Supporting Information

Defining Oxyanion Reactivities in Base-promoted Glycosylations

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2,3,4,6-tetra-*O*-methyl-α-D-galactopyranosyl chloride (**9**)	S-12	S-46 S-47
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Methyl 3-*O*-acetyl-4,6-di-*O*-methyl-2-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (**14**)	S-14	S-50 S-51
Methyl 6-*O*-acetyl-2,3-di-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (**15**), Methyl 4-*O*-acetyl-2,3-di-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (**16**)	S-14	S-52 S-53
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Methyl 4,6-*O*-benzylidene-3-*O*-methyl-α-D-glucopyranoside (**32**)	S-22	S-76 S-77
Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**33**)	S-23	S-78 S-79
Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**34**)	S-24	S-80 S-81
Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**35**)	S-24	S-82 S-83
Methyl 2,3,4-tri-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (**36**)	S-25	S-84 S-85
Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside (**37**)	S-25	S-86 S-87
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Methyl 2,3-di-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (**39**)	S-26	S-90 S-91
Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-methyl-α-D-glucopyranoside (**40**)	S-26	S-92 S-93
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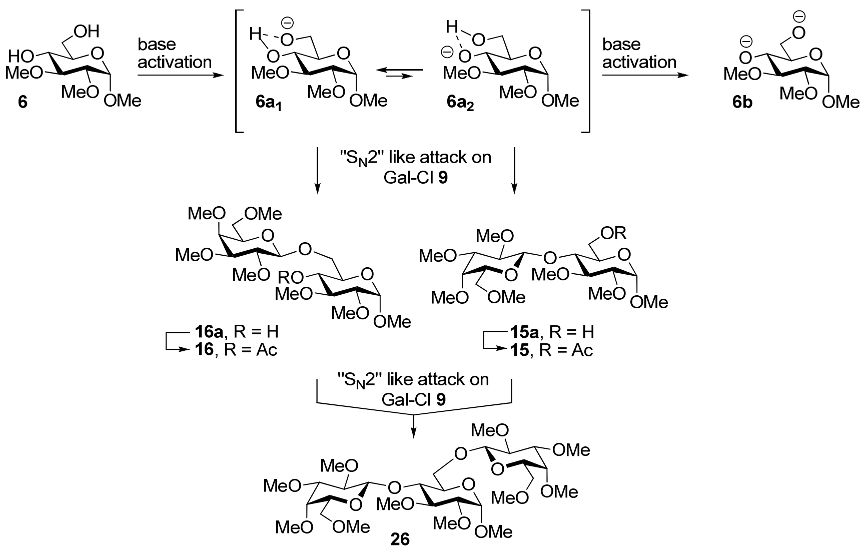
Methyl 4-*O*-benzyl-2,3-di-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (**43**)	S-28	S-98 S-99

Proposed mechanism for base-promoted glycosylation on acceptors containing vicinal hydroxyl groups exemplary shown for the 4,6-diol 6

In the case of **6** deprotonation of one hydroxyl group resulted in the formation of compound **6a**. Using a systematic study of the acidic behaviour (K_e)[1] of partially methylated glucopyranosides **1** – **8** allowed to conclude that in such anionic species the negative charge was dispersed by hydrogen bonding from the unreacted hydroxyl group, i.e. stabilized by a mesomeric effect (**6a$_1$** and **6a$_2$**). In general it could be observed that adjacent hydroxyl groups of sugars exhibit a higher acidity relative to isolated ones. This suggests that diol and triol structures are likely to show hydrogen bonding.

Further deprotonation would lead to the proposed dianionic species **6b** the formation of which was most likely hindered due to the incorporation of the unreacted hydrogen by dispersion of negative charge. Both disaccharides **15** and **16** were formed by nucleophilic attack of the sugar alkoholate **6a$_1$** and **6a$_2$** in β-position at the α-glycosylchloride in a "S_N2-like" manner. The equilibrium between **6a$_1$** and **6a$_2$** is most likely shifted to structure **6a$_1$** in which the negative charge is located on the less basic oxyanion. Accordingly, O-6 acts mainly as a hydrogen-bond acceptor which enhances its reactivity.[2] Consequently, the 6-position exhibited a higher reactivity relative to the 4-position giving rise to a ratio of 1:4 for **15a** and **16a.** After monoglycosylation the presence of an excess of base and donor concentration leads to deprotonation of the remaining, now isolated hydroxyl groups of disaccharides **15a** and **16a**. Again, donor **9** was attacked in a "S_N2-like" manner resulting in the formation of trisaccharide **26**, in which disaccharide **16a** is the main reactant for a second glycosylation due to its excess.



Scheme 1: Proposed mechanism for base-promoted glycosylation

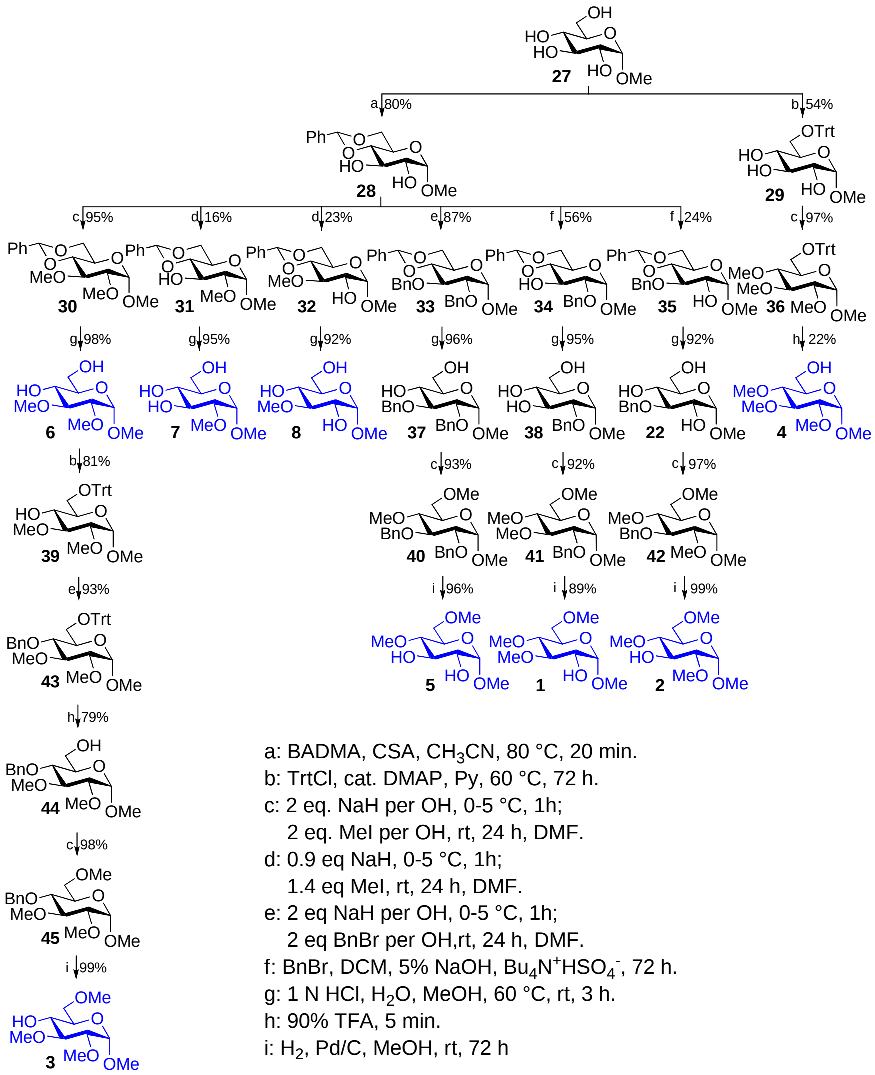
Experimental:

General:

All reagents were purchased from commercial sources and used as received. Sodium hydride (NaH) was purchased and used as 60% suspension in paraffine. Glycosylation reactions were conducted under an atmosphere of dry argon. Solvents for chromatography were distilled prior to use. Thin layer chromatography was performed on *Merck* silica gel 60 F_{254} plates. Column chromatography was performed on *Merck/Fluka* silica gel 60 (230 – 400 mesh). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a *Bruker AMX-400* or *Bruker AV-400* spectrometers (400 MHz for ^{1}H, 101 MHz for ^{13}C). Melting points were measured on a Apotec® melting point apparatous. Optical rotation were obtained using a Krüss Optronic P8000 polarimeter (c = [g 100cm^{-1}]). ESI HRMS were recorded on Thermo Finnigan MAT 95XL mass spectrometer.

Relative yields of disaccharide mixtures were determined by ^{1}H-NMR-integration of the anomeric or other well separated proton signals.

Partially methylated methyl α-D-glucopyranosides **1** – **8**,[3,4] and methyl 3-*O*-benzyl-α-D-glucopyranoside (**22**) were synthesized applying standard protecting group chemistry (see Scheme 2).[5,6]



Scheme 2: Synthesis of partially methylated methyl α-D-glucopyranosides **1** – **8**.

9[7], **23**[7,8], **28**[9], **34**[10] and **35**[10] were synthesized as described in the cited literature.

A) General procedure for methylation/benzylation:

The starting material (1 mmol) was dissolved in anhydrous *N*,*N*-dimethylformamide (10 mL), treated with sodium hydride (2 – 2.5 eq. per OH group) at 0 °C and stirred for 1 h. Subsequently MeI/BnBr (2 – 2.5 eq. per OH group) was addedat 0 °C, the mixture warmed to ambient temperature and stirred for 12 – 18 h. The reaction was quenched by addition of methanol (5 mL) and the solvents were removed under reduced pressure. The residue was taken up in H_2O/DCM 1:1 and the aqueous layer extracted twice with DCM. The organic phase was washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash column chromatography (gradient petrol ether/ethyl acetate) to yield the corresponding methylated/benzylated derivatives **30**[11], **33**[10], **36**[16], **40**[16], **41**, **42**[12], **43** and **45**.

B) General procedure for cleavage of the benzylidene group:

The 4,6-*O*-benzylidene protected derivative (1 mmol) was dissolved or suspended in distilled methanol (10 mL), treated with 0.5 mL H_2O and 1 mL 1 N HCl. The mixture was stirred for 3 h at 55 °C, neutralized by addition of $NaHCO_3$-solution. Solvents were evaporated *in vacuo*, azeotroping with toluene, and the residue purified by flash silica gel chromatography (gradient petrol ether/ethyl acetate) to yield the compounds **6**[16], **7**[16], **8**, **22**[13], **37**[14] and **38**[13].

C) General procedure for cleavage of the benzyl groups:

To a solution of the benzylated intermediate (1 mmol) in distilled methanol (20 mL) 30 mg Pd(10%)/C was added and the mixture stirred under an atmosphere of hydrogen at room temperature for 24 - 96 h. The catalyst was filtered off, the solvents evaporated *in vacuo* and the residue purified by flash silica gel chromatography (gradient petrol ether/ethyl acetate) to yield the compounds **1**, **2**, **3**[16], and **5**[16].

D) General procedure for tritylation:

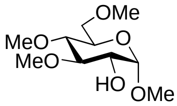
To a solution of 1 mmol starting material in anhydrous pyridine (3 mL) Chlorotriphenylmethane (1.1 eq.) and catalytic amounts of 4-*N*,*N*-dimethylaminopyridine (DMAP) were added. The mixture was stirred at 60 °C for 72 h, evaporated *in vacuo*, azeotroping with toluene and purified by flash silica gel chromatography (gradient petrol ether/ethyl acetate) to yield the compounds **29**[15] and **39**[16].

E) Standard procedure for base-promoted glycosylation:

The acceptor (0.1 mmol) was dissolved in anhydrous *N*,*N*-dimethylformamide (2.0 mL), treated with the specified amount of base (2 – 4 eq.) and stirred for 1 h. Subsequently the donor (2 – 4 eq.), dissolved in anhydrous *N*,*N*-dimethylformamide (2.0 mL), was added and the mixture stirred for 4 h. The reaction was quenched by addition of methanol (1 mL) and the solvents were removed under reduced pressure. The remaining syrup was taken up in pyridine and acetic anhydride (2:1 v/v, 6 mL) and stirred for 18 h. Pyridine was removed under reduced pressure and by codistilling with toluene. The remaining residue was purified using flash-column chromatography (eluent: petrol ether/ethyl acetate 2:1 to only ethylacetate) to give the disaccharide mixtures. The subsequent analysis of the disaccharide mixtures by ^{1}H-NMR afforded their relative yields.

Characterization data for partially methylated methyl α-D-glucopyranosides 1 – 8 and donor 2,3,4,6-Tetra-*O*-methyl α-D-galactopyranosyl chloride (9).

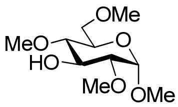
Methyl 3,4,6-tri-*O*-methyl-α-D-glucopyranoside (1)



1

Prepared following procedure C. 1.12 g (3.44 mmol) **41**, 110 mg Pd(10%)/C, 50 mL MeOH. Yield: 720 mg (3.05 mmol, 89%), colourless syrup, $[\alpha]_D^{23}$ = + 179.0° (c = 0.92 in $CHCl_3$), R_f (PE/EE 2:1, v/v) = 0.10, ESI HRMS for $C_{10}H_{20}O_6$ $[M+Na^+]$: found 259.1162, calcd. 259.1152. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 4.75 (d, $^3J_{1,2}$ = 4.0 Hz, 1H, H-1), 3.61-3.57 (m, 4H, H-5, H-6, H-2), 3.35 (dd, 1H, H-3), 3.19 (dd, $^3J_{3,4}$ = 9.1, $^3J_{4,5}$ = 9.1 Hz 1H, H-4), 3.65, 3.52, 3.41, 3.40 (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 99.3 (C-1), 84.4 (C-3), 79.3 (C-4), 72.3 (C-2), 70.9 (C-6), 70.2 (C-5), 60.8, 60.2, 59.1, 55.2 (O<u>C</u>H$_3$) ppm.

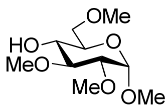
Methyl 2,4,6-tri-*O*-methyl-α-D-glucopyranoside (2)



2

Prepared following procedure C. 1.44 g (4.41 mmol) **42**, 117 mg Pd(10%)/C, 50 mL MeOH. Yield: 1.04 g (4.40 mmol, 99%) colourless syrup, $[\alpha]_D^{23}$ = + 165.3° (c = 0.19 in $CHCl_3$), R_f (ethyl acetate) = 0.17, ESI HRMS for $C_{10}H_{20}O_6$ $[M+Na^+]$: found 259.1152, calcd. 259.1152. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 4.89 (d, $^3J_{1,2}$ = 3.5 Hz, 1H, H-1), 3.91 (dd, $^3J_{2,3}$ = 9.4 Hz, $^3J_{3,4}$ = 9.2 Hz, 1H, H-3), 3.64 – 3.58 (m, 3H, H-5, H-6), 3.26 (dd, 1H, H-4), 3.21 (dd, 1H, H-2), 3.57, 3.49, 3.43, 3.41 (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 96.8 (C-1), 81.3 (C-2), 79.1 (C-4), 73.1 (C-3), 71.1 (C-6), 69.6 (C-5), 60.5, 59.2, 58.4, 55.2 (O<u>C</u>H$_3$) ppm.

Methyl 2,3,6-tri-*O*-methyl-α-D-glucopyranoside (3)

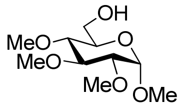


3

Prepared following procedure C. 937 mg (2.87 mmol) **45**, 220 mg Pd(10%)/C, 50 mL MeOH. Yield: 672 mg (2.84 mmol, 99%), colourless syrup, $[\alpha]_D^{23}$ = + 129.0° (c = 0.2, MeOH), Lit.[16]: $[\alpha]_D$ = + 149.0° (MeOH), R_f (PE/EE 2:1, v/v) = 0.05, ESI HRMS for $C_{10}H_{20}O_6$ $[M+Na^+]$: found 259.1155, calcd. 259.1152. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 4.86 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 3.71 (ddd, $^3J_{4,5}$ = 9.2 Hz,

$^{3}J_{5,6a}$ = 4.1 Hz, $^{3}J_{5,6b}$ = 3.6 Hz, 1H, H-5), 3.67 – 3.60 (m, 2H, H-6), 3.52 (dd, $^{3}J_{3,4}$ = 9.4 Hz, $^{3}J_{4,5}$ = 9.2 Hz, 1H, H-4), 3.46 (dd, $^{3}J_{2,3}$ = 9.4 Hz, $^{3}J_{3,4}$ = 9.4 Hz, 1H, H-3), 3.26 (dd, $^{3}J_{1,2}$ = 3.6 Hz, $^{3}J_{2,3}$ = 9.4 Hz, 1H, H-2), 3.64, 3.50, 3.44, 3.42 ($OC\underline{H}_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 97.6 (C-1), 82.8 (C-3), 81.7 (C-2), 72.0 (C-6), 70.6 (C-4), 69.6 (C-5), 61.2, 59.4, 58.5, 55.2 ($O\underline{C}H_3$) ppm.

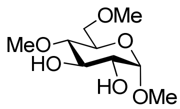
Methyl-2,3,4-tri-*O*-methyl-α-D-glucopyranosid (4)



4

3.66 g (7.64 mmol) **36** were deprotected and purified by flash silica gel chromatography with 5% TfOH in chloroform as eluent.[17] Yield: 390 mg (1.65 mmol, 22%), colourless syrup, $[\alpha]_D^{23}$ = + 158.0° (c = 0.26, $CHCl_3$), R_f (ethyl acetate) = 0.16, ESI HRMS for $C_{10}H_{20}O_6$ [M+Na$^+$]: found 259.1153, calcd. 259.1152. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 4.80 (d, $^{3}J_{1,2}$ = 3.5 Hz, 1H, H-1), 3.83 (dd, $^{3}J_{5,6a}$ = 2.1 Hz, $^{2}J_{6a,6b}$ = 11.7 Hz, 1H, H-6a), 3.74 (dd, $^{3}J_{5,6b}$ = 4.2 Hz, $^{2}J_{6a,6b}$ = 11.7 Hz, 1H, H-6b), 3.56 – 3.50 (m, 2H, H-3, H-5), 3.21 – 3.12 (m, 2H, H-2, H-4), 3.63, 3.56, 3.52, 3.40 ($OC\underline{H}_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 97.5 (C-1), 83.4 (C-3), 81.8 (C-2), 79.7 (C-4), 70.5 (C-5), 62.0 (C-6), 60.9, 60.6, 59.0, 55.2 ($O\underline{C}H_3$) ppm.

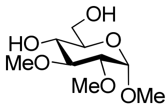
Methyl-4,6-di-*O*-methyl-α-D-glucopyranoside (5)



5

Prepared following procedure C. 1.33 g (3.30 mmol) **40**, 111 mg Pd(10%)/C, 50 mL MeOH. Yield: 704 mg (3.17 mmol, 96%), colourless syrup, $[\alpha]_D^{23}$ = + 152.0° (c = 1.0, $CHCl_3$), Lit.[16]: $[\alpha]_D$ = + 157° ($CHCl_3$), R_f (PE/EE 1:1, v/v) = 0.04, ESI HRMS for $C_9H_{18}O_6$ [M+Na$^+$]: found 245.0991, calcd. 245.0996. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 4.79 (d, $^{3}J_{1,2}$ = 3.8 Hz, 1H, H-1), 3.75 (dd, $^{3}J_{2,3}$ = 9.4 Hz, $^{3}J_{3,4}$ = 9.2 Hz, 1H, H-3), 3.64 – 3.58 (m, 3H, H-5, H-6), 3.55 (dd, $^{3}J_{1,2}$ = 3.8 Hz, $^{3}J_{2,3}$ = 9.4 Hz, 1H, H-2), 3.26 – 3.19 (dd, $^{3}J_{3,4}$ = 9.2 Hz, $^{3}J_{4,5}$ = 9.2 Hz, 1H, H-4), 3.57, 3.43, 3.42 ($OC\underline{H}_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 99.1 (C-1), 79.0 (C-4), 75.0 (C-3), 72.5 (C-2), 71.0 (C-6), 70.0 (C-5), 60.6, 59.2, 55.4 ($O\underline{C}H_3$) ppm.

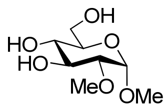
Methyl-2,3-di-*O*-methyl-α-D-glucopyranoside (6)



6

Prepared following procedure B. 2.00 g (6.44 mmol) **30**, 40 mL MeOH, 4 mL H_2O, 1 mL 1 N HCl. Yield: 1.40 g (6.32 mmol, 98%), white solid, $[\alpha]_D^{23}$ = + 146.4° (c = 1.0, H_2O), Lit.[16]: $[\alpha]_D$ = + 143° (H_2O), m.p.: 83 – 85 °C, Lit.[16]: m.p.: 83 – 85 °C, R_f (ethyl acetate) = 0.12, ESI HRMS for $C_9H_{18}O_6$ [M+Na$^+$]: found 245.0990, calcd. 245.0996. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 4.85 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 3.86 (dd, $^3J_{5,6a}$ = 3.6 Hz, $^2J_{6a,6b}$ = 12.0 Hz, 1H, H-6a), 3.81 (dd, $^3J_{5,6b}$ = 4.2 Hz, $^2J_{6a,6b}$ = 12.0 Hz, 1H, H-6b), 3.70 – 3.61 (m, 1H, H-5), 3.55-3.44 (m, 2H, H-3, H-4), 3.23 (dd, $^3J_{1,2}$ = 3.6, $^3J_{2,3}$ = 9.4 Hz, 1H, H-2), 3.64, 3.50, 3.44 (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 97.6 (C-1), 82.7 (C-3), 82.0 (C-2), 70.7 (C-5), 70.6 (C-4), 62.6 (C-6), 61.2, 58.5, 55.3 (O<u>C</u>H$_3$) ppm.

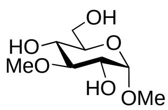
Methyl-2-*O*-methyl-α-D-glucopyranoside (7)



7

Prepared following procedure B. 1.07 g (3.61 mmol) **31**, 30 mL MeOH, 2 mL H_2O, 1 mL 1 N HCl. Yield: 712 mg (3.42 mmol, 95%), white solid, $[\alpha]_D^{23}$ = + 139.0° (c = 0.2, H_2O), Lit.[16]: $[\alpha]_D$ = + 155° (H_2O), m.p.: 144 – 145 °C, Lit.[16]: m.p.: 147 – 148 °C, R_f (DCM/MeOH 9:1, v/v) = 0.15, ESI HRMS for $C_8H_{16}O_6$ [M+Na$^+$]: found 231.0844, calcd. 231.0839. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 4.91 (d, $^3J_{1,2}$ = 3.5 Hz, 1H, H-1), 3.91 – 3.80 (m, 3H, H-3, H-6), 3.69 - 3.56 (m, 2H, H-5, H-4), 3.17 (dd, $^3J_{1,2}$ = 3.5 Hz, $^3J_{2,3}$ = 9.7 Hz 1H, H-2), 3.50, 3.44 (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 96.9 (C-1), 81.1 (C-2), 73.0 (C-3), 70.8 (C-4), 70.7 (C-5), 62.5 (C-6), 58.3, 55.3 (O<u>C</u>H$_3$) ppm.

Methyl-3-*O*-methyl-α-D-glucopyranoside (8)



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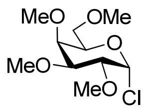
Prepared following procedure B. 1.35 g (4.56 mmol) **32**, 30 mL MeOH, 2 mL H_2O, 1 mL 1 N HCl. Yield: 876 mg (4.21 mmol, 92%), white solid, $[\alpha]_D^{23}$ = + 146.0° (c = 0.5, $CHCl_3$), m.p.: 79 °C, R_f (DCM/MeOH 9:1, v/v) = 0.18, ESI HRMS for $C_8H_{16}O_6$ [M+Na$^+$]: found 231.0833, calcd. 231.0839. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 4.74 (d, $^3J_{1,2}$ = 3.8 Hz, 1H, H-1), 3.87 (dd, $^3J_{5,6a}$ = 3.8 Hz, $^2J_{6a,6b}$ = 11.7 Hz, 1H, H-6a), 3.81 (dd, $^3J_{5,6b}$ = 4.6 Hz, $^2J_{6a,6b}$ = 11.7 Hz, 1H, H-6b), 3.69 – 3.62 (m, 1H, H-5), 3.62 – 3.55 (m, 1H, H-2), 3.52 (dd, $^3J_{3,4}$ = 9.2 Hz, $^3J_{4,5}$ = 9.5 Hz, 1H, H-4), 3.34 (dd, $^3J_{2,3}$ = 9.2 Hz, $^3J_{3,4}$ = 9.2 Hz, 1H, H-3), 3.68, 3.44 (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 99.6 (C-1), 84.2 (C-3), 72.8 (C-2), 70.9 (C-5), 70.2 (C-4), 62.5 (C-6), 60.9, 55.4 (O<u>C</u>H$_3$) ppm.

2,3,4,6-Tetra-*O*-methyl-α-D-galactopyranosyl chloride (9)[7]



9

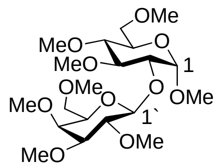
Prepared as described in the literature.[7] 516 mg (2.18 mmol) 2,3,4,6-Tetra-*O*-methyl α-D-galactopyranose[18,19], 50 µL (0.64 mmol) abs. DMF, 500 µL (5.71 mmol) Oxalylchlorid, 10 mL abs. DCM, Yield: 511 mg (2.01 mmol, 92%), colourless oil, $[\alpha]_D^{23}$ = + 203.3° (c = 0.66, $CHCl_3$), R_f (ethyl acetate) = 0.55, **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 6.28 (d, $^3J_{1,2}$ = 3.8 Hz, 1H, H-1), 4.22 – 4.16 (m, 1H, H-5), 3.83 (dd, $^3J_{1,2}$ = 3.8 Hz, $^3J_{2,3}$ = 9.9 Hz, 1H, H-2), 3.77 (dd, $^3J_{3,4}$ = 2.5 Hz, $^3J_{4,5}$ = 0.8 Hz, 1H, H-4), 3.62 – 3.56 (m, 2H, H-3, H-6a), 3.56 – 3.50 (m, 1H, H-6b), 3.59, 3.55, 3.52, 3.41, (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 94.1 (C-1), 79.8 (C-3), 77.8 (C-2), 75.4 (C-4), 72.1 (C-5), 70.3 (C-6), 61.5, 59.2, 58.5, 58.4 (O<u>C</u>H$_3$) ppm.

Characterization data for disaccharides 10 – 21 and 24 – 25.

Methyl 3,4,6-tri-*O*-methyl-2-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (10), methyl 2,4,6-tri-*O*-methyl-3-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galacto-pyranosyl)-α-D-glucopyranoside (11), methyl 2,3,6-tri-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (12) and methyl 2,3,4-tri-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (13)

Prepared following procedure E. 25.3 mg (0.107 mmol) methyl 3,4,6-tri-*O*-methyl-α-D-glucopyranoside (**1**), 25.3 mg (0.107 mmol) methyl 2,4,6-tri-*O*-methyl-α-D-glucopyranoside (**2**), 25.2 mg (0.107 mmol) methyl 2,3,6-tri-*O*-methyl-α-D-glucopyranoside (**3**), 25.2 mg (0.107 mmol) methyl 2,3,4-tri-*O*-methyl-α-D-glucopyranoside (**4**), 34.2 mg (0.856, 2.0 eq.) NaH, 218 mg (0.857 mmol, 2.0 eq.) 2,3,4,6-tetra-*O*-methyl-α-D-galactopyranosyl chloride (**9**); Yield (**10** – **13**): 38.4 mg (0.0845 mmol, 20%), yellow syrup; Relative yield (**10**/**11**/**12**/**13**): 40:11:26:23; R_f (ethyl acetate) = 0.17; ESI HRMS for $C_{20}H_{38}O_{11}$ [M+Na$^+$]: found 477.2303, calcd. 477.2306; Disaccharides **10** and **12** were fully characterized by NMR-spectroscopy.

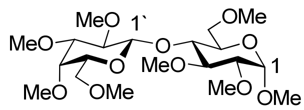
Methyl 3,4,6-tri-*O*-methyl-2-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (**10**)



10

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 4.82 (d, $^3J_{1,2}$ = 2.8 Hz, 1H, H-1), 4.39 (d, $^3J_{1`,2`}$ = 7.8 Hz, 1H, H-1`), 3.64 – 3.60 (m, 1H, H-4`), 3.60 – 3.50 (m, 6H, H-5, H-6a, H-6b, H-6a`, H-3, H-2), 3.48 – 3.42 (m, 2H, H-6b`, H-5`), 3.38 – 3.33 (m, 1H, H-2`), 3.23 – 3.16 (m, 1H, H-4), 3.13 (dd, $^3J_{3`,2`}$ = 9.7 Hz, $^3J_{3`,4`}$ = 3.2 Hz, 1H, H-3`), 3.63, 3.62, 3.55, 3.54, 3.52, 3.41, 3.36, 3.36 (OC<u>H</u>$_3$) ppm; **$^{13}$C-NMR** (101 MHz, $CDCl_3$) δ = 105.1 (C-1`), 99.7 (C-1), 84.2 (C-3`), 83.3 (C-3), 80.6 (C-2`), 80.0 (C-4), 79.6 (C-2), 74.9 (C-4`), 72.9 (C-5`), 71.1 (C-6), 70.7 (C-6`), 69.7 (C-5), 61.2, 60.8, 60.7, 60.4, 59.2, 59.1, 58.3, 55.1 (O<u>C</u>H$_3$) ppm.

Methyl 2,3,6-tri-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (**12**)

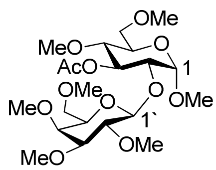


12

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 4.82 (d, $^3J_{1,2}$ = 3.5 Hz, 1H, H-1), 4.32 (d, $^3J_{1`,2`}$ = 7.6 Hz, 1H, H-1`), 3.77 (dd, $^3J_{6a,5}$ = 4.1 Hz, $^2J_{6a,6b}$ = 10.4 Hz, 1H, H-6a), 3.69 (ddd, $^3J_{5,4}$ = 9.8 Hz, $^3J_{5,6a}$ = 4.1 Hz, $^3J_{5,6b}$ = 1.6 Hz, 1H, H-5), 3.68 – 3.65 (m, 1H, H-4`), 3.65 – 3.60 (m, 3H, H-6b, H-4, H-6a`), 3.57 - 3.52 (m, 2H, H-3, H-6b`), 3.50 – 3.46 (m, 1H, H-5`), 3.27 (dd, $^3J_{2`,1`}$ = 7.6 Hz, $^3J_{2`,3`}$ = 9.8 Hz, 1H, H-2`), 3.21 (dd, 1H, H-2), 3.14 (dd, $^3J_{3`,2`}$ = 9.8 Hz, $^3J_{3`,4`}$ = 3.2 Hz, 1H, H-3`), 3.59, 3.58, 3.56, 3.52, 3.51, 3.42, 3.40, 3.39 (OC<u>H</u>$_3$) ppm; **$^{13}$C-NMR** (101 MHz, $CDCl_3$) δ = 103.8 (C-1`), 97.4 (C-1), 84.5 (C-3`), 81.7 (C-3), 81.5 (C-2), 81.0 (C-2`), 78.5 (C-4), 74.4 (C-4`), 72.7 (C-5`), 70.5 (C-6), 70.3 (C-6`), 69.7 (C-5), 61.2, 61.0, 60.9, 59.1, 59.0, 59.0, 58.0, 55.2 (O<u>C</u>H$_3$) ppm.

Methyl 3-*O*-acetyl-4,6-di-*O*-methyl-2-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (14)

Prepared following procedure E. 52.3 mg (0.235 mmol) methyl 4,6-di-*O*-methyl-α-D-glucopyranoside (**5**), 28.5 mg (0.713, 3.0 eq.) NaH, 175 mg (0.687 mmol, 3.0 eq.) 2,3,4,6-tetra-*O*-methyl-α-D-galactopyranosyl chloride (**9**); Yield (**14**): 19.2 mg (0.0398 mmol, 17%), colourless syrup; $[\alpha]_D^{23}$ = + 67.2° (c = 0.06, in $CHCl_3$); R_f (ethyl acetate) = 0.23; ESI HRMS for $C_{21}H_{38}O_{12}$ [M+Na$^+$]: found 505.2258, calcd. 505.2255.



14

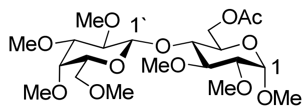
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 5.47 (dd, $^3J_{3,2}$ = 9.8 Hz, $^3J_{3,4}$ = 9.9 Hz, 1H, H-3), 4.88 (d, $^3J_{1,2}$ = 3.4 Hz, 1H, H-1), 4.20 (d, $^3J_{1`,2`}$ = 7.8 Hz, 1H, H-1`), 3.73 – 3.69 (m, 1H, H-5), 3.62 – 3.52 (m, 5H, H-4, H-4`, H-6, H-6a`), 3.45 – 3.33 (m, 3H, H-2, H-5`, H-6b`), 3.30 (dd, 1H, H-2`), 3.06 (dd, $^3J_{3`,2`}$ = 9.8 Hz, $^3J_{3`,4`}$ = 3.1 Hz, 1H, H-3`), 3.54, 3.50, 3.48, 3.41, 3.41, 3.36, 3.36 (OC<u>H</u>$_3$), 2.11 (C<u>H</u>$_3$-OAc) ppm. **$^{13}$C-NMR** (101 MHz, $CDCl_3$) δ = 169.9 (C=O), 105.6 (C-1`), 99.6 (C-1), 84.1 (C-3`), 80.0 (C-2`), 78.6 (C-4), 77.8 (C-2), 74.9 (C-4`), 73.0 (C-5`), 72.8 (C-3), 70.8 (C-6), 70.7 (C-6`), 69.3 (C-5), 61.2, 61.0, 59.5, 59.2, 59.1, 58.3, 55.2 (O<u>C</u>H$_3$), 21.1 (<u>C</u>H$_3$-OAc) ppm.

Methyl 6-*O*-acetyl-2,3-di-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (15),

Methyl 4-*O*-acetyl-2,3-di-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (16),

Prepared following procedure E. 51.6 mg (0.232 mmol) methyl 2,3-di-*O*-methyl-α-D-glucopyranoside (**6**), 24.0 mg (0.600, 2.6 eq.) NaH, 159 mg (0.624 mmol, 2.7 eq.) 2,3,4,6-tetra-*O*-methyl-α-D-galactopyranosyl chloride (**9**); Yield (**15, 16**): 69.4 mg (0.144 mmol, 62%), white solid; Relative yield (**15**/**16**): 20:80; R_f (ethyl acetate) = 0.23; ESI HRMS for $C_{21}H_{38}O_{12}$ [M+Na$^+$]: found 505.2252, calcd. 505.2255.

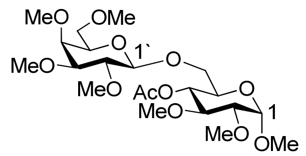
Methyl 6-*O*-acetyl-2,3-di-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (**15**)



15

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 4.81 (d, $^3J_{1,2}$ = 3.8 Hz, 1H, H-1), 4.51 (dd, $^3J_{6a,5}$ = 1.9 Hz, $^2J_{6a,6b}$ = 12.0 Hz, 1H, H-6a), 4.34 (d, $^3J_{1`,2`}$ = 7.9 Hz ,1H, H-1`), 4.29 (dd, $^3J_{6b,5}$ = 5.4 Hz, $^2J_{6b,6a}$ = 12.0 Hz, 1H, H-6b), 3.81 (ddd, $^3J_{5,4}$ = 9.8 Hz, $^3J_{5,6a}$ = 1.9 Hz, $^3J_{5,6b}$ = 5.4 Hz, 1H, H-5), 3.67 – 3.64 (m, 1H, H-4`), 3.64 – 3.46 (m, 5H, H-6a`, H-3, H-4, H-6b`, H-5`), 3.26 (dd, $^3J_{2`,1`}$ = 7.9 Hz, $^3J_{2`,3`}$ = 9.7 Hz, 1H, H-2`), 3.21 (dd, $^3J_{2,1}$ = 3.8 Hz, $^3J_{2,3}$ = 9.5 Hz, 1H, H-2), 3.14 (dd, $^3J_{3`,2`}$ = 9.7 Hz, $^3J_{3`,4`}$ = 3.0 Hz, 1H, H-3`), 3.60, 3.56, 3.56, 3.52, 3.51, 3.42, 3.39 (OC<u>H</u>$_3$), 2.09 (C<u>H</u>$_3$-OAc) ppm. **$^{13}$C-NMR** (101 MHz, $CDCl_3$) δ = 170.8 (C=O), 104.0 (C-1`), 97.2 (C-1), 84.9 (C-3`), 81.9 (C-3), 81.8 (C-2), 81.0 (C-2`), 79.3 (C-4), 74.3 (C-4`), 72.8 (C-5`), 70.4 (C-6`), 68.4 (C-5), 63.2 (C-6), 61.2, 61.2, 61.1, 59.1, 59.0, 57.9, 55.2 (O<u>C</u>H$_3$), 20.9 (<u>C</u>H$_3$-OAc) ppm.

Methyl 4-*O*-acetyl-2,3-di-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (**16**)



16

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 4.83 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.72 (dd, $^3J_{4,3}$ = 9.4 Hz, $^2J_{4,5}$ = 10.1 Hz, 1H, H-4), 4.27 (d, $^3J_{1`,2`}$ = 7.6 Hz, 1H, H-1`), 3.93 – 3.84 (m, 2H, H-5, H-6a), 3.67 – 3.63 (m, 1H, H-4`), 3.63 – 3.44 (m, 5H, H-6a`, H-3, H-6b`, H-6b, H-5`), 3.30 (dd, $^3J_{2`,1`}$ = 7.6 Hz, $^3J_{2`,3`}$ = 9.8 Hz, 1H, H-2`), 3.27 (dd, $^3J_{2,1}$ = 3.6 Hz, $^3J_{2,3}$ = 9.7 Hz, 1H, H-2), 3.13 (dd, 1H, $^3J_{3`,2`}$ = 9.8 Hz, $^3J_{3`,4`}$ = 3.0 Hz, H-3`), 3.59, 3.56, 3.52, 3.52, 3.51, 3.43, 3.40 (OC<u>H</u>$_3$), 2.08 (C<u>H</u>$_3$-OAc) ppm. **$^{13}$C-NMR** (101 MHz, $CDCl_3$) δ = 170.0 (C=O), 103.9 (C-1`), 97.1 (C-1), 83.6 (C-3`), 81.5 (C-2), 80.8 (C-3), 80.6 (C-2`), 74.6

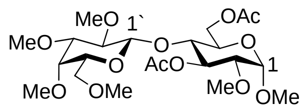
(C-4`), 72.9 (C-5`), 70.9 (C-4), 70.5 (C-6`), 68.9 (C-5), 68.6 (C-6), 61.2, 60.8, 60.7, 59.2, 59.1, 58.3, 55.1 (O<u>C</u>H$_3$), 20.9 (<u>C</u>H$_3$-OAc) ppm.

Methyl 3,6-di-*O*-acetyl-2-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (17)

Methyl 3,4-di-*O*-acetyl-2-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (18)

Prepared following procedure E. 42.0 mg (0.202 mmol) methyl 2-*O*-methyl-α-D-glucopyranoside (**7**), 24.0 mg (0.600, 3.0 eq.) NaH, 160 mg (0.624 mmol, 3.0 eq.) 2,3,4,6-tetra-*O*-methyl-α-D-galactopyranosyl chloride (**9**); Yield (**17, 18**): 31.0 mg (0.0607 mmol, 30%), white solid; Relative yield (**17**/**18**): 39:61; R_f (ethyl acetate) = 0.26; ESI HRMS for $C_{22}H_{38}O_{13}$ [M+Na$^+$]: found 533.2211, calcd. 533.2205.

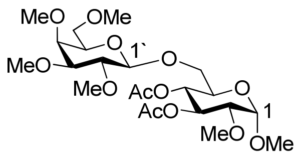
Methyl 3,6-di-*O*-acetyl-2-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (**17**)



17

^{1}H-NMR (400 MHz, CDCl$_3$) δ = 5.35 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 9.5 Hz, 1H, H-3), 4.84 (d, $^3J_{1,2}$ = 3.5 Hz, 1H, H-1), 4.53 (dd, $^3J_{6a,5}$ = 2.0 Hz, $^2J_{6a,6b}$ = 11.8 Hz, 1H, H-6a), 4.30 (dd, $^3J_{6b,5}$ = 5.2 Hz, $^2J_{6b,6a}$ = 11.8 Hz, 1H, H-6b), 4.10 (d, $^3J_{1`,2`}$ = 7.6 Hz, 1H, H-1`), 3.92 – 3.84 (m, 1H, H-5), 3.73 – 3.31 (m, 6H, H-4, H-4`, H-6`, H-5`, H-2), 3.20 (dd, $^3J_{2`,1`}$ = 7.6 Hz, $^3J_{2`,3`}$ = 9.7 Hz, 1H, H-2`), 3.07 (dd, $^3J_{3`,2`}$ = 9.7 Hz, $^3J_{3`,4`}$ = 3.2 Hz, 1H, H-3`), 3.51, 3.50, 3.48, 3.41, 3.41, 3.38 (OC<u>H</u>$_3$), 2.09, 2.07 (C<u>H</u>$_3$-OAc) ppm. **^{13}C-NMR** (101 MHz, CDCl$_3$) δ = 170.5, 169.8 (C=O), 103.4 (C-1`), 97.2 (C-1), 84.3 (C-3`), 80.5 (C-2`), 79.3 (C-2), 76.3 (C-4), 74.5 (C-4`), 73.1 (C-5`), 71.6 (C-3), 70.7 (C-6`), 68.6 (C-5), 62.4 (C-6), 61.0, 60.9, 59.0, 58.7, 58.2, 55.2 (O<u>C</u>H$_3$), 21.1, 20.8 (<u>C</u>H$_3$-OAc) ppm.

Methyl 3,4-di-*O*-acetyl-2-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (**18**)



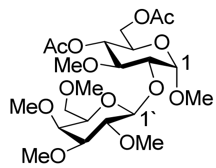
18

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 5.36 (dd, $^{3}J_{3,2}$ = $^{3}J_{3,4}$ = 9.5 Hz, 1H, H-3), 4.87 (d, $^{3}J_{1,2}$ = 3.5 Hz, 1H, H-1), 4.82 (dd, $^{3}J_{4,3}$ = 9.5 Hz, $^{3}J_{4,5}$ = 9.8 Hz, 1H, H-4), 4.24 (d, $^{3}J_{1`,2`}$ = 7.5 Hz, 1H, H-1`), 4.00 – 3.93 (m, 1H, H-5), 3.88 (dd, $^{3}J_{6a,5}$ = 1.9 Hz, $^{2}J_{6a,6b}$ = 10.9 Hz, 1H, H-6a), 3.73 – 3.31 (m, 6H, H-4`, H-6`, H-6b, H-5`, H-2), 3.30 (dd, $^{3}J_{2`,1`}$ = 7.5 Hz, $^{3}J_{2`,3`}$ = 9.8 Hz, 1H, H-2`), 3.12 (dd, $^{3}J_{3`,2`}$ = 9.8 Hz, $^{3}J_{3`,4`}$ = 3.0 Hz, 1H, H-3`), 3.58, 3.54, 3.51, 3.43, 3.43, 3.38 (OC<u>H</u>$_3$), 2.02, 1.99 (C<u>H</u>$_3$-OAc) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 170.0, 170.0 (C=O), 103.9 (C-1`), 96.8 (C-1), 83.7 (C-3`), 80.5 (C-2`), 79.1 (C-2), 74.7 (C-4`), 73.0 (C-5`), 72.2 (C-3), 70.6 (C-6`), 69.7 (C-4), 68.5 (C-5), 68.4 (C-6), 61.2, 60.7, 59.1, 58.9, 58.3, 55.2 (O<u>C</u>H$_3$), 20.8, 20.6 (<u>C</u>H$_3$-OAc) ppm.

Methyl 4,6-di-*O*-acetyl-3-*O*-methyl-2-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (19),
Methyl 2,6-di-*O*-acetyl-3-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (20),
Methyl 2,4-di-*O*-acetyl-3-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (21)

Prepared following procedure E. 40.5 mg (0.195 mmol) methyl 3-*O*-methyl-α-D-glucopyranoside (**8**), 75.7 mg (0.800, 4.0 eq.) NaH, 202 mg (0.793 mmol, 4.0 eq.) 2,3,4,6-tetra-*O*-methyl α-D-galactopyranosyl chloride (**9**); Yield (**19 - 21**): 39.7 mg (0.0778 mmol, 40%), white solid; Relative yield (**19**/**20**/**21**): 32:10:58; R_f (ethyl acetate) = 0.30; ESI HRMS for $C_{22}H_{38}O_{13}$ [M+Na$^+$]: found 533.2211, calcd. 533.2205. Disaccharide **21** was fully characterized by NMR-spectroscopy. Disaccharide **19** was characterized by ^{13}C-NMR-spectroscopy.

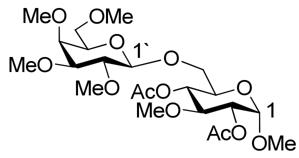
Methyl 4,6-di-*O*-acetyl-3-*O*-methyl-2-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (**19**)



19

^{13}C-NMR (101 MHz, $CDCl_3$) δ = 170.7, 169.6 (C=O), 104.8 (C-1`), 99.6 (C-1), 84.1 (C-3`), 80.4 (C-2`), 80.2 (C-3), 78.7 (C-2), 74.9 (C-4`), 72.9 (C-4), 70.7 (C-6`), 70.3 (C-5`), 67.3 (C-5), 62.4 (C-6), 61.2, 60.7, 60.4, 59.1, 58.3, 55.3 (O<u>C</u>H$_3$), 20.8, 20.7 (<u>C</u>H$_3$-OAc) ppm.

Methyl 2,4-di-*O*-acetyl-3-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (**21**)



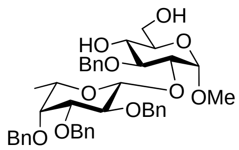
21

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 4.89 (d, $^{3}J_{1,2}$ = 3.8 Hz, 1H, H-1), 4.79 (dd, $^{3}J_{4,3}$ = 9.8 Hz, $^{3}J_{4,5}$ = 10.0 Hz, 1H, H-4), 4.77 (dd, $^{3}J_{2,1}$ = 3.8 Hz, $^{3}J_{2,3}$ = 10.0 Hz, 1H, H-2), 4.28 (d, $^{3}J_{1`,2`}$ = 7.5 Hz, 1H, H-1`), 3.93 (ddd, $^{3}J_{5,4}$ = 10.0 Hz, $^{3}J_{5,6a}$ = 1.5 Hz, $^{3}J_{5,6b}$ = 8.2 Hz, 1H, H-5), 3.87 (dd, $^{3}J_{6a,5}$ = 1.5 Hz, $^{2}J_{6a,6b}$ = 10.8 Hz, 1H, H-6a), 3.71 (dd, $^{3}J_{3,2}$ = 10.0 Hz, $^{3}J_{3,4}$ = 9.8 Hz, 1H, H-3), 3.67 – 3.64 (m, 1H, H-4`), 3.64 – 3.44 (m, 4H, H-6b, H-6`, H-5`), 3.30 (dd, $^{3}J_{2`,1`}$ = 7.5 Hz, $^{3}J_{2`,3`}$ = 9.8 Hz, 1H, H-2`), 3.13 (dd, $^{3}J_{3`,2`}$ = 9.8 Hz, $^{3}J_{3`,4`}$ = 3.0 Hz, 1H, H-3`), 3.58, 3.56, 3.52, 3.45, 3.40, 3.39 (OC$\underline{H}_3$), 2.14, 2.08 (C$\underline{H}_3$-OAc) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 170.1, 169.8 (C=O), 103.8 (C-1`), 96.5 (C-1), 83.6 (C-3`), 80.7 (C-2`), 78.5 (C-3), 74.6 (C-4`), 73.0 (C-2), 72.9 (C-4), 70.7 (C-5`), 70.5 (C-6`), 69.0 (C-5), 68.5 (C-6), 61.2, 60.7, 60.3, 59.2, 58.4, 55.1 (O$\underline{C}H_3$), 21.0, 20.9 ($\underline{C}H_3$-OAc) ppm.

Methyl 3-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (24),
Methyl 3-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (25)

Prepared following procedure E. 100 mg (0.352 mmol) methyl 3-*O*-benzyl-α-D-glucopyranoside (**22**) was dissolved in 5 mL anhydrous *N*,*N*-dimethylformamide and treated with 42.0 mg (0.650 mmol, 3.0 eq.) NaH. The mixture was stirred for 1 h. Subsequently 500 mg (1.10 mmol, 3.1 eq.) 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl chloride (**23**), dissolved in 5 mL anhydrous *N*,*N*-dimethylformamide, was added and the mixture stirred for 20 h. The reaction was stopped with methanol and the solvents were removed under reduced pressure. The remaining syrup was purified using flash-column chromatography (eluent: petrol ether/ethyl acetate 2:1 → ethylacetate) to give **24** and **25** (119 mg, 0.170 mmol, 48%) white solid; Relative yield (**24**/**25**): 13:87.

