Contents

1. General Information

Methods and Reagents. All reactions were performed in oven-dried flasks fitted with septa under a positive pressure of nitrogen atmosphere. Organic solutions were concentrated using a Buchi rotary evaporator below 40 °C at 25 torr. Analytical thin-layer chromatography was routinely utilized to monitor the progress of the reactions and performed using pre-coated glass plates with 230-400 mesh silica gel impregnated with a fluorescent indicator (250 nm). Visualization was then achieved using UV light, iodine, or ceric ammonium molybdate. Flash column chromatography was performed using 40-63 μm silica gel (SiliaFlash F60 from Silicycle). Dry solvents were obtained from a SG Waters solvent system utilizing activated alumina columns under an argon pressure. All other commercial reagents were used as received from Sigma Aldrich, Alfa Aesar, Acros Organics, TCI, and Combi-Blocks, unless otherwise noted.

Instrumentation. All new compounds were characterized by Nuclear Magnetic Resonance (NMR) spectroscopy and High-Resolution Mass spectrometry (HRMS). All ^{1}H NMR spectra were recorded on either Bruker 400 or 500 MHz spectrometers or DRX-400 (400 MHz) spectrometer. All ^{13}C NMR spectra were recorded on either Bruker 100 or 125 MHz spectrometer or DRX-400 (100 MHz) spectrometer. All ^{19}F NMR spectra were recorded on DRX-400 (376 MHz) spectrometer. Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent ($CDCl_3$: δ 7.26 ppm, δ 77.00 ppm). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and bs = broad singlet), integration, and coupling constant in hertz (Hz).

High resolution (ESI-TOF) mass spectrometry was performed at the University of Iowa and at Wayne State University.

Abbreviations were used as follows: MTBE (*tert*-butyl methyl ether), IBO (isobutylene oxide) and DFT (density functional theory).

2. Optimization Studies

Figure S1. Screening of Small-Molecule Catalysts

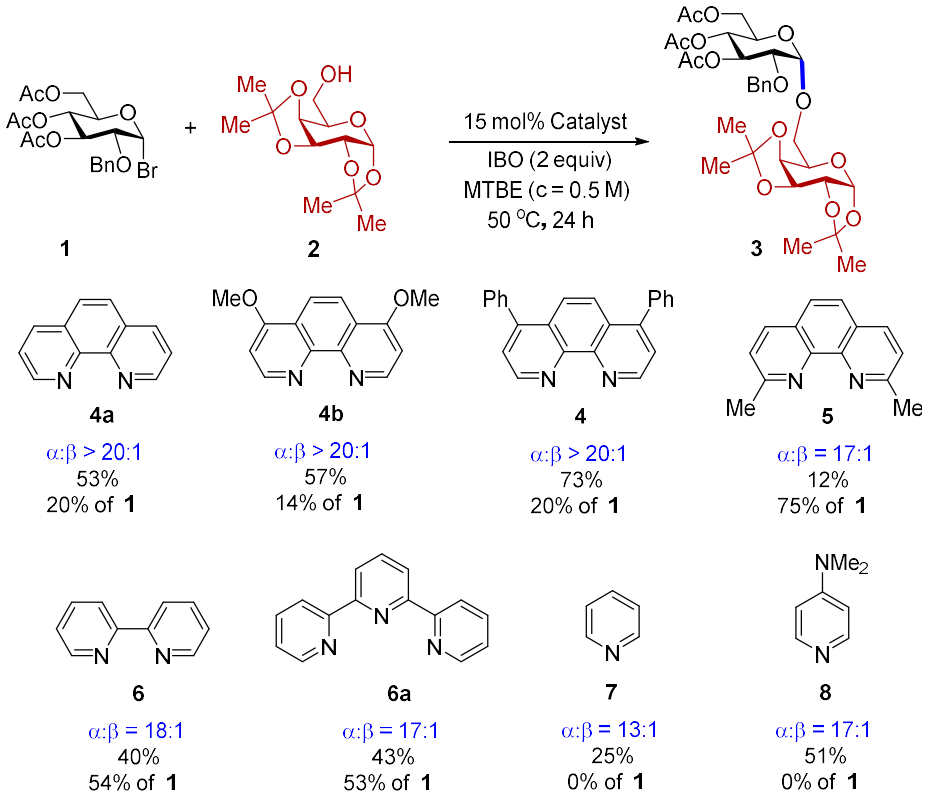
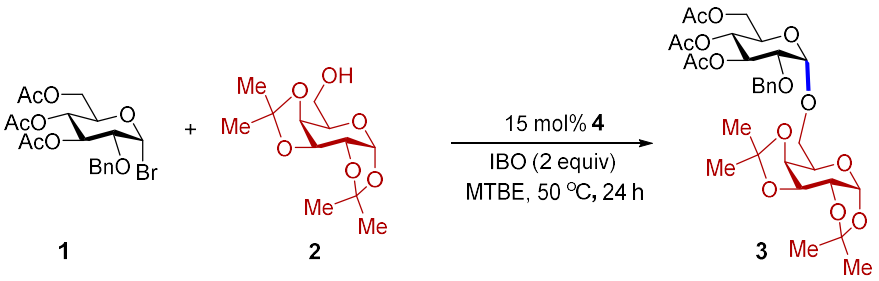


Figure S2. Screening of Hydrogen Bromide (HBr) Scavengers



1 **2** **3**

Entry	Additive	Recovered Donor (%)	Yield (%)	α:β
1	None	0	50	17:1
2	Molecular Sieve	26	70	17:1
3	β-(-)-Pinene (1 equiv.)	0	68	17:1
4	IBO (1 equiv.)	23	71	>20:1
5	IBO (2 equiv.)	20	73	>20:1

β-(-)-Pinene

iso-Butyl Oxide (IBO)

Figure S3. Increasing Catalyst Loading

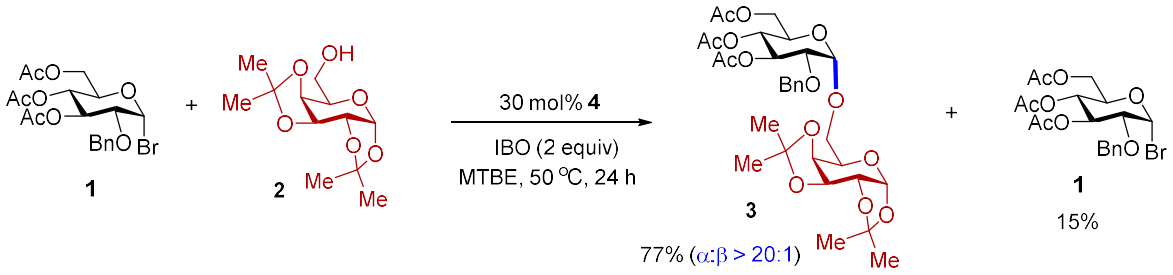
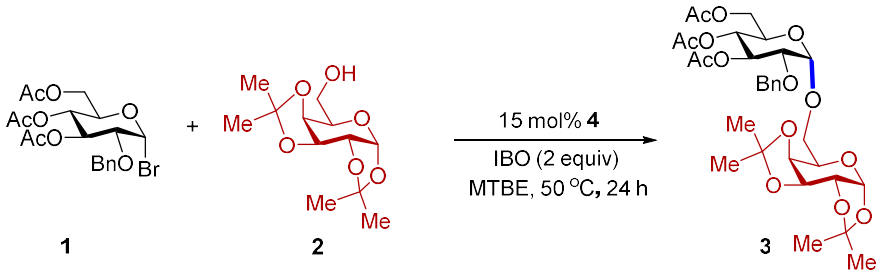


Figure S4. Effect of Concentration

(c = 0.2 M)	50% (α:β > 20:1)	45%
(c = 0.3 M)	53% (α:β > 20:1)	42%
(c = 0.5 M)	73% (α:β > 20:1)	20%
(c = 1.0 M)	79% (α:β > 20:1)	0%

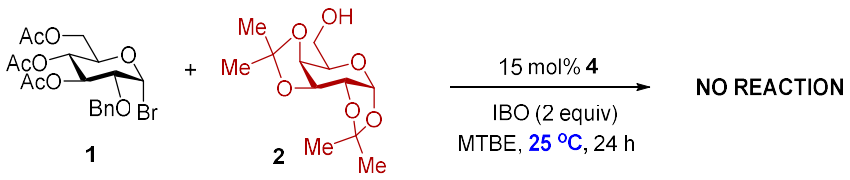
Figure S5. Effect of Solvent



1 2 3

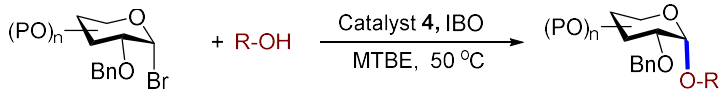
Entry	Solvent	Recovered Donor **1** (%)	**3** Yield (%)	α:β
1	MTBE	20	73	>20:1
2	CPME	13	72	>20:1
3	Toluene	30	63	>20:1
4	DCE	-	71	>20:1

Figure S6. Effect of Reaction Temperature



1 2

3. Phenanthroline-Catalyzed Glycosylation Reactions
General Procedure



Standard Conditions A:

A 10 mL Schlenk flask was charged with glycosyl bromide (0.2 mmol, 1.0 equiv), alcohol (0.4 mmol, 3.0 equiv), catalyst **4** (0.03 mmol, 15 mol%), IBO (0.4 mmol, 2.0 equiv.) and MTBE (0.4 mL). The resulting solution was stirred at 50 ºC for 24 h, diluted with toluene, and purified by silica gel flash chromatography (toluene/ethyl acetate: 5/1→3/1) to give the desired product.

Standard Conditions B:

A 10 mL Schlenk flask was charged with glycosyl bromide (0.4 mmol, 2.0 equiv), alcohol (0.2 mmol, 1.0 equiv), catalyst **4** (0.06 mmol, 30 mol%), IBO (0.4 mmol, 2.0 equiv.) and MTBE (0.2 mL). The resulting solution was stirred at 50 ºC for 48 h, diluted with toluene, and purified by silica gel flash chromatography (toluene/ethyl acetate: 5/1→3/1) to give the desired product.

Standard Conditions B':

A 10 mL Schlenk flask was charged with glycosyl bromide (0.4 mmol, 2.0 equiv), alcohol (0.2 mmol, 1.0 equiv), catalyst **4** (0.06 mmol, 30 mol%), IBO (0.4 mmol, 2.0 equiv.) and MTBE (0.4 mL). The resulting solution was stirred at 50 ºC for 24 h, diluted with toluene, and purified by silica gel flash chromatography (toluene/ethyl acetate: 9/1→4/1) to give the desired product.

Standard Conditions C:

A 10 mL Schlenk flask was charged with glycosyl bromide (0.6 mmol, 3.0 equiv), alcohol (0.2 mmol, 1.0 equiv), catalyst **4** (0.1 mmol, 50 mol%), IBO (0.6 mmol, 3.0 equiv.) and MTBE (0.2 mL). The resulting solution was stirred at 50 ºC for 48 h, diluted with toluene, and purified by silica gel flash chromatography (toluene/ethyl acetate: 5/1→3/1) to give the desired product.

Standard Conditions D:

A 10 mL Schlenk flask was charged with glycosyl bromide (0.2 mmol, 2.0 equiv), alcohol (0.1 mmol, 1.0 equiv), catalyst **4** (0.02 mmol, 20 mol%), IBO (0.2 mmol, 2.0 equiv.) and MTBE (0.2 mL). The resulting solution was stirred at 25 ºC for 24 h, diluted with toluene, and purified by silica gel flash chromatography (toluene/ethyl acetate: 9/1→4/1) to give the desired product.

Standard Conditions D':

A 10 mL Schlenk flask was charged with glycosyl bromide (0.2 mmol, 2.0 equiv), alcohol (0.1 mmol, 1.0 equiv), catalyst **4** (0.02 mmol, 20 mol%), IBO (0.2 mmol, 2.0 equiv.) and MTBE (0.2 mL). The resulting solution was stirred at 25 ºC for 48 h, diluted with toluene, and purified by silica gel flash chromatography (toluene/ethyl acetate: 9/1→4/1) to give the desired product.

Standard Conditions E:

A 10 mL Schlenk flask was charged with glycosyl bromide (0.2 mmol, 1.0 equiv), alcohol (0.6 mmol, 3.0 equiv), catalyst **4** (0.04 mmol, 20 mol%), IBO (0.4 mmol, 2.0 equiv.) and MTBE

(0.4 mL). The resulting solution was stirred at 25 °C for 24 h, diluted with toluene, and purified by silica gel flash chromatography (toluene/ethyl acetate: 9/1→4/1) to give the desired product.

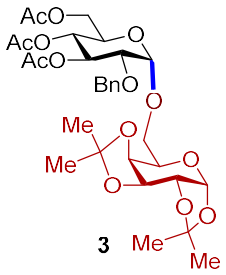
Standard Conditions F:

A 10 mL Schlenk flask was charged with glycosyl bromide (0.2 mmol, 1.0 equiv), alcohol (0.6 mmol, 3.0 equiv), catalyst **4** (0.04 mmol, 20 mol%), IBO (0.4 mmol, 2.0 equiv.) and MTBE (0.4 mL). The resulting solution was stirred at 50 °C for 24 h, diluted with toluene, and purified by silica gel flash chromatography (toluene/ethyl acetate: 9/1→4/1) to give the desired product.

Standard Conditions G:

A 10 mL Schlenk flask was charged with glycosyl bromide (0.22 mmol, 1.1 equiv), alcohol (0.2 mmol, 1.0 equiv), catalyst **4** (0.03 mmol, 15 mol%), IBO (0.4 mmol, 2.0 equiv.) and MTBE (0.4 mL). The resulting solution was stirred at 50 °C for 24 h, diluted with toluene, and purified by silica gel flash chromatography (toluene/ethyl acetate: 33/1→9/1) to give the desired product.

The α/β ratio of the desired products were determined by ^{1}H NMR analysis based on the ratio of the anomeric protons of both α- and β-anomers. When the anomeric protons are overlapped, other protons of both anomers were analyzed. In some cases, we utilized prep-TLC to separate the α-anomer from the β-anomer so that we can accurately determine the α/β ratio of the mixture.

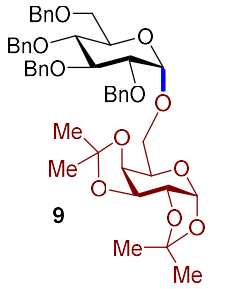


3

Conditions A: 73% (117 mg), α:β >20:1

^{1}H and ^{13}C NMR of disaccharide **3** has been reported.[1]

^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.30-7.27 (m, 5 H), 5.49 (d, *J* = 5.2 Hz, 1 H), 5.43 (t, *J* = 10.0 Hz, 1 H), 5.00-4.90 (m, 2 H), 4.70-4.55 (m, 3 H), 4.34-4.28 (m, 3 H), 4.12-4.06 (m,1 H), 4.04-4.00 (m, 2 H), 3.80-3.72 (m, 2 H), 3.55 (dd, *J* = 10.0, 3.6 Hz, 1 H), 2.07 (s, 3 H), 2.01 (s, 3 H), 2.00 (s, 3 H), 1.56 (s, 3 H), 1.43 (s, 3 H), 1.33 (s, 3 H), 1.28 (s, 3 H). ^{1}H NMR matches with the literature report.[1]

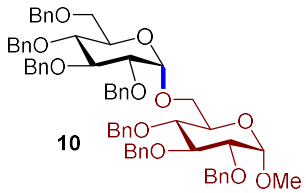


9

Conditions D: 95% (74.6 mg), α:β = 14:1

^{1}H and ^{13}C NMR of disaccharide **9** has been reported.[2]

^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.40 – 7.09 (m, 20H), 5.53 (d, *J* = 5.0 Hz, 1H), 4.99 (m, 2H), 4.82 (m, 2H), 4.73 (m, 2H), 4.66 – 4.57 (m, 2H), 4.48 (m, 2H), 4.40 – 4.29 (m, 2H), 4.09 – 3.96 (m, 2H), 3.88 – 3.56 (m, 7H), 1.54 (s, 3H), 1.46 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H). ^{1}H NMR matches with the literature report.[2]

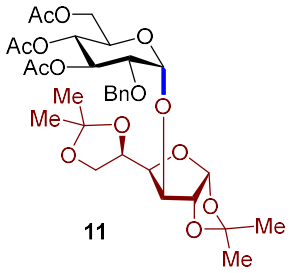


10

Conditions E: 63% (124.2 mg), α:β = 14:1

^{1}H and ^{13}C NMR of disaccharide **10** has been reported.[2]

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.44 – 7.16 (m, 35H), 5.08 – 4.97 (m, 4H), 4.93 – 4.83 (m, 3H), 4.81 – 4.70 (m, 4H), 4.67 – 4.61 (m, 3H), 4.56 – 4.46 (m, 2H), 4.10 – 4.01 (m, 2H), 3.93 – 3.83 (m, 3H), 3.82 – 3.66 (m, 4H), 3.65 – 3.58 (m, 2H), 3.52 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.43 (s, 3H). ^{1}H NMR matches with the literature report.[2]

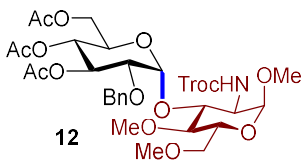


11

Conditions B: 63% (100 mg), α only

^{1}H and ^{13}C NMR of disaccharide **11** has been reported.[3]

^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.38-7.22 (m, 5 H), 5.94 (d, *J* = 3.6 Hz, 1 H), 5.39 (t, *J* = 10.0 Hz, 1 H), 5.31 (d, *J* = 3.6 Hz, 1 H), 4.92 (t, *J* = 10.0 Hz, 1 H), 4.71 (d, *J* = 12.0 Hz, 1 H), 4.60-4.52 (m, 2 H), 4.47-4.41 (m, 1 H), 4.26-4.4.02 (m, 2 H), 4.13-3.97 (m, 5 H), 3.57 (dd, *J* = 10.0, 3.6 Hz, 1 H), 2.09 (s, 3 H), 2.02 (s, 3 H), 1.97 (s, 3 H), 1.49 (s, 3 H), 1.41 (s, 3 H), 1.32 (s, 3 H), 1.24 (s, 3 H). ^{1}H NMR matches with the literature report.[3]

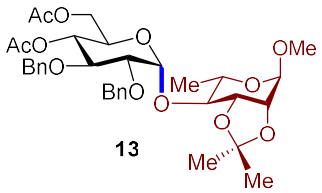


12

Conditions B: 50% (87 mg), α only

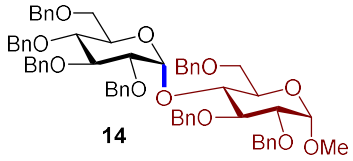
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.31-7.27 (m, 5 H), 5.47-5.35 (m, 3 H), 4.91 (t, *J* = 10.0 Hz, 1 H), 4.93 (d, *J* = 12.0 Hz, 1 H), 4.77-4.60 (m, 4 H), 4.33-4.19 (m, 2 H), 4.08 (dd, *J* = 12.0, 2.0 Hz,

1 H), 3.98-3.90 (m, 1 H), 3.85 (t, *J* = 10.0 Hz, 1 H), 3.65 (dd, *J* = 10.0, 4.0 Hz, 1 H), 3.62-3.59 (m, 3 H), 3.57-3.40 (m, 1 H), 3.39 (s, 3 H), 3.35 (s, 6 H), 2.10 (s, 3 H), 2.01 (s, 3 H), 1.91 (s, 3 H).
^{13}C NMR (CDCl3, 100 MHz): δ = 170.3, 169.8, 154.0, 137.6, 128.4, 128.2, 127.8, 98.3, 98.2, 95.3, 90.9, 80.2, 74.6, 73.7, 71.9, 71.7, 70.7, 70.6, 68.9, 67.1, 62.9, 60.4, 59.1, 55.1, 54.4, 20.74, 20.71, 20.6.
HRMS (ESI): calc. for $C_{31}H_{43}NO_{15}Cl_3$ (M+H): 774.1698; found: 774.1703.



13

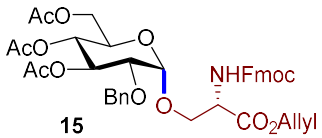
Conditions B: 73% (141 mg), α only
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.40-7.22 (m, 10 H), 5.14 (t, *J* = 10.0 Hz, 1 H), 4.96 (d, *J* = 4.0 Hz, 1 H), 4.90-4.60 (m, 5 H), 4.36 (dd, *J* = 12.0, 2.8 Hz, 1 H), 4.22-4.09 (m, 3 H), 4.00-3.88 (m, 2 H), 3.8-3.60 (m, 1 H), 3.63 (dd, *J* = 10.0, 3.2 Hz, 1 H), 3.34 (s, 3 H), 3.38-3.30 (m, 1 H), 2.08 (s, 3 H), 1.91 (s, 3 H), 1.51 (s, 3 H), 1.33 (d, *J* = 4.4 Hz, 3 H), 1.32 (s, 3 H).
^{13}C NMR (CDCl3, 100 MHz): δ = 170.9, 169.5, 138.3, 137.5, 128.4, 128.3, 128.2, 128.0, 127.7, 127.6, 109.1, 98.3, 97.7, 81.2, 79.5, 79.4, 76.8, 75.9, 75.3, 74.3, 69.3, 67.6, 64.6, 61.6, 54.6, 28.1, 26.3, 20.74, 20.72, 17.3.
HRMS (ESI): calc. for $C_{34}H_{44}O_{12}Na$ (M+Na): 667.2730; found: 667.2735.



14

Conditions B': 55% (54.3mg) α:β = 7:1

^{1}H and ^{13}C NMR of disaccharide **14** has been reported.[2]
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.37 – 7.05 (m, 35H), 5.69 (d, *J* = 3.5 Hz, 1H), 5.03 (d, *J* = 11.6 Hz, 1H), 4.91 – 4.39 (m, 13H), 4.27 (d, *J* = 12.2 Hz, 1H), 4.11 – 4.01 (m, 2H), 3.93 – 3.80 (m, 3H), 3.74 – 3.69 (m, 1H), 3.67 – 3.56 (m, 3H), 3.51 – 3.46 (m, 2H), 3.41 – 3.39 (m, 1H), 3.37 (s, 3H). ^{1}H NMR matches with the literature report.[2]

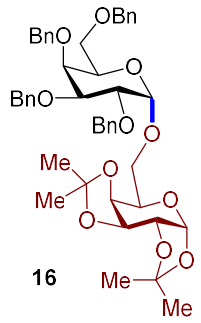


15

Conditions B: 79% (147 mg), α:β = 20:1

^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.76 (d, *J* = 7.6 Hz, 2 H), 7.63(dd, *J* = 7.6, 3.2 Hz, 2 H), 7.40-7.23 (m, 9 H), 6.04 (d, *J* = 8.8 Hz, 1 H), 5.94-5.83 (m, 1 H), 5.40 (t, *J* = 9.6 Hz, 1 H), 5.32 (d, *J* = 16.0 Hz, 1 H), 5.24 (d, *J* = 9.6 Hz, 1 H), 4.95 (t, *J* = 10.0 Hz, 1 H), 4.77 (d, *J* = 3.2 Hz, 1 H), 4.68-4.38 (m, 5 H), 4.45-4.40 (m, 2 H), 4.26-3.95 (m, 5 H), 3.90 (dd, *J* = 10.0, 3.2 Hz, 1 H), 3.57 (dd, *J* = 10.0, 3.6 Hz, 1 H), 2.05 (s, 3 H), 2.02 (s, 6 H).

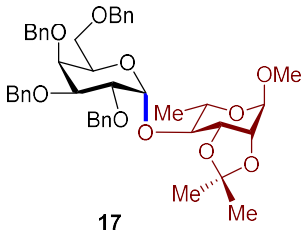
^{13}C NMR (CDCl3, 100 MHz): δ = 170.5, 170.0, 169.7, 169.4, 155.9, 143.70, 143.67, 141.2, 137.5, 131.4, 128.9, 129.5, 128.4, 128.1, 128.0, 127.7, 127.6, 127.0, 125.1, 119.9, 119.0, 98.1, 76.6, 72.8, 71.6, 70.2, 68.4, 67.8, 67.2, 66.4, 61.9, 54.5, 47.0, 20.7, 20.59, 20.57.
HRMS (ESI): calc. for $C_{40}H_{44}NO_{13}$ (M+H): 746.2813; found: 746.2810.



16

Conditions E: 77% (120.4mg) α:β = 10:1

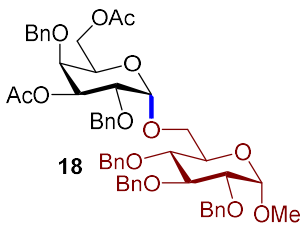
^{1}H and ^{13}C NMR of disaccharide **16** has been reported.[4]
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.43 – 7.10 (m, 20H), 5.53 (d, *J* = 5.0 Hz, 1H), 5.03 (d, *J* = 3.6 Hz, 1H), 4.95 (d, *J* = 11.4 Hz, 1H), 4.85 (d, *J* = 11.7 Hz, 1H), 4.78 – 4.72 (m, 3H), 4.62 – 4.56 (m, 2H), 4.52 – 4.40 (m, 2H), 4.35 – 4.29 (m, 2H), 4.10 – 3.95 (m, 5H), 3.84 – 3.73 (m, 2H), 3.62 – 3.51 (m, 2H), 1.54 (s, 3H), 1.45 (s, 3H), 1.35 – 1.29 (m, 6H). ^{1}H NMR matches with the literature report.[4]



17

Conditions F: 58% (86.4mg), α only

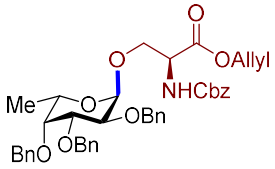
^{1}H and ^{13}C NMR of disaccharide **17** has been reported.[2]
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.39 – 7.21 (m, 20H), 4.98 – 4.92 (m, 2H), 4.87 – 4.81 (m, 2H), 4.75 – 4.68 (m, 3H), 4.59 (d, *J* = 11.3 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.39 (d, *J* = 11.9 Hz, 1H), 4.24 (dd, *J* = 9.2, 4.5 Hz, 1H), 4.16 – 4.04 (m, 4H), 3.96 (dd, *J* = 10.2, 2.7 Hz, 1H), 3.77 – 3.60 (m, 2H), 3.50 (dd, *J* = 8.3, 4.6 Hz, 1H), 3.36 – 3.27 (m, 4H), 1.37 (s, 3H), 1.30 (d, *J* = 6.3 Hz, 3H), 1.25 (s, 3H). ^{1}H NMR matches with the literature report.[2]



18

Conditions A: 85% (151 mg), α only

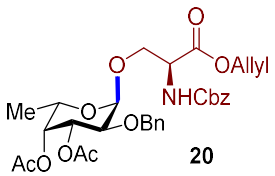
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.41-7.21 (m, 25 H), 5.30 (dd, *J* = 10.8, 3.2 Hz, 1 H), 5.05 (d, *J* = 3.2 Hz, 1 H), 5.01 (d, *J* = 11.2 Hz, 1 H), 4.96 (d, *J* = 11.2 Hz, 1 H), 4.85 (d, *J* = 11.2 Hz, 1 H), 4.78-4.60 (m, 7 H), 4.53 (d, *J* = 11.6 Hz, 1 H), 4.17-4.00 (m, 6 H), 3.85-3.70 (m, 3 H), 3.61 (t, *J* = 9.6 Hz, 1 H), 3.45 (dd, *J* = 9.6, 3.6 Hz, 1 H), 3.41 (s, 3 H), 2.05 (s, 3 H), 1.96 (s, 3 H).
^{13}C NMR (CDCl3, 100 MHz): δ = 170.3, 170.2, 138.6, 138.3, 138.2, 138.0, 137.5, 128.3, 128.25, 128.21, 128.18, 128.0, 127.9, 127.82, 127.77, 127.7, 127.6, 127.5, 127.4, 97.7, 97.3, 81.9, 79.8, 77.8, 75.5, 74.98, 74.95, 74.9, 73.6, 73.1, 72.2, 70.1, 67.8, 66.1, 62.7, 55.0, 20.9, 20.6.
HRMS (ESI): calc. for $C_{52}H_{58}O_{13}Na$ (M+Na): 913.3775; found: 913.3787.



19

Conditions D: 80% (55.7 mg), α:β = 6:1

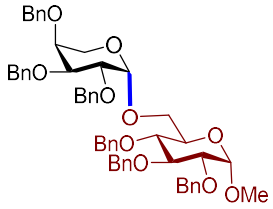
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.42 – 7.19 (m, 20H), 6.08 (d, *J* = 9.0 Hz, 1H), 5.90 – 5.80 (m, 1H), 5.29 (d, *J* = 17.2 Hz, 1H), 5.21 – 5.12 (m, 3H), 4.97 (d, *J* = 11.6 Hz, 1H), 4.85 – 4.77 (m, 2H), 4.73 – 4.53 (m, 7H), 4.20 (dd, *J* = 9.9, 2.2 Hz, 1H), 4.01 (dd, *J* = 10.1, 3.6 Hz, 1H), 3.80 (dd, *J* = 10.1, 2.7 Hz, 1H), 3.73 (q, *J* = 6.4 Hz, 1H), 3.60 – 3.52 (m, 2H), 1.07 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (CDCl3, 100 MHz): δ = 170.0, 156.2, 138.8, 138.5, 138.4, 136.3, 131.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.6, 127.5, 118.6, 98.9, 79.0, 77.6, 76.4, 74.8, 73.3, 73.2, 69.0, 67.0, 66.8, 66.0, 54.4, 16.5.
HRMS (ESI): calc. for $C_{41}H_{45}NO_9Na$ (M+Na): 718.2987; found: 718.2967.



20

Conditions B: 88% (107 mg), α:β = 20:1

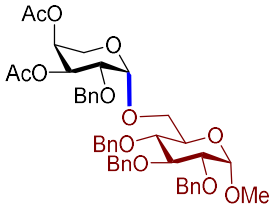
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.38-7.20 (m, 10 H), 6.00-5.93 (m, 2 H), 5.40-5.07 (m, 6 H), 4.74-4.52 (m, 6 H), 4.25 (dd, *J* = 10.0, 6.4 Hz, 1 H), 4.04-3.98 (m, 1 H), 3.81 (dd, *J* = 10.0, 3.6 Hz, 1 H), 3.57 (dd, *J* = 10.0, 3.2 Hz, 1 H), 2.13 (s, 3 H), 1.97 (s, 3 H), 1.08 (d, *J* = 6.4 Hz, 3 H).
^{13}C NMR (CDCl3, 100 MHz): δ = 170.3, 169.8, 169.5, 156.0, 137.9, 136.2, 131.4, 128.39, 128.36, 128.0, 127.8, 127.6, 119.1, 98.5, 73.4, 73.1, 71.2, 69.9, 69.1, 67.0, 66.2, 64.6, 54.3, 20.7, 20.6, 15.7.
HRMS (ESI): calc. for $C_{31}H_{37}NO_{11}Na$ (M+Na): 622.2264; found: 622.2265.



21

Conditions D': 47% (61mg), α only

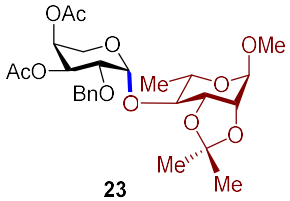
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.42-7.22 (m, 30 H), 5.00-4.60 (m, 14 H), 4.03-3.96 (m, 2 H), 3.88-3.58 (m, 8 H), 3.46 (dd, *J* = 12.0, 4.0 Hz, 1 H), 3.32 (s, 3 H).
^{13}C NMR (CDCl3, 100 MHz): δ = 138.82, 138.76, 138.6, 138.4, 138.3, 138.1, 128.32, 128.26, 128.24, 128.18, 127.91, 127.89, 127.8, 127.6, 127.4, 98.3, 97.8, 82.0, 80.0, 77.9, 76.3, 76.2, 75.6, 74.9, 73.9, 73.3, 72.8, 72.4, 71.6, 70.2, 66.4, 60.5, 54.9.
HRMS (ESI): calc. for $C_{54}H_{58}O_{10}Na$ (M+Na): 889.3922; found: 889.3943.



22

Conditions B: 84% (130 mg), α only

^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.42-7.22 (m, 20 H), 5.39-5.32 (m, 2 H), 5.05 (d, *J* = 3.6 Hz, 1 H), 5.02 (d, *J* = 10.8 Hz, 1 H), 4.97 (d, *J* = 11.2 Hz, 1 H), 4.86 (d, *J* = 11.2 Hz, 1 H), 4.76 (d, *J* = 11.2 Hz, 1 H), 4.71-4.58 (m, 5 H), 4.01 (t, *J* = 10.0 Hz, 1 H), 3.96-3.53 (m, 7 H), 3.46 (dd, *J* = 9.6, 3.6 Hz, 1 H), 3.41 (s, 3 H), 2.13 (s, 3 H), 2.04 (s, 3 H).
^{13}C NMR (CDCl3, 100 MHz): δ = 107.1, 169.9, 138.7, 138.3, 138.1, 138.0, 128.3, 128.21, 128.20, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 97.8, 97.7, 82.0, 79.9, 77.7, 75.5, 74.9, 73.7, 73.2, 72.2, 70.2, 69.4, 69.0, 66.2, 60.3, 55.0, 20.8, 20.7.
HRMS (ESI): calc. for $C_{44}H_{50}O_{12}Na$ (M+Na): 793.3200; found: 793.3211.

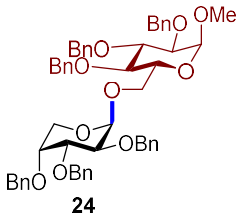


23

Conditions B: 73% (76 mg), α only

^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.38-7.25 (m, 5 H), 5.36-5.30 (m, 2 H), 5.08 (d, *J* = 3.6 Hz, 1 H), 4.85 (s, 1 H), 4.72-4.63 (m, 2 H), 4.37 (d, *J* = 13.2 Hz, 1 H), 4.19-4.10 (m, 2 H), 3.73 (dd, *J* = 10.0, 6.4 Hz, 1 H), 3.77-3.55 (m, 2 H), 3.40 (dd, *J* = 10.0, 6.4 Hz, 1 H), 3.53 (s, 3 H), 2.11 (s, 3 H), 2.00 (s, 3 H), 1.50 (s, 3 H), 1.34 (s, 3 H), 1.31 (d, *J* = 6.4 Hz, 3 H).

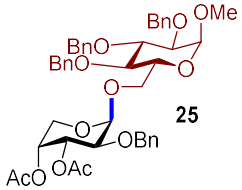
^{13}C NMR (CDCl3, 100 MHz): δ = 170.2, 169.9, 137.8, 128.3, 127.83, 127.78, 109.0, 98.4, 97.7, 80.2, 76.8, 76.1, 74.0, 73.7, 69.8, 69.4, 64.8, 61.0, 54.6, 27.7, 26.3, 20.9, 20.8, 17.3.
HRMS (ESI): calc. for $C_{26}H_{36}O_{11}Na$ (M+Na): 547.2155; found: 547.2156.



24

Conditions D': 48% (62mg), α:β = 9:1

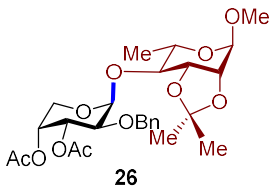
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.42-7.22 (m, 30 H), 5.00-4.60 (m, 14 H), 4.03-3.56 (m, 10 H), 3.50 (dd, *J* = 8.0, 4.0 Hz, 1 H), 3.32 (s, 3 H).
^{13}C NMR (CDCl3, 100 MHz): δ = 138.7, 138.62, 138.58, 138.4, 138.3, 138.2, 128.4, 128.31, 128.28, 128.2, 128.1, 1287.94, 127.90, 127.83, 127.75, 127.7, 127.6, 127.5, 98,.3, 97.9, 82.0, 80.0, 77.7, 76.2, 75.7, 74.9, 73.7, 73.4, 73.2, 72.3, 71.7, 70.0, 66.4, 60.4, 55.0.
HRMS (ESI): calc. for $C_{54}H_{58}O_{10}Na$ (M+Na): 889.3922; found: 889.3959.



25

Conditions A: 83% (128 mg), α only

^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.43-7.20 (m, 20 H), 5.39-5.36 (m, 2 H), 5.02-4.94 (m, 2 H), 4.87-4.80 (m, 3 H), 4.75-4.60 (m, 5 H), 4.07-3.97 (m, 2 H), 3.95-3.88 (m, 2 H), 3.81 (dd, *J* = 10.0, 3.2 Hz, 1 H), 3.76-3.57 (m, 4 H), 3.37 (s, 3 H), 2.15 (s, 3 H), 2.03 (s, 3 H).
^{13}C NMR (CDCl3, 100 MHz): δ = 170.2, 170.0, 138.7, 138.5, 138.2, 137.9, 128.3, 128.22, 128.19, 128.0, 127.8, 127.7, 127.53, 127.46, 127.41, 127.38, 127.3, 98.0, 97.9, 81.8, 80.2, 77.4, 75.6, 74.8, 73.8, 73.4, 73.0, 69.6, 69.4, 66.6, 60.4, 55.0, 20.9, 20.8.
HRMS (ESI): calc. for $C_{44}H_{50}O_{12}Na$ (M+Na): 793.3200; found: 793.3204.

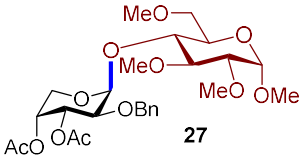


26

Conditions B: 71% (74 mg), α only

^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.39-7.28 (m, 5 H), 5.75 (d, *J* = 3.6 Hz, 1 H), 5.34-5.31 (m, 1 H), 5.25 (dd, *J* = 10.4, 3.6 Hz, 1 H), 4.86 (s, 1 H), 4.77 (d, *J* = 12.0 Hz, 1 H), 4.65 (d, *J* = 12.0 Hz, 1 H), 4.26 (dd, *J* = 6.8, 5.6 Hz, 1 H), 4.10 (d, *J* = 5.6 Hz, 1 H), 3.99 (dd, *J* = 12.8, 1.2 Hz, 1 H), 3.90 (dd, *J* = 10.4, 3.6 Hz, 1 H), 3.78-3.70 (m, 1 H), 3.67 (dd, *J* = 12.8, 2.0 Hz, 1 H), 3.55 (dd, *J* =

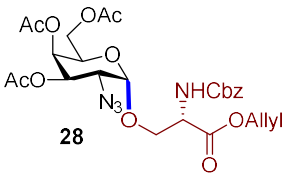
10.0, 6.4 Hz, 1 H), 3.36 (s, 3 H), 2.11 (s, 3 H), 2.03 (s, 3 H), 1.54 (s, 3 H), 1.36 (s, 3 H), 1.33 (d, *J* = 6.4 Hz, 3 H).
^{13}C NMR (CDCl3, 100 MHz): δ = 170.2, 169.9, 138.0, 128.2, 127.7, 109.2, 97.9, 95.7, 78.4, 77.9, 76.0, 73.3, 72.6, 69.4, 68.8, 63.5, 60.7, 54.6, 27.9, 26.3, 20.9, 20.8, 18.2.
HRMS (ESI): calc. for $C_{26}H_{36}O_{11}Na$ (M+Na): 547.2155; found: 547.2150.



27

Conditions B: 82% (90 mg), α only

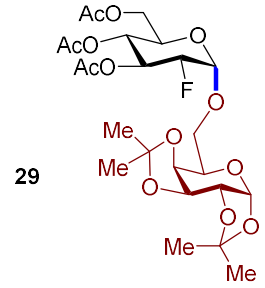
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.39-7.27 (m, 5 H), 5.35-5.30 (m, 2 H), 5.08 (d, *J* = 4.0 Hz, 1 H), 4.82 (d, *J* = 3.2 Hz, 1 H), 4.75-4.63 (m, 2 H), 4.29 (d, *J* = 13.2 Hz, 1 H), 3.95 (dd, *J* = 10.0, 4.0, Hz, 1 H), 3.76-3.40 (m, 6 H), 3.59 (s, 3 H), 3.49 (s, 3 H), 3.40 (s, 3 H), 3.27 (dd, *J* = 10.0, 4.0 Hz, 1 H), 3.21 (s, 3 H), 2.12 (s, 3 H), 1.99 (s, 3 H).
^{13}C NMR (CDCl3, 100 MHz): δ = 170.3, 169.9, 137.8, 128.4, 128.0, 127.9, 98.5, 97.2, 82.5, 81.2, 75.2, 74.2, 74.1, 70.0, 69.8, 69.7, 60.9, 60.7, 58.8, 58.6, 55.1, 20.9, 20.8.
HRMS (ESI): calc. for $C_{26}H_{38}O_{12}Na$ (M+Na): 565.2261; found: 564.2260.



