

Electronic Supplemental Information (ESI)

Barton radical reactions of 2-C-branched carbohydrates

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General methods:

All reactions requiring anhydrous conditions were performed under a positive pressure of argon using oven-dried glassware (110 °C), which was cooled under argon. Solvents for anhydrous reactions were dried according to Perrin *et al.* Benzene and dichloromethane were distilled from calcium hydride and stored over molecular sieves. All commercial reagents were obtained from Sigma-Aldrich, Acros or Fluka Chemical Co. Progress of the reactions was monitored by tlc. Column chromatographies were performed on silica gel 60-120/ 100-200/ 230-400 mesh obtained from ACROS Organics Belgium. Typical syringe and cannula techniques were used to transfer air- and moisture-sensitive reagents. IR spectra were recorded on a Perkin – Elmer infrared spectrometer model 599-B and model 1620 FT-IR. NMR spectra were recorded either on a Bruker Avance 300 or Avance 500 or Avance 600 instrument using deuterated chloroform solvent. Elemental analyses were performed on a vario EL III analyzer (Elementar Analysensysteme GmbH, Hanau, Germany). Optical rotations were measured on a JASCO P-1020 digital polarimeter at 589 nm, melting points on a Electrothermal MEL-TEMP apparatus (uncorrected).

Experimental procedures:

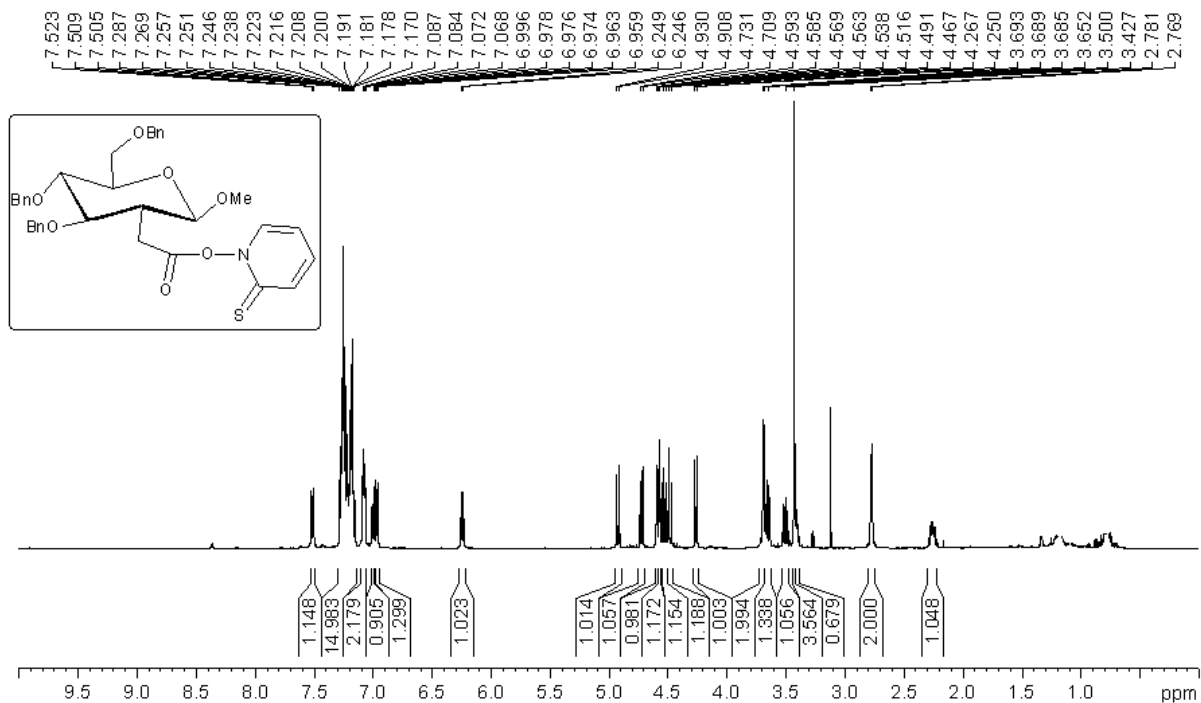
General procedure for the synthesis of Barton esters 4a: The sugar carboxylic acid **1a** (2.0 mmol) was dissolved in 30 mL of dry dichloromethane and was protected from light with an aluminum foil at 0 °C. 2-Mercaptopyridine N-oxide (390 mg, 2.5 mmol), *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide (EDCI) (620 mg, 4.0 mmol) and a catalytic amount of 4-(dimethylamino)pyridine (DMAP) (20 mg) were added and the mixture was stirred at 0 °C for 1-2 h until tlc showed complete conversion of the starting material. Then a saturated solution of sodium bicarbonate was added, and the mixture was extracted with dichloromethane (3x10 mL). The combined organic extracts were dried using sodium sulfate, filtered and concentrated under reduced pressure at 30 °C. The desired product was isolated by flash chromatography in analytically pure form.

General procedure for the reduction of Barton ester 4a: The Barton ester **4a** (2.0 mmol) was dissolved in 20 mL of dry benzene and was protected from light with aluminium foil under argon atmosphere. *tert*-Butanethiol (360 mg, 4.0 mmol) was added at 25 °C. The reaction mixture was subsequently exposed to light using a 250 W low- pressure mercury lamp. After completion of the reaction (approximately 1-2 h), the crude reaction mixture was concentrated and the residue was purified by flash chromatography, affording the product **5**.

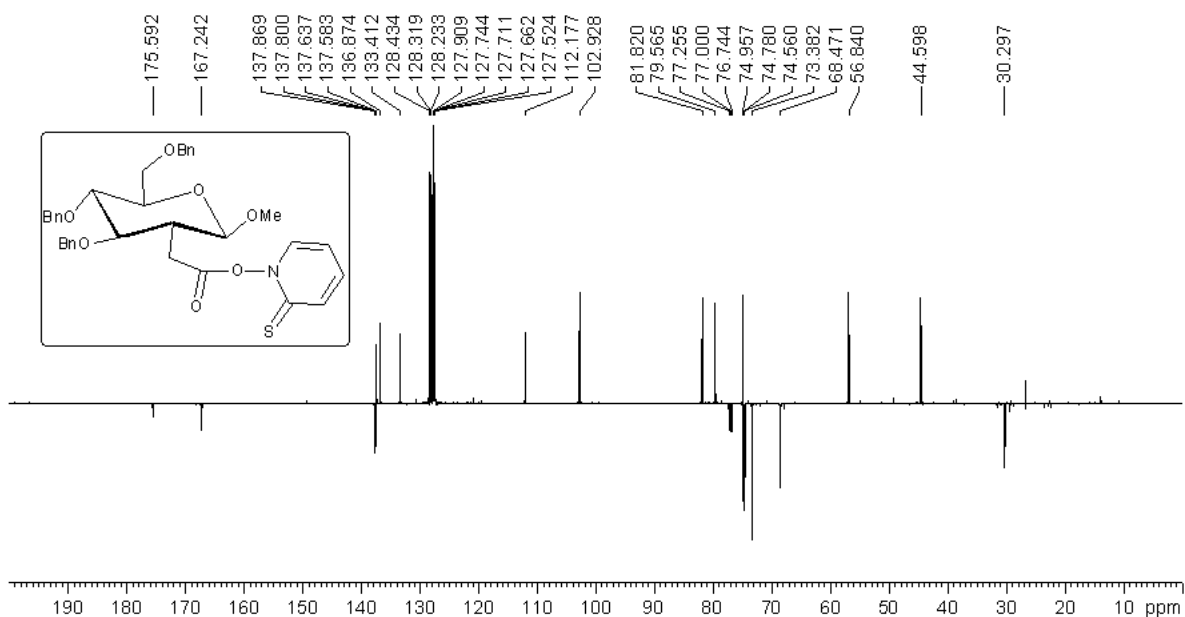
General procedure for the bromination of Barton ester 4a: The Barton ester **4a** (2.0 mmol) was dissolved in 20 mL of dry benzene and was protected from light with aluminium foil under argon atmosphere. Bromotrichloromethane (795 mg, 4.0 mmol) was added at 25 °C. The reaction mixture was subsequently exposed to light using a 250 W low- pressure mercury lamp. After completion of the reaction (approximately 1-2 h), the crude reaction mixture was concentrated and the residue was purified by flash chromatography, affording the product **6**.

