Regioselective Activation of Glycosyl Acceptors by a Diarylborinic Acid-Derived Catalyst

Christina Gouliaras, Doris Lee, Lina Chan and Mark S. Taylor

Department of Chemistry, Lash Miller Laboratories, University of Toronto
80 St. George St., Toronto ON M5S 3H6 Canada

Supporting Information

General: Reactions were carried out without effort to exclude air or moisture, unless otherwise indicated. Stainless steel syringes were used to transfer air- and moisture-sensitive liquids. Flash chromatography was carried out using silica gel (Silicycle P60 40–63 μM, 60 Å).

Materials: HPLC grade acetonitrile was dried and purified using a solvent purification system equipped with columns of activated alumina, under argon (Innovative Technology, Inc.). Deionized water was obtained from an in-house supply. All other reagents and solvents were purchased from Sigma-Aldrich, Caledon, Carbosynth or Alfa Aesar, and used without further purification.

Instrumentation: ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker Avance III 400 MHz or Varian Mercury 400 MHz spectrometer, referenced to residual protium in the solvent. Spectral features are tabulated in the following order: chemical shift (δ, ppm); multiplicity (s-singlet, br s-broad singlet, d-doublet, t-triplet, q-quartet, m-complex multiplet); coupling constants (*J*, Hz); number of protons; assignment. Assignments are based on analysis of coupling constants and COSY spectra. In cases of uncertain assignments, structural confirmation was secured through NOESY experiments. High-resolution mass spectra (HRMS) were conducted on an AB/Sciex QStar spectrometer (ESI). Infrared (IR) spectra were obtained on a Perkin-Elmer Spectrum 100 instrument equipped with a single-reflection diamond / ZnSe ATR accessory, either in the solid state or as neat liquids, as indicated. Spectral features are tabulated as follows: wavenumber (cm^{-1}); intensity (s-strong, m-medium, w-weak, br-broad).

I. Reaction Development

Evaluation of Solvents for Glycosylation

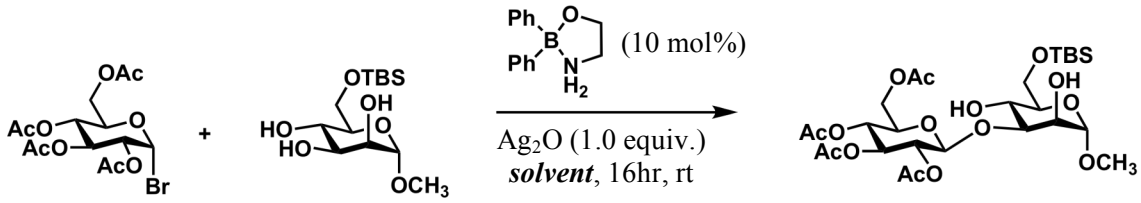


Table 1. Evaluation of solvents for glycosylation.

Entry	Solvent	NMR yield (%)[a]
1	dichloromethane	>95
2	tetrahydrofuran	>95
3	toluene	70
4	acetonitrile	>95

[a] Yields determined by ^{1}H NMR with mesitylene as a quantitative internal standard.

Evaluation of Ag(I) Promoters for Glycosylation

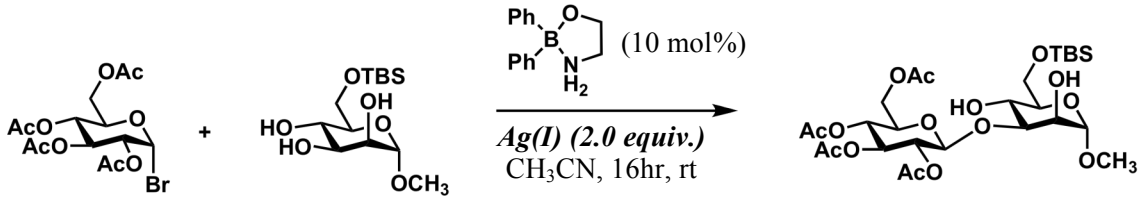


Table 2. Evaluation of Ag(I) promoters for glycosylation.

Entry	Ag(I) promoter	NMR yield (%)[a]
1	Ag_2CO_3	85
2	AgOAc	15
3	AgOTf + *i*-Pr_2NEt (1.1 equiv.)	<5
4	Ag_2O	>95

[a] Yields determined by ^{1}H NMR with mesitylene as a quantitative internal standard.

II. General Experimental Procedures

Preparation of Glycosyl Acceptors

The following carbohydrate acceptor substrates were prepared by literature methods[1]: methyl-6-*O*-*tert*-butyldimethysilyl-α-*D*-mannopyranose (**2a**), methyl-6-*O*-*tert*-butyldimethysilyl-β-*D*-galactopyranose, and methyl-6-*O*-*tert*-butyldimethysilyl-α-*D*-galactopyranose. Spectral data were

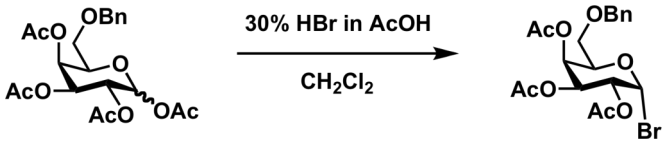
[1] Lee, D.; Taylor, M.S. *J. Am. Chem. Soc.* **2011**, *133*, 3724-3727.

consistent with those presented in the literature[1]. The following glycosyl acceptors were purchased from Carbosynth: methyl *β*-*D*-arabinopyranoside, methyl *α*-*L*-fucopyranoside, and 1,6-anhydro-*β*-*D*-galactopyranose; and Alfa Aesar: methyl *α*-*L*-rhamnopyranoside.

Preparation of Glycosyl Donors

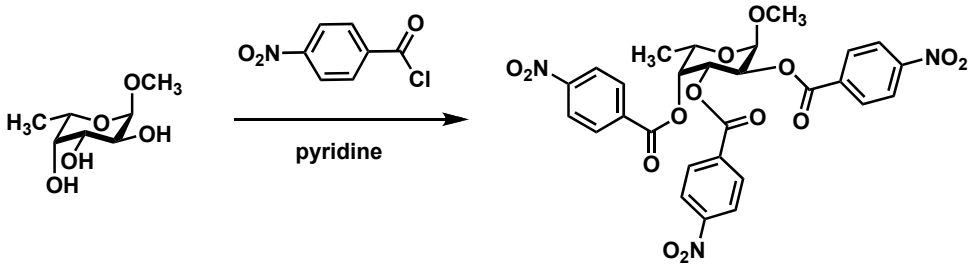
The following glycosyl bromides were purchased from Carbosynth: 2,3,4,6-tetra-*O*-acetyl-*α*-*D*-glucopyranosyl bromide, 2,3,4,6-tetra-*O*-acetyl-*α*-*D*-galactopyranosyl bromide, and 2,3,4,6-tetra-*O*-pivaloyl-*α*-*D*-glucopyranosyl bromide.

2,3,4-Tri-*O*-acetyl-6-*O*-benzyl-*α*-*D*-galactopyranosyl bromide was prepared as follows:



30% HBr in acetic acid (2.3 mL) was added dropwise to a stirred solution of 1,2,3,4-tetra-*O*-acetyl-6-*O*-benzyl-*D*-galactopyranose[2] (3.15 mmol, 1.38 g) in dichloromethane (25 mL) at 0 ºC over a period of 30 minutes. The resulting mixture was stirred at 0 ºC for 1 h, then at room temperature for 2 h. The mixture was then diluted with dichloromethane and poured slowly into ice water. The organic layer was separated and washed sequentially with dilute $NaHCO_{3(aq)}$, saturated $NaHCO_{3(aq)}$, and brine; dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude material was purified over a short pad of silica gel using ethyl acetate/pentane 2:8 to yield the glycosyl bromide in 38% yield. Spectral data were in agreement with those previously reported.[3] **^{1}H NMR (400 MHz, $CDCl_3$):** *δ* 7.37–7.26 (m, 5H, Ph*H*), 6.70 (d, *J* = 3.9 Hz, 1H, *H*-1), 5.58 (dd, *J* = 3.3, 1.0 Hz, 1H, *H*-4), 5.40 (dd, *J* = 10.6, 3.3 Hz, 1H, *H*-3), 5.03 (dd, *J* = 10.6, 3.9 Hz, 1H, *H*-2), 4.56 (d, *J* = 12.0 Hz, 1H, OC*H*Ph), 4.47–4.45 (m, 1H, *H*-5), 4.42 (d, *J* = 12.0 Hz, 1H, OC*H*Ph), 3.56–3.46 (m, 2H, *H*-6a and *H*-6b) 3.84 (dd, *J* = 9.3, 5.0 Hz, 1H, *H*-6a), 2.11 (s, 3H, COCH_3), 2.04 (s, 3H, COCH_3), 2.01 (s, 3H, COCH_3).

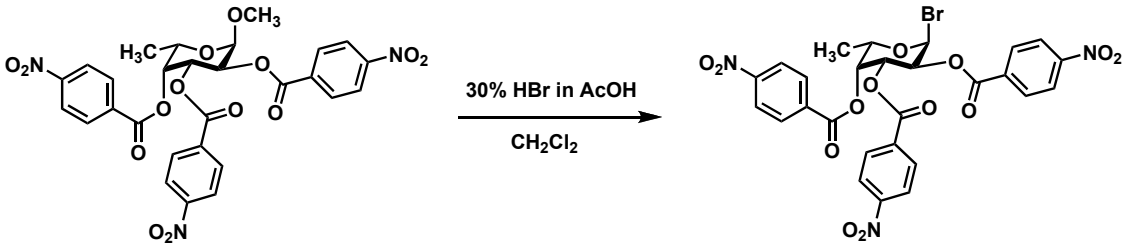
2,3,4-Tri-*O*-*para*-nitrobenzoyl-*α*-*L*-fucopyranosyl bromide was prepared in two steps from methyl-*α*-*L*-fucopyranose as follows:



Methyl-(2,3,4-tri-*O*-*para*-nitrobenzoyl)-*α*-*L*-fucopyranose. To a solution of methyl-*α*-*L*-fucopyranose (1.5 mmol, 0.27 g) in pyridine (3.7 mL), was added 4-nitrobenzoyl chloride (7.5

[2] Pannecoucke, X.; Schmitt, G.; Luu, B. *Tetrahedron* **1994**, *50*, 6569–6578.
[3] Xia, J.; Srikrishnan, T.; Alderfer, J. L.; Jain, R. K.; Piskorz, C. F.; Matta, K. L.; *Carbohydr, Res.* **2000**, *329*, 561–577.

mmol, 1.4 g). The mixture was stirred at 60 °C for 20 hours, diluted in dichloromethane and washed twice with water. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Toluene was added and the solution was concentrated *in vacuo* to azeotrope pyridine. The resulting crude material was purified by silica gel chromatography to yield the desired product as a pale yellow solid in quantitative yield. **^{1}H NMR (400MHz, $CDCl_3$):** δ 8.38–8.35 (m, 2H, OC*H*Ph), 8.28–8.22 (m, 4H, OC*H*Ph), 8.17–8.12 (m, 4H, OC*H*Ph), 7.96–7.93 (m, 2H, OC*H*Ph), 5.97 (dd, 1H, J = 10.7, 3.4 Hz, *H*-3), 5.78 (dd, 1H, J = 3.4, 1.1 Hz, *H*-4), 5.67 (dd, 1H, J = 10.7, 3.6 Hz, *H*-2), 5.22 (d, 1H, J = 3.6 Hz, *H*-1), 4.44 (q, 1H, J = 6.9 Hz, *H*-5), 3.51 (s, 3H, OCH_3), 1.32 (d, 3H, J = 6.6 Hz, CH_3). **R_f:** 0.3 (ethyl acetate/toluene 1:19).



2,3,4-Tri-*O*-*para*-nitrobenzoyl-α-*L*-fucopyranosyl bromide. To a solution of methyl-(2,3,4-tri-*O*-*para*-nitrobenzoyl)-α-*L*-fucopyranose (0.80 mmol, 0.50 g) in dichloromethane (5.7 mL), was added hydrogen bromide (33% solution in acetic acid, 1.9 mL). The mixture was stirred for 24 hours at 35 °C. The crude mixture was cooled to room temperature, diluted in dichloromethane and washed twice with ice-cold water to pH neutral. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude material was purified over a plug of silica (10 cm) to yield the desired product as a yellow solid in 14% yield. **^{1}H NMR (400MHz, $CDCl_3$):** δ 8.39–8.36 (m, 2H, OC*H*Ph), 8.28–8.23 (m, 4H, OC*H*Ph), 8.19–8.14 (m, 4H, OC*H*Ph), 7.98–7.94 (m, 2H, OC*H*Ph), 6.89 (d, 1H, J = 4.0 Hz, *H*-1), 6.02 (dd, 1H, J = 10.5, 3.3 Hz, *H*-3), 5.86 (dd, 1H, J = 3.2, 1.1 Hz, *H*-4), 5.64 (dd, 1H, J = 10.5, 4.0 Hz, *H*-2), 4.73 (q, 1H, J = 6.6 Hz, *H*-5), 1.39 (d, 3H, J = 6.5 Hz, CH_3). **R_f:** 0.7 (ethyl acetate/pentanes 1:5).

The following glycosyl chlorides were prepared according to previous reports:[4]

2,3,4-tri-*O*-acetyl-α-*L*-fucopyranosyl chloride[5] was synthesized from 2,3,4-tri-*O*-acetyl-*L*-fucopyranose[6] according to TCT–DMF chlorination protocol A (see below);

2,3,4-tri-*O*-acetyl-β-*L*-arabinopyranosyl chloride[7] was synthesized from 2,3,4-tri-*O*-acetyl-*L*-arabinopyranose according to TCT–DMF chlorination protocol A;

2,3,4,6-tetra-*O*-benzyl-α-*D*-galactopyranosyl chloride[4] was synthesized from 2,3,4,6-tetra-*O*-benzyl-*D*-galactopyranose[8] according to TCT–DMF chlorination protocol B;

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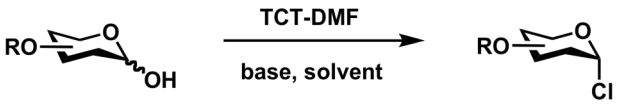
[4] Chang, C.-W.; Chang, S.-S.; Chao, C.-S.; Mong, K.-K. T. *Tetrahedron Lett.* **2009**, *50*, 4536–4540.
[5] Dekany, G.; Ward, P.; Toth, I. *J. Carbohydr. Chem.* **1995**, *14*, 227–236.
[6] Nishi, Y.; Yamane, N.; Tanimoto, T. *Carbohydr. Res.* **2007**, *342*, 2173–2181.
[7] Collins, P. M.; Overend, W. G.; Rayner, B. A. *Carbohydr. Res.* **1973**, *31*, 1–16.

2,3,4,6-tetra-*O*-benzyl-*α*-*D*-glucopyranosyl chloride[9] was synthesized from 2,3,4,6-tetra-*O*-benzyl-*D*-glucopyranose[10] according to TCT–DMF chlorination protocol B (see below);

2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl chloride was prepared from β-D-glucose pentaacetate using a modification of the literature procedure.[11]



TCT–DMF chlorination protocol A: DMF (4.0 equiv.) was added to 2,4,6-trichloro-[1,3,5]-triazine (TCT) (1.1 equiv.) and the resulting suspension was stirred at room temperature for 15 minutes under argon. Glycosyl hemiacetal (1.0 equiv.) in dichloroethane (0.2 M) was added to the TCT–DMF suspension followed by addition of DBU (1.1 equiv.). The reaction mixture was stirred at 60 ºC for 4 hours. Upon completion of chlorination, the temperature was brought to room temperature and Et_2O was added to the mixture for the precipitation of cyanuric salt. After removal of cyanuric salt by filtration, the filtrate was concentrated to yield the crude glycosyl chloride. Further purification was performed by brief flash chromatography over a short pad of silica gel to furnish the respective *α*-glycosyl chloride.
TCT–DMF chlorination protocol B: Similar to protocol A except that DCM and 5 equiv. of K_2CO_3 were used as solvent and proton scavenger, respectively, to replace DCE and DBU in protocol A. The reaction was conducted at 45 ºC. Subsequent workup followed the same procedure as described in protocol A above, and the respective *α*-glycosyl chloride was obtained.

General Procedure A: Borinic Acid-Catalyzed Glycosylation

Glycosyl donor (1 equiv.), acceptor (1.1 equiv.), silver (I) oxide (1 equiv.) and 2-aminoethyl diphenylborinate (10 mol %) were added to an oven-dried round bottom flask, under an argon atmosphere. Dry acetonitrile (0.13 M) was added and the resulting mixture was stirred at room temperature (unless otherwise noted). After 16 hours, the reaction was quenched with a few drops of methanol, diluted with dichloromethane and filtered through a plug of Celite®. The resulting crude material was purified by silica gel chromatography.

III. Comparison of Crude ^{1}H NMR Spectra of Catalyzed vs. Uncatalyzed Glycosylations

In all of the cases shown below, the glycosylation reaction was carried out using 2,3,4,6-tetra-*O*-acetyl-*α*-*D*-glucopyranosyl bromide as donor and methyl-6-*O*-*tert*-butyldimethysilyl-*α*-*D*-

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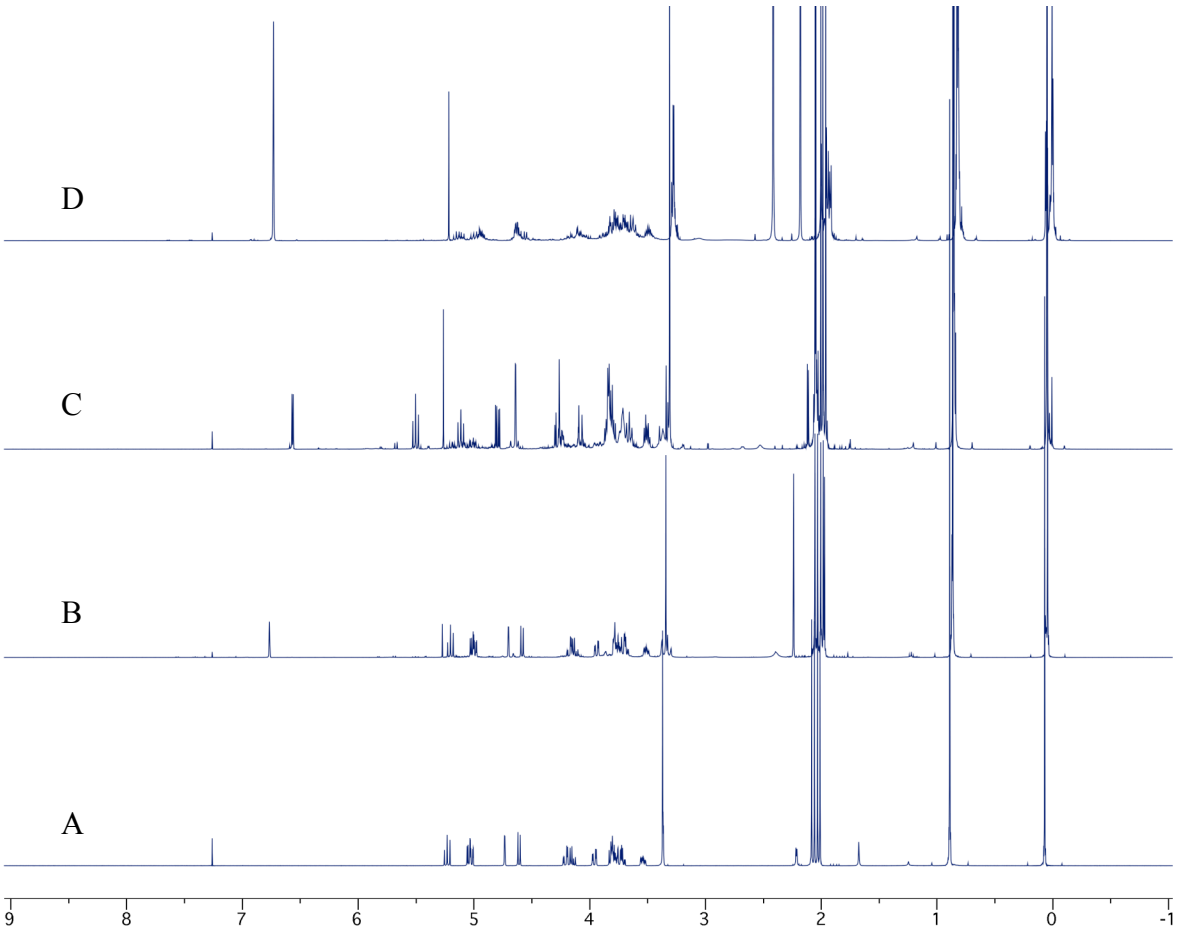
[8] Ye, X.-S.; Sun, F.; Liu, M.; Li, Q.; Wang, Y.; Zhang, G.; Zhang, L.-H.; Zhang, X.-L. *J. Med. Chem.* **2005**, *48*, 3688–3691.
[9] Zhang, Z.; Magnusson, G. *Carbohydr. Res.* **1996**, *925*, 41–55.
[10] Bernardes, G. J. L.; Grayson, E. J.; Thompson, S.; Chalker, J. M.; Errey, J. C.; El Oualid, F.; Claridge, T. D. W.; Davis, B. G. *Angew. Chem. Int. Ed.* **2008**, *47*, 2244–2247.
[11] Kortynyk, W.; Mills, J. A. *J. Chem. Soc*. **1959**, 636–649.

mannopyranose as acceptor. Spectra A, B and C are of reactions run according to general procedure A. Spectrum A is of the purified disaccharide. Spectrum B is the crude ^{1}H NMR under optimized conditions. Spectrum C is the crude ^{1}H NMR of the reaction run without catalyst. Spectrum D is the crude ^{1}H NMR of the reaction run under Hanessian's reported glycosylation conditions (AgOTf, tetramethylurea, CH_2Cl_2, 0 °C).[12] Mesitylene was added as a quantitative internal standard and appears at approximately 6.7 ppm in spectra B, C and D.