28

Conditions C: 50% (59 mg), α only

^{1}H and ^{13}C NMR of disaccharide **28** has been reported.[5]
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.40-7.30 (m, 5 H), 5.98-5.87 (m, 1 H), 5.82 (d, *J* = 8.0 Hz, 1 H), 5.46-5.23 (m, 4 H), 5.20-5.10 (m, 2 H), 4.97 (d, *J* = 3.6 Hz, 1 H), 4.70-4.56 (m, 3 H), 4.22-4.00 (m, 5 H), 3.62 (dd, *J* = 11.2, 3.6 Hz, 1 H), 2.14 (s, 3 H), 2.05 (s, 3 H), 2.02 (s, 3 H). ^{1}H NMR matches with the literature report.[5]

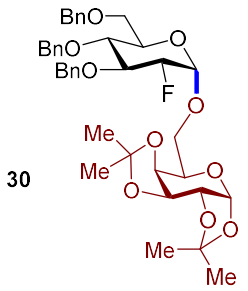


29

Conditions B: 61% (50 mg), α:β > 20:1

^{1}H and ^{13}C NMR of disaccharide **29** has been reported. [6]
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 5.58-5.45 (m, 2 H), 5.11 (d, *J* = 4.0 Hz, 1 H), 5.01 (t, *J* = 8.0 Hz, 1 H), 4.60 (dd, *J* = 8.0, 4.0 Hz, 1 H), 4.48 (ddd, *J* = 48.0, 8.0, 4.0 Hz, 1 H), 4.34-4.25 (m, 3

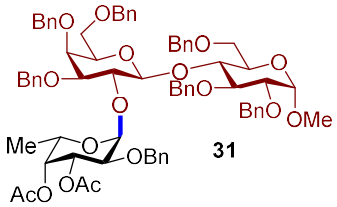
H), 4.18-4.00 (m, 3 H), 3.90-3.73 (m, 2 H), 2.07(s, 3 H), 2.05 (s, 3 H), 2.02 (s, 3 H), 1.55 (s, 3 H), 1.41 (s, 3 H), 1.32 (s, 3 H), 1.31 (s, 3 H). ^{1}H NMR matches with the literature report. [6]
^{19}F NMR (CDCl$_3$, 376 MHz): δ = -201.4.



30

Conditions D': 83% (85 mg), α:β = 16:1

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.39-7.15 (m, 15H), 5.52 (d, *J* = 4.8 Hz, 1H), 5.11 (d, *J* = 4.0 Hz, 1H), 4.90 (d, *J* = 10.8 Hz, 1H), 4.84 (d, *J* = 11.2 Hz, 1H), 4.76 (d, *J* = 10.8 Hz, 1H), 4.66-4.57 (m, 2.5H), 4.51-4.45 (m, 2.5H), 4.33-4.29 (m, 2H), 4.10 (dt, *J* = 12.4, 9.2 Hz, 1H), 4.02 (t, *J* = 6.0 Hz, 1H), 3.90 (dt, *J* = 10.0, 2.0 Hz, 1H), 3.84 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.81-3.66 (m, 4H), 1.55 (s, 3H), 1.45 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H)
^{13}C NMR (CDCl3, 100 MHz): δ = 138.5, 138.2, 137.9, 128.4, 128.3, 127.9, 127.9, 127.8, 127.7, 127.7, 127.7, 127.7, 109.3, 108.6, 96.8 (d, $J_{c\text{-}F}$ = 20.9 Hz), 96.3, 91.1 (d, $J_{c\text{-}F}$ = 191.0 Hz), 80.6 (d, $J_{c\text{-}F}$ = 16.1 Hz), 76.8 (d, $J_{c\text{-}F}$ = 8.3 Hz), 75.1 (d, $J_{c\text{-}F}$ = 2.7 Hz), 75.0, 73.5, 70.74, 70.68, 70.6, 70.2, 68.1, 66.9, 66.2, 26.2, 26.0, 25.0, 24.5
^{19}F NMR (376 MHz, CDCl$_3$): δ -199.09 (dd, *J* = 49.5, 12.2 Hz).
HRMS (ESI): calc. for $C_{38}H_{47}O_{10}FNa$ (M+Na): 717.3051; found: 713.3044.



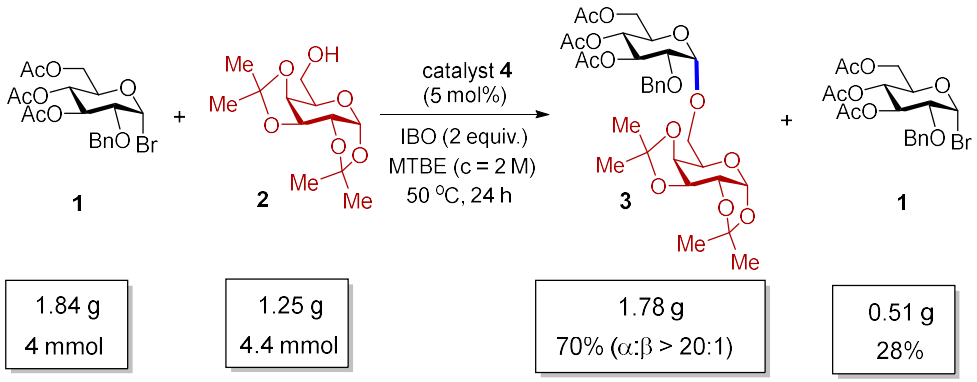
31

Conditions B: 86% (213 mg), α only

^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.42-6.98 (m, 35 H), 5.72 (d, *J* = 2.4 Hz, 1 H), 5.32 (dd, *J* = 10.8, 2.8 Hz, 1 H), 5.18 (s 1 H), 5.04 (d, *J* = 9.6 Hz, 1 H), 4.90-4.58 (m, 8 H), 4.50-4.40 (m, 5 H), 4.36-4.25 (m, 3 H), 4.17-4.06 (m, 3 H), 3.95 (s, 1 H), 3.82-3.58 (m, 5 H), 3.55-3.45 (m, 2 H), 3.43 (s, 3 H), 3.39-3.30 (m, 2 H), 2.10 (s, 3 H), 1.99 (s, 3 H), 1.08 (d, *J* = 6.4 Hz, 3 H).
^{13}C NMR (CDCl3, 100 MHz): δ = 170.5, 170.0, 140.0, 138.6, 138.3, 138.03, 138.01, 137.9, 128.5, 128.30, 128.27, 128.2, 128.1, 128.0, 127.8, 127.7, 127.64, 127.58, 127.56, 127.5, 127.31, 127.28, 127.2, 127.02, 126.97, 126.1, 100.2, 98.3, 96.8, 83.8, 80.3, 78.7, 75.6, 75.0, 74.6, 73.7, 73.3, 73.2, 73.03, 72.98, 72.8, 72.2, 71.7, 70.7, 69.7, 69.6, 67.9, 67.6, 64.2, 55.3, 20.7, 20.5, 15.5.
HRMS (ESI): calc. for $C_{31}H_{37}NO_{11}Na$ (M+Na): 622.2264; found: 622.2265.

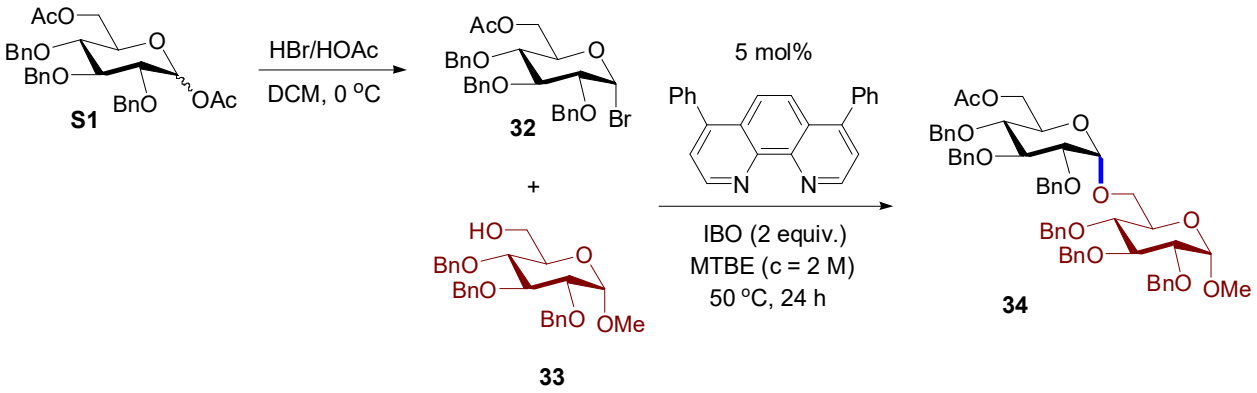
Gram Scale synthesis

Figure S7. Gram Scale Synthesis of Disaccharide 3



A 50 mL round-bottom flask was charged with glycosyl bromide **1** (1.83 g, 4.0 mmol, 1.0 equiv), alcohol **2** (1.25 g, 4.8 mmol, 1.2 equiv), catalyst **4** (66 mg, 0.2 mmol, 15 mol%), IBO (0.7 mL, 8.0 mmol, 2.0 equiv.) and MTBE (2.0 mL). The resulting solution was stirred at 50 °C for 24 h under open-air atmosphere, diluted with toluene, and purified by silica gel flash chromatography (toluene/ethyl acetate: 5/1→3/1) to give the desired disaccharide **3** (1.784 g, 70%, α:β > 20:1) and recovered **1** (0.515 g, 28%).

Synthesis of Octasaccharides 40

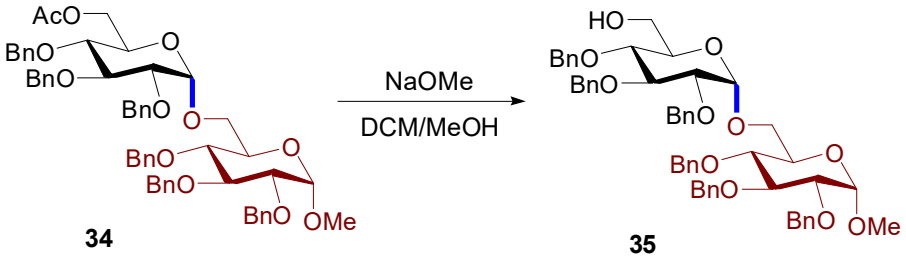


A 500 mL round-bottom flask was charged with **S1** (8.03 g, 15.0 mmol, 1.5 equiv.) and DCM (150 mL). The solution was cooled to 0 °C, then HBr/HOAc (33% wt, 15 mL) was added. The solution was stirred at 0 °C for 30 minutes till the reaction was complete as monitored by TLC. The solution was diluted with ethyl acetate, washed with saturated $NaHCO_3$ solution for two times, dried over Na_2SO_4, concentrated in vacuo, and the afforded glycosyl bromide **32** was used directly.

A 50 mL round-bottom flask was charged with glycosyl bromide **32** (15.0 mmol, 1.5 equiv), alcohol **33** (4.63 g, 10.0 mmol, 1.0 equiv), BPhen (166 mg, 0.5 mmol, 5 mol%), IBO (1.78 mL, 20.0 mmol, 2.0 equiv.) and MTBE (2.0 mL). The resulting solution was stirred at 50 °C for 24 h under open-air atmosphere, diluted with toluene, and purified by silica gel flash chromatography (toluene/ethyl acetate: 20/1→10/1) to give the desired disaccharide **34** (8.36 g, 89%, α:β > 20:1):

^{1}H and ^{13}C NMR of disaccharide **34** has been reported.[7]

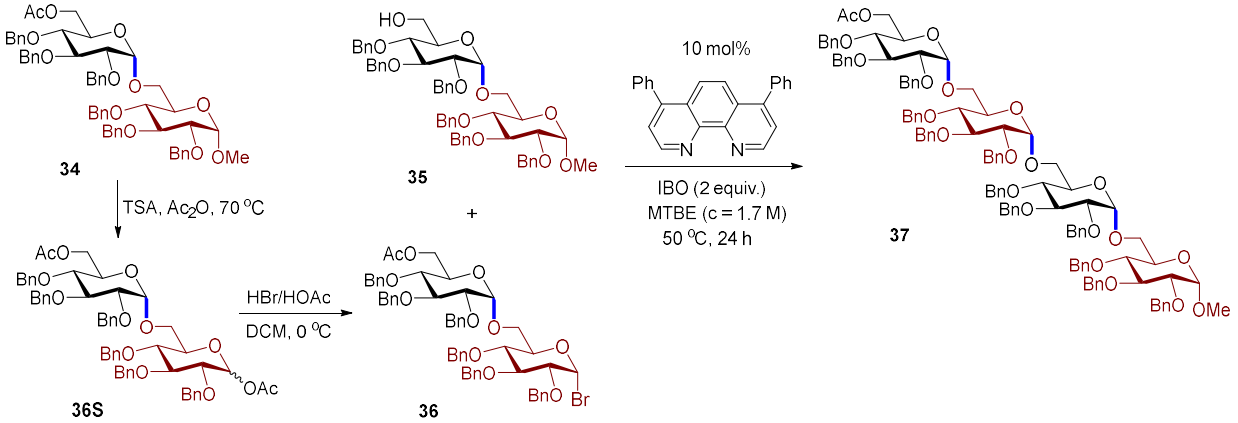
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.40-7.28 (m, 30 H), 5.00-4.60 (m, 14 H), 4.28-4.22 (m, 2 H), 4.05-4.00 (m 2 H), 3.90-3.80 (m, 3 H), 3.78-3.66 (m, 2 H), 3.55-3.46 (m, 3 H), 3.40 (s, 3 H), 2.01 (s, 3 H).



A 50 mL oven-dried RBF was charged with **34** (350 mg, 0.37 mmol, 1.0 equiv.), MeONa (10 mg, 0.19 mmol, 0.5 equiv.), and CH_2Cl_2/MeOH (1 mL/1 mL). The solution was stirred at room temperature overnight. When the reaction was complete as monitored by TLC, the reaction mixture was evaporated, and purified by flash chromatography on silica gel (hexane/ethyl acetate: 2/1→1/1) to afford 341 mg (99%) of **35**:

^{1}H and ^{13}C NMR of disaccharide **35** has been reported.[7]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.40-7.28 (m, 30 H), 5.00-4.52 (m, 14 H), 4.28-4.22 (m, 2 H), 4.05-3.46 (m, 10 H), 3.35 (s, 3 H).



A 50 mL round-bottom flask was charged with **34** (940 mg, 1.0 mmol, 1.0 equiv.), PTSA·H_2O (248 mg, 1.3 mmol, 1.3 equiv.), and Ac_2O (6 mL). The solution was stirred at 70 °C for 2 hours. The solution was diluted with ethyl acetate, washed with saturated $NaHCO_3$ (aq.) for three times, concentrated in vacuo, and the residue was purified by silica gel flash chromatography (hexane/ethyl acetate = 4/1 ~ 2/1) to afford 572 mg (61%) of **36S**:

^{1}H and ^{13}C NMR of disaccharide **36S** has been reported.[7]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.40-7.28 (m, 30 H), 6.28 (d, *J* = 4.0 Hz, 1 H), 5.00-4.60 (m, 13 H), 4.28-4.22 (m, 2 H), 4.05-3.46 (m, 11 H), 2.13 (s, 3 H), 1.99 (s, 3 H).

A 50 mL round-bottom flask was charged with **36S** (500 mg, 0.51 mmol, 1.5 equiv.) and DCM (30 mL). The solution was cooled to 0 °C, then HBr/HOAc (33% wt, 0.5 mL) was added. The solution was stirred at 0 °C for 20 minutes till the reaction was complete as monitored by TLC. The solution was diluted with ethyl acetate, washed with saturated $NaHCO_3$ solution for two times, dried over Na_2SO_4, concentrated in vacuo, and the afforded glycosyl bromide **36** was used directly.

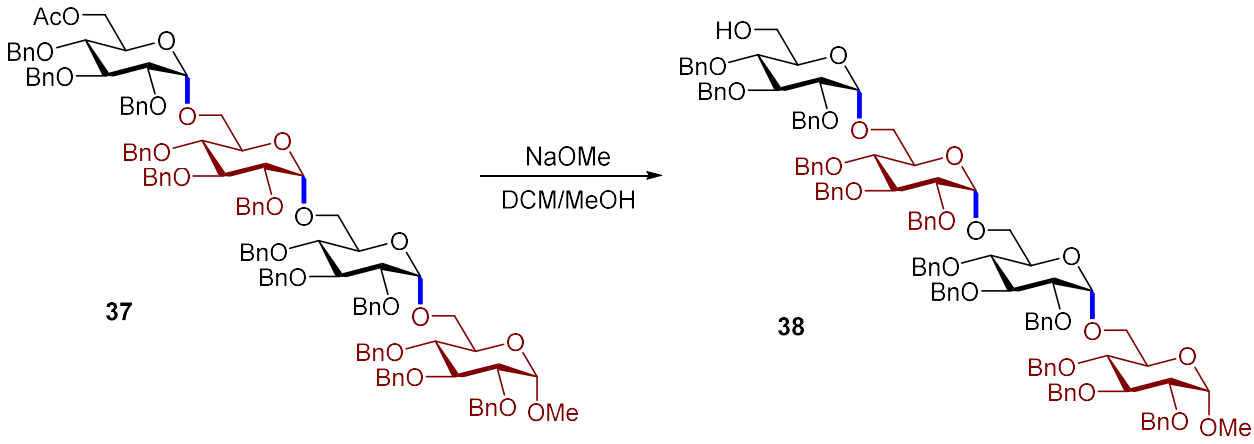
A 50 mL round-bottom flask was charged with glycosyl bromide **36** (0.51 mmol, 1.5 equiv), alcohol **33** (320 mg, 0.34 mmol, 1.0 equiv), BPhen (11 mg, 0.034 mmol, 10 mol%), IBO (0.06 mL, 0.68 mmol, 2.0 equiv.) and MTBE (0.2 mL). The resulting solution was stirred at 50 °C for 24 h under open-air atmosphere, diluted with toluene, and purified by silica gel flash chromatography (toluene/ethyl acetate: 20/1→10/1) to give the desired tetraccharide **37** (520 mg, 86%, α:β > 20:1):

^{1}H and ^{13}C NMR of disaccharide **37** has been reported.[7]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.42-7.28 (m, 60 H), 5.11 (d, *J* = 4.0 Hz, 1 H), 5.05-4.60 (m, 27 H), 4.28-4.22 (m, 2 H), 4.08-4.00 (m, 4 H), 3.90-3.75 (m 12 H), 3.60-3.42 (m, 6 H), 3.40 (s, 3 H), 2.03 (s, 3 H).

^{13}C NMR (CDCl3, 100 MHz): δ = 170.6, 138.8, 138.6, 138.5, 138.4, 138.3, 138.1, 137.9, 128.30, 128.25, 128.2, 128.0, 127.94, 127.88, 127.73, 127.70, 127.65, 127.6, 127.5, 127.44, 127.41, 127.37, 127.32, 127.28, 97.9, 97.00, 96.95, 82.0, 81.5, 80.3, 80.2, 80.1, 80.0, 77.6, 77.4, 75.6, 75.5, 75.3, 74.9, 74.8, 73.3, 72.3, 72.2, 72.1, 70.71, 70.64, 70.5, 70.3, 68.6, 65.6, 65.5, 65.5, 62.9, 55.1, 20.8.

HRMS (ESI): calc. for $C_{111}H_{118}O_{22}Na$ (M+Na): 1825.8007; found: 1925.8009.

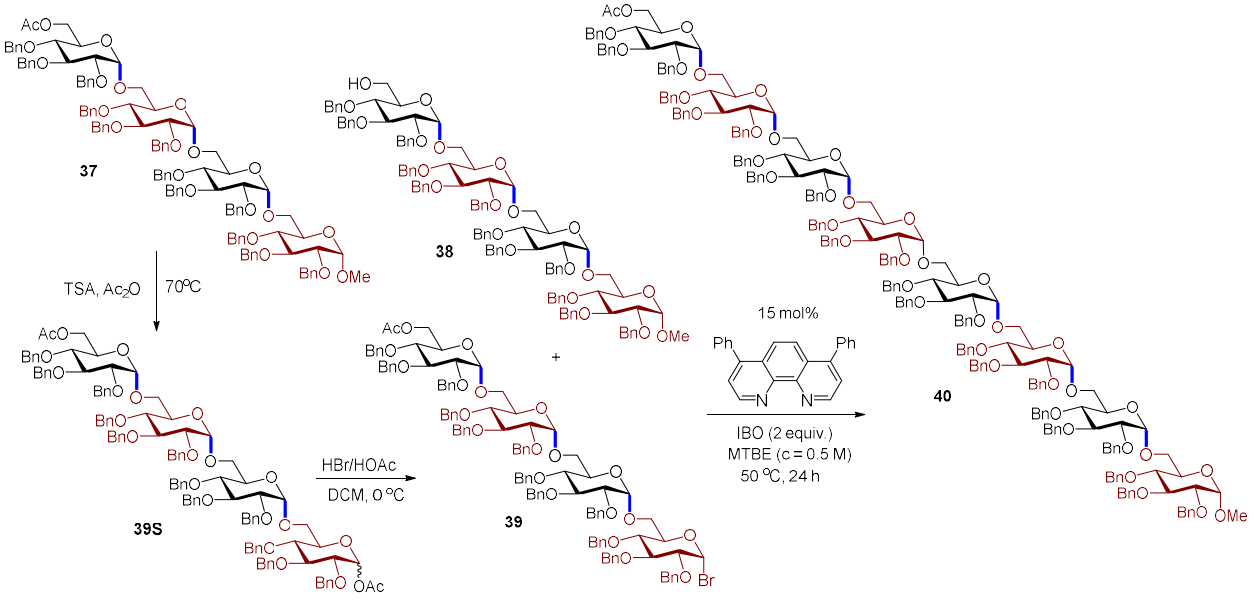


A 50 mL oven-dried RBF was charged with **37** (250 mg, 0.14 mmol, 1.0 equiv.), MeONa (4 mg, 0.07 mmol, 0.5 equiv.), and CH_2Cl_2/MeOH (1 mL/1 mL). The solution was stirred at room temperature. When the reaction was complete as monitored by TLC, the reaction mixture was evaporated, and purified by flash chromatography on silica gel (toluene/ethyl acetate: 5/1→3/1) to afford 170 mg (70%) of **38**:

^{1}H and ^{13}C NMR of disaccharide **38** has been reported.[7]

^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.42-7.28 (m, 60 H), 5.05-4.60 (m, 28 H), 4.05-3.40 (m, 24 H), 3.37 (s, 3 H).

^{13}C NMR (CDCl3, 100 MHz): δ = 138.8, 128.7, 138.6, 138.54, 138.45, 138.4, 138.3, 138.2, 138.1, 128.33, 128.30, 128.27, 128.2, 127.94, 127.91, 127.8, 127.64, 127.57, 127.5, 127.40, 127.35, 127.1, 98.0, 97.1, 97.0, 82.0, 81.5, 81.4, 77.7, 77.5, 75.6, 75.42, 75.37, 74.9, 73.3, 72.31, 72.25, 72.2, 70.82, 70.75, 70.7, 70.5, 65.8, 65.6, 65.4, 61.8, 55.1.



A 50 mL round-bottom flask was charged with **37** (500 mg, 0.27 mmol, 1.0 equiv.), PTSA·H_2O (67 mg, 0.35 mmol, 1.3 equiv.), and Ac_2O (3 mL). The solution was stirred at 70 ºC for 2 hours. The solution was diluted with ethyl acetate, washed with saturated $NaHCO_3$ (aq.) for

three times, concentrated in vacuo, and the residue was purified by silica gel flash chromatography (toluene/ethyl acetate = 8/1 ~ 5/1) to afford 249 mg (51%) of **39S**:

^{1}H and ^{13}C NMR of disaccharide **S3** has been reported.[7]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.40-7.28 (m, 60 H), 6.34 (d, *J* = 4.0 Hz, 1 H), 5.00-4.60 (m, 27 H), 4.28-4.22 (m, 2 H), 4.05-3.46 (m, 22 H), 2.08 (s, 3 H), 2.02 (s, 3 H).

A 25 mL round-bottom flask was charged with **39S** (110 mg, 0.06 mmol, 1.5 equiv.) and DCM (6 mL). The solution was cooled to 0 ºC, then HBr/HOAc (33% wt, 0.06 mL) was added. The solution was stirred at 0 ºC for 15 minutes till the reaction was complete as monitored by TLC. The solution was diluted with ethyl acetate, washed with saturated $NaHCO_3$ solution for two times, dried over Na_2SO_4, concentrated in vacuo, and the afforded glycosyl bromide **39** was used directly.

A 50 mL round-bottom flask was charged with glycosyl bromide **39** (0.06 mmol, 1.5 equiv), alcohol **38** (70 mg, 0.04 mmol, 1.0 equiv), BPhen (2 mg, 0.006 mmol, 15 mol%), IBO (0.007 mL, 0.08 mmol, 2.0 equiv.) and MTBE (0.08 mL). The resulting solution was stirred at 50 ºC for 24 h under open-air atmosphere, diluted with toluene, and purified by silica gel flash chromatography (toluene/ethyl acetate: 20/1→10/1) to give the desired octasaccharide **40** (109 mg, 77%, α:β > 20:1):

^{1}H and ^{13}C NMR of disaccharide **40** has been reported.[7]

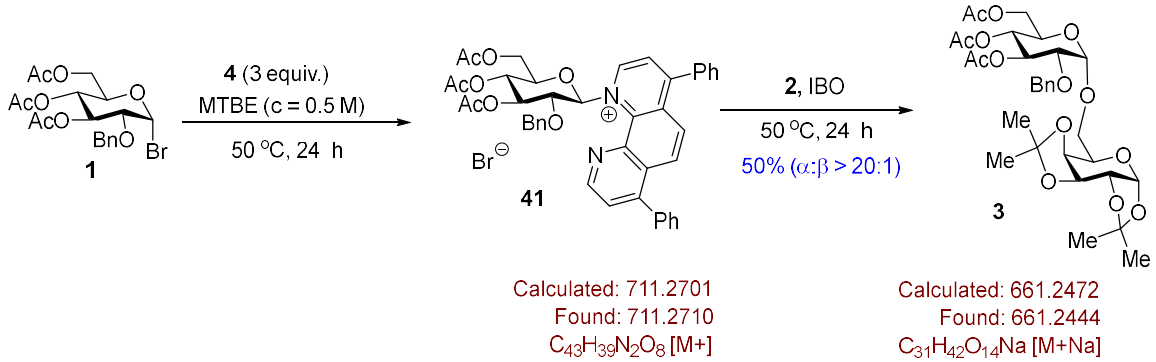
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.42-7.28 (m, 120 H), 5.05 (d, *J* = 4.0 Hz, 1 H), 5.05-4.40 (m, 54 H), 4.25-4.18 (m, 2 H), 4.08-4.00 (m, 8 H), 3.90-3.30 (m 39 H), 3.32 (s, 3 H), 1.98 (s, 3 H).

^{13}C NMR (CDCl3, 100 MHz): δ = 170.7, 138.8, 138.6, 138.54, 138.46, 138.4, 138.2, 138.0, 128.38, 128.36, 128.3, 128.2, 128.04, 127.99, 127.9, 127.8, 127.6, 127.5, 127.4, 127.34, 127.27, 98.0, 97.30, 97.25, 97.18, 97.16, 97.1, 97.0, 82.1, 81.5, 80.4, 80.3, 80.2, 80.0, 75.7, 75.5, 75.4, 75.0, 74.9, 73.4, 72.2, 72.13, 72.07, 70.88, 70.87, 70.8, 70.7, 70.6, 68.7, 65.5, 63.0, 55.1, 20.8.

HRMS (ESI): calc. for $C_{219}H_{230}O_{42}Na$ (M+Na): 3554.5754; found: 3554.5867.

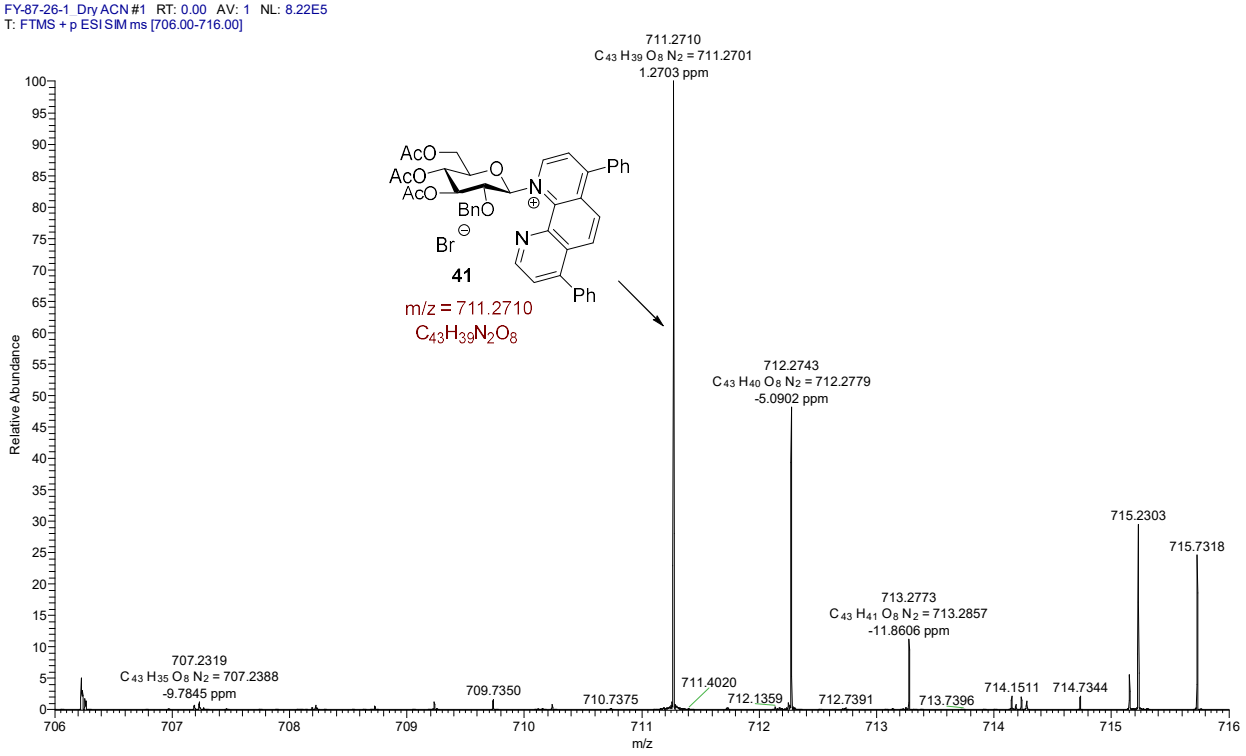
4. Mechanistic Studies

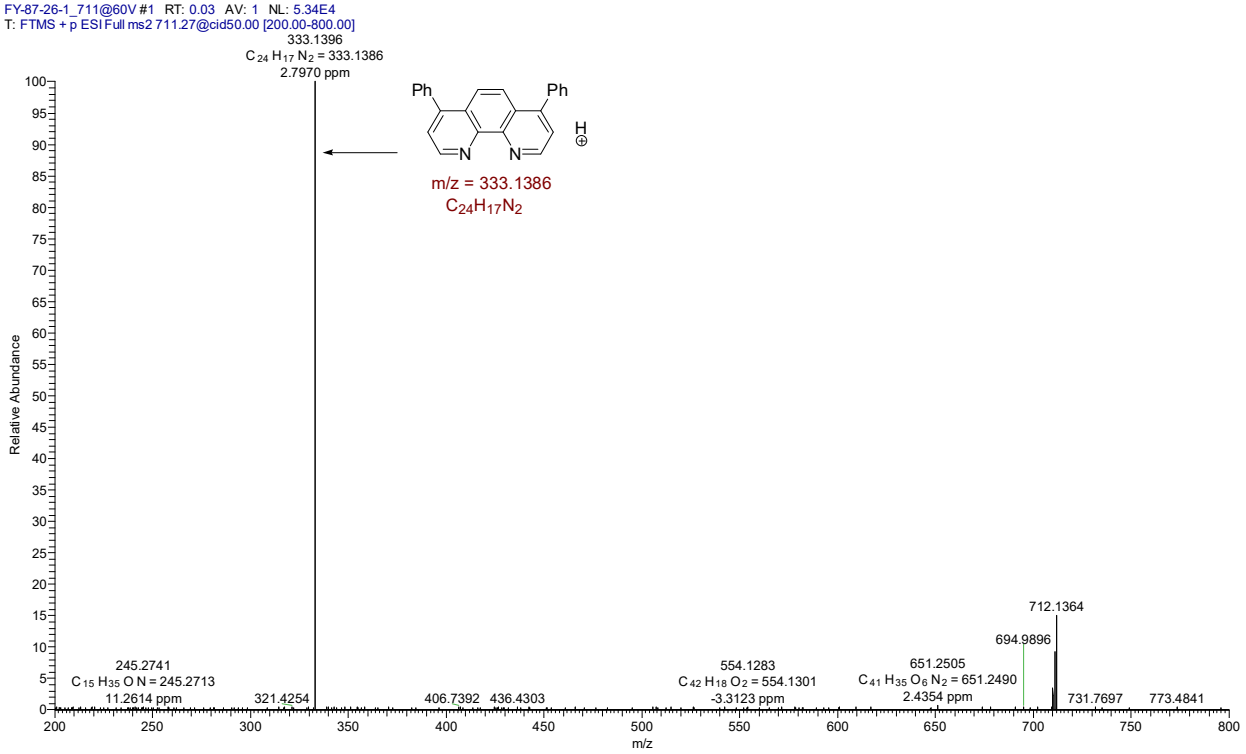
Figure S8. High Resolution Mass Spectrometry Analysis of Glycosyl Phenanthrolium 41



A 10 mL bottle was charged with glycosyl bromide **1** (46 mg, 0.1 mmol, 1.0 equiv), **4** (100 mg, 0.3 mmol, 3.0 equiv.), and MTBE (1.2 mL). The reaction mixture was stirred at 50 °C for 24 h. Formation of the glycosyl phenanthrolinium ion **41** was confirmed using electrospray ionization (ESI) with an m/z ratio of 711.2710 (see below). Subsequent fragmentation of **41** using collision induced dissociation (CID) led to the formation of various fragment ions, most notably the phenanthroline species with an m/z ratio of 331.1396 (see below). The mixture was concentrated and dried *in vacuo*. The resulting residue was mixed with alcohol **2** (39 mg, 0.15 mmol, 1.5 equiv.), and MTBE (0.4 mL). The reaction mixture was stirred at 50 °C for 12 h, formation of the desired disaccharide **3** was confirmed by high resolution electrospray ionization (ESI), diluted with toluene, and purified by silica gel flash chromatography (toluene/ethyl acetate: 5/1→3/1) to give the desired disaccharide **3** (31 mg, 50%, α:β > 20:1).

Sample Preparation for ESI: 50 µL of a solution of glycosyl bromide **1** (46 mg, 0.1 mmol, 1.0 equiv), catalyst **4** (100 mg, 0.3 mmol, 3.0 equiv.), and MTBE (1.2 mL) was diluted with 1 mL of dry acetonitrile (ACN). The resulting acetonitrile sample was infused at a rate of 5 µl/min via syringe pump.


FY-87-26-1 Dry ACN #1 RT: 0.00 AV: 1 NL: 8.22E5
T: FTMS + p ESI SIM ms [706.00-716.00]
711.2710
C43 H39 O8 N2 = 711.2701
1.2703 ppm
AcO
AcO
AcO
O
BnO
Br
N
Ph
N
Ph
41
m/z = 711.2710
C43H39N2O8
712.2743
C43 H40 O8 N2 = 712.2779
-5.0902 ppm
715.2303
715.7318
713.2773
C43 H41 O8 N2 = 713.2857
-11.8606 ppm
707.2319
C43 H35 O8 N2 = 707.2388
-9.7845 ppm
709.7350
710.7375
711.4020
712.1359
712.7391
713.7396
714.1511
714.7344
Relative Abundance
m/z


FY-87-26-1_711@60V #1 RT: 0.03 AV: 1 NL: 5.34E4
T: FTMS + p ESI Full ms2 711.27@cid50.00 [200.00-800.00]
333.1396
C24 H17 N2 = 333.1386
2.7970 ppm
Ph
Ph
N
N
H
m/z = 333.1386
C24H17N2
712.1364
694.9896
245.2741
C15 H35 O N = 245.2713
11.2614 ppm
321.4254
406.7392
436.4303
554.1283
C42 H18 O2 = 554.1301
-3.3123 ppm
651.2505
C41 H35 O6 N2 = 651.2490
2.4354 ppm
731.7697
773.4841
Relative Abundance
m/z

FY 87-31 #1 RT: 0.01 AV: 1 NL: 4.79E3
T: FTMS + p ESI Full ms [50.00-1500.00]

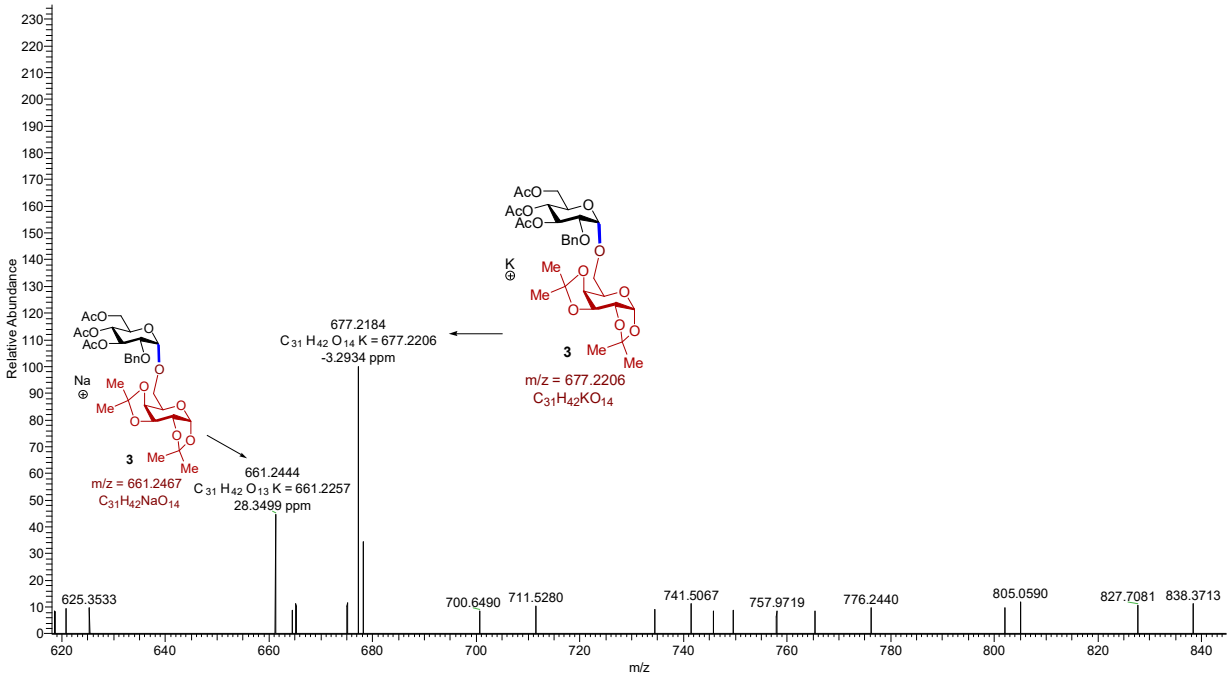


Figure S9. Attempted Isomerization of Disaccharide 3.

