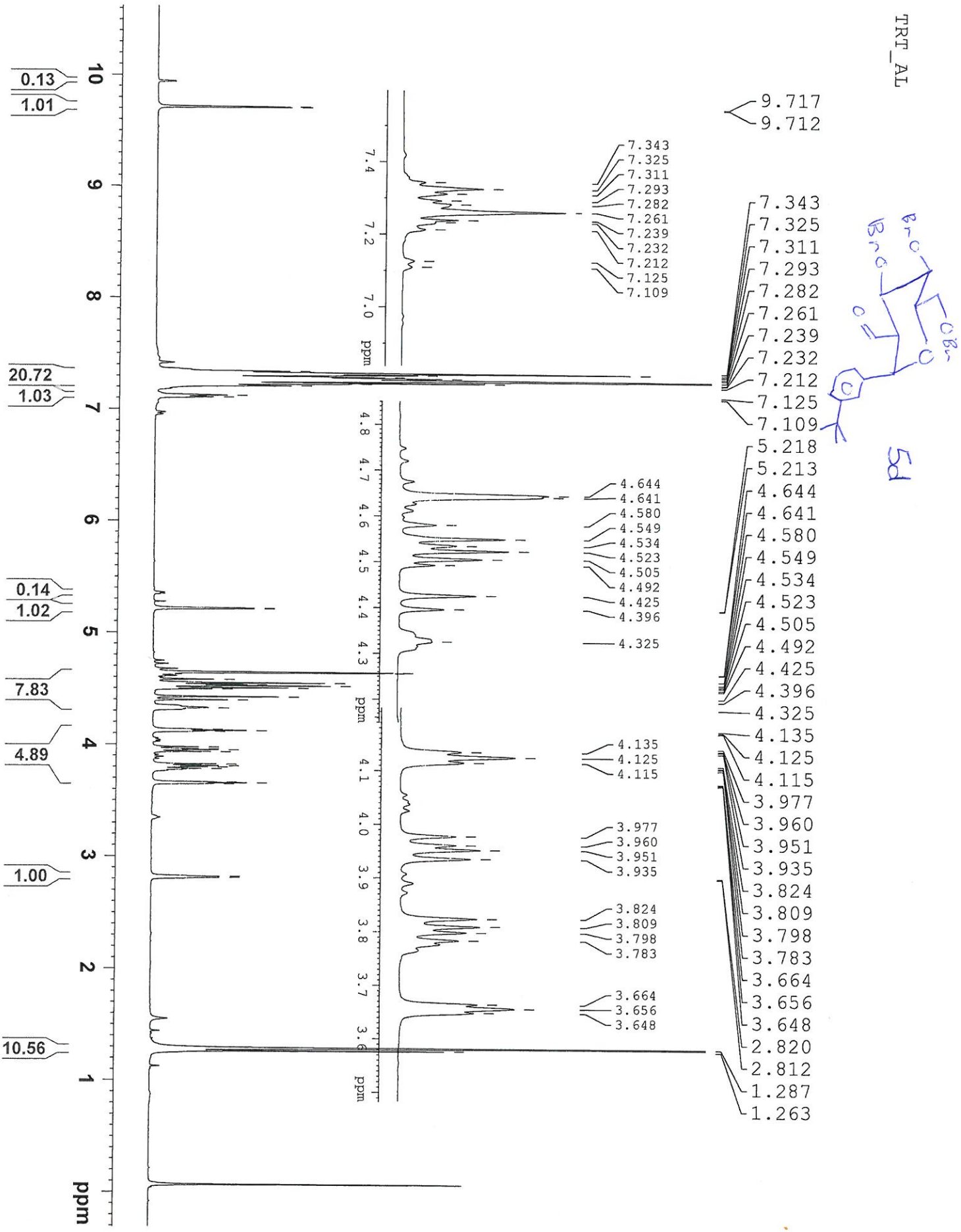
1.03
1.00
3.21

methoxy_al_rn






TRT_AL
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7.239
7.232
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7.125
7.109
5.218
5.213
4.644
4.641
4.580
4.549
4.534
4.523
4.505
4.492
4.425
4.396
4.325
4.135
4.125
4.115
3.977
3.960
3.951
3.935
3.824
3.809
3.798
3.783
3.664
3.656
3.648
2.820
2.812
1.287
1.263
0.13
1.01
20.72
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0.14
1.02
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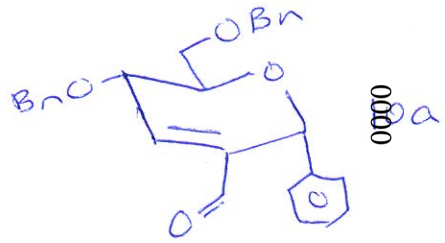
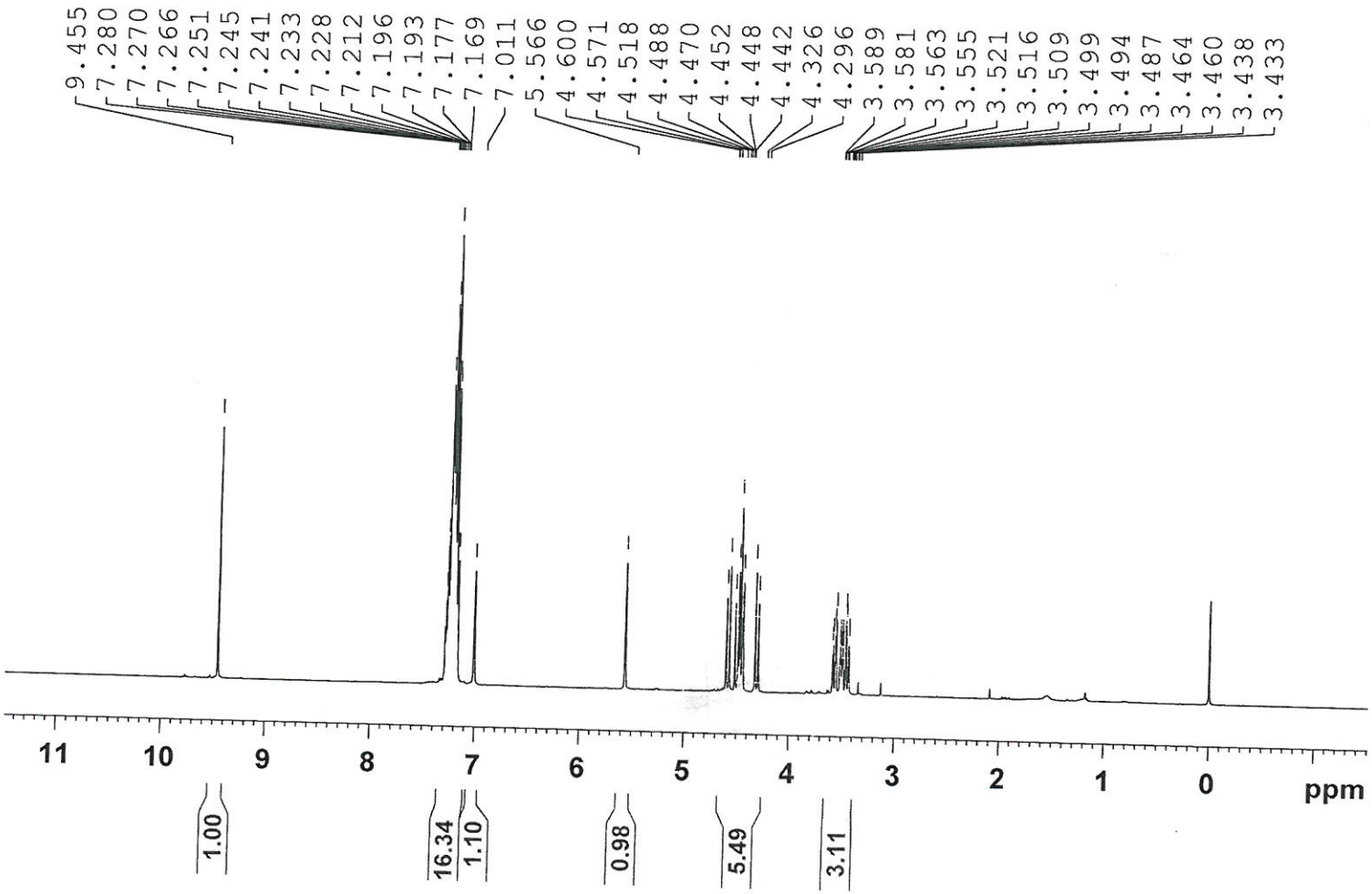
1.00
10.56
ppm
5d

