

Supporting Information for

3-(Dimethylamino)-1-propylamine(DMAPA): a Cheap and Versatile Reagent for Removal of By-Products in Carbohydrate Chemistry

*Sofie Meng Andersen, Mads Heuckendorff and Henrik H. Jensen**

Contribution from the Department of Chemistry, Aarhus University, Langelandsgade 140

DK-8000 Aarhus C, Denmark

E-mail: hhj@chem.au.dk

General Methods	S3
Experimental	S3
General procedure for deacetylation	S3
Procedure for solvent and nucleophile screening	S3
Procedure for extraction studies	S3
Table 1. Solvent and nucleophile screening	S4
Table 2. Extraction studies	S5
2,3,4,6-tetra- <i>O</i> -acetyl- α/β -D-glucopyranose (2)	S5
2,3,4,6-tetra- <i>O</i> -acetyl- α/β -D-glucopyranose (2) from 1,2,3,4,6-penta- <i>O</i> -acetyl- α -D-glucopyranose (3)	S6
2,3,4,6-tetra- <i>O</i> -acetyl- α/β -D-galactopyranose (5)	S6
Synthesis of 1,2,3,4,6-penta- <i>O</i> -acetyl- α/β -D-mannopyranose (6)	S7
2,3,4,6-tetra- <i>O</i> -acetyl- α/β -D-mannopyranose (7)	S7
3,4,6-tri- <i>O</i> -acetyl-2-azido-2-deoxy- α/β -D-glucopyranose (9)	S8
2-acetamido-2-deoxy-1,3,4,6-tetra- <i>O</i> -acetyl- α/β -D-glucopyranose (10)	S8
2-acetamido-2-deoxy-3,4,6-tri- <i>O</i> -acetyl- α/β -D-glucopyranose (11)	S9
4- <i>O</i> -(2,3,4,6-tetra- <i>O</i> -acetyl- β -D-galactopyranosyl)-2,3,6-tri- <i>O</i> -acetyl- α/β -D-glycopyranose (13)	S9
1,2,3,4,6-penta- <i>O</i> -benzoyl- β -D-mannopyranose (14)	S10
2,3,4,6-tetra- <i>O</i> -benzoyl- α/β -D-mannopyranose (15)	S11
2,3,4,6-tetra- <i>O</i> -acetyl-D- α -glucopyranosyl trichloroacetimidate (16)	S11
2,3,4,6-tetra- <i>O</i> -acetyl-D- α -galactopyranosyl trichloroacetimidate (17)	S12
6- <i>O</i> -benzoyl-1,2;3,4-di- <i>O</i> -isopropylidene- α -D-galactopyranose	S13
1,2;3,4-di- <i>O</i> -isopropylidene-6- <i>O</i> -tosyl- α -D-galactopyranose	S14
1- <i>O</i> -benzoyl-2,3;4,5-di- <i>O</i> -isopropylidene- β -D-fructopyranose	S14
2,3;4,5-di- <i>O</i> -isopropylidene-1- <i>O</i> -tosyl- β -D-fructopyranose	S15
3,5-di- <i>O</i> -benzoyl-1,2- <i>O</i> -isopropylidene-D-xylofuranose	S16
1,2- <i>O</i> -Isopropylidene-3,5-di- <i>O</i> -tosyl-D-xylofuranose	S17
2,3,4,6-tetra- <i>O</i> -acetyl-D-glucopyranosyl 1-(<i>N</i> -phenyl)-2,2,2-trifluoroacetimidate	S18
2,3,4,6-Tetra- <i>O</i> -benzoyl-D-mannopyranosyl 1-(<i>N</i> -phenyl)-2,2,2-trifluoroacetimidate	S19
2,3,4,6-tetra- <i>O</i> -benzyl-D-glucopyranosyl 1-(<i>N</i> -phenyl)-2,2,2-trifluoroacetimidate	S19
¹ H and ¹³ C NMR Spectra for Compounds.	S21

General Methods

All reagents were used as purchased without further purification. Dry solvents were taken from an MBraun SPS-800 solvent purification system. Glassware used for water-free reactions were dried for 12 h at 120 °C before use. Columns were packed with silica gel 60 (230–400 mesh) as the stationary phase. TLC plates (Merck, 60, F254) were visualized by 10% H₂SO₄ in EtOH and heating until spots appeared. NMR chemical shifts (δ) are reported in ppm relative to the residual solvent signal. High-resolution mass spectral (HRMS) data were obtained on an electrospray (ES) mass spectrometer analyzing time-of-flight. NMR assignments were based on COSY and HSQC NMR experiments.

Experimental

General procedure for deacetylation

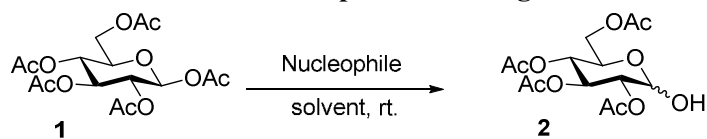
A solution of 1-*O*-acylated sugar (0.50 mmol) and DMAPA (5 equiv., 2.5 mmol) in THF (2.5 mL) was stirred at room temperature until TLC analysis showed until full conversion. The reaction mixture was diluted in CH₂Cl₂ and washed once with hydrochloric acid (1 M) and once with brine. The organic layer was dried with Na₂SO₄, filtered and evaporated to dryness giving the product.

Procedure for solvent and nucleophile screening

A solution of 1-*O*-acylated sugar (0.50 mmol) and nucleophile (5 equiv., 2.5 mmol) in 2.5 mL solvent was stirred at room temperature until TLC analysis showed until full conversion. The reaction mixture was diluted in CH₂Cl₂ and washed once with hydrochloric acid (1 M) and once with brine. The organic layer was dried with Na₂SO₄, filtered and evaporated to dryness giving the product.

Procedure for extraction studies

A solution of 1-*O*-acylated sugar (0.50 mmol) and DMAPA (5 equiv., 2.5 mmol) in THF (2.5 mL) was stirred at room temperature until TLC analysis showed until full conversion. The reaction mixture was diluted in CH₂Cl₂ and washed twice with acid and once with brine. The organic layer was dried with Na₂SO₄, filtered and evaporated to dryness giving the product.

Table 1. Solvent and nucleophile screening

Entry	Solvent	Nucleophile	Equiv.	Time	Yield
1	THF	DMAPA	1.3	72 h	- ^b
2	THF	DMAPA	1.5	24 h	95% ^a
3	THF	DMAPA	3	3 h	88% ^a
4	THF	DMAPA	5	1.5 h	92% ^a
5	DMF	Hydrazinium acetate	1.5	1 h	70% ^c
6	DMF	Hydrazinium acetate	5	½ h	83% ^c
7	THF	BnNH ₂	1.5	24 h	75% ^c
8	THF	BnNH ₂	5	3 ½ h	86% ^c
9	CH ₂ Cl ₂	DMAPA	5	3 h	83% ^a
10	Toluene	DMAPA	5	1.5 h	52% ^a
11	EtOAc	DMAPA	5	1.5 h	75% ^a
12	Et ₂ O	DMAPA	5	1.5 h	30% ^a
13	CH ₃ CN	DMAPA	5	1.5 h	48% ^a
14	2-MeTHF	DMAPA	5	1.5 h	75% ^a
15	<i>Tert</i> -butyl methyl ether	DMAPA	5	1.5 h	50% ^a
16	Cyclopentyl methyl ether	DMAPA	5	1.5	41% ^a

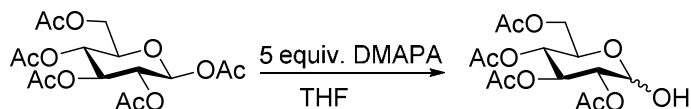
^aYield after acidic work-up without chromatographic purification; ^bReaction did not go to completion according to TLC analysis; ^cYield after column chromatography.

Table 2. Extraction studies

Entry	DMAPA (equiv.)	Reaction time	Organic phase	Acidic aqueous phase	Yield
1	5	1.5 h	THF/CH ₂ Cl ₂	1M HCl	95% ^a
2	5	1.5 h	THF/CH ₂ Cl ₂	0.1M phosphate buffer, pH=5.8	84% ^a
3	5	1.5 h	THF/CH ₂ Cl ₂	1M citric acid	73% ^a
4	5	1.5 h	THF/CH ₂ Cl ₂	1M tartaric acid	80% ^a

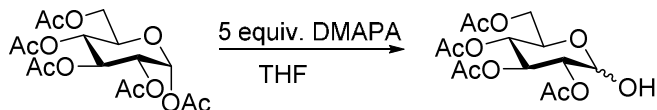
^aYield after acidic work-up without chromatographic purification

2,3,4,6-tetra-*O*-acetyl- α/β -D-glucopyranose (2)



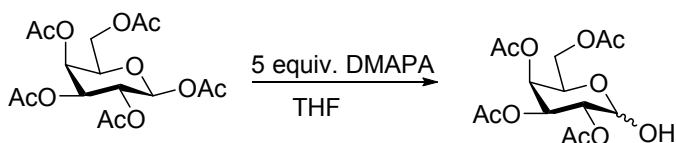
Reaction time 1½ h. Yield: 0.162 g, 92%, α/β 3:1, syrup. R_f : 0.53 (pentane/EtOAc 1:1), ¹H NMR (400 MHz, CDCl₃): δ_H 5.44 (t, 1H, J 9.9 Hz, H3 α), 5.35 (t, 1H, J 3.5 Hz, H1 α), 5.14 (t, 1H, J 9.8 Hz, H β), 4.99 (t, 2H, J 9.9 Hz, H4 α + β), 4.93 (d, 1H, J 8.2 Hz, H β) 4.79 (dd, 2H, J 10.1 Hz, 3.5 Hz), 4.20-4.14 (m, 2H), 4.07 (m, 2H), 3.66 (t, 2H, J 6.6 Hz), 2.00, 2.00, 1.95, 1.93 (s, 24H). ¹³C NMR (100 MHz, CDCl₃): δ_C 171.0, 170.9, 170.3, 170.3, 170.3, 169.8, 169.6, (β -anomer): 95.2 (C1), 72.9 (C2), 72.5 (C3), 71.8 (C4), 68.4 (C5), 67.9 (C6). (α -anomer): 89.9 (C1), 71.2 (C2), 69.9 (C3), 68.5 (C4), 66.9 (C5), 62.0 (C6), 25.49, 20.7, 20.6, 20.6, 20.6, 20.5. HRMS(ES): calcd. for C₁₄H₂₀O₁₀Na 371.0949; found 371.0955. Spectral values were in accordance with those reported in ref. i & ii.

2,3,4,6-tetra-*O*-acetyl- α/β -D-glucopyranose (2) from 1,2,3,4,6-penta-*O*-acetyl- α -D-glucopyranose (3)



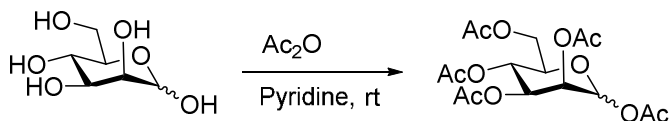
Reaction time 1½ h. Yield (0.168 g, 90%, α/β 3:1).

2,3,4,6-tetra-*O*-acetyl- α/β -D-galactopyranose (5)



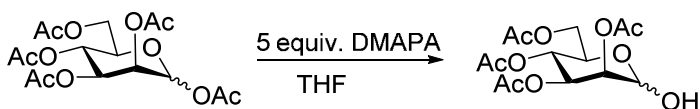
Reaction time 1½ h, Yield: 0.146 g, 84%, α/β 2.2:1, oil. R_f : 0.43 (pentane/EtOAc 1:1), ^1H NMR (400 MHz, CDCl_3): δ_{H} (α -anomer): 5.45 (t, 1H, J 3.5 Hz, H1), 5.41 (d, 1H, J 2.5 Hz), 5.34 (d, 1H, J 3.2 Hz), 5.08 (dd, 1H, J 10.7 Hz, 3.2 Hz), 4.42 (t, 1H, J 6.6 Hz, H4), 4.26 (s, 1H, OH), 4.04 (dd, 2H, J 6.5 Hz, 1.4 Hz, H6). (β -anomer): 5.37 (d, 1H, J 3.3 Hz), 5.04 (s, 1H, OH), 5.02 (d, 1H, J 4.4 Hz), 4.68 (t, 1H, J 7.6 Hz, H1), 4.47 (s, 1H), 4.10 (d, 1H, J 6.5 Hz), 3.39 (t, 1H, J 6.5 Hz), 2.11, 2.10, 2.04, 2.00, 1.94 (20H, s). ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 170.8, 170.8, 170.6, 170.5, 170.5, 170.3, 170.2. (α -anomer): 90.5, 68.4, 68.2, 67.3 (C2, C3, C5), 65.9 (C4), 61.8 (C6). (β -anomer): 95.7 (C1), 70.8, 70.7, 70.6 (C2, C3, C5), 67.2 (C4), 61.5 (C6), 20.8, 20.7, 20.7, 20.6, 20.6, 20.6. HRMS (ES): calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_{10}\text{Na}$ 371.0949; found 371.0948. Spectral values were in accordance with those reported in ref. iii & iv.

Synthesis of 1,2,3,4,6-penta-*O*-acetyl- α/β -D-mannopyranose (6)



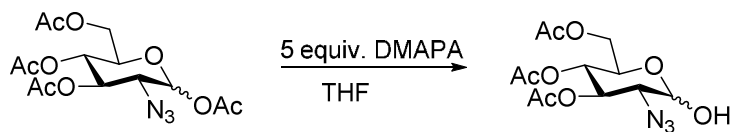
D-mannose (1.00 g, 5.55 mmol) was dissolved in a solution of pyridine (10 mL) and acetic anhydride (10 mL). The reaction was stirred under an argon atmosphere overnight and then quenched with water. The reaction was diluted with ethyl acetate and washed five times with hydrochloric acid. The organic layer was dried over Na_2SO_4 , filtered and concentrated under reduced pressure. **6** was isolated as an oil. Yield: 1.91 g, 88 %, α/β 1:2. R_f : 0.57 (pentane/EtOAc 1:1). ^1H NMR (400 MHz, CDCl_3): δ_{H} 5.83 (d, 1H, J 1.8 Hz, H1 β), 5.71 (s, 1H, H1 α), 5.24 (d, 1H, J 2.2 Hz), 5.10-5.09 (m, 2H), 5.03-4.99 (m, 2H), 4.08-4.01 (m, 2H) 3.90-3.83 (m, 3H), 3.68-3.64 (m, 1H), 1.96, 1.94, 1.86, 1.84, 1.82, 1.76, 1.75. ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 170.3, 170.3, 169.9, 169.6, 169.5, 169.4, 169.3, 168.2, 168.1, 167.8, 90.3 (C1 β), 90.1 (C1 α), 72.8 (C5 α), 70.3(C5 β), 70.3, 68.8, 65.2 (C2, C3, C4 α), 68.5, 68.0, 65.2 (C2, C3, C4 β), 61.9 (C6 β), 61.8 (C6 α), 20.5, 20.5, 20.4, 20.4, 20.4, 20.4, 20.4, 20.3, 20.3, 20.2. HRMS(ES): calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_{11}\text{Na}$ 413.1054; found 413.1057. Spectral values were in accordance with those reported in ref.v & vi.

2,3,4,6-tetra-*O*-acetyl- α/β -D-mannopyranose (7)



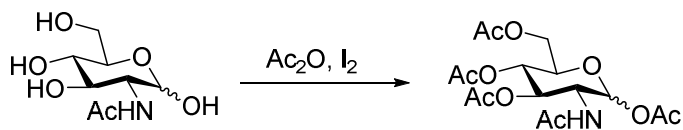
Reaction time 1½ h. Yield: 0.150 g, 86%, α/β 9:1, R_f : 0.43 (pentane/EtOAc 1:1). ^1H NMR (400 MHz, CDCl_3): δ_{H} 5.39 (dd, 1H, J 9.9 Hz, H α), 5.27 (t, 1H, J 9.9 Hz, H α), 5.24-5.19 (m, 3H), 5.07 (dd, 1H, J 4.0 Hz), 4.98 (s, 1H, H1 β), 4.25-4.19 (m, 3H), 4.13-4.10 (m, 3H), 3.72-3.67 (m, 1H), 2.19, 2.14, 2.08, 2.03, 1.98 (s, 24H). ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 171.1, 171.8, 170.4, 170.3, 170.0, 169.8, 21.0, 20.9, 20.9, 20.8, 20.7. α -anomer: 92.1(C1), 70.2, 68.9, 68.4, 66.2, 62.7. β -anomer: 92.9 (C1), 72.5, 71.2, 70.1, 65.7, 62.5. HRMS(ES): calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_{10}\text{Na}$ 371.0949; found 371.0948. Spectral values were in accordance with those reported in ref. vii & i.

3,4,6-tri-*O*-acetyl-2-azido-2-deoxy- α/β -D-glucopyranose (9)



Reaction time 1½ h, Yield 0.193 g, 82%, α/β 1.7:1, white foam R_f : 0.60 (pentane/EtOAc 1:1). ^1H NMR (400 MHz, CDCl_3): δ_{H} 5.50 (t, 1H, J 9.9 Hz), 5.37 (s, 1H), 5.05 (m, 3H), 4.73 (d, 1H, J 8.0 Hz), 4.27-4.18 (m, 3H), 4.11 (t, 2H, J 11.6 Hz), 3.70 (bs, 1H, OH), 3.47 (t, 1H, J 7.0 Hz), 3.41 (d, 1H, J 13.3 Hz), 2.07, 2.02, 2.00 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 171.2, 171.1, 170.4, 170.3, 170.0, 169.9, 96.2, 92.1, 72.7, 71.9, 70.6, 68.7, 68.4, 67.5, 64.9, 62.1, 61.5, 20.8, 20.8, 20.8, 20.7, 20.7. HRMS(ES): calcd. for $\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_8\text{NH}_4$ 349.1354; found 349.1357. Spectral values were in accordance with those reported in ref. viii.

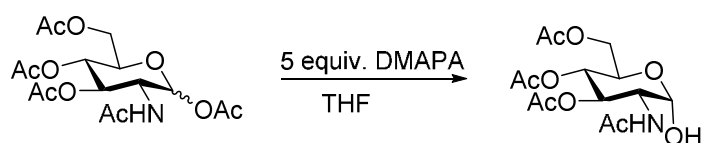
2-acetamido-2-deoxy-1,3,4,6-tetra-*O*-acetyl- α/β -D-glucopyranose (10)



A solution of 2-acetamido-2-deoxy- α/β -D-glucopyranose (1 g, 4.5 mmol) and iodine (0.32 mmol, 0.397 g) were dissolved in acidic anhydride (1.7 mL) at 40 °C and was stirred under a nitrogen atmosphere. The reaction was followed by TLC analysis until full conversion. The reaction was quenched with methanol and the mixture was stirred for 30 min. The solution was diluted with CH_2Cl_2 and washed with aq. 10 % sodium thiosulfate and aqueous saturated bicarbonate solution. The organic layer was dried with Na_2SO_4 , filtered and evaporated to dryness giving the product. Yield 1.75 g, 89%, R_f : 0.55 (toluene/acetone 2:1), α/β 1:1.7. ^1H NMR (400 MHz, CDCl_3): δ_{H} 6.55 (d, 1H, J 9.5 Hz), 6.10 (d, 1H, J 9.0 Hz), 6.05 (d, 1H, J 3.6 Hz), 5.65 (d, 1H, J 8.8), 5.14 (t, 1H, J 10.0 Hz), 5.07 (t, 1H, J 9.8 Hz), 4.98 (t, 1H, J 9.7 Hz), 4.37 (ddd, 1H, J 10.7 Hz, 9.0 Hz, 3.6 Hz), 4.20-4.11 (m, 2H), 4.02 (d, 1H, J 2.3 Hz), 3.97 (dd, 1H, J 11.0 Hz, 2.3 Hz), 3.94-3.90 (m, 1H), 3.78 (ddd, 1H, J 10.1 Hz, 4.7 Hz, 2.4 Hz), 2.07, 1.99, 1.95, 1.93, 1.81 (s, 30H). ^{13}C NMR (100 MHz,

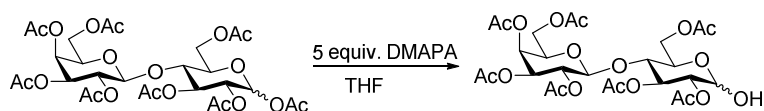
CDCl₃): δ_C 171.2, 170.7, 170.6, 170.3, 170.2, 169.3, 169.2, 169.1, 168.7, 92.2(C1 β), 90.5(C1 α), 72.5(C β), 70.4(C α), 69.5(C α), 68.1(C β), 67.6(C α), 61.7(C β), 61.5(C α), 52.6(C β), 50.8(C α), 22.9, 22.7, 20.8, 20.7, 20.6, 20.5, 20.5, 20.4, 20.4. Spectral values were in accordance with those reported in ref. ix & x.

2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl- α/β -D-glucopyranose (11)



Reaction time 2 h, Yield: 0.145 g, 83%, white foam, $[\alpha]_D^{RT}$ 50.2 (*c* 1.0, CHCl₃), Lit. 52.2.^{xi} *R*_f 0.36 (toluene/acetone 2:1). ¹H NMR (400 MHz, CDCl₃): δ_H 6.15 (d, 1H, *J* 9.3 Hz, NH), 5.25 (t, 1H, *J* 10.1 Hz, H3), 5.19 (s, 1H, H1), 5.07 (t, 1H, *J* 9.4 Hz, H4), 4.26-4.05 (4H, m, H2, H5, H6), 2.04, 1.99, 1.98, 1.93 (s, 12H). ¹³C NMR (100 MHz, CDCl₃): δ_C 171.4, 171.1, 170.9, 169.6, 91.5 (C1), 71.1, 68.4, 67.4, 62.2, 52.4, 23.0, 20.7, 20.7, 20.6. HRMS(ES): calcd. for C₁₄H₂₁NO₉H 348.1289; found 348.1292. Spectral values were in accordance with those reported in ref. xii & xiii.