Spectral charts

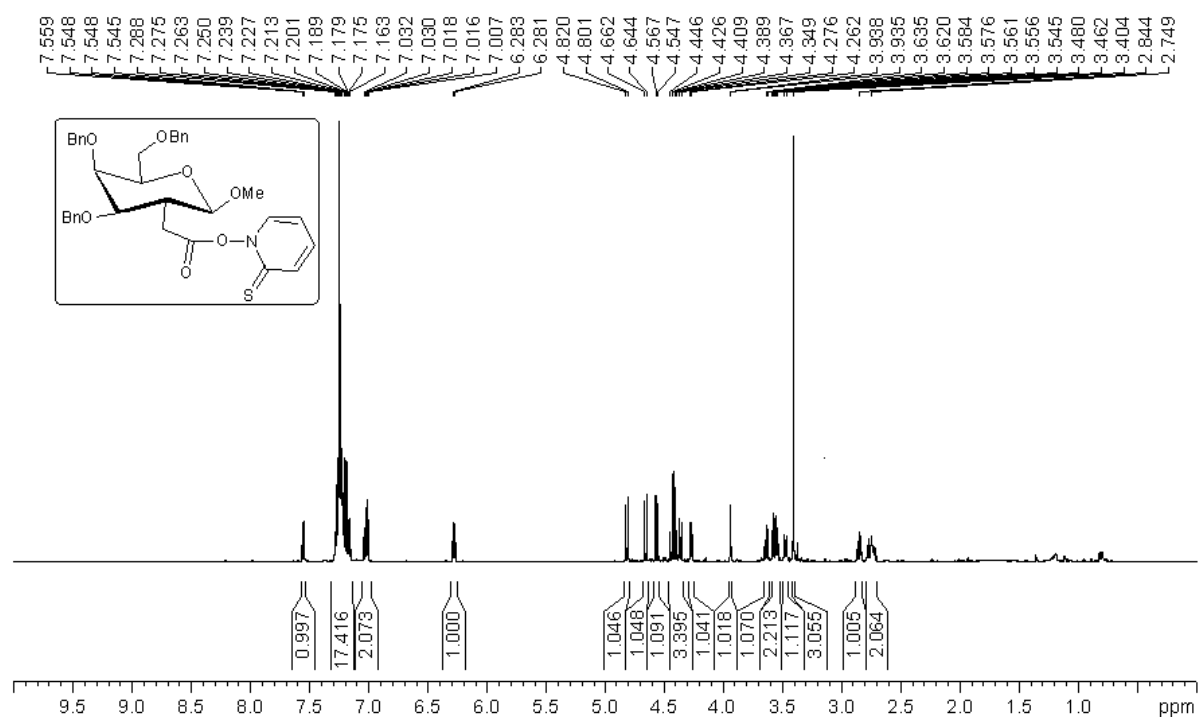
^1H NMR (500 MHz, CDCl_3) of *gluco-4a*



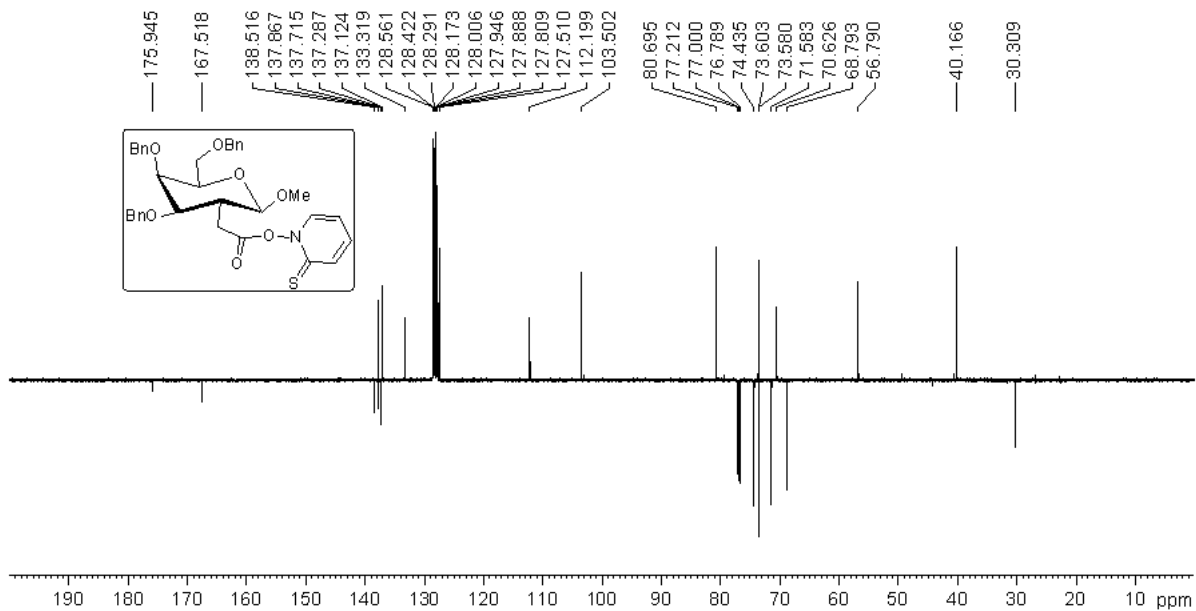
DEPT NMR (125 MHz, CDCl_3) of *gluco-4a*



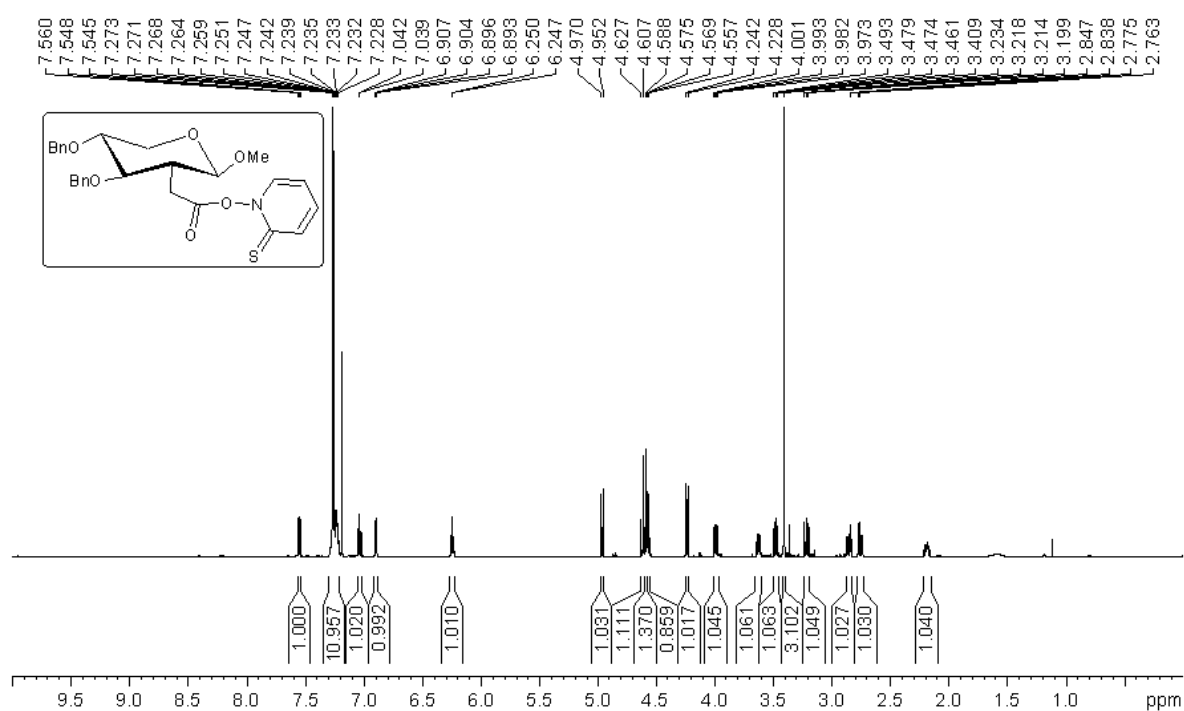
^1H NMR (600 MHz, CDCl_3) of *galacto-4a*



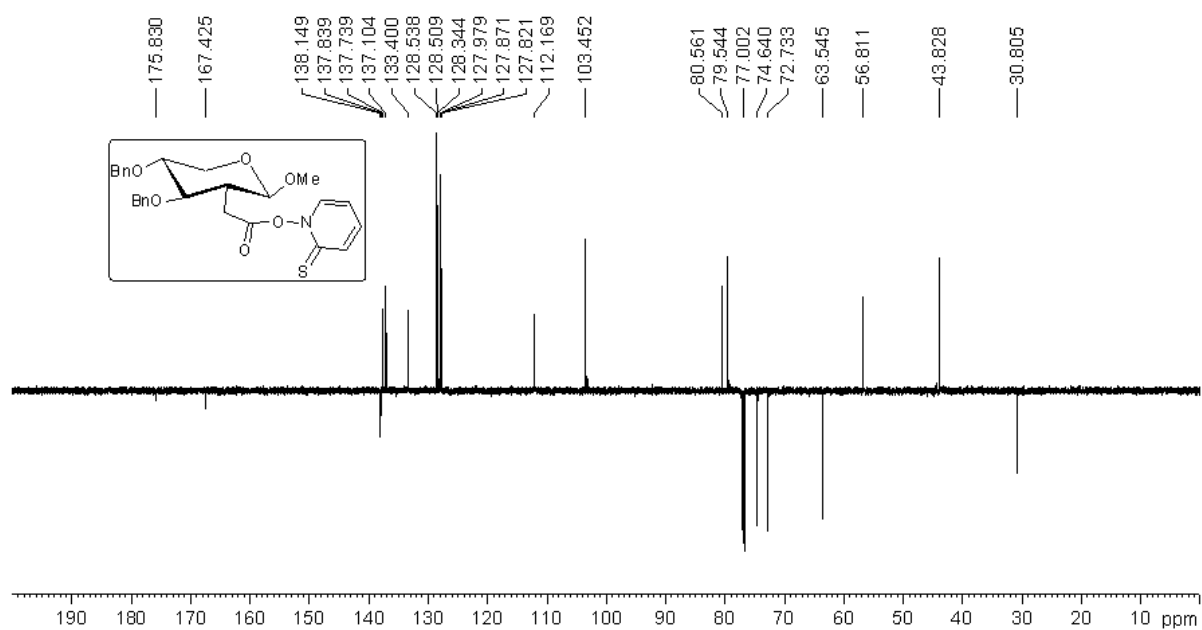
DEPT NMR (150 MHz, CDCl_3) of *galacto-4a*