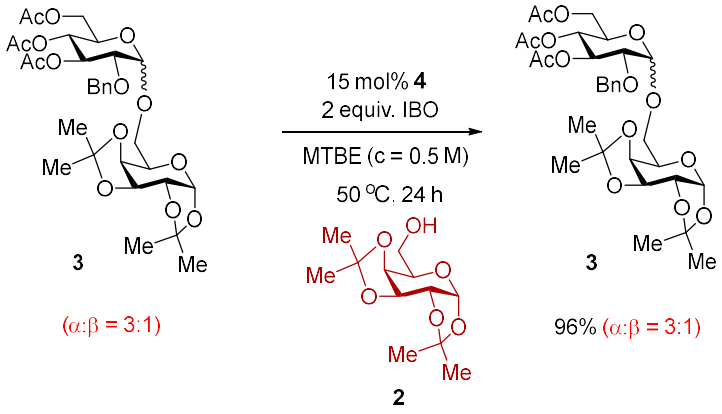
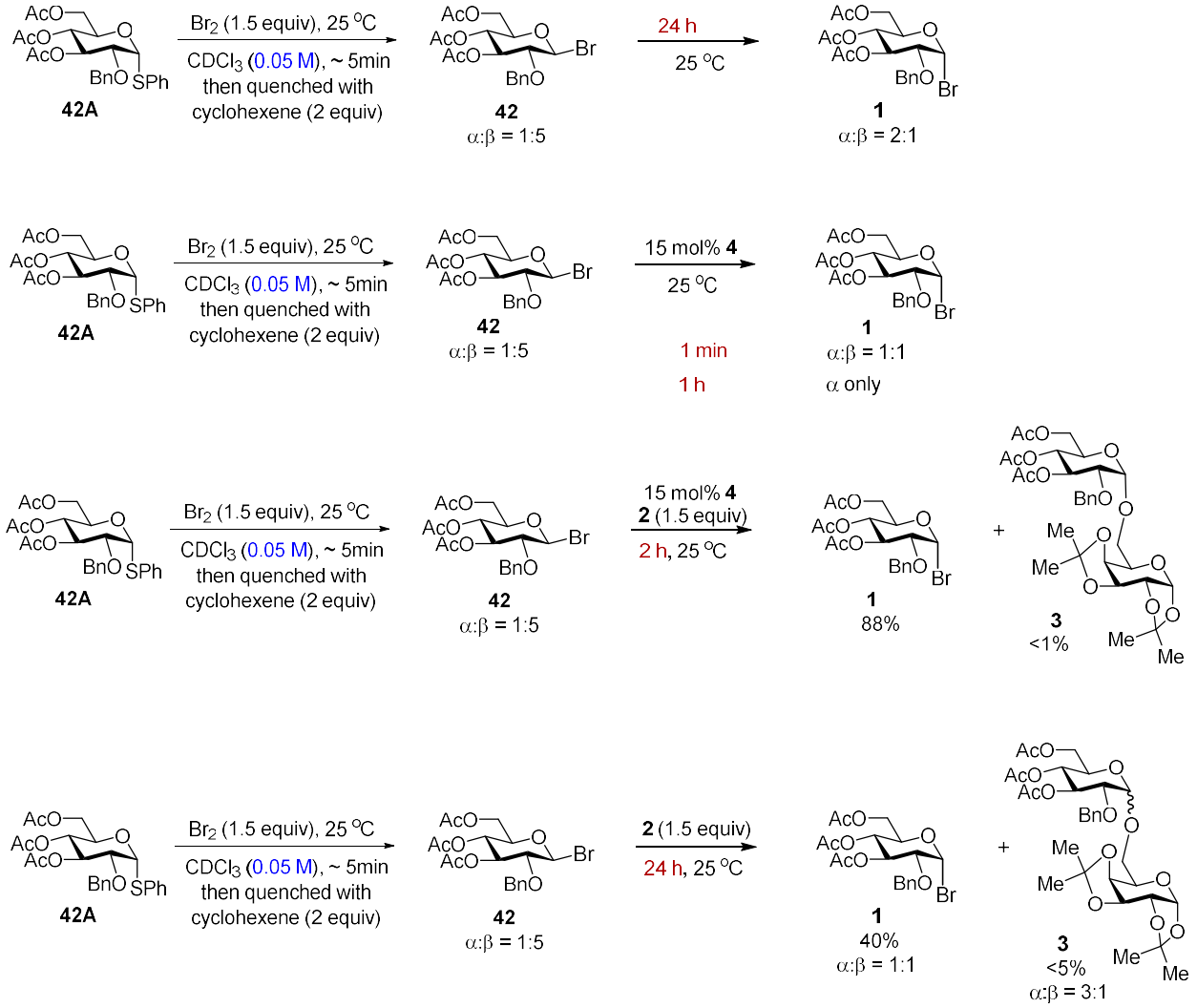
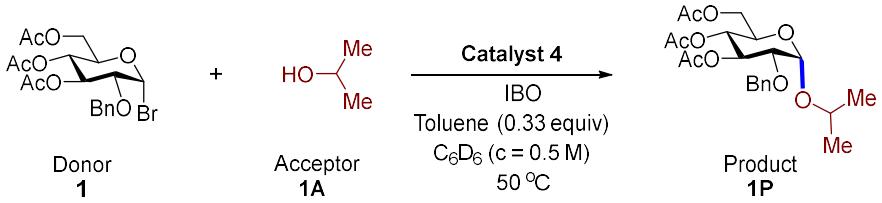


Figure S10. Anomerization of β-Bromide to α-Bromide



5. Kinetic Study

General Experimental Procedure for Kinetic Studies

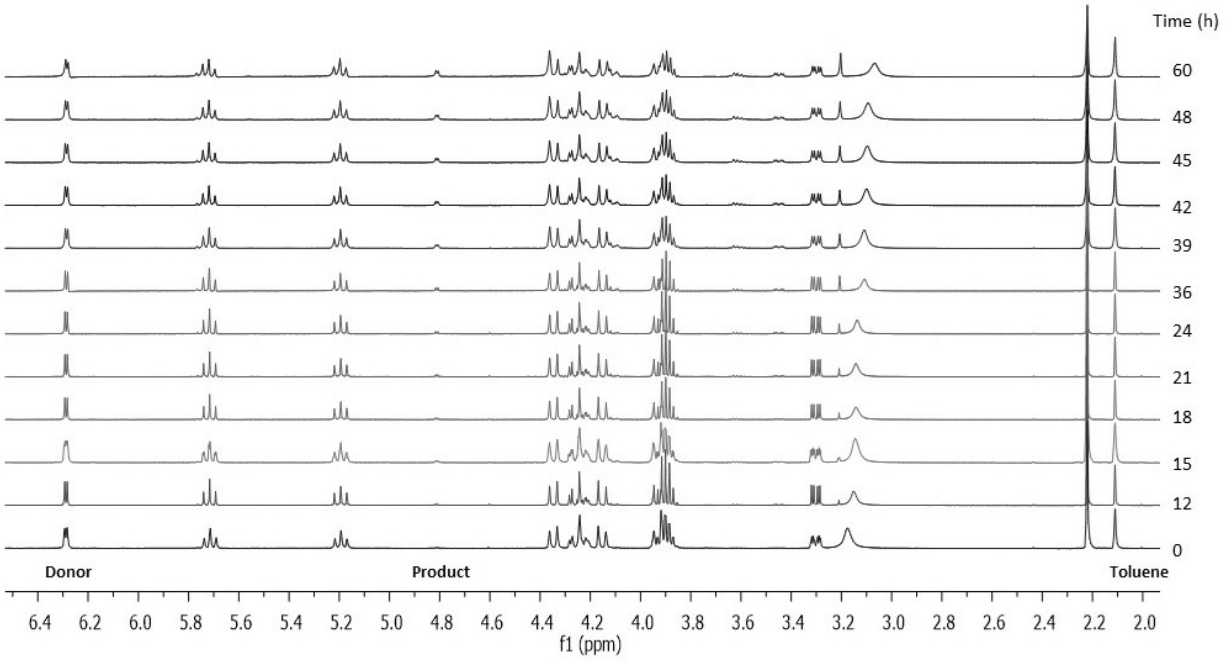


A 10 mL scintillation vial was charged with glycosyl bromide **1** (fixed amount, 0.25 mmol, 1.0 equiv), isopropanol acceptor **1A** (vary amount from 0.5 to 5 equiv), catalyst **4** (vary amount from 2 to 20 mol%), IBO (vary amount from 1.5 to 3 equiv), toluene (internal standard, 0.083mmol, 0.33 equiv), and C_6D_6 (0.5 mL). The resulting solution was then transferred to a 5 mm NMR tube. ^{1}H NMR spectrum was acquired on a 400 MHz instrument before heating. Then the mixture in NMR tube was then consistently shaken and heated in a 50 °C water bath. Between 3 and 60 h, spectra were obtained depending on the experiment. Example spectra and example rate plot were based on standard condition: 0.25 mmol glycosyl bromide **1** (1.0 equiv), 0.75 mmol acceptor (3.0 equiv), 15 mol% catalyst **4**, 0.5 mmol IBO (2 equiv), 0.083 mmol toluene (0.33 equiv) as an internal standard, and 0.5 mL C_6D_6 (0.5 M). The kinetic runs were repeated twice.

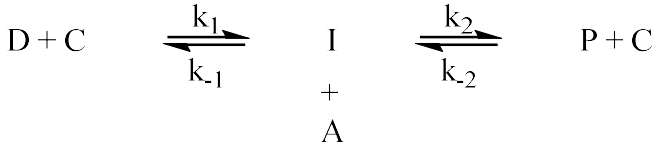
Spectra Processing

The spectra for each kinetic experiment were processed using MestReNova (v. 6.0.2, Mestrelab Research S.L.). The concentrations of product were measured by integration of its H-1 proton against the toluene internal standard, δ = 2.1 ppm. Peak fitting or deconvolution algorithms were not used for integration.

Figure S11: Example Spectra Array for a Kinetic Experiment



Rate Equation Derivation



D = Donor C = Catalyst I = Intermediate A = Acceptor P = Product

$$\frac{d[P]}{dt} = k_2[I][A] - k_{-2}[P][C]$$

$$\frac{d[I]}{dt} = k_1[D][C] - k_{-1}[I] - k_2[I][A] + k_{-2}[P][C]$$

Assume steady state,

$$\frac{d[I]}{dt} = 0$$

Therefore,

$$[I] = \frac{k_1[D][C] + k_{-2}[P][C]}{k_{-1} + k_2[A]}$$

Since $k_{-2} \approx 0$,

$$\frac{d[P]}{dt} = k_2[I][A]$$

$$[I] = \frac{k_1[D][C]}{k_{-1} + k_2[A]}$$

Substitute $[I]$ into rate equation,

$$\boldsymbol{\frac{d[P]}{dt} = \frac{k_1 k_2[D][C][A]}{k_{-1} + k_2[A]}}$$

For fixed donor and acceptor concentration,

$$\boldsymbol{\frac{d[P]}{dt} = k'[C]}$$

where $k' = \frac{k_1 k_2[D][A]}{k_{-1}+k_2[A]}$

For fixed donor and catalyst concentration,

$$\boldsymbol{\frac{d[P]}{dt} = \frac{k''[A]}{k_{-1} + k_2[A]}}$$

where $k'' = k_1 k_2[D][C]$

Graphing

For each kinetic experiment, the concentration of product versus time were plotted on Excel 2016. Linear regression was obtained by best fitting with all points (Figure S12). Slope of the best-fit line represents the initial rate of reaction for each kinetic experiment. The initial rate was then graphed against catalyst concentration for fixed acceptor concentration (Figure S13), and against acceptor concentration for fixed catalyst concentration (Figure S14). The product formation versus time was also compared at different equivalent of IBO (Figure S15).

Figure S12: Example Rate Plot: Product concentration versus time for a kinetic experiment

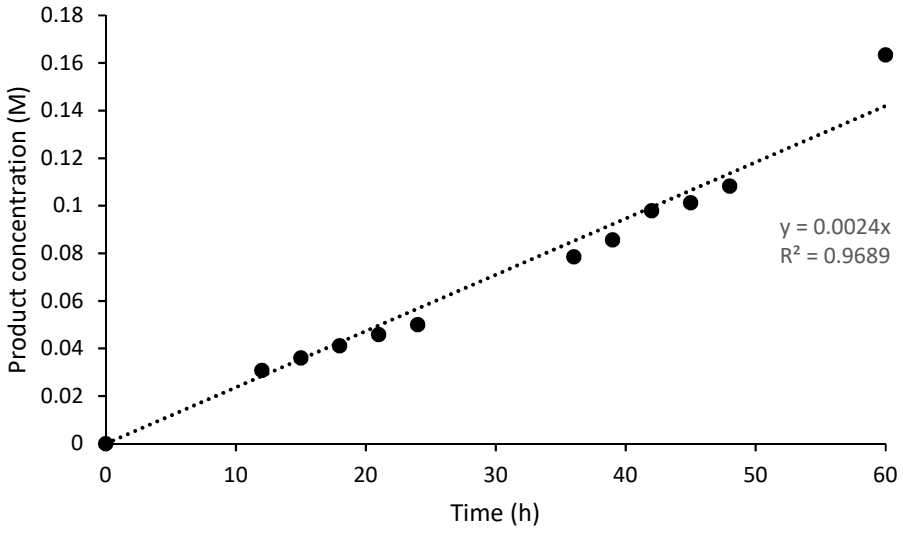


Figure S13: Rate of Reaction versus Catalyst concentration

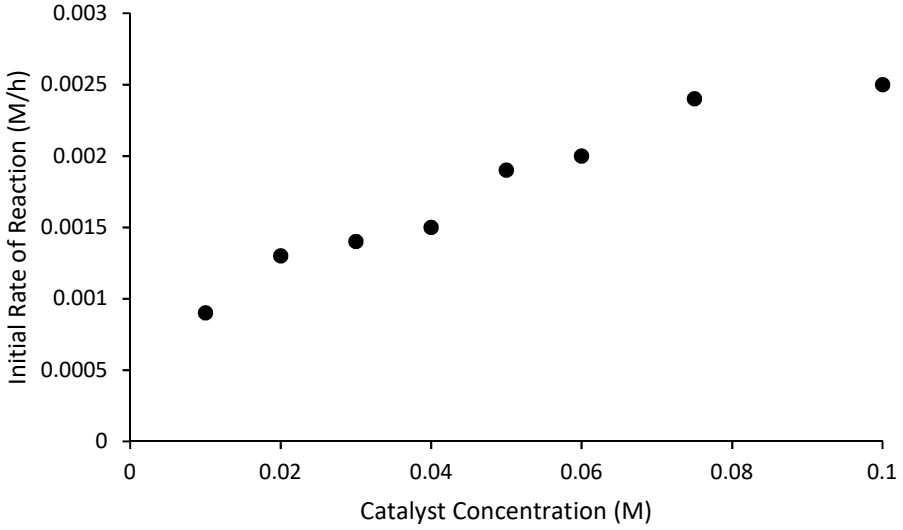


Figure S14: Rate of Reaction versus Acceptor concentration

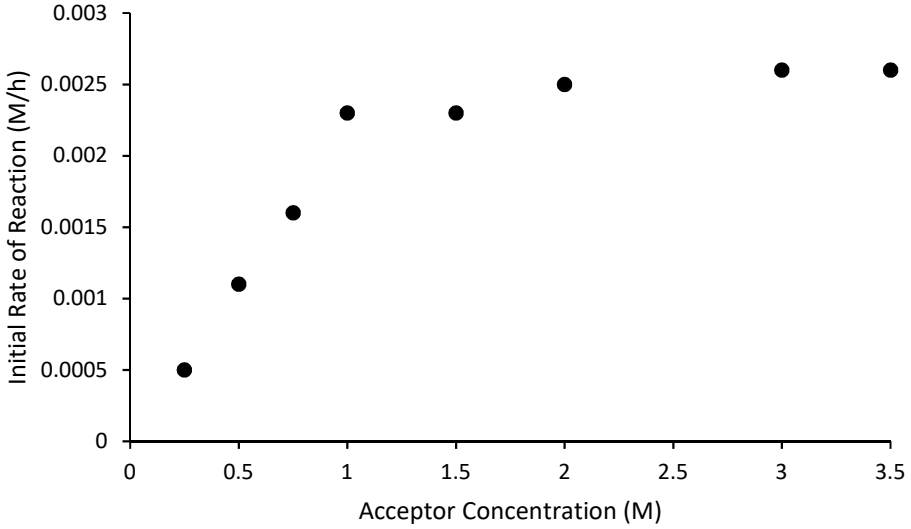
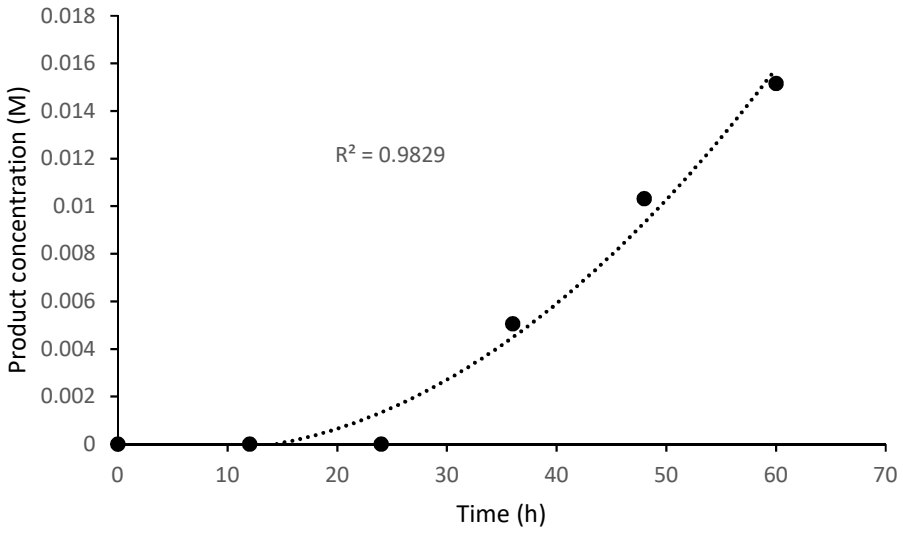
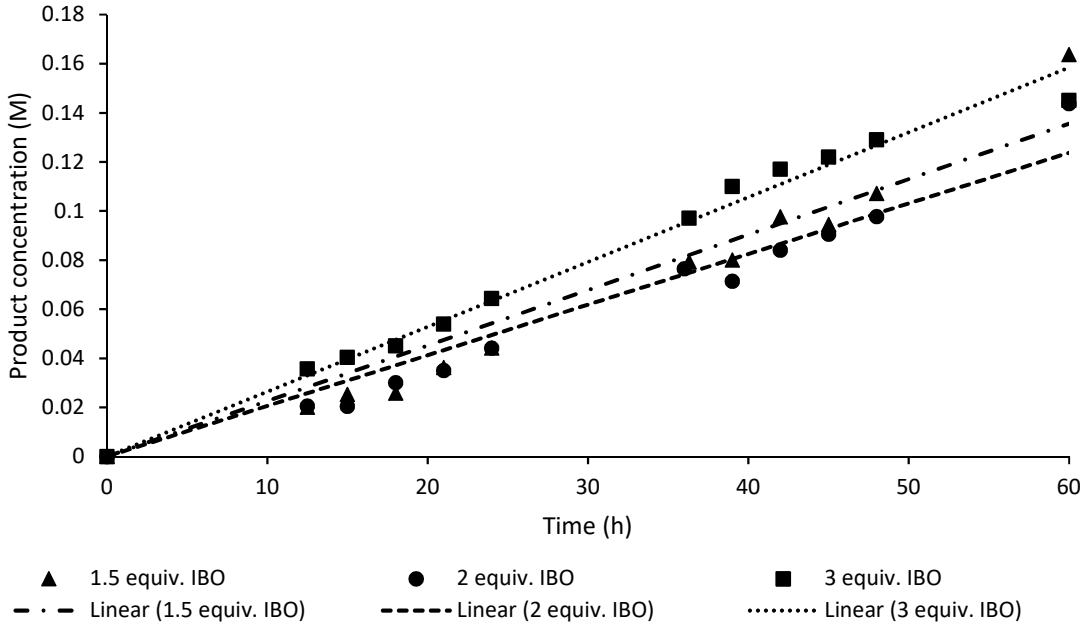


Figure S15: Product formation versus time at 0 mol% catalyst



As shown in Figure S15, the desired product was not observed even after 24 h. This result is consistent with our control experiment illustrated in Table 1 in the main text. After 24 h, the desired product was slowly formed in the reaction. Even after 60 h, only 3% conversion was observed. Collectively, these results suggest that the background reaction only takes place after a long period.

Figure S16: Product formation versus time at different equivalent of IBO

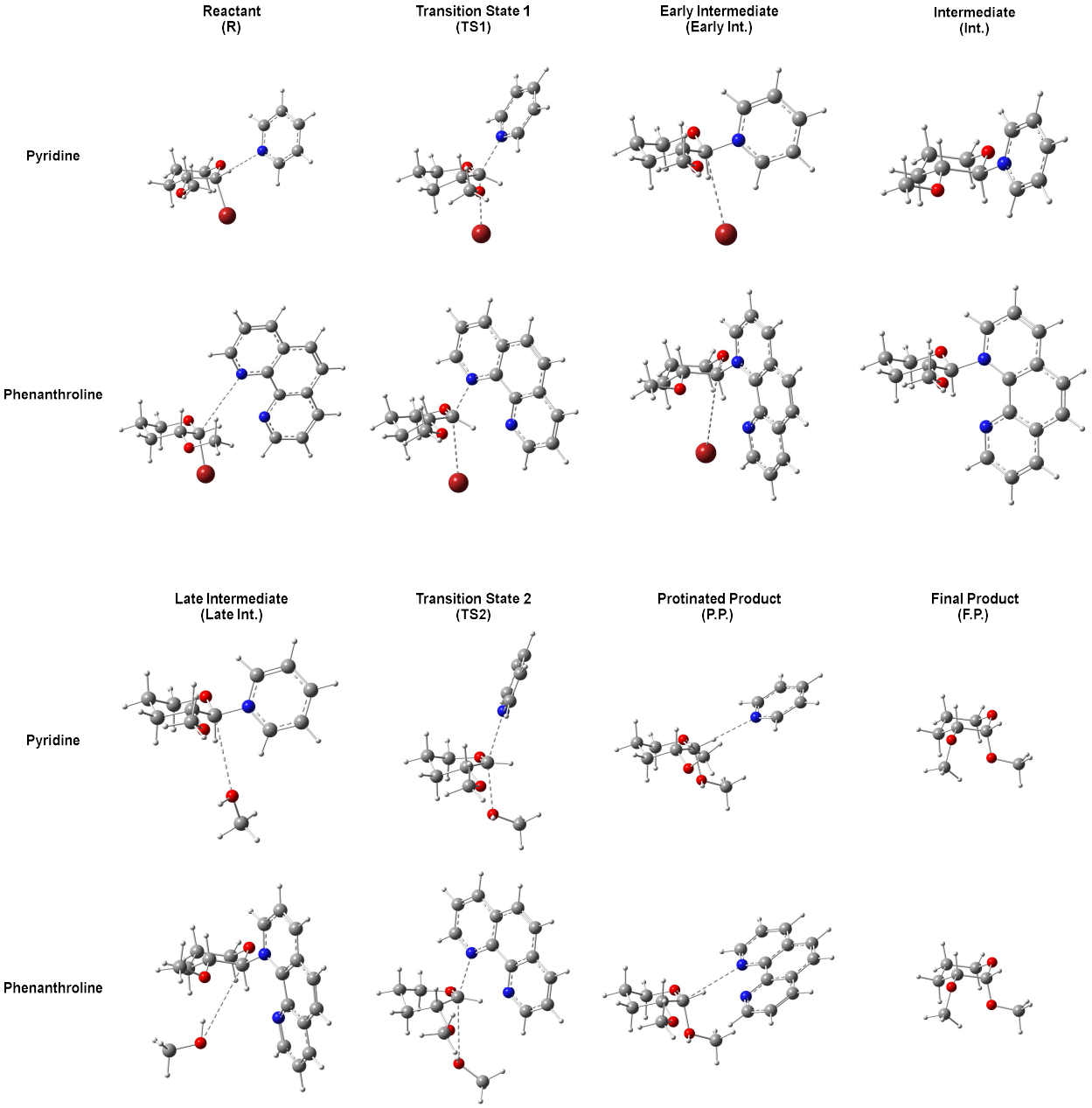


As shown in Figure S16, the rate of reactions does not change significantly with varying amounts of IBO.

6. DFT Calculations

All calculations were carried out with Gaussian 09.[8] Geometry optimization for reactant, intermediates, transition states, and products were computed at the B3LYP/6-31+G(d,p) level of theory [9-19] with the SMD implicit solvation model [20] in diethyl ether. There is only one imaginary frequency for transition state structures and no imaginary frequency for reactant, intermediates, and products. Non-covalent interactions (NCI) were calculated with the NCIPLOT program [21].

Figure S17. Optimized Structures



Cartesian coordinate

R_PY

Charge = 0 Multiplicity = 1

E(RB3LYP) = -3205.781567 A.U.

C	3.165678	-0.862673	0.914227
C	1.702113	-0.529111	1.187095
C	0.918667	-0.302628	-0.120761
C	2.458617	-1.656448	-1.359637
C	3.264411	-1.998425	-0.113949
H	-0.154033	-0.165863	0.013853
H	1.206831	-1.407443	1.641965
H	3.665818	0.037347	0.538657
H	3.649743	-1.141440	1.856002
H	2.374567	-2.505276	-2.041685
H	2.905739	-0.813732	-1.901420
H	2.889110	-2.934871	0.318076
H	4.308677	-2.168287	-0.401121
O	1.090023	-1.309635	-1.038264
O	1.650421	0.552641	2.095004
C	0.352833	0.864031	2.594682
H	0.496524	1.572110	3.414703
H	-0.280182	1.333903	1.831964
H	-0.152285	-0.033922	2.979810
Br	1.469670	1.518986	-0.913602
C	-3.171264	-1.357526	-0.003801
C	-4.561412	-1.491805	0.013727
C	-5.343616	-0.339545	-0.084219
C	-4.702561	0.895954	-0.193114
C	-3.306148	0.925624	-0.199057
N	-2.543906	-0.175163	-0.103079
H	-6.428108	-0.402898	-0.075930
H	-2.532836	-2.235889	0.066227
H	-5.012868	-2.475585	0.098166
H	-5.267353	1.819697	-0.273660
H	-2.775699	1.871569	-0.283247

TS1_Pyridine

Charge = 0 Multiplicity = 1

E(RB3LYP) = -3205.742135 A.U.

C	-5.165043	-1.057924	4.224031
C	-3.880020	-1.893345	4.131315
C	-3.157567	-1.632197	2.822409
C	-4.145048	0.569000	2.602085
C	-4.774478	0.404940	3.972188
H	-2.892909	-2.452994	2.172671

H	-3.212357	-1.536053	4.932933
H	-5.878555	-1.411047	3.474269
H	-5.604370	-1.165295	5.220105
H	-3.633380	1.524705	2.479966
H	-4.879408	0.431134	1.803687
H	-4.087127	0.754456	4.752987
H	-5.657945	1.052425	4.007178
O	-3.114332	-0.439298	2.296118
O	-4.024068	-3.295490	4.244385
C	-4.393226	-3.739654	5.545971
H	-4.330271	-4.830192	5.530396
H	-3.707183	-3.349535	6.313441
H	-5.419995	-3.451648	5.803900
Br	-5.236851	-2.441940	0.860721
C	-0.297338	-0.789112	3.133226
C	-0.651211	-2.860559	4.112630
C	1.065146	-0.831422	3.427556
H	-0.745591	0.052266	2.611427
C	0.698961	-2.987454	4.434549
H	-1.373753	-3.634712	4.355379
C	1.570872	-1.952079	4.088848
H	1.708896	-0.009216	3.133177
H	1.052359	-3.879117	4.941661
H	2.628145	-2.020504	4.326862
N	-1.128338	-1.774789	3.486910

Early-Int_Pyridine

Charge = 0 Multiplicity = 1

E(RB3LYP) = -3205.780059 A.U.

C	-0.977437	-0.014877	-0.234492
C	0.507013	-0.414415	-0.264780
C	1.157591	0.307525	-1.456687
C	-0.320577	2.144483	-1.351567
C	-1.118441	1.516693	-0.213707
H	0.708897	-0.038540	-2.399584
H	1.001389	-0.077003	0.663104
H	-1.461162	-0.430267	-1.127199
H	-1.465638	-0.453476	0.641522
H	-0.274356	3.232799	-1.271206
H	-0.746465	1.879807	-2.328632
H	-0.760918	1.916962	0.743750
H	-2.172137	1.802310	-0.312824
O	1.058957	1.705878	-1.311847
O	0.728302	-1.803501	-0.443279
C	0.474076	-2.595682	0.712863
H	0.783671	-3.614213	0.467393

H	1.057879	-2.240204	1.575075
H	-0.589903	-2.606685	0.980826
Br	0.142230	-1.083344	-4.614798
C	3.017332	-0.883664	-2.497979
C	4.354840	-1.246640	-2.572974
C	5.268691	-0.694632	-1.676783
C	4.821866	0.222686	-0.719592
C	3.479705	0.553053	-0.676767
N	2.610260	-0.006352	-1.551971
H	6.317988	-0.968214	-1.723704
H	2.248107	-1.239918	-3.185574
H	4.663093	-1.948971	-3.338823
H	5.502336	0.681639	-0.011709
H	3.063093	1.258113	0.030411

Late-Int_Pyridine

Charge = 1 Multiplicity = 1

E(RB3LYP) = -749.617112 A.U.

C	-0.730893	-0.389269	4.670408
C	-0.333098	-0.690589	3.216943
C	-0.094231	0.647053	2.492105
C	0.531658	1.775469	4.480249
C	0.303691	0.534413	5.332661
H	0.605764	-1.268423	3.200938
H	-1.718309	0.090559	4.665501
H	-0.823993	-1.324027	5.231621
H	1.364813	2.380695	4.842692
H	-0.369349	2.404585	4.443091
H	1.255809	0.005776	5.464295
H	-0.039576	0.838365	6.327928
H	-1.040014	1.196161	2.409346
O	0.898466	1.410611	3.126324
O	-1.335530	-1.372948	2.478171
C	-1.452830	-2.763861	2.782135
H	-2.185689	-3.174753	2.084416
H	-0.492994	-3.280352	2.641497
H	-1.805560	-2.931050	3.806916
C	1.666038	0.067618	0.873161
C	2.113625	-0.173183	-0.413657
C	1.222770	-0.045093	-1.482694
C	-0.097738	0.328148	-1.229975
C	-0.502734	0.563726	0.074513
N	0.378672	0.427699	1.093359
H	1.556730	-0.229354	-2.498762
H	2.302223	-0.002066	1.745215

H	3.148400	-0.456313	-0.567634
H	-0.817715	0.445097	-2.031551
H	-1.510158	0.868789	0.342437
O	-3.234962	1.622885	1.420355
H	-3.821605	0.921727	1.738478
C	-4.027480	2.773498	1.087036
H	-3.334761	3.544764	0.742493
H	-4.740076	2.550720	0.283639
H	-4.571612	3.151124	1.961002

TS2_Pyridine

Charge = 1 Multiplicity = 1

E(RB3LYP) = -749.576283 A.U.

C	-2.855387	0.118082	4.147442
C	-1.554162	-0.226211	3.414612
C	-1.131059	0.884767	2.481254
C	-2.524633	2.537315	3.580265
C	-2.721342	1.542013	4.702108
H	-0.741961	-0.296768	4.154747
H	-3.697911	0.049101	3.451550
H	-3.021321	-0.594358	4.958946
H	-2.159265	3.508415	3.912918
H	-3.419443	2.670430	2.968309
H	-1.888109	1.601405	5.411953
H	-3.627893	1.833705	5.242449
H	-0.467473	0.675293	1.650944
O	-1.493953	2.097752	2.592761
O	-1.580067	-1.411349	2.632948
C	-1.530213	-2.623084	3.399128
H	-1.458846	-3.438124	2.676809
H	-0.647442	-2.636196	4.050844
H	-2.435196	-2.754604	4.002588
C	2.109344	0.254125	3.708084
C	3.426568	0.499526	4.097540
C	3.872134	1.821972	4.146036
C	2.985934	2.844177	3.801244
C	1.687177	2.501101	3.422824
N	1.251901	1.233013	3.379777
H	1.725830	-0.762742	3.655572
H	4.080993	-0.327368	4.353543
H	3.289193	3.885915	3.822274
H	0.969768	3.269275	3.142570
O	-2.850613	0.222568	0.870337
H	-2.707990	-0.728504	1.005998
C	-2.607727	0.559128	-0.504016

H	-1.607524	0.246037	-0.827881
H	-3.358523	0.096501	-1.154871
H	-2.688353	1.645070	-0.587301
H	4.890686	2.051081	4.444885

P.P._Pyridine

Charge = 1 Multiplicity = 1

E(RB3LYP) = -749.581689 A.U.

C	-3.870530	0.739542	4.458652
C	-2.660633	0.040344	3.845857
C	-2.189057	0.710469	2.541629
C	-3.365879	2.751078	3.057606
C	-3.640692	2.257309	4.465847
H	-1.807475	0.078033	4.534291
H	-4.765690	0.498941	3.872454
H	-4.028989	0.354954	5.470139
H	-3.064117	3.798323	3.029713
H	-4.232135	2.611828	2.402189
H	-2.800661	2.518573	5.120919
H	-4.525641	2.775177	4.850162
H	-1.230917	0.342825	2.159945
O	-2.229592	2.043806	2.450052
O	-2.986489	-1.322379	3.528731
C	-1.990378	-2.301681	3.885473
H	-2.372762	-3.265374	3.545084
H	-1.030785	-2.092770	3.400001
H	-1.860258	-2.323500	4.972479
C	1.572925	-1.253546	0.976549
C	2.828676	-1.277656	0.367203
C	3.405759	-0.066887	-0.019891
C	2.703447	1.115253	0.220561
C	1.453109	1.035796	0.836746
N	0.885017	-0.123190	1.212223
H	1.099192	-2.181772	1.289003
H	3.336675	-2.222856	0.203253
H	3.110720	2.081270	-0.060965
H	0.883305	1.940267	1.038472
O	-3.250482	0.081728	1.487456
H	-3.378996	-0.828706	1.876640
C	-2.852456	0.057015	0.071358
H	-2.697791	1.092985	-0.223977
H	-1.941053	-0.530584	-0.045306
H	-3.689622	-0.378341	-0.474093
H	4.381066	-0.044923	-0.497414

R_Phenanthroline

Charge = 0 Multiplicity = 1

E(RB3LYP) = -3529.131672 A.U.

C	-3.993558	1.500050	0.470229
C	-2.569535	1.137649	0.879646
C	-1.958005	0.072863	-0.050844
C	-3.436644	0.676151	-1.834739
C	-4.043595	1.817929	-1.030854
H	-0.902486	-0.125992	0.130853
H	-1.913404	2.015235	0.733408
H	-4.651604	0.654809	0.703013
H	-4.330500	2.355153	1.065414
H	-3.317745	0.933174	-2.889613
H	-4.051955	-0.229490	-1.760809
H	-3.493841	2.744299	-1.240905
H	-5.078536	1.971915	-1.358092
O	-2.100055	0.350633	-1.385021
O	-2.572927	0.781270	2.247415
C	-1.283959	0.585559	2.825891
H	-1.444944	0.438945	3.896946
H	-0.778460	-0.298565	2.419823
H	-0.643028	1.465185	2.672583
Br	-2.805047	-1.765816	0.398445
C	1.714344	2.940687	0.211854
C	2.970910	3.567448	0.082207
C	4.080702	2.772231	-0.120422
C	3.926853	1.368636	-0.194964
N	1.530963	1.628708	0.149740
H	5.071582	3.206541	-0.225356
H	0.823998	3.545925	0.373971
H	3.050089	4.648305	0.142821
C	2.611964	0.835820	-0.054473
C	3.566797	-1.438132	-0.352504
C	5.045565	0.493954	-0.409042
C	4.872493	-0.855385	-0.483967
H	6.034435	0.933174	-0.511232
H	5.720335	-1.515626	-0.647084
C	2.427172	-0.609197	-0.137590
C	3.359376	-2.834547	-0.434978
C	1.022254	-2.437342	-0.087463
C	2.082447	-3.341283	-0.303166
H	4.209556	-3.491266	-0.601170
H	0.003282	-2.802317	0.022860
H	1.884973	-4.406934	-0.362760
N	1.180580	-1.122825	-0.003998

TS1_Phenanthroline

Charge = 0 Multiplicity = 1

E(RB3LYP) = -3529.084393 A.U.

C	-4.832837	-1.136532	-0.140903
C	-4.303745	-0.769552	-1.514306
C	-2.122037	-0.282629	-0.532137
C	-2.599154	-0.723233	0.843558
C	-3.723997	-1.763530	0.711842
H	-4.108011	-1.663546	-2.112895
H	-4.962598	-0.090317	-2.058418
H	-5.247817	-0.254187	0.363888
H	-5.658730	-1.842705	-0.284324
H	-1.108411	-0.506712	-0.837674
H	-3.036928	0.157551	1.342279
H	-3.326255	-2.665176	0.236734
H	-4.104714	-2.017156	1.705850
O	-3.002586	-0.081185	-1.490781
O	-1.460566	-1.145939	1.567035
C	-1.664216	-1.224333	2.972681
H	-2.045852	-0.273438	3.375875
H	-2.354892	-2.031828	3.248503
H	-0.688564	-1.433368	3.417941
C	-0.263071	3.520834	0.601485
C	-1.431935	4.313269	0.617952
C	-2.633262	3.773092	0.208256
C	-2.655467	2.422931	-0.167697
N	-1.579505	1.647940	-0.171724
H	-3.547830	4.355343	0.186540
H	-1.366314	5.346314	0.947825
C	-0.358111	2.167247	0.156693
C	2.092672	1.960155	0.479007
C	1.000322	4.059662	1.019385
C	2.131222	3.302978	0.979323
H	1.028773	5.087483	1.369350
H	3.084715	3.710742	1.303531
H	-3.585596	1.949036	-0.467952
C	0.864090	1.385193	0.043225
C	1.915529	-0.567230	-0.594471
C	3.259025	1.165428	0.375887
C	3.174125	-0.105738	-0.153823
H	1.810356	-1.553311	-1.040913
H	4.210041	1.572092	0.709375
H	4.049257	-0.740782	-0.246443
N	0.807330	0.150323	-0.501538
Br	-1.509336	-3.098709	-1.937457

Early-Int_Phenanthroline
Charge = 0 Multiplicity = 1
E(RB3LYP) = -3529.117038 A.U.

C	3.413047	-1.615412	0.157217
C	2.730066	-1.289559	-1.165587
C	0.621486	-1.036414	-0.116946
C	1.163775	-1.413635	1.273045
C	2.637886	-0.984231	1.326668
H	2.778037	-0.211542	-1.364888
H	3.163791	-1.839863	-2.004129
H	3.480130	-2.704501	0.284276
H	4.436301	-1.223479	0.133495
H	0.632982	0.042238	-0.253042
H	1.092668	-2.507866	1.404565
H	2.690083	0.108903	1.252686
H	3.079820	-1.286894	2.281772
O	1.336241	-1.705391	-1.134053
O	0.326505	-0.773834	2.227565
C	0.566309	-1.155354	3.578381
H	0.537703	-2.249383	3.694402
H	1.528206	-0.780345	3.948803
H	-0.235231	-0.713082	4.175176
C	-3.213101	-1.298790	-0.237435
C	-3.310406	-2.702530	-0.317783
C	-2.171879	-3.475019	-0.407028
C	-0.941174	-2.834135	-0.364426
N	-0.816108	-1.496803	-0.267639
H	-2.206728	-4.554814	-0.488265
H	-4.295584	-3.159589	-0.316734
C	-1.930940	-0.666277	-0.244183
C	-3.118578	1.514077	-0.170416
C	-4.417531	-0.523149	-0.160447
C	-4.374520	0.833649	-0.113672
H	-5.362310	-1.056986	-0.143424
H	-5.285944	1.421191	-0.053090
H	-0.012150	-3.384695	-0.409170
C	-1.888026	0.793759	-0.248401
C	-0.670384	2.763919	-0.365159
C	-3.053118	2.928412	-0.177673
C	-1.832211	3.560297	-0.273587
H	0.328258	3.192543	-0.449560
H	-3.977120	3.496562	-0.115464
H	-1.753229	4.642633	-0.283105
N	-0.709938	1.442268	-0.353247
Br	2.966011	2.469945	-0.561160

Late-Int_Phenanthroline

Charge = 1 Multiplicity = 1

E(RB3LYP) = -1072.953844 A.U.

C	3.948746	0.006459	-0.600737
C	2.738404	-0.753398	-0.036707
C	1.666931	-0.844725	-1.139819
C	3.268131	-0.775464	-2.888302
C	4.427835	-0.640844	-1.910023
H	1.284929	0.143133	-1.385831
H	3.047814	-1.765906	0.260604
H	3.652559	1.047386	-0.783395
H	4.754107	0.018587	0.140380
H	3.537440	-1.359901	-3.770562
H	2.907806	0.209865	-3.216492
H	4.851043	-1.633361	-1.710807
H	5.218884	-0.034976	-2.365866
O	2.169425	-1.498264	-2.283796
O	2.137065	-0.101851	1.083636
C	2.788461	-0.357602	2.335317
H	2.174019	0.106721	3.109131
H	2.848500	-1.436870	2.525286
H	3.795812	0.073725	2.364849
C	-1.674590	-2.016109	0.295172
C	-1.330875	-3.364414	0.524382
C	-0.117094	-3.858388	0.092077
C	0.780475	-2.971038	-0.484598
N	0.489658	-1.670838	-0.687550
H	-2.043836	-4.007321	1.031896
H	0.166742	-4.895859	0.221216
H	1.771238	-3.280822	-0.787921
C	-0.767191	-1.154374	-0.394254
C	-2.946512	-1.531671	0.745482
C	-2.507212	0.606390	-0.292660
C	-3.337579	-0.256391	0.489375
H	-3.585785	-2.216981	1.292473
H	-4.296324	0.115571	0.837841
C	-1.233404	0.175534	-0.772599
C	-0.952656	2.149067	-1.948778
C	-2.950053	1.899417	-0.660739
C	-2.174147	2.680677	-1.487706
H	-0.323896	2.725273	-2.623544
H	-3.910336	2.250639	-0.293896
H	-2.487028	3.673773	-1.791963
N	-0.501063	0.954106	-1.604767
C	2.460689	3.392179	1.902387
H	2.263773	4.467325	1.861927

H	3.485275	3.217565	1.544107
H	2.394301	3.071400	2.951962
O	1.487303	2.751086	1.081629
H	1.685955	1.798711	1.045207

TS2_Phenanthroline

Charge = 1 Multiplicity = 1

E(RB3LYP) = -1072.925835 A.U.