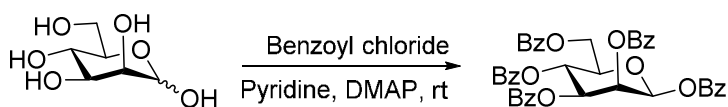
4-*O*-(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-2,3,6-tri-*O*-acetyl- α/β -D-glycopyranose (13)



Reaction time 1 ½ h, Yield: 0.318 g, 89%, α/β 2.7:1, white foam, *R*_f 0.45 (pentane/EtOAc 1:2). ¹H NMR (400 MHz, CDCl₃): δ_H 5.42, (t, 1H, *J* 9.6 Hz), 5.26 (d, 1H, *J* 3.2 Hz), 5.11 (t, 1H, *J* 9.2), 5.03 (m), 4.86 (dd, *J* 10.2, 3.2), 4.72-4.69 (m), 4.62 (s), 4.45-4.41 (m), 4.38 (s), 4.11-3.97 (m), 3.84-3.80

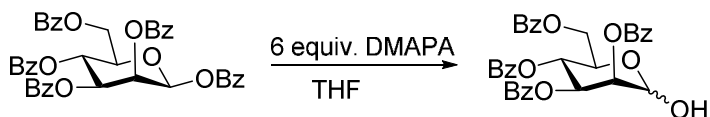
(m), 3.73-3.63 (m), 2.07, 2.04, 2.03, 1.98, 1.97, 1.96, 1.96, 1.87 (42H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ_C 170.6, 170.5, 170.5, 170.4, 170.3, 170.1, 170.1, 169.8, 169.7, 169.2, 169.1, 100.9, 100.8, 94.9, 89.8, 76.3, 76.1, 73.1, 72.7, 72.5, 71.4, 71.0, 70.9, 70.5, 69.6, 69.1, 67.9, 68.8, 66.6, 61.9, 60.8, 20.8, 20.8, 20.7, 20.7, 20.6, 20.5, 20.4. HRMS (ES): calcd. for C₂₆H₃₆O₁₈Na 659.1794; found 659.1794. Spectral values were in accordance with those reported in ref. xiv & xv.

1,2,3,4,6-penta-*O*-benzoyl-β-D-mannopyranose (**14**)



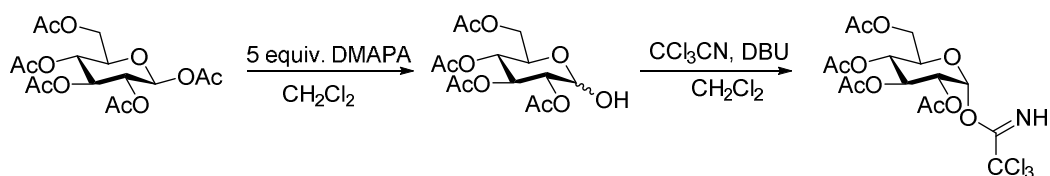
D-mannose (2.00 g, 11.1 mmol) was dissolved in pyridine (20 mL) and benzoyl chloride (9.67 mL, 83.3 mmol). The reaction was stirred for 5 min. before DMAP (13.6 mg, 1.11 mmol) was added to the reaction mixture. The reaction was allowed to stir overnight under argon atmosphere. The reaction was quenched with water and extracted twice with ethyl acetate (40 mL). The combined organic phases were washed thrice with hydrochloric acid (1 M) and brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure to give a white solid. The crude product was recrystallized (methanol and acetone) to give **14** as white crystals. Yield: 6.53 g, 84%, [α]_D^{RT} -76 (*c* 1.0, CHCl₃), Lit. -84.2.^{xvi} Mp. (uncorr): 160.7-161.3 °C; *R*_f: 0.47 (pentane/EtOAc 2:1). ¹H NMR (400 MHz, CDCl₃): δ_H 8.17-8.11 (m, 4H), 7.95-7.85 (m, 6H), 7.66-7.27 (m, 15H), 6.44 (s, 1H, H1), 6.18 (t, 1H, *J* 9.8 Hz, H4), 6.11 (d, 1H, *J* 3.2 Hz, H2), 5.81 (dd, 1H, *J* 9.8 Hz, 3.2 Hz, H3), 4.76 (dd, 1H, *J* 12.3 Hz, 2.7 Hz, H6a), 4.55 (dd, 1H, *J* 12.3 Hz, 4.2 Hz, H6b), 4.40-4.36 (m, 1H, H5). ¹³C NMR (100 MHz, CDCl₃): δ_C 166.2, 165.7, 165.6, 165.4, 164.2 (C=O), 133.4, 133.7, 133.7, 133.5, 133.2, 130.3, 130.2, 130.0, 130.0, 129.5, 128.9, 128.8, 128.8, 128.6, 128.6, 128.6, 128.5, 91.4 (C1), 73.5 (C5), 71.7 (C3), 69.5 (C2), 66.5 (C4), 62.8 (C6). HRMS(ES) calculated C₄₁H₃₂O₁₁Na 723.1837; found 723.1847. Spectral values were in accordance with those reported in ref. xvi & xvii.

2,3,4,6-tetra-O-benzoyl- α/β -D-mannopyranose (15)



A solution of **14** (0.50 mmol, 0.700 g) and DMAPA (6 equiv., 3.0 mmol) in THF (2.5 mL) was stirred for 18 h at room temperature. The reaction was followed by TLC analysis until full conversion. Then the reaction mixture was diluted in toluene and washed once with hydrochloric acid (1 M) and once with brine. The organic layer was dried with Na₂SO₄, filtered and concentrated under reduced pressure. Yield: 0.469 g, 79%, white foam. *R*_f: 0.32 (pentane/ethyl acetate 2:1) ¹H NMR (400 MHz, CDCl₃): δ_H 8.14-7.97 (m, 8H), 7.88-7.86 (m, 2H), 7.58 (t, 2H), 7.51-7.27 (m, 14H), 6.22 (t, 1H, *J* 10.1 Hz, H4), 6.06 (dd, 1H, *J* 10.1 Hz, 3.3 Hz, H3), 5.79 (dd, 1H, *J* 3.1 Hz, 1.9 Hz, H2), 5.56 (d, 1H, *J* 1.8 Hz, H1), 4.79 (dd, 1H, *J* 12.3 Hz, 2.7 Hz, H6b), 4.71 (dt, 1H, *J* 10.1 Hz, 2.9 Hz, H5), 4.46 (dd, 1H, *J* 12.3 Hz, 3.5 Hz). ¹³C NMR (100 MHz, CDCl₃): δ_C 171.3, 166.6, 165.8, 165.7, 165.6, 133.7, 133.5, 133.3, 133.2, 130.2, 129.9, 129.9, 129.8, 129.5, 129.4, 129.1, 128.6, 128.5, 128.5, 128.4, 128.3, 125.4. (α-anomer): 92.4 (C1), 72.2 (C5), 70.1 (C3), 68.8 (C2), 67.0 (C4), 62.9 (C6). (β-anomer): 92.2 (C1), 74.3, 73.6, 72.7, 68.5. HRMS (ESI): calcd. for C₃₄H₂₈O₁₀Na 619.1575; found 619.1578. Spectral values were in accordance with those reported in ref. xviii & xix.

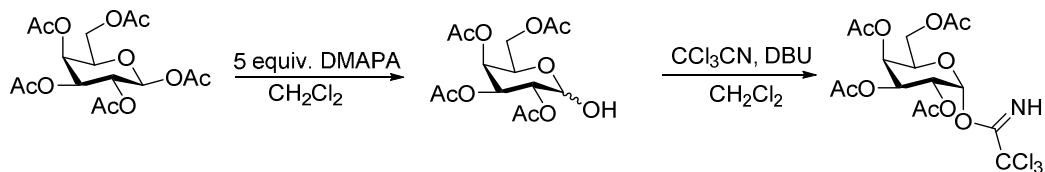
2,3,4,6-tetra-O-acetyl-D- α -glucopyranosyl trichloroacetimidate (16)



A solution of glucose pentaacetate (0.50 mmol) and DMAPA (5 equiv., 2.5 mmol) in CH₂Cl₂ (2.5 mL) was stirred at room temperature. The reaction was followed by TLC analysis until full conversion. After 3 hours CCl₃CN (10 equiv. 0.5 mL, 5 mmol) and DBU (0.2 equiv., 0.05 mL 0.4

mmol) were added to the reaction and the reaction changed to a yellow color. The reaction was stirred under an argon atmosphere for another 45 min. The reaction mixture was diluted in DCM and the organic phase was washed with hydrochloric acid (1 M) by saturated aqueous bicarbonate. The combined organic phases were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (pentane/ethyl acetate 1:1) and **16** was isolated as a yellow oil. Yield: 0.194 g, 78%. $[\alpha]_D^{RT} +67.2$ (*c* 1.0, CHCl₃), *R*_f: 0.50 (pentane/EtOAc 1:1). ¹H NMR (400 MHz, CDCl₃): δ_H 8.68 (s, 1H, NH), 6.51 (d, 1H, *J* 3.7 Hz, H1), 5.51 (t, 1H, *J* 9.9 Hz, H4), 5.13 (t, 1H, *J* 9.9 Hz, H3), 5.09 (dd, 1H, *J* 10.3 Hz, 3.7 Hz, H2), 4.24 (dd, 1H, *J* 12.0 Hz, 3.8 Hz, H6a), 4.19-4.15 (m, 1H, H5), 4.09 (dd, 1H, *J* 12.0 Hz, 1.8 Hz, H6b), 2.02, 2.00, 1.98, 1.97 (12H, s, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ_C 170.5, 170.0, 169.8, 169.5 (C=O), 160.7 (C=N), 92.9 (C1), 90.7 (C-Cl₃), 70.0 (C5), 69.8 (C3), 69.7 (C2), 67.7 (C4), 61.4 (C6), 20.7, 20.6, 20.5. Spectral values were in accordance with those reported in ref. xx & xxi.

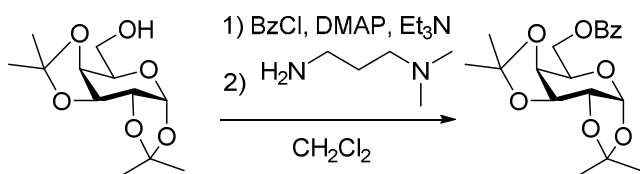
2,3,4,6-tetra-*O*-acetyl-D-α-galactopyranosyl trichloracetimidate (**17**)



A solution of glucose pentaacetate (0.50 mmol) and DMAPA (5 equiv., 2.5 mmol) in CH₂Cl₂ (2.5 mL) was stirred at room temperature. The reaction was followed by TLC analysis until full conversion. After 3 hours CCl₃CN (10 equiv. 0.5 mL, 5 mmol) and DBU (0.8 equiv., 0.05 mL 0.4 mmol) were added to the reaction and the reaction mixture changed to yellow. The reaction was stirred under an argon atmosphere for another 45 min. The reaction mixture was diluted in DCM and the organic phase was washed with hydrochloric acid (1 M) followed by saturated aqueous bicarbonate. The combined organic phases were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (pentane/ethyl acetate 1:1) and **17** was isolated as a yellow oil. Yield 0.201 g, 82%. $[\alpha]_D^{RT} +83.4$ (*c* 1, CHCl₃). *R*_f: 0.52 (pentane/EtOAc 1:1). ¹H NMR (400 MHz, CDCl₃): δ_H 8.66 (s, 1H, NH), 6.57 (s, 1H, H1), 5.52 (s, 1H, H4), 5.38 (m, 2H, H3, H2), 4.21 (t, 1H, *J* 6.5 Hz, H5), 4.15-4.02 (m, 2H, H6), 2.13 (s, 3H,

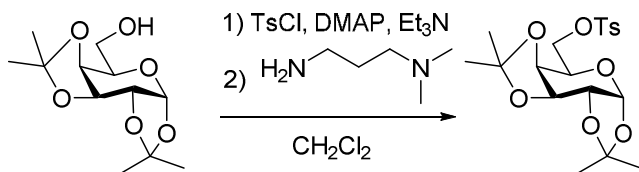
CH₃), 1.99 (s, 9H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ_C 170.3, 170.1, 170.1, 170.0 (C=O), 160.9 (C=N), 93.6 (C1), 90.8 (CCl₃), 69.1 (C5), 67.6 (C3), 67.4 (C2), 67.0 (C4), 61.3 (C6), 20.7, 20.7, 20.6, 20.6 (CH₃). Spectral values were in accordance with those reported in ref. xxii & xxiii.

6-*O*-benzoyl-1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranose



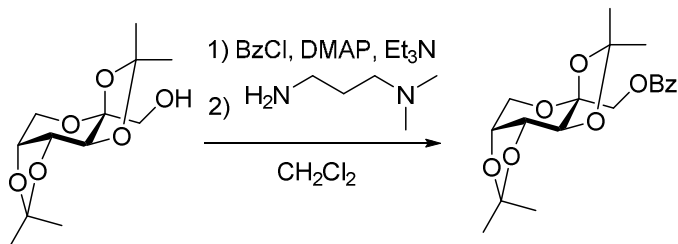
1,2;3,4-Di-*O*-isopropylidene-α-D-galactopyranose^{xxiv} (0.20 g, 0.77 mmol) was dissolved in dry CH₂Cl₂ (2.5 mL). To the mixture was added DMAP (0.1 equiv. 0.01 g, 0.077 mmol), Et₃N (1.5 equiv. 1.2 mmol, 0.16 mL) and finally benzoyl chloride (4 equiv. 3.1 mmol, 0.36 mL). The solution was stirred at room temperature for 1½ hours and then quenched by addition of 3-(dimethylamino)-1-propylamine (4 equiv. 3.1 mmol, 0.39 mL). The mixture was stirred for an additional 30 min. before diluted with CH₂Cl₂ and washed thrice with hydrochloric acid (1 M), aqueous saturated bicarbonate solution and then brine. The organic layer was dried with MgSO₄, filtered and evaporated to dryness giving the product (0.278 g, 99%) as a syrup. *R*_f: 0.71(pentane/EtOAc, 5:1). [α]_D^{RT} -57 (*c* 1.0, CHCl₃). Lit.- 59.4.^{xxv} ¹H NMR (400 MHz, CDCl₃) δ_H 8.06 – 8.03 (m, 1H), 8.03-8.00 (m, 1H), 7.55-7.48 (m, 1H), 7.42-7.36 (m, 2H), 5.54 (d, 1H, *J* 5.0 Hz, 1H), 4.63 (dd, 1H, *J* 7.9 Hz, 2.5 Hz), 4.50 (dd, 1H, *J* 11.5 Hz, 4.9 Hz, H6a), 4.41 (dd, 1H, *J* 11.5 Hz, 7.5 Hz, H6b), 4.36-4.27 (m, 2H), 4.16 (ddd, 1H, *J* 7.5 Hz, 4.9 Hz, 1.8 Hz, H5), 1.49 (s, 3H), 1.45 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ_C 166.4 (C=O), 133.0, 130.1, 129.7, 128.4, 109.7, 108.8, 96.3 (C1), 71.2, 70.7, 70.5, 66.2 (C5), 63.9 (C6), 26.0, 26.0, 25.0, 24.5. HRMS(ES): calcd. for C₁₉H₂₅O₇ 369.1595; found: 369.1598. Spectral values were in accordance with those reported in ref. xxv

1,2;3,4-di-*O*-isopropylidene-6-*O*-tosyl- α -D-galactopyranose



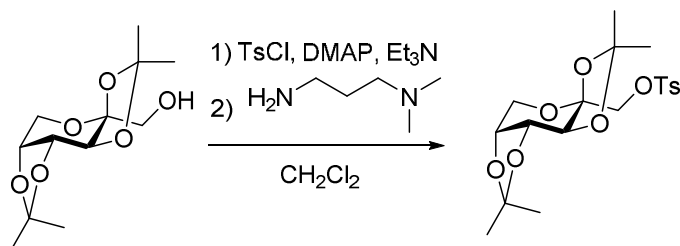
1,2;3,4-Di-*O*-isopropylidene- α -D-galactopyranose^{xxiv} (0.20 g, 0.77 mmol) was dissolved in dry CH₂Cl₂ (2.5 mL). To the mixture was added DMAP (0.1 equiv. 0.01 g, 0.077 mmol), Et₃N (1.5 equiv. 1.2 mmol, 0.16 mL) and finally tosyl chloride (4 equiv. 0.31 mmol, 0.59 g). The solution was stirred at room temperature for 2 hours and then quenched by addition of 3-(dimethylamino)-1-propylamine (4 equiv. 3.1 mmol, 0.39 mL). The mixture was stirred for an additional 30 min. before diluted with CH₂Cl₂ and washed thrice with hydrochloric acid (1 M), aqueous saturated bicarbonate solution then brine. The organic layer was dried with MgSO₄, filtered and evaporated to dryness giving the product (0.318 g, 99%) as a syrup. *R*_f: 0.36(pentane/EtOAc 5:1). [α]_D^{RT} -64.2 (*c* 1.0, CHCl₃). Lit.- 52.7.^{xxvi} ¹H NMR (400 MHz, CDCl₃) δ _H 7.72 (d, 1H, *J* 8.3 Hz), 7.25 (d, 2H, *J* 8.1 Hz), 5.37 (d, 1H, *J* 4.9 Hz, H1), 4.51 (dd, 1H, *J* 7.9 Hz, 2.5 Hz, H3), 4.22 (dd, 1H, *J* 4.9 Hz, 2.5 Hz, H2), 4.19-4.09 (m, 2H, H4, H6a), 4.10-3.91 (m, 2H, H5, H6b), 2.36 (s, 3H), 1.42 (s, 3H), 1.26 (s, 3H), 1.23 (s, 3H), 1.20 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ _C 144.8, 133.0, 129.8, 128.1, 109.6, 109.0, 96.2 (C1), 70.6, 70.5, 70.4, 68.3 (C6), 65.9 (C5), 26.0, 25.9, 25.0, 24.4, 21.6. HRMS(ES): calcd. for C₁₉H₃₀O₈NS 432.1687; found: 432.1691. Spectral values were in accordance with those reported in ref. xxvi & xxvii.

1-*O*-benzoyl-2,3;4,5-di-*O*-isopropylidene- β -D-fructopyranose



2,3;4,5-Di-*O*-isopropylidene- β -D-fructopyranose^{xxviii} (0.20 g, 0.77 mmol) was dissolved in dry CH_2Cl_2 (2.5 mL). To the mixture was added DMAP (0.1 equiv. 0.01 g, 0.077 mmol), Et_3N (1.5 equiv. 1.2 mmol, 0.16 mL) and finally benzoyl chloride (4 equiv. 3.1 mmol, 0.36 mL). The solution was stirred at room temperature for 2 hours and then quenched by addition of 3-(dimethylamino)-1-propylamine (4 equiv. 3.1 mmol, 0.39 mL). The mixture was stirred for an additional 30 min. before diluted with CH_2Cl_2 and washed thrice with hydrochloric acid (1 M), aqueous saturated bicarbonate solution and then brine. The organic layer was dried over MgSO_4 , filtered and evaporated to dryness giving the product (0.279 g, 100%) as a syrup. R_f : 0.64 (pentane/EtOAc 5:1) $[\alpha]_D^{RT}$ -17.0 (c 1.0, CHCl_3). Lit. -20.6.^{xxix} ^1H NMR (400 MHz, CDCl_3) δ_H 8.06 (d, 2H, J 7.1 Hz), 7.54 (t, 1H, J 7.4 Hz), 7.41 (t, 2H, J 7.6 Hz), 4.67 (d, 1H, J 11.8 Hz, H1a), 4.63 (dd, 1H, J 7.8 Hz, 2.3 Hz, H4), 4.46 (d, 1H, J 2.3 Hz, H3), 4.31 (d, 1H J 11.8 Hz, H1b), 4.24 (dd, 1H, J 7.8 Hz, 1.0 Hz, H5), 3.94 (dd, 1H, J 13.0 Hz, 1.0 Hz, H6a), 3.78 (d, 1H, J 13.0 Hz, H6b), 1.53 (s, 3H), 1.44 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ_C 166.0 (C=O), 133.2, 129.9, 129.8, 128.5, 109.2, 108.9, 101.7 (C2), 70.9 (C5), 70.6 (C3), 70.2 (C4), 65.3 (C1), 61.4 (C6), 26.6, 25.9, 25.6, 24.1. HRMS(ES): calcd. for $\text{C}_{19}\text{H}_{25}\text{O}_7$ 365.1595; found: 365.1600. Spectral values were in accordance with those reported in ref. xxx.

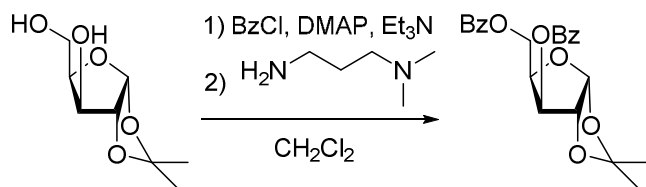
2,3;4,5-di-*O*-isopropylidene-1-*O*-tosyl- β -D-fructopyranose



2,3;4,5-Di-*O*-isopropylidene- β -D-fructopyranose^{IV} (0.20 g, 0.77 mmol) was dissolved in dry CH_2Cl_2 (2.5 mL). To the mixture was added DMAP (1 equiv. 0.1 g, 0.77 mmol), Et_3N (2 equiv. 1.5 mmol, 0.21 mL) and finally tosyl chloride (4 equiv. 3.1 mmol, 0.59 g). The solution was stirred at room temperature for 2 hours and then quenched by addition of 3-(dimethylamino)-1-propylamine (4 equiv. 3.1 mmol, 0.39 mL). The mixture was stirred for an additional 30 min. before diluted with CH_2Cl_2 and washed thrice with hydrochloric acid (1 M), aqueous saturated bicarbonate solution and then brine. The organic layer was dried over MgSO_4 , filtered and evaporated to dryness giving the product (0.306 g, 96%) as a syrup. R_f : 0.72 (pentane/EtOAc 5:1). $[\alpha]_D^{RT}$ -21.4 (c 1.0, CHCl_3). NMR

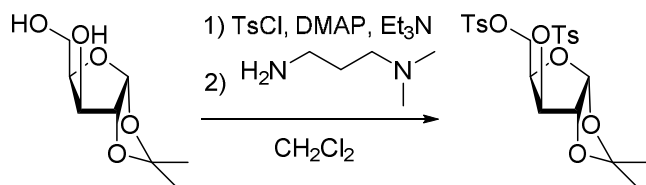
(400 MHz, CDCl₃) δ_H 7.76 (d, 2H, J 8.2 Hz), 7.32 (d, 2H, J 8.2 Hz), 4.53 (dd, 1H, J 7.9 Hz, 2.2 Hz, H4), 4.26 (d, 1H, J 2.2 Hz, H5), 4.17 (d, 1H, J 7.9 Hz, H3), 4.03 (d, 1H, J 10.2 Hz, H1a), 3.98 (d, 1H, J 10.2 Hz, H1b), 3.83 (dd, 1H, J 13.0 Hz, 1.4 Hz, H6a), 3.67 (d, 1H, J 13.0 Hz, H6b), 2.42 (s, 3H), 1.47 (s, 3H), 1.33 (s, 6H), 1.28 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ_C 145.0, 132.4, 129.8, 128.1, 109.14, 109.0, 100.6 (C2), 70.5 (C3), 69.9, 69.8, 69.1 (C1), 61.2 (C2), 26.5, 25.7, 25.1, 23.9, 21.6. HRMS(ES): calcd. for C₁₉H₃₀NO₈S 432.1687; found: 432.1697.

