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Supporting Information

Efficient O-Functionalization of Carbohydrates with Electrophilic Reagents

*Gergely L. Tolnai, Ulf J. Nilsson, and Berit Olofsson**

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I. Experimental Procedures

I.1 General experimental procedures

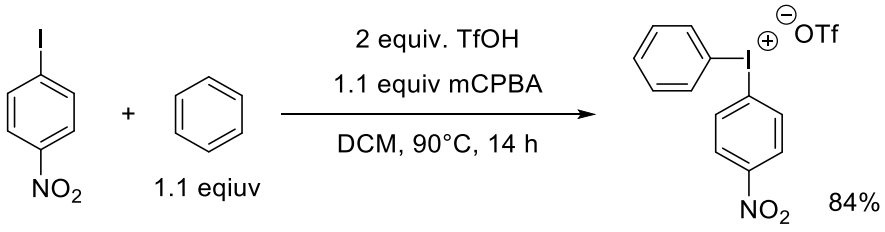
All reactions were carried out in non-dried glassware unless otherwise noted. All solvents and reagents were synthesized via literature protocols or purchased from commercial sources and used without further purifications, unless otherwise noted. *m*CPBA (Aldrich, 77% active oxidant) was dried at RT on high vacuum for several hours, and titrated by iodometric titration[1] prior to use. TLC analysis was performed on pre-coated Merck silica gel 60 F254 plates using UV light and anisaldehyde stain (1 mL anisaldehyde/1 mL cc. H_2SO_4/18 mL EtOH). Column chromatography was conducted by flash column chromatography using 40-60 µm, 60 Å silica gel as stationary phase. Flash column chromatography was done on SiO_2 purchased from Aldrich (technical grade, 60 Å pore size, 230-400 mesh, 40-63 µm). Melting points were measured using a STUART SMP3 and are reported uncorrected. The melting point measurements refer to the solidified materials as the result of the given experimental procedures, no additional recrystallization was done. All NMR spectra were recorded using a 400 or 500 MHz Bruker AVANCE II with a BBO probe at 298 K using $CDCl_3$, CD_3OD or DMSO-d_6 as solvents. Chemical shifts are given in ppm relative to the residual solvent peak (^{1}H NMR: $CDCl_3$ δ 7.26; CD_3OD 3.31; DMSO-d_6 2.50, CD_3CN 1.93; ^{13}C NMR: $CDCl_3$ δ 77.16; CD_3OD 49.00, DMSO-d_6 39.52, CD_3CN 119.00) with multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, hept = heptet, m = multiplet, app = apparent), coupling constants (in Hz) and integration. High resolution mass analyses were obtained using a Bruker microTOF ESI. Analytical data is given if the compound is novel or not fully characterized in the literature.

[1] See http://www.organ.su.se/bo/Gruppfiler/Iodometric%20titration.pdf and Vogel, A. I.; Furniss, B. S.; Hannaford, A. J.; Rogers, V.; Smith, P. W. G.; Tatchell, A. R., *Vogel's Textbook of Practical Organic Chemistry* (4th Ed) **1978**, p. 308. *Org. Synth, Coll. Vol. 6,* **1988***, 276; Org. Synth.* **1970**, *50,* 15.

I.2 Diaryliodonium salts 2

Most diaryliodonium salts discussed in present work were synthesized by one-pot methods, developed by our group.[2] For others, separate references are given below.

I.2.1 4-Nitrophenyl(phenyl)iodonium triflate (2a)

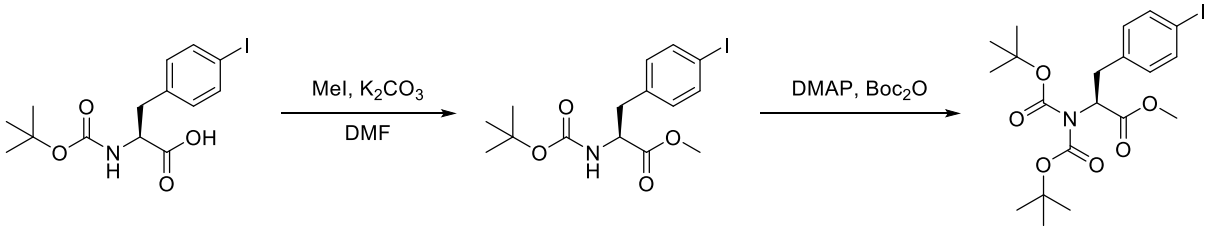


4-Iodonitrobenzene (10 mmol, 2.49 g) and *m*CPBA (11 mmol, 2.21 g, 87% active oxidant) was filled into a 100 mL bomb flask equipped with a stir bar. DCM (50 mL) was added, following by benzene (1.01 mL, 11 mmol). The reaction mixture was cooled to 0 °C, then trifluoromethanesulfonic acid (1.77 mL, 20 mmol) was added dropwise. Then the flask was sealed, and moved to a 90 °C oil-bath.[3] The reaction mixture was stirred overnight, then cooled to ambient temperature and poured into Et_2O (300 mL) Left to precipitate for 15 min. The solid was filtered off and washed with Et_2O (3x50 mL) dried on the funnel, then dried under high-vac, to give **2a** as an almost white solid (4.02 g, 8.4 mmol, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 9.1 Hz, 2H), 8.28 – 8.20 (m, 4H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 135.8, 134.8, 131.8, 131.3, 125.6, 122.0, 116.2.

I.2.2 Amino acid-derived diaryliodonium salt (2b)

I.2.2.1 N,N-Bis-Boc-4-iodo-L-phenylalanine methyl ester



The solution of Boc-4-iodo-*L*-phenylalanine (2.0 g, 6.83 mmol, 1.1 equiv) in anhydrous DMF (40 mL) was stirred at RT, then $NaHCO_3$ (1.29 g, 15.4 mmol, 2.5 equiv) was added. MeI (388 µL, 6.22 mmol, 1 equiv) was added dropwise. The reaction mixture was stirred overnight at 60 °C, then diluted with DCM (100 mL) and extracted with water (100 mL). The phases were separated and the aqueous phase was extracted with DCM (100 mL), and the combined organic phases were washed with brine, dried on Na_2SO_4, and filtered. The solvent was evaporated to give Boc-4-iodo-*L*-phenylalanine methyl ester as a white solid (1.93 g, 4.76 mmol, 70% yield).

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[2] M. Bielawski, B. Olofsson, *Chem. Commun.* **2007**, 2521-2523; M. Bielawski, M. Zhu, B. Olofsson, *Adv. Synth. Catal.* **2007**, *349*, 2610-2618; M. Zhu, N. Jalalian, B. Olofsson, *Synlett* **2008**, *2008*, 592-596.
[3] Our previous protocoll at lower concentration at 80°C gave somewhat lower yields (61-78%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.1 Hz, 2H), 5.00 (d, *J* = 8.3 Hz, 1H), 4.58 (q, *J* = 6.6 Hz, 1H), 3.73 (s, 3H), 3.14 – 2.92 (m, 2H), 1.44 (s, 9H).

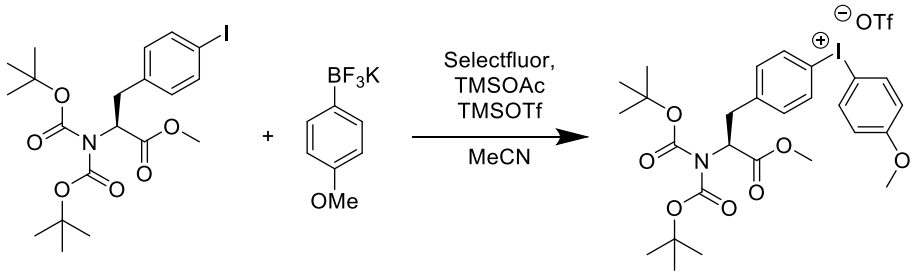
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 155.0, 137.6, 135.7, 131.3, 92.5, 80.1, 54.2, 52.3, 37.9, 28.3.

Boc-4-iodo-*L*-phenylalanine methyl ester (810 mg, 2 mmol) and DMAP (244 mg, 2 mmol) were dissolved in MeCN, and Boc_2O (689 µL, 3 mmol) was added. The reaction mixture was stirred overnight, then diluted with EtOAc (100 mL), washed with water (100 mL) and brine (100 mL). The solvent was evaporated, and the remaining crude was subjected to column chromatography (50 g SiO_2, 10:1 to 8:1 hexanes/EtOAc), to give *N,N*-bis-Boc-4-iodo-*L*-phenylalanine methyl ester (800 mg, 1.58 mmol, 79%) as white crystals.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 5.12 (dd, *J* = 10.3, 5.1 Hz, 1H), 3.76 (s, 3H), 3.38 (dd, *J* = 14.0, 5.1 Hz, 1H), 3.16 (dd, *J* = 14.0, 10.3 Hz, 1H), 2.06 (s, 1H), 1.41 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 151.7, 137.4, 137.2, 131.7, 92.0, 83.3, 59.0, 52.4, 35.8, 27.9.

*I.2.2.2 [(S)4-(2-(Di-(tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenyl] (4'-methoxyphenyl)iodonium triflate (**2b**)*



In a slight modification of a reported procedure,[4] N,N-bis-Boc-4-iodo-*L*-phenylalanine methyl ester (506 mg, 1.00 mmol) and SelectFluor (CAS: 140681-55-6, 463 mg, 1.30 mmol) were filled into a flame-dried round-bottom flask. The atmosphere was changed to argon 3 times, then dry MeCN (5 mL) was cannulated in. A solution of TMSOAc (2.60 mmol, 389 µL) in dry MeCN (2 mL) was added to the stirring mixture. The stirring was continued for 24 h, then solid potassium (4-methoxyphenyl)trifluoroborate (213 mg, 1.00 mmol) was added with a flow of argon. After 5 minutes a solution of TMSOTf (182 µL, 0.90 mmol) in dry MeCN (3 mL) was added dropwise, and the reaction mixture was stirred at RT for 20 minutes. The volatile was removed under reduced pressure, and the residue was redissolved in DCM (50 mL). The solution was washed with an acetate buffer (pH 5, 50 mL), then the aqueous layer was extracted with DCM (3x50 mL). The combined organic layers were washed with water, then with NaOTf solution [2x(500 mg in 50 mL water)]. The organic layer was dried over Na_2SO_4, then the solvent was evaporated under reduced pressure to give **2b** as a white solid (300 mg, 0.39 mmol, 39%).

[4] L. Qin, B. Hu, K. D. Neumann, E. J. Linstad, K. McCauley, J. Veness, J. J. Kempinger, S. G. DiMagno, *Eur. J. Org. Chem.* **2015**, *2015*, 5919-5924.

Mp: 102-107 °C (no mp in literature[4]).

^{1}H NMR (400 MHz, CD_3CN) δ 8.02 (d, *J* = 9.1 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 9.1 Hz, 2H), 5.16 (dd, *J* = 10.9, 4.8 Hz, 1H), 3.83 (s, 3H), 3.69 (s, 3H), 3.42 (dd, *J* = 14.0, 4.8 Hz, 1H), 3.21 (dd, *J* = 14.0, 10.9 Hz, 1H), 1.27 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 164.4, 152.5, 144.7, 138.8, 135.9, 134.5, 112.6, 102.6, 84.1, 59.6, 56.8, 53.1, 36.3, 28.0.

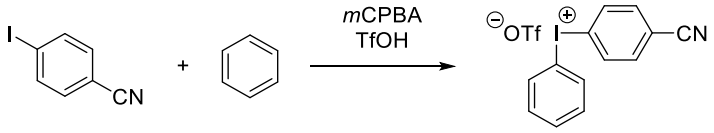
The analytical data correspond to the reported data.[4]

I.2.3 (3-(Trifluoromethyl)phenyl)(4-methoxyphenyl)iodonium tosylate (2p)

[Hydroxyl(tosyloxy)iodo]-3-trifluoromethylbenzene[5] (1.84 g, 4 mmol) was dissolved in TFE/DCM (1:1, 20 mL) and cooled to 0 °C. Anisole (443 µL, 41 mmol) was added dropwise to the cooled mixture, while it turned greyish blue. The reaction mixture was stirred at ambient temperature for 16 h, the solvent was removed under reduced pressure and the diaryliodonium salt was precipitated with diethyl ether (30 mL). The resulting white solid was stirred at ambient temperature for 30 min, then filtered, washed with diethyl ether (3x30 mL), dried on the funnel and to give the product as a white solid in 2.10 g (95% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.71 (d, *J* = 2.1 Hz, 1H), 8.51 (d, *J* = 8.1 Hz, 1H), 8.25 (d, *J* = 9.0 Hz, 2H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 8.6 Hz, 4H), 3.80 (s, 3H), 2.28 (s, 3H).
^{19}F NMR (376 MHz, DMSO-d_6) δ -61.21.
^{13}C NMR (101 MHz, DMSO-d_6) δ 162.5, 146.1, 139.4, 138.1, 137.9, 132.9, 132.0, 132.0, 131.8, 131.4, 129.0, 128.5, 125.9, 124.8, 122.1, 118.0, 117.8, 106.3, 56.2, 21.2.

I.2.4 4-Cyanophenyl(phenyl)iodonium triflate (2q)



To a solution of 4-iodobenzonitrile (1.0 mg, 4.4 mmol) in DCM (9 mL) was added benzene (440 µL, 4.9 mmol) and *m*CPBA (86% active oxidant, 1.00 g, 5.0 mmol). Additional DCM (3 mL) was added and the solution was cooled to 0 °C. TfOH (780 µL, 8.8 mmol) was added dropwise at 0 °C over 30 min. After that the reaction was allowed to reach room temperature and stirred overnight. Then the volatiles were removed under reduced pressure. Et_2O (5 mL) was added, and the mixture was stirred at 0 °C for 20 min. The precipitate was filtered off with a sintered glass funnel and washed with additional cold Et_2O. The crystals were dried in high-vacuum, to afford **2q** (1.59 g, 79%) as a pale brown solid.

[5] Jalalian, N.; Olofsson, B., *Org. Synth.* **2013**, *90*, 1-9

Mp 115-117 °C (lit.: 110-112 °C).

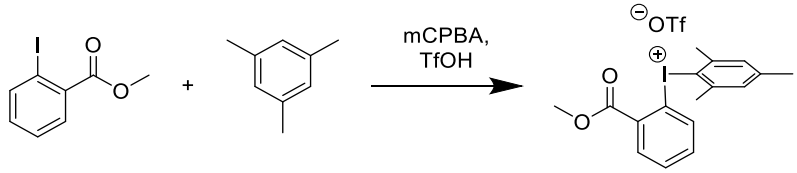
^{1}H NMR (400 MHz, CD_3OD) δ 8.36-8.30 (m, 2H), 8.25-8.20 (m, 2H), 7.90-7.84 (m, 2H), 7.77-7.70 (m, 1H), 7.61-7.53 (m, 2H).

^{13}C NMR (100 MHz, CD_3OD) δ 137.1, 136.8, 136.2, 134.1, 133.4, 120.3, 117.9, 117.5, 116.2.

^{19}F (376 MHz, CD_3OD) δ -80.1.

The analytical data are consistent with the literature data.[6]

I.2.5 2-Methoxycarbonylphenyl(mesityl)iodonium triflate (2r)

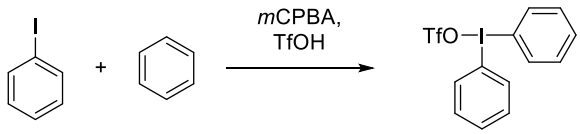


2-Iodobenzoic acid methyl ester (367 µL, 2.5 mmol), *m*CPBA (665 mg, 84% active oxidant, 3.2 mmol) and mesitylene (695 µL, 5 mmol) were dissolved in DCM. The mixture was cooled to 0 °C, and TfOH (442 µL, 0.5 mmol) was added dropwise. The reaction mixture was stirred for another 10 minutes at 0 °C, then warmed to 40 °C, and stirred for 3 h. The volatiles were removed under reduced pressure, and the residue was treated with Et_2O (50 mL). The reddish solid was filtered off and washed with Et_2O to afford **2r** (1.00 g, 1.88 mmol, 75%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.34 (dd, J = 7.5, 1.9 Hz, 1H), 7.84 – 7.72 (m, 2H), 7.42 (s, 2H), 6.90 (dd, J = 8.0, 1.3 Hz, 1H), 4.08 (s, 3H), 2.52 (s, 6H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 168.4, 145.0, 143.7, 137.8, 133.4, 131.9, 130.6, 129.1, 128.0, 118.3, 114.1, 54.9, 26.6, 21.3.

I.2.6 Diphenyliodonium triflate (2s)



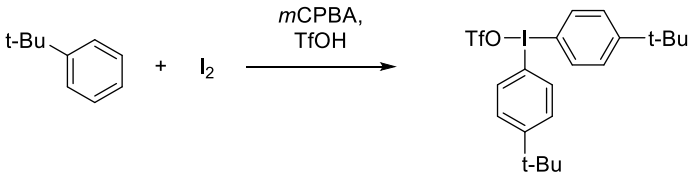
In a round-bottomed flask, iodobenzene (640 µL, 5.75 mmol), benzene (1.025 mL, 11.5 mmol) and *m*CPBA (1.250 g, 86% active oxidant, 6.25 mmol) were dissolved in DCM (50 mL). TfOH (1.525 mL, 17.25 mmol) was added dropwise to the stirring solution at RT. After 10 minutes the mixture was warmed to 40 °C and stirred for 1 h. The volatile components were removed under reduced pressure, and the remaining solid was treated with Et_2O. After cooling 20 minutes in the freezer, the precipitated solid was filtered off, washed with Et_2O, and dried under high vacuum, to give **2s** (2.30 g, 5.35 mmol, 93%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.25 (dd, J = 8.4, 1.2 Hz, 4H), 7.68 (t, J = 7.5 Hz, 2H), 7.54 (t, J = 7.8 Hz, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 135.6, 132.5, 132.2, 116.9.

[6] Ghosh, R.; Lindstedt, E.; Jalalian, N.; Olofsson, B., *ChemistryOpen* **2014**, *3*, 54.

I.2.7 Di(4-tert-butylphenyl)iodonium triflate (2t)

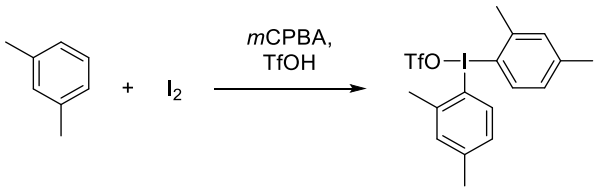


To a solution of iodine (2.15 g, 8.48 mmol) in DCM (93 mL) *m*CPBA (5.41 g, 83% active oxidant, 3.1 equiv) was added, then the mixture was cooled to 0 °C. *tert*-Butylbenzene (5.4 mL, 35 mmol, 4.1 equiv) was added. The mixture was stirred for 5 minutes, then TfOH (3.7 mL, 42 mmol, 5 equiv) was added dropwise. After continued stirring for 5 minutes at 0 °C, the mixture was left to warm up to RT and stirred for 2 h. The reaction mixture was quenched with water (20 mL), the phases were separated and the aqueous phase was extracted with DCM (2x15 mL). The combined organic phases were dried, and the volatiles were removed under reduced pressure. Et_2O was added to the crude, and while the precipitation started, the volatiles were removed again under reduced pressure. Adding Et_2O again caused immediate precipitation. The mixture was stirred for 1 hour, then kept in the freezer at -18 °C, then the solids were filtered off and washed with Et_2O. The resulting yellowish solid was dissolved in minimal amount of DCM, and precipitated with Et_2O. The precipitate was filtered off, and washed with Et_2O, to provide **2u** (5.2 g, 9.6 mmol, 57%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 140.2, 134.1, 118.1, 40.1, 35.9.

I.2.8 Di(2,4-dimethylphenyl)iodonium triflate (2u)

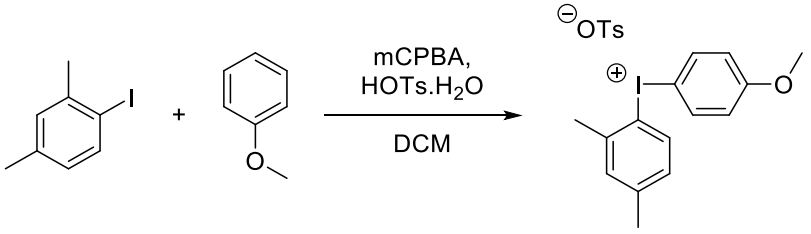


*m*CPBA (90% active oxidant, 5.75 g, 30 mmol), iodine (2.54 g, 10 mmol) and *m*-xylene (4.89 mL, 4.25 g, 40 mmol) were dissolved in DCM (100 mL). The mixture was cooled to 0 °C followed by dropwise addition of TfOH (4.42 mL, 50 mmol). The solution was let to warm to ambient temperature, while being stirred overnight, resulting a purple mixture. The volatiles were evaporated under reduced pressure, and Et_2O was added to crystallize the salt. The solid was filtered off and washed with Et_2O to obtain **2v** (5.71 g, 11.8 mmol, 59%) as a greyish solid. The product contains around 5-8% of (2,4-dimethylphenyl)(2,6-dimethylphenyl)-iodonium triflate.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (d, J = 8.2 Hz, 1H), 7.36 (d, J = 2.1 Hz, 1H), 7.11 (dd, J = 8.3, 2.2 Hz, 1H), 2.56 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 143.5, 140.7, 137.4, 132.6, 130.3, 117.5, 25.2, 21.1.

I.2.9 (2,4-dimethylphenyl)(4-methoxyphenyl)iodonium tosylate (2uu)

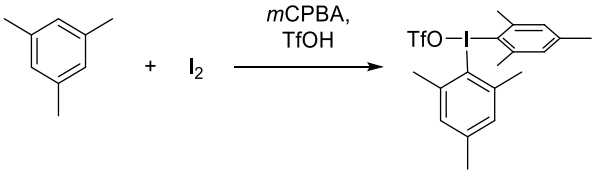


mCPBA (870 mg, 4.4 mmol, 87% active oxidant) was dissolved in DCM (40 mL). 1-iodo-2,4-dimethylbenzene (570 µL, 928 mg, 4 mmol) was added with stirring. Anisole (2.17 mL, 2.16 g, 20 mmol) was added, followed by $TsOH.H_2O$ (836 mg, 4.4 mmol). Stirred for 3 h at RT, then the solvent was evaporated. Precipitated by addition of Et_2O (50 mL), filtered, washet with Et_2O and dried on the funnel, to give **2uu** (1.76 g, 3.4 mmol, 73%) as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.2 Hz, 1H), 8.09 (d, J = 9.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.14 – 7.06 (m, 3H), 7.03 (d, J = 9.0 Hz, 2H), 3.77 (s, 3H), 2.55 (s, 3H), 2.30 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 150.9, 148.2, 145.4, 142.8, 142.1, 142.0, 137.1, 135.0, 133.2, 130.7, 123.6, 122.6, 110.2, 60.9, 30.0, 26.0, 25.9.

I.2.10 Dimesityliodonium triflate (2v)



In a round bottom-flask mesitylene (1.47 mL, 10.25 mmol), iodine (635 mg, 2.5 mmol) and *m*CPBA (2.00 g, 86% active oxidant, 10 mmol) were dissolved in DCM (50 mL). The mixture was cooled to 0 °C, and TfOH (1.32 mL, 15 mmol) was added dropwise. The mixture was stirred for 3 h at RT, then the volatiles were removed under reduced pressure. Precipitation by Et_2O (50 mL), the solid was filtered off and washed with Et_2O (3x25 mL) to give **2w** as a brownish solid (1.46 g, 2.84 mmol, 56% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.20 (s, 4H), 2.47 (s, 12H), 2.30 (s, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 143.2, 142.4, 130.7, 119.3, 25.8, 20.8.

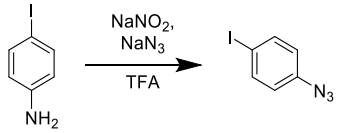
^{19}F NMR (376 MHz, DMSO-d_6) δ -77.75.

I.2.11 4-Azidophenyl(4'-methoxyphenyl)iodonium tosylate (2w)[7]

While we have never observed any issues, it is important to note, that there are two fairly reactive functionalities in the compounds below (**2w**, **2ww**, **2x**). It is important to make safety planning prior preparing/handling these compounds.

[7] This compound had been reported earlier, using similarly conditions as our one-pot method, by J.-H. Chun, V. W. Pike, *Eur. J. Org. Chem.* **2012**, *2012*, 4541-4547. We modified their method to obtain a higher yield.

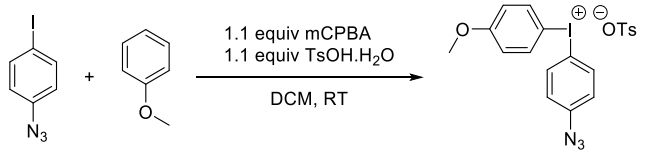
I.2.11.1 4-Azidoiodobenzene



Iodoaniline (6.0 g, 27.4 mmol) was dissolved in TFA (25 mL), then cooled to 0 °C. $NaNO_2$ (2.07 g, 30.1 mmol) was added portion-wise, while the temperature was kept below 5 °C with a salt-ice bath. The mixture was stirred for 30 min, then ice-cold NaN_3 (1.87 g, 28.8 mmol in 10 mL H_2O) was added portion-wise. Immediate foaming occurred. The bubbling brownish suspension was stirred for 1 h at 0 °C, then let to warm up with stirring. The mixture was concentrated under reduced pressure, and the residue was dissolved in DCM (300 mL). It was washed with water (3x100 mL) and brine (100 mL); flash column chromatography (SiO_2, pentane) resulted in a brownish oil (5.48 g, 82%), that crystallized in the refrigerator upon storing for days.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 138.5, 120.8, 88.0.

*I.2.11.2 4-Azidophenyl(4'-methoxyphenyl)iodonium tosylate (**2w**)*

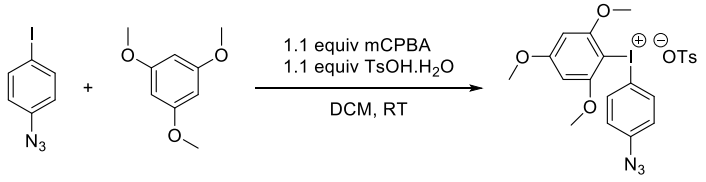


4-Azidoiodobenzene (0.49 g, 2.0 mmol) and *m*CPBA (0.42g, 88% active oxidant, 2.2 mmol) were filled into a round-bottomed flask. DCM (20 mL) was added and the mixture was stirred for 15 min. $TsOH{\cdot}H_2O$ (0.42 g, 2.2 mmol) was added, then anisole (1.1 mL, 10 mmol). The mixture was stirred at 40 °C for 2 h, then the volatile was removed under reduced pressure. The residue was dissolved in MeOH (~1 mL), then precipitated with Et_2O (100 mL). The solid was filtered off and washed with Et_2O to afford **2x** (770 mg, 1.46 mmol, 73%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 12.3, 8.9 Hz, 4H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 3.77 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 143.6, 142.6, 139.3, 137.3, 136.7, 128.4, 126.0, 121.7, 117.3, 110.1, 104.7, 55.5, 21.2.

I.2.12 4-Azidophenyl(2',4'6'-trimethoxyphenyl)iodonium tosylate (2ww) [8]



[8] M. Reitti, P. Villo, B. Olofsson, *Angew. Chem., Int. Ed.* **2016,** 10.1002/anie.201603175

4-Azidoiodobenzene (0.98 g, 4.0 mmol) and *m*CPBA (0.89 g, 85% active oxidant, 4.4 mmol) were filled into a round-bottomed flask. DCM (40 mL) was added and the reaction mixture was stirred for 15 min. $TsOH \cdot H_2O$ (0.84 g, 4.4 mmol) was added, then trimethoxybenzene (1.1 mL, 20 mmol). The mixture was stirred at 40 °C for 4 h, then the volatiles were removed under reduced pressure. The residue was dissolved in DCM:MeOH (1:1, ~5 mL), then precipitated with Et_2O (100 mL). The solid was filtered off and washed with Et_2O to afford **2xx** (326 mg, 0.56 mmol, 14%) as a white solid.

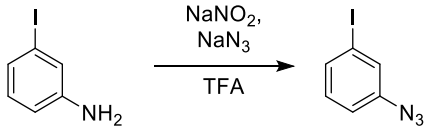
Mp:178-179 °C (decomp).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 9.0 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 6.18 (s, 2H), 3.90 (s, 6H), 3.88 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 160.5, 143.6, 143.0, 139.3, 135.8, 128.5, 126.1, 121.8, 109.6, 91.5, 84.4, 56.9, 56.0, 21.3.

I.2.13 3-Azidophenyl(4'-methoxyphenyliodonium tosylate (2x)

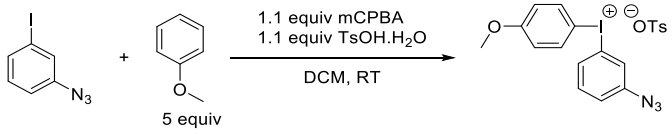
I.2.13.1 3-Azidoiodobenzene



3-Iodoaniline (3 g, 13.7 mmol) was dissolved in TFA (15 mL) and cooled to 0 °C. $NaNO_2$ (1.04 g, 15 mmol in H_2O (5 mL)) was added over a period of 15 min. The mixture was stirred for 30 min at 0 °C. An ice-cold solution of NaN_3 (0.935 g, 14.4 mmol) in H_2O (5 mL) was added over a period of 10 min, then the mixture was stirred at 0 °C for 1 h. The solvent was evaporated under reduced pressure, and the residue was redissolved in DCM (150 mL). The solution was washed with water (100 mL), and the water-phase was back-extracted with DCM (150 mL). The combined organic layers were washed with water (100 mL), and brine (50 mL), and dried on Na_2SO_4. Filtration followed by concentration under reduced pressure afforded a brown oil (2.50 g, 10.3 mmol, 75%) that was used without further purification.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (ddd, J = 7.7, 1.6, 1.0 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.07 (t, J = 7.9 Hz, 1H), 6.99 (ddd, J = 8.1, 2.2, 1.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 134.0, 131.1, 127.9, 118.4, 94.6.

*I.2.13.2 3-Azidophenyl(4'-methoxyphenyl)iodonium tosylate (**2x**)*[7]



3-Azidoiodobenzene (0.98 g, 4.0 mmol) was dissolved in DCM (40 mL). *m*CPBA (880 mg, 86% active oxidant, 4.4 mmol) was added at RT. The mixture was stirred for 10 minutes, followed by the addition of $TsOH \cdot H_2O$ (840 mg, 4.4 mmol), and anisole (2.2 mL, 20 mmol). The reaction mixture was heated to 40 °C, and stirred for 4 hours. The solvent was evaporated, and Et_2O (50 mL) was added. The mixture was agitated to help precipitation, then

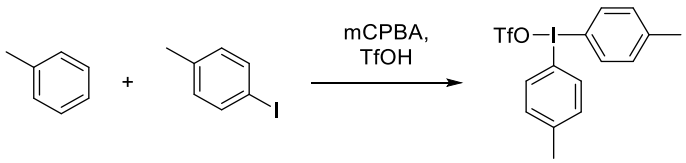
the solid was filtered off and washed with Et_2O (3x20 mL). The solid was further purified by dissolving in MeOH (4 mL) and precipitation by Et_2O (100 mL) to afford **2y** as a white powder (1.54 g, 2.94 mmol, 74%).

Mp: 127-128 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.1 Hz, 2H), 7.70 (ddd, *J* = 8.0, 1.8, 0.9 Hz, 1H), 7.57 (t, *J* = 1.9 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.29 (t, *J* = 8.1 Hz, 1H), 7.08 (ddd, *J* = 8.2, 2.2, 0.9 Hz, 1H), 7.04 (dd, *J* = 7.9, 0.9 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 3.81 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 142.7, 142.5, 139.4, 137.5, 132.2, 130.6, 128.4, 126.0, 124.9, 121.8, 117.5, 116.5, 104.2, 55.6, 21.3.

I.2.14 Di(4-Tolyl)iodonium triflate (2ac)



*m*CPBA (85% active oxidant, 2.68 g, 13.2 mmol) was dissolved in DCM (52 mL). 4-Iodotoluene (2.61 g, 12 mmol) and toluene (1.4 mL, 13.2 mmol) were added, and the mixture was cooled to 0 °C. TfOH (2.1 mL, 24 mmol) was added dropwise. Efficient stirring was necessary to maintain the mixing of the slurry. After 5 minutes of the addition, the ice-bath was removed and the mixture was stirred for an additional 35 min. The volatiles were removed under reduced pressure and the residue was stirred in Et_2O for sufficient precipitation of the salt. The solid was filtered off and washed with Et_2O to obtain **2t** (3.70 g, 67%) as a grey powder.

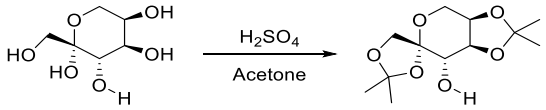
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.09 (d, *J* = 8.3 Hz, 2H), 7.33 (dd, *J* = 8.4, 0.8 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 142.9, 135.4, 132.8, 113.5, 21.3.

I.3 Carbohydrate substrates 1

The starting protected carbohydrates were purchased from commercial sources (**1a-c, 1f, 1h**) or prepared via literature protocols (**1e**,[9] **1i**,[10] **1j**,[11] **1k**,[12] **1l**[13]).

I.3.1 1,2:4,5-Di-O-isopropylidene-β-D-fructopyranose (1d)[14]



To a suspension of D-fructose (3.0 g, 16 mmol) in acetone (60 mL), H_2SO_4 (96%, 300 µL) was added. The mixture was stirred for 2 hours at RT, and cooled to 0 °C, then NaOH (0.95 g) and H_2O (8.4 mL) were added to quench the reaction. The volatiles were evaporated under reduced pressure, and the residue was extracted with DCM (2x 10 mL). The organic fraction was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The resulting white solid was recrystallized by Hex-EtOAc, to afford the title compound as white crystals (1.1 g, 2.1 mmol, 13%).

Mp.: 117-119 °C (lit:[14] 117-118 °C).

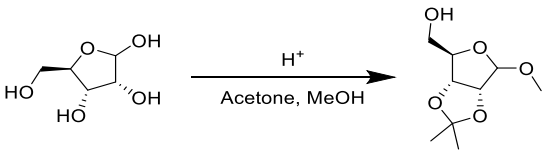
$[\alpha^{31}{}_D]$(c 1.3, $CHCl_3$)= -141.3, (Lit[14] $[\alpha^{28}{}_D]$= -156° (c 1.0, acetone).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 – 4.20 (m, 1H), 4.18 (d, *J* = 8.8 Hz, 1H), 4.15 – 4.09 (m, 2H), 4.03 – 3.96 (m, 2H), 3.67 (dd, *J* = 8.3, 6.9 Hz, 1H), 1.97 (d, *J* = 8.3 Hz, 1H), 1.53 (s, 3H), 1.52 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 111.8, 109.4, 104.5, 73.3, 72.4, 70.4, 60.8, 27.9, 26.5, 26.2, 25.9.

Spectroscopic data correspond to the literature values.[14]

I.3.2 1-O-Methyl-2,3-O-isopropylidene-α-D-riboside (1g)[15]



Following a reported procedure, D-ribose (2.50 g, 16.5 mmol) was stirred in a mixture of acetone and MeOH (1:1, 20 mL). Concentrated HCl was added (250 µL), and the reaction mixture was heated to 75 °C and stirred for 4 hours. After cooling to RT, pyridine (2.5 mL) was added to the mixture. The volatiles were removed under reduced pressure, and the residue was diluted with EtOAc (20 mL). saturated $NaHCO_3$ solution (20 mL) was added, then the

[9] A. S. Henderson, S. Medina, J. F. Bower, M. C. Galan, *Org. Lett.* **2015**, *17*, 4846-4849.
[10] Kohata, Katsunori; Abbas, Saeed A.; Matta, Khushi L. *Carbohydr. Res*. **1984**, *132*, 127-35.
[11] Jansson, Karl et al *J. Org. Chem*., **1988,** *53*, 5629-47
[12] G. J. L. Bernardes, E. J. Grayson, S. Thompson, J. M. Chalker, J. C. Errey, F. El-Oualid, T. D. W. Claridge, B. G. Davis, *Angew. Chem., Int. Ed.* **2008**, *47*, 2244-2247.
[13] Fuerstner, Alois; Konetzki, Ingo *Tetrahedron Lett*. **1998**, *39*, 5721-5724; Yamasaki, Kazuaki; Hishiki, Ryogo; Kato, Eisuke; Jun, Kawabata ACS Med. Chem. Lett. **2011**, *2*, 17-21
[14] J. Kang, G. J. Lim, S. K. Yoon, M. Y. Kim, *J. Org. Chem.* **1995**, *60*, 564-577.
[15] M. J. Lambrecht, M. Brichacek, E. Barkauskaite, A. Ariza, I. Ahel, P. J. Hergenrother, *J. Am. Chem. Soc.* **2015**, *137*, 3558-3564.

aqueous layer was extracted with EtOAc (5x20 mL). The combined organic layers were dried on $MgSO_4$, then the solvent was evaporated under reduced pressure. The liquid was distilled under high vacuum (~1 mbar, 100 °C), then additional column chromatography (SiO_2, PET:EtOAc 3:1 to 2:1) gave **1g** (1.57 g, 49%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97 (s, 1H), 4.83 (dt, *J* = 5.9, 0.6 Hz, 1H), 4.58 (d, *J* = 5.9 Hz, 1H), 4.46 – 4.39 (m, 1H), 3.69 (dd, *J* = 12.5, 2.3 Hz, 1H), 3.65 – 3.54 (m, 1H), 3.43 (s, 3H), 3.23 (t, *J* = 7.6 Hz, 1H), 1.48 (d, *J* = 0.8 Hz, 3H), 1.31 (q, *J* = 0.7 Hz, 3H).

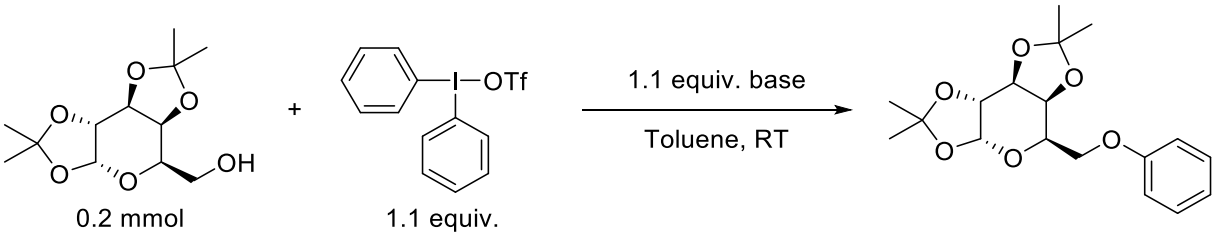
^{13}C NMR (101 MHz, $CDCl_3$) δ 112.1, 110.0, 88.4, 85.8, 81.5, 64.0, 55.5, 26.3, 24.7.

Analytical data correspond to the reported data.

I.4 *O*-Nitroarylation of carbohydrates

I.4.1 Additional optimization data

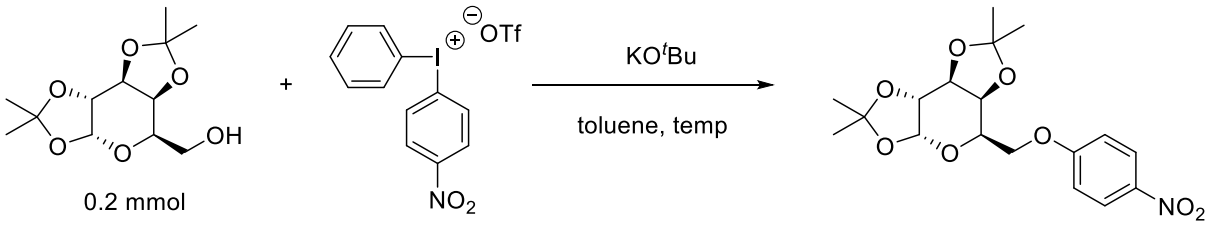
I.4.1.1 Base screen on primary OH with diphenyliodonium triflate



base	isolated yield
KO^{t}Bu	63 %
Di*iso*propylethylamine	-
2,6-Di*tert*butylpyridine	-
Triethylamine	-
NaO^{t}Bu	52 %
LiO^{t}Bu	12 %
Cs_2CO_3	34 %

As an initial setup, primary OH group of a protected galactose(**1h**) was chosen for arylation with diphenyliodonium triflate (**2s**) Although the use of the screened organic bases did not result in product formation (remaining starting materials). The use of *tert*-butoxides generated the product, potassium and sodium *tert*-butoxides gave similar results, while the use of the corresponding lithium base gave only minor amounts of product.

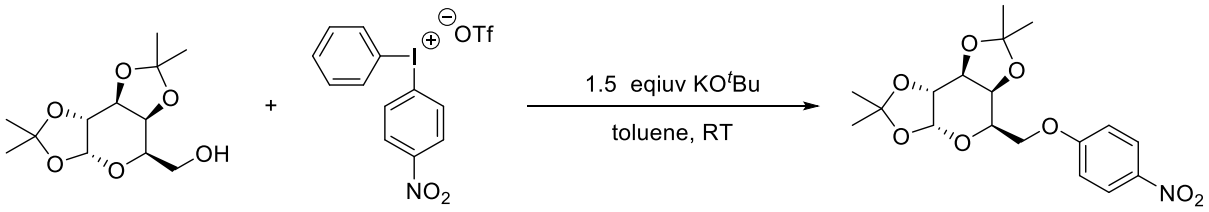
I.4.1.2 Nitroarylation on primary OH



equiv KO^{t}Bu	equiv salt	temp.	yield	
1.1	1.1	RT	79 %	
1.3	1.1	RT	87 %	
1.5	1.1	RT	92 %	89% on 0.5 mmol
1.6	1.1	RT	65 %	
2.0	1.1	RT	78 %	with impurity
1.5	1.2	RT	89 %	
1.5	1.1	40 °C	78%	
1.5	1.1	0°C	93 %	
1.5	1.1	RT, 4A MS	86%	90% on 0.5 mmol

The hypothesized higher activity of the nitroaryl salt (**2a**) was confirmed, as the yield with this salt was 79% for first trial. Increasing the amount of base increased the yield as well, until 1.5 equiv. Addition of more base was not beneficial. With the fixed amount of base the increasing of the amount of the salt did not improve the yield. When the temperature was increased from RT to 40 °C the yield dropped to 78% (entry 7), but lowering the temperature

to 0 °C did not have any effect on the yield (entry 8). Also, only negligible effect was observed when molecular sieves were used (entry 9).

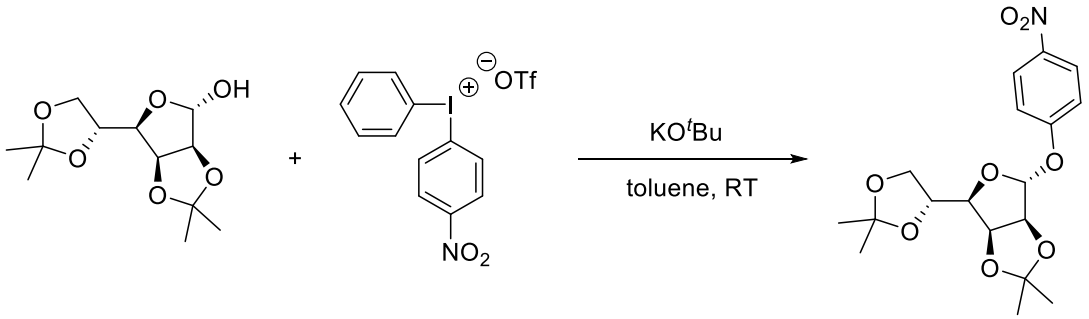


0.2 mmol 1.1 equiv

water added	Yield
-	93%
1 equiv	93%
3 equiv	92%

No effect on the yield was observed upon water addition, showing the robustness of the reaction.

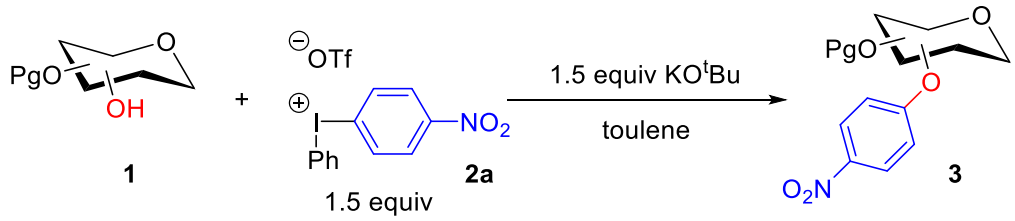
I.4.1.3 Arylation of glycosylic OH group



Iodonium salt	KO^{t}Bu	isolated yield
1.1 equiv.	1.5 equiv	65 %
2 equiv.	2 equiv	91 %
1.5 equiv	1.5 equiv	95 %

Slight increase of the amount of salt and base from 1.1 to 1.5 equiv increased the yield from 65 to 91 %, but further increasing to 2 equiv was not beneficial.

I.4.2 General procedure for nitroarylation with salt 2a

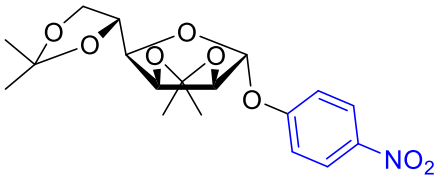


1 **2a** 1.5 equiv **3**

The carbohydrate derivative **1** (0.4-0.04 mmol) was stirred in a 20 mL screw-cap vial in toluene (4-0.4 mL) for 3 minutes. A mixture of 4-nitrophenyl(phenyl) iodonium triflate (**2a**, 0.06-0.8 mmol, 1.5 equiv/OH) and potassium *tert*-butoxide (0.06-0.8 mmol, 1.5 equiv/OH) were added under air over a period of 2-3 minutes, while the mixture turned yellow. The

reaction was stirred for 10-120 min, followed by TLC analysis.[16] The mixture was transferred to a round-bottom flask with EtOAc (3 x 10 mL) and Celite was added. Then the volatiles were removed under reduced pressure, and the residue was subjected to column chromatography to provide the purified product.

I.4.3 (4-Nitrophenyl)-2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside (3a)



2,3:5,6-Di-*O*-isopropylidene-α-D-mannofuranose (**1a**) (104 mg, 0.4 mmol) was arylated according to the general procedure in toluene (2 mL) for 20 minutes. Purified by column chromatography (10 g SiO_2, PET/EtOAc 10:1 to 8:1), to give **3a** (144 mg, 0.380 mmol, 95%) as a white solid.

Mp: 83-85 °C. (Lit:[17] 81-83 °C).

R_f= 0.3 (PET/EtOAc 4/1).