Methyl 3-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (**24**)

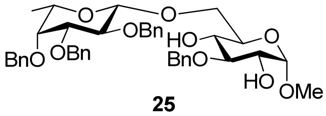


24

15.8 mg (0.0225 mmol, 6%), $[\alpha]_D^{23}$ = + 50.0° (c = 0.30, in $CHCl_3$); m.p. 150 °C; R_f (ethyl acetate) = 0.50; ESI HRMS for $C_{41}H_{48}O_{10}$ [M+Na$^+$]: found 723.3133, calcd. 723.3140. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.40 – 7.12 (m, 20H, $H_{arom.}$), 5.01 (d, $^{2}J_{A,A`}$ = 11.6 Hz, 1H, OC$\underline{H}_2$Ph-A), 4.98 (d, $^{2}J_{B,B`}$ = 11.8 Hz, 1H, OC$\underline{H}_2$Ph-B), 4.93 – 4.88 (m, 2H, OC$\underline{H}_2$Ph-A`, C`), 4.90 (d, $^{3}J_{1,2}$ = 3.5 Hz, 1H, H-1), 4.77 (d, $^{2}J_{D,D`}$ = 11.8

Hz, 1H, OC<u>H</u>$_2$Ph-D), 4.72 (d, $^{2}J_{D`,D}$ = 11.8 Hz, 1H, OC<u>H</u>$_2$Ph-D`), 4.72 (d, $^{2}J_{B`,B}$ = 11.8 Hz, 1H, OC<u>H</u>$_2$Ph-B`), 4.59 (d, $J_{1`,2`}$ = 7.8 Hz, 1H, H-1`), 4.49 (d, $^{2}J_{C`,C}$ = 11.8 Hz, 1H, OC<u>H</u>$_2$Ph-C`), 3.90 (dd, $^{3}J_{2`,1`}$ = 7.8 Hz, $^{3}J_{2`,3`}$ = 9.3 Hz, 1H, H-2`), 3.85 – 3.63 (m, 5H, H-3, H-6, H-2, H-5), 3.58 – 3.44 (m, 4H, H-4`, H-3`, H-4, H-5`), 3.43 (OC<u>H</u>$_3$), 1.17 (d, $^{3}J_{5`,6`}$ = 6.3 Hz, 3H, H-6′) ppm. **$^{13}$C-NMR** (101 MHz, $CDCl_3$) δ = 128.5, 128.4, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.2 (<u>C</u>H$_{arom.}$), 104.1 (C-1`), 100.0 (C-1), 82.8 (C-3`), 81.5 (C-3), 79.1 (C-2`), 78.9 (C-2), 76.4 (C-4`), 75.0 (OCH$_2$Ph-A), 75.0 (OCH$_2$Ph-C), 74.7 (OCH$_2$Ph-B), 73.1 (OCH$_2$Ph-D), 70.9 (C-4), 70.5 (C-5), 70.5 (C-5`), 62.7 (C-6), 55.3 (O<u>C</u>H$_3$), 16.9 (C-6`) ppm.

Methyl 3-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (**25**)

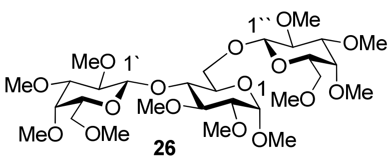


25

103 mg (0.147 mmol, 42%), $[\alpha]_D^{23}$ = + 37.6° (c = 1.00, in $CHCl_3$); m.p. 146 °C; R_f (ethyl acetate) = 0.56; ESI HRMS for $C_{41}H_{48}O_{10}$ [M+Na$^+$]: found 723.3133, calcd. 723.3140. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.42 – 7.26 (m, 20H, H$_{arom.}$), 4.99 (d, $^{2}J_{A,A`}$ = 11.8 Hz, 1H, OC<u>H</u>$_2$Ph-A), 4.97 – 4.91 (m, 2H, OC<u>H</u>$_2$Ph-B, OC<u>H</u>$_2$Ph-C), 4.82 – 4.70 (m, 5H, OC<u>H</u>$_2$Ph-B`, OC<u>H</u>$_2$Ph-C`, OC<u>H</u>$_2$Ph-D, H-1, OC<u>H</u>$_2$Ph-D`), 4.68 (d, $^{2}J_{A`,A}$ = 11.8 Hz, 1H, OC<u>H</u>$_2$Ph-A`), 4.41 (d, $J_{1`,2`}$ = 7.5 Hz, 1H, H-1`), 4.15 - 4.06 (m, 1H, H-6a), 3.85 (dd, $^{3}J_{2`,1`}$ = 7.5 Hz, $^{3}J_{2`,3`}$ = 9.3 Hz, 1H, H-2`), 3.81 – 3.74 (m, 2H, H-5, H-6b), 3.67 – 3.45 (m, 6H, H-2, H-3, H-4, H-4`, H-3`, H-5`), 3.38 (OC<u>H</u>$_3$), 1.21 (d, $^{3}J_{5`,6`}$ = 6.3 Hz, 3H, H-6`) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 138.7, 138.6 (C$_{arom.}$,), 128.5, 128.4, 128.3, 128.1, 128.1, 128.0, 127.8, 127.6, 127.6, 127.5 (<u>C</u>H$_{arom.}$), 103.9 (C-1`), 99.3 (C-1), 82.6 (C-3`), 82.6 (C-3), 79.1 (C-2`), 76.4 (C-4`), 75.1 (OCH$_2$Ph-B), 74.9 (OCH$_2$Ph-C), 74.6 (OCH$_2$Ph-A), 73.1 (OCH$_2$Ph-D), 72.6 (C-2), 71.0 (C-4), 70.5 (C-5), 70.2 (C-5`), 68.9 (C-6), 55.3 (O<u>C</u>H$_3$), 16.8 (C-6`) ppm.

Methyl 2,3-di-*O*-methyl-4,6-di-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (26)

Trisaccharide isolated after base-promoted glycosylation of methyl 2,3-di-*O*-methyl-α-D-glucopyranoside (**6**). 4 – 24% yield as white solid; $[\alpha]_D^{23}$ = + 41.7° (c = 0.23, in $CHCl_3$); R_f (ethyl acetate) = 0.05; ESI HRMS for $C_{29}H_{54}O_{16}$ [M+Na$^+$]: found 681.3306, calcd. 681.3304.

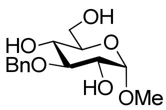


26

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 4.79 (d, $^3J_{1,2}$ = 3.8 Hz, 1H, H-1), 4.35 (d, $^3J_{1`,2`}$ = 7.6 Hz, 1H, H-1`), 4.29 (d, $^3J_{1``,2``}$ = 7.6 Hz, 1H, H-1``), 4.27 – 4.22 (m, 1H, H-6a), 3.79 – 3.72 (m, 2H, H-5, H-6b), 3.67 – 3.46 (m, 10H, H-4`, H-4``, H-6a`, H-6a``, H-3, H-4, H-6b`, H-6b``, H-5`, H-5``), 3.34 (dd, $^3J_{2``,1``}$ = 7.6 Hz, $^3J_{2``,3``}$ = 9.8 Hz, 1H, H-2``), 3.24 (dd, $^3J_{2`,1`}$ = 7.6 Hz, $^3J_{2`,3`}$ = 9.8 Hz, 1H, H-2`), 3.19 (dd, $^3J_{2,1}$ = 3.8 Hz, $^3J_{2,3}$ = 9.5 Hz, 1H, H-2), 3.13 (dd, $^3J_{3`,2`}$ = 9.8 Hz, $^3J_{3`,4`}$ = 3.2 Hz, 1H, H-3`), 3.11 (dd, $^3J_{3``,2``}$ = 9.8 Hz, $^3J_{3``,4``}$ = 3.2 Hz, 1H, H-3``), 3.59, 3.58, 3.57, 3.55, 3.54, 3.52, 3.52, 3.51, 3.40, 3.39, 3.38 (s, 3H, OC$\underline{H}_3$) ppm. **$^{13}$C-NMR** (101 MHz, $CDCl_3$) δ = 103.9 (C-1`), 103.9 (C-1``), 97.1 (C-1), 84.5 (C-3`), 83.8 (C-3``), 81.8 (C-3), 81.5 (C-2), 81.1 (C-2`), 80.6 (C-2``), 79.3 (C-4), 74.6 (C-4`), 74.5 (C-4``), 72.8 (C-5`), 72.6 (C-5``), 70.7 (C-6`), 70.4 (C-6``), 69.6 (C-5), 68.1 (C-6), 61.2, 61.1, 61.1, 61.0, 60.9, 59.1, 59.1, 59.0, 58.1, 57.9, 55.1 (O$\underline{C}H_3$) ppm.

Characterization data for donor 23 and intermediates 22, 28 – 45.

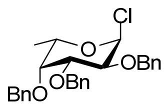
Methyl 3-*O*-benzyl-α-D-glucopyranoside (22)[13]



22

Prepared following procedure B. 2.00 g (5.37 mmol) **35**, 50 mL MeOH, 4.0 mL H_2O, 1 mL 1 N HCl. Yield: 1.40 g (4.92 mmol, 92%), white solid, $[\alpha]_D^{23}$ = + 102.5° (c = 0.2, $CHCl_3$), Lit.[13]: $[\alpha]_D^{23}$ = + 90.3° (c = 0.66, $CHCl_3$), m.p.: 94 °C, Lit.[13]: m.p.: 89 – 91 °C, R_f (EE) = 0.23. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.41 – 7.29 (m, 5H, $H_{arom.}$), 5.03 (d, 1H, OC$\underline{H}_2$Ph-A), 4.76 (d, $^3J_{1,2}$ = 3.8 Hz, 1H, H-1), 4.73 (d, $^2J_{A,A`}$ = 11.5 Hz, 1H, OC$\underline{H}_2$Ph-A`), 3.85 (dd, $^3J_{5,6a}$ = 3.6 Hz, $^2J_{6a,6b}$ = 11.7 Hz, 1H, H-6a), 3.78 (dd, $^3J_{5,6b}$ = 4.6 Hz, $^2J_{6a,6b}$ = 11.7 Hz, 1H, H-6b), 3.71 – 3.61 (m, 2H, H-2, H-5), 3.60 – 3.54 (m, 2H, H-3, H-4), 3.44 (OC$\underline{H}_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 138.5 ($C_{arom.}$), 128.7, 128.0, 128.0 ($\underline{C}H_{arom.}$), 99.6 (C-1), 82.8 (C-3), 75.0 (O$\underline{C}H_2$Ph-A), 72.9 (C-2), 70.9 (C-5), 70.3 (C-4), 62.6 (C-6), 55.4 (O$\underline{C}H_3$) ppm.

2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl chloride (23)[8]

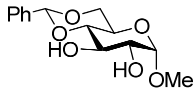


23

Prepared as described in the literature.[7] 1.00 g (2.30 mmol) 2,3,4-tri-*O*-benzyl α-L-fucopyranose, 53 µL (0.69 mmol) abs. DMF, 550 µL (6.44 mmol) oxalylchloride, 8 mL abs. DCM. Yield: 917 mg (2.02 mmol, 88%), colourless oil, $[\alpha]_D^{23}$ = - 180.0° (c = 0.2, $CHCl_3$), Lit.[8]: $[\alpha]_D^{23}$ = - 169.0° (c = 1.0, CH_2Cl_2), R_f (PE/EE

4:1, v/v) = 0.29. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.44 – 7.28 (m, 15H, $H_{arom.}$), 6.17 (d, $^3J_{1,2}$ = 3.8 Hz, 1H, H-1), 5.01 (d, $^2J_{A,A`}$ = 11.4 Hz, 1H, OC<u>H</u>$_2$Ph-A), 4.91 (d, $^2J_{B,B`}$ = 11.9 Hz, 1H, OC<u>H</u>$_2$Ph-B), 4.82 – 4.72 (m, 3H, OC<u>H</u>$_2$Ph-B′,C,C′), 4.67 (d, $^2J_{A,A`}$ = 11.4 Hz, 1H, OC<u>H</u>$_2$Ph-A′), 4.23 (dd, $^3J_{1,2}$ = 3.8 Hz, $^3J_{2,3}$ = 9.8 Hz, 1H, H-2), 4.21 – 4.16 (m, 1H H-5), 4.00 (dd, $^3J_{2,3}$ = 9.8 Hz, $^3J_{3,4}$ = 2.6 Hz, 1H, H-3), 3.74 – 3.68 (m, 1H, H-4), 1.07 (d, $^3J_{5,6}$ = 6.5Hz, 3H, H-6) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 138.5, 138.2, 137.8 ($C_{arom.}$), 128.4, 128.4, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5 (<u>C</u>$H_{arom.}$), 95.4 (C-1), 78.6 (C-3), 77.1 (C-4), 76.1 (C-2), 75.0 (OC<u>H</u>$_2$Ph-A), 73.5 (OC<u>H</u>$_2$Ph-B), 72.9 (OC<u>H</u>$_2$Ph-C), 69.9 (C-5), 16.3 (C-6) ppm.

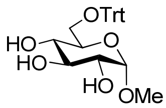
Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (28)[9]



28

Prepared as described in the literature[9]. 20.0 g (103 mmol) **27**, 320 mL CH_3CN, 28.0 mL (186 mmol) benzaldehyde dimethylacetal, 1.2 g (5.0 mmol) camphor-10-sulfonic acid. Yield: 23.1 g (82.0 mmol, 80%), white solid, $[\alpha]_D^{23}$ = + 112.6° (c = 1.0, $CHCl_3$), Lit.[9]: $[\alpha]_D^{23}$ = + 110° (c = 2.0, $CHCl_3$), m.p.: 160 °C, Lit.[9]: m.p.: 161 – 162 °C, R_f (DCM/MeOH 9:1, v/v) = 0.45. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.53 – 7.47 (m, 2H, $H_{arom.}$), 7.42-7.35 (m, 3H, $H_{arom.}$), 5.54 (s, 1H, PhC<u>H</u>OO), 4.80 (d, $^3J_{1,2}$ = 4.0 Hz, 1H, H-1), 4.30 (dd, $^3J_{5,6a}$ = 4.4 Hz, $^2J_{6a,6b}$ = 9.7 Hz, 1H, H-6a), 3.94 (dd, $^2J_{2,3}$ = 9.2 Hz, $^2J_{3,4}$ = 9.3 Hz, 1H, H-3), 3.82 (ddd, $^3J_{4,5}$ = 9.2 Hz, $^3J_{5,6a}$ = 4.4 Hz, $^3J_{5,6b}$ = 10.3 Hz, 1H, H-5), 3.75 (dd, $^3J_{5,6b}$ = 10.3 Hz, $^2J_{6a,6b}$ = 9.7 Hz, 1H, H-6b), 3.64 (dd, $^3J_{1,2}$ = 4.0 Hz, $^3J_{2,3}$ = 9.2 Hz, 1H, H-2), 3.50 (dd, $^3J_{3,4}$ = 9.3 Hz, $^3J_{4,5}$ = 9.2 Hz, 1H, H-4), 3.47 (OC<u>H</u>$_3$) ppm, **^{13}C-NMR** (100 MHz, $CDCl_3$): δ = 137.1 ($C_{arom.}$), 129.3, 128.3, 126.3 (<u>C</u>$H_{arom.}$), 102.0 (Ph<u>C</u>HOO), 99.7 (C-1), 80.8 (C-4), 72.9 (C-2), 71.9 (C-3), 68.9 (C-6), 62.4 (C-5), 55.6 (O<u>C</u>H_3) ppm.

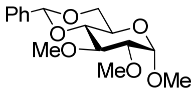
Methyl 6-*O*-triphenylmethyl-α-D-glucopyranoside (29)[15]



29

Prepared following procedure D. 3.00 g (15.4 mmol) **27**, 4.33 g (15.5 mmol) Chlorotriphenylmethane, 20 mg DMAP, 40 mL pyridine. Yield: 3.66 g (8.38 mmol, 54%), white solid, $[\alpha]_D^{23}$ = + 53.6° (c = 0.56, $CHCl_3$), m.p.: 134 °C, Lit.[15]: m.p.: 151 – 152 °C, R_f (EE) = 0.16, MALDI TOF MS for $C_{26}H_{28}O_6$ $[M+Na^+]$: found 459.0, calcd. 459.2. **^{1}H-NMR** (400 MHz, MeOD) δ = 4.71 (d, $^3J_{1,2}$ = 3.8 Hz, 1H, H-1), 3.75 (ddd, $^3J_{4,5}$ = 9.8 Hz, $^3J_{5,6a}$ = 1.7 Hz, $^3J_{5,6b}$ = 6.8 Hz, 1H, H-5), 3.59 (dd, $^3J_{2,3}$ = 9.3 Hz, $^3J_{3,4}$ = 9.0 Hz, 1H, H-3), 3.51 (OC<u>H</u>$_3$), 3.45-3.36 (m, 2H, H-2, H-6a), 3.25 (dd, $^3J_{3,4}$ = 9.0 Hz, $^3J_{4,5}$ = 9.8 Hz, 1H, H-4), 3.22 (dd, $^3J_{5,6b}$ = 6.8 Hz, $^2J_{6a,6b}$ = 9.8 Hz, 1H, H-6b) ppm. **^{13}C-NMR** (101 MHz, MeOD) δ = 145.8 ($C_{arom.}$), 130.1, 128.9, 128.2 ($\underline{C}H_{arom.}$), 101.3 (C-1), 75.6 (C-3), 73.8 (C-2), 72.7 (C-5), 72.5 (C-4), 65.1 (C-6), 55.6 ($O\underline{C}H_3$).

Methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-α-D-glucopyranoside (30)[11]



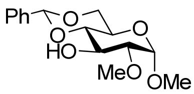
30

Prepared following procedure A. 6.0 g (21 mmol) **28**, 3.8 g (96 mmol) NaH, 6.0 mL (96 mmol) MeI, 50 mL DMF. Yield: 6.29 g (20.3 mmol, 97%), white solid, $[\alpha]_D^{23}$ = + 95.1° (c = 1.0, $CHCl_3$), Lit.[11]: $[\alpha]_D^{23}$ = + 97.9° (c = 1.5, acetone), m.p.: 123 – 124 °C, Lit.[11]: m.p.: 121 – 122 °C, R_f (PE/EE 1:1, v/v) = 0.30 **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.53 – 7.49 (m, 2H, $H_{arom.}$), 7.41-7.33 (m, 3H, $H_{arom.}$), 5.55 (s, 1H, PhC$\underline{H}$OO), 4.87 (d, $^3J_{1,2}$ = 3.7 Hz, 1H, H-1), 4.30 (dd, $^3J_{5,6a}$ = 4.6 Hz, $^2J_{6a,6b}$ = 9.9 Hz, 1H, H-6a), 3.83 (ddd, $^3J_{4,5}$ = 9.4 Hz, $^3J_{5,6a}$ = 4.6 Hz, $^3J_{5,6b}$ = 10.2 Hz, 1H, H-5), 3.74 (dd, $^3J_{5,6b}$ = 10.2 Hz, $^2J_{6a,6b}$ = 9.9 Hz 1H, H-6b), 3.70 (dd, $^3J_{2,3}$ = 9.2 Hz, $^3J_{3,4}$ = 9.4 Hz, 1H, H-3), 3.54 (dd, $^3J_{3,4}$ = 9.4 Hz, $^3J_{4,5}$ = 9.4 Hz, 1H, H-4), 3.31 (dd, $^3J_{1,2}$ = 3.7 Hz, $^3J_{2,3}$ = 9.2 Hz, 1H, H-2), 3.64, 3.56, 3.46 ($OC\underline{H}_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 137.3 ($C_{arom.}$), 128.9, 128.2, 126.1 ($\underline{C}H_{arom.}$), 101.4 (Ph$\underline{C}$HOO), 98.4 (C-1), 82.1 (C-4), 81.4 (C-2), 79.8 (C-3), 69.1 (C-6), 62.2 (C-5), 61.0, 59.3, 55.3 ($O\underline{C}H_3$) ppm.

Methyl 4,6-*O*-benzylidene-2-*O*-methyl-α-D-glucopyranoside (31) and Methyl 4,6-*O*-benzylidene-3-*O*-methyl-α-D-glucopyranoside (32).

Prepared following procedure A with substoichiometric amounts of base and methylating agent, 9.40 g (33.3 mmol) **28**, 1.24 g NaH (31.0 mmol, 0.9 eq), 2.80 mL (45.0 mmol) MeI, 100 mL DMF.

Methyl 4,6-*O*-benzylidene-2-*O*-methyl-α-D-glucopyranoside (**31**).

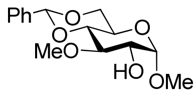


31

Yield: 1.51 g (5.10 mmol, 16 %), white solid, $[\alpha]_D^{20}$ = + 100.2 ° (c = 0.5, $CHCl_3$), m.p.: 165 – 166 °C, R_f (PE/EE 1:1, v/v) = 0.14, ESI HRMS for $C_{15}H_{20}O_6$ [M+Na$^+$]: found 319.1147, calcd. 319.1152. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.53 – 7.46 (m, 2H, H_{arom}), 7.40 – 7.32 (m, 3H, H_{arom}), 5.54 (s, 1H, PhC$\underline{H}$OO), 4.92 (d, $^3J_{1,2}$ = 3.5 Hz, 1H, H-1), 4.29 (dd, $^3J_{5,6a}$ = 4.6 Hz, $^2J_{6a,6b}$ = 9.9 Hz, 1H, H-6a), 4.10 (dd, $^3J_{2,3}$ = 9.4 Hz, $^3J_{3,4}$ = 9.2 Hz, 1H, H-3), 3.83 (ddd, $^3J_{4,5}$ = 9.4 Hz, $^3J_{5,6a}$ = 4.6 Hz, $^3J_{5,6b}$ = 10.4 Hz, 1H, H-5), 3.74 (dd, $^3J_{5,6b}$ = 10.4 Hz, $^3J_{6a,6b}$ = 9.9 Hz, 1H, H-6b), 3.52 (dd, $^3J_{3,4}$ = 9.2 Hz, $^3J_{4,5}$ = 9.4 Hz, 1H, H-4), 3.54, 3.46

(OC<u>H</u>$_3$), 3.31 (dd, $^3J_{1,2}$ = 3.5 Hz, $^3J_{2,3}$ = 9.4 Hz, 1H, H-2) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 137.2 ($C_{arom.}$), 129.4, 128.5, 126.5 (<u>C</u>$H_{arom.}$), 102.2 (Ph<u>C</u>HOO), 97.9 (C-1), 81.8 (C-2), 81.4 (C-4), 70.4 (C-3), 69.1 (C-6), 62.2 (C-5), 58.9, 55.5 (O<u>C</u>H_3) ppm.

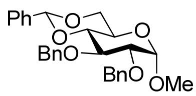
Methyl 4,6-*O*-benzylidene-3-*O*-methyl-α-D-glucopyranoside (**32**).



32

Yield: 2.08 g (7.02 mmol, 23 %), white solid, $[\alpha]_D^{20}$ = + 123.0 ° (c = 1.0, $CHCl_3$), m.p.: 143 – 145 °C, R_f (PE/EE 1:1, v/v) = 0.18, ESI HRMS for $C_{15}H_{20}O_6$ [M+Na$^+$]: found 319.1153, calcd. 319.1152. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.52 – 7.45 (m, 2H, $H_{arom.}$), 7.41 – 7.33 (m, 3H, $H_{arom.}$), 5.55 (s, 1H, PhC<u>H</u>OO), 4.81 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.29 (dd, $^3J_{5,6a}$ = 4.5 Hz, $^2J_{6a,6b}$ = 9.8 Hz, 1H, H-6a), 3.83 (ddd, $^3J_{5,6a}$ = 4.5 Hz, $^3J_{5,6b}$ = 10.2 Hz, $^2J_{6a,6b}$ = 9.8 Hz, 1H, H-5), 3.75 (dd, $^3J_{5,6b}$ = 10.2 Hz, $^2J_{6a,6b}$ = 9.8 Hz, 1H, H-6b), 3.66 – 3.61 (m, 1H, H-2), 3.60 – 3.54 (m, 2H, H-3, H-4), 3.67, 3.46 (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 137.5 ($C_{arom.}$), 129.1, 128.4, 126.2 (<u>C</u>$H_{arom.}$), 101.5 (Ph<u>C</u>HOO), 99.9 (C-1), 82.2 (C-4), 80.8 (C-3), 72.5 (C-2), 69.2 (C-6), 62.7 (C-5), 61.3, 55.6, (O<u>C</u>H_3) ppm.

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (33)[10]



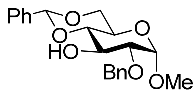
33

Prepared following procedure A. 8.0 g (28 mmol) **28**, 3.2 g (80 mmol) NaH, 9.4 mL (80 mmol) BnBr, 80 mL DMF. Yield: 11.4 g (24.7 mmol, 87%), white solid, $[\alpha]_D^{23}$ = - 31.5° (c = 1.0, $CHCl_3$), Lit.[10]: $[\alpha]_D^{23}$ = -32 ° ($CHCl_3$), m.p. = 98 – 99 °C, Lit.[10]: m.p. = 99 °C, R_f (PE/EE 3:1, v/v) = 0.39. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.52 – 7.48 (m, 2H, $H_{arom.}$), 7.43-7.26 (m, 13H, $H_{arom.}$), 5.56 (s, 1H, PhC<u>H</u>OO), 4.93 (d, $^2J_{A,A`}$ = 11.3 Hz, 1H, OC<u>H</u>$_2$Ph-A), 4.87 (d, $^2J_{B,B`}$ = 12.1 Hz, 1H, OC<u>H</u>$_2$Ph-B), 4.85 (d, $^2J_{A,A`}$ = 11.3 Hz, 1H, OC<u>H</u>$_2$Ph-A`), 4.71 (d, $^2J_{B,B`}$ = 12.1 Hz, 1H, OC<u>H</u>$_2$Ph-B`), 4.61 (d, $^3J_{1,2}$ = 3.8 Hz, 1H, H-1), 4.28 (dd, $^3J_{5,6a}$ = 4.7 Hz, $^2J_{6a,6b}$ = 10.1 Hz, 1H, H-6a), 4.06 (dd, $^3J_{2,3}$ = 9.4 Hz, $^3J_{3,4}$ = 9.4 Hz, 1H, H-3), 3.84 (ddd, $^3J_{4,5}$ = 9.4 Hz, $^3J_{5,6a}$ = 4.7 Hz, $^3J_{5,6b}$ = 10.1 Hz, 1H, H-5), 3.72 (dd, $^3J_{5,6b}$ = 10.1 Hz, $^2J_{6a,6b}$ = 10.1 Hz, 1H, H-6b), 3.62 (dd, $^3J_{3,4}$ = 9.4 Hz, $^3J_{4,5}$ = 9.4 Hz, 1H, H-4), 3.57 (dd, $^3J_{1,2}$ = 3.8 Hz, $^3J_{2,3}$ = 9.4 Hz, 1H, H-2), 3.42 (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 138.8, 138.2, 137.4 ($C_{arom.}$), 128.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 126.0 (<u>C</u>$H_{arom.}$), 101.3 (Ph<u>C</u>HOO), 99.3 (C-1), 82.2 (C-4), 79.2 (C-2), 78.6 (C-3), 75.3 (O<u>C</u>H_2Ph-A), 73.8 (O<u>C</u>H_2Ph-B), 69.1 (C-6), 62.3 (C-5), 55.3 (O<u>C</u>H_3) ppm.

Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (34)[10] **and Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (35)**[10]

Prepared as described in the literature[10]. 5.00 g (17.7 mmol) **28**, 1.20 g (3.50 mmol) tetrabutylammonium hydrogensulfate, 300 mL DCM, 3.6 mL (30.3 mmol) benzyl bromide, 25 mL aq. NaOH solution (5%).

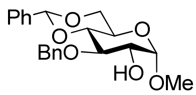
Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**34**)[10]



34

Yield: 3.69 g (9.91 mmol, 56 %), white solid, $[\alpha]_D^{23}$ = + 33.8 ° (c = 0.5, $CHCl_3$), Lit.[10]: $[\alpha]_D^{23}$ = + 35 ° ($CHCl_3$), m.p. = 129 – 130 °C, Lit.[10]: m.p. = 131 – 132 °C, R_f (PE/EE 2:1, v/v) = 0.27. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.52 – 7.46 (m, 2H, $H_{arom.}$), 7.39 – 7.29 (m, 8H, $H_{arom.}$), 5.52 (s, 1H, PhC<u>H</u>OO), 4.79 (d, $^2J_{A,A`}$ = 12.2 Hz, 1H, OC<u>H</u>$_2$Ph-A), 4.71 (d, $^2J_{A,A`}$ = 12.2 Hz, 1H, OC<u>H</u>$_2$Ph-A`), 4.62 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.26 (dd, $J_{5,6a}$ = 4.8 Hz, $^2J_{6a,6b}$ = 10.0 Hz, 1H, H-6a), 4.16 (dd, $^2J_{2,3}$ = 9.2 Hz, $^2J_{3,4}$ = 9.4 Hz, 1H, H-3), 3.82 (ddd, $^3J_{4,5}$ = 9.7 Hz, $^3J_{5,6a}$ = 4.8 Hz, $^3J_{5,6b}$ = 10.1 Hz, 1H, H-5), 3.70 (dd, $^3J_{5,6b}$ = 10.1 Hz, $^3J_{6a,6b}$ = 10.0 Hz, 1H, H-6b), 3.50 (dd, $^3J_{3,4}$ = 9.4 Hz, $^3J_{4,5}$ = 9.7 Hz, 1H, H-4), 3.47 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.2 Hz, 1H, H-2), 3.38 (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (100 MHz, $CDCl_3$) δ = 137.9, 137.1 ($C_{arom.}$), 129.2, 128.6, 128.6, 128.3, 128.2, 128.1, 127.7, 127.0, 126.3 (<u>C</u>$H_{arom.}$), 102.0 (Ph<u>C</u>HOO), 98.6 (C-1), 81.3 (C-4), 79.6 (C-2), 73.4 (O<u>C</u>H$_2$Ph), 70.3 (C-3), 69.0 (C-6), 62.0 (C-5), 55.4 (O<u>C</u>H$_3$) ppm.

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**35**)[10]



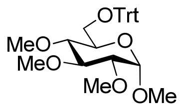
35

Yield: 1.58 g (4.25 mmol, 24 %), white solid, $[\alpha]_D^{23}$ = + 82.6 ° (c = 0.5, $CHCl_3$), Lit.[10]: $[\alpha]_D^{23}$ = + 78 ° ($CHCl_3$), m.p. = 184 °C, Lit.[10]: m.p. = 187 – 188 °C, R_f (PE/EE 2:1, v/v) = 0.16. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.52 – 7.47 (m, 2H, $H_{arom.}$), 7.42 – 7.26 (m, 8H, $H_{arom.}$), 5.57 (s, 1H, PhC<u>H</u>OO), 4.96 (d, $^2J_{A,A`}$ = 11.7 Hz, 1H, OC<u>H</u>$_2$Ph-A), 4.81 (d, $^3J_{1,2}$ = 4.1 Hz, 1H, H-1), 4.80 (d, $^2J_{A,A`}$ = 11.7 Hz, 1H, OC<u>H</u>$_2$Ph-A`), 4.30 (dd, $^3J_{5,6a}$ = 4.4 Hz, $^2J_{6a,6b}$ = 9.9 Hz, 1H, H-6a), 3.84 (ddd, $^3J_{4,5}$ = 9.2 Hz, $^3J_{5,6a}$ = 4.4 Hz, $^3J_{5,6b}$ = 10.2 Hz, 1H, H-5), 3.83 (dd, $^3J_{2,3}$ = 9.1 Hz, $^3J_{3,4}$ = 9.1 Hz, 1H, H-3), 3.76 (dd, $^3J_{5,6b}$ = 10.2, $^2J_{6a,6b}$ = 9.9 Hz, 1H, H-6b), 3.77 – 3.70 (m, 1H, H-2), 3.65 (dd, $^3J_{3,4}$ = 9.1 Hz, $^3J_{4,5}$ = 9.2 Hz, 1H, H-4), 3.45 (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (100 MHz, $CDCl_3$) δ = 138.6, 137.5 ($C_{arom.}$), 129.1, 128.6, 128.4, 128.2, 127.9, 126.2 (<u>C</u>$H_{arom.}$),

Electronic Supplementary Material (ESI) for Chemical Communications

101.5 (Ph$\underline{C}$HOO), 100.0 (C-1), 82.1 (C-4), 79.0 (C-3), 75.0 (O$\underline{C}H_2$Ph), 72.6 (C-2), 69.2 (C-6), 62.7 (C-5), 55.6 (O$\underline{C}H_3$) ppm.

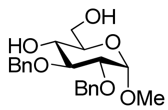
Methyl 2,3,4-tri-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (36)[16]



36

Prepared following procedure A. 3.54 g (8.11 mmol) **29**, 1.85 g (46.3 mmol) NaH, 2.9 mL (80 mmol) MeI, 80 mL DMF. Yield: 3.74 g (7.82 mmol, 97%), white solid, $[\alpha]_D^{23}$ = + 90.4° (c = 0.88, $CHCl_3$), Lit.[16]: $[\alpha]_{546}$ = + 88.9° (Aceton), m.p. = 105 °C, Lit.[16]: m.p. = 151 – 152 °C, R_f (PE/EE 3:1, v/v) = 0.16, MALDI TOF MS for $C_{29}H_{34}O_6$ $[M+Na^+]$: found 501.0, calcd. 501.2. **^{1}H-NMR** (400 MHz, MeOD) δ = 7.51 – 7.45 (m, 6H, $H_{arom.}$), 7.33 – 7.26 (m, 6H, $H_{arom.}$), 7.26 – 7.20 (m, 3H, $H_{arom.}$), 4.95 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 3.60 – 3.55 (m, 1H, H-5), 3.41 – 3.34 (m, 2H, H-3, H-6a), 3.30 – 3.22 (m, 2H, H-2, H-4), 3.11 (dd, $^3J_{5,6b}$ = 4.8 Hz, $^2J_{6a,6b}$ = 10.0 Hz, 1H, H-6b), 3.56, 3.50, 3.44, 3.26 (OC$\underline{H}_3$) ppm. **^{13}C-NMR** (101 MHz, MeOD) δ = 145.6 ($C_{arom.}$), 130.7, 128.9, 128.3 ($\underline{C}H_{arom.}$), 98.7 (C-1), 85.0 (C-3), 83.2 (C-2), 81.4 (C-4), 71.6 (C-5), 63.9 (C-6), 61.2, 60.9, 59.0, 55.5 (O$\underline{C}H_3$).

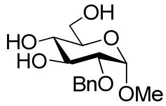
Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside (37)[14]



37

Prepared following procedure B. 2.07 g (4.48 mmol) **33**, 50 mL MeOH, 5.0 mL H_2O, 1 mL 1 N HCl. Yield: 1.62 g (4.32 mmol, 96%), white solid, $[\alpha]_D^{23}$ = + 14.9° (c = 1.0, $CHCl_3$), Lit.[14]: $[\alpha]_D^{23}$ = + 18.8° (c = 1.01, $CHCl_3$), m.p. = 72 – 75 °C, Lit.[14]: m.p. = 75 – 76 °C, R_f (PE/EE 2:1, v/v) = 0.05, MALDI TOF MS for $C_{21}H_{26}O_6$ $[M+Na^+]$: found 397.6, calcd. 397.2. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.41 – 7.28 (m, 10H, $H_{arom.}$), 5.04 (d, $^2J_{A,A`}$ = 11.6 Hz, 1H, OC$\underline{H}_2$Ph-A), 4.78 (d, $^2J_{B,B`}$ = 12.1 Hz, 1H, OC$\underline{H}_2$Ph-B), 4.71 (d, $^2J_{A,A`}$ = 11.6 Hz, 1H, OC$\underline{H}_2$Ph-A`), 4.67 (d, $^2J_{B,B`}$ = 12.1 Hz, 1H, OC$\underline{H}_2$Ph-B`), 4.61 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 3.81 (dd, $^3J_{5,6a}$ = 3.8 Hz, $^2J_{6a,6b}$ = 11.7 Hz, 1H, H-6a), 3.80 (dd, $^3J_{2,3}$ = 9.4 Hz, $^3J_{3,4}$ = 8.9 Hz, 1H, H-3), 3.75 (dd, $^3J_{5,6b}$ = 4.6 Hz, $^2J_{6a,6b}$ = 11.7 Hz, 1H, H-6b), 3.63 (ddd, $^3J_{4,5}$ = 9.7 Hz, $^3J_{5,6a}$ = 3.8 Hz, $^3J_{5,6b}$ = 4.6 Hz, 1H, H-5), 3.52 (dd, $^3J_{3,4}$ = 8.9 Hz, $^3J_{4,5}$ = 9.7 Hz, 1H, H-4), 3.51 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.4 Hz, 1H, H-2), 3.39 (s, 3H, OC$\underline{H}_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 138.7, 137.9 ($C_{arom.}$), 128.6, 128.5, 128.1, 128.0, 128.0, 127.9 ($\underline{C}H_{arom}$), 98.2 (C-1), 81.3 (C-3), 79.8 (C-2), 75.4 (O$\underline{C}H_2$Ph-A), 73.1 (O$\underline{C}H_2$Ph-B), 70.6 (C-5), 70.4 (C-4), 62.4 (C-6), 55.2 (O$\underline{C}H_3$) ppm.

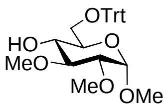
Methyl 2-*O*-benzyl-α-D-glucopyranoside (38)[13]



38

Prepared following procedure B. 1.49 g (4.03 mmol) **34**, 50 mL MeOH, 4.0 mL H_2O, 1 mL 1 N HCl. Yield: 1.09 g (3.83 mmol, 95%), white solid, $[\alpha]_D^{23}$ = + 85.2° (c = 1.0, $CHCl_3$), Lit.[13]: $[\alpha]_D^{23}$ = + 86.8° (c = 1.1, $CHCl_3$), m.p. = 120 °C, Lit.[13]: m.p. = 120 °C, R_f (EE) = 0.17. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.38 – 7.29 (m, 5H, $H_{arom.}$), 4.70 (d, $^2J_{A,A`}$ = 12.2 Hz, 1H, OC<u>H</u>$_2$Ph-A), 4.66 (d, $^2J_{A,A`}$ = 12.2 Hz, 1H, OC<u>H</u>$_2$Ph-A`), 4.61 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 3.91 (dd, $^3J_{2,3}$ = 9.7 Hz, $^3J_{3,4}$ = 8.8 Hz, 1H, H-3), 3.84 (dd, $^3J_{5,6a}$ = 3.6 Hz, $^2J_{6a,6b}$ = 11.7 Hz, 1H, H-6a), 3.79 (dd, $^3J_{5,6b}$ = 4.1 Hz, $^2J_{6a,6b}$ = 11.7 Hz, 1H, H-6b), 3.62 (ddd, $^3J_{4,5}$ = 9.7 Hz, $^3J_{5,6a}$ = 3.6 Hz, $^3J_{5,6b}$ = 4.1 Hz, 1H, H-5), 3.55 (dd, $^3J_{3,4}$ = 8.8 Hz, $^3J_{4,5}$ = 9.7 Hz, 1H, H-4), 3.35 (OC<u>H</u>$_3$), 3.34 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.7 Hz, 1H, H-2) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 137.8 ($C_{arom.}$), 128.6, 128.2, 128.1 (<u>C</u>$H_{arom.}$), 97.7 (C-1), 79.3 (C-2), 73.0 (O<u>C</u>H_2Ph-A), 72.9 (C-3), 70.6 (C-4), 70.6 (C-5), 62.3 (C-6), 55.3 (O<u>C</u>H_3) ppm.

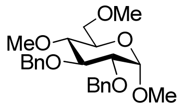
Methyl 2,3-di-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (39)[16]



39

Prepared following procedure D. 2.08 g (9.36 mmol) **6**, 2.65 g (9.51 mmol) Chlorotriphenylmethane, 20 mg DMAP, 25 mL pyridine. Yield: 3.52 g (7.58 mmol, 81%), white solid, $[\alpha]_D^{23}$ = + 66.2° (c = 1.0, $CHCl_3$), Lit.[16]: $[\alpha]_D^{23}$ = + 66.4° ($CHCl_3$), m.p.:174 °C, Lit.[16]: m.p. = 169 – 170 °C, R_f (PE/EE 2:1, v/v) = 0.14, MALDI TOF MS for $C_{28}H_{32}O_6$ [M+Na$^+$]: found 487.1, calcd. 487.2. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.49 – 7.44 (m, 6H, $H_{arom.}$), 7.34 – 7.21 (m, 9H, $H_{arom.}$), 4.87 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 3.70 (ddd, $^3J_{4,5}$ = 9.4 Hz, $^3J_{5,6a}$ = 4.1 Hz, $^3J_{5,6b}$ = 5.1 Hz, 1H, H-5), 3.52 (ddd, $^3J_{3,4}$ = 8.9 Hz, $^3J_{4,5}$ = 9.4 Hz, $^3J_{4,OH}$ = 2.3 Hz, 1H, H-4), 3.44 (dd, $^3J_{2,3}$ = 9.4 Hz, $^3J_{3,4}$ = 8.9 Hz, 1H, H-3), 3.39 (dd, $^3J_{5,6a}$ = 4.1 Hz, $^2J_{6a,6b}$ = 9.9 Hz, 1H, H-6a), 3.35 (dd, $^3J_{5,6b}$ = 5.1 Hz, $^2J_{6a,6b}$ = 9.9 Hz, 1H, H-6b), 3.25 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.4 Hz, 1H, H-2), 3.63, 3.51, 3.45 (OC<u>H</u>$_3$), 2.52 (d, $J_{4,OH}$ = 2.3 Hz, 1H, O<u>H</u>) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 143.8 ($C_{arom.}$), 128.7, 127.9, 127.1 (<u>C</u>H_{arom}), 97.3 (C-1), 87.0 (Ph_3<u>C</u>O), 82.8 (C-3), 81.7 (C-2), 71.9 (C-4), 69.8 (C-5), 64.1 (C-6), 61.2, 58.6, 55.1 (O<u>C</u>H_3) ppm.

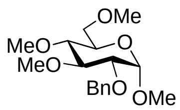
Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-methyl-α-D-glucopyranoside (40)[16]



40

Prepared following procedure A. 1.35 g (3.61 mmol) **37**, 594 mg (14.9 mmol) NaH, 0.9 mL (14.5 mmol) MeI, 40 mL DMF. Yield: 1.36 g (3.37 mmol, 93%), colourless syrup, $[\alpha]_D^{23}$ = + 30.6° (c = 0.5, $CHCl_3$), Lit.[16]: $[\alpha]_D^{23}$ = + 32.9° ($CHCl_3$), R_f (PE/EE 2:1, v/v) = 0.35, MALDI TOF MS for $C_{23}H_{30}O_6$ [M+Na$^+$]: found 426.2, calcd. 425.2. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.42 – 7.25 (m, 10H, $H_{arom.}$), 4.94 (d, $^2J_{A,A`}$ = 11.1 Hz, 1H, OC<u>H</u>$_2$Ph-A), 4.82 (d, $^2J_{A,A`}$ = 11.1 Hz, 1H, OC<u>H</u>$_2$Ph-A`), 4.79 (d, $^2J_{B,B`}$= 12.4 Hz, 1H, OC<u>H</u>$_2$Ph-B), 4.64 (d, $^2J_{B,B`}$= 12.4 Hz, 1H, OC<u>H</u>$_2$Ph-B`), 4.58 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 3.86 (dd, $^3J_{2,3}$ = 9.7 Hz, $^3J_{3,4}$ = 9.4 Hz, 1H, H-3), 3.64 – 3.55 (m, 3H, H-5, H-6), 3.50 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.7 Hz, 1H, H-2), 3.28 (dd, $^3J_{3,4}$ = 9.4 Hz, $^3J_{4,5}$ = 9.4 Hz, 1H, H-4), 3.54, 3.40, 3.38 (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 139.0, 138.2 ($C_{arom.}$), 128.4, 128.3, 128.1, 127.9, 127.8, 127.5 (<u>C</u>H_{arom}), 98.3 (C-1), 81.9 (C-3), 79.6 (C-2), 79.5 (C-4), 75.6 (O<u>C</u>H$_2$Ph-A), 73.4 (O<u>C</u>H$_2$Ph-B), 71.1 (C-6), 69.9 (C-5), 60.6, 59.2, 55.2 (O<u>C</u>H$_3$) ppm.

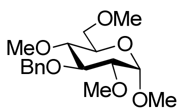
Methyl 2-*O*-benzyl-3,4,6-tri-*O*-methyl-α-D-glucopyranoside (41)



41

Prepared following procedure A. 1.06 g (3.73 mmol) **38**, 896 mg (22.4 mmol) NaH, 1.4 mL (22 mmol) MeI, 40 mL DMF. Yield: 1.12 g (3.44 mmol, 92%), colourless syrup, $[\alpha]_D^{23}$ = + 129.0° (c = 0.84, $CHCl_3$), R_f (PE/EE 2:1, v/v) = 0.27, ESI HRMS for $C_{17}H_{26}O_6$ [M+Na$^+$]: found 349.1596, calcd. 349.1622. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.39 – 7.25 (m, 5H, $H_{arom.}$), 4.79 (d, $^2J_{A,A`}$ = 12.2 Hz, 1H, OC<u>H</u>$_2$Ph-A), 4.63 (d, $^2J_{A,A`}$ = 12.2 Hz, 1H, OC<u>H</u>$_2$Ph-A`), 4.55 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 3.60 – 3.52 (m, 4H, H-3, H-5, H-6), 3.39 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.7 Hz, 1H, H-2), 3.18 (dd, $^3J_{3,4}$ = 9.0 Hz, $^3J_{4,5}$ = 8.8 Hz, 1H, H-4), 3.67, 3.54, 3.40, 3.36 (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 138.3 ($C_{arom.}$), 128.4, 128.2, 127.8 (<u>C</u>$H_{arom.}$), 98.3 (C-1), 83.6 (C-3), 79.4 (C-4), 79.4 (C-2), 73.3 (O<u>C</u>H$_2$Ph-A), 71.1 (C-6), 69.8 (C-5), 61.0, 60.4, 59.2, 55.2 (O<u>C</u>H$_3$) ppm.

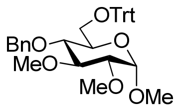
Methyl 3-*O*-benzyl-2,4,6-tri-*O*-methyl-α-D-glucopyranoside (42)[12]



42

Prepared following procedure A. 1.32 g (4.64 mmol) **22**, 1.16 mg (29.0 mmol) NaH, 1.70 mL (27.4 mmol) MeI, 50 mL DMF. Yield: 1.47 g (4.50 mmol, 97%), colourless syrup, $[\alpha]_D^{23}$ = + 102.0° (c = 0.2, $CHCl_3$), Lit.[12]: $[\alpha]_{578}$ = + 133.0° (c = 0.47, $CHCl_3$), R_f (PE/EE 1:1, v/v) = 0.37. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.43 – 7.26 (m, 5H, $H_{arom.}$), 4.89 (d, $^2J_{A,A`}$ = 11.0 Hz, 1H, OC<u>H</u>$_2$Ph-A), 4.86 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.79 (d, $^2J_{A,A`}$ = 11.0 Hz, 1H, OC<u>H</u>$_2$Ph-A\`), 3.80 (dd, $^3J_{2,3}$ = 9.7 Hz, $^3J_{3,4}$ = 9.3 Hz, 1H, H-3), 3.66 – 3.58 (m, 3H, H-5, H-6), 3.31 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.7 Hz, 1H, H-2), 3.29 (dd, $^3J_{3,4}$ = 9.3 Hz, $^3J_{4,5}$ = 9.3 Hz, 1H, H-4), 3.54, 3.53, 3.43, 3.42 (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 139.0 ($C_{arom.}$), 128.3, 127.9, 127.4 (<u>C</u>$H_{arom.}$), 97.6 (C-1), 82.0 (C-2), 81.9 (C-3), 79.3 (C-4), 75.4 (O<u>C</u>H_2Ph-A), 71.1 (C-6), 70.0 (C-5), 60.7, 59.2, 59.2, 55.2 (O<u>C</u>H_3) ppm.

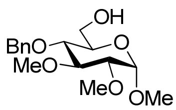
Methyl 4-*O*-benzyl-2,3-di-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (43).



43

Prepared following procedure A. 3.46 g (7.45 mmol) **6**, 653 mg (15.2 mmol) NaH, 2.0 mL (17 mmol) BnBr, 40 mL DMF. Yield: 3.84 g (6.93 mmol, 93%), white solid, $[\alpha]_D^{23}$ = + 117.6° (c = 0.5, $CHCl_3$), m.p.: 57 °C, R_f (PE/EE 5:1, v/v) = 0.13, ESI HRMS for $C_{35}H_{38}O_6$ [M+Na$^+$]: found 577.2553, calcd. 577.2561. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.52 – 7.47 (m, 6H, $H_{arom.}$), 7.32 – 7.18 (m, 12H, $H_{arom.}$), 6.97 – 6.92 (m, 2H, $H_{arom.}$), 4.95 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.67 (d, $^2J_{A,A`}$ = 10.4 Hz, 1H, OC<u>H</u>$_2$Ph-A), 4.30 (d, $^2J_{A,A`}$ = 10.4 Hz, 1H, OC<u>H</u>$_2$Ph-A\`), 3.77 (ddd, $^3J_{4,5}$ = 9.4 Hz, $^3J_{5,6a}$ = 1.8 Hz, $^3J_{5,6b}$ = 4.8 Hz, 1H, H-5), 3.60 (dd, $^3J_{2,3}$ = 9.2 Hz, $^3J_{3,4}$ = 8.9 Hz, 1H, H-3), 3.56 (dd, $^3J_{3,4}$ = 8.9 Hz, $^3J_{4,5}$ = 9.4 Hz, 1H, H-4), 3.50 (dd, $^3J_{5,6a}$ = 1.8 Hz, $^2J_{6a,6b}$ = 10.2 Hz, 1H, H-6a), 3.34 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.2 Hz, 1H, H-2), 3.20 (dd, $^3J_{5,6b}$ = 4.8 Hz, $^2J_{6a,6b}$ = 10.2 Hz, 1H, H-6b), 3.65, 3.59, 3.47 (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 144.0, 138.1 ($C_{arom.}$), 128.8, 128.2, 128.1, 127.9, 127.8, 127.6, 126.9 (<u>C</u>$H_{arom.}$), 97.3 (C-1), 86.3 (Ph_3<u>C</u>O), 83.9 (C-3), 82.2 (C-2), 78.2 (C-4), 74.9 (O<u>C</u>H_2Ph-A), 70.2 (C-5), 62.6 (C-6), 61.1, 59.0, 54.9 (O<u>C</u>H_3) ppm.

