Flexible 1,2-cis α-Glycosylation Strategy Based on *in situ* Adduct Transformation

Jhe-Cyuan Hu,[a] Ai-Fen Wendy Feng,[a] Bo-Yao Chang,[a] Chun-Hung Lin, *[,b] and Kwok-Kong Tony Mong*[,a]

[a] *Applied Chemistry Department, National Chiao Tung University, 1001, University Road, Taiwan, Republic of China.*

[b] *Institute of Biological Chemistry, Academia Sinica, Room 802, 128, Academia Road Sec. 2, Nankang, Taipei 115, Taiwan, Republic of China.*

Supporting Information

Contents

1 General Experimental

Reagent-grade chemicals were purchased from commercial vendors and used without further purification. Dichloromethane (CH_2Cl_2) was dried by Asianwong solvent purification system (AWS-1000). *N*-Formyl morpholine (NFM) and 2,6-lutidine was purchased from vendor and was treated with activated molecular sieves (MS) under N_2 before use. Progress of reactions was monitored by thin layer chromatography on silica gel 60 F-254 plate and visualized under UV illumination and/or by staining with acidic ceric ammonium molybdate or *p*-anisaldehyde. HPLC analysis was performed over Mightysil Si 60 (250 mm L × 4.6 mm I.D.) obtained from KANTO CHEMICAL CO. INC. and eluted with EtOAc/hexanes/CH_2Cl_2 or EtOAc/hexanes mixture at a 1 mL/min flow rate. Gradient pump (L-2130) and UV detector (L-2400) from Hitachi were employed for solvent elution and detection respectively. 0.063-0.200 mm Silica gel for column chromatography was obtained from Merck (Geduran Si-60). NMR spectroscopy analysis of saccharide building blocks and glycosylation products were recorded by 300 (Büchi console), 400 (Varian console), 500 (Varian console), or 600 (Varian console) MHz NMR spectrometers. The proton chemical shifts (in ppm) of reported were calibrated against the proton signal of TMS standard and the carbon chemical shift was calibrated against the ^{13}C signals of deuterated chloroform ($CDCl_3$). Coupling constants (in Hz) was calculated from chemical shifts of ^1H NMR spectra. Diacetonide protected galactosyl acceptor **15**, cholesterol **33**, and diosgenine **17** are commercially available. Preparation of glycosyl donors/acceptors **1**[1], **2**[2], **3**[3], **4**[4], **9**[5], **11**[2], **16**[6], **18**[7], **30**[8], **31**[9], and **42**[3] followed the literature procedures. On some occasions, low concentration glycosylation method is applied to obtain the β-anomers of the glycosylation product as standard for determination of α:β ratio.[7]

2 Experimental procedures and spectroscopic data

2.1 One-pot *in situ* adduct transformation and glycosylation protocol for thioglycosyl donors (1, 2, 9-14, 30, and 32).

Thioglycoside donor (1.0 equiv), *N*-formylmorpholine (2.0 equiv), and activated 4Å molecular sieve (MS) were added to dried CH_2Cl_2 such that final concentration of the donor was 50 mM. Resulting mixture was stirred at room temperature for 10 min and at 0 °C (for **1**, **2**, **9**-**13**, **30**) or at -20 °C (for **14**, **32**) for additional 20-30 min. Subsequently, NIS (1.5 equiv.) and TMSOTf (1.0 equiv.) were added, and the reaction progress was monitored by TLC. Upon the complete formation of the NFM imidinium ion (by TLC examination), TBAI (5.0 equiv.) was added. The mixture was stirred at 0 °C for 0.5 to 2 h. Glycosyl iodides from donors **1**, **2**, **9**-**12** were detectable by TLC, but glycosyl iodides from **13**, **14**, **30** and **32** were not detectable. After 0.5 - 2 h, an acceptor (1.5 equiv.) and a base (DTBP, DIEA, or lutidine) (2.0 equiv.) were added to the reaction mixture. The reaction temperature was then raised to 30 °C and the resulting mixture was continuously stirred for ~ 18 - 24 h (for **14**, a lower 15 ºC was applied), followed by the addition of satd. $NaHCO_3$ and $Na_2S_2O_3$(s). The mixture was vigorously stirred until the red color of the solution changed to the pale yellow. The mixture was diluted with CH_2Cl_2, followed by filtration, and concentrated for flash chromatography purification over silica gel to furnish the glycosylation product.

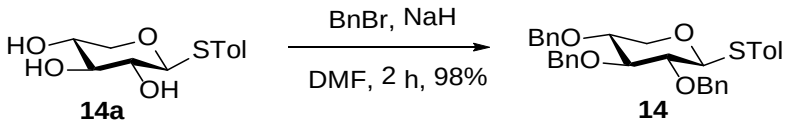
2.2 One-pot *in situ* adduct transformation and glycosylation procedure for 2-azido-2-deoxythioglucoside donor (31)

Mixture of 2-azido-2-deoxythioglucoside donor **31** (2.0 equiv.), *N*-formylmorpholine (4.0 equiv.), and activated 4Å molecular sieve (MS) was suspended in dried CH_2Cl_2 ([**31**] = 50 mM). Then, the resulting mixture was stirred at room temperature for 10 min and at 0 °C for an additional 20 min, followed by addition of NIS (3.0 equiv.) and TMSOTf (2.6 equiv.). The formation of the NFM imidinium ion intermediate was monitored by TLC. Upon complete formation of the imidinium ion, TBAI (10.0 equiv.) was added and the mixture was stirred ng mixture was stirred at room temperature for 10 min and at 0 °C until the formation of glycosyl iodide (detectable by TLC). At this stage, acceptor (1.0 equiv.) and lutidine (5.2 equiv.) were

added and the reaction temperature was raised to 30 °C. After 24 h reaction, satd. $NaHCO_3$ and $Na_2S_2O_3$(s) were added to the mixture, followed by vigorous stirring until the color of the solution changed from the deep red to pale yellow. The resulting mixture was dried (over $MgSO_4$), filtered, and concentrated for flash chromatography purification over silica gel to furnish the glycosylation product.

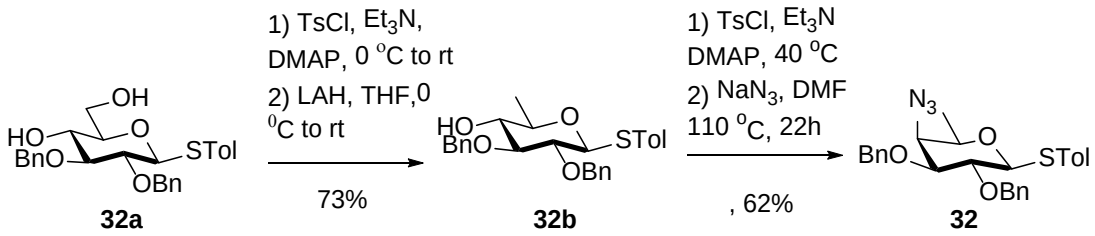
2.3 Preparation of thioglycosyl substrates

2.3.1 *p*-Tolyl 2,3,4-Tri-*O*-benzyl-1-thio-α-D-xylopyranoside (14)



To a solution of thioxylopyranoside **14a** (2 g, 7.8 mmol) in dried DMF (5 mL), NaH (1.2 g, 31 mmol) was added at ice bath temperature and the mixture was stirred under N_2 atmosphere. And then benzyl bromide (BnBr) (3.36 mL, 28 mmol) was added and the stirring was continued for 2 h. The reaction was quenched with ice water and diluted with CH_2Cl_2 (20 mL). The CH_2Cl_2 solution was washed with water (20 mL × 2), brine, dried over $MgSO_4$, filtered, and concentrated for flash chromatography (Hexanes/EtOAc 9:1). Desired thioxylopyranoside **14** (3.9 g) was afforded in 98% yield as a yellowish liquid. For thioxylopyranoside **14**: R_f 0.30 (Hexanes/EtOAc 9:1); $[\alpha]_D^{20}$ +20.4 (*c* 0.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 17.3, 8.6 Hz, 4H), 7.39 – 7.27 (m, 13H), 7.13 (d, *J* = 7.9 Hz, 2H), 4.97 – 4.82 (m, 3H), 4.83 – 4.70 (m, 2H), 4.64 (dt, *J* = 9.4, 6.7 Hz, 2H), 4.14 – 4.01 (m, 1H), 3.70 – 3.59 (m, 2H), 3.48 – 3.38 (m, 1H), 3.29 – 3.16 (m, 1H), 2.35 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.49, 138.15, 138.09, 137.84, 132.64, 132.25, 129.79, 129.76, 129.73, 128.49, 128.42, 128.41, 128.35, 128.19, 128.09, 128.06, 127.96, 127.89, 127.83, 127.71, 127.61, 88.75 (C-1), 85.44, 80.43, 76.74, 75.67, 75.44, 73.23, 67.51, 21.35 (*C*H$_3$). HRMS (ESI): calcd for $C_{33}H_{34}NaO_4S^+$ requires 549.2070; found: *m/z* 549.2068 $[M + Na]^+$.

