Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Photocatalytic, Site-Selective Oxidation of Carbohydrates

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General Information

Materials

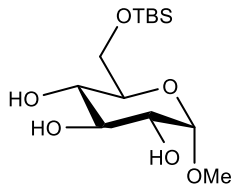
Stainless steel needles and syringes were used to transfer air and moisture-sensitive liquids. Schlenk flasks were dried at 140 °C for at least 24 hours prior to use. Acetonitrile was HPLC grade and purified using a solvent purification system equipped with columns of activated alumina under nitrogen (Innovative Technology, Inc.). 4 Å molecular sieves were stored for at least 24 hours at 140 °C prior to use. Other reagents and solvents were used without further purification. Flash column chromatography was carried out using neutral silica gel (60 Å, 230–400 mesh, Silicycle). Analytical thin layer chromatography was carried out using aluminum-backed silica gel 60 F254 plates (EMD), and compounds were visualized using UV light and aqueous basic $KMnO_4$ stain.

Instrumentation

^{1}H and ^{13}C NMR and 2D NMR spectra were recorded using a Varian Mercury 400 MHz, Bruker Avance III 400 MHz, Agilent DD2 600 (600 MHz), or Agilent DD2-500 (500 MHz) spectrometer equipped with a XSens cryoprobe. ^{1}H NMR are reported in parts per million (ppm) relative to tetramethylsilane and referenced to residual protium in the solvent. Spectral features are tabulated in the following order: chemical shift (δ, ppm); multiplicity (s-singlet, d-doublet, t-triplet, q-quartet, m-complex multiplet); coupling constant(s) (J, Hz); number of protons; assignment. Assignments were made on the basis of coupling constants and 2D NMR spectra. High-resolution mass spectra (HRMS) were obtained on a JEOL AccuTOF JMS- T1000LC mass spectrometer equipped with a DART (direct analysis in real time) ion source. Infrared (IR) spectra were obtained on a Perkin-Elmer Spectrum 100 instrument equipped with a single-bounce diamond/ZnSe ATR accessory as neat samples, or as thin film from CH_2Cl_2 as indicated. Spectral features are tabulated as follows: wavenumber (cm^{-1}); intensity (br-broad, s-strong, m-medium, w-weak). Specific rotations were measured with a Rudolph Autopol IV digital polarimeter equipped with a sodium lamp source (589 nm) and concentration (c) is reported in g/100 mL. Oxidation reactions were all run in 1 or 2 dram vials and placed approximately 4 inches from a Kessil® LED lamp (either: A160WE Tuna Blue (40 W), H150-Blue (32 W) or PR160L-390nm (52 W)

Substrate Synthesis

Methyl 6-O-(tert-butyldimethylsilyl)-α-D-glucopyranoside (1a)

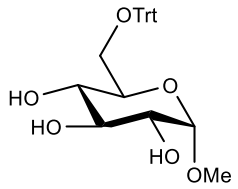


Prepared according to previous literature.[1]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = δ 4.72 (d, J = 3.8 Hz, 1H), 4.11 (d, J = 3.5 Hz, 1H), 3.90 – 3.82 (m, 2H), 3.80 (dd, J = 11.0, 5.4 Hz, 1H), 3.75 (m, 1H), 3.56 (ddd, J = 9.3, 5.2, 3.8 Hz, 1H), 3.50 (m, 1H), 3.43 (dd, J = 9.3, 2.9 Hz, 1H), 3.40 (s, 3H), 0.89 (s, 9H), 0.08 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = δ 99.4, 74.5, 72.2, 71.5, 71.5, 63.7, 55.2, 26.0, 18.5, -5.2.

Methyl 6-O-(trityl)-α-D-glucopyranoside (1b)

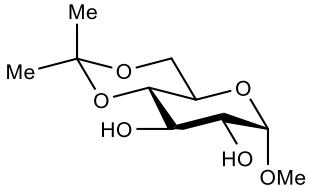


Prepared according to previous literature.[2]

^{1}H NMR (400 MHz, CD_3OD): δ (ppm) = 7.54 – 7.46 (m, 6H), 7.34 – 7.27 (m, 6H), 7.27 – 7.21 (m, 3H), 4.77 (d, *J* = 3.8 Hz, 1H), 3.78 (ddd, *J* = 9.9, 6.7, 1.8 Hz, 1H), 3.67 – 3.58 (m, 1H), 3.54 (s, 3H), 3.50 – 3.39 (m, 2H), 3.28 (ddd, *J* = 12.2, 10.0, 7.8 Hz, 2H).

^{13}C NMR (100 MHz, CD_3OD): δ (ppm) = 145.6, 129.9, 128.7, 128.0, 101.1, 87.7, 75.4, 73.6, 72.5, 72.3, 64.9, 55.4,

Methyl 4,6-O-isopropylidene-α-D-glucopyranoside (1c)

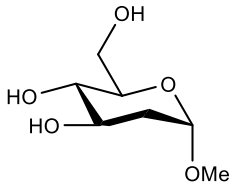


Prepared according to previous literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.74 (d, J = 3.9 Hz, 1H), 3.85 (dd, J = 10.5, 5.2 Hz, 1H), 3.80 – 3.66 (m, 2H), 3.67 – 3.53 (m, 2H), 3.53 – 3.47 (m, 1H), 3.40 (s, 3H), 1.49 (s, 3H), 1.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 99.9, 99.9, 73.6, 73.1, 72.1, 63.4, 62.4, 55.5, 29.2, 19.2.

Methyl 2-deoxy-α-D-glucopyranoside (1d)

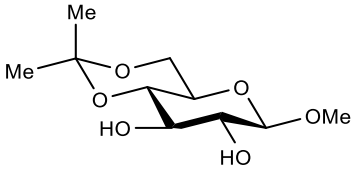


Prepared according to previous literature.[4]

^{1}H NMR (500 MHz, CD_3OD): δ (ppm) = 4.79 (d, J = 3.1 Hz, 1H), 3.86 – 3.78 (m, 2H), 3.71 (dd, J = 11.8, 5.6 Hz, 1H), 3.52 – 3.47 (m, 1H), 3.34 (s, 3H), 3.27 – 3.22 (m, 1H), 2.06 (ddd, J = 13.0, 5.1, 1.0 Hz, 1H), 1.61 (ddd, J = 13.0, 11.8, 3.6 Hz, 1H).

^{13}C NMR (126 MHz, CD_3OD): δ (ppm) = 99.8, 73.8, 73.3, 69.9, 62.8, 54.9, 38.8.

Methyl 4,6-O-isopropylidene-β-D-glucopyranoside (1f)

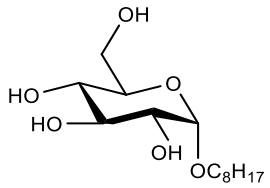


Prepared according to previous literature.[3]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = δ 4.26 (d, J = 7.7 Hz, 1H), 3.92 (dd, J = 10.8, 5.4 Hz, 1H), 3.81 – 3.74 (m, 1H), 3.69 – 3.61 (m, 1H), 3.58 – 3.52 (m, 4H), 3.45 – 3.38 (m, 1H), 3.38 – 3.33 (m, 1H), 3.30 – 3.22 (m, 2H), 1.50 (s, 3H), 1.43 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = δ 104.3, 100.0, 74.7, 73.6, 73.3, 67.3, 62.2, 57.5, 29.1, 19.2.

Octyl α-D-glucopyranoside (1h)

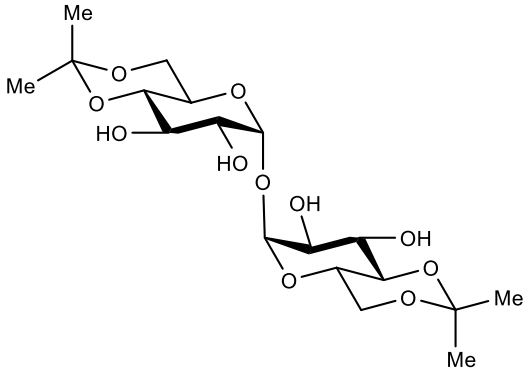


Prepared according to previous literature.[5]

^{1}H NMR (500 MHz, CD_3OD): δ (ppm) = 4.79 (d, J = 3.8 Hz, 1H), 3.81 (dd, J = 11.8, 2.4 Hz, 1H), 3.78 – 3.72 (m, 1H), 3.72 – 3.62 (m, 2H), 3.59 (ddd, J = 9.9, 5.5, 2.4 Hz, 1H), 3.49 – 3.43 (m, 1H), 3.40 (dd, J = 9.7, 3.8 Hz, 1H), 3.35 – 3.27 (m, 1H), 1.73 – 1.56 (m, 2H), 1.47 – 1.23 (m, 10H), 0.96 – 0.88 (m, 3H).

^{13}C NMR (126 MHz, CD_3OD): δ (ppm) = 100.1, 75.1, 73.6, 73.6, 71.8, 69.1, 62.7, 33.0, 30.6, 30.6, 30.4, 27.3, 23.7, 14.4.

4,6:4',6'-di-O-isopropylidene-α,α'-trehalose (1i)

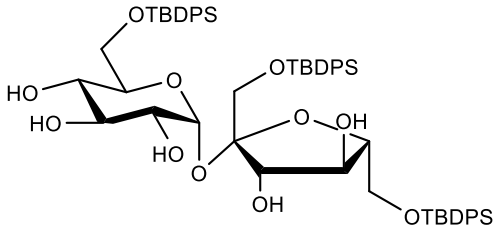


Prepared according to previous literature.[6]

^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 5.01 (d, J = 3.8 Hz, 2H), 3.81 – 3.65 (m, 8H), 3.65 – 3.54 (m, 4H), 3.53 – 3.45 (m, 4H), 1.46 (s, 6H), 1.35 (s, 6H).

^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 100.3, 95.5, 74.7, 73.6, 71.7, 64.8, 63.0, 29.6, 19.5.

6,1',6'-tri-O-tertbutyldiphenylsilyl sucrose (1j)

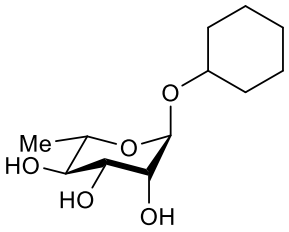


Prepared according to previous literature.[7]

^{1}H NMR (500 MHz, CD_3Cl_3): δ (ppm) = 7.74 – 7.64 (m, 12H), 7.42 – 7.30 (m, 18H), 5.66 (d, J = 4.1 Hz, 1H), 4.27 – 4.15 (m, 2H), 3.92 (ddd, J = 11.3, 6.8, 2.9 Hz, 2H), 3.88 – 3.80 (m, 2H), 3.77 – 3.67 (m, 4H), 3.66 – 3.58 (m, 1H), 3.40 – 3.33 (m, 2H), 1.15 – 0.99 (m, 27H).

^{13}C NMR (126 MHz, CD_3Cl_3): δ (ppm) = 135.8, 135.8, 135.8, 135.7, 135.7, 135.6, 133.3, 133.1, 132.9, 132.9, 132.8, 130.0, 130.0, 130.0, 130.0, 129.9, 128.0, 128.0, 127.9, 127.9, 127.9, 104.8, 91.0, 80.4, 78.3, 74.9, 74.4, 72.3, 71.5, 71.1, 65.8, 64.7, 63.3, 27.0, 27.0, 26.9, 19.4, 19.3, 19.3.

Cyclohexyl α-L-rhamnopyranoside (1l)

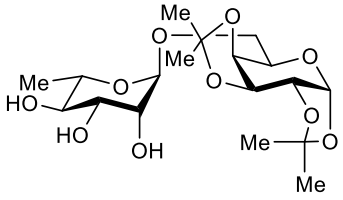


Prepared according to previous literature.[8]

^{1}H NMR (400 MHz, CD_3OD): δ (ppm) = 4.82 (d, J = 1.7 Hz, 1H), 3.75 (dd, J = 3.3, 1.7 Hz, 1H), 3.70 – 3.63 (m, 2H), 3.63 – 3.54 (m, 1H), 3.39 – 3.33 (m, 1H), 1.94 – 1.79 (m, 2H), 1.79 – 1.65 (m, 2H), 1.59 – 1.47 (m, 1H), 1.46 – 1.17 (m, 8H).

^{13}C NMR (100 MHz, CD_3OD): δ (ppm) = 99.6, 76.1, 74.1, 72.8, 72.4, 69.8, 34.5, 32.5, 26.8, 25.1, 24.8, 17.9.

1,2:3,4-di-O-isopropylidene-6-O-α-L-rhamnopyranosyl-α-D-galactopyranose (1m)

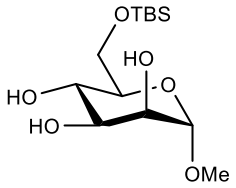


Prepared according to previous literature.[8]

^{1}H NMR (400 MHz, CD_3OD): δ (ppm) = 4.66 (dd, J = 7.9, 2.4 Hz, 1H), 4.39 (dd, J = 5.0, 2.4 Hz, 1H), 4.30 (dd, J = 7.9, 1.9 Hz, 1H), 4.05 – 3.97 (m, 1H), 3.90 – 3.81 (m, 2H), 3.75 – 3.61 (m, 2H), 3.54 (dd, J = 10.2, 6.9 Hz, 1H), 1.53 (s, 3H), 1.44 (s, 3H), 1.40 – 1.33 (m, 6H), 1.29 (d, J = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ (ppm) = 110.4, 109.9, 101.9, 97.7, 73.9, 72.4, 72.2, 72.0, 72.0, 69.9, 68.5, 67.0, 26.4, 26.4, 25.2, 24.6, 18.0.

Methyl-6-(tert-butyldimethylsilyloxy)-α-D-mannopyranoside (1n)



Prepared according to previous literature.[9]

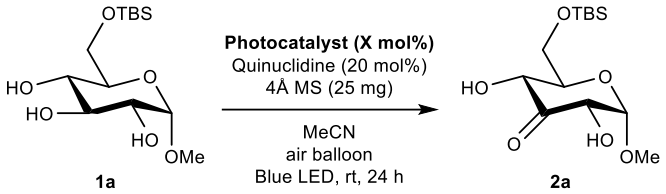
^{1}H NMR (400 MHz, CD_3OD): δ (ppm) = 4.64 (d, J = 1.6 Hz, 1H), 4.01 (dd, J = 11.1, 1.9 Hz, 1H), 3.84 – 3.76 (m, 2H), 3.67 (dd, J = 8.9, 3.5 Hz, 1H), 3.60 – 3.48 (m, 2H), 3.39 (s, 3H), 0.95 (s, 9H), 0.13 (s, 3H), 0.13 (s, 3H).

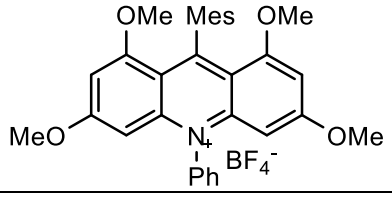
^{13}C NMR (100 MHz, CD_3OD): δ (ppm) = 102.6, 74.9, 72.8, 72.0, 68.8, 64.6, 55.0, 26.4, 19.2, -5.1.

Reaction Optimization

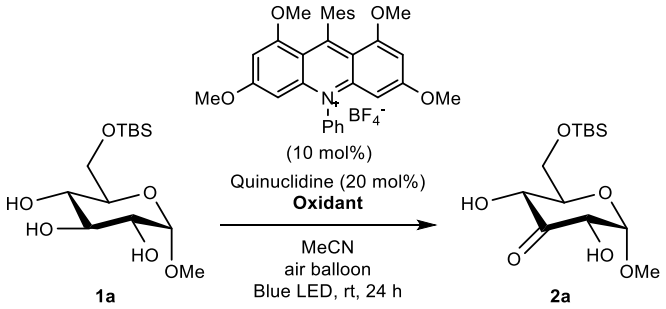
Methyl 6-O-(tert-butyldimethylsilyl)-α-D-glucopyranoside

Photocatalyst Screen



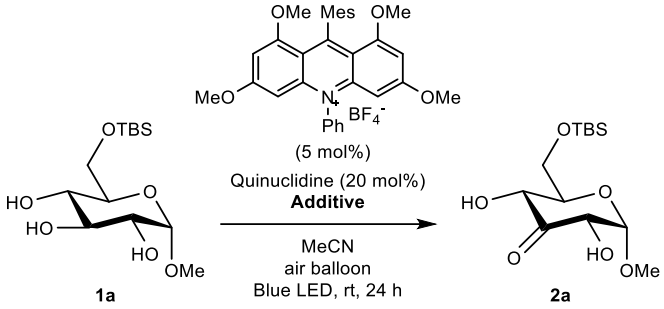
Photocatalyst	Loading	%2a	%1a
$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	2.5 mol%	63	13
4-CzIPN	5.0 mol%	51	0
	5.0 mol%	65	22

Oxidant Screen



Oxidant	%2a	%1a	Notes:
None	38	39	
O_2 balloon (instead of air)	27	64	
Selectfluor (1.0 equiv.)	9	90	
DMSO (10:1 MeCN:DMSO)	-	-	over-oxidation
K_2S_2O (1.0 equiv.)	-	-	over-oxidation

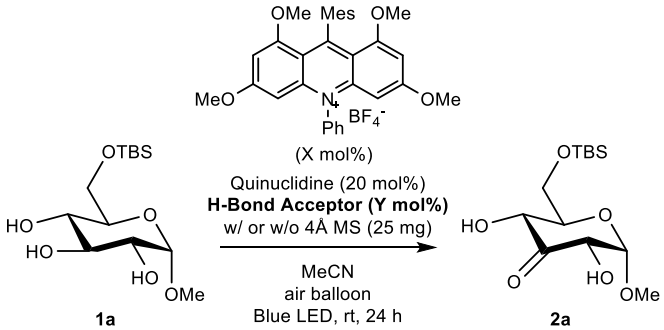
Additive Screen



1a 2a

Additive	%2a	%1a
None	40	40
4Å MS (powder, 25 mg)	65	22
4Å MS (powder, 50 mg)	47	38
4Å MS (beads, 25 mg)	46	37
MnO_2 (0.2 equiv)	54	0
KI (0.2 equiv)	<5	91

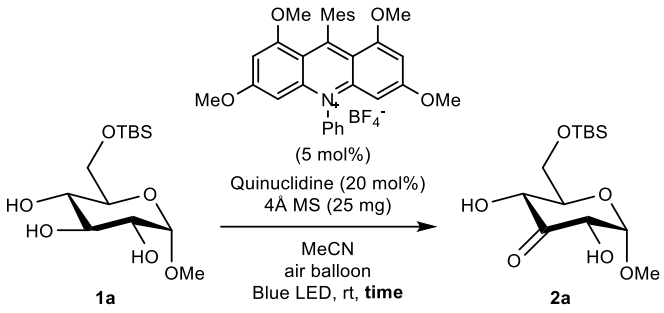
Hydrogen Bond Acceptor Screen



1a 2a

Photocatalyst Loading	Acceptor (Y mol%)	4Å MS?	%2a	%1a
10 mol%	None	No	38	39
	$Bu_4NH_2PO_4$ (25 mol%)		30	41
	Bu_4NOBz (25 mol%)		27	40
5 mol%	None	Yes	65	22
	$Bu_4NOPO(OBu)_2$ (25 mol%)		62	15

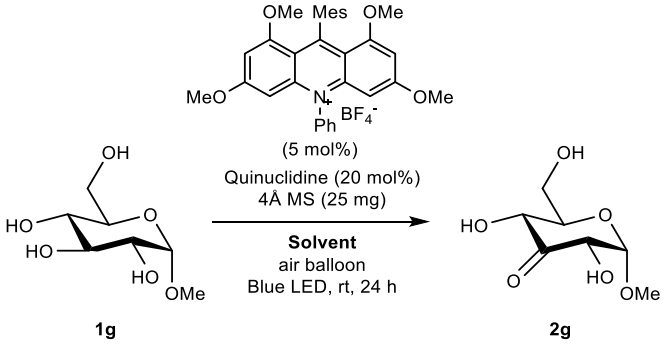
Time Screen



Time (h)	%2a	%1a
24	65	22
48	67	11

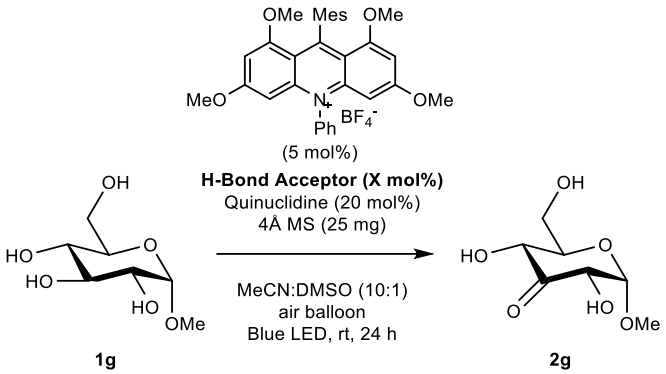
Methyl α-D-glucopyranoside

Solvent Screen



Solvent	%2g	%1g
MeCN	16	58
DMSO	30	52
MeCN:DMSO (10:1)	33	48
MeCN:DMSO (4:1)	40	30
MeCN:DMSO (1:1)	32	47
MeCN:H_2O (10:1)	11	51
MeCN:MeOH (10:1)	20	64
MeCN:TFE (10:1)	21	60

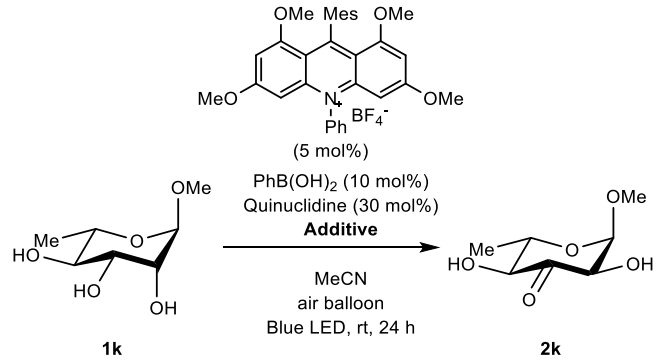
Hydrogen Bond Acceptor Screen:



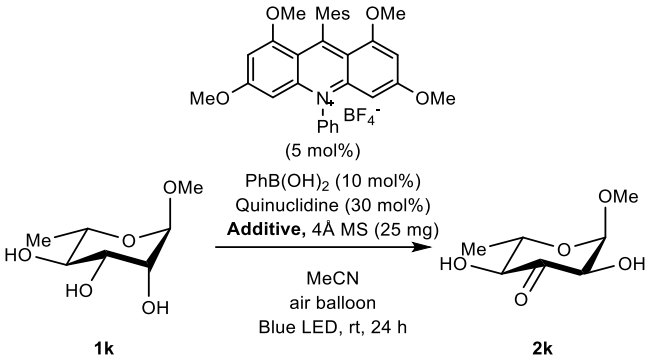
H-Bond Acceptor (X mol%)	%2g	% 1g
None	14	62
4-ClOBzBu_4N (25 mol%)	18	51
$Bu_4NH_2PO_4$ (25 mol%)	33	48
$Bu_4NOPO(OPh)_2$ (25 mol%)	45	20
$Bu_4NOPO(OBu)_2$ (25 mol%)	56	<5
$NaOPO(OBu)_2$ (25 mol%)	44	<5
$KOPO(OBu)_2$ (25 mol%)	53	<5

Methyl α-L-rhamnopyranoside

Additive Screen

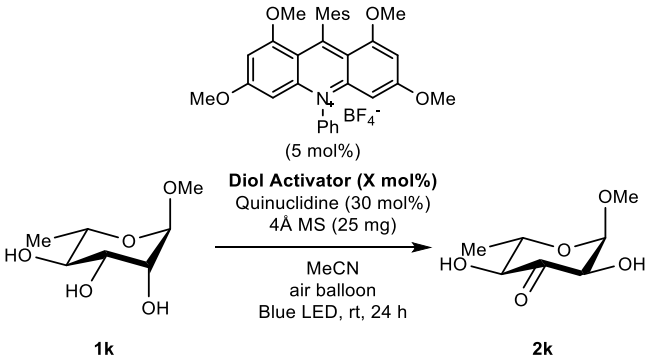


Additive	%2k	%1k
None	22	22
4Å MS (powder, 25 mg)	28	28



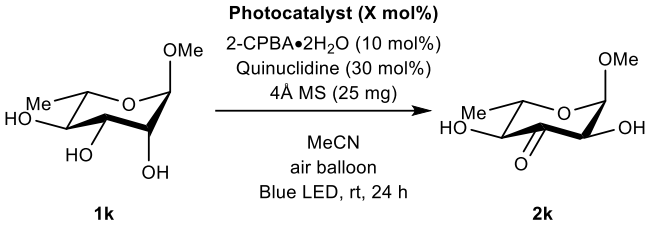
Additive	%2k	% 1k
None	28	28
Phthalimide (20 mol%)	22	35
$(CH_3)_3CCO_2H$ (1.0 equiv.)	36	25
TsOH●H2O (1.0 equiv.)	11	86
Bu_3PO (30 mol%)	18	24
Pyridine-N-oxide (30 mol%)	11	16

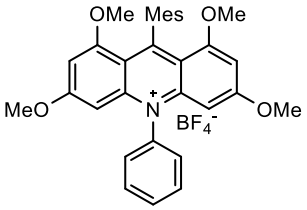
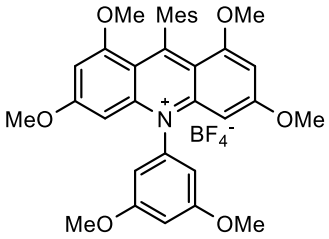
Diol Activator Screen



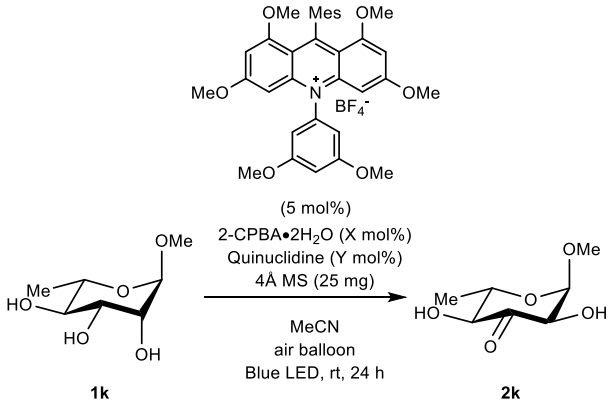
Additive	%2k
$PhB(OH)_2$ (10 mol%)	22
Ph_2SnCl_2 (10 mol%) + 1.5 equiv. $KHCO_3$	31
$(Ph_2B)_2O$ (5 mol%)	10
2-CPBA●$2H_2O$ (10 mol%)	52

Photocatalyst Screen



Photocatalyst (X mol%)	%2k	%1k
(Ir[dF(CF3)ppy]2(dtbpy))PF6 (2.0 mol%)	27	27
4-CzIPN (5 mol%)	32	15
 (5 mol%)	52	11
 (5 mol%)	53	7

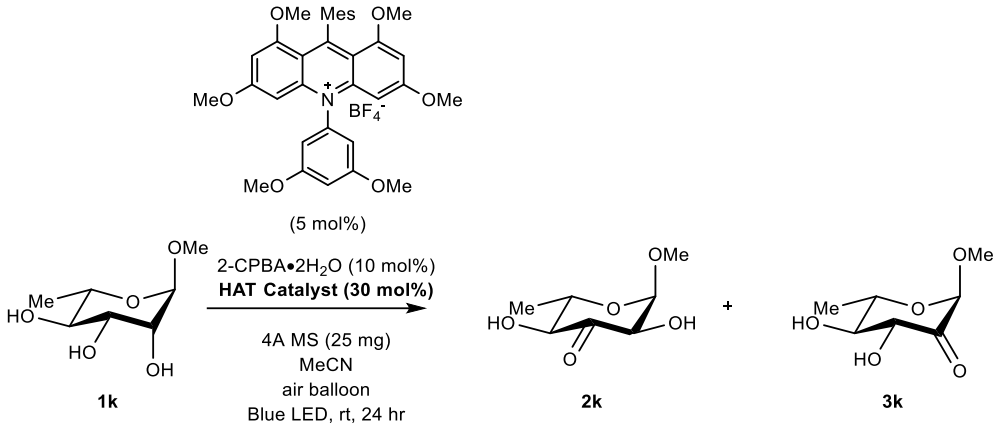
Boron-Quinuclidine Loading Screen

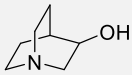
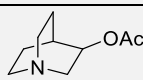
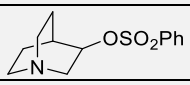
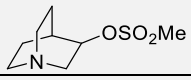
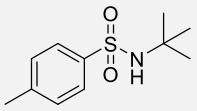
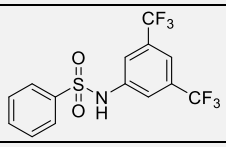
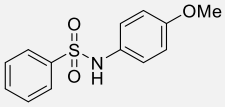
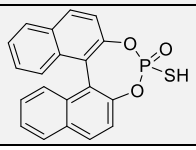


		2-CPBA•2H2O (mol%)	
		10	20
Quinuclidine (mol%)	20	21	
	30	53	48
	40	57	48

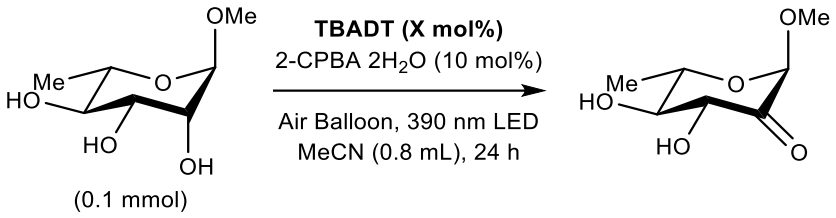
Methyl α-L-rhamnopyranoside (C2 Oxidation)

HAT Catalyst Screen



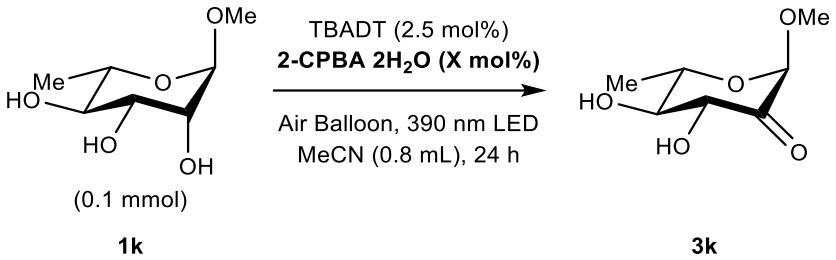
HAT Catalyst	% 2k	%3k	%1k
	51	0	11
	0	8	81
	35	4	22
	17	0	60
	13	0	51
	0	0	95
	0	0	76
	0	0	83
	0	0	85

TBADT Loading



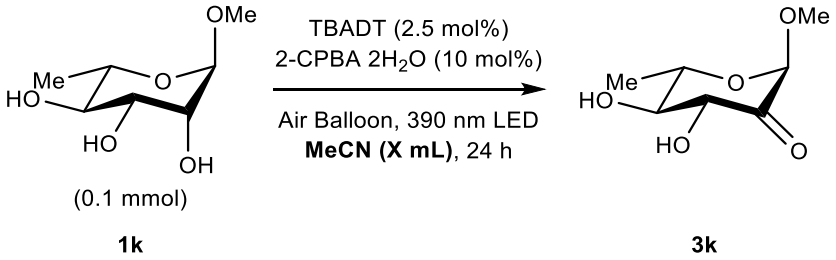
TBADT (X mol%)	%3k	%1k
5	17	0
4.5	21	17
3.5	34	20
2.5	30	26

Boronic Acid Loading



2-CPBA $2H_2O$ (X mol%)	%3k	%1k
5	27	28
10	30	26
20	20	29

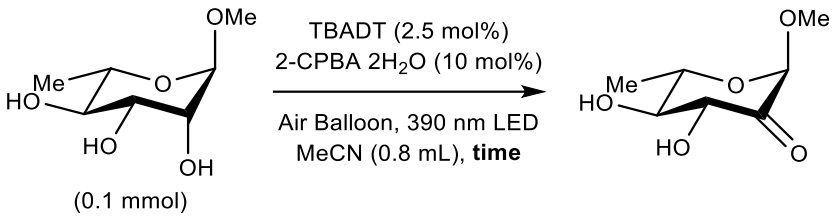
Concentration Screen



MeCN (X mL)	%3k	%1k
0.4	20	22
0.8	30	26

1.6	28	29

Time Screen



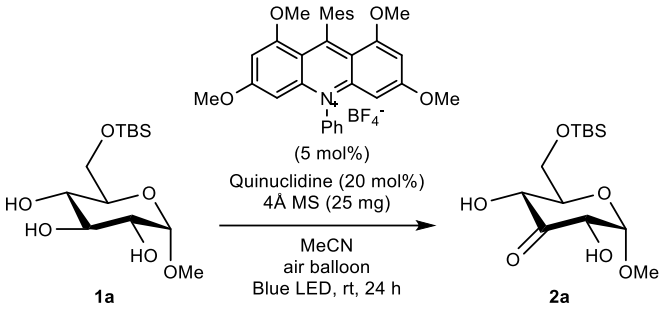
(0.1 mmol)

1k **3k**

Time (h)	%3k	%1k
2	15	66
6	17	55
13	24	40
24	30	26
30	29	21
48	28	7

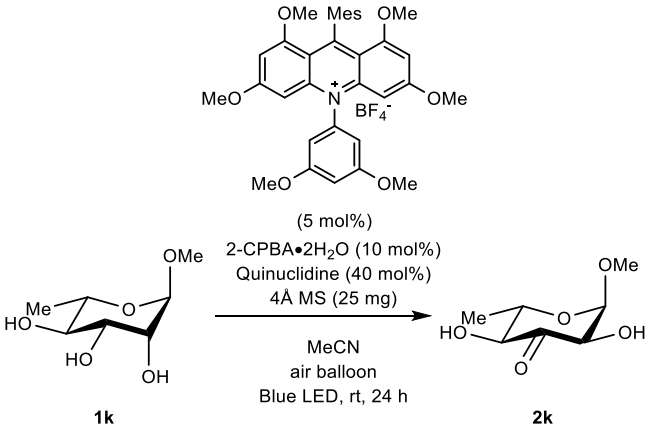
Control Experiments

Methyl 6-O-(tert-butyldimethylsilyl)-α-D-glucopyranoside



Changes to Above Conditions:	%2a
None	65
No Photocatalyst	<5
No Quinuclidine	<5
No MS	40
No Blue Light	<5

Methyl α-L-rhamnopyranoside



Changes to Above Conditions:	%2k
None	57
No Photocatalyst	<5
No 2-CPBA•2H_2O	<5
No Quinuclidine	<5
No MS	26
No Blue Light	<5

Product Characterization

General Procedure A:

Carbohydrate (0.2 mmol, 1.0 equiv.), acridinium photocatalyst (0.01 mmol, 0.05 equiv.), quinuclidine (4.4 mg, 0.04 mmol, 0.2 equiv.), 4Å molecular sieves (powder, 25 mg) and a small, magnetic stir bar were transferred to a 2-dram vial. The vial was sealed with a rubber septum and an air balloon was inserted into it. 1.6 mL of anhydrous acetonitrile was transferred into the vial and the solution was sonicated for 5 seconds. Subsequently, the vial was placed 4 inches from a blue LED Kessil lamp and stirred at 1050 rpm (the temperature under the light was monitored and remained at ~25 °C throughout the course of the reaction) for 24 – 48 hours. After 16 hours, a needle was inserted into the septum and the vial was flushed with air from the balloon for 10 seconds. The needle was then removed. After 24 – 48 hours, the crude mixture was diluted with acetonitrile, filtered through a small celite plug and the filtrate was concentrated under reduced pressure. Following ^{1}H NMR analysis, the crude material was subjected to flash chromatography on silica gel.

