

Stereospecific Reagent-Controlled Approach of 2-Deoxy- β -Linked Sugars with *p*-Toluenesulfonyl Chloride: A Mild Practical Glycosylation Method for Oligosaccharide Synthesis

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S1. General Experimental

Prior to running the glycosylation reactions, all solid reagents were dried by azeotropic removal of water using toluene and a rotary evaporator then set under pressure 16 h before use. All reactions were performed under inert argon atmosphere, unless otherwise noted. Solvents for reactions were dried through a commercial solvent purification system immediately prior to use. All other chemicals were purchased at the highest possible quality and used as received. Flash column chromatography was performed on 230–400 mesh silica gel. Analytical and preparative thin layer chromatography was carried out on silica gel 60 F-254 plates. Products were visualized using UV or by staining with either 5% aqueous sulfuric acid or ceric ammonium molybdate. NMR spectra were recorded on a NMR spectrometer at 500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR. Chemical shifts are reported in ppm relative to TMS (for ^1H NMR in CDCl_3) or CDCl_3 (for ^{13}C NMR in CDCl_3). For ^1H NMR spectra, data are reported as follows: δ shift, multiplicity (s = singlet, m = multiplet, t = triplet, d = doublet, q = quartet, brs = broad singlet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublets, tdd = triplet of doublet of doublets), coupling constants are reported in Hz. Low-resolution mass spectra (LRMS) were recorded using a ESI-MS with an additional APCI source. High-resolution mass spectra (HRMS) were obtained on ElectroSpray Ionization (ESI) on a Waters Qtof Premier instrument in the positive mode or Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR-MS) with direct analysis in real time (DART) ionization source. Optical rotations were measured at 589 nm in a 5 cm cell at room temperature. Compounds **1**,^[1] **3**,^[1] **4**,^[1] **12**^[2] and **13**^[3] were prepared according to literature methods. TsNO_2IM ^[4] and TsMeOTf ^[5] was prepared according to literature methods.

S1.1 Recrystallization of Sulfonyl Chlorides

S1.1.1 Recrystallization of *p*-toluenesulfonyl chloride

A solution of *p*-toluenesulfonyl chloride (40g) in diethyl ether (400 mL) was washed twice with aqueous 2M NaOH (2 x100 mL), then dried over Na_2SO_4 , and filtered. The receiving flask was covered with parafilm, and placed in a crystalizing dish. The crystalizing dish was packed with powdered dry ice, and the flask left there for at least 4 h, refreshing dry ice as needed. The resulting colorless crystals were filtered then placed under high vacuum overnight. The recrystallized material should be stored in the dark in a sealed container that had been purged with argon.

S1.1.2 Recrystallization of 2,4,6-triisopropylbenzenesulfonyl chloride (Trisyl Chloride)

2,4,6-Triisopropylbenzenesulfonyl chloride (5g) was dissolved in 20 mL of anhydrous pentane by heating, then allowed to cool to room temperature and left to crystallize overnight. The resulting crystals were filtered and dried under high vacuum overnight. The recrystallized material should be stored in the dark in a sealed container that had been purged with argon.

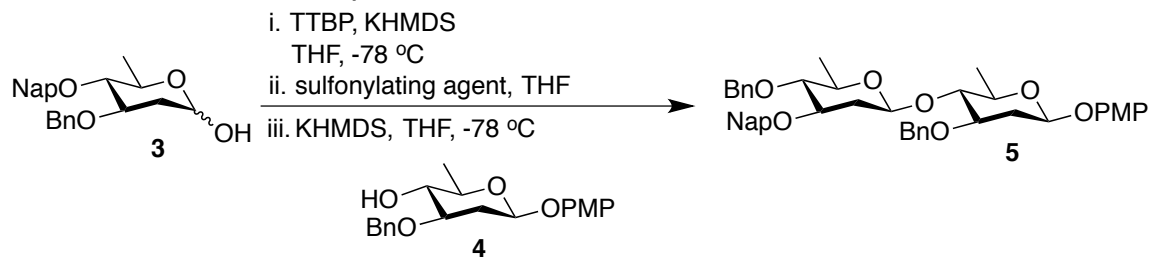
S2. Glycosylation screening

S2.1 General procedure for screening glycosylation conditions

A solution of donor (1.5 equiv.) and proton scavenger (1.5 equiv.) in THF was cooled to -78°C and treated dropwise with potassium hexamethyldisilazane (1M in THF, 1.5 equiv.). After 15 minutes, a solution of sulfonylating agent (1.5 equiv.) in THF was added slowly to the reaction. The flask containing the sulfonylating agent solution was then rinsed with THF, and the rinse added to the reaction vessel. The solution was maintained at -78°C for indicated activation time. Meanwhile in a separate flask, the acceptor (1 equiv.) and any additive (see Table S2.3.3) was dissolved in THF, cooled to -78°C , and treated with potassium hexamethyldisilazane (1 M in THF, 1 equiv.). After the activation time, this solution was transferred to the primary reaction vessel. The flask containing the acceptor was rinsed with THF, which was allowed to cool before addition to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 4 to 6 h. The reaction was quenched with saturated aqueous NH_4Cl .

S2.2 Reaction optimizations of 5

Table S2.2.1 Reaction optimization of 5 with Ts₂O and TsCl

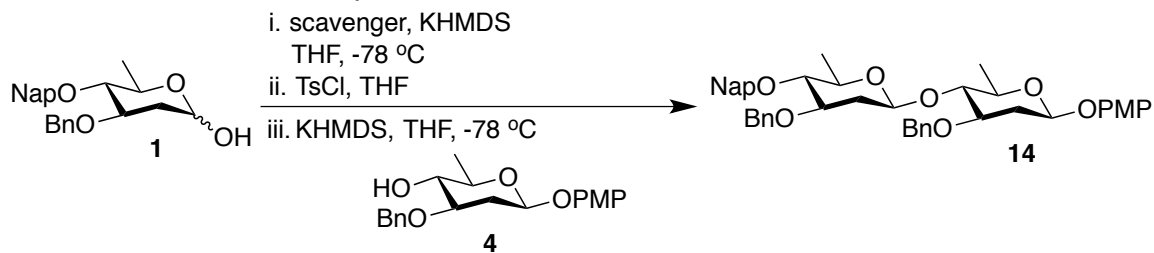


entry	sulfonylating agent	acceptor scale	yield (β:α) ^[a]
1	Ts ₂ O	84 mg	76% (β-only)
2 ^[c]	Ts ₂ O	84 mg	50% (β-only)
3	TsCl	84 mg	50% (β only)
4	Ts ₂ O	116 mg	64% (β only)
5	Ts ₂ O	500 mg	32% (β only)
6 ^[d]	Ts ₂ O	500 mg	23% (β only)
7 ^[e]	TsCl	500 mg	72% (13:1)

[a]Yield of isolated product. Selectivity determined by ¹H NMR spectroscopy. [b] Used 0.5 h activation time unless otherwise noted. [c] Repeat of entry 1. [d] Repeat of entry 5. [e] Used 1.5 h activation time. TTBP= 2,4,6-tri-*tert*-butylpyrimidine; KHMDS= potassium hexamethyldisilazane.

S2.3 Reaction optimizations of **14**

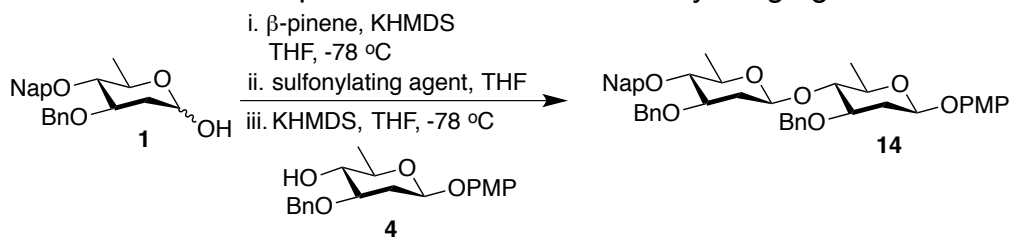
Table S2.3.1 Reaction optimization of **14** with TsCl



entry	scavenger	acceptor scale	[rxn 1]	[rxn 2]	yield (β:α) ^[a]
1	TTBP	171 mg	0.075 M	0.054 M	76% (β-only)
2	TTBP	100 mg	0.061 M	0.043 M	75% (β-only)
3	DTBP	100 mg	0.061 M	0.043 M	53% (β-only)
4	TTBpyridine	100 mg	0.061 M	0.043 M	61% (β-only)
5	β-pinene	100 mg	0.061 M	0.043 M	75% (9:1)
6 ^[d]	β-pinene	100 mg	0.061 M	0.043 M	62 (2.7:1)
7 ^[e]	β-pinene	100 mg	0.061 M	0.043 M	---
8	β-pinene	100 mg	0.096 M	0.066 M	73 (6:1)
9 ^[f]	β-pinene	100 mg	0.096 M	0.066 M	41 (45:1)
10	β-pinene	500 mg	0.072 M	0.052 M	76% (5.4:1)
11	β-pinene	500 mg	0.136 M	0.090 M	59% (4:1)
12 ^[g]	β-pinene	500 mg	0.136 M	0.090 M	65% (9:1)
13	β-pinene	500 mg	0.056 M	0.043 M	87% (3.8:1)
14	TTBP	500 mg	0.057 M	0.043 M	66% (β-only)

[a]Yield of isolated product. Selectivity determined by ¹H NMR spectroscopy. [b] Used donor:acceptor ratio 1.5:1 unless otherwise noted. [c] Used 1 h activation time unless otherwise noted. [d] Donor:acceptor ratio 2:1. [e] Used Et₂Zn instead of KHMDS. [f] TsCl present during donor metalation. [g] Used 1.5 h activation time. KHMDS= potassium hexamethyldisilazane; TTBP= 2,4,6-tri-*tert*-butylpyrimidine; DTBP= 2,6-di-*tert*-butylpyridine; TTBpyridine= 2,4,6-tri-*tert*-butylpyridine

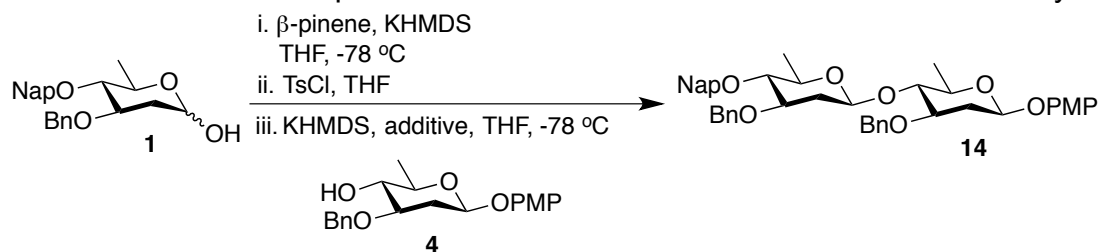
Table S2.3.2 Reaction optimization of **14** with sulfonylating agents



entry	sulfonylating agent	yield (β : α) ^[a]
1 ^[d]	TsCl	75% (β -only)
2	TsCl	75% (9:1)
3	TsIm	37% (18:1)
4	Ts ₂ O	14% (β -only)
5	TsNO ₂ Im	Trace
6	TsImMe	---
7	TsMeOTf	---
8 ^[e]	TsMeOTf	---
9	TrisylCl	18% (3:1)

[a]Yield of isolated product. Selectivity determined by ¹H NMR spectroscopy. [b] Donor:acceptor ratio 1.5:1. [c] Used 1 h activation time. [d] Used TTBP instead of β -pinene. [e] Made sulfonylating agent in situ. KHMDS= potassium hexamethyldisilazane; TsCl= *p*-toluenesulfonyl chloride; Ts₂O= *p*-toluenesulfonic anhydride; TsIm= 1-(*p*-toluenesulfonyl)imidazole; TsNO₂Im= 1-(*p*-toluenesulfonyl)-4-nitroimidazole; TsMeOTf= 1-methyl-3-[(4-methylbenzene)sulfonyl]imidazolium triflate; TrisylCl= triisopropylbenzenesulfonyl chloride

Table S2.3.3 Reaction optimization of **14** with additives to increase reactivity of **4**

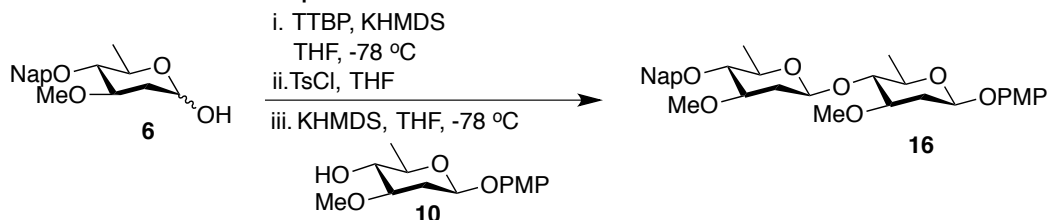


entry	additive	additive equiv.	% yield (β : α) ^[a]
1 ^[e]	---	---	75 (β -only)
2	18-crown-6	1	50 (6:1)
3	diglyme	10	49 (7:1)
4	glyme	10	57 (β -only)
5	glyme	Cosolvent w/ acceptor	48 (4.1:1)
6	glyme	Cosolvent	43 (3.6:1)
7 ^[e]	glyme	10	52 (11:1)
8	glyme	10	41 (5:1)
9	AuCl ₃	0.1	---
10 ^[f]	AuCl ₃	0.1	---
11	CuI	1	---
12 ^[g]	CuI	1	Trace

[a] Yield of isolated product. Selectivity determined by ¹H NMR spectroscopy. [b] Donor:acceptor ratio 1.5:1 [c] Used 1 h activation time. [d] Additive was present in acceptor flask before addition to main reaction flask. [e] Used TTBP instead of β -pinene. [f] Acceptor not metalated. [g] Metalated acceptor with LiHMDS (1M in THF) instead of KHMDS. KHMDS= Potassium hexamethyldisilazane; TTBP= 2,4,6-tri-*tert*-butylpyrimidine; LiHMDS= lithium hexamethyldisilazane

S2.4 Reaction optimizations of 16

Table S2.4.1 Reaction optimization of 16

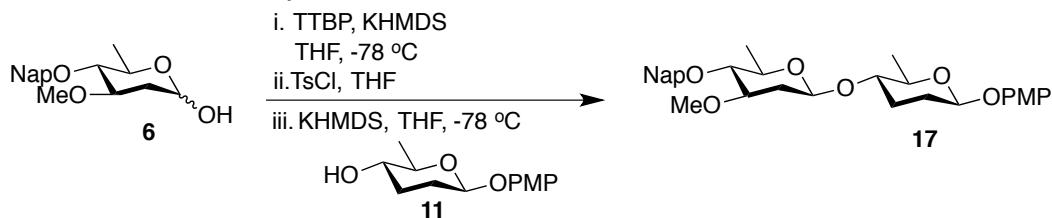


entry	donor:acceptor	[Rxn 1]	[Rxn 2]	activation time	yield (β:α) ^[a]
1	1.5:1	0.059 M	0.042 M	1 h	53% (β-only)
2 ^[c]	1.5:1	0.059 M	0.042 M	1 h	37% (24:1)
3 ^[d]	1.5:1	0.059 M	0.042 M	1 h	38% (7:1)
4	1.5:1	0.059 M	0.042 M	1.5 h	46% (β-only)
5	1.5:1	0.059 M	0.042 M	0.5 h	33% (21:1)
6	1.5:1	0.059 M	0.042 M	0.25 h	57% (14:1)
7 ^[e]	1.5:1	0.059 M	0.042 M	0.25 h	20% (β-only)
8 ^[f]	1.5:1	0.059 M	0.042 M	0.25 h	35% (β-only)
9 ^[g]	1.5:1	0.059 M	0.042 M	0.25 h	20% (β-only)
10	1.5:1	0.073 M	0.052 M	0.25 h	60% (β-only)
11	2:1	0.062 M	0.045 M	0.25 h	80% (8:1)
12	2:1	0.078 M	0.055 M	0.25 h	71% (β-only)
13	2:1	0.065 M	0.050 M	0.25 h	75% (β-only)
14 ^[h]	2:1	0.065 M	0.050 M	0.25 h	66% (β-only)
15 ^[i]	2:1	0.065 M	0.050 M	0.25 h	48% (β-only)
16 ^[j]	2:1	0.065 M	0.050 M	0.25 h	54% (β-only)
17 ^[k]	2:1	0.065 M	0.050 M	0.25 h	62% (β-only)
18 ^[k,l]	2:1	0.065 M	0.050 M	0.25 h	58% (β-only)
19 ^[k]	2:1	0.065 M	0.050 M	0.3 h	57% (β-only)

[a]Yield of isolated product. Selectivity determined by ¹H NMR spectroscopy. [b] Used 100 mg acceptor scale unless otherwise noted. [c] Stirred reaction overnight. [d] Used β-pinene instead of TTBP. [e] No scavenger used. [f] Held reaction at temperature at -78 °C. [g] Added donor to TsCl solution. [h] Added KHMDS immediately after addition of acceptor. [i] Metalated acceptor 5 min prior to addition. [j] Added KHMDS 3 h after addition of acceptor. [k] Used 1.1 g donor scale and 500 mg acceptor scale. [l] Used KHMDS solution freshly prepared in a glovebox. TTBP= 2,4,6-tri-*tert*-butylpyrimidine; KHMDS= potassium hexamethyldisilazane.

S2.5 Reaction optimizations of 17

Table S2.5.1 Reaction optimization of 17

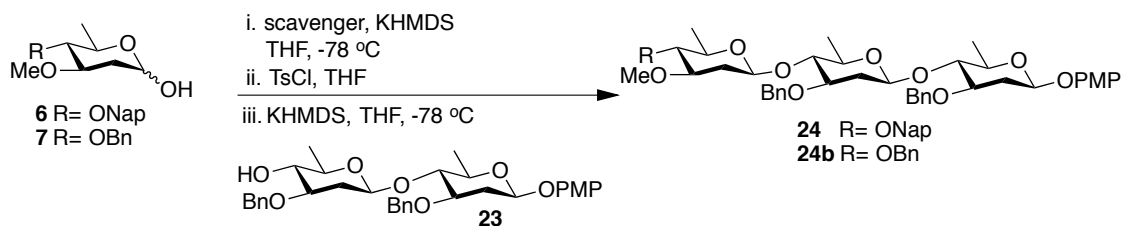


entry	donor:acceptor	activation time	yield ($\beta:\alpha$) ^[a]
1	1.5:1	1 h	48% (β -only)
2	1.5:1	1 h	52% (β -only)
3 ^[c]	1.5:1	1 h	44% (β -only)
4 ^[d]	1.5:1	1 h	35% (β -only)
5 ^[e]	1.5:1	1 h	---
6 ^[f]	1.5:1	1 h	---
7	2:1	1 h	50% (β -only)
8	2:1	0.5 h	51% (β -only)
9	2:1	0.25 h	55% (β -only)
10 ^[g]	2:1	0.25 h	41% (β -only)
11 ^[h]	2:1	0.25 h	44% (β -only)
13 ^[i]	2:1	0.25 h	59% (5.4:1)
14 ^[j]	2:1	0.25 h	75% (5:1)
15 ^[k]	2:1	0.25 h	61% (5:1)
16 ^[l,m]	2:1	0.25 h	59% (4:1)
17 ^[l]	2:1	0.25 h	62% (5:1)
18 ^[l]	2:1	0.4 h	50% (β -only)

[a] Yield of isolated product. Selectivity determined by ¹H NMR spectroscopy. [b] Used 254 mg donor and 100 mg scale unless otherwise noted. [c] Metalated acceptor with NaHMDS (1M in THF) instead of KHMDS. [d] Used NaHMDS (1M in THF) instead of KHMDS for the entire reaction. [e] Metalated acceptor with LiHMDS (1M in THF) instead of KHMDS. [f] Used LiHMDS (1M in THF) instead of KHMDS for the entire reaction. [g] Used 1,2,2,6,6-pentamethylpiperidine instead of TTBP. [h] Used tetramethylethylenediamine as an additive with acceptor. [i] Controlled temperature ramp increase: 3 h at -78 °C, then 2 h -60 °C and 1 h -40 °C. [j] Addition of acceptor in three portions. [k] Added KHMDS immediately after addition of acceptor. [l] Used 1.2 g donor and 500 mg acceptor scale. TTBP= 2,4,6-tri-*tert*-butylpyrimidine; KHMDS= potassium hexamethyldisilazane; NaHMDS= sodium hexamethyldisilazane; LiHMDS= lithium hexamethyldisilazane.

S2.6 Reaction optimizations of **24** and **24b**

Table S2.6.1 Reaction optimization of **24** and **24b** with activation times and reaction concentrations

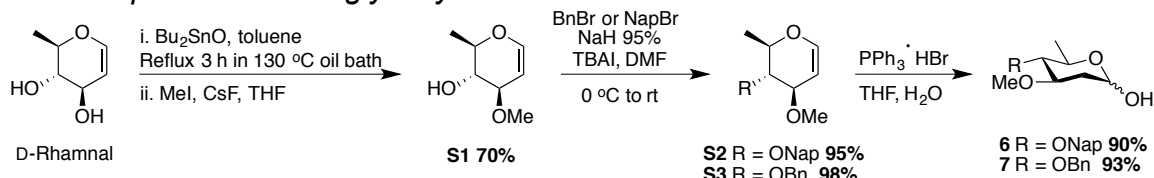


entry	donor:acceptor	scavenger	[Rxn 1]	[Rxn 2]	activation time	yield (β : α) ^[a]	
24:	1	1.5:1	TTBP	0.090 M	0.067 M	1 h	40% (β only)
	2	1.5:1	TTBP	0.090 M	0.067 M	0.5 h	34% (β only)
	3	1.5:1	TTBP	0.090 M	0.067 M	0.25 h	33% (β only)
	5	2:1	TTBP	0.090 M	0.067 M	1 h	43% (β only)
	6	2:1	TTBP	0.090 M	0.067 M	1 h	35% (β only)
	7	2:1	TTBP	0.090 M	0.067 M	0.5 h	75% (β only)
	8	2:1	TTBP	0.090 M	0.067 M	0.25 h	40% (β only)
	24b:	1	1.5:1	TTBP	0.090 M	0.067 M	1 h
2		1.5:1	β -pinene	0.090 M	0.067 M	1 h	50% (β only)
3		1.5:1	β -pinene	0.090 M	0.067 M	1.5 h	48% (β only)
4		1.5:1	β -pinene	0.141 M	0.091 M	1 h	44% (3.4:1)
5		1.5:1	β -pinene	0.043 M	0.033 M	1 h	35% (β only)
6 ^[c]		1.5:1	β -pinene	0.092 M	0.068 M	1 h	49% (16:1)

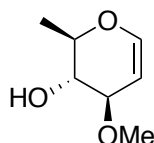
[a] Yield of isolated product. Selectivity determined by ¹H NMR spectroscopy. [b] 67 mg donor scale and 100 mg acceptor scale unless otherwise noted. [c] Used 335 mg donor and 500 mg acceptor scale. TTBP= 2,4,6-tri-*tert*-butylpyrimidine; KHMDS= potassium hexamethyldisilazane.

S3 Experimental Procedure

S3.1 Preparation of the glycosyl donor **6** and **7**.



3-O-Methyl-6-deoxy-D-glucal (**S1**)



Synthesis of compound **S1** was performed using procedures adapted from Toerien et al.^[6] D-Rhamnal (5 g, 38.4 mmol) and Bu₂SnO (10.4 g, 42.2 mmol) were suspended in toluene (250 mL) at room temperature. The reaction mixture was stirred at reflux at 130 °C under Dean-Stark conditions for 5 h, then cooled to room temperature. The solvent was removed *in vacuo*. The resulting solid and CsF (11.6 g, 76.8 mmol) was suspended in THF (250 mL), then iodomethane was added to reaction at room temperature. The reaction was stirred for 43 h, then imidazole (4.9 g, 72.9 mmol) was added to reaction allowed to stir for 1 h. The crude residue was filtered through a silica gel plug and washed with ethyl acetate (750 mL) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel (30% to 70% ethyl acetate in hexanes) to afford compound **S1** (3.6 g, 65%) as a clear oil. The spectroscopic data is in good agreement with previously reported data.^[7]

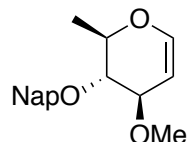
$[\alpha]_D^{24} = -19.7^\circ$ (c 1.80, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ = 6.35 (dd, *J*=6.1, 1.5, 1H), 4.84 (dd, *J*=6.1, 2.1, 1H), 3.94 – 3.87 (m, 1H), 3.85 (dt, *J*=7.1, 1.9, 1H), 3.53 (ddd, *J*=10.1, 7.1, 3.5, 1H), 3.40 (s, 3H), 2.41 (m, 1H), 1.39 (d, *J*=6.4, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 145.2, 99.3, 78.6, 74.6, 72.0, 55.9, 17.3.

HRMS (ESI, pos. ion) *m/z*: calcd. for C₇H₁₁O₃ (M-H) 143.0703, found 143.0715.

3-O-Methyl-4-O-(2-naphthylmethyl)-6-deoxy-D-glucal (**S2**)



Sodium hydride (60% in mineral oil, 2.1 g, 52.5 mmol) and tetrabutylammonium iodide (1.9 g, 5.2 mmol) were suspended in DMF (90 mL). The suspension was cooled to 0 °C and treated with a solution of **S1** (3.8 g, 26.2 mmol) in DMF (25 mL), while additional DMF (20 mL) was simultaneously added. After the mixture

was stirred for 15 min at 0 °C, 2-(bromomethyl)naphthalene (8.6 g, 39.3 mmol) in DMF (25 mL) was added dropwise to the mixture and the reaction was then allowed to warm to room temperature. After being stirred for 4 h, the reaction mixture was quenched with saturated aqueous NH₄Cl and extracted three times with diethyl ether. The pooled organic layers were washed with water and brine, and then dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (2% to 5% to 10% ethyl acetate in hexanes) afforded compound **S2** (6.5 g, 89%) as an amorphous solid.

$[\alpha]_D^{22} = +8.6^\circ$ (c 1.32, CH₂Cl₂).

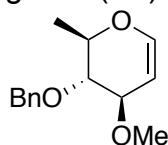
¹H NMR (500 MHz, CDCl₃) δ = 7.86 – 7.79 (m, 4H), 7.52 – 7.43 (m, 3H), 6.37 (d, *J*=5.5, 1H), 5.03 (d, *J*=11.6, 1H), 4.90 – 4.83 (m, 2H), 4.06 – 4.00 (m, 1H), 3.96 (dq, *J*=8.9, 6.4, 1H), 3.44 (dd, *J*=9.0, 6.5, 1H), 3.41 (s, 3H), 1.38 (d, *J*=6.4, 3H).

¹³C NMR (125 MHz, CDCl₃) δ = 145.0, 135.9, 133.4, 133.1, 128.2, 128.0, 127.8, 126.7, 126.2, 126.1, 126.0, 99.9, 79.2, 78.4, 74.0, 55.9, 17.7.

LRMS (ESI, pos. ion) *m/z*: calcd. for C₁₈H₂₄NO₃ (M+NH₄) 302.18, found 302.02.

HRMS (ESI, pos. ion) *m/z*: calcd. for C₁₈H₂₄NO₃ (M+NH₄) 302.1751, found 302.1766.

3-O-Methyl-4-O-benzyl-6-deoxy-D-glucal (**S3**)



Sodium hydride (60% in mineral oil, 1.7 g, 44.4 mmol) and tetrabutylammonium iodide (1.6 g, 4.4 mmol) were suspended in DMF (102 mL). The suspension was cooled to 0 °C and treated with a solution of **S1** (3.2 g, 22.2 mmol) in DMF (20 mL), while additional DMF (10 mL) was simultaneously added. After the mixture was stirred for 25 min at 0 °C, benzyl bromide (5.2 mL, 44.4 mmol) was added dropwise to the mixture and the reaction was then allowed to warm to room temperature. After being stirred for 3 h, the reaction mixture was quenched with saturated aqueous NH₄Cl and extracted three times with diethyl ether. The pooled organic layers were washed with water and brine, and then dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (2% ethyl acetate in hexanes) afforded compound **S3** (4.9 g, 95%) as a clear oil.

$[\alpha]_D^{24} = +1.7^\circ$ (c 1.34, CH₂Cl₂).

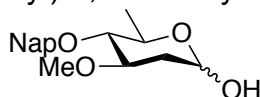
^1H NMR (500 MHz, CDCl_3) δ = 7.39 – 7.23 (m, 5H), 6.34 (dd, $J=6.2, 1.4$, 1H), 4.86 (d, $J=11.5$, 1H), 4.82 (dd, $J=3.6, 2.9$, 1H), 4.69 (d, $J=11.6$, 1H), 3.98 (d, $J=6.3$, 1H), 3.95 – 3.88 (m, 1H), 3.42 – 3.33 (m, 4H), 1.36 (d, $J=6.4$, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 144.9, 138.5, 128.5, 128.0, 127.8, 99.9, 79.2, 78.4, 74.0, 73.9, 55.9, 17.6.

LRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{14}\text{H}_{22}\text{NO}_3$ ($\text{M}+\text{NH}_4$) 252.16, found 251.73.

HRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{14}\text{H}_{17}\text{O}_3$ ($\text{M}-\text{H}$) 233.1172, found 233.1188.

3-O-Methyl-4-O-(2-naphthylmethyl)-2,6-dideoxy-D-*arabino*-hexopyranose (**6**)



Synthesis of **6** was performed using procedures adapted from Blumenstein et al.^[8] To a solution of **S2** (12.3 g, 43.2 mmol) in THF (255 ml), $\text{P}(\text{Ph}_3)_3\text{HBr}$ (2.9 g, 8.6 mmol) was added to the reaction and allowed to stir at room temperature. After 10 min, H_2O (3.8 ml, 216 mmol) was added to the reaction. The reaction was stirred for 4 h. The reaction was quenched with saturated aqueous NaHCO_3 , diluted with ethyl acetate and water, and extracted three times with ethyl acetate. The pooled organic layer was washed with H_2O , brine, and dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (30% to 60% ethyl acetate in hexanes) to afford **6** (11.3 g, 87%) as a white solid.

m.p. 116-117 °C.

$[\alpha]_D^{22} = +60.3^\circ$ (c 1.13, CH_2Cl_2).

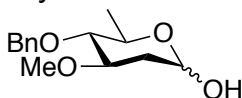
^1H NMR (500 MHz, CDCl_3) δ = 7.87 – 7.78 (m, 5H), 7.52 – 7.43 (m, 4H), 5.35 (s, 1H), 5.07 (d, $J=9.8$, 1H), 4.82 (d, $J=9.8$, 1H), 4.00 (dq, $J=9.4, 6.2$, 1H), 3.78 (ddd, $J=11.4, 8.7, 5.0$, 1H), 3.50 – 3.38 (m, 4H), 3.15 – 3.06 (m, 1H), 2.32 (dd, $J=12.9, 5.2$, 1H), 1.63 – 1.53 (m, 1H), 1.29 (d, $J=6.2$, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ = 136.3, 133.5, 133.1, 128.2, 128.1, 128.0, 127.8, 126.7, 126.6, 126.2, 126.1, 126.0, 125.9, 94.0, 92.1, 84.4, 83.4, 81.2, 78.5, 75.2, 75.2, 71.5, 67.4, 57.3, 57.1, 37.8, 35.2, 18.4.

LRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{18}\text{H}_{22}\text{NaO}_4$ ($\text{M}+\text{Na}$) 325.14, found 325.20.

HRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{18}\text{H}_{26}\text{NO}_4$ ($\text{M}+\text{NH}_4$) 320.1856, found 320.1842.

3-O-Methyl-4-O-benzyl-2,6-dideoxy-D-*arabino*-hexopyranose (**7**)



Synthesis of **7** was performed using procedures adapted from Blumenstein et al.^[8] To a solution of **S3** (4.5 g, 19.2 mmol) in THF (75 ml), P(Ph₃)₃·HBr (1.3 g, 3.8 mmol) was added to the reaction and allowed to stir at room temperature. After 10 min, H₂O (1.7 ml, 96.0 mmol) was added to the reaction. The reaction was stirred for 4 h. The reaction was quenched with saturated aqueous NaHCO₃, diluted with ethyl acetate and water, and extracted three times with ethyl acetate. The pooled organic layer was washed with H₂O, brine, and dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (30% ethyl acetate in hexanes) to afford **7** (4.5 g, 93%) as a white solid.

m.p. 76-77 °C.

$[\alpha]_D^{22} = +65.7^\circ$ (c 1.05, CH₂Cl₂).

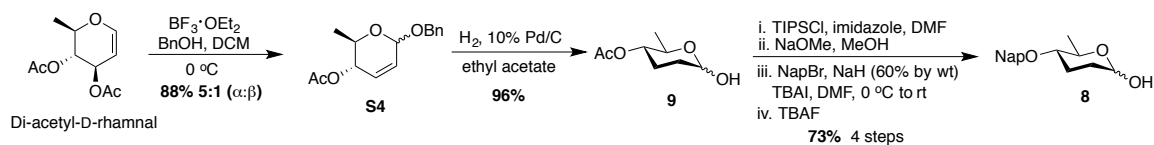
¹H NMR (500 MHz, CDCl₃) δ = 7.40 – 7.26 (m, 7H), 5.33 (s, 1H), 4.90 (dd, *J*=11.1, 5.7, 1H), 4.64 (dd, *J*=11.1, 5.6, 1H), 3.96 (dq, *J*=9.4, 6.2, 1H), 3.73 (ddd, *J*=11.3, 8.7, 5.0, 1H), 3.45 (s, 3H), 3.44 – 3.34 (m, 1H), 3.08 – 2.99 (m, 1H), 2.29 (dd, *J*=10.9, 7.5, 1H), 1.61 – 1.51 (m, 1H), 1.26 (d, *J*=6.2, 3H).

¹³C NMR (125 MHz, CDCl₃) δ = 138.7, 128.5, 128.1, 128.1, 128.0, 127.8, 127.7, 94.0, 92.1, 84.3, 83.3, 81.2, 78.5, 75.1, 75.1, 71.5, 67.4, 57.4, 57.1, 37.8, 35.2, 18.3.

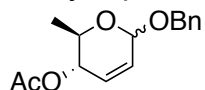
LRMS (ESI, pos. ion) *m/z*: calcd. for C₁₄H₂₄NO₄ (M+NH₄) 270.17, found 270.02.

HRMS (ESI, pos. ion) *m/z*: calcd. for C₁₄H₂₄NO₄ (M+NH₄) 270.1700, found 270.1708.

S3.2 Preparation of the glycosyl donors **8** and **9**.



Benzyl 4-O-acetyl-6-deoxy-2,3-dideoxy- α/β -D-erythro-hex-2-enopyranoside (**S4**)



Synthesis of **S4** was performed using procedures adapted from Brimacombe et al. [9] To a solution of di-acetyl-D-rhamnal^[10] (5 g, 23.3 mmol) and benzyl alcohol (3.6 mL, 35.0 mmol) was dissolved in DCM (24 mL) and cooled to 0 °C. After 5 min, boron trifluoride ether complex (1.2 mL, 9.3 mmol) was dropwise added to reaction at 0 °C. During addition, each drop produced a red swirl and then the reaction turned red in color, after 1.25 h the solution turned a dark purple color. The reaction was quenched with saturated aqueous NaHCO₃ (12 mL), during which time reaction turned blue then yellow. The solution was diluted with DCM (50 mL) and water (25 mL), and extracted three times with DCM. The pooled organic layers were washed with saturated NaHCO₃ (50 mL), water (50 mL) and dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (5% to 10% ethyl acetate in hexanes) to afford compound **S4** (5 g, 82%, 6.3:1 $\alpha:\beta$) as a slight yellow oil. The spectroscopic data is in good agreement with previously reported data.^[11]

¹H NMR (500 MHz, CDCl₃) δ = 7.40 – 7.26 (m, 5H), 5.89 – 5.79 (m, 2H), 5.10 – 5.03 (m, 2H), 4.79 (d, $J=11.8$, 1H), 4.60 (d, $J=11.9$, 1H), 4.05 – 3.96 (m, 1H), 2.08 (s, 3H), 1.19 (d, $J=6.2$, 3H).

¹³C NMR (125 MHz, CDCl₃) δ = 170.7, 138.1, 129.9, 128.6, 128.1, 127.9, 127.9, 93.8, 71.1, 70.3, 65.1, 21.2, 18.0.

4-O-Acetyl-2,3,6-trideoxy-D-erythro-hexopyranose (**9**)



To a suspension of palladium on carbon (875 mg, 0.73 mmol) in ethyl acetate (47 mL), was treated with a solution of **S4** (4.8 g, 18.4 mmol) in ethyl acetate (47 mL). After 10 min, H₂ gas was bubbled into the reaction three times and left under H₂ gas atmosphere. The reaction was allowed to stir under H₂ gas for 15 h before filtering the reaction through silica gel and rinsed with ethyl acetate (500 mL) and concentrated *in vacuo*. Without further purification, afforded **9** (3.1 g, 96%) as an amorphous solid:

m.p. 59-60 °C.

$[\alpha]_{\text{D}}^{22} = +129.59^\circ$ (c 1.37, CH₂Cl₂).

^1H NMR (500 MHz, CDCl_3) δ = 5.24 (s, 1H), 4.53 – 4.41 (m, 1H), 4.04 (dq, $J=9.5$, 6.3, 1H), 2.47 (s, 1H), 2.06 (s, 4H), 2.03 – 1.75 (m, 5H), 1.64 – 1.46 (m, 1H), 1.15 (d, $J=6.3$, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ = 170.4, 95.9, 91.0, 73.6, 73.6, 72.8, 66.8, 31.9, 29.3, 27.5, 23.5, 21.3, 18.3.

LRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_8\text{H}_{18}\text{NO}_4$ ($\text{M}+\text{NH}_4$) 192.12, found 192.00.

HRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_8\text{H}_{14}\text{NaO}_4$ ($\text{M}+\text{Na}$) 197.0790, found 197.0797.

4-O-(2-Naphthylmethyl)-2,3,6-trideoxy-D-erythro-hexopyranose (**8**)



Compound **9** (5.8g, 33 mmol) and imidazole (4.5 g, 66 mmol) were dissolved in DMF (90 mL). After 25 min, triisopropylsilyl chloride (10 mL, 49 mmol) was dropwise added to reaction at room temperature. After 4 h, the solution was diluted with diethyl ether (100 mL) and water (100 mL), and extracted with diethyl ether (3 x 100 mL). The pooled organic layers were washed with water (2 x 100 mL), brine and dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The crude residue was passed through a silica gel plug and used without further purifications. The resulting oil was dissolved in anhydrous methanol (100 mL), and then powdered sodium methoxide (0.27 g, 4.9 mmol) was added to reaction at room temperature. After 5.5 h, the solution was concentrated *in vacuo*. This solid was azeotroped with toluene and then sufficiently dried by placing on high vacuum for 5 h. The solid was then dissolved in DMF (75 mL) and cannulated slowly to a suspension of sodium hydride (60% in mineral oil, 2.6 g, 66.4 mmol) and tetrabutylammonium iodide (2.4 g, 6.6 mmol) in DMF (120 mL) at 0 °C. After the mixture was stirred for 20 min at 0 °C, 2-(bromomethyl)naphthalene (11 g, 49.8 mmol) in DMF (35 mL) was added dropwise to the mixture and the reaction was then allowed to warm to room temperature. After being stirred for 16 h, the reaction mixture was quenched with of saturated aqueous NH_4Cl (5 mL) and extracted three times with diethyl ether. The pooled organic layers were washed with water and brine, and then dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting residue was subjected to a 1M solution TBAF in THF (66.4 mL, 66.4 mmol). After 2 h, the reaction was diluted with water (250 mL) and extracted with dichloromethane (3 x 150 mL). The pooled organic layers were washed with water and brine and then dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (25% ethyl acetate in hexanes to 100% ethyl acetate) to afford **8** (6.6 g, 73% over 4 steps) as a white powder.

m.p. 93-94 °C.

$[\alpha]_D^{22} = +86.3^\circ$ (c 1.14, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ = 7.86 – 7.74 (m, 7H), 7.52 – 7.42 (m, 6H), 5.21 (s, 1H), 4.85 – 4.75 (m, 3H), 4.66 (d, *J*=5.6, 1H), 4.64 (d, *J*=5.4, 1H), 4.01 (dq, *J*=8.9, 6.2, 1H), 3.53 (dq, *J*=8.9, 6.2, 1H), 3.17 – 3.08 (m, 2H), 2.93 (s, 1H), 2.50 – 2.46 (m, 1H), 2.31 – 2.21 (m, 1H), 2.08 – 1.95 (m, 2H), 1.93 – 1.79 (m, 2H), 1.75 – 1.64 (m, 1H), 1.57 (dd, *J*=3.1, 1.7, 1H), 1.55 – 1.47 (m, 1H), 1.47 – 1.41 (m, 0H), 1.35 (d, *J*=6.1, 3H), 1.28 (d, *J*=6.2, 3H).

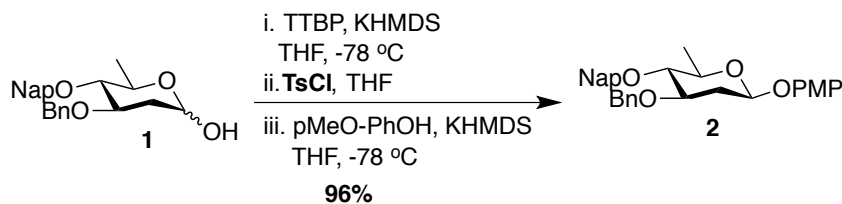
¹³C NMR (125 MHz, CDCl₃) δ = 136.2, 135.9, 133.4, 133.1, 133.1, 128.3, 128.3, 128.0, 127.8, 126.5, 126.5, 126.3, 126.2, 126.1, 126.0, 126.0, 125.9, 95.9, 91.0, 79.0, 78.3, 75.0, 71.5, 70.9, 68.2, 32.1, 29.5, 27.6, 23.4, 18.7, 18.6.

LRMS (ESI, pos. ion) *m/z*: calcd. for C₁₇H₂₀NaO₃ (M+Na) 295.13, found 295.18.

HRMS (ESI, pos. ion) *m/z*: calcd. for C₁₇H₂₀NaO₃ (M+Na) 295.1310, found 295.1309.

S3.3 Synthesis of monosaccharides **2**, **15**, **19**, **20**

Synthesis of **2**



β -*p*-Methoxyphenyl 3-O-benzyl-4-O-(2-naphthylmethyl)-2,6-di-deoxy-D-*arabino*-hexopyranose (**2**)

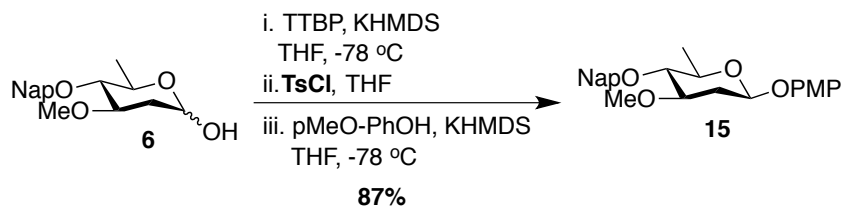


A solution of **1**^[1] (4.5 g, 12 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 1.9 g, 12 mmol) in THF (96 mL) was cooled to -78 °C and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 12 mL, 12 mmol). The solution was maintained at -78 °C for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (2.3 g, 12.0 mmol) in THF (44 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (20 mL), and the rinse added to the reaction mixture. The solution was maintained at -78 °C for 30 min. Meanwhile in a separate flask, *p*-methoxyphenol (500 mg, 4.0 mmol) was dissolved in THF (44 mL), cooled to -78 °C, and treated with potassium hexamethyldisilazane (1 M in THF, 8 mL, 8.0 mmol). After 30 min, this solution was cannulated to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (20 mL), which was then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 4.5 h. The reaction was quenched with saturated aqueous NH_4Cl (1 mL), diluted with water, and extracted three times with Et_2O . The pooled organic layers were washed with H_2O and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (5% ethyl acetate in hexanes to 10% ethyl acetate in hexanes) to afford **2** as a single β -anomer (3.2 g, 96%) as a white powder. The spectroscopic data is in good agreement with previously reported data.^[1]

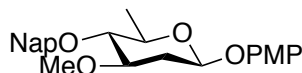
^1H NMR (500 MHz, CDCl_3) δ = 7.86–7.75 (m, 4H), 7.52–7.43 (m, 3H), 7.41–7.26 (m, 5H), 6.98–6.92 (m, 2H), 6.84–6.78 (m, 2H), 5.13 (d, $J=11.1$ Hz, 1H), 4.97 (dd, $J=9.9, 2.1$ Hz, 1H), 4.85 (d, $J=11.1$ Hz, 1H), 4.75 (d, $J=11.7$ Hz, 1H), 4.66 (d, $J=11.7$ Hz, 1H), 3.76 (s, 3H), 3.76–3.69 (m, 1H), 3.54–3.45 (m, 1H), 3.28 (t, $J=8.9$ Hz, 1H), 2.53 (ddd, $J=12.5, 5.0, 2.1$ Hz, 1H), 1.90 (td, $J=12.0, 9.8$ Hz, 1H), 1.39 (d, $J=6.2$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ = 155.1, 151.4, 138.4, 135.9, 133.4, 133.1, 128.6, 128.3, 128.1, 127.9, 127.8, 126.9, 126.22, 126.2, 118.0, 114.6, 98.5, 83.6, 79.2, 75.5, 71.7, 55.8, 37.0, 18.5.

Synthesis of **15**



β -*p*-Methoxyphenyl 3-O-(2-naphthylmethyl)-4-O-methyl-2,6-dideoxy-D-*arabino*-hexopyranose (**15**)



A solution of **6** (3.6 g, 4.0 mmol) and 2,4,6-*tert*-butylpyrimidine (TTBP, 2.9 g, 12 mmol) in THF (96 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 12 mL, 12 mmol). The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (2.3 g, 12 mmol) in THF (44 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (20 mL), and the rinse added to the reaction mixture. The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 30 min. Meanwhile in a separate flask, *p*-methoxyphenol (1 g, 8 mmol) was dissolved in THF (44 mL), cooled to $-78\text{ }^{\circ}\text{C}$, and treated with potassium hexamethyldisilazane (1 M in THF, 8 mL, 8 mmol). After 30 min, this solution was cannulated to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (20 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 4.5 h. The reaction was quenched with saturated aqueous NH_4Cl (3 mL), diluted with water, and extracted three times with Et_2O . The pooled organic layers were washed with H_2O and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (10% ethyl acetate in hexanes) to afford **15** as a single β -anomer (2.8 g, 87%) as a white powder.

m.p. 130-131 $^{\circ}\text{C}$.

$[\alpha]_{\text{D}}^{22} = -11.4^{\circ}$ (c 0.97, CH_2Cl_2).

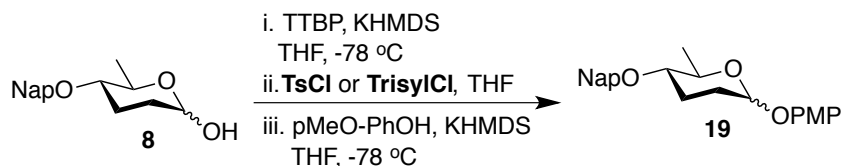
^1H NMR (500 MHz, CDCl_3) δ = 7.86 – 7.79 (m, 4H), 7.51 – 7.43 (m, 3H), 7.00 – 6.93 (m, 2H), 6.85 – 6.77 (m, 2H), 5.08 (d, $J=11.2$, 1H), 4.98 (dd, $J=9.9$, 2.1, 1H), 4.83 (d, $J=11.3$, 1H), 3.77 (s, 3H), 3.55 – 3.43 (m, 5H), 3.18 (t, $J=8.9$, 1H), 2.53 (ddd, $J=12.4$, 5.0, 2.1, 1H), 1.79 (td, $J=12.1$, 9.9, 1H), 1.38 (d, $J=6.2$, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ = 155.2, 151.4, 136.2, 133.5, 133.2, 128.3, 128.1, 127.8, 126.8, 126.2, 126.2, 126.0, 118.1, 114.7, 98.6, 83.5, 81.4, 75.4, 71.7, 57.2, 55.8, 36.4, 18.5.

LRMS (ESI, pos. ion) m/z : calcd. for $C_{25}H_{28}NaO_5$ (M+Na) 431.18, found 431.18.

HRMS (ESI, pos. ion) m/z : calcd. for $C_{25}H_{32}NO_5$ (M+NH₄) 426.2275, found 426.2286.

Synthesis of **19**



TsCl conditions 100mg acceptor scale: A solution of **8** (305 mg, 1.12 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 278 mg, 1.12 mmol) in THF (9 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 1.1 mL, 1.12 mmol). The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (213 mg, 1.12 mmol) in 5 mL THF was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (1 mL), and the rinse added to the reaction mixture. The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. Meanwhile in a separate flask, *p*-methoxyphenol (93 mg, 0.75 mmol) was dissolved in THF (3 mL), cooled to $-78\text{ }^{\circ}\text{C}$, and treated with potassium hexamethyldisilazane (1 M in THF, 0.75 mL, 0.75 mmol). After 15 min, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (3 mL), which was then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 4.5 h. The reaction was quenched with saturated aqueous NH₄Cl (0.3 mL), diluted with water, and extracted three times with Et₂O. The pooled organic layers were washed with H₂O and dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (5% ethyl acetate in hexanes to 10% ethyl acetate in hexanes) to afford **19** and **19a** as separate anomers (226 mg, 80%, 1:8 α : β) as white powders.

TsCl conditions 930 mg acceptor scale: A solution of **8** (3 g, 11 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 2.7 g, 11.2 mmol) in THF (87.2 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ for 10 min and then treated dropwise with potassium hexamethyldisilazane (1M in THF, 11.2 mL, 11.2 mmol). The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (2.1 g, 11.2 mmol) in THF (50 mL) cooled to $-78\text{ }^{\circ}\text{C}$ was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (10 mL) that was allowed to cool, and the cooled rinse added to the reaction mixture. The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. Meanwhile in a separate flask, *p*-methoxyphenol (930 mg, 7.5 mmol) was dissolved in THF (30 mL) was cooled to $-78\text{ }^{\circ}\text{C}$, and treated with potassium hexamethyldisilazane (1 M in THF, 0.75 mL, 0.75 mmol). After 15 min, this solution was cannulated to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (30 mL),

which was cooled and then added to the primary reaction mixture. The reaction mixture was held at $-78\text{ }^{\circ}\text{C}$ for 3 h and then allowed to gradually warm over the course of 2 h. The reaction was quenched with saturated aqueous NH_4Cl (3 mL), diluted with water, and extracted three times with Et_2O . The pooled organic layers were washed with H_2O and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (5% ethyl acetate in hexanes to 10% ethyl acetate in hexanes) to afford **19** and **19a** as separate anomers (1.5 g, 50%, 1:16 α : β) as white powders.

Trisyl chloride conditions: A solution of **8** (305 mg, 1.1 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 278 mg, 1.1 mmol) in THF (9 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 1.1 mL, 1.1 mmol). The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. After 15 min, a solution of 2,4,6-triisopropylbenzenesulfonyl chloride, (340 mg, 1.1 mmol) in THF (5 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (1 mL), and the rinse added to the reaction mixture. The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 30 min. Meanwhile in a separate flask, *p*-methoxyphenol (93 mg, 0.75 mmol) was dissolved in THF (3 mL), cooled to $-78\text{ }^{\circ}\text{C}$, and treated with potassium hexamethyldisilazane (1 M in THF, 0.75 mL, 0.75 mmol). After 30 min, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (3 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 5 h. The reaction was quenched with saturated aqueous NH_4Cl (0.3 mL), diluted with water, and extracted three times with Et_2O . The pooled organic layers were washed with H_2O , brine and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (15% ethyl acetate in hexanes to 30% ethyl acetate in hexanes) to afford **19** and **19a** as separate α - and β -anomer (119 mg, 42%, 1:5 α : β) as white powders.

β -*p*-Methoxyphenyl 4-*O*-(2-naphthylmethyl)-2,3,6-trideoxy-*D*-erythro-hexopyranose (**19**)



m.p. 87-88 $^{\circ}\text{C}$.

$[\alpha]_{\text{D}}^{22} = -12.9^{\circ}$ (c 1.08, CH_2Cl_2).

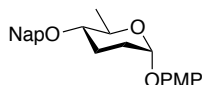
^1H NMR (500 MHz, CDCl_3) δ = 7.86 – 7.75 (m, 4H), 7.52 – 7.44 (m, 3H), 7.00 – 6.93 (m, 2H), 6.85 – 6.78 (m, 2H), 5.04 (dd, $J=9.2, 2.3$, 1H), 4.80 (d, $J=11.7$, 1H), 4.67 (d, $J=11.7$, 1H), 3.77 (s, 3H), 3.61 (dq, $J=8.6, 6.2$, 1H), 3.21 (ddd, $J=10.5, 8.6, 4.4$, 1H), 2.33 (dq, $J=12.7, 4.1$, 1H), 2.13 – 2.04 (m, 1H), 1.81 (tdd, $J=13.3, 9.2, 4.3$, 1H), 1.64 – 1.55 (m, 1H), 1.38 (d, $J=6.2$, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ = 154.9, 151.4, 136.0, 133.4, 133.2, 128.4, 128.0, 127.8, 126.6, 126.3, 126.1, 125.9, 117.9, 114.6, 100.2, 78.2, 74.9, 71.6, 55.8, 30.3, 27.4, 18.8.

LRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{24}\text{H}_{30}\text{NO}_4$ ($\text{M}+\text{NH}_4$) 396.22, found 395.91.

HRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{24}\text{H}_{26}\text{NaO}_4$ ($\text{M}+\text{Na}$) 401.1729, found 401.1725.

α -*p*-Methoxyphenyl 4-*O*-(2-naphthylmethyl)-2,3,6-trideoxy-*D*-erythro-hexopyranose (**19a**)



m.p. 80-81 °C.

$[\alpha]_{\text{D}}^{22} = +151.1^\circ$ (c 0.96, CH_2Cl_2).

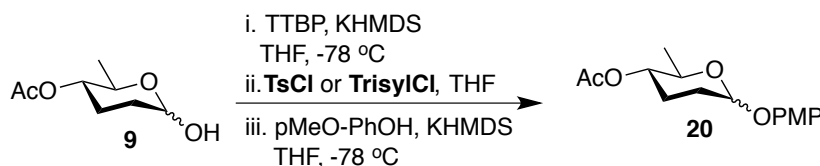
^1H NMR (500 MHz, CDCl_3) δ = 7.86 – 7.75 (m, 4H), 7.51 – 7.43 (m, 3H), 7.03 – 6.96 (m, 2H), 6.85 – 6.78 (m, 2H), 5.36 (d, $J=2.5$, 1H), 4.83 (d, $J=11.8$, 1H), 4.67 (d, $J=11.8$, 1H), 3.91 (dq, $J=9.1$, 6.2, 1H), 3.76 (s, 3H), 3.19 (ddd, $J=10.6$, 9.2, 4.5, 1H), 2.17 – 2.10 (m, 1H), 2.10 – 1.93 (m, 2H), 1.87 – 1.76 (m, 1H), 1.25 (d, $J=6.2$, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ = 154.6, 151.0, 136.1, 133.4, 133.1, 128.3, 128.0, 127.8, 126.5, 126.2, 126.0, 125.9, 117.9, 114.6, 95.5, 78.9, 71.0, 68.8, 55.8, 29.6, 24.0, 18.5.

LRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{24}\text{H}_{26}\text{NaO}_4$ ($\text{M}+\text{Na}$) 401.17, found 401.27.

HRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{24}\text{H}_{26}\text{NaO}_4$ ($\text{M}+\text{Na}$) 401.1729, found 401.1727.

Synthesis of **20**

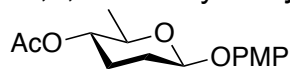


TsCl conditions: A solution of **9** (195 mg, 1.12 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 278 mg, 1.12 mmol) in THF (9 mL) was cooled to -78°C and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 1.1 mL, 1.1 mmol). The solution was maintained at -78°C for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (213 mg, 1.1 mmol) in THF (5 mL) was added slowly to the reaction. The flask containing the *TsCl* solution was then

rinsed with THF (1 mL), and the rinse added to the reaction mixture. The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 30 min. Meanwhile in a separate flask, *p*-methoxyphenol (93 mg, 0.75 mmol) was dissolved in THF (3 mL), cooled to $-78\text{ }^{\circ}\text{C}$, and treated with potassium hexamethyldisilazane (1 M in THF, 0.75 mL, 0.75 mmol). After 30 min, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (3 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 4.5 h. The reaction was quenched with saturated aqueous NH_4Cl (0.3 mL), diluted with water, and extracted three times with Et_2O . The pooled organic layers were washed with H_2O and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (5% ethyl acetate in hexanes to 10% ethyl acetate in hexanes) to afford **20** and **20a** as separate anomers (128 mg, 61%, 2.2:1 α : β) as a white powders.

TrisylCl conditions: A solution of **9** (195 mg, 1.12 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 278 mg, 1.12 mmol) in THF (9 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 1.1 mL, 1.1 mmol). The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. After 15 min, a solution of 2,4,6-triisopropylbenzenesulfonyl chloride, (340 mg, 1.12 mmol) in THF (5 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (1 mL), and the rinse added to the reaction mixture. The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 30 min. Meanwhile in a separate flask, *p*-methoxyphenol (93 mg, 0.75 mmol) was dissolved in THF (3 mL), cooled to $-78\text{ }^{\circ}\text{C}$, and treated with potassium hexamethyldisilazane (1 M in THF, 0.75 mL, 0.75 mmol). After 30 min, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (3 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 5 h. The reaction was quenched with saturated aqueous NH_4Cl (0.3 mL), diluted with water, and extracted three times with Et_2O . The pooled organic layers were washed with H_2O , brine and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (15% ethyl acetate in hexanes to 30% ethyl acetate in hexanes) to afford **20** as a single α -anomer (177 mg, 84%) as a white powder.

β -*p*-Methoxyphenyl 4-*O*-acetyl-2,3,6-trideoxy-D-*erythro*-hexopyranose (**20**)



m.p. 93-94 $^{\circ}\text{C}$.

$[\alpha]_{\text{D}}^{22} = -35.9^{\circ}$ (*c* 1.19, CH_2Cl_2).

$^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 7.02 - 6.93$ (m, 2H), 6.85 - 6.78 (m, 2H), 5.06 (dd, $J=8.8, 2.4$, 1H), 4.54 (ddd, $J=10.2, 8.6, 4.6$, 1H), 3.77 (s, 3H), 3.65 (dq,

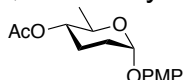
$J=8.7, 6.3, 1\text{H}$), 2.26 (dq, $J=13.1, 4.4, 1\text{H}$), 2.11 – 2.03 (m, 4H), 1.90 (tdd, $J=13.2, 8.8, 4.4, 1\text{H}$), 1.64 – 1.52 (m, 1H), 1.26 (d, $J=6.3, 3\text{H}$).

^{13}C NMR (125 MHz, CDCl_3) $\delta = 170.4, 155.0, 151.3, 117.9, 114.6, 99.9, 73.5, 72.6, 55.8, 29.8, 26.8, 21.3, 18.4$.

LRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{15}\text{H}_{24}\text{NO}_5$ ($\text{M}+\text{NH}_4$) 298.17, found 298.18.

HRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{15}\text{H}_{20}\text{NaO}_5$ ($\text{M}+\text{Na}$) 303.1208, found 303.1196 .

α -*p*-Methoxyphenyl 4-*O*-acetyl-2,3,6-trideoxy-*D*-erythro-hexopyranose (**20a**)



m.p. 85-86 °C.

$[\alpha]_{\text{D}}^{22} = +156.6^\circ$ (c 1.09, CH_2Cl_2).

^1H NMR (500 MHz, CDCl_3) $\delta = 7.04 - 6.96$ (m, 2H), 6.87 – 6.79 (m, 2H), 5.39 (d, $J=2.8, 1\text{H}$), 4.60 – 4.52 (m, 1H), 3.93 (dq, $J=9.9, 6.2, 1\text{H}$), 3.78 (s, 3H), 2.06 (s, 3H), 2.06 – 1.87 (m, 4H), 1.12 (d, $J=6.2, 3\text{H}$).

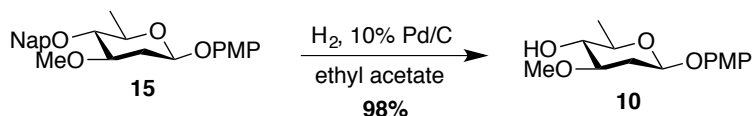
^{13}C NMR (125 MHz, CDCl_3) $\delta = 170.4, 154.7, 151.0, 117.8, 114.7, 95.5, 73.5, 67.3, 55.8, 29.5, 24.1, 21.3, 18.0$.

LRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{15}\text{H}_{24}\text{NO}_5$ ($\text{M}+\text{NH}_4$) 298.17, found 298.16.

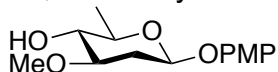
HRMS (DART, pos. ion) m/z : calcd. for $\text{C}_{15}\text{H}_{21}\text{O}_5$ ($\text{M}+\text{H}$) 281.1384, found 281.1391.

S3.4 Preparation of the glycosyl acceptors **10** and **11**

Synthesis of **10**



β -*p*-Methoxyphenyl 4-O-methyl-2,6-dideoxy-D-*arabino*-hexopyranose (**10**)



Compound **15** (0.5 g, 1.2 mmol) dissolved in ethyl acetate (10 mL) was added to a suspension of palladium on carbon (58 mg, 0.04 mmol) in ethyl acetate (3 mL) under argon atmosphere. The flask was evacuated and then purged with hydrogen gas three times. After 3 h under hydrogen atmosphere, the reaction was filtered with silica gel and rinsed with ethyl acetate and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (30% ethyl acetate in hexanes to 50% ethyl acetate in hexanes) to afford compound **10** (315 mg, 98%) as a white powder.

m.p. 105-106 °C.

$[\alpha]_{\text{D}}^{22} = -73.9^\circ$ (*c* 1.27, CH₂Cl₂).

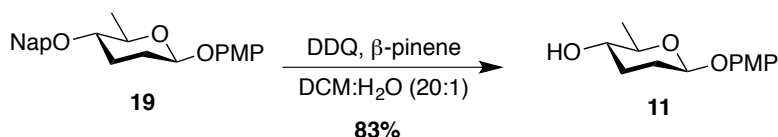
¹H NMR (500 MHz, CDCl₃) δ = 7.00 – 6.93 (m, 2H), 6.85 – 6.79 (m, 2H), 5.01 (dd, *J*=9.8, 2.2, 1H), 3.77 (s, 3H), 3.48 – 3.39 (m, 4H), 3.32 – 3.20 (m, 2H), 2.55 – 2.48 (m, 2H), 1.77 – 1.67 (m, 1H), 1.39 (d, *J*=6.2, 3H).

¹³C NMR (125 MHz, CDCl₃) δ = 155.2, 151.3, 118.0, 114.6, 98.7, 80.7, 75.5, 71.9, 56.5, 55.8, 35.2, 18.1.

LRMS (ESI, pos. ion) *m/z*: calcd. for C₁₄H₂₀NaO₅ (M+Na) 291.12, found 291.09.

HRMS (ESI, pos. ion) *m/z*: calcd. for C₁₄H₁₉O₅ (M-H) 267.1227, found 267.1240.

Synthesis of **11**.



β -*p*-Methoxyphenyl 2,3,6-trideoxy-D-*erythro*-hexopyranose (**11**)



To a solution of **19** (1 g, 2.6 mmol) and β -pinene (1.4 mL, 8.9 mmol) in DCM (260 mL) and H₂O (13 mL), was added DDQ (1.2 g, 5.2 mmol). The reaction was

stirred at room temperature under argon for 1.5 h and monitored by TLC. The reaction mixture was then diluted with DCM (250 mL), and the organic layer was washed with 2M NaOH (3 x 300 mL) and saturated NaHCO₃ (3 x 300 mL), dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (25% to 30% ethyl acetate in hexanes) to afford **11** (522 mg, 83%) as an off-white powder.

m.p. 61-62 °C.

$[\alpha]_D^{22} = -51.6^\circ$ (c 1.28, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ = 7.00 – 6.93 (m, 2H), 6.85 – 6.78 (m, 2H), 5.02 (dd, *J*=9.3, 2.3, 1H), 3.77 (s, 3H), 3.48 – 3.33 (m, 2H), 2.16 (dq, *J*=12.5, 4.1, 1H), 2.11 – 2.02 (m, 1H), 1.87 (tdd, *J*=13.4, 9.3, 4.3, 1H), 1.63 – 1.47 (m, 2H), 1.35 (d, *J*=6.0, 3H).

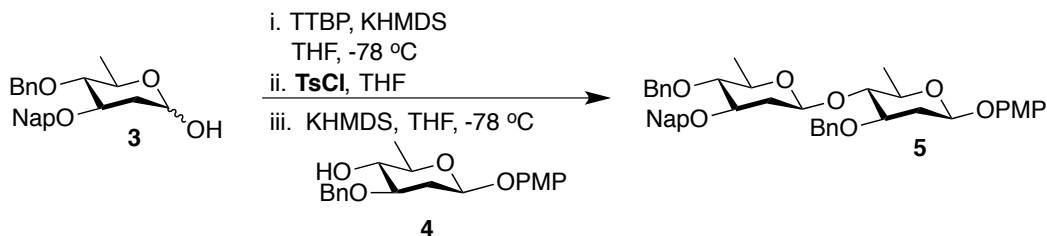
¹³C NMR (125 MHz, CDCl₃) δ = 154.9, 151.4, 117.9, 114.6, 100.2, 76.1, 71.4, 55.8, 30.9, 30.6, 18.3.

LRMS (ESI, pos. ion) *m/z*: calcd. for C₁₃H₂₂NO₄ (M+NH₄) 256.15, found 255.73.

HRMS (ESI, pos. ion) *m/z*: calcd. for C₁₃H₁₉O₄ (M+H) 239.1283, found 239.1285.

S3.5 Synthesis of disaccharides **5**, **14**, **16**, **17**, **18**, **21**, **22**

Synthesis of **5**

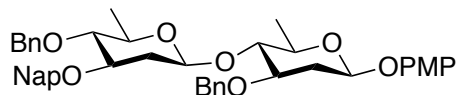


Method for 100 mg acceptor scale: A solution of **3**^[1] (282 mg, 0.74 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 183 mg, 0.74 mmol) in THF (10 mL) was cooled to -78 °C and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 0.74 mL, 0.74 mmol). The solution was maintained at -78 °C for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (141 mg, 0.74 mmol) in THF (3.5 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (0.5 mL), and the rinse added to the reaction mixture. The solution was maintained at -78 °C for 1 h. Meanwhile in a separate flask, the acceptor **4**^[1] (171 mg, 0.49 mmol) was dissolved in 2 mL THF, cooled to -78 °C, and treated with potassium hexamethyldisilazane (1 M in THF, 0.49 mL, 0.49 mmol). After 1 h, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (2 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 5 h. The reaction was quenched with saturated aqueous NH₄Cl (0.3 mL), diluted with water, and extracted three times with DCM. The pooled organic layers were washed with H₂O and dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (20% ethyl acetate in hexanes) to afford **5** as a single β-anomer (220 mg, 64%) as a white powder. The spectroscopic data is in good agreement with previously reported data.^[1]

Method for 500 mg acceptor scale: A solution of **3**^[1] (820 mg, 2.1 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 539 mg, 2.1 mmol) in THF (18 mL) was cooled to -78 °C and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 2.1 mL, 2.1 mmol). The solution was maintained at -78 °C for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (413 mg, 2.1 mmol) in THF (8 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (3 mL), and the rinse added to the reaction mixture. The solution was maintained at -78 °C for 1 h. Meanwhile in a separate flask, the acceptor **4**^[1] (500 mg, 1.4 mmol) was dissolved in THF (8 mL), cooled to -78 °C, and treated with potassium hexamethyldisilazane (1 M in THF, 1.4 mL, 1.4 mmol). After 1 h, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (3 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 5 h. The reaction was

quenched with saturated aqueous NH_4Cl (0.3 mL), diluted with water, and extracted three times with DCM. The pooled organic layers were washed with H_2O and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (10% ethyl acetate in hexanes) to afford **5** as a single β -anomer (620 mg, 60%) as a white powder. The spectroscopic data is in good agreement with previously reported data.^[1]

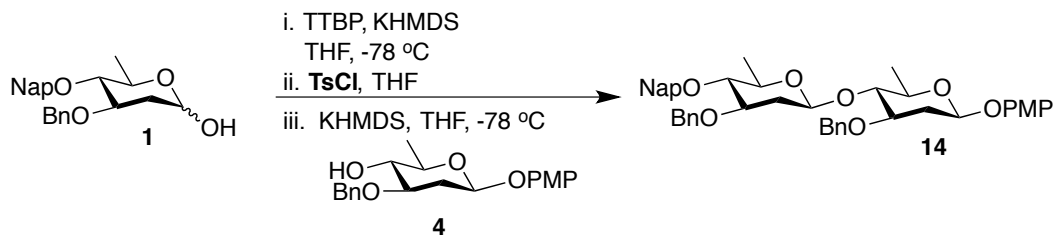
β -*p*-Methoxyphenyl 4-(3'-O-naphthylmethyl-4'-O-benzyl-2',6'-dideoxy- β -D-*arabino*-hexopyranoyl)-3-O-benzyl-2,6-dideoxy-D-*arabino*-hexopyranose (**5**)



^1H NMR (500 MHz, CDCl_3) δ = 7.86 – 7.72 (m, 4H), 7.49 – 7.43 (m, 3H), 7.40 – 7.33 (m, 2H), 7.33 – 7.22 (m, 6H), 6.94 (d, $J=9.4$, 2H), 6.80 (d, $J=9.7$, 2H), 5.00 – 4.91 (m, 2H), 4.85 – 4.63 (m, 6H), 3.76 (s, 3H), 3.69 – 3.59 (m, 2H), 3.49 – 3.39 (m, 1H), 3.38 – 3.25 (m, 2H), 3.15 (t, $J=9.0$, 1H), 2.45 (ddd, $J=12.6$, 5.2, 2.1, 1H), 2.39 (ddd, $J=12.1$, 8.3, 4.0, 1H), 1.86 (td, $J=12.4$, 10.0, 1H), 1.63 (td, $J=12.1$, 9.8, 1H), 1.34 (d, $J=8.9$, 3H), 1.30 (d, $J=6.1$, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ = 155.2, 151.3, 138.7, 138.6, 136.0, 128.5, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.7, 126.5, 126.3, 126.0, 125.9, 118.1, 114.6, 100.3, 98.5, 83.9, 82.4, 79.3, 77.8, 75.4, 72.0, 71.8, 71.7, 71.4, 55.8, 37.6, 37.1, 18.6, 18.4.

Synthesis of **14**

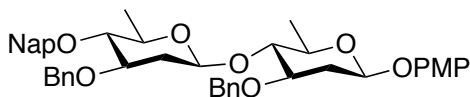


Method for 100 mg acceptor scale: A solution of **1**^[1] (164 mg, 0.43 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 106 mg, 0.43 mmol) in THF (4 mL) was cooled to -78 °C and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 0.43 mL, 0.43 mmol). The solution was maintained at -78 °C for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (83 mg, 0.43 mmol) in 2.5 mL THF was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (0.5 mL), and the rinse added to the reaction mixture. The solution was maintained at -78 °C for 1 h. Meanwhile in a separate flask, **4**^[1] (100 mg, 0.29 mmol) was dissolved in THF (1.5 mL), cooled to -78 °C, and treated with potassium hexamethyldisilazane (1 M in THF, 0.29 mL, 0.29

mmol). After 1 h, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (1.5 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 4.5 h. The reaction was quenched with saturated aqueous NH₄Cl (0.3 mL), diluted with water, and extracted three times with DCM. The pooled organic layers were washed with H₂O and dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (20% ethyl acetate in hexanes) to afford **14** as a single β-anomer (152 mg, 75%) as a white powder.

Method for 500 mg acceptor scale: A solution of **1**^[1] (820 mg, 2.11 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 539 mg, 2.11 mmol) in THF (26 mL) was cooled to -78 °C and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 0.43 mL, 2.1 mmol). The solution was maintained at -78 °C for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (413 mg, 2.11 mmol) in THF (10 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (2 mL), and the rinse added to the reaction mixture. The solution was maintained at -78 °C for 1 h. Meanwhile in a separate flask, **4**^[1] (500 mg, 1.40 mmol) was dissolved in THF (8 mL), cooled to -78 °C, and treated with potassium hexamethyldisilazane (1 M in THF, 1.4 mL, 1.4 mmol). After 1 h, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (4 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 4.5 h. The reaction was quenched with saturated aqueous NH₄Cl (0.3 mL), diluted with water, and extracted three times with DCM. The pooled organic layers were washed with H₂O and dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (15% ethyl acetate in hexanes to 20% ethyl acetate in hexanes) to afford **14** as a single β-anomer (660 mg, 66%) as a white powder.

β-*p*-Methoxyphenyl 4-(3'-O-benzyl-4'-(2-naphthylmethyl)-2',6'-dideoxy-β-D-*arabino*-hexopyranoyl)-3-O-benzyl-2,6-dideoxy-D-*arabino*-hexopyranose (**14**)



m.p. 124-125 °C.

$[\alpha]_D^{24} = -23.2^\circ$ (c 0.96, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ = 7.85 – 7.68 (m, 4H), 7.50 – 7.41 (m, 3H), 7.40 – 7.28 (m, 8H), 6.97 – 6.91 (m, 2H), 6.84 – 6.78 (m, 2H), 5.09 (d, *J*=10.9, 1H), 4.95 (dd, *J*=10.1, 2.0, 1H), 4.82 (d, *J*=11.0, 1H), 4.78 – 4.59 (m, 5H), 3.77 (s, 3H), 3.71 – 3.56 (m, 2H), 3.47 – 3.43 (m, 1H), 3.39 – 3.29 (m, 2H), 3.19 (t, *J*=8.8, 1H),

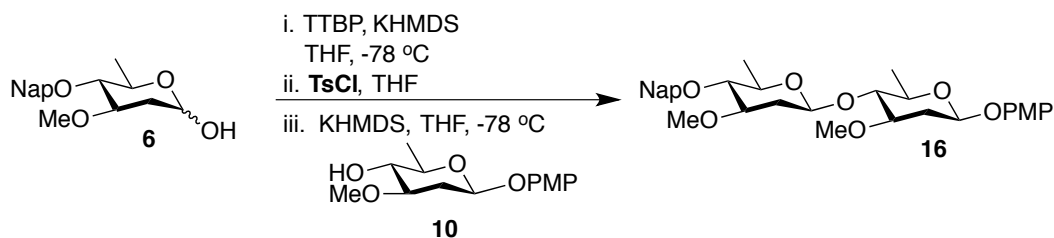
2.45 (dd, $J=11.5, 4.2$, 1H), 2.37 (dd, $J=11.9, 4.2$, 1H), 1.87 (q, $J=11.3$, 1H), 1.61 (q, $J=11.1, 10.6$, 1H), 1.36 (d, $J=5.5$, 3H), 1.31 (d, $J=5.5$, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ = 155.1, 151.2, 138.7, 138.5, 136.0, 133.4, 133.1, 128.5, 128.4, 128.2, 128.0, 127.8, 127.8, 127.7, 127.6, 126.8, 126.2, 126.1, 126.0, 118.0, 114.6, 100.3, 98.5, 83.8, 82.3, 79.4, 77.7, 75.4, 71.9, 71.7, 71.7, 71.4, 55.7, 37.5, 37.1, 18.6, 18.5.

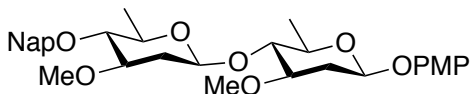
LRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{44}\text{H}_{48}\text{NaO}_8$ ($\text{M}+\text{Na}$) 727.32, found 727.45.

HRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{44}\text{H}_{52}\text{NO}_8$ ($\text{M}+\text{NH}_4$) 722.3667, found 722.3671.

Synthesis of **16**



β -*p*-Methoxyphenyl 4-(3'-*O*-methyl-4'-(2-naphthylmethyl)-2',6'-dideoxy- β -*D*-*arabino*-hexopyranoyl)-3-*O*-methyl-2,6-dideoxy-*D*-*arabino*-hexopyranose (**16**)



Method for 100 mg acceptor scale: A solution of **6** (225 mg, 0.74 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 185 mg, 0.74 mmol) in THF (7.9 mL) was cooled to $-78\text{ }^\circ\text{C}$ and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 0.74 mL, 0.74 mmol). The solution was maintained at $-78\text{ }^\circ\text{C}$ for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (142 mg, 0.74 mmol) in THF (2 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (1.5 mL), and the rinse added to the reaction mixture. The solution was maintained at $-78\text{ }^\circ\text{C}$ for 15 min. Meanwhile in a separate flask, the acceptor **10** (100 mg, 0.37 mmol) was dissolved in THF (2 mL), cooled to $-78\text{ }^\circ\text{C}$, and treated with potassium hexamethyldisilazane (1 M in THF, 0.37 mL, 0.37 mmol). After 15 min, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (1.5 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 4.5 h. The reaction was quenched with saturated aqueous NH_4Cl (0.3 mL), diluted with water, and extracted three times with DCM. The pooled organic layers were

washed with H₂O and dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (20% ethyl acetate in hexanes to 30% ethyl acetate in hexanes) to afford **16** as a single β-anomer (155 mg, 75%) as a white powder.

Method for 500 mg acceptor scale: A solution of **6** (1.1 g, 3.7 mmol) and 2,4,6-*tert*-butylpyrimidine (TTBP, 924 mg, 3.7 mmol) in THF (39.5 mL) was cooled to -78 °C and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 3.7 mL, 3.7 mmol). The solution was maintained at -78 °C for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (704 mg, 3.7 mmol) in THF (10 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (7.5 mL), and the rinse added to the reaction mixture. The solution was maintained at -78 °C for 15 min. Meanwhile in a separate flask, the acceptor **10** (500 mg, 1.8 mmol) was dissolved in THF (10 mL), cooled to -78 °C, and treated with potassium hexamethyldisilazane (1 M in THF, 1.8 mL, 1.8 mmol). After 25 min, this solution was transferred to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (7.5 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 4.5 h. The reaction was quenched with saturated aqueous NH₄Cl (0.3 mL), diluted with water, and extracted three times with DCM. The pooled organic layers were washed with H₂O and dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (20% ethyl acetate in hexanes to 30% ethyl acetate in hexanes) to afford **16** as a single β-anomer (570 mg, 57%) as a white powder.

m.p. 119-120 °C.

$[\alpha]_D^{22} = -23.6^\circ$ (c 1.12, CH₂Cl₂).

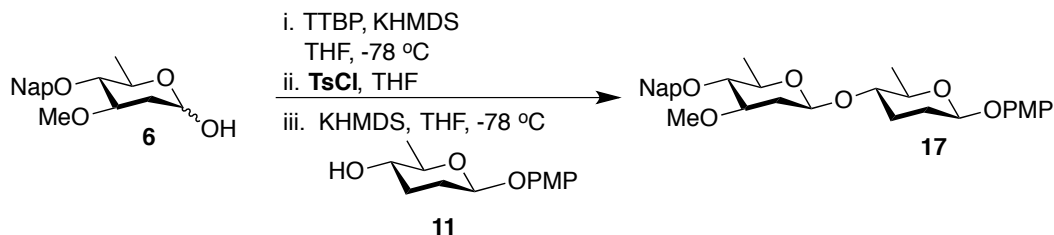
¹H NMR (500 MHz, CDCl₃) δ = 7.86 – 7.75 (m, 4H), 7.51 – 7.42 (m, 3H), 7.00 – 6.91 (m, 2H), 6.85 – 6.78 (m, 2H), 5.06 (d, *J*=11.3, 1H), 4.96 (dd, *J*=9.8, 2.1, 1H), 4.80 (d, *J*=11.3, 1H), 4.73 (dd, *J*=9.9, 2.0, 1H), 3.77 (s, 3H), 3.51 – 3.34 (m, 10H), 3.26 (t, *J*=8.8, 1H), 3.10 (t, 8.9, 1H), 2.49 (ddd, *J*=12.5, 5.2, 2.1, 1H), 2.36 (ddd, *J*=12.5, 4.9, 2.0, 1H), 1.77 (td, *J*=12.2, 9.9, 1H), 1.51 (td, *J*=12.1, 9.9, 1H), 1.36 (dd, *J*=6.2, 4.1, 6H).

¹³C NMR (125 MHz, CDCl₃) δ 155.1, 151.3, 136.2, 133.4, 133.1, 128.2, 128.0, 127.8, 126.7, 126.2, 126.1, 125.9, 118.0, 114.6, 100.3, 98.5, 83.6, 82.4, 81.5, 79.3, 75.2, 71.5, 71.3, 57.2, 56.9, 55.7, 36.8, 36.1, 18.5.

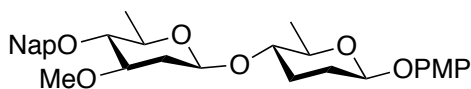
LRMS (ESI, pos. ion) *m/z*: calcd. for C₃₂H₄₀NaO₈ (M+Na) 575.26, found 575.45.

HRMS (ESI, pos. ion) *m/z*: calcd. for C₃₂H₄₀NaO₈ (M+Na) 575.2621, found 575.2621.

Synthesis of 17



β -*p*-Methoxyphenyl 4-(3'-*O*-methyl-4'-(2-naphthylmethyl)-2',6'-dideoxy- β -D-*arabino*-hexopyranoyl)-2,3,6-trideoxy-D-*erythro*-hexopyranose (**17**)



Method of 100mg acceptor scale: A solution of **6** (254 mg, 0.83 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 208 mg, 0.83 mmol) in THF (8.2 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 0.83 mL, 0.83 mmol). The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (213 mg, 0.83 mmol) in THF (2.5 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (2.5 mL), and the rinse added to the reaction mixture. The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. Meanwhile in a separate flask, a stock solution of the acceptor was made: **11** (300 mg, 1.23 mmol) was dissolved in THF (9.5 mL), cooled to $-78\text{ }^{\circ}\text{C}$, and treated with potassium hexamethyldisilazane (1 M in THF, 1.23 mL, 1.23 mmol). After 15 min, a portion (3.5 mL) of the stock solution was transferred by syringe to the primary reaction vessel. The reaction mixture was then allowed to gradually warm over the course of 4.5 h. The reaction was quenched with saturated aqueous NH_4Cl (0.3 mL), diluted with water, and extracted three times with DCM. The pooled organic layers were washed with H_2O and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (15% ethyl acetate in hexanes to 20% ethyl acetate in hexanes) to afford **17** as a single β -anomer (118 mg, 55%) as a white powder.

Method of 500mg acceptor scale: A solution of **6** (1.2 g, 4.1 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 1 g, 4 mmol) in THF (41 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 4 mL, 4 mmol). The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (704 mg, 4.1 mmol) in THF (20 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (5 mL), and the rinse added to the reaction mixture. The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. Meanwhile in a separate flask, a solution of **11** (500 mg, 2 mmol) was dissolved in THF (15 mL), cooled to $-78\text{ }^{\circ}\text{C}$, and treated with potassium hexamethyldisilazane (1 M in THF, 2 mL, 2 mmol). After

25min, the solution was cannulated to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (10 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was maintained at $-78\text{ }^{\circ}\text{C}$ for 3 h and then allowed to gradually warm over the course of 3.5 h. The reaction was quenched with saturated aqueous NH_4Cl (3 mL), diluted with water, and extracted three times with DCM. The pooled organic layers were washed with H_2O and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (15% ethyl acetate in hexanes to 20% ethyl acetate in hexanes) to afford **17** as a single β -anomer (500 mg, 50%) as a white powder.

m.p. 83-84 $^{\circ}\text{C}$.

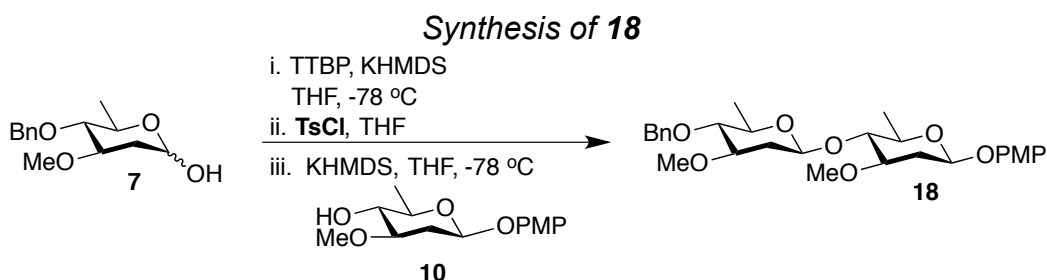
$[\alpha]_{\text{D}}^{22} = -37.4^{\circ}$ (c 1.09, CH_2Cl_2).

^1H NMR (500 MHz, CDCl_3) $\delta = 7.88 - 7.80$ (m, 4H), 7.54 - 7.45 (m, 3H), 7.02 - 6.92 (m, 2H), 6.87 - 6.80 (m, 2H), 5.08 (d, $J=11.2$, 1H), 5.02 (dd, $J=9.2$, 2.2, 1H), 4.83 (d, $J=11.3$, 1H), 4.55 (dd, $J=9.9$, 2.0, 1H), 3.79 (s, 3H), 3.55 (dq, $J=8.8$, 6.2, 1H), 3.49 (s, 3H), 3.47 - 3.36 (m, 2H), 3.34 - 3.25 (m, 1H), 3.13 (t, $J=8.9$, 1H), 2.41 - 2.30 (m, 2H), 2.07 (dd, $J=11.5$, 4.1, 1H), 1.85 (tdd, $J=13.3$, 9.1, 4.2, 1H), 1.74 - 1.62 (m, 1H), 1.61 - 1.50 (m, 1H), 1.36 (d, $J=6.2$, 3H), 1.34 (d, $J=6.2$, 3H).

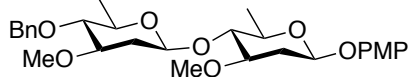
^{13}C NMR (125 MHz, CDCl_3) $\delta = 154.9$, 151.4, 136.2, 133.4, 133.1, 128.2, 128.1, 127.8, 126.8, 126.3, 126.2, 126.0, 117.9, 114.6, 101.1, 100.2, 83.5, 81.4, 80.2, 75.3, 74.6, 71.4, 57.1, 55.8, 36.7, 30.5, 29.6, 18.6, 18.5.

LRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{31}\text{H}_{42}\text{NO}_7$ ($\text{M}+\text{NH}_4$) 540.30, found 540.10.

HRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{31}\text{H}_{38}\text{NaO}_7$ ($\text{M}+\text{Na}$) 545.2515, found 545.2488.



β -*p*-Methoxyphenyl 4-(3'-O-methyl-4'-benzyl-2',6'-dideoxy- β -D-*arabino*-hexopyranoyl)-3-O-methyl-2,6-dideoxy-D-*arabino*-hexopyranose (**18**)



A solution of **7** (186 mg, 0.74 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 185 mg, 0.74 mmol) in THF (7.9 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated dropwise with

potassium hexamethyldisilazane (1 M in THF, 0.74 mL, 0.74 mmol). The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (142 mg, 0.74 mmol) in THF (2 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (1.5 mL), and the rinse added to the reaction mixture. The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. Meanwhile in a separate flask, **10** (100 mg, 0.37 mmol) was dissolved in 2 mL THF, cooled to $-78\text{ }^{\circ}\text{C}$, and treated with potassium hexamethyldisilazane (1 M in THF, 0.37 mL, 0.37 mmol). After 15 min, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (1.5 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 6 h. The reaction was quenched with saturated aqueous NH_4Cl (0.3 mL), diluted with water, and extracted three times with DCM. The pooled organic layers were washed with H_2O and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (15% ethyl acetate in hexanes to 30% ethyl acetate in hexanes) to afford **18** as a single β -anomer (130 mg, 70%) as a white powder.

m.p. 117-118 $^{\circ}\text{C}$.

$[\alpha]_{\text{D}}^{22} = -14.04^{\circ}$ (c 1.90, CH_2Cl_2).

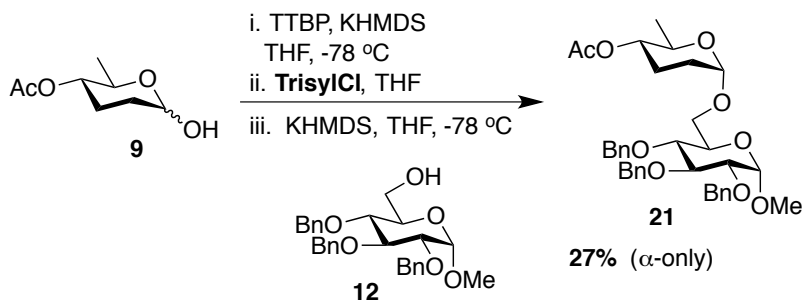
^1H NMR (500 MHz, CDCl_3) $\delta = 7.38 - 7.27$ (m, 5H) 6.99 – 6.92 (m, 2H), 6.85 – 6.78 (m, 2H), 4.95 (dd, $J=9.8, 2.1$, 1H), 4.90 (d, $J=11.1$, 1H), 4.71 (dd, $J=9.9, 2.1$, 1H), 4.63 (d, $J=11.0$, 1H), 3.77 (s, 3H), 3.51 – 3.40 (m, 8H) 3.40 – 3.30 (m, 2H), 3.26 (t, $J=8.8$, 1H), 3.04 (t, $J=8.9$, 1H), 2.49 (ddd, $J=12.6, 5.3, 2.1$, 1H), 2.34 (ddd, $J=12.4, 5.0, 2.1$, 1H), 1.76 (td, $J=11.9, 9.9$, 1H) 1.49 (td, $J=12.1, 9.9$, 1H), 1.36 (d, $J=6.2$, 3H), 1.34 (d, $J=6.1$, 3H).

^{13}C NMR (125 MHz, CDCl_3) $\delta = 155.1, 151.3, 138.7, 128.5, 128.1, 127.8, 118.0, 114.6, 100.3, 98.5, 83.5, 82.4, 81.4, 79.3, 75.1, 71.5, 71.3, 57.1, 56.9, 55.7, 36.8, 36.1, 18.5, 18.4$.

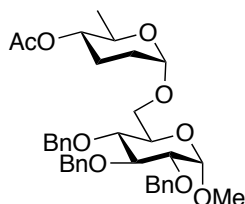
LRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{28}\text{H}_{38}\text{NaO}_8$ (M+Na) 525.25, found 525.36.

HRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{28}\text{H}_{38}\text{NaO}_8$ (M+Na) 525.2464, found 525.2463.

Synthesis of **21**



Methyl 6-O-(2',3',6'-trideoxy-D-*erythro*-hexopyranoyl)-2,3,4-tri-O-benzyl- α -D-glucopyranoside (**21**)



A solution of **9** (195 mg, 1.12 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 278 mg, 1.12 mmol) in THF (9 mL) was cooled to -78 °C and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 1.1 mL, 1.1 mmol). The solution was maintained at -78 °C for 15 min. After 15 min, a solution of 2,4,6-triisopropylbenzenesulfonyl chloride, (340 mg, 1.12 mmol) in THF (5 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (1 mL), and the rinse added to the reaction mixture. The solution was maintained at -78 °C for 30 min. Meanwhile in a separate flask, **12**^[2] (348 mg, 0.75 mmol) was dissolved in THF (3 mL), cooled to -78 °C, and treated with potassium hexamethyldisilazane (1 M in THF, 0.75 mL, 0.75 mmol). After 30 min, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (3 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 6 h. The reaction was quenched with saturated, aqueous NH_4Cl (0.3 mL), diluted with water, and extracted three times with Et_2O . The pooled organic layers were washed with H_2O , brine and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (25% ethyl acetate in hexanes to 40% ethyl acetate in hexanes) to afford **21** as a single α -anomer (131 mg, 27%) as an amorphous solid.

$[\alpha]_{\text{D}}^{22} = +98.3^\circ$ (*c* 1.08, CH_2Cl_2).

$^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 7.41 - 7.27$ (m, 15H), 5.00 (dd, $J=10.9, 6.4$, 2H), 4.84 - 4.75 (m, 3H), 4.68 (d, $J=11.7$, 2H), 4.65 - 4.61 (m, 1H), 4.45 - 4.11 (m, 1H), 4.02 (t, $J=9.3$, 1H), 3.90 (dd, $J=11.4, 4.0$, 1H), 3.80 - 3.68 (m, 2H), 3.64 -

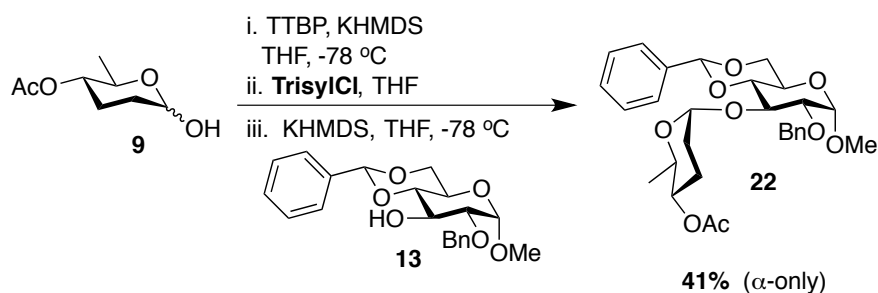
3.56 (m, 2H), 3.55 (dd, $J=9.6, 3.6$, 1H), 3.38 (s, 3H), 2.01 (s, 3H), 1.93 – 1.83 (m, 2H), 1.83 – 1.70 (m, 2H), 1.02 (d, $J=6.2$, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ = 170.4, 138.8, 138.6, 138.3, 128.6, 128.6, 128.5, 128.2, 128.1, 127.8, 127.8, 127.6, 98.2, 96.7, 82.4, 80.2, 77.9, 76.0, 75.0, 73.6, 73.5, 70.0, 66.8, 65.7, 55.3, 29.2, 24.2, 21.3, 17.9.

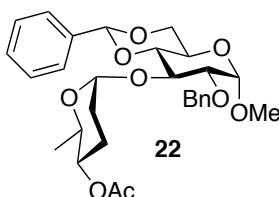
LRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{36}\text{H}_{44}\text{NaO}_9$ ($\text{M}+\text{Na}$) 643.29, found 643.45.

HRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{36}\text{H}_{44}\text{NaO}_9$ ($\text{M}+\text{Na}$) 643.2883, found 643.2878.

Synthesis of **22**



Methyl 3-(2',3',6'-trideoxy-D-erythro-hexopyranoyl)-2-O-benzyl-4,6-O-benzylidene- α -D-glucopyranoside (**22**)



A solution of **9** (195 mg, 1.12 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 278 mg, 1.12 mmol) in THF (9 mL) was cooled to $-78\text{ }^\circ\text{C}$ and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 1.1 mL, 1.1 mmol). The solution was maintained at $-78\text{ }^\circ\text{C}$ for 15 min. After 15 min, a solution of 2,4,6-triisopropylbenzenesulfonyl chloride, (340 mg, 1.12 mmol) in THF (5 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (1 mL), and the rinse added to the reaction mixture. The solution was maintained at $-78\text{ }^\circ\text{C}$ for 30 min. Meanwhile in a separate flask, **13**^[3] (279 mg, 0.75 mmol) was dissolved in THF (3 mL), cooled to $-78\text{ }^\circ\text{C}$, and treated with potassium hexamethyldisilazane (1 M in THF, 0.75 mL, 0.75 mmol). After 30 min, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (3 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 6 h. The reaction was quenched with saturated aqueous NH_4Cl (0.3 mL), diluted with water, and extracted three times

with Et₂O. The pooled organic layers were washed with H₂O, brine and dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (15% ethyl acetate in hexanes to 30% ethyl acetate in hexanes) to afford **22** as a single α-anomer (162 mg, 41%) as a white powder.

m.p. 148-149 °C.

$[\alpha]_D^{22} = +95.7^\circ$ (c 1.28, CH₂Cl₂).

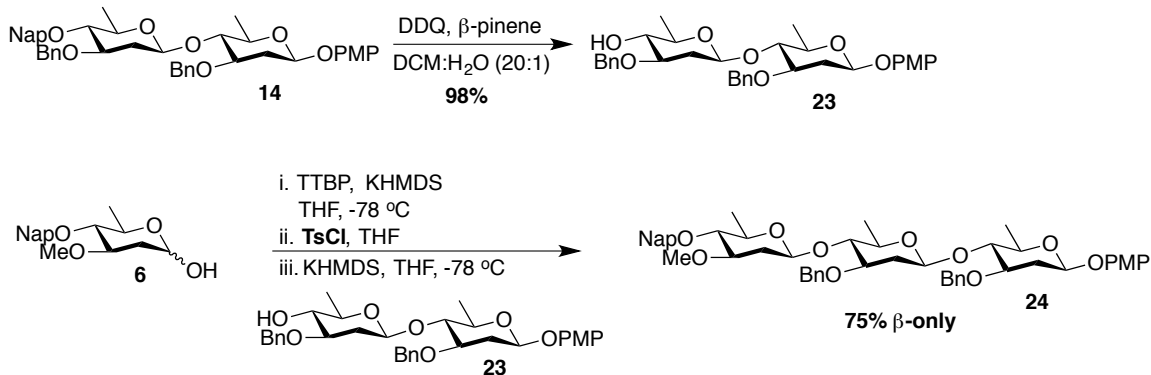
¹H NMR (500 MHz, CDCl₃) δ = 7.45 – 7.40 (m, 4H), 7.40 – 7.28 (m, 6H), 5.49 (s, 1H), 5.29 (d, *J*=2.9, 1H), 4.83 (d, *J*=11.9, 1H), 4.68 (d, *J*=11.9, 1H), 4.61 (d, *J*=3.6, 1H), 4.46 (td, *J*=10.1, 4.7, 1H), 4.30 (t, *J*=9.4, 1H), 4.25 (dd, *J*=10.2, 4.9, 1H), 3.53 – 3.45 (m, 1H), 3.82 (td, *J*=10.0, 4.8, 1H), 3.69 (t, *J*=10.3, 1H), 3.56 (t, *J*=9.4, 1H), 3.50 (dd, *J*=9.5, 3.7, 1H), 3.40 (s, 3H), 2.02 (s, 3H), 1.96 – 1.71 (m, 4H), 1.06 (d, *J*=6.2, 3H).

¹³C NMR (125 MHz, CDCl₃) δ = 170.4, 138.1, 137.4, 129.1, 128.6, 128.5, 128.4, 128.1, 126.1, 101.5, 100.1, 99.1, 96.1, 83.3, 78.3, 73.9, 73.8, 72.6, 69.2, 66.5, 62.1, 55.4, 29.3, 24.0, 21.4, 18.1.

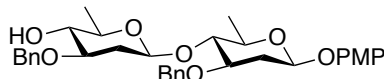
LRMS (ESI, pos. ion) *m/z*: calcd. for C₂₉H₃₆NaO₉ (M+Na) 551.23, found 551.36.

HRMS (ESI, pos. ion) *m/z*: calcd. for C₂₉H₃₆NaO₉ (M+Na) 551.2257, found 551.2257.

S3.6 Synthesis of trisaccharides **24** and **24b**



β -*p*-Methoxyphenyl 4-(3'-O-benzyl-2',6'-dideoxy- β -D-*arabino*-hexopyranoyl)-3-O-benzyl-2,6-dideoxy-D-*arabino*-hexopyranose (**23**)



To a solution of **14** (1 g, 1.4 mmol) and β -pinene (0.75 mL, 4.8 mmol) in DCM (140 mL) and H₂O (7 mL), was added DDQ (635 mg, 2.8 mmol). The reaction was stirred at room temperature under argon for 1 h and monitored by TLC. The reaction mixture was then diluted with DCM (100 mL), and the organic layer was washed with 2M NaOH (3 x 150 mL) and once with saturated NaHCO₃ (150 mL), dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (100% dichloromethane then 10% to 30% ethyl acetate in hexanes) to afford **23** (772 mg, 98%) as a white powder.

m.p. 120-121 °C.

$[\alpha]_{\text{D}}^{24} = -46.8^\circ$ (c 1.34, CH₂Cl₂).

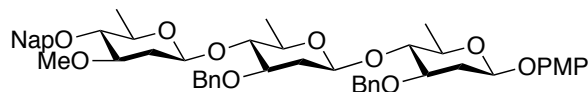
¹H NMR (500 MHz, CDCl₃) δ = 7.41 – 7.25 (m, 10H), 6.98 – 6.91 (m, 2H), 6.85 – 6.77 (m, 2H), 4.95 (dd, *J*=9.8, 2.1, 1H), 4.77 (dd, *J*=9.8, 2.1, 1H), 4.75 – 4.64 (m, 3H), 4.47 (d, *J*=11.6, 1H), 3.77 (s, 3H), 3.71 – 3.62 (m, 1H), 3.50 – 3.41 (m, 1H), 3.40 – 3.31 (m, 2H), 3.28 – 3.16 (m, 2H), 2.47 (ddd, *J*=12.6, 5.2, 2.1, 1H), 2.39 – 2.31 (m, 1H), 1.87 (td, *J*=12.2, 9.9, 1H), 1.53 (td, *J*=11.9, 9.7, 2H), 1.35 (d, *J*=6.1, 3H), 1.30 (d, *J*=5.6, 3H).

¹³C NMR (125 MHz, CDCl₃) δ = 155.2, 151.3, 138.7, 138.2, 128.7, 128.5, 128.1, 127.9, 127.7, 127.7, 118.1, 114.6, 100.4, 98.5, 82.3, 79.1, 77.8, 75.7, 72.0, 72.0, 71.4, 71.1, 55.8, 37.1, 36.5, 18.6, 18.1.

LRMS (ESI, pos. ion) *m/z*: calcd. for C₃₃H₄₀NaO₈ (M+Na) 587.26, found 587.45.

HRMS (ESI, pos. ion) m/z : calcd. for $C_{33}H_{44}NO_8$ ($M+NH_4$) 582.3061, found 582.3058.

β -*p*-Methoxyphenyl 4-(4'-O-(4''-O-(2-naphthylmethyl)-3''-O-methyl-2'',6''-dideoxy- β -D-*arabino*-hexopyranoyl)-3'-O-benzyl-2',6'-dideoxy- β -D-*arabino*-hexopyranoyl)-3-O-benzyl-2,6-dideoxy-D-*arabino*-hexopyranose (**24**)



A solution of **6** (107 mg, 0.35 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 86 mg, 0.35 mmol) in THF (2.5 mL) was cooled to -78 °C and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 0.35 mL, 0.35 mmol). The solution was maintained at -78 °C for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (66 mg, 0.35 mmol) in THF (0.7 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (0.7 mL), and the rinse added to the reaction mixture. The solution was maintained at -78 °C for 30 min. Meanwhile in a separate flask, a stock solution of the acceptor was made: the acceptor **23** (400 mg, 0.68 mmol) was dissolved in THF (5.6 mL), cooled to -78 °C, and treated with potassium hexamethyldisilazane (1 M in THF, 0.68 mL, 0.68 mmol). After 30 min, a portion (1.5 mL) of the stock solution was transferred by syringe to the primary reaction vessel. The reaction mixture was then allowed to gradually warm over the course of 5 h. The reaction was quenched with saturated, aqueous NH_4Cl (0.3 mL), diluted with water, and extracted three times with DCM. The pooled organic layers were washed with H_2O and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (25% ethyl acetate in hexanes to 30% ethyl acetate in hexanes) to afford **24** as a single β -anomer (114 mg, 75%) as a white powder.

m.p. 153-154 °C.

$[\alpha]_D^{22} = -7.5^\circ$ (c 0.98, CH_2Cl_2).

1H NMR (500 MHz, $CDCl_3$) δ = 7.86 – 7.76 (m, 4H), 7.51 – 7.42 (m, 3H), 7.39 – 7.21 (m, 10H), 6.99 – 6.90 (m, 2H), 6.84 – 6.77 (m, 2H), 5.03 (d, $J=11.3$, 1H), 4.94 (dd, $J=9.8, 2.1$, 1H), 4.79 (d, $J=11.3$, 1H), 4.76 – 4.70 (m, 4H), 4.67 (d, $J=11.6$, 1H), 4.62 (d, $J=11.6$, 1H), 3.76 (s, 3H), 3.68 – 3.59 (m, 1H), 3.58 – 3.49 (m, 1H), 3.47 – 3.40 (m, 4H), 3.39 – 3.24 (m, 5H), 3.07 (t, $J=8.9$, 1H), 2.45 (ddd, $J=12.6, 5.2, 2.1$, 1H), 2.36 (ddd, $J=12.5, 5.0, 2.1$, 1H), 2.30 (ddd, $J=12.7, 5.2, 2.1$, 1H), 1.86 (td, $J=12.2, 9.8$, 1H), 1.63 – 1.55 (m, 1H), 1.47 (td, $J=12.1, 9.8, 2H$), 1.33 (d, $J=6.6$, 3H), 1.30 – 1.23 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 155.2, 151.3, 138.9, 138.8, 136.2, 133.4, 133.1, 128.5, 128.4, 128.2, 128.0, 127.8, 127.7, 127.6, 127.6, 126.7, 126.2, 126.2,

126.0, 118.1, 114.6, 100.4, 98.5, 83.7, 82.6, 82.4, 81.4, 77.9, 77.7, 75.2, 72.1, 72.0, 71.6, 71.5, 71.4, 57.2, 55.8, 37.7, 37.1, 36.8, 18.5, 18.5, 18.5.

LRMS (ESI, pos. ion) m/z : calcd. for $C_{51}H_{60}NaO_{11}$ (M+Na) 871.40, found 871.45.

HRMS (ESI, pos. ion) m/z : calcd. for $C_{51}H_{60}NaO_{11}$ (M+Na) 871.4033, found 871.4008.

β -*p*-Methoxyphenyl 4-(4'-O-(4''-O-benzyl-3''-O-methyl-2'',6''-dideoxy- β -D-*arabino*-hexopyranoyl)-3'-O-benzyl-2',6'-dideoxy- β -D-*arabino*-hexopyranoyl)-3-O-benzyl-2,6-dideoxy-D-*arabino*-hexopyranose (**24b**)



A solution of **7** (67 mg, 0.26 mmol) and β -pinene (0.26 mL, 0.26 mmol) in THF (1.9 mL) was cooled to -78 °C and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 0.26 mL, 0.26 mmol). The solution was maintained at -78 °C for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (83 mg, 0.26 mmol) in THF (1 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (0.5 mL), and the rinse added to the reaction mixture. The solution was maintained at -78 °C for 1 h. Meanwhile in a separate flask, **23** (100 mg, 0.17 mmol) was dissolved in THF (0.5 mL), cooled to -78 °C, and treated with potassium hexamethyldisilazane (1 M in THF, 0.17 mL, 0.17 mmol). After 1 h, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (0.5 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 6 h. The reaction was quenched with saturated aqueous NH_4Cl (0.3 mL), diluted with water, and extracted three times with DCM. The pooled organic layers were washed with H_2O and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (20% ethyl acetate in hexanes) to afford **24b** as a single β -anomer (71 mg, 50%) as a white powder.

m.p. 124-125 °C.

$[\alpha]_D^{24} = -6.6^\circ$ (c 1.12, CH_2Cl_2).

1H NMR (500 MHz, $CDCl_3$) δ = 7.40 – 7.24 (m, 15H), 6.97 – 6.90 (m, 2H), 6.84 – 6.76 (m, 2H), 4.94 (dd, $J=9.9, 2.0$, 1H), 4.88 (d, $J=11.1$, 1H), 4.76 – 4.64 (m, 5H), 4.61 (d, $J=11.3$, 2H), 3.75 (s, 3H), 3.68 – 3.58 (m, 1H), 3.58 – 3.49 (m, 1H), 3.42 (s, 4H), 3.37 – 3.28 (m, 3H), 3.28 – 3.21 (m, 2H), 3.01 (t, $J=8.9$, 1H), 2.45 (ddd, $J=12.6, 5.2, 2.1$, 1H), 2.38 – 2.27 (m, 2H), 1.86 (td, $J=12.1, 9.9$, 1H), 1.64 – 1.52 (m, 1H), 1.46 (td, $J=12.0, 9.8$, 1H), 1.33 (d, $J=6.1$, 3H), 1.27 (dd, $J=9.5, 5.4$, 6H).

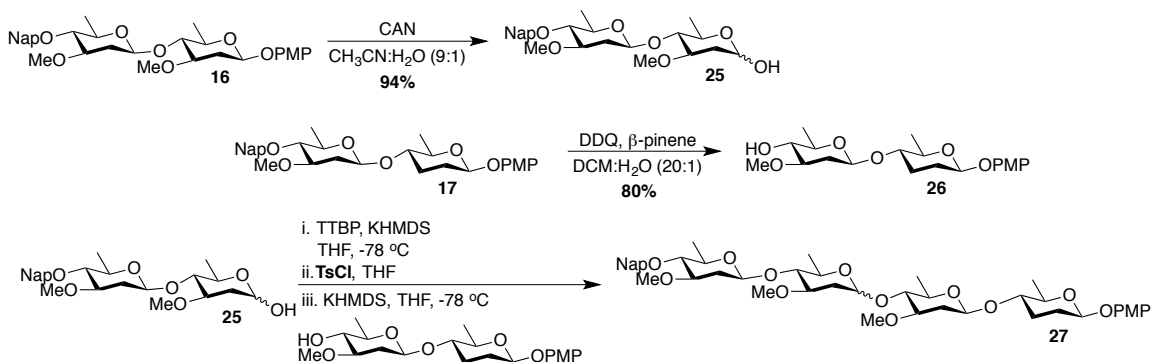
^{13}C NMR (125 MHz, CDCl_3) δ = 155.2, 151.3, 138.9, 138.8, 138.7, 128.5, 128.5, 128.4, 128.1, 127.8, 127.7, 127.6, 127.6, 118.1, 114.6, 100.4, 98.6, 83.7, 82.6, 82.4, 81.3, 77.9, 77.8, 75.2, 72.1, 72.0, 71.6, 71.5, 71.4, 57.2, 55.8, 37.7, 37.1, 36.8, 18.6, 18.5, 18.4.

LRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{47}\text{H}_{58}\text{NaO}_{11}$ (M+Na) 821.39, found 821.41.

HRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{47}\text{H}_{62}\text{NO}_{11}$ (M+ NH_4) 816.4317, found 816.4336.

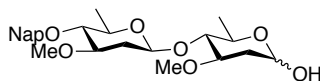
S3.7 Synthesis of tetrasaccharide **27**

S3.7.1 Convergent synthesis of tetrasaccharide **27**



Synthesis of **25**

4-(3'-O-Methyl-4'-(2-naphthylmethyl)-2',6'-dideoxy-β-D-*arabino*-hexopyranoyl)-3-O-methyl-2,6-dideoxy-D-*arabino*-hexopyranose (**25**)



To a solution **16** (250 mg, 0.45 mmol) in acetonitrile (24.1 mL) and water (2.67 mL) was added ceric ammonium nitrate. Within 45 min, the reaction was quenched with saturated NaHCO₃ (8 ml) and diluted with water (125 ml) and extracted with EtOAc (3 x 50 ml) and DCM (2 x 50 ml). The pooled yellow EtOAc layers were washed with 10% Na₂SO₃ aqueous solution (until colorless), water, dried over Na₂SO₄, and combined with dried pooled DCM layers, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (50% ethyl acetate in hexanes) to afford **25** (188 mg, 94%) as a colorless solid.

m.p. 87-88 °C.

$[\alpha]_D^{23} = +27.76^\circ$ (c 1.04, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ = 7.85 – 7.78 (m, 5H), 7.50 – 7.43 (m, 4H) 7.26 (s, 3H), 5.31 (s, 1H), 5.06 (d, *J*=11.3, 1H), 4.84 – 4.77 (m, 2H), 4.70 (d, *J*=9.9, 2.9, 1H), 4.00 – 3.91 (m, 1H), 3.73 (ddd, *J*=10.6, 8.0, 5.0, 1H), 3.47 (d, *J*=1.2, 4H), 3.45 – 3.33 (m, 7H), 3.25 – 3.17 (m, 1H), 3.10 (td, *J*=9.0, 3.4, 1H), 2.96 (dd, *J*=6.6, 3.5, 0H), 2.43 – 2.31 (m, 3H), 2.23 (ddd, *J*=13.4, 4.9, 2.0, 1H), 1.65 – 1.58 (m, 1H), 1.57 – 1.42 (m, 5H), 1.37 – 1.30 (m, 5H), 1.27 (d, *J*=6.3, 3H).

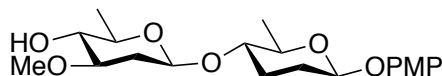
¹³C NMR (125 MHz, CDCl₃) δ = 136.2, 133.4, 133.1, 128.2, 128.0, 127.8, 126.7, 126.2, 126.1, 125.9, 100.3, 93.9, 91.7, 83.6, 83.3, 82.3, 81.5, 79.2, 76.7, 75.2, 71.4, 71.1, 66.9, 57.3, 57.1, 56.9, 37.3, 36.7, 34.9, 18.4.

LRMS (ESI, pos. ion) m/z : calcd. for $C_{25}H_{34}NaO_7$ (M+Na) 469.22, found 469.36.

HRMS (ESI, pos. ion) m/z : calcd. for $C_{25}H_{34}NaO_7$ (M+Na) 469.2202, found 469.2207.

Synthesis of **26**

β -*p*-Methoxyphenyl 4-(3'-O-methyl-2',6'-dideoxy- β -D-*arabino*-hexopyranoyl)-2,3,6-trideoxy-D-*erythro*-hexopyranose (**26**)



To a solution of **17** (500 mg, 0.95 mmol) and β -pinene (0.5 mL, 3.2 mmol) in DCM (95 mL) and H_2O (4.75 mL), was added DDQ (431 mg, 1.9 mmol). The reaction was stirred at room temperature under argon for 1.25 h and monitored by TLC. The reaction mixture was then diluted with DCM (250 mL), and the organic layer was washed with 2M NaOH (3 x 250 mL) and of saturated $NaHCO_3$ (2 x 250 mL), dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (30% ethyl acetate in hexanes to 50% ethyl acetate in hexanes) to afford **26** (290 mg, 80%) as a white powder m.p. 146-147 °C.

$[\alpha]_D^{22} = -77.1^\circ$ (c 1.02, CH_2Cl_2).

1H NMR (500 MHz, $CDCl_3$) δ = 6.99 – 6.92 (m, 2H), 6.85 – 6.78 (m, 2H), 5.00 (dd, $J=9.2, 2.3$, 1H), 4.54 (dd, $J=9.9, 2.0$, 1H), 3.77 (s, 3H), 3.52 (dq, $J=8.8, 6.2$, 1H), 3.40 (s, 3H), 3.37 – 3.24 (m, 2H), 3.23 – 3.12 (m, 2H), 2.47 (*brs*, 1H), 2.38 – 2.29 (m, 2H), 2.10 – 2.01 (m, 1H), 1.83 (tdd, $J=13.3, 9.2, 4.2$, 1H), 1.72 – 1.58 (m, 1H), 1.46 (td, $J=11.6, 9.7$, 1H), 1.35 (d, $J=6.1$, 3H), 1.31 (d, $J=6.1$, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.9, 151.4, 117.9, 114.6, 101.2, 100.2, 80.8, 80.3, 75.5, 74.5, 71.7, 56.5, 55.8, 35.5, 30.5, 29.6, 18.5, 18.1.

LRMS (ESI, pos. ion) m/z : calcd. for $C_{20}H_{34}NO_7$ (M+ NH_4) 400.23, found 400.00.

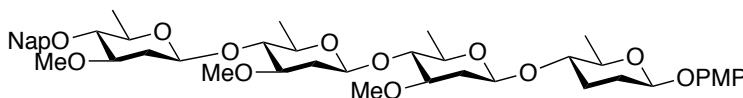
HRMS (ESI, pos. ion) m/z : calcd. for $C_{20}H_{30}NaO_7$ (M+Na) 405.1889, found 405.1884.

Synthesis of **27**

[2+2] conditions: A solution of **25** (233 mg, 0.52 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 129 mg, 0.52 mmol) in THF (3.8 mL) was cooled to $-78^\circ C$ and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 0.52 mL, 0.52 mmol). The solution was maintained at $-78^\circ C$ for 15 min. After 15 min,

a solution of *p*-toluenesulfonyl chloride (99 mg, 0.52 mmol) in THF (1 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (1 mL), and the rinse added to the reaction mixture. The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 30 min. Meanwhile in a separate flask, a stock solution of the acceptor was made: the acceptor **26** (200 mg, 0.52 mmol) was dissolved in THF (4 mL), cooled to $-78\text{ }^{\circ}\text{C}$, and treated with potassium hexamethyldisilazane (1 M in THF, 0.52 mL, 0.52 mmol). After 30 min, a portion of the stock solution (2.26 mL) was transferred by syringe to the primary reaction vessel. The reaction mixture was then allowed to gradually warm over the course of 6 h. The reaction was quenched with saturated aqueous NH_4Cl (0.3 mL), diluted with water, and extracted three times with DCM. The pooled organic layers were washed with H_2O and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (15% ethyl acetate in hexanes to 30% ethyl acetate in hexanes) to afford **27** and **27a** as separate α - and β -anomers (106 mg, 50%, 1.3:1 α : β) as white powders.

β -*p*-Methoxyphenyl 4-(4'-O-(4''-O-(4'''-O-(2-naphthmethyl)-3'''-O-methyl-2''',6'''-dideoxy- β -D-*arabino*-hexopyranoyl)-3''-O-methyl-2'',6''-dideoxy- β -D-*arabino*-hexopyranoyl)-3'-O-methyl-2',6'-dideoxy- β -D-*arabino*-hexopyranoyl)-2,3,6-trideoxy-D-*erythro*-hexopyranose (**27**)



$[\alpha]_{\text{D}}^{22} = -34.1^{\circ}$ (*c* 1.18, CH_2Cl_2).

^1H NMR (500 MHz, CDCl_3) $\delta = 7.85 - 7.77$ (m, 4H), $7.51 - 7.42$ (m, 3H), $6.99 - 6.92$ (m, 2H), $6.84 - 6.77$ (m, 2H), 5.05 (d, $J=11.3$, 1H), 4.99 (dd, $J=9.2$, 2.3 , 1H), 4.80 (d, $J=11.3$, 1H), 4.68 (ddd, $J=14.0$, 9.9 , 2.0 , 2H), 4.49 (dd, $J=9.8$, 2.0 , 1H), 3.76 (s, 3H), 3.51 (dq, $J=8.6$, 6.2 , 1H), 3.46 (s, 3H), $3.44 - 3.30$ (m, 11H), 3.26 (ddd, $J=10.3$, 8.7 , 4.6 , 1H), 3.17 (td, $J=8.9$, 4.1 , 2H), 3.09 (t, $J=8.9$, 1H), $2.38 - 2.26$ (m, 4H), $2.08 - 2.00$ (m, 1H), 1.82 (tdd, $J=13.3$, 9.2 , 4.2 , 1H), $1.70 - 1.59$ (m, 2H), $1.56 - 1.43$ (m, 3H), $1.38 - 1.27$ (m, 12H).

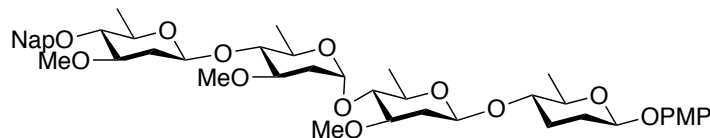
^{13}C NMR (125 MHz, CDCl_3) $\delta = 154.9$, 151.4 , 136.2 , 133.4 , 133.1 , 128.1 , 128.0 , 127.7 , 126.6 , 126.1 , 126.1 , 125.9 , 117.9 , 114.5 , 101.0 , 100.2 , 100.1 , 83.6 , 82.6 , 82.5 , 81.5 , 80.1 , 79.3 , 79.3 , 75.2 , 74.5 , 71.4 , 71.2 , 71.1 , 57.1 , 56.8 , 56.8 , 55.7 , 36.8 , 36.6 , 36.5 , 30.4 , 29.8 , 29.6 , 18.5 , 18.5 .

LRMS (ESI, pos. ion) *m/z*: calcd. for $\text{C}_{45}\text{H}_{62}\text{NaO}_{13}$ (M+Na) 833.41, found 833.45.

HRMS (ESI, pos. ion) *m/z*: calcd. for $\text{C}_{45}\text{H}_{62}\text{NaO}_{13}$ (M+Na) 833.4088, found 833.4077.

β -*p*-Methoxyphenyl 4-(4'-O-(4''-O-(4'''-O-(2-naphthmethyl)-3'''-O-methyl-2''',6'''-dideoxy- β -D-*arabino*-hexopyranoyl)-3''-O-methyl-2'',6''-dideoxy- α -D-*arabino*-

hexopyranoyl)-3'-O-methyl-2',6'-dideoxy- β -D-*arabino*-hexopyranoyl)-2,3,6-trideoxy-D-*erythro*-hexopyranose (**27a**)



m.p. 140-141 °C.

$[\alpha]_D^{22} = +6.8^\circ$ (c 1.09, CH₂Cl₂).

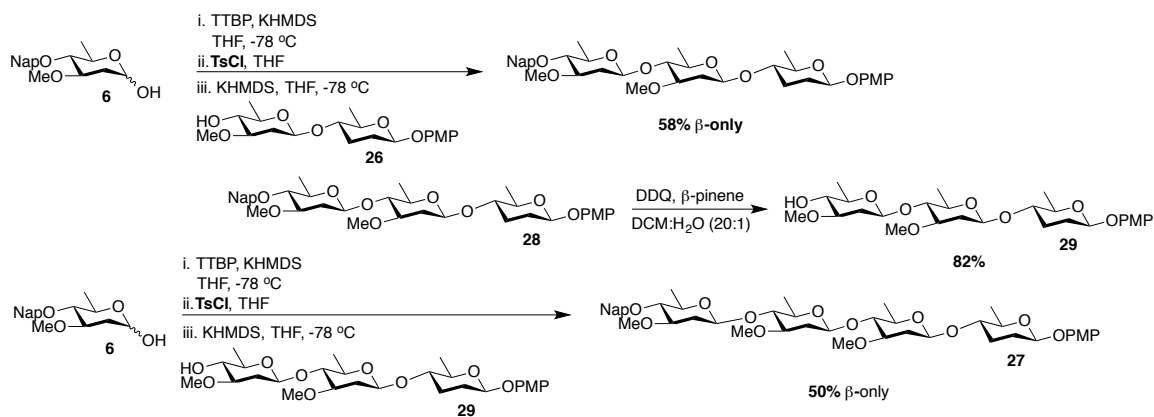
¹H NMR (500 MHz, CDCl₃) δ = 7.86 – 7.77 (m, 4H), 7.52 – 7.43 (m, 3H), 6.99 – 6.93 (m, 2H), 6.85 – 6.78 (m, 2H), 5.31 (d, $J=4.7$, 1H), 5.06 (d, $J=11.3$, 1H), 5.00 (dd, $J=9.2, 2.4$, 1H), 4.80 (d, $J=11.4$, 1H), 4.68 (dd, $J=9.9, 2.0$, 1H), 4.49 (dd, $J=9.8, 1.8$, 1H), 3.77 (s, 3H), 3.56 – 3.45 (m, 4H), 3.45 – 3.33 (m, 8H), 3.32 – 3.13 (m, 6H), 3.10 (t, $J=8.9$, 1H), 2.40 – 2.27 (m, 4H), 2.24 – 2.12 (m, 1H), 2.05 (t, $J=6.7$, 1H), 1.83 (tdd, $J=13.2, 9.1, 4.0$, 1H), 1.71 – 1.60 (m, 2H), 1.54 – 1.41 (m, 2H), 1.37 – 1.24 (m, 12H).

¹³C NMR (125 MHz, CDCl₃) δ = 154.9, 151.4, 136.2, 133.4, 133.1, 128.2, 128.0, 127.8, 126.7, 126.2, 126.2, 126.0, 117.9, 114.6, 101.0, 100.5, 100.2, 98.1, 83.6, 83.4, 81.7, 81.5, 80.2, 79.9, 75.2, 74.5, 71.5, 71.0, 57.1, 57.1, 56.4, 55.8, 36.8, 36.2, 34.8, 30.5, 29.6, 18.7, 18.5, 18.3.

LRMS (ESI, pos. ion) m/z : calcd. for C₄₅H₆₂NaO₁₃ (M+Na) 833.41, found 833.45.

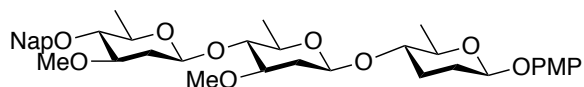
HRMS (ESI, pos. ion) m/z : calcd. for C₄₅H₆₂NaO₁₃ (M+Na) 833.4088, found 833.4119.

S3.7.2 Linear synthesis of tetrasaccharide **27**



Synthesis of **28**

β -*p*-Methoxyphenyl 4-(4'-O-(4''-O-(2-naphthmethyl)-3''-O-methyl-2'',6''-dideoxy- β -D-*arabino*-hexopyranoyl)-3'-O-methyl-2',6'-dideoxy- β -D-*arabino*-hexopyranoyl)-2,3,6-trideoxy-D-*erythro*-hexopyranose (**28**)



A solution of **6** (158 mg, 0.52 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 129 mg, 0.52 mmol) in THF (3.7 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 0.52 mL, 0.52 mmol). The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (83 mg, 0.52 mmol) in THF (1.1 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (1 mL), and the rinse added to the reaction mixture. The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 30 min. Meanwhile in a separate flask, **26** (100 mg, 0.26 mmol) was dissolved in THF (1.5 mL), cooled to $-78\text{ }^{\circ}\text{C}$, and treated with potassium hexamethyldisilazane (1 M in THF, 0.26 mL, 0.26 mmol). After 30 min, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (0.5 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 6.5 h. The reaction was quenched with saturated aqueous NH_4Cl (0.3 mL), diluted with water, and extracted three times with DCM. The pooled organic layers were washed with H_2O and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (25% ethyl acetate in hexanes to 40% ethyl acetate in hexanes) to afford **28** as a single β -anomer (100 mg, 58%) as a white powder.

m.p. 124-125 $^{\circ}\text{C}$.

$[\alpha]_{\text{D}}^{22} = -22.0^{\circ}$ (*c* 1.30, CH_2Cl_2).

^1H NMR (500 MHz, CDCl_3) δ = 7.84 – 7.78 (m, 4H), 7.52 – 7.43 (m, 3H), 6.99 – 6.92 (m, 2H), 6.85 – 6.78 (m, 2H), 5.06 (d, $J=11.5$, 1H), 4.99 (dd, $J=9.2$, 2.2, 1H), 4.81 (d, $J=11.4$, 5.7, 1H), 4.70 (dd, $J=9.8$, 2.0, 1H), 4.49 (dd, $J=9.9$, 2.0, 1H), 3.77 (s, 3H), 3.56 – 3.45 (m, 5H), 3.43 – 3.30 (m, 7H), 3.29 – 3.22 (m, 1H), 3.18 (t, $J=8.9$, 1H), 3.10 (t, $J=9.0$, 1H), 2.39 – 2.27 (m, 3H), 2.08 – 2.02 (m, 1H), 1.83 (tdd, $J=13.3$, 9.2, 4.2, 1H), 1.71 – 1.56 (m, 1H), 1.50 (tdd, $J=12.1$, 9.9, 4.6, 1H), 1.37 – 1.28 (m, 9H).

^{13}C NMR (125 MHz, CDCl_3) δ = 154.9, 151.4, 136.2, 133.4, 133.1, 128.2, 128.0, 127.8, 126.7, 126.2, 126.2, 126.0, 117.9, 114.6, 101.1, 100.3, 100.2, 83.6, 82.5, 81.5, 80.2, 79.3, 75.2, 74.5, 71.5, 71.1, 57.2, 56.8, 55.8, 36.8, 36.5, 30.5, 29.6, 18.5.

LRMS (ESI, pos. ion) m/z : calcd. for $C_{38}H_{50}NaO_{10}$ (M+Na) 689.33, found 689.45.

HRMS (ESI, pos. ion) m/z : calcd. for $C_{38}H_{50}NaO_{10}$ (M+Na) 689.3302, found 689.3309.

Synthesis of **29**

β -*p*-Methoxyphenyl 4-(4'-O-(3''-O-methyl-2'',6''-dideoxy- β -D-*arabino*-hexopyranoyl)-3'-O-methyl-2',6'-dideoxy- β -D-*arabino*-hexopyranoyl)-2,3,6-trideoxy-D-*erythro*-hexopyranose (**29**)



To a solution of **28** (50 mg, 0.07 mmol) and β -pinene (0.03 mL, 0.25 mmol) in DCM (7.5 mL) and H_2O (0.37 mL), was added DDQ (33 mg, 0.15 mmol). The reaction was stirred at room temperature under argon for 45 min and monitored by TLC. The reaction mixture was then diluted with DCM (25 mL), and the organic layer was washed with 2M NaOH (3 x 20 mL) and saturated $NaHCO_3$ (2 x 20 mL), dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (50% ethyl acetate in hexanes) to afford **29** (32 mg, 82%) as a white powder.

m.p. 173-174 °C.

$[\alpha]_D^{22} = -63.6^\circ$ (c 0.94, CH_2Cl_2).

1H NMR (500 MHz, $CDCl_3$) δ = 6.99 – 6.92 (m, 2H), 6.85 – 6.78 (m, 2H), 4.99 (dd, $J=9.2, 2.3$, 1H), 4.73 (dd, $J=9.8, 2.1$, 1H), 4.50 (dd, $J=9.8, 2.0$, 1H), 3.77 (s, 3H), 3.51 (dq, $J=8.7, 6.3$, 1H), 3.41 (d, $J=4.8$, 7H), 3.40 – 3.29 (m, 2H), 3.29 – 3.22 (m, 1H), 3.22 – 3.11 (m, 3H), 2.40 (d, $J=1.7$, 1H), 2.36 – 2.27 (m, 3H), 2.08 – 2.01 (m, 1H), 1.83 (tdd, $J=13.2, 9.1, 4.1$, 1H), 1.71 – 1.59 (m, 1H), 1.56 – 1.38 (m, 2H), 1.35 (d, $J=6.1$, 3H), 1.31 (dd, $J=9.6, 6.2$, 6H).

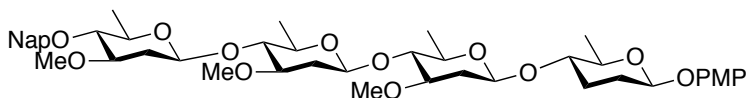
^{13}C NMR (126 MHz, $CDCl_3$) δ = 155.0, 151.4, 117.9, 114.6, 101.1, 100.4, 100.2, 82.5, 80.8, 80.2, 79.4, 75.6, 74.5, 71.8, 71.1, 56.8, 56.5, 55.8, 36.5, 35.6, 30.5, 29.8, 29.6, 18.6, 18.5, 18.1.

LRMS (ESI, pos. ion) m/z : calcd. for $C_{27}H_{42}NaO_{10}$ (M+Na) 549.27, found 549.45.

HRMS (ESI, pos. ion) m/z : calcd. for $C_{27}H_{42}NaO_{10}$ (M+Na) 549.2676, found 549.2681.

Synthesis of 27

β -*p*-Methoxyphenyl 4-(4'-O-(4''-O-(4'''-O-(2-naphthmethyl)-3'''-O-methyl-2''',6'''-dideoxy- β -D-*arabino*-hexopyranoyl)-3''-O-methyl-2'',6''-dideoxy- β -D-*arabino*-hexopyranoyl)-3'-O-methyl-2',6'-dideoxy- β -D-*arabino*-hexopyranoyl)-2,3,6-trideoxy-D-*erythro*-hexopyranose (**27**)

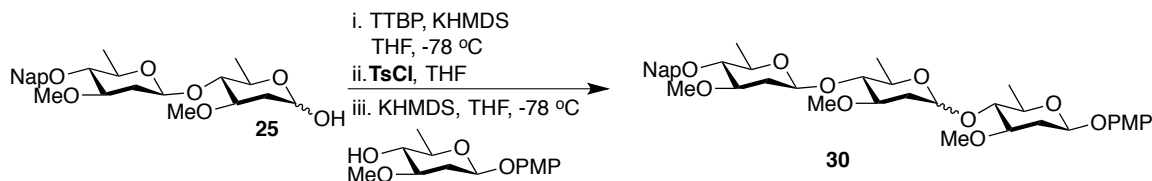


Linear conditions: A solution of **6** (114 mg, 0.37 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 94 mg, 0.37 mmol) in THF (2.66 mL) was cooled to -78 °C and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 0.37 mL, 0.37 mmol). The solution was maintained at -78 °C for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (72 mg, 0.37 mmol) in THF (0.76 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (0.76 mL), and the rinse added to the reaction mixture. The solution was maintained at -78 °C for 30 min. Meanwhile in a separate flask, **29** (100 mg, 0.18 mmol) was dissolved in THF (1.16 mL), cooled to -78 °C, and treated with potassium hexamethyldisilazane (1 M in THF, 0.18 mL, 0.18 mmol). After 30 min, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (0.36 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 5.5 h. The reaction was quenched with saturated aqueous NH_4Cl (0.3 mL), diluted with water, and extracted three times with DCM. The pooled organic layers were washed with H_2O and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (30% ethyl acetate in hexanes) to afford **27** as a single β -anomer (78 mg, 50%) as a white powder. The spectroscopic data is in good agreement with data as shown above.

^1H NMR (500 MHz, CDCl_3) δ = 7.85 – 7.77 (m, 4H), 7.51 – 7.42 (m, 3H), 6.99 – 6.92 (m, 2H), 6.84 – 6.77 (m, 2H), 5.05 (d, $J=11.3$, 1H), 4.99 (dd, $J=9.2$, 2.3, 1H), 4.80 (d, $J=11.3$, 1H), 4.68 (ddd, $J=14.0$, 9.9, 2.0, 2H), 4.49 (dd, $J=9.8$, 2.0, 1H), 3.76 (s, 3H), 3.51 (dq, $J=8.6$, 6.2, 1H), 3.46 (s, 3H), 3.44 – 3.30 (m, 11H), 3.26 (ddd, $J=10.3$, 8.7, 4.6, 1H), 3.17 (td, $J=8.9$, 4.1, 2H), 3.09 (t, $J=8.9$, 1H), 2.38 – 2.26 (m, 4H), 2.08 – 2.00 (m, 1H), 1.82 (tdd, $J=13.3$, 9.2, 4.2, 1H), 1.70 – 1.59 (m, 2H), 1.56 – 1.43 (m, 3H), 1.38 – 1.27 (m, 12H).

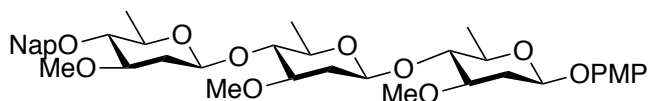
^{13}C NMR (125 MHz, CDCl_3) δ = 154.9, 151.4, 136.2, 133.4, 133.1, 128.1, 128.0, 127.7, 126.6, 126.1, 126.1, 125.9, 117.9, 114.5, 101.0, 100.2, 100.1, 83.6, 82.6, 82.5, 81.5, 80.1, 79.3, 79.3, 75.2, 74.5, 71.4, 71.2, 71.1, 57.1, 56.8, 56.8, 55.7, 36.8, 36.6, 36.5, 30.4, 29.8, 29.6, 18.5, 18.5.

S4. Test glycosylation of trisaccharide **30**



A solution of **16** (249 mg, 0.55 mmol) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 136 mg, 0.55 mmol) in THF (4.5 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 0.55 mL, 0.55 mmol). The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. After 15 min, a solution of *p*-toluenesulfonyl chloride (104 mg, 0.55 mmol) in THF (2 mL) was added slowly to the reaction. The flask containing the TsCl solution was then rinsed with THF (1 mL), and the rinse added to the reaction mixture. The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 15 min. Meanwhile in a separate flask, **10** (100 mg, 0.37 mmol) was dissolved in THF (2 mL), cooled to $-78\text{ }^{\circ}\text{C}$, and treated with potassium hexamethyldisilazane (1 M in THF, 0.37 mL, 0.37 mmol). After 15 min, this solution was transferred by syringe to the primary reaction vessel. The flask containing the acceptor was rinsed with THF (1 mL), which was cooled and then added to the primary reaction mixture. The reaction mixture was then allowed to gradually warm over the course of 6.5 h. The reaction was quenched with saturated aqueous NH_4Cl (0.3 mL), diluted with water, and extracted three times with DCM. The pooled organic layers were washed with H_2O and dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (15% ethyl acetate in hexanes to 30% ethyl acetate in hexanes) to afford **30** and **30a** as separate α - and β -anomers (122 mg, 47%, 1:1 α : β) as an amorphous solid and a white powder, respectively.

β -*p*-Methoxyphenyl 4-(4'-O-(4''-O-(2-naphthylmethyl)-3''-O-methyl-2'',6''-dideoxy- β -D-*arabino*-hexopyranoyl)-3'-O-methyl-2',6'-dideoxy- β -D-*arabino*-hexopyranoyl)-3-O-methyl-2,6-dideoxy-D-*arabino*-hexopyranose (**30**)



m.p. $152\text{--}153\text{ }^{\circ}\text{C}$.

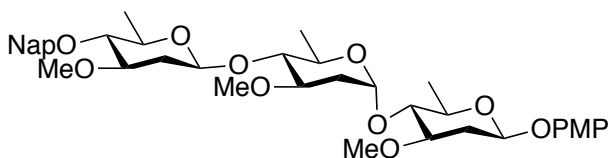
$[\alpha]_{\text{D}}^{23} = -22.9^{\circ}$ (*c* 1.69, CH_2Cl_2).
 $^1\text{H NMR}$ (500 MHz, CDCl_3) δ = 7.85 – 7.77 (m, 4H), 7.51 – 7.42 (m, 3H), 6.99 – 6.91 (m, 2H), 6.85 – 6.77 (m, 2H), 5.05 (d, $J=11.3$, 1H), 4.95 (dd, $J=9.8$, 2.0, 1H), 4.80 (d, $J=11.3$, 1H), 4.70 (d, $J=9.9$, 2H), 3.76 (s, 3H), 3.47 – 3.34 (m, 15H), 3.25 (t, $J=8.8$, 1H), 3.18 (t, $J=8.8$, 1H), 3.10 (t, $J=8.9$, 1H), 2.48 (ddd, $J=12.7$, 5.2, 2.1, 1H), 2.33 (tdd, $J=14.2$, 5.1, 2.1, 2H), 1.81 – 1.71 (m, 1H), 1.50 (tdd, $J=12.1$, 9.8, 4.2, 2H), 1.38 – 1.32 (m, 9H).

^{13}C NMR (125 MHz, CDCl_3) δ = 155.2, 151.3, 136.2, 133.4, 133.1, 128.2, 128.0, 127.8, 126.7, 126.2, 126.0, 118.1, 114.6, 100.3, 98.6, 83.7, 82.6, 82.4, 81.5, 79.4, 79.3, 75.2, 71.5, 71.3, 57.1, 56.9, 56.9, 55.8, 36.8, 36.6, 36.1, 18.6, 18.5.

LRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{39}\text{H}_{52}\text{NaO}_{11}$ (M+Na) 719.34, found 719.45.

HRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{39}\text{H}_{52}\text{NaO}_{11}$ (M+Na) 719.3407, found 719.3407.

β -*p*-Methoxyphenyl 4-(4'-O-(4''-O-(2-naphthylmethyl)-3''-O-methyl-2'',6''-dideoxy- β -D-*arabino*-hexopyranoyl)-3'-O-methyl-2',6'-dideoxy- α -D-*arabino*-hexopyranoyl)-3-O-methyl-2,6-dideoxy-D-*arabino*-hexopyranose (**30a**)



$[\alpha]_{\text{D}}^{23} = +10.6^\circ$ (c 0.93, CH_2Cl_2).

^1H NMR (500 MHz, CDCl_3) δ = 7.88 – 7.80 (m, 4H), 7.54 – 7.45 (m, 3H), 7.02 – 6.94 (m, 2H), 6.88 – 6.81 (m, 2H), 5.37 (s, 1H), 5.08 (d, $J=11.3$, 1H), 4.98 (dd, $J=9.8$, 2.0, 1H), 4.83 (d, $J=11.3$, 1H), 4.71 (dd, $J=9.8$, 9.3, 1H), 3.89 – 3.76 (m, 4H), 3.70 – 3.61 (m, 1H), 3.53 – 3.36 (m, 13H), 3.36 – 3.28 (m, 1H), 3.28 – 3.20 (m, 1H), 3.13 (t, $J=8.9$, 1H), 2.51 (ddd, $J=12.6$, 4.9, 2.1, 1H), 2.43 – 2.31 (m, 1H), 2.22 (ddd, $J=13.3$, 4.8, 2.3, 1H), 1.82 – 1.63 (m, 2H), 1.63 – 1.46 (m, 1H), 1.38 (dd, $J=6.2$, 2.6, 6H), 1.29 (dd, $J=6.7$, 2.0, 3H).

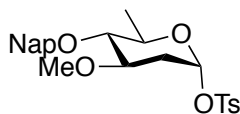
^{13}C NMR (125 MHz, CDCl_3) δ = 155.1, 151.3, 136.2, 133.4, 133.1, 128.2, 128.0, 127.8, 126.7, 126.2, 126.1, 125.9, 118.0, 118.0, 114.6, 100.5, 98.5, 98.2, 83.6, 83.3, 81.6, 81.5, 79.9, 75.2, 71.5, 71.2, 67.3, 57.1, 56.5, 55.7, 36.7, 35.8, 34.7, 18.7, 18.5, 18.2.

LRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{39}\text{H}_{52}\text{NaO}_{11}$ (M+Na) 719.34, found 719.55.

HRMS (ESI, pos. ion) m/z : calcd. for $\text{C}_{39}\text{H}_{52}\text{NaO}_{11}$ (M+Na) 719.3407, found 719.3406.

S5. Low temperature NMR experiment

S5.1 Synthesis of α -*p*-toluenesulfonyl 3-O-methyl-4-O-(2-naphthylmethyl)-2,6-dideoxy-D-*arabino*-hexopyranose



A solution of donor **6** (15 mg, 0.05 mmol, 1.0 equiv.) and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 12 mg, 0.05 mmol, 1.0 equiv.) in THF- d_8 (0.50 mL) was cooled to $-78\text{ }^\circ\text{C}$ in a dry ice/acetone bath and treated dropwise with potassium hexamethyldisilazane (1 M in THF, 50 μl , 0.05 mmol, 1.0 equiv.). After 15 minutes, a solution of *p*-toluenesulfonyl chloride (9 mg, 0.05 mmol, 1.05 equiv.) in THF- d_8 (0.50 mL) was added rapidly to the reaction. The reaction was maintained at $-78\text{ }^\circ\text{C}$ for 15 min, transferred by syringe to a pre-cooled 5 mm Screw Capped NMR tube, and promptly inserted into the NMR instrument probe pre-cooled to $-78\text{ }^\circ\text{C}$ for ^1H NMR, ^{13}C NMR, and 2D-Gradient HSQC data acquisition.

S5.2 NMR spectra of α -glucosyl toluenesulfonate

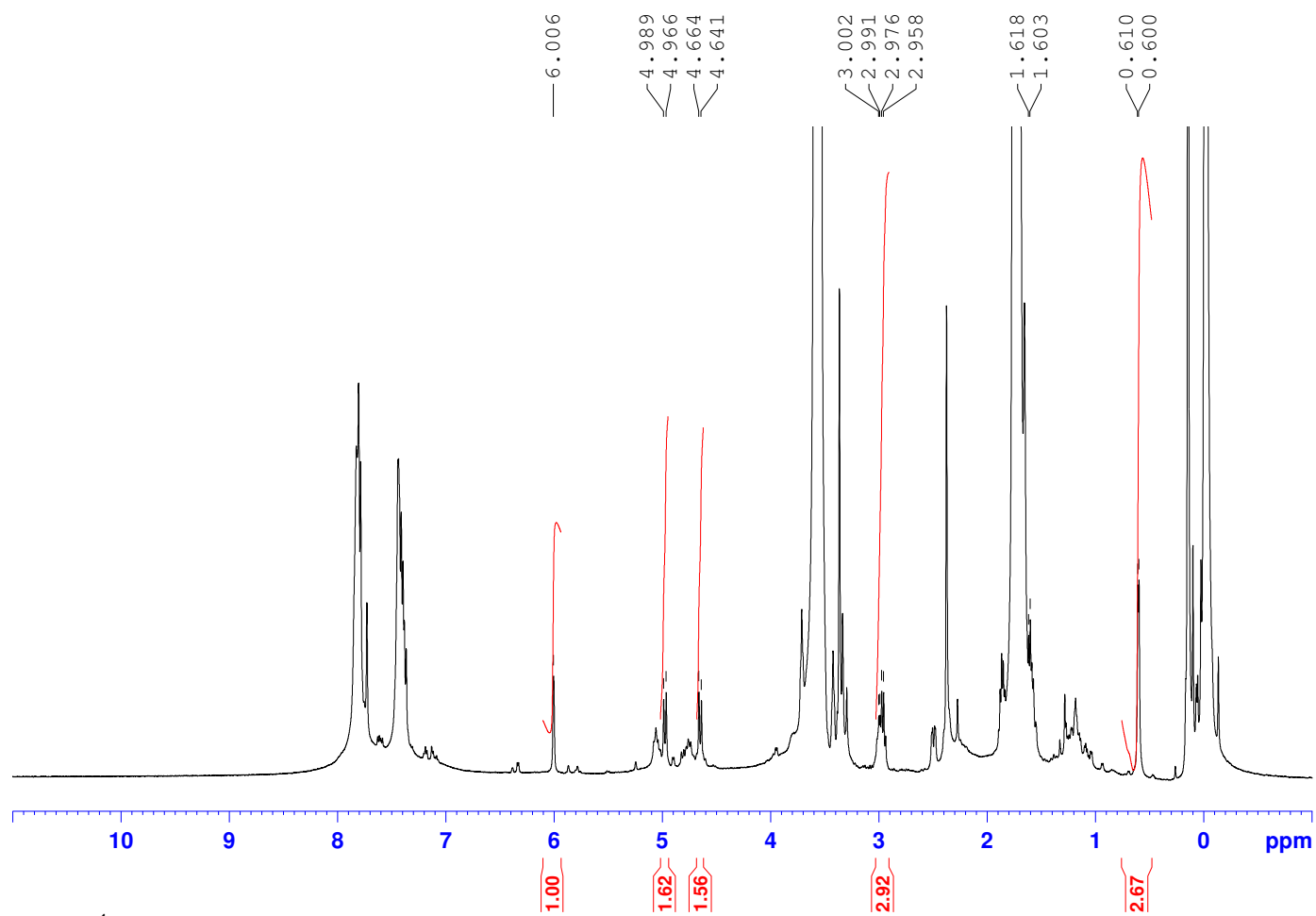


Figure S5.2.1 ^1H NMR spectra of α -glucosyl toluenesulfonate in THF-d_3 at 500 MHz at -78°C

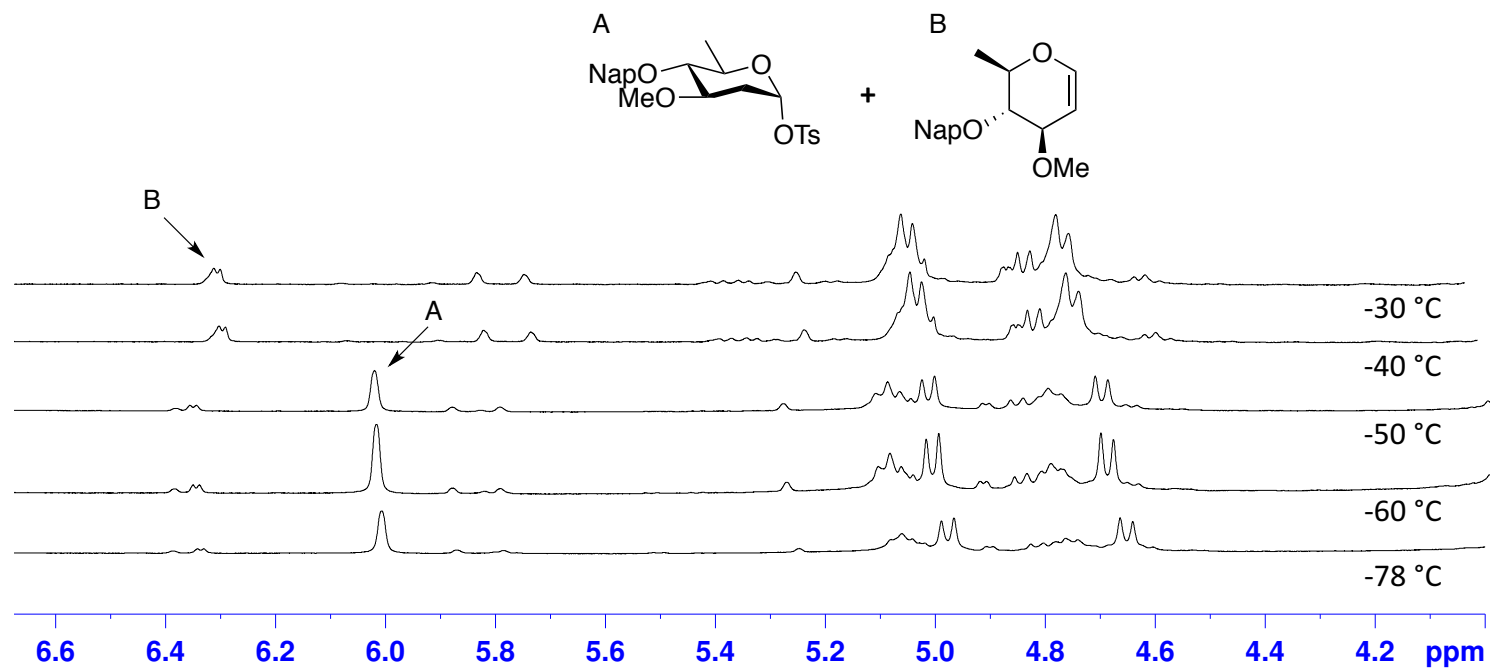


Figure S5.2.2 ^1H NMR spectra of α -glucosyl tosylate in THF-d_8 at 500 MHz at $-78\text{ }^\circ\text{C}$ to $-30\text{ }^\circ\text{C}$. Above $-50\text{ }^\circ\text{C}$ spectrum shows complete decomposition of the tosylate to corresponding glycal elimination product.

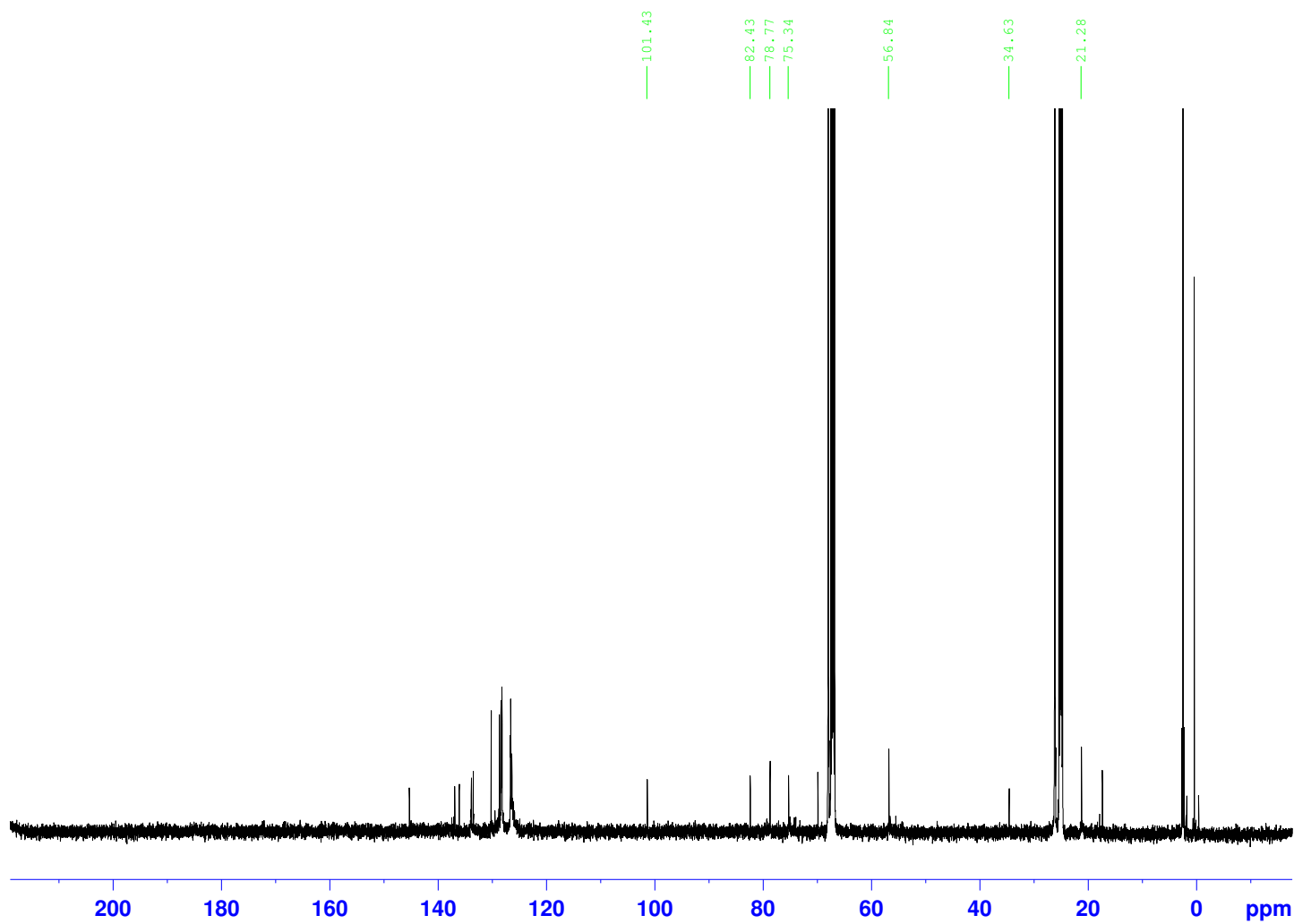


Figure S5.2.3 ^{13}C NMR spectra of α -glucosyl toluenesulfonate at $-78\text{ }^\circ\text{C}$. The signal at δ 101.1 ppm is indicative of the anomeric carbon.

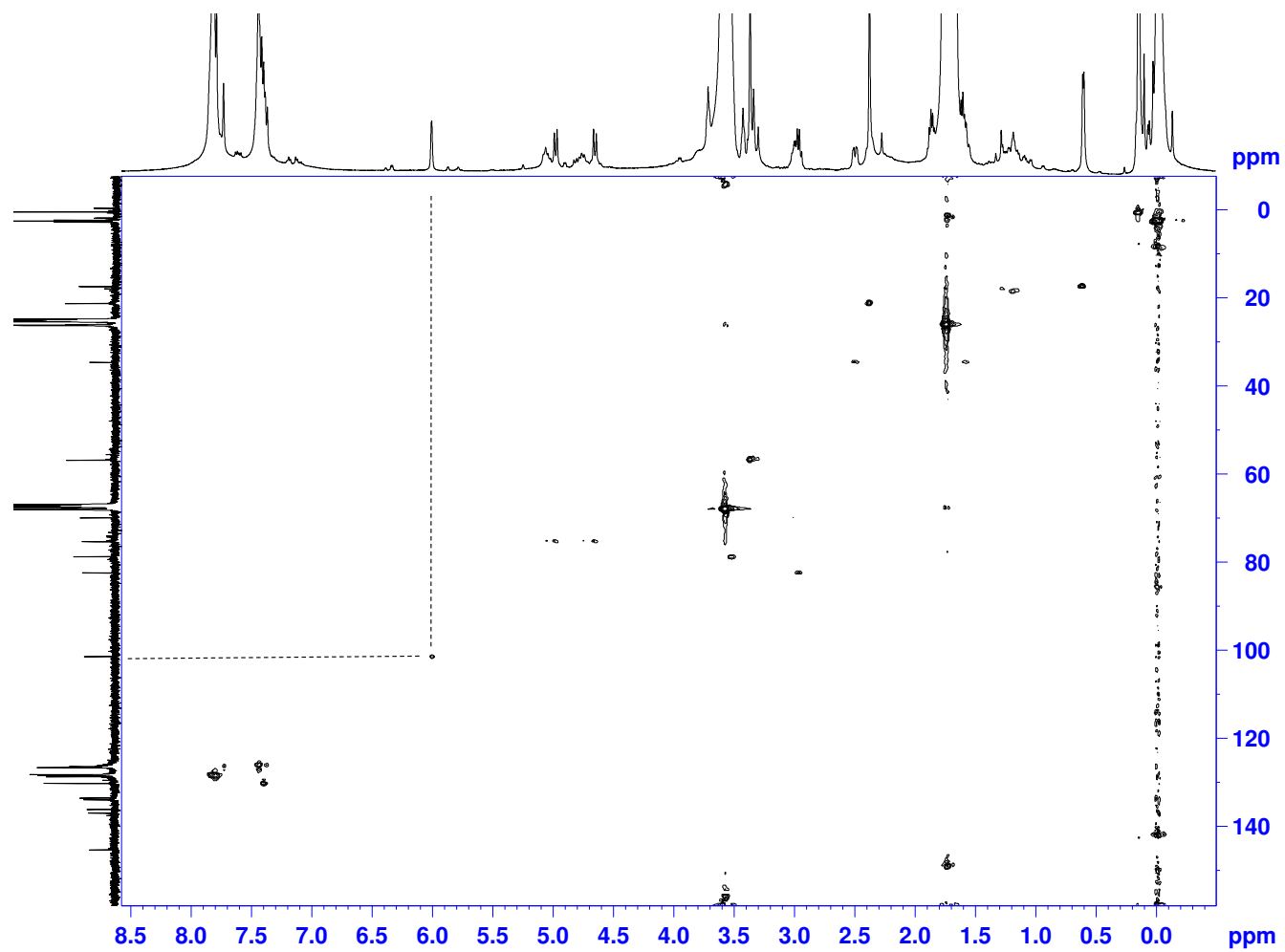
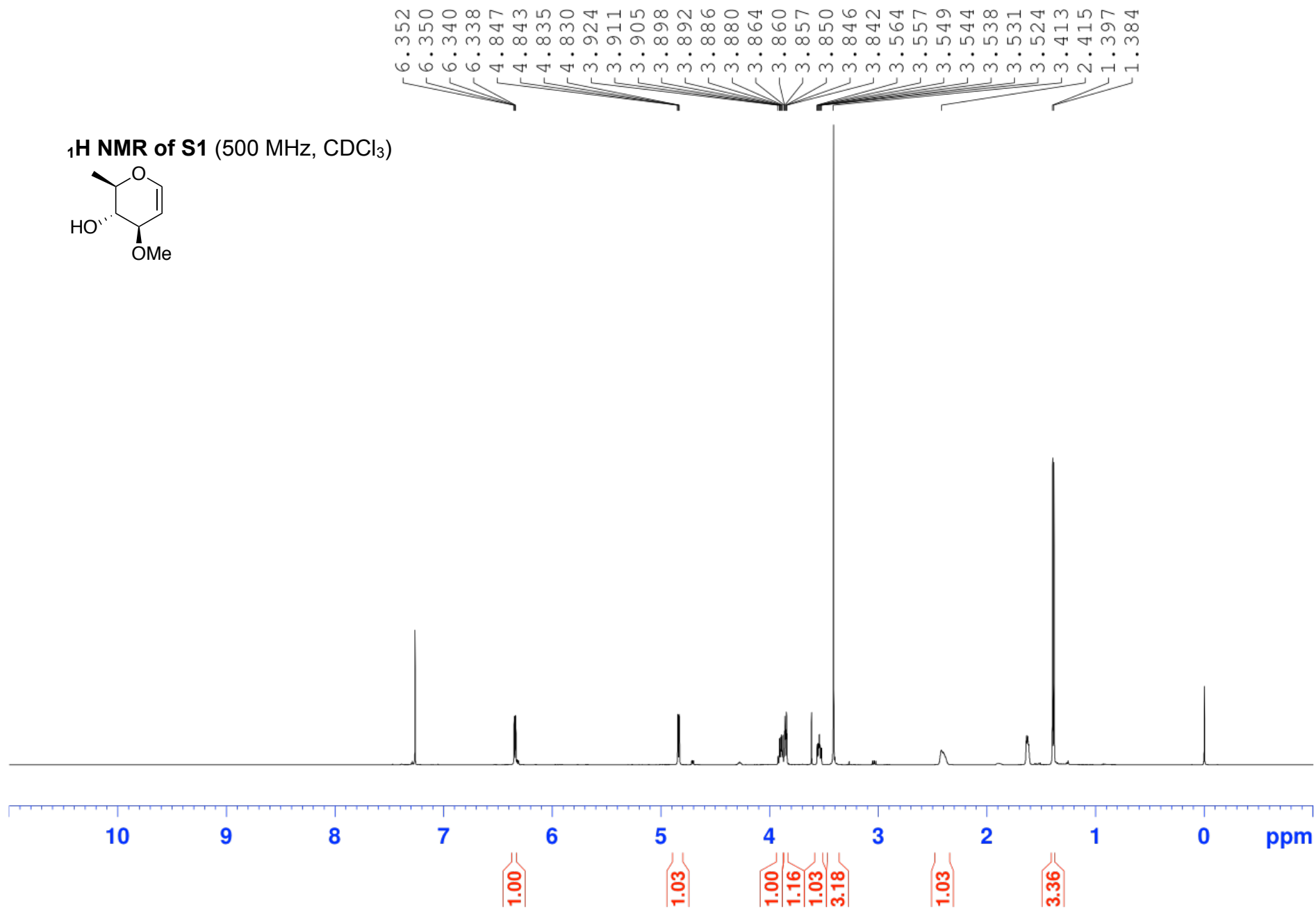
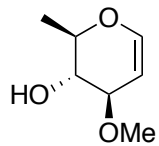


Figure S5.2.4 2D Gradient HSQC NMR spectrum of α -glucosyl toluenesulfonate at $-78\text{ }^{\circ}\text{C}$.