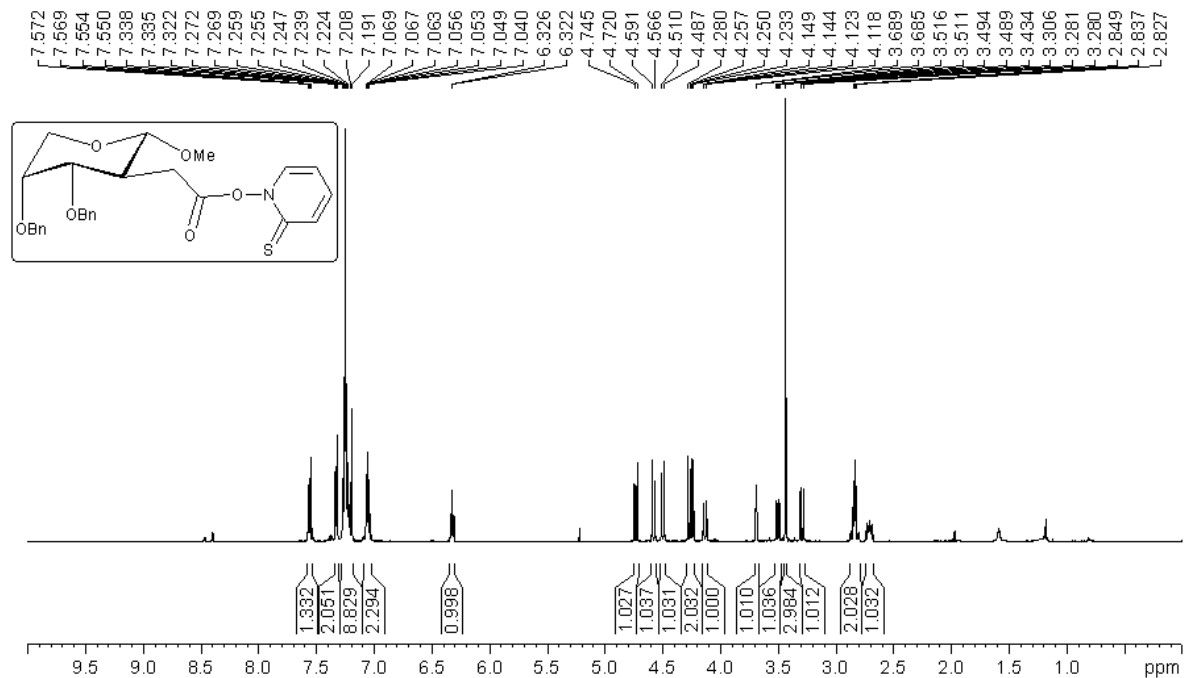
¹H NMR (600 MHz, CDCl₃) of *xylo-4a*



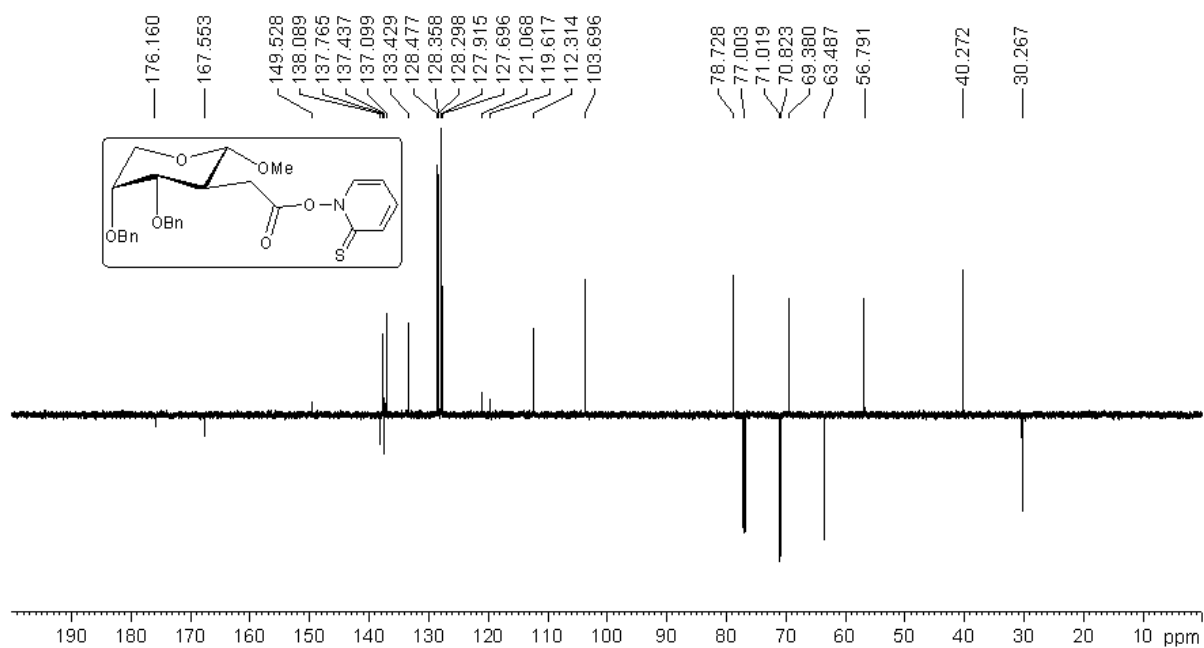
DEPT NMR Spectrum (150 MHz, CDCl₃) of *xylo-4a*



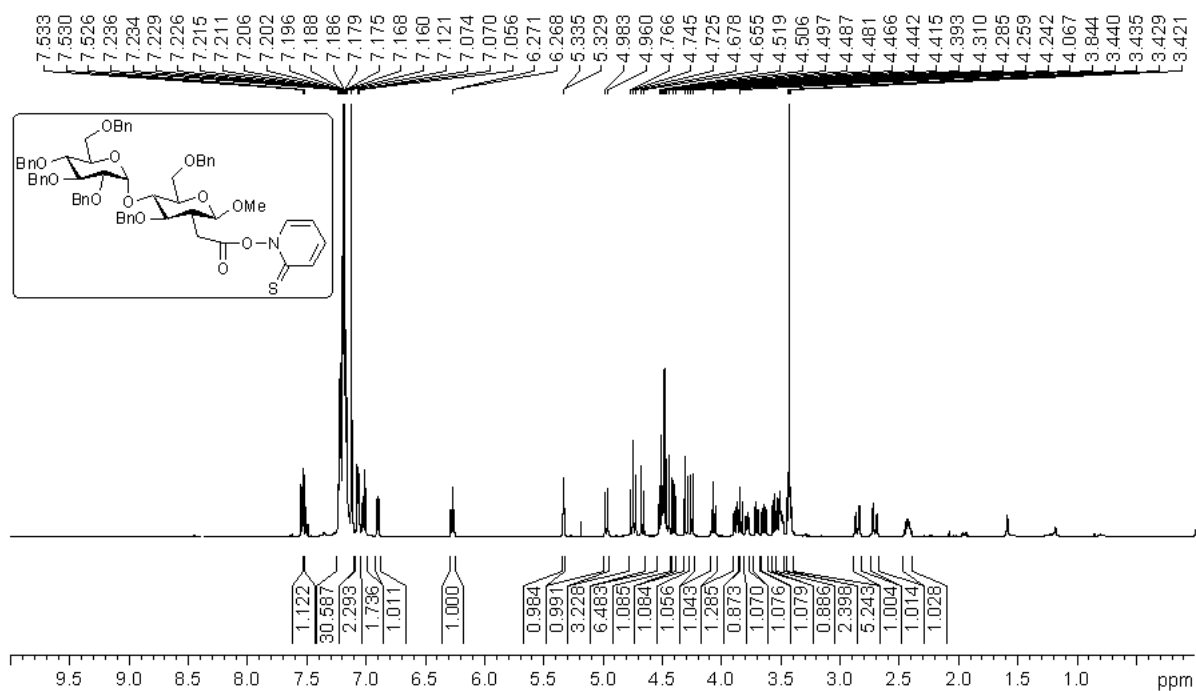
^1H NMR (500 MHz, CDCl_3) of *arabino-4a*



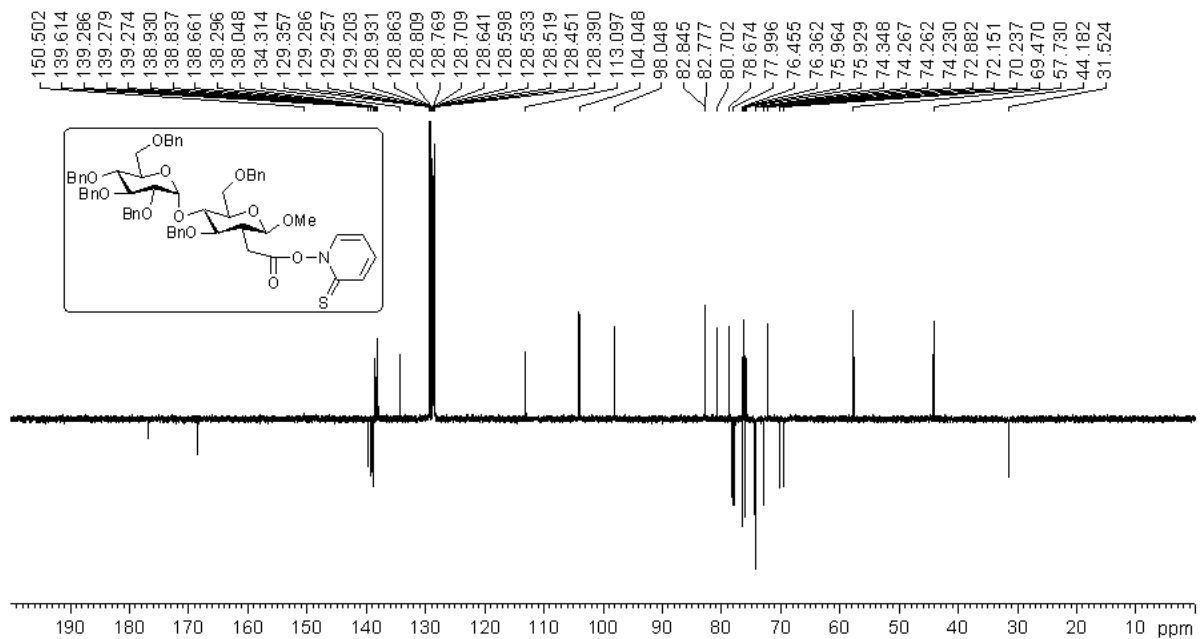
DEPT NMR (125 MHz, CDCl_3) of *arabino-4a*



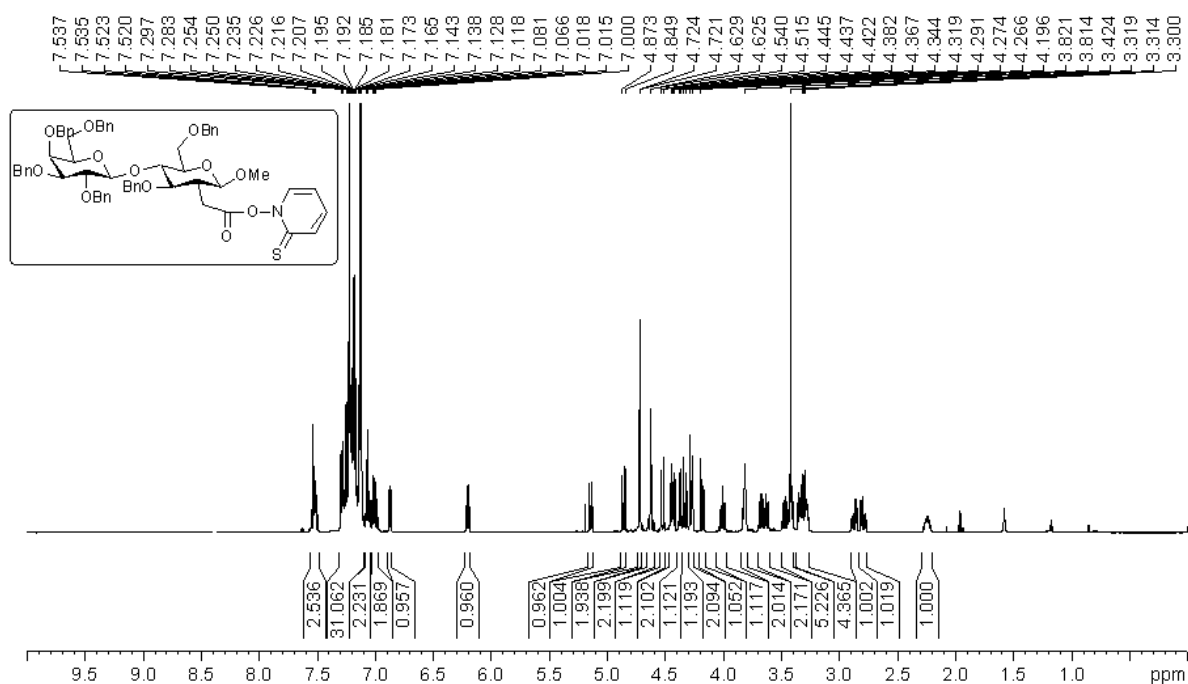
^1H NMR (500 MHz, CDCl_3) of *malto-4a*



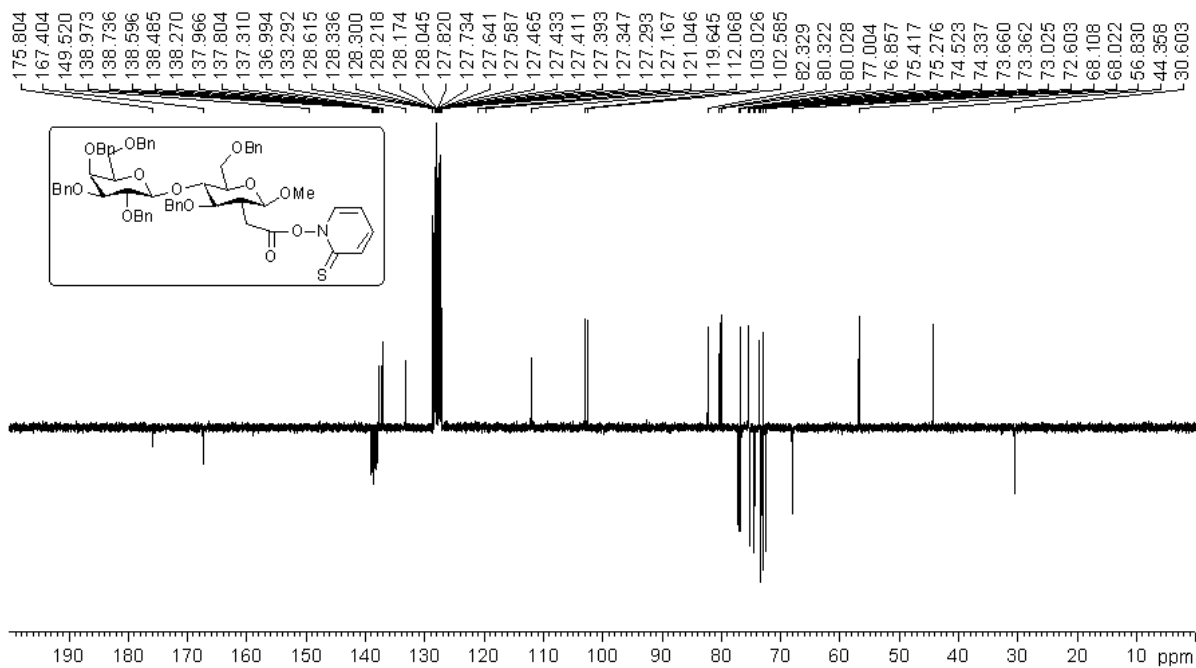
DEPT NMR (125 MHz, CDCl_3) of *malto-4a*