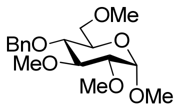
Methyl 4-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranoside (44)



44

2.86 g (5.17 mmol) **43** was stirred in 15 mL trifluoroacetic acid (90%) for 5 min. The mixture was diluted with DCM, neutralized by washing with sat. $NaHCO_3$, dried and concentrated in vacuo. The residue was purified by flash column chromatography (gradient petrol ether/ethyl acetate). Yield: 1.27 g (4.08 mmol, 79%), white solid, $[\alpha]_D^{23}$ = + 151.8° (c = 0.5, $CHCl_3$), m.p.: 98 °C, R_f (PE/EE 1:1, v/v) = 0.12, ESI HRMS for $C_{16}H_{24}O_6$ [M+Na$^+$]: found 335.1465, calcd. 335.1458. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.40 – 7.28 (m, 5H, $H_{arom.}$), 4.89 (d, $^2J_{A,A`}$ = 11.1 Hz, 1H, OC<u>H</u>$_2$Ph-A), 4.83 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.66 (d, $^2J_{A,A`}$ = 11.1 Hz, 1H, OC<u>H</u>$_2$Ph-A`), 3.80 (dd, $^3J_{5,6a}$ = 2.8 Hz, $^2J_{6a,6b}$ = 11.8 Hz, 1H, H-6a), 3.71 (dd, $^3J_{5,6b}$ = 4.1 Hz, $^2J_{6a,6b}$ = 11.8 Hz, 1H, H-6b), 3.64 (dd, $^3J_{2,3}$ = 9.4 Hz, $^3J_{3,4}$ = 9.1 Hz, 1H, H-3), 3.63 (ddd, $^3J_{4,5}$ = 9.9 Hz, $^3J_{5,6a}$ = 2.8 Hz, $^3J_{5,6b}$ = 4.1 Hz, 1H, H-5), 3.44 (dd, $^3J_{3,4}$ = 9.1 Hz, $^3J_{4,5}$ = 9.9 Hz, 1H, H-4), 3.22 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.4 Hz, 1H, H-2), 3.66, 3.55, 3.41 (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 138.2 ($C_{arom.}$), 128.5, 128.1, 127.9, (<u>C</u>$H_{arom.}$), 97.5 (C-1), 83.7 (C-3), 82.1 (C-2), 77.4 (C-4), 74.9 (O<u>C</u>H_2Ph-A), 70.6 (C-5), 61.9 (C-6), 61.1, 59.0, 55.1 (O<u>C</u>H_3) ppm.

Methyl 4-*O*-benzyl-2,3,6-tri-*O*-methyl-α-D-glucopyranoside (45)

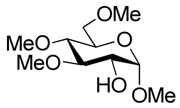


45

Prepared following procedure A. 1.27 g (4.08 mmol) **44**, 326 mg (8.16 mmol) NaH, 0.51 mL (8.2 mmol) MeI 50 mL DMF. Yield: 1.31 g (4.03 mmol, 98%), colourless syrup, $[\alpha]_D^{23}$ = + 158.4° (c = 0.5, $CHCl_3$), R_f (PE/EE 1:1, v/v) = 0.34, ESI HRMS for $C_{17}H_{26}O_6$ [M+Na$^+$]: found 349.1618, calcd. 349.1622. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.40 – 7.28 (m, 5H, $H_{arom.}$), 4.87 (d, $^2J_{A,A`}$ = 11.1 Hz, 1H, OC<u>H</u>$_2$Ph-A), 4.85 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.62 (d, $^2J_{A,A`}$ = 11.1 Hz, 1H, OC<u>H</u>$_2$Ph-A`), 3.68 (ddd, $^3J_{4,5}$ = 9.9 Hz, $^3J_{5,6a}$ = 3.6 Hz, $^3J_{5,6b}$ = 2.0 Hz, 1H, H-5), 3.62 (dd, $^3J_{2,3}$ = 9.4 Hz, $^3J_{3,4}$ = 8.9 Hz, 1H, H-3), 3.62 (dd, $^3J_{5,6a}$ = 3.6 Hz, $^2J_{6a,6b}$ = 10.4 Hz, 1H, H-6a), 3.56 (dd, $^3J_{5,6b}$ = 2.0 Hz, $^2J_{6a,6b}$ = 10.4 Hz, 1H, H-6b), 3.51 (dd, $^3J_{3,4}$ = 8.9 Hz, $^3J_{4,5}$ = 9.9 Hz, 1H, H-4), 3.26 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.4 Hz, 1H, H-2), 3.65, 3.53, 3.42, 3.37 (OC<u>H</u>$_3$) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 138.4 ($C_{arom.}$), 128.4, 128.0, 127.7 (<u>C</u>$H_{arom.}$), 97.6 (C-1), 83.7 (C-3), 81.9 (C-2), 77.5 (C-4), 75.0 (O<u>C</u>H_2Ph-A), 70.9 (C-6), 69.8 (C-5), 61.1, 59.2, 59.0, 55.1 (O<u>C</u>H_3) ppm.

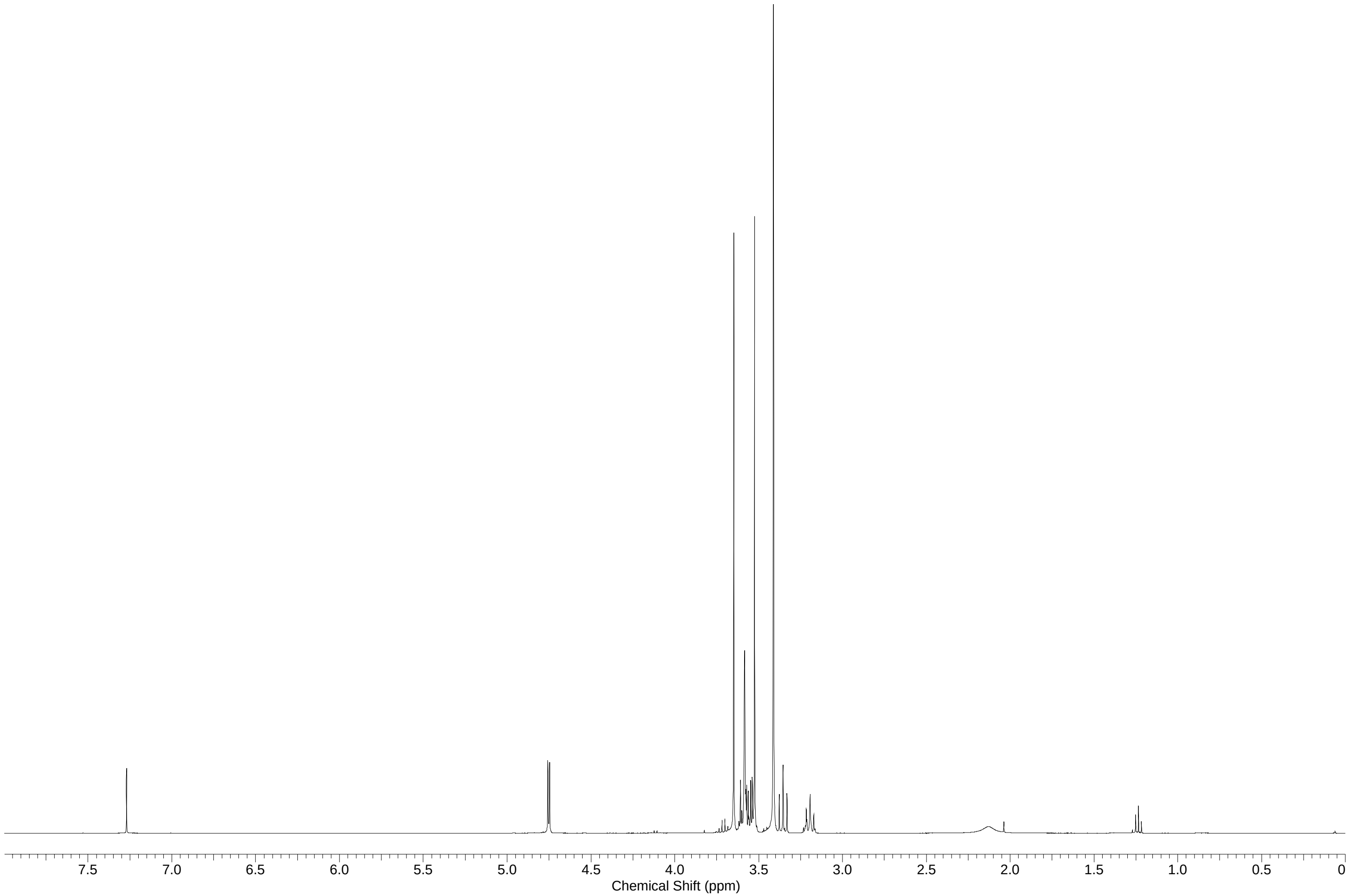
Electronic Supplementary Material (ESI) for Chemical Communications

Methyl 3,4,6-tri-*O*-methyl-α-D-glucopyranoside (1)

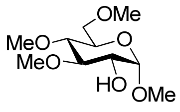


1

^{1}H-NMR (400 MHz, $CDCl_3$)

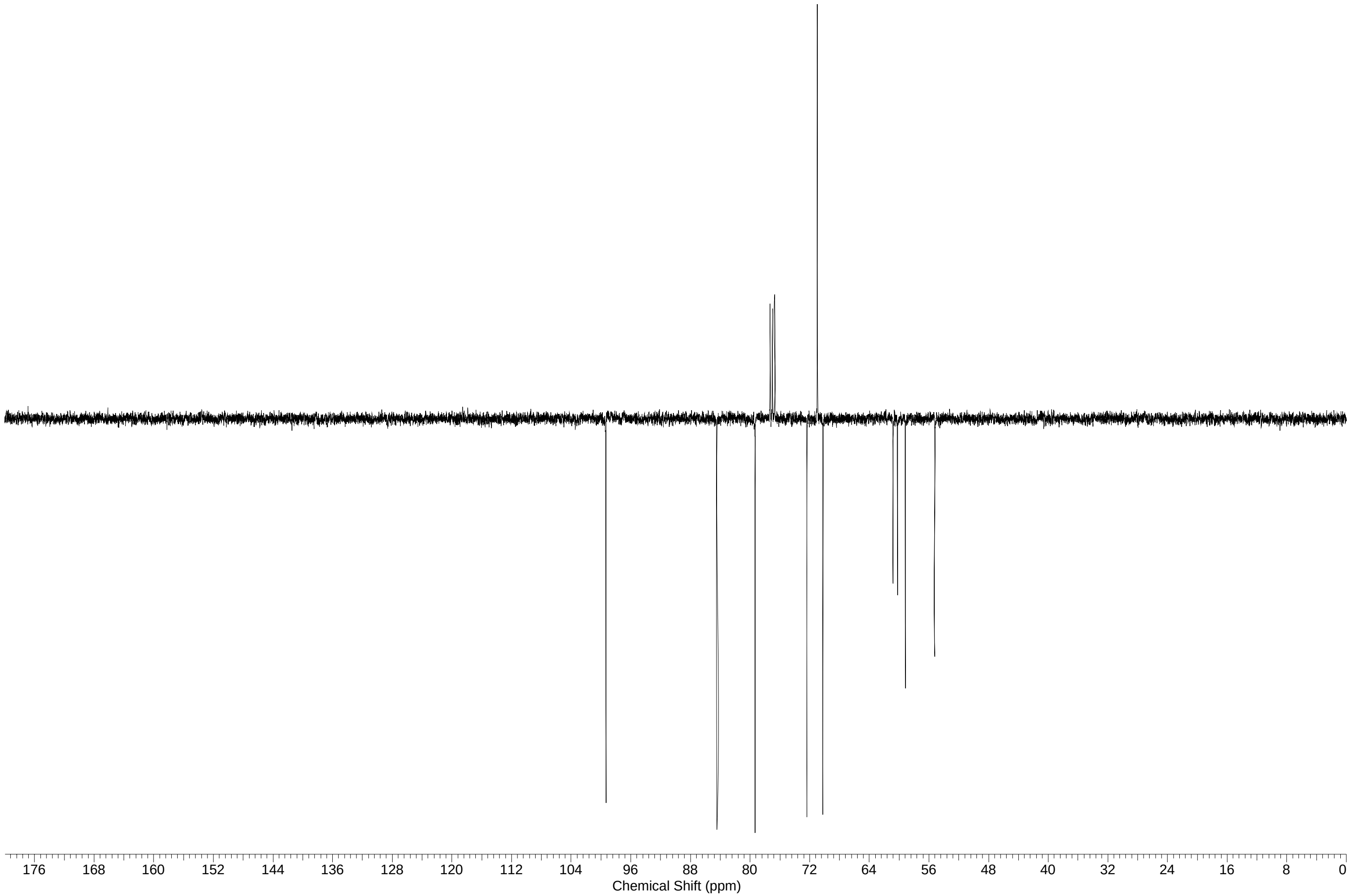


Methyl 3,4,6-tri-*O*-methyl-α-D-glucopyranoside (1)

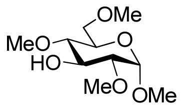


1

^{13}C-NMR (101 MHz, $CDCl_3$)

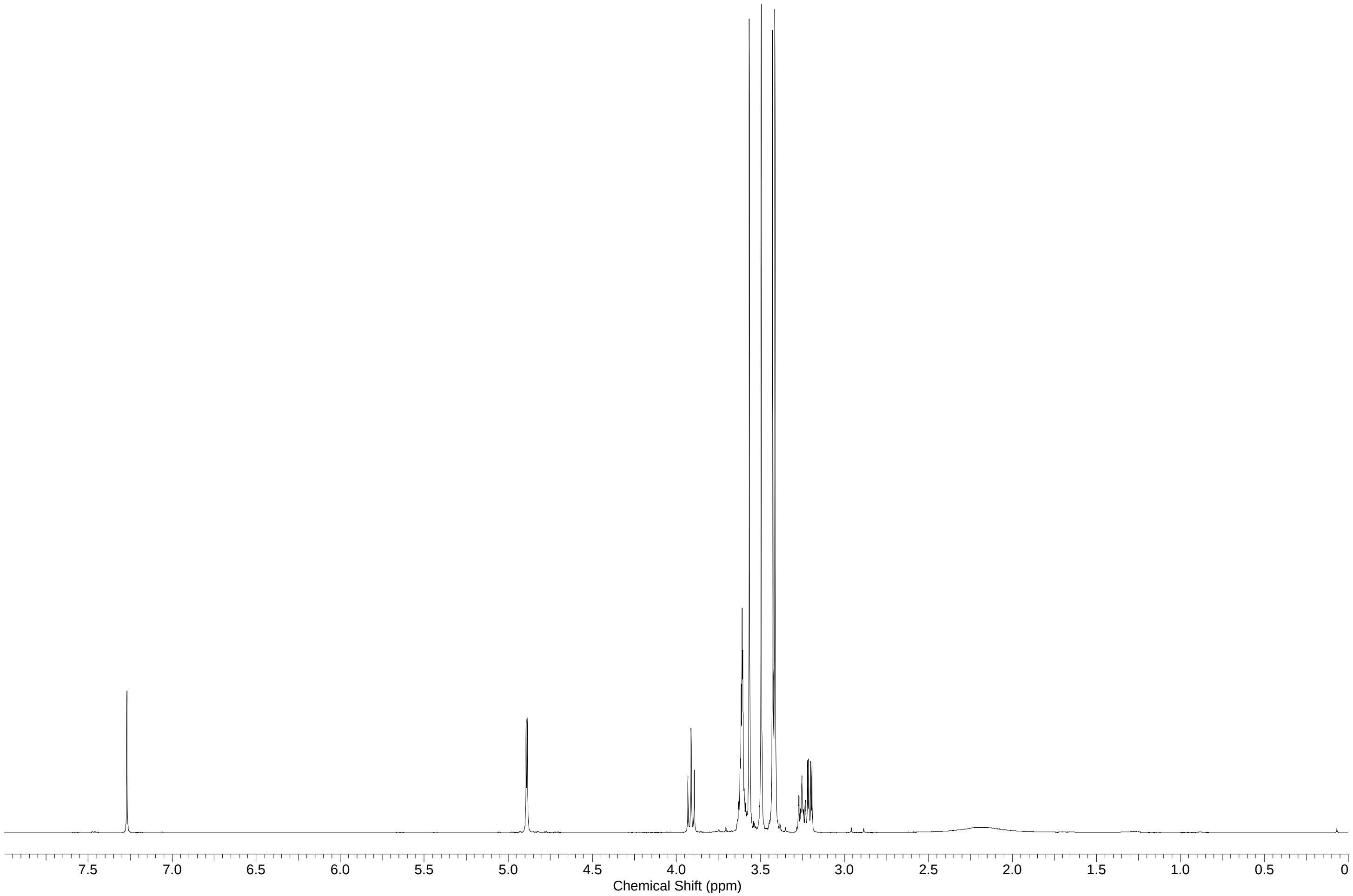


Methyl 2,4,6-tri-*O*-methyl-α-D-glucopyranoside (2)



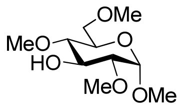
2

^{1}H-NMR (400 MHz, $CDCl_3$)



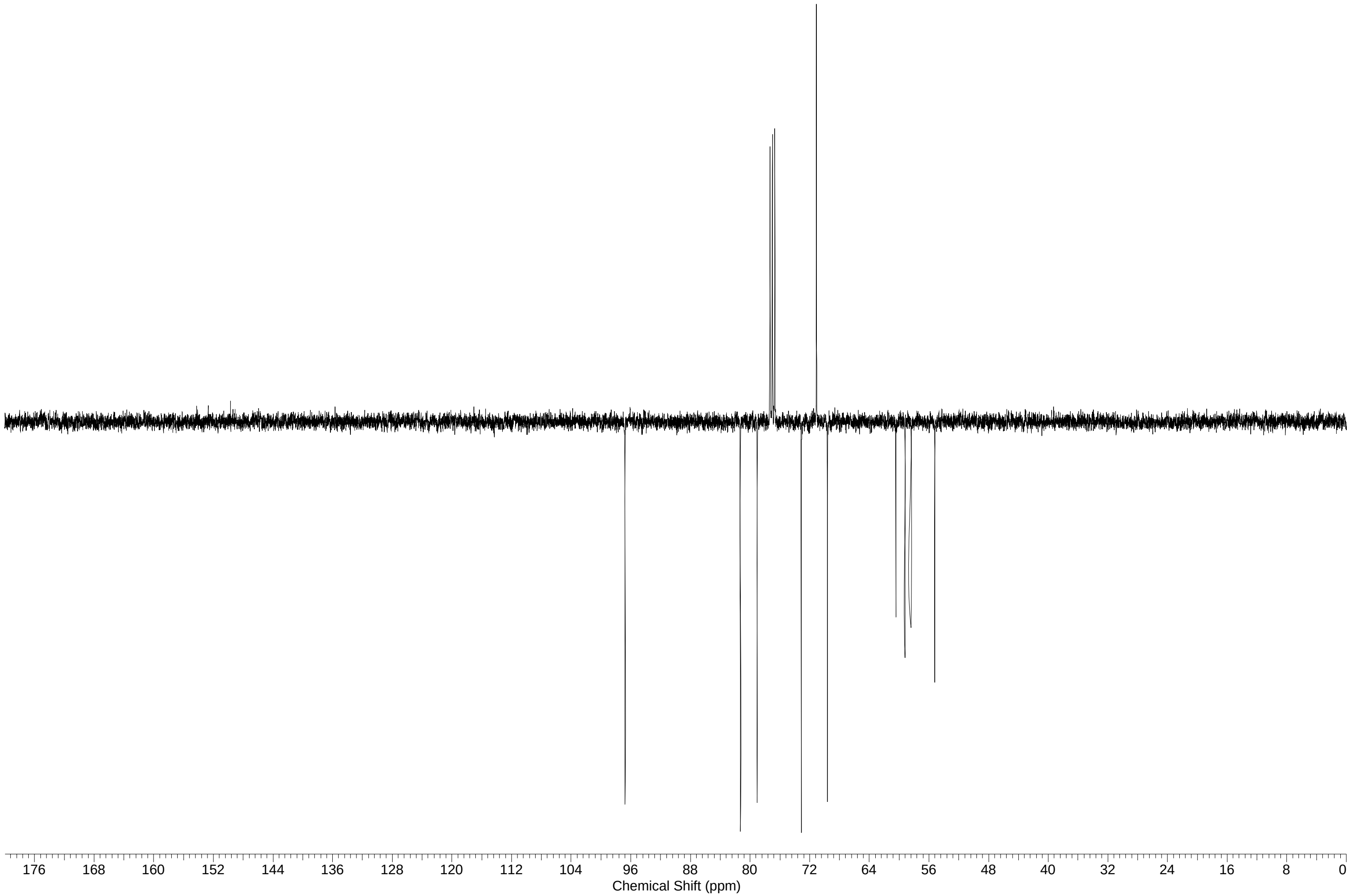
Electronic Supplementary Material (ESI) for Chemical Communications

Methyl 2,4,6-tri-*O*-methyl-α-D-glucopyranoside (2)

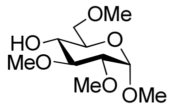


2

^{13}C-NMR (101 MHz, $CDCl_3$)

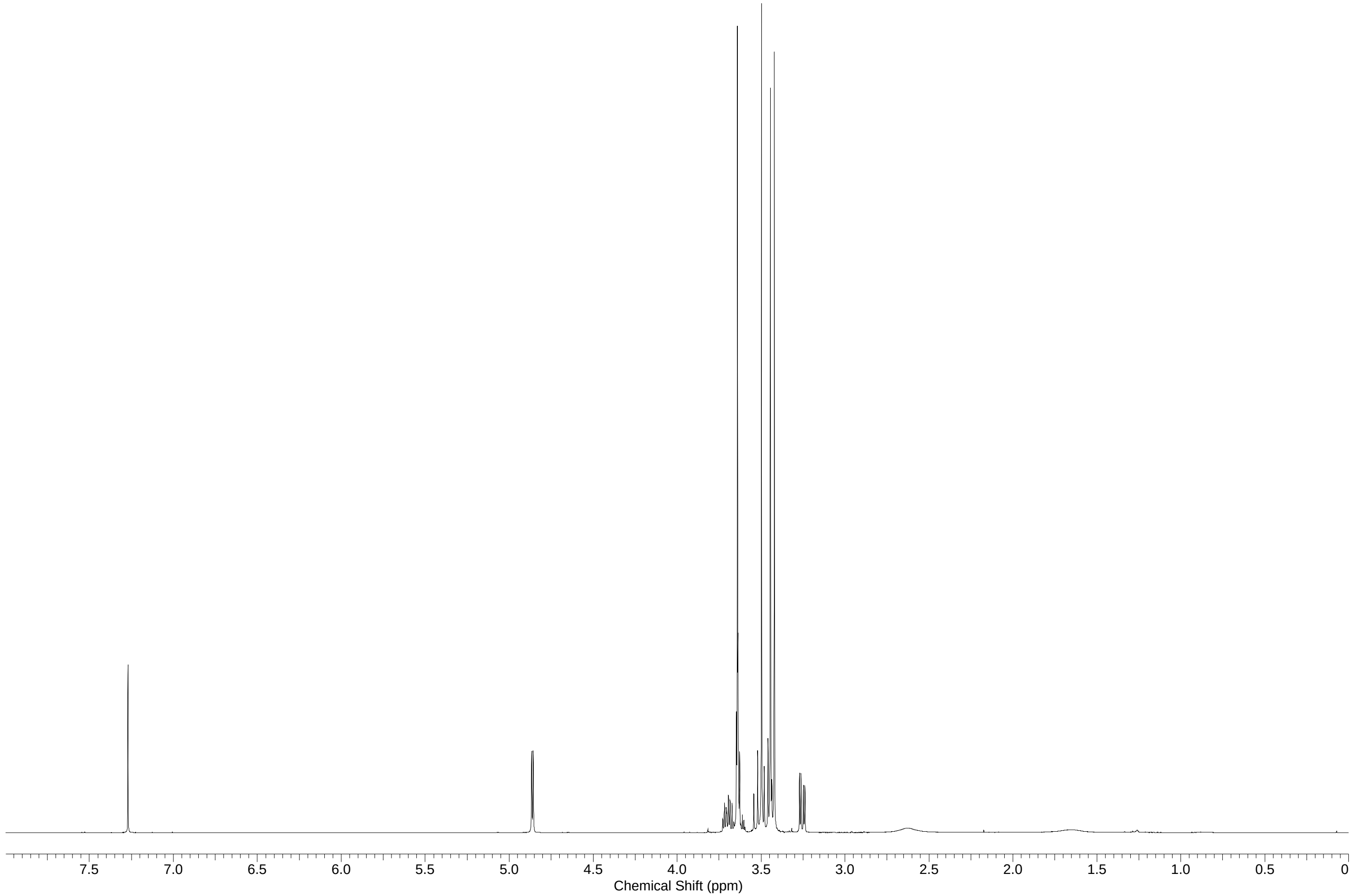


Methyl 2,3,6-tri-*O*-methyl-α-D-glucopyranoside (3)

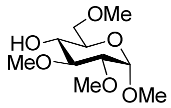


3

^{1}H-NMR (400 MHz, $CDCl_3$)

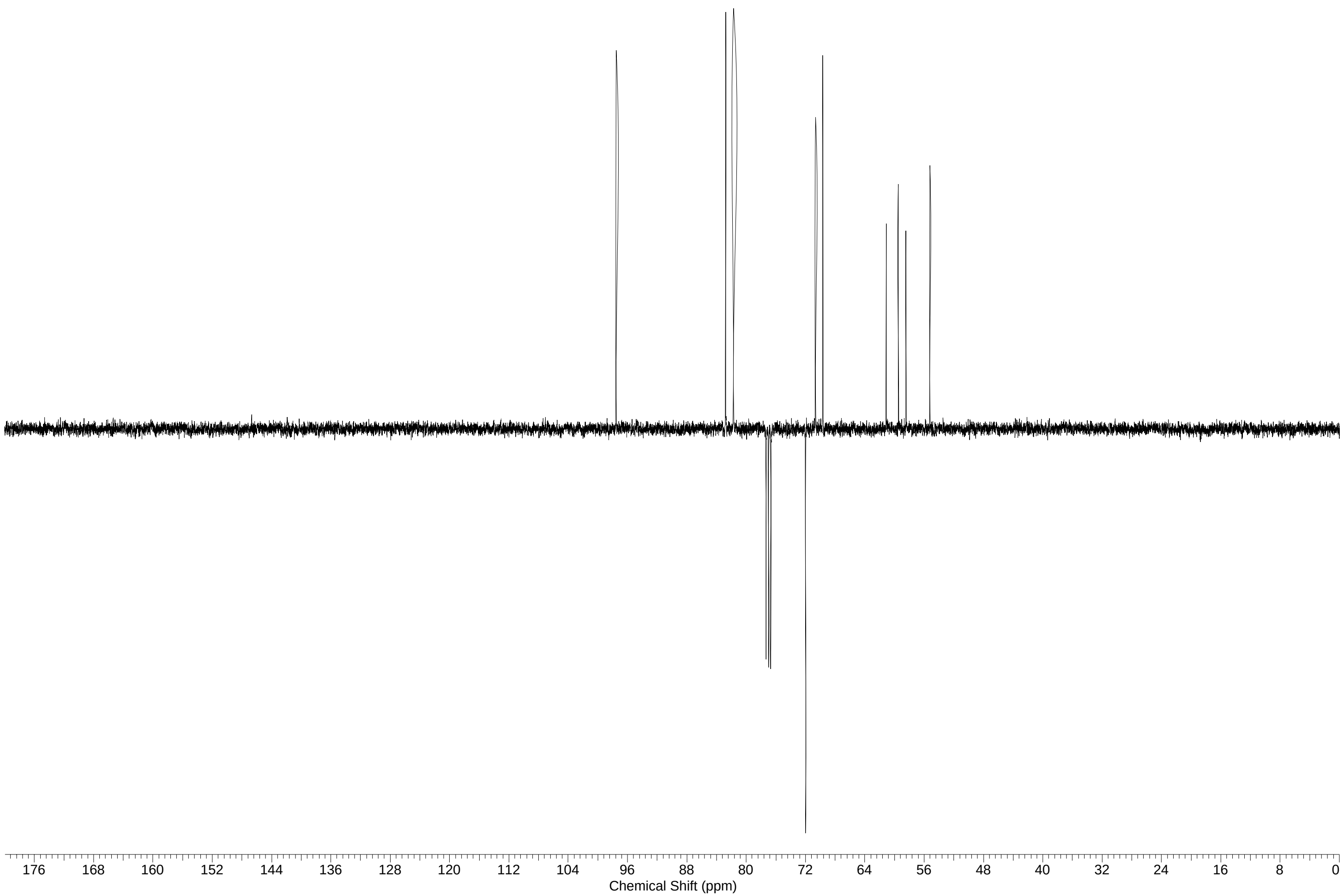


Methyl 2,3,6-tri-*O*-methyl-α-D-glucopyranoside (3)

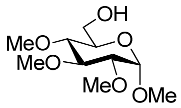


3

^{13}C-NMR (101 MHz, $CDCl_3$)

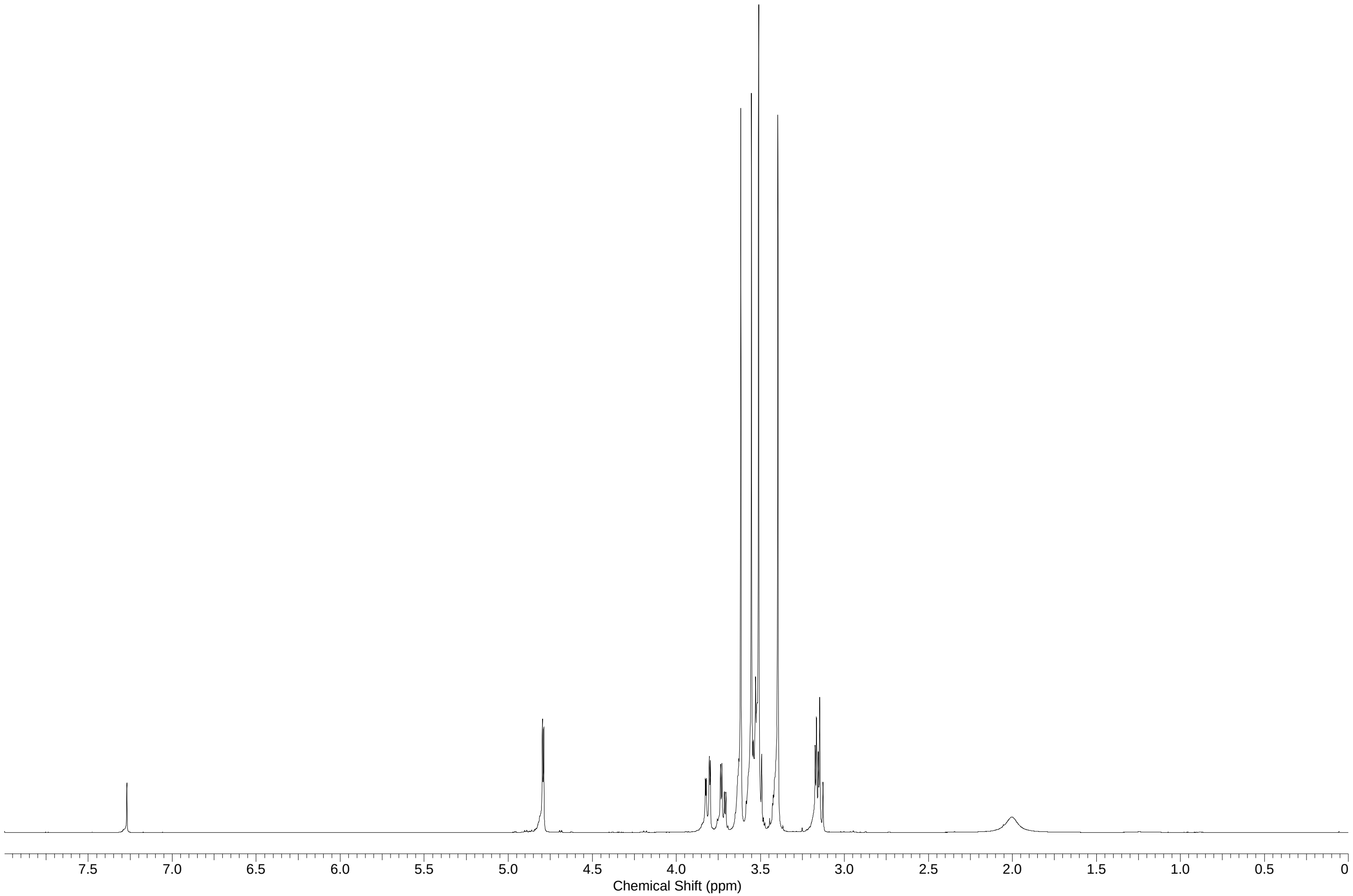


Methyl 2,3,4-tri-*O*-methyl-α-D-glucopyranoside (4)

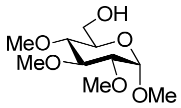


4

^{1}H-NMR (400 MHz, $CDCl_3$)

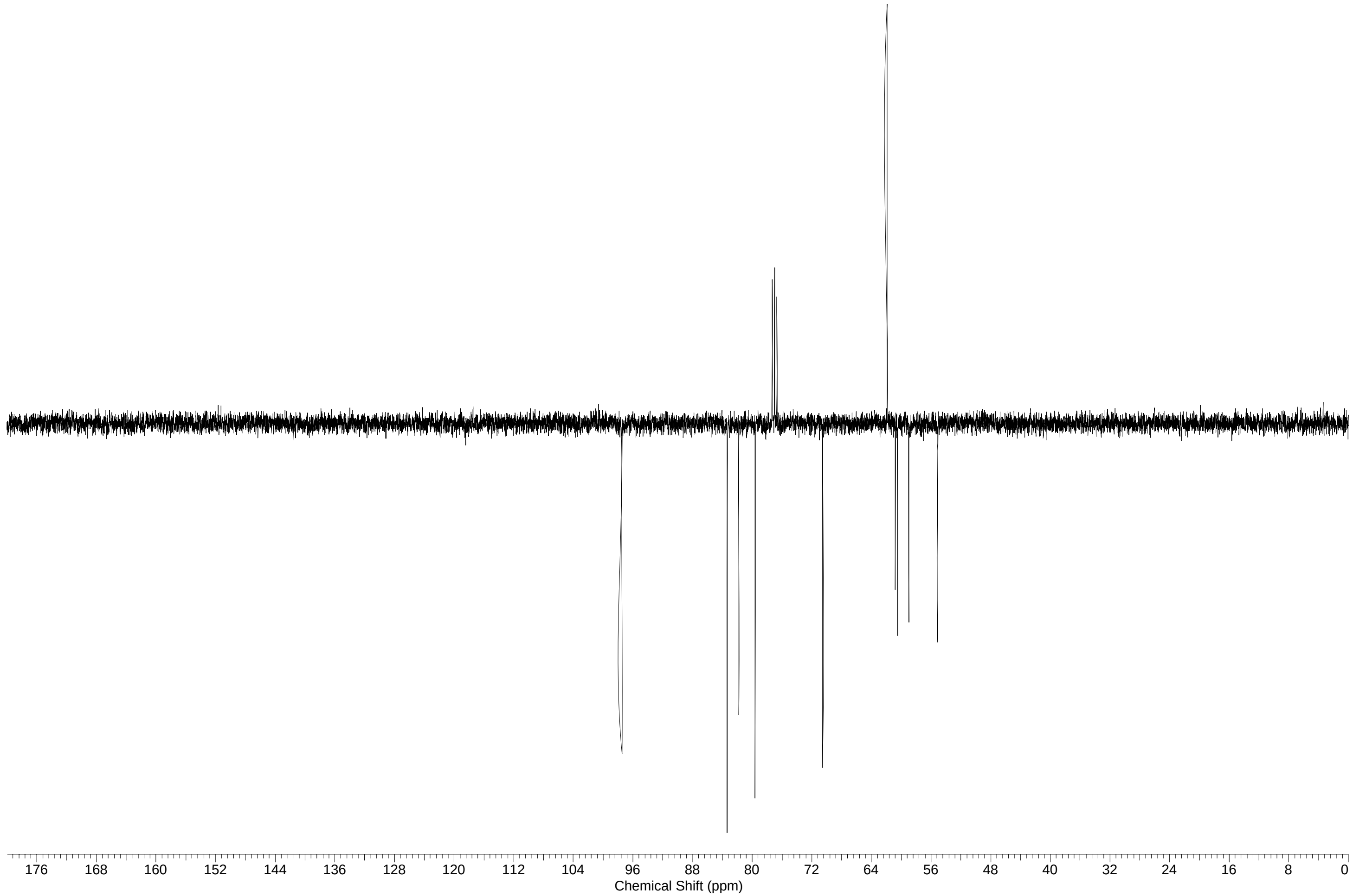


Methyl 2,3,4-tri-*O*-methyl-α-D-glucopyranoside (4)

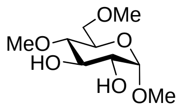


4

^{13}C-NMR (101 MHz, $CDCl_3$)

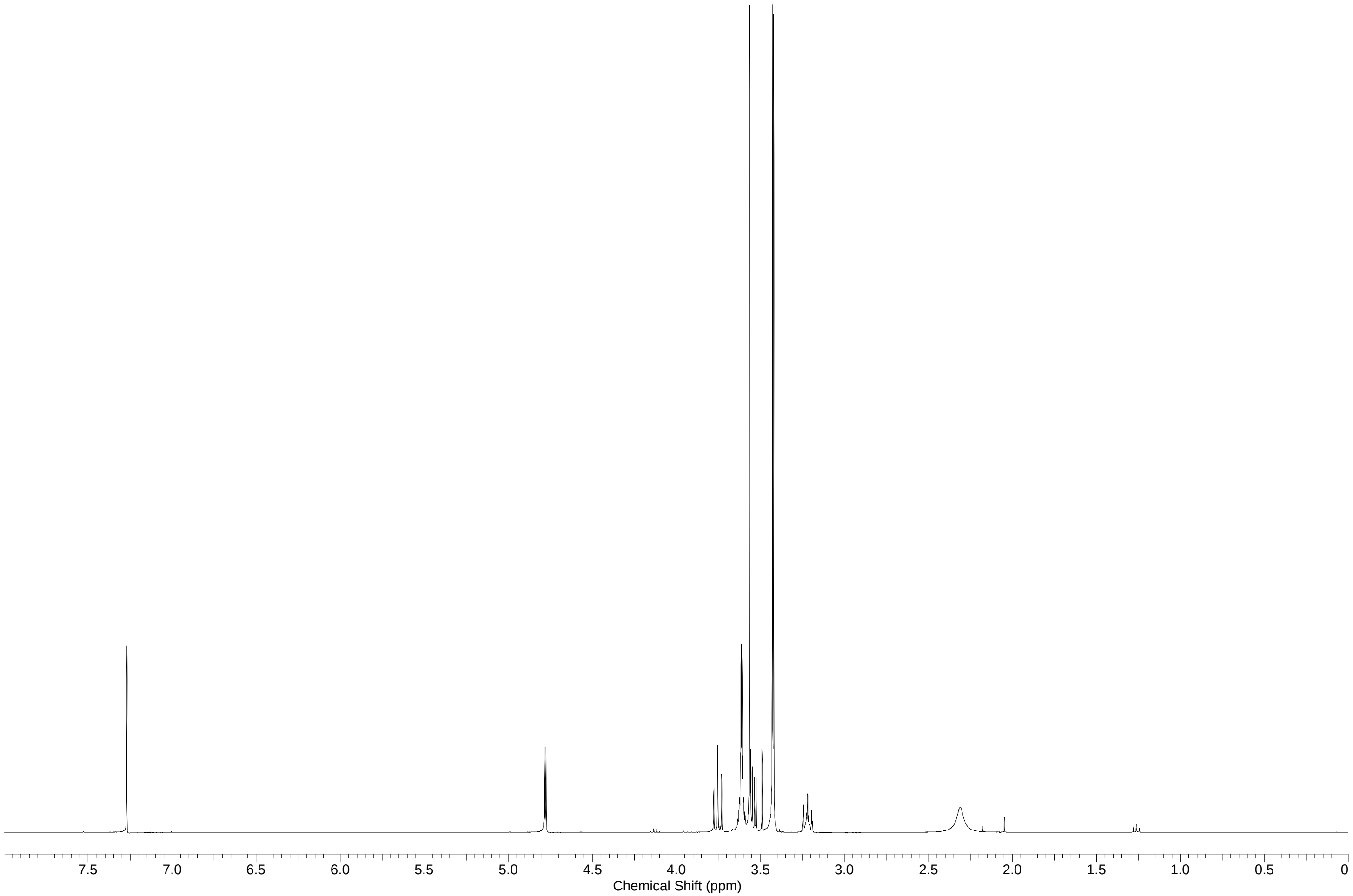


Methyl 4,6-di-*O*-methyl-α-D-glucopyranoside (5)



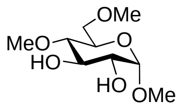
5

^{1}H-NMR (400 MHz, $CDCl_3$)



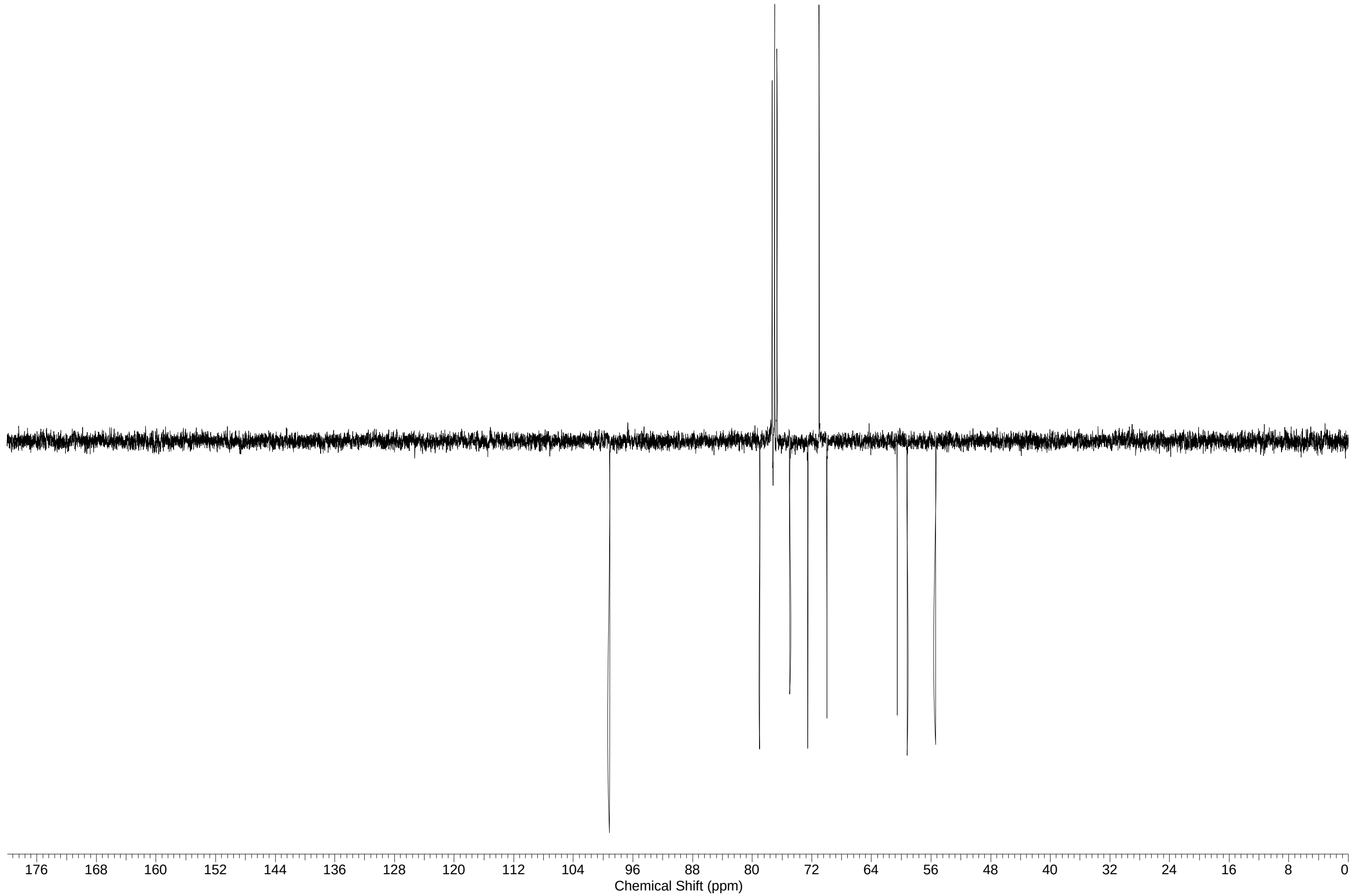
Electronic Supplementary Material (ESI) for Chemical Communications

Methyl 4,6-di-*O*-methyl-α-D-glucopyranoside (5)

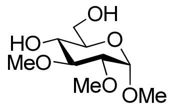


5

^{13}C-NMR (101 MHz, $CDCl_3$)

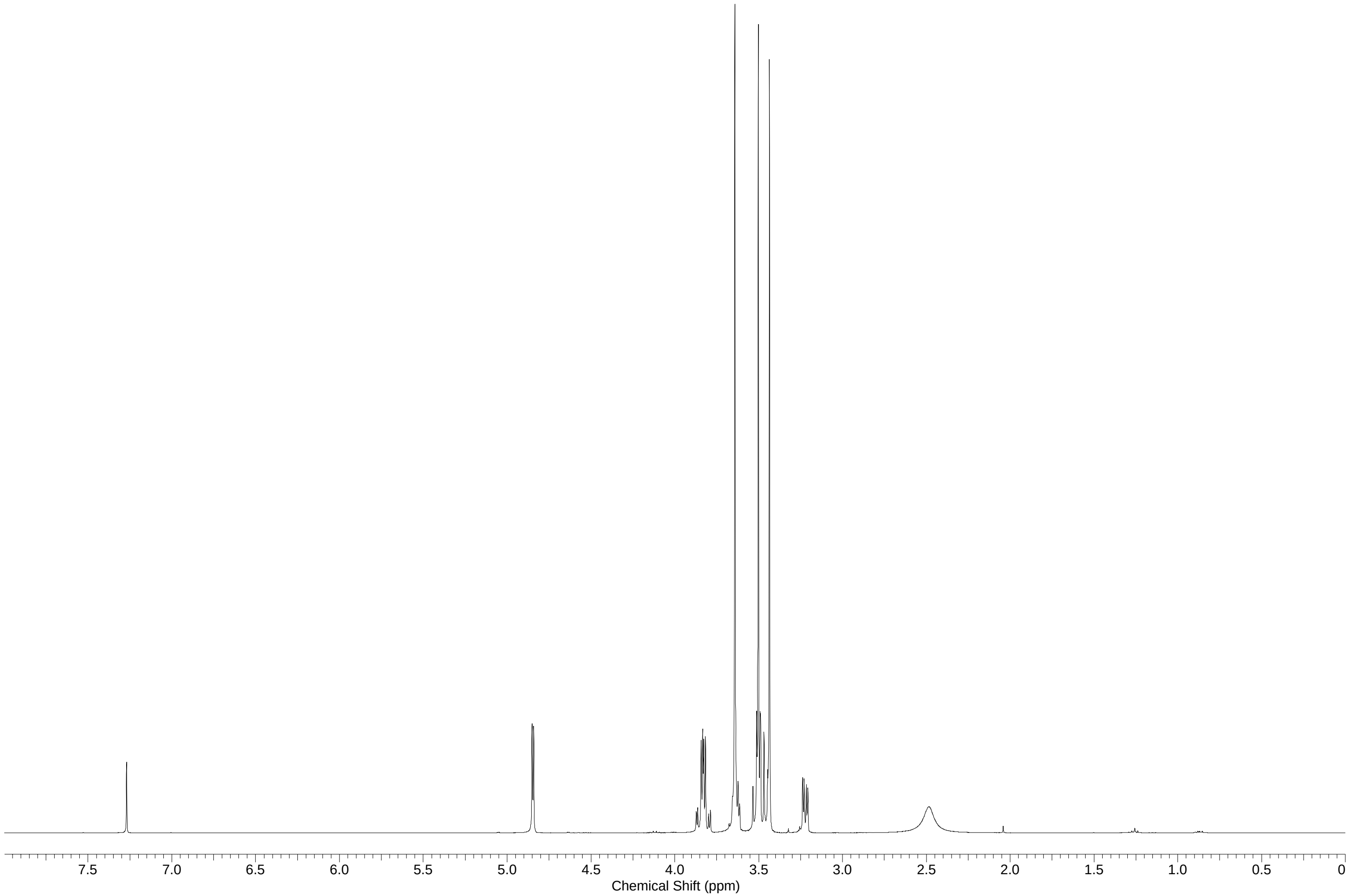


Methyl 2,3-di-*O*-methyl-α-D-glucopyranoside (6)

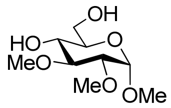


6

^{1}H-NMR (400 MHz, $CDCl_3$)

