BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Supporting Information

for

Indium-mediated C-allylation of melibiose

Christian Denner, Manuel Gintner, Hanspeter Kählig and Walther Schmid

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General instructions, NMR spectra, mass analysis data and X-ray data

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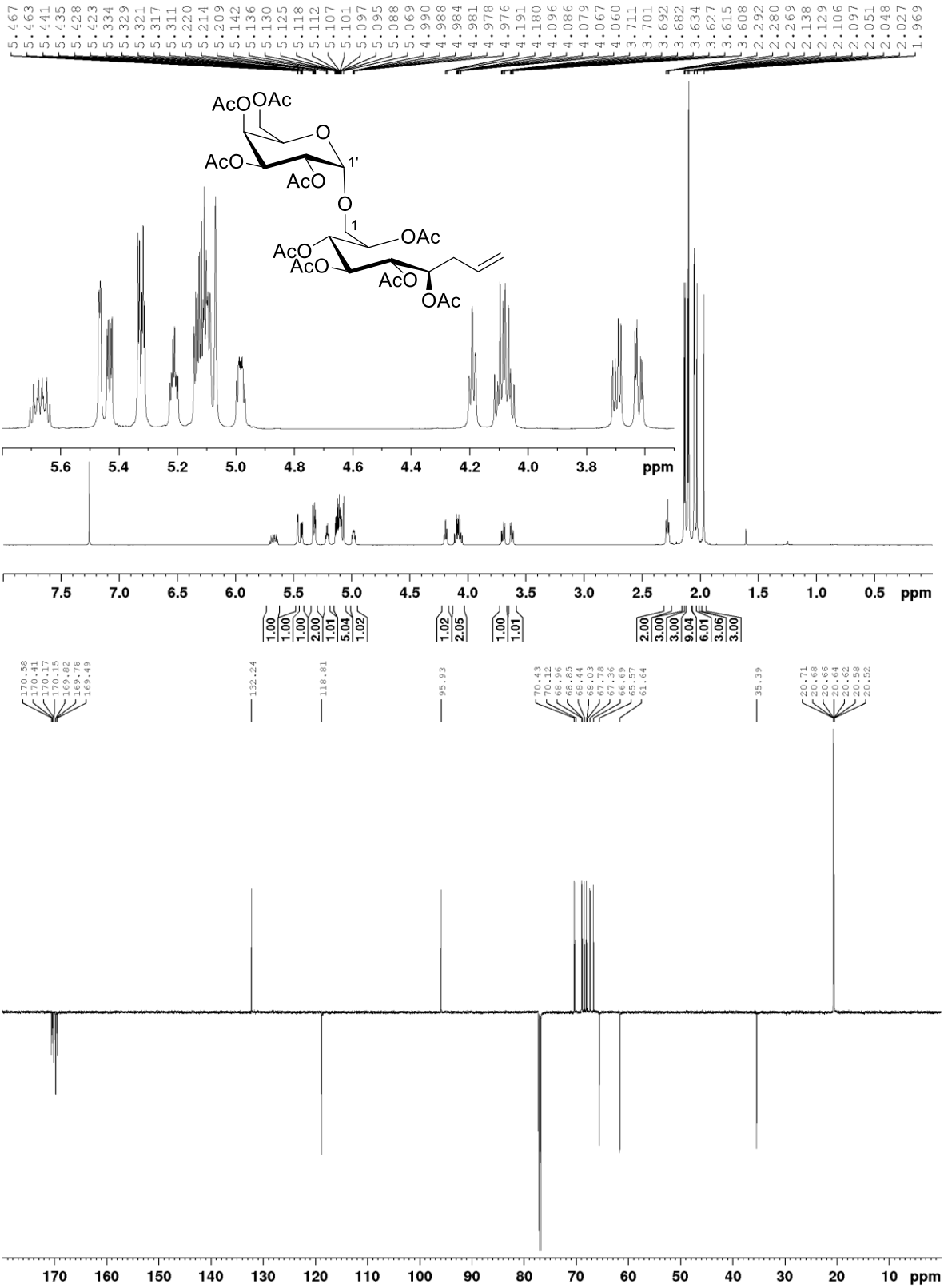
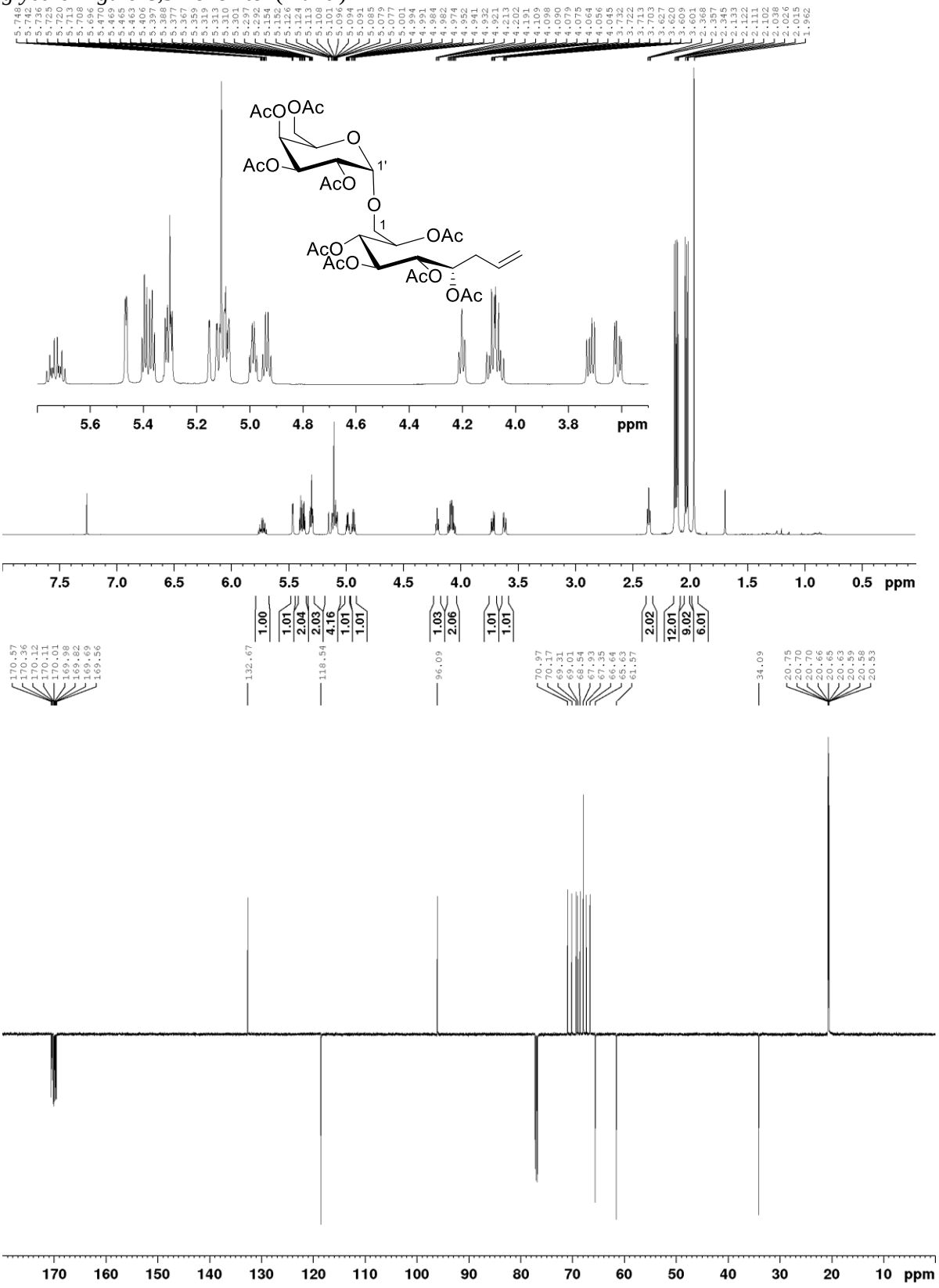
General instructions: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV III 600. Chemical shifts (δ) are reported in parts per million (ppm) and spectra were calibrated using solvent signal of $CDCl_3$. Signal multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet); q (quartet). NMR analysis was assisted by the spin simulation software DAISY (part of Bruker Top Spin software). High resolution mass spectra (HRMS) were recorded on a Bruker maXis UHR-TOF spectrometer in ESI mode. Optical rotations were measured on a Schmidt-Haensch Digital Polarimeter Unipol L 2000. Ozonolysis was performed operating an Anseros COM-AD-04 ozone generator. Column chromatography was performed using Macherey-Nagel silica gel 60 (0.04–0.063 mm, 240–400 mesh). TLC monitoring was carried out on precoated Merck silica gel 60 F_{254} glass plates. Compounds were visualized by treatment with a Mo–$Ce(SO_4)_2$ complex solution (48 g $(NH_4)_6Mo_7O_{24}$ and 2 g $CeSO_4$ in 1 dm^3 10% H_2SO_4) followed by heating. Filtrations over celite were performed with Celite® S by Sigma-Aldrich®. Solvents were distilled, if necessary, prior to use. Reagents were purchased from commercial suppliers and were used without further purification.