THIOPHENOL_FERRIER

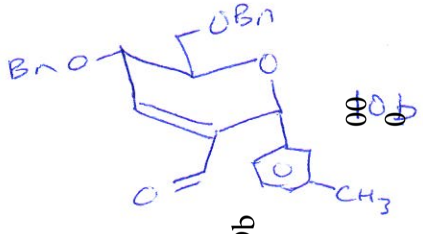


9a

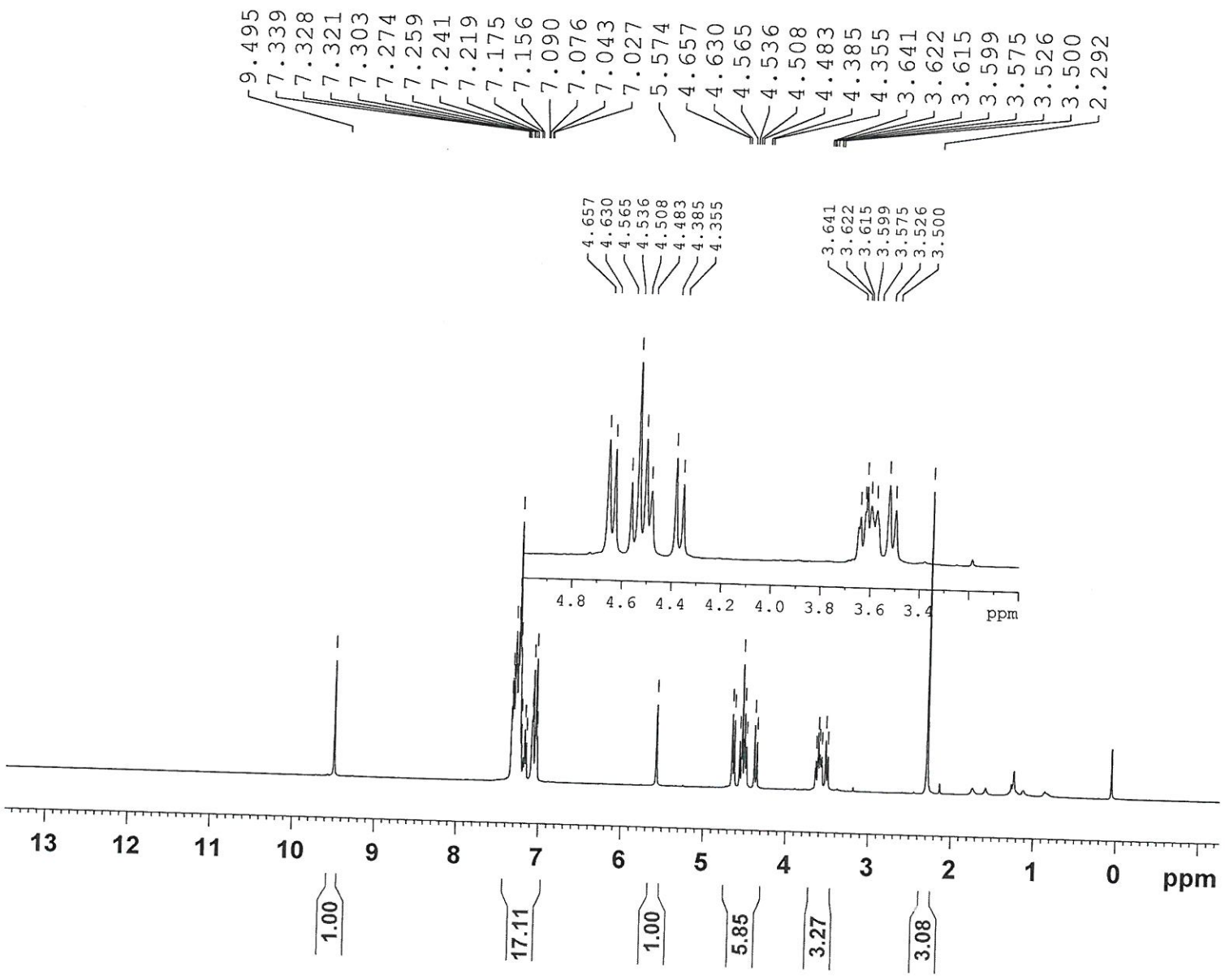
NAME	THIOPHENOL_FERRRIER
EXPNO	10
PROCNO	1
Date_	20140703
Time	18.09
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	50.8
DW	60.800 usec
DE	6.50 usec
TE	286.8 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	9.30 usec
PL1	-3.50 dB
SFO1	400.1724712 MHz
SI	32768
SF	400.1700446 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