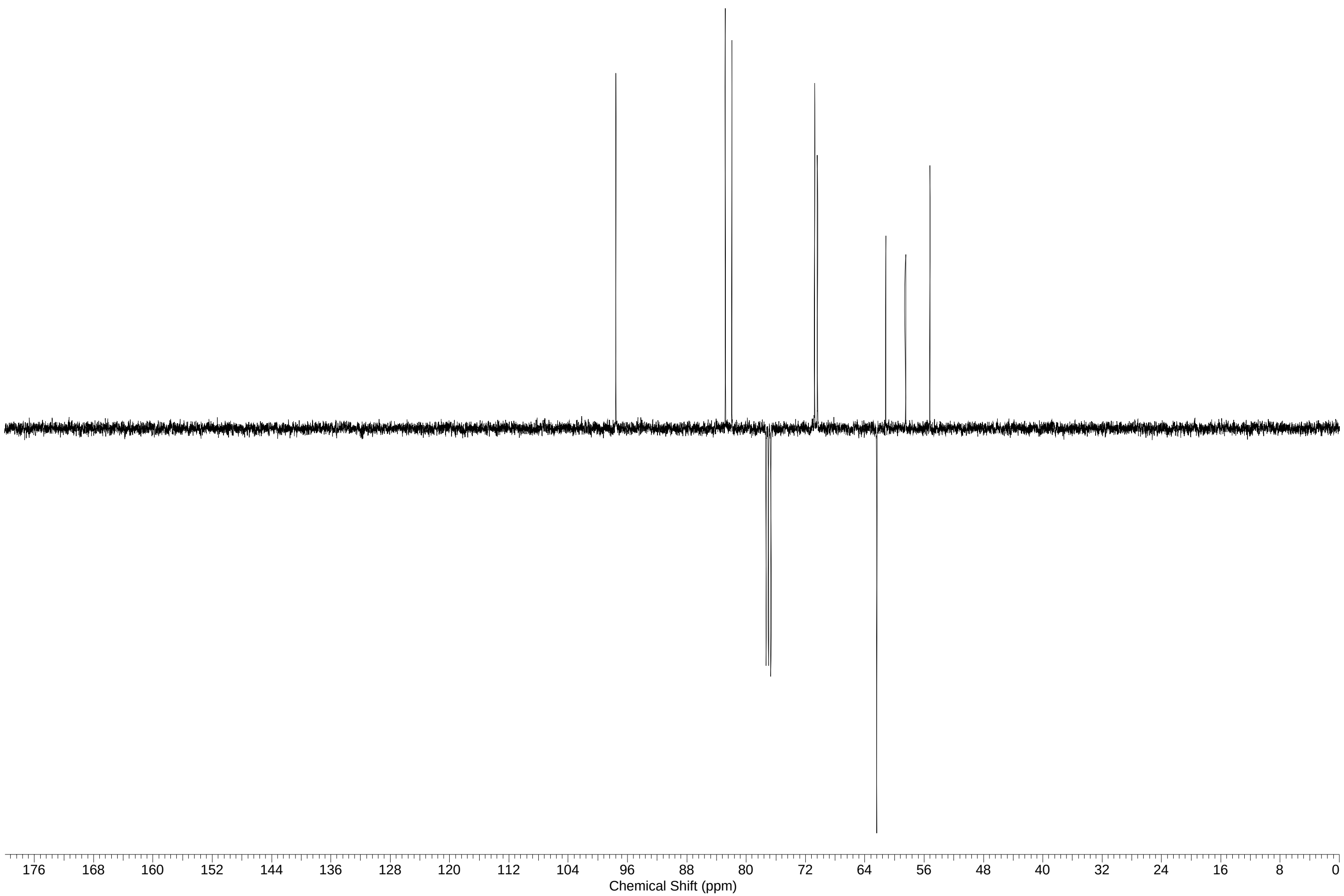


Methyl 2,3-di-*O*-methyl-α-D-glucopyranoside (6)

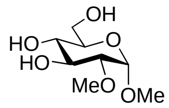


6

^{13}C-NMR (101 MHz, $CDCl_3$)

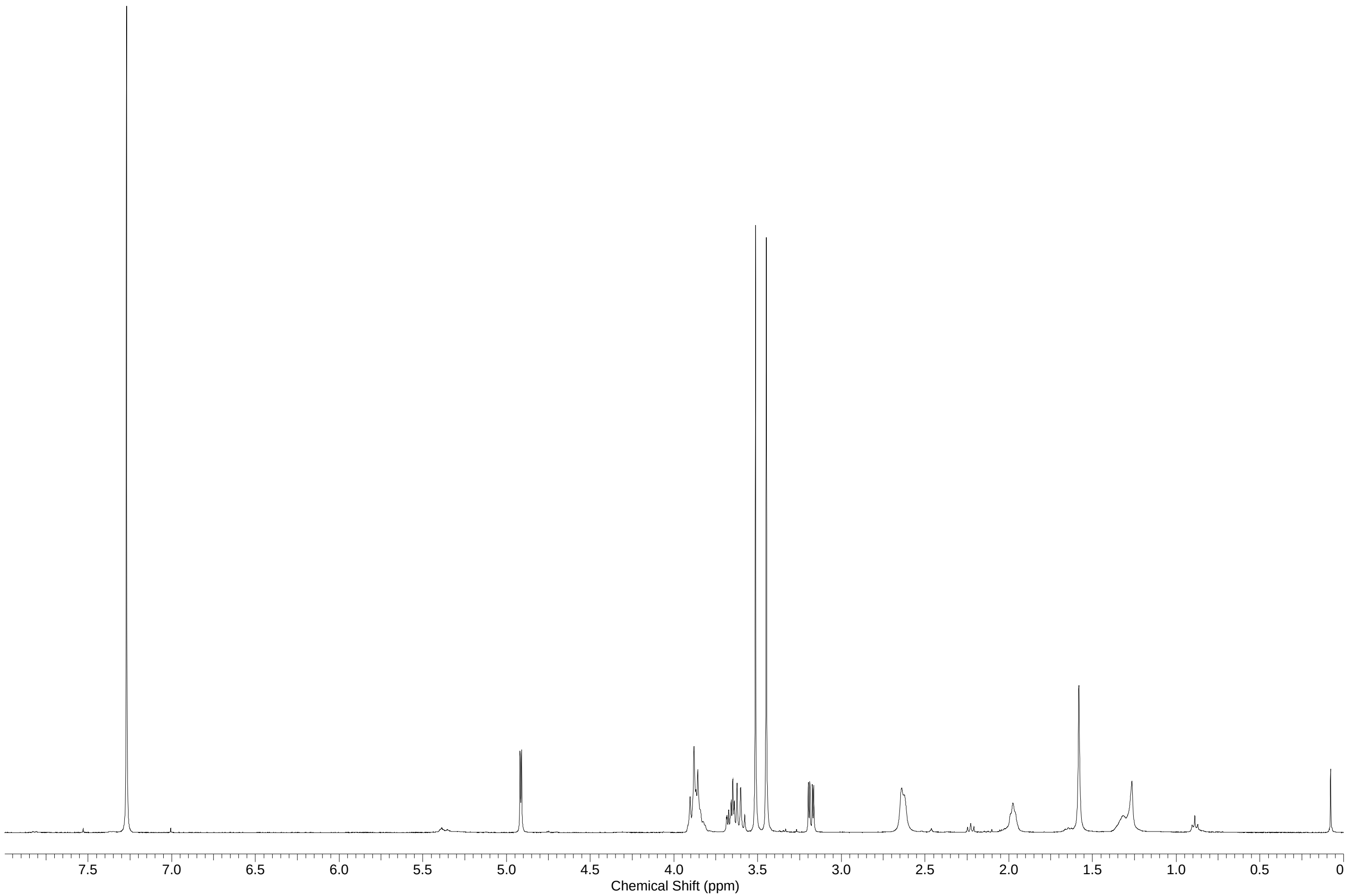


Methyl 2-*O*-methyl-α-D-glucopyranoside (7)

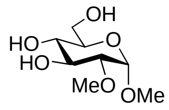


7

^{1}H-NMR (400 MHz, $CDCl_3$)

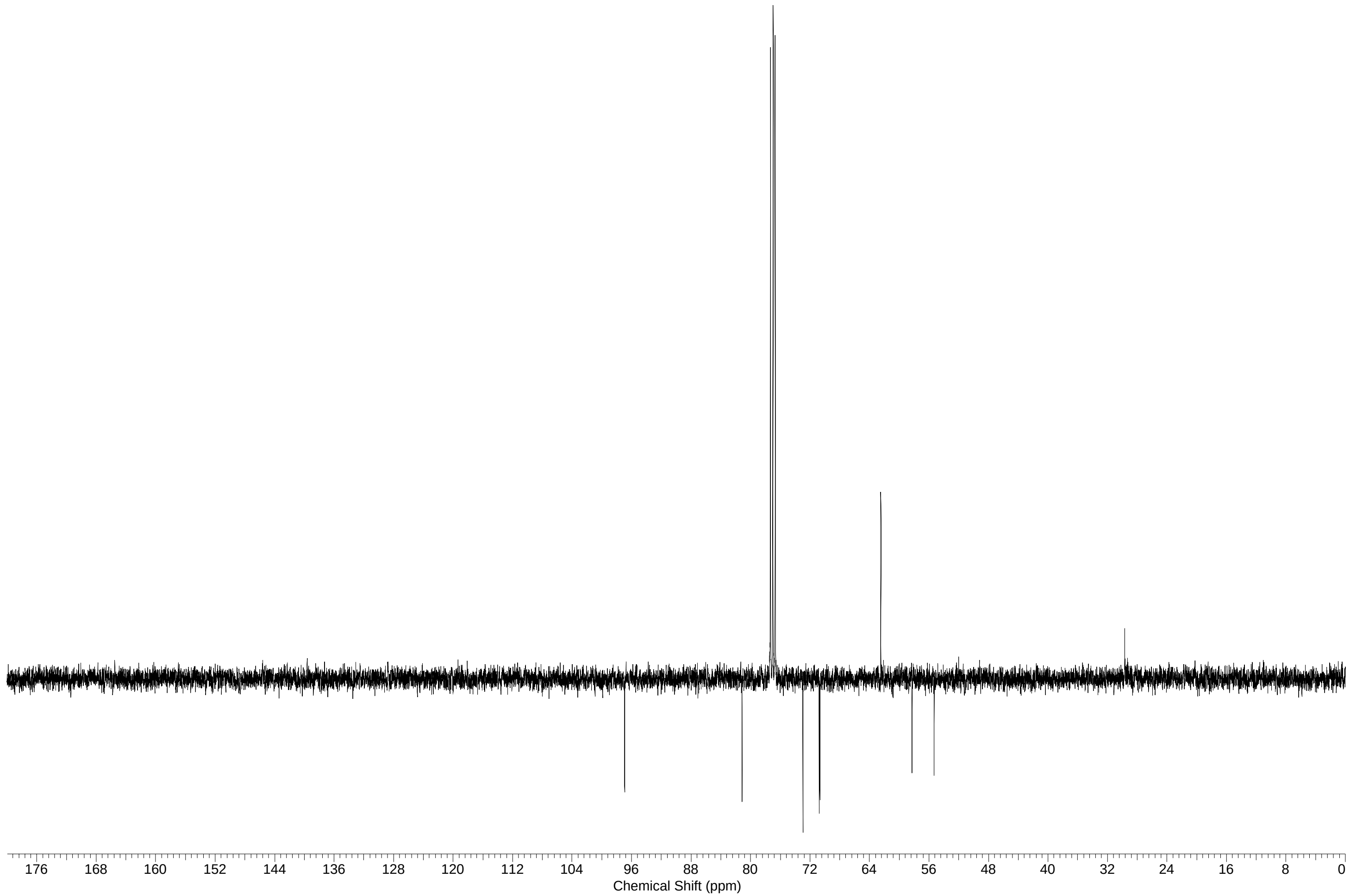


Methyl 2-*O*-methyl-α-D-glucopyranoside (7)

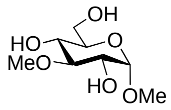


7

^{13}C-NMR (101 MHz, $CDCl_3$)

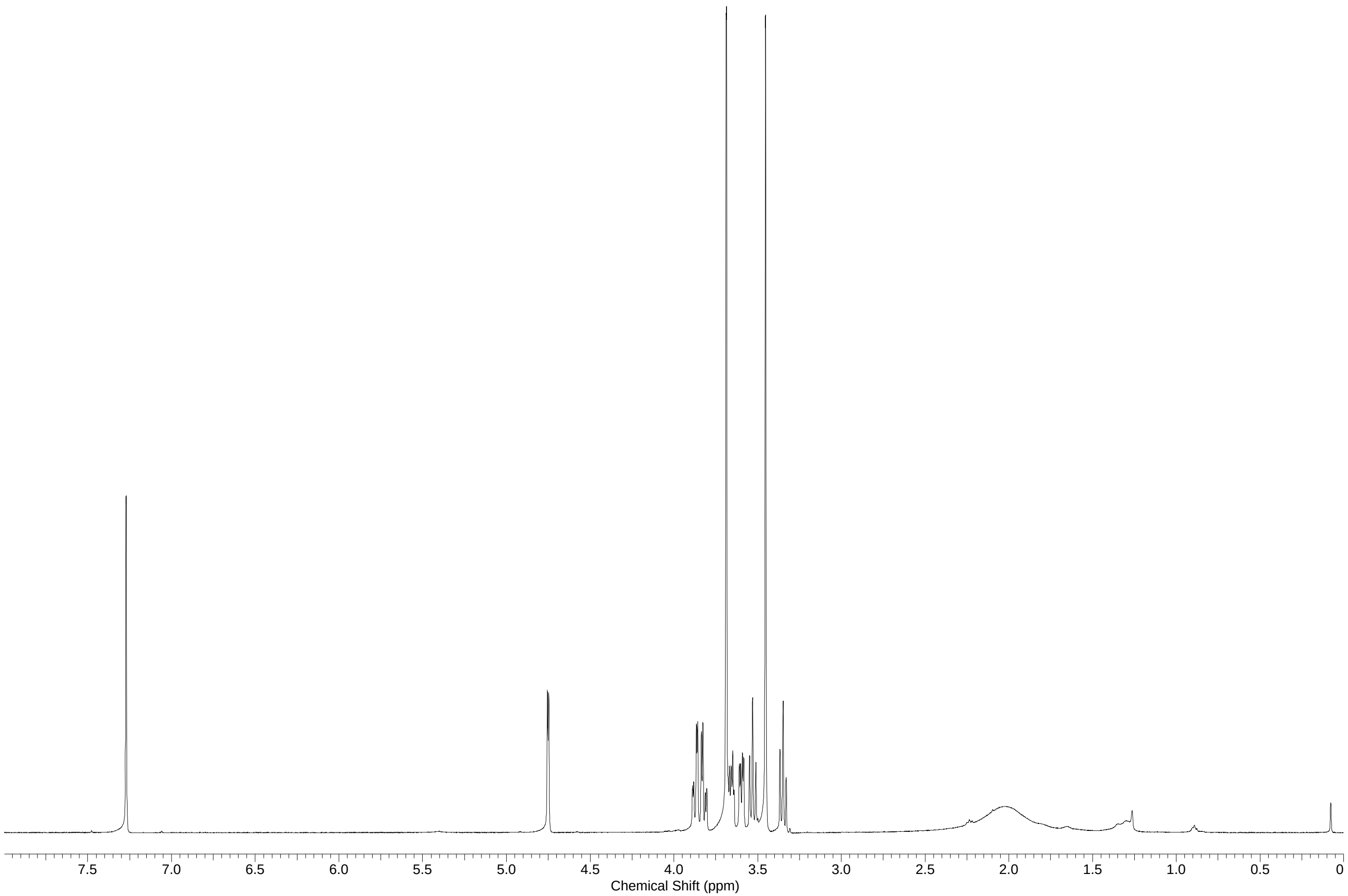


Methyl 3-*O*-methyl-α-D-glucopyranoside (8)

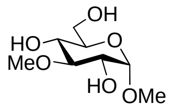


8

^{1}H-NMR (400 MHz, $CDCl_3$)

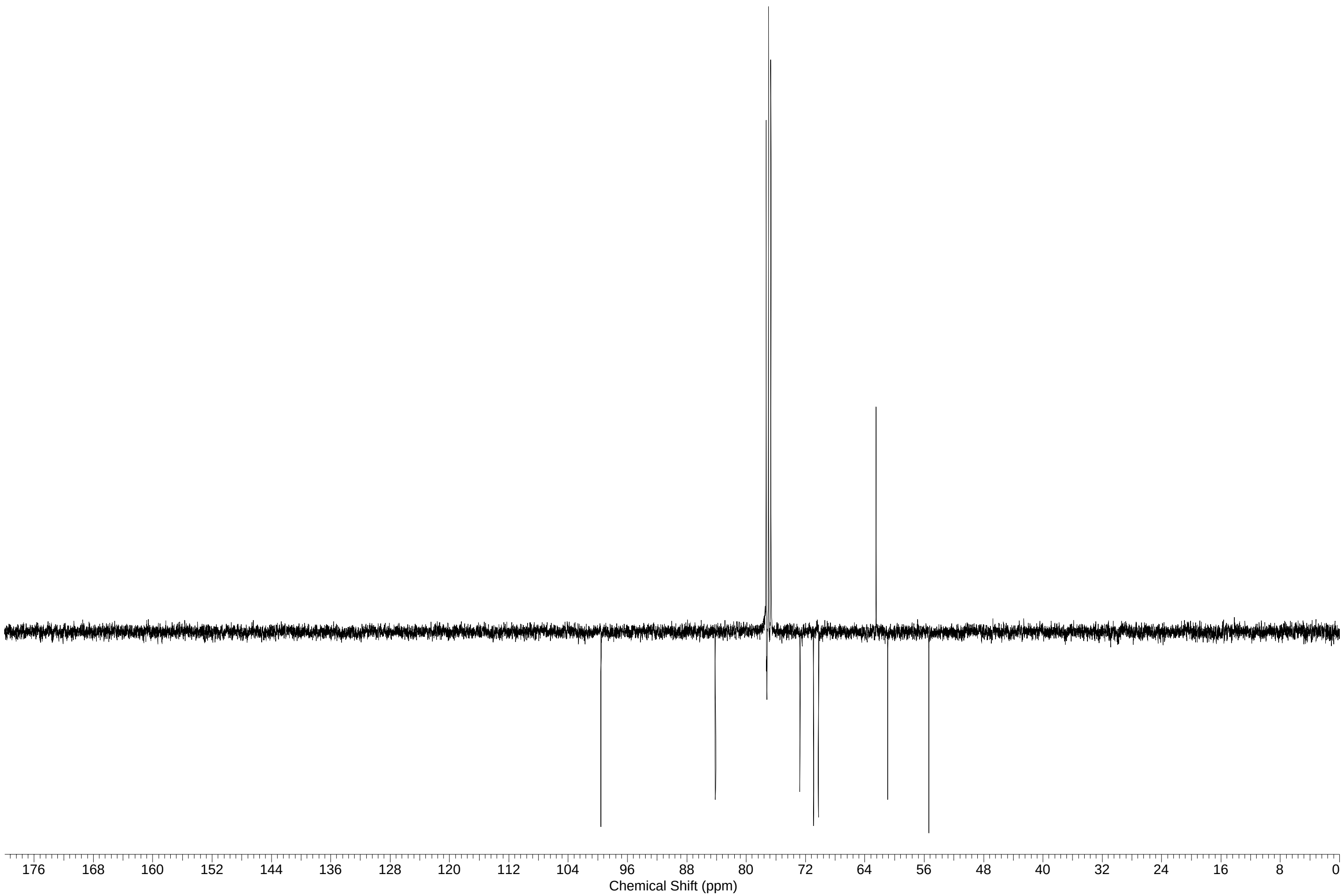


Methyl 3-*O*-methyl-α-D-glucopyranoside (8)

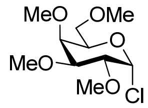


8

^{13}C-NMR (101 MHz, $CDCl_3$)

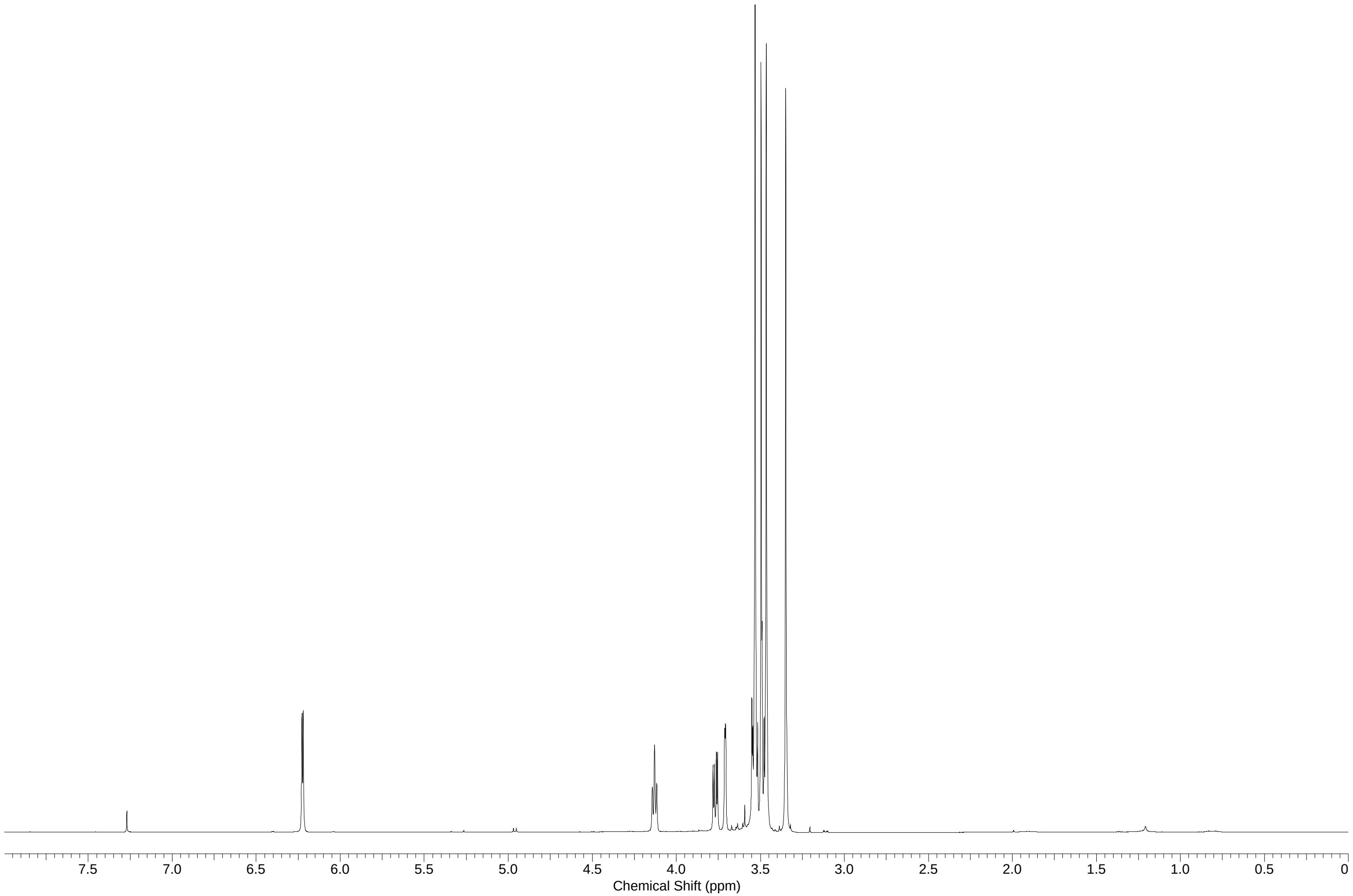


2,3,4,6-Tetra-*O*-methyl α-D-galactopyranosyl chloride (9)

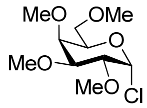


9

^{1}H-NMR (400 MHz, $CDCl_3$)

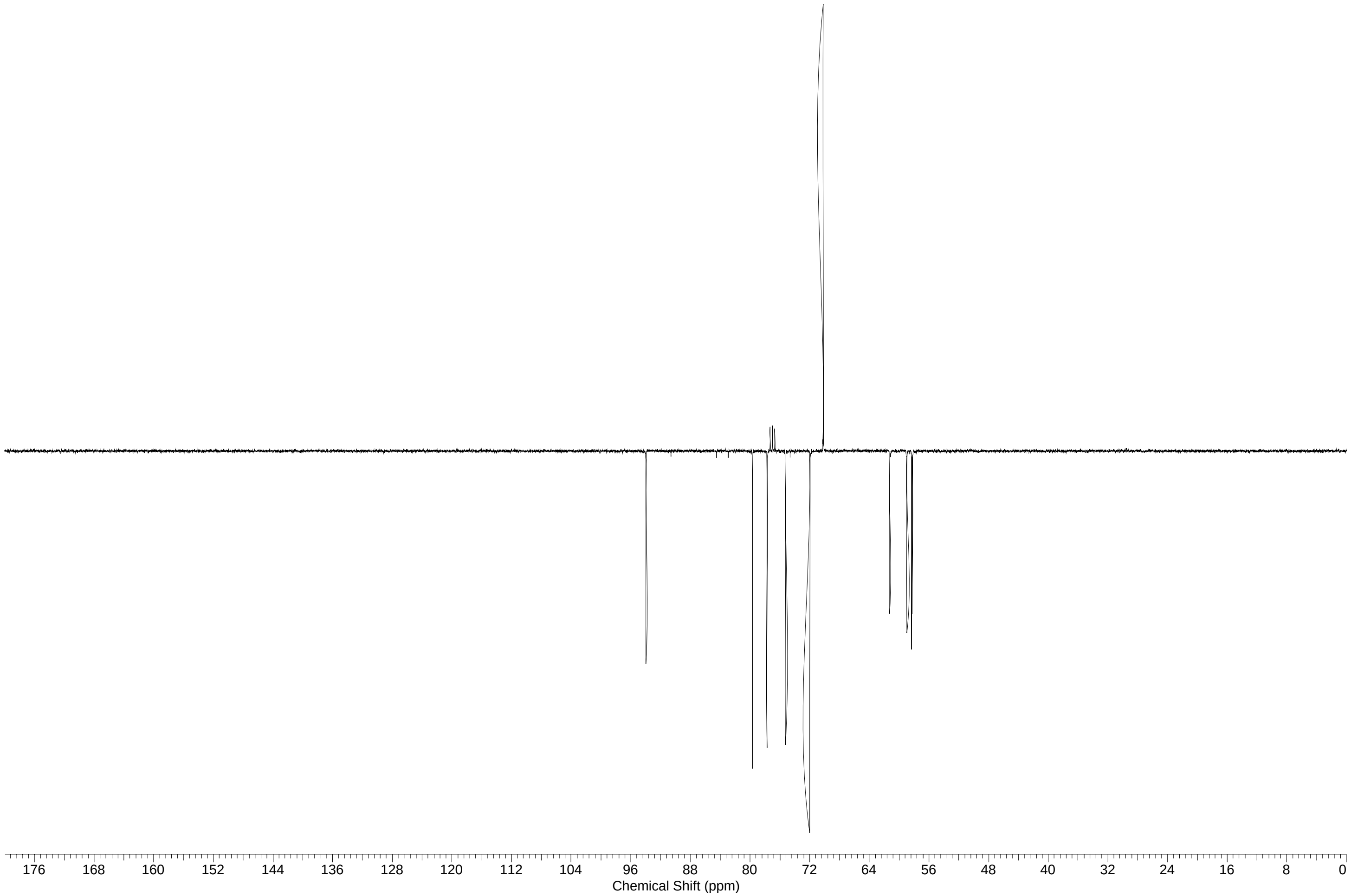


2,3,4,6-Tetra-*O*-methyl α-D-galactopyranosyl chloride (9)



9

^{13}C-NMR (101 MHz, $CDCl_3$)

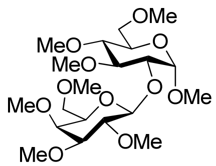


Methyl 3,4,6-tri-*O*-methyl-2-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (10)

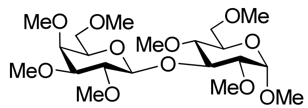
Methyl 2,4,6-tri-*O*-methyl-3-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (11)

Methyl 2,3,6-tri-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (12)

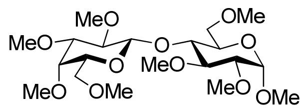
Methyl 2,3,4-tri-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (13)



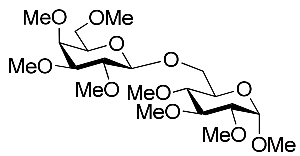
10



11

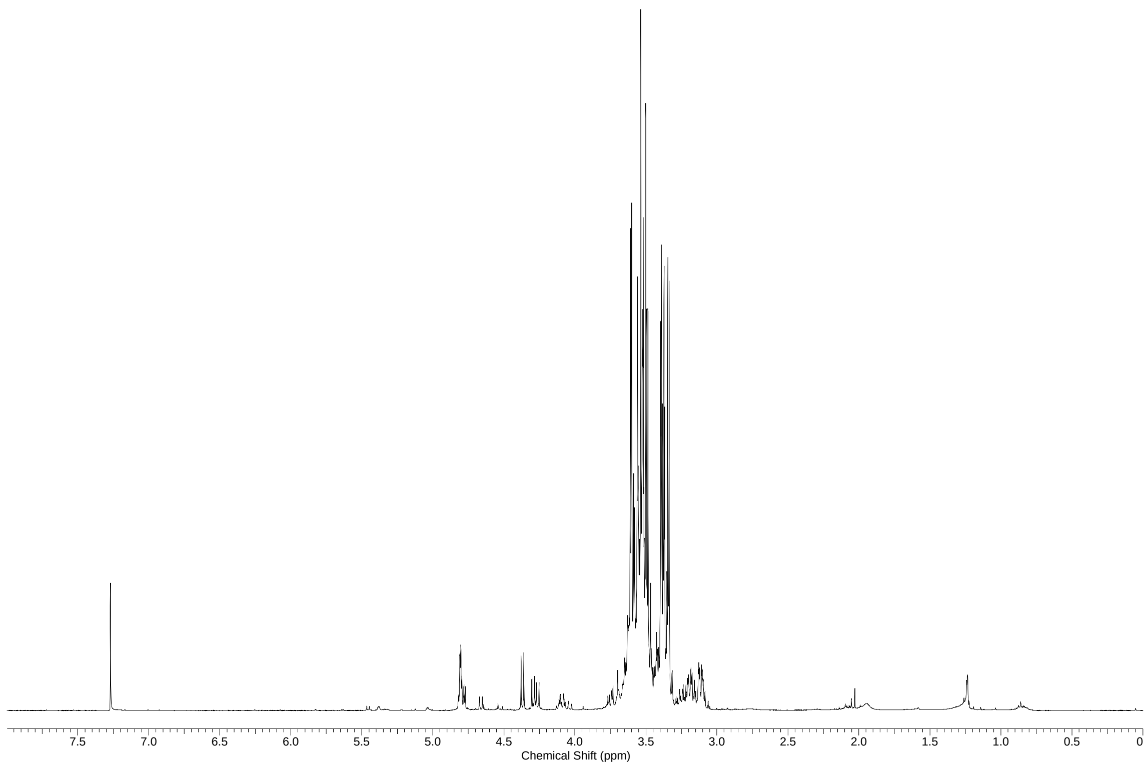


12



13

^{1}H-NMR (400 MHz, $CDCl_3$)

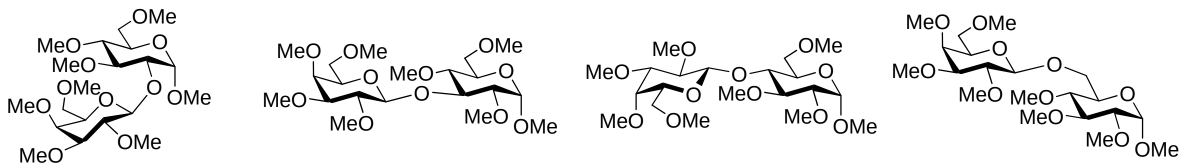


Methyl 3,4,6-tri-*O*-methyl-2-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (10)

Methyl 2,4,6-tri-*O*-methyl-3-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (11)

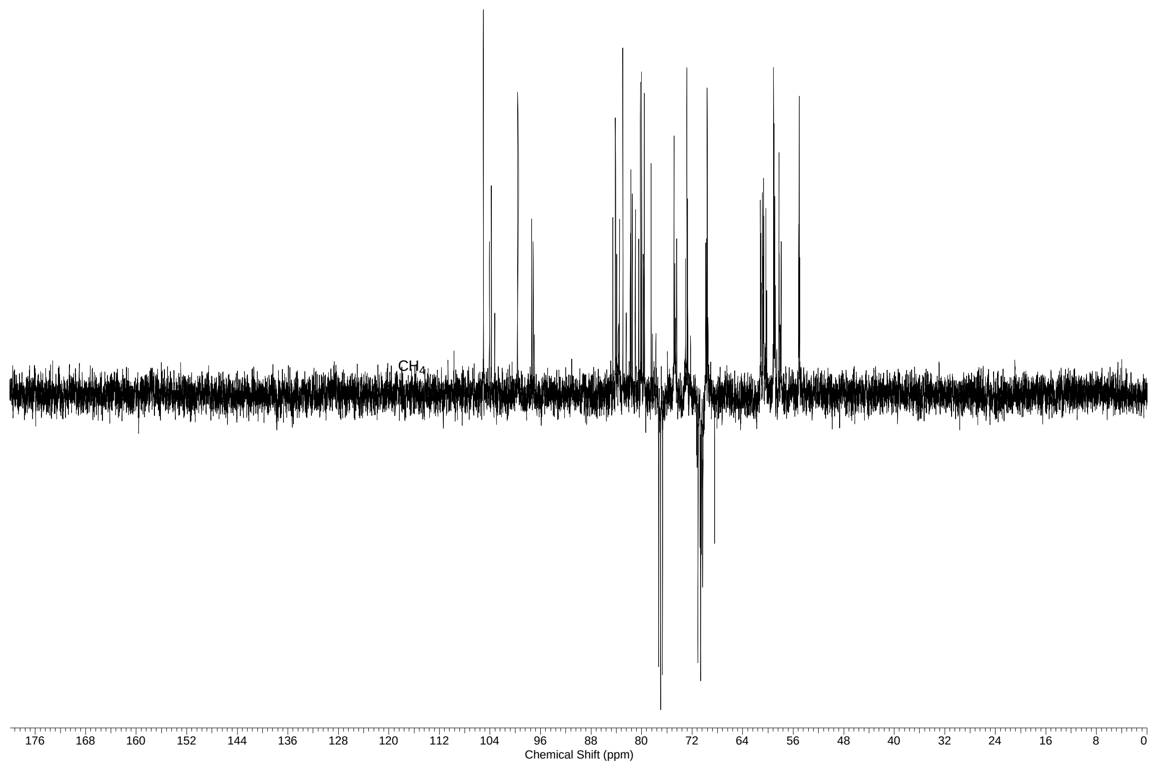
Methyl 2,3,6-tri-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (12)

Methyl 2,3,4-tri-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (13)

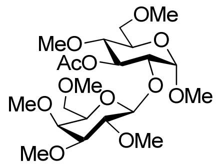


10 **11** **12** **13**

^{13}C-NMR (101 MHz, $CDCl_3$)

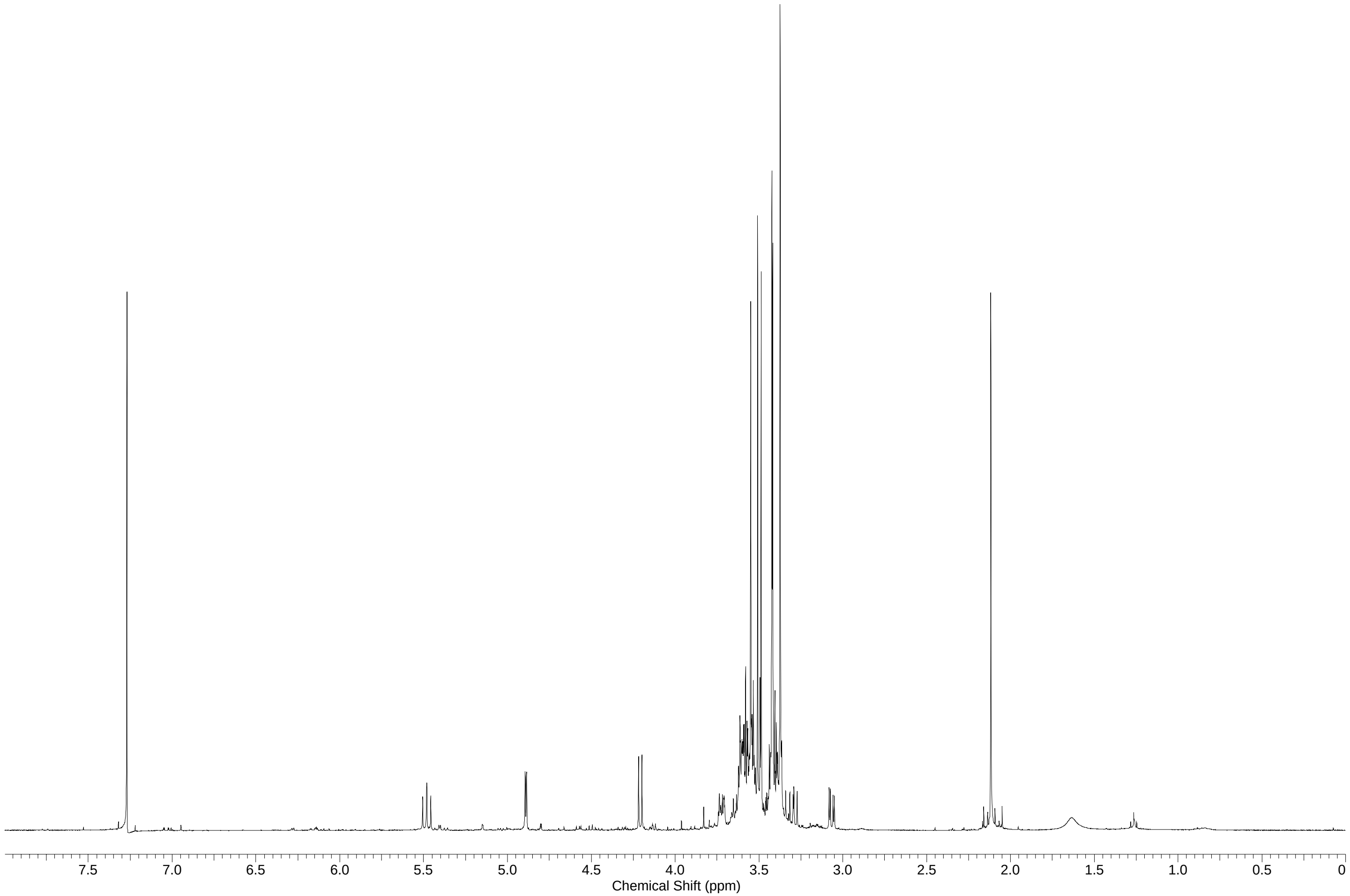


Methyl 3-*O*-acetyl-4,6-di-*O*-methyl-2-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (14)

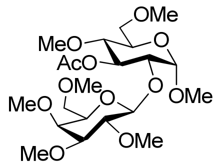


14

^{1}H-NMR (400 MHz, $CDCl_3$)

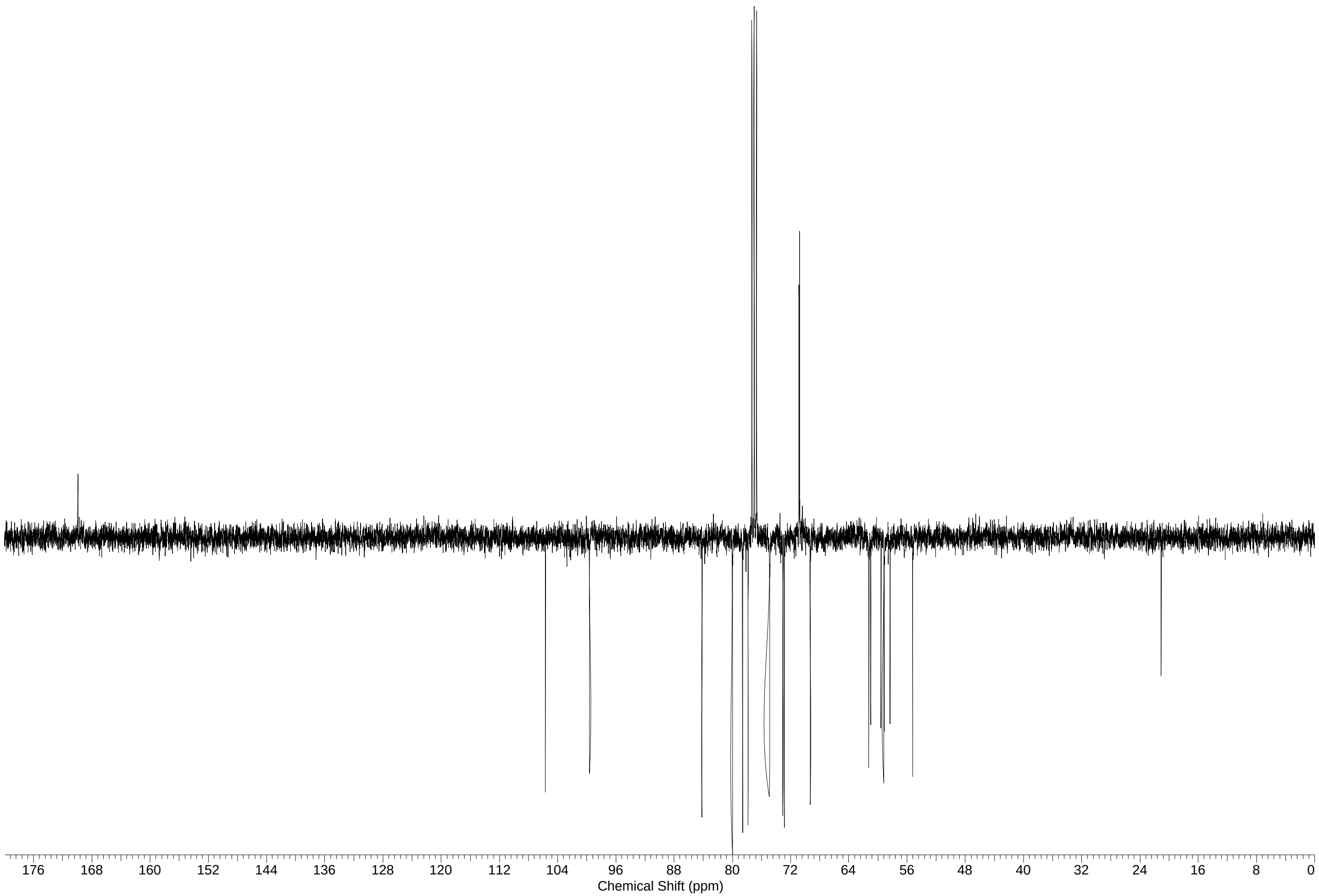


Methyl 3-*O*-acetyl-4,6-di-*O*-methyl-2-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (14)



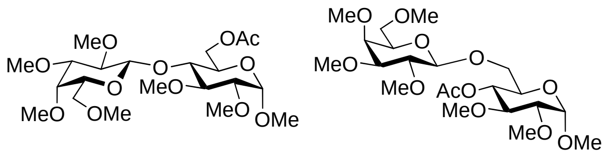
14

^{13}C-NMR (101 MHz, $CDCl_3$)



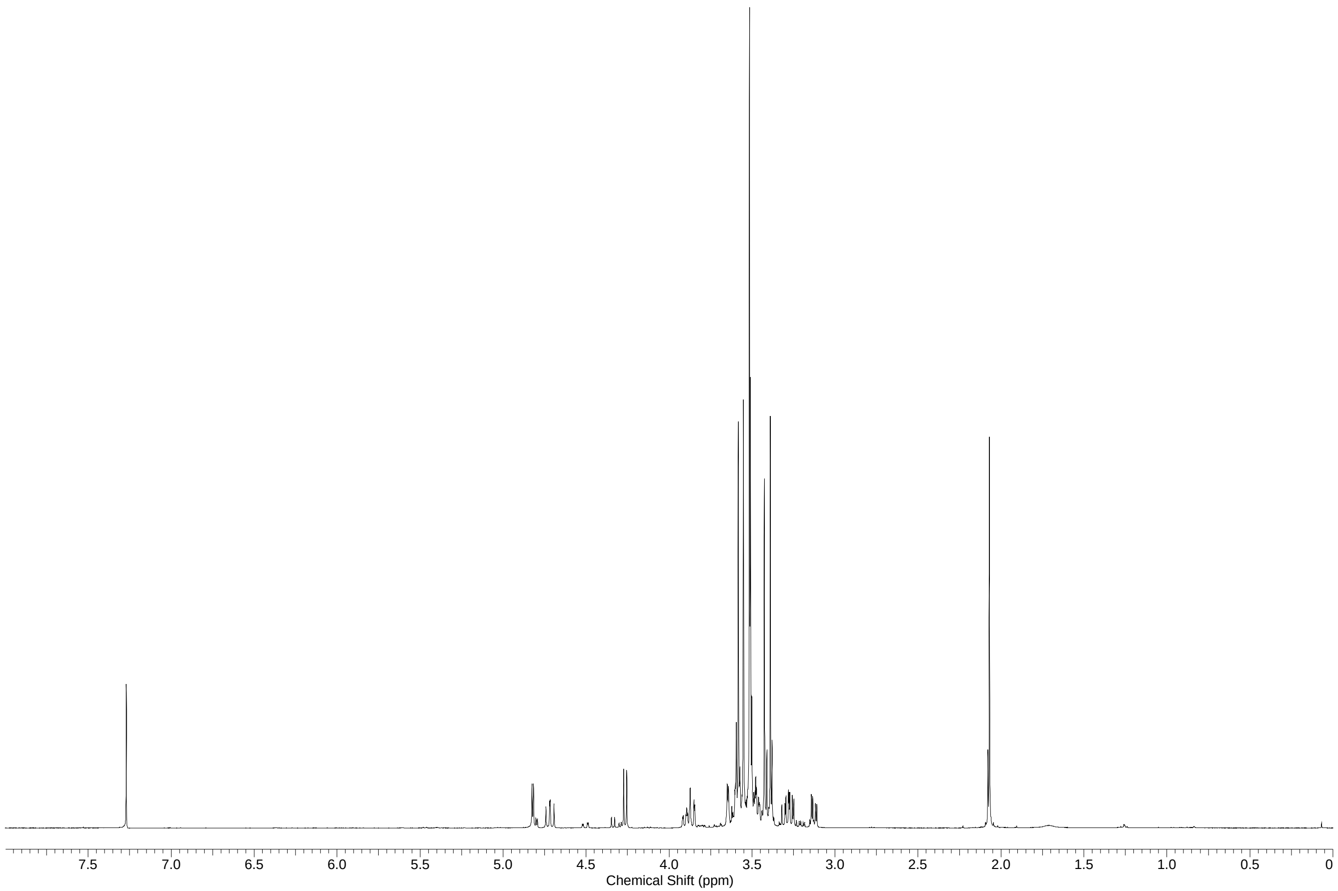
Methyl 6-*O*-acetyl-2,3-di-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (15)

Methyl 4-*O*-acetyl-2,3-di-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (16)



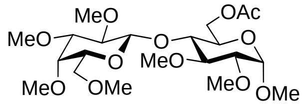
15 **16**

^{1}H-NMR (400 MHz, $CDCl_3$)

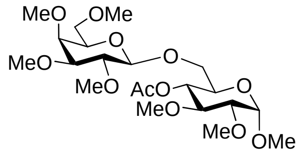


Methyl 6-*O*-acetyl-2,3-di-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (15)

Methyl 4-*O*-acetyl-2,3-di-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (16)

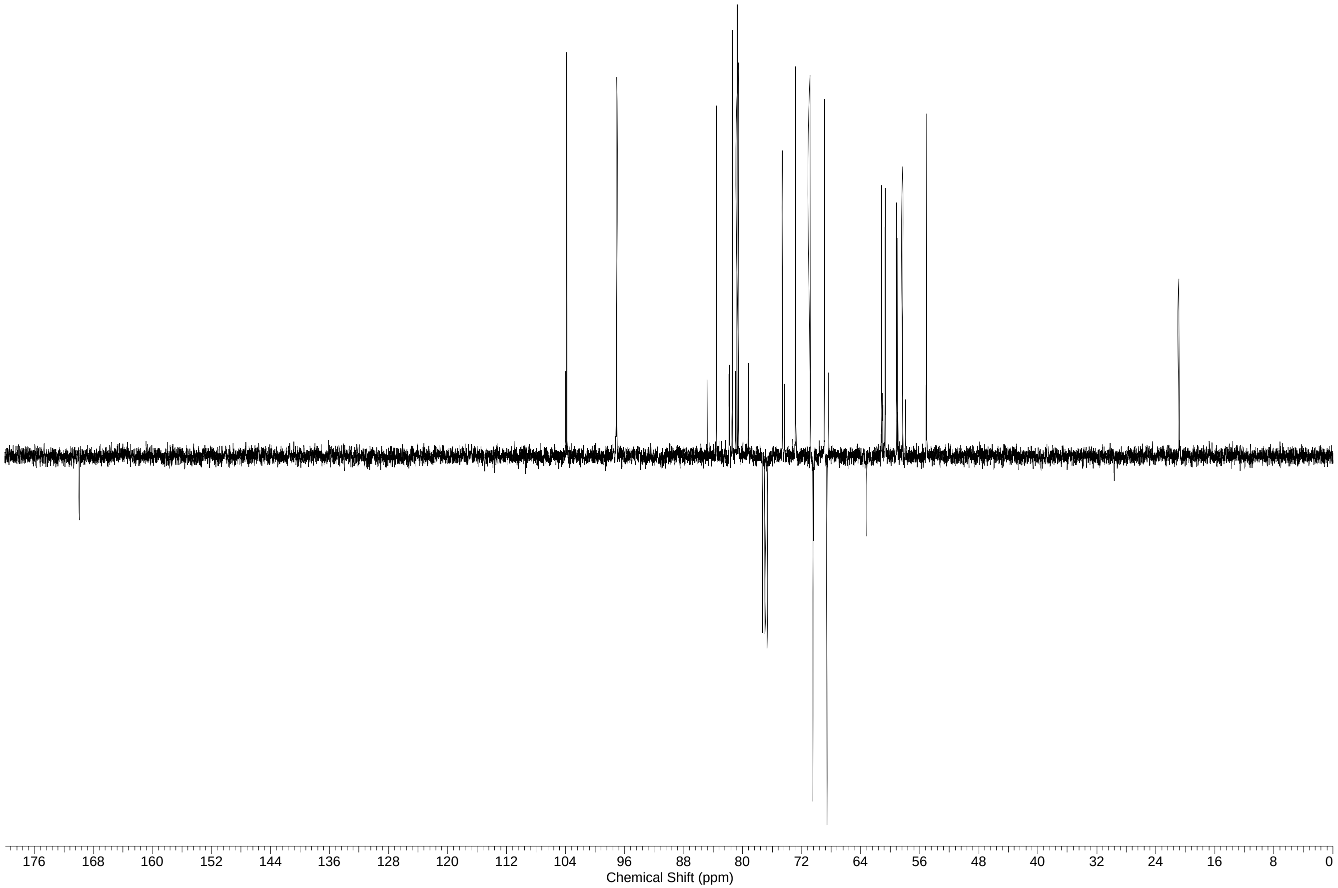


15



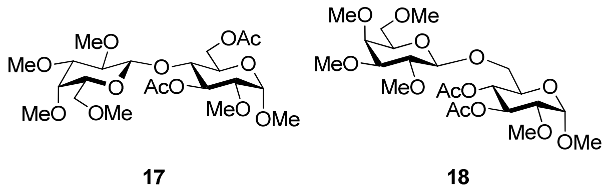
16

^{13}C-NMR (101 MHz, $CDCl_3$)