General Procedure B:

Carbohydrate (0.2 mmol, 1.0 equiv.), acridinium photocatalyst (0.01 mmol, 0.05 equiv.), $NBu_4OPO(OBu)_2$ (22.6 mg, 0.05 mmol, 0.25 equiv.), quinuclidine (4.4 mg, 0.04 mmol, 0.2 equiv.), 4Å molecular sieves (powder, 25 mg) and a small, magnetic stir bar were transferred to a 2-dram vial. The vial was sealed with a rubber septum and an air balloon was inserted into it. 1.6 mL of anhydrous acetonitrile was transferred into the vial and the solution was sonicated for 5 seconds. Subsequently, the vial was placed 4 inches from a blue LED Kessil lamp and stirred at 1050 rpm (the temperature under the light was monitored and remained at ~25 °C throughout the course of the reaction) for 24 – 48 hours. After 16 hours, a needle was inserted into the septum and the vial was flushed with air from the balloon for 10 seconds. The needle was then removed. After 24 – 48 hours, the crude mixture was diluted with acetonitrile, filtered through a small celite plug and the filtrate was concentrated under reduced pressure. Following ^{1}H NMR analysis, the crude material was subjected to flash chromatography on silica gel.

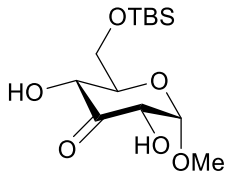
General Procedure C:

Carbohydrate (0.2 mmol, 1.0 equiv.), acridinium photocatalyst (0.01 mmol, 0.05 equiv.), $NBu_4OPO(OBu)_2$ (22.6 mg, 0.05 mmol, 0.25 equiv.), quinuclidine (4.4 mg, 0.04 mmol, 0.2 equiv.), 4Å molecular sieves (powder, 25 mg) and a small, magnetic stir bar were transferred to a 2-dram vial. The vial was sealed with a rubber septum and an air balloon was inserted into it. 1.6 mL of anhydrous acetonitrile and 0.16 mL of anhydrous dimethyl sulfoxide were transferred into the vial and the solution was sonicated for 5 seconds. Subsequently, the vial was placed 4 inches from a blue LED Kessil lamp and stirred at 1050 rpm (the temperature under the light was monitored and remained at ~25 °C throughout the course of the reaction) for 24 – 48 hours. After 16 hours, a needle was inserted into the septum and the vial was flushed with air from the balloon for 10 seconds. The needle was then removed. After 24 – 48 hours, the crude mixture was diluted with acetonitrile, filtered through a small celite plug and the filtrate was concentrated under reduced pressure. Following ^{1}H NMR analysis, the crude material was peracylated using acetic anhydride (2.5 equiv./hydroxyl group) and pyridine (3 mL). After quenching the reaction mixture with methanol and azeotropic removal of pyridine using toluene, the crude material was subjected to flash chromatography on silica gel.

General Procedure D:

Carbohydrate (0.2 mmol, 1.0 equiv.), acridinium photocatalyst (0.01 mmol, 0.05 equiv.), 2-carboxyphenylboronic acid dihydrate (4.0 mg, 0.02 mmol, 0.1 equiv.), quinuclidine (8.8 mg, 0.08 mmol, 0.4 equiv.), 4Å molecular sieves (powder, 25 mg) and a small, magnetic stir bar were transferred to a 2-dram vial. The vial was sealed with a rubber septum and an air balloon was inserted into it. 1.6 mL of anhydrous acetonitrile was transferred into the vial and the solution was sonicated for 5 seconds. Subsequently, the vial was placed 4 inches from a blue LED Kessil lamp and stirred at 1050 rpm (the temperature under the light was monitored and remained at ~25 °C throughout the course of the reaction) for 24 hours. After 16 hours, a needle was inserted into the septum and the vial was flushed with air from the balloon for 10 seconds. The needle was then removed. After 24 hours, the crude mixture was diluted with acetonitrile, filtered through a small celite plug and the filtrate was concentrated under reduced pressure. Following ^{1}H NMR analysis, the crude material was subjected to flash chromatography on silica gel.

(6-O-tert-butyldimethylsilyl)-methyl-α-D-ribo-hexapyranoside-3-ulose (2a)



Prepared according to **General Procedure A** (24 hours) from **1a** (61.6 mg, 0.2 mmol, 1 equiv.). **2a** was obtained as a white solid (39.2 mg, 64%) after flash chromatography on silica gel (25% to 55% ethyl acetate in hexanes).

^{1}H NMR (500 MHz, CD_3CN): δ (ppm) = 5.03 (d, *J* = 4.3 Hz, 1H, H1), 4.34 (ddd, *J* = 8.4, 4.3, 1.6 Hz, 1H, H2), 4.23 (ddd, *J* = 9.7, 5.3, 1.6 Hz, 1H, H4), 3.97 – 3.82 (m, 2H, $H6_a$, $H6_b$), 3.65 (d, *J* = 5.3 Hz, 1H, OH), 3.56 – 3.49 (m, 2H, H5, OH), 3.34 (s, 3H, OCH_3), 0.91 (s, 9H, CH_3), 0.10 (s, 6H, CH_3).

^{13}C NMR (126 MHz, CD_3CN): δ (ppm) = 207.3 (C3), 103.3 (C1), 76.7 (C5), 75.8 (C2), 72.9 (C4), 63.4 (C6), 55.7 (OCH_3), 26.2 (CH_3), 19.0 ($C(CH_3)_3$), -5.0 (CH_3), -5.2 (CH_3).

IR (thin film, cm^{-1}): 3493 (w), 3401 (w), 2953 (w), 2931 (w), 2856 (w), 1738 (s), 1478 (w), 1461 (w), 1393 (w), 1249 (m), 1129 (m), 1113 (m), 1055 (s), 997 (m), 829 (s), 785 (s).

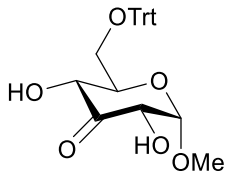
HRMS ($DART^+$, m/z): calculated for $C_{13}H_{27}O_6Si$ $[M+H]^+$: 307.1571, found 307.1567.

1.0 mmol scale reaction with 4-CzIPN:

Due to unforeseen shortages in the commercial supply of acridinium photocatalysts, 4-CzIPN was used as the photocatalyst for large scale reactions. Yields are expected to be 5% to 10% higher with the acridinium photocatalysts.

1a (308.4 mg, 1.0 mmol, 1.0 equiv.), 4-CzIPN (39.4 mg, 0.05 mmol, 0.05 equiv.), quinuclidine (22.2 mg, 0.2 mmol, 0.2 equiv.), 4Å molecular sieves (powder, 50 mg) and a magnetic stir bar were transferred to a 10-dram vial. The vial was sealed with a rubber septum and an air balloon was inserted into it. 8.0 mL of anhydrous acetonitrile was transferred into the vial and the solution was sonicated for 5 seconds. Subsequently, the vial was placed 4 inches from two blue LED Kessil lamp and stirred at 1050 rpm (the temperature under the light was monitored and remained at ~25 °C throughout the course of the reaction) for 36 hours. After 16 hours, a needle was inserted into the septum and the vial was flushed with air from the balloon for 20 seconds. The needle was then removed. After 36 hours, the crude mixture was diluted with acetonitrile, filtered through a celite plug and the filtrate was concentrated under reduced pressure. After flash chromatography on silica gel (25% to 55% ethyl acetate in hexanes), **2a** was obtained as a pale-yellow solid (159.5 mg, 52%).

(6-O-trityl)-methyl-α-D-ribo-hexapyranoside-3-ulose (2b)



Prepared according to **General Procedure A** (24 hours) from **1b** (87.2 mg, 0.2 mmol, 1 equiv.). **2b** was obtained as a white solid (47.6 mg, 55%) after flash chromatography on silica gel (25% to 55% ethyl acetate in hexanes).

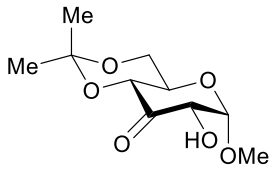
^{1}H NMR (500 MHz, CD_3CN): δ (ppm) = 7.55 – 7.45 (m, 6H, H_{Ar}), 7.38 – 7.31 (m, 6H, H_{Ar}), 7.31 – 7.25 (m, 3H, H_{Ar}), 5.12 (d, *J* = 4.7 Hz, 1H, H1), 4.45 (ddd, *J* = 8.1, 4.3, 1.4 Hz, 1H, H2), 4.29 (ddd, *J* = 9.8, 5.2, 1.5 Hz, 1H, H4), 3.78 – 3.71 (m, 1H, H5), 3.62 (d, *J* = 5.4 Hz, 1H, OH), 3.57 (d, *J* = 8.4 Hz, 1H, OH), 3.42 (s, 3H, OCH_3), 3.37 (dd, *J* = 10.2, 1.9 Hz, 1H, $H6_a$), 3.32 (dd, *J* = 10.2, 5.6 Hz, 1H, $H6_b$).

^{13}C NMR (126 MHz, CD_3CN): δ (ppm) = 206.9 (C3), 145.0 (C_{Ar}), 129.6 (C_{Ar}), 128.9 (C_{Ar}), 128.2 (C_{Ar}), 103.2 (C1), 87.4 ($C(Ph)_3$), 75.9 (C2), 75.3 (C5), 73.6 (C4), 64.4 (C6), 55.8 (OCH_3).

IR (thin film, cm^{-1}): 3435 (w, br), 2927 (w), 1732 (s), 1491 (m), 1447 (s), 1220 (w), 1186 (w), 1118 (s), 1045 (s), 900 (w), 873 (w), 764 (s), 701 (s), 631 (s).

HRMS ($DART^+$, m/z): calculated for $C_{26}H_{26}NaO_6$ $[M+Na]^+$: 457.1622, found 457.1625.

(4aR,6S,7S,8aR)-7-hydroxy-6-methoxy-2,2-dimethyltetrahydropyrano[3,2-d][1,3]dioxin-8(4H)-one (2c)



Prepared according to **General Procedure B** (48 hours) from **1c** (46.8 mg, 0.2 mmol, 1 equiv.). **2c** was obtained as a white solid (27.6 mg, 60%) after flash chromatography on silica gel (60% to 80% ethyl acetate in hexanes).

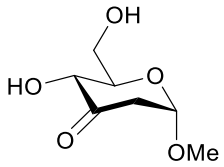
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.11 (d, *J* = 4.4 Hz, 1H, H1), 4.42 – 4.27 (m, 2H, H2, H4), 4.00 – 3.91 (m, 2H, $H6_a$, $H6_b$), 3.88 – 3.82 (m, 1H, H5), 3.40 (s, 3H, OCH_3), 1.50 (s, 3H, CH_3), 1.48 (s, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 199.6 (C3), 103.5 (C1), 100.5 ($\underline{C}(CH_3)_2$), 75.7 (C4), 75.0 (C2), 66.8 (C5), 62.9 (C6), 55.8 (OCH_3), 28.9 (CH_3), 18.9 (CH_3).

IR (thin film, cm^{-1}): 3439 (w, br), 2939 (w), 1743 (s), 1458 (w), 1379 (w), 1354 (w), 1261 (w), 1190 (m), 1162 (m), 1120 (m), 1040 (s), 966 (s), 956 (s), 882 (m), 829 (m), 730 (w), 646 (w).

HRMS ($DART^+$, m/z): calculated for $C_{10}H_{17}O_6$ $[M+H]^+$: 233.1019, found 233.1017.

Methyl-2-deoxy-α-D-erythro-hexopyranosid-3-ulose (2d)

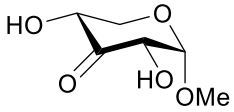


Prepared according to **General Procedure B** (48 hours) from **1d** (35.6 mg, 0.2 mmol, 1 equiv.). **2d** was obtained as a white solid (19.6 mg, 56%) after flash chromatography on silica gel (60% to 90% ethyl acetate in hexanes). Spectral features match with previous literature.[10]

^{1}H NMR (500 MHz, CD_3OD): δ (ppm) = 5.22 (d, *J* = 4.2 Hz, 1H), 4.26 (dd, *J* = 9.9, 1.0 Hz, 1H), 3.92 (m, 2H), 3.80 – 3.72 (m, 1H), 3.42 (s, 3H), 2.97 (ddd, *J* = 14.1, 4.5, 1.3 Hz, 1H), 2.57 (dd, *J* = 14.1, 1.1 Hz, 1H).

^{13}C NMR (126 MHz, CD_3OD): δ (ppm) = 207.5, 101.1, 76.3, 74.1, 62.6, 55.0, 46.6.

Methyl α-D-xylo-hexopyranosid-3-ulose (2e)

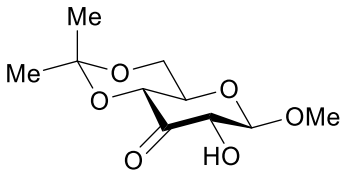


Prepared according to **General Procedure B** (48 hours) from **1e** (32.8 mg, 0.2 mmol, 1 equiv.). **2e** was obtained as a white solid (19.4 mg, 60%) after flash chromatography on silica gel (60% to 90% ethyl acetate in hexanes). Spectral features match with previous literature.[11]

^{1}H NMR (500 MHz, CD_3CN): δ (ppm) = 5.00 (d, *J* = 4.2 Hz, 1H), 4.40 – 4.28 (m, 2H), 4.03 (dd, *J* = 10.4, 8.0 Hz, 1H), 3.64 (d, *J* = 5.0 Hz, 1H), 3.54 (d, *J* = 8.4 Hz, 1H), 3.50 – 3.43 (m, 1H), 3.34 (s, 3H).

^{13}C NMR (126 MHz, CD_3CN): δ (ppm) = δ 206.9, 104.0, 76.1, 72.9, 65.2, 55.8.

(4aR,6R,7S,8aR)-7-hydroxy-6-methoxy-2,2-dimethyltetrahydropyrano[3,2-d][1,3]dioxin-8(4H)-one (2f)



Prepared according to **General Procedure B** (48 hours) from **1f** (46.8 mg, 0.2 mmol, 1 equiv.). A 5:1 mixture of C3 (**2f**):C2 regioisomers were obtained as a colorless oil (22.0 mg, 47%) after flash chromatography on silica gel (60% to 80% ethyl acetate in hexanes).

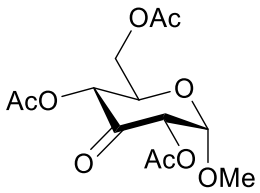
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.42 (dd, *J* = 10.2, 2.0 Hz, 1H, H4), 4.34 (d, *J* = 7.5 Hz, 1H, H1), 4.13 – 4.10 (m, 1H, H2), 4.07 (dd, *J* = 11.0, 5.4 Hz, 1H, $H6_a$), 3.95 (d, *J* = 10.0 Hz, 1H, $H6_b$), 3.60 (s, 3H, OCH_3), 3.40 (ddd, *J* = 10.1, 5.3 Hz, 1H, H5), 1.51 (s, 3H, CH_3), 1.49 (s, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 199.7 (C3), 107.1 (C1), 100.6 ($\underline{C}(CH_3)_2$), 77.3 (C2), 75.3 C4), 67.8 (C5), 62.5 (C6), 57.9 (OCH_3), 28.8 (CH_3), 18.8 (CH_3).

IR (thin film, cm^{-1}): 3405 (w, br), 2939 (w), 1743 (m), 1455 (w), 1380 (m), 1199 (m), 1124 (m), 1085 (s), 1013 (s), 849 (m), 728 (w).

HRMS ($DART^+$, m/z): calculated for $C_{10}H_{17}O_6$ $[M+H]^+$: 233.1019, found 233.1021.

(2R,3R,5S,6S)-2-(acetoxymethyl)-6-methoxy-4-oxotetrahydro-2H-pyran-3,5-diyl diacetate (2g)



Prepared according to **General Procedure C** (24 hours) from **1g** (38.8 mg, 0.2 mmol, 1 equiv.). **2g** was obtained as a pale-yellow oil (35.6 mg, 56%) after flash chromatography on silica gel (20% to 50% ethyl acetate in hexanes).

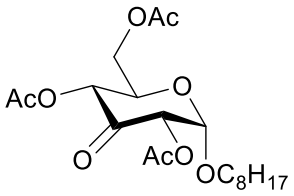
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.41 (dd, *J* = 4.1, 1.1 Hz, 1H, H2), 5.30 (dd, *J* = 10.3, 1.1 Hz, 1H, H4), 5.16 (d, *J* = 4.1 Hz, 1H, H1), 4.33 – 4.28 (m, 2H, H6), 4.20 – 4.14 (m, 1H, H5), 3.43 (s, 3H, OCH_3), 2.17 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.10 (s, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 193.0 (C3), 170.6 (Ac C=O), 169.4 (Ac C=O), 168.9 (Ac C=O), 99.9 (C1), 74.7 (C2), 72.2 (C4), 69.7 (C5), 62.2 (C6), 55.8 (OCH_3), 20.8 (CH_3), 20.5 (CH_3), 20.3 (CH_3).

IR (thin film, cm^{-1}): 2942 (w), 1740 (s), 1440 (w), 1371 (m), 1218 (s), 1115 (m), 1090 (s), 915 (m), 731 (w), 639 (w).

HRMS ($DART^+$, m/z): calculated for $C_{13}H_{19}O_9$ $[M+H]^+$: 319.1024, found 319.1025.

(2R,3R,5S,6S)-2-(acetoxymethyl)-6-octyloxy-4-oxotetrahydro-2H-pyran-3,5-diyl diacetate (2h)



Prepared according to **General Procedure C** (36 hours) from **1h** (58.4 mg, 0.2 mmol, 1 equiv.). **2h** was obtained as a pale-yellow oil (48.8 mg, 54%) after flash chromatography on silica gel (20% to 50% ethyl acetate in hexanes).

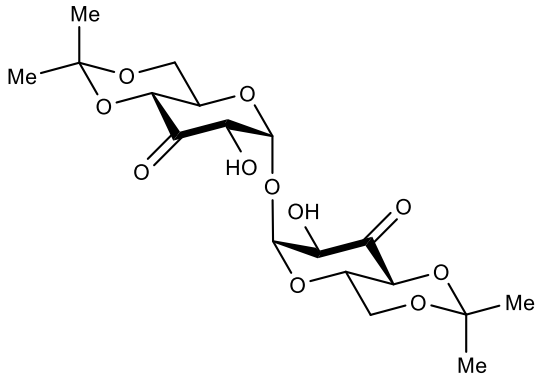
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.40 (dd, *J* = 4.2, 1.1 Hz, 1H, H2), 5.29 (dd, *J* = 10.3, 1.1 Hz, 1H, H4), 5.25 (d, *J* = 4.1 Hz, 1H, H1), 4.30 (d, *J* = 3.2 Hz, 2H, H6), 4.23 – 4.18 (m, 1H, H5), 3.72 – 3.65 (m, 1H, CH_a), 3.52 – 3.46 (m, 1H, CH_b), 2.17 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 1.61 – 1.54 (m, 2H, CH_2), 1.30 – 1.22 (m, 10H, CH_2), 0.88 – 0.84 (m, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 193.2 (C3), 170.6 (Ac C=O), 169.6 (Ac C=O), 169.0 (Ac C=O), 98.8 (C1), 74.8 (C2), 72.3 (C4), 69.7 (C5), 69.2 (CH_2), 62.3 (C6), 31.9 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 26.0 (CH_2), 22.7 (CH_2), 20.8 (CH_3), 20.5 (CH_3), 20.4 (CH_3), 14.2 (CH_3).

IR (thin film, cm^{-1}): 2927 (w), 2857 (w), 1745 (s), 1444 (w), 1370 (m), 1220 (s), 1159 (w), 1113 (w), 1066 (s), 1028 (s), 639 (w).

HRMS ($DART^+$, m/z): calculated for $C_{20}H_{32}NaO_9$ $[M+Na]^+$: 439.1939, found 439.1947.

(6R,7S)-7-hydroxy-6-(((4aR,6R,7S,8aR)-7-hydroxy-2,2-dimethyl-8-oxohexahydropyrano[3,2-d][1,3]dioxin-6-yl)oxy)-2,2-dimethyltetrahydropyrano[3,2-d][1,3]dioxin-8(4H)-one (2i)



Prepared according to **General Procedure B** (0.1 mmol scale, 48 hours) from **1i** (42.2 mg, 0.1 mmol, 1 equiv.). **2i** was obtained as a colorless solid (14.6 mg, 35%) after flash chromatography on silica gel (70% to 90% ethyl acetate in hexanes).

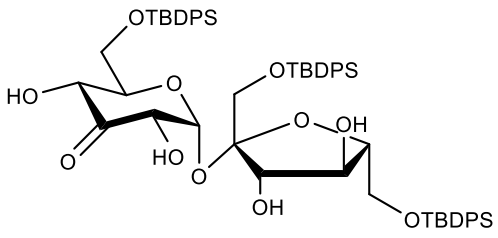
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.50 (d, *J* = 4.7 Hz, 2H, H1), 4.45 – 4.34 (m, 4H, H2, H4), 4.14 – 4.07 (m, 2H, H5), 3.99 (dd, *J* = 10.6, 5.1 Hz, 2H, $H6_a$), 3.90 (t, *J* = 10.4 Hz, 2H, $H6_b$), 3.54 (d, *J* = 6.7 Hz, 2H, OH), 1.51 (s, 6H, CH_3), 1.50 (s, 6H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 199.0 (C3), 100.7 ($\underline{C}(CH_3)_2$), 98.3 (C1), 75.5 (C4), 74.1 (C2), 67.7 (C5), 62.7 (C6), 28.7 (CH_3), 19.0 (CH_3).

IR (thin film, cm^{-1}): 3480 (w, br), 2929 (w), 1746 (s), 1378 (w), 1261 (w), 1175 (w), 1044 (s), 977 (s), 953 (s), 852 (s), 709 (w).

HRMS ($DART^+$, m/z): calculated for $C_8H_{27}O_{11}$ $[M+H]^+$: 419.1548, found 419.1548.

(2R,3S,5R,6R)-2-(((2S,3S,4S,5R)-2,5-bis(((tert-butyldiphenylsilyl)oxy)methyl)-3,4-dihydroxytetrahydrofuran-2-yl)oxy)-6-(((tert-butyldiphenylsilyl)oxy)methyl)-3,5-dihydroxytetrahydro-4H-pyran-4-one (2j)



Prepared according to **General Procedure A** (0.1 mmol scale, 48 hours) from **1j** (105.7 mg, 0.1 mmol, 1 equiv.). **2j** was obtained as a colorless solid (41 mg, 39%) after flash chromatography on silica gel (10% to 50% ethyl acetate in hexanes).

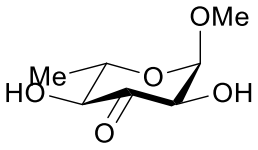
^{1}H NMR (500 MHz, CD_3CN): δ (ppm) = 7.77 – 7.64 (m, 12H, H_{Ar}), 7.47 – 7.29 (m, 18H, H_{Ar}), 5.78 (d, *J* = 4.7 Hz, 1H, Gluc-H1), 4.42 (ddd, *J* = 9.7, 5.3, 1.5 Hz, 1H, Gluc-H4), 4.34 – 4.25 (m, 1H, Fruc-CH), 4.13 (ddd, *J* = 8.8, 4.7, 1.6 Hz, 1H, Gluc-H2), 4.02 – 3.93 (m, 2H, Gluc-H5, Fruc-CH), 3.91 – 3.83 (m, 4H, Gluc-$H6_a$, Gluc-$H6_b$, Fruc-CH, Fruc-CH_a), 3.79 (dd, *J* = 11.2, 1.7 Hz, 1H, Fruc-CH_b), 3.72 (d, *J* = 10.8 Hz, 1H, Fruc-CH_a), 3.67 – 3.60 (m, 2H, OH, Fruc-CH_b), 3.54 (d, *J* = 8.8 Hz, 1H, OH), 3.39 (d, *J* = 5.5 Hz, 1H, OH), 3.23 (d, *J* = 8.8 Hz, 1H, OH), 1.05 (s, 9H, CH_3), 1.04 (s, 9H, CH_3), 1.00 (s, 9H, CH_3).

^{13}C NMR (126 MHz, CD_3CN): δ (ppm) = 207.3 (Gluc-C3), 136.6 (C_{Ar}), 136.4 (C_{Ar}), 136.4 (C_{Ar}), 136.4 (C_{Ar}), 136.4 (C_{Ar}), 134.4 (C_{Ar}), 134.3 (C_{Ar}), 134.2 (C_{Ar}), 134.2 (C_{Ar}), 134.1 (C_{Ar}), 133.8 (C_{Ar}), 130.9 (C_{Ar}), 130.8 (C_{Ar}), 130.8 (C_{Ar}), 130.8 (C_{Ar}), 130.8 (C_{Ar}), 128.9 (C_{Ar}), 128.8 (C_{Ar}), 128.8 (C_{Ar}), 128.8 (C_{Ar}), 128.7 (C_{Ar}), 105.7 (Fruc-C), 95.6 (Gluc-C1), 83.2, 77.5 (Fruc-C), 77.3, 75.1, 75.1 (Gluc-H2), 72.7 (Gluc-H4), 65.6, 65.0 (Fruc-CH_2), 64.1, 27.3 (CH_3), 27.2 (CH_3), 27.2 (CH_3), 19.9 ($\underline{C}(CH_3)_3$), 19.8 ($\underline{C}(CH_3)_3$).

IR (thin film, cm^{-1}): 3450 (w, br), 2911 (w), 1732 (w), 1466 (w), 1427 (m), 1098 (s), 999 (s), 815 (m), 699 (s), 611 (m).

HRMS ($DART^+$, m/z): calculated for $C_{60}H_{74}NaO_{11}Si_3$ $[M+Na]^+$: 1077.4431, found 1077.4441.

(2R,3R,5S,6S)-3,5-dihydroxy-2-methoxy-6-methyltetrahydro-4H-pyran-4-one (2k)

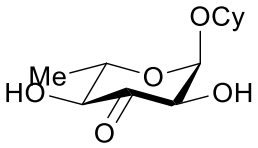


Prepared according to **General Procedure D** from **1k** (35.6 mg, 0.2 mmol, 1 equiv.). **2k** was obtained as a colorless solid (17.5 mg, 50%) after flash chromatography on silica gel (60% to 80% ethyl acetate in hexanes). Spectral features match with previous literature.[11]

^{1}H NMR (500 MHz, CD_3CN): δ (ppm) = 4.98 (d, *J* = 4.4 Hz, 1H), 4.41 – 4.32 (m, 1H), 3.90 – 3.81 (m, 1H), 3.68 – 3.58 (m, 2H), 3.52 (d, *J* = 8.4 Hz, 1H), 3.34 (s, 3H), 1.36 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (126 MHz, CD_3CN): δ (ppm) = 206.7, 103.2, 78.5, 75.9, 72.0, 55.7, 18.9.

(2R,3R,5S,6S)-2-(cyclohexyloxy)-3,5-dihydroxy-6-methyltetrahydro-4H-pyran-4-one (2l)



Prepared according to **General Procedure D** from **1l** (49.2 mg, 0.2 mmol, 1 equiv.). **2l** was obtained as a colorless solid (24.4 mg, 50%) after flash chromatography on silica gel (20% to 60% ethyl acetate in hexanes).

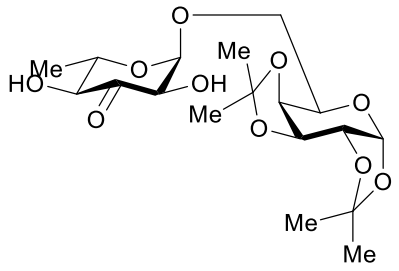
^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 5.22 (d, *J* = 4.6 Hz, 1H, H1), 4.33 (ddd, *J* = 9.3, 4.5, 1.5 Hz, 1H, H2), 3.84 (ddd, *J* = 9.3, 4.9, 1.4 Hz, 1H, H4), 3.80 – 3.67 (m, 1H, H5), 3.65 – 3.51 (m, 2H, CH, OH), 3.39 (d, *J* = 9.4 Hz, 1H, OH), 1.88 – 1.76 (m, 2H, CH_2), 1.76 – 1.60 (m, 2H, CH_2), 1.55 – 1.43 (m, 1H, CH_2), 1.35 – 1.16 (m, 8H, CH_3, CH_2).

^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 207.0 (C3), 100.6 (C1), 78.6 (C4), 77.3 (CH), 75.8 (C2), 72.3 (C5), 34.0 (CH_2), 32.1 (CH_2), 26.3 (CH_2), 24.7 (CH_2), 24.5 (CH_2), 18.9 (CH_3).

IR (thin film, cm^{-1}): 3415 (m, br), 2930 (m), 2857 (m), 1729 (s), 1449 (w), 1424 (w), 1380 (w), 1358 (w), 1343 (w), 1160 (w), 1122 (m), 1102 (m), 1063 (s), 1033 (s), 1004 (s), 967 (m), 933 (m), 878 (m), 853 (m), 678 (w).