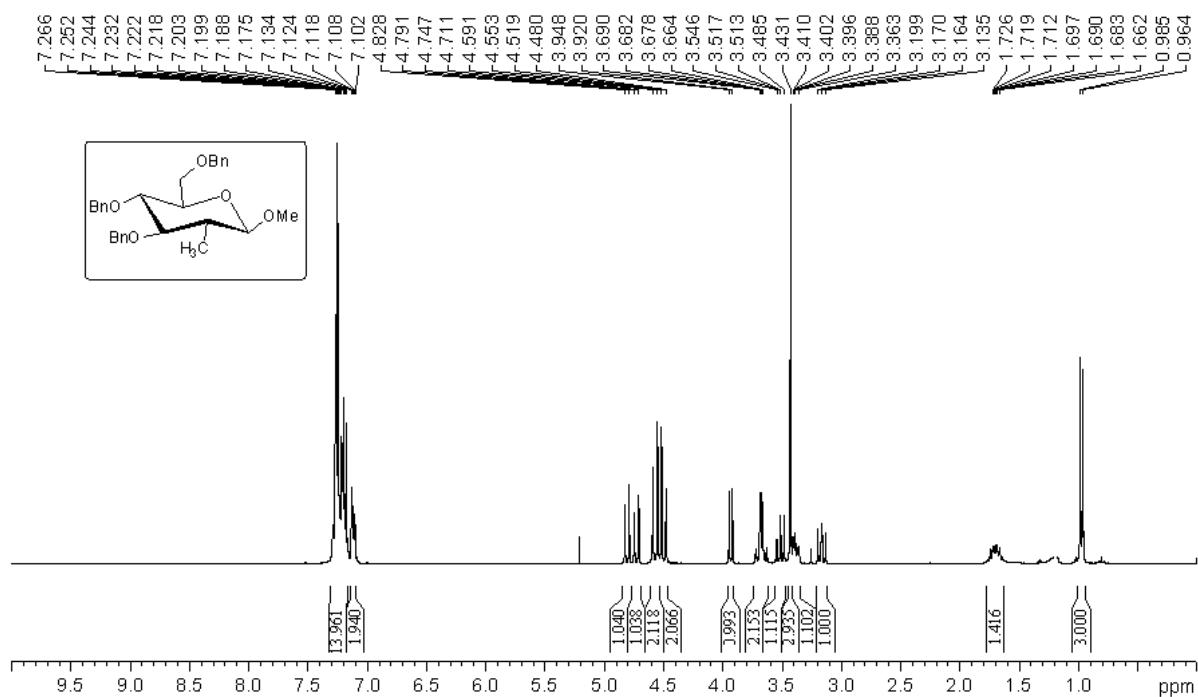
^1H NMR (500 MHz, CDCl_3) of *lacto-4a*



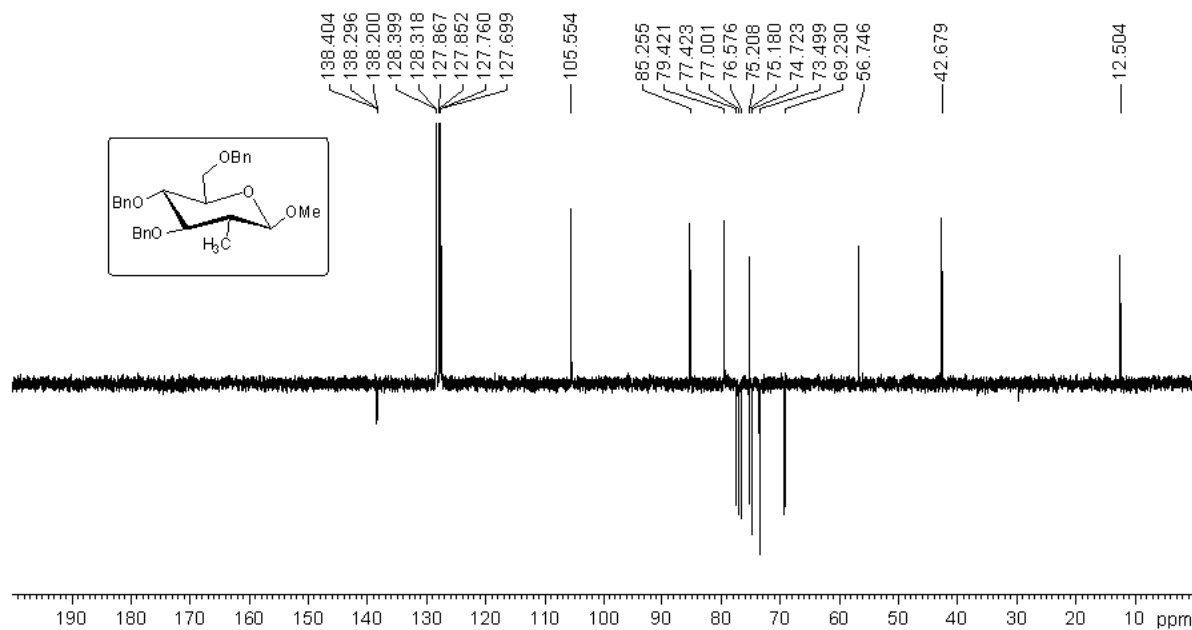
DEPT NMR (125 MHz, CDCl_3) of *lacto-4a*



