Synthesis of Thiourea-Tethered *C*-Glycosyl Amino Acids by Isothiocyanate-Amine Coupling

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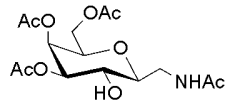
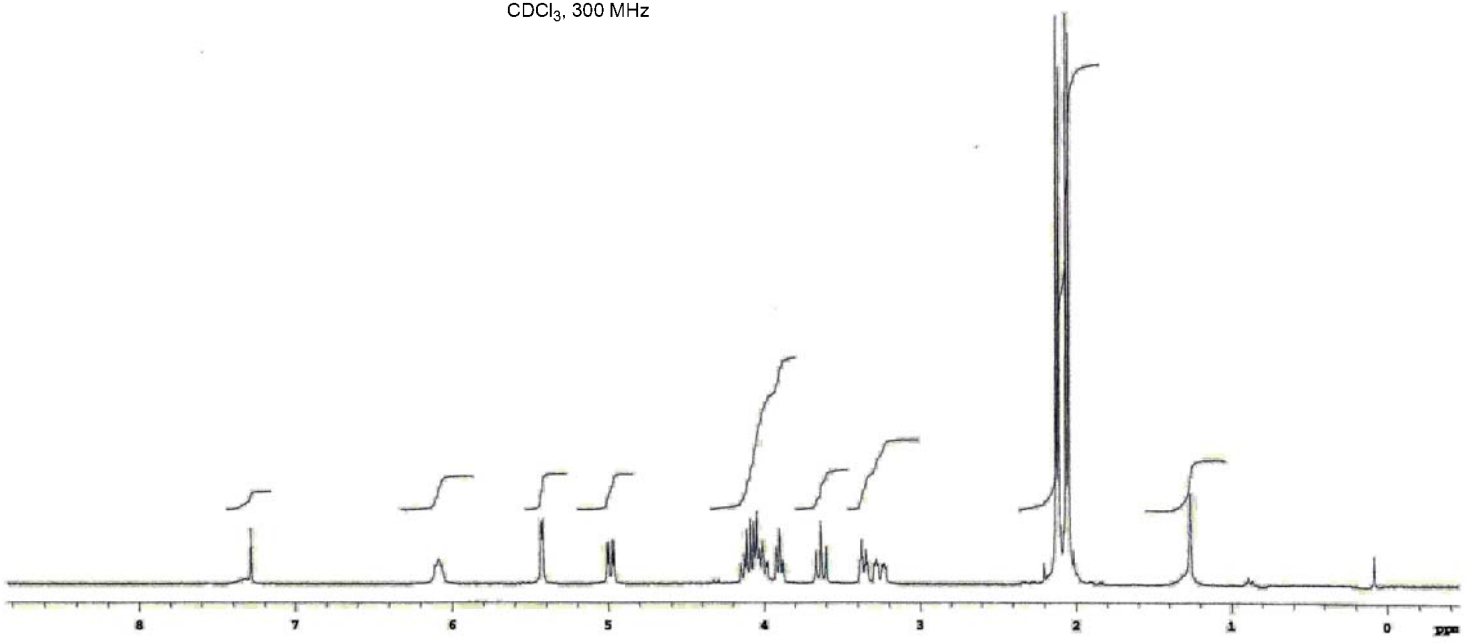
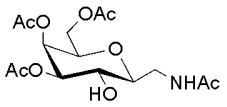
Supporting Information



10

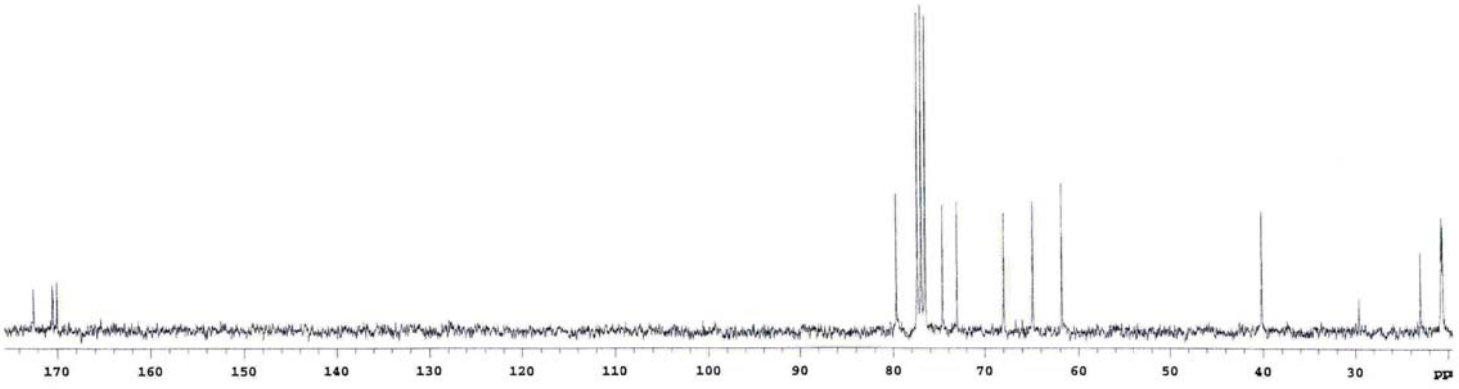
$CDCl_3$, 300 MHz

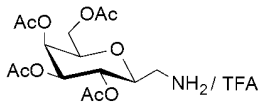




10

$CDCl_3$, 75 MHz





β-1a

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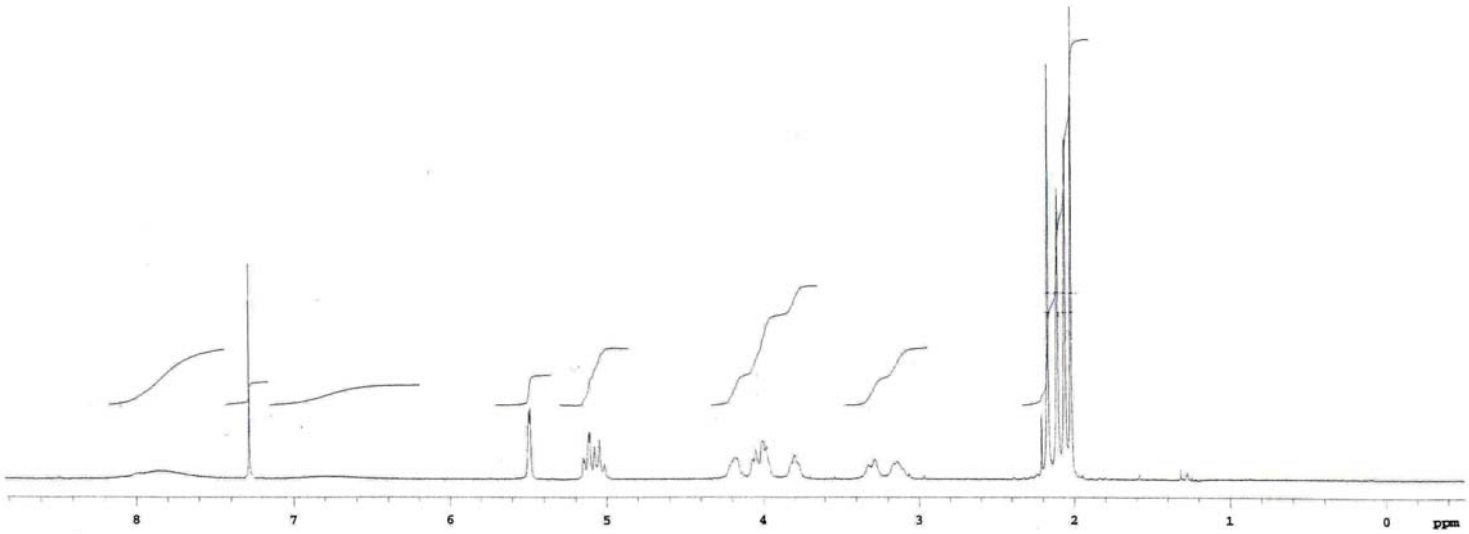
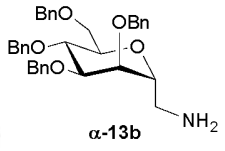
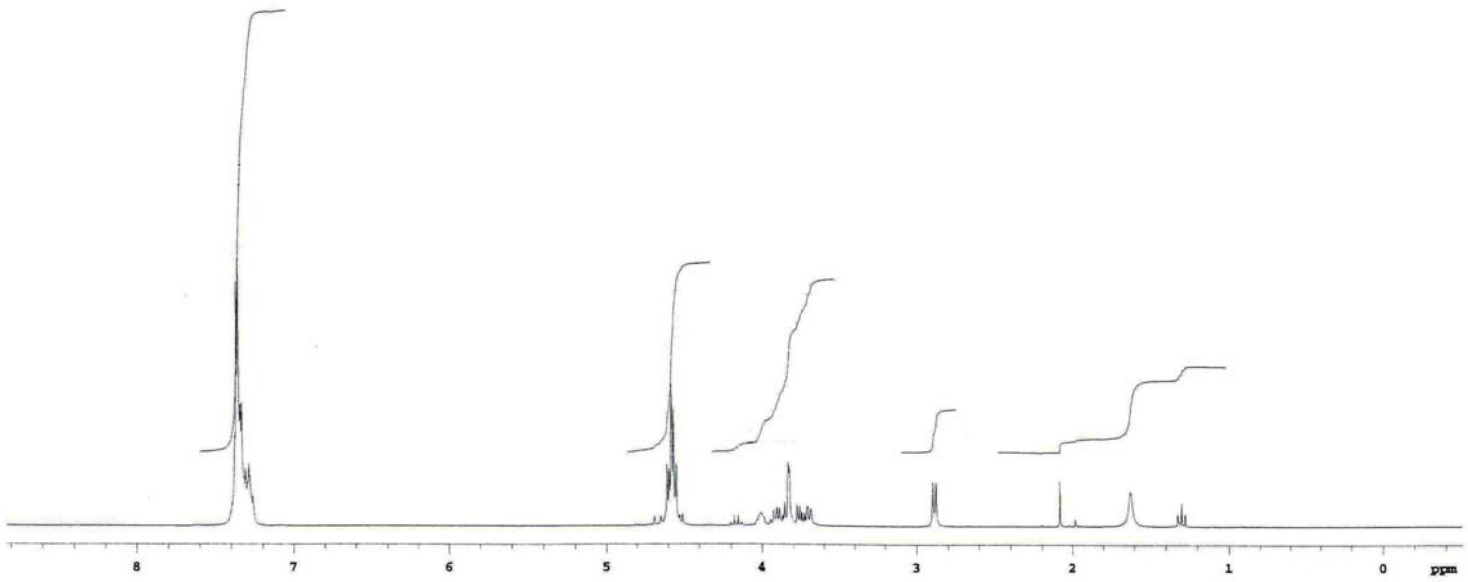
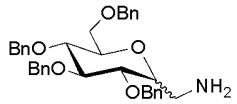




α-13b

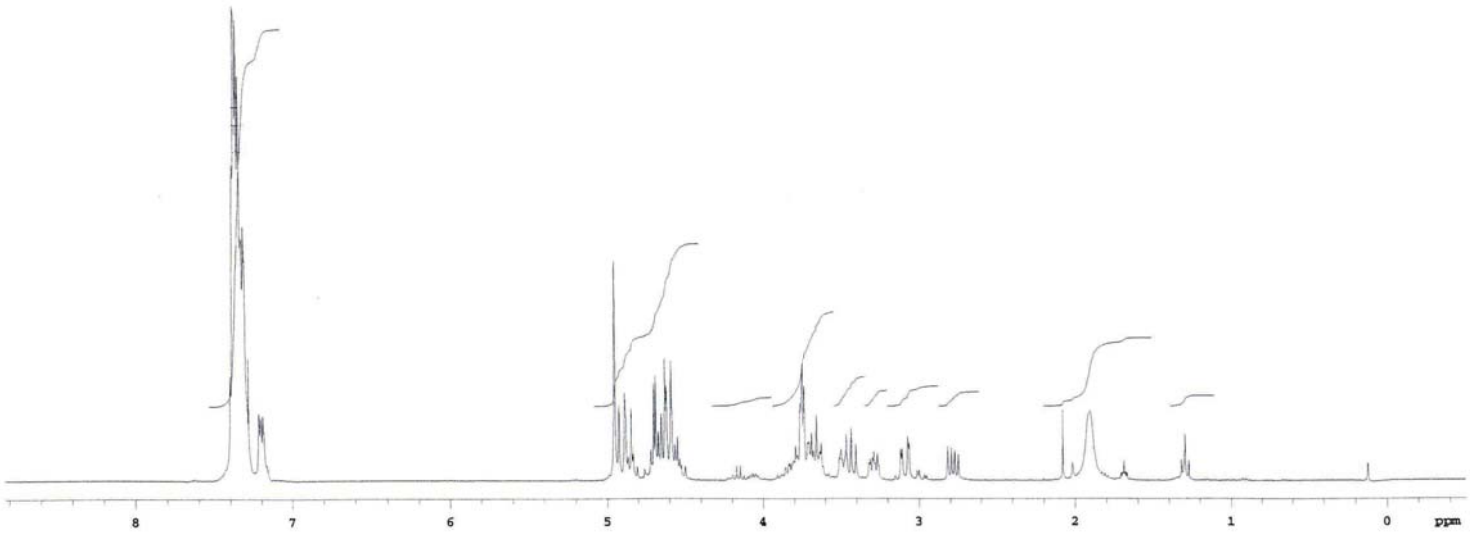
$CDCl_3$, 300 MHz

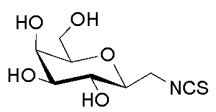




α,β-13c

$CDCl_3$, 300 MHz



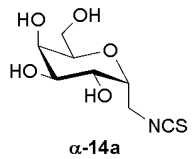


β-14a

D_2O, 300 MHz

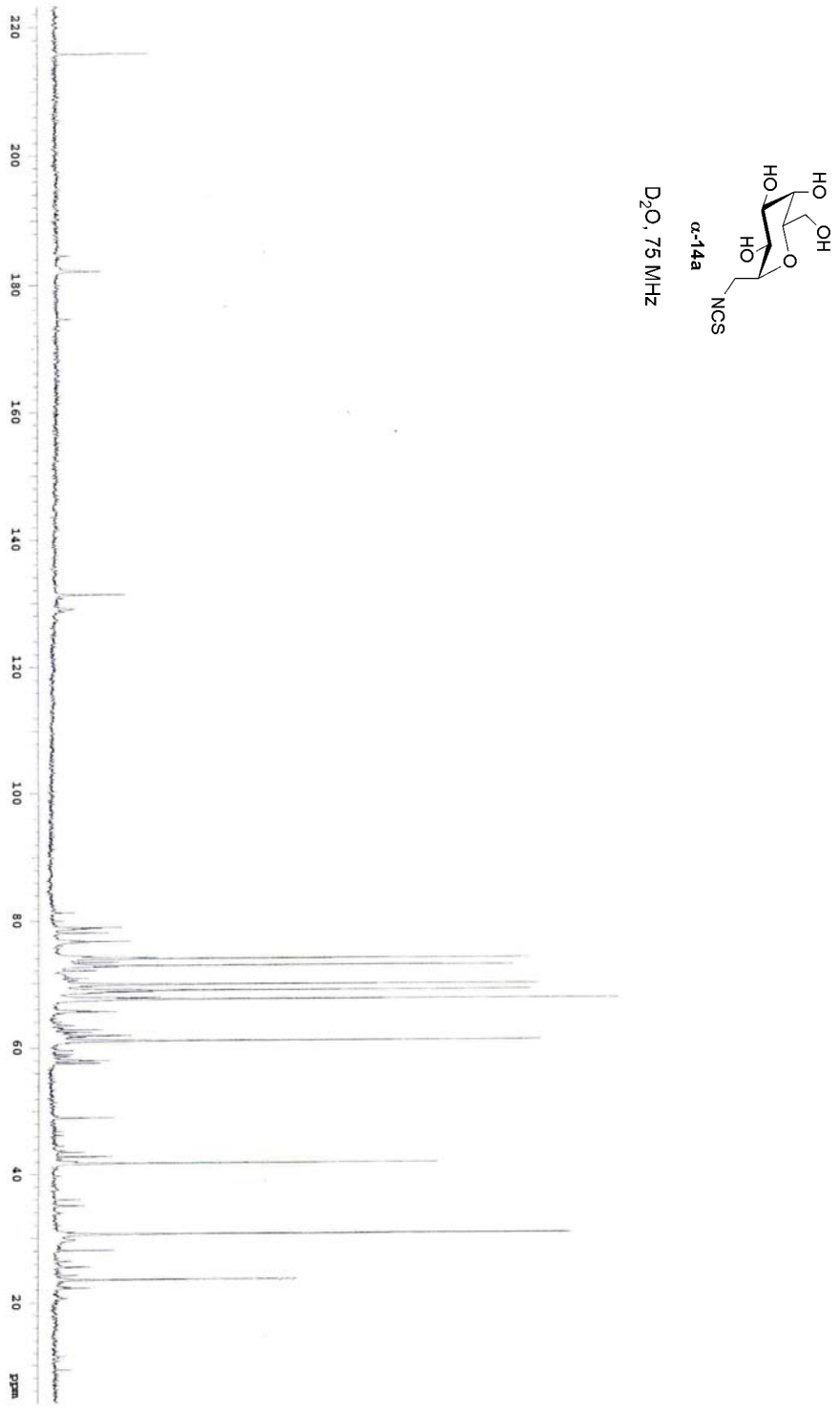
HO
OH
HO
HO
O
NCS
β-14a
D2O, 75 MHz

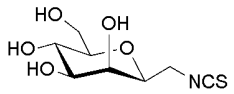
130
120
110
100
90
80
70
60
50
40
30
ppm



