Electronic Supplementary Information for:

Enzymatically Triggered Chromogenic Cross-Linking Agents Under Physiological Conditions

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(1) X-ray single crystal structures

Summary of the crystal data for 1-acetyl-4-bromo-5-hydroxy-1*H*-indol-3-yl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (17)

CCDC registry	1902489
Formula	$C_{26}H_{30}BrNO_{12.50}$
Formula Weight (g/mol)	636.42
Crystal Dimensions (mm)	0.130×0.229×0.321
Crystal System	orthorhombic
Space Group	P 21 21 21
Temperature (K)	100(2)
a (Å)	13.3401(8)
b (Å)	14.3756(9)
c (Å)	28.9203(19)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	5546.1(6)
Number of reflections to determine final unit cell	9951
Min and Max 2θ for cell determination (°)	4.398, 51.23
Z	8
F(000)	2624
ρ (g/cm^3)	1.524
λ (Å, Mo Kα)	0.71073
μ (mm^{-1})	1.550
Max 2θ for data collection (°)	56.66
Measured fraction of data	0.999
Number of reflections measured	113542
Unique reflections measured	13811
R_{merge}	6.44%
Number of parameters in least-squares	788
R_1	0.0324
wR_2	0.0684
R_1 (all data)	0.0423
wR_2 (all data)	0.0712

Summary of the crystal data for 1-acetyl-4,6-dibromo-5-hydroxy-1*H*-indol-3-yl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (18)

CCDC registry	1902488
Formula	$C_{25.50}H_{28}Br_2NO_{12.50}$
Formula Weight (g/mol)	708.31
Crystal Dimensions (mm)	0.072×0.290×0.302
Crystal System	orthorhombic
Space Group	P 21 21 21
Temperature (K)	100
a (Å)	13.4601(5)
b (Å)	14.6763(5)
c (Å)	12.7603 (4)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	5670.5(3)
Number of reflections to determine final unit cell	9915
Min and Max 2θ for cell determination (°)	4.991, 62.78
Z	8
F(000)	2864
ρ (g/cm^3)	1.659
λ (Å, Mo Kα)	0.71073
μ (mm^{-1})	2.926
Max 2θ for data collection (°)	66.38
Measured fraction of data	0.999
Number of reflections measured	116273
Unique reflections measured	21707
R_{merge}	4.48%
Number of parameters in least-squares	757
R_1	0.0297
wR_2	0.0604
R_1 (all data)	0.0380
wR_2 (all data)	0.0627

(2) Time course of indigogenic reactions selected from Table 1

Figure S1 shows the time course of the indigogenic reaction of known indoxyl-glucoside **1** or **45** with β-glucosidase from almonds. The formation of indigoid products was monitored by absorption spectroscopy over the course of 16 h due to the slow reaction rate.

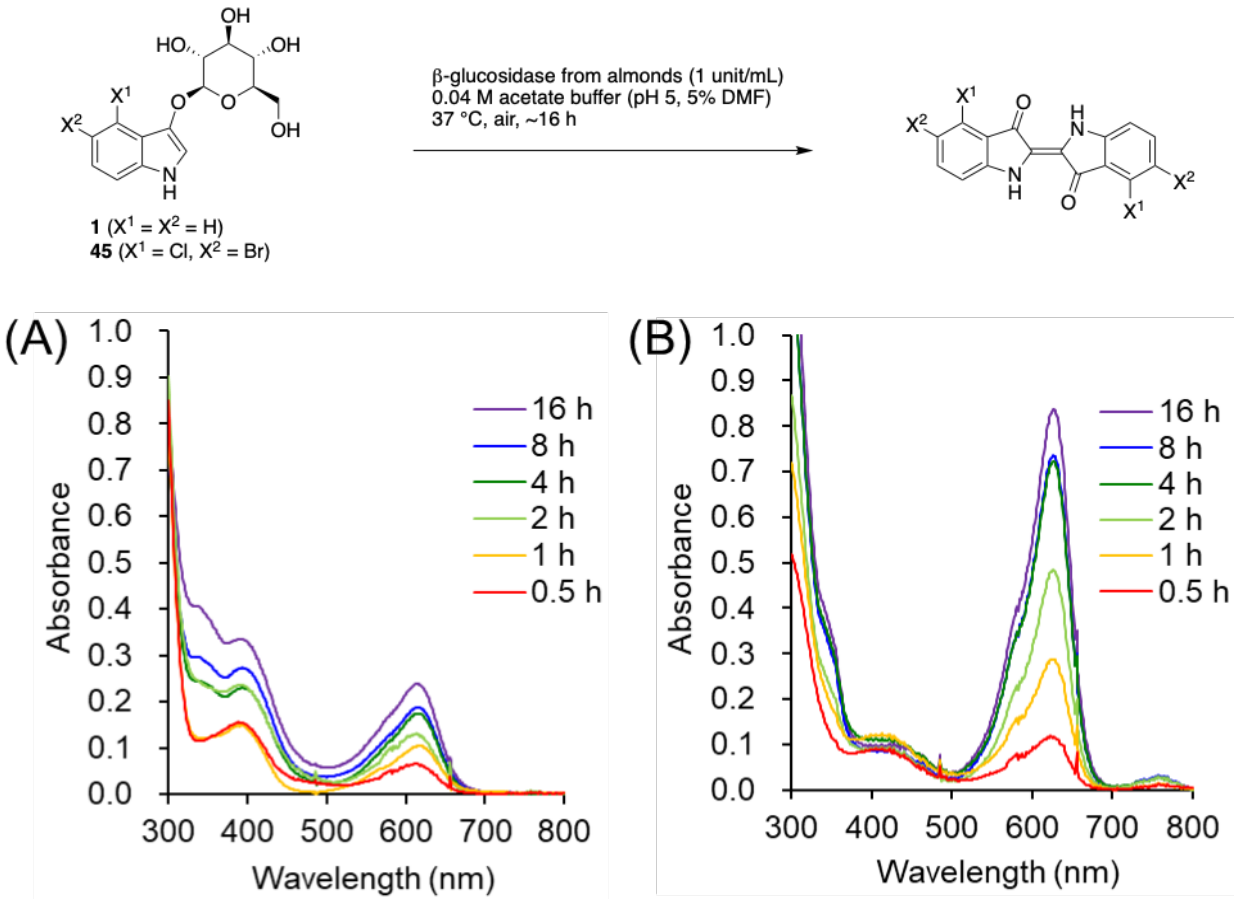
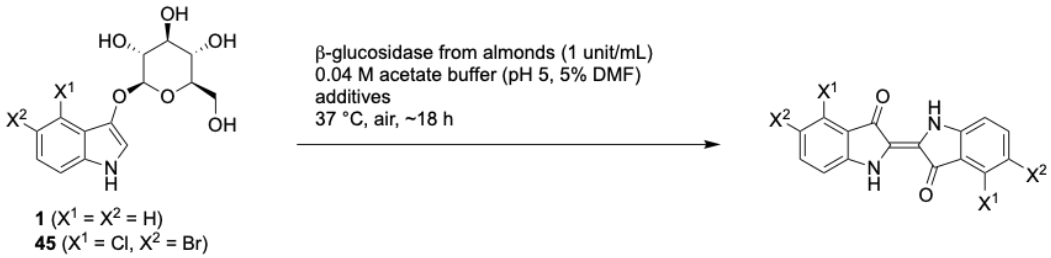


Figure S1. Time course of absorption spectra of indigogenic reactions with β-glucosidase from almonds (1 unit/mL) in 40 mM acetate buffer (pH 5.0, containing 5% DMF) at 37 °C. (A) The reaction of **1** (1 mM). After incubation, the reaction mixture was diluted four times with DMF and used for absorption spectroscopy. (B) The reaction of **45** (1 mM). After incubation, the reaction mixture was diluted ten times with DMF and used for absorption spectroscopy.

(3) Indigogenic reactions examined in the presence of oxidants or with tritosomes

To improve the yield and reaction rate of the indigogenic reaction, addition of oxidizing agents was attempted (Figure S2). However, $K_2Fe(CN)_6/K_3Fe(CN)_6$, peroxidase/H_2O_2, 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl tetrazolium chloride (**S2**, Chart S1), or phenazine methosulfate (**S3**) did not increase the yield of the indigogenic reaction with **1** (Figure S2A). As shown in Figure S2B, the reaction rate of the indigogenic reaction with **45** was not increased by inclusion of $K_2Fe(CN)_6/K_3Fe(CN)_6$ or peroxidase/H_2O_2.



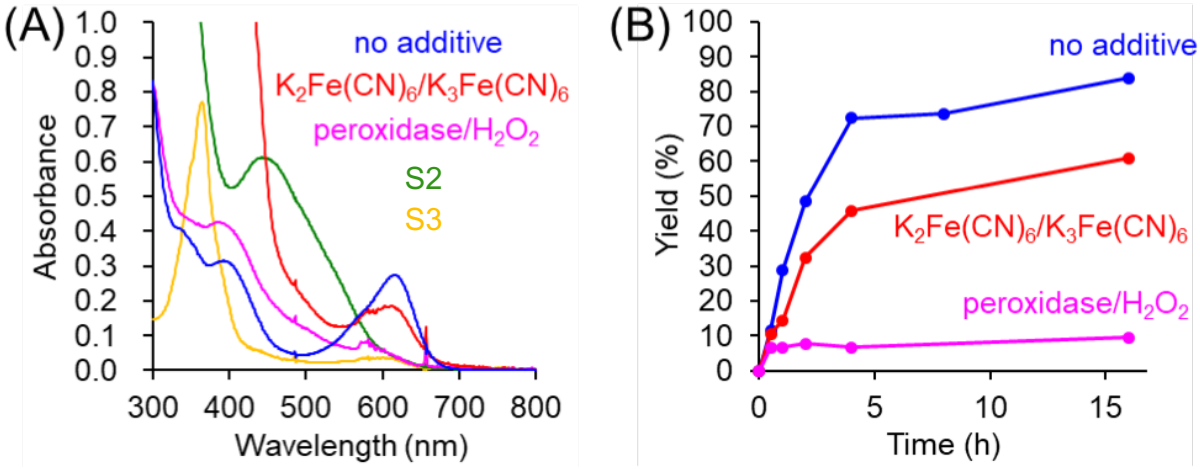


Figure S2. Indigogenic reactions in the presence of oxidizing agents. (A) Absorption spectra from the reaction with **1** (1 mM) without additives or with $K_2Fe(CN)_6$ (3 mM)/$K_3Fe(CN)_6$ (3 mM), peroxidase (1 unit/mL)/H_2O_2 (5 mM), **S2** (3 mM), or **S3** (3 mM). After incubation, the reaction mixture was diluted with DMF 4 times (for no additive; $K_2Fe(CN)_6$)/$K_3Fe(CN)_6$; or peroxidase), 12 times (**S2**) or 20 times (**S3**) and used for absorption spectroscopy. (B) Time course of the reaction with **45** (1 mM) without additives, with $K_2Fe(CN)_6$ (3 mM)/$K_3Fe(CN)_6$ (3 mM), and with peroxidase (1 unit/mL)/H_2O_2 (5 mM). Yields were estimated from absorption spectroscopy with $\varepsilon = 2.00\times10^4$ $M^{-1}cm^{-1}$ reported for 5,5′-dibromo-4,4′-dichloroindigo.[40]

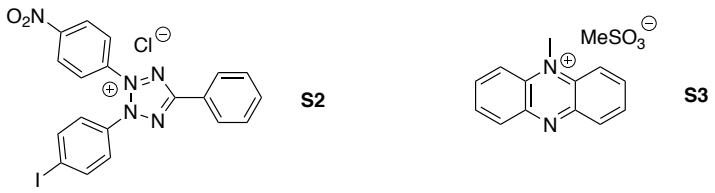
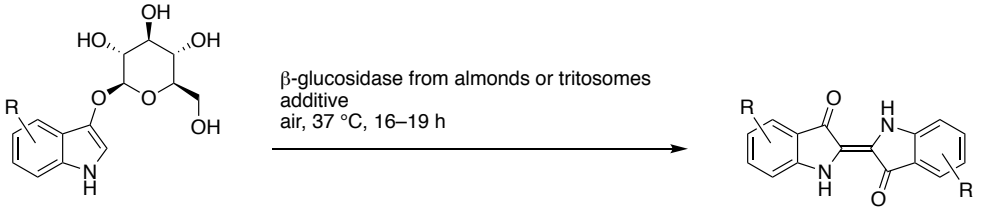
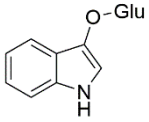
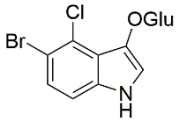
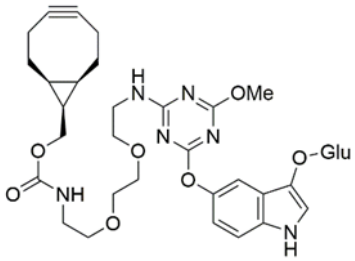
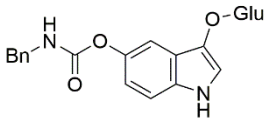
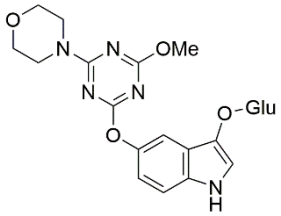
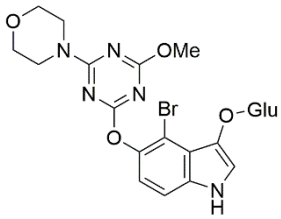


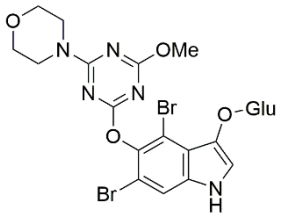
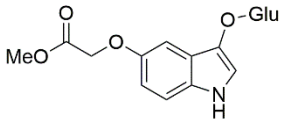
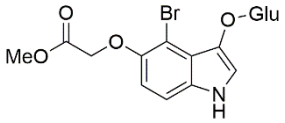
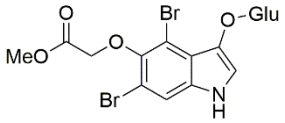
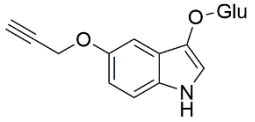
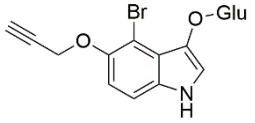
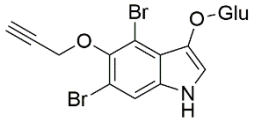
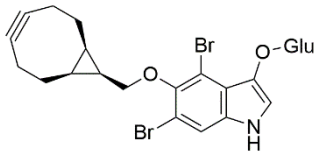
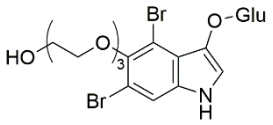
Chart S1. Structures of additives for indigogenic reactions.

A set of indigogenic reactions was examined where oxidants were included along with the β-glucosidase.

Table S1. Indigogenic reactions of indoxyl derivatives.



Entry	Indoxyl	Structure	Yield (%)[a]		
			β-glucosidase from almonds with **S2**[b]	tritosomes[c]	tritosomes with catabolic buffer[d]
1	**1**		Poor	< 1	< 1
2	**45**		Good	< 1[e]	8[e]
3	**15**		Poor	< 1	< 1
4	**16**		Poor	8	< 5
5	**19**		Poor	15	11
6	**20**		Poor	< 1	< 1

7	**21**		Poor	< 1	< 1
8	**22**		Poor	< 1	< 1
9	**23**		Good	< 1	< 1
10	**24**		Fair	< 1	< 5
11	**25**		Poor	< 5	< 5
12	**26**		Good	< 1	< 1
13	**27**		Good	< 1	11 (6)[g]
14	**30**		Poor	< 1	< 1
15	**33**		Good[g]	–[f]	–[f]

[a]The yield was estimated by absorption spectroscopy with ε = 1.27×10^4 $M^{-1}cm^{-1}$ (DMF/H_2O = 2:1) measured for the parent indigo **4** unless otherwise noted. A yield of <1% implies no color was observed by visual inspection and no absorption was observed spectroscopically. A yield of <5% implies a faint blue color was observed by visual inspection but the absorption was too weak for reliable spectroscopic determination. [b]A mixture of the indoxyl (1 mM), **S2** (3 mM), and β-glucosidase from almonds (1 unit/mL) in 40 mM acetate buffer (pH 5.0, containing 5% DMF) was incubated at 37 °C for 16–19 h. The yield of indigoid compounds was roughly evaluated by

absorption spectroscopy as products from **S2** have a shoulder absorption in the region 600–650 nm. [c]A mixture of the indoxyl (1 mM) and tritosomes (0.13 mg protein/mL) in 20 mM acetate buffer (pH 5.0, containing 5% DMF) was incubated at 37 °C for 16–19 h. [d]A mixture of the indoxyl (1 mM) and tritosomes (0.13 mg protein/mL) in 20 mM acetate buffer (pH 5.0, containing 5% DMF) in the presence of 1x catabolic buffer was incubated at 37 °C for 16–19 h. [e]The yield was estimated from absorption spectroscopy with $\varepsilon = 2.00\times10^4$ $M^{-1}cm^{-1}$ reported for 5,5′-dibromo-4,4′-dichloroindigo.[40] [f]Not conducted. [g]The yield was estimated from absorption spectroscopy with $\varepsilon = 2.6\times10^4$ $M^{-1}cm^{-1}$ (DMF/H_2O = 2:1) measured for **46**.

Figure S3 shows the effect of the nonionic surfactant tyloxapol (Triton WR1339) over a 1000-fold concentration range on the indigogenic reaction of **45** with β-glucosidase from almonds. The effect was measurable but rather small over the very large range of concentration examined.

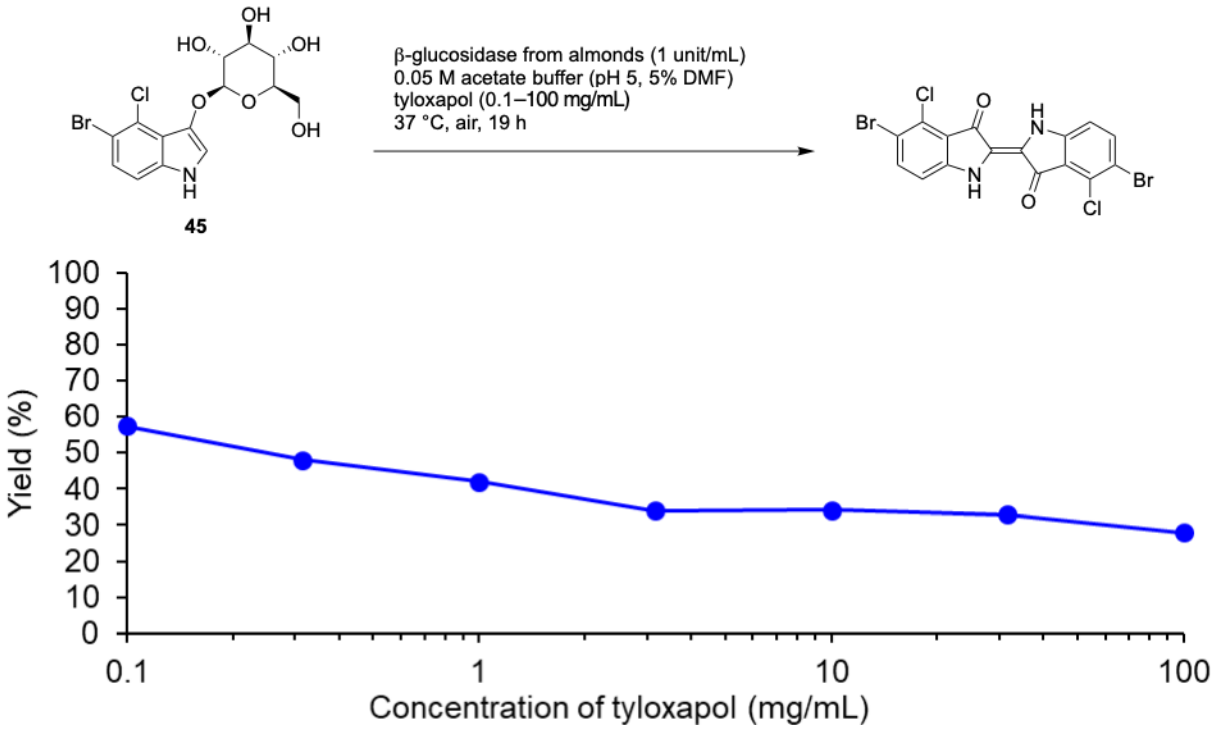


Figure S3. Effect of tyloxapol on the indigogenic reaction of **45** with β-glucosidase from almonds.

(4) pH Profile of β-glucosidase from *Agrobacterium*.

Following a reported procedure[43] with slight modification, a solution of 4-nitrophenyl β-D-glucopyranoside (2 mM) in 45 mM phosphate buffers (pH 4.0, 5.0, 6.0, 7.0, 8.0, or 9.0) was incubated at 37 °C for 10 min. A solution of β-glucosidase from *Agrobacterium* in NaPi-NaCl buffer (10 μL, 1 μM, pH 7.0, 10 mM NaPi and 50 mM NaCl) was added. The reaction mixture was incubated at 37 °C for 5 min and then quenched by the addition of 1.2 M aqueous NaOH (120, 100, 90, 60, 30, or 20 μL for the reaction at pH 4.0, 5.0, 6.0, 7.0, 8.0, or 9.0, respectively) at room temperature. The solution was diluted two times with H_2O. The absorption at 400 nm was measured to calculate the activity of the enzyme (Figure S4).

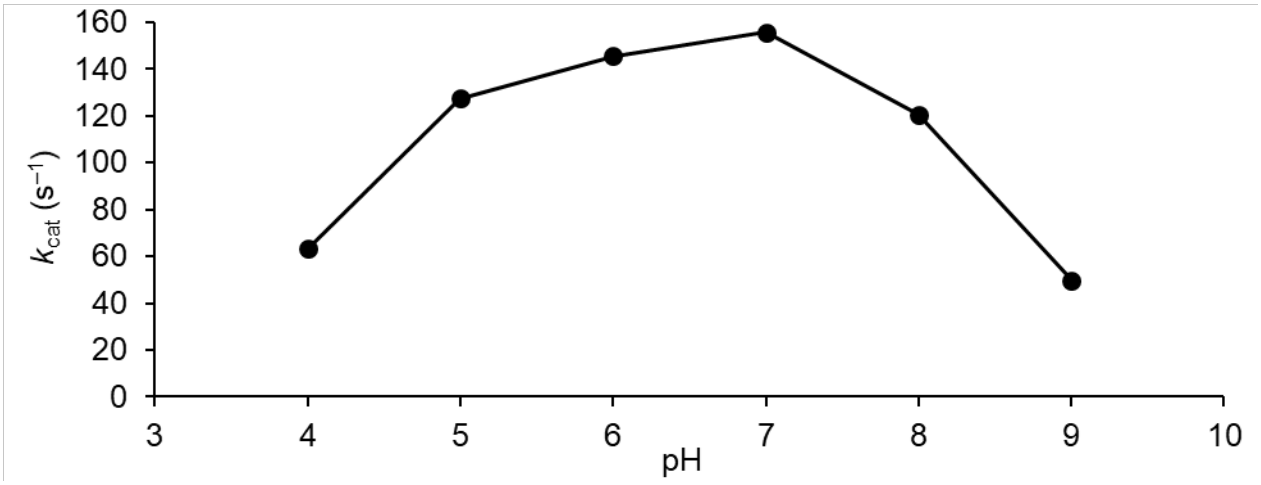


Figure S4. pH profile of β-glucosidase from *Agrobacterium*.

(5) HPLC data from oligomerization studies

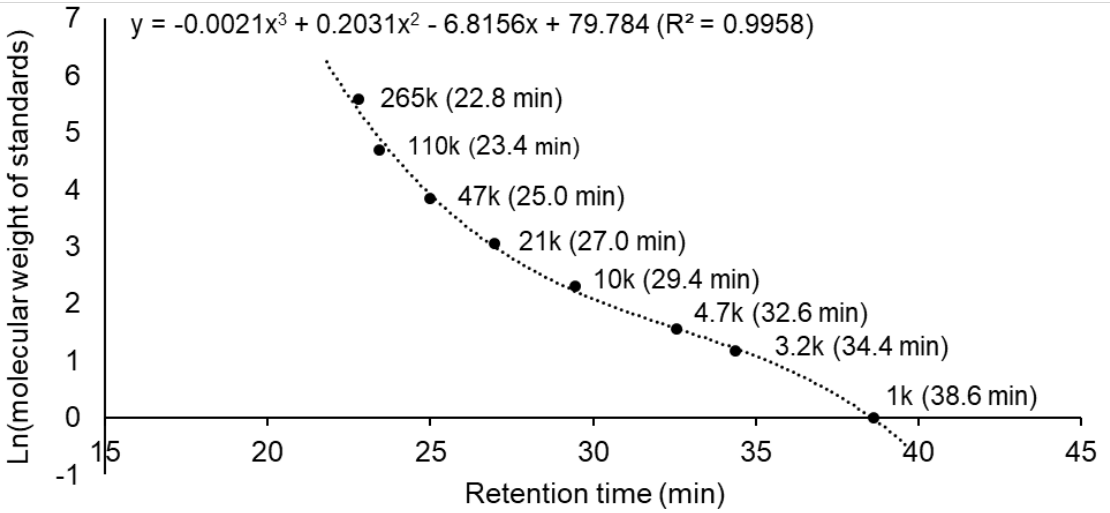


Figure S5. Calibration curve for SEC analysis.

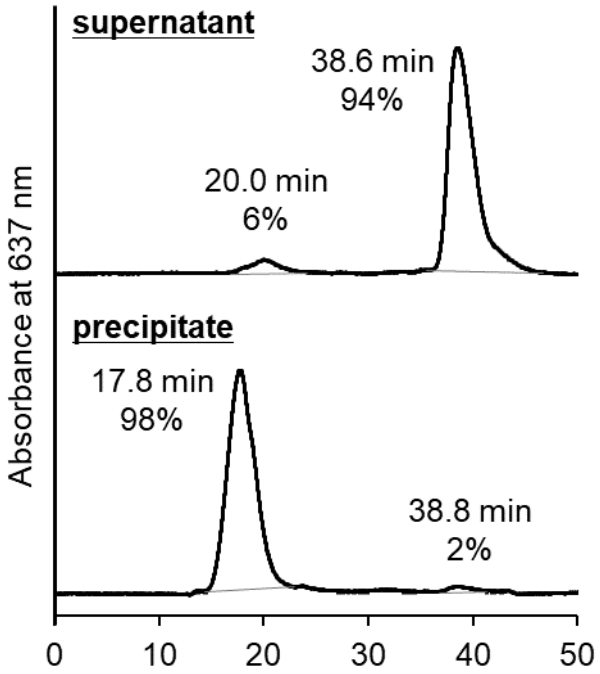


Figure S6. Analytical SEC traces for the supernatant and precipitate samples from 50 μM of **49**.

(6) Mass spectrometry of the oligomer supernatant

ESI-MS analysis was carried out of the supernatant in the negative-ion mode using MeCN/H_2O (0.1% TFA). The spectrum is shown in Figure S7. Peaks consistent with the monomer and the dimer were detected. The putative monomer and dimer structures are shown in Figure S8.

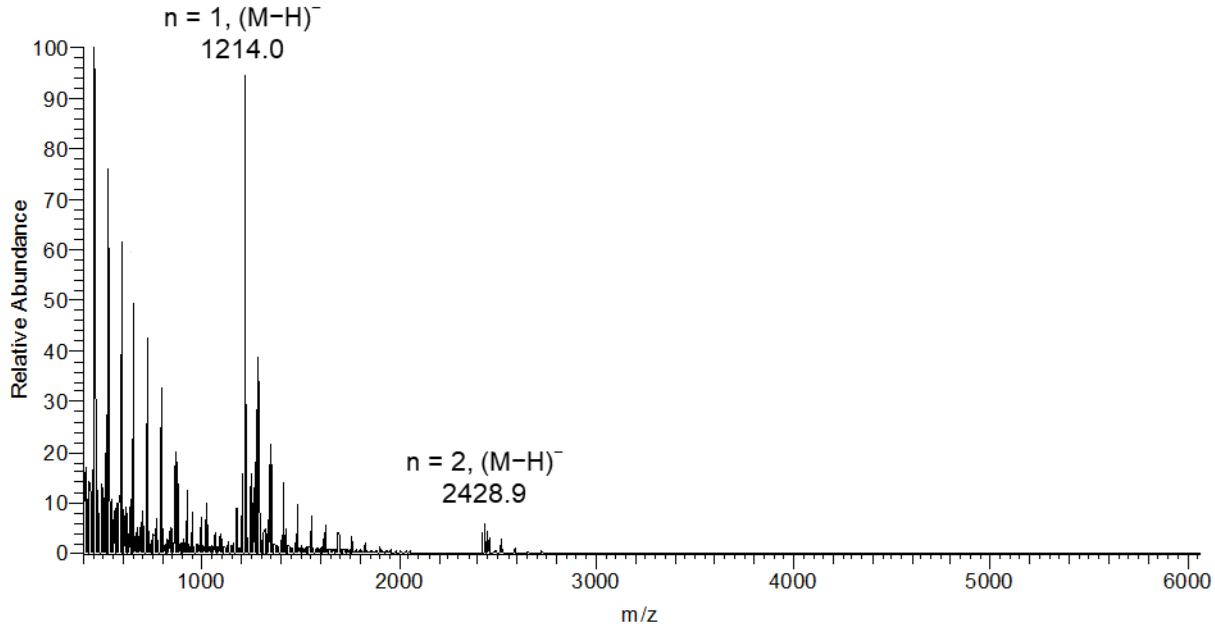
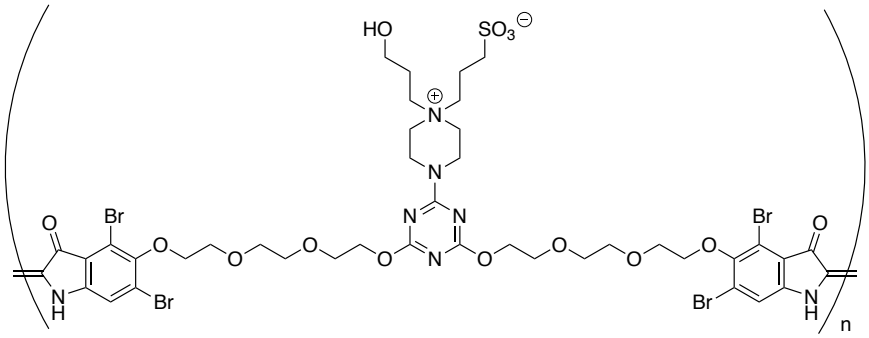


Figure S7. ESI-MS spectrum (negative-ion mode) of the supernatant derived from 300 μM of **49**.



$(C_{41}H_{49}Br_4N_7O_{14}S)_n$, *m/z*: 1214.98 when n = 1

Figure S8. Cyclic monomer and dimer structures where n = 1 and 2, respectively.

MALDI-MS analysis (positive-ion mode) was carried out of the supernatant derived from 300 μM of **49** using CHCA as a matrix and calibration with peptide standards. The spectrum is shown in Figure S9. The observed peak masses are compared with calculated masses in Table S2.

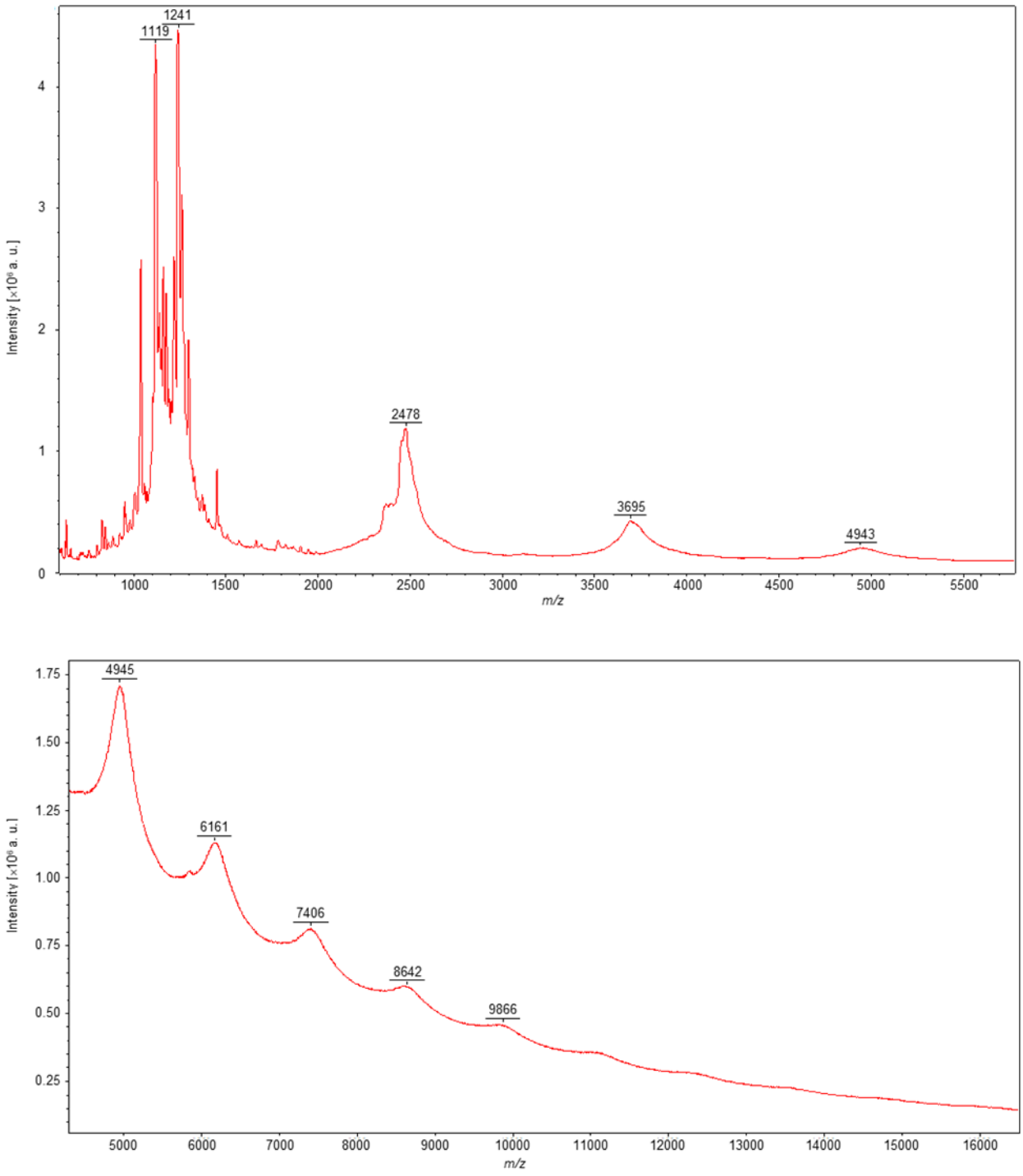


Figure S9. Peaks in the MALDI-MS spectrum of the supernatant derived from 300 μM of **49**.

Table S2. Comparison of observed and calculated peak masses.

n	Calculated *m/z* for $[M + Na]^+$	Observed	Difference
1	1238	1241	3
2	2453	2478	25
3	3669	3695	26
4	4884	4943, 4945	59, 61
5	6098	6161	63
6	7315	7406	91
7	8528	8642	114
8	9746	9866	120

(7) Final concentrations of each ingredient in buffered solutions

Table 1
Reactions with β-glucosidase from almonds.

Ingredient	**Final concentration**
Indoxyl compound	1 mM
β-Glucosidase from almonds	1 unit/mL
Sodium acetate buffer (pH 5.0)	42.5 mM
DMF	5%

Reactions with β-glucosidase from *Agrobacterium*.

Ingredient	**Final concentration**
Indoxyl compound	100 μM
β-Glucosidase from *Agrobacterium*	200 nM
Sodium phosphate buffer (pH 7.0)	48.2 mM
DMF	2%
NaCl	1 mM
$(NH_4)_2SO_4$	12 mM

Reactions in rat liver homogenate.

Ingredient	**Final concentration**
Indoxyl compound	100 μM
Rat liver homogenate	95%
DMF	5%

Reaction of 33 with β-glucosidase from *Agrobacterium* in rat liver homogenate.

Ingredient	**Final concentration**
33	100 μM
β-Glucosidase from *Agrobacterium*	200 nM
Sodium phosphate buffer (pH 7.0)	200 μM
Rat liver homogenate	96%
DMF	2%
NaCl	1 mM
$(NH_4)_2SO_4$	12 mM

Figure 6
Effect of pH (Figure 6A).

Ingredient	**Final concentration**
33	100 μM
β-Glucosidase from *Agrobacterium*	200 nM
Sodium phosphate buffer (pH 4.0, 5.0, 6.0, 7.0, 8.0, or 9.0)	48.2 mM
DMF	2%
NaCl	1 mM
$(NH_4)_2SO_4$	12 mM

Effect of the enzyme concentration (Figure 6B).

Ingredient	**Final concentration**
33	100 μM
β-Glucosidase from *Agrobacterium*	10 nM
Sodium phosphate buffer (pH 4.0, 5.0, 6.0, 7.0, 8.0, or 9.0)	48.6 mM
DMF	2%
NaCl	0.5 mM
$(NH_4)_2SO_4$	0.59 mM

Effect of the concentration of 33 (Figure 6C).

Ingredient	**Final concentration**
33	1.00, 1.78, 3.16, 5.62, 10.0, 17.8, 31.6, or 56.2 μM)
β-Glucosidase from *Agrobacterium*	200 nM
Sodium phosphate buffer (pH 7.0)	9.8 mM
DMF	2%
NaCl	50 mM
$(NH_4)_2SO_4$	12 mM

Table 2
Oligomerization of 49 in NaPi-NaCl buffer.

Ingredient	**Final concentration**
49	300, 100, 50 or 10 μM
β-Glucosidase from *Agrobacterium*	200 nM
Sodium phosphate buffer (pH 7.0)	10 mM
NaCl	50 mM
$(NH_4)_2SO_4$	12 mM

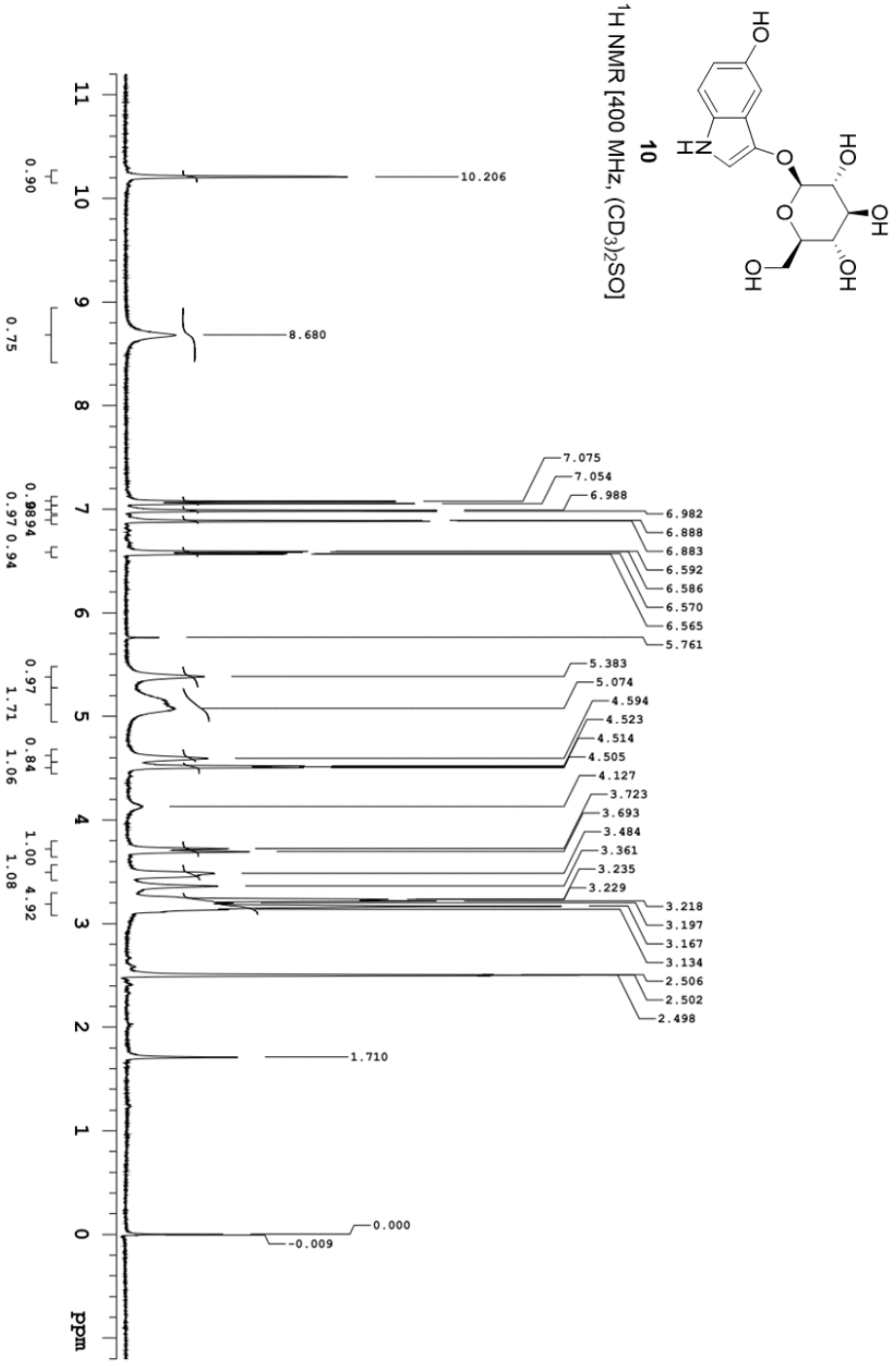
Low-salt oligomerization of 49.

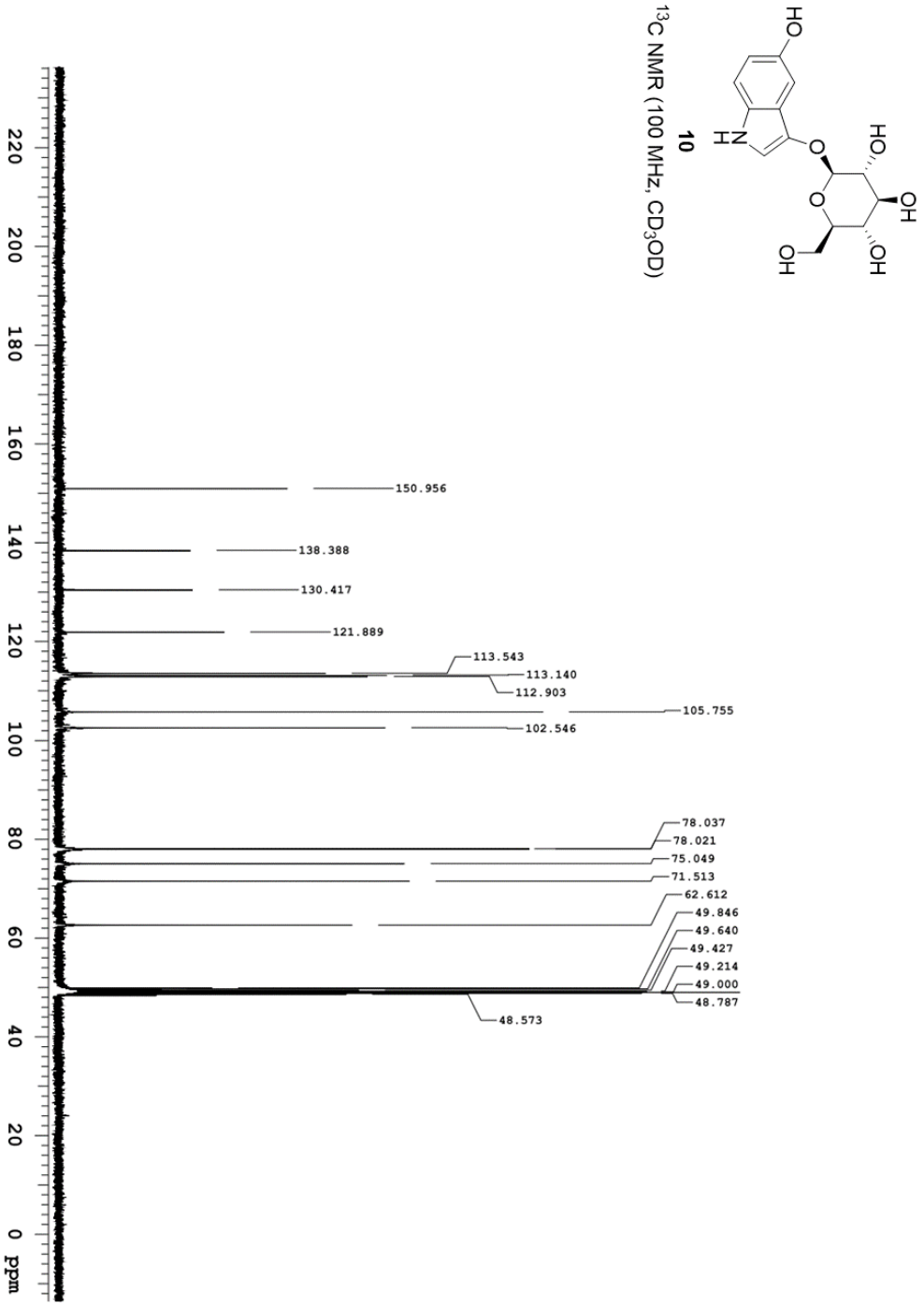
Ingredient	**Final concentration**
49	300 μM
β-Glucosidase from *Agrobacterium*	200 nM
Sodium phosphate buffer (pH 7.0)	9.9 mM
DMF	0.6%
NaCl	1 mM
$(NH_4)_2SO_4$	12 mM

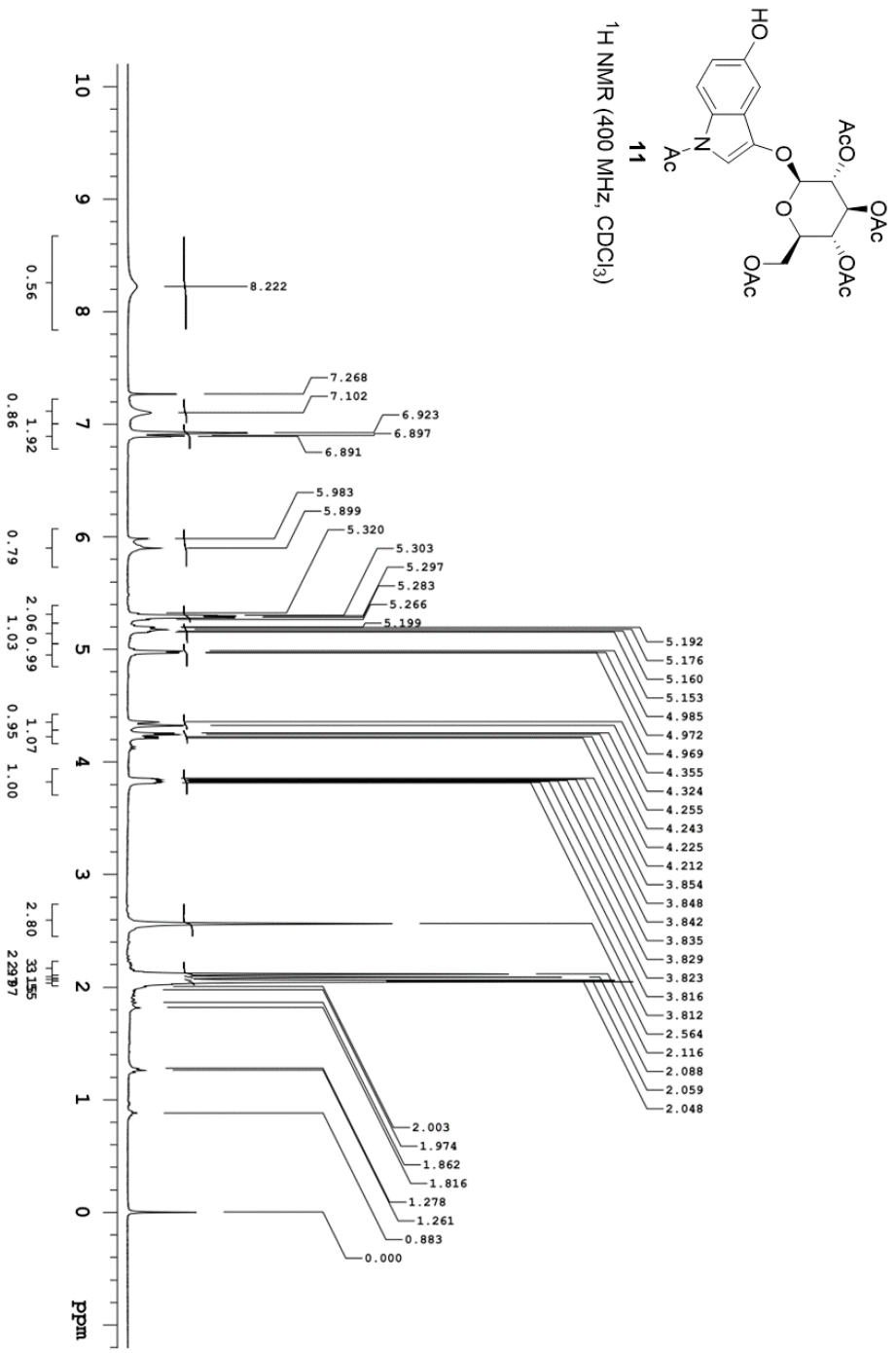
Figure S4
pH Profile of β-glucosidase from *Agrobacterium*.

