SUPPORTING INFORMATION

NHC-Catalysed Synthesis of Hydroxy Methylene Bridged Formyl-Di-Xylofuranose: Access to Tetrakis and Spiro Tricyclic Xylofuranose

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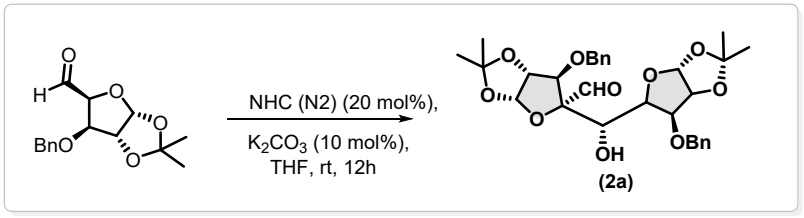
1. General information:

^{1}H and ^{13}C NMR spectra were recorded on 400, 101 and 126 MHz spectrometers with TMS as internal standard. Chemical shifts are expressed in parts per million (δ ppm). Silica gel coated aluminium plates were used for TLC. The products were purified by column chromatography on silica gel (60-120/100-200 mesh) using hexane–ethyl acetate and DCM-MeOH as the eluent to obtain the pure products. Mass spectra were obtained using Q-TOF-LC/MS spectrometer using electron spray ionization. Reagents used were mostly purchased from Sigma Aldrich, TCI and Alfa Aesar.

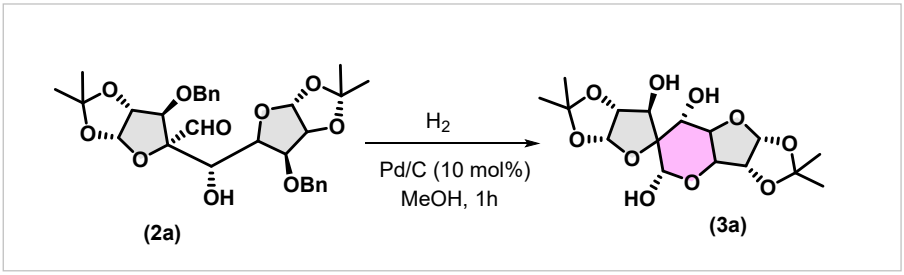
2. General Procedures:

2A. General Procedure for the synthesis of hydroxyl methylene bridged formyl-di-glucofuranose



In a round bottomed flask was added sugar based aldehyde (1.0 equiv) dissolved in THF and then charged with NHC (20 mol%) and K_2CO_3 (10 mol%). The reaction was allowed to stir at rt for 12h. After the completion of the reaction as monitored by TLC, the reaction mixture was extracted with ethyl acetate and the residue was purified by column chromatography.

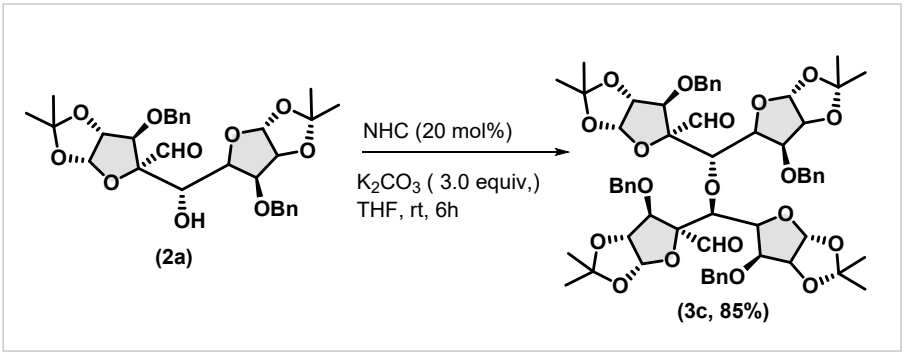
2B. General Procedure for the synthesis of Spiro[furano-4,5-pyrano[3,2-b]furanose](3a):



In a borosilicate glass reaction bottle with tooled neck was charged with Compound dissolved in HPLC Methanol and Pd/C (10 mol%). The reaction bottle was placed tightly in the hydrogenation

apparatus and the continuous supply of H_2 was given over a period of 1 h. After the completion of the reaction as monitored by TLC, the reaction mixture was filtered using celite and then evaporated on a rotavapour.

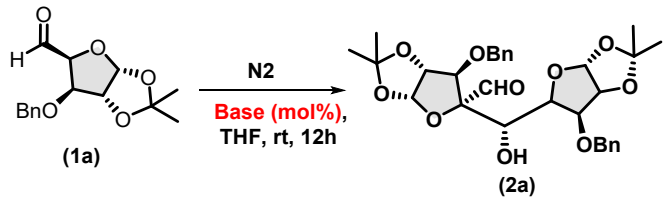
2C. General Procedure for the synthesis of oxymethylene bridged di-formyl-tetrakis-glucofuranose (3c):



In a round bottomed flask was added compound (1.0 equiv) dissolved in THF and then charged with NHC (20 mol%) and K_2CO_3 (3.0 equiv.). The reaction was allowed to stir at rt for 6h. After the completion of the reaction as monitored by TLC, the reaction mixture was extracted with ethyl acetate and the residue was purified by column chromatography.

3. Optimization studies:

3A. Screening of Base[a]

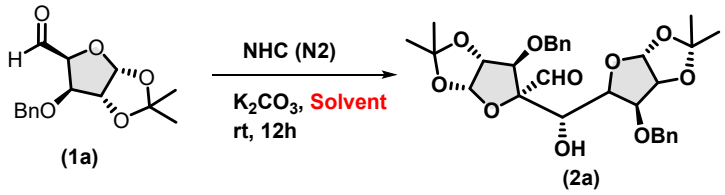


Entry	Base (mol%)	Yield[b] (%)
01	Et_3N (50 mol%)	42
02	DBU (50 mol%)	53
03	K_2CO_3 (50 mol%)	72
04	**K_2CO_3 (10 mol%)**	**90**
04	NaOMe (50 mol%)	32
05	KOH (50 mol%)	40
06	DIPEA (50 mol%)	28
08	Cs_2CO_3 (50 mol%)	60

[a]Reaction conditions, unless otherwise stated: **1a** (1 equiv.), NHC (**N2**) (20 mol%), base (10 mol%) in THF for 12h.

[b]Yields of the purified products after column chromatography.

3B. **Screening of Solvent**[a]



Entry	Solvent	Yield[b] (%)
01	Toluene	20
02	DCM	12
03	DMF	18
04	EtOH	50
04	**THF**	**90**
05	ACN	40
06	Xylene	28
08	DCE	35
09	DME	42

[a]Reaction conditions, unless otherwise stated: **1a** (1 equiv.), NHC (**N2;** 20 mol%), K_2CO_3 (10 mol%) in solvent. [b]Yields of the purified products after column chromatography.

4. Computational details:

In the present study all density functional theory (DFT) calculations were performed utilizing Gaussian 16 program suite [1]. Ground state geometry optimizations of the of pyran derivative, furan derivative, intermediates were performed at B3LYP D3/6-31+G(d)level of theory. Previous studies reported that non-covalently bonded interaction energies like hydrogen bonding, π–π stacking are nicely accounted by Hybrid B3LYP D3/6-31+G(d)level of theory[2-3]. During ground state energy minimization, solvent effects (THF) was introduced by applying the Polarizable Continuum Model (PCM) [4-5] using the integral equation formalism variant. Furthermore, Vibration frequency analysis was accomplished at the same level of theory to confirm that the optimized geometries resemble to global minima on the potential energy surfaces. To account the

weak interactions like H-bonding, van der Waals ,staric interactions functioning at ground state geometries, Non Covalent Interaction (NCI) [6] index plots of the reduced density gradient (RDG *or* s) vs. molecular density ρ were analyzed using the Multiwfn 2.6 [7]. To understand the type of interactions in the complexes molecular electrostatic potential (MESP) maps were generated at the same level of theory.

References:

1. Frisch M, Trucks G, Schlegel H, Scuseria G, Robb M, Cheeseman J*, et al.* Gaussian 16, Gaussian. *Inc, Wallingford CT* 2016, **2016**.

2. Deb, Mousumi, Shrestha Roy, Nadira Hassan, Joy Sankar Deb Roy, Narendra Nath Ghosh, Pijush Kanti Chattopadhyay, Dilip K. Maiti, and Nayan Ranjan Singha. "Chromo-Fluorogenic Sensing of Fe (III), Cu (II), and Hg (II) Using a Redox-Mediated Macromolecular Ratiometric Sensor." *ACS Applied Polymer Materials* 5, no. 7 (2023): 4820-4837.

3. Ghosh A, Dubey SK, Patra M, Mandal J, Ghosh NN, Das P, Bhowmick A, Sarkar K, Mukherjee S, Saha R, Bhattacharjee S. Solvent-and Substrate-Induced Chiroptical Inversion in Amphiphilic, Biocompatible GlycoconjugateSupramolecules: Shape-Persistent Gelation, Self-Healing, and Antibacterial Activity. *Chemistry–A European Journal.* 2022 Nov 11;28(63):e202201621.

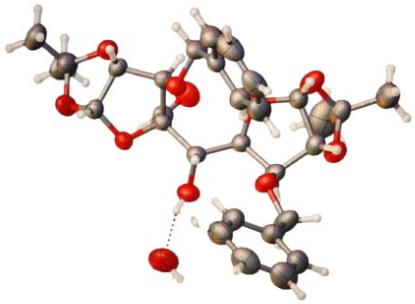
4. Ghosh, N.N., Habib, M., Pramanik, A., Sarkar, P. and Pal, S. Molecular engineering of anchoring groups for designing efficient triazatruxene-based organic dye-sensitized solar cells. *New Journal of Chemistry*, **2019***, 43*(17), pp.6480-6491.]

5. M. Cossi, V. Barone, R. Cammi and J. Tomasi, Ab initio study of solvated molecules: a new implementation of the polarizable continuum model, Chem. Phys. Lett., 1996, 255, 327–335

6. Grimme, S. Wiley Interdisciplinary Reviews: *Computational Molecular Science*. **2011,** *1*, 211-228.

7. Contreras-García, J.; Johnson, E. R.; Keinan, S.; Chaudret,R.; Piquemal, J.-P.; Beratan, D.N.; Yang, W. NCIPLOT: a program for plotting noncovalent interaction regions. *J. chem. theory comput.* **2011,** *7*, 625-632.

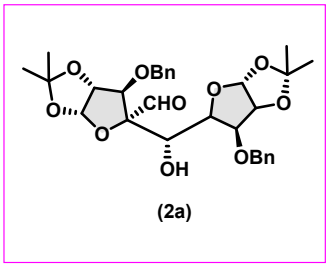
5. Crystal data and structure refinement of 2a.



Identification code	2a **CCDC 2388758**
Formula weight	574.6230
Temperature/K	297.19
Crystal system	orthorhombic
Space group	'P 212121'
a/Å	8.44401(12)
b/Å	14.3851(2)
c/Å	25.1080(3)
α/°	90
β/°	89.96
γ/°	90
Volume/Å^3	3048.33(7)
Z	13
Goodness-of-fit on F2	1.062
Crystal size/mm^3	0.4 × 0.16 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.146 to 56.59

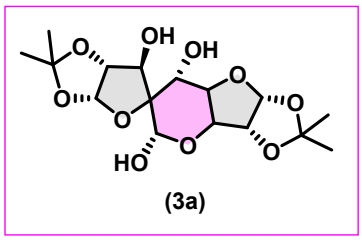
6. Characterization:

6-(benzyloxy)-5-((6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)(hydroxy)methyl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole-5-carbaldehyde (2a)



Prepared according to the general procedure **2A** to get compound **2a** as white crystalline solid in 90% yield**;** 545 mg. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 9.67 (s, 1H) 7.29 (dt, *J* = 15.0, 5.0 Hz, 12H), 6.11 (d, *J* = 4.0 Hz, 1H), 5.83 (d, *J* = 3.7 Hz, 1H), 4.72 (s, 2H), 4.68 – 4.63 (m, 2H), 4.55 (dd, *J* = 10.8, 7.8 Hz, 2H),4.49 – 4.42 (m, 2H), 4.33 (dd, *J* = 9.3, 3.0 Hz, 1H), 4.05 (d, *J* = 3.1 Hz, 1H), 3.48 (s, 1H), 3.41 (d, *J* = 2.8 Hz, 1H), 1.50 (s, 3H), 1.44 (s, 3H), 1.33 (s, 3H), 1.29 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 200.6, 137.7, 136.5, 128.7, 128.4, 128.4, 127.9, 127.8, 127.6, 113.1, 112.1, 105.4, 105.2, 94.5, 88.0, 84.8, 82.2, 81.4, 73.6, 72.5, 70.5, 27.0, 26.9, 26.5 (2C). **HRMS** calcd for $C_{30}H_{37}O_{10}$ $[M + H]^+$ 557.2387, found 557.2389.

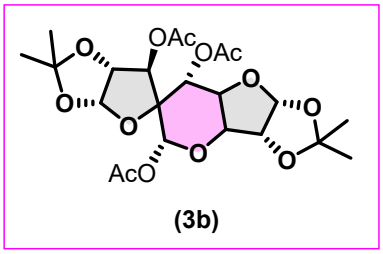
2,2,2',2'-tetramethylhexahydro-5'H,6H,7'H-spiro[furo[2,3-d][1,3]dioxole-5,6'-[1,3]dioxolo[4',5':4,5]furo[3,2-b]pyran]-5',6,7'-triol (3a)



Prepared according to the general procedure **2B** to get compound **3a** as whitish solid in 88% yield; 178.11 mg**. ^{1}H NMR (400 MHz, $CDCl_3$ + MeOD)** δ 6.08 – 5.94 (m, 2H), 5.17 (d, *J* = 3.3 Hz, 1H), 4.59 (dt, *J* = 4.0, 2.3 Hz, 2H), 4.45 (d, *J* = 0.9 Hz, 1H), 4.40 (dd, *J* = 9.0, 3.1 Hz, 2H), 4.33 (d, *J* = 3.5 Hz, 1H), 3.41 (s, 1H), 1.50 (s, 6H), 1.32 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$ + MeOD)** δ

112.5, 111.7, 105.5, 104.8, 94.9, 87.0, 86.7, 84.1, 79.4, 76.3, 72.7, 63.6, 26.6, 26.4, 26.0. **HRMS** calcd for $C_{16}H_{25}O_{10}$ $[M + H]^+$ 377.1448, found 377.1450.

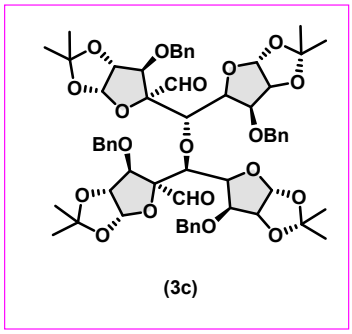
2,2,2',2'-tetramethylhexahydro-5'H,6H,7'H-spiro[furo[2,3-d][1,3]dioxole-5,6'-[1,3]dioxolo[4',5':4,5]furo[3,2-b]pyran]-5',6,7'-triyl triacetate (3b)



(3b)

Prepared by acetylation of compound **3a** in pyridine to get compound **3b** as yellowish gummy liquid in 90% yield; 360.00 mg. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.06 (s, 2H), 5.96 (t, J = 7.5 Hz, 1H), 5.23 (d, J = 4.2 Hz, 1H), 5.19 (d, J = 1.6 Hz, 1H), 4.52 (d, J = 3.6 Hz, 1H), 4.48 (dd, J = 4.1, 2.4 Hz, 1H), 4.47 – 4.44 (m, 1H), 4.19 (d, J = 1.8 Hz, 1H), 2.14 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.51 (s, 3H), 1.39 (s, 3H), 1.29 (s, 3H), 1.23 (s, 3H). **^{13}C NMR (101 MHz, CDCl3)** δ 169.6, 168.7, 168.4, 114.4, 112.0, 105.4, 104.9, 94.3, 86.6, 83.3, 83.0, 78.1, 75.6, 74.2, 65.5, 27.8, 27.3, 26.6, 26.1, 21.3, 20.6, 20.5. **HRMS** calcd for $C_{22}H_{31}O_{13}$ $[M + H]^+$ 503.1765, found 503.1769.

5,5'-(oxybis((6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)methylene))bis(6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole-5-carbaldehyde) (3c)

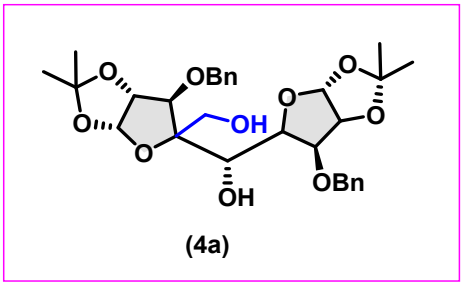


(3c)

Prepared according to the general procedure **2C** to get compound **3c** as yellowish gummy liquid in 85% yield; 502.93 mg**. ^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.67 (s, 1H), 9.50 (s, 1H), 7.31 – 7.09 (m, 20H), 6.10 (d, *J* = 4.3 Hz, 1H), 5.85 (dd, *J* = 7.9, 3.7 Hz, 3H), 4.77 – 4.70 (m, 2H), 4.66 – 4.59 (m, 3H), 4.58 (s, 1H), 4.55 – 4.47 (m, 8H), 4.46 – 4.39 (m, 3H), 4.35 (s, 1H), 4.29 (dd, *J* = 6.2, 3.5

Hz, 1H), 4.23 (d, *J* = 11.3 Hz, 1H), 4.03 (t, *J* = 5.4 Hz, 2H), 3.83 (d, *J* = 3.5 Hz, 1H), 3.30 (d, *J* = 11.1 Hz, 1H), 2.92 (s, 1H), 1.94 (s, 1H), 1.47 (s, 3H), 1.40 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H), 1.28 (s, 3H), 1.23 (s, 3H), 1.21 (s, 3H), 1.18 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.6, 200.4, 137.68, 137.0, 136.8, 136.7, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.90, 127.87, 12.78, 127.7, 127.5 (2C), 114.6, 112.3, 112.2, 112.0, 105.7, 105.0, 104.8, 104.6, 93.1, 91.4, 85.7, 85.5, 84.6, 83.8, 83.4, 83.0, 82.6, 82.3, 79.8, 73.9, 72.9, 72.2, 71.1, 70.3, 68.7, 27.7, 27.3, 27.1, 26.8, 26.6, 26.3, 25.7, 25.5. **HRMS** calcd for $C_{60}H_{71}O_{19}$ $[M + H]^+$ 1095.4590, found 1095.4596.