2.4.2 *p*-Tolyl 4-Azido-2,3-di-*O*-benzyl-4,6-dideoxy-1-thio-β-D-galactopyranoside (32)

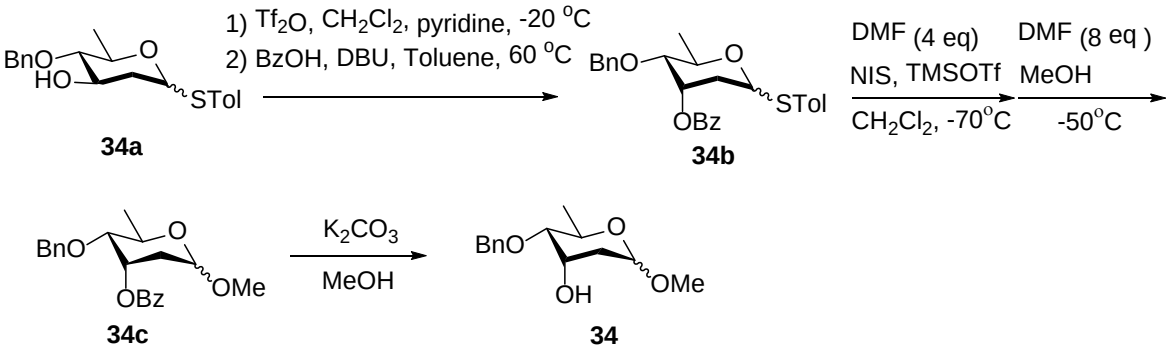


To a solution of **32a**[10] (7.8 g, 16.7 mmol), NEt_3 (5.77 mL, 41.75 mmol), and DAMP (0.2 g, 1.67 mmol) in dried CH_2Cl_2 (33 mL) was added tosyl chloride (TsCl) (4.77 g, 25.1 mmol) at 0 °C. The reaction mixture was stirred at RT for 6 h, and then diluted with EtOAc (100 mL). The mixture was washed with 10% $HCl_{(aq)}$ (100 mL × 2), brine, dried (over $MgSO_4$), concentrated, and dried under *vacuo* to give crude C6-tosylated derivative. The crude tosylated derivative was dissolved in dried THF (65 mL) and to which lithium aluminum hydride ($LiAlH_4$) (1.26 g, 33.4 mmol) was added at 0 °C. The reaction mixture was stirred at RT for overnight and then quenched with EtOAc. The mixture was filtered and the filtrate obtained was diluted with EtOAc (200 mL), which was washed with H_2O (100 mL ×2), brine, dried (over $MgSO_4$), and concentrated for flash chromatography (Hexanes/EtOAc = 10/1) to give **32b** (5.3 g, 73%) as a white glassy solid. For **32b**, R_f 0.42 (Hexane/EtOAc = 3/1); $[\alpha]_D^{35}$ –2.1 (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 4H, Ar*H*), 7.36 – 7.26 (m, 8H, Ar*H*), 7.10 (d, *J* = 7.9 Hz, 2H, Ar*H*), 4.95 (d, *J* = 10.5 Hz, 1H, benzyl-H), 4.93 (d, *J* = 11.5 Hz, 1H, benzyl-H), 4.71 (d, *J* = 14.5 Hz, 1H, benzyl-H), 4.68 (d, *J* = 15.0 Hz, 1H, benzyl-H), 4.59 (d, *J* = 9.0 Hz, 1H, H-1), 3.48 – 3.40 (m, 2H, H-4, H-2), 3.29 (dq, *J* = 9.5, 6.0 Hz, 1H, H-5), 3.22 (t, *J* = 8.5 Hz, 1H, H-3), 2.32 (s, 3H, C*H*$_3$), 2.22 (br-s, 1H, OH), 1.31 (d, *J* = 6.0 Hz, 1H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3, 137.9, 137.6, 132.3, 129.9, 129.6, 128.6, 128.4, 128.2, 127.9, 127.8, 87.9 (C-1), 86.0, 81.0, 75.6, 75.2, 75.2, 74.8, 21.0, 17.9; HRMS (ESI): calcd for $C_{27}H_{30}O_4SNa^+$ $[M + Na]^+$ requires 473.1757, found 473.1762 *m/z*.

To a solution of **32b** (0.5g, 1.11 mmol), NEt_3 (0.46 mL, 3.33 mmol) and DAMP (0.67g, 0.555 mmol) in dried CH_2Cl_2 (5 mL) was added tosylchloride (TsCl) (0.42 g, 2.22 mmol) at 0 °C. The reaction mixture was stirred at 40 °C for 24 h, and then diluted with EtOAc (10 mL). The

mixture was washed with 10% $HCl_{(aq)}$ (10 mL × 2), brine, dried (over $MgSO_4$), concentrated, and dried under *vacuo* to give crude C4-tosylated derivative. The crude tosylated derivative was dissolved in dried DMF (10 mL), followed by sodium nitrate ($NaNO_3$) (0.65 g, 9.99 mmol) was added at 110 °C and the reaction mixture was stirred for 22h. After completion reaction mixture was diluted with EtOAc (10 mL) and water (10mL). Organic layer was washed with saturated $NaHCO_{3(aq)}$ (10 mL × 2) and brine (10 mL), dried (over $MgSO_4$), and concentrated for flash chromatography (Hexane/EtOAc = 9/1) to give **32** (0.86 g, 85%) as a white glassy solid. For **32**, R_f 0.25 (Hexanes/EtOAc = 6/1); $[\alpha]_D^{35}$ –8.19 (*c* 0.39, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.41 – 7.24 (m, 10H, Ar*H*), 7.09 (d, *J* = 7.9 Hz, 2H, Ar*H*), 4.80 (d, *J* = 10.0 Hz, 1H, benzyl-*H*), 4.74–4.72 (m, 3H, benzyl-*H*), 4.48 (dd, *J* = 6.7, 2.7 Hz, 1H, H-1), 3.71 – 3.67 (m, 3H, H-2, H-3, H-4), 3.52 (q, *J* = 6.3 Hz, 1H, H-5), 2.31 (s, 3H, C*H*$_3$), 1.32 (d, *J* = 6.4 Hz, 3H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 137.6, 137.5, 132.6, 129.7, 129.6, 129.5, 128.5, 128.3, 128.2, 127.9, 127.8, 127.7, 126.9, 87.9 (C-1), 83.1 (C-2), 77.3, 77.0, 76.8 (C-3), 76.7, 75.7 (C-5), 73.0, 72.7, 63.6 (C-4), 21.1, 17.8; HRMS (ESI): calcd for $C_{27}H_{29}N_3O_3SNa^+$ [M + Na]$^+$ requires 498.1822, found 498.1822 *m/z*.

2.4.3 Methyl 4-*O*-Benzyl-2,6-dideoxy-α-D-*ribo*-hexopyranoside (34)



To a solution of α/β anomers of **34a**[11] (0.848 g, 2.47 mmol) in dry CH_2Cl_2 (10 mL) containing pyridine (0.89 mL), triflic anhydride (Tf_2O) (0.14 mL, 3.69 mmol) was added dropwise at -20 °C. The reaction mixture was stirred at -20 °C for 2 h and then diluted in EtOAc (30 mL) followed by washing with water (30 mL). The organic layer was further washed with satd. $NaHCO_3$ (30 mL) and brine, dried (over $MgSO_4$), filtered, concentrated, and dried under