α-14a

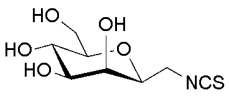
D_2O, 300 MHz


HO
HO
OH
HO
O
NCS
α-14a
D2O, 75 MHz
220
200
180
160
140
120
100
80
60
40
20
ppm



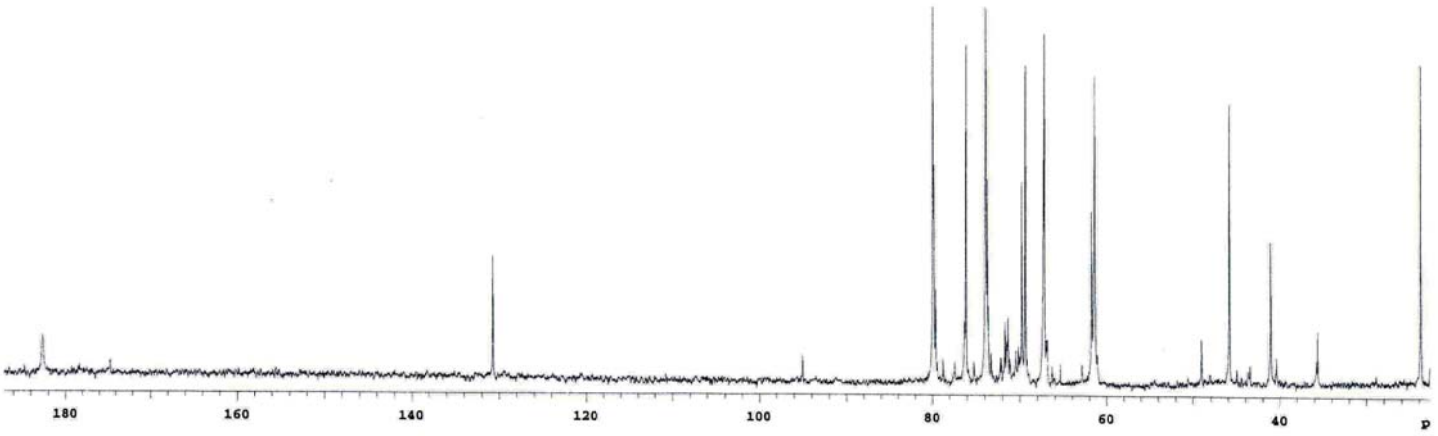
β-14b

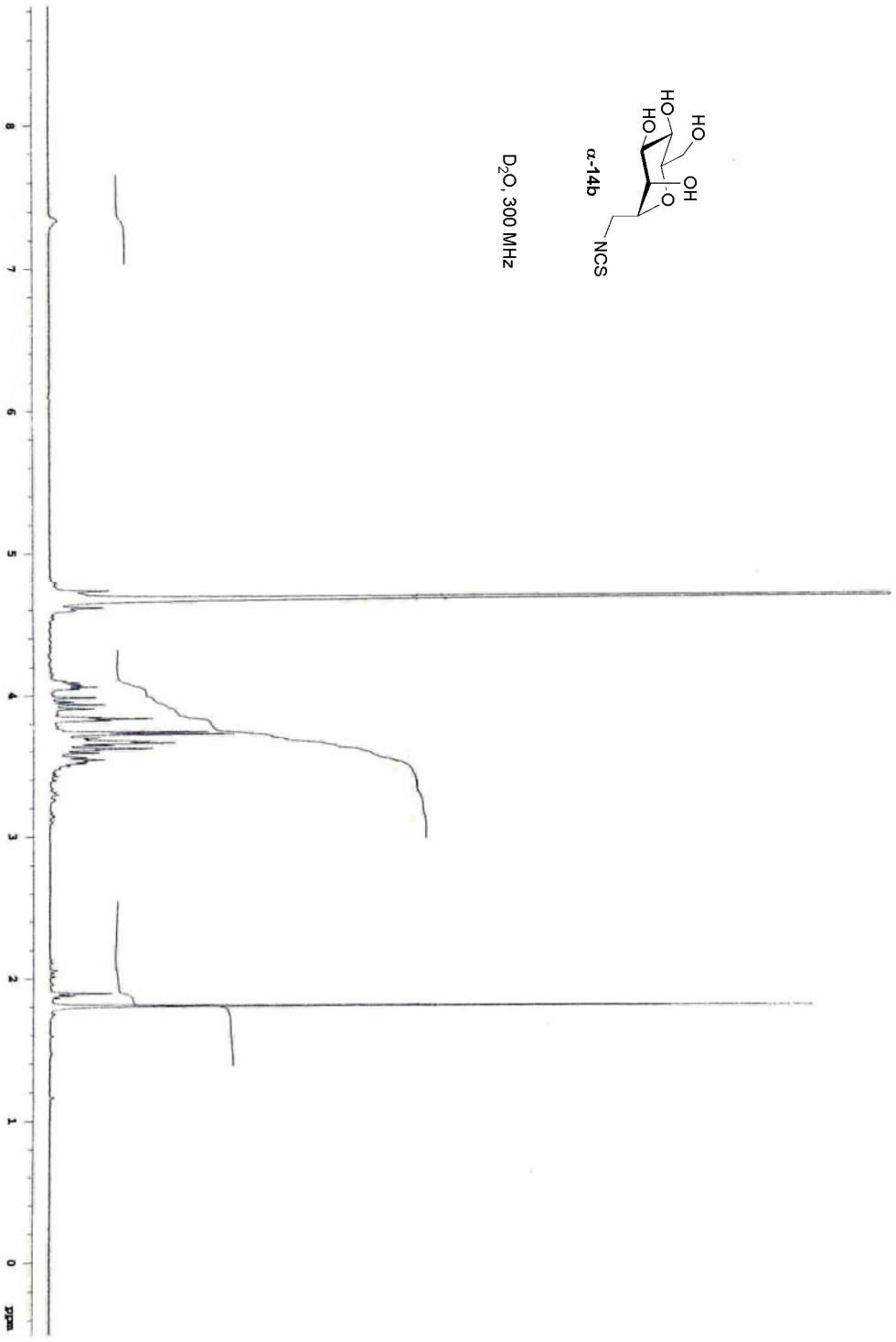
D_2O, 300 MHz

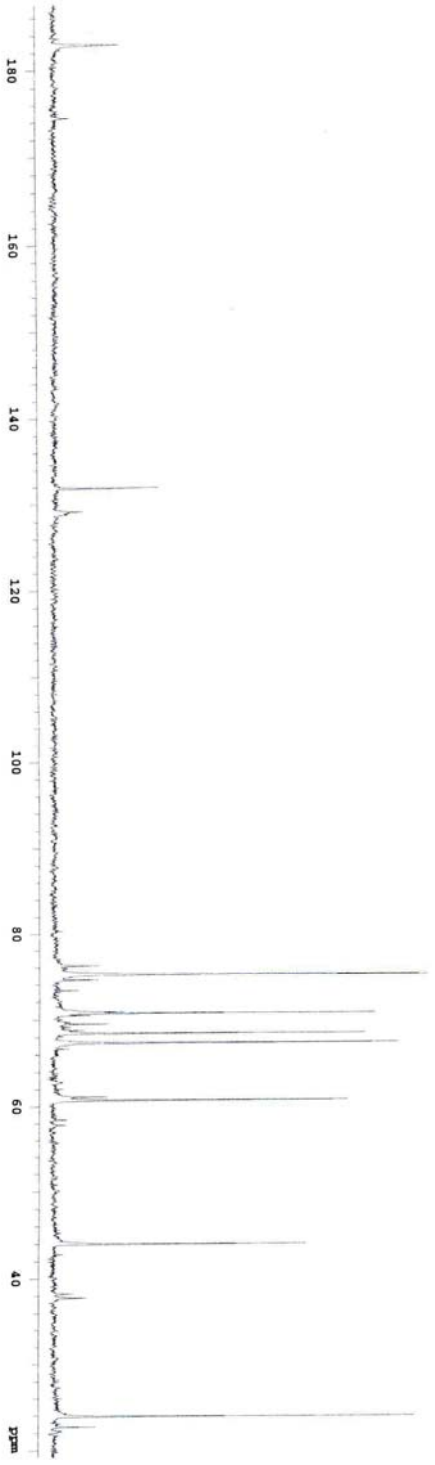


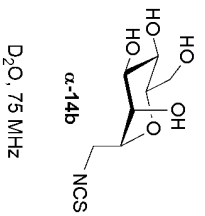
β-14b

D_2O, 75 MHz



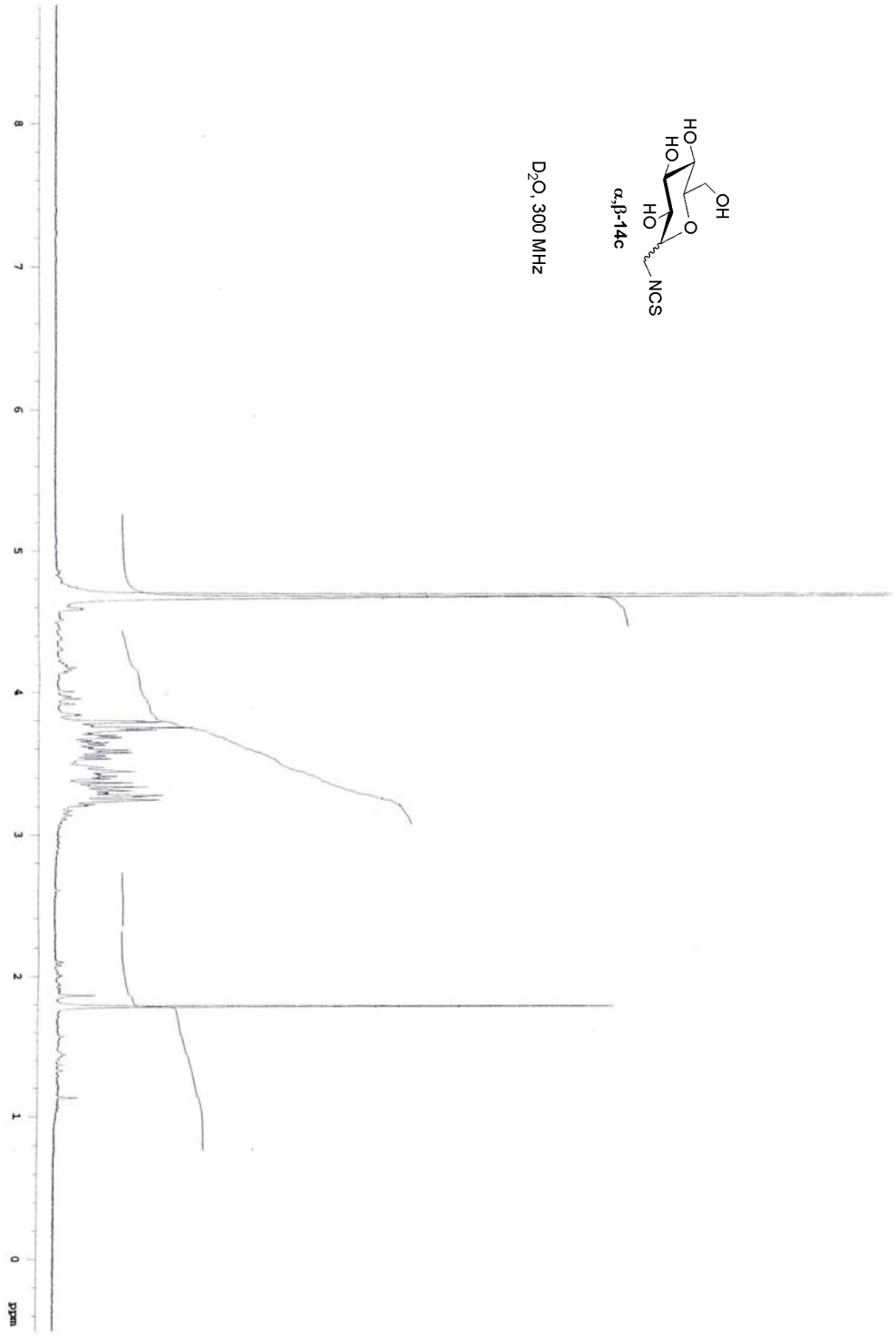

α-14b
NCS
HO
OH
HO
HO
D2O, 300 MHz
ppm

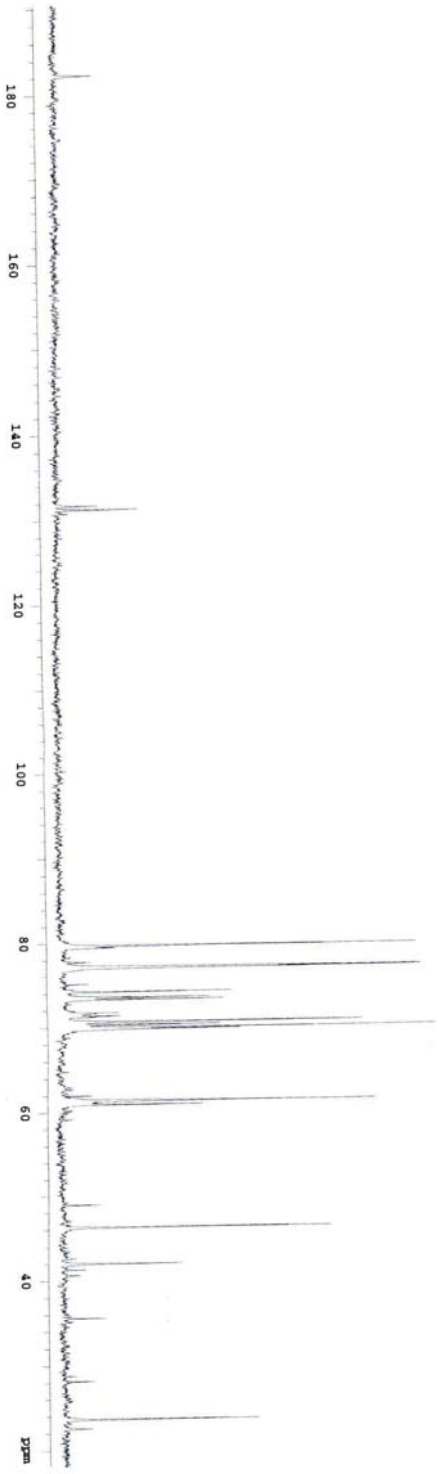


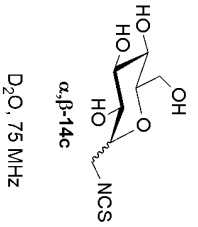


α-14b

D_2O, 75 MHz

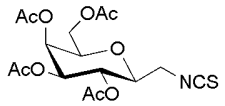

D2O, 300 MHz
α,β-14c
HO
HO
HO
OH
O
NCS
ppm





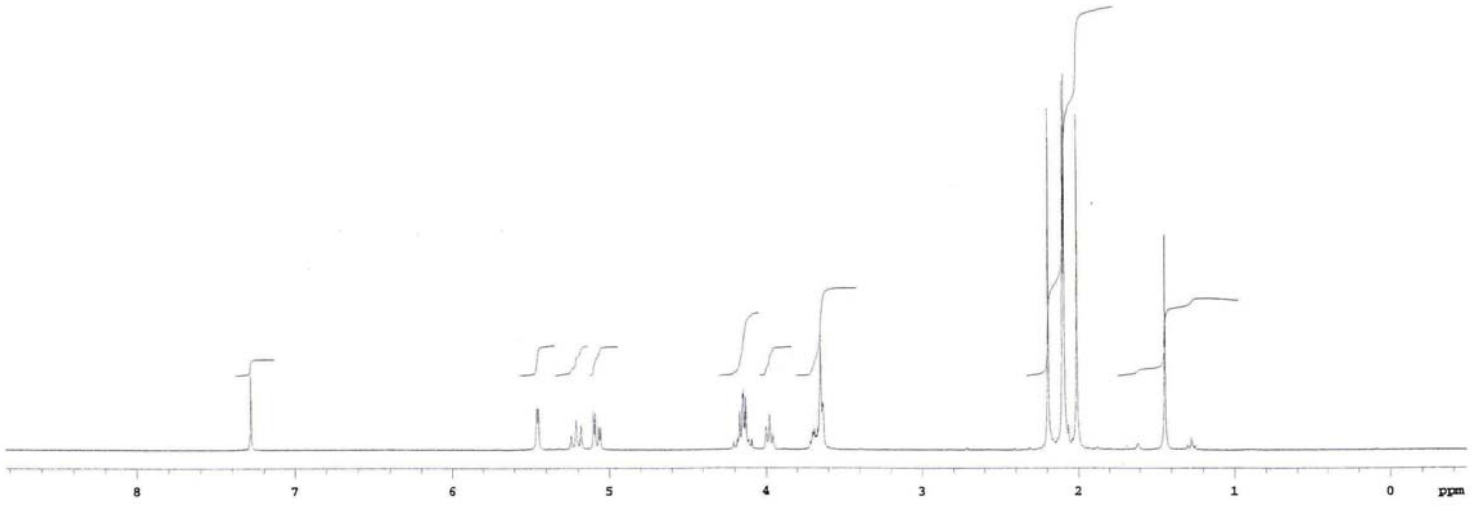
α,β-14c

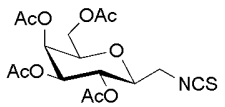
D_2O, 75 MHz



β-4a