[12] Hanessian, S.; Banoub, J. *Carbohydr. Res.* **1977**, *53*, C13–C16.

IV. Kinetics Experiments

Initial rate kinetic studies were carried out to determine the order for each reagent in the coupling of 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide and methyl-6-*O*-*tert*-butyldimethysilyl-*α*-*D*-mannopyranose **2a**. Using 2-aminoethyl diphenylborinate **1d** as the pre-catalyst and Ag_2O as promoter in acetonitrile solvent, the concentration of each reaction component was varied and the progression of the reaction at room temperature was monitored.

General protocol for kinetics experiments:

Into an oven-dried 1 dram vial were added 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide, methyl-6-*O*-*tert*-butyldimethysilyl-*α*-*D*-mannopyranose **2a**, 2-aminoethyl diphenylborinate **1d** and Ag_2O. The reaction vial was capped with a septum and purged with argon. Dry acetonitrile (0.13 M) was added and the resulting mixture was stirred vigorously (750 rpm) at room temperature. The initial time of each kinetic run corresponds to the time at which dry acetonitrile was added to the reaction vial. During the course of the reaction, aliquots of the reaction mixture were removed and filtered over Celite® to remove the silver oxide, thus stopping the reaction. The solvent was then removed and the resulting samples were analyzed by ^{1}H-NMR spectroscopy for the formation of product with mesitylene as an internal standard. Integrations for the internal standard peak and the anomeric peak of the product were used to calculate moles of product formed and therefore % conversion.

Pseudo first-order kinetics in glycosyl acceptor 2a:

The conversion of 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide to product was monitored over a period of 10 hours using three equivalents of methyl-6-*O*-*tert*-butyldimethysilyl-*α*-*D*-mannopyranose **2a** and Ag_2O, and 10 mol % 2-aminoethyl diphenylborinate **1d** in 0.13 M acetonitrile. A plot of the concentration of 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide over time could be fit to an exponential function $[\mathbf{2a}](t) = [\mathbf{2a}]_0 e^{-kt}$, indicating the reaction follows pseudo-first-order kinetics under these conditions (Figure 1).

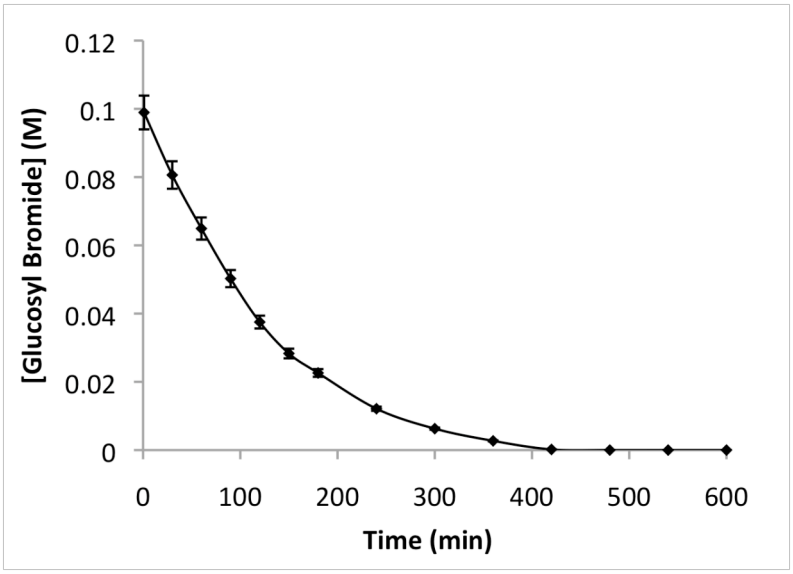


Figure 1. Plot of the consumption of 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide over 10 hours.

Dependence of the initial rate on the concentration of 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide:

The reactions were carried out using varying concentrations of 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide (0.75–5.0 equiv) with 0.22 mmol of methyl-6-*O*-*tert*-butyldimethysilyl-*α*-*D*-mannopyranose **2a**, 10 mol % of 2-aminoethyl diphenylborinate **1d**, and 0.2 mmol of Ag_2O in 0.13 M dry acetonitrile. The concentration of product formed was calculated and values not exceeding 10% conversion were used to calculate the initial rate (Figure 2). The order in 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide was then determined by plotting the initial rates against the concentration of 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide (Figure 3). The linear relationship between the initial k_{obs} and the initial concentration of glycosyl bromide indicates first-order kinetics in glycosyl donor.

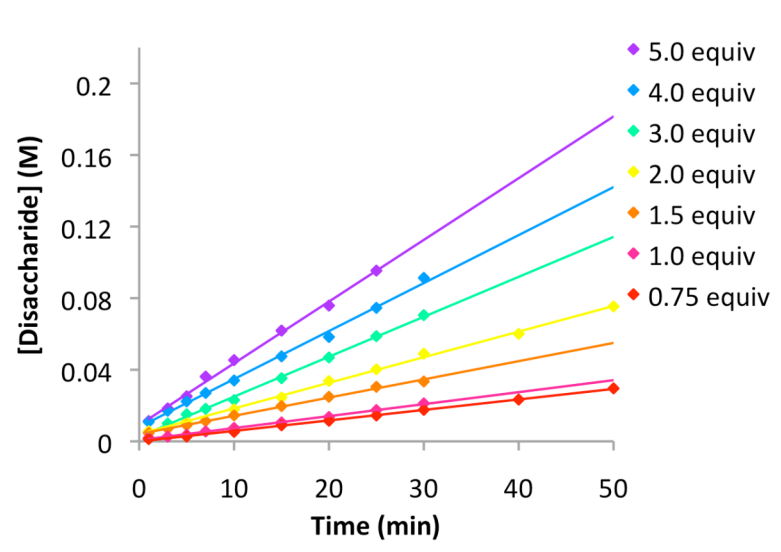


Figure 2. Plot of the formation of product over time with variation in the concentration of 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide (0.75–5.0 equivalents).

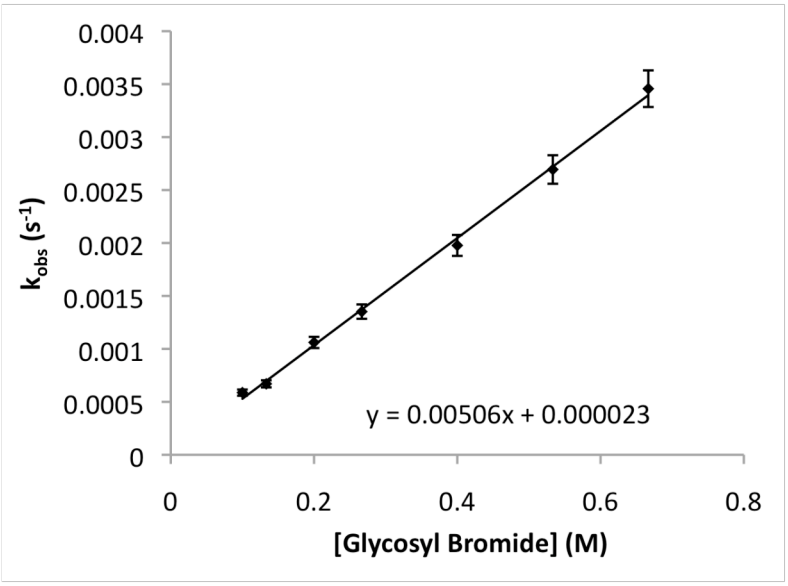


Figure 3. Plot of the initial rate dependence on the concentration of 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide.

Dependence of the initial rate on the concentration of methyl-6-*O*-*tert*-butyldimethysilyl-*α*-*D*-mannopyranose **2a:**

The reactions were carried out using varying concentrations of methyl-6-*O*-*tert*-butyldimethysilyl-*α*-*D*-mannopyranose **2a** (1.0–6.0 equiv) with 0.2 mmol of 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide, 10 mol % of 2-aminoethyl diphenylborinate **1d**, and 0.2 mmol of Ag_2O in 0.13 M acetonitrile. The concentration of product formed was calculated and values not exceeding 10% conversion were used to calculate the initial rate (Figure 4). The order in methyl-6-*O*-*tert*-butyldimethysilyl-*α*-*D*-mannopyranose **2a** was then determined by plotting the initial rates against the concentration of methyl-6-*O*-*tert*-butyldimethysilyl-*α*-*D*-mannopyranose **2a** (Figure 5). The linear relationship between the initial k_{obs} and the initial concentration of glycosyl acceptor indicates first-order kinetics in glycosyl acceptor.

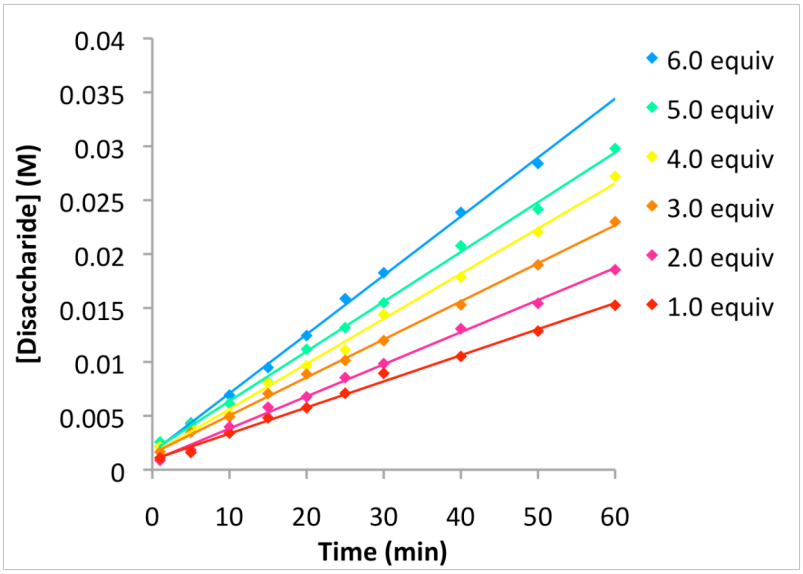


Figure 4. Plot of the formation of product over time with variation in the concentration of methyl-6-*O*-*tert*-butyldimethysilyl-*α*-*D*-mannopyranose **2a** (1.0–6.0 equivalents).

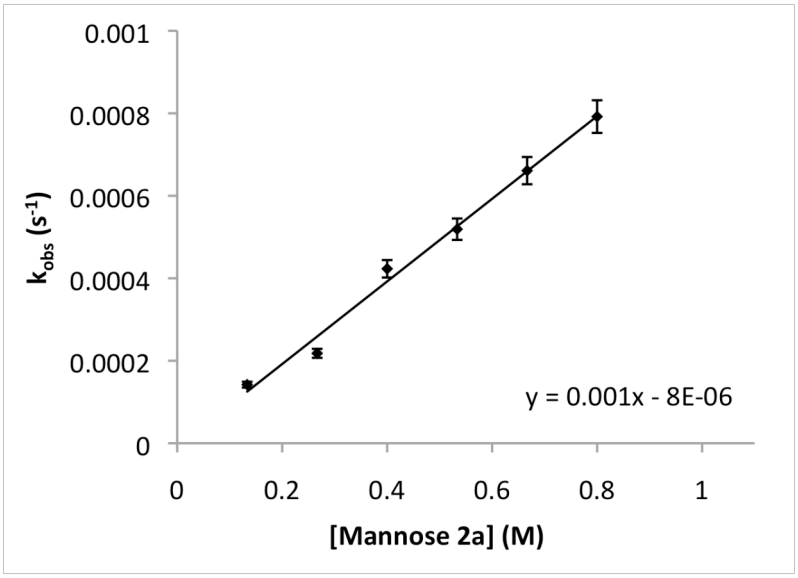


Figure 5. Plot of the initial rate dependence on the concentration of methyl-6-*O*-*tert*-butyldimethysilyl-*α*-*D*-mannopyranose **2a**.

Dependence of the initial rate on the concentration of 2-aminoethyl diphenylborinate 1d:

The reactions were carried out using a range of catalyst loadings from 7 to 13 mol % with 0.2 mmol of 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide, 0.22 mmol of methyl-6-*O*-*tert*-butyldimethysilyl-*α*-*D*-mannopyranose **2a**, and 0.2 mmol of Ag_2O in 0.13 M acetonitrile. The concentration of product formed was calculated and values not exceeding 10% conversion were used to calculate the initial rate (Figure 6). The order in 2-aminoethyl diphenylborinate **1d** was then determined by plotting the initial rates against the concentration of 2-aminoethyl diphenylborinate **1d** (Figure 7). The linear relationship between the initial k_{obs} and the catalyst concentration indicates first-order kinetics in catalyst.

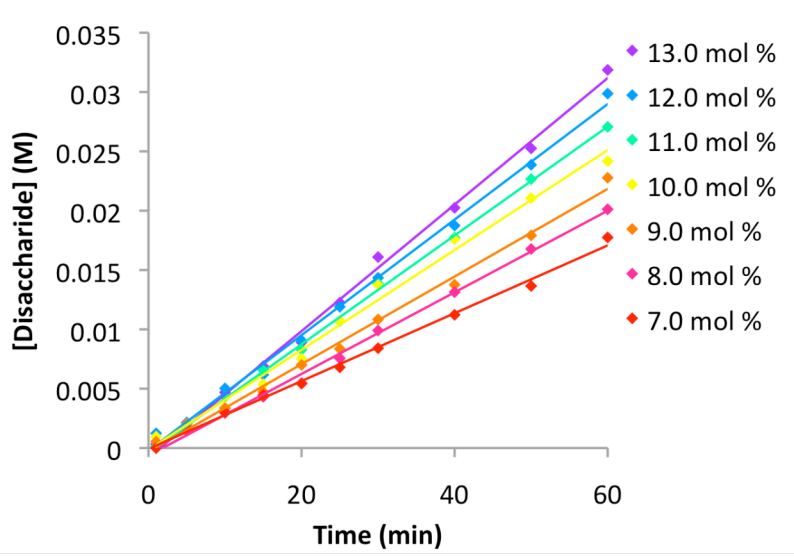


Figure 6. Plot of the formation of product over time with variation in the concentration of 2-aminoethyl diphenylborinate **1d** (7.0–13.0 mol %).

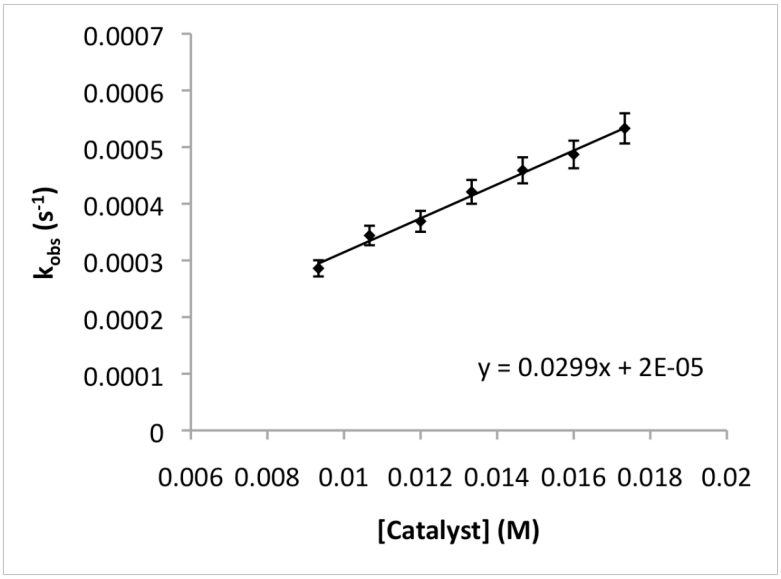


Figure 7. Plot of the initial rate dependence on the concentration of 2-aminoethyl diphenylborinate **1d**.

Dependence of the initial rate on the concentration of Ag_2O:

The reactions were carried out using varying concentrations of Ag_2O (0.5–5.0 equiv) with 0.2 mmol of 2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide, 0.22 mmol of methyl-6-*O*-*tert*-butyldimethysilyl-*α*-*D*-mannopyranose **2a**, and 10 mol % of 2-aminoethyl diphenylborinate **1d** in 0.13 M acetonitrile. The concentration of product formed was calculated and values not exceeding 10% conversion were used to calculate the initial rate (Figure 8). The order in Ag_2O was then determined by plotting the initial rates against the concentration of Ag_2O (Figure 9). The invariant values of the initial k_{obs} as a function of Ag_2O concentration indicate zero-order kinetics in Ag_2O.

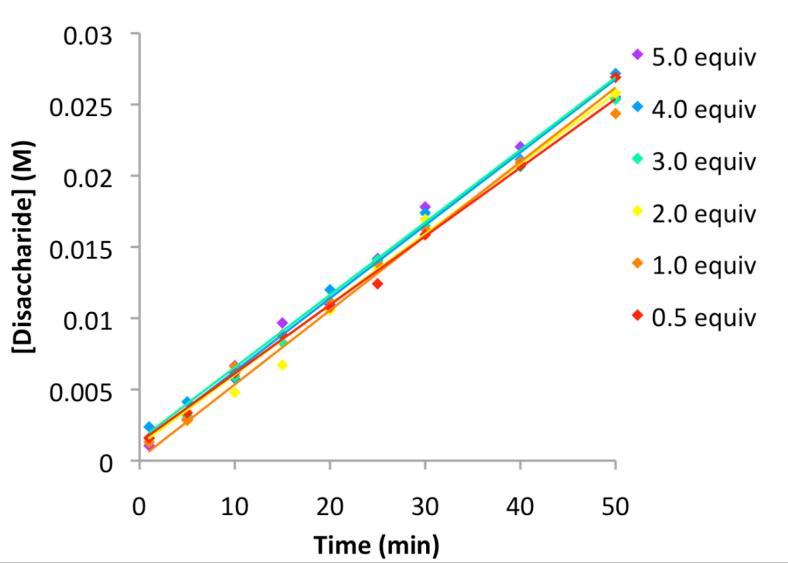


Figure 8. Plot of the formation of product over time with variation in the concentration of Ag_2O (0.5–5.0 equivalents).

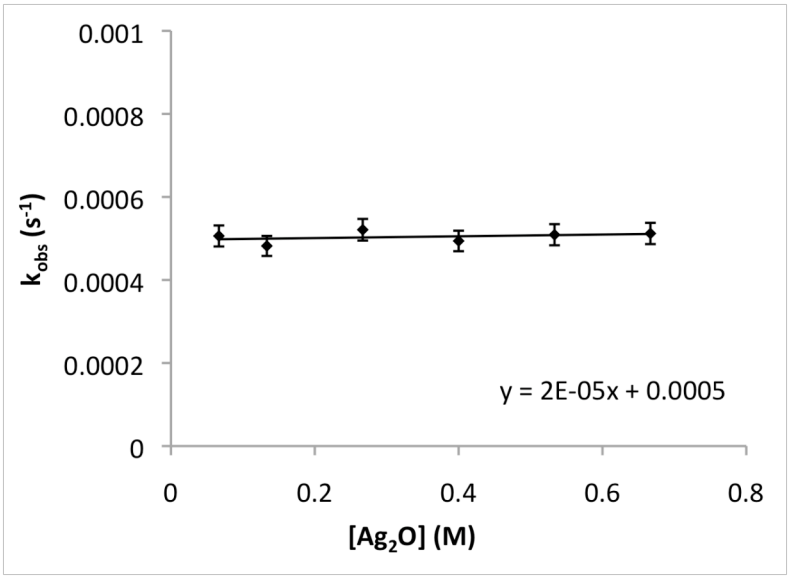


Figure 9. Plot of the initial rate dependence on the concentration of Ag_2O.

Dependence of rate on the nature of the catalyst used:

Further experiments were performed to examine the effect the nature of the borinic acid catalyst has on the reaction rate. The reactions were carried out using 0.2 mmol 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide, 0.22 mmol methyl-6-*O*-*tert*-butyldimethysilyl-α-*D*-mannopyranose **2a**, 0.2 mmol of Ag_2O, 0.13 M dry acetonitrile, and either 10 mol % diphenyl borinic acid or 10 mol % 2-aminoethyl diphenylborinate **1d**. A plot of the concentration of product formed versus time indicates that the initial rate is lower with 2-aminoethyl diphenylborinate **1d** compared to diphenyl borinic acid (Figure 10). This is consistent with the hypothesis that 2-aminoethyl diphenylborinate **1d** acts as a pre-catalyst under the reaction conditions.