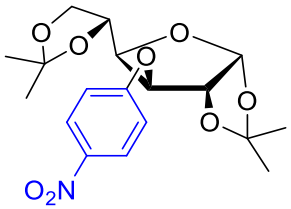
$[\alpha^{31}_D]$(c 1.3, $CHCl_3$)= +168.4, (Lit[17] $[\alpha^{20}_D]$($CHCl_3$=+186).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 9.3 Hz, 2H), 7.10 (d, *J* = 9.3 Hz, 2H), 5.74 (s, 1H), 5.03 – 4.85 (m, 2H), 4.45 (ddd, *J* = 7.7, 6.2, 4.1 Hz, 1H), 4.16 – 4.05 (m, 2H), 3.97 (dd, *J* = 8.8, 4.2 Hz, 1H), 1.54 (s, 3H), 1.44 (s, 3H), 1.40 (s, 3H), 1.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 142.5, 125.8, 116.3, 113.3, 109.4, 104.8, 85.3, 81.8, 79.4, 72.8, 66.7, 26.9, 25.9, 25.1, 24.6.

HRMS(ESI): calcd for [$C_{18}H_{23}NO_8Na^+$]: 404.1316 found: 404.1307.

I.4.4 3-O-(4-Nitrophenyl)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3b)



1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (**1b**) (0.4 mmol, 104 mg) was arylated according to the general procedure in toluene (4 mL) for 40 minutes. Purified by column chromatography (15 g SiO_2, PET/EtOAc 8:1 to 7:1), to give **3b** (140 mg, 0.38 mmol, 92%), as white crystals.

Mp: 133-135 °C. (Amorphous solid in Lit, no mp. given).**Error! Bookmark not defined.**

R_f= 0.2 (PET/EtOAc 4/1).

[16] usually not complete conversion, iodonium salt and related compounds are not visible with anisaldehyde stain.
[17] G. Grynkiewicz, *Carbohydr. Res.* **1977**, *53*, C11-C12. No NMR data available.

$[\alpha^{31}{}_D]$= -25.7 (c 1.0, $CHCl_3$) Lit:[18] $[\alpha]^{21}{}_D$ = -45 (c = 1.0, $CHCl_3$).

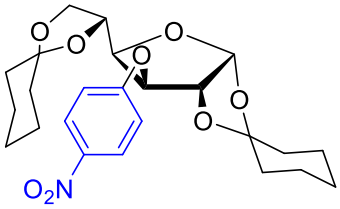
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 9.2 Hz, 2H), 7.07 (d, *J* = 9.3 Hz, 2H), 5.95 (d, *J* = 3.8 Hz, 1H), 4.82 (d, *J* = 3.0 Hz, 1H), 4.57 (d, *J* = 3.8 Hz, 1H), 4.41 (ddd, *J* = 8.3, 6.1, 5.0 Hz, 1H), 4.29 (dd, *J* = 8.3, 3.0 Hz, 1H), 4.19 – 4.05 (m, 2H), 1.56 (s, 3H), 1.43 (s, 3H), 1.32 (s, 3H), 1.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 142.3, 126.0, 115.4, 112.5, 109.5, 105.2, 82.2, 80.6, 80.3, 71.9, 67.3, 26.9, 26.7, 26.2, 25.2.

HRMS(ESI) [$C_{18}H_{23}NNaO_8^+$] 404.1321 found: 404.1322.

Corresponds to the literature values.[18]

I.4.5 3-O-(4-Nitrophenyl)-1,2:5,6-di-O-cyclohexylidene-α-D-glucofuranose (3c)



1,2:5,6-Di-*O*-cyclohexylidene-α-D-glucofuranose (**1c**) (136 mg, 0.4 mmol) was arylated according to the general procedure in toluene (2 mL) for 10 minutes. Purified by column chromatography (20 g SiO_2, PET/EtOAc 10:1), to give **3c** (179 mg, 0.388 mmol, 97%), as a white foam.

Mp: 110-113 °C.

R_f= 0.6 (PET/EtOAc 4/1).

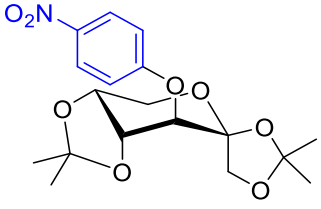
$[\alpha^{31}{}_D]$= -16.1 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.16 (m, 2H), 7.13 – 7.06 (m, 2H), 5.96 (d, *J* = 3.8 Hz, 1H), 4.85 (d, *J* = 2.9 Hz, 1H), 4.58 (d, *J* = 3.8 Hz, 1H), 4.36 (ddd, *J* = 8.4, 6.0, 4.9 Hz, 1H), 4.27 (dd, *J* = 8.4, 2.9 Hz, 1H), 4.16 – 4.02 (m, 2H), 1.94 – 0.66 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 142.2, 125.9, 115.6, 113.2, 110.1, 104.9, 82.0, 81.0, 80.6, 71.5, 67.0, 36.6, 36.3, 35.7, 34.6, 25.1, 24.8, 24.1, 23.9, 23.7, 23.5.

HRMS(ESI): calcd for [$C_{24}H_{31}NNaO_8^+$]: 484.1942 found: 484.1963.

I.4.6 3-O-(4-Nitrophenyl)-1,2:4,5-di-O-isopropylidene-β-D-fructopyranose (3d)



[18] A. S. Henderson, S. Medina, J. F. Bower, M. C. Galan, *Org. Lett.* **2015**, *17*, 4846-4849.

1,2:4,5-Di-*O*-isopropylidene-*β*-D-fructopyranose (**1d**) (104 mg, 0.400 mmol) was arylated according to the general procedure in toluene (2 mL) for 10 minutes. Purified by column chromatography (20 g SiO_2, PET/EtOAc 10:1 to 8:1), to give **3d** (151 mg, 0.396 mmol, 99%) as white crystals.

Mp: 110-112 °C.

R_f = 0.35 (PET/EtOAc 4/1).

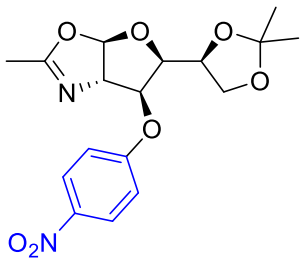
$[\alpha^{31}{}_D]$= -90.2 (c 1.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 9.3 Hz, 2H), 7.17 (d, *J* = 9.2 Hz, 2H), 4.47 (dd, *J* = 7.2, 5.6 Hz, 1H), 4.39 (d, *J* = 7.2 Hz, 1H), 4.35 (dd, *J* = 5.7, 2.7 Hz, 1H), 4.24 (dd, *J* = 13.5, 2.8 Hz, 1H), 4.12 (d, *J* = 13.5 Hz, 1H), 3.99 (d, *J* = 8.9 Hz, 1H), 3.90 (d, *J* = 8.9 Hz, 1H), 1.65 (s, 3H), 1.54 (s, 3H), 1.49 (s, 3H), 1.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 142.2, 125.9, 116.3, 112.7, 109.5, 103.8, 77.7, 76.2, 73.8, 71.8, 60.4, 28.0, 26.6, 26.0, 25.9.

HRMS(ESI) calcd. for $[C_{18}H_{23}NNaO_8^+]$: 404.1321, found: 404.1344.

I.4.7 (3aR,5R,6S,6aS)-5-((S)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2-methyl-6-(4-nitrophenoxy)-3a,5,6,6a-tetrahydrofuro[3,2-d]oxazole (3e)



(3a*R*,5*R*,6*S*,6a*S*)-5-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2-methyl-3a,5,6,6a-tetrahydrofuro-[3,2-d]oxazol-6-ol (**1e**) (97 mg, 0.4 mmol) was arylated according to the general procedure in toluene (2 mL) for 15 min. Purified by column chromatography (15 g SiO_2, PET/EtOAc 2:1 to 1:1), to give **3e** (123 mg, 0.338 mmol, 85%), as a white foam.

Mp.: 50-54 °C.

R_f = 0.4 (PET/EtOAc 1/1).

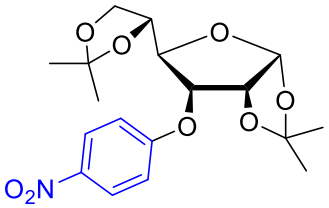
$[\alpha^{31}{}_D]$= -68.5 (c 1.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 9.2 Hz, 2H), 7.12 (d, *J* = 9.2 Hz, 2H), 6.17 (d, *J* = 5.2 Hz, 1H), 4.87 (d, *J* = 3.2 Hz, 1H), 4.53 (dd, *J* = 5.1, 1.8 Hz, 1H), 4.49 – 4.40 (m, 1H), 2.09 (d, *J* = 1.5 Hz, 3H), 1.41 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 161.6, 142.2, 126.0, 115.5, 109.5, 107.0, 80.6, 80.2, 75.1, 71.9, 66.9, 26.9, 25.1, 14.2.

HRMS(ESI): calcd for $[C_{17}H_{20}N_2NaO_7^+]$: 387.1163 found: 387.1147.

I.4.8 3-O-(4-Nitrophenyl)-1,2:5,6-di-O-isopropylidene-α-D-allofuranose (3f)



1,2:5,6-Di-*O*-isopropylidene-α-D-allofuranose (**1f**) (0.4 mmol, 104 mg) was arylated according to the general procedure in toluene (2 mL) for 60 minutes. Purified by column chromatography (15 g SiO_2, PET/EtOAc 8:1 to 4:1), to give **3f** (110 mg, 0.291 mg, 72%), as white crystals.

Mp: 120-122 °C.

R_f= 0.1 (PET/EtOAc 4/1).

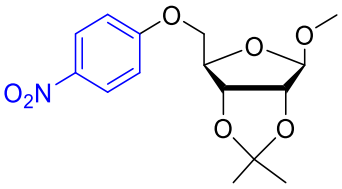
$[\alpha^{31}{}_D]$= +208.6 (c 1.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 9.2 Hz, 2H), 7.08 (d, *J* = 9.3 Hz, 2H), 5.96 (d, *J* = 3.9 Hz, 1H), 4.92 (dd, *J* = 5.0, 3.9 Hz, 1H), 4.71 (dd, *J* = 7.8, 5.0 Hz, 1H), 4.48 – 4.35 (m, 2H), 4.13 (dd, *J* = 8.6, 6.9 Hz, 1H), 3.99 (dd, *J* = 8.6, 6.1 Hz, 1H), 1.59 (s, 3H), 1.39 – 1.31 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 142.3, 126.0, 115.4, 113.6, 110.1, 104.5, 78.8, 77.3, 76.5, 74.7, 65.5, 26.8, 26.5, 26.2, 25.0.

HRMS(ESI): calcd for $[C_{18}H_{23}NO_8Na^+]$: 404.1316 found: 404.1331.

I.4.9 Methyl-5-O-(4-nitrophenyl)-2,3-O-isopropylidene-α-D-ribofuranoside (3g)



Methyl-2,3-*O*-isopropylidene-α-D-ribofuranoside (**3a**) (81.6 mg, 0.400 mmol) was arylated according to the general procedure in toluene (2 mL) for 30 minutes. Purified by column chromatography (15 g SiO_2, PET/EtOAc 8:1 to 6:1), to give **3g** (116 mg, 0.357 mmol, 89%), as white crystals.

Mp: 139-142 °C.

R_f= 0.6 (PET/EtOAc 4/1).

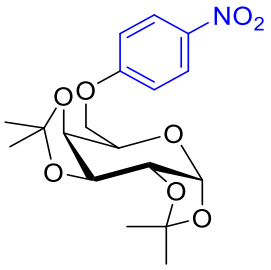
$[\alpha^{31}{}_D]$= -34.5 (c 1.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 9.2 Hz, 2H), 7.00 (d, *J* = 9.3 Hz, 2H), 5.05 (s, 1H), 4.80 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.66 (d, *J* = 6.0 Hz, 1H), 4.57 (ddd, *J* = 8.2, 6.1, 1.1 Hz, 1H), 4.17 – 4.02 (m, 2H), 3.36 (s, 3H), 1.55 – 1.53 (m, 3H), 1.38 – 1.36 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 141.9, 125.9, 114.5, 112.8, 109.5, 85.1, 84.2, 81.9, 69.0, 55.1, 26.4, 25.0.

HRMS(ESI) calcd for [$C_{15}H_{19}NNaO_7^+$]: 348.1054, found: 348.1059.

I.4.10 6-O-(4-Nitrophenyl)- 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (3h)



1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranose (**1h**) (104 mg, 0.400 mmol) was arylated according to the general procedure in toluene (1 mL) for 30 minutes. Purified by column chromatography (15 g SiO_2, PET/EtOAc 10:1 to 8:1), to give **3h** (123 mg, 0.325 mmol, 81%), as pale yellow oil.

R_f= 0.25 (PET/EtOAc 4/1).

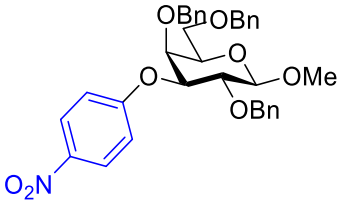
[$\alpha^{31}{}_D$]= -103.9 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 9.2 Hz, 2H), 7.03 (d, *J* = 9.3 Hz, 2H), 5.59 (d, *J* = 5.0 Hz, 1H), 4.69 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.41 – 4.35 (m, 2H), 4.31 – 4.19 (m, 3H), 1.56 (s, 3H), 1.49 (s, 3H), 1.38 (s, 3H), 1.37 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 141.7, 125.8, 114.7, 109.7, 108.9, 96.3, 70.9, 70.6, 70.5, 67.6, 66.2, 26.1, 26.0, 24.9, 24.4.

HRMS(ESI): calcd for [$C_{18}H_{23}NO_8Na^+$]: 404.1316 found: 404.1316.

I.4.11 Methyl-3-O-(4-nitrophenyl)-2,3,6-O-tribenzyl-β-D-glucopyranoside (3i)



Methyl-2,3,6-*O*-tribenzyl-β-D-glucopyranoside (**1i**) (18.6 mg, 0.04 mmol) was arylated according to the general procedure in toluene (400 µL) in a 2 mL microwave vial for 20 min. Purified by column chromatography (SiO_2, PET/EtOAc 5:1 to 4:1), to give **3i** (18 mg, 0.03128 mmol, 78%), as a yellowish oil.

R_f= 0.45 (PET/EtOAc 4/1).

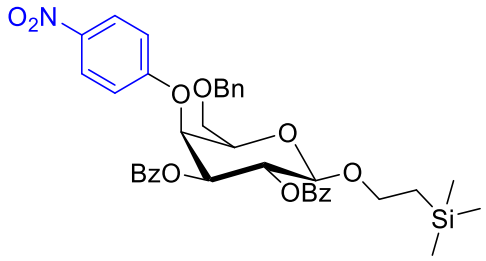
[$\alpha^{31}{}_D$]= +18.3 (c 0.7, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 9.2 Hz, 2H), 7.40 – 7.22 (m, 13H), 7.18 – 7.11 (m, 2H), 6.99 (d, *J* = 9.3 Hz, 2H), 4.85 (d, *J* = 11.1 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 11.1 Hz, 1H), 4.57 – 4.39 (m, 5H), 4.04 (d, *J* = 3.1 Hz, 1H), 3.95 (dd, *J* = 9.7, 7.6 Hz, 1H), 3.74 – 3.64 (m, 3H), 3.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 141.7, 137.9, 137.9, 137.6, 128.5, 128.2, 128.2, 128.0, 127.9, 127.8, 127.7, 125.9, 115.7, 104.8, 80.6, 78.2, 75.1, 75.1, 73.7, 73.5, 73.0, 68.1, 57.2.

HRMS(ESI) calcd for [$C_{34}H_{35}NNaO_8^+$]: 608.2255, found: 608.2293.

I.4.12 2-Trimethylsilylethyl-4-O-(4-nitrophenyl)-2,3-O-benzoyl-6-O-benzyl-β-D-galactopyranoside (3j)



2-Trimethylsilylethyl-2,3-*O*-benzoyl-6-*O*-benzyl-β-D-galactopyranoside (**1j**) (39.4 mg, 0.068 mmol) was arylated according to the general procedure with **2a** (1.76 equiv) in toluene (0.8 mL) in a 4 mL screw-cap vial for 5 min at 0 °C. Purified by column chromatography (10 g SiO_2, PET/EtOAc 20:1 to 8:1), to give **3j** (23 mg, 0.0329 mmol, 48%), as a yellow oil.

R_f= 0.4 (PET/EtOAc 4/1).

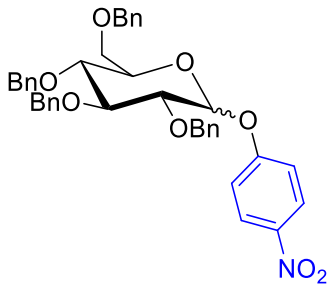
[α^{30}_D]= +105.2 (c 0.6, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 8.4, 1.3 Hz, 2H), 8.08 (d, *J* = 9.2 Hz, 2H), 7.94 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.65 (ddt, *J* = 8.7, 6.9, 1.3 Hz, 1H), 7.58 – 7.47 (m, 3H), 7.44 – 7.37 (m, 2H), 7.31 – 7.20 (m, 6H), 6.96 (d, *J* = 9.3 Hz, 2H), 5.98 (dd, *J* = 3.5, 1.1 Hz, 1H), 5.75 (dd, *J* = 9.9, 8.0 Hz, 1H), 4.83 – 4.76 (m, 2H), 4.54 (d, *J* = 11.7 Hz, 1H), 4.47 (d, *J* = 11.7 Hz, 1H), 4.14 – 4.04 (m, 2H), 3.78 – 3.61 (m, 3H), 1.00 – 0.88 (m, 2H), -0.03 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 165.0, 162.7, 142.4, 137.3, 133.5, 133.3, 130.1, 129.6, 129.4, 129.1, 128.6, 128.4, 128.4, 128.0, 127.9, 125.8, 116.4, 100.9, 78.1, 73.8, 72.6, 71.2, 67.8, 67.7, 67.6, 29.7, 18.0, -1.5.

HRMS(ESI): calcd for [$C_{38}H_{41}NNaO_{10}Si^+$]: 722.2392, found: 722.2415.

I.4.13 4-Nitrophenyl-2,3,4,6-tetra-O-benzyl-D-glucopyranoside (3k)



2,3,4,6-tetra-O-benzyl-D-glucopyranoside (**1k**) was arylated according to the general procedure in toluene (2 mL) for 10 minutes. Purified by column chromatography (20 g SiO_2, PET/EtOAc 10:1 to 8:1), to give **3k** (218 mg, 0.330 mmol, 83%), as a colorless oil.

Alpha to Beta ratio: 1 to 0.82

R_f= 0.35 (PET/EtOAc 4/1).

$[\alpha^{31}{}_D]$= +58.6 (c 1.5, $CHCl_3$) for the mixture of anomers.

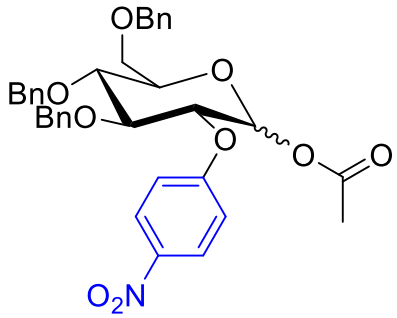
^{1}H NMR (400 MHz, $CDCl_3$) 8.21 (d, *J* = 9.3 Hz, 2H, beta nitrophenyl), δ 8.20 (d, *J* = 9.3 Hz, 2H, alpha nitrophenyl), 7.45 – 7.26 (m, 18H, beta benzyl), 7.39 – 7.27 (m, 18H, alpha benzyl), 7.24 – 7.29 (m, 2H, alpha benzyl), 7.19 – 7.14 (m, 4H, beta benzyl+nitrophenyl), 7.11 (d, *J* = 9.2 Hz, 2H, alpha nitrophenyl), 5.48 (d, *J* = 3.5 Hz, 1H, beta anomeric), 5.15 – 5.08 (m, 1H), 5.08 (d, *J* = 10.8 Hz, 1H, alpha anomeric), 4.98 (dd, *J* = 11.0, 1.4 Hz, 2H), 4.97 – 4.84 (m, 3H), 4.92 – 4.84 (m, 3H), 4.67 (d, *J* = 12.1 Hz, 1H), 4.62 – 4.57 (m, 2H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 11.9 Hz, 1H), 4.52 (d, *J* = 10.7 Hz, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.20 (dd, *J* = 9.6, 8.3 Hz, 1H), 3.86 – 3.68 (m, 4H), 3.87 – 3.65 (m, 6H). 3.56 (dd, *J* = 10.7, 1.8 Hz, 1H).

In correspondence with the reported data.[19]

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 161.5, 142.8, 142.6, 138.6, 138.3, 138.0, 137.9, 137.9, 137.8, 137.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.2, 128.2, 128.1, 128.0, 128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 125.8, 125.8, 116.6, 116.5, 100.8 (beta C1), 95.7 (alfa C1), 84.6, 81.8, 79.6, 75.9, 75.9, 75.4, 75.3, 75.2, 73.8, 73.6, 73.5, 71.5, 68.7, 68.0.

HRMS(ESI): calcd for $[C_{40}H_{39}NNaO_8^+]$: 684.2568 found: 684.2565.

I.4.14 1-O-Acetyl-2-O-(4-nitrophenyl)-3,4,6-O-benzylglucopyranose (3l)



1-*O*-Acetyl-3,4,6-*O*-benzylglucopyranose (**1l**) (197 mg, 0.400 mmol) was arylated according to the general procedure in toluene (4 mL) for 5 min. Purified by column chromatography (20 g SiO_2, PET/EtOAc 8:1 to 5:1), to give **3l** (197 mg, 0.32 mmol, 80%) as a yellow oil.

Alpha to Beta ratio: 1 to 0.9

R_f= 0.6 (PET/EtOAc 1/1).

$[\alpha^{31}{}_D]$= +72.8 (c 1.0, $CHCl_3$) for the mixture of anomers.

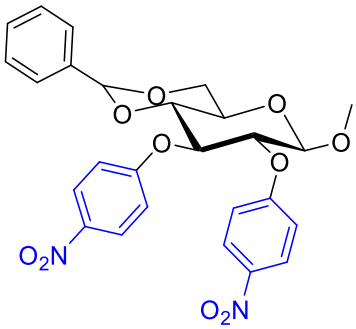
[19] K. Briner, A. Vasella, *Helv. Chim. Acta* **1990**, *73*, 1764-1778.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 9.2 Hz, 2H), 8.17 (d, *J* = 9.2 Hz, 2H), 7.33 (dddd, *J* = 15.9, 11.5, 8.4, 5.2 Hz, 25H), 7.18 (s, 6H), 7.09 (d, *J* = 9.2 Hz, 2H), 5.85 (d, *J* = 3.6 Hz, 1H, H-1 alfa anomer), 5.33 (dd, *J* = 9.3, 7.6 Hz, virtual couplings, 0.8H, H-2 beta anomer), 5.08 (d, *J* = 7.7 Hz, 0.8H, H-1 beta anomer), 5.08 (dd, *J* =10.01, 3.6 Hz, 1H, H-2 alfa anomer), 4.95 – 4.82 (m, 5H), 4.73 (d, *J* = 11.4 Hz, 1H), 4.66 – 4.44 (m, 6H), 4.23 (dd, *J* = 10.1, 8.6 Hz, 1H, H-3 alfa anomer), 3.90 (t, *J* = 8.8, 1H, H-4, alfa anomer), 3.87 – 3.68 (m, 7H), 3.63 (dd, *J* = 1.83, 10.87, 1H, H-6, alfa anomer), 2.05 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 169.4, 161.7, 161.1, 142.9, 142.8, 138.4, 137.9, 137.8, 137.6, 137.6, 128.5, 128.5, 128.5, 128.4, 128.1, 128.1, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 125.8, 125.8, 125.7, 116.6, 116.6, 116.5, 98.4 (beta C1), 94.7 (alfa C1), 82.6, 79.9, 77.6, 77.2, 75.7, 75.7, 75.3, 75.2, 75.2, 73.6, 73.5, 72.8, 72.6, 71.7, 68.5, 68.0, 20.8; only one acetyl CH_3 apparent in the ^{13}C NMR.

HRMS(ESI): calcd for [$C_{35}H_{35}NO_9$ Na^+]: 636.2204, found: 636.2212.

I.4.15 Methyl-2,3-O-di(4-nitrophenyl)-4,6-O-benzylidene-α-D-glucopyranoside (3m)



Methyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**1m**) (139 mg, 0.400 mmol, 1 equiv) was arylated according to the general procedure with **2a** (3 equiv) in toluene (8 mL) for 2 h. Purified by column chromatography (20 g SiO_2, PET/EtOAc 5:1 to 3:1), to give **3m** (150 mg, 0.287 mmol, 72%), as an amorphous solid.

Mp: 100-104 °C.

R_f= 0.8 (PET/EtOAc 1/1); R_f= 0.5 (PET/EtOAc 2/1).

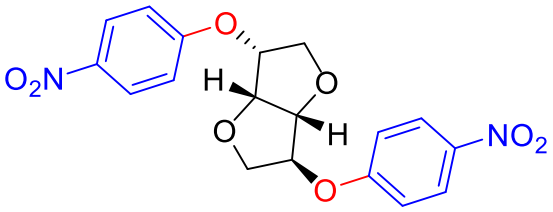
[α^{30}_D]= -148.9 (c 0.9, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 9.3 Hz, 2H), 8.10 (d, *J* = 9.2 Hz, 2H), 7.40 – 7.29 (m, 5H), 7.06 (d, *J* = 9.2 Hz, 2H), 7.04 (d, *J* = 9.2 Hz, 2H), 5.59 (s, 1H), 4.75 (t, *J* = 9.1 Hz, 1H), 4.66 (d, *J* = 7.6 Hz, 1H), 4.54 – 4.45 (m, 2H), 3.91 (td, *J* = 10.4, 9.9, 8.5 Hz, 2H), 3.65 (td, *J* = 9.7, 5.0 Hz, 1H), 3.56 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 163.7, 142.5, 142.4, 136.5, 129.2, 128.3, 125.8, 125.7, 125.6, 116.7, 116.5, 103.3, 101.5, 80.8, 80.7, 79.7, 68.5, 66.2, 57.8.

HRMS(ESI): calcd for [$C_{26}H_{24}N_2NaO_{10}^+$]: 547.1323 found: 547.1330.

I.4.16 2,5-O-Di(4-nitrophenyl)-dianhydro-D-glucitol (3n)



Dianhydro-D-glucitol (**1n**) (58 mg, 0.4 mmol, 1 equiv) was arylated according to the general procedure with **2a** (3 equiv) in toluene (4 mL) for 20 min. Purified by column chromatography (15 g SiO_2, PET/EtOAc 2:1 to 1:1), to give **3n** (73 mg, 0.188 mmol, 47%) as a beige solid.

Mp.: 142-145 °C (no literature data reported).

R_f= 0.2 (PET/EtOAc 2/1).

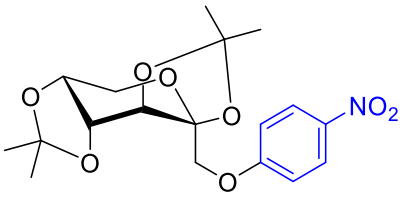
$[\alpha^{31}{}_D]$= +117.4 (c 0.9, $CHCl_3$) (no literature data reported).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 9.2 Hz, 2H), 8.19 (d, *J* = 9.2 Hz, 2H), 7.04 (d, *J* = 9.2 Hz, 2H), 7.00 (d, *J* = 9.2 Hz, 2H), 5.09 (t, *J* = 5.3 Hz, 1H), 4.98 – 4.88 (m, 2H), 4.65 (d, *J* = 5.2 Hz, 1H), 4.21 – 4.02 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 161.8, 142.1, 142.0, 126.1, 125.9, 115.2, 115.1, 86.2, 82.0, 81.7, 77.9, 73.3, 71.9.

HRMS(ESI): calcd for [$C_{18}H_{16}N_2NaO_8^+$]: 411.0799 found: 411.0812.
Analytical data correspond to the literature values.[20]

I.4.17 1-O-(4-Nitrophenyl)-2,3:4,5-di-O-isopropylidene-β-D-fructopyranose (3o)



2,3:4,5-Di-*O*-isopropylidene-β-D-fructopyranose (**1o**) (104 mg, 0.4 mmol) was arylated according to the general procedure in toluene (2 mL) for 30 minutes. Purified by column chromatography (15 g SiO_2, PET/EtOAc 10:1 to 7:1), to give **3o** (139 mg, 0.367 mmol, 92%), as an amorphous foam.

Mp: 70-72 °C.

R_f= 0.4 (PET/EtOAc 4/1).

$[\alpha^{31}{}_D]$= -25.4 (c 1.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 9.3 Hz, 2H), 7.02 (d, *J* = 9.3 Hz, 2H), 4.68 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.53 (d, *J* = 2.6 Hz, 1H), 4.34 – 4.25 (m, 2H), 4.16 (d, *J* = 10.4 Hz, 1H), 3.99

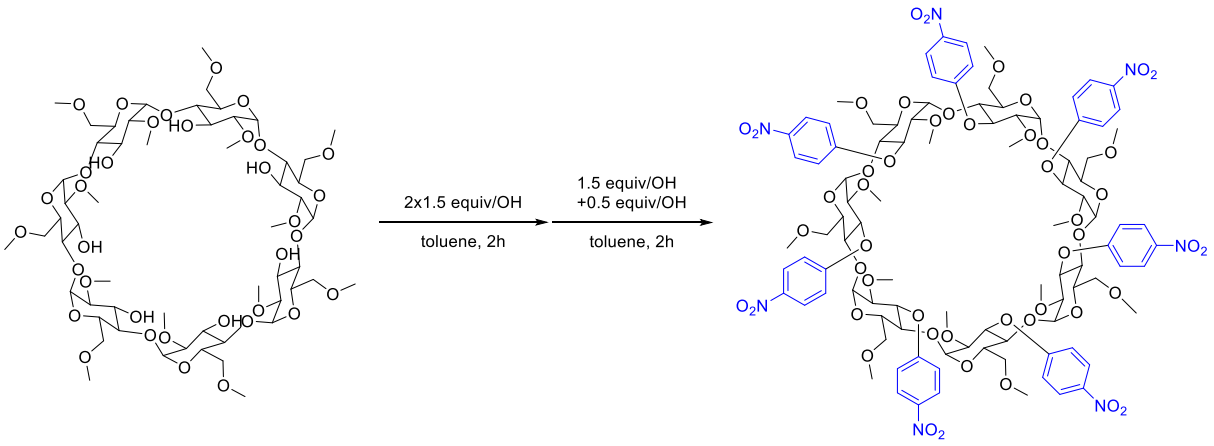
[20] R. Medimagh, S. Mghirbi, A. Saadaoui, A. Fildier, M. Desloir-Bonjour, G. Raffin, H. R. Kricheldorf, S. Chatti, *C. R. Chim.* **2013**, *16*, 1127-1139.

(dd, *J* = 13.0, 1.9 Hz, 1H), 3.82 (dd, *J* = 13.0, 0.8 Hz, 1H), 1.59 (s, 3H), 1.51 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 141.9, 125.9, 114.7, 109.2, 109.1, 101.7, 70.8, 70.1, 70.0, 69.4, 61.3, 26.6, 25.9, 25.3, 24.0.

HRMS(ESI): calcd for [$C_{18}H_{23}NO_8Na^+$]: 404.1316 found: 404.1315.

I.4.18 Heptakis(2,6-di-O-mehtyl-4-nitrophenyl)-ß-cyclodextrine (4)

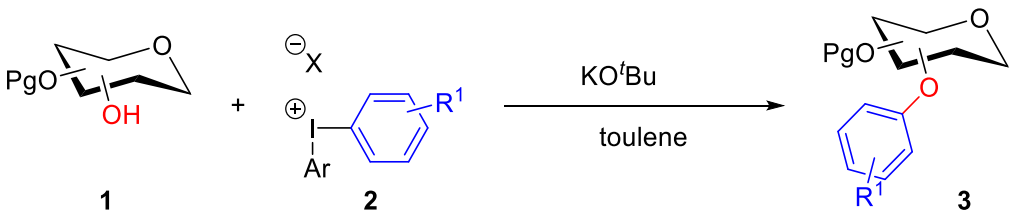


Heptakis(2,6-di-*O*-mehtyl)-β-cyclodextrine (78 mg, 0.059 mmol) was dissolved in toluene (4 mL). **2a** (285 mg, 0.6 mmol, 1.5 equiv/OH) and KO^{t}Bu (67 mg, 0.60 mmol, 1.5 equiv/OH) were added, and the reaction mixture was stirred for 1 h. Another 1.5 equiv of **2a** and KO^{t}Bu were added, and the reaction mixture was stirred for 1 h. It was then diluted with EtOAc, and Celite was added. The volatiles were removed under reduced pressure and submitted to column chromatography (SiO_2, DCM:MeOH 100:1 to 20:1). After concentration, the anisaldehyde visible fractions were dissolved in toluene (4 mL) and resubmitted to the reaction with 1.5 equiv of **2a** (285 mg, 0.6 mmol) and KO^{t}Bu (67 mg, 0.60 mmol, 1.5 equiv/OH). The reaction mixture was stirred for 1 h, then another 0.5 equiv of **2a** (95 mg) and KO^{t}Bu (22 mg) were added, and the reaction mixture was stirred for 1 h. It was then diluted with EtOAc, evaporated to Celite, subjected to column chromatography, (SiO_2, DCM/MeOH) to give **4** (72 mg, 0.033 mmol, 57%) as a yellowish oil, solidifying upon storing at 4°C.

[α^{30}_D]= -32.1 (c 0.6, $CHCl_3$).

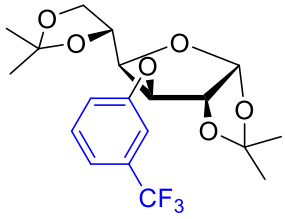
HRMS(ESI): calcd for [$C_{98}H_{119}N_7O_{49}$ Na^+]: 2201.6961, found: 2201.6950.

I.5 Other *O*-arylations of carbohydrates



The starting carbohydrate derivative **1** (0.04-0.4 mmol) was stirred in toluene (0.4-4 mL) for 3 minutes, then a mixture of the iodonium salt **2** (1.5-2 equiv) and KO^{t}Bu (1.5-2 equiv) was added in portions under air in 2-3 minutes. The vial was capped, and the reaction was stirred at RT for the time indicated (5 min-4 h). The mixture was transferred to a flask by EtOAc, and evaporated to Celite. Column chromatography afforded the purified product.

I.5.1 3-O-(3-Trifluoromethylphenyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3p)



1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.4 mmol, 104 mg) was arylated according to the general procedure with 3-trifluoromethylphenyl(4-methoxyphenyl)iodonium tosylate (**2p**, 2 equiv, 416 mg, 0.8 mmol) and KO^{t}Bu (2 equiv, 89.6 mg, 0.800 mmol) in toluene (4 mL) for 1 h. Purified by column chromatography (10 g SiO_2, PET/EtOAc 10:1 to 8:1), to give **3p** (161 mg, 0.39 mmol, 99%), as a colorless oil.

R_f= 0.6 (PET/EtOAc 4/1).

$[\alpha^{31}{}_D]$= -29.7 (c 1.5, $CHCl_3$).

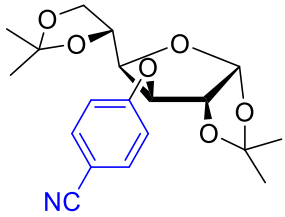
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (td, *J* = 8.3, 1.0 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.22 – 7.17 (m, 1H), 5.97 (d, *J* = 3.8 Hz, 1H), 4.79 (d, *J* = 3.0 Hz, 1H), 4.61 (d, *J* = 3.8 Hz, 1H), 4.44 (ddd, *J* = 8.2, 6.1, 5.2 Hz, 1H), 4.32 (dd, *J* = 8.1, 3.0 Hz, 1H), 4.21 – 4.08 (m, 2H), 1.58 (s, 3H), 1.46 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.76.

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 132.1 (q, *J* = 32 Hz), 130.2, 123.8(q, *J* =273 Hz), 118.7(d, *J* = 0.57 Hz), 118.5(q, *J* = 3.6 Hz), 112.9 (q, *J* = 3.8 Hz), 112.3, 109.4, 105.3, 82.3, 80.5, 80.4, 72.0, 67.3, 26.9, 26.7, 26.2, 25.2.

HRMS(ESI): calcd for [$C_{19}H_{23}F_3NaO_6^+$]: 427.1339 found: 427.1346.

I.5.2 3-O-(4-Cyanophenyl)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3q)



1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.4 mmol, 104 mg) was arylated according to the general procedure with 4-cyanophenyl(phenyl)iodonium triflate **2q,** (272 mg, 0.6 mmol, 1.5 equiv.) and KO^{t}Bu (1.5 equiv) in toluene (4 mL) for 3 h. Purified by column

chromatography (15 g SiO_2, PET/EtOAc 10:1 to 8:1), to give **3q** (112 mg, 0.310 mmol, 78%) as a colorless oil.

R_f= 0.4 (PET/EtOAc 4/1).

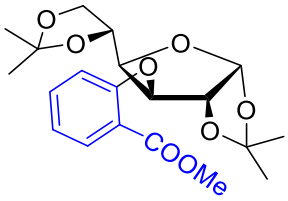
$[\alpha^{30}{}_D]$= -36.5 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.9 Hz, 2H), 7.07 (d, *J* = 8.9 Hz, 2H), 5.95 (d, *J* = 3.8 Hz, 1H), 4.79 (d, *J* = 3.1 Hz, 1H), 4.57 (d, *J* = 3.8 Hz, 1H), 4.42 (ddd, *J* = 8.2, 6.1, 5.0 Hz, 1H), 4.30 (dd, *J* = 8.2, 3.0 Hz, 1H), 4.17 – 4.08 (m, 2H), 1.57 (s, 3H), 1.44 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 134.1, 118.8, 116.1, 112.4, 109.4, 105.2, 105.2, 82.1, 80.3, 80.2, 71.9, 67.2, 26.9, 26.7, 26.2, 25.2.

HRMS(ESI): calcd for $[C_{19}H_{23}NNaO_6^+]$: 384.1418 found: 384.1427.

I.5.3 3-O-(2-Carbmethoxyphenyl)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3r)



1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (**1b**) (0.4 mmol, 104 mg) was arylated according to the general procedure with 2-carbethoxyphenyl(mesityl)iodonium triflate (**2r**, 2 equiv, 424 mg, 0.8 mmol) and KO^{t}Bu (2 equiv, 89.6 mg, 0.800 mmol) in toluene (4 mL) for 3 h **at 50 °C**. Purified by column chromatography (15 g SiO_2, PET/EtOAc 10:1 to 8:1), to give **3r** (92 mg, 0.234 mmol, 59%), as a colorless oil.

R_f= 0.4 (PET/EtOAc 3/1).

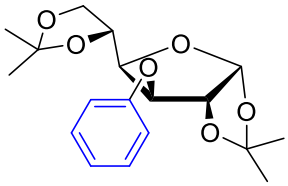
$[\alpha^{30}{}_D]$= -24.9 (c 1.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.50 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.16 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.06 (td, *J* = 7.6, 1.0 Hz, 1H), 5.99 (d, *J* = 3.8 Hz, 1H), 4.83 (d, *J* = 3.2 Hz, 1H), 4.66 (d, *J* = 3.8 Hz, 1H), 4.59 (ddd, *J* = 8.0, 6.1, 5.2 Hz, 1H), 4.33 (dd, *J* = 8.0, 3.1 Hz, 1H), 4.21 – 4.08 (m, 2H), 3.89 (s, 3H), 1.57 (s, 3H), 1.46 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 156.4, 133.4, 131.9, 121.6, 121.4, 114.7, 112.1, 109.2, 105.4, 82.2, 81.2, 80.7, 72.2, 67.3, 52.0, 26.9, 26.8, 26.3, 25.3.

HRMS(ESI): calcd. for $[C_{20}H_{26}NaO_8^+]$: 417.1520 found: 417.1522.

I.5.4 3-O-(Phenyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3s)



1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.4 mmol, 104 mg) was arylated according to the general procedure with diphenyliodonium triflate (**2s**) (2 equiv, 344 mg, 0.8 mmol) and KO^{t}Bu (2 equiv, 89.6 mg, 0.800 mmol) in toluene (4 mL) for 3 h. Purified by column chromatography (15 g SiO_2, PET/EtOAc 20:1 to 10:1), to give **3s** (76 mg, 0.226 mmol, 57%), as a white solid.

R_f= 0.25 (PET/EtOAc 10/1).

Mp.: 93-95 °C, Lit:.[21] 95-98 °C.

$[\alpha^{31}{}_D]$= -38.3 (c 1.1, $CHCl_3$), Lit[21] $[\alpha_D]$= -45.8 (c 1.7, $CHCl_3$).

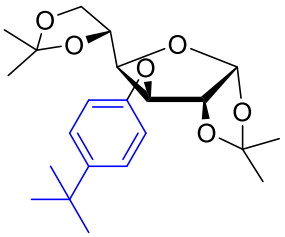
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.07 – 6.98 (m, 3H), 5.96 (d, *J* = 3.8 Hz, 1H), 4.76 (d, *J* = 3.1 Hz, 1H), 4.63 (d, *J* = 3.8 Hz, 1H), 4.51 (dt, *J* = 7.4, 5.8 Hz, 1H), 4.36 (dd, *J* = 7.4, 3.1 Hz, 1H), 4.22-4.08 (m, 2H), 1.58 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 129.7, 121.7, 115.5, 112.0, 109.1, 105.3, 82.1, 80.5, 79.8, 72.3, 67.0, 26.8, 26.7, 26.3, 25.3.

HRMS(ESI): calcd for $[C_{18}H_{24}NaO_6^+]$: 359.1465 found: 359.1461.

The analytical data correspond to the literature data.[21]

I.5.5 3-O-(4-tert-Butylphenyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3t)



1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.4 mmol, 104 mg) was arylated according to the general procedure with di(4-*tert*-butoxyphenyl)iodonium triflate (**2u**, 2 equiv, 433 mg, 0.8 mmol) and KO^{t}Bu (2 equiv, 89.6 mg, 0.800 mmol) in toluene (4 mL) for 3 h. Purified by column chromatography (15 g SiO_2, PET/EtOAc 100:0 to 20:1), to give **3u** (108 mg, 0.276 mmol, 69%) as a colorless oil.

R_f= 0.75 (PET/EtOAc 4/1).

$[\alpha^{30}{}_D]$= -22.5 (c 1.1, $CHCl_3$).

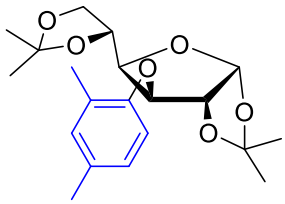
[21] D. H. R. Barton, J.-P. Finet, W. B. Motherwell, C. Pichon, *J. Chem, Soc., Perkin Trans. 1* **1987**, 251-259.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 5.95 (d, *J* = 3.8 Hz, 1H), 4.74 (d, *J* = 3.2 Hz, 1H), 4.64 (d, *J* = 3.9 Hz, 1H), 4.50 (dt, *J* = 7.4, 5.9 Hz, 1H), 4.36 (dd, *J* = 7.4, 3.1 Hz, 1H), 4.21 – 4.09 (m, 2H), 1.58 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.34 – 1.32 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 144.5, 126.5, 114.9, 112.0, 109.1, 105.3, 82.1, 80.5, 79.7, 72.3, 67.0, 34.1, 31.5, 26.8, 26.7, 26.3, 25.3.

HRMS(ESI): calcd for [$C_{22}H_{32}NaO_6^+$]: 415.2091 found: 415.2091.

I.5.6 3-O-(1,4-Dimethylphenyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3u)



1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.4 mmol, 104 mg) was arylated according to the general procedure with (2,4-dimethylphenyl)(4-methoxyphenyl)iodonium tosylate (**2uu**, 2 equiv, 388 mg, 0.8 mmol) and KO^{t}Bu (2 equiv, 89.6 mg, 0.800 mmol) in toluene (4 mL) for 2 h. Purified by column chromatography (20 g SiO_2, PET/EtOAc 40:1 to 15:1), to give **3u** (110 mg, 0.305 mmol, 76%) as a colorless oil.

*Product **3u** can also be obtained by arylation with the symmetric xylyliodonium salt **3u**. The synthesis of salt **3u** from xylene and iodine gives a minor amount of the 2,6-regioisomer as a byproduct, see section I.2.8. The arylation proceeded smoothly, but provided **3u**.together with minor amounts of the corresponding 2,6-dimethylphenylated product. To obtain this salt in a pure form, it should be prepared from 1-iodo-2,4-dimethylbenzene and 1,3-dimethylbenzene instead.*

1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.4 mmol, 104 mg) was arylated according to the general procedure with di(2,4-dimethylphenyl)iodonium triflate (**2u**, 2 equiv, 388 mg, 0.8 mmol, contains 5-8% regioisomer) and KO^{t}Bu (2 equiv, 89.6 mg, 0.800 mmol) in toluene (4 mL) for 30 minutes. Purified by column chromatography (15 g SiO_2, PET/EtOAc 20:1 to 15:1), to give **3u** (144 mg, 90% in 10:1 ratio with 2,6-dimethylphenylated product) as a yellow oil.

R_f= 0.85 (PET/EtOAc 4/1).

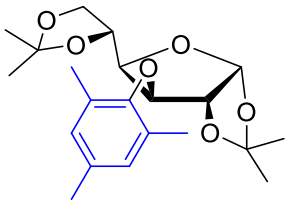
[$\alpha^{29}{}_D$]= -37.1 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 – 6.95 (m, 2H), 6.87 (d, *J* = 8.8 Hz, 1H), 5.93 (d, *J* = 3.8 Hz, 1H), 4.71 (d, *J* = 3.2 Hz, 1H), 4.59 (d, *J* = 3.8 Hz, 1H), 4.52 (dt, *J* = 7.5, 5.8 Hz, 1H), 4.35 (dd, *J* = 7.4, 3.2 Hz, 1H), 4.20 – 4.09 (m, 2H), 2.27 (s, 3H), 2.18 (s, 3H), 1.56 (s, 3H), 1.44 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 131.9, 130.6, 127.3, 127.1, 112.0, 111.9, 109.1, 105.3, 82.2, 80.8, 79.9, 72.5, 67.2, 26.8, 26.8, 26.2, 25.2, 20.4, 16.3.

HRMS(ESI): calcd for [$C_{20}H_{28}NaO_6^+$]: 387.1778 found: 387.1783.

I.5.7 3-O-(Mesityl)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3v)



1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.4 mmol, 104 mg) was arylated according to the general procedure with dimesityliodonium triflate (**2v**)(2 equiv, 414 mg, 0.8 mmol) and KO^{t}Bu (2 equiv, 89.6 mg, 0.800 mmol) in toluene (4 mL) for 3 h. Purified by column chromatography (15 g SiO_2, PET/EtOAc 20:1 to 10:1), to give **3v** (124 mg, 0.328 mmol, 84%), as white crystals.

Mp: 97-100 °C.

R_f= 0.3 (PET/EtOAc 10/1).