3,5-di-*O*-benzoyl-1,2-*O*-isopropylidene-D-xylofuranose



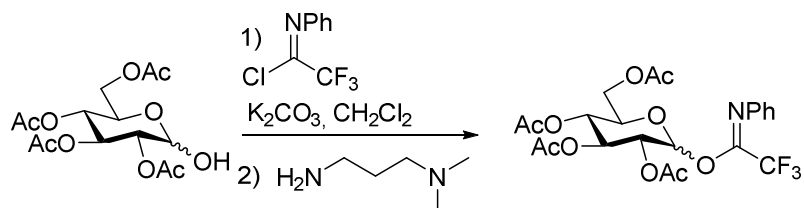
1,2-*O*-Isopropylidene-D-xylofuranose^{xxxi} (0.20 g, 1.1 mmol) was dissolved in dry CH₂Cl₂ (3 mL). To the mixture was added DMAP (0.2 equiv. 0.03 g, 0.21 mmol), Et₃N (3 equiv. 3.2 mmol, 0.44 mL) and finally benzoyl chloride (8 equiv. 8.4 mmol, 1 mL). The solution was stirred at room temperature for 2 hours and then quenched by addition of 3-(dimethylamino)-1-propylamine (8 equiv. 8.4 mmol, 1.1 mL). The mixture was stirred for an additional 30 min. before diluted with CH₂Cl₂ and washed thrice with hydrochloric acid (1 M), aqueous saturated bicarbonate solution and then brine. The organic layer was dried over MgSO₄, filtered and evaporated to dryness giving the product (0.404 g, 98%) as a syrup. R_f : 0.59 (pentane/EtOAc 5:1). $[\alpha]_D^{RT}$ -35.0 (c 1.0, CHCl₃). Lit. -28.^{xxxii} NMR (400 MHz, CDCl₃) δ_H 8.07-7.97 (m, 4H), 7.59-7.51 (m, 2H), 7.46-7.34 (m, 4H), 6.06 (s, 1H, H1), 5.60 (s, 1H), 4.83-4.74 (m, 1H), 4.70 (s, 1H, H2), 4.64-4.56 (m, 2H, H5), 1.57 (s, 3H), 1.33 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ_C 166.2(C=O), 165.3(C=O) 133.7, 133.2, 129.8, 129.6, 129.0, 128.6, 128.4, 112.4, 105.1 (C1), 83.5 (C2), 77.1, 76.8, 62.0 (C5), 26.8, 26.3. HRMS(ES): calcd. for C₂₂H₂₃O₇ 399.1438; found: 399.1441. Spectral values were in accordance with those reported in ref. xxxiii.

1,2-*O*-Isopropylidene-3,5-di-*O*-tosyl-D-xylofuranose



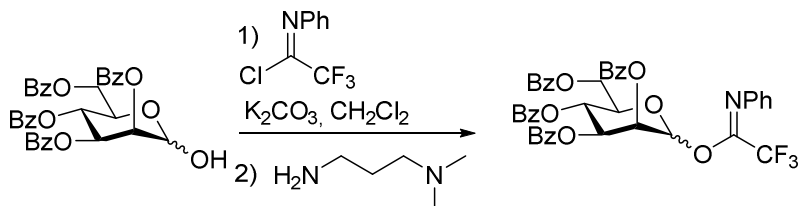
1,2-*O*-isopropylidene-D-xylofuranose^{xxxix} (0.20 g, 1.1 mmol) was dissolved in dry CH₂Cl₂ (3 mL). To the mixture was added DMAP (0.2 equiv. 0.03 g, 0.21 mmol), Et₃N (3 equiv. 3.2 mmol, 0.44 mL) and finally tosyl chloride (8 equiv. 8.4 mmol, 1.6 g). The solution was stirred at room temperature for 24 hours and then quenched by addition of 3-(dimethylamino)-1-propylamine (8 equiv. 8.4 mmol, 1.1 mL). The mixture was stirred for an additional 30 min. before diluted with CH₂Cl₂ and washed thrice with hydrochloric acid (1 M), aqueous saturated bicarbonate solution then brine. The organic layer was dried over MgSO₄, filtered and evaporated to dryness giving the product (0.504 g, 96%) as a syrup. *R*_f: 0.53 (pentane/EtOAc 3:1). [α]_D^{RT} -30.0 (*c* 1.0, CHCl₃). Lit. - 30.^{xxxiv} ¹H NMR (400 MHz, CDCl₃) δ_H 7.76 (d, 1H, *J* 8.5 Hz), 7.69 (d, 1H, *J* 8.4 Hz), 7.37 (d, 1H, *J* 8.5 Hz), 7.32 (d, 1H, *J* 8.4 Hz), 5.84 (d, 1H, *J* 3.7 Hz, H1), 4.74 (d, 1H, *J* 3.0 Hz, H3), 4.65 (d, 1H, *J* 3.7 Hz, H2), 4.31 (td, 1H, *J* 6.1, 3.0 Hz, H4), 4.02 (dd, 1H, *J* 10.6, 6.4 Hz, H5a), 3.97 (dd, 1H, *J* 10.6, 5.8 Hz, H5b), 2.45 (s, 3H), 2.42 (s, 3H), 1.39 (s, 3H), 1.24 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ_C 146.0, 145.3, 132.3, 132.1, 130.3, 123.0, 128.0, 112.8, 104.8 (C1), 83.0 (C2), 81.3 (C3), 76.2 (C4), 66.0 (C5), 26.6, 26.2, 21.8, 21.7. HRMS(ES): calcd. for C₂₂H₃₀O₉S₂N 516.1356; found: 516.1358. Spectral values were in accordance with those reported in xxxiv & xxxv.

2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl 1-(*N*-phenyl)-2,2,2-trifluoroacetimidate



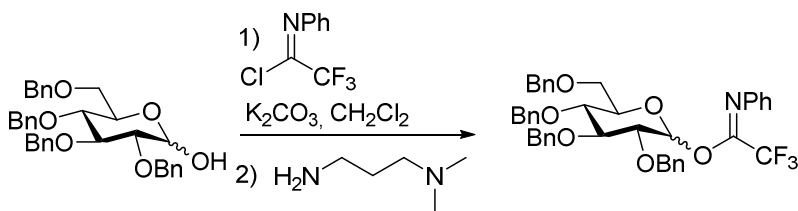
2,3,4,6-Tetra-*O*-acetyl-D-glucopyranose (0.22 g, 0.63 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride^{xxxvii} (2 equiv. 0.262 g, 1.26 mmol) was dissolved in CH₂Cl₂ (3 mL). To the mixture was added K₂CO₃ (2 equiv. 0.174 g, 1.26 mmol) and the solution was stirred at room temperature for 4 hours before quenched by addition of 3-(dimethylamino)-1-propylamine (1.5 equiv. 0.95 mmol, 0.12 mL). The mixture was stirred for an additional 10 minutes before diluted with CH₂Cl₂ and washed twice with hydrochloric acid (0.1 M), aqueous saturated bicarbonate solution then brine. The organic layer was dried over MgSO₄, filtered and evaporated to dryness giving the product (0.304 g, 93%) as a syrup. *R*_f: 0.33 (pentane/EtOAc 5:1). ¹H NMR (400 MHz, CDCl₃) δ_H 7.30 (t, 2H, *J* 7.7 Hz), 7.12 (t, 1H, *J* 7.3 Hz), 6.83 (d, 1H, *J* 7.0 Hz), 5.24 (s, 1H), 5.17 (d, 1H, *J* 9.0 Hz), 4.26 (d, 1H, *J* 12.3 Hz), 4.12 (d, 1H, *J* 12.2 Hz), 2.06 (s, 6H), 2.01 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ_C 170.7, 170.2, 169.4, 169.1, 143.0, 129.4, 128.9, 126.3, 124.8, 120.6, 119.3, 94.1, 94.4, 72.8, 72.6, 70.2, 67.8, 61.5, 20.7, 20.6, 20.6, 20.5. Spectral values were in accordance with those reported in ref. xxxvi.

2,3,4,6-Tetra-*O*-benzoyl-D-mannopyranosyl 1-(*N*-phenyl)-2,2,2-trifluoroacetimidate



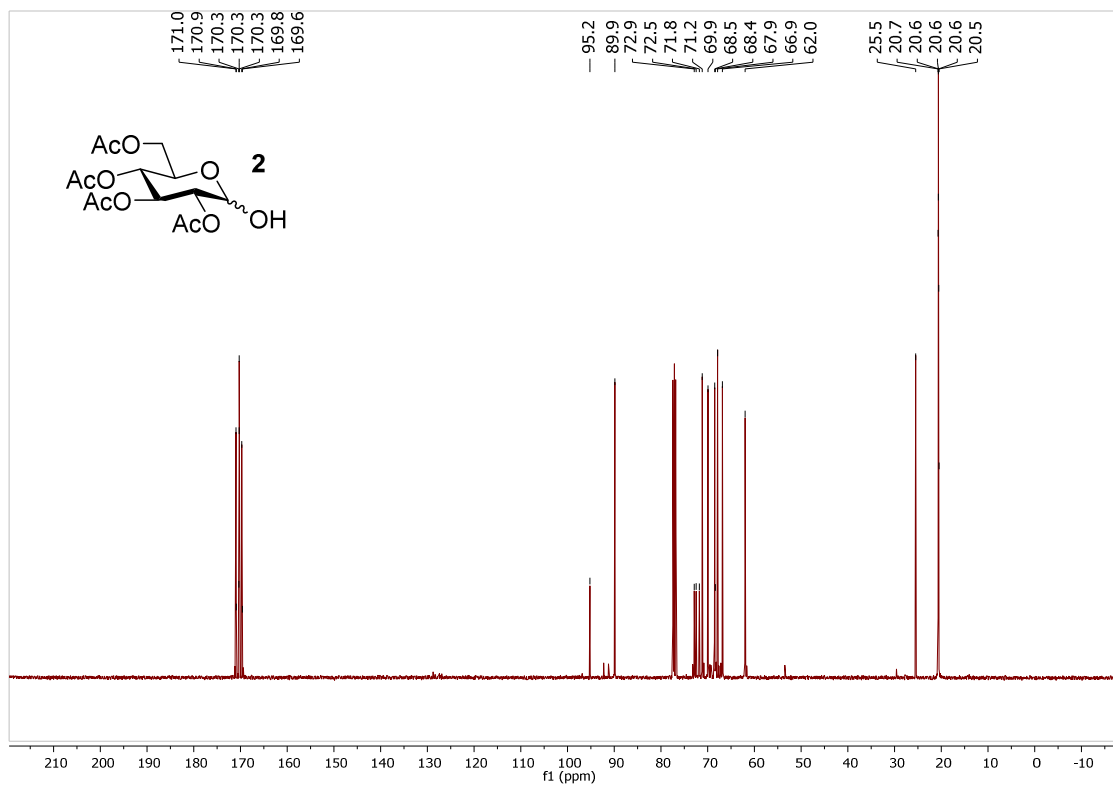
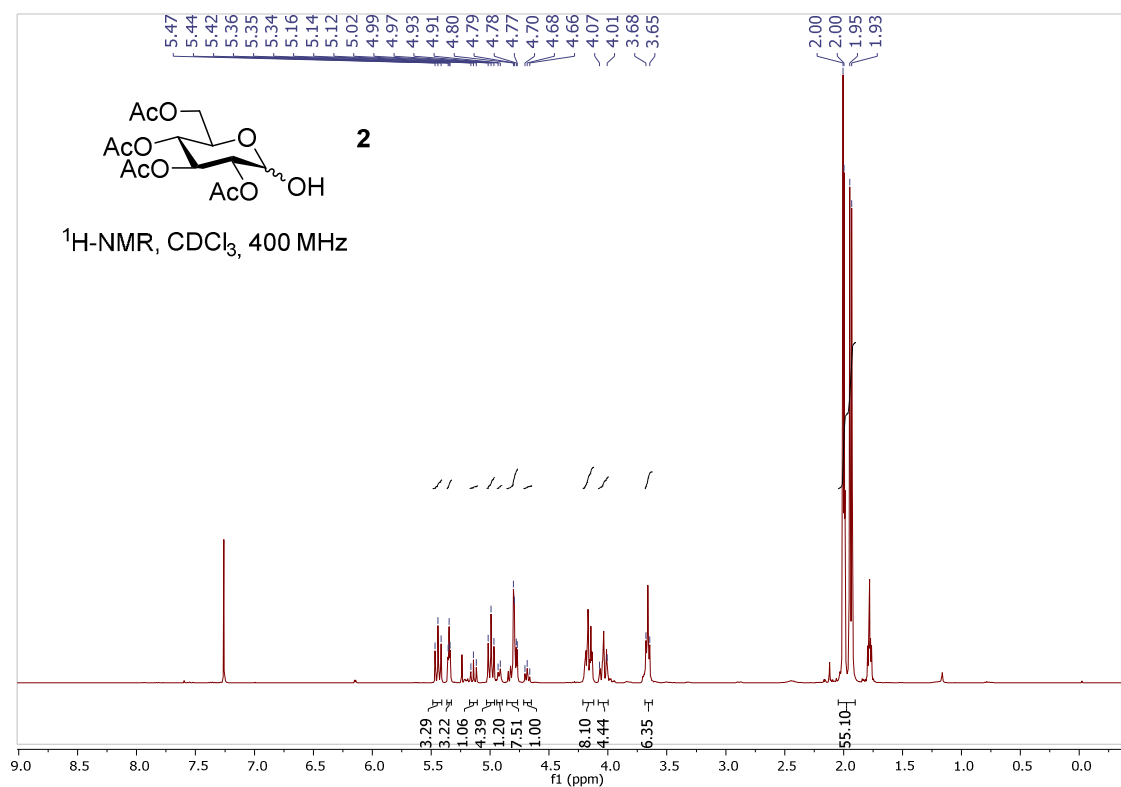
2,3,4,6-Tetra-*O*-benzoyl-D-mannopyranose (0.10 g, 0.17 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride^{xxxvii} (2 equiv. 0.071 g, 0.35 mmol) was dissolved in CH₂Cl₂ (3 mL). To the mixture was added K₂CO₃ (2 equiv. 0.05 g, 0.35 mmol). The solution was stirred at room temperature for 4 hours and then quenched by addition of 3-(dimethylamino)-1-propylamine (1.5 equiv. 0.26 mmol, 0.033 mL). The mixture was stirred for an additional 10 minutes before diluted with CH₂Cl₂ and washed twice with hydrochloric acid (0.1 M), aqueous saturated bicarbonate solution and then brine. The organic layer was dried over MgSO₄, filtered and evaporated to dryness giving the product (0.1 g, 77 %) as a syrup. *R*_f: 0.63 (pentane/EtOAc 5:1). ¹H NMR (400 MHz, CDCl₃) δ_H 8.15 (dd, 1H *J* 8.2 Hz, 1.1 Hz), 8.11-8.06 (m, 1H), 8.05-7.98 (m, 1H), 7.89 (dd, 1H, *J* 8.3 Hz, 1.1 Hz), 7.67-7.59 (m, 1H), 7.56-7.51 (m, 1H), 7.48-7.38 (m, 4H), 7.32-7.28 (m, 2H), 7.16-7.10 (m, 1H), 6.84 (d, 1H, *J* 7.6 Hz), 6.59 (s, 1H), 6.26 (t, 1H, *J* 10.8 Hz), 6.02-6.00 (m, 1H), 4.79-4.76 (m, 1H), 4.65-4.49 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ_C 166.1, 165.6, 165.5, 165.2, 142.9, 133.9, 133.8, 133.5, 133.3, 130.1, 130.0, 130.0, 130.0, 130.0, 129.8, 129.4, 128.9, 128.9, 128.9, 128.9, 128.8, 128.8, 128.7, 128.6, 128.6, 128.6, 128.5, 124.8, 120.6, 119.4, 110.1, 93.6, 71.4, 71.1, 69.8, 68.9, 66.6, 66.2, 62.6.

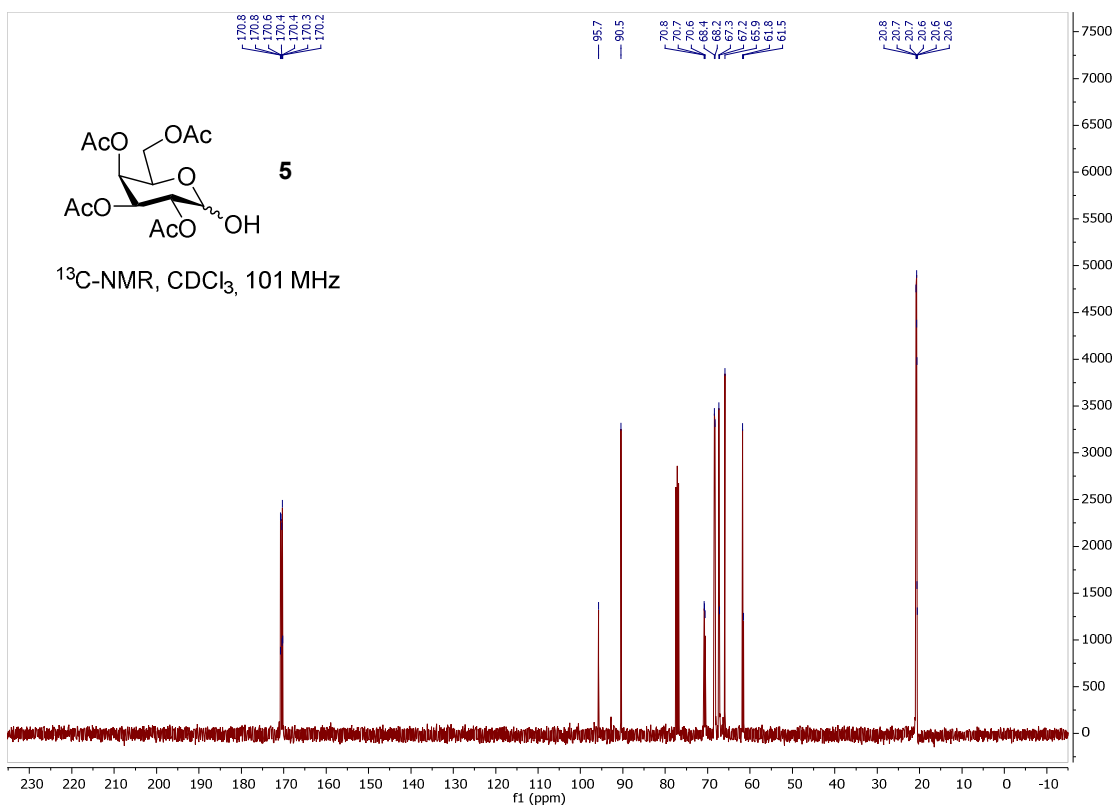
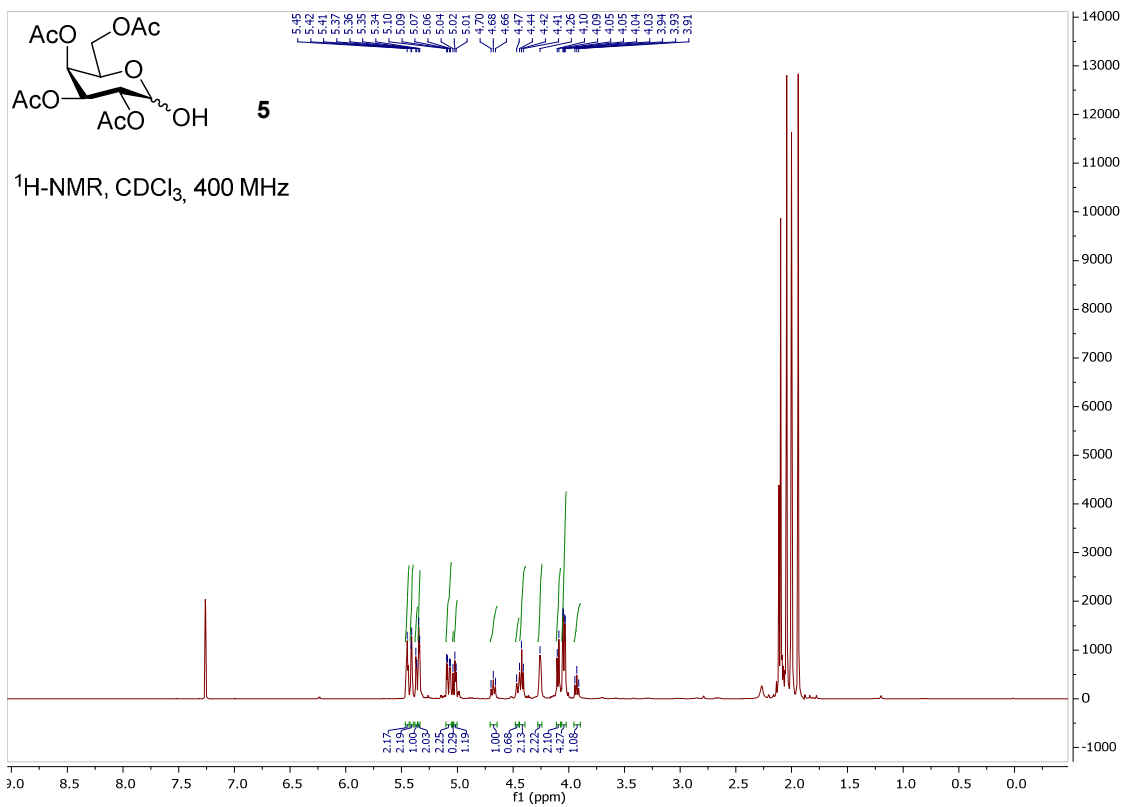
2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl 1-(*N*-phenyl)-2,2,2-trifluoroacetimidate