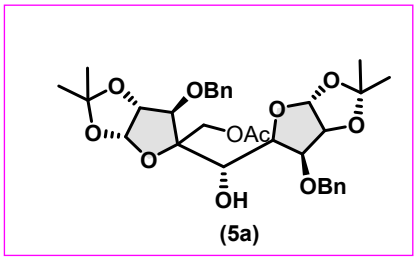
(6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)(6-(benzyloxy)-5-(hydroxymethyl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)methanol (4a)



(4a)

Prepared by the reduction of compound **2a** using $NaBH_4$ (1.2 equiv.) in MeOH for 30 min at 0 °C to get compound **4a** as yellowish gummy liquid in 88%, 265.03 mg. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26 – 7.17 (m, 10H), 5.91 (d, *J* = 4.4 Hz, 1H), 5.82 (d, *J* = 3.7 Hz, 1H), 4.65 (d, *J* = 11.3 Hz, 2H), 4.60 – 4.52 (m, 2H), 4.48 – 4.43 (m, 2H), 4.32 – 4.26 (m, 2H), 4.23 – 4.17 (m, 1H), 4.02 (d, *J* = 2.6 Hz, 1H), 3.77 – 3.68 (m, 2H), 2.89 (s, 1H), 2.63 (s, 1H), 1.47 (d, *J* = 4.9 Hz, 3H), 1.40 (s, 3H), 1.26 (s, 3H), 1.19 (d, *J* = 10.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.7, 137.3, 128.5, 128.5, 128.0, 127.9, 127.8, 127.6, 113.5, 112.1, 105.5, 105.3, 91.2, 87.3, 87.2, 82.7, 81.5, 78.4, 77.5, 77.2, 76.8, 73.2, 72.6, 69.4, 63.9, 27.7, 27.3, 26.9, 26.4. **HRMS** calcd for $C_{30}H_{39}O_{10}$ $[M + H]^+$ 559.2543, found 559.2546.

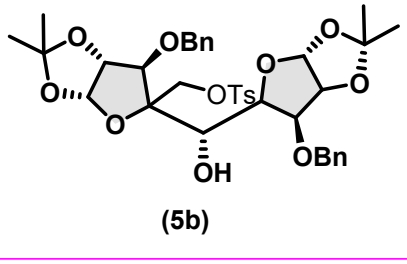
(6-(benzyloxy)-5-((6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)(hydroxy)methyl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)methyl acetate (5a)



(5a)

Prepared by acetylation of compound **4a** in pyridine to get compound **5a** as yellowish gummy liquid in 92% yield; 279.21 mg. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 (s, 5H), 7.20 (s, 5H), 5.94 (d, *J* = 4.7 Hz, 1H), 5.83 (d, *J* = 3.8 Hz, 1H), 4.74 (dd, *J* = 4.6, 2.9 Hz, 1H), 4.70 (d, *J* = 11.5 Hz, 1H), 4.61 (d, *J* = 11.7 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.46 (dd, *J* = 7.7, 3.9 Hz, 1H), 4.33 (d, *J* = 12.4 Hz, 1H), 4.26 (dd, *J* = 8.7, 2.9 Hz, 1H), 4.18 (d, *J* = 2.9 Hz, 1H), 4.15 – 4.10 (m, 2H), 4.02 (d, *J* = 3.0 Hz, 1H), 2.79 (d, *J* = 5.0 Hz, 1H), 1.86 (s, 3H), 1.52 (s, 3H), 1.40 (s, 3H), 1.32 (s, 3H), 1.22 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.3, 137.6, 137.1, 128.5, 128.5, 127.8, 127.7, 114.4, 111.8, 105.4, 105.3, 88.9, 87.9, 85.5, 83.0, 81.3, 77.7, 77.4, 72.8, 72.3, 70.0, 63.5, 28.0, 27.9, 26.8, 26.3, 20.8. **HRMS** calcd for $C_{32}H_{41}O_{11}$ $[M + H]^+$ 601.2649, found 601.2652.

(6-(benzyloxy)-5-((6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)(hydroxy)methyl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)methyl-4-methylbenzenesulfonate (5b)



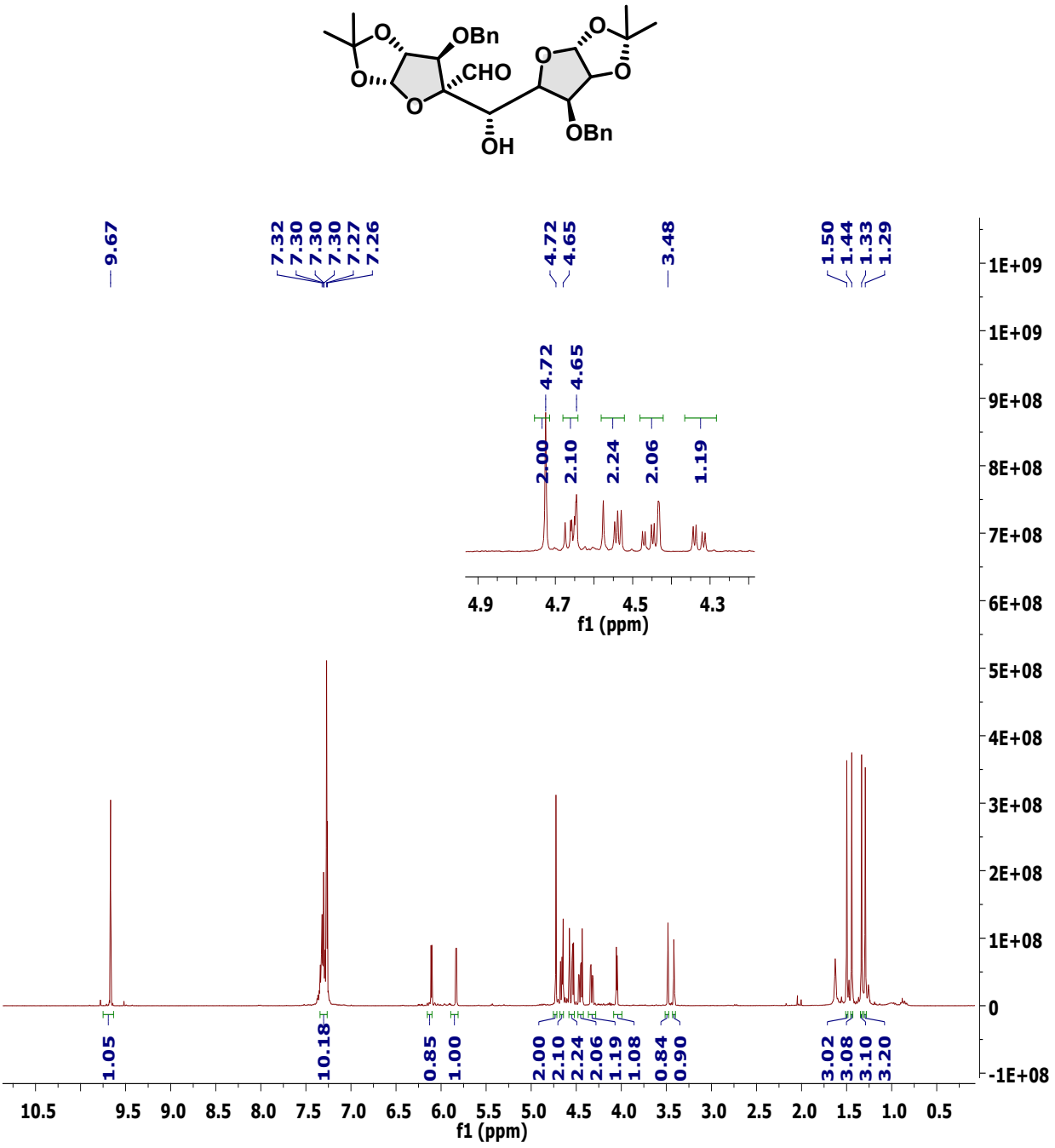
(5b)

Prepared by tosylation of compound **4a** using tosyl chloride, Et_3N, DMAP in DCM for 2h at rt to get compound **5b** as yellowish gummy liquid in 94% yield; 364.23 mg. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.25 (dd, *J* = 3.9, 1.7 Hz, 5H), 7.21 (d, *J* = 0.6 Hz, 1H), 7.18 (d, *J* = 4.2 Hz, 3H), 7.13 – 7.10 (m, 3H), 5.90 (d, *J* = 4.6 Hz, 1H), 5.65 (d, *J* = 3.7 Hz, 1H), 4.68 – 4.60 (m, 2H), 4.53 (dd, *J* = 14.8, 11.4 Hz, 2H), 4.39 (dd, *J* = 9.8, 7.7 Hz, 2H), 4.30 (dd, *J* = 6.8, 4.1 Hz, 2H), 4.20 – 4.11 (m, 2H), 4.01 (dd, *J* = 9.2, 4.7 Hz, 1H), 3.92 (d, *J* = 3.0 Hz, 1H), 2.63 (d, *J* = 4.8 Hz, 1H), 2.31 (s, 3H), 1.45 (s, 3H), 1.35 (s, 3H), 1.29 (s, 3H), 1.20 (s, 3H). **^{13}C NMR (101**

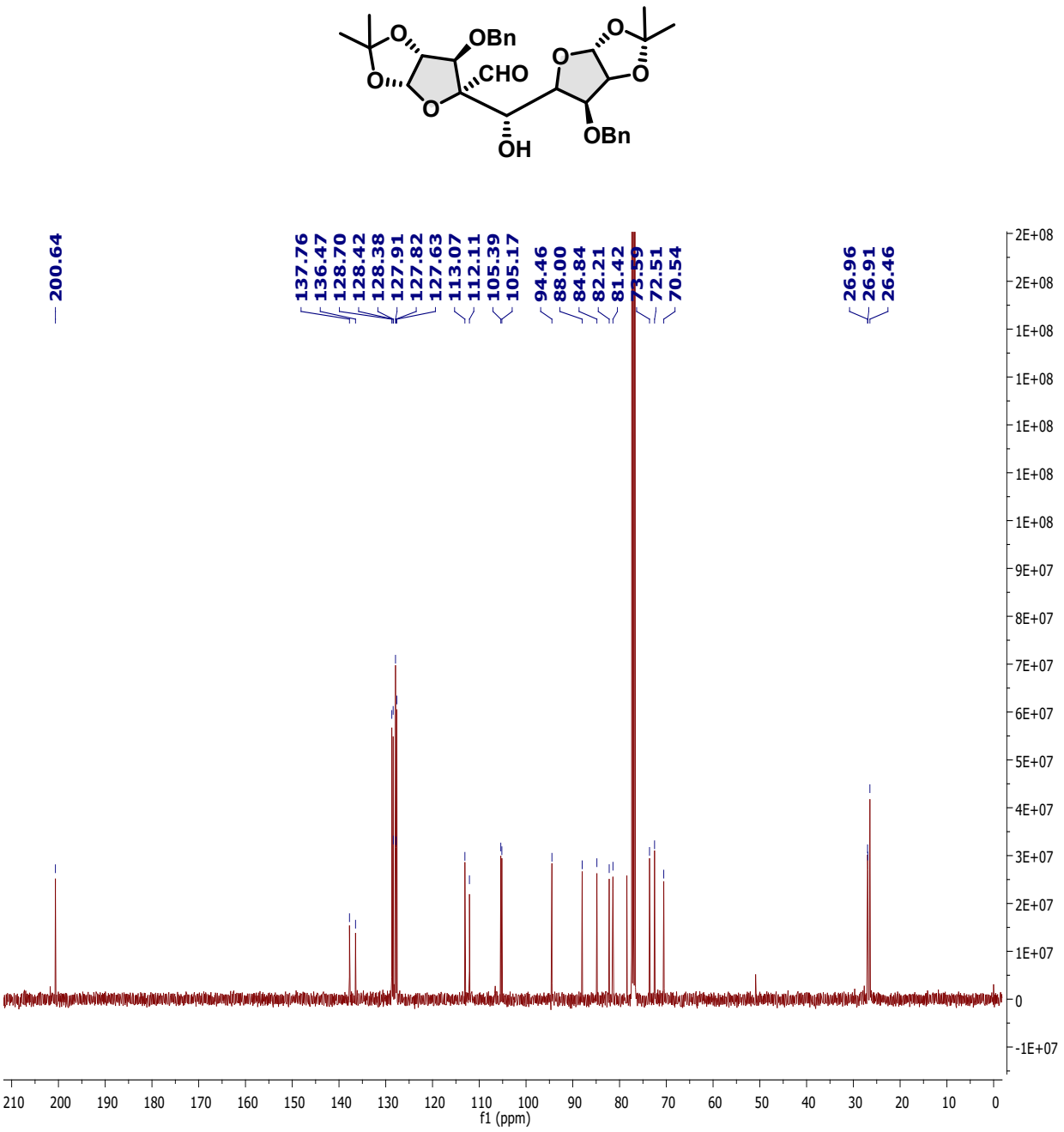
MHz, $CDCl_3$) δ 143.7, 136.5, 136.1, 131.7, 128.7, 127.50, 127.47, 127.1, 127.0, 126.9, 126.7, 126.6, 113.7, 110.8, 104.4, 104.2, 87.7, 86.8, 85.7, 81.5, 80.2, 76.6, 72.4, 71.4, 68.4, 67.7, 26.9, 26.8, 25.8, 25.3, 20.5. **HRMS** calcd for $C_{37}H_{45}O_{12}S$ $[M + H]^+$ 713.2632, found 713.2635.

7. NMR Spectrum

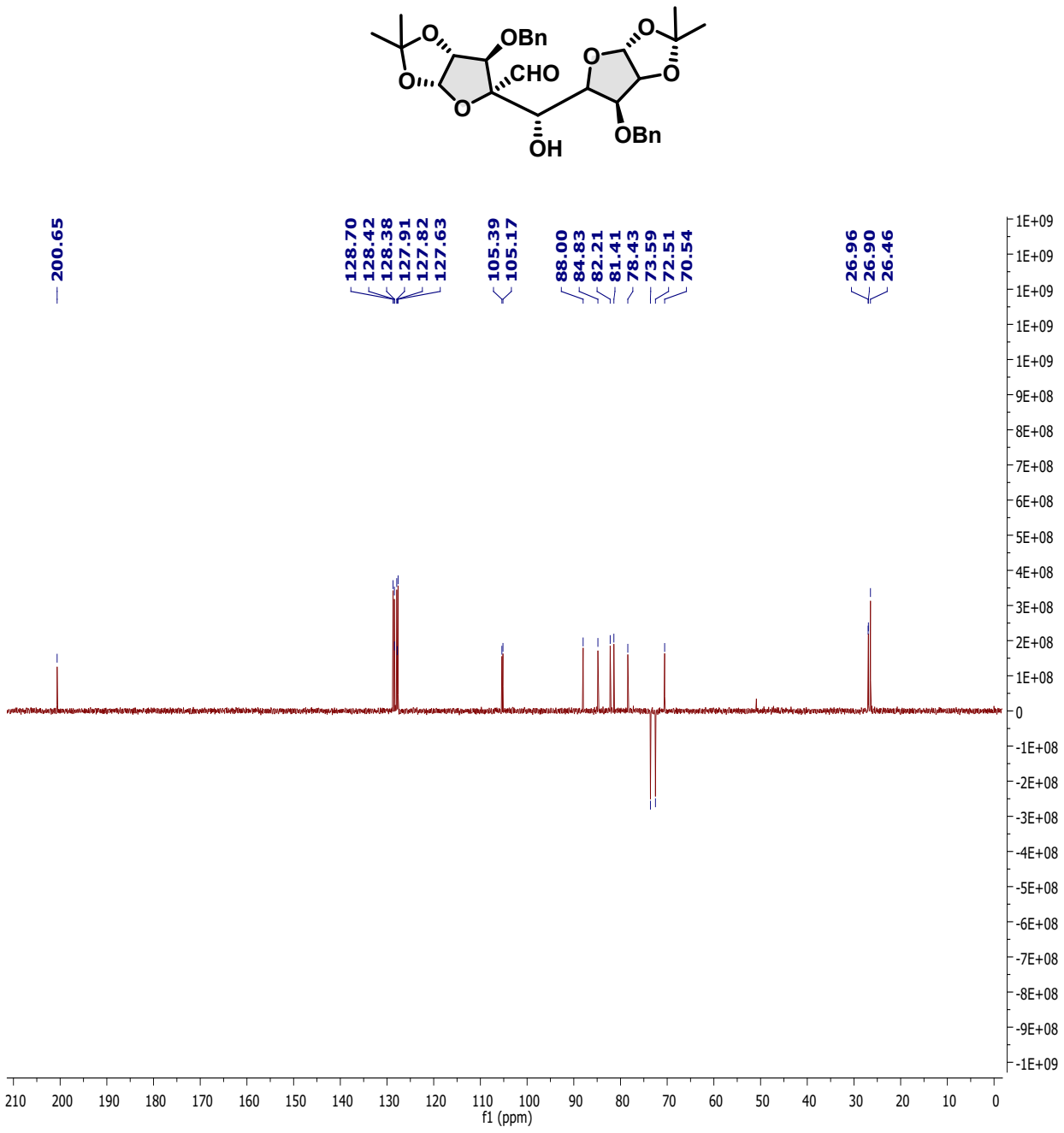
^{1}H NMR (400 MHz, $CDCl_3$) of compound 2a