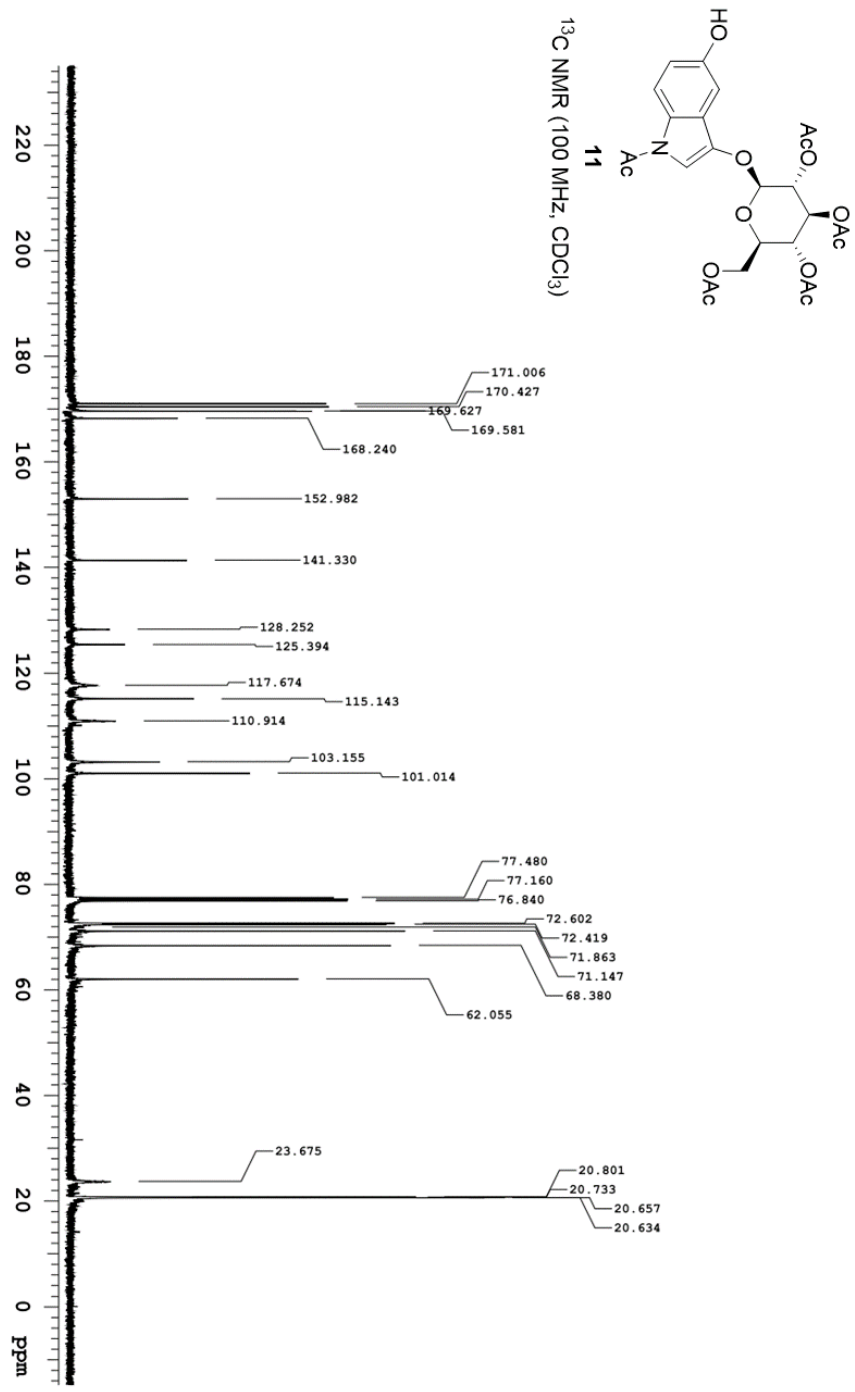
Ingredient	**Final concentration**
4-nitrophenyl β-D-glucopyranoside	2 mM
β-Glucosidase from *Agrobacterium*	5 nM
Sodium phosphate buffer (pH 4.0, 5.0, 6.0, 7.0, 8.0, or 9.0)	45 mM
NaCl	0.025 mM
$(NH_4)_2SO_4$	0.029 mM

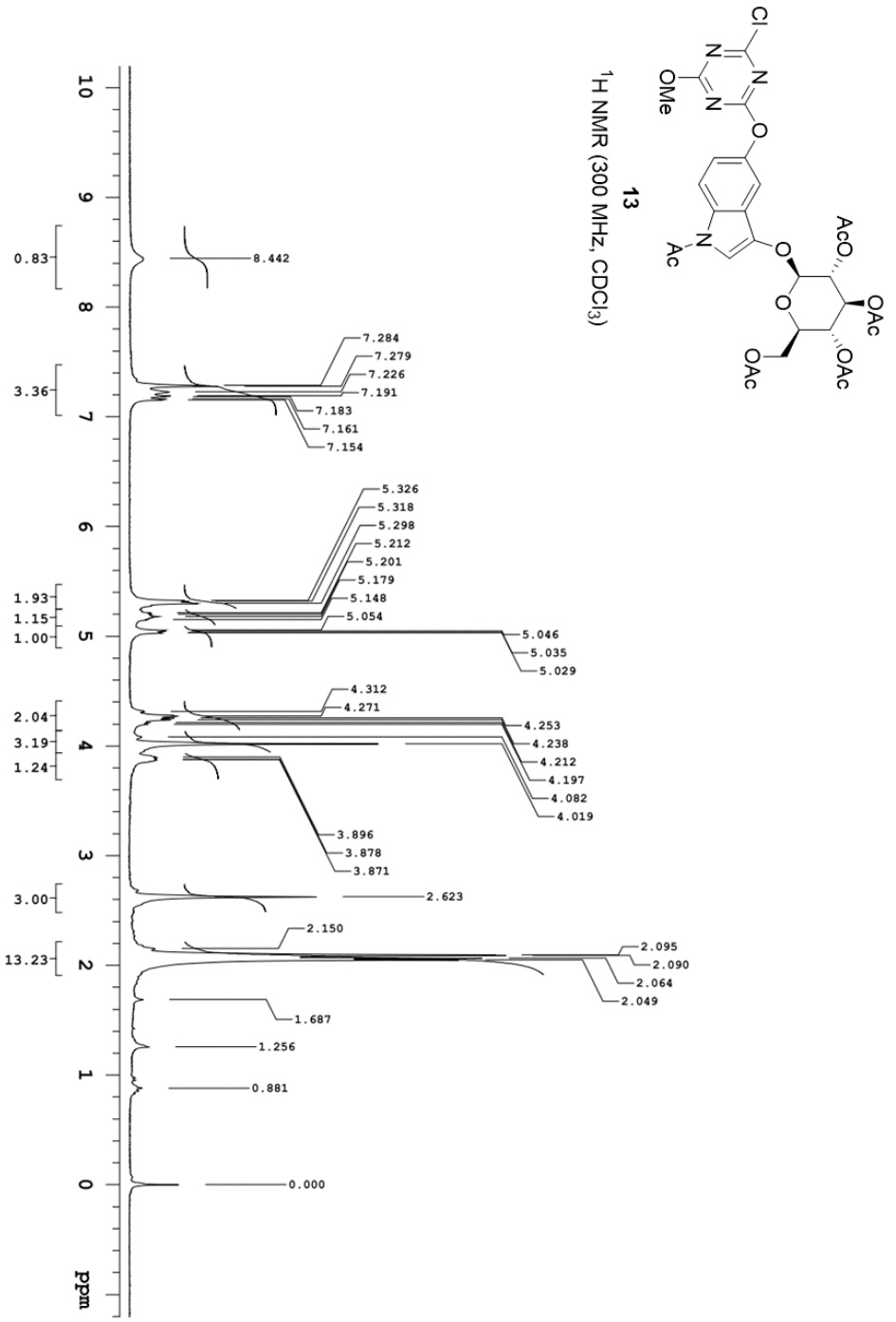
(8) Spectral data

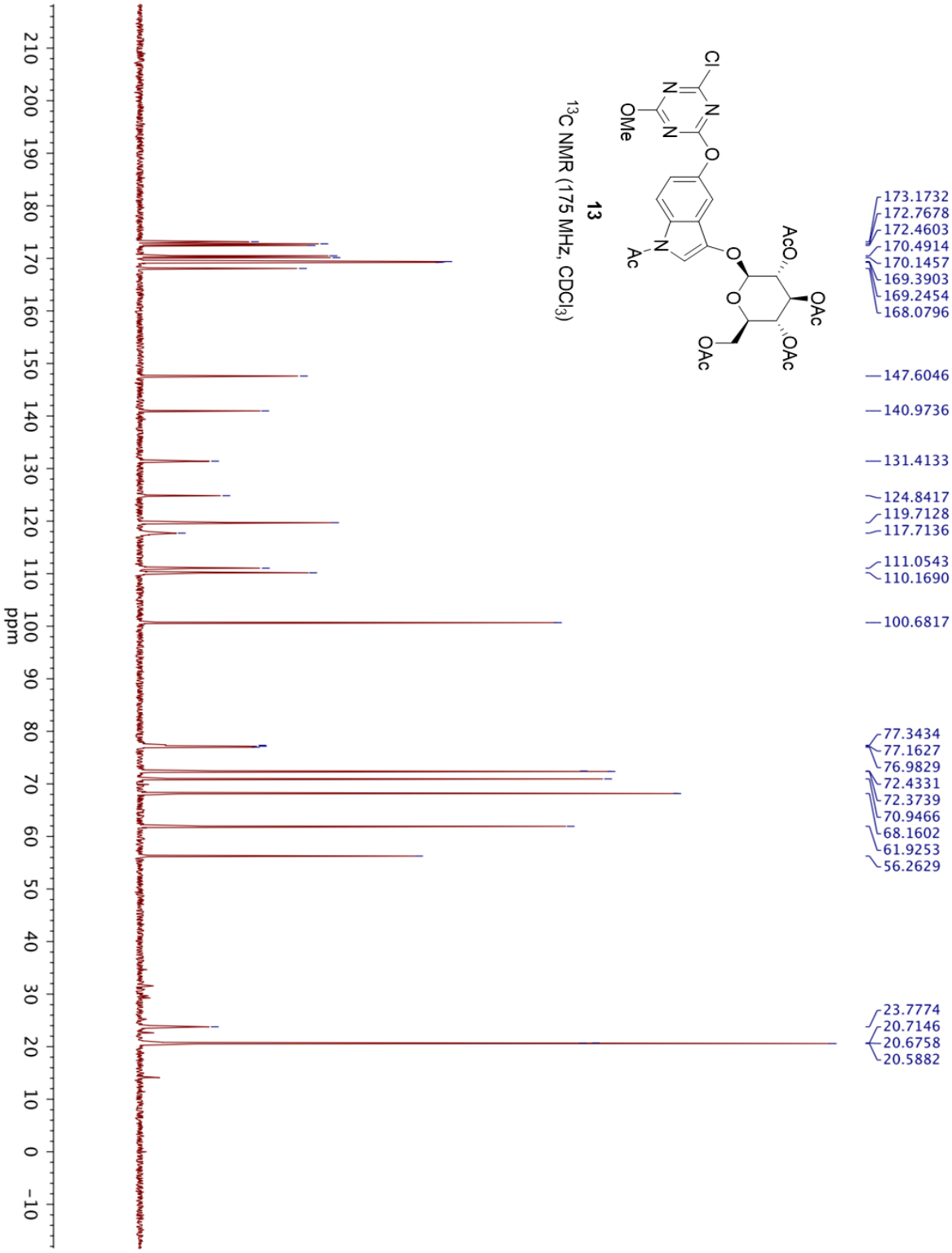

10
^{1}H NMR [400 MHz, $(CD_3)_2SO$]
10.206
8.680
7.075
7.054
6.988
6.982
6.888
6.883
6.592
6.586
6.570
6.565
5.761
5.383
5.074
4.594
4.523
4.514
4.505
4.127
3.723
3.693
3.484
3.361
3.235
3.229
3.218
3.197
3.167
3.134
2.506
2.502
2.498
1.710
0.000
-0.009
ppm

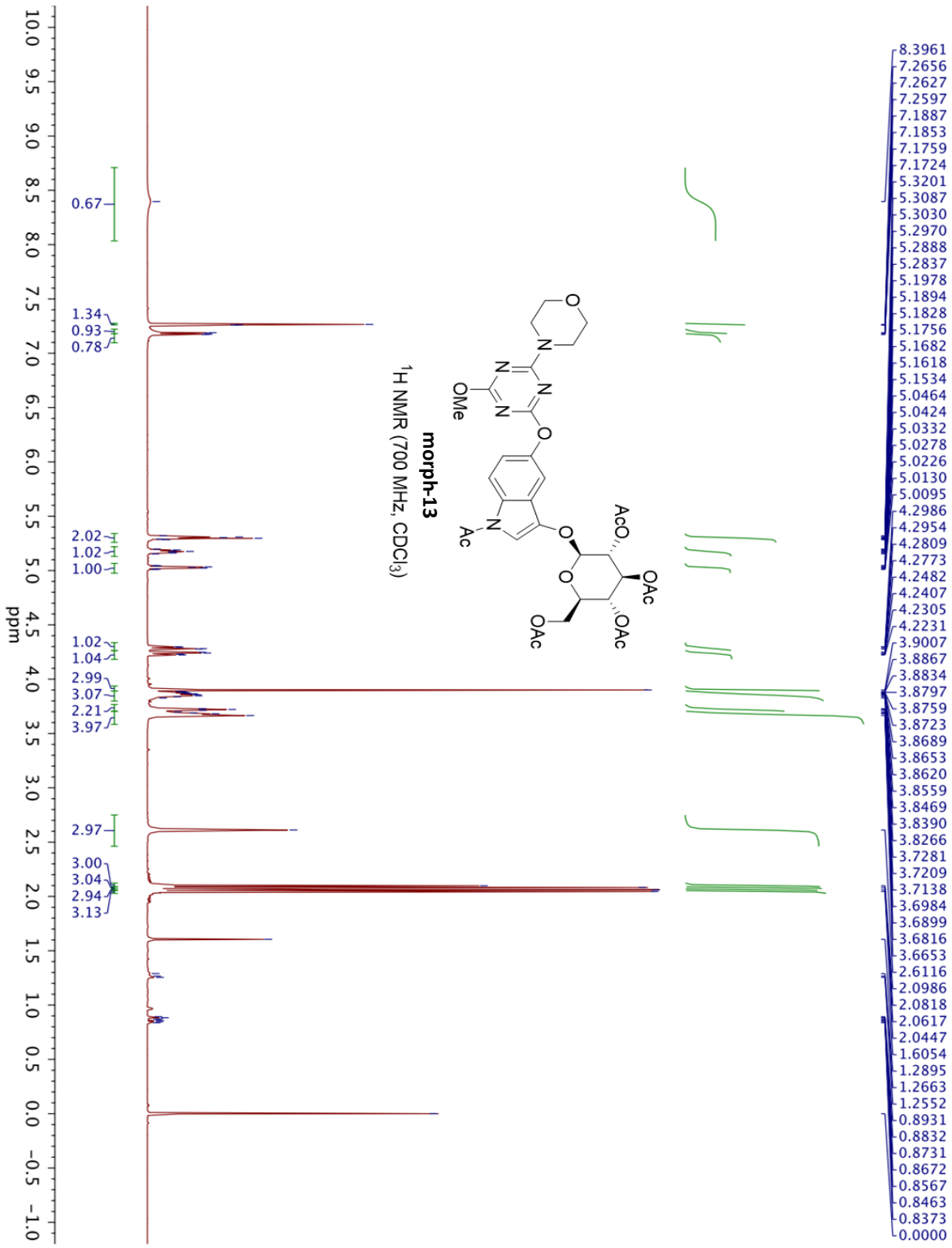

10
^{13}C NMR (100 MHz, CD_3OD)
150.956
138.388
130.417
121.889
113.543
113.140
112.903
105.755
102.546
78.037
78.021
75.049
71.513
62.612
49.846
49.640
49.427
49.214
49.000
48.787
48.573
220
200
180
160
140
120
100
80
60
40
20
0
ppm

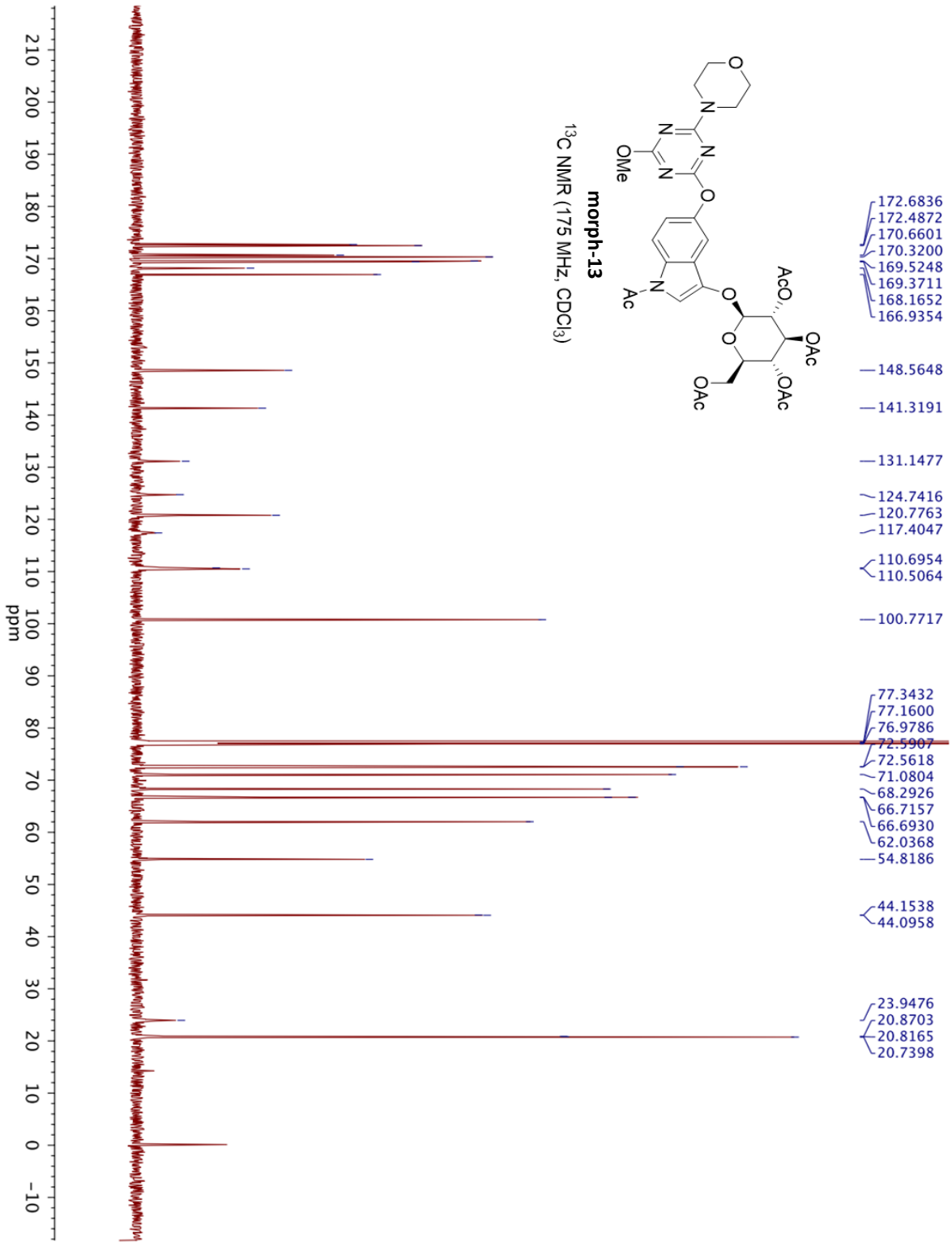

HO
AcO
OAc
OAc
OAc
N
Ac
O
O
11
^{1}H NMR (400 MHz, CDCl$_3$)
8.222
7.268
7.102
6.923
6.897
6.891
5.983
5.899
5.320
5.303
5.297
5.283
5.266
5.199
5.192
5.176
5.160
5.153
4.985
4.972
4.969
4.355
4.324
4.255
4.243
4.225
4.212
3.854
3.848
3.842
3.835
3.829
3.823
3.816
3.812
2.564
2.116
2.088
2.059
2.048
2.003
1.974
1.862
1.816
1.278
1.261
0.883
0.000
ppm

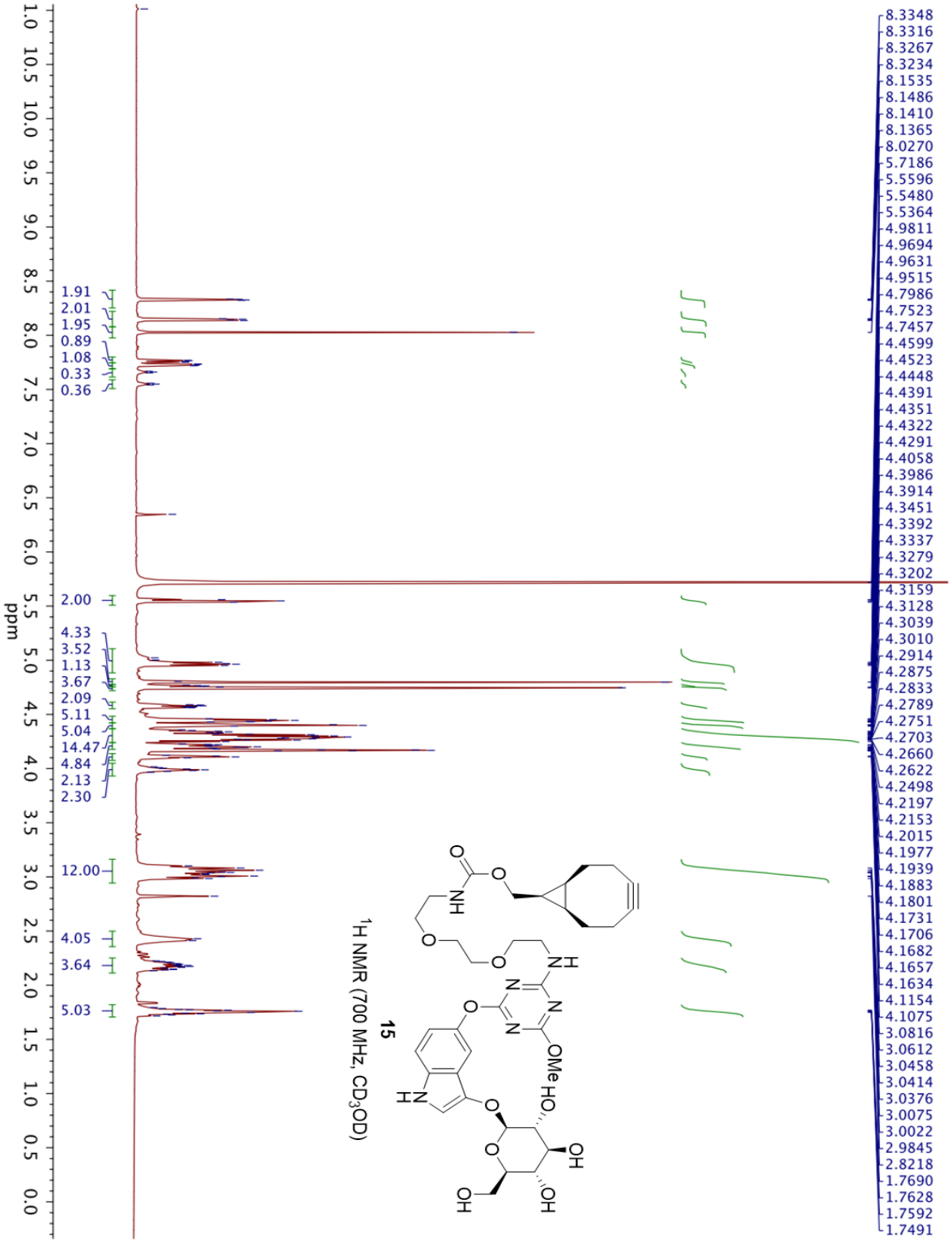

^{13}C NMR (100 MHz, CDCl$_3$)
11
HO
N
Ac
O
AcO
OAc
O
OAc
OAc
171.006
170.427
169.627
169.581
168.240
152.982
141.330
128.252
125.394
117.674
115.143
110.914
103.155
101.014
77.480
77.160
76.840
72.602
72.419
71.863
71.147
68.380
62.055
23.675
20.801
20.733
20.657
20.634
220
200
180
160
140
120
100
80
60
40
20
0
ppm

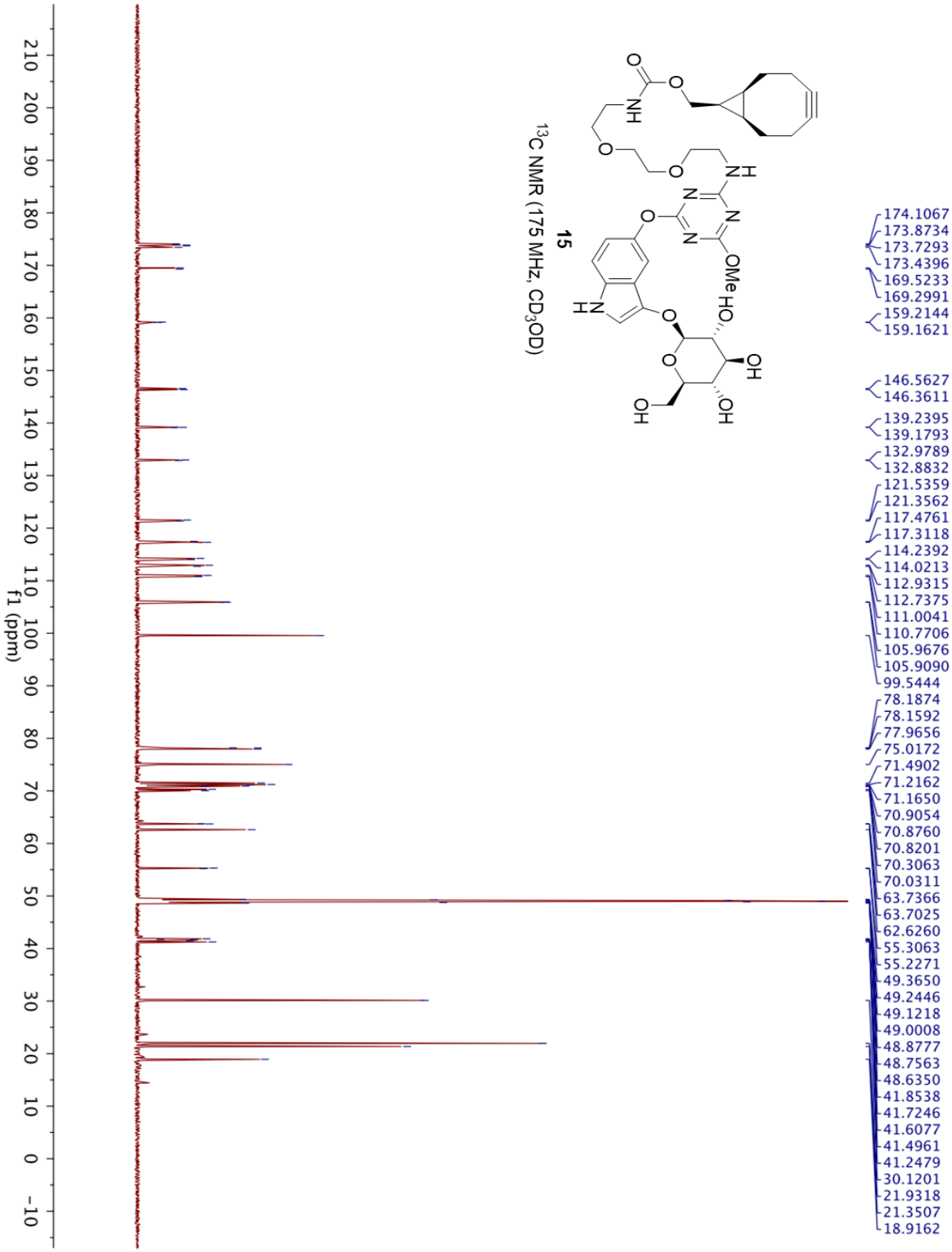

13
^{1}H NMR (300 MHz, CDCl$_3$)
Cl
N
N
OMe
N
O
O
N
Ac
O
AcO
OAc
O
OAc
OAc
ppm
0.83
3.36
1.93
1.15
1.00
2.04
3.19
1.24
3.00
13.23
8.442
7.284
7.279
7.226
7.191
7.183
7.161
7.154
5.326
5.318
5.298
5.212
5.201
5.179
5.148
5.054
5.046
5.035
5.029
4.312
4.271
4.253
4.238
4.212
4.197
4.082
4.019
3.896
3.878
3.871
2.623
2.150
2.095
2.090
2.064
2.049
1.687
1.256
0.881
0.000

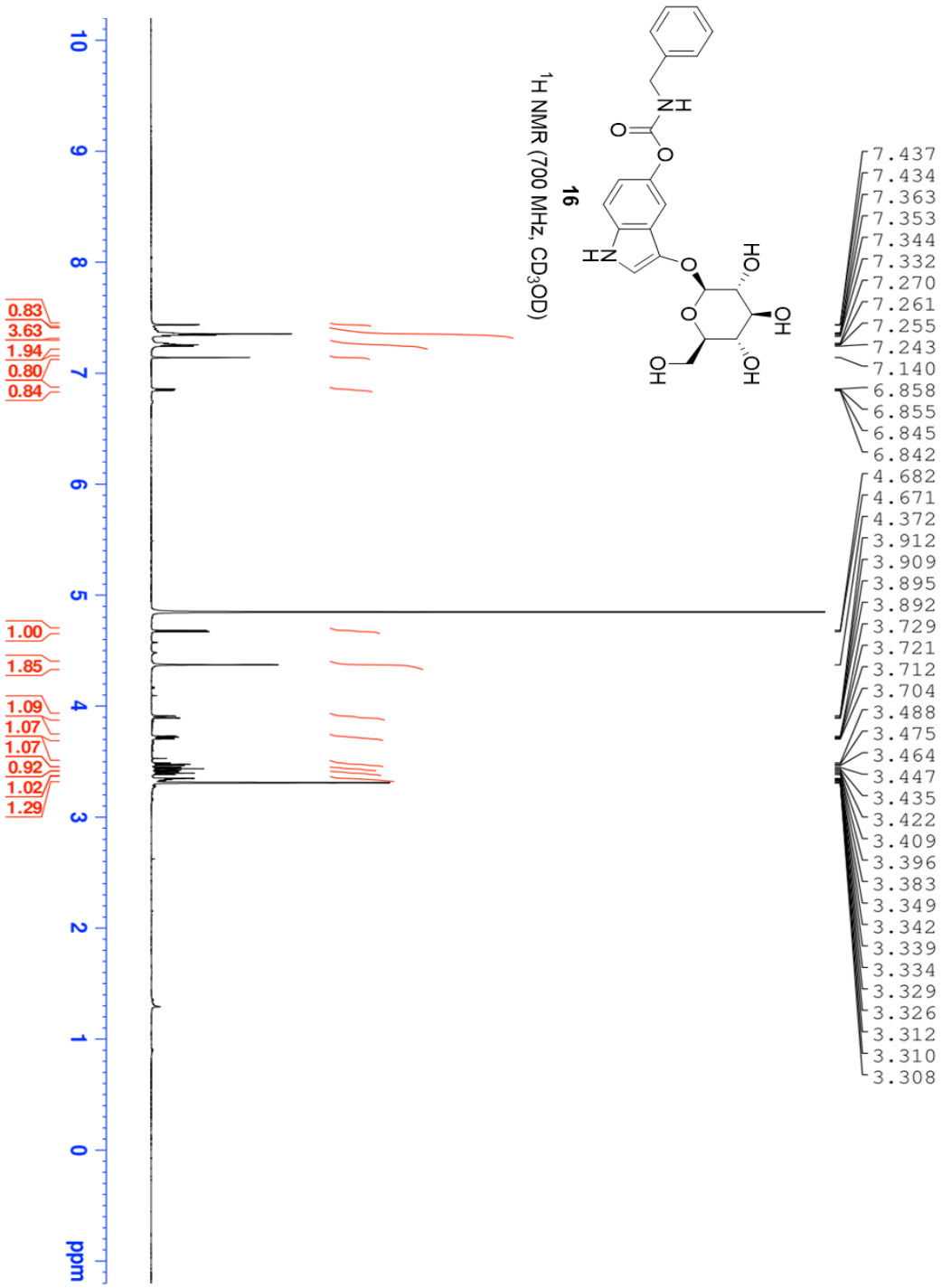

13
^{13}C NMR (175 MHz, CDCl$_3$)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
173.1732
172.7678
172.4603
170.4914
170.1457
169.3903
169.2454
168.0796
147.6046
140.9736
131.4133
124.8417
119.7128
117.7136
111.0543
110.1690
100.6817
77.3434
77.1627
76.9829
72.4331
72.3739
70.9466
68.1602
61.9253
56.2629
23.7774
20.7146
20.6758
20.5882
Cl
N
N
N
OMe
O
N
Ac
O
AcO
OAc
O
OAc
OAc

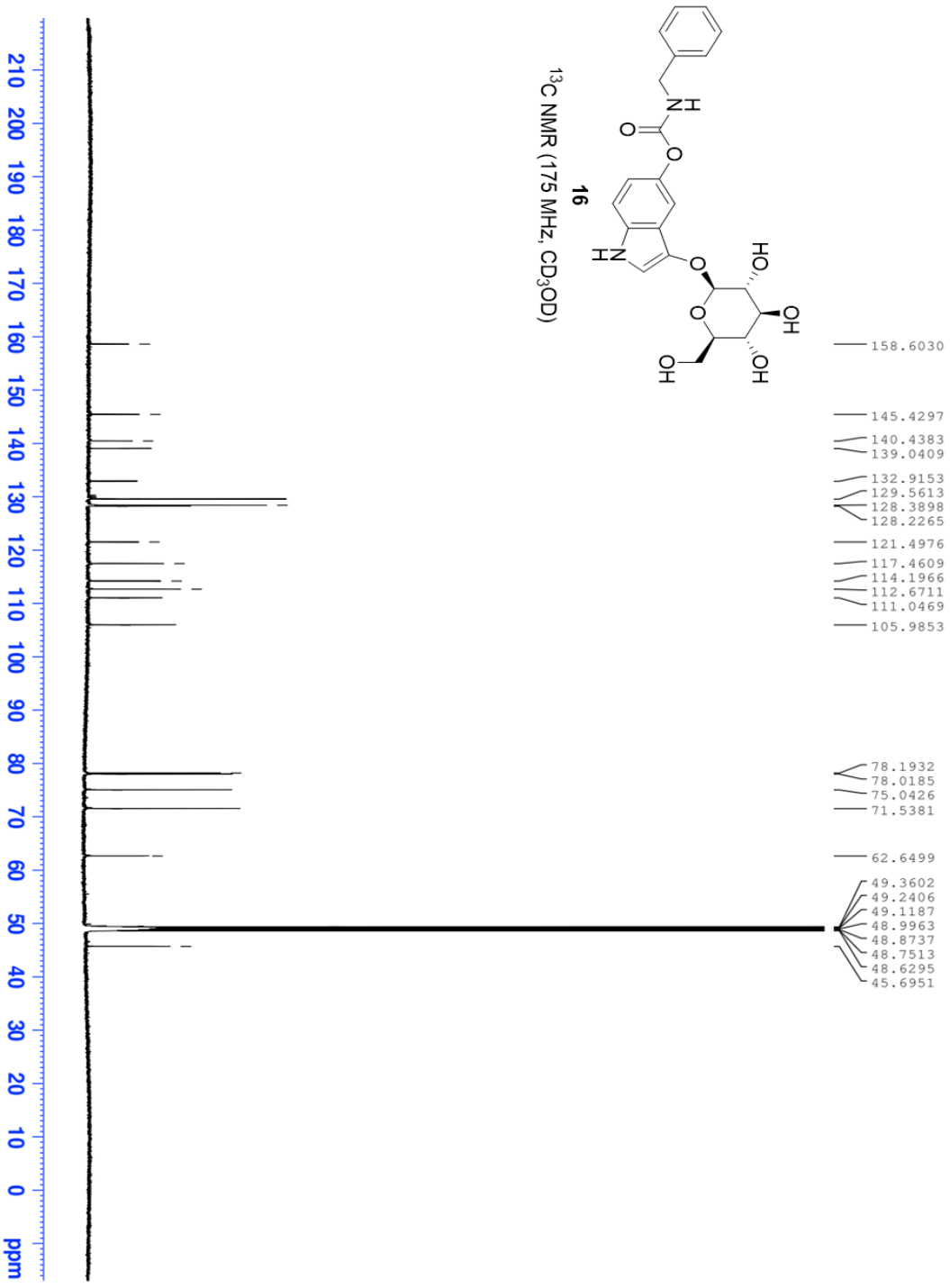

morph-13
^{1}H NMR (700 MHz, CDCl$_3$)
OMe
Ac
AcO
OAc
OAc
OAc
ppm
0.67
1.34
0.93
0.78
2.02
1.02
1.00
1.02
1.04
2.99
3.07
2.21
3.97
2.97
3.00
3.04
2.94
3.13
8.3961
7.2656
7.2627
7.2597
7.1887
7.1853
7.1759
7.1724
5.3201
5.3087
5.3030
5.2970
5.2888
5.2837
5.1978
5.1894
5.1828
5.1756
5.1682
5.1618
5.1534
5.0464
5.0424
5.0332
5.0278
5.0226
5.0130
5.0095
4.2986
4.2954
4.2809
4.2773
4.2482
4.2407
4.2305
4.2231
3.9007
3.8867
3.8834
3.8797
3.8759
3.8723
3.8689
3.8653
3.8620
3.8559
3.8469
3.8390
3.8266
3.7281
3.7209
3.7138
3.6984
3.6899
3.6816
3.6653
2.6116
2.0986
2.0818
2.0617
2.0447
1.6054
1.2895
1.2663
1.2552
0.8931
0.8832
0.8731
0.8672
0.8567
0.8463
0.8373
0.0000

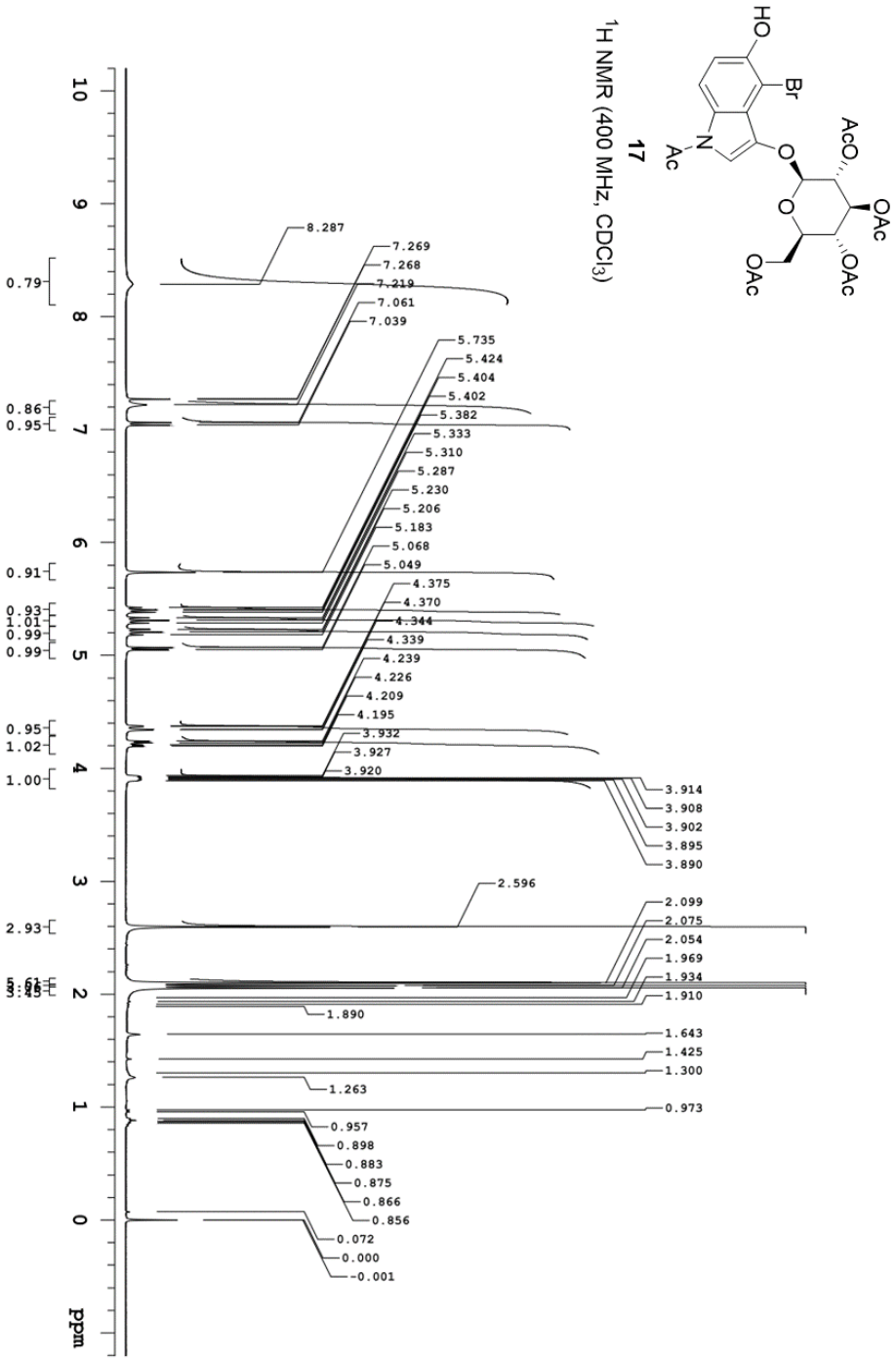

morph-13
^{13}C NMR (175 MHz, CDCl$_3$)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
OMe
Ac
AcO
OAc
OAc
OAc
172.6836
172.4872
170.6601
170.3200
169.5248
169.3711
168.1652
166.9354
148.5648
141.3191
131.1477
124.7416
120.7763
117.4047
110.6954
110.5064
100.7717
77.3432
77.1600
76.9786
72.5907
72.5618
71.0804
68.2926
66.7157
66.6930
62.0368
54.8186
44.1538
44.0958
23.9476
20.8703
20.8165
20.7398