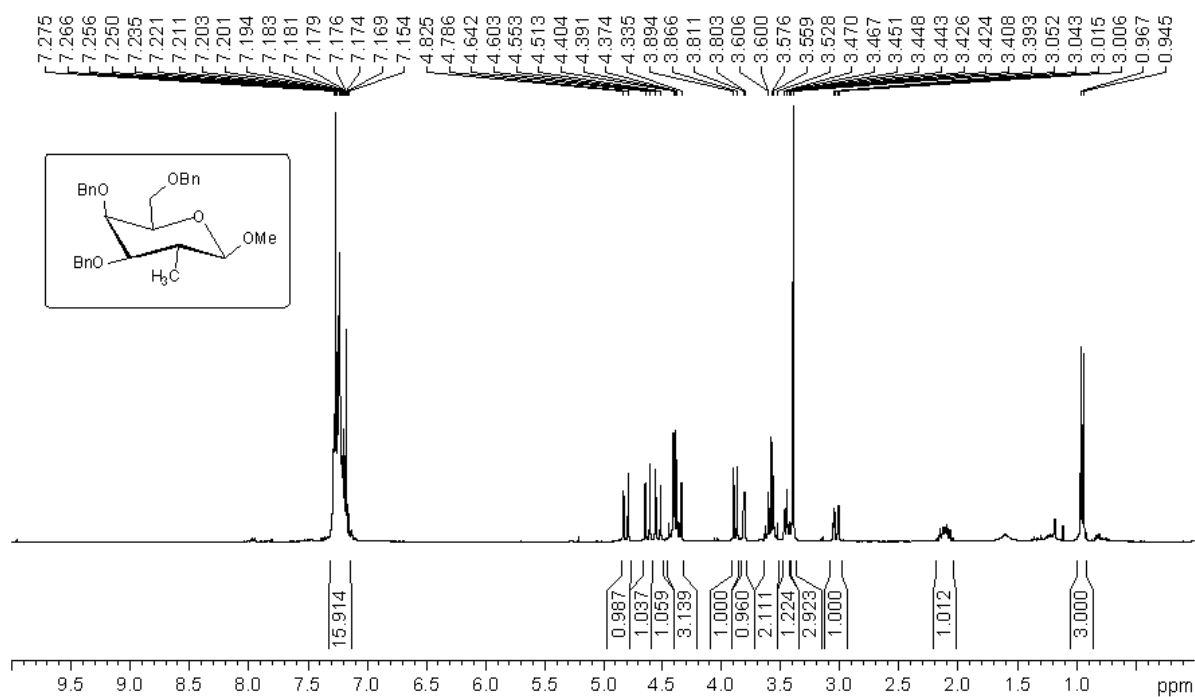
^1H NMR (300 MHz, CDCl_3) of *gluco-5*



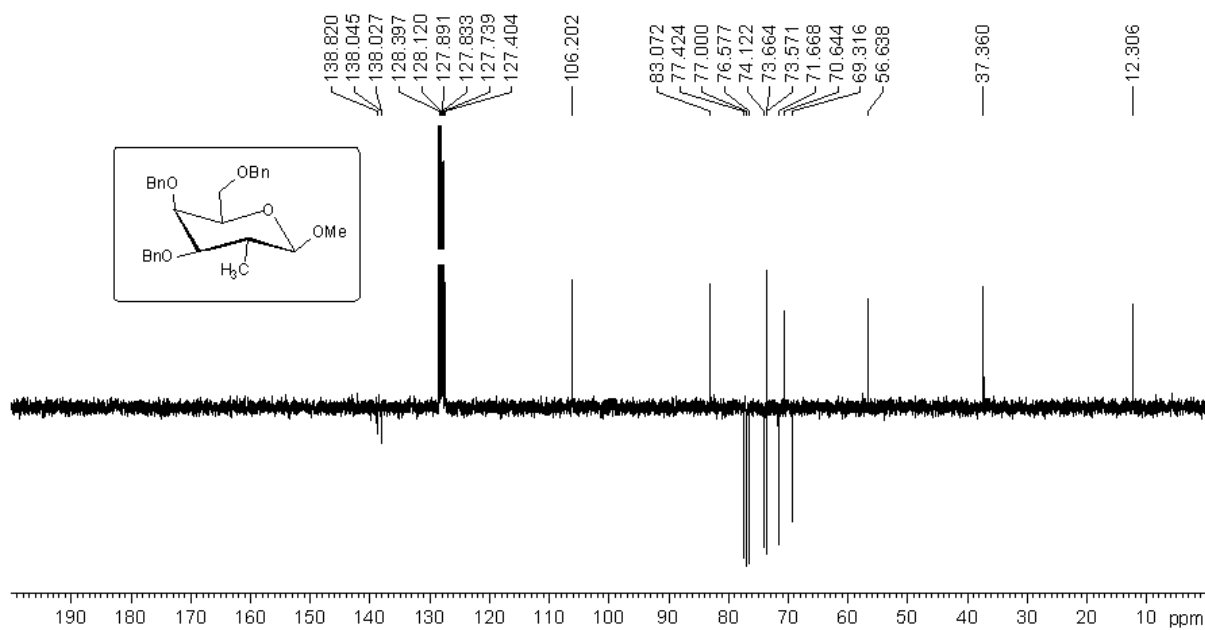
DEPT NMR (75 MHz, CDCl_3) of *gluco-5*



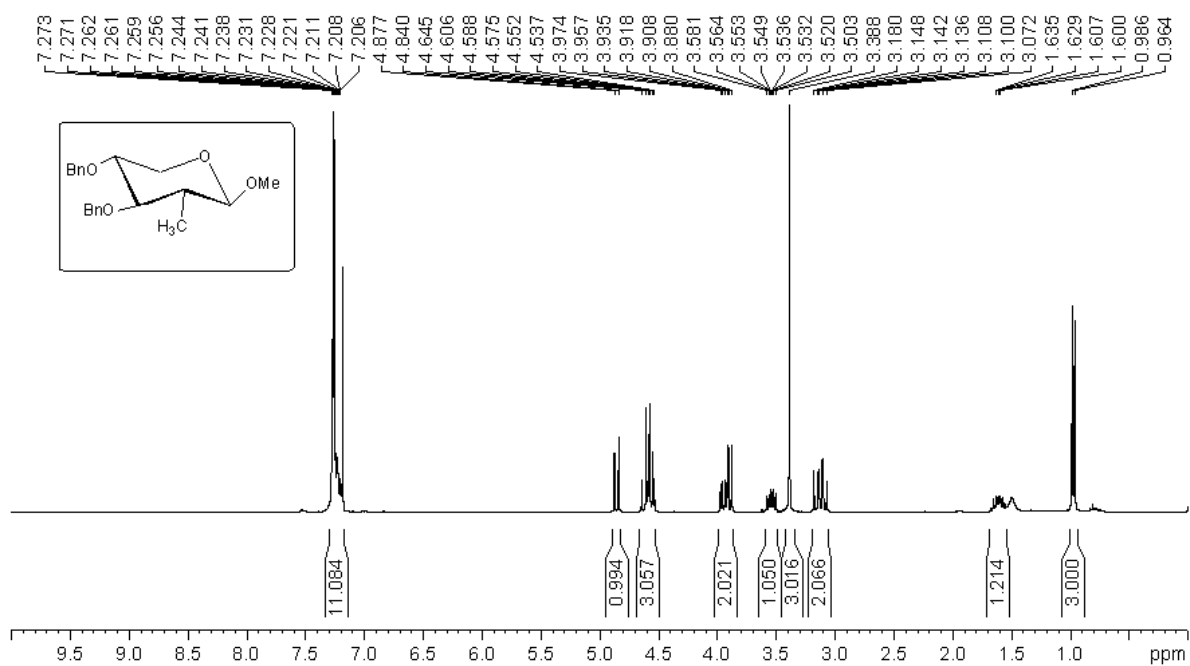
^1H NMR (300 MHz, CDCl_3) of *galacto-5*



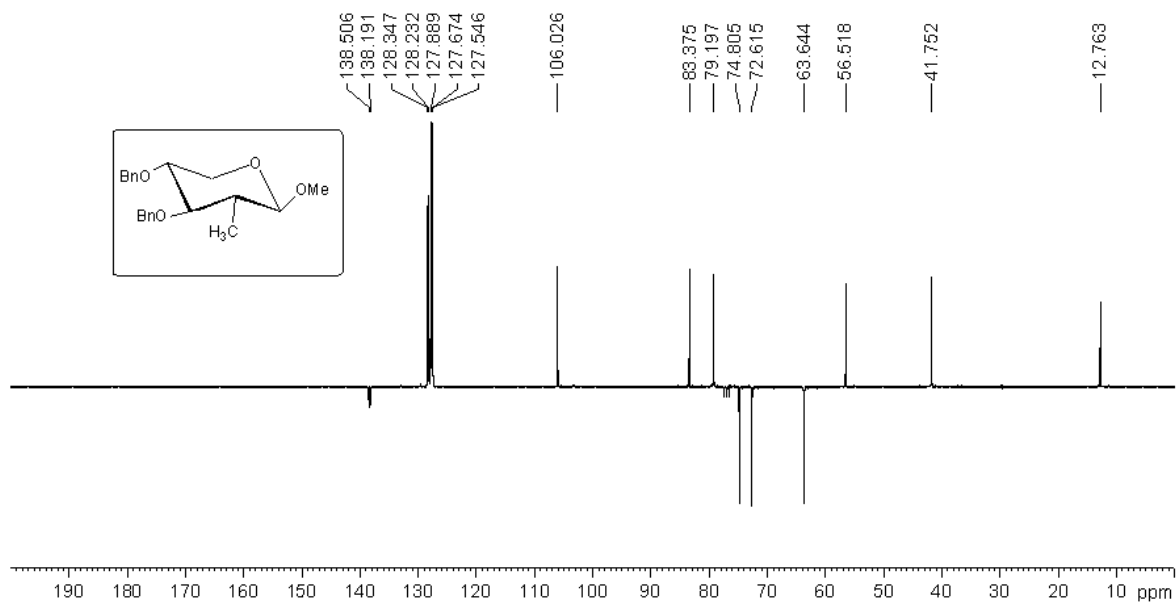
DEPT NMR (75 MHz, CDCl_3) of *galacto-5*