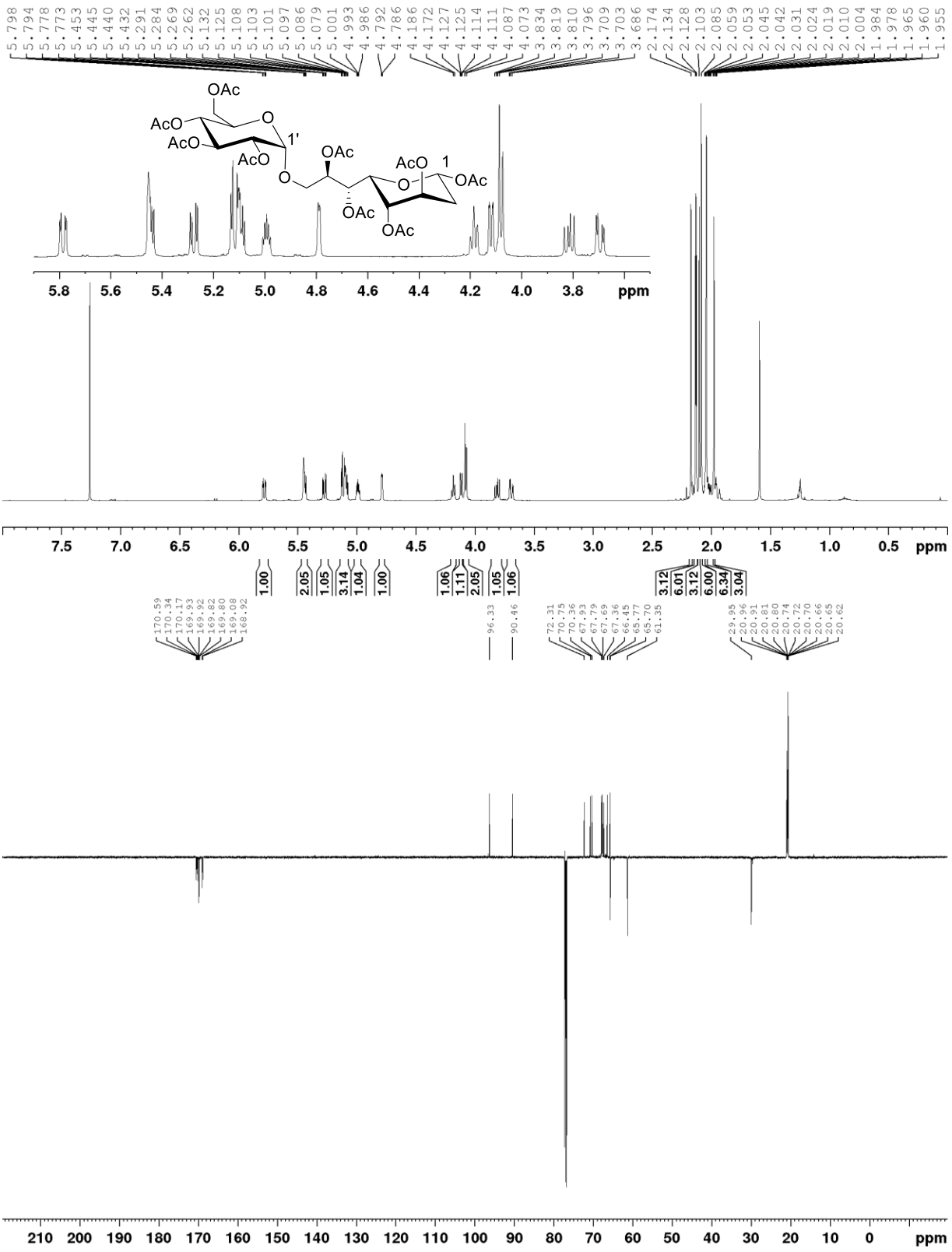
2’,3’,4’,6’-Tetra-*O*-acetyl-α-D-galactopyranosyl-(1’→1)-2,3,4,5,6-penta-*O*-acetyl-7,8,9-trideoxy-D-*glycero*-L-*gulo*-8,9-nonenitol (**2-*syn***)