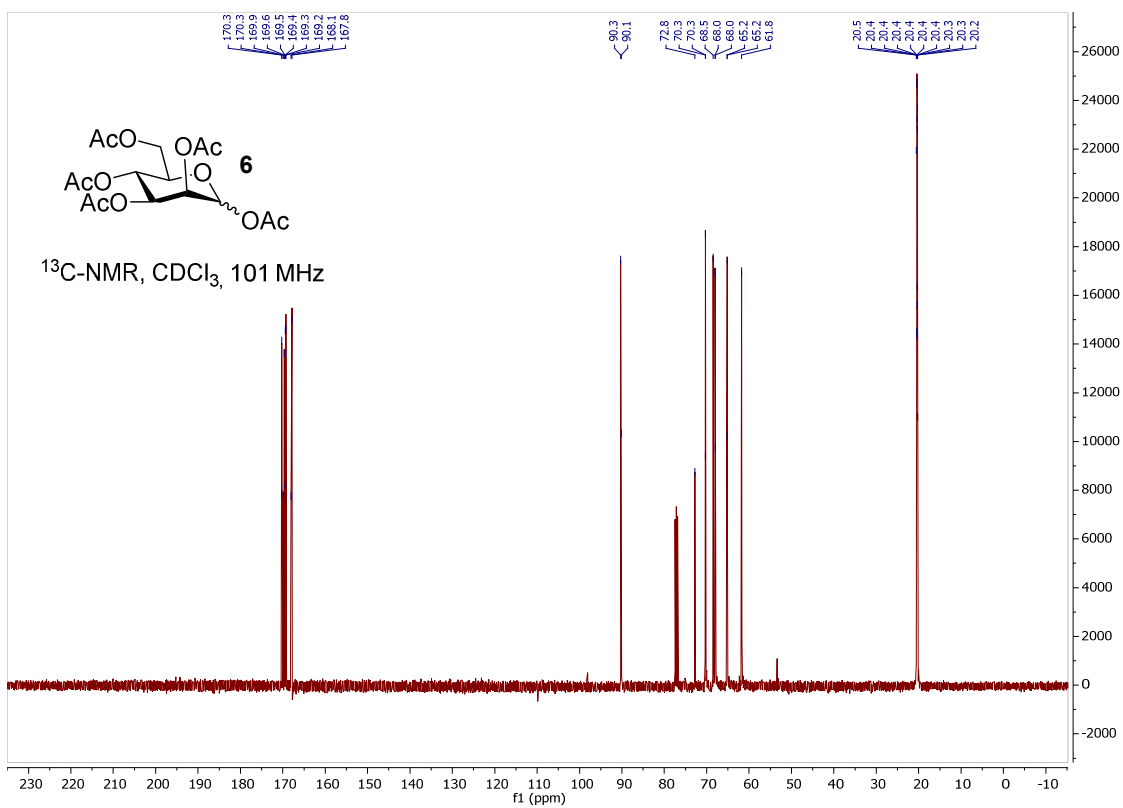
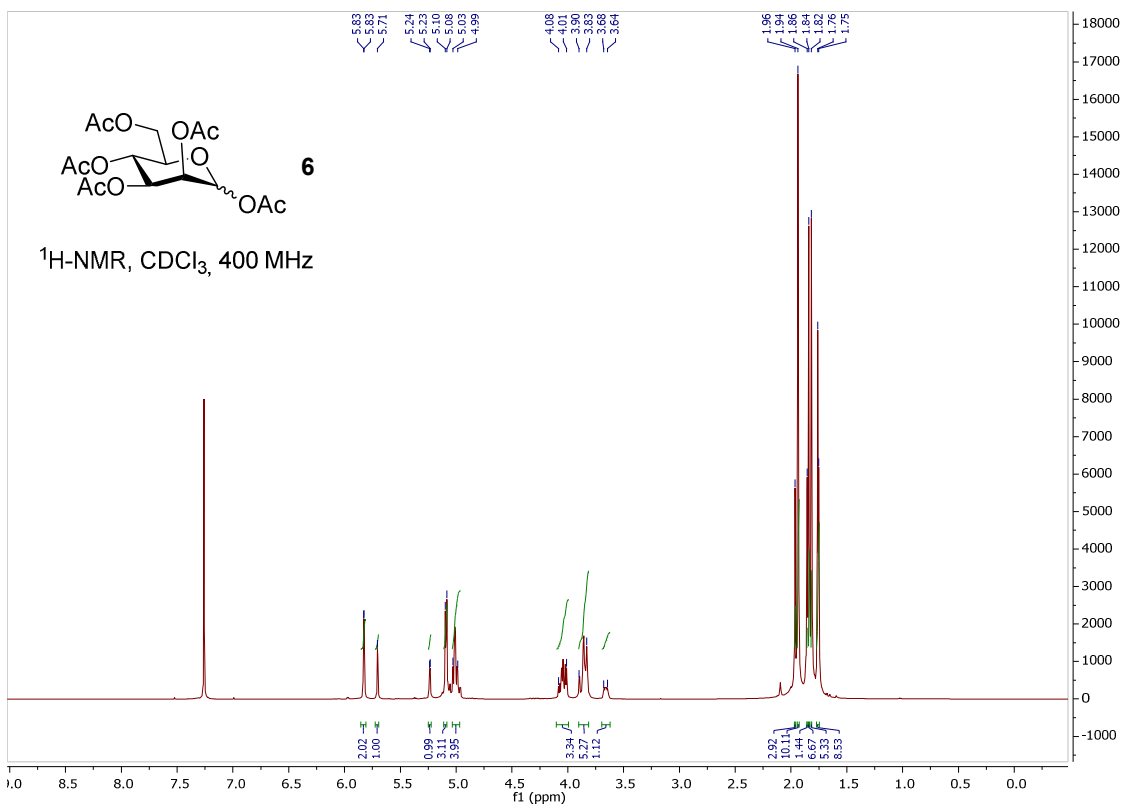


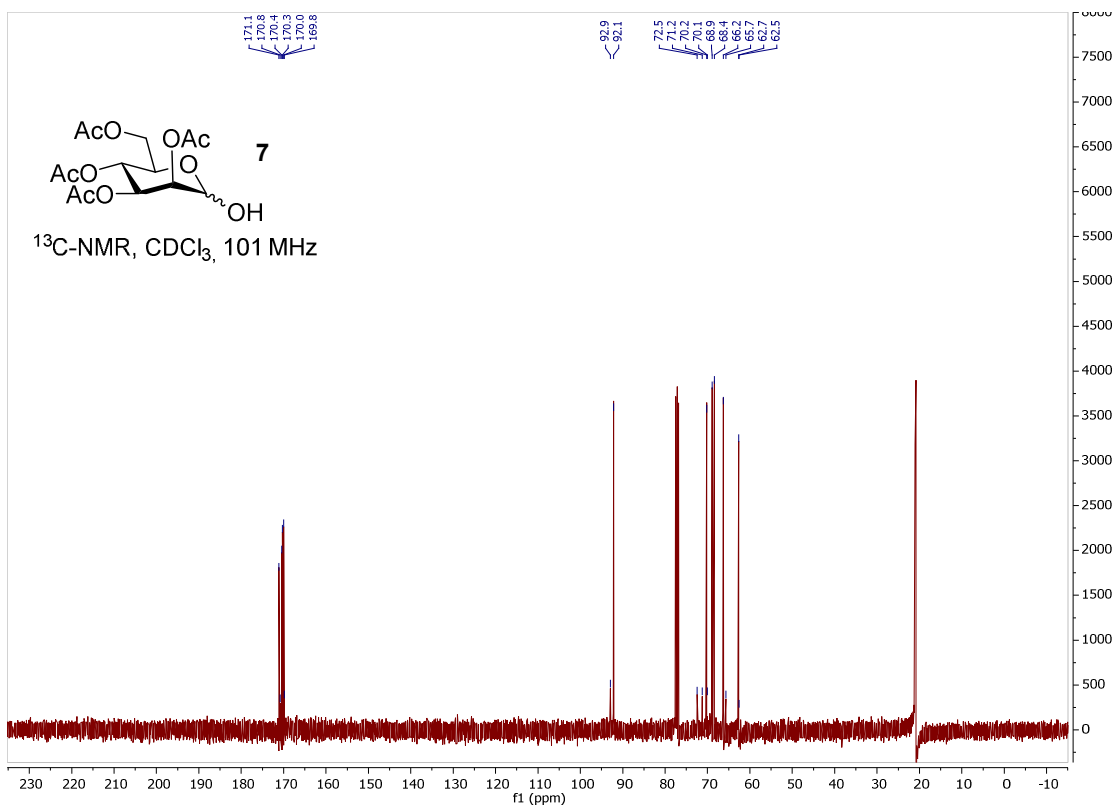
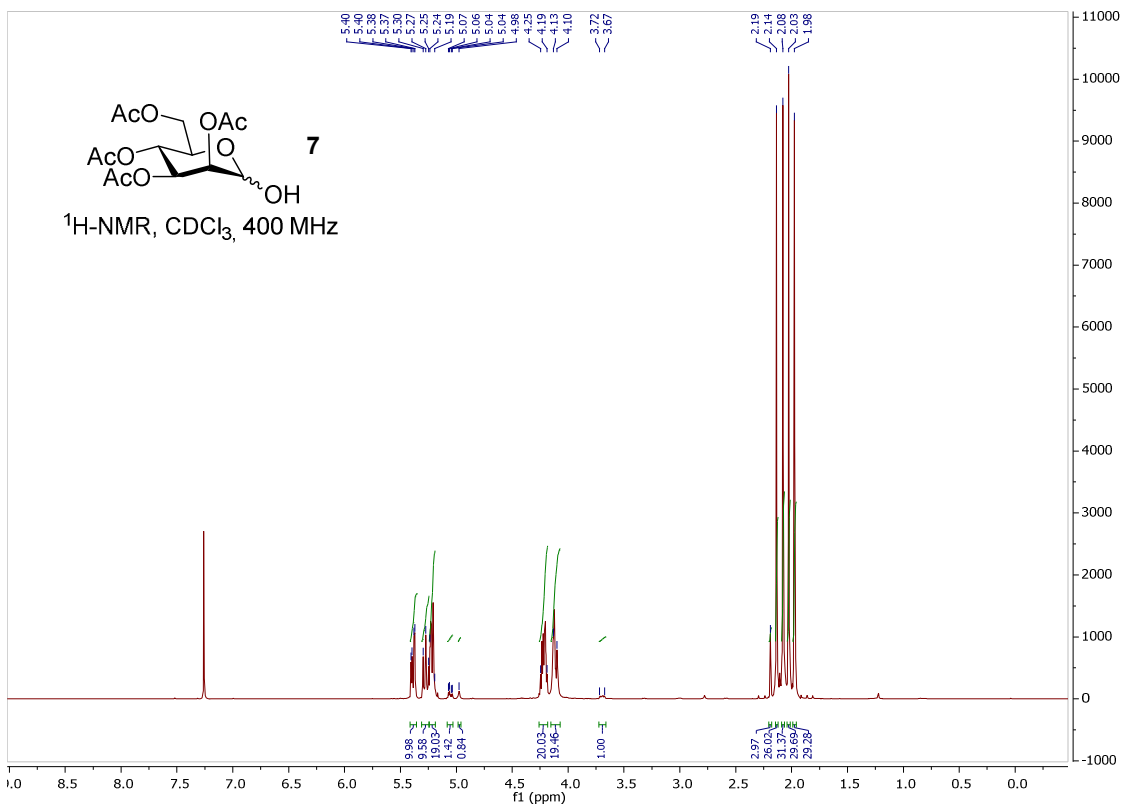
2,3,4,6-Tetra-*O*-benzyl-D-glucopyranose^{xxxviii} (0.10 g, 0.19 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride^{xxxvii} (2 equiv. 0.078 g, 0.38 mmol) was dissolved in CH₂Cl₂ (3 mL). To the mixture was added K₂CO₃ (2 equiv. 0.053 g, 0.38 mmol). The solution was stirred at room temperature for 24 hours and then quenched by addition of 3-(dimethylamino)-1-propylamine (1.5 equiv. 0.29 mmol, 0.04 mL). The mixture was stirred for an additional 10 minutes before diluted with CH₂Cl₂ and washed twice with hydrochloric acid (0.1 M), aqueous saturated bicarbonate solution and then brine. The organic layer was dried over MgSO₄, filtered and evaporated to dryness giving the product (0.126 g, 92%) as a syrup. *R*_f: 0.7 (pentane/EtOAc 10:1). ¹H NMR (400 MHz, CDCl₃) δ_H 7.53-7.33 (m, 20H), 7.27 (s, 2H), 7.18 (t, 1H, *J* 7.0 Hz), 6.92 (d, 1H, *J* 7.3 Hz), 5.09-4.85 (m, 4H), 4.74 (d, 1H, *J* 12.1 Hz), 4.67-4.67 (m, 2H), 3.83 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ_C 138.4, 138.0, 137.9, 137.8, 129.3, 128.8, 128.6, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 126.3, 124.3, 120.6, 119.4, 84.5, 81.0, 75.8, 75.7, 75.6, 75.4, 75.2, 75.1, 73.6, 73.5, 73.4, 68.1. Spectral values were in accordance with those reported in ref. xxxix.

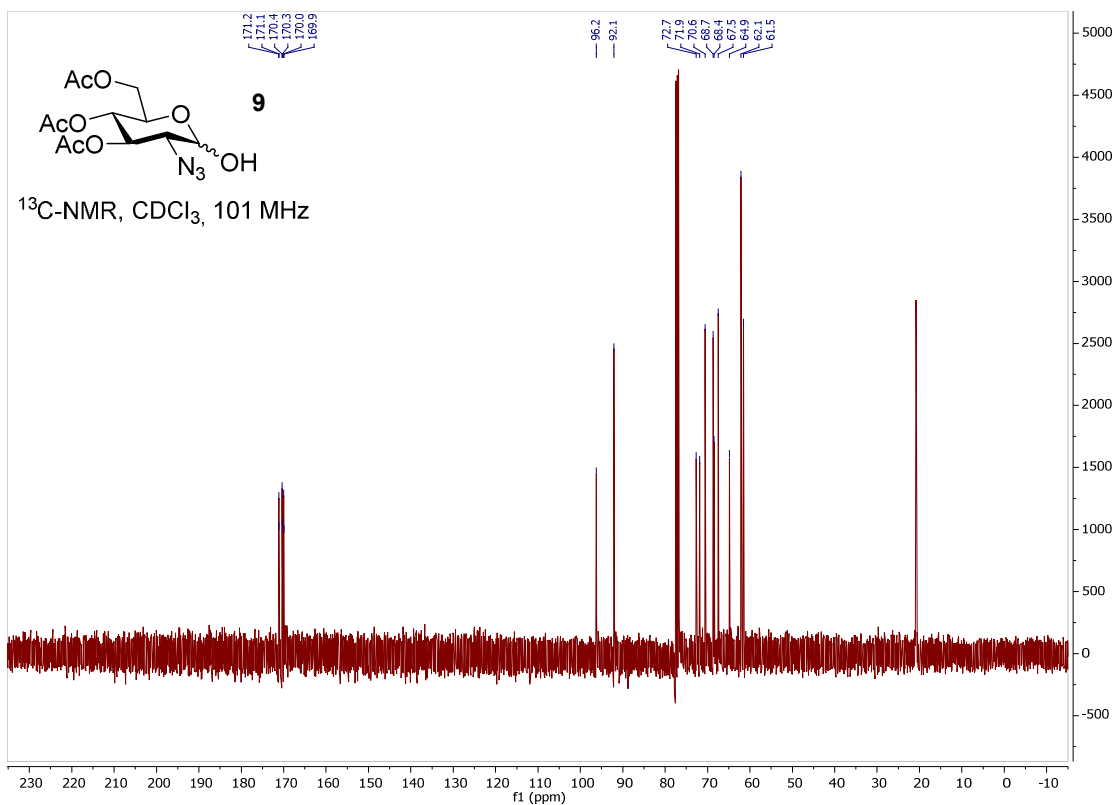
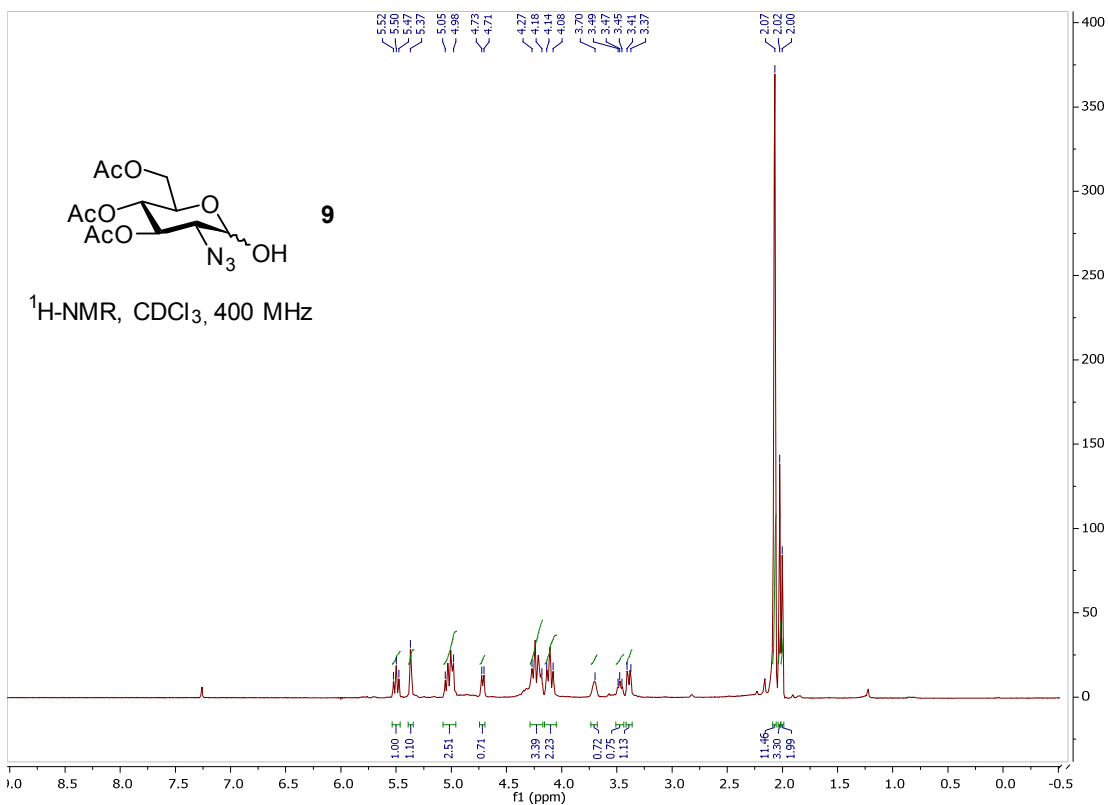
^1H and ^{13}C NMR Spectra for Compounds.

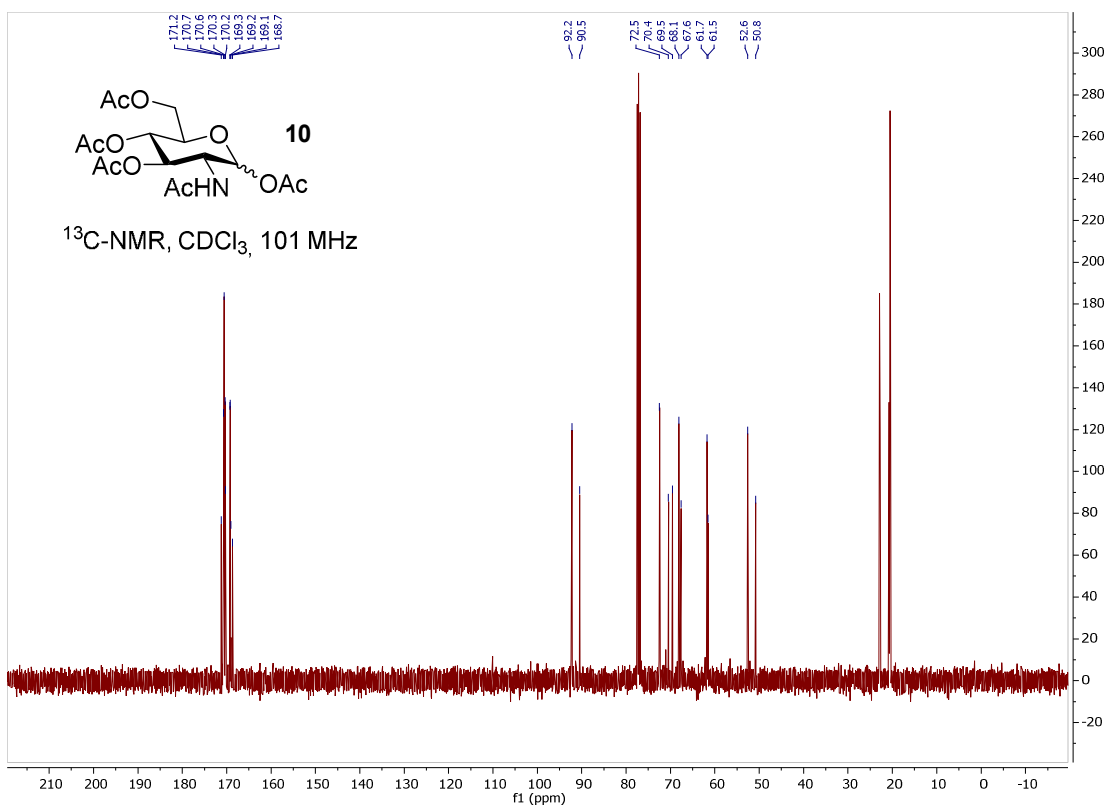
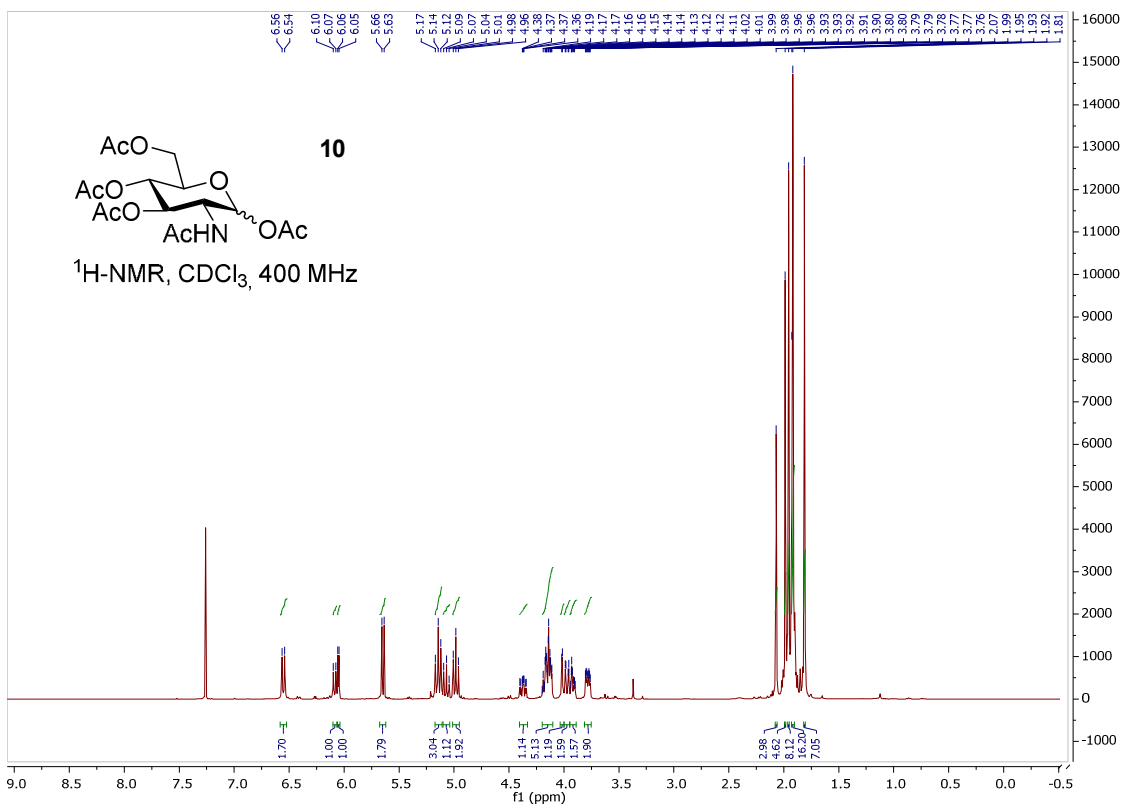