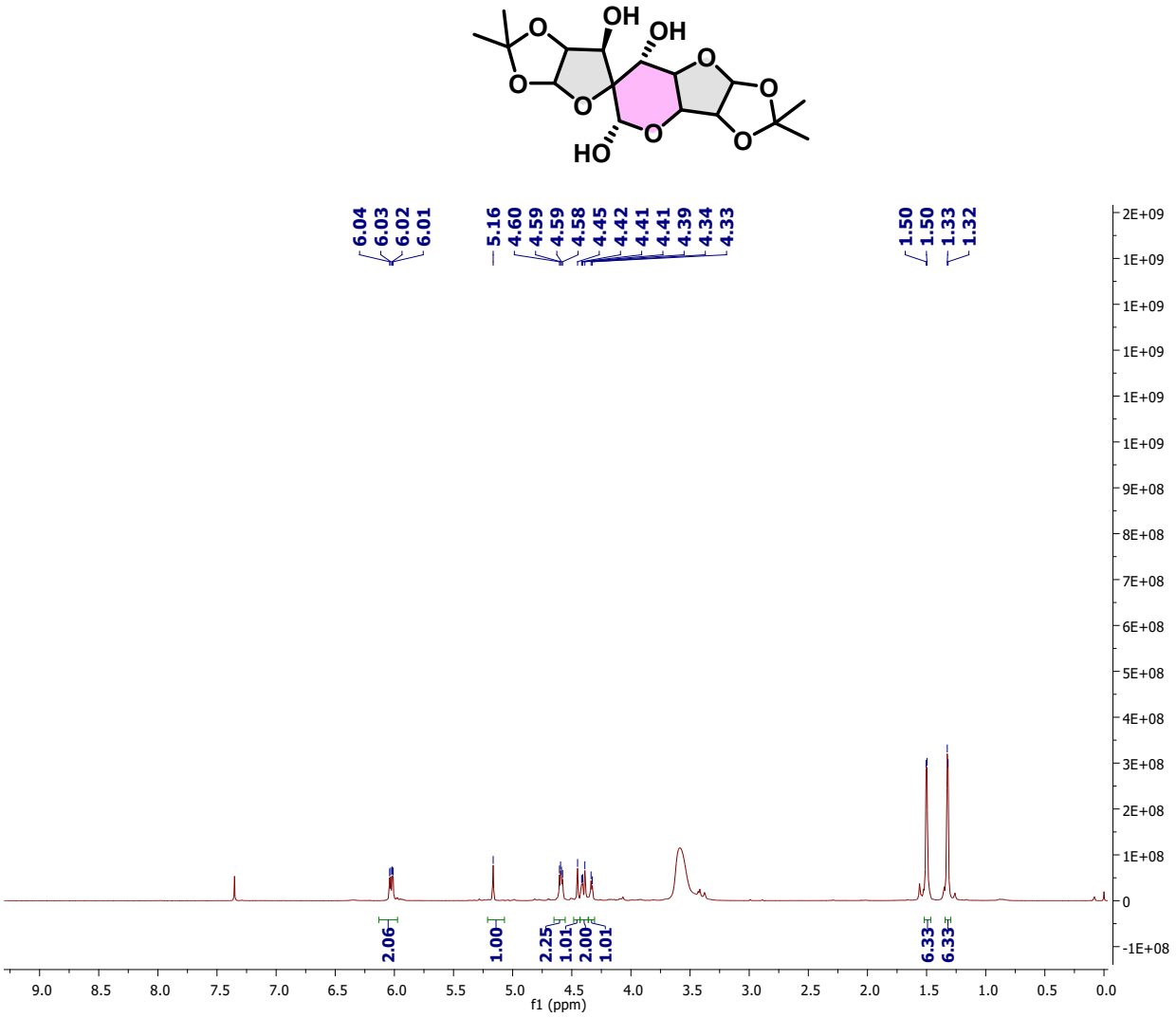
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 2a



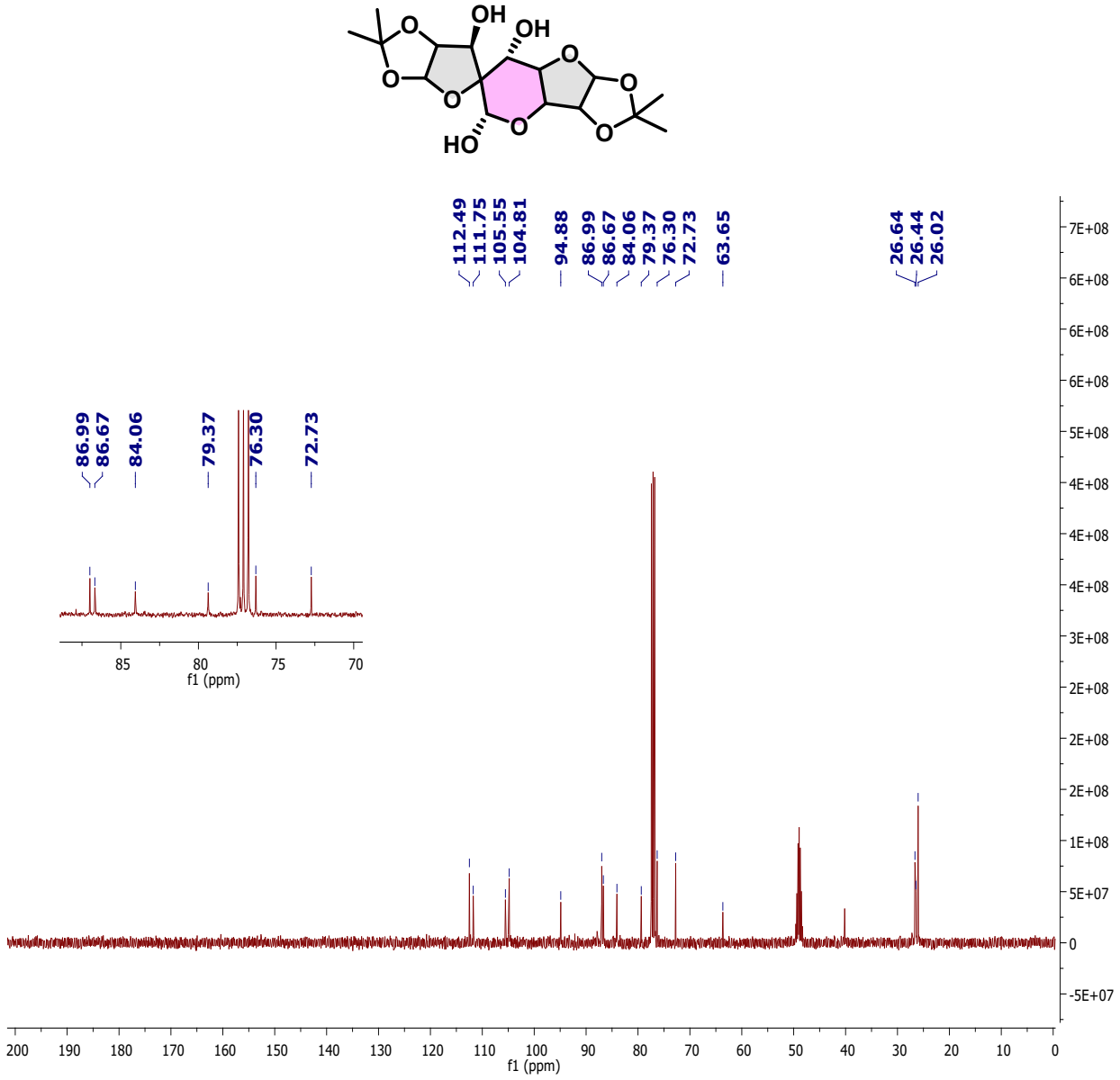
DEPT NMR (101 MHz, $CDCl_3$) of compound 2a



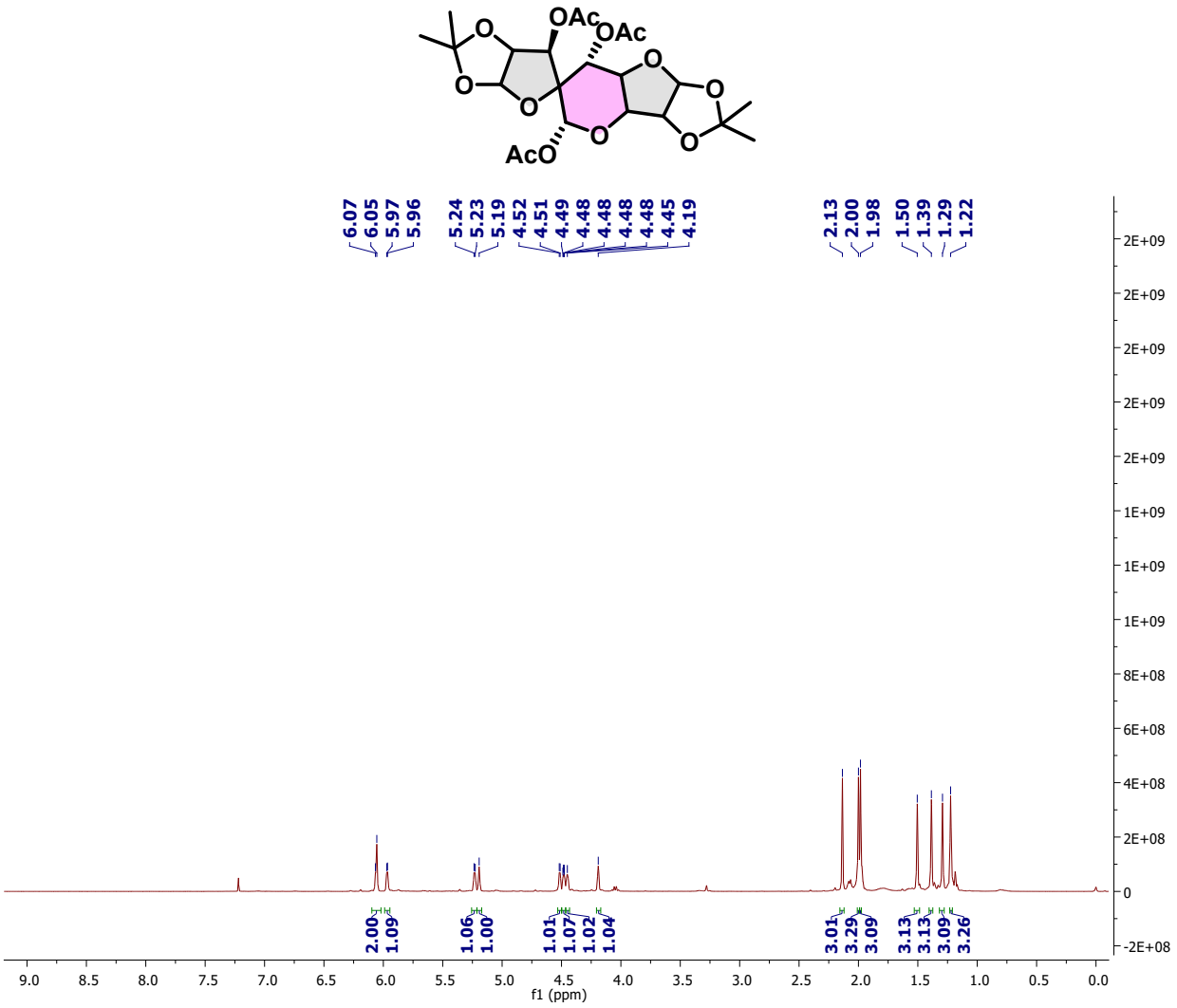
^{1}H NMR (400 MHz, $CDCl_3$ + MeOD) of compound 3a



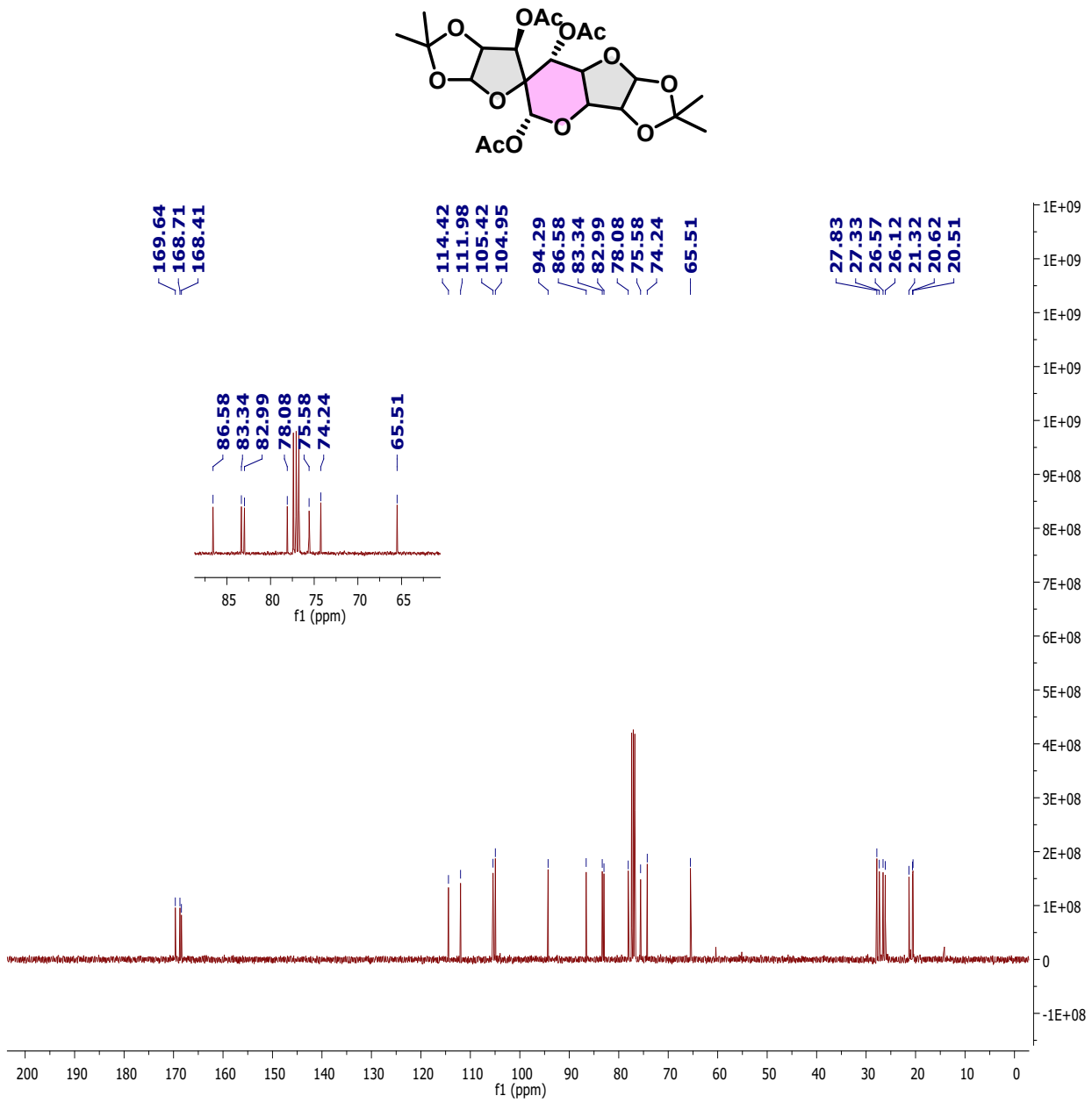
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$ + MeOD) of compound 3a



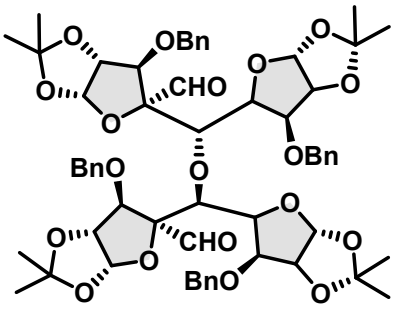
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3b