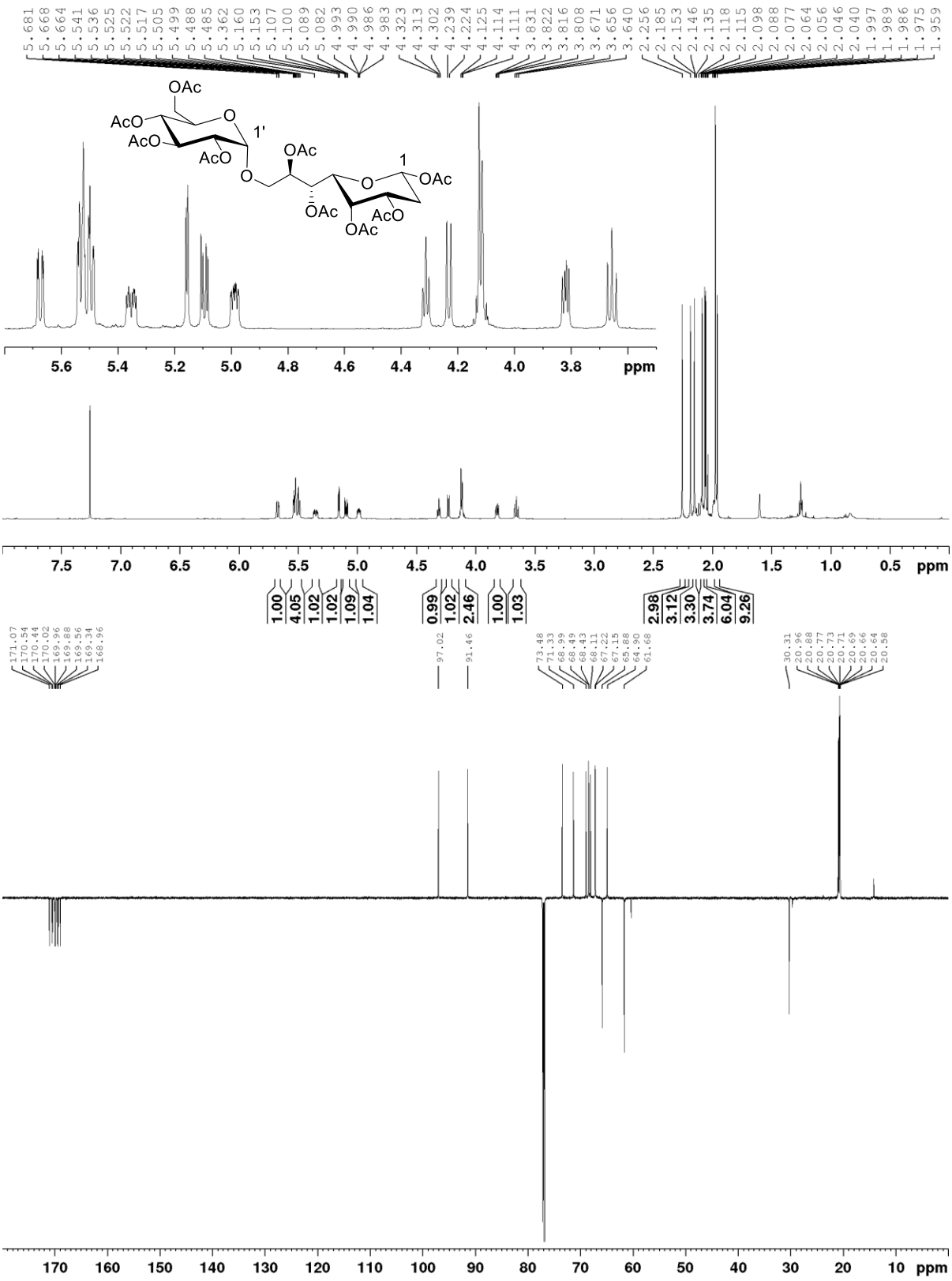
2’,3’,4’,6’-Tetra-*O*-acetyl-α-D-galactopyranosyl-(1’→1)-2,3,4,5,6-penta-*O*-acetyl-7,8,9-trideoxy-L-*glycero*-L-*gulo*-8,9-nonenitol (**2-*anti***)