HRMS ($DART^+$, m/z): calculated for $C_{12}H_{21}O_5$ $[M+H]^+$: 245.1383, found 245.1380.

(2S,3S,5R,6R)-3,5-dihydroxy-2-methyl-6-(((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methoxy)tetrahydro-4H-pyran-4-one (2m)



Prepared according to **General Procedure D** (0.1 mmol scale) from **1m** (40.6 mg, 0.1 mmol, 1 equiv.). **2m** was obtained as a colorless solid (20.5 mg, 51%) after flash chromatography on silica gel (50% to 80% ethyl acetate in hexanes).

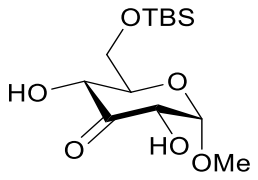
^{1}H NMR (500 MHz, CD_3CN): δ (ppm) = 5.44 (d, J = 5.0 Hz, 1H, Gal-H1), 5.16 (d, J = 4.4, 1H, Rham-H1), 4.59 (dd, J = 7.9, 2.4 Hz, 1H, Gal-H3), 4.36 (s, 1H, Rham-H2), 4.32 (dd, J = 5.0, 2.4 Hz, 1H, Gal-H2), 4.17 (dd, J = 7.9, 1.9 Hz, 1H, Gal-H4), 3.94 – 3.89 (m, 1H, Gal-H5), 3.88 – 3.82 (m, 1H, Rham-H4), 3.80 – 3.73 (m, 2H, Gal-$H6_a$, Rham-H5), 3.53 (dd, J = 10.3, 6.6 Hz, 1H, Gal-$H6_b$), 1.48 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.35 (d, J = 6.1 Hz, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.29 (s, 3H, CH_3).

^{13}C NMR (126 MHz, CD_3CN): δ (ppm) = 206.7 (Rham-C3), 109.8 (Gal-$\underline{C}(CH_3)_2$), 109.4 (Gal-$\underline{C}(CH_3)_2$), 102.2 (Rham-C1), 97.1 (Gal-C1), 78.5 (Rham-C4), 75.8 (Rham-C2), 72.4 (Rham-C5), 71.7 (Gal-C4), 71.5 (Gal-C3), 71.4 (Gal-C2), 67.5 (Gal-C5), 67.2 (Gal-C6), 26.3 (CH_3), 26.3 (CH_3), 25.2 (CH_3), 24.6 (CH_3), 18.9 (CH_3).

IR (thin film, cm^{-1}): 3450 (w, br), 2965 (w), 2931 (w), 1734 (m), 1378 (m), 1254 (m), 1166 (m), 1114 (m), 1058 (s), 999 (s), 918 (m), 889 (m), 860 (m), 805 (m), 763 (w).

HRMS ($DART^+$, m/z): calculated for $C_{18}H_{28}NO_{10}$ $[M+NH_4]^+$: 422.2020, found 422.2016.

(6-O-tert-butyldimethylsilyl)-methyl-α-D-ribo-hexapyranoside-3-ulose (2n) from 1n



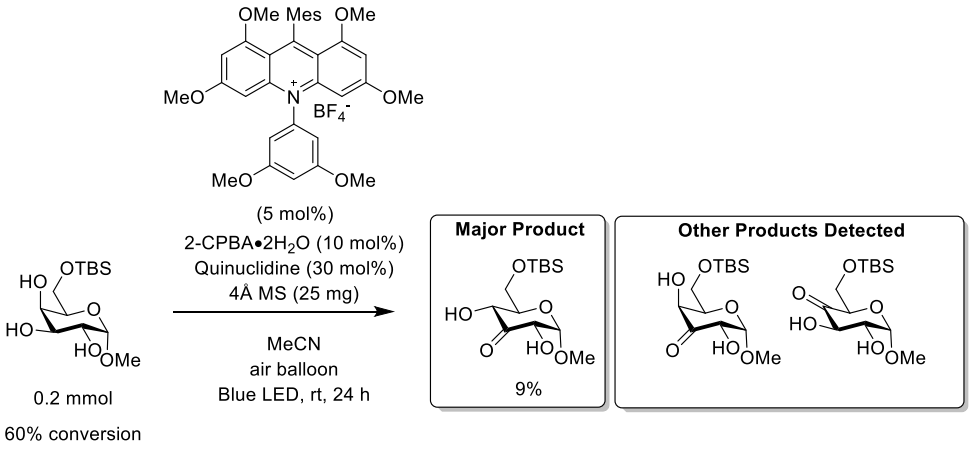
Prepared according to **General Procedure D** from **1n** (61.6 mg, 0.2 mmol, 1 equiv.). **2n** was obtained as a colorless solid (28.2 mg, 46%) after flash chromatography on silica gel (20% to 40% ethyl acetate in hexanes).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.13 (d, J = 4.4 Hz, 1H), 4.44 – 4.36 (m, 1H), 4.35 – 4.26 (m, 1H), 4.01 – 3.89 (m, 2H), 3.60 (ddd, J = 9.4, 4.0, 2.3 Hz, 1H), 3.45 – 3.35 (m, 4H), 3.18 (d, J = 8.2 Hz, 1H), 0.91 (s, 9H), 0.10 (s, 6H).

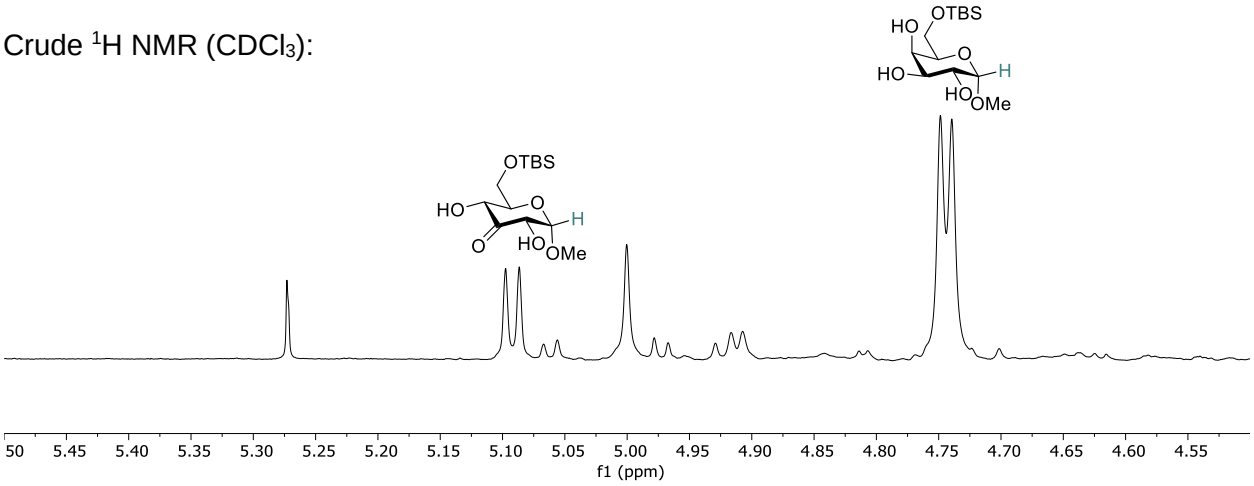
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 206.5, 102.3, 76.1, 74.8, 72.3, 62.6, 55.6, 26.0, 18.6, -5.1, -5.2.

Substrate Limitations

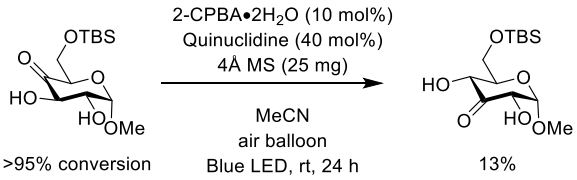
α-Galactopyranosides:



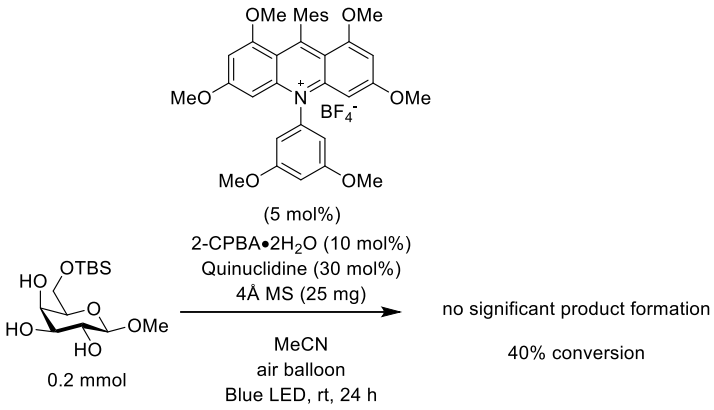
Crude ^{1}H NMR ($CDCl_3$):



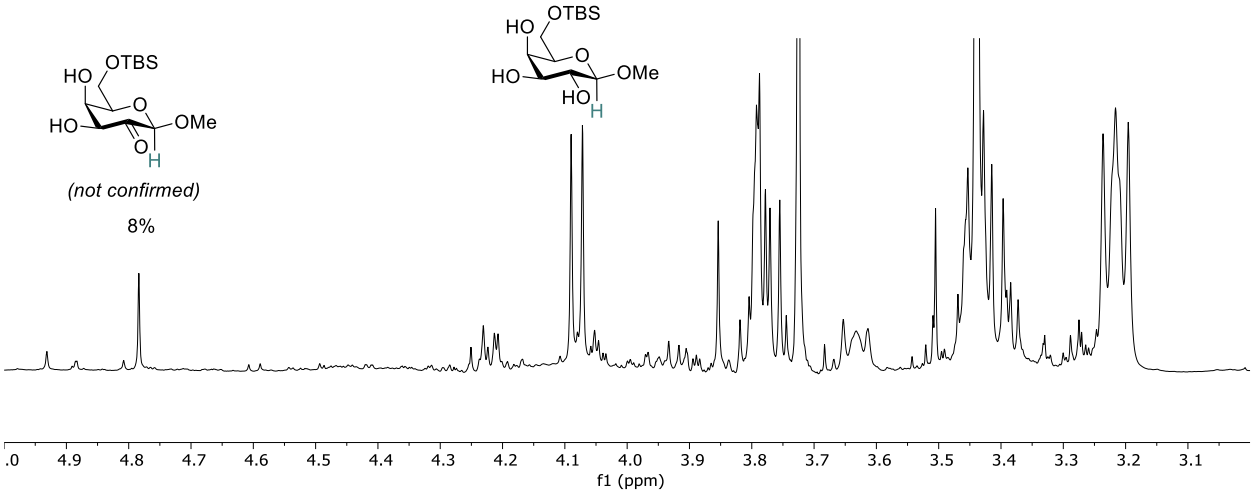
Base-mediated isomerization:



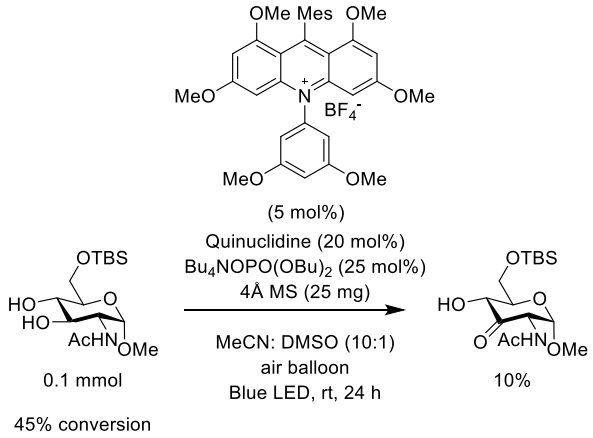
β-Galactopyranosides:



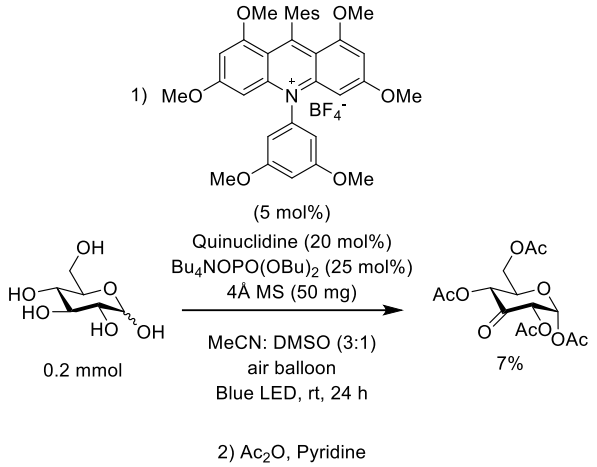
Crude ^{1}H NMR (CD_3CN):



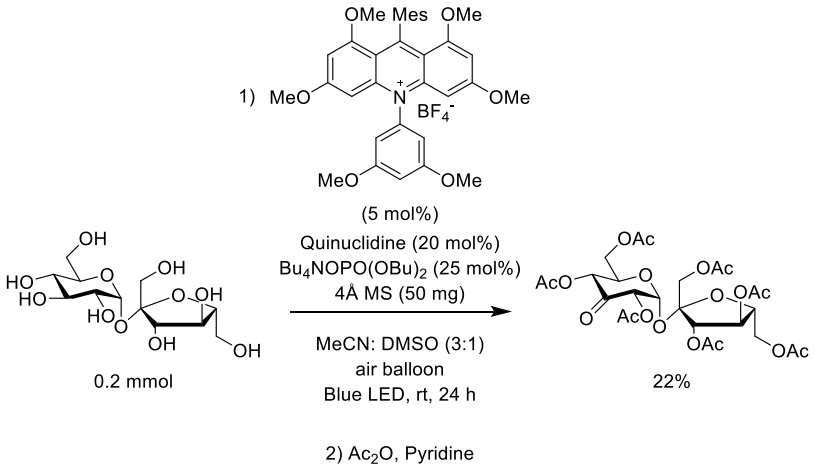
N-Acetylglucosamine:



Glucopyranose:



Sucrose:



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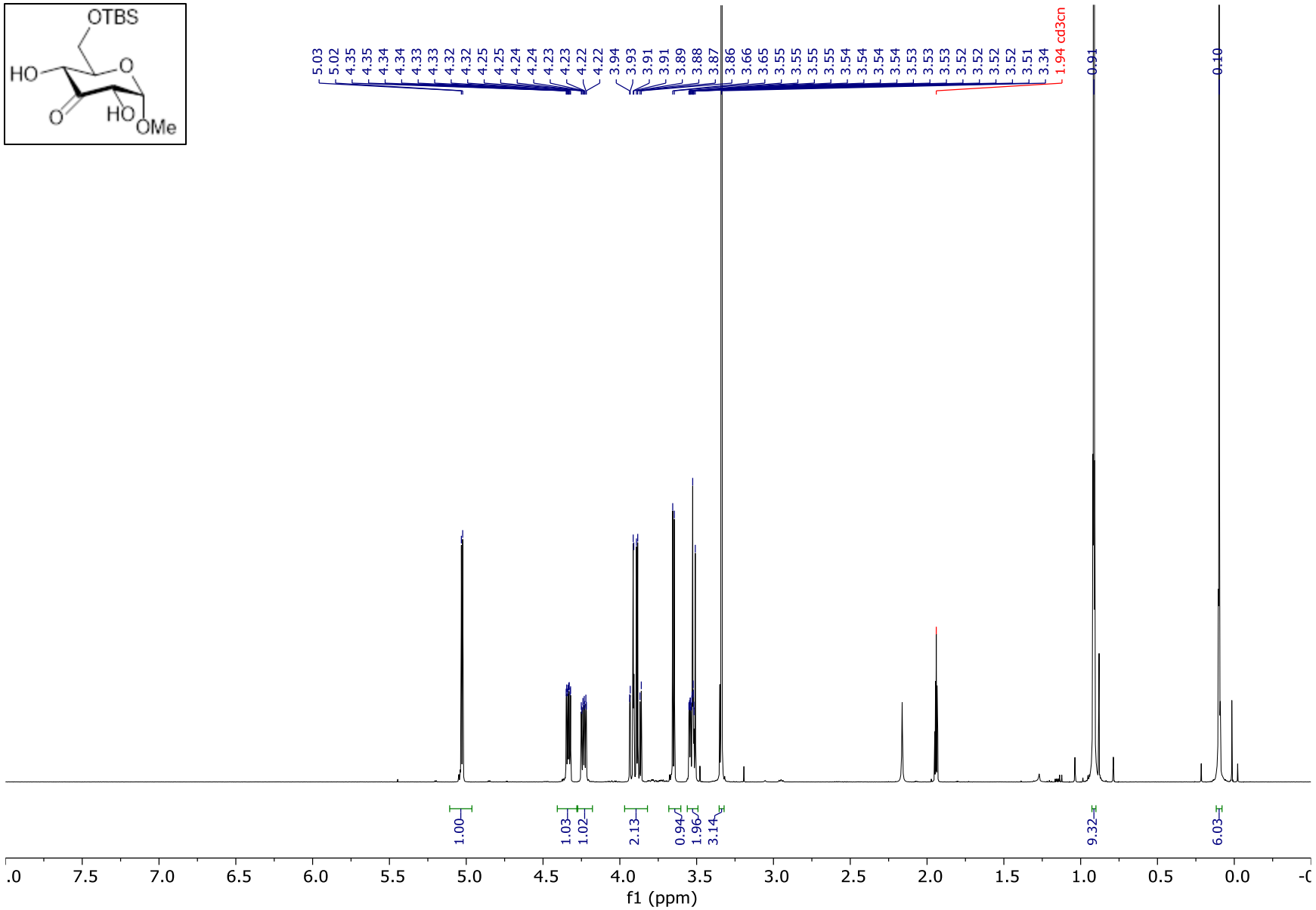
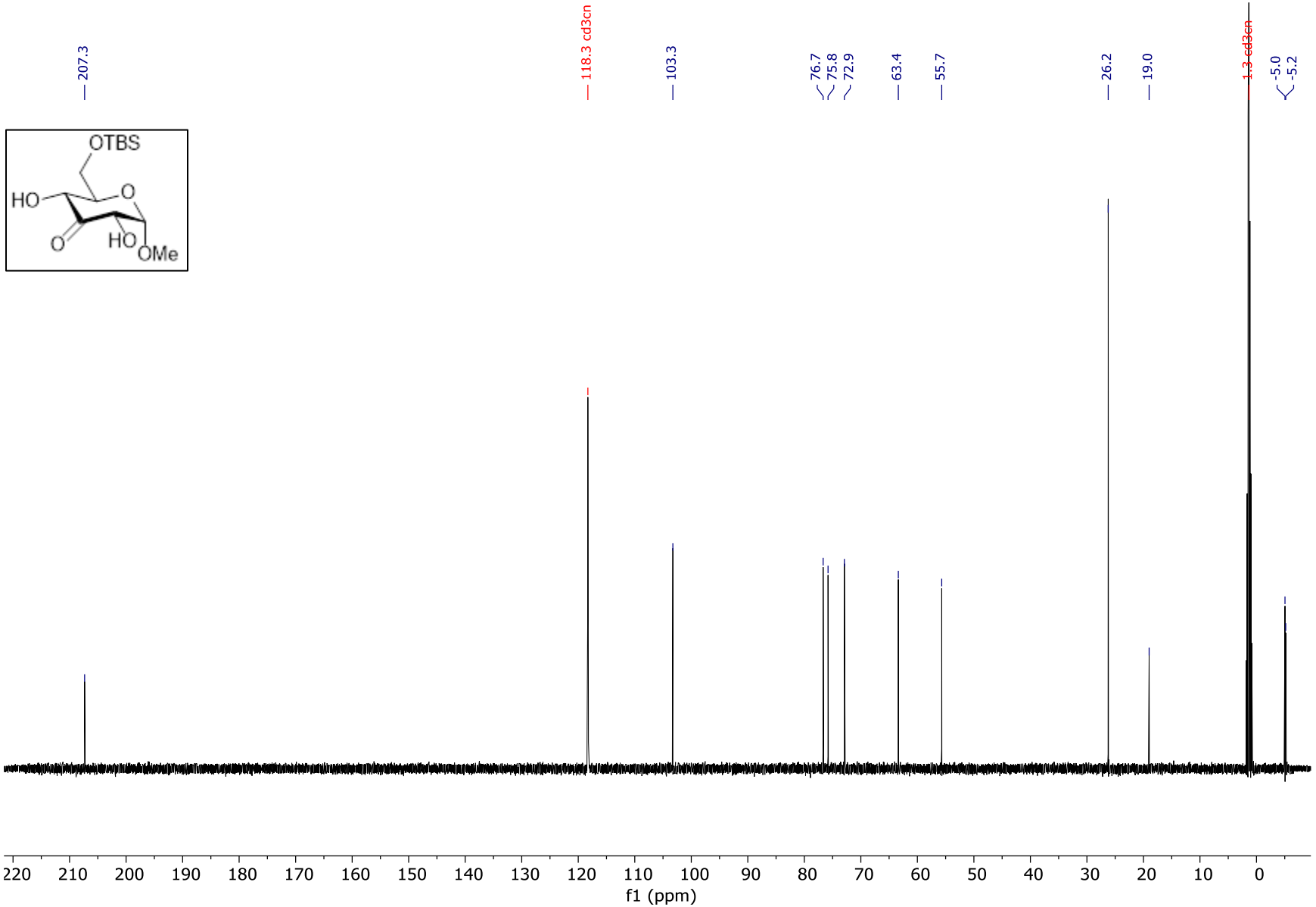
NMR Files

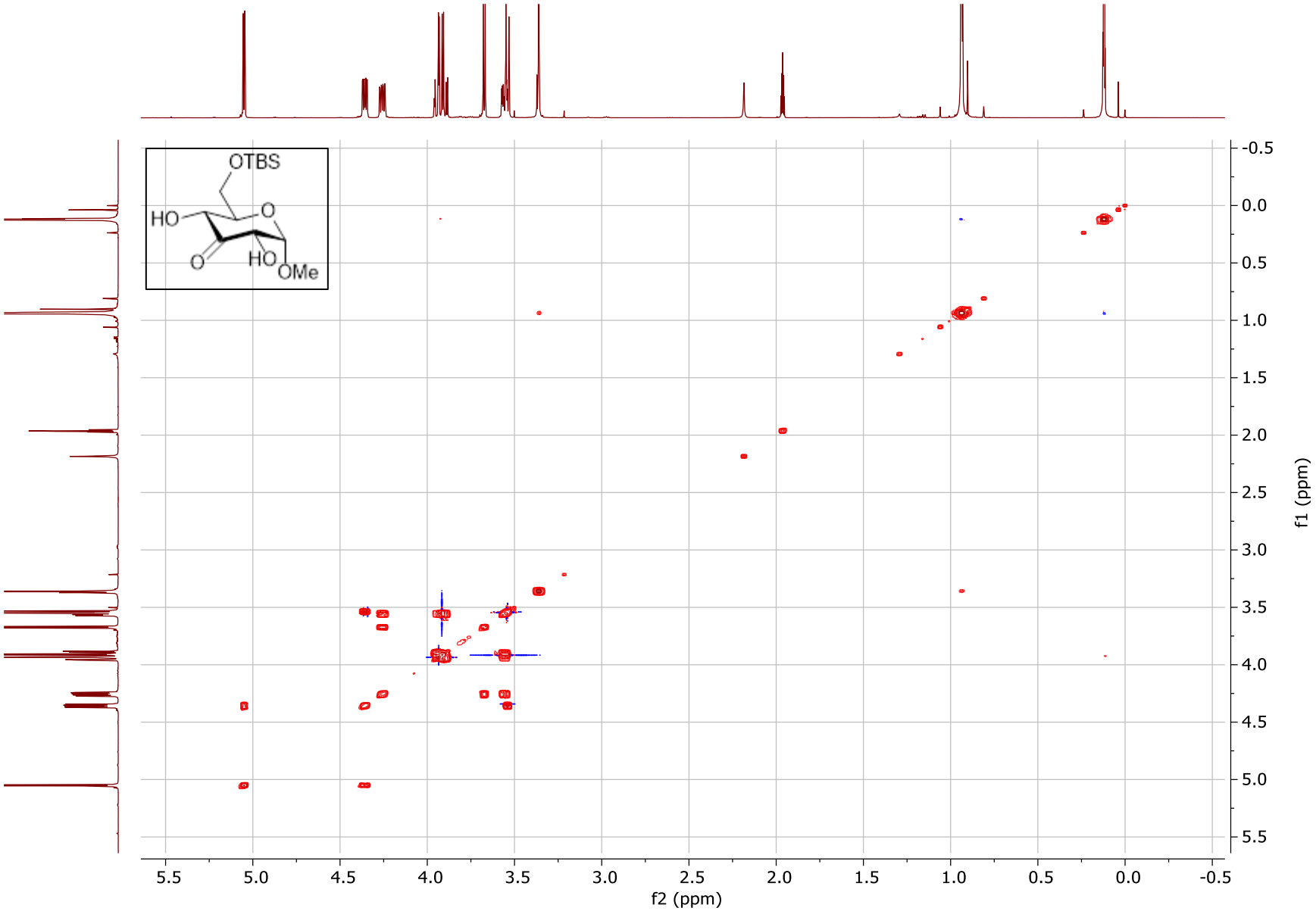
2a – ^{1}H NMR (500 MHz, CD_3CN)



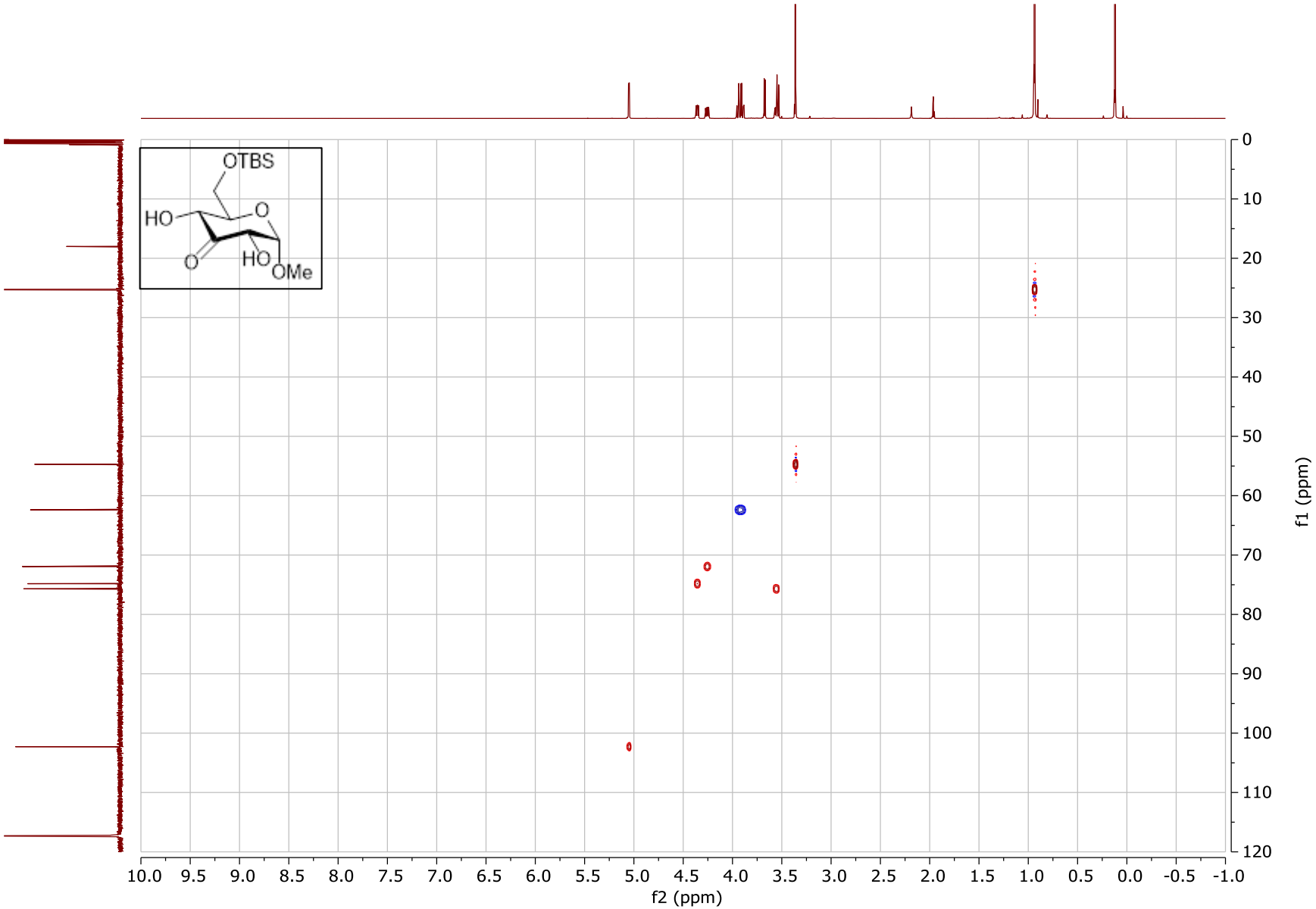
2a – ^{13}C NMR (126 MHz, CD_3CN)



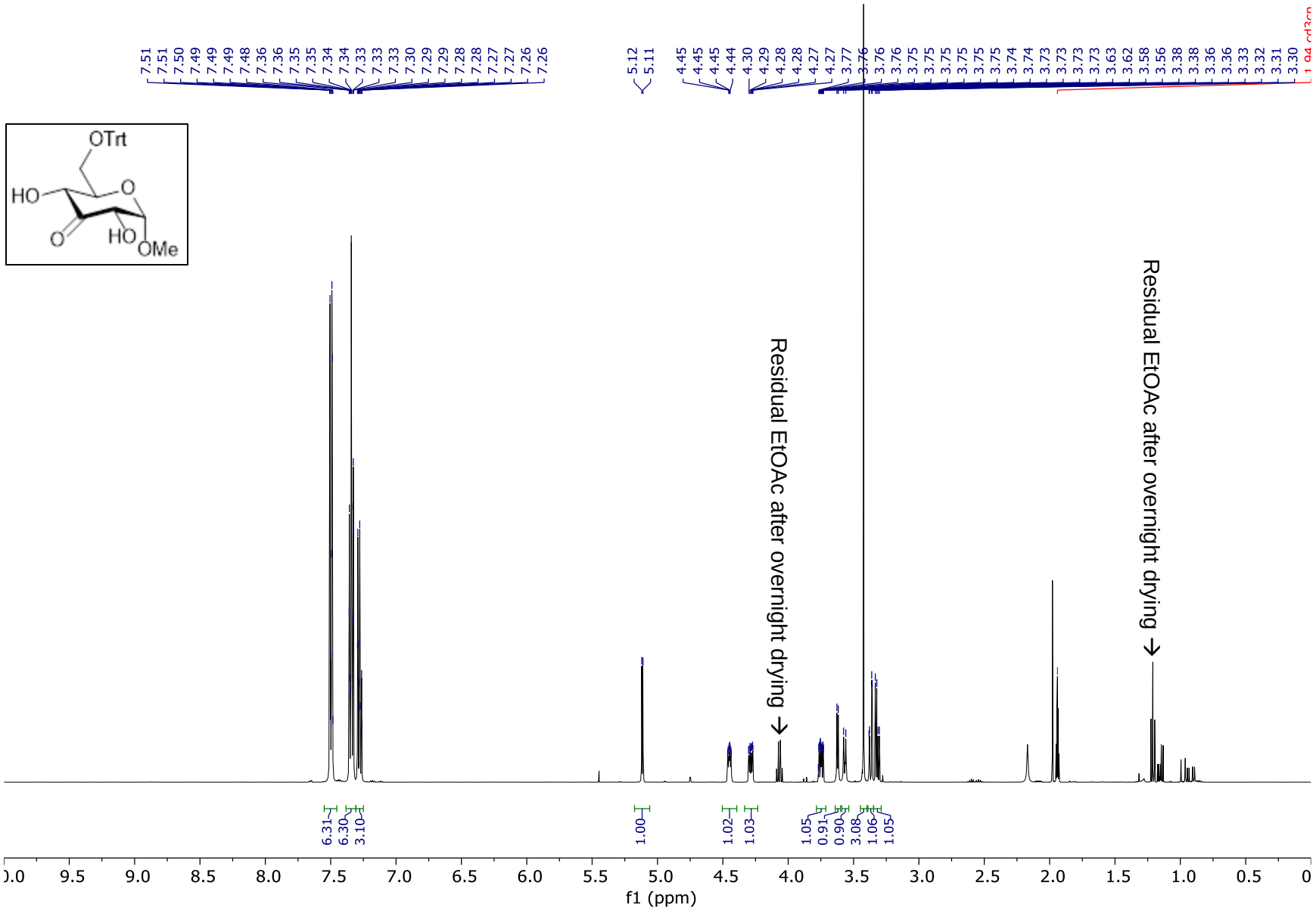
2a – COSY (500 MHz, CD_3CN)