C	3.041997	-1.145325	1.339295
C	1.879416	-0.202137	1.004107
C	1.661776	-0.064409	-0.495591
C	3.128566	-1.944227	-1.018879
C	2.982154	-2.371789	0.423766
H	1.199705	0.848806	-0.859277
H	0.944991	-0.593364	1.423993
H	3.985838	-0.609668	1.190767
H	2.984313	-1.437963	2.390568
H	2.853009	-2.710168	-1.743885
H	4.129879	-1.571742	-1.247143
H	2.046096	-2.923772	0.569718
H	3.801693	-3.062246	0.648375
O	2.246623	-0.789953	-1.368239
O	2.097863	1.126162	1.468289
C	1.581499	1.393847	2.779342
H	1.816992	2.437283	2.996186
H	0.494537	1.252751	2.804039
H	2.057113	0.754587	3.532703
C	-2.980646	-0.856853	-0.780681
C	-2.946317	-2.239871	-1.067468
C	-1.731675	-2.878409	-1.206344
C	-0.560020	-2.121933	-1.031315
N	-0.555133	-0.826461	-0.745513
H	-3.880864	-2.781780	-1.182656
H	-1.663734	-3.935692	-1.438388
H	0.408258	-2.604693	-1.128247
C	-1.741801	-0.164190	-0.637365
C	-4.224652	-0.153918	-0.643256
C	-3.026414	1.924645	-0.260732
C	-4.247870	1.182742	-0.384936
H	-5.147608	-0.715865	-0.752666
H	-5.190724	1.711767	-0.279239
C	-1.767906	1.269674	-0.390458
C	-0.625666	3.250610	-0.085594
C	-3.019499	3.318584	-0.021693
C	-1.816516	3.988663	0.069210

H	0.338047	3.752282	-0.027570
H	-3.963945	3.845245	0.083682
H	-1.774974	5.057931	0.249485
N	-0.595692	1.943300	-0.307167
C	4.369886	3.221619	-0.792391
H	4.791029	3.908122	-0.045279
H	3.421306	3.636085	-1.161327
H	5.067002	3.153985	-1.631673
O	4.207772	1.902889	-0.269087
H	3.573140	1.924271	0.467067

P.P._Phenanthroline

Charge = 1 Multiplicity = 1

E(RB3LYP) = -1072.934271 A.U.

C	-4.461771	0.118736	-0.668452
C	-2.978264	0.497048	-0.652404
C	-2.114274	-0.468339	0.171724
C	-3.833932	-2.158233	0.149110
C	-4.608942	-1.390854	-0.904615
H	-1.035916	-0.335866	0.048101
H	-2.564408	0.457458	-1.670845
H	-4.915734	0.392003	0.292270
H	-4.978064	0.683617	-1.449854
H	-3.807940	-3.230831	-0.045232
H	-4.235250	-1.988095	1.153859
H	-4.245808	-1.664524	-1.902618
H	-5.662653	-1.684133	-0.850087
O	-2.419447	-1.769544	0.158155
O	-2.722091	1.783634	-0.079002
C	-3.134058	2.910277	-0.866027
H	-2.813483	3.800659	-0.322860
H	-2.647884	2.885207	-1.848412
H	-4.221739	2.935473	-0.988627
C	1.175683	-2.790508	-0.223724
C	2.385232	-3.484857	-0.429725
C	3.555516	-2.756553	-0.501630
C	3.509066	-1.349521	-0.368291
N	1.093102	-1.472249	-0.093095
H	4.512323	-3.246483	-0.661196
H	0.238555	-3.340168	-0.164982
H	2.382239	-4.565578	-0.529185
C	2.235641	-0.744250	-0.162245
C	3.358826	1.468823	-0.109203
C	4.692921	-0.539909	-0.438446
C	4.620504	0.815012	-0.314947
H	5.648936	-1.032003	-0.594729

H	5.517349	1.425970	-0.370482
C	2.158604	0.704883	-0.024875
C	3.256544	2.873420	0.016207
C	0.891444	2.605158	0.285692
C	2.017536	3.449753	0.212342
H	4.155635	3.481058	-0.044065
H	-0.097703	3.032939	0.438384
H	1.900196	4.524253	0.310169
N	0.947608	1.283463	0.176168
O	-2.356588	0.093293	1.686307
H	-2.431456	1.070481	1.532070
C	-1.313559	-0.240655	2.671156
H	-1.636175	0.194337	3.617258
H	-1.288839	-1.326541	2.736050
H	-0.358028	0.163756	2.337060

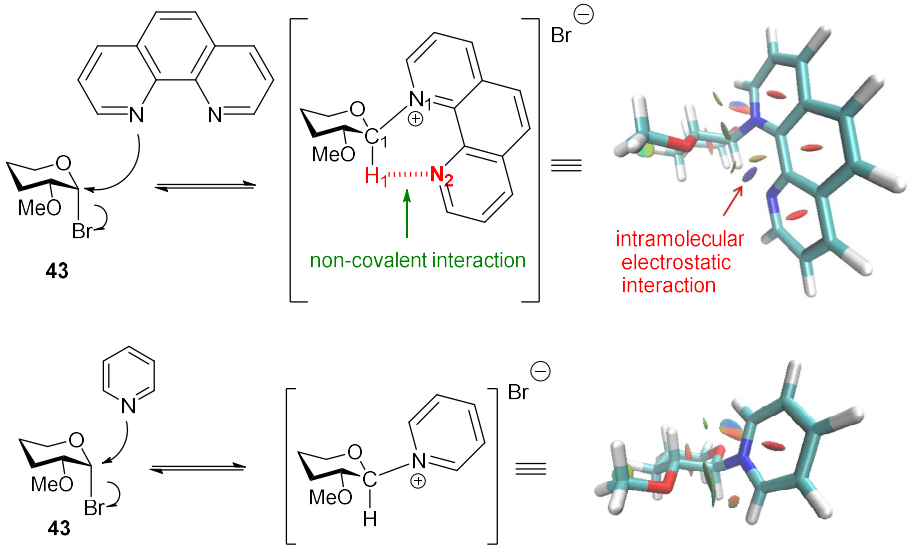
F.P.

Charge = 0 Multiplicity = 1

E(RB3LYP) = -500.857189 A.U.

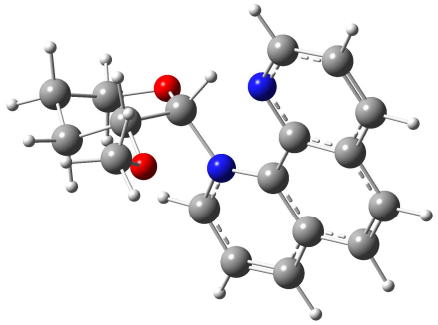
C	-0.971857	2.777809	0.206469
C	0.143537	1.891855	-0.340900
C	-0.402564	2.420275	-2.617915
C	-1.564834	3.322628	-2.158680
C	-1.289012	3.920576	-0.775019
H	1.093404	2.442269	-0.374092
H	0.286058	0.999275	0.274321
H	-1.869481	2.167448	0.370149
H	-0.669375	3.180538	1.180988
H	-0.679505	1.884649	-3.536240
H	-2.423899	2.646692	-2.069705
H	-0.440830	4.612784	-0.816608
H	-2.164644	4.487563	-0.438355
O	-0.171255	1.394694	-1.657549
O	-1.971671	4.247518	-3.169780
C	-1.274600	5.489851	-3.273648
H	-1.444181	6.128026	-2.396592
H	-0.199287	5.349351	-3.420718
H	-1.695065	5.991785	-4.149668
C	1.806428	2.500481	-3.498558
H	2.602142	3.227343	-3.678294
H	1.470061	2.088219	-4.460408
H	2.194024	1.685755	-2.876070
O	0.746794	3.202677	-2.847322

Figure S18. Non-Covalent Interaction (NCI) Plot



Non-covalent interactions plot (reduced density gradient isosurface = 0.3) for the optimized structure at B3LYP/6-31+G(d,p). Blue surfaces represent attractive interactions, and red surfaces represent repulsive interactions.

Figure S19. α-Phenanthrolinium Ion Complex



Cartesian coordinate

Charge = 1 Multiplicity = 1

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C	4.086881	-0.473795	1.063480
C	3.948378	-0.865978	-0.395503
C	1.507094	-0.314190	-0.297910
C	1.738606	0.372746	1.081503
C	3.200836	0.743180	1.338816
H	4.416635	-0.108746	-1.038505
H	4.424230	-1.824800	-0.613053
H	3.796730	-1.311996	1.709529
H	5.139878	-0.252583	1.269229
H	1.434340	-0.381216	1.822433
H	3.491811	1.579591	0.690013
H	3.304992	1.084245	2.373517
O	2.566786	-1.066868	-0.802839
O	0.873471	1.496010	1.162405
C	0.396212	1.774747	2.477277
H	-0.183311	0.930033	2.873686
H	1.214702	2.008021	3.170599
H	-0.253776	2.648778	2.394501
C	-2.744152	0.654767	-1.468700
C	-3.848522	0.038739	-0.833144
C	-3.642805	-0.826952	0.217777
C	-2.315528	-1.061228	0.627755
N	-1.262677	-0.498310	0.056632
H	-4.467824	-1.314480	0.726314
H	-4.850053	0.264515	-1.187833
C	-1.432556	0.344288	-0.991055
C	-0.549776	1.895644	-2.710343
C	-2.950416	1.566943	-2.549713
C	-1.889094	2.172815	-3.139651
H	-3.965843	1.768384	-2.877275
H	-2.023079	2.877420	-3.953941
H	-2.109883	-1.731477	1.459715
C	-0.287031	0.968310	-1.654181

C	2.038401	1.368866	-1.983280
C	0.513801	2.557314	-3.357233
C	1.815517	2.302823	-2.987059
H	3.042471	1.118257	-1.682457
H	0.285304	3.264720	-4.148495
H	2.660303	2.792718	-3.456058
N	1.047694	0.724056	-1.345547
H	0.661735	-0.983060	-0.219510

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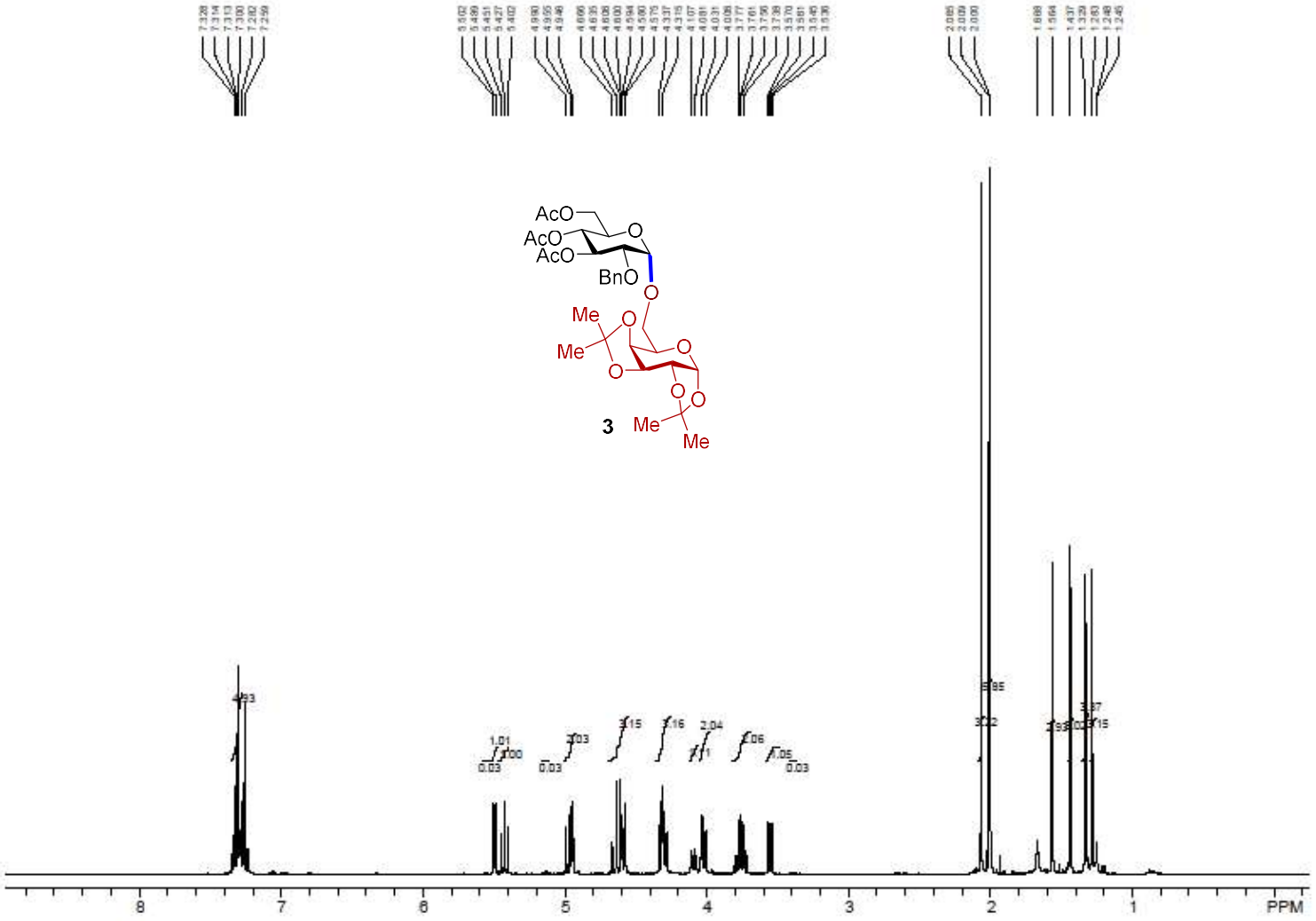
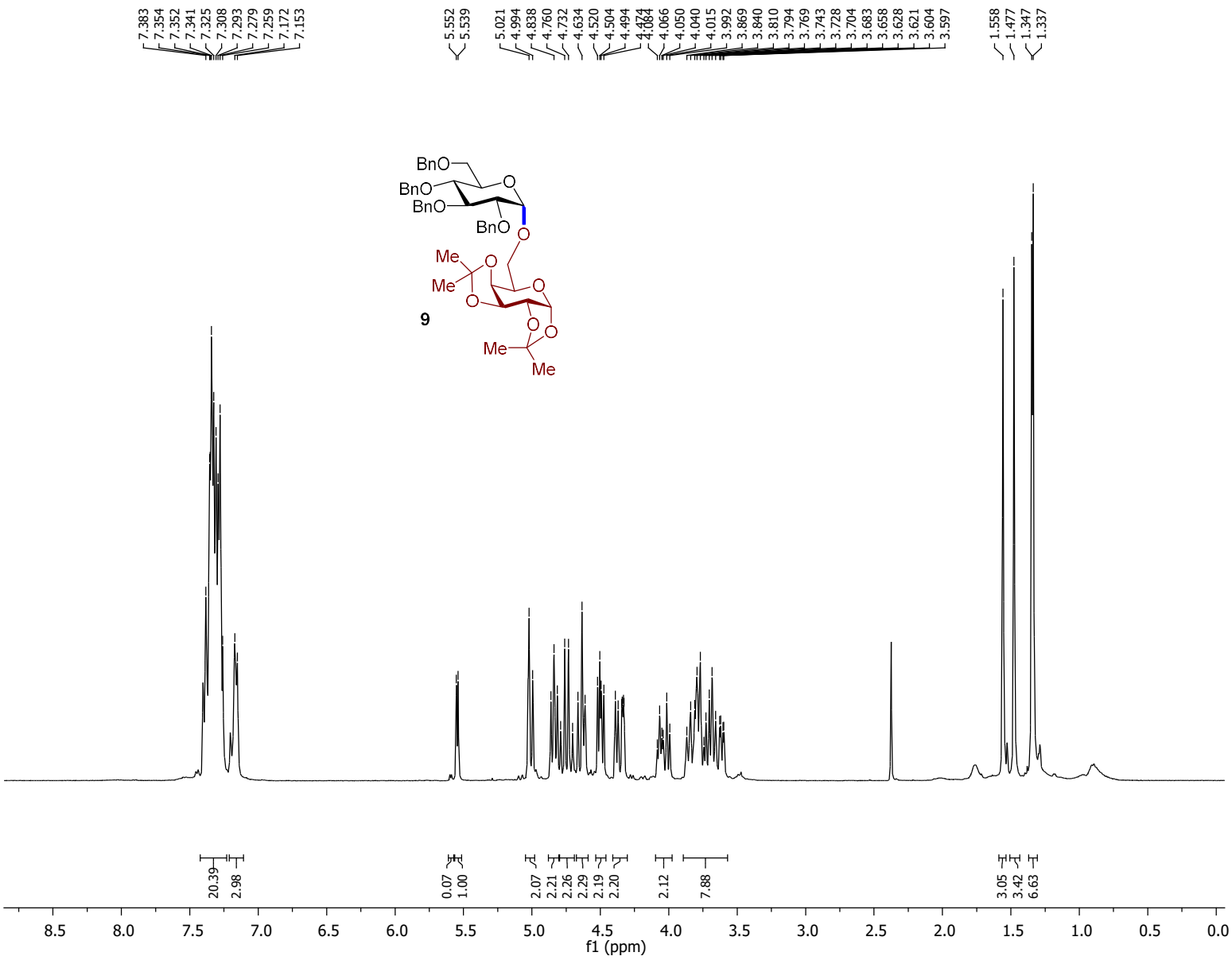
8. Spectral Data

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1.337
BnO
BnO
BnO
BnO
O
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Me
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O
O
O
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O
Me
Me
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0.07
1.00
2.07
2.21
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3.05
3.42
6.63
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6.5
6.0
5.5
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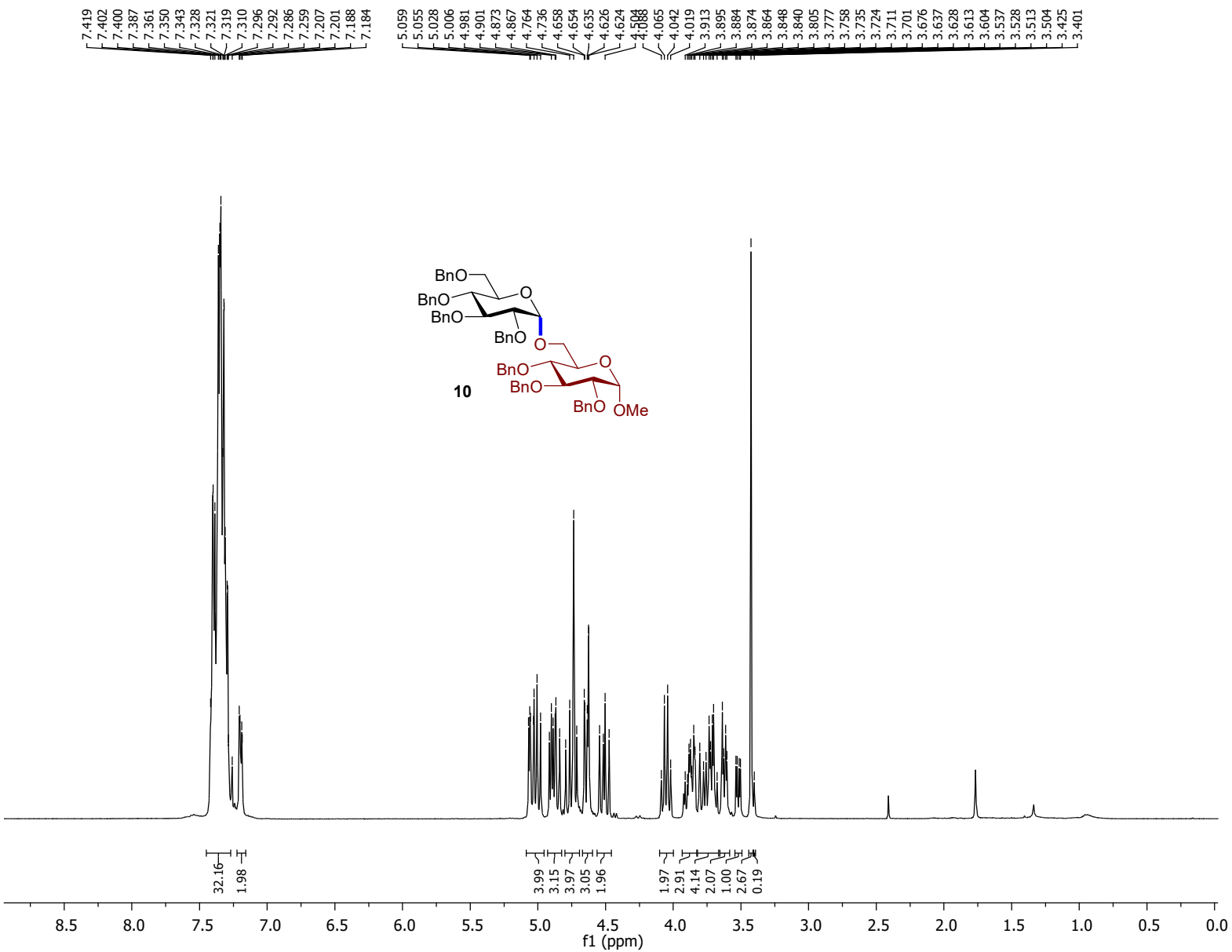
f1 (ppm)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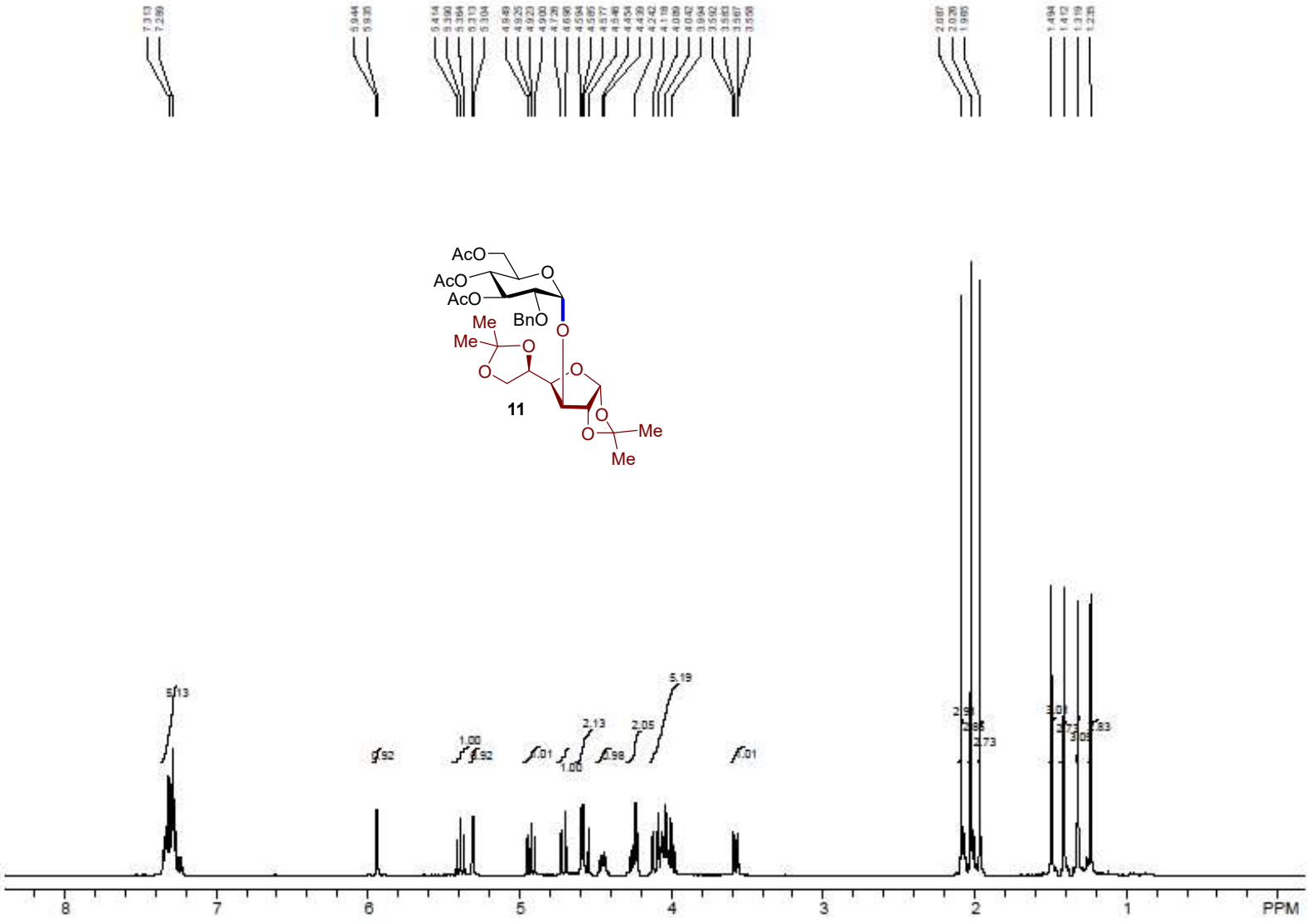
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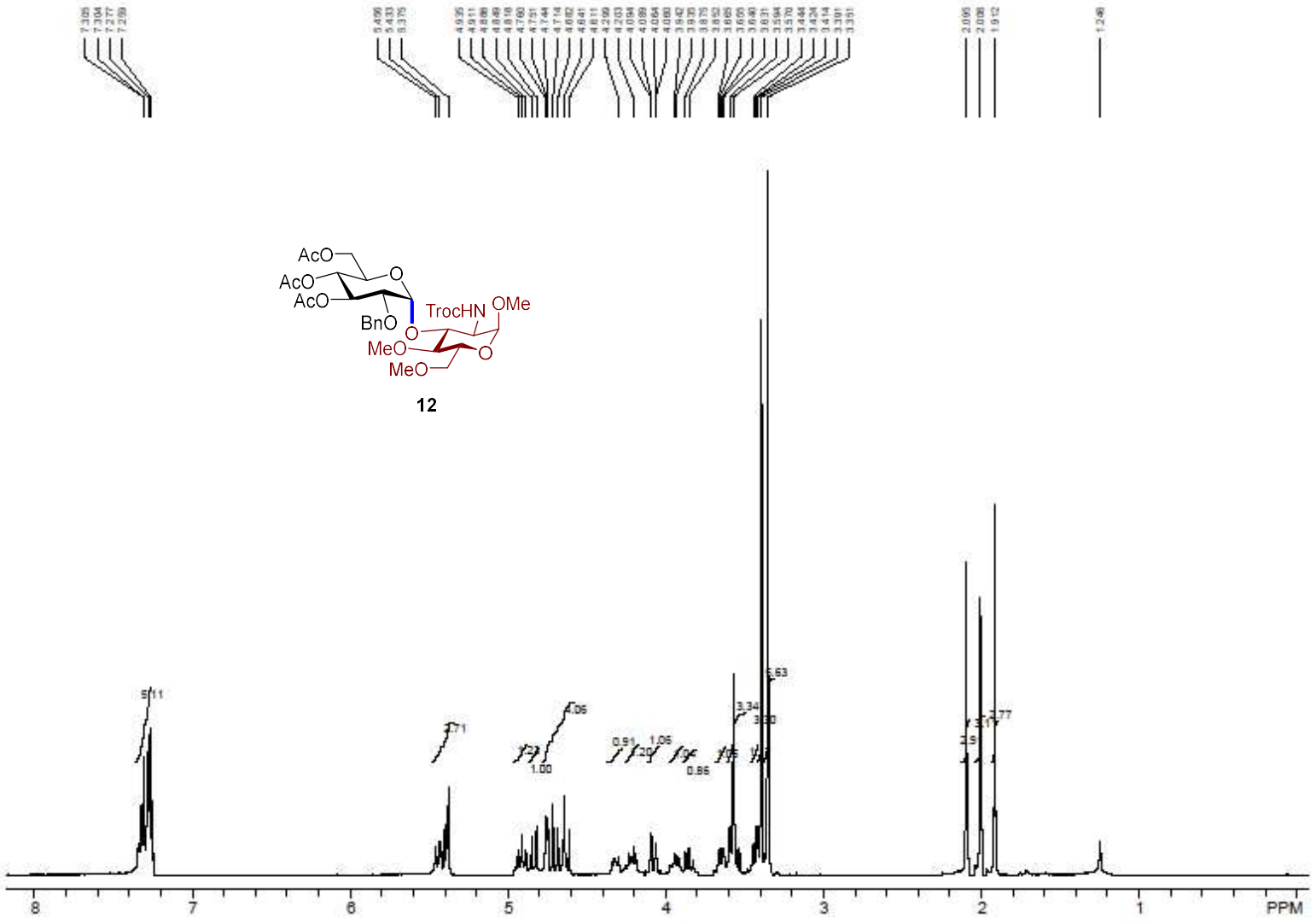
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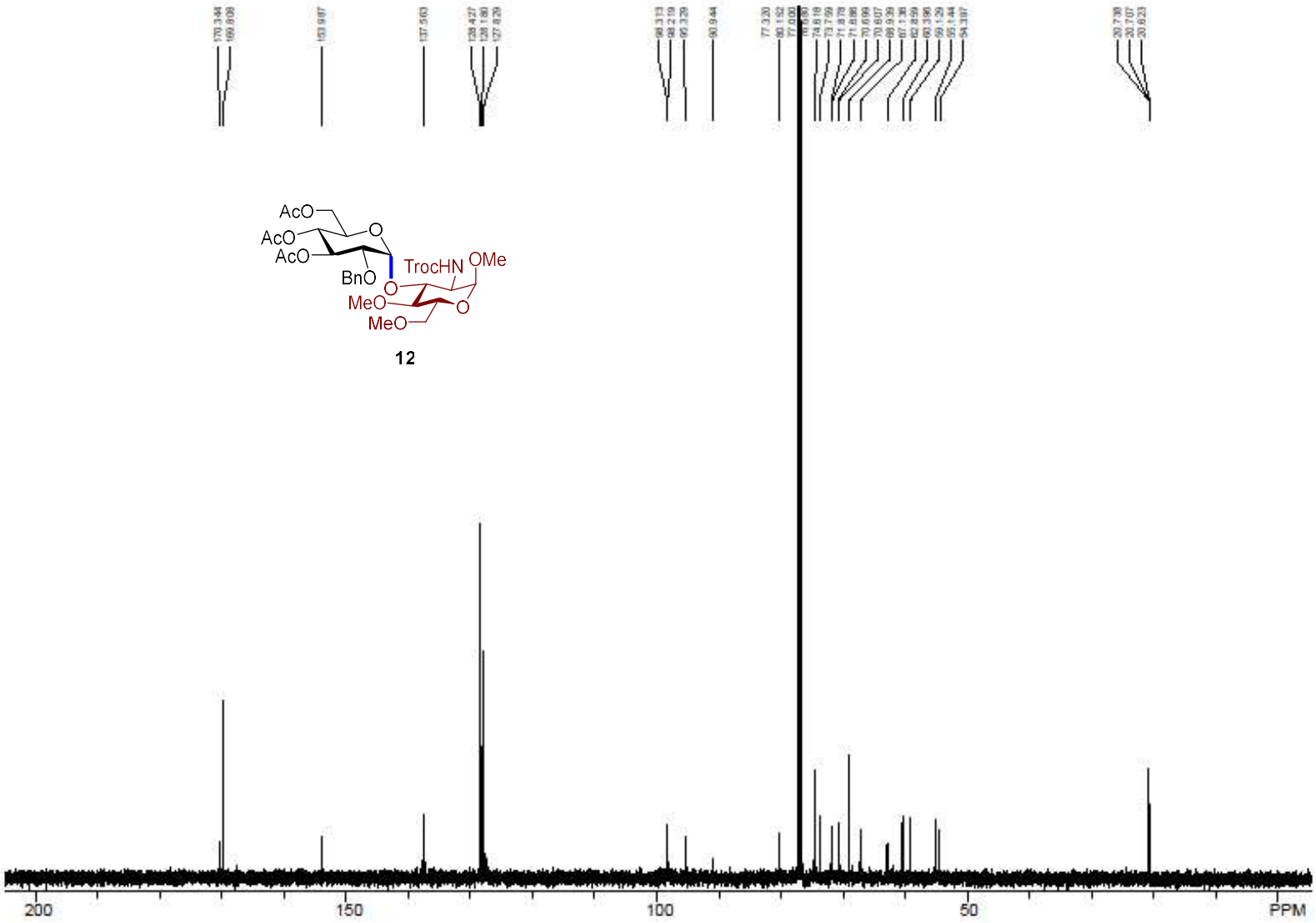