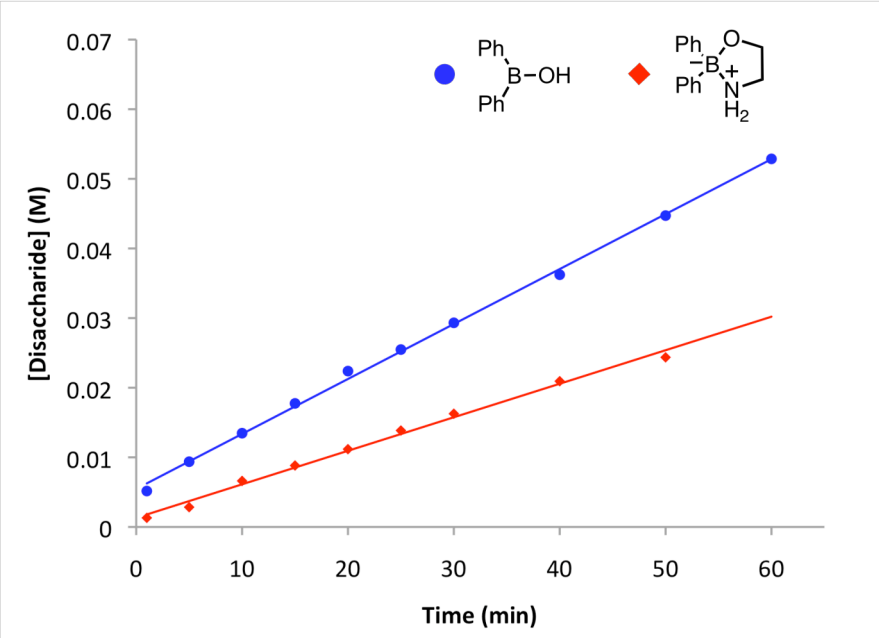
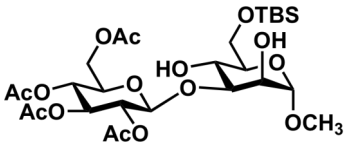
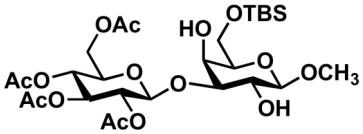


Figure 10. Dependence of rate on the nature of the organoboron catalyst.

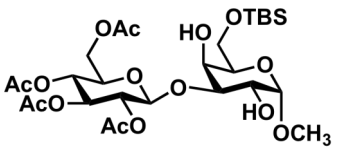
V. Characterization Data



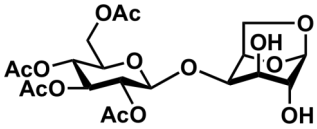
Methyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-(2',3',4',6'-tetra-*O*-acetyl-*β*-*D*-glucopyranosyl)-*α*-*D*-mannopyranoside (3a). Synthesized according to general procedure A, from 2,3,4,6-tetra-*O*-acetyl-*α*-*D*-glucopyranosyl bromide (1.0 mmol) and methyl-6-*O*-*tert*-butyldimethysilyl-*α*-*D*-mannopyranose, 99% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** *δ* 5.23 (dd, *J* = 9.6, 9.6 Hz, 1H, *H*-3'), 5.06–5.01 (m, 2H, *H*-4' and *H*-2'), 4.73 (d, *J* = 1.6 Hz, 1H, *H*-1), 4.61 (d, *J* = 8.0 Hz, 1H, *H*-1'), 4.21 (dd, *J* = 12.4, 2.4 Hz, 1H, *H*-6a'), 4.15 (dd, *J* = 12.4, 6.0 Hz, 1H, *H*-6b'), 3.96 (dd, *J* = 11.2, 2.4 Hz, 1H, *H*-6a), 3.83–3.69 (m, 5H, *H*-6b, *H*-2, *H*-3, *H*-5' and *H*-4), 3.54 (ddd, *J* = 8.8, 6.0, 2.4 Hz, 1H, *H*-5), 3.37 (s, 3H, OCH_3), 3.36 (d, *J* = 1.6 Hz, 1H, C_4-O*H*), 2.21 (d, *J* = 3.6 Hz, 1H, C_2-O*H*), 2.08 (s, 3H, OCOCH_3), 2.06 (s, 3H, OCOCH_3), 2.03 (s, 3H, OCOCH_3), 2.01 (s, 3H, OCOCH_3), 0.89 (s, 9H, Si(C(CH_3)$_3$)(CH_3)$_2$), 0.07 (s, 6H, Si(C(CH_3)$_3$)(CH_3)$_2$). **^{13}C NMR (100 MHz, $CDCl_3$):** *δ* 170.7, 170.2, 169.7, 169.5, 101.5, 100.2, 84.3, 72.6, 72.4, 72.2, 71.5, 70.0, 68.6, 66.2, 63.3, 62.1, 54.8, 26.1, 20.8, 20.7, 20.7, 20.7, 18.5, -5.1. **R_f:** 0.4 (isopropanol/toluene 1:9). **IR (Powder, cm^{-1}):** 3522 (w), 2929 (w), 1751 (s), 1367 (m), 1212 (s), 1135 (m), 1104 (m), 1035 (s). **HRMS (ESI, m/z):** Calculated for $C_{27}H_{47}O_{15}Si$ ($(M+H)^+$): 639.2678; Found: 639.2702.



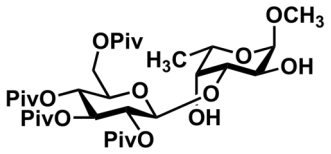
Methyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-(2',3',4',6'-tetra-*O*-acetyl-*β*-*D*-glucopyranosyl)-*β*-*D*-galactopyranoside (3b). Synthesized according to general procedure A, from 2,3,4,6-tetra-*O*-acetyl-*α*-*D*-glucopyranosyl bromide (1.0 mmol) and methyl-6-*O*-*tert*-butyldimethysilyl-*β*-*D*-galactopyranose, 94% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** *δ* 5.25 (dd, *J* = 9.2, 9.2 Hz, 1H, *H*-3'), 5.09 (dd, *J* = 9.6, 9.6 Hz, 1H, *H*-4'), 5.04 (dd, *J* = 10.0, 8.0 Hz, 1H, *H*-2'), 4.88 (d, *J* = 8.0 Hz, 1H, *H*-1'), 4.25 (dd, J = 12.4, 4.4 Hz, 1H, *H*-6a'), 4.15 (d, *J* = 7.6 Hz, 1H, *H*-1), 4.12 (dd, *J* = 12.4, 2.4 Hz, 1H, *H*-6b'), 4.03 (dd, *J* = 2.4, 2.4 Hz, 1H, *H*-4), 3.92 (dd, *J* = 10.0, 6.4 Hz, 1H, *H*-6a), 3.82 (dd, *J* = 10.0, 5.6 Hz, 1H, *H*-6b), 3.75 (ddd, *J* = 9.6, 8.0, 2.4 Hz, 1H, *H*-2), 3.71 (ddd, *J* = 6.8, 4.4, 2.4 Hz, 1H, *H*-5'), 3.60 (dd, *J* = 9.2, 3.2 Hz, 1H, *H*-3), 3.54 (s, 3H, OCH_3), 3.49 (dd, *J* = 6.4, 5.6 Hz, 1H, *H*-5), 2.54 (dd, *J* = 2.4, 1.6 Hz, 1H, C_4-O*H*), 2.33 (d, *J* = 2.4 Hz, 1H, C_2-O*H*), 2.09 (s, 3H, OCOCH_3), 2.04 (s, 3H, OCOCH_3), 2.03 (s, 3H, OCOCH_3), 2.02 (s, 3H, OCOCH_3), 0.89 (s, 9H, Si(C(CH_3)$_3$)(CH_3)$_2$), 0.08 (s, 6H, Si(C(CH_3)$_3$)(CH_3)$_2$). **^{13}C NMR (100 MHz, $CDCl_3$):** *δ* 170.8, 170.4, 169.9, 169.5, 103.8, 101.4, 82.5, 74.8, 72.5, 72.1, 71.5, 70.9, 68.4, 67.8, 62.0, 61.8, 57.0, 26.0, 20.8, 20.8, 20.8, 20.7, 18.4, -5.2, -5.3. **R_f:** 0.3 (isopropanol/toluene 1:9). **IR (Powder, cm^{-1}):** 3597 (w), 2928 (w), 1747 (s), 1367 (m), 1213 (s), 1034 (s). **HRMS (ESI, m/z):** Calculated for $C_{27}H_{50}NO_{15}Si$ ($(M+NH_4)^+$): 656.2944; Found: 656.2972.



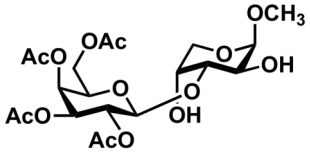
Methyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-(2',3',4',6'-tetra-*O*-acetyl-*β*-*D*-glucopyranosyl)-*α*-*D*-galactopyranoside (3c). Synthesized according to general procedure A, from 2,3,4,6-tetra-*O*-acetyl-*α*-*D*-glucopyranosyl bromide (1.0 mmol) and methyl-6-*O*-*tert*-butyldimethysilyl-*α*-*D*-galactopyranose, 74% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.23 (dd, J = 9.6, 9.6 Hz, 1H, *H*-3'), 5.07 (dd, J = 10, 9.6 Hz, 1H, *H*-4'), 5.02 (dd, J = 10, 8 Hz, 1H, *H*-2'), 4.81 (d, J = 8 Hz, 1H, *H*-1'), 4.79 (d, J = 3.6 Hz, 1H, *H*-1), 4.23 (dd, J = 12.4, 4.8 Hz, 1H, *H*-6a'), 4.12 (dd, J = 12.4, 2.4 Hz, 1H, *H*-6b'), 4.06 (d, J = 3.2 Hz, 1H, *H*-4), 3.97 (dd, J = 9.2, 3.6 Hz, 1H, *H*-2), 3.85 (ddd, J = 8.8, 4.8, 4.8 Hz, 1H, *H*-5), 3.80–3.74 (m, 3H, *H*-6a, *H*-6b, and *H*-3), 3.71 (ddd, J = 10, 4.8, 2.4 Hz, 1H, *H*-5'), 3.42 (s, 3H, OCH_3), 2.08 (s, 3H, OCOCH_3), 2.05 (s, 3H, OCOCH_3), 2.02 (s, 3H, OCOCH_3), 2.01 (s, 3H, OCOCH_3), 0.88 (s, 9H, Si(C(CH_3)$_3$)(CH$_3$)$_2$), 0.07 (s, 6H, Si(C(CH$_3$)$_3$)(CH_3)$_2$). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.7, 170.3, 170.0, 169.5, 101.6, 99.4, 81.1, 72.5, 72.0, 71.6, 70.3, 68.5, 68.4, 68.2, 62.5, 61.8, 55.3, 26.0, 20.9, 20.8, 20.7, 20.7, 18.4, -5.2, -5.3. **R_f:** 0.35 (isopropanol/toluene 1:9). **IR (Powder, cm^{-1}):** 3527 (w), 2931 (w), 2856 (w), 1747 (s), 1434 (w), 1366 (m), 1215 (s), 1147 (m), 1034 (s). **HRMS (ESI, m/z):** Calculated for $C_{27}H_{50}NO_{15}Si$ ((M+NH$_4$)$^+$): 656.2950; Found: 656.2958.



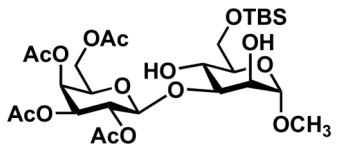
1,6-Anhydro-4-*O*-(2',3',4',6'-tetra-*O*-acetyl-*β*-*D*-glucopyranosyl)-*β*-*D*-galactopyranoside (3d). Synthesized according to general procedure A at 60 °C, from 2,3,4,6-tetra-*O*-acetyl-*α*-*D*-glucopyranosyl bromide (1.0 mmol) and 1,6-anhydro-*β*-*D*-galactopyranose, 73% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.38 (dd, J = 1.2, 1.2 Hz, 1H, *H*-1), 5.23 (dd, J = 9.6, 9.6 Hz, 1H, *H*-3'), 5.05 (dd, J = 10.0, 9.2 Hz, 1H, *H*-4'), 5.00 (dd, J = 9.6, 8.0 Hz, 1H, *H*-2'), 4.69 (d, J = 8.0 Hz, 1H, *H*-1'), 4.54 (apparent t, J = 5.2 Hz, 1H, *H*-5), 4.29 (d, J = 7.6 Hz, 1H, *H*-6a), 4.22 (dd, J = 12.0, 4.8 Hz, 1H, *H*-6a'), 4.16 (dd, J = 12.0, 2.4 Hz, 1H, *H*-6b'), 4.04–4.00 (m, 2H, *H*-4 and *H*-3), 3.83 (br s, 1H, *H*-2), 3.74 (ddd, J = 10, 4.8, 2.4 Hz, 1H, *H*-5'), 3.67 (dd, J = 7.2, 5.2 Hz, 1H, *H*-6b), 2.46 (br s, 1H, C$_3$-O*H*), 2.09–2.08 (m, 1H, C$_2$-O*H*), 2.09 (s, 3H, OCOCH_3), 2.05 (s, 3H, OCOCH_3), 2.03 (s, 3H, OCOCH_3), 2.01 (s, 3H, OCOCH_3). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.7, 170.2, 169.8, 169.5, 101.4, 100.7, 73.9, 73.3, 72.4, 72.3, 71.7, 71.5, 70.0, 68.4, 64.5, 61.9, 20.8, 20.8, 20.7, 20.7. **R_f:** 0.25 (isopropanol/toluene 3:17). **IR (Powder, cm^{-1}):** 3472 (w), 2940 (w), 1747 (s), 1725 (s), 1435 (w), 1368 (m), 1228 (s), 1207 (s), 1122 (m), 1034 (s). **HRMS (ESI, m/z):** Calculated for $C_{20}H_{32}NO_{14}$ ((M+NH$_4$)$^+$): 510.1823; Found: 510.1832. **m.p.:** 172–174 °C.



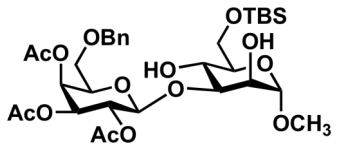
Methyl-3-*O*-(2',3',4',6'-tetra-*O*-pivaloyl-*β*-*D*-glucopyranosyl)-*α*-*L*-fucopyranoside (3e). Synthesized according to general procedure A, from 2,3,4,6-tetra-*O*-pivaloyl-*α*-*D*-glucopyranosyl bromide (1.0 mmol) and methyl-*α*-*L*-fucopyranose, 81% yield, white solid. Inseparable unidentified regioisomer, 9% yield, ^{1}H NMR peaks visible at δ 4.66 (d, J = 4.0 Hz, 1H), 4.60 (d, J = 8.0 Hz, 1H). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.34 (dd, J = 9.6, 9.6 Hz, 1H, *H*-3'), 5.15 (dd, J = 10.0, 9.6 Hz, 1H, *H*-4'), 5.08 (dd, J = 9.6, 8.0 Hz, 1H, *H*-2'), 4.82 (d, J = 3.6 Hz, 1H, *H*-1), 4.69 (d, J = 7.6 Hz, 1H, *H*-1'), 4.30 (dd, J = 12.8, 2.0 Hz, 1H, *H*-6a'), 4.03 (dd, J = 12.4, 4.8 Hz, 1H, *H*-6b'), 3.95 (ddd, J = 10.0, 8.0, 4.0 Hz, 1H, *H*-2), 3.89 (q, J = 6.8 Hz, 1H, *H*-5), 3.81 (dd, J = 9.6, 3.2 Hz, 1H, *H*-3), 3.76 (ddd, J = 10.0, 4.8, 1.6 Hz, 1H, *H*-5'), 3.68 (ddd, J = 3.2, 1.6, 1.6 Hz, 1H, *H*-4), 3.40 (s, 3H, OCH_3), 3.10 (d, J = 4.0 Hz, 1H, C_2-O*H*), 2.22 (dd, J = 1.6, 1.6 Hz, 1H, C_4-O*H*), 1.28 (d, J = 6.8 Hz, 3H, CH_3), 1.22 (s, 9H, OCOC(CH_3)$_3$), 1.16 (s, 9H, OCOC(CH_3)$_3$), 1.14 (s, 9H, OCOC(CH_3)$_3$), 1.11 (s, 9H, OCOC(CH_3)$_3$). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 178.2, 177.2, 177.1, 176.4, 100.8, 99.6, 81.9, 72.7, 72.0, 71.6, 70.8, 67.5, 67.2, 65.2, 61.3, 55.5, 39.1, 39.0, 38.9, 38.9, 27.3, 27.3, 27.2, 27.2, 16.1. **R_f:** 0.2 (isopropanol/toluene 1:19). **IR (Powder, cm^{-1}):** 3562 (w), 2970 (w), 1730 (s), 1482 (m), 1279 (m), 1141 (s), 1082 (s), 1037 (s). **HRMS (ESI, m/z):** Calculated for $C_{33}H_{60}NO_{14}$ ((M+NH_4)$^+$): 694.4014; Found: 694.3983. **m.p.:** 210–211 °C.



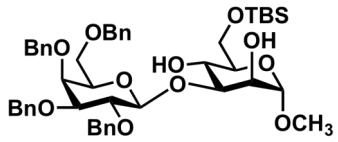
Methyl-3-*O*-(2',3',4',6'-tetra-*O*-acetyl-*β*-*D*-galactopyranosyl)-*β*-*D*-arabinopyranoside (3f). Synthesized according to general procedure A, from 2,3,4,6-tetra-*O*-acetyl-*α*-*D*-galactopyranosyl bromide (1.0 mmol) and methyl-*β*-*D*-arabinopyranose, 78% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.40 (dd, J = 3.6, 1.2 Hz, 1H, *H*-4'), 5.24 (dd, J = 10.8, 8.0 Hz, 1H, *H*-2'), 5.03 (dd, J = 10.4, 3.2 Hz, 1H, *H*-3'), 4.85 (d, J = 3.6 Hz, 1H, *H*-1), 4.61 (d, J = 8.0 Hz, 1H, *H*-1'), 4.17 (dd, J = 11.2, 6.0 Hz, 1H, *H*-6a'), 4.13 (dd, J = 11.6, 7.2 Hz, 1H, *H*-6b'), 4.01 (ddd, J = 9.2, 3.6, 3.6 Hz, 1H, *H*-2), 3.97 (ddd, J = 7.2, 6.4, 1.2 Hz, 1H, *H*-5'), 3.89 (m, 1H, *H*-4), 3.84 (dd, J = 9.2, 3.6 Hz, 1H, *H*-3), 3.80–3.76 (m, 1H, *H*-5a), 3.73 (dd, J = 12.4, 2.0 Hz, 1H, *H*-5b), 3.43 (s, 3H, OCH_3), 3.20 (d, J = 3.6 Hz, 1H, C_2-O*H*), 2.43 (br s, 1H, C_4-O*H*), 2.16 (s, 3H, OCOCH_3), 2.08 (s, 3H, OCOCH_3), 2.06 (s, 3H, OCOCH_3), 1.99 (s, 3H, OCOCH_3). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.5, 170.2, 170.1, 169.9, 101.8, 99.8, 82.1, 71.4, 70.6, 69.3, 68.4, 67.7, 66.9, 61.7, 61.5, 55.6, 20.9, 20.8, 20.7, 20.7. **R_f:** 0.2 (isopropanol/toluene 1:9). **IR (Powder, cm^{-1}):** 3507 (w), 2934 (w), 1741 (s), 1432 (w), 1368 (m), 1214 (s), 1139 (m), 1054 (s). **HRMS (ESI, m/z):** Calculated for $C_{20}H_{34}NO_{14}$ ((M+NH_4)$^+$): 512.1979; Found: 512.1961.



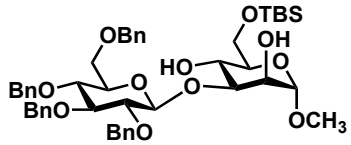
Methyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-(2',3',4',6'-tetra-*O*-acetyl-*β*-*D*-galactopyranosyl)-*α*-*D*-mannopyranoside (3g). Synthesized according to general procedure A, from 2,3,4,6-tetra-*O*-acetyl-*α*-*D*-galactopyranosyl bromide (1.0 mmol) and methyl-6-*O*-*tert*-butyldimethylsilyl-*α*-*D*-mannopyranoside, 80% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.40 (dd, J = 3.4, 0.9 Hz, 1H, *H*-4'), 5.25 (dd, J = 10.5, 8.0 Hz, 1H, *H*-2'), 5.03 (dd, J = 10.5, 3.4 Hz, 1H, *H*-3'), 4.74 (d, J = 1.4 Hz, 1H, *H*-1), 4.56 (d, J = 8.0 Hz, 1H, *H*-1'), 4.18–4.08 (m, 2H, *H*-6a' and *H*-6b'), 4.01–3.95 (m, 2H, *H*-3 and *H*-5'), 3.84–3.79 (m, 2H, *H*-2 and *H*-6a), 3.76 (dd, J = 9.4, 1.2 Hz, 1H, *H*-6b), 3.69 (dd, J = 8.9, 3.3 Hz, 1H, *H*-4), 3.56–3.52 (m, 1H, *H*-5), 3.42 (d, J = 1.3 Hz, 1H, C_4-O*H*), 3.38 (s, 3H, OCH_3), 2.22 (d, J = 2.7 Hz, 1H, C_2-O*H*), 2.16 (s, 3H, COCH_3), 2.08 (s, 3H, COCH_3), 2.06 (s, 3H, COCH_3), 1.99 (s, 3H, COCH_3), 0.90 (s, 9H, Si(C(CH_3)$_3$)(CH_3)$_2$), 0.08 (s, 6H, Si(C(CH_3)$_3$)(CH_3)$_2$). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.6, 170.2, 170.1, 169.9, 102.2, 100.2, 84.6, 72.7, 71.4, 70.6, 70.1, 69.2, 67.0, 66.2, 63.3, 61.7, 54.8, 26.1, 20.9, 20.8, 20.7, 20.7, 18.5, -5.1. **R_f:** 0.2 (ethyl acetate/pentane 40:60). **IR (Powder, cm^{-1}):** 3481 (br), 2929 (w), 2857 (w), 1747 (s), 1369 (m), 1215 (s), 1049 (s), 835 (m), 777 (m). **HRMS (ESI, m/z):** Calculated for $C_{27}H_{50}NO_{15}Si$ ((M+NH_4)$^+$): 656.2950; Found: 656.2966.