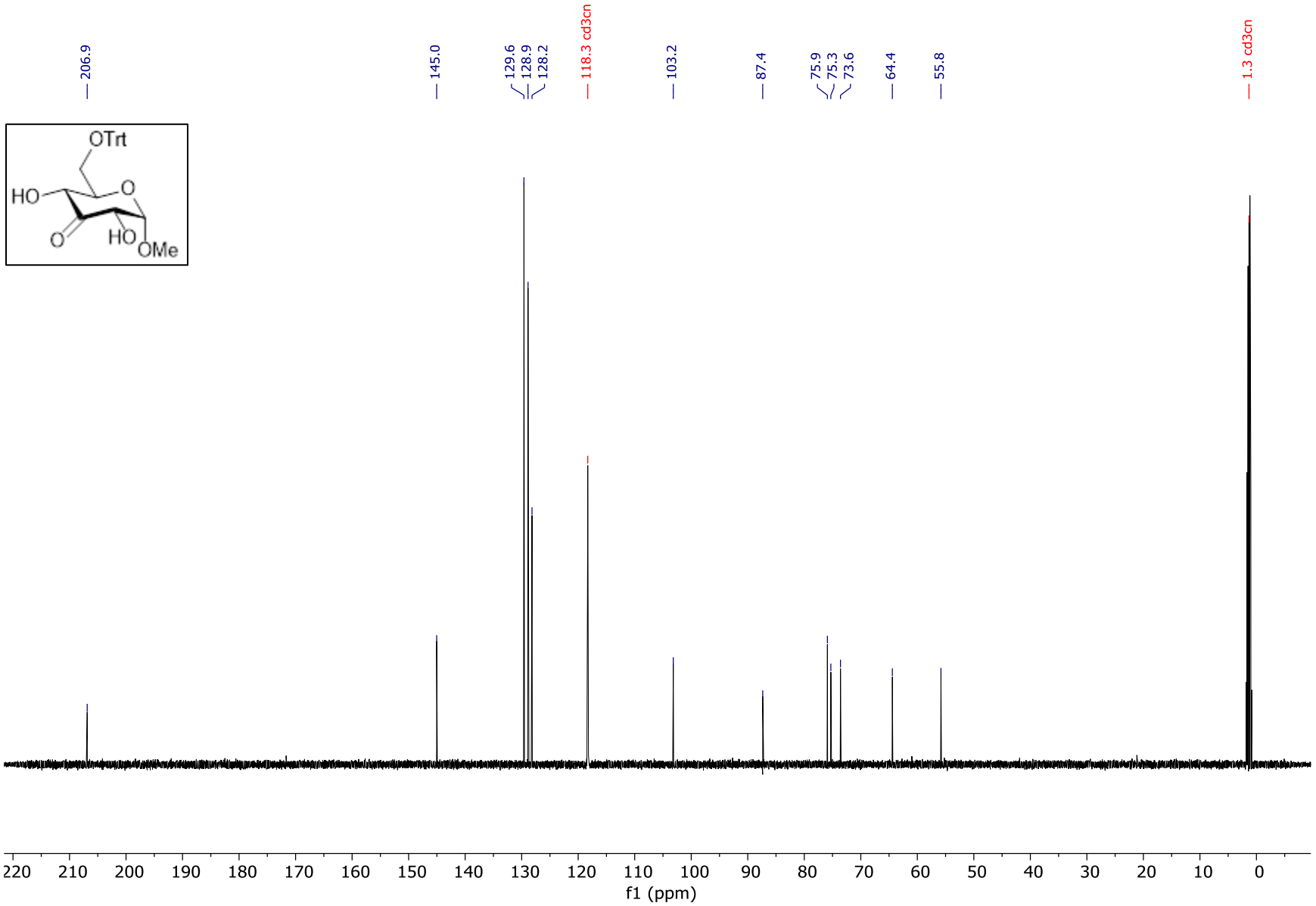
2a – HSQC (500 MHz, CD_3CN)



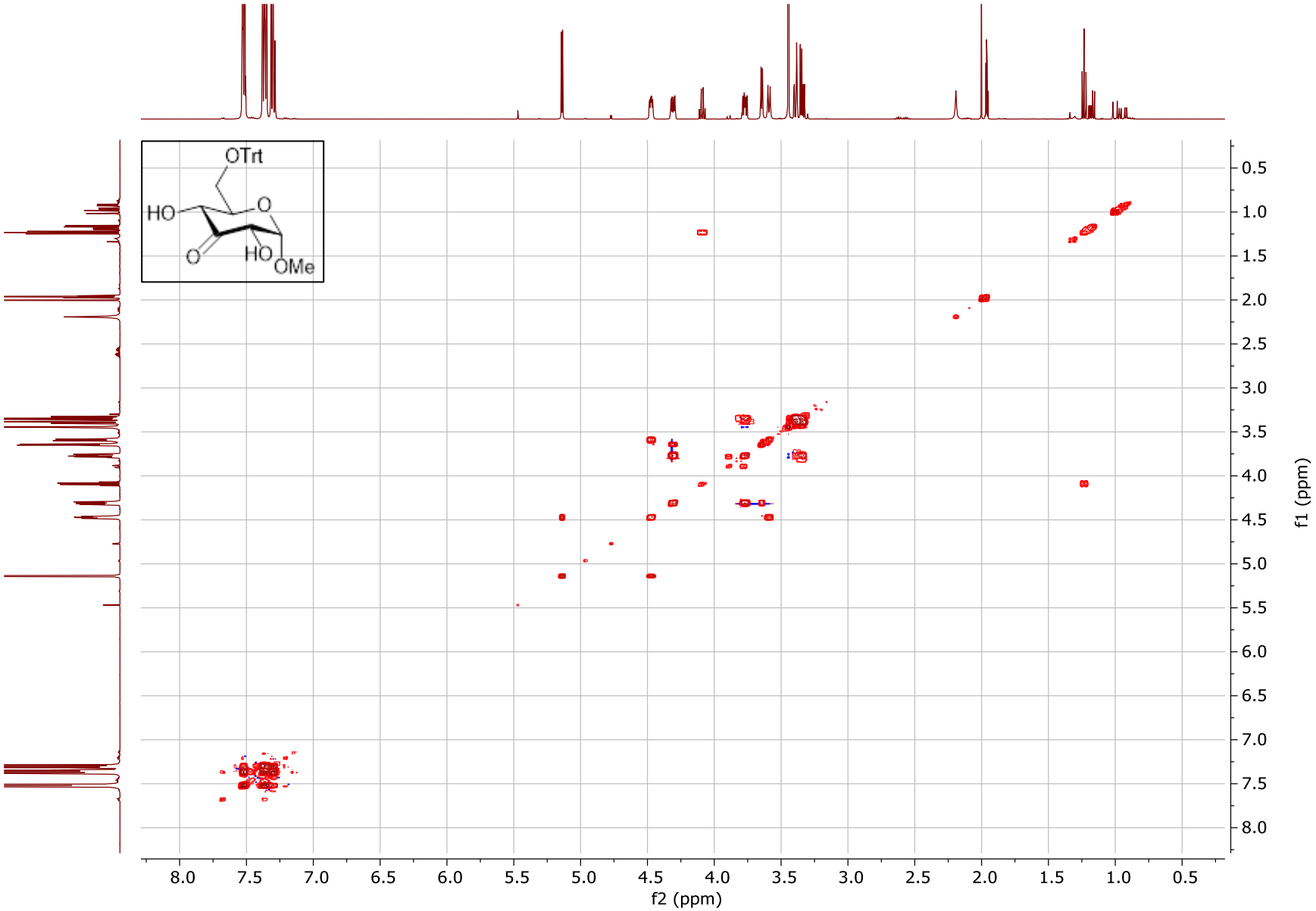
2b – ^{1}H NMR (500 MHz, CD_3CN)



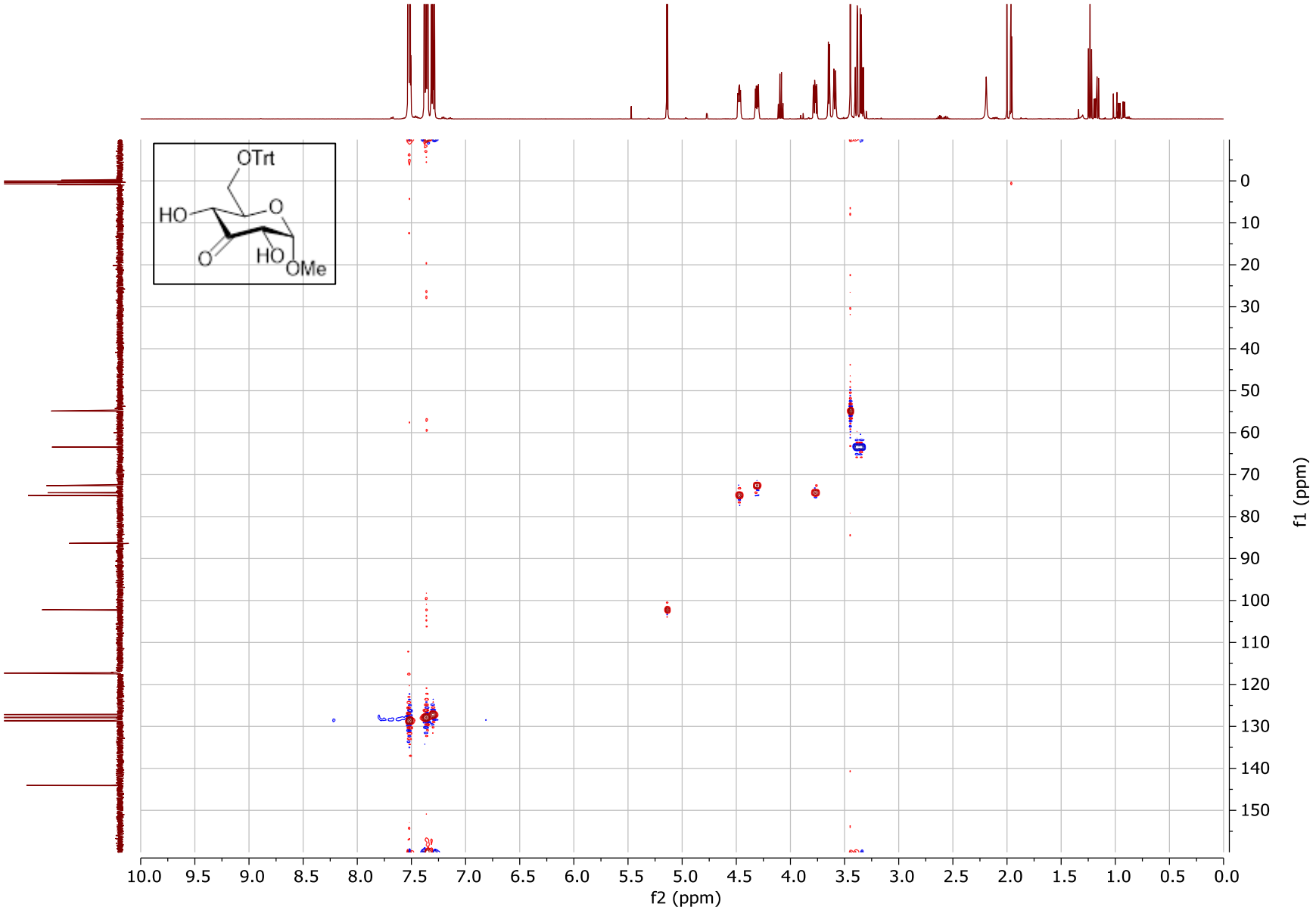
2b – ^{13}C NMR (126 MHz, CD_3CN)



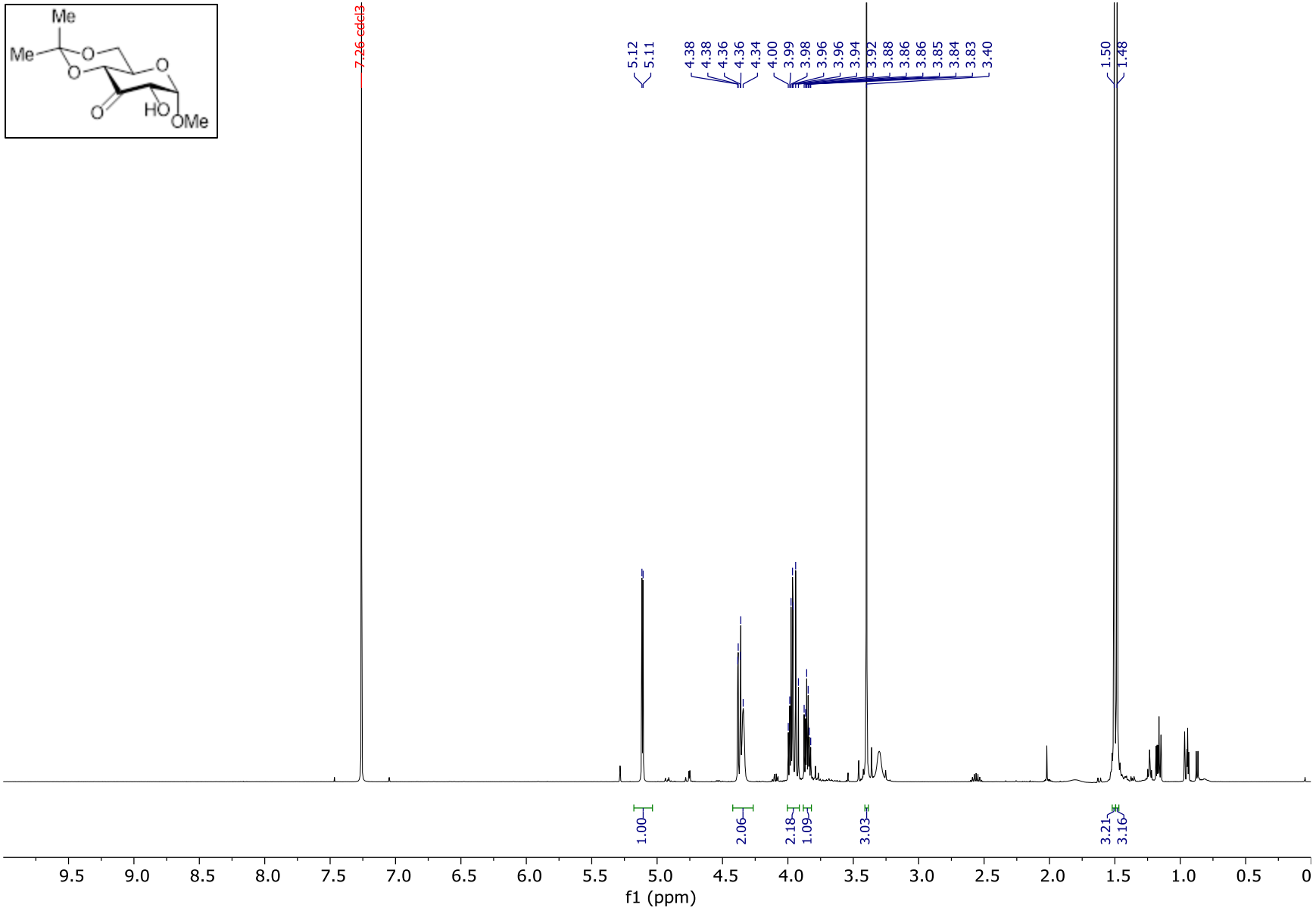
2b – COSY (500 MHz, CD_3CN)



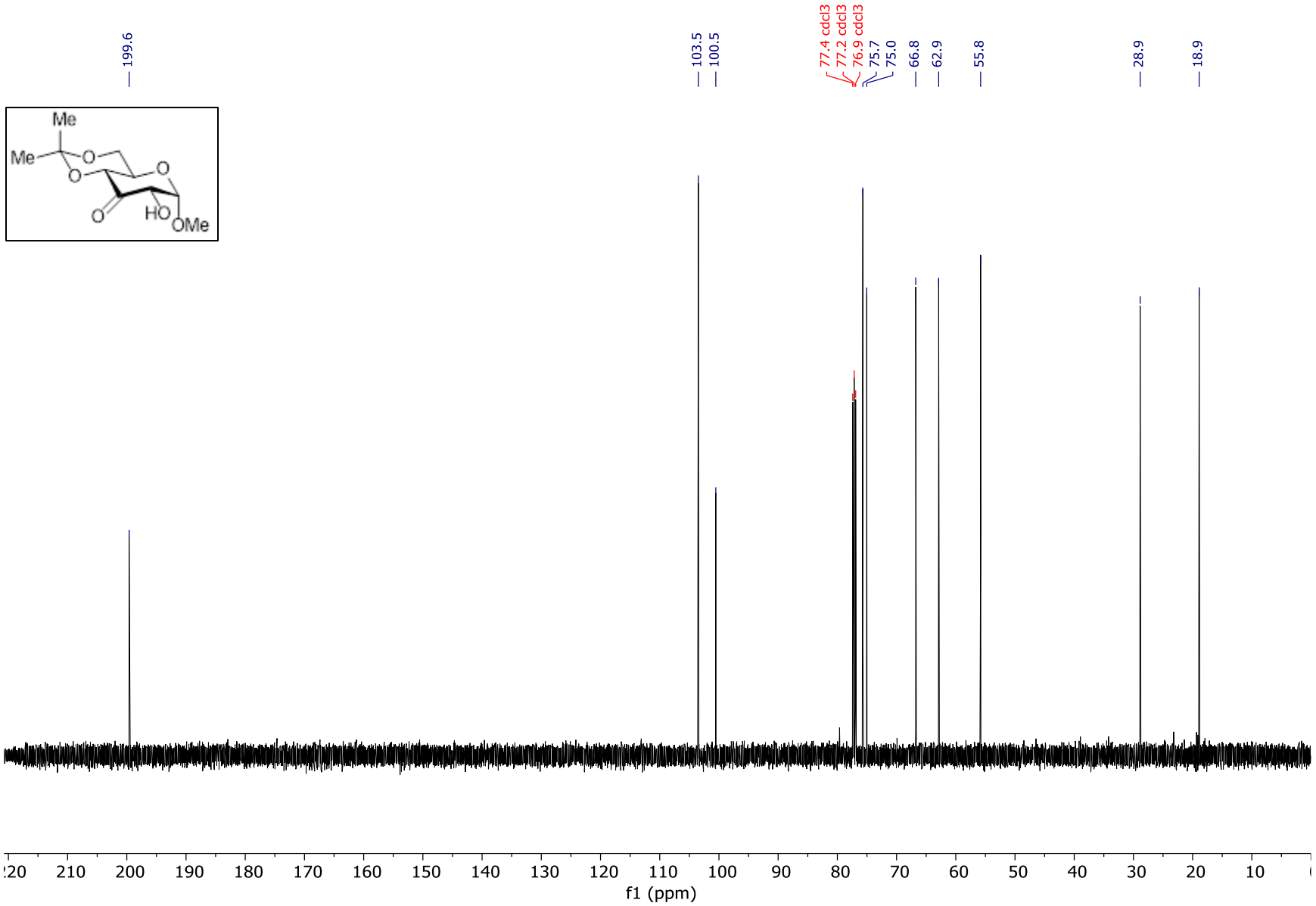
2b – HSQC (500 MHz, CD_3CN)



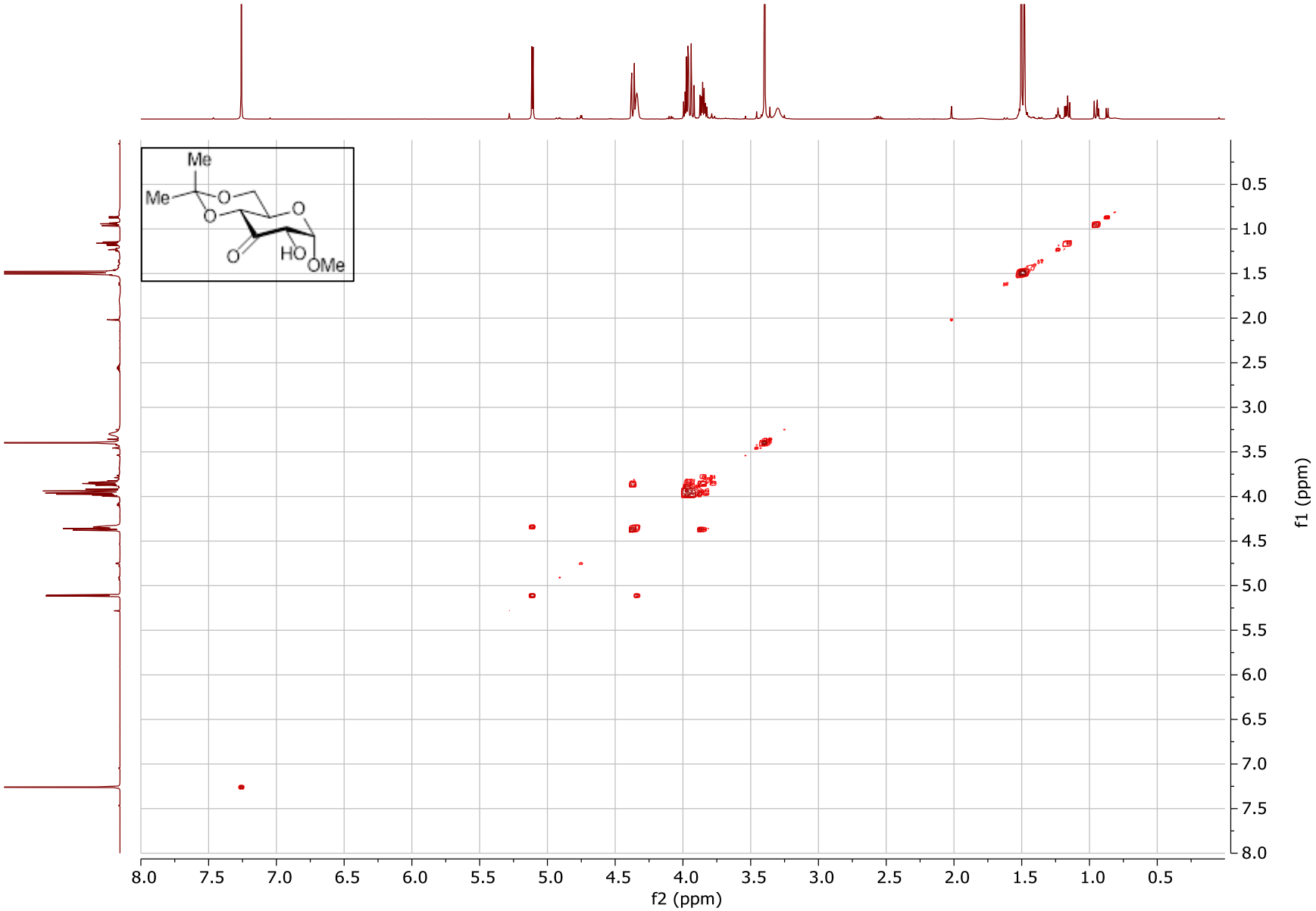
2c – ^{1}H NMR (500 MHz, $CDCl_3$)



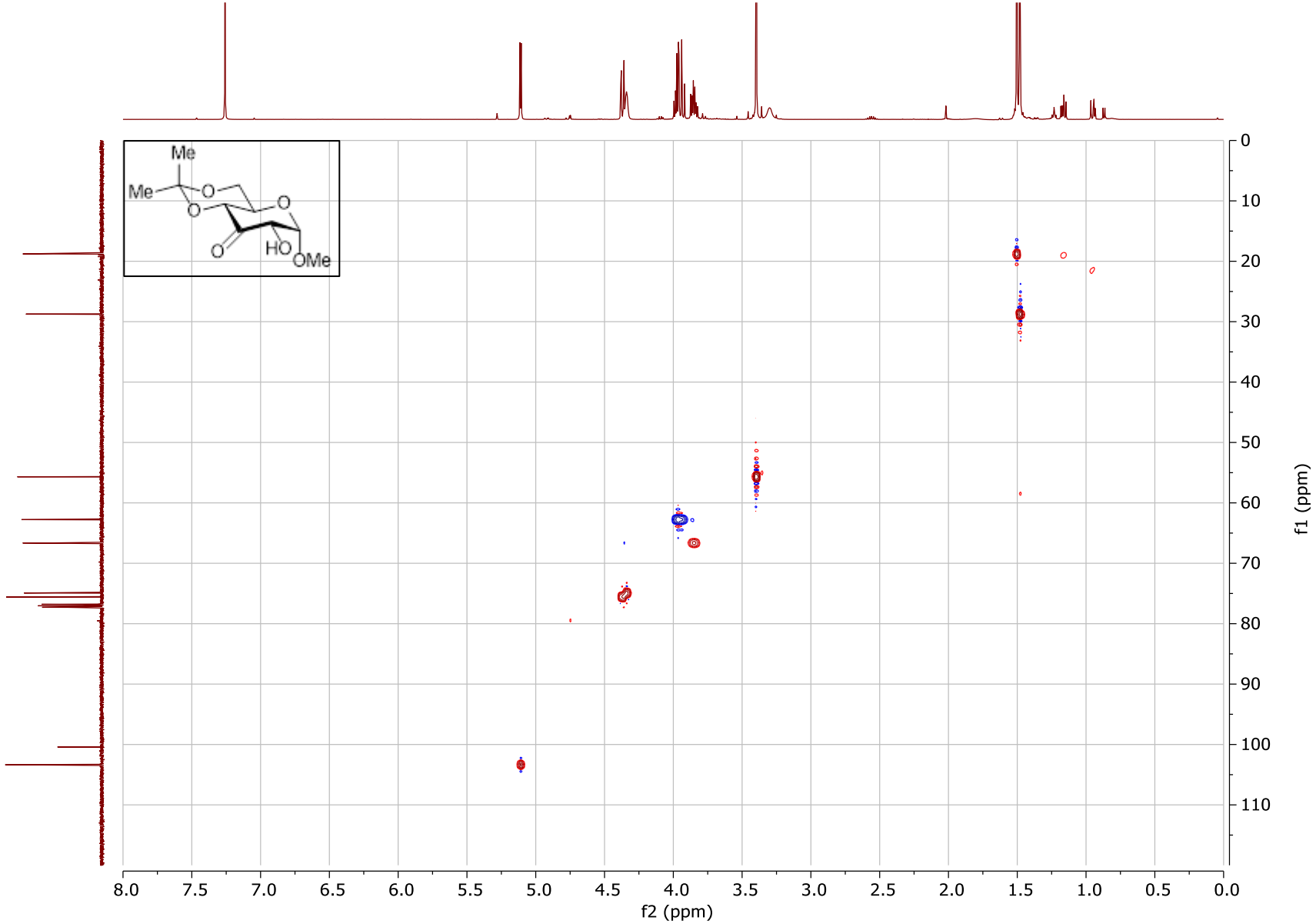
2c – ^{13}C NMR (126 MHz, $CDCl_3$)



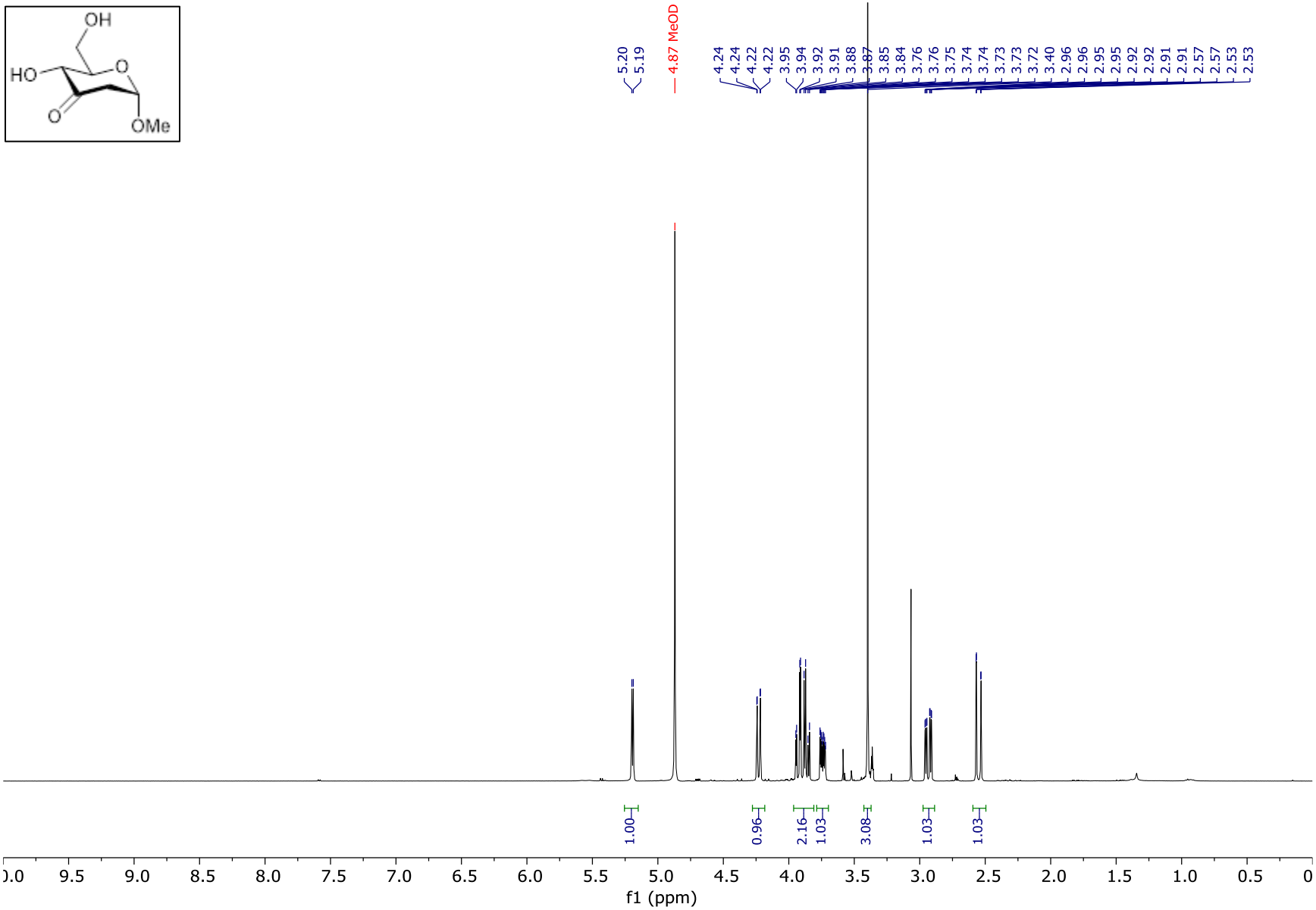
2c – COSY (500 MHz, $CDCl_3$)