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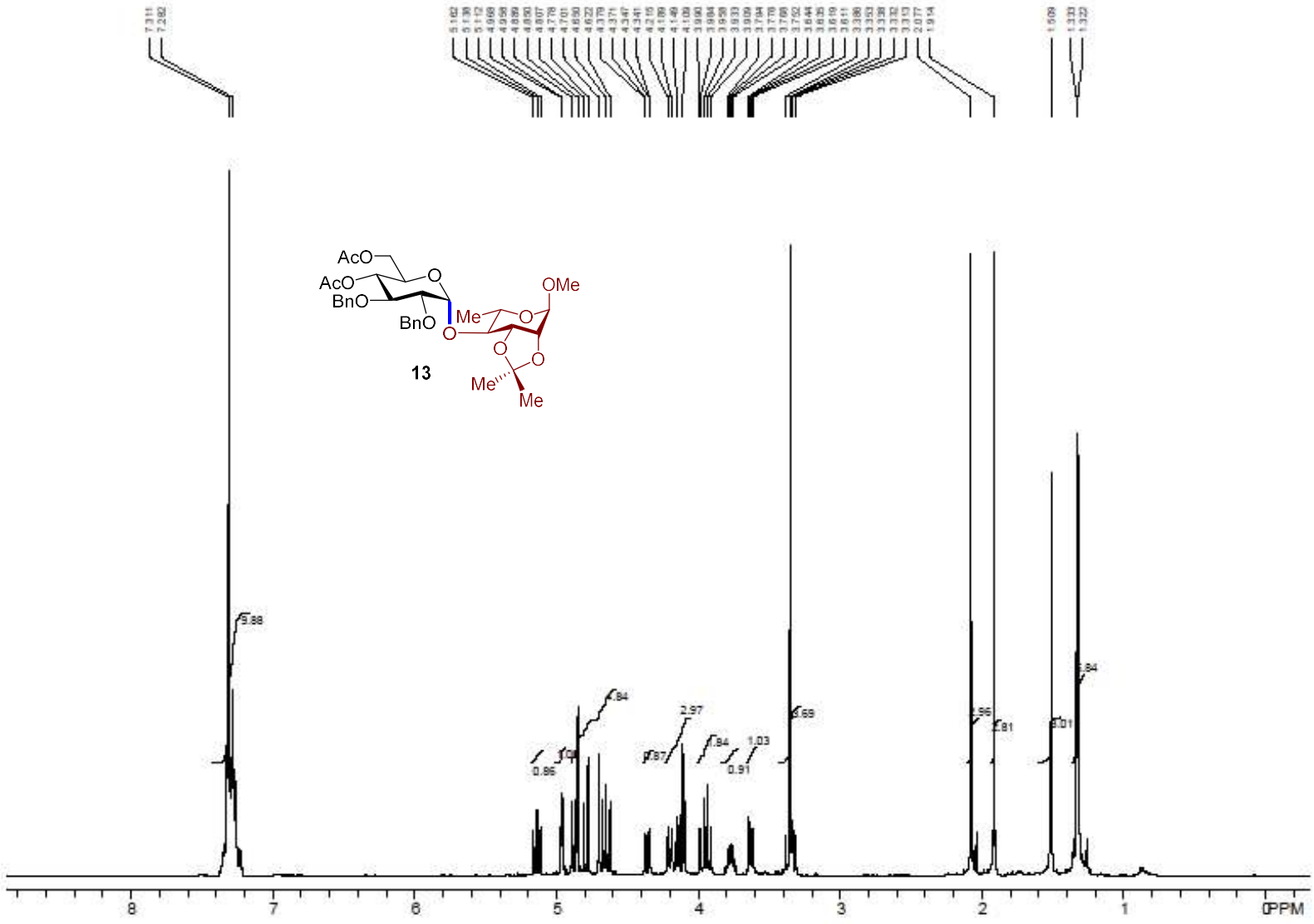
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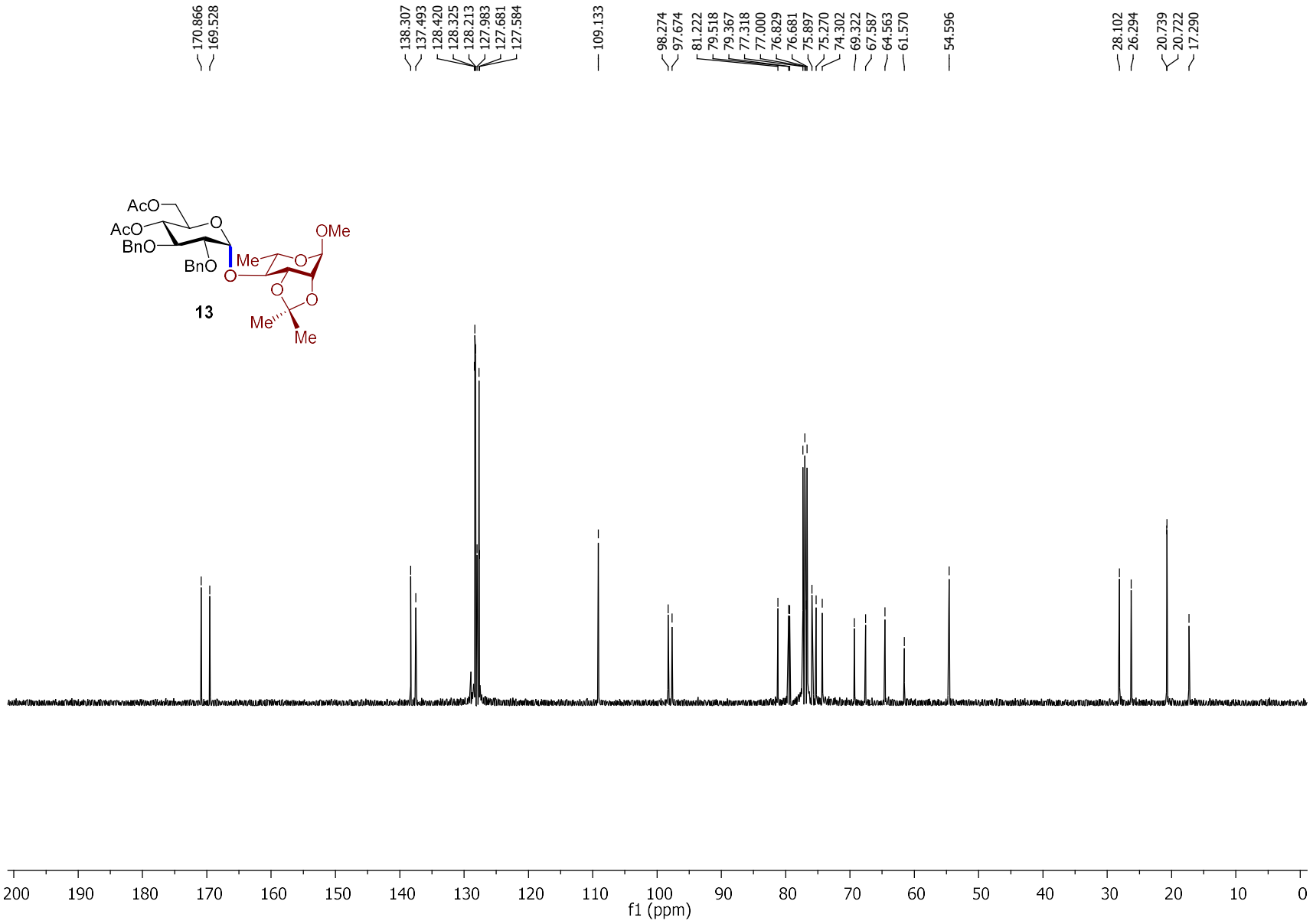
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BnO
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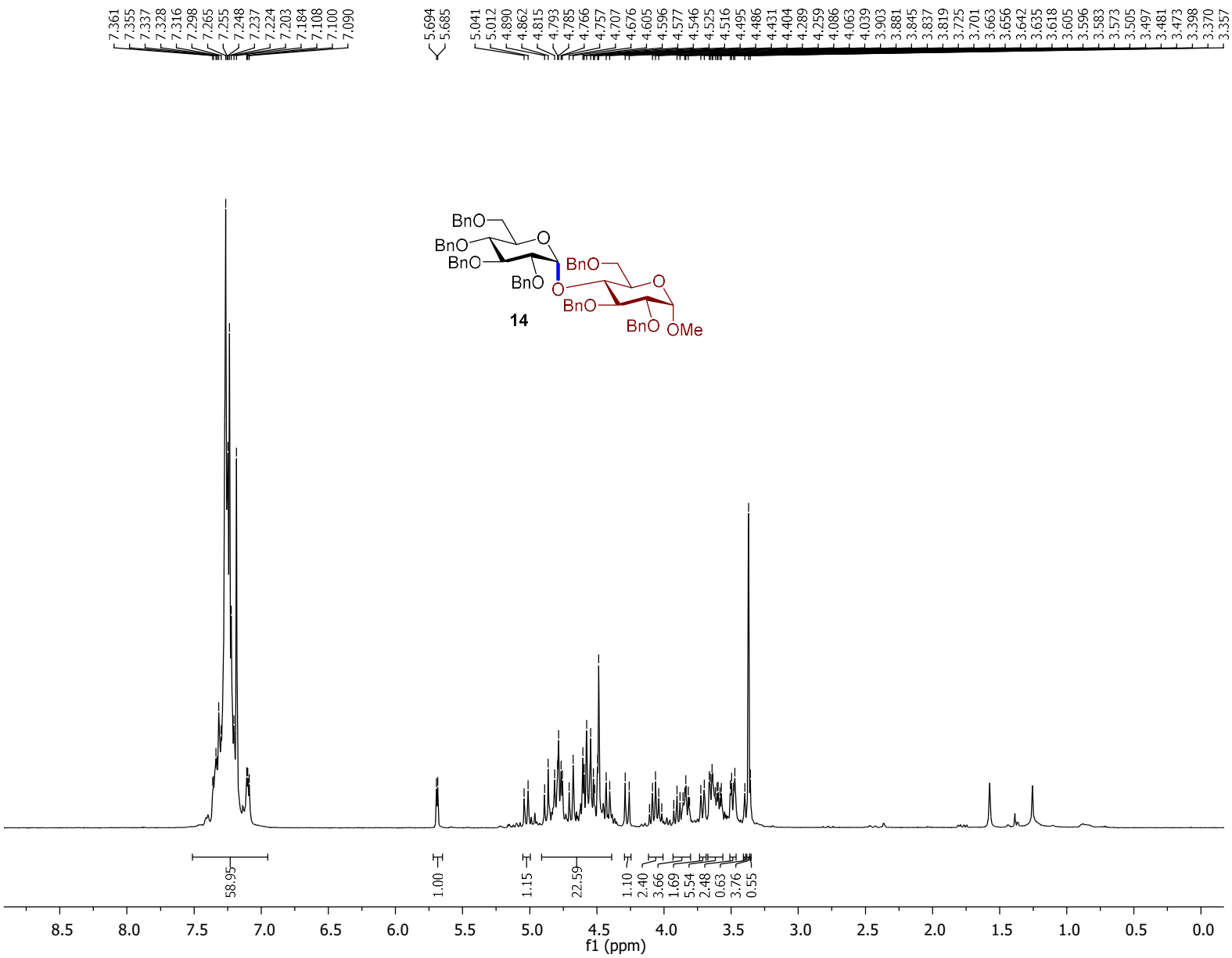
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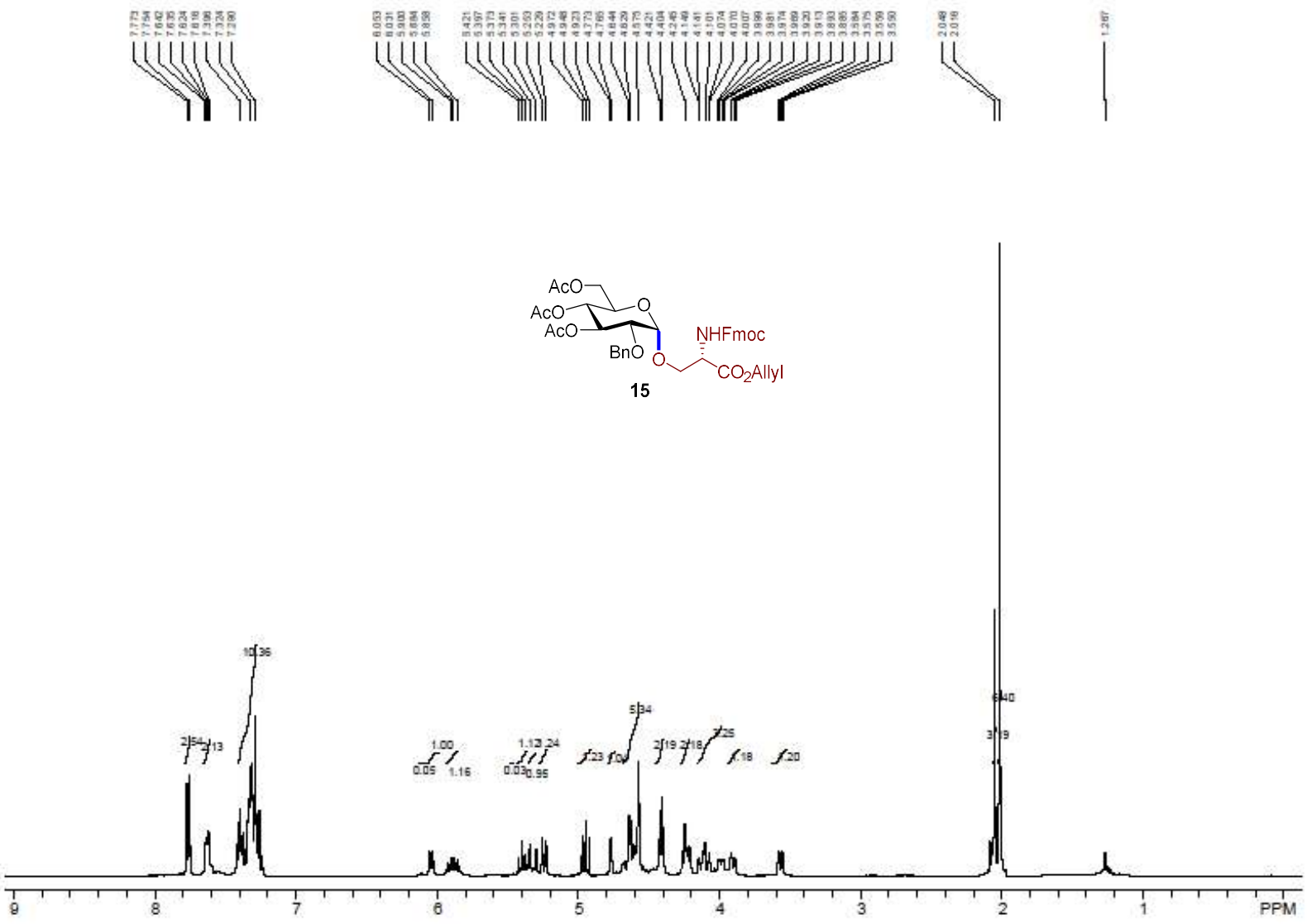
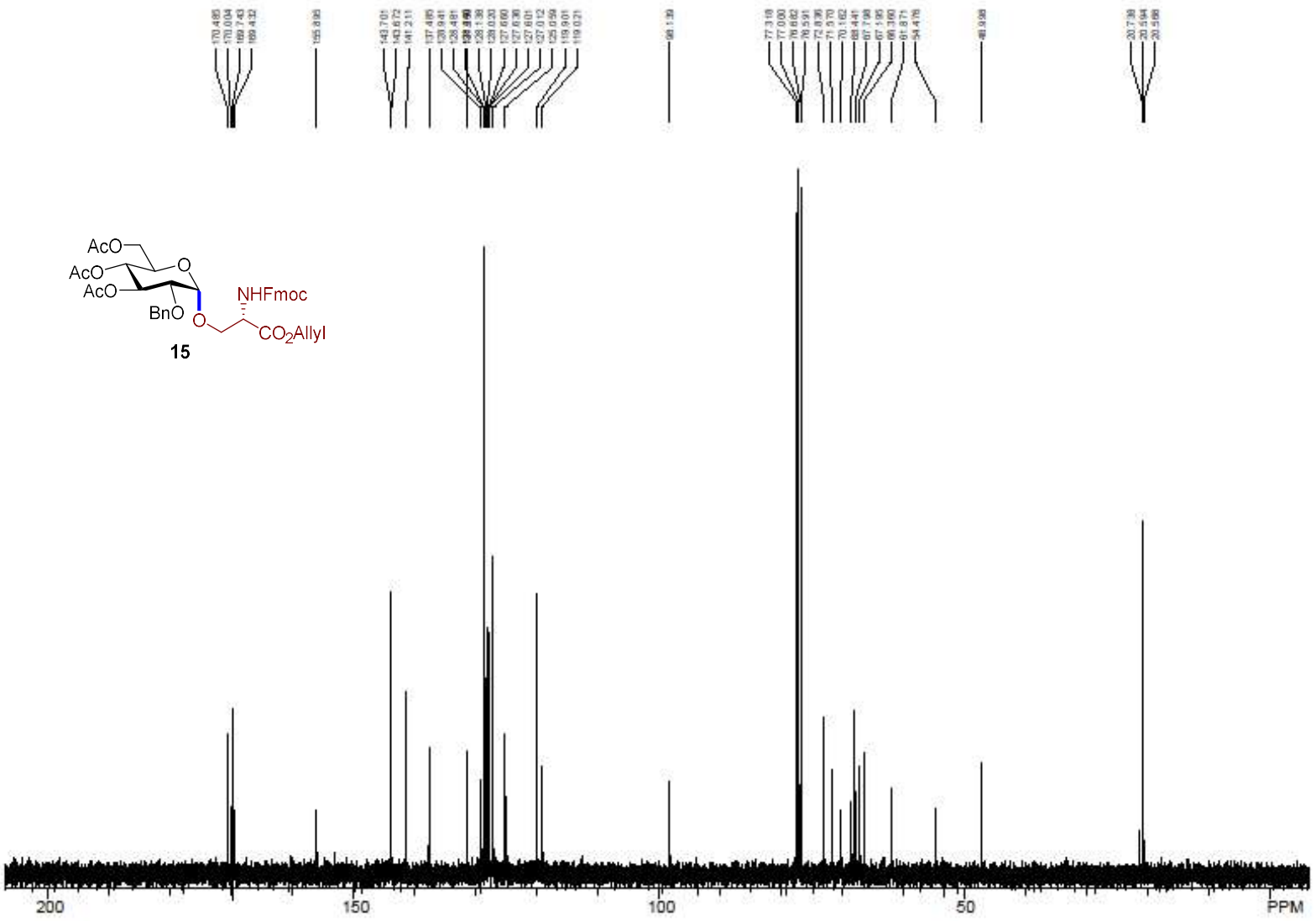
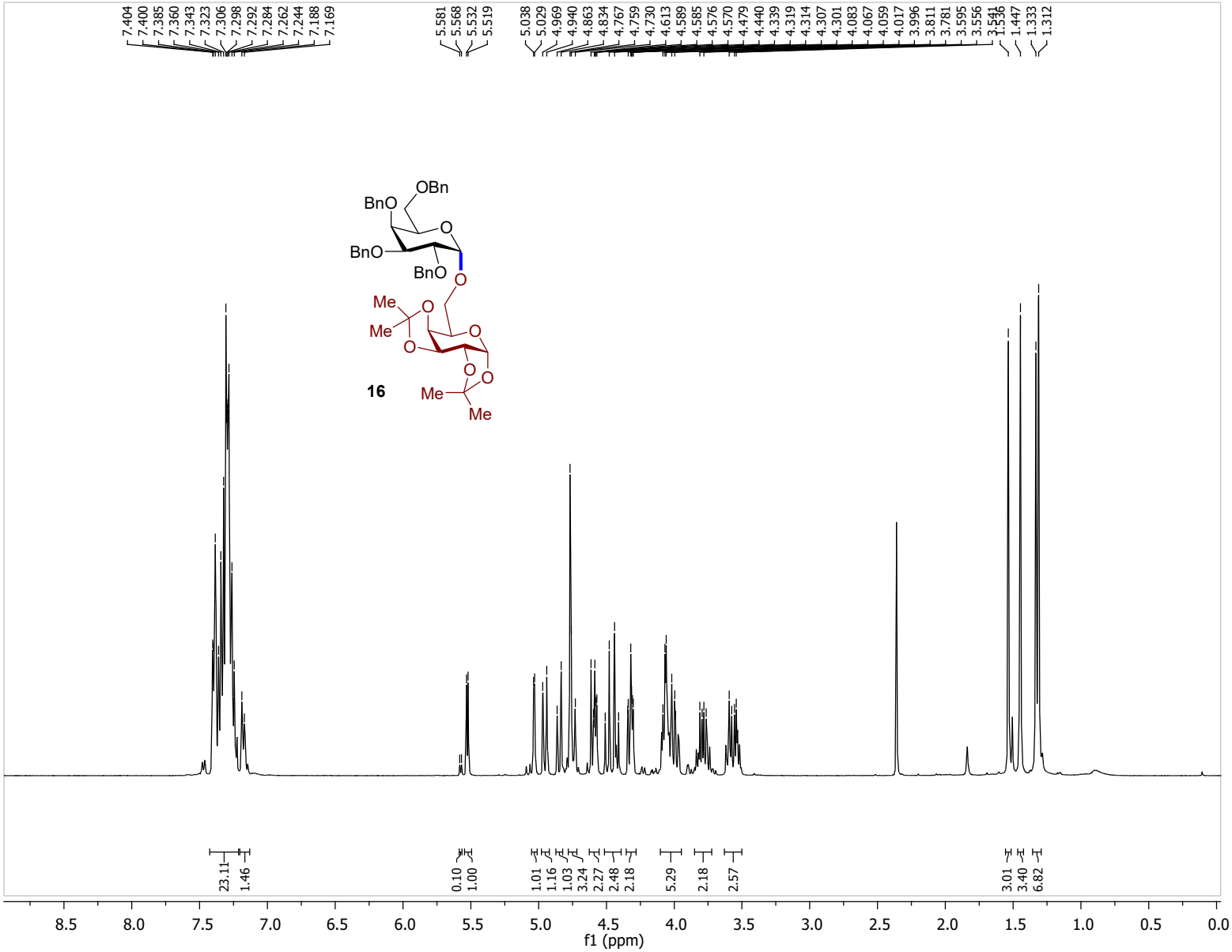
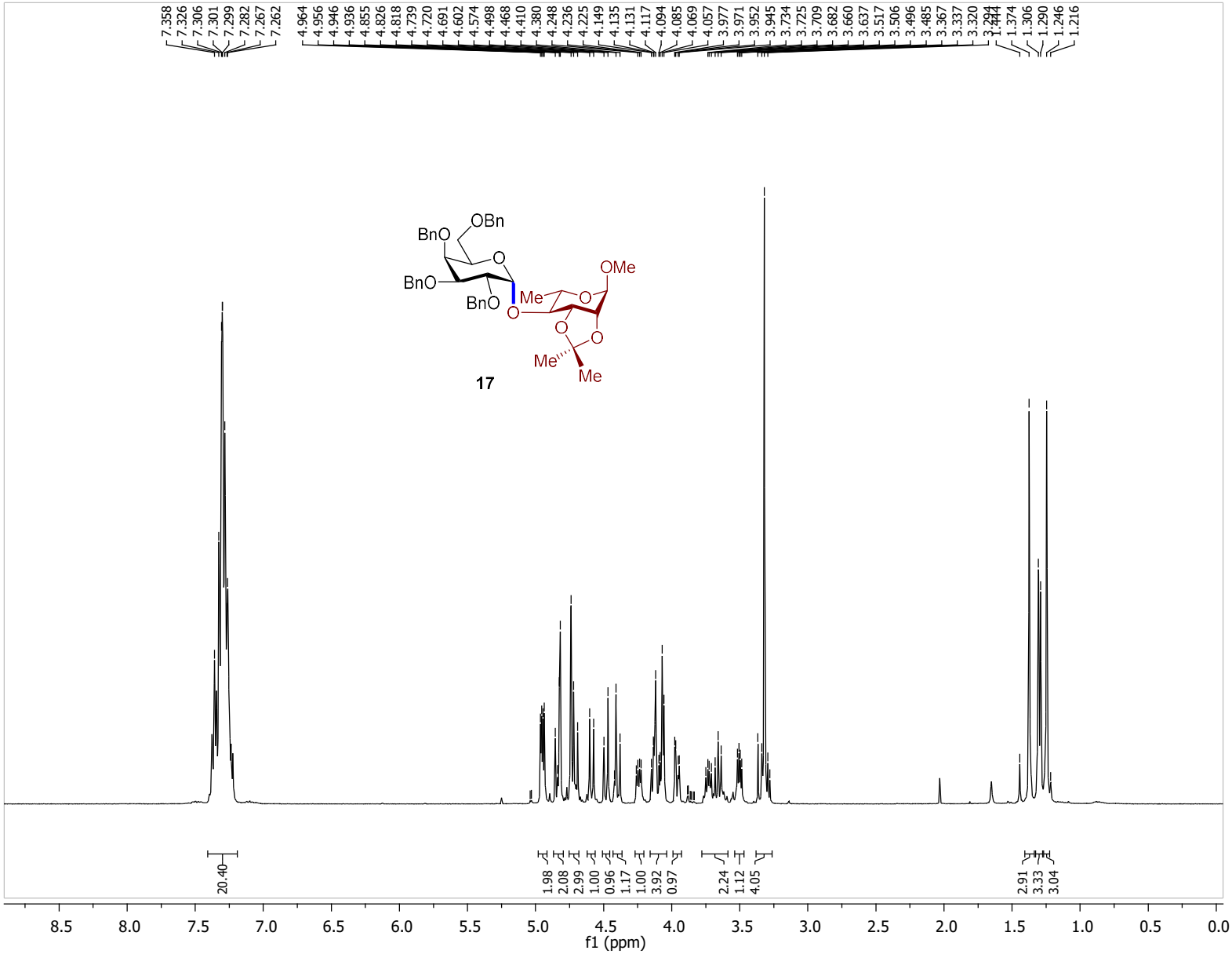
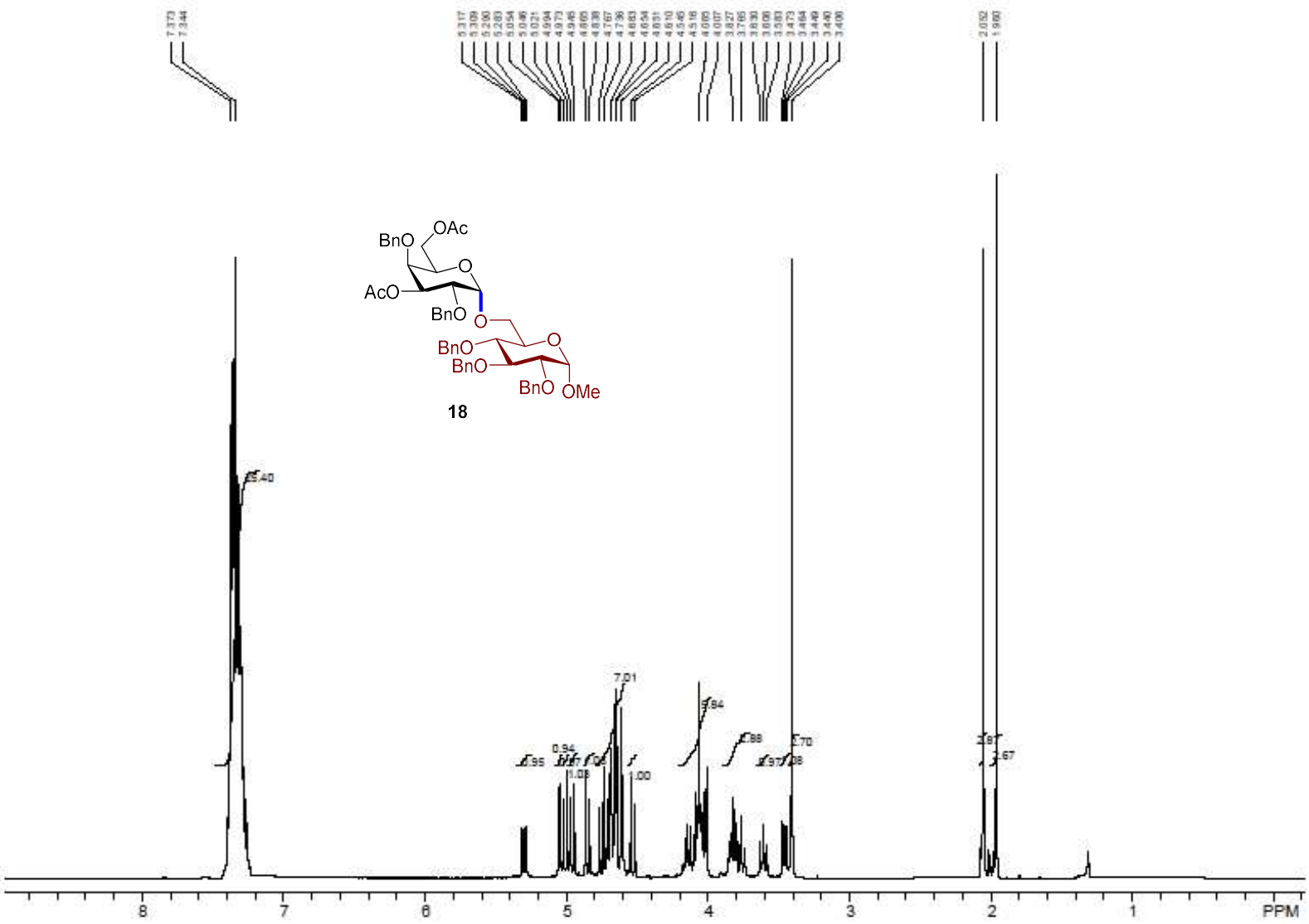
3.656
3.642
3.635
3.618
3.605
3.596
3.583
3.573
3.505
3.497
3.481
3.473
3.398
3.370
3.357
BnO
BnO
BnO
BnO
O
BnO
O
O
BnO
BnO
OMe
14
58.95
1.00
1.15
22.59
1.10
2.40
3.66
1.69
5.54
2.48
0.63
3.76
0.55
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

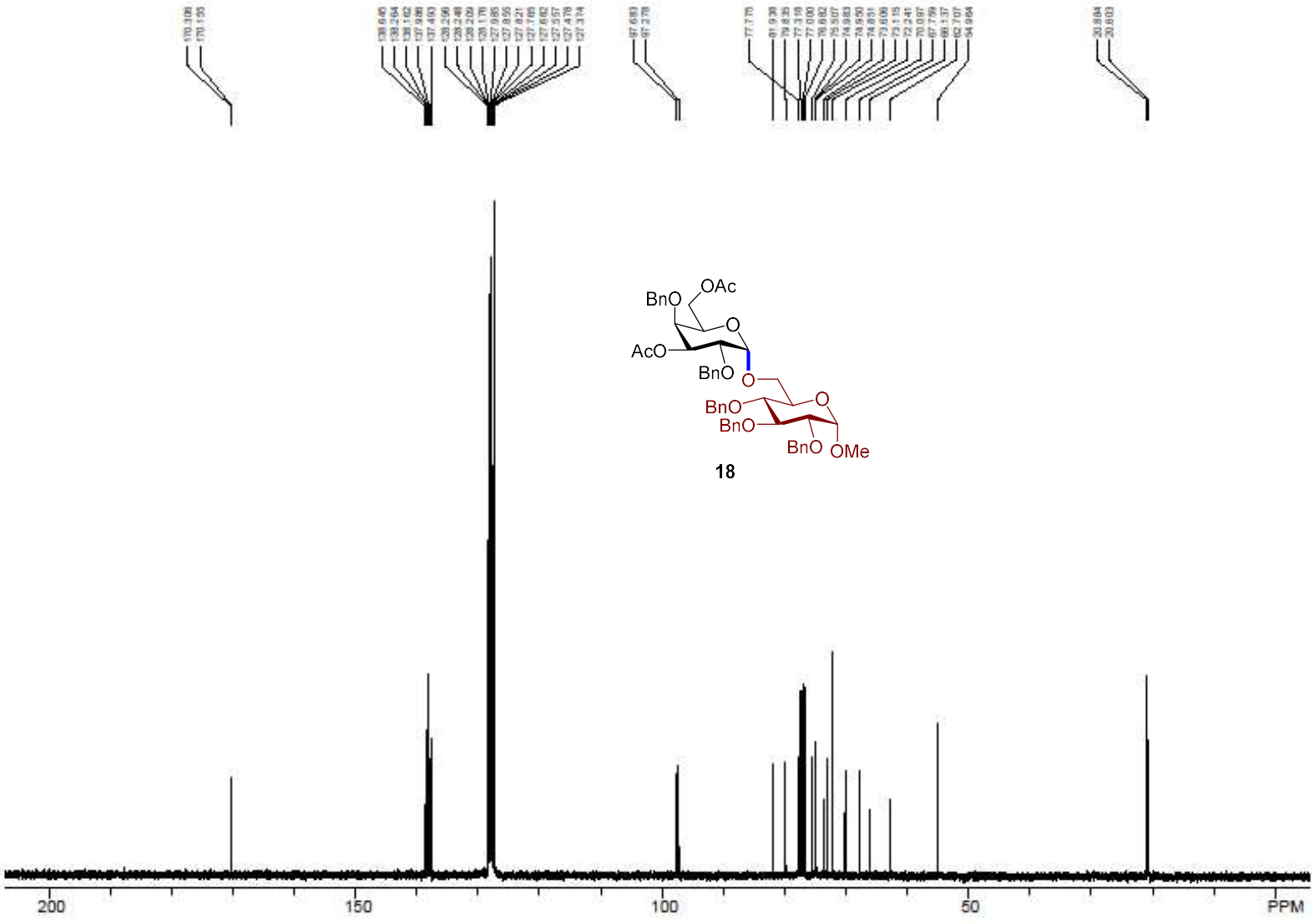

AcO
AcO
AcO
BnO
O
O
NHFmoc
CO2Allyl
15
9
8
7
6
5
4
3
2
1
PPM


AcO
AcO
AcO
BnO
O
NHFmoc
CO2Allyl
15
200
150
100
50
PPM

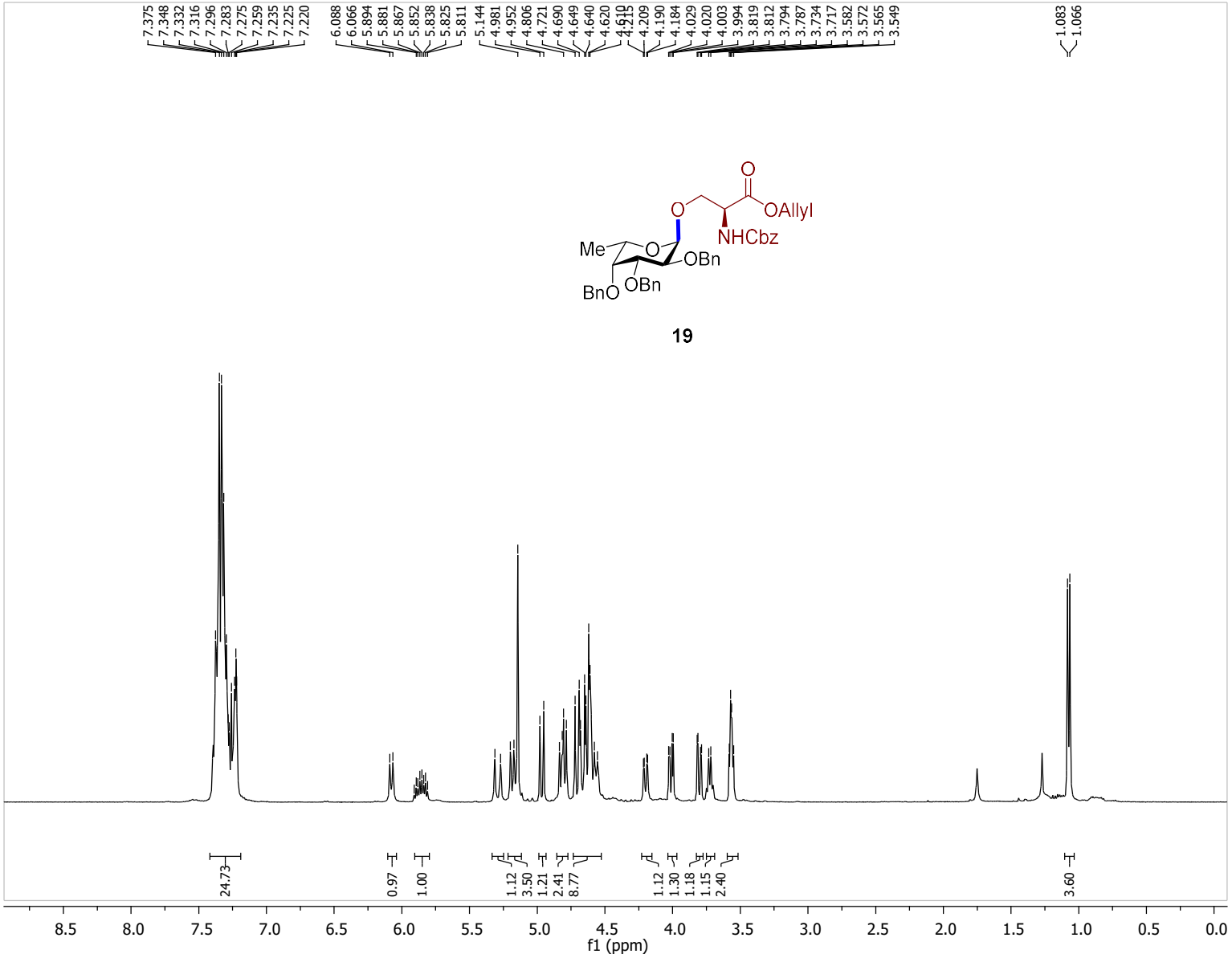

7.404
7.400
7.385
7.360
7.343
7.323
7.306
7.298
7.292
7.284
7.262
7.244
7.188
7.169
5.581
5.568
5.532
5.519
5.038
5.029
4.969
4.940
4.863
4.834
4.767
4.759
4.730
4.613
4.589
4.585
4.576
4.570
4.479
4.440
4.339
4.319
4.314
4.307
4.301
4.083
4.067
4.059
4.017
3.996
3.811
3.781
3.595
3.556
3.541
1.536
1.447
1.333
1.312
OBn
BnO
BnO
BnO
O
O
Me
Me
O
O
O
O
O
Me
Me
16
23.11
1.46
0.10
1.00
1.01
1.16
1.03
3.24
2.27
2.48
2.18
5.29
2.18
2.57
3.01
3.40
6.82
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

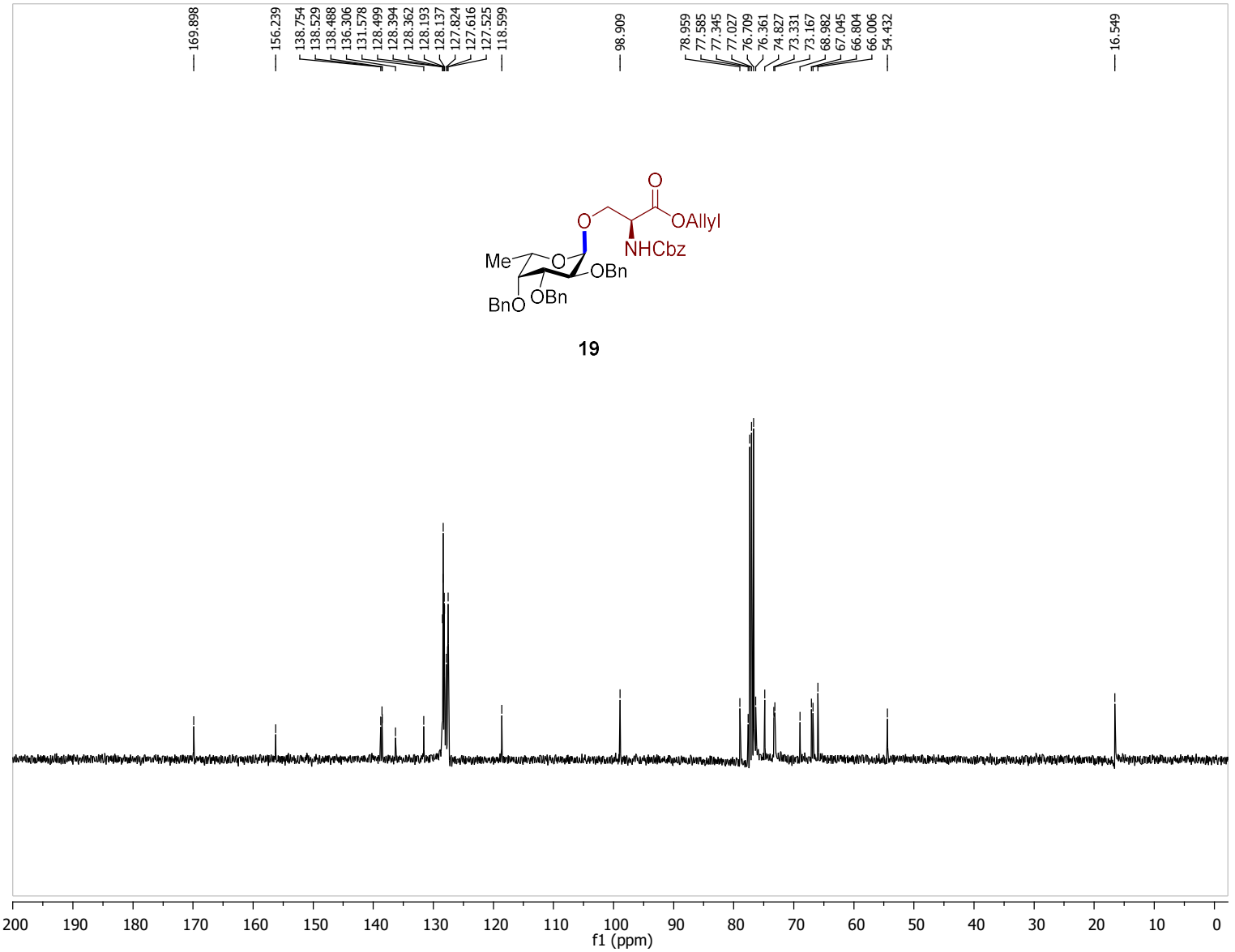

7.358
7.326
7.306
7.301
7.299
7.282
7.267
7.262
4.964
4.956
4.946
4.936
4.855
4.826
4.818
4.739
4.720
4.691
4.602
4.574
4.498
4.468
4.410
4.380
4.248
4.236
4.225
4.149
4.135
4.131
4.117
4.094
4.085
4.069
4.057
3.977
3.971
3.952
3.945
3.734
3.725
3.709
3.682
3.660
3.637
3.517
3.506
3.496
3.485
3.367
3.337
3.320
1.444
1.374
1.306
1.290
1.246
1.216
BnO
OBn
O
BnO
BnO
O
Me
O
OMe
O
O
Me
Me
17
20.40
1.98
2.08
2.99
1.00
0.96
1.17
1.00
3.92
0.97
2.24
1.12
4.05
2.91
3.33
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

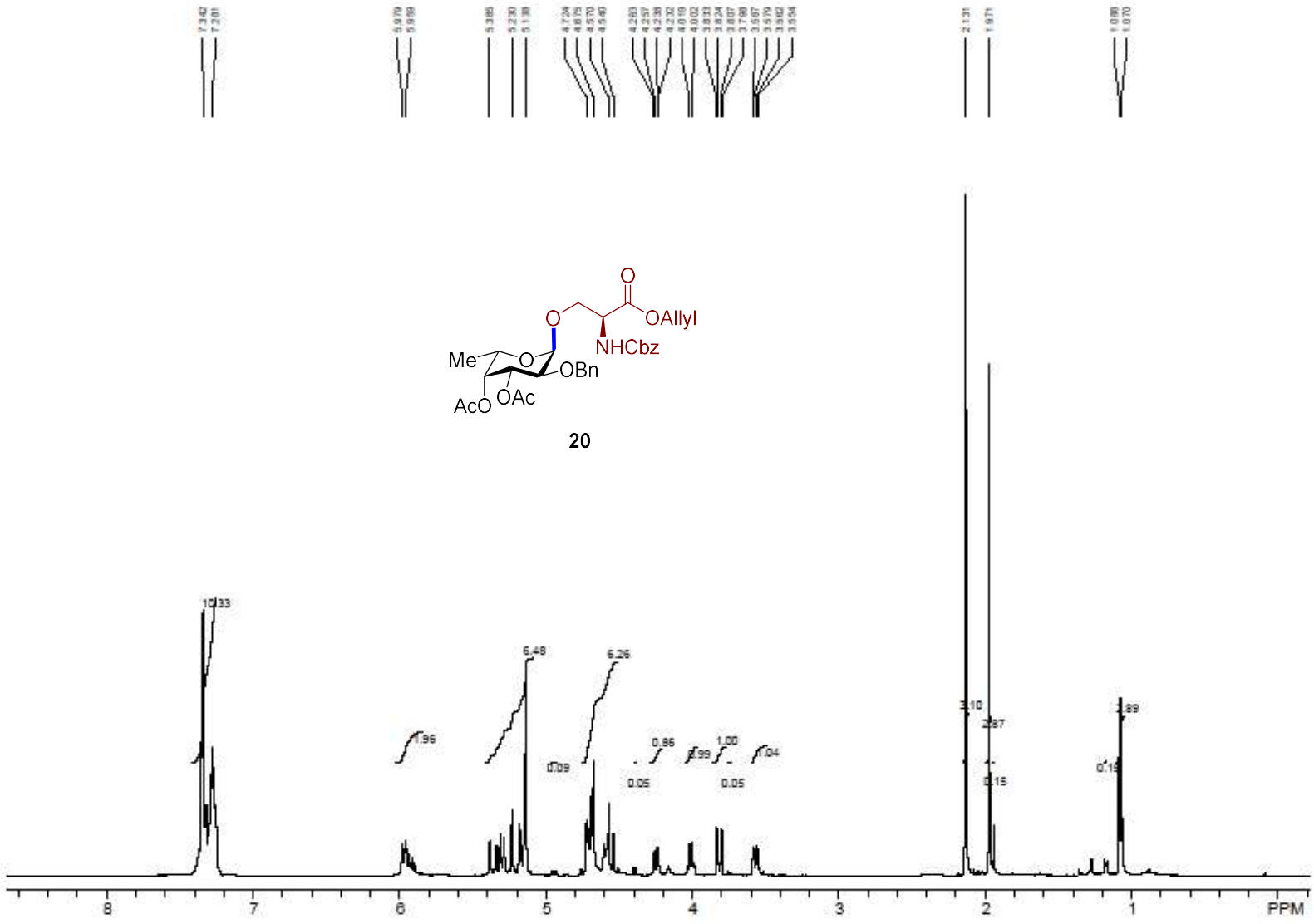

BnO
OAc
O
AcO
BnO
O
BnO
BnO
O
BnO
OMe
18
PPM



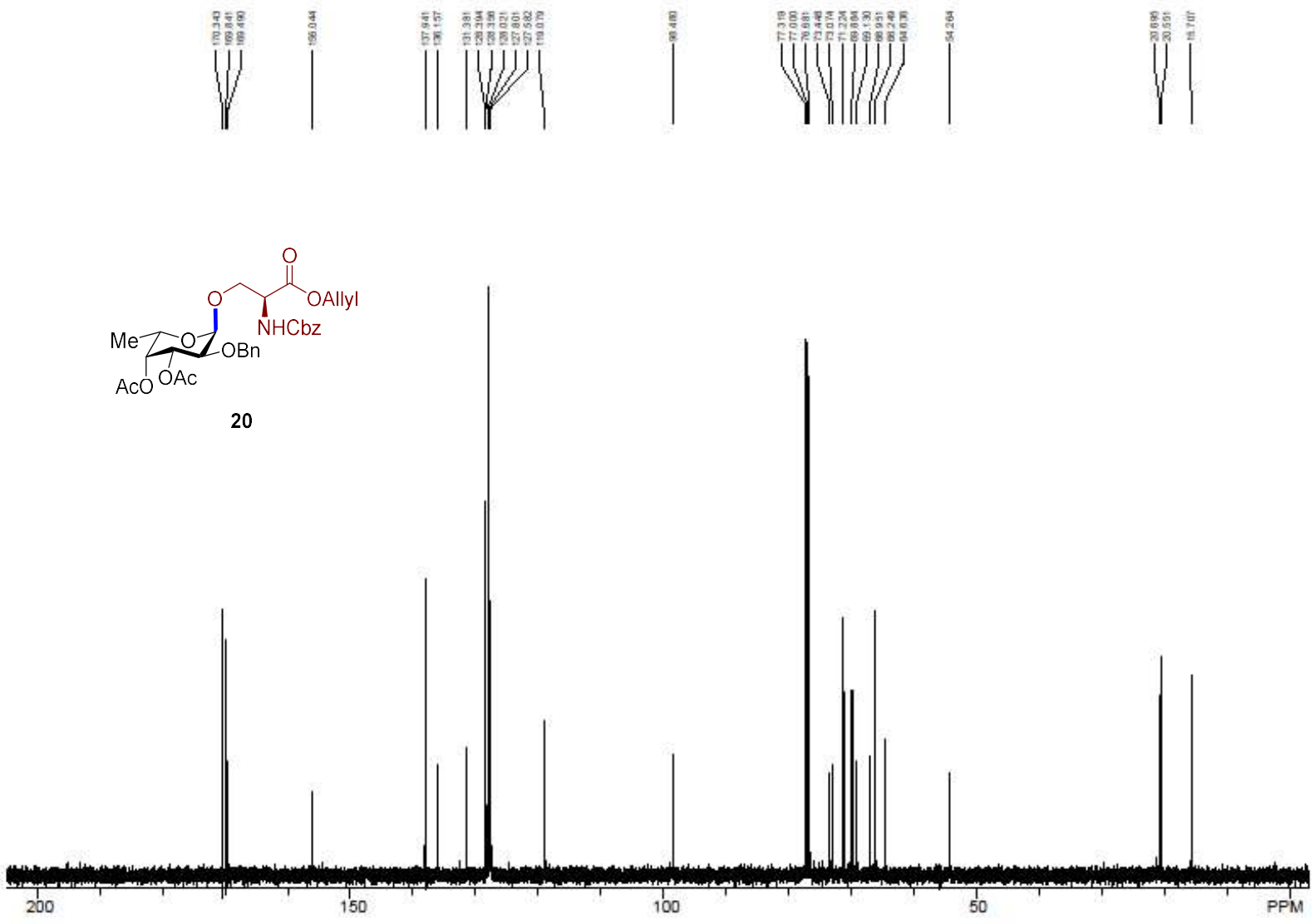
18


7.375
7.348
7.332
7.316
7.296
7.283
7.275
7.259
7.235
7.225
7.220
6.088
6.066
5.894
5.881
5.867
5.852
5.838
5.825
5.811
5.144
4.981
4.952
4.806
4.721
4.690
4.649
4.640
4.620
4.610
4.209
4.190
4.184
4.029
4.020
4.003
3.994
3.819
3.812
3.794
3.787
3.734
3.717
3.582
3.572
3.565
3.549
1.083
1.066
O
O
OAllyl
NHCbz
Me
O
OBn
BnO
OBn
19
24.73
0.97
1.00
1.12
3.50
1.21
2.41
8.77
1.12
1.30
1.18
1.15
2.40
3.60
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