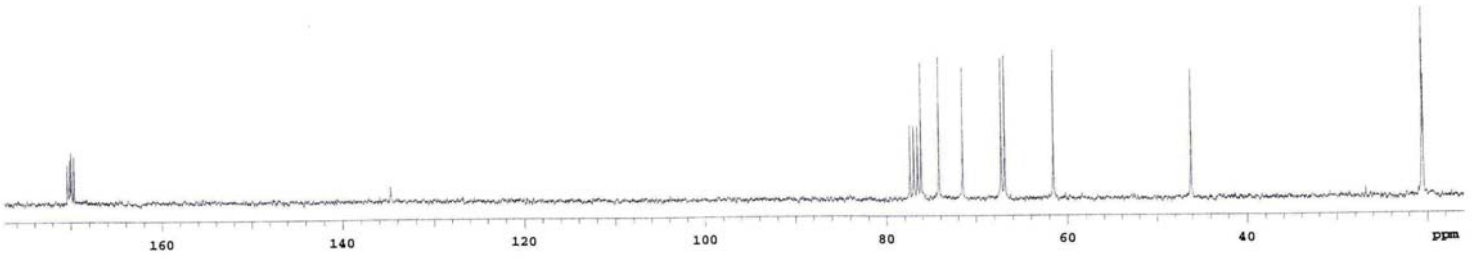
$CDCl_3$, 300 MHz

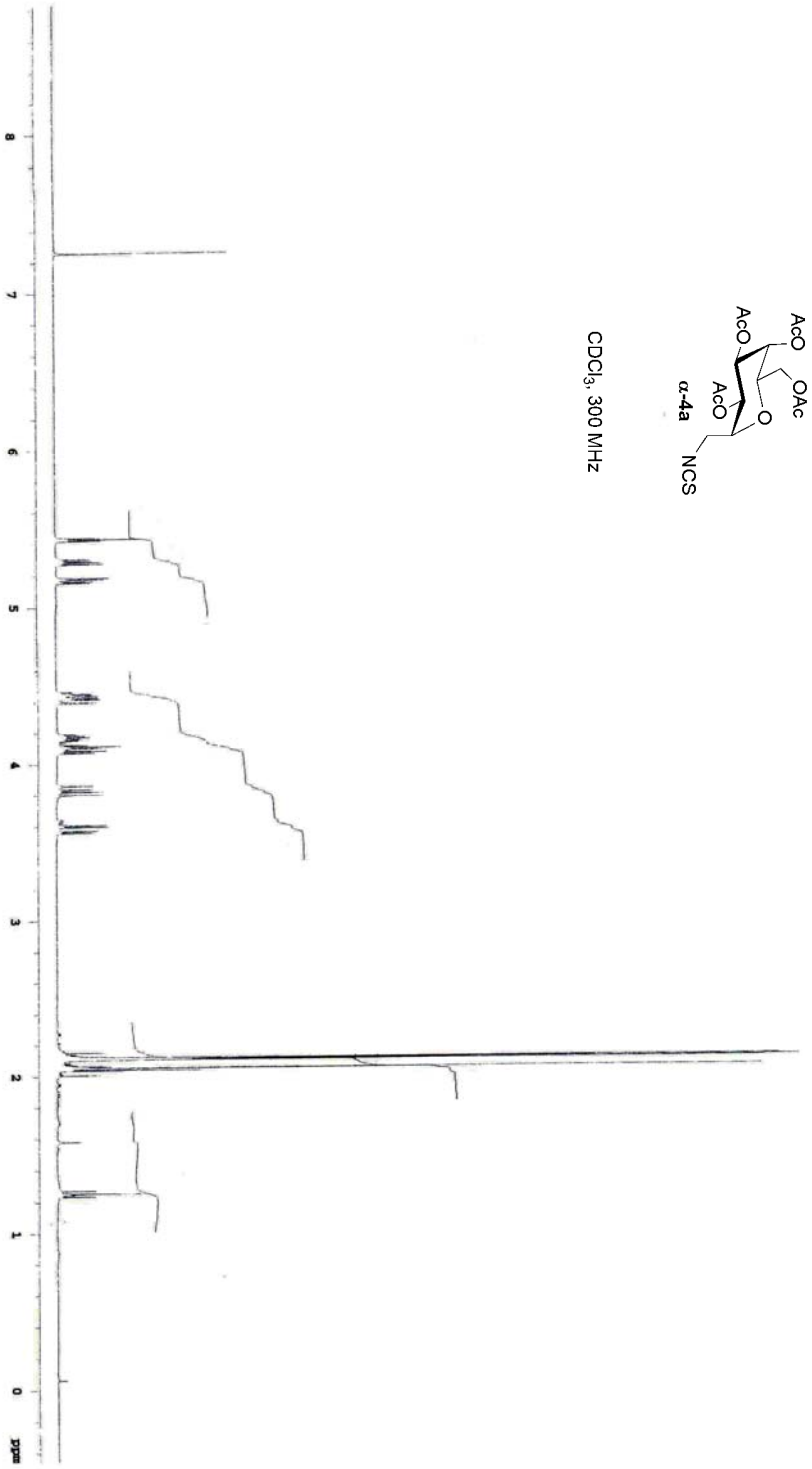


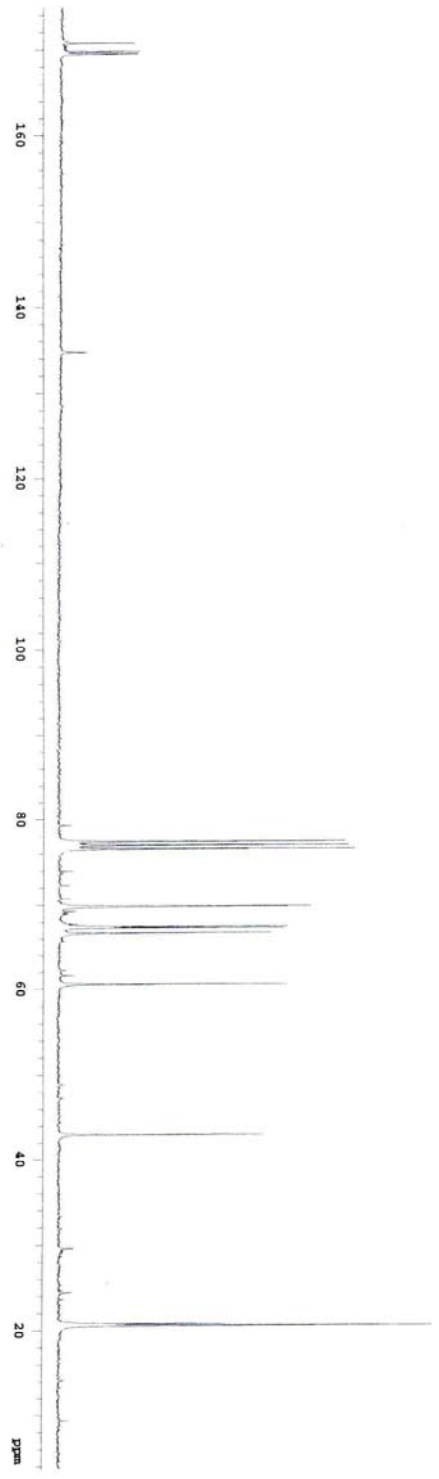


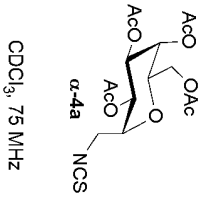
β-4a

$CDCl_3$, 75 MHz



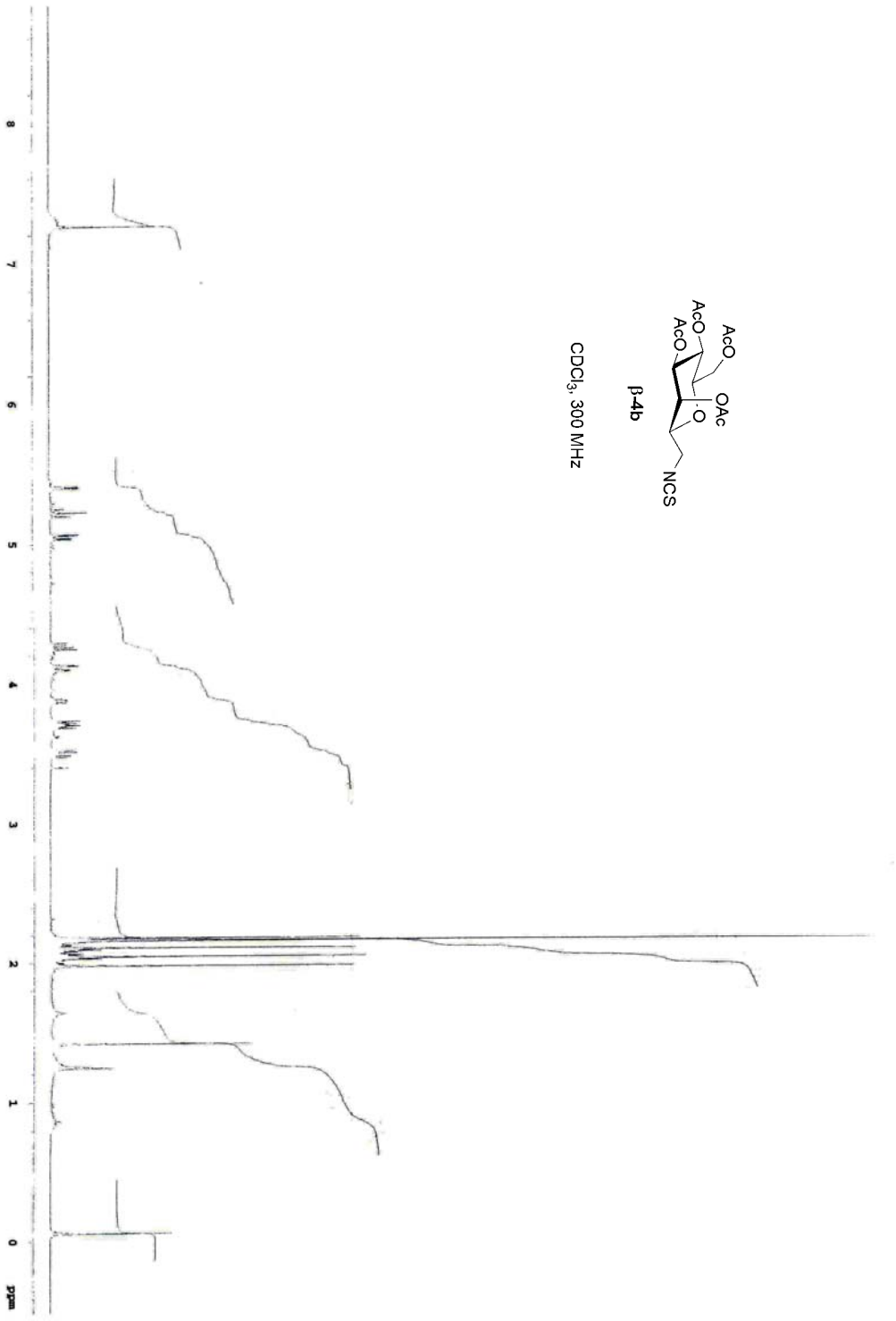

AcO
AcO
OAc
AcO
O
α-4a
NCS
CDCl3, 300 MHz
8
7
6
5
4
3
2
1
0
ppm

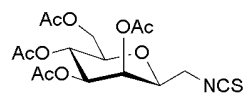




α-4a

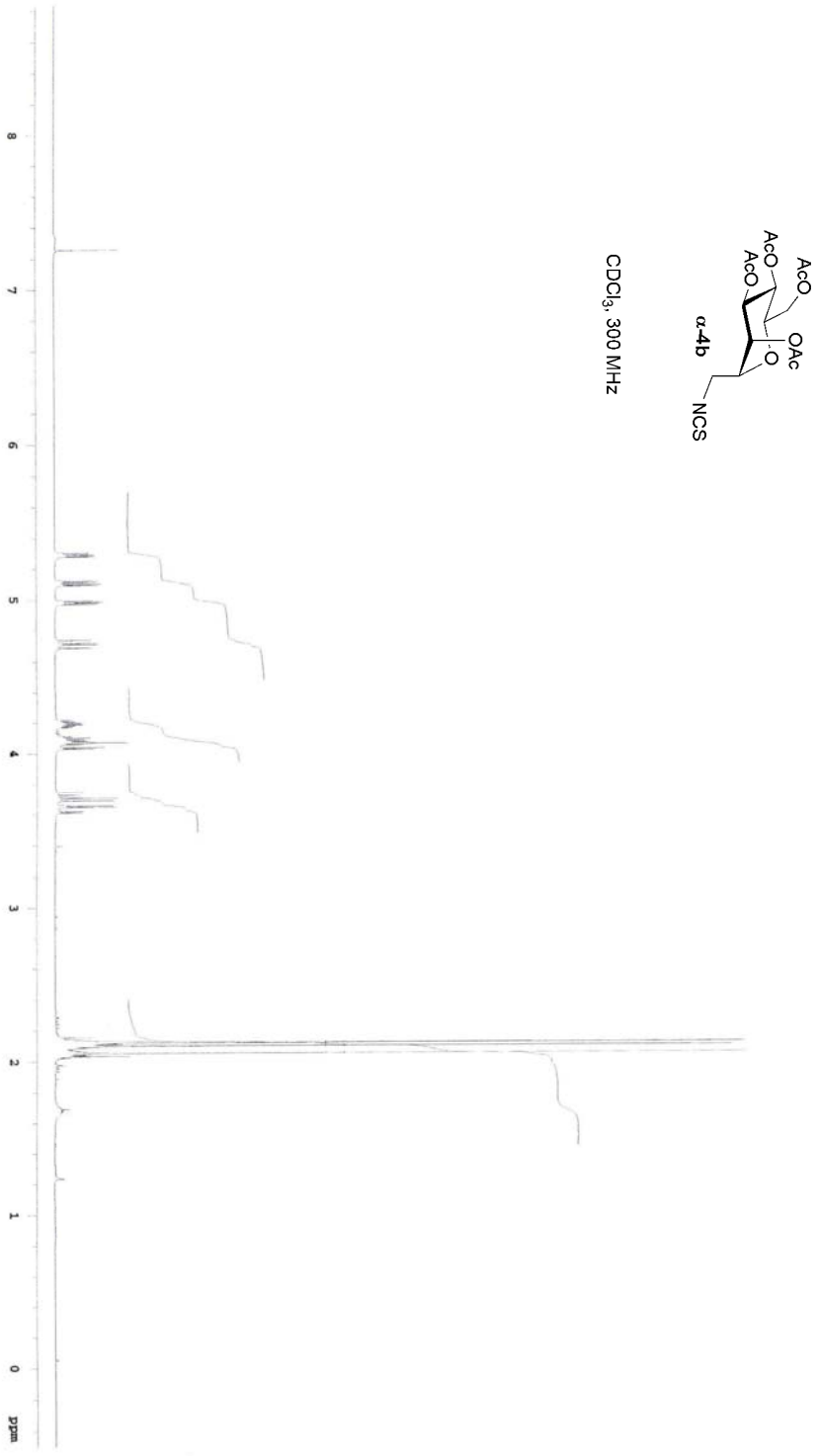
$CDCl_3$, 75 MHz

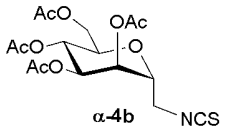

AcO
AcO
AcO
OAc
O
NCS
β-4b
CDCl3, 300 MHz
8
7
6
5
4
3
2
1
0
ppm



β-4b

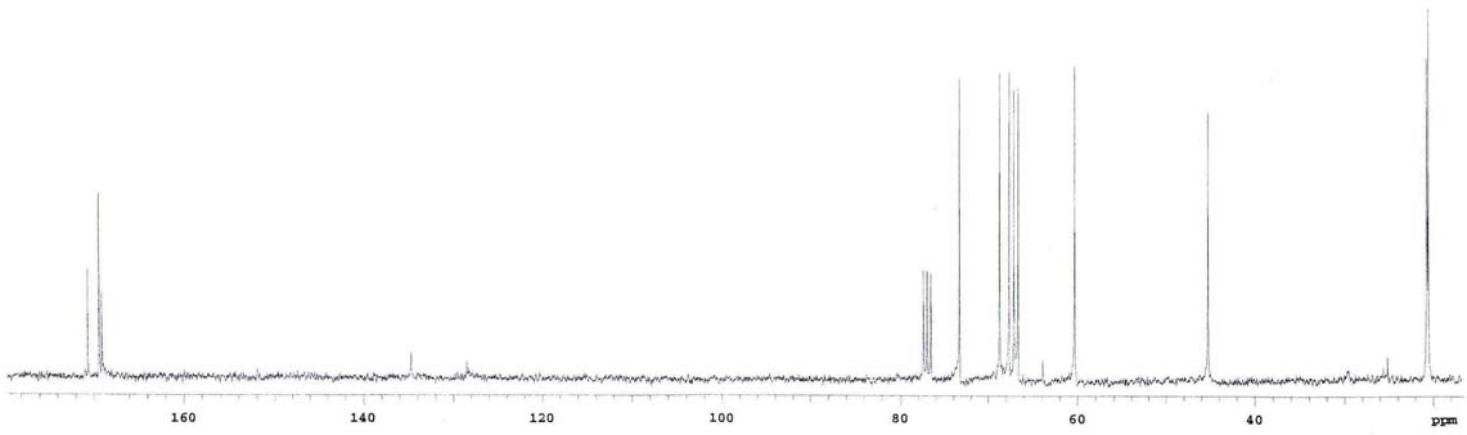
$CDCl_3$, 75 MHz

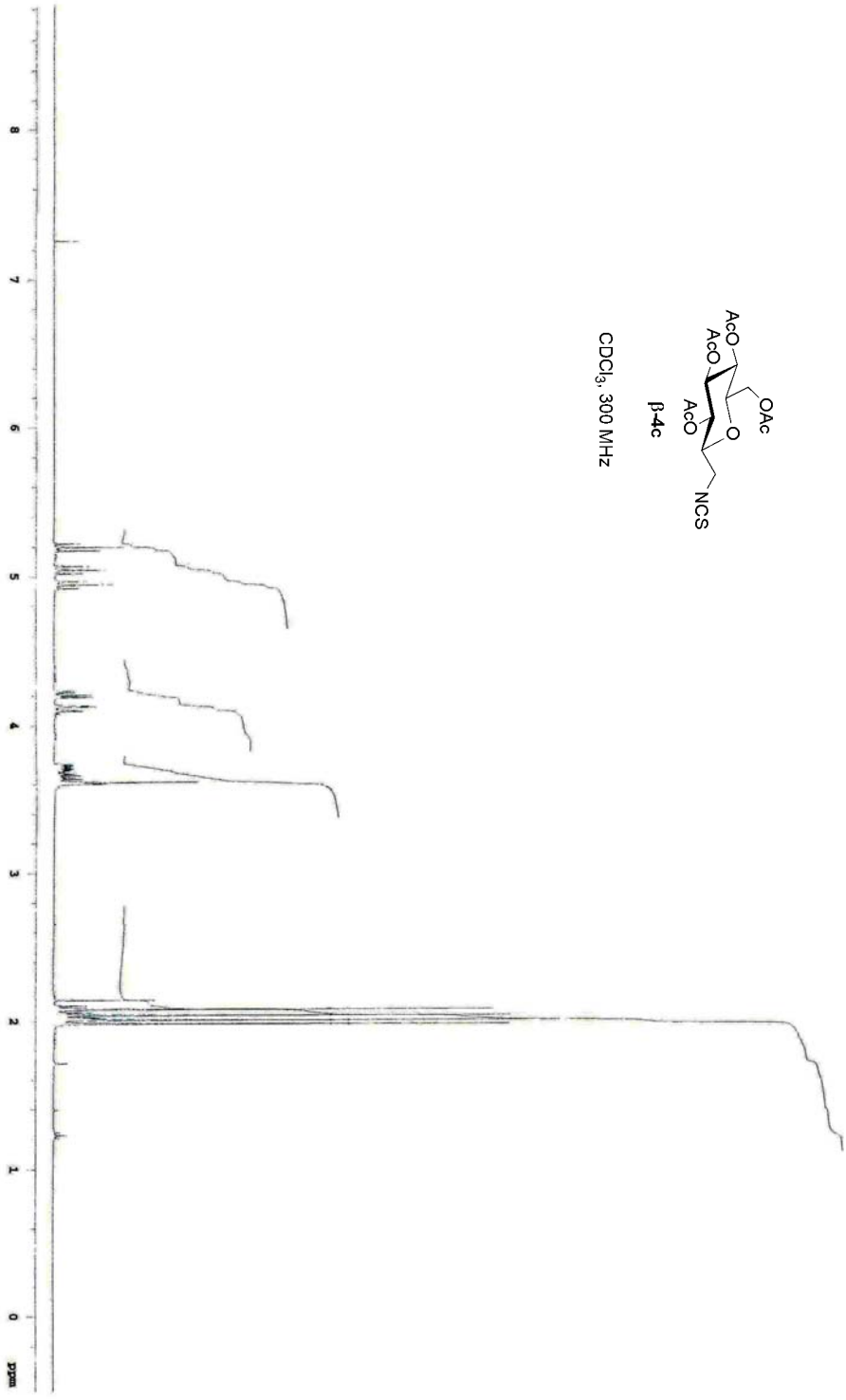

AcO
AcO
AcO
OAc
O
α-4b
NCS
CDCl3, 300 MHz
8
7
6
5
4
3
2
1
0
ppm

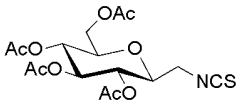


α-**4b**

$CDCl_3$, 75 MHz