2’,3’,4’,6’-Tetra-*O*-acetyl-α-D-galactopyranosyl-(1’→8)-1,3,4,6,7-penta-*O*-acetyl-2-deoxy-α-D-*glycero*-D-*ido*-octopyranose (**5-*syn*-β**)

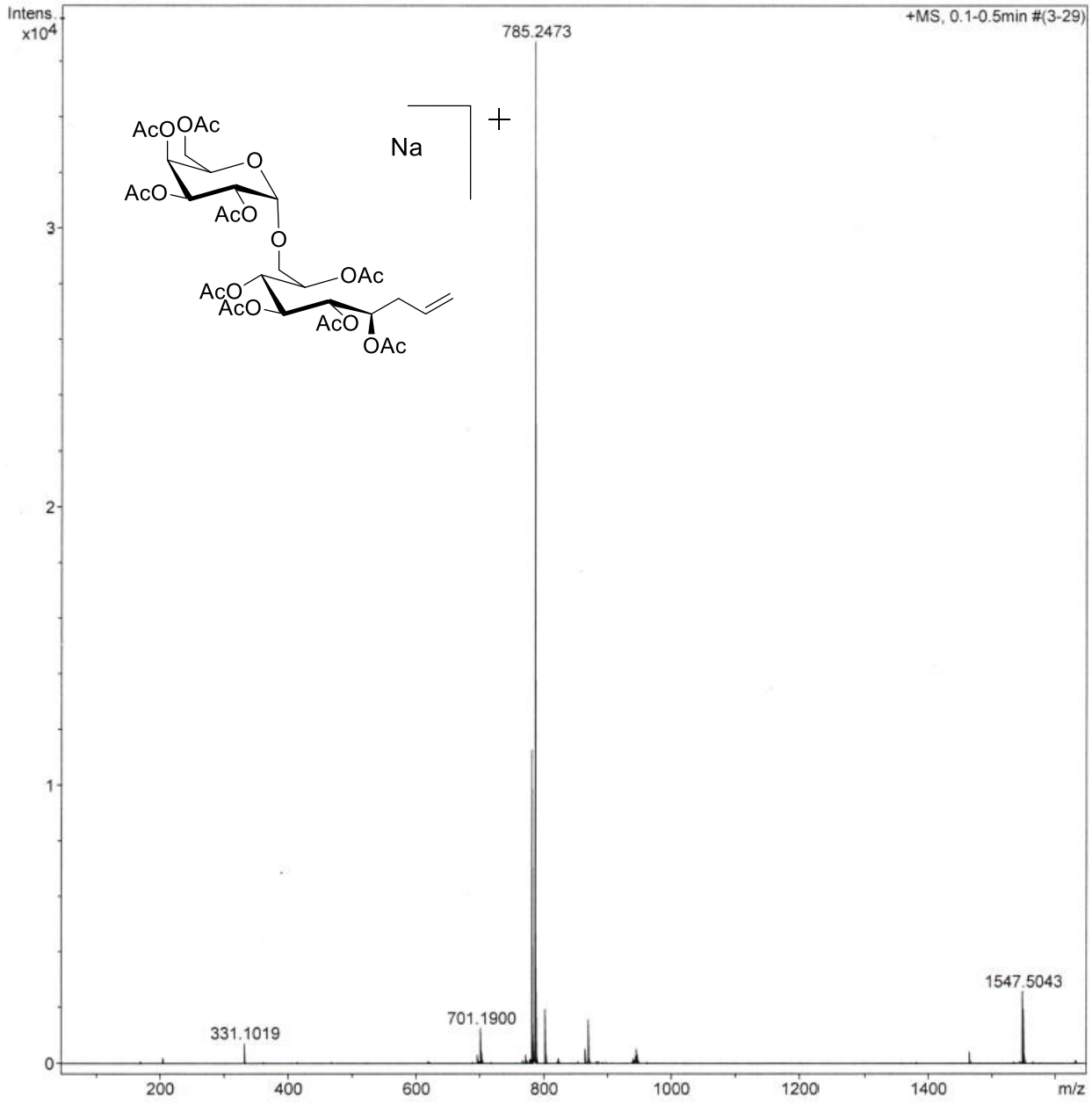


2’,3’,4’,6’-Tetra-*O*-acetyl-α-D-galactopyranosyl-(1’→8)-1,3,4,6,7-penta-*O*-acetyl-2-deoxy-α-D-*glycero*-D-*gulo*-octopyranose (**5-*anti*-β**)