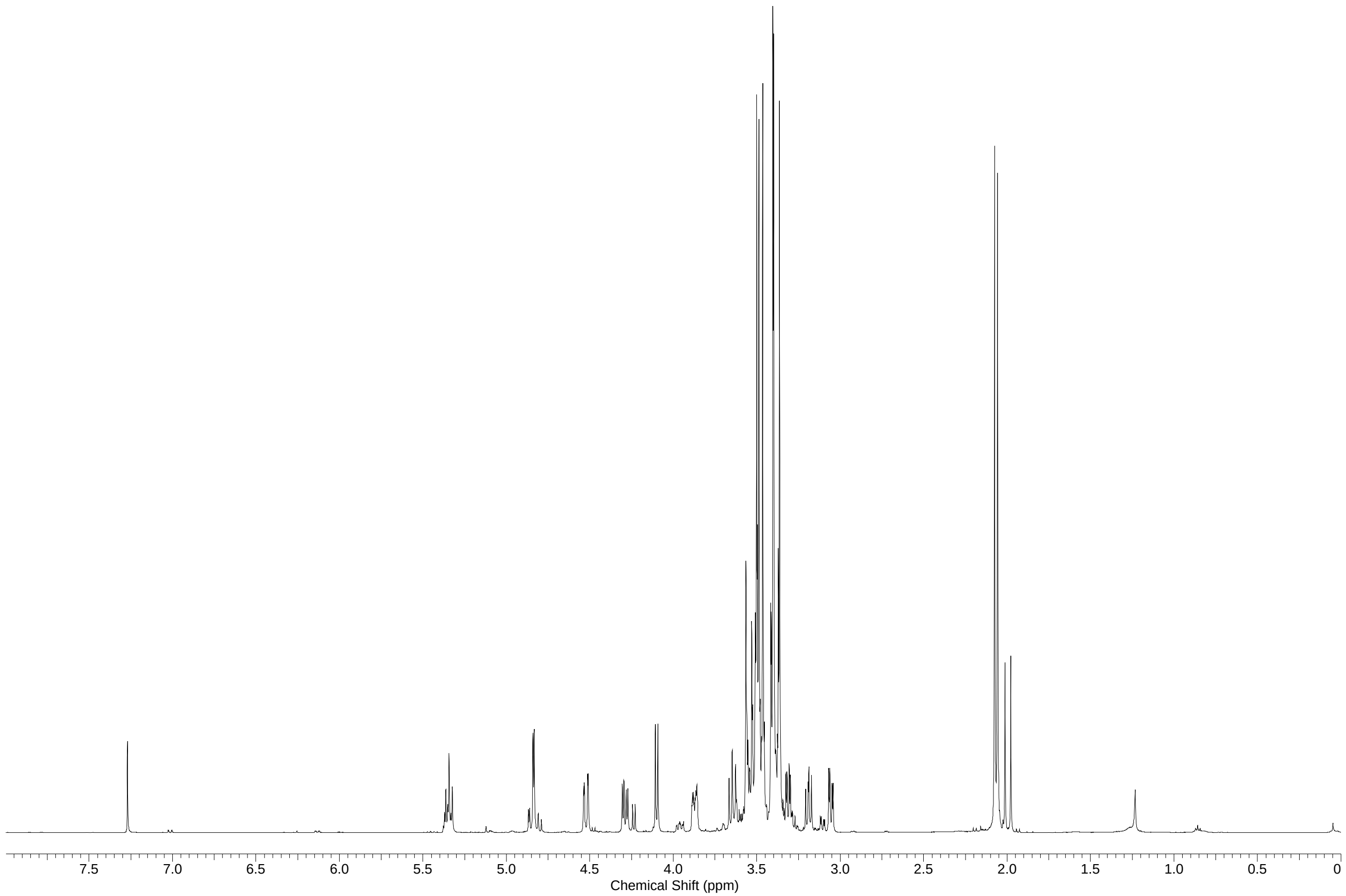


Methyl 3,6-di-*O*-acetyl-2-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (17)

Methyl 3,4-di-*O*-acetyl-2-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (18)

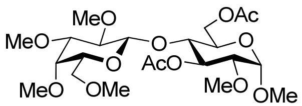


^{1}H-NMR (400 MHz, $CDCl_3$)

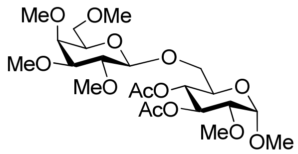


Methyl 3,6-di-*O*-acetyl-2-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (17)

Methyl 3,4-di-*O*-acetyl-2-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (18)

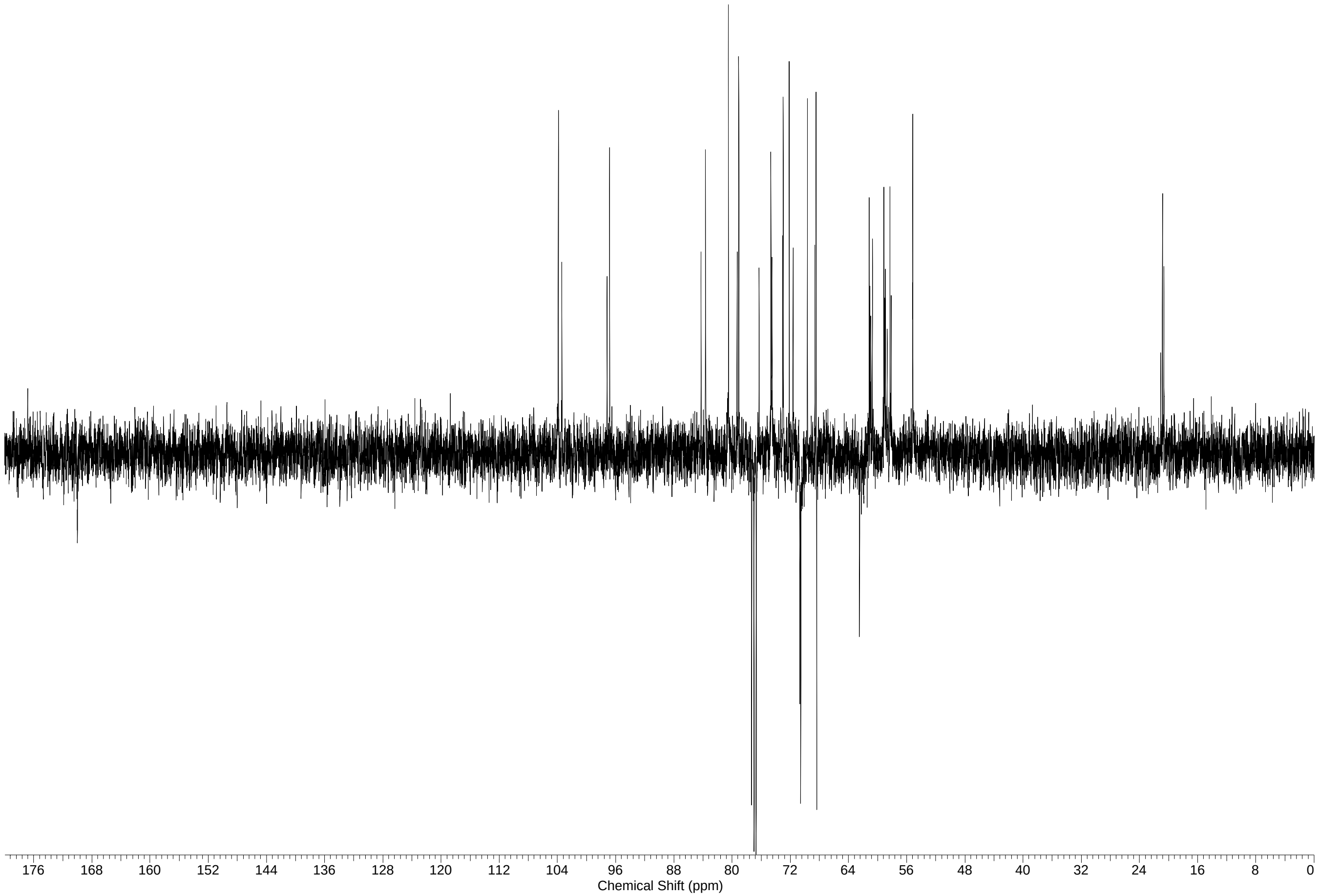


17



18

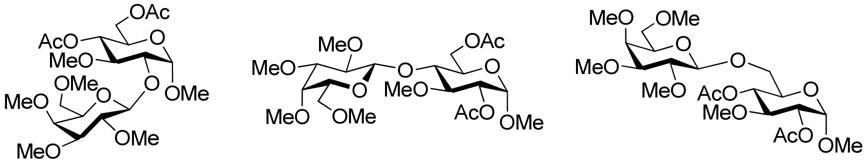
^{13}C-NMR (101 MHz, $CDCl_3$)



Methyl 4,6-di-*O*-acetyl-3-*O*-methyl-2-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (19)

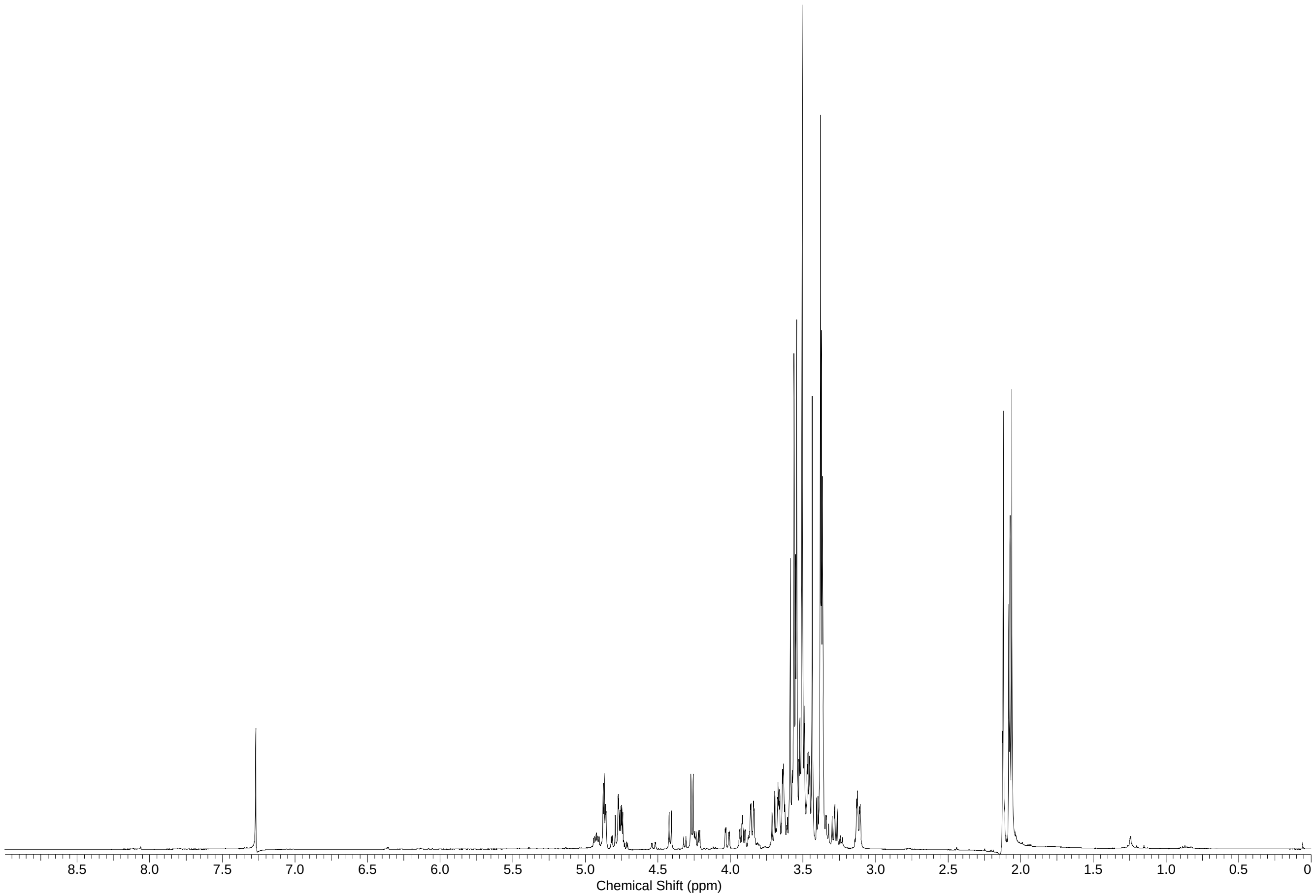
Methyl 2,6-di-*O*-acetyl-3-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (20)

Methyl 2,4-di-*O*-acetyl-3-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (21)



19 **20** **21**

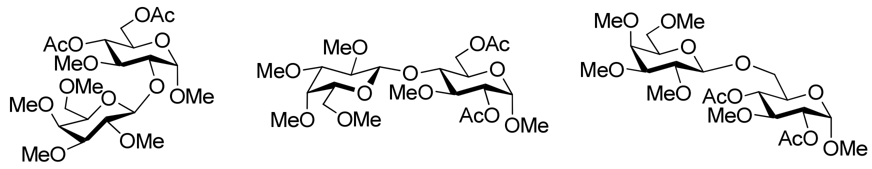
^{1}H-NMR (400 MHz, $CDCl_3$)



Methyl 4,6-di-*O*-acetyl-3-*O*-methyl-2-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (19)

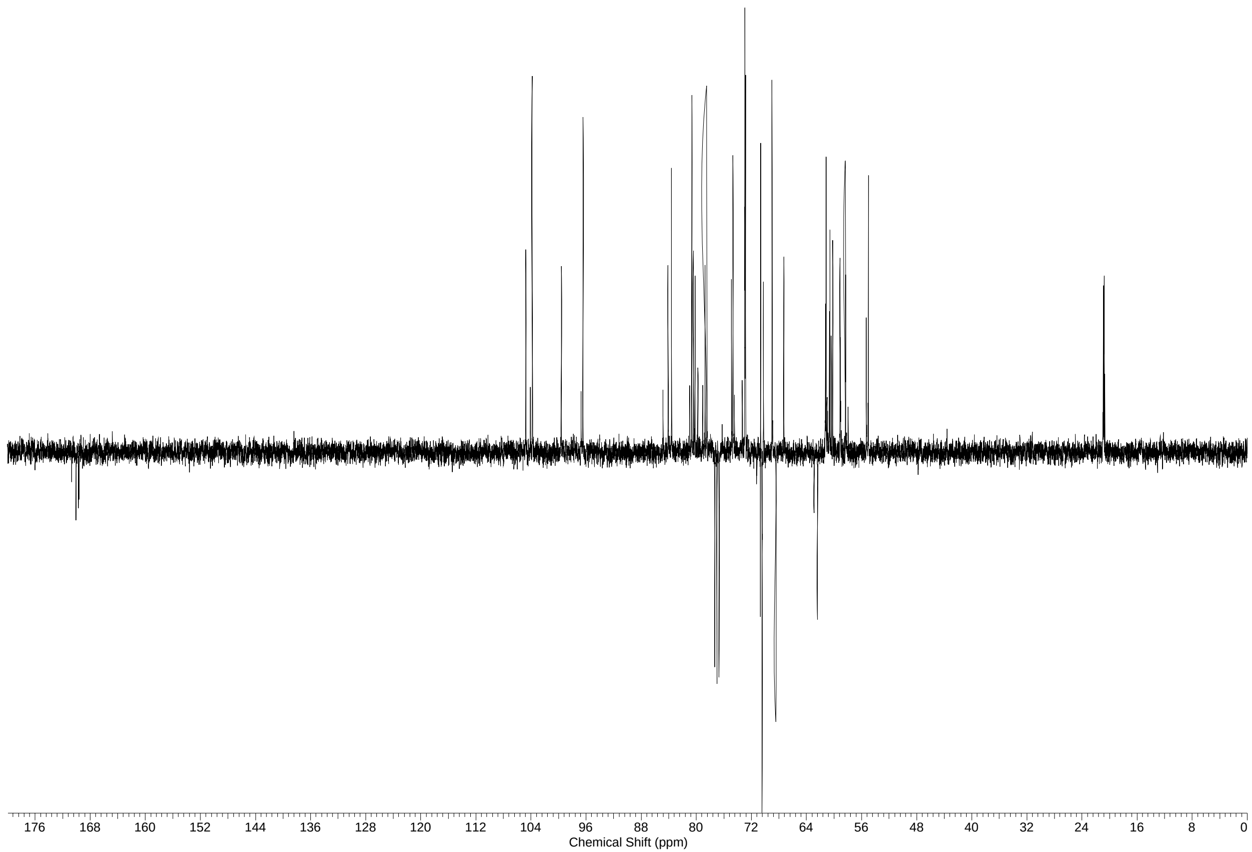
Methyl 2,6-di-*O*-acetyl-3-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (20)

Methyl 2,4-di-*O*-acetyl-3-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (21)

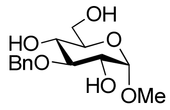


19 **20** **21**

^{13}C-NMR (101 MHz, $CDCl_3$)

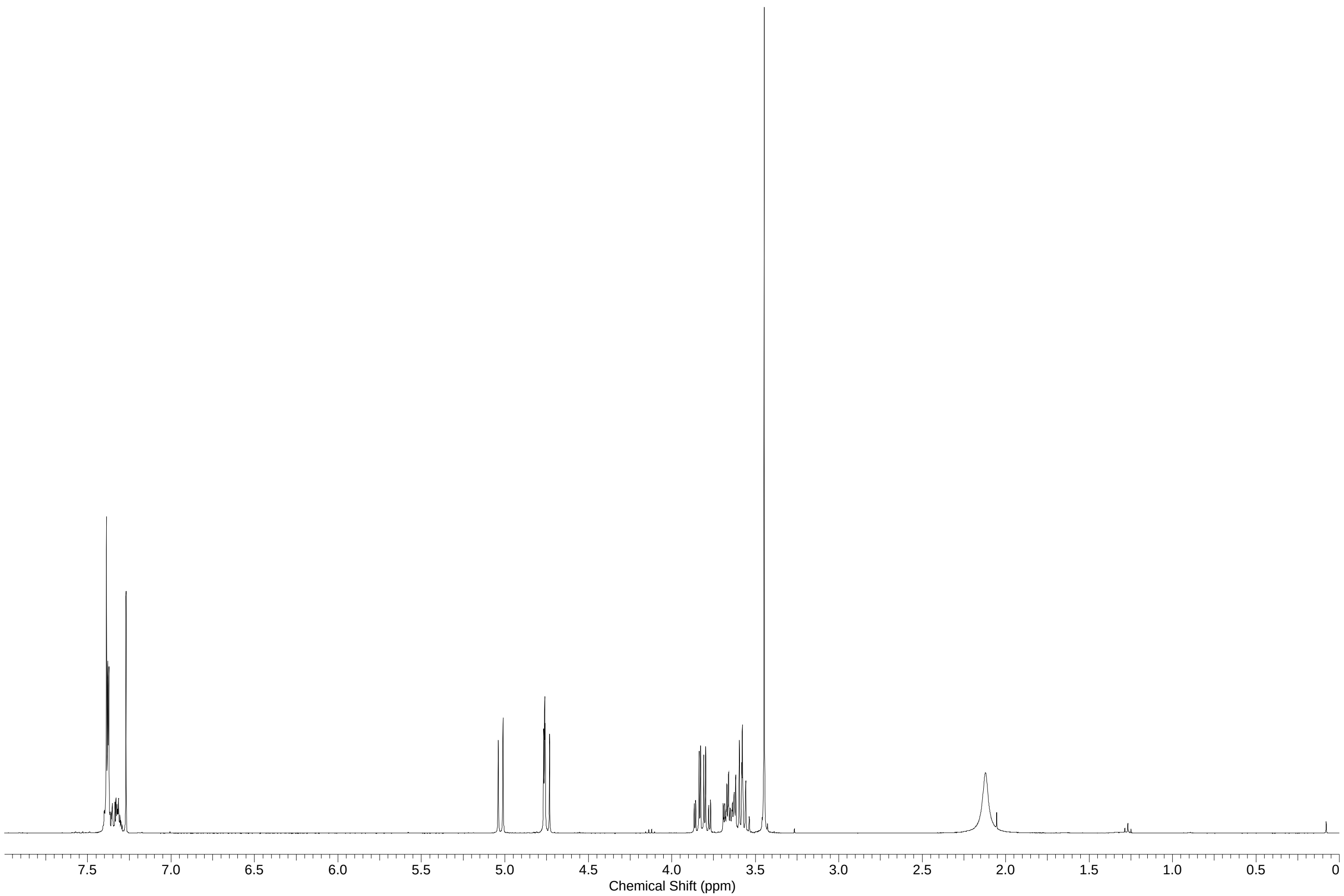


Methyl 3-*O*-benzyl-α-D-glucopyranoside (22)

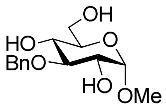


22

^{1}H-NMR (400 MHz, $CDCl_3$)

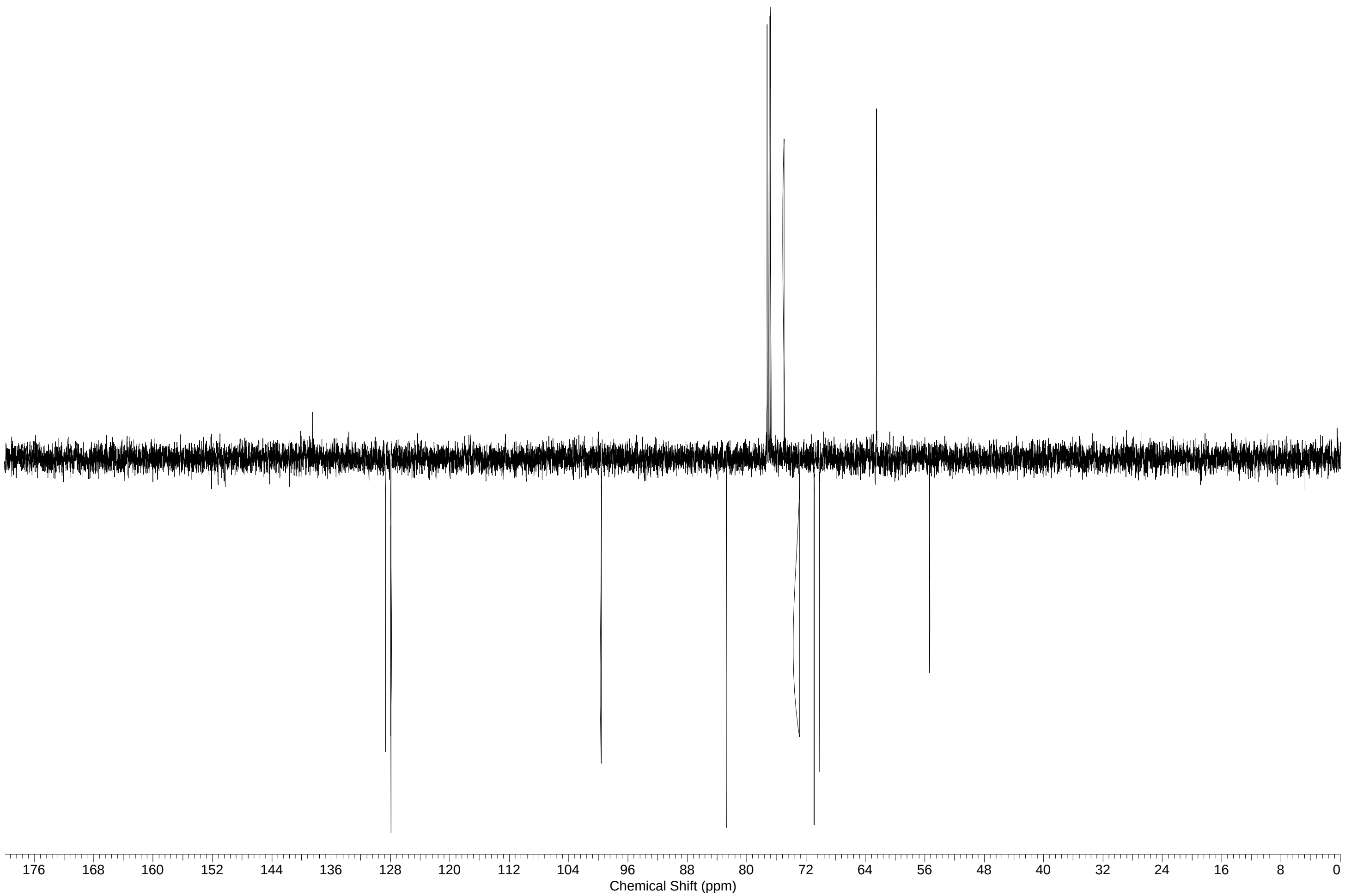


Methyl 3-*O*-benzyl-α-D-glucopyranoside (22)

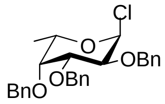


22

^{13}C-NMR (101 MHz, $CDCl_3$)

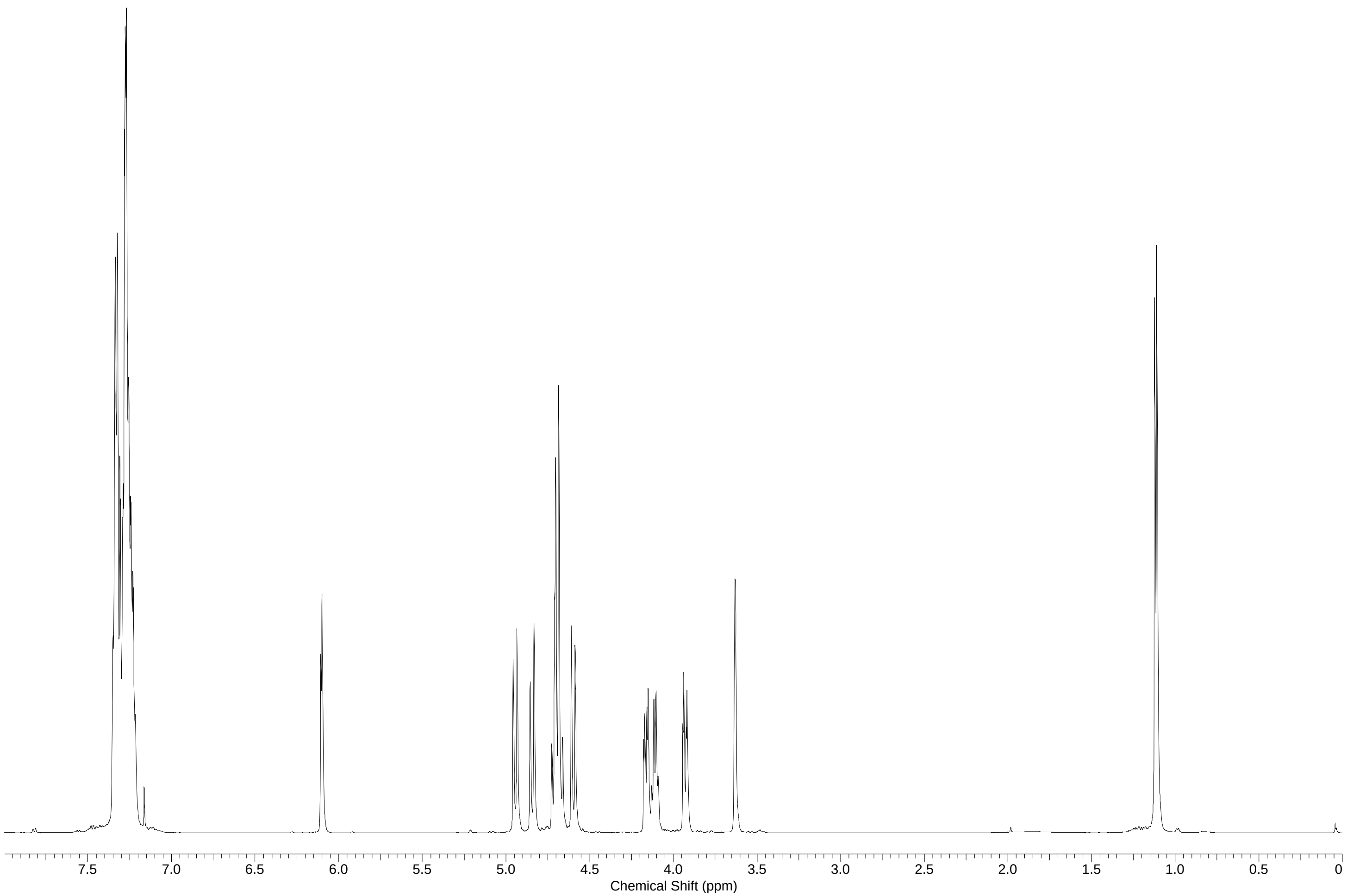


2,3,4-Tri-*O*-benzyl-α-L-fucopyranosyl chloride (23)

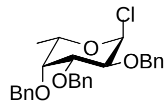


23

^{1}H-NMR (400 MHz, $CDCl_3$)

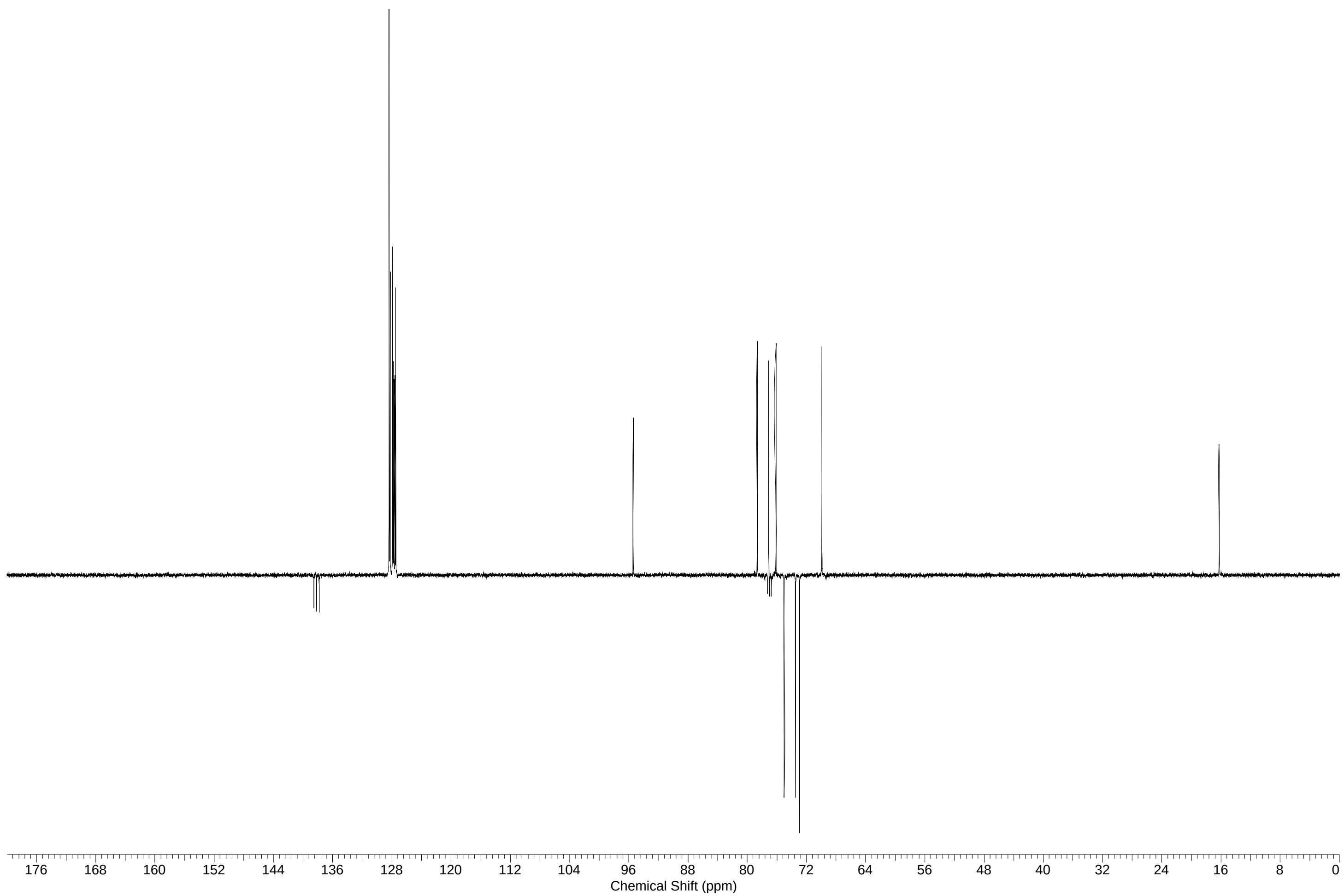


2,3,4-Tri-*O*-benzyl-α-L-fucopyranosyl chloride (23)

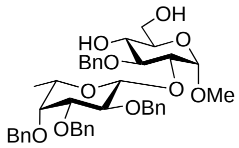


23

^{13}C-NMR (101 MHz, $CDCl_3$)

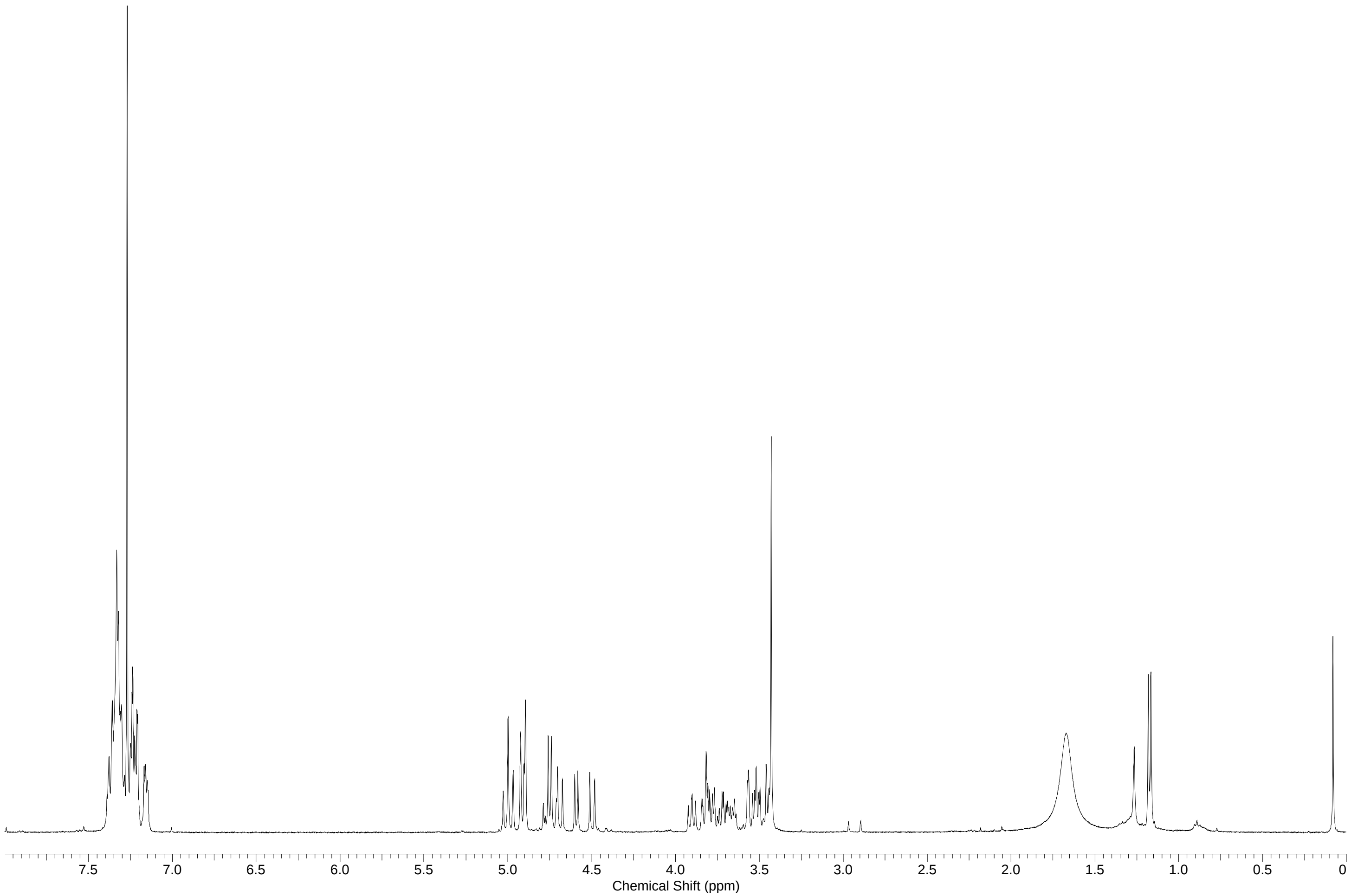


Methyl 3-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (24)

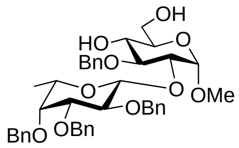


24

^{1}H-NMR (400 MHz, $CDCl_3$)

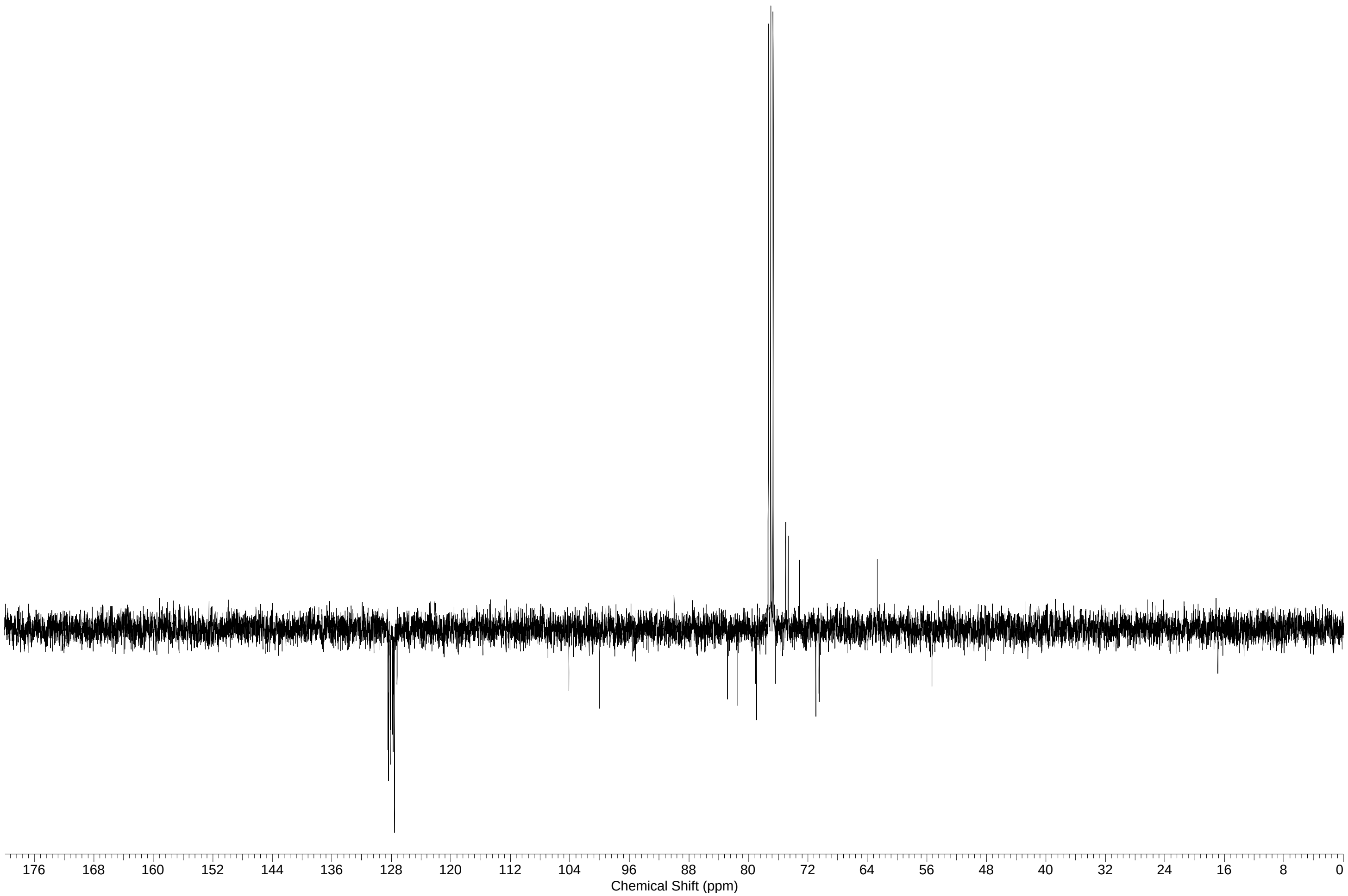


Methyl 3-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (24)

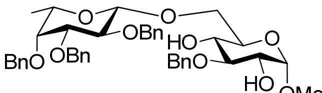


24

^{13}C-NMR (101 MHz, $CDCl_3$)

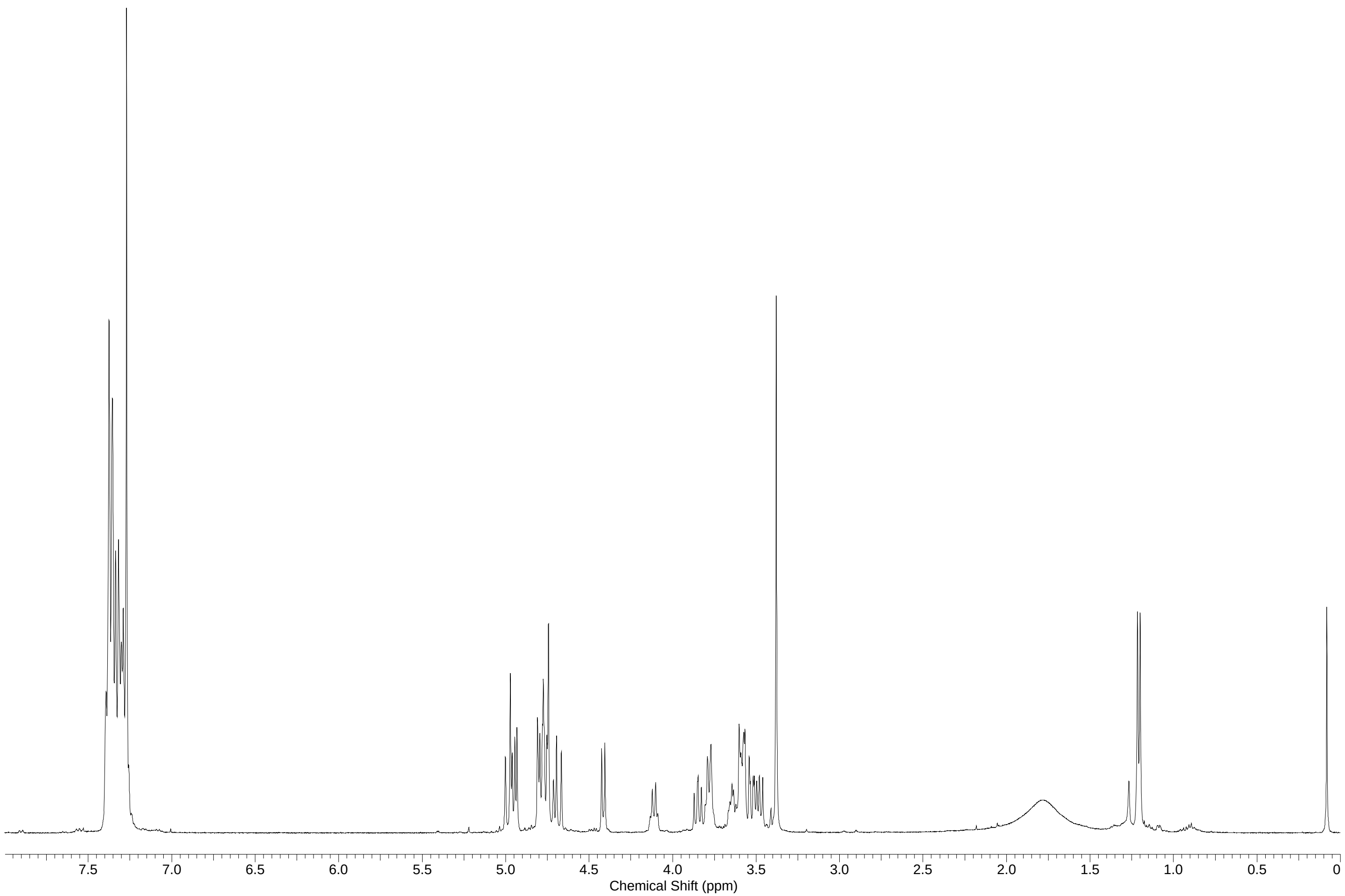


Methyl 3-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (25)

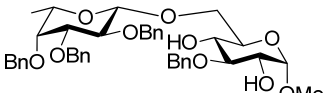


25

^{1}H-NMR (400 MHz, $CDCl_3$)

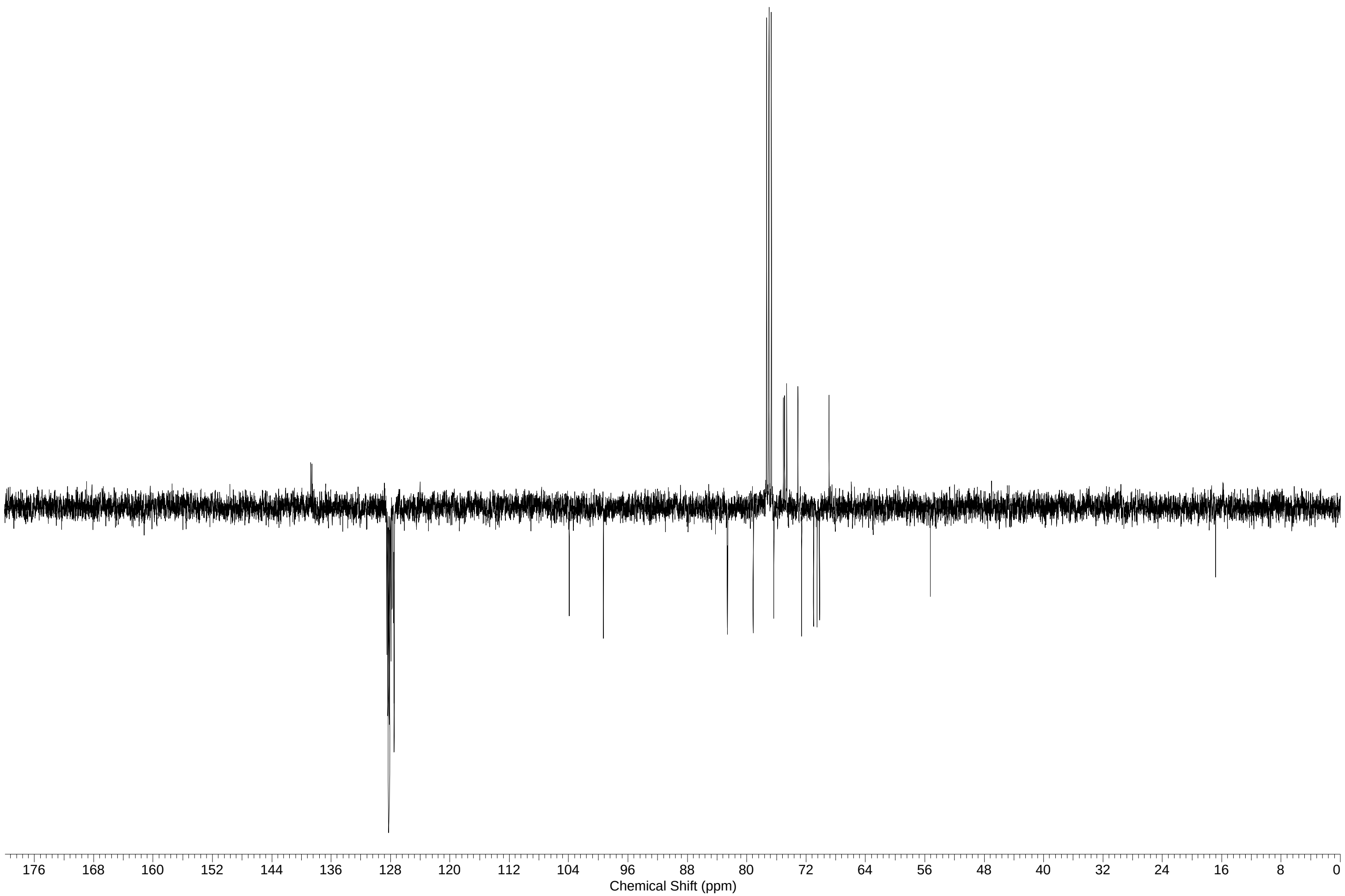


Methyl 3-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (25)

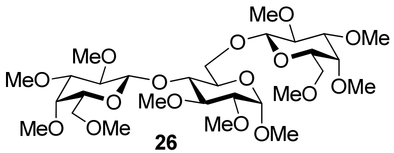


25

^{13}C-NMR (101 MHz, $CDCl_3$)