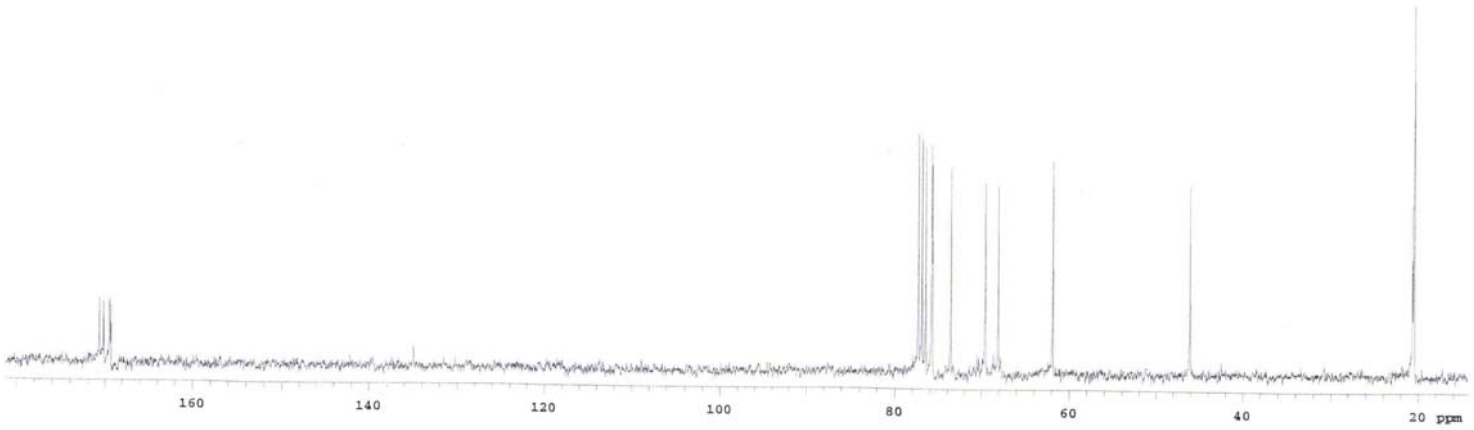


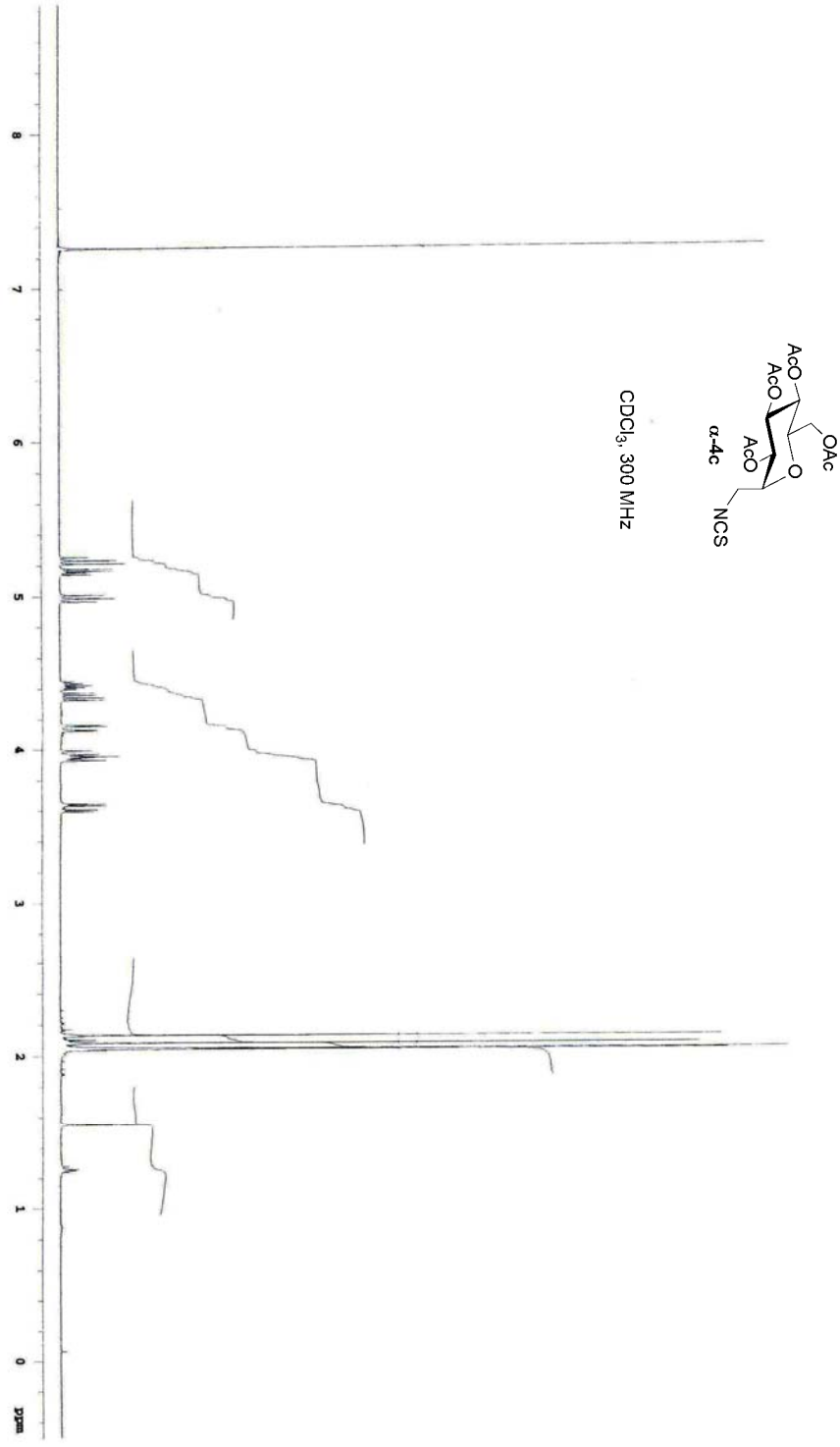

AcO
AcO
AcO
OAc
O
NCS
β-4c
CDCl3, 300 MHz
8
7
6
5
4
3
2
1
0
ppm

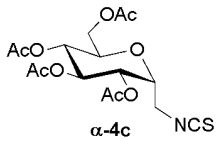


β-4c

$CDCl_3$, 75 MHz

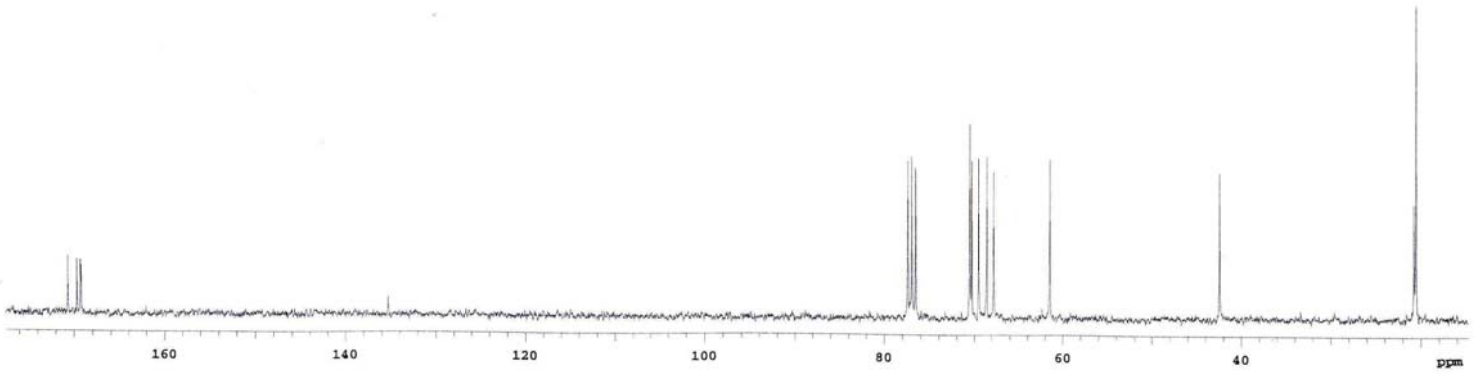


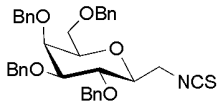

AcO
AcO
AcO
OAc
O
NCS
α-4c
CDCl3, 300 MHz
8
7
6
5
4
3
2
1
0
ppm



α-4c

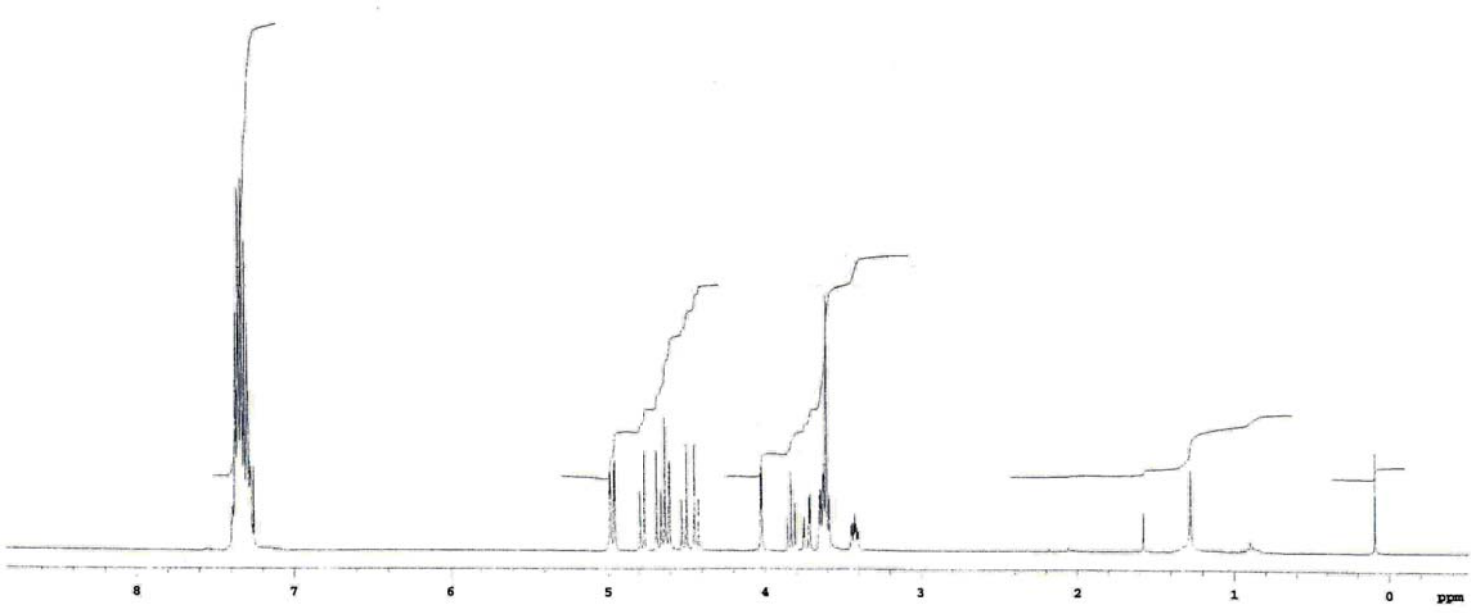
$CDCl_3$, 75 MHz

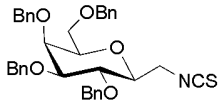




β-15a

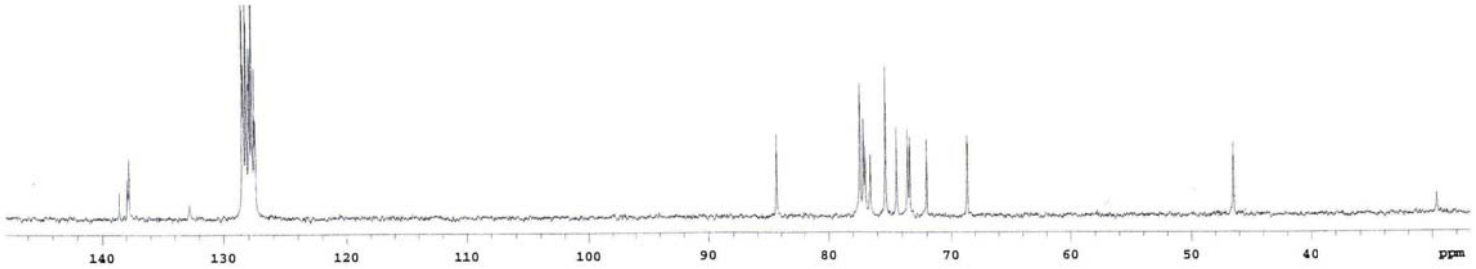
$CDCl_3$, 300 MHz

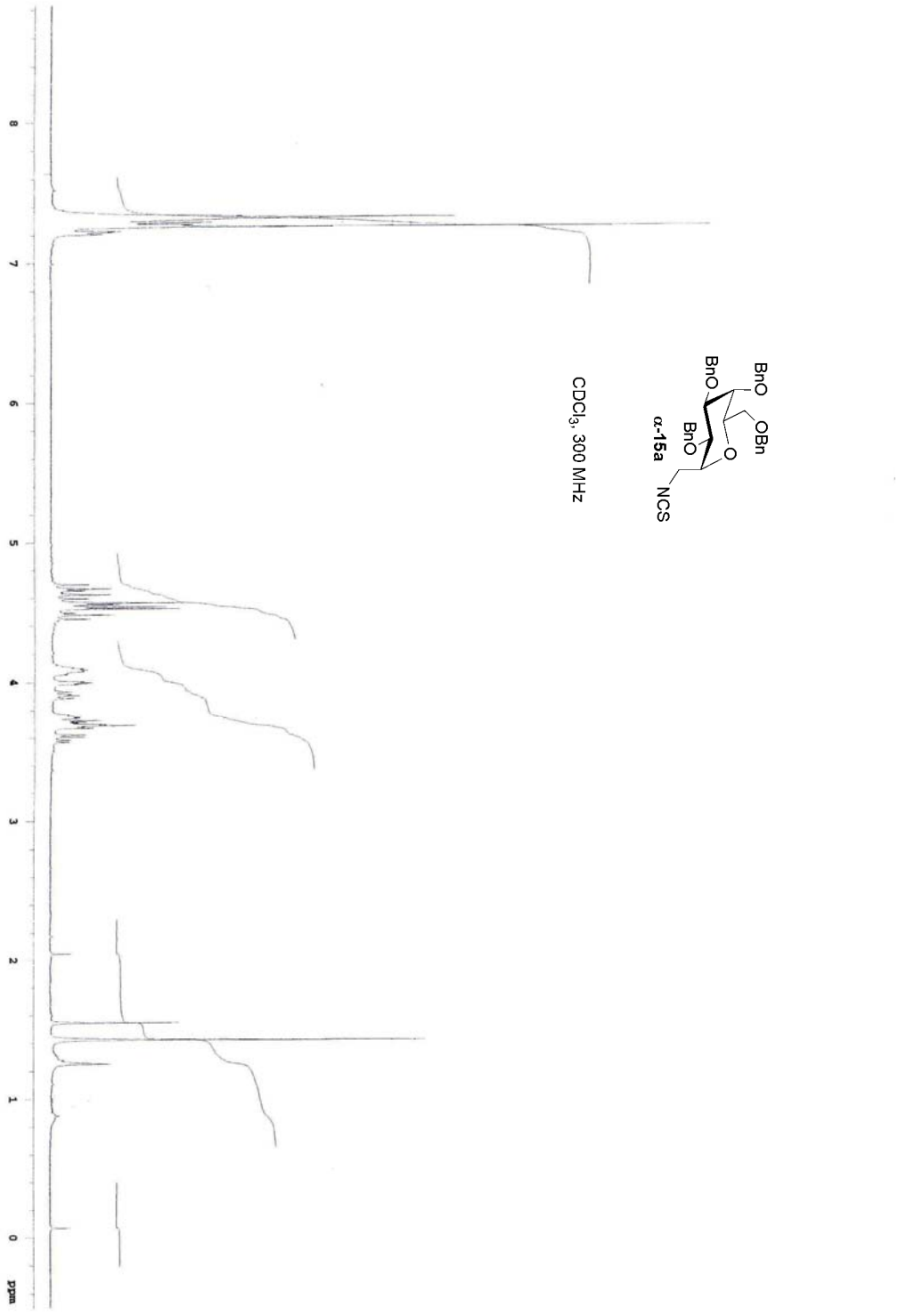


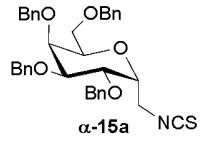


β-15a

$CDCl_3$, 75 MHz

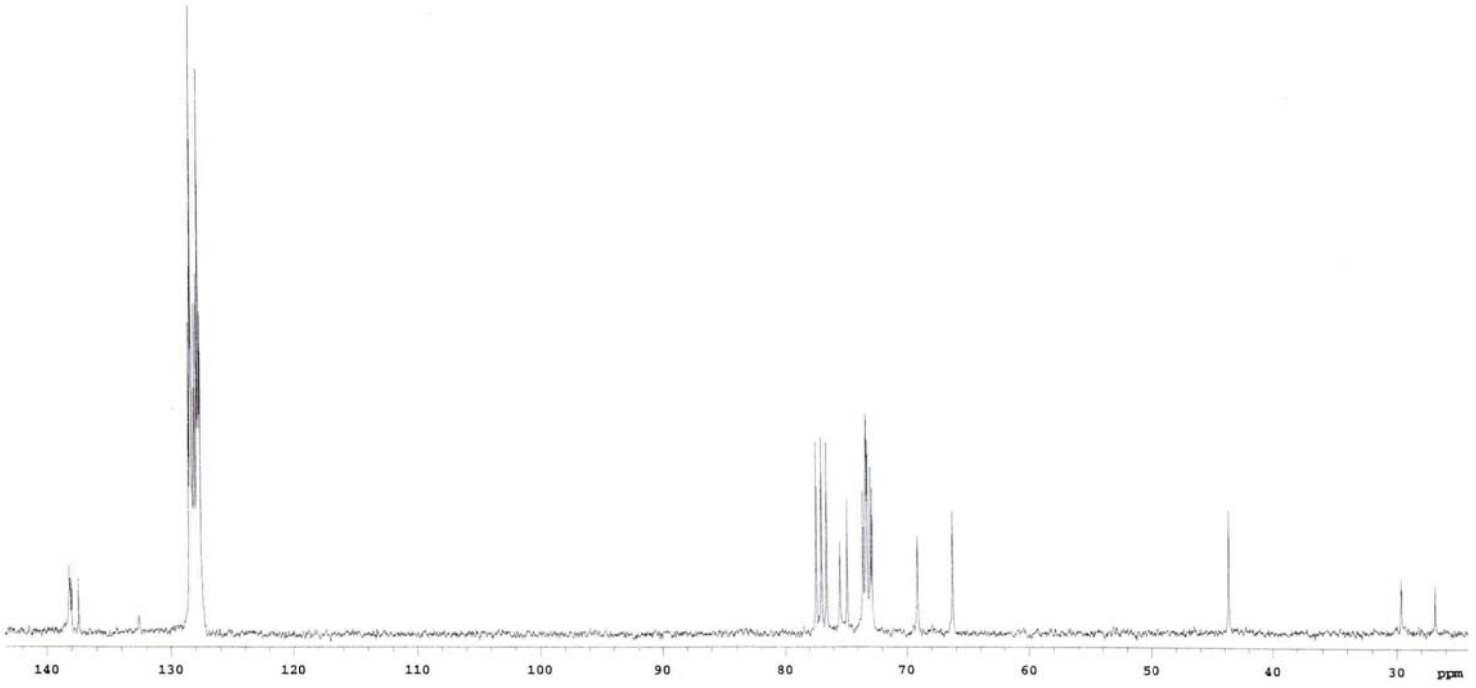


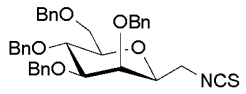

BnO
OBn
BnO
O
BnO
α-15a
NCS