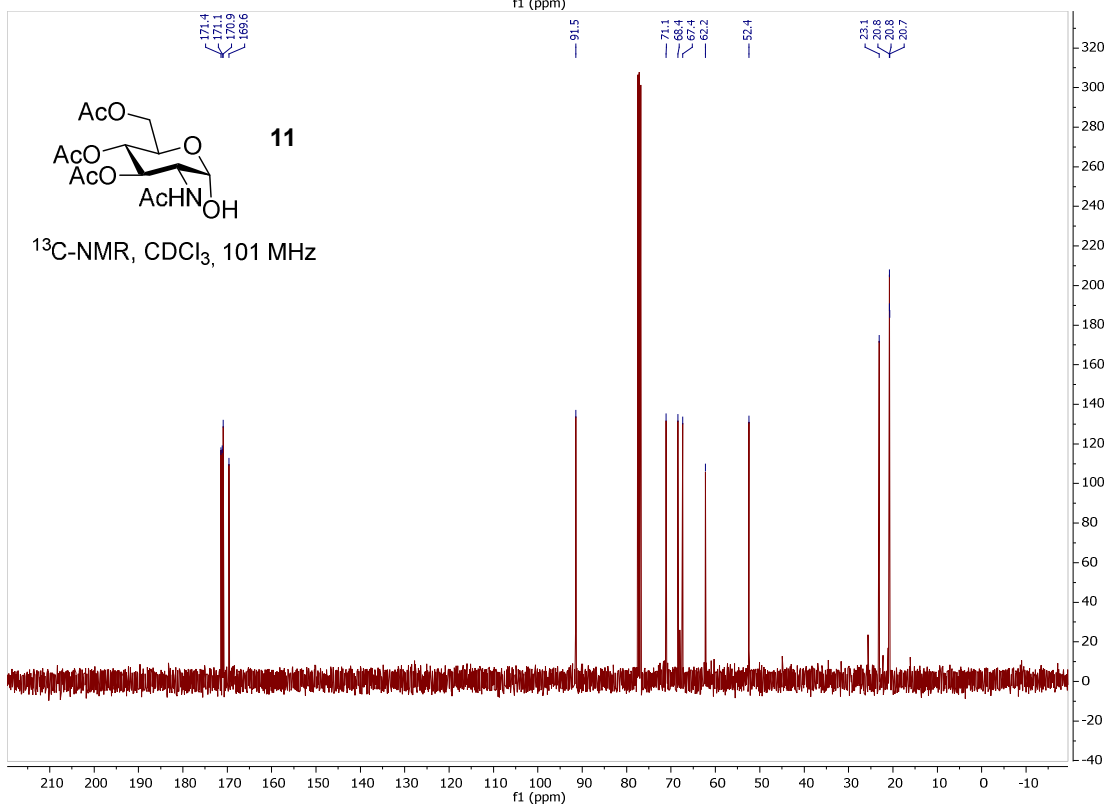
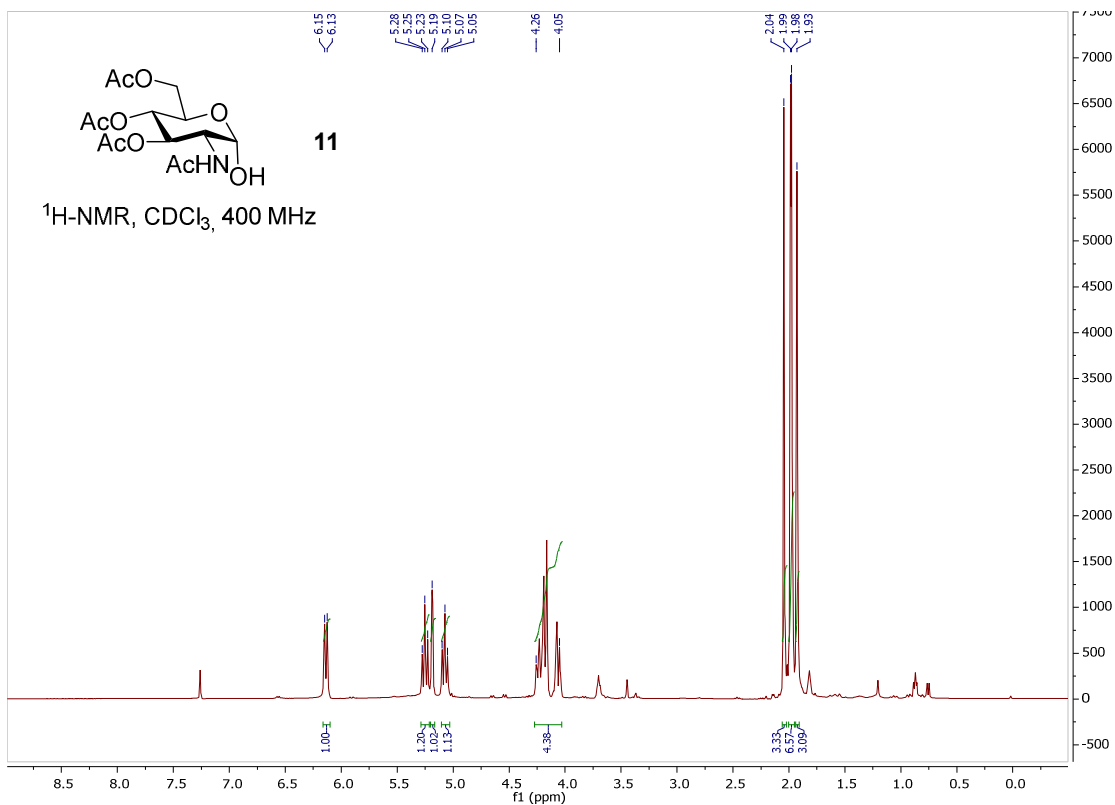


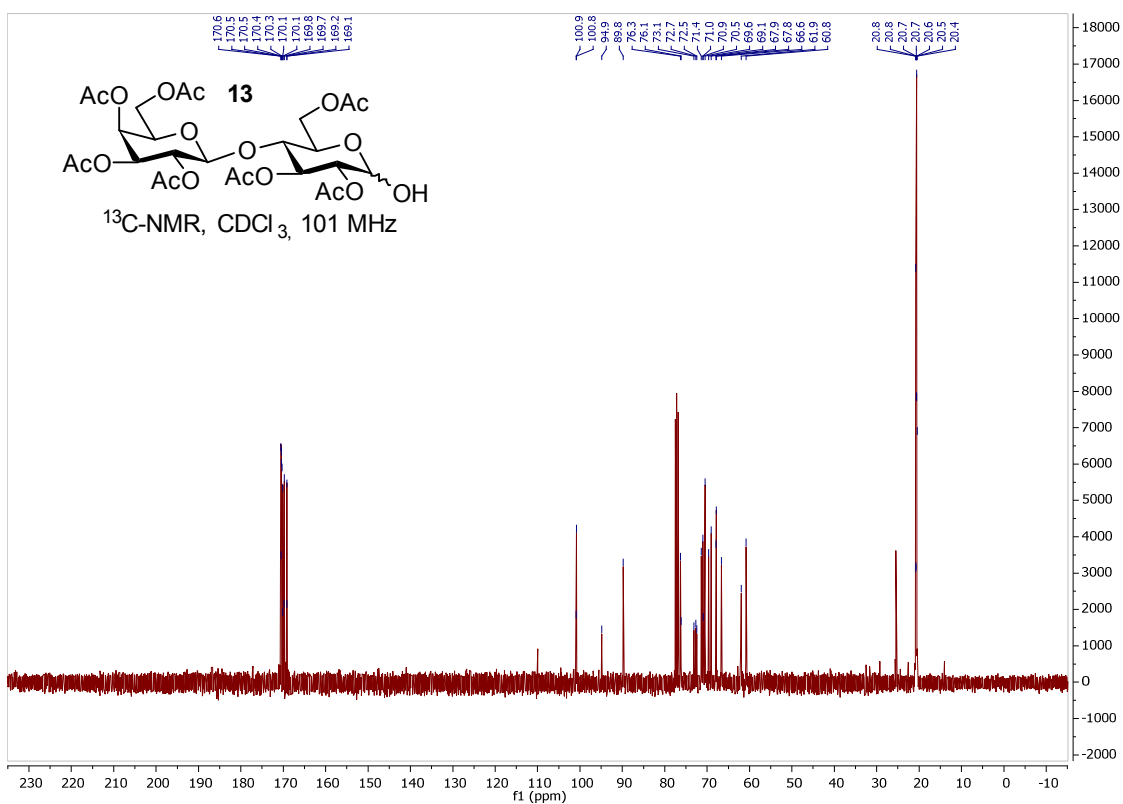
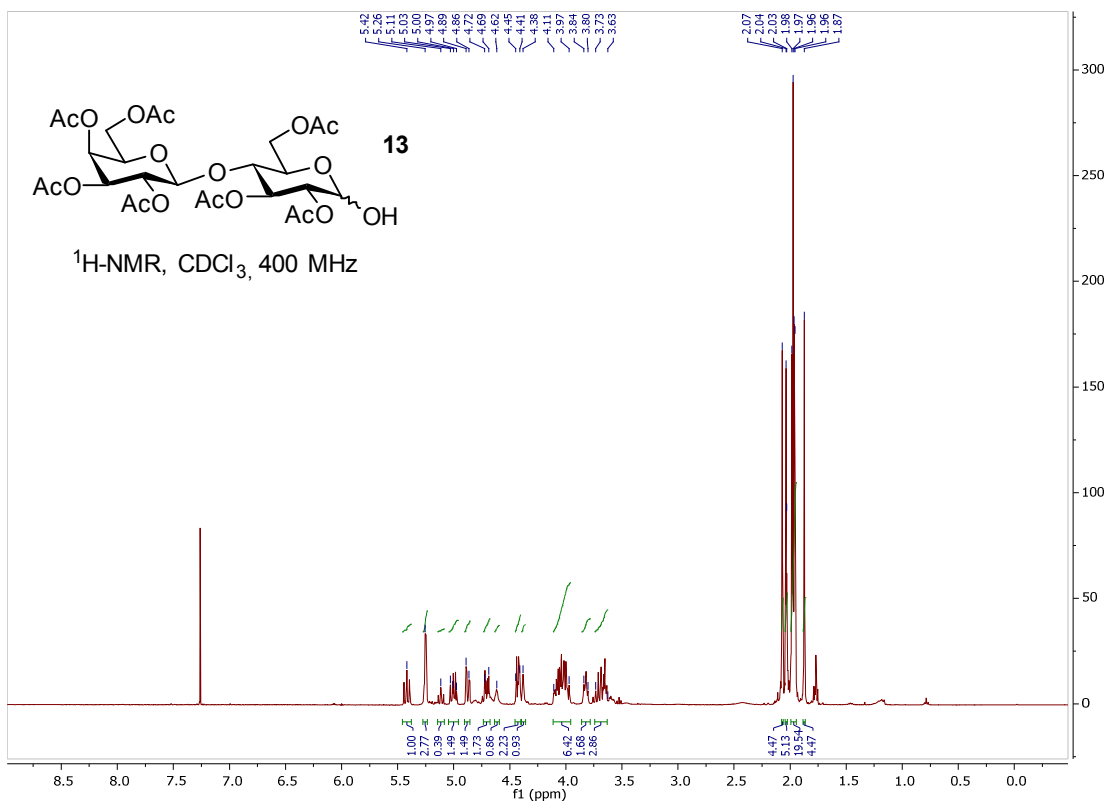


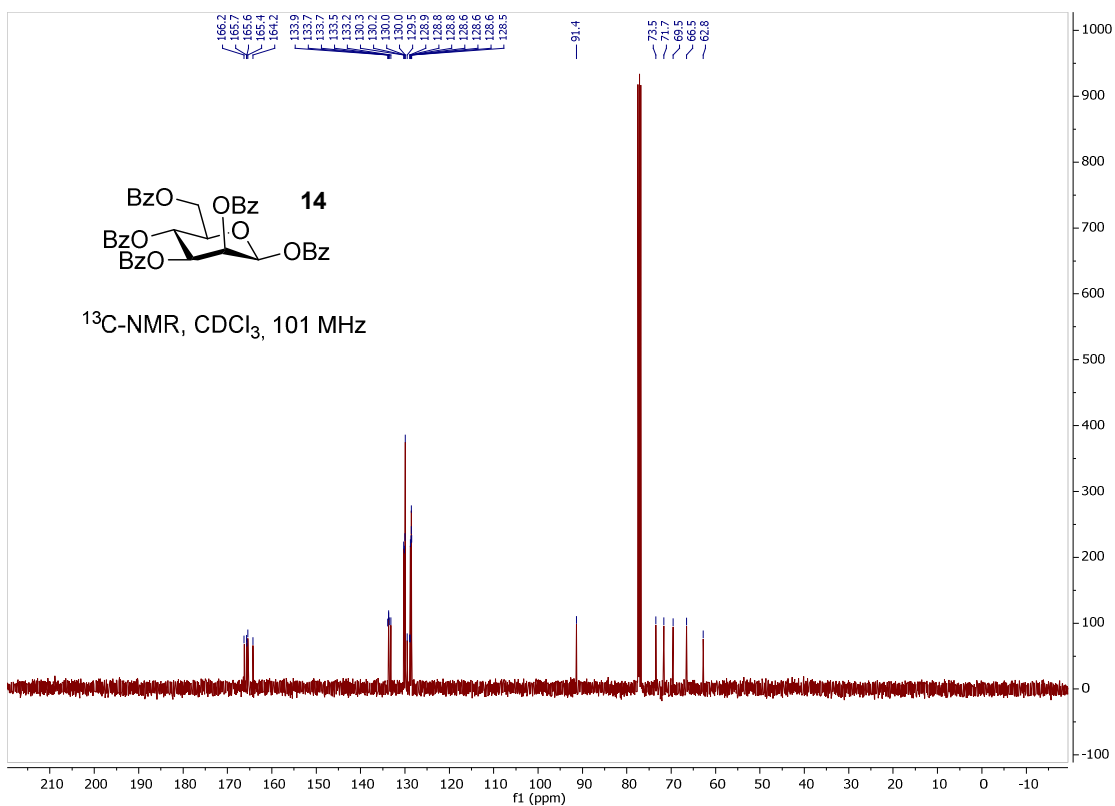
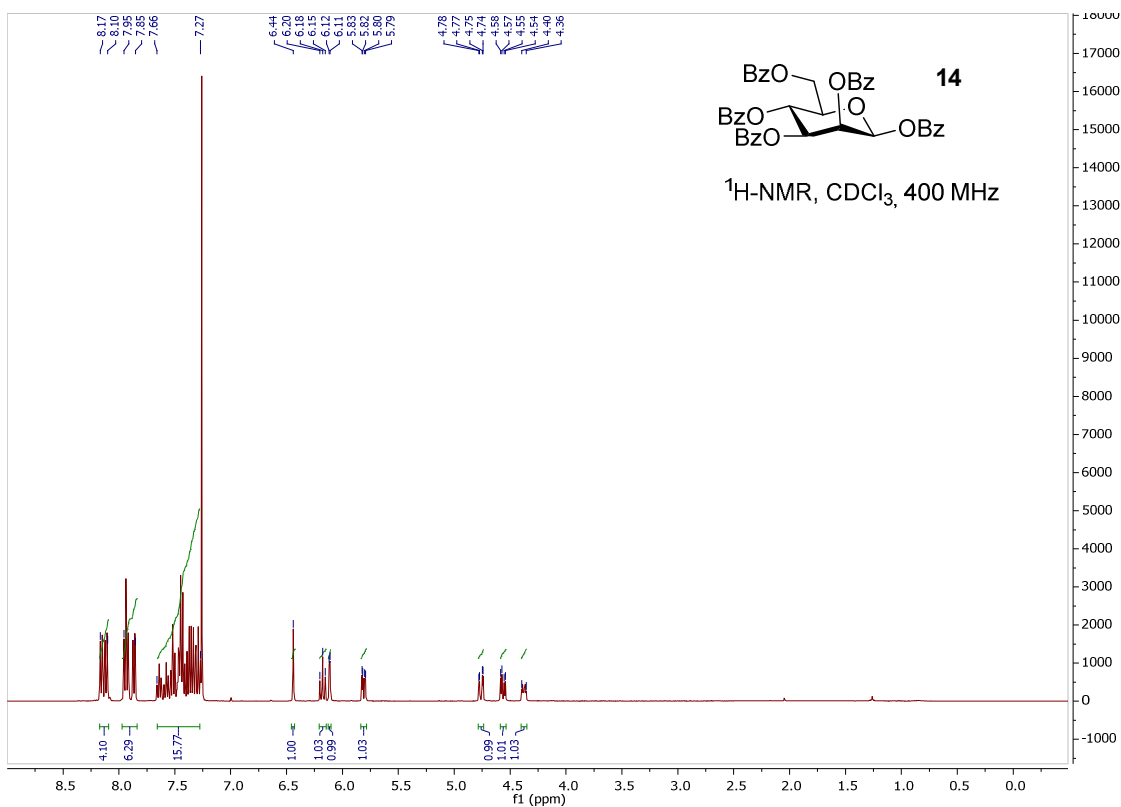


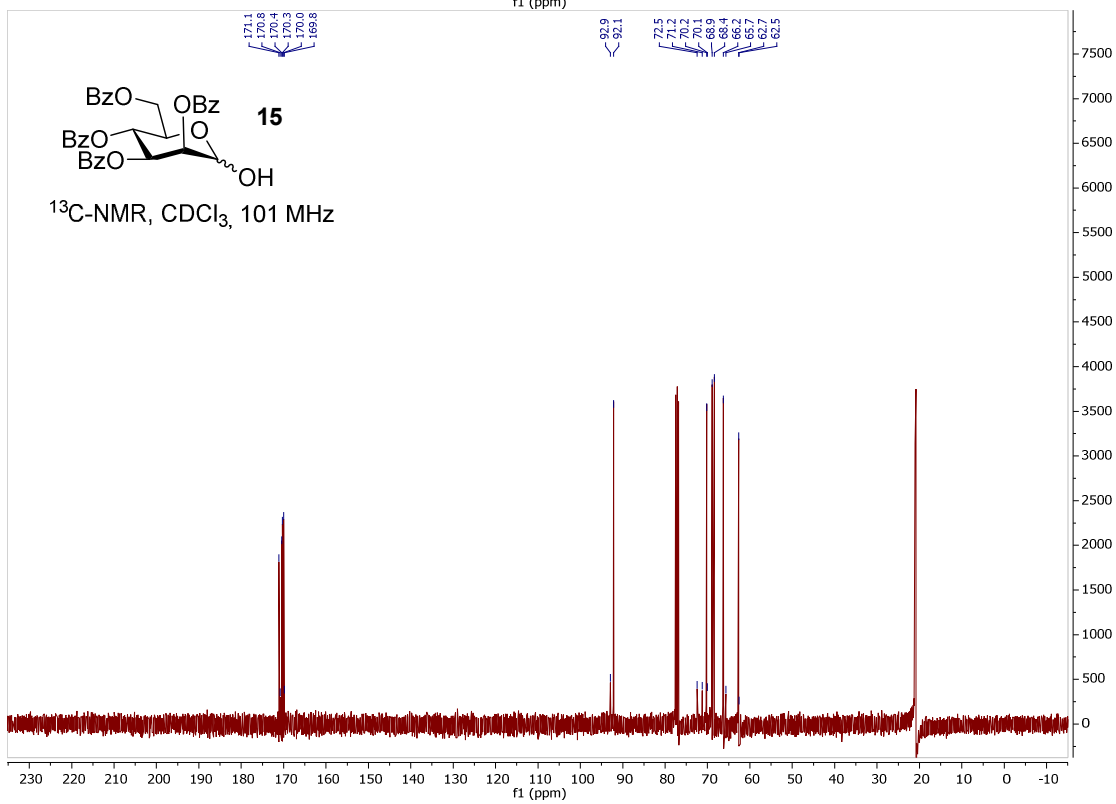
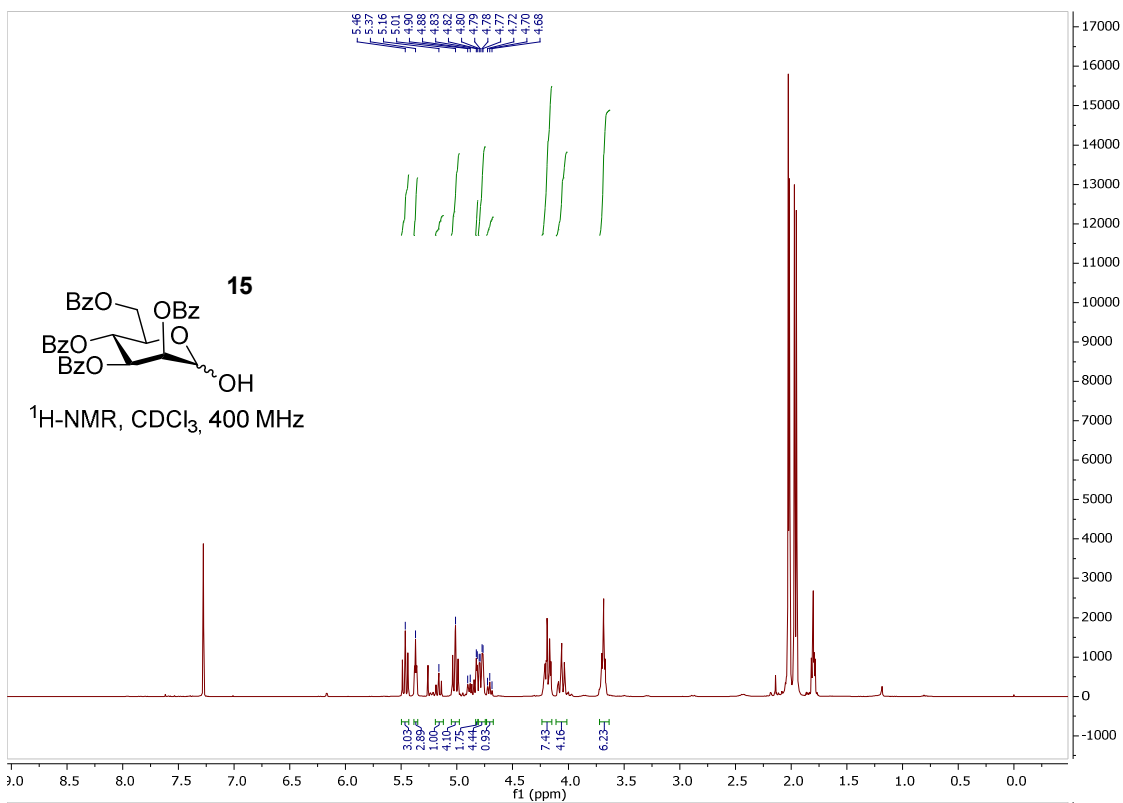