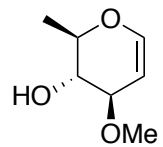
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¹H NMR of S1 (500 MHz, CDCl₃)



¹³C NMR of S1 (125 MHz, CDCl₃)



145.22

99.31

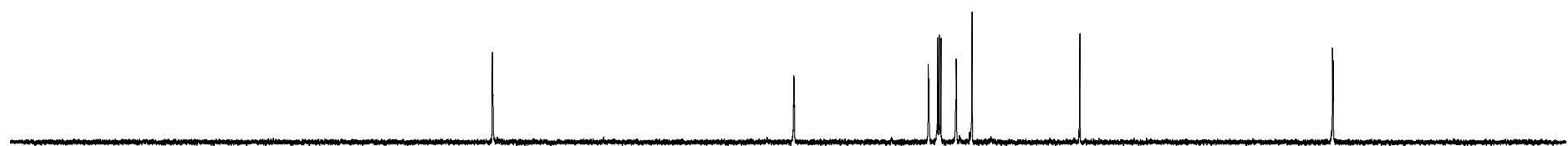
78.64

74.62

72.06

55.96

17.37



200

180

160

140

120

100

80

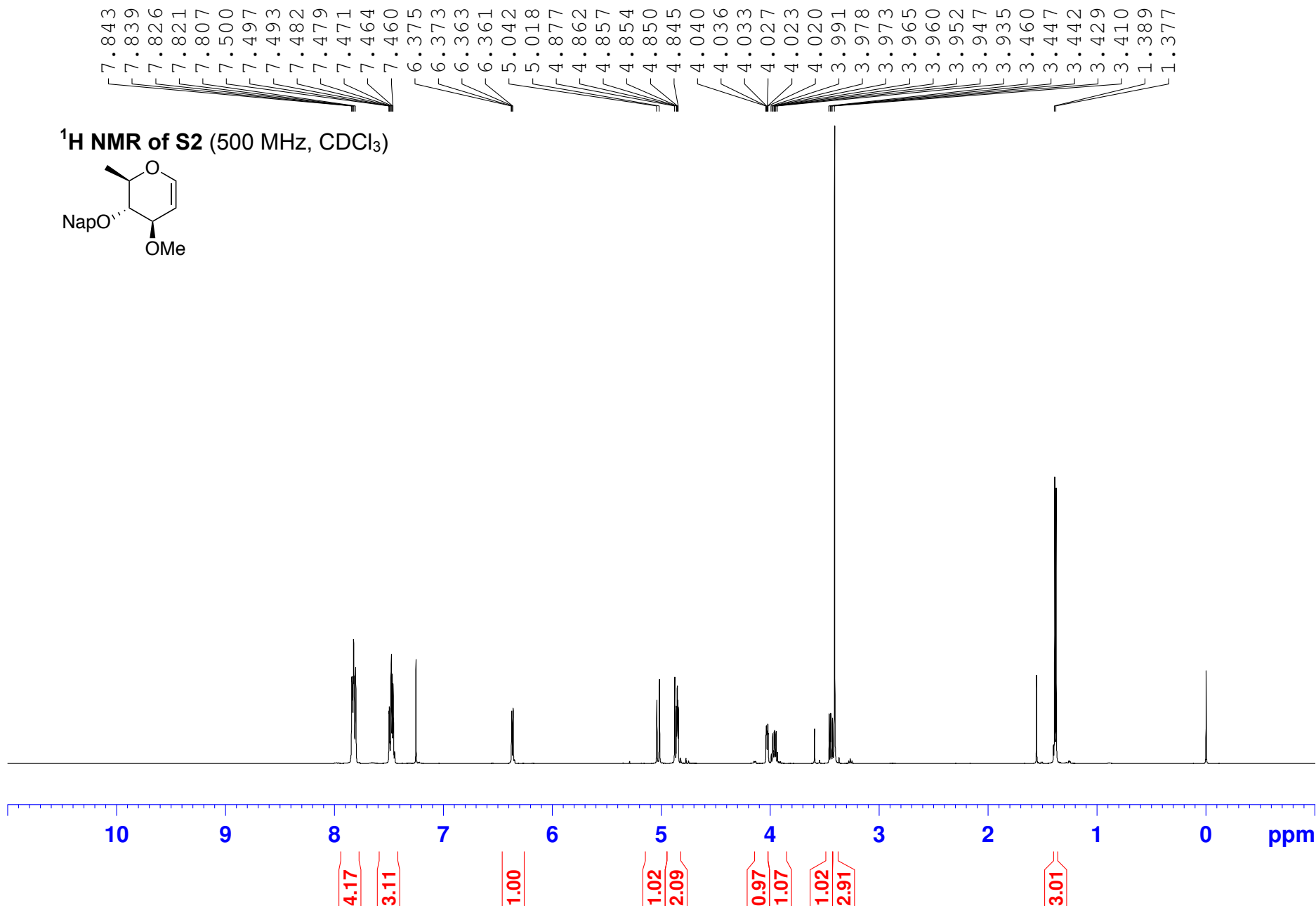
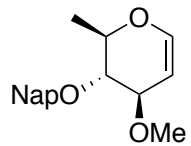
60

40

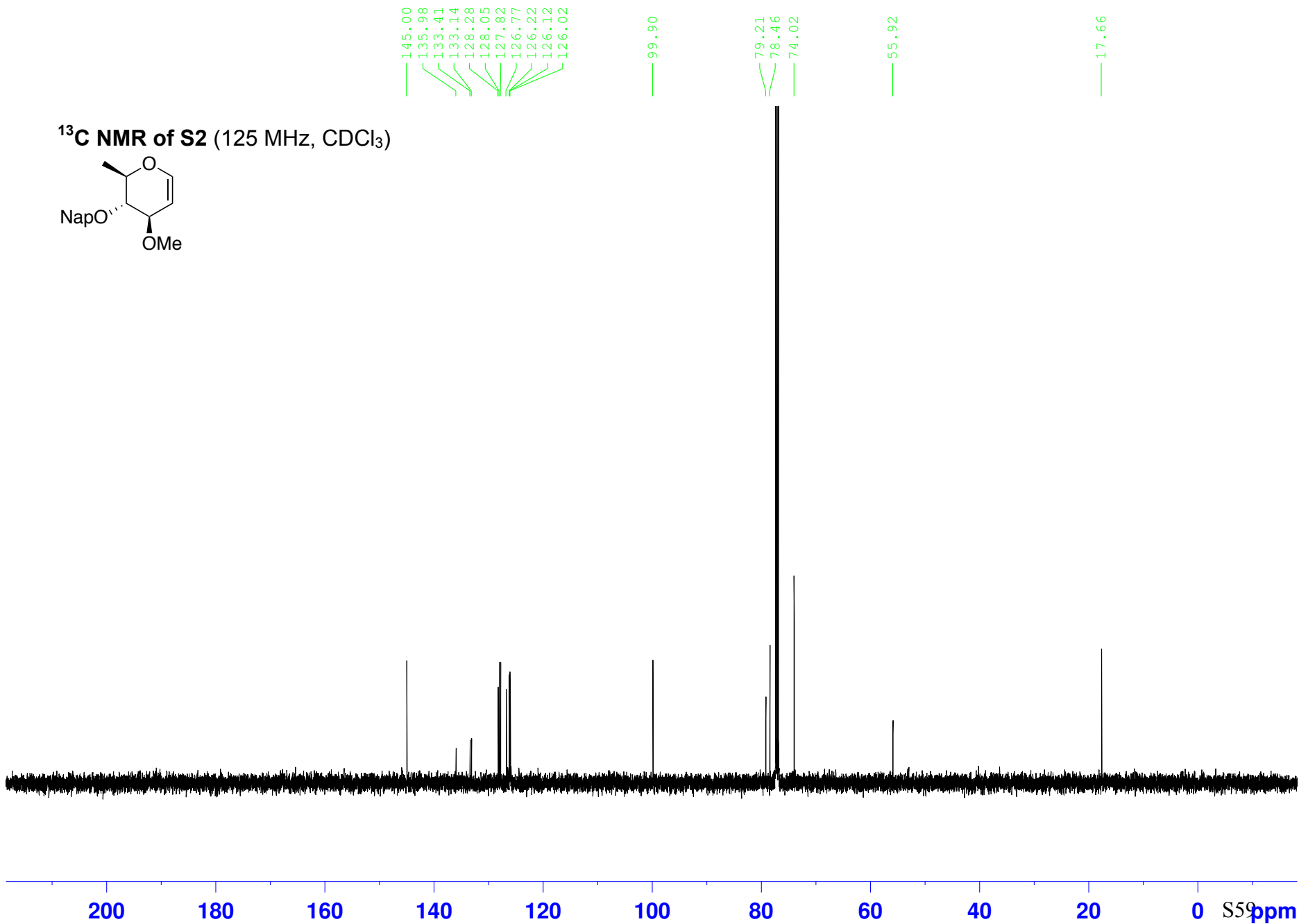
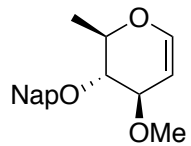
20

0 ppm

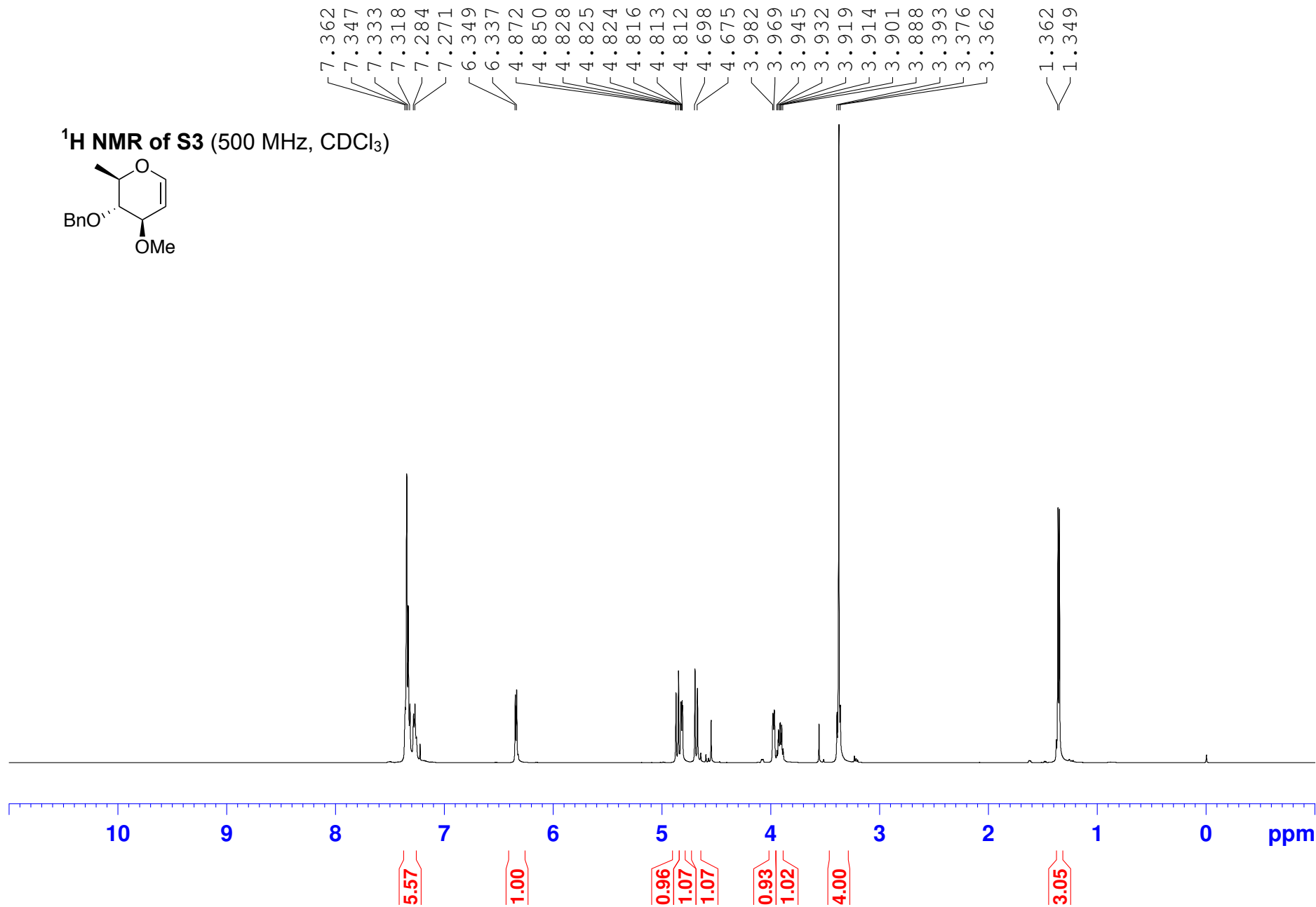
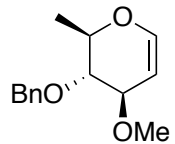
¹H NMR of S2 (500 MHz, CDCl₃)



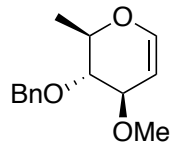
¹³C NMR of S2 (125 MHz, CDCl₃)



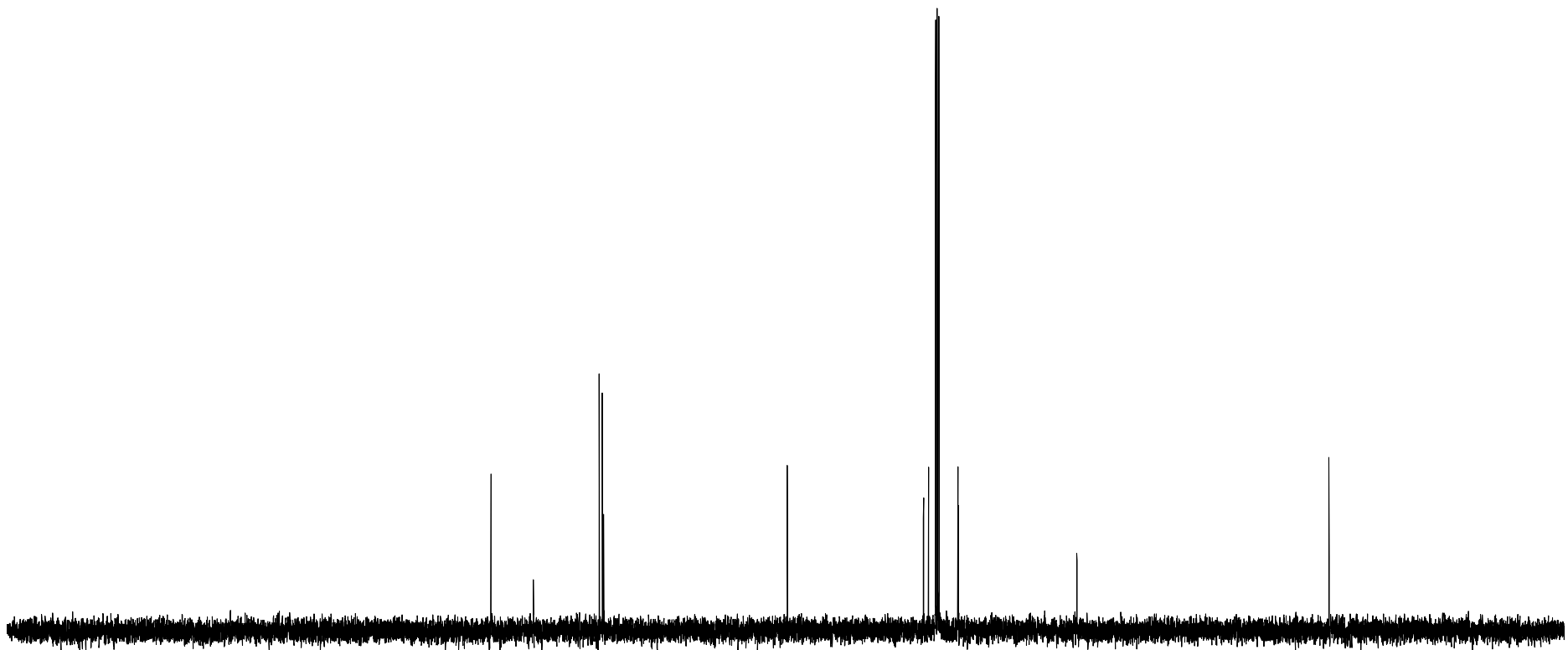
¹H NMR of S3 (500 MHz, CDCl₃)



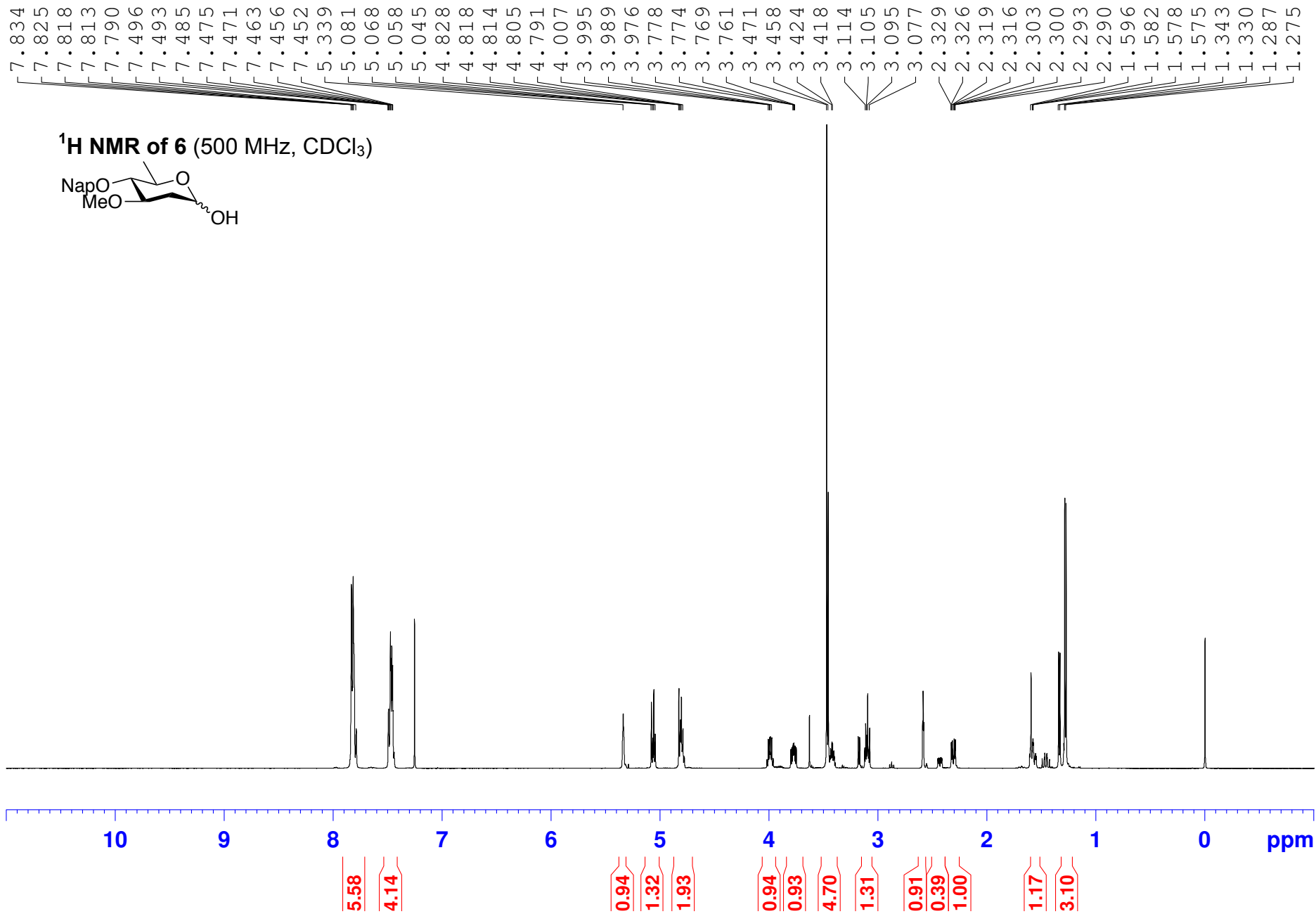
¹³C NMR of S3 (125 MHz, CDCl₃)



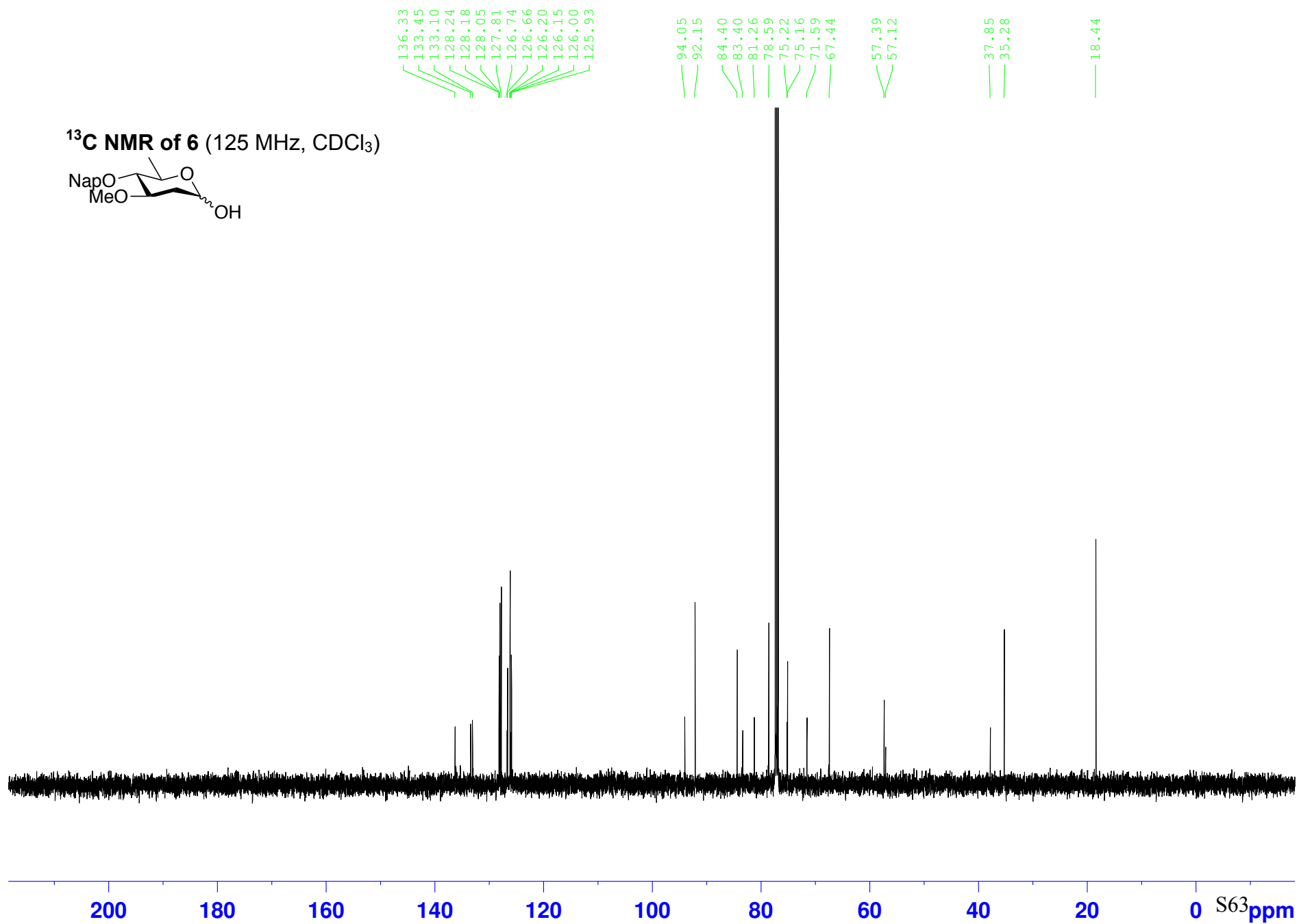
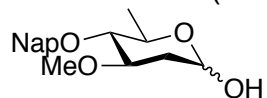
144.96
138.51
128.52
128.05
127.85
99.92
79.22
78.44
74.00
73.95
55.92
17.60

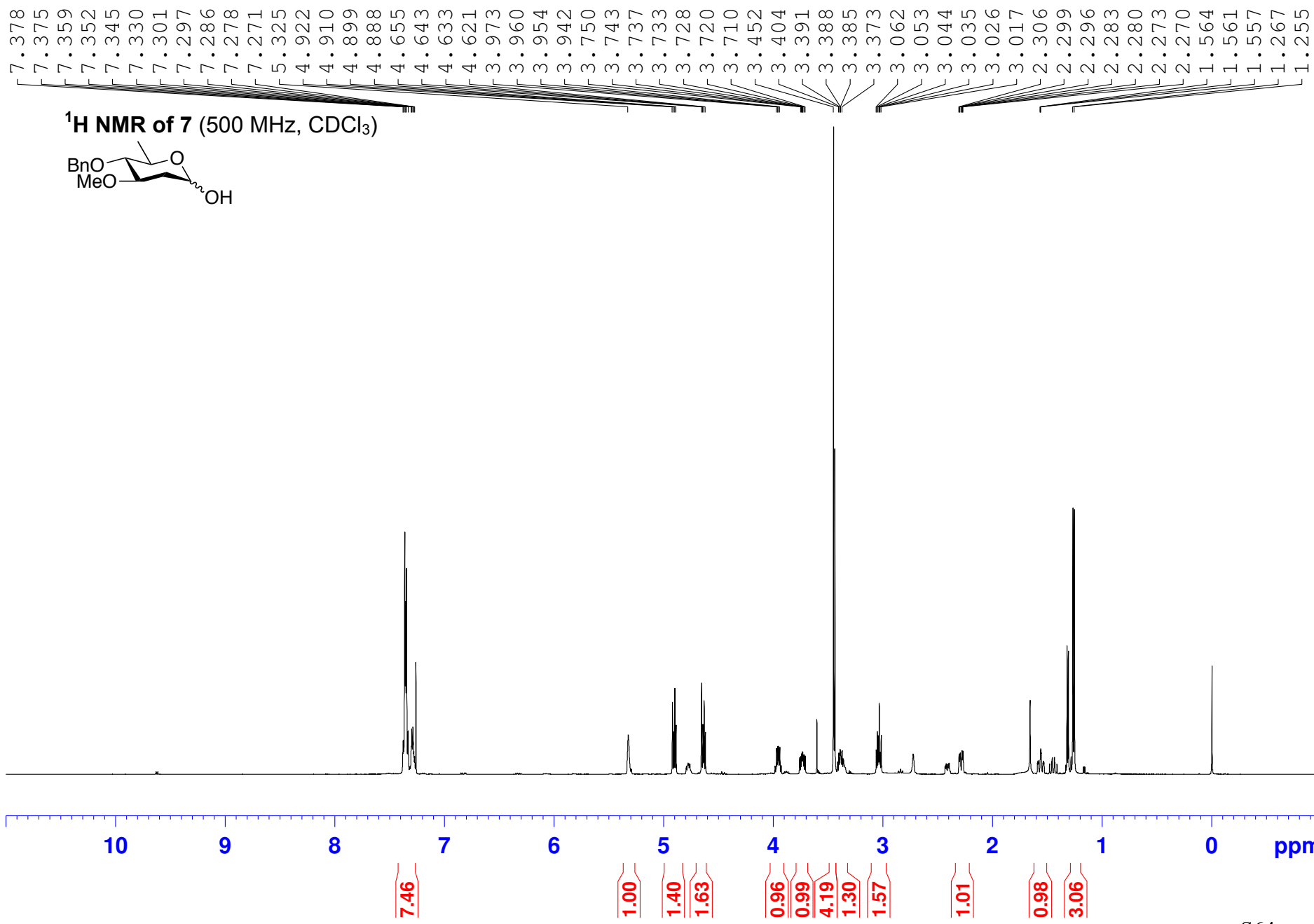


200 180 160 140 120 100 80 60 40 20 0 ppm

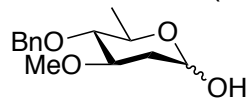


¹³C NMR of 6 (125 MHz, CDCl₃)





¹³C NMR of 7 (125 MHz, CDCl₃)

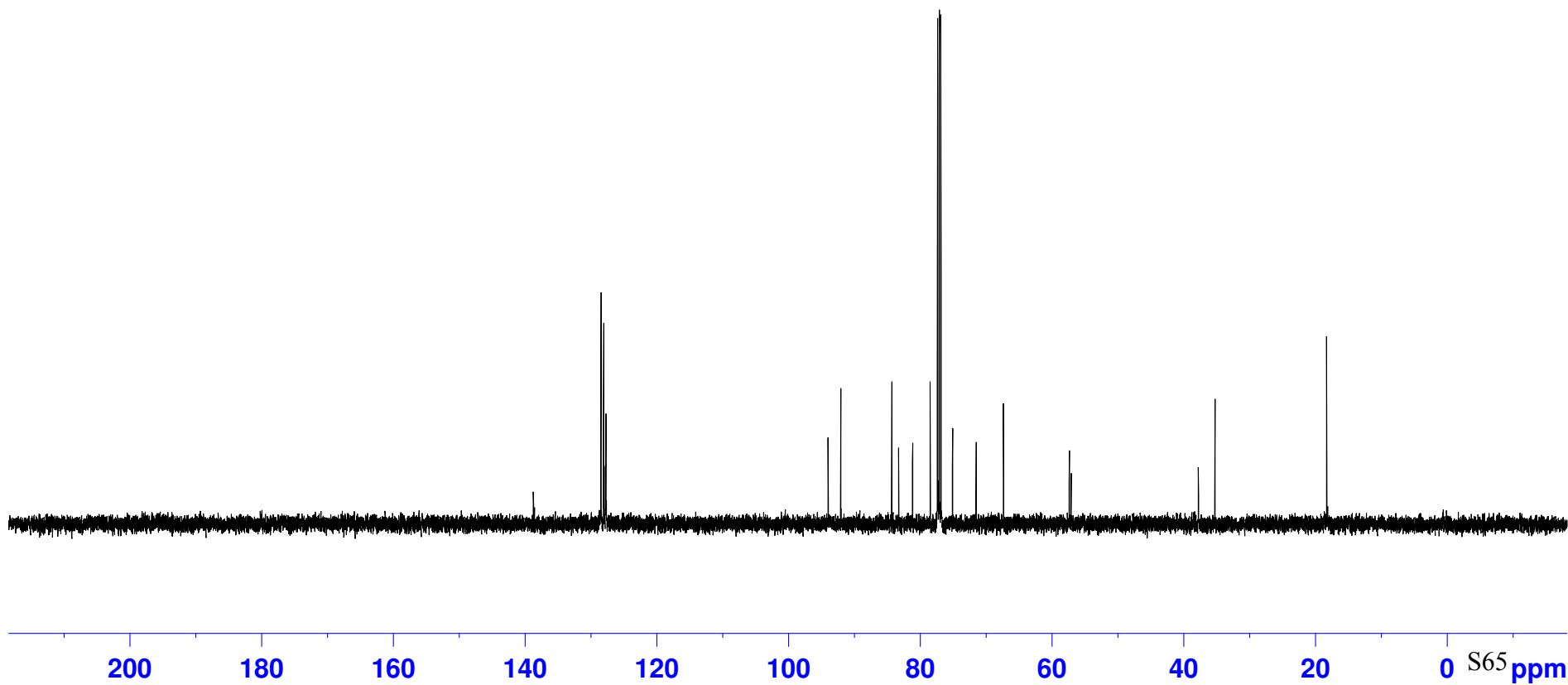


138.78
128.51
128.48
128.13
128.08
127.85
127.76

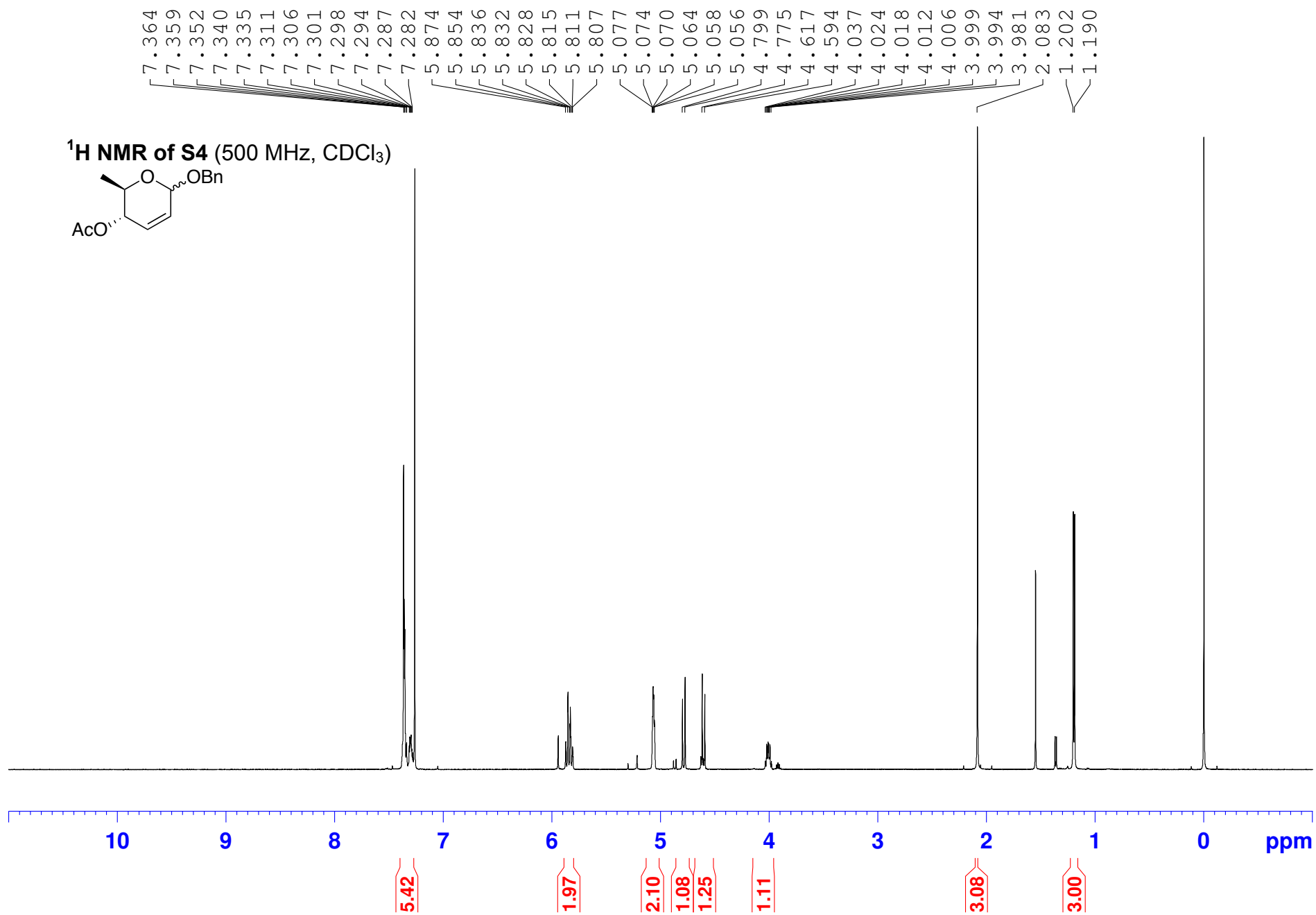
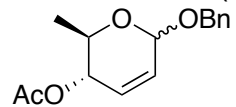
94.02
92.11
84.36
83.32
81.20
78.53
75.16
75.11
71.55
67.40
57.40
57.12

37.81
35.28

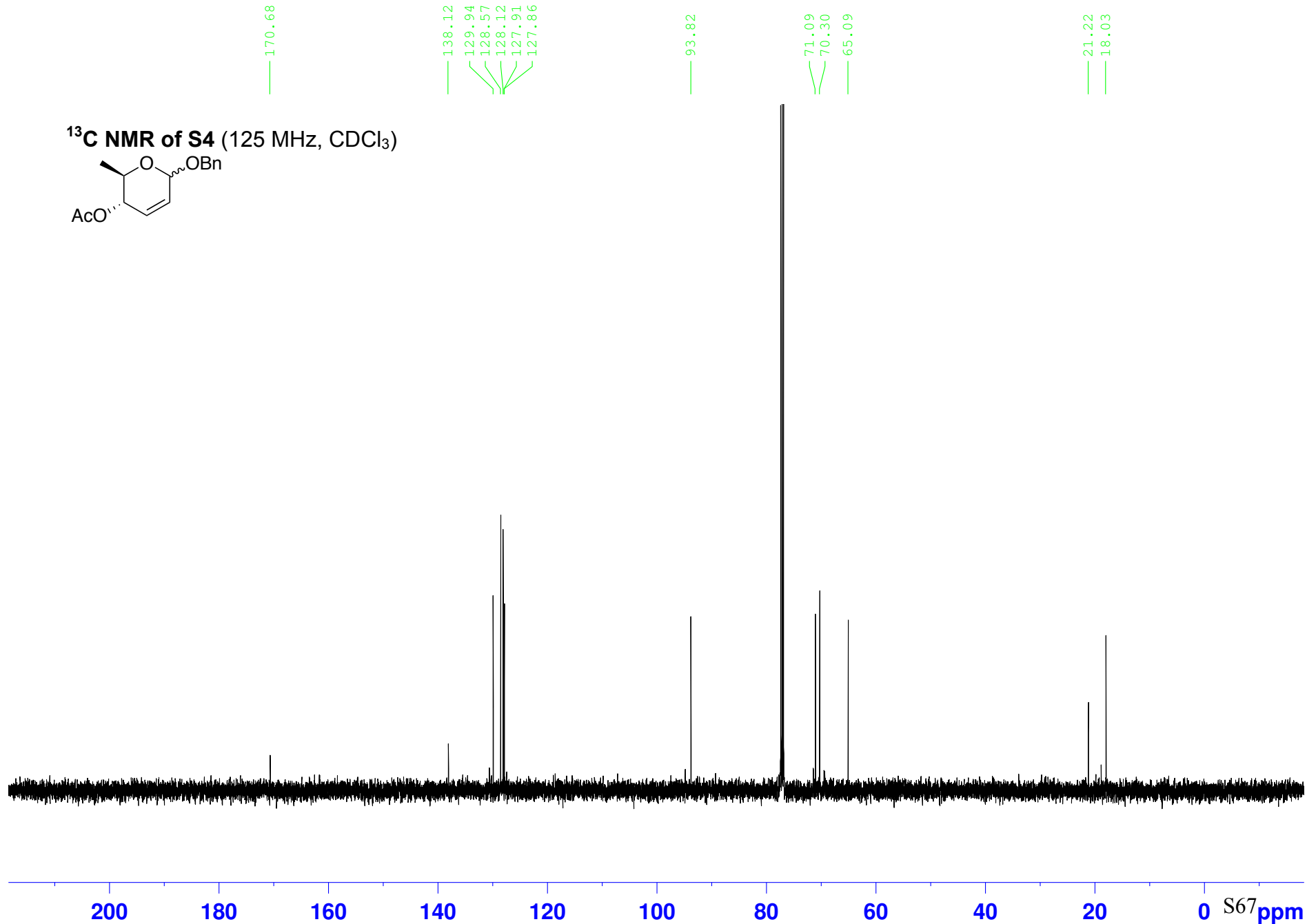
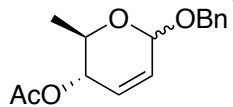
18.34



¹H NMR of S4 (500 MHz, CDCl₃)

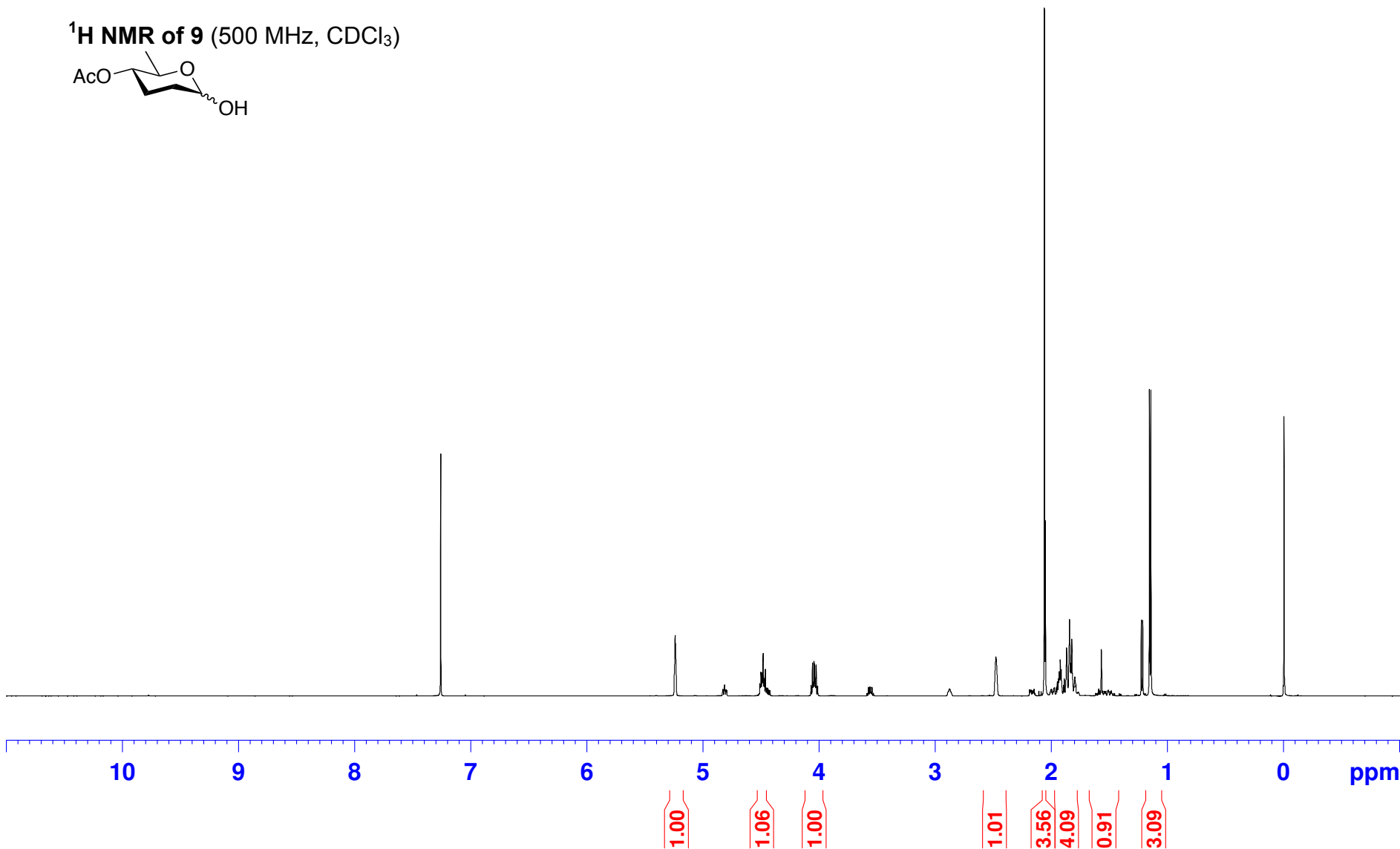
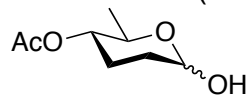


¹³C NMR of S4 (125 MHz, CDCl₃)

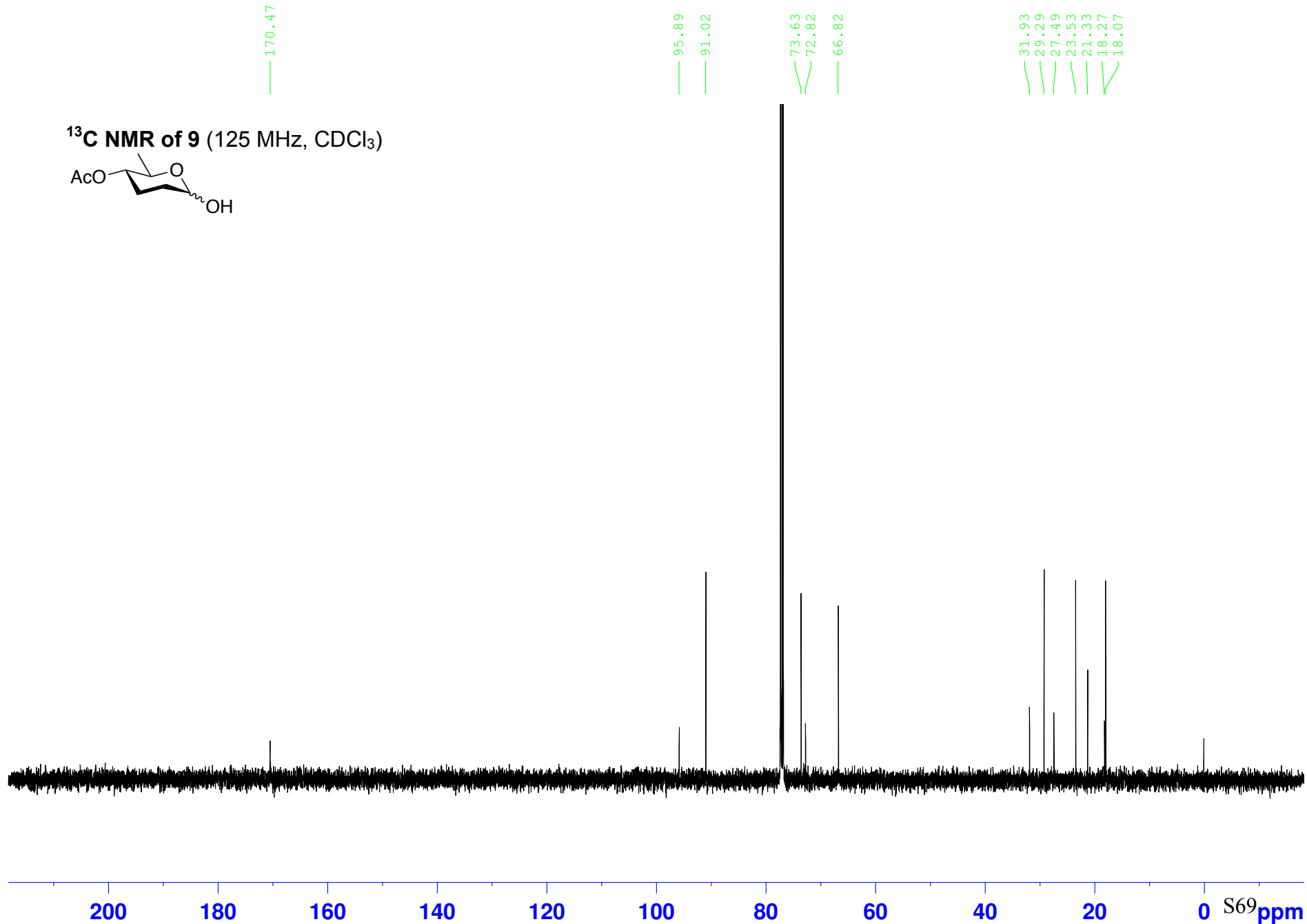
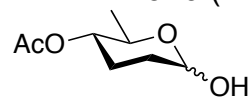


5.241
 4.512
 4.503
 4.492
 4.483
 4.473
 4.464
 4.453
 4.444
 4.071
 4.058
 4.052
 4.046
 4.040
 4.033
 4.027
 4.014
 2.479
 2.061
 2.052
 1.957
 1.949
 1.942
 1.934
 1.925
 1.916
 1.898
 1.890
 1.870
 1.867
 1.846
 1.843
 1.835
 1.826
 1.820
 1.808
 1.799
 1.789
 1.601
 1.593
 1.584
 1.559
 1.548
 1.543
 1.537
 1.531
 1.517
 1.514
 1.510
 1.506
 1.493
 1.484
 1.457
 1.156
 1.144

¹H NMR of 9 (500 MHz, CDCl₃)

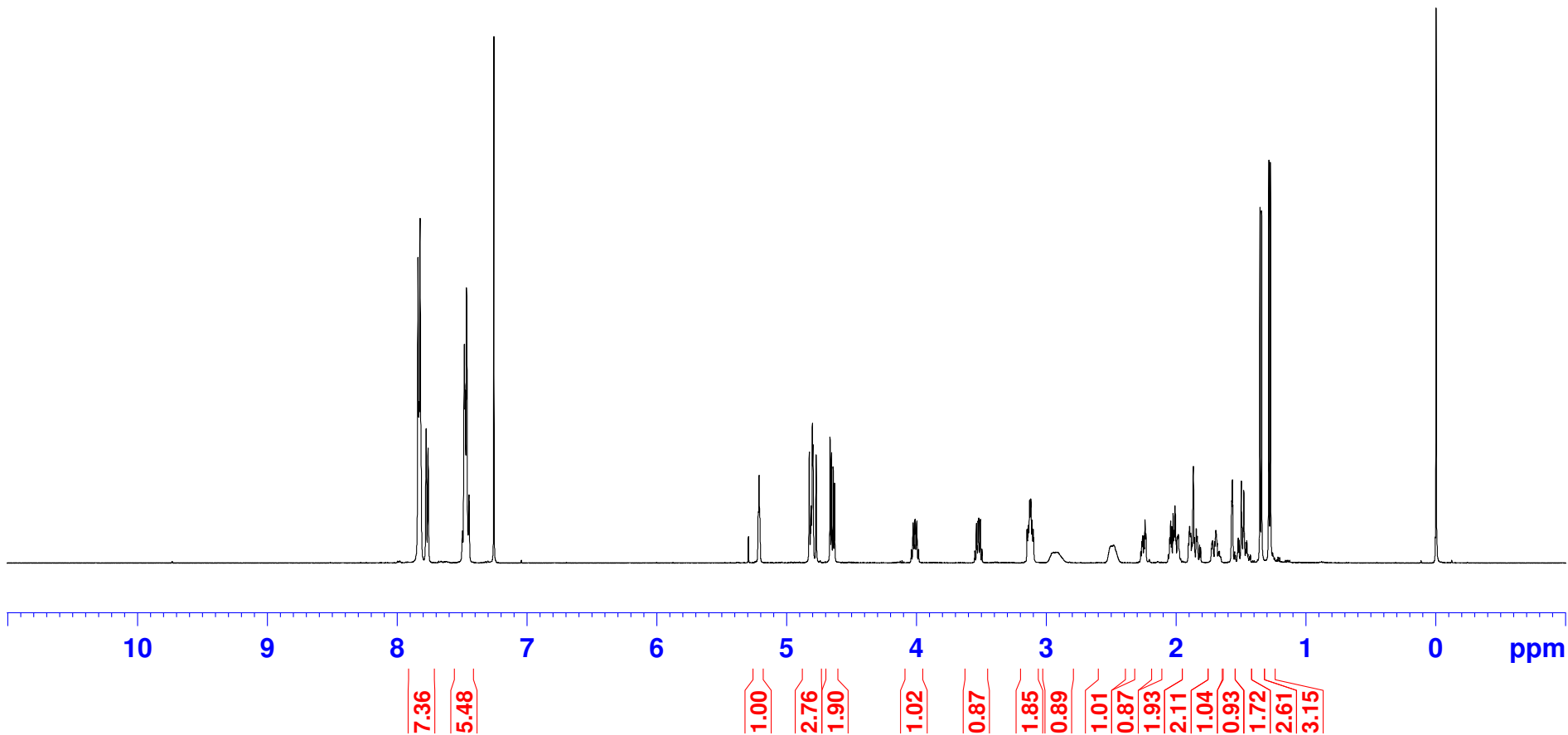
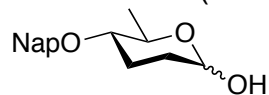


^{13}C NMR of 9 (125 MHz, CDCl_3)

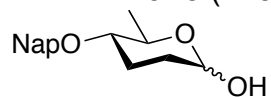


7.839
7.830
7.822
7.776
7.761
7.483
7.480
7.476
7.473
7.465
7.451
7.446
7.443
5.220
5.215
4.827
4.818
4.812
4.804
4.799
4.775
4.667
4.656
4.644
4.633
4.029
4.016
4.011
3.998
3.540
3.527
3.522
3.510
3.150
3.142
3.137
3.130
3.120
3.112
3.103
2.242
2.043
2.035
2.025
2.011
1.898
1.871
1.868
1.846
1.499
1.480
1.355
1.343
1.287
1.275

¹H NMR of 8 (500 MHz, CDCl₃)



¹³C NMR of 8 (125 MHz, CDCl₃)

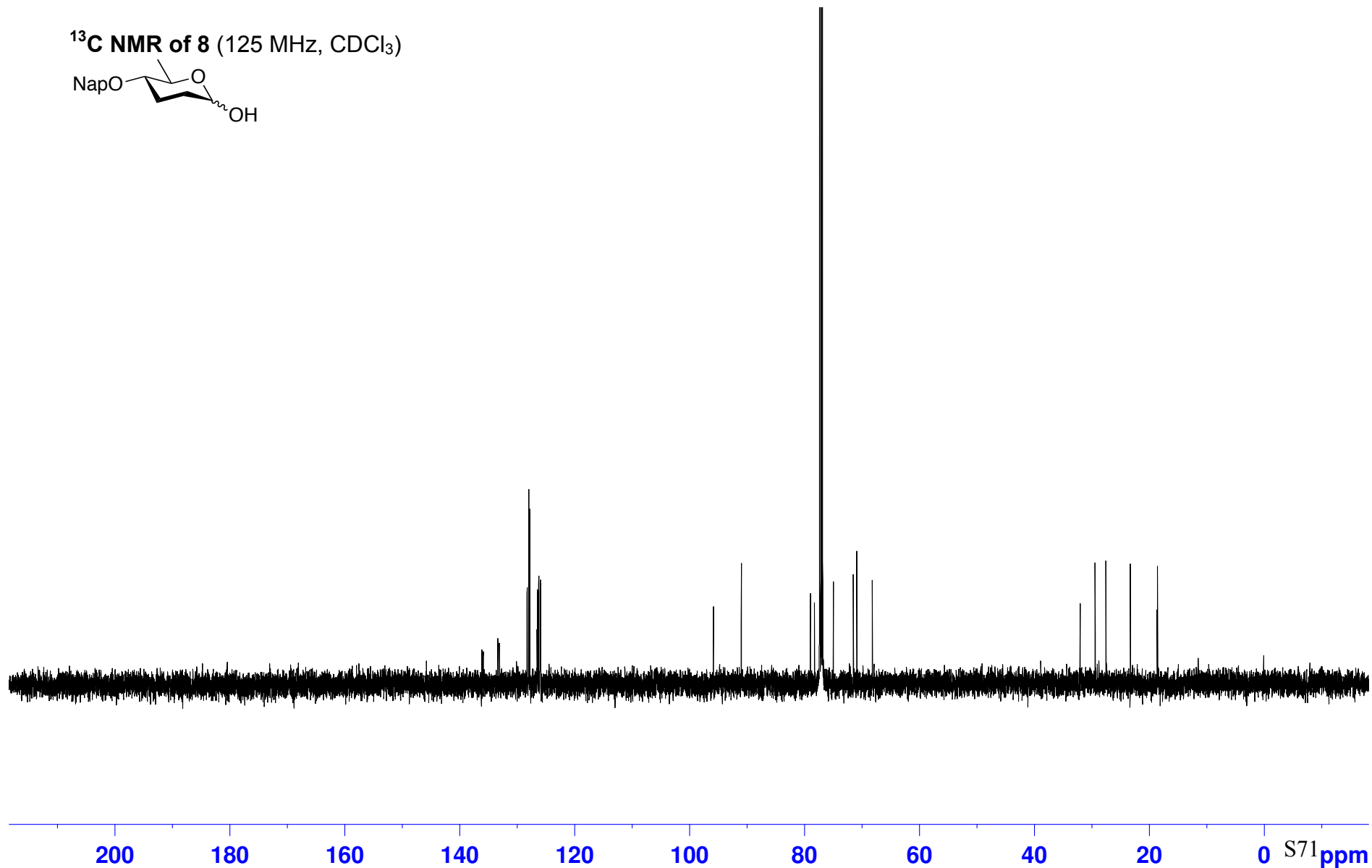


136.16
135.94
133.40
133.14
133.12
128.35
128.29
128.00
127.84
126.55
126.49
126.29
126.24
126.07
126.00
125.97
125.93