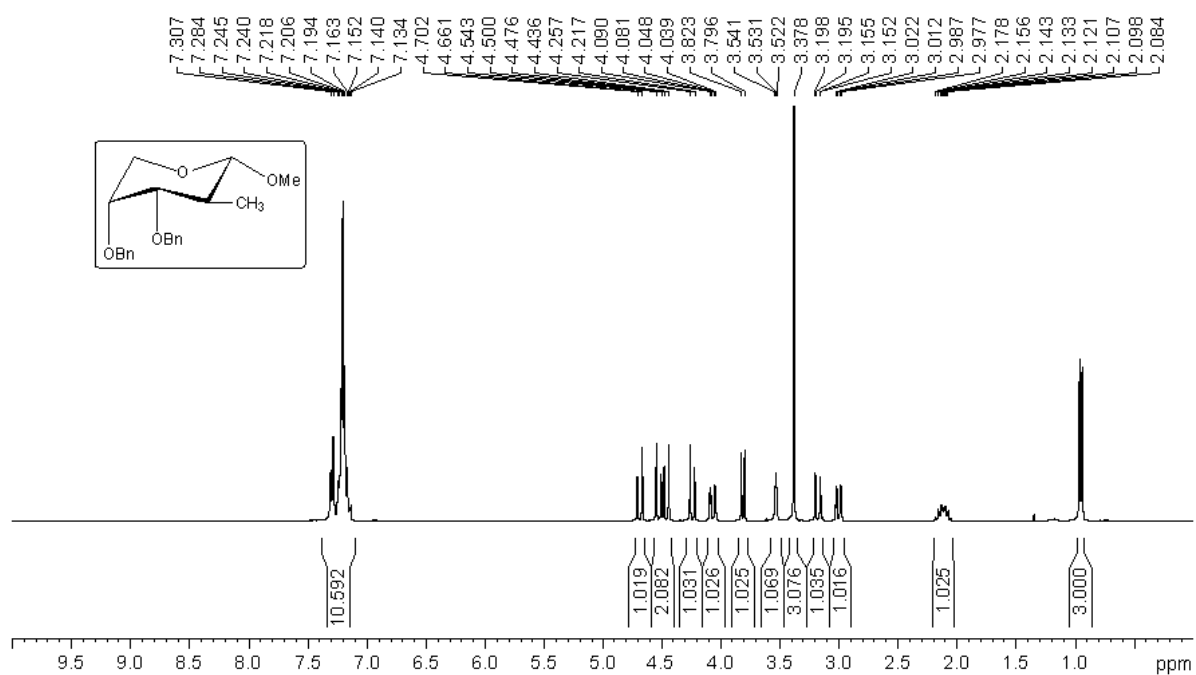
^1H NMR (300 MHz, CDCl_3) of *xylo-5*



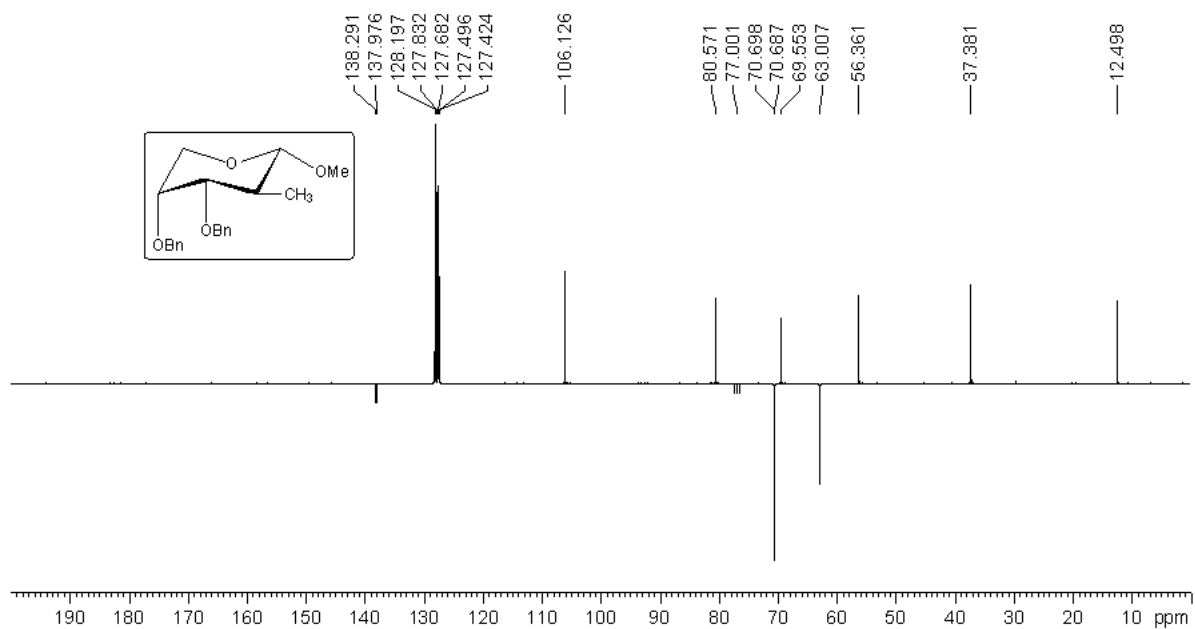
DEPT NMR (75 MHz, CDCl_3) of *xylo-5*



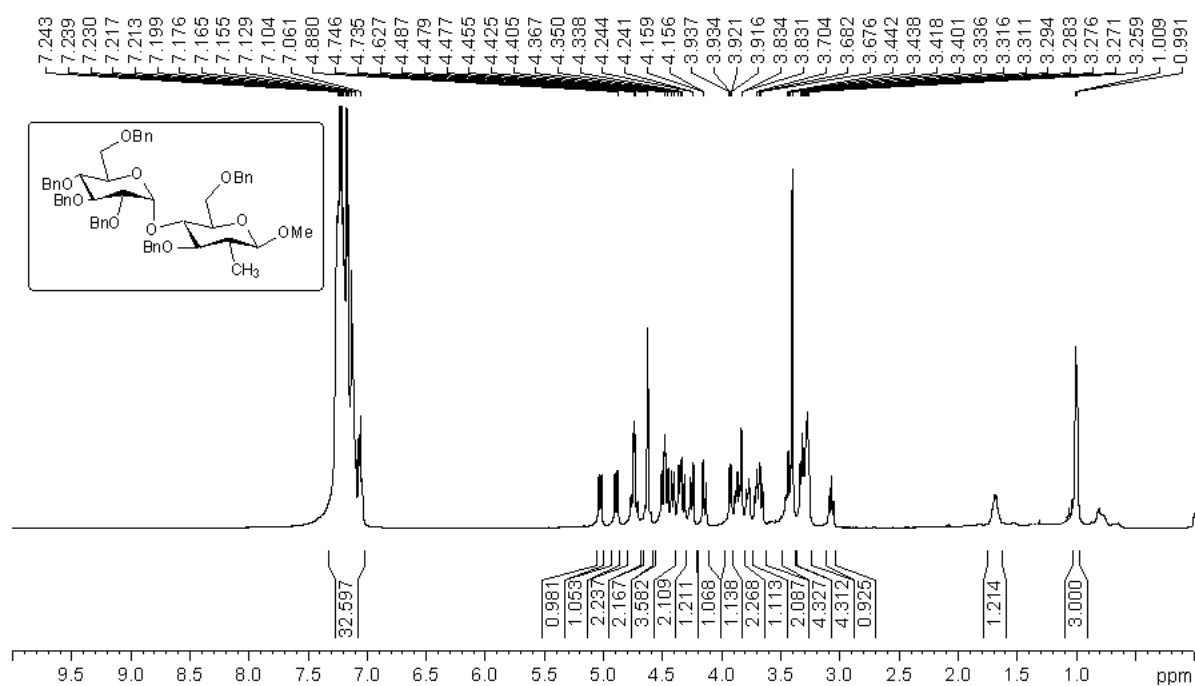
^1H NMR (300 MHz, CDCl_3) of *arabino-5*



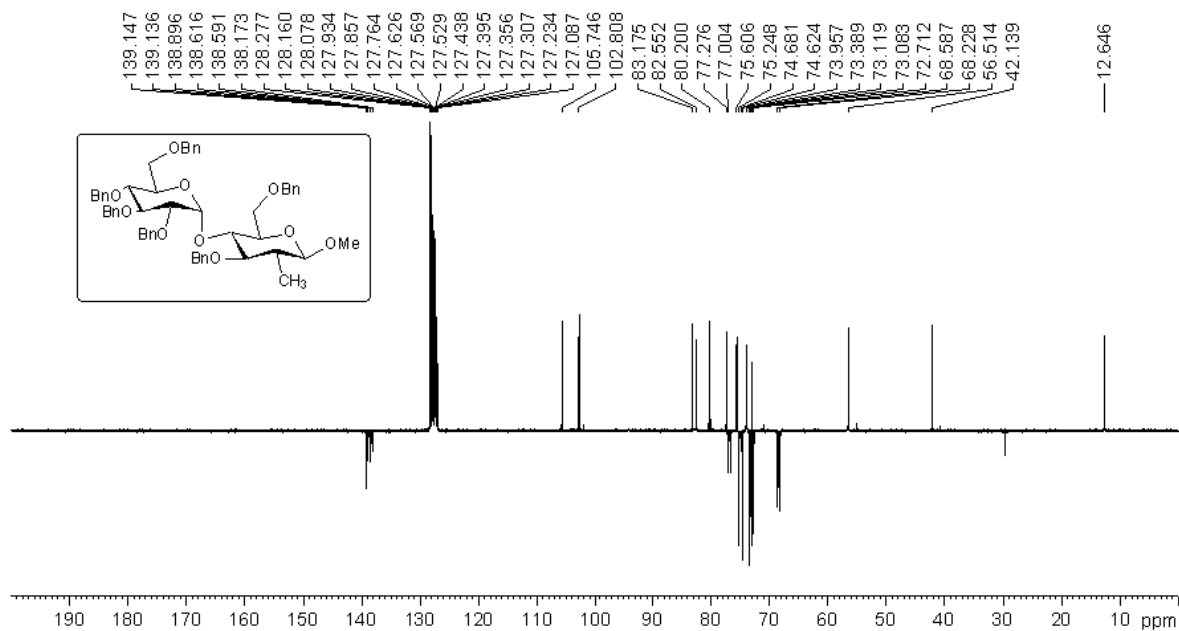
DEPT NMR (75 MHz, CDCl_3) of *arabino-5*