vacuo to give crude 3-*O*-triflyl intermediate. The triflyl intermediate in dry toluene was added DBU (1.1 mL, 7.40 mmol) and benzoic acid (2.70 g, 22.17 mmol) and the mixture was stirred at room temperature for 30 min. The reaction mixture was stirred at 60 °C for 9 h. After then, the reaction mixture was cooled down to rt and diluted with EtOAc (10 mL). The EtOAc solution was washed satd. $NaHCO_3$ (30 mL × 3), brine, dried (over $MgSO_4$), and concentrated for flash chromatography (Hexanes/EtOAc = 20/1) to give 3-*O*-benzoyl intermediate **34b** (0.71 g, 64%, α/β = 1:1 based on checking TLC) as an oily yellow liquid. For α anomer of **34b**, R_f 0.35 (Hexanes/CH_2Cl_2/EtOAc = 10/1/1); $[\alpha]_D^{35}$ +288.0 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (dd, *J* = 8.1, 1.1 Hz, 2H, Ar*H*), 7.56 – 7.51 (m, 1H, Ar*H*), 7.48 – 7.37 (m, 4H, Ar*H*), 7.30 – 7.21 (m, 5H, Ar*H*), 7.09 (d, *J* = 7.9 Hz, 2H, Ar*H*), 5.84 (d, *J* = 2.8 Hz, 1H, H-3), 5.43 – 5.39 (t, 1H, H-1), 4.74 (d, *J* = 11.5 Hz, 1H, benzyl-H), 4.69 (m, 1H, H-5), 4.45 (d, *J* = 11.5 Hz, 1H, benzyl-H), 3.26 (dd, *J* = 9.6, 2.8 Hz, 1H, H-4), 2.44-2.42 (m, 2H, H-2), 2.30 (s, 3H, C*H*$_3$), 1.32 (d, *J* = 6.4 Hz, 3H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9 (C=O), 137.6, 137.0, 132.9, 131.6, 130.2, 129.5, 128.3, 128.2, 128.1, 127.7, 83.3 (C-1), 78.4 (C-4), 70.9, 65.1 (C-3), 64.1 (C-5), 35.4 (C-2), 21.0 (*C*H$_3$), 17.9 (C-6). For β anomer of **34b**, R_f 0.45 (Hexanes/CH_2Cl_2/EtOAc = 10/1/1); $[\alpha]_D^{35}$ +9.74 (*c* 1.08, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 4.5, 3.8 Hz, 2H, Ar*H*), 7.53 (ddd, *J* = 6.9, 4.1, 1.3 Hz, 1H, Ar*H*), 7.45 – 7.38 (m, 4H, Ar*H*), 7.28 – 7.23 (m, 5H, Ar*H*), 7.11 (d, *J* = 8.0 Hz, 2H, Ar*H*), 5.80 (d, *J* = 2.8 Hz, 1H, H-3), 5.12 (d, *J* = 10.4 Hz, 1H, H-1), 4.70 (d, *J* = 11.5 Hz, 1H, benzyl-H), 4.42 (d, *J* = 11.5 Hz, 1H, benzyl-H), 4.05 – 3.97 (dq, *J* = 9.6 , 6.4 Hz, 1H, H-5), 3.24 (dd, *J* = 9.6, 2.8 Hz, 1H, H-4), 2.32 (s, 3H, C*H*$_3$ including H-2$_{eq}$), 2.00 (ddd, *J* = 12.0, 14.4, 2.8 Hz, 1H, H-2$_{ax}$), 1.34 (d, *J* = 6.4 Hz, 3H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6 (C=O), 137.7, 137.5, 133.1, 132.5, 129.7, 129.5, 128.3, 128.3, 128.1, 127.7, 80.1 (C-1), 78.2 (C-4), 72.4 (C-5), 71.1, 66.6 (C-3), 36.3, 21.1 (*C*H$_3$), 18.5 (C-6); HRMS (ESI): calcd for $C_{27}H_{28}O_4SNa^+$ $[M + Na]^+$ requires 471.1601, found 471.1620 *m/z*.

A suspension of **34b** (0.46 g, 1.03 mmol) and activated molecular sieve (4Å) in dried CH_2Cl_2 (4.0 mL) was treated with DMF (0.33 mL, 4.1 mmol). The resulting mixture was stirred at rt for 10 min and then at −70 °C for 30 min. Subsequently, *N*-iodosuccinimide (NIS) (0.277 g, 1.23 mmol) and trimethylsilyl triflate (TMSOTf) (0.22 mL, 1.23 mmol) were added. Progress of

the reaction was monitored by TLC (EtOAc/Hexanes/CH_2Cl_2 = 1/10/1). After activation of **34b** activation, additional DMF (0.63 mL, 8.21 mmol) and MeOH (0.2 mL, 5.13 mmol) was added to the donor activation mixture, which was then stirred at –50 °C under N_2 till the formation of the product. The reaction was quenched with addition of satd. $NaHCO_3$ and small lumps of $Na_2S_2O_{3(s)}$, followed by vigorous stirring until the color of the reaction mixture turned from dark red to pain yellow. The resulting mixture was dried (over $MgSO_{4(s)}$), filtered, and concentrated for flash chromatography (Hexanes/EtOAc = 20/1) to to give **34b** (0.31 g, 85%, α/β = 1/1 based on checking TLC) as an oily yellow liquid. For α anomer of **34b**, R_f 0.23 (Hexanes/CH_2Cl_2/EtOAc = 10/1/1); $[\alpha]_D^{35}$ +184.85 (*c* 4.55, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.2 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.23 (m, 5H), 5.71 (q, *J* = 3.2 Hz, 1H, H-3), 4.73 (d, *J* = 11.6 Hz, H, benzyl-H), 4.71 (s, H-1), 4.45 (d, *J* = 11.6 Hz, 1H, benzyl-H), 4.32 – 4.23 (dq, *J* = 11.5, 6.0, 1H, H-5), 3.38 (s, 3H, O*CH*$_3$), 3.25 (dd, *J* = 9.2, 3.2 Hz, 1H, H-4), 2.25 (dd, *J* = 15.2, 3.2 Hz, 1H, H-2$_{eq}$), 1.99 (dt, *J* = 15.2, 4.0 Hz, 1H, H-2$_{ax}$), 1.29 (d, *J* = 6.0 Hz, 3H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 137.7, 132.7, 130.6, 129.8, 128.3, 128.2, 128.1, 127.7, 96.9(C-1), 78.1 (C-4), 70.8, 65.1 (C-3), 62.9 (C-5), 55.0 (O*C*H$_3$), 33.6 (C-2), 17.9 (C-6). For β anomer of **34b**, R_f 0.28 (Hexanes/CH_2Cl_2/EtOAc = 10/1/1); $[\alpha]_D^{35}$ +91.49 (*c* 2.95, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.48 – 7.42 (m, 2H), 7.29 – 7.23 (m, 5H), 5.83 (dd, *J* = 6.4, 2.8 Hz, 1H, H-3), 4.80 (dd, *J* = 9.6, 2.0 Hz, 1H, H-1), 4.72 (d, *J* = 11.4 Hz, 1H, benzyl-H), 4.43 (d, *J* = 11.4 Hz, 1H, benzyl-H), 4.01 (dq, *J* = 9.2, 6.4 Hz, 1H, H-5),3.51(s, 3H, O*CH*$_3$), 3.26 (dd, *J* = 9.2, 2.8 Hz, 1H, H-4), 2.24 (ddd, *J* = 14.2, 6.0, 2.0 Hz, 1H, H-2$_{eq}$), 1.84 (ddd, *J* = 14.2, 9.6, 2.8 Hz, 1H, H-2$_{ax}$), 1.33 (d, *J* = 6.4 Hz, 3H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ165.6 (C=O), 137.5, 133.0, 130.2, 129.7, 128.4, 128.3, 128.1, 127.8, 99.0 (C-1), 78.6, 71.3, 69.5, 66.7, 56.4, 35.8, 18.3; HRMS (ESI): calcd for $C_{21}H_{24}O_5Na^+$ $[M + Na]^+$ requires 379.1518, found 379.1529 *m/z*.

To a solution of **34b** (0.31 g, 0.87 mmol) in MeOH (5 mL), potassium carbonate (0.06 g, 0.87 mmol) was added at 0 °C. The reaction mixture was stirred at rt for 6 h and neutralized with resin IR-120 H^+. The neutralization solution was filtered and concentrated for flash chromatography (Hexanes/EtOAc = 9/1) to give **34** (0.178 g, 81%, α/β = 1/1 based on checking