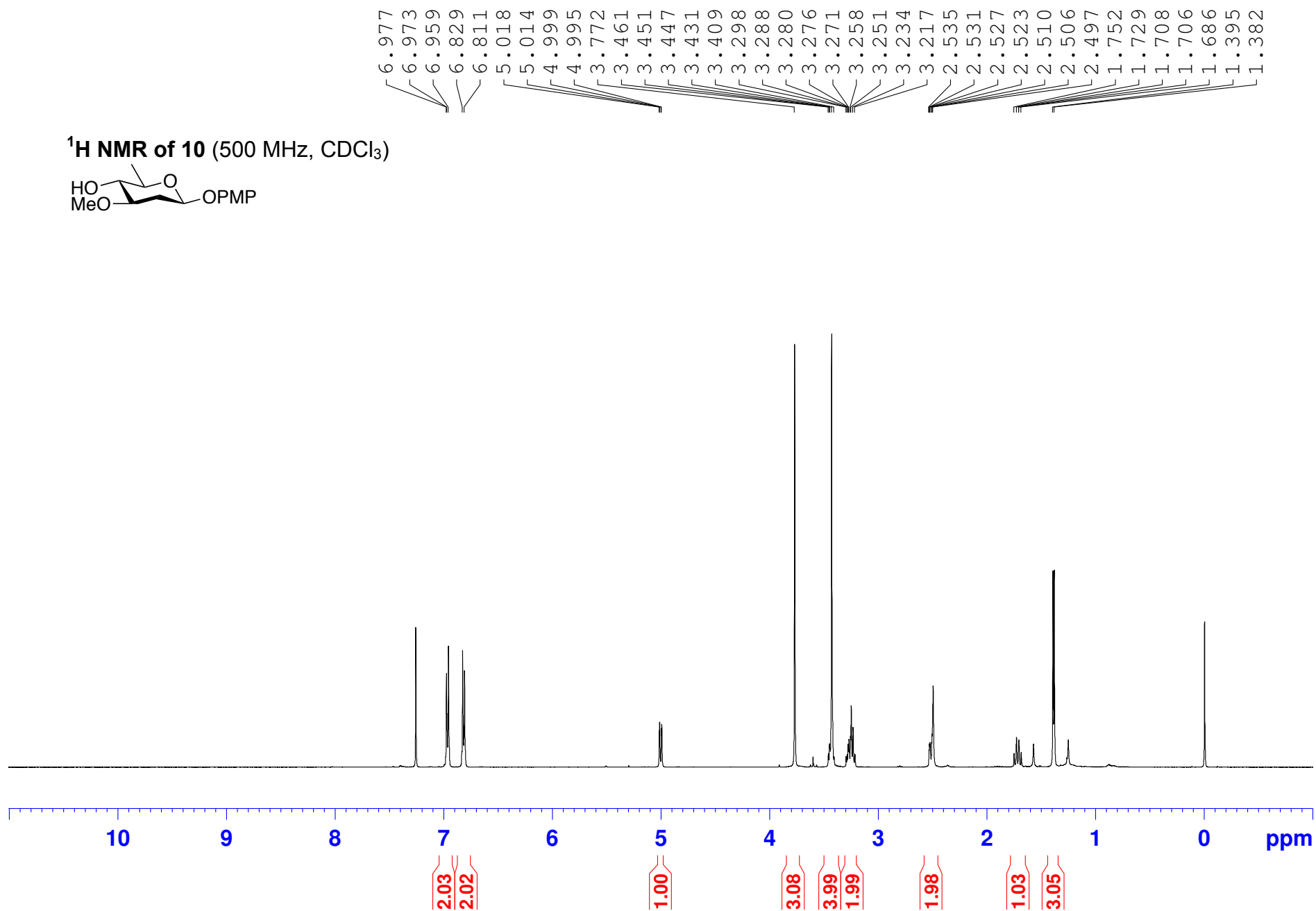
95.89
91.04

79.02
78.31
75.02
71.54
70.95
68.25

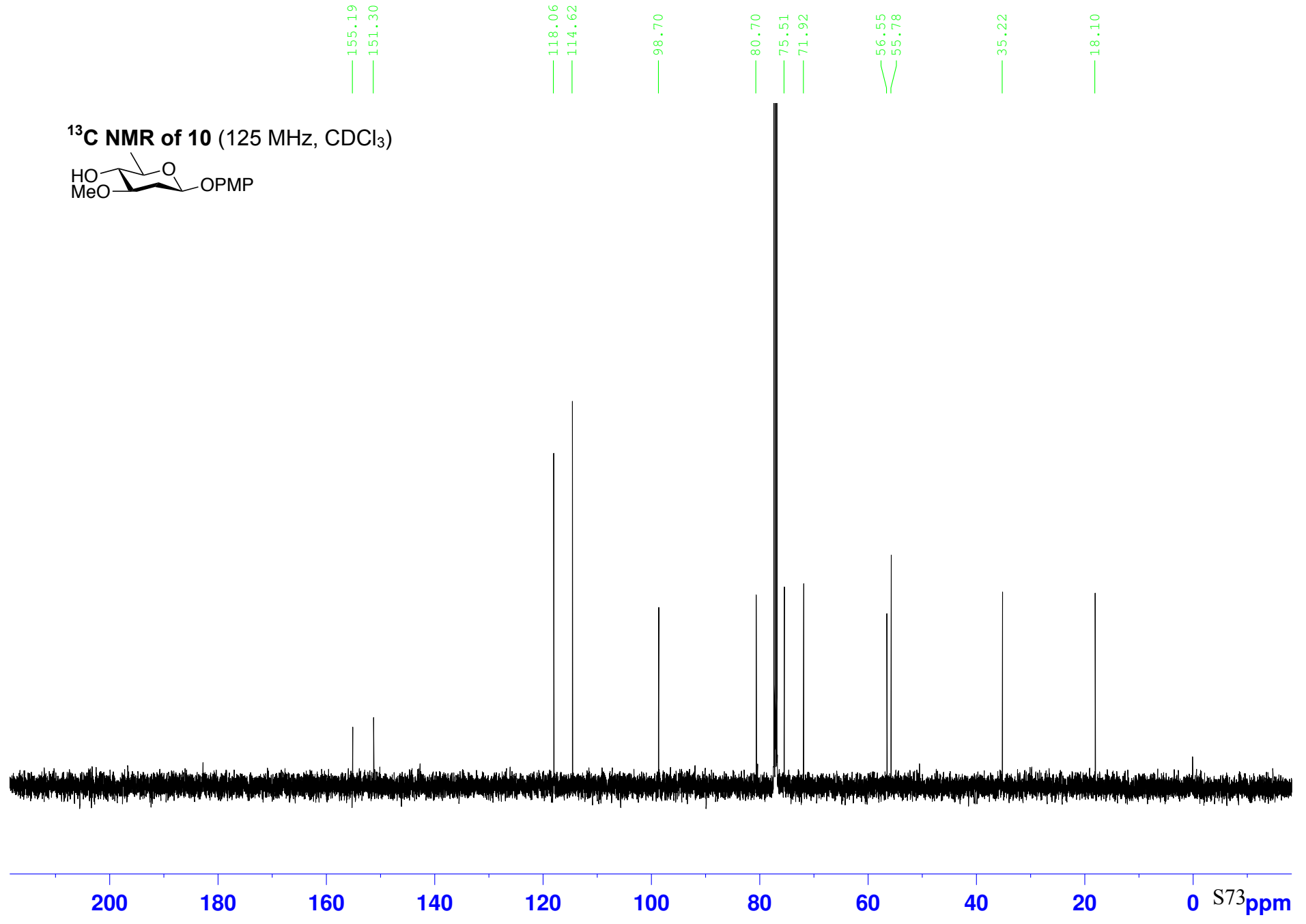
32.08
29.47
27.61
23.36
18.67
18.61

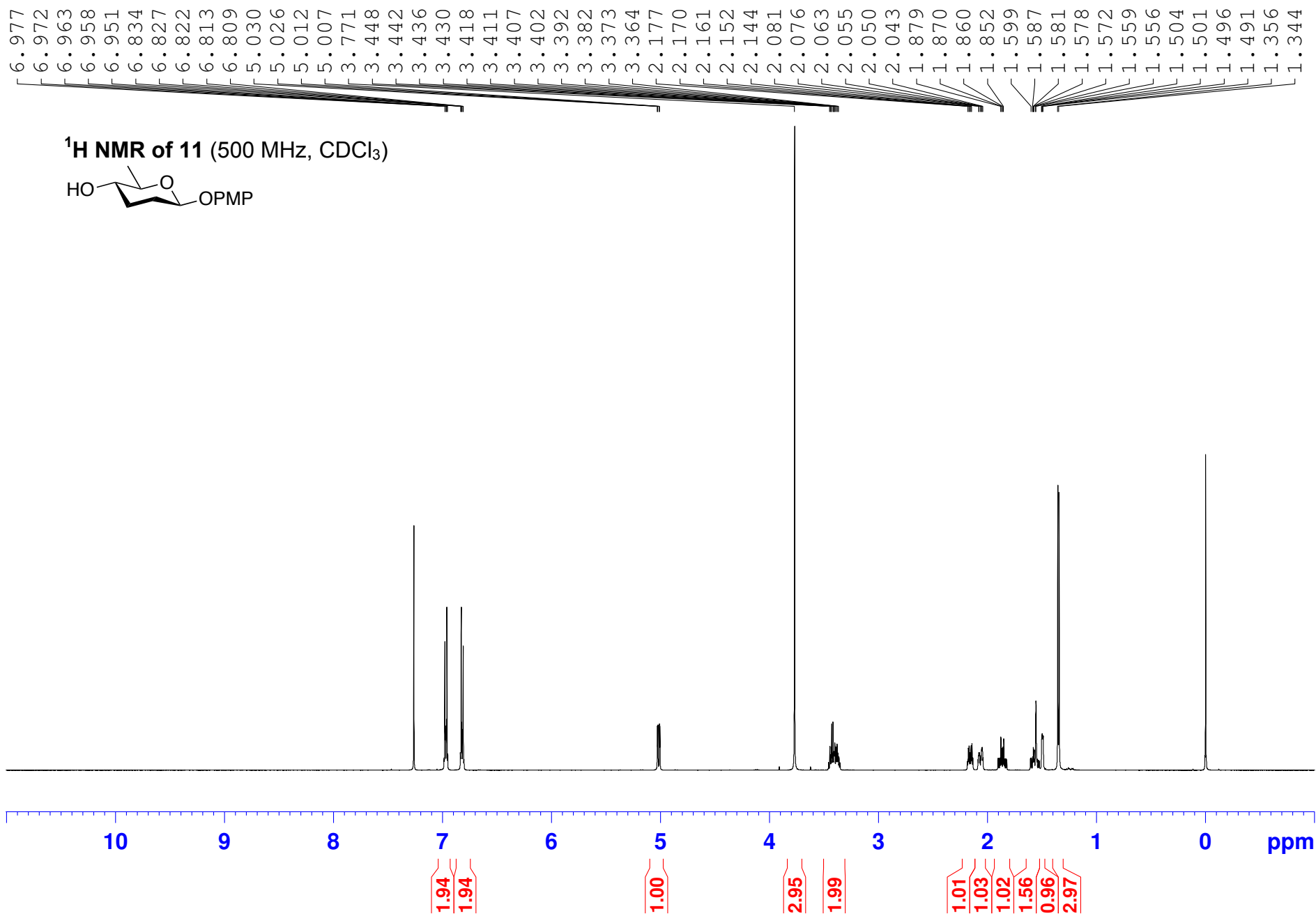


¹H NMR of 10 (500 MHz, CDCl₃)

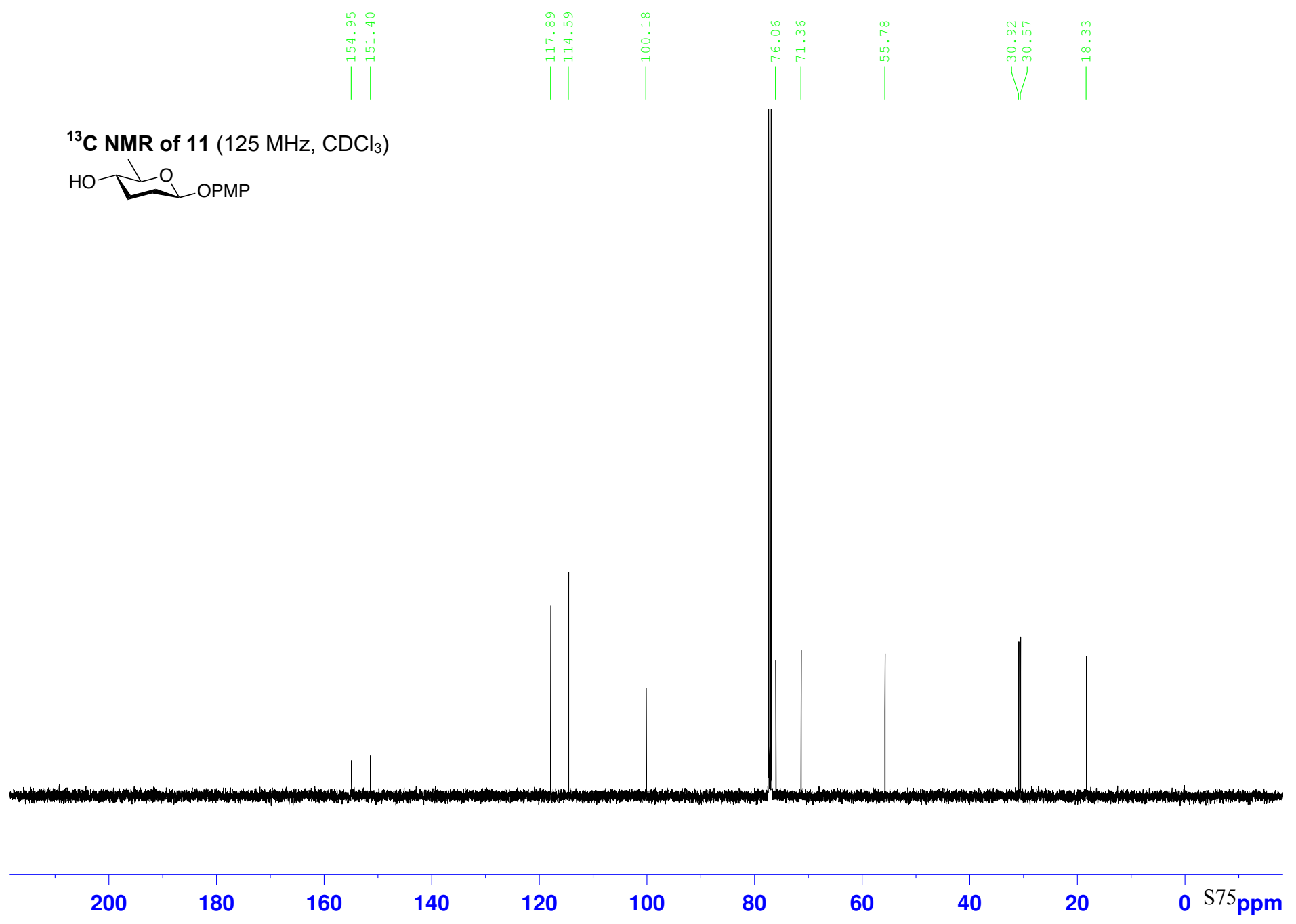


¹³C NMR of 10 (125 MHz, CDCl₃)



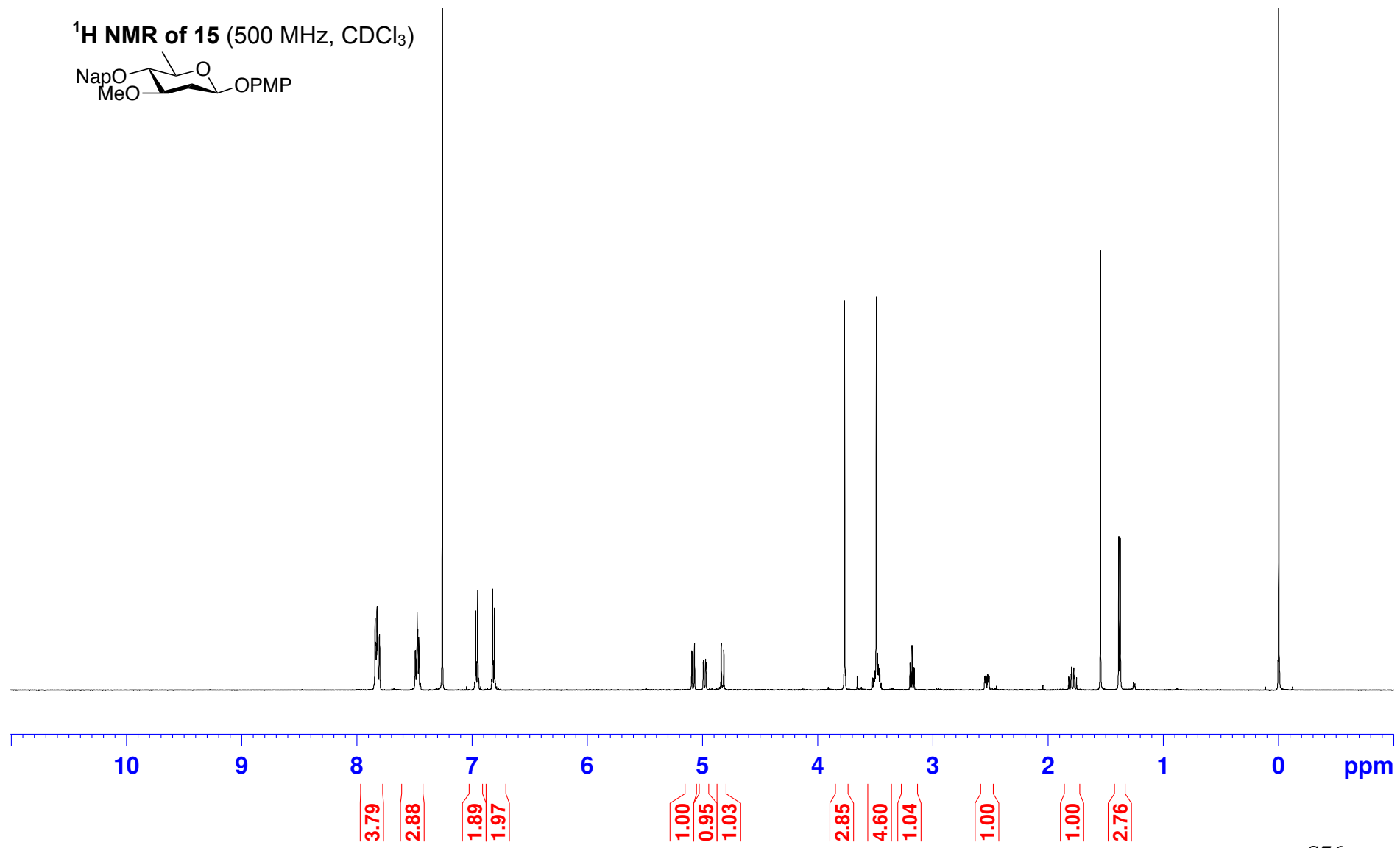
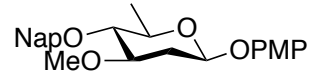


¹³C NMR of 11 (125 MHz, CDCl₃)

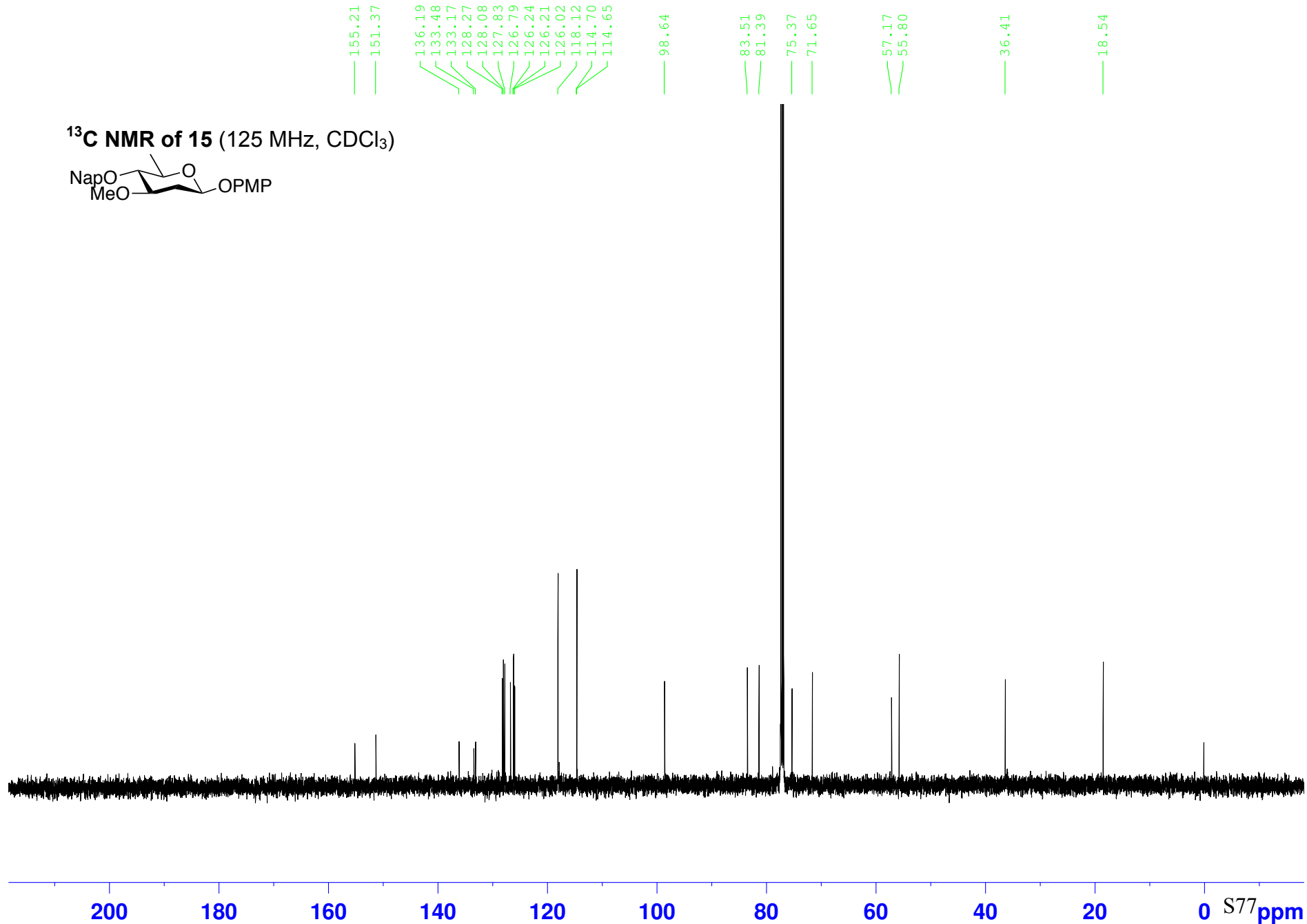
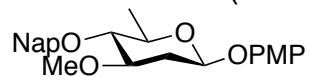


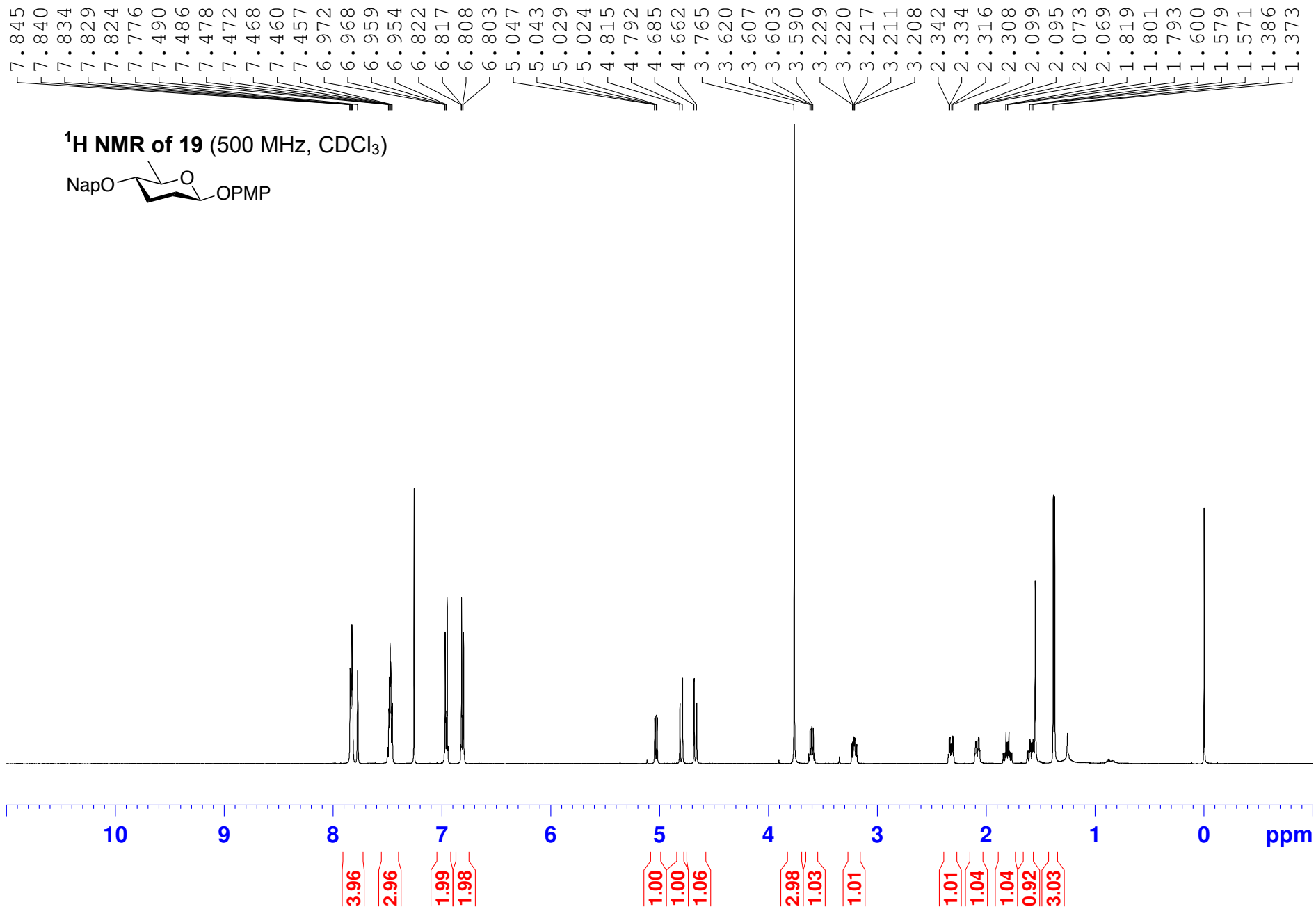
7.844
7.838
7.827
7.806
7.495
7.484
7.480
7.473
7.465
7.461
6.971
6.966
6.957
6.952
6.825
6.820
6.811
6.806
5.094
5.071
4.995
4.991
4.975
4.971
4.839
4.816
3.769
3.530
3.522
3.512
3.505
3.492
3.482
3.476
3.471
3.463
3.200
3.182
3.164
2.552
2.548
2.542
2.538
2.527
2.523
2.518
2.513
1.822
1.802
1.798
1.779
1.774
1.754

¹H NMR of 15 (500 MHz, CDCl₃)

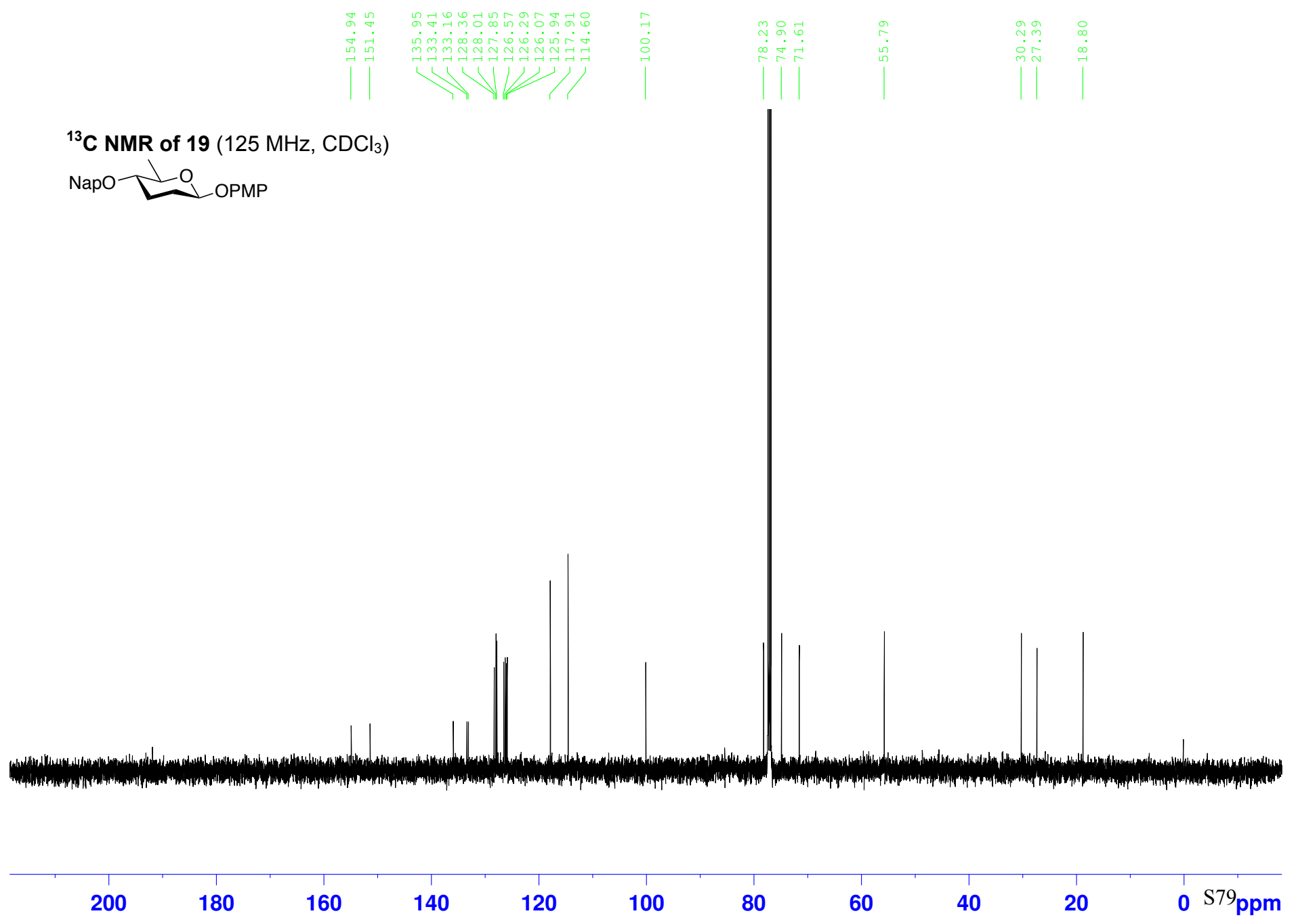
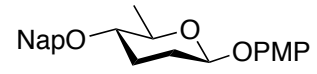


¹³C NMR of 15 (125 MHz, CDCl₃)



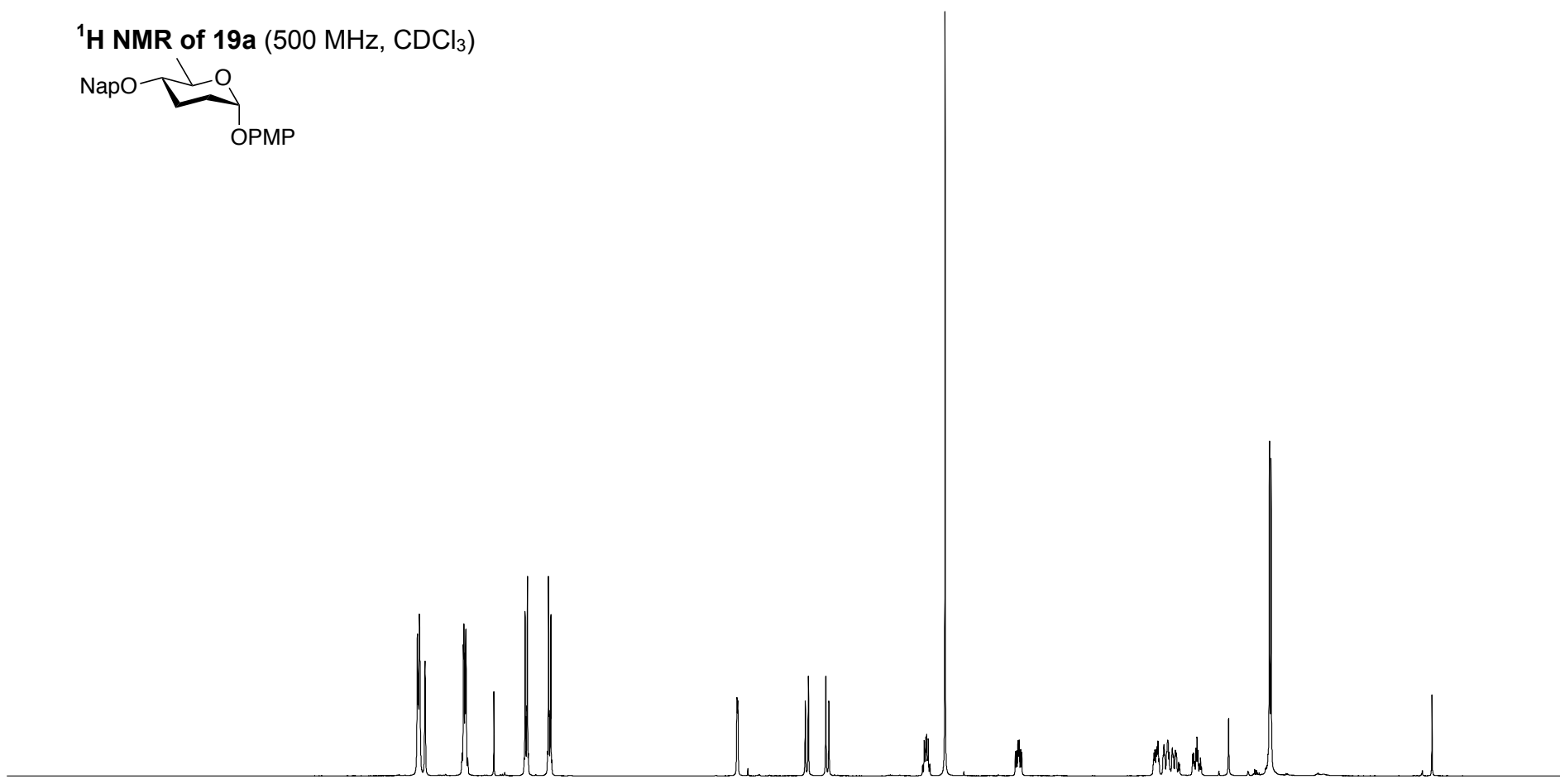
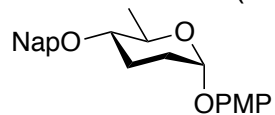


¹³C NMR of 19 (125 MHz, CDCl₃)



7.837
7.829
7.822
7.778
7.482
7.478
7.470
7.463
7.005
7.001
6.992
6.987
6.824
6.820
6.811
6.806
5.368
5.362
4.841
4.817
4.682
4.658
3.922
3.909
3.903
3.891
3.761
3.217
3.208
3.196
3.189
3.177
3.169
2.147
2.140
2.131
2.127
2.122
2.116
2.070
2.048
2.043
2.041
2.038
2.030
2.005
1.982
1.974
1.849
1.842
1.823
1.815
1.807
1.255
1.243

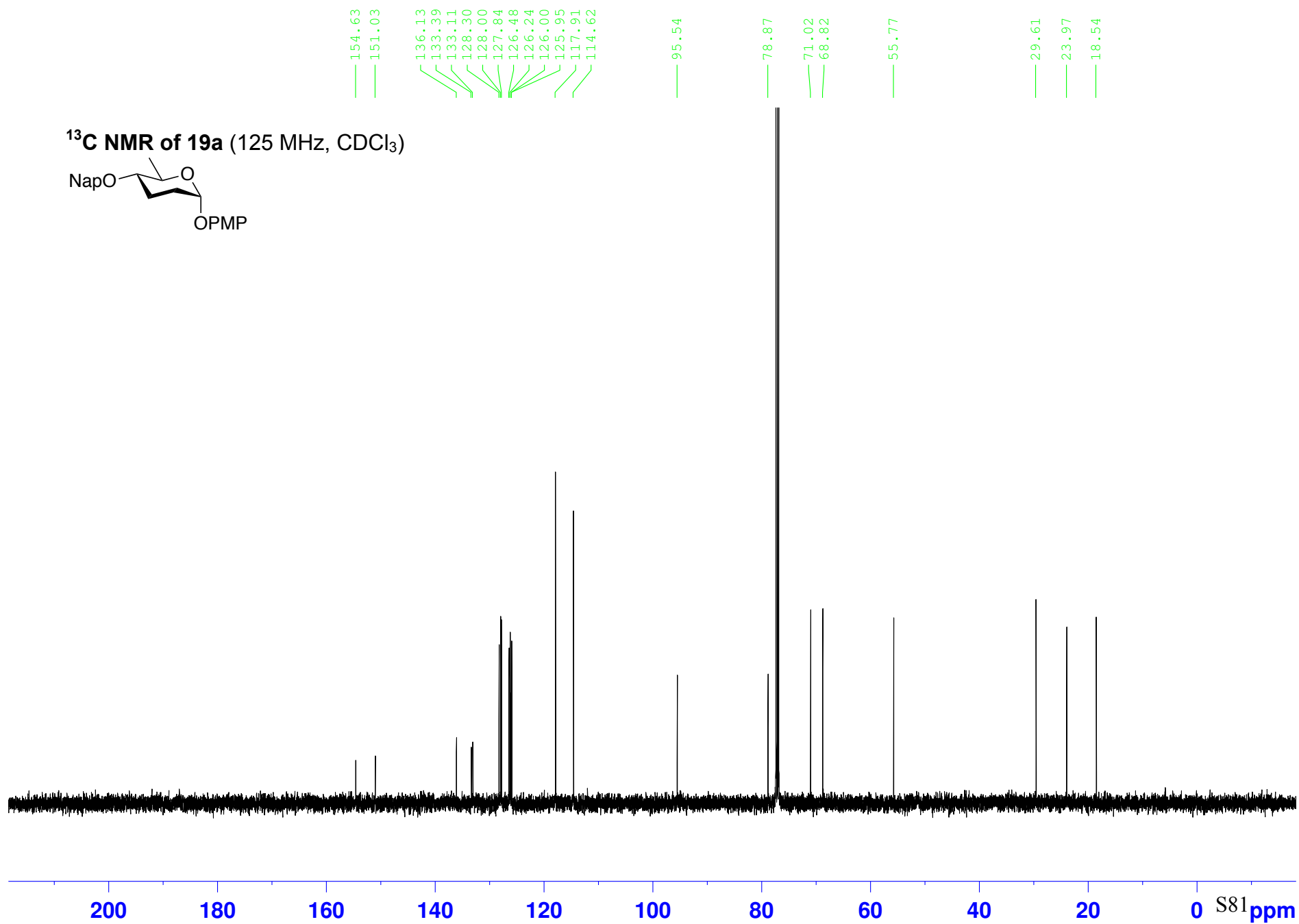
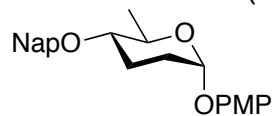
¹H NMR of 19a (500 MHz, CDCl₃)

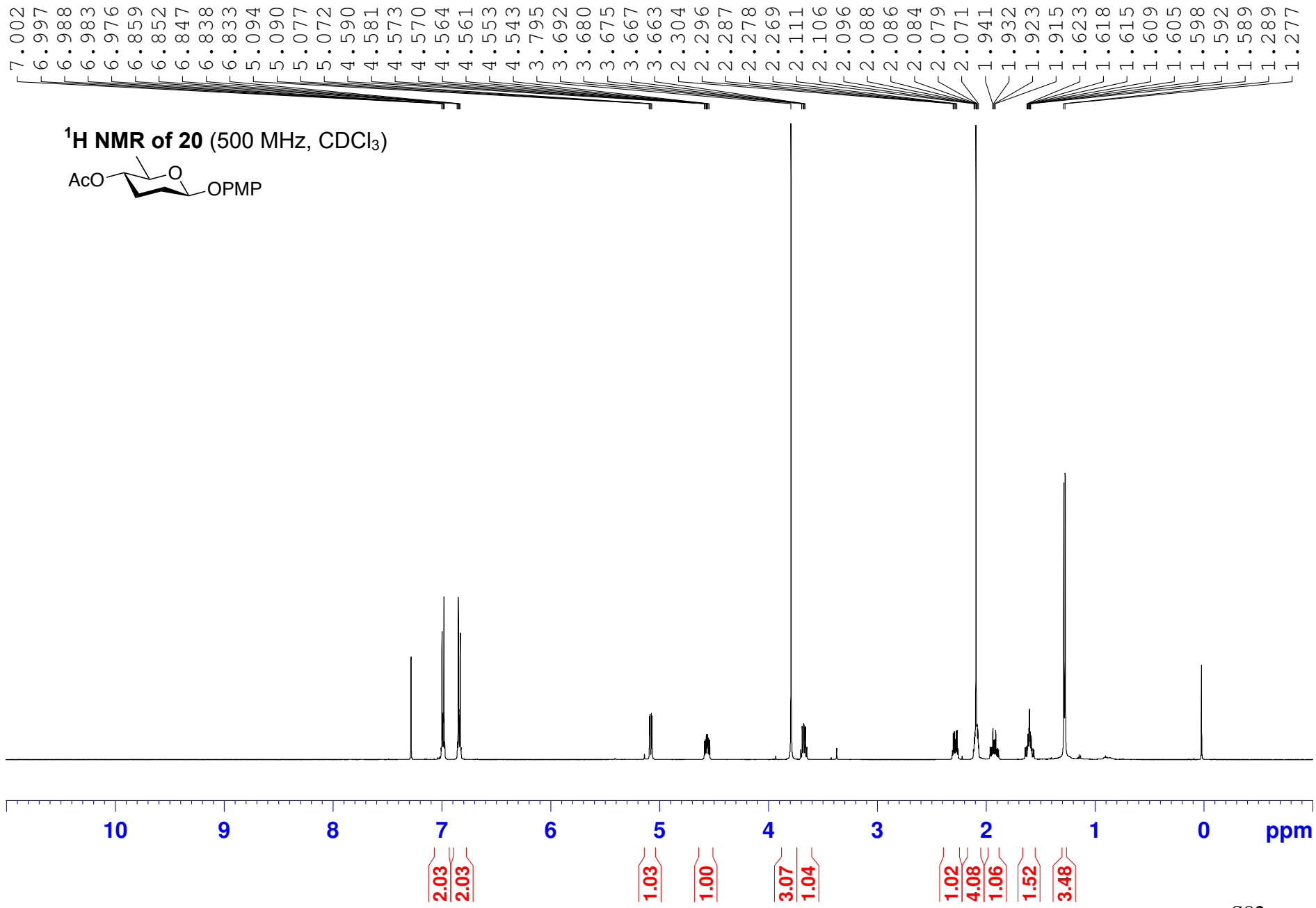


10 9 8 7 6 5 4 3 2 1 0 ppm

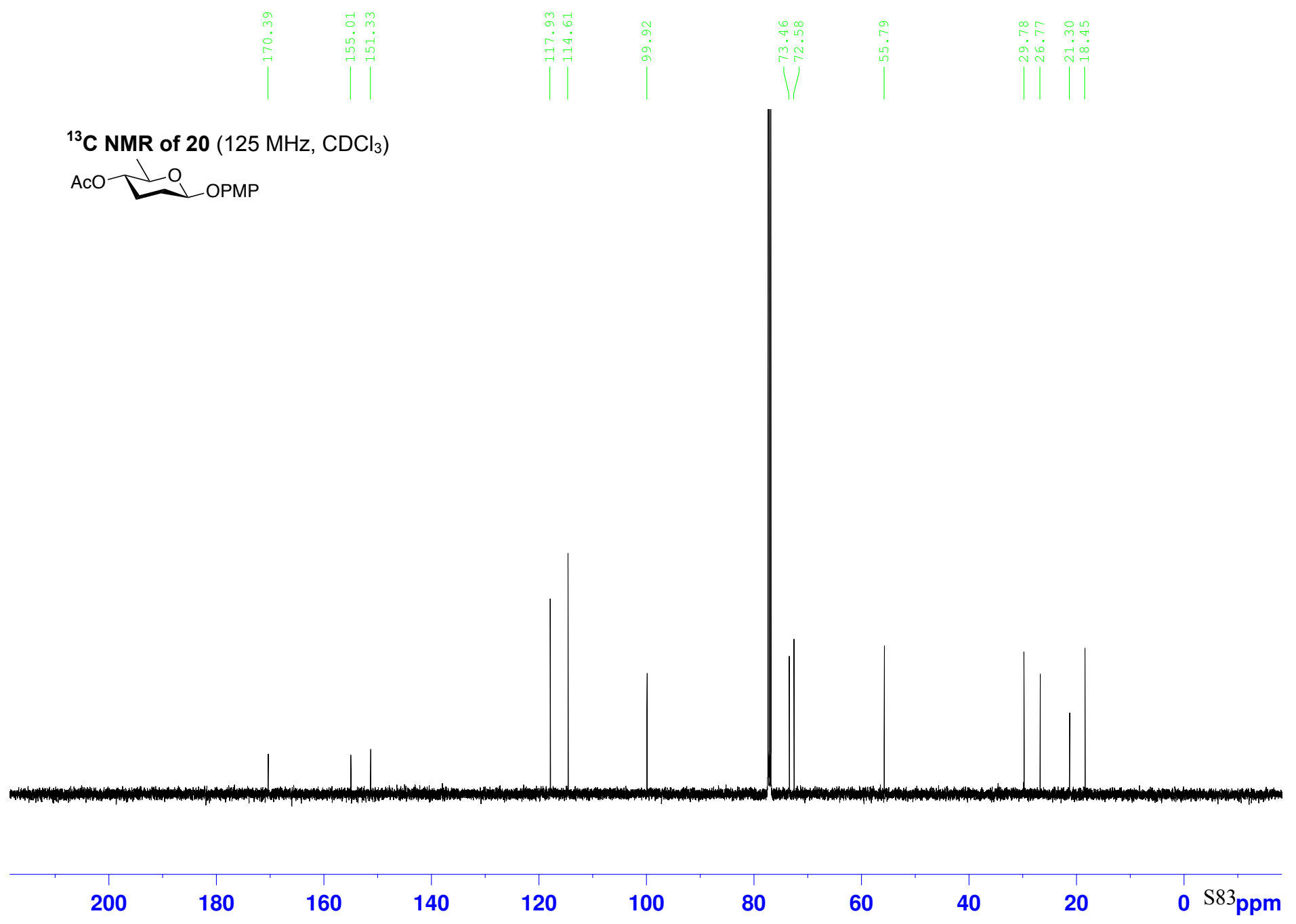
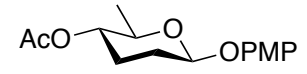
4.08
3.02
2.01
2.01
1.00
1.03
1.03
1.00
3.04
1.00
1.01
2.12
1.06
3.15

¹³C NMR of 19a (125 MHz, CDCl₃)

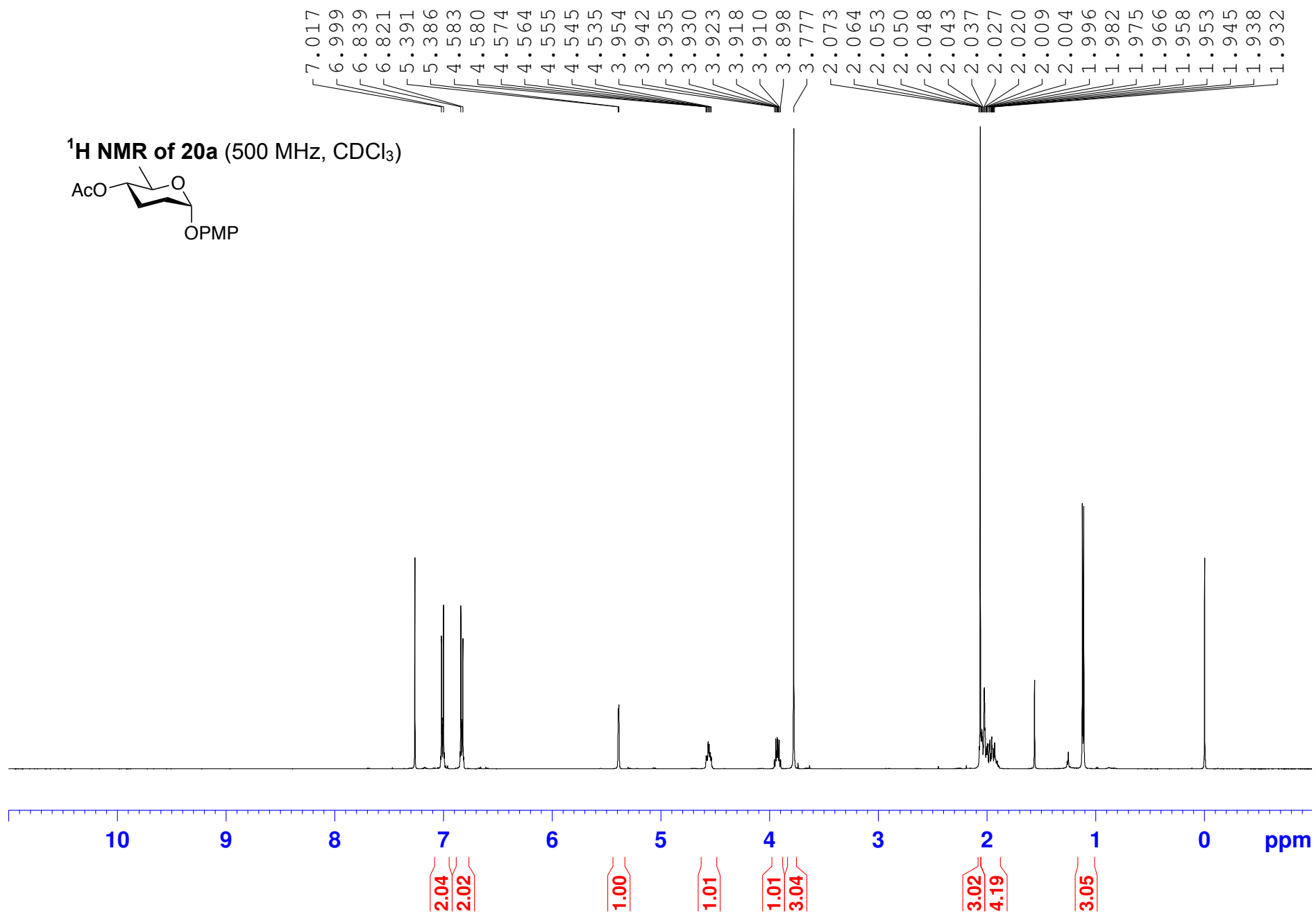
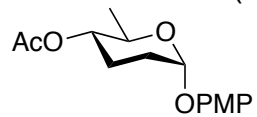




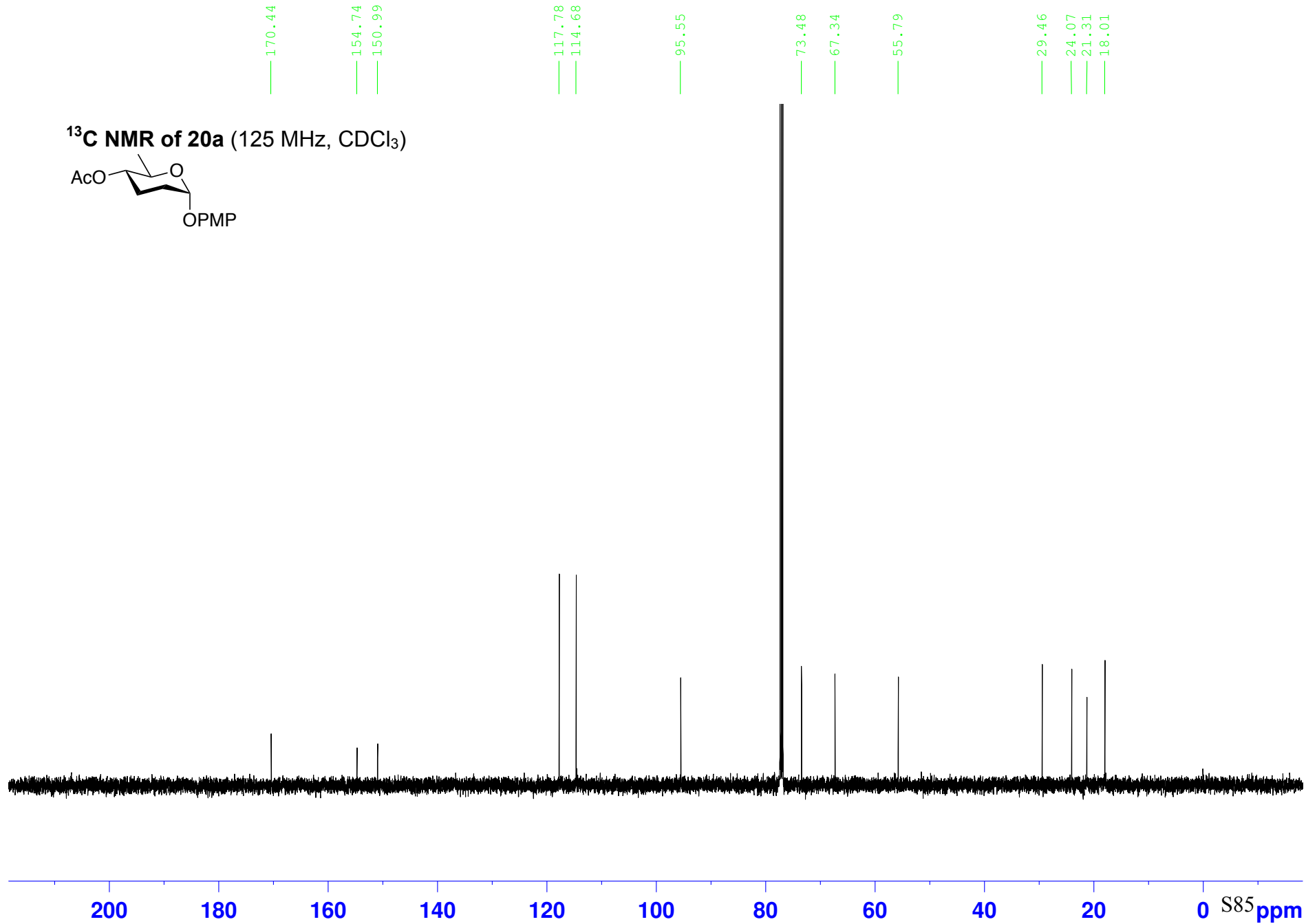
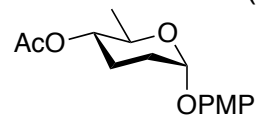
¹³C NMR of 20 (125 MHz, CDCl₃)



¹H NMR of 20a (500 MHz, CDCl₃)

