SUPPORTING INFORMATION

Investigations into the decomposition of aminoacyl-substituted monosaccharide scaffolds from a drug discovery library

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Figure S1. LC/MS analysis of the decomposition product of compound **1** after >2 years of storage in DMSO.

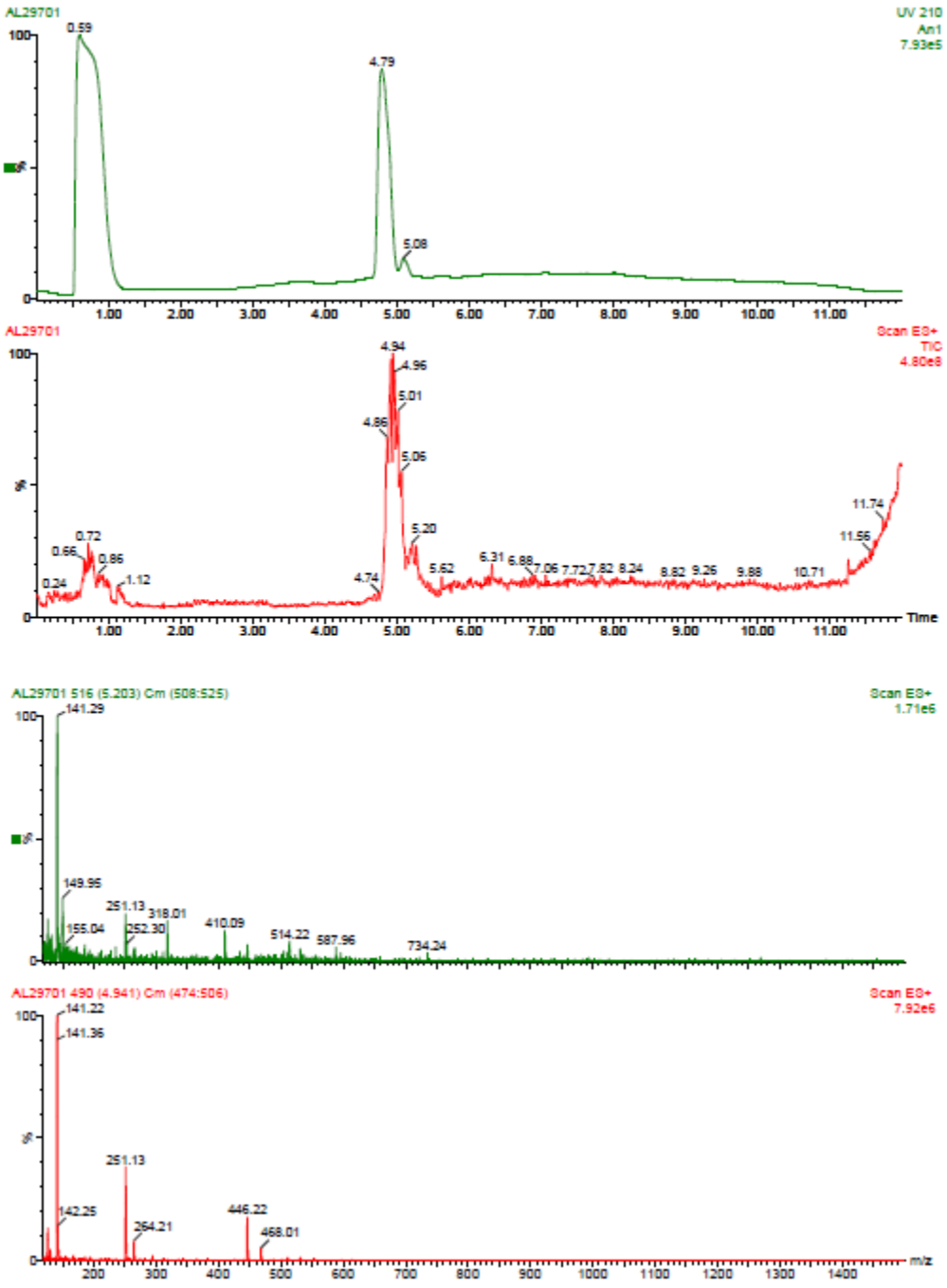


Figure S2. LC/MS analysis of resynthesized compound **1**.

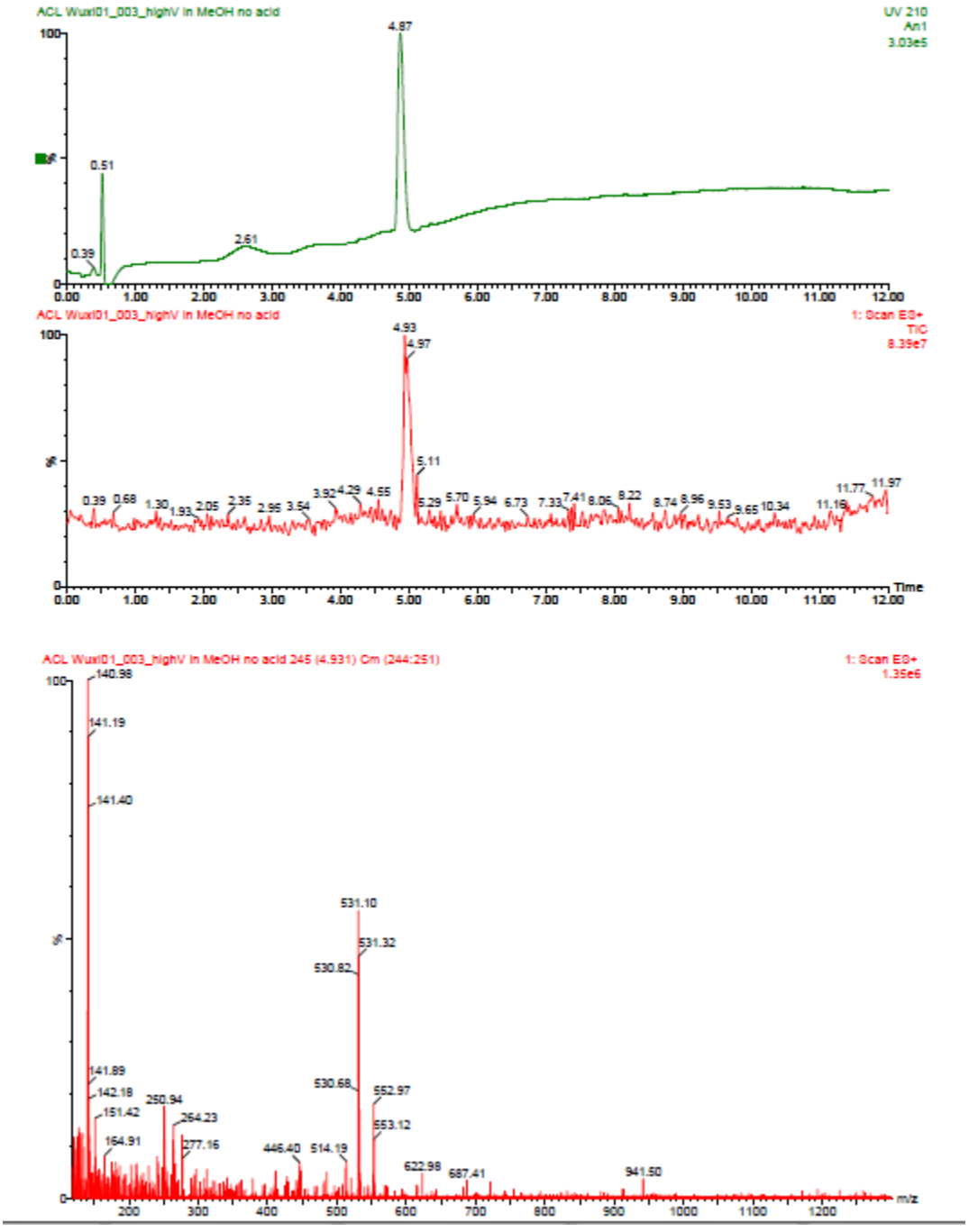


Figure S3. LC/MS analysis of **1** (10 mM) in DMSO + 5% H_2O at pH 1 and 50 °C at various time points.

(d) 10 months

(c) 13 d

(b) 2 d

(a) 1 h

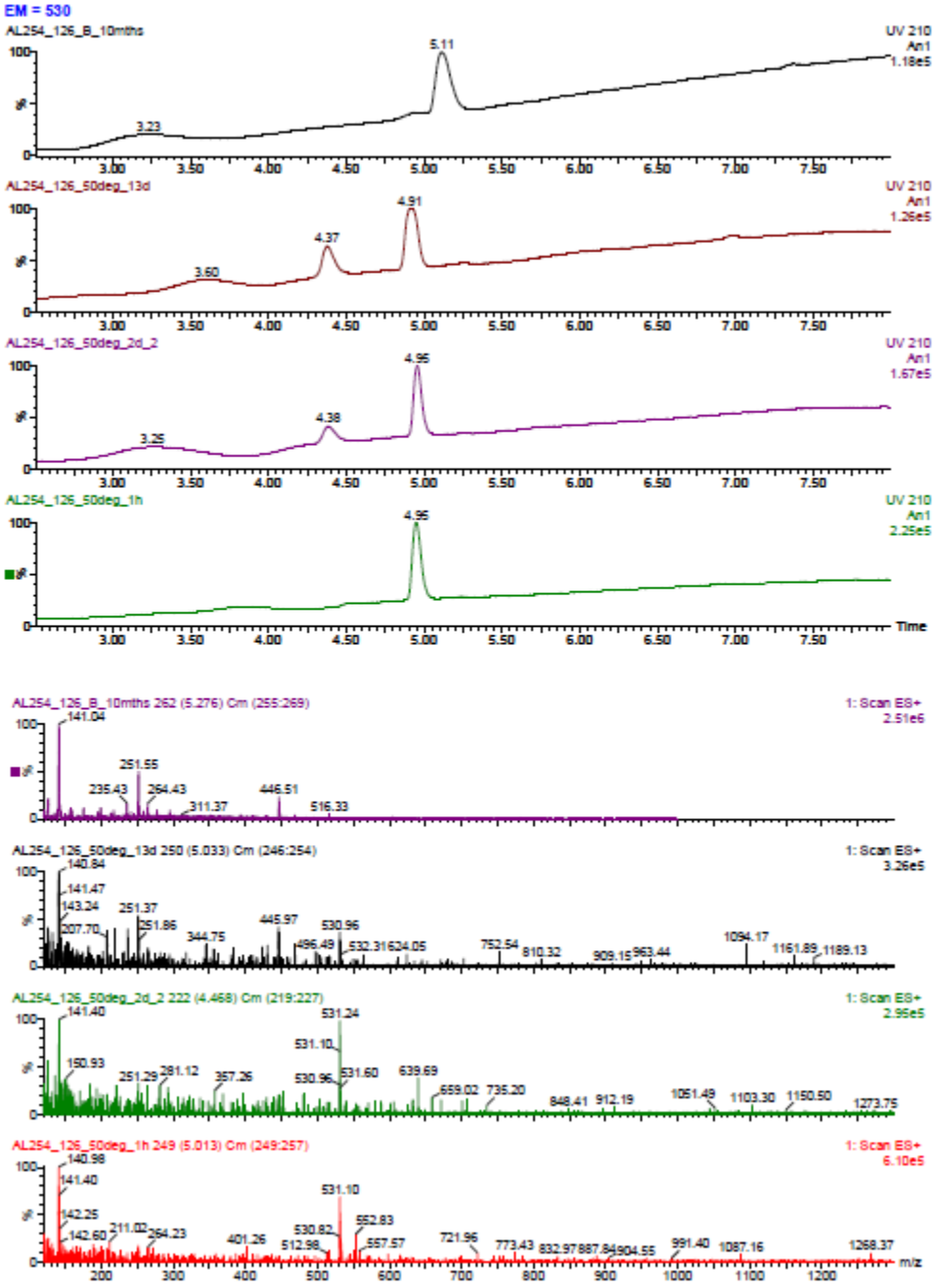
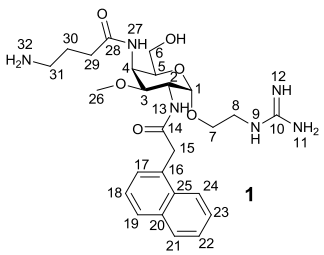


Table S1. ^{1}H and ^{13}C NMR data **(DMSO-d_6)** for compound **1**.

	^{13}C NMR, ppm	**^{1}H NMR,** ppm (mult., *J*, Hz)	**COSY** ^{1}H–^{1}H connections	**HMBC** ^{13}C – ^{1}H long range correlations
1	97.1	4.70 (d, 3.5)	H-2	H-1 < - - > C-3, C-4, C-5, C-7
2	49.1	4.12 (m)	H-1, H-3, H-13	H-2 < - - > C-3
3	75.3	3.67 (m)	H-2, H-4	H-3 < - - > C-2, C-26
4	45.3	4.55 (dd, 4.0, 11.0)	H-3, H-5, H-27	H-4 < - - > C-2, C-3
5	70.3	3.89 (t, 6.5)	H-4, H-6	H-5 < - - > C-6
6	60.9	3.28 (m)	H-5	H-6 < - - > C-5
7	65.4	3.67, 3.40 (m)	H-8	H-7 < - - > C-8
8	40.7	3.40, 3.28 (m)	H-7, H-9	H-8 < - - > C-7
9, NH		8.23 (t, 5.0)	H-8	
10, C=N	157.5			
11, NH_2				
12, NH				
13, NH		8.54 (d, 8.5)	H-2	H-13 < - - > C-2, C-14
14, C=O	170.3			
15	40.0	4.04 (dd, 17.5, 14.5)		H-15 < - - > C-14, C-16, C-17, C-25
16	132.1			
17	128.0	7.45 (m)	H-18	H-17 < - - > C-16, C-18, C-15, C-25
18	125.5	7.47 (m)	H-17, H-19	H-18 < - - > C-16, C-17, C-19
19	126.9	7.80 (d, 7.80)	H-18	H-19 < - - > C-18, C-20, C-21
20	133.3			
21	128.3	7.91 (m)	H-22	H-21 < - - > C-19, C-20, C-22
22	125.6	7.49 (m)	H-21, H-23	H-22 < - - > C-20, C-21, C-23
23	125.7	7.48 (m)	H-22, H-24	H23 < - - > C-21, C-22, C-24
24	124.6	8.15 (d, 8.5)	H-23	H-24 < - - > C-22, C-23, C-25
25	133.3			
26	56.3	3.26 (s)		H-26 < - - > C-3
27, NH		7.90 (m)	H-4	H-27 < - - > C-4, C-28
28, C=O	172.3			
29	32.0	2.24 (t, 7.0)	H-30	H-29 < - - > C-30, C-31
30	23.6	1.74 (q, 7.0, 14.5)	H-29, H-31	H-30 < - - > C-29, C-31
31	38.4	2.71 (m)	H-30, H-32	H-31 < - - > C-30
32, NH_2		7.84 (br. s)	H-31	



1

Table S2. ^{1}H and ^{13}C NMR data (**MeOH-d_4**) for compound **1**.

	^{13}C NMR, ppm	**^{1}H NMR,** ppm (mult., *J*, Hz)	**COSY** ^{1}H–^{1}H connections	**HMBC** ^{13}C – ^{1}H long range correlations
1	99.2	4.78 (overlap with MeOD)	H-2	H-1 < - - > C-3, C-5, C-7
2	50.8	4.15 (dd, 3.9, 11.3)	H-1, H-3, H-13	H-2 < - - > C-1, C-3
3	77.8	3.61 (dd, 4.9, 11.3)	H2, H-4	H-3 < - - > C-2, C-4, C-26
4	47.6	4.67 (d, 4.9)	H-3, H-5, H-27	H-4 < - - > C-1, C-3, C-2
5	71.6	3.94 (t, 6.7)	H-4, H-6	H-5 < - - > C-6
6	62.8	3.50 (m)	H-5	H-6 < - - > C-5
7	67.6	3.71, 3.45 (m)	H-8	H-7 < - - > C-1, C-8
8	42.3	3.44, 3.32 (m)	H-7, H-9	H-8 < - - > C-7
9, NH		7.52 (t, 5.6)	H-8	
10, C=N	158.9			
11, NH_2				
12, NH				
13, NH		7.97 (d, 8.9)	H-2	
14, C=O	174.3			
15	41.4	4.03 (dd, 19.9, 15.4)		H-15 < - - > C-14, C-16, C-17, C-25
16	133.2			
17	129.1	7.40 (m)	H-18	H-17 < - - > C-16, C-18, C-15, C-25
18	126.6	7.43 (m)	H-17, H-19	H-18 < - - > C-16, C-17, C-19
19	128.9	7.73 (d, 7.9)	H-18	H-19 < - - > C-18, C-20, C-21
20	135.4			
21	129.7	7.81 (d, 7.7)	H-22	H-21 < - - > C-19, C-20, C-22
22	126.8	7.45 (m)	H-21, H-23	H-22 < - - > C-20, C-21, C-23
23	127.2	7.47 (m)	H-22, H-24	H23 < - - > C-21, C-22, C-24
24	125.1	8.01 (d, 8.2)	H-23	H-24 < - - > C-22, C-23, C-25
25	133.6			
26	57.7	3.29 (s)		H-26 < - - > C-3
27, NH		8.02 (d, 10.0)	H-4	
28, C=O	175.5			
29	33.6	2.33 (m)	H-30	H-29 < - - > C-31, C-30
30	24.8	1.84 (q, 7.0, 14.7)	H-29, H-31	H-30 < - - > C-29, C-31
31	40.2	2.87 (t, 7.6)	H-30	H-31 < - - > C-29, C-30
32, NH_2				

Table S3. ^{1}H and ^{13}C NMR data **(DMSO-d_6)** for resynthesized decomposition product **2**

	^{13}C NMR, ppm	**^{1}H NMR,** ppm (mult., *J*, Hz)	**COSY** $^{1}H - ^{1}H$ connections
1, CH	97.2	4.70 (d, 4.0)	H-2
2, CH	48.0	4.14 (dd, 4.0, 11.0)	H-1, H-3, H-13
3, CH	75.3	3.57 (m)	H-2, H-4
4, CH	**47.9**	**3.58 (m)**	**H-3, H-5**
5, CH	68.4	3.83 (t, 5.5)	H-4, H-6
6, CH_2	60.6	3.51 (d, 6.5)	H-5
7, CH_2	66.0	3.64, 3.45 (m)	H-8
8, CH_2	56.6	3.42, 3.34 (m)	H-7, H-9
9, NH		7.86 (br. s)	H-8
10, C=N	157.3		
11, NH_2			
12, NH			
13, NH		8.24 (d, 9.0)	H-2
14, C=O	170.3		
15, CH_2	39.8	3.96 (dd, 27.5, 15.0)	
16	132.0		
17	127.8	7.43 (m)	H-18
18	125.5	7.44 (m)	H-17, H-19
19	127.0	7.80 (t, 4.5)	H-18
20	133.3		
21	128.3	7.91 (m)	H-22
22	125.6	7.49 (m)	H-21, H-23
23	125.8	7.51 (m)	H-22, H-24
24	125.2	8.07 (m)	H-23
25	132.9		
26	40.8	3.34 (s)	
27, NH_2			

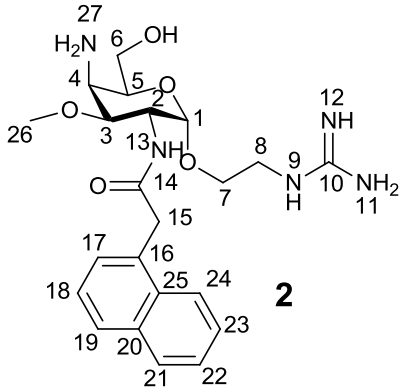


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Table S4. ^{1}H and ^{13}C NMR data **(MeOH-d_4)** for resynthesized decomposition product **2**