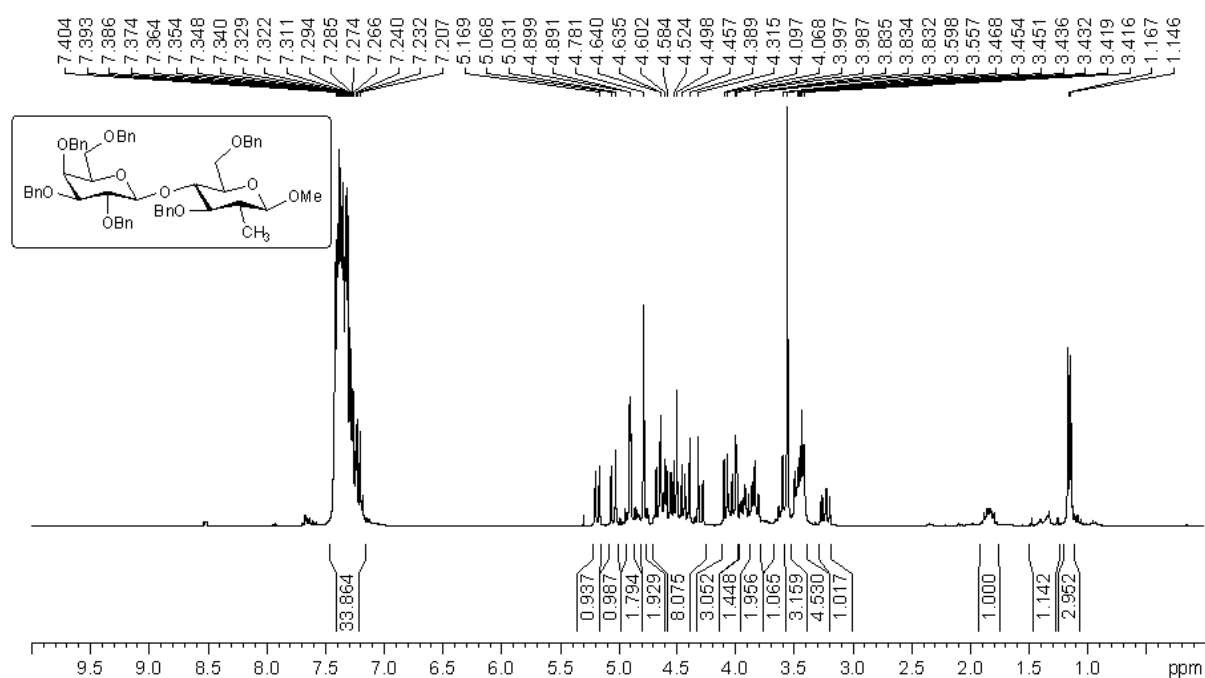
¹H NMR (500 MHz, CDCl₃) of *malto-5*



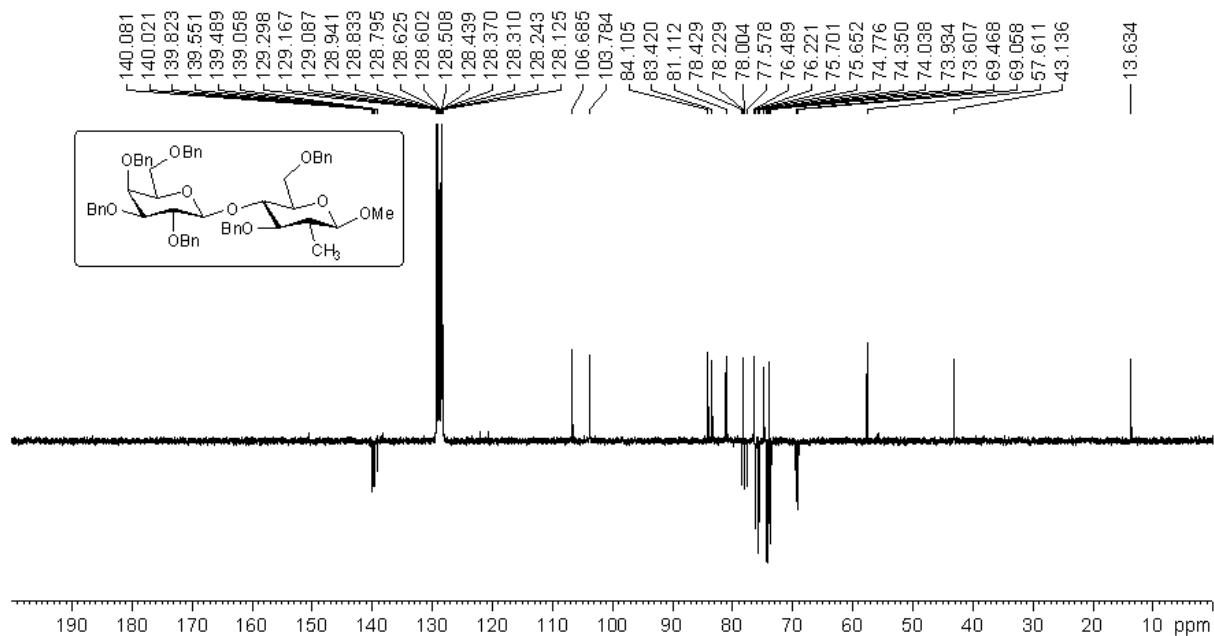
DEPT NMR (150 MHz, CDCl₃) of *malto-5*



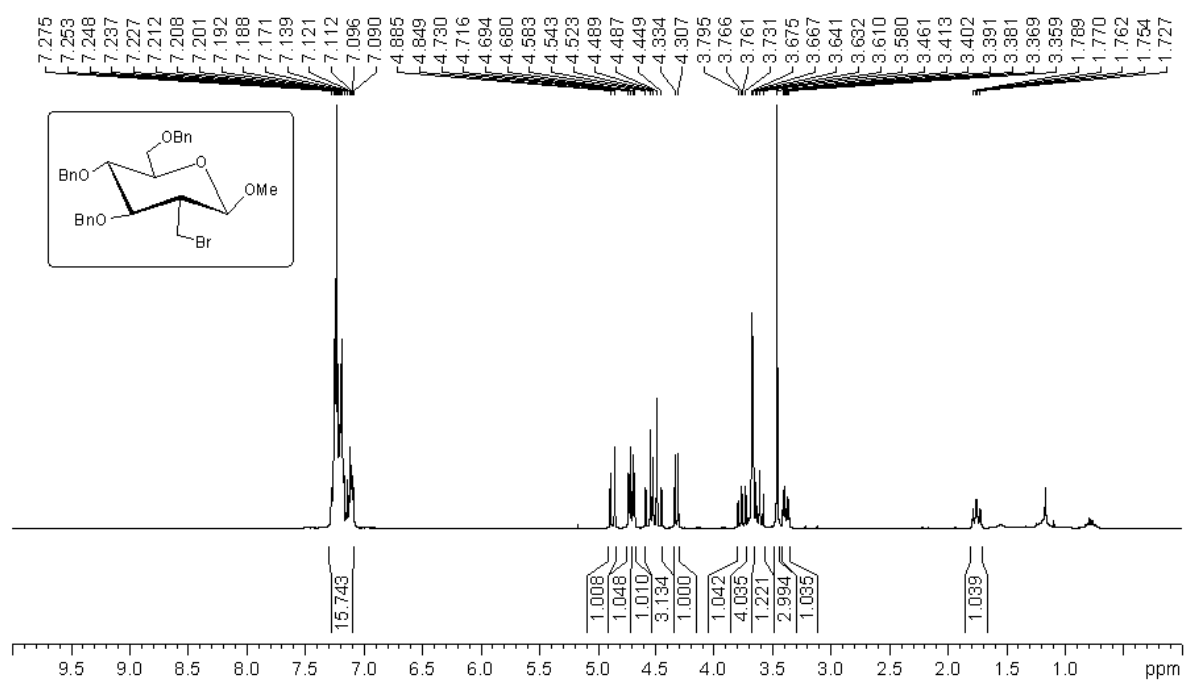
¹H NMR (300 MHz, CDCl₃) of *lacto-5*



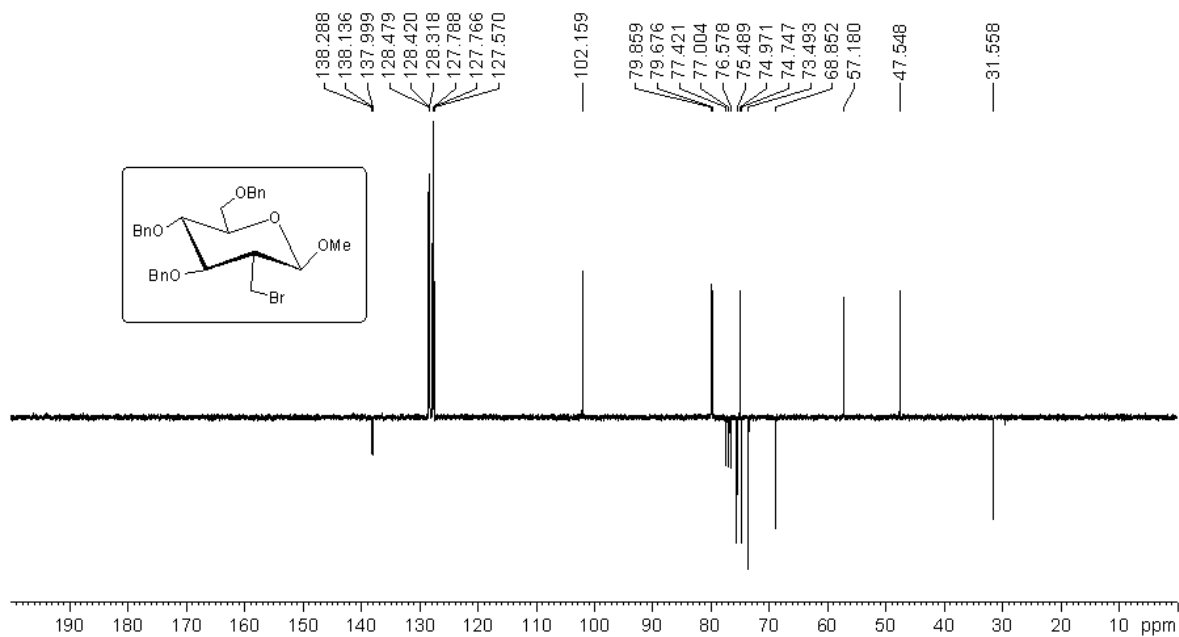
DEPT NMR (75 MHz, CDCl₃) of *lacto-5*



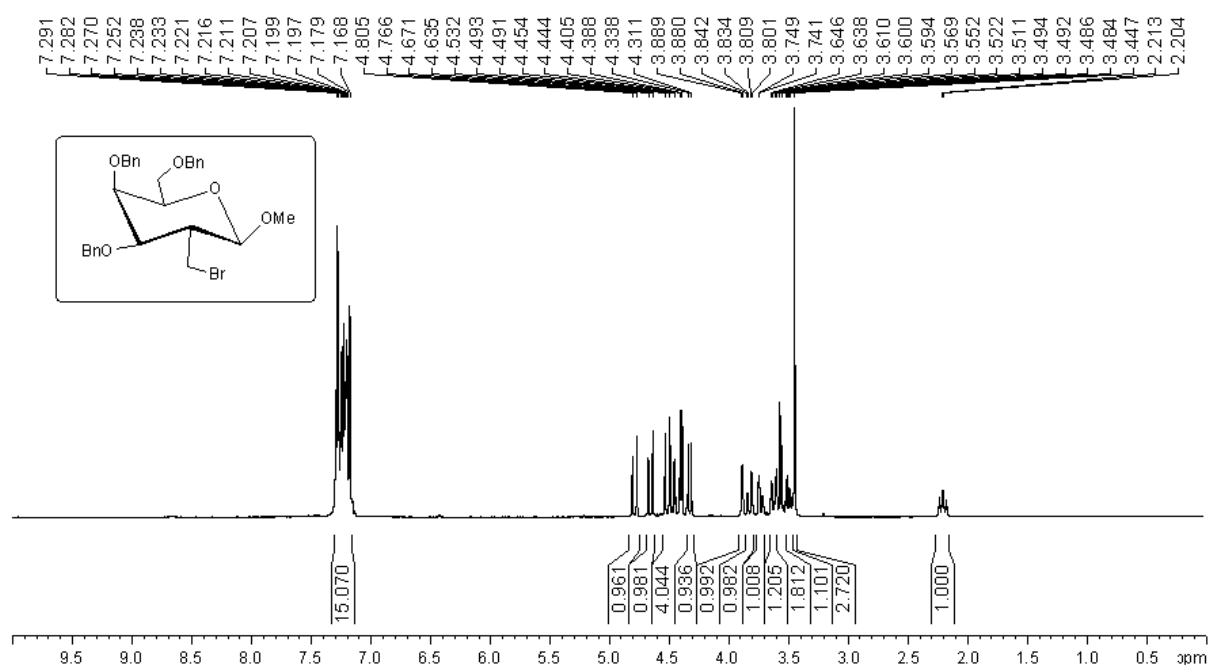
^1H NMR (300 MHz, CDCl_3) of *gluco-6*



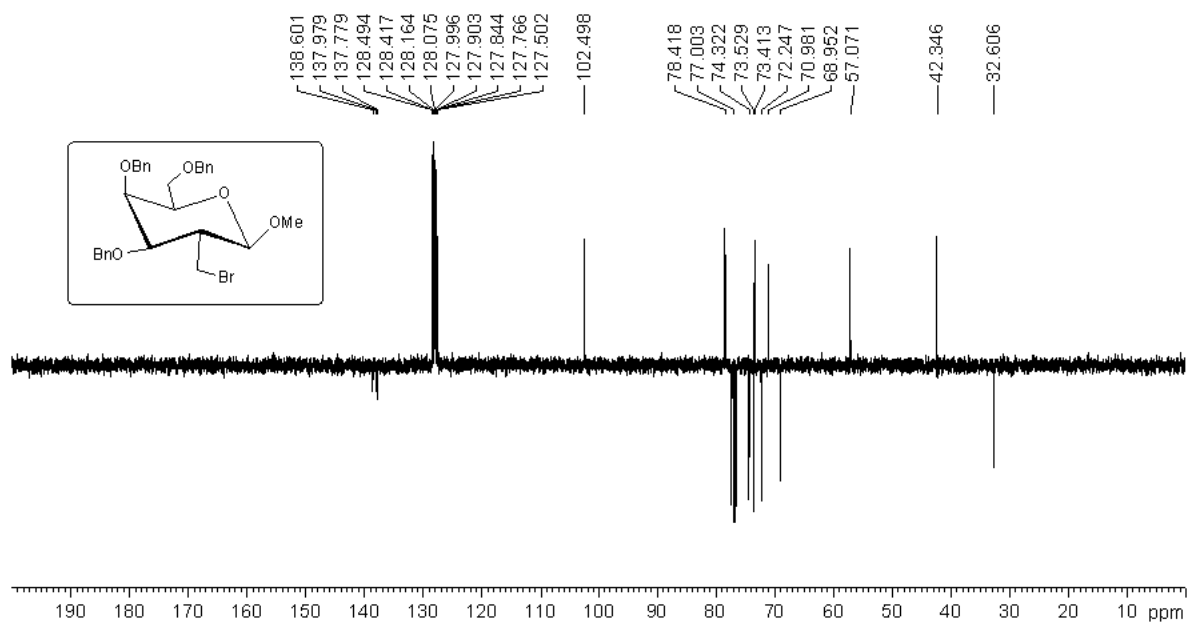
DEPT NMR (75 MHz, CDCl_3) of *gluco-6*



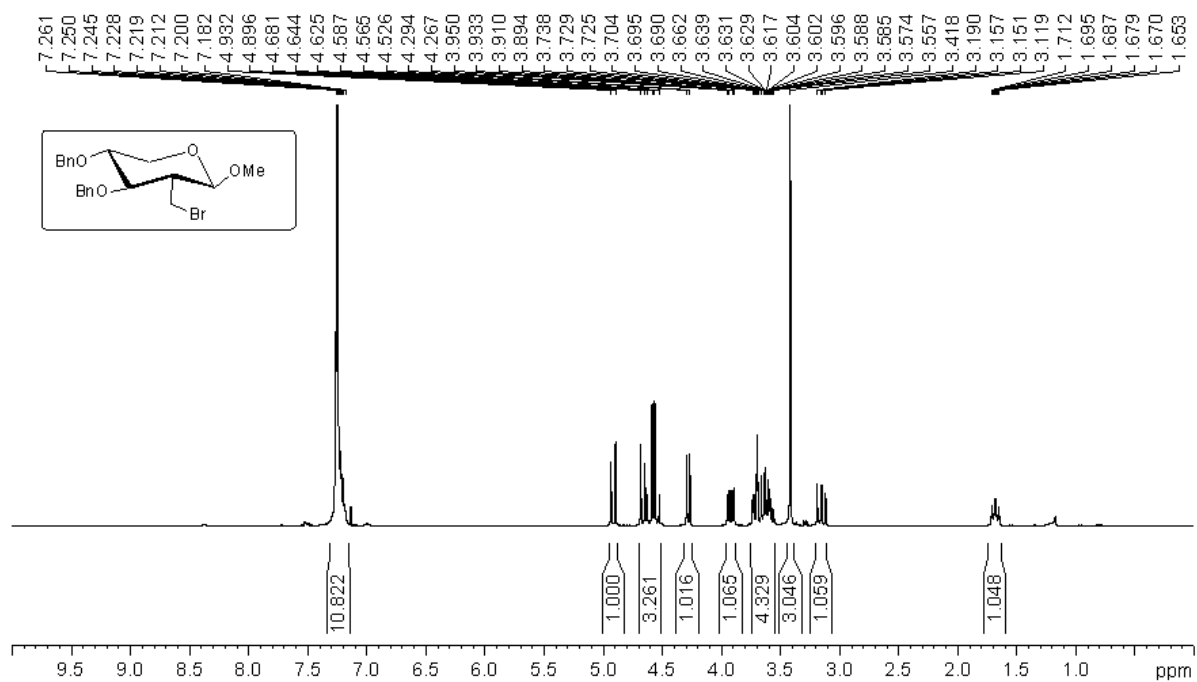