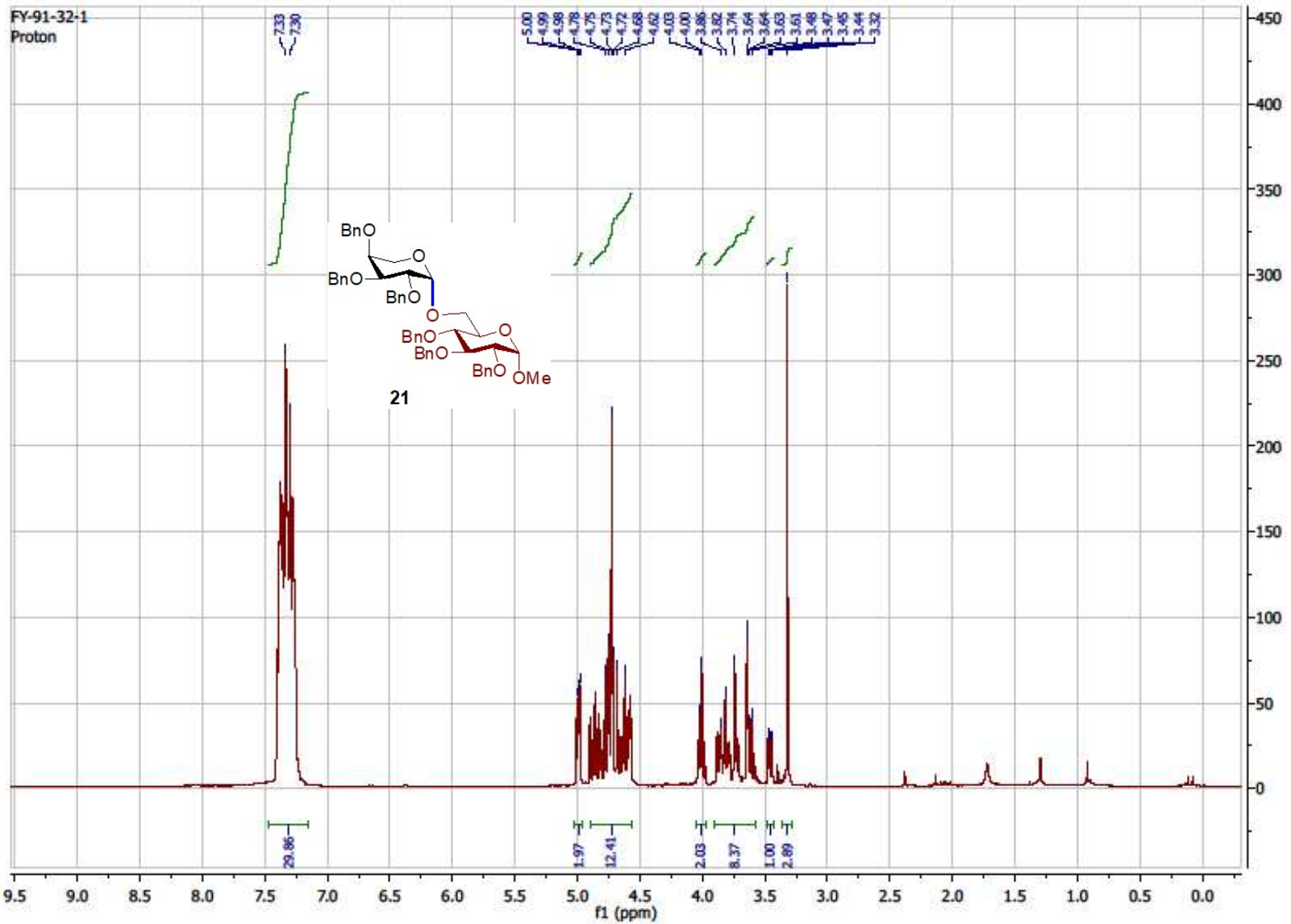

169.898
156.239
138.754
138.529
138.488
136.306
131.578
128.499
128.394
128.362
128.193
128.137
127.824
127.616
127.525
118.599
98.909
78.959
77.585
77.345
77.027
76.709
76.361
74.827
73.331
73.167
68.982
67.045
66.804
66.006
54.432
16.549
O
O
OAllyl
NHCbz
Me
O
OBn
BnO
OBn
19
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

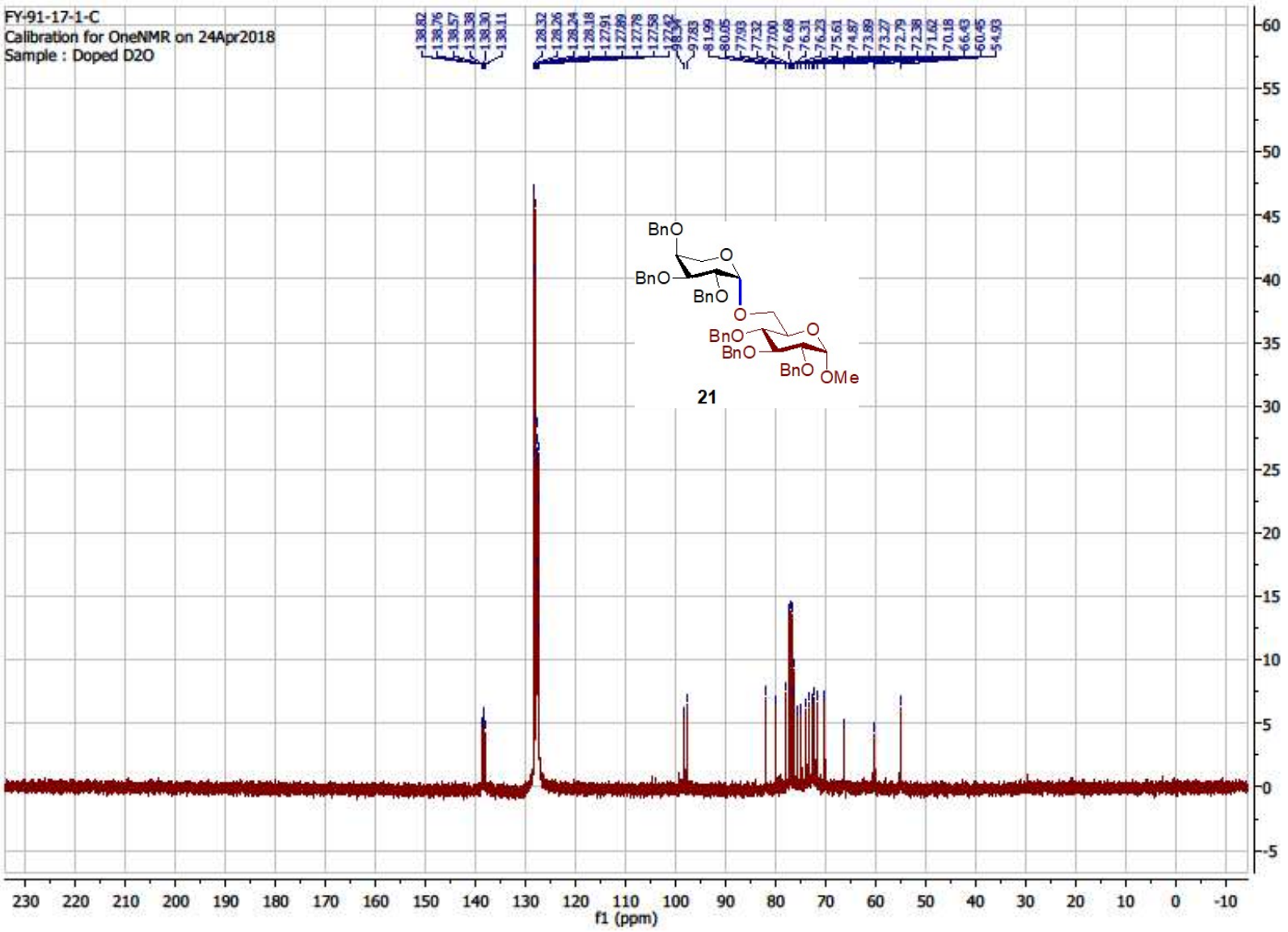


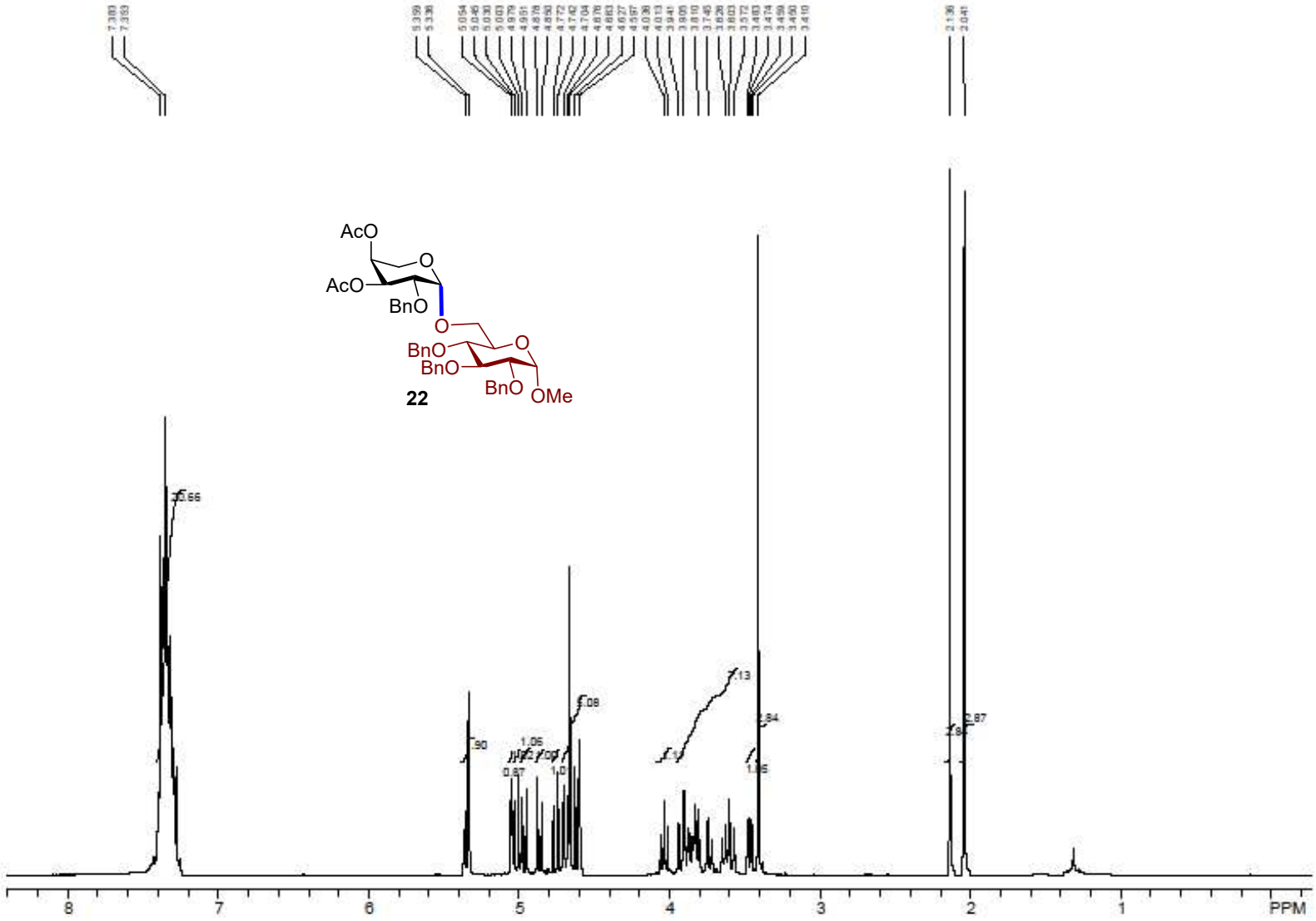
20

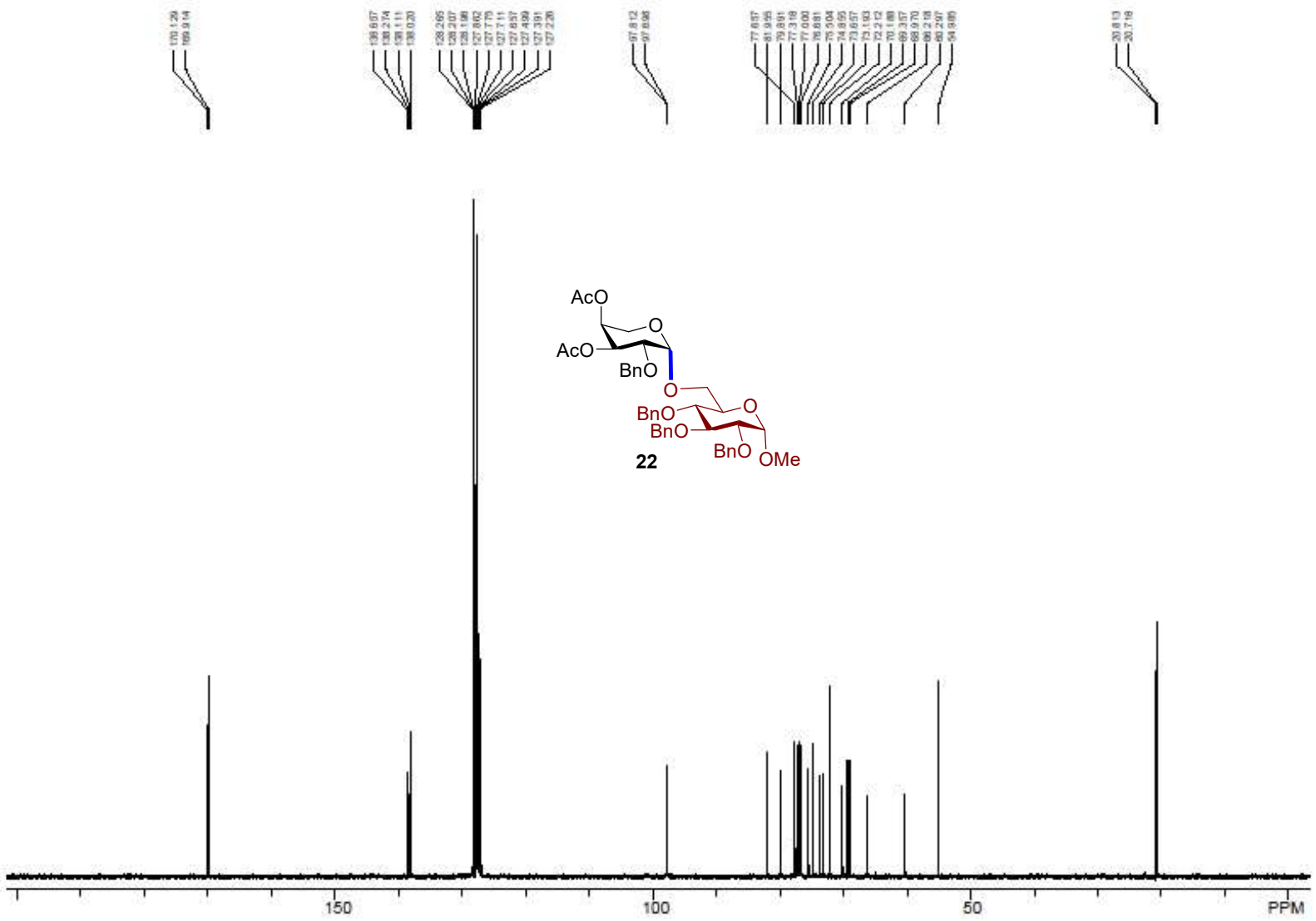


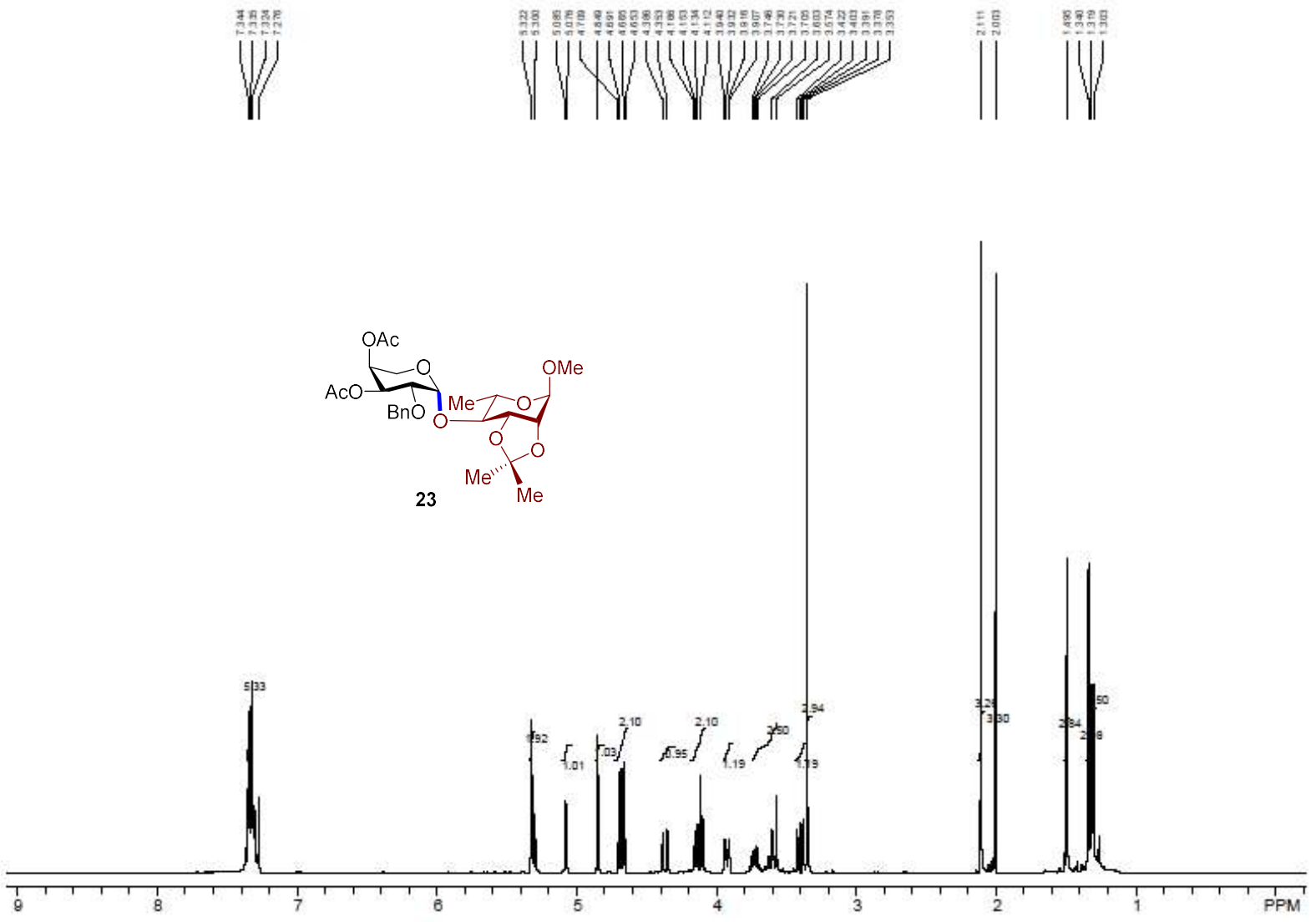
20

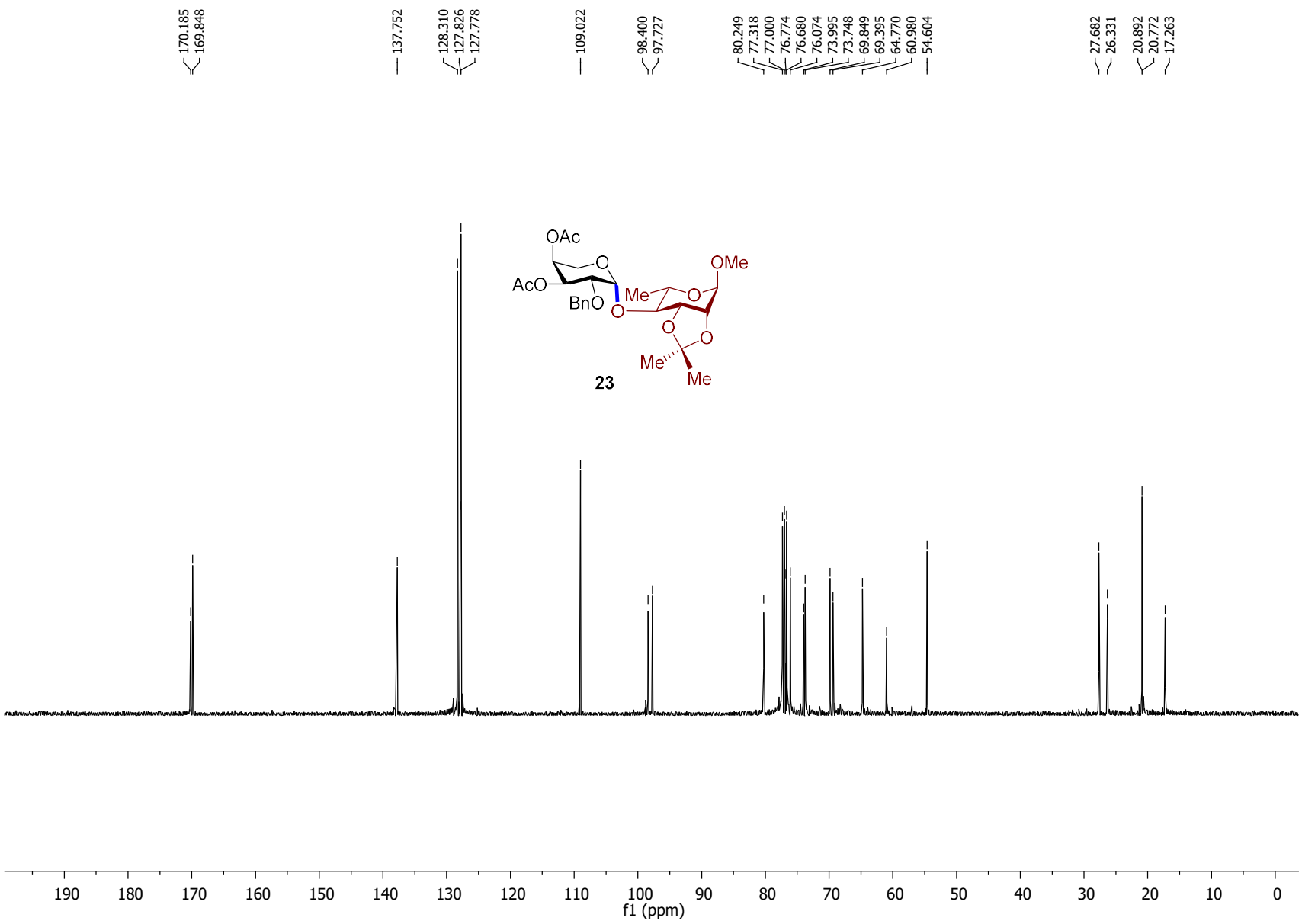

FY-91-32-1
Proton
7.33
7.30
5.00
4.99
4.98
4.78
4.75
4.73
4.72
4.68
4.62
4.03
4.00
3.86
3.82
3.74
3.64
3.64
3.63
3.61
3.48
3.47
3.45
3.44
3.32
BnO
BnO
BnO
O
BnO
BnO
BnO
O
OMe
21
29.86
1.97
12.41
2.03
8.37
1.00
2.89
f1 (ppm)

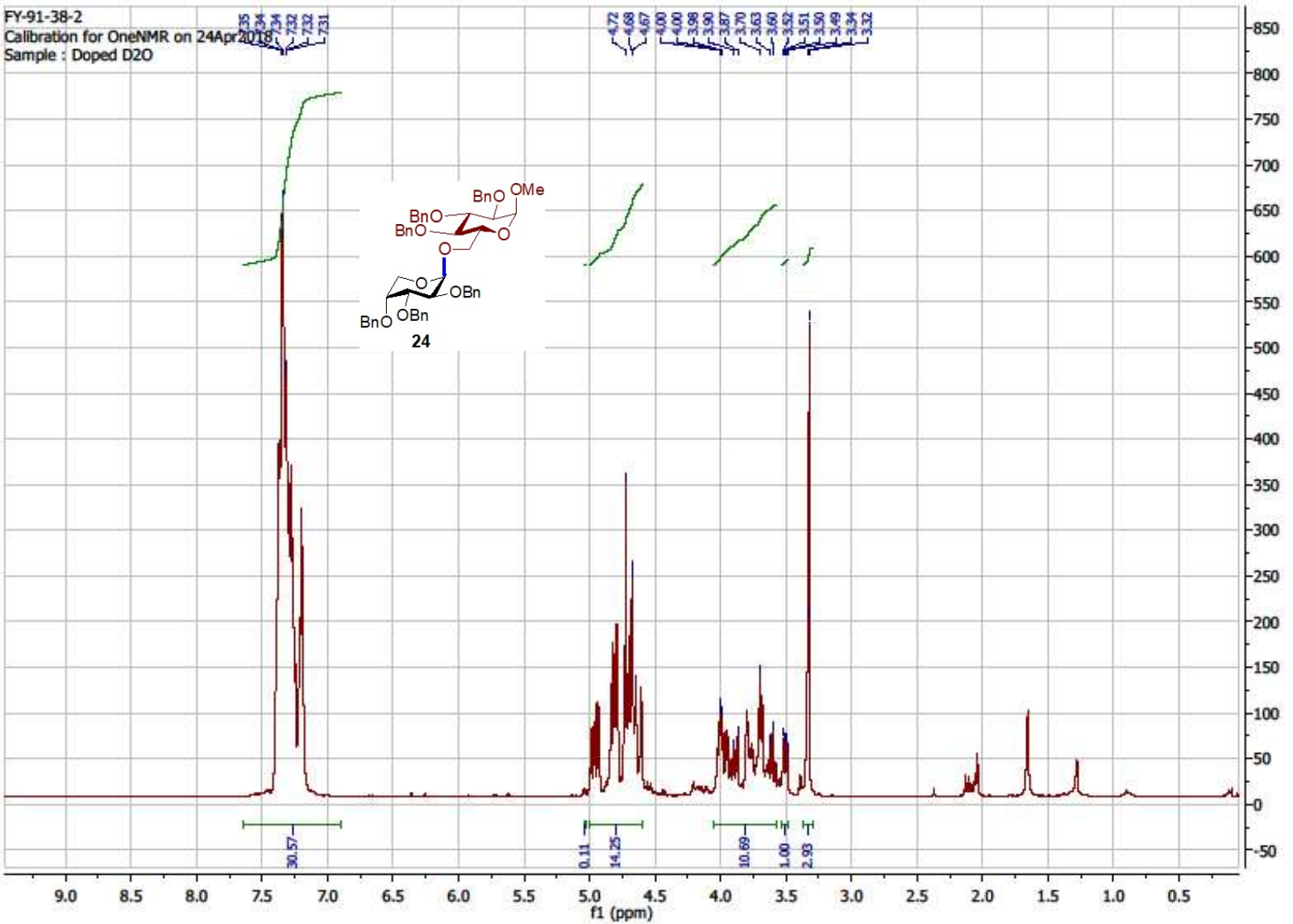

FY-91-17-1-C
Calibration for OneNMR on 24Apr2018
Sample : Doped D2O
BnO
BnO
BnO
O
O
BnO
BnO
BnO
OMe
21
f1 (ppm)

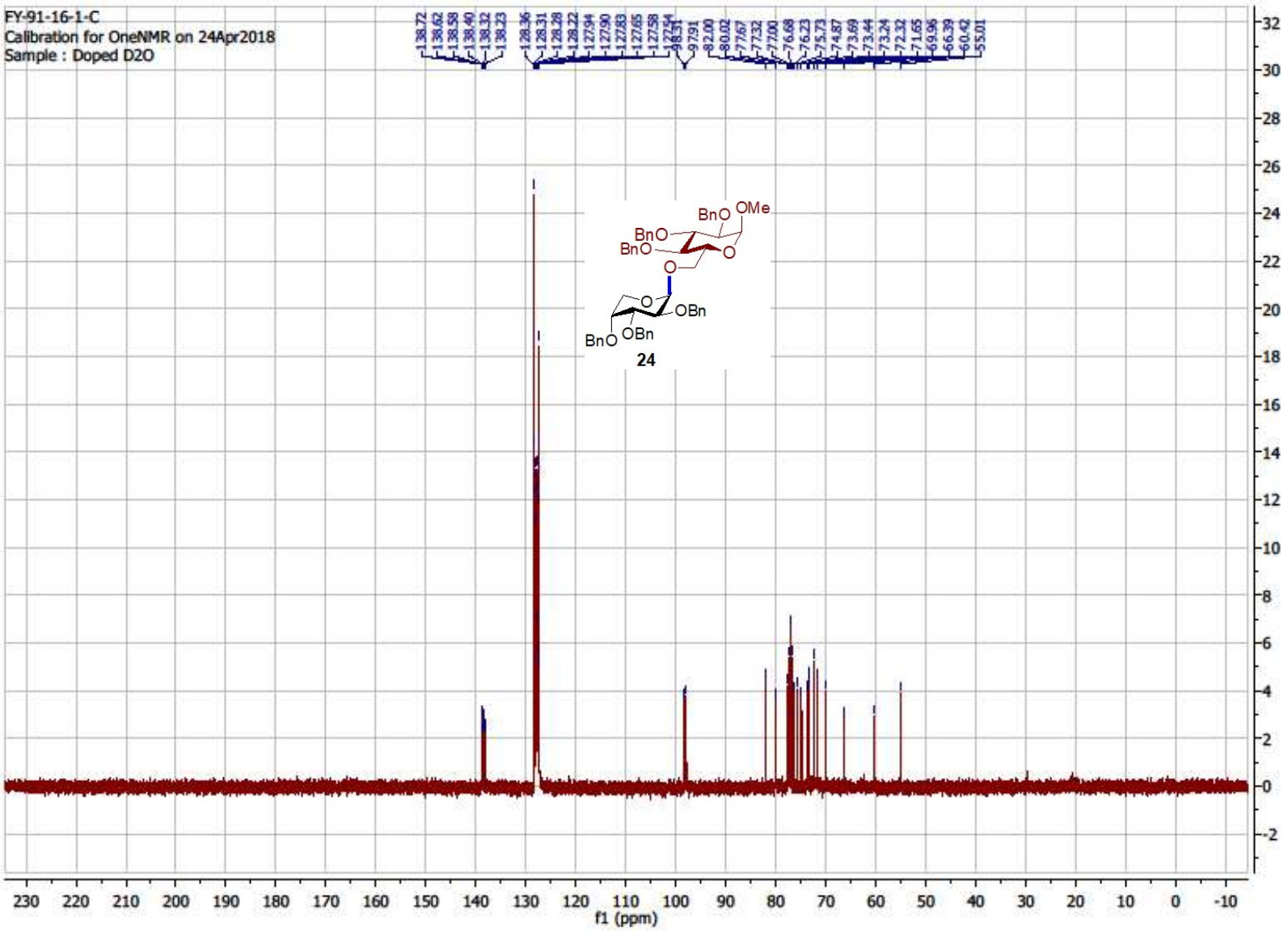

AcO
AcO
O
BnO
O
BnO
BnO
O
BnO
OMe
22
8
7
6
5
4
3
2
1
PPM

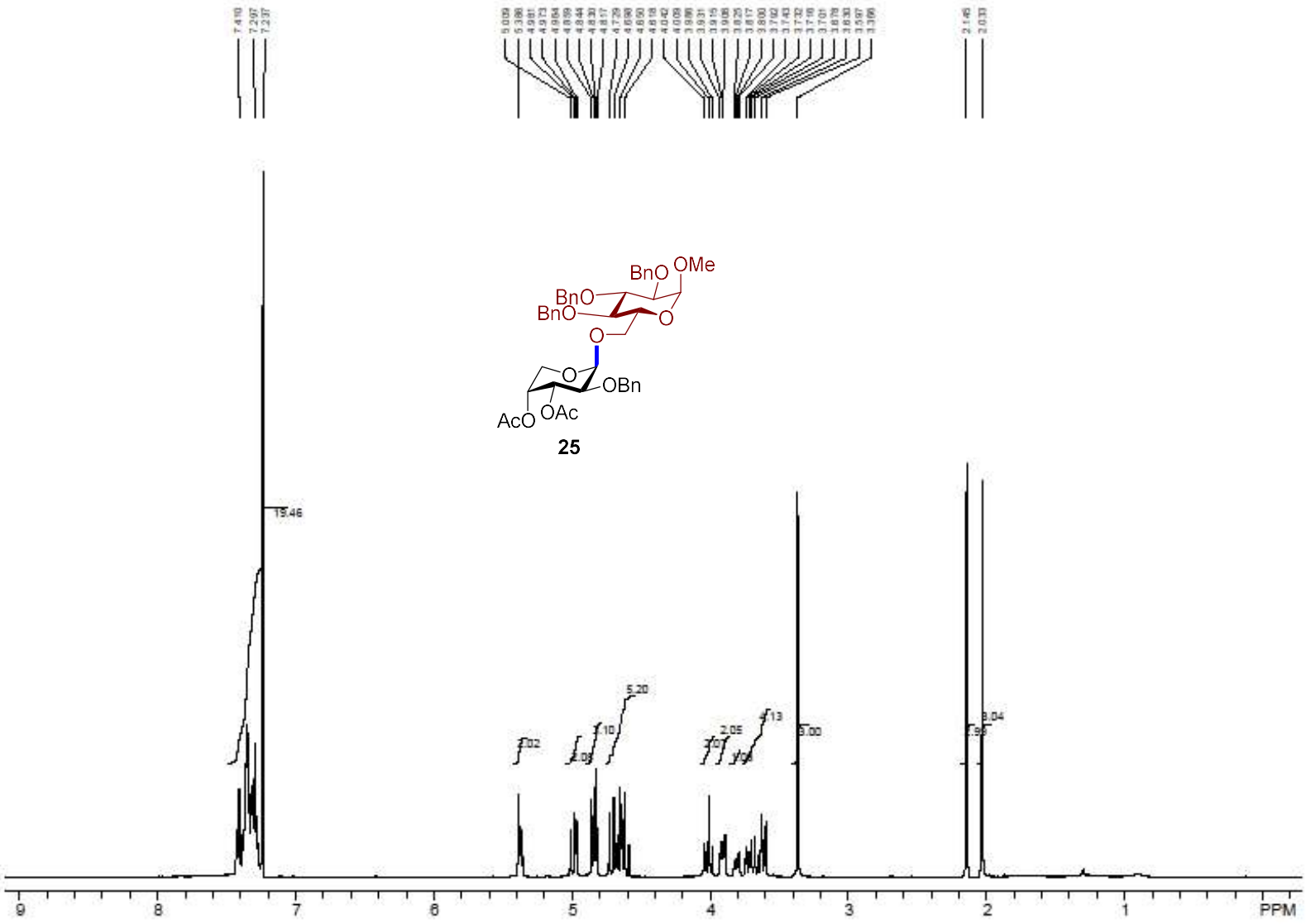

AcO
O
AcO
BnO
O
BnO
O
BnO
BnO
OMe
22
150
100
50
PPM

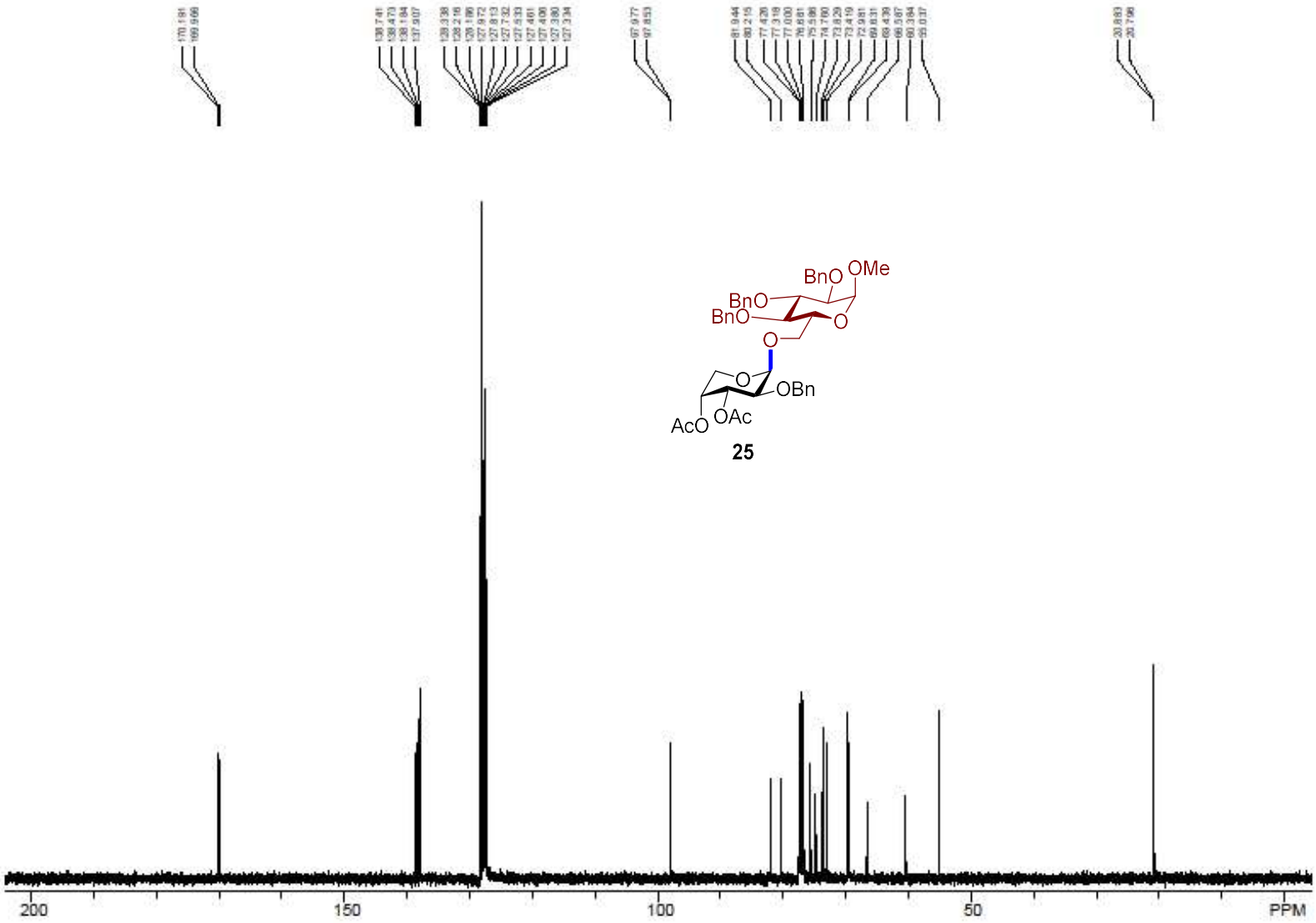

OAc
AcO
BnO
Me
OMe
Me
Me
23
PPM

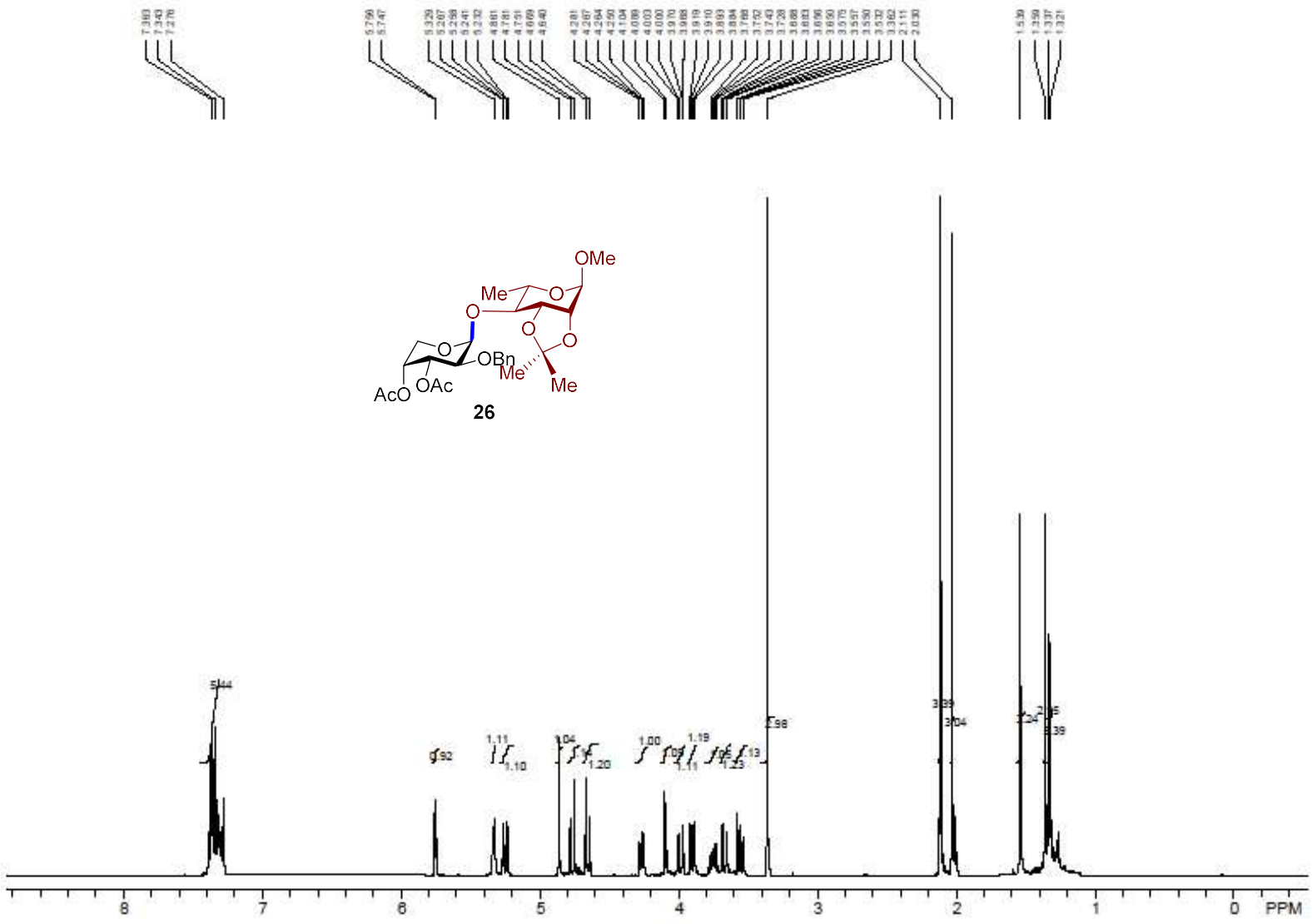

170.185
169.848
137.752
128.310
127.826
127.778
109.022
98.400
97.727
80.249
77.318
77.000
76.774
76.680
76.074
73.995
73.748
69.849
69.395
64.770
60.980
54.604
27.682
26.331
20.892
20.772
17.263
OAc
AcO
BnO
O
Me
OMe
Me
Me
23
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