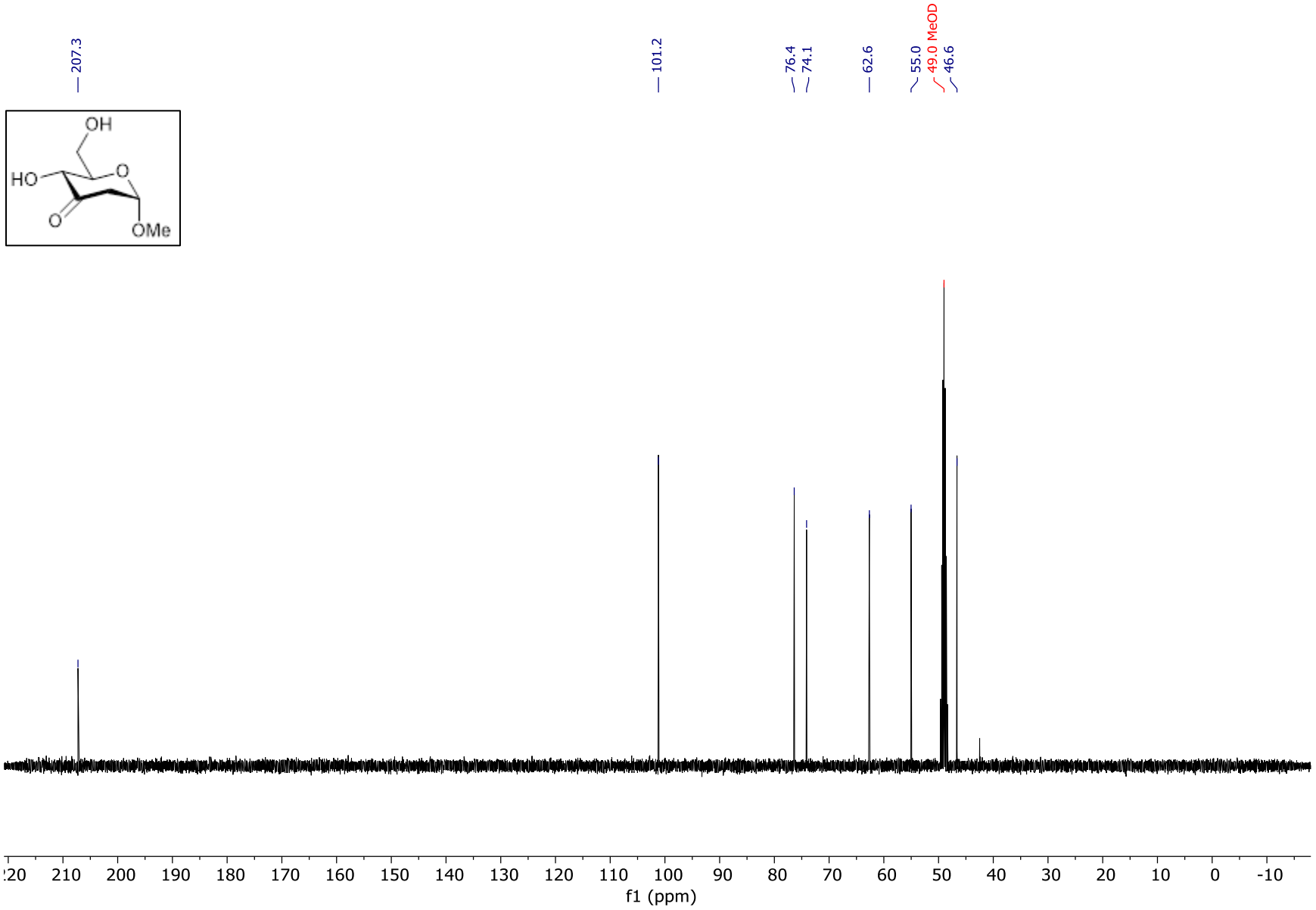
2c - HSQC (500 MHz, $CDCl_3$)



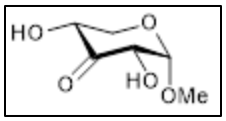
2d – ^{1}H NMR (500 MHz, CD_3OD)



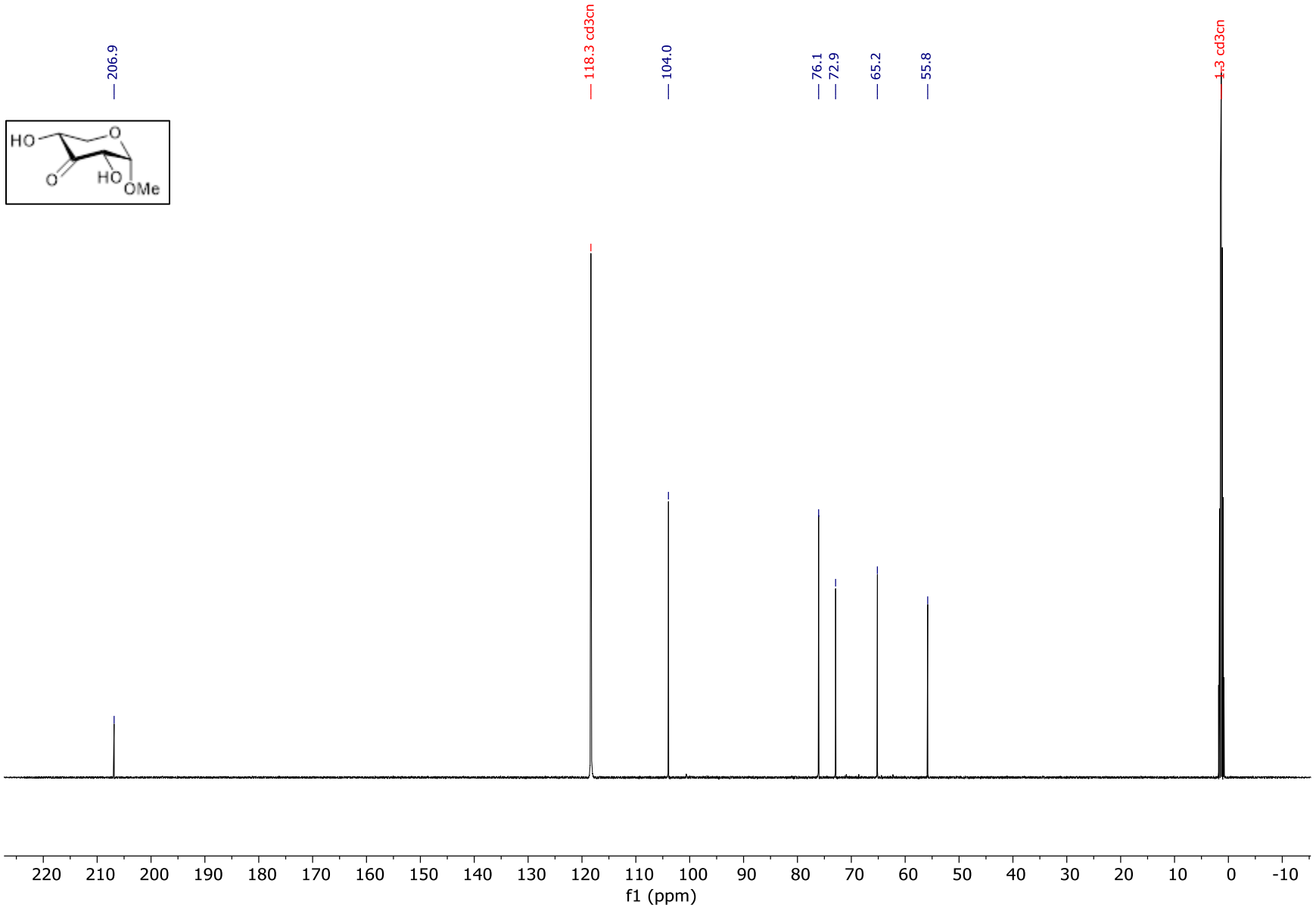
2d – ^{13}C NMR (126 MHz, CD_3OD)



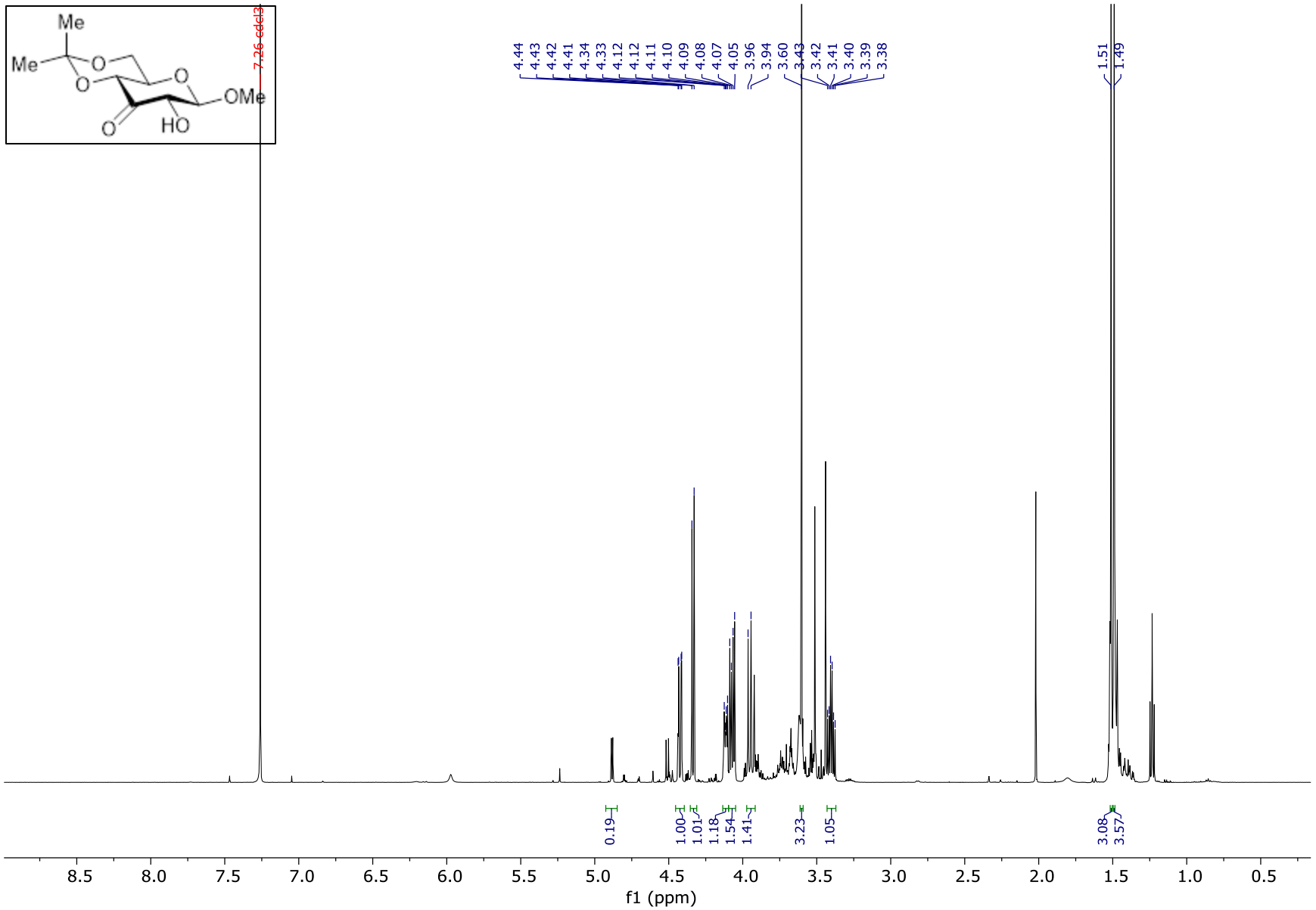
2e – ^{1}H NMR (500 MHz, CD_3CN)



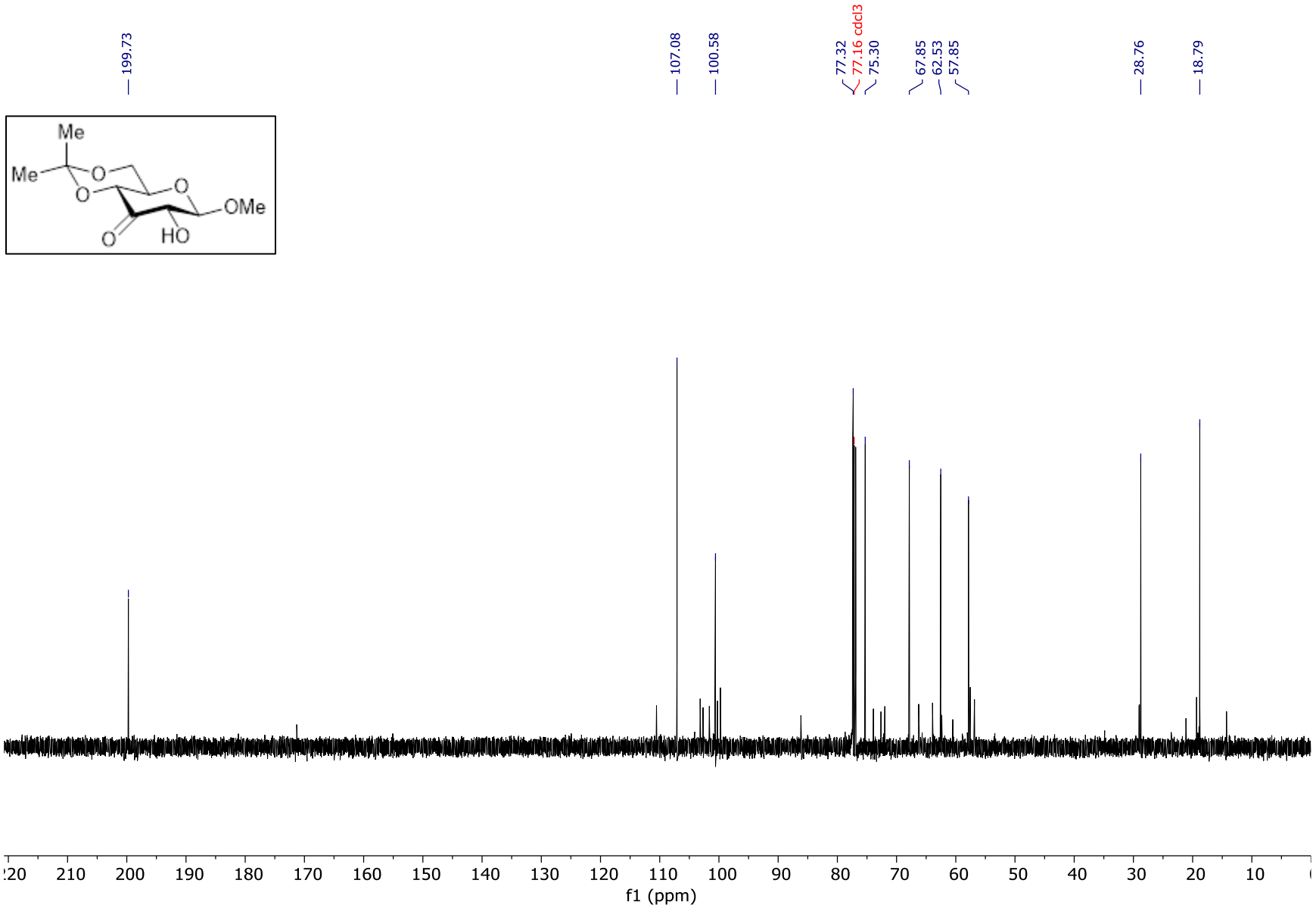
2e – ^{13}C NMR (126 MHz, CD_3CN)



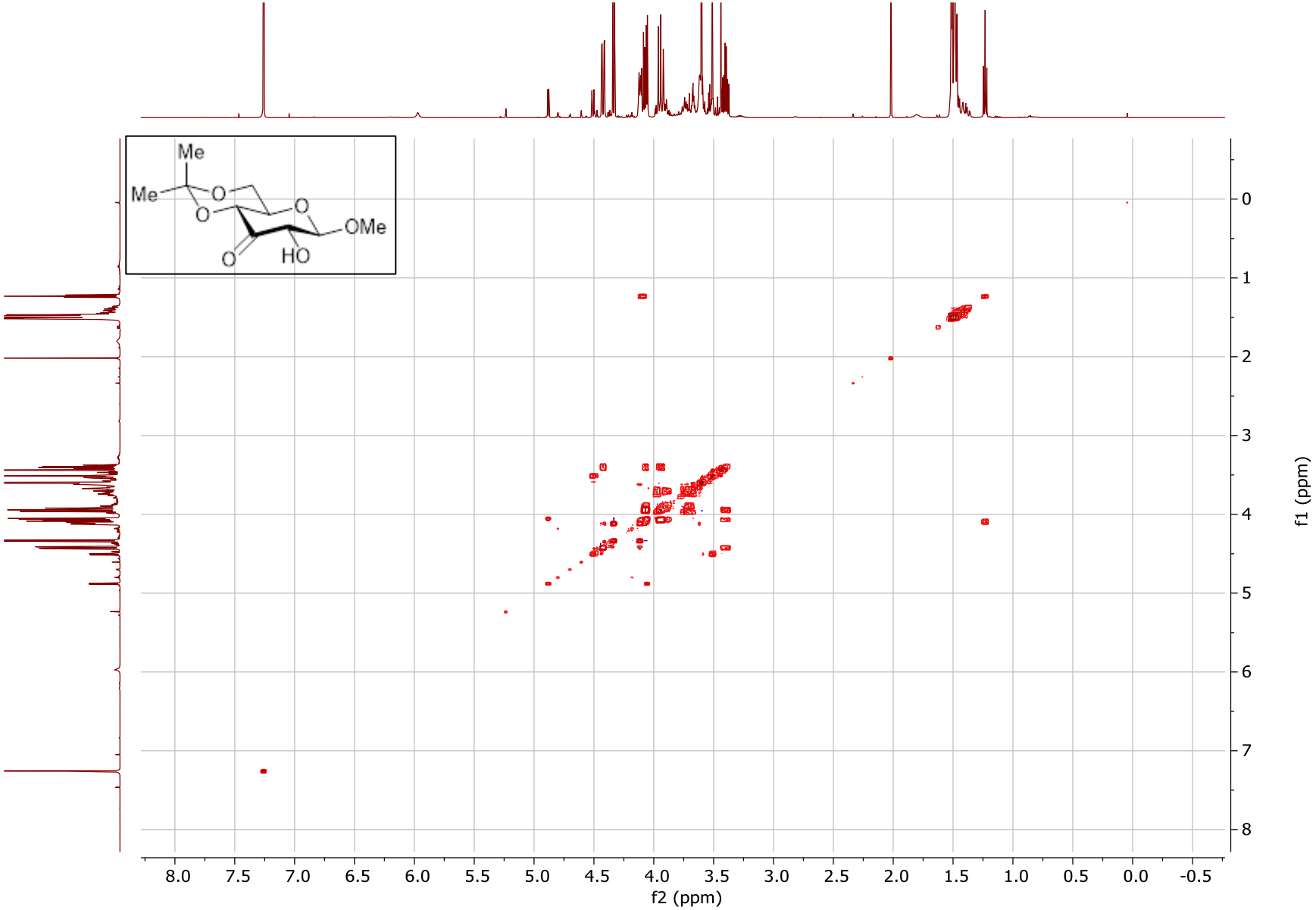
2f – ^{1}H NMR (500 MHz, $CDCl_3$)



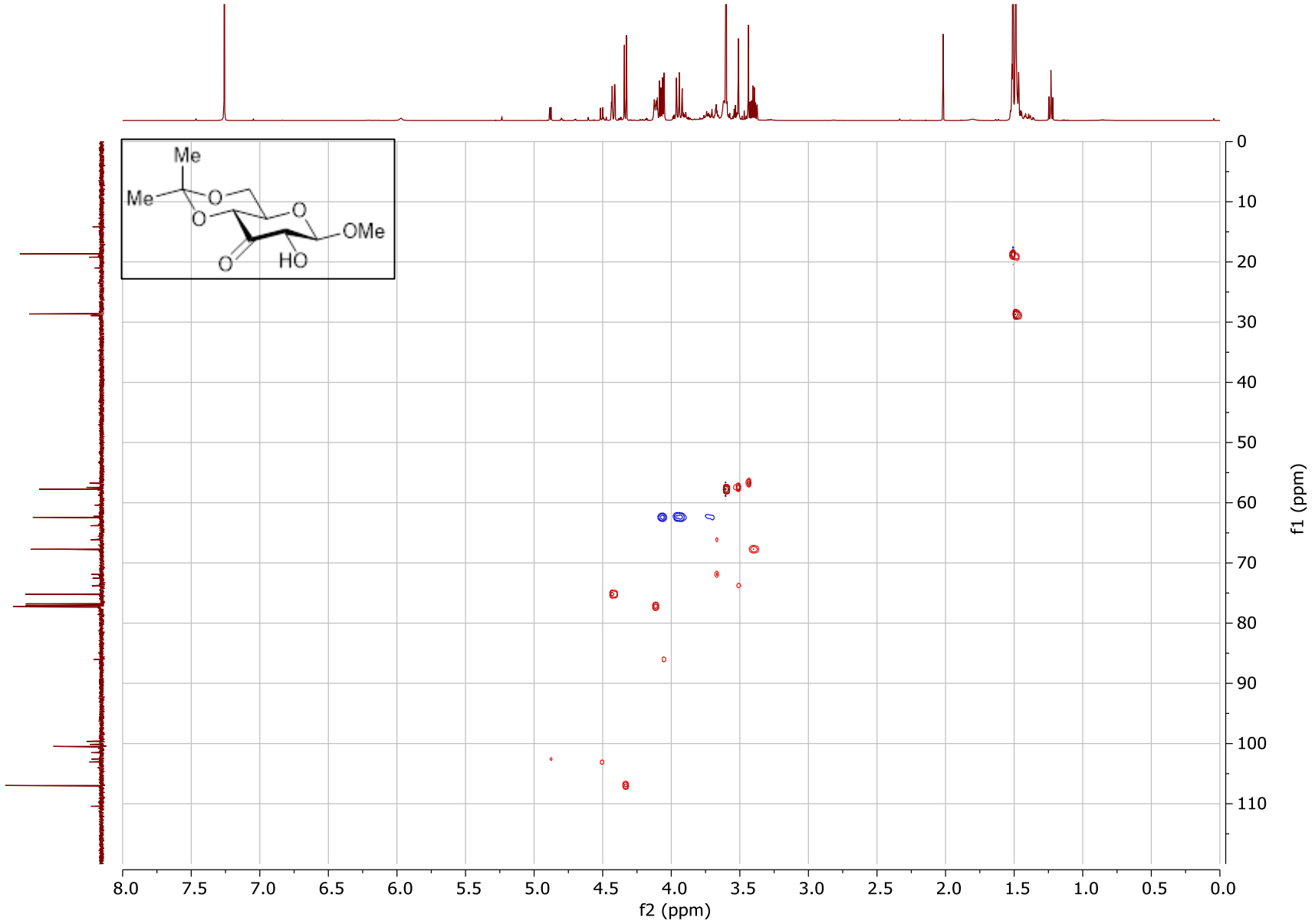
2f – ^{13}C NMR (126 MHz, $CDCl_3$)



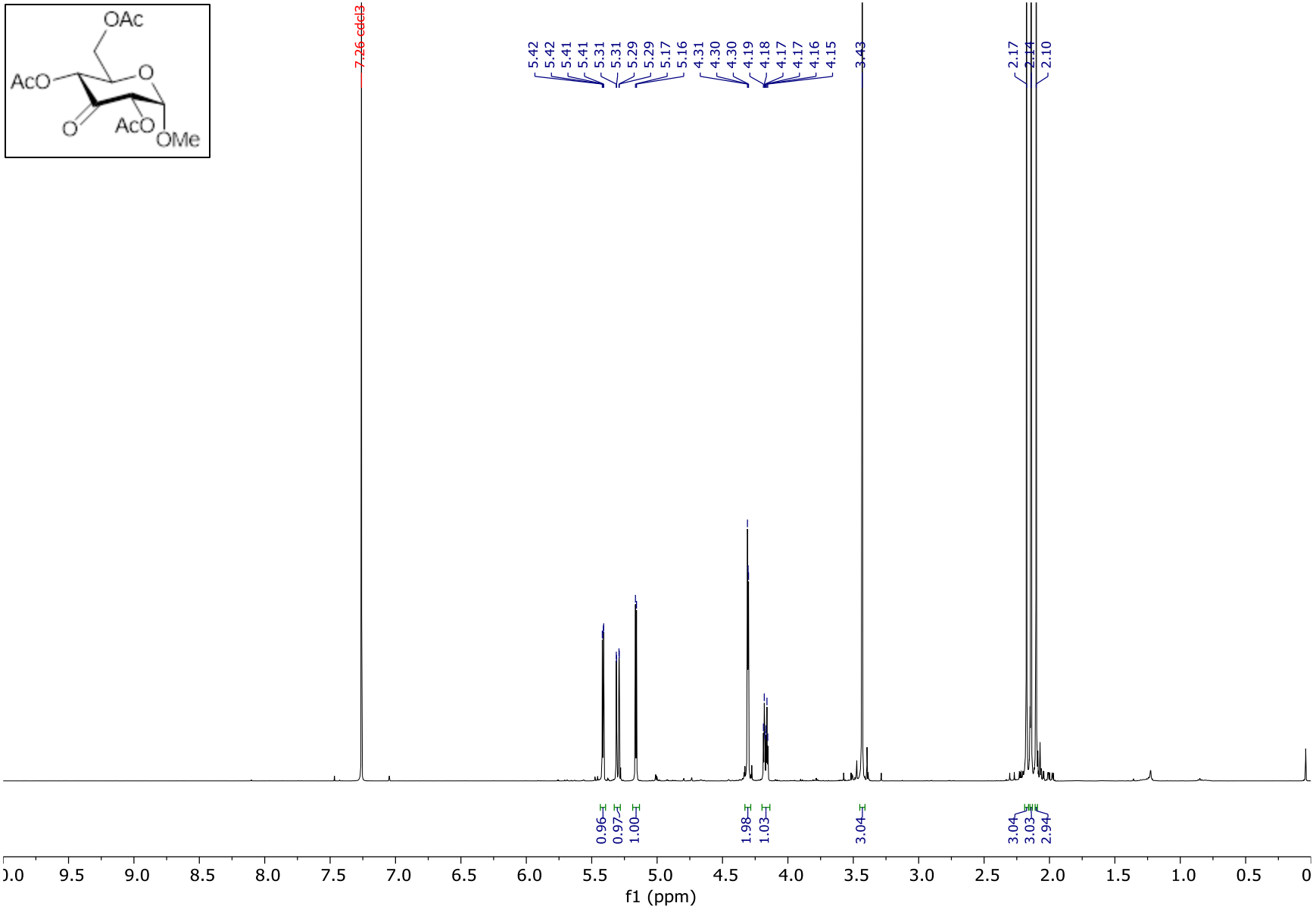
2f - COSY (500 MHz, $CDCl_3$)



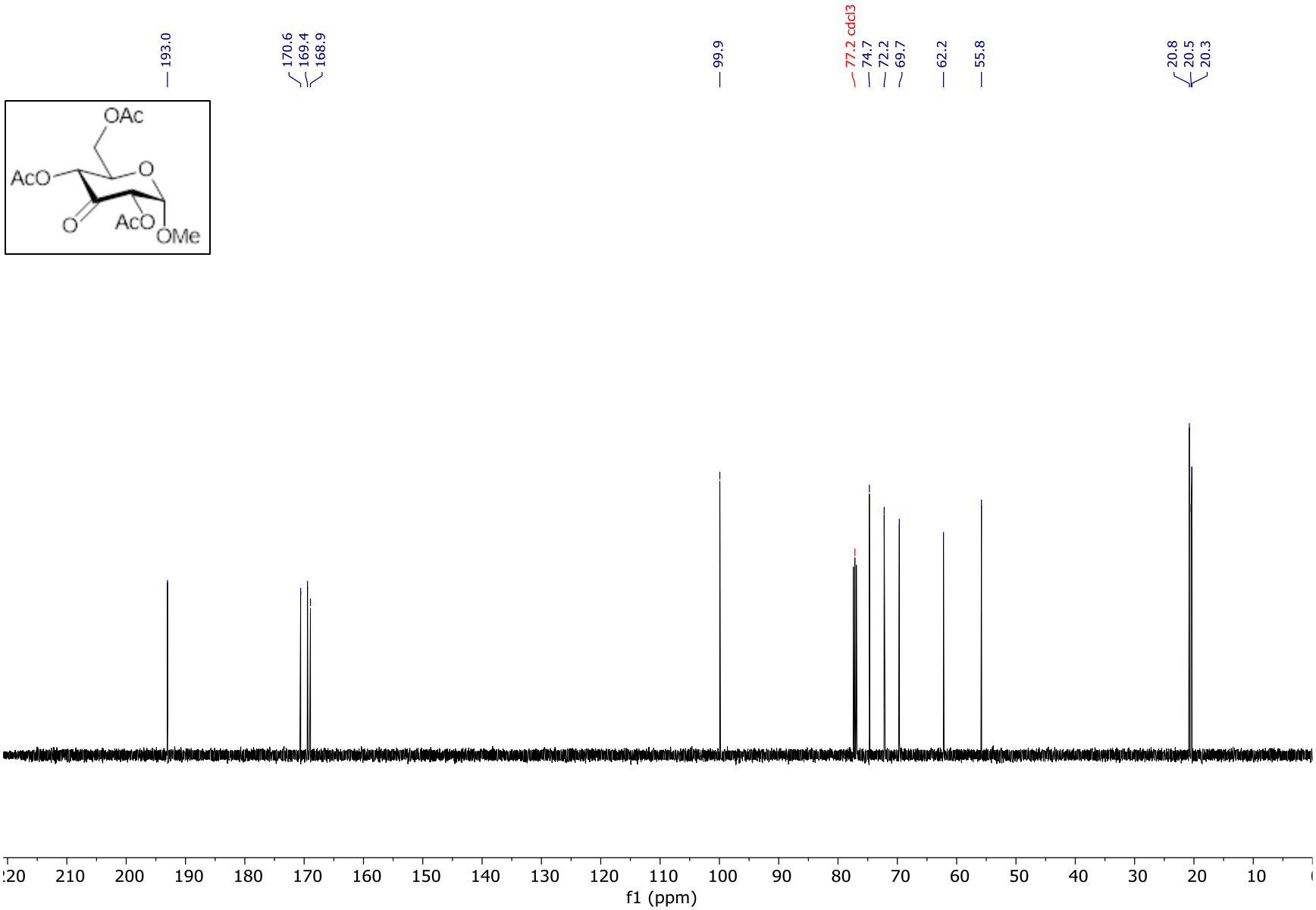
2f - HSQC (500 MHz, $CDCl_3$)



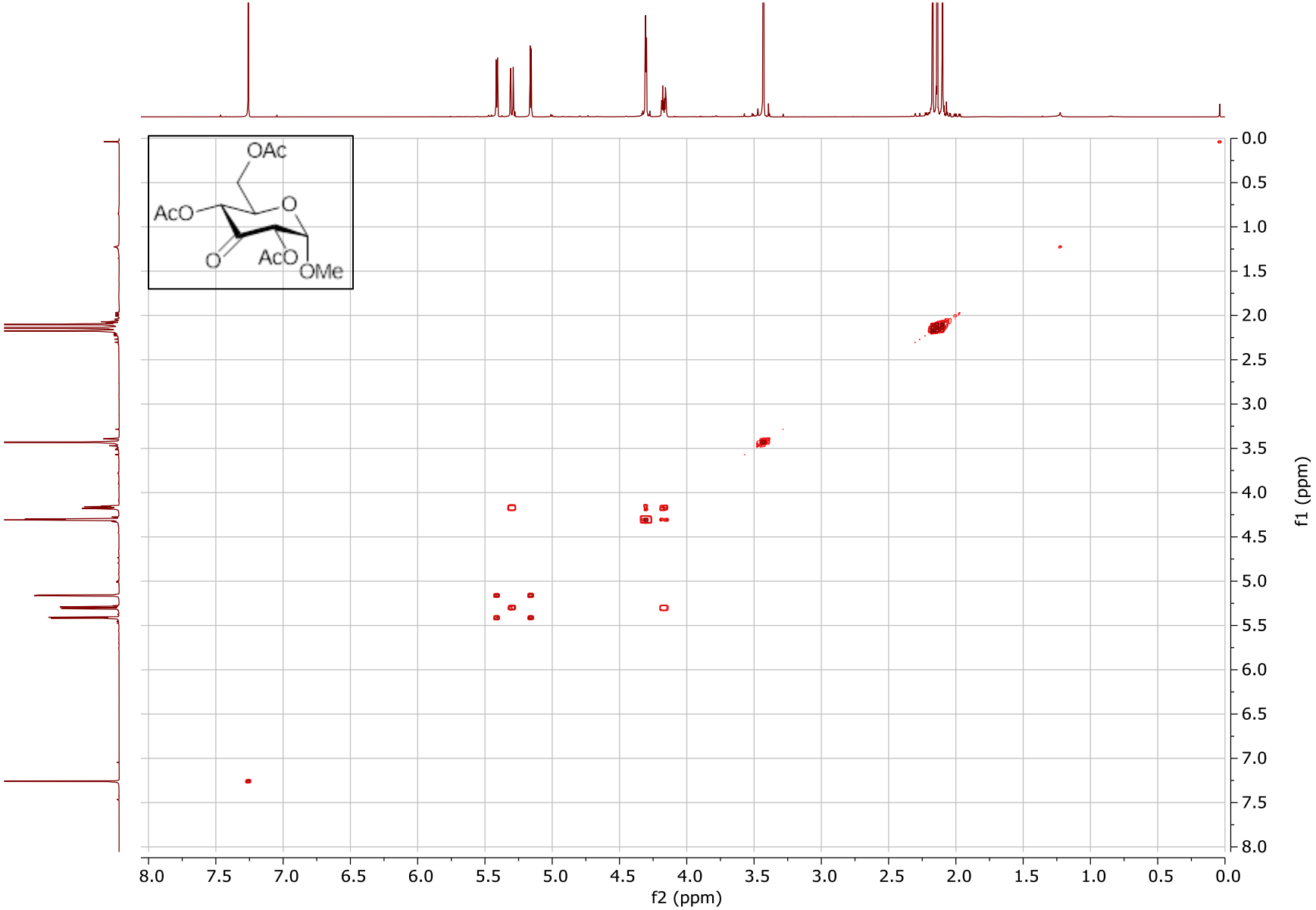
2g – ^{1}H NMR (500 MHz, $CDCl_3$)