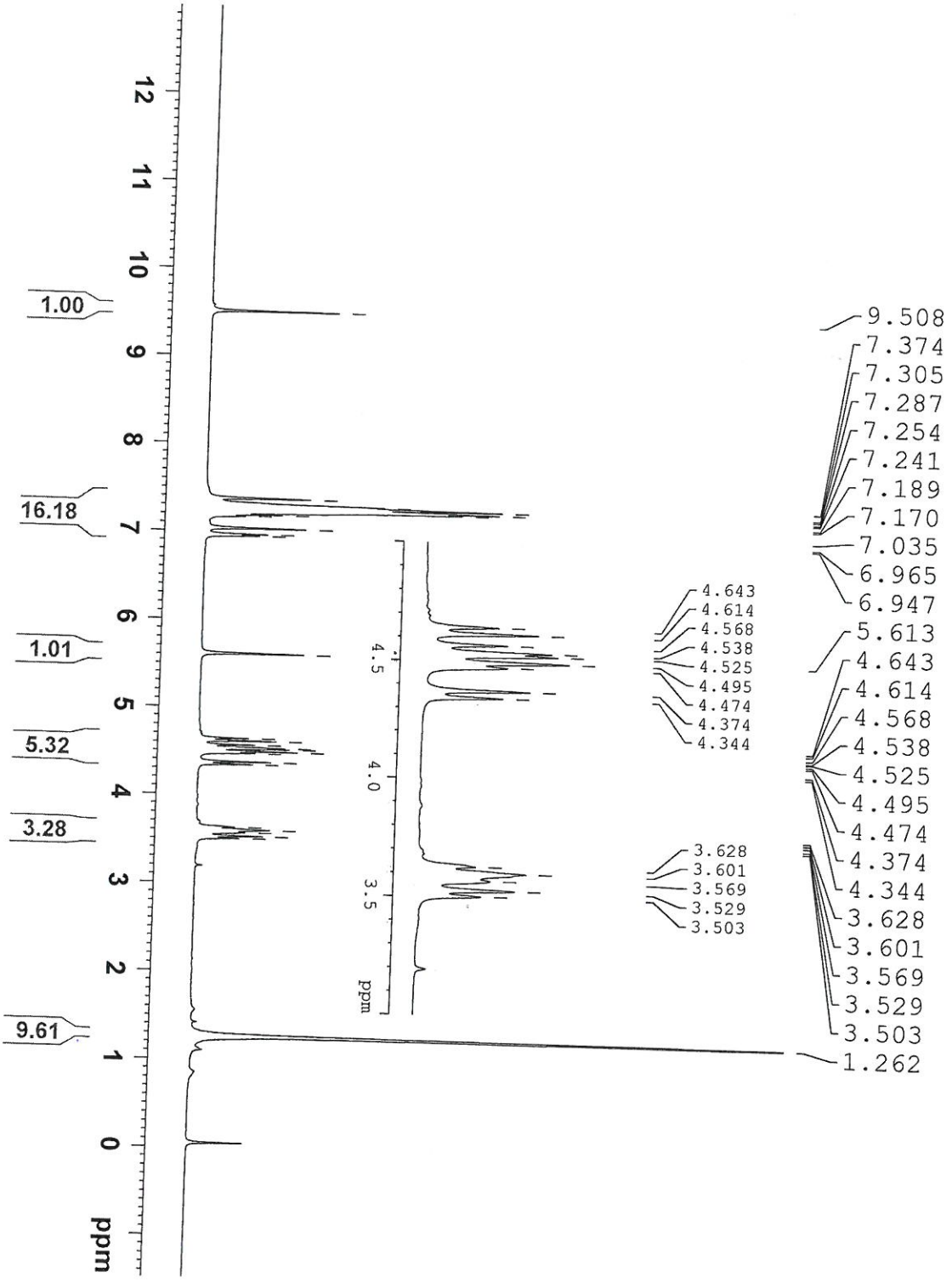
4M_FERRIER

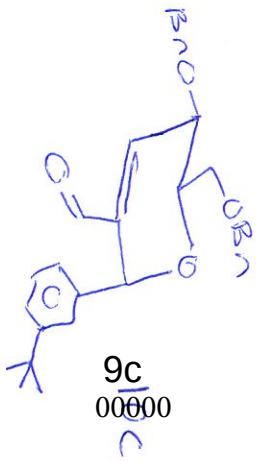


9b



TRT_FERRIER

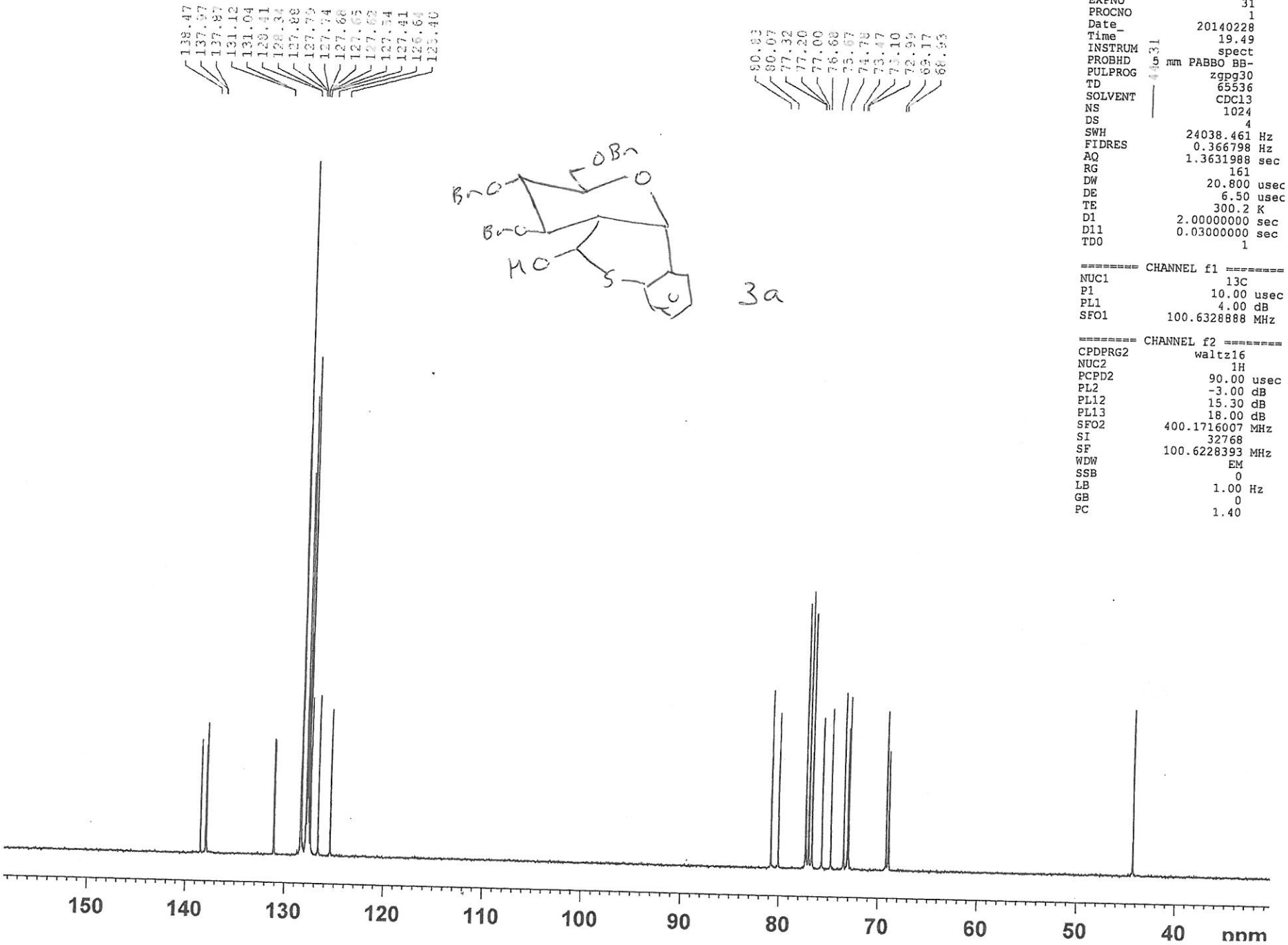




9c

00000

H_HO-Pummerer



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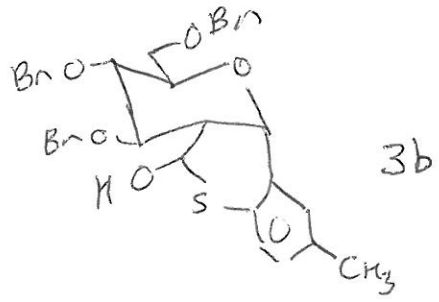
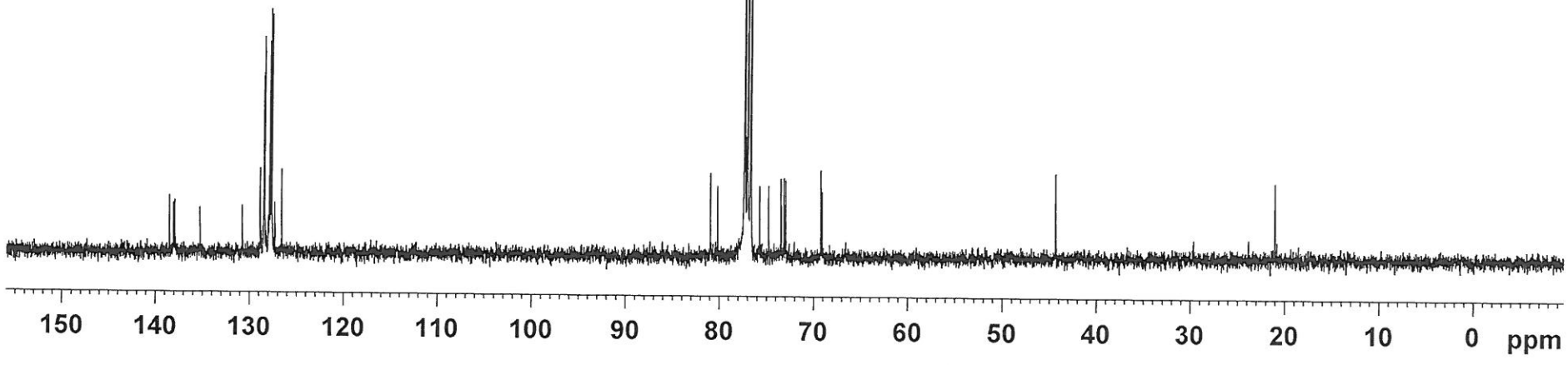
EXPNO	31
PROCNO	1
Date_	20140228
Time	19.49
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	161
DW	20.800 usec
DE	6.50 usec
TE	300.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	13C
P1	10.00 usec
PL1	4.00 dB
SFO1	100.6328888 MHz
========	CHANNEL f2 ========
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-3.00 dB
PL12	15.30 dB
PL13	18.00 dB
SFO2	400.1716007 MHz
SI	32768
SF	100.6228393 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

4-Methyl_HO-Pummerer

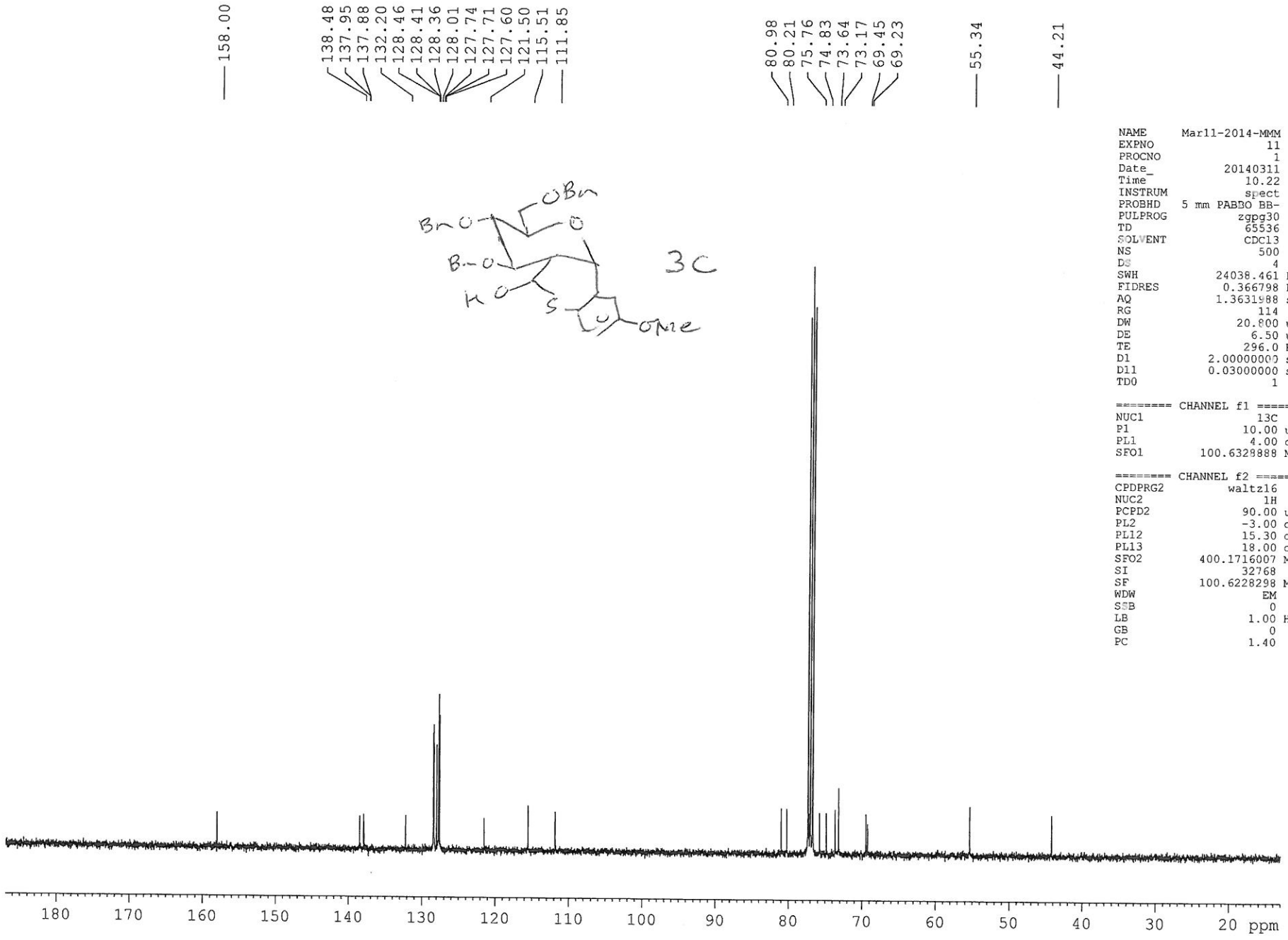


3b

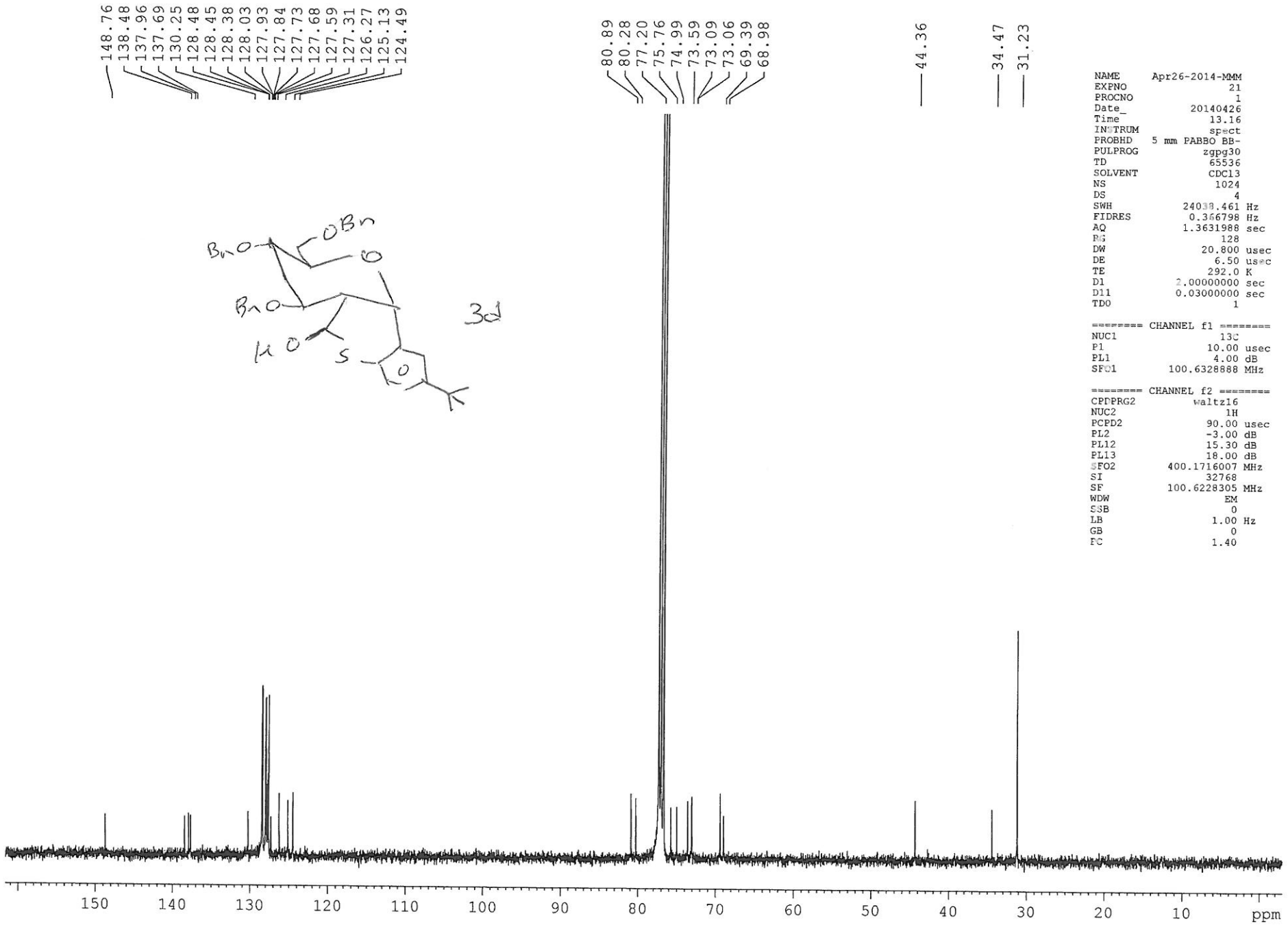
NAME	Feb23-2014-MMM
EXPNO	32
PROCNO	1
Date_	20140224
Time	6.39
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	80.6
DW	20.800 usec
DE	6.50 usec
TE	297.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	4.00 dB
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-3.00 dB
PL12	15.30 dB
PL13	18.00 dB
SFO2	400.1716007 MHz
SI	32768
SF	100.6226267 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