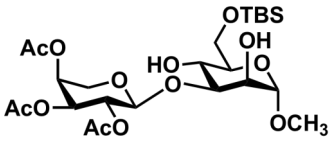
Methyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-(2',3',4'-tri-*O*-acetyl-6'-*O*-benzyl-*β*-*D*-galactopyranosyl)-*α*-*D*-mannopyranoside (3h). Synthesized according to general procedure A, from 2,3,4-tri-*O*-acetyl-6-*O*-benzyl-*α*-*D*-galactopyranosyl bromide (0.20 mmol) and methyl-6-*O*-*tert*-butyldimethylsilyl-*α*-*D*-mannopyranoside, 75% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.36–7.27 (m, 5H, Ph*H*), 5.43 (dd, J = 3.4, 0.5 Hz, 1H, *H*-4'), 5.23 (dd, J = 10.5, 7.9 Hz, 1H, *H*-2'), 5.02 (dd, J = 10.5, 3.4 Hz, 1H, *H*-3'), 4.74 (d, J = 1.2 Hz, 1H, *H*-1), 4.57–4.54 (m, 2H, *H*-1' and OC*H*Ph), 4.43 (d, J = 11.9 Hz, 1H, OC*H*Ph), 3.97–3.91 (m, 2H, *H*-6a and *H*-5'), 3.83–3.76 (m, 3H, *H*-2, *H*-3 and *H*-6b), 3.72 (dd, J = 9.0, 3.3 Hz, 1H, *H*-4), 3.60 (d, J = 1.4 Hz, 1H, C_4-O*H*), 3.57–3.53 (m, 2H, *H*-5 and *H*-6a'), 3.48 (dd, J = 9.6, 5.5 Hz, 1H, *H*-6b'), 3.37 (s, 3H, OCH_3), 2.23 (d, J = 3.1 Hz, 1H, C_2-O*H*), 2.08 (s, 3H, COCH_3), 2.07 (s, 3H, COCH_3), 1.99 (s, 3H, COCH_3), 0.90 (s, 9H, Si(C(CH_3)$_3$)(CH_3)$_2$), 0.08 (s, 6H, Si(C(CH_3)$_3$)(CH_3)$_2$). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.2, 170.1, 170.0, 137.3, 128.6, 128.1, 128.1, 101.9, 100.1, 84.2, 73.8, 72.7, 72.6, 70.8, 70.1, 69.4, 67.7, 67.4, 66.2, 63.2, 54.7, 26.1, 20.9, 20.8, 20.7, 18.5, -5.1. **R_f:** 0.3 (ethyl acetate/pentane 30:70). **IR (Powder, cm^{-1}):** 3483 (br), 2929 (w), 2857 (w), 1747 (s), 1368 (m), 1216 (s), 1057 (s), 835 (m), 778 (m), 698 (w). **HRMS (ESI, m/z):** Calculated for $C_{32}H_{54}NO_{14}Si$ ((M+NH_4)$^+$): 704.3314; Found: 704.3316.



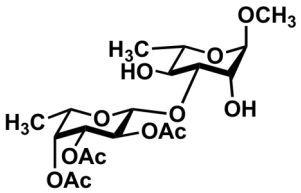
Methyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-(2',3',4',6'-tetra-*O*-benzyl-*β*-*D*-galactopyranosyl)-*α*-*D*-mannopyranoside (3i). Synthesized according to general procedure A, from 2,3,4,6-tetra-*O*-benzyl-*α*-*D*-galactopyranosyl chloride (0.30 mmol) and methyl-6-*O*-*tert*-butyldimethylsilyl-*α*-*D*-mannopyranoside, 68% yield, viscous yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.36–7.27 (m, 20H, Ph*H*), 4.93 (d, J = 11.7 Hz, 1H, OC*H*Ph), 4.88 (d, J = 10.8 Hz, 1H, OC*H*Ph), 4.83 (d, J = 11.2 Hz, 1H, OC*H*Ph), 4.74–4.73 (m, 3H, *H*-1, OC*H*Ph, and OC*H*Ph), 4.60 (d, J = 11.7 Hz, 1H, OC*H*Ph), 4.45 (d, J = 12.0 Hz, 1H, OC*H*Ph), 4.44 (d, J = 7.6 Hz, 1H, *H*-1'), 4.38 (d, J = 11.6 Hz, 1H, OC*H*Ph), 3.98–3.76 (m, 8H, *H*-6a, *H*-2, *H*-6b, *H*-3, *H*-2', *H*-3', *H*-4', and *H*-5'), 3.61–3.52 (m, 4H, *H*-6a', *H*-4, *H*-5 and C_4-O*H*), 3.41 (dd, J = 12.4, 8.4 Hz, 1H, *H*-6b'), 3.35 (s, 3H, OCH_3), 2.22 (d, J = 4.0 Hz, C_2-O*H*), 0.90 (s, 9H, Si(C(CH_3)$_3$)(CH$_3$)$_2$), 0.08 (s, 6H, Si(C(CH$_3$)$_3$)(CH_3)$_2$). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 138.4, 138.3, 138.3, 137.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.2, 128.2, 128.0, 127.9, 127.9, 127.8, 127.8, 103.5, 100.4, 83.5, 82.6, 79.0, 75.7, 74.7, 74.0, 73.8, 73.3, 73.2, 72.9, 70.0, 68.9, 66.0, 63.2, 54.7, 26.1, 18.5, -5.1. **R_f:** 0.2 (ethyl acetate/pentane 20:80). **IR (Neat, cm^{-1}):** 3452 (br), 2928 (w), 2857 (w), 1454 (w), 1362 (w), 1251 (w), 1057 (s), 835 (m), 733 (s), 696 (s). **HRMS (ESI, m/z):** Calculated for $C_{47}H_{66}NO_{11}Si$ ((M+NH$_4$)$^+$): 848.4405; Found: 848.4418.



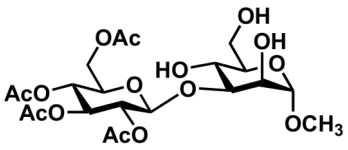
Methyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-(2',3',4',6'-tetra-*O*-benzyl-*β*-*D*-glucopyranosyl)-*α*-*D*-mannopyranoside (3j). Synthesized according to general procedure A, from 2,3,4,6-tetra-*O*-benzyl-*α*-*D*-glucopyranosyl chloride (0.8 mmol) and methyl-6-*O*-*tert*-butyldimethylsilyl-*α*-*D*-mannopyranoside, 71% yield, viscous colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.34–7.14 (m, 20H, Ph*H*), 4.92 (d, J = 10.9 Hz, 2H, OC*H*Ph and OC*H*Ph), 4.83–4.77 (m, 3H, OC*H*Ph, OC*H*Ph, and OC*H*Ph), 4.73 (d, J = 1.5 Hz, 1H, *H*-1), 4.56–4.49 (m, 4H, OC*H*Ph, OC*H*Ph, OC*H*Ph, and *H*-1'), 3.99–3.93 (m, 3H, *H*-2, *H*-5, and *H*-6a), 3.86–3.75 (m, 3H, *H*-3, *H*-6b, and *H*-3'), 3.69–3.64 (m, 2H, *H*-5' and *H*-6a'), 3.58–3.50 (m, 5H, *H*-4, *H*-2', *H*-4', *H*-6b', and C_4-O*H*), 3.36 (s, 3H, OCH_3), 2.13 (d, J = 4.8 Hz, 1H, C_2-O*H*), 0.91 (s, 9H, Si(C(CH_3)$_3$)(CH$_3$)$_2$), 0.09 (s, 6H, Si(C(CH$_3$)$_3$)(CH_3)$_2$). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 138.5, 138.1, 137.9, 137.8, 128.7, 128.6, 128.6, 128.5, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 103.2, 100.4, 84.9, 83.4, 81.8, 77.9, 75.9, 75.3, 75.2, 74.7, 73.7, 72.9, 70.1, 69.0, 66.1, 63.2, 54.8, 26.1, 18.5, -5.1. **R_f:** 0.3 (ethyl acetate/pentane 20:80). **IR (Neat, cm^{-1}):** 3466 (br), 2929 (w), 2857 (w), 1455 (w), 1361 (w), 1251 (w), 1059 (s), 835 (m), 734 (m), 696 (s). **HRMS (ESI, m/z):** Calculated for $C_{47}H_{66}NO_{11}Si$ ((M+NH$_4$)$^+$): 848.4405; Found: 848.4415.



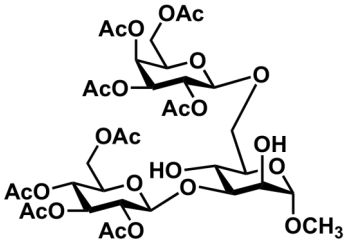
Methyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-(2',3',4'-tri-*O*-acetyl-*α*-*L*-arabinopyranosyl)-*α*-*D*-mannopyranoside (3k). Synthesized according to general procedure A, from 2,3,4-tri-*O*-acetyl-*β*-*L*-arabinopyranosyl chloride (0.50 mmol) and methyl-6-*O*-*tert*-butyldimethylsilyl-*α*-*D*-mannopyranoside, 86% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** *δ* 5.29–5.27 (m, 1H, *H*-4'), 5.24 (dd, *J* = 10.1, 7.5 Hz, 1H, *H*-2'), 5.04 (dd, *J* = 10.1, 3.5 Hz, 1H, *H*-3'), 4.75 (d, *J* = 1.3 Hz, 1H, *H*-1), 4.49 (d, *J* = 7.5 Hz, 1H, *H*-1'), 4.08 (dd, *J* = 13.3, 2.4 Hz, 1H, *H*-5a'), 3.94 (dd, *J* = 11.0, 3.2 Hz, 1H, *H*-3), 3.85–3.81 (m, 2H, *H*-2 and *H*-4), 3.78 (dd, *J* = 9.6, 9.6 Hz, 1H, *H*-6a), 3.74 (dd, *J* = 9.1, 3.3 Hz, 1H, *H*-6b), 3.69 (dd, *J* = 13.3, 1.3 Hz, 1H, *H*-5b'), 3.58–3.53 (m, 1H, *H*-5), 3.37 (s, 3H, OCH_3), 3.34 (d, *J* = 0.7 Hz, 1H, C_4-O*H*), 2.19 (d, *J* = 3.1 Hz, 1H, C_2-O*H*), 2.15 (s, 3H, COCH_3), 2.09 (s, 3H, COCH_3), 2.03 (s, 3H, COCH_3), 0.90 (s, 9H, Si(C(CH_3)$_3$)(CH$_3$)$_2$), 0.08 (s, 6H, Si(C(CH$_3$)$_3$)(CH_3)$_2$). **^{13}C NMR (100 MHz, $CDCl_3$):** *δ* 170.4, 170.2, 170.0, 101.7, 100.2, 83.2, 72.3, 70.3, 69.7, 69.6, 67.7, 66.4, 64.4, 63.6, 54.8, 26.1, 21.1, 20.9, 20.8, 18.5, -5.2. **R_f:** 0.5 (ethyl acetate/pentane 50:50). **IR (Powder, cm^{-1}):** 3503 (br), 2929 (w), 2856 (w), 1745 (s), 1370 (m), 1218 (s), 1049 (s), 835 (s), 777 (m). **HRMS (ESI, m/z):** Calculated for $C_{24}H_{46}NO_{13}Si$ ((M+NH$_4$)$^+$): 584.2738; Found: 584.2729.



Methyl-3-*O*-(2',3',4'-tri-*O*-acetyl-*β*-*L*-fucopyranosyl)-*α*-*L*-rhamnopyranoside (3l). Synthesized according to general procedure A, from 2,3,4-tri-*O*-acetyl-*α*-*L*-fucopyranosyl chloride (0.20 mmol) and methyl-*α*-*L*-rhamnopyranoside at 40 ºC, 71% yield, white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** *δ* 5.26 (dd, *J* = 3.4, 0.7 Hz, 1H, *H*-4'), 5.20 (dd, *J* = 10.5, 7.9 Hz, 1H, *H*-2'), 5.03 (dd, *J* = 10.5, 3.4 Hz, 1H, *H*-3'), 4.70 (d, *J* = 1.3 Hz, 1H, *H*-1), 4.50 (d, *J* = 7.9 Hz, 1H, *H*-1'), 3.89 (qd, *J* = 6.4, 0.7 Hz, 1H, *H*-5'), 3.83–3.81 (m, 1H, *H*-2), 3.65–3.54 (m, 3H, *H*-3, *H*-4 and *H*-5), 3.50 (s, 1H, C_4-O*H*), 3.37 (s, 3H, OCH_3), 2.28 (d, *J* = 1.9 Hz, 1H, C_2-O*H*), 2.18 (s, 3H, COCH_3), 2.08 (s, 3H, COCH_3), 2.00 (s, 3H, COCH_3), 1.35 (d, *J* = 5.9 Hz, 3H, C_6-CH_3), 1.24 (d, *J* = 6.4 Hz, 3H, C_6'-CH_3). **^{13}C NMR (100 MHz, $CDCl_3$):** *δ* 170.6, 170.2, 170.2, 102.0, 100.2, 84.0, 70.9, 70.9, 70.4, 69.9, 69.9, 69.4, 67.7, 54.9, 21.0, 20.8, 20.8, 17.8, 16.1. **R_f:** 0.3 (ethyl acetate/pentane 60:40). **IR (Powder, cm^{-1}):** 3425 (br), 2977 (w), 2908 (w), 1746 (s), 1368 (m), 1219 (s), 1135 (m), 1060 (s), 911 (m), 811 (w). **HRMS (ESI, m/z):** Calculated for $C_{19}H_{34}NO_{12}$ ((M+NH$_4$)$^+$): 468.2081; Found: 468.2090. **m.p.:** 170–172 °C.

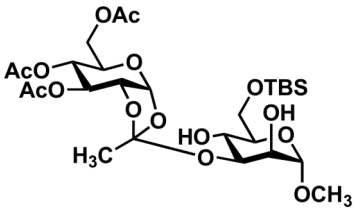


Methyl-3-*O*-(2',3',4',6'-tetra-*O*-acetyl-*β*-*D*-glucopyranosyl)-*α*-*D*-mannopyranoside. An 80% aqueous acetic acid solution (14.5 mL) was added to a stirred solution of **3a** (0.61 mmol, 0.39 g) in acetonitrile (7.3 mL). The solution was stirred at 40 ºC for 18 hours, cooled to room temperature then diluted in ethyl acetate and washed twice with brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography to yield the TBS-deprotected product as a white solid in 75% yield. **^{1}H NMR (400MHz, $CDCl_3$):** δ 5.23 (dd, *J* = 9.6, 9.6 Hz, 1H, *H*-3'), 5.05–5.00 (m, 2H, *H*-4' and *H*-2'), 4.74 (d, *J* = 1.2 Hz, 1H, *H*-1), 4.61 (d, *J* = 8.0 Hz, 1H, *H*-1'), 4.22 (dd, *J* = 12.4, 2.8 Hz, 1H, *H*-6a'), 4.14 (dd, *J* = 12.4, 6.4 Hz, 1H, *H*-6b'), 3.93–3.83 (m, 4H, *H*-6a, *H*-6b, *H*-4 and *H*-2), 3.79 (ddd, *J* = 9.6, 6.4, 2.4 Hz, 1H, *H*-5'), 3.72 (dd, *J* = 9.2, 3.6 Hz, 1H, *H*-3), 3.59–3.55 (m, 2H, *H*-5 and C_4-O*H*), 3.37 (s, 3H, OCH_3), 2.76 (br s, 1H, C_2-O*H*), 2.48 (br s, 1H, C_6-O*H*), 2.08 (s, 3H, OCOCH_3), 2.06 (s, 3H, OCOCH_3), 2.03 (s, 3H, OCOCH_3), 2.01 (s, 3H, OCOCH_3). **^{13}C NMR (100MHz, $CDCl_3$):** δ 170.7, 170.2, 169.9, 169.5, 101.6, 100.4, 84.4, 72.3, 72.2, 71.6, 71.6, 70.1, 68.6, 66.3, 62.6, 62.1, 55.0, 20.8, 20.7, 20.7, 20.7. **R_f:** 0.25 (isopropanol/toluene 1:5). **IR (Powder, cm^{-1}):** 2922, 1754, 1369, 1212, 1130, 1053, 1029, 970, 805. **HRMS (ESI, m/z):** Calculated for $C_{21}H_{32}O_{15}Na$ ($M+Na^+$): 547.1633; Found: 547.1627. **m.p.:** 68–70 °C.

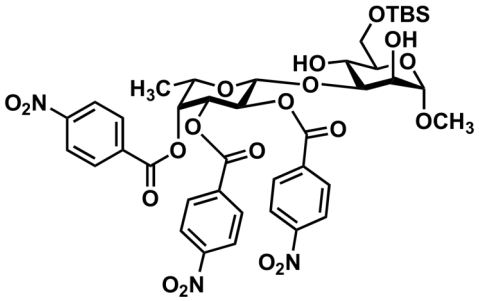


Methyl-3-*O*-(2',3',4',6'-tetra-*O*-acetyl-*β*-*D*-glucopyranosyl)-6-*O*-(2'',3'',4'',6''-tetra-*O*-acetyl-*β*-*D*-galactopyranosyl)-*α*-*D*-mannopyranoside (3m). Synthesized according to general procedure A in an oven-dried 2-dram vial from 2,3,4,6-tetra-*O*-acetyl-*α*-*D*-galactopyranosyl bromide (0.20 mmol) and methyl-3-*O*-(2',3',4',6'-tetra-*O*-acetyl-*β*-*D*-glucopyranosyl)-*α*-*D*-mannopyranoside, 88% yield, white solid. **^{1}H NMR (400MHz, $CDCl_3$):** *δ* 5.38 (dd, *J* = 3.2, 0.8 Hz, 1H, *H*-4''), 5.26–5.21 (m, 2H, *H*-2'' and *H*-3'), 5.05–4.98 (m, 3H, *H*-4', *H*-2' and *H*-3''), 4.71 (d, *J* = 1.6 Hz, 1H, *H*-1), 4.59 (d, *J* = 8.0 Hz, 1H, *H*-1'), 4.58 (d, *J* = 8.0 Hz, 1H, *H*-1''), 4.25–4.10 (m, 5H, *H*-6a', *H*-6b', *H*-6a'', *H*-6b'' and *H*-6a), 3.91 (ddd, *J* = 6.4, 6.4, 0.8 Hz, 1H, *H*-5''), 3.81–3.68 (m, 6H, *H*-6b, *H*-2, *H*-3, *H*-5', *H*-4 and *H*-5), 3.36 (s, 3H, OCH_3), 3.34 (br s, 1H, C_4-O*H*), 2.30 (d, *J* = 3.6 Hz, 1H, C_2-O*H*), 2.13 (s, 3H, OCOCH_3), 2.08 (s, 3H, OCOCH_3), 2.06 (s, 3H, OCOCH_3), 2.04 (s, 3H, OCOCH_3), 2.04 (s, 3H, OCOCH_3), 2.03 (s, 3H, OCOCH_3), 2.01 (s, 3H, OCOCH_3), 1.97 (s, 3H, OCOCH_3). **^{13}C NMR (100MHz, $CDCl_3$):** *δ* 170.7, 170.5, 170.4, 170.3, 170.2, 169.8, 169.7, 169.5, 102.0, 101.5, 100.2, 84.2, 72.3, 72.2, 71.5, 71.1, 71.0, 70.7, 69.9, 69.5, 69.1, 68.5, 67.2, 65.9, 62.0, 61.4, 55.0, 20.9, 20.8, 20.8, 20.8, 20.7, 20.7, 20.7, 20.7. **R_f:** 0.2 (isopropanol/toluene 1:9). **IR (Powder, cm^{-1}):** 2942

(w), 1740 (s), 1367 (m), 1212 (s), 1132 (m), 1033 (s). **HRMS (ESI, m/z):** Calculated for $C_{35}H_{50}O_{24}Na$ ($(M+Na)^+$): 877.2584; Found: 877.2600. **m.p.:** 90–91 °C.

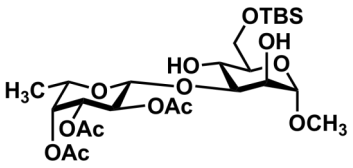


Methyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-(3',4',6'-tri-*O*-acetyl-α-*D*-glucopyranose-1,2-orthoacetyl)-α-*D*-mannopyranoside (4a). 2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl bromide (1.0 mmol, 0.41 g), **2a** (1.1 mmol, 0.34 g), silver (I) oxide (1.0 mmol, 0.23 g) and phenylboronic acid (0.10 mmol, 12 mg) were added to an oven-dried round bottom flask, under an argon atmosphere. Dry acetonitrile (7.5 mL) was added and the resulting mixture was stirred at room temperature. After 16 hours, the mixture was quenched with a few drops of methanol, diluted with dichloromethane and filtered through a plug of celite. The resulting crude material was purified by silica gel chromatography to yield **4a** as a white solid in 15% yield. **^{1}H NMR (400MHz, $CDCl_3$):** δ 5.86 (d, J = 5.2 Hz, 1H, *H*-1'), 5.18 (apparent t, J = 3.2 Hz, 1H, *H*-3'), 4.91 (ddd, J = 9.6, 3.2, 0.4 Hz, 1H, *H*-4'), 4.68 (d, J = 1.6 Hz, 1H, *H*-1), 4.46 (ddd, J = 5.2, 3.2, 0.8 Hz, 1H, *H*-2'), 4.22 (dd, J = 12.4, 5.2 Hz, 1H, *H*-6a'), 4.17 (dd, J = 12.4, 2.8 Hz, 1H, *H*-6b'), 3.96–3.76 (m, 6H, *H*-5', *H*-2, *H*-3, *H*-6a, *H*-6b and *H*-4), 3.60 (ddd, J = 9.6, 5.6, 5.6 Hz, 1H, *H*-5), 3.37 (s, 3H, OCH_3), 3.03 (d, J = 2.0 Hz, 1H, C_4-O*H*), 2.21 (d, J = 3.2 Hz, 1H, C_2-O*H*), 2.11 (s, 3H, $OCOCH_3$), 2.09 (s, 3H, $OCOCH_3$), 2.09 (s, 3H, $OCOCH_3$), 1.80 (s, 3H, $OCOCH_3$), 0.90 (s, 9H, $Si(C(CH_3)_3)(CH_3)_2$), 0.09 (s, 6H, $Si(C(CH_3)_3)(CH_3)_2$). **^{13}C NMR (100MHz, $CDCl_3$):** δ 170.7, 170.2, 169.8, 169.5, 101.5, 100.2, 84.3, 72.6, 72.4, 72.2, 71.5, 70.0, 68.6, 66.2, 63.3, 62.1, 54.8, 26.1, 20.8, 20.7, 20.7, 20.7, 18.5, -5.2. **R_f:** 0.3 (isopropanol/toluene 1:9). **IR (Powder, cm^{-1}):** 3507 (w), 2930 (w), 1749 (s), 1368 (m), 1214 (s), 1135 (m), 1036 (s). **HRMS (ESI, m/z):** Calculated for $C_{27}H_{50}NO_{15}Si$ ($(M+NH_4)^+$): 656.2950; Found: 656.2948.