	^{13}C NMR, ppm	**^{1}H NMR**, ppm (mult, *J*, Hz),	**COSY** ^{1}H–^{1}H connections	**HMBC** ^{13}C – ^{1}H long range correlations
1, CH	99.0	4.78 (overlap with MeOD)	H-2	H-1 < - - > C-3, C-5, C-7
2, CH	50.0	4.16 (dd, 4.0, 11.5)	H-1, H-3	H-2 < - - > C-3
3, CH	76.1	3.67 (m)	H-2, H-4	H-3 < - - > C-4
4, CH	**50.5**	**3.77 (d, 3.0)**	**H-3, H-5**	**H-4 < - - > C-3**
5, CH	68.6	3.96 (t, 7.0)	H-6. H-4	
6, CH_2	62.5	3.68 (m)	H-5	
7, CH_2	67.7	3.68, 3.40 (m)	H-8	H-7 < - - > C-8
8, CH_2	42.2	3.30, 3.26 (m)	H-7	H-8 < - - > C-7
9, NH				
10, C=N	158.9			
11, NH_2				
12, NH				
13, NH				
14, C=O	174.3			
15, CH_2	41.3	4.00 (dd, 15.5, 18.0)		H-15 < - - > C-14, C-16, C-17, C-25
16	133.0			
17	129.1	7.38 (m)	H-18	H-17 < - - > C-16, C-18, C-15, C-25
18	126.6	7.40 (m)	H-17, H-19	H-18 < - - > C-16, C-17, C-19
19	129.0	7.74 (dd, 7.5, 1.5)	H-18	H-19 < - - > C-18, C-20, C-21
20	135.4			
21	129.8	7.80 (d, 7.5)	H-22	H-21 < - - > C-19, C-20, C-22
22	126.8	7.45 (m)	H-21, H-23	H-22 < - - > C-20, C-21, C-23
23	127.2	7.46 (m)	H-22, H-24	H-23 < - - > C-21, C-22, C-24
24	125.0	7.98 (d, 8.0)	H-23	H-24 < - - > C-22, C-23, C-25
25	133.6			
26	57.9	3.33 (s)		H-26 < - - > C-3
27, NH_2				

Table S5. ^{1}H and ^{13}C NMR data of the reaction mixture of **1** in 10% TFA in anhydrous DMSO-d_6 (pH 1) at 80°C for 6 h (**1**: Intermediate **5** = 3:2)

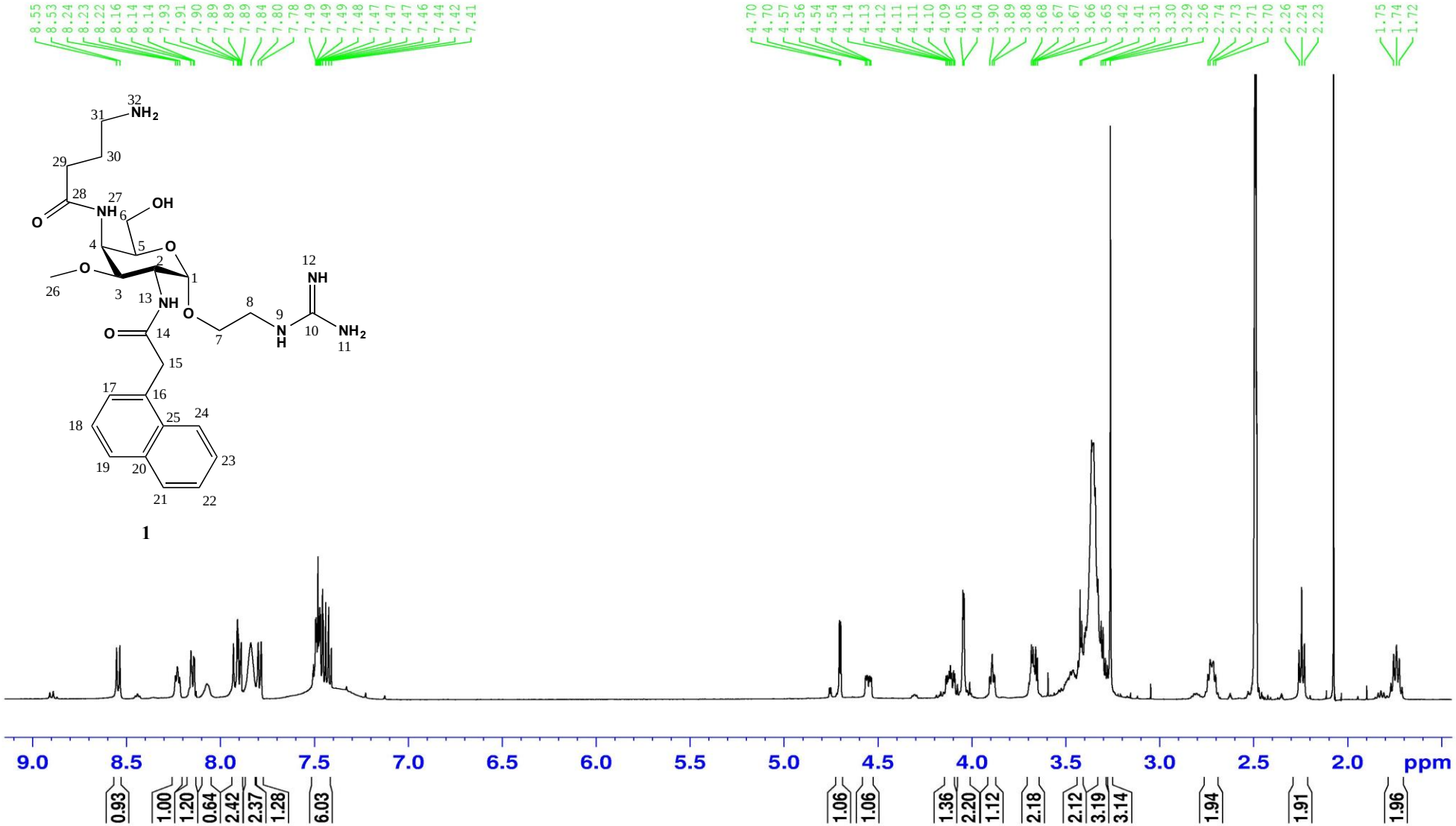
	1 (starting material)		**Intermediate 5**	
	^{13}C NMR, ppm	**^{1}H NMR**, ppm (mult., *J*, Hz)	**^{13}C NMR**, ppm	**^{1}H NMR**, ppm (mult., *J*, Hz)
1	97.6	4.75 (d, 3.5)	97.3	4.78 (d, 3.5)
2	48.7	4.13 (m)	49.4	4.13 (m)
3	75.8	3.58 (dd, 4.0, 11.0)	74.1	3.88 (m)
4	**45.6**	**4.56 (dd, 4.0, 9.5)**	**48.4**	**3.88 (m)**
5	**70.5**	**3.88 (m)**	**65.0**	**4.27 (t, 7.0)**
6	**61.2**	**3.31 (m)**	**63.1**	**4.13 (m)**
7	66.3	3.65, 3.45 (m)	66.3	3.65, 3.45 (m)
8	41.1	3.44, 3.37 (m)	41.1	3.44, 3.37 (m)
9, NH		7.87 (m)		8.19 (m)
10, C=N	157.5		157.6	
11, NH_2				
12, NH				
13, NH		8.19 (m)		8.54 (d, 9.0)
14, C=O	170.6		170.9	
15	40.9	3.97 (s)	40.9	4.03 (s)
16	132.3		132.3	
17	128.1	7.42 (m)	128.2	7.42 (m)
18	125.7	7.43 (m)	125.7	7.43 (m)
19	127.2	7.77 (dd, 2.5, 7.5)	127.3	7.77 (dd, 2.5, 7.5)
20	133.7		133.3	
21	128.6	7.87 (m)	128.6	7.87 (m)
22	125.8	7.49 (m)	125.8	7.49 (m)
23	126.1	7.47 (m)	126.1	7.47 (m)
24	124.6	8.09 (m)	124.6	8.09 (m)
25	133.2		133.2	
26	56.4	3.25 (s)	57.5	3.40 (s)
27, NH		**7.94 (d, 10.0, 1H)**		**8.03 (br. s, 2H)**
28, C=O	172.8		172.1	
29	32.3	2.25 (t, 7.0)	30.4	2.43 (t, 7.0)
30	23.9	1.73 (m)	22.6	1.78 (m)
31	38.5	2.75 (m)	38.5	2.82 (m)
32, NH_2		7.70 (br. s)		7.83 (br. s)

Table S6. COSY and HMBC data of the reaction mixture of **1** in 10% TFA in anhydrous DMSO-d_6 (pH 1) at 80°C for 6 h (**1**: Intermediate **5** = 3:2)

	1 (starting material)		**Intermediate 5**	
	COSY ^{1}H – ^{1}H connections	**HMBC** ^{13}C – ^{1}H long range correlations	**COSY** ^{1}H – ^{1}H connections	**HMBC** ^{13}C – ^{1}H long range correlations
1	H-2	H-1 < - - > C-3, C-5	H-2	H-1 < - - > C-3, C-5
2	H-1, H-3, H-13	H-2 < - - > C-3	H-1, H-3, H-13	H-2 < - - > C-3
3	H-2, H-4	H-3 < - - > C-2, C-26	H-2, H-4	H-3 < - - > C-2, C-26
4	H-3, H-5, H-27	H-4 < - - > C-3, C-5	H-3, H-5, H-27	H-4 < - - > C-3, C-5
5	H-4, H-6	H-5 < - - > C-6	H-4, H-6	H-5 < - - > C-6
6	**H-5**	**H-6 < - - > C-5**	**H-5**	**H-6 < - - > C-5, C-28**
7	H-8	H-7 < - - > C-8	H-8	H-7 < - - > C-8
8	H-7, H-9	H-8 < - - > C-7	H-7, H-9	H-8 < - - > C-7
9, NH	H-8		H-8	
10, C=N				
11, NH_2				
12, NH				
13, NH	H-2	H-13 < - - > C-14	H-2	H-13 < - - > C-14
14, C=O				
15		H-15 < - - > C-14, C-16, C-17, C-25		H-15 < - - > C-14, C-16, C-17, C-25
16				
17	H-18	H-17 < - - > C-16, C-18, C-15, C-25	H-18	H-17 < - - > C-16, C-18, C-15, C-25
18	H-17, H-19	H-18 < - - > C-16, C-17, C-19	H-17, H-19	H-18 < - - > C-16, C-17, C-19
19	H-18	H-19 < - - > C-18, C-20, C-21	H-18	H-19 < - - > C-18, C-20, C-21
20				
21	H-22	H-21 < - - > C-19, C-20, C-22	H-22	H-21 < - - > C-19, C-20, C-22
22	H-21, H-23	H-22 < - - > C-20, C-21, C-23	H-21, H-23	H-22 < - - > C-20, C-21, C-23
23	H-22, H-24	H23 < - - > C-21, C-22, C-24	H-22, H-24	H23 < - - > C-21, C-22, C-24
24	H-23	H-24 < - - > C-22, C-23, C-25	H-23	H-24 < - - > C-22, C-23, C-25
25				
26		H-26 < - - > C-3		H-26 < - - > C-3
27, NH	**H-4**	**H-27 < - - > C-4, C-28**	**H-4**	**H-27 < - - > C-4**
28, C=O				
29	H-30	H-29 < - - > C-30, C-31	H-30	H-29 < - - > C-30, C-31
30	H-29, H-31	H-30 < - - > C-29, C-31	H-29, H-31	H-30 < - - > C-29, C-31
31	H-30, H-32	H-31 < - - > C-30	H-30, H-32	H-31 < - - > C-30
32, NH_2	H-31		H-31	

^{1}H and ^{13}C NMR spectra for compounds **1 - 5, 11- 22**

500 MHz, ^{1}H NMR, DMSO-d_6



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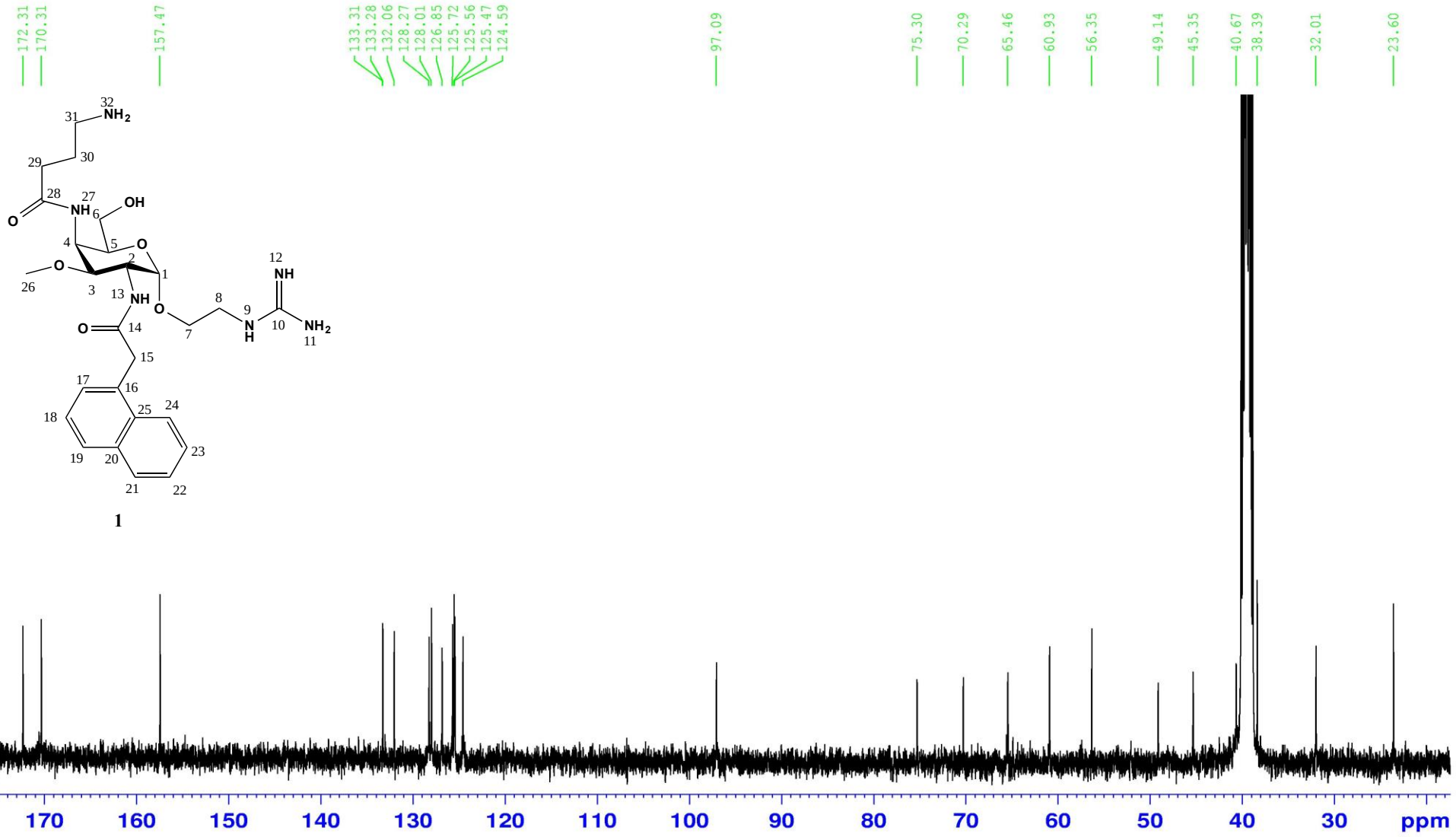
100 MHz, ^{13}C NMR, DMSO-d_6



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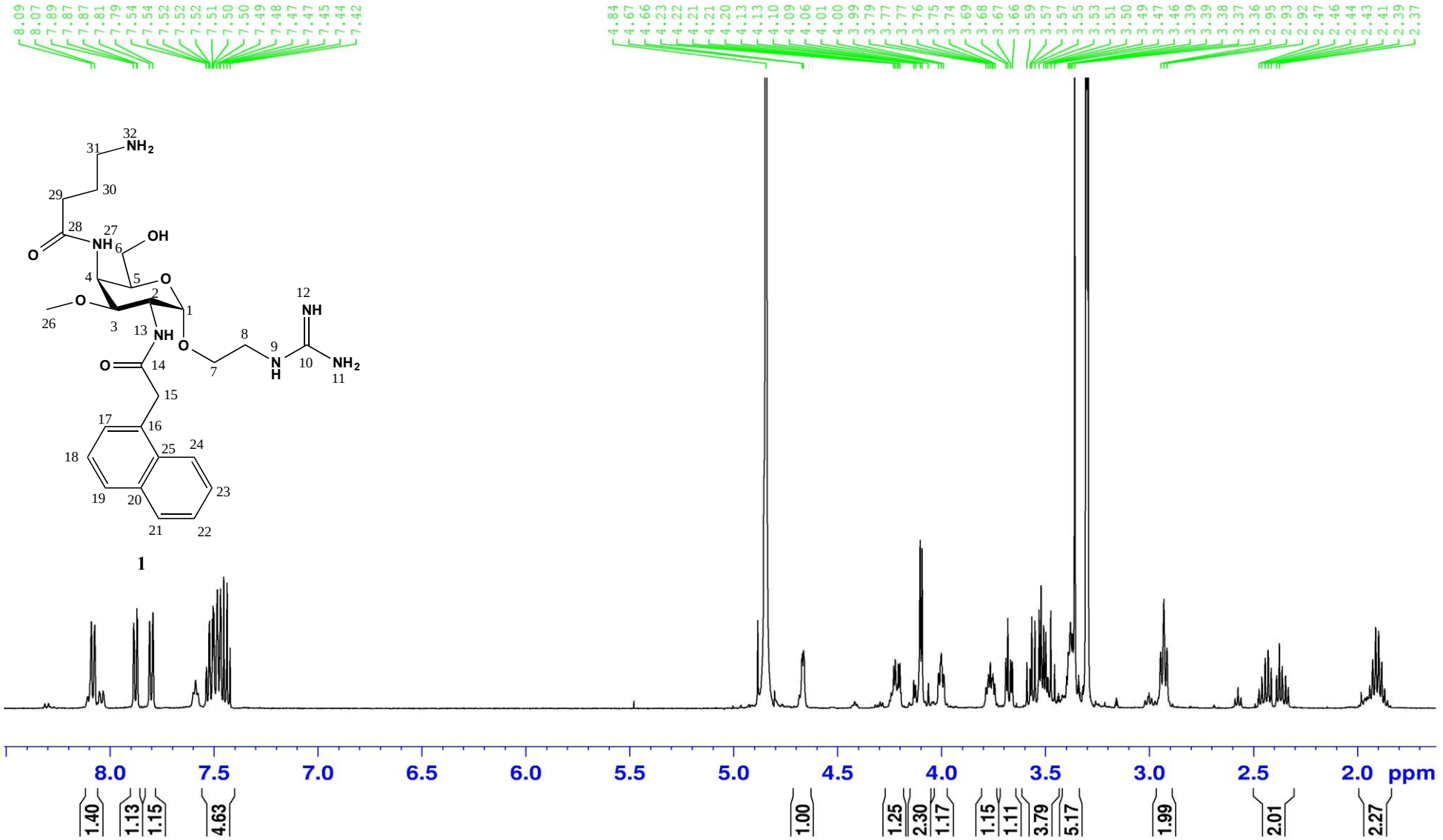
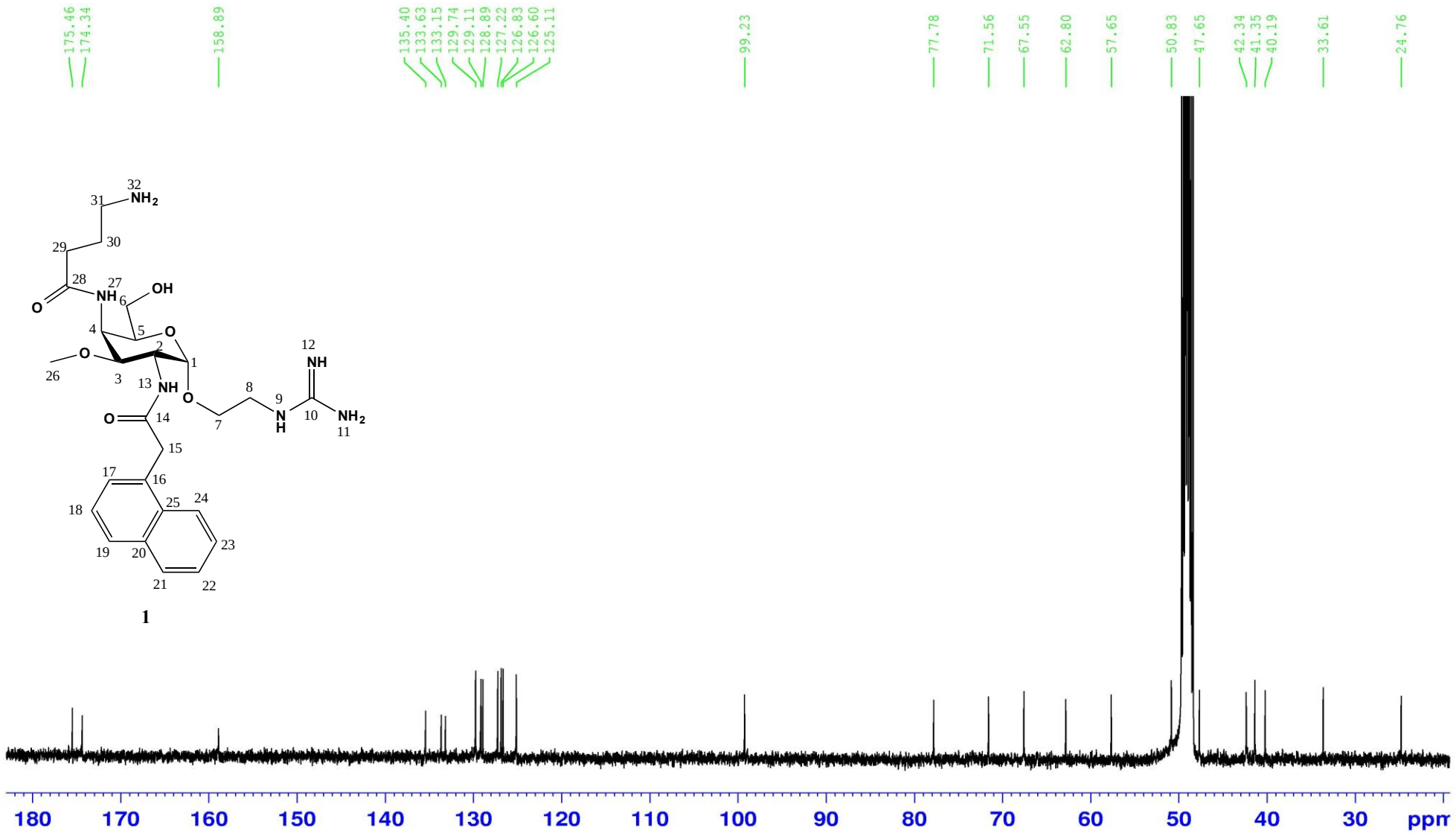
500 MHz, ^{1}H NMR, MeOH-d_4