4-MeO_HO-Pummerer

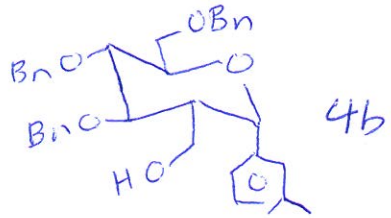


tert-Butyl_HO-Pum



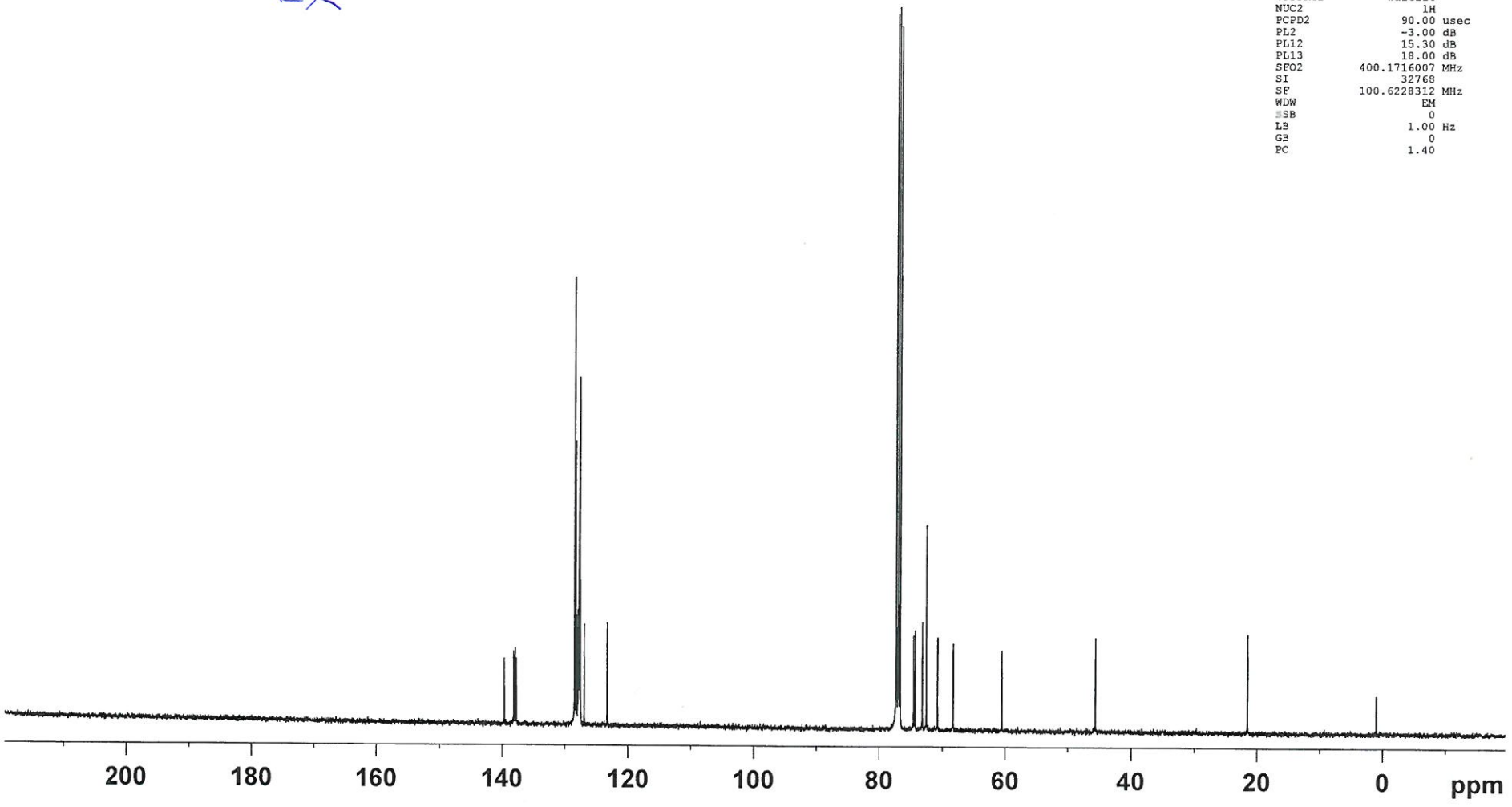
BnO
BnO
HO
OBn
O
O
4a
139.77
138.18
138.09
137.72
128.49
128.30
128.25
127.84
127.79
127.74
127.63
127.54
127.17
126.25
77.32
77.00
76.88
76.68
74.56
74.26
73.15
72.53
72.49
70.71
68.26
60.41
45.60
200
180
160
140
120
100
80
60
40
20
0
ppm

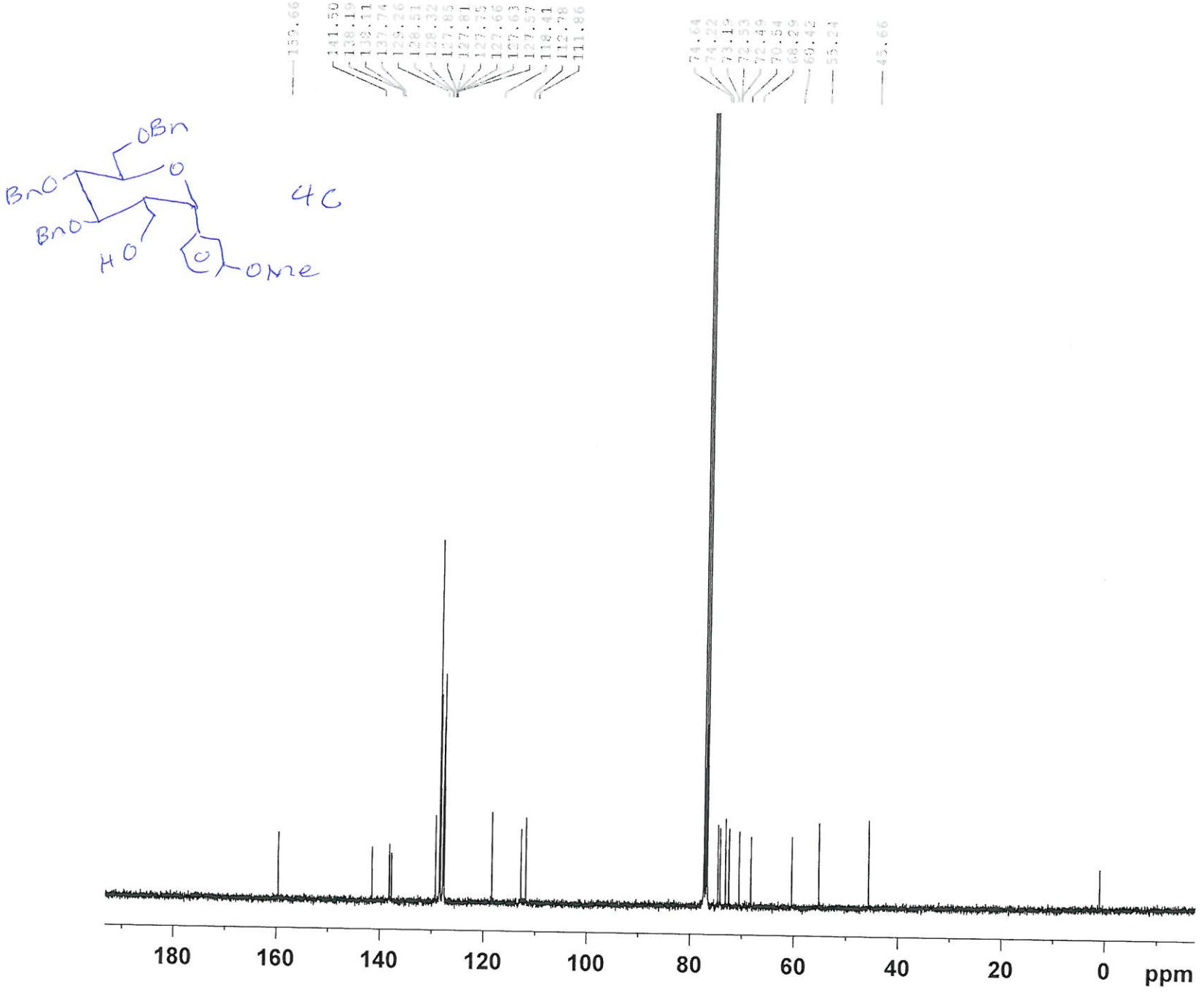
4M_OH



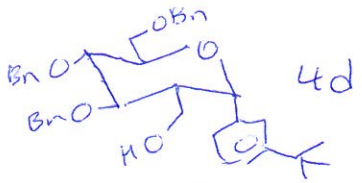
4b

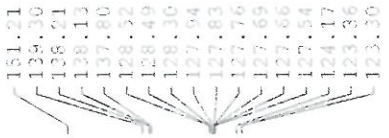
NAME	4M_OH
EXPNO	20
PROCNO	1
Date_	20140605
Time	2.20
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	2000
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	144
DW	20.800 usec
DE	6.50 usec
TE	294.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	4.00 dB
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-3.00 dB
PL12	15.30 dB
PL13	18.00 dB
SFO2	400.1716007 MHz
SI	32768
SF	100.6228312 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