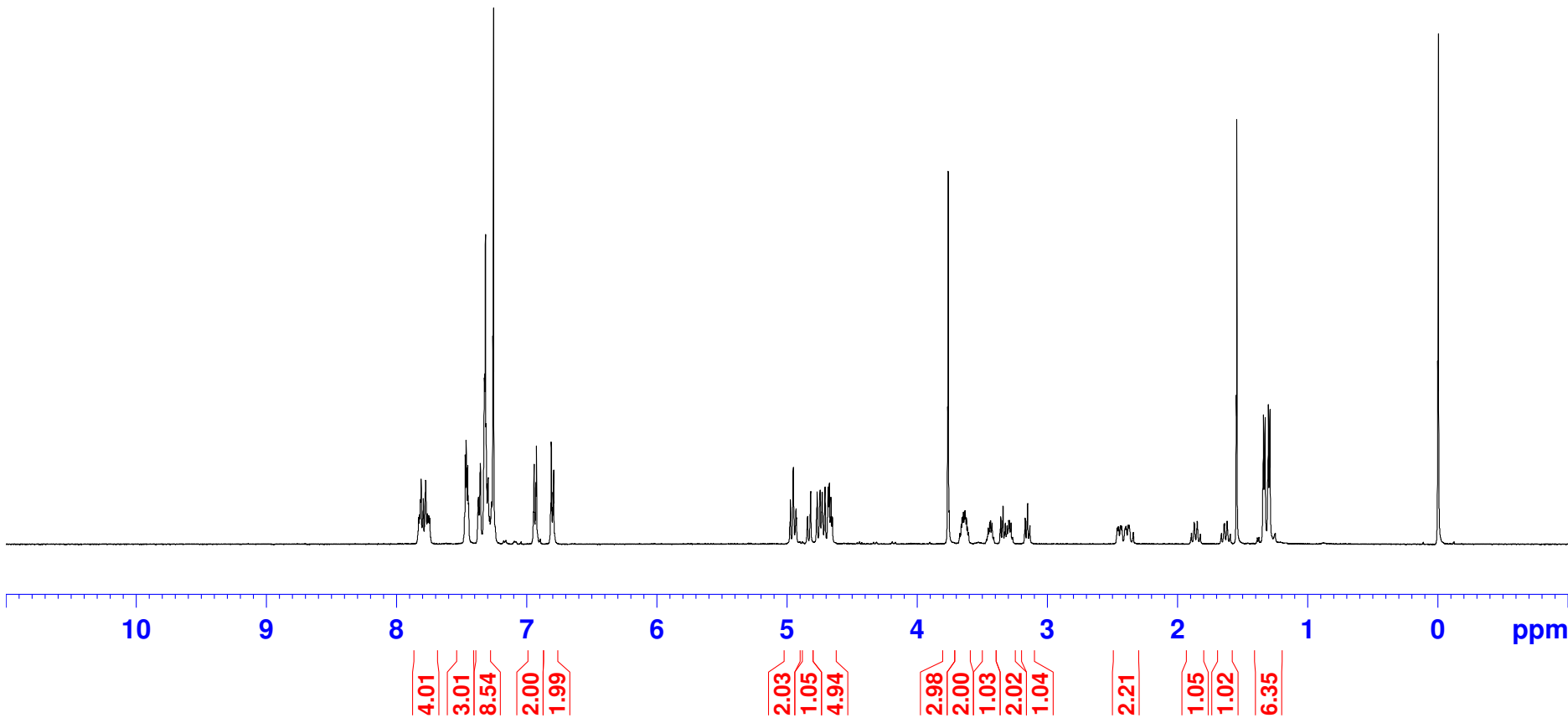
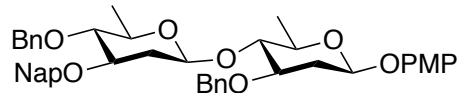


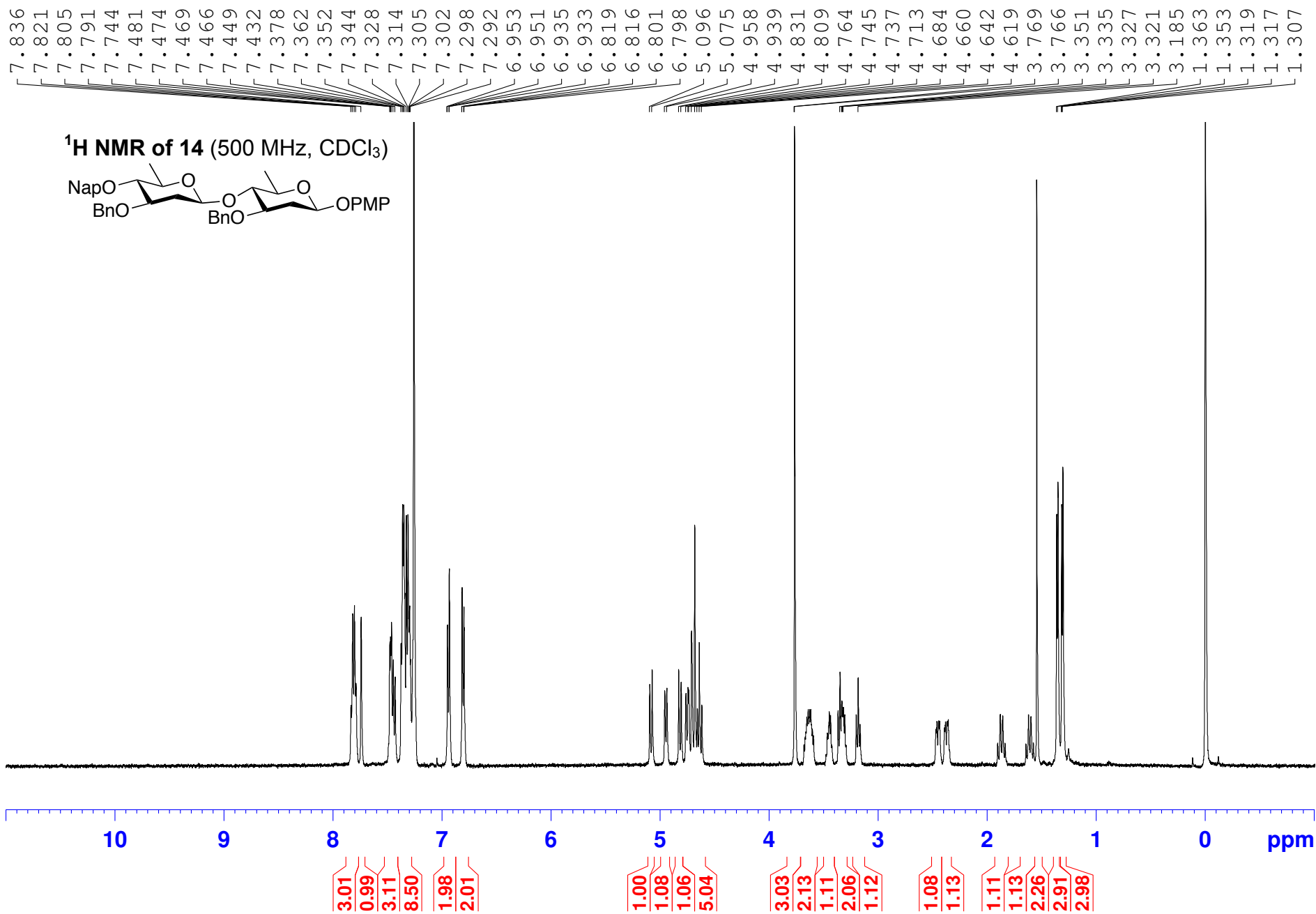
¹³C NMR of 20a (125 MHz, CDCl₃)



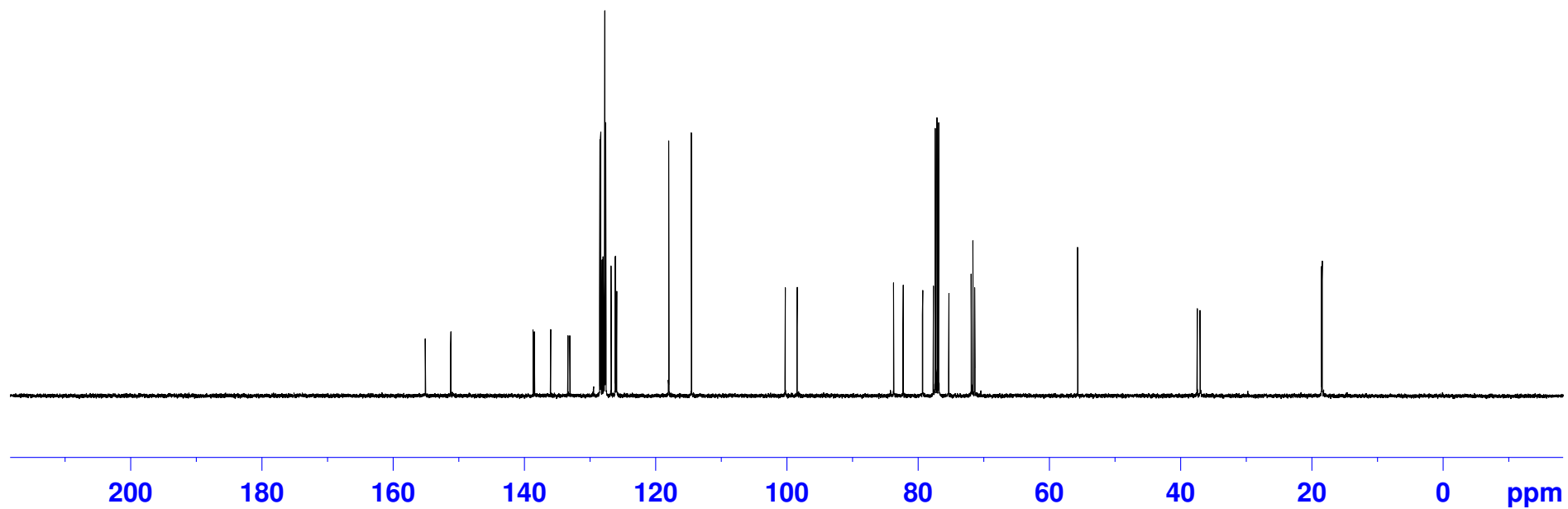
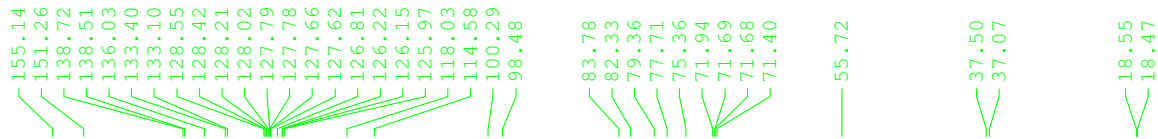
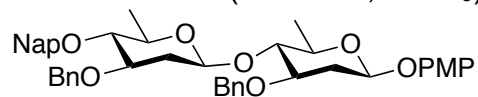
7.819
7.813
7.796
7.778
7.473
7.467
7.461
7.455
7.451
7.447
7.375
7.372
7.358
7.327
7.324
7.319
7.314
7.303
7.298
7.271
7.262
7.257
6.945
6.941
6.932
6.927
6.813
6.808
6.799
6.795
4.976
4.954
4.933
4.820
4.771
4.747
4.731
4.709
4.686
4.677
4.664
3.768
3.763
3.756
3.647
3.640
3.634
3.343
3.154
1.551
1.546
1.341
1.329
1.304
1.292

¹H NMR of 5 (500 MHz, CDCl₃)



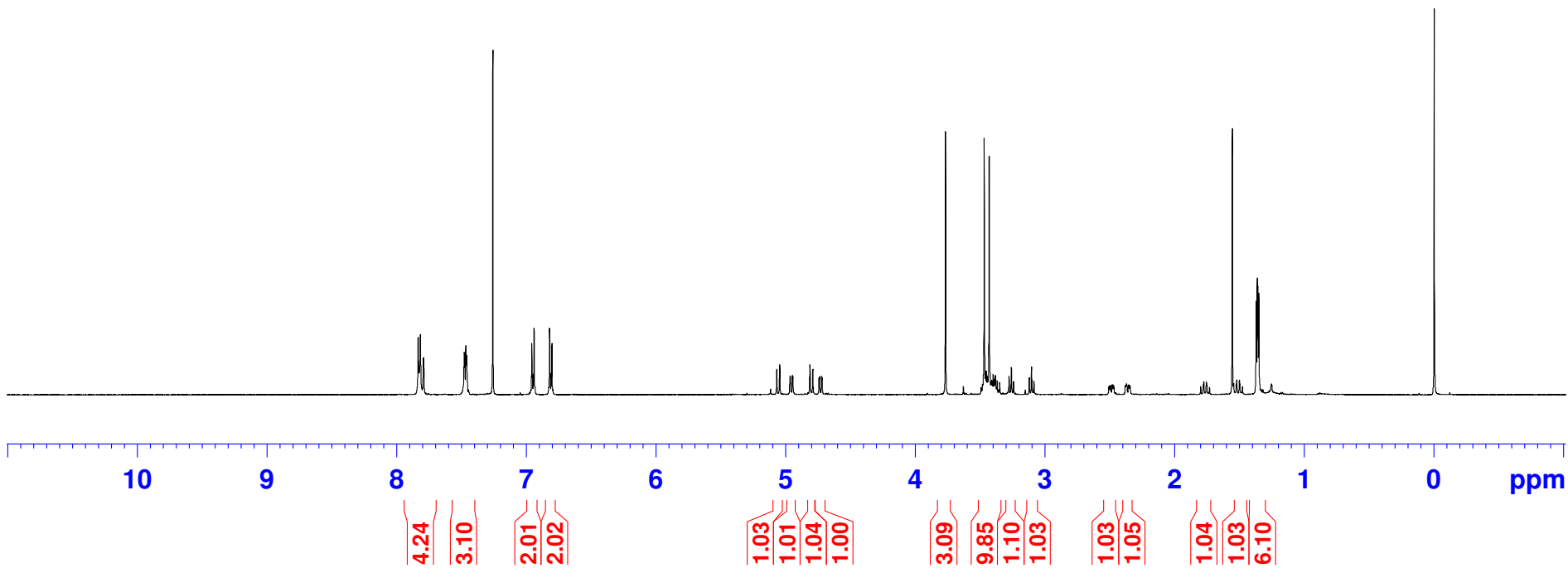
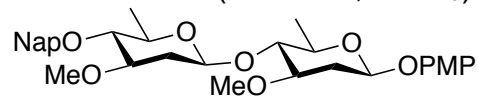


¹³C NMR of 14 (125 MHz, CDCl₃)

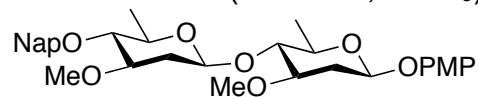


7.836
7.827
7.819
7.795
7.480
7.476
7.468
7.462
7.458
6.960
6.956
6.947
6.942
6.823
6.818
6.809
6.805
5.070
5.048
4.969
4.965
4.950
4.946
4.815
4.792
4.744
4.741
4.725
4.721
3.769
3.470
3.460
3.454
3.449
3.443
3.432
3.418
3.412
3.408
3.402
3.395
3.389
3.383
3.370
3.279
3.261
3.123
3.105
3.087
1.522
1.502
1.372
1.364
1.360
1.352

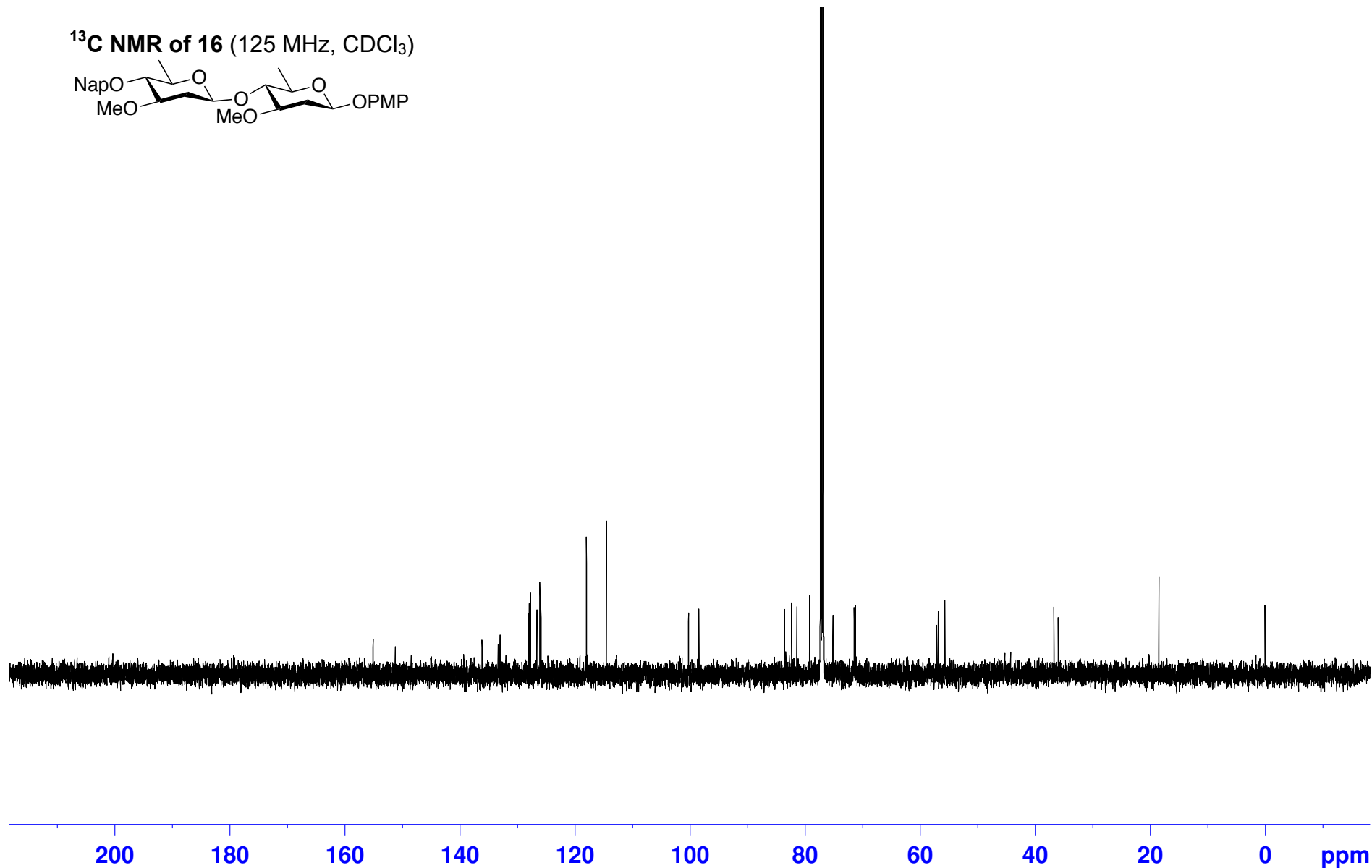
¹H NMR of 16 (500 MHz, CDCl₃)



¹³C NMR of 16 (125 MHz, CDCl₃)

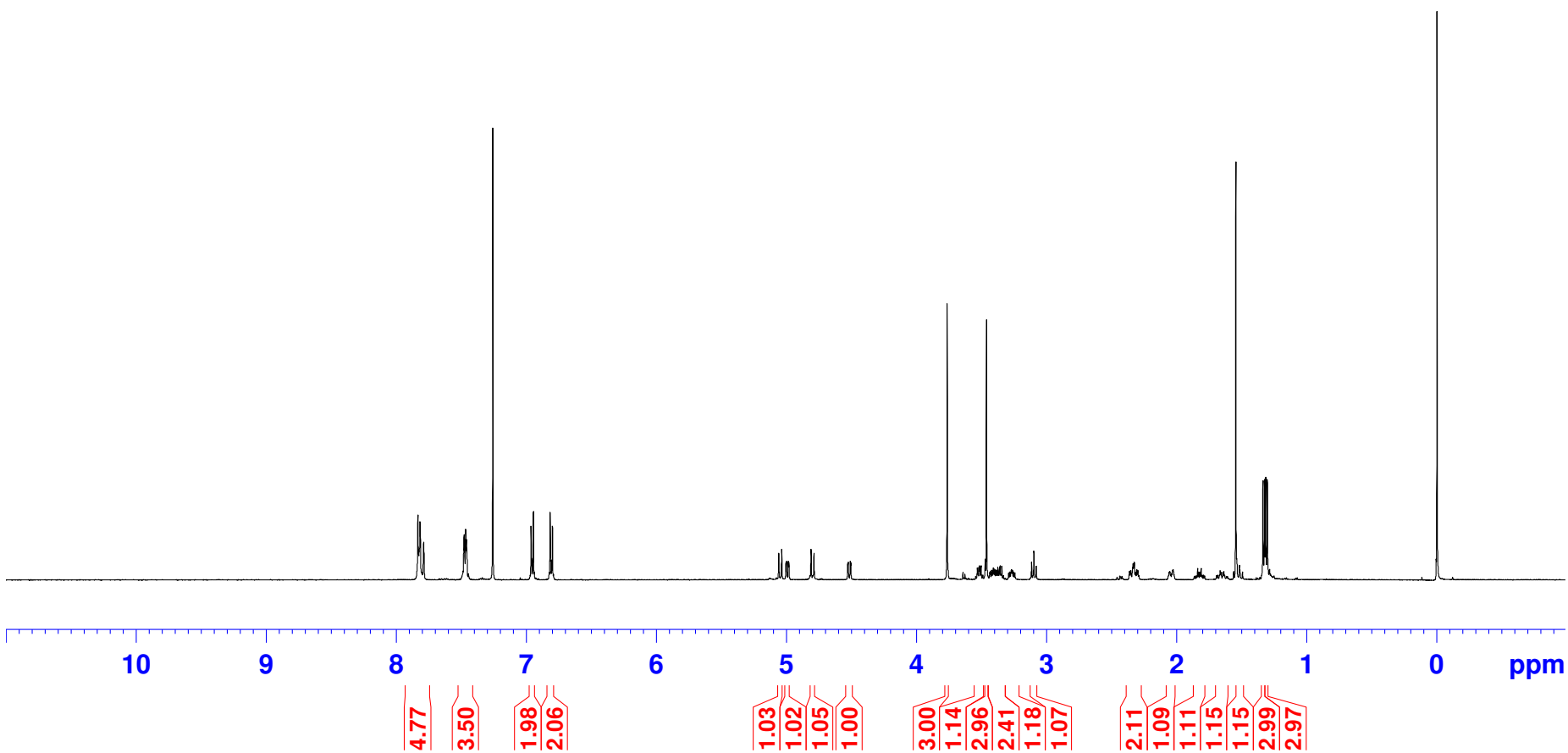
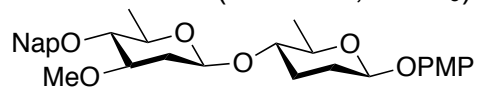


- 155.15
- 151.29
- 136.20
- 133.42
- 133.08
- 128.19
- 128.02
- 127.78
- 126.68
- 126.17
- 126.15
- 125.95
- 118.06
- 114.59
- 100.31
- 98.54
- 83.63
- 82.38
- 81.47
- 79.26
- 75.21
- 71.51
- 71.30
- 57.15
- 56.90
- 55.75
- 36.80
- 36.06
- 18.53

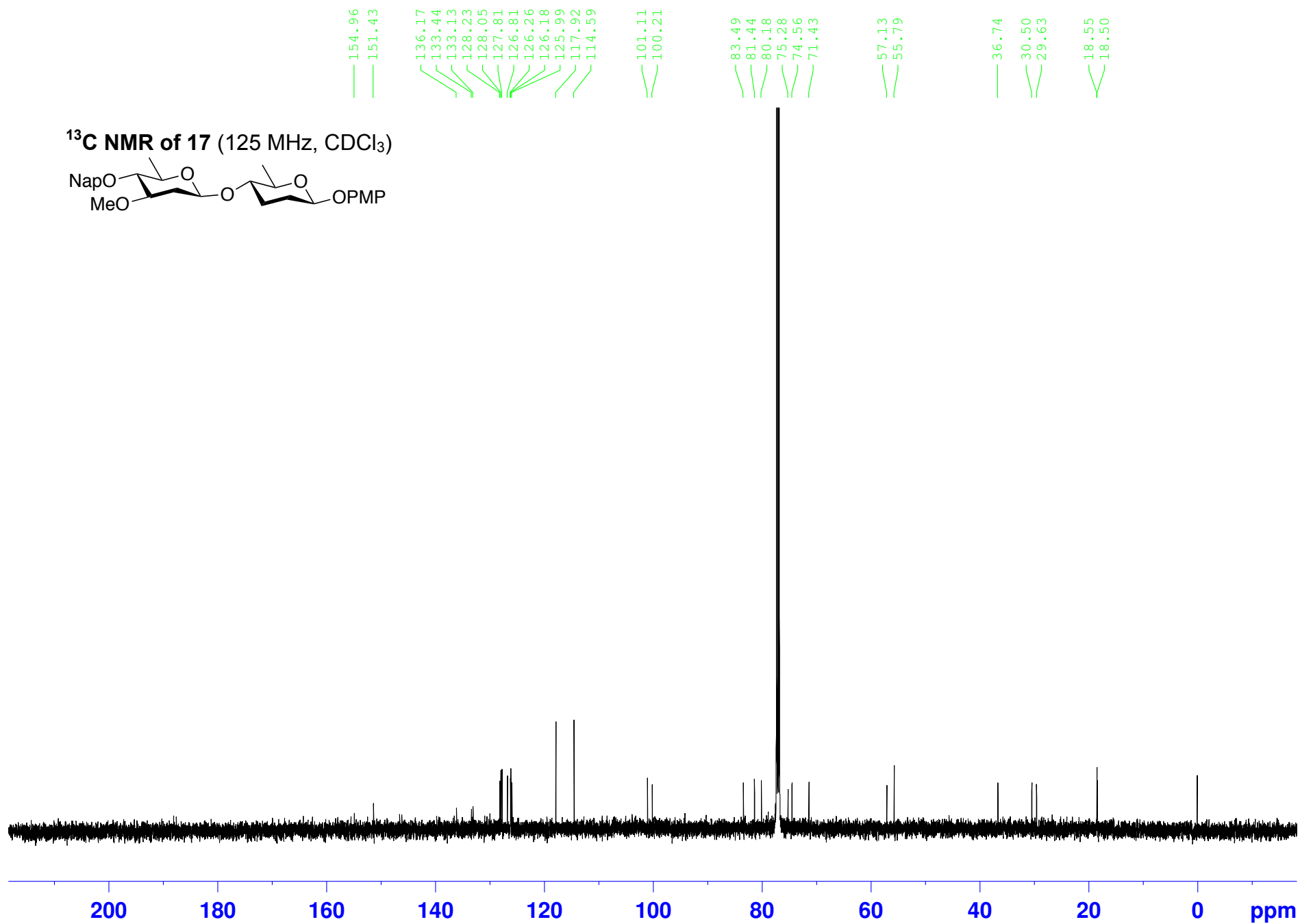
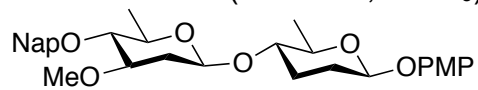


7.836
7.820
7.791
7.481
7.476
7.468
7.462
7.458
6.966
6.961
6.952
6.948
6.819
6.815
6.806
6.801
5.061
5.039
5.006
5.002
4.988
4.983
4.813
4.790
4.530
4.527
4.511
4.507
3.766
3.535
3.522
3.517
3.505
3.473
3.464
3.411
3.407
3.377
3.364
3.358
3.346
3.117
3.099
3.082
2.341
2.336
2.327
1.840
1.813
1.539
1.519
1.338
1.326
1.317
1.305

¹H NMR of 17 (500 MHz, CDCl₃)

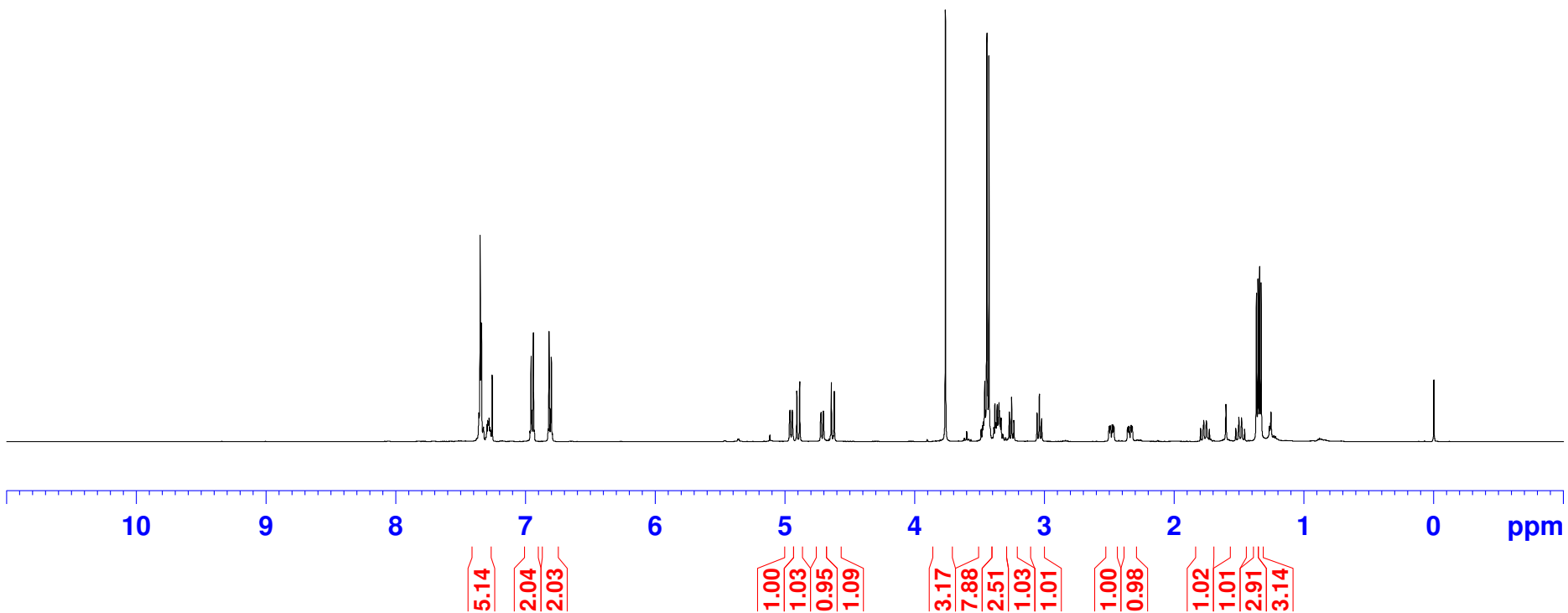
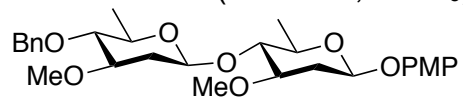


¹³C NMR of 17 (125 MHz, CDCl₃)

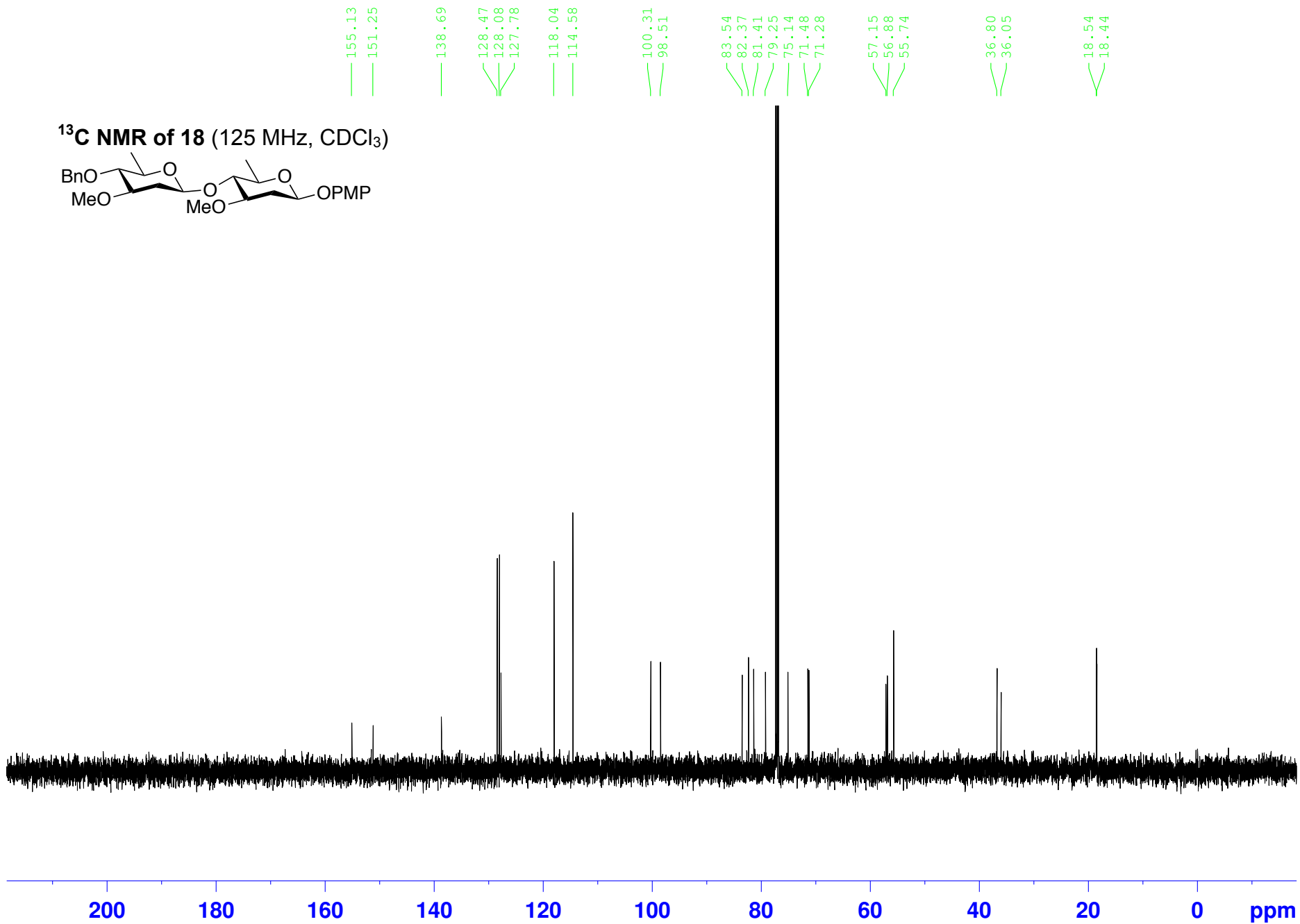
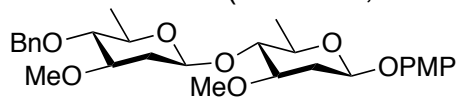


7.361
7.352
7.345
7.341
7.294
7.287
7.282
6.959
6.955
6.945
6.941
6.821
6.816
6.807
6.803
4.966
4.962
4.947
4.943
4.910
4.888
4.726
4.723
4.707
4.703
4.644
4.622
3.765
3.473
3.462
3.456
3.446
3.439
3.430
3.384
3.366
3.359
3.352
3.348
3.342
3.335
3.273
3.255
3.237
3.059
3.041
3.023
1.774
1.754
1.503
1.483
1.368
1.355
1.343
1.331

¹H NMR of 18 (500 MHz, CDCl₃)

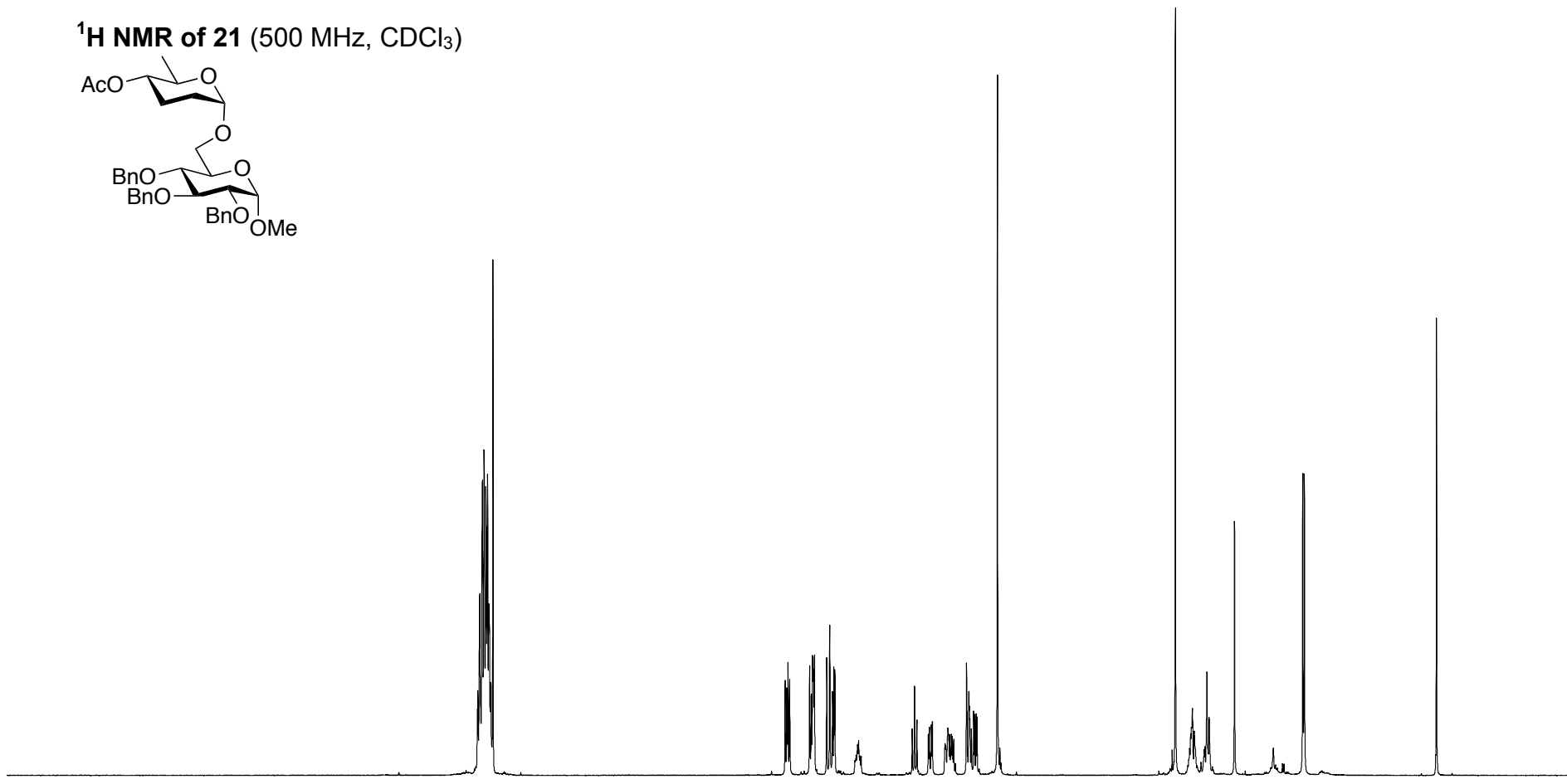
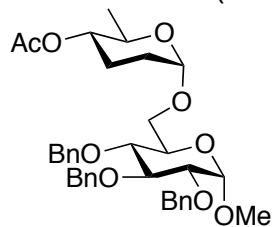


^{13}C NMR of 18 (125 MHz, CDCl_3)



7.375
7.360
7.342
7.340
7.328
7.325
7.319
7.313
7.309
7.300
7.290
7.287
7.275
5.013
5.001
4.992
4.978
4.825
4.812
4.803
4.795
4.788
4.693
4.670
4.649
4.638
4.631
4.036
4.017
3.999
3.903
3.888
3.880
3.762
3.758
3.618
3.614
3.599
3.595
3.591
3.580
3.563
3.556
3.543
3.536
3.379
2.010
1.892
1.887
1.878
1.865
1.767
1.750
1.029
1.017

¹H NMR of 21 (500 MHz, CDCl₃)



10 9 8 7 6 5 4 3 2 1 0 ppm

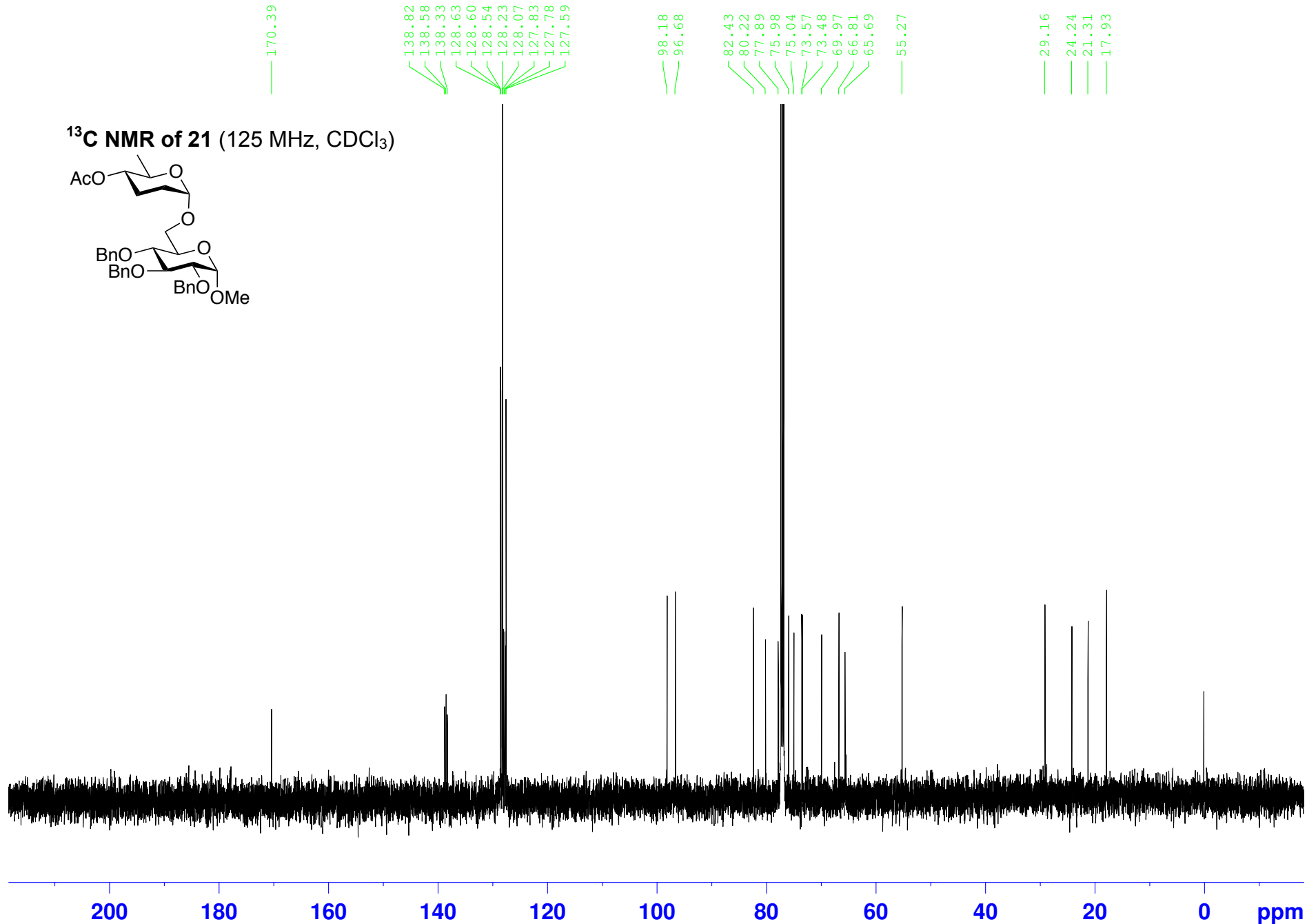
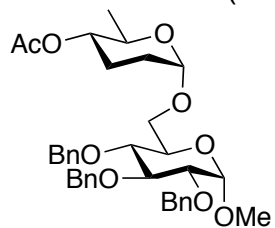
15.45

1.99
2.96
1.47
1.35
0.99
1.02
1.00
2.00
1.89
1.02
3.05

3.06
1.92
2.09

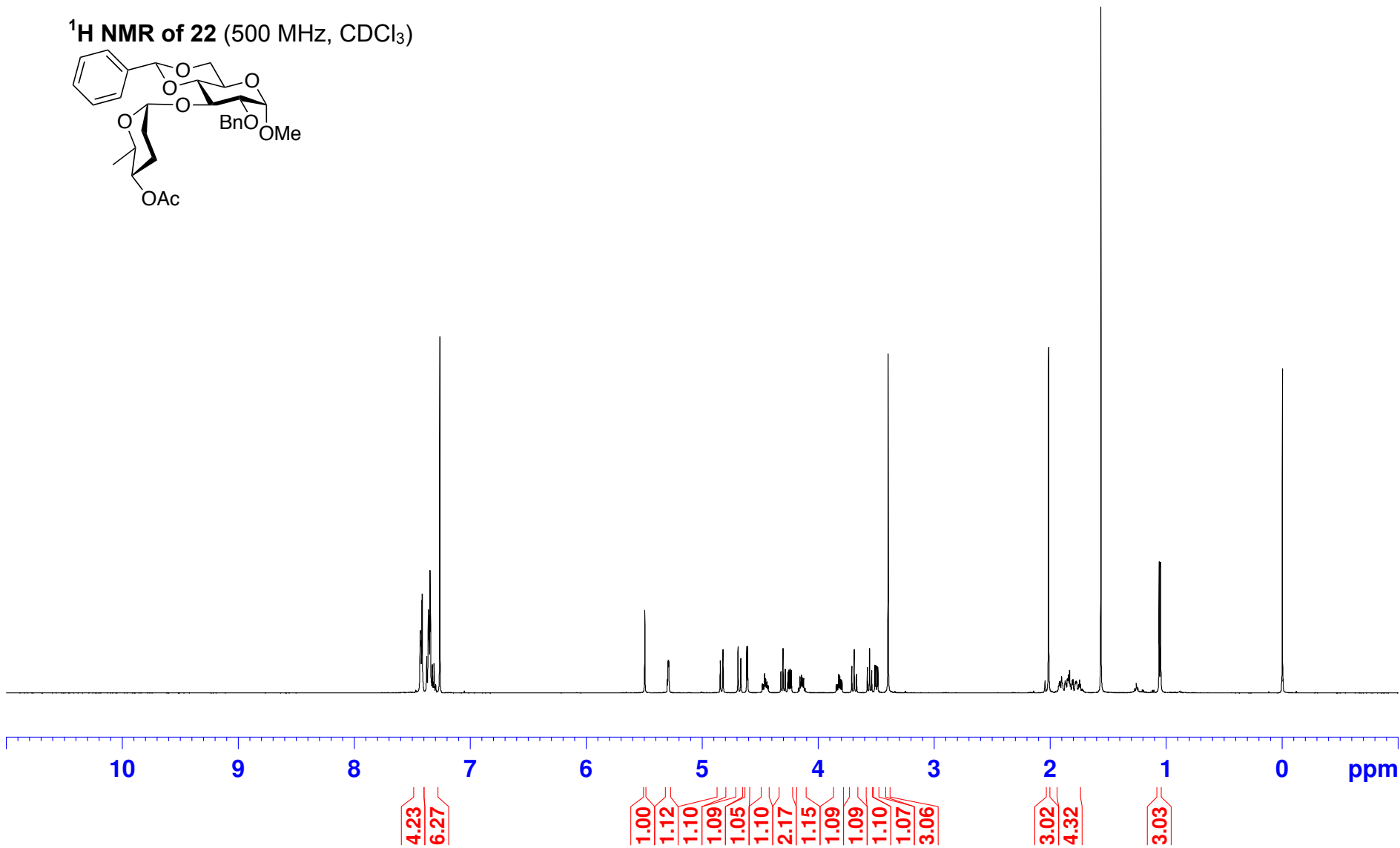
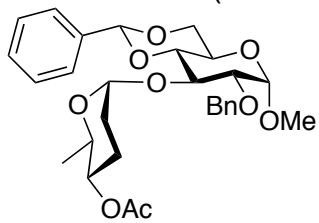
2.89

¹³C NMR of 21 (125 MHz, CDCl₃)

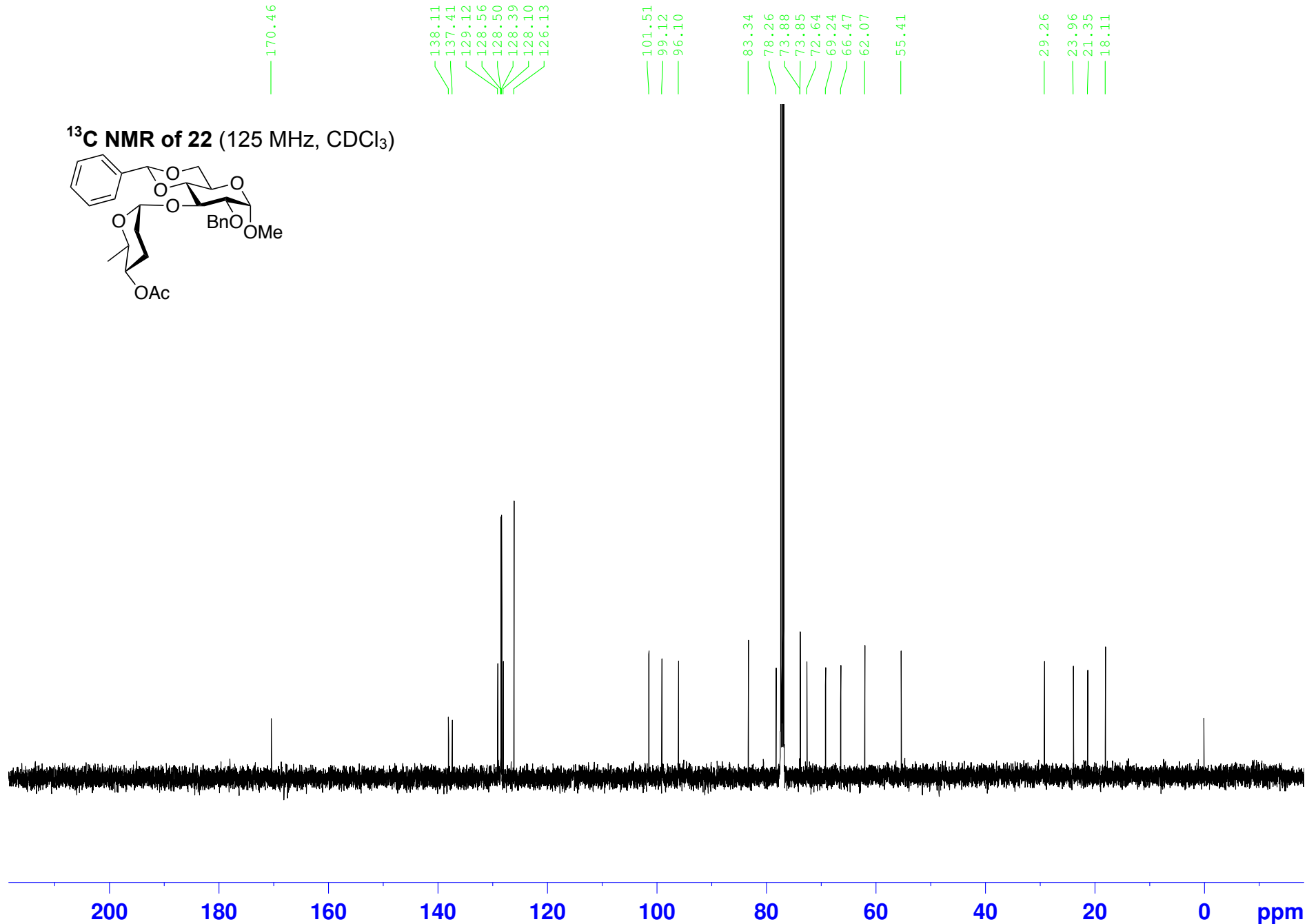
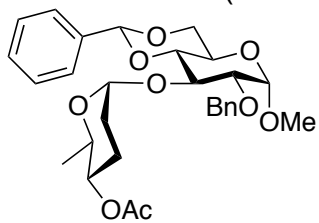


7.431
7.428
7.424
7.415
7.413
7.376
7.374
7.370
7.360
7.356
7.352
7.345
7.341
7.325
7.322
7.311
5.494
5.293
5.287
4.843
4.819
4.690
4.666
4.614
4.607
4.460
4.320
4.301
4.282
4.260
4.250
4.239
4.230
4.156
4.143
4.136
3.822
3.813
3.708
3.688
3.667
3.574
3.556
3.537
3.511
3.503
3.492
3.484
3.396
2.016
1.905
1.843
1.834
1.062
1.050

¹H NMR of 22 (500 MHz, CDCl₃)

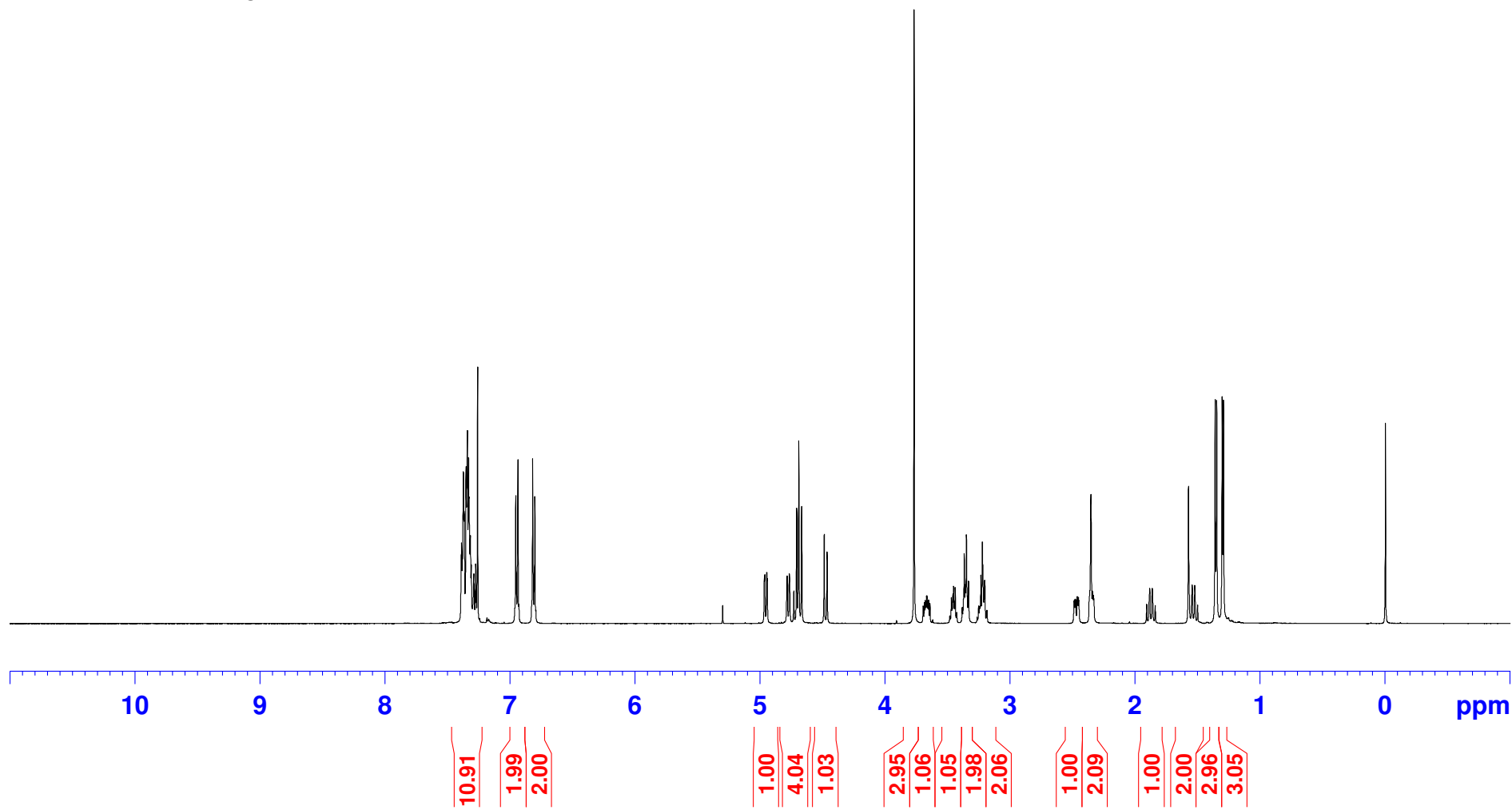
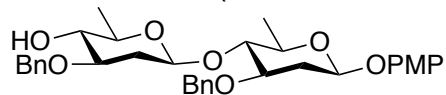