100 MHz, ^{13}C NMR, MeOH-d_4



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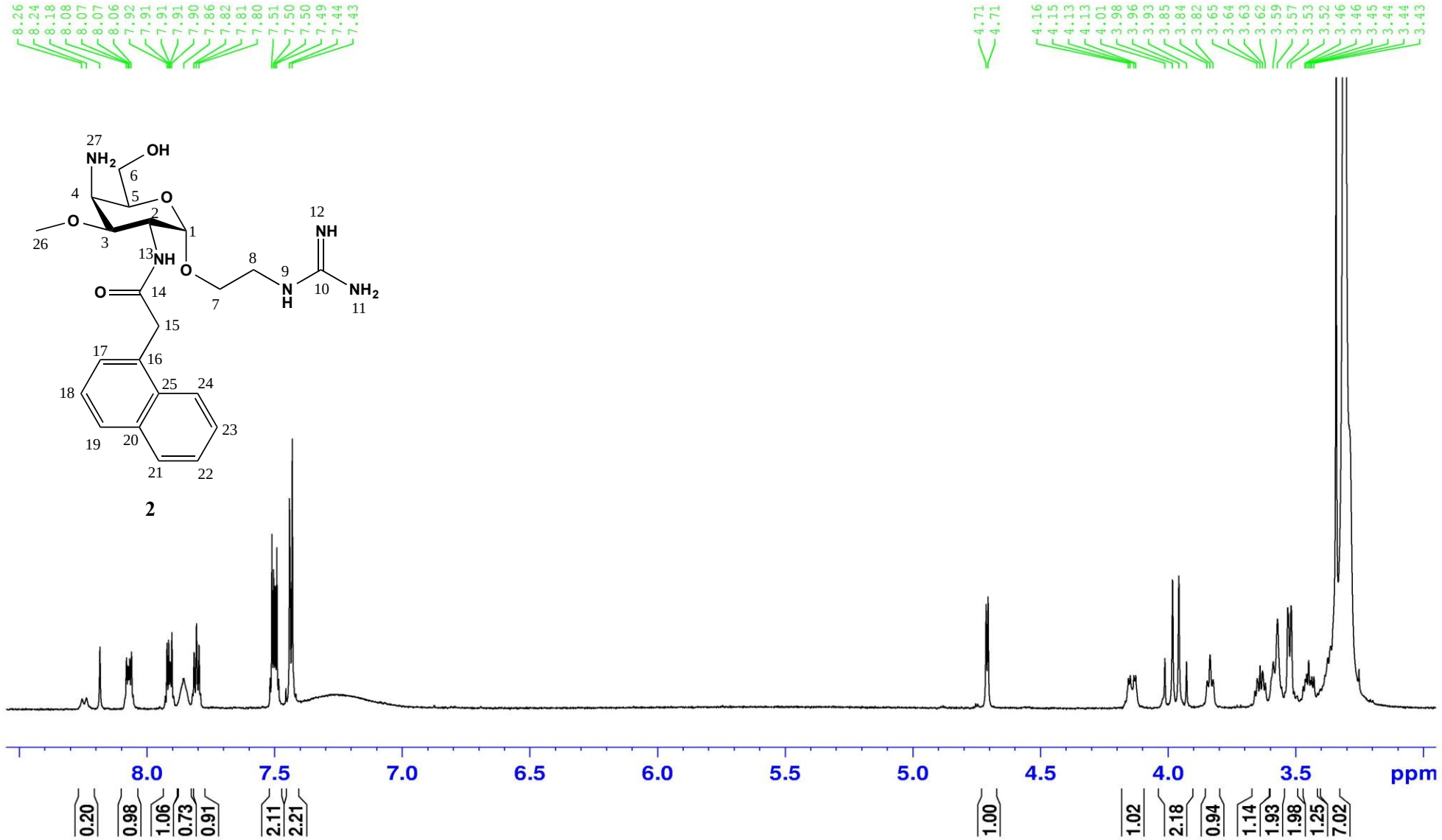
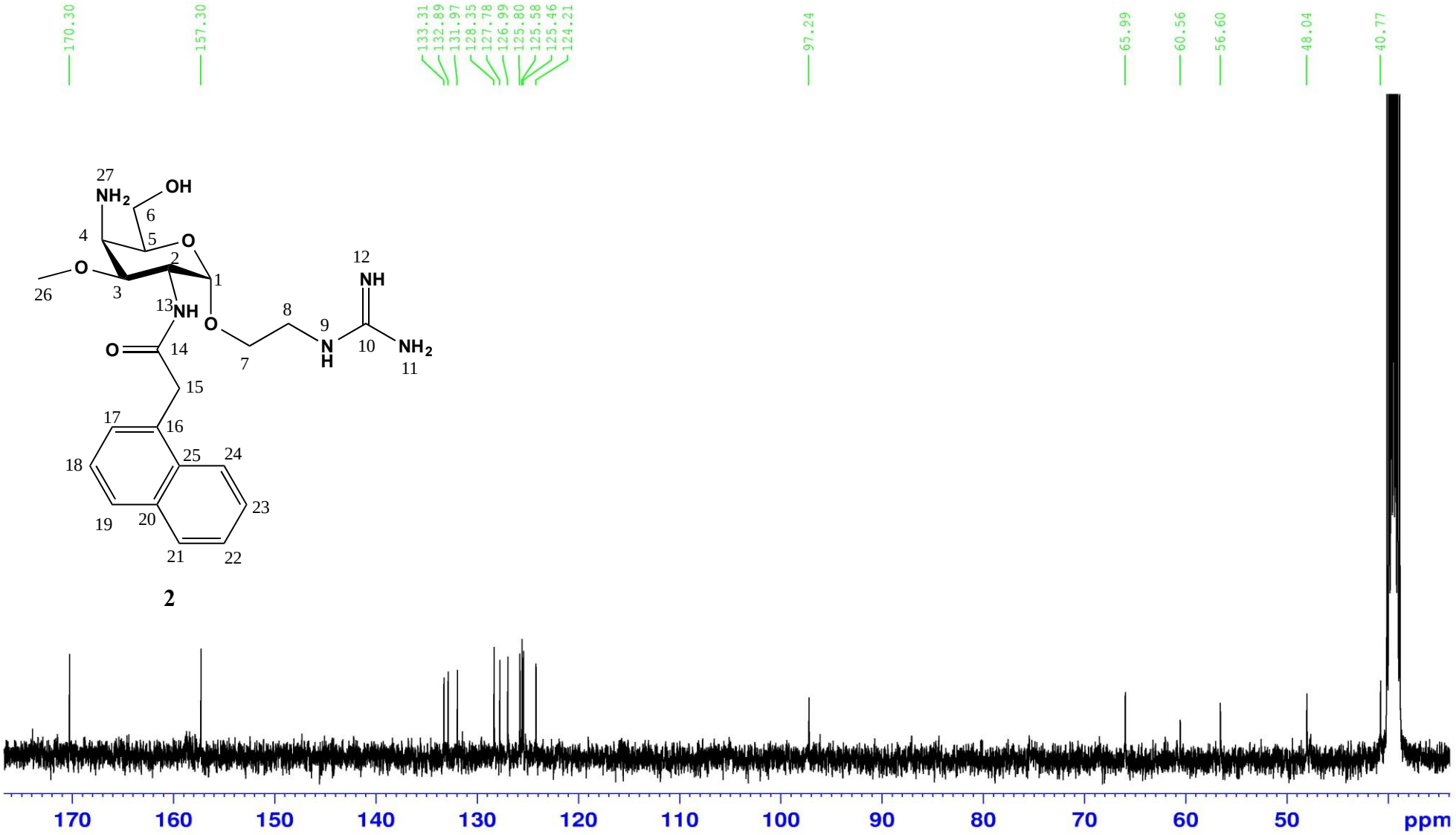
500 MHz, ^{1}H NMR, DMSO-d_6



100 MHz, ^{13}C NMR, DMSO-d_6



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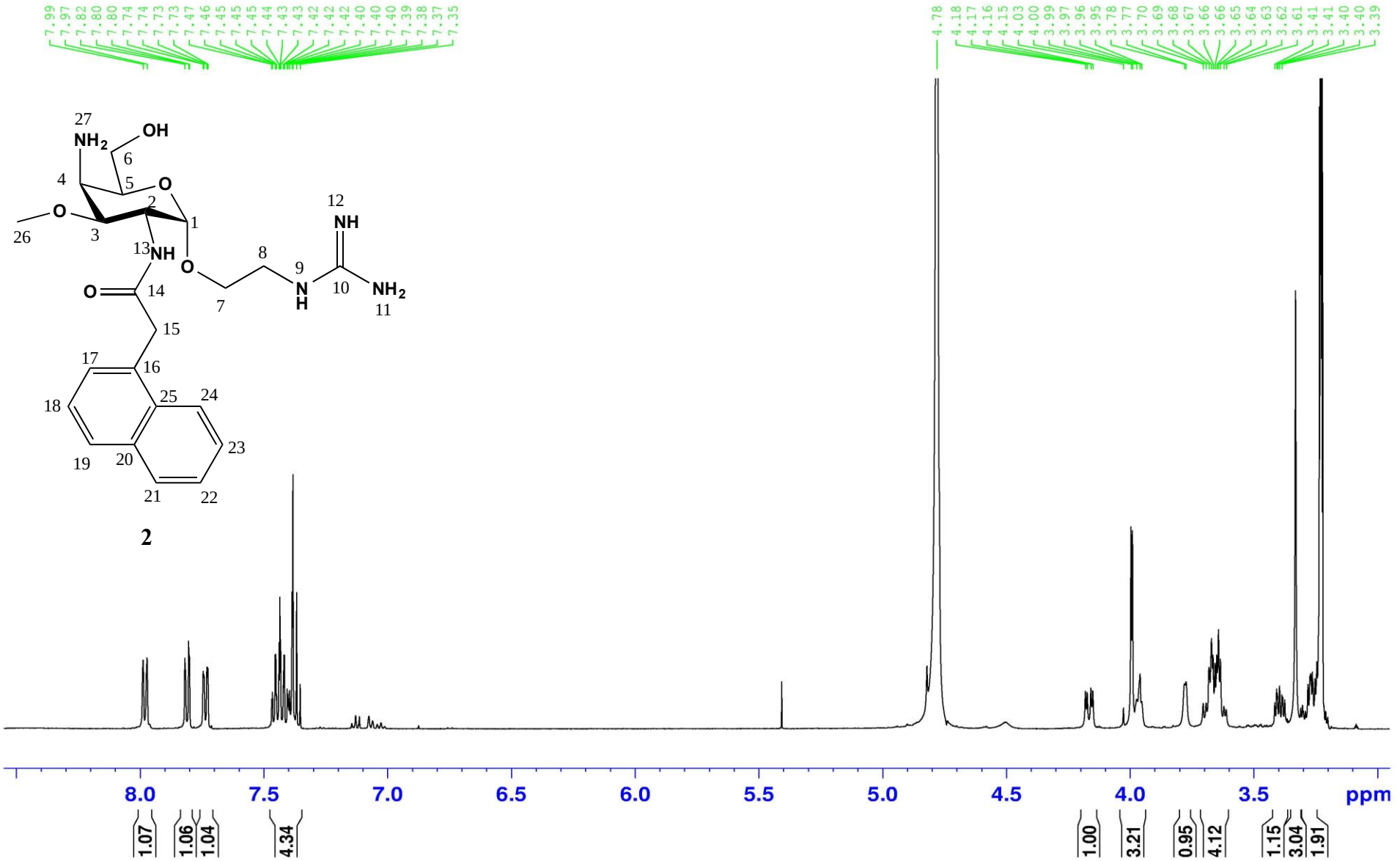
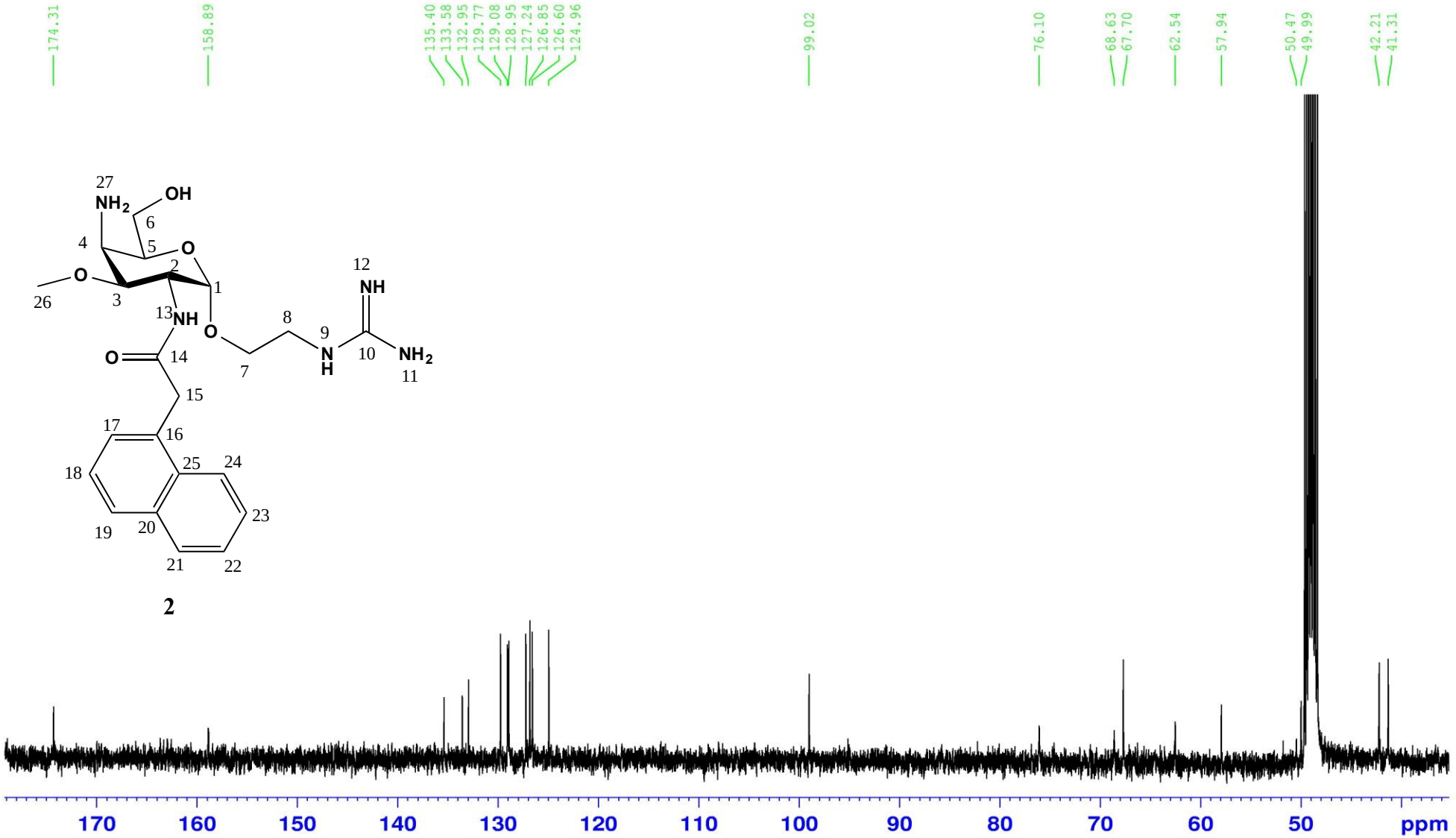
500 MHz, ^{1}H NMR, MeOH-d_4