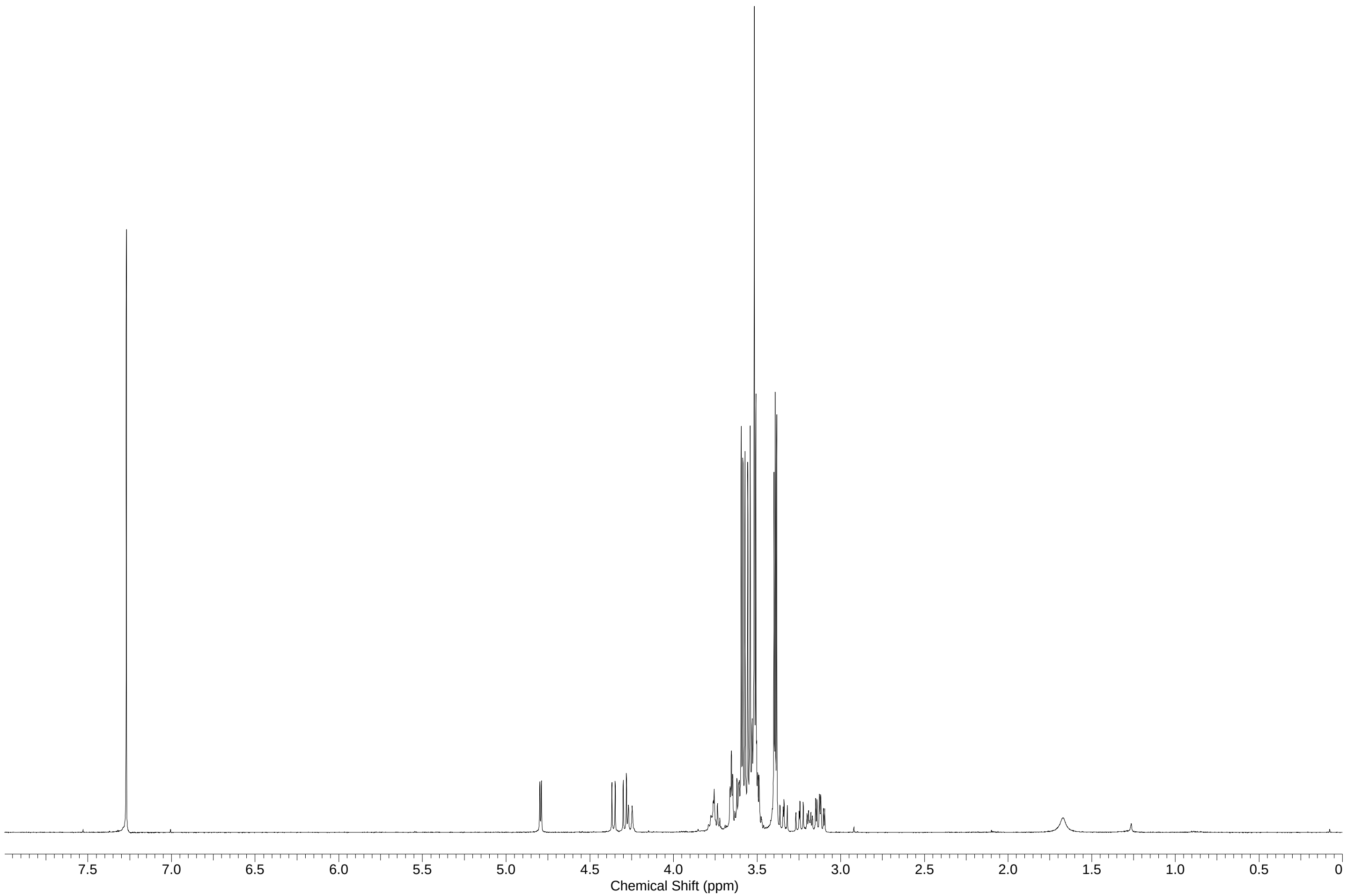


Methyl 2,3-di-*O*-methyl-4,6-di-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (26)



26

^{1}H-NMR (400 MHz, $CDCl_3$)



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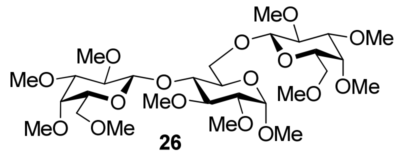
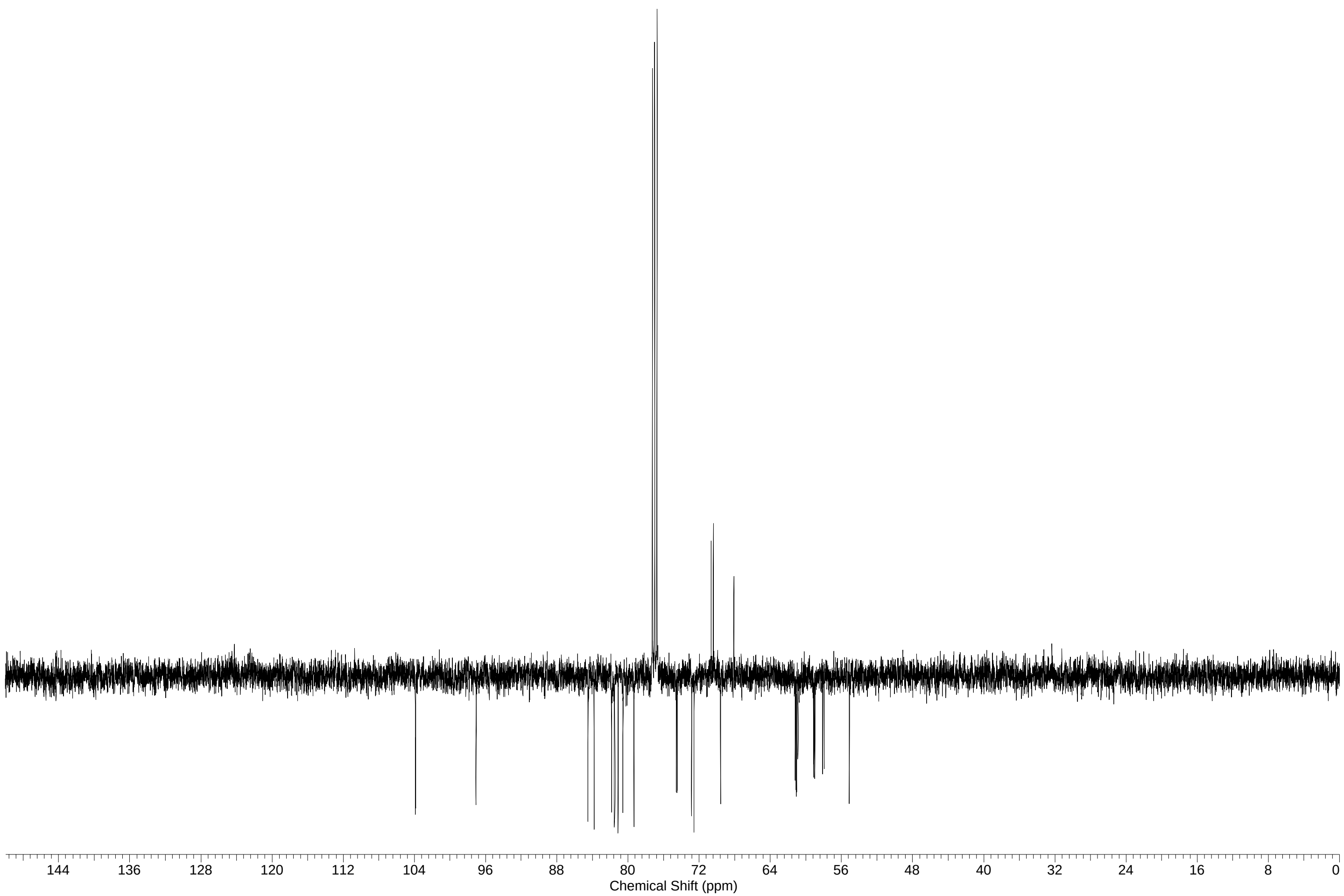
Methyl 2,3-di-*O*-methyl-4,6-di-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (26)

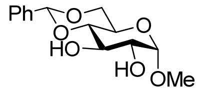


26

^{13}C-NMR (101 MHz, $CDCl_3$)

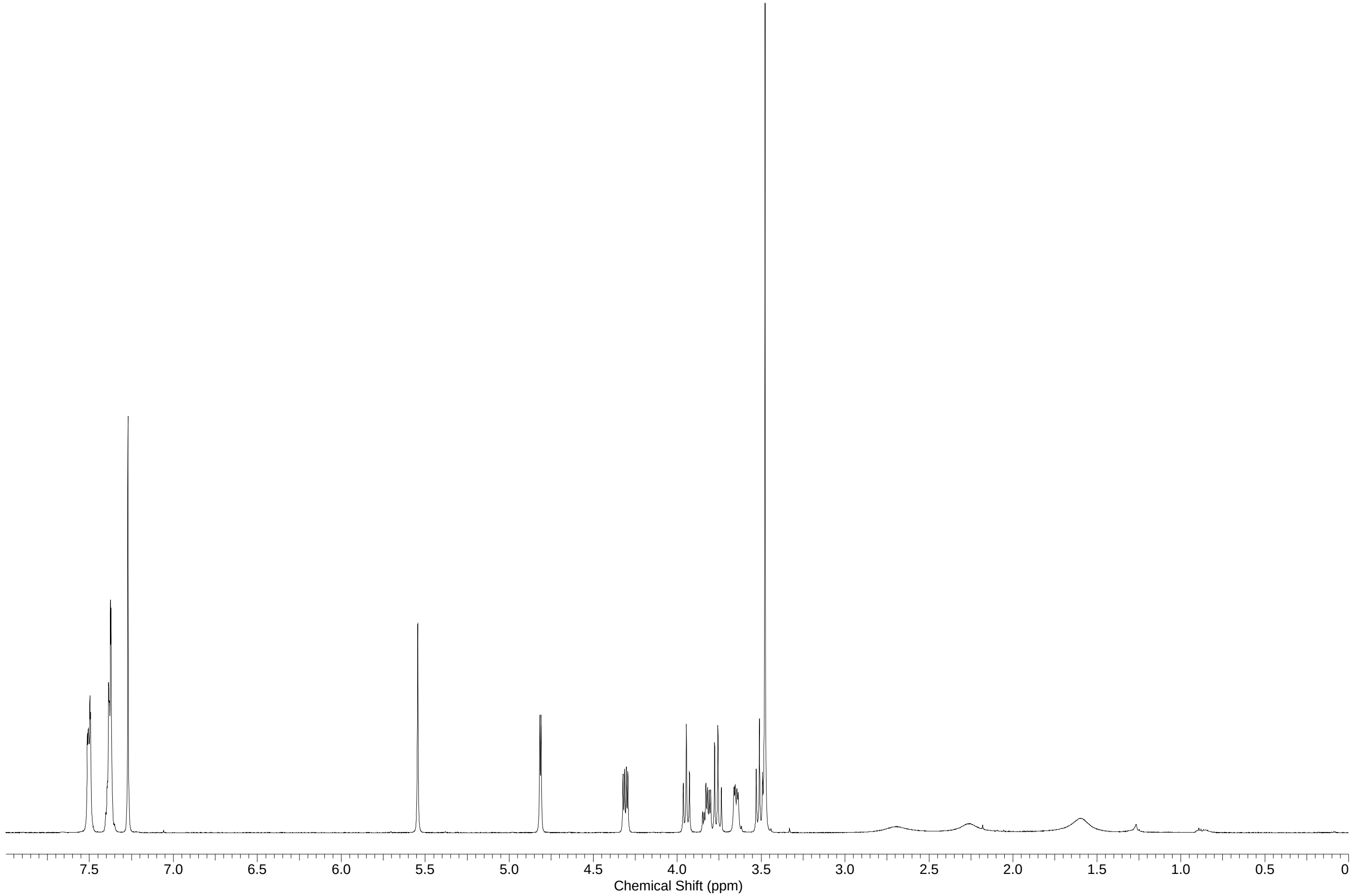


Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (28)

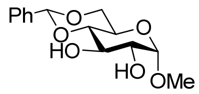


28

^{1}H-NMR (400 MHz, $CDCl_3$)

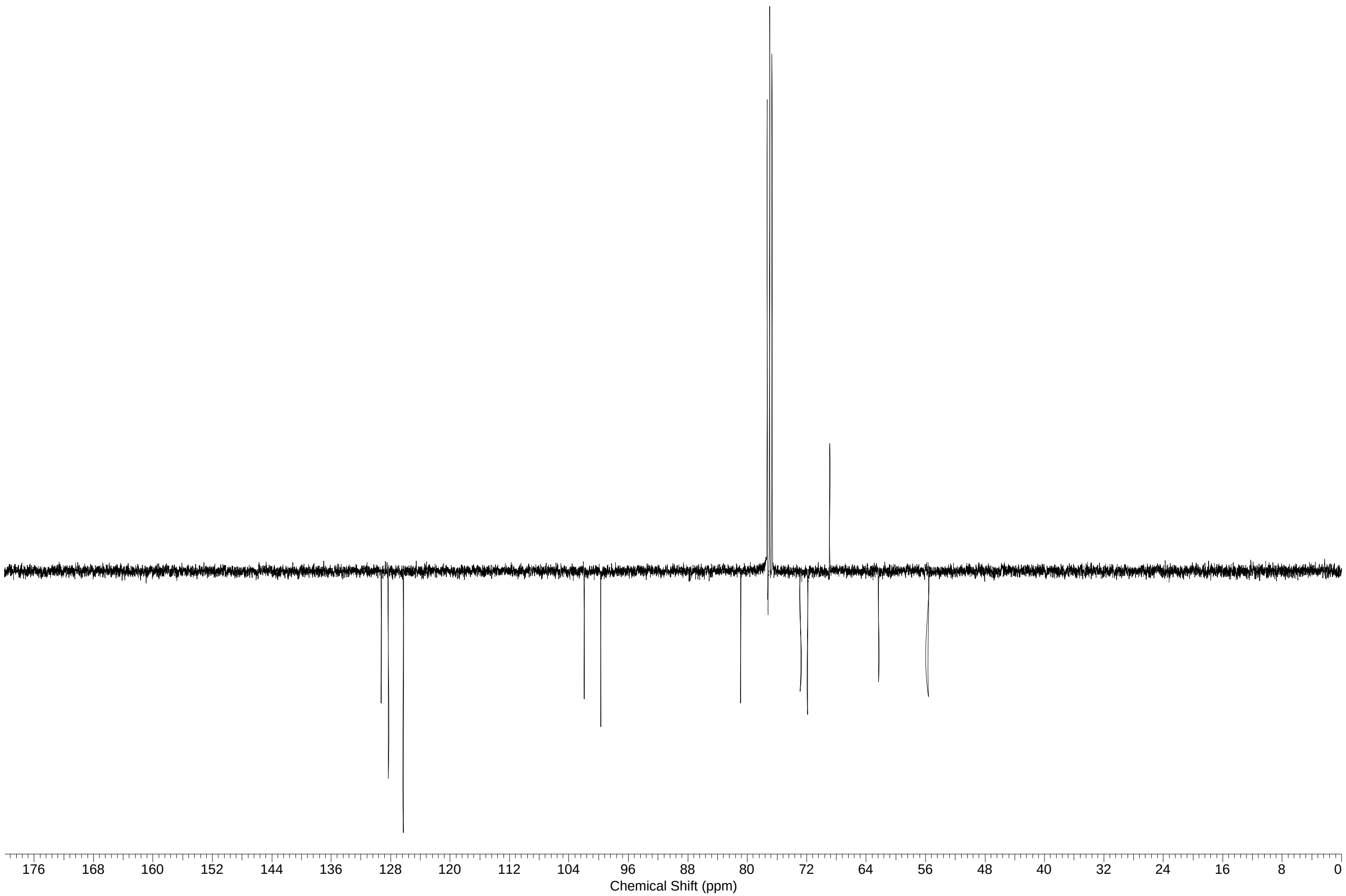


Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (28)

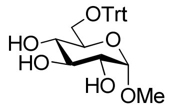


28

^{13}C-NMR (101 MHz, $CDCl_3$)

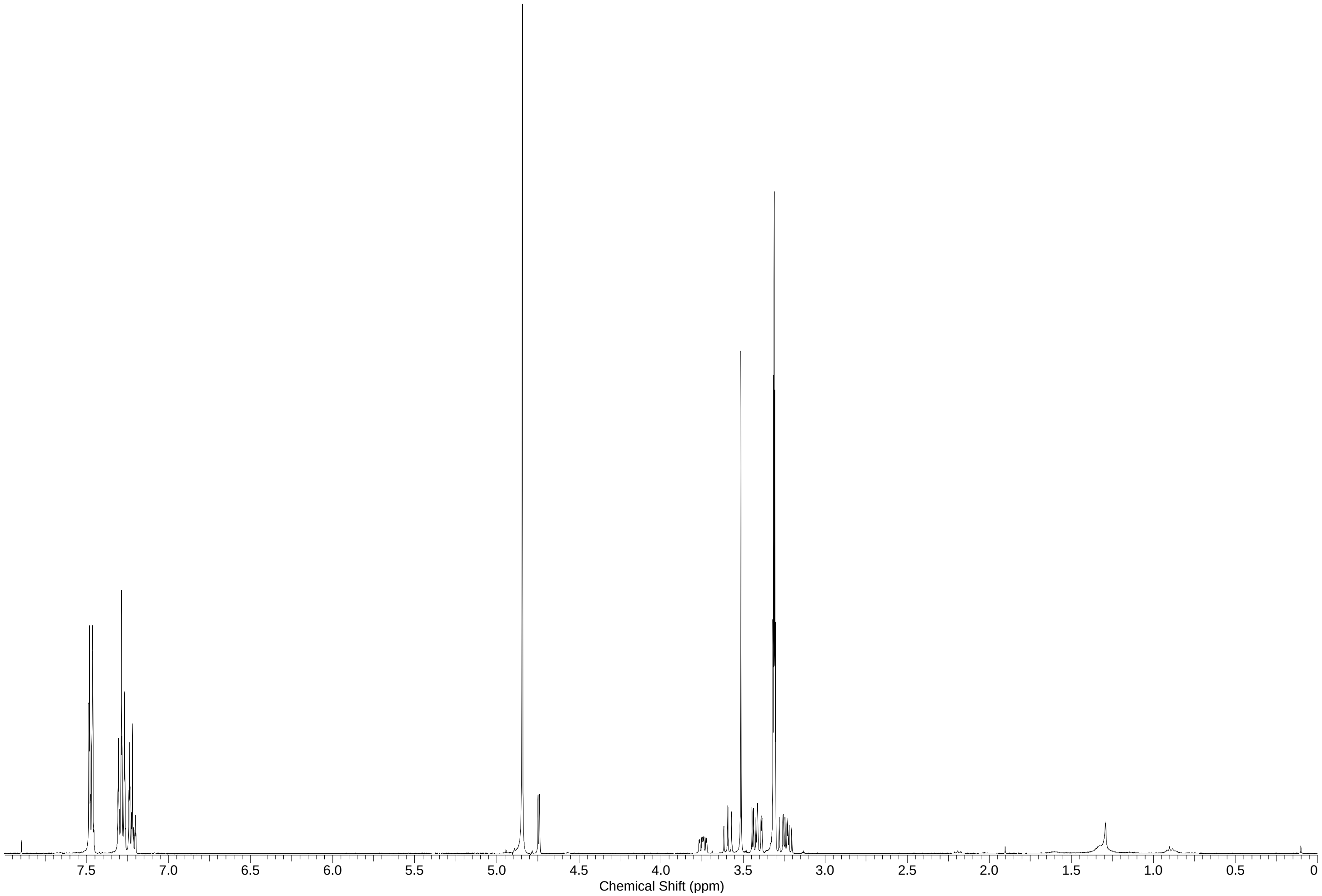


Methyl 6-*O*-triphenylmethyl-α-D-glucopyranoside (29)



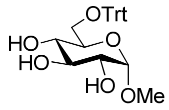
29

^{1}H-NMR (400 MHz, MeOD)



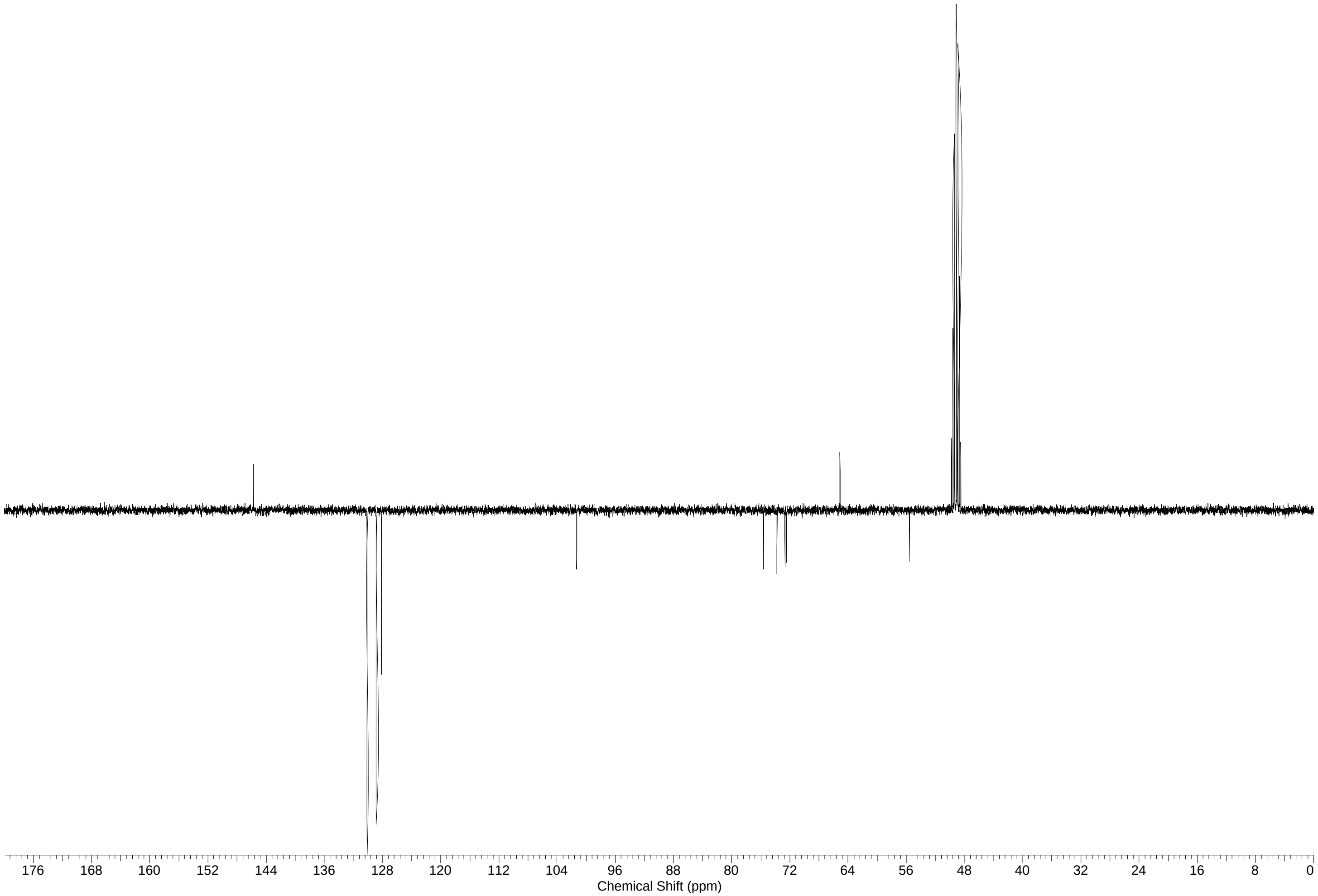
Electronic Supplementary Material (ESI) for Chemical Communications

Methyl 6-*O*-triphenylmethyl-α-D-glucopyranoside (29)

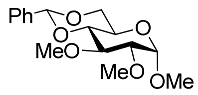


29

^{13}C-NMR (400 MHz, MeOD)

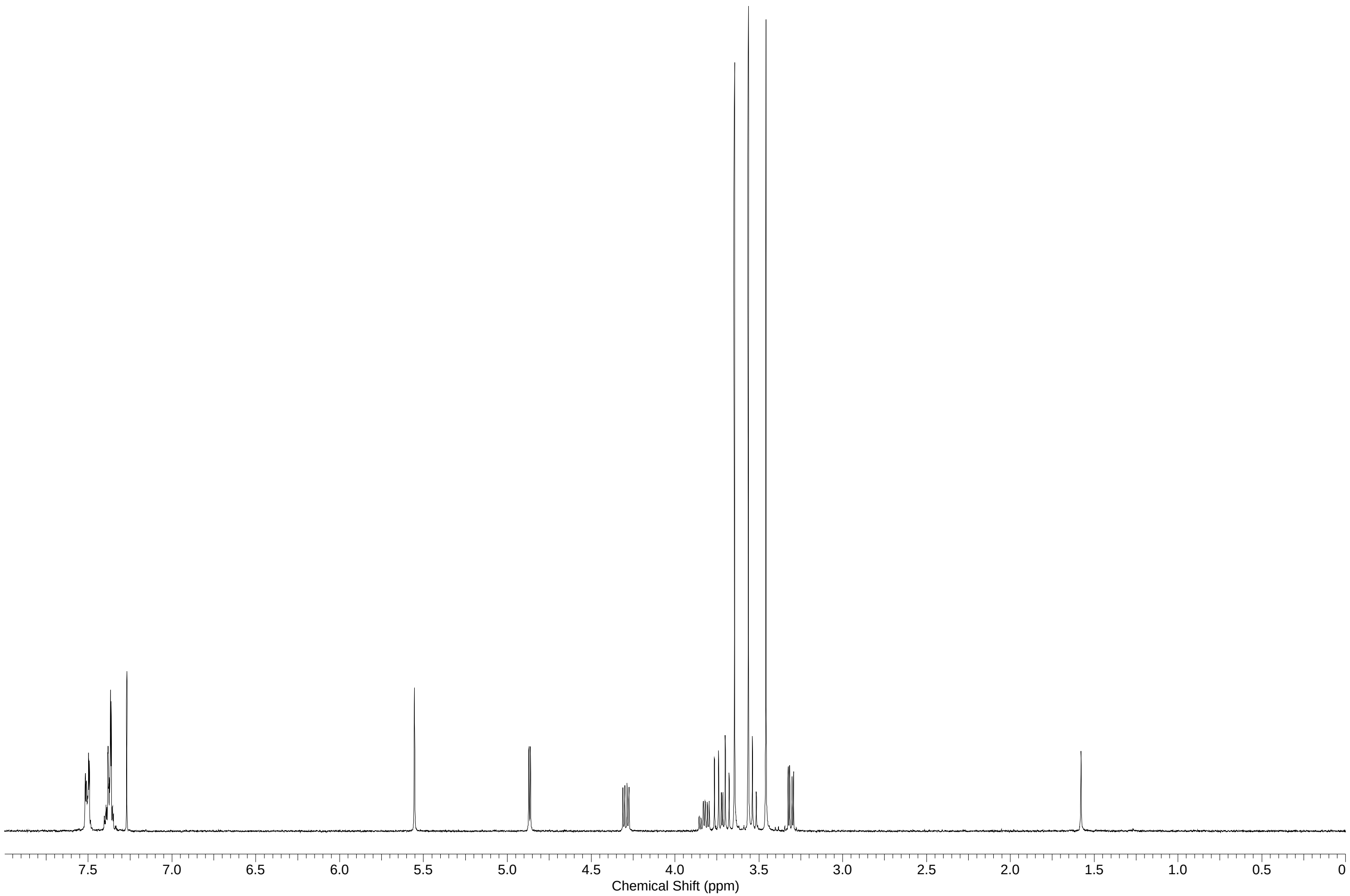


Methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-α-D-glucopyranoside (30)

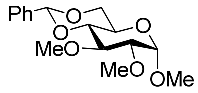


30

^{1}H-NMR (400 MHz, $CDCl_3$)

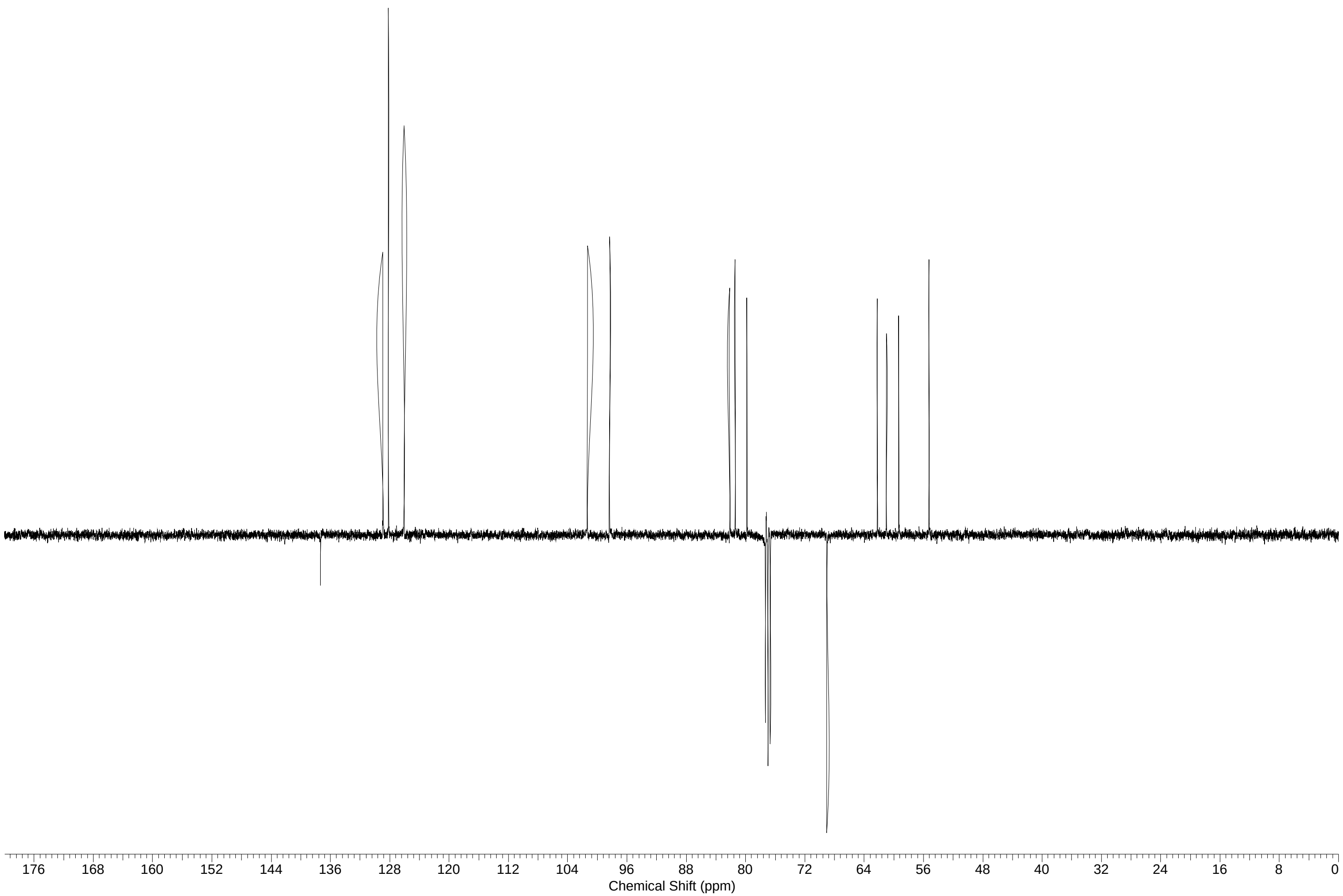


Methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-α-D-glucopyranoside (30)

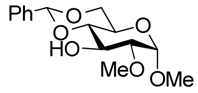


30

^{13}C-NMR (101 MHz, $CDCl_3$)

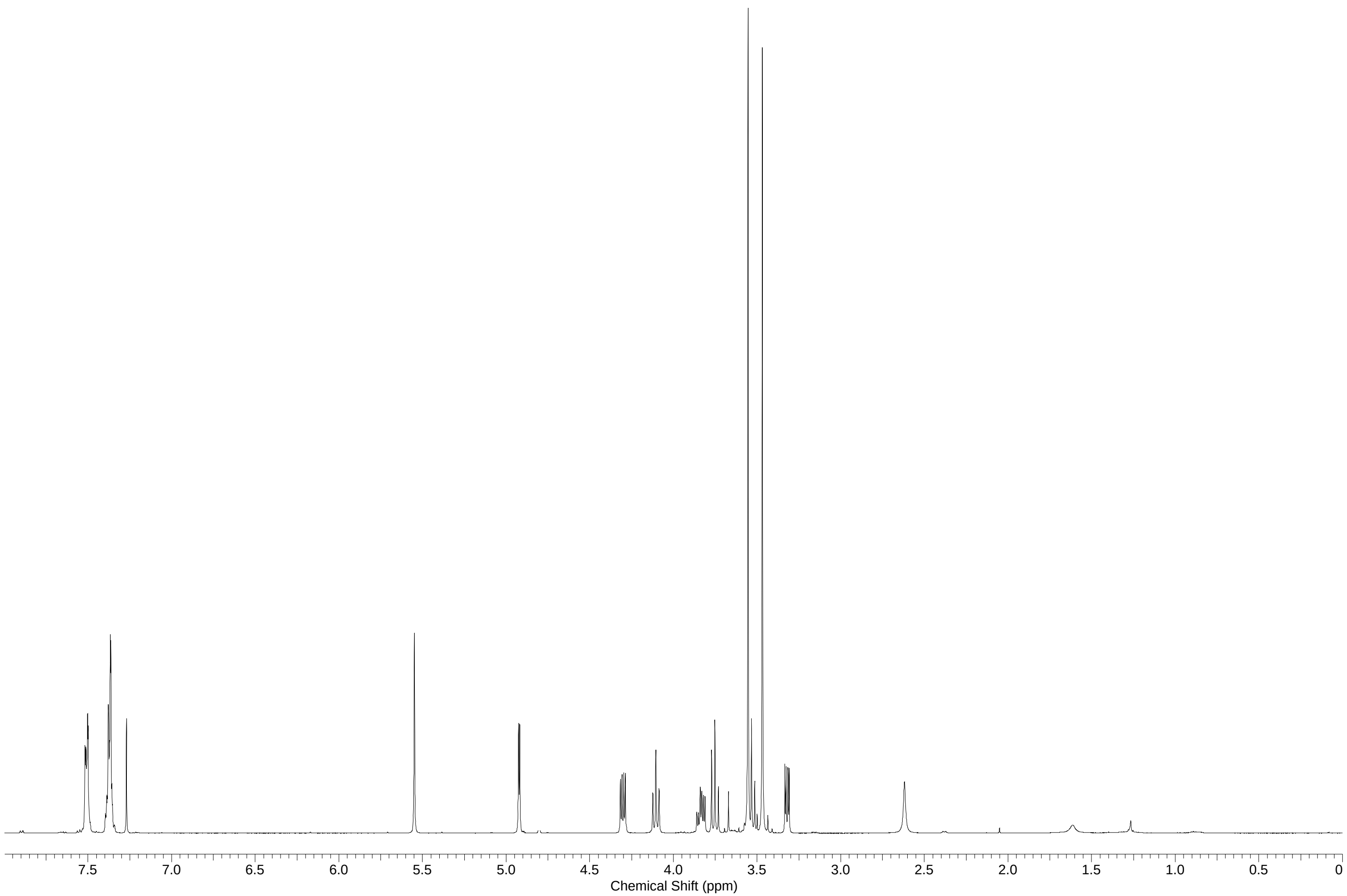


Methyl 4,6-*O*-benzylidene-2-*O*-methyl-α-D-glucopyranoside (31)

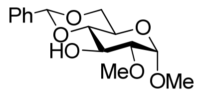


31

^{1}H-NMR (400 MHz, $CDCl_3$)

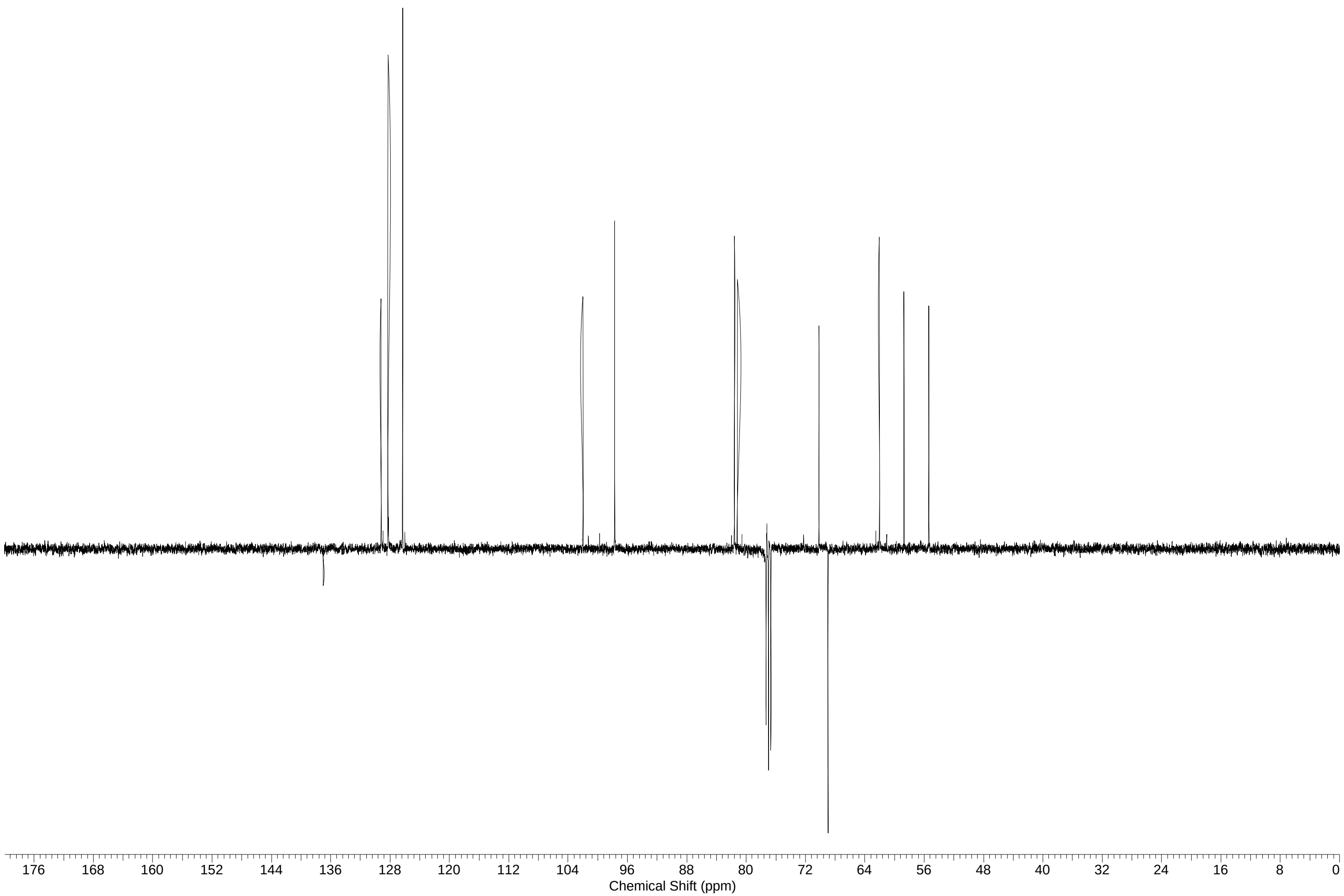


Methyl 4,6-*O*-benzylidene-2-*O*-methyl-α-D-glucopyranoside (31)

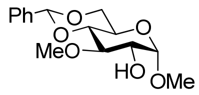


31

^{13}C-NMR (101 MHz, $CDCl_3$)

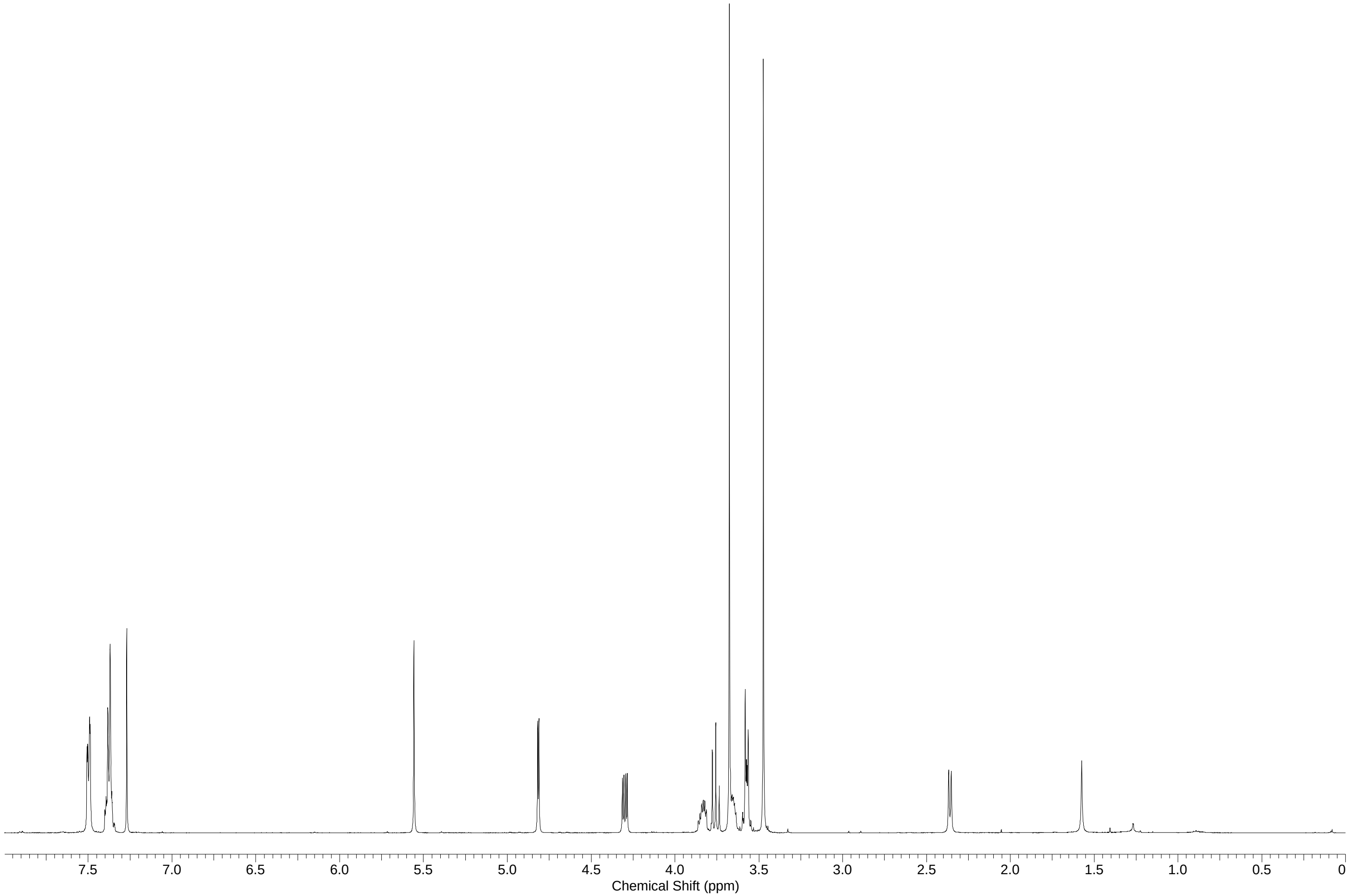


Methyl 4,6-*O*-benzylidene-3-*O*-methyl-α-D-glucopyranoside (32)

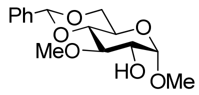


32

^{1}H-NMR (400 MHz, $CDCl_3$)

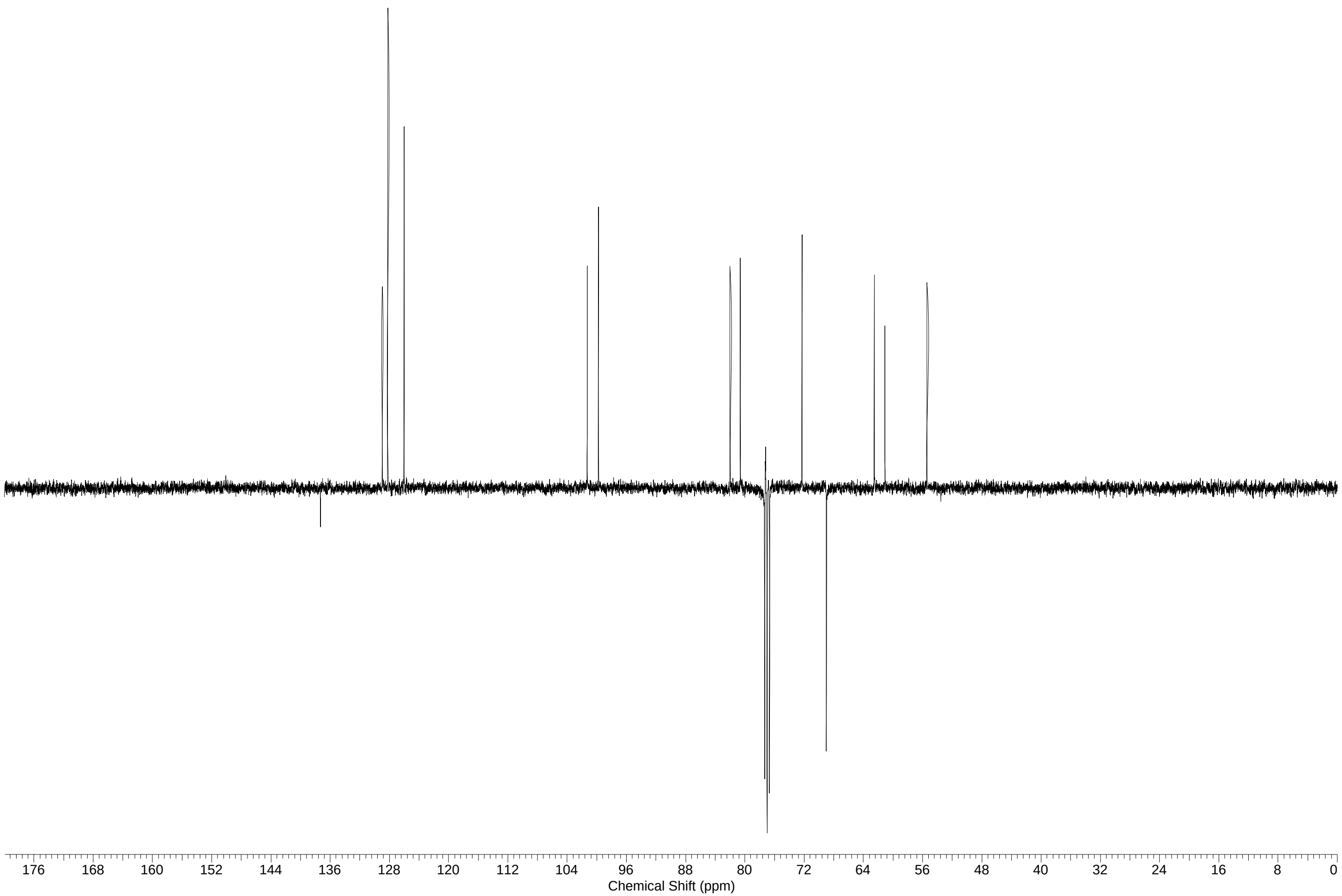


Methyl 4,6-*O*-benzylidene-3-*O*-methyl-α-D-glucopyranoside (32)

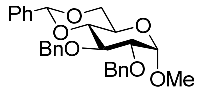


32

^{13}C-NMR (101 MHz, $CDCl_3$)

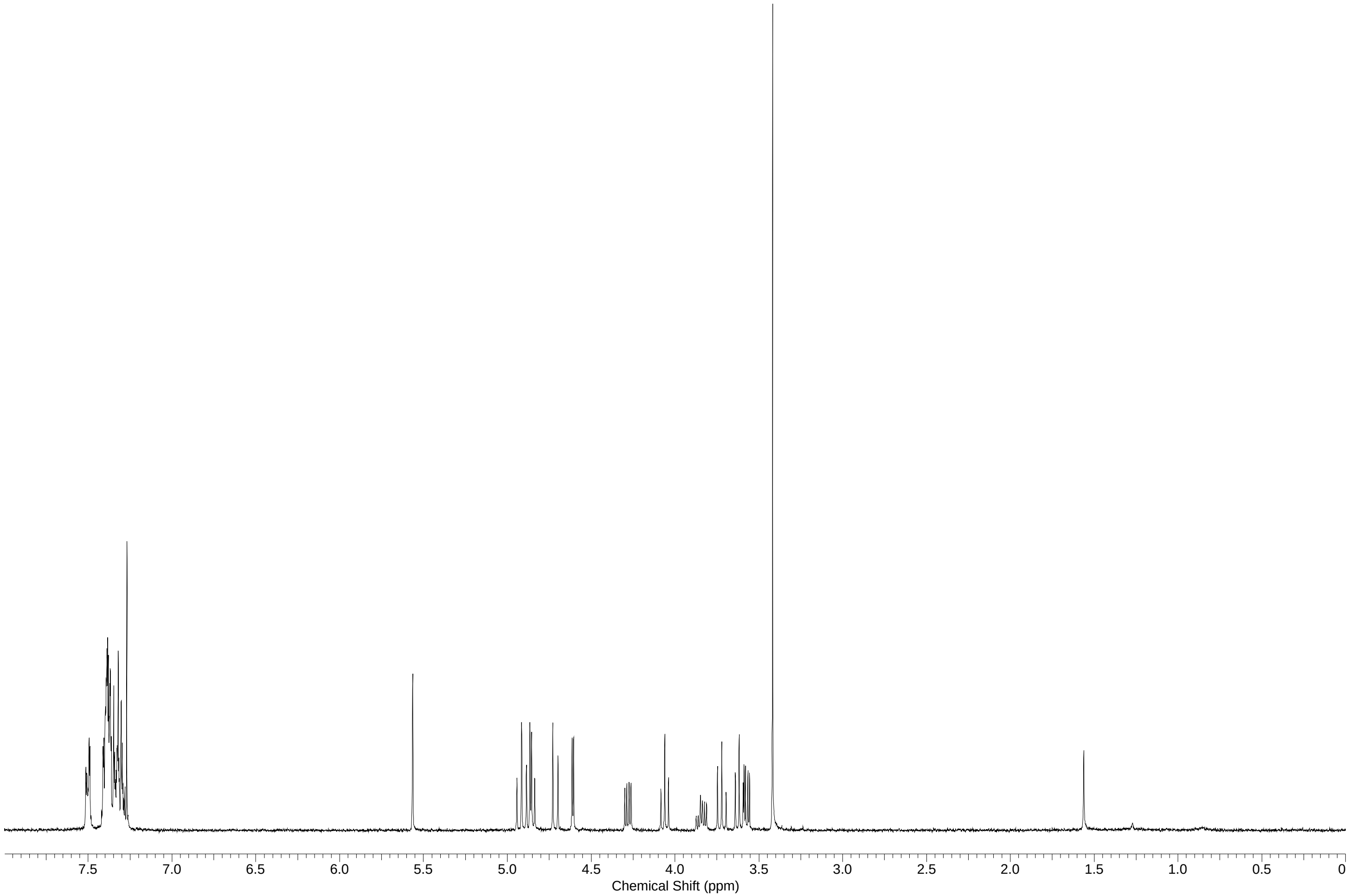


Methyl 4,6-*O*-benzylidene-2,3-di-*O*-benzyl-α-D-glucopyranoside (33)