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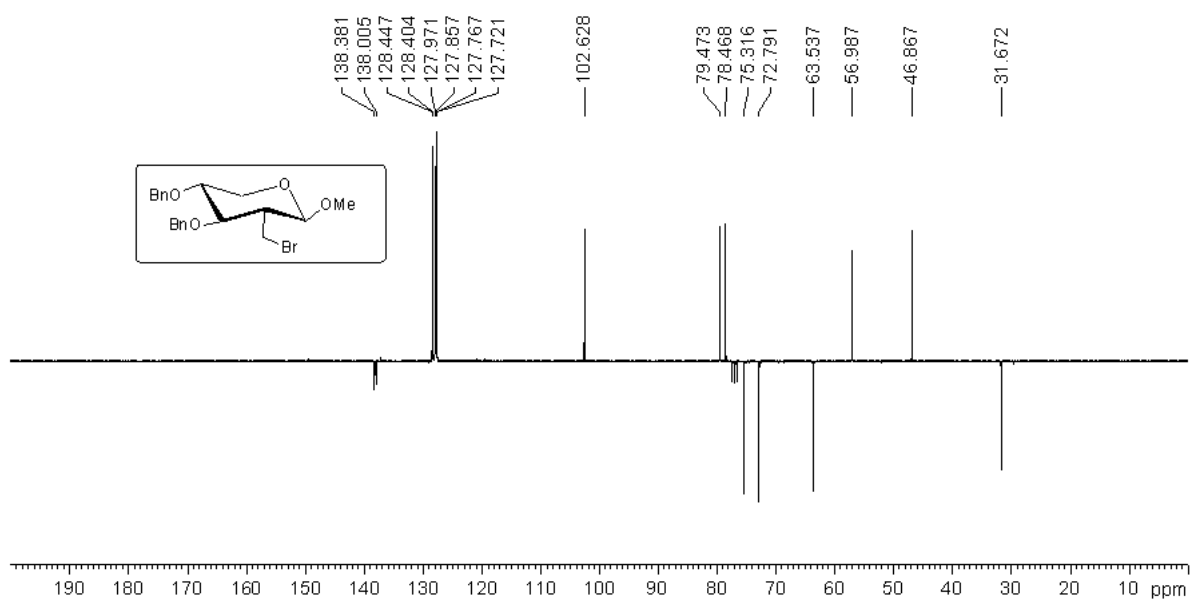
DEPT NMR (75 MHz, CDCl_3) of *galacto-6*



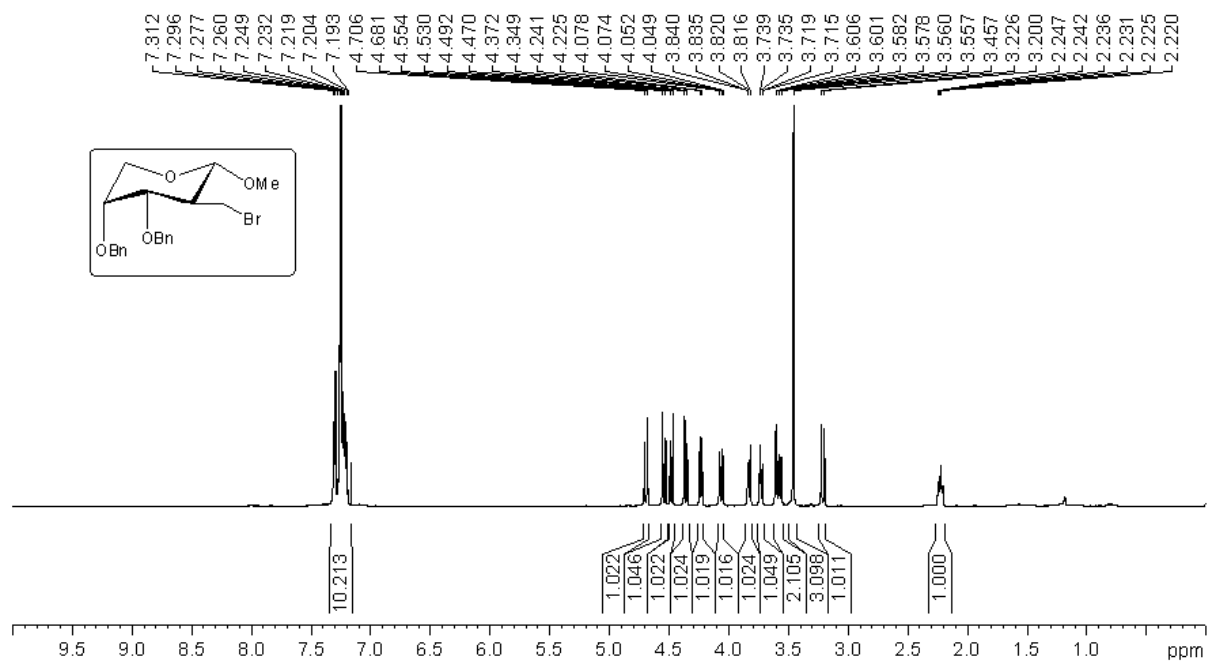
^1H NMR (300 MHz, CDCl_3) of *xylo-6*



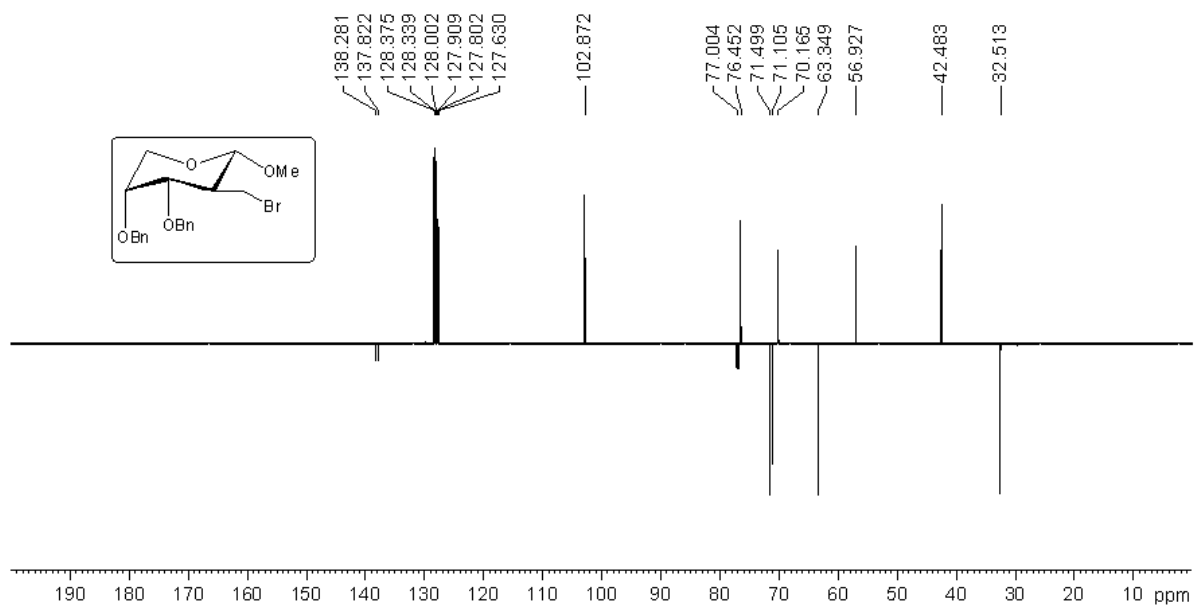
DEPT NMR (75 MHz, CDCl_3) of *xylo-6*



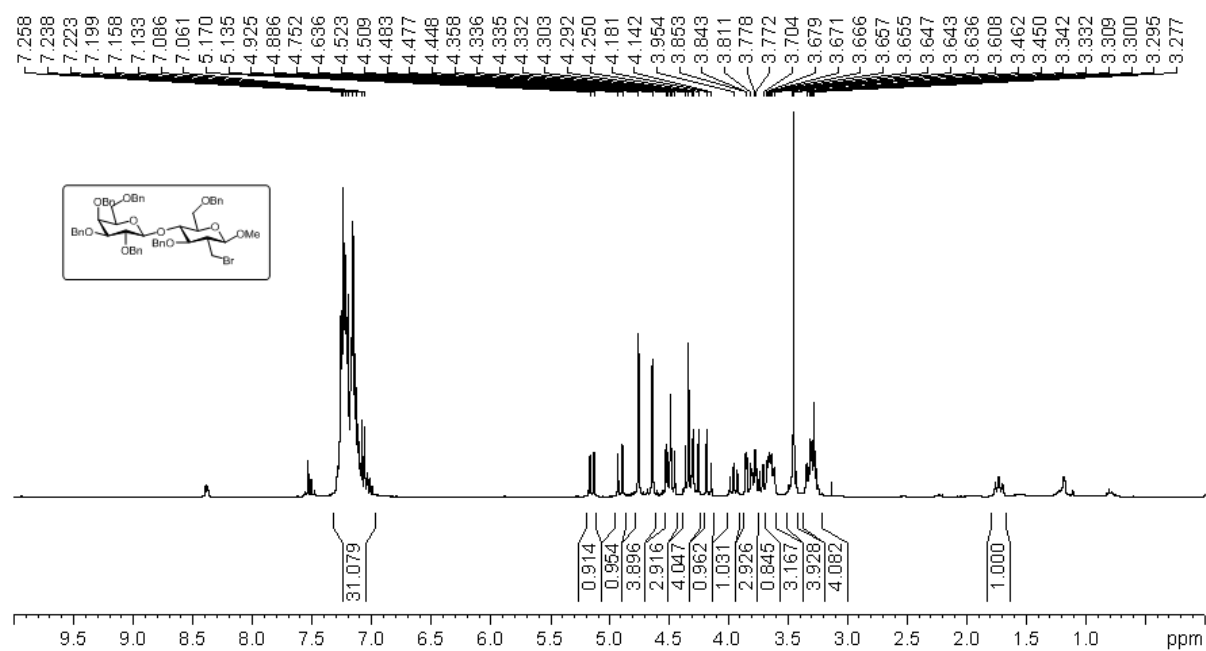
^1H NMR (500 MHz, CDCl_3) of *arabino-6*



DEPT NMR (125 MHz, CDCl_3) of *arabino-6*



^1H NMR (300 MHz, CDCl_3) of *lacto-6*



DEPT NMR (75 MHz, CDCl_3) of *lacto-6*