TLC) as an oily yellow liquid. For α anomer of **34,** R_f 0.28 (Hexanes/ EtOAc = 3/1); $[\alpha]_D^{35}$ +75.10 (*c* 4.76, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.23 (m, 5H, Ar*H*), 4.71 (d, *J* = 11.8 Hz, 2H, benzyl-H), 4.70 (d, *J* = 4.0 Hz, 1H, H-1) 4.49 (d, *J* = 11.8 Hz, 2H, benzyl-H), 4.15 (d, *J* = 3.0 Hz, 1H, H-3), 4.00 (dq, *J* = 9.6, 6.4 Hz, 1H, H-5), 3.33 (s, 3H, O*CH*$_3$), 3.27 (br-s, 1H, OH), 3.04 (dd, *J* = 9.6, 3.2 Hz, 1H, H-4), 2.12 (dd, *J* = 14.8, 3.6 Hz, 1H, H-2$_{eq}$), 1.80 (dt, *J* = 14.8, 3.6 Hz, 1H, H-2$_{ax}$), 1.28 (d, *J* = 6.0 Hz, 3H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 128.3, 127.8, 127.7, 98.1 (C-1), 79.7, 70.4, 63.8, 62.1, 55.0, 35.0, 17.9. For β anomer of **34**, R_f 0.38 (Hexanes/ EtOAc = 3/1); $[\alpha]_D^{35}$ +23.80 (*c* 2.11, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.28 (m, 5H, Ar*H*), 4.72 (dd, *J* = 9.2, 1.6 Hz, 1H, H-1), 4.61 (d, *J* = 11.4 Hz, 1H, benzyl-H), 4.51 (d, *J* = 11.5 Hz, 1H, benzyl-H), 4.19 (d, *J* = 2.0 Hz, 1H, H-3), 3.82 (dq, *J* = 9.4, 6.2 Hz, 1H, H-5), 3.46(s, 1H, O*CH*$_3$), 3.13 – 3.09 (dq, 1H, *J* = 9.2, 3.2, 1.6) Hz, H-4), 2.55 (br-s, 1H, OH), 2.15 (d, *J* = 14.0 Hz, 1H, H-2$_{eq}$), 1.65 – 1.56 (ddd, 1H, *J* = 9.6, 3.2, H-2$_{ax}$), 1.29 (d, *J* = 6.4 Hz, 3H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 128.4, 128.0, 127.8, 98.7 (C-1), 80.48, 71.6, 68.0, 64.4, 56.3, 36.5, 18.1; HRMS (ESI): calcd for $C_{14}H_{20}O_4Na^+$ $[M + Na]^+$ requires 275.1254, found 275.1245 *m/z*.

2.4 HPLC chromatograms and α/β ratio determination for glycosylations of Table 1

2.4.1 Amount of TBAI

Glycosylation without TBAI and base addition (Table 1, entry 1 in article): HPLC conditions - flow rate 1.0 mL/min and elution with 3/1 hexanes/EtOAc. Retention time for α anomer of **5** = 9.3 min and for β anomer of **5** = 7.7 min, thus α/β = 2/1 (Figure S1).

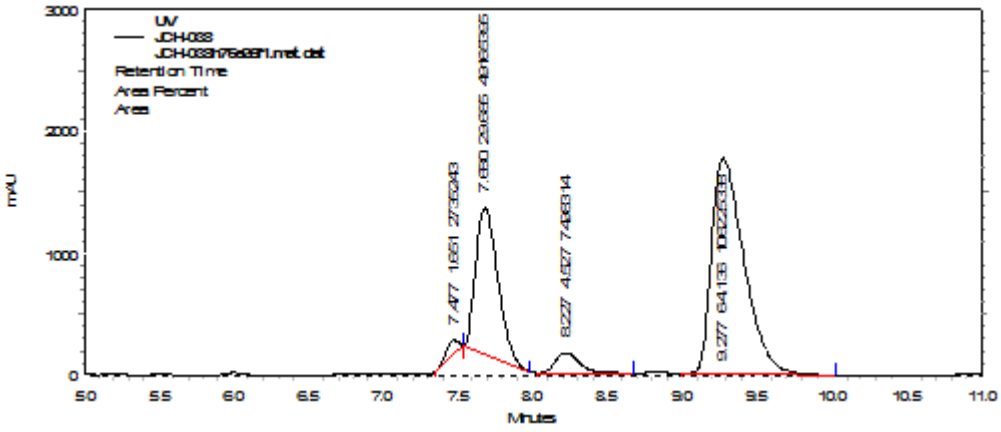


Figure S1. Partial HPLC chromatogram for **5** obtained from glycosylation without iodide substitution.

Glycosylation with addition of 2.0 equiv. TBAI (Table 1, entry 2 in article): HPLC conditions - flow rate 1.0 mL/min and 3/1 hexanes/EtOAc elution. Retention time for α anomer of **5** = 9.0 min and β anomer of **5** = 7.4 min, thus α/β = 5/1 (Figure S2).

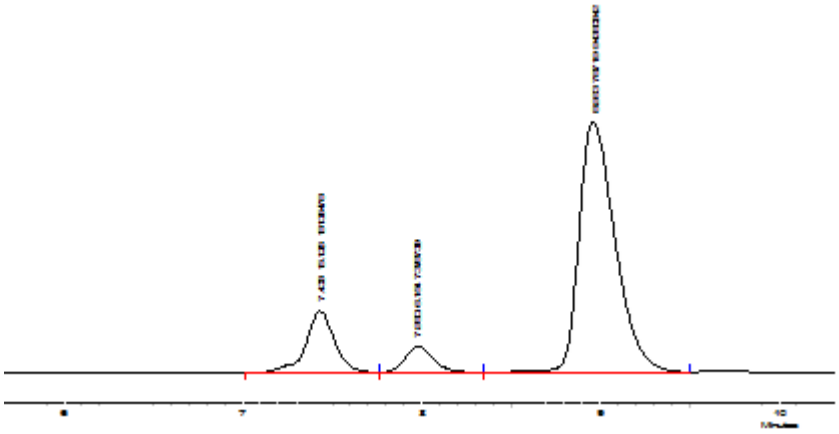


Figure S2. HPLC chromatogram for sample **5** obtained from glycosylation with 2.0 equiv of TBAI.

Glycosylation with addition of 5.0 equiv. TBAI (Table 1, entry 3 in article): HPLC conditions: flow rate 1.0 mL/min and 3/1 hexanes/EtOAc elution. Retention time for α anomer of **5** = 8.9 min and β anomer of **5** = 7.4, thus α/β = 11/1 (Figure S3).

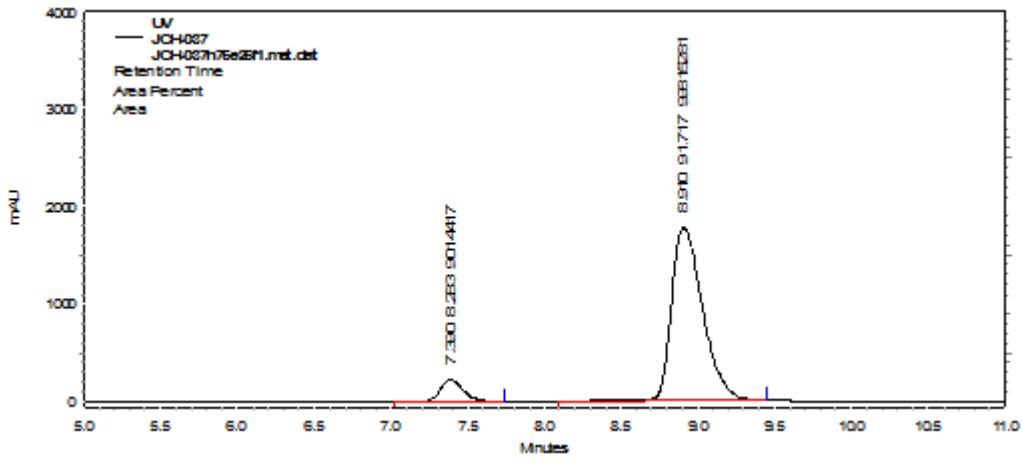


Figure S3. HPLC chromatogram for crude sample **5** obtained from glycosylation with 5.0 equiv of TBAI.

Glycosylation with addition of 10 equiv. TBAI (Table 1, entry 4 in article): HPLC conditions: flow rate 1.0 mL/min and 3/1 hexanes/EtOAc elution. Retention time for α anomer of **5** = 9.1 min and β anomer of **5** = 7.6 min, thus α/β = 13/1 (Figure S4)