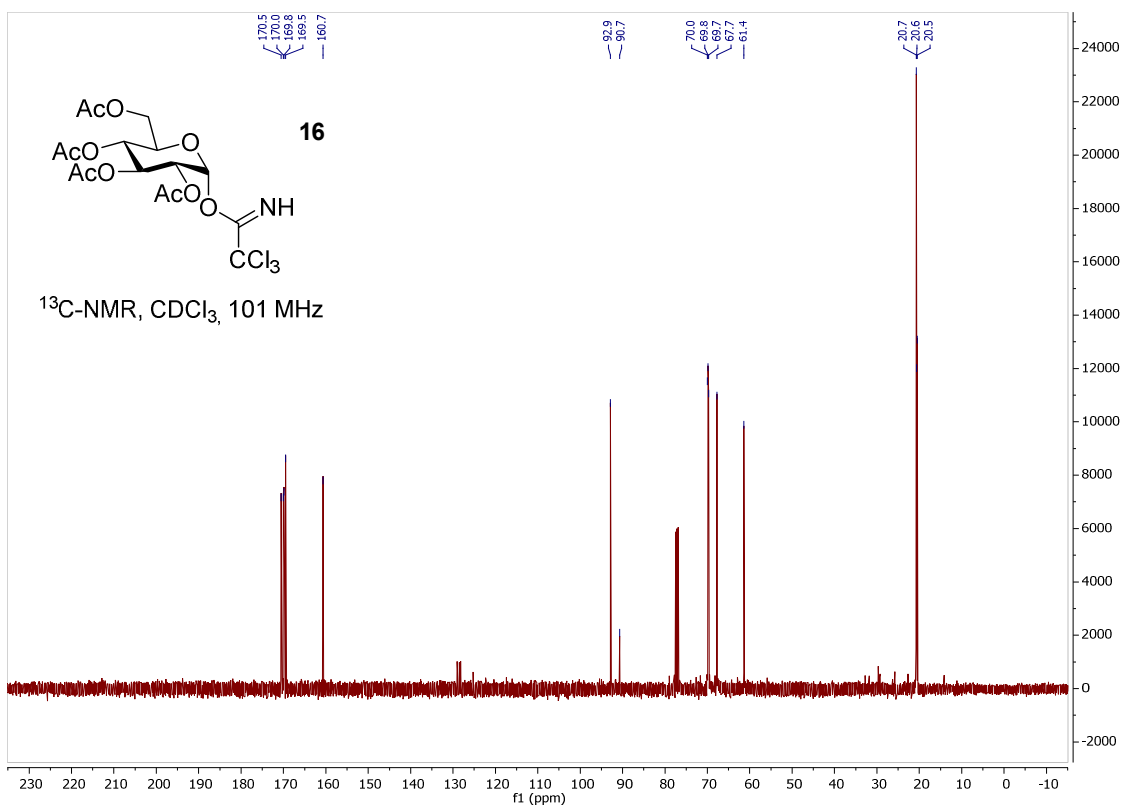
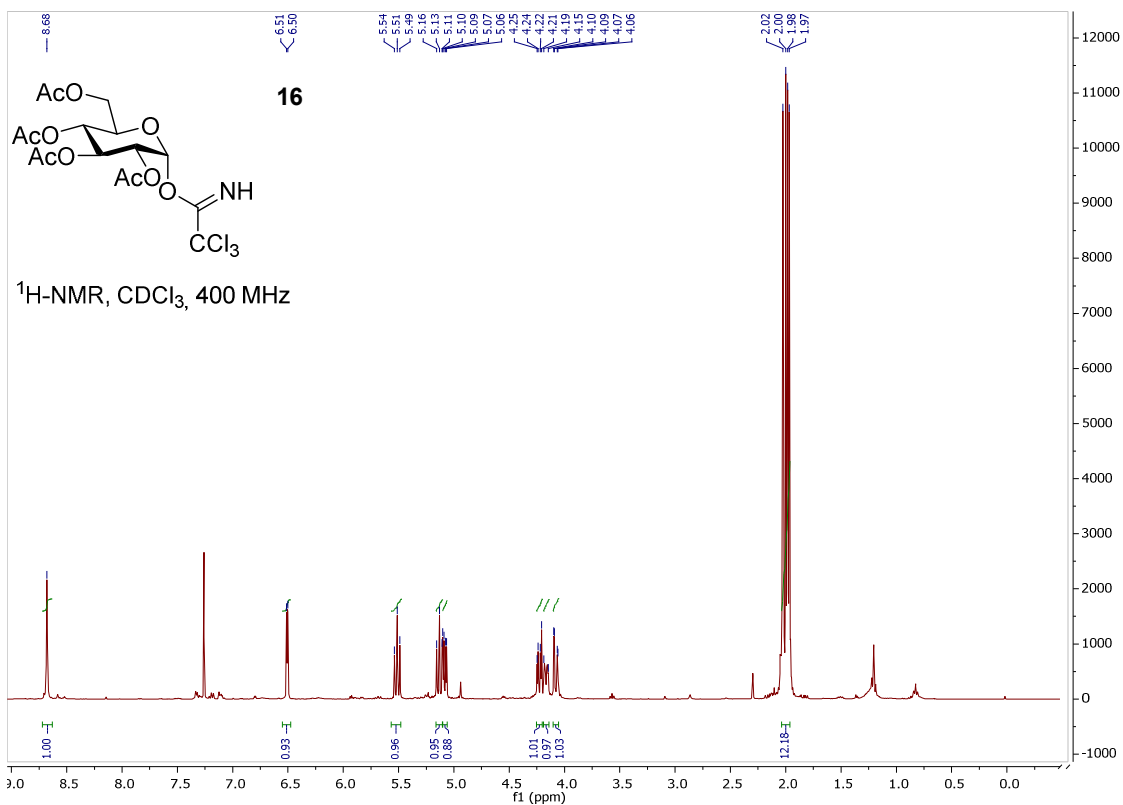


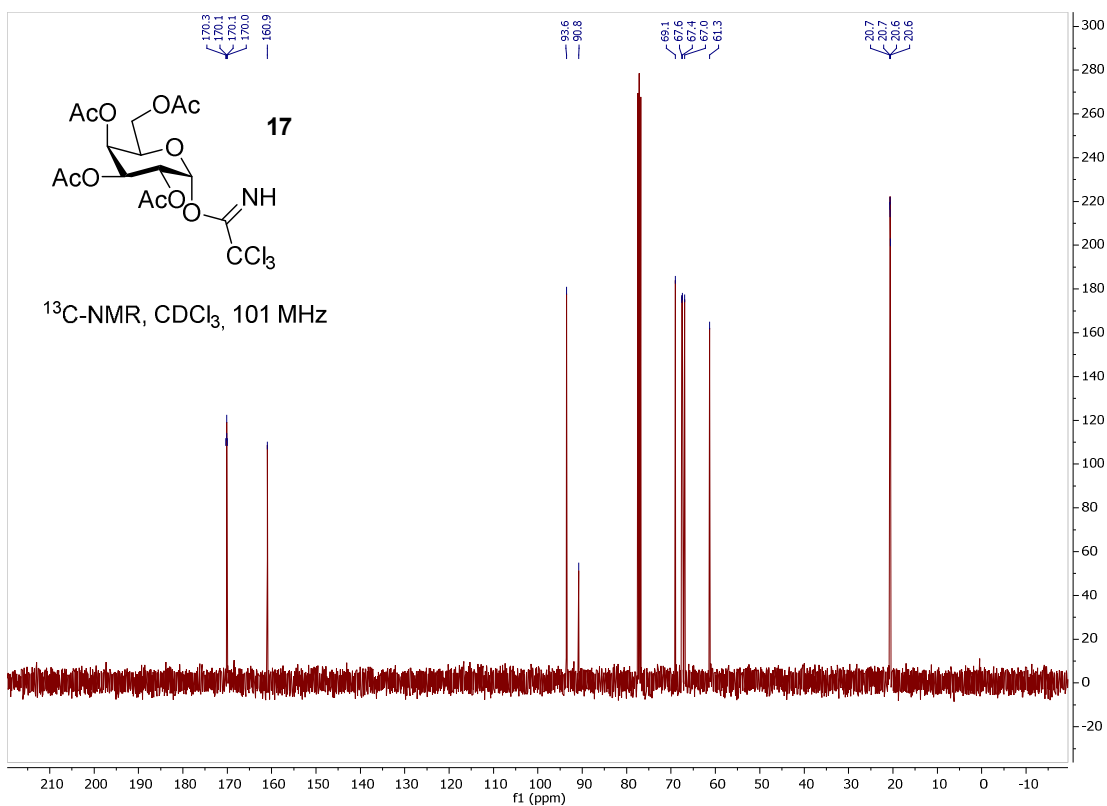
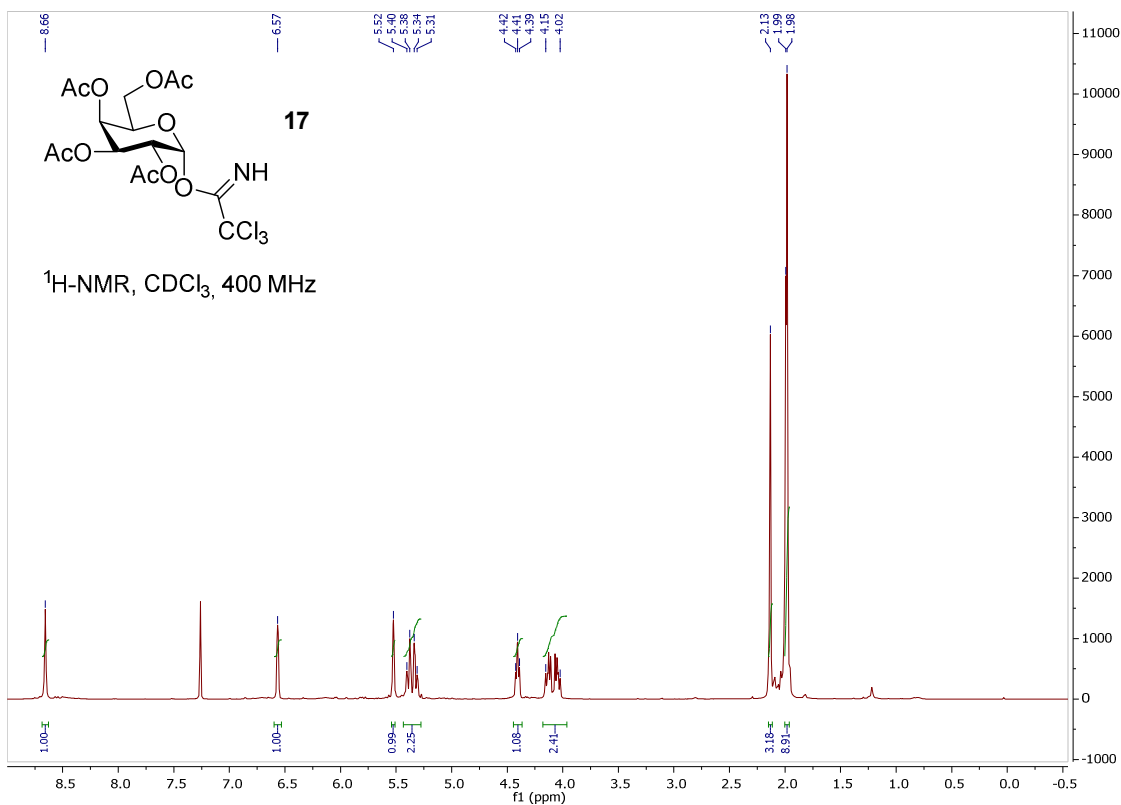


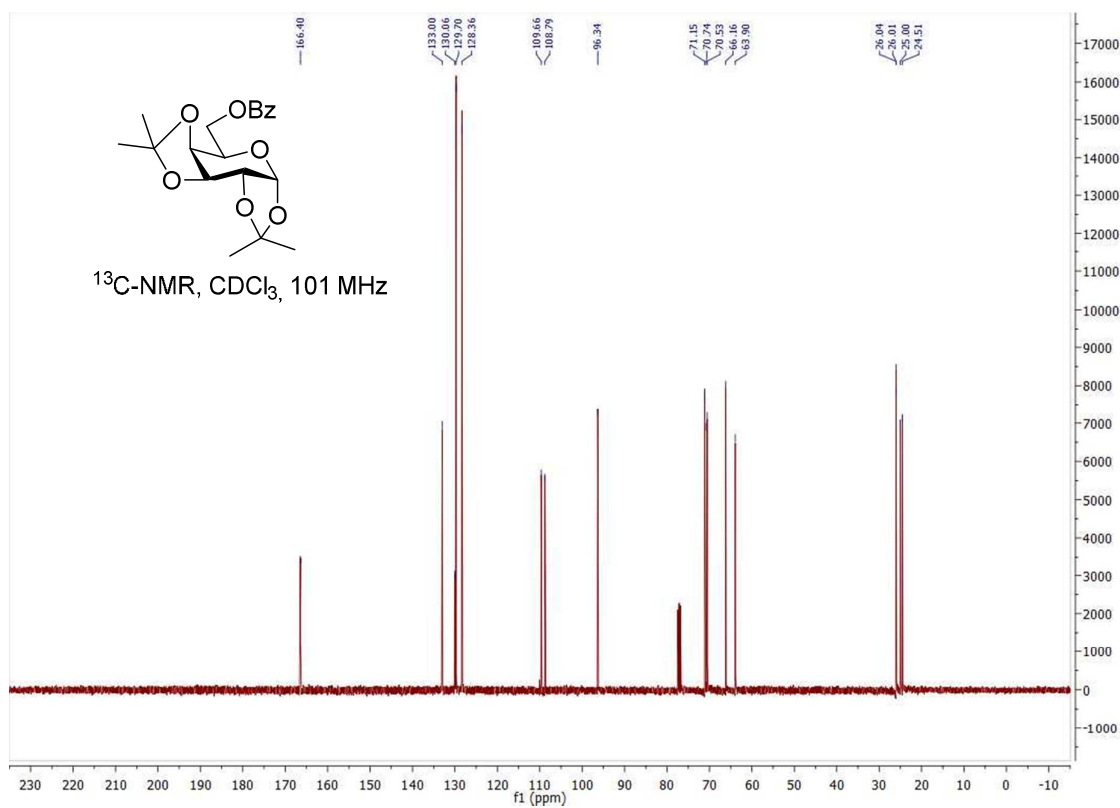
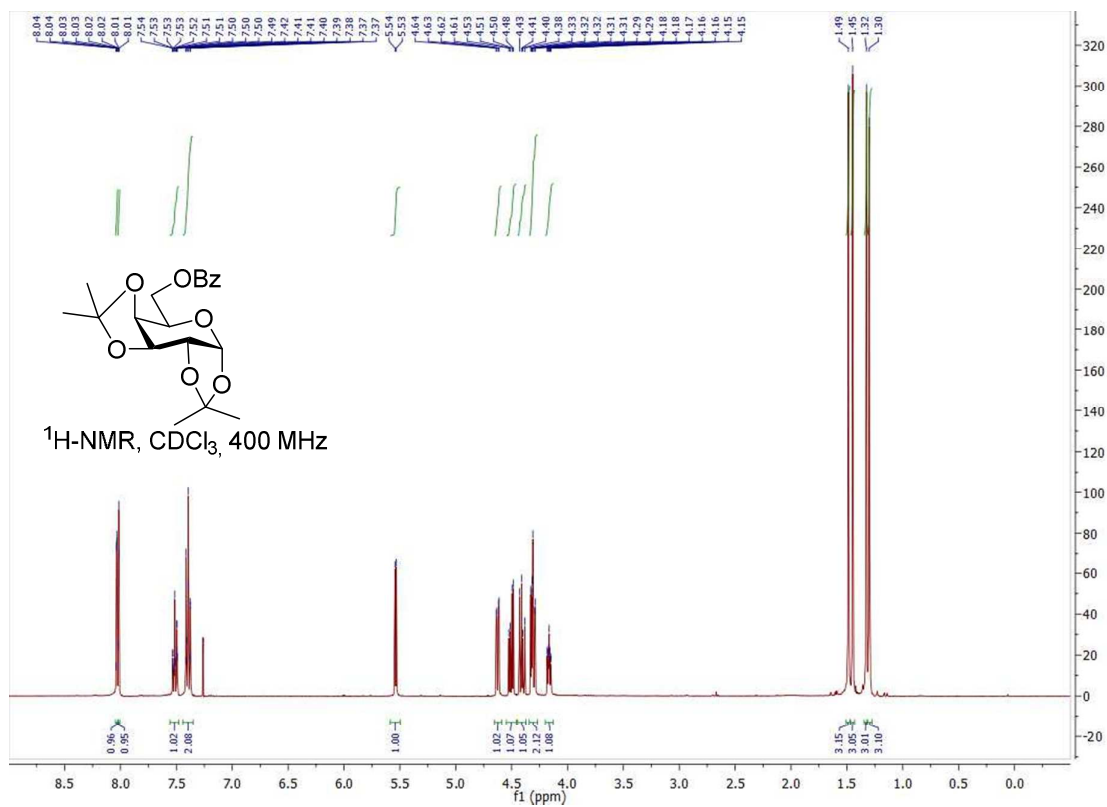


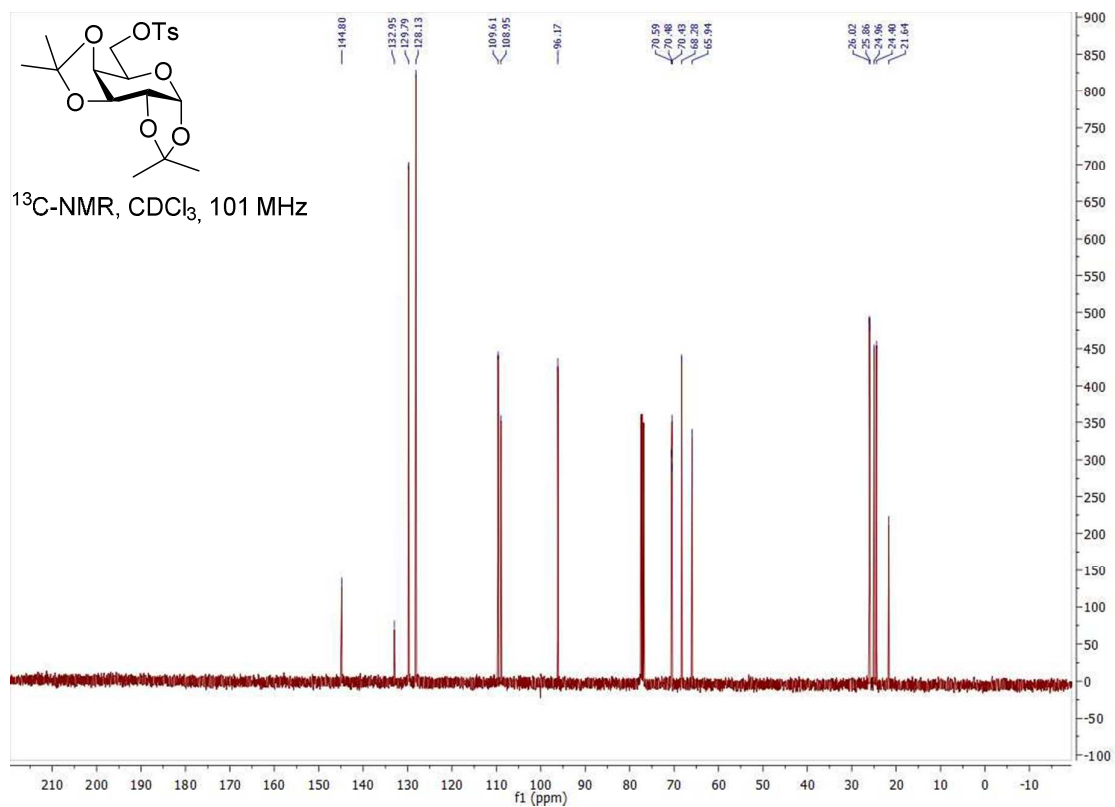
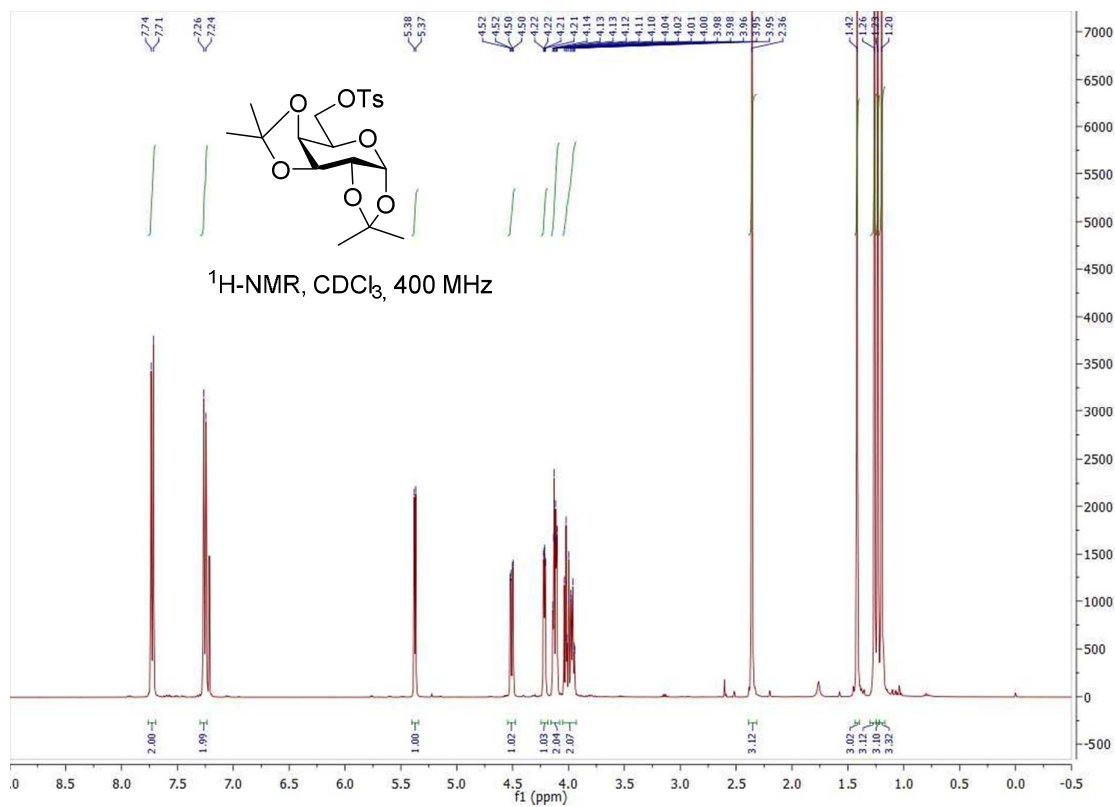