100 MHz, ^{13}C NMR, MeOH-d_4



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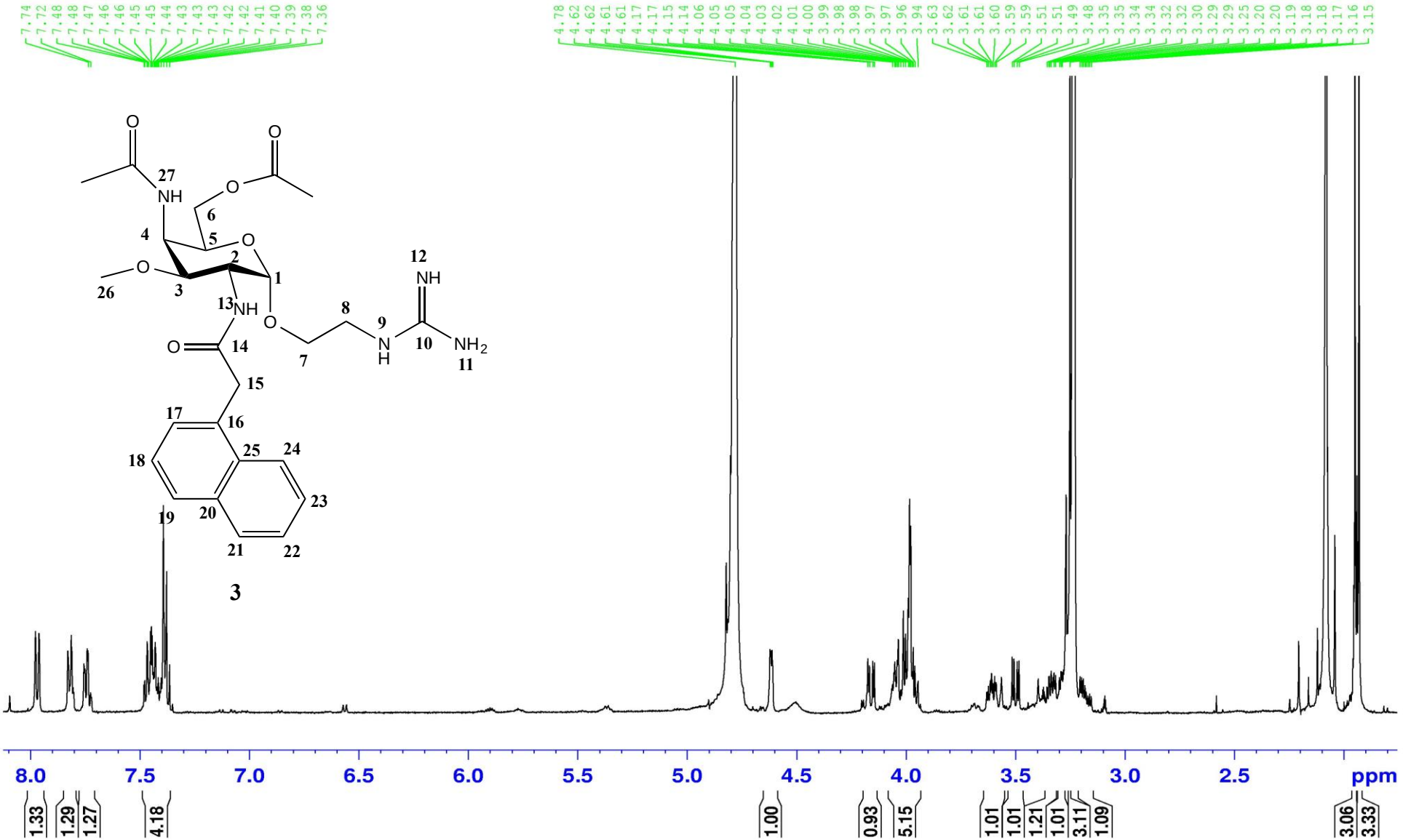
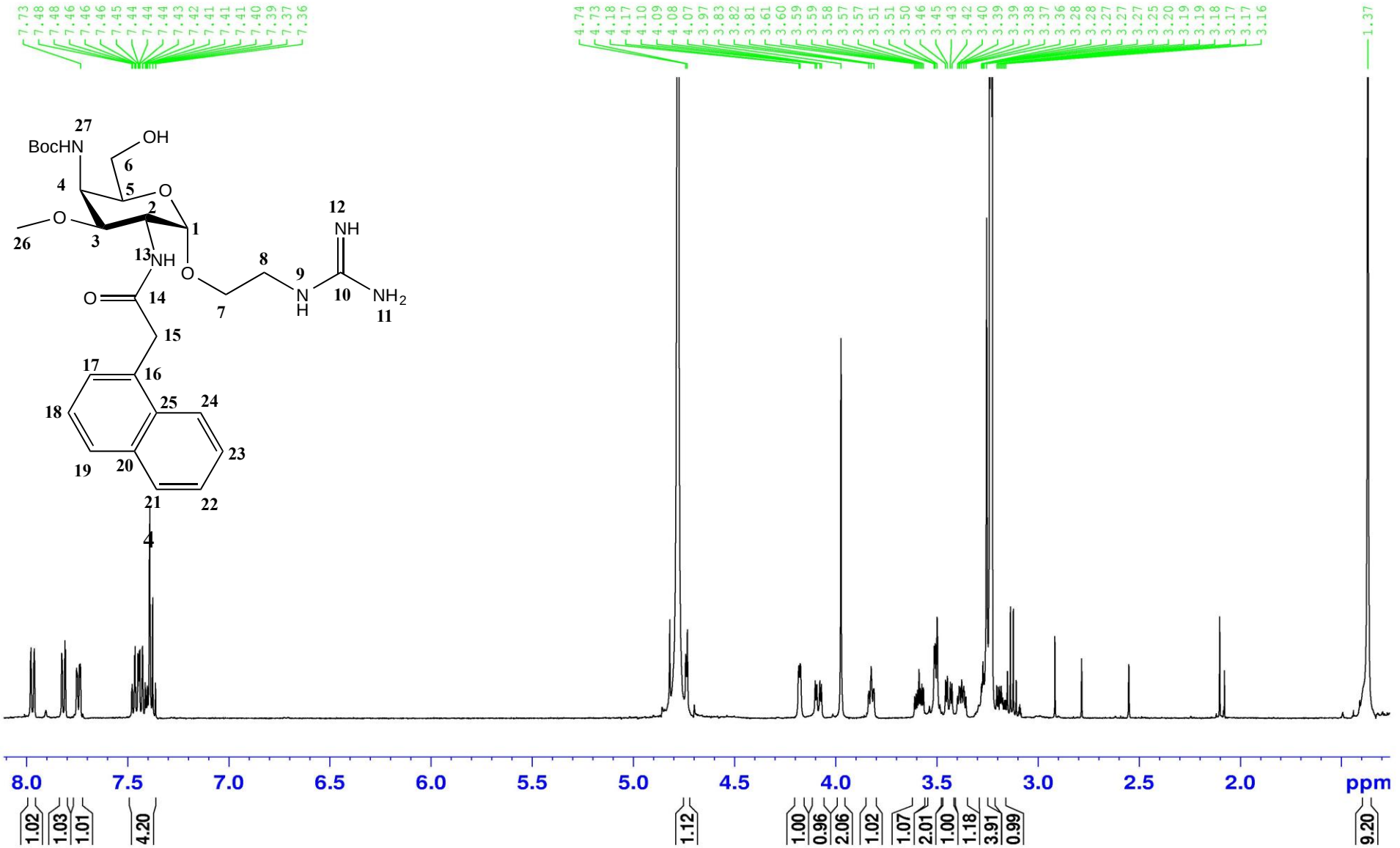
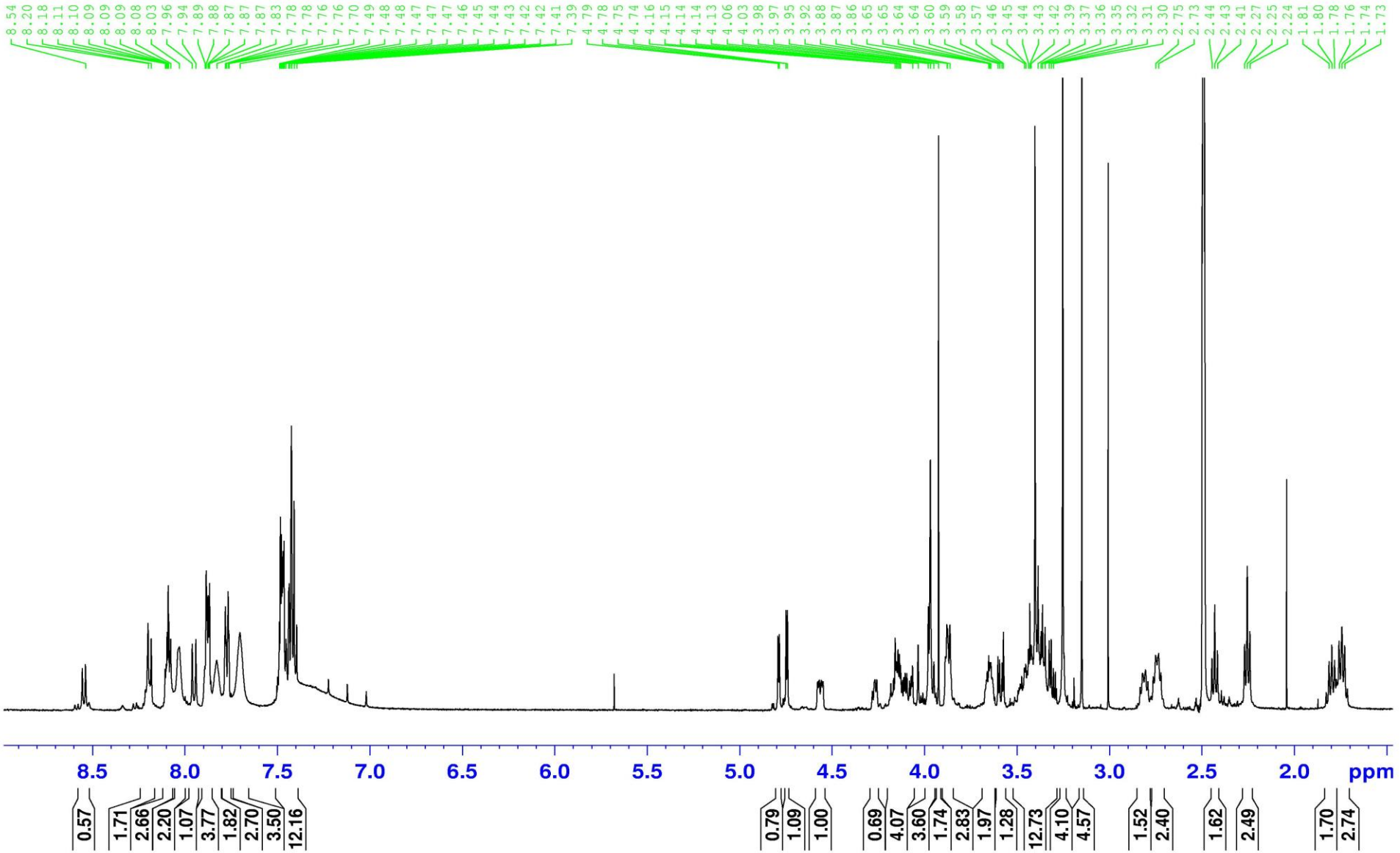
500 MHz, ^{1}H NMR, MeOH-d_4



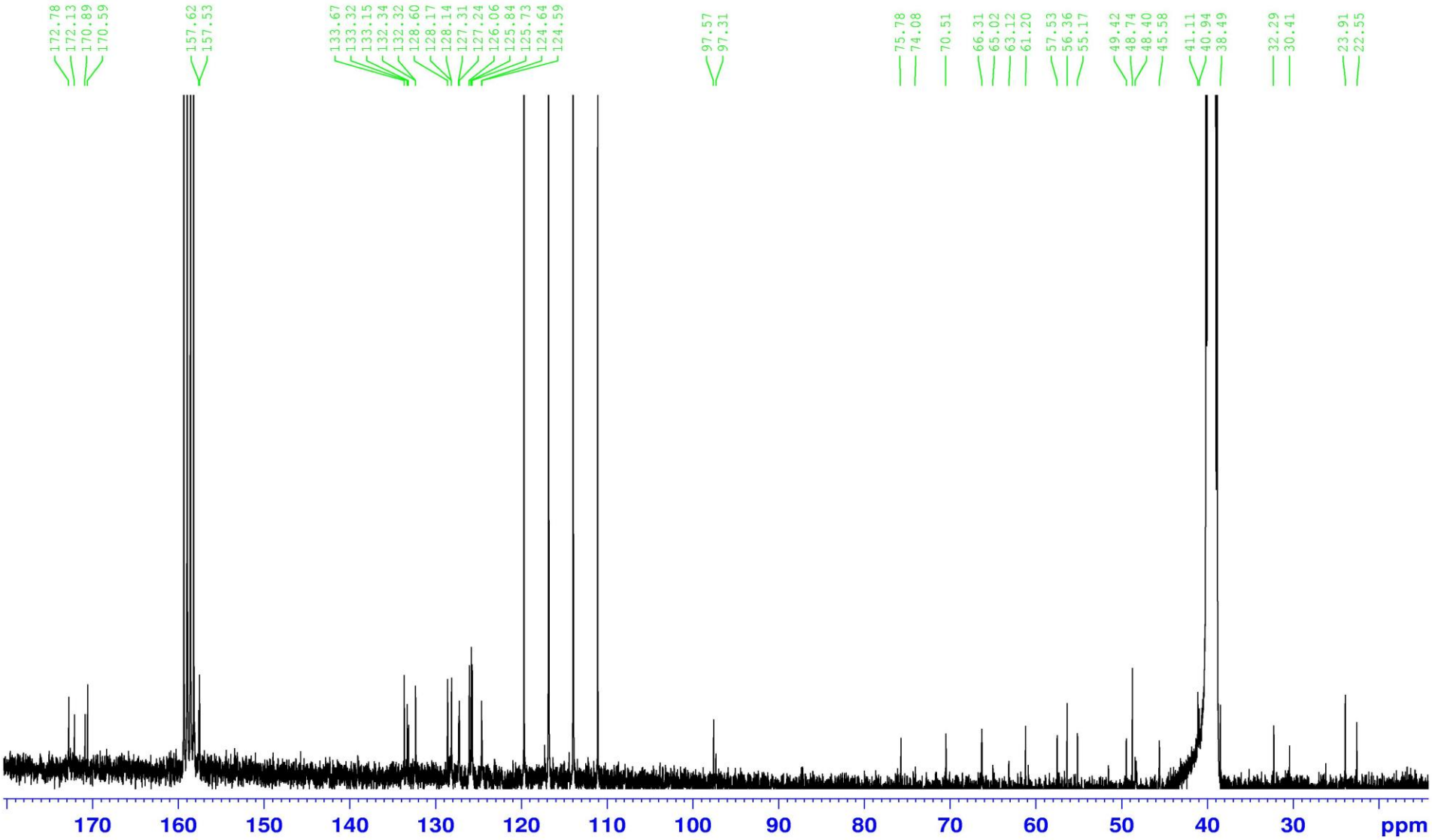
500 MHz, ^{1}H NMR, MeOH-d_4



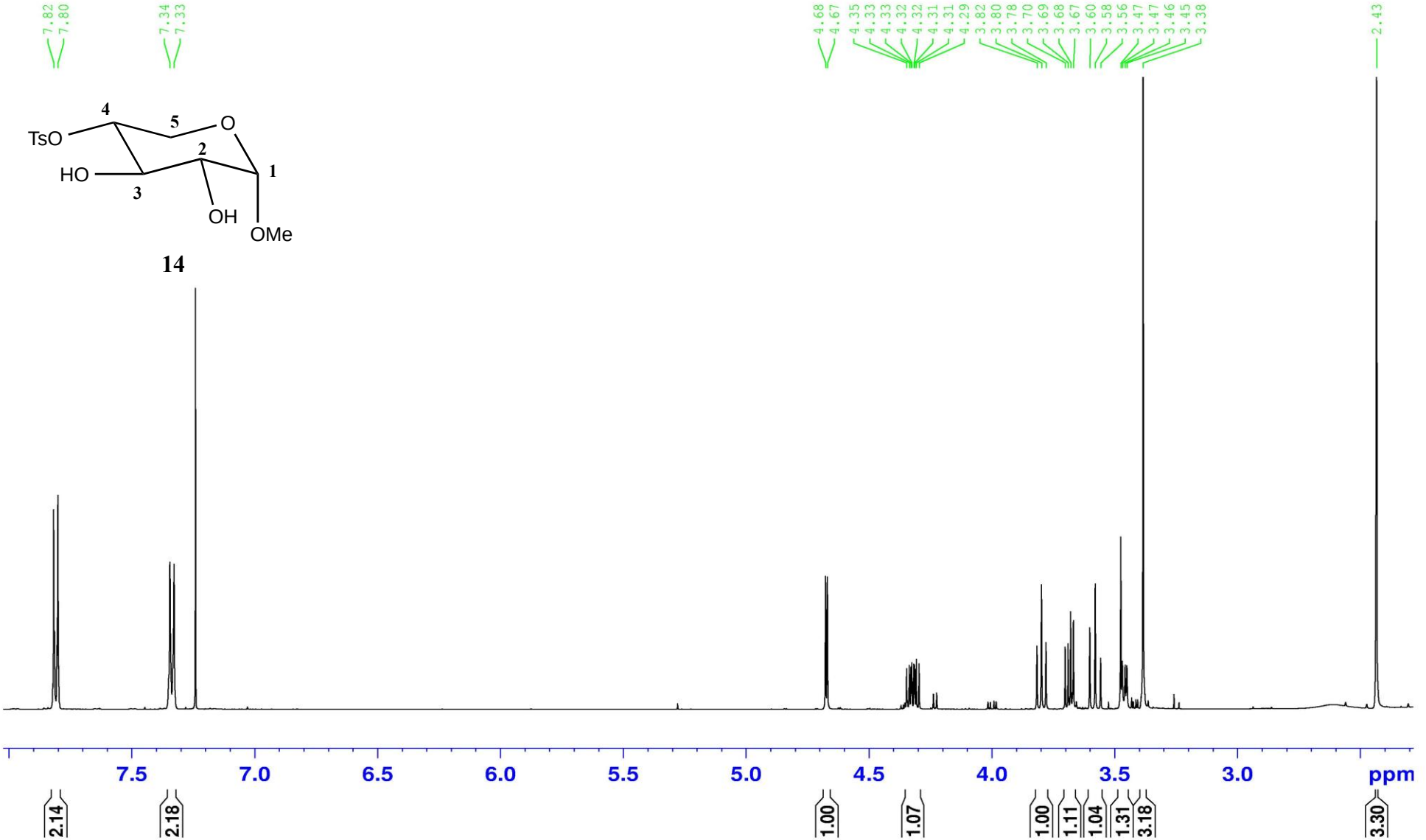
500 MHz, ^{1}H NMR, reaction mixture of **1** in 10% TFA in DMSO-d_6 at 80 °C for 6 h (**1**: Intermediate **5** = 3:2)