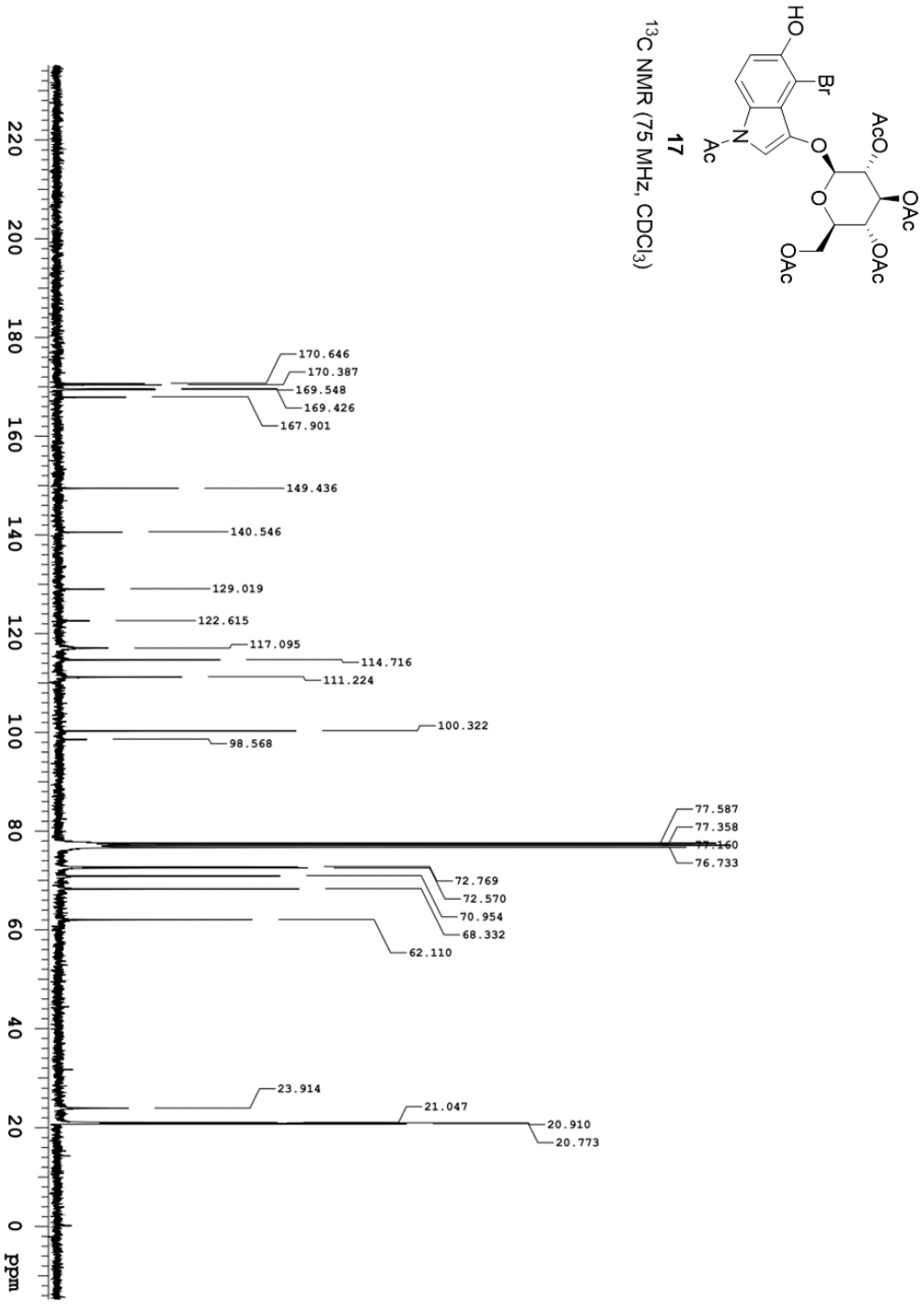

1.91
2.01
1.95
0.89
1.08
0.33
0.36
2.00
4.33
3.52
1.13
3.67
2.09
5.11
5.04
14.47
4.84
2.13
2.30
12.00
4.05
3.64
5.03
ppm
8.3348
8.3316
8.3267
8.3234
8.1535
8.1486
8.1410
8.1365
8.0270
5.7186
5.5596
5.5480
5.5364
4.9811
4.9694
4.9631
4.9515
4.7986
4.7523
4.7457
4.4599
4.4523
4.4448
4.4391
4.4351
4.4322
4.4291
4.4058
4.3986
4.3914
4.3451
4.3392
4.3337
4.3279
4.3202
4.3159
4.3128
4.3039
4.3010
4.2914
4.2875
4.2833
4.2789
4.2751
4.2703
4.2660
4.2622
4.2498
4.2197
4.2153
4.2015
4.1977
4.1939
4.1883
4.1801
4.1731
4.1706
4.1682
4.1657
4.1634
4.1154
4.1075
3.0816
3.0612
3.0458
3.0414
3.0376
3.0075
3.0022
2.9845
2.8218
1.7690
1.7628
1.7592
1.7491
15
1H NMR (700 MHz, CD3OD)

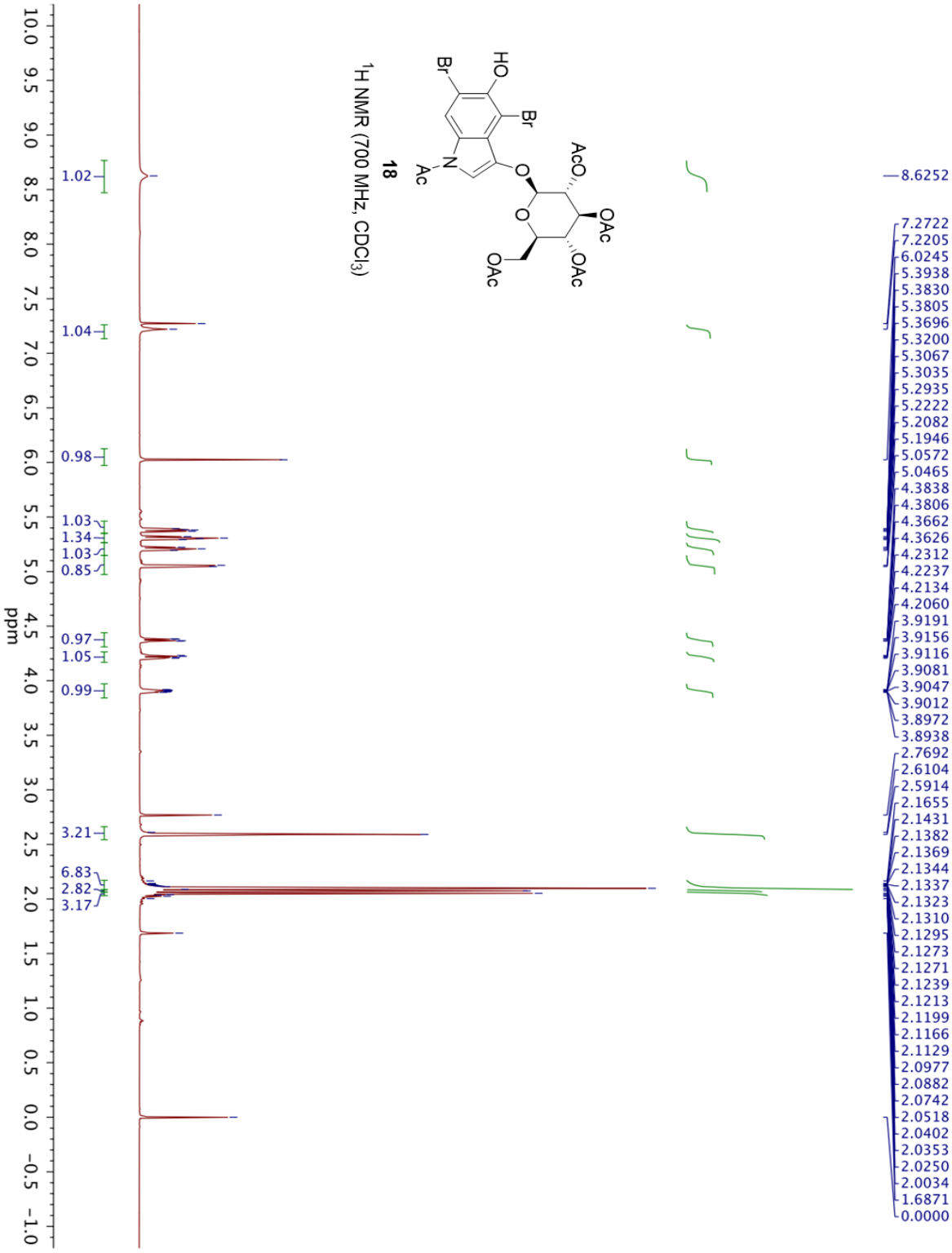

15
^{13}C NMR (175 MHz, CD_3OD)
f1 (ppm)
174.1067
173.8734
173.7293
173.4396
169.5233
169.2991
159.2144
159.1621
146.5627
146.3611
139.2395
139.1793
132.9789
132.8832
121.5359
121.3562
117.4761
117.3118
114.2392
114.0213
112.9315
112.7375
111.0041
110.7706
105.9676
105.9090
99.5444
78.1874
78.1592
77.9656
75.0172
71.4902
71.2162
71.1650
70.9054
70.8760
70.8201
70.3063
70.0311
63.7366
63.7025
62.6260
55.3063
55.2271
49.3650
49.2446
49.1218
49.0008
48.8777
48.7563
48.6350
41.8538
41.7246
41.6077
41.4961
41.2479
30.1201
21.9318
21.3507
18.9162

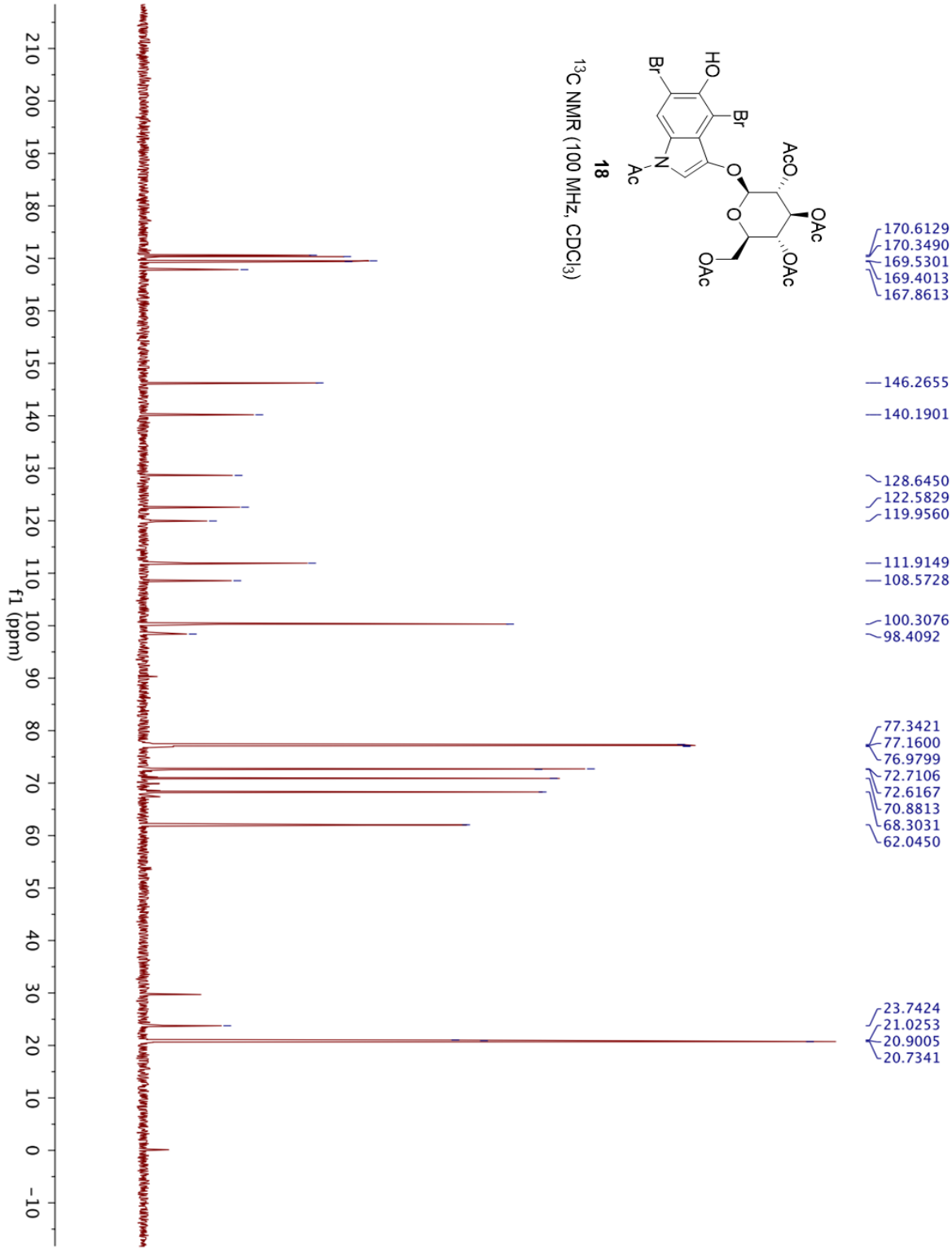

16
^{1}H NMR (700 MHz, CD_3OD)
7.437
7.434
7.363
7.353
7.344
7.332
7.270
7.261
7.255
7.243
7.140
6.858
6.855
6.845
6.842
4.682
4.671
4.372
3.912
3.909
3.895
3.892
3.729
3.721
3.712
3.704
3.488
3.475
3.464
3.447
3.435
3.422
3.409
3.396
3.383
3.349
3.342
3.339
3.334
3.329
3.326
3.312
3.310
3.308
0.83
3.63
1.94
0.80
0.84
1.00
1.85
1.09
1.07
1.07
0.92
1.02
1.29
ppm

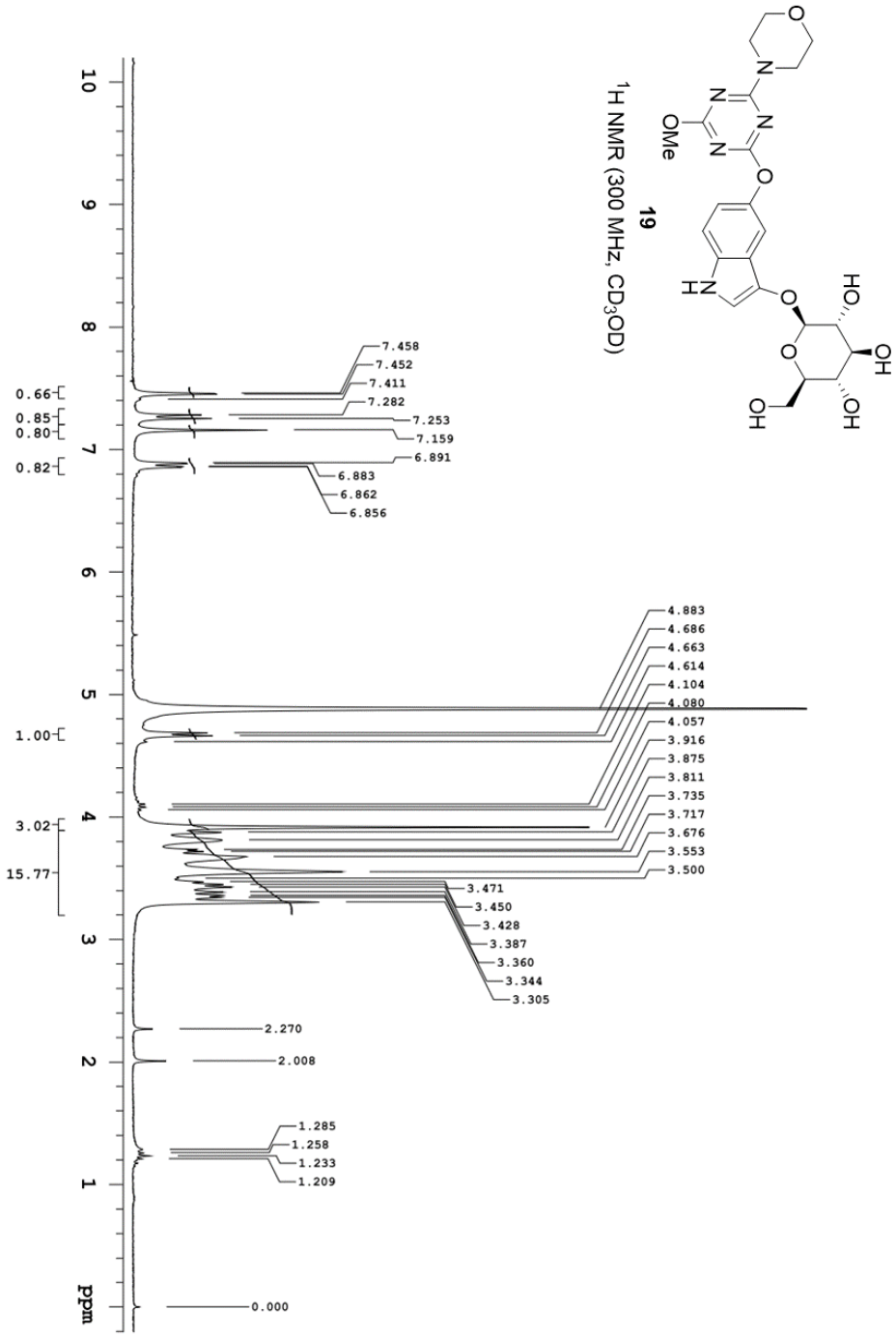

^{13}C NMR (175 MHz, CD_3OD)
16
158.6030
145.4297
140.4383
139.0409
132.9153
129.5613
128.3898
128.2265
121.4976
117.4609
114.1966
112.6711
111.0469
105.9853
78.1932
78.0185
75.0426
71.5381
62.6499
49.3602
49.2406
49.1187
48.9963
48.8737
48.7513
48.6295
45.6951
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

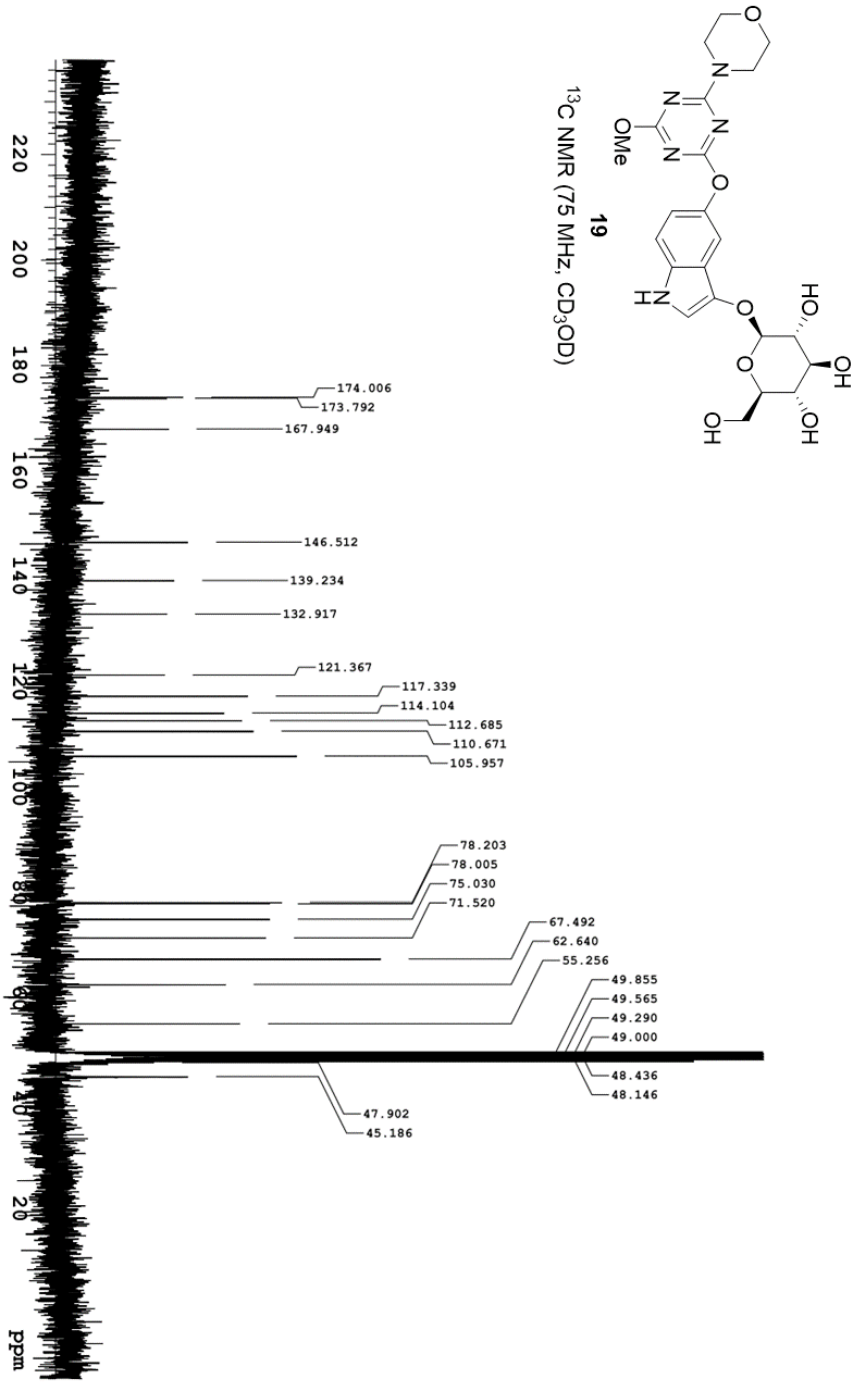

17
^{1}H NMR (400 MHz, CDCl$_3$)
HO
Br
N
Ac
O
AcO
OAc
OAc
OAc
O
8.287
7.269
7.268
7.219
7.061
7.039
5.735
5.424
5.404
5.402
5.382
5.333
5.310
5.287
5.230
5.206
5.183
5.068
5.049
4.375
4.370
4.344
4.339
4.239
4.226
4.209
4.195
3.932
3.927
3.920
3.914
3.908
3.902
3.895
3.890
2.596
2.099
2.075
2.054
1.969
1.934
1.910
1.890
1.643
1.425
1.300
1.263
0.973
0.957
0.898
0.883
0.875
0.866
0.856
0.072
0.000
-0.001
0.79
0.86
0.95
0.91
0.93
1.01
0.99
0.99
0.95
1.02
1.00
2.93
ppm

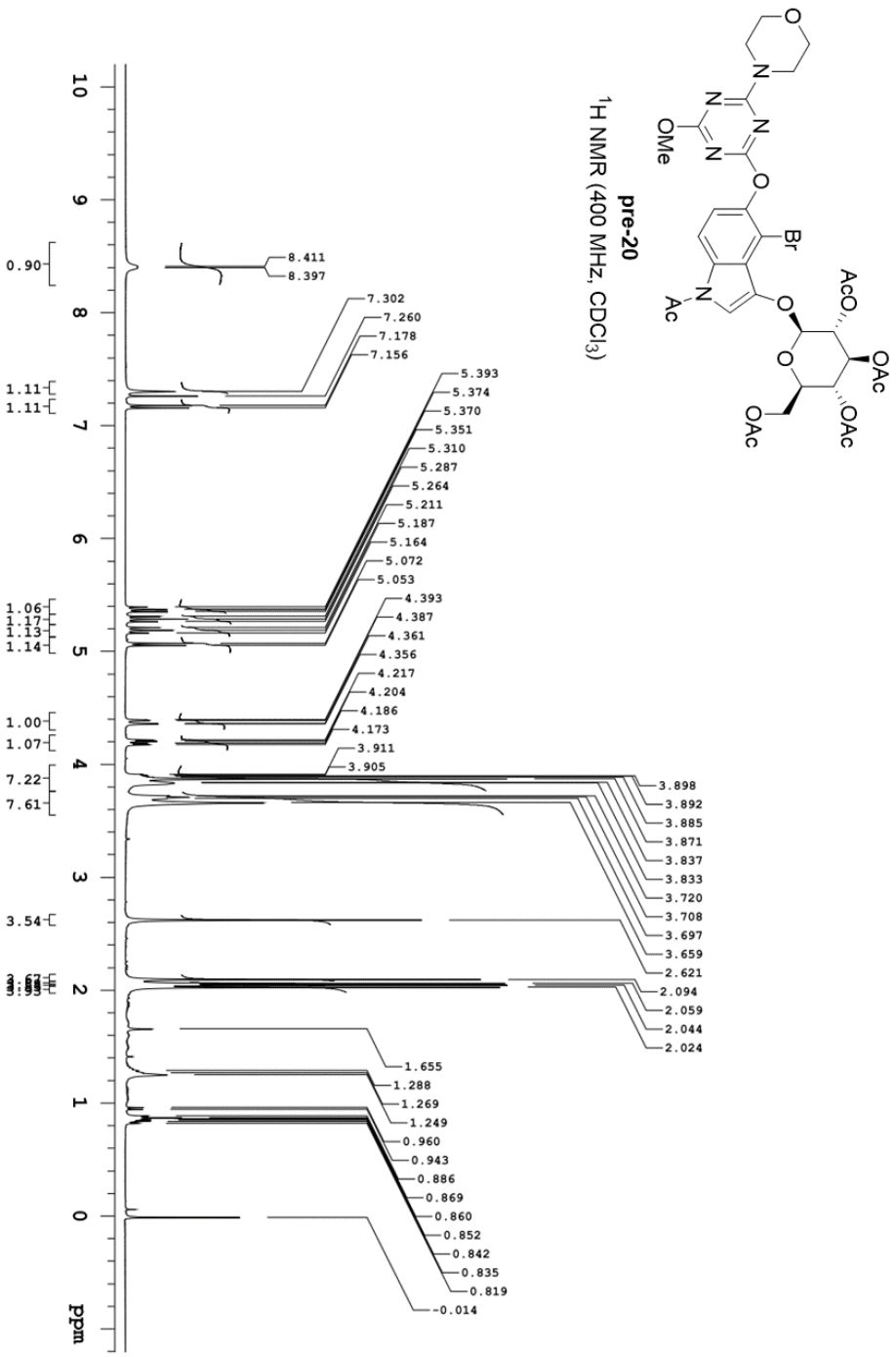

HO
Br
N
Ac
O
AcO
OAc
O
OAc
OAc
17
^{13}C NMR (75 MHz, CDCl$_3$)
170.646
170.387
169.548
169.426
167.901
149.436
140.546
129.019
122.615
117.095
114.716
111.224
100.322
98.568
77.587
77.358
77.160
76.733
72.769
72.570
70.954
68.332
62.110
23.914
21.047
20.910
20.773
220
200
180
160
140
120
100
80
60
40
20
0
ppm

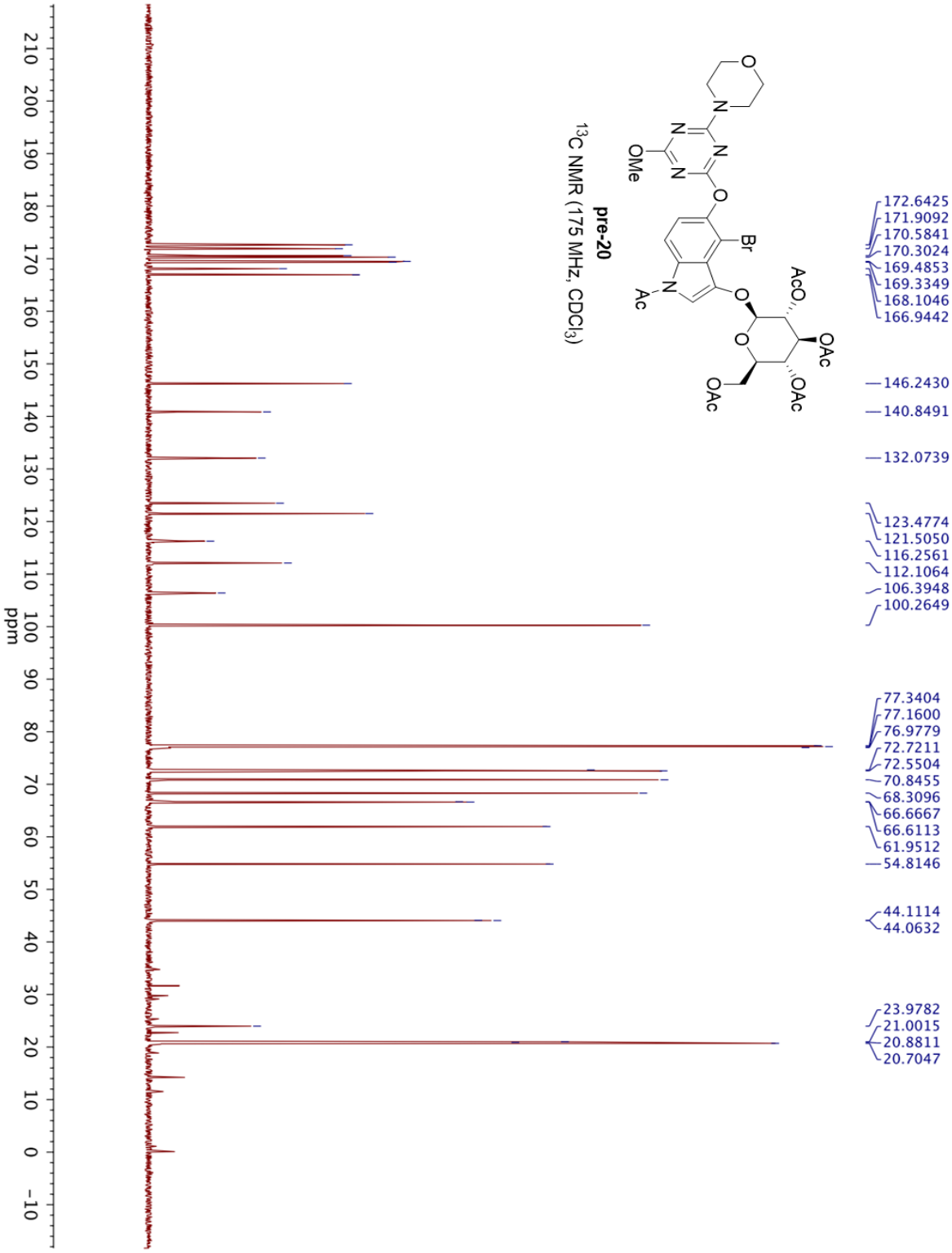

18
^{1}H NMR (700 MHz, CDCl$_3$)
ppm
1.02
1.04
0.98
1.03
1.34
1.03
0.85
0.97
1.05
0.99
3.21
6.83
2.82
3.17
8.6252
7.2722
7.2205
6.0245
5.3938
5.3830
5.3805
5.3696
5.3200
5.3067
5.3035
5.2935
5.2222
5.2082
5.1946
5.0572
5.0465
4.3838
4.3806
4.3662
4.3626
4.2312
4.2237
4.2134
4.2060
3.9191
3.9156
3.9116
3.9081
3.9047
3.9012
3.8972
3.8938
2.7692
2.6104
2.5914
2.1655
2.1431
2.1382
2.1369
2.1344
2.1337
2.1323
2.1310
2.1295
2.1273
2.1271
2.1239
2.1213
2.1199
2.1166
2.1129
2.0977
2.0882
2.0742
2.0518
2.0402
2.0353
2.0250
2.0034
1.6871
0.0000

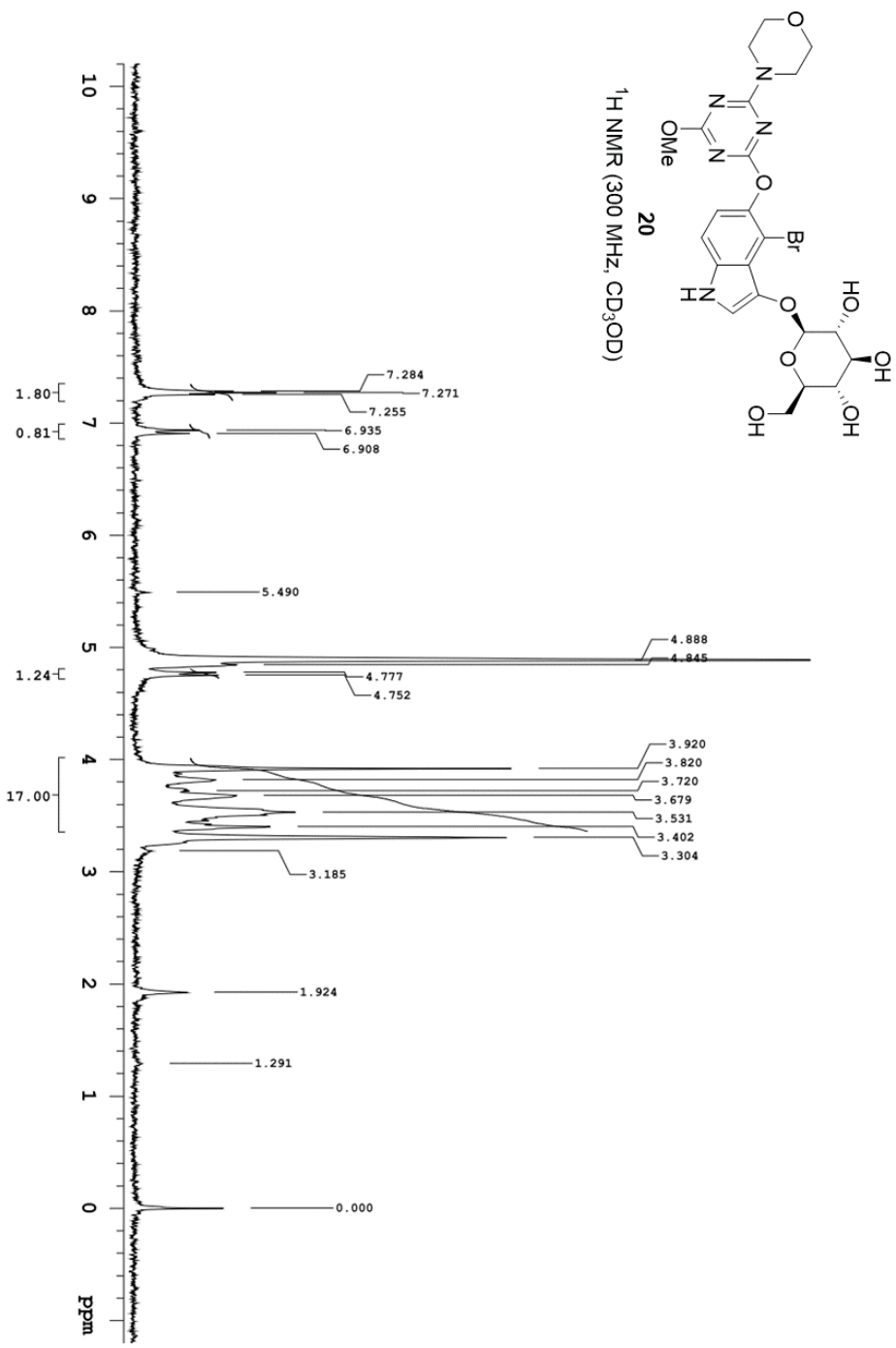

18
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)
170.6129
170.3490
169.5301
169.4013
167.8613
146.2655
140.1901
128.6450
122.5829
119.9560
111.9149
108.5728
100.3076
98.4092
77.3421
77.1600
76.9799
72.7106
72.6167
70.8813
68.3031
62.0450
23.7424
21.0253
20.9005
20.7341

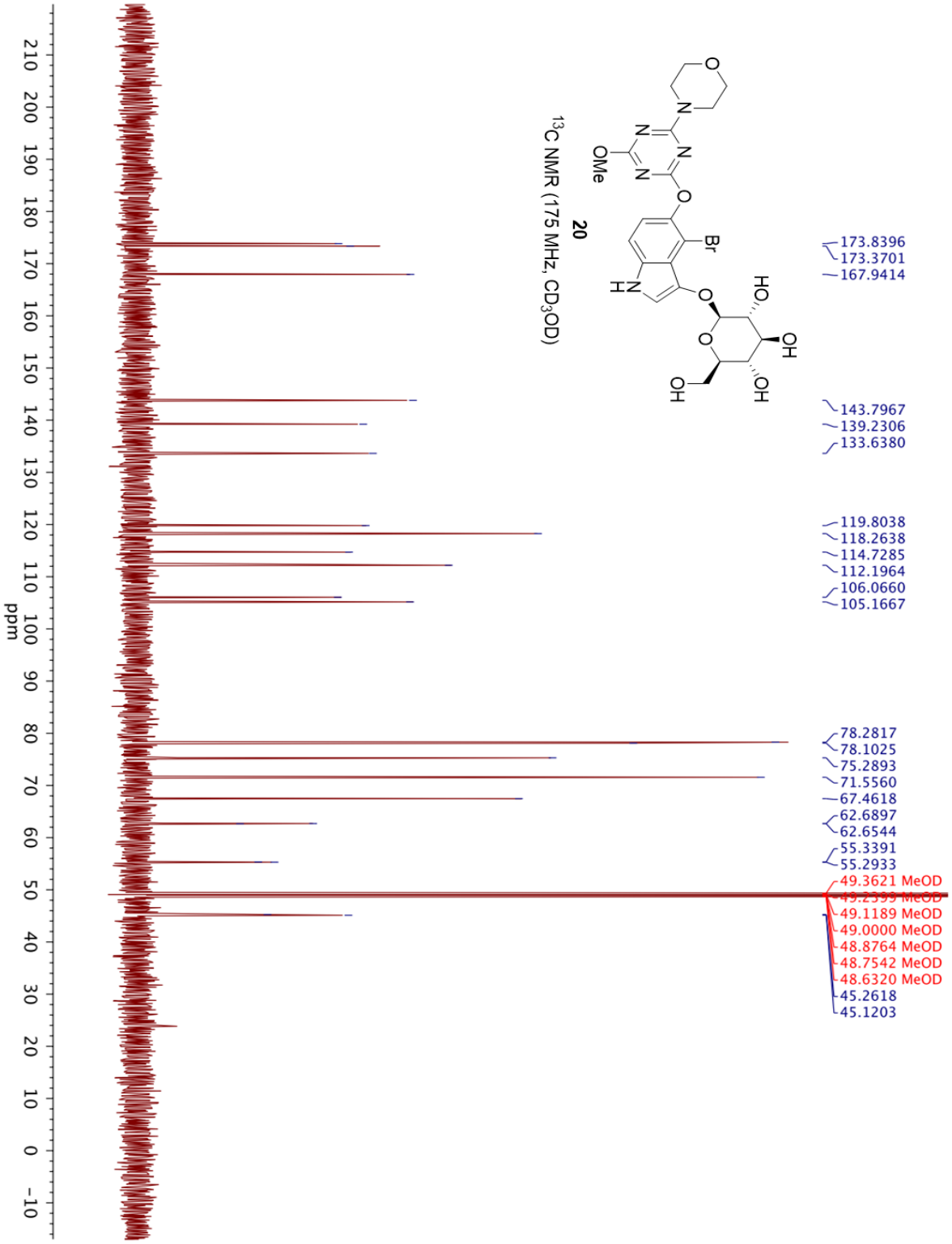

19
1H NMR (300 MHz, CD3OD)
OMe
7.458
7.452
7.411
7.282
7.253
7.159
6.891
6.883
6.862
6.856
4.883
4.686
4.663
4.614
4.104
4.080
4.057
3.916
3.875
3.811
3.735
3.717
3.676
3.553
3.500
3.471
3.450
3.428
3.387
3.360
3.344
3.305
2.270
2.008
1.285
1.258
1.233
1.209
0.000
0.66
0.85
0.80
0.82
1.00
3.02
15.77
ppm

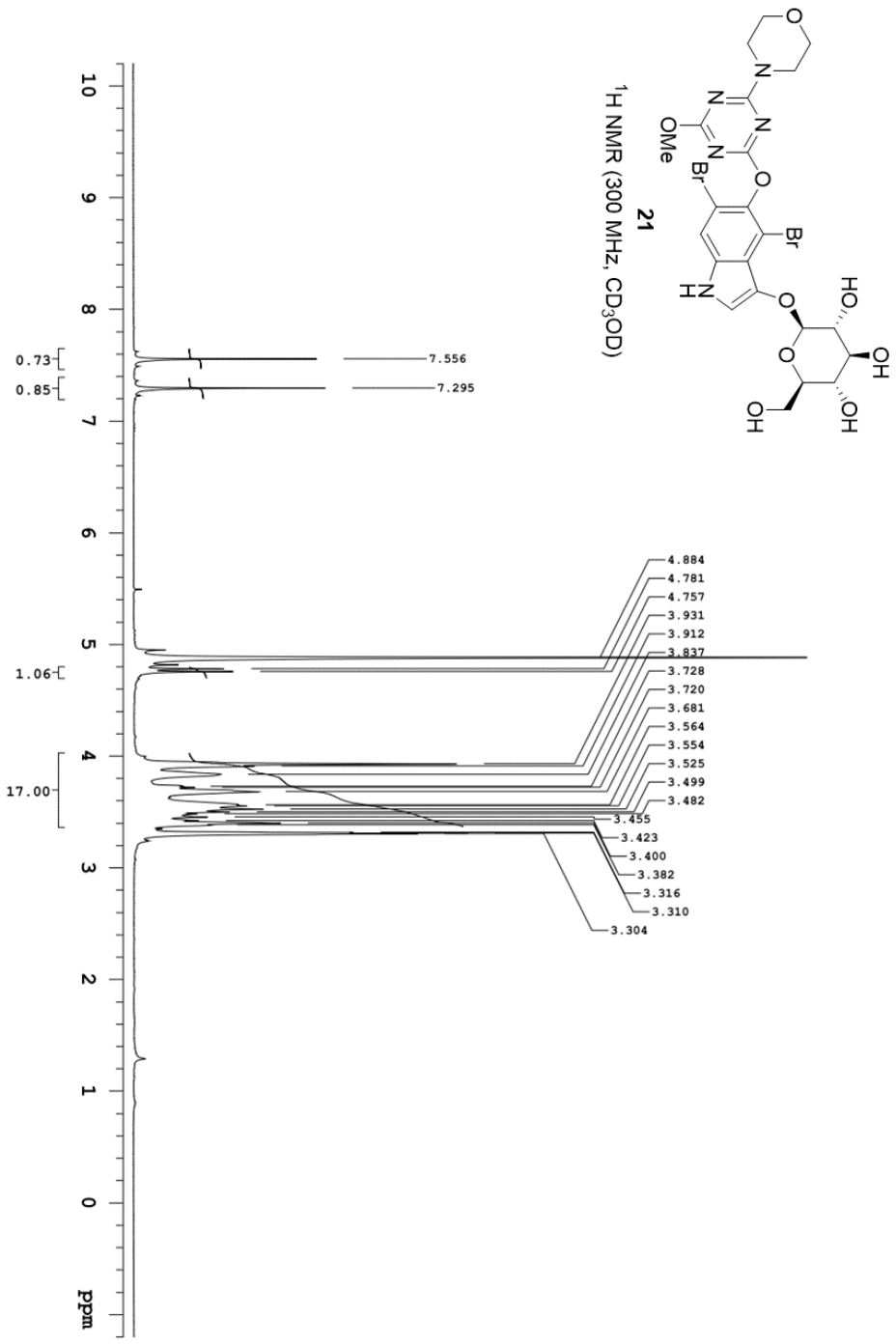

19
^{13}C NMR (75 MHz, CD$_3$OD)
OMe
HO
OH
OH
OH
174.006
173.792
167.949
146.512
139.234
132.917
121.367
117.339
114.104
112.685
110.671
105.957
78.203
78.005
75.030
71.520
67.492
62.640
55.256
49.855
49.565
49.290
49.000
48.436
48.146
47.902
45.186
220
200
180
160
140
120
100
80
60
40
20
ppm

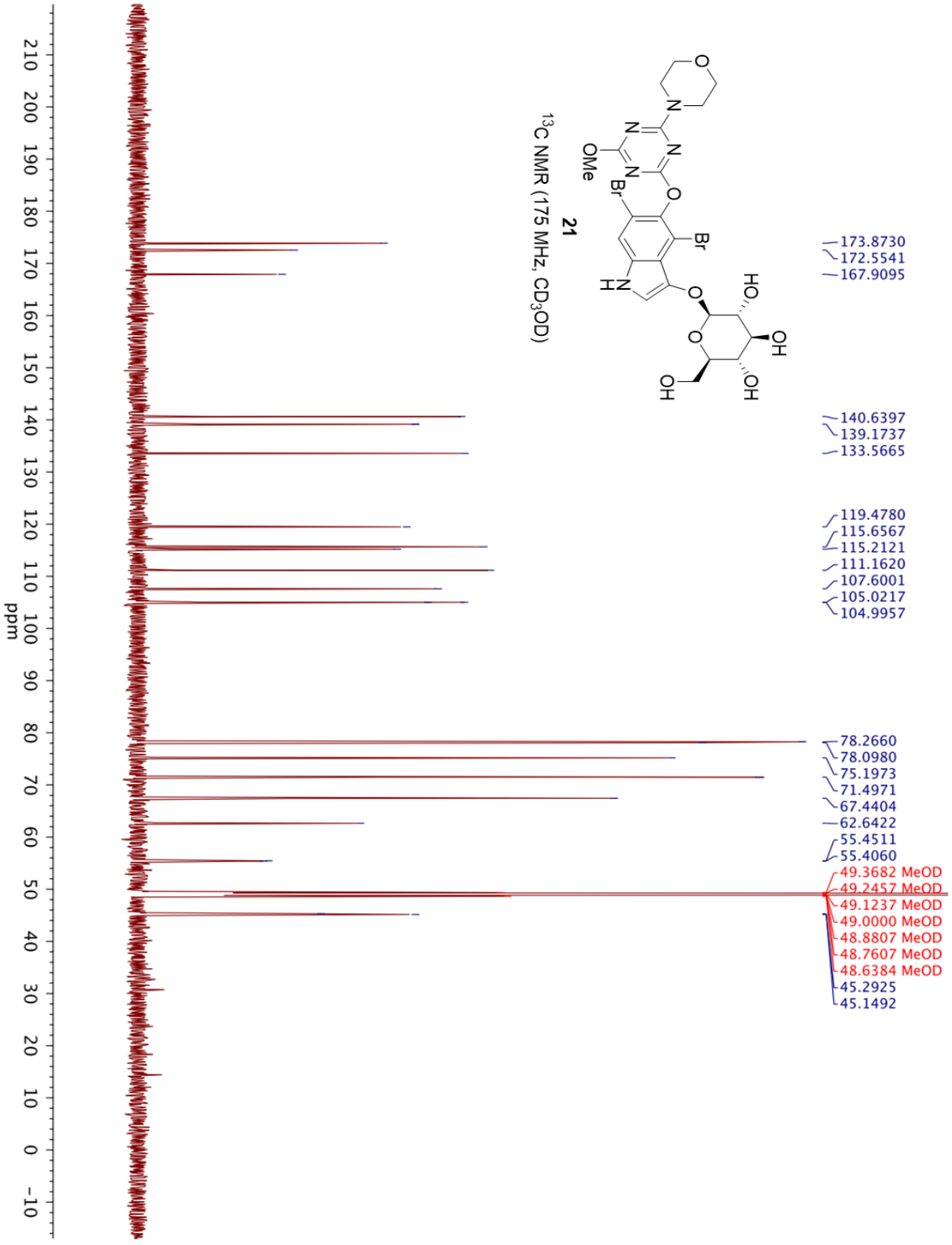

pre-20
^{1}H NMR (400 MHz, CDCl$_3$)
OMe
Br
Ac
AcO
OAc
OAc
OAc
8.411
8.397
7.302
7.260
7.178
7.156
5.393
5.374
5.370
5.351
5.310
5.287
5.264
5.211
5.187
5.164
5.072
5.053
4.393
4.387
4.361
4.356
4.217
4.204
4.186
4.173
3.911
3.905
3.898
3.892
3.885
3.871
3.837
3.833
3.720
3.708
3.697
3.659
2.621
2.094
2.059
2.044
2.024
1.655
1.288
1.269
1.249
0.960
0.943
0.886
0.869
0.860
0.852
0.842
0.835
0.819
-0.014
0.90
1.11
1.11
1.06
1.17
1.13
1.14
1.00
1.07
7.22
7.61
3.54
ppm