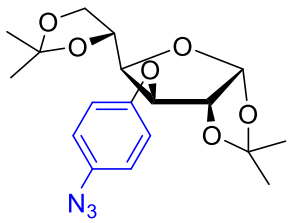
$[\alpha^{30}{}_D]$= -5.8 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 6.02 (d, *J* = 3.7 Hz, 1H), 4.63 – 4.56 (m, 2H), 4.43 (d, *J* = 3.6 Hz, 1H), 4.29 (dd, *J* = 7.4, 3.1 Hz, 1H), 4.19 – 4.08 (m, 2H), 2.24 (s, 3H), 2.23 (s, 6H), 1.49 (s, 3H), 1.48 (s, 3H), 1.38 (s, 3H), 1.24 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 133.4, 130.4, 129.9, 111.7, 109.0, 105.4, 82.5, 81.3, 81.1, 72.5, 67.3, 26.9, 26.8, 26.2, 25.4, 20.6, 16.7.

HRMS(ESI): calcd. for $[C_{21}H_{30}NaO_6^+]$: 401.1935 found: 401.1952.

I.5.8 3-O-(4-Azidophenyl)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3w)

This product has been obtained using two different salts (**2w** and **2ww**). The synthesis of salt **2x** is considerably more efficient, and we have hence reported the arylation yield with that salt in the article even though the arylation yield with salt **2ww** is higher yielding.



1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.2 mmol, 52 mg) was arylated according to the general procedure with 4-azidophenyl(4-methoxyphenyl)iodonium tosylate (**2w**, 2 equiv 209 mg, 0.4 mmol) and KO^{t}Bu (2 equiv, 44.8 mg, 0.400 mmol) in toluene (2 mL) for 4 h. Purified by column chromatography (10 g SiO_2, PET/EtOAc/TEA 10:1:1), to give **3w** (36 mg, 0.095 mmol, 46%) as a yellow oil.

Product **3w** can also be obtained using 4-azidophenyl(2,4,6-trimethoxyphenyl)iodonium tosylate (**2ww**, 175 mg, 0.3 mmol, 1.5 equiv) and KO^{t}Bu (33 mg, 0.30 mmol, 1.5 equiv). in toluene (2 mL) for 4 h. Purified by column chromatography (10 g SiO_2, PET/EtOAc/TEA 20:1:1), to give **3w** (42 mg, 0.11 mmol, 56%) as a yellow oil.

R_f= 0.65 (PET/EtOAc 4/1).

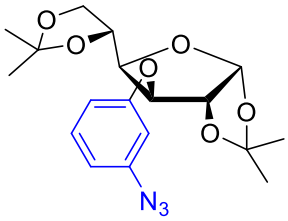
$[\alpha^{29}{}_D]$= -33.3 (c 0.4, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (app. s, 4H), 5.95 (d, *J* = 3.8 Hz, 1H), 4.69 (d, *J* = 3.1 Hz, 1H), 4.59 (d, *J* = 3.8 Hz, 1H), 4.47 (ddd, *J* = 7.8, 6.1, 5.3 Hz, 1H), 4.32 (dd, *J* = 7.7, 3.1 Hz, 1H), 4.19 – 4.09 (m, 2H), 1.57 (s, 3H), 1.46 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 133.6, 120.2, 117.0, 112.1, 109.2, 105.2, 82.1, 80.5, 80.5, 72.2, 67.1, 26.9, 26.7, 26.2, 25.3.

HRMS(ESI): calcd for $[C_{22}H_{32}NaO_6^+]$: 400.1479 found: 400.1488.

I.5.9 3-O-(3-Azidophenyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3x)



1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.2 mmol, 52 mg) was arylated according to the general procedure with 3-azidophenyl(4-methoxyphenyl)iodonium tosylate (**2x**, 2 equiv, 209 mg, 0.4 mmol) and KO^{t}Bu (2 equiv, 44.8 mg, 0.400 mmol) in toluene (2 mL) for 30 min. Purified by column chromatography (15 g SiO_2, PET/EtOAc/ 20:1:1), to give **3x** (42 mg, 0.11 mmol, 56%) as a yellow oil.

R_f= 0.6 (PET/EtOAc 4/1).

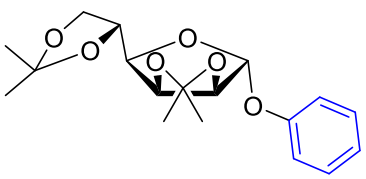
$[\alpha^{30}{}_D]$= -27.3 (c 0.7, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 1H), 6.80 (ddd, *J* = 8.3, 2.4, 0.8 Hz, 1H), 6.72 (ddd, *J* = 8.0, 2.1, 0.8 Hz, 1H), 6.69 (t, *J* = 2.2 Hz, 1H), 5.95 (d, *J* = 3.8 Hz, 1H), 4.73 (d, *J* = 3.0 Hz, 1H), 4.60 (d, *J* = 3.8 Hz, 1H), 4.45 (ddd, *J* = 7.9, 6.1, 5.3 Hz, 1H), 4.31 (dd, *J* = 7.9, 3.0 Hz, 1H), 4.19 – 4.09 (m, 2H), 1.57 (s, 3H), 1.46 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 141.6, 130.7, 112.4, 112.2, 111.9, 109.3, 106.9, 105.2, 82.2, 80.4, 80.2, 72.1, 67.1, 26.9, 26.7, 26.2, 25.3.

HRMS(ESI): calcd for $[C_{22}H_{32}NaO_6^+]$: 400.1479 found: 400.1489.

I.5.10 Phenyl-2,3:5,6-Di-O-isopropylidene-α-D-mannofuranoside (3y)



2,3:5,6-Di-*O*-isopropylidene-α-D-mannofuranose (**1a**) (0.4 mmol, 104 mg) was arylated according to the general procedure with diphenyliodonium triflate (**2s**, 2 equiv, 344 mg, 0.8 mmol) and KO^{t}Bu (2 equiv, 89.6 mg, 0.800 mmol) in toluene (4 mL) for 4 h. Purified by column chromatography (15 g SiO_2, PET/EtOAc 10:1), to give **3y** (27 mg, 20%), as a yellowish oil.

R_f= 0.5 (PET/EtOAc 10/1).

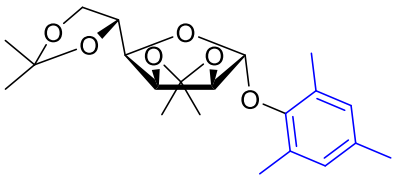
$[\alpha^{30}{}_D]$= +101.0 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.07 – 7.01 (m, 3H), 5.66 (s, 1H), 4.97 – 4.85 (m, 2H), 4.45 (ddd, *J* = 8.0, 6.2, 4.2 Hz, 1H), 4.16 – 4.07 (m, 2H), 4.01 (dd, *J* = 8.8, 4.3 Hz, 1H), 1.54 (s, 3H), 1.46 (s, 3H), 1.40 (s, 3H), 1.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 129.5, 122.2, 116.6, 113.0, 109.4, 104.9, 85.5, 81.1, 79.6, 73.0, 66.9, 26.9, 26.0, 25.2, 24.6.

HRMS(ESI): calcd for $[C_{18}H_{24}NaO_6^+]$: 359.1465 found: 359.1466.

I.5.11 Mesityl-2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside (3z)



2,3:5,6-Di-*O*-isopropylidene-α-D-mannofuranose (**1a**) (0.4 mmol, 104 mg) was arylated according to the general procedure with dimesityliodonium triflate (**2v**, 2 equiv, 414 mg, 0.8 mmol) and KO^{t}Bu (2 equiv, 89.6 mg, 0.800 mmol) in toluene (4 mL) for 4 h. Purified by column chromatography (15 g SiO_2, PET/EtOAc 10:1), to give **3z** (72 mg, 0.191 mmol, 47%), as colorless oil.

R_f = 0.7 (hex/EtOAc 4/1).

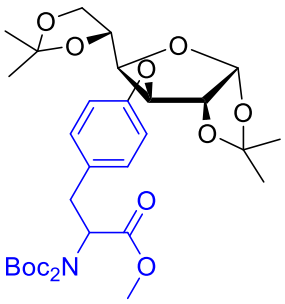
$[\alpha^{31}{}_D]$= +111.0 (c 1.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 2H), 5.23 (s, 1H), 5.04 – 4.94 (m, 2H), 4.48 – 4.37 (m, 2H), 4.14 – 4.04 (m, 2H), 2.27 (s, 6H), 2.26 (s, 3H), 1.49 (s, 3H), 1.48 (s, 3H), 1.42 (s, 3H), 1.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 133.7, 130.4, 129.5, 113.0, 110.0, 109.2, 85.9, 81.3, 79.7, 73.3, 66.6, 26.9, 26.0, 25.3, 24.8, 20.6, 17.2.

HRMS(ESI): calcd for $[C_{21}H_{30}NaO_6^+]$: 401.1935 found: 401.1938.

I.5.12 3-O-(N-Boc$_2$-COOMe-L-phenylalanyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3aa)



1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.04 mmol, 10.4 mg) was arylated according to the general procedure with N-Boc$_2$-COOMe-L-phenylalanyl(4-methoxyphenyl)iodonium triflate (**2b**, 2 equiv, 60.9 mg, 0.08 mmol) and KO^{t}Bu (2 equiv, 8.9 mg, 0.08 mmol) in toluene (0.4 mL) for 4 h. Purified by column chromatography (10 g SiO_2, PET/EtOAc 10:1 to 5:1), to give **3aa** (10.2 mg, 0.016 mmol, 40%) as a colorless oil. Starting glucofuranose (5.2 mg, 50%) was recovered.

R_f= 0.7 (PET/EtOAc 4/1).

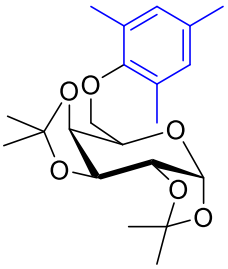
$[\alpha^{30}{}_D]$= -61.4 (c 0.9, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.90 (d, *J* = 3.8 Hz, 1H), 5.09 (dd, *J* = 10.1, 5.1 Hz, 1H), 4.66 (d, *J* = 3.1 Hz, 1H), 4.54 (d, *J* = 3.8 Hz, 1H), 4.44 (dt, *J* = 7.5, 5.8 Hz, 1H), 4.30 (dd, *J* = 7.5, 3.1 Hz, 1H), 4.18-4.05 (m, 2H), 3.74 (s, 3H), 3.38 (dd, *J* = 14.1, 5.1 Hz, 1H), 3.14 (dd, *J* = 14.2, 10.1 Hz, 1H), 1.54 (s, 3H), 1.42 (s, 3H), 1.41 (s, 18H), 1.31 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 155.7, 151.7, 130.9, 130.8, 115.4, 112.1, 109.1, 105.3, 83.0, 82.1, 80.5, 79.8, 72.3, 67.0, 59.5, 52.3, 35.4, 27.9, 26.8, 26.7, 26.2, 25.3.

HRMS(ESI): calcd. [$C_{32}H_{47}NO_{12}Na^+$] calcd: 660.2990, found: 660.3002.

I.5.13 6-O-(Mesityl)- 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (3ab)



1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranose (0.2 mmol, 52 mg) was arylated according to the general procedure with dimesityliodonium triflate (**2v**, 1.1 equiv, 113 mg, 0.22 mmol) and KO^{t}Bu (1.5 equiv, 33 mg, 0.300 mmol) in toluene (1 mL) for 3 hours. Purified by column chromatography (15 g SiO_2, PET/EtOAc/ 20:1:1), to give **3ab** (46 mg, 0.12 mmol, 61%), as a colorless oil.

R_f= 0.65 (PET/EtOAc 4/1).

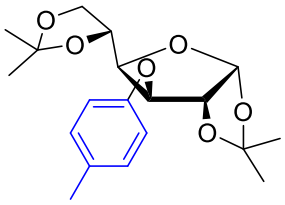
$[\alpha^{31}{}_D]$= -79.5 (c 0.7, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 2H), 5.58 (d, *J* = 5.0 Hz, 1H), 4.65 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.42 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.35 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.19 (td, *J* = 6.3, 1.9 Hz, 1H), 4.04 (dd, *J* = 9.7, 6.0 Hz, 1H), 3.88 (dd, *J* = 9.7, 6.5 Hz, 1H), 2.27 (s, 6H), 2.23 (s, 3H), 1.57 (s, 3H), 1.46 (s, 3H), 1.36 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 132.9, 130.5, 129.3, 109.3, 108.6, 96.4, 71.1, 70.9, 70.7, 67.0, 26.1, 26.0, 25.0, 24.5, 20.6, 16.3.

HRMS(ESI): calcd. $[C_{21}H_{30}O_6Na^+]$ calcd: 401.1935, found: 401.1937.

I.5.14 3-O-(4-Tolyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3ac)



1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (**1b**) (0.4 mmol, 104 mg) was arylated according to the general procedure with di(4-tolyl)iodonium triflate (**2t**, 2 equiv, 366 mg, 0.8 mmol) and KO^{t}Bu (2 equiv, 89.6 mg, 0.800 mmol) in toluene (4 mL) for 3 h. Purified by column chromatography (15 g SiO_2, PET/EtOAc 20:1 to 10:1), to give **3ac** (126 mg, including about 10% inseparable impurity, 0.324 mmol, 81%), as a yellow oil.

R_f= 0.7 (PET/EtOAc 4/1).

$[\alpha^{29}{}_D]$= -27.4 (c 1.5, $CHCl_3$).

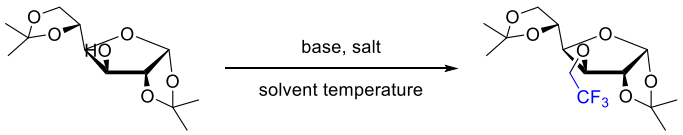
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 5.95 (d, *J* = 3.8 Hz, 1H), 4.72 (d, *J* = 3.1 Hz, 1H), 4.63 (d, *J* = 3.8 Hz, 1H), 4.51 (dt, *J* = 7.4, 5.8 Hz, 1H), 4.36 (dd, *J* = 7.3, 3.1 Hz, 1H), 4.18 (dd, *J* = 2.2 Hz, 1H), 4.16(d, *J* = 2.2 Hz, 1H), 2.32 (s, 3H), 1.58 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 131.1, 130.2, 115.2, 112.0, 109.2, 105.2, 81.9, 80.3, 79.6, 72.3, 66.9, 26.9, 26.7, 26.2, 25.3, 20.6.

HRMS(ESI): calcd for $[C_{19}H_{26}NaO_6]$: 373.1622 found: 373.1628.

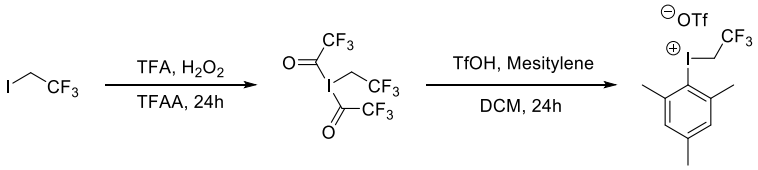
I.6 *O*-Trifluoroethylation of carbohydrates

I.6.1 Optimization data for the trifluoroethylation



base (equiv)	salt (equiv)	solvent	temperature	isolated yield (%)
2 equiv $NHCO_3$	2	toluene	RT	-
-	2	toluene	RT	-
2 equiv DTBPy	2	toluene	RT	-
2 equiv Cs_2CO_3	2	DCM	RT	traces
2 equiv.TMG	2	toluene	RT	The TMG got alkylated
1.25 equiv.NaH	2	toluene	RT	35
2 equiv KOtBu	2	toluene	RT(30 min)	~60, with inseparable impurity
2 equiv KOtBu	2	DCM	RT	45 with many other products
1.1 equiv KOtBu	1.5	toluene	RT	traces
2 equiv LiOtBu	2	toluene	RT	28
2 equiv NaOtBu	2	toluene	RT	41
2 equiv NaOtBu	2	DCM	RT	42
2 equiv NaOtBu	2	toluene	0 °C	63
2 equiv NaOtBu	2	DCM	0 °C	78

I.6.2 2,2,2-Trifluoroethyl(mesityl)iodonium triflate (5)



Synthesized according to a known procedure.[22] Into a 50 mL round-bottom flask 2,2,2-trifluoroacetic anhydride (18 mL, 210 mmol) and trifluoroacetic acid (153 µL, 2 mmol, 10 mol%) were added and the mixture was cooled to 0 °C. Then H_2O_2 (8 mL, 50% aqueous solution, 118 mmol) was added dropwise and the mixture was stirred for 5 minutes. 2,2,2-Trifluoroiodoethane (2 mL, 20 mmol) was added, then the reaction was allowed to warm up to room temperature and it was stirred for 20 hours. The volatiles were evaporated under reduced pressure and white oil was obtained, which crystallized upon storage at 4°C to give (2,2,2-trifluoroethyl)-λ^3-iodanediyl bis(2,2,2-trifluoroacetate) as a white solid in quantitative yield that was used without further purification.

In a 100 mL round-bottom flask the λ^3-iodane (3.92 g, 9 mmol) was dissolved in DCM (15 mL), then the solution was cooled to 0 °C and mesitylene (1.94 mL, 14 mmol) was added. Then TfOH (1.6 mL, 18 mmol) was added dropwise. The reaction mixture turned into a dark red solution and it was kept at 0 °C for 24 hours. The solvent was evaporated under reduced

[22] G. L. Tolnai, A. Szekely, Z. Mako, T. Gati, J. Daru, T. Bihari, A. Stirling, Z. Novak, *Chem. Commun.* **2015**, *51*, 4488-4491.

pressure, then Et_2O (30 mL) was added. White crystals precipitated from the mixture. The product was filtered off and washed with Et_2O and a white solid was obtained. This was recrystallized by precipitation by Et_2O from concentrated MeOH solution to give 5 (3.1g, 72%) as a white solid.

Mp 112-114 °C (Lit:[22] 114 °C).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.04 – 6.91 (m, 2H), 5.01 (q, J = 8.7 Hz, 2H), 2.36 (s, 6H), 2.20 (s, 3H).

^{19}F NMR (377 MHz, DMSO-d_6) δ -73.01 (t, J = 8.8 Hz), -77.77.

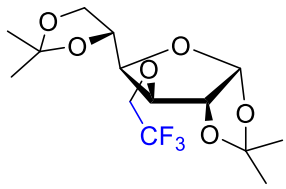
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 137.1, 128.1 (q, J = 320 Hz), 121.0, 104.2, 69.4 (q, J = 34 Hz), 29.0, 20.2.

Data correspond to the reported values.[22]

I.6.3 General procedure for the O trifluoroethylation of carbohydrates

The starting carbohydrate derivative **1** (0.2 mmol) was stirred in a 20 mL screw-cap vial in DCM (2 mL) at 0 °C. NaO^{t}Bu (0.4 mmol, 38 mg, 2 equiv) was added, then iodonium salt **5** (191 mg, 0.4 mmol, 2 equiv) was added under air during 1 min. The reaction mixture was stirred for 2-5 h at 0 °C, after which the whole reaction mixture was transferred to a round bottom flask by EtOAc and evaporated onto Celite. Column chromatography afforded the purified product.

I.6.4 3-O-(2,2,2-Trifluoroethyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (6a)



1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.2 mmol, 52 mg) was trifluoroethylated according to the general procedure for 4 h. Purified by column chromatography (10 g SiO_2, PET/EtOAc 20:1 to 10:1) to give **6a** (53 mg, 0.155 mmol, 78%), as a colorless oil.

R_f = 0.65 (PET/EtOAc 4/1).

$[\alpha^{31}{}_D]$= -10.7 (c 0.8, $CHCl_3$).

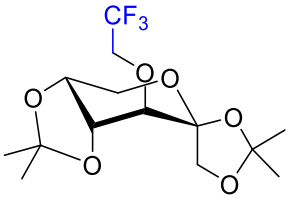
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (d, J = 3.7 Hz, 1H), 4.59 (d, J = 3.6 Hz, 1H), 4.26 (ddd, J = 8.3, 6.1, 5.4 Hz, 1H), 4.17 – 3.94 (m, 6H), 1.51 (s, 3H), 1.44 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 123.7 (q, J=277 Hz), 112.1, 109.2, 105.3, 84.3, 83.1, 81.1, 72.3, 68.4 (q, J=34 Hz), 67.5, 26.8, 26.8, 26.2, 25.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -74.71 (t, J = 8.5 Hz).

HRMS(ESI): calcd[$C_{14}H_{21}F_3NaO_6^+$] calcd: 365.1182, found: 365.1185.

I.6.5 3-O-(2,2,2-Trifluoroethy)-1,2:4,5-Di-O-isopropylidene-β-D-fructopyranose (6b)



1,2:4,5-Di-*O*-isopropylidene-β-D-fructopyranose (52 mg, 0.200 mmol) was trifluoroethylated according to the general procedure for 5 h. Purified by column chromatography (10 g SiO_2, PET/EtOAc 20:1 to 10:1), to give **6b** (33 mg, 0.096 mmol, 48%) as a colorless oil. 18 mg (34%) of starting fructopyranose was recovered from the column.

R_f = 0.8 (PET/EtOAc 4/1).

$[\alpha^{31}{}_D]$= -95.6 (c 0.7, $CHCl_3$).

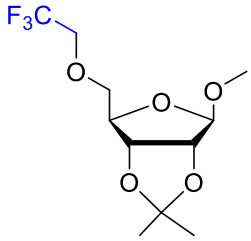
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (dd, *J* = 7.3, 5.6 Hz, 1H), 4.27 – 3.99 (m, 6H), 3.96 (d, *J* = 8.6 Hz, 1H), 3.55 (d, *J* = 7.3 Hz, 1H), 1.54 (s, 3H), 1.50 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 123.9 (q, *J* = 279 Hz), 112.5, 109.4, 103.7, 77.9, 73.8, 71.4, 67.8 (q, *J* = 34 Hz), 60.1, 28.1, 27.0, 26.1, 25.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -74.65 (t, *J* = 8.6 Hz).

HRMS(ESI): calcd. [$C_{14}H_{21}F_3NaO_6^+$] calcd: 365.1182, found: 365.1184.

I.6.6 5-O-(2,2,2-Trifluoroethyl)-1-O-Methyl-2,3-O-isopropylidene-α-D-riboside (6c)



Starting from 1-*O*-Methyl-2,3-*O*-isopropylidene-α-D-riboside (41 mg, 0.40 mmol) was trifluoroethylated according to the general procedure for 4 h. Purified by column chromatography (10 g SiO_2, PET/EtOAc 20:1 to 10:1), to give **6d** (41 mg, 0.143 mmol, 72%) as a colorless oil.

R_f = 0.75 (PET/EtOAc 4/1).

$[\alpha^{30}{}_D]$= -60,4 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.99 (s, 1H), 4.68 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.60 (d, *J* = 6.0 Hz, 1H), 4.35 (ddd, *J* = 7.6, 6.4, 1.1 Hz, 1H), 3.89 (qd, *J* = 8.7, 0.7 Hz, 2H), 3.66 (qd, *J* = 9.7, 7.1 Hz, 2H), 3.34 (s, 3H), 1.53 – 1.48 (m, 3H), 1.34 (d, *J* = 0.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 123.9 (q, *J* = 279 Hz), 112.6, 109.4, 85.1, 84.7, 81.8, 73.4, 68.7 (q, *J* = 33 Hz), 54.9, 26.4, 25.0.

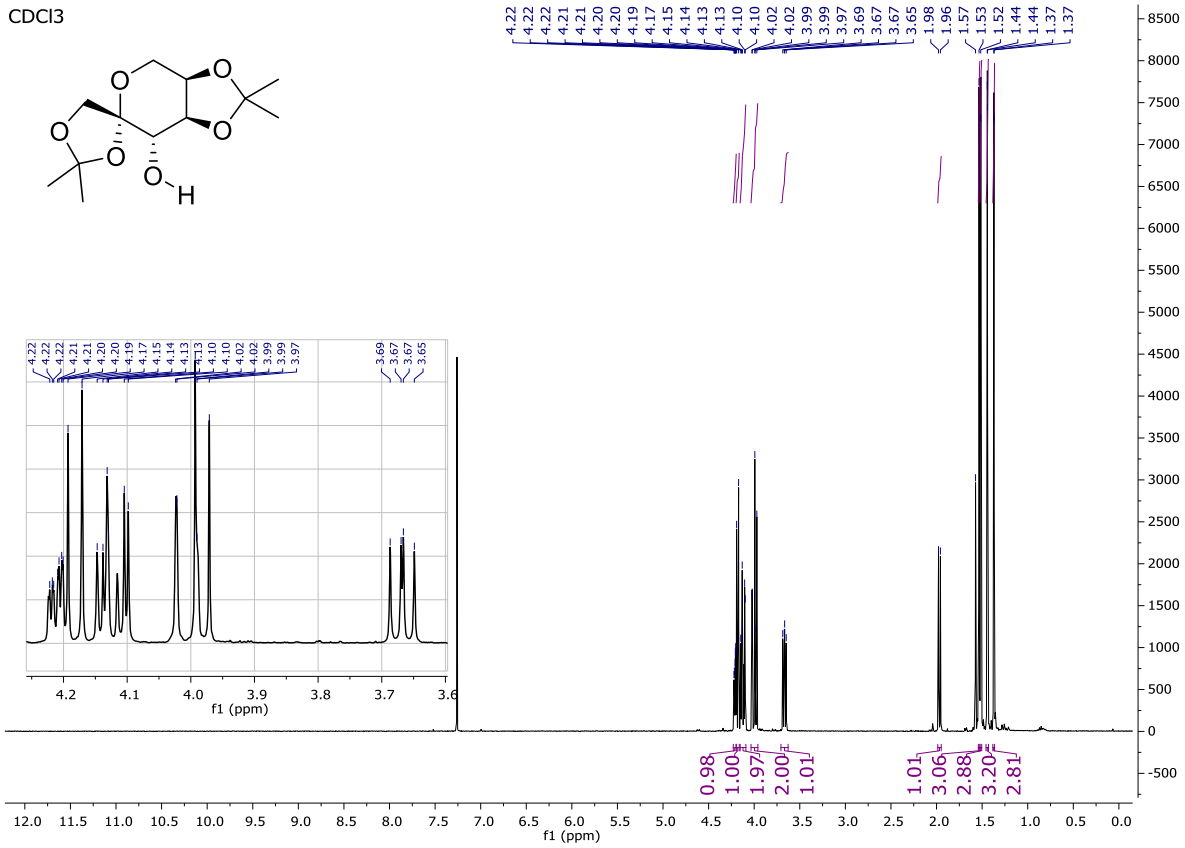
^{19}F NMR (377 MHz, $CDCl_3$) δ -74.13 (t, *J* = 8.7 Hz).

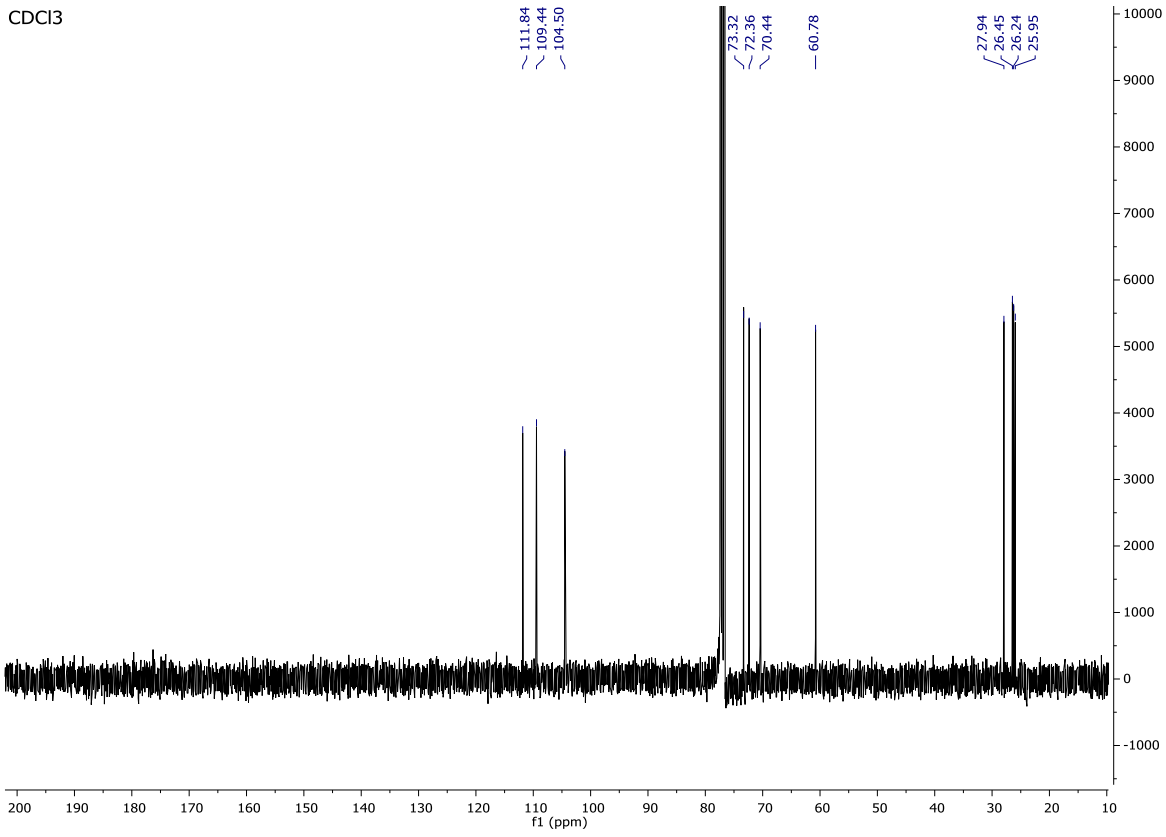
HRMS(ESI): calcd. [$C_{11}H_{17}F_3NaO_5^+$] calcd: 309.0920, found: 309.0919.

II. Spectra

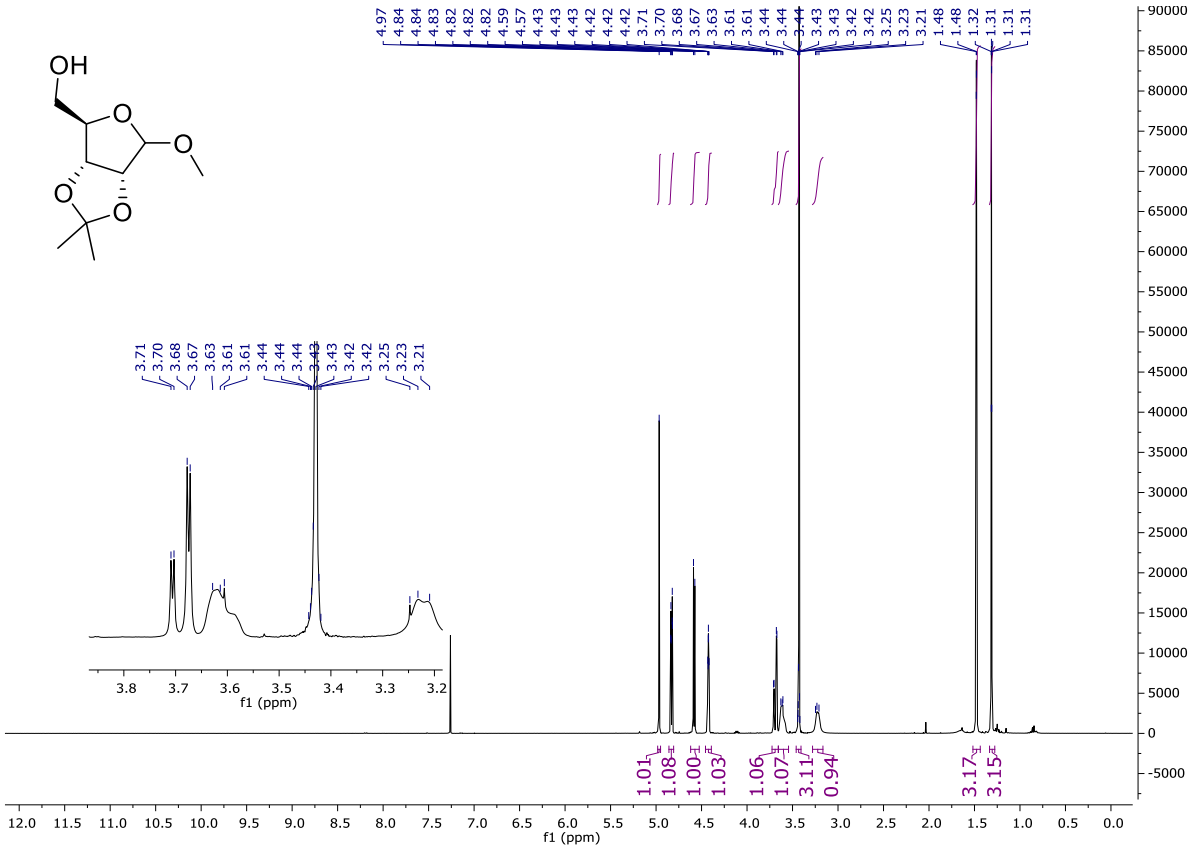
II. Spectra

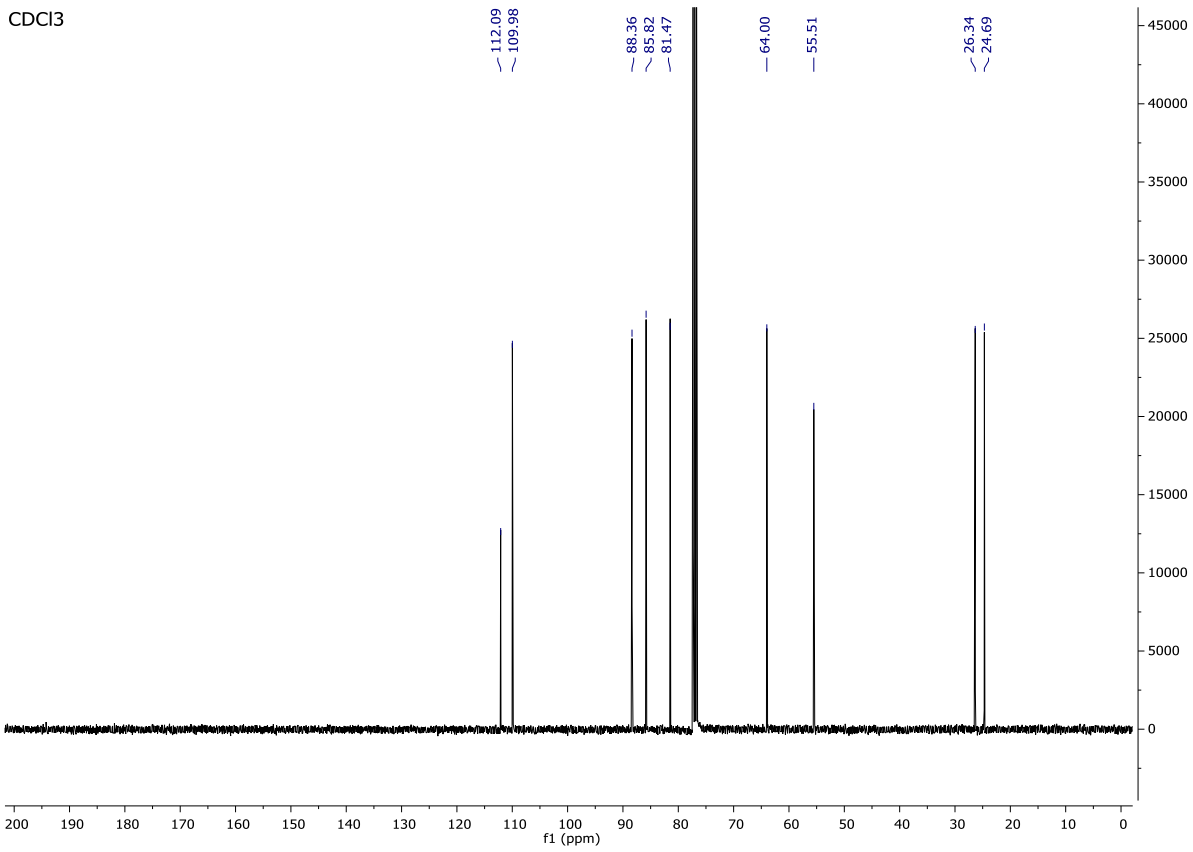
II.1.1 1,2:4,5-Di-O-isopropylidene-β-D-fructopyranose (1d)





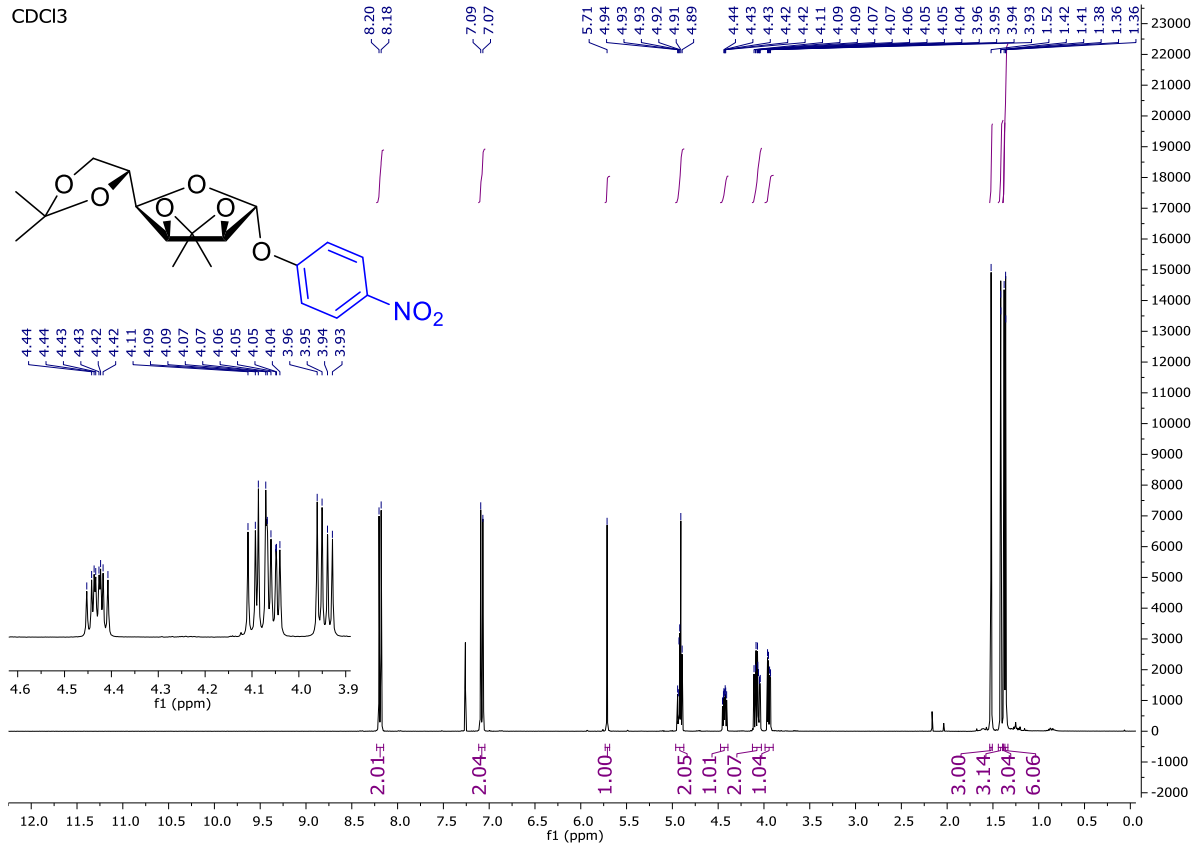
II.1.2 1-O-Methyl-2,3-O-isopropylidene-α-D-riboside (1g)

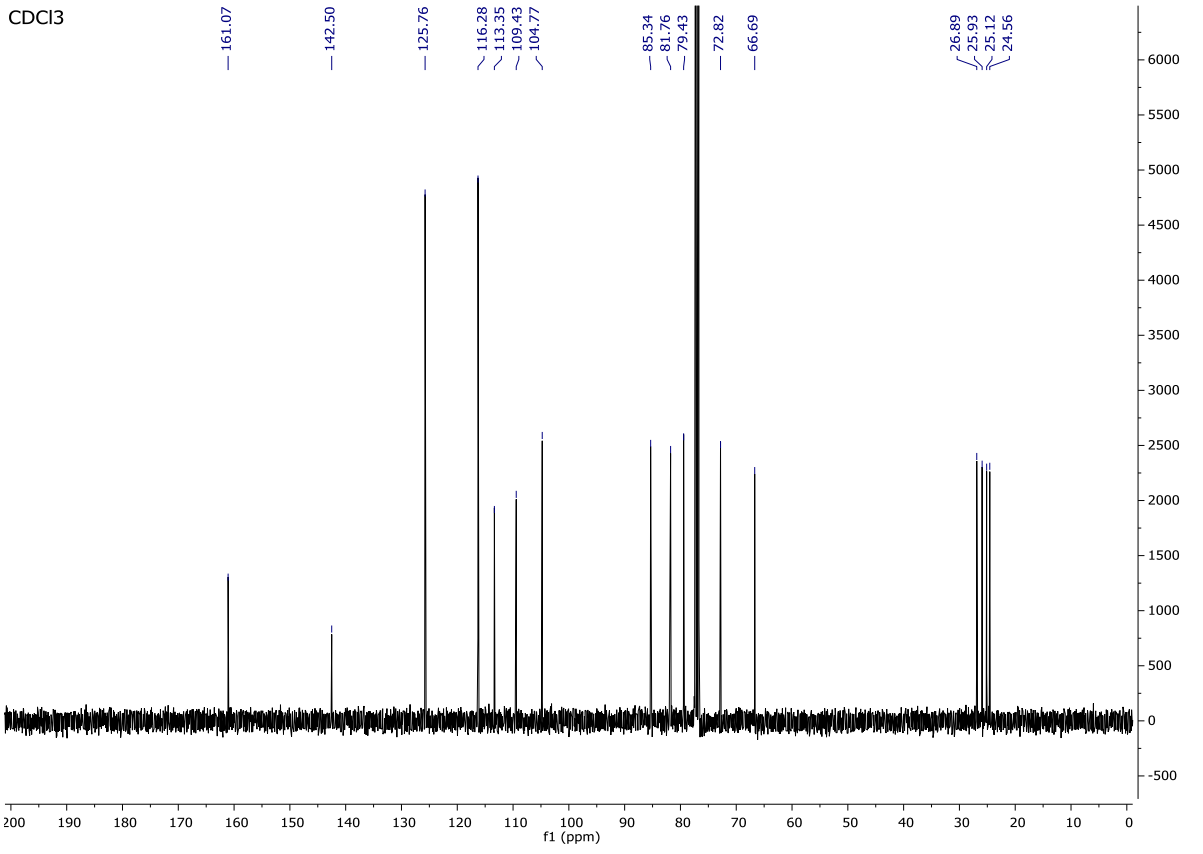




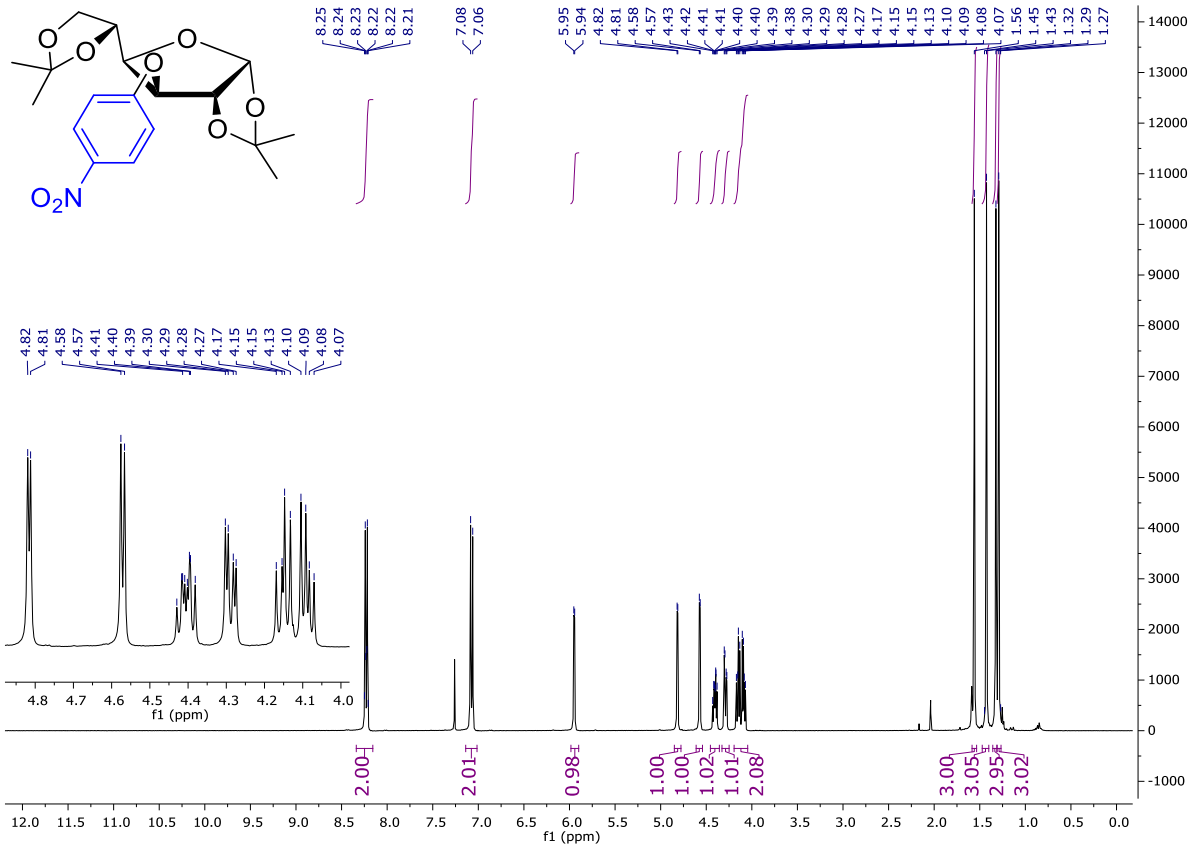
II.2 Nitroaryl spectra

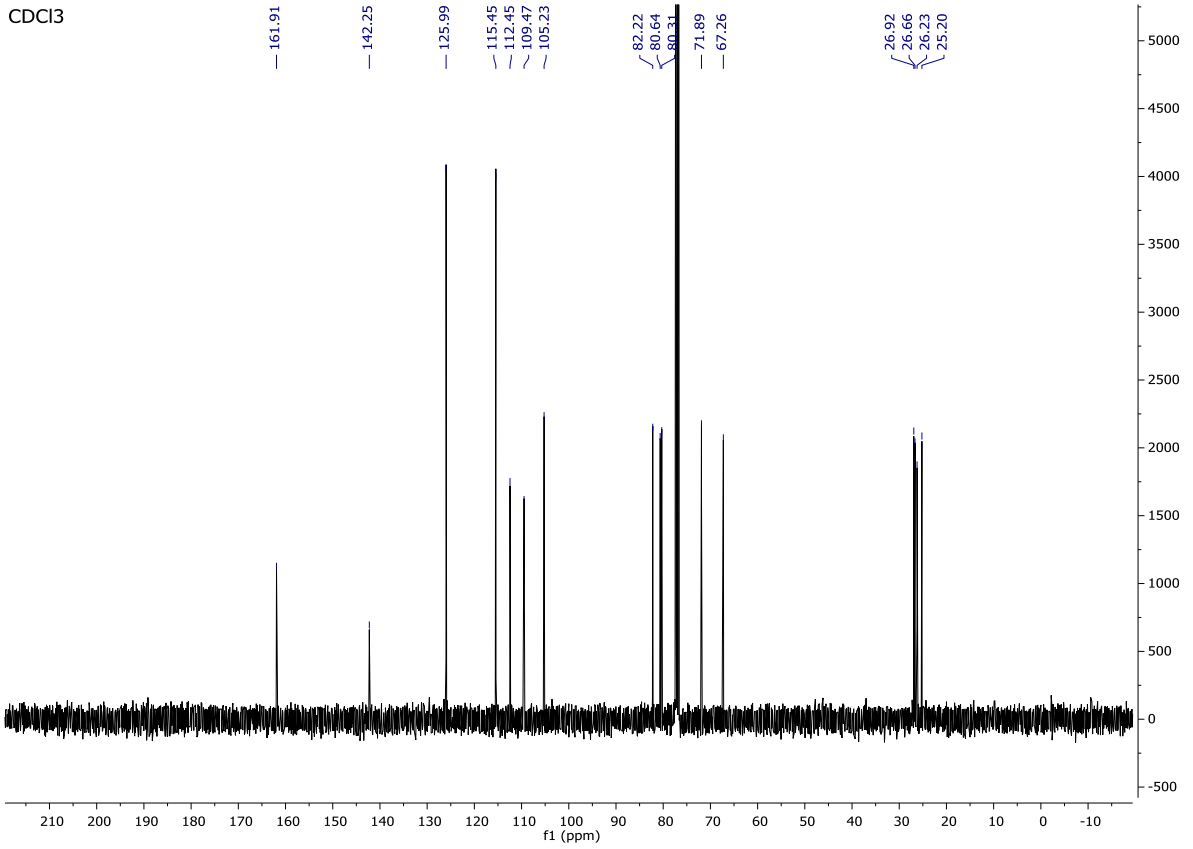
II.2.1 (4-Nitrophenyl)-2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside (3a)