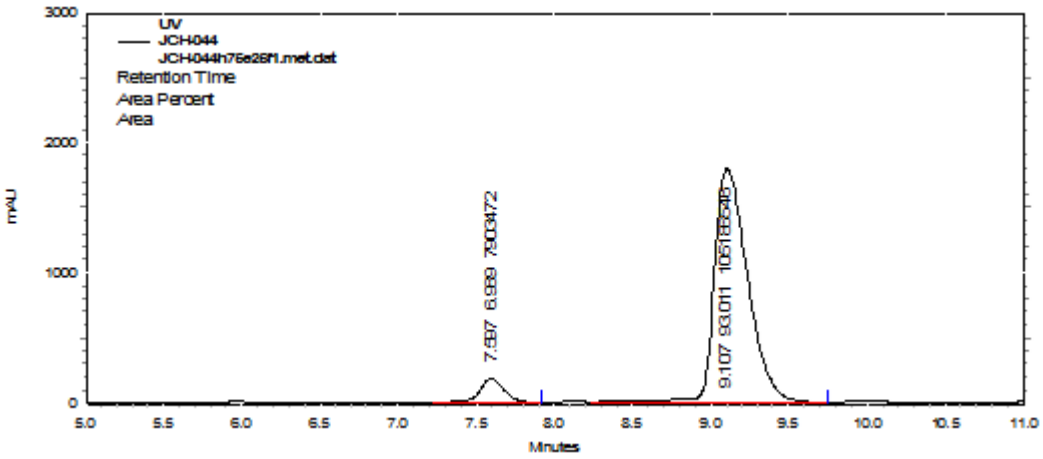
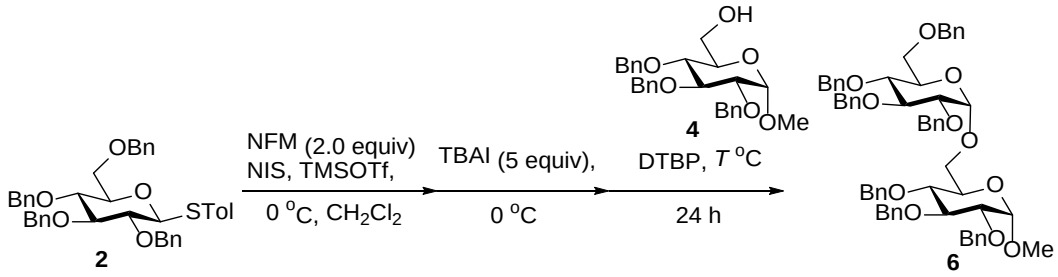


Figure S4. HPLC chromatogram for crude sample **5** from glycosylation with 10.0 equiv. of TBAI.

2.4.2 Effect of temperature in glycosylation



Glycosylation at 15 ºC (Table 1, entry 6 in article)**:** HPLC conditions: flow rate 1.0 mL/min and 4/1 hexanes/EtOAc elution. Retention time for β anomer of **6** obtained from low concentration glycosylation = 10.7 min (Figure S6-1). Retention time for α-anomer of **6** = 12.5 min and no β-anomer of **6** was detected at 10.7 min, thus α/β = >19/1(Figure S6-2).

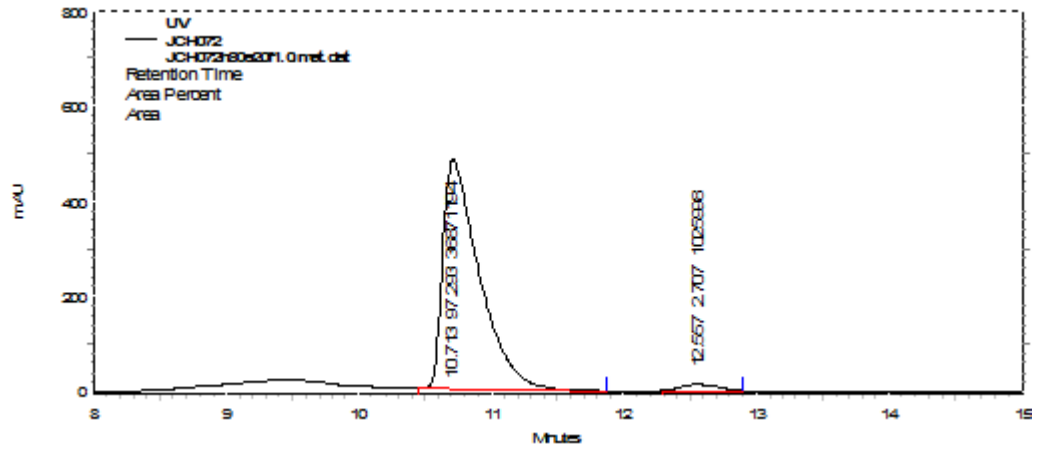


Figure S6-1. HPLC chromatogram of β anomer of **6**.

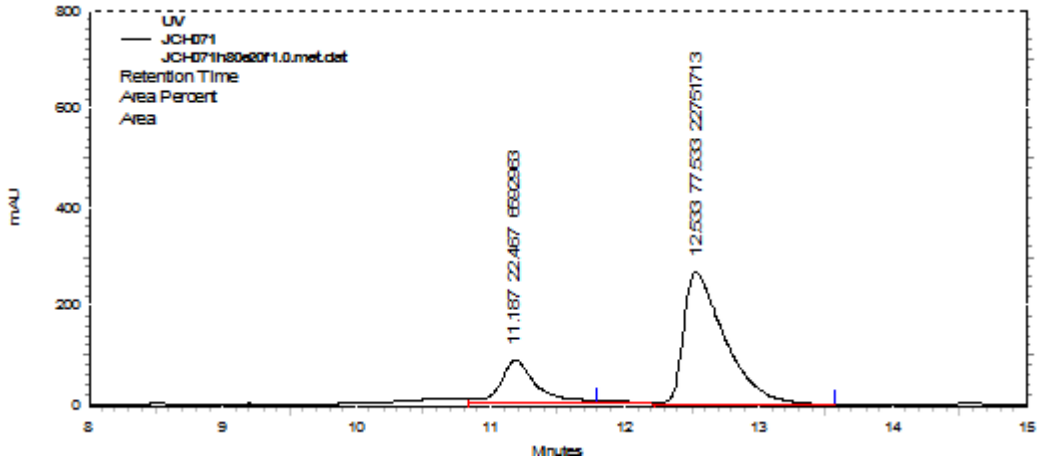


Figure S6-2. HPLC chromatogram for crude sample **6** from one-pot *in situ* adduct transformation and glycosylation procedure at 15 ºC.

Glycosylation at 30 ºC (Table 1, entry 7 in article): HPLC conditions: flow rate 1.0 mL/min and 4/1 hexanes/EtOAc elution. Retention time for β anomer **6** obtained from low concentration glycosylation = 10.7 min (Figure S7-1). For crude product obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention time for α-anomer of **6** = 12.8 min and no β-anomer of **6** was detected at 10.7 min, thus α/β = >19/1 (Figure S7-2).

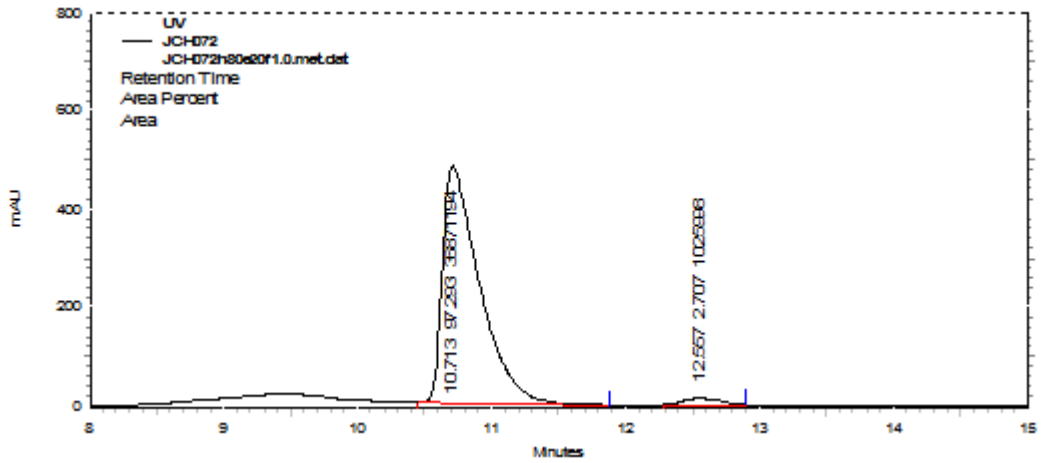


Figure S7-1. HPLC chromatogram of β anomer of **6**.

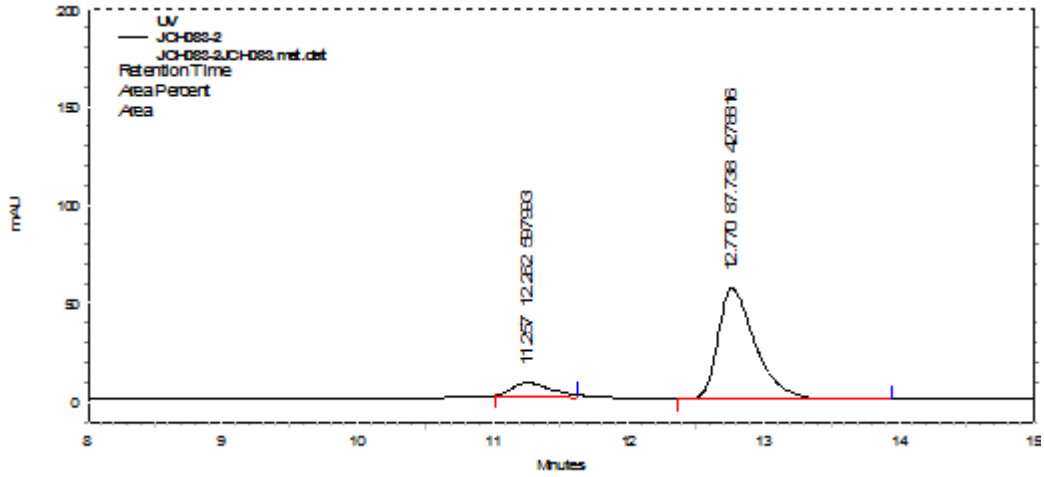


Figure S7-2. HPLC chromatogram for crude sample **6** from one-pot *in situ* adduct transformation and glycosylation procedure at 30 ºC.