100 MHz, ^{13}C NMR, reaction mixture of **1** in 10% TFA in DMSO-d_6 at 80 °C for 6 h (**1**: Intermediate **5** = 3:2)

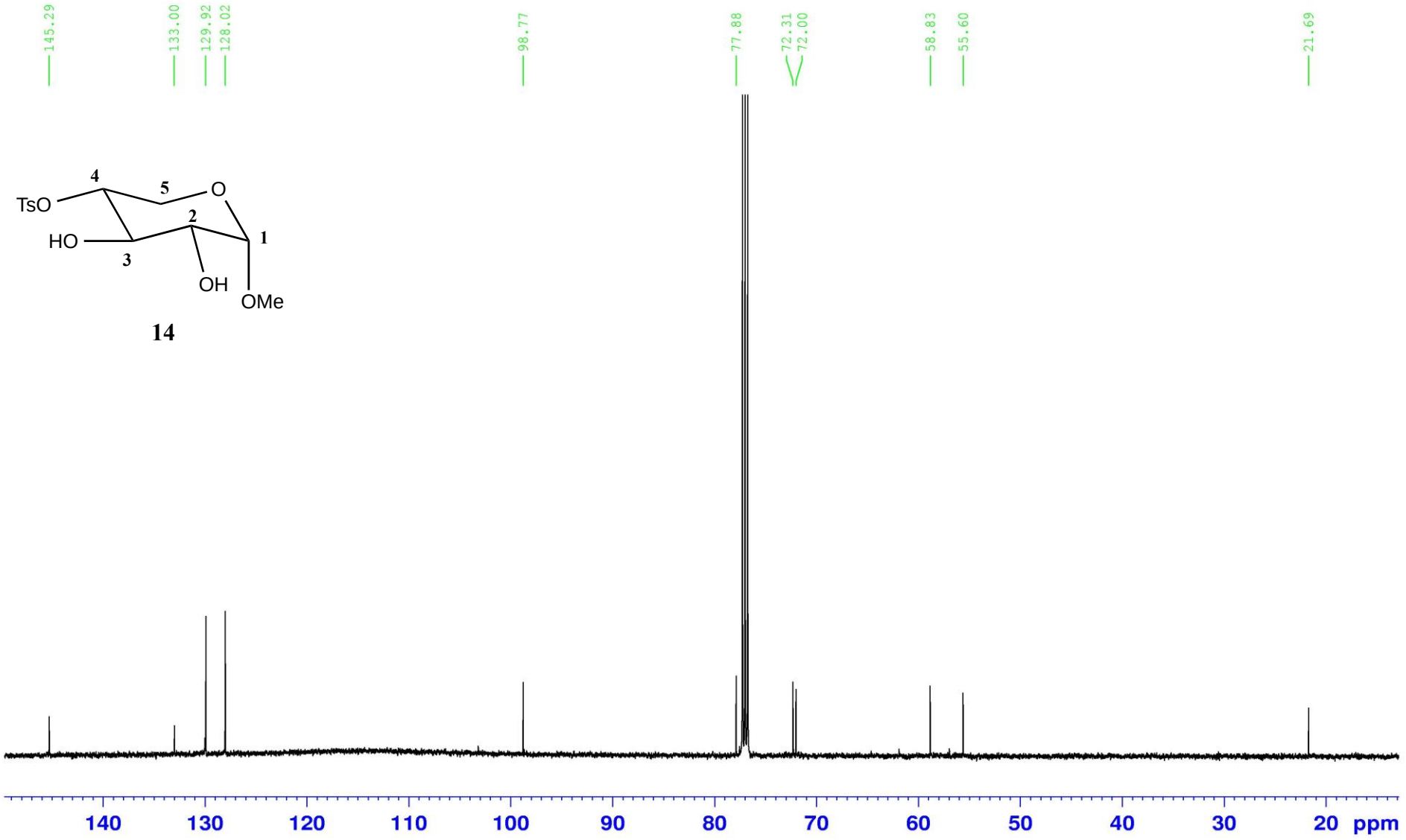


500 MHz, ^{1}H NMR, $CDCl_3$



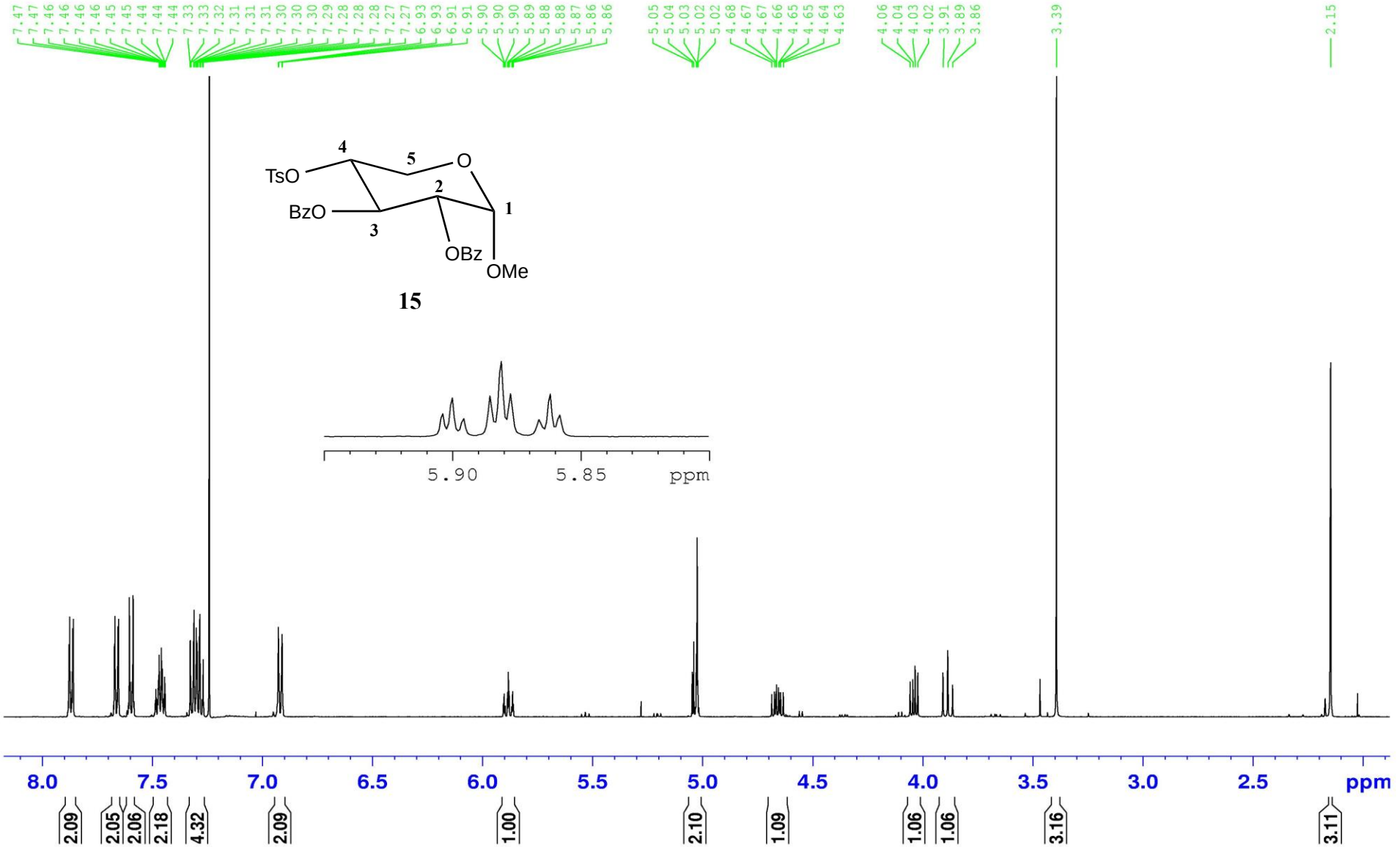
14

100 MHz, ^{13}C NMR, $CDCl_3$

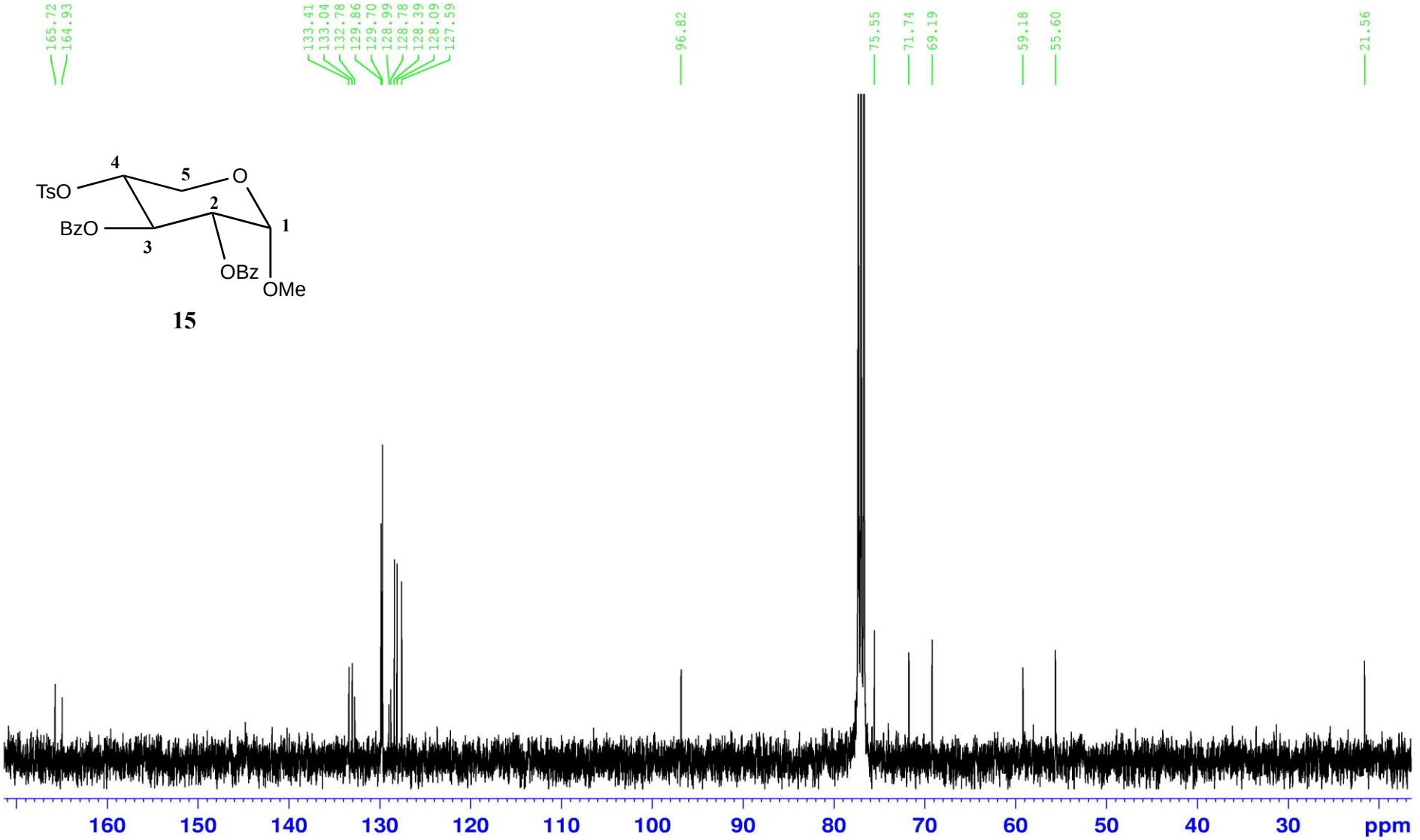


14

500 MHz, ^{1}H NMR, $CDCl_3$

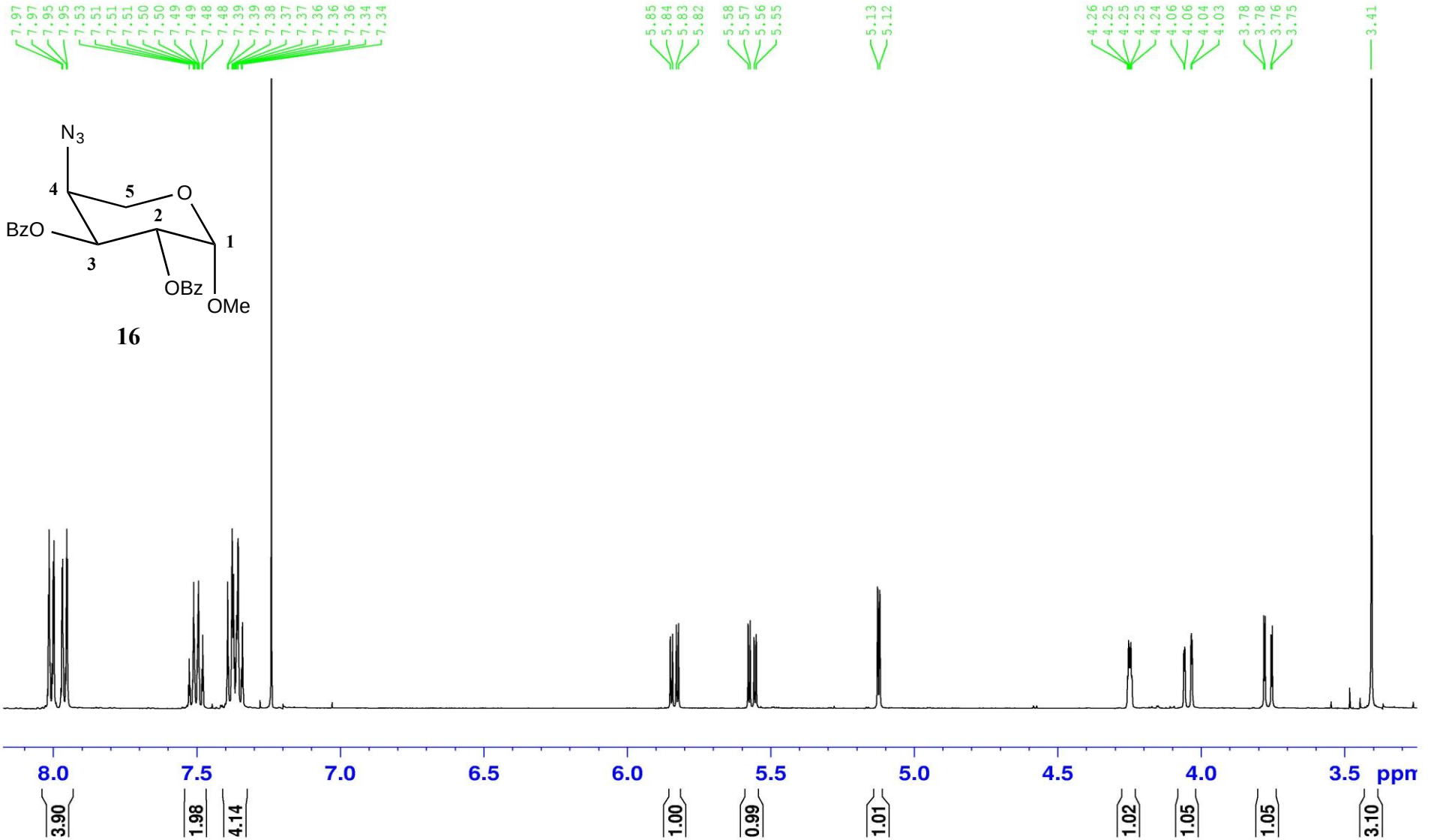


100 MHz, ^{13}C NMR, $CDCl_3$

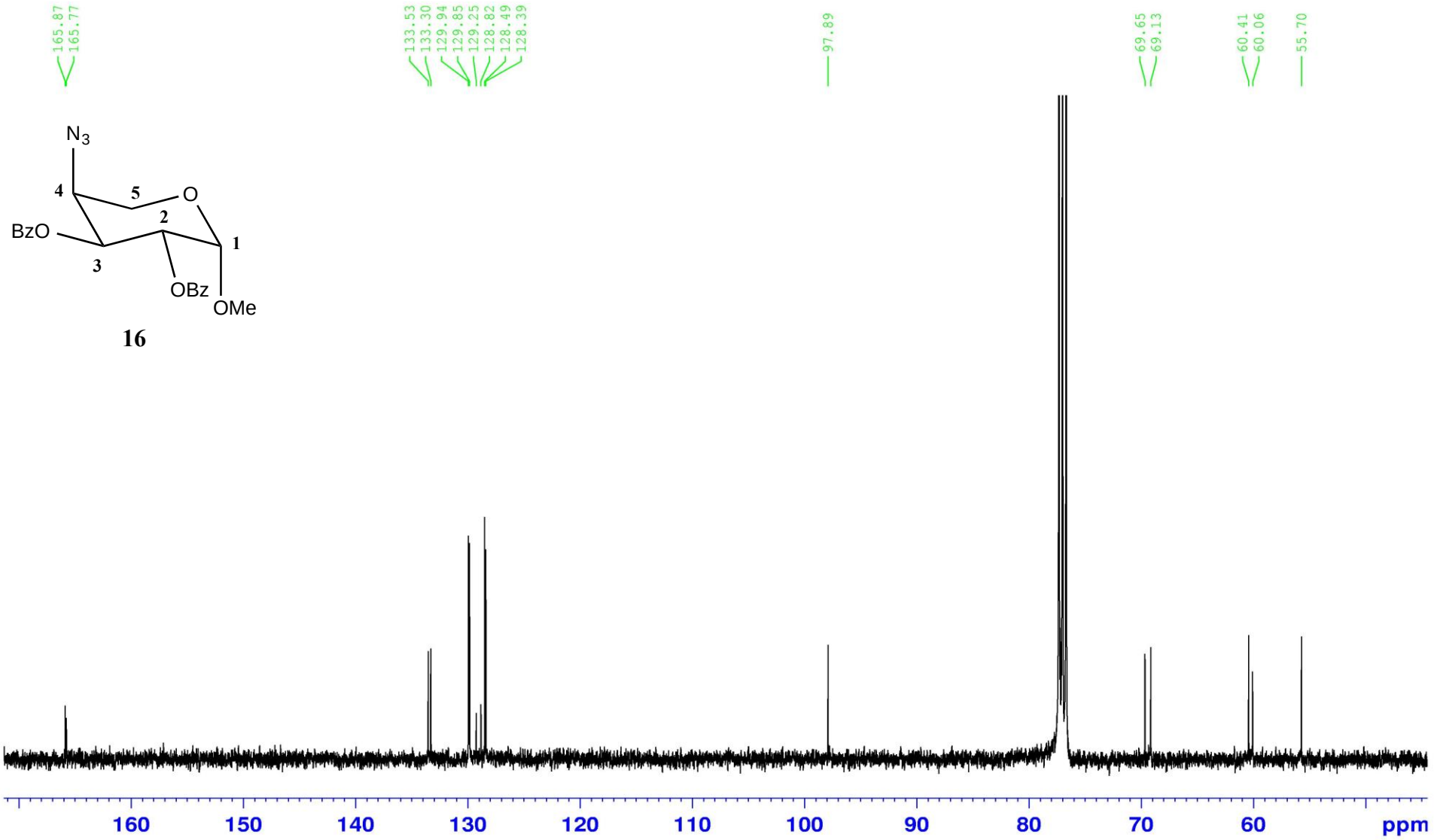


15

500 MHz, ^{1}H NMR, $CDCl_3$

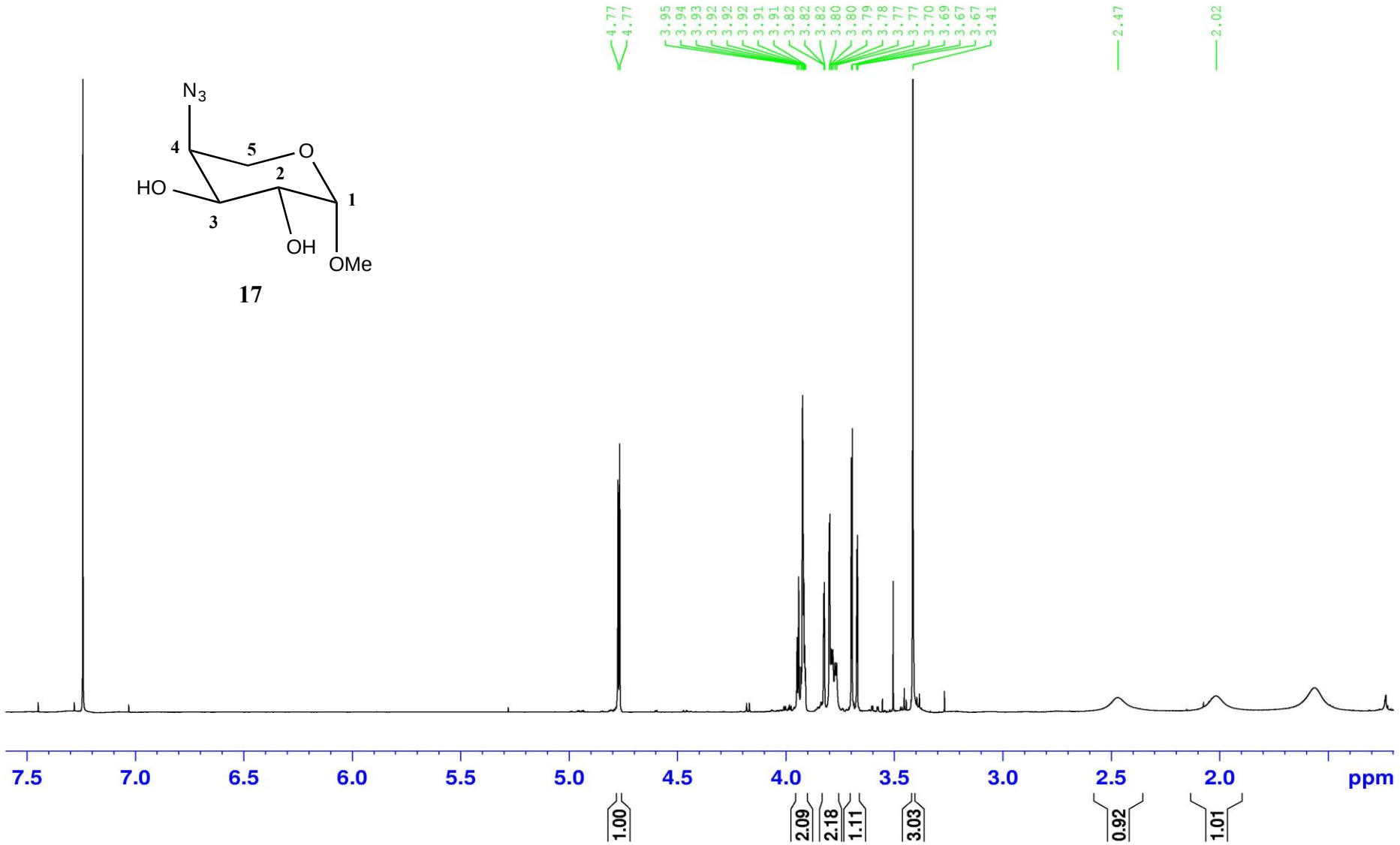