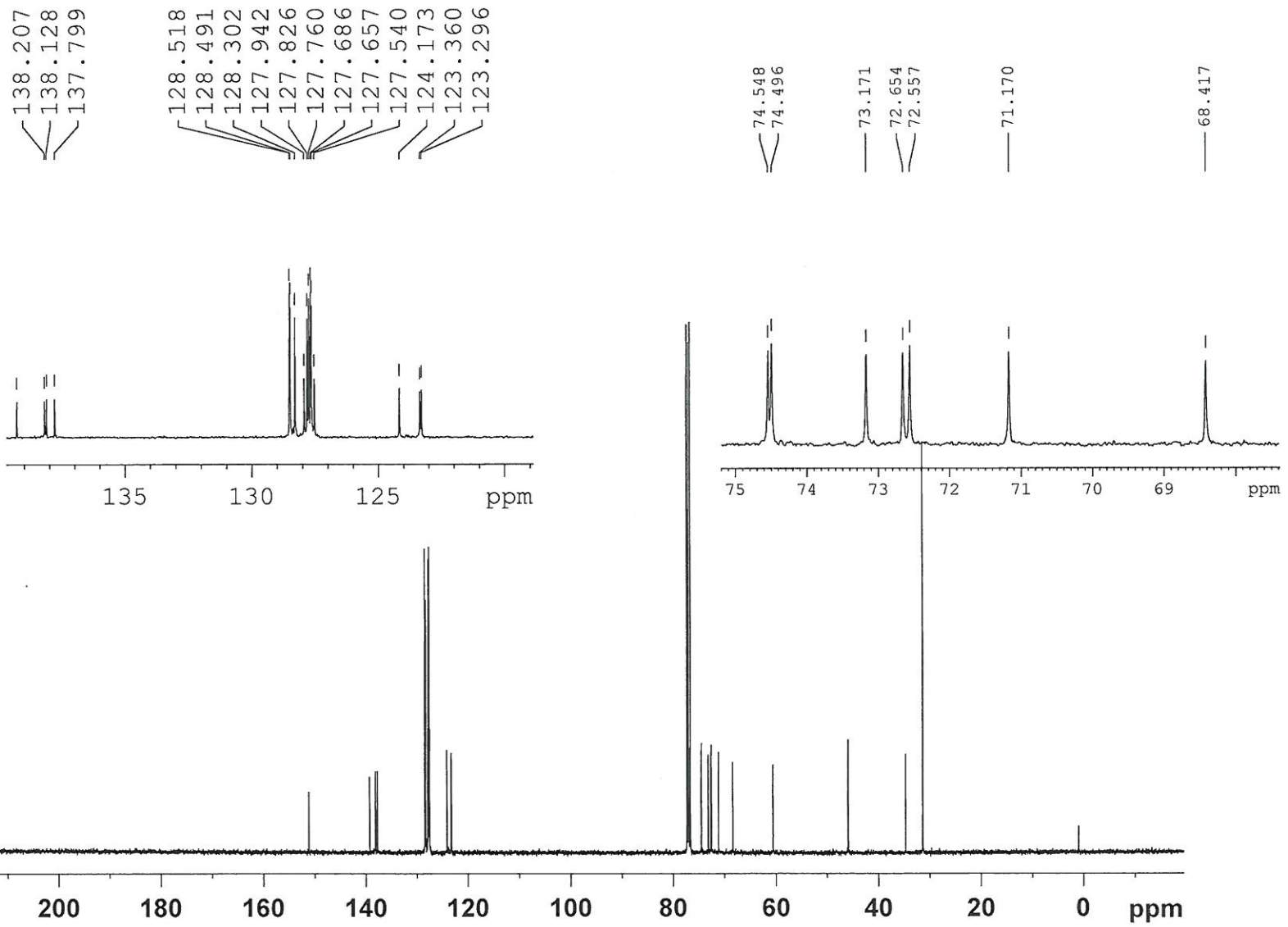



159.66
141.50
138.19
138.11
137.74
134.26
128.51
128.32
127.85
127.81
127.75
127.66
127.63
127.57
118.41
112.78
111.86
74.64
74.22
73.15
72.53
72.49
70.54
68.29
69.42
55.21
45.66
OBn
BnO
BnO
HO
OMe
4C
180
160
140
120
100
80
60
40
20
0
ppm

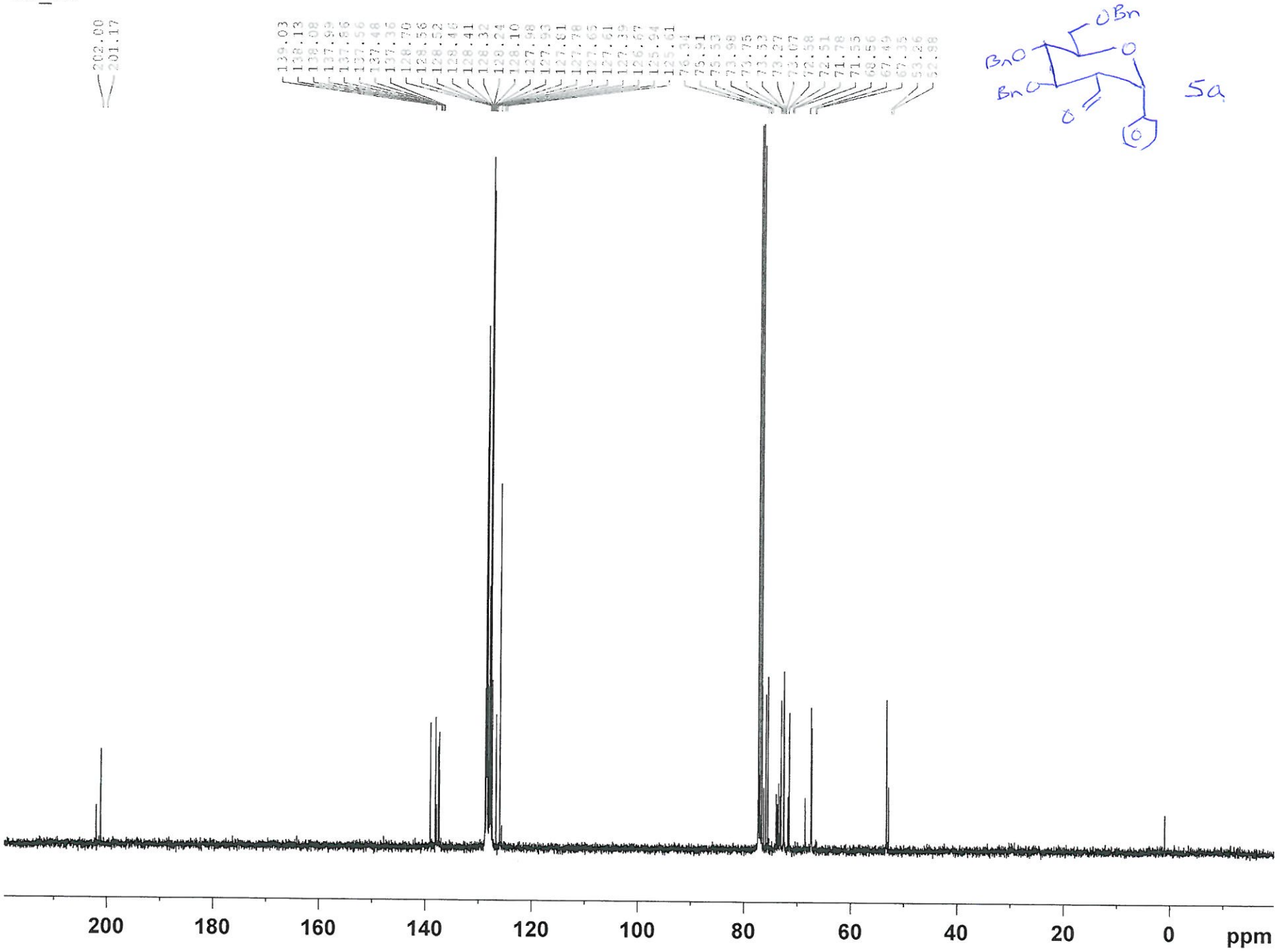
DSL_PM_OH


OBn
BnO
BnO
HO
4d

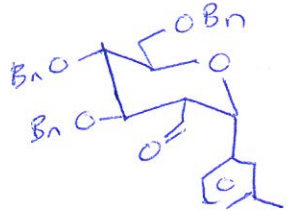

151.21
139.30
138.21
138.13
137.80
128.52
128.49
128.30
127.94
127.83
127.76
127.69
127.66
127.54
124.17
123.36
123.30
74.55
74.50
73.17
72.65
72.56
71.17
68.42
60.60
45.93
34.70
31.37


138.207
138.128
137.799
128.518
128.491
128.302
127.942
127.826
127.760
127.686
127.657
127.540
124.173
123.360
123.296
74.548
74.496
73.171
72.654
72.557
71.170
68.417
135
130
125
ppm
75
74
73
72
71
70
69
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