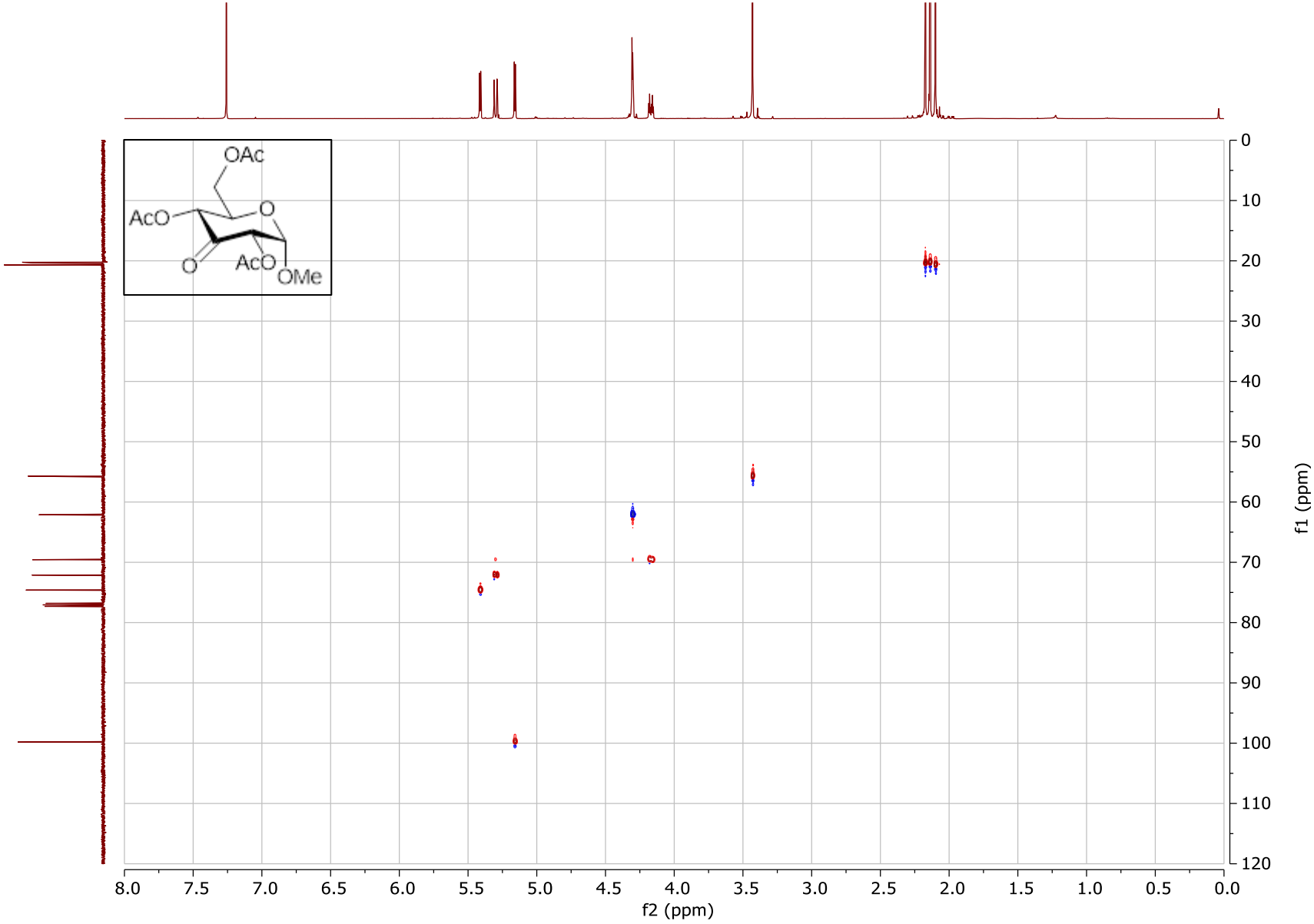
2g – ^{13}C NMR (126 MHz, $CDCl_3$)



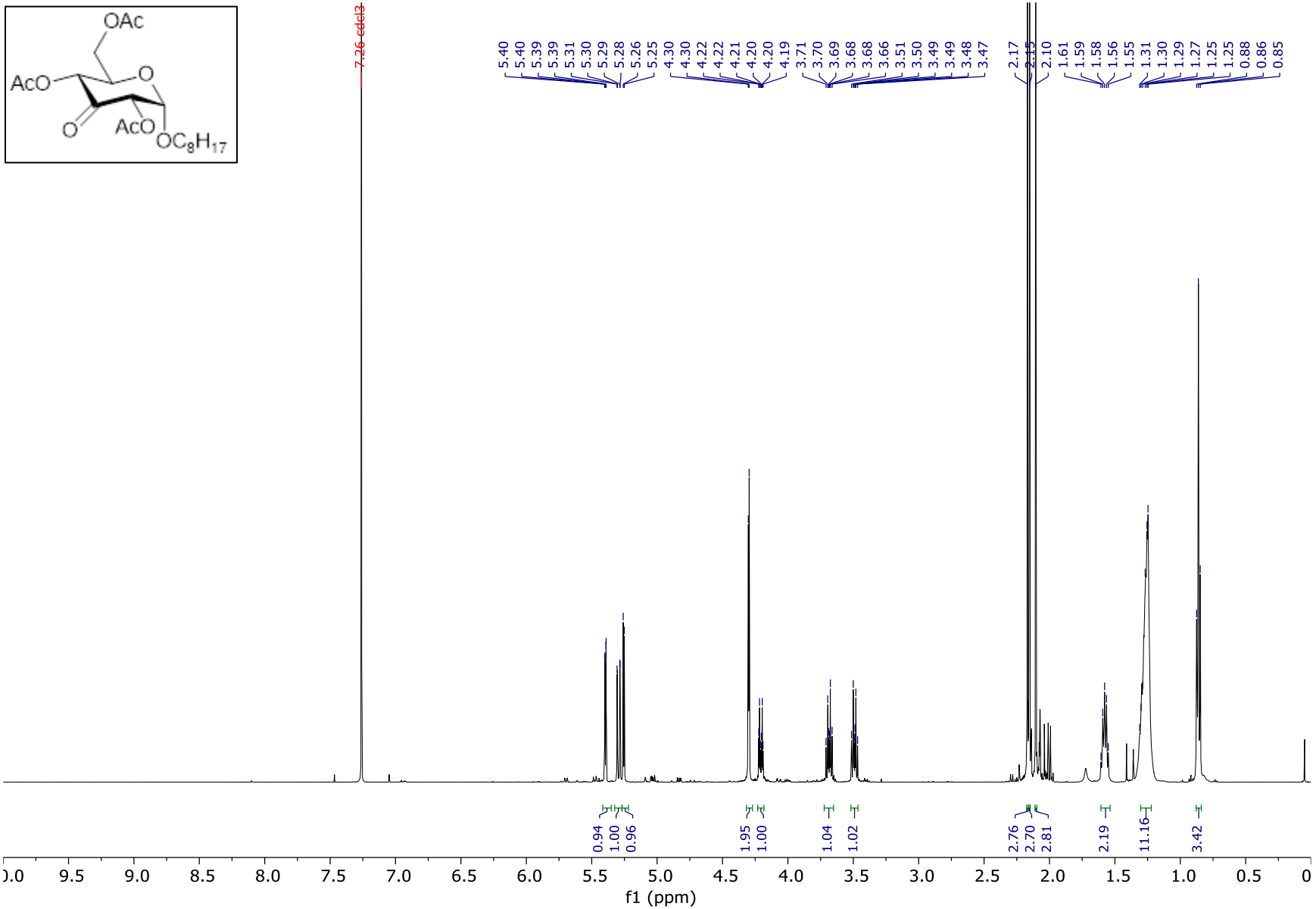
2g – COSY (500 MHz, $CDCl_3$)



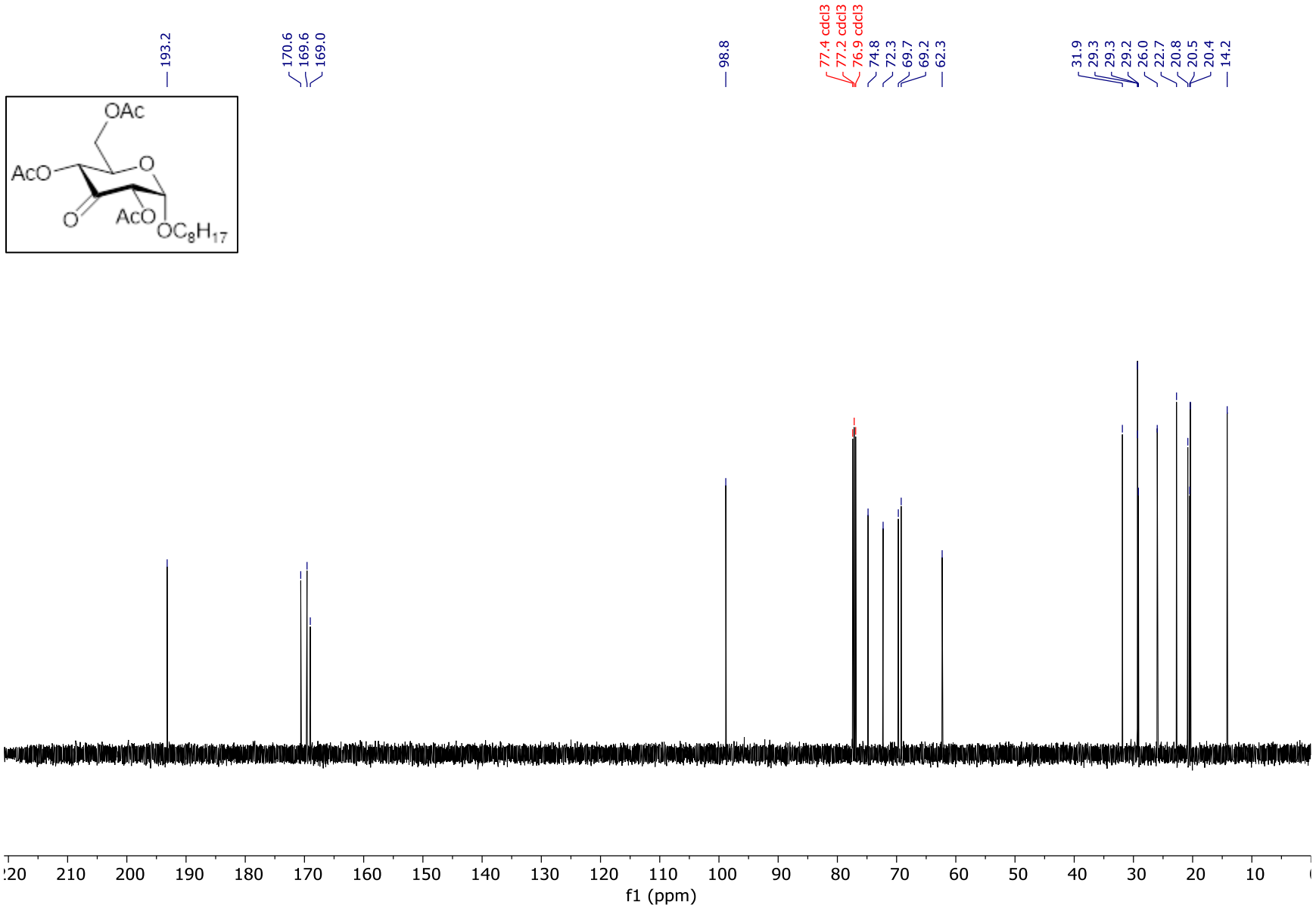
2g – HSQC (500 MHz, $CDCl_3$)



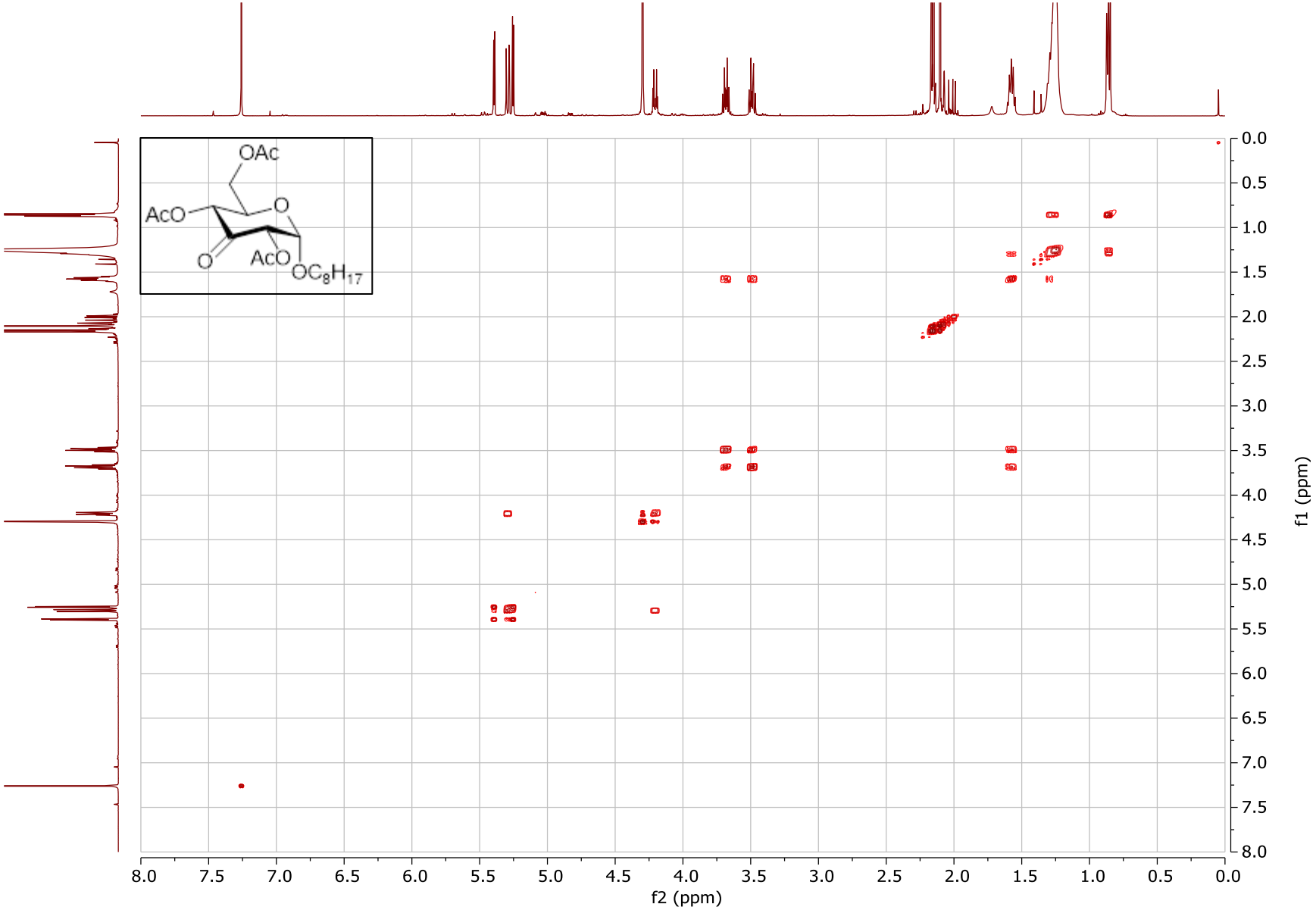
2h – ^{1}H NMR (500 MHz, $CDCl_3$)



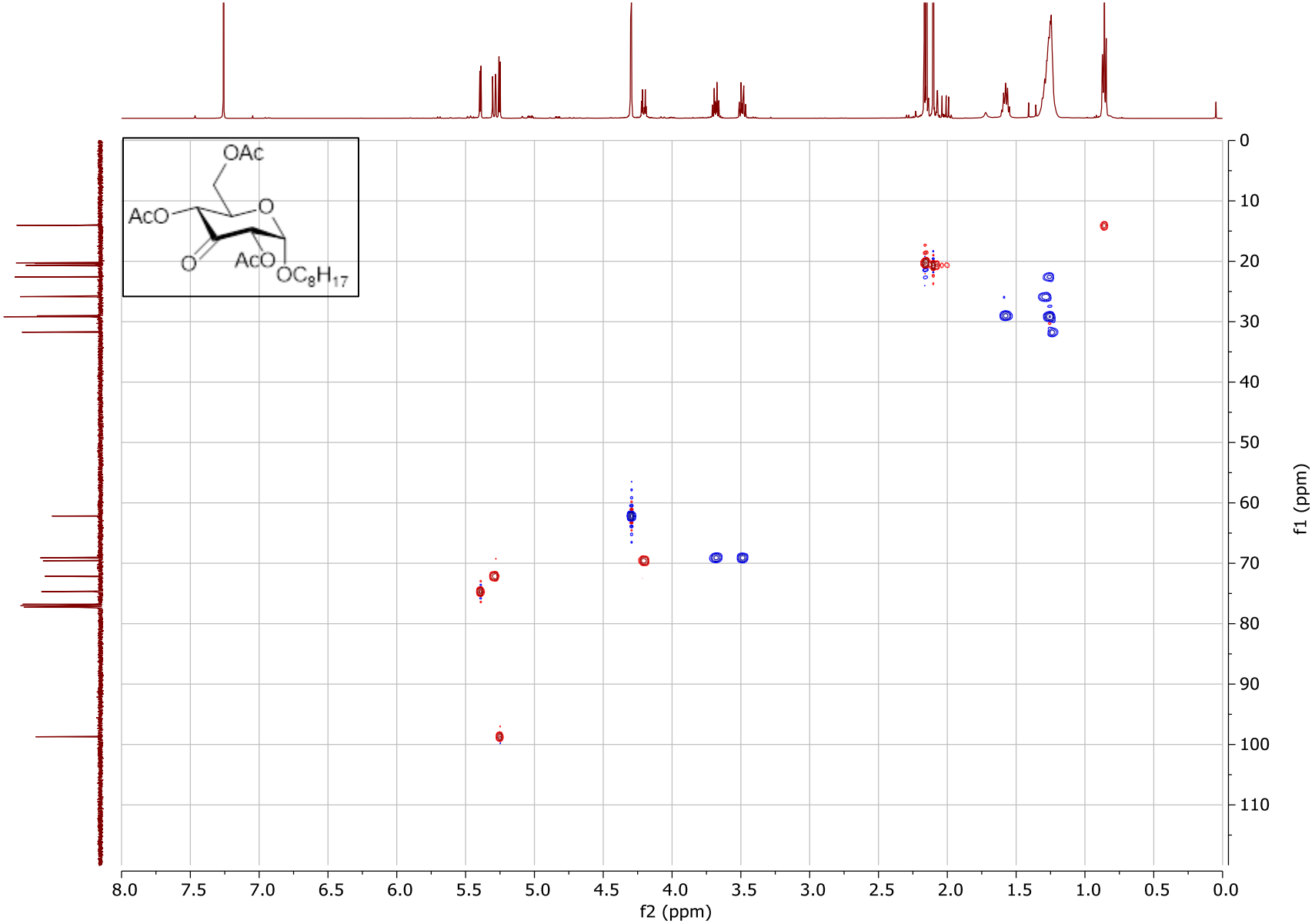
2h – ^{13}C NMR (126 MHz, $CDCl_3$)



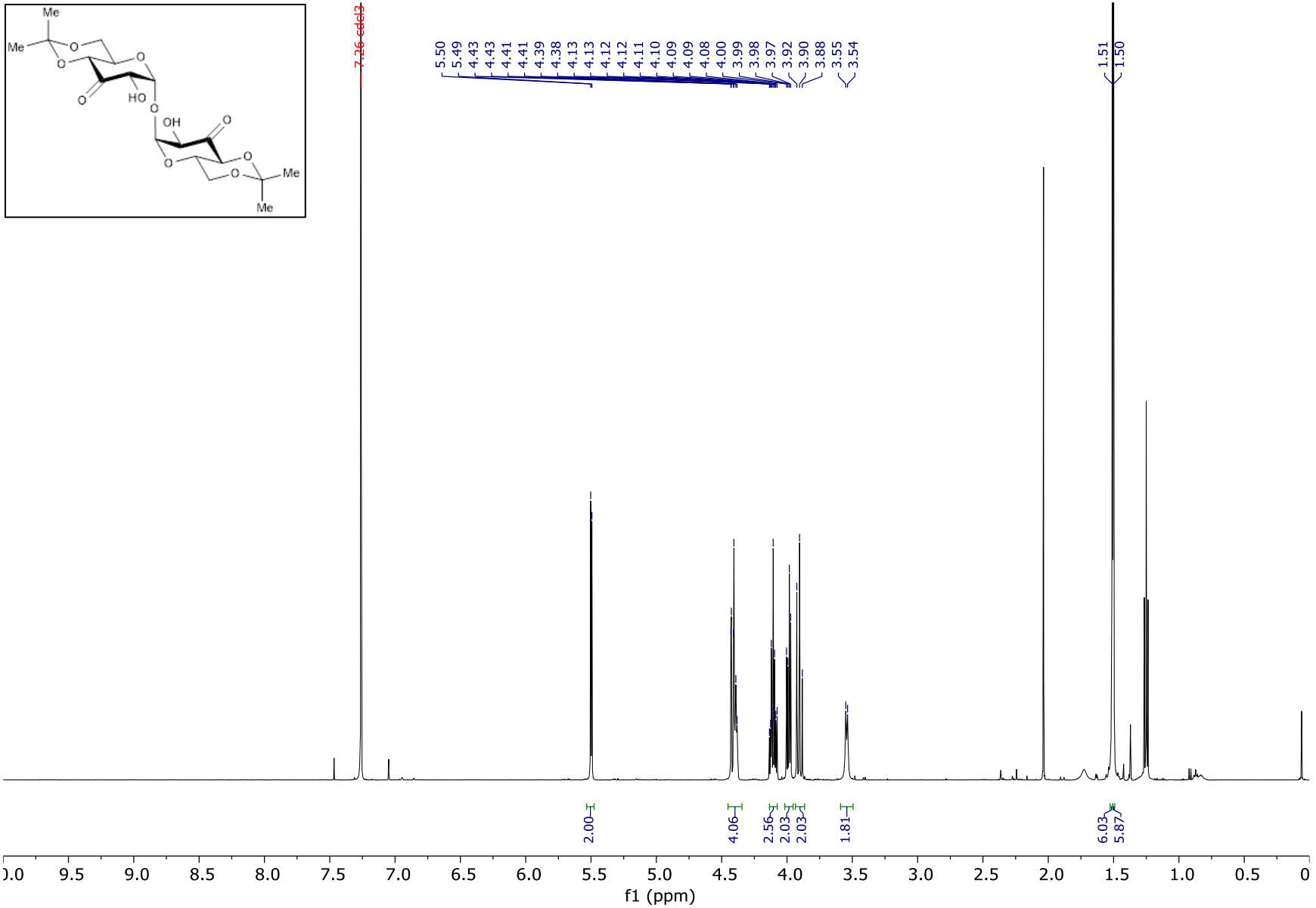
2h – COSY (500 MHz, $CDCl_3$)



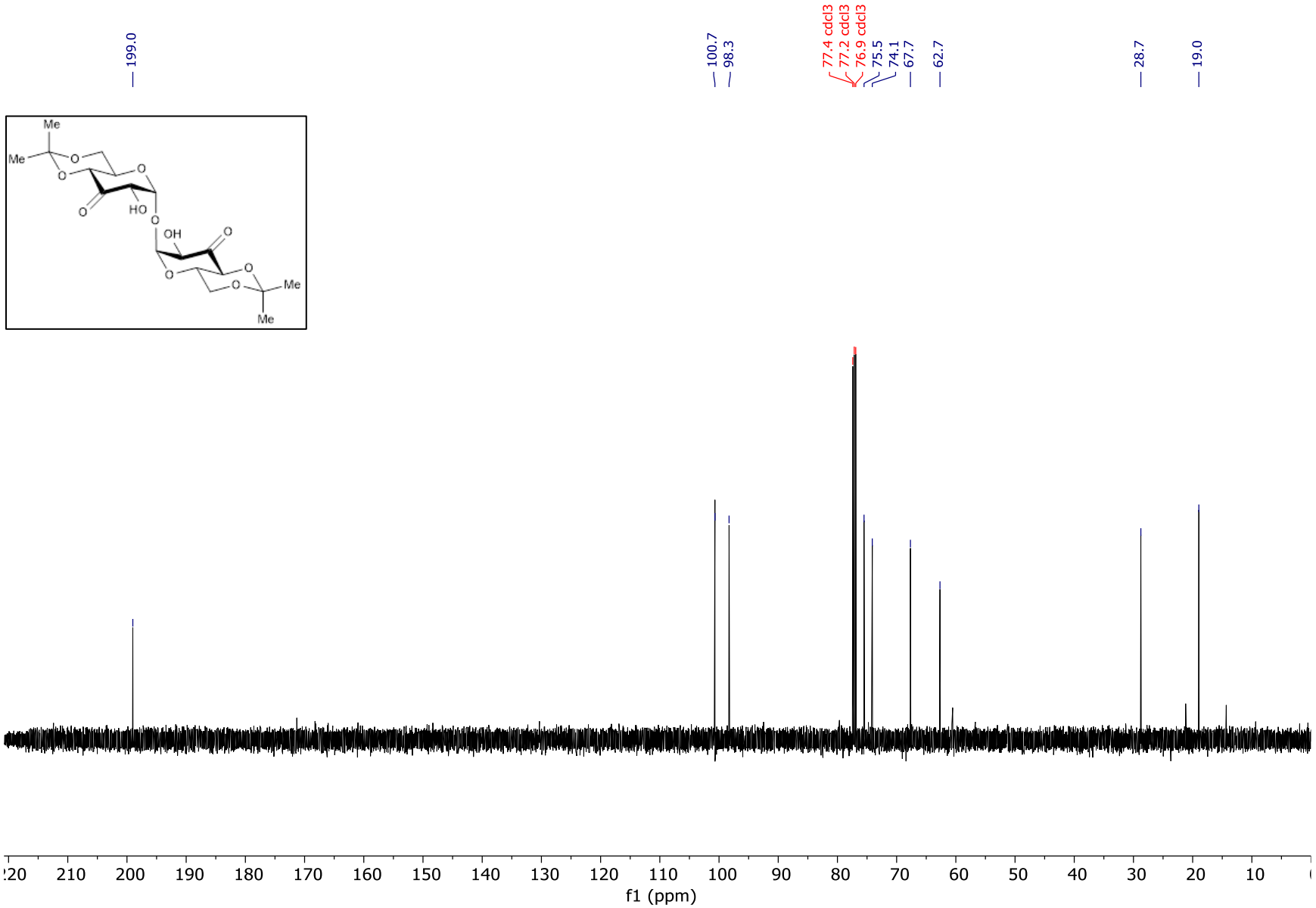
2h – HSQC (500 MHz, $CDCl_3$)



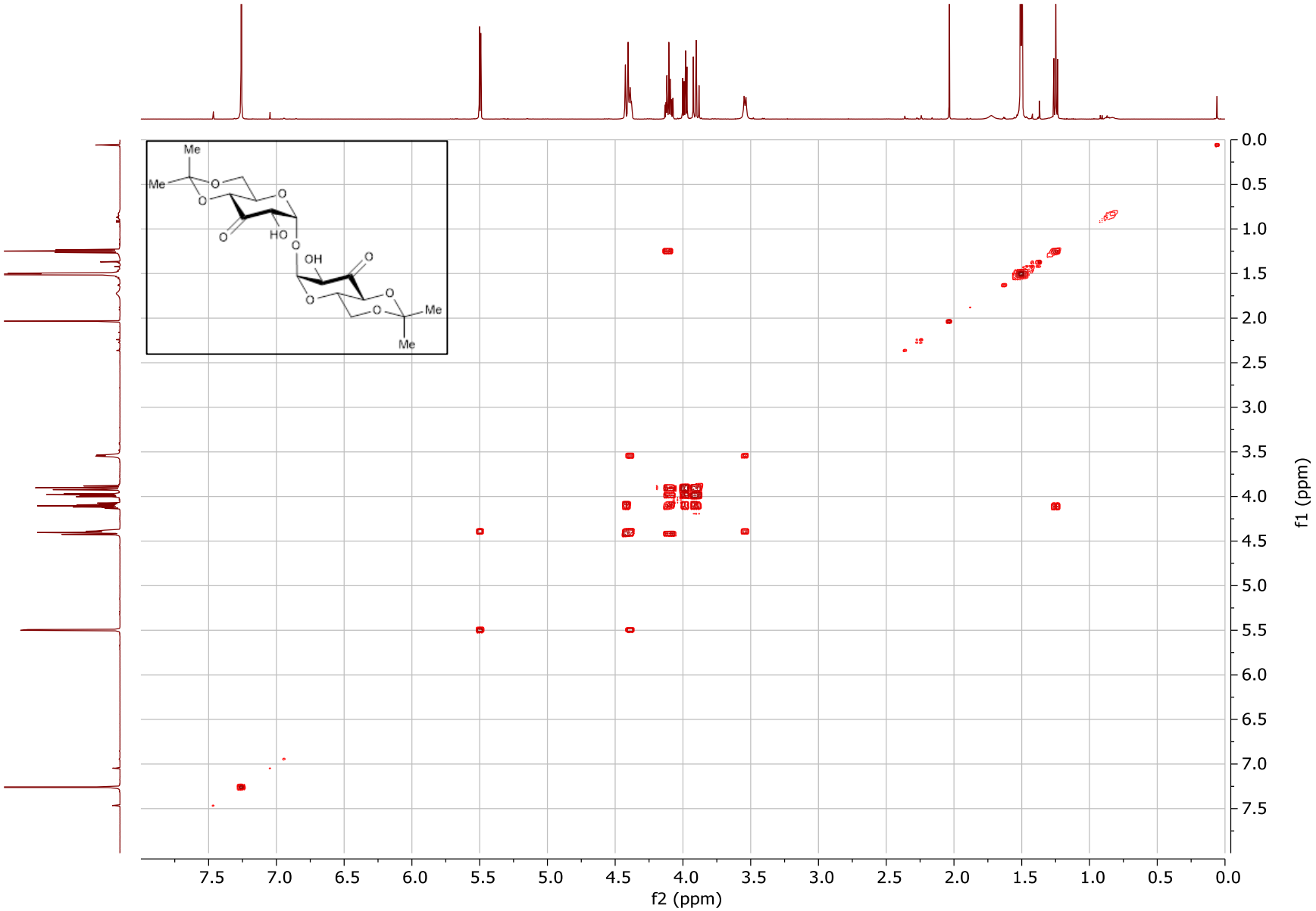
2i – ^{1}H NMR (500 MHz, $CDCl_3$)