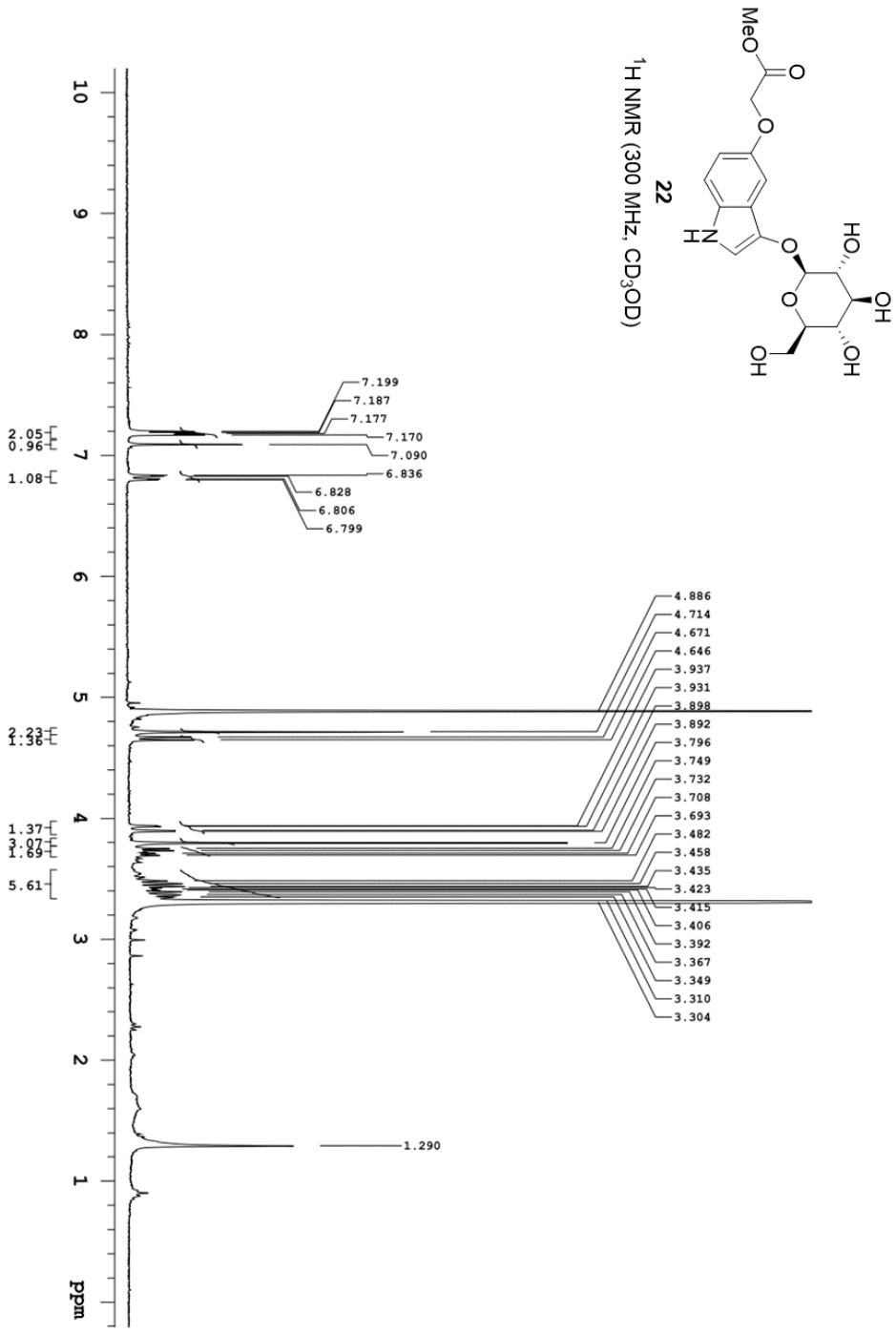

pre-20
^{13}C NMR (175 MHz, CDCl$_3$)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
172.6425
171.9092
170.5841
170.3024
169.4853
169.3349
168.1046
166.9442
146.2430
140.8491
132.0739
123.4774
121.5050
116.2561
112.1064
106.3948
100.2649
77.3404
77.1600
76.9779
72.7211
72.5504
70.8455
68.3096
66.6667
66.6113
61.9512
54.8146
44.1114
44.0632
23.9782
21.0015
20.8811
20.7047
OMe
Br
Ac
AcO
OAc
OAc
OAc

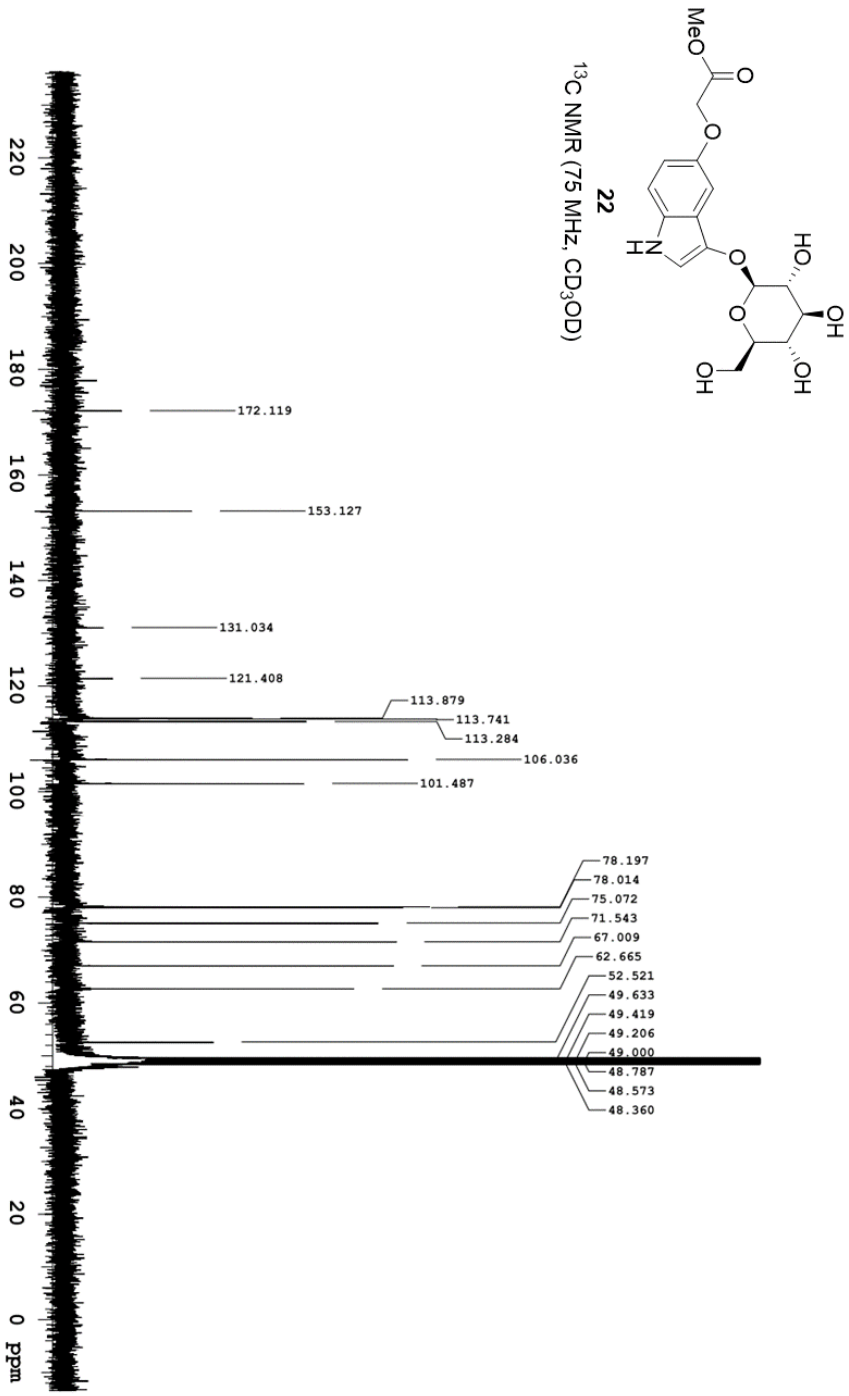

20
^{1}H NMR (300 MHz, CD_3OD)
OMe
Br
HO
OH
OH
OH
1.80
0.81
1.24
17.00
7.284
7.271
7.255
6.935
6.908
5.490
4.888
4.845
4.777
4.752
3.920
3.820
3.720
3.679
3.531
3.402
3.304
3.185
1.924
1.291
0.000
ppm

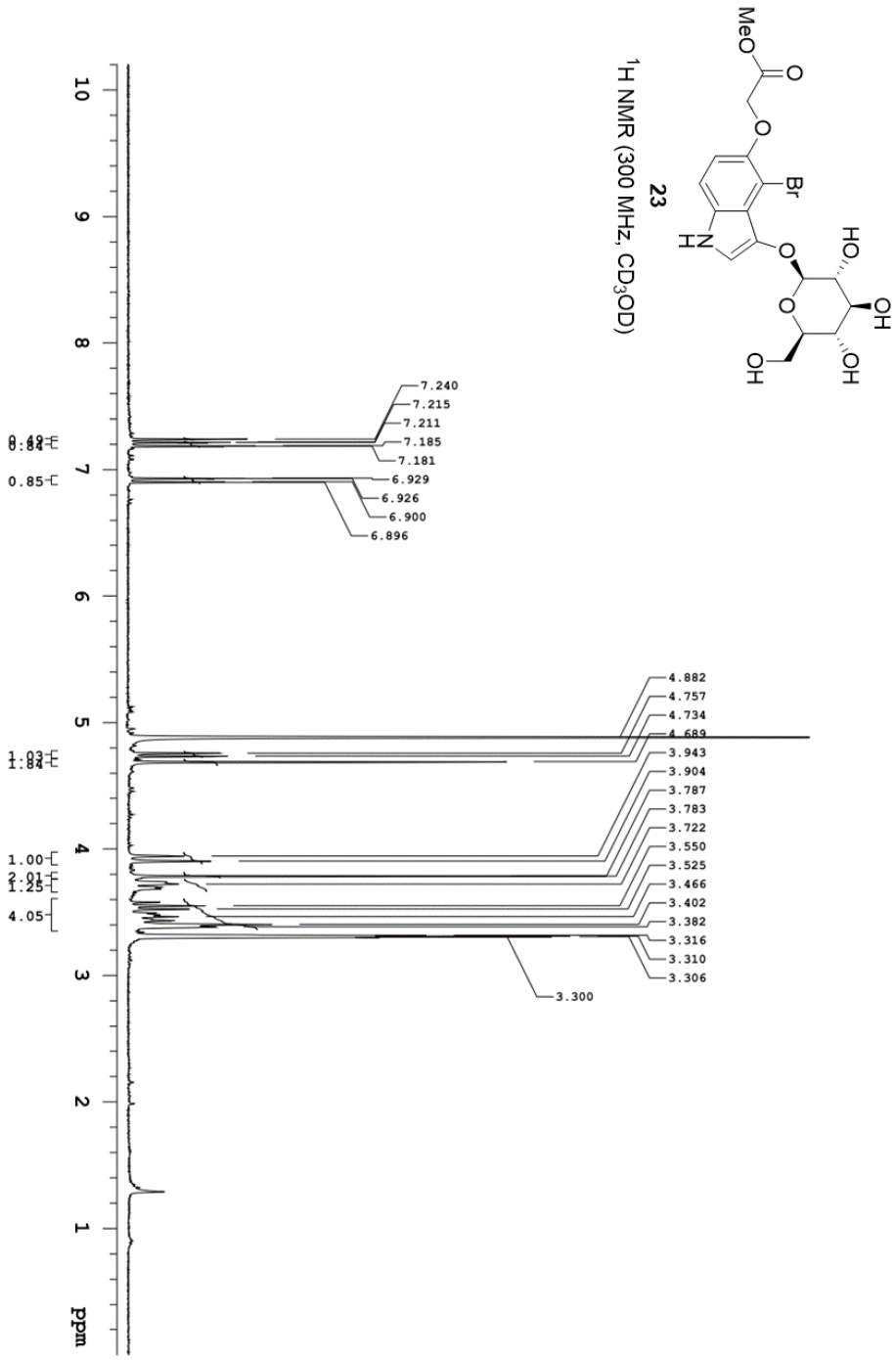

20
^{13}C NMR (175 MHz, CD$_3$OD)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
173.8396
173.3701
167.9414
143.7967
139.2306
133.6380
119.8038
118.2638
114.7285
112.1964
106.0660
105.1667
78.2817
78.1025
75.2893
71.5560
67.4618
62.6897
62.6544
55.3391
55.2933
49.3621 MeOD
49.2339 MeOD
49.1189 MeOD
49.0000 MeOD
48.8764 MeOD
48.7542 MeOD
48.6320 MeOD
45.2618
45.1203

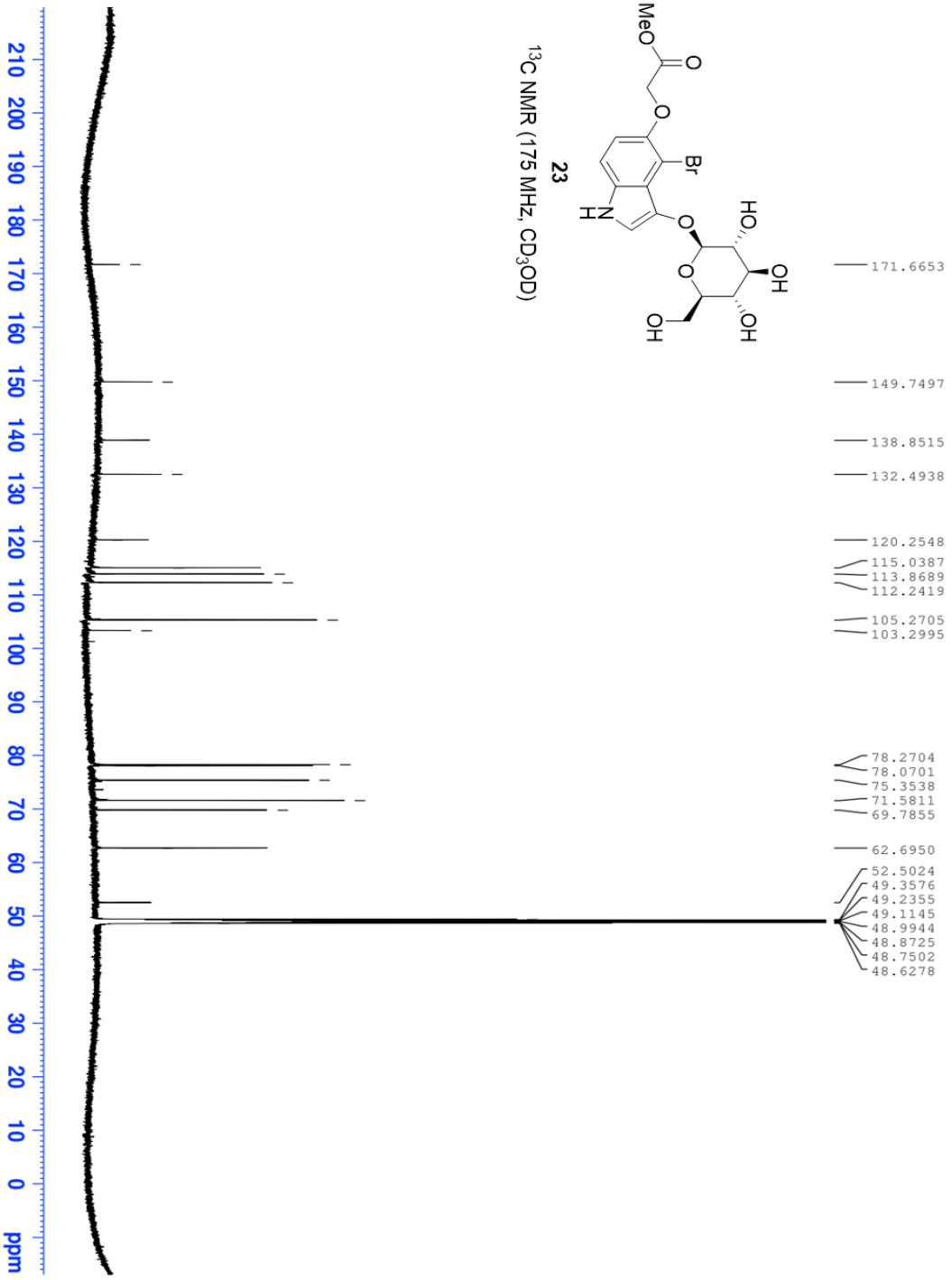

21
^{1}H NMR (300 MHz, CD$_3$OD)
OMe
Br
Br
HO
OH
OH
OH
0.73
0.85
1.06
17.00
7.556
7.295
4.884
4.781
4.757
3.931
3.912
3.837
3.728
3.720
3.681
3.564
3.554
3.525
3.499
3.482
3.455
3.423
3.400
3.382
3.316
3.310
3.304
ppm

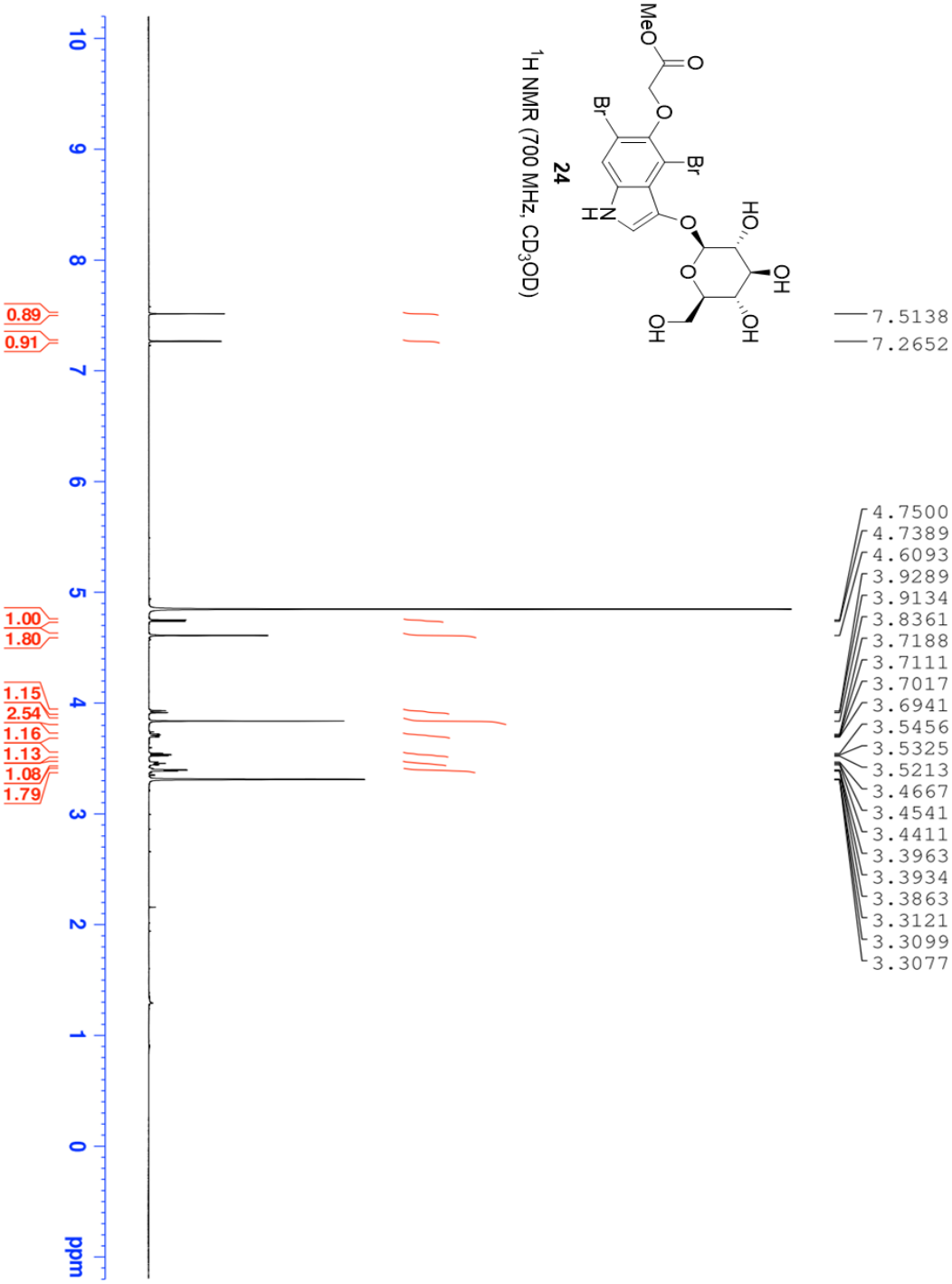

21
^{13}C NMR (175 MHz, CD$_3$OD)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
173.8730
172.5541
167.9095
140.6397
139.1737
133.5665
119.4780
115.6567
115.2121
111.1620
107.6001
105.0217
104.9957
78.2660
78.0980
75.1973
71.4971
67.4404
62.6422
55.4511
55.4060
49.3682 MeOD
49.2457 MeOD
49.1237 MeOD
49.0000 MeOD
48.8807 MeOD
48.7607 MeOD
48.6384 MeOD
45.2925
45.1492

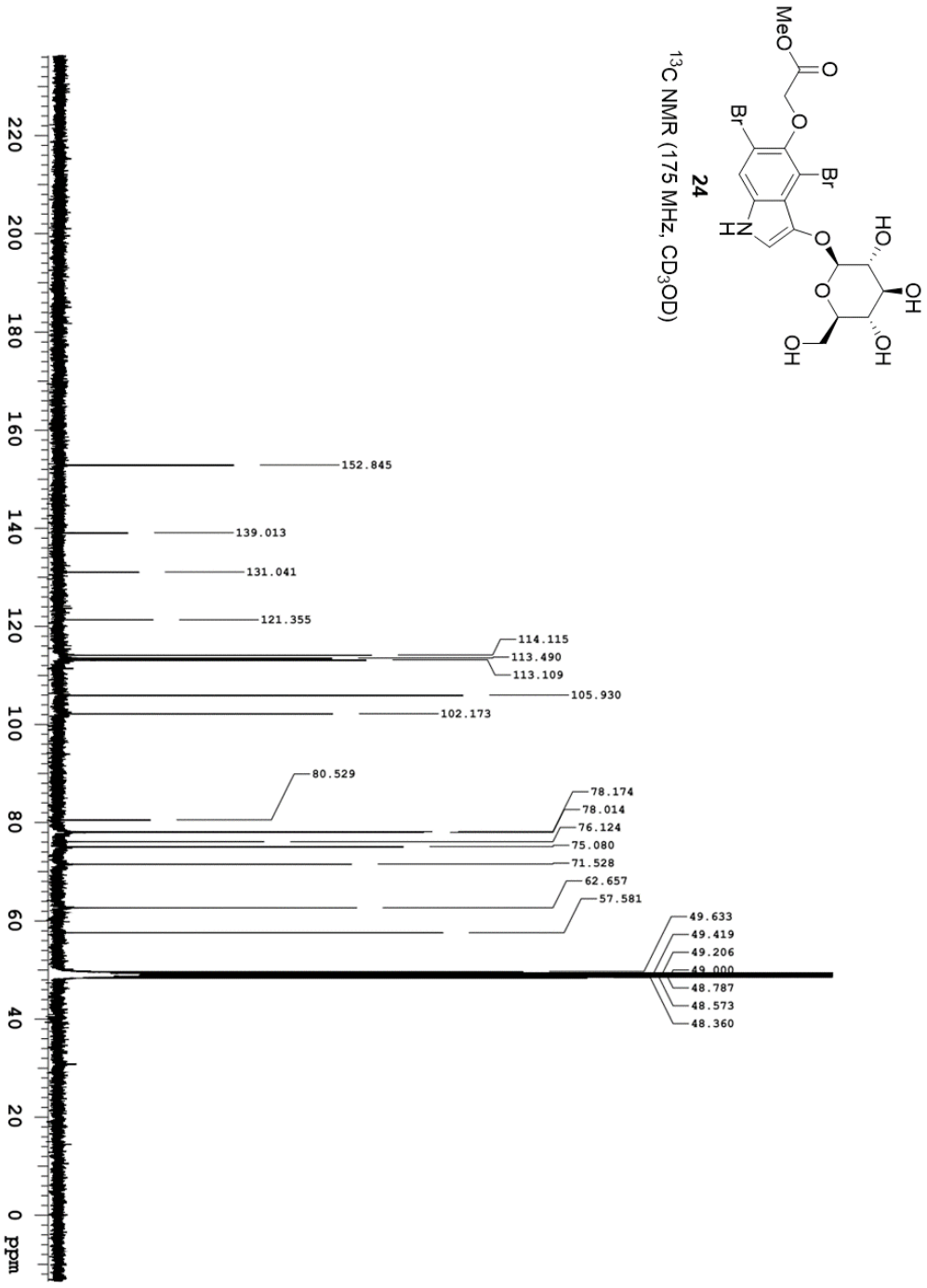

22
^{1}H NMR (300 MHz, CD_3OD)
MeO
O
O
N
H
O
HO
OH
OH
O
7.199
7.187
7.177
7.170
7.090
6.836
6.828
6.806
6.799
4.886
4.714
4.671
4.646
3.937
3.931
3.898
3.892
3.796
3.749
3.732
3.708
3.693
3.482
3.458
3.435
3.423
3.415
3.406
3.392
3.367
3.349
3.310
3.304
1.290
2.05
0.96
1.08
2.23
1.36
1.37
3.07
1.69
5.61
ppm

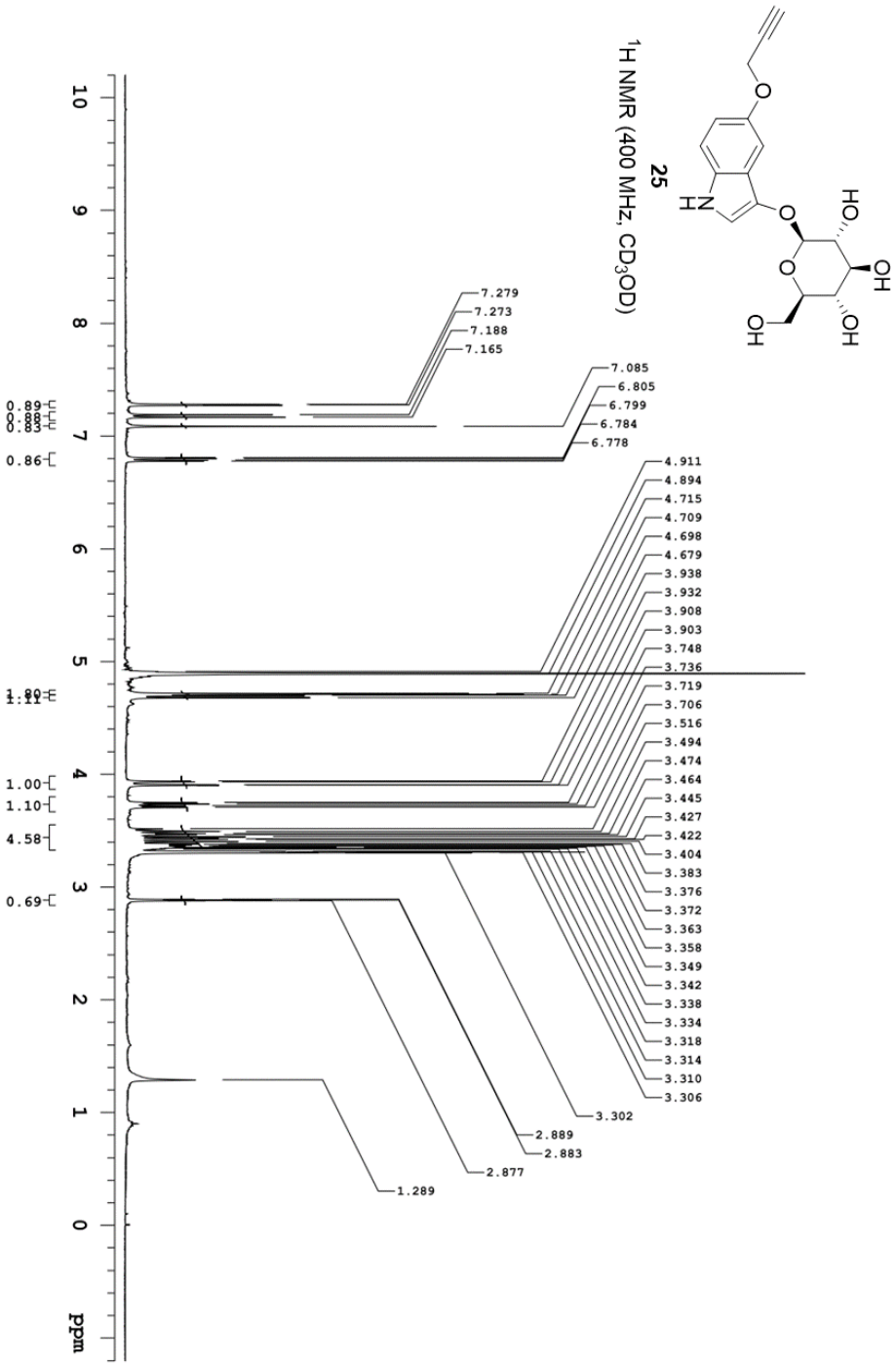

22
^{13}C NMR (75 MHz, CD_3OD)
MeO
O
O
N
H
O
HO
OH
OH
O
220
200
180
160
140
120
100
80
60
40
20
0 ppm
172.119
153.127
131.034
121.408
113.879
113.741
113.284
106.036
101.487
78.197
78.014
75.072
71.543
67.009
62.665
52.521
49.633
49.419
49.206
49.000
48.787
48.573
48.360

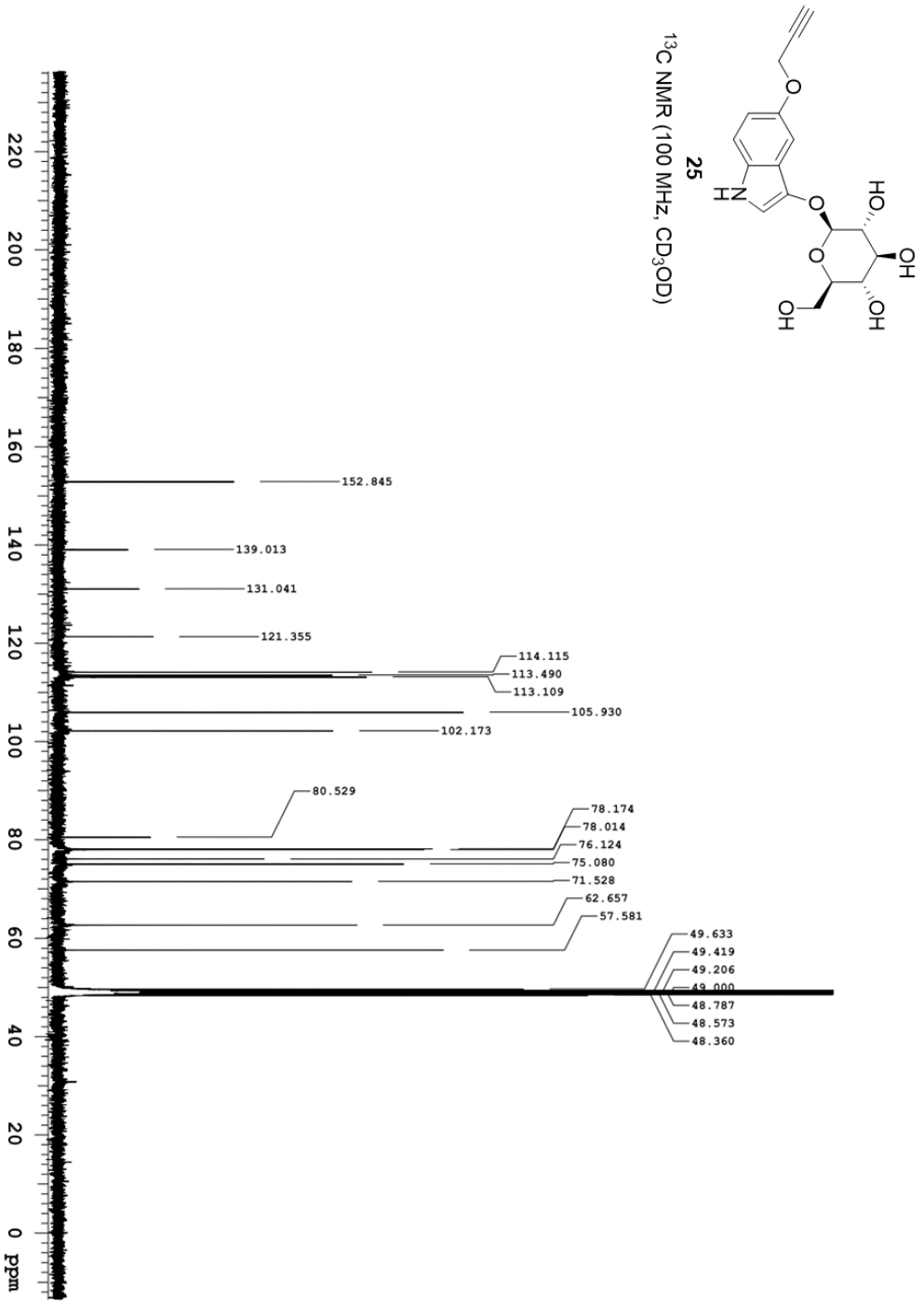

23
^{1}H NMR (300 MHz, CD_3OD)
MeO
O
O
Br
N
H
O
HO
OH
OH
OH
7.240
7.215
7.211
7.185
7.181
6.929
6.926
6.900
6.896
4.882
4.757
4.734
4.689
3.943
3.904
3.787
3.783
3.722
3.550
3.525
3.466
3.402
3.382
3.316
3.310
3.306
3.300
0.85
1.00
2.01
1.25
4.05
ppm

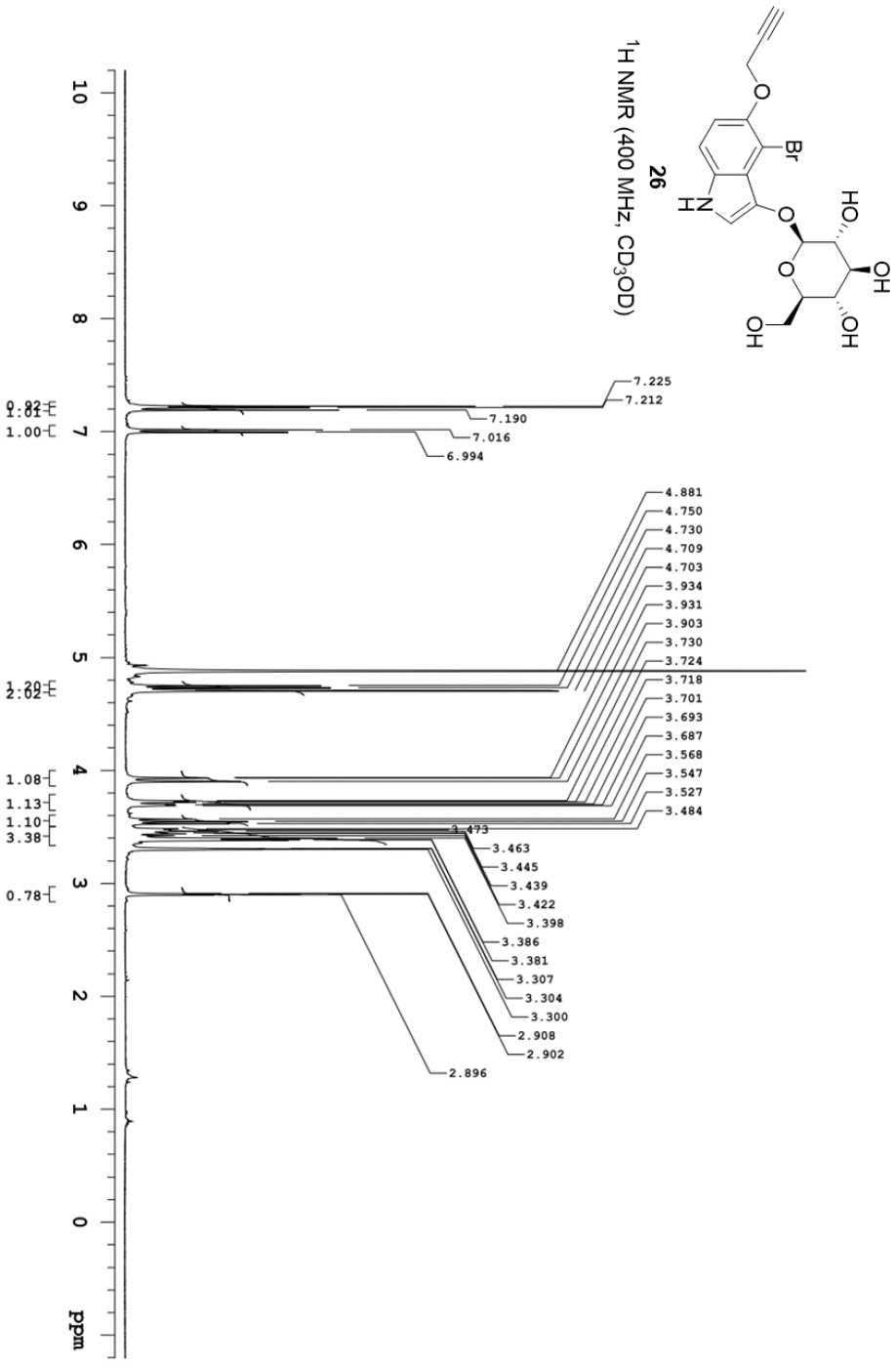

23
^{13}C NMR (175 MHz, CD_3OD)
MeO
O
O
Br
N
H
O
HO
OH
OH
OH
171.6653
149.7497
138.8515
132.4938
120.2548
115.0387
113.8689
112.2419
105.2705
103.2995
78.2704
78.0701
75.3538
71.5811
69.7855
62.6950
52.5024
49.3576
49.2355
49.1145
48.9944
48.8725
48.7502
48.6278
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

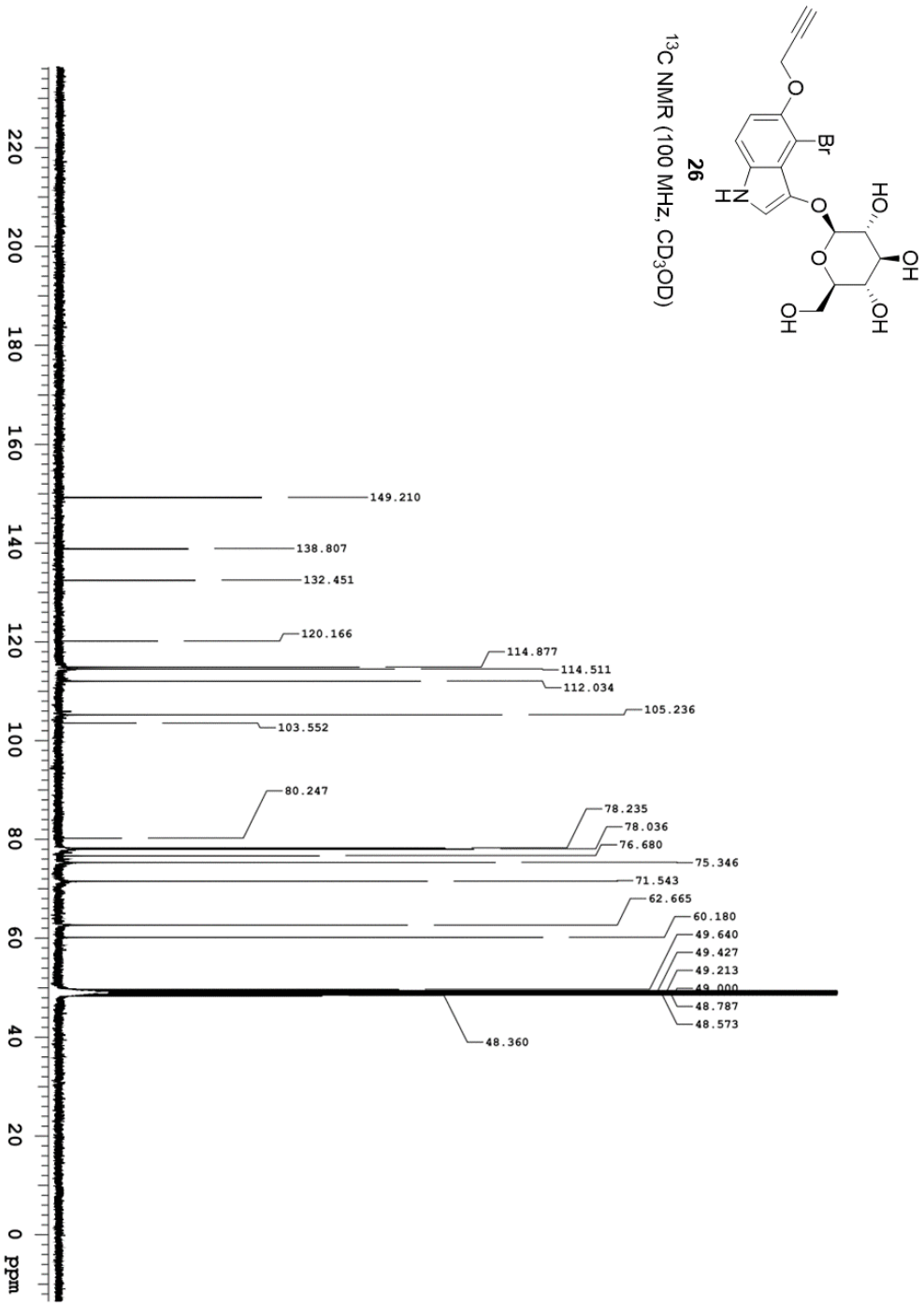

24
^{1}H NMR (700 MHz, CD_3OD)
MeO
O
O
Br
Br
N
H
O
HO
OH
O
OH
OH
7.5138
7.2652
4.7500
4.7389
4.6093
3.9289
3.9134
3.8361
3.7188
3.7111
3.7017
3.6941
3.5456
3.5325
3.5213
3.4667
3.4541
3.4411
3.3963
3.3934
3.3863
3.3121
3.3099
3.3077
0.89
0.91
1.00
1.80
1.15
2.54
1.16
1.13
1.08
1.79
10
9
8
7
6
5
4
3
2
1
0
ppm

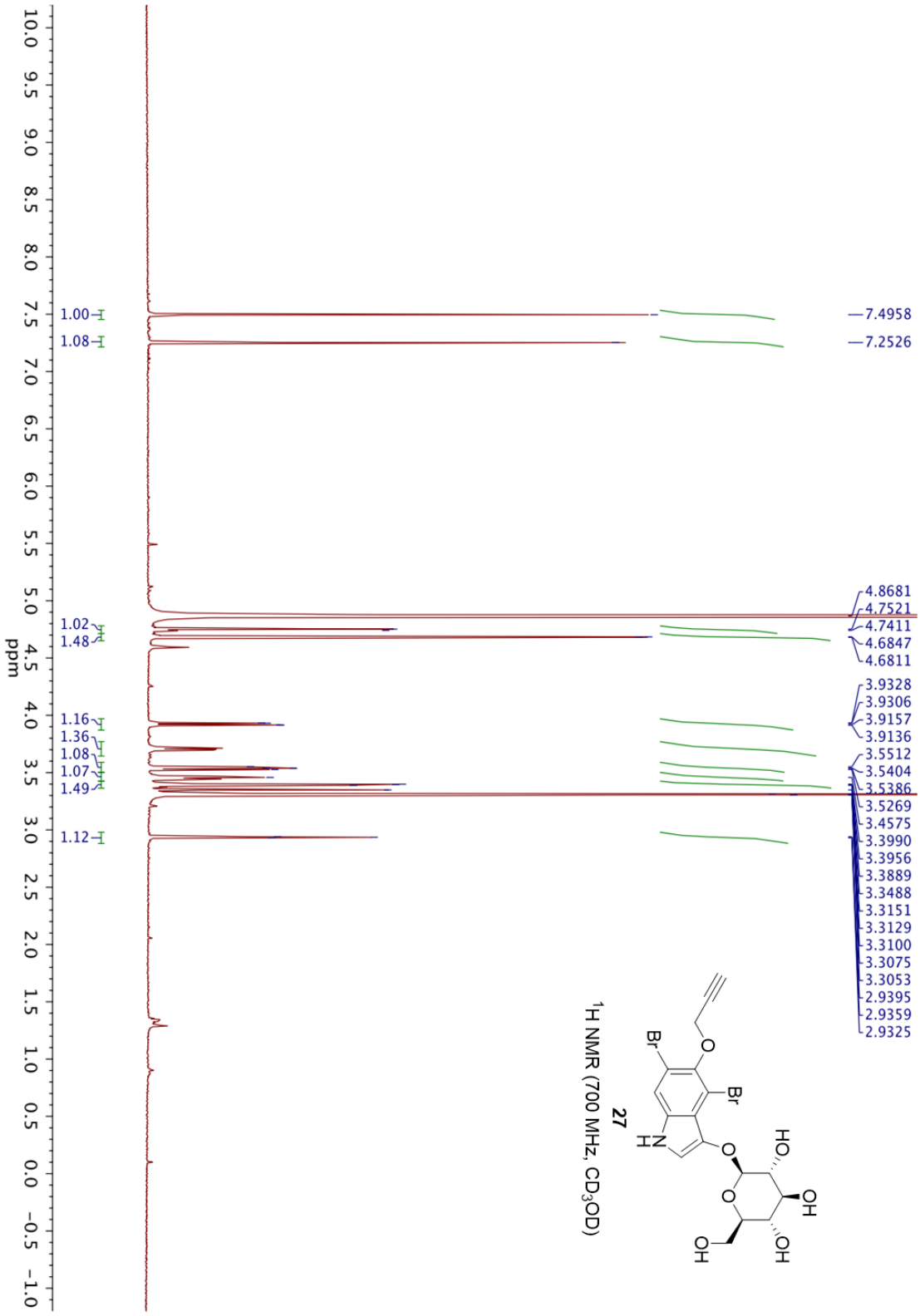

24
^{13}C NMR (175 MHz, CD_3OD)
MeO
O
O
Br
Br
N
H
O
HO
OH
O
OH
OH
220
200
180
160
140
120
100
80
60
40
20
0
ppm
152.845
139.013
131.041
121.355
114.115
113.490
113.109
105.930
102.173
80.529
78.174
78.014
76.124
75.080
71.528
62.657
57.581
49.633
49.419
49.206
49.000
48.787
48.573
48.360