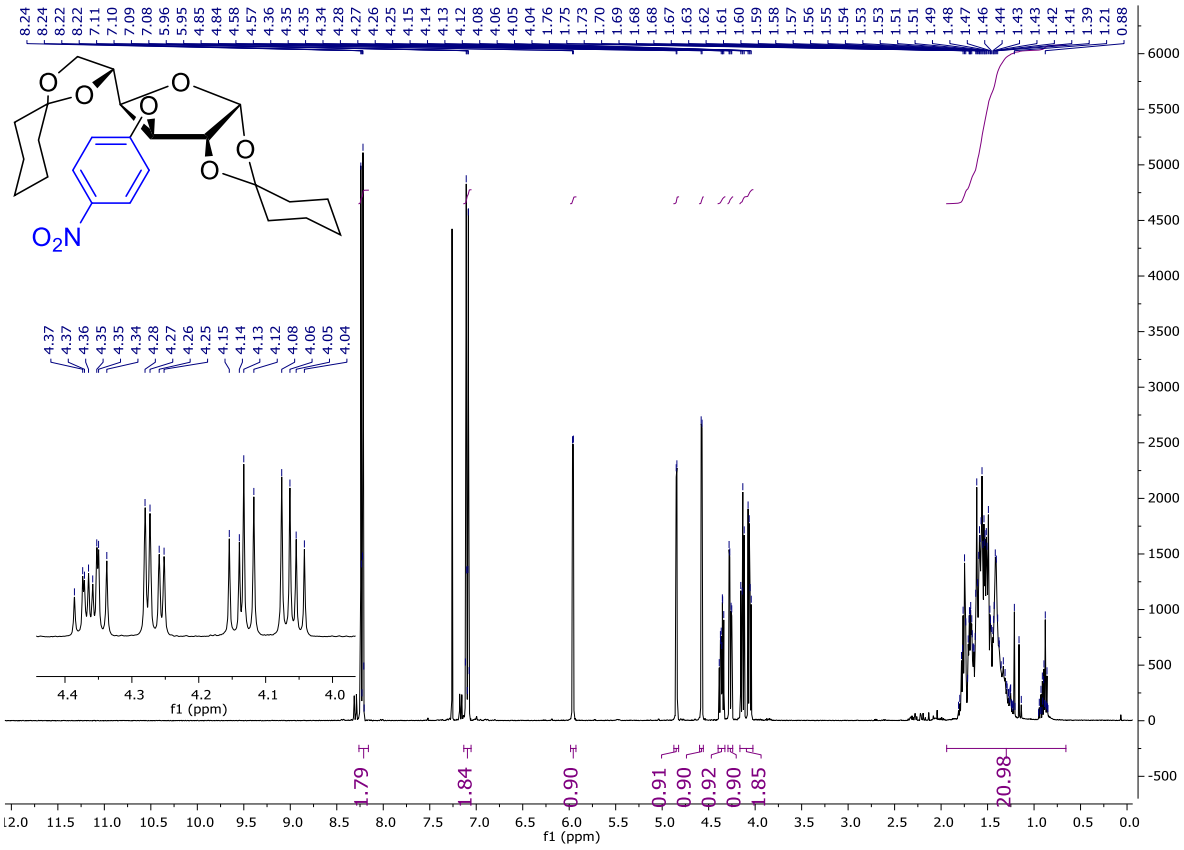


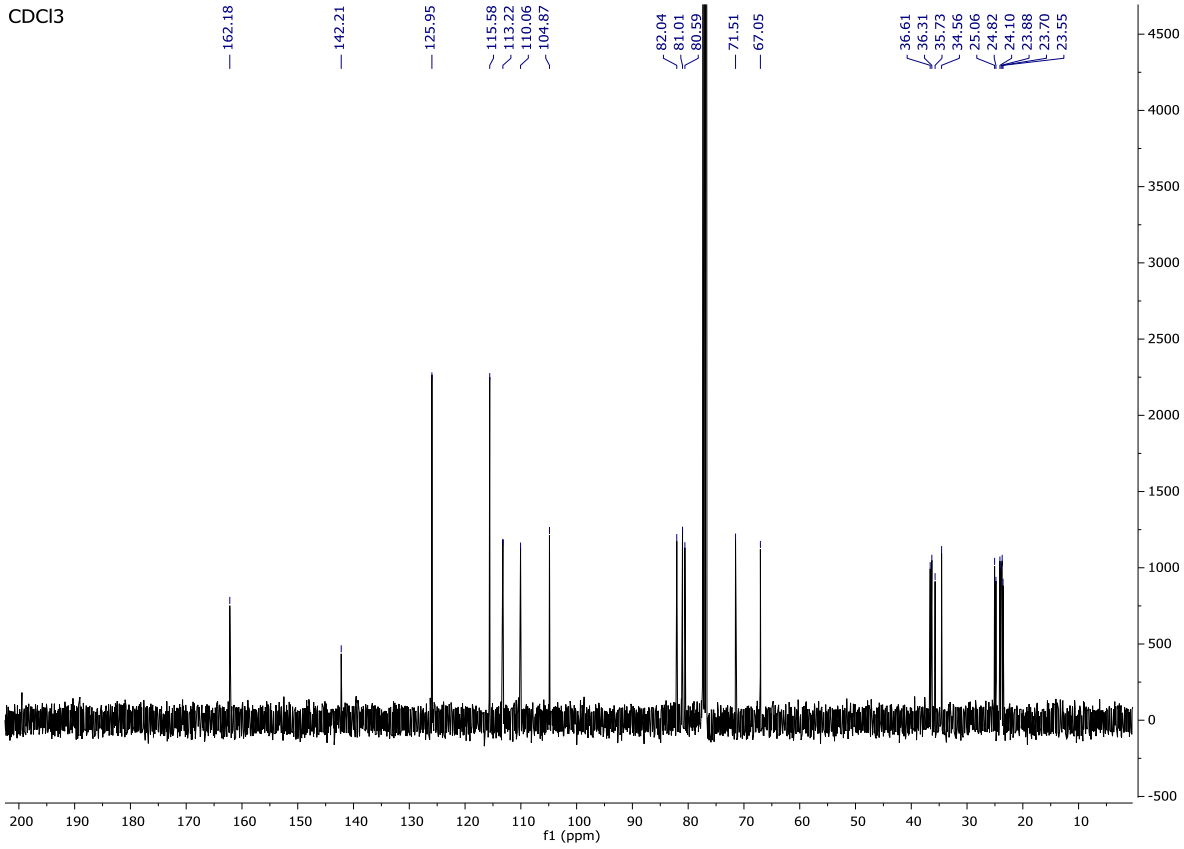
II.2.2 3-O-(4-nitrophenyl)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3b)



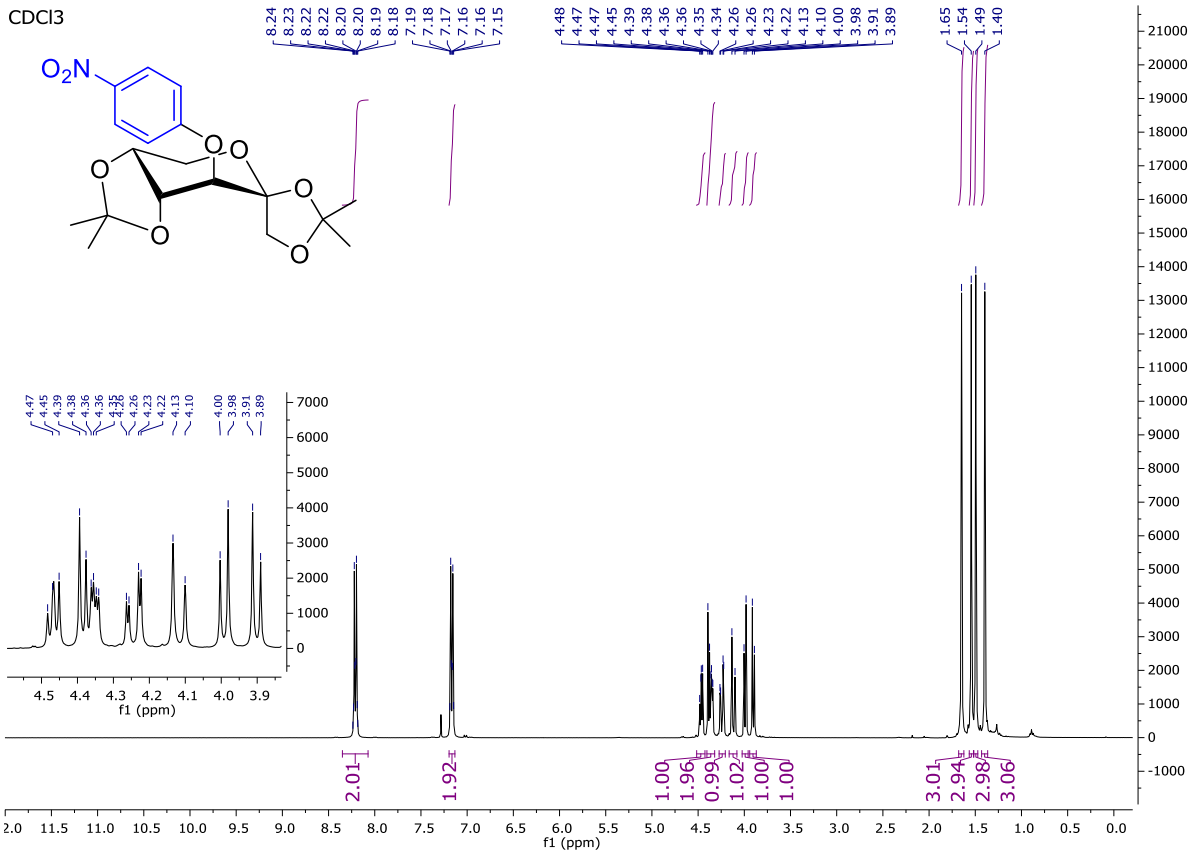


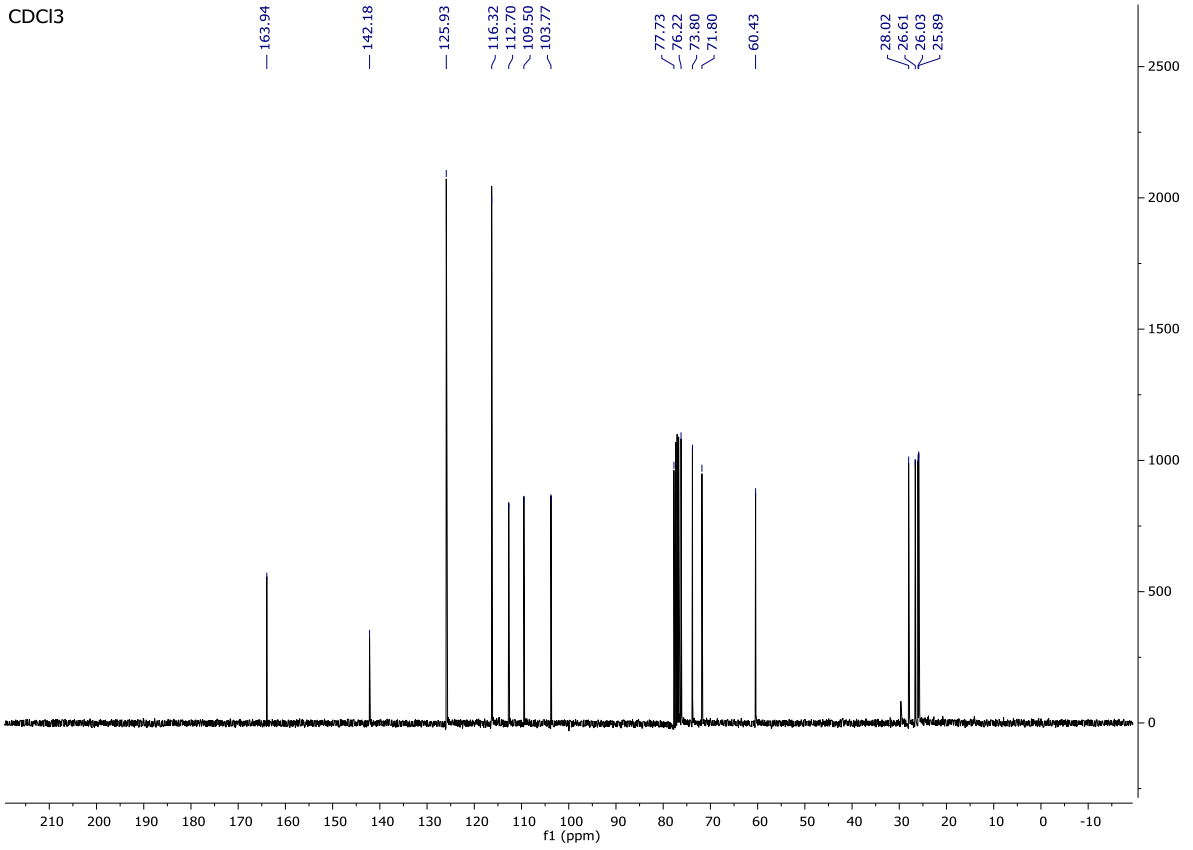
II.2.3 3-O-(4-Nitrophenyl)- 1,2:5,6-di-O-cyclohexylidene-α-D-glucofuranose (3c)



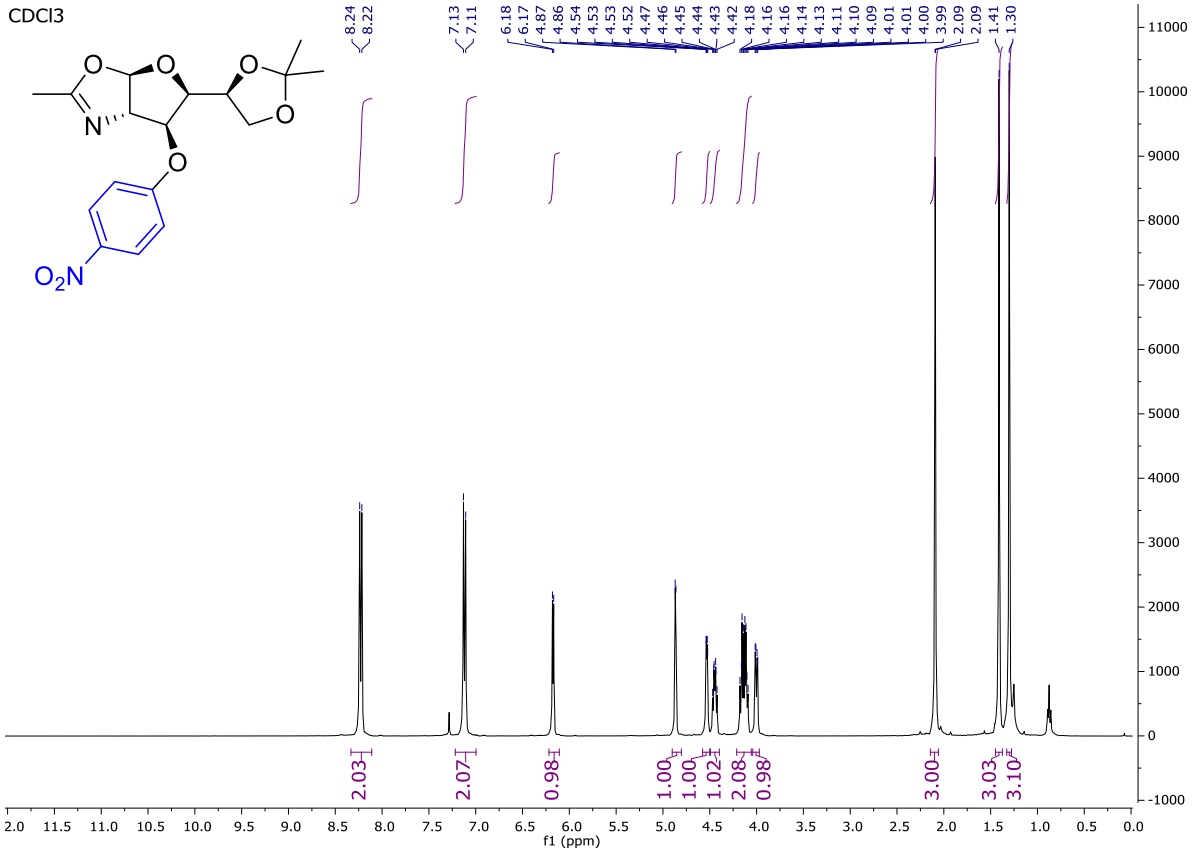


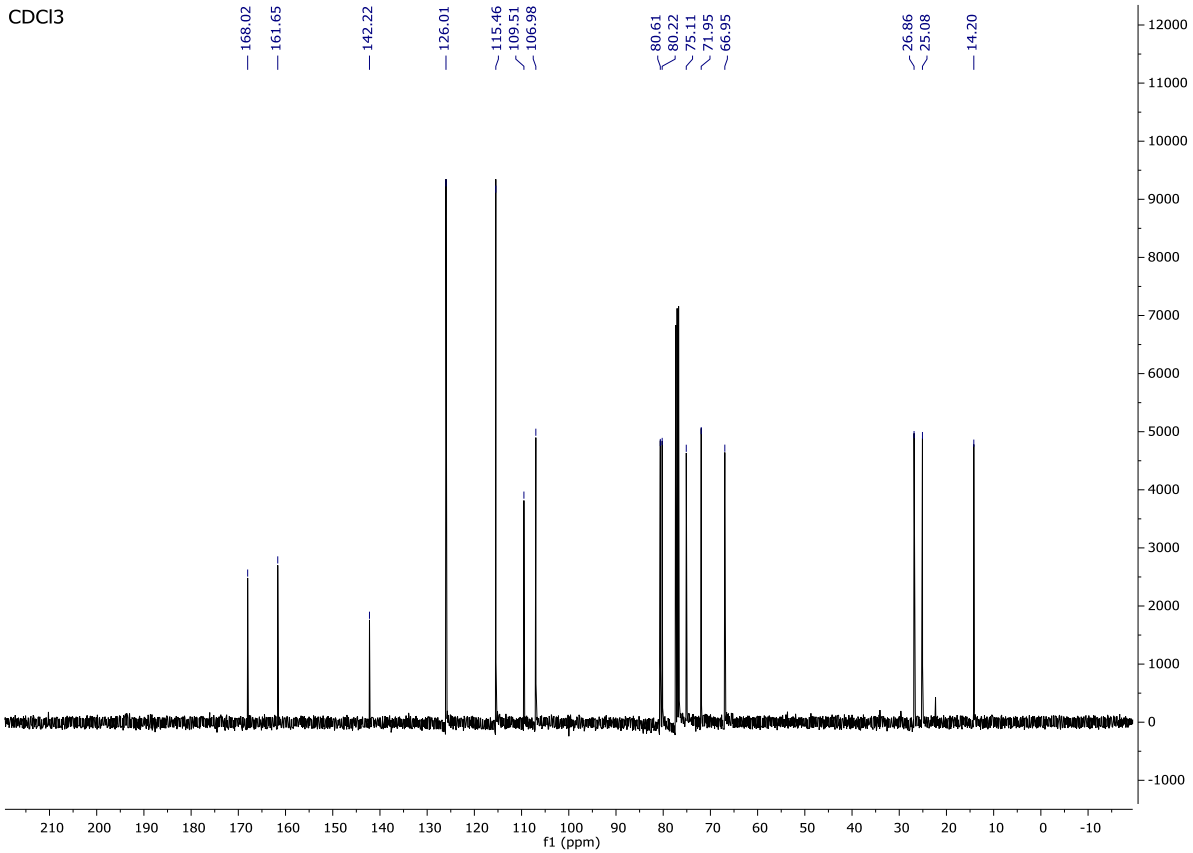
II.2.4 3-O-(4-Nitrophenyl)-1,2:4,5-di-O-isopropylidene-β-D-fructopyranose (3d)



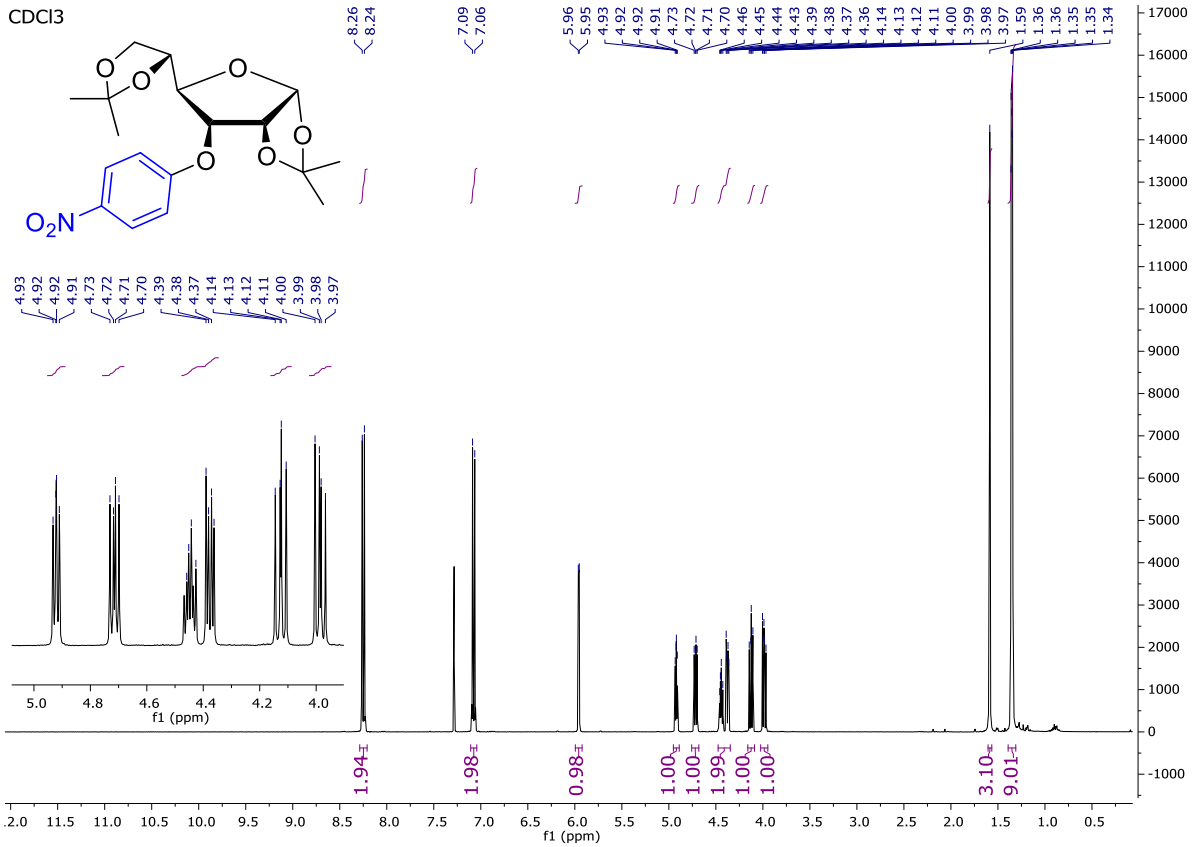


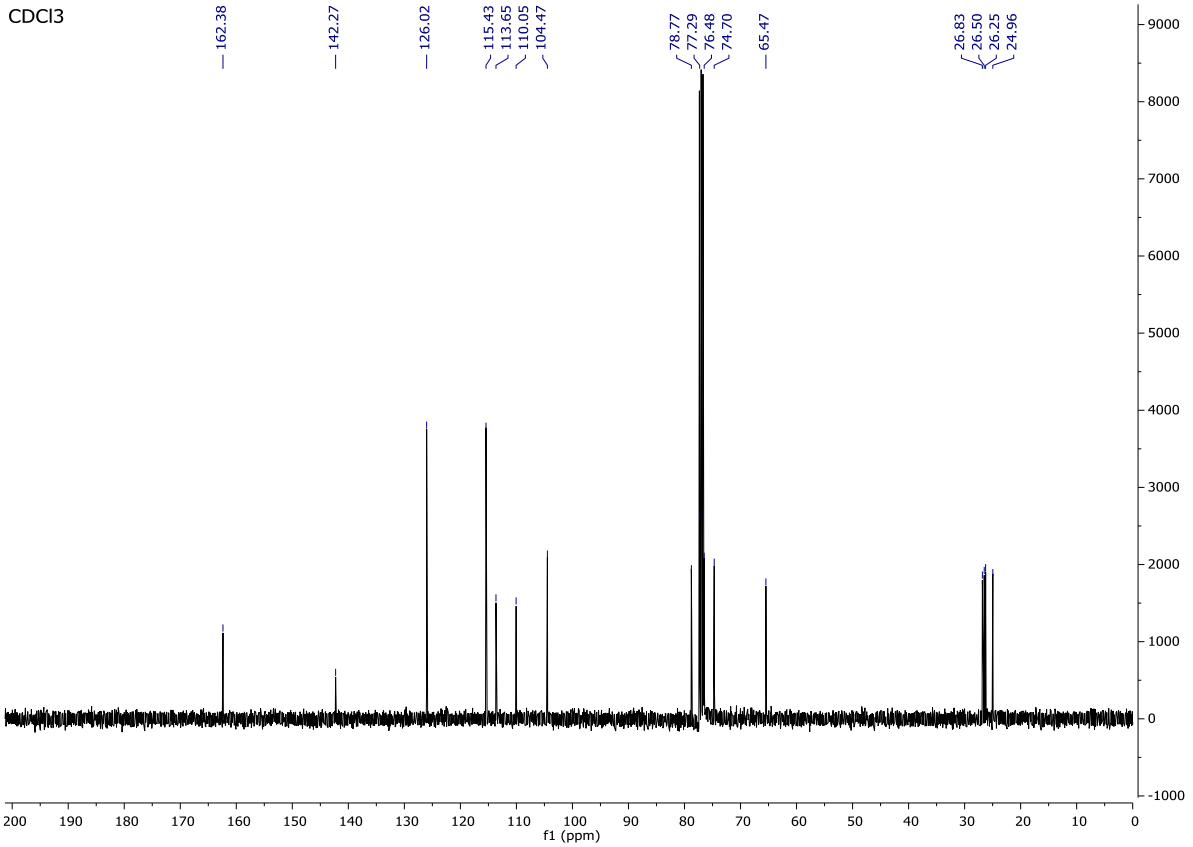
II.2.5 (3aR,5R,6S,6aS)-5-((S)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2-methyl-6-(4-nitrophenoxy)-3a,5,6,6a-tetrahydrofuro[3,2-d]oxazole (3e)



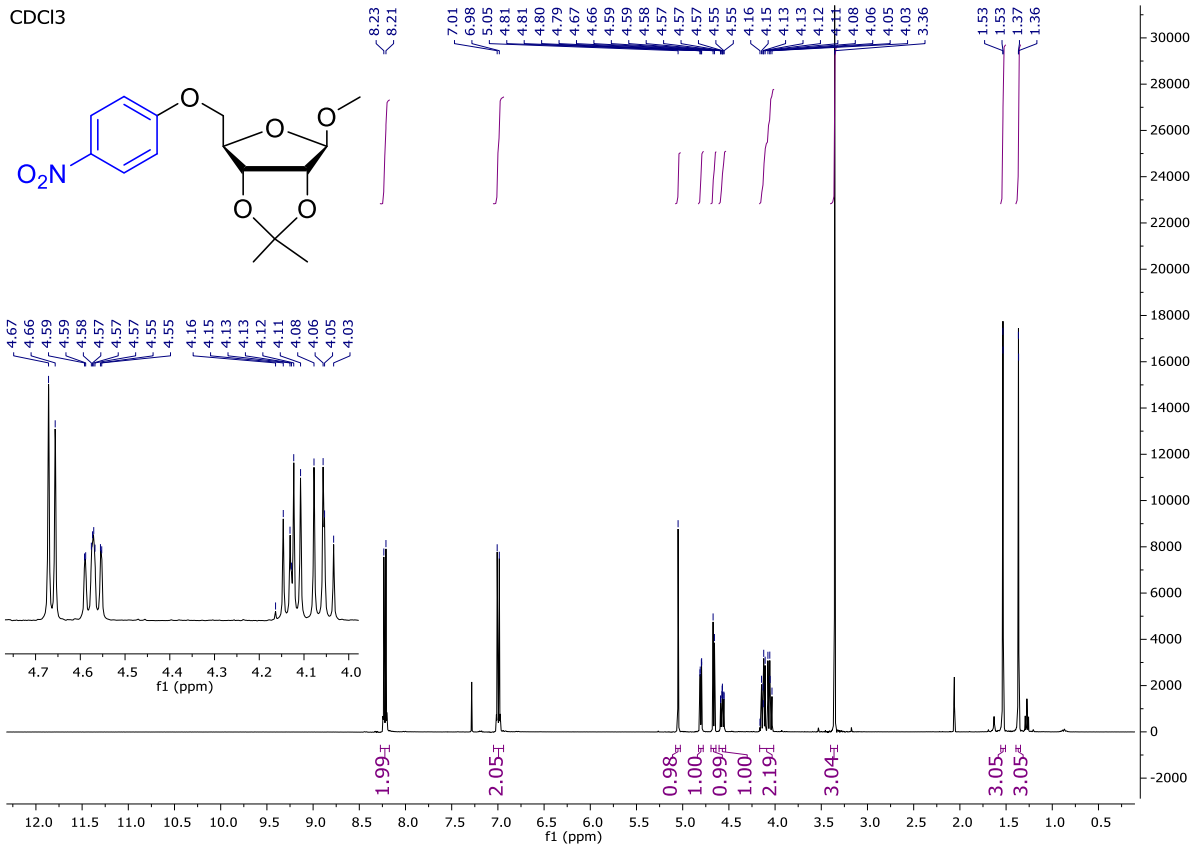


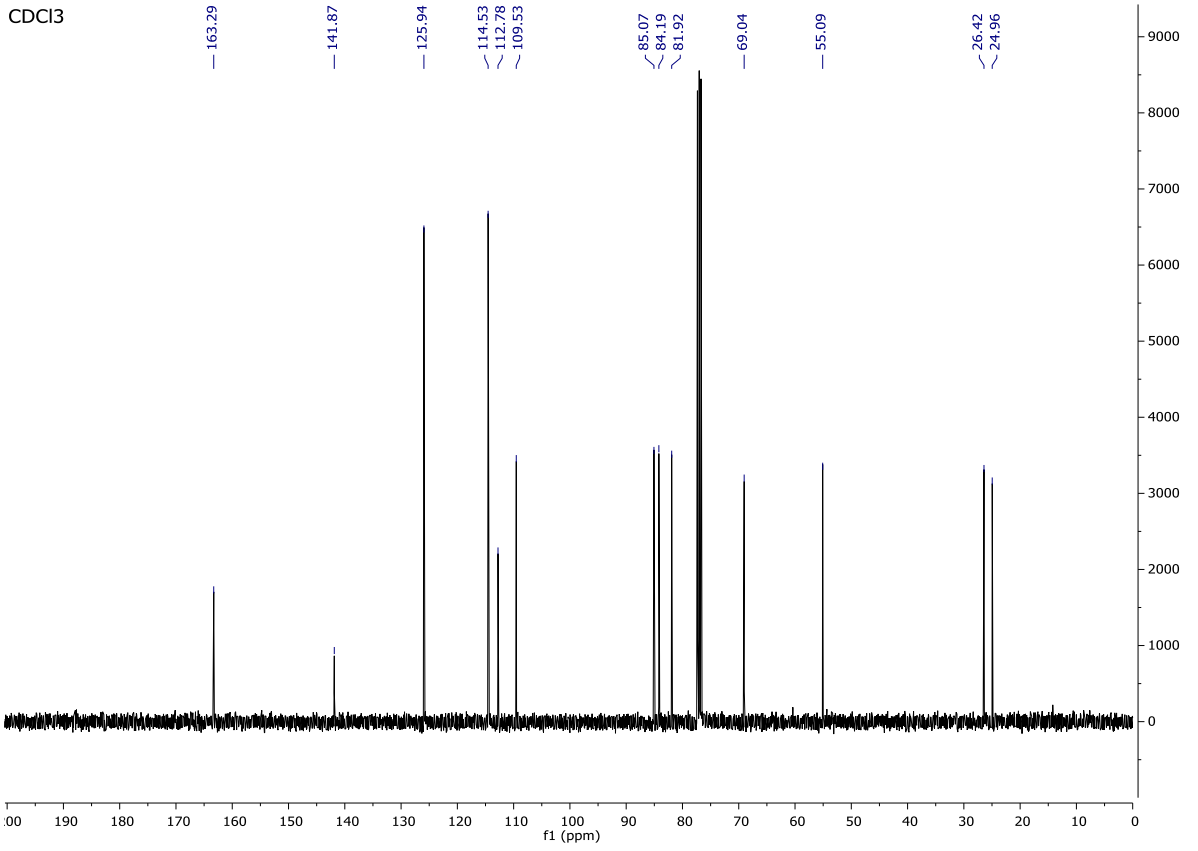
II.2.6 3-O-(4-nitrophenyl)-1,2:5,6-di-O-isopropylidene-α-D-allofuranose (3f)



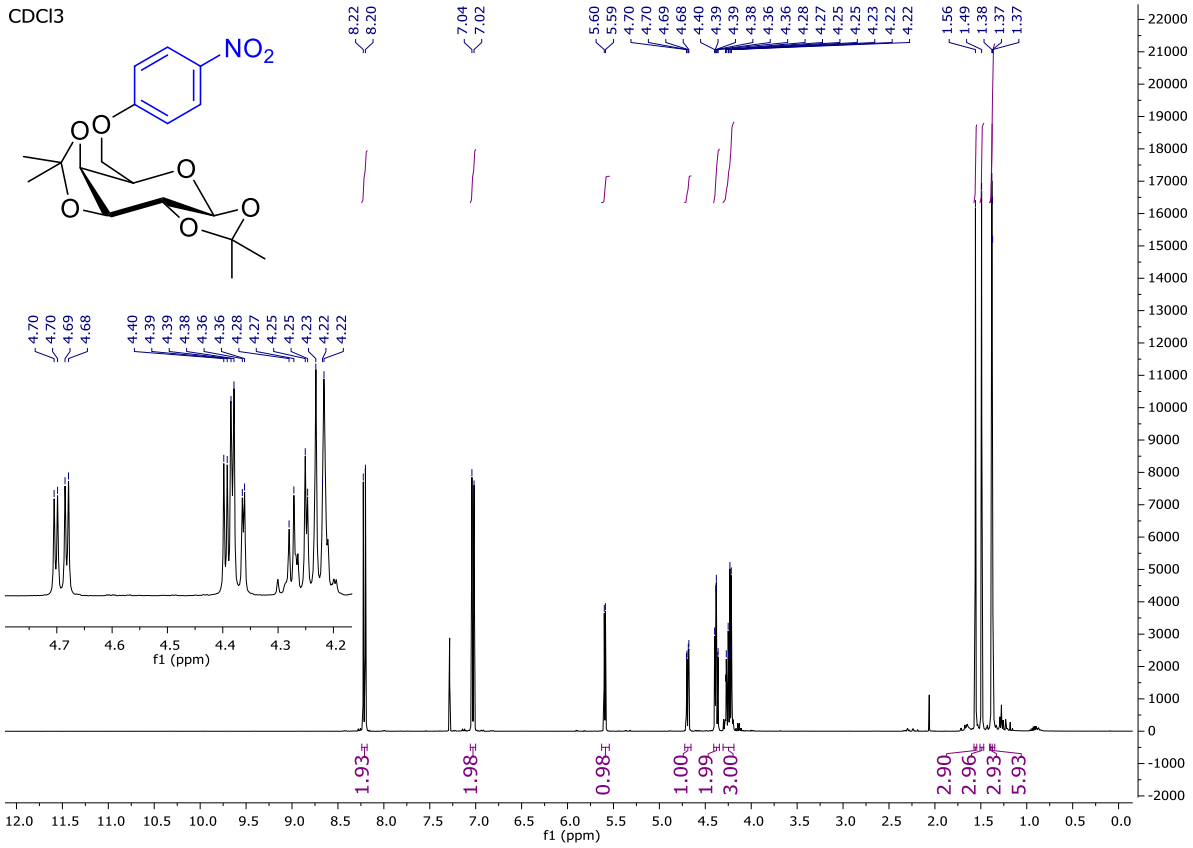


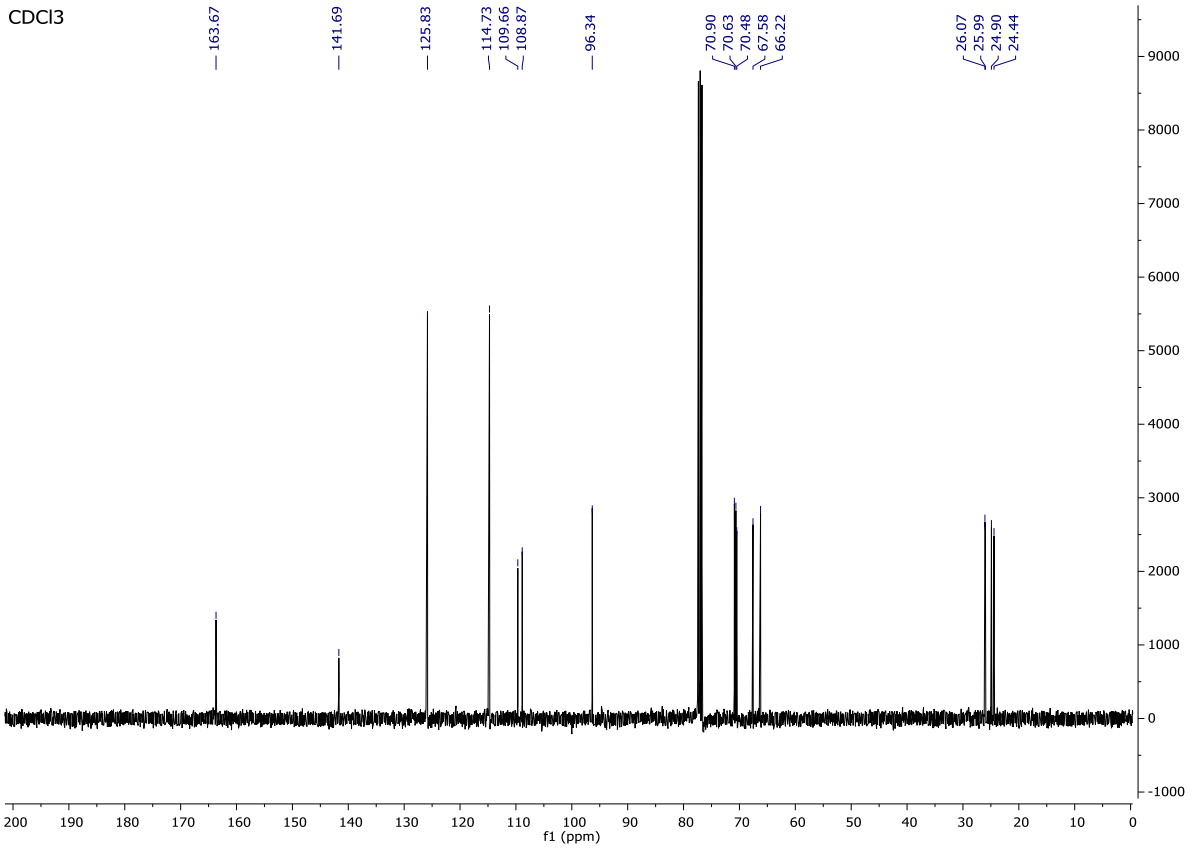
II.2.7 Methyl-5-O-(4-nitrophenyl)-2,3-O-isopropylidene-α-D-ribofuranoside (3g)



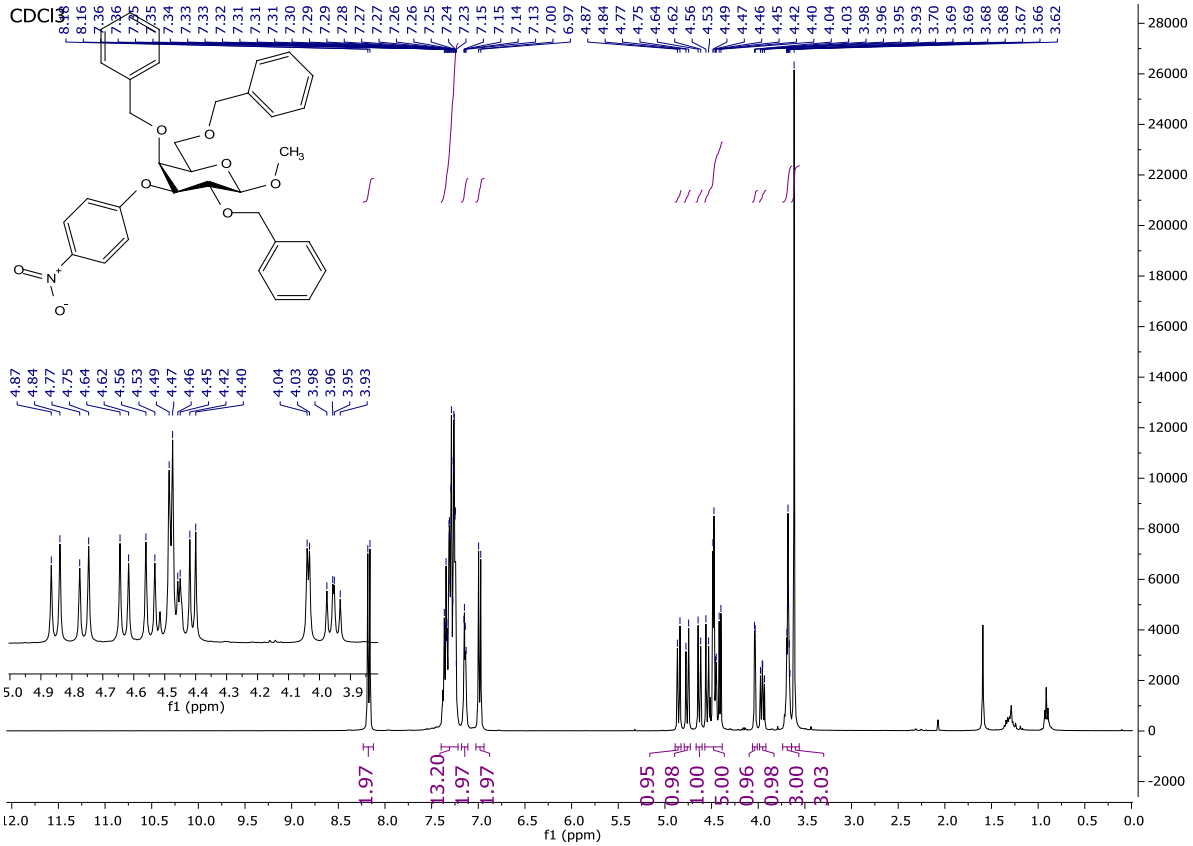


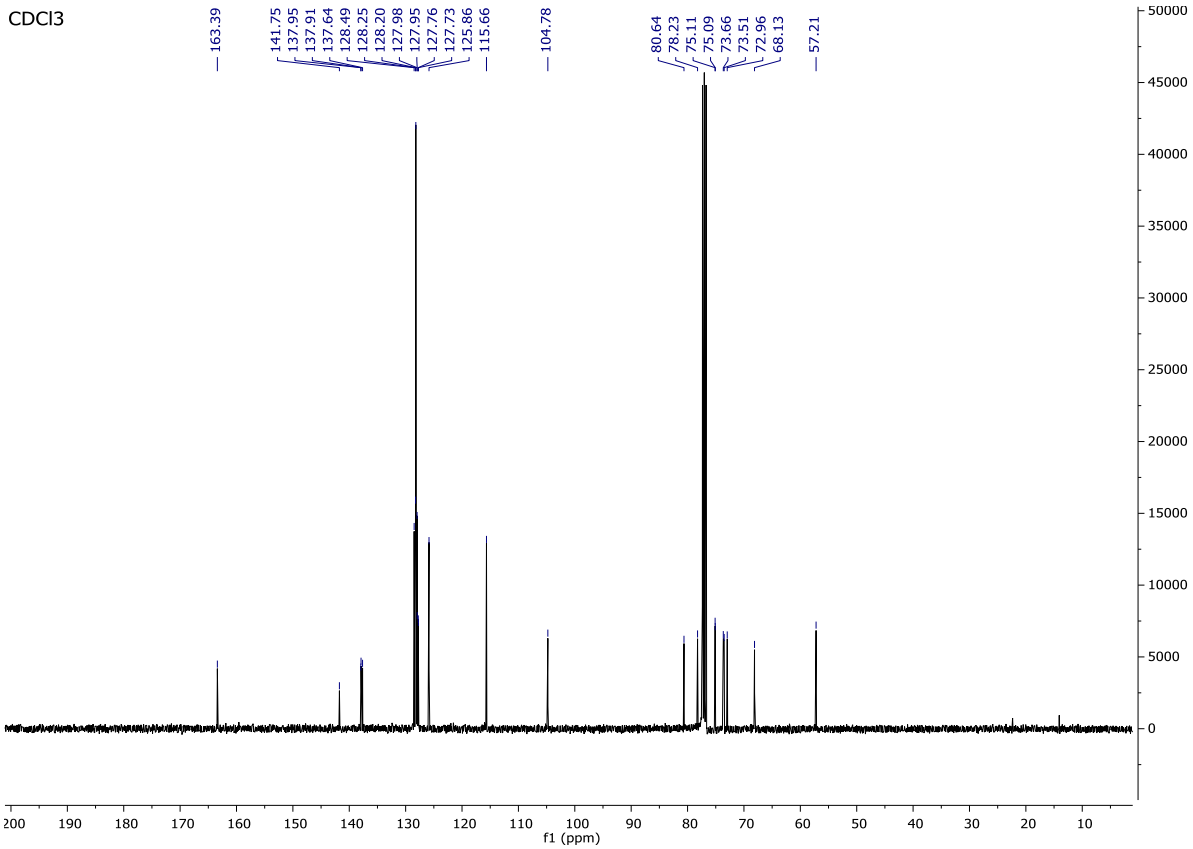
II.2.8 6-O-(4-nitrophenyl)- 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (3h)