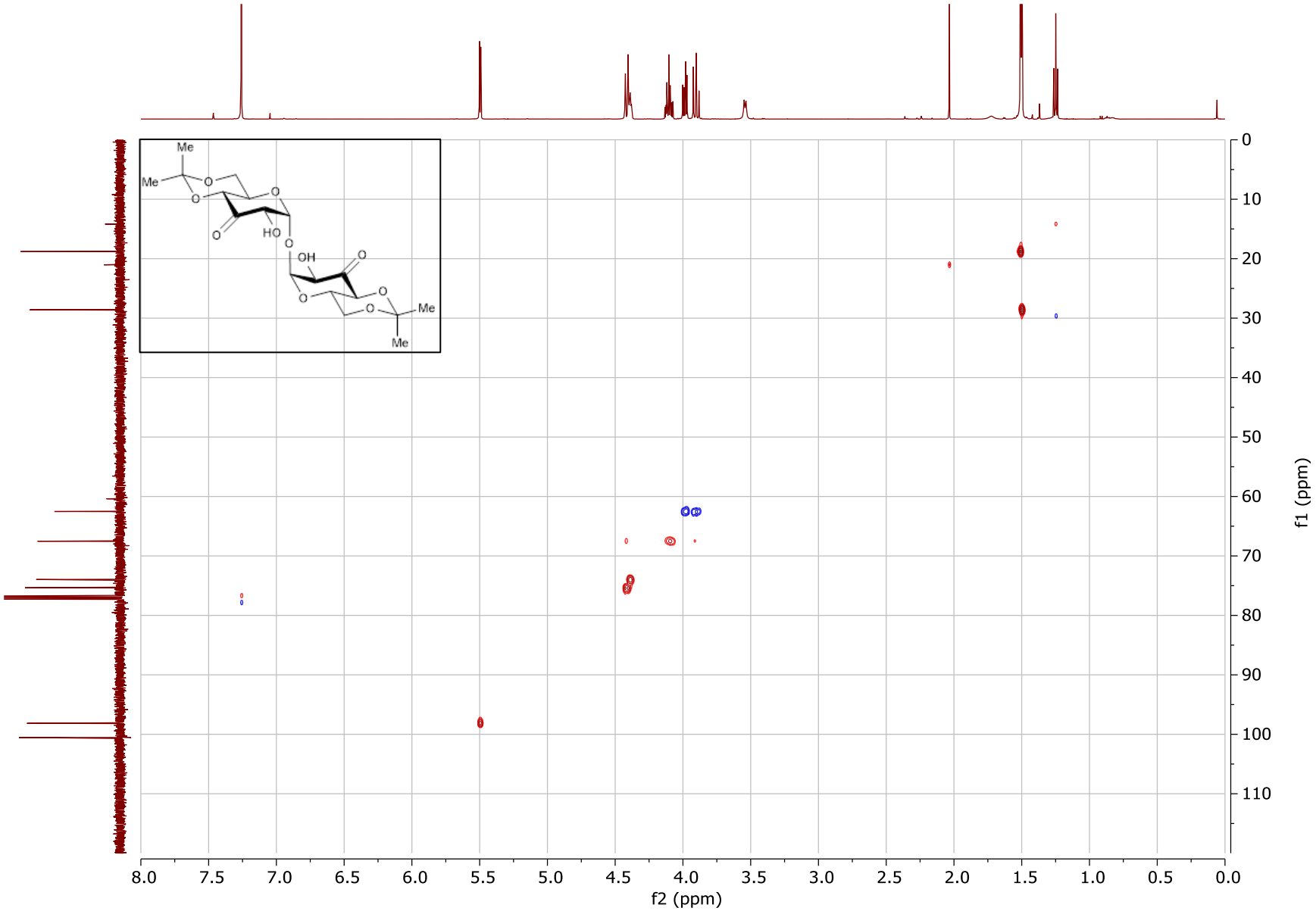
2i – ^{13}C NMR (126 MHz, $CDCl_3$)



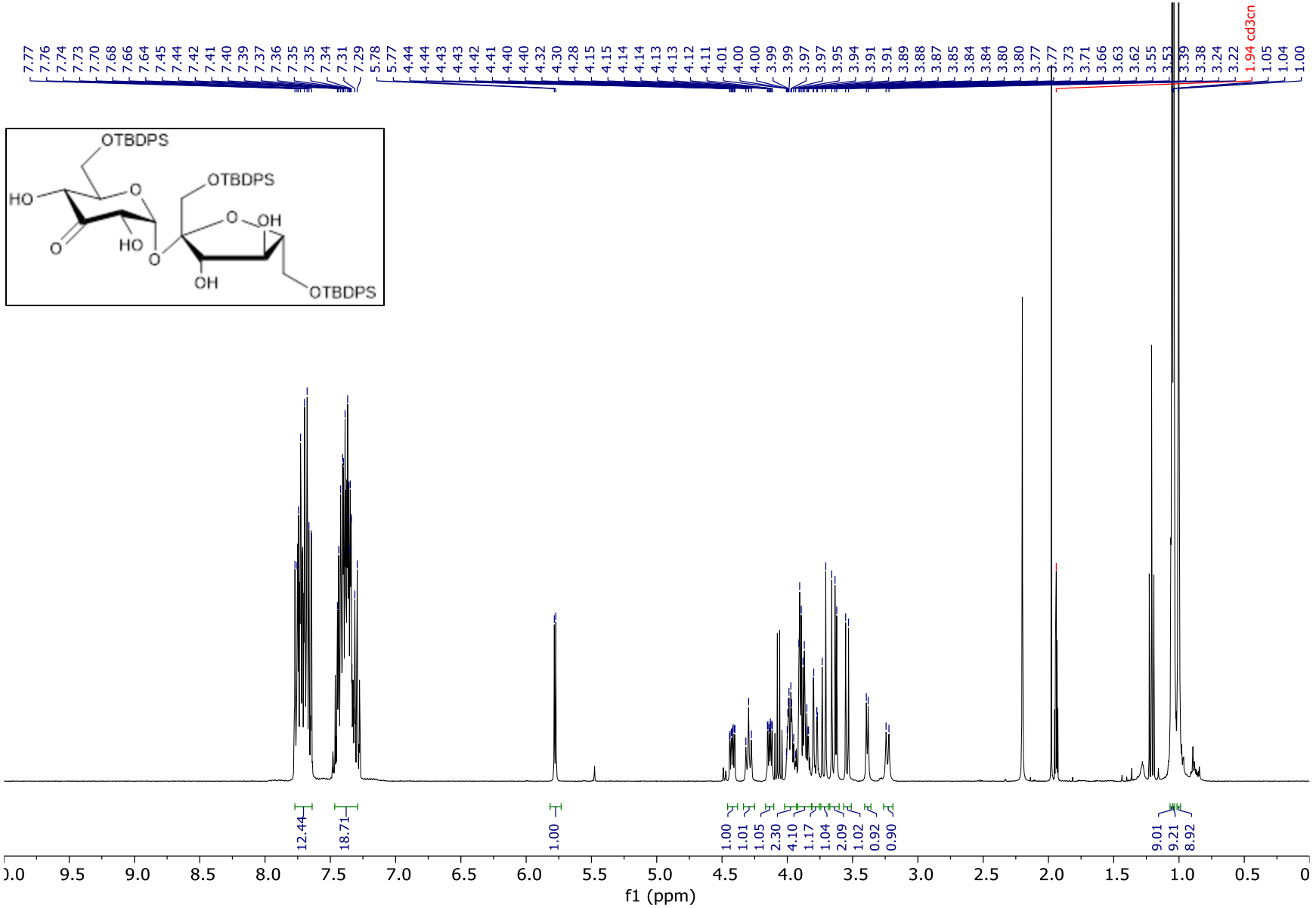
2i –COSY (500 MHz, $CDCl_3$)



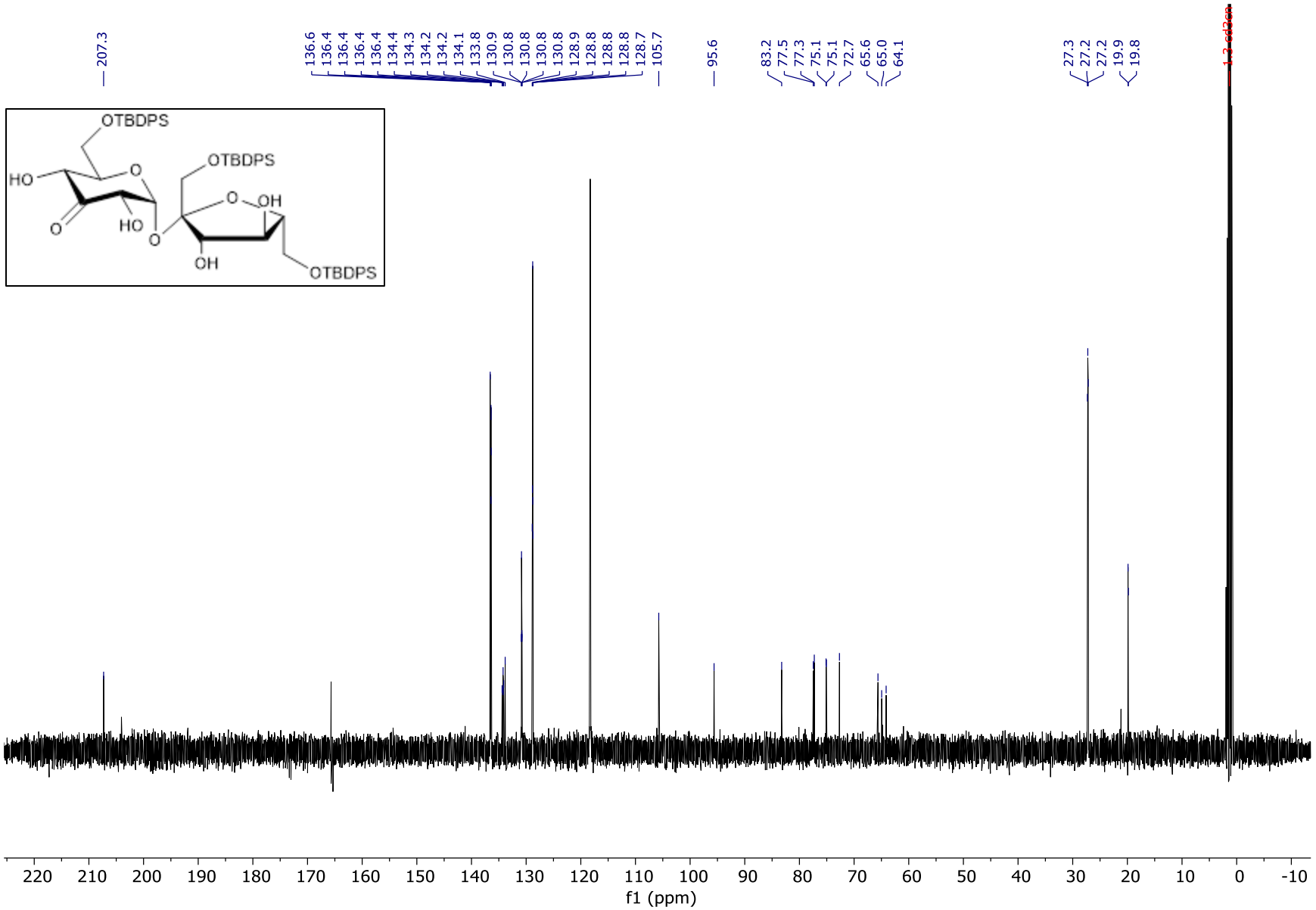
2i – HSQC (500 MHz, $CDCl_3$)



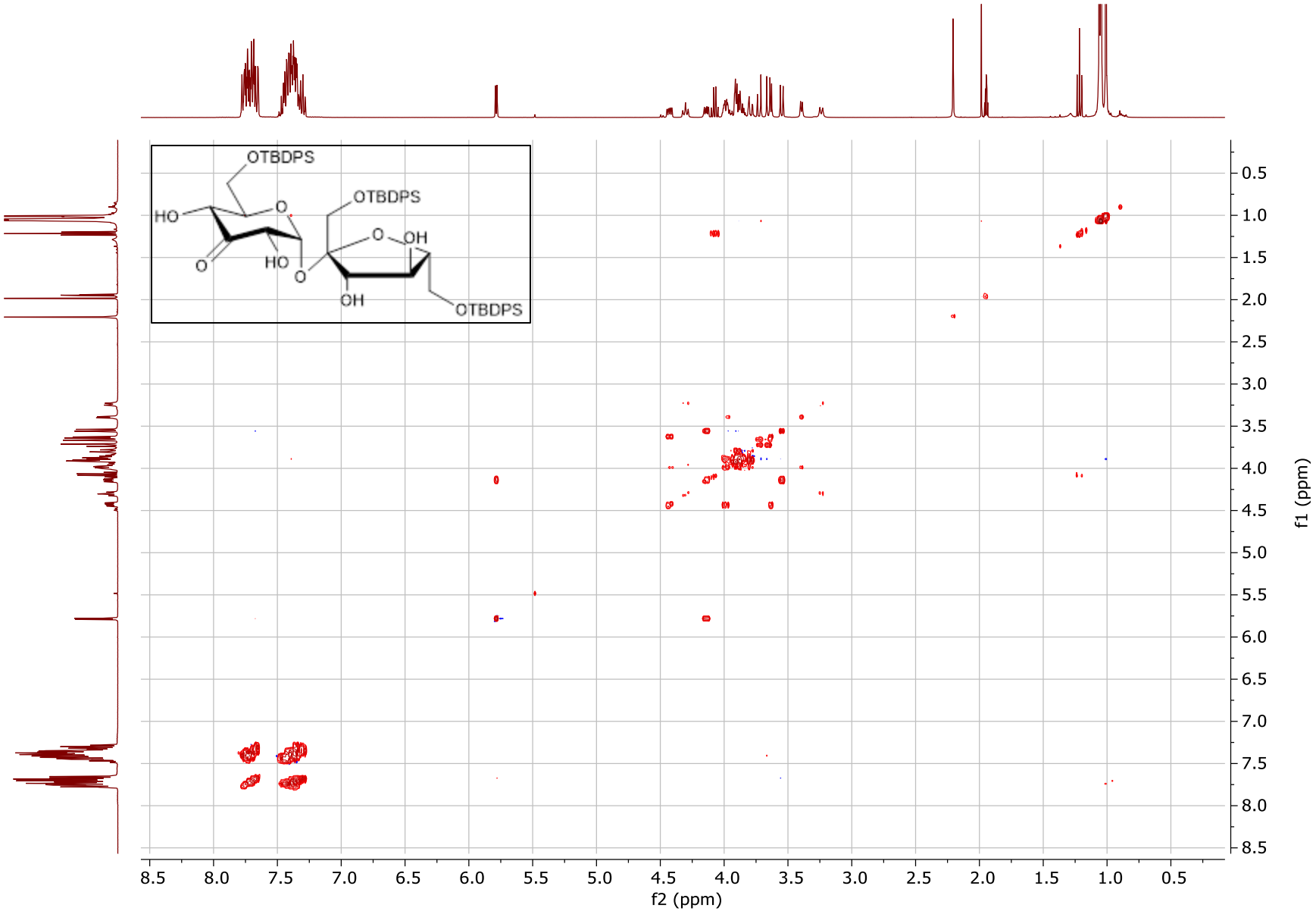
2j –^{1}H NMR (500 MHz, CD_3CN)



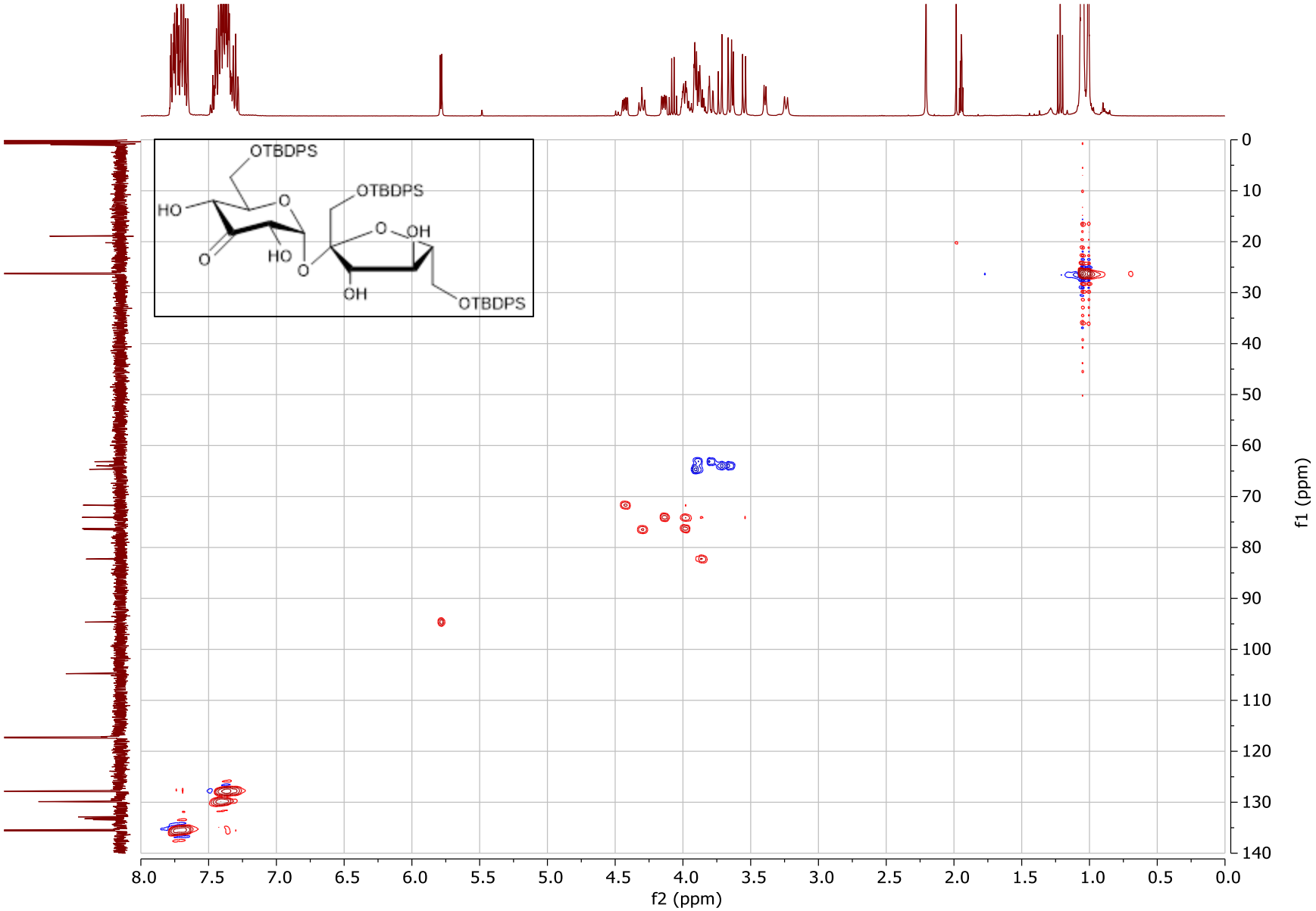
2j –^{13}C NMR (126 MHz, CD_3CN)



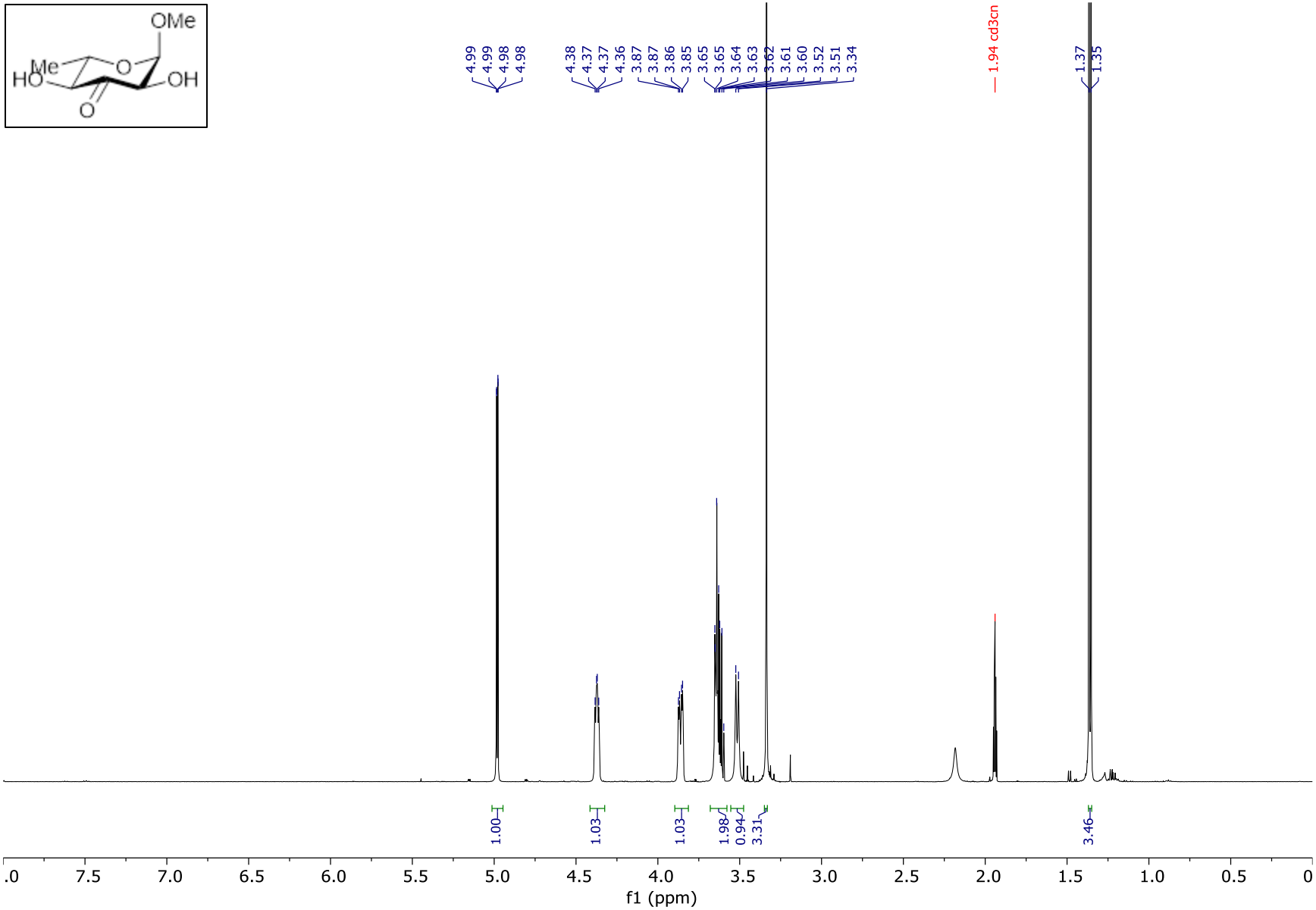
2j – COSY (500 MHz, CD_3CN)



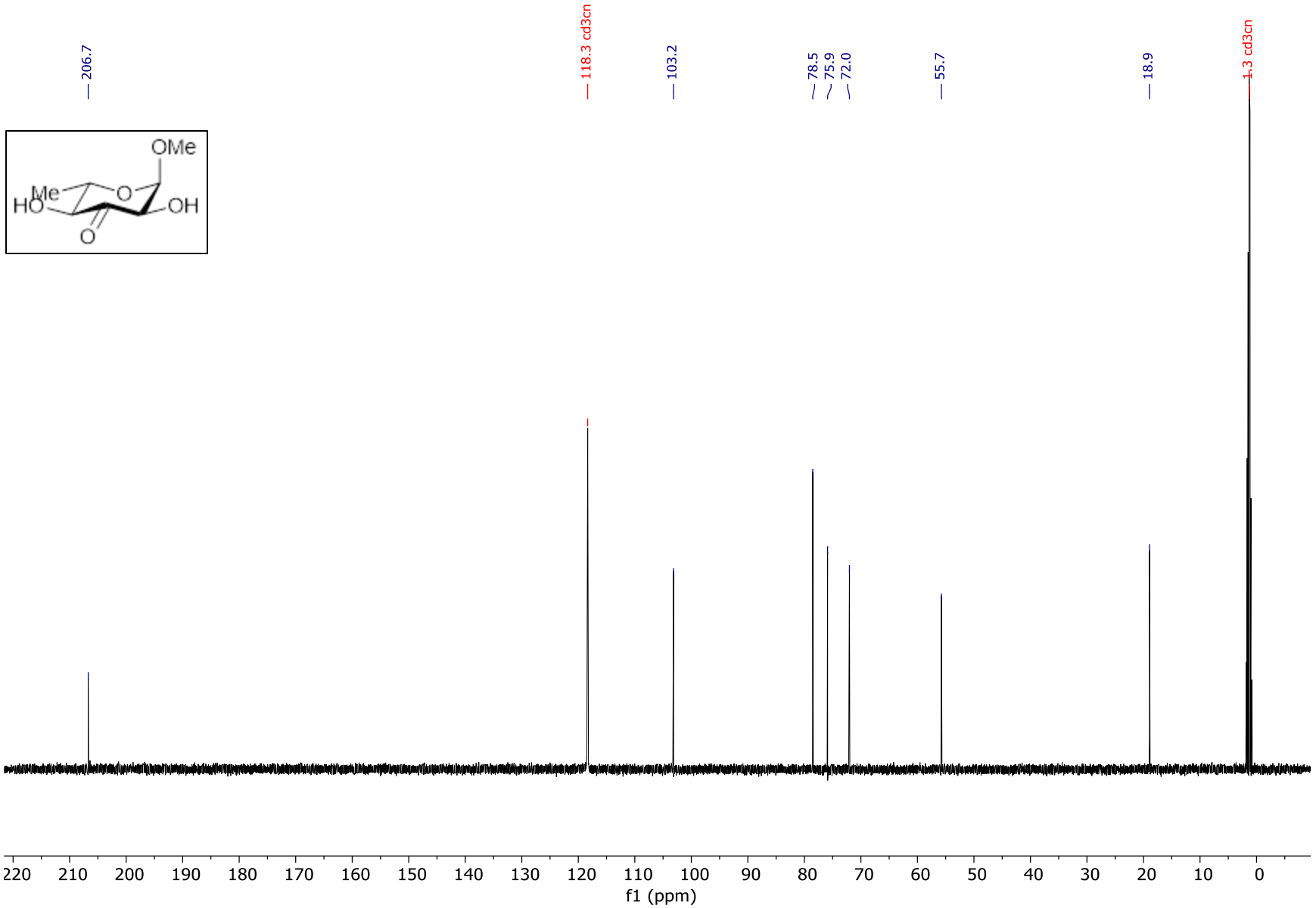
2j – HSQC (500 MHz, CD_3CN)



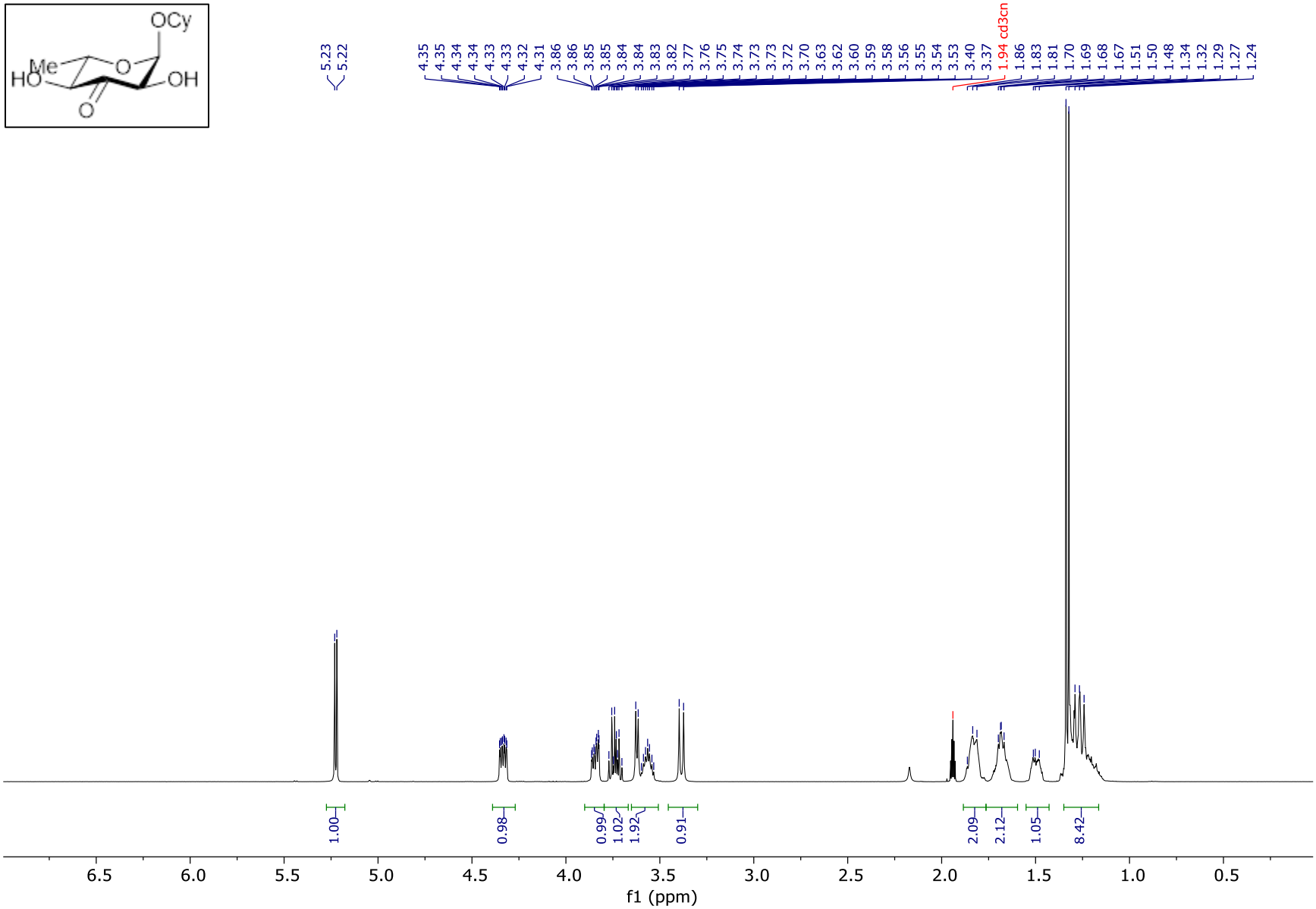
2k – ^{1}H NMR (500 MHz, CD_3CN)



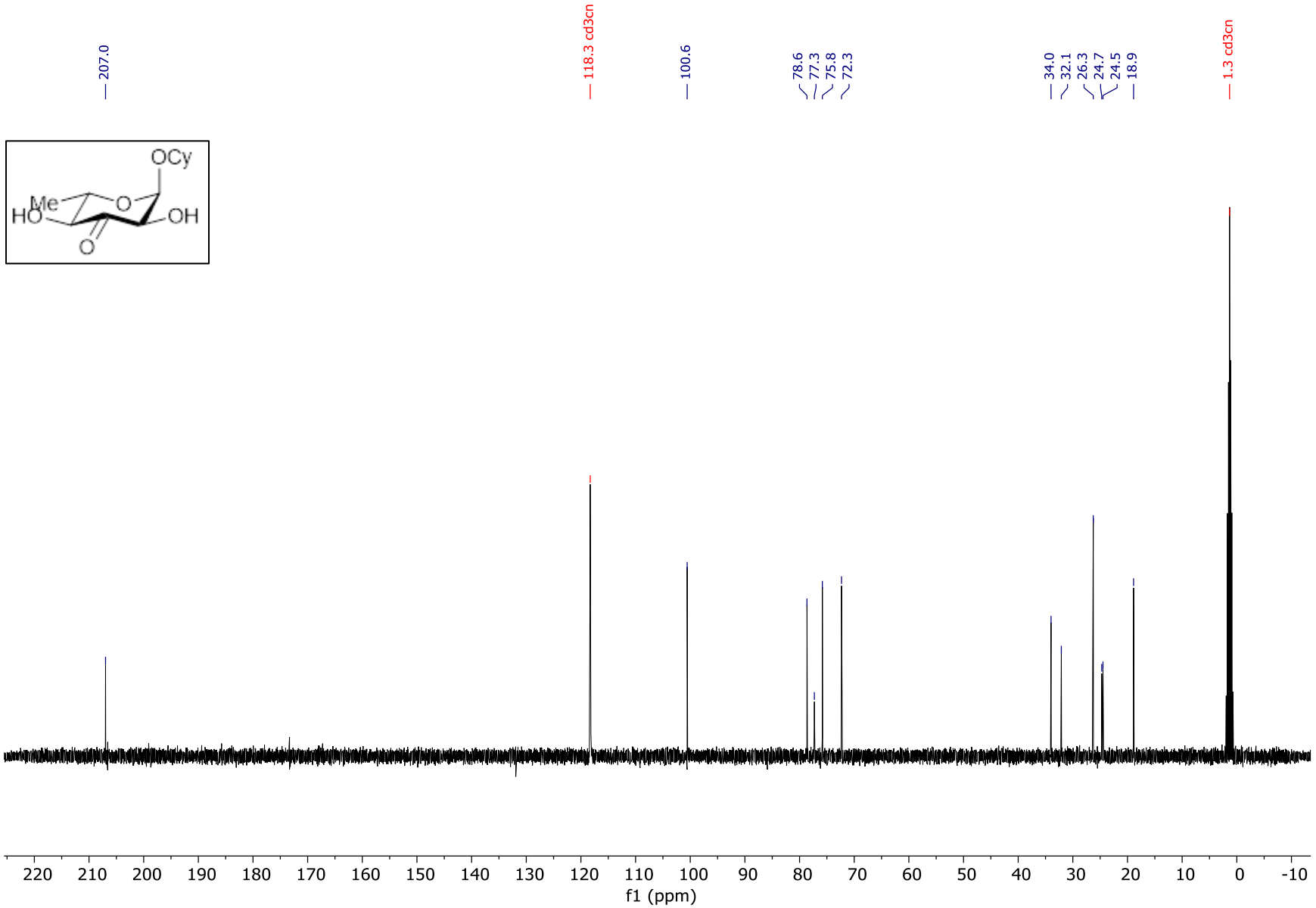
2k – ^{13}C NMR (126 MHz, CD_3CN)