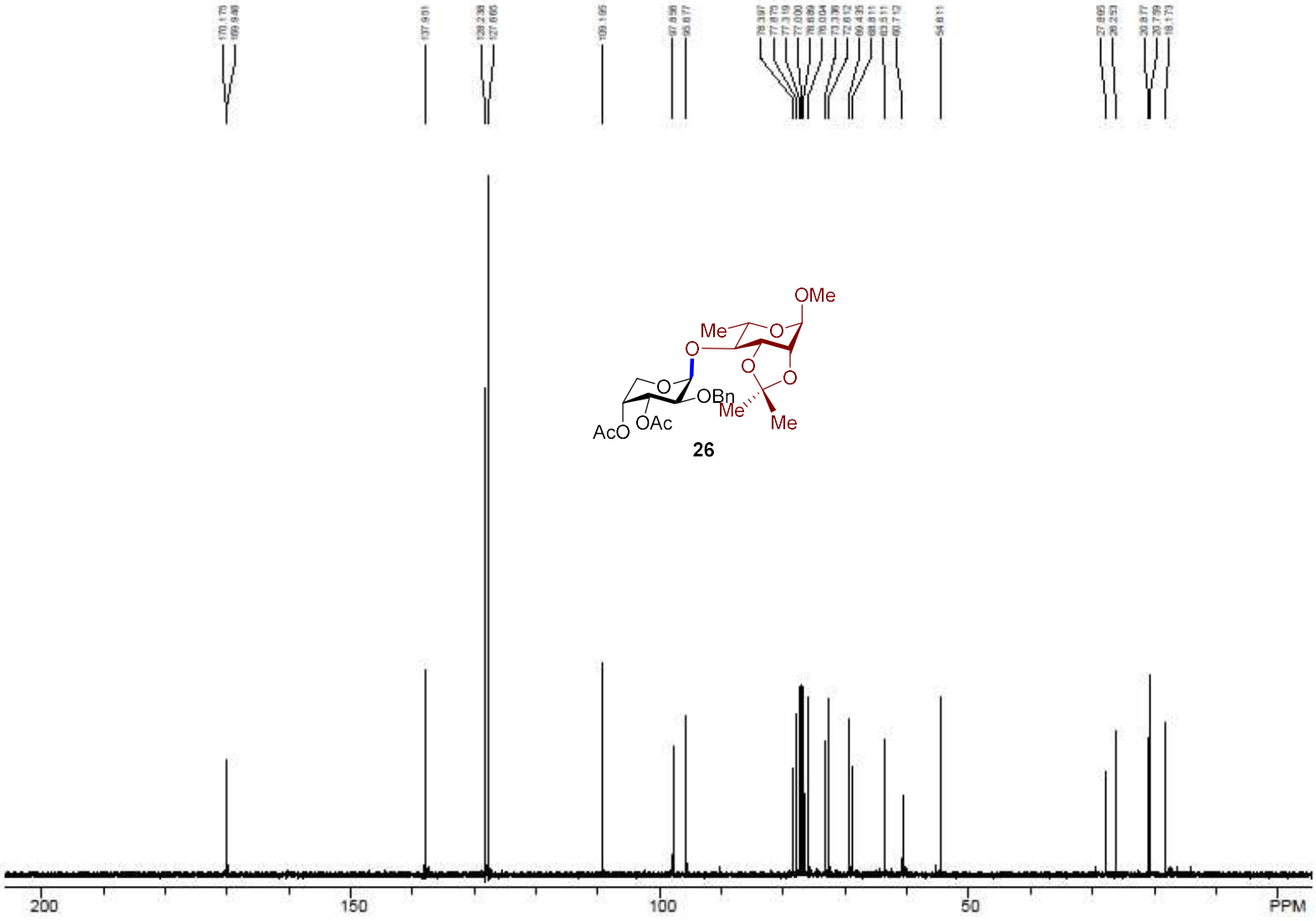

FY-91-38-2
Calibration for OneNMR on 24Apr2018
Sample : Doped D2O
7.35
7.34
7.34
7.32
7.32
7.31
4.72
4.68
4.67
4.00
4.00
3.98
3.90
3.87
3.70
3.63
3.60
3.52
3.51
3.50
3.49
3.34
3.32
BnO
OMe
BnO
BnO
O
O
OBn
BnO
OBn
24
30.57
0.11
14.25
10.69
1.00
2.93
f1 (ppm)

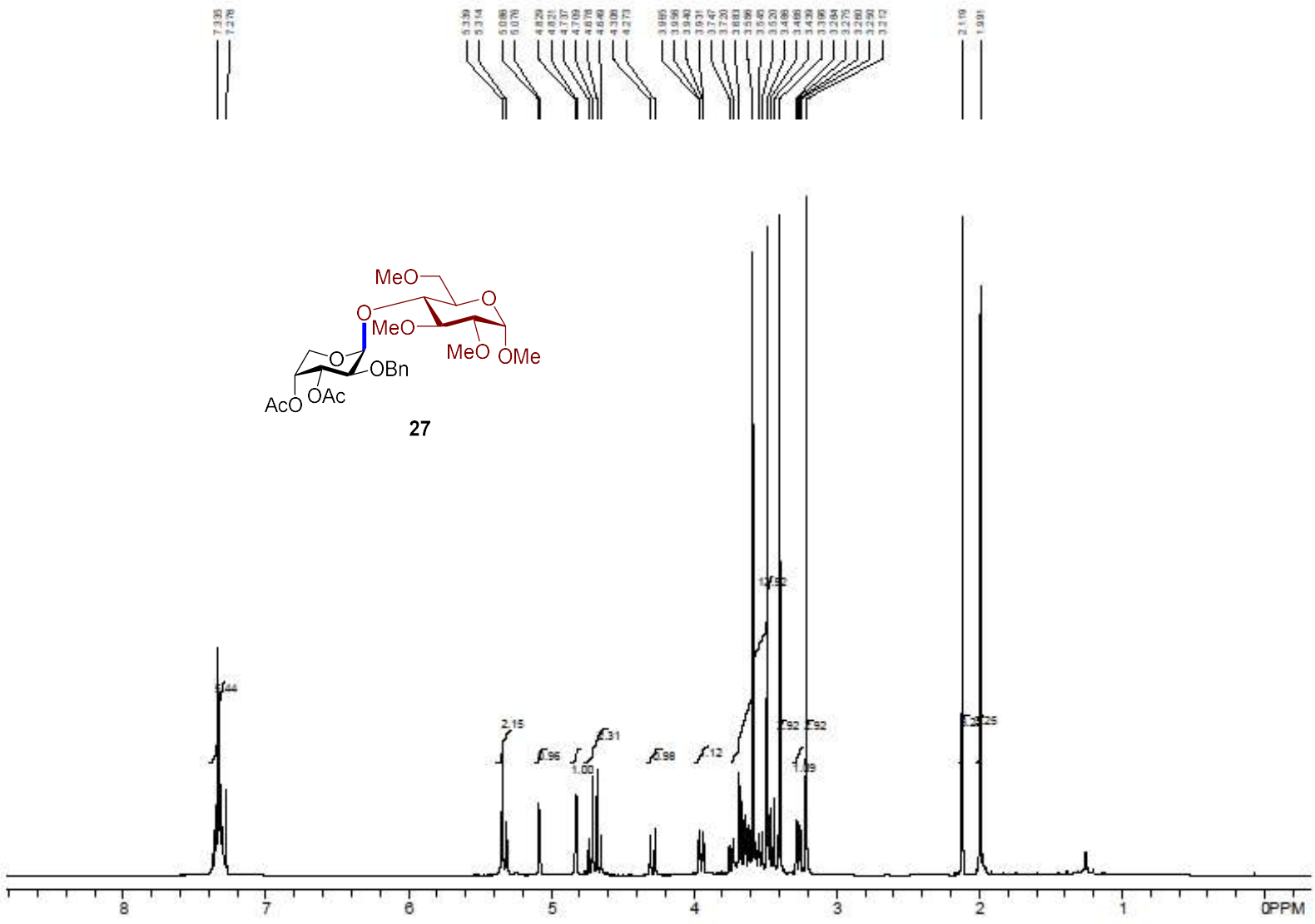

FY-91-16-1-C
Calibration for OneNMR on 24Apr2018
Sample : Doped D2O
BnO
OMe
BnO
BnO
O
O
O
OBn
BnO
OBn
24
f1 (ppm)

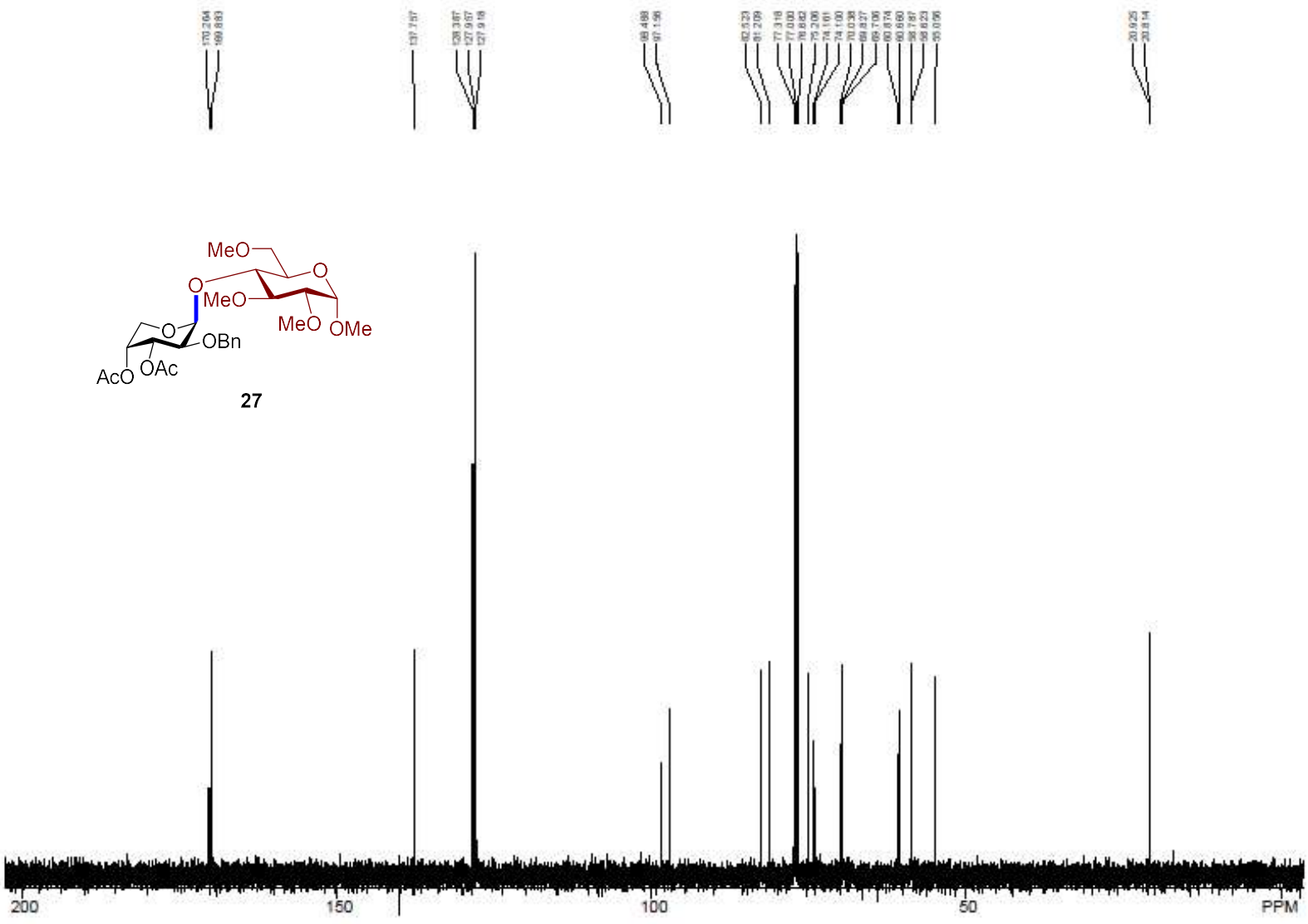

BnO
OMe
BnO
BnO
O
O
O
OBn
AcO
OAc
25
15.46
5.20
2.10
2.05
3.13
3.00
3.04
9
8
7
6
5
4
3
2
1
PPM


BnO
OMe
BnO
BnO
O
O
O
OBn
AcO
OAc
25
200
150
100
50
PPM

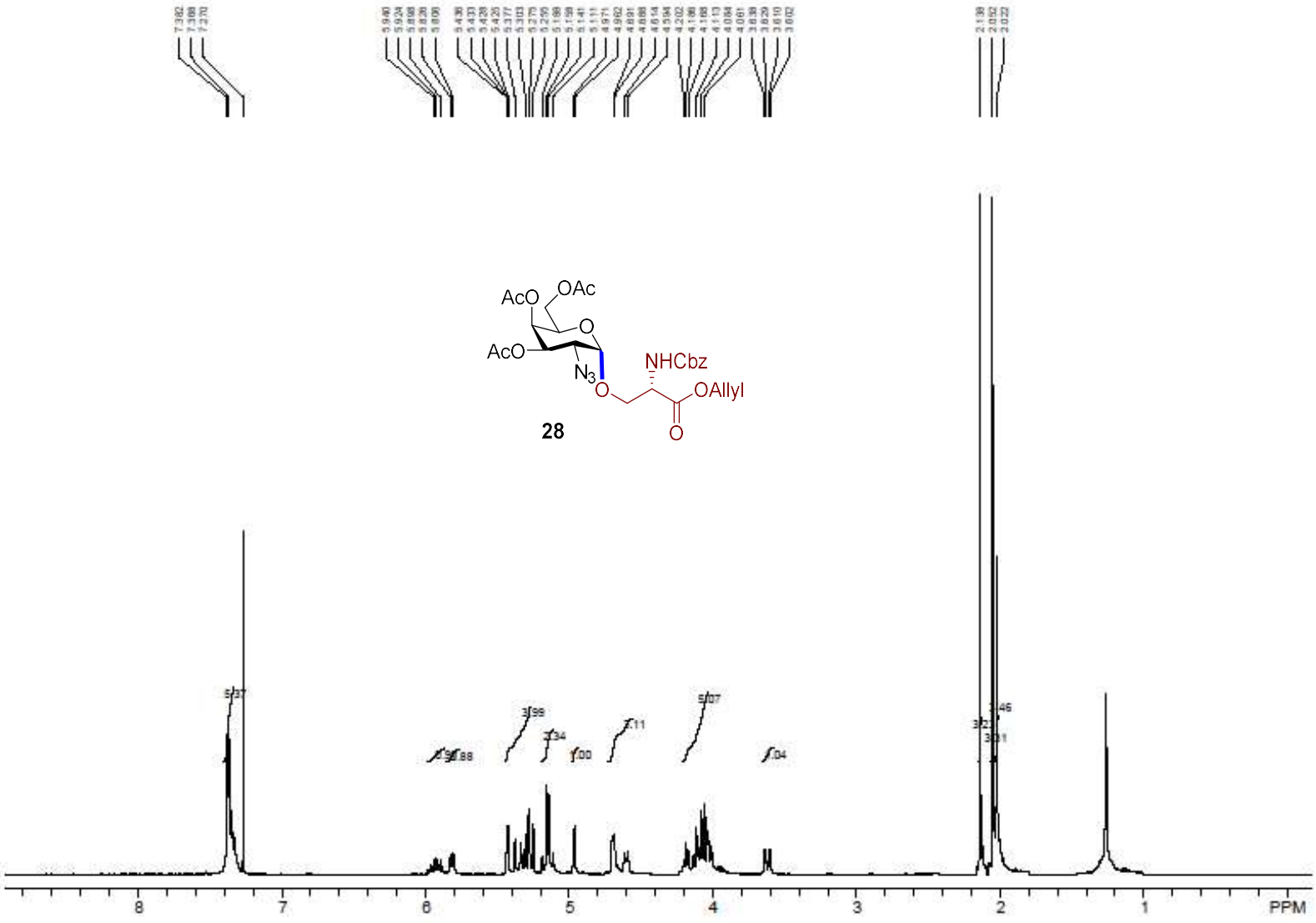

OMe
Me
O
O
O
O
O
OBn
Me
Me
AcO
OAc
26
PPM

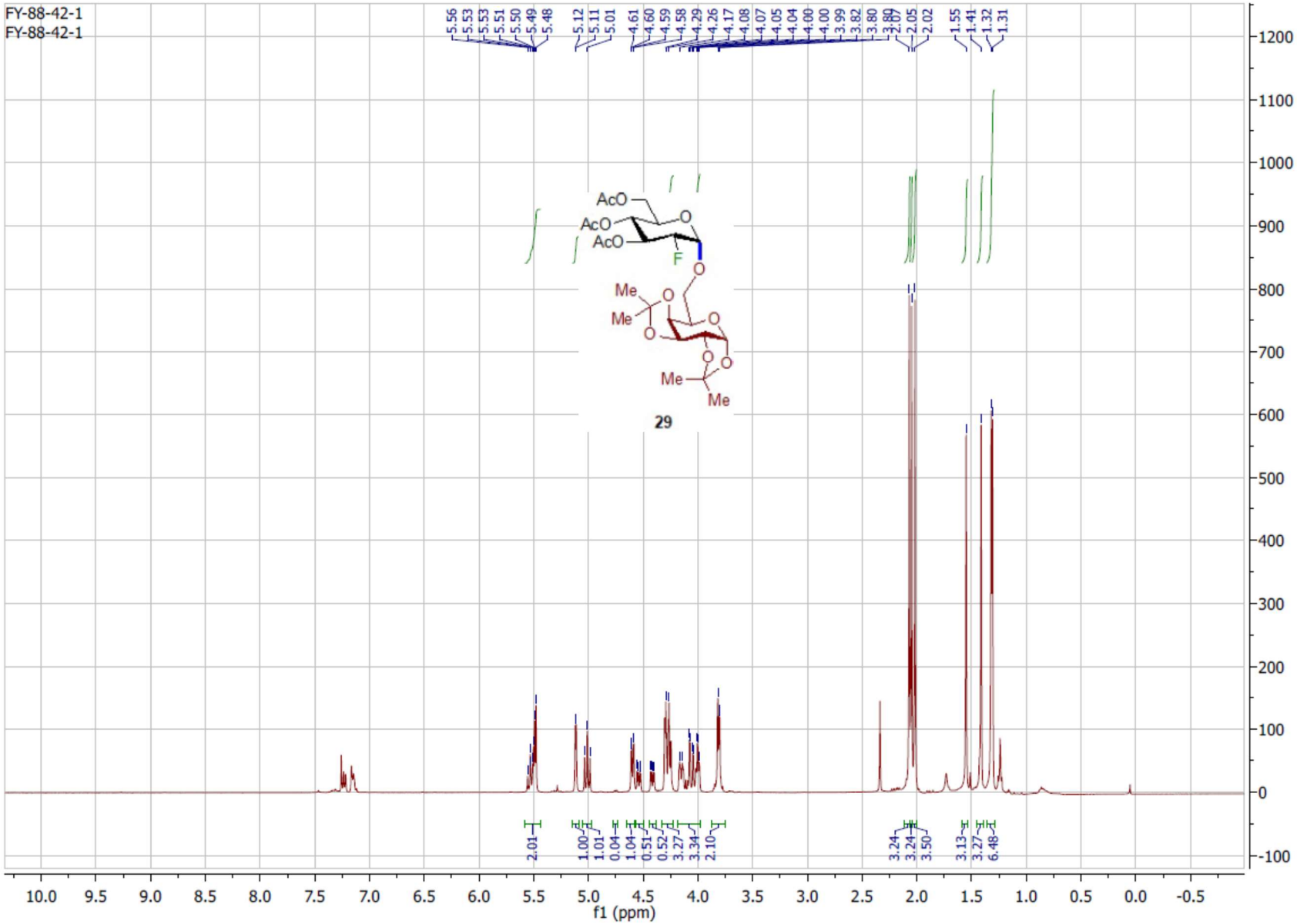

OMe
Me
O
O
O
O
O
OBn
Me
Me
AcO
OAc
26
200
150
100
50
PPM

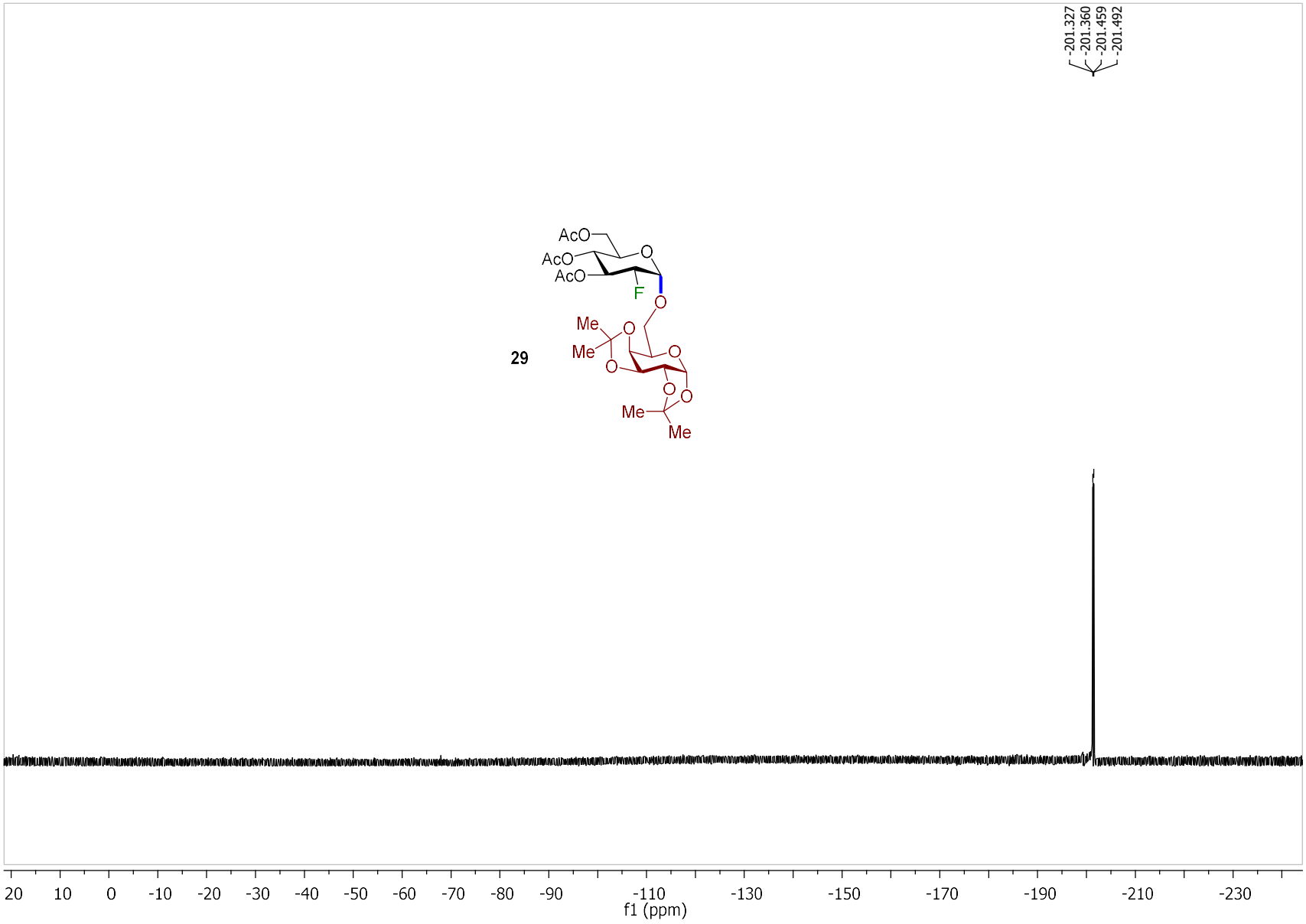

MeO
O
O
MeO
MeO
OMe
O
OBn
AcO
OAc
27
8
7
6
5
4
3
2
1
0PPM



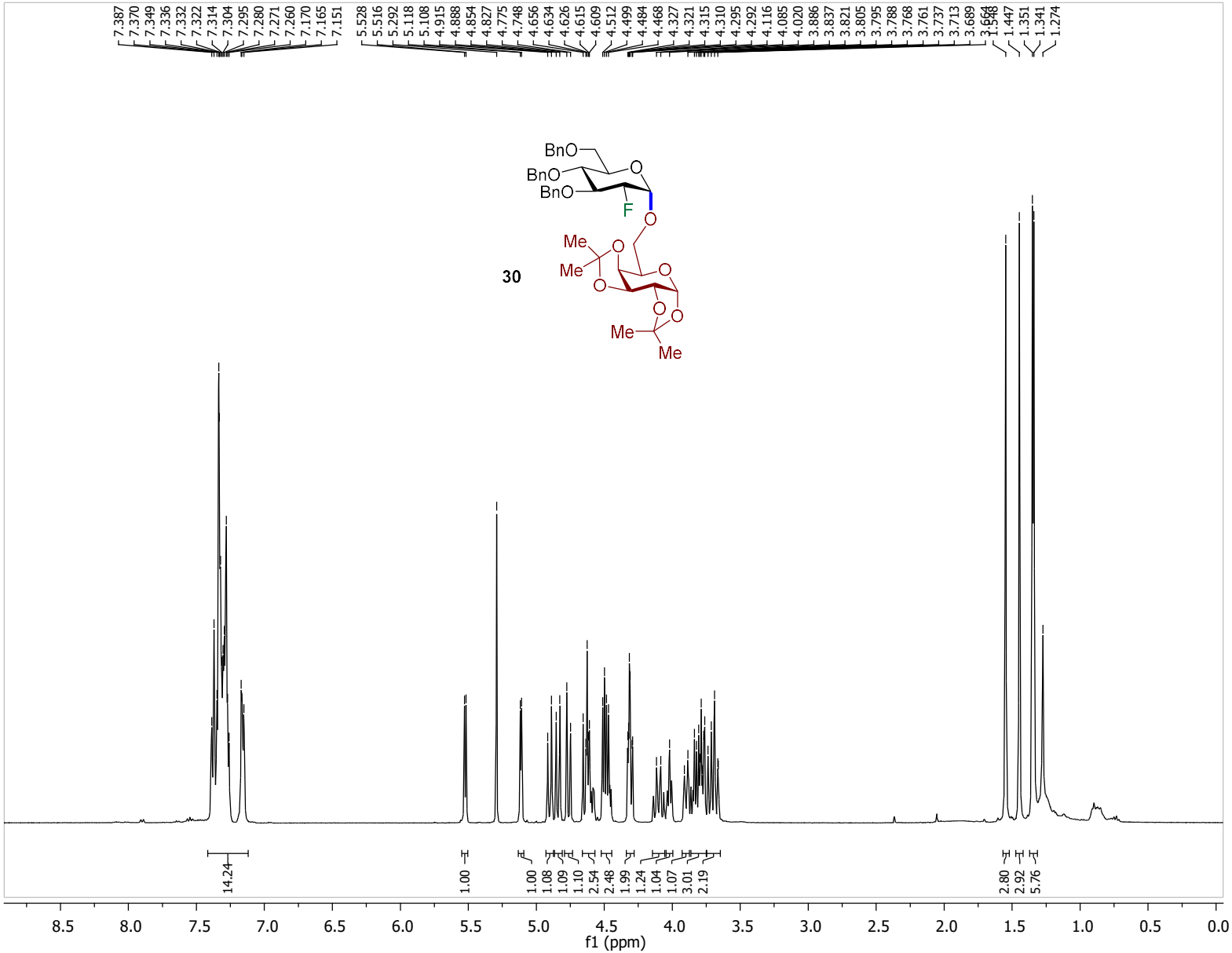
27

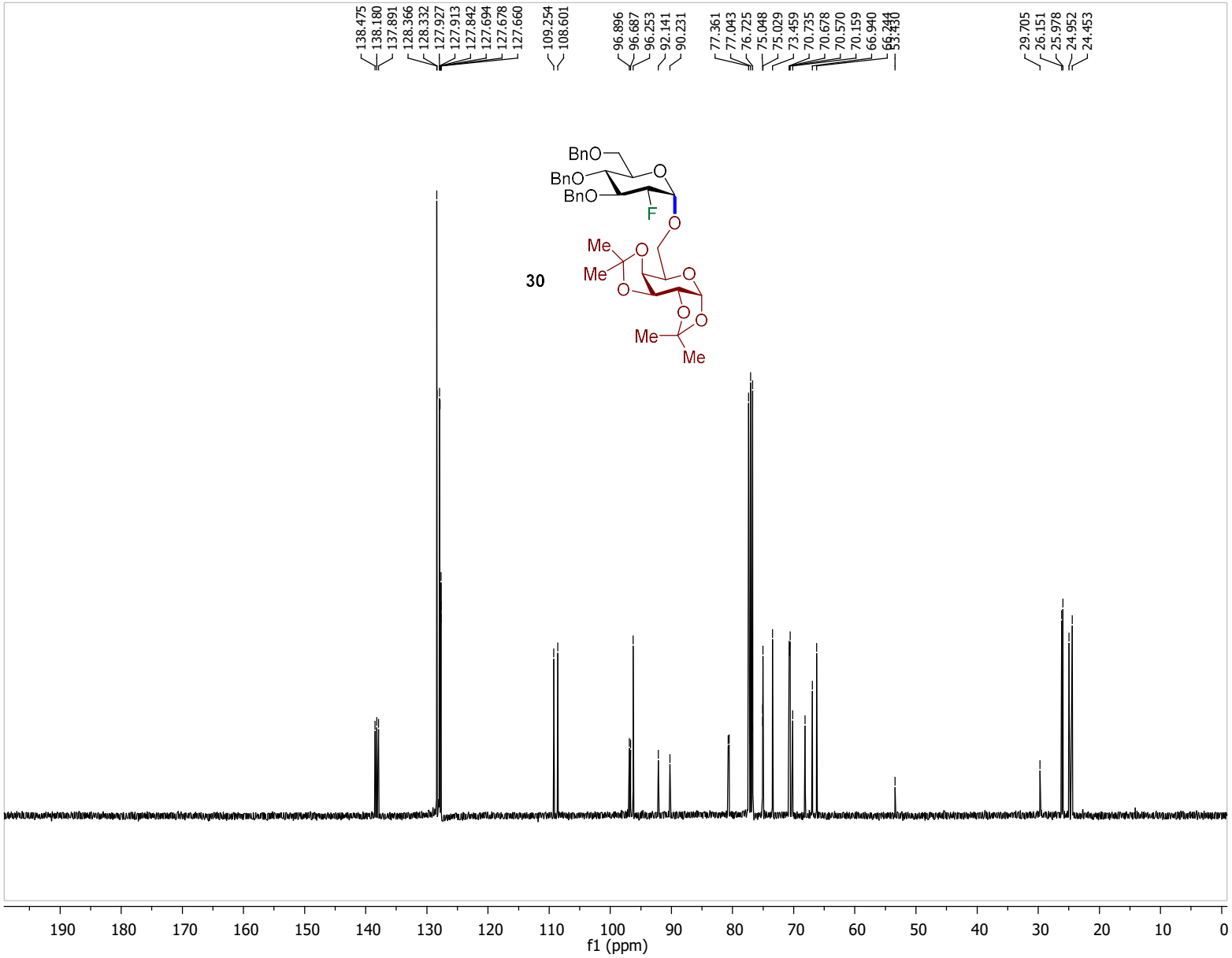

AcO
OAc
O
AcO
N3
O
NHCbz
OAllyl
O
28
8
7
6
5
4
3
2
1
PPM

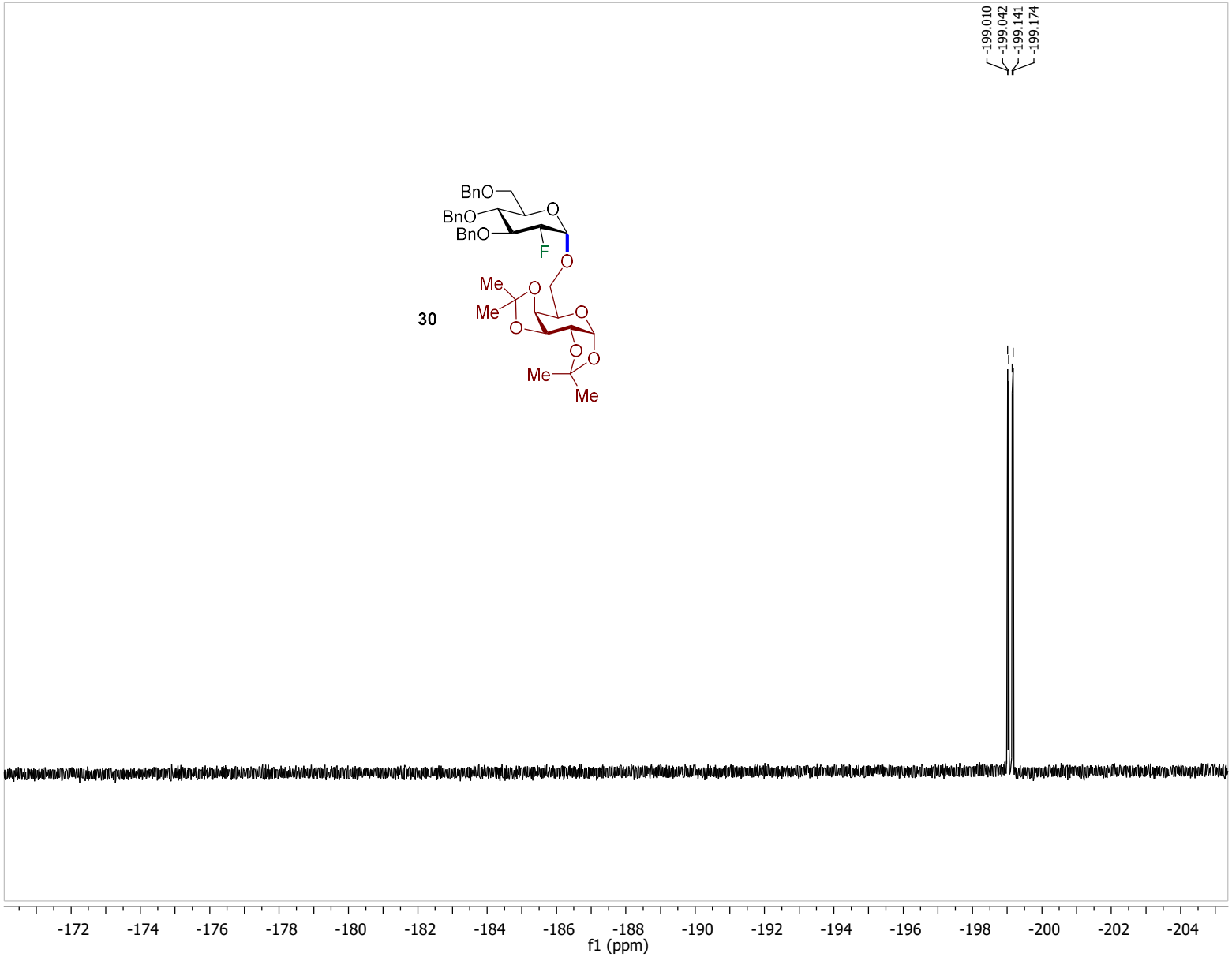

FY-88-42-1
FY-88-42-1
AcO
AcO
AcO
O
F
O
Me
Me
O
O
O
O
O
Me
Me
29
f1 (ppm)