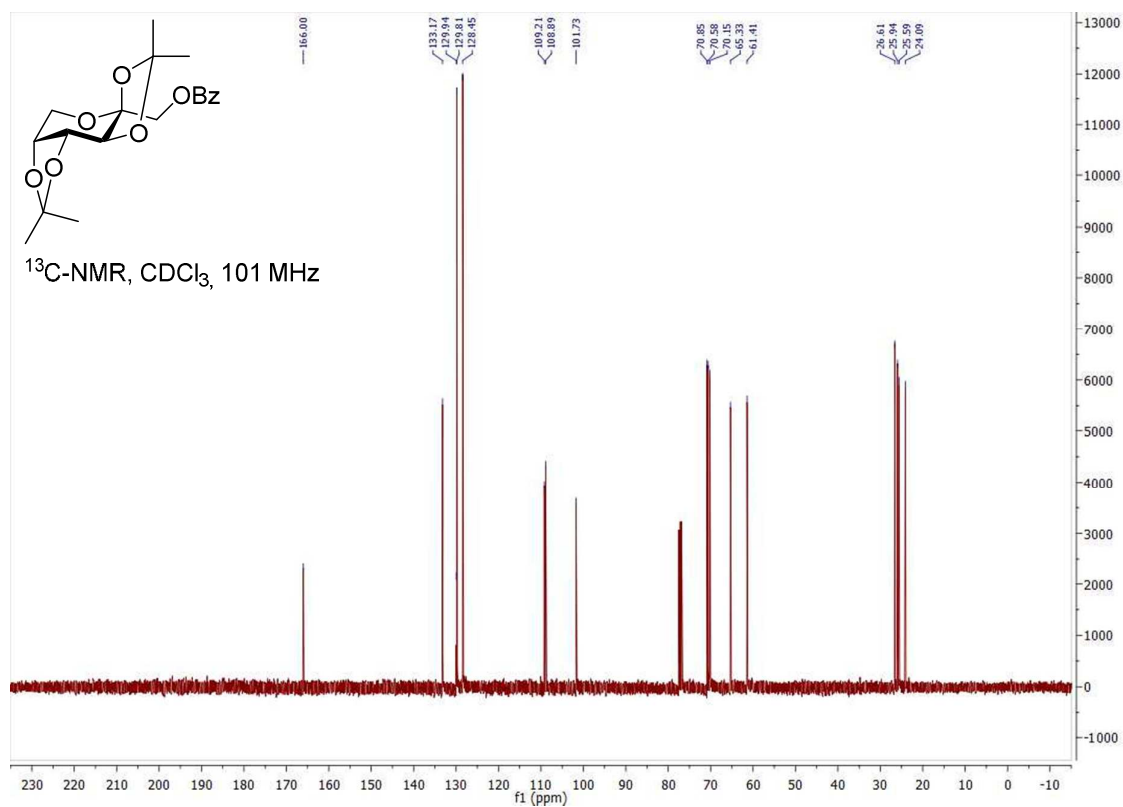
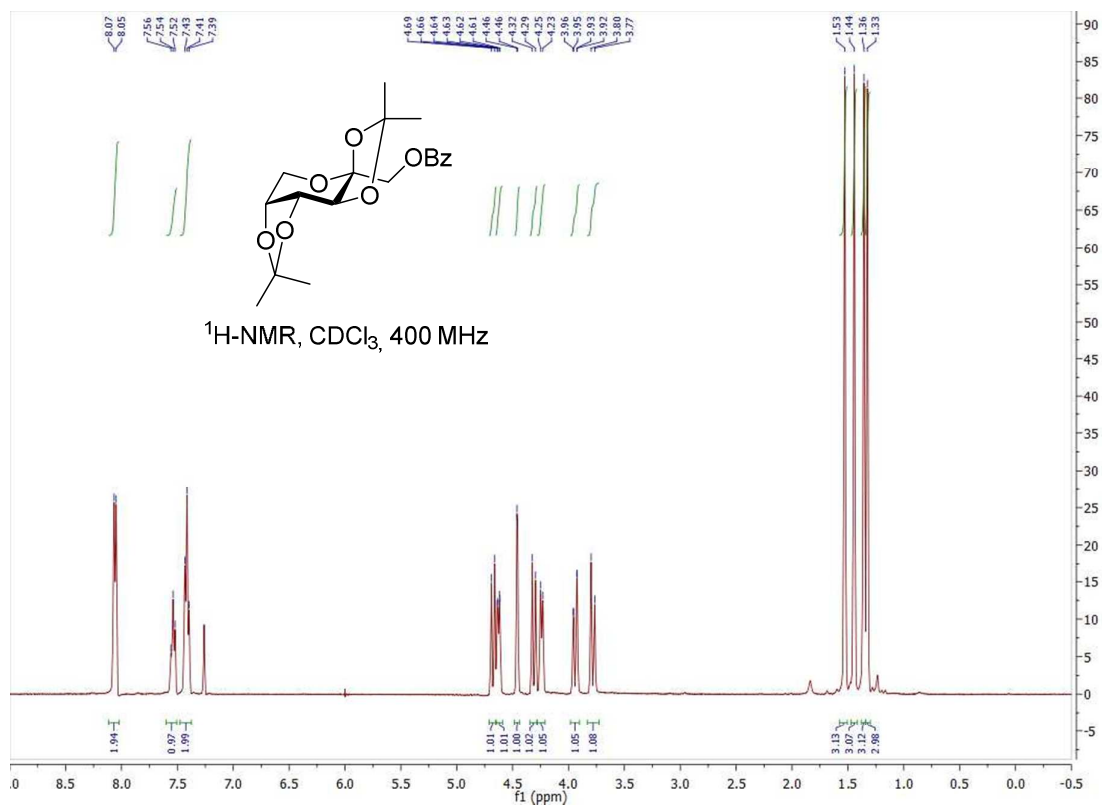


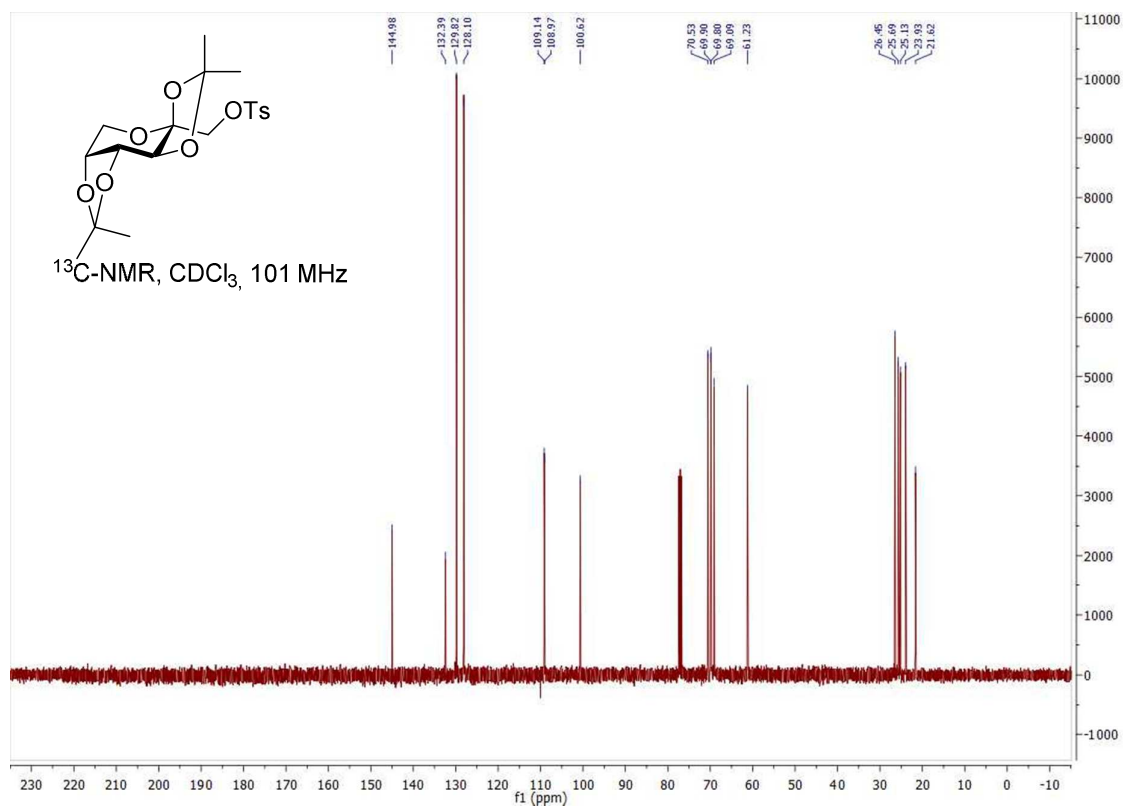
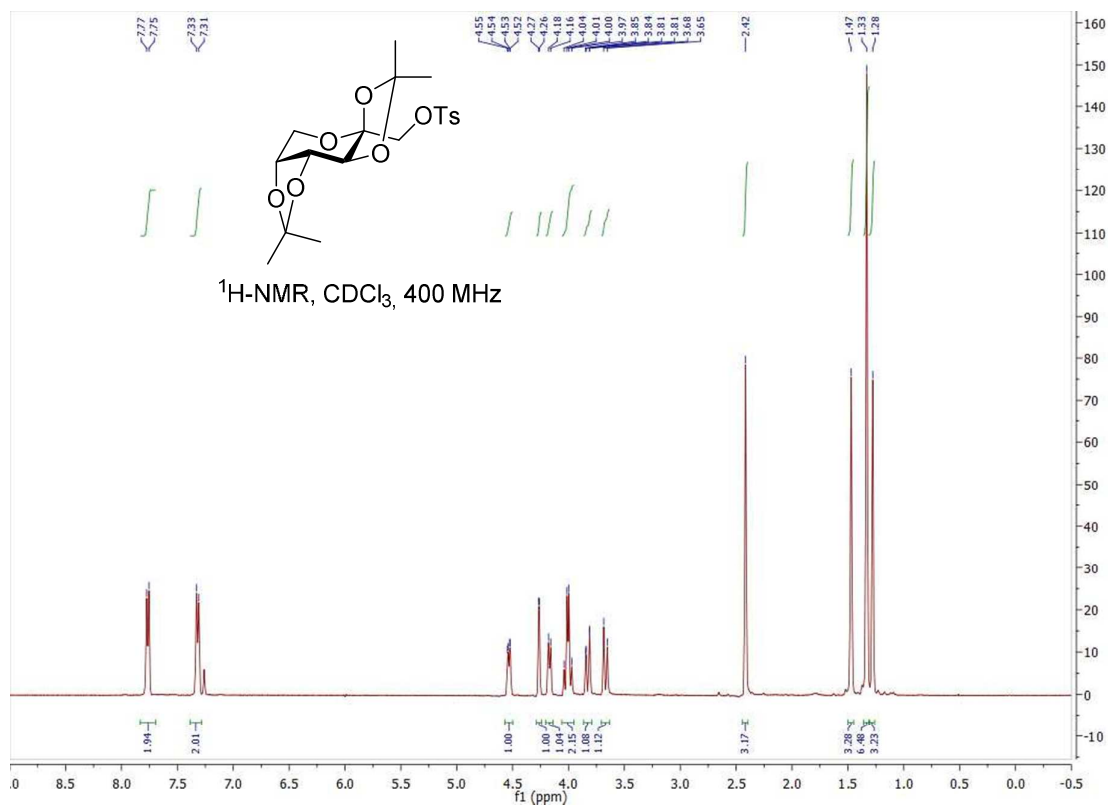


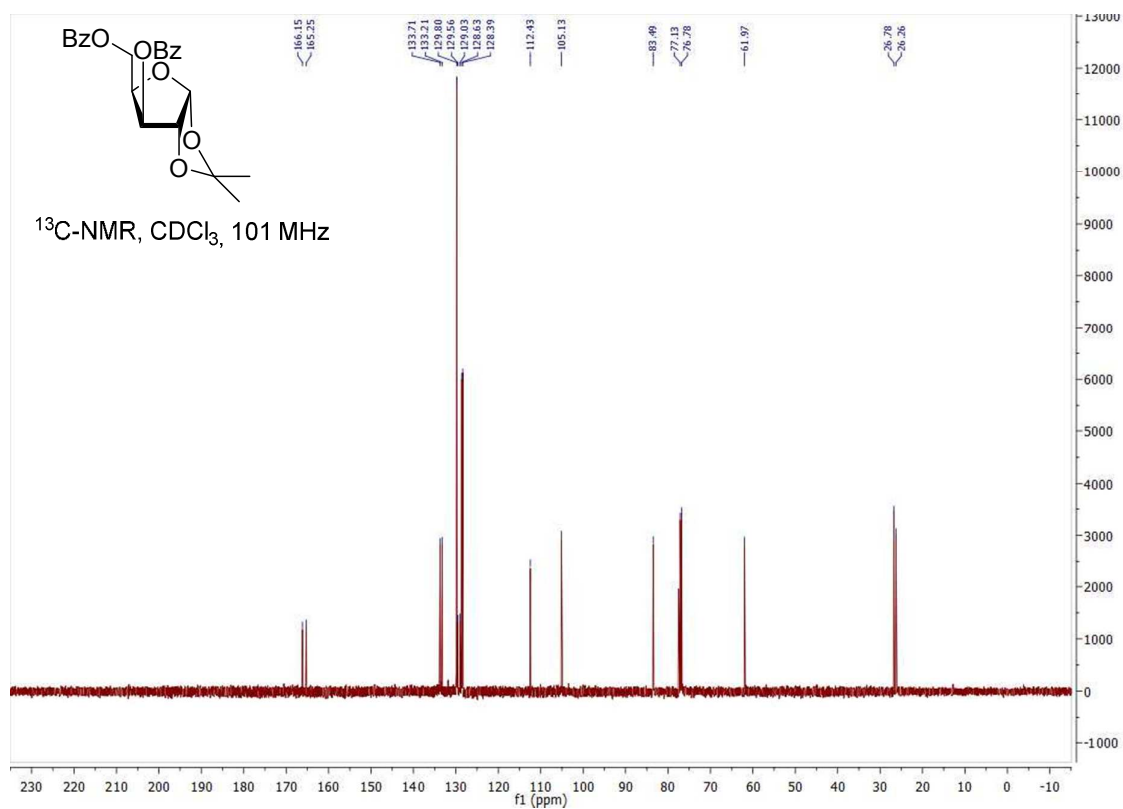
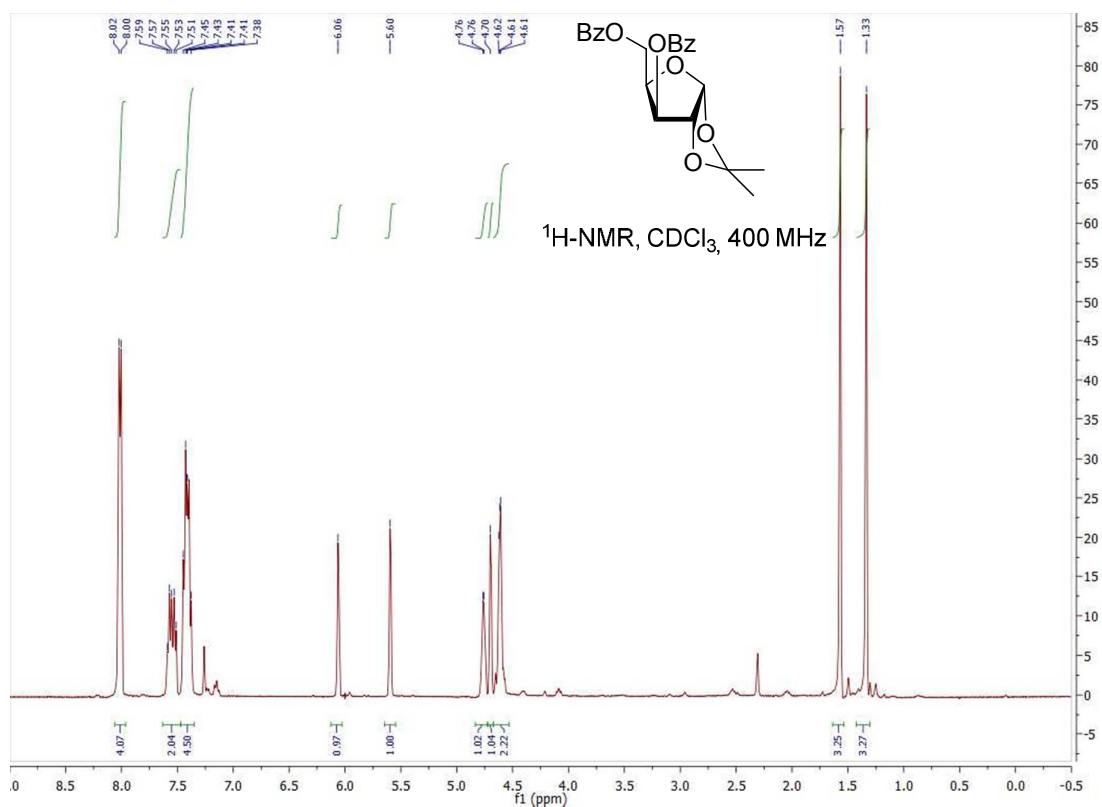


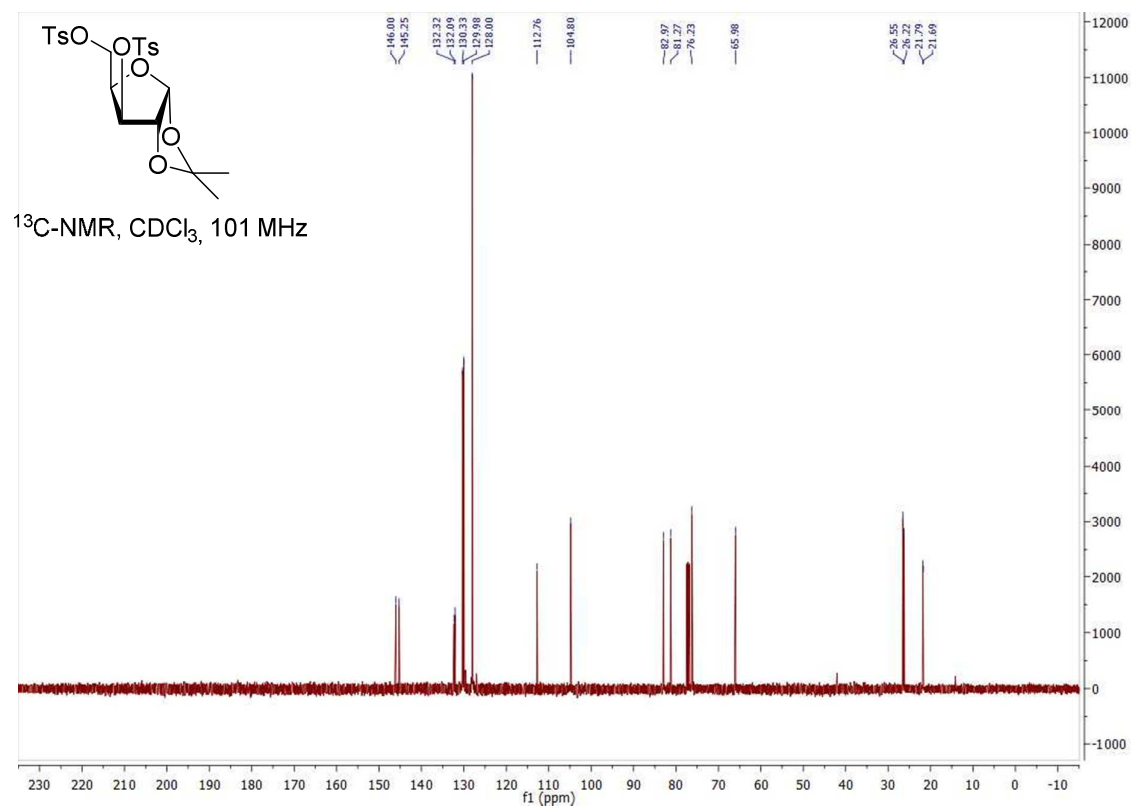
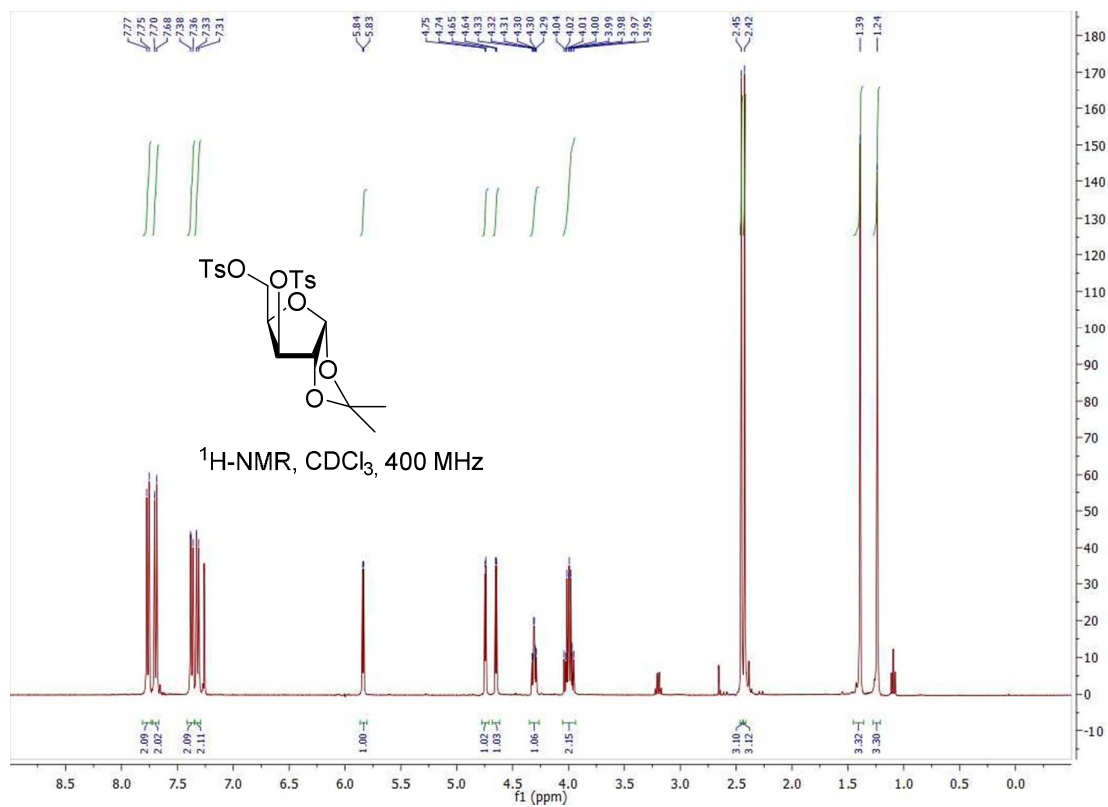