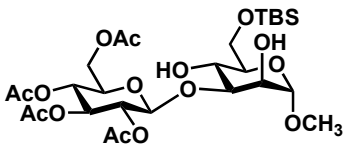
Methyl-3-*O*-(2',3',4'-tri-*O*-*para*-nitrobenzoyl-β-*L*-fucopyranosyl)-α-*D*-mannopyranoside. Synthesized according to general procedure A, from 2,3,4-tri-*O*-*para*-nitrobenzoyl-α-*L*-fucopyranosyl bromide (0.10 mmol) and methyl 6-*O*-*tert*-butyldimethylsilyl-α-*D*-mannopyranoside, 40% yield, white solid. **^{1}H NMR (400MHz, $CDCl_3$):** δ 8.39–8.36 (m, 2H, OC*H*Ph), 8.28–8.20 (m,

4H, OC*H*Ph), 8.18–8.13 (m, 4H, OC*H*Ph), 7.98–7.94 (m, 2H, OC*H*Ph), 5.73 (dd, *J* = 3.4, 0.8 Hz, 1H, *H*-4'), 5.69 (dd, *J* = 10.5, 7.8 Hz, 1H, *H*-2'), 5.60 (dd, *J* = 10.4, 3.4 Hz, 1H, *H*-3'), 5.16 (d, *J* = 7.8 Hz, 1H, *H*-1'), 4.72 (d, *J* = 1.5 Hz, 1H, *H*-1), 4.17–4.12 (m, 1H, *H*-5'), 4.08–4.06 (m, 1H, *H*-2), 3.92 (dd, *J* = 9.1, 3.4 Hz, 1H, *H*-3), 3.87–3.79 (m, 2H, *H*-6a and *H*-4), 3.71 (dd, *J* = 10.0, 7.6 Hz, 1H, *H*-6b), 3.55 (ddd, *J* = 9.0, 7.7, 4.9 Hz, 1H, *H*-5), 3.38 (s, 3H, OCH_3), 3.14 (d, *J* = 1.0 Hz, 1H, C_4-O*H*), 2.52 (d, *J* = 2.4 Hz, 1H, C_2-O*H*), 1.36 (d, *J* = 6.4 Hz, 3H, CH_3), 0.83 (s, 9H, Si(C(CH_3)$_3$)(CH$_3$)$_2$), 0.04 (s, 3H, Si(C(CH$_3$)$_3$)(CH_3)$_2$), 0.02 (s, 3H, Si(C(CH$_3$)$_3$)(CH_3)$_2$). **R_f:** 0.3 (ethyl acetate/toluene 1:3).



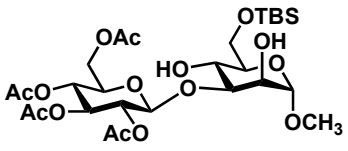
Methyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-(2',3',4'-tri-*O*-acetyl-*β*-*L*-fucopyranosyl)-*α*-*D*-mannopyranoside. Synthesized according to general procedure A, from 2,3,4-tri-*O*-acetyl-*α*-*L*-fucopyranosyl chloride (0.2 mmol) and methyl-6-*O*-*tert*-butyldimethylsilyl-*α*-*D*-mannopyranoside at 40 ºC, 69% yield, white solid. **^{1}H NMR (400 MHz, CDCl$_3$):** *δ* 5.24 (dd, *J* = 3.4, 0.7 Hz, 1H, *H*-4'), 5.20 (dd, *J* = 10.5, 7.9 Hz, 1H, *H*-2'), 5.03 (dd, *J* = 10.5, 3.4 Hz, 1H, *H*-3'), 4.74 (d, *J* = 1.3 Hz, 1H, *H*-1), 4.68 (d, *J* = 7.9 Hz, 1H, *H*-1'), 4.01–3.98 (m, 1H, *H*-2), 3.89–3.80 (m, 4H, *H*-3, *H*-4, *H*-6a, and *H*-5'), 3.77 (dd, *J* = 9.1, 3.4 Hz, 1H, *H*-6b), 3.61–3.56 (m, 1H, *H*-5), 3.37 (s, 3H, OCH_3), 2.88 (d, *J* = 1.6 Hz, 1H, C_4-O*H*), 2.62 (d, *J* = 1.6 Hz, 1H, C_2-O*H*), 2.18 (s, 3H, COCH_3), 2.06 (s, 3H, COCH_3), 1.99 (s, 3H, COCH_3), 1.20 (d, *J* = 6.4 Hz, 3H, C_6'-CH_3), 0.90 (s, 9H, Si(C(CH_3)$_3$)(CH$_3$)$_2$), 0.09 (s, 6H, Si(C(CH$_3$)$_3$)(CH_3)$_2$). **^{13}C NMR (100 MHz, CDCl$_3$):** *δ* 170.6, 170.3, 170.1, 101.8, 100.2, 82.0, 70.9, 70.7, 70.0, 69.4, 69.4, 69.2, 68.6, 64.7, 54.8, 25.8, 20.8, 20.7, 20.6, 18.2, 16.1, -5.4, -5.5. **R_f:** 0.2 (ethyl acetate/pentane 40:60). **IR (Powder, cm^{-1}):** 3511 (br), 2933 (w), 2858 (w), 1747 (s), 1368 (m), 1219 (s), 1053 (s), 972 (m), 835 (s), 777 (m). **HRMS (ESI, m/z):** Calculated for $C_{25}H_{48}NO_{13}Si$ ((M+NH$_4$)$^+$): 598.2895; Found: 598.2875.

VI. ^{1}H, ^{13}C and COSY NMR Spectra



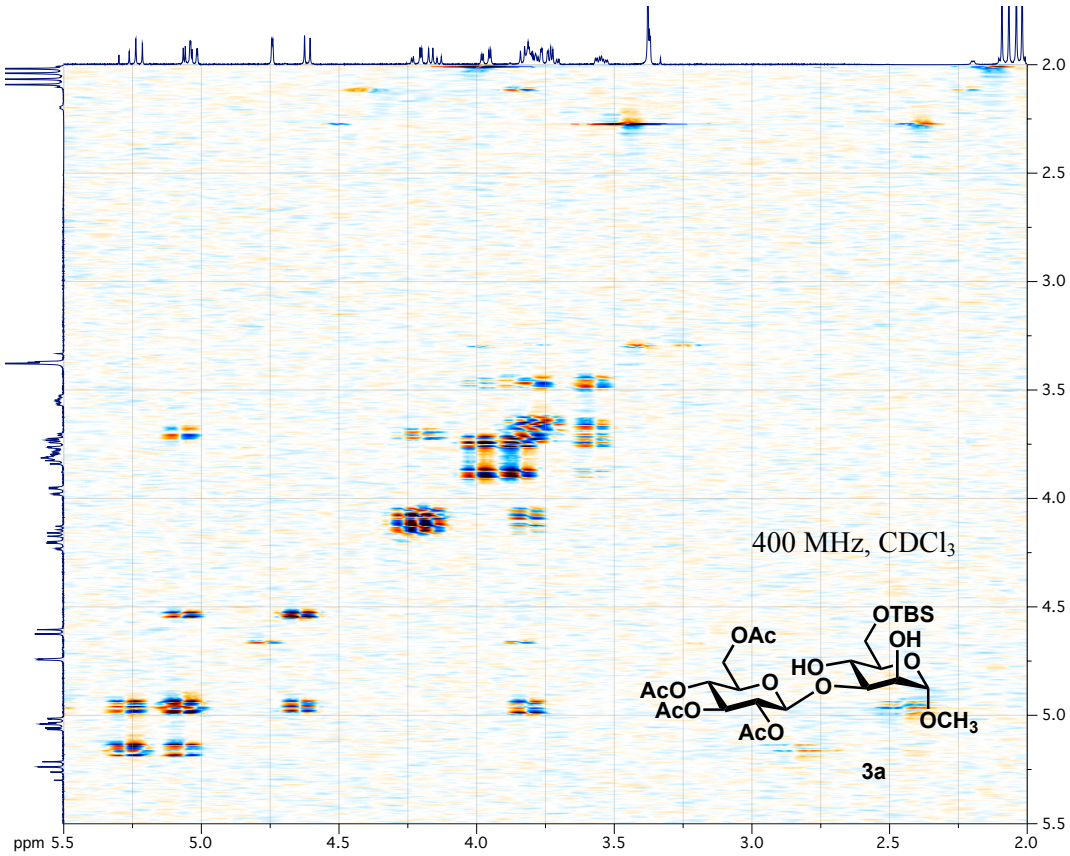
3a

400 MHz, $CDCl_3$

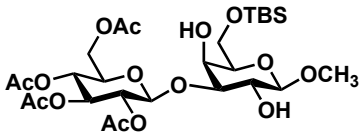


3a

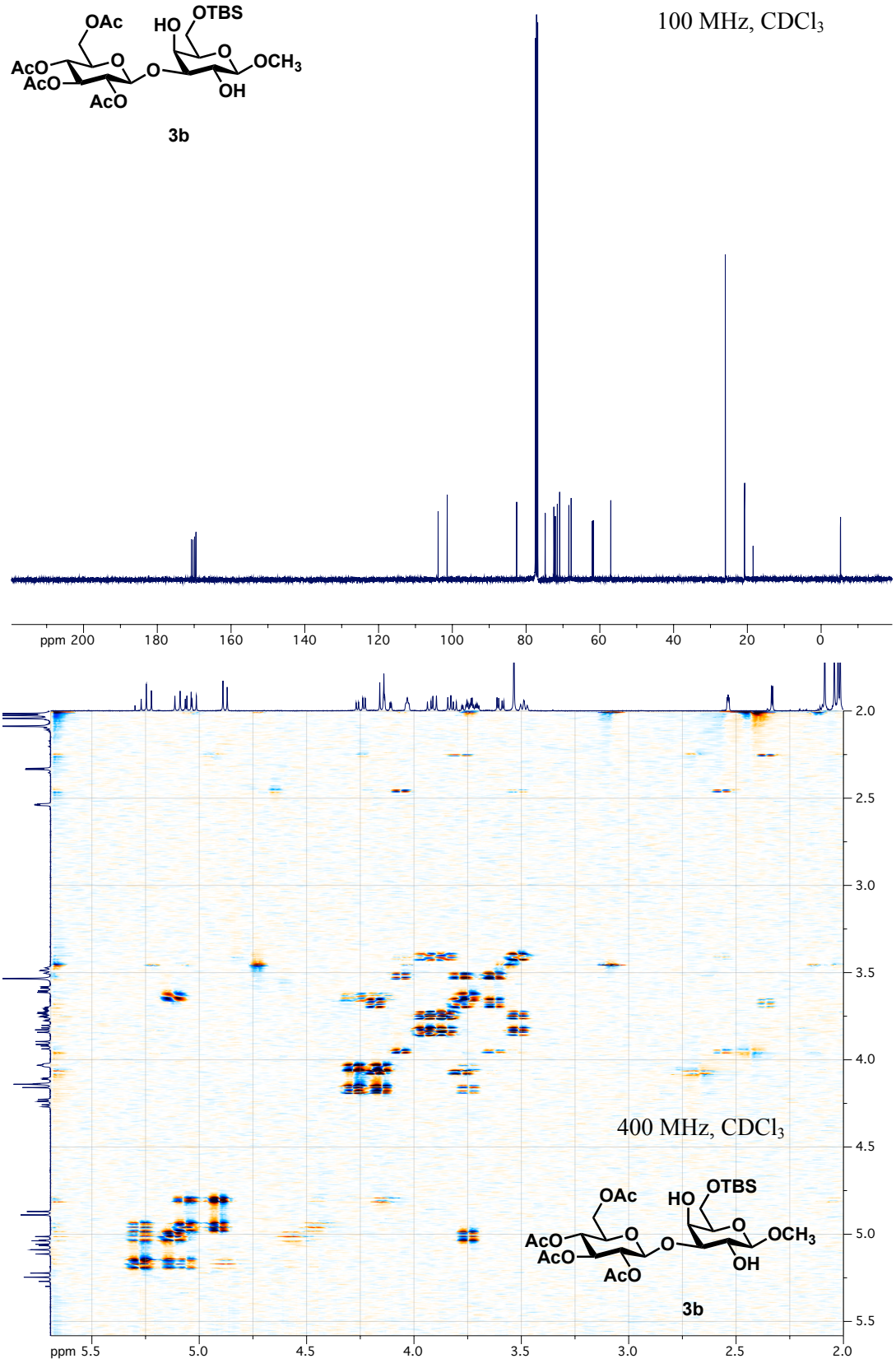
100 MHz, $CDCl_3$



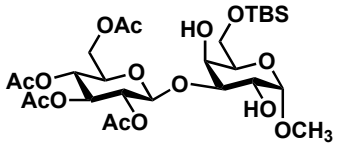
400 MHz, $CDCl_3$



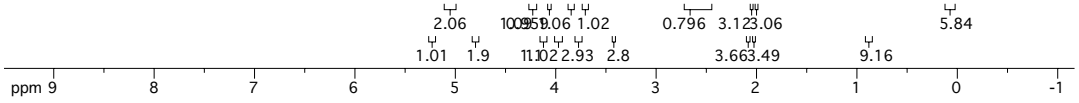
3b


OAc
HO
OTBS
AcO
AcO
AcO
O
O
O
OCH3
OH
3b
100 MHz, CDCl3
ppm 200
180
160
140
120
100
80
60
40
20
0
400 MHz, CDCl3
ppm 5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