CDCl3, 300 MHz
8
7
6
5
4
3
2
1
0
ppm



α-15a

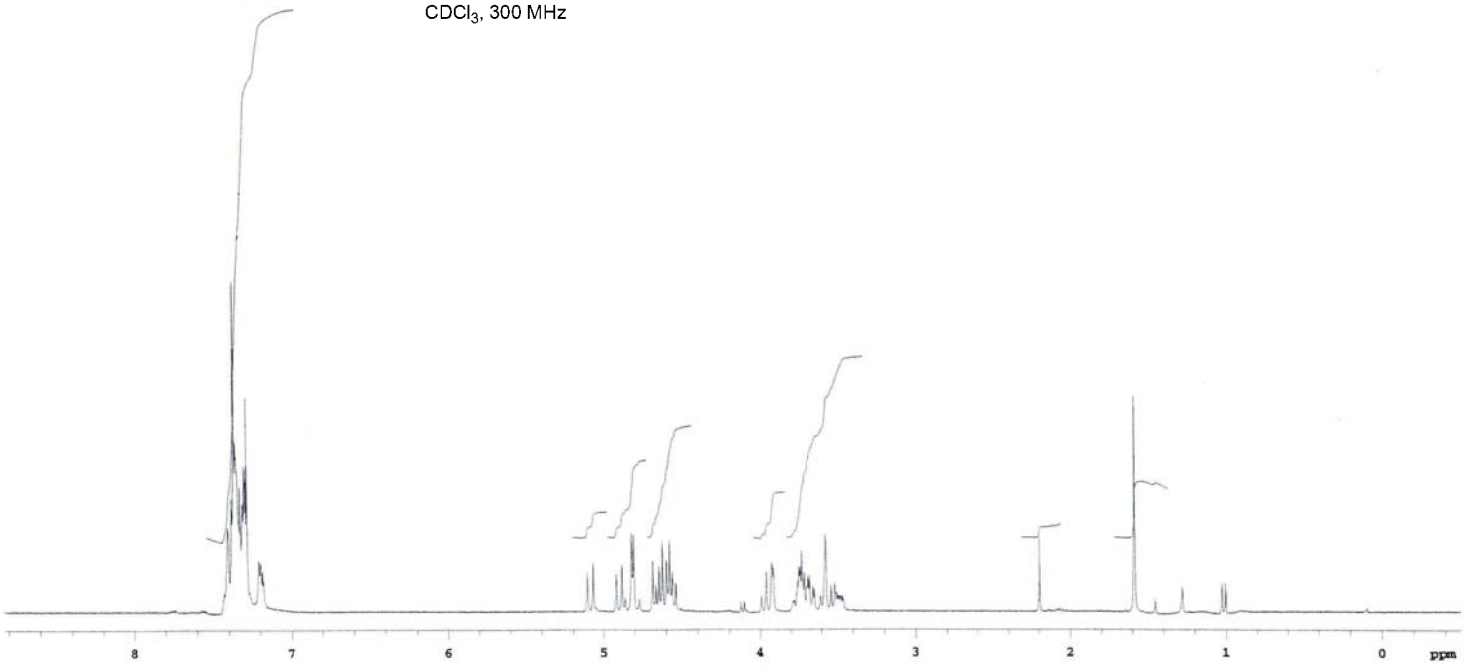
$CDCl_3$, 75 MHz

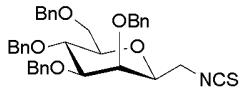




β-15b

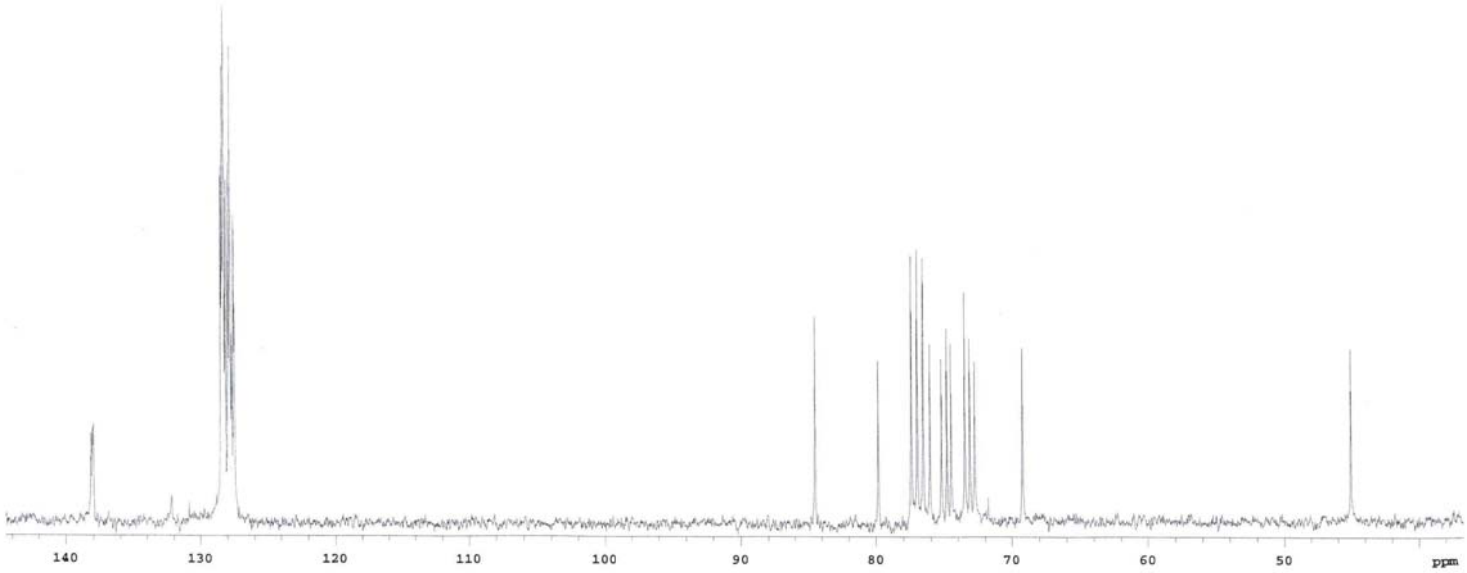
$CDCl_3$, 300 MHz

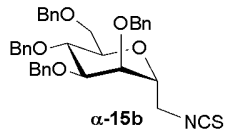




β-15b

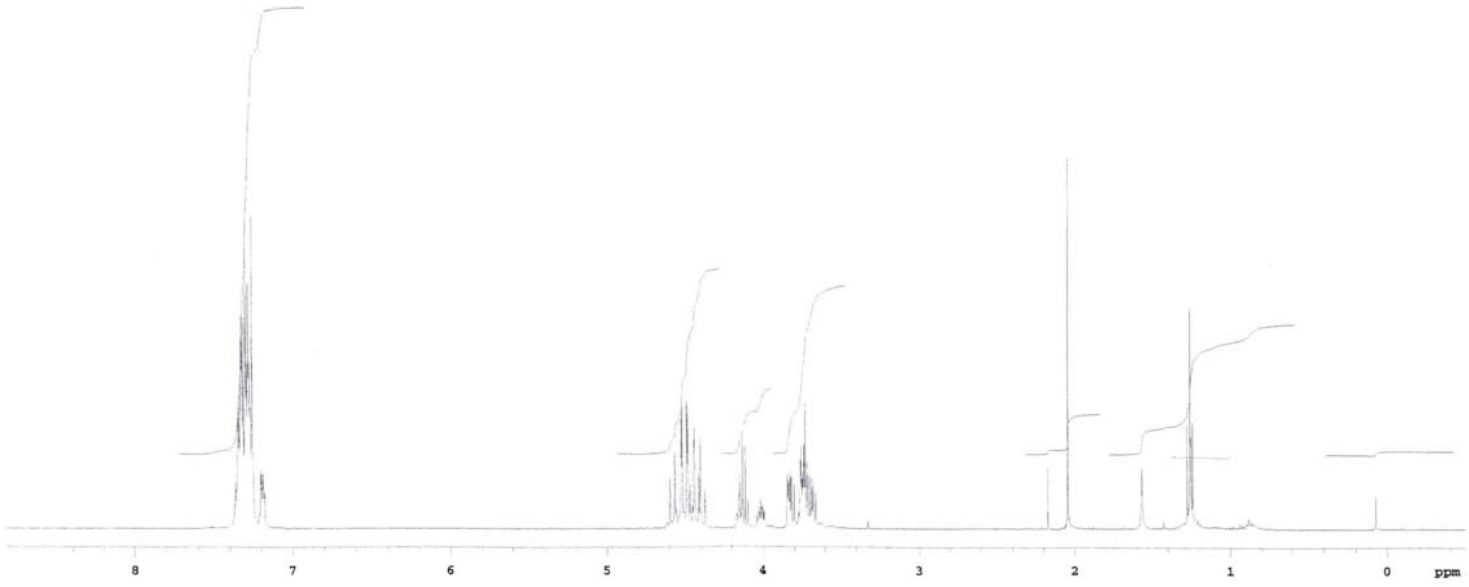
$CDCl_3$, 75 MHz

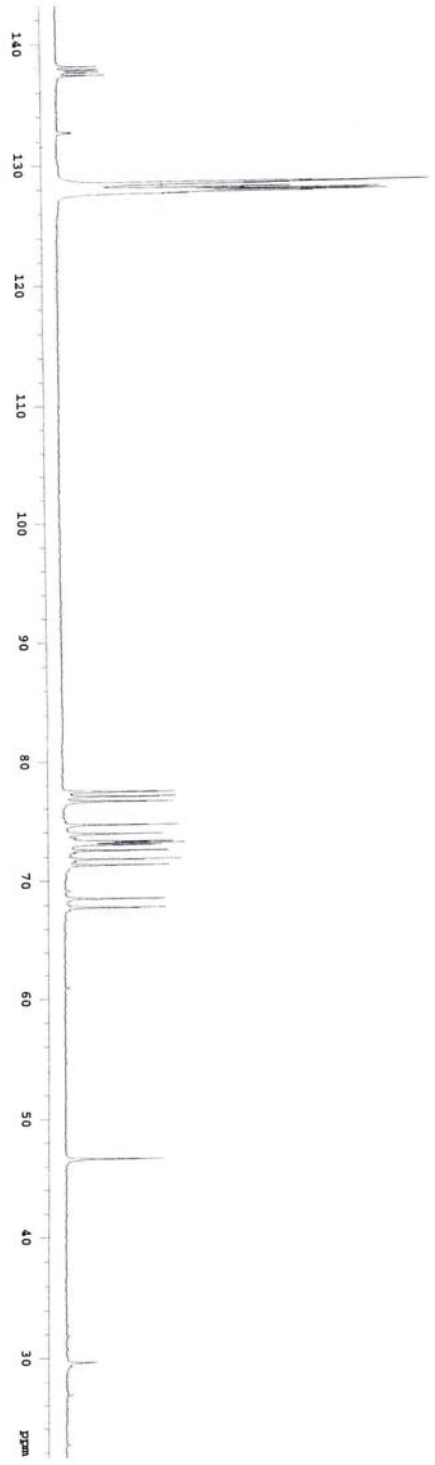


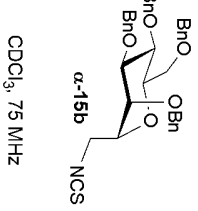


α-15b

$CDCl_3$, 300 MHz

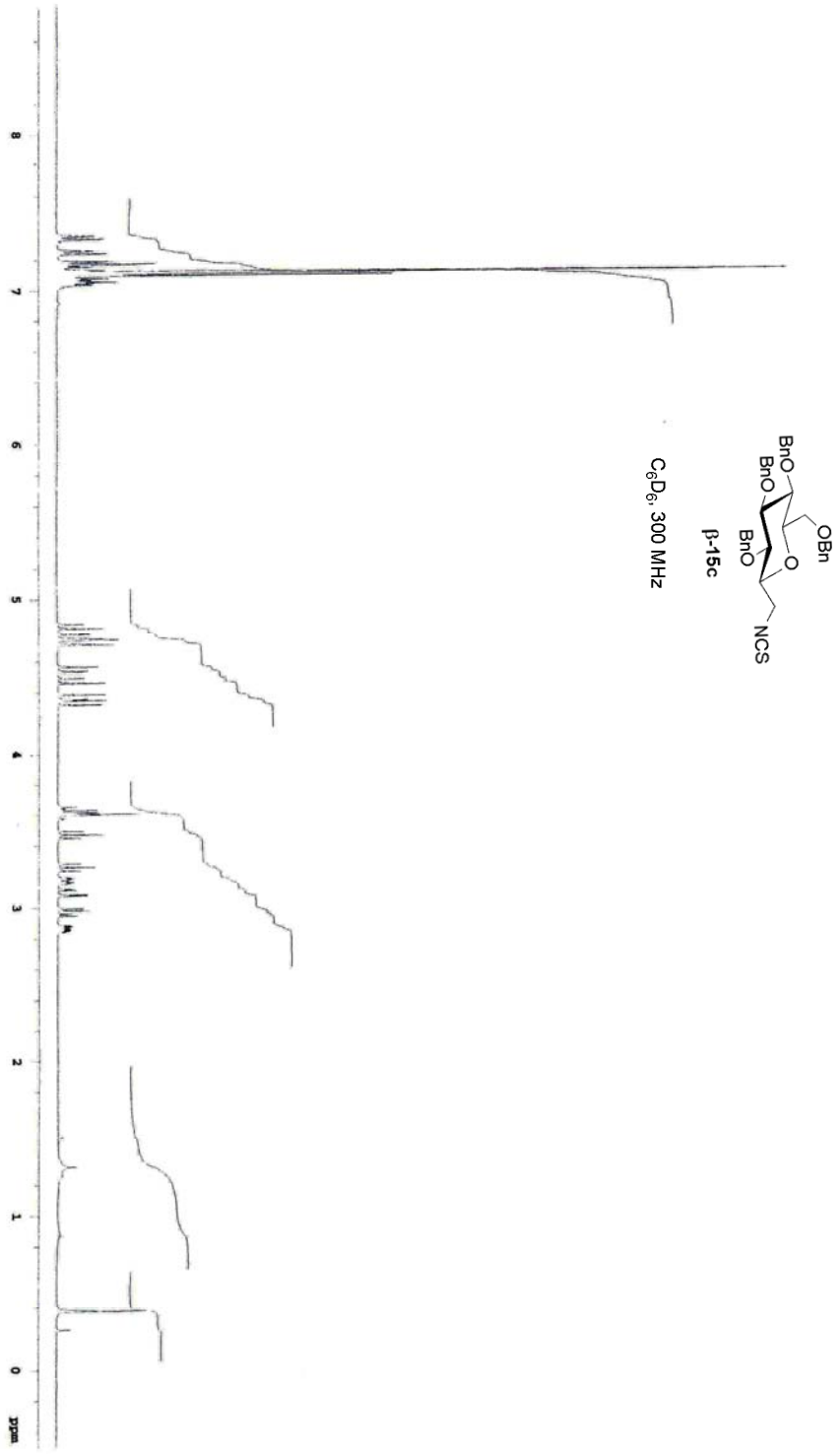


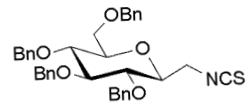




α-15b

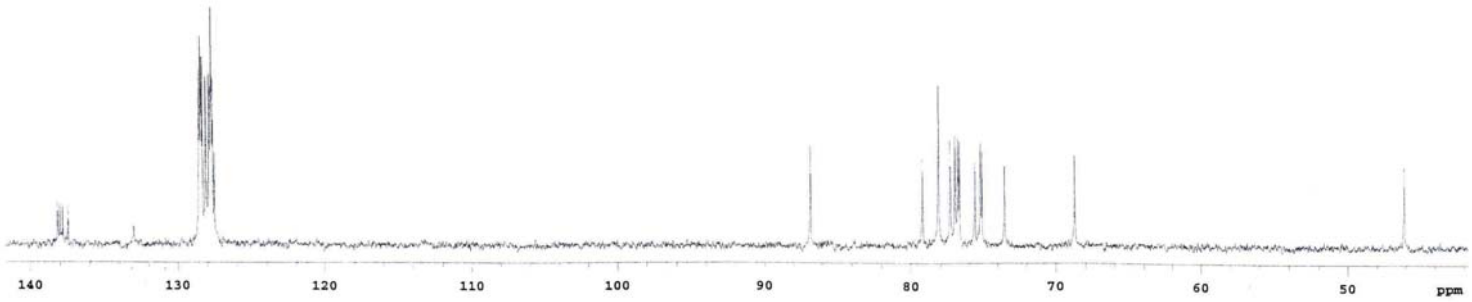
$CDCl_3$, 75 MHz

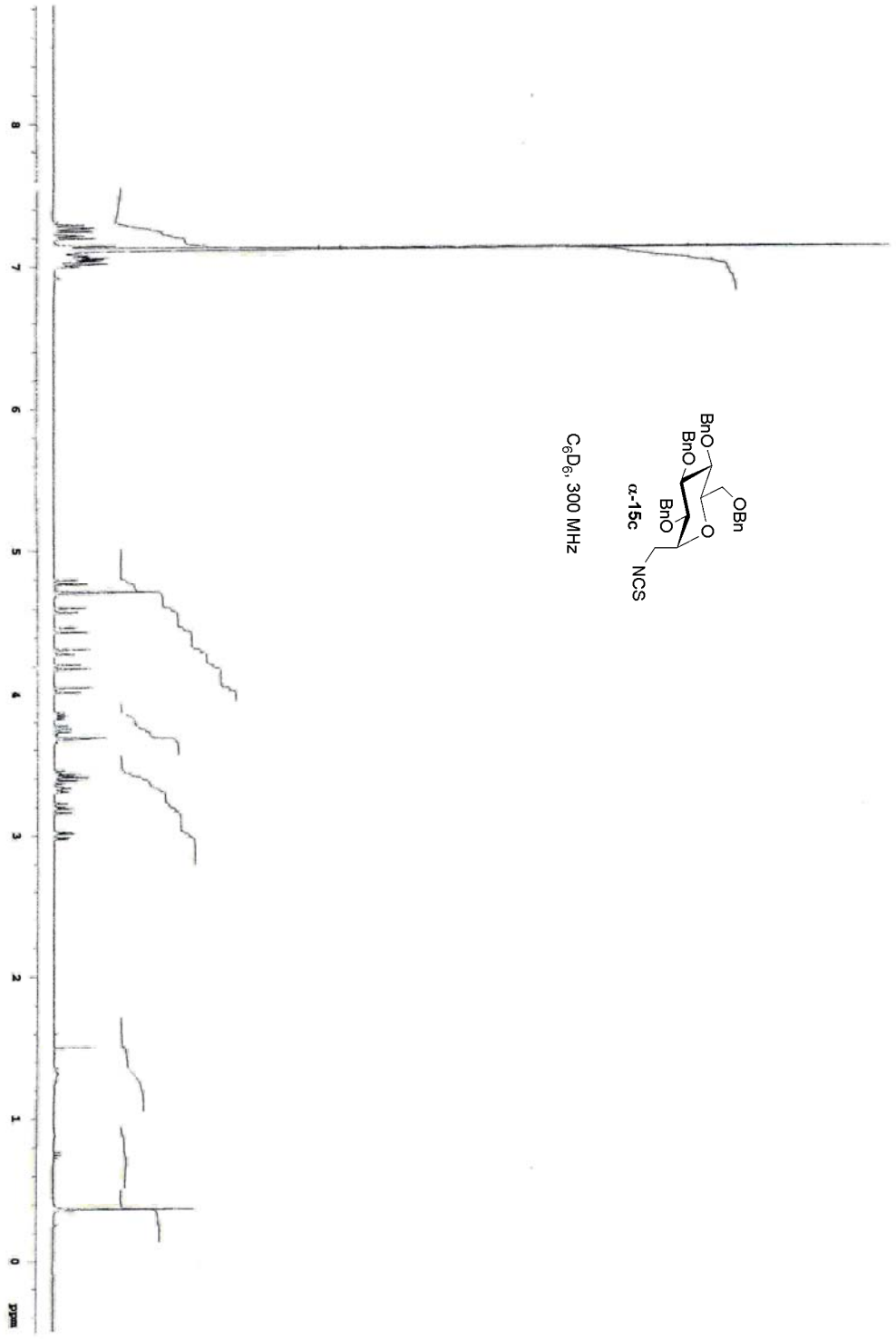

BnO
BnO
BnO
OBn
O
NCS
β-15c
C6D6, 300 MHz
8
7
6
5
4
3
2
1
0
ppm

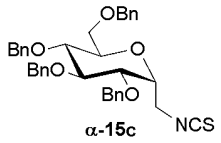


β-15c

$CDCl_3$, 75 MHz