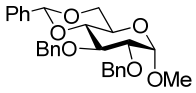


33

^{1}H-NMR (400 MHz, $CDCl_3$)

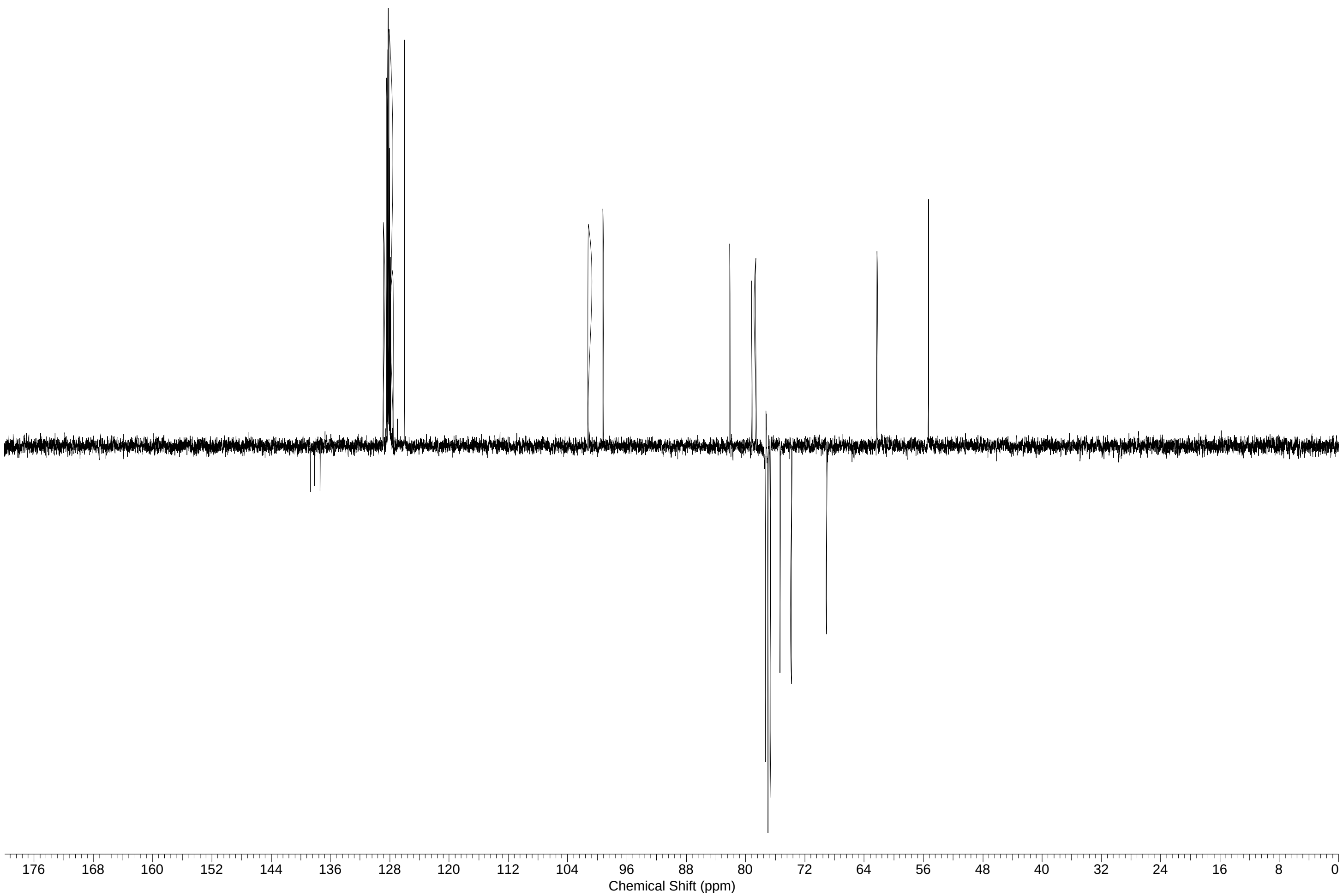


Methyl 4,6-*O*-benzylidene-2,3-di-*O*-benzyl-α-D-glucopyranoside (33)

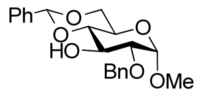


33

^{13}C-NMR (101 MHz, $CDCl_3$)

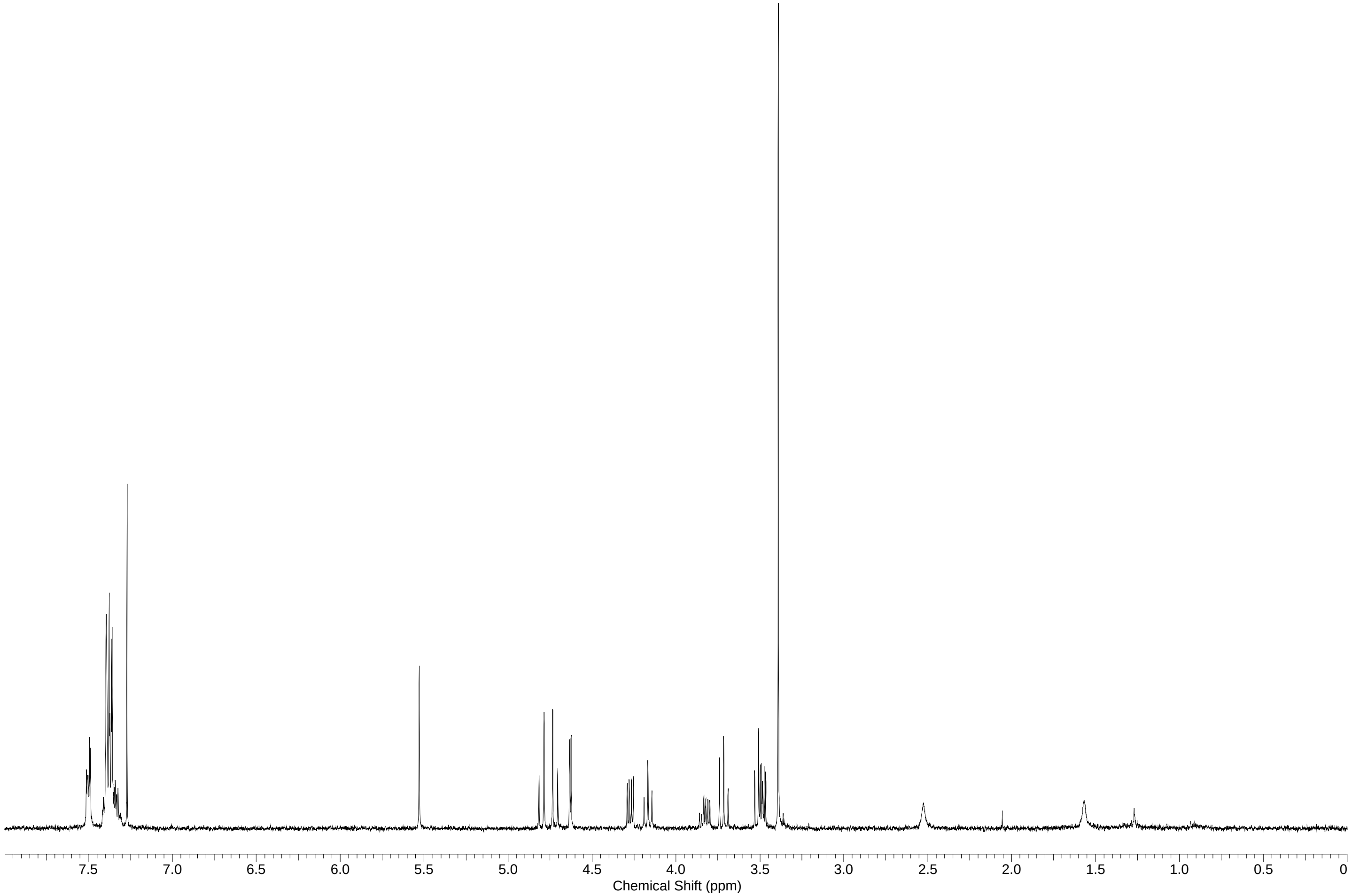


Methyl 4,6-*O*-benzylidene-2-*O*-benzyl-α-D-glucopyranoside (34)

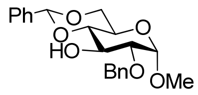


34

^{1}H-NMR (400 MHz, $CDCl_3$)

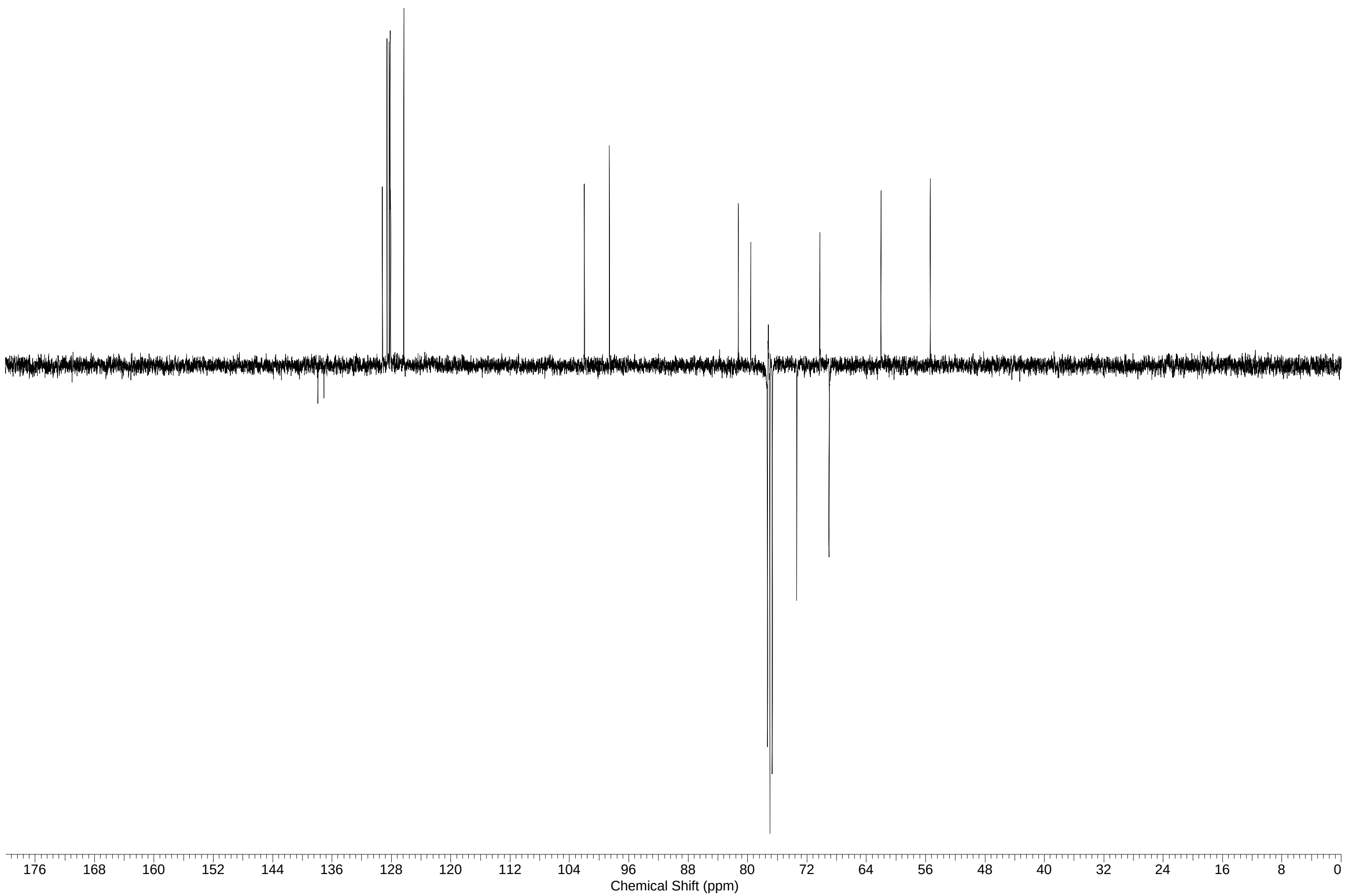


Methyl 4,6-*O*-benzylidene-2-*O*-benzyl-α-D-glucopyranoside (34)

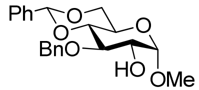


34

^{13}C-NMR (101 MHz, $CDCl_3$)

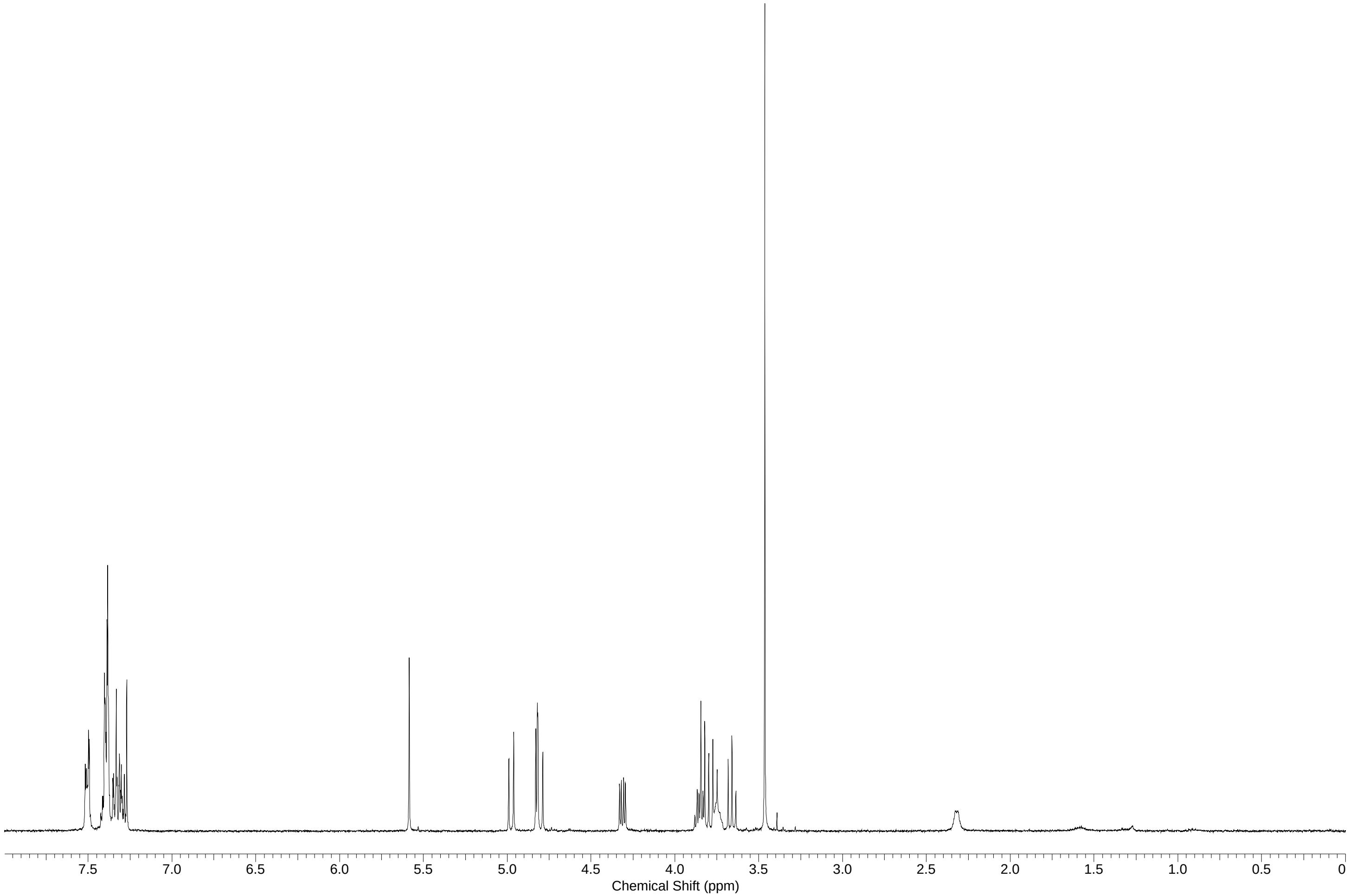


Methyl 4,6-*O*-benzylidene-3-*O*-benzyl-α-D-glucopyranoside (35)



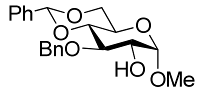
35

^{1}H-NMR (400 MHz, $CDCl_3$)



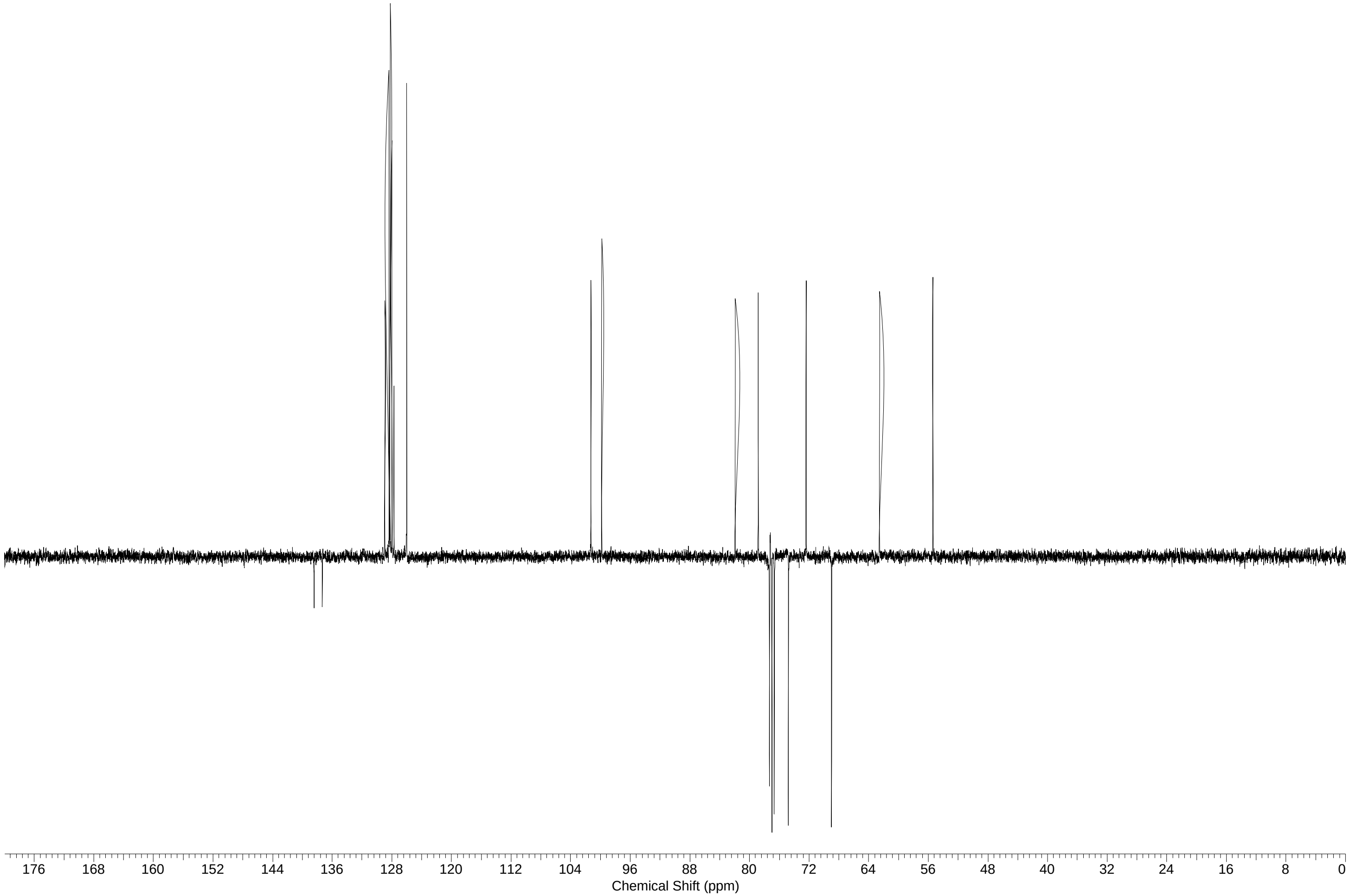
Electronic Supplementary Material (ESI) for Chemical Communications

Methyl 4,6-*O*-benzylidene-3-*O*-benzyl-α-D-glucopyranoside (35)



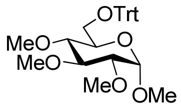
35

^{13}H-NMR (101 MHz, $CDCl_3$)



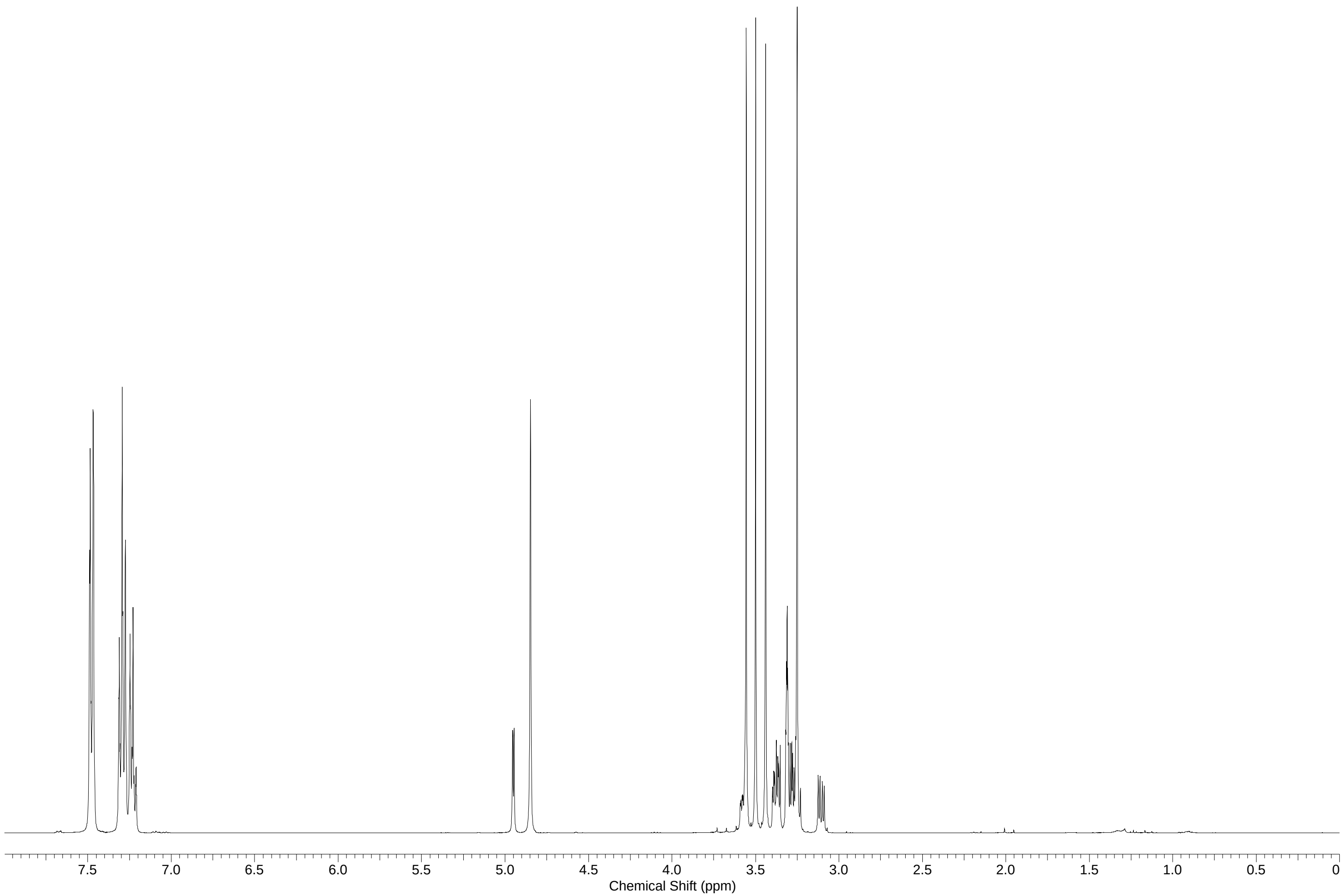
Electronic Supplementary Material (ESI) for Chemical Communications

Methyl 2,3,4-tri-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (36)



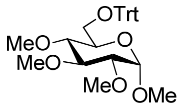
36

^{1}H-NMR (400 MHz, MeOD)



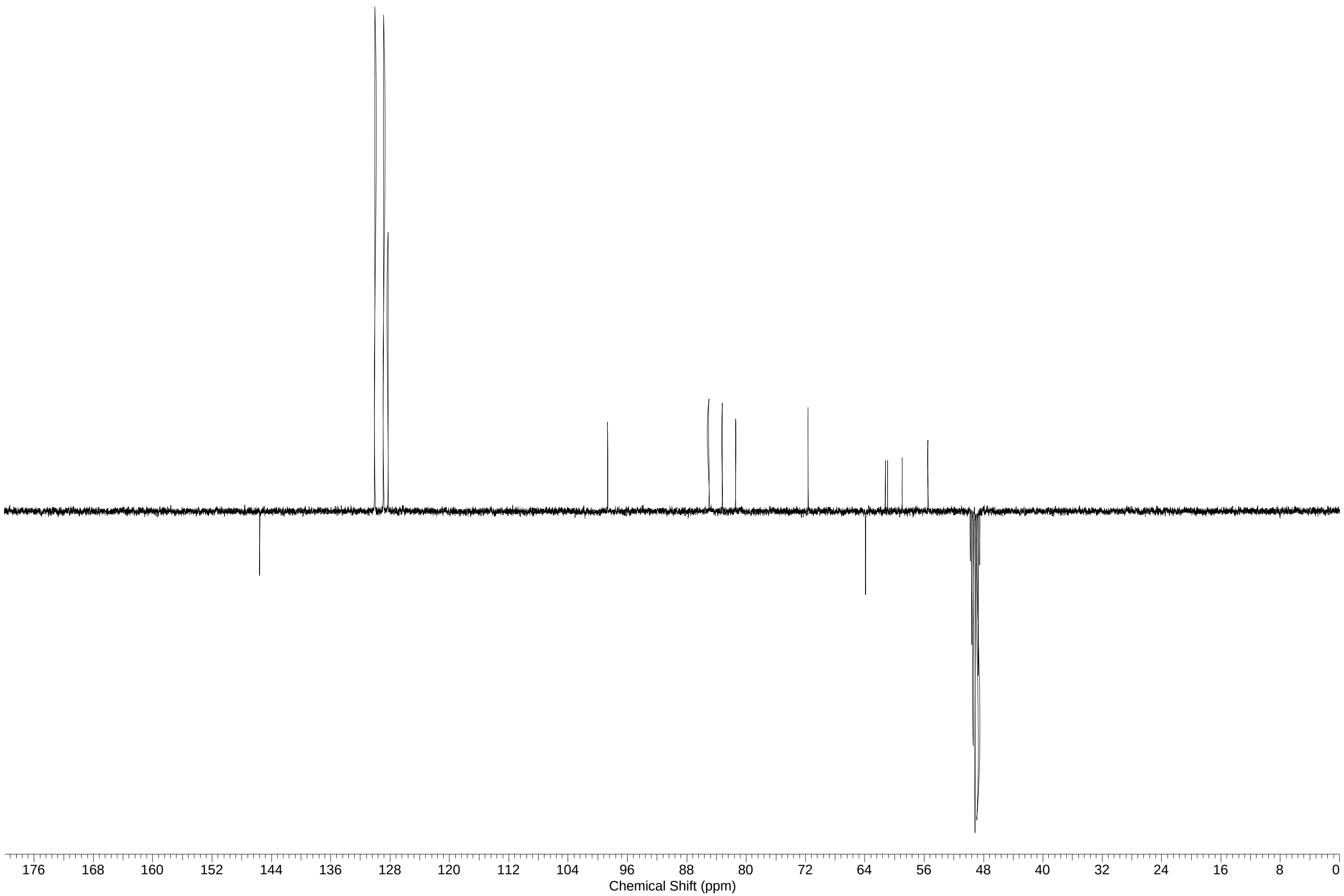
Electronic Supplementary Material (ESI) for Chemical Communications

Methyl 2,3,4-tri-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (36)

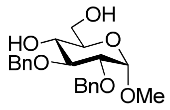


36

^{13}C-NMR (101 MHz, MeOD)

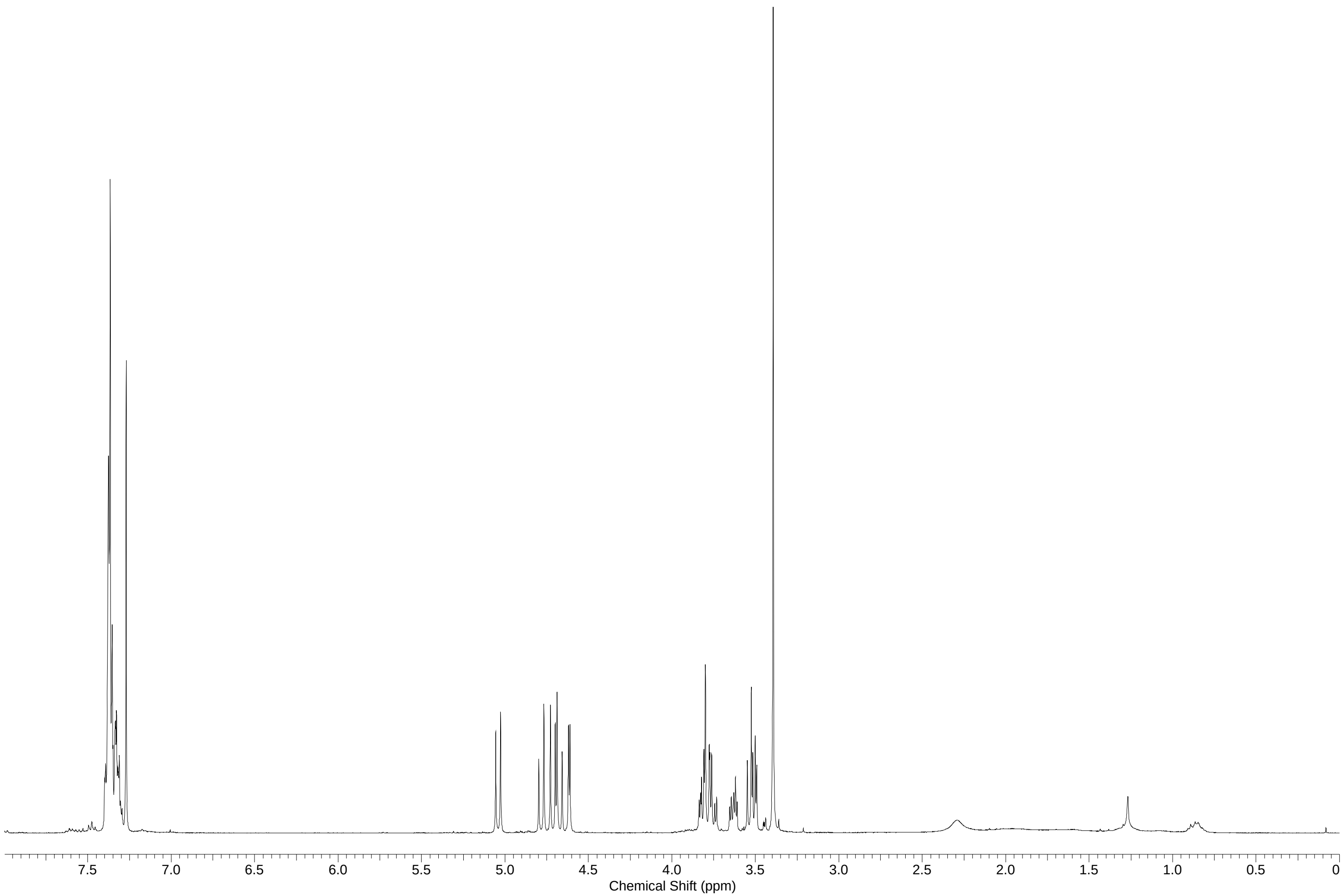


Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside (37)



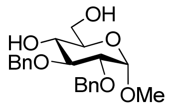
37

^{1}H-NMR (400 MHz, $CDCl_3$)



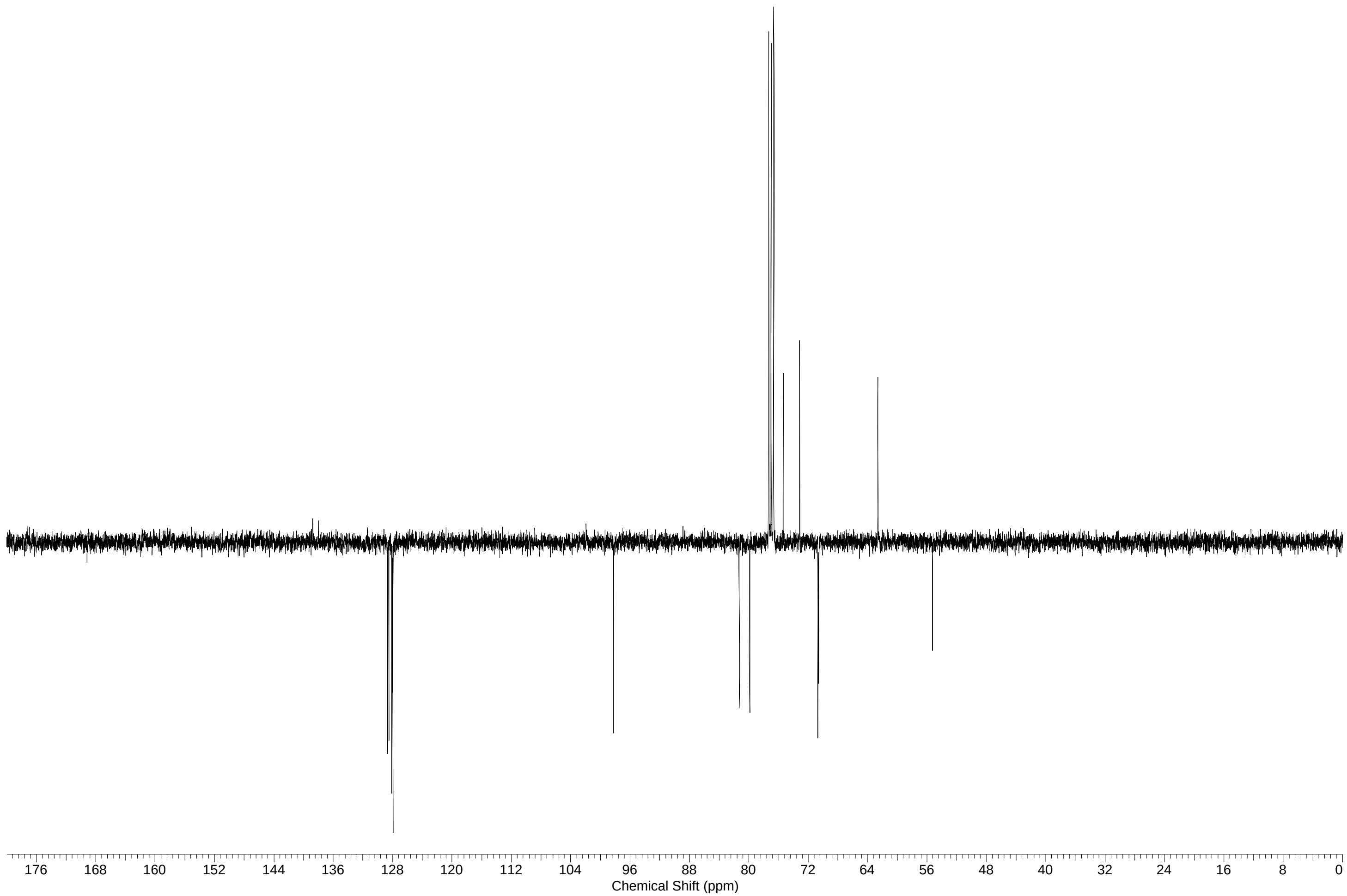
Electronic Supplementary Material (ESI) for Chemical Communications

Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside (37)

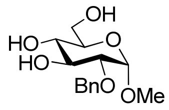


37

^{13}C-NMR (101 MHz, $CDCl_3$)

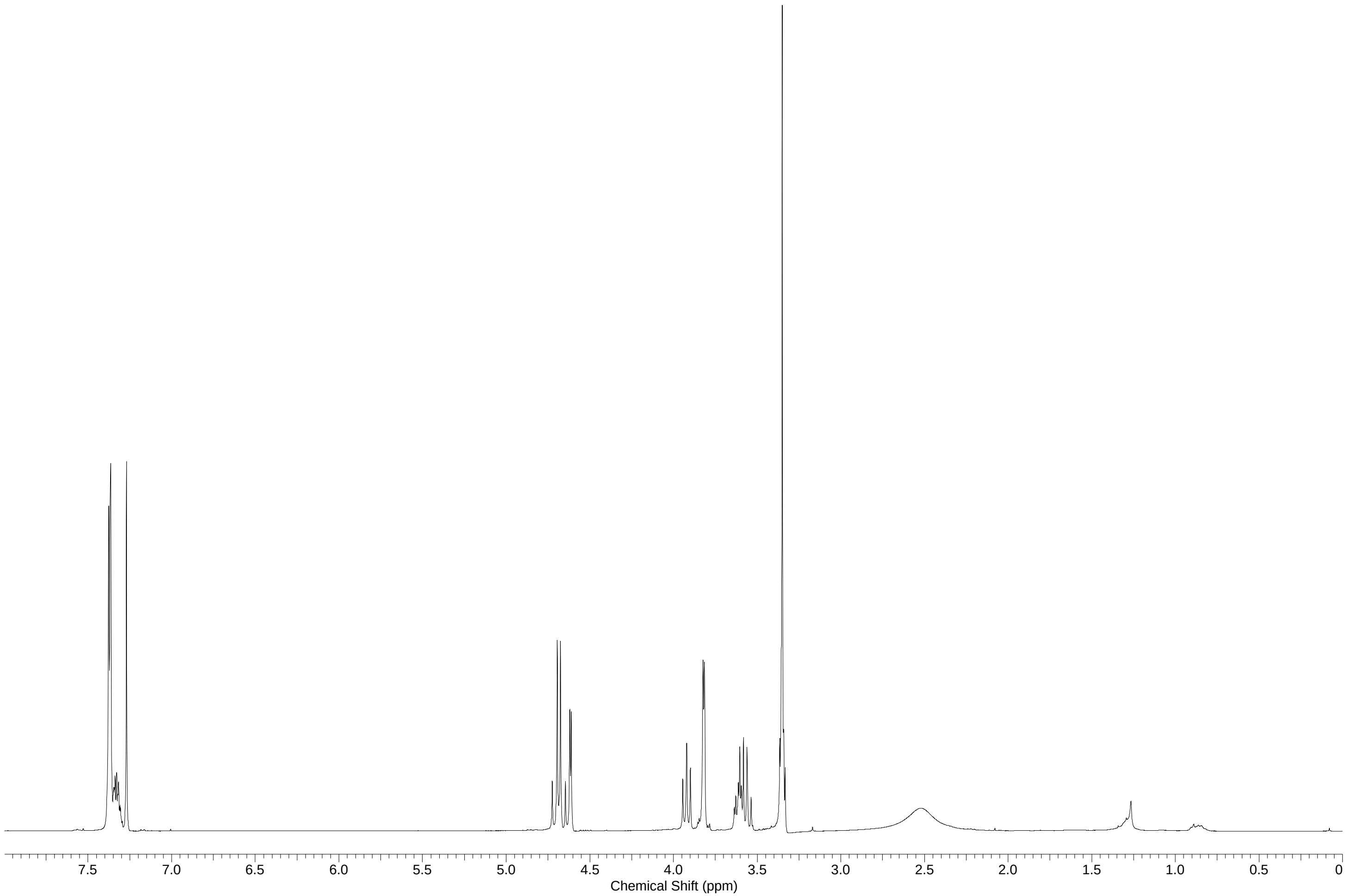


Methyl 2-*O*-benzyl-α-D-glucopyranoside (38)



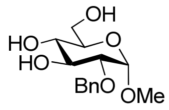
38

^{1}H-NMR (400 MHz, $CDCl_3$)



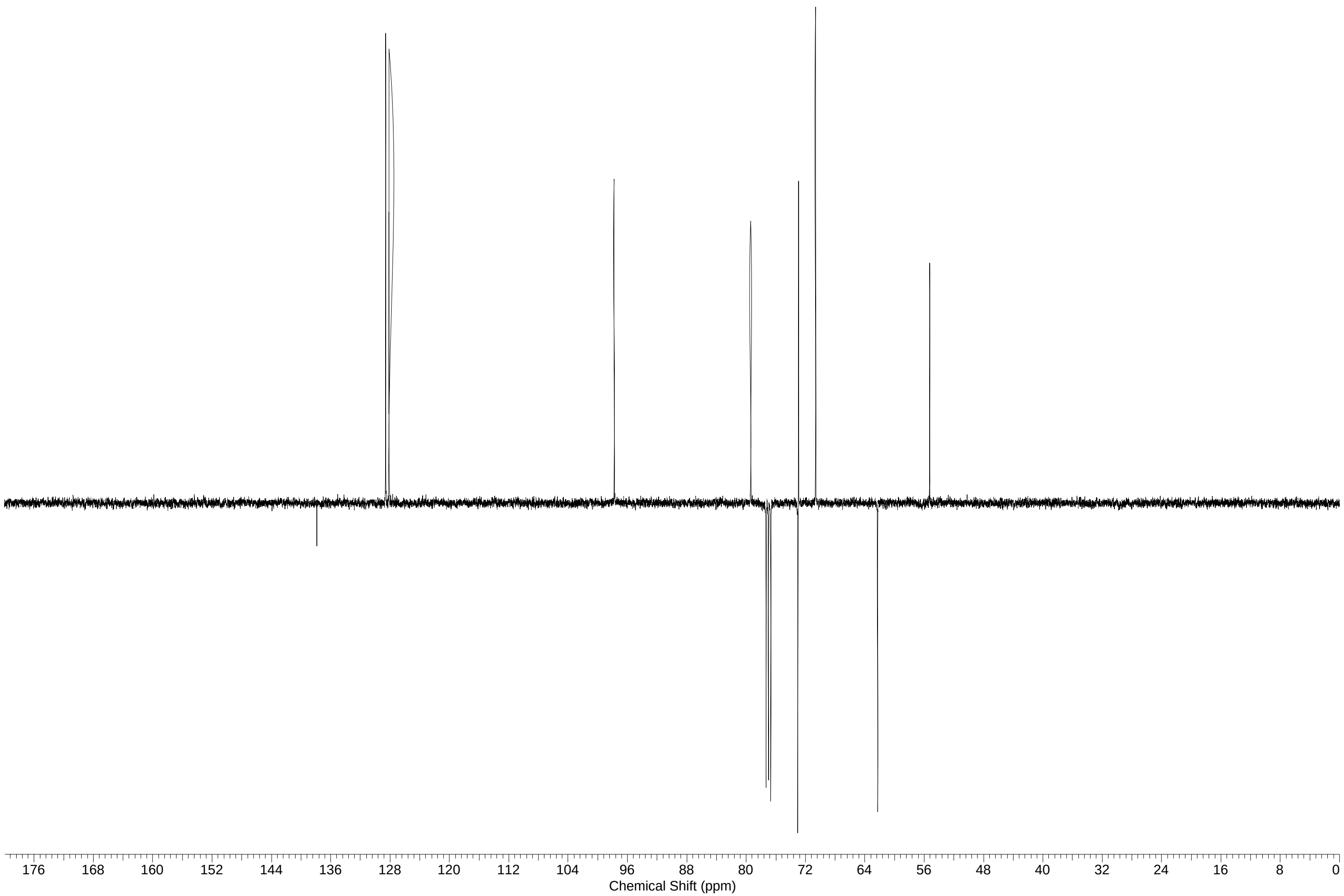
Electronic Supplementary Material (ESI) for Chemical Communications

Methyl 2-*O*-benzyl-α-D-glucopyranoside (38)

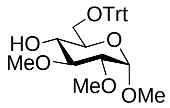


38

^{13}C-NMR (101 MHz, $CDCl_3$)

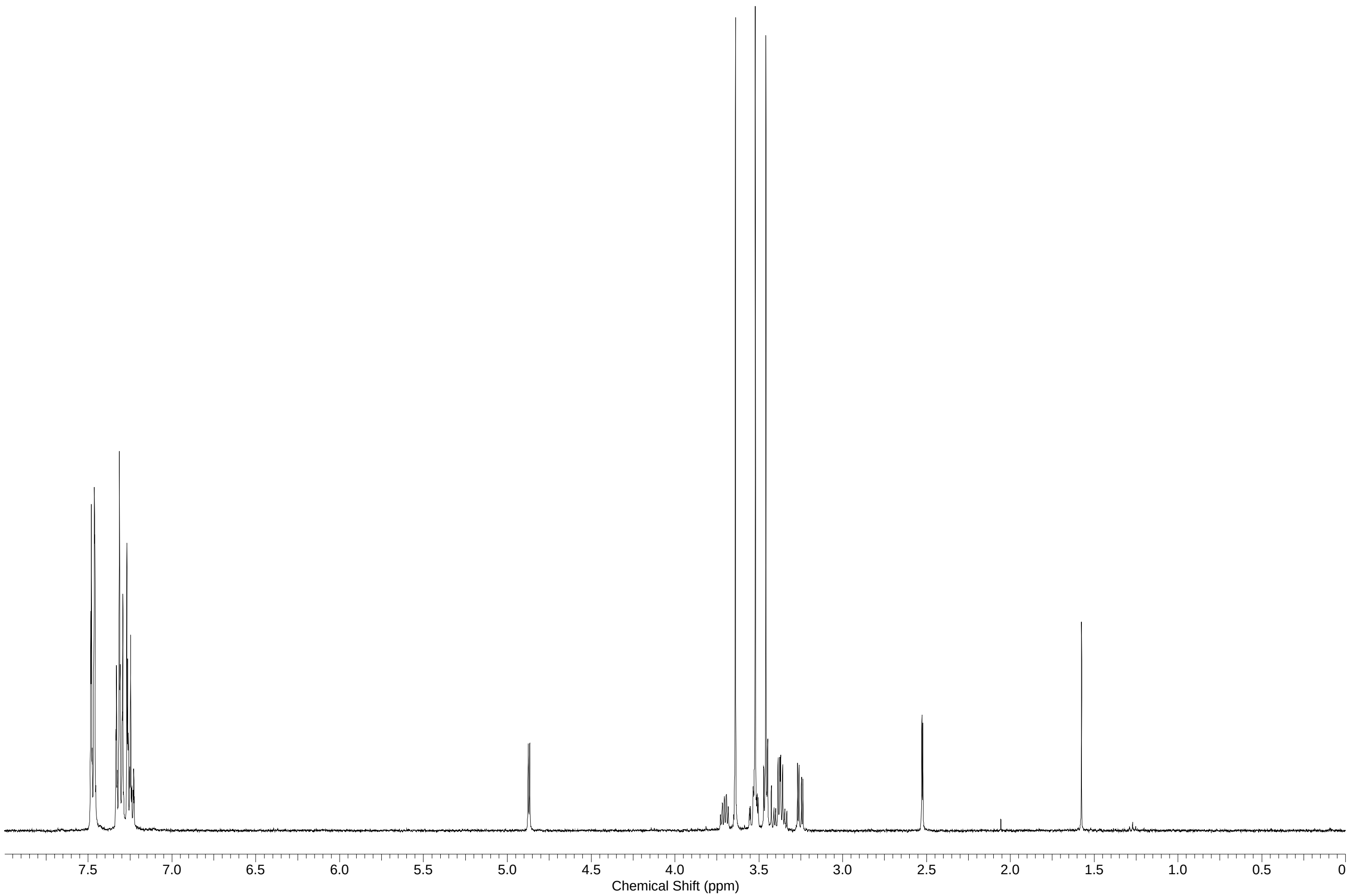


Methyl 2,3-di-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (39)

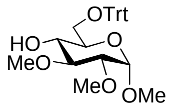


39

^{1}H-NMR (400 MHz, $CDCl_3$)