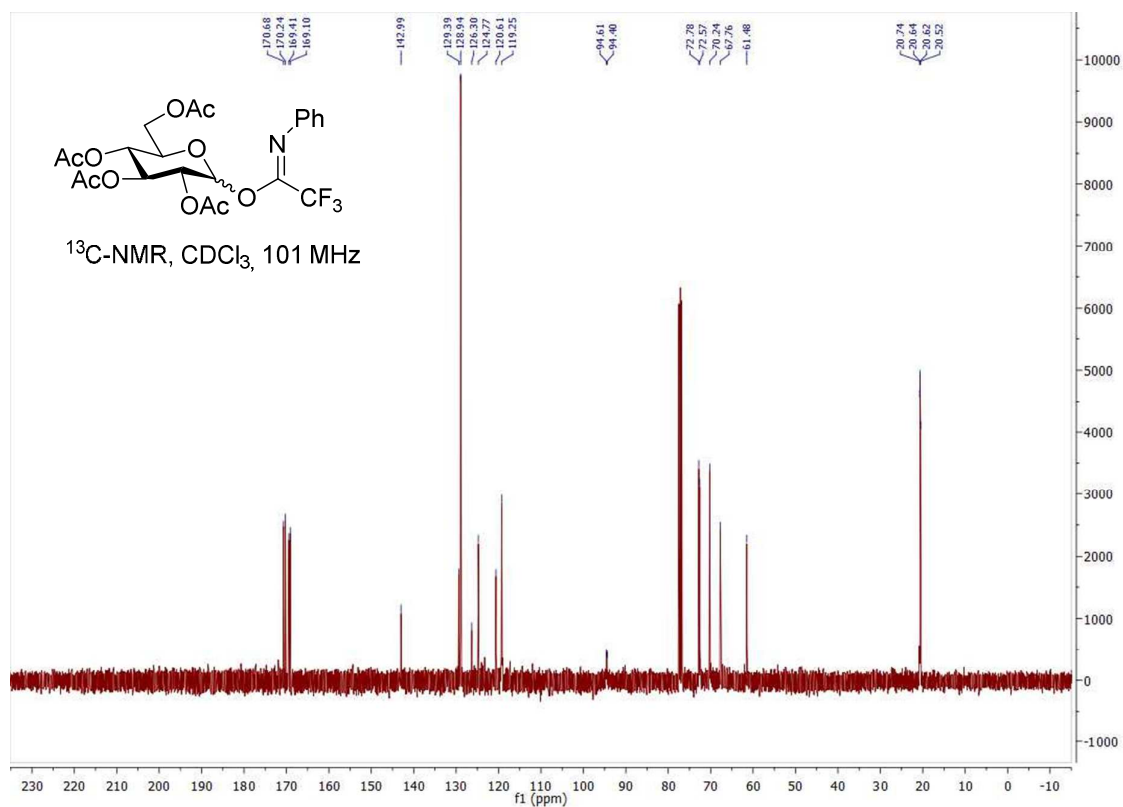
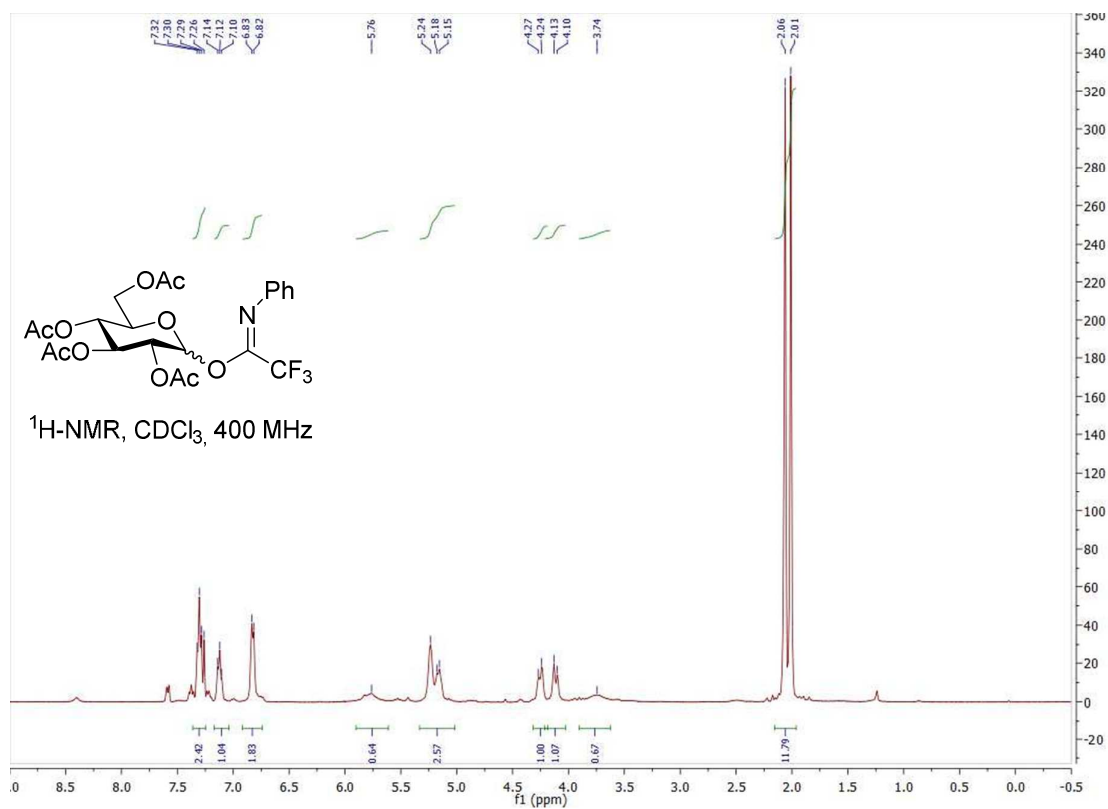


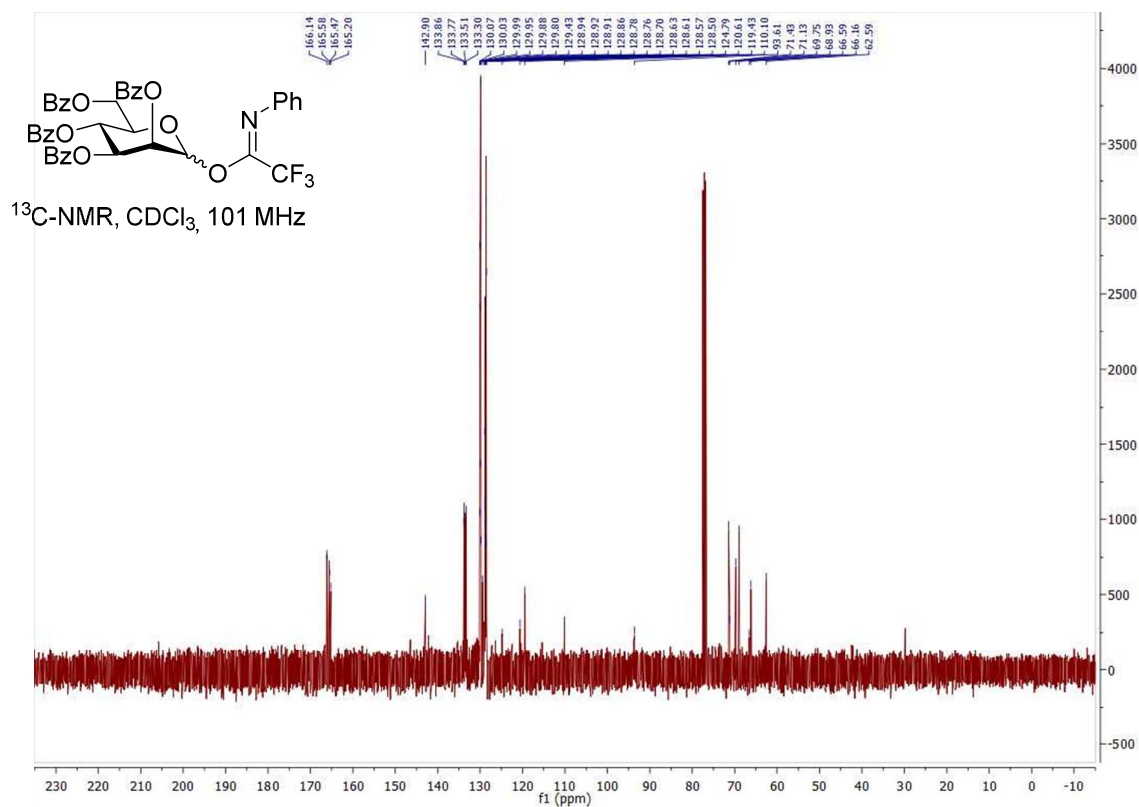
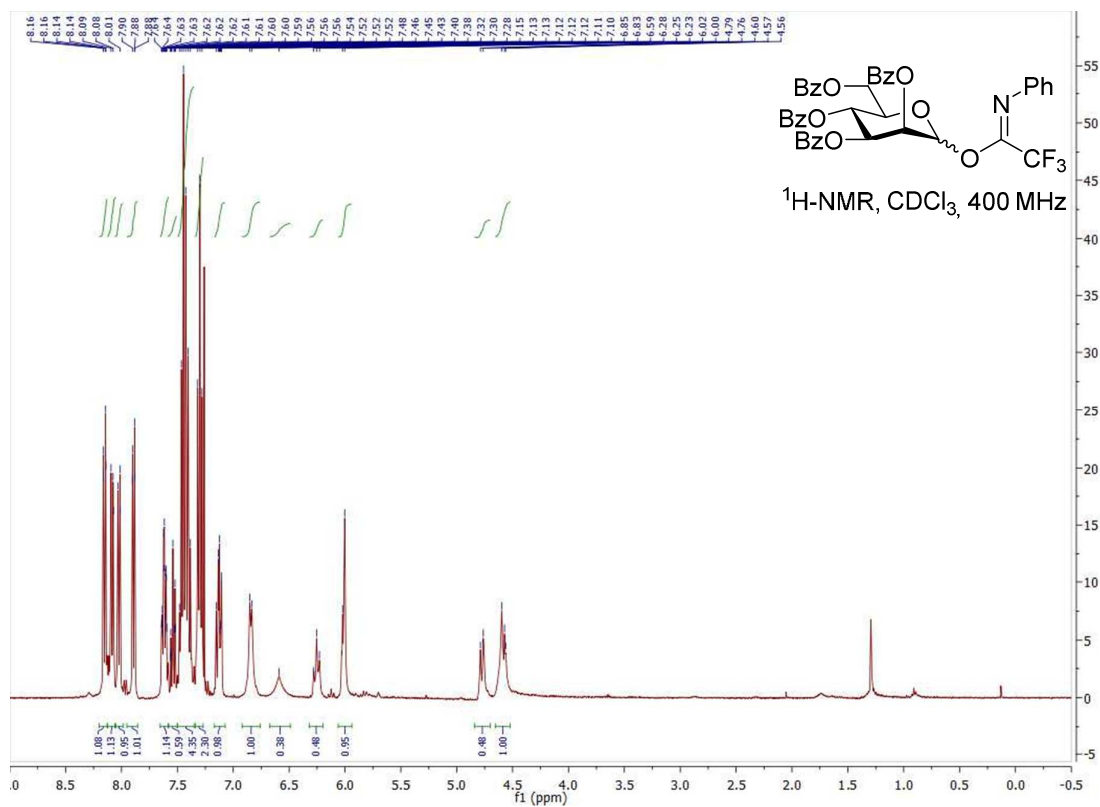


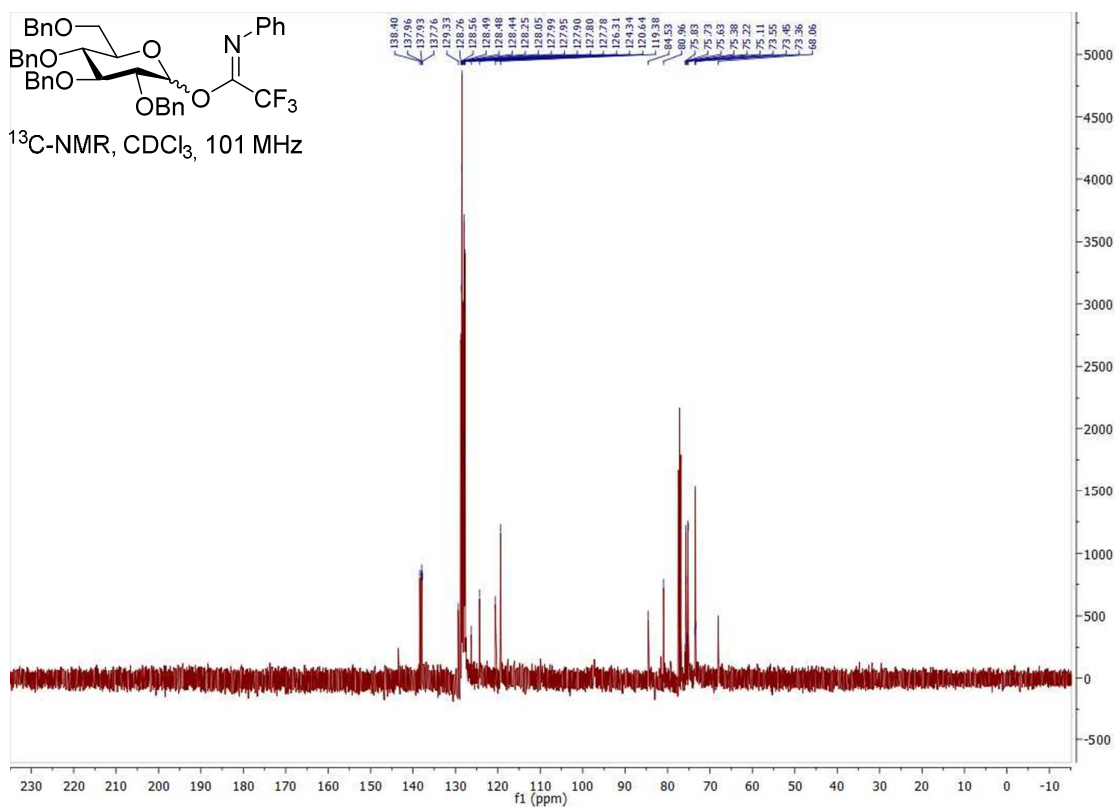
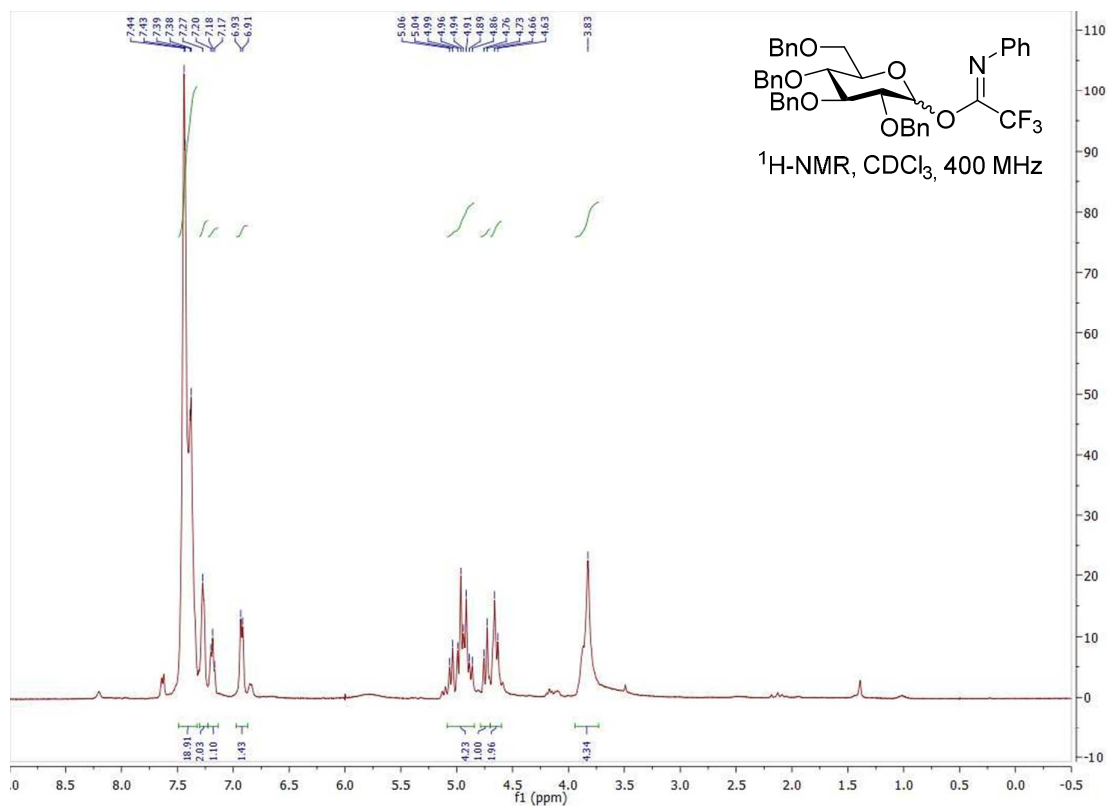












- ⁱ Sim, M. M.; Kondo, H.; Wong, C. H. *J. Am. Chem. Soc.* **1993**, *115*, 2260–2267.
- ⁱⁱ Sudibya, H. G.; Ma, J.; Dong, X.; Ng, S.; Li, L.-J.; Liu, X.-W.; Chen, P.; *Angew. Chem.*, **2009**, *121*, 2761–2764
- ⁱⁱⁱ Watanabe, K.; Itoh, K.; Araki, Y.; Ishido, Y. *Carbohydr. Res.* **1986**, *154*, 165–176.
- ^{iv} Vankayalapati, H.; Singh, G.; *J. Chem. Soc. Perkin Trans.* **2000**, *1*, 2187–2193
- ^v Dowlut, M.; Hall, D. G.; Hindsgaul, O. *J. Org. Chem.* **2005**, *70*, 9809–9813.
- ^{vi} Sardzik, R.; Noble, G. T.; Weissenborn, M. J.; Martin, A.; Webb, S.; Flitsch, S. L., *Beilstein J. Org. Chem.*, **2010**, *6*, 699–703
- ^{vii} Hennen, W. J.; Sweers, H. M.; Wang, Y. F.; Wong, C. H. *J. Org. Chem.* **1988**, *53*, 4939–4945.
- ^{viii} Iyer, S. S.; Rele, S. M.; Baskaran, S.; Chaikof, E. L., *Tetrahedron*, **2003**, *59*, 631–638
- ^{ix} Horton, D. *J. Org. Chem.* **1964**, *29*, 1776–1782.
- ^x Kartha, K. P. R.; Field, R. A., *Tetrahedron*, **1997**, *53*, 11753–11768
- ^{xi} Giovanni, N.; Spatafora, C.; Tringali, C., *Tetrahedron: Asymmetry*, 1999, *10*, 2891–2897
- ^{xii} Fiandor, J.; García-López, M. T.; De Las Heras, F. G.; Méndez-Castrillón, P. P. *Synthesis (Stuttg.)*. **1985**, *1985*, 1121–1123.
- ^{xiii} Palomo, J. M.; Filice, M.; Fernandez-Lafuente, R.; Terreni, M.; Gaisan, J. M., *Adv. Synth. Catal.* **2007**, *349*, 1969–1976
- ^{xiv} Jansson, K.; Ahlfors, S.; Frejd, T.; Kihlberg, J.; Magnusson, G.; Dahmen, J.; Noori, G.; Stenvall, K. *J. Org. Chem.* **1988**, *53*, 5629–5647.
- ^{xv} Brabcova, J.; Carrasco-Lopez, C.; Bavaro, T.; Hermoso, J. A.; Palomo, J. M.; *Journal of molecular Catalysis B: Enzymatic*, **2014**, *107*, 31–37
- ^{xvi} Onodera, K.; Hirano, S.; Masuda, F.; Kashimura, N. *J. Org. Chem.* **1966**, *31*, 2403–2406.
- ^{xvii} Sail, D.; Kováč, P., *Carbohydr. Res.* **2012**, *357*, 47–52
- ^{xviii} Pozsgay, V. *Tetrahedron Lett.* **1993**, *34*, 7175–7178.
- ^{xix} Hartmann, M.; Betz, P.; Sun, Y.; Gorb, S. N.; Lindhorst, T. K.; Krueger, A.; *Chem. Eur. J.*, 2012, *18*, 6485–6492
- ^{xx} (Schmidt, R. R.; Michel, J. *Angew. Chemie* **1980**, *92*, 763–764.
- ^{xxi} Ita, H.; Kamachi, T.; Yashima, E., *Chem. Commun.* **2012**, *48*, 5650–5652
- ^{xxii} Schmidt, R. R.; Stumpp, M. *Liebigs Ann. der Chemie* **1983**, *1983*, 1249–1256.
- ^{xxiii} Yu, H.; Chen, X., *Org Lett*, **2006**, *8*, 2393–2396
- ^{xxiv} Commercial available
- ^{xxv} Asaoka, S.; Horiguchi, H.; Wada, T.; Inoue, Y. *J. Chem. Soc. Perkin Trans. 2*, **2000**, 737–747.
- ^{xxvi} Hevey, R.; Ling, C.-C. *Org. Biomol. Chem.* **2013**, *11*, 1887–1895.
- ^{xxvii} Girard, P.; Kagan, H.; David, S. *Tetrahedron* **1971**, *27*, 5911–5920.
- ^{xxviii} Patent: WO2005/121114 A2, **2005**
- ^{xxix} Wieslaw, S. *Pol. J. Chem.*, **1980**, *54*, 1301–1304
- ^{xxx} Meng, X.-B.; Li, Y.-F.; Li, Z.-J. *Carbohydr. Res.* **2007**, *342*, 1101–1104.
- ^{xxxi} Ma, X.; Tang, Q.; Ke, J.; Yang, X.; Zhang, J.; Shao, H. *Org. Lett.* **2013**, *15*, 5170–5173.
- ^{xxxii} Collins, P. M.; Hurford, J. R.; Overend, W. G. *J. Chem. Soc. Perkin Trans. 1* **1975**, 2163.
- ^{xxxiii} Prudhomme, D. R.; Wang, Z.; Rizzo, C. J. *J. Org. Chem.* **1997**, *62*, 8257–8260.
- ^{xxxiv} Ozols, A. M.; Azhayev, A. V.; Krayevsky, A. A.; Ushakov, A. S.; Gnuchev, N. V.; Gottikh, B. P. *Synthesis* **1980**, *1980*, 559–561.
- ^{xxxv} Zhao, M.-L.; Zhang, E.; Gao, J.; Zhang, Z.; Zhao, Y.-T.; Qu, W.; Liu, H.-M. *Carbohydr. Res.* **2012**, *351*, 126–129.
- ^{xxxvi} Thomas, M.; Gesson, J.; Papot, S. *J. Org. Chem.* **2007**, *72*, 4262–4264.
- ^{xxxvii} Commercial available
- ^{xxxviii} 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. Engl.* **2008**, *47*, 2244–2247.
- ^{xxxix} Nigudkar, S. S.; Stine, K. J.; Demchenko, A. V. *J. Am. Chem. Soc.* **2014**, *136*, 921–923.