100 MHz, ^{13}C NMR, $CDCl_3$

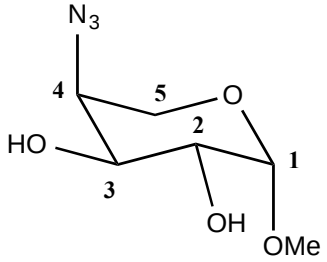


16

500 MHz, ^{1}H NMR, $CDCl_3$

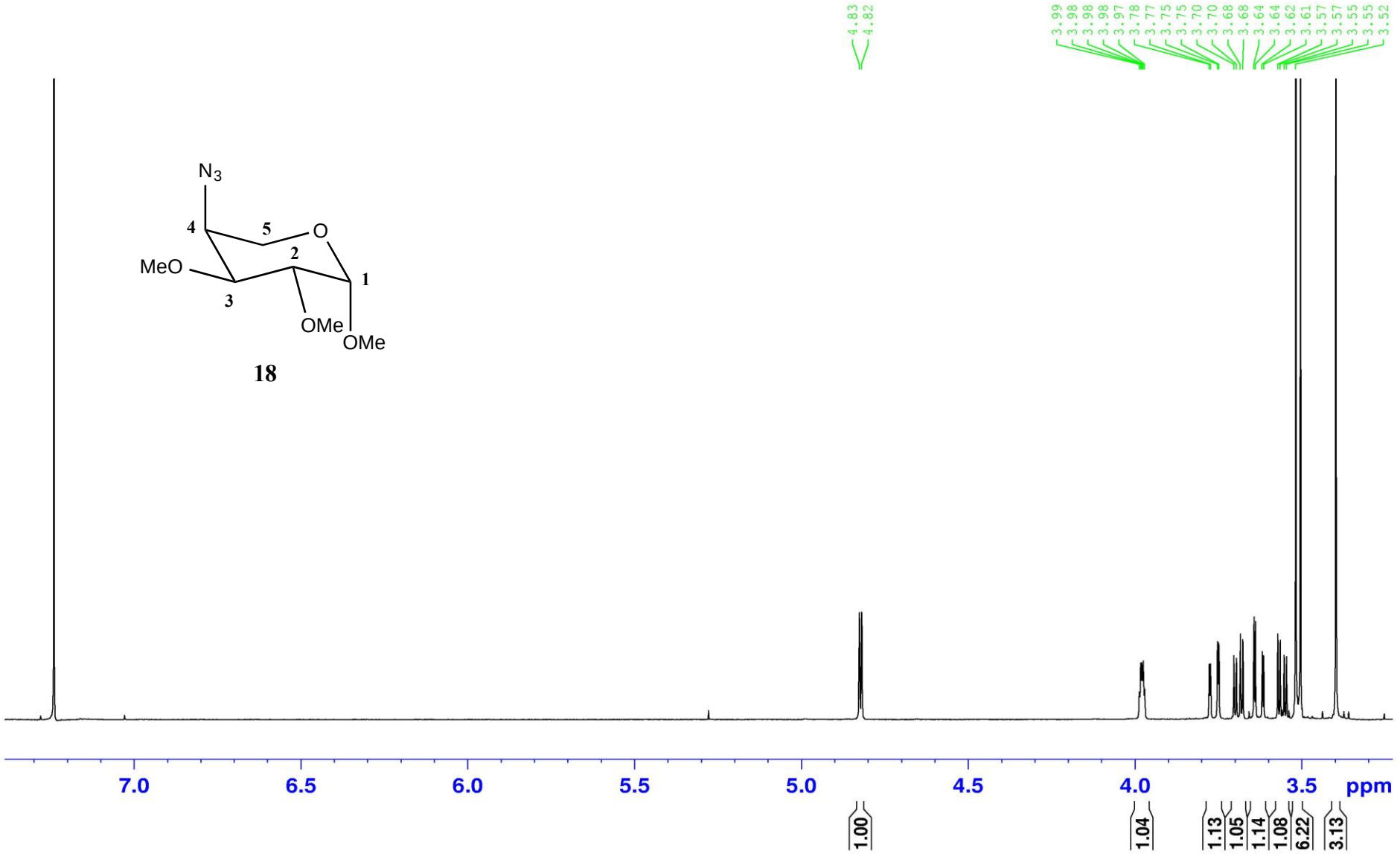


100 MHz, ^{13}C NMR, $CDCl_3$



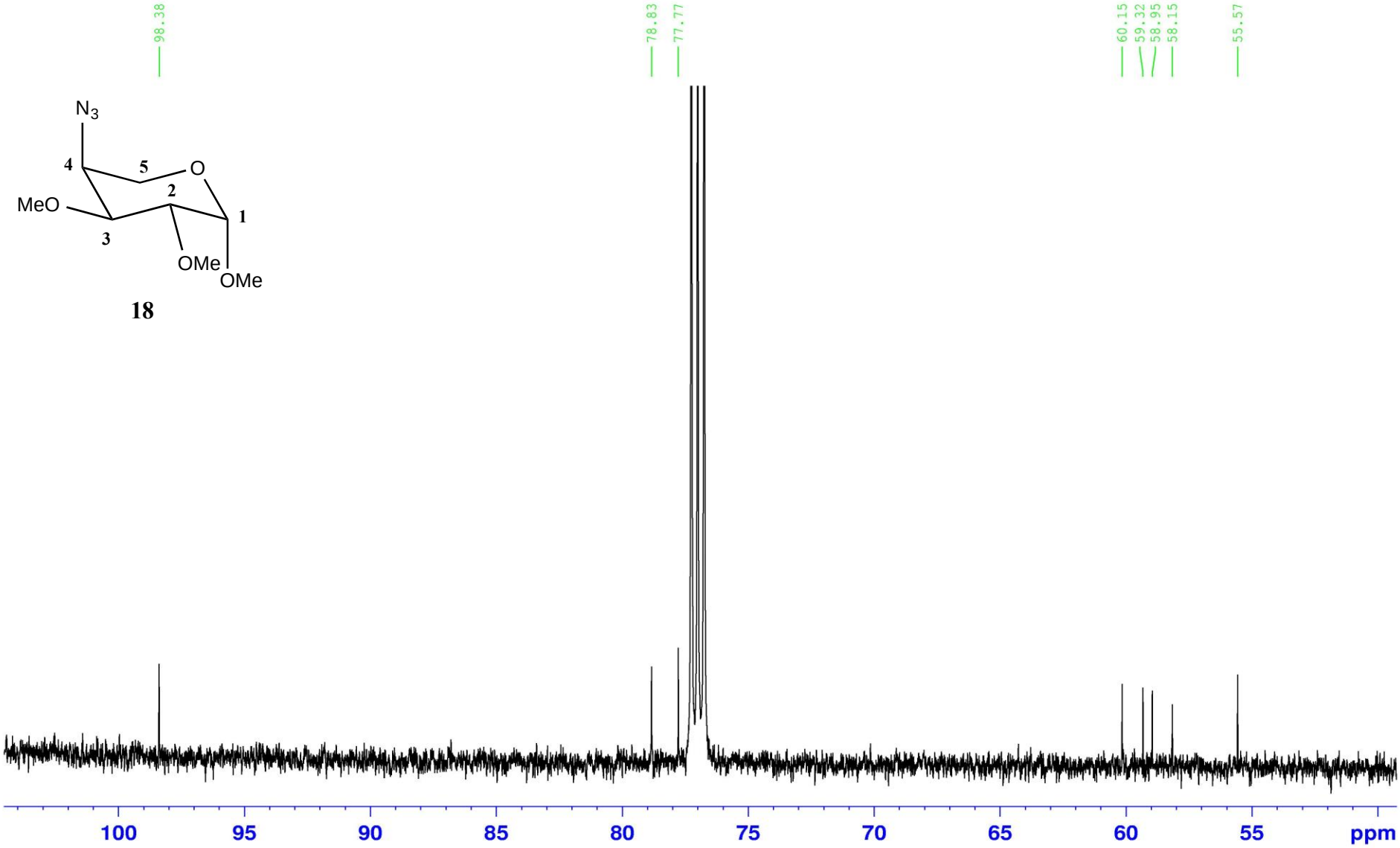
17

500 MHz, ^{1}H NMR, $CDCl_3$



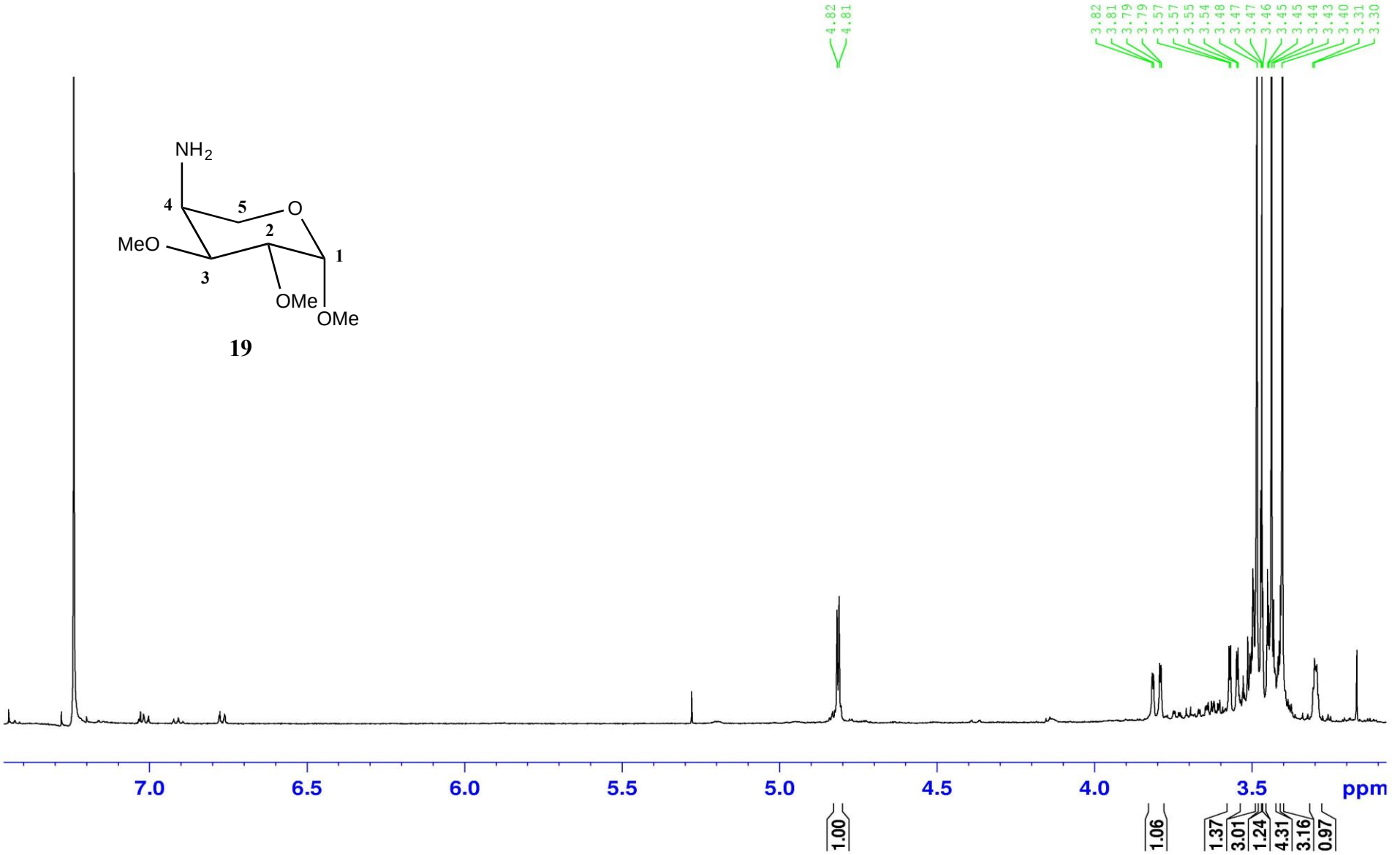
18

100 MHz, ^{13}C NMR, $CDCl_3$



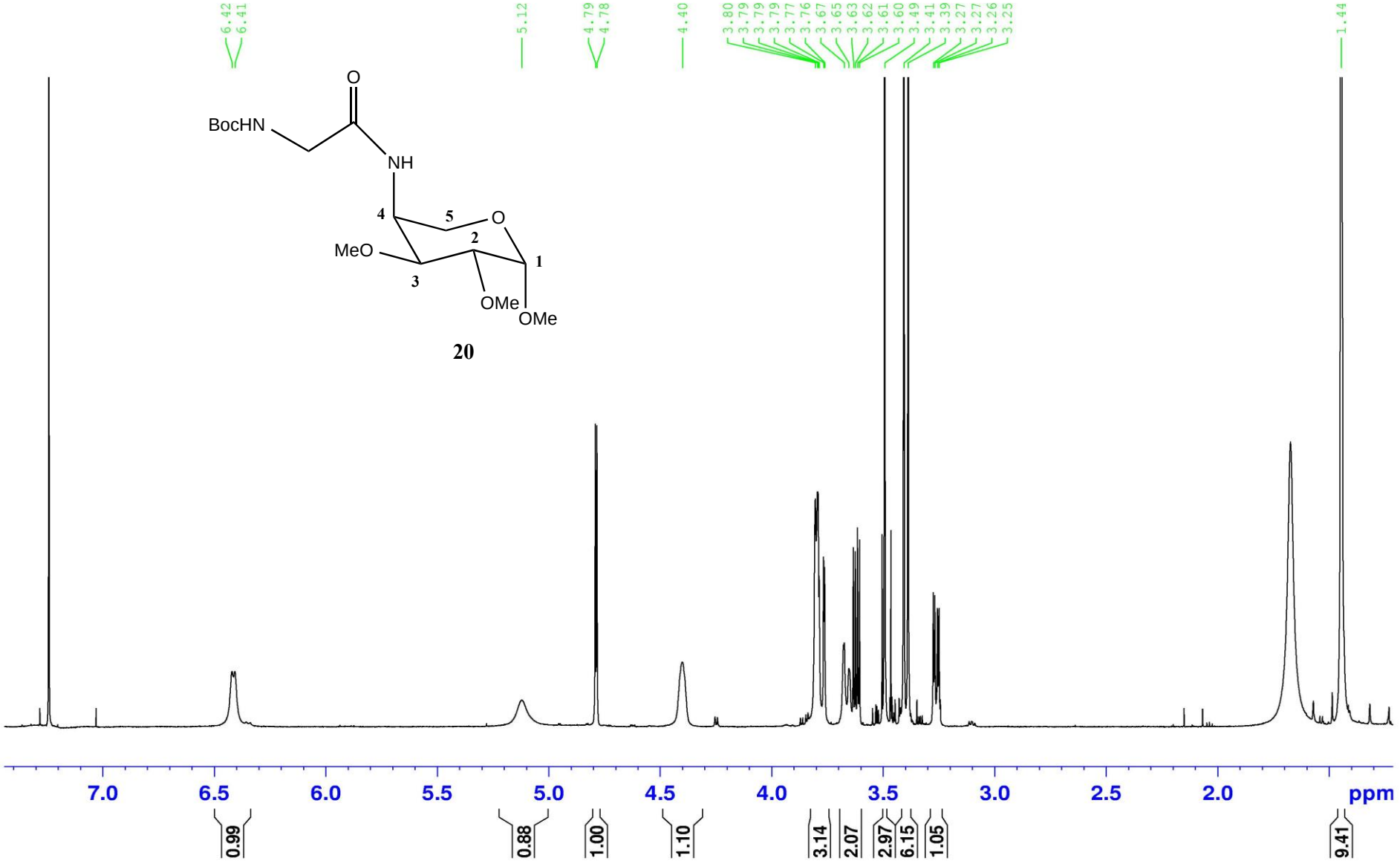
18

500 MHz, ^{1}H NMR, $CDCl_3$

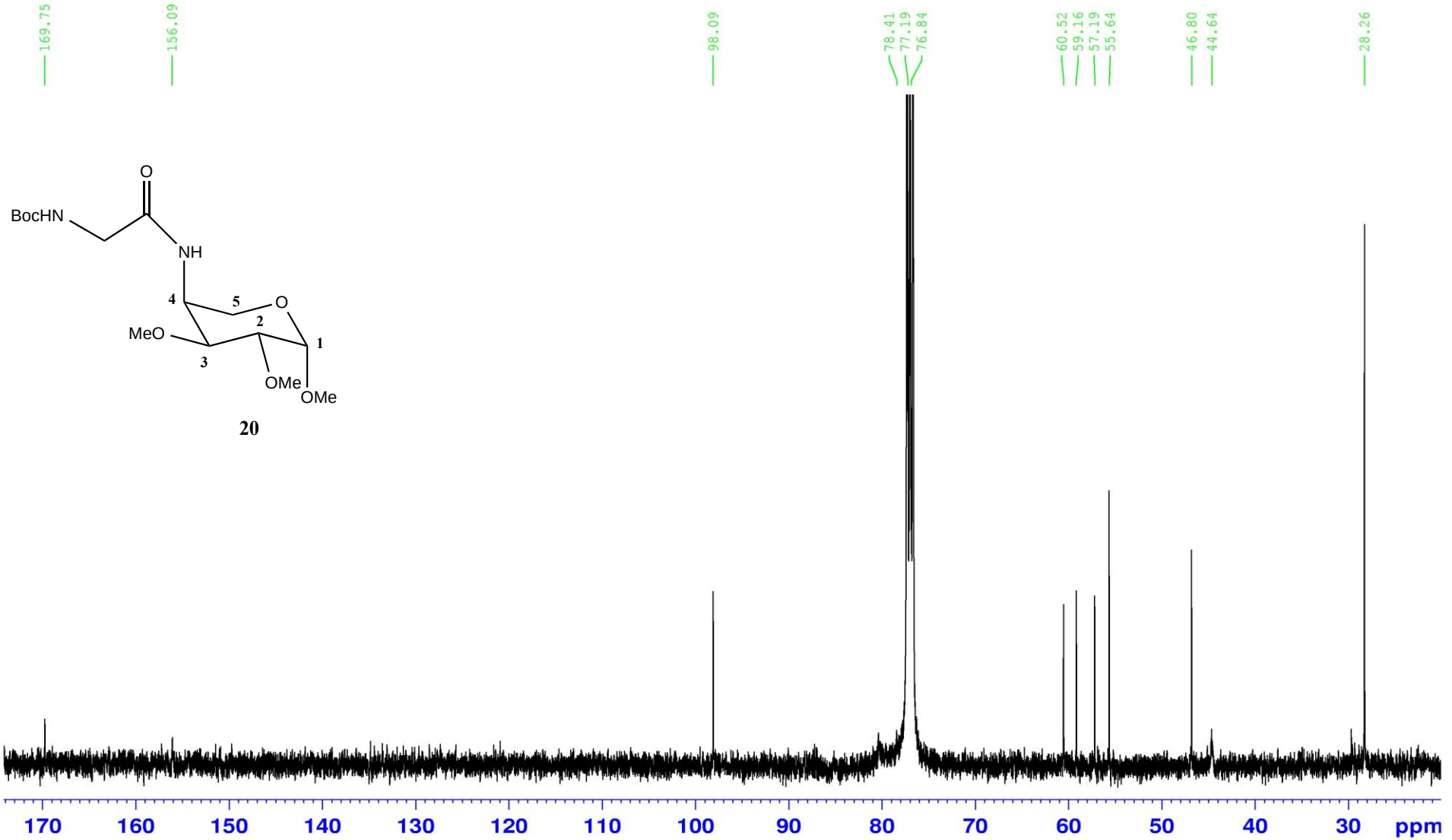


19

500 MHz, ^{1}H NMR, $CDCl_3$

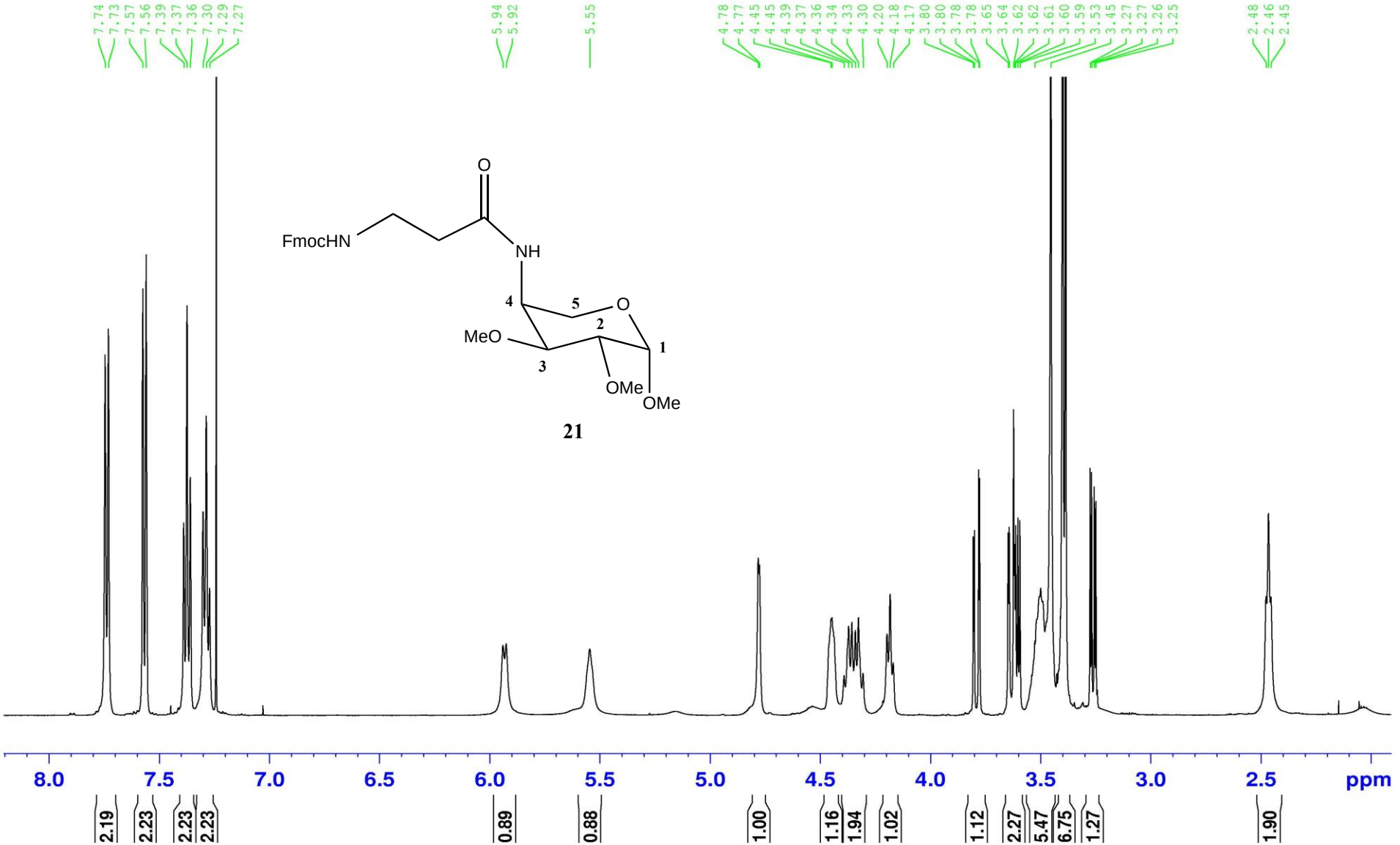