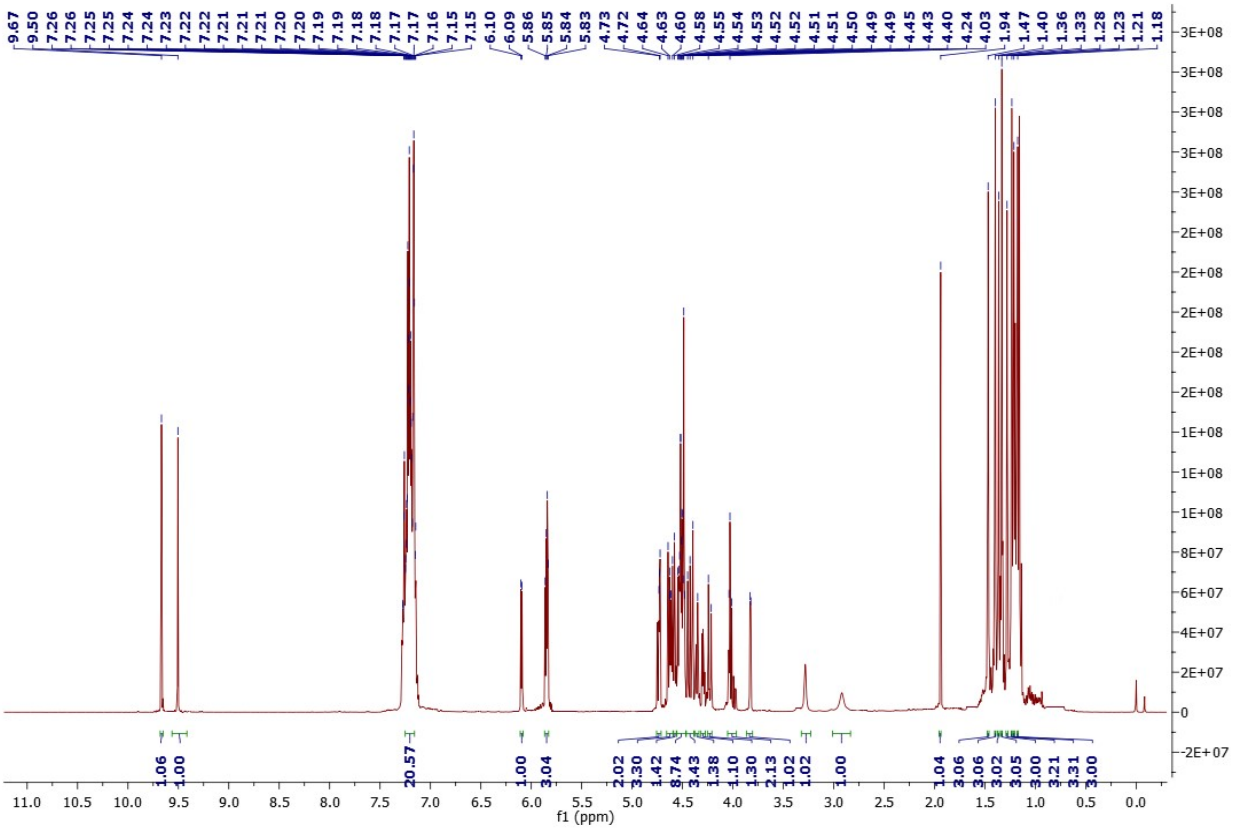


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3b

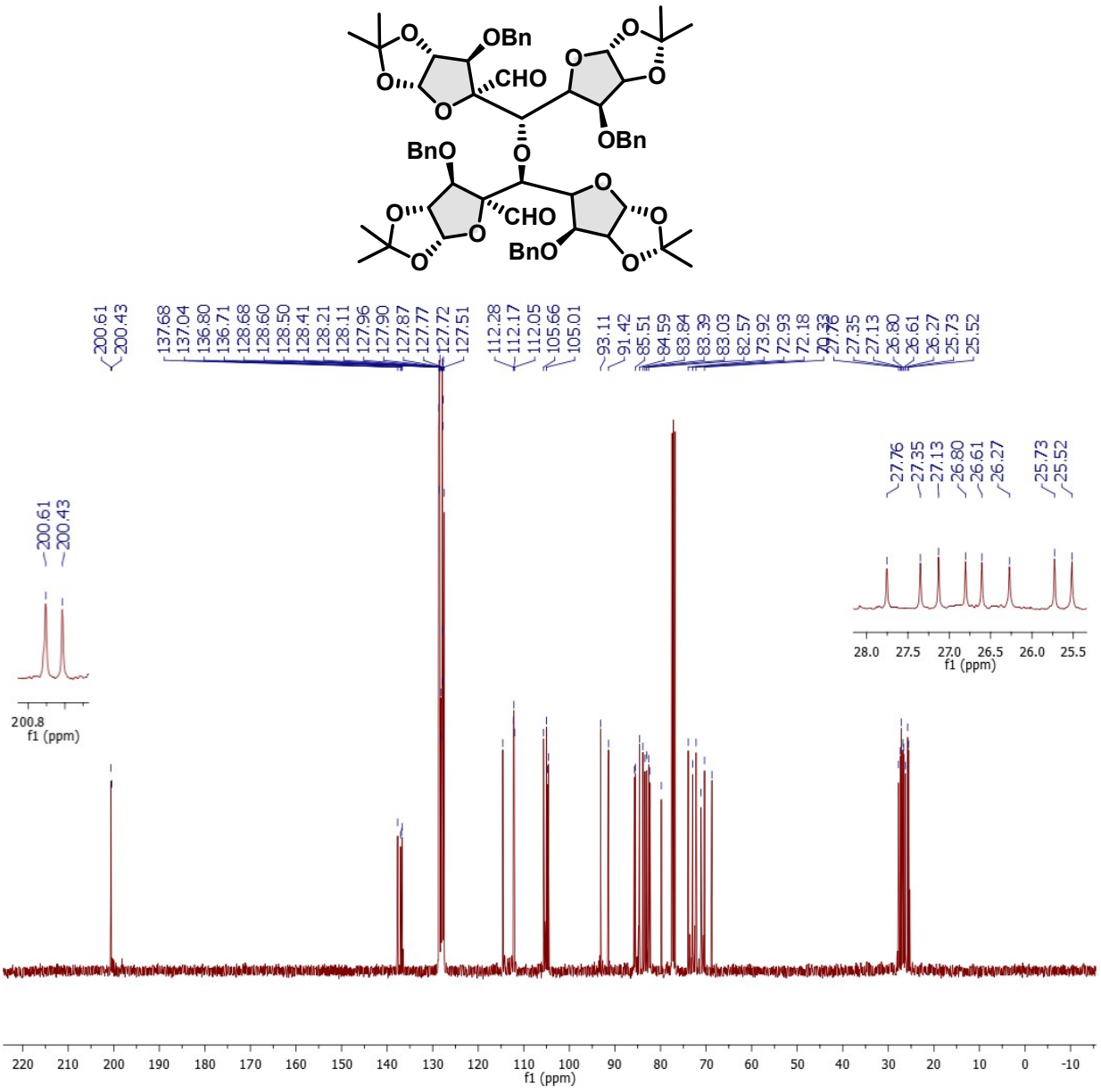


^{1}H NMR (400 MHz, $CDCl_3$) of compound 3c

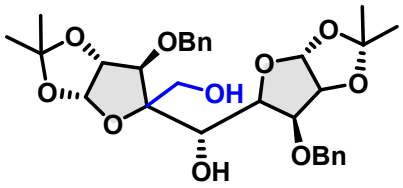


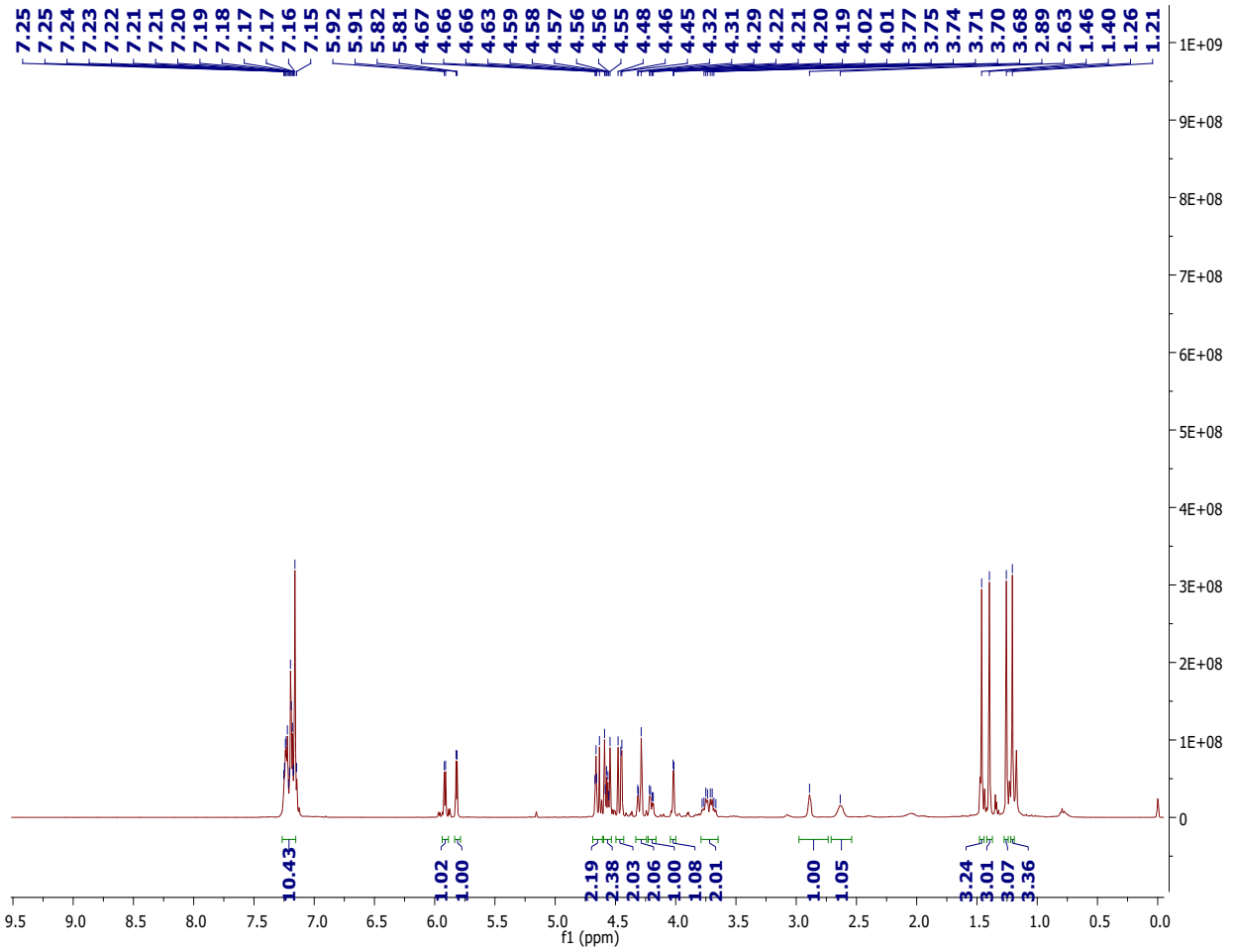


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3c

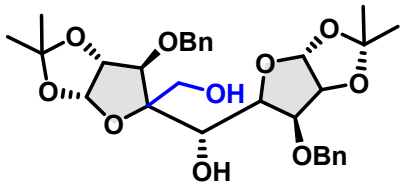


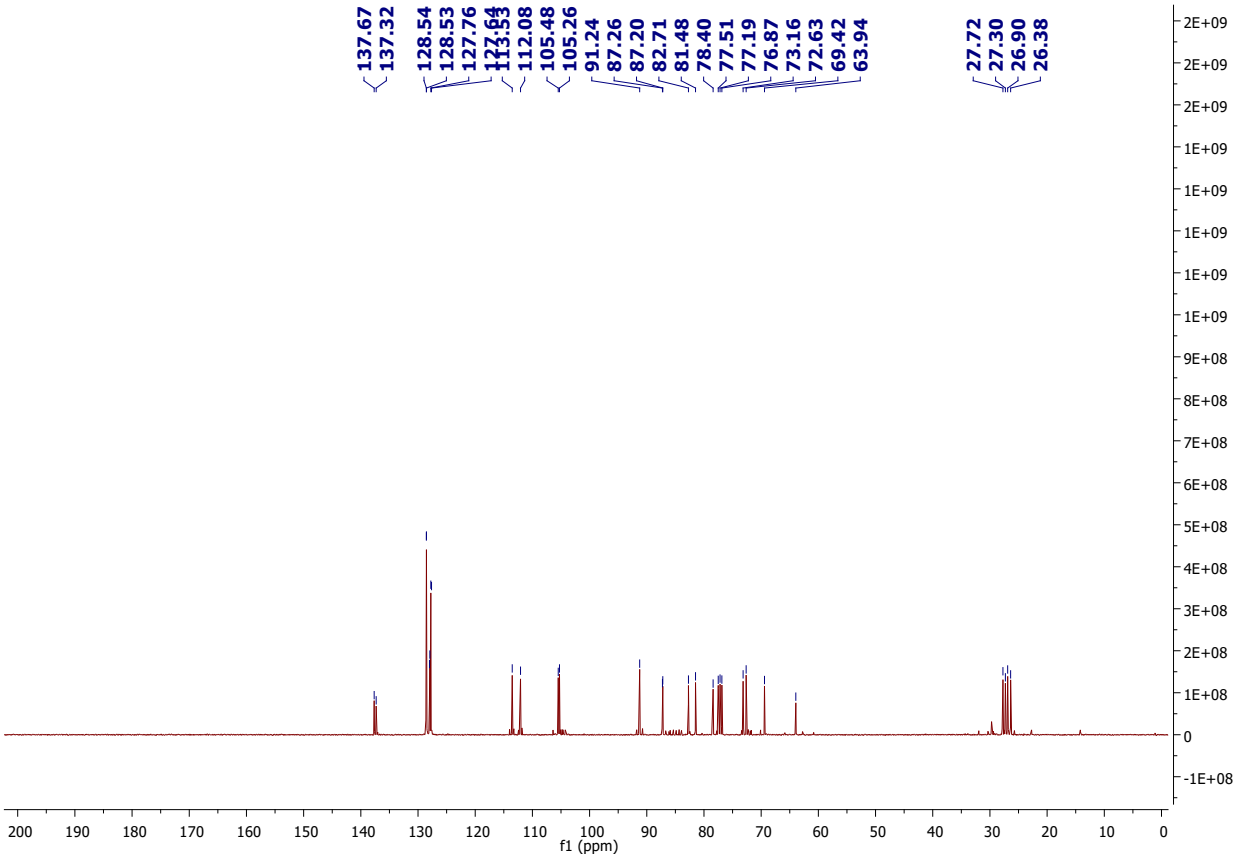
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4a