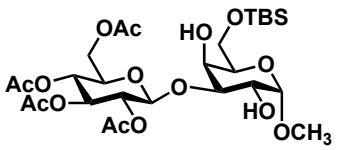
400 MHz, $CDCl_3$



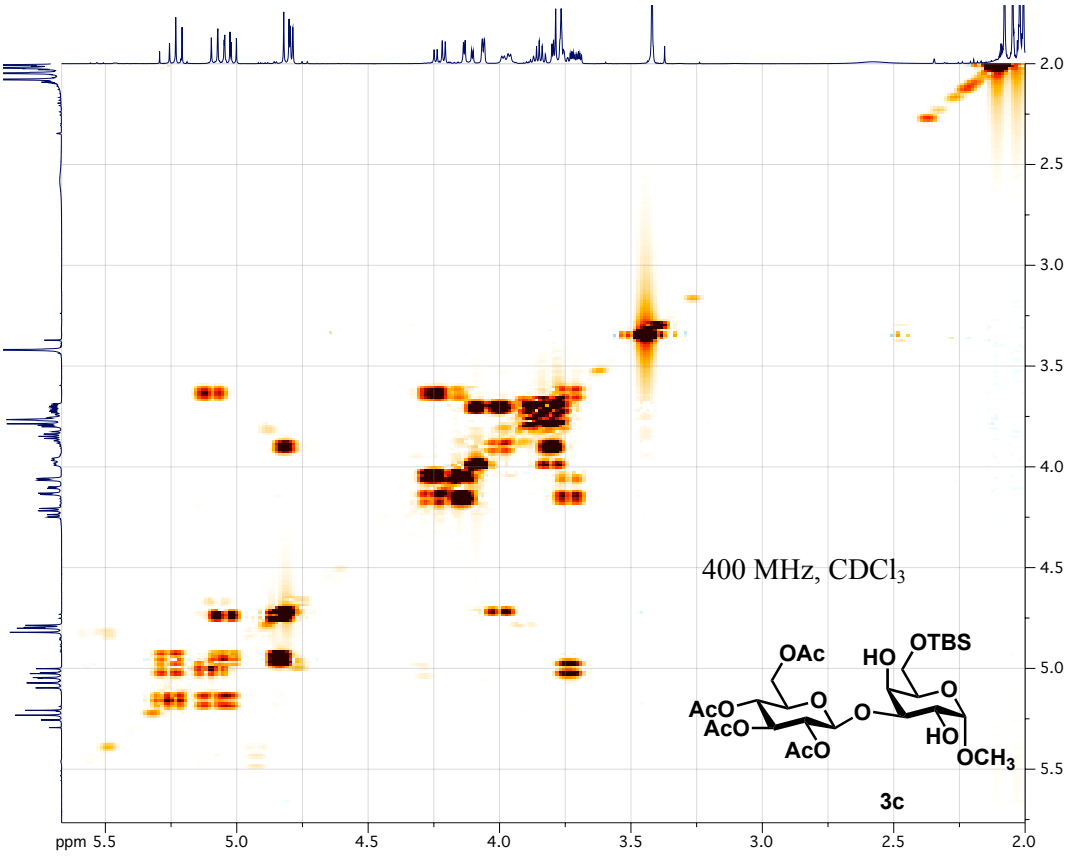
3c

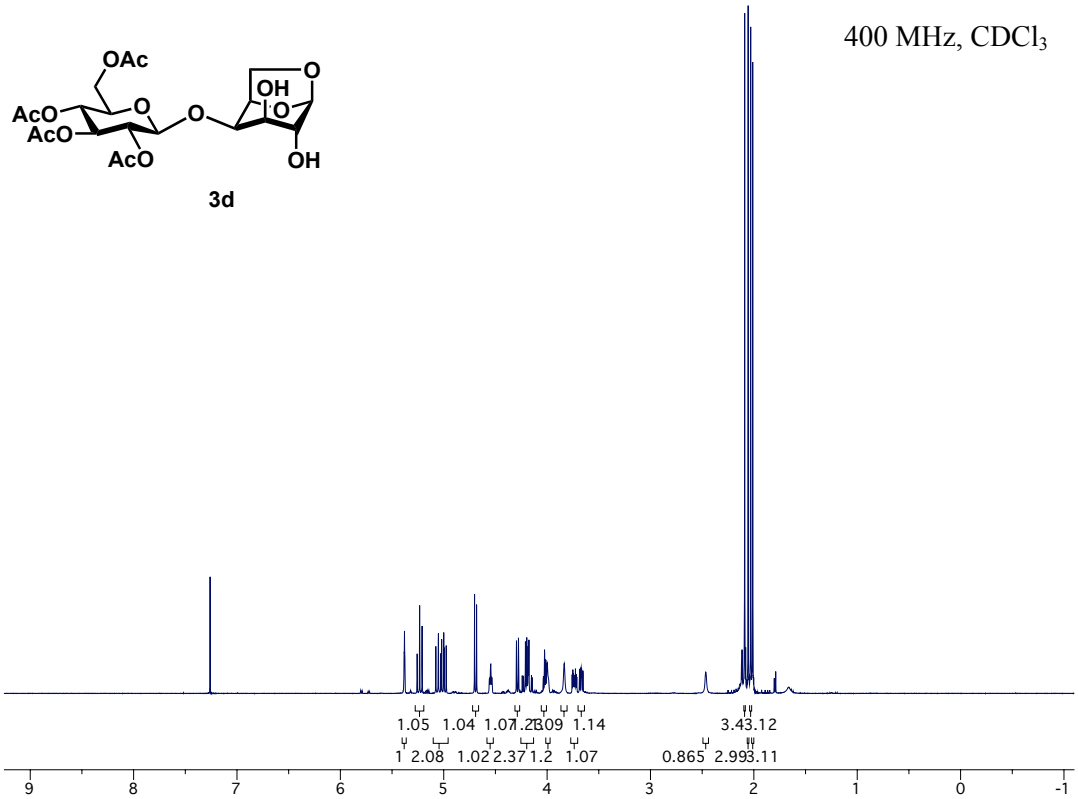


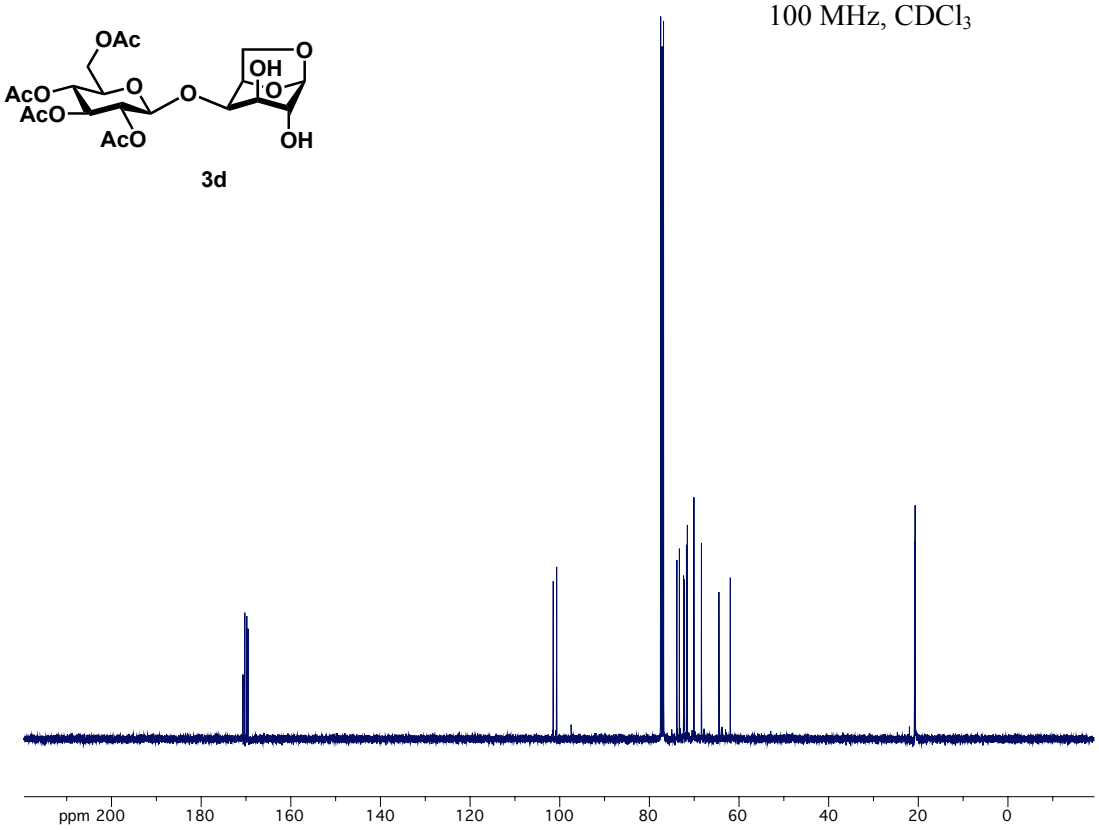
100 MHz, $CDCl_3$

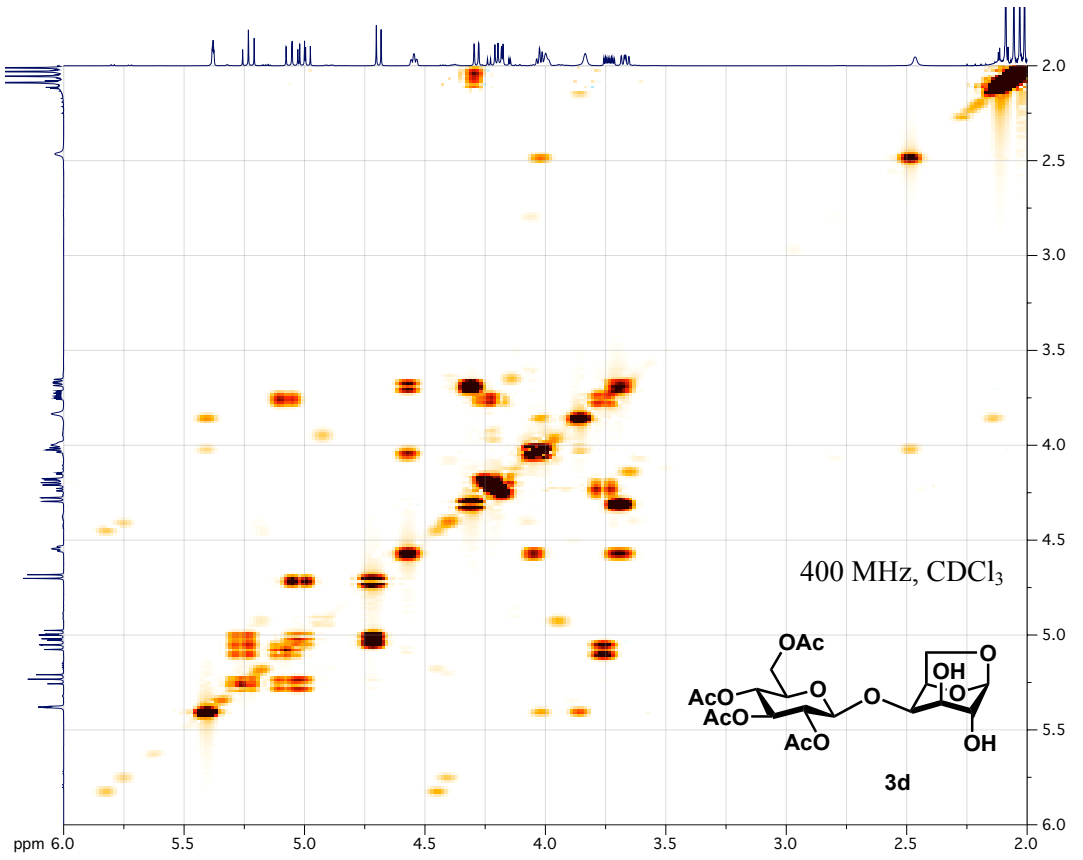


3c

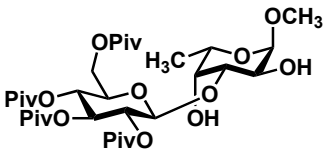

400 MHz, CDCl3
OAc
HO
OTBS
AcO
AcO
AcO
HO
OCH3
3c
ppm 5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0


400 MHz, CDCl3
OAc
AcO
AcO
AcO
OH
OH
3d
1.05 1.04 1.07 1.23 1.09 1.14
3.43 12
1 2.08 1.02 2.37 1.2 1.07
0.865 2.99 3.11

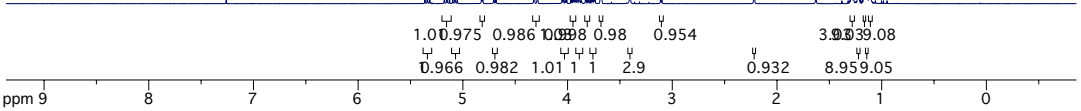

100 MHz, CDCl3
OAc
AcO
AcO
AcO
O
O
OH
O
OH
3d
ppm 200
180
160
140
120
100
80
60
40
20
0


400 MHz, CDCl3
OAc
AcO
AcO
AcO
O
O
OH
O
OH
3d
ppm 6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

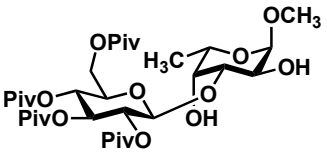
400 MHz, $CDCl_3$



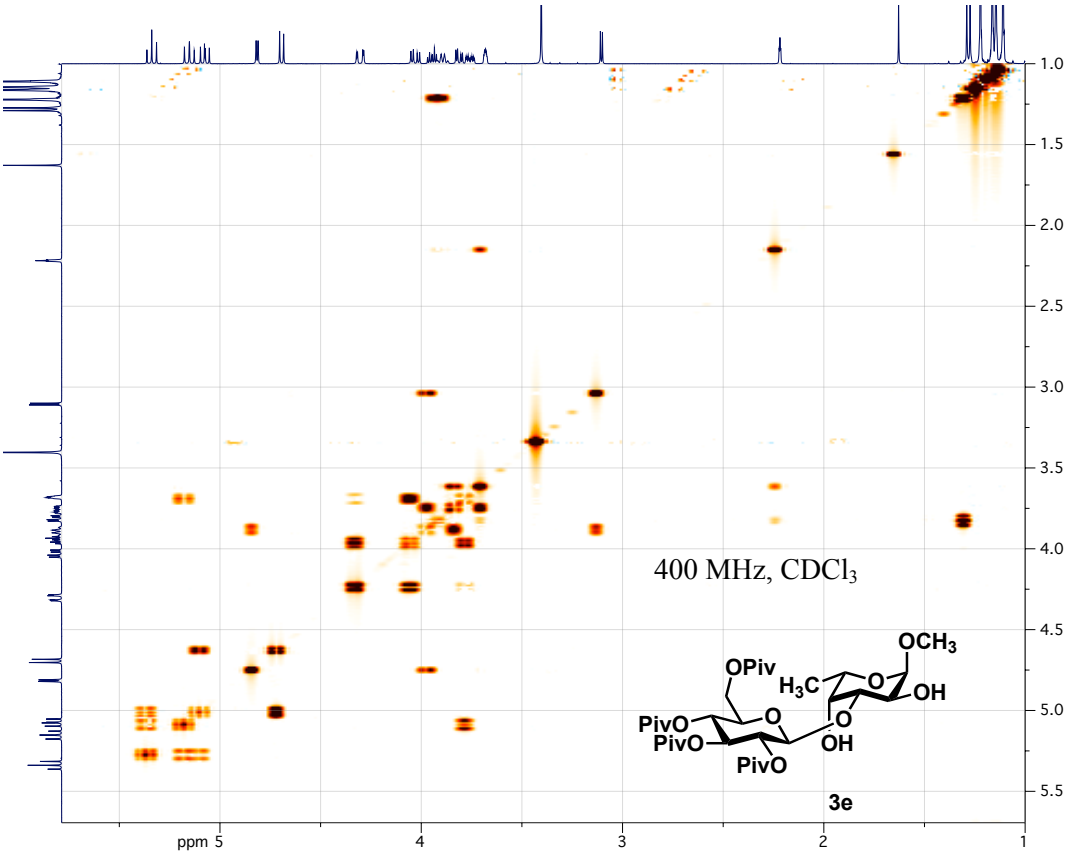
3e

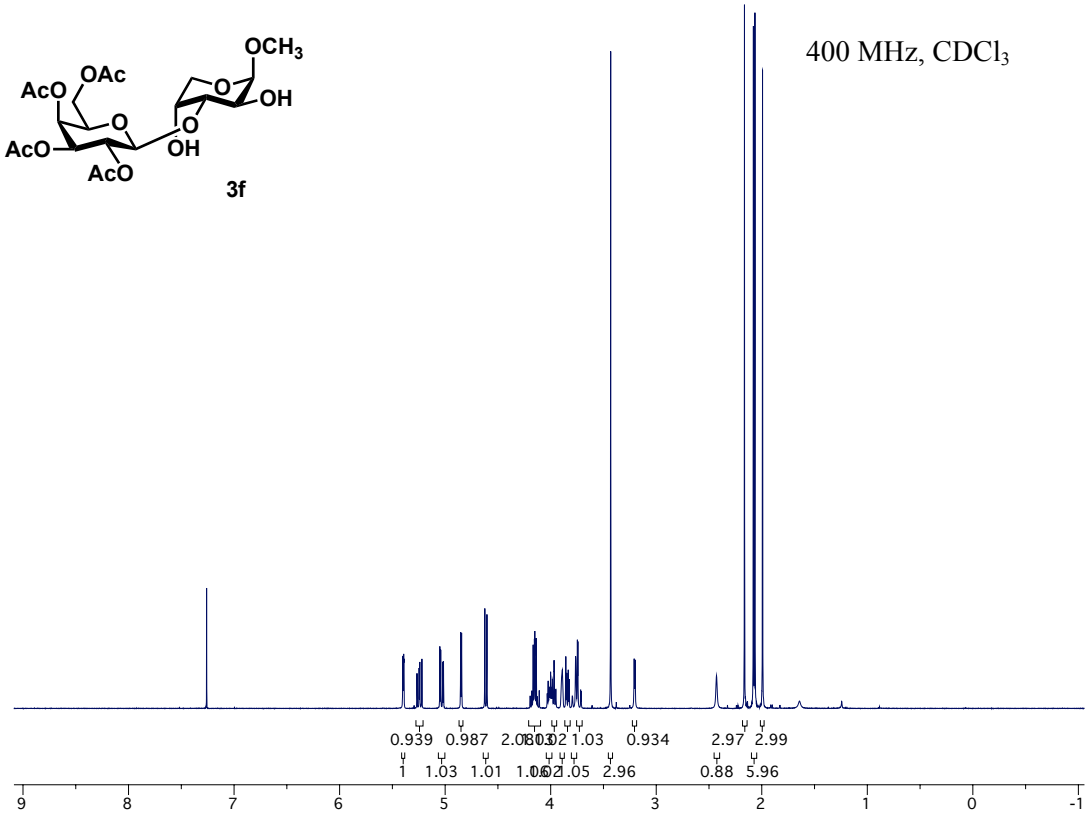


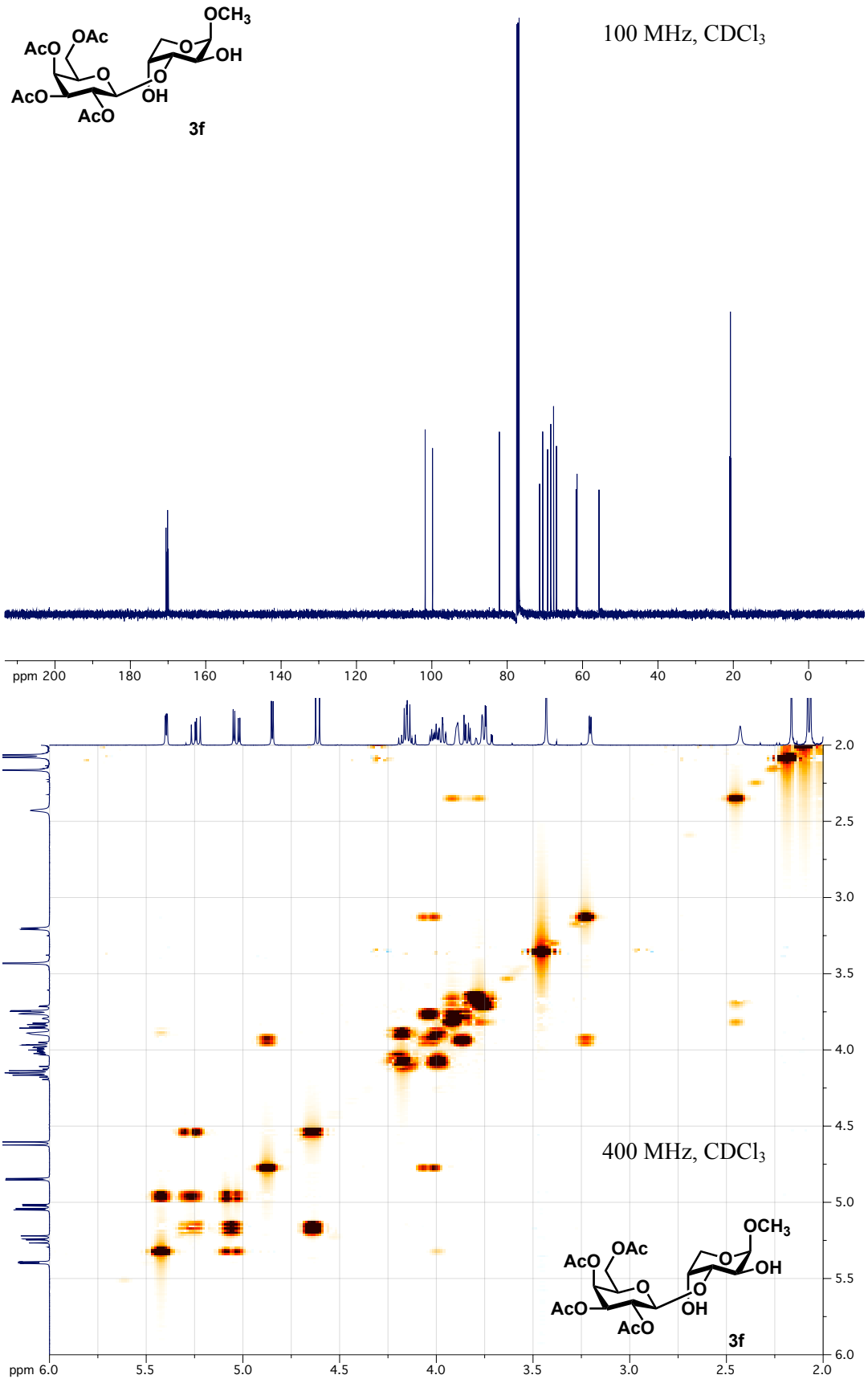
100 MHz, $CDCl_3$



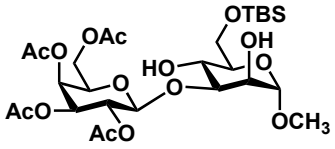
3e


400 MHz, CDCl3
OPiv
H3C
OCH3
O
OH
PivO
PivO
PivO
O
O
OH
3e
ppm 5
4
3
2
1

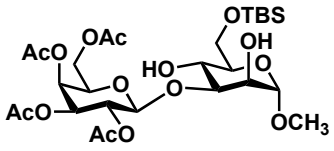

400 MHz, CDCl3
OCH3
AcO
OAc
O
OH
AcO
O
OH
AcO
3f
0.939
0.987
2.03
1.03
0.934
2.97
2.99
1
1.03
1.01
1.05
2.96
0.88
5.96
9
8
7
6
5
4
3
2
1
0
-1


OCH3
AcO
OAc
O
OH
AcO
O
OH
AcO
3f
100 MHz, CDCl3
ppm 200
180
160
140
120
100
80
60
40
20
0
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
400 MHz, CDCl3
OCH3
AcO
OAc
O
OH
AcO
O
OH
AcO
3f
ppm 6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