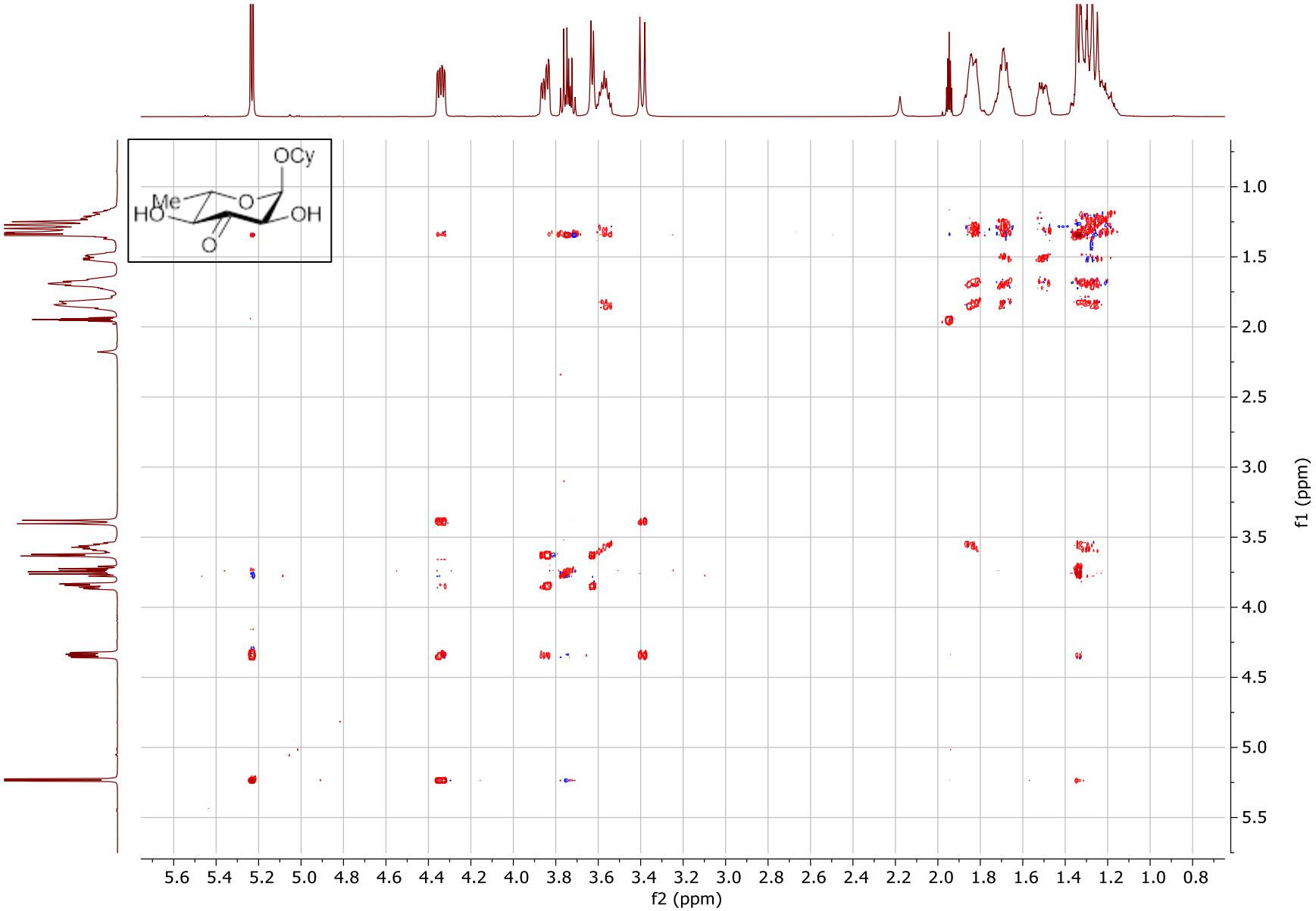
2l – ^{1}H NMR (400 MHz, CD_3CN)



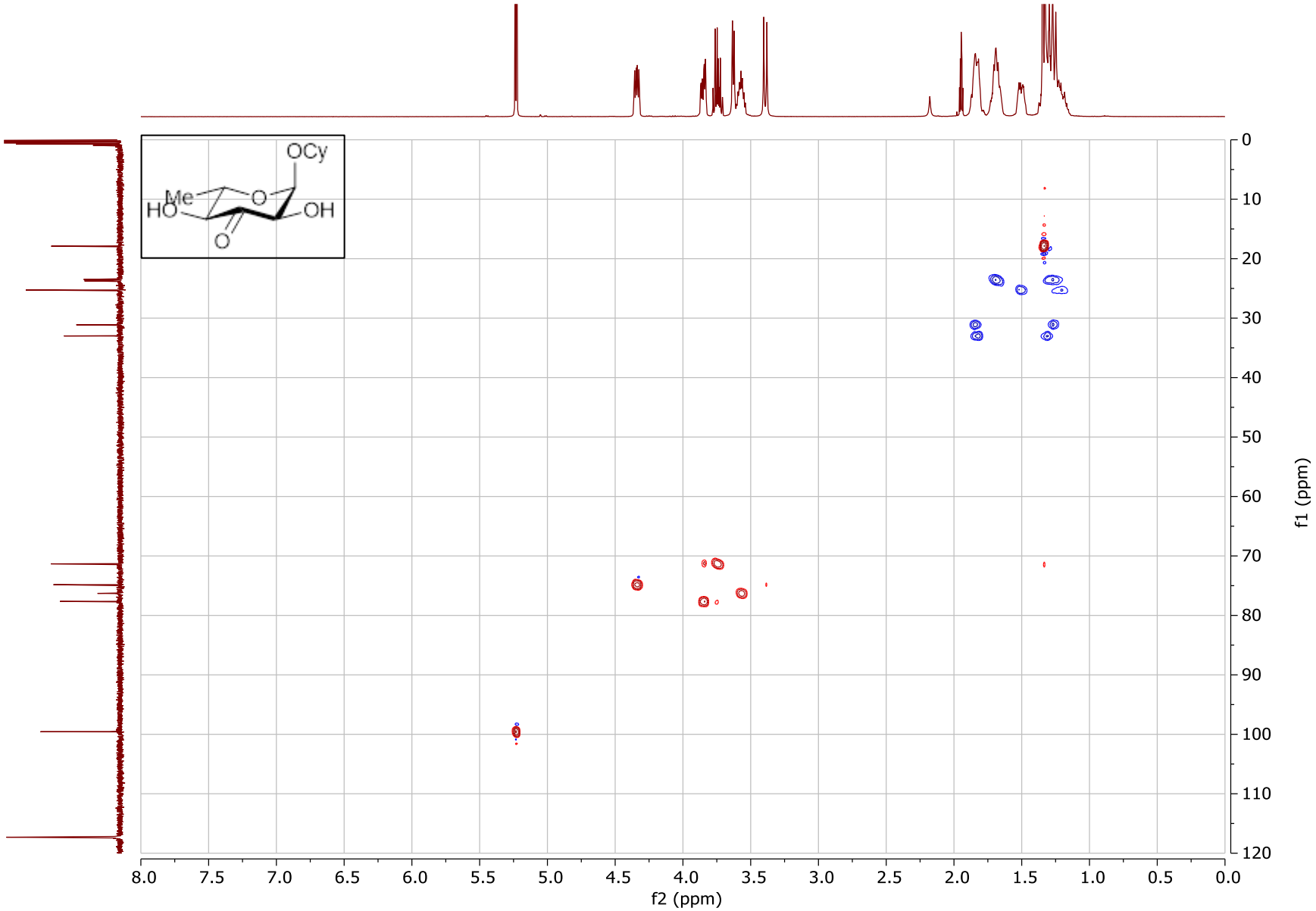
2l – ^{13}C NMR (100 MHz, CD_3CN)



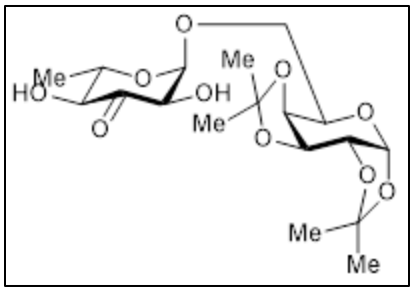
2l – COSY (400 MHz, CD_3CN)



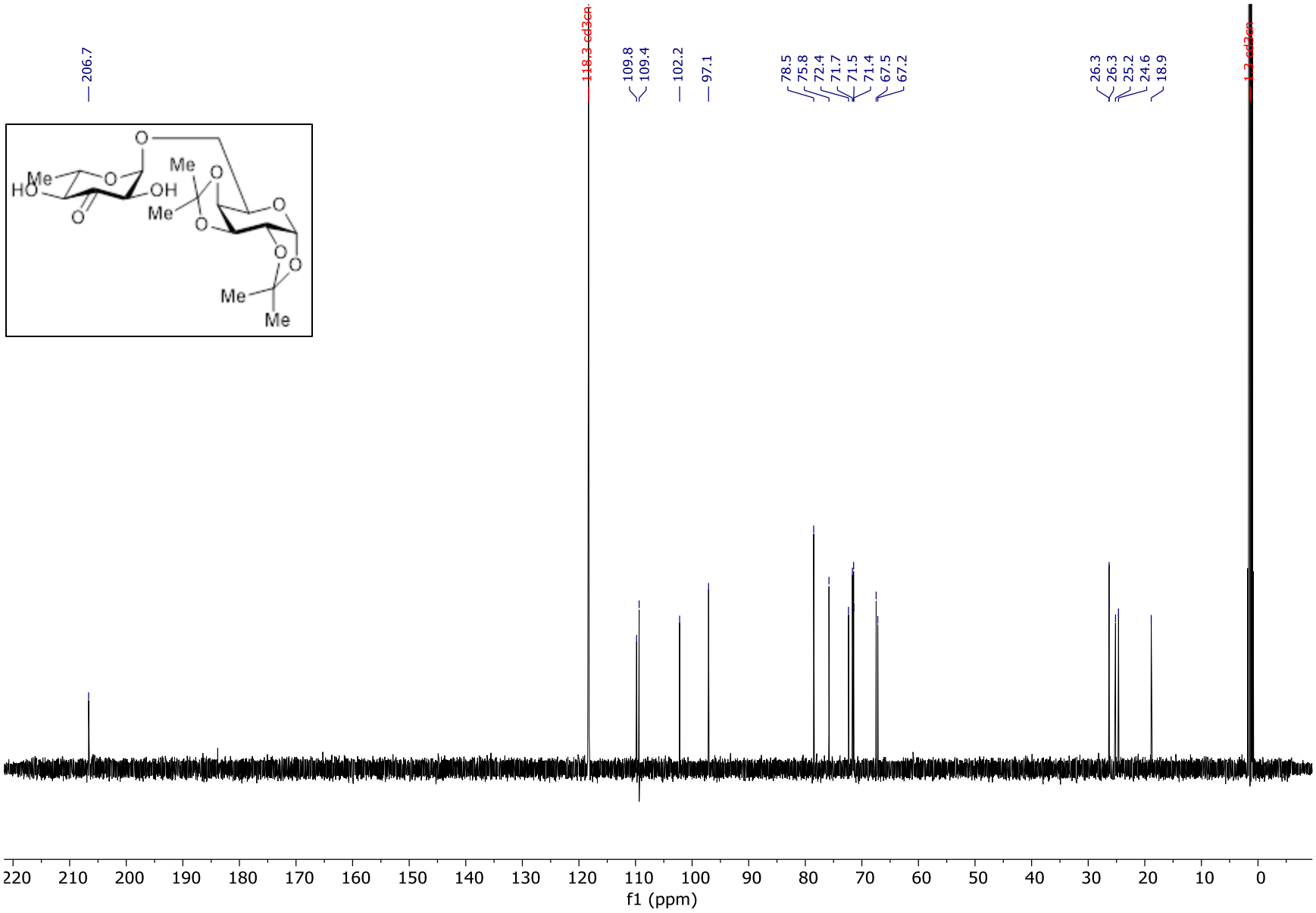
2l – HSQC (400 MHz, CD_3CN)



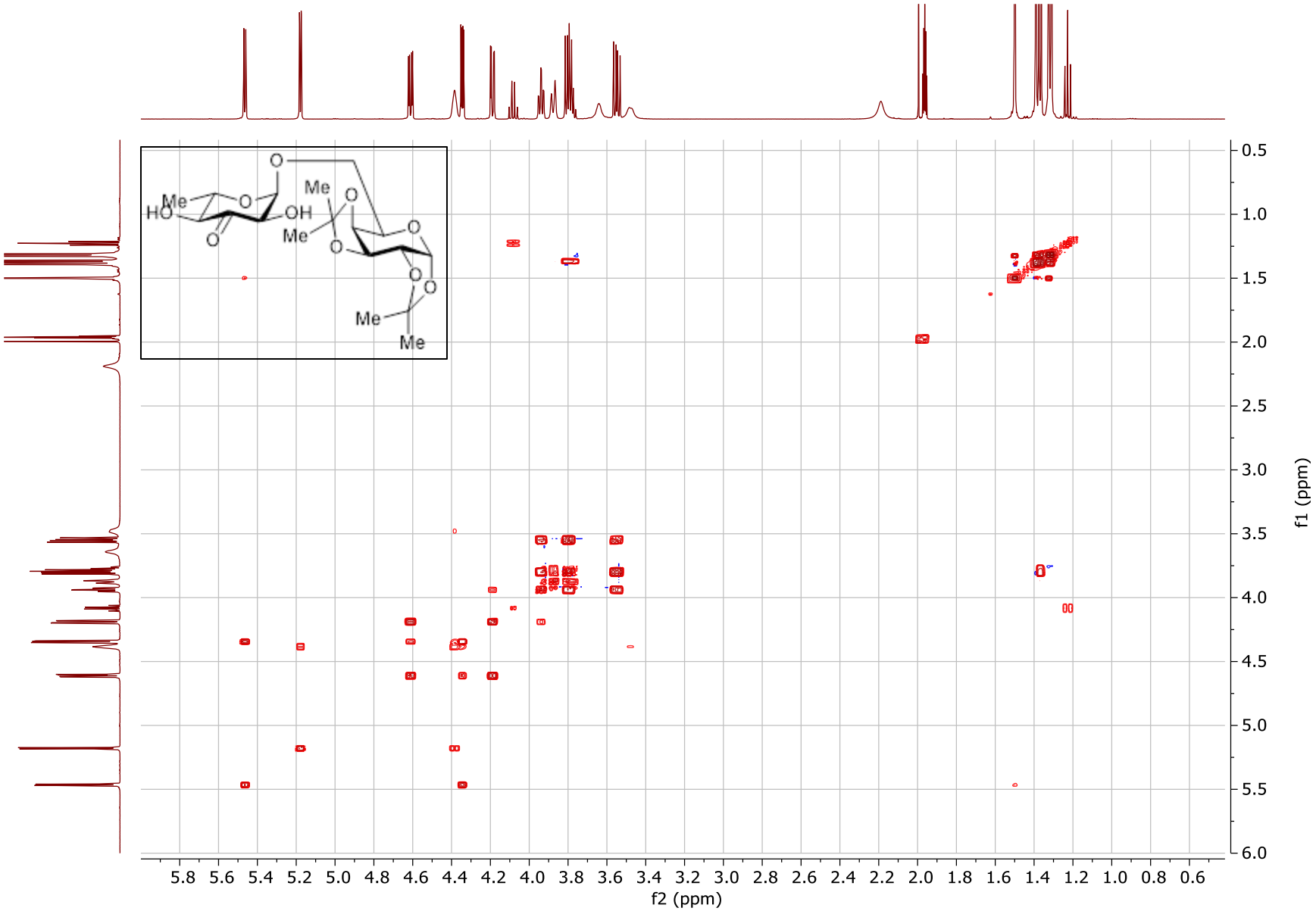
2m – ^{1}H NMR (500 MHz, CD_3CN)



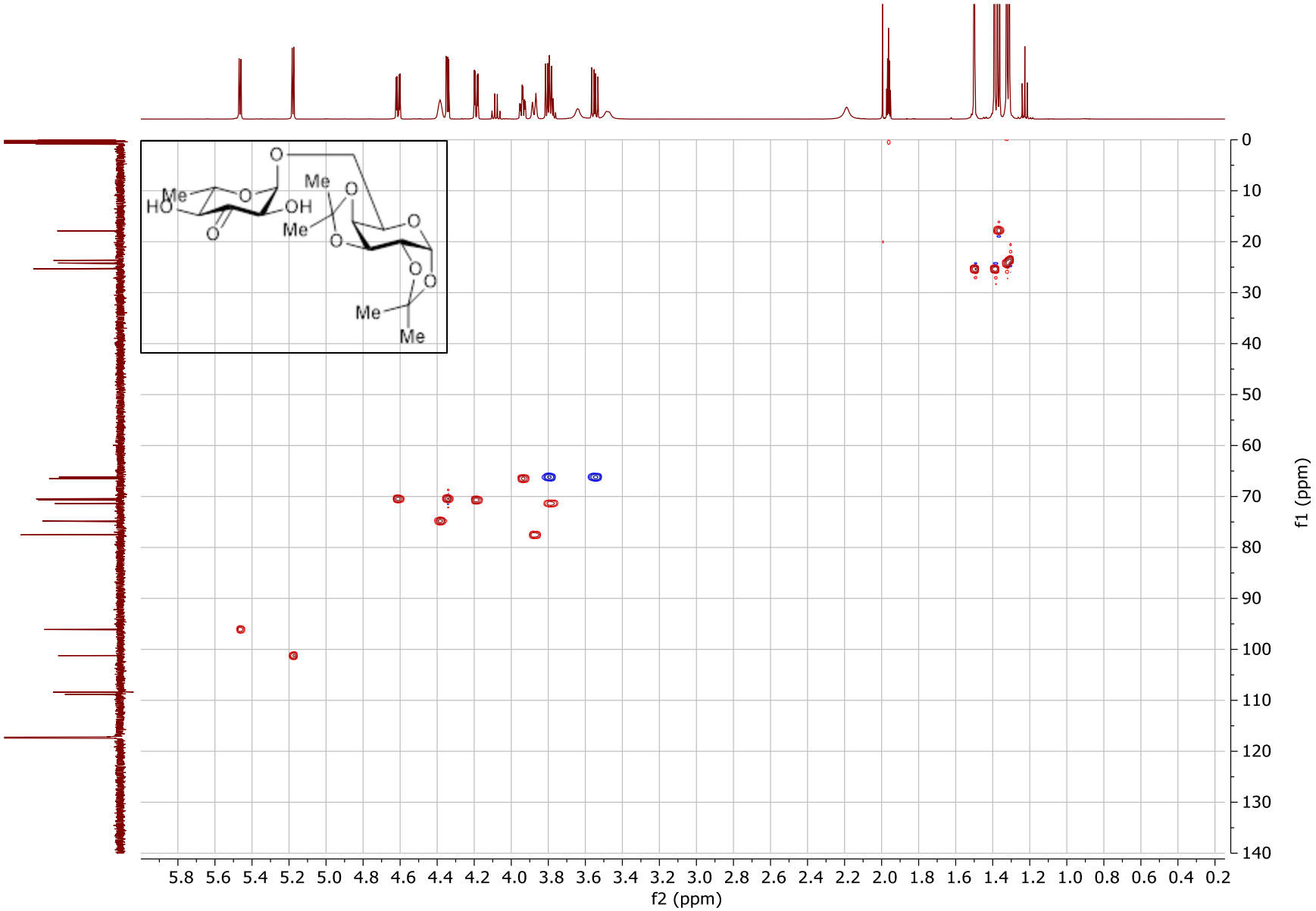
2m – ^{13}C NMR (126 MHz, CD_3CN)



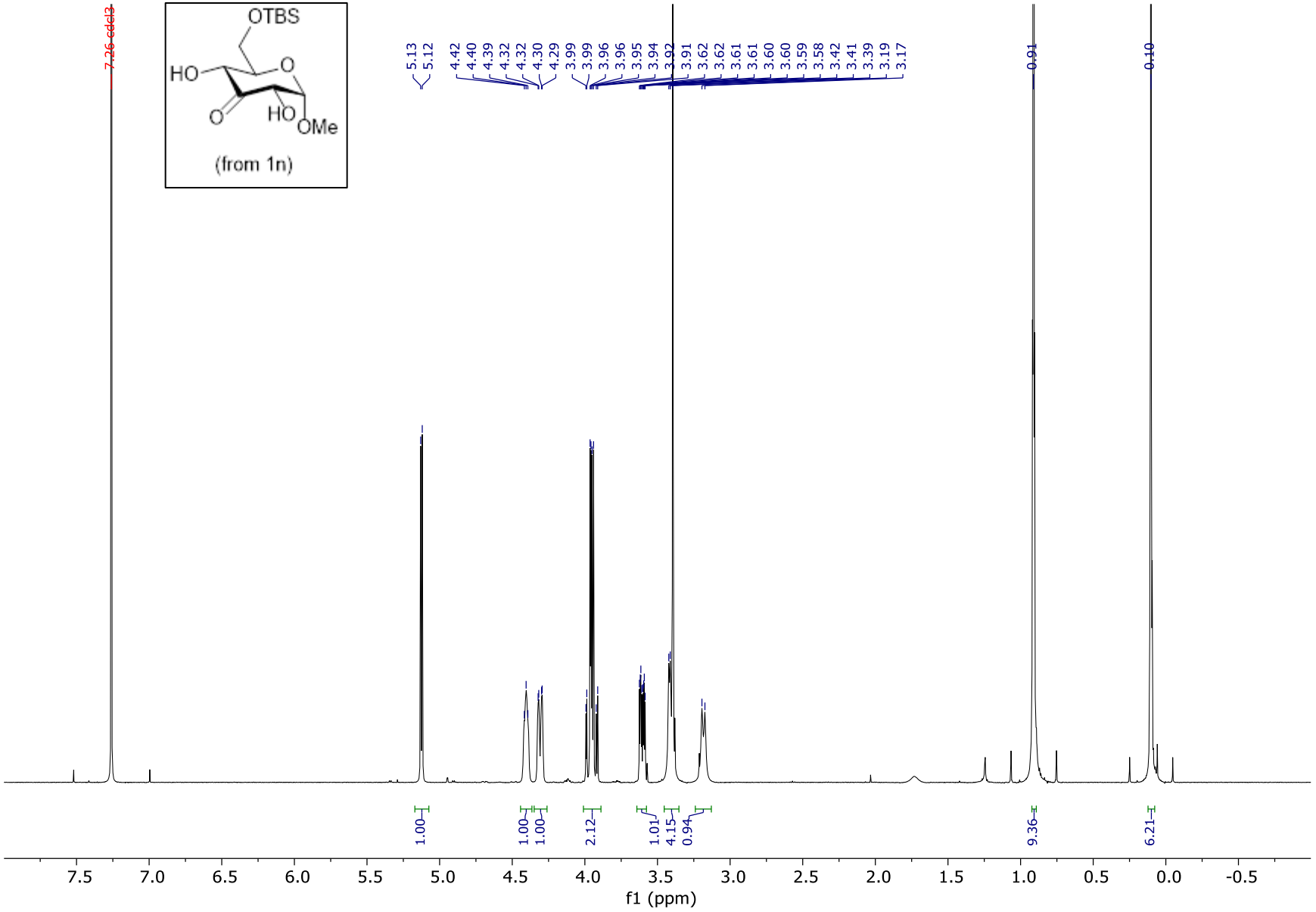
2m – COSY (500 MHz, CD_3CN)



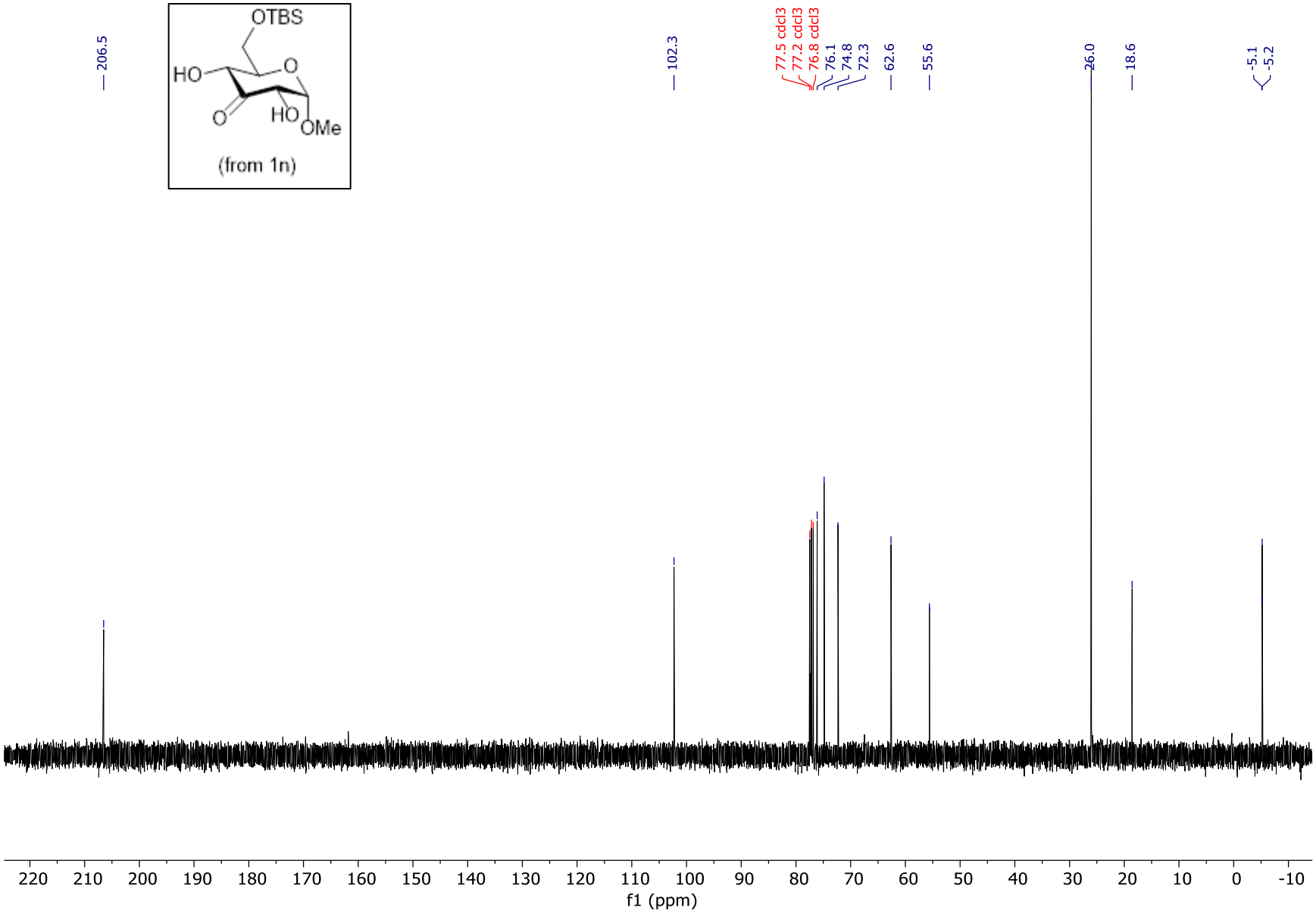
2m – HSQC (500 MHz, CD_3CN)



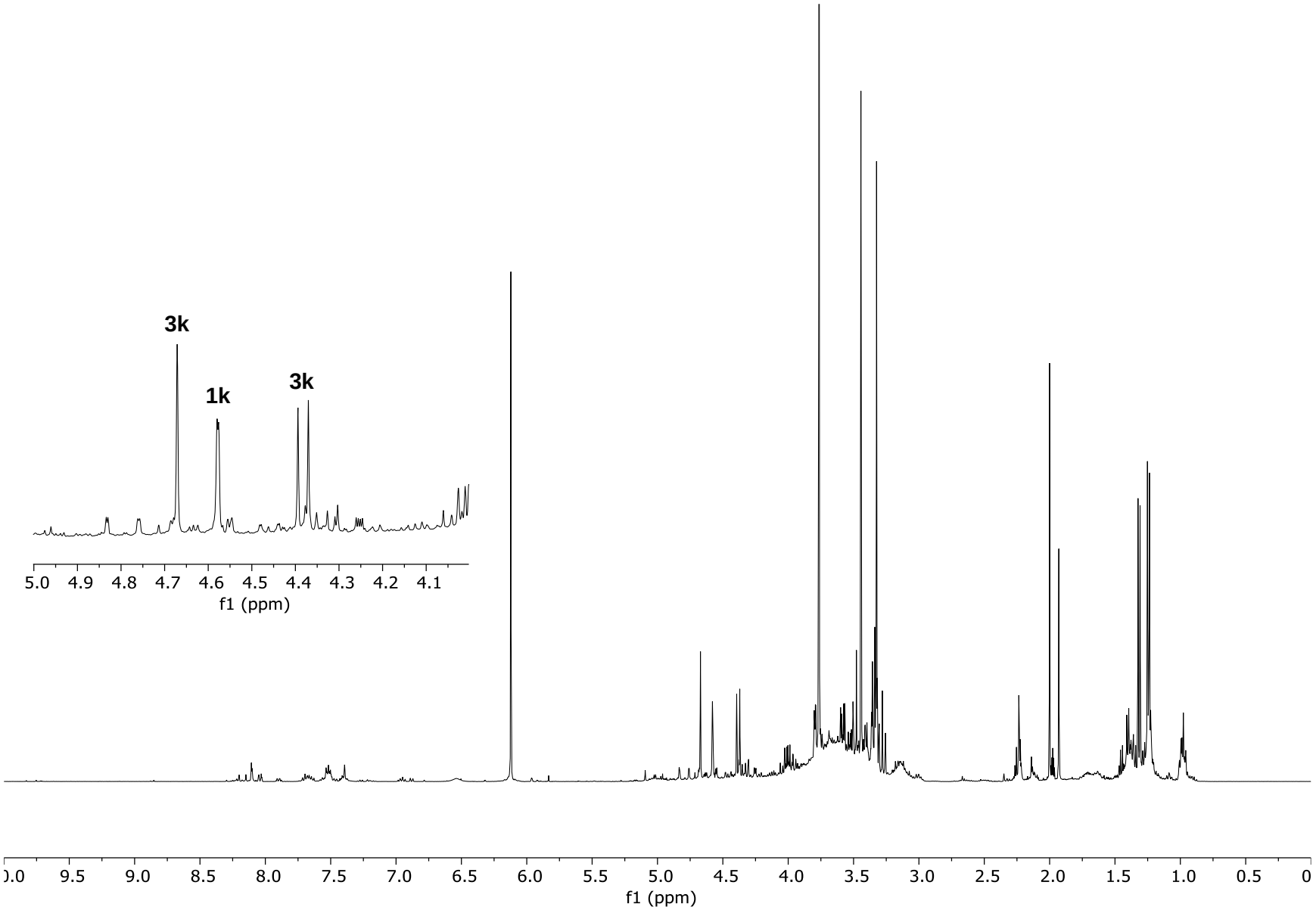
2n – ^{1}H NMR (500 MHz, $CDCl_3$)



2n – ^{13}C NMR (126 MHz, $CDCl_3$)



3k – Crude ^{1}H NMR (500 MHz, CD_3CN)



3n – Crude ^{1}H NMR (500 MHz, CD_3CN)