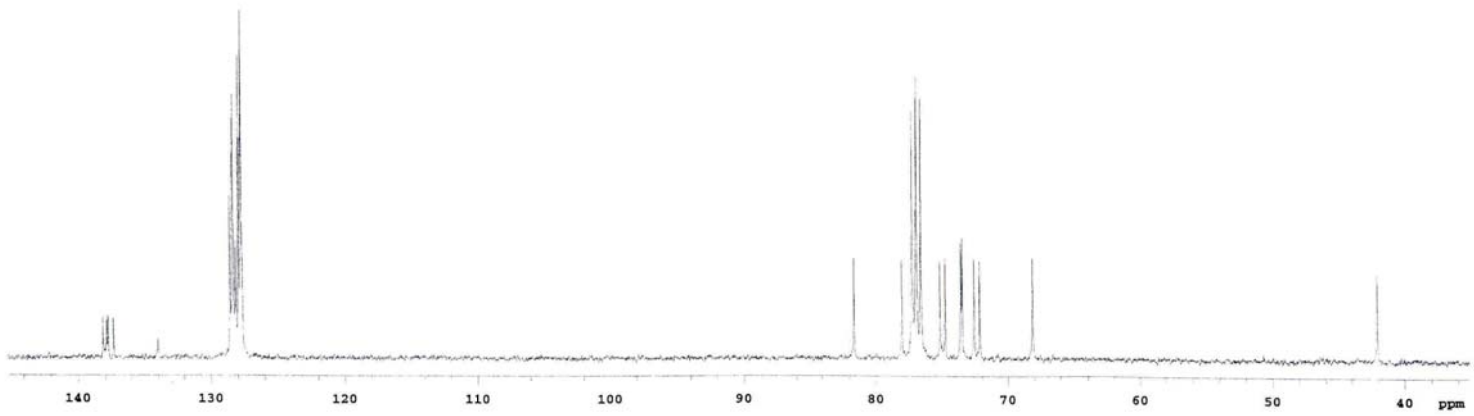


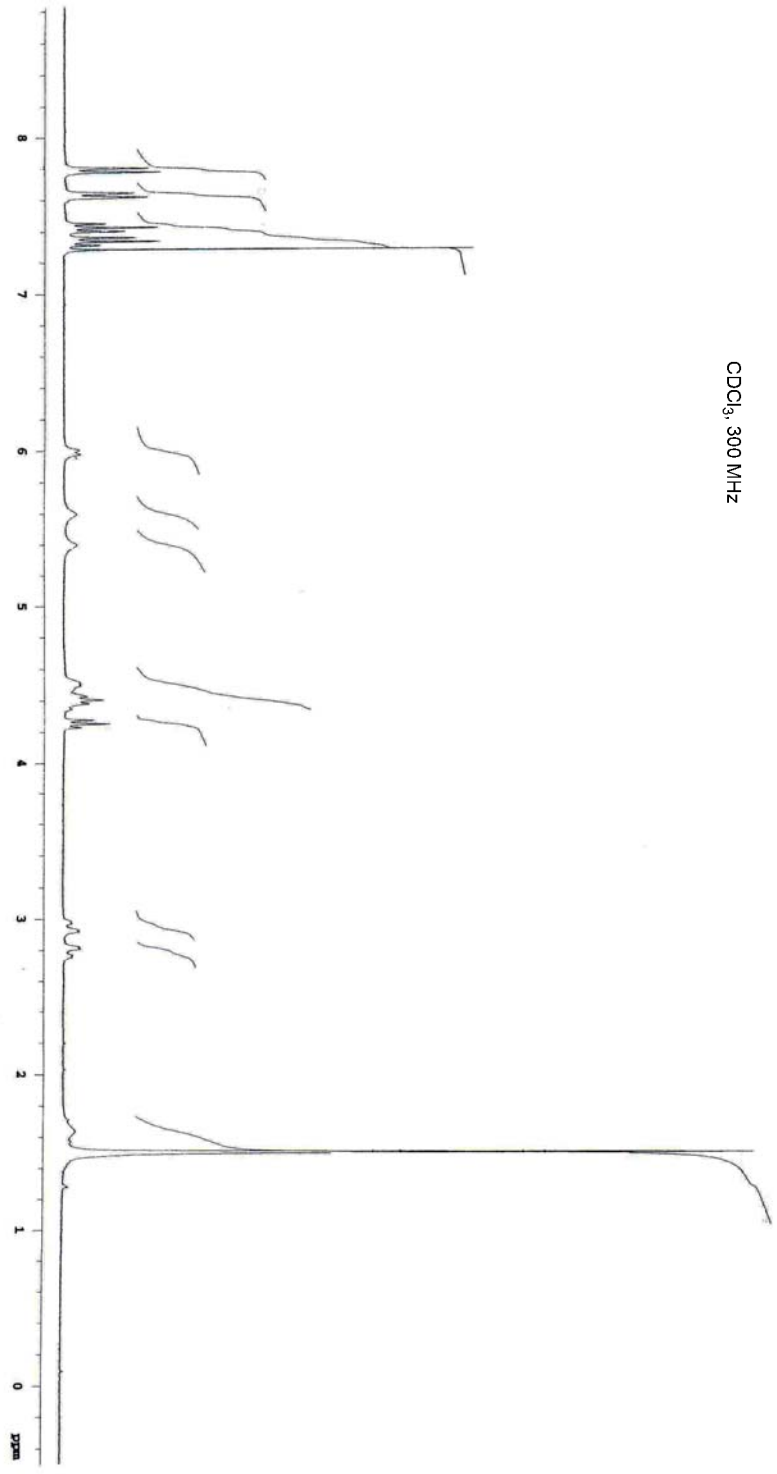

BnO
BnO
BnO
OBn
O
NCS
α-15c
C6D6, 300 MHz
ppm

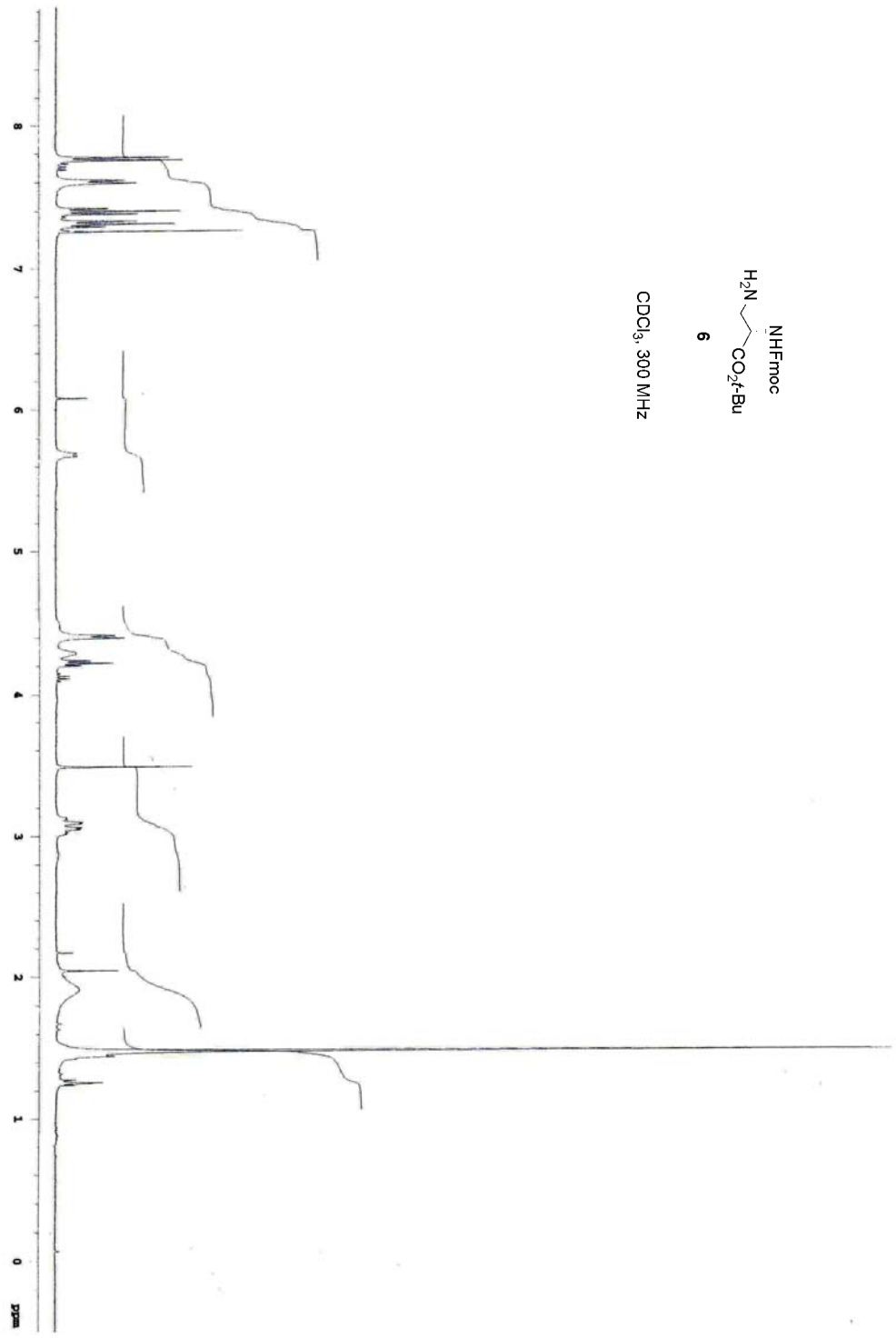


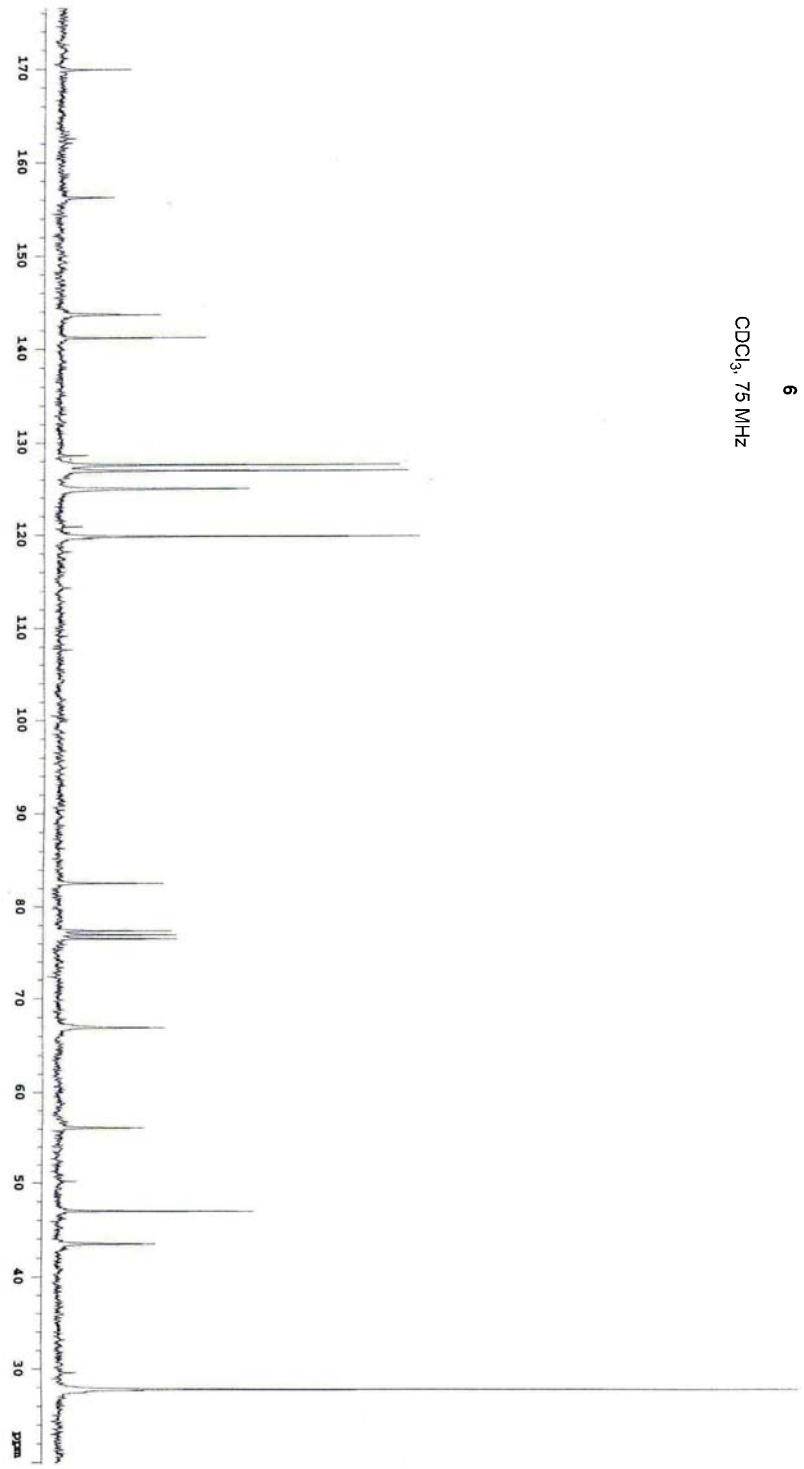
α-15c

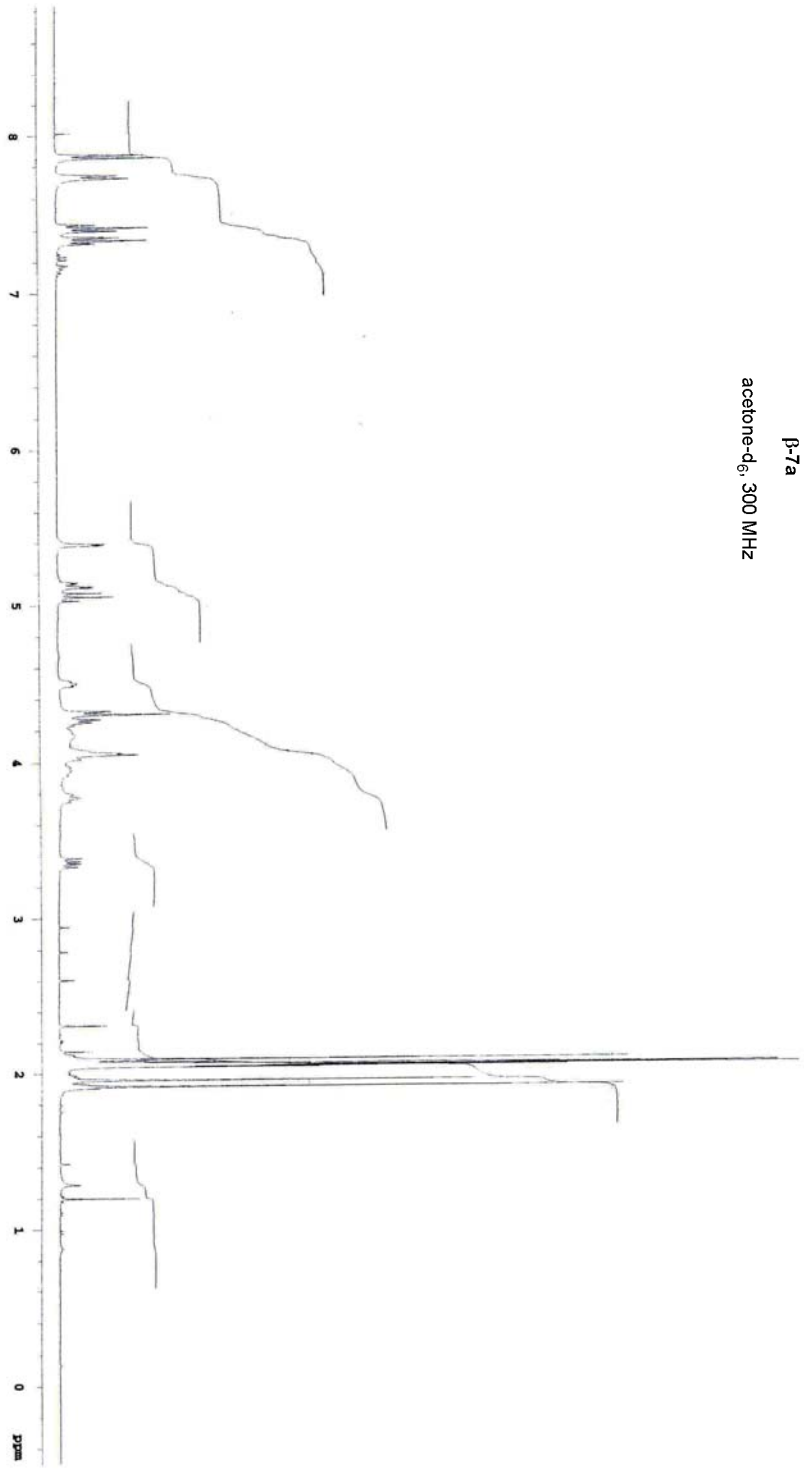
$CDCl_3$, 75 MHz

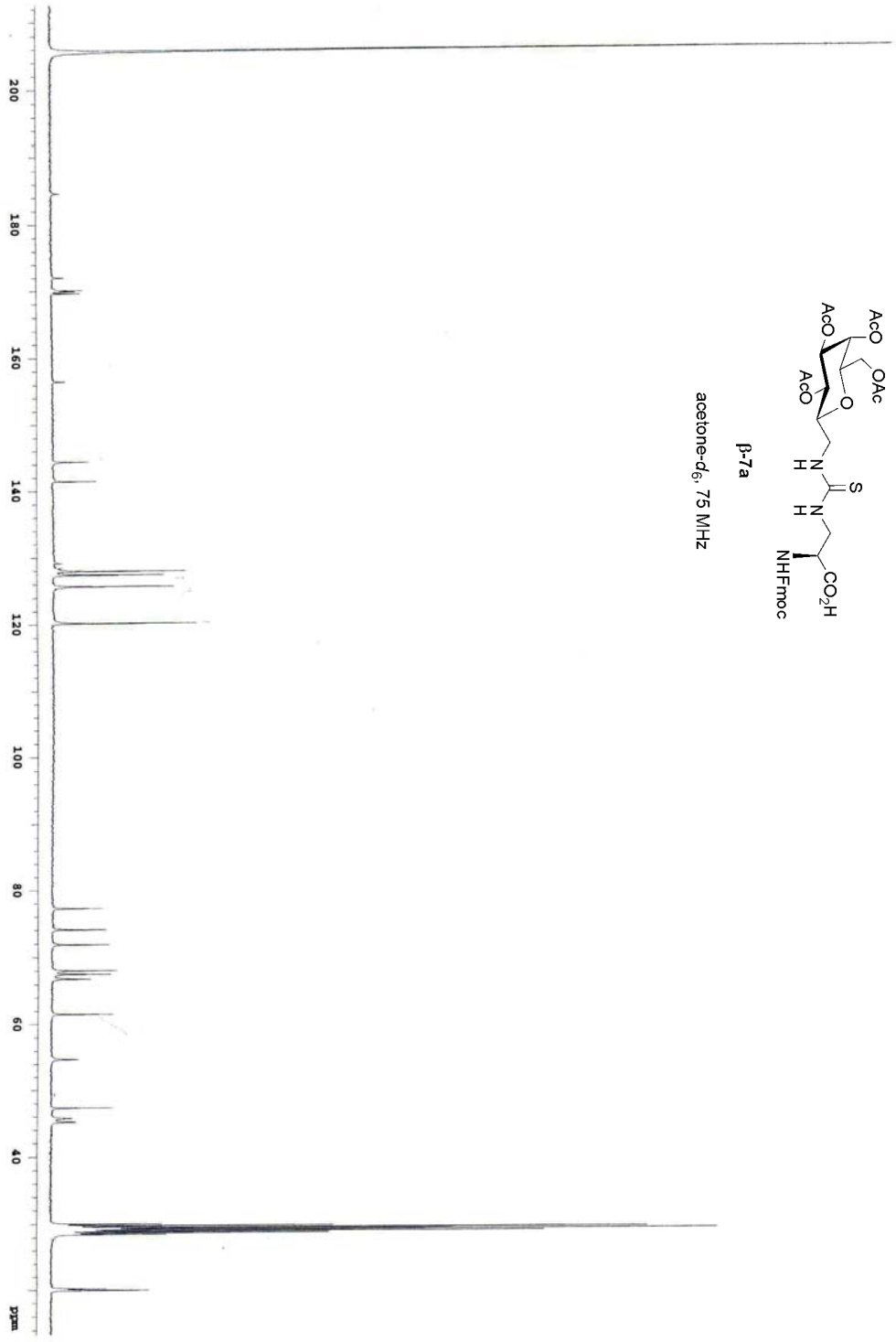


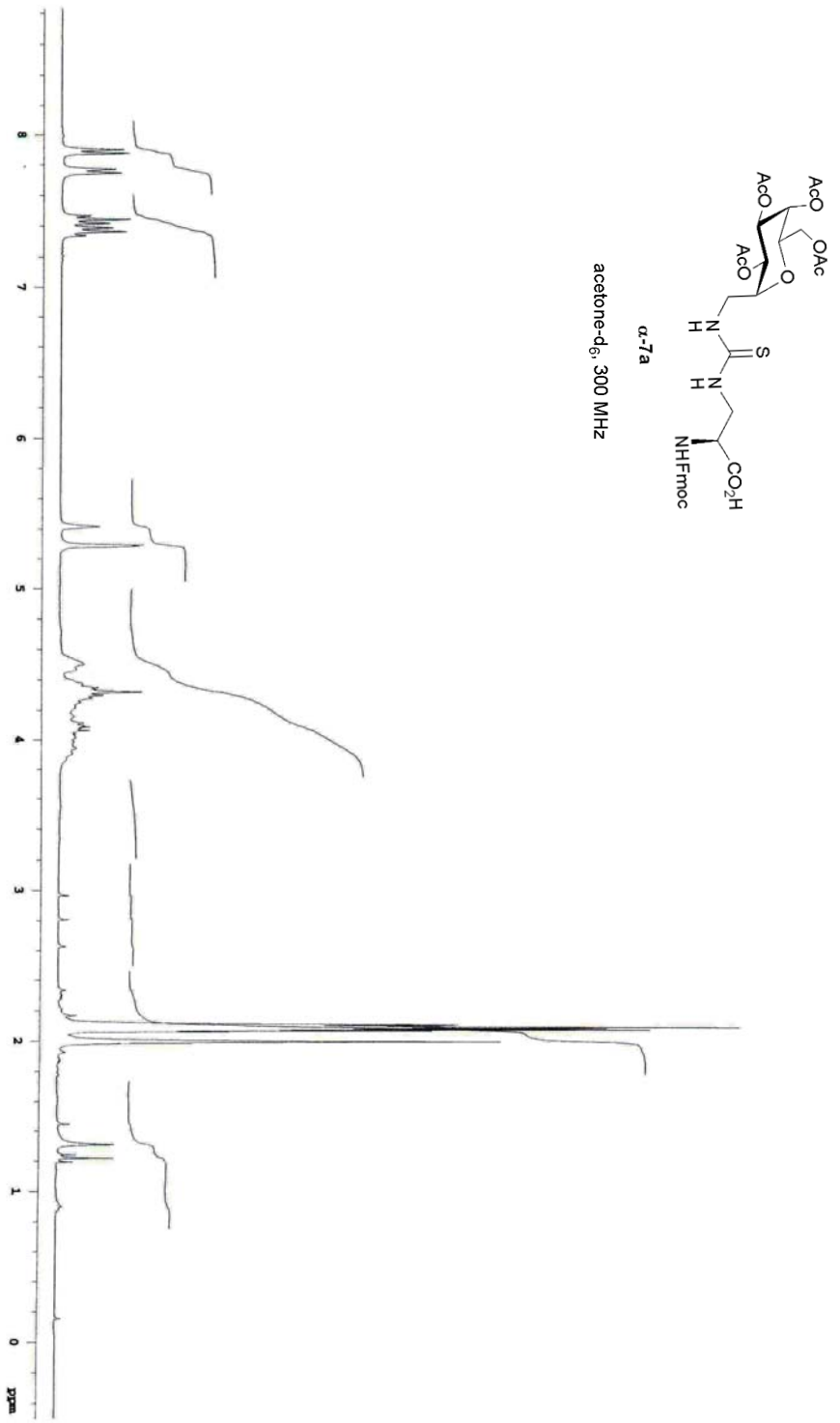

O
NHFmoc
H2N
CO2t-Bu
16
CDCl3, 300 MHz
8
7
6
5
4
3
2
1
0
ppm

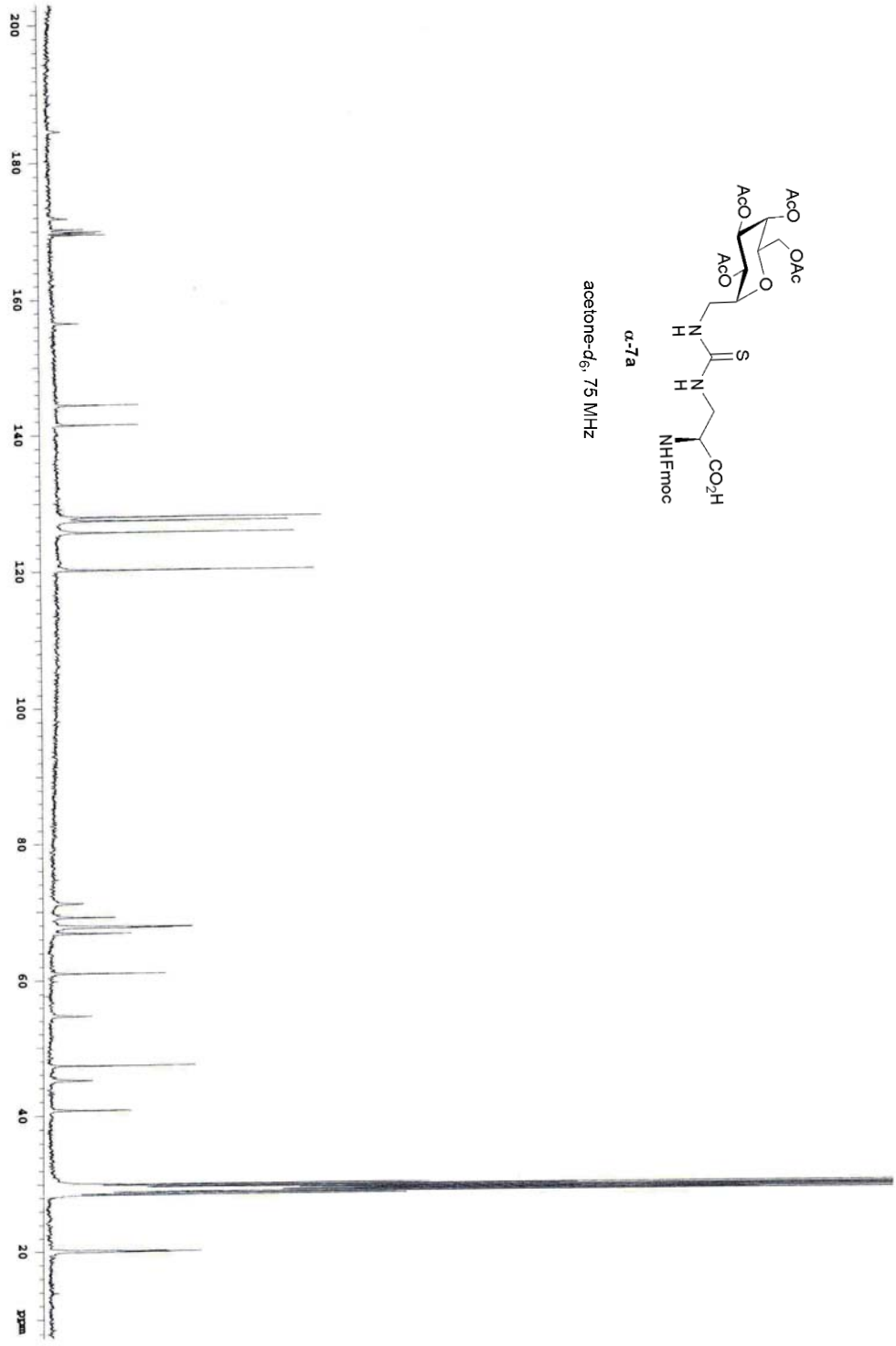

NHFmoc
H2N
CO2t-Bu
6
CDCl3, 300 MHz
8
7
6
5
4
3
2
1
0
ppm

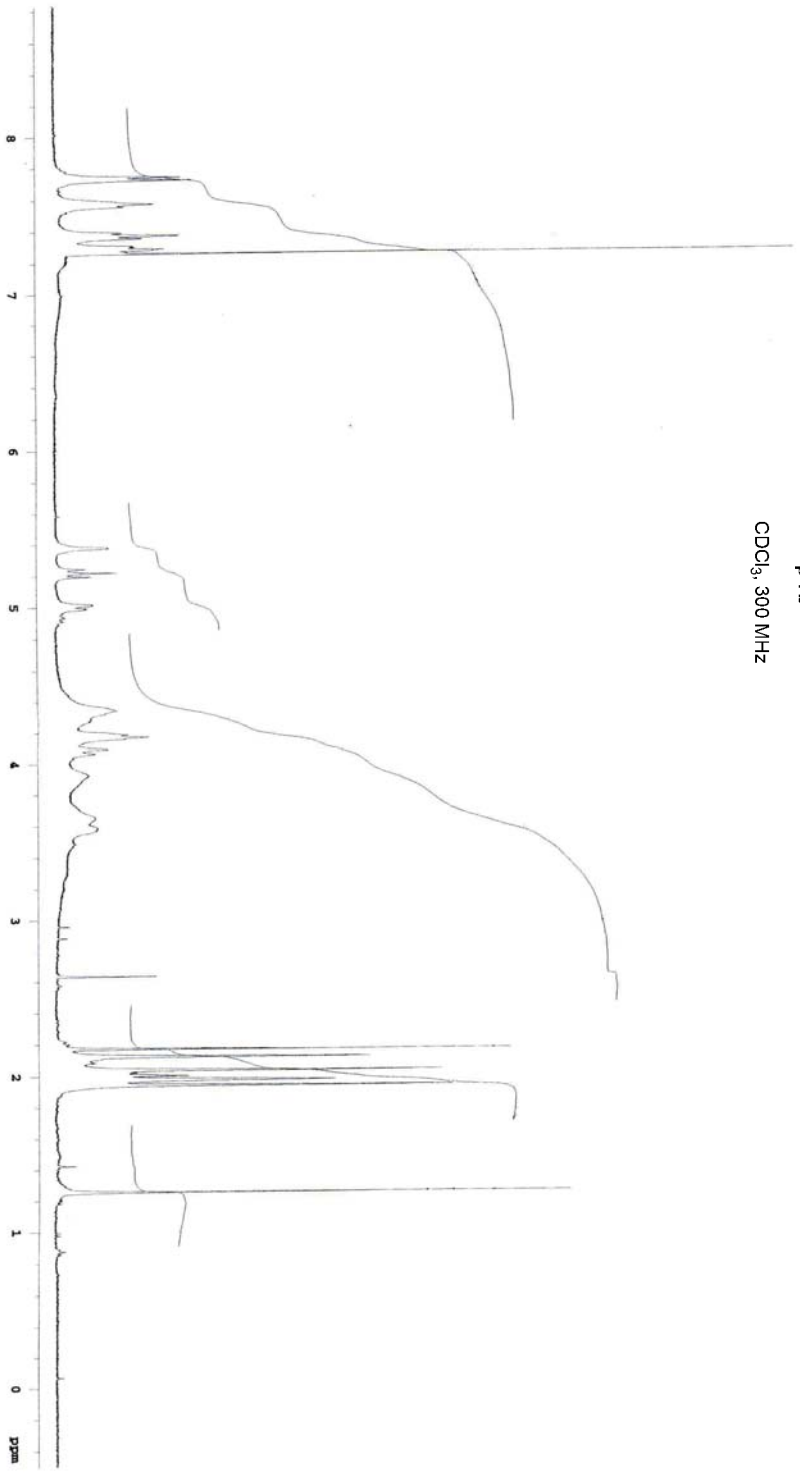

NHFmoc
H2N
CO2t-Bu
6
CDCl3, 75 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

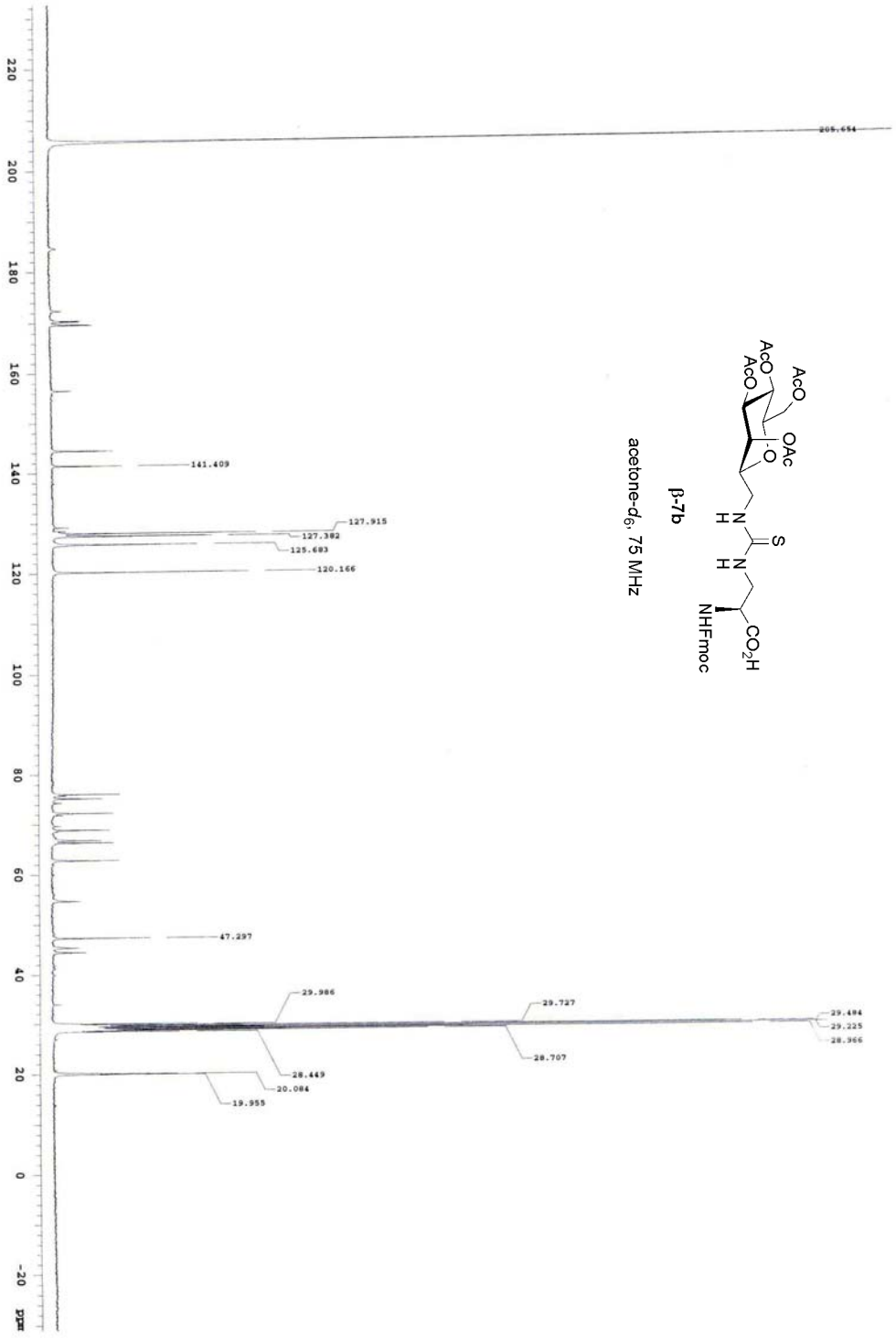

AcO
OAc
AcO
AcO
O
N
H
S
N
H
NHFmoc
CO2H
β-7a
acetone-d6, 300 MHz