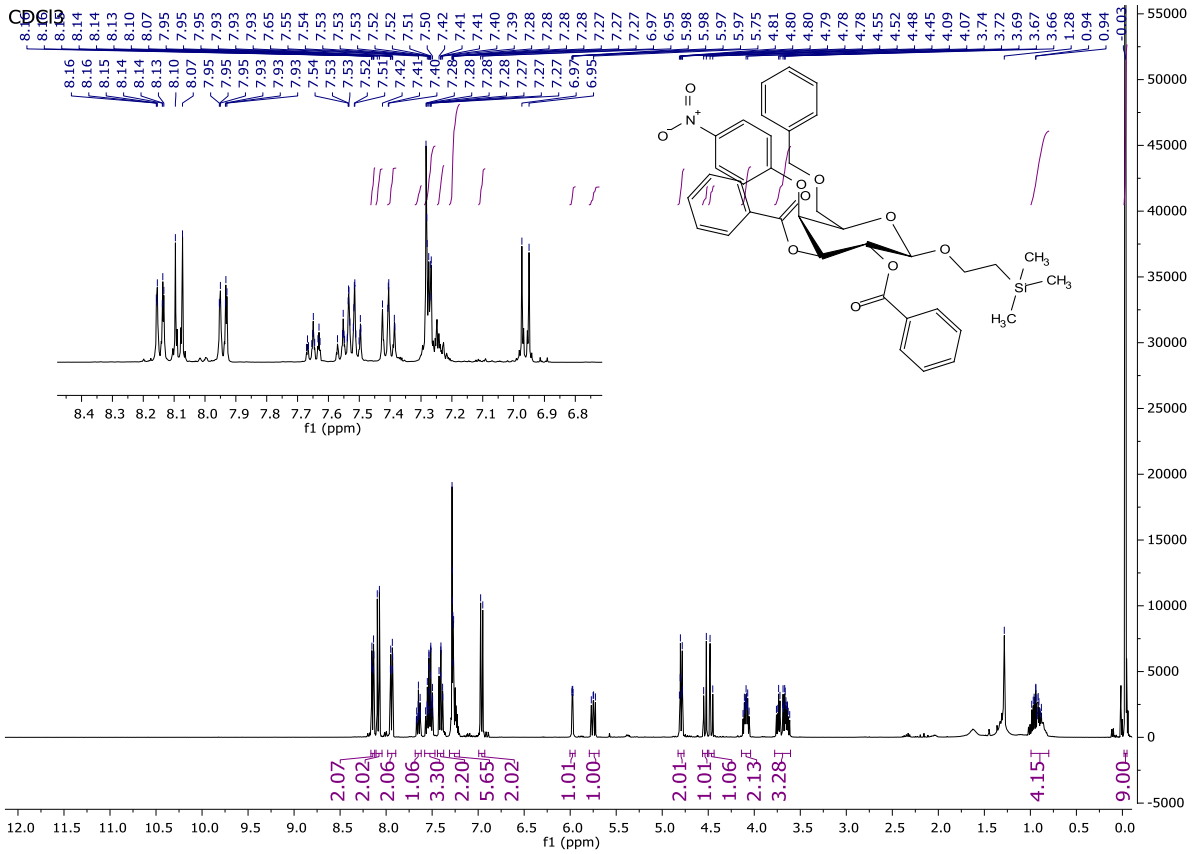


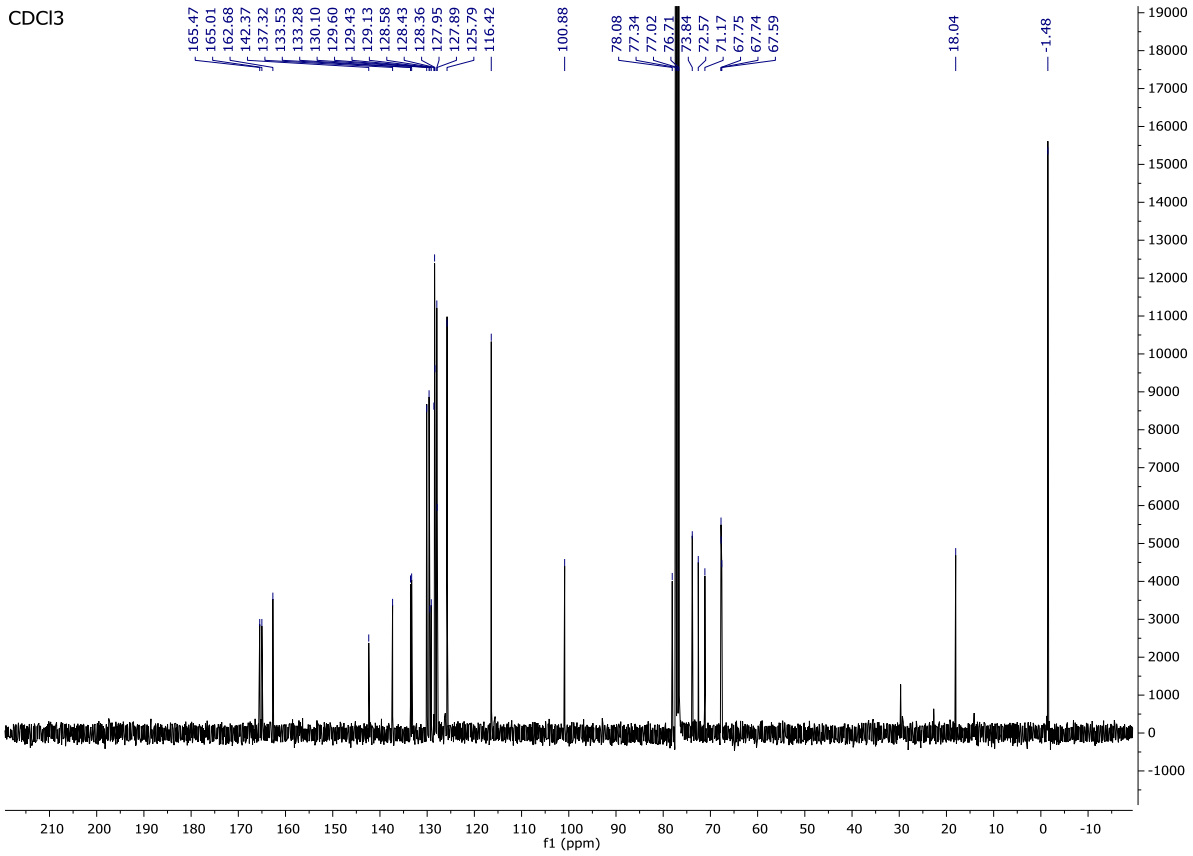
II.2.9 Methyl-3-O-(4-nitrophenyl)-2,3,6-O-tribenzyl-β-D-glucopyranoside (3i)



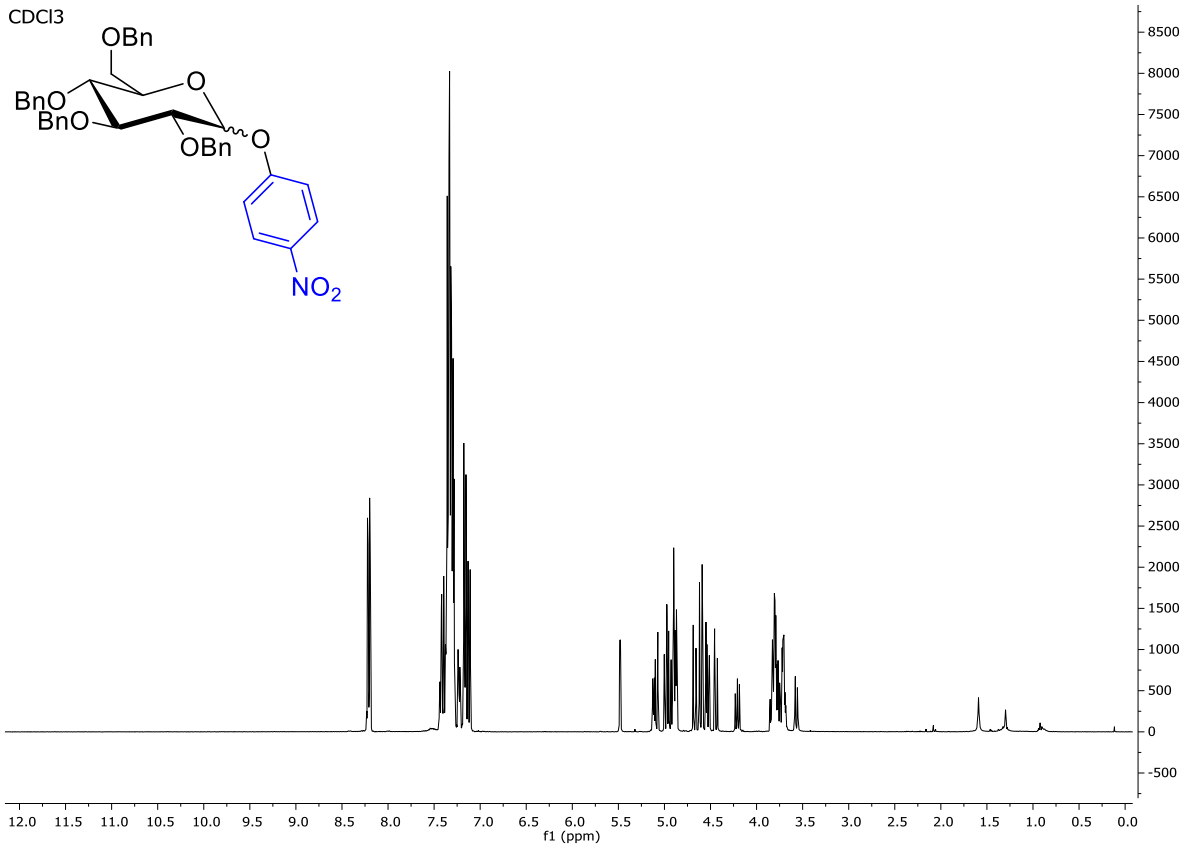


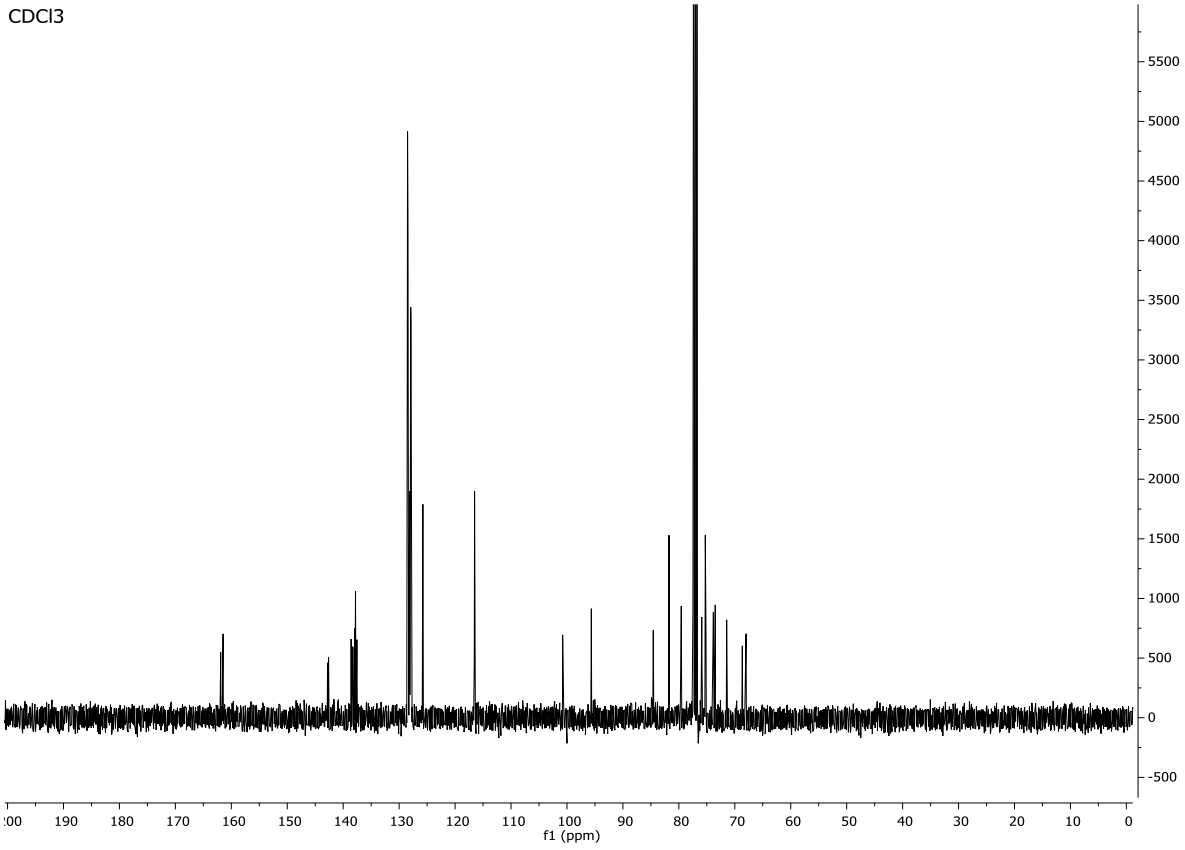
II.2.10 2-Trimethylsilylethyl-4-O-(4-nitrophenyl)-2,3-O-benzoyl-6-O-benzyl-ß-D-galactopyranoside (3j)



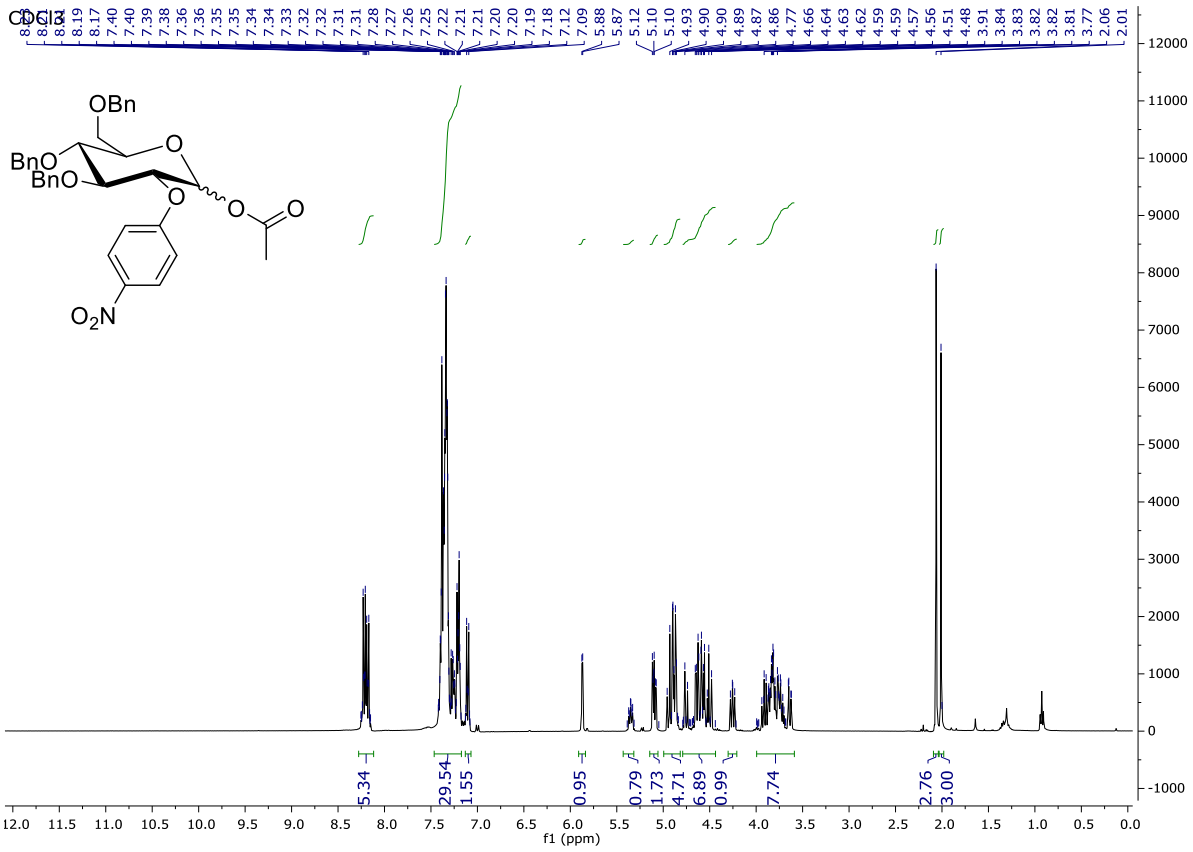


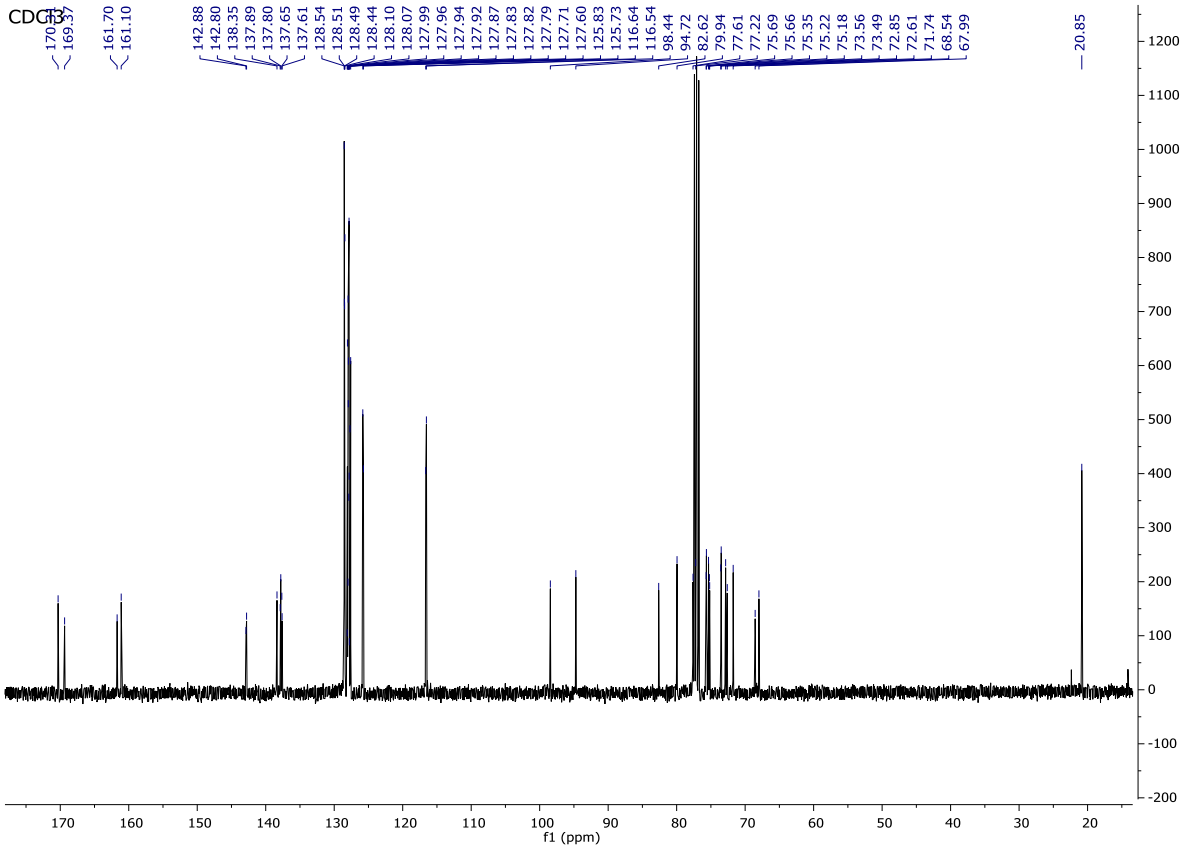
II.2.11 ***4-Nitrophenyl-2,3,4,6-tetra-O-benzyl-D-glucopyranoside (3k)***



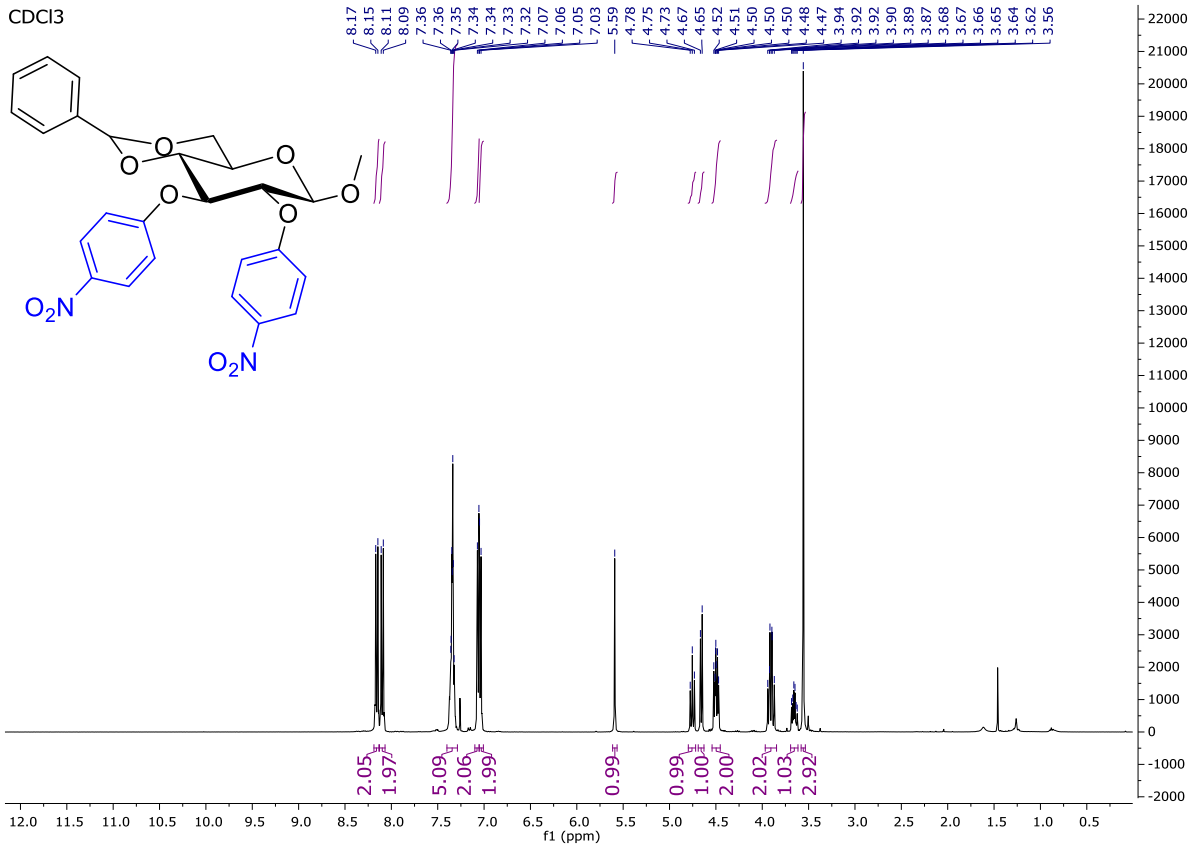


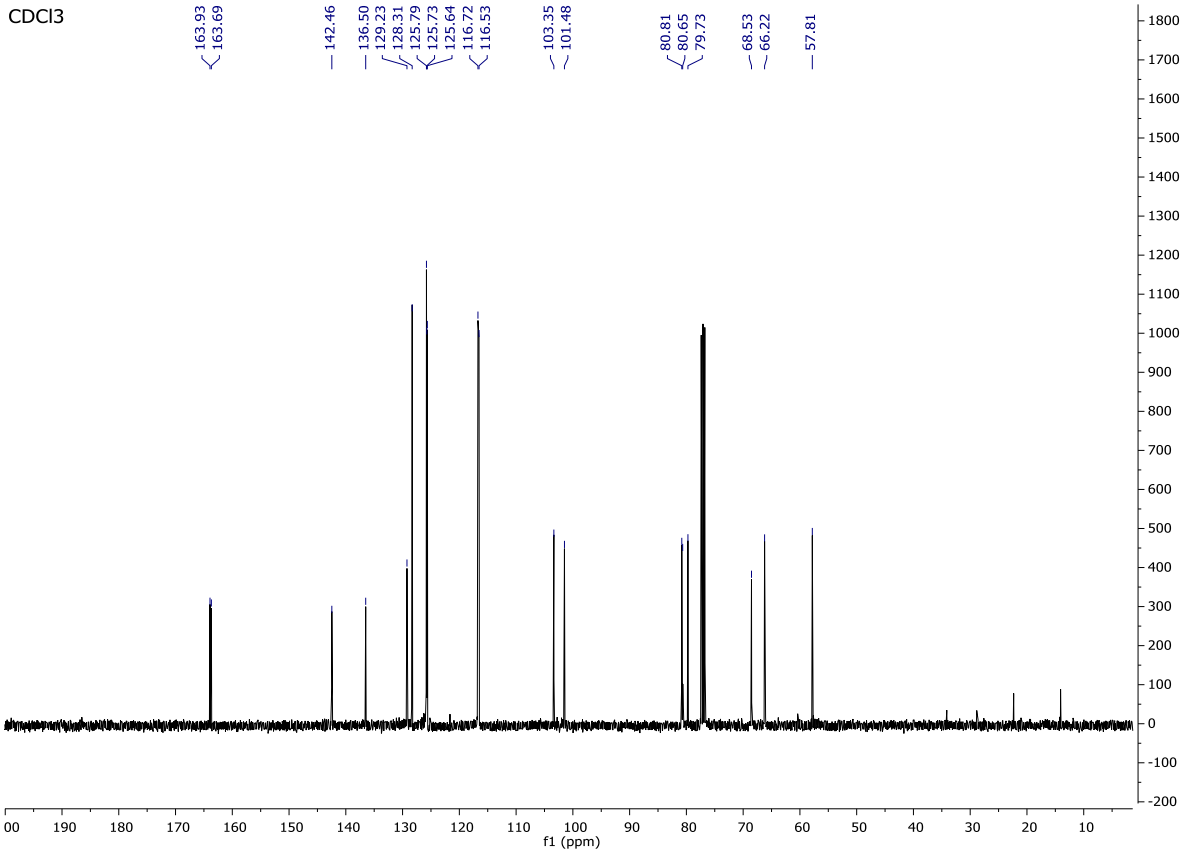
II.2.12 1-O-Acetyl-2-O-(4-nitrophenyl)-3,4,6-O-benzylglucopyranose (3l)



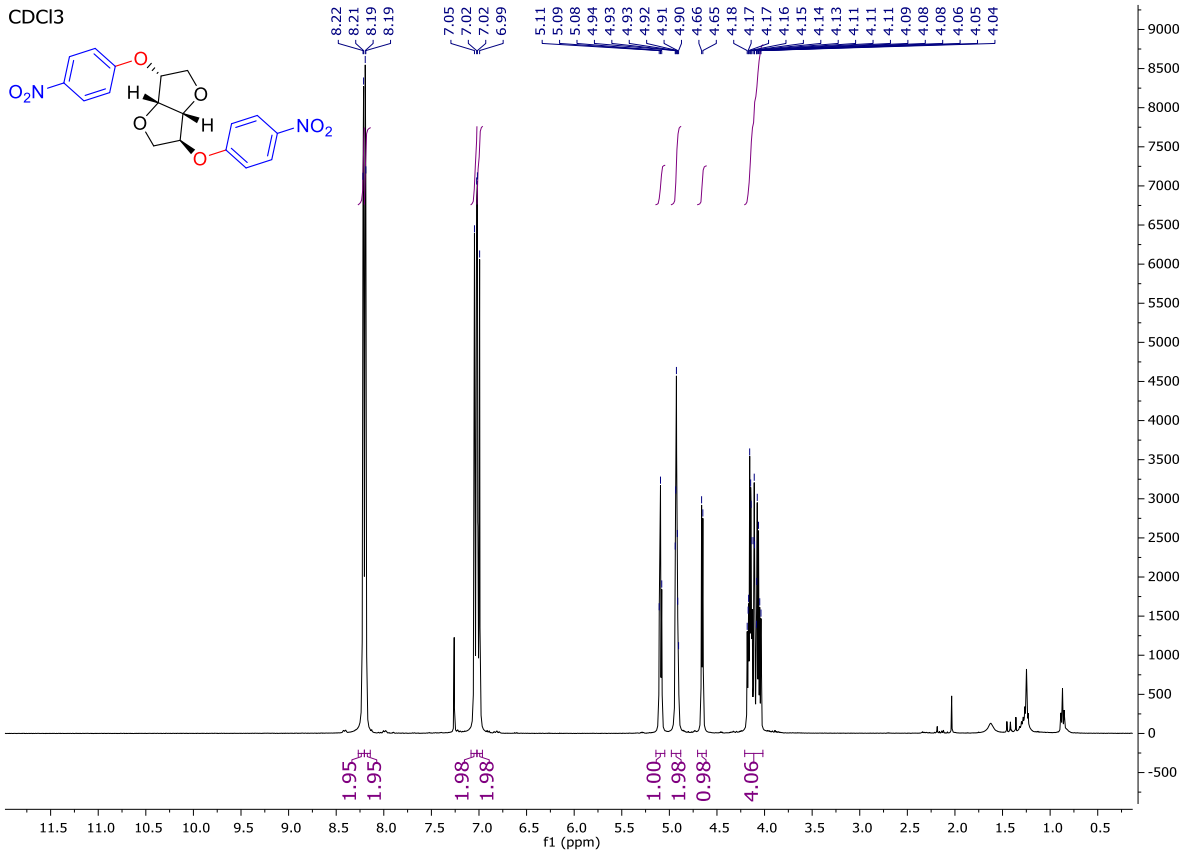


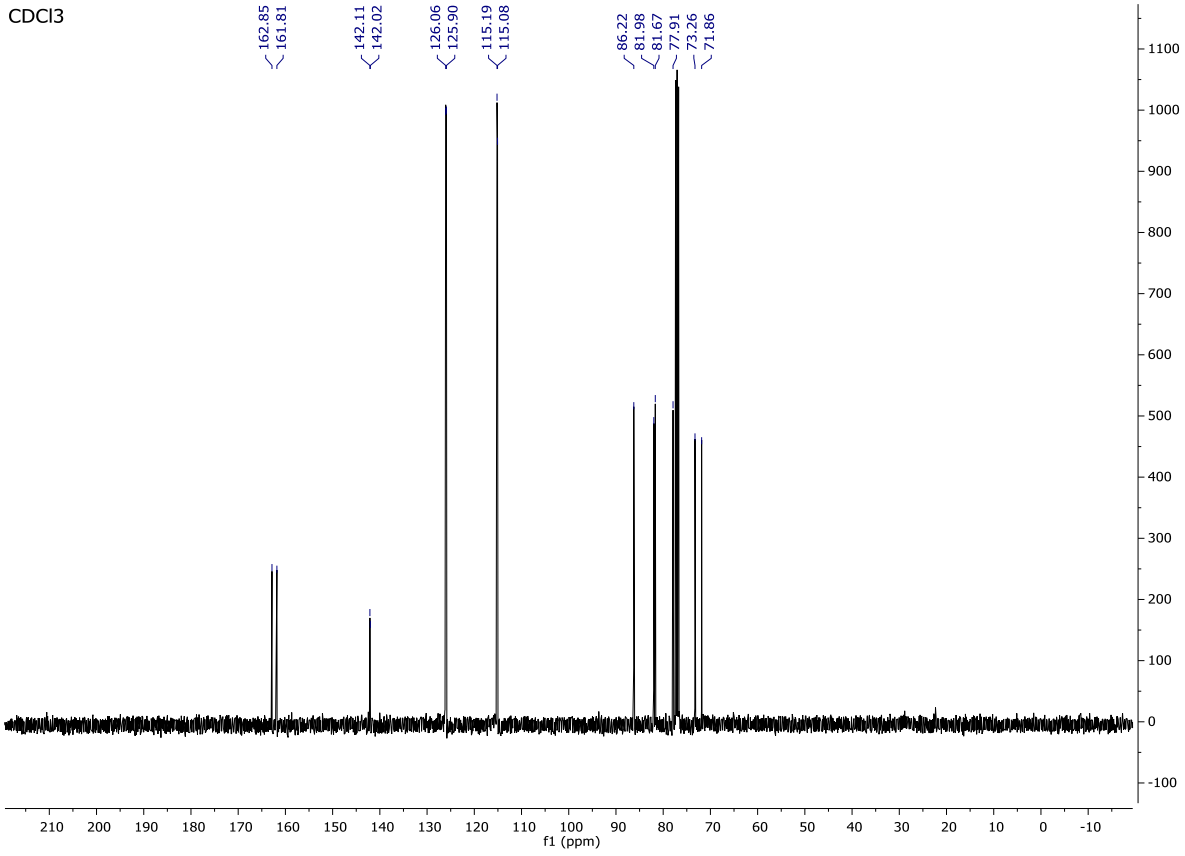
II.2.13 ***Methyl-2,3-O-di(4-nitrophenyl)-4,6-O-benzylidene-α-D-glucopyranoside (3m)***



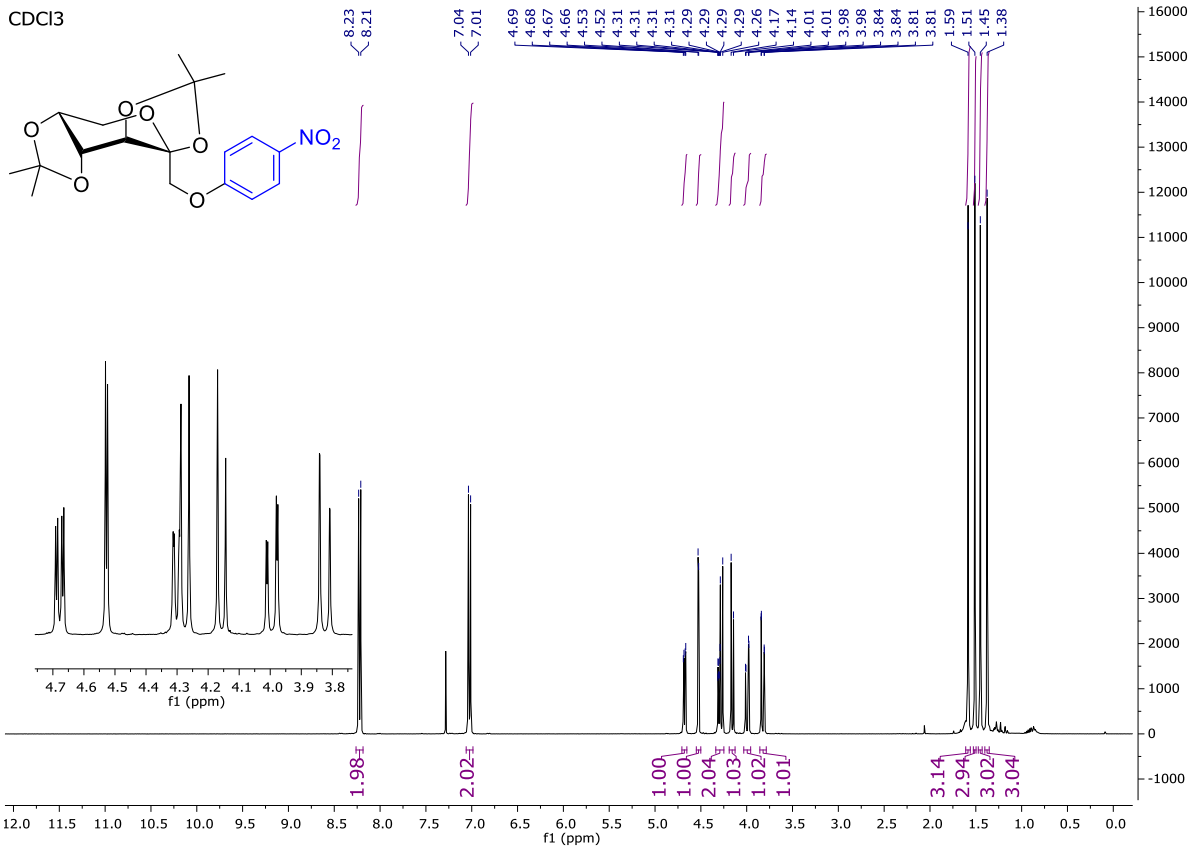


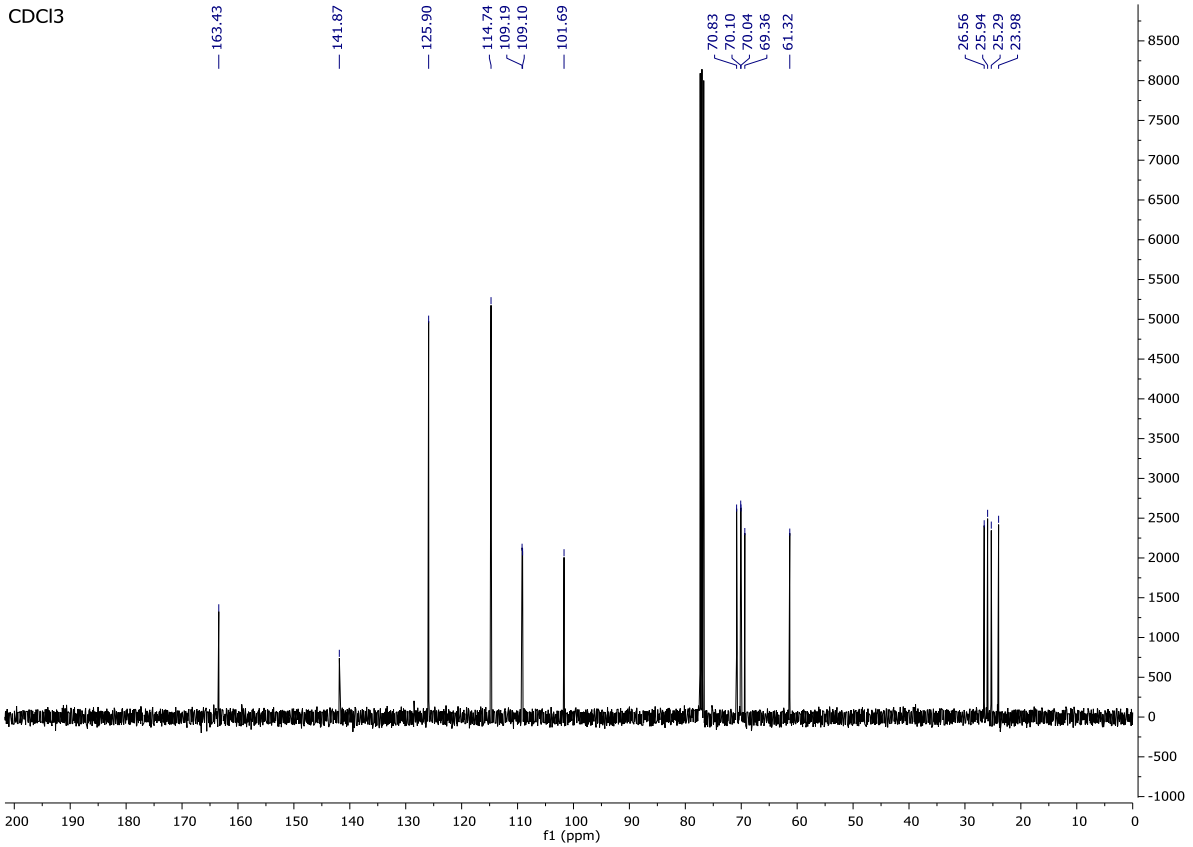
II.2.14 *2,5-O-Di(4-nitrophenyl)-dianhydro-D-glucitol (3n)*



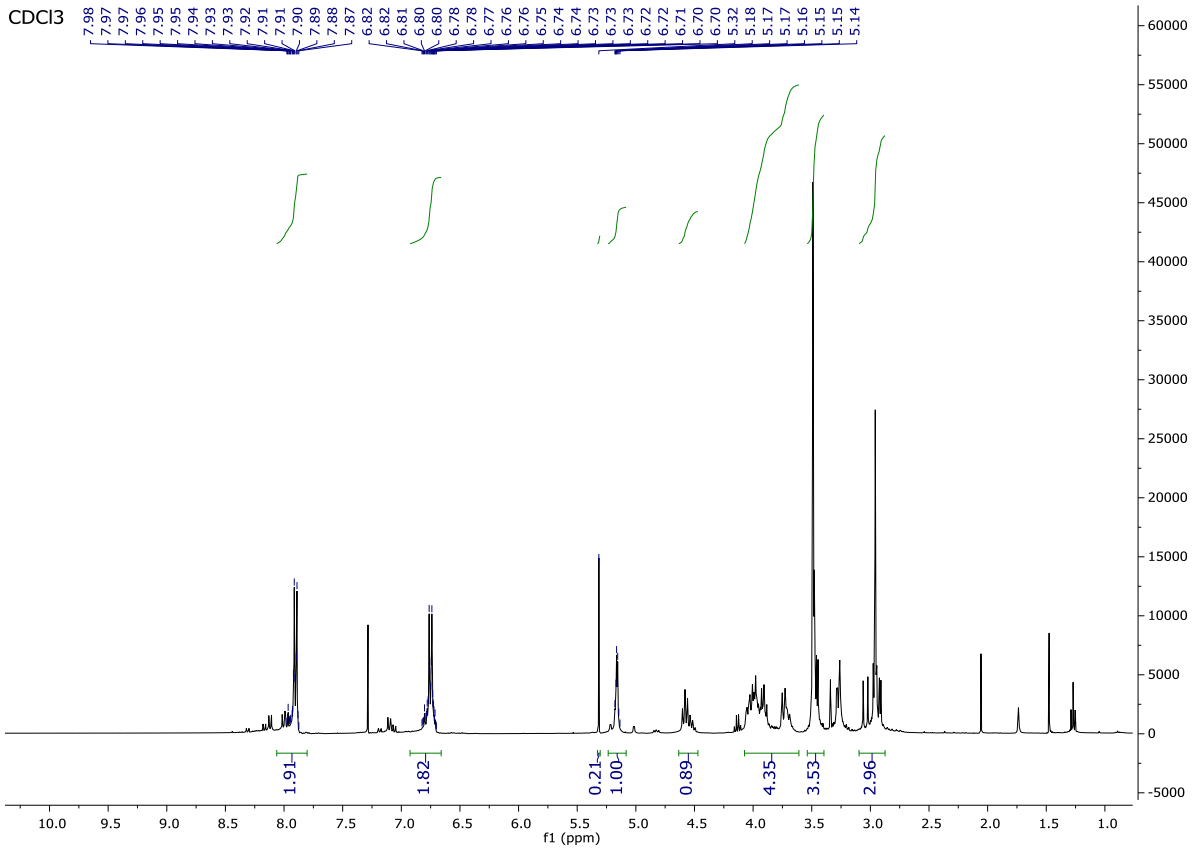


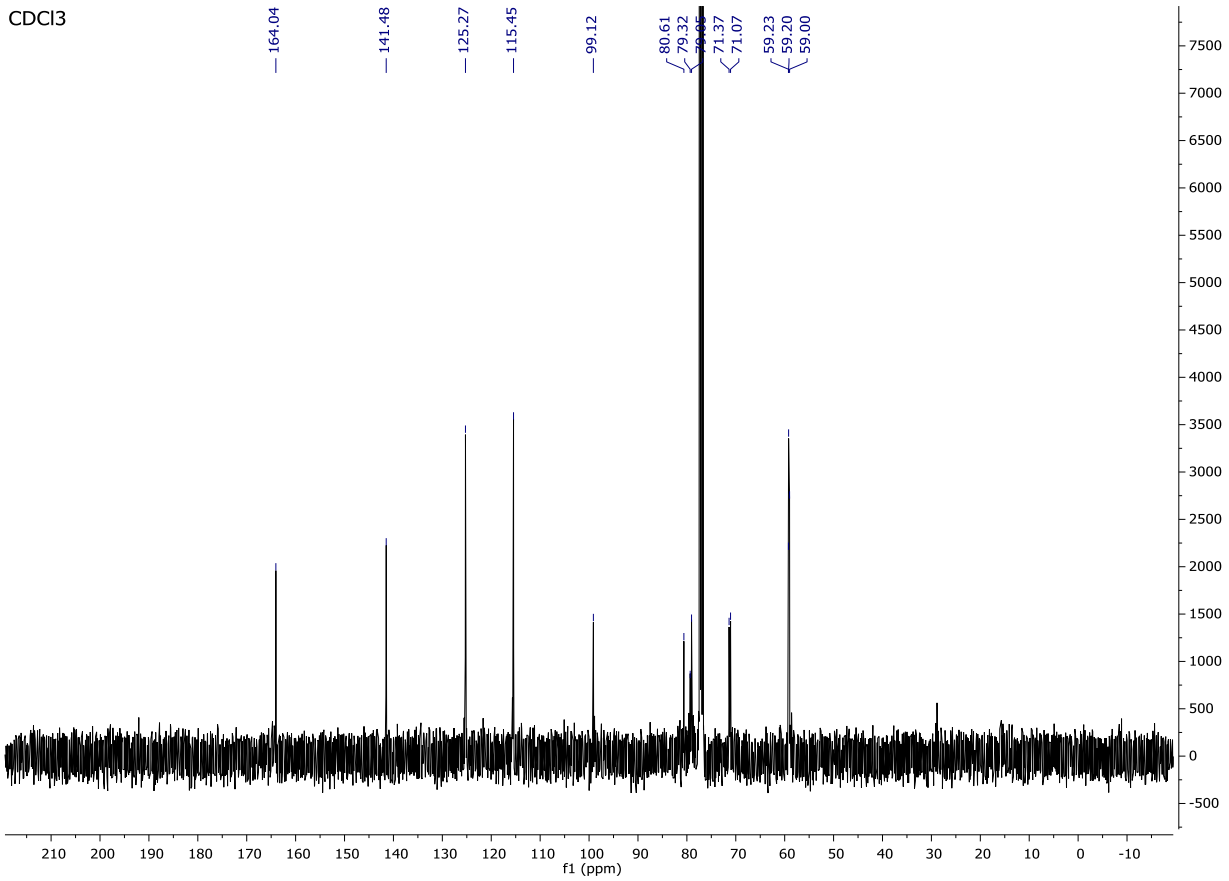
II.2.15 *1-O-(4-Nitrophenyl)- 2,3:4,5-di-O-isopropylidene-β-D-fructopyranose (3o)*