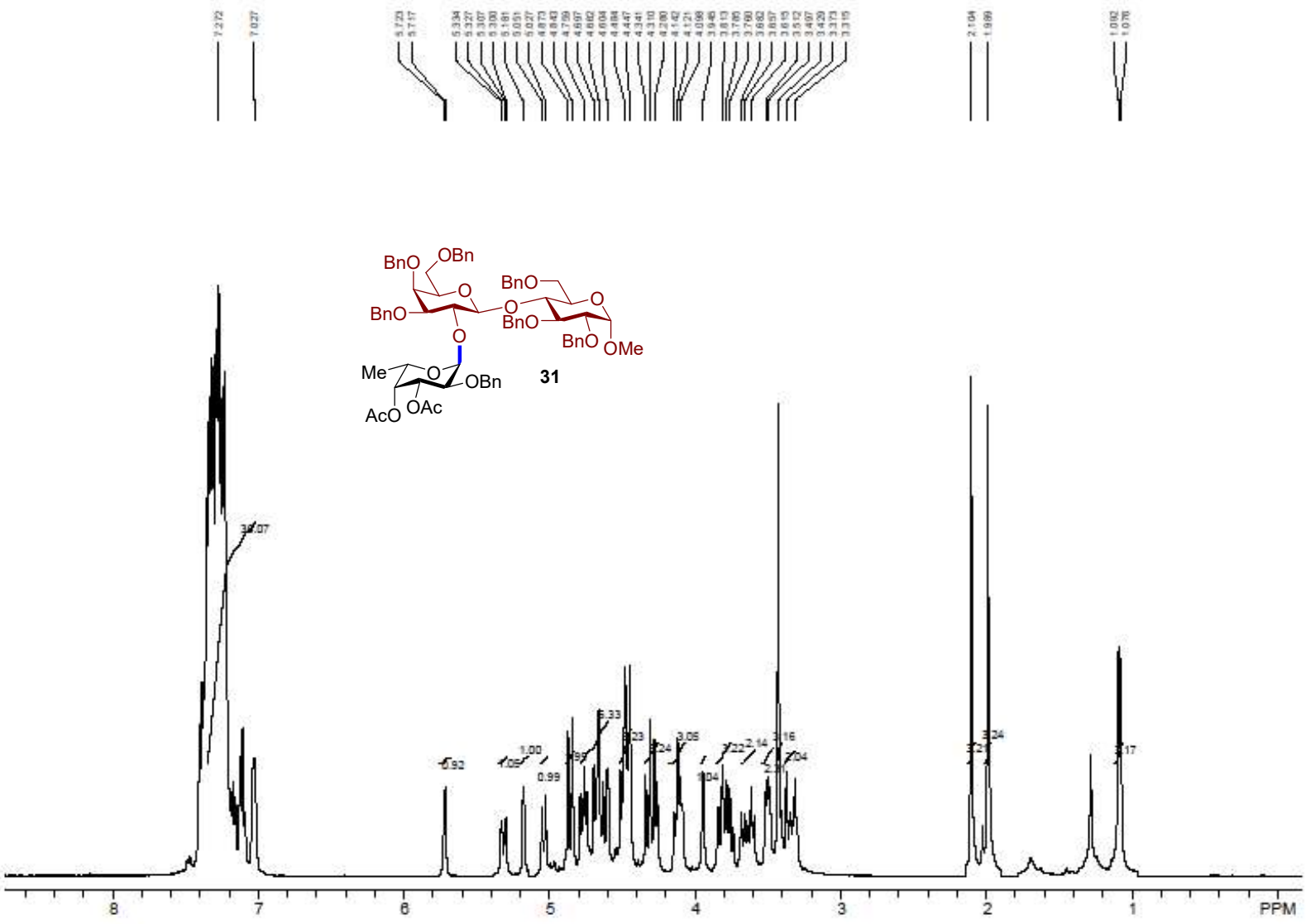

-201.327
-201.360
-201.459
-201.492
AcO
AcO
AcO
O
F
O
Me
Me
O
O
O
O
O
Me
Me
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

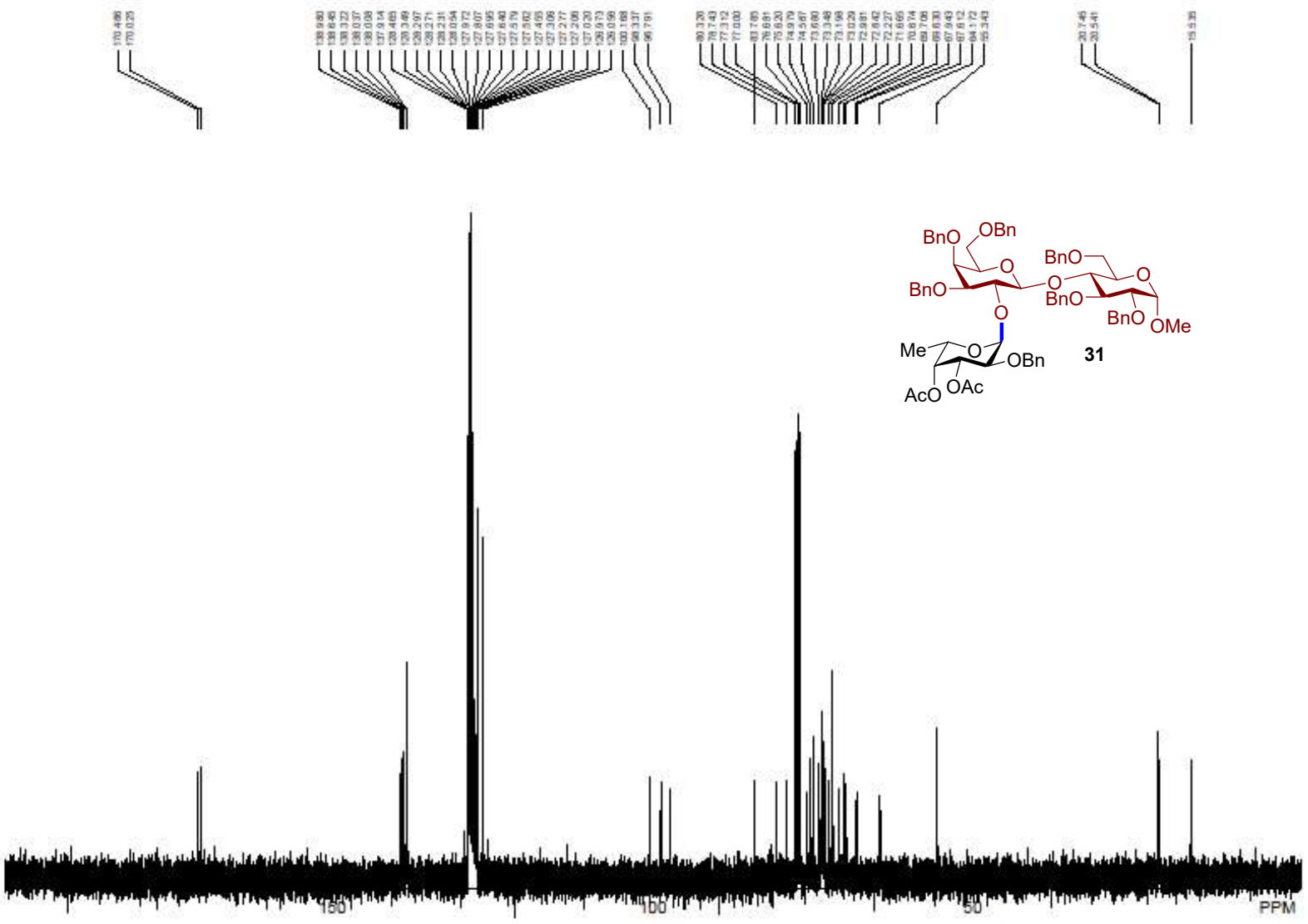
29

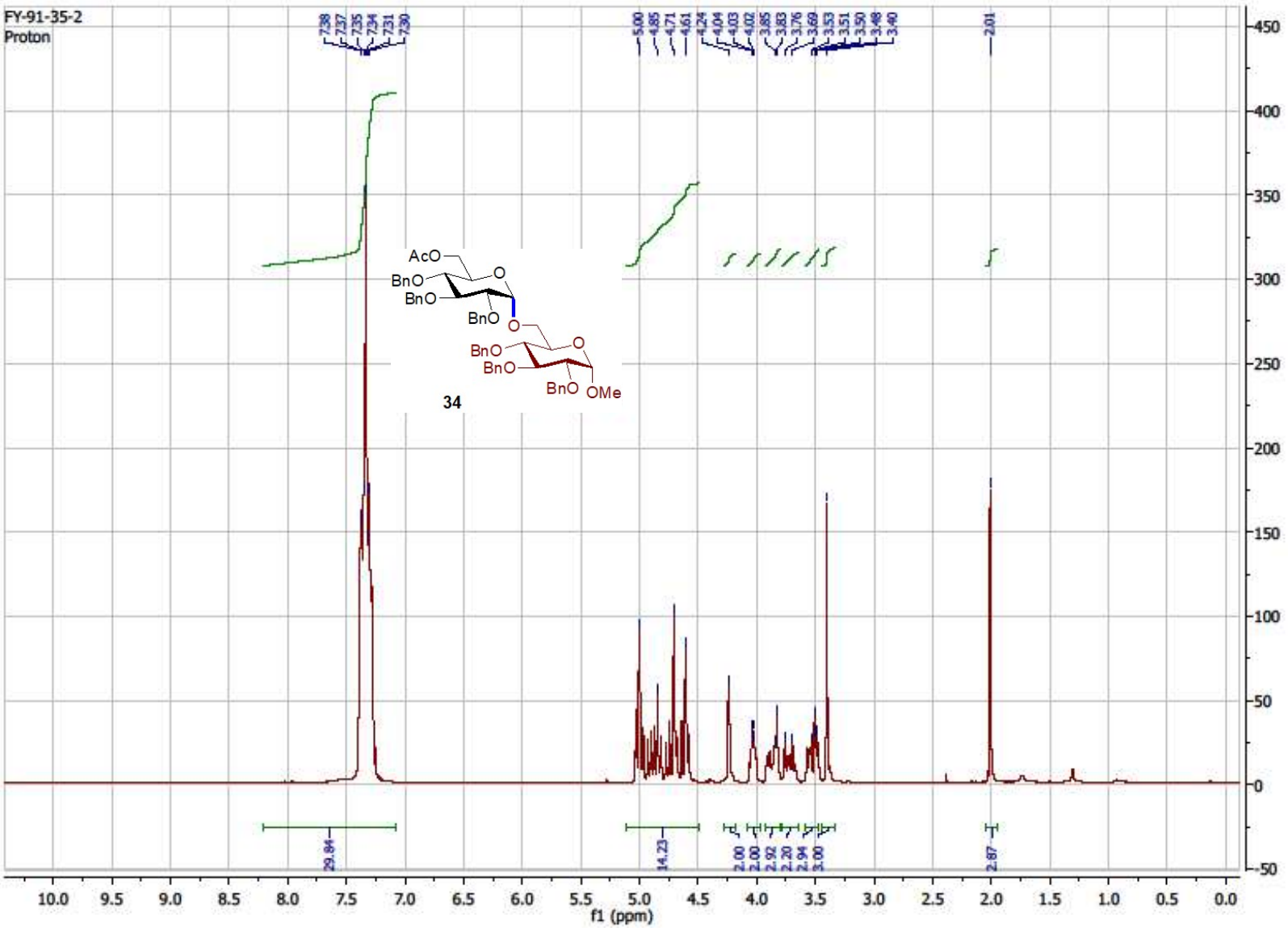

7.387
7.370
7.349
7.336
7.332
7.322
7.314
7.304
7.295
7.280
7.271
7.260
7.170
7.165
7.151
5.528
5.516
5.292
5.118
5.108
4.915
4.888
4.854
4.827
4.775
4.748
4.656
4.634
4.626
4.615
4.609
4.512
4.499
4.484
4.468
4.327
4.321
4.315
4.310
4.295
4.292
4.116
4.085
4.020
3.886
3.837
3.821
3.805
3.795
3.788
3.768
3.761
3.737
3.713
3.689
1.447
1.351
1.341
1.274
BnO
BnO
BnO
O
F
O
Me
Me
O
O
O
O
O
Me
Me
30
14.24
1.00
1.00
1.08
1.09
1.10
2.54
2.48
1.99
1.24
1.04
1.07
3.01
2.19
2.80
2.92
5.76
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

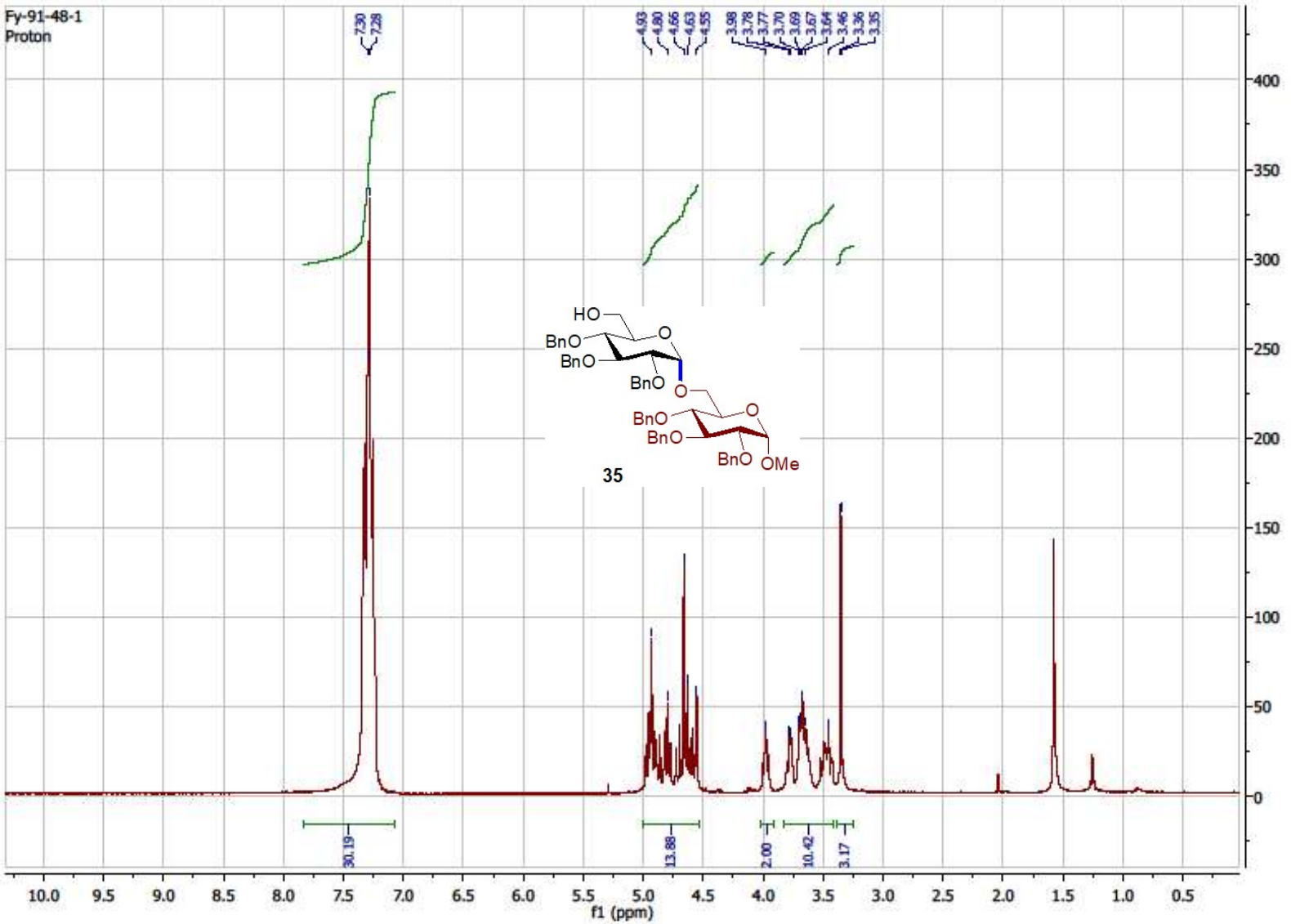

138.475
138.180
137.891
128.366
128.332
127.927
127.913
127.842
127.694
127.678
127.660
109.254
108.601
96.896
96.687
96.253
92.141
90.231
77.361
77.043
76.725
75.048
75.029
73.459
70.735
70.678
70.570
70.159
66.940
66.244
55.430
29.705
26.151
25.978
24.952
24.453
BnO
BnO
BnO
O
F
O
Me
Me
O
O
O
O
O
Me
Me
30
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

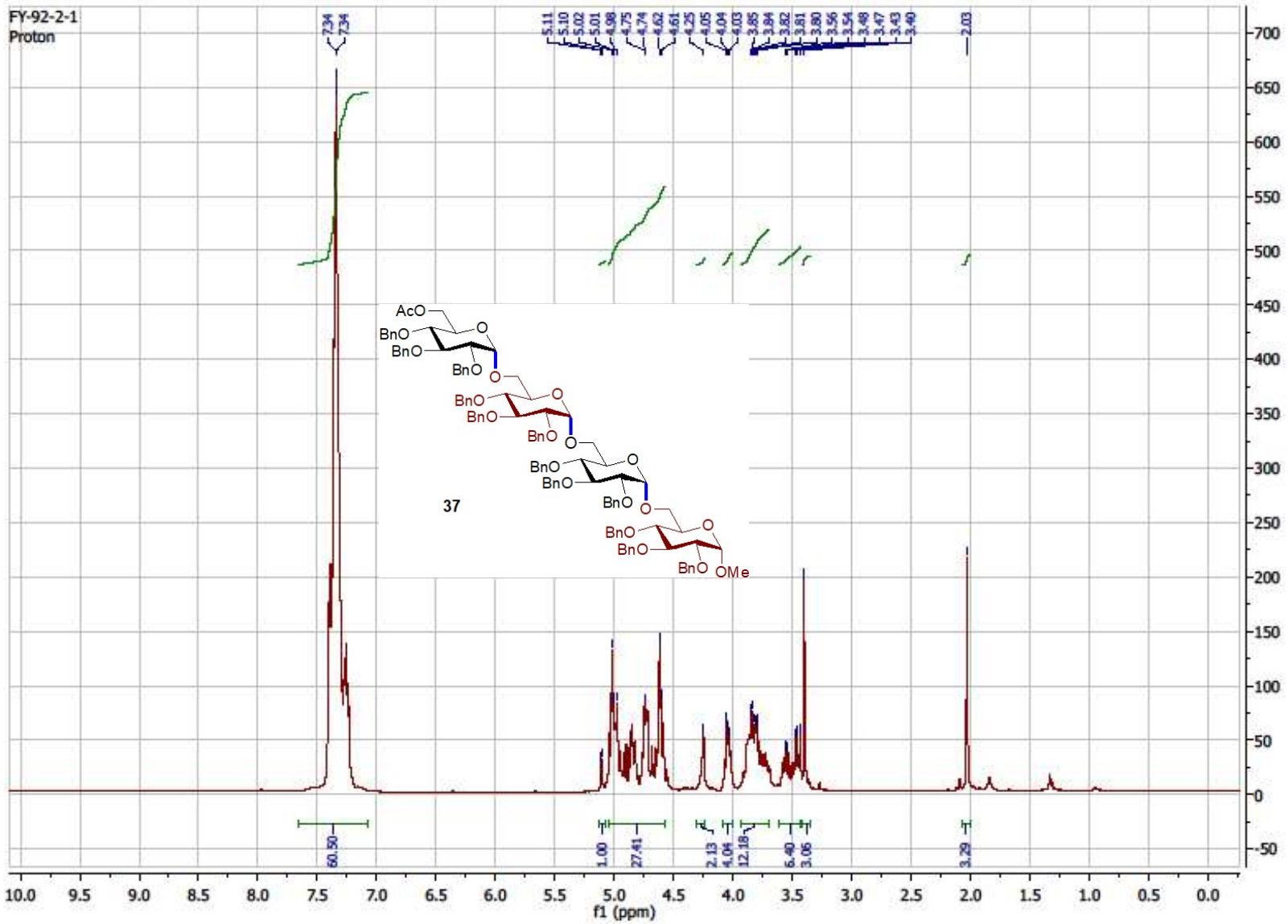

-199.010
-199.042
-199.141
-199.174
BnO
BnO
BnO
O
F
O
Me
Me
O
O
O
O
O
Me
Me
30
-172
-174
-176
-178
-180
-182
-184
-186
-188
-190
-192
-194
-196
-198
-200
-202
-204
f1 (ppm)

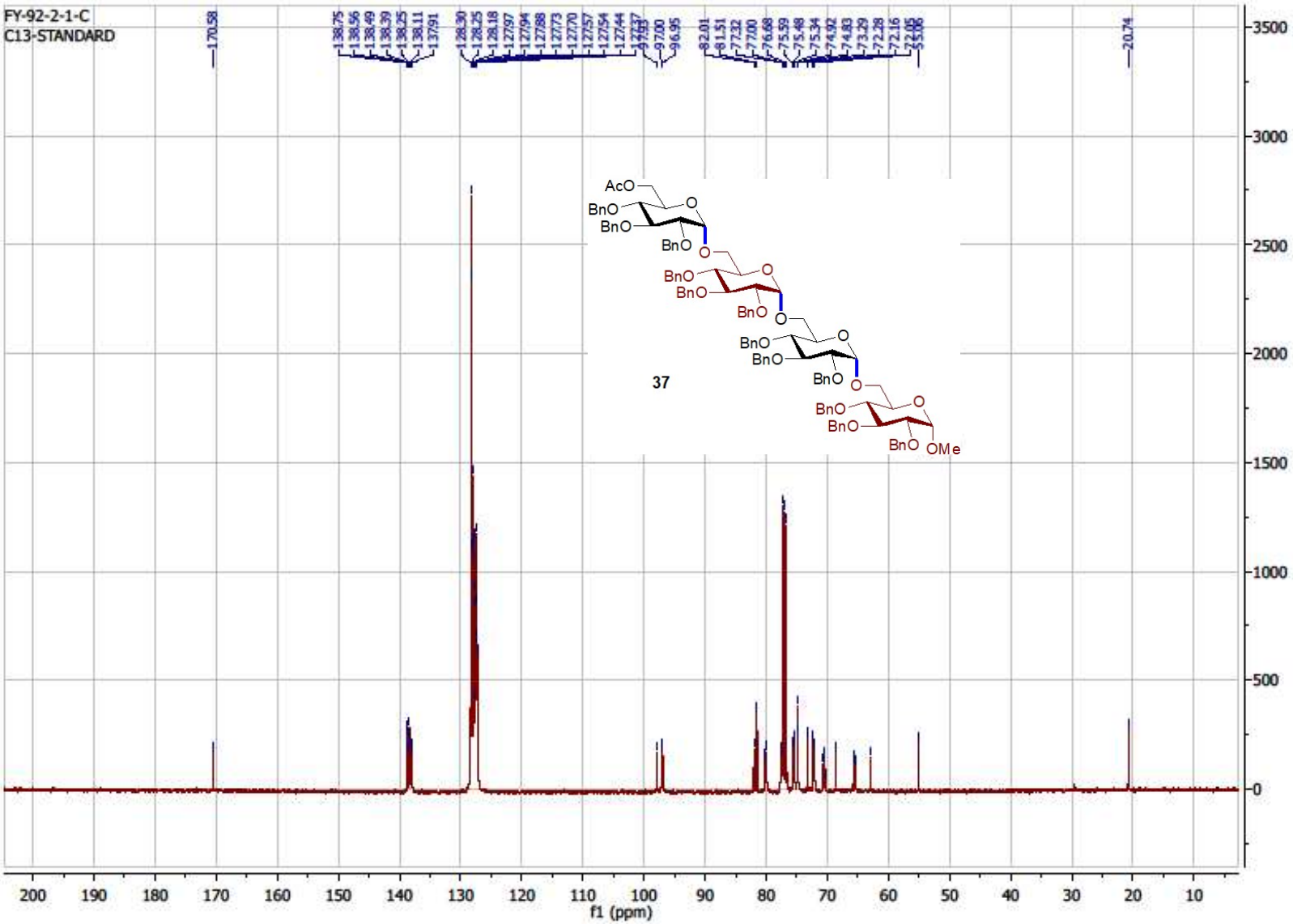

BnO
OBn
BnO
O
BnO
O
O
BnO
BnO
OMe
Me
O
OBn
AcO
OAc
31
PPM

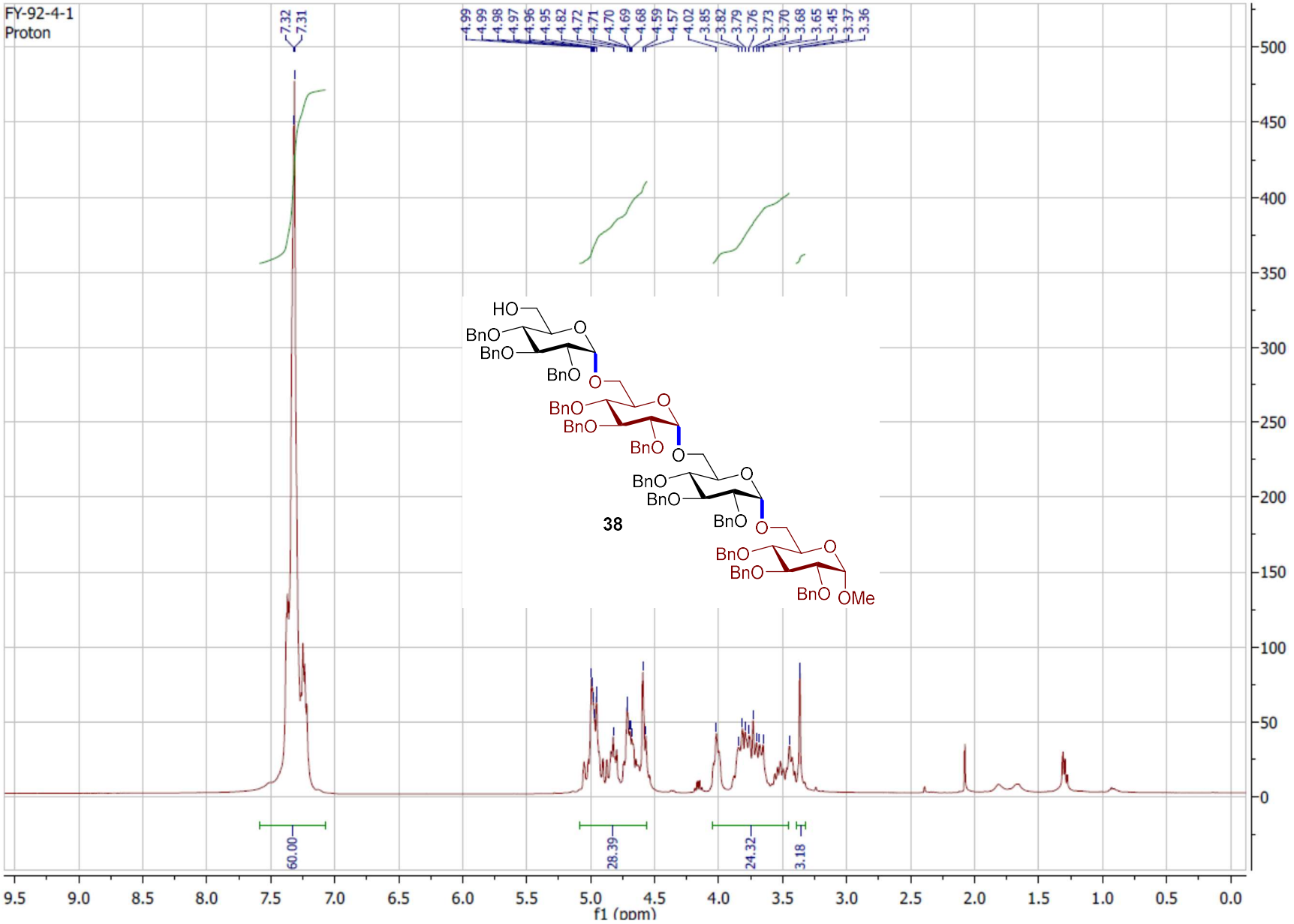

BnO
OBn
BnO
O
O
BnO
O
BnO
BnO
OMe
Me
O
OBn
AcO
OAc
31
150
100
50
PPM

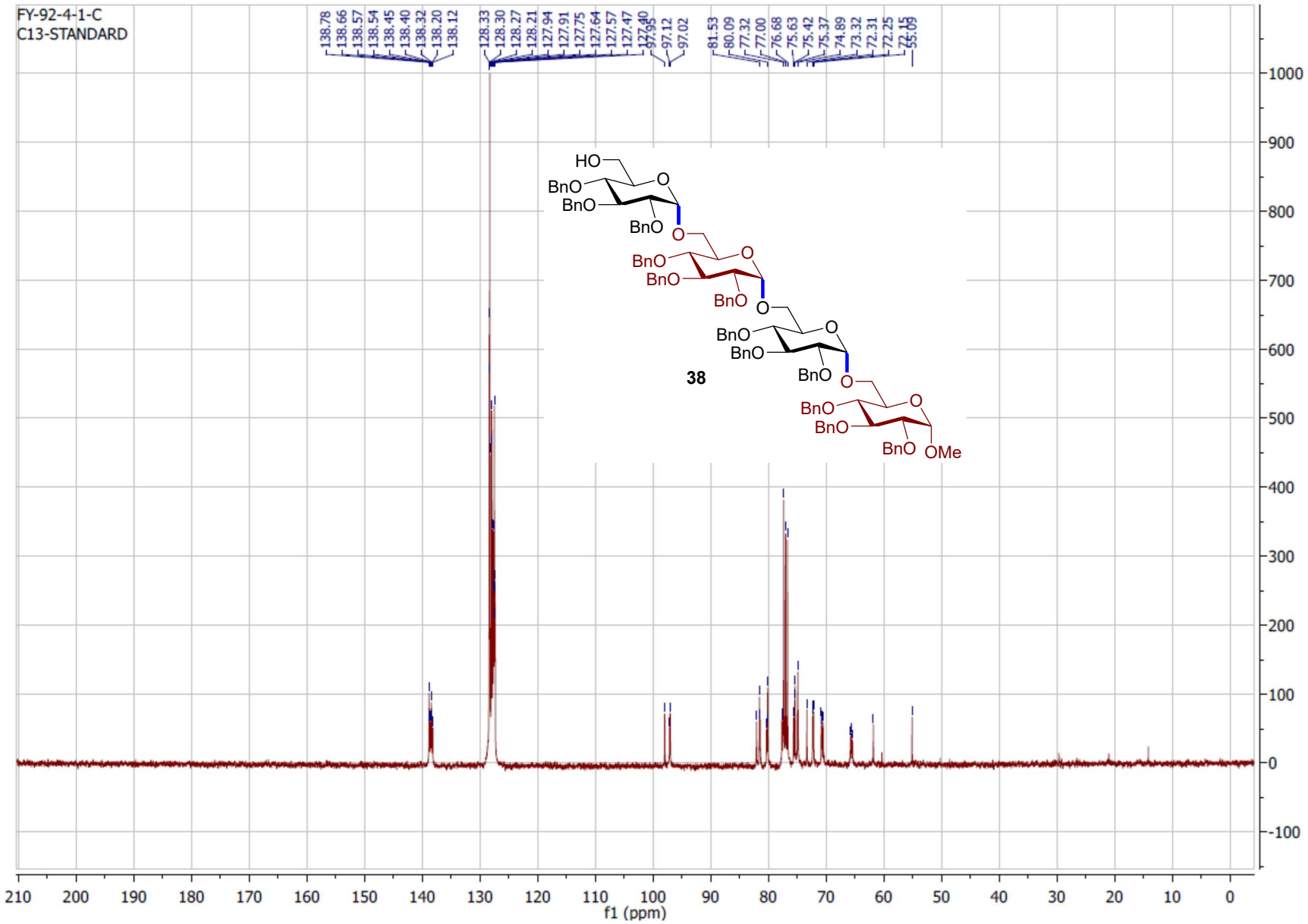

FY-91-35-2
Proton
7.38
7.37
7.35
7.34
7.31
7.30
5.00
4.85
4.71
4.61
4.24
4.04
4.03
4.02
3.85
3.83
3.76
3.69
3.53
3.51
3.50
3.48
3.40
2.01
AcO
BnO
BnO
BnO
O
BnO
BnO
BnO
O
O
OMe
34
29.84
14.23
2.00
2.00
2.92
2.20
2.94
3.00
2.87
f1 (ppm)

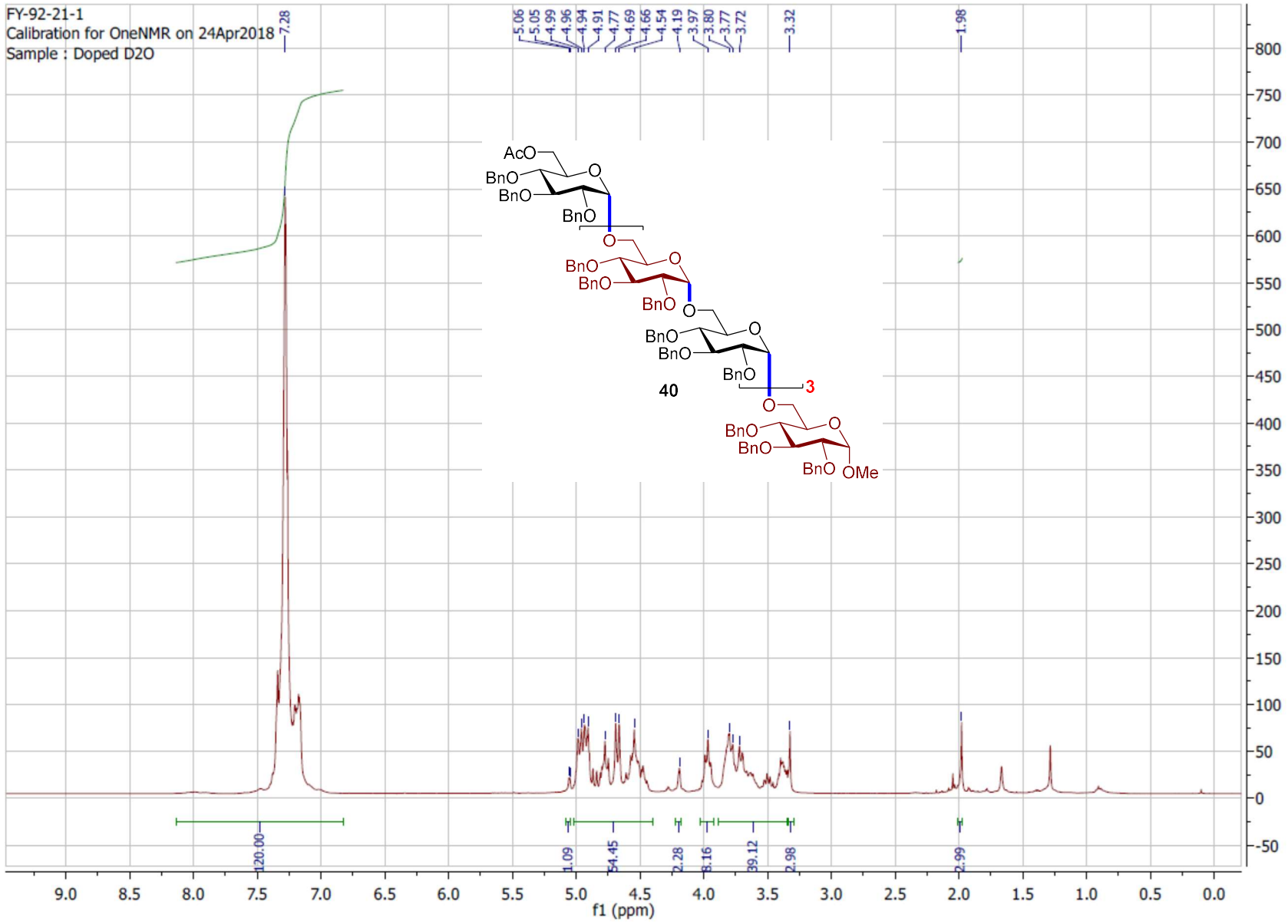

Fy-91-48-1
Proton
7.30
7.28
4.93
4.80
4.66
4.63
4.55
3.98
3.78
3.77
3.70
3.69
3.67
3.64
3.46
3.36
3.35
HO
BnO
BnO
BnO
O
O
BnO
BnO
BnO
OMe
35
30.19
13.88
2.00
10.42
3.17
f1 (ppm)

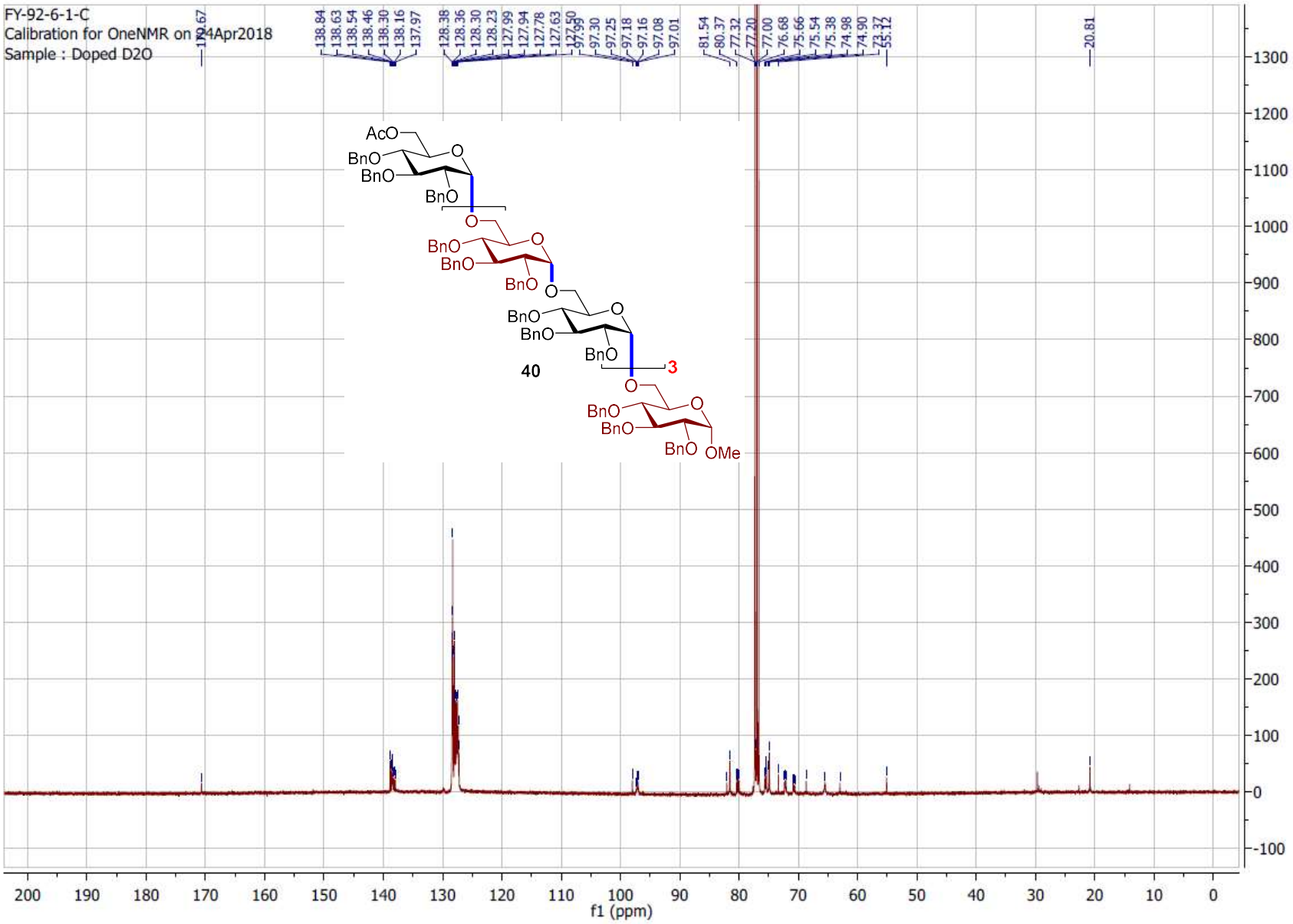

FY-92-2-1
Proton
37
f1 (ppm)


FY-92-2-1-C
C13-STANDARD
AcO
BnO
BnO
BnO
O
OMe
37
f1 (ppm)


FY-92-4-1
Proton
7.32
7.31
4.99
4.99
4.98
4.97
4.96
4.95
4.82
4.72
4.71
4.70
4.69
4.68
4.59
4.57
4.02
3.85
3.82
3.79
3.76
3.73
3.70
3.68
3.65
3.45
3.37
3.36
HO
BnO
BnO
BnO
O
O
BnO
BnO
BnO
O
O
BnO
BnO
BnO
O
O
BnO
BnO
BnO
OMe
38
60.00
28.39
24.32
3.18
f1 (ppm)


FY-92-4-1-C
C13-STANDARD
138.78
138.66
138.57
138.54
138.45
138.40
138.32
138.20
138.12
128.33
128.30
128.27
128.21
127.94
127.91
127.75
127.64
127.57
127.47
127.40
97.95
97.12
97.02
81.53
80.09
77.32
77.00
76.68
75.63
75.42
75.37
74.89
73.32
72.31
72.25
55.09
HO
BnO
BnO
BnO
O
O
BnO
BnO
BnO
O
O
BnO
BnO
BnO
O
O
BnO
BnO
BnO
OMe
38
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


FY-92-21-1
Calibration for OneNMR on 24Apr2018
Sample : Doped D2O
7.28
5.06
5.05
4.99
4.96
4.94
4.91
4.77
4.69
4.66
4.54
4.19
3.97
3.80
3.77
3.72
3.32
1.98
AcO
BnO
BnO
BnO
O
O
BnO
BnO
BnO
O
O
BnO
BnO
BnO
3
O
O
BnO
BnO
BnO
OMe
40
120.00
1.09
54.45
2.28
8.16
39.12
2.98
2.99
f1 (ppm)


FY-92-6-1-C
Calibration for OneNMR on 24Apr2018
Sample : Doped D2O
AcO
BnO
BnO
BnO
O
BnO
BnO
BnO
O
BnO
BnO
BnO
O
BnO
BnO
BnO
OMe
40
3
f1 (ppm)