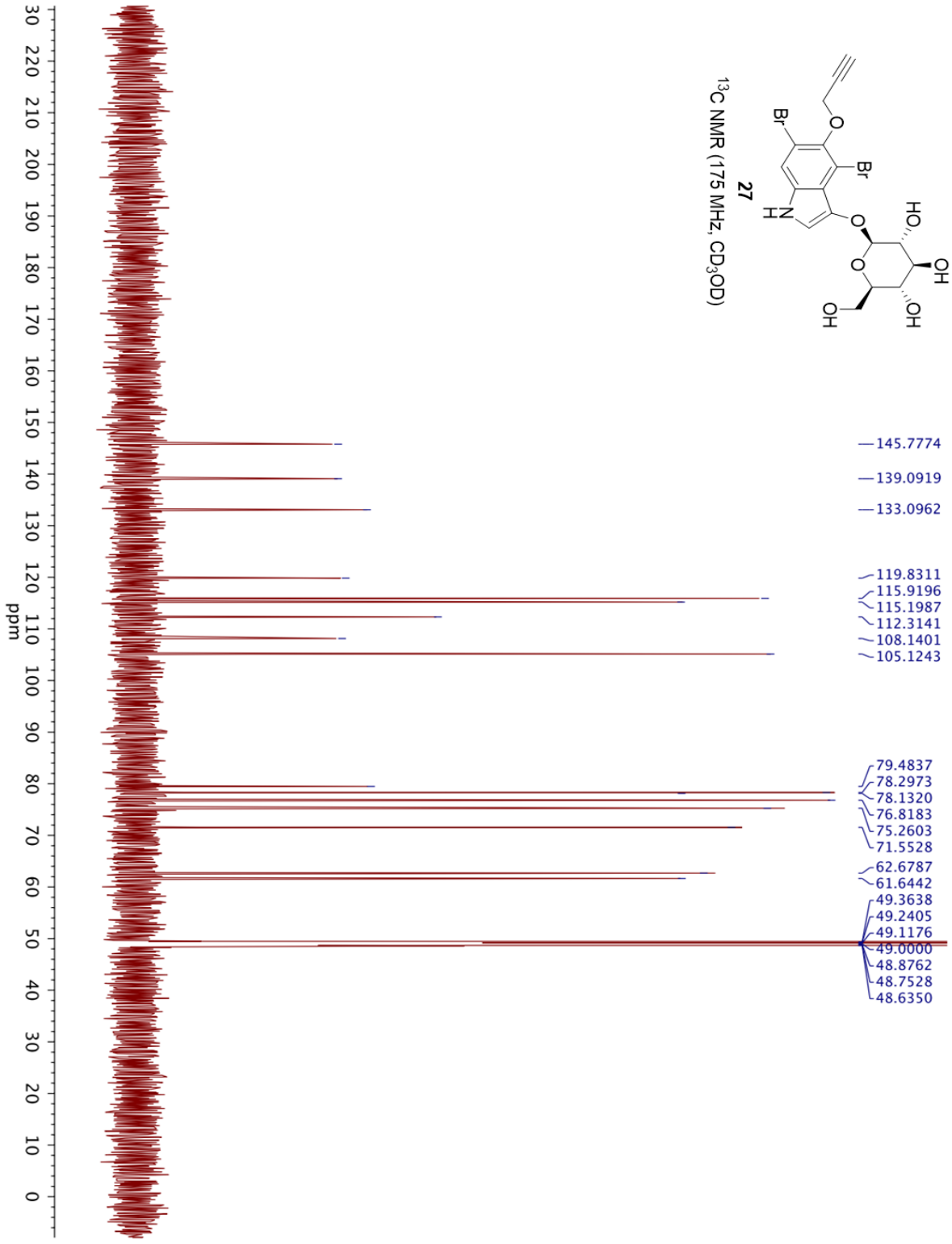

25
^{1}H NMR (400 MHz, CD_3OD)
7.279
7.273
7.188
7.165
7.085
6.805
6.799
6.784
6.778
4.911
4.894
4.715
4.709
4.698
4.679
3.938
3.932
3.908
3.903
3.748
3.736
3.719
3.706
3.516
3.494
3.474
3.464
3.445
3.427
3.422
3.404
3.383
3.376
3.372
3.363
3.358
3.349
3.342
3.338
3.334
3.318
3.314
3.310
3.306
3.302
2.889
2.883
2.877
1.289
0.89
0.88
0.86
1.00
1.10
4.58
0.69
ppm

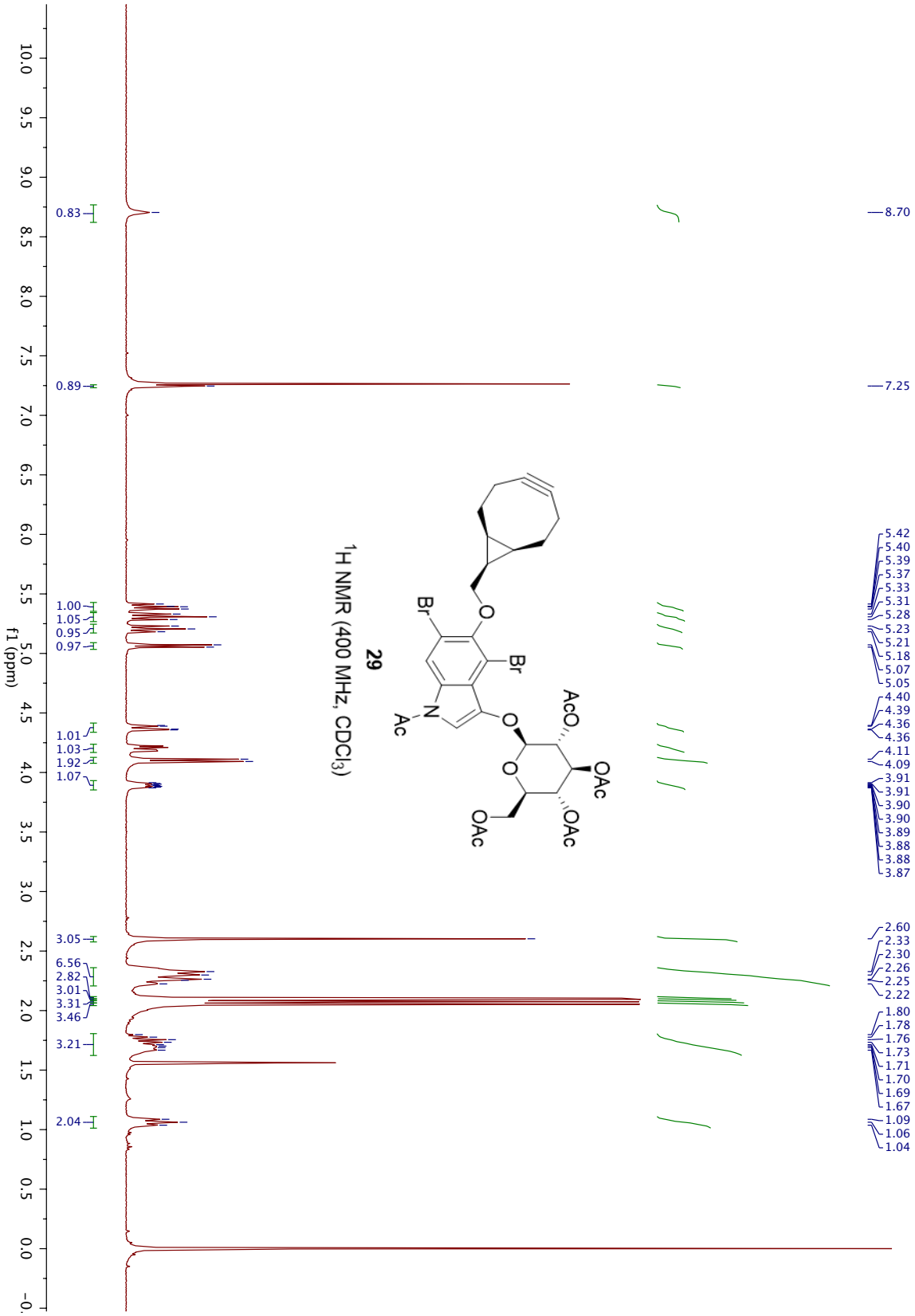

25
^{13}C NMR (100 MHz, CD_3OD)
152.845
139.013
131.041
121.355
114.115
113.490
113.109
105.930
102.173
80.529
78.174
78.014
76.124
75.080
71.528
62.657
57.581
49.633
49.419
49.206
49.000
48.787
48.573
48.360
220
200
180
160
140
120
100
80
60
40
20
0
ppm

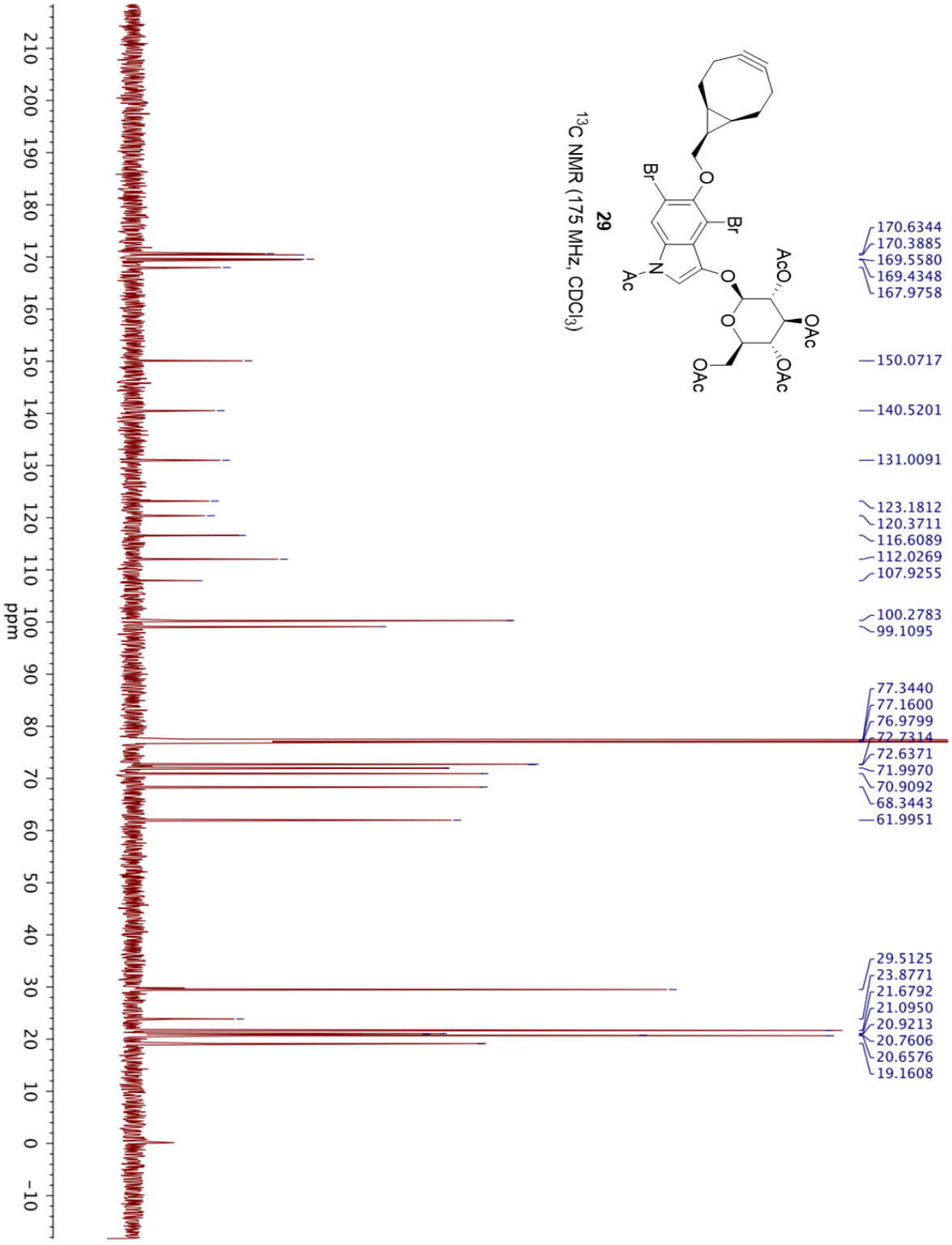

26
^{1}H NMR (400 MHz, CD_3OD)
Br
HO
OH
OH
OH
7.225
7.212
7.190
7.016
6.994
4.881
4.750
4.730
4.709
4.703
3.934
3.931
3.903
3.730
3.724
3.718
3.701
3.693
3.687
3.568
3.547
3.527
3.484
3.473
3.463
3.445
3.439
3.422
3.398
3.386
3.381
3.307
3.304
3.300
2.908
2.902
2.896
0.82
1.01
1.00
1.20
2.02
1.08
1.13
1.10
3.38
0.78
ppm

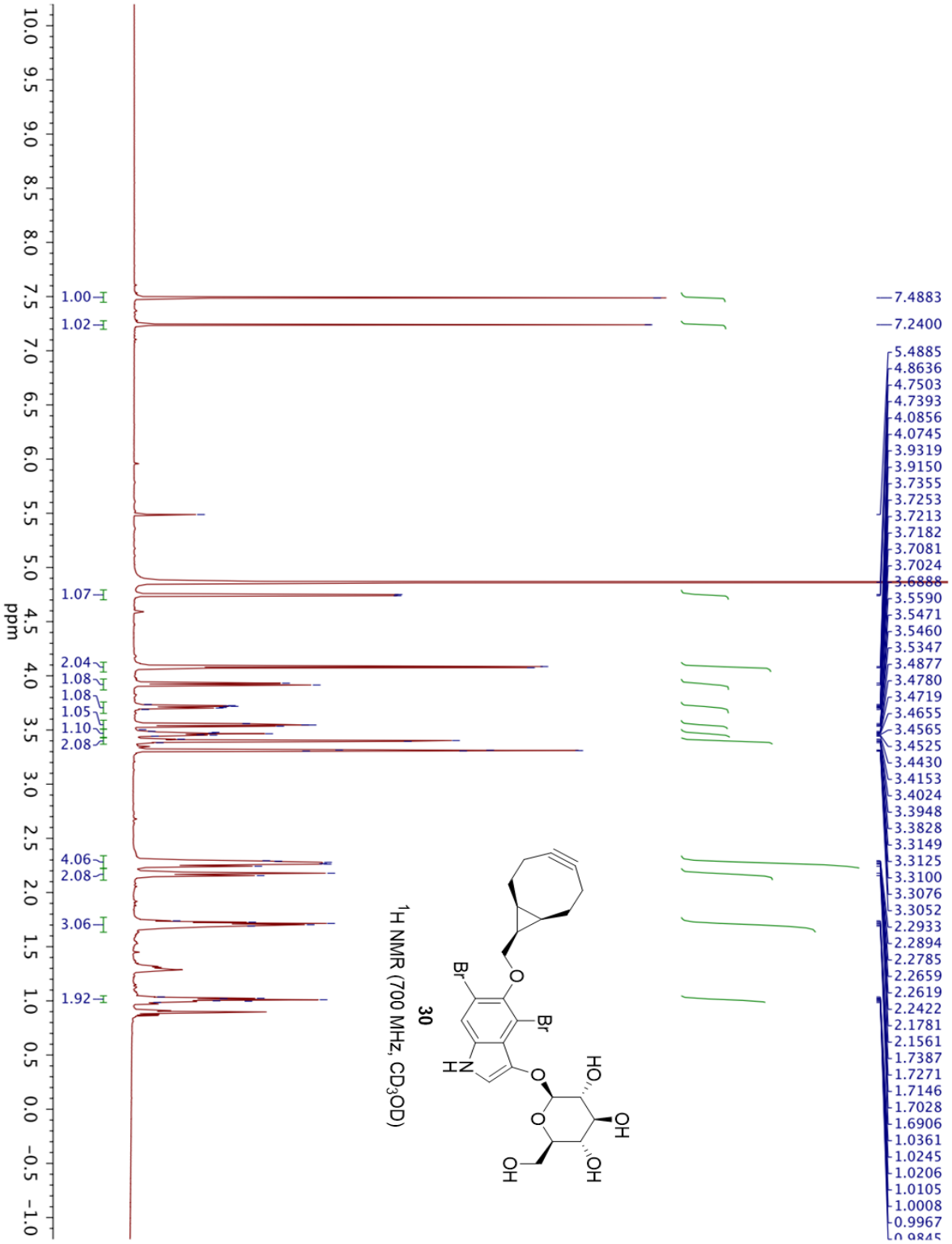

26
^{13}C NMR (100 MHz, CD_3OD)
149.210
138.807
132.451
120.166
114.877
114.511
112.034
105.236
103.552
80.247
78.235
78.036
76.680
75.346
71.543
62.665
60.180
49.640
49.427
49.213
49.000
48.787
48.573
48.360
220
200
180
160
140
120
100
80
60
40
20
0
ppm

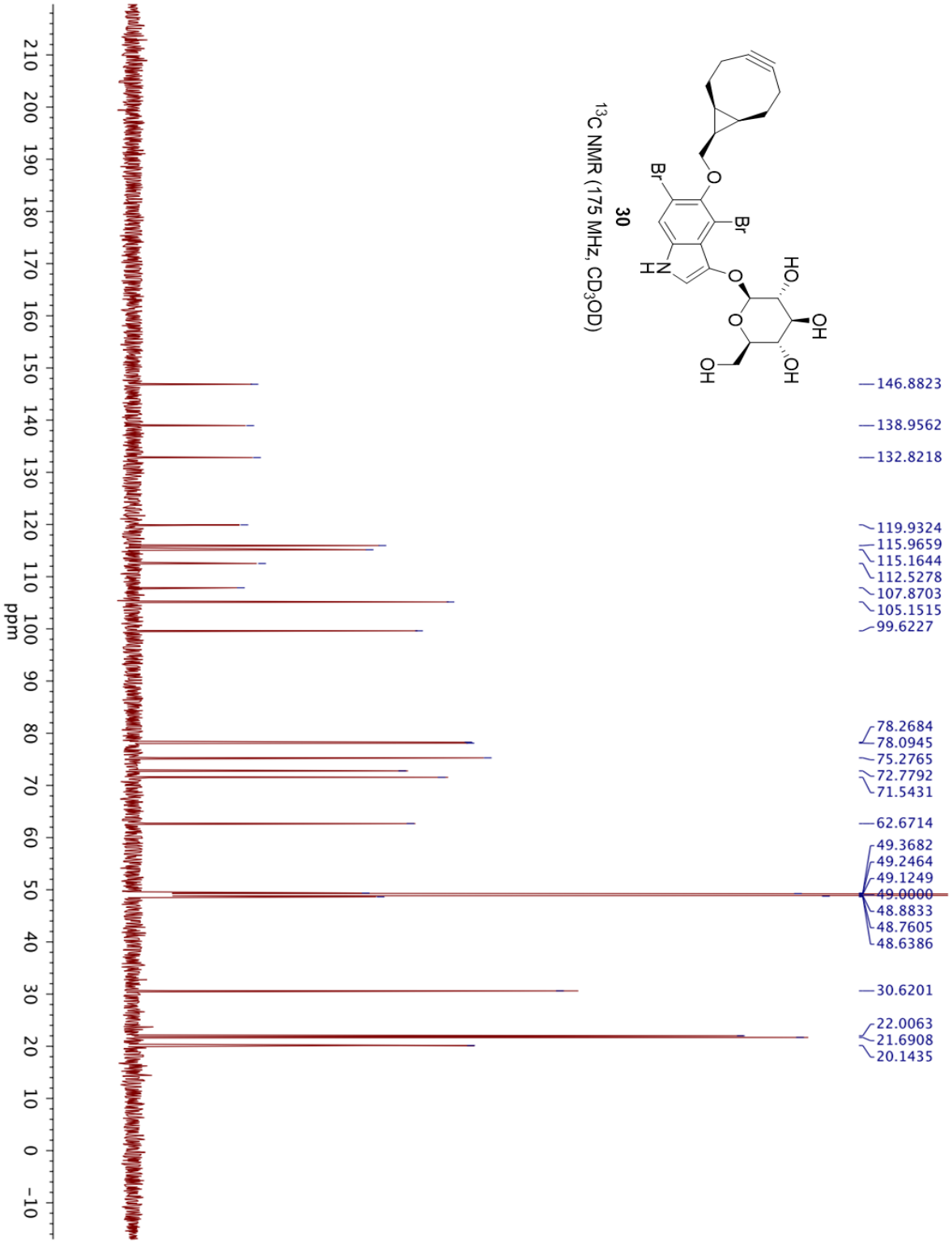

1H NMR (700 MHz, CD3OD)
27
ppm
1.00
1.08
1.02
1.48
1.16
1.36
1.08
1.07
1.49
1.12
7.4958
7.2526
4.8681
4.7521
4.7411
4.6847
4.6811
3.9328
3.9306
3.9157
3.9136
3.5512
3.5404
3.5386
3.5269
3.4575
3.3990
3.3956
3.3889
3.3488
3.3151
3.3129
3.3100
3.3075
3.3053
2.9395
2.9359
2.9325
Br
Br
O
N
H
O
O
HO
OH
OH
OH

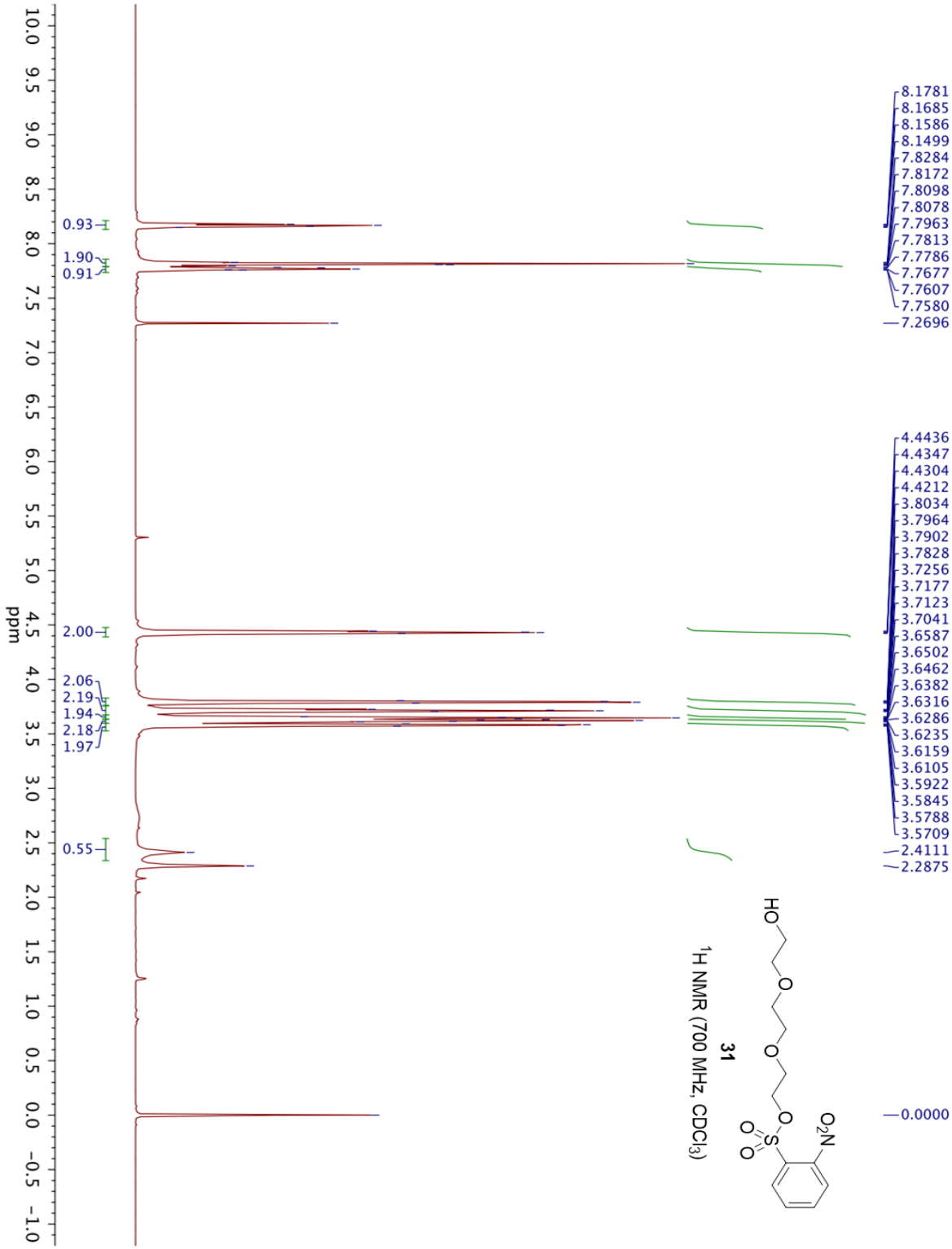

27
^{13}C NMR (175 MHz, CD_3OD)
Br
Br
O
N
H
O
HO
OH
OH
OH
O
ppm
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
145.7774
139.0919
133.0962
119.8311
115.9196
115.1987
112.3141
108.1401
105.1243
79.4837
78.2973
78.1320
76.8183
75.2603
71.5528
62.6787
61.6442
49.3638
49.2405
49.1176
49.0000
48.8762
48.7528
48.6350

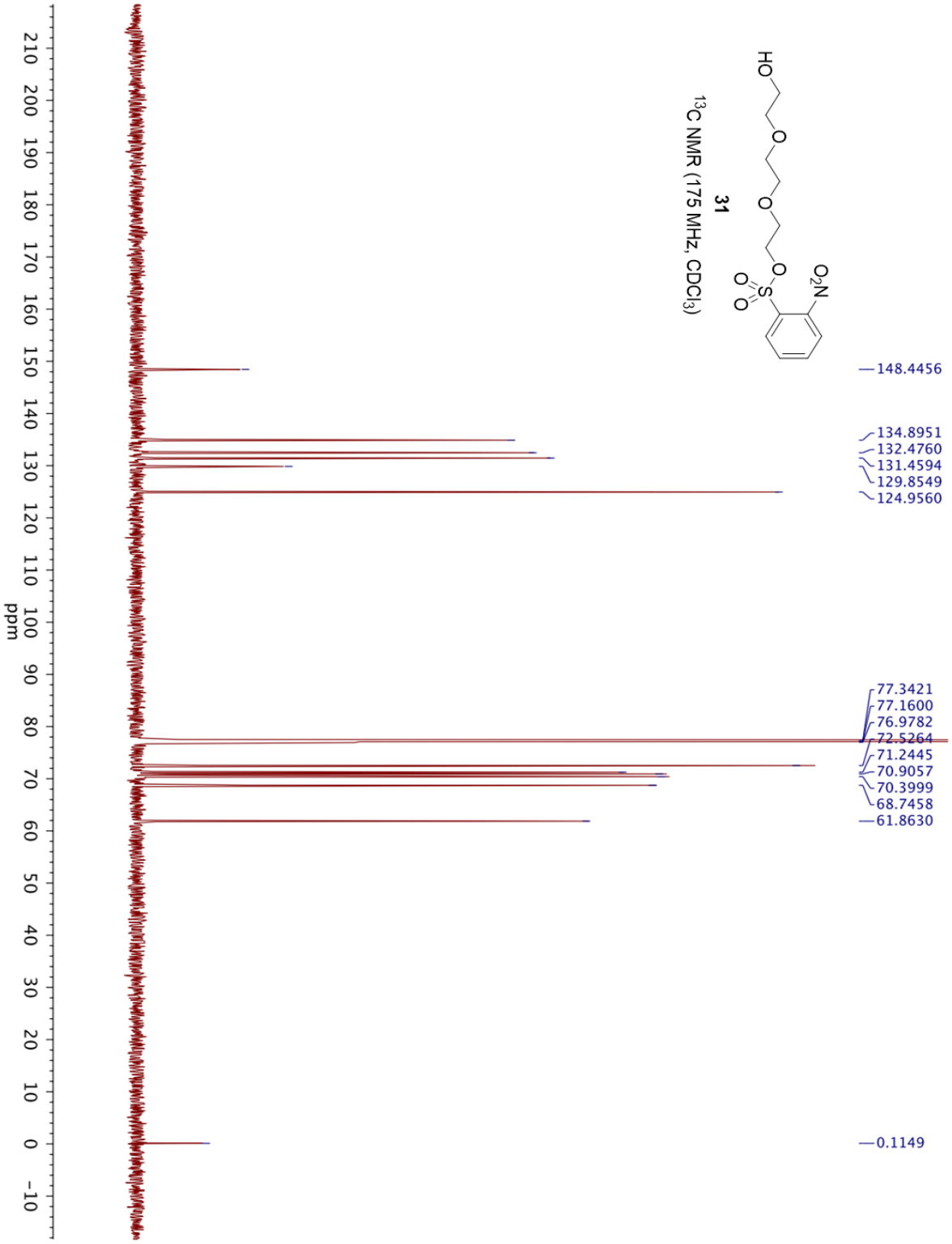

29
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)
Br
Br
N
Ac
O
O
AcO
OAc
OAc
OAc
0.83
0.89
1.00
1.05
0.95
0.97
1.01
1.03
1.92
1.07
3.05
6.56
2.82
3.01
3.31
3.46
3.21
2.04
8.70
7.25
5.42
5.40
5.39
5.37
5.33
5.31
5.28
5.23
5.21
5.18
5.07
5.05
4.40
4.39
4.36
4.36
4.11
4.09
3.91
3.91
3.90
3.90
3.89
3.88
3.88
3.87
2.60
2.33
2.30
2.26
2.25
2.22
1.80
1.78
1.76
1.73
1.71
1.70
1.69
1.67
1.09
1.06
1.04

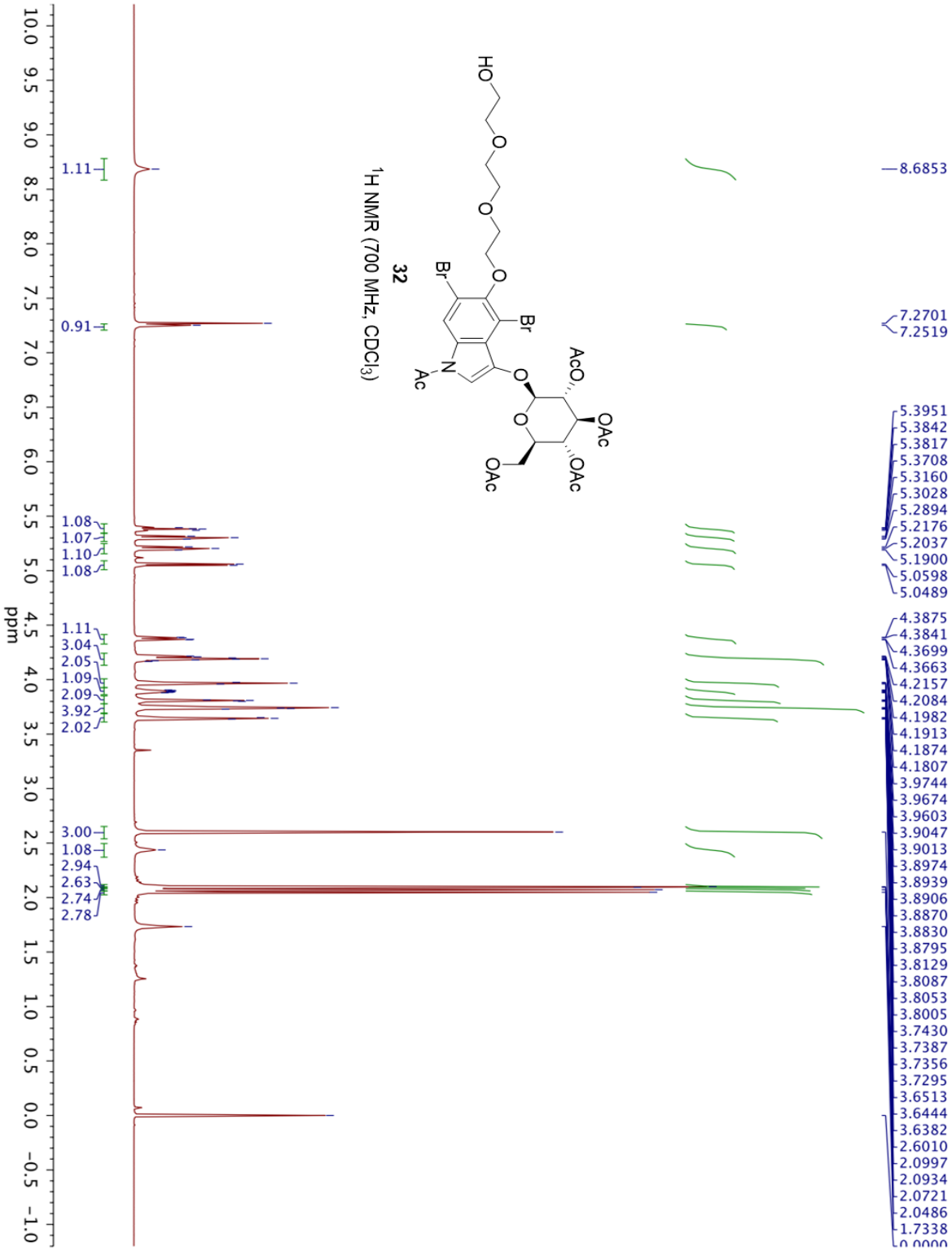

29
^{13}C NMR (175 MHz, CDCl$_3$)
Br
Br
O
N
Ac
O
AcO
OAc
O
OAc
OAc
170.6344
170.3885
169.5580
169.4348
167.9758
150.0717
140.5201
131.0091
123.1812
120.3711
116.6089
112.0269
107.9255
100.2783
99.1095
77.3440
77.1600
76.9799
72.7314
72.6371
71.9970
70.9092
68.3443
61.9951
29.5125
23.8771
21.6792
21.0950
20.9213
20.7606
20.6576
19.1608
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

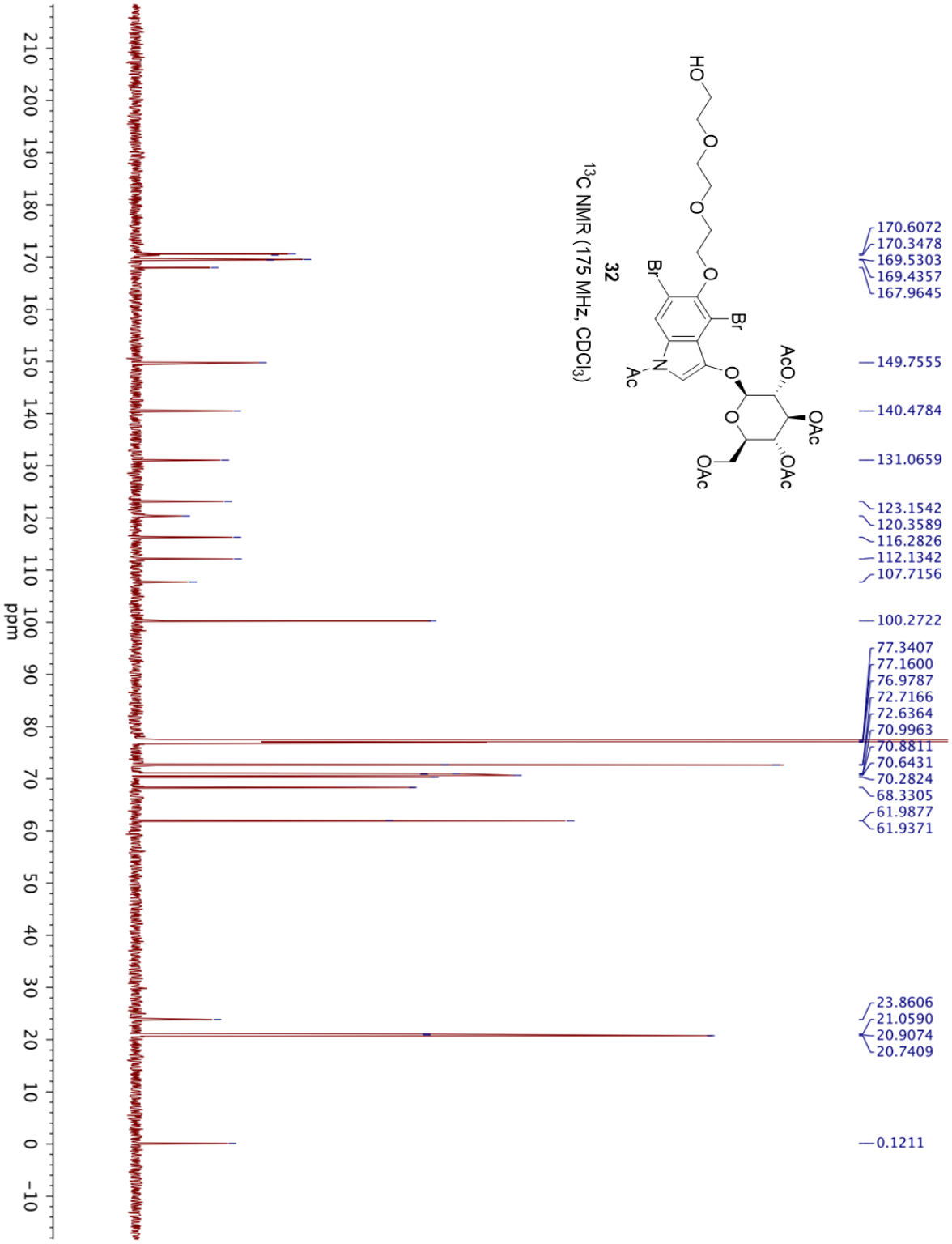

1H NMR (700 MHz, CD3OD)
30
ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
1.00
1.02
1.07
2.04
1.08
1.08
1.05
1.10
2.08
4.06
2.08
3.06
1.92
7.4883
7.2400
5.4885
4.8636
4.7503
4.7393
4.0856
4.0745
3.9319
3.9150
3.7355
3.7253
3.7213
3.7182
3.7081
3.7024
3.6888
3.5590
3.5471
3.5460
3.5347
3.4877
3.4780
3.4719
3.4655
3.4565
3.4525
3.4430
3.4153
3.4024
3.3948
3.3828
3.3149
3.3125
3.3100
3.3076
3.3052
2.2933
2.2894
2.2785
2.2659
2.2619
2.2422
2.1781
2.1561
1.7387
1.7271
1.7146
1.7028
1.6906
1.0361
1.0245
1.0206
1.0105
1.0008
0.9967
Br
Br
O
N
H
O
HO
OH
OH
OH
O

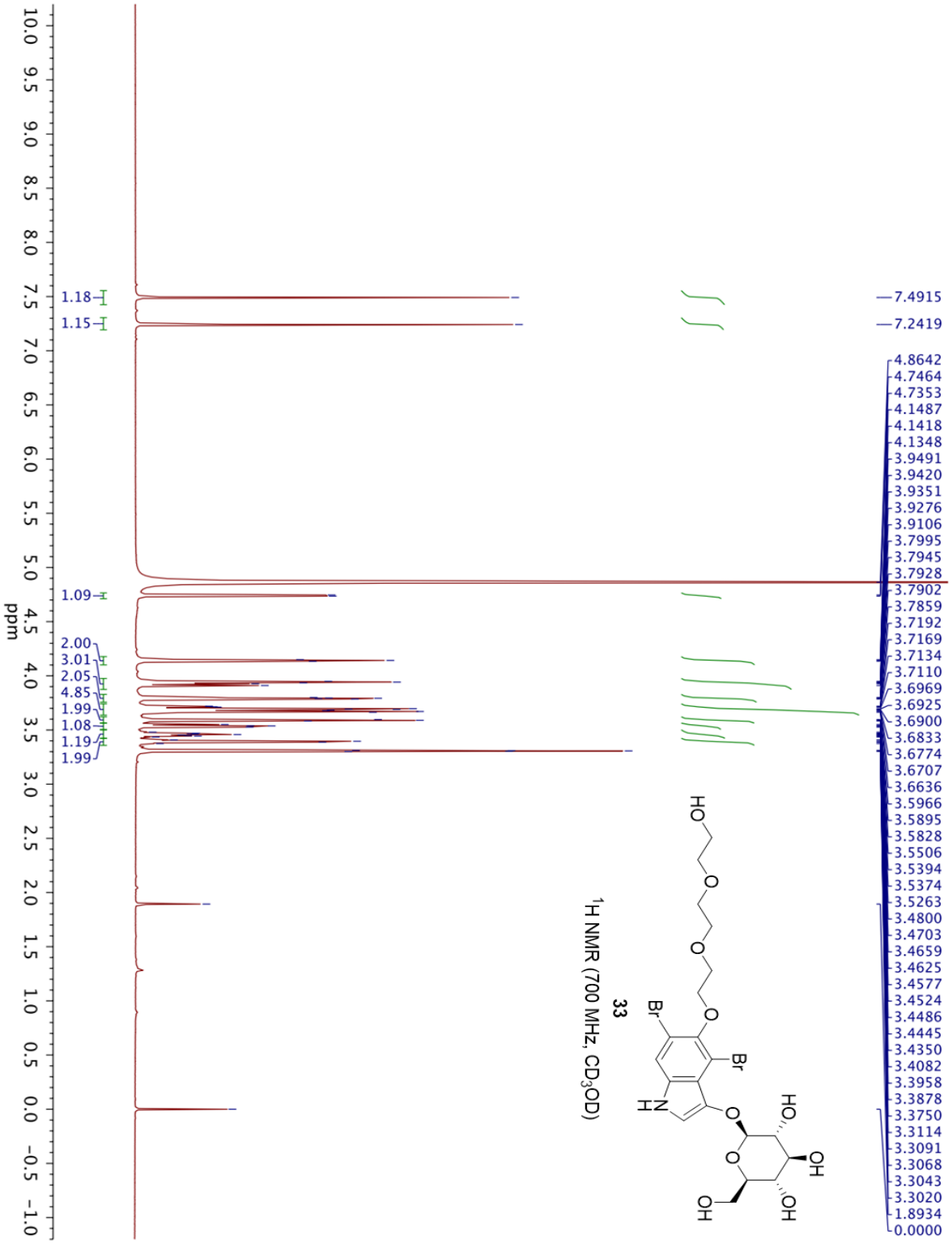

30
^{13}C NMR (175 MHz, CD$_3$OD)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
146.8823
138.9562
132.8218
119.9324
115.9659
115.1644
112.5278
107.8703
105.1515
99.6227
78.2684
78.0945
75.2765
72.7792
71.5431
62.6714
49.3682
49.2464
49.1249
49.0000
48.8833
48.7605
48.6386
30.6201
22.0063
21.6908
20.1435

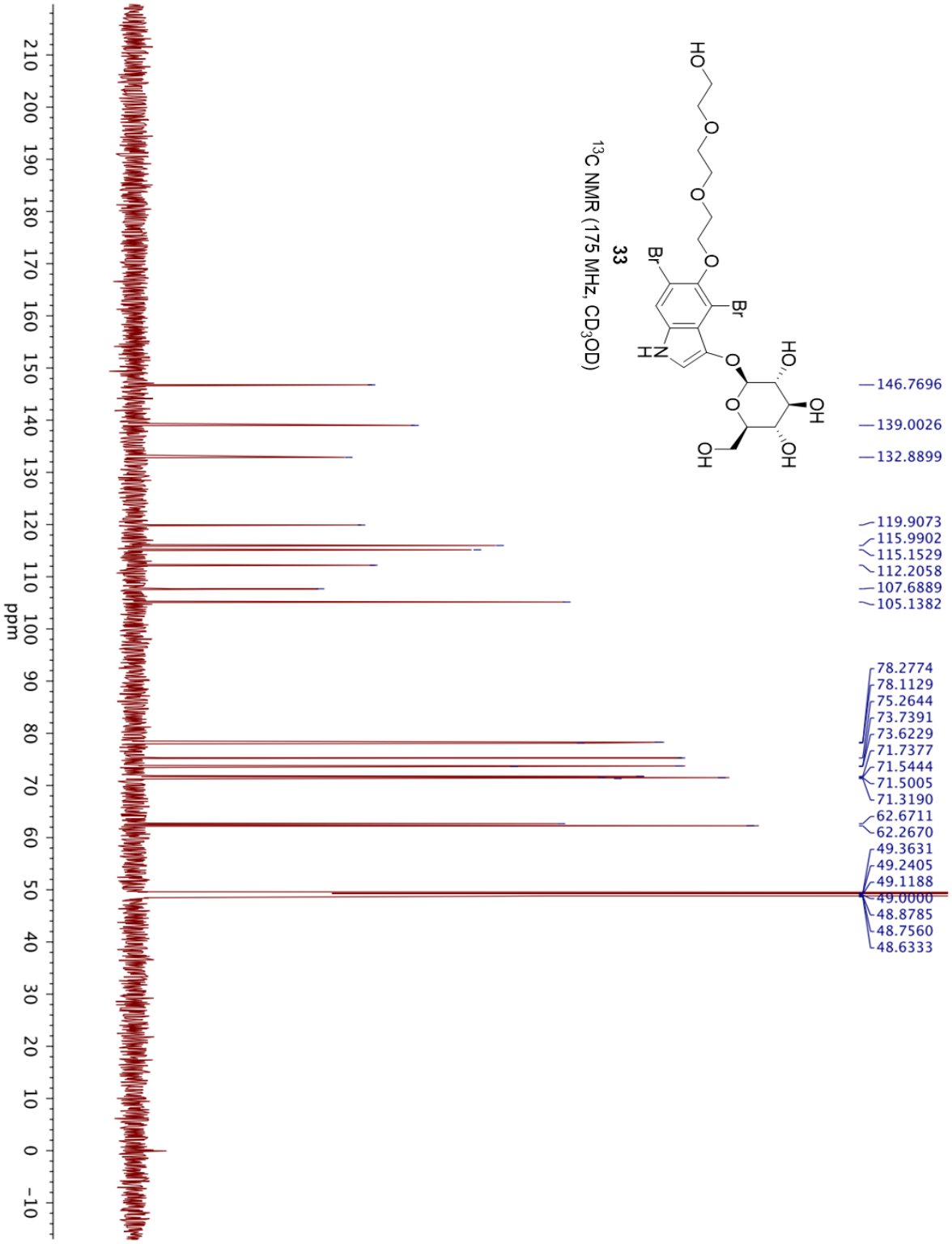

8.1781
8.1685
8.1586
8.1499
7.8284
7.8172
7.8098
7.8078
7.7963
7.7813
7.7786
7.7677
7.7607
7.7580
7.2696
4.4436
4.4347
4.4304
4.4212
3.8034
3.7964
3.7902
3.7828
3.7256
3.7177
3.7123
3.7041
3.6587
3.6502
3.6462
3.6382
3.6316
3.6286
3.6235
3.6159
3.6105
3.5922
3.5845
3.5788
3.5709
2.4111
2.2875
0.0000
0.93
1.90
0.91
2.00
2.06
2.19
1.94
2.18
1.97
0.55
ppm
10.0 9.5 9.0 8.5 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 1.5 1.0 0.5 0.0 -0.5 -1.0
HO
O
O
O
O
S
O
O
O2N
31
1H NMR (700 MHz, CDCl3)