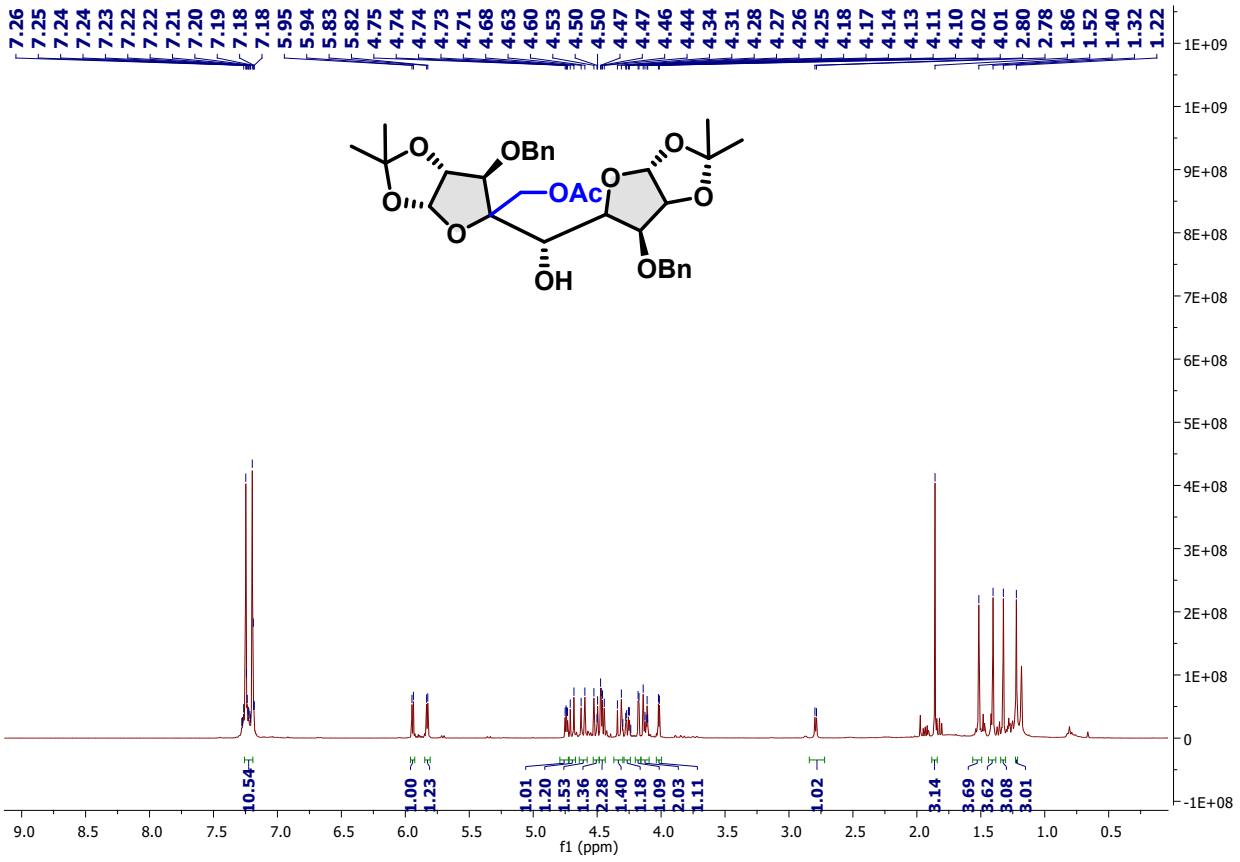


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 4a

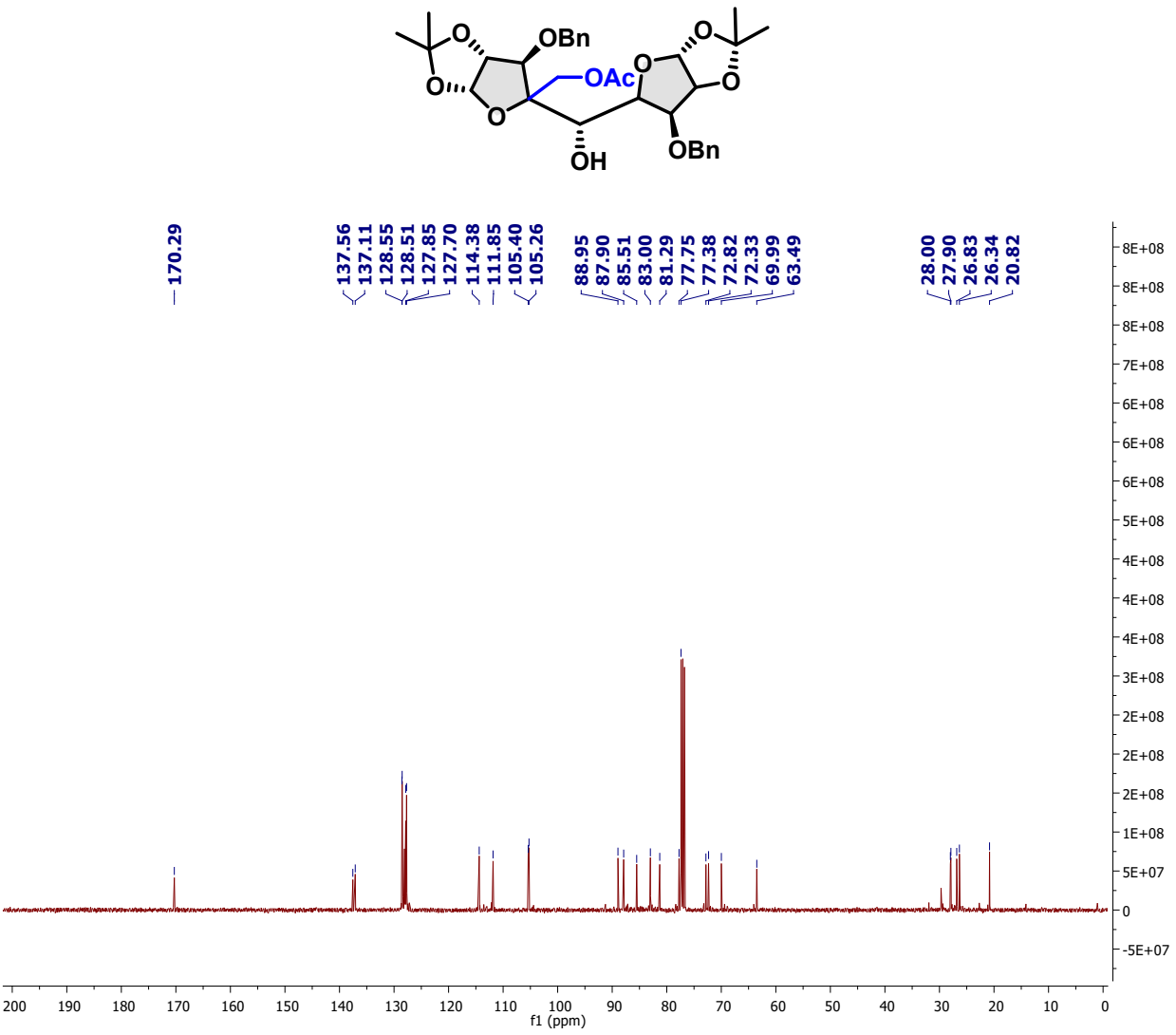




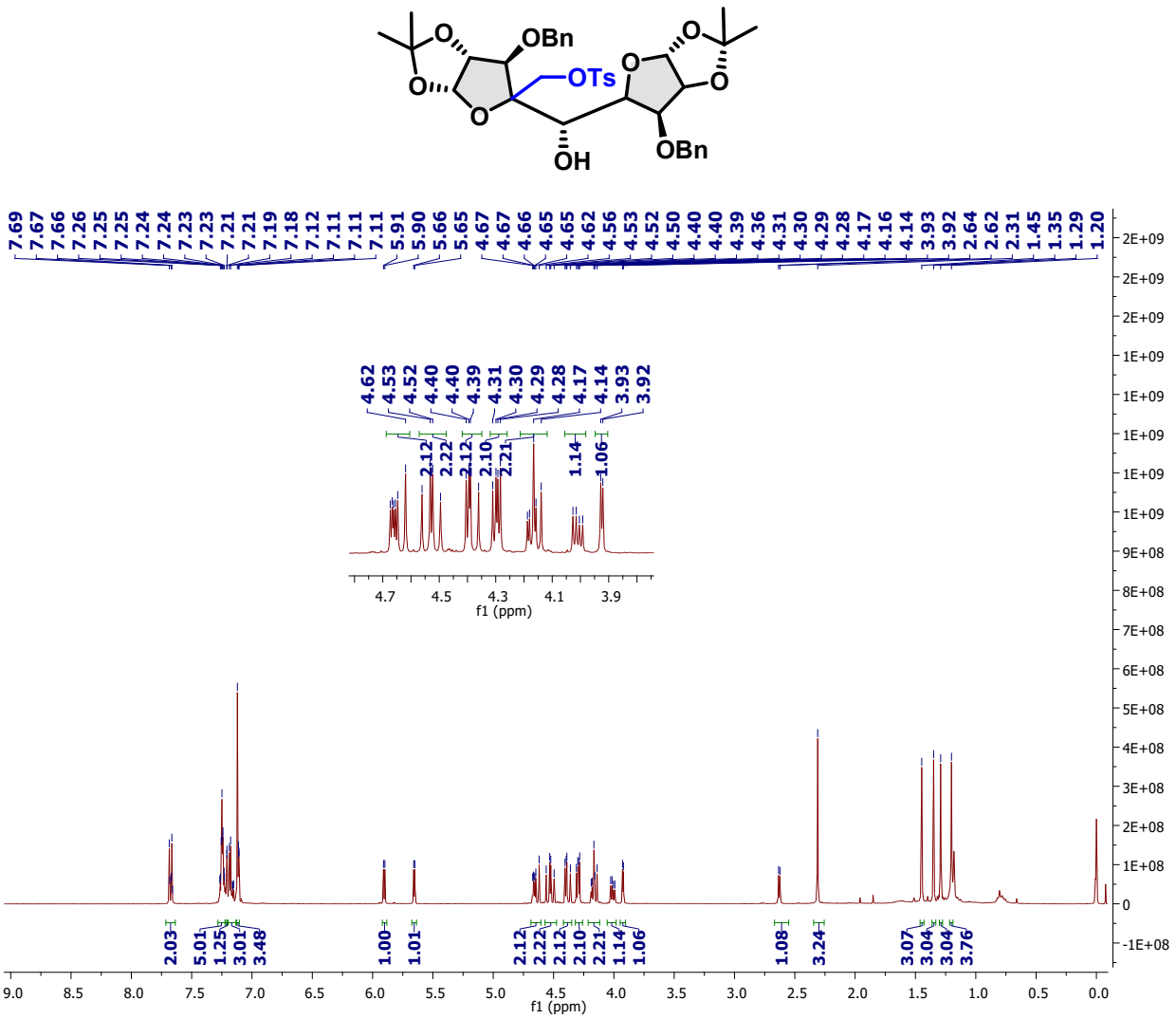
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5a



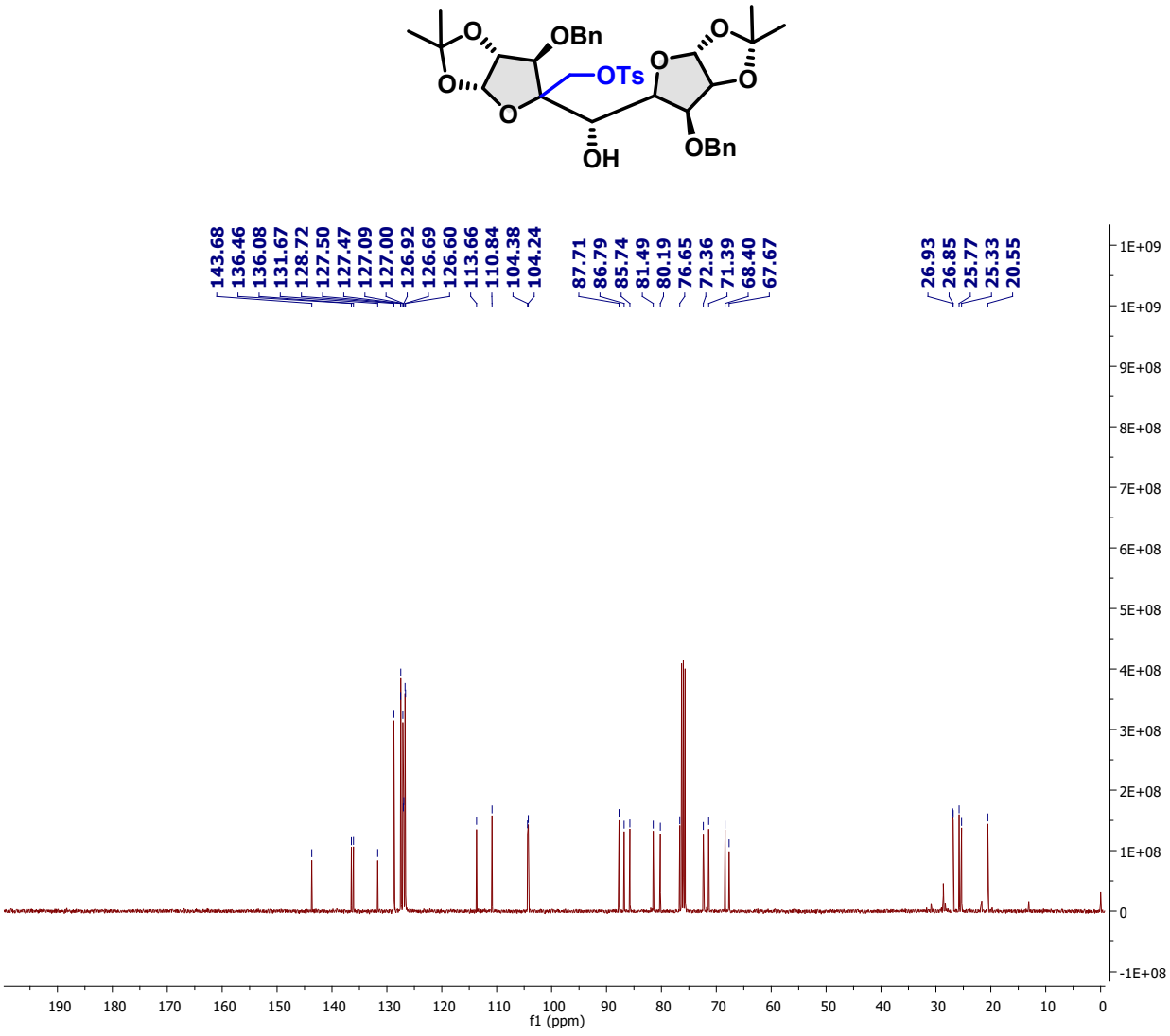
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5a



^{1}H NMR (400 MHz, $CDCl_3$) of compound 5b



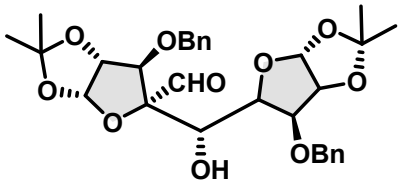
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5b