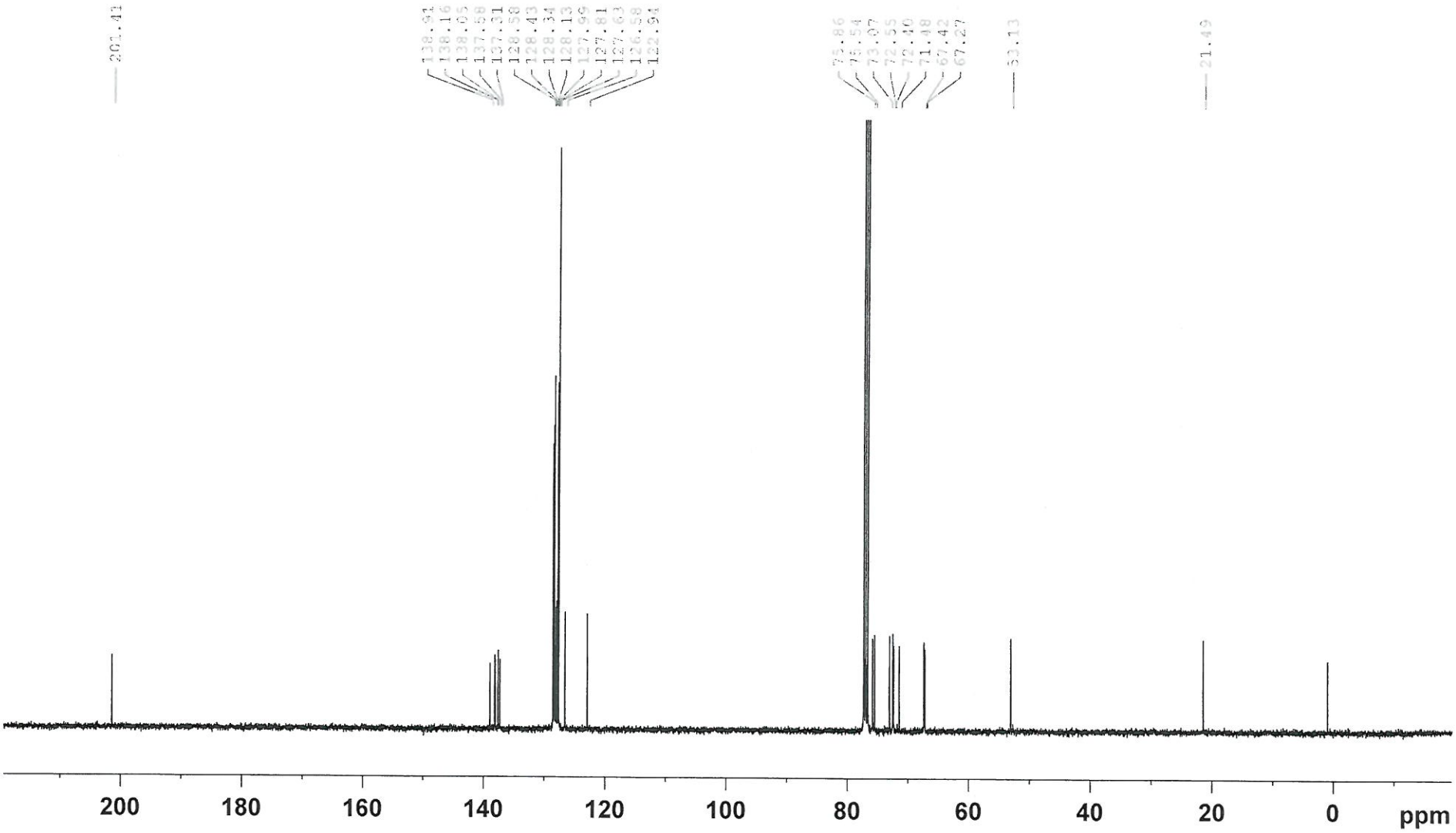
RN_AL

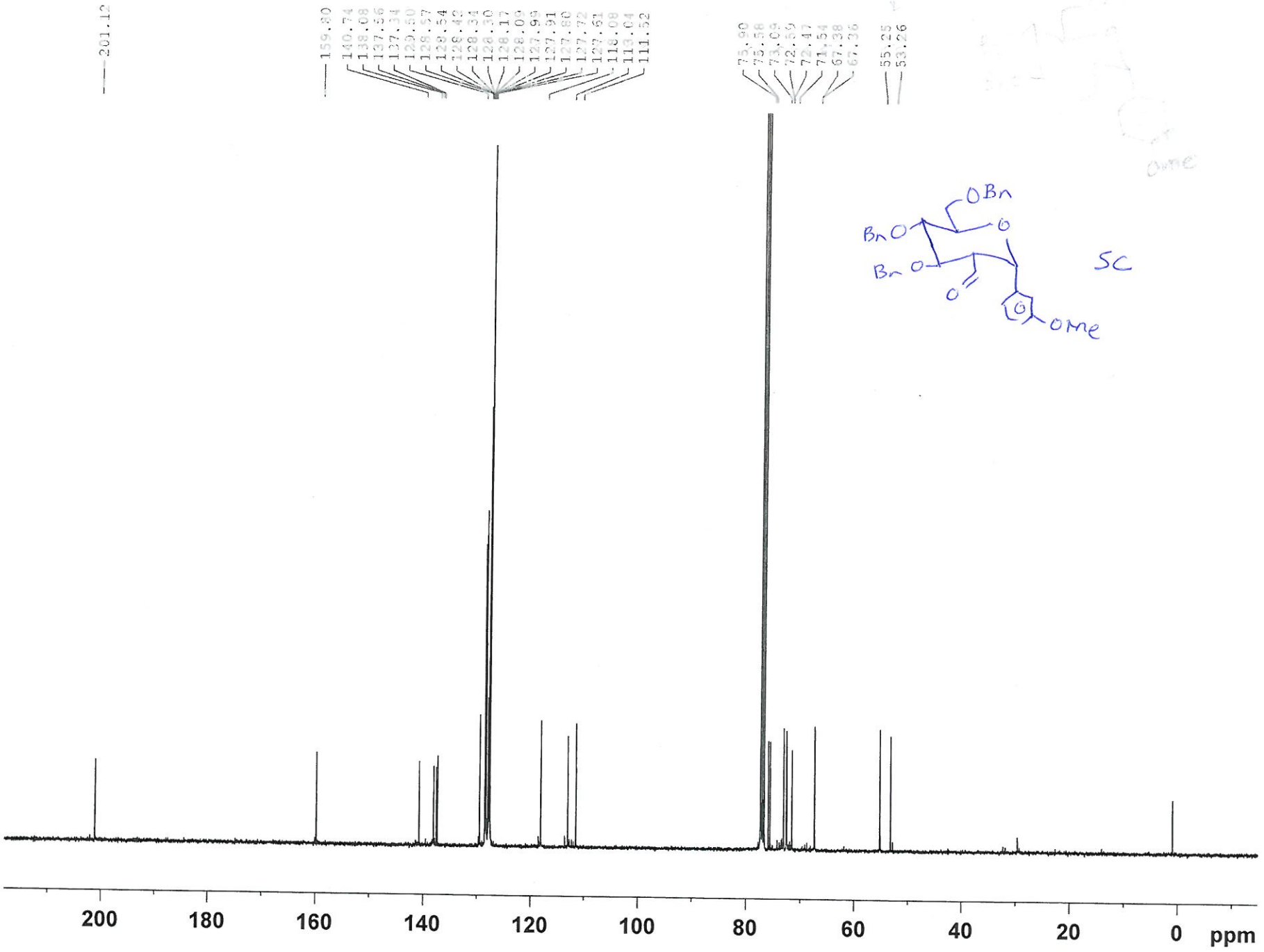

202.00
201.17
139.03
138.13
138.08
137.99
137.86
137.56
137.48
137.36
128.70
128.56
128.52
128.46
128.41
128.32
128.24
128.10
127.98
127.93
127.81
127.78
127.65
127.61
127.39
126.67
125.94
125.61
76.34
75.91
75.53
73.98
73.75
73.53
73.27
73.07
72.58
72.51
71.78
71.53
68.56
67.49
67.35
53.26
52.98
OBn
BnO
BnO
O
O
O
5a
200
180
160
140
120
100
80
60
40
20
0
ppm

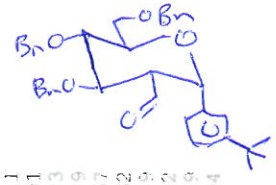
4M_ALDEHYDE



5b




methoxy_al_rn
201.12
159.80
140.74
138.08
137.56
137.34
129.50
128.57
128.54
128.46
128.34
128.30
128.17
128.05
127.99
127.91
127.80
127.72
127.61
118.08
113.04
111.52
75.90
75.58
73.05
72.59
72.47
71.54
67.38
67.36
55.25
53.26
OBn
BnO
OBn
O
O
OMe
5C
200
180
160
140
120
100
80
60
40
20
0
ppm



TRT_AL

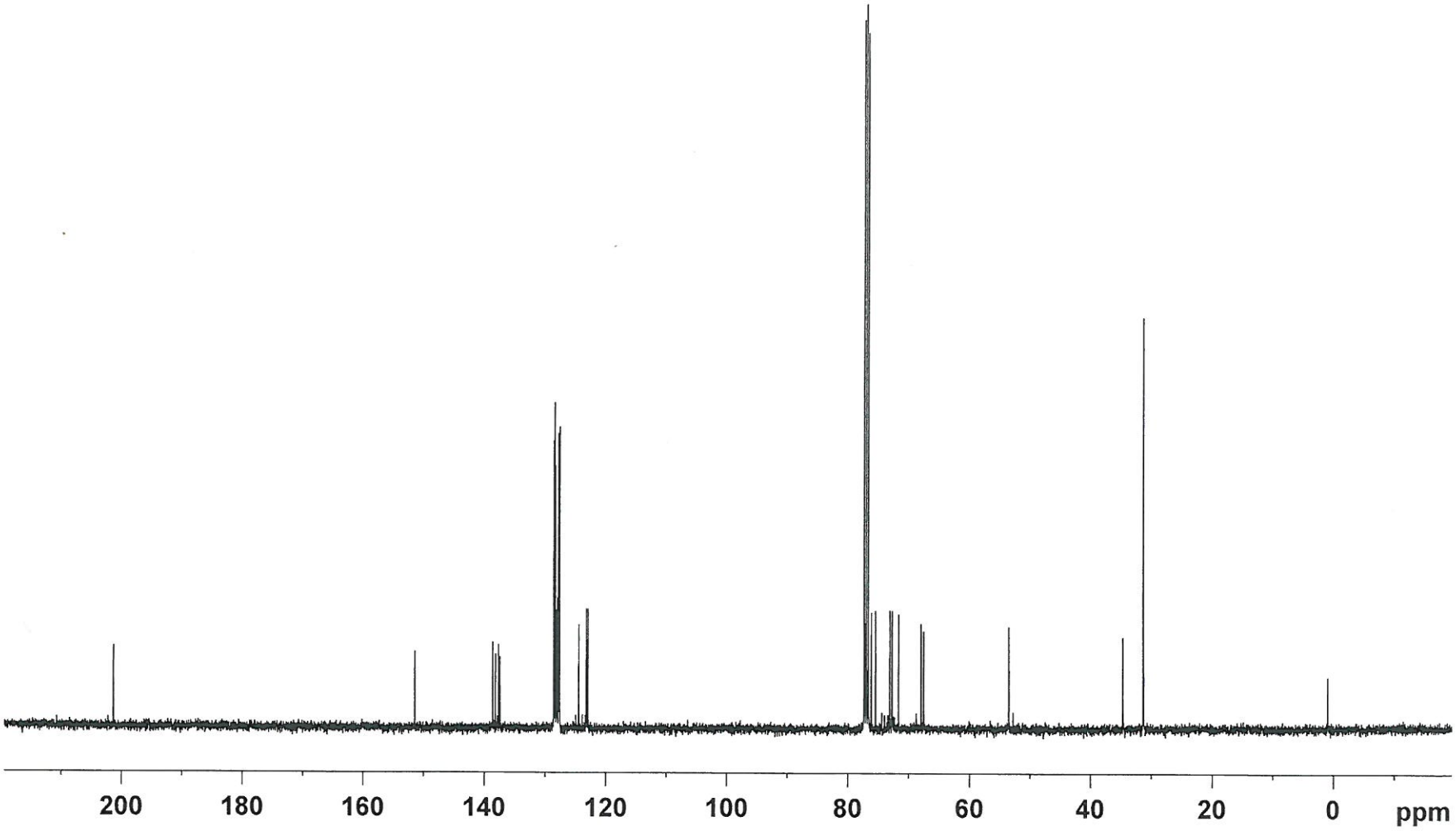
201.34

151.46
138.65
138.17
137.67
137.46
128.59
128.54
128.43
128.34
128.15
128.11
128.01
127.83
127.79
127.67
127.62
127.59
124.42
123.19
122.94