8
7
6
5
4
3
2
1
0
ppm

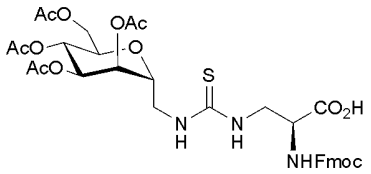

AcO
OAc
AcO
AcO
O
N
H
S
N
H
NHFmoc
CO2H
β-7a
acetone-d6, 75 MHz
200
180
160
140
120
100
80
60
40
ppm


AcO
AcO
AcO
OAc
O
N
H
S
N
H
NHFmoc
CO2H
α-7a
acetone-d6, 300 MHz
8
7
6
5
4
3
2
1
0
ppm


AcO
AcO
AcO
OAc
O
N
H
S
N
H
NHFmoc
CO2H
α-7a
acetone-d6, 75 MHz
200
180
160
140
120
100
80
60
40
20
ppm

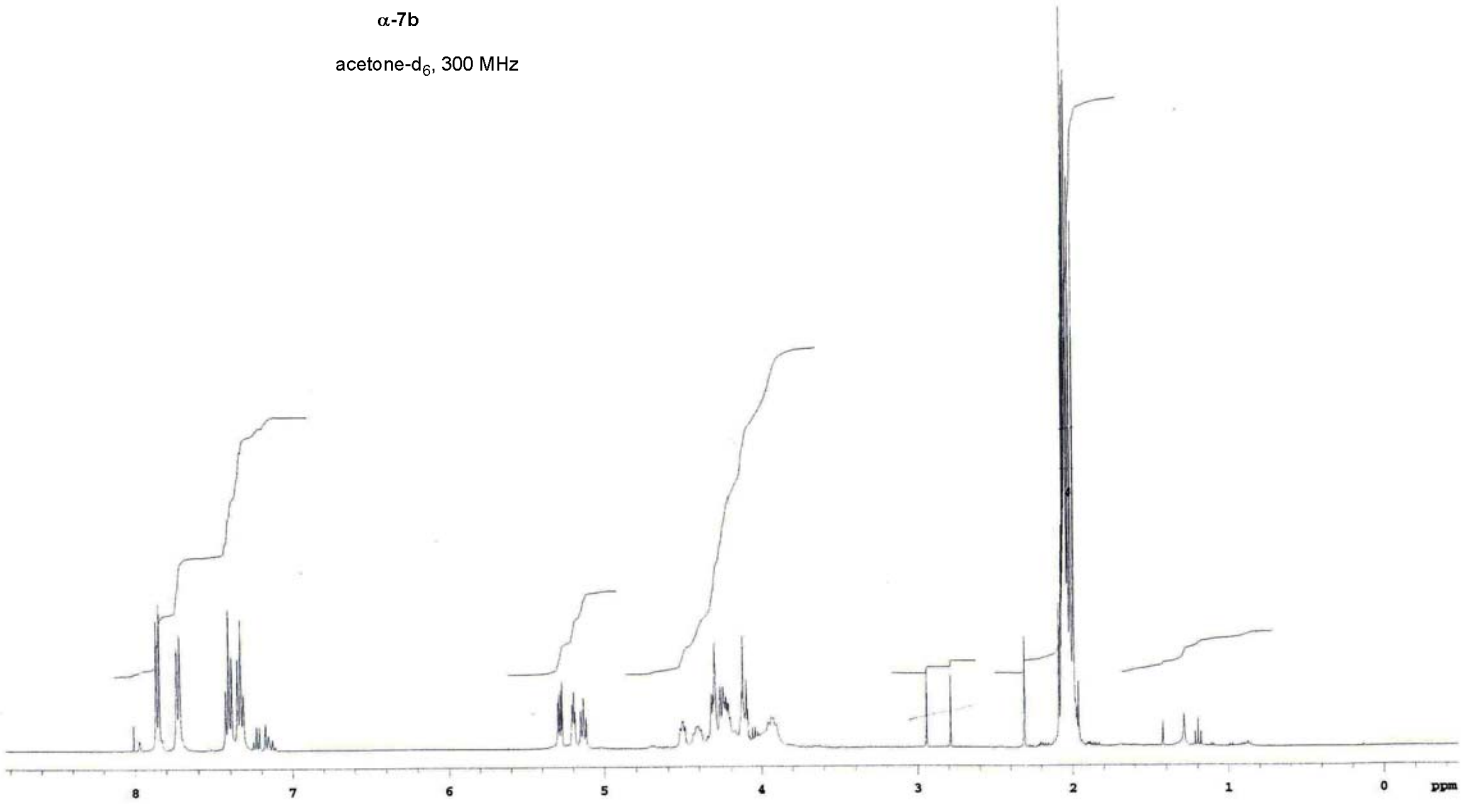

AcO
AcO
AcO
OAc
O
N
H
S
N
H
NHFmoc
CO2H
β-7b
CDCl3, 300 MHz
8
7
6
5
4
3
2
1
0
ppm

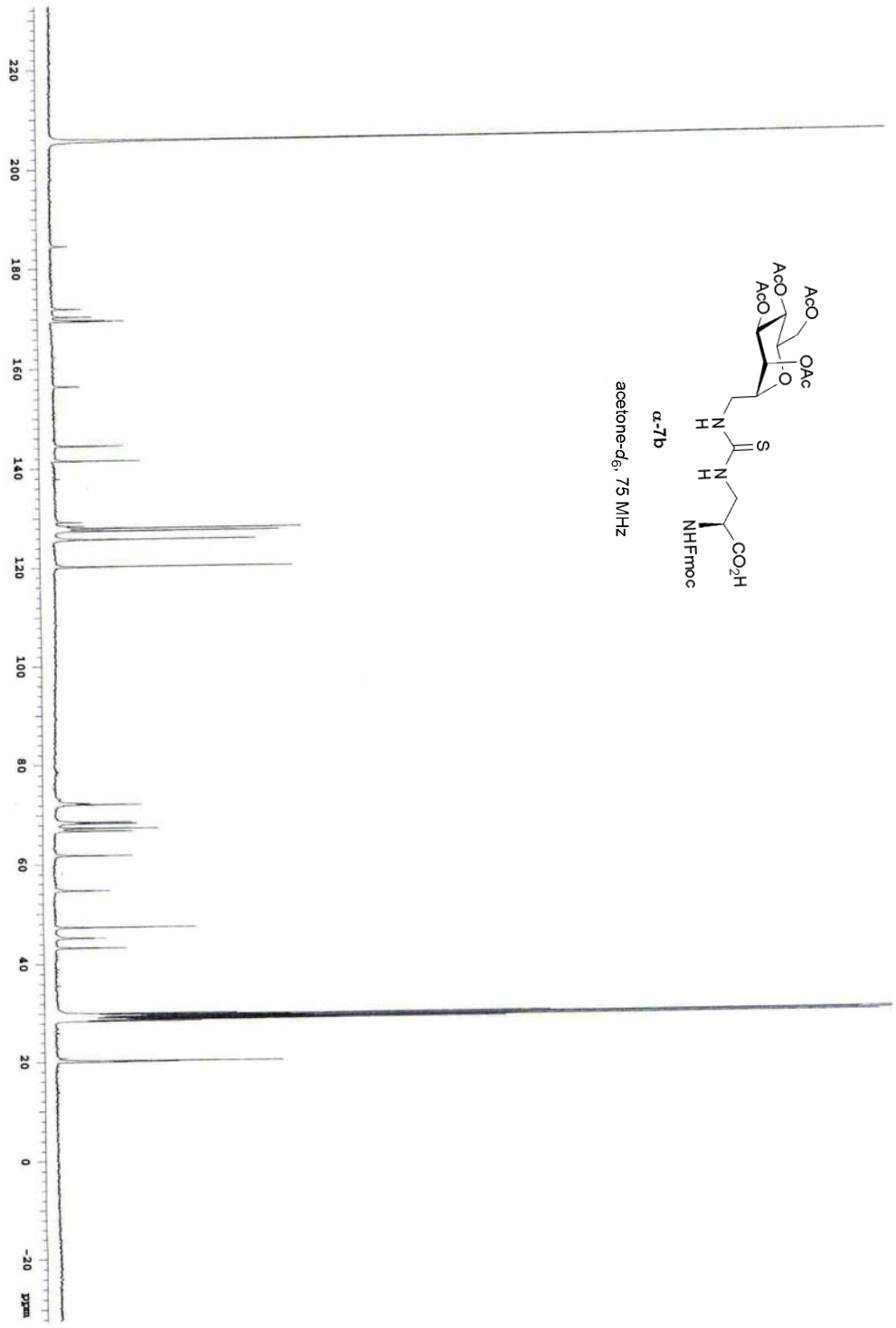

205.654
141.409
127.915
127.382
125.683
120.166
47.297
29.986
29.727
29.494
29.225
28.966
28.707
28.449
20.084
19.955
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm
AcO
AcO
AcO
OAc
O
N
H
N
H
S
NHFmoc
CO2H
β-7b
acetone-d6, 75 MHz