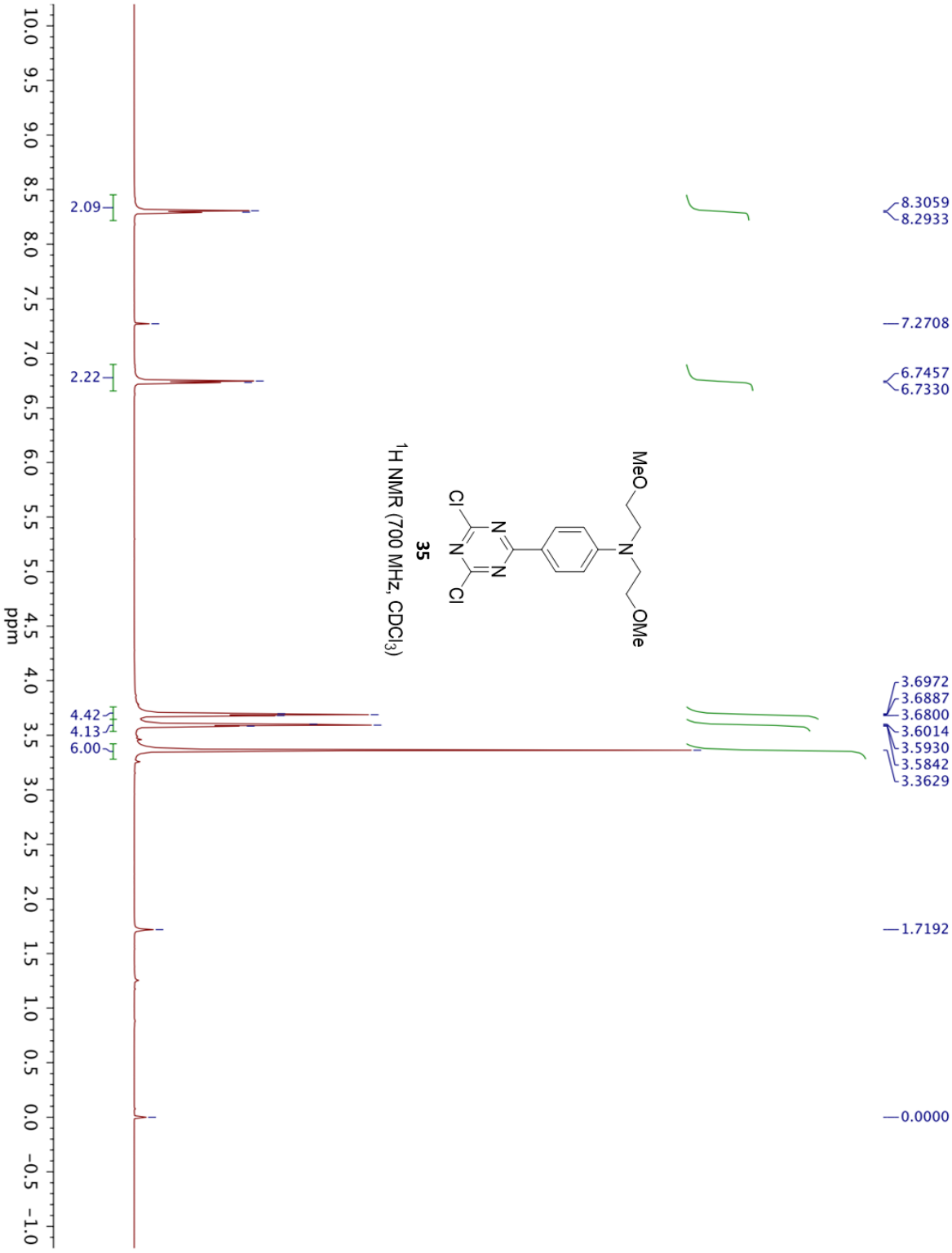

31
^{13}C NMR (175 MHz, CDCl$_3$)
HO
O
O
O
O
S
O
O
O_2N
148.4456
134.8951
132.4760
131.4594
129.8549
124.9560
77.3421
77.1600
76.9782
72.5264
71.2445
70.9057
70.3999
68.7458
61.8630
0.1149
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

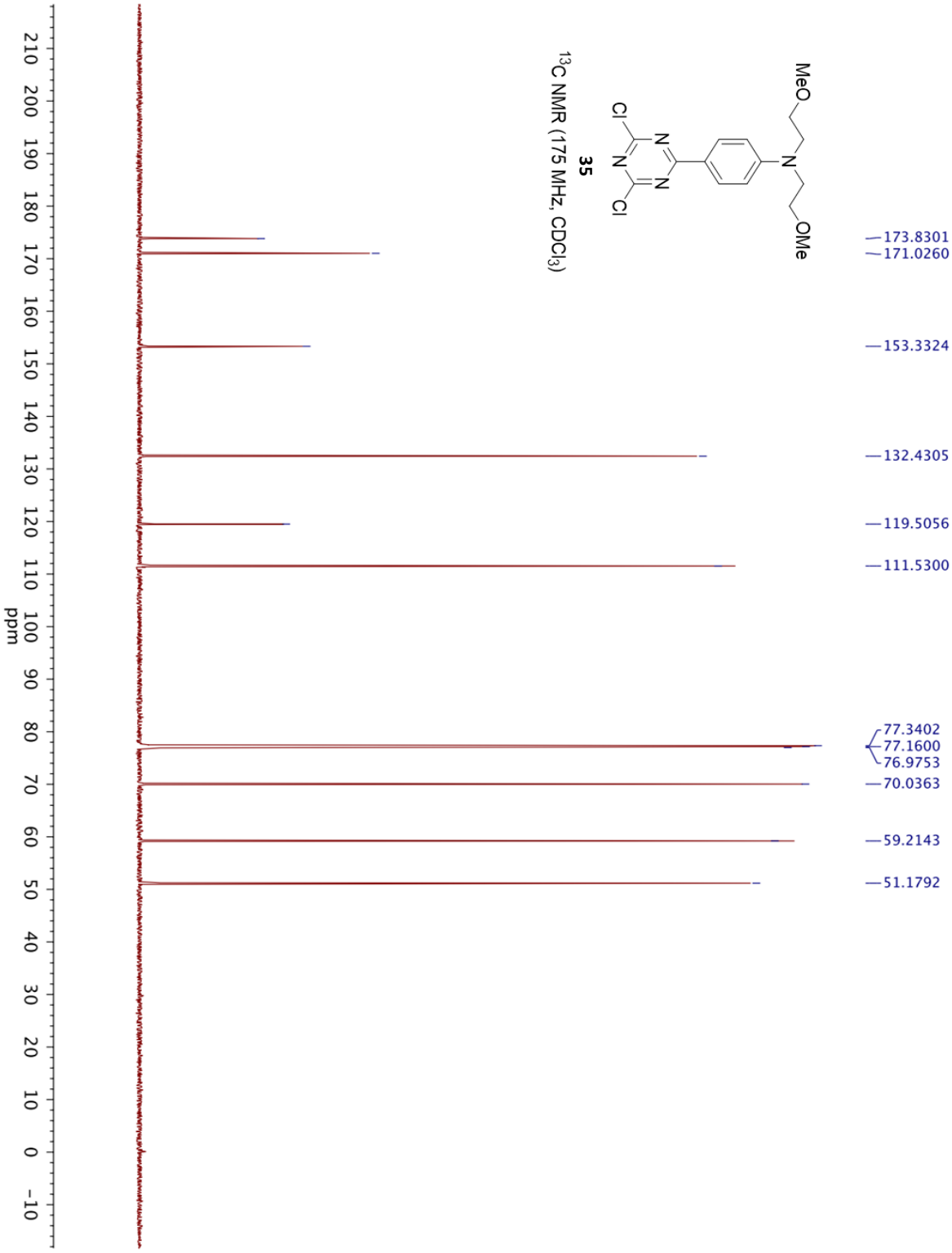

32
^{1}H NMR (700 MHz, CDCl$_3$)
ppm

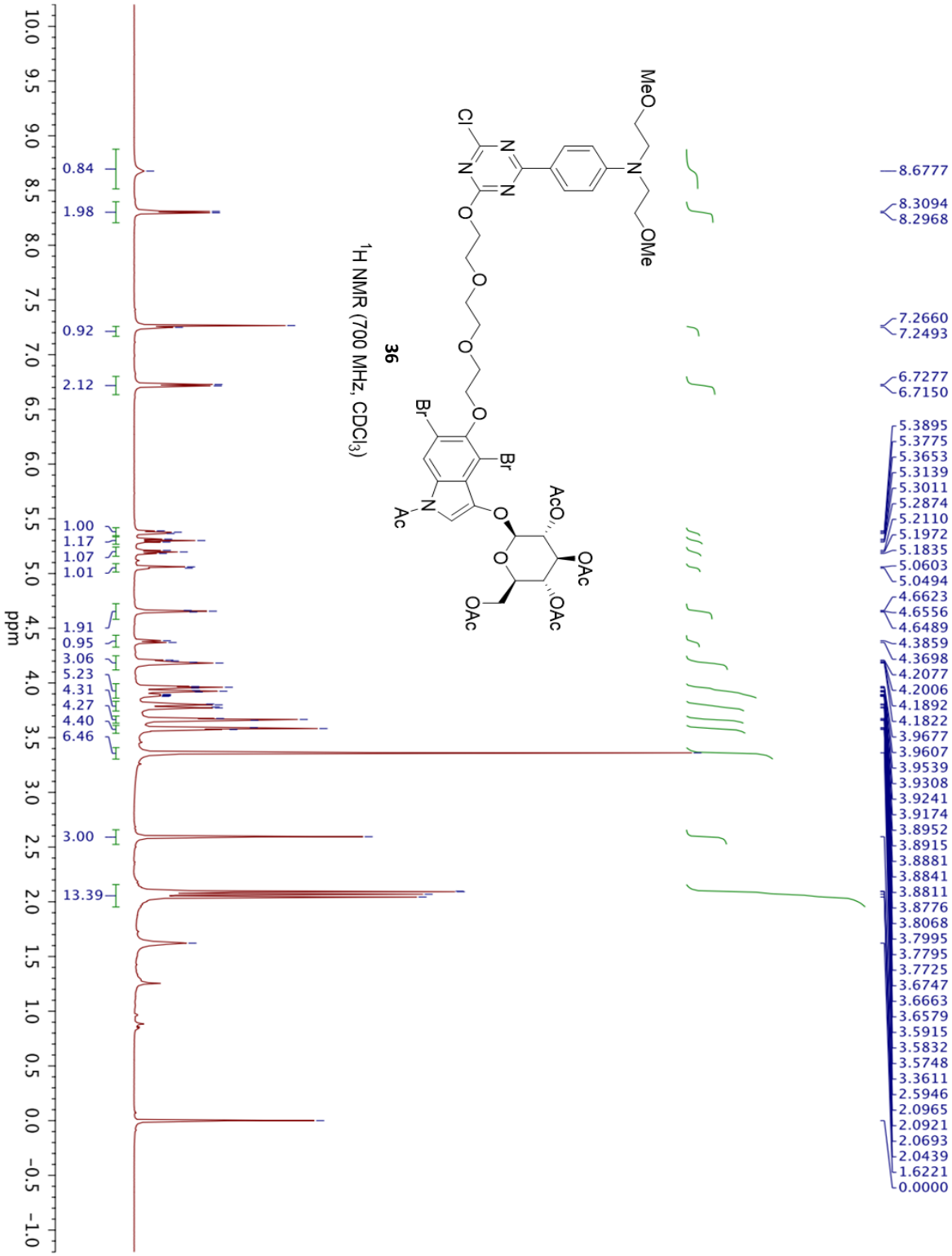

32
^{13}C NMR (175 MHz, CDCl$_3$)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
170.6072
170.3478
169.5303
169.4357
167.9645
149.7555
140.4784
131.0659
123.1542
120.3589
116.2826
112.1342
107.7156
100.2722
77.3407
77.1600
76.9787
72.7166
72.6364
70.9963
70.8811
70.6431
70.2824
68.3305
61.9877
61.9371
23.8606
21.0590
20.9074
20.7409
0.1211

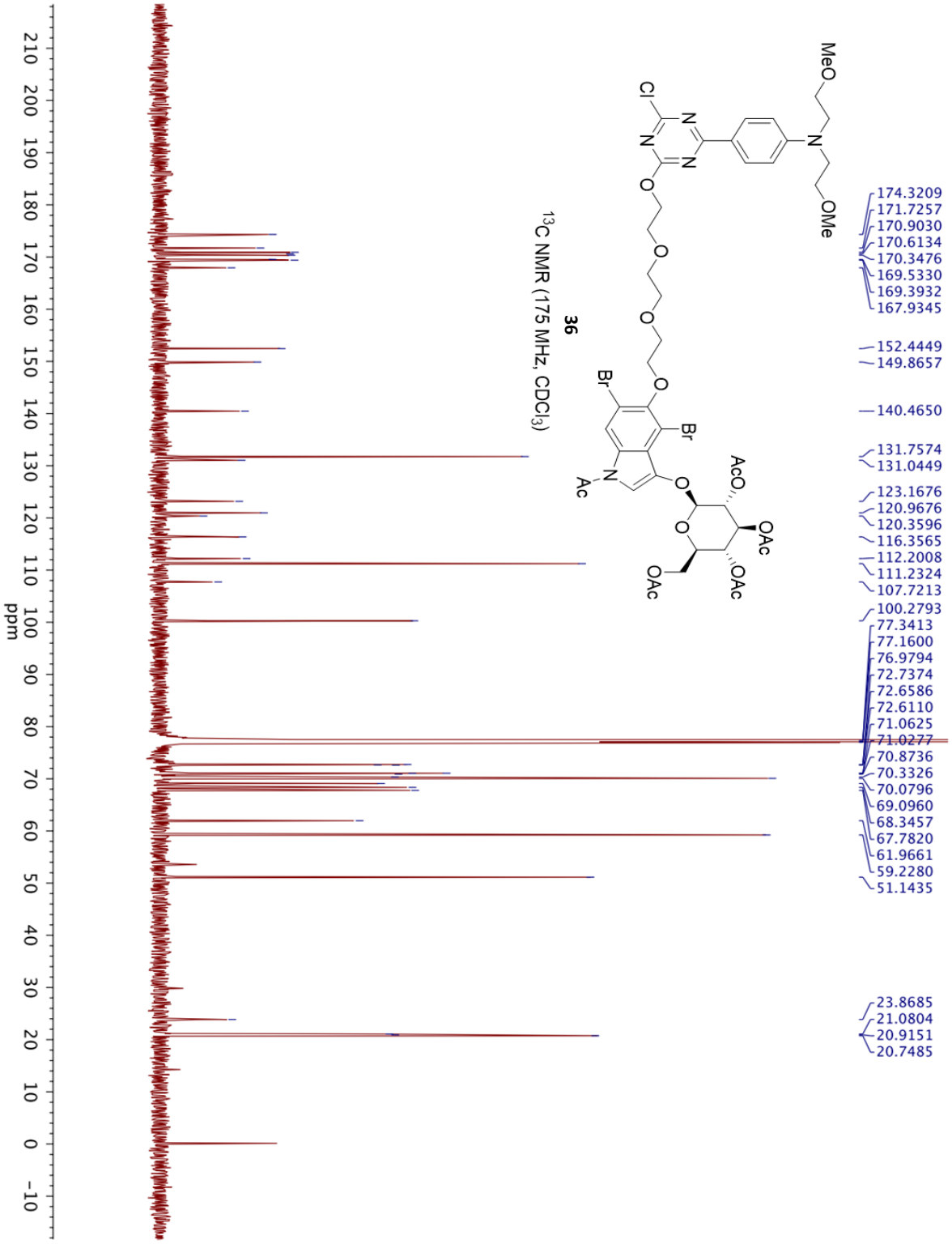

33
^{1}H NMR (700 MHz, CD_3OD)
ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
1.18
1.15
1.09
2.00
3.01
2.05
4.85
1.99
1.08
1.19
1.99
7.4915
7.2419
4.8642
4.7464
4.7353
4.1487
4.1418
4.1348
3.9491
3.9420
3.9351
3.9276
3.9106
3.7995
3.7945
3.7928
3.7902
3.7859
3.7192
3.7169
3.7134
3.7110
3.6969
3.6925
3.6900
3.6833
3.6774
3.6707
3.6636
3.5966
3.5895
3.5828
3.5506
3.5394
3.5374
3.5263
3.4800
3.4703
3.4659
3.4625
3.4577
3.4524
3.4486
3.4445
3.4350
3.4082
3.3958
3.3878
3.3750
3.3114
3.3091
3.3068
3.3043
3.3020
1.8934
0.0000
HO
O
O
O
Br
Br
N
H
O
HO
OH
O
OH
OH

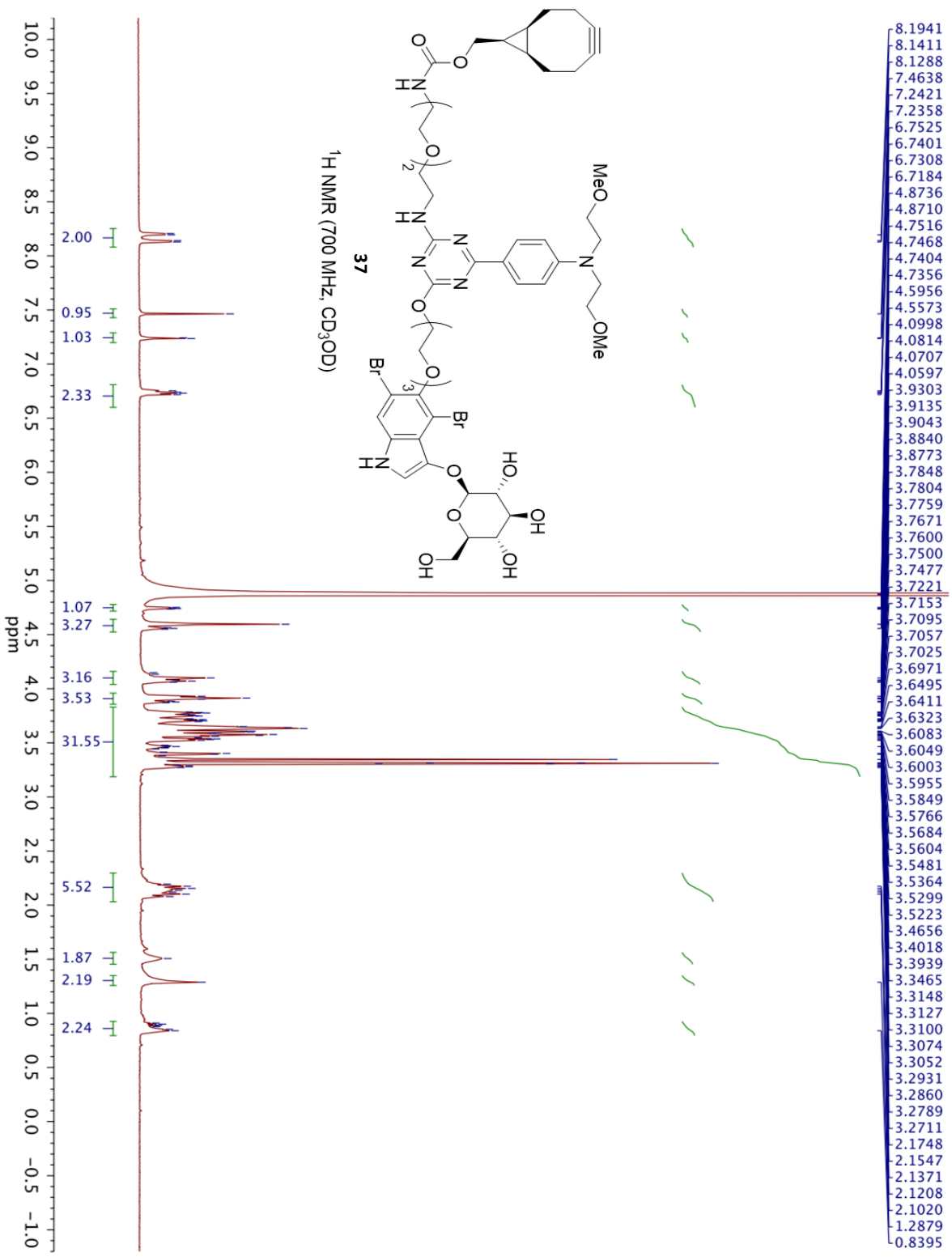

33
^{13}C NMR (175 MHz, CD_3OD)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
146.7696
139.0026
132.8899
119.9073
115.9902
115.1529
112.2058
107.6889
105.1382
78.2774
78.1129
75.2644
73.7391
73.6229
71.7377
71.5444
71.5005
71.3190
62.6711
62.2670
49.3631
49.2405
49.1188
49.0000
48.8785
48.7560
48.6333

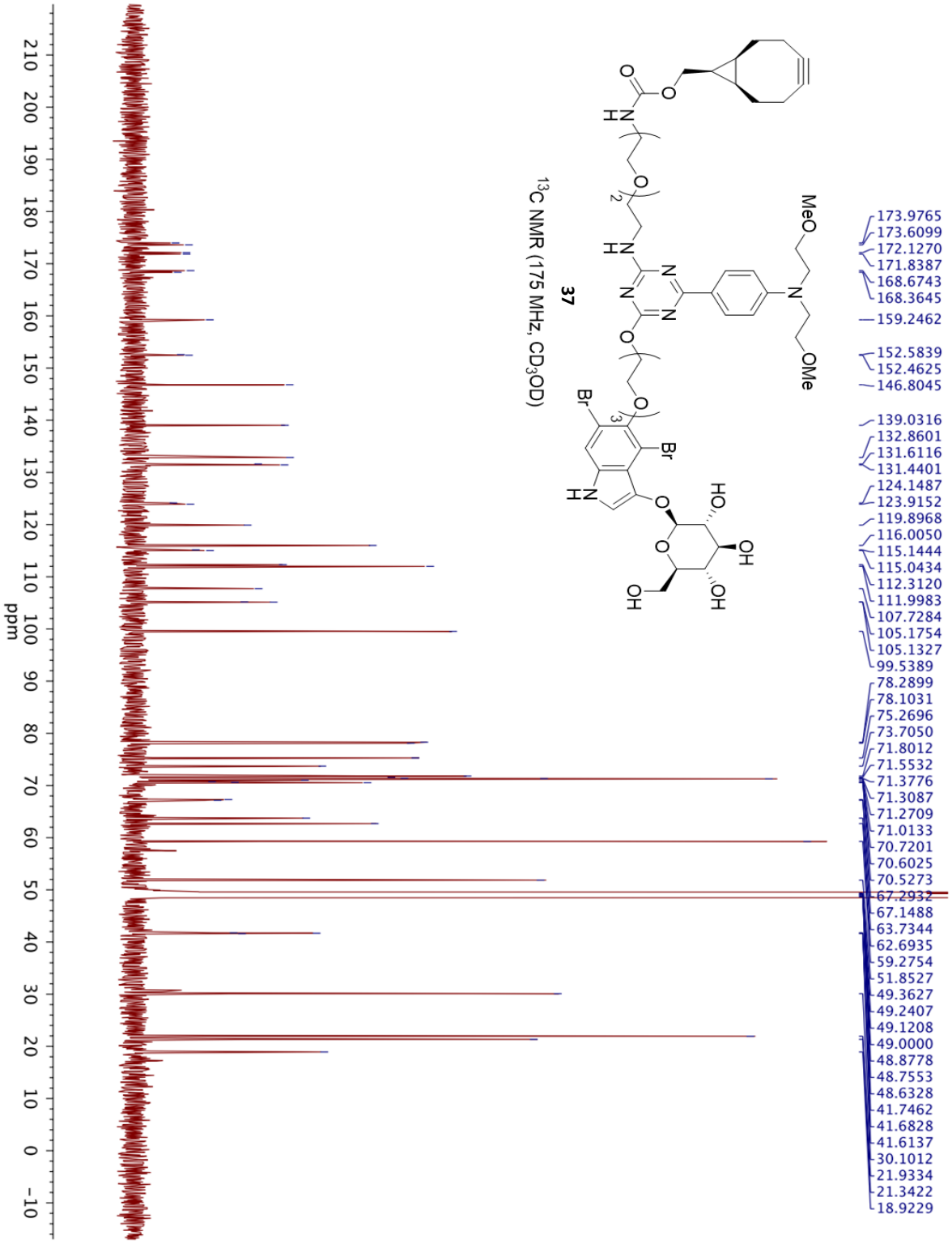

35
^{1}H NMR (700 MHz, CDCl$_3$)
MeO
OMe
Cl
Cl
N
N
N
N
ppm
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
2.09
2.22
4.42
4.13
6.00
8.3059
8.2933
7.2708
6.7457
6.7330
3.6972
3.6887
3.6800
3.6014
3.5930
3.5842
3.3629
1.7192
0.0000

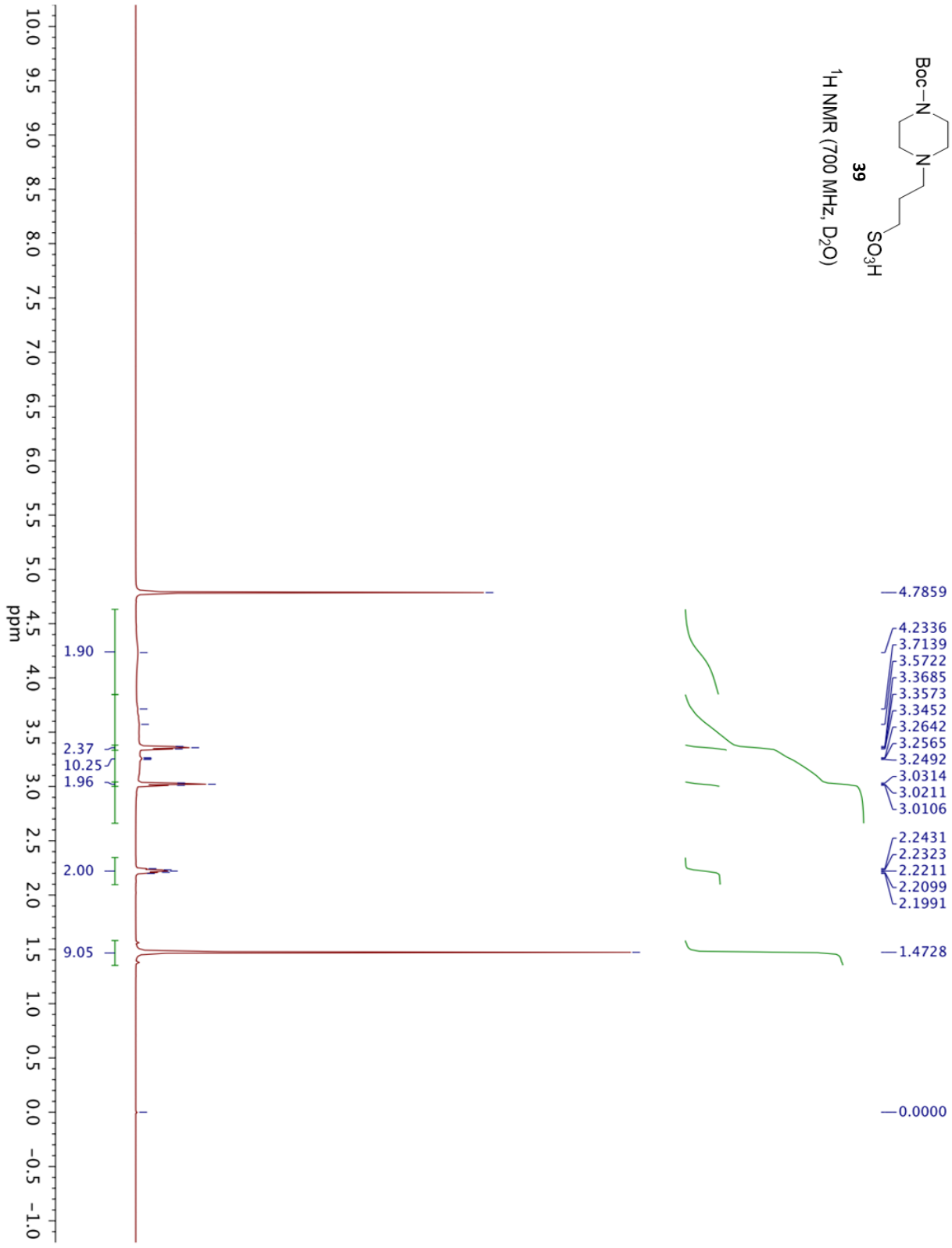

35
^{13}C NMR (175 MHz, CDCl$_3$)
MeO
OMe
Cl
Cl
N
N
N
N
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
173.8301
171.0260
153.3324
132.4305
119.5056
111.5300
77.3402
77.1600
76.9753
70.0363
59.2143
51.1792

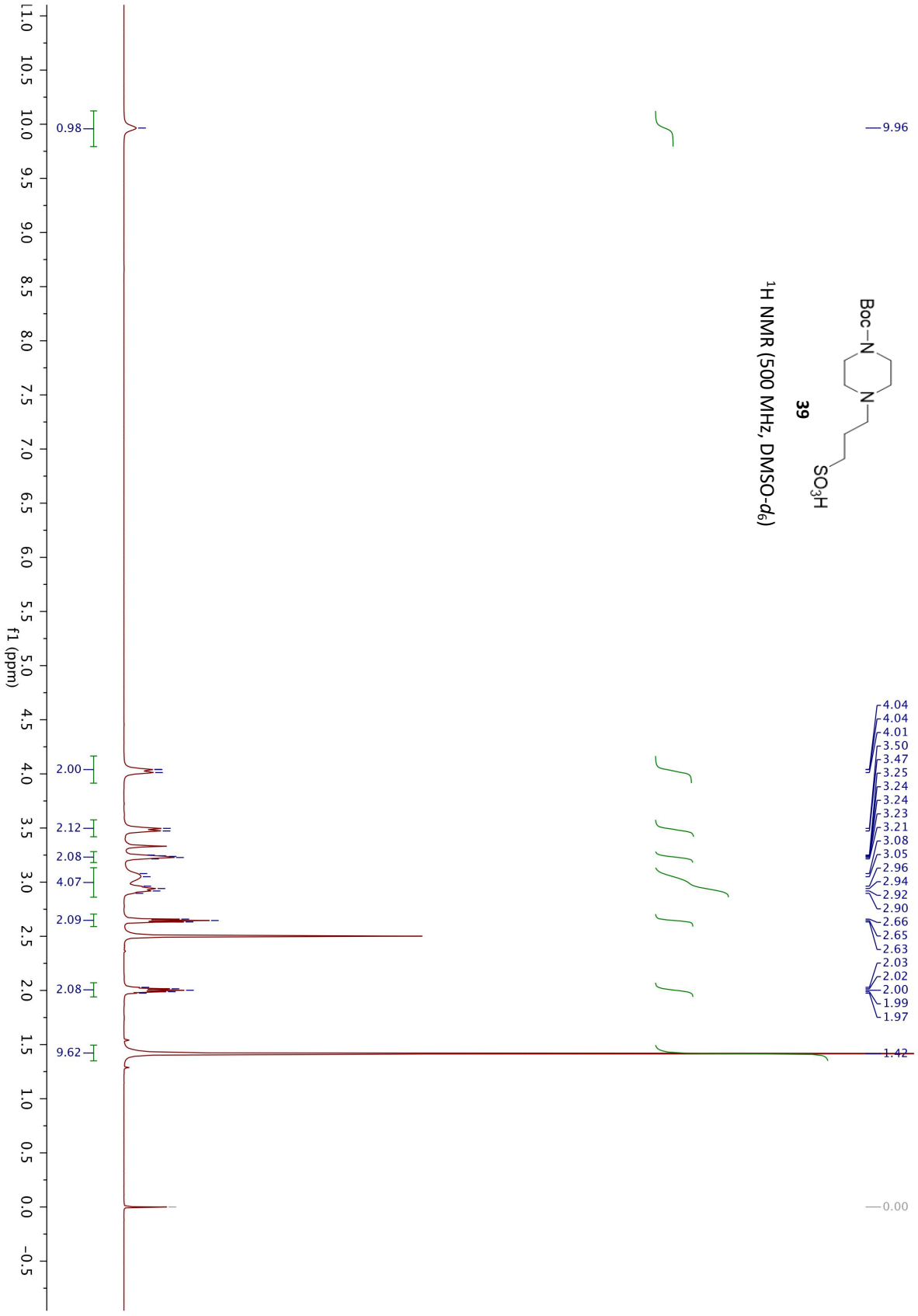

36
^{1}H NMR (700 MHz, CDCl$_3$)
ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
0.84
1.98
0.92
2.12
1.00
1.17
1.07
1.01
1.91
0.95
3.06
5.23
4.31
4.27
4.40
6.46
3.00
13.39
8.6777
8.3094
8.2968
7.2660
7.2493
6.7277
6.7150
5.3895
5.3775
5.3653
5.3139
5.3011
5.2874
5.2110
5.1972
5.1835
5.0603
5.0494
4.6623
4.6556
4.6489
4.3859
4.3698
4.2077
4.2006
4.1892
4.1822
3.9677
3.9607
3.9539
3.9308
3.9241
3.9174
3.8952
3.8915
3.8881
3.8841
3.8811
3.8776
3.8068
3.7995
3.7795
3.7725
3.6747
3.6663
3.6579
3.5915
3.5832
3.5748
3.3611
2.5946
2.0965
2.0921
2.0693
2.0439
1.6221
0.0000

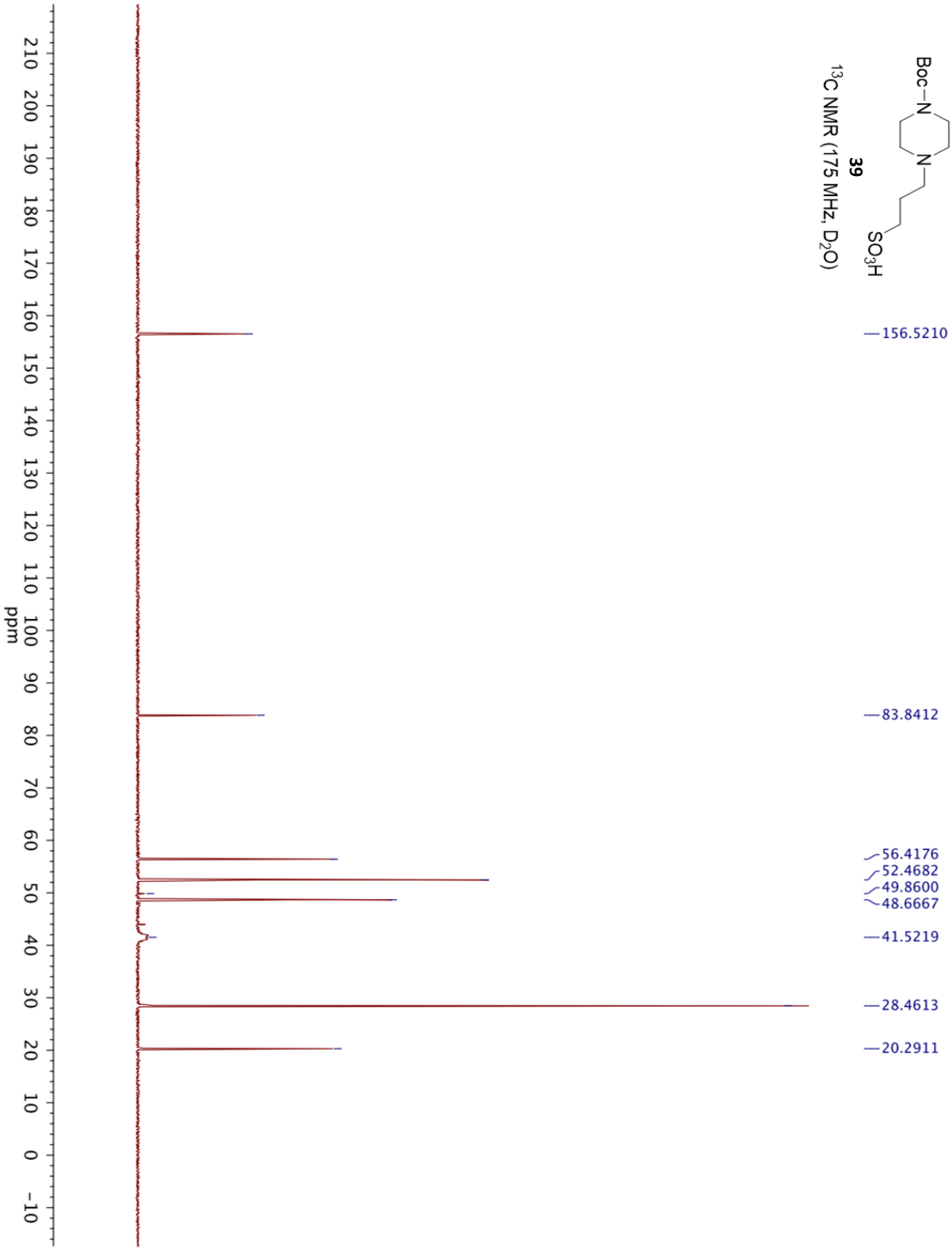

36
^{13}C NMR (175 MHz, CDCl$_3$)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
174.3209
171.7257
170.9030
170.6134
170.3476
169.5330
169.3932
167.9345
152.4449
149.8657
140.4650
131.7574
131.0449
123.1676
120.9676
120.3596
116.3565
112.2008
111.2324
107.7213
100.2793
77.3413
77.1600
76.9794
72.7374
72.6586
72.6110
71.0625
71.0277
70.8736
70.3326
70.0796
69.0960
68.3457
67.7820
61.9661
59.2280
51.1435
23.8685
21.0804
20.9151
20.7485

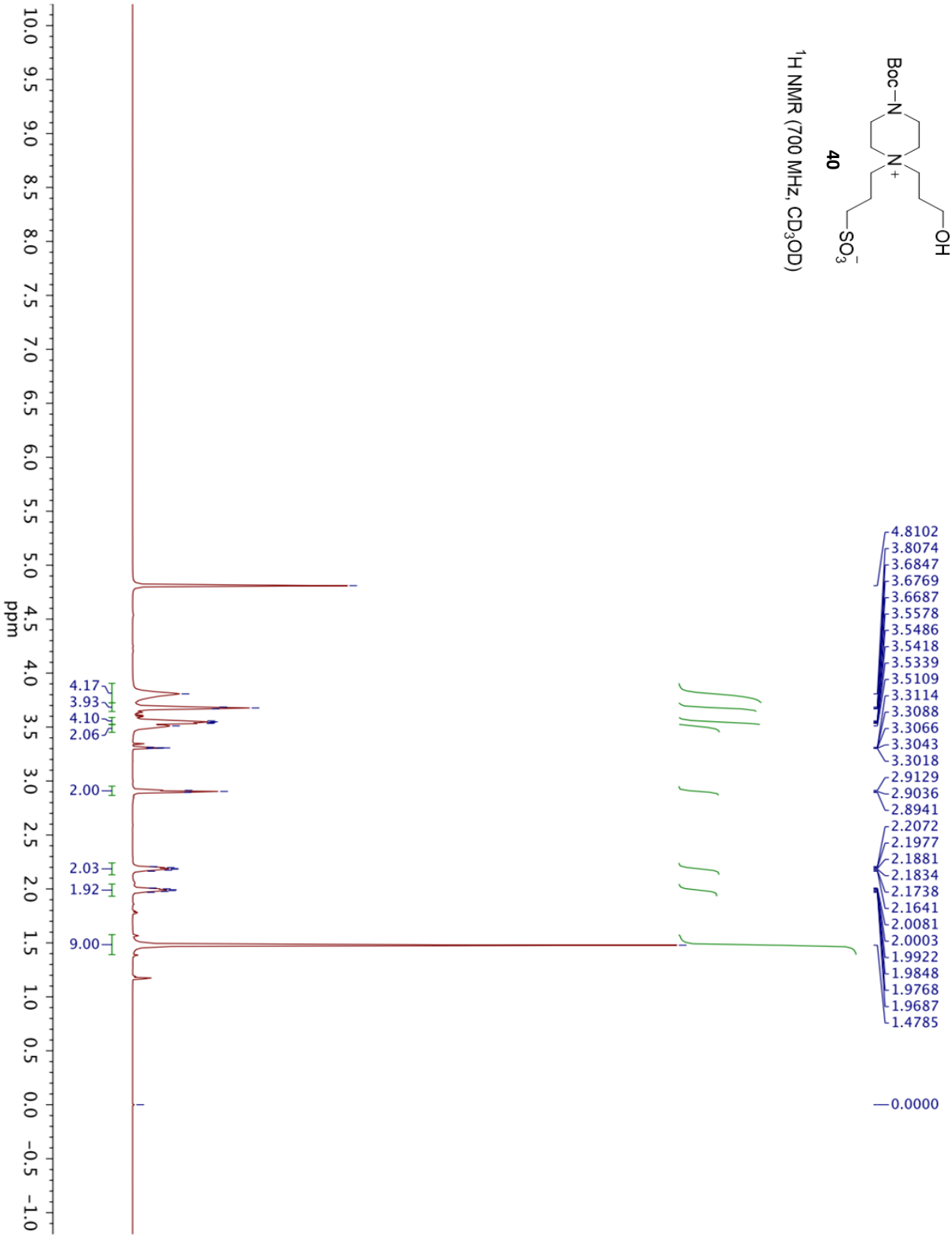

37
^{1}H NMR (700 MHz, CD$_3$OD)
ppm
2.00
0.95
1.03
2.33
1.07
3.27
3.16
3.53
31.55
5.52
1.87
2.19
2.24
MeO
OMe
Br
Br
HO
OH
OH
OH
8.1941
8.1411
8.1288
7.4638
7.2421
7.2358
6.7525
6.7401
6.7308
6.7184
4.8736
4.8710
4.7516
4.7468
4.7404
4.7356
4.5956
4.5573
4.0998
4.0814
4.0707
4.0597
3.9303
3.9135
3.9043
3.8840
3.8773
3.7848
3.7804
3.7759
3.7671
3.7600
3.7500
3.7477
3.7221
3.7153
3.7095
3.7057
3.7025
3.6971
3.6495
3.6411
3.6323
3.6083
3.6049
3.6003
3.5955
3.5849
3.5766
3.5684
3.5604
3.5481
3.5364
3.5299
3.5223
3.4656
3.4018
3.3939
3.3465
3.3148
3.3127
3.3100
3.3074
3.3052
3.2931
3.2860
3.2789
3.2711
2.1748
2.1547
2.1371
2.1208
2.1020
1.2879
0.8395

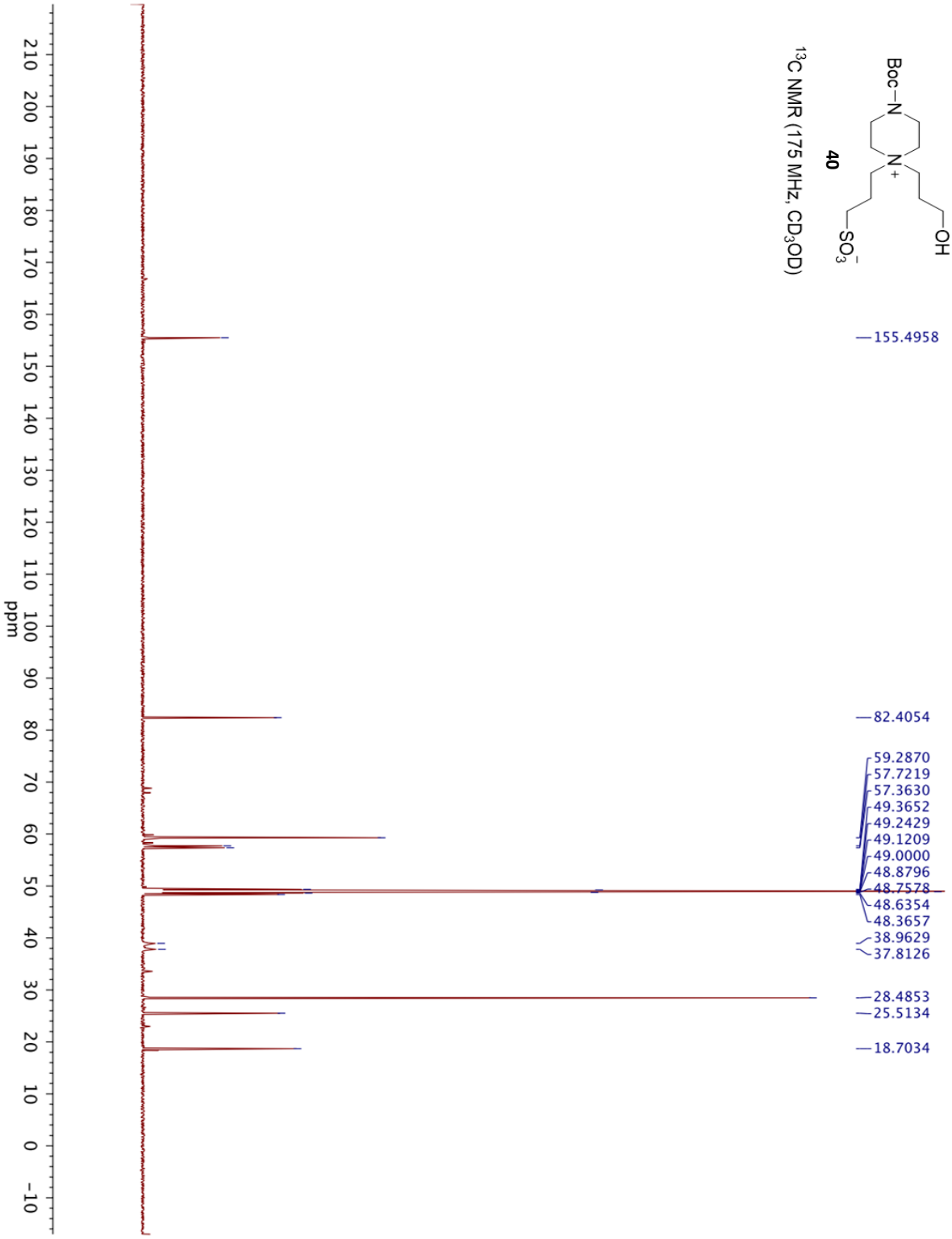

37
^{13}C NMR (175 MHz, CD_3OD)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
MeO
OMe
Br
Br
HO
OH
OH
OH
173.9765
173.6099
172.1270
171.8387
168.6743
168.3645
159.2462
152.5839
152.4625
146.8045
139.0316
132.8601
131.6116
131.4401
124.1487
123.9152
119.8968
116.0050
115.1444
115.0434
112.3120
111.9983
107.7284
105.1754
105.1327
99.5389
78.2899
78.1031
75.2696
73.7050
71.8012
71.5532
71.3776
71.3087
71.2709
71.0133
70.7201
70.6025
70.5273
67.2932
67.1488
63.7344
62.6935
59.2754
51.8527
49.3627
49.2407
49.1208
49.0000
48.8778
48.7553
48.6328
41.7462
41.6828
41.6137
30.1012
21.9334
21.3422
18.9229