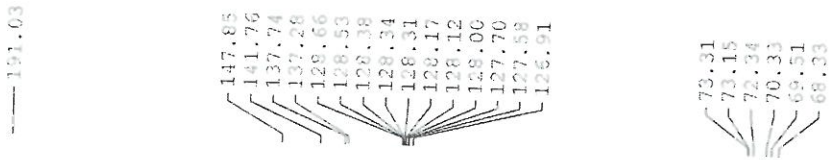
76.15
75.46
73.12
72.80
72.72
71.67
68.02
67.60

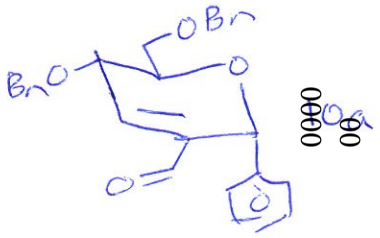
53.53

34.74
31.36



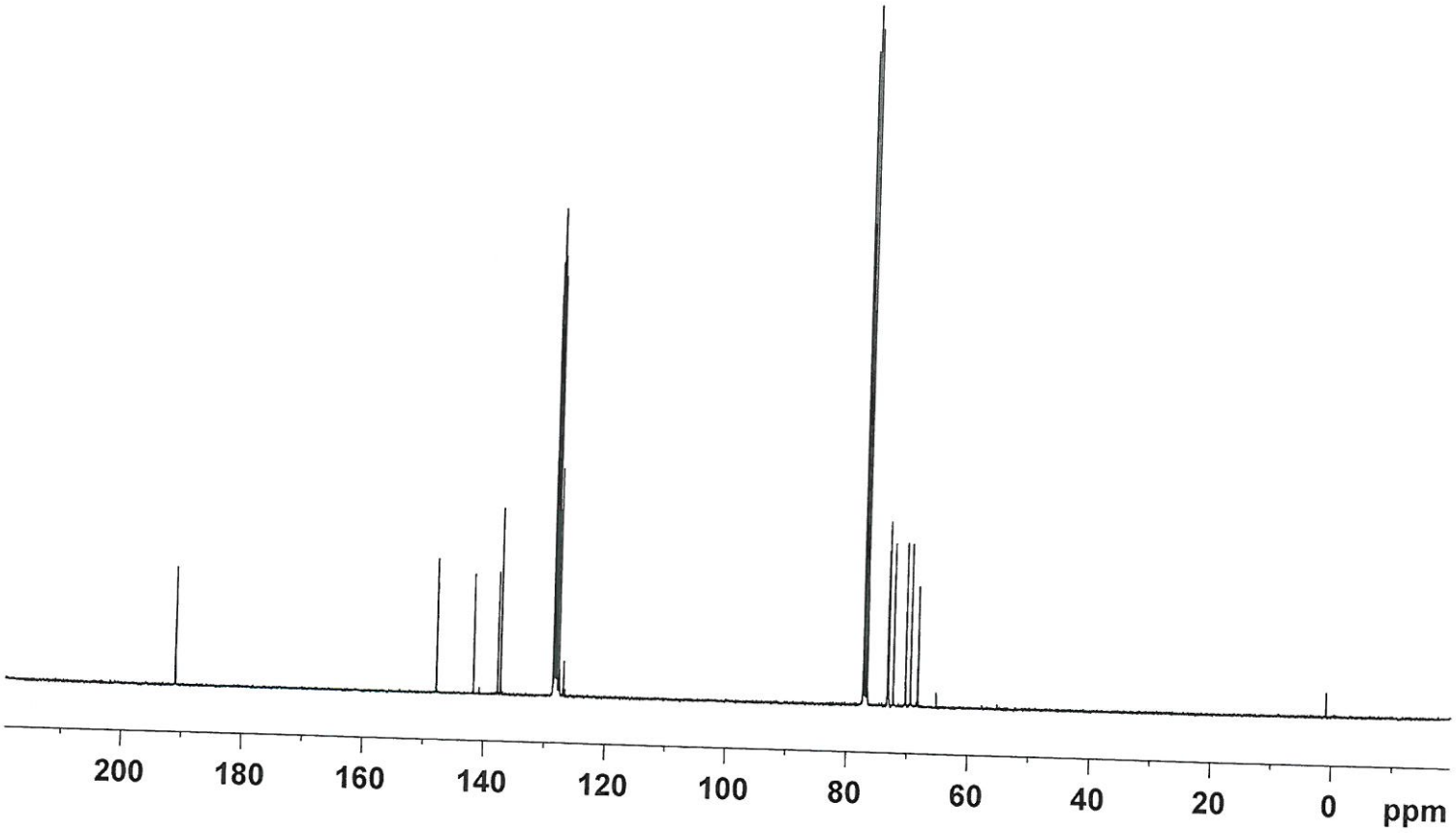
THIOPHENOL_FERRIER



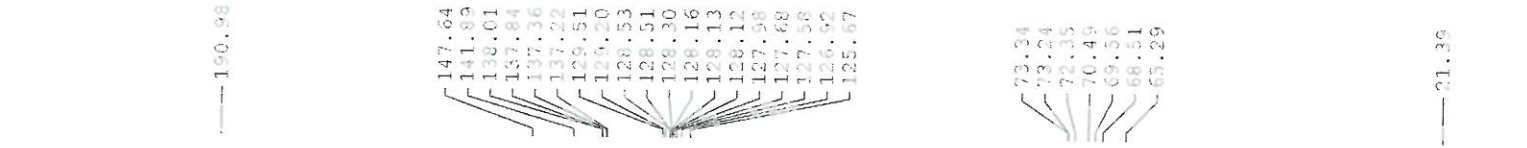


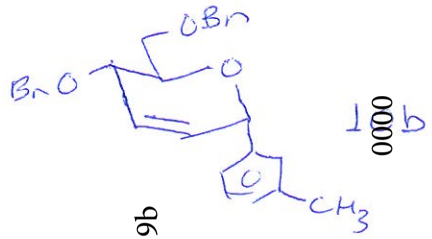
9a

```
NAME          THIOPHENOL_FERRRIER
EXPNO                          11
PROCNO                          1
Date_                    20140703
Time                        21.02
INSTRUM                     spect
PROBHD  5 mm PABBO BB-
PULPROG                    zgpg30
TD                          65536
SOLVENT                     CDCl3
NS                           3000
DS                              4
SWH                    24038.461 Hz
FIDRES                  0.366798 Hz
AQ                      1.3631988 sec
RG                            101
DW                       20.800 usec
DE                        6.50 usec
TE                          287.6 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                          13C
P1                          10.00 usec
PL1                          4.00 dB
SFO1                100.6328888 MHz

======== CHANNEL f2 ========
CPDPRG2                    waltz16
NUC2                           1H
PCPD2                       90.00 usec
PL2                         -3.00 dB
PL12                        15.30 dB
PL13                        18.00 dB
SFO2                400.1716007 MHz
SI                          32768
SF                  100.6228370 MHz
WDW                            EM
SSB                             0
LB                           1.00 Hz
GB                              0
PC                           1.40
```