Glycosylation at 50 ºC (Table 1, entry 8 in article): HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 4/1. For crude product obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention time of β anomer of **6** = 11.3 min (Figure S8-1). Retention time for α anomer of **6** = 13.5 min and for β anomer of **6** = 11.6 min, thus α/β = 3/1 (Figure S8-2).

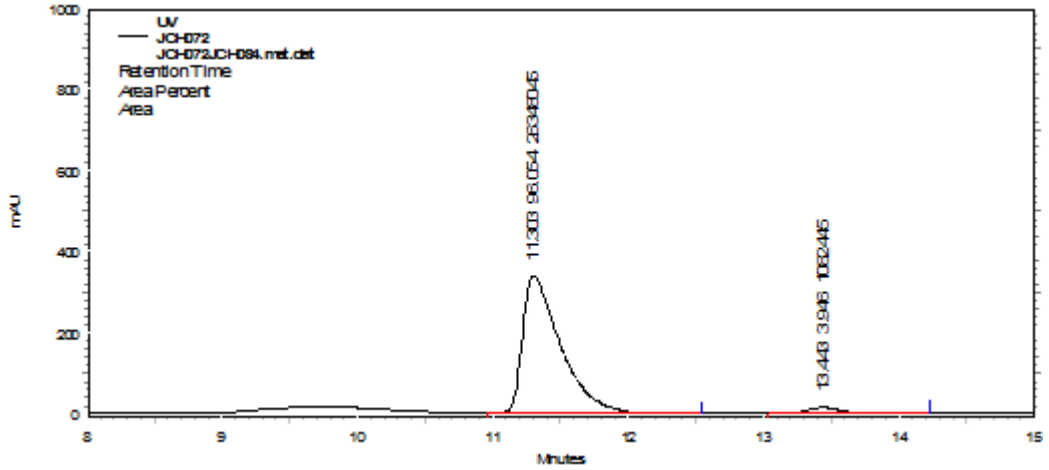


Figure S8-1. Partial HPLC chromatogram of β anomer of **6.**

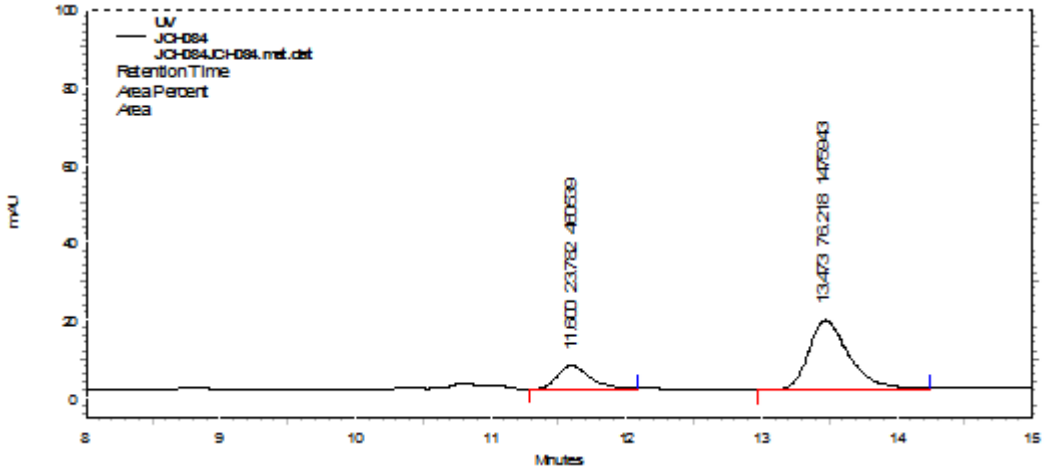
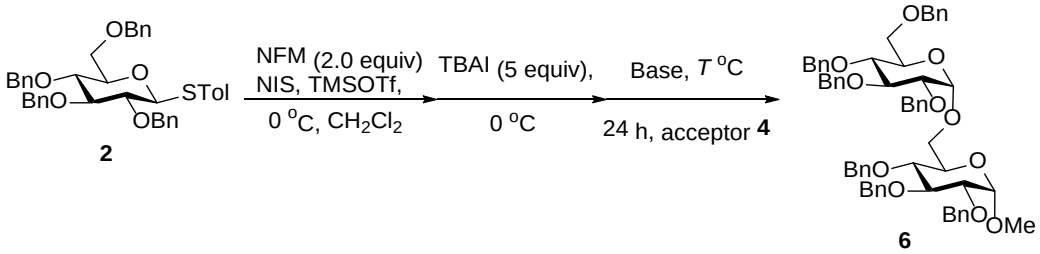


Figure S8-2. HPLC chromatogram for crude sample **6** from one-pot *in situ* adduct transformation and glycosylation procedure at 50 °C.

2.4.3 Effect of base in glycosylation



Glycosylation without base addition (Table 1, entry 9 in article): HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 4/1. Retention time for β-anomer **6** from low concentration glycosylation = 14.4 min (Figure S9-1). For crude product obtained from one-pot *in situ* adduct

transformation and glycosylation procedure in the absence of base, retention time for α anomer of **6** = 16.7 min and β anomer of **6** = 14.7 min, thus α/β = 5/1 (Figure S9-2).

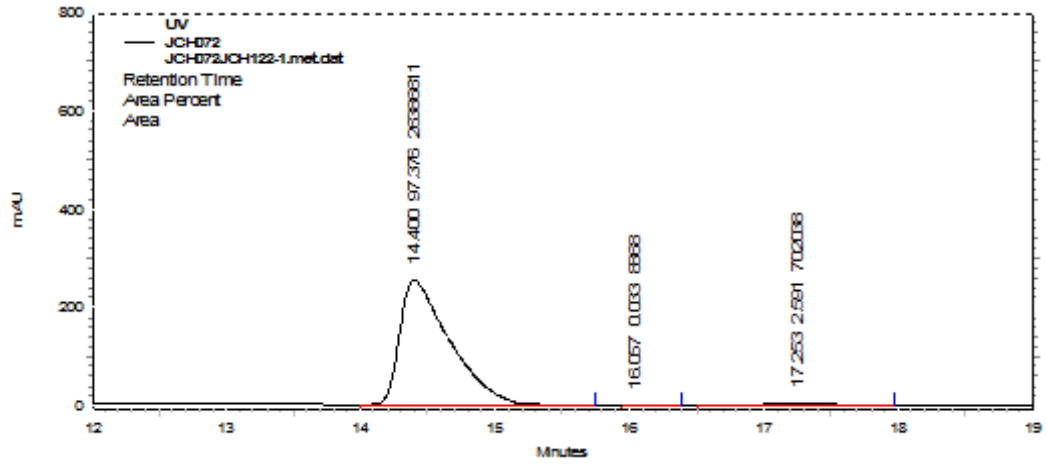


Figure S9-1. HPLC chromatogram of β anomer of **6**.

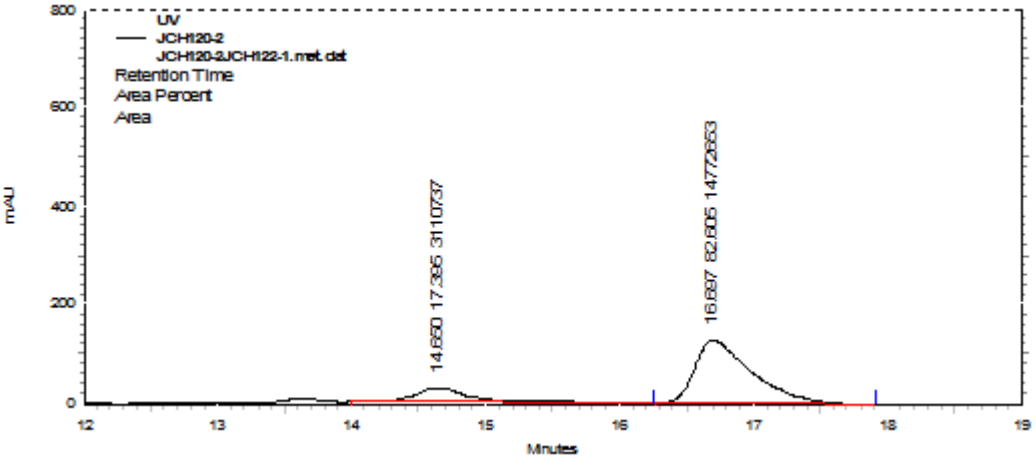


Figure S9-2. HPLC chromatogram for crude sample **6** from one-pot *in situ* adduct transformation and glycosylation procedure in the absence of base.