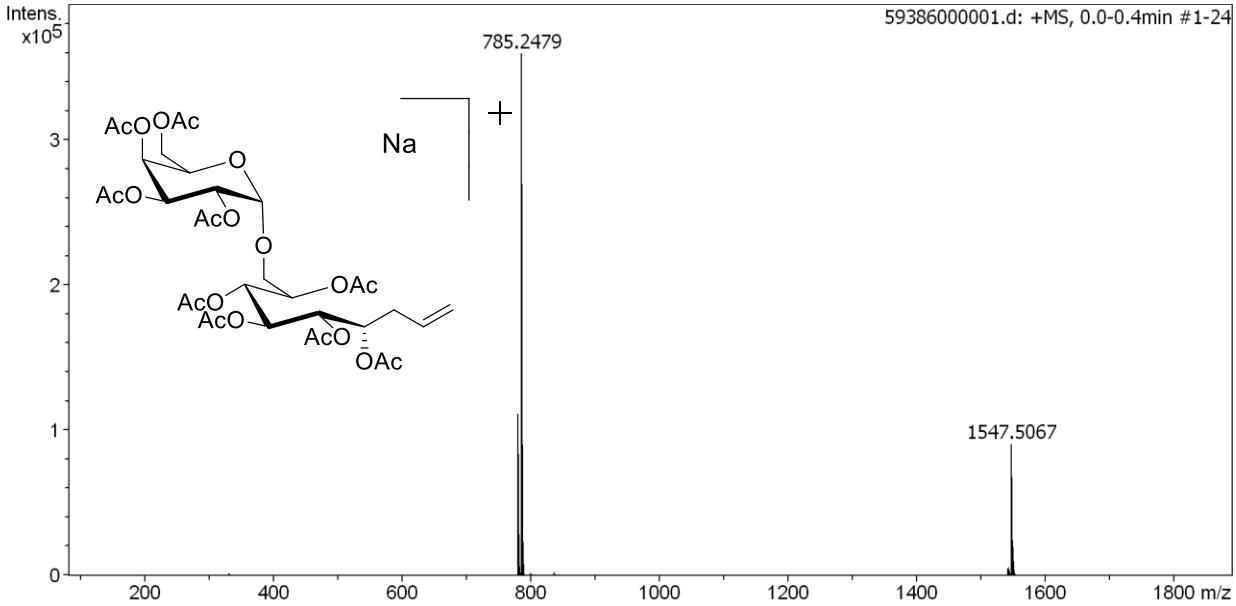
2’,3’,4’,6’-Tetra-*O*-acetyl-α-D-galactopyranosyl-(1’→1)-2,3,4,5,6-penta-*O*-acetyl-7,8,9-trideoxy-D-*glycero*-L-*gulo*-8,9-nonenitol (**2-*syn***)

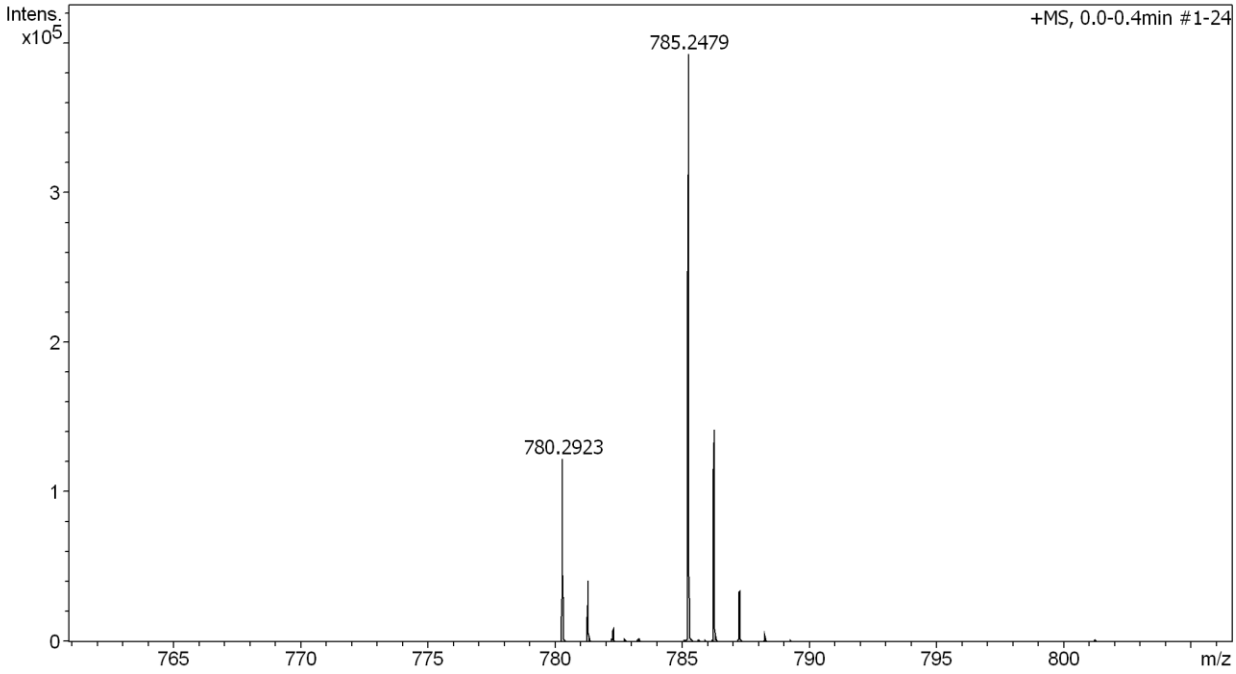
HRMS (ESI$^+$) m/z = 785.2473 [M+Na]$^+$ calcd. for $C_{33}H_{46}O_{20}Na^+$: 785.2475.