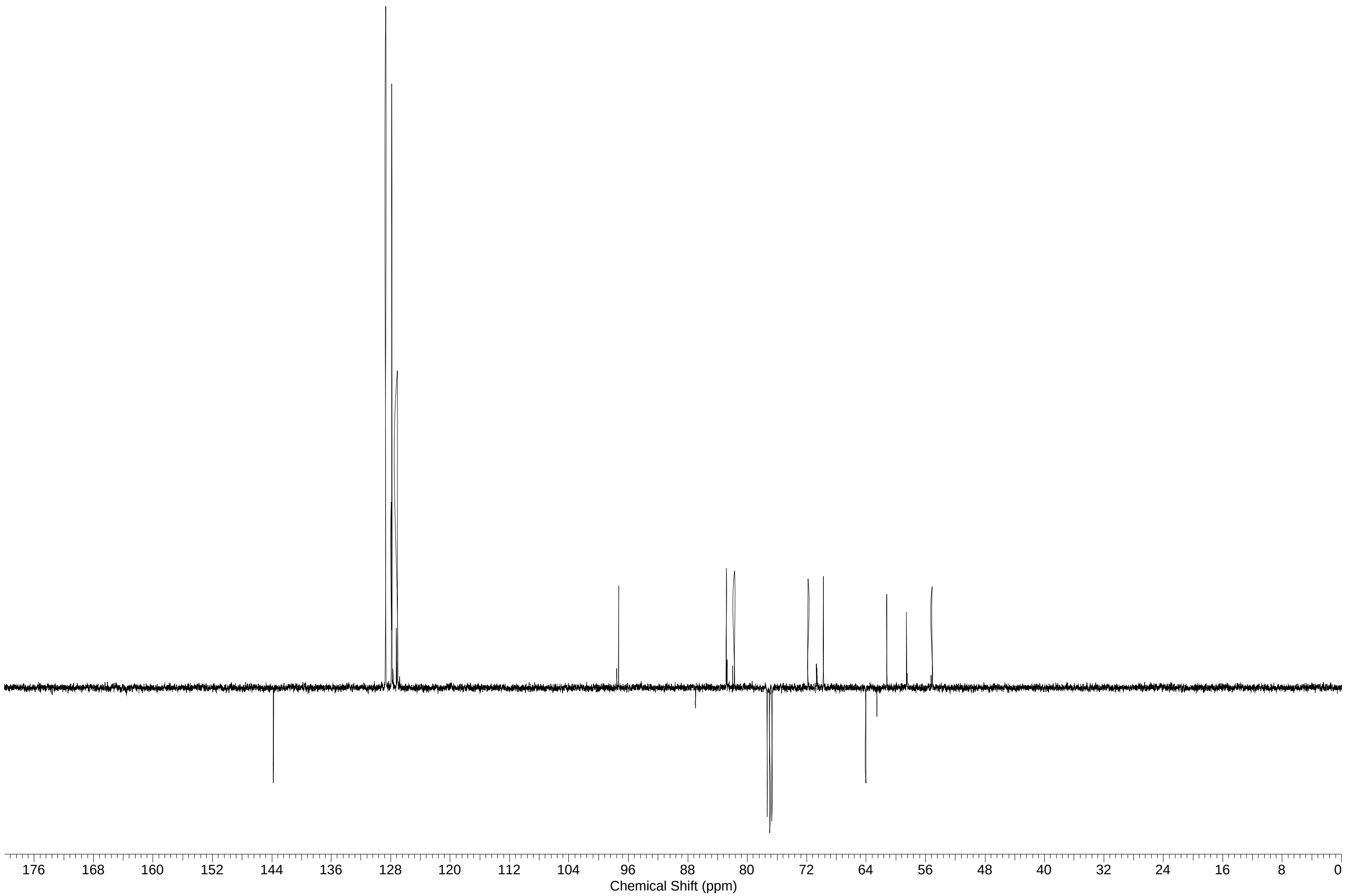


Methyl 2,3-di-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (39)

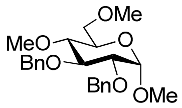


39

^{13}C-NMR (101 MHz, $CDCl_3$)

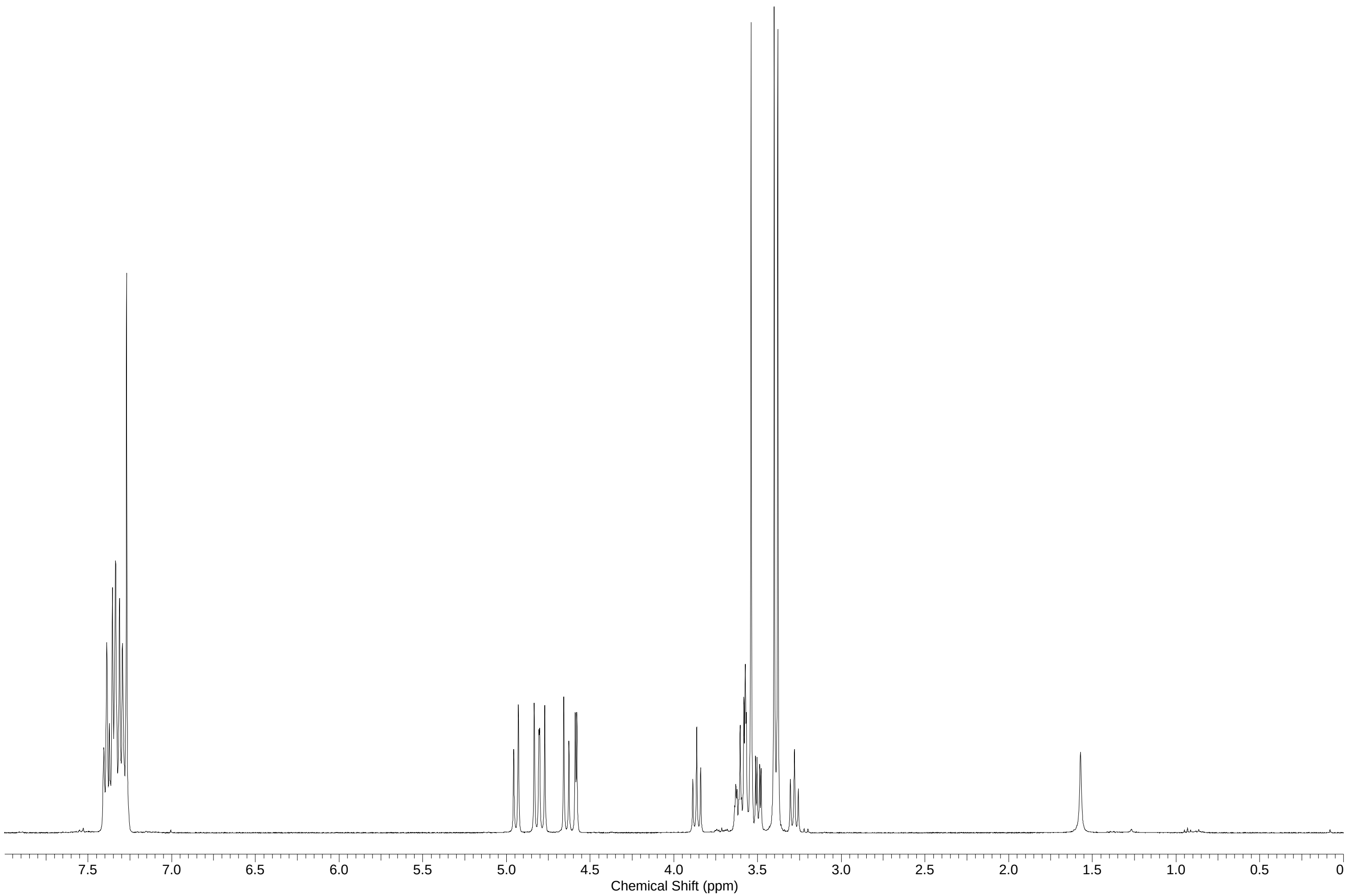


Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-methyl-α-D-glucopyranoside (40)

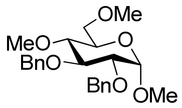


40

^{1}H-NMR (400 MHz, $CDCl_3$)

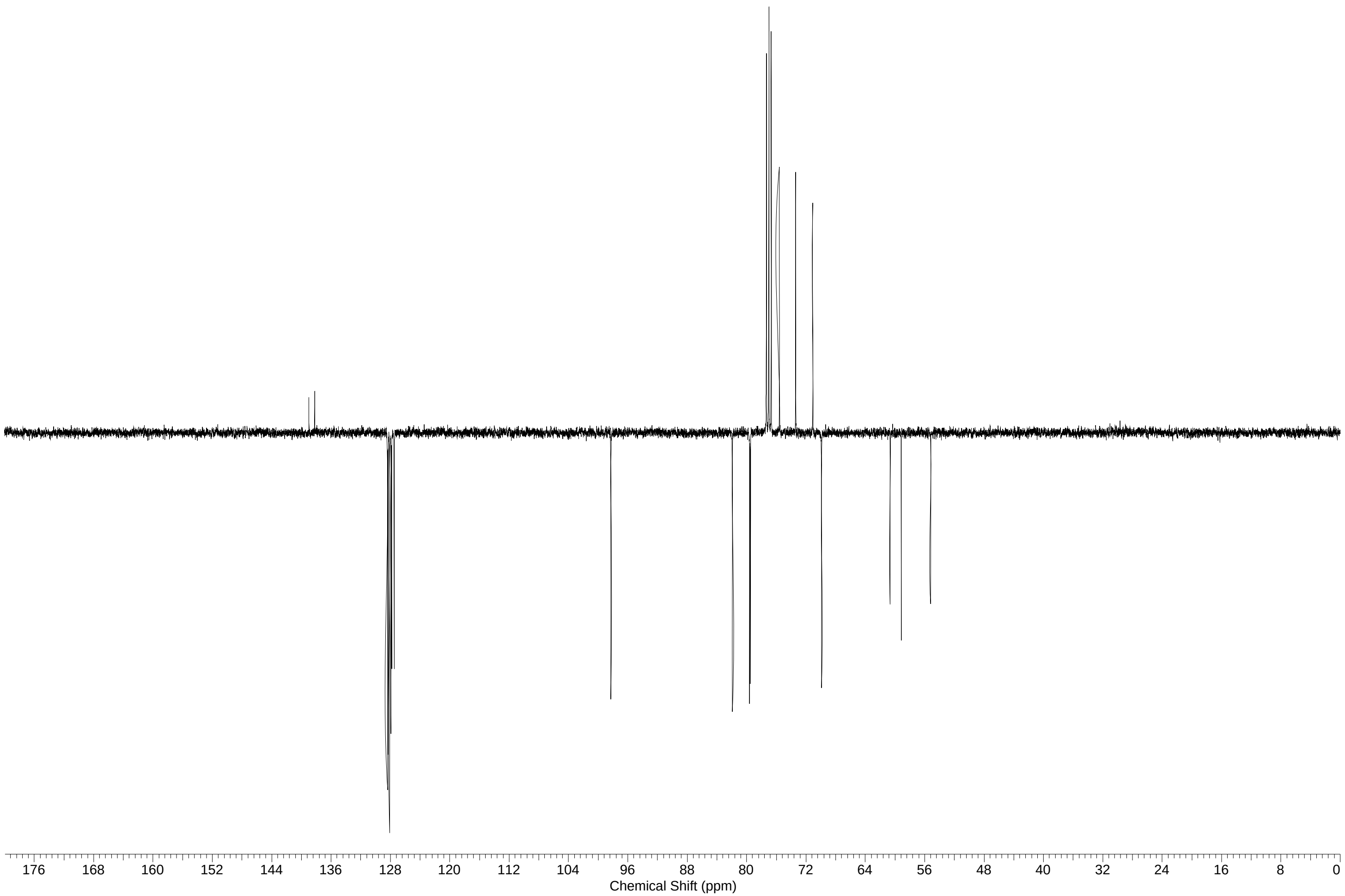


Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-methyl-α-D-glucopyranoside (40)

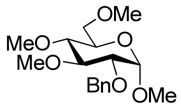


40

^{13}C-NMR (101 MHz, $CDCl_3$)

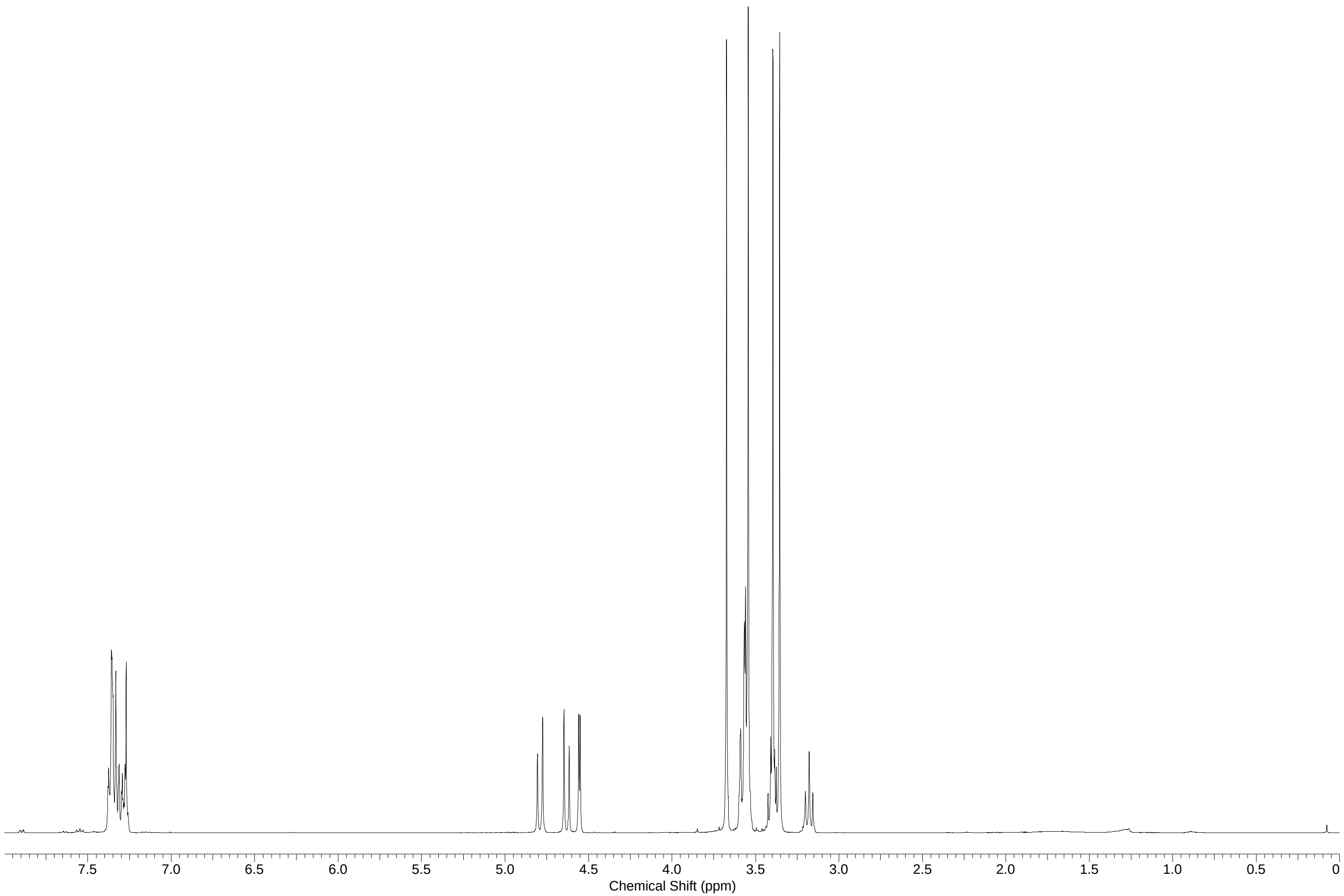


Methyl 2-*O*-benzyl-3,4,6-tri-*O*-methyl-α-D-glucopyranoside (41)

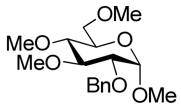


41

^{1}H-NMR (400 MHz, $CDCl_3$)

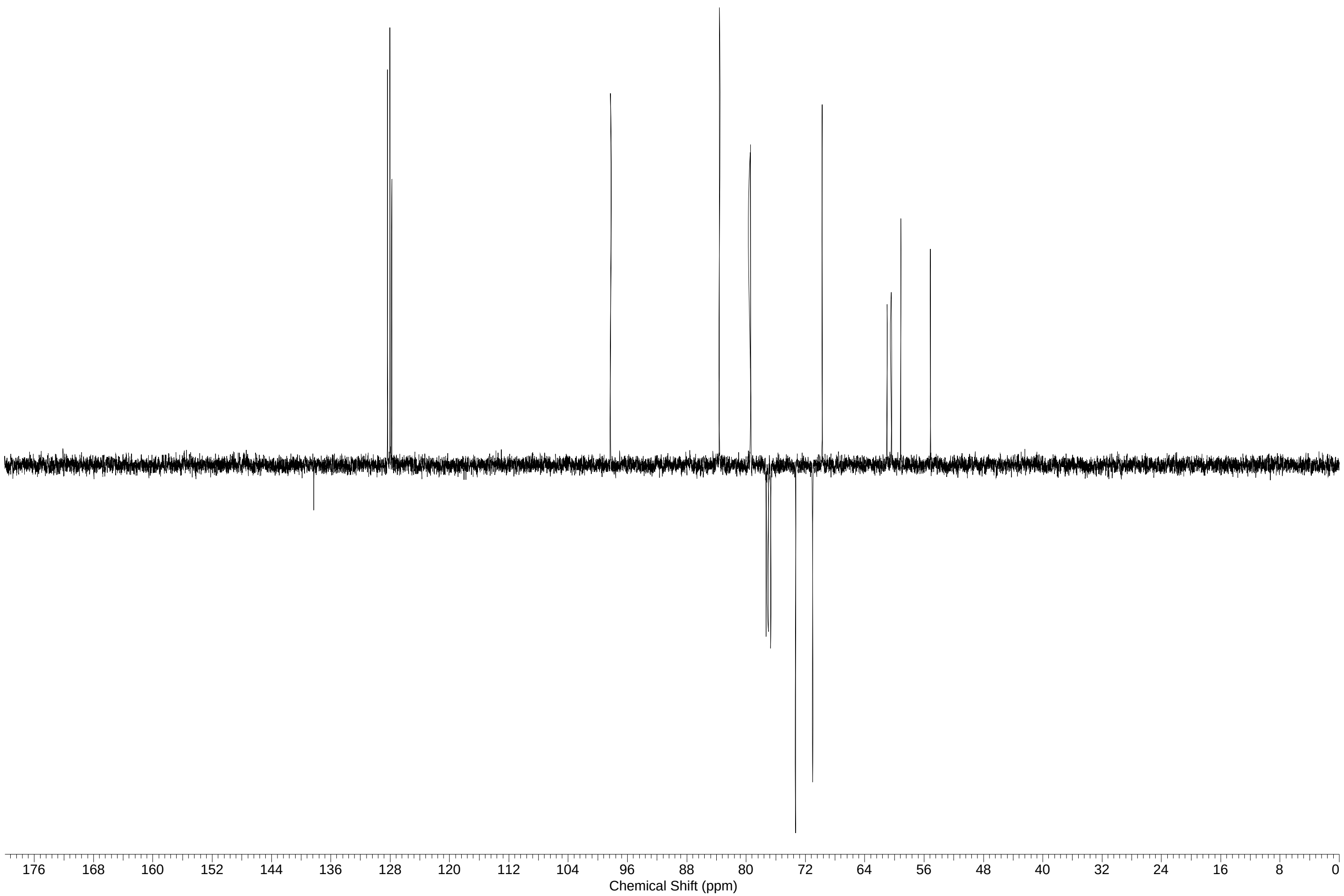


Methyl 2-*O*-benzyl-3,4,6-tri-*O*-methyl-α-D-glucopyranoside (41)



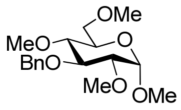
41

^{13}C-NMR (101 MHz, $CDCl_3$)



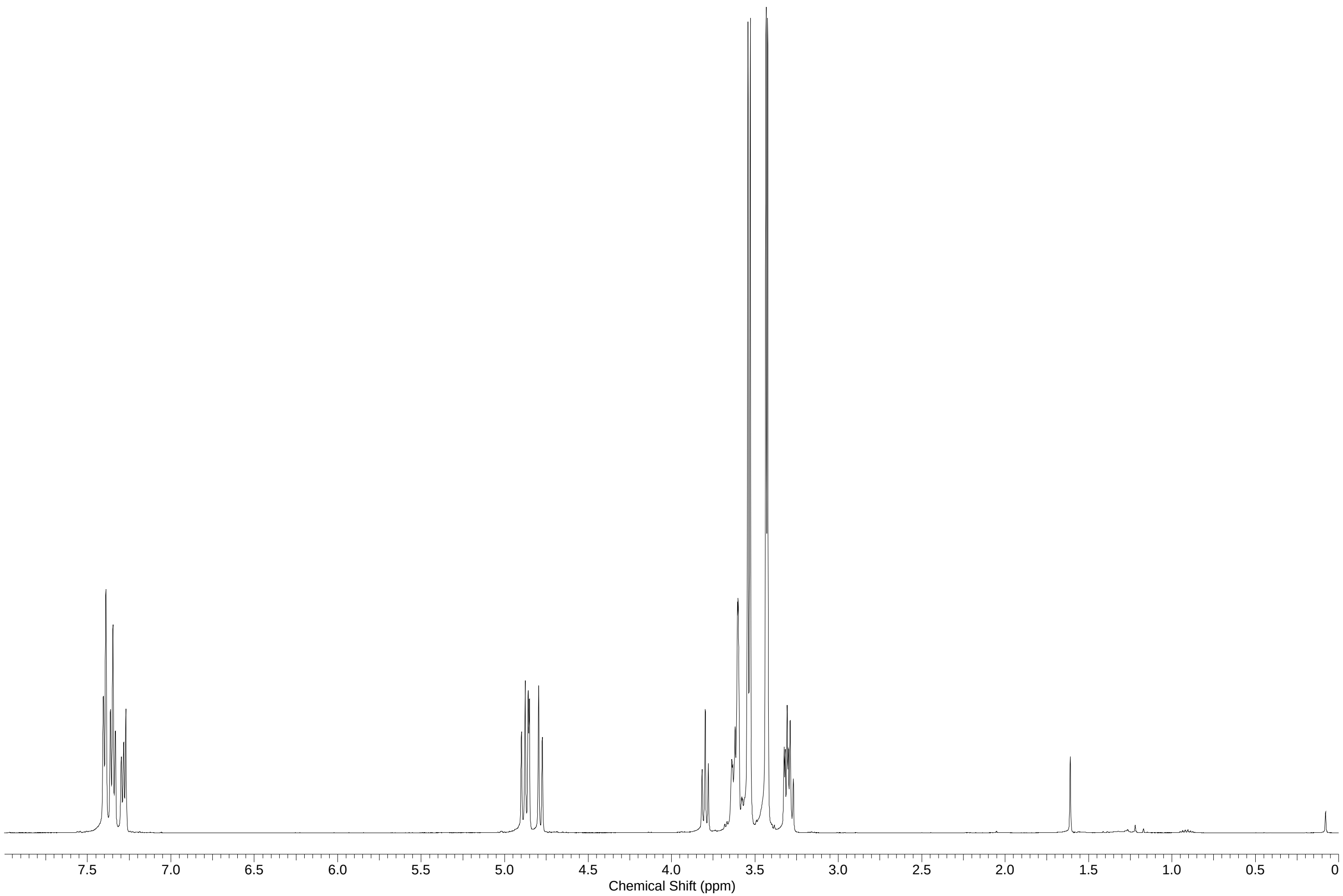
Electronic Supplementary Material (ESI) for Chemical Communications

Methyl 3-*O*-benzyl-2,4,6-tri-*O*-methyl-α-D-glucopyranoside (42)

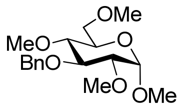


42

^{1}H-NMR (400 MHz, $CDCl_3$)

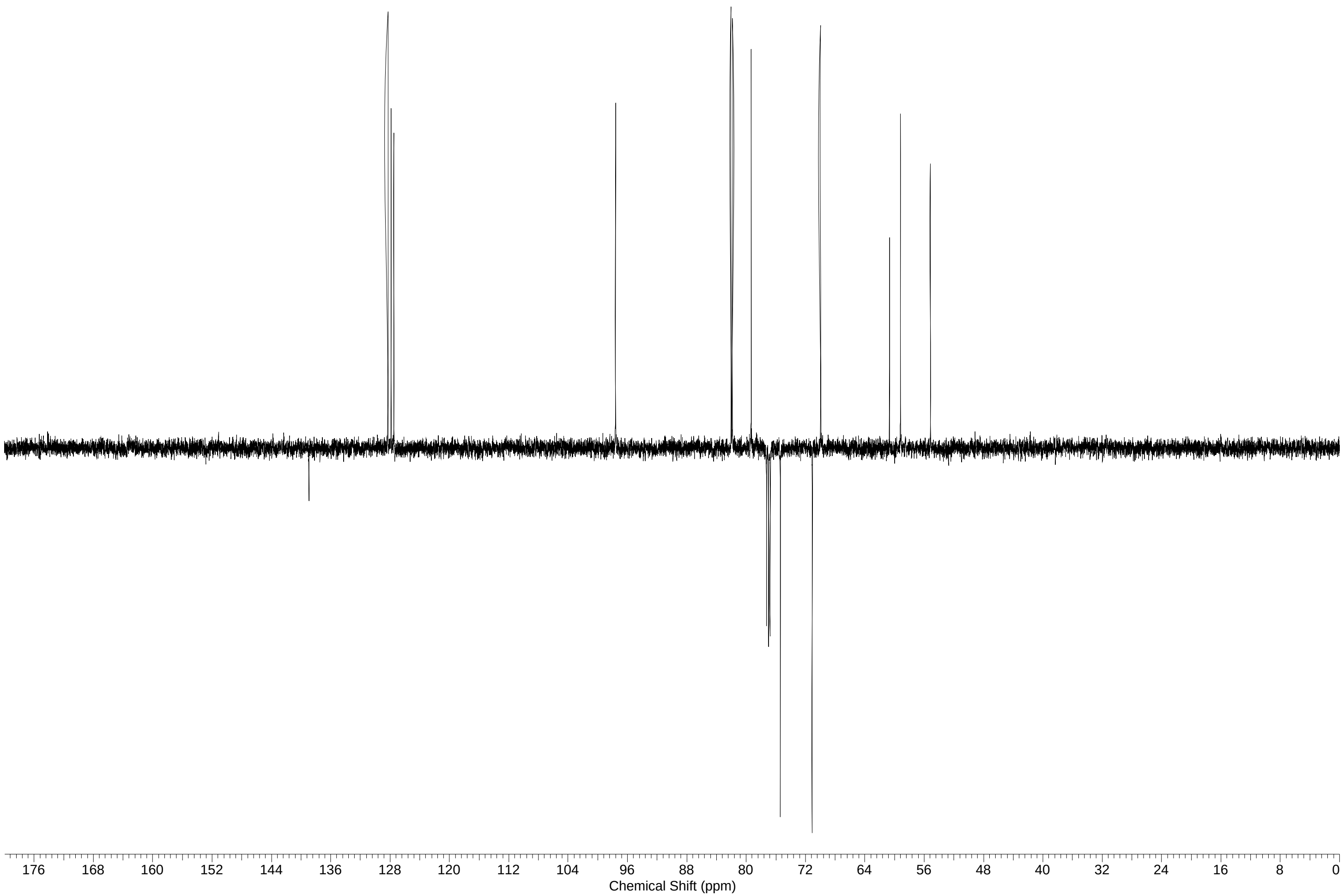


Methyl 3-*O*-benzyl-2,4,6-tri-*O*-methyl-α-D-glucopyranoside (42)

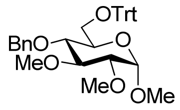


42

^{13}C-NMR (101 MHz, $CDCl_3$)

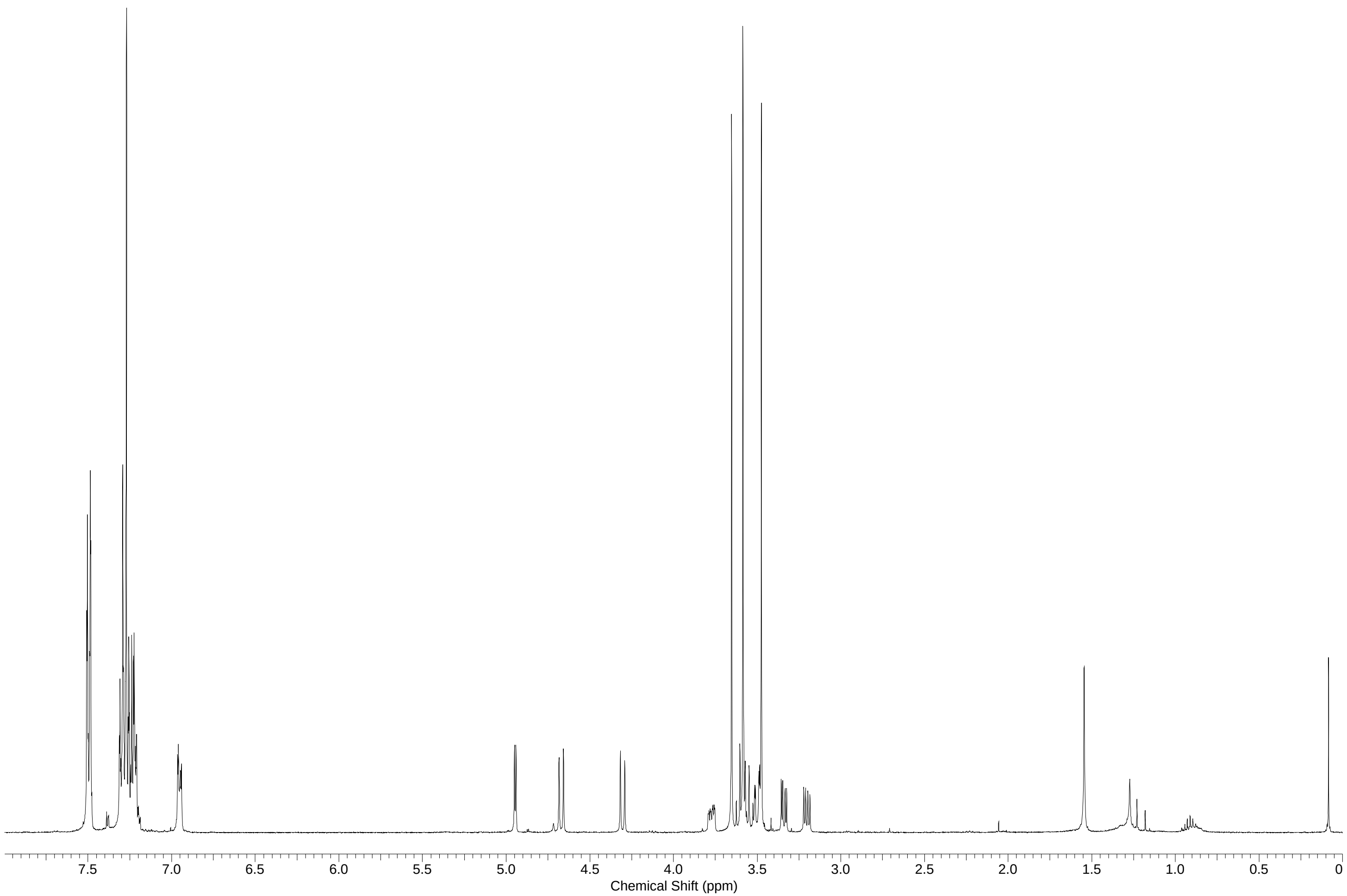


Methyl 4-*O*-benzyl-2,3-di-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (43)



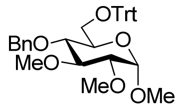
43

^{1}H-NMR (400 MHz, $CDCl_3$)



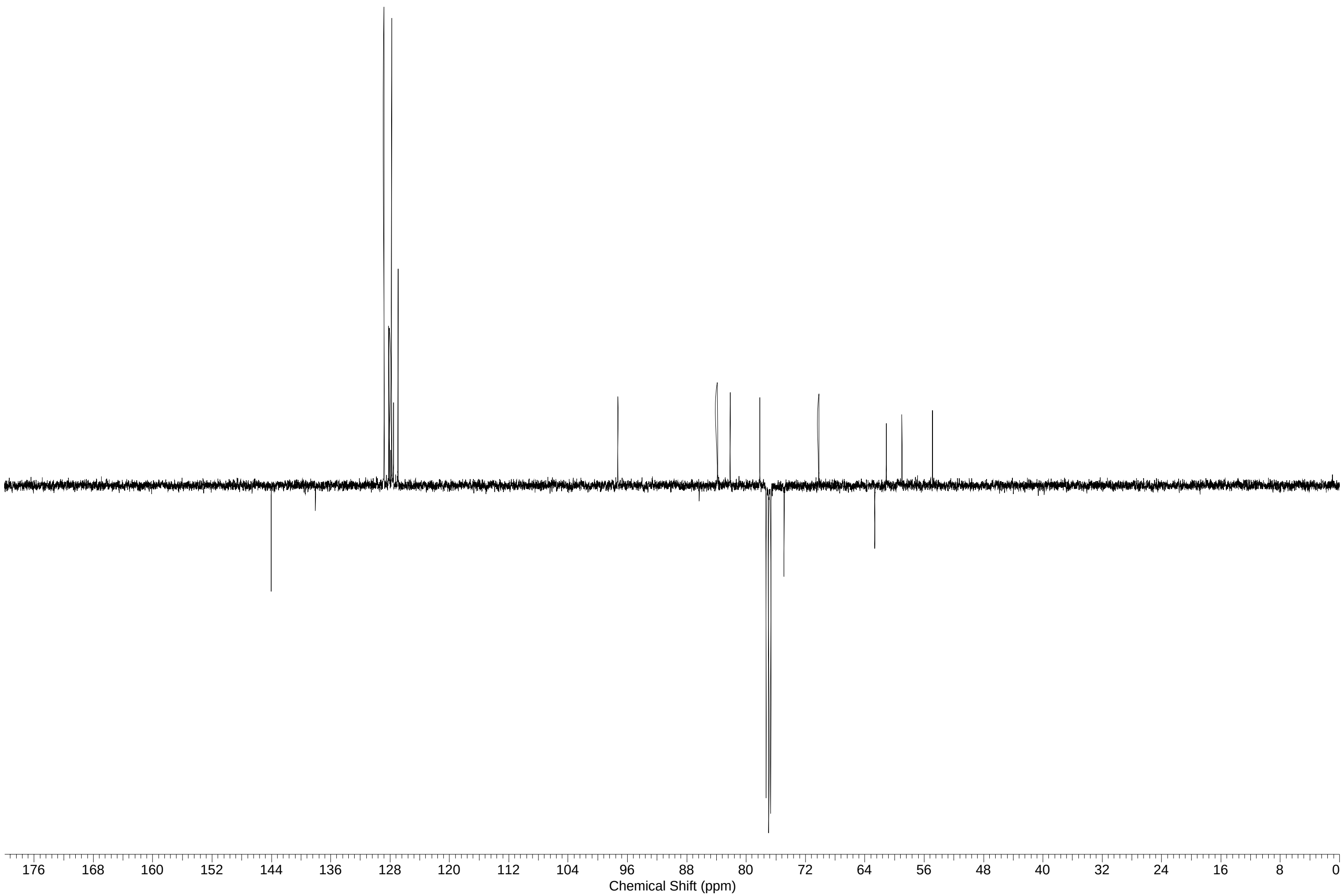
Electronic Supplementary Material (ESI) for Chemical Communications

Methyl 4-*O*-benzyl-2,3-di-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (43)

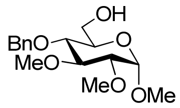


43

^{13}C-NMR (101 MHz, $CDCl_3$)

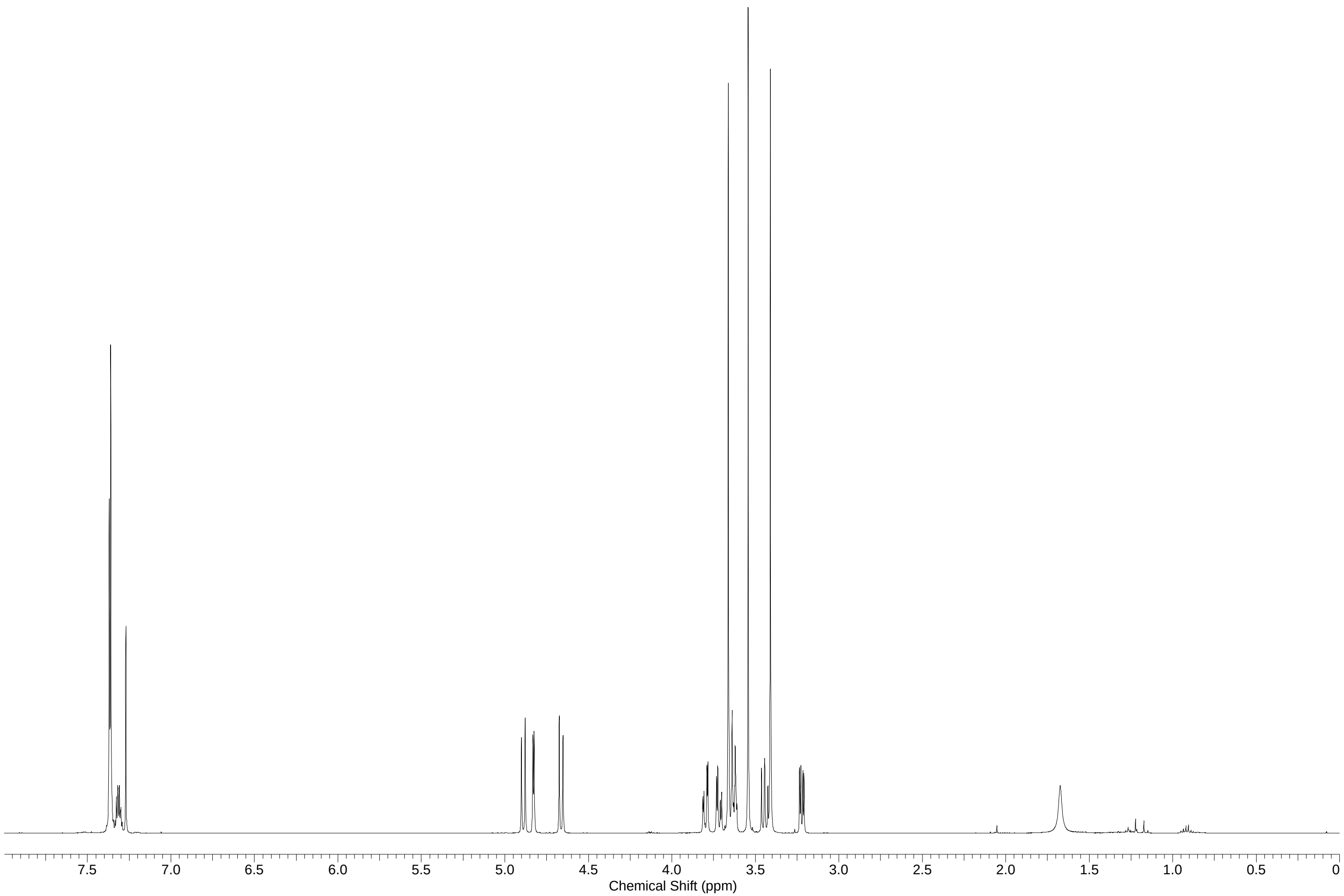


Methyl 4-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranoside (44)

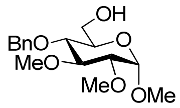


44

^{1}H-NMR (400 MHz, $CDCl_3$)

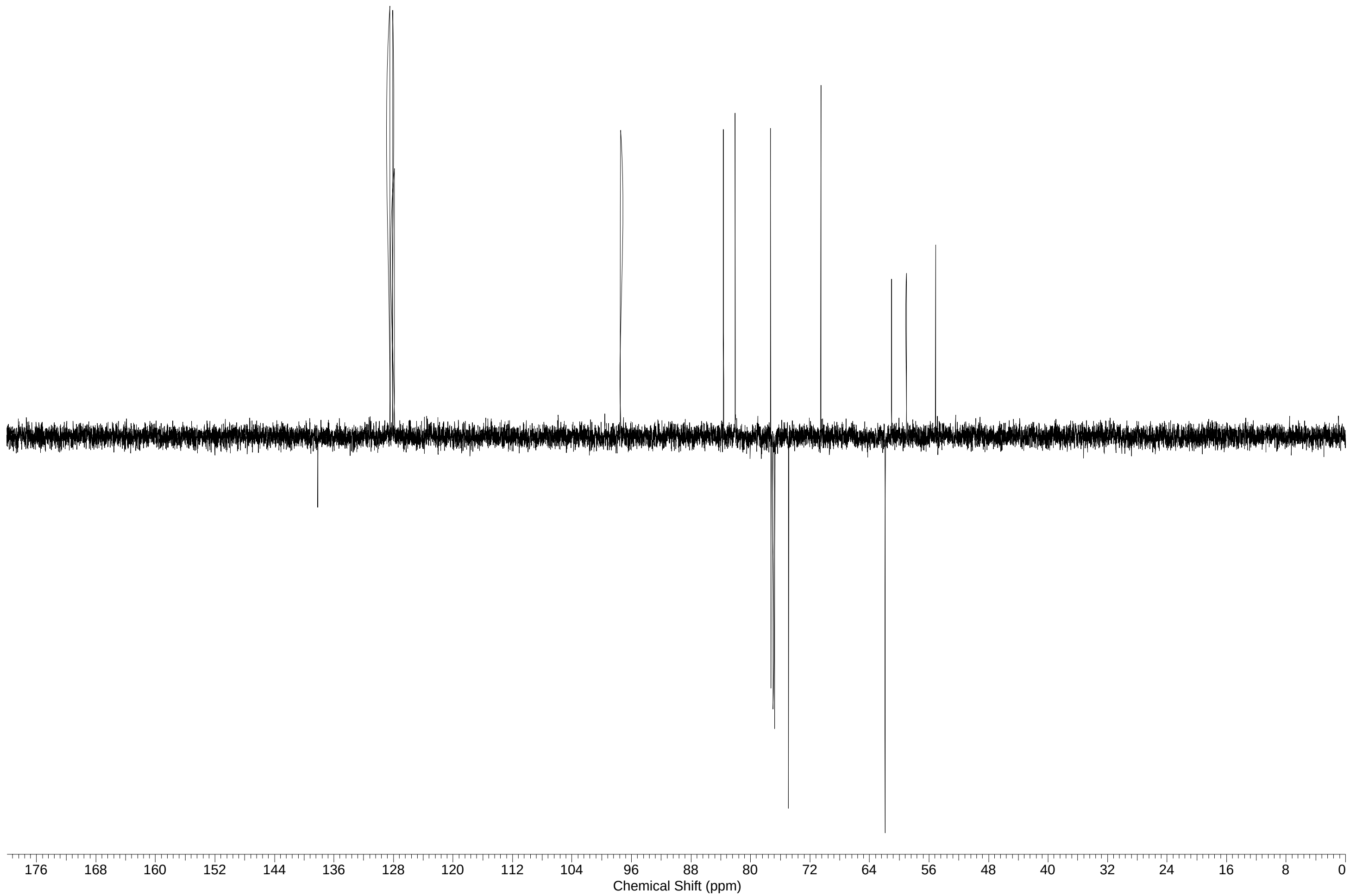


Methyl 4-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranoside (44)

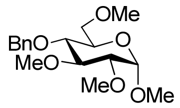


44

^{13}C-NMR (101 MHz, $CDCl_3$)

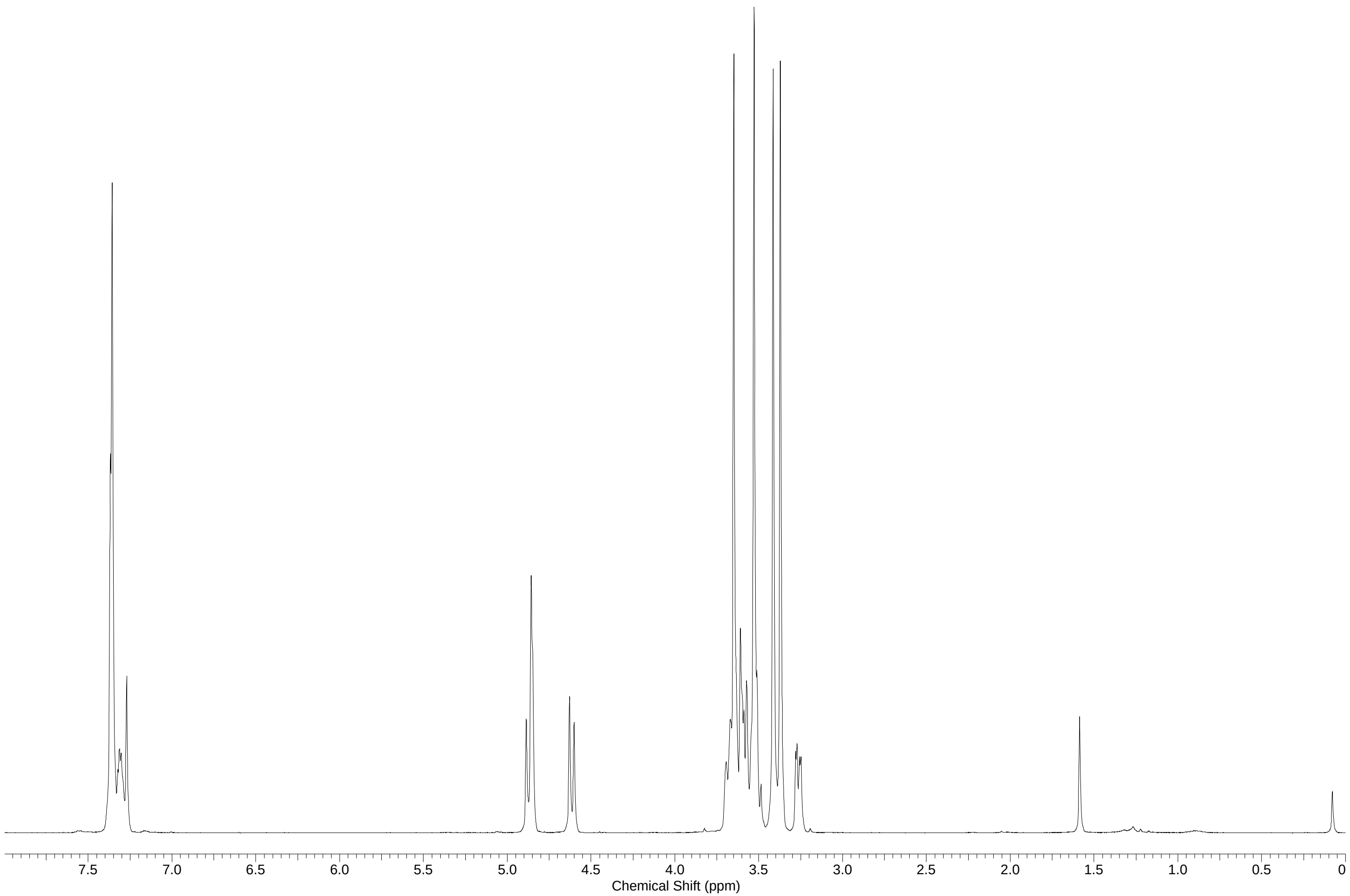


Methyl 4-*O*-benzyl-2,3,6-tri-*O*-methyl-α-D-glucopyranoside (45)

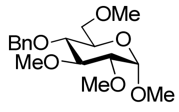


45

^{1}H-NMR (400 MHz, $CDCl_3$)

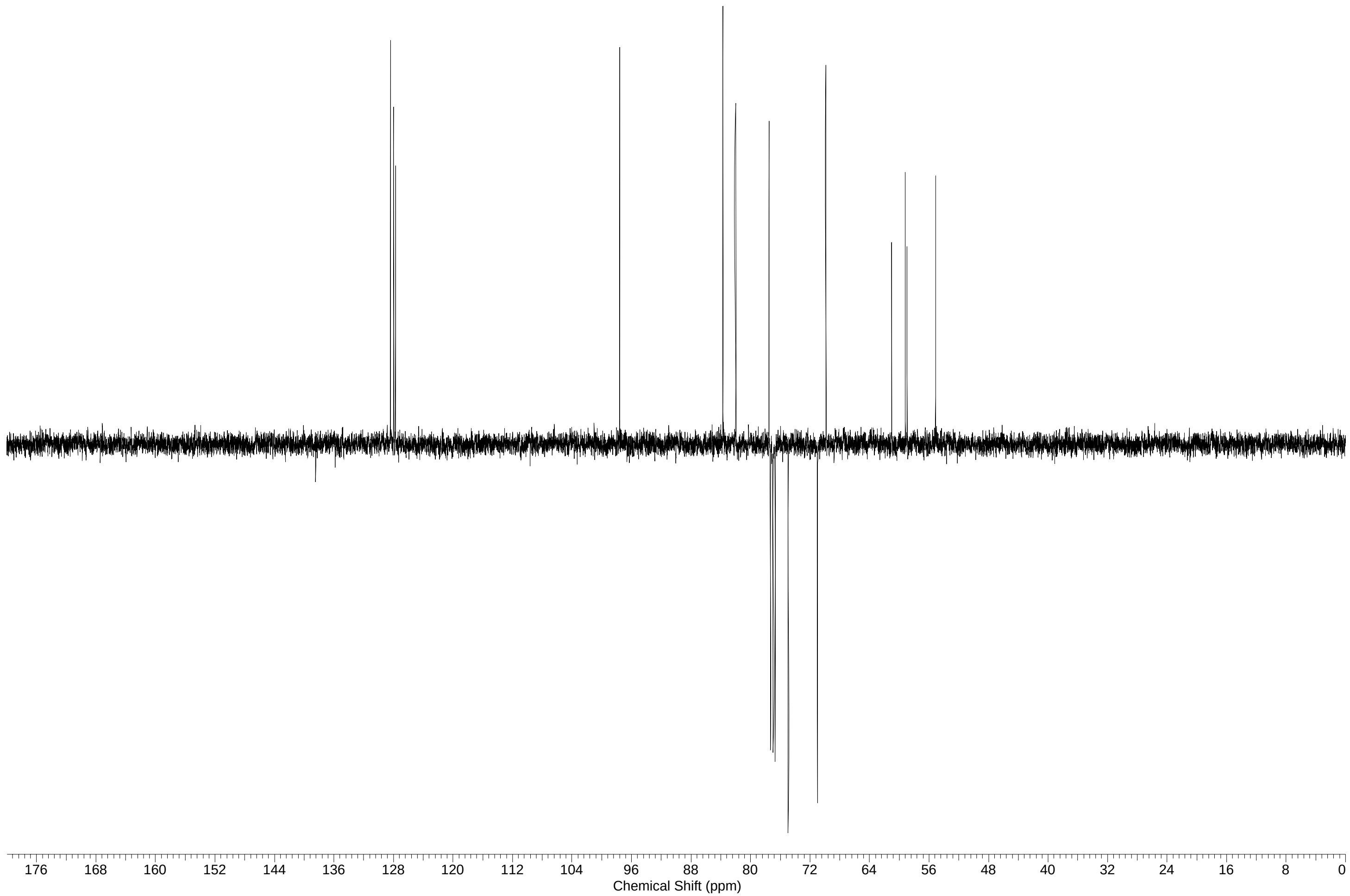


Methyl 4-*O*-benzyl-2,3,6-tri-*O*-methyl-α-D-glucopyranoside (45)



45

^{13}C-NMR (101 MHz, $CDCl_3$)



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