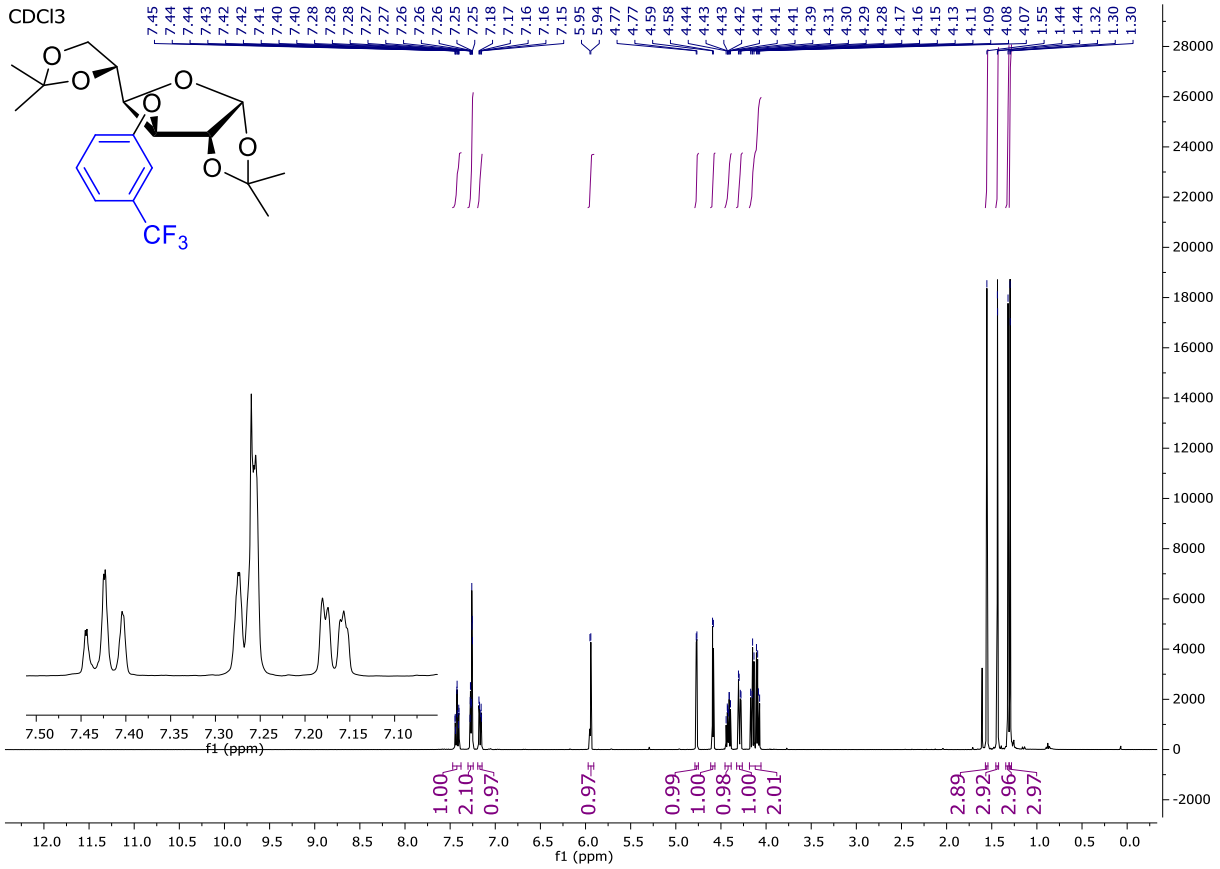
II.2.16 Heptakis(2,6-di-O-mehtyl-4-nitrophenyl)-β-cyclodextrine (4)

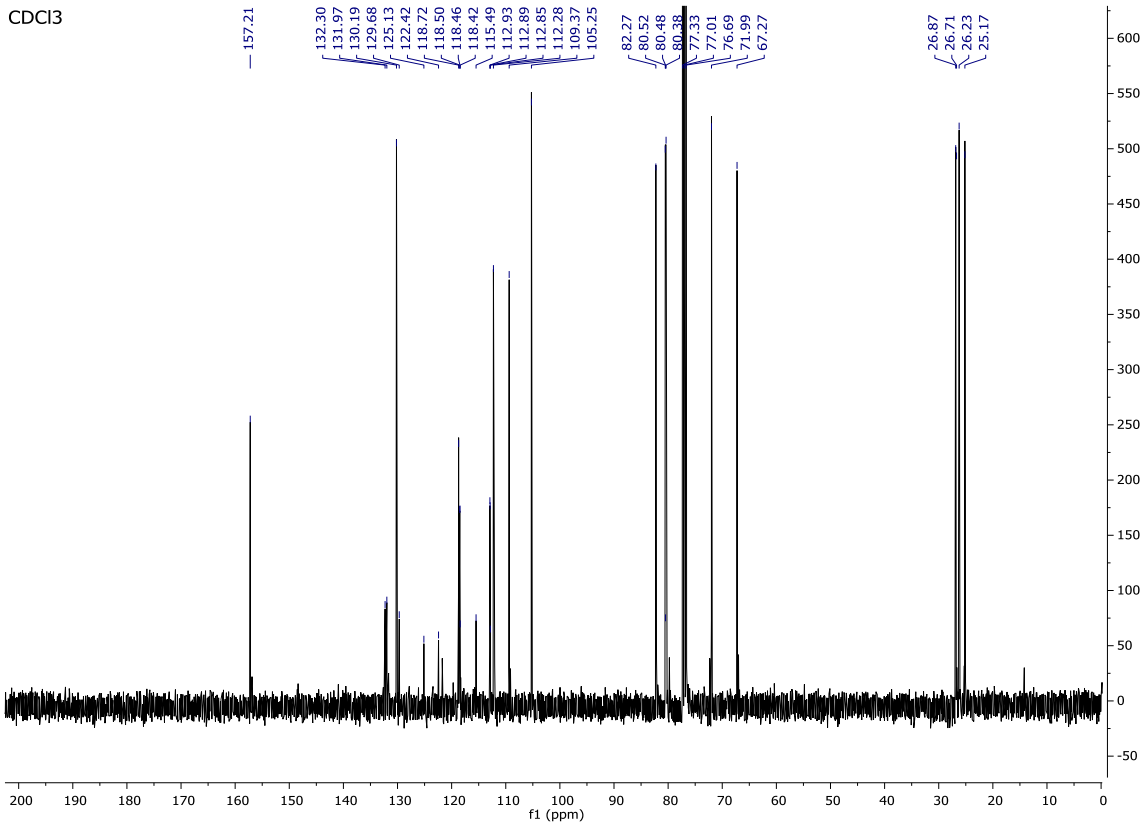


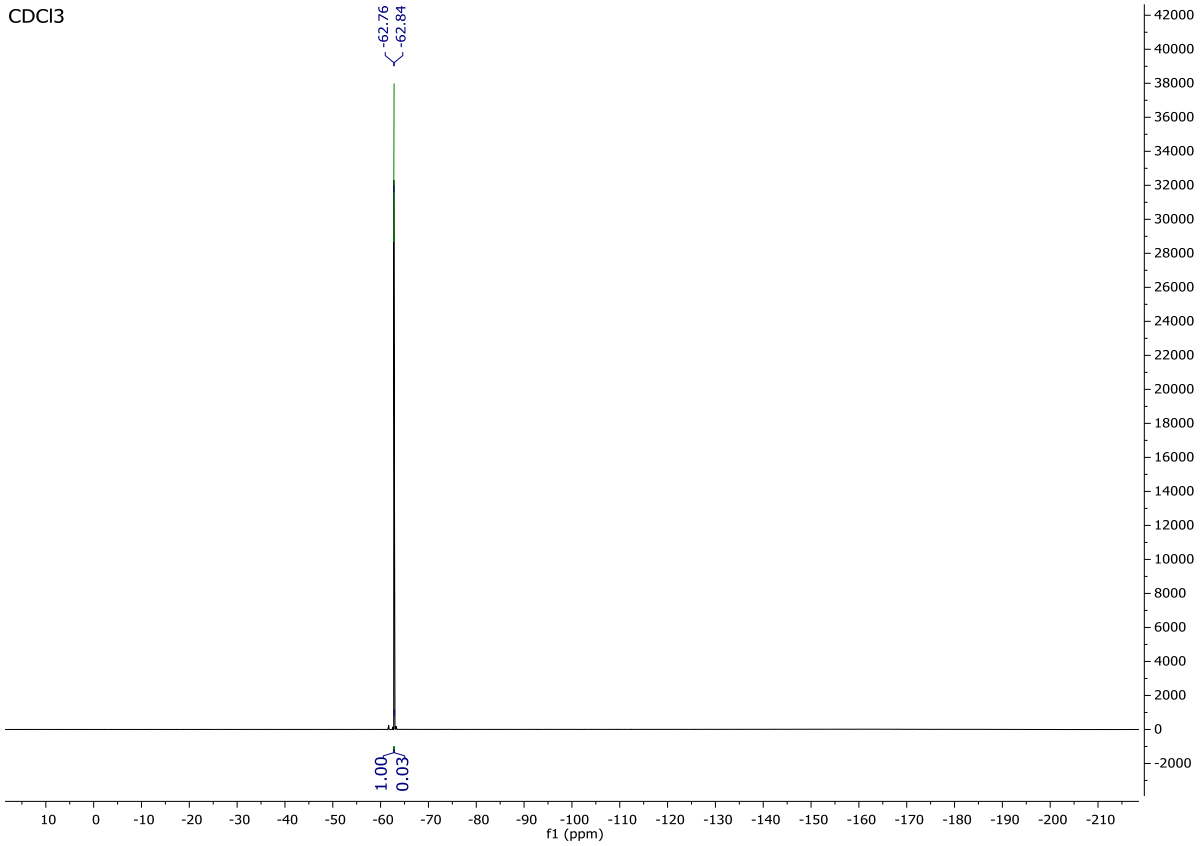


II.3 Spectra of other arylations

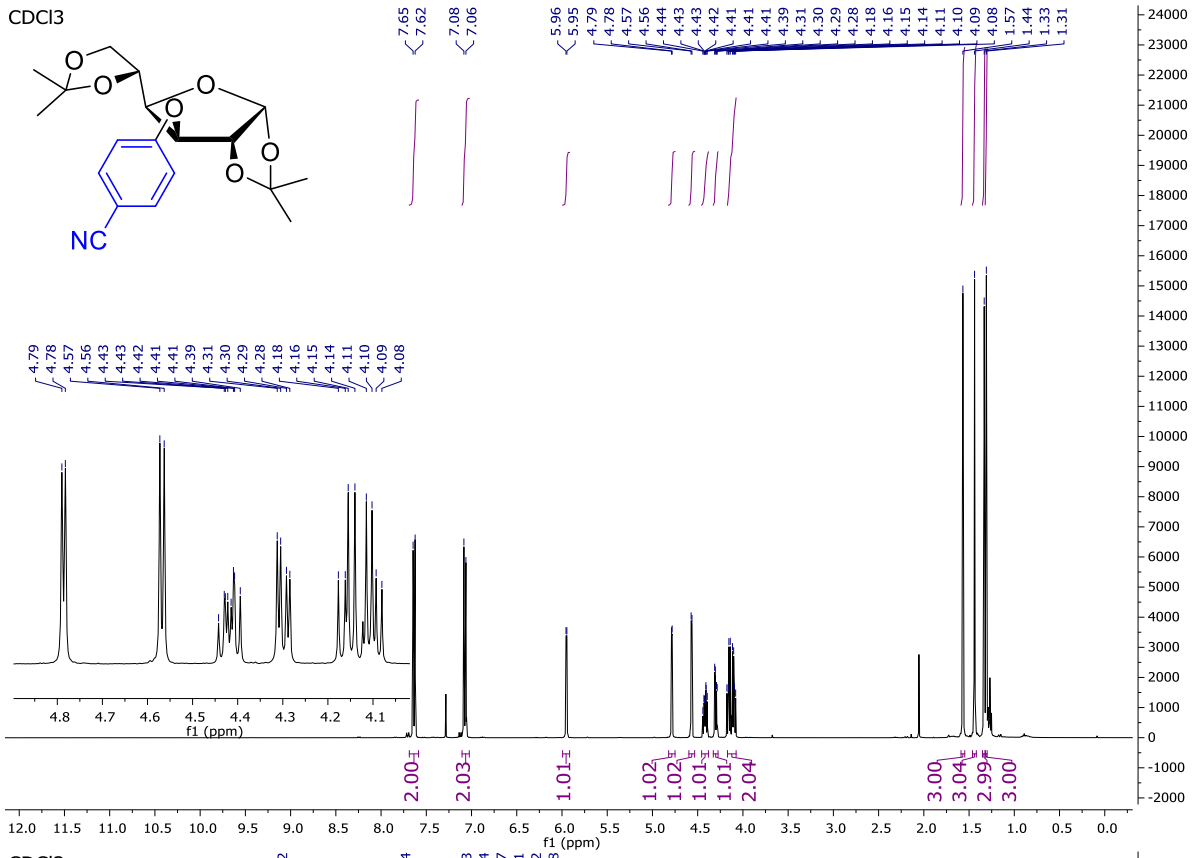
II.3.1 3-O-(3-Trifluoromethylphenyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3p)

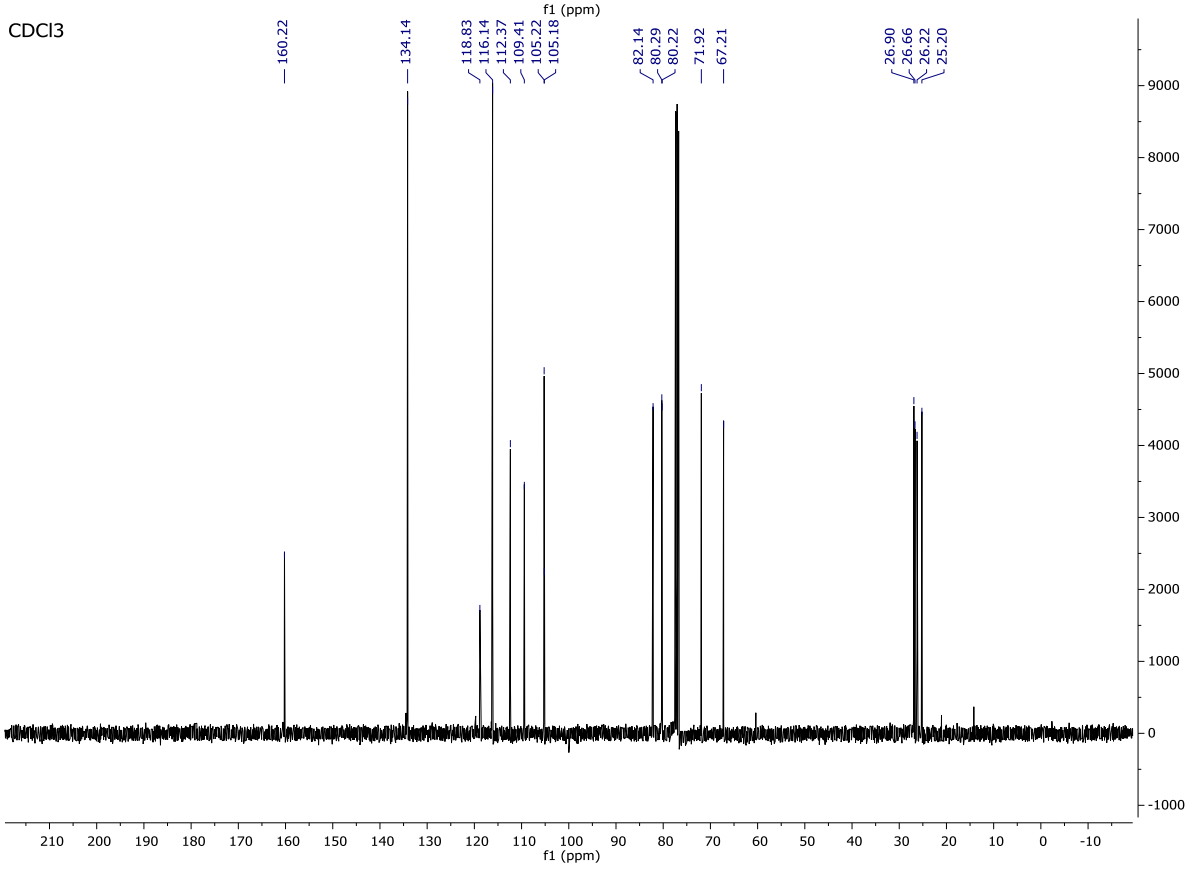




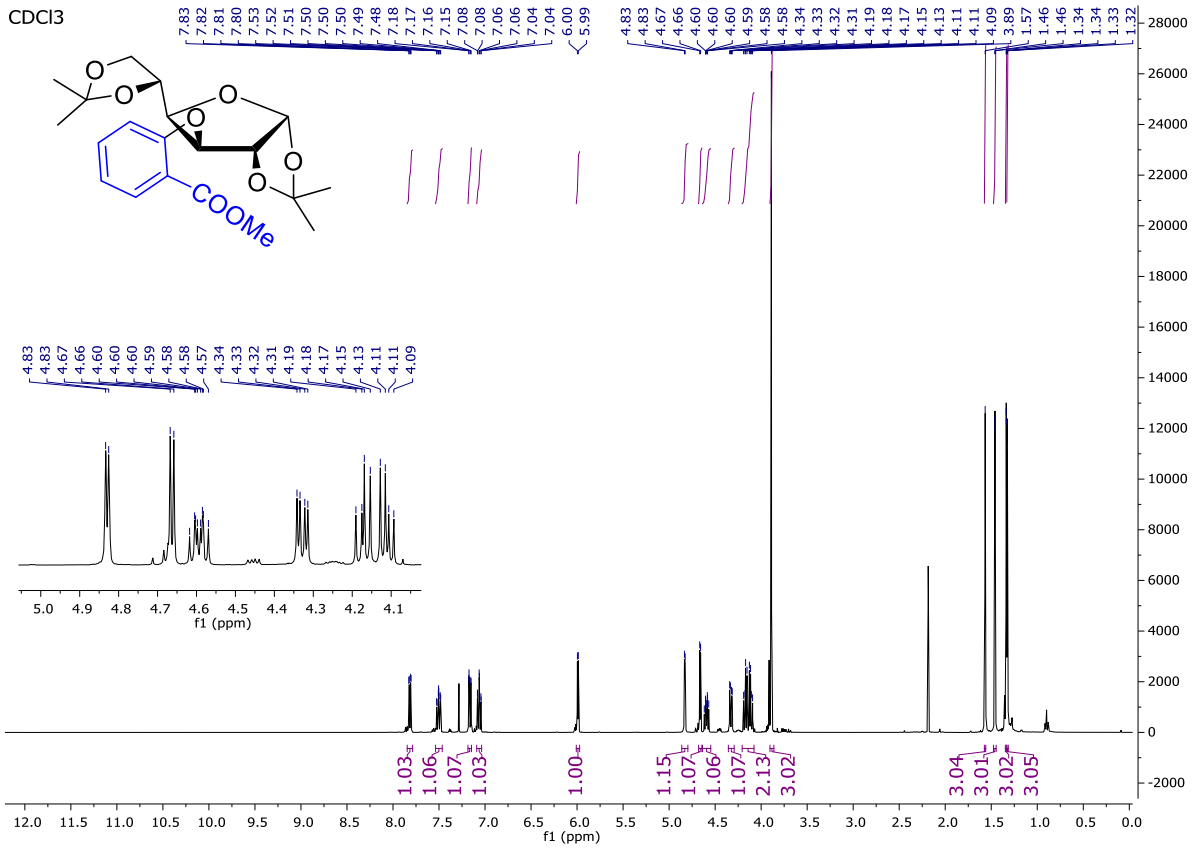

CDCl3
-62.76
-62.84
1.00
0.03
f1 (ppm)

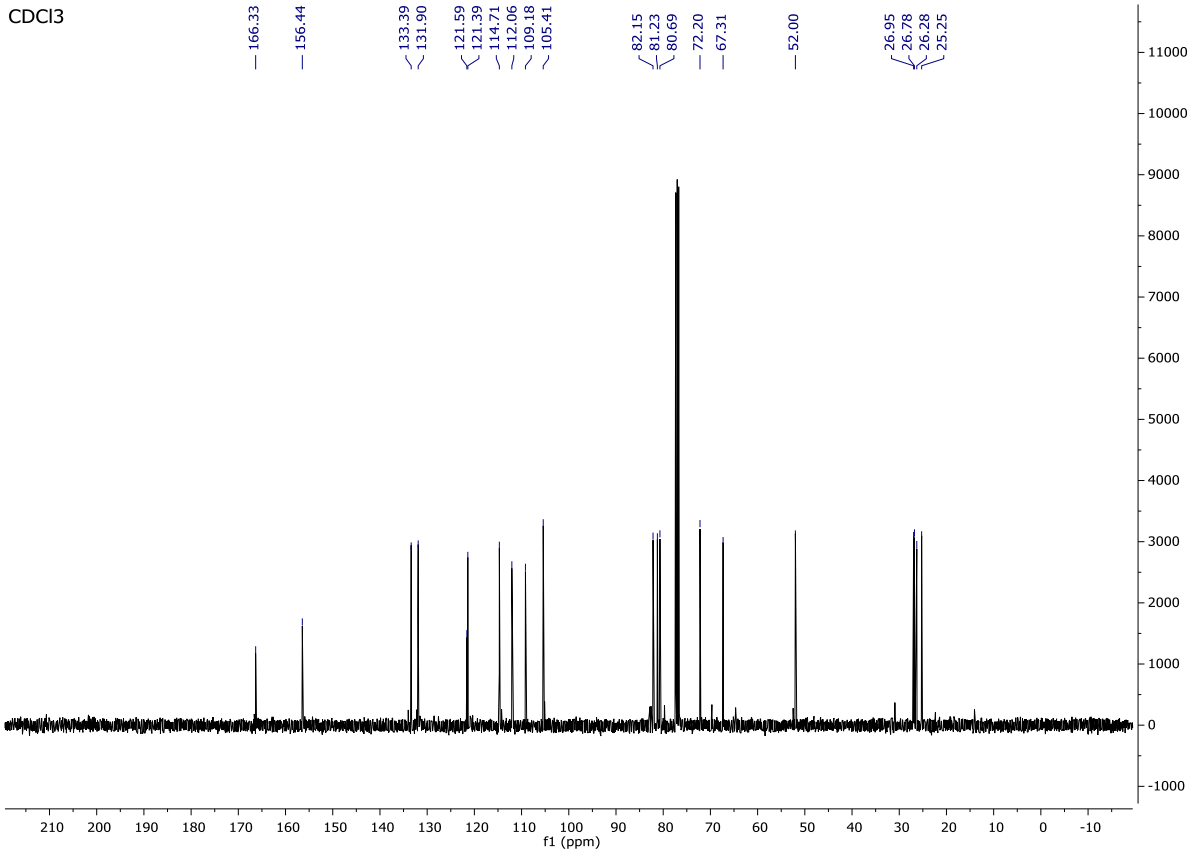
II.3.2 3-O-(4-Cyanophenyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3g)



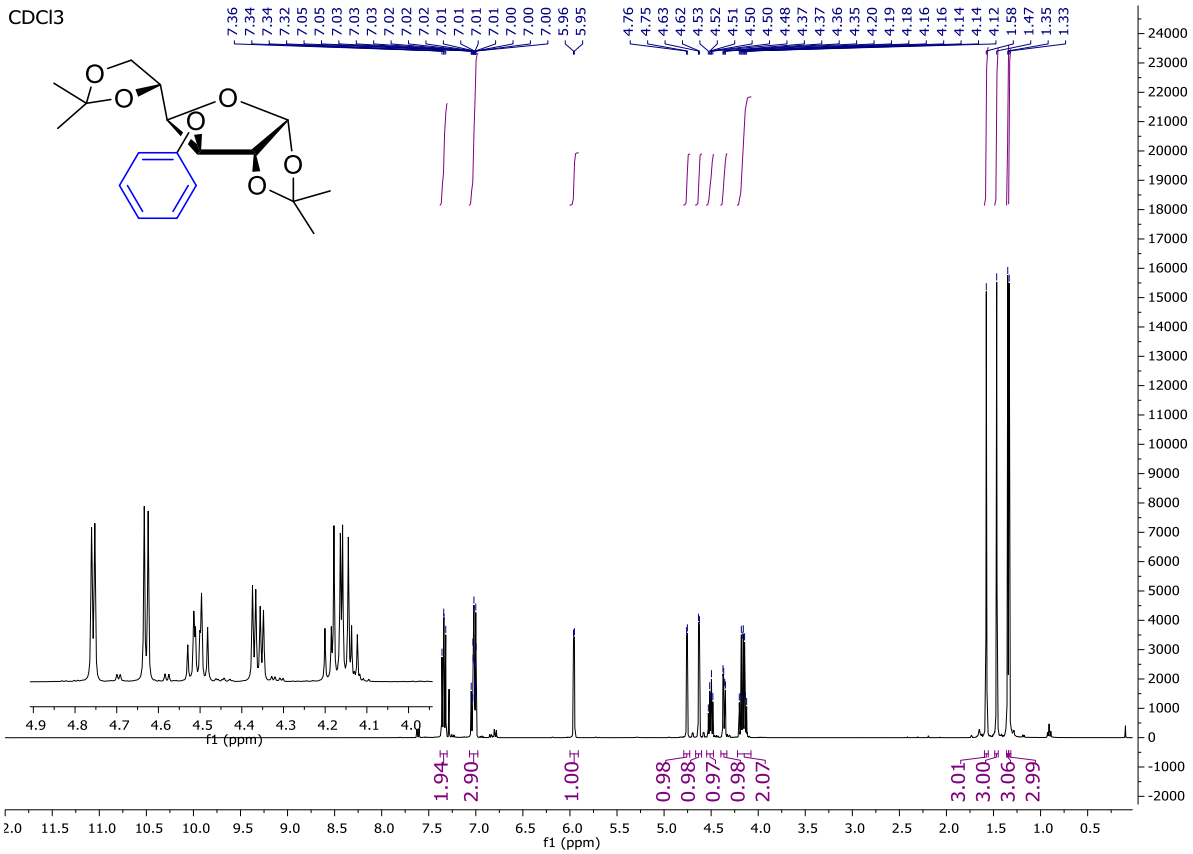


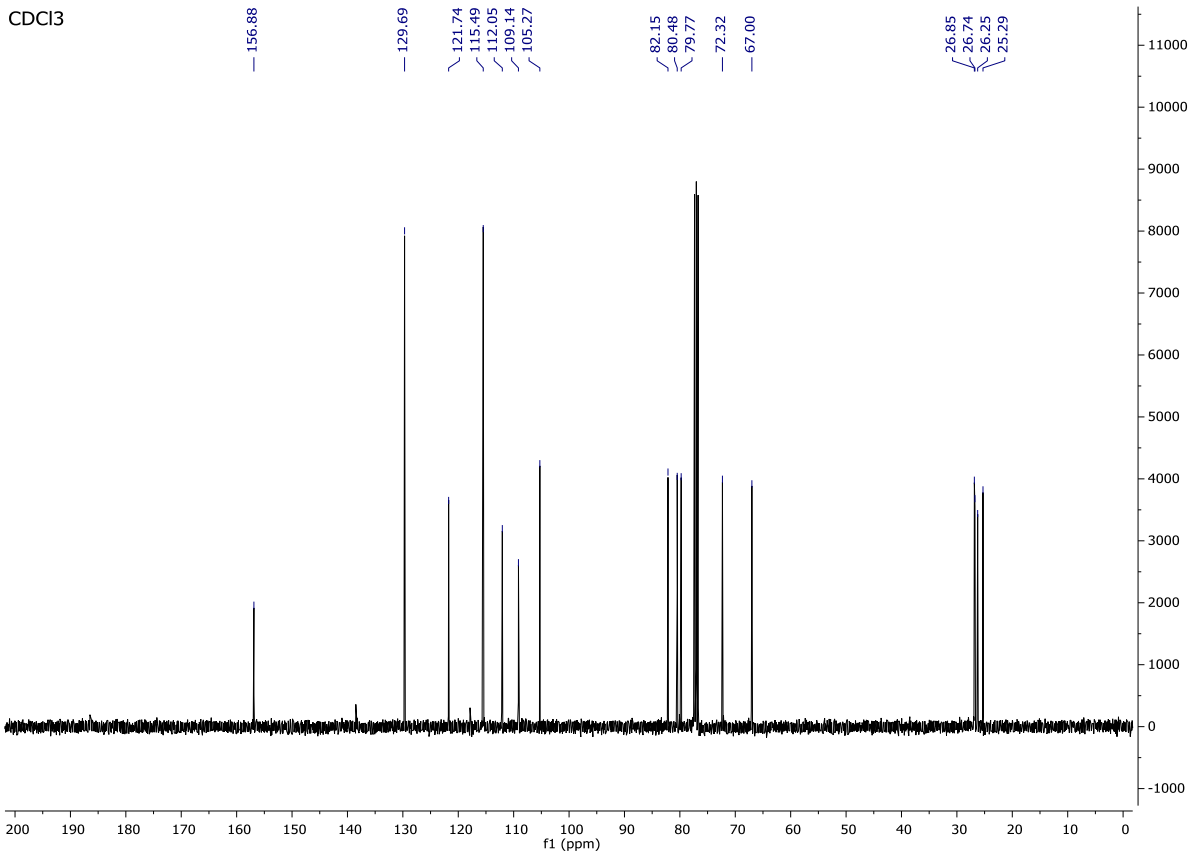
II.3.3 3-O-(2-Carbethoxyphenyl)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3r)



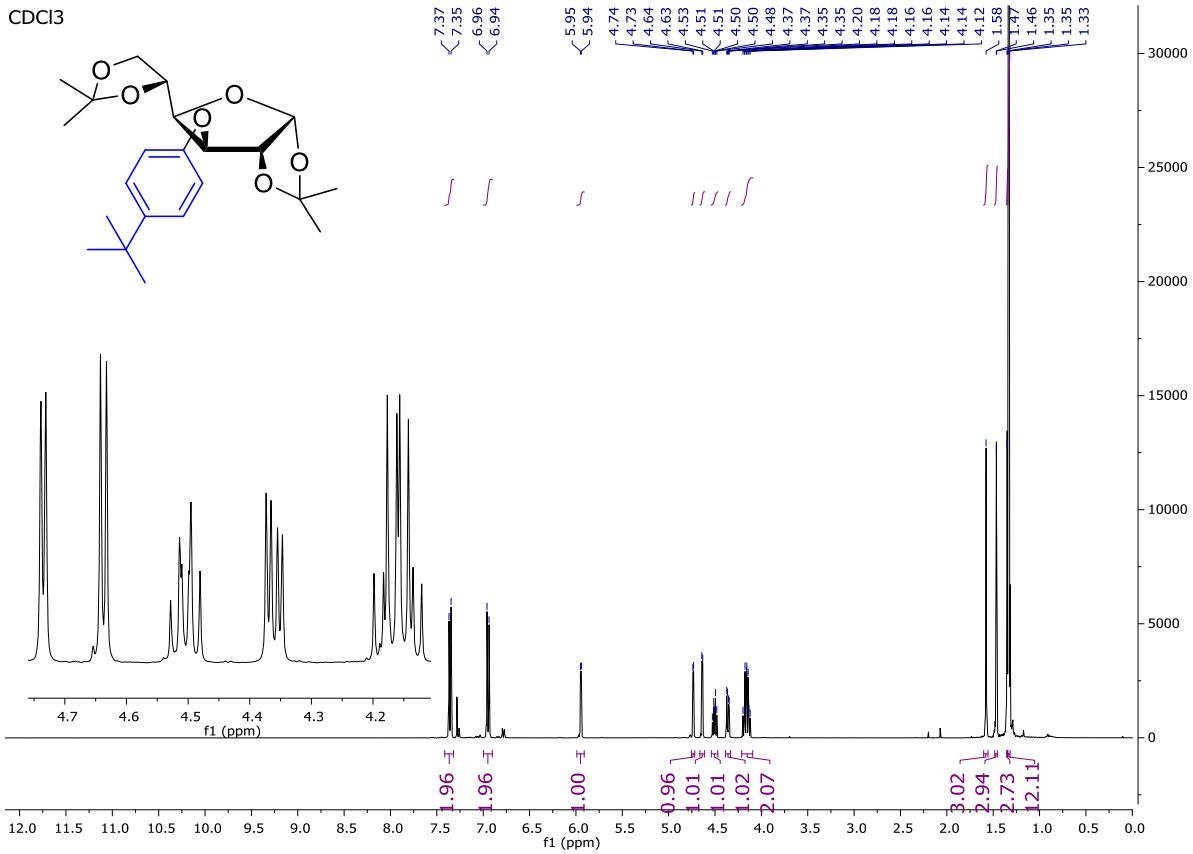


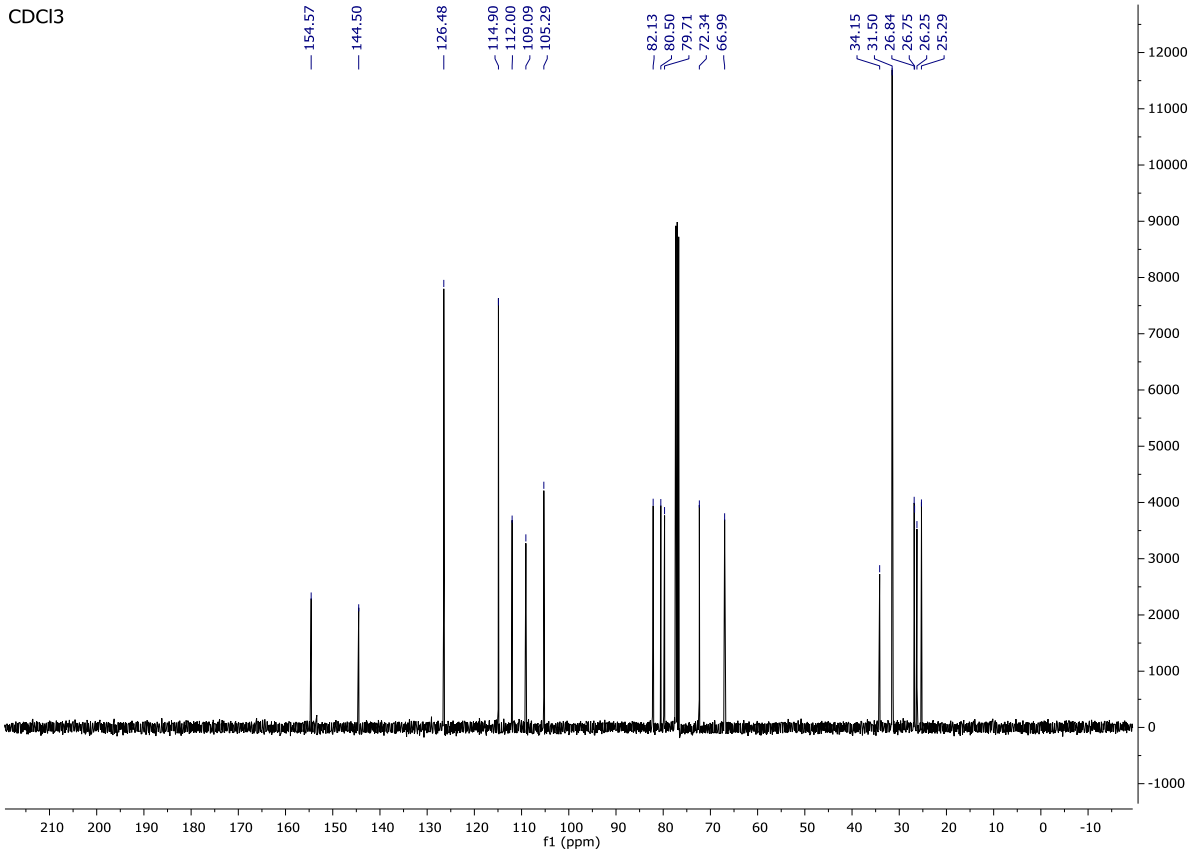
II.3.4 3-O-(Phenyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3s)



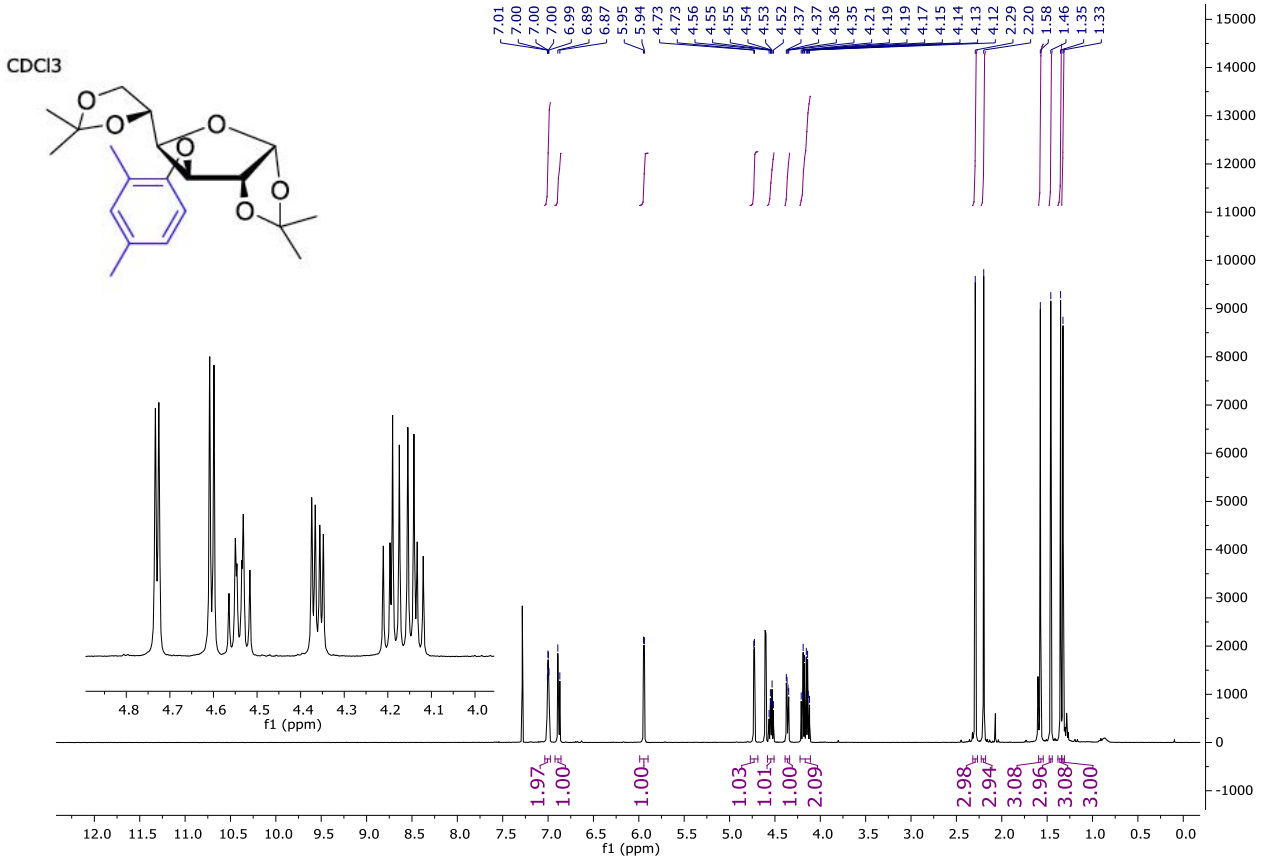


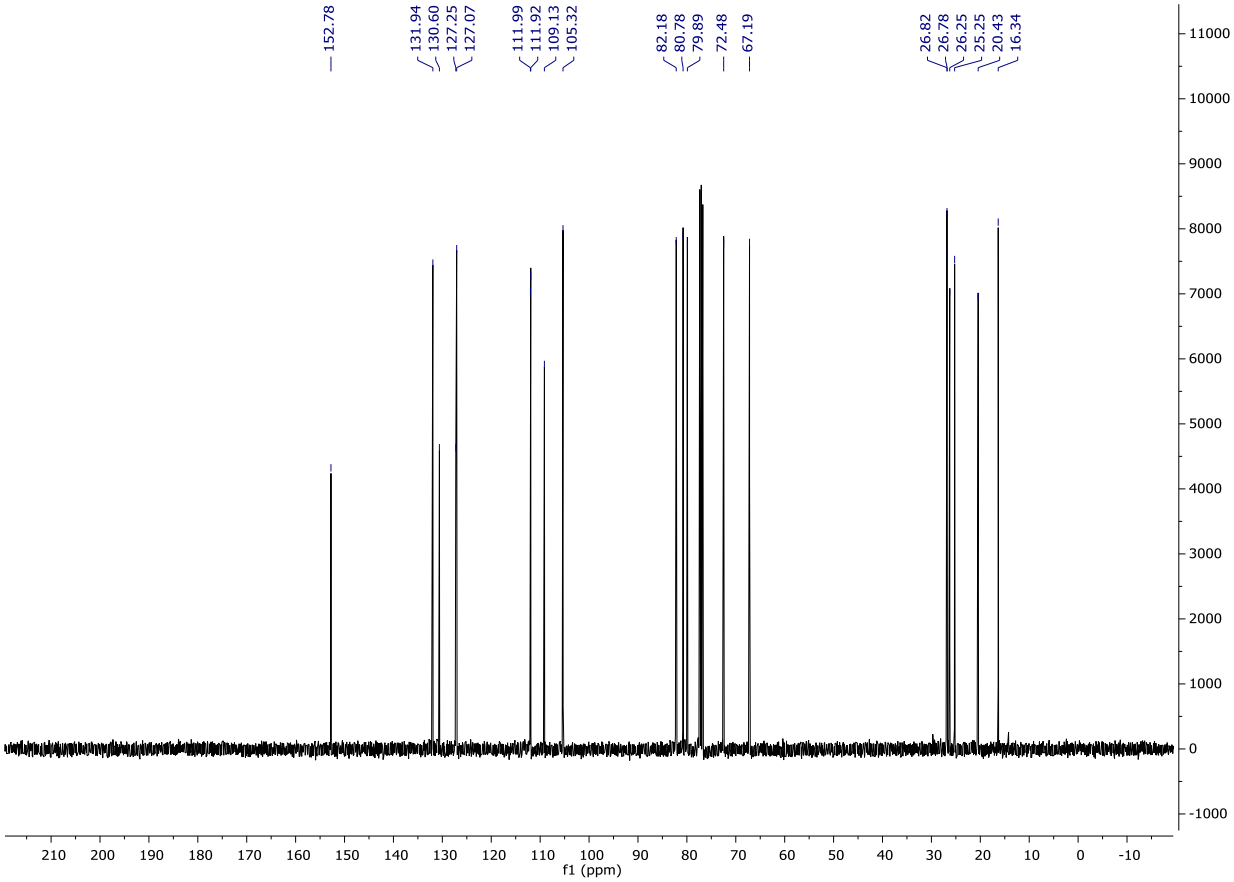
II.3.5 3-O-(4-Tertbutylphenyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3t)



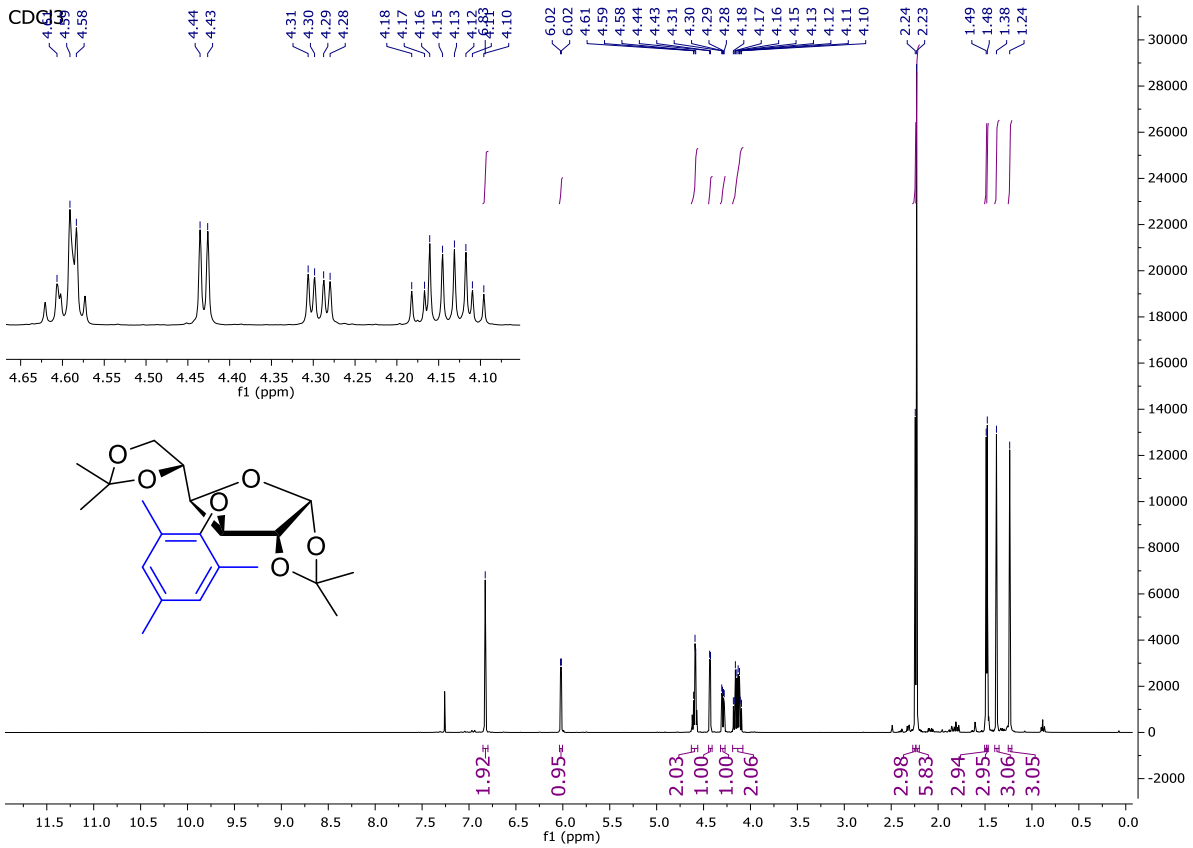


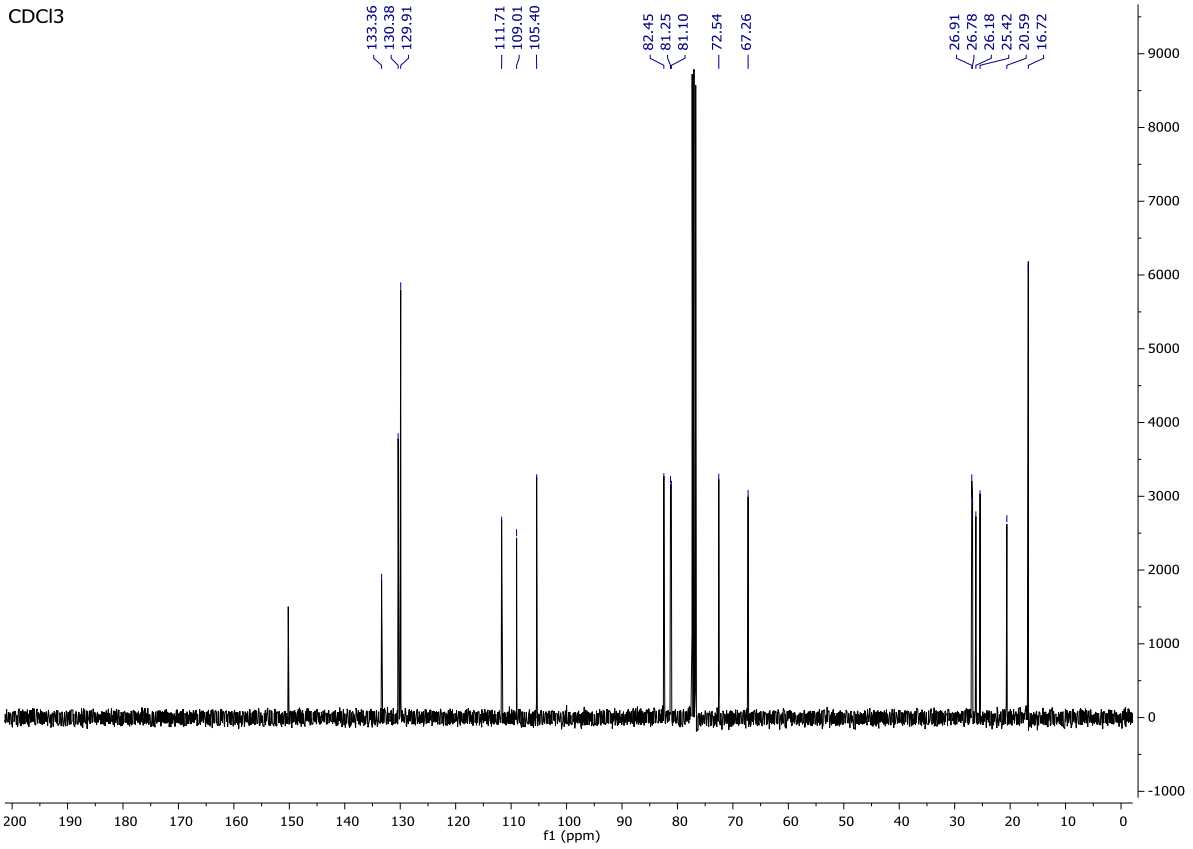
II.3.6 3-O-(1,4-Dimethylphenyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3u)