100 MHz, ^{13}C NMR, $CDCl_3$



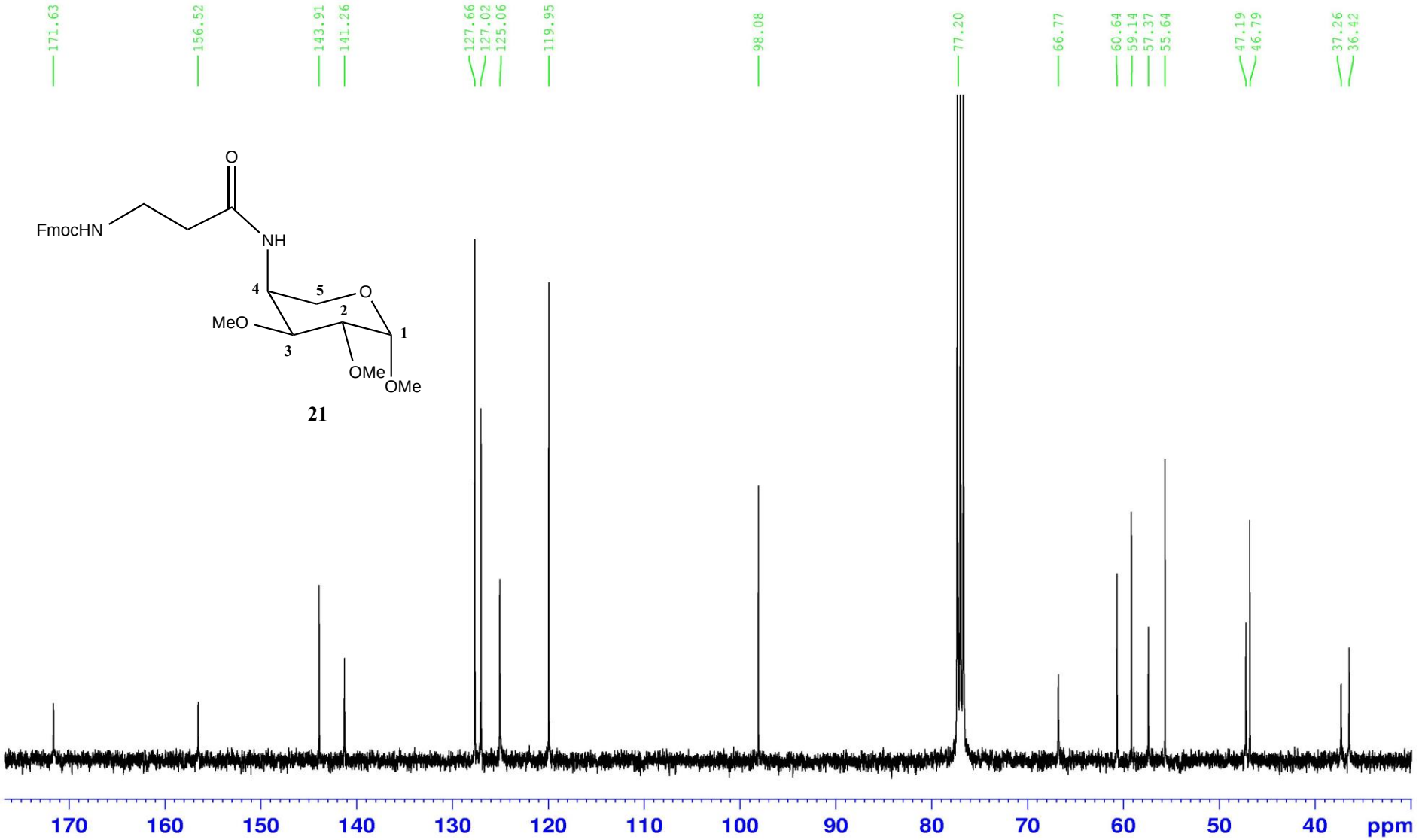
20

500 MHz, ^{1}H NMR, $CDCl_3$



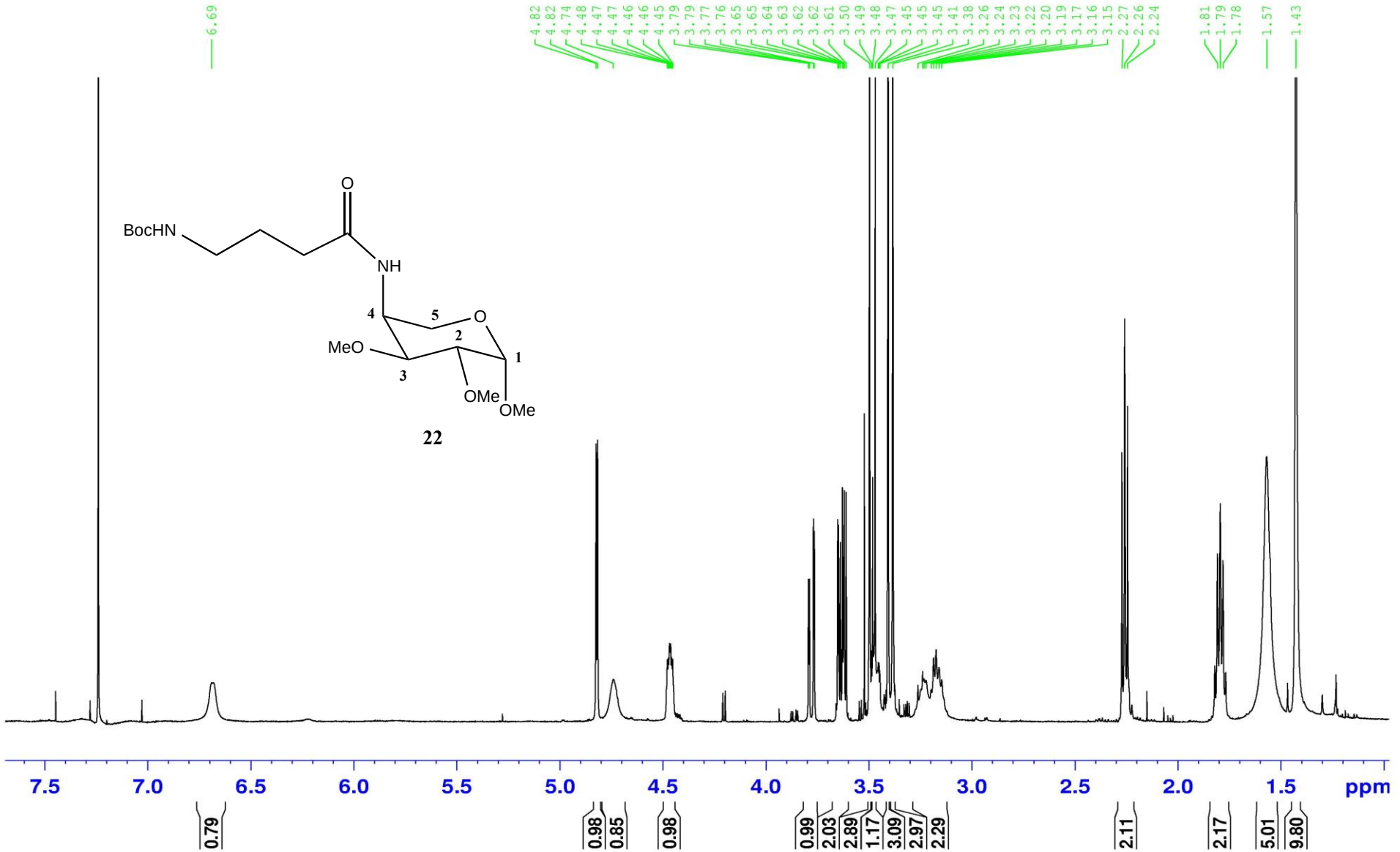
21

100 MHz, ^{13}C NMR, $CDCl_3$

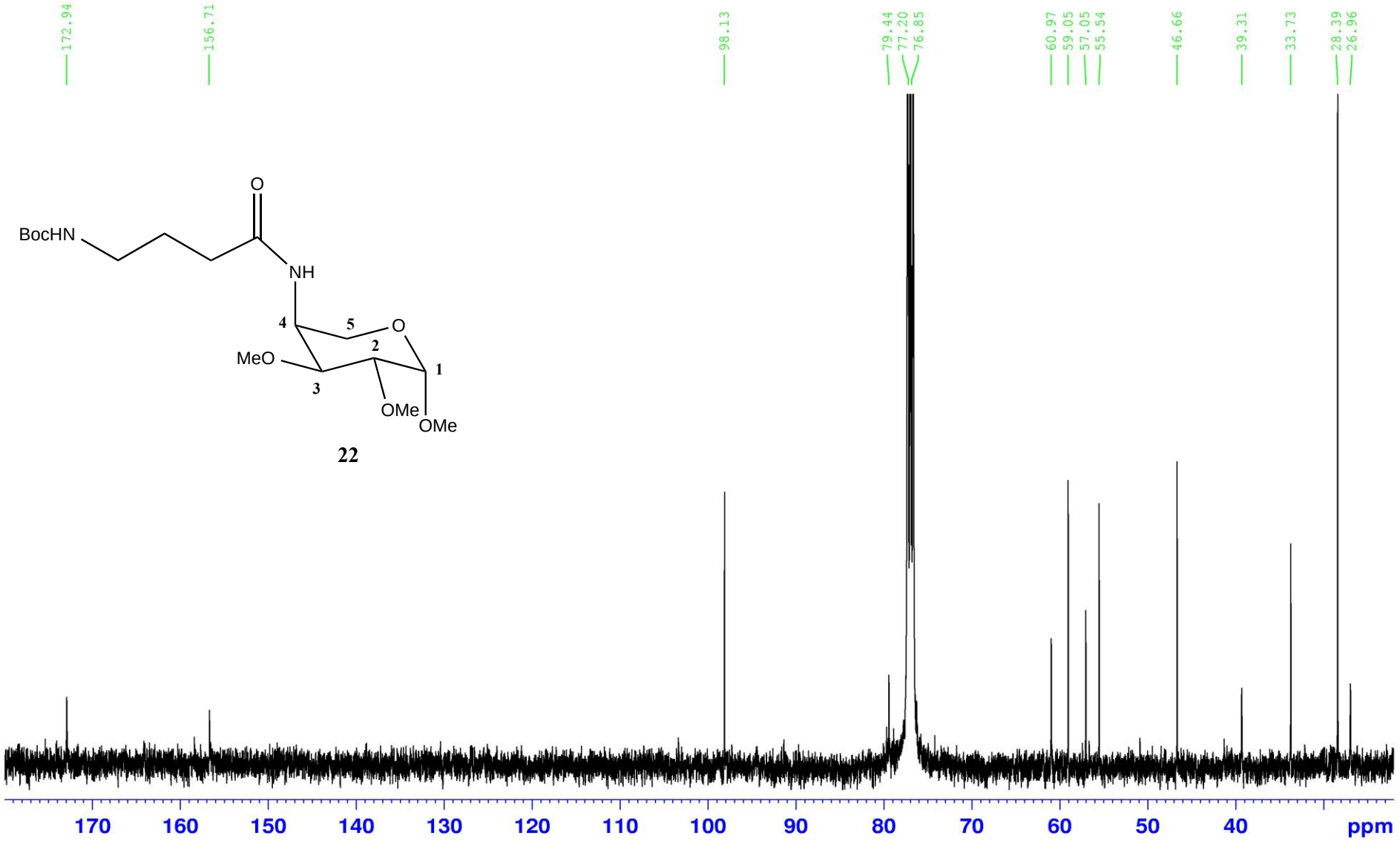


21

500 MHz, ^{1}H NMR, $CDCl_3$

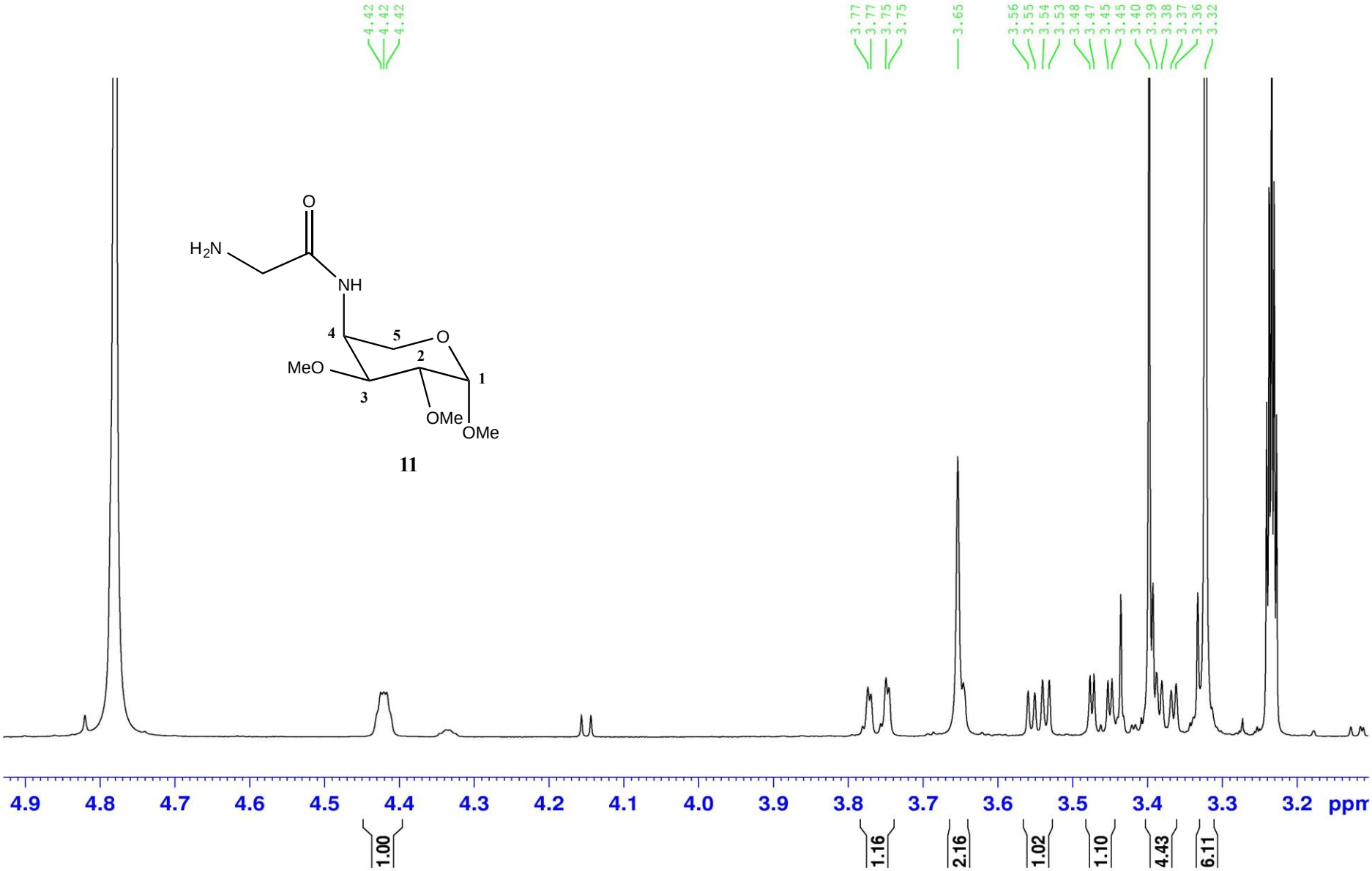


100 MHz, ^{13}C NMR, $CDCl_3$



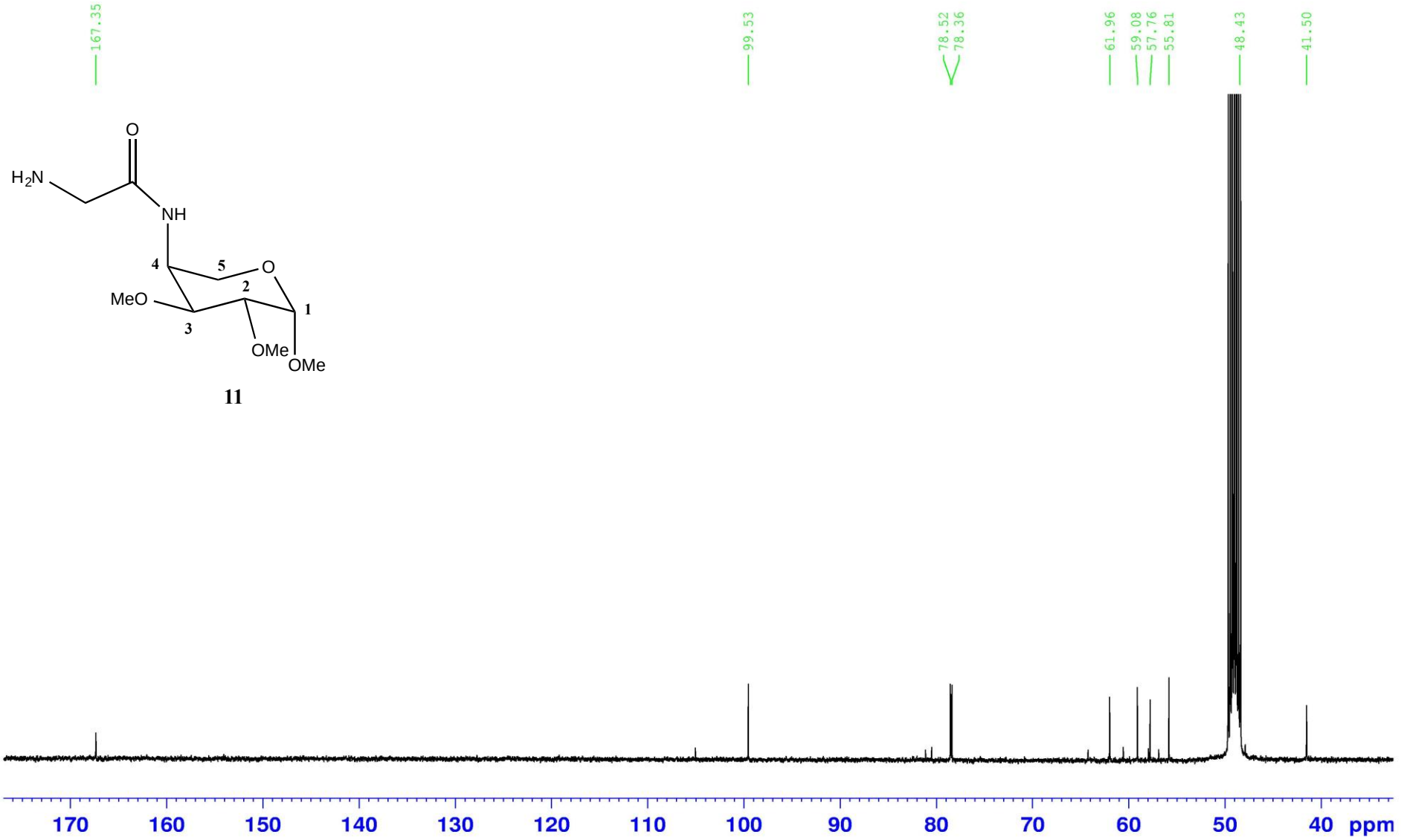
22

500 MHz, ^{1}H NMR, $CDCl_3$



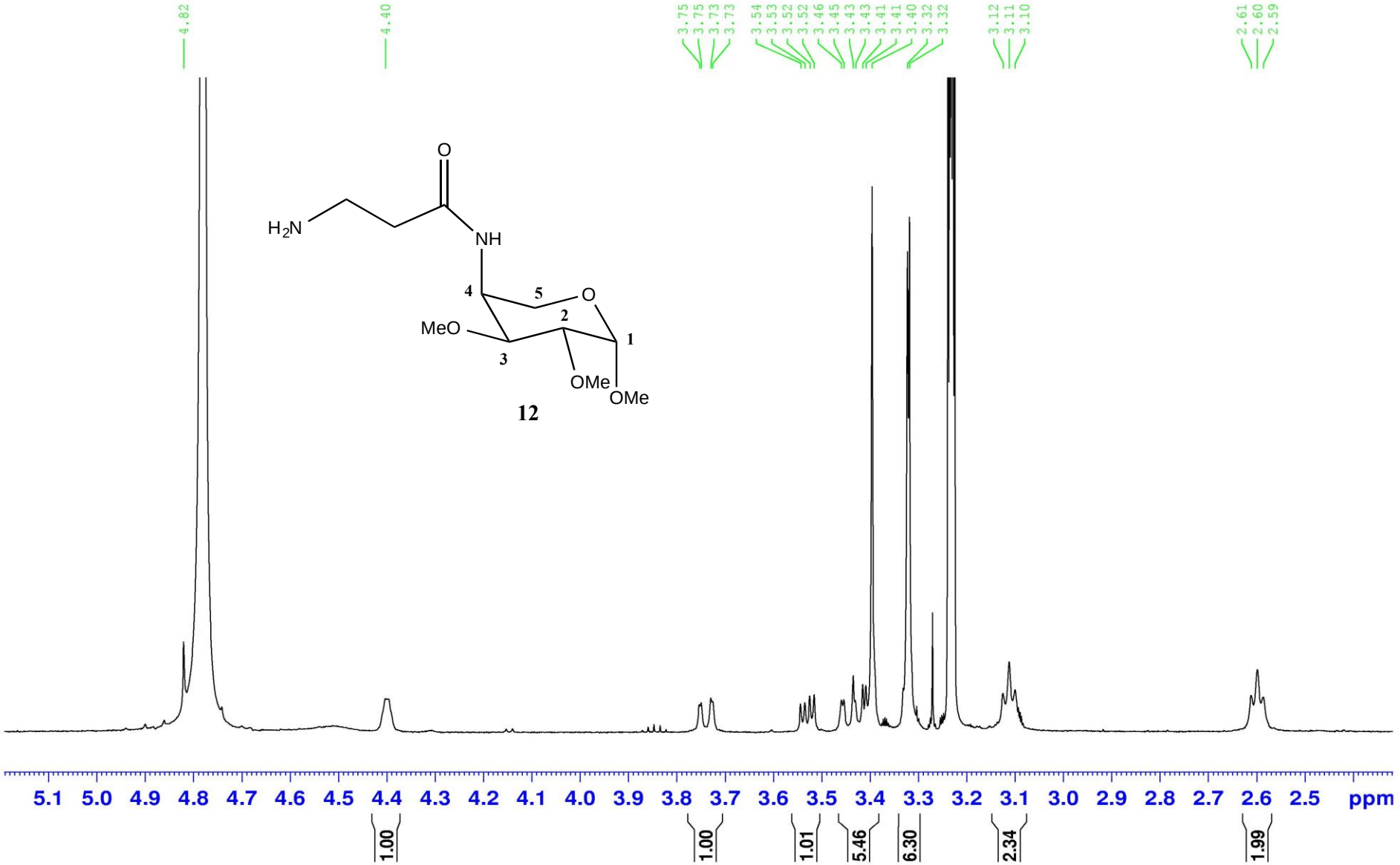
11

100 MHz, ^{13}C NMR, $CDCl_3$

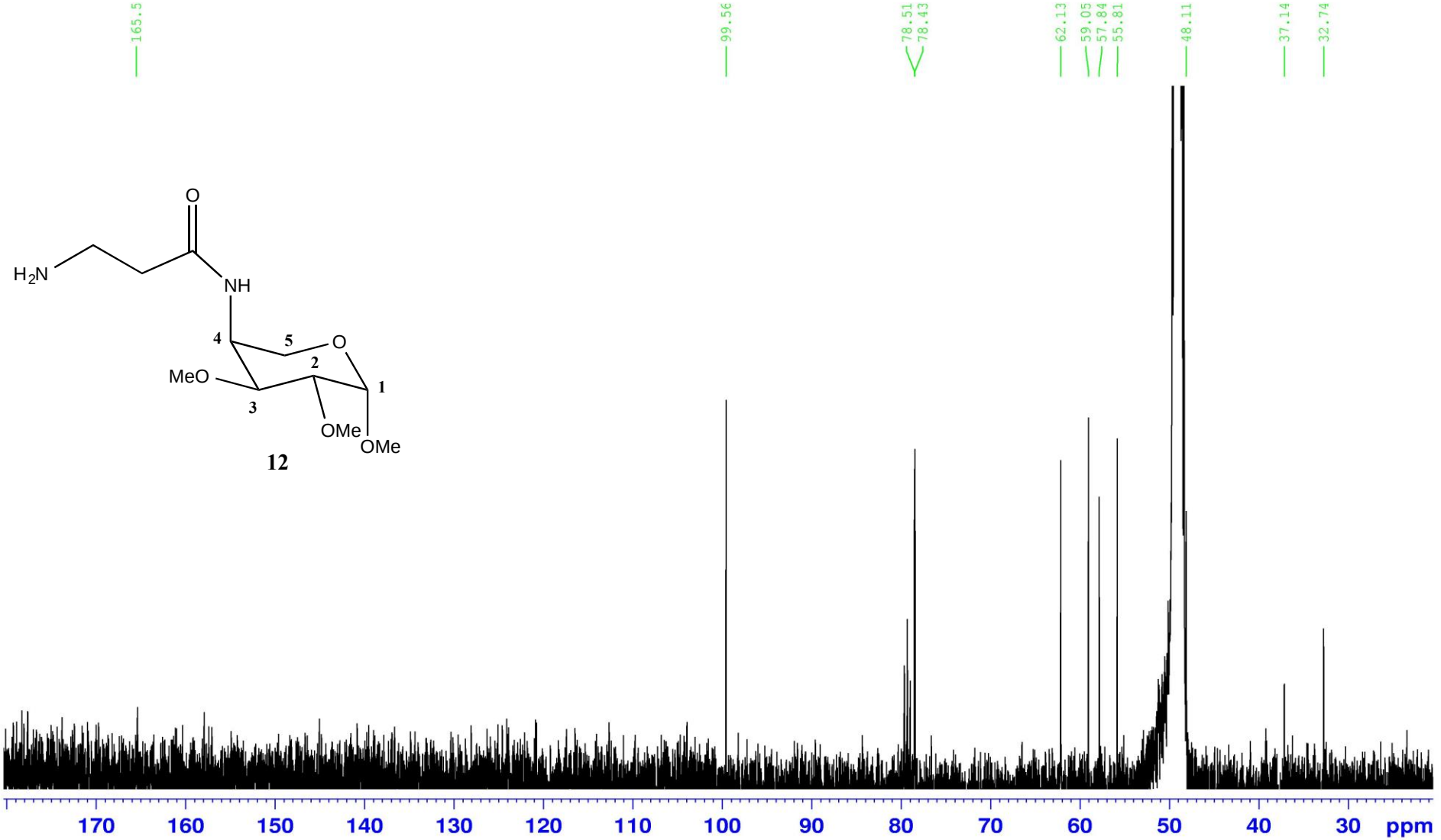


11

500 MHz, ^{1}H NMR, $CDCl_3$