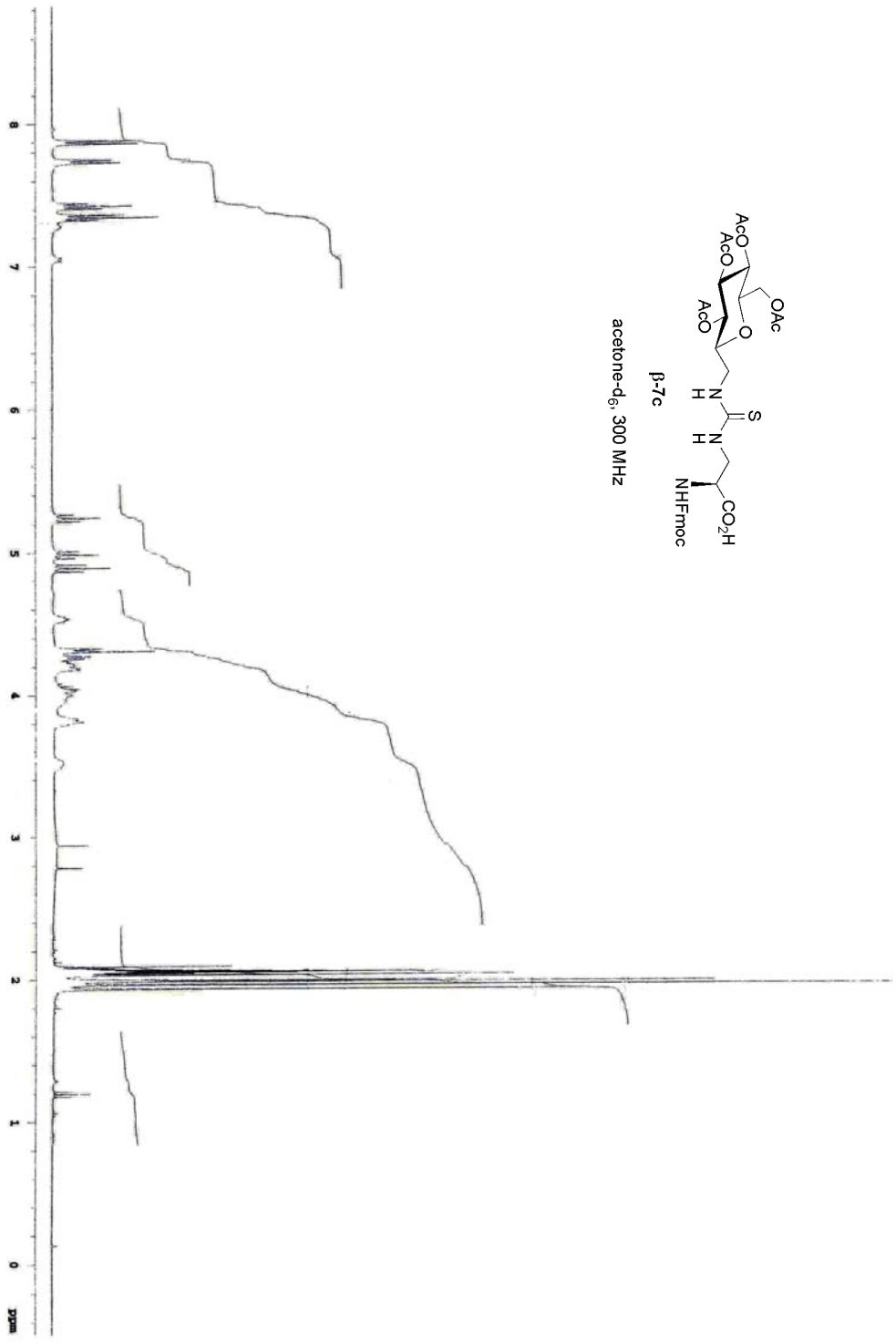


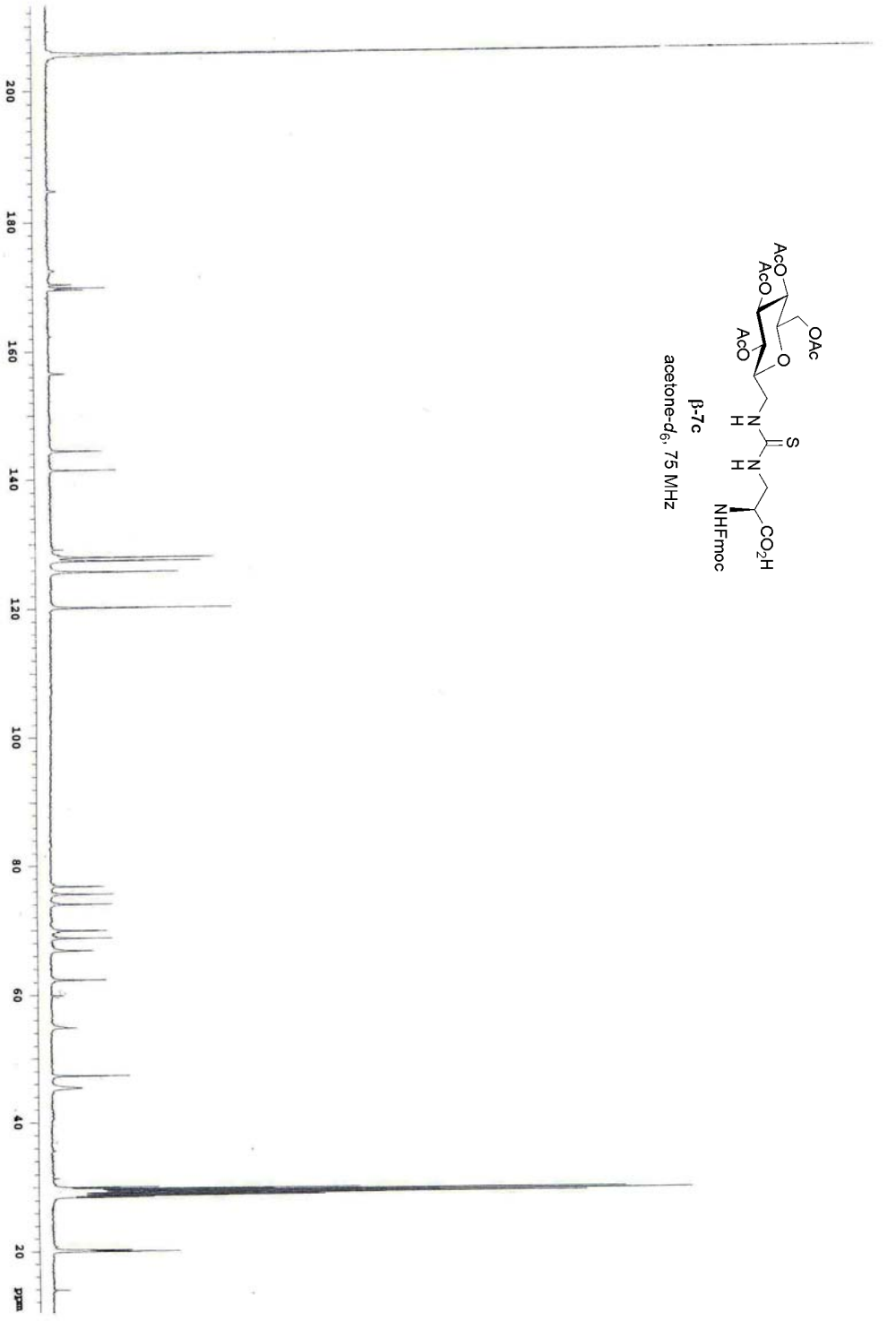
α-7b

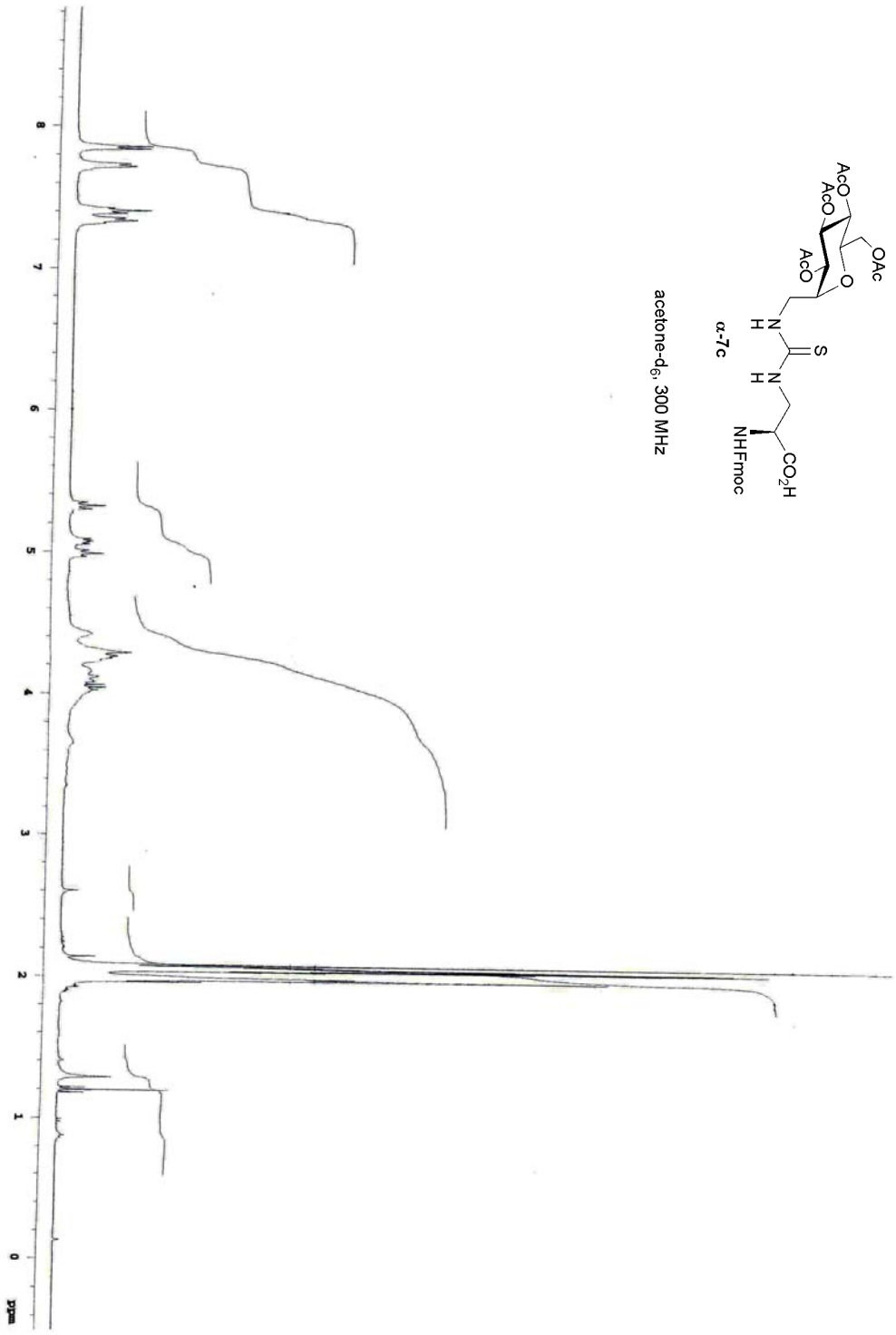
acetone-d_6, 300 MHz

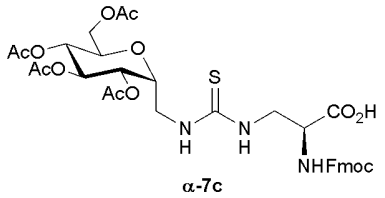



AcO
AcO
AcO
OAc
O
S
N
H
N
H
NHFmoc
CO2H
α-7b
acetone-d6, 75 MHz
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm


AcO
AcO
AcO
OAc
O
N
H
S
N
H
NHFmoc
CO2H
β-7c
acetone-d6, 300 MHz
8
7
6
5
4
3
2
1
0
ppm

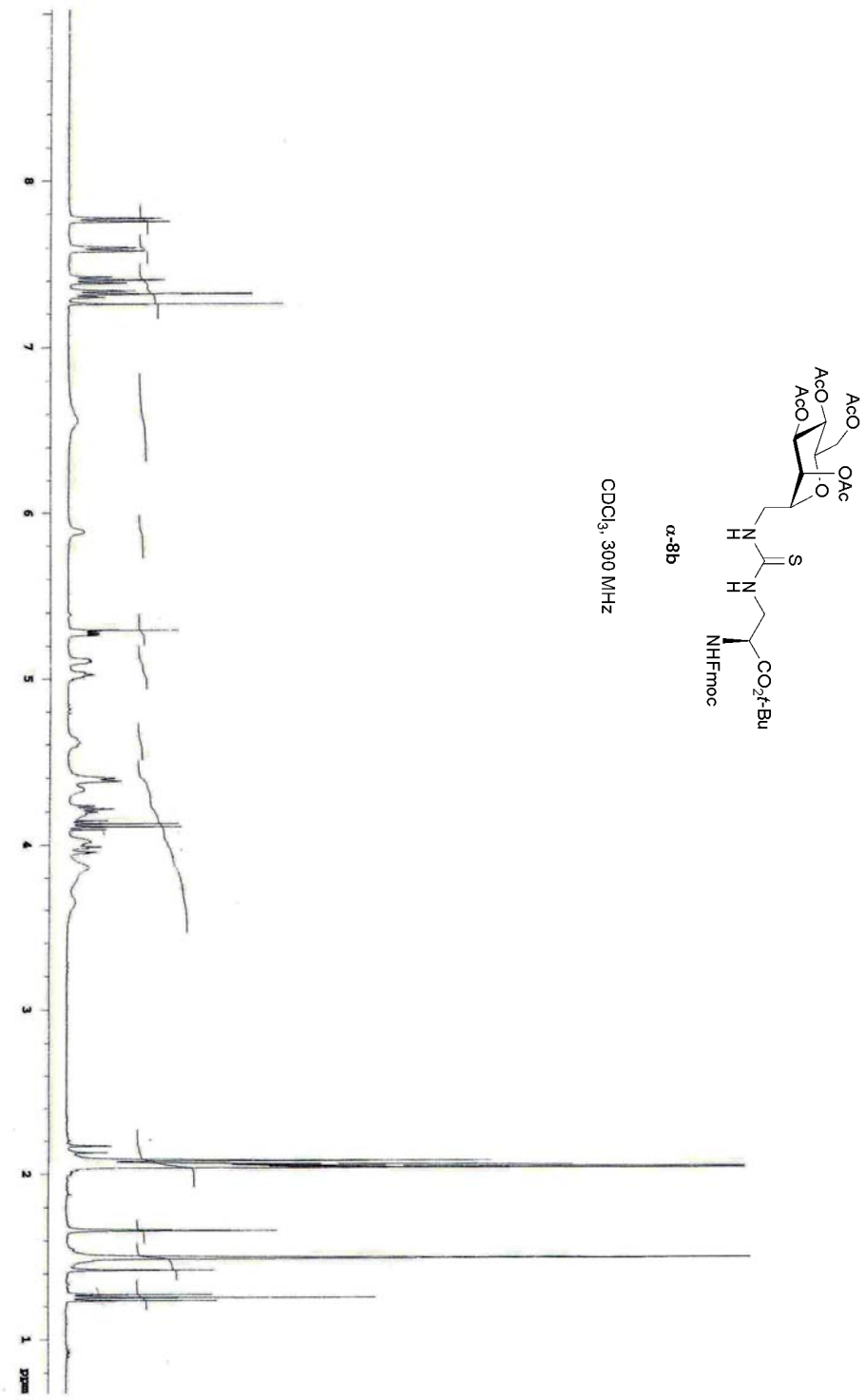

AcO
AcO
AcO
OAc
O
N
H
S
N
H
NHFmoc
CO2H
β-7c
acetone-d6, 75 MHz
200
180
160
140
120
100
80
60
40
20
ppm

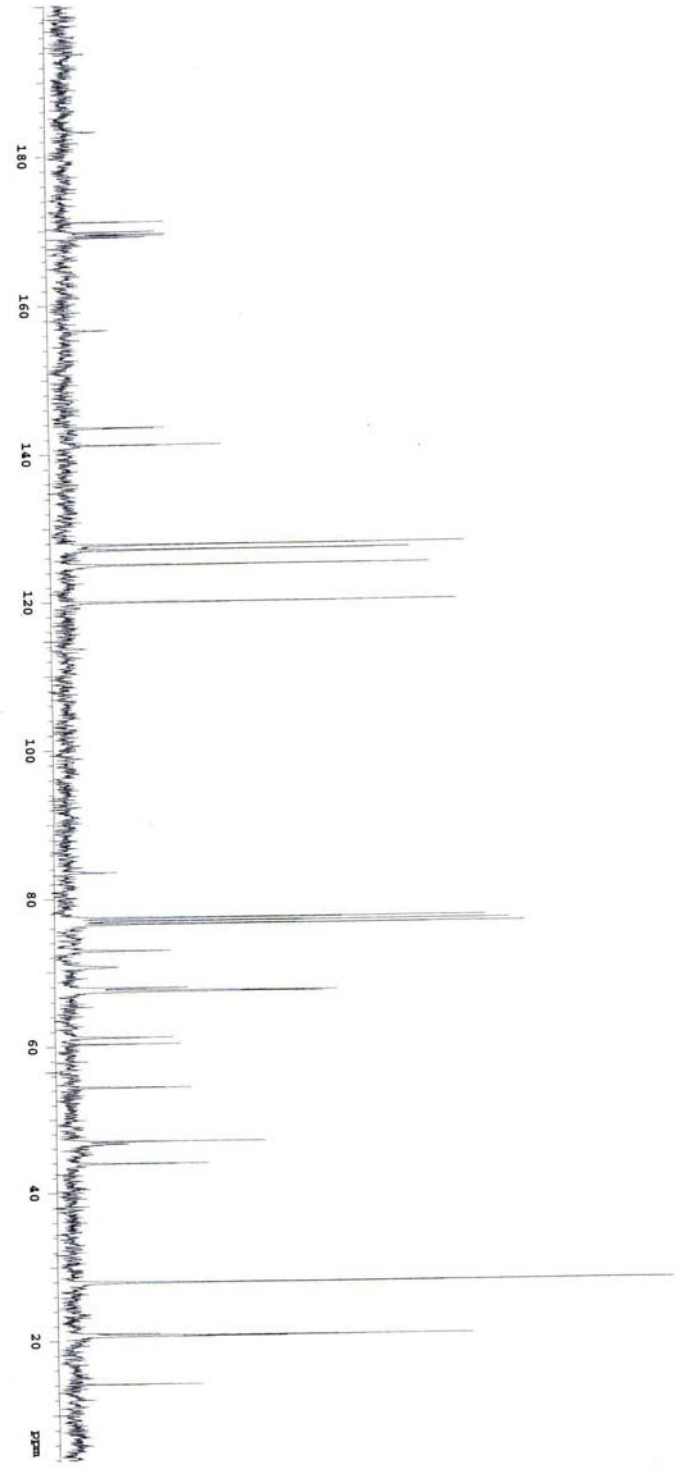

AcO
AcO
AcO
OAc
O
N
H
S
N
H
NHFmoc
CO2H
α-7c
acetone-d6, 300 MHz
8
7
6
5
4
3
2
1
0
ppm

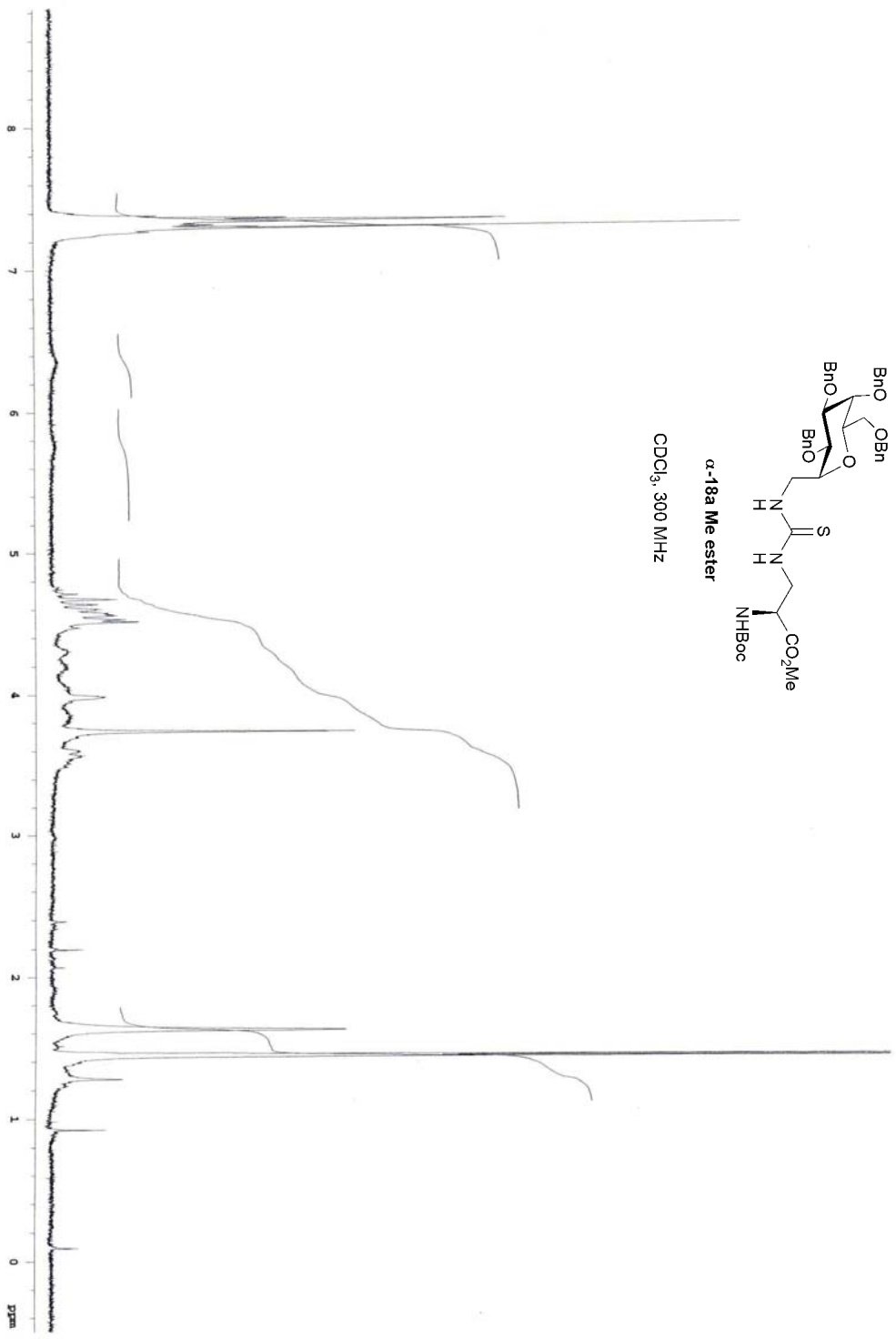


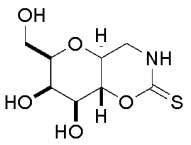
α-7c

acetone-d_6, 75 MHz


AcO
AcO
AcO
OAc
O
N
H
S
N
H
NHFmoc
CO2t-Bu
α-8b
CDCl3, 300 MHz
8
7
6
5
4
3
2
1
ppm

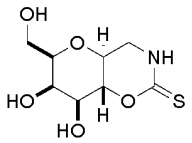

AcO
AcO
AcO
OAc
O
N
H
S
N
H
NHFmoc
CO2t-Bu
α-8b
CDCl3, 75 MHz
180
160
140
120
100
80
60
40
20
ppm


BnO
OBn
BnO
BnO
O
N
H
S
N
H
NHBoc
CO2Me
α-18a Me ester
CDCl3, 300 MHz
8
7
6
5
4
3
2
1
0
ppm



β-20a

D_2O, 300 MHz



β-20a

D_2O, 75 MHz