¹³C NMR of 22 (125 MHz, CDCl₃)

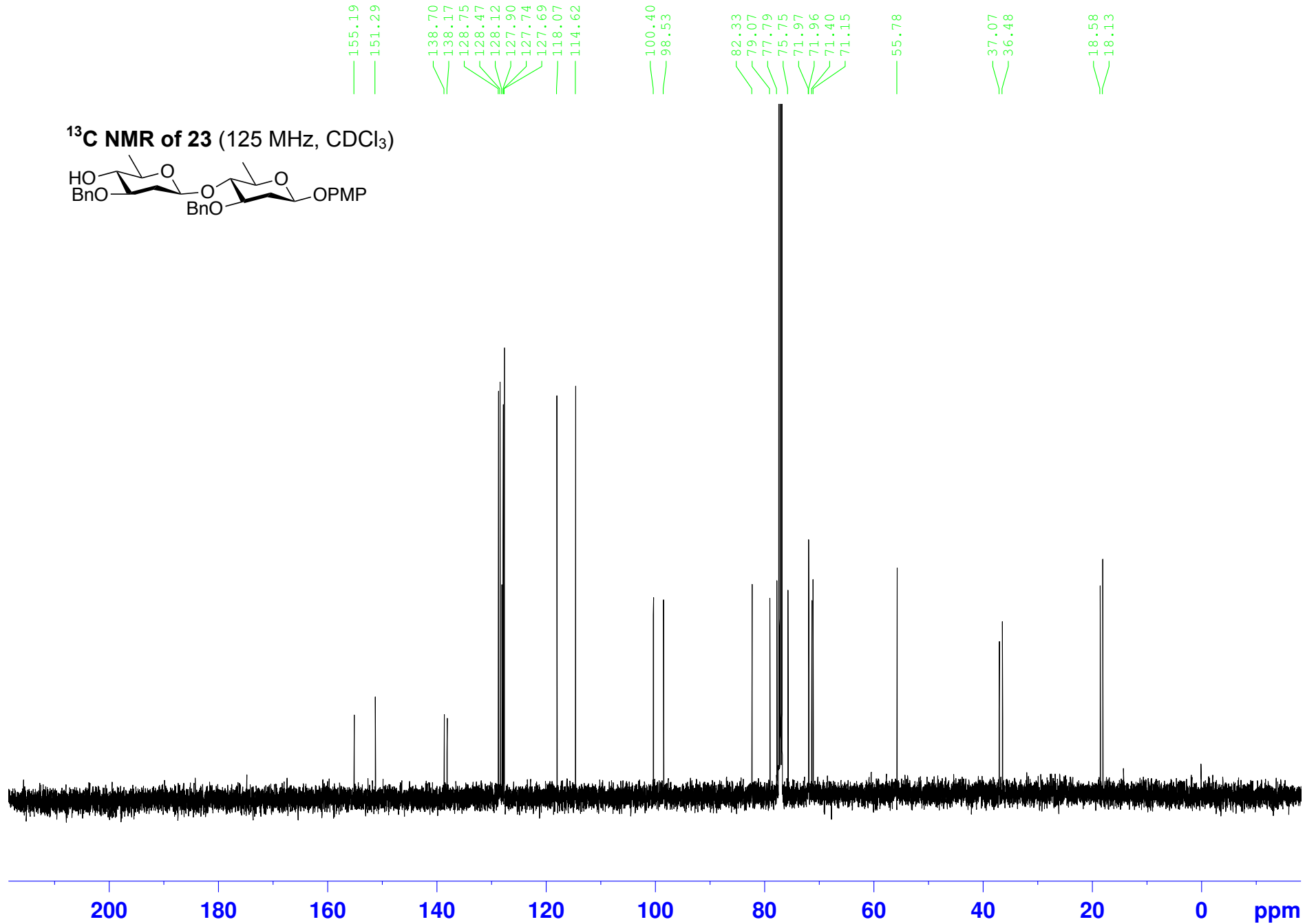
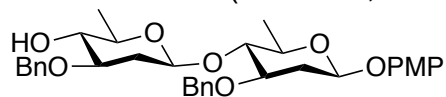


7.386
7.382
7.372
7.365
7.350
7.338
7.330
7.326
7.315
7.308
7.287
7.273
7.258
6.952
6.948
6.934
6.817
6.799
4.963
4.960
4.944
4.941
4.784
4.780
4.764
4.761
4.728
4.705
4.688
4.665
4.484
4.461
3.765
3.459
3.453
3.440
3.368
3.359
3.350
3.333
3.235
3.223
3.206
3.204
2.354
2.343
2.339
1.884
1.863
1.544
1.524
1.360
1.348
1.304
1.293

¹H NMR of 23 (500 MHz, CDCl₃)

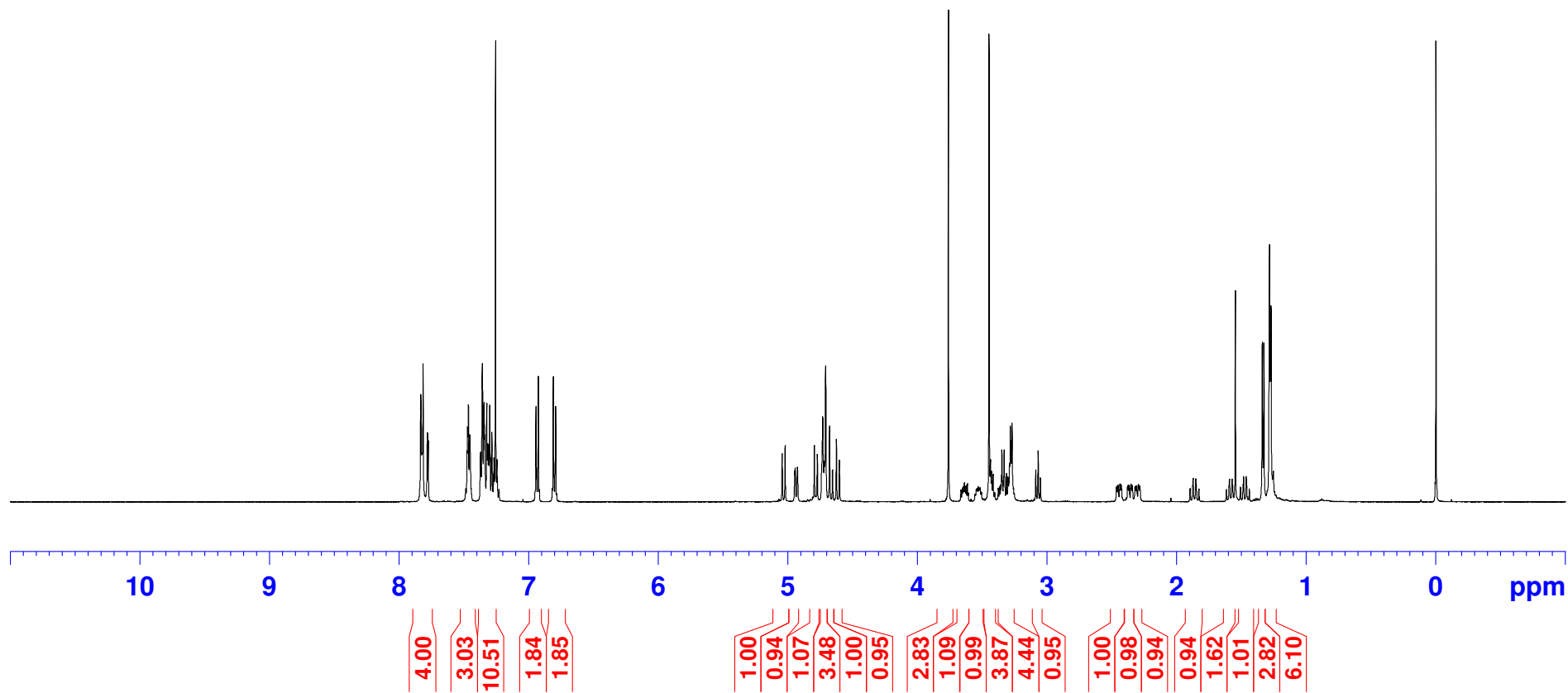
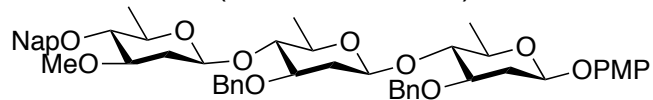


¹³C NMR of 23 (125 MHz, CDCl₃)



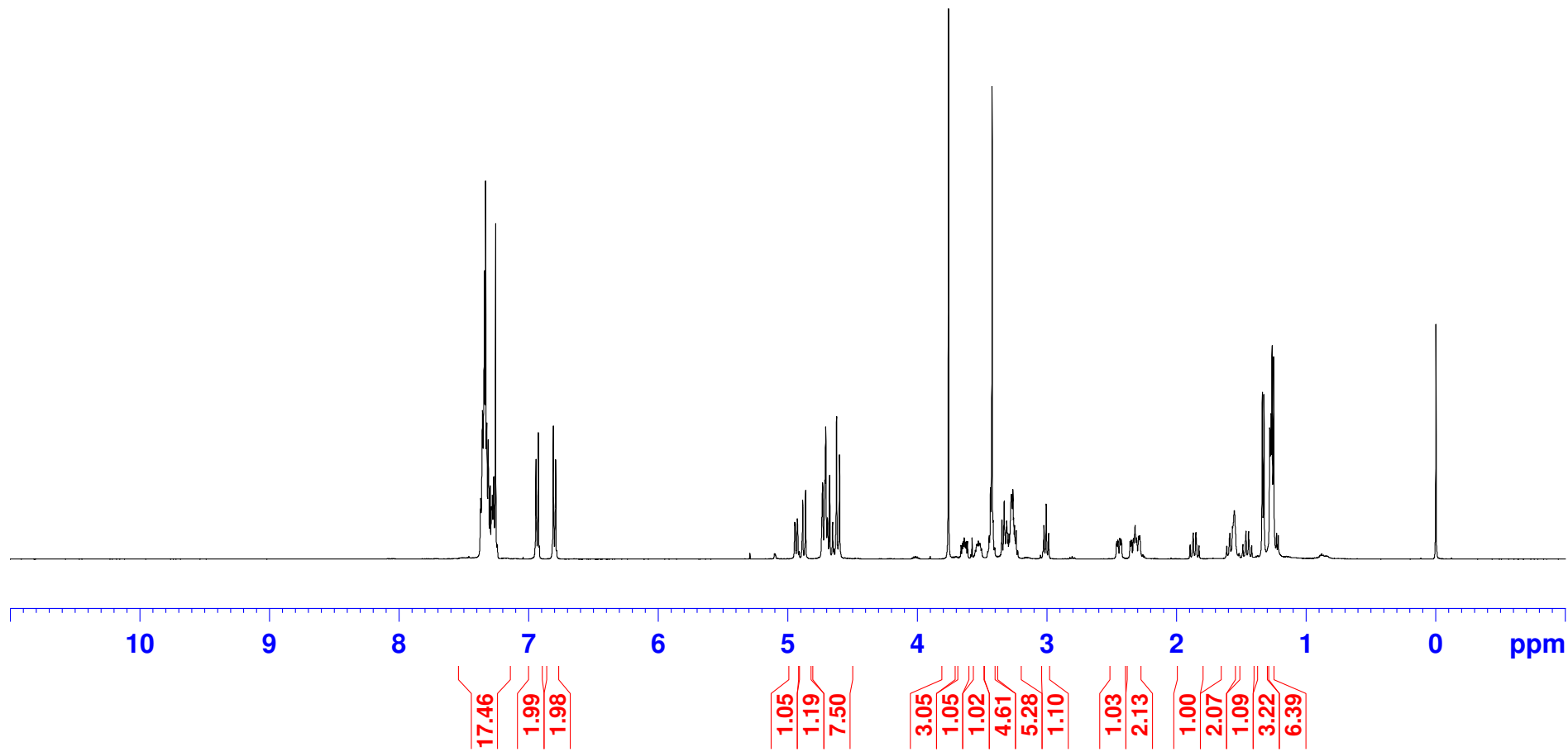
7.831
7.822
7.814
7.780
7.477
7.474
7.467
7.459
7.455
7.373
7.359
7.346
7.339
7.325
7.316
7.310
7.302
7.287
7.270
7.246
6.945
6.932
6.927
6.812
6.807
6.798
6.794
5.045
5.022
4.945
4.929
4.797
4.774
4.732
4.722
4.718
4.709
4.679
4.627
4.604
3.762
3.449
3.437
3.350
3.332
3.290
3.284
3.281
3.272
3.070
1.340
1.328
1.284
1.276
1.272

¹H NMR of 24 (500 MHz, CDCl₃)



7.371
7.358
7.343
7.334
7.328
7.324
7.314
7.299
7.288
7.283
7.281
7.271
7.256
6.945
6.927
6.811
6.797
6.793
4.948
4.944
4.928
4.925
4.886
4.864
4.733
4.715
4.709
4.696
4.693
4.679
4.656
4.625
4.603
3.761
3.437
3.425
3.417
3.349
3.332
3.313
3.279
3.273
3.265
3.259
3.252
3.025
3.007
2.321
1.569
1.555
1.339
1.327
1.272
1.264
1.252

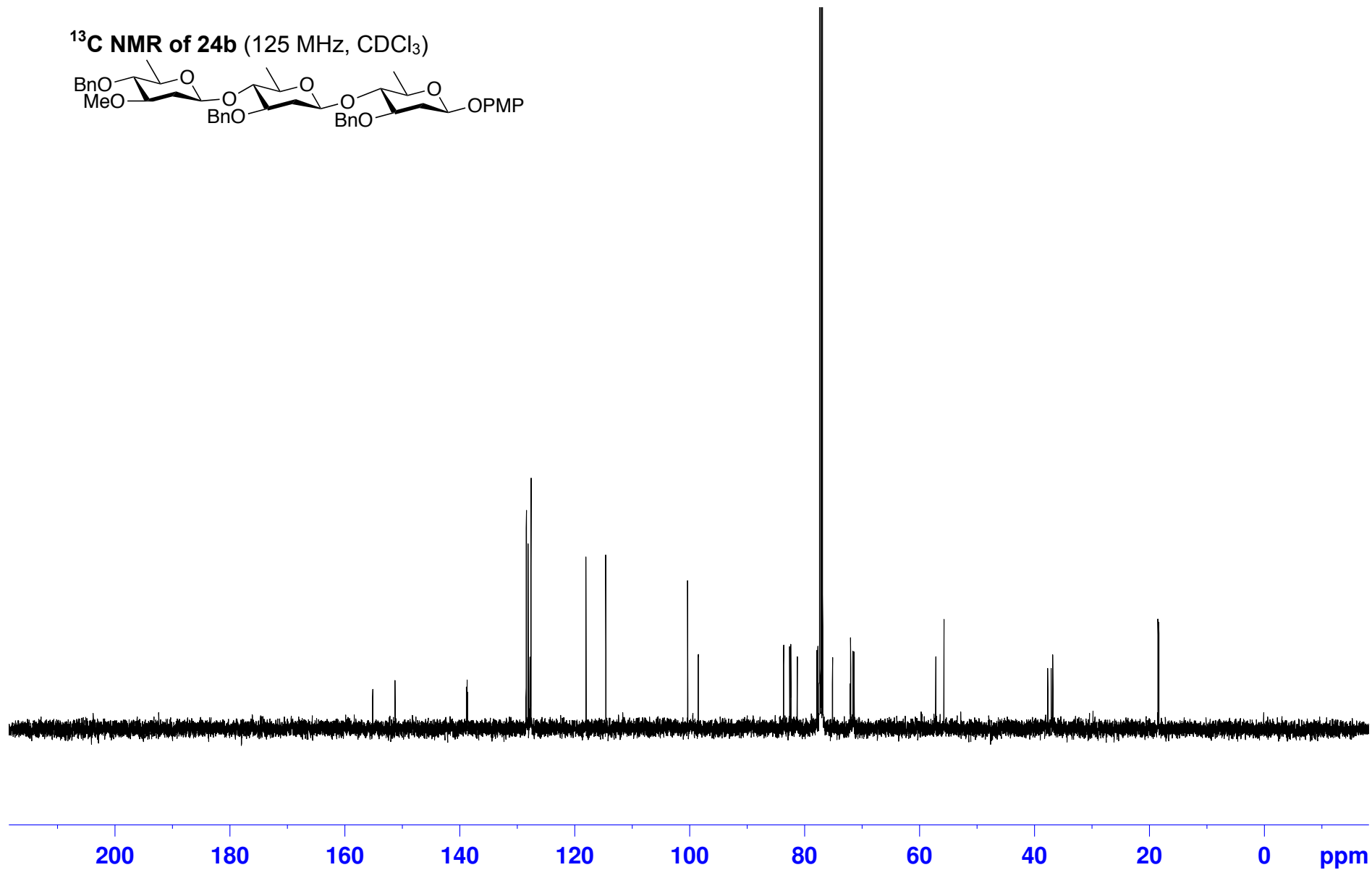
¹H NMR of 24b (500 MHz, CDCl₃)



¹³C NMR of 24b (125 MHz, CDCl₃)

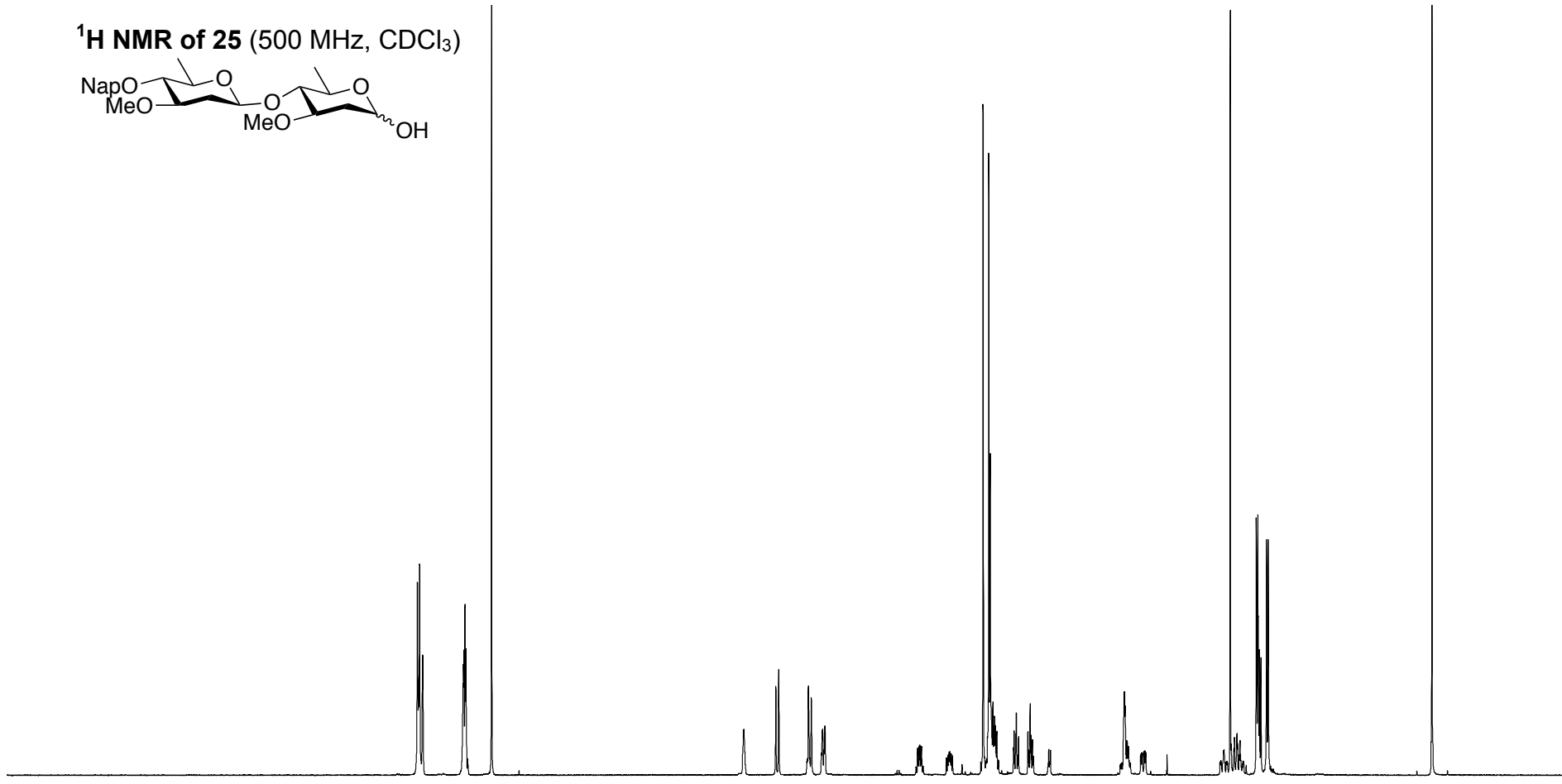
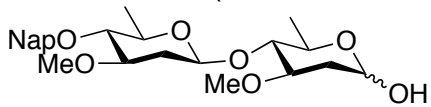


- 155.19
- 151.31
- 138.89
- 138.77
- 138.72
- 128.51
- 128.47
- 128.43
- 128.14
- 127.82
- 127.71
- 127.64
- 127.63
- 118.09
- 114.63
- 100.39
- 98.55
- 83.69
- 82.65
- 82.42
- 81.31
- 77.91
- 77.75
- 75.18
- 72.08
- 72.02
- 71.63
- 71.52
- 71.42
- 57.20
- 55.78
- 37.72
- 37.13
- 36.85
- 18.55
- 18.53
- 18.40



7.833
7.825
7.816
7.792
7.478
7.474
7.466
7.459
7.455
5.315
5.311
5.066
5.043
4.814
4.792
4.707
4.703
4.688
4.684
3.959
3.953
3.466
3.431
3.422
3.410
3.390
3.377
3.371
3.359
3.226
3.209
3.191
3.120
3.102
3.095
3.084
2.378
2.372
2.368
2.357
2.353
2.343
1.549
1.525
1.505
1.500
1.481
1.357
1.353
1.344
1.341
1.333
1.320
1.277
1.265

¹H NMR of 25 (500 MHz, CDCl₃)



10

9

8

7

6

5

4

3

2

1

0

ppm

5.24

3.89

1.00

1.39

1.85

1.40

0.98

0.90

11.29

1.48

1.42

0.50

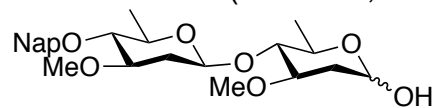
2.68

1.02

5.88

8.24

¹³C NMR of 25 (125 MHz, CDCl₃)

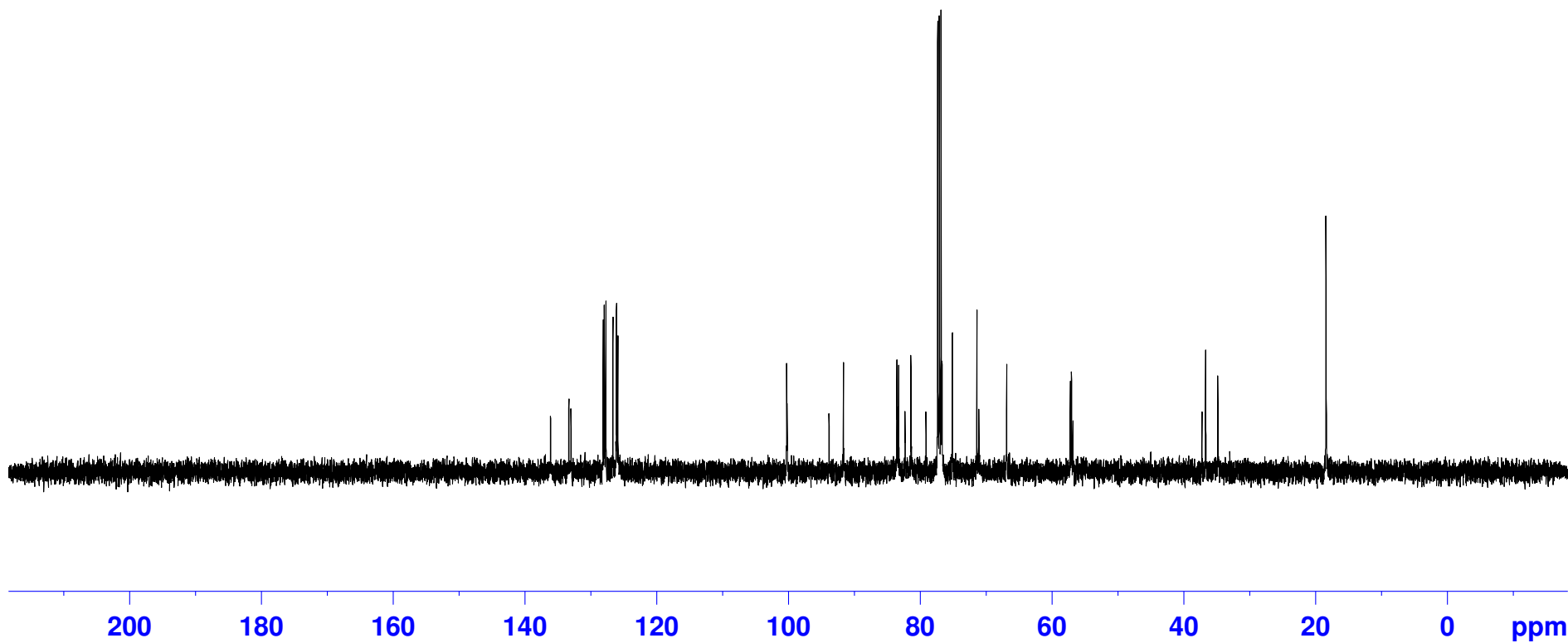


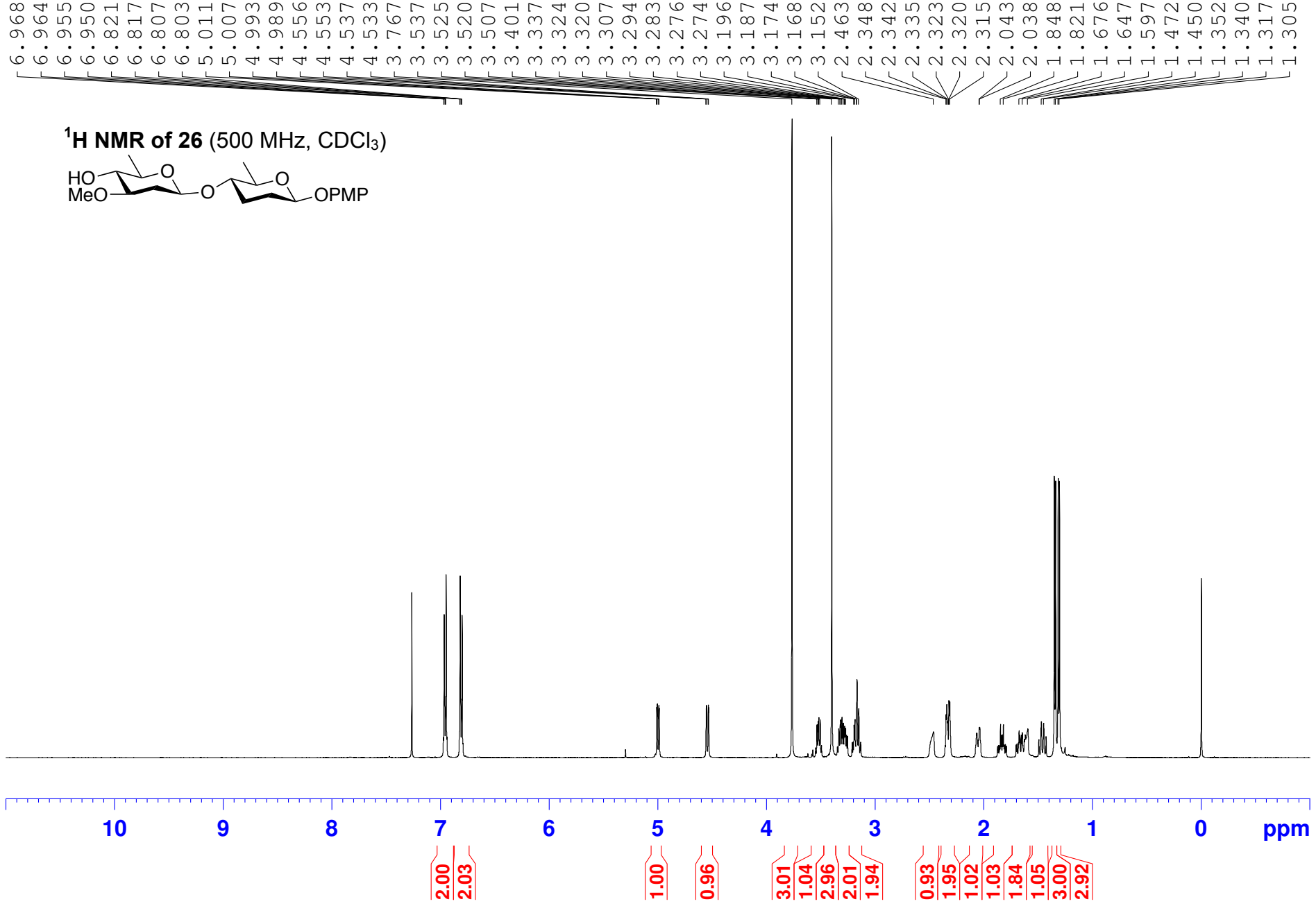
136.15
133.37
133.05
128.16
127.99
127.75
126.69
126.17
126.12
125.92

100.41
93.89
91.69
83.60
83.31
82.35
81.46
79.17
76.73
75.17
71.44
71.15
66.92
57.27
57.08
56.87

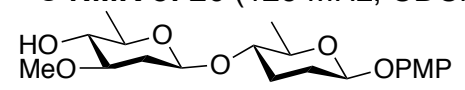
37.28
36.71
34.87

18.47





¹³C NMR of 26 (125 MHz, CDCl₃)



154.93
151.40

117.88
114.57

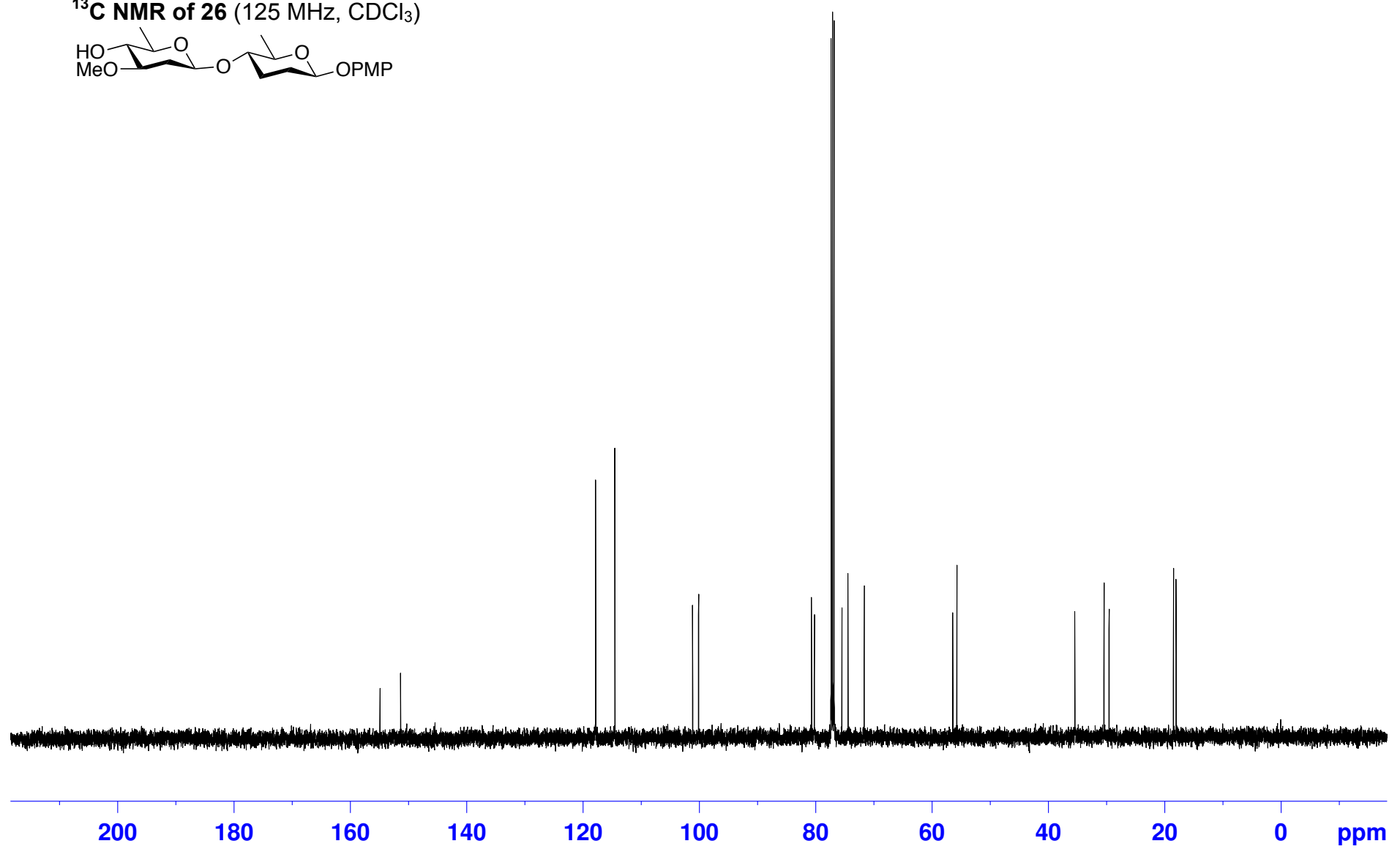
101.19
100.17

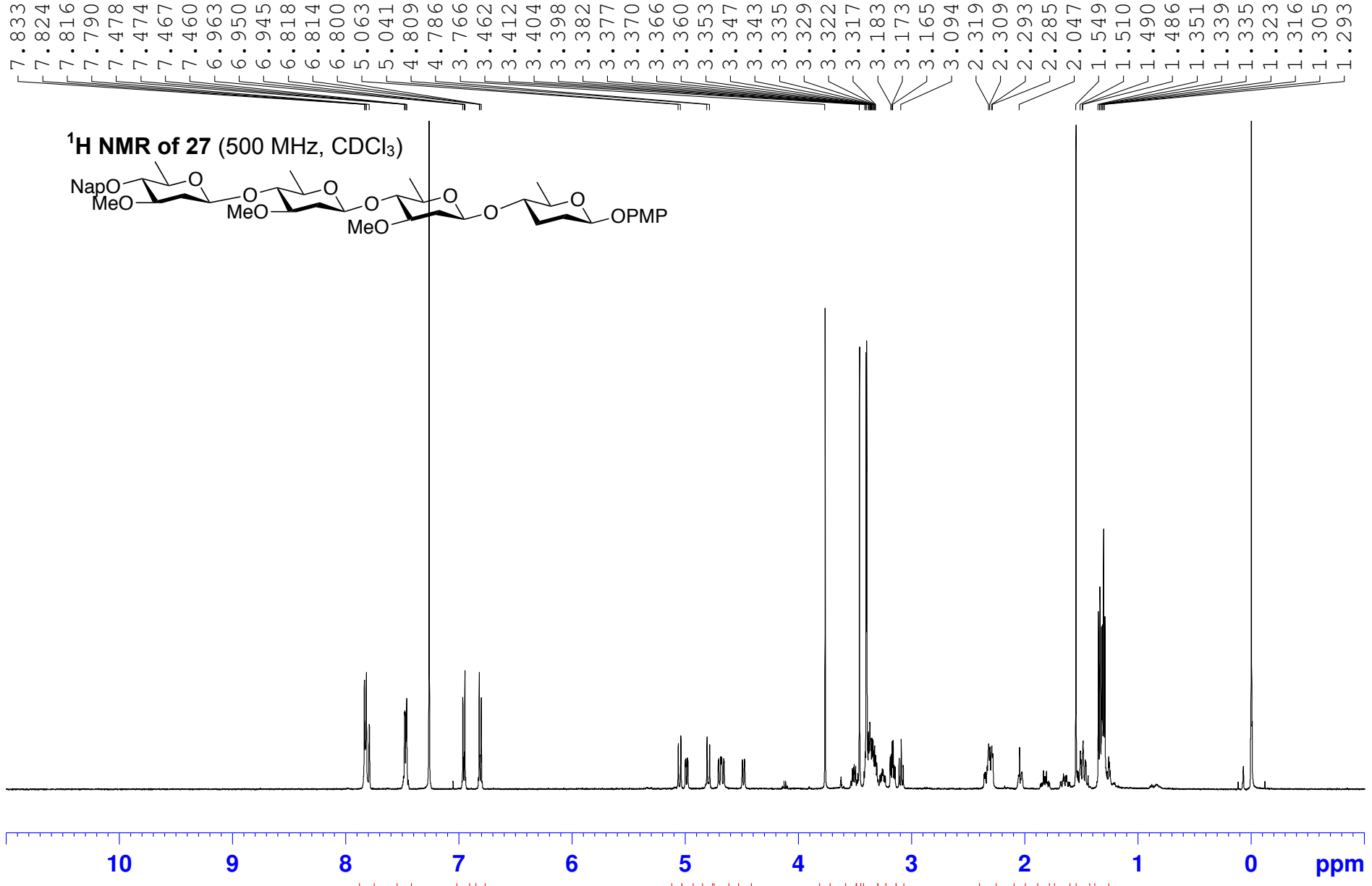
80.76
80.26
75.53
74.50
71.70

56.47
55.77

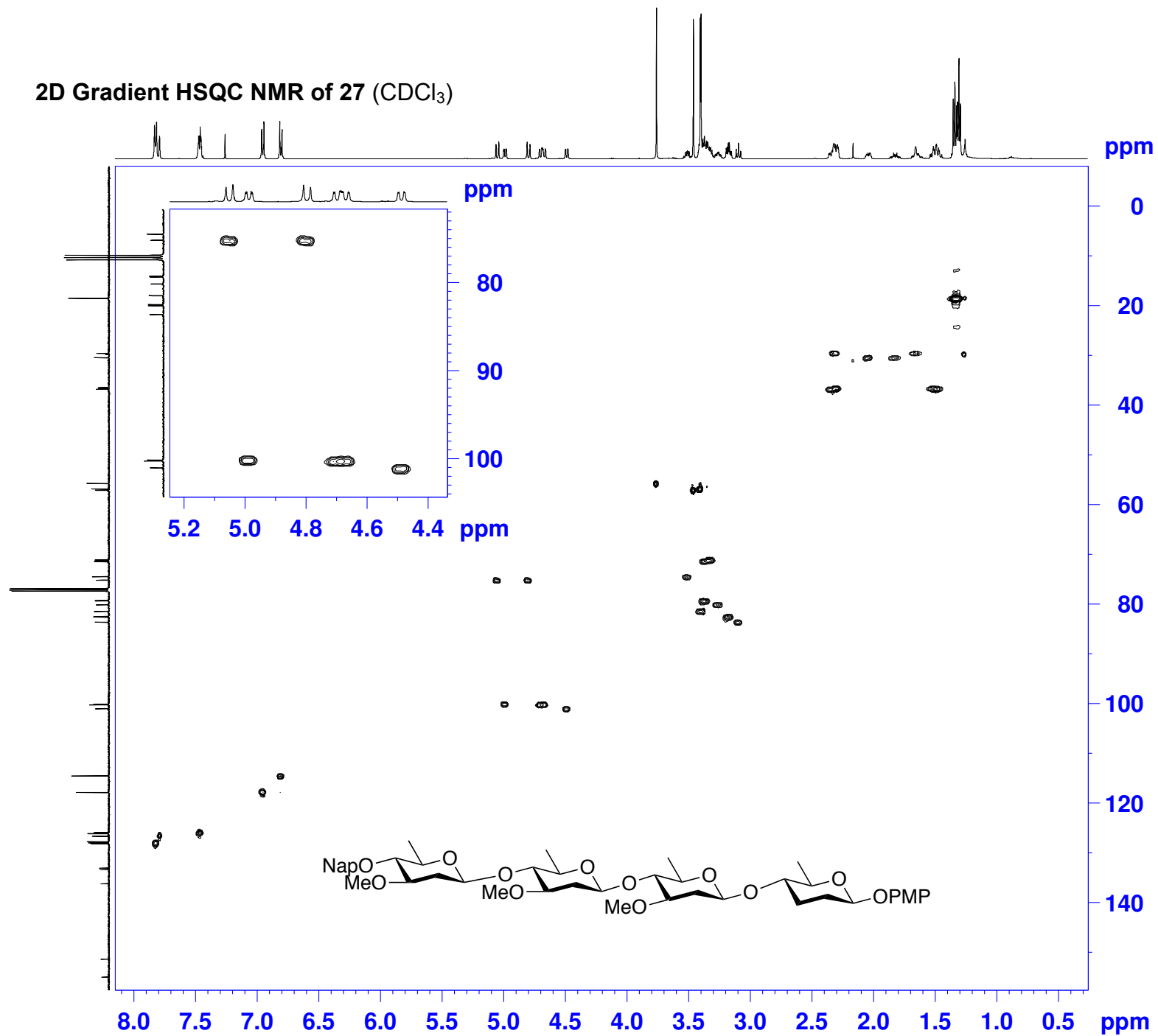
35.50
30.48
29.61

18.54
18.08



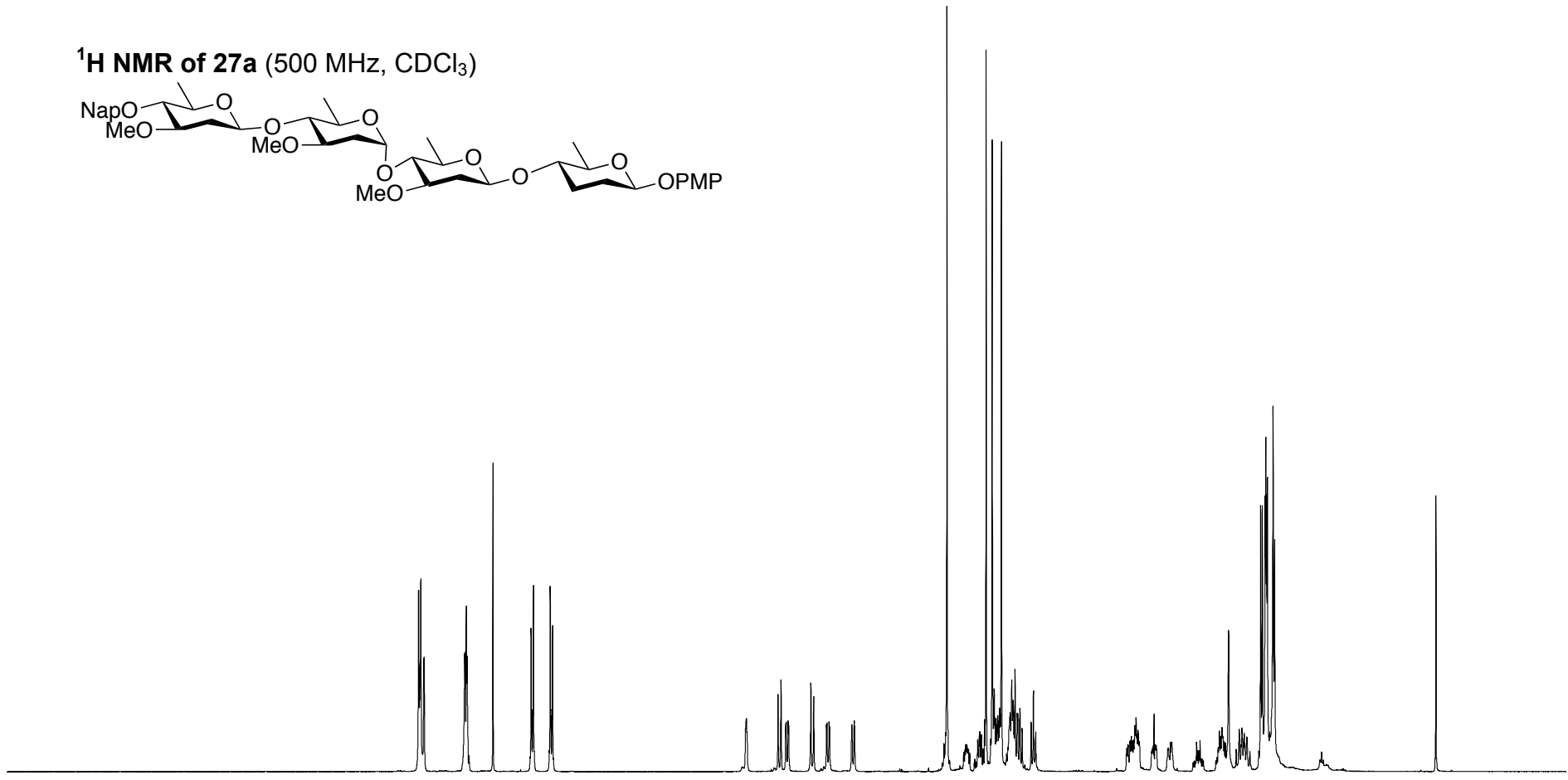
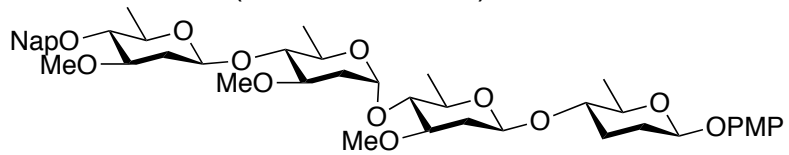


2D Gradient HSQC NMR of 27 (CDCl₃)



7.833
7.824
7.816
7.791
7.478
7.473
7.465
7.458
7.455
6.967
6.962
6.953
6.949
6.819
6.815
6.806
6.801
5.311
5.308
5.065
5.043
4.813
4.790
3.765
3.475
3.463
3.416
3.405
3.401
3.395
3.386
3.373
3.367
3.359
3.355
3.345
3.279
3.265
3.256
3.253
3.240
3.223
3.219
3.204
3.099
2.309
2.170
1.349
1.336
1.314
1.310
1.303
1.297
1.254
1.241

¹H NMR of 27a (500 MHz, CDCl₃)



10

9

8

7

6

5

4

3

2

1

0

ppm

4.56

3.39

2.02

2.02

1.00

1.18

1.04

1.14

1.12

0.99

4.06

1.10

1.08

12.32

5.38

1.28

3.30

1.24

1.11

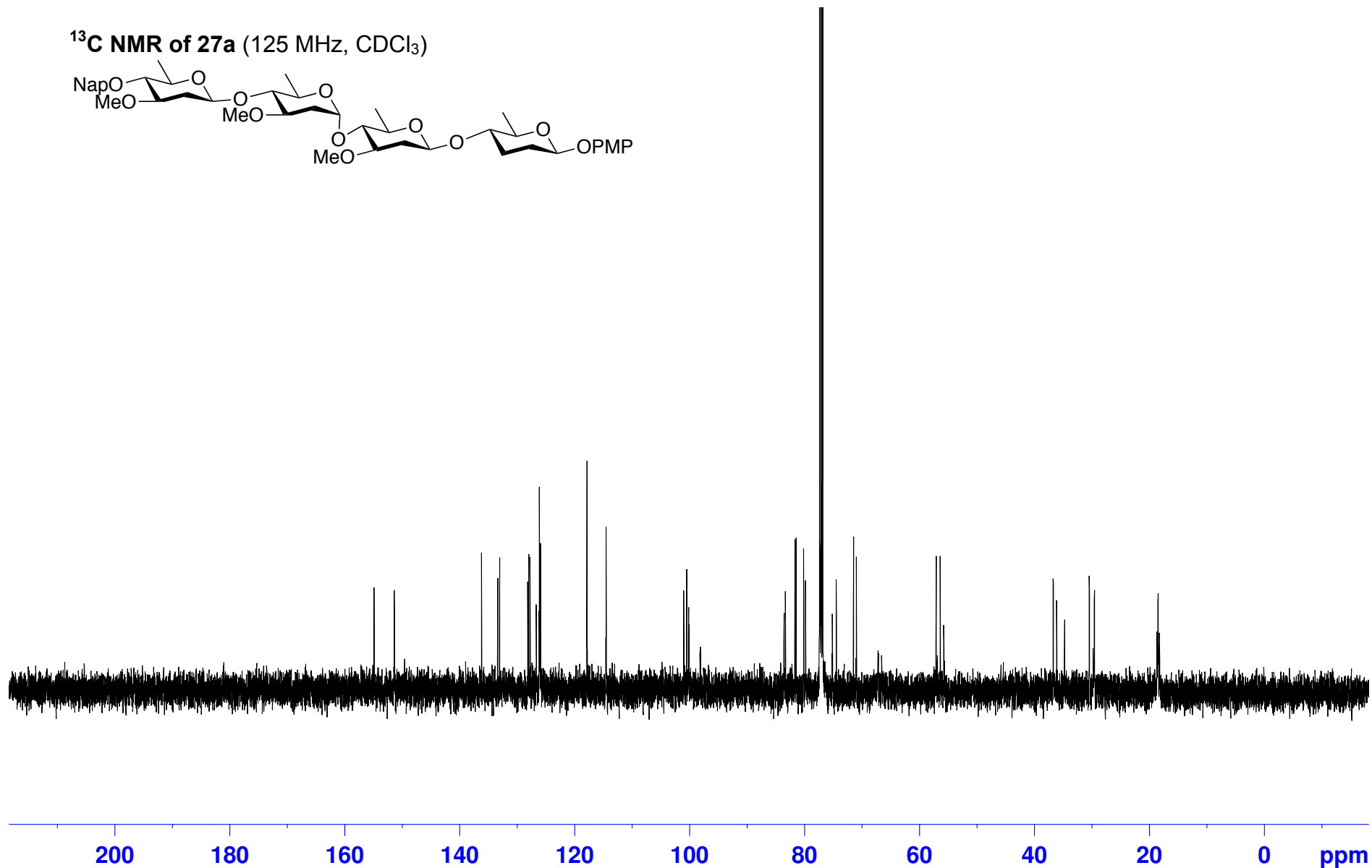
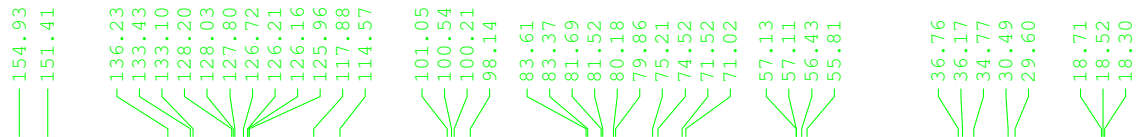
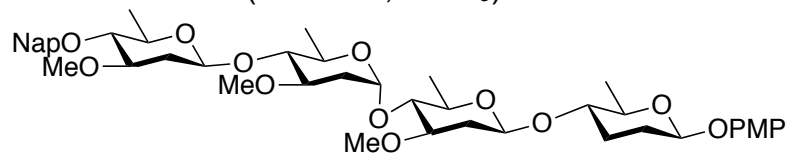
1.01