400 MHz, $CDCl_3$

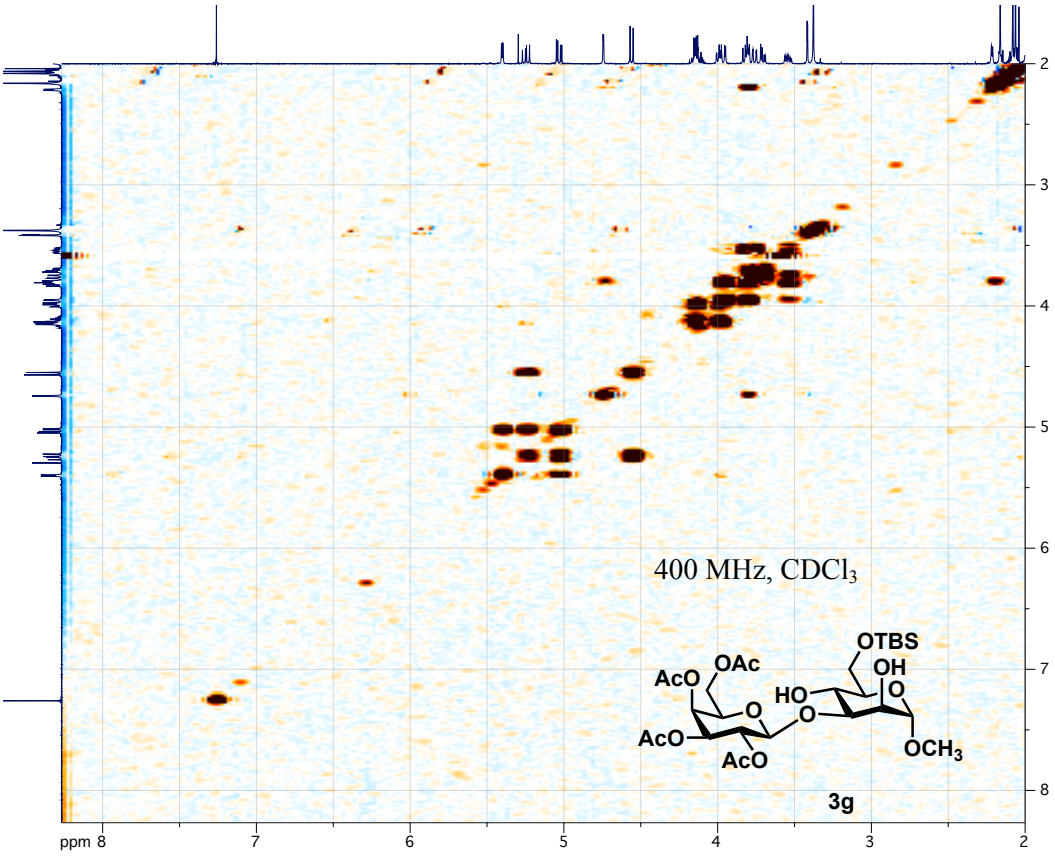


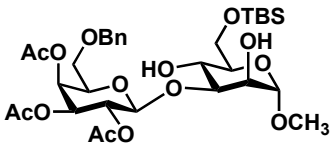
3g



3g

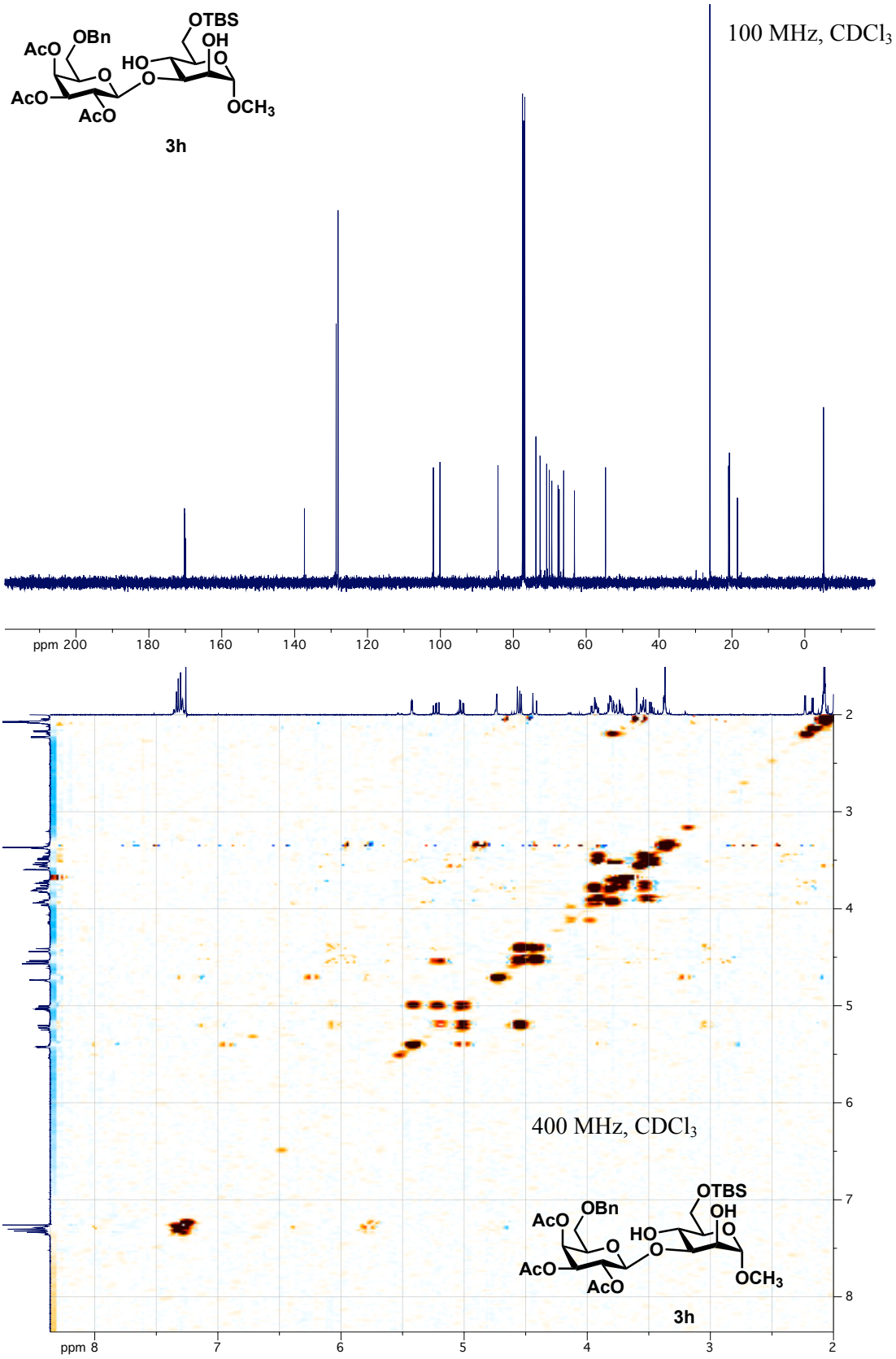
100 MHz, $CDCl_3$


400 MHz, CDCl3
OTBS
OH
HO
OAc
AcO
AcO
AcO
OCH3
3g
ppm 8
7
6
5
4
3
2

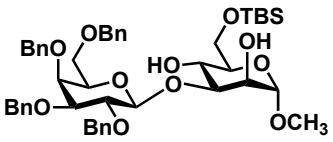

OTBS
OH
OBn
AcO
HO
AcO
AcO
OCH3

3h

400 MHz, CDCl3
1
1.19
2.11
2.71
6.07
11
4.86
1.09
1.12
1.09
0.998
0.973
2.94
6.76
9
8
7
6
5
4
3
2
1
0
-1

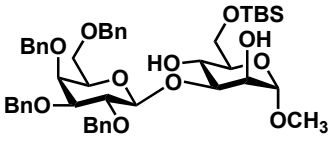

OTBS
OH
OBn
AcO
HO
O
AcO
AcO
OCH3
3h
100 MHz, CDCl3
ppm 200
180
160
140
120
100
80
60
40
20
0
2
3
4
5
6
7
8
400 MHz, CDCl3
ppm 8
7
6
5
4
3
2

400 MHz, $CDCl_3$

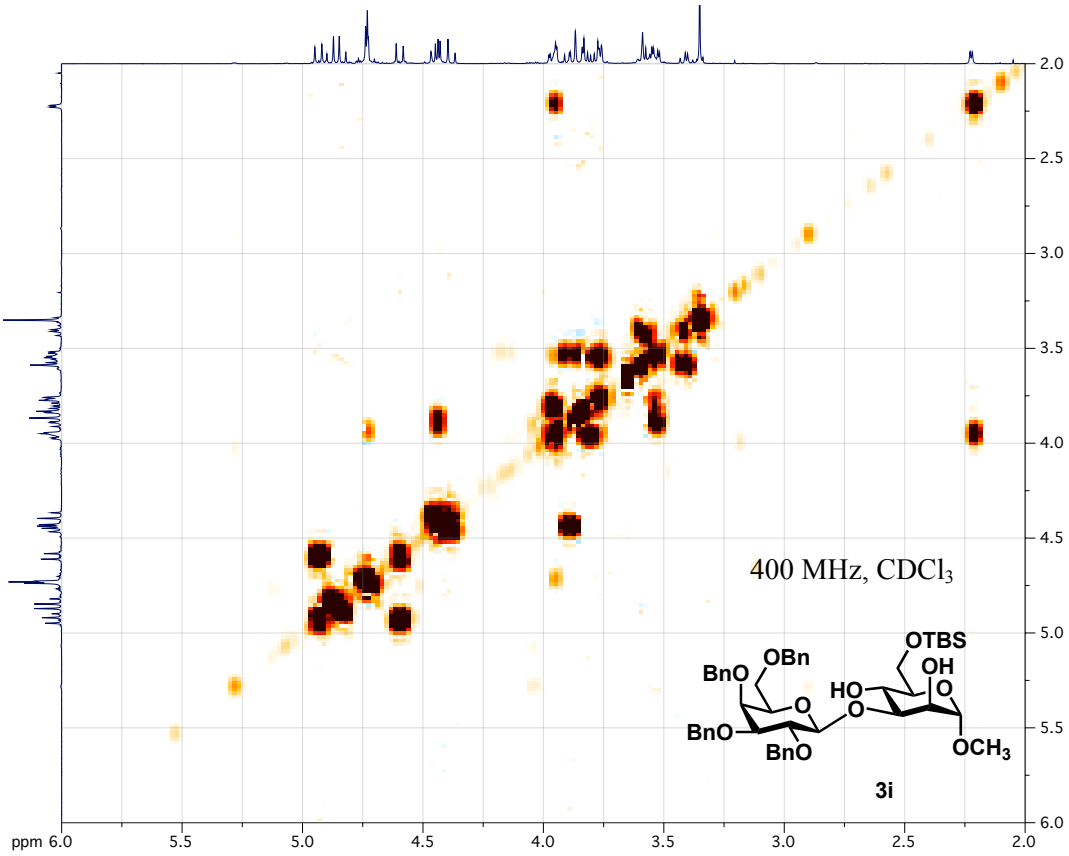


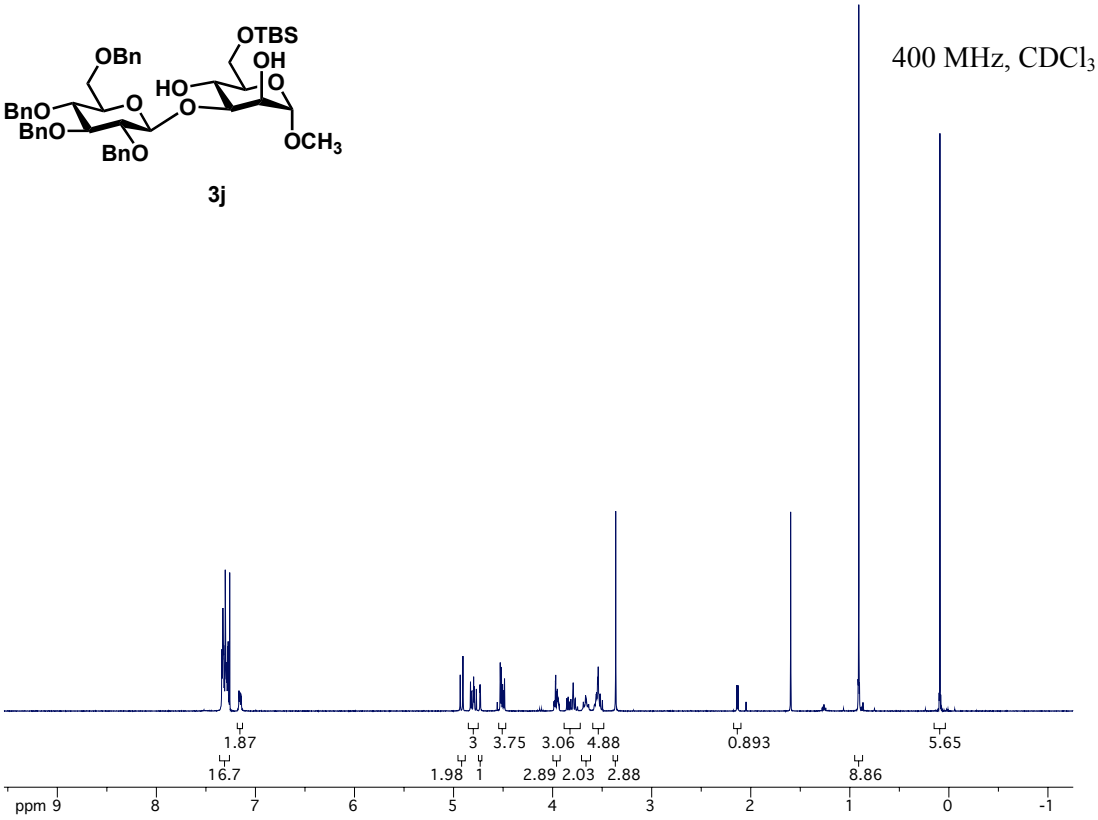
3i

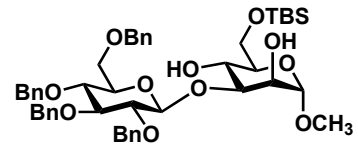
100 MHz, $CDCl_3$



3i

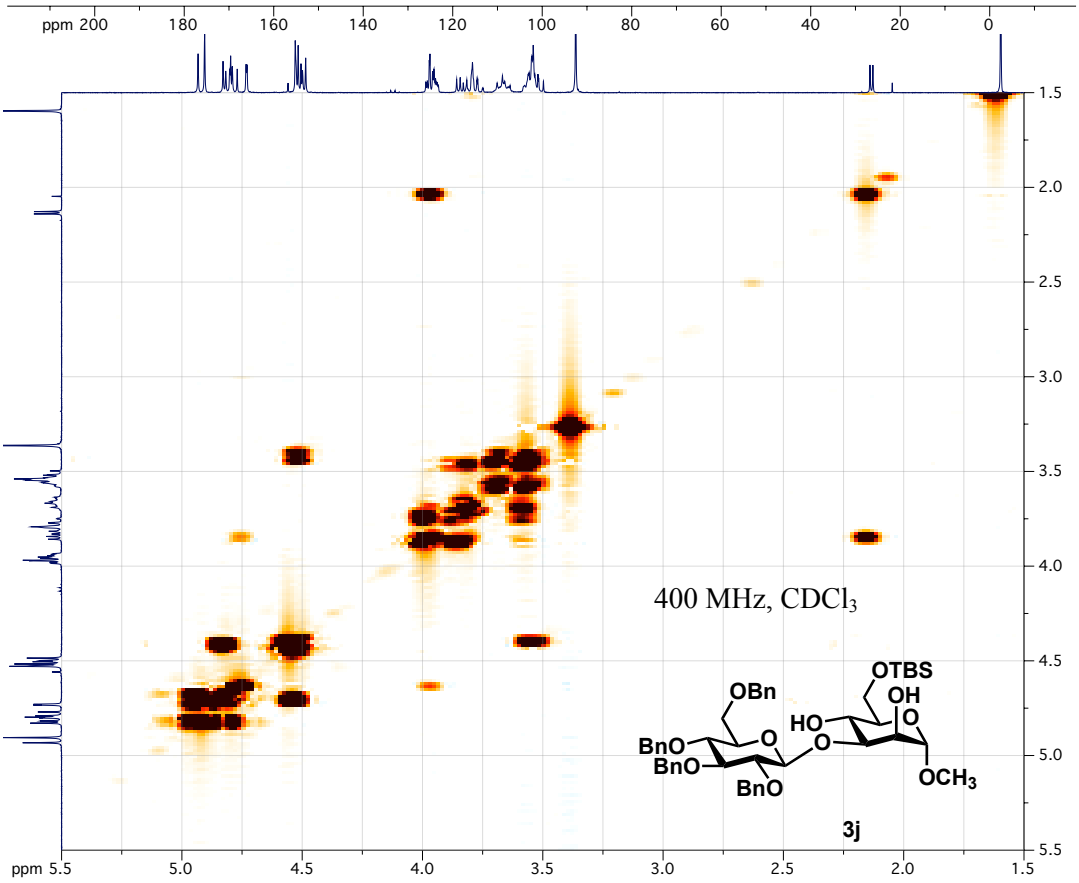

400 MHz, CDCl3
OBn
BnO
BnO
BnO
O
HO
O
OTBS
OH
O
OCH3
3i
ppm 6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0


OBn
BnO
BnO
BnO
O
HO
O
OTBS
OH
O
OCH3
3j
400 MHz, CDCl3
1.87
16.7
3
1.98
3.75
1
3.06
2.89
4.88
2.03
2.88
0.893
5.65
8.86
ppm 9
8
7
6
5
4
3
2
1
0
-1



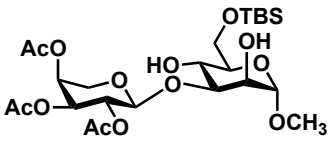
3j

100 MHz, $CDCl_3$



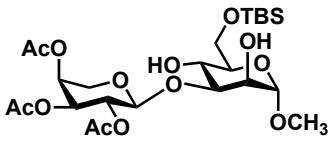
400 MHz, $CDCl_3$

3j



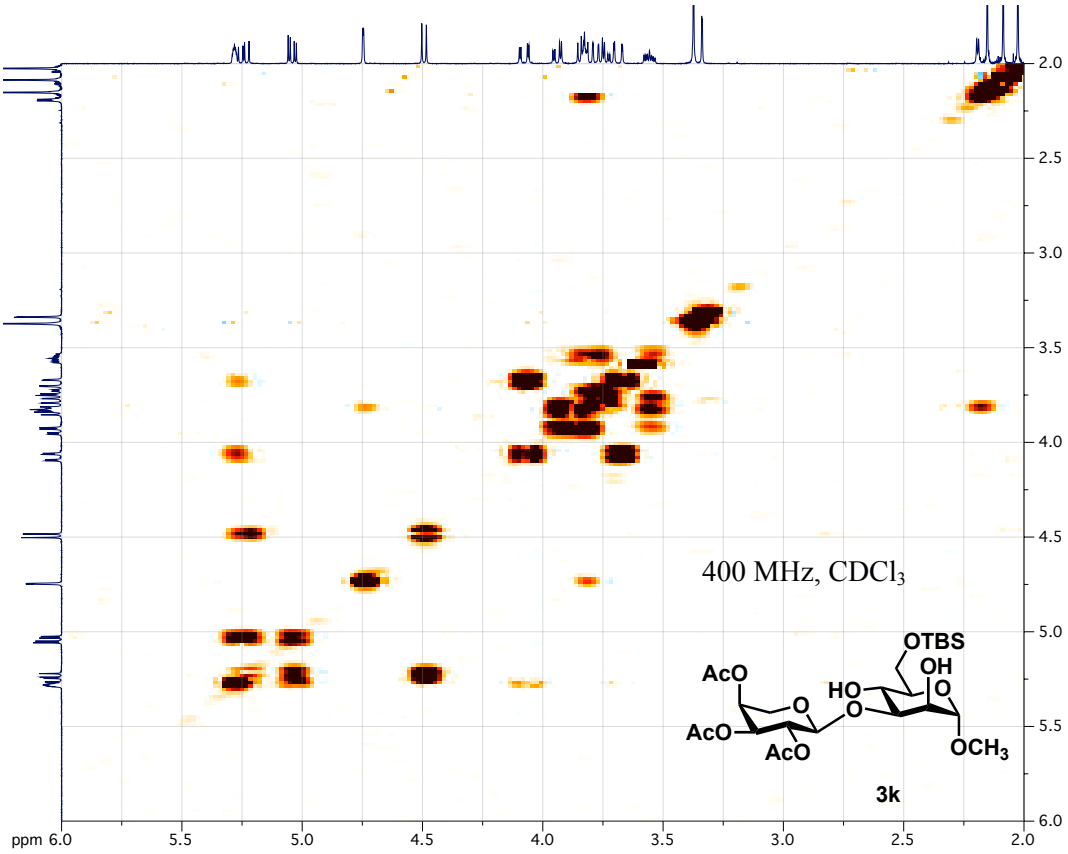
3k

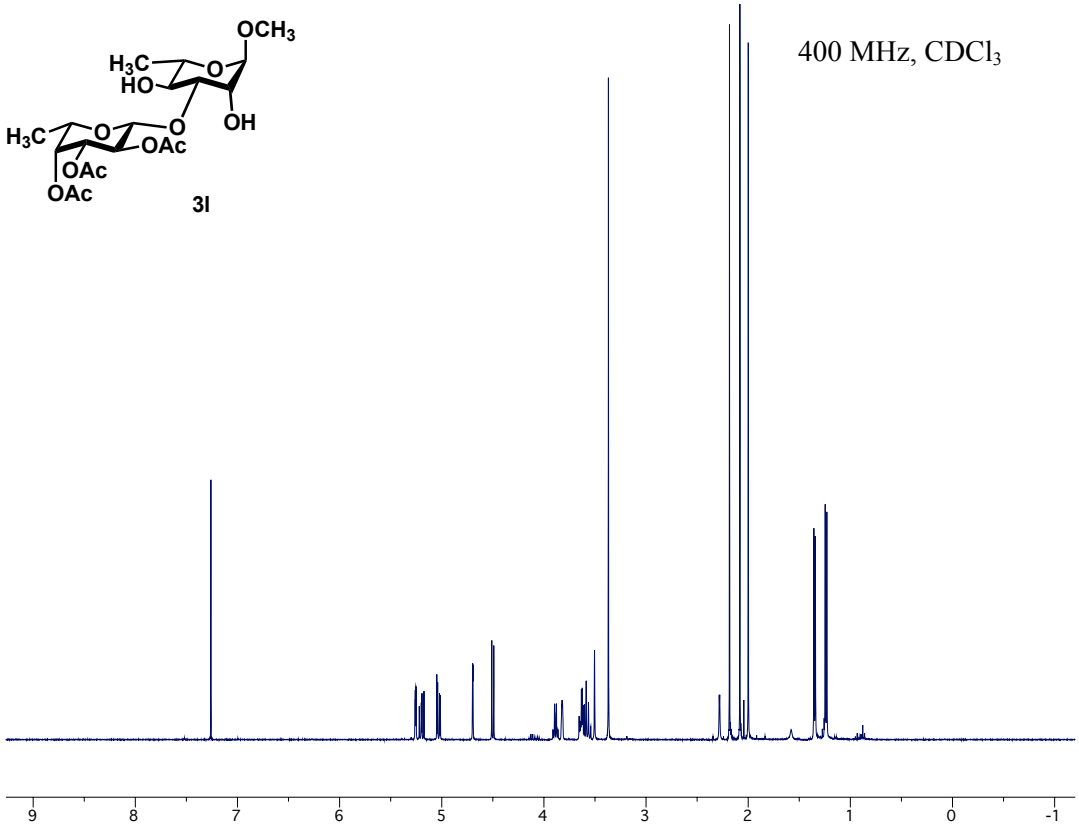
400 MHz, $CDCl_3$

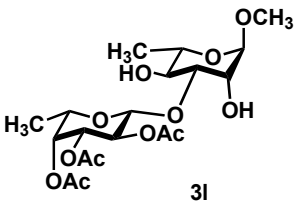


3k

100 MHz, $CDCl_3$

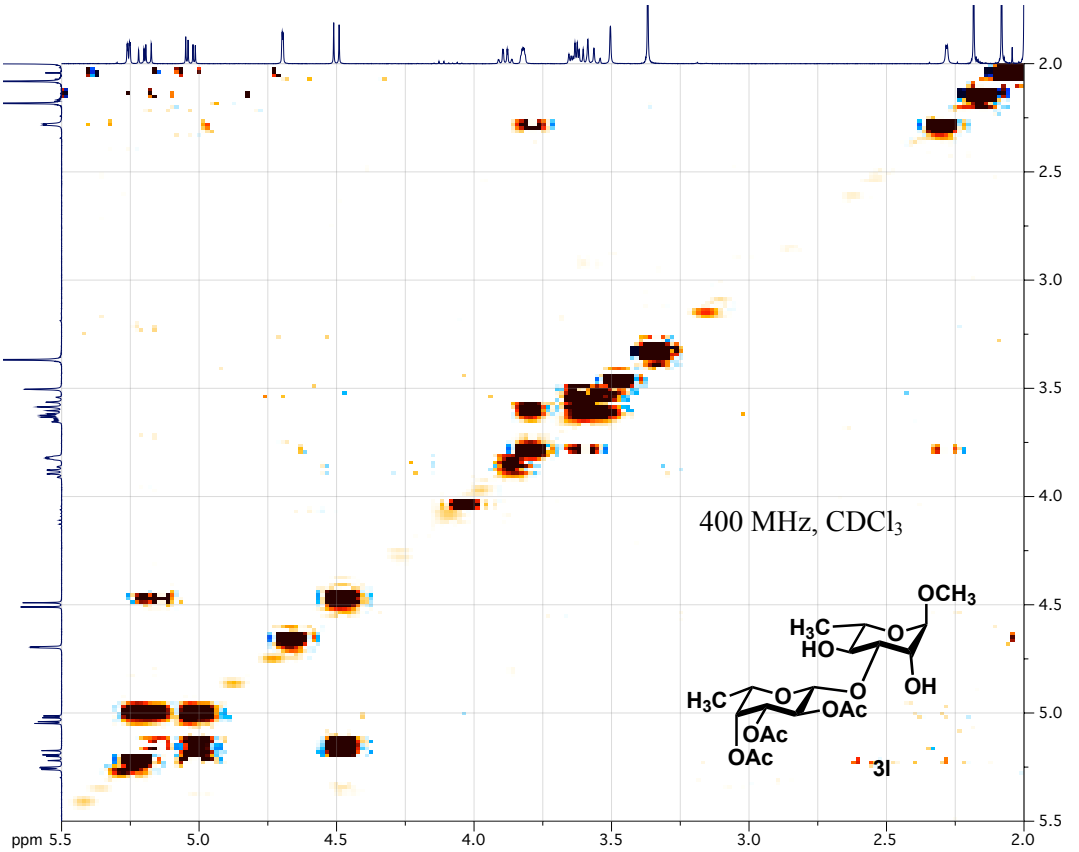

400 MHz, CDCl3
AcO
AcO
AcO
O
HO
O
OTBS
OH
O
OCH3
3k
ppm 6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

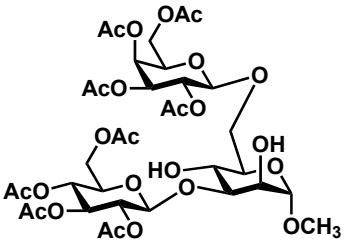

OCH3
H3C
HO
O
OH
H3C
O
O
OAc
OAc
OAc
3l
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
-1