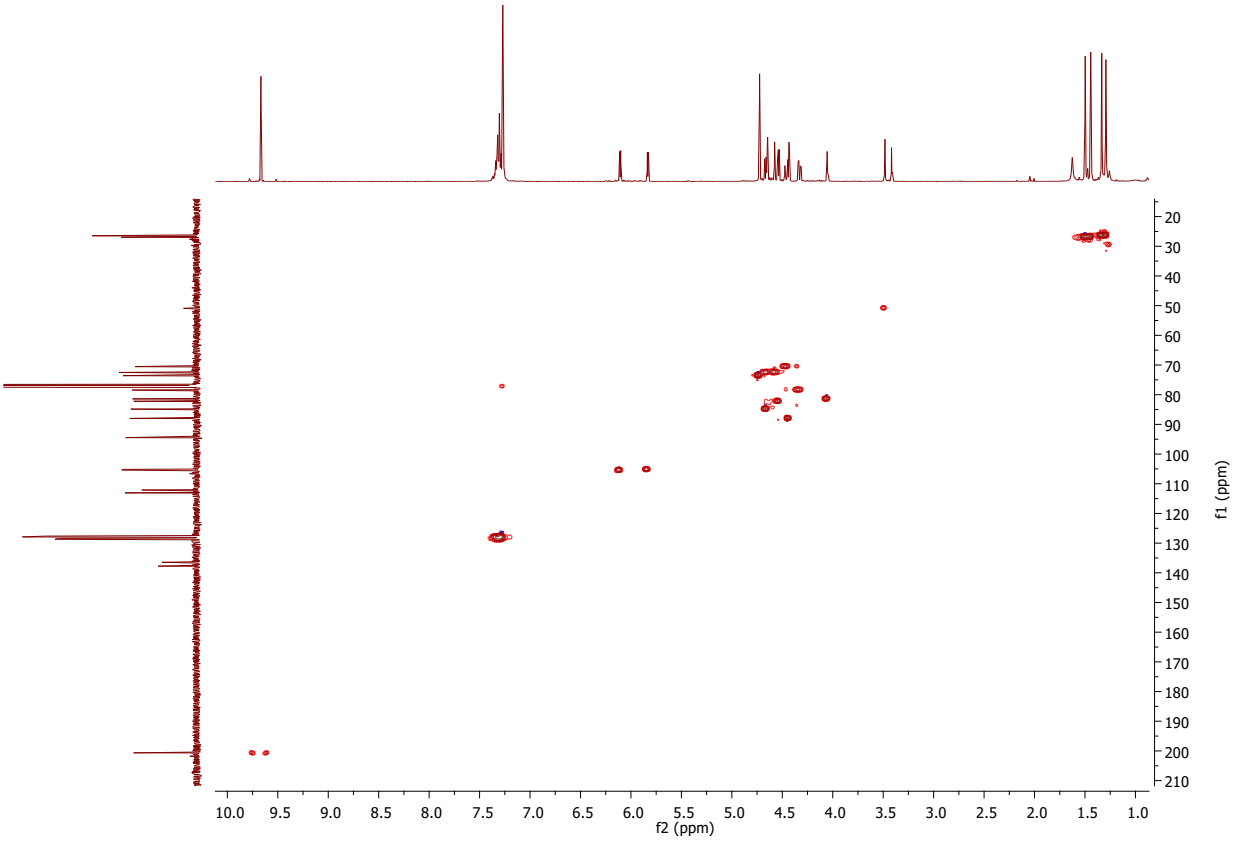


8. 2D-Data

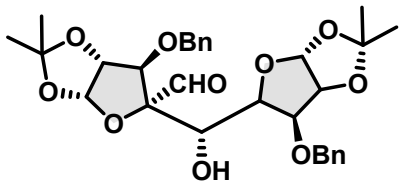
7A. 2D Spectrum of Compound 2a

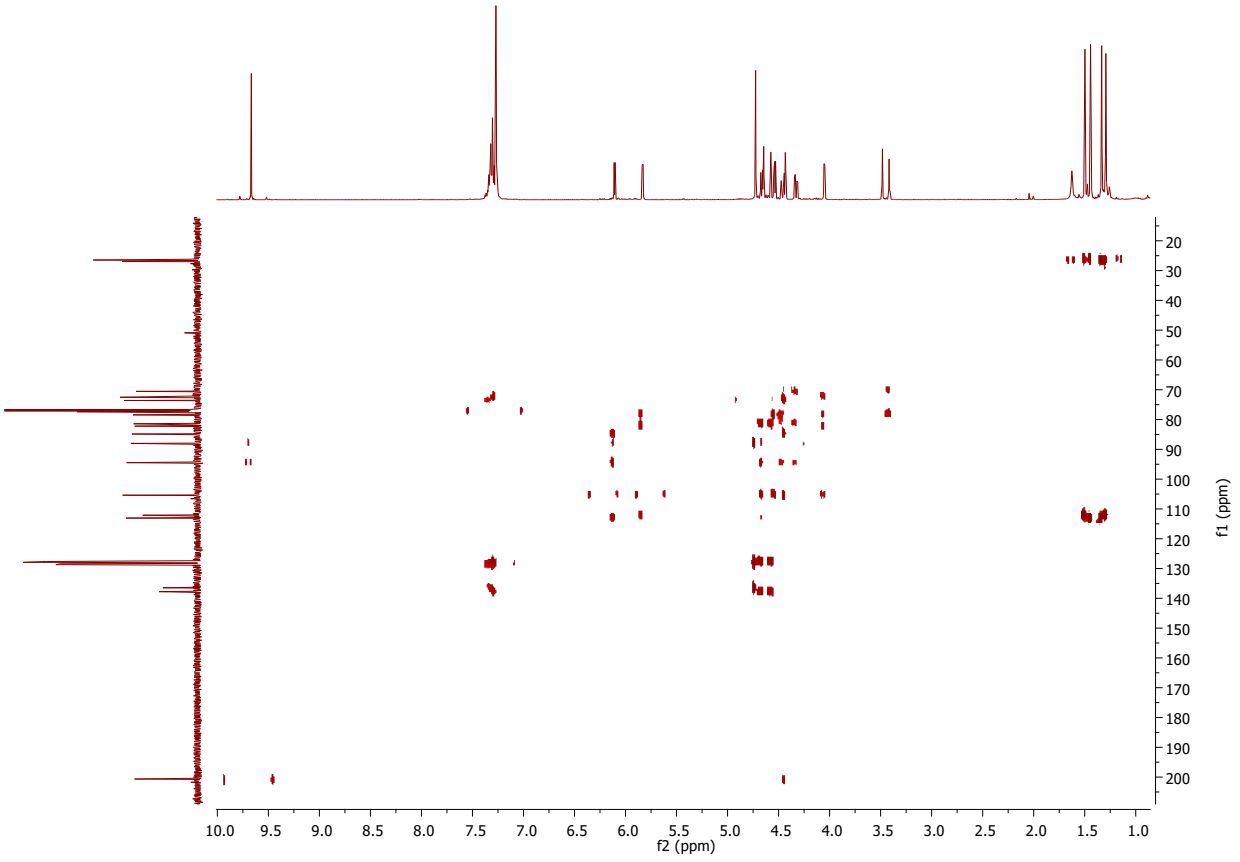
HSQC Spectrum of 2a



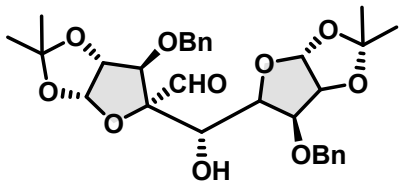


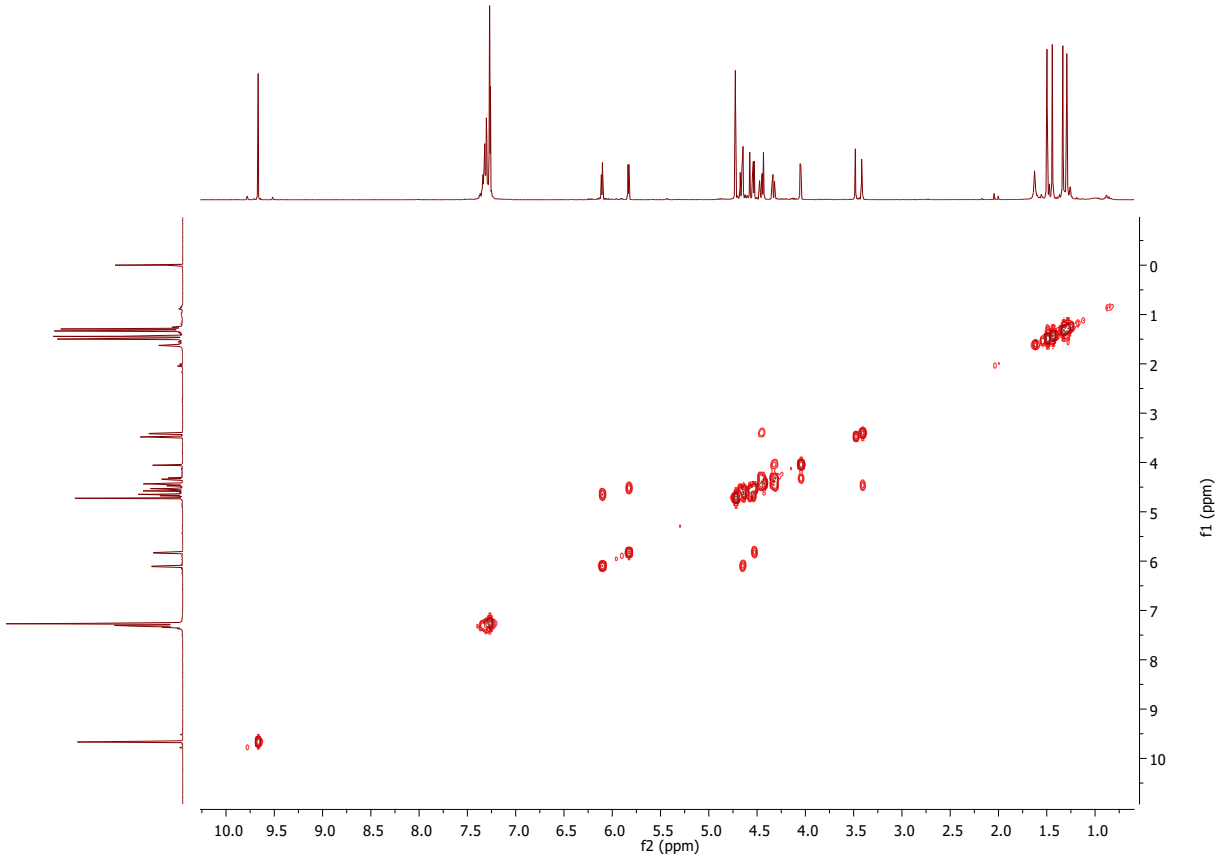
HMBC Spectrum of 2a



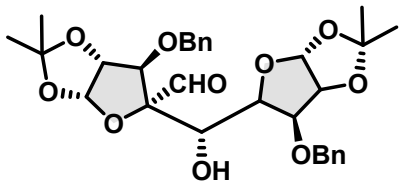


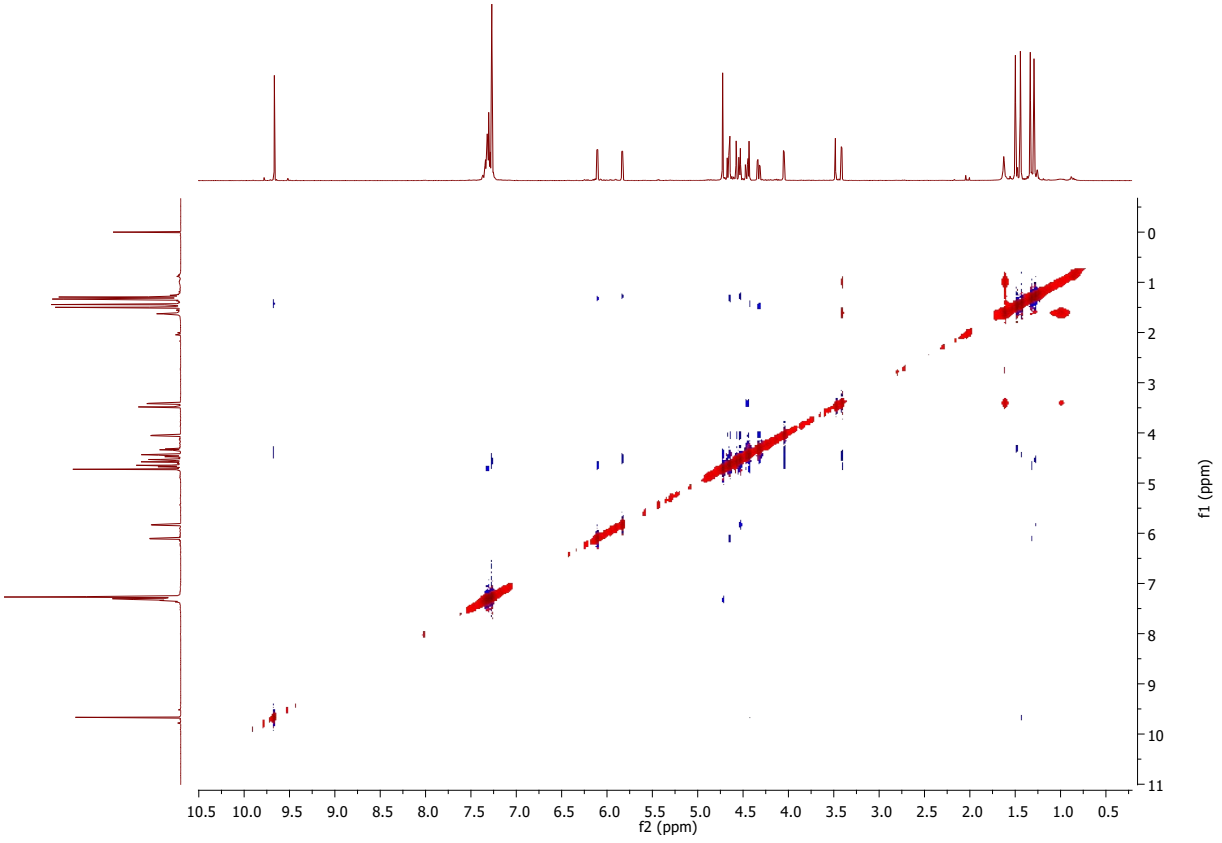
COSY Spectrum of 2a





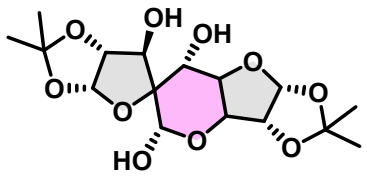
NOESY Spectrum of 2a

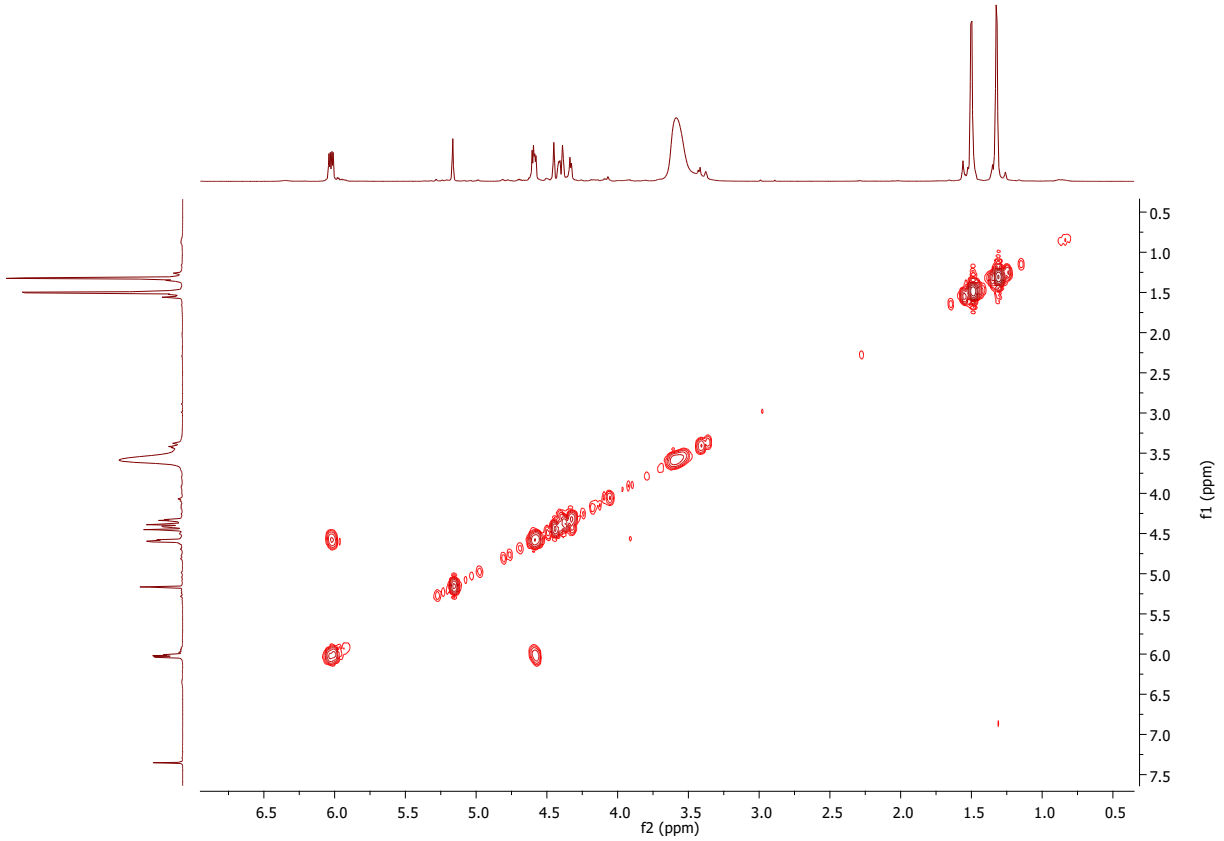




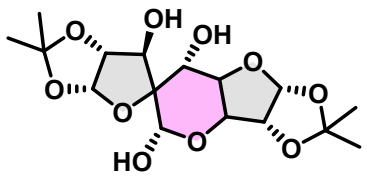
7B. 2D Spectrum of compound 3a

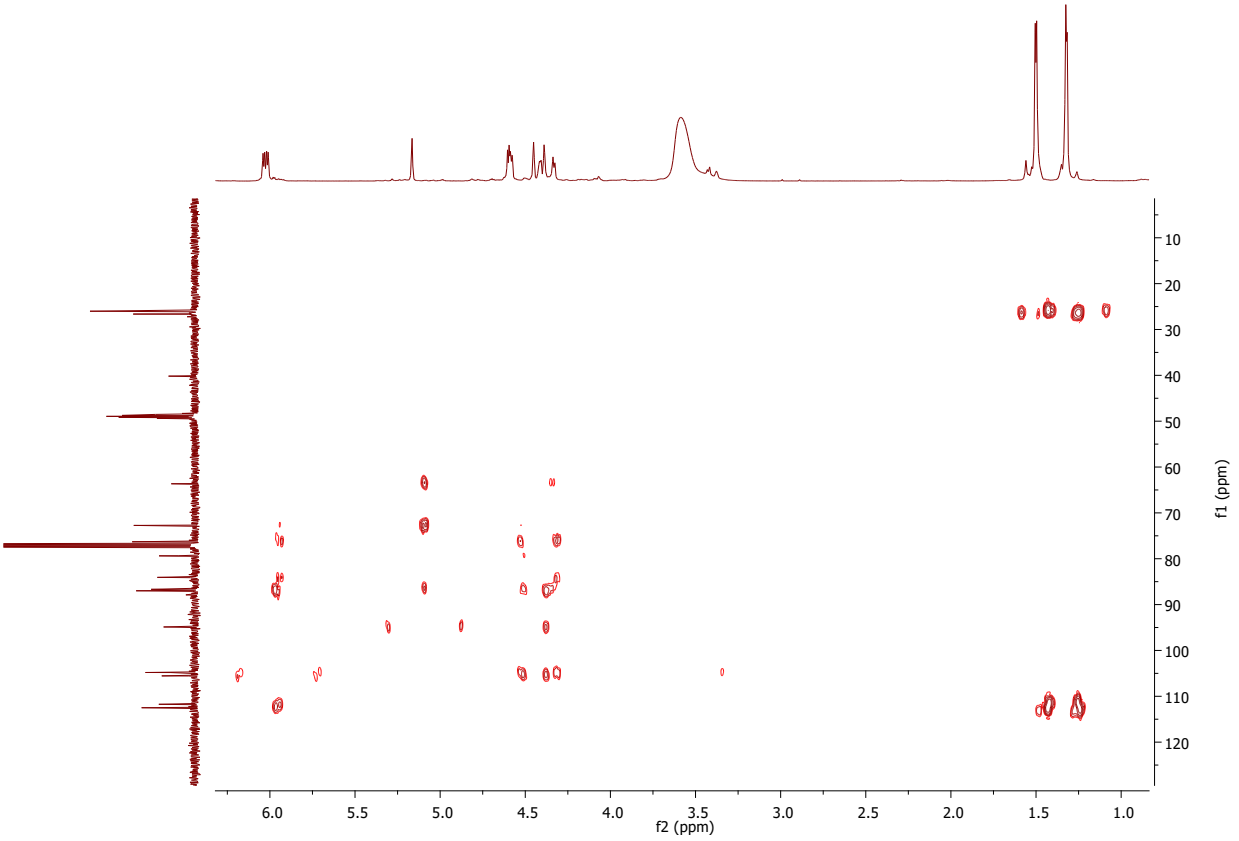
COSY Spectrum of 3a



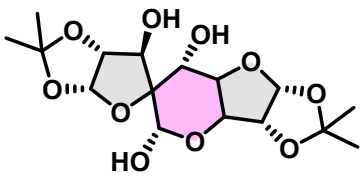