2’,3’,4’,6’-Tetra-*O*-acetyl-α-D-galactopyranosyl-(1’→1)-2,3,4,5,6-penta-*O*-acetyl-7,8,9-trideoxy-L-*glycero*-L-*gulo*-8,9-nonenitol (**2-*anti***)

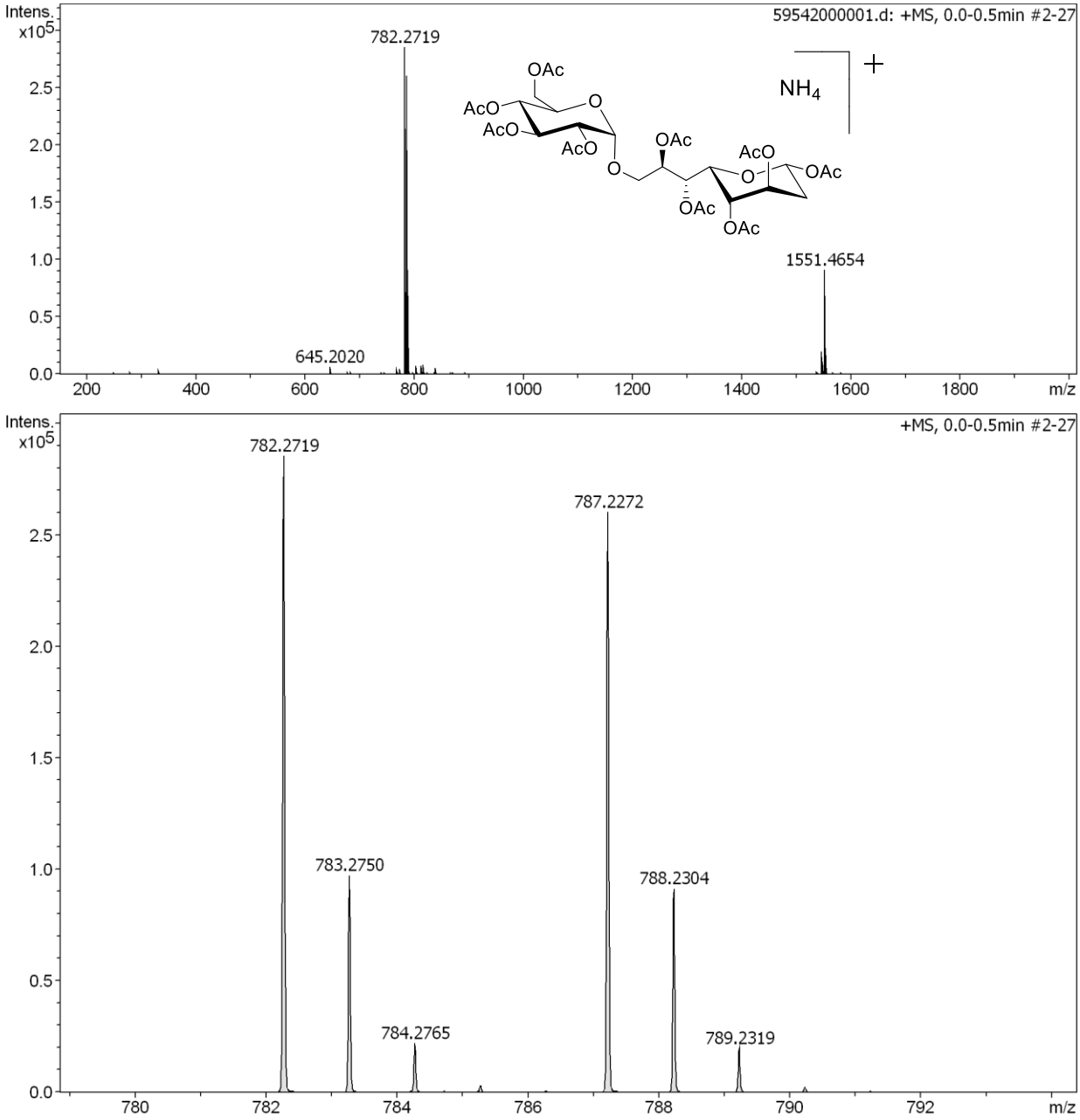
HRMS (ESI$^+$) m/z = 785.2479 $[M+Na]^+$ calcd. for $C_{33}H_{46}O_{20}Na^+$: 785.2475.





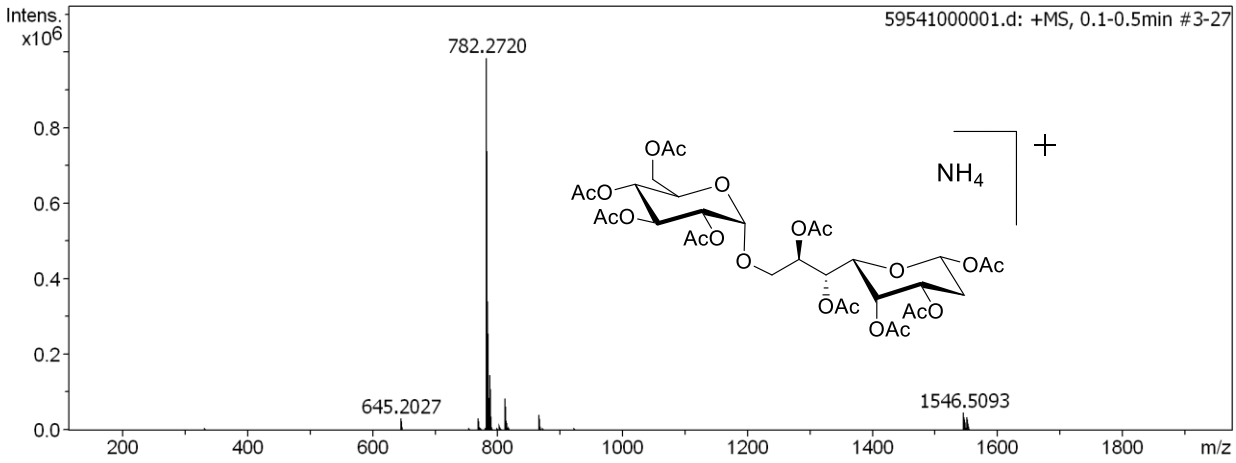
2’,3’,4’,6’-Tetra-*O*-acetyl-α-D-galactopyranosyl-(1’→8)-1,3,4,6,7-penta-*O*-acetyl-2-deoxy-α-D-*glycero*-D-*ido*-octopyranose (**5-*syn*-β**)