Glycosylation with 2,6-lutidine addition (Table 1, entry 10 in article): HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 4/1. Retention time for β anomer standard **6** obtained from low concentration glycosylation = 12.6 min (Figure S11-1). For sample obtained from one-pot *in situ* adduct transformation and glycosylation procedure with 2,6-Lutidine addition, retention time for α anomer of **6** = 14.8 min; β anomer of **6** = 12.3 min, thus α/β > 19/1 (Figure S11-2).

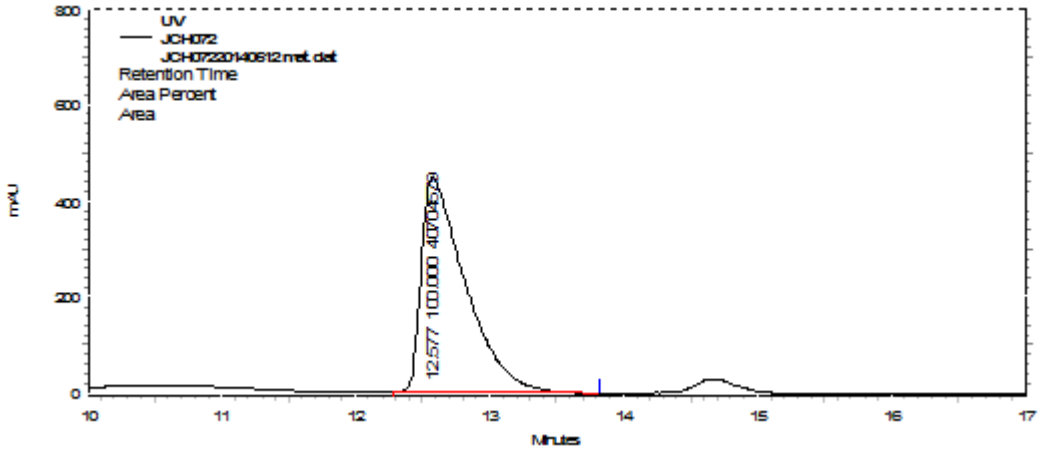


Figure S11-1. HPLC chromatogram of β anomer of **6**.

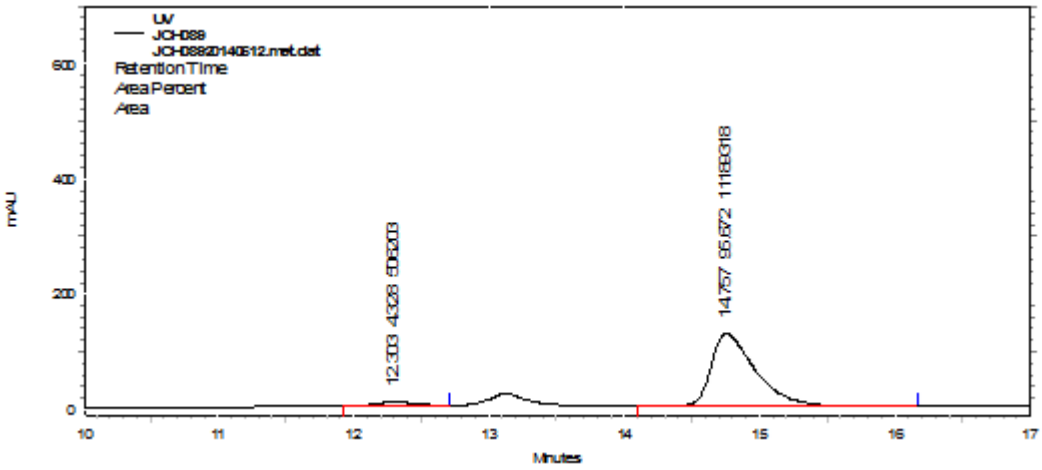


Figure S11-2. HPLC chromatogram for crude sample **6** from one-pot *in situ* adduct transformation and glycosylation procedure with lutidine addition.

Glycosylation with DIEA addition (Table 1, entry 11 in article**)**: HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 4/1. Retention time for β anomer standard of **6** obtained from low concentration glycosylation = 12.6 min (Figure S12-1). For sample obtained from one-pot *in situ* adduct transformation and glycosylation procedure with DIEA addition, retention time for α anomer of **6** = 15.0 min; β anomer of **6** = 12.4 min, thus α/β > 19/1 (Figure S12-1).

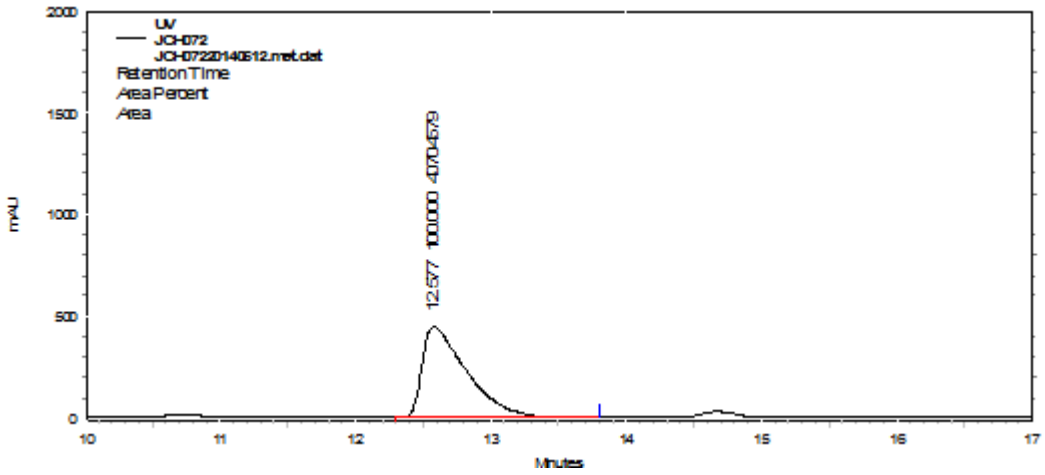


Figure S12-1. HPLC chromatogram of β anomer standard of **6**.

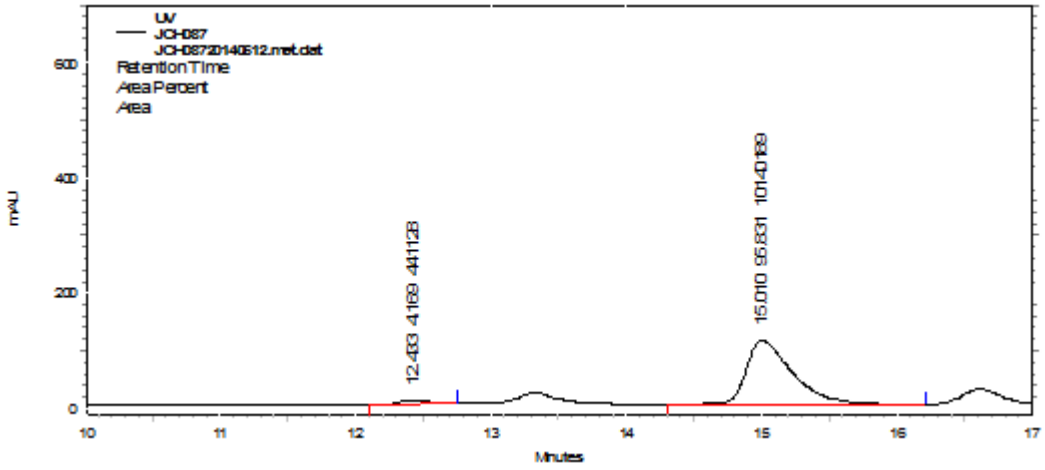
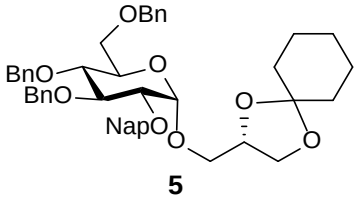


Figure S12-2. HPLC chromatogram for crude product **6** obtained from one-pot *in situ* adduct transformation and glycosylation with DIEA addition.