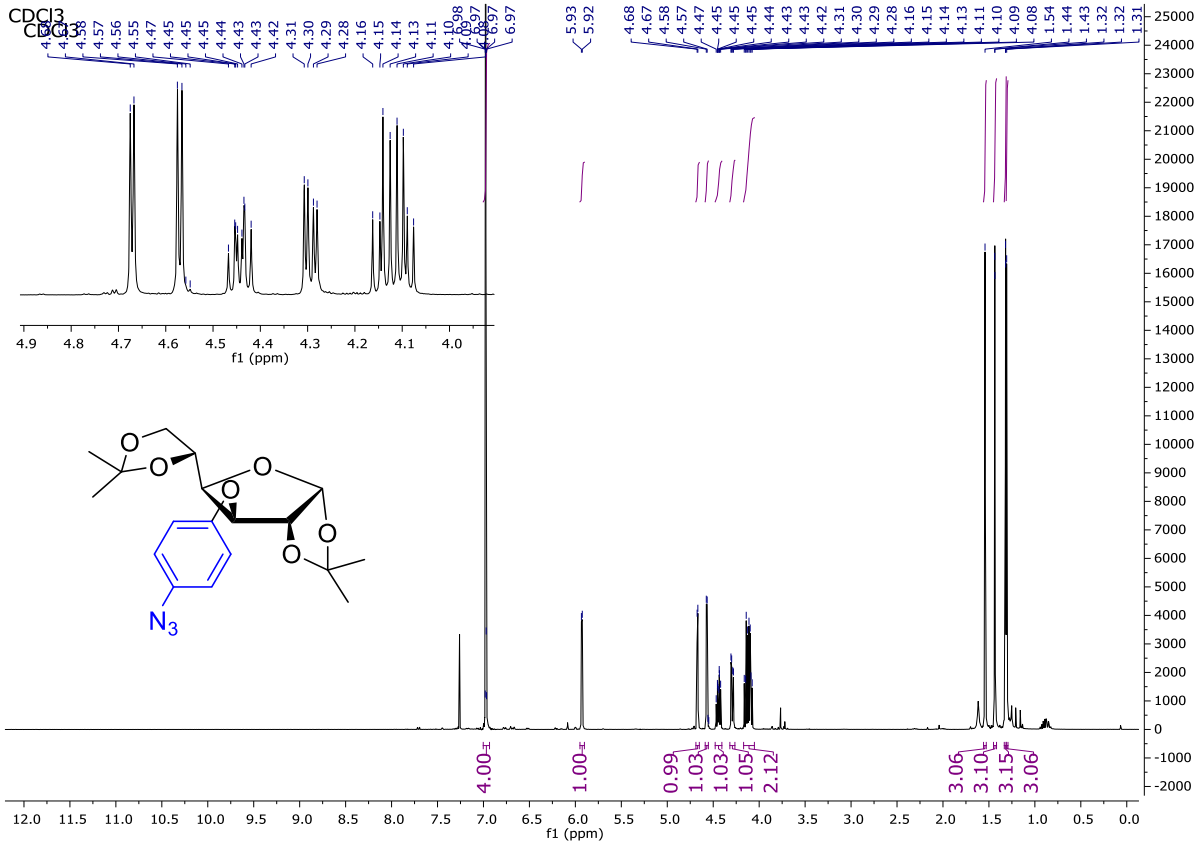


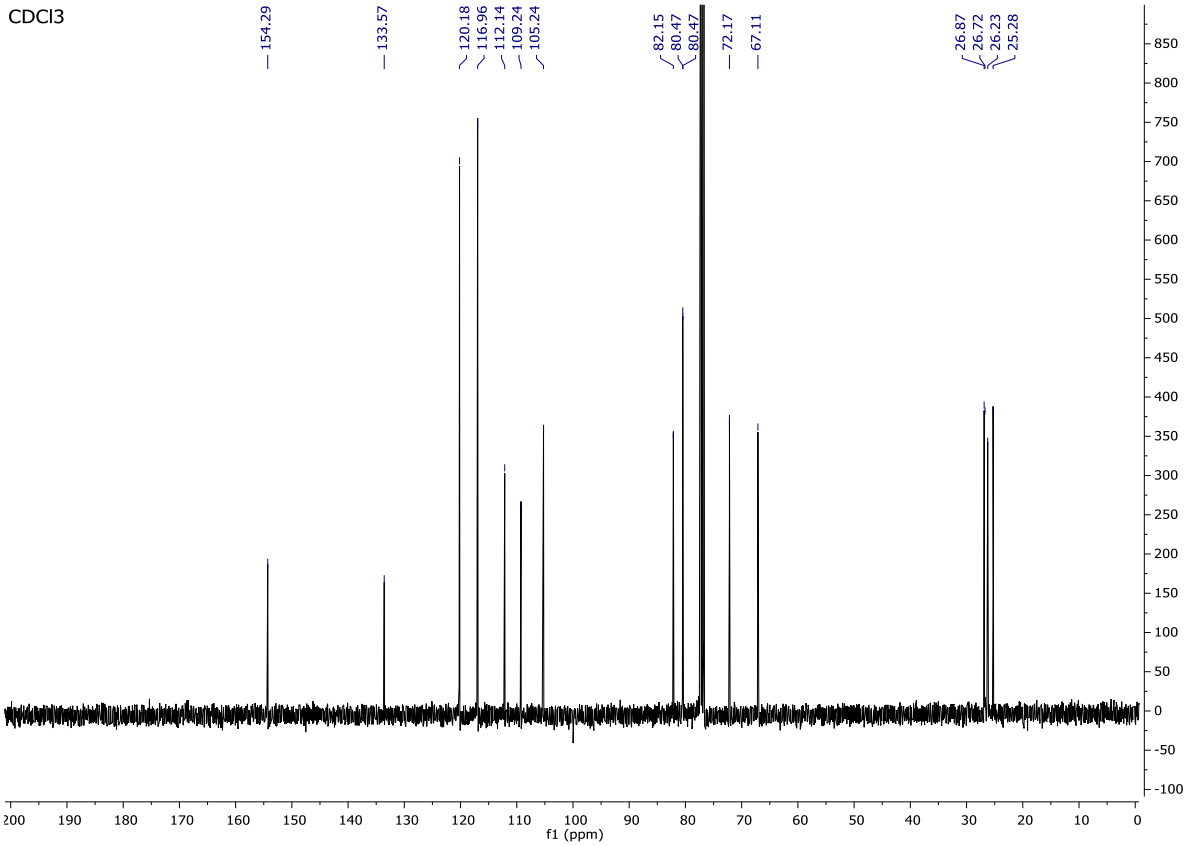
II.3.7 3-O-(Mesityl)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3v)



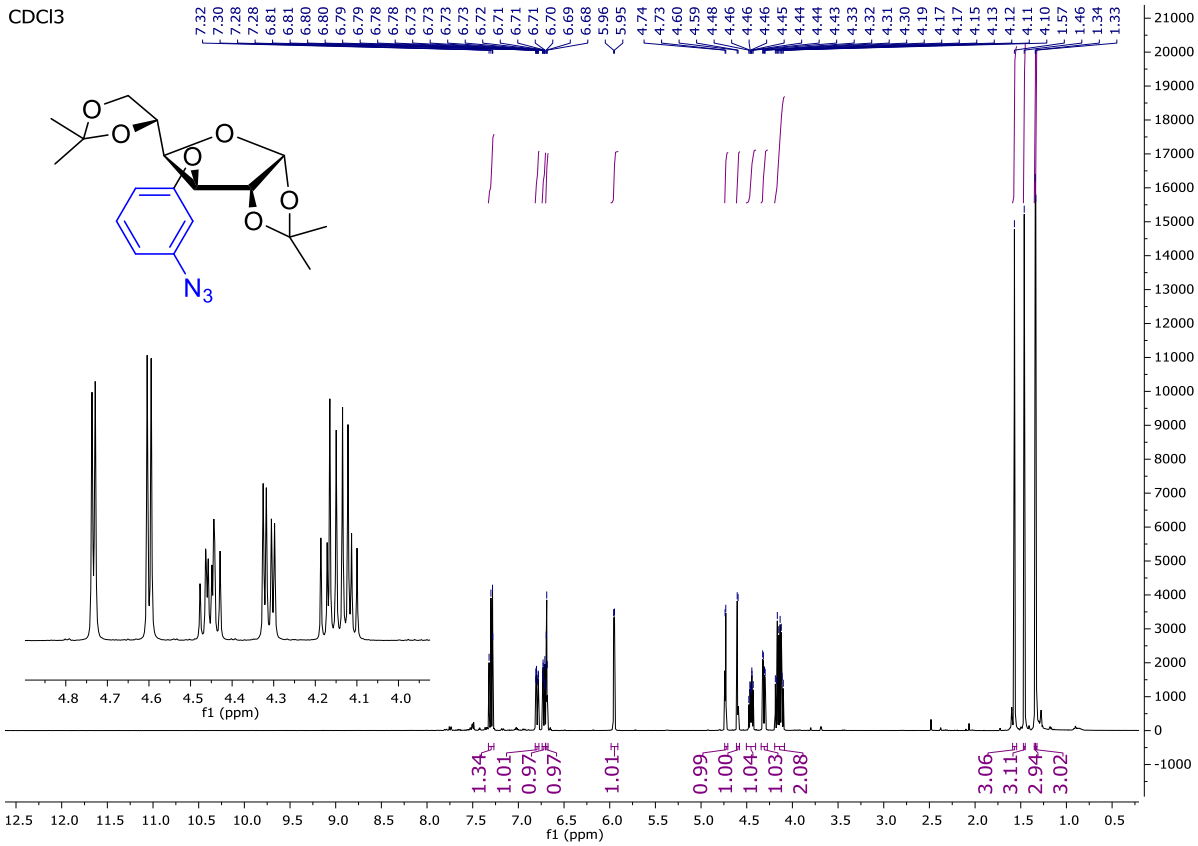


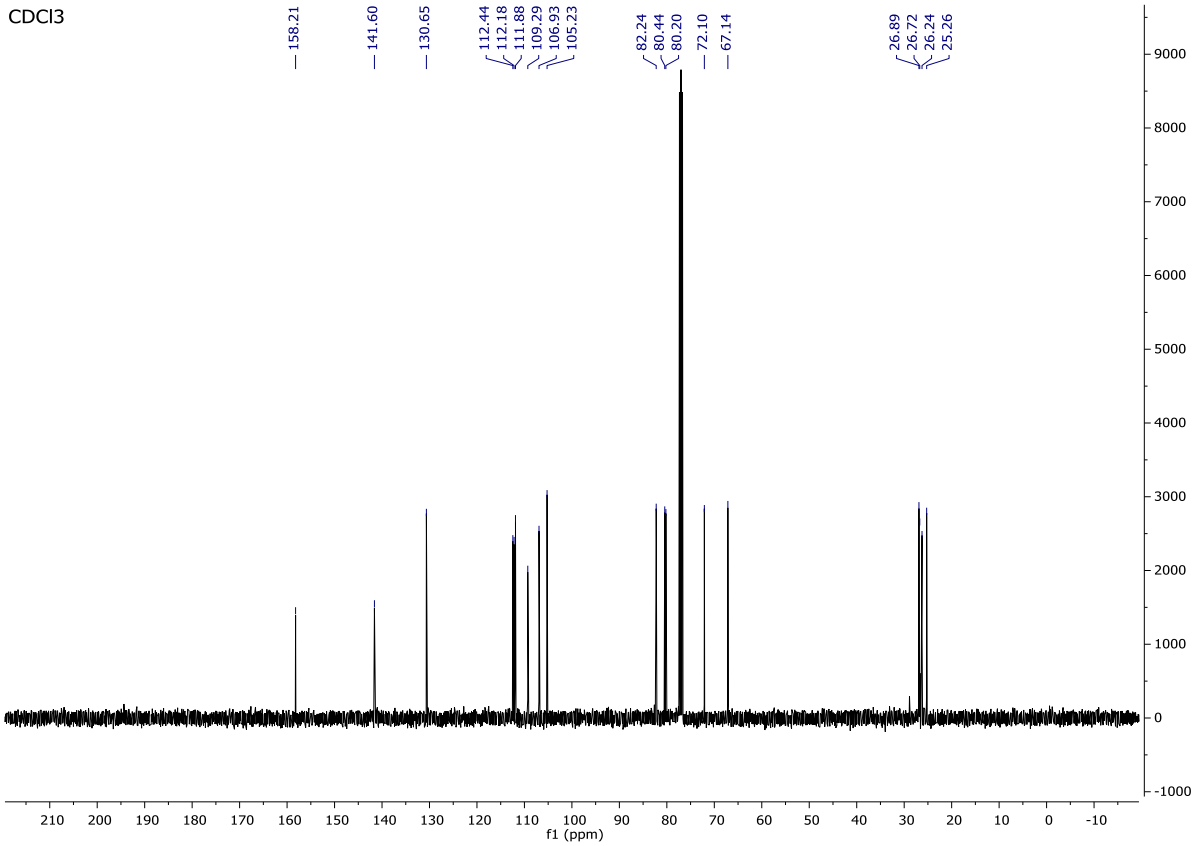
II.3.8 3-O-(4-Azidophenyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3w)



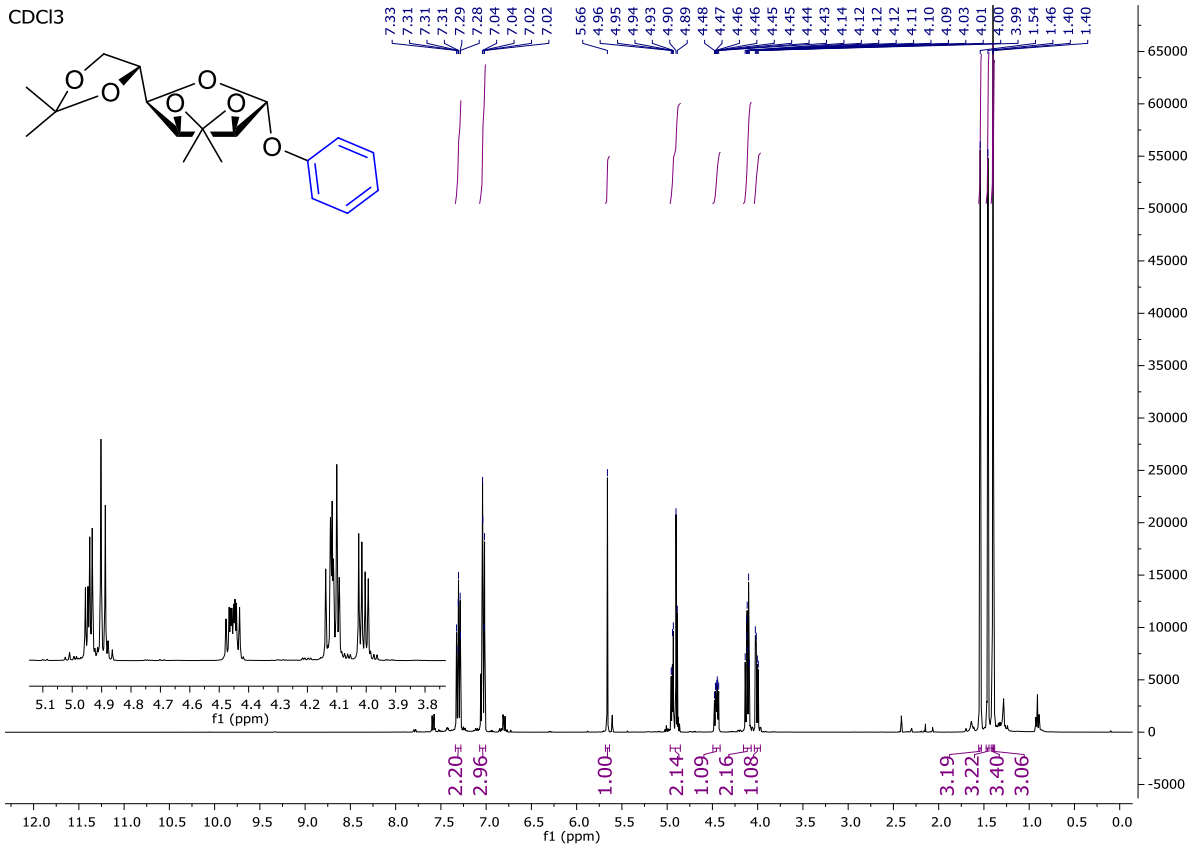


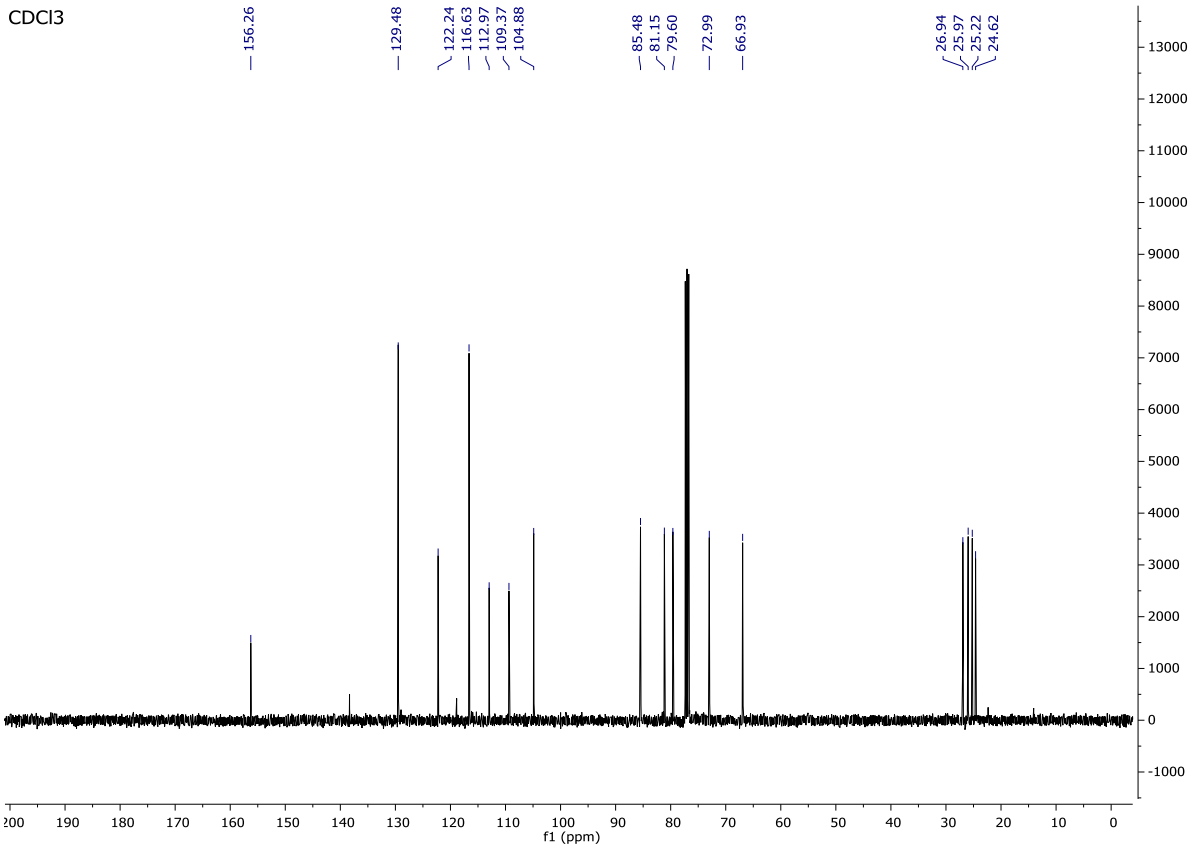
II.3.9 3-O-(3-Azidophenyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3x)



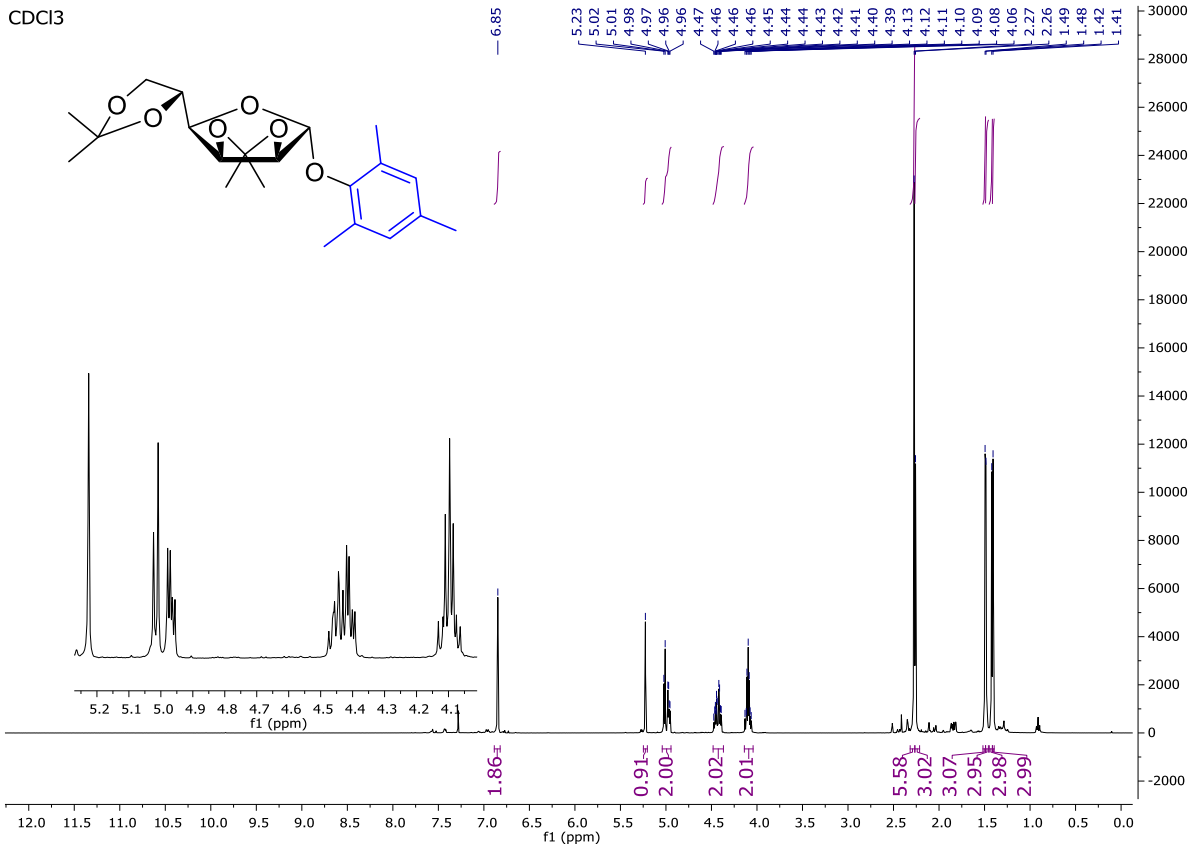


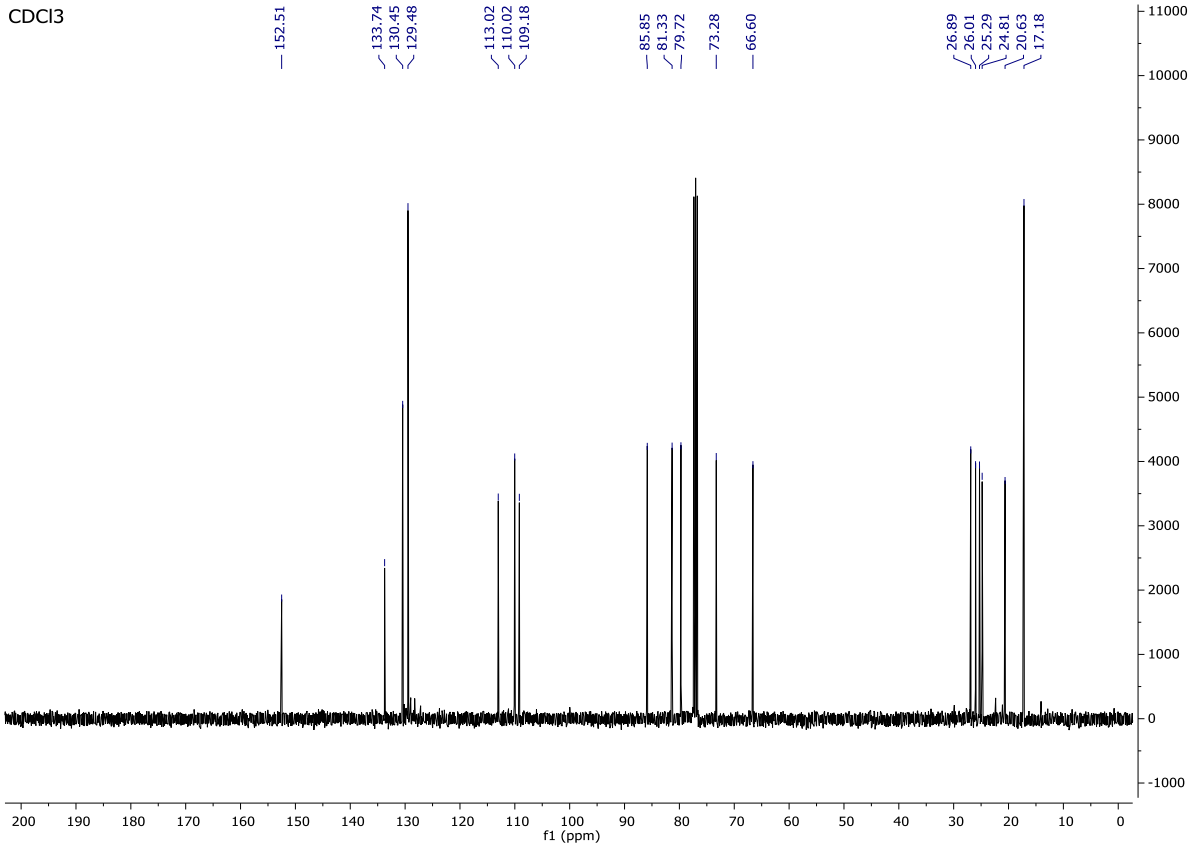
II.3.10 Phenyl-2,3:5,6-Di-O-isopropylidene-α-D-mannofuranoside (3y)



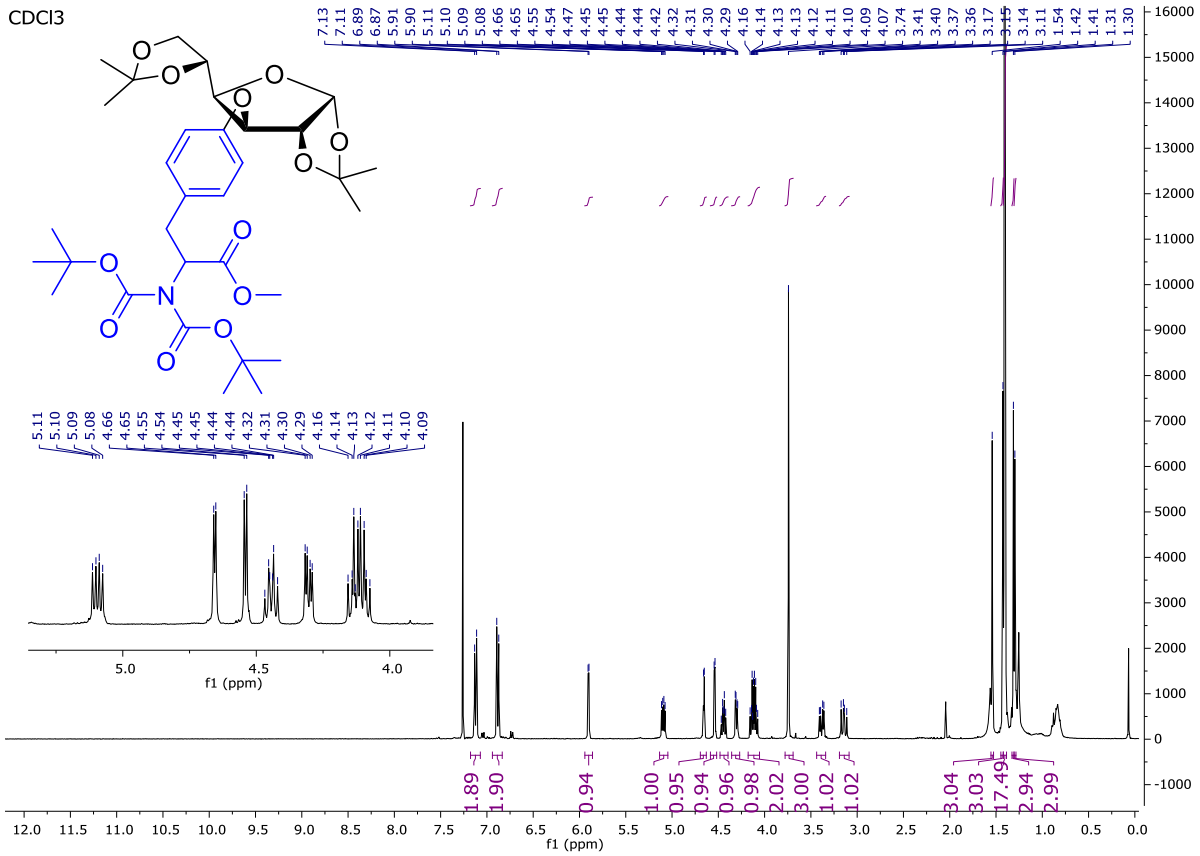


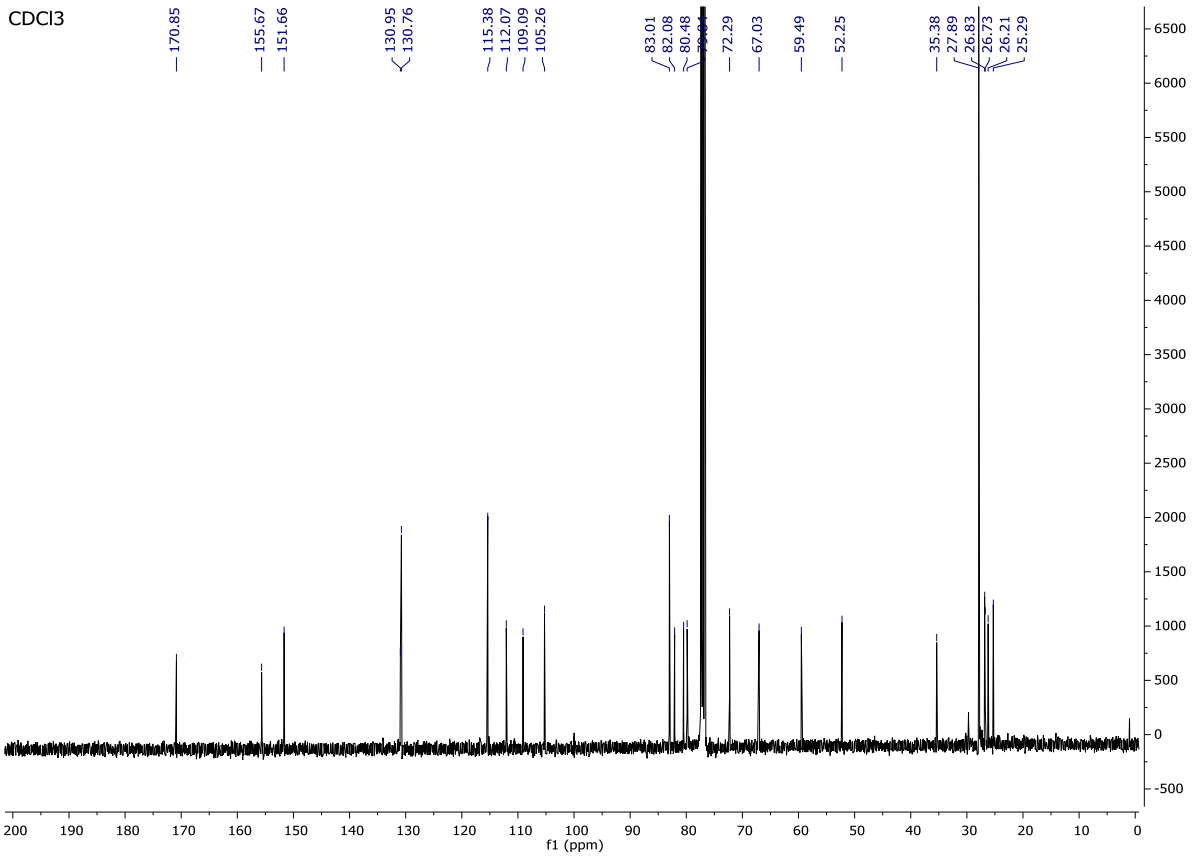
II.3.11 Mesityl-2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside (3z)



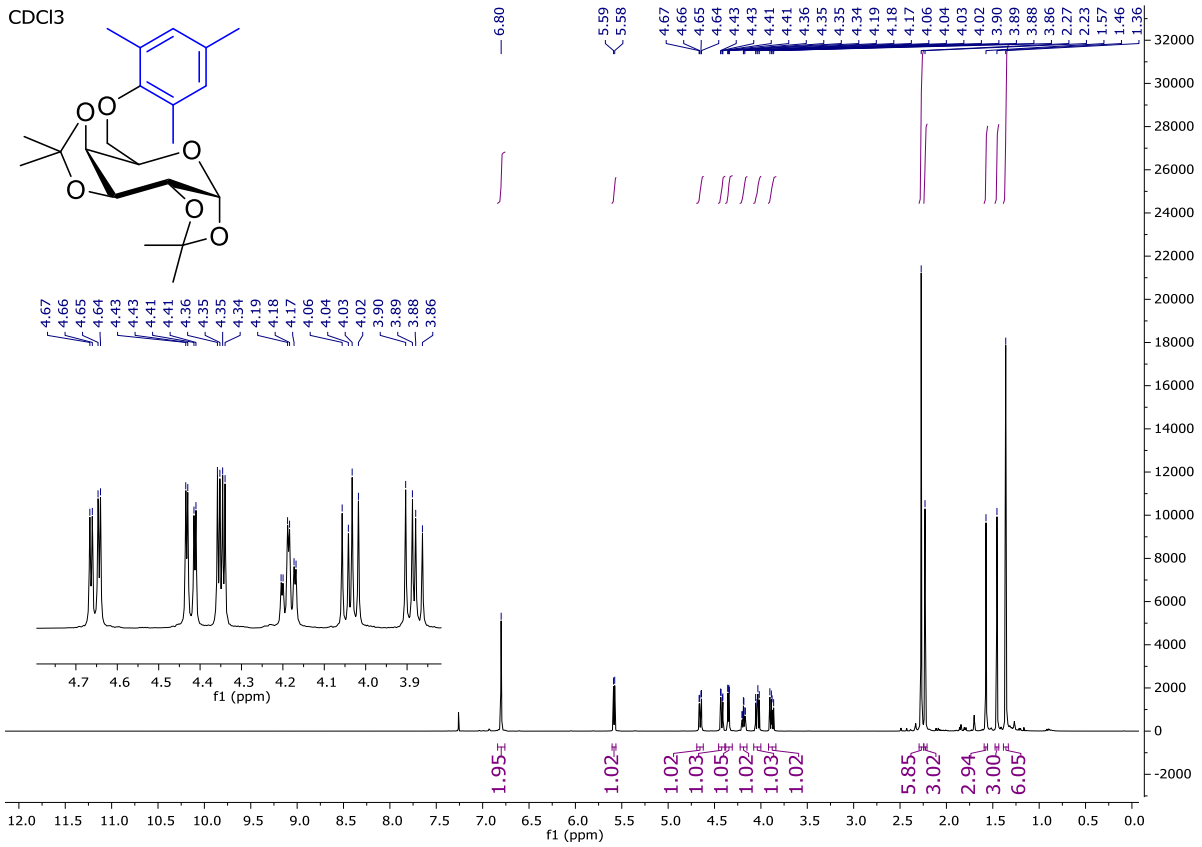


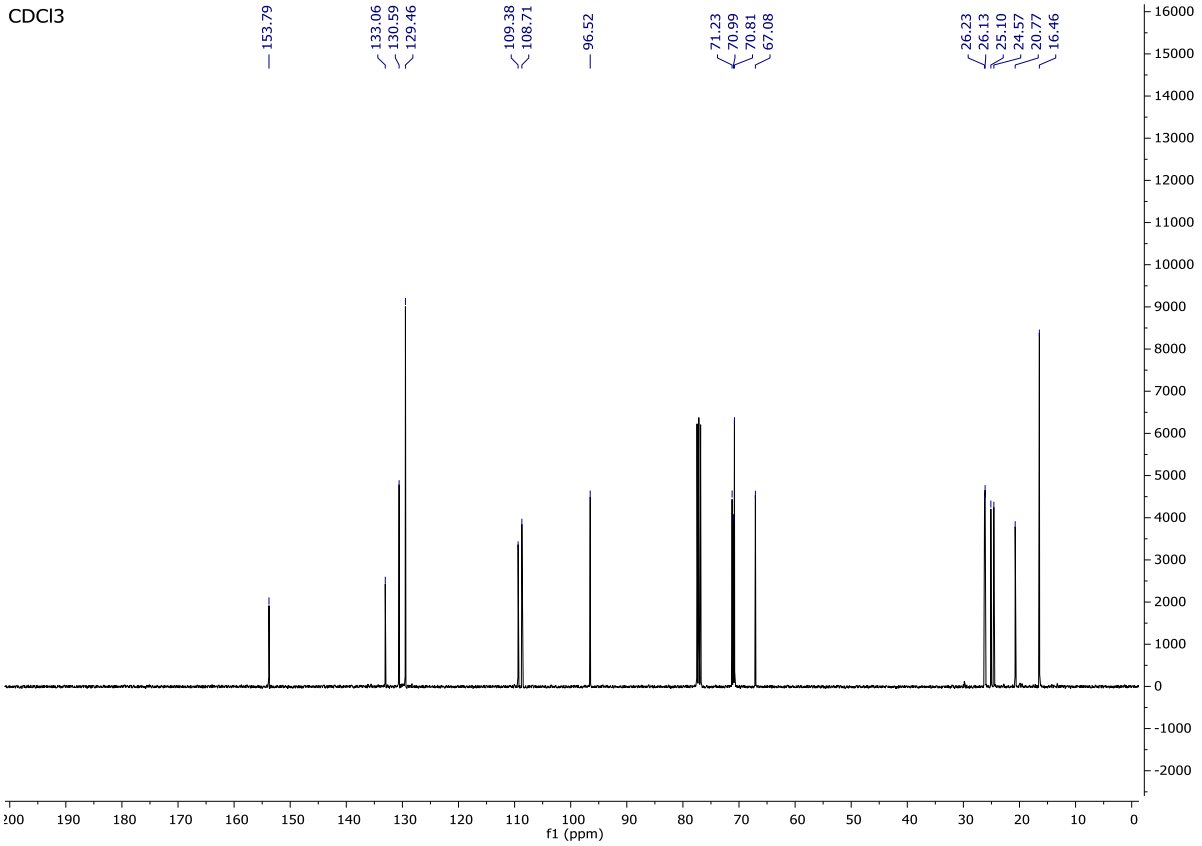
II.3.12 3-O-(N-Boc$_2$-COOMe-L-phenylalanyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3aa)



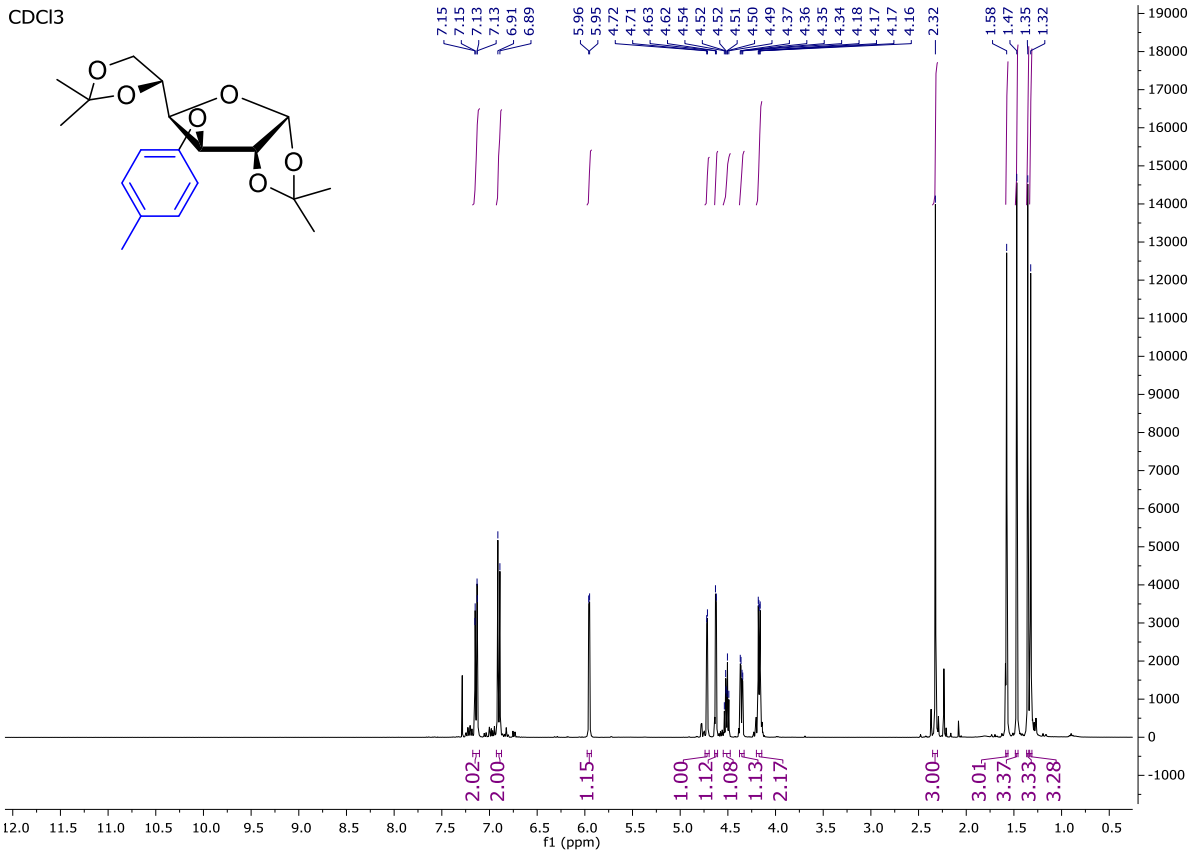


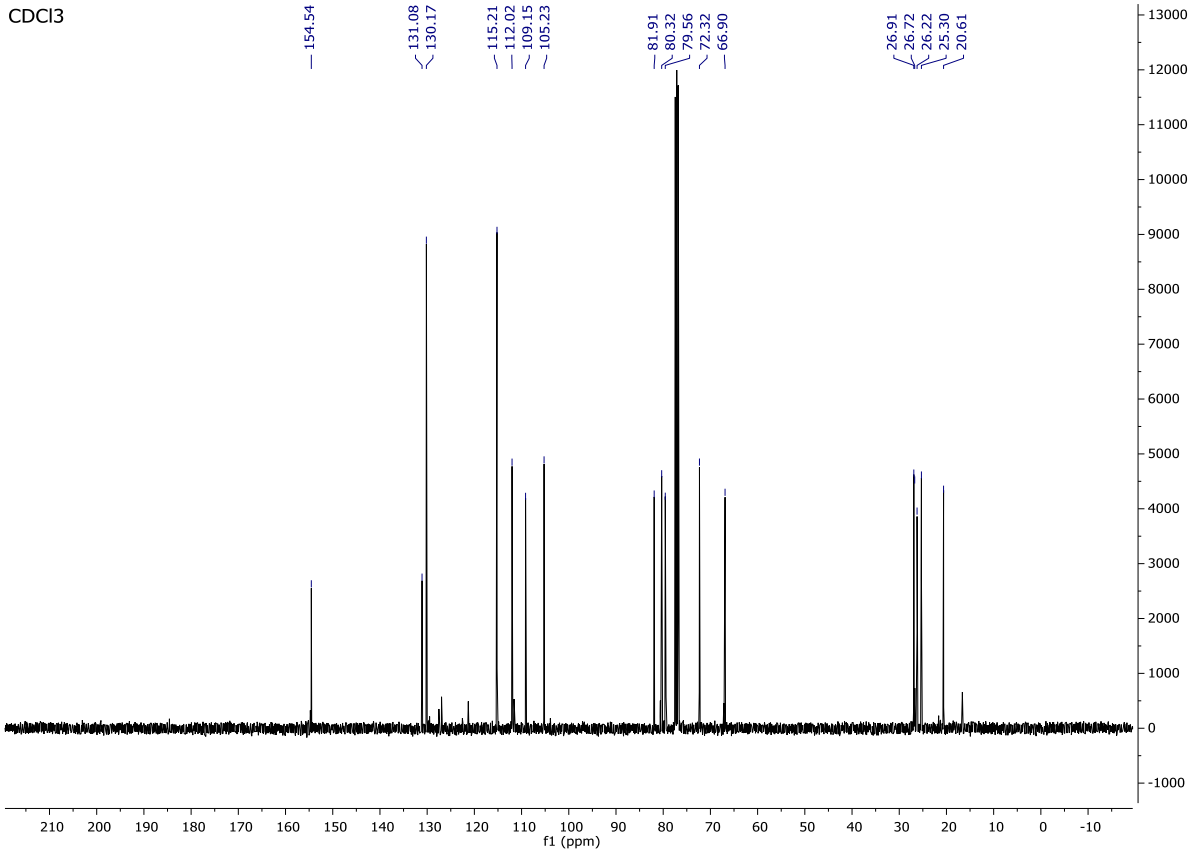
II.3.13 6-O-(Mesityl)- 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (3ab)