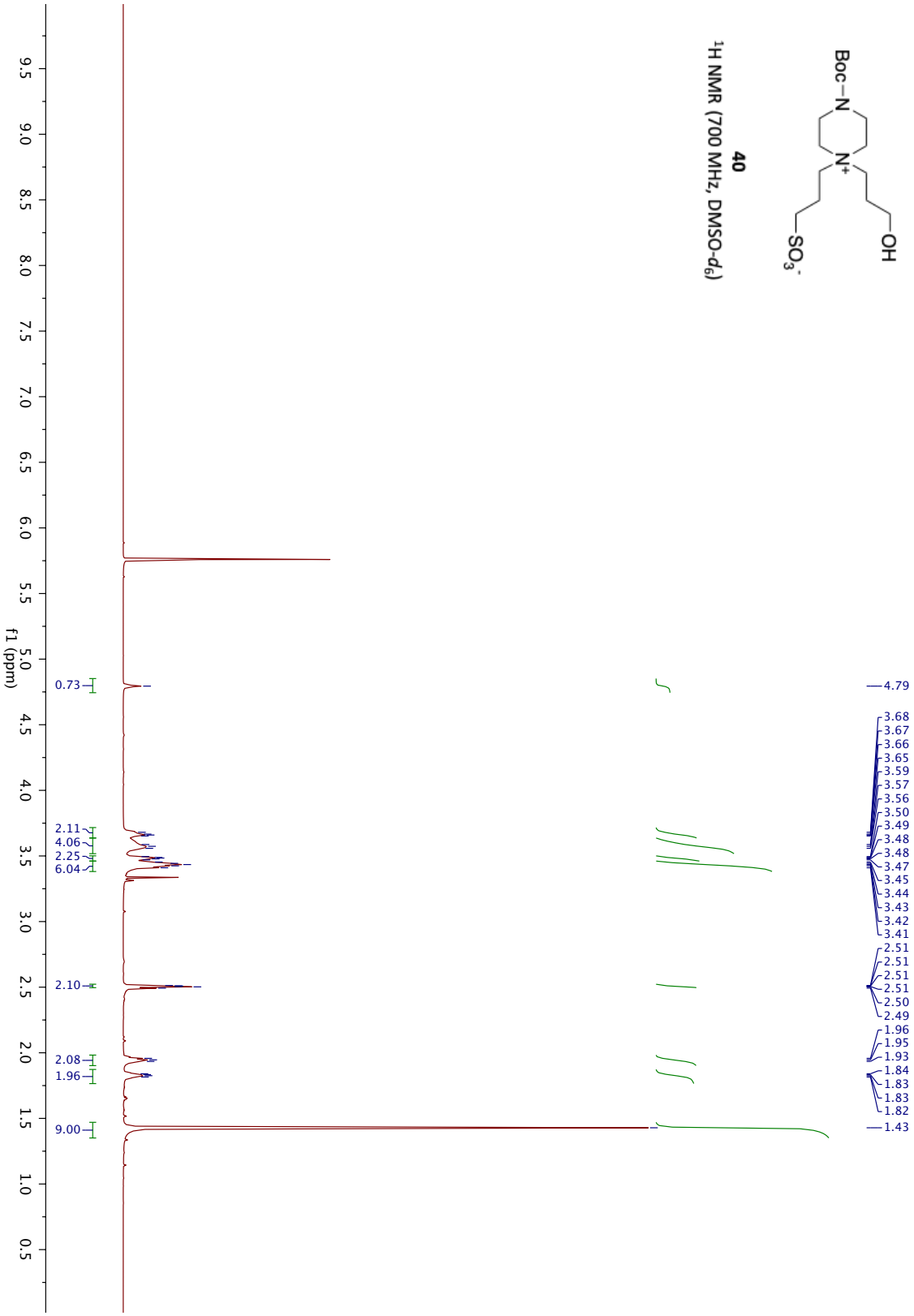

Boc–N
N
SO3H
39
1H NMR (700 MHz, D2O)
ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
1.90
2.37
10.25
1.96
2.00
9.05
4.7859
4.2336
3.7139
3.5722
3.3685
3.3573
3.3452
3.2642
3.2565
3.2492
3.0314
3.0211
3.0106
2.2431
2.2323
2.2211
2.2099
2.1991
1.4728
0.0000

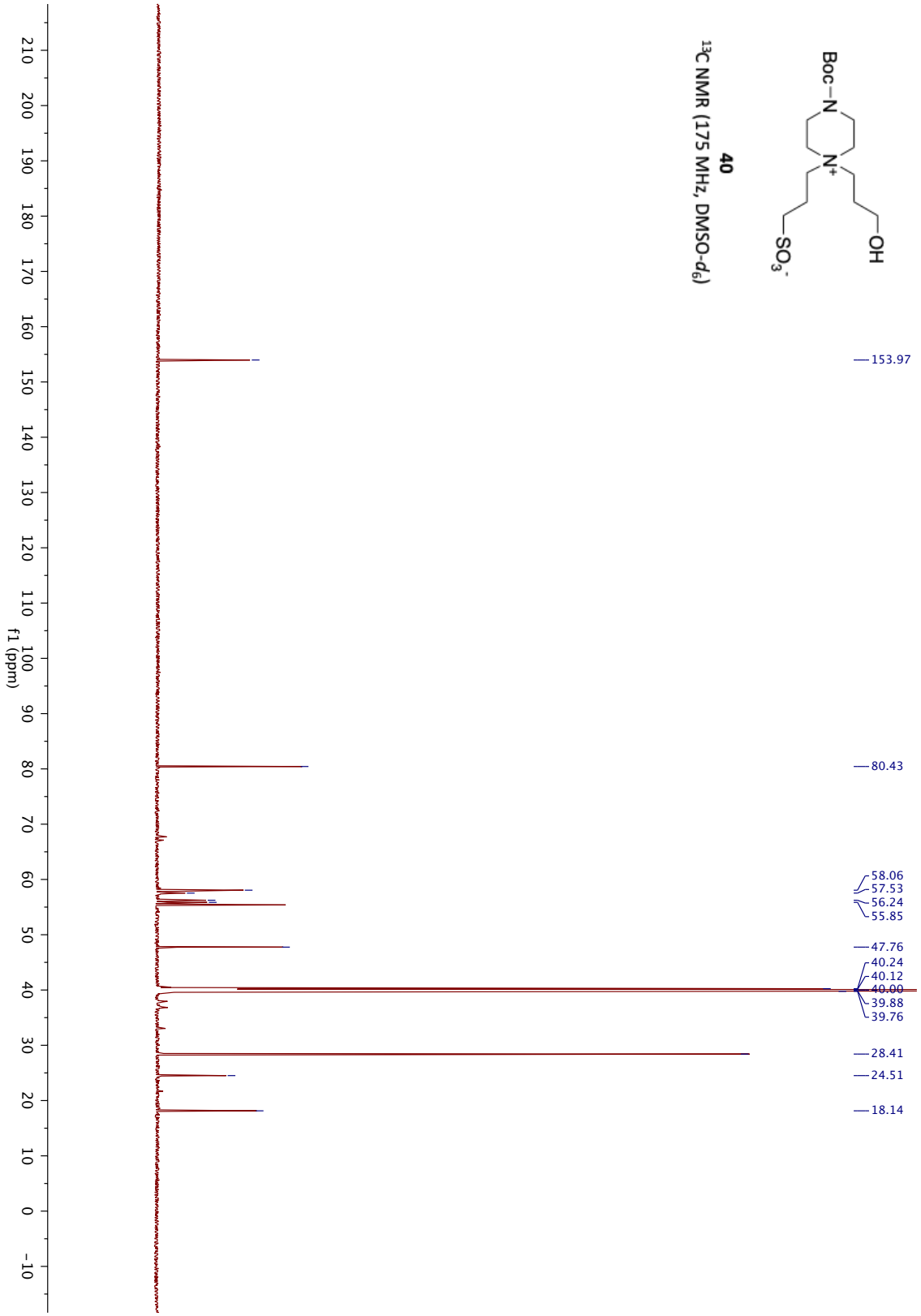

Boc—N
N
SO3H
39
1H NMR (500 MHz, DMSO-d6)
f1 (ppm)
0.98
2.00
2.12
2.08
4.07
2.09
2.08
9.62
9.96
4.04
4.04
4.01
3.50
3.47
3.25
3.24
3.24
3.23
3.21
3.08
3.05
2.96
2.94
2.92
2.90
2.66
2.65
2.63
2.03
2.02
2.00
1.99
1.97
1.42
0.00

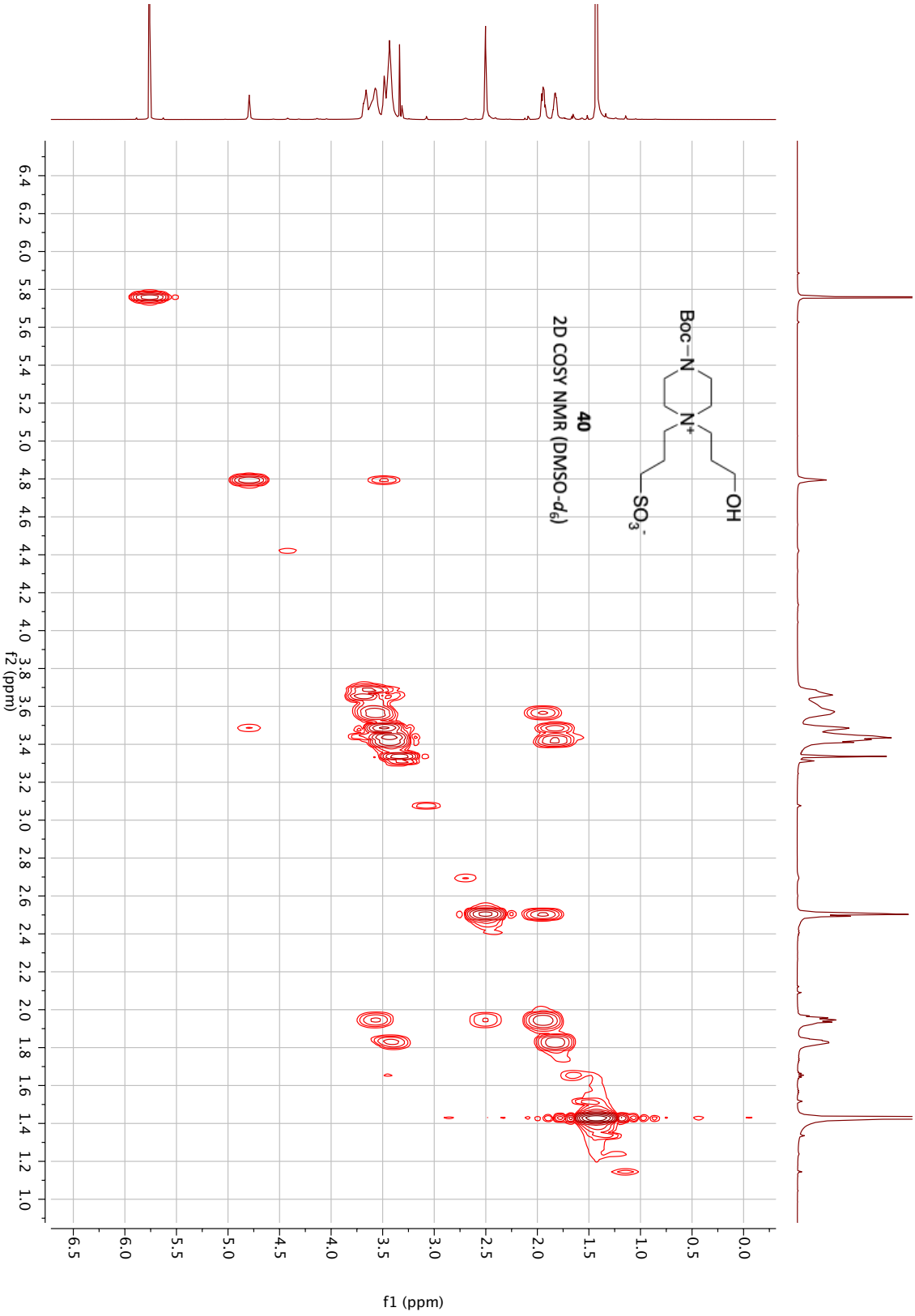

Boc–N
N
SO3H
39
13C NMR (175 MHz, D2O)
156.5210
83.8412
56.4176
52.4682
49.8600
48.6667
41.5219
28.4613
20.2911
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

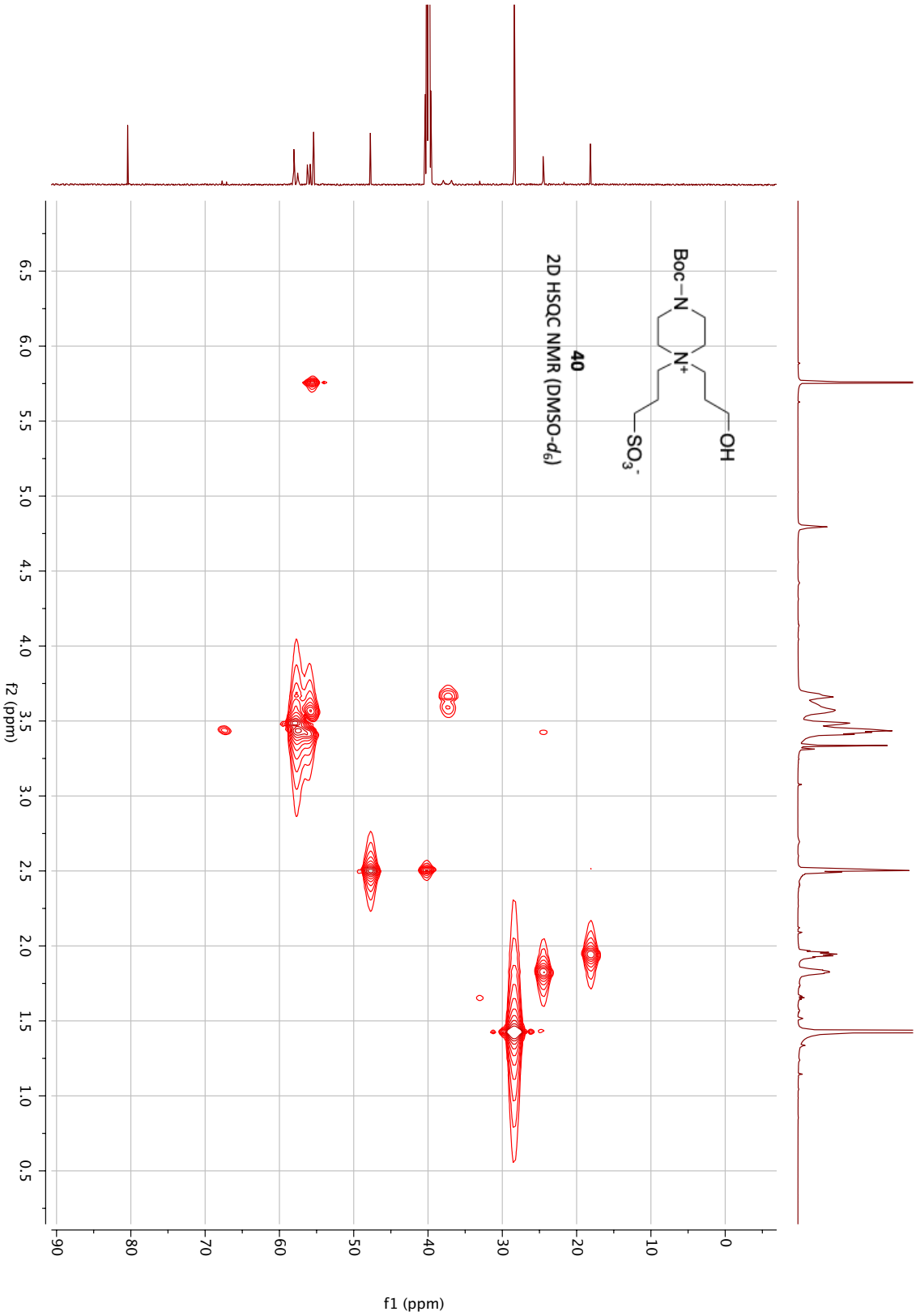

Boc—N
N+
SO3−
OH
40
1H NMR (700 MHz, CD3OD)
ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
4.17
3.93
4.10
2.06
2.00
2.03
1.92
9.00
4.8102
3.8074
3.6847
3.6769
3.6687
3.5578
3.5486
3.5418
3.5339
3.5109
3.3114
3.3088
3.3066
3.3043
3.3018
2.9129
2.9036
2.8941
2.2072
2.1977
2.1881
2.1834
2.1738
2.1641
2.0081
2.0003
1.9922
1.9848
1.9768
1.9687
1.4785
0.0000

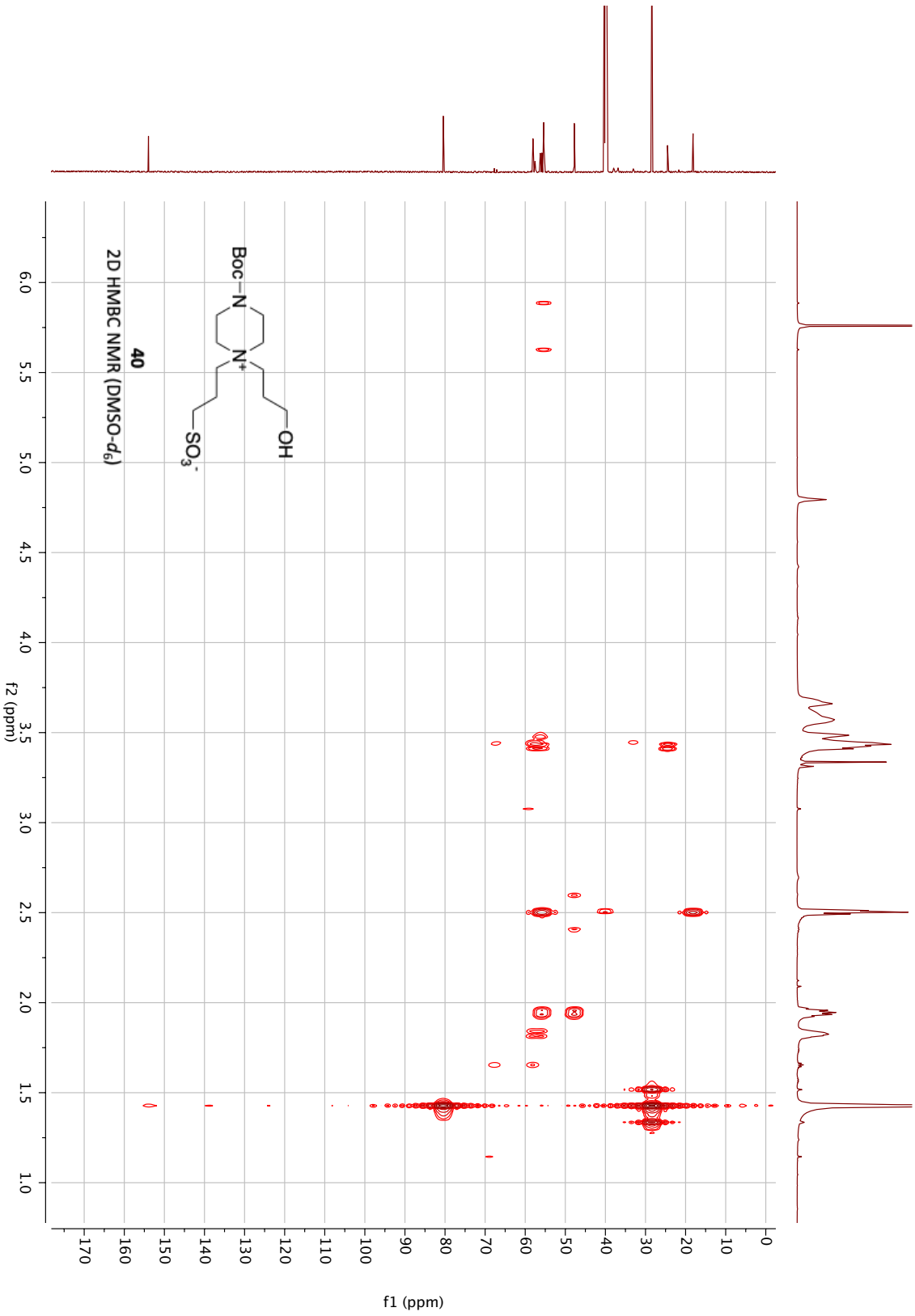

^{13}C NMR (175 MHz, CD_3OD)
40
Boc–N
N+
SO3−
OH
155.4958
82.4054
59.2870
57.7219
57.3630
49.3652
49.2429
49.1209
49.0000
48.8796
48.7578
48.6354
48.3657
38.9629
37.8126
28.4853
25.5134
18.7034
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

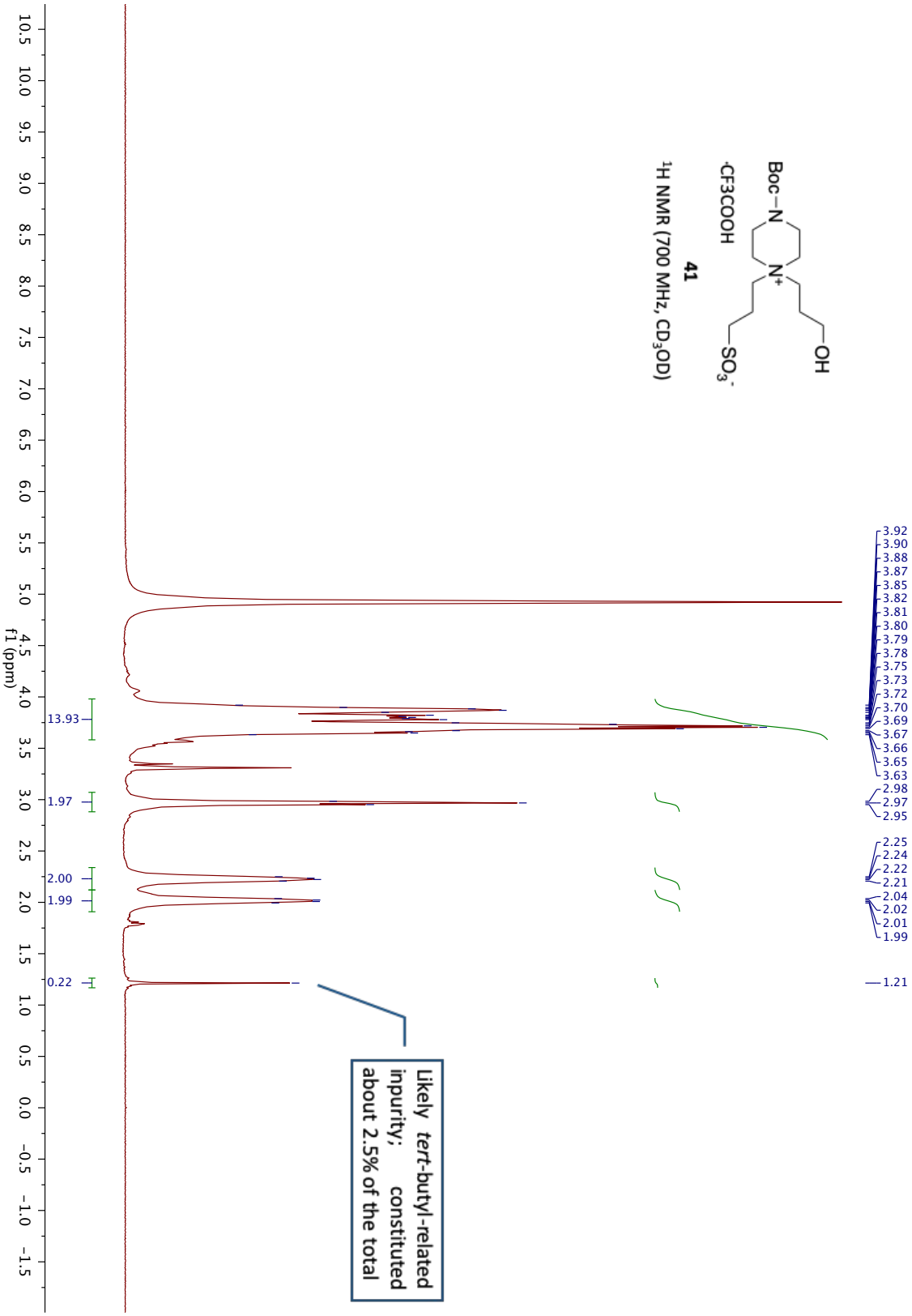

40
^{1}H NMR (700 MHz, DMSO-d_6)
Boc
N
N+
SO3-
OH
f1 (ppm)
0.73
2.11
4.06
2.25
6.04
2.10
2.08
1.96
9.00
4.79
3.68
3.67
3.66
3.65
3.59
3.57
3.56
3.50
3.49
3.48
3.48
3.47
3.45
3.44
3.43
3.42
3.41
2.51
2.51
2.51
2.51
2.50
2.49
1.96
1.95
1.93
1.84
1.83
1.83
1.82
1.43

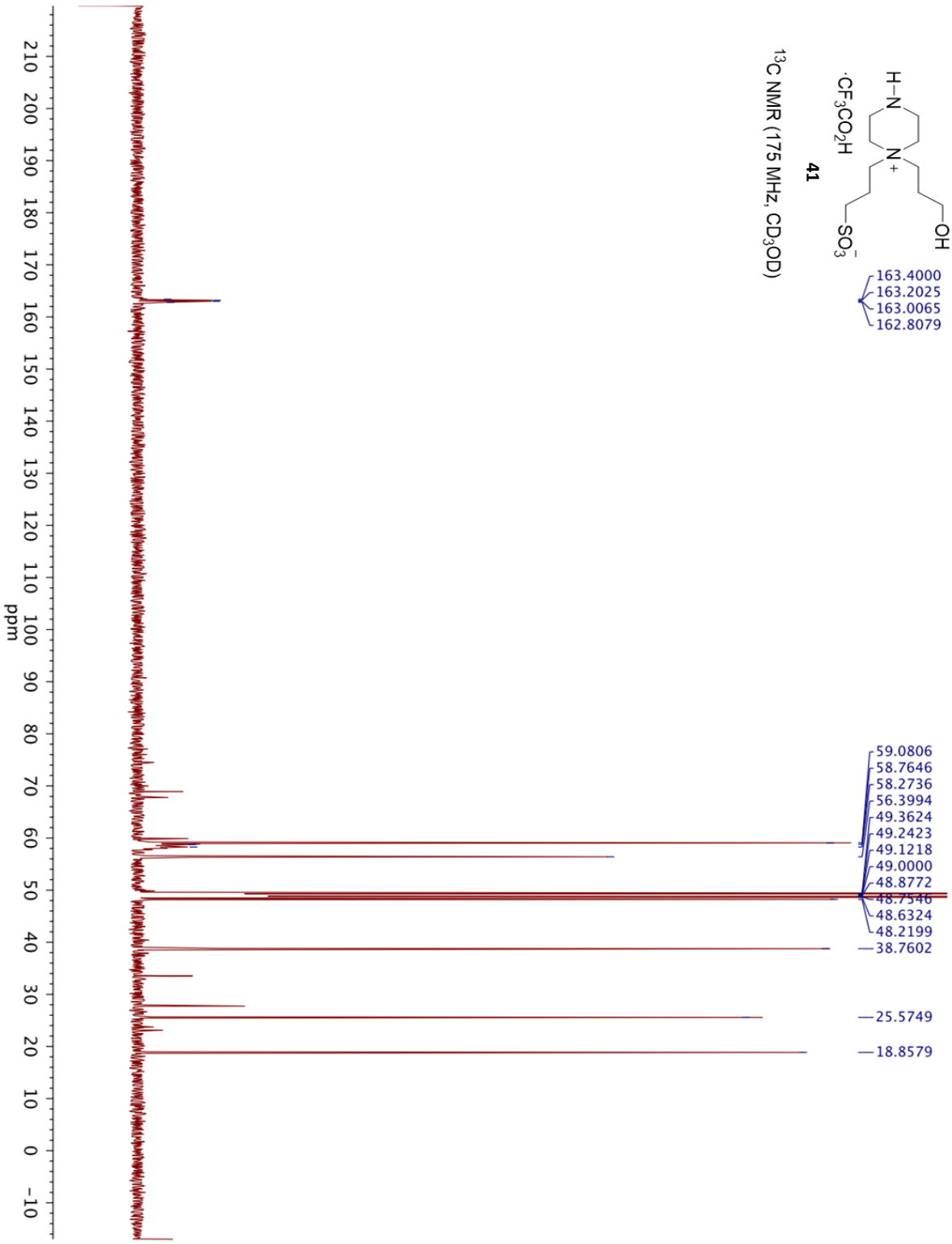

40
^{13}C NMR (175 MHz, DMSO-d_6)
Boc
N
N+
SO3-
OH
153.97
80.43
58.06
57.53
56.24
55.85
47.76
40.24
40.12
40.00
39.88
39.76
28.41
24.51
18.14
f1 (ppm)

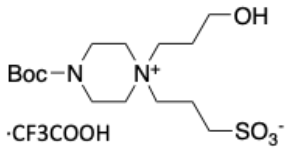

40
2D COSY NMR (DMSO-d_6)
Boc–N
N+
OH
SO_3^-
f2 (ppm)
f1 (ppm)


40
2D HSQC NMR (DMSO-d_6)
Boc–N
N+
SO3-
OH
f1 (ppm)
f2 (ppm)


40
2D HMBC NMR (DMSO-d_6)
Boc—N
N+
OH
SO3-
f2 (ppm)
f1 (ppm)

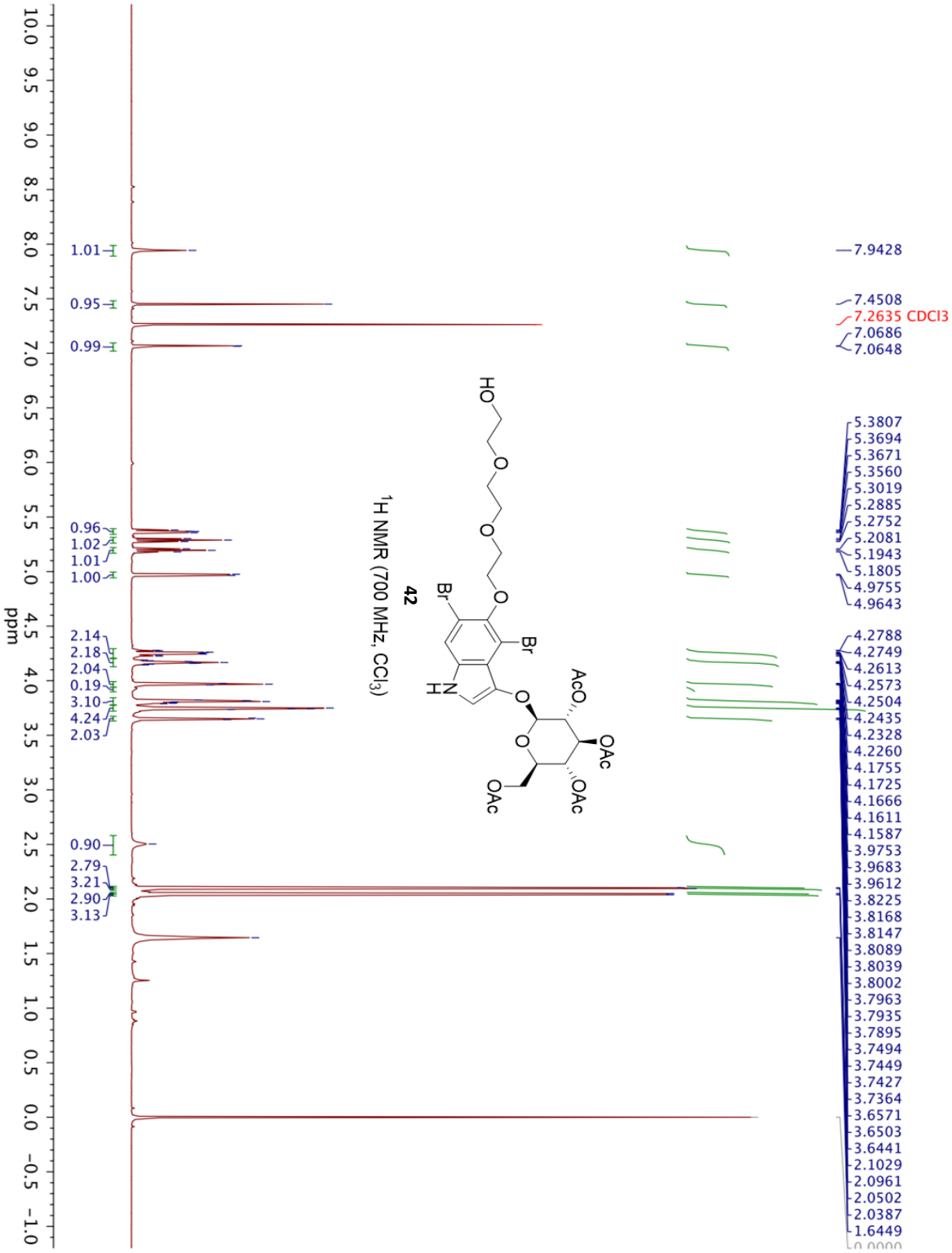

41
^{1}H NMR (700 MHz, CD_3OD)
Likely *tert*-butyl-related inpurity; constituted about 2.5% of the total
f1 (ppm)
13.93
1.97
2.00
1.99
0.22
1.21

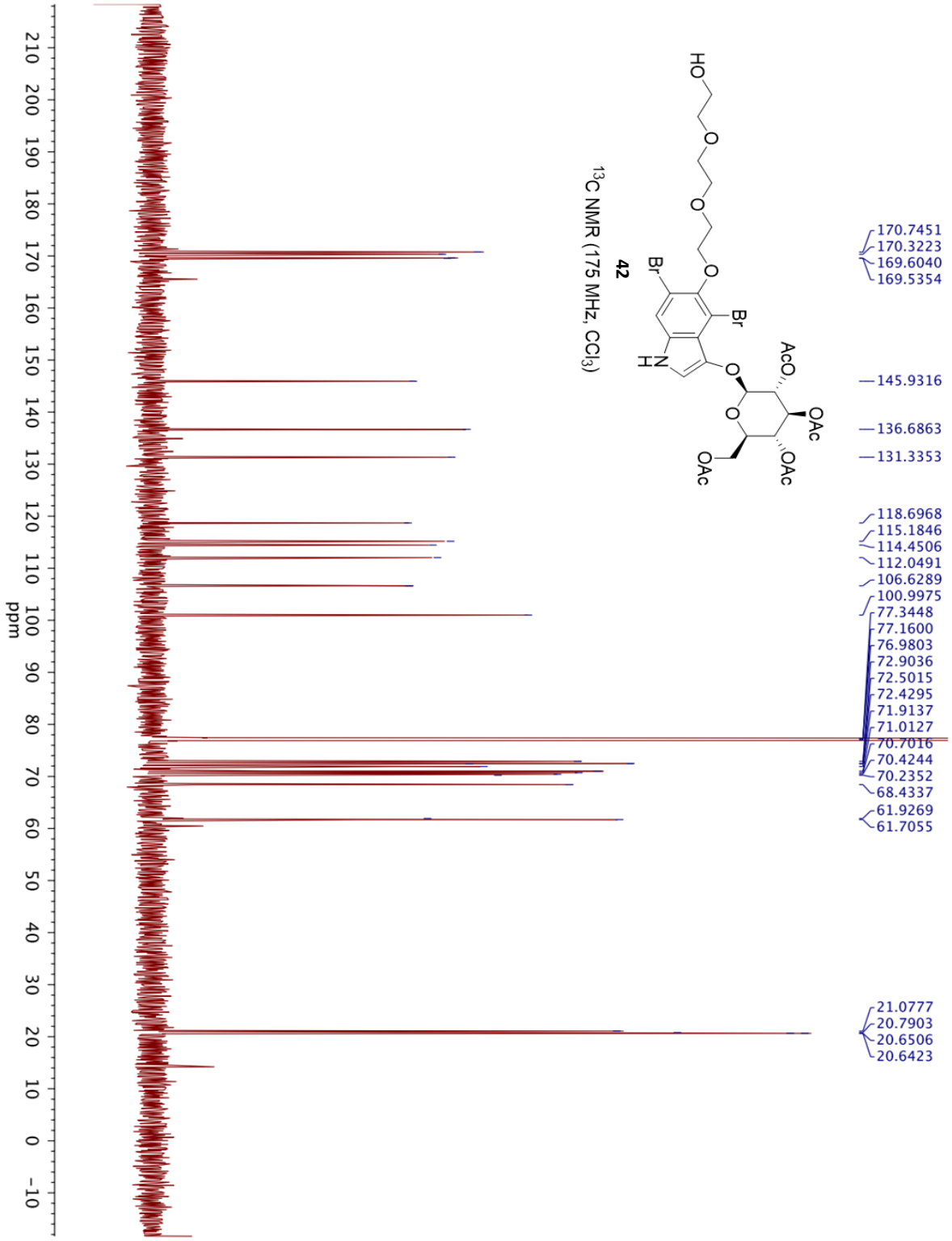

^{13}C NMR (175 MHz, CD_3OD)
41
$\cdot CF_3CO_2H$
H–N
N+
SO_3^-
OH
163.4000
163.2025
163.0065
162.8079
59.0806
58.7646
58.2736
56.3994
49.3624
49.2423
49.1218
49.0000
48.8772
48.7546
48.6324
48.2199
38.7602
25.5749
18.8579
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

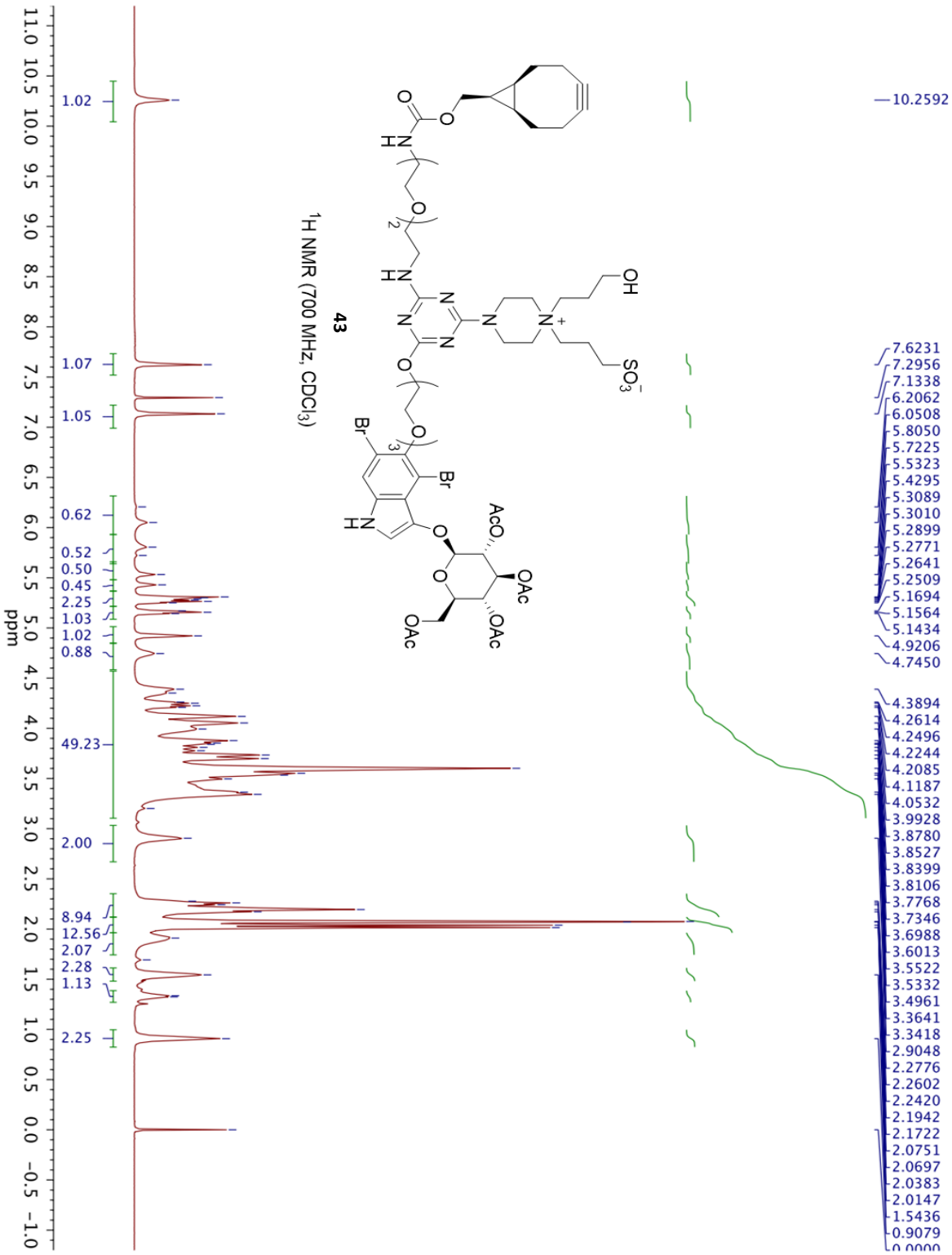


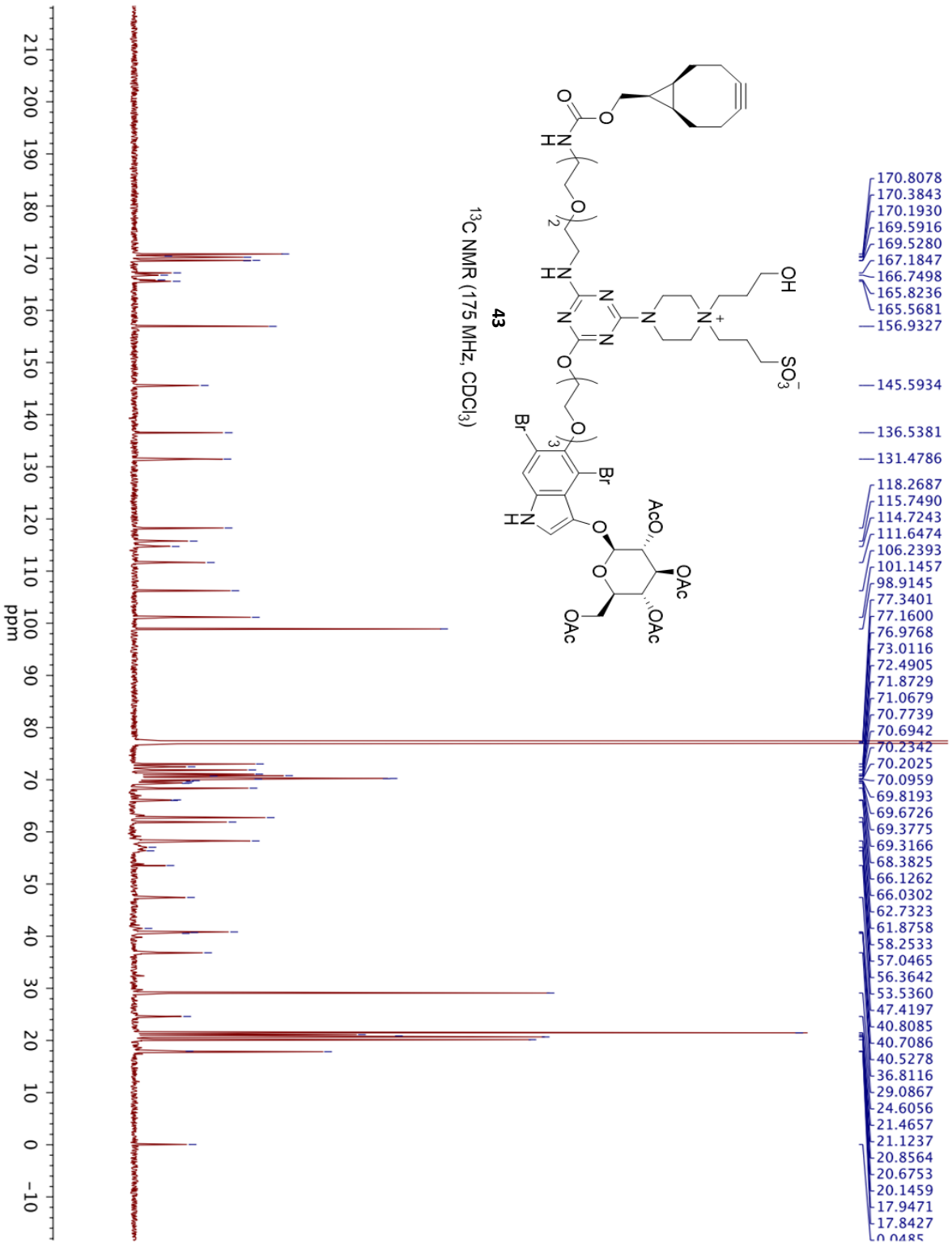
41

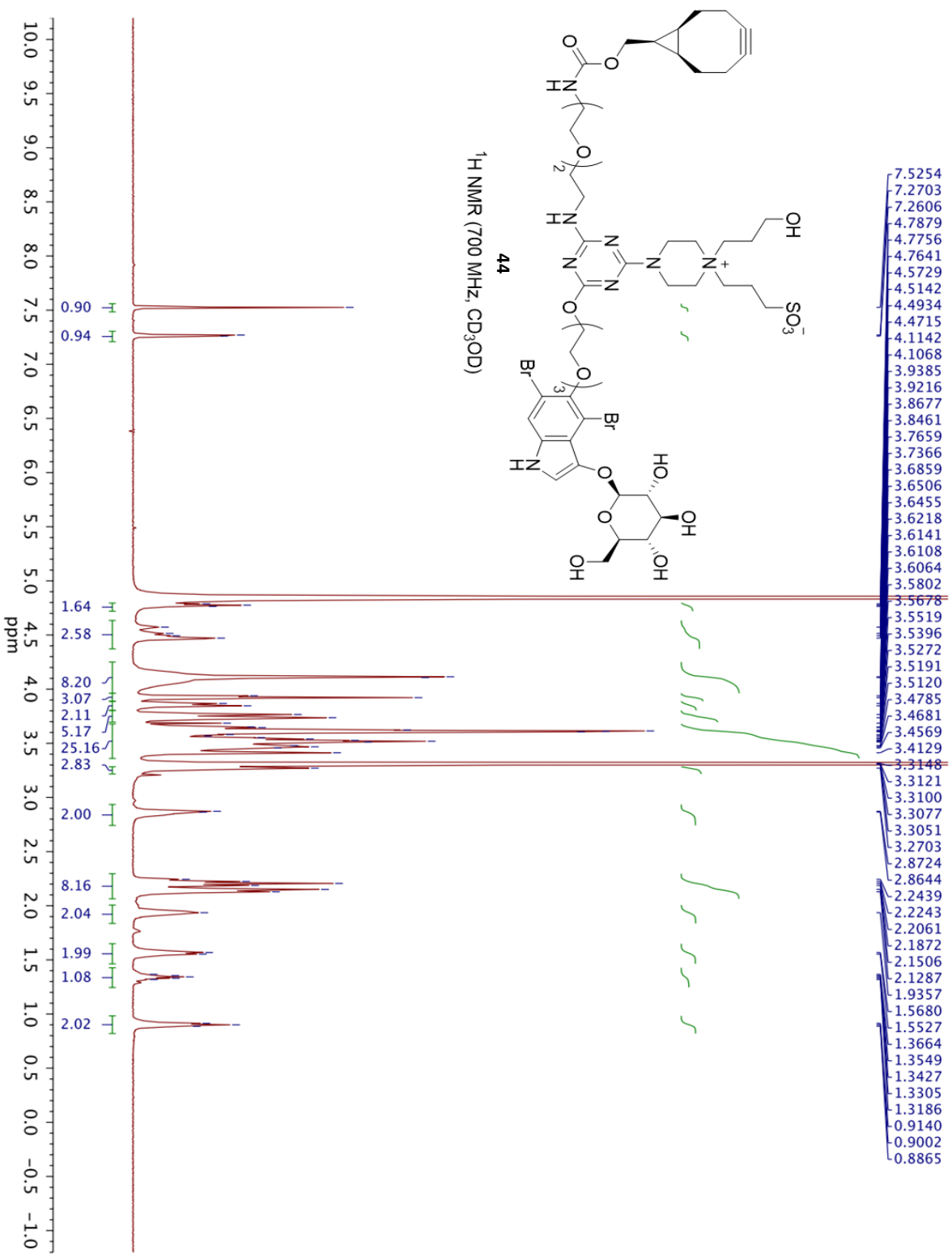
^{19}F NMR (564 MHz, CD_3OD)