3l

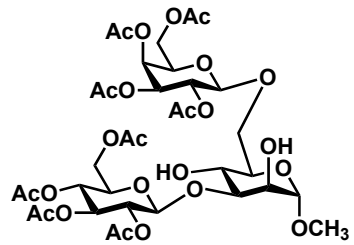
100 MHz, $CDCl_3$





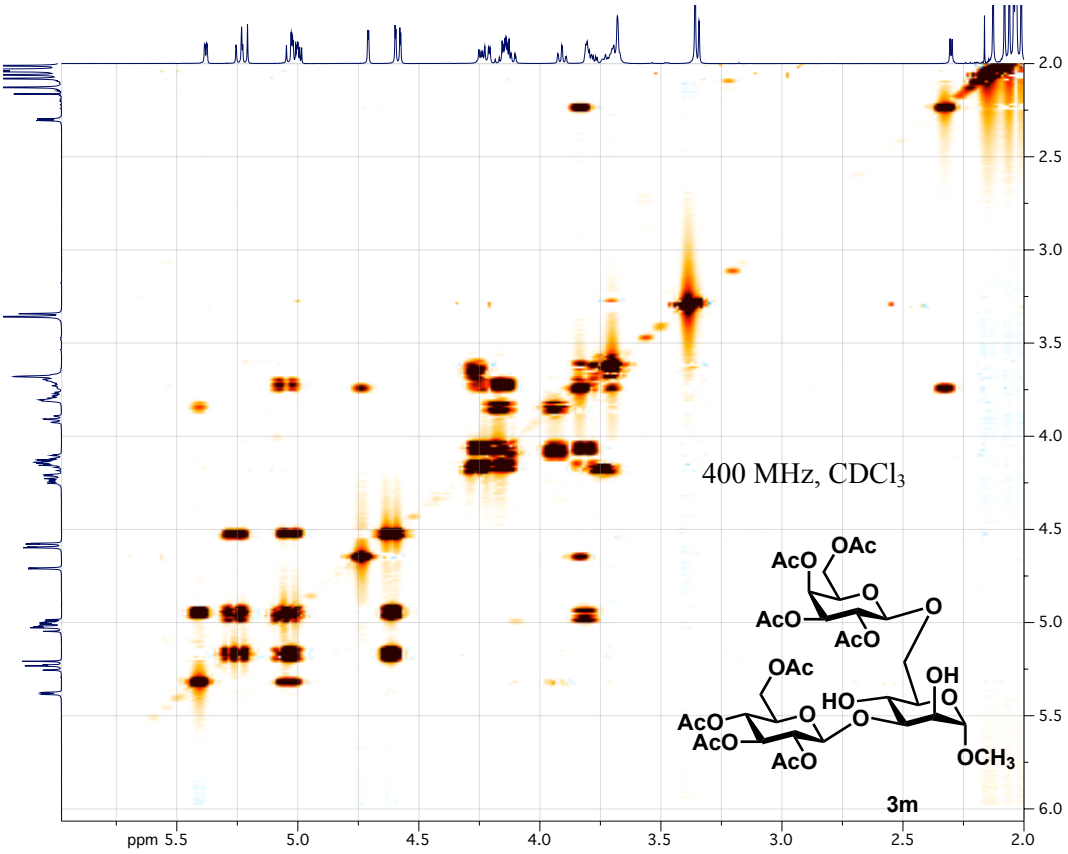
3m

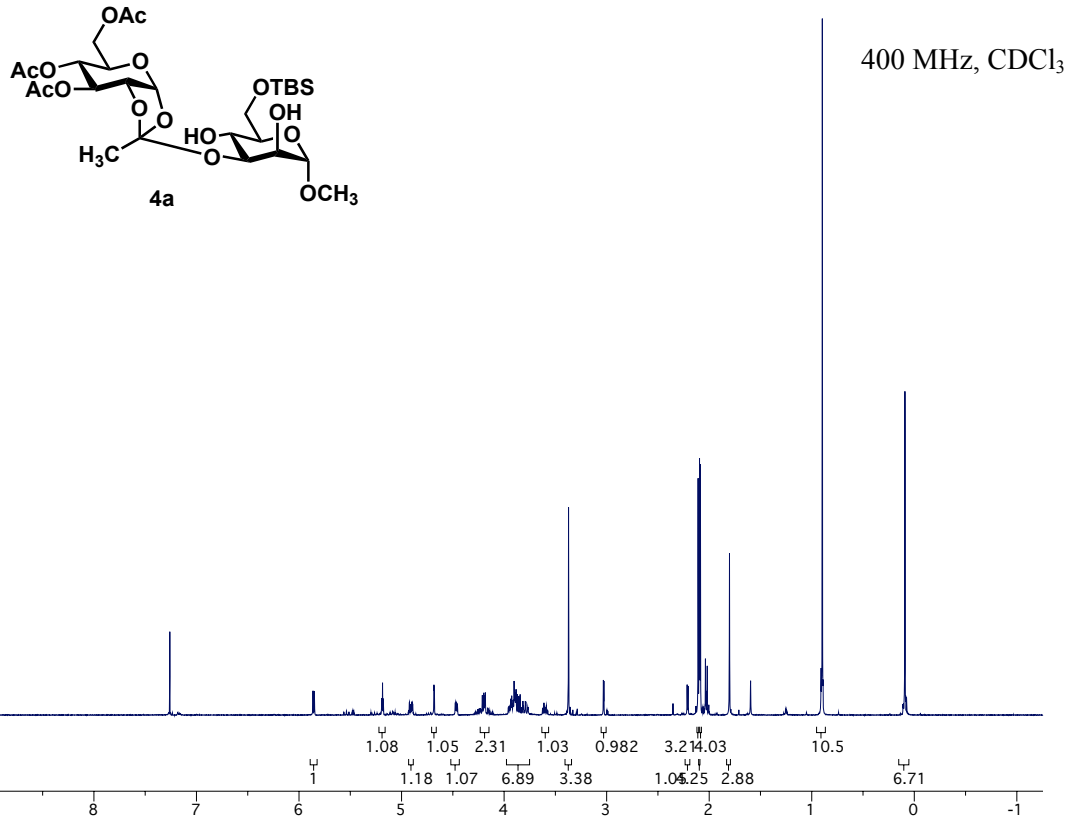
400 MHz, $CDCl_3$

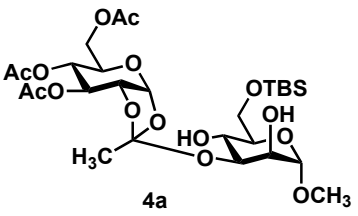


3m

100 MHz, $CDCl_3$

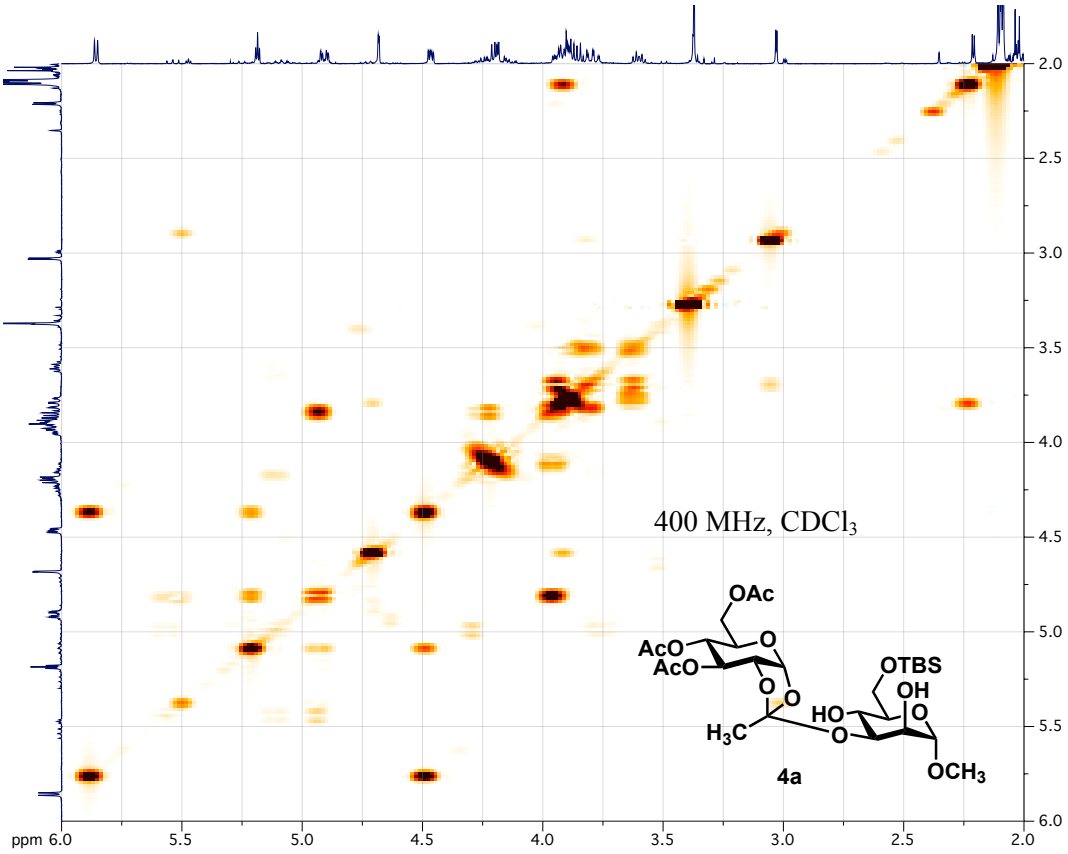

400 MHz, CDCl3
AcO
OAc
AcO
AcO
OAc
HO
OH
AcO
AcO
AcO
OCH3
3m
ppm 5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
6.0


OAc
AcO
AcO
OTBS
OH
HO
H3C
OCH3
4a
400 MHz, CDCl3
1.08
1.05
2.31
1.03
0.982
3.21
4.03
10.5
1
1.18
1.07
6.89
3.38
1.04
5.25
2.88
6.71
9
8
7
6
5
4
3
2
1
0
-1



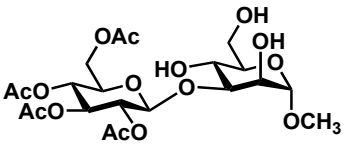
4a

100 MHz, $CDCl_3$

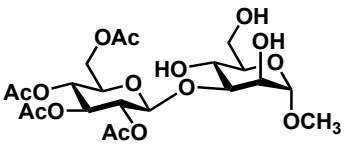


400 MHz, $CDCl_3$

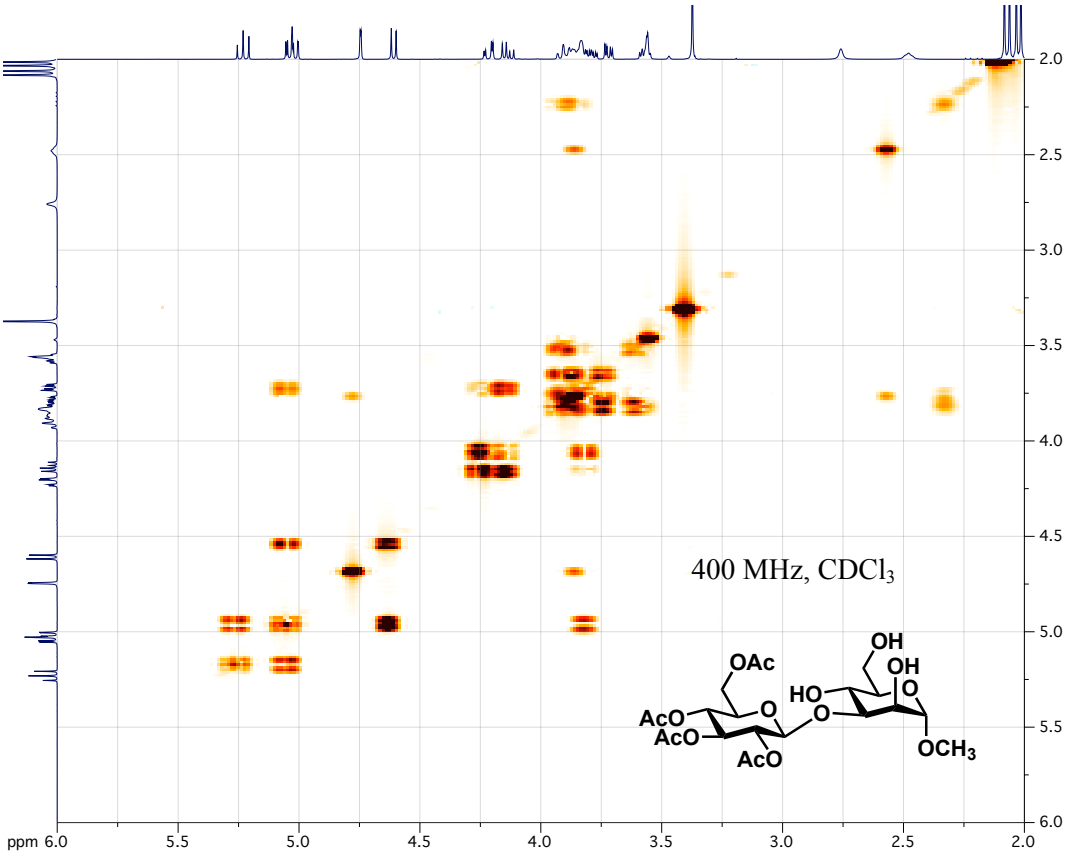
4a

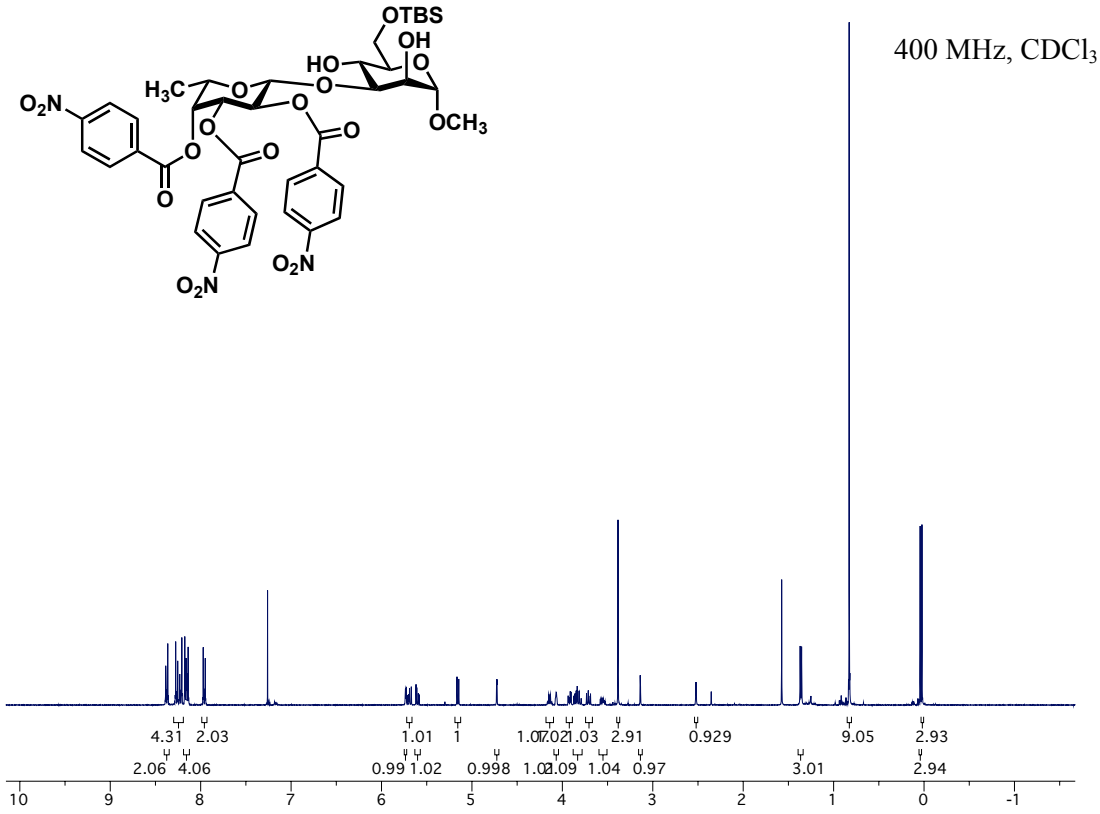


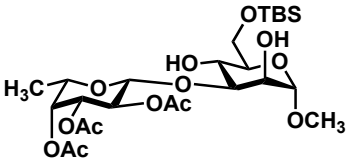
400 MHz, $CDCl_3$



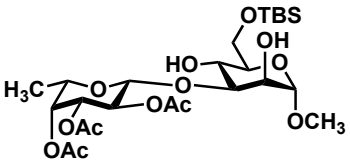
100 MHz, $CDCl_3$


400 MHz, CDCl3
OAc
AcO
AcO
AcO
O
HO
O
OH
OH
O
OCH3
ppm 6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

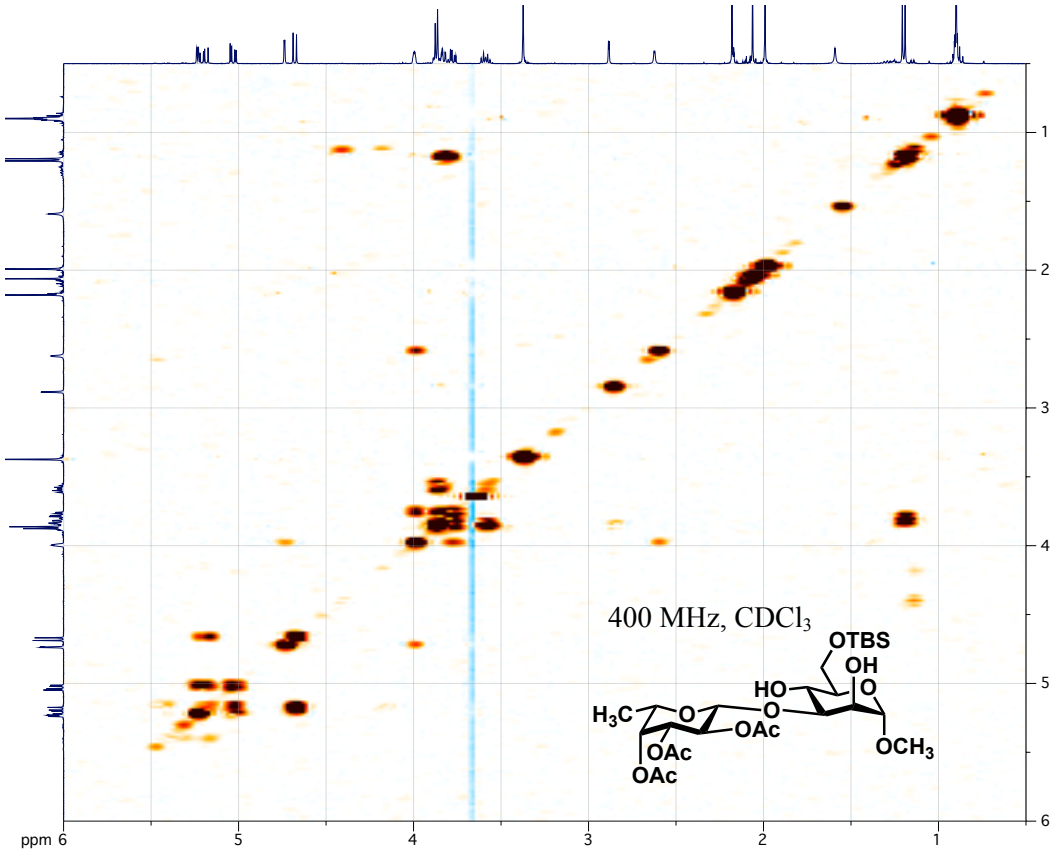

400 MHz, CDCl3
OTBS
OH
HO
O
H3C
O
O
O
O
O
O
O2N
O2N
O2N
OCH3
4.31
2.03
2.06
4.06
1.01
1
0.99
1.02
0.998
1.02
1.09
1.03
1.04
2.91
0.97
0.929
9.05
3.01
2.93
2.94
10
9
8
7
6
5
4
3
2
1
0
-1



400 MHz, $CDCl_3$



100 MHz, $CDCl_3$


400 MHz, CDCl3
OTBS
OH
HO
O
H3C
O
O
OAc
OAc
OAc
OCH3
ppm 6
5
4
3
2
1