2.5 Glycosylation products (5, 6, 19-29, 35-41, 43, 45)

2.5.1 3-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(2-naphthylmethyl)-α-D-glucopyranosyl]-1,2-*O*-cyclohexylidene-*sn*-glycerol (5)



5

α-Glucoside **5**[1] was (126 mg, 60%) prepared from and glycosylation of *sn*-glycerol acceptor **3** (72 mg, 0.42 mmol)[1] with thioglucoside **1** (200 mg, 0.28 mmol)[1] according to one-pot

in situ adduct transformation and glycosylation procedure (with DTBP as the base). For **5**, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 – 7.73 (m, 4H), 7.51 – 7.44 (m, 3H), 7.39 – 7.21 (m, 13H), 7.16 – 7.12 (m, 2H), 5.00 (d, *J* = 10.9 Hz, 1H, OC*H*Ph), 4.93 – 4.89 (m, 2H, including H-1′), 4.86 – 4.80 (m, 3H), 4.58 (d, *J* = 12.1 Hz, 1H, OC*H*Ph), 4.49 – 4.44 (m, 2H), 4.40 – 4.34 (m, 1H), 4.06 (dd, *J* = 8.3, 6.4 Hz, 1H), 3.98 (t, *J* = 9.3 Hz, 1H), 3.81 – 3.76 (m, *J* = 8.9 Hz, 1H), 3.75 – 3.68 (m, 2H), 3.66 – 3.55 (m, 5H), 1.64 – 1.56 (m, 10H)); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8, 138.3, 137.9, 135.6, 133.2, 133.1, 128.4, 128.3, 128.2, 127.90, 127.86, 127.8, 127.7, 127.6, 127.5, 126.8, 126.1, 126.0, 125.9, 110.1, 97.3 (C-1′, $J_{CH'}$ = 167.8 Hz), 81.9, 79.9, 77.6, 75.7, 75.0, 74.3, 73.5, 73.1, 70.4, 69.0, 68.5, 66.6, 36.5, 35.0, 25.1, 24.0, 23.9. The α:β ratio of **5** was determined to be 11:1 by HPLC analysis (Table 1, entry 3). HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 3:1. Retention time of α anomer of **5** = 8.9 min and β anomer of **5** = 7.4 min (Figure S13).

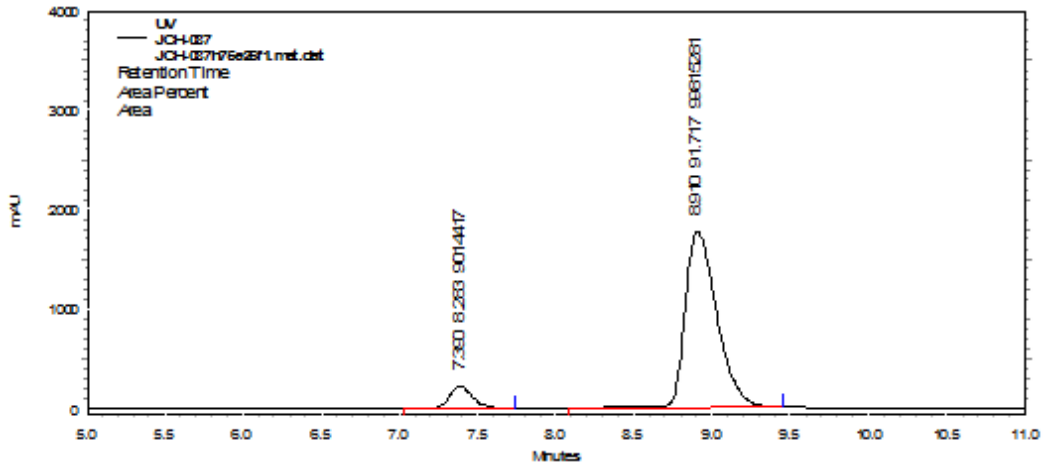
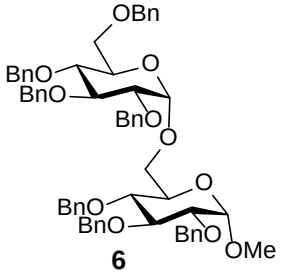


Figure S13. HPLC chromatogram for sample **5** obtained from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.2 Methyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (6)



6

α-Anomer of disaccharide **6**[12] was (78 mg, 55%) synthesized from Glc donor **2** (100 mg, 0.15 mmol) and Glc acceptor **4** (105 mg, 0.23 mmol) using the one-pot *in situ* adduct transformation and glycosylation procedure (with DTBP as the base) (76% yield was achieved from DIEA or lutidine as the base). For α-anomer of **6**, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.20 (m, 33H, Ar*H*), 7.15 – 7.10 (m, 2H, Ar*H*), 5.00 – 4.89 (m, 4H, including H-1′), 4.85 – 4.75 (m, 3H), 4.70 (d, *J* = 12.1 Hz, 1H, OC*H*Ph), 4.68 – 4.62 (m, 3H), 4.58 (d, *J* = 3.7 Hz, 1H), 4.55 (d, *J* = 3.7 Hz, 2H, including H-1), 4.45 (d, *J* = 11.0 Hz, 1H), 4.41 (d, *J* = 12.1 Hz, 1H, OC*H*Ph), 4.02 – 3.93 (m, 2H), 3.82 (dd, *J* = 11.5, 4.4 Hz, 1H), 3.80 – 3.76 (m, 2H), 3.71 (d, *J* = 11.1 Hz, 1H, OC*H*Ph), 3.68 – 3.59 (m, 3H), 3.57 – 3.52 (m, 2H, including H-2′), 3.44 (dd, *J* = 9.6, 3.5 Hz, 1H, H-2), 3.35 (s, 3H, OC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.7, 138.41, 138.37, 138.36, 138.1, 137.9, 128.38, 128.35, 128.30, 128.26, 128.24, 128.21, 128.0, 127.94, 127.91, 127.88, 127.81, 127.78, 127.66, 127.65, 127.57 127.56, 127.54, 127.52, 127.49, 127.47, 127.4, 97.9 (C-1, J_{CH} = 166.3 Hz), 97.2 (C-1′, $J_{CH'}$ = 167.8 Hz), 82.1, 81.6, 80.1, 79.9, 77.7, 77.6, 75.7, 75.4, 74.9, 74.8, 73.3, 73.3, 72.3, 70.3, 70.2, 68.4, 66.0, 55.1 (O*C*H$_3$). The α/β ratio of **6a** was determined to be >19/1 by HPLC analysis (Table 1, entries 7, 10, and 11). HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 4/1. For sample obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention time for α anomer = 12.8 min and no β anomer was detected (Figure S14-2). β-Anomer of disaccharide **6** was synthesized from **2** and **4** using low concentration glycosylation procedure.[7]

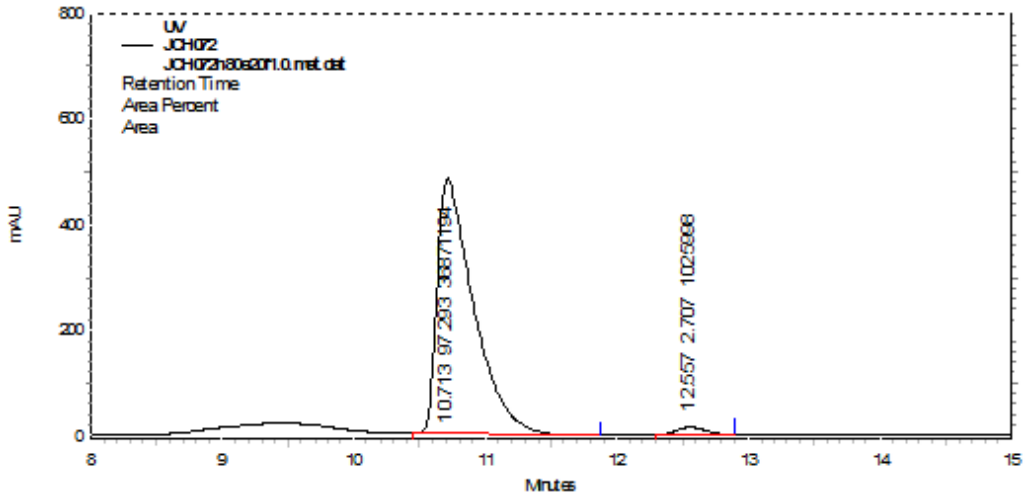


Figure S14-1. HPLC chromatogram for β anomer of **6**.