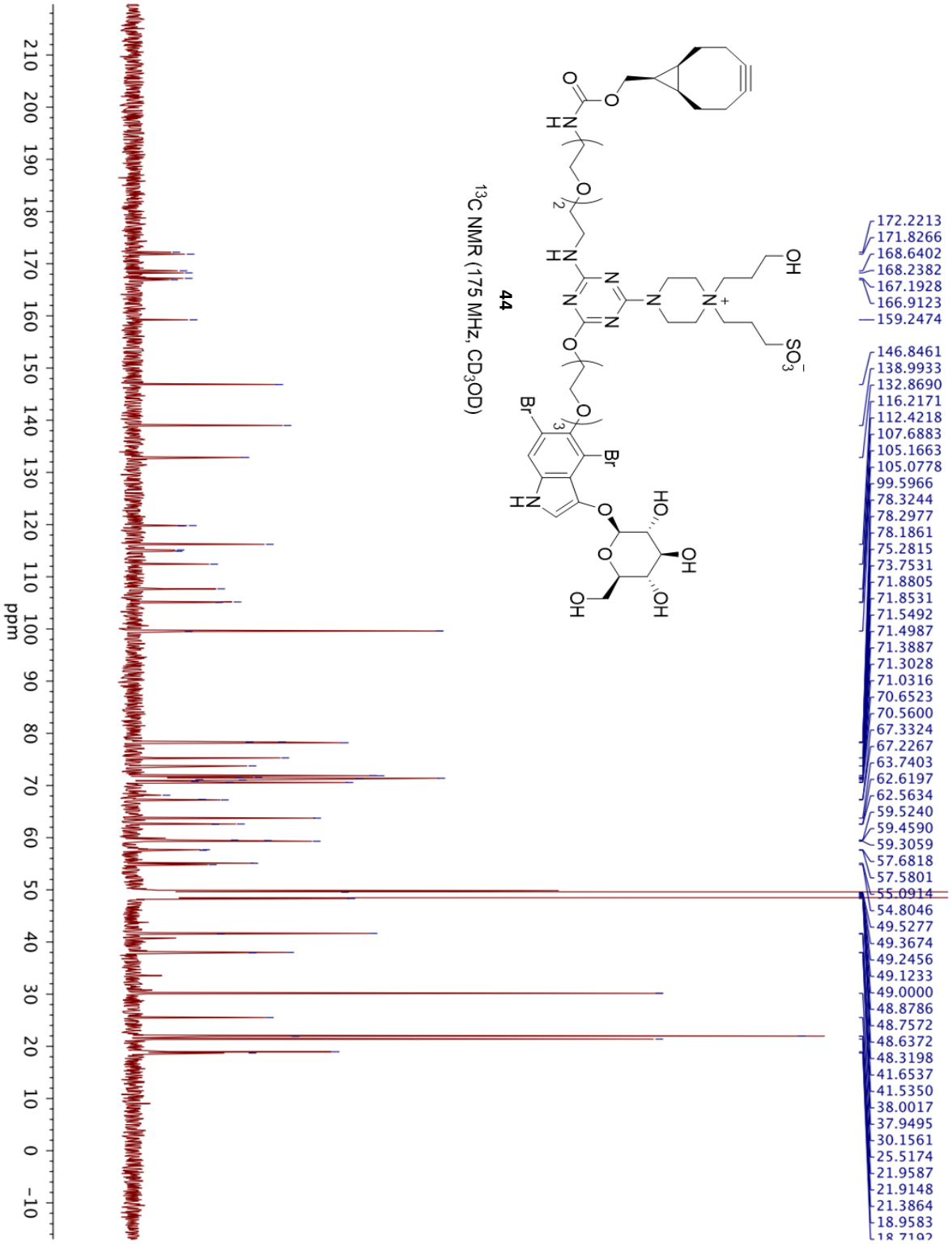

42
^{1}H NMR (700 MHz, CCl_3)
ppm
7.9428
7.4508
7.2635 CDCl3
7.0686
7.0648
5.3807
5.3694
5.3671
5.3560
5.3019
5.2885
5.2752
5.2081
5.1943
5.1805
4.9755
4.9643
4.2788
4.2749
4.2613
4.2573
4.2504
4.2435
4.2328
4.2260
4.1755
4.1725
4.1666
4.1611
4.1587
3.9753
3.9683
3.9612
3.8225
3.8168
3.8147
3.8089
3.8039
3.8002
3.7963
3.7935
3.7895
3.7494
3.7449
3.7427
3.7364
3.6571
3.6503
3.6441
2.1029
2.0961
2.0502
2.0387
1.6449
1.01
0.95
0.99
0.96
1.02
1.01
1.00
2.14
2.18
2.04
0.19
3.10
4.24
2.03
0.90
2.79
3.21
2.90
3.13

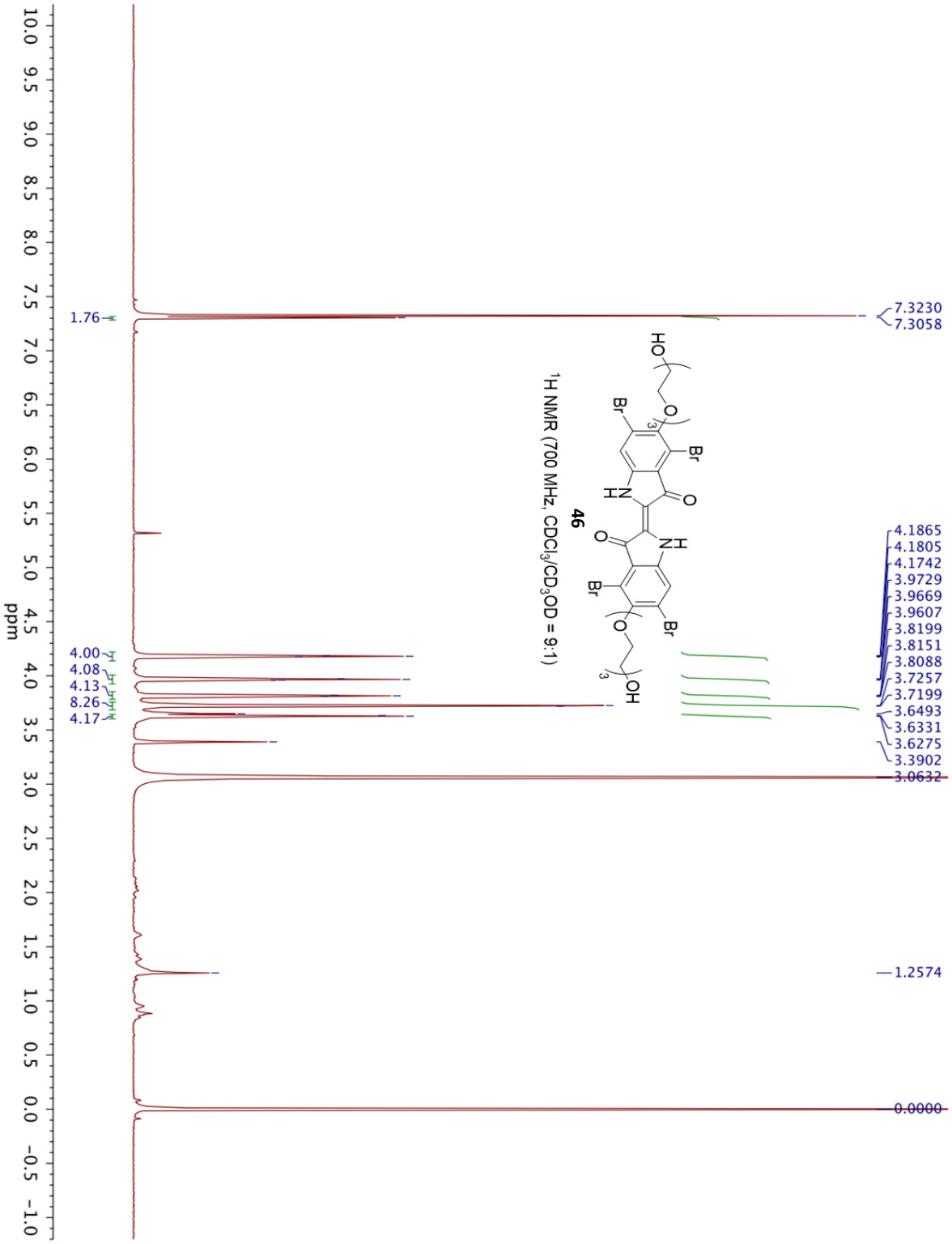

42
^{13}C NMR (175 MHz, CCl_3)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
170.7451
170.3223
169.6040
169.5354
145.9316
136.6863
131.3353
118.6968
115.1846
114.4506
112.0491
106.6289
100.9975
77.3448
77.1600
76.9803
72.9036
72.5015
72.4295
71.9137
71.0127
70.7016
70.4244
70.2352
68.4337
61.9269
61.7055
21.0777
20.7903
20.6506
20.6423

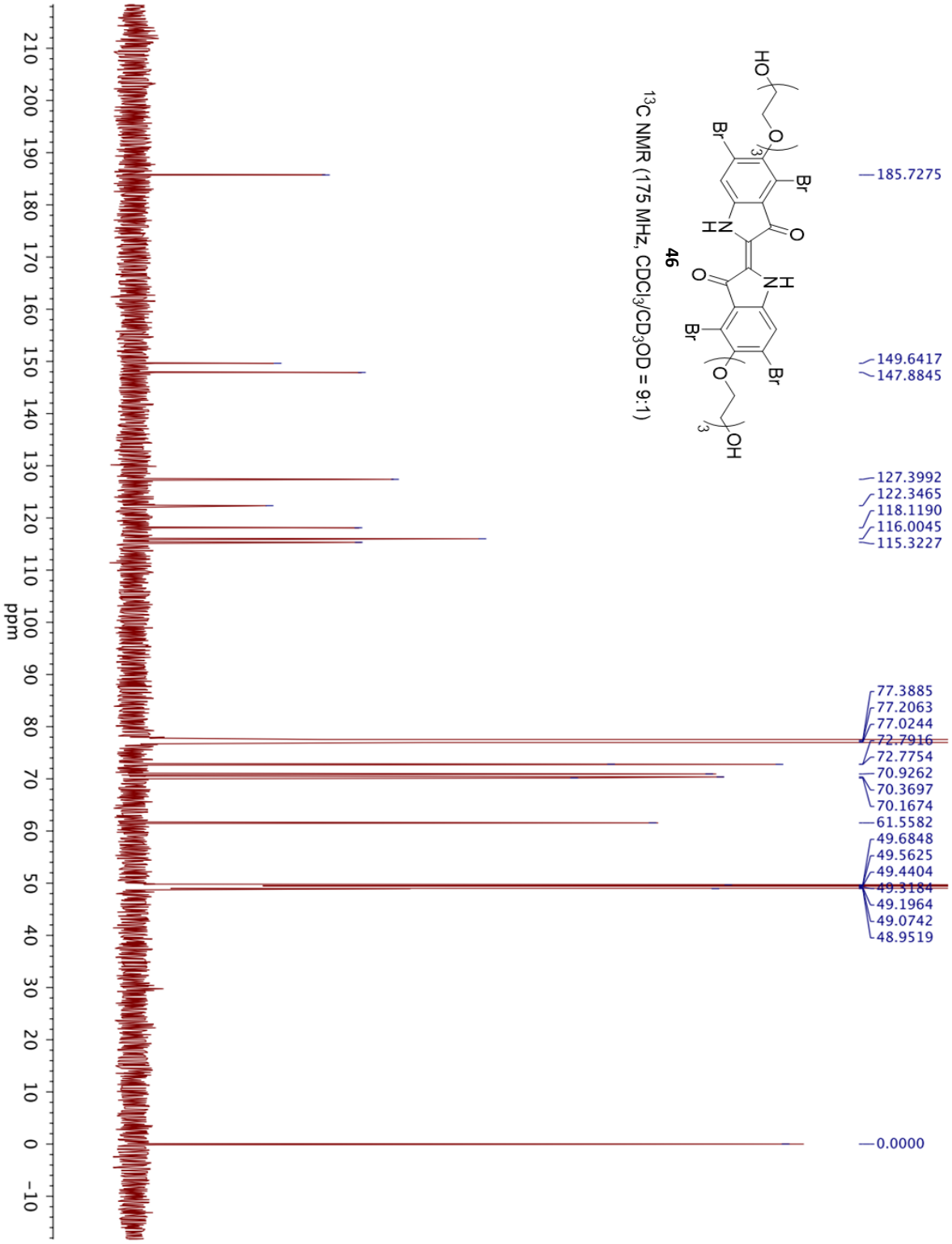

43
^{1}H NMR (700 MHz, CDCl$_3$)
ppm
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
1.02
1.07
1.05
0.62
0.52
0.50
0.45
2.25
1.03
1.02
0.88
49.23
2.00
8.94
12.56
2.07
2.28
1.13
2.25
10.2592
7.6231
7.2956
7.1338
6.2062
6.0508
5.8050
5.7225
5.5323
5.4295
5.3089
5.3010
5.2899
5.2771
5.2641
5.2509
5.1694
5.1564
5.1434
4.9206
4.7450
4.3894
4.2614
4.2496
4.2244
4.2085
4.1187
4.0532
3.9928
3.8780
3.8527
3.8399
3.8106
3.7768
3.7346
3.6988
3.6013
3.5522
3.5332
3.4961
3.3641
3.3418
2.9048
2.2776
2.2602
2.2420
2.1942
2.1722
2.0751
2.0697
2.0383
2.0147
1.5436
0.9079
0.0000

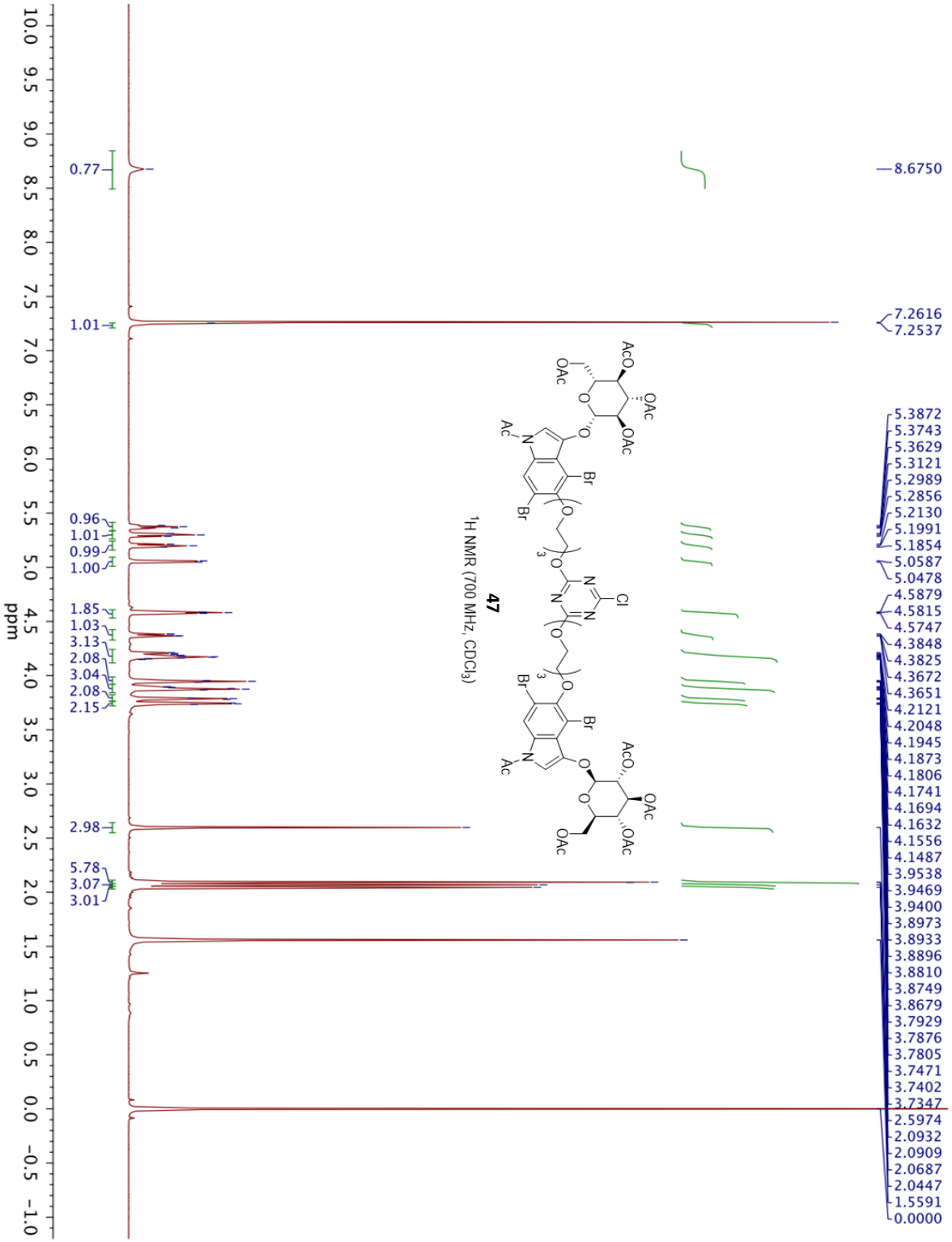

43
^{13}C NMR (175 MHz, CDCl$_3$)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
170.8078
170.3843
170.1930
169.5916
169.5280
167.1847
166.7498
165.8236
165.5681
156.9327
145.5934
136.5381
131.4786
118.2687
115.7490
114.7243
111.6474
106.2393
101.1457
98.9145
77.3401
77.1600
76.9768
73.0116
72.4905
71.8729
71.0679
70.7739
70.6942
70.2342
70.2025
70.0959
69.8193
69.6726
69.3775
69.3166
68.3825
66.1262
66.0302
62.7323
61.8758
58.2533
57.0465
56.3642
53.5360
47.4197
40.8085
40.7086
40.5278
36.8116
29.0867
24.6056
21.4657
21.1237
20.8564
20.6753
20.1459
17.9471
17.8427

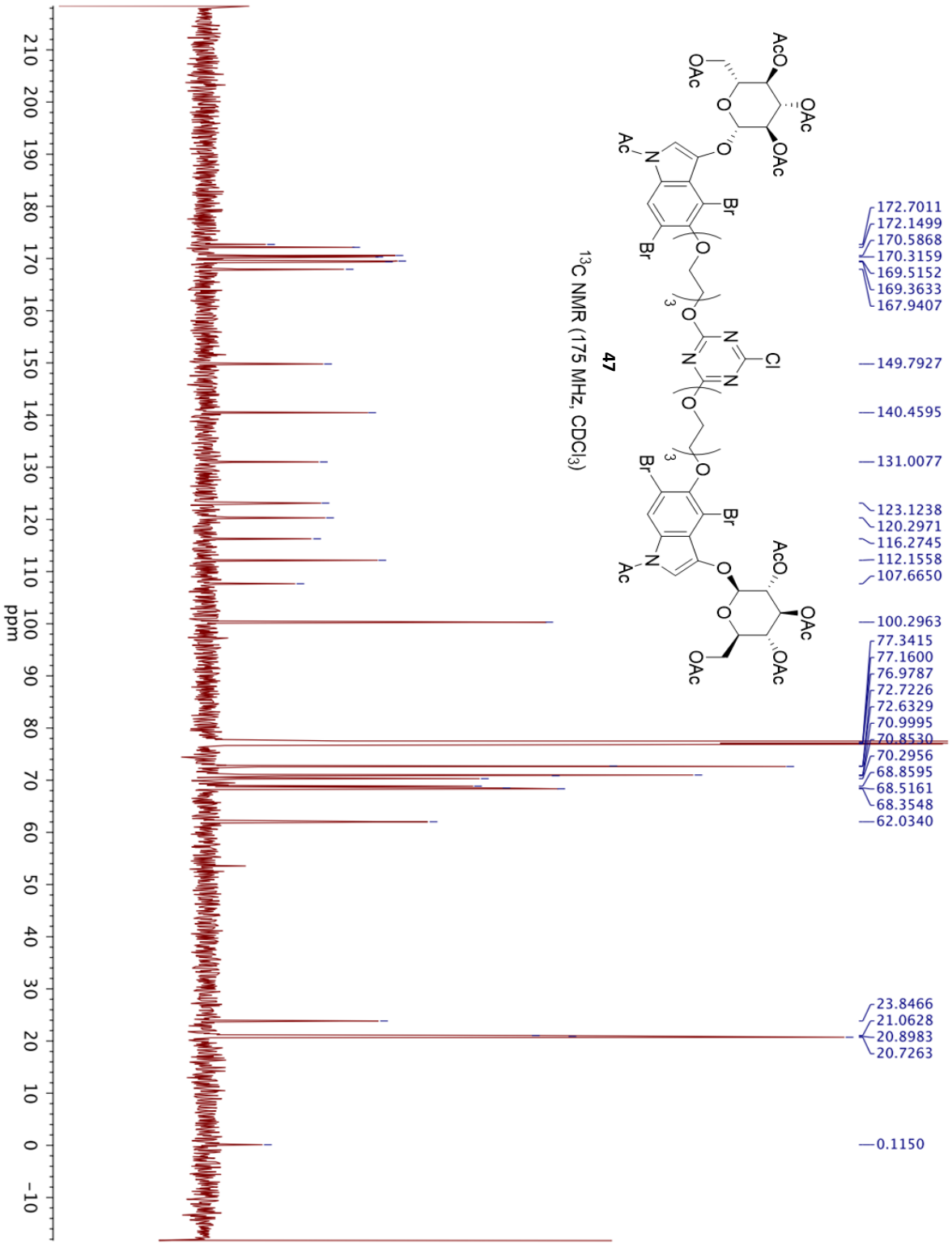

44
^{1}H NMR (700 MHz, CD_3OD)
ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
0.90
0.94
1.64
2.58
8.20
3.07
2.11
5.17
25.16
2.83
2.00
8.16
2.04
1.99
1.08
2.02
7.5254
7.2703
7.2606
4.7879
4.7756
4.7641
4.5729
4.5142
4.4934
4.4715
4.1142
4.1068
3.9385
3.9216
3.8677
3.8461
3.7659
3.7366
3.6859
3.6506
3.6455
3.6218
3.6141
3.6108
3.6064
3.5802
3.5678
3.5519
3.5396
3.5272
3.5191
3.5120
3.4785
3.4681
3.4569
3.4129
3.3148
3.3121
3.3100
3.3077
3.3051
3.2703
2.8724
2.8644
2.2439
2.2243
2.2061
2.1872
2.1506
2.1287
1.9357
1.5680
1.5527
1.3664
1.3549
1.3427
1.3305
1.3186
0.9140
0.9002
0.8865

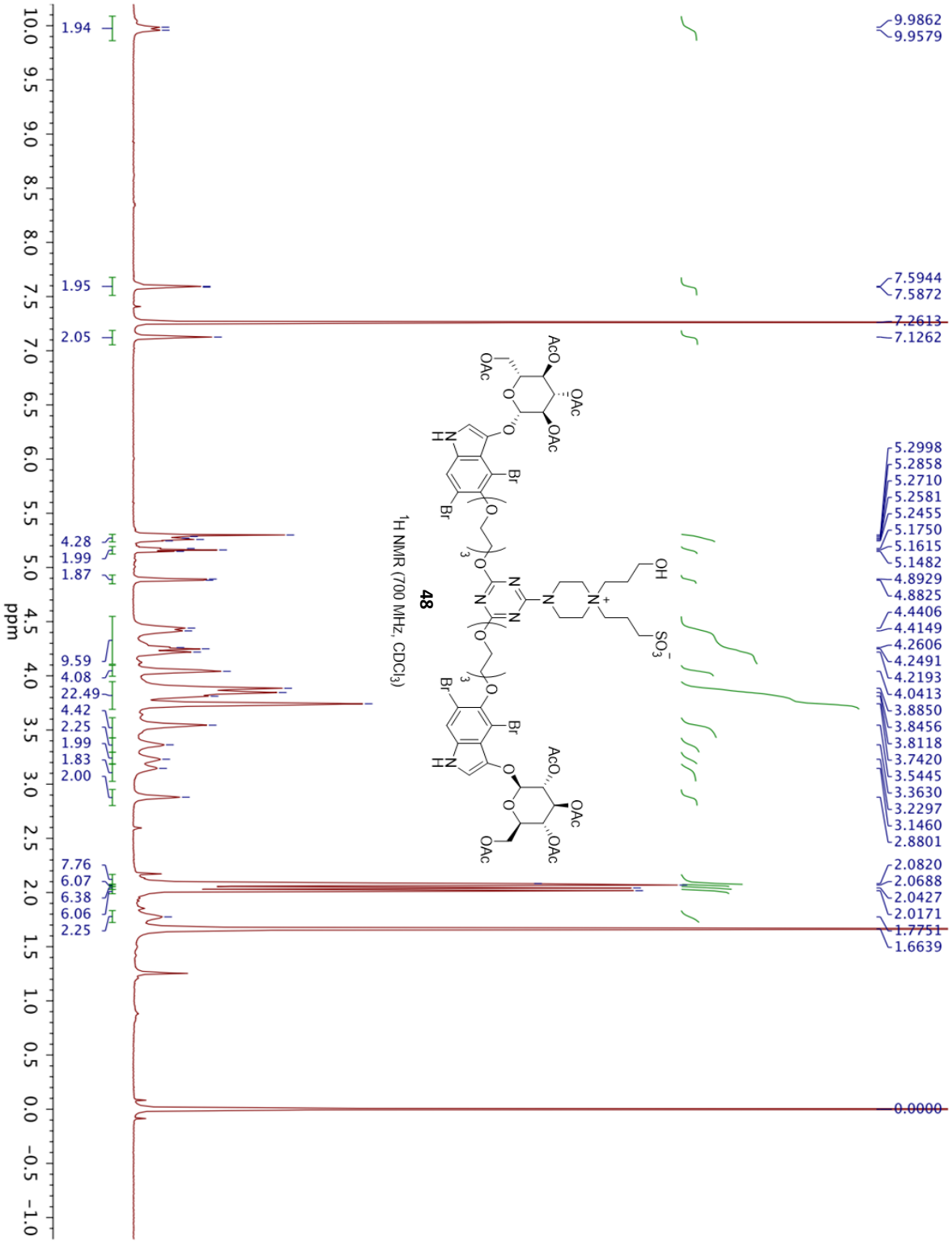

44
^{13}C NMR (175 MHz, CD$_3$OD)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
172.2213
171.8266
168.6402
168.2382
167.1928
166.9123
159.2474
146.8461
138.9933
132.8690
116.2171
112.4218
107.6883
105.1663
105.0778
99.5966
78.3244
78.2977
78.1861
75.2815
73.7531
71.8805
71.8531
71.5492
71.4987
71.3887
71.3028
71.0316
70.6523
70.5600
67.3324
67.2267
63.7403
62.6197
62.5634
59.5240
59.4590
59.3059
57.6818
57.5801
55.0914
54.8046
49.5277
49.3674
49.2456
49.1233
49.0000
48.8786
48.7572
48.6372
48.3198
41.6537
41.5350
38.0017
37.9495
30.1561
25.5174
21.9587
21.9148
21.3864
18.9583

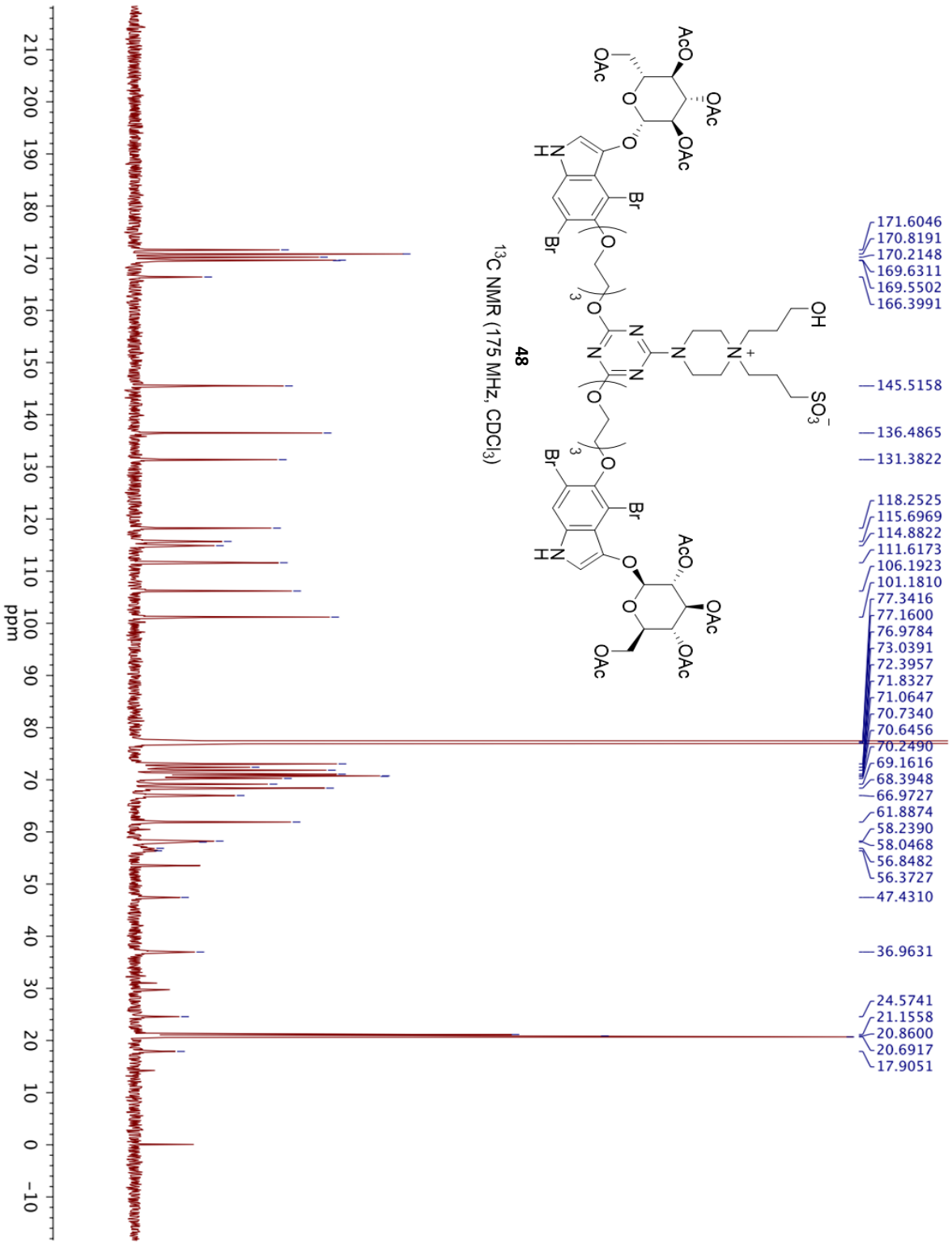

^{1}H NMR (700 MHz, $CDCl_3$/CD_3OD = 9:1)
46
ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
1.76
4.00
4.08
4.13
8.26
4.17
7.3230
7.3058
4.1865
4.1805
4.1742
3.9729
3.9669
3.9607
3.8199
3.8151
3.8088
3.7257
3.7199
3.6493
3.6331
3.6275
3.3902
3.0632
1.2574
0.0000

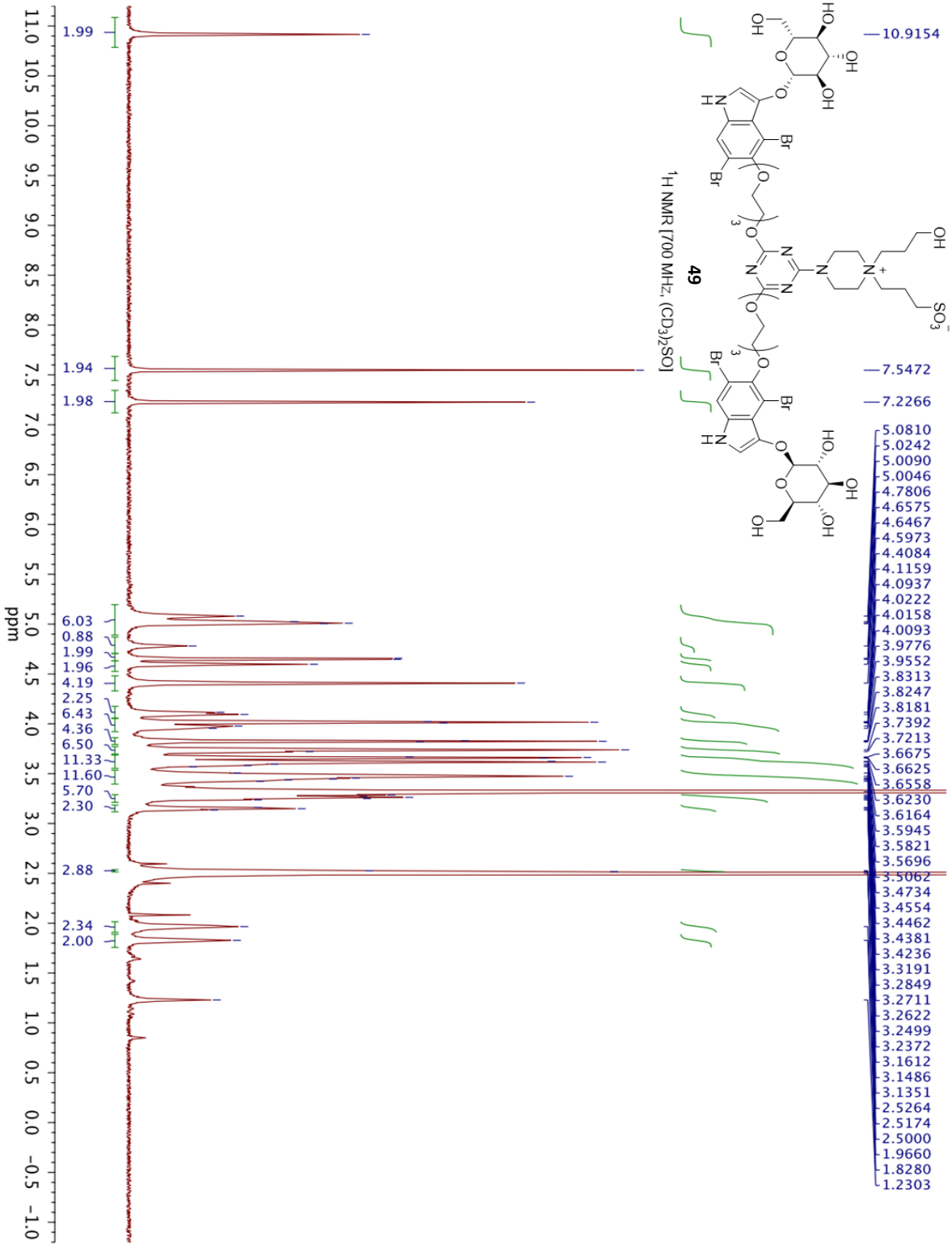

46
^{13}C NMR (175 MHz, CDCl$_3$/CD$_3$OD = 9:1)
185.7275
149.6417
147.8845
127.3992
122.3465
118.1190
116.0045
115.3227
77.3885
77.2063
77.0244
72.7916
72.7754
70.9262
70.3697
70.1674
61.5582
49.6848
49.5625
49.4404
49.3184
49.1964
49.0742
48.9519
0.0000
ppm

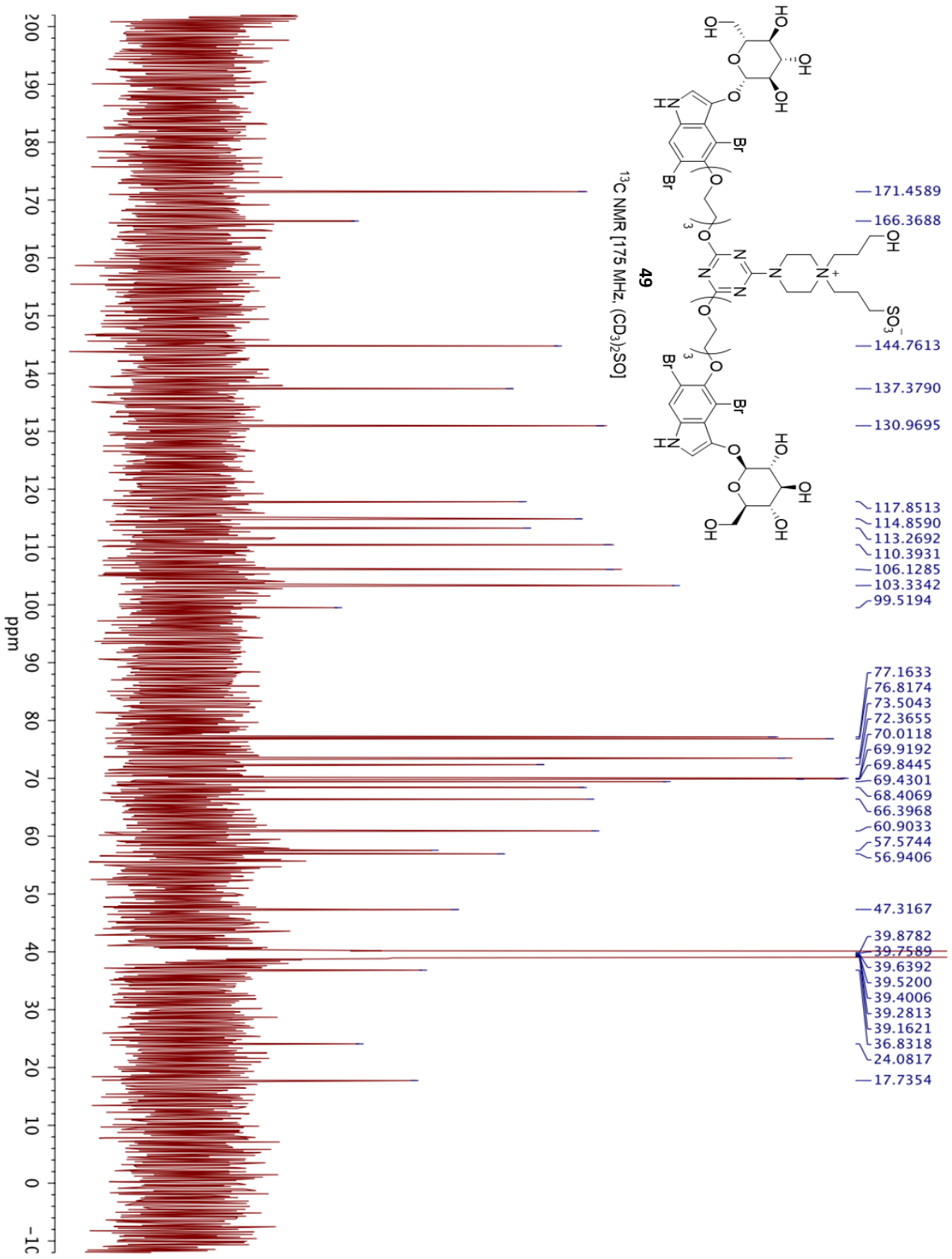

47
^{1}H NMR (700 MHz, CDCl$_3$)
ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
0.77
1.01
0.96
1.01
0.99
1.00
1.85
1.03
3.13
2.08
3.04
2.08
2.15
2.98
5.78
3.07
3.01
8.6750
7.2616
7.2537
5.3872
5.3743
5.3629
5.3121
5.2989
5.2856
5.2130
5.1991
5.1854
5.0587
5.0478
4.5879
4.5815
4.5747
4.3848
4.3825
4.3672
4.3651
4.2121
4.2048
4.1945
4.1873
4.1806
4.1741
4.1694
4.1632
4.1556
4.1487
3.9538
3.9469
3.9400
3.8973
3.8933
3.8896
3.8810
3.8749
3.8679
3.7929
3.7876
3.7805
3.7471
3.7402
3.7347
2.5974
2.0932
2.0909
2.0687
2.0447
1.5591
0.0000


47
^{13}C NMR (175 MHz, CDCl$_3$)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
172.7011
172.1499
170.5868
170.3159
169.5152
169.3633
167.9407
149.7927
140.4595
131.0077
123.1238
120.2971
116.2745
112.1558
107.6650
100.2963
77.3415
77.1600
76.9787
72.7226
72.6329
70.9995
70.8530
70.2956
68.8595
68.5161
68.3548
62.0340
23.8466
21.0628
20.8983
20.7263
0.1150


48
^{1}H NMR (700 MHz, CDCl$_3$)
ppm
10.0 9.5 9.0 8.5 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 1.5 1.0 0.5 0.0 -0.5 -1.0
1.94
1.95
2.05
4.28
1.99
1.87
9.59
4.08
22.49
4.42
2.25
1.99
1.83
2.00
7.76
6.07
6.38
6.06
2.25
9.9862
9.9579
7.5944
7.5872
7.2613
7.1262
5.2998
5.2858
5.2710
5.2581
5.2455
5.1750
5.1615
5.1482
4.8929
4.8825
4.4406
4.4149
4.2606
4.2491
4.2193
4.0413
3.8850
3.8456
3.8118
3.7420
3.5445
3.3630
3.2297
3.1460
2.8801
2.0820
2.0688
2.0427
2.0171
1.7751
1.6639
0.0000


48
^{13}C NMR (175 MHz, CDCl$_3$)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
171.6046
170.8191
170.2148
169.6311
169.5502
166.3991
145.5158
136.4865
131.3822
118.2525
115.6969
114.8822
111.6173
106.1923
101.1810
77.3416
77.1600
76.9784
73.0391
72.3957
71.8327
71.0647
70.7340
70.6456
70.2490
69.1616
68.3948
66.9727
61.8874
58.2390
58.0468
56.8482
56.3727
47.4310
36.9631
24.5741
21.1558
20.8600
20.6917
17.9051


49
^{1}H NMR [700 MHz, $(CD_3)_2SO$]
10.9154
7.5472
7.2266
1.99
1.94
1.98
6.03
0.88
1.99
1.96
4.19
2.25
6.43
4.36
6.50
11.33
11.60
5.70
2.30
2.88
2.34
2.00
ppm


49
^{13}C NMR [175 MHz, (CD$_3$)$_2$SO]
171.4589
166.3688
144.7613
137.3790
130.9695
117.8513
114.8590
113.2692
110.3931
106.1285
103.3342
99.5194
77.1633
76.8174
73.5043
72.3655
70.0118
69.9192
69.8445
69.4301
68.4069
66.3968
60.9033
57.5744
56.9406
47.3167
39.8782
39.7589
39.6392
39.5200
39.4006
39.2813
39.1621
36.8318
24.0817
17.7354
ppm

precipitate from oligomerization with **49**

^{1}H NMR [700 MHz, $(CD_3)_2SO$]