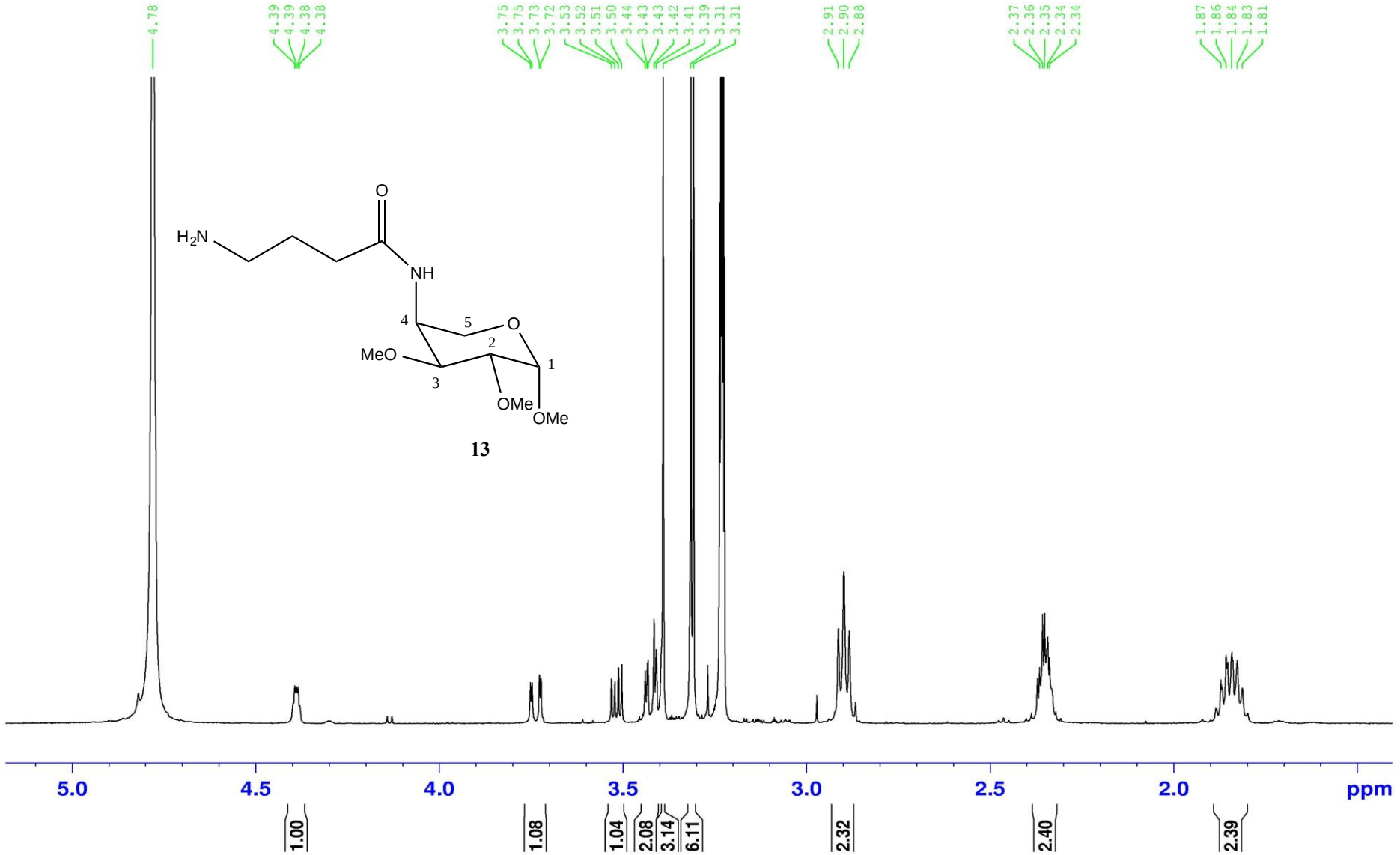


100 MHz, ^{13}C NMR, $CDCl_3$



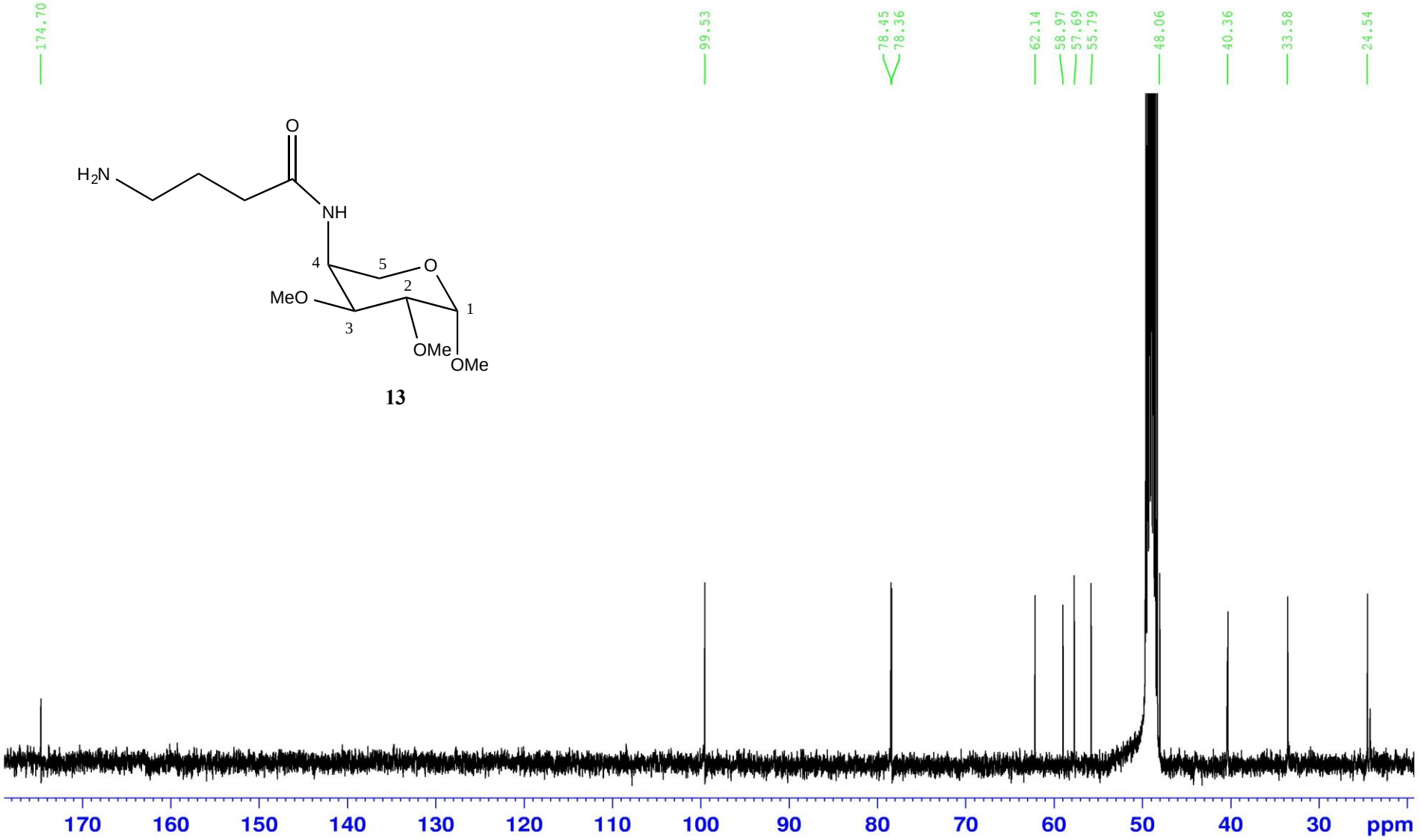
12

500 MHz, ^{1}H NMR, $CDCl_3$



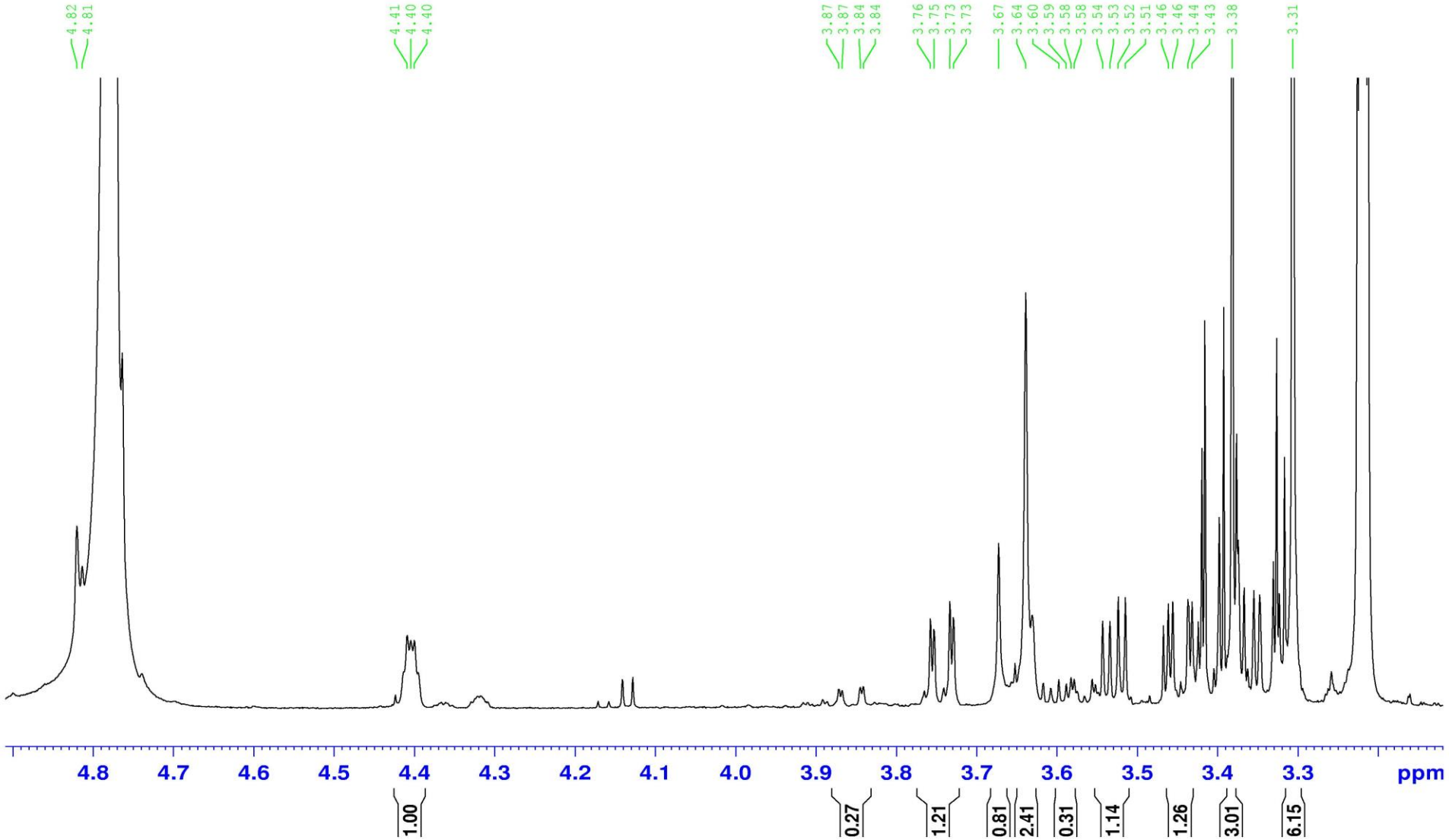
13

100 MHz, ^{13}C NMR, $CDCl_3$

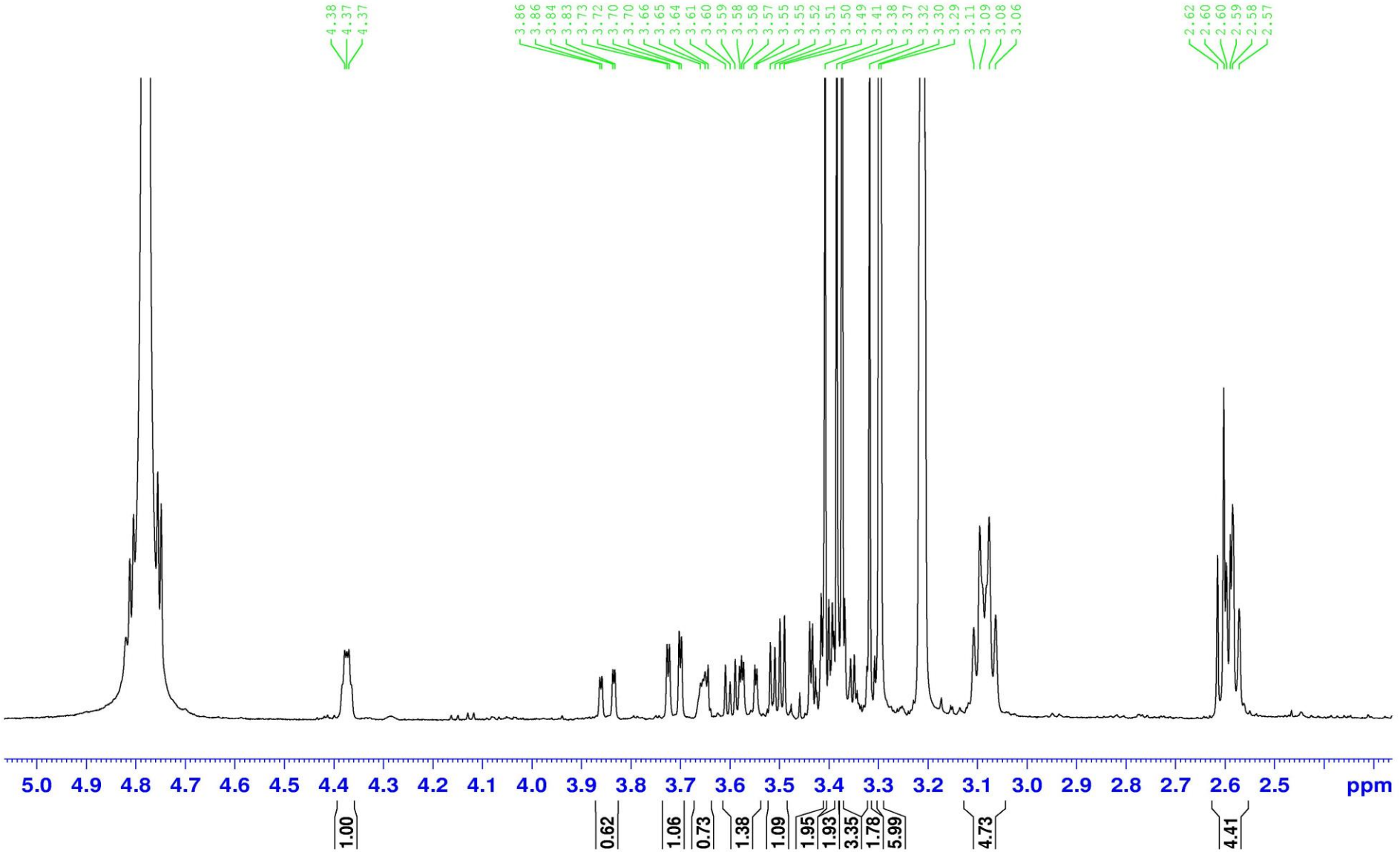


13

500 MHz, ^{1}H NMR, $CDCl_3$, reaction mixture of amine **11** under acidic conditions



500 MHz, ^{1}H NMR, $CDCl_3$, reaction mixture of amine **12** under acidic conditions



500 MHz, ^{1}H NMR, $CDCl_3$, reaction mixture of amine **13** under acidic conditions