1.91

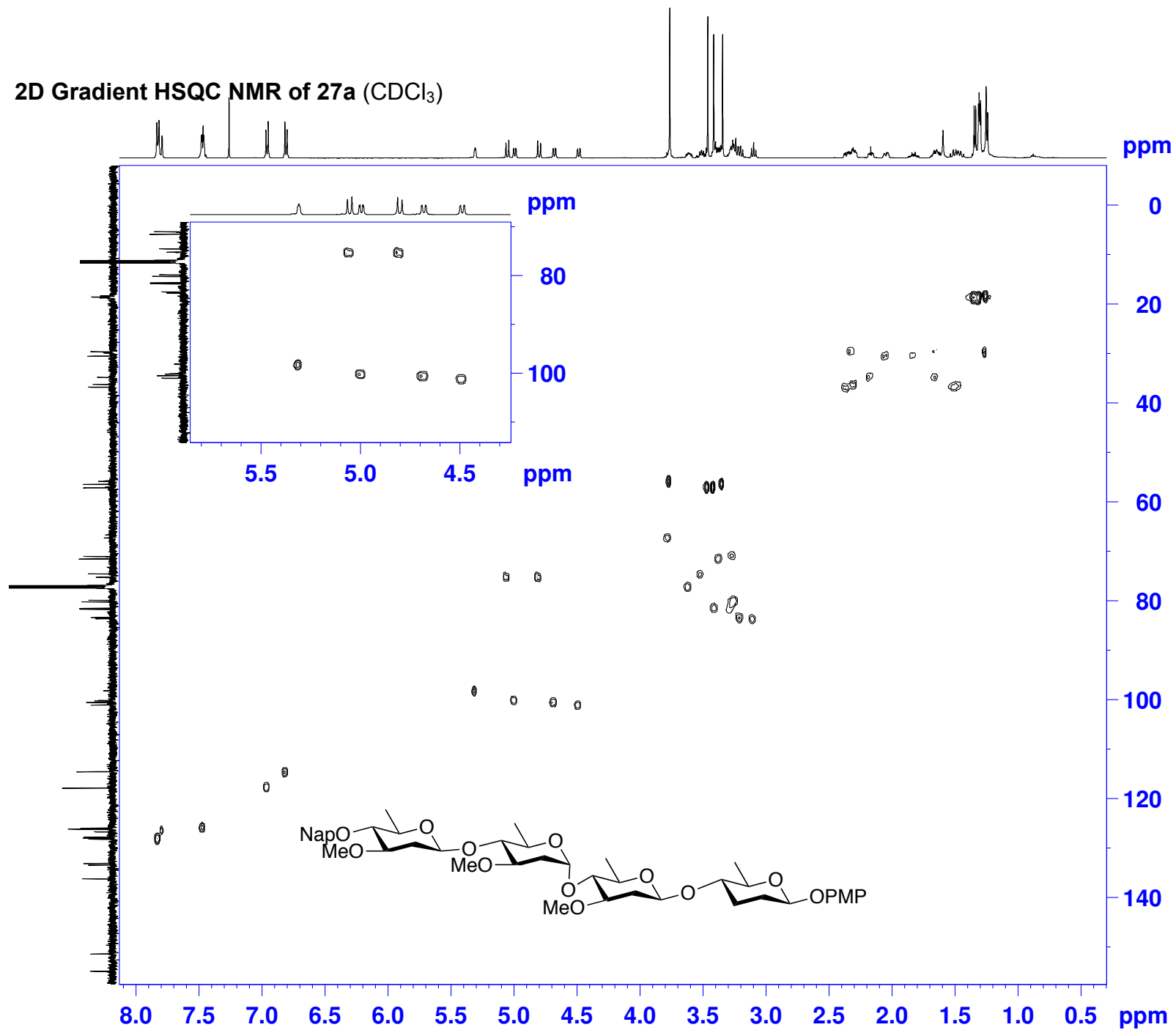
2.47

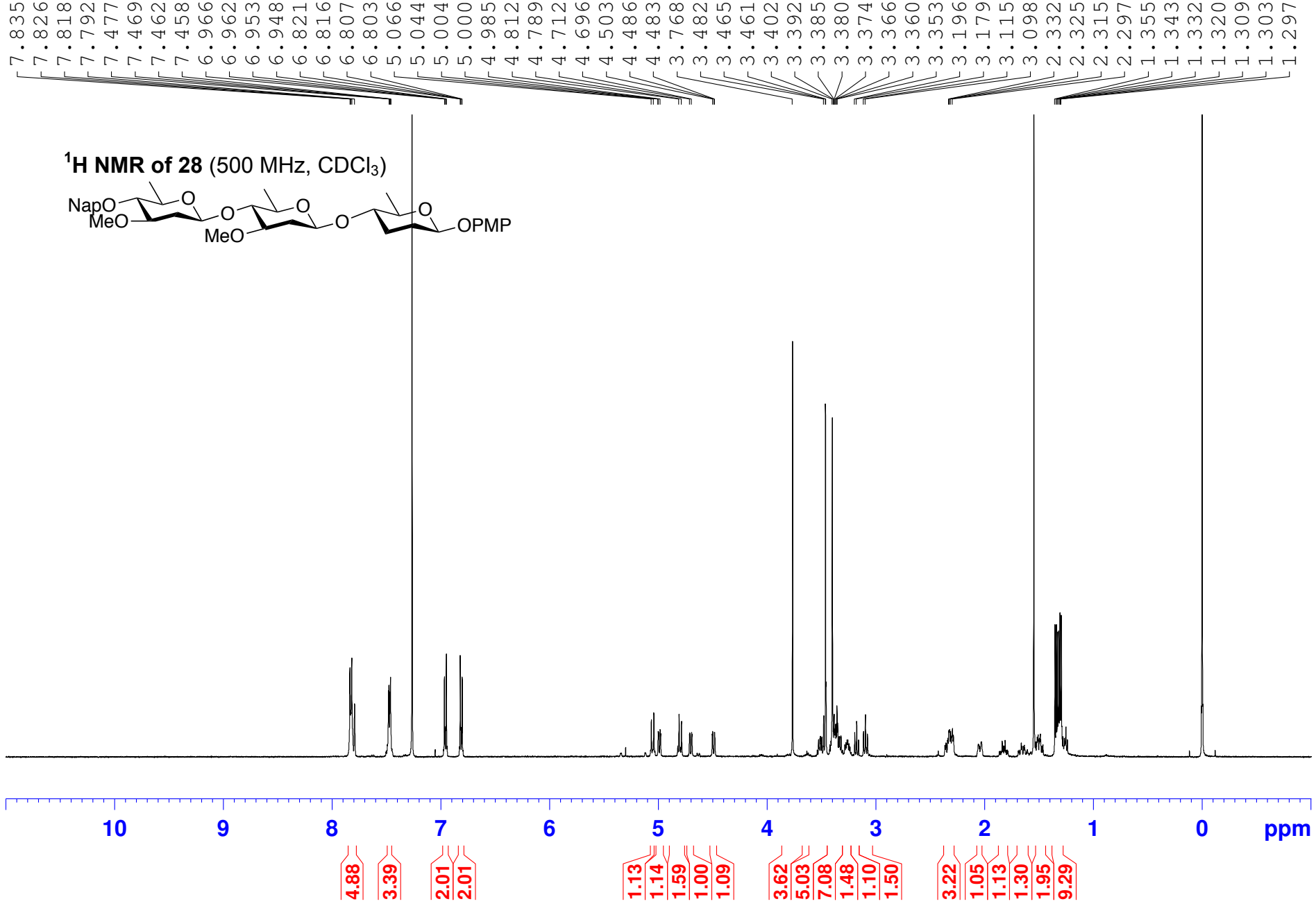
12.92

¹³C NMR of 27a (125 MHz, CDCl₃)

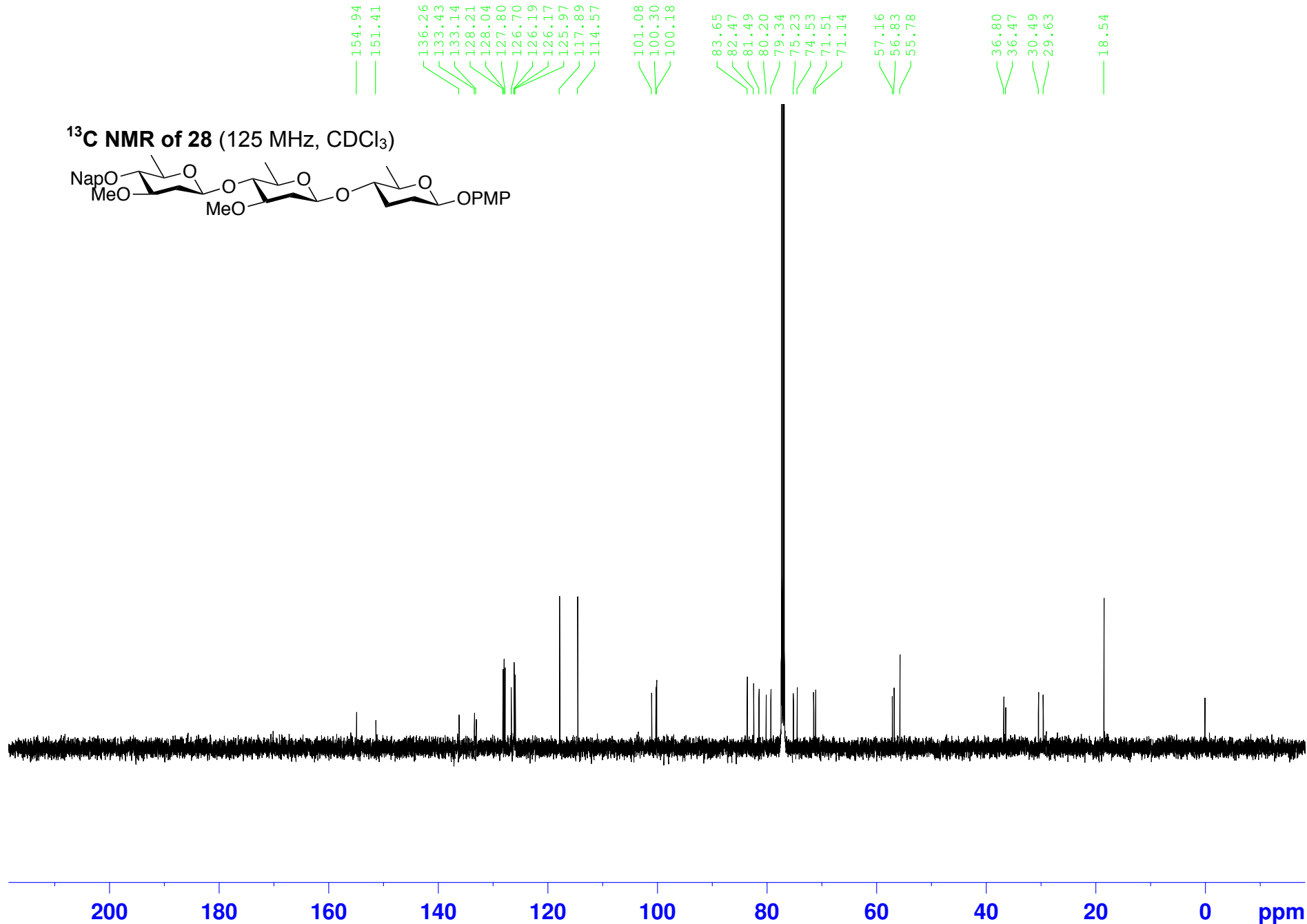
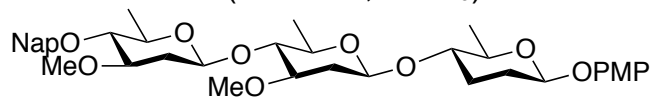


2D Gradient HSQC NMR of 27a (CDCl₃)



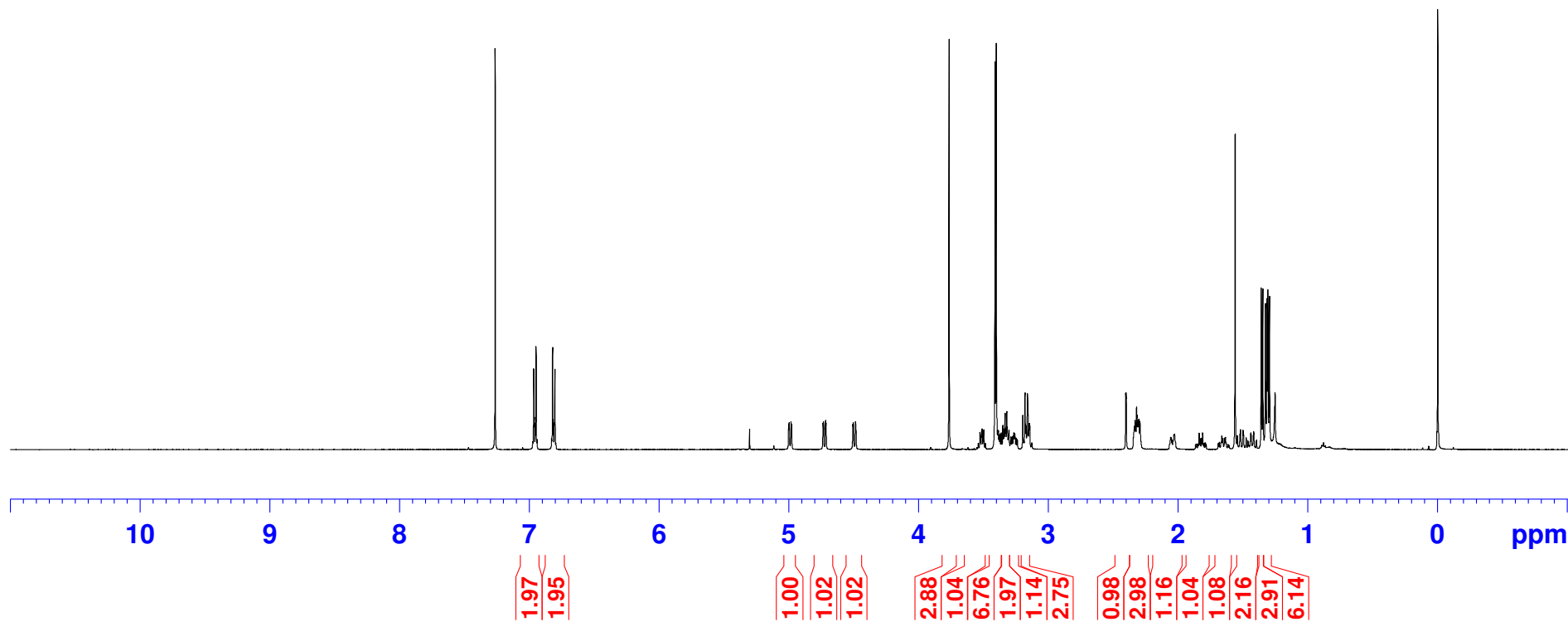
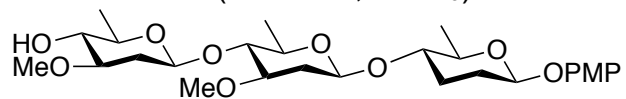


¹³C NMR of 28 (125 MHz, CDCl₃)

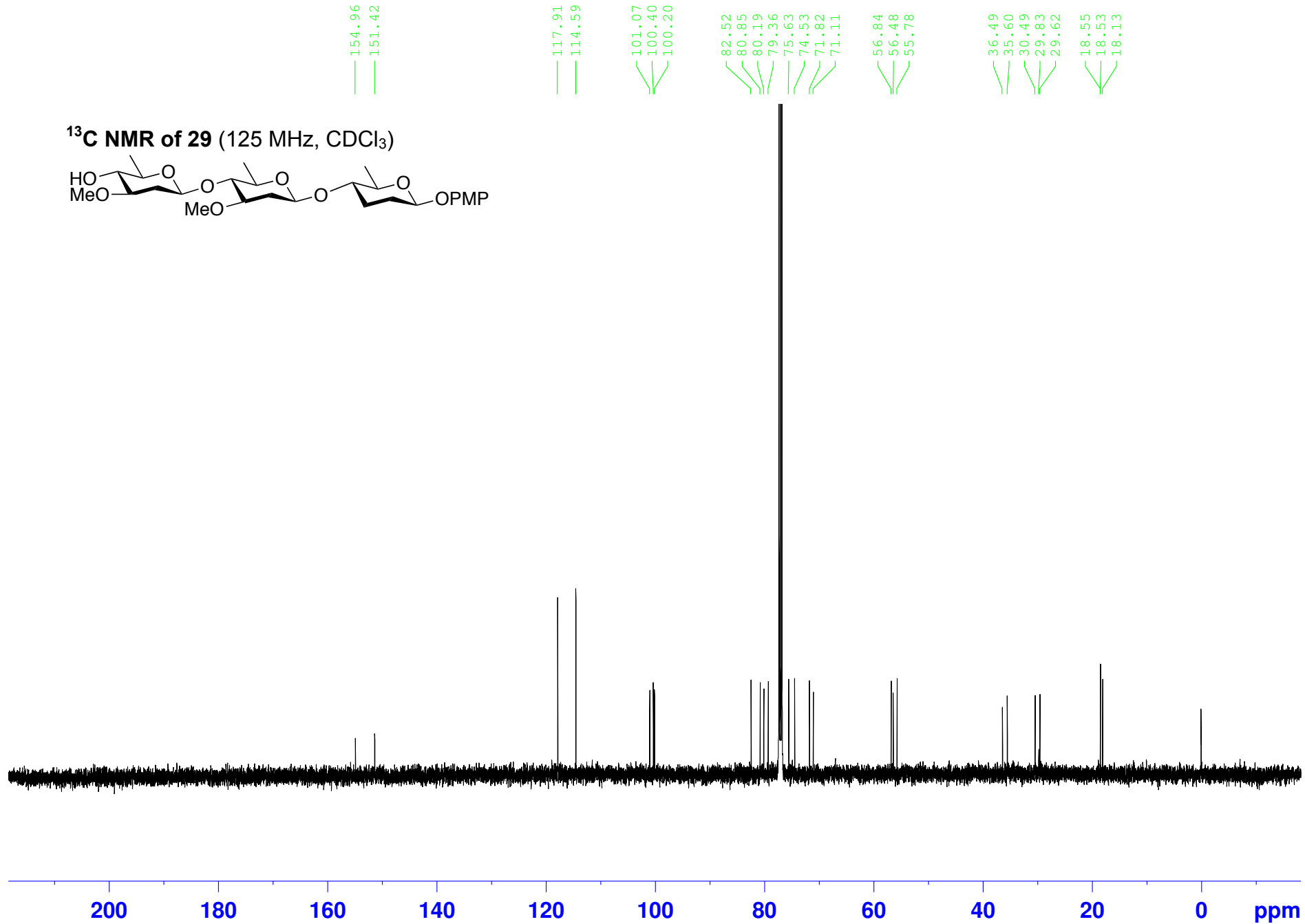


6.965
6.960
6.951
6.947
6.819
6.815
6.806
6.801
5.003
4.999
4.984
4.980
4.738
4.734
4.719
4.715
4.508
4.504
4.488
4.485
3.766
3.511
3.499
3.413
3.403
3.353
3.341
3.334
3.322
3.317
3.305
3.199
3.181
3.173
3.162
3.148
3.145
2.404
2.401
2.338
2.332
2.321
2.318
2.313
2.308
2.303
2.296
1.521
1.500
1.360
1.348
1.328
1.316
1.309
1.297

¹H NMR of 29 (500 MHz, CDCl₃)

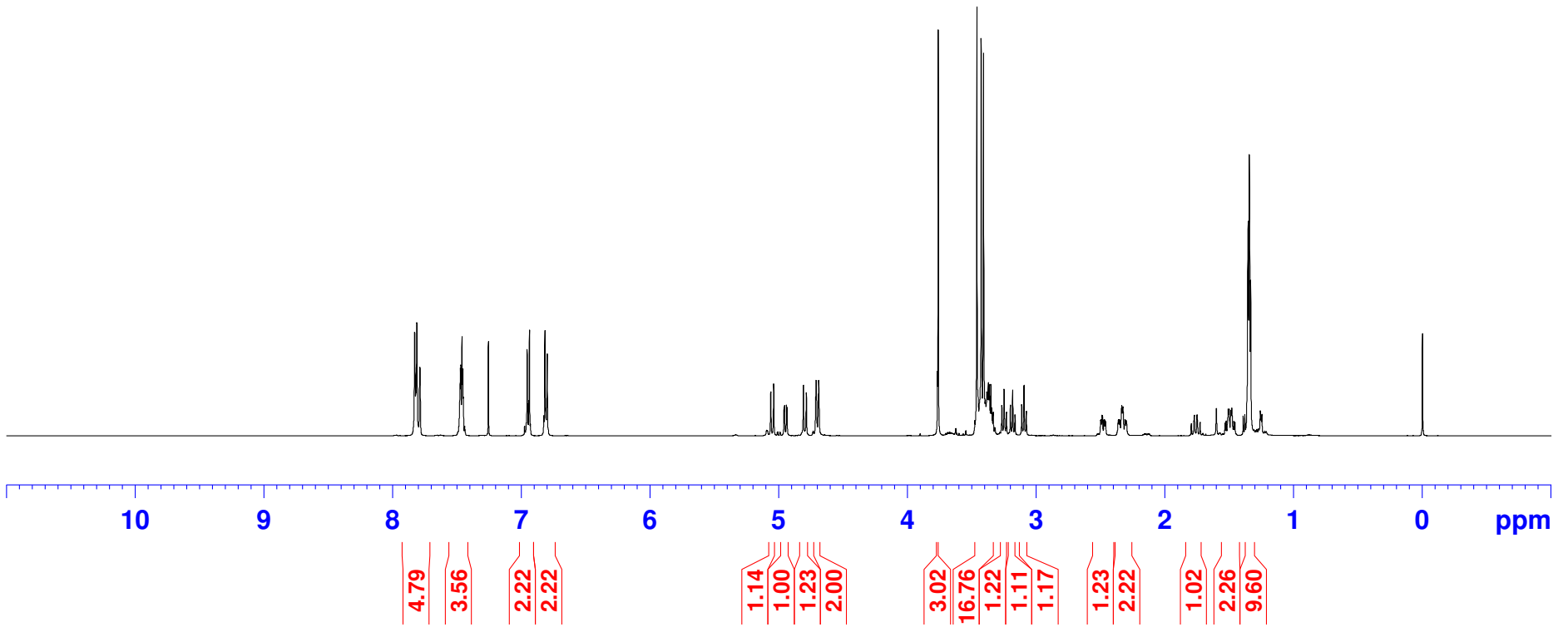


¹³C NMR of 29 (125 MHz, CDCl₃)

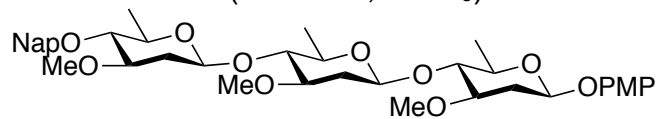


7.831
7.822
7.814
7.790
7.475
7.471
7.463
7.456
7.452
6.957
6.952
6.943
6.939
6.818
6.814
6.805
6.800
5.063
5.041
4.960
4.957
4.941
4.937
4.810
4.787
4.711
4.691
3.768
3.762
3.462
3.441
3.429
3.410
3.396
3.390
3.385
3.373
3.366
3.353
3.347
3.268
3.251
3.201
3.184
3.114
3.096
2.337
2.327
1.510
1.481
1.357
1.354
1.346
1.342
1.335

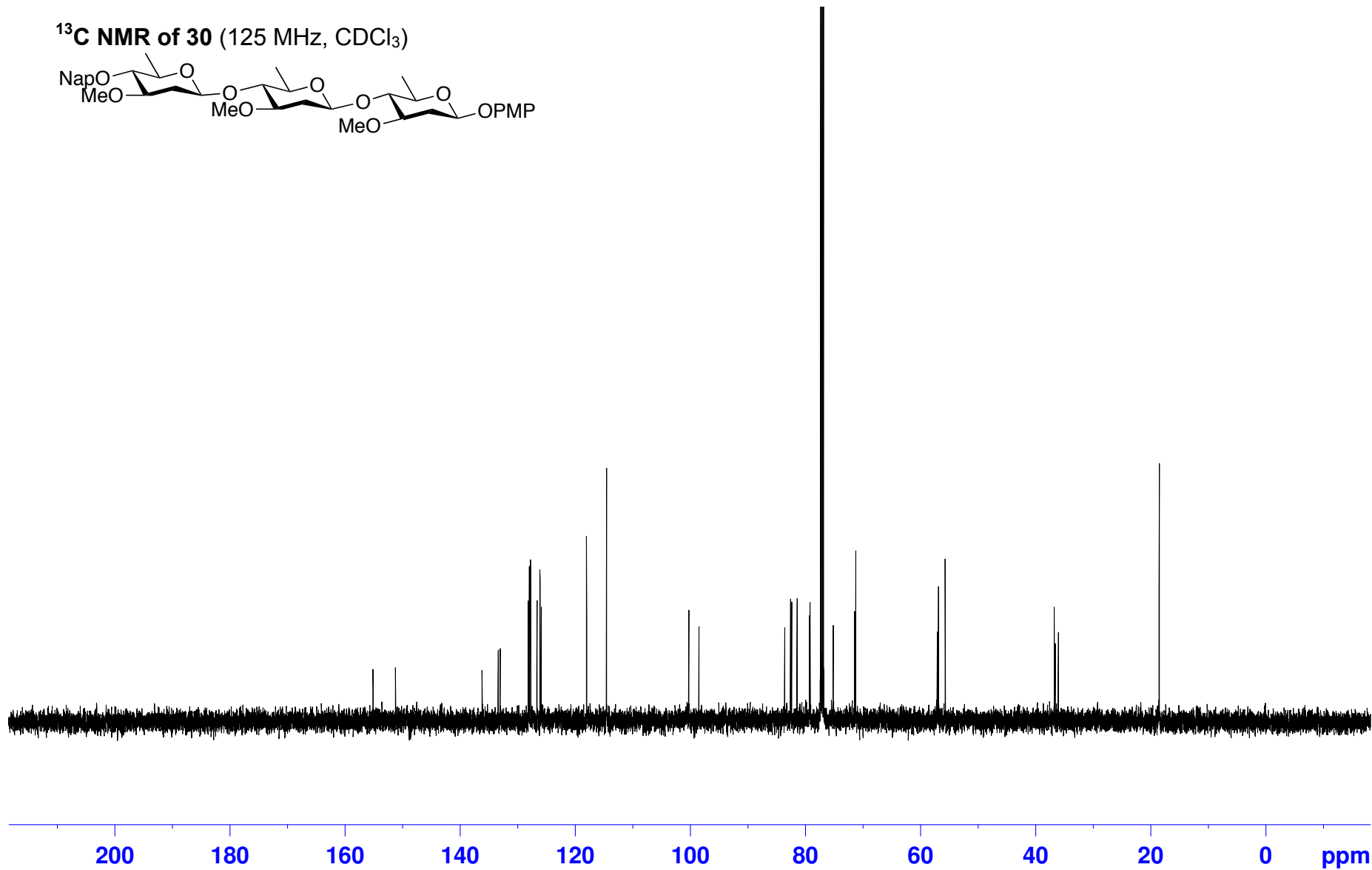
¹H NMR of 30 (500 MHz, CDCl₃)



¹³C NMR of 30 (125 MHz, CDCl₃)

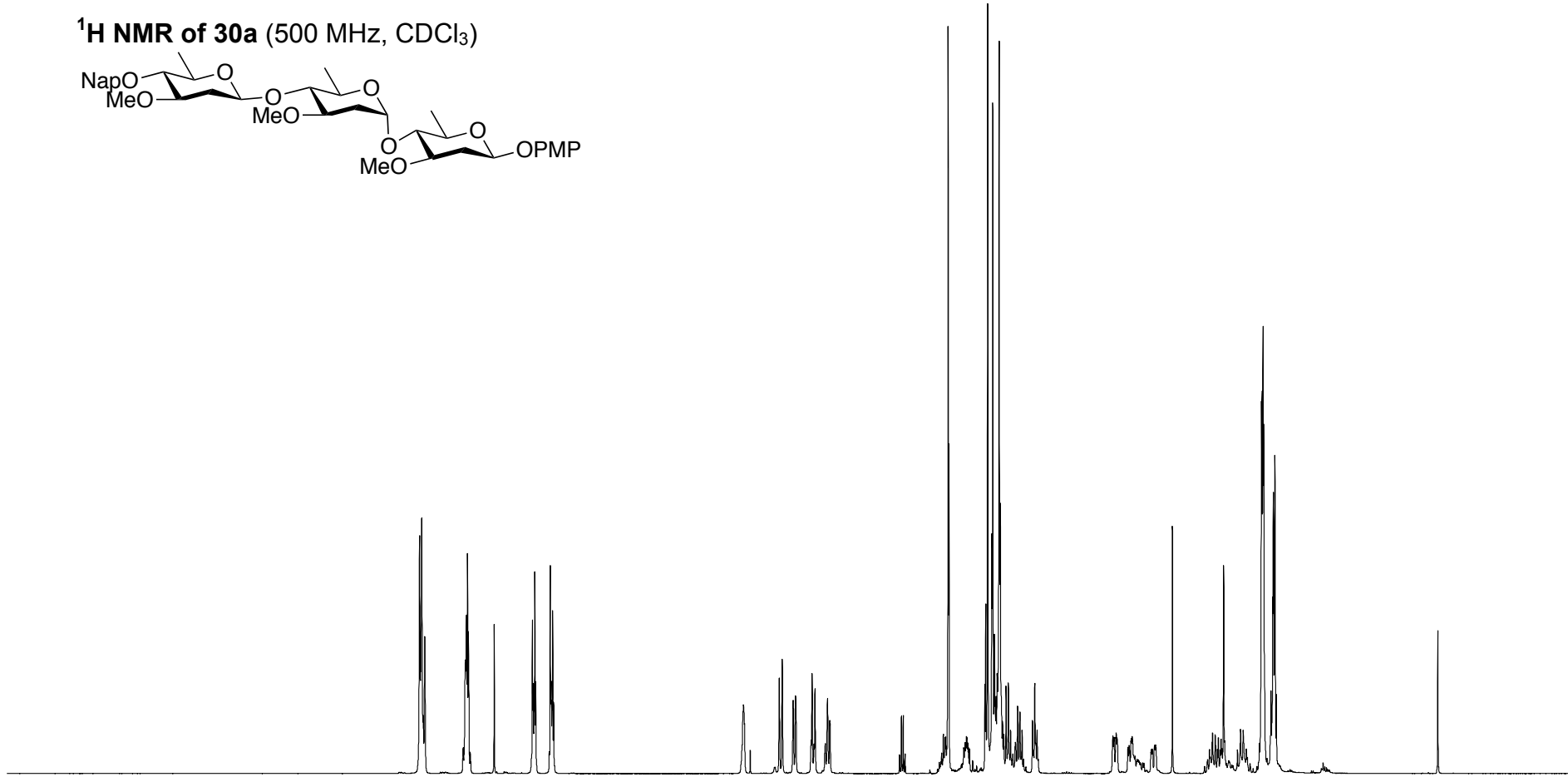
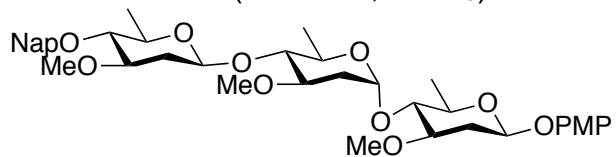


- 155.17
- 151.28
- 136.23
- 133.43
- 133.09
- 128.20
- 128.03
- 127.79
- 126.69
- 126.19
- 126.16
- 125.95
- 118.07
- 114.60
- 100.29
- 98.55
- 83.65
- 82.64
- 82.44
- 81.50
- 79.38
- 79.25
- 75.21
- 71.49
- 71.29
- 57.14
- 56.94
- 56.90
- 55.76
- 36.82
- 36.61
- 36.09
- 18.59
- 18.54



7.860
7.851
7.843
7.820
7.508
7.504
7.499
7.492
7.484
6.992
6.986
6.974
6.967
6.855
6.850
6.847
6.841
6.837
6.829
5.369
5.094
5.071
4.987
4.984
4.968
4.841
4.819
4.722
3.795
3.789
3.512
3.506
3.491
3.460
3.452
3.439
3.426
3.418
3.414
3.403
3.394
3.388
3.350
3.332
3.260
3.129
1.385
1.381
1.373
1.368
1.312
1.299
1.294
1.282
1.270

¹H NMR of 30a (500 MHz, CDCl₃)



10

9

8

7

6

5

4

3

2

1

0

ppm

4.40
3.26
2.02
2.01

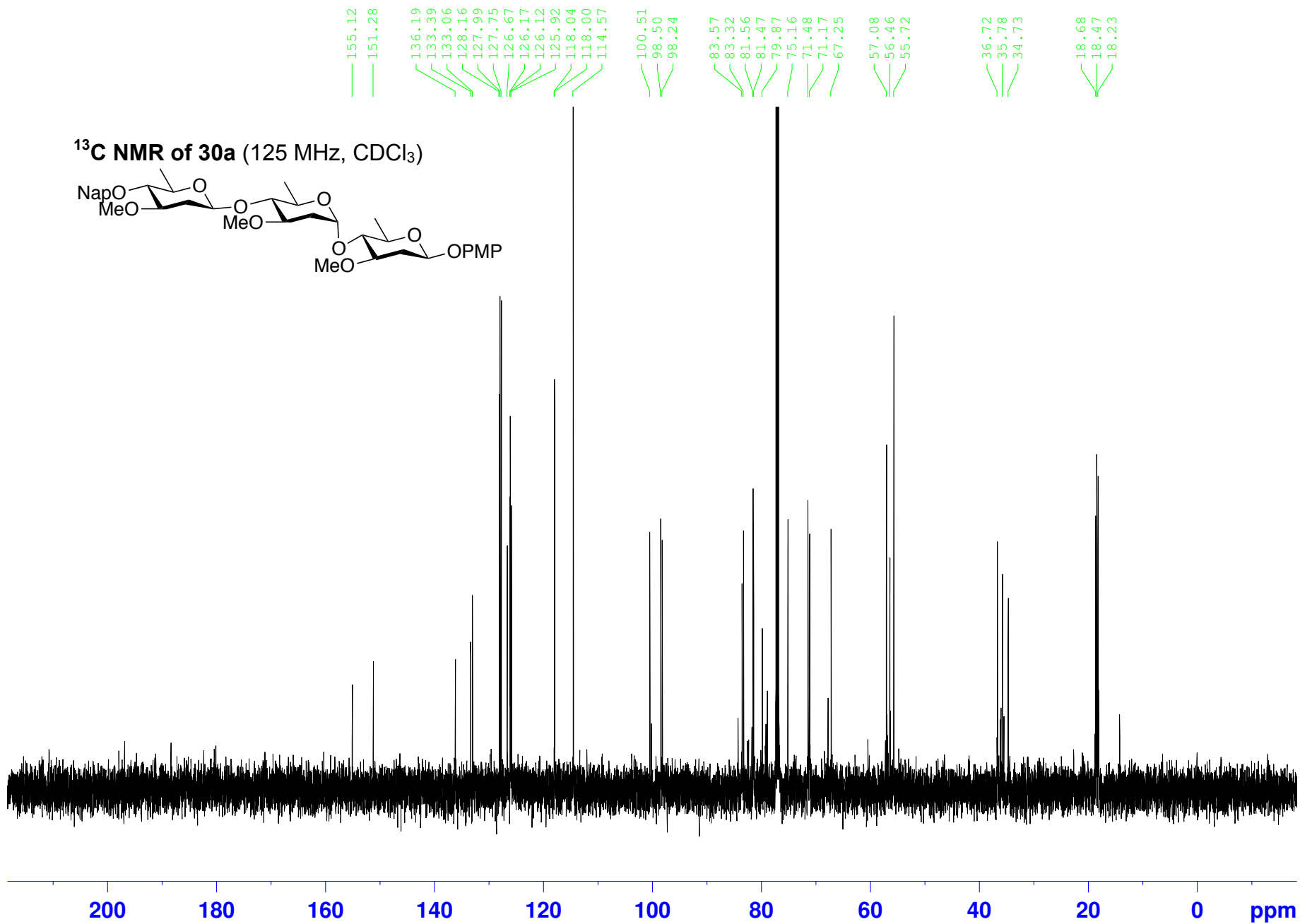
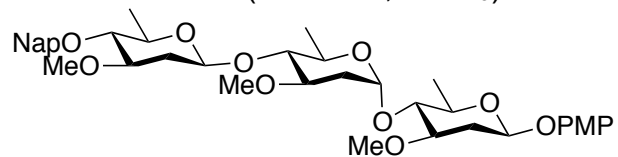
0.94
1.09
1.00
1.08
1.06

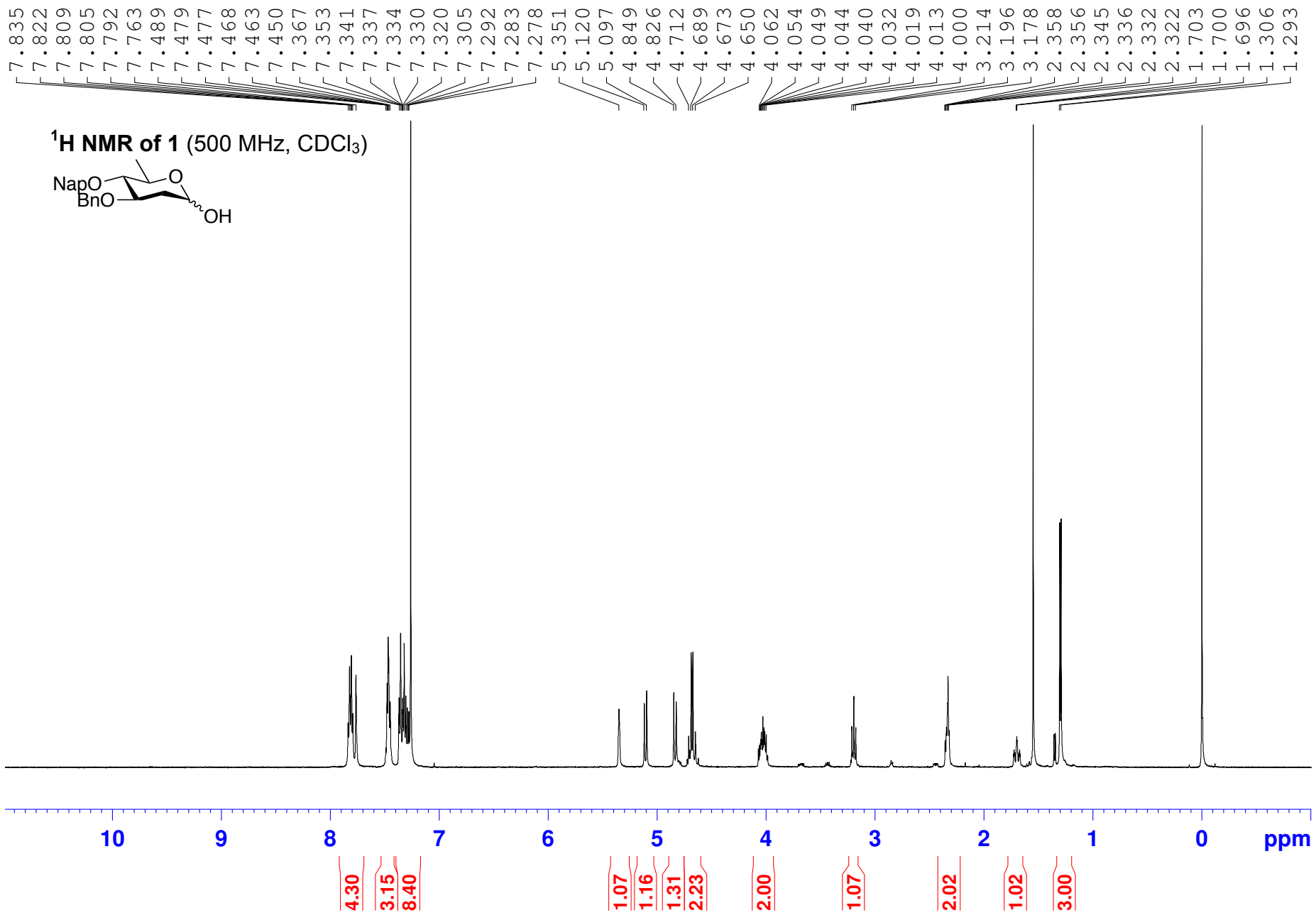
4.00
1.07
13.49
1.24
1.18
1.11

0.98
1.46
0.70

1.33
1.19
6.58
3.39

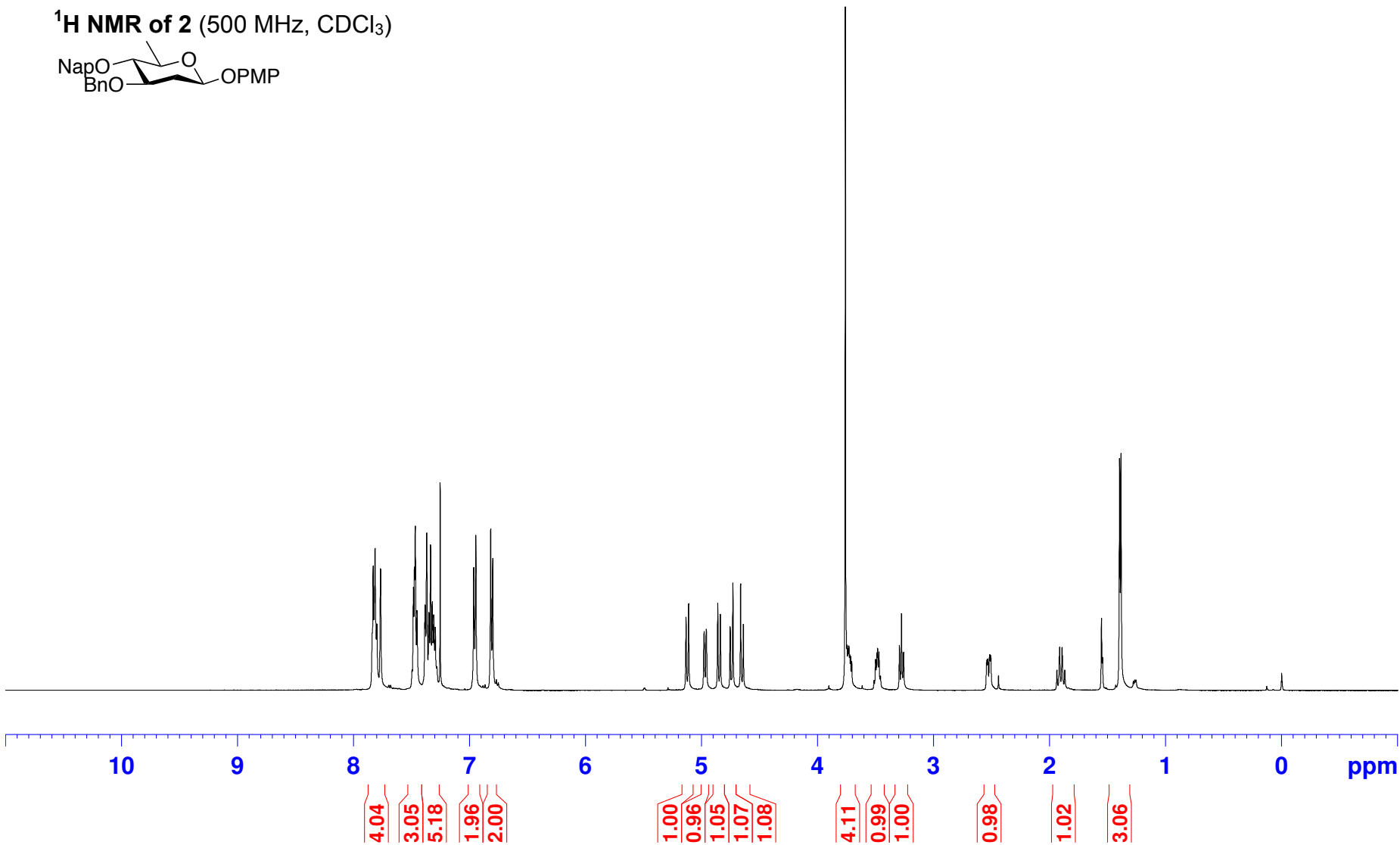
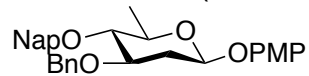
¹³C NMR of 30a (125 MHz, CDCl₃)





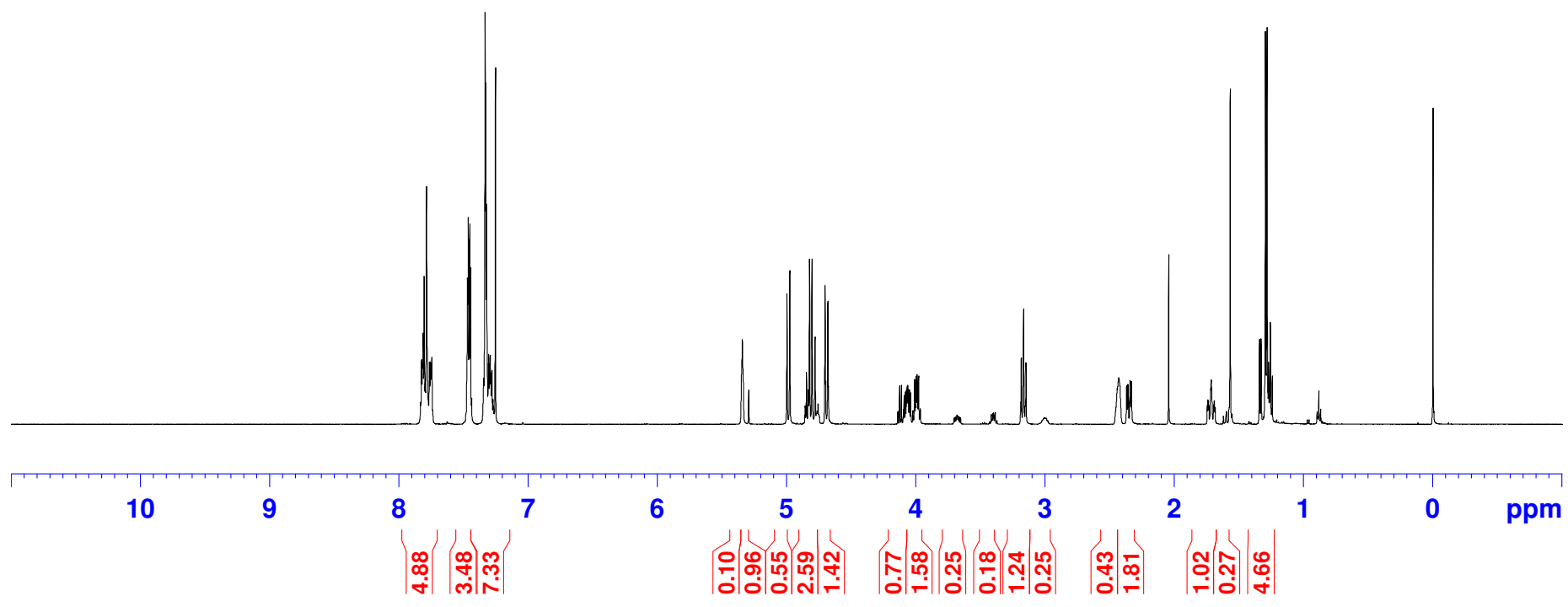
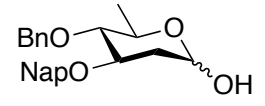
7.829
7.813
7.797
7.766
7.481
7.473
7.466
7.452
7.382
7.367
7.348
7.334
7.319
7.308
7.294
7.251
6.962
6.944
6.819
6.802
5.135
5.113
4.981
4.978
4.962
4.959
4.862
4.839
4.755
4.731
4.664
4.641
3.762
3.748
3.740
3.733
3.731
3.724
3.717
3.502
3.489
3.483
3.471
3.295
3.277
3.260
2.541
2.535
2.532
2.517
2.510
1.914
1.893
1.398
1.386

¹H NMR of 2 (500 MHz, CDCl₃)



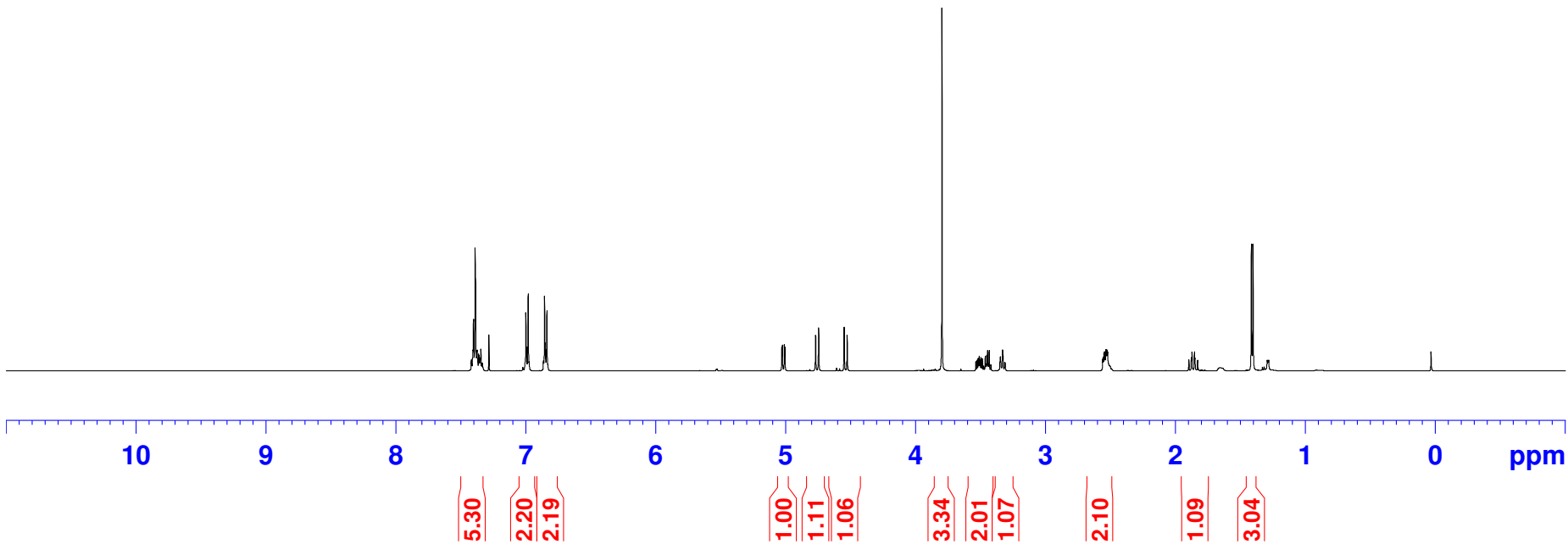
7.826
7.819
7.814
7.806
7.798
7.788
7.765
7.758
7.753
7.746
7.476
7.471
7.465
7.458
7.452
7.446
7.345
7.334
7.329
7.322
7.317
7.307
7.299
7.294
7.289
7.282
5.344
4.998
4.976
4.848
4.824
4.804
4.781
4.704
4.699
4.682
4.011
3.998
3.992
3.979
3.185
3.167
3.148
2.431
2.343
2.333
2.044
1.715
1.341
1.329
1.296
1.283
1.271
1.257
1.242

¹H NMR of **3** (500 MHz, CDCl₃)



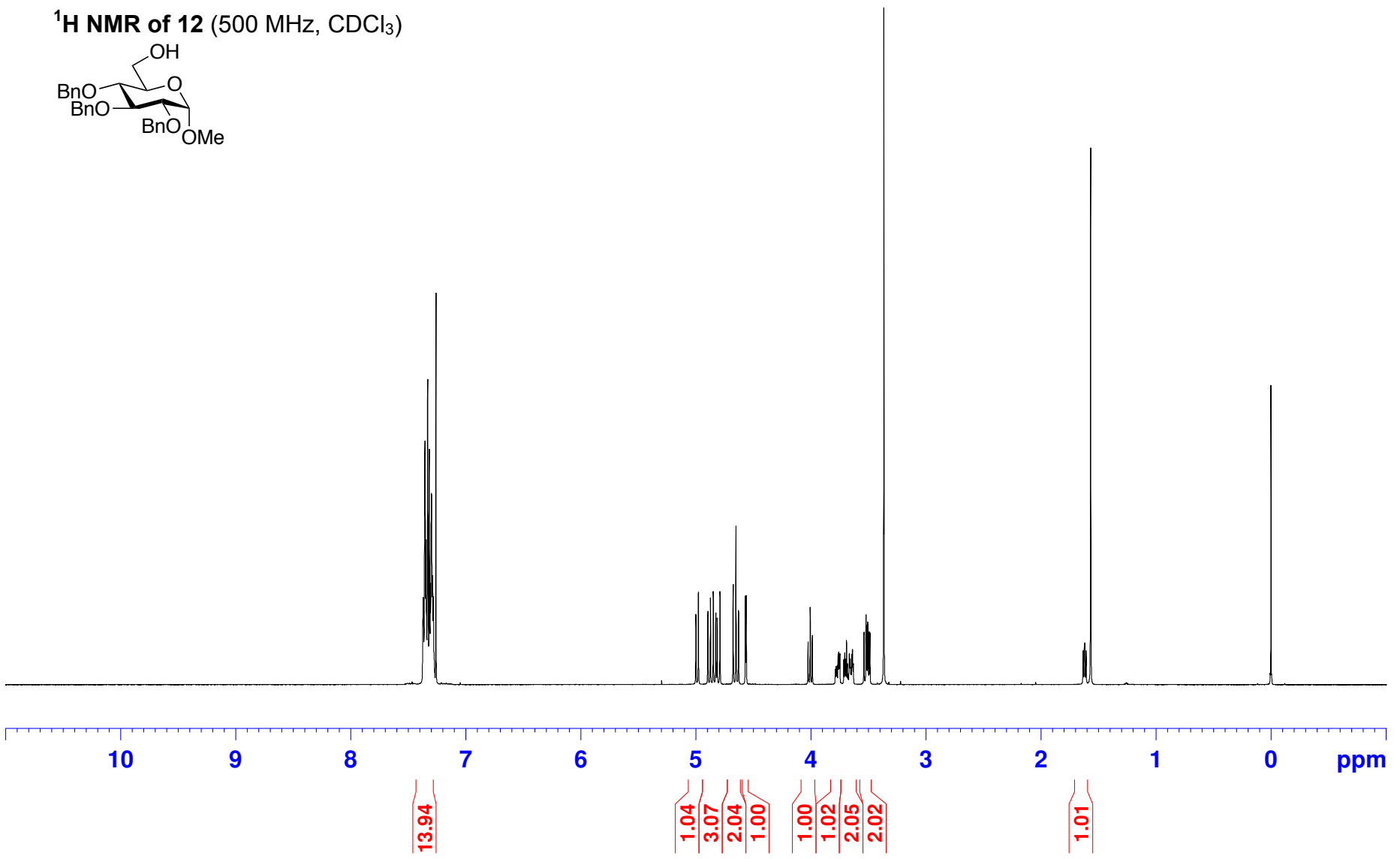
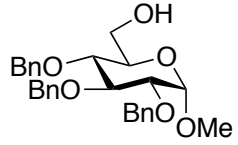
7.412
7.409
7.406
7.404
7.392
7.389
7.379
7.376
7.365
7.362
7.355
7.348
7.286
7.002
6.997
6.988
6.983
6.858
6.853
6.844
6.840
5.031
5.027
5.012
5.007
4.771
4.748
4.552
4.529
3.803
3.799
3.520
3.514
3.511
3.497
3.465
3.453
3.447
3.435
3.351
3.348
3.331
2.557
2.552
2.548
2.537
2.533
2.527
2.523
1.879
1.875
1.855
1.851
1.417
1.405

¹H NMR of 4 (500 MHz, CDCl₃)



7.373
7.357
7.349
7.347
7.333
7.319
7.314
7.309
7.300
7.291
7.285
5.002
4.980
4.897
4.875
4.850
4.829
4.816
4.792
4.678
4.653
4.631
4.571
4.564
4.027
4.008
3.989
3.773
3.765
3.760
3.755
3.750
3.716
3.708
3.700
3.692
3.684
3.669
3.666
3.661
3.646
3.640
3.633
3.541
3.522
3.514
3.507
3.503
3.495
3.488
3.368
1.636
1.625
1.621
1.610

¹H NMR of 12 (500 MHz, CDCl₃)



7.498
7.493
7.489
7.487
7.486
7.482
7.479
7.400
7.396
7.383
7.380
7.374
7.370
7.365
7.357
7.352
7.349
7.343
7.339
7.331
7.327
7.314
5.516
4.798
4.774
4.717
4.693
4.616
4.609
4.274
4.264
4.254
4.244
4.169
4.154
4.150
4.136
4.131
3.819
3.809
3.799
3.790
3.723
3.702
3.682
3.513
3.494
3.480
3.475
3.473
3.462
3.454
3.375
2.548
2.543

¹H NMR of 13 (500 MHz, CDCl₃)