4M_FERRIER

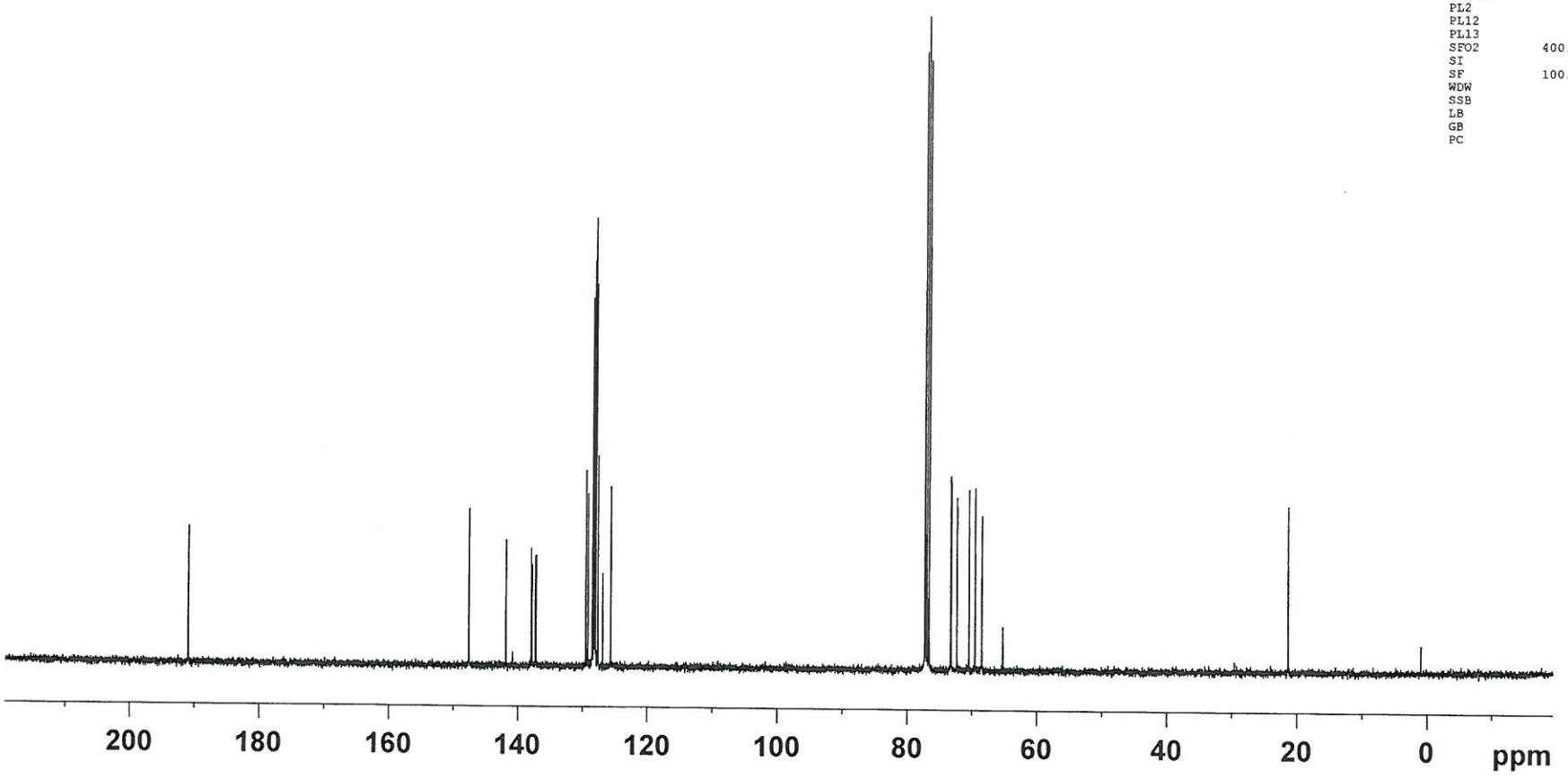




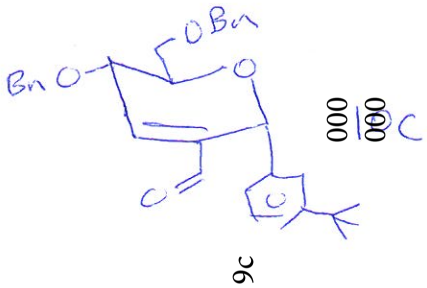
9b

1000b

NAME	FERREIR_4M
EXPNO	11
PROCNO	1
Date_	20140626
Time	18.14
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	500
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	101
DW	20.800 usec
DE	6.50 usec
TE	295.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	4.00 dB
SFO1	100.6328898 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-3.00 dB
PL12	15.30 dB
PL13	18.00 dB
SFO2	400.1716007 MHz
SI	32768
SF	100.6228341 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

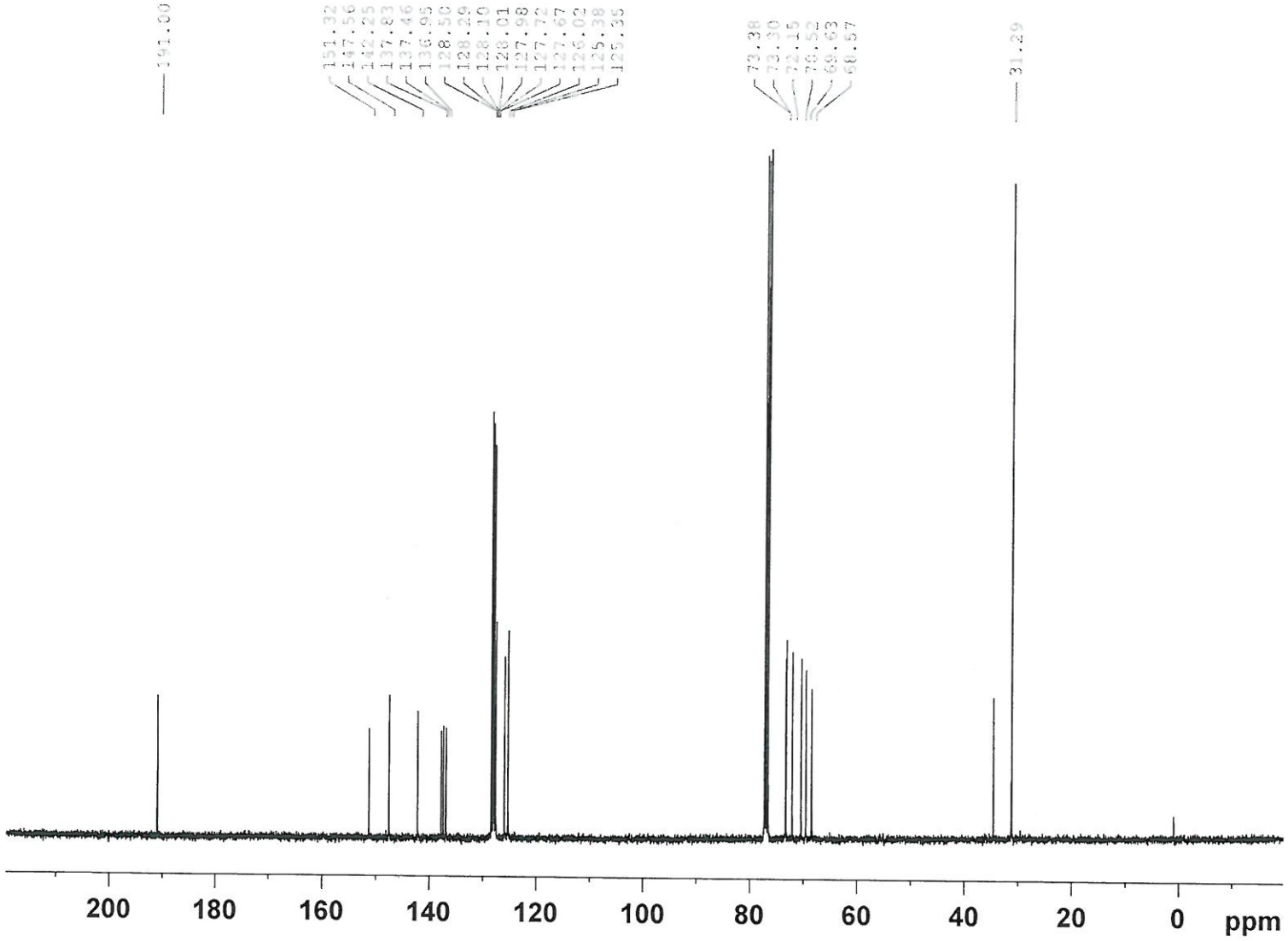


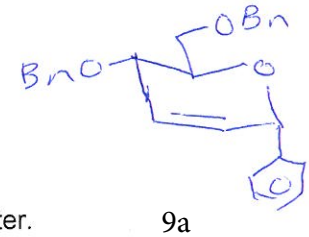
TRT_FERRIER



9c

```
NAME          FERRIER_TRT_FINAL
EXPNO                        11
PROCNO                        1
Date_                  20140625
Time                      17.33
INSTRUM                   spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         500
DS                           4
SWH                  24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                         101
DW                      20.800 usec
DE                       6.50 usec
TE                      295.3 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                      10.00 usec
PL1                      4.00 dB
SFO1           100.6328889 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   90.00 usec
PL2                     -3.00 dB
PL12                    15.30 dB
PL13                    18.00 dB
SFO2           400.1716007 MHz
SI                       32768
SF             100.6228737 MHz
WDW                         EM
SSB                          0
LB                      1.00 Hz
GB                           0
PC                        1.40
```





00000

Requested: H. Kinfe (UJ)
Report No: HK_UJ_150211

9a

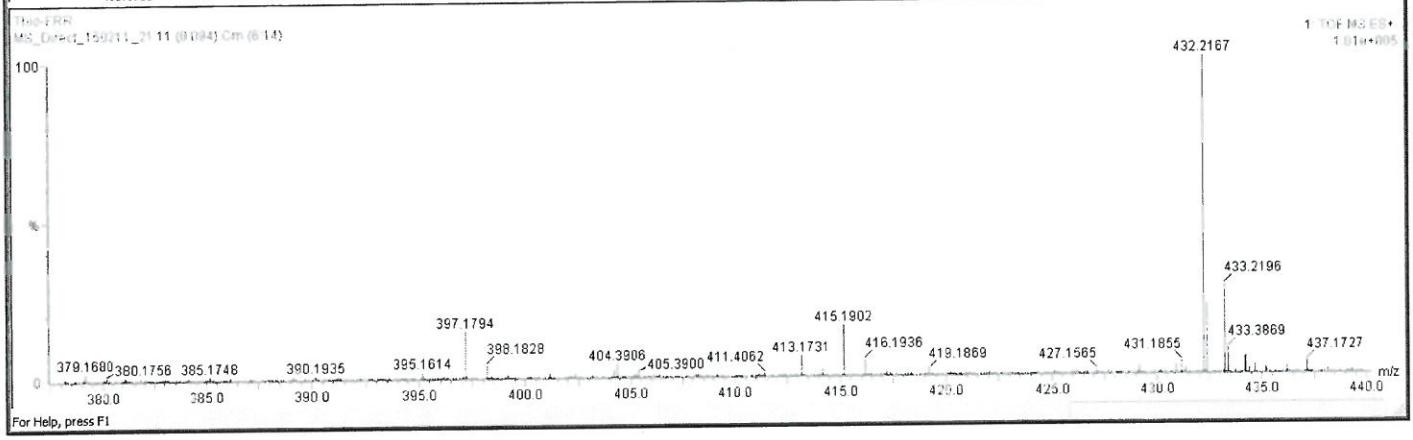
Instrument: Waters Synapt G2
Introduction: ESI probe injected into a stream of acetonitrile with 5 % water.
Source: ESI positive, Cone Voltage 15 V
Lock mass: leucine enkephalin

Elemental Composition

File Edit View Process Help

Single Mass Analysis
Tolerance = 80.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
219 formula(e) evaluated with 16 results within limits (all results (up to 1000) for each mass)
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O
415.1902	415.1902	-0.7	-1.7	14.5	C27 H27 O4	248.5	1.053	19.15	27	27		4
	415.1882	2.0	4.8	15.5	C23 H23 N6 O2	250.2	3.377	3.41	23	23	6	2
	415.1923	-2.1	-5.1	19.5	C28 H23 N4	249.5	2.614	7.33	28	23	4	
	415.1961	-7.9	-19.0	10.5	C21 H27 N4 O5	250.9	4.072	1.70	21	27	4	5
	415.1810	9.2	22.2	19.5	C29 H23 N2 O	249.2	2.402	9.05	29	23	2	1
	415.2022	-12.0	-28.9	14.5	C26 H27 N2 O3	249.1	2.257	10.46	26	27	2	3
	415.1770	13.2	31.8	15.5	C24 H23 N4 O3	249.9	3.038	4.79	24	23	4	3
	415.2062	-16.0	-38.5	18.5	C31 H27 O	249.7	2.859	5.73	31	27		1
	415.1730	17.2	41.4	11.5	C19 H23 N6 O5	251.6	4.756	0.86	19	23	6	5



For Help, press F1