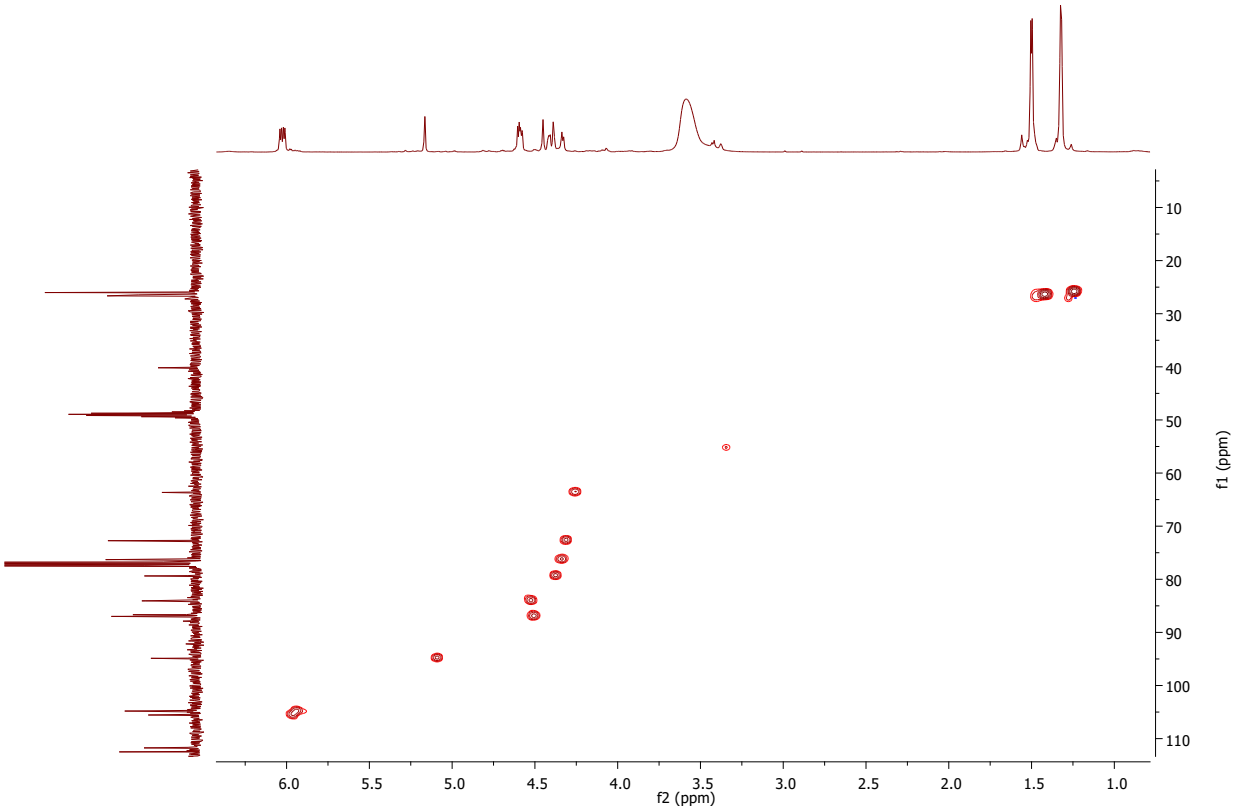
HMBC Spectrum of 3a



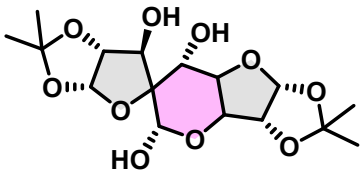


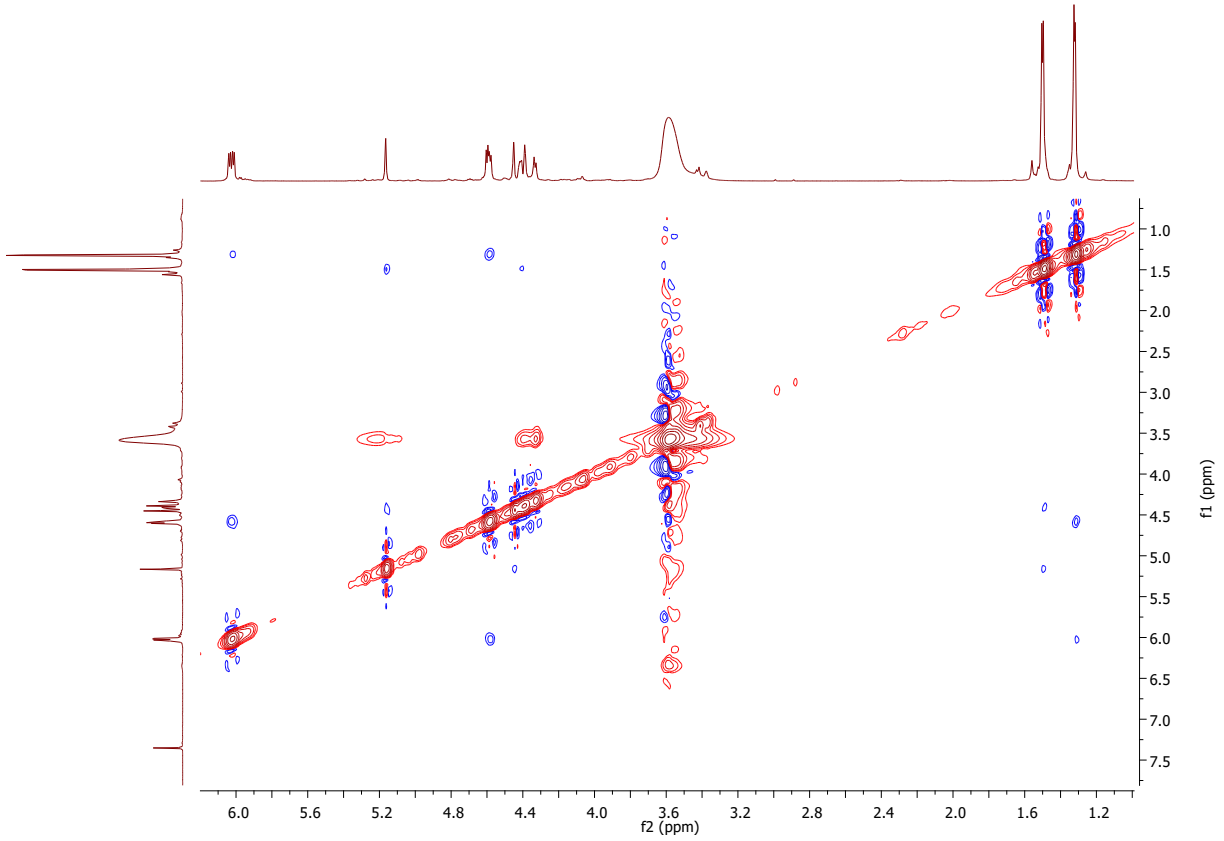
HSQC Spectrum of 3a





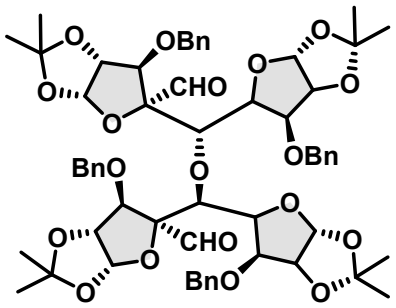
NOESY Spectrum of 3a

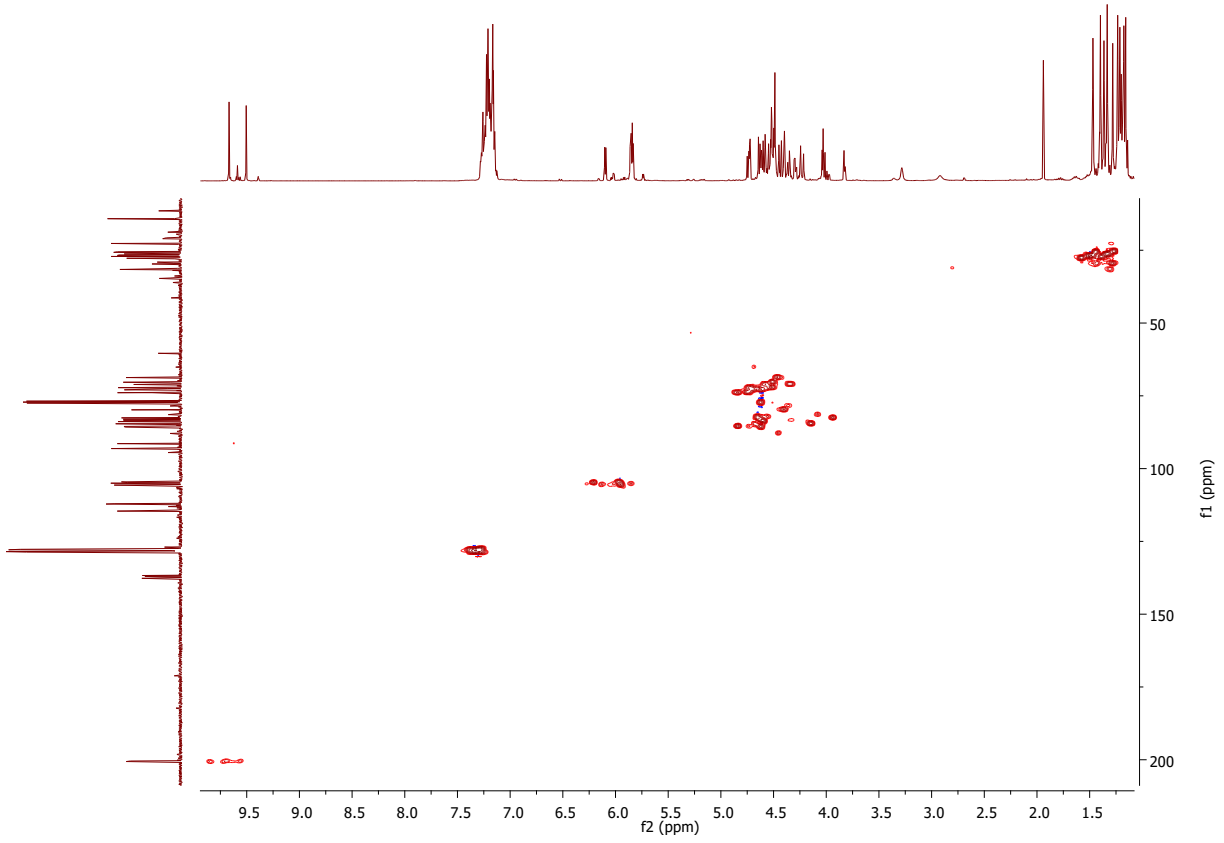




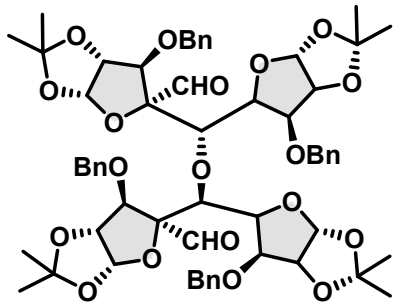
7C. 2D spectrum of compound 3c

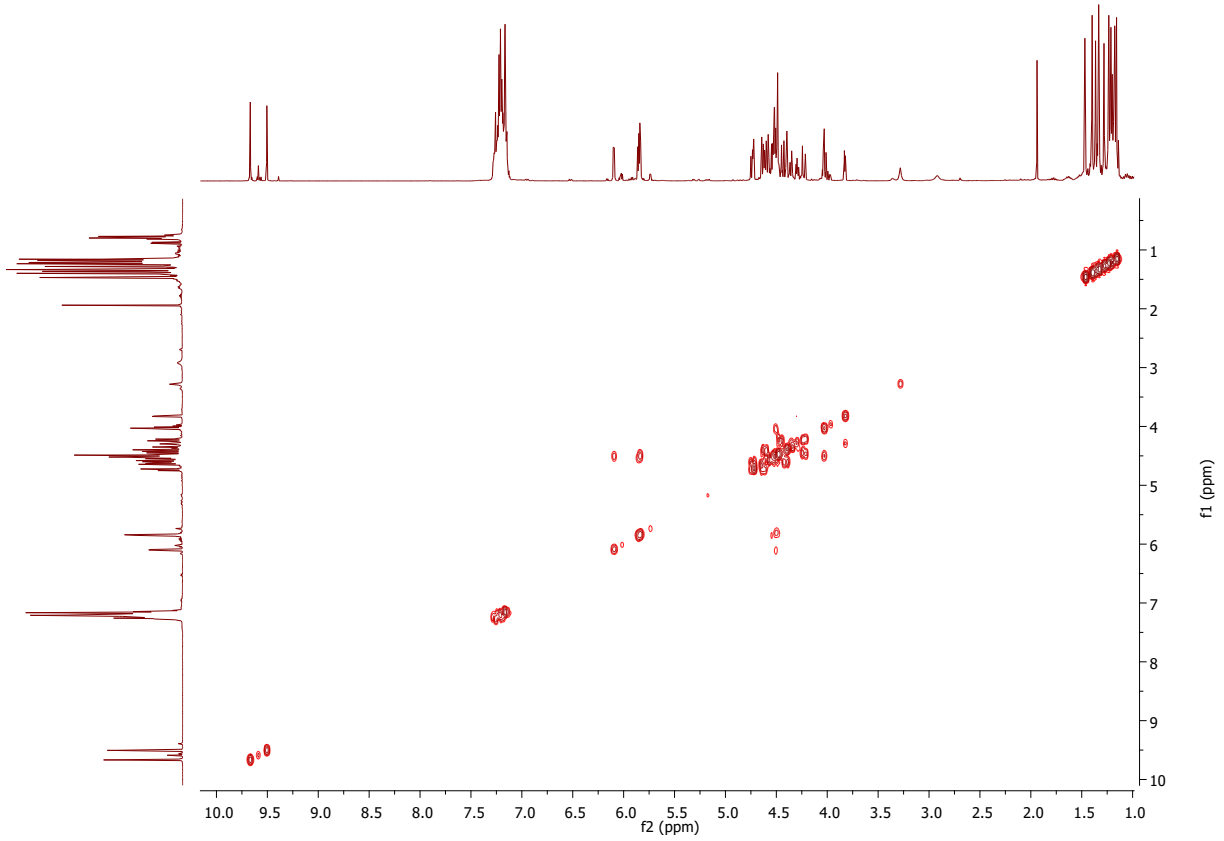
HSQC Spectrum of 3c



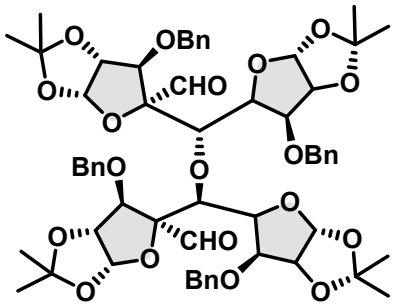


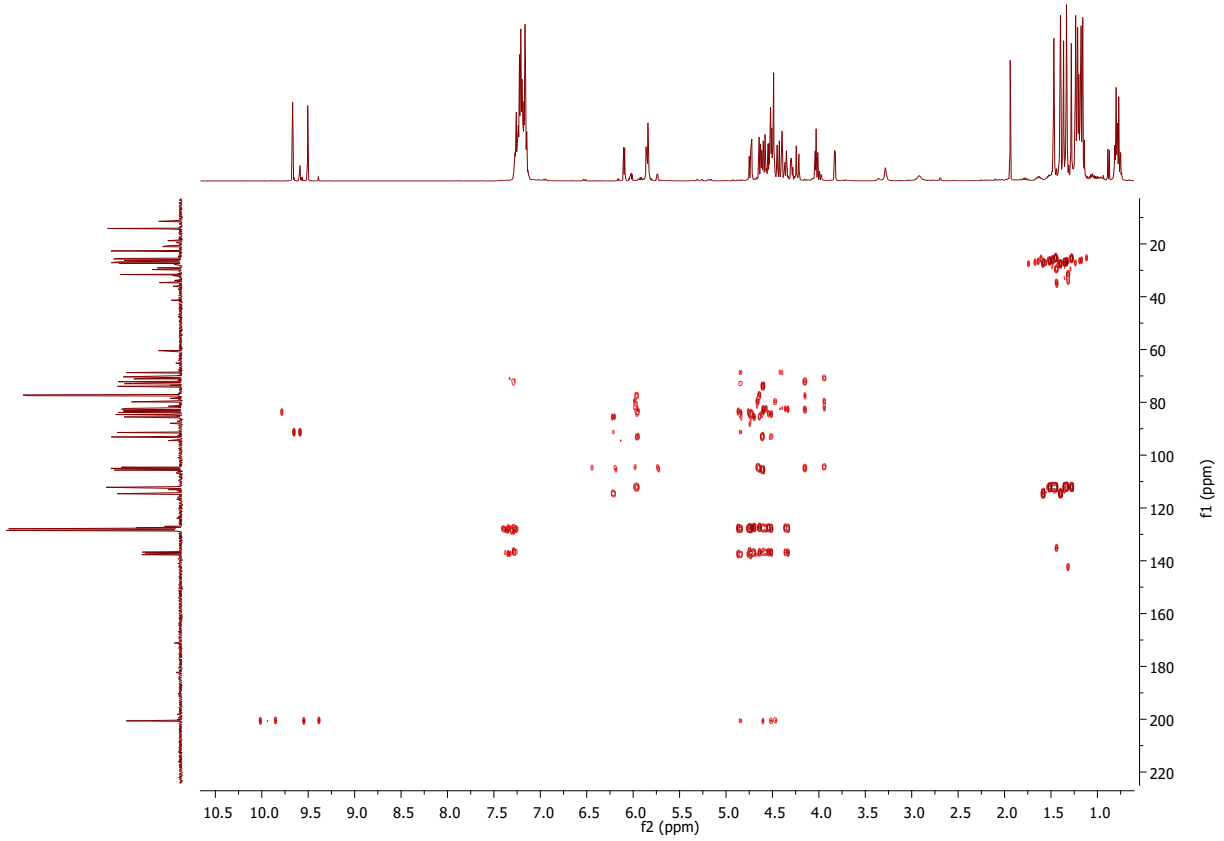
COSY Spectrum of 3c



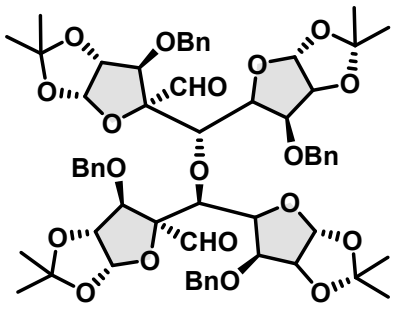


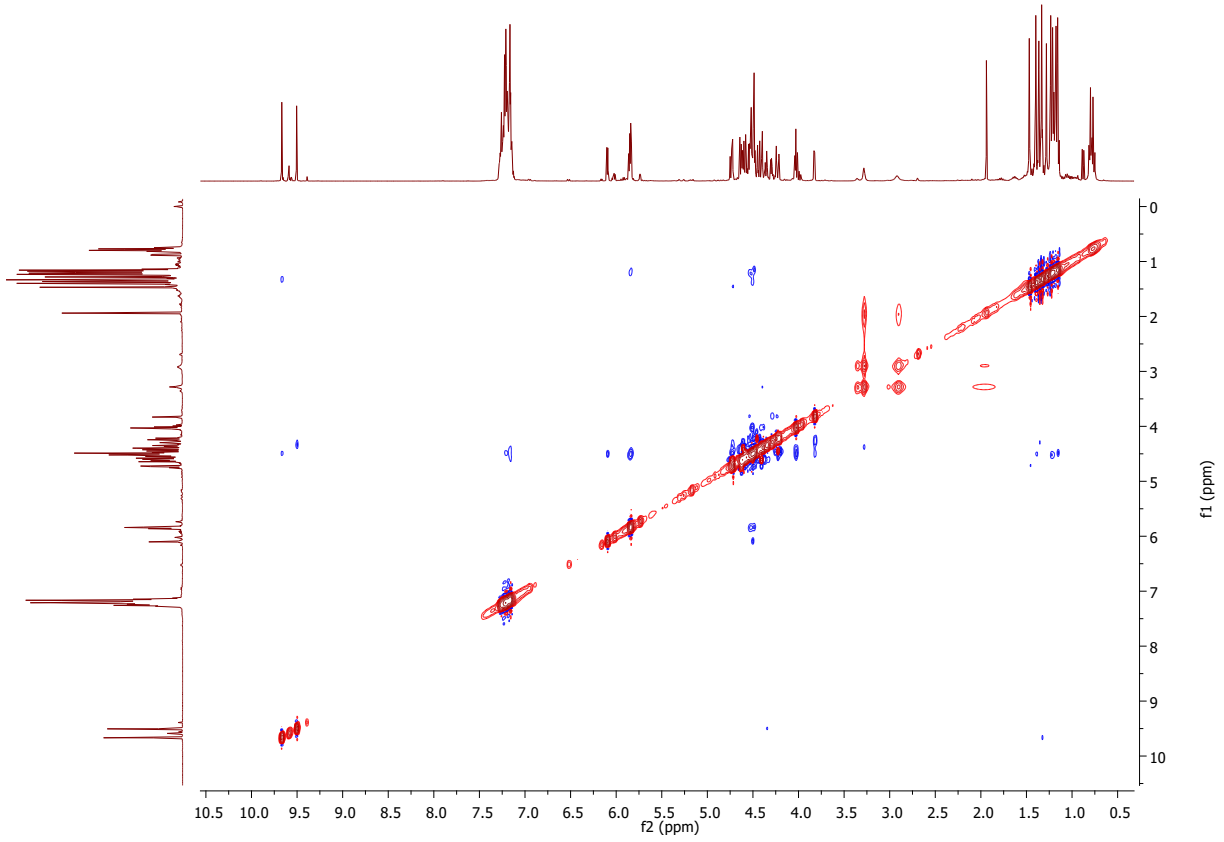
HMBC Spectrum of 3c





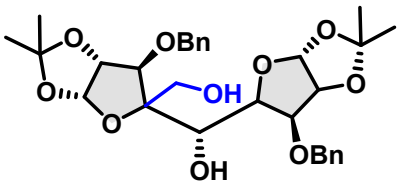
NOESY Spectrum of 3c

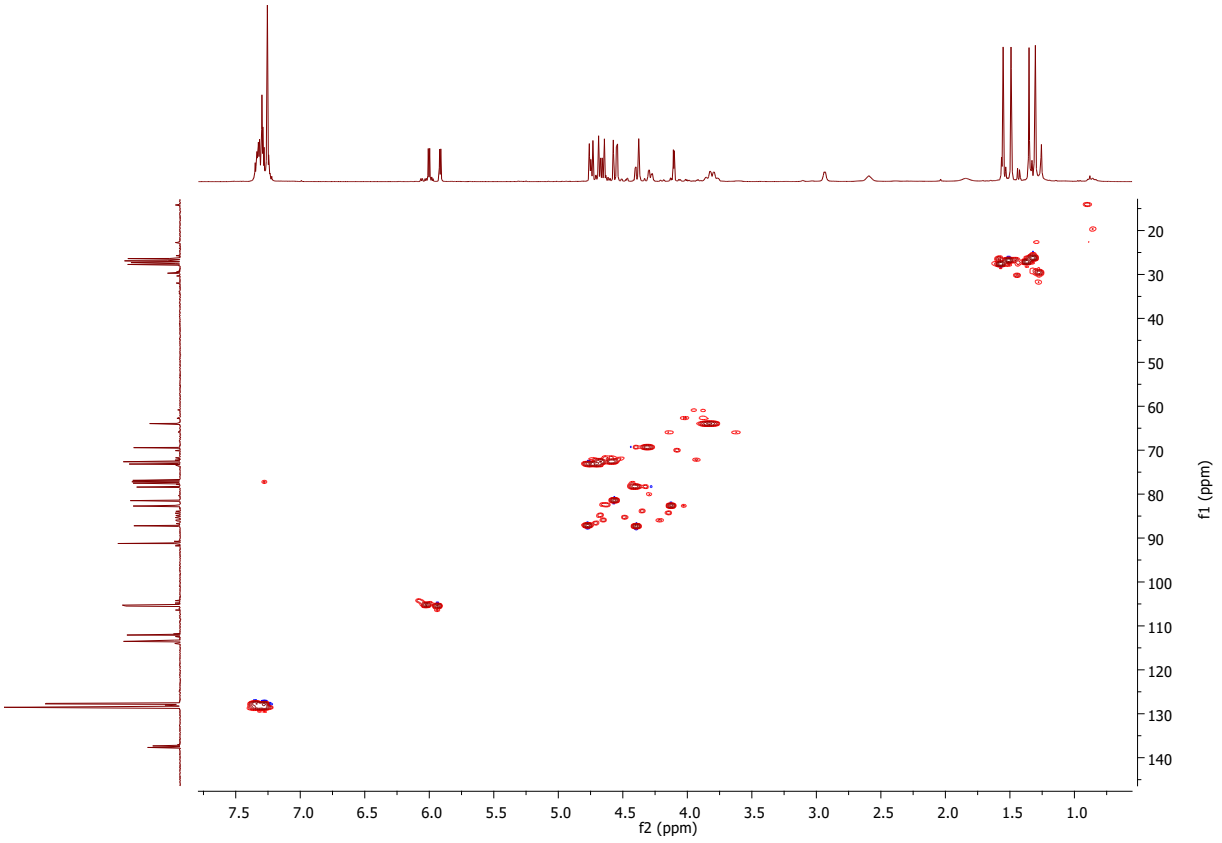




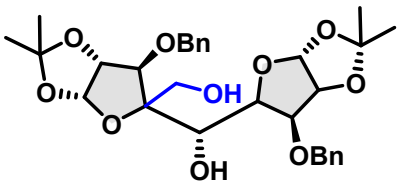
7D. 2D Spectrum of compound 4a

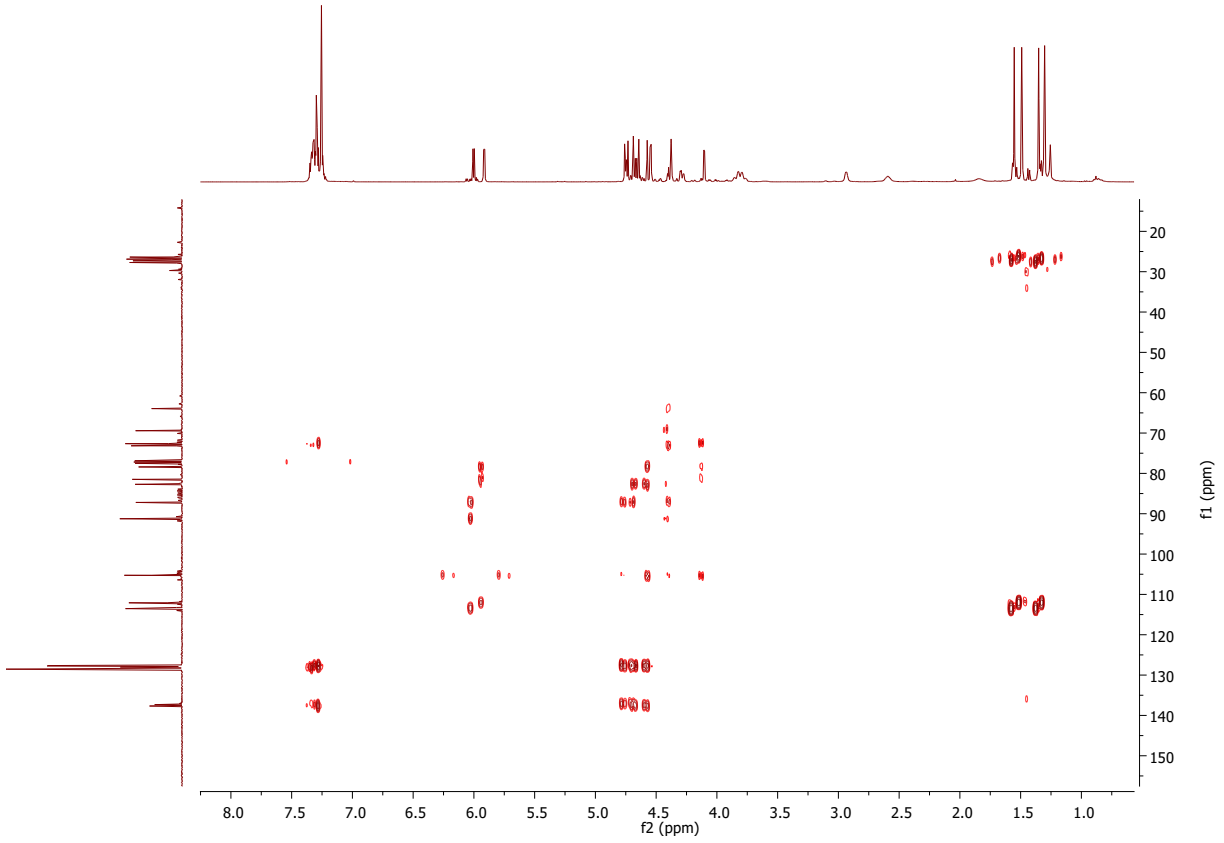
HSQC Spectrum of 4a



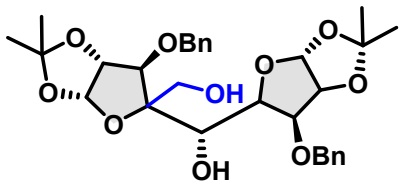


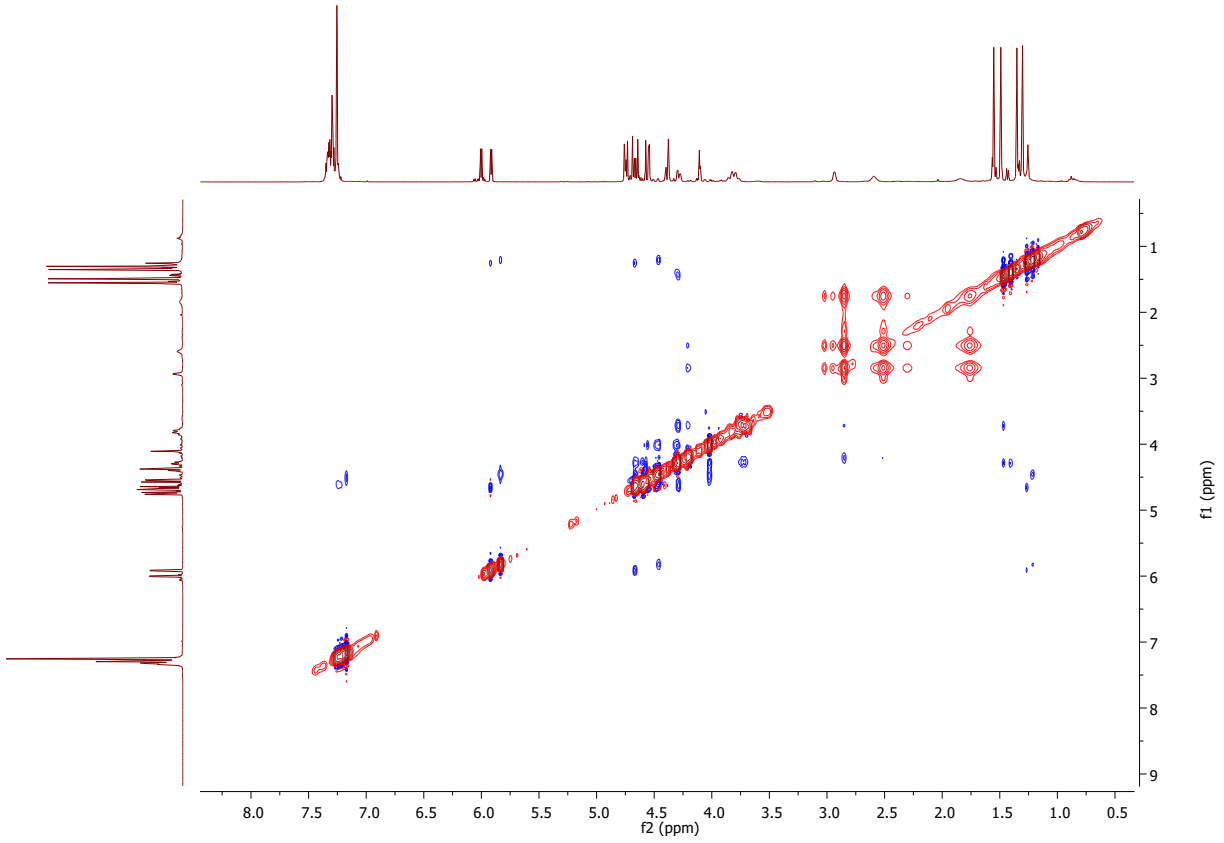
HMBC Spectrum of 4a





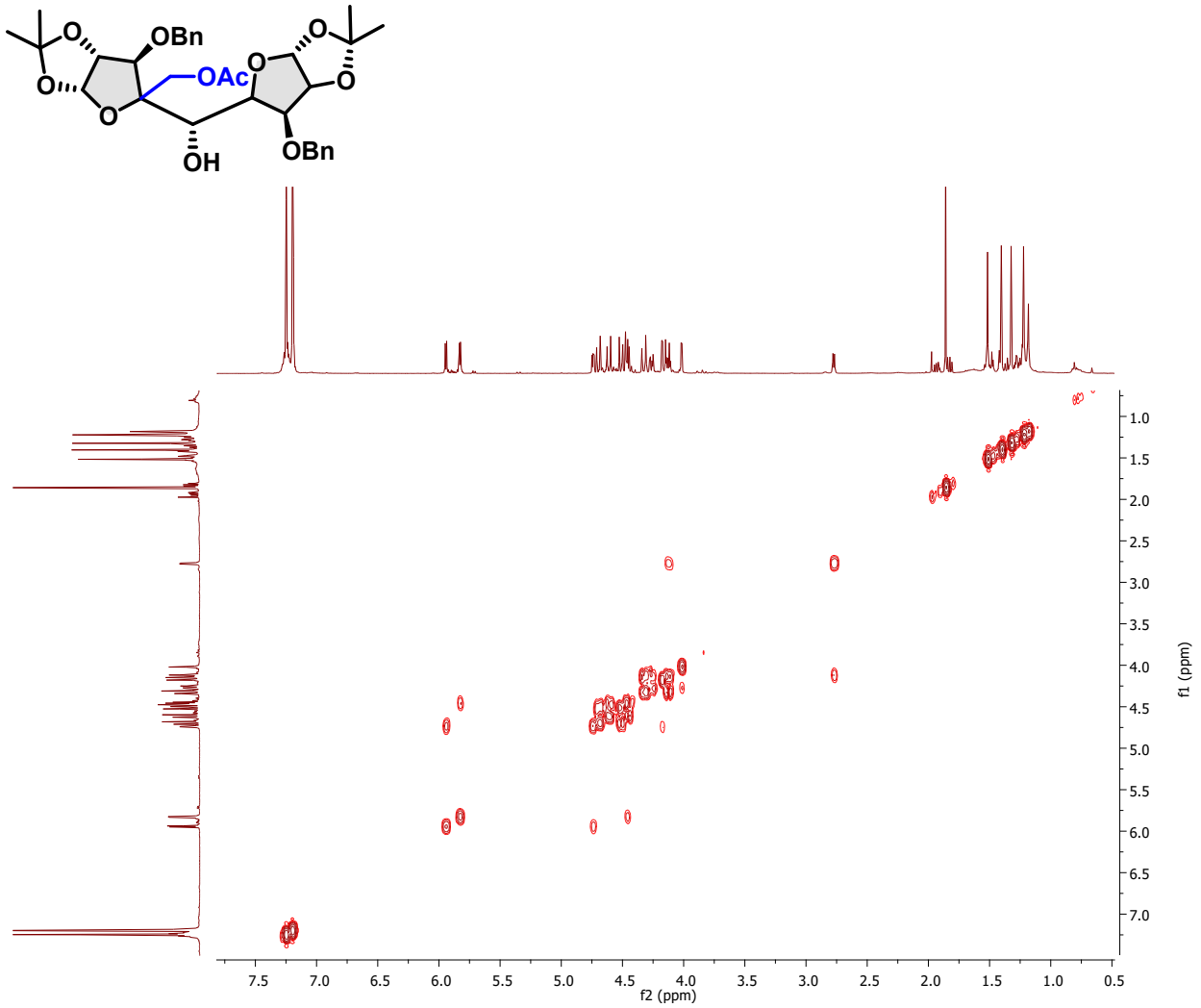
NOESY Spectrum of 4a



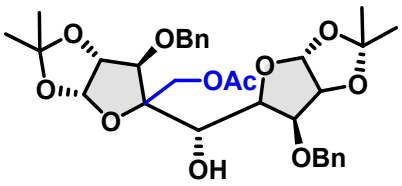


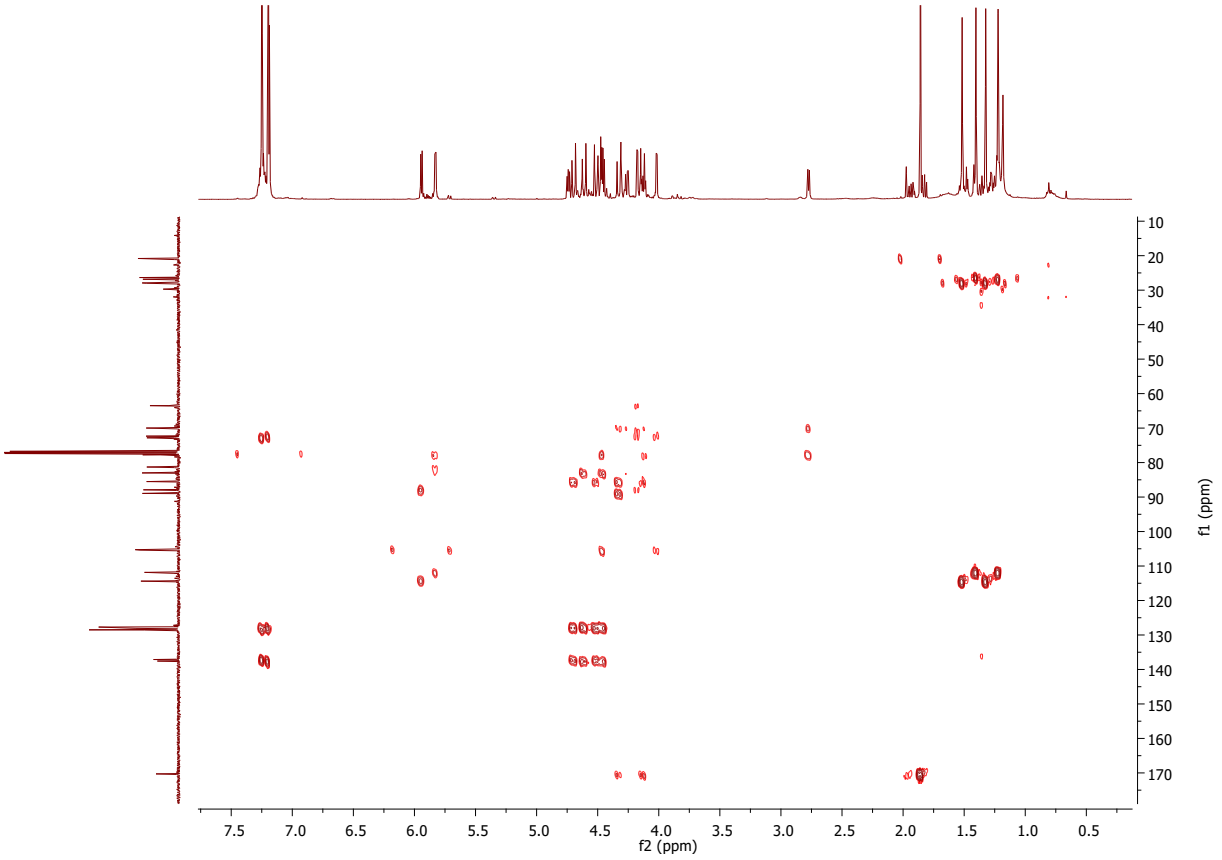
7E. 2D Spectrum of compound 5a

COSY Spectrum of 5a

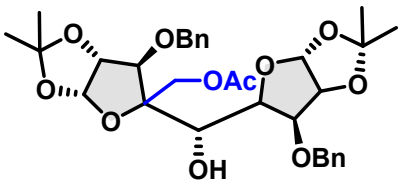


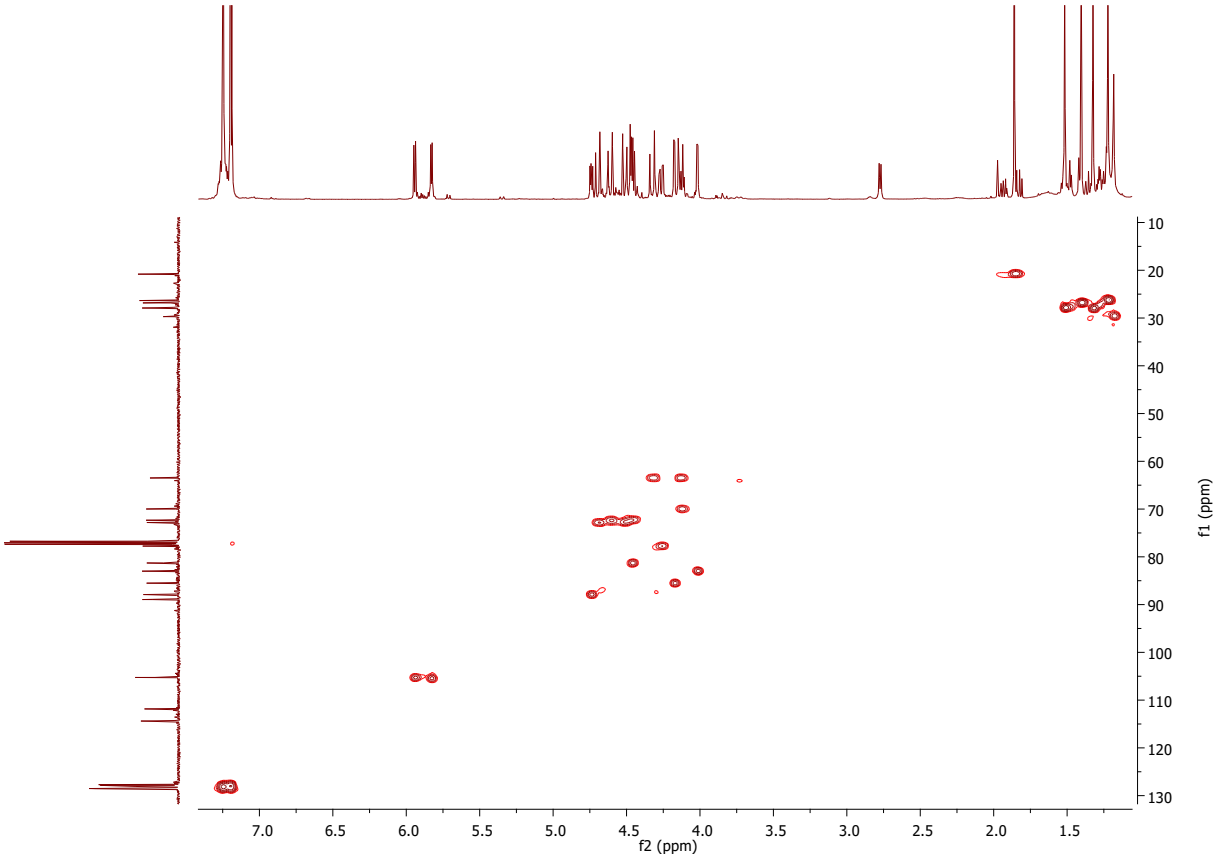
HMBC Spectrum of compound 5a





HSQC Spectrum of 5a





NOESY Spectrum of 5a