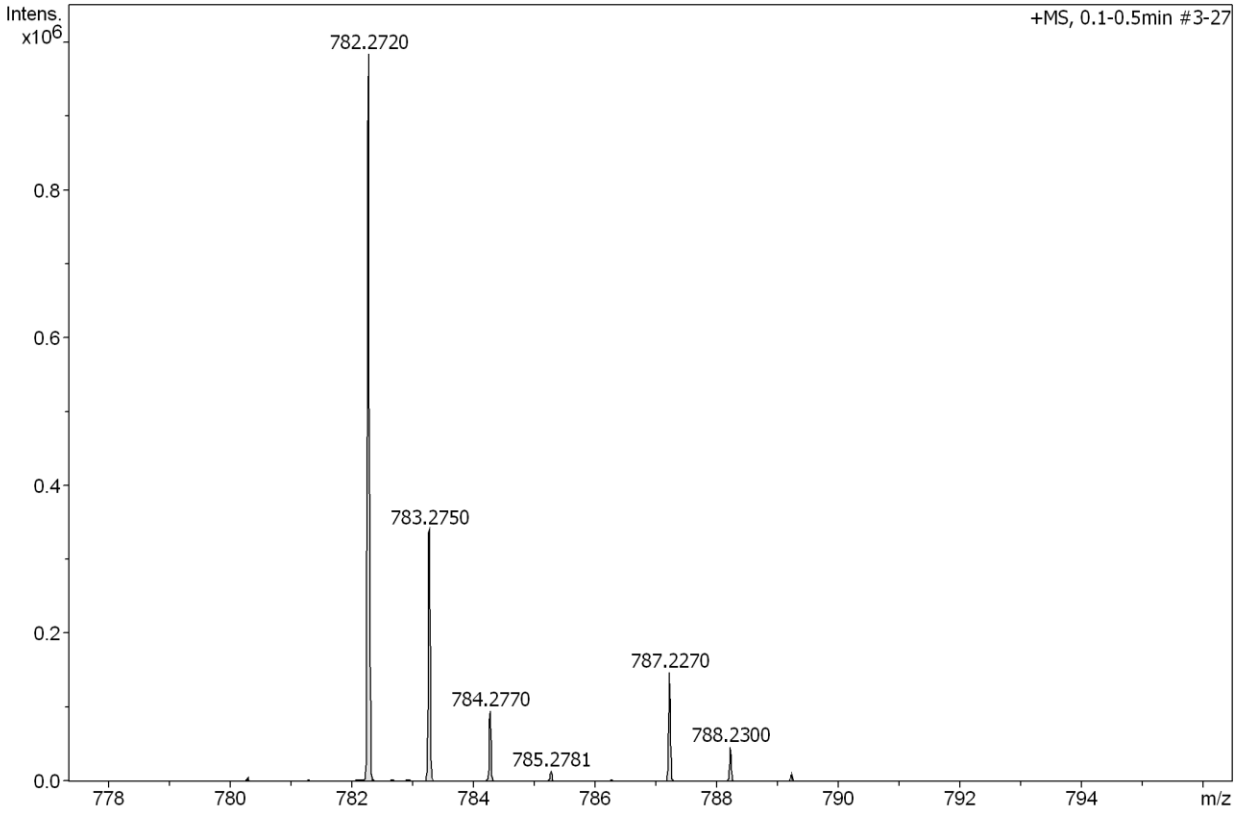
HRMS (ESI$^+$) m/z = 782.2719 [M+ NH_4]$^+$ calcd. for $C_{32}H_{48}NO_{21}^+$: 782.2713.



2’,3’,4’,6’-Tetra-*O*-acetyl-α-D-galactopyranosyl-(1’→8)-1,3,4,6,7-penta-*O*-acetyl-2-deoxy-α-D-*glycero*-D-*gulo*-octopyranose (**5-*anti*-β**)

HRMS (ESI$^+$) m/z = 782.2720 $[M+NH_4]^+$ calcd. for $C_{32}H_{48}NO_{21}^+$: 782.2713.





X-ray analysis

The X-ray intensity data were measured on Bruker D8 Venture diffractometer equipped with multilayer monochromator, Mo Kα INCOATEC micro focus sealed tube and Oxford cooling system. The structure was solved by *charge flipping* and refined by *full-matrix least-squares techniques*. Non-hydrogen atoms were refined with *anisotropic displacement parameters*. Hydrogen atoms were inserted at calculated positions and refined with riding model. The following software was used: *Bruker SAINT software package*[i] using a narrow-frame algorithm for frame integration, *SADABS*[ii] for absorption correction, *OLEX2*[iii] for structure solution, molecular diagrams and graphical user-interface, *Shelxle*[iv] for refinement and graphical user-interface, *SHELXL-2015*[v] for refinement, *Platon*[vi] for symmetry check. Experimental data and CCDC-Codes Experimental data and CCDC-Code (Available online: http://www.ccdc.cam.ac.uk/conts/retrieving.html) can be found in Table S1. Crystal data, data collection parameters, and structure refinement details are given in Tables S2 and S3. Crystal structure is visualized in Figure S1.

Table S1 Experimental parameter and CCDC-Code.