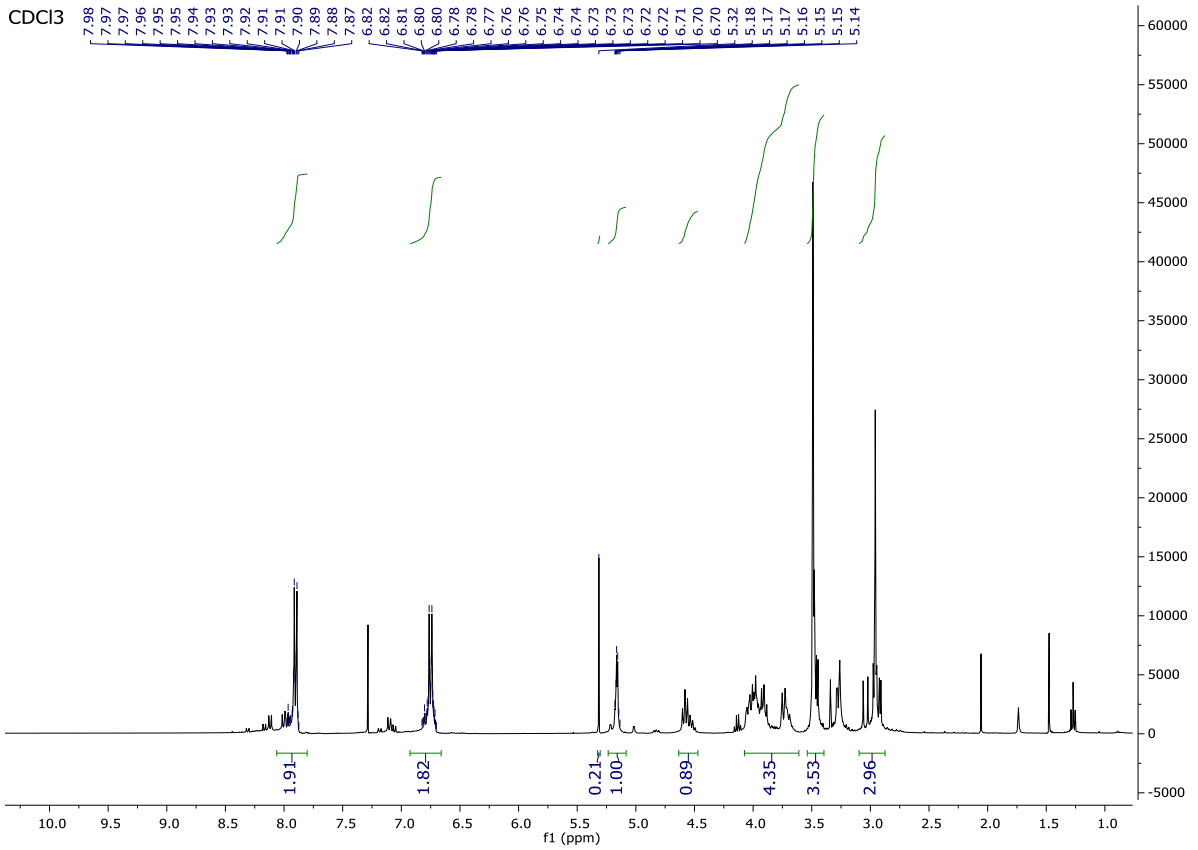


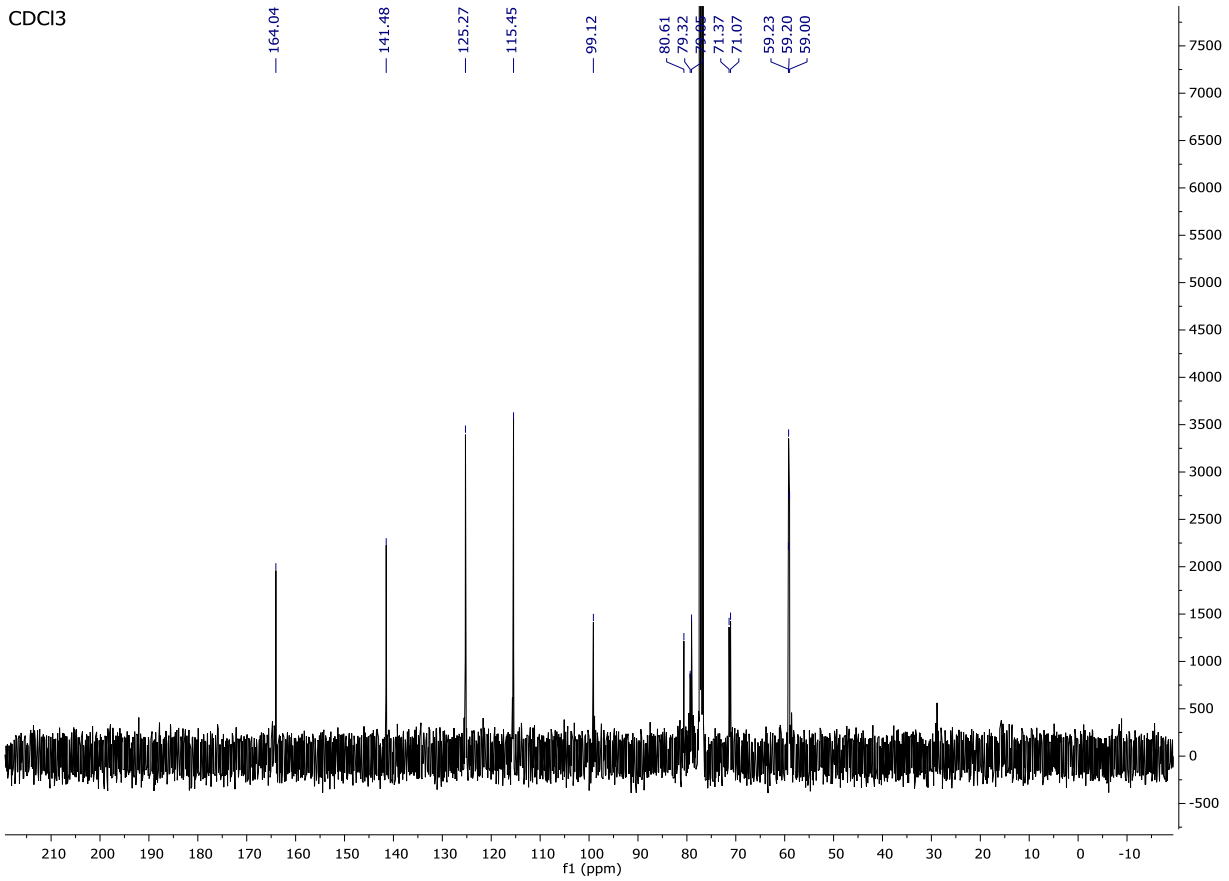
II.3.14 3-O-(4-Tolyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (3ac)





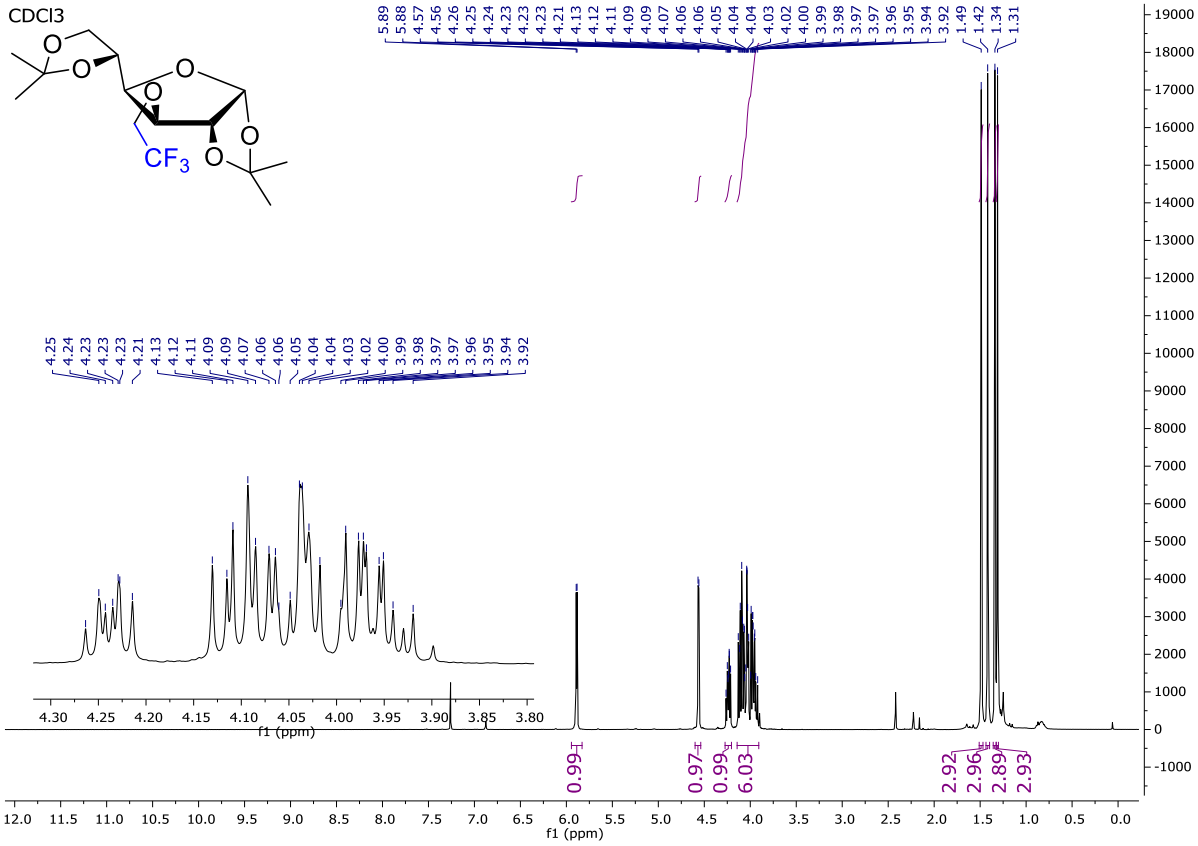
II.2.16 Heptakis(2,6-di-O-mehtyl-4-nitrophenyl)-β-cyclodextrine (4)

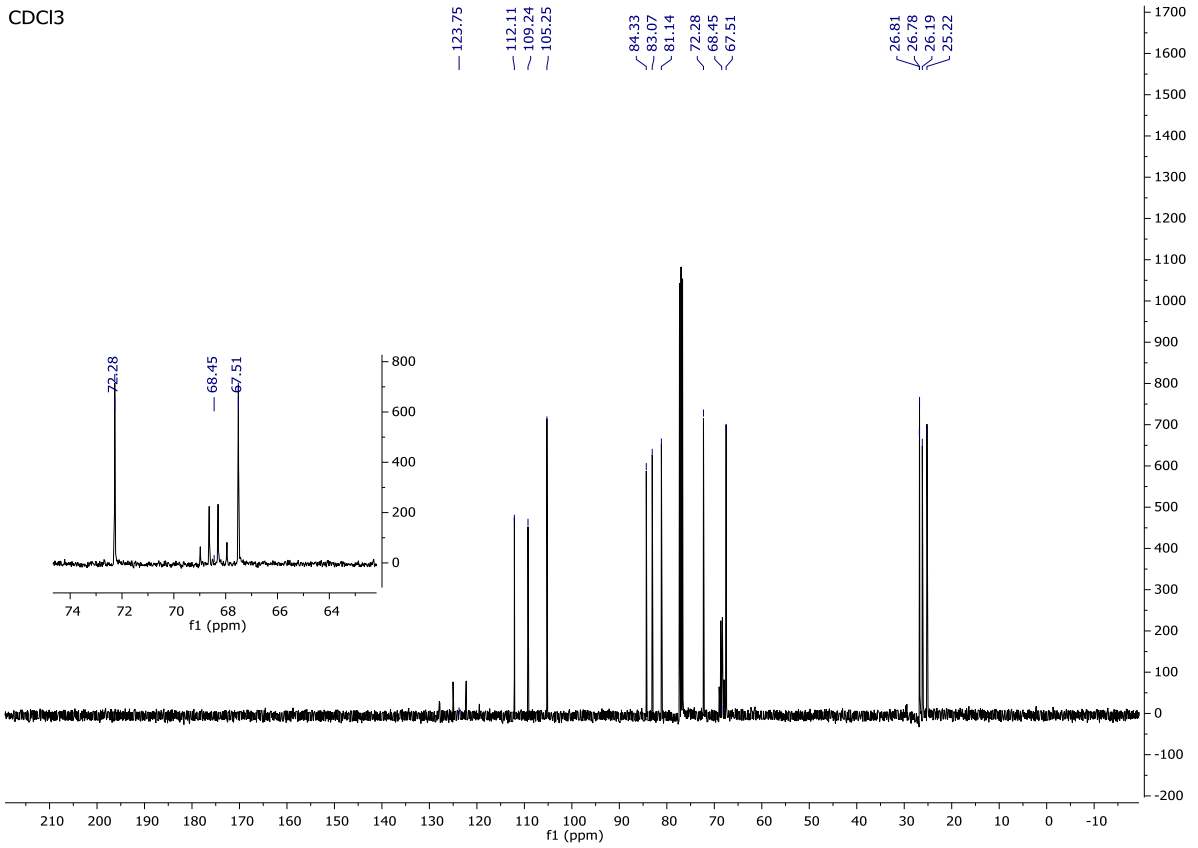


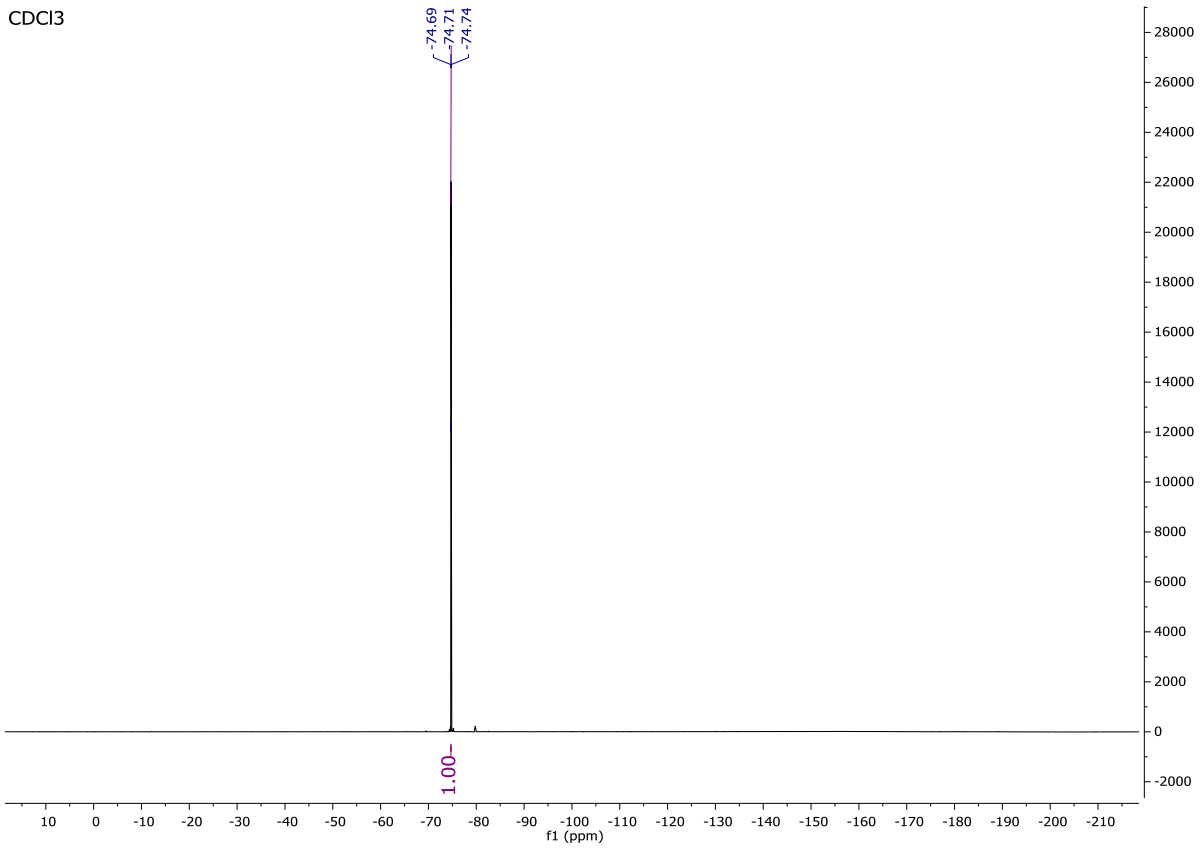


II.4 Spectra of Trifluoroethylations

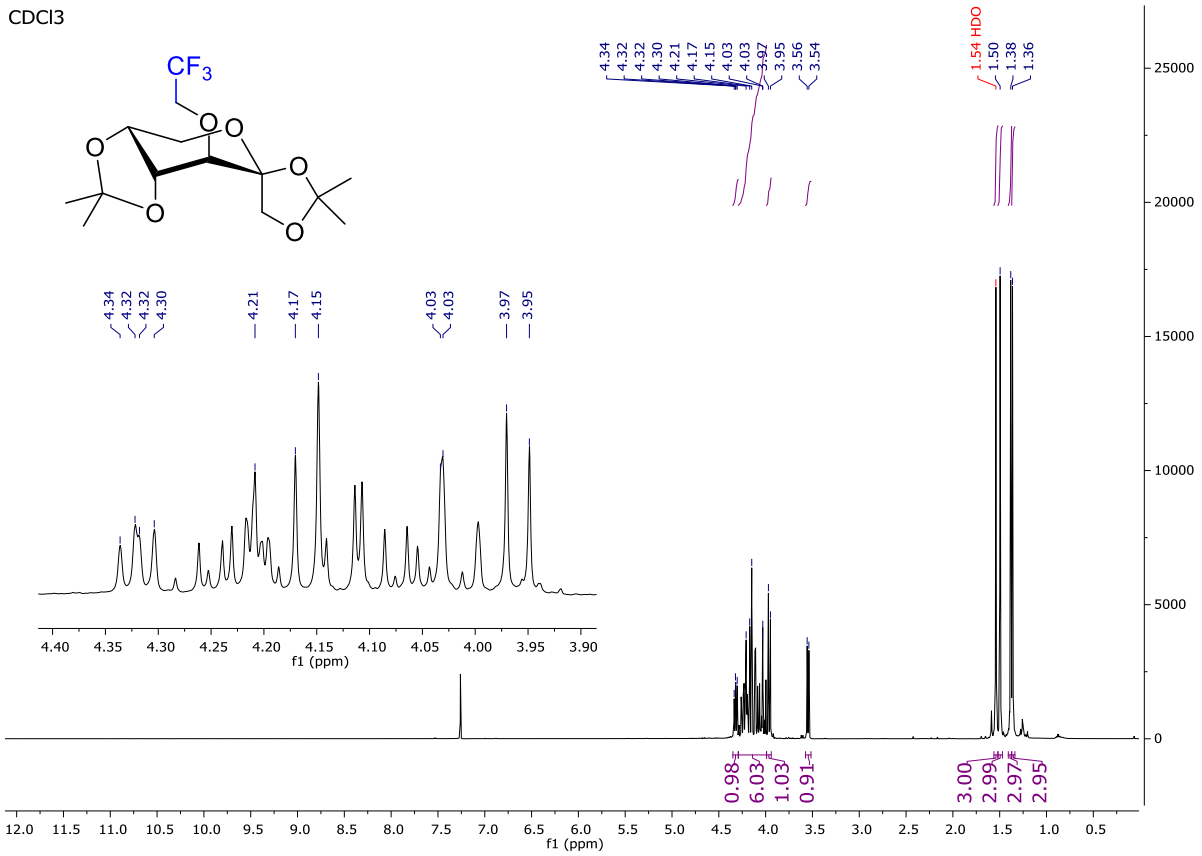
II.4.1 3-O-(2,2,2-Trifluoroethyl)- 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (6a)

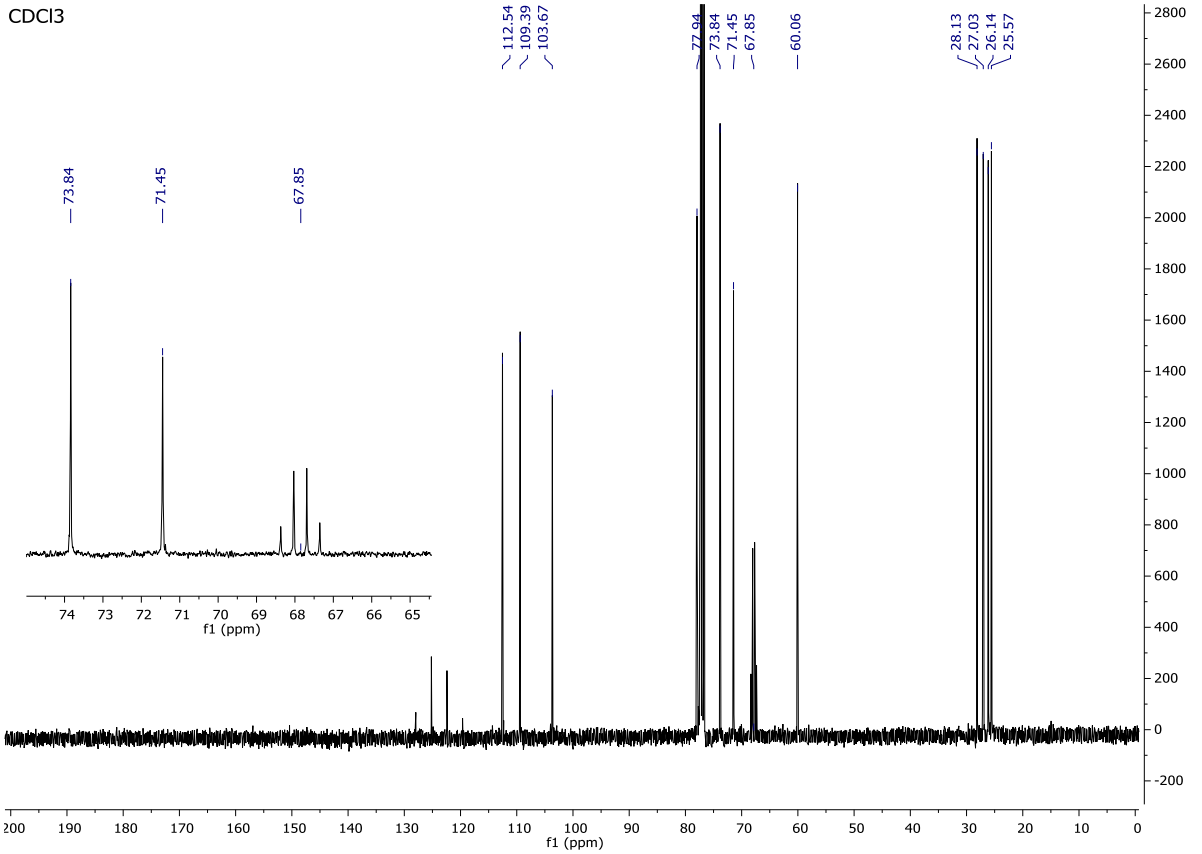


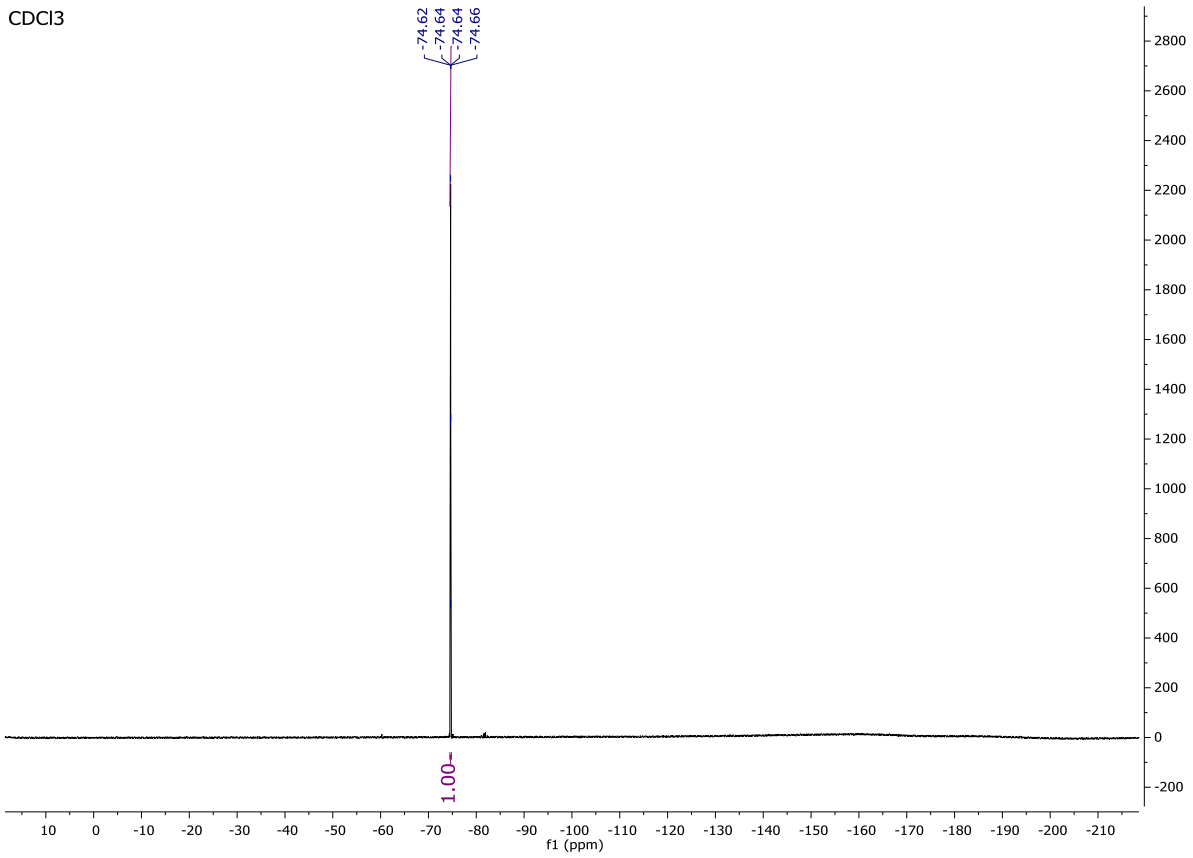



CDCl3
-74.69
-74.71
-74.74
1.00
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

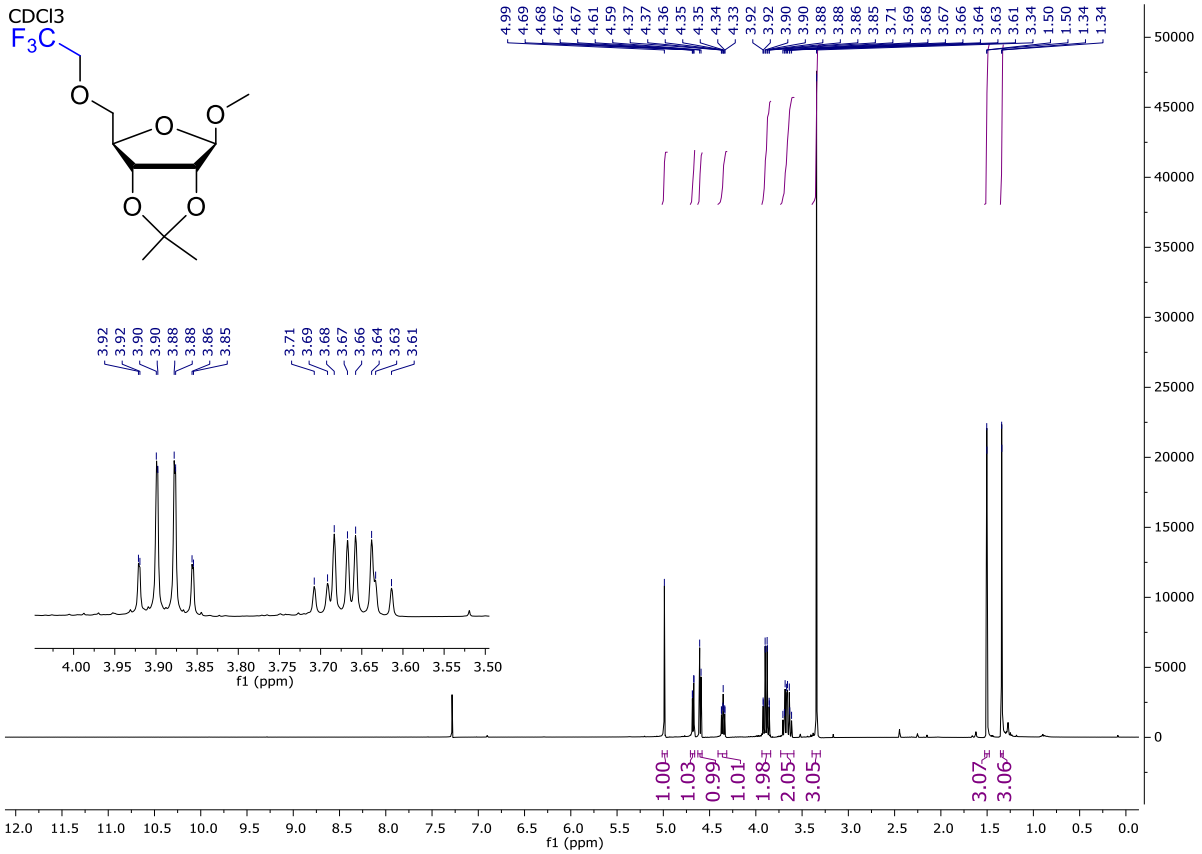
II.4.2 3-O-(2,2,2-Trifluoroethy)-1,2:4,5-Di-O-isopropylidene-ß-D-fructopyranose (6b)

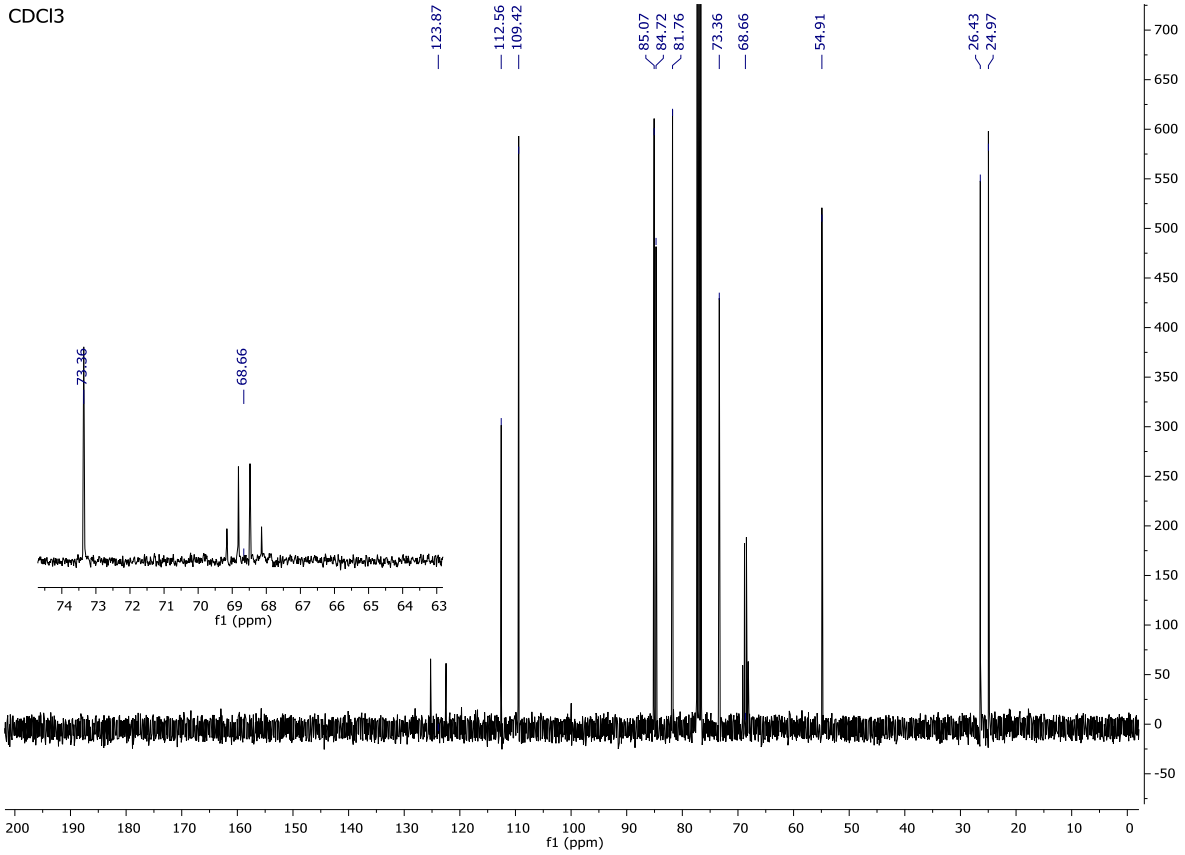


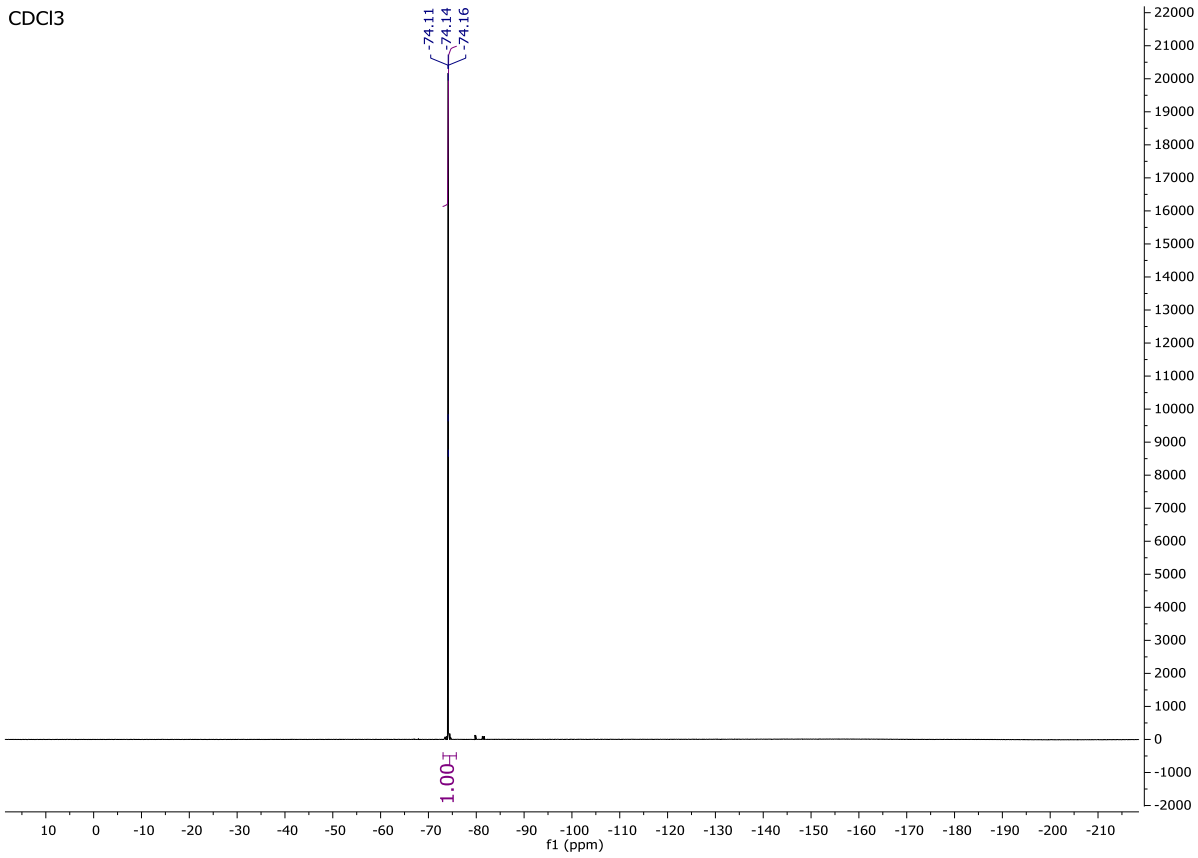



CDCl3
-74.62
-74.64
-74.64
-74.66
1.00
f1 (ppm)

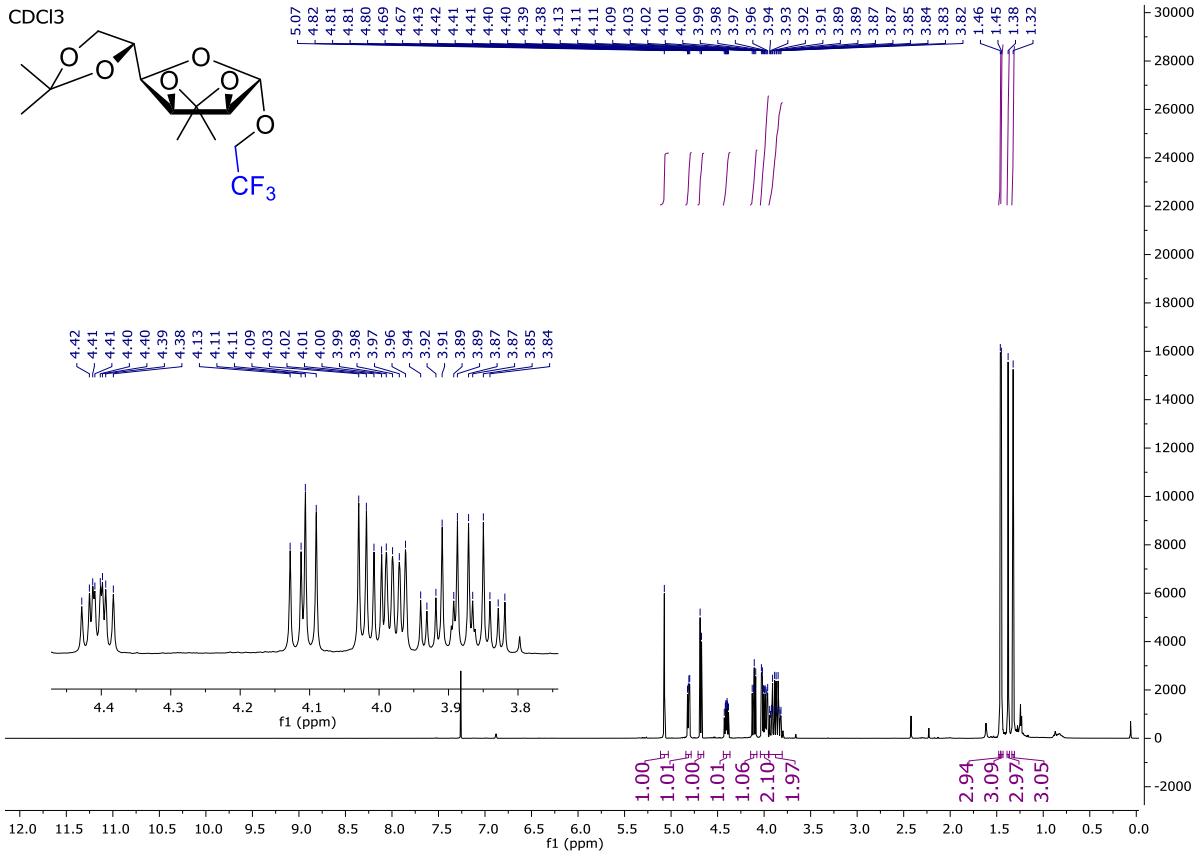
II.4.3 5-O-(2,2,2-Trifluoroethyl)-1-O-Methyl-2,3-O-isopropylidene-α-D-riboside (6c)

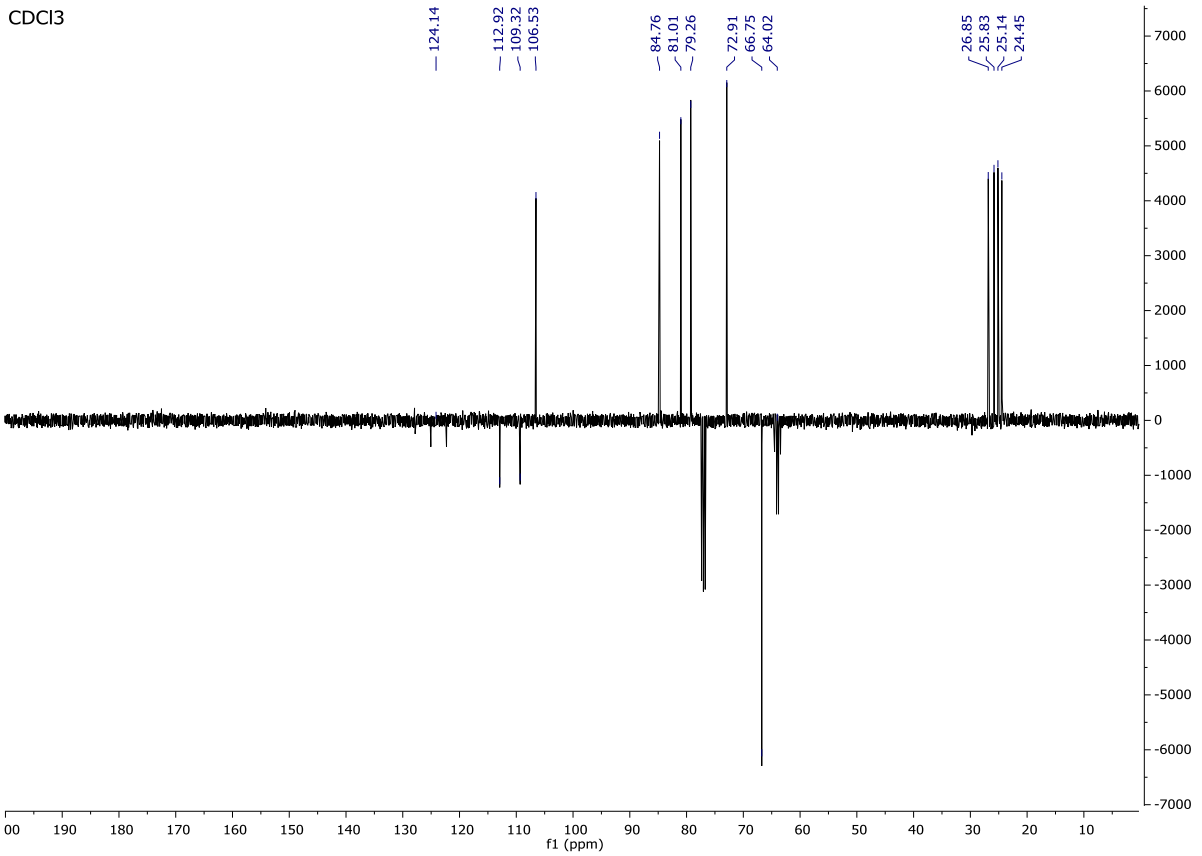


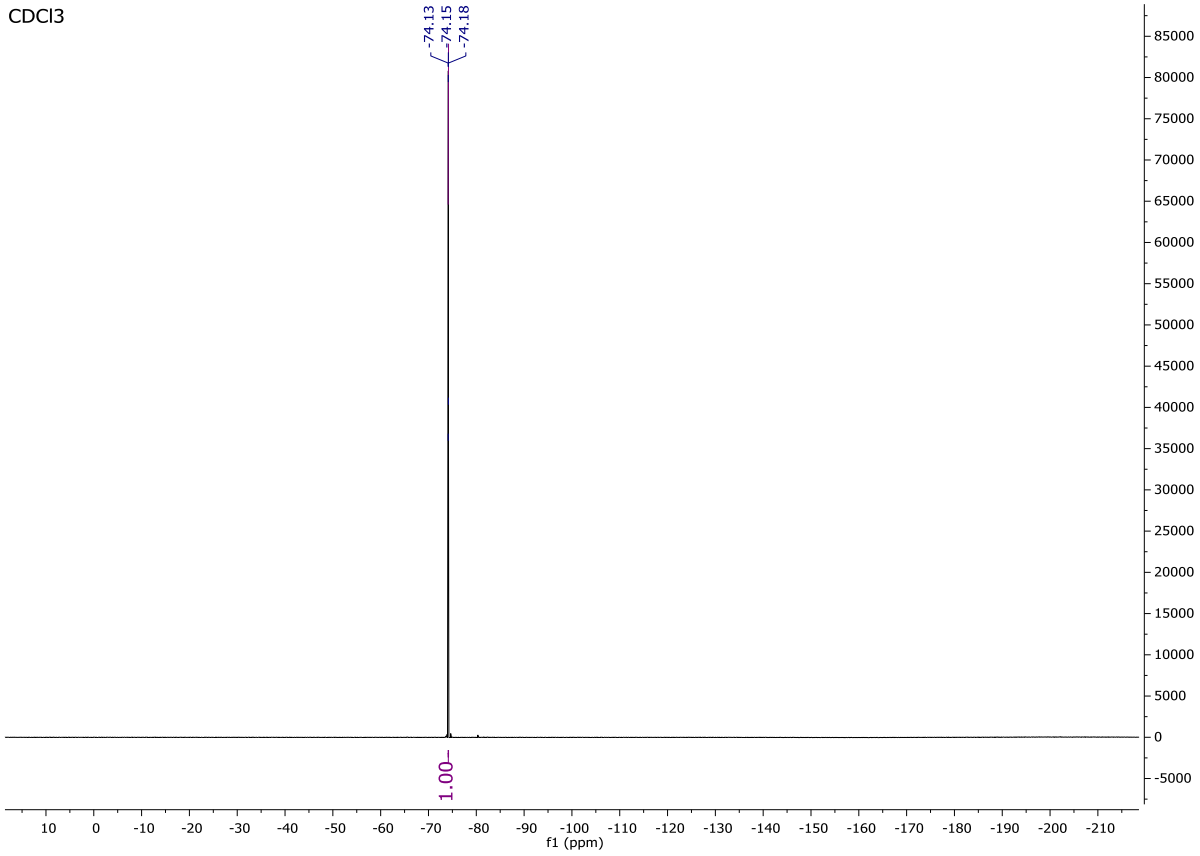



CDCl3
-74.11
-74.14
-74.16
1.00
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

II.4.4 2,2,2-Trifluoroethyl-2,3:5,6-Di-O-isopropylidene-α-D-mannofuranoside (6d)






CDCl3
-74.13
-74.15
-74.18
1.00
f1 (ppm)