Sample	Machine	Source	Temp.	Detector Distance	Time/ Frame	#Frames	Frame width	CCDC
	Bruker		[K]	[mm]	[s]		[°]	
2-syn	D8	Mo	100	37	8	6216	0.500	1922520

2-syn

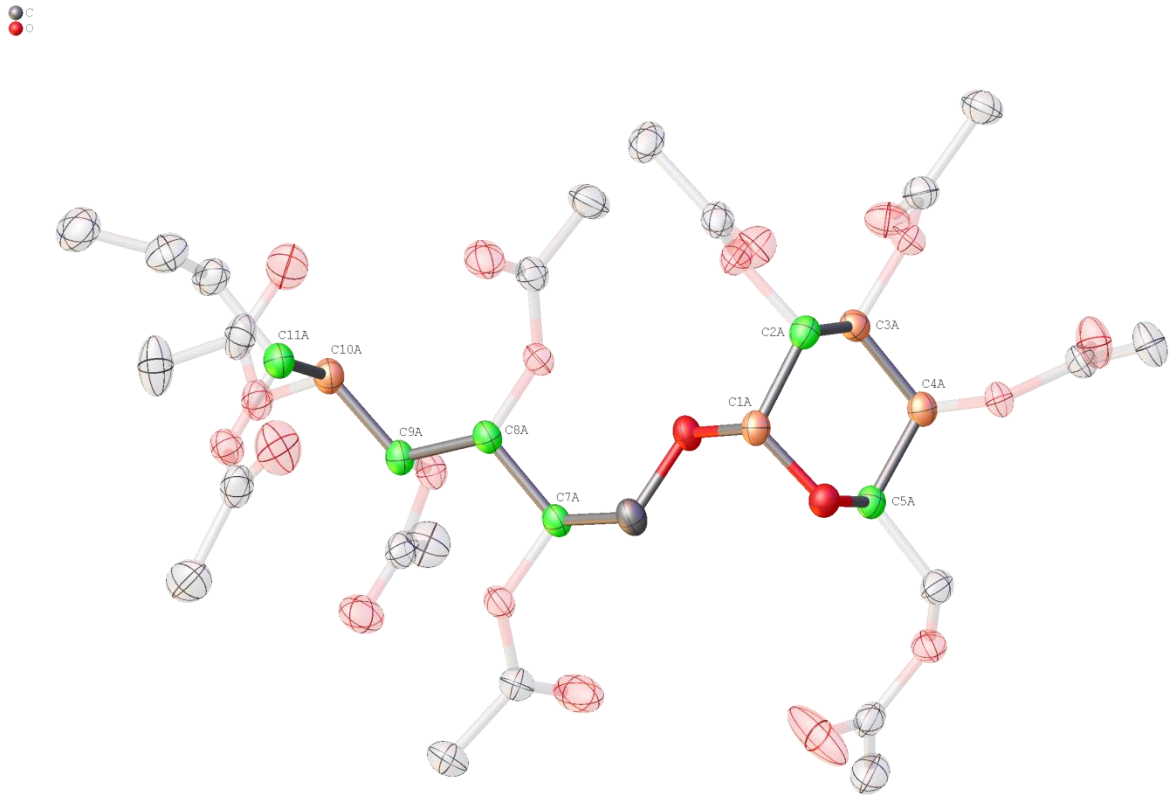


Figure S1 Crystal structure of [**2-syn**], drawn with 50% displacement ellipsoid. Backbone highlighted, side chains translucent. The green carbons are in R conformation, the orange ones are S. Chirality is proofed by reference molecule and AD. The bond precision for C–C single bonds is 0.0033 Å. Second independent molecule in the AU, Hydrogen Atoms and Disorder omitted for clarity. Main residue disorder is 9%.

Table S2 Sample and crystal data [**2-syn**].

Chemical formula	C33H46O20	**Crystal system**	monoclinic	
Formula weight [g/mol]	762.7	**Space group**	*P21*	
Temperature [K]	100	**Z**	4	
Measurement method	\f and \w scans	**Volume [Å^3]**	3800.8(3)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	**Unit cell dimensions [Å] and [°]**	14.1418(6)	90
Crystal size / [mm^3]	0.35 × 0.23 × 0.211		9.0704(3)	91.8306(15)
Crystal habit	clear colourless block		29.6461(12)	90
Density (calculated) / [g/cm^3]	1.333	**Absorption coefficient / [mm^{-1}]**	0.111	
Abs. correction Tmin	0.7191	**Abs. correction Tmax**	0.746	
Abs. correction type	multiscan	**F(000) [e$^-$]**	1616	

Table S3 Data collection and structure refinement[**2-syn**]..

Index ranges	$-19 \leq h \leq 19$, $-12 \leq k \leq 12$, $-41 \leq l \leq 41$	**Theta range for data collection [°]**	4.124 to 60.124	
Reflections number	489568	**Data / restraints / parameters**	22249/5/1051	
Refinement method	Least squares	**Final R indices**	all data	R1 = 0.0483, wR2 = 0.1031
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$		$I>2\sigma(I)$	R1 = 0.0384, wR2 = 0.0925
Goodness-of-fit on F^2	1.093	**Weighting scheme**	$w=1/[\sigma^2(F_o^2)+(0.0403P)^2+1.2026P]$	
Largest diff. peak and hole [e $Å^{-3}$]	0.47/-0.25		where $P=(F_o^2+2F_c^2)/3$	

[i] Bruker SAINT v8.38B Copyright © 2005-2019 Bruker AXS
[ii] Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
[iii] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J; Howard, J.A.K.; Puschmann, H. OLEX2, (2009), *J. Appl. Cryst.* **2009,** *42,* 339-341
[iv] Huebschle, C. B.; Sheldrick, G. M.; Dittrich, B. ShelXle: a Qt graphical user interface for SHELXL, *J. Appl. Cryst.* **2011,** *44,* 1281-1284
[v] Sheldrick, G. M. (2015). *SHELXL* v 2016/4 University of Göttingen, Germany.
[vi] Spek, A. L. *Acta Cryst.* **2009,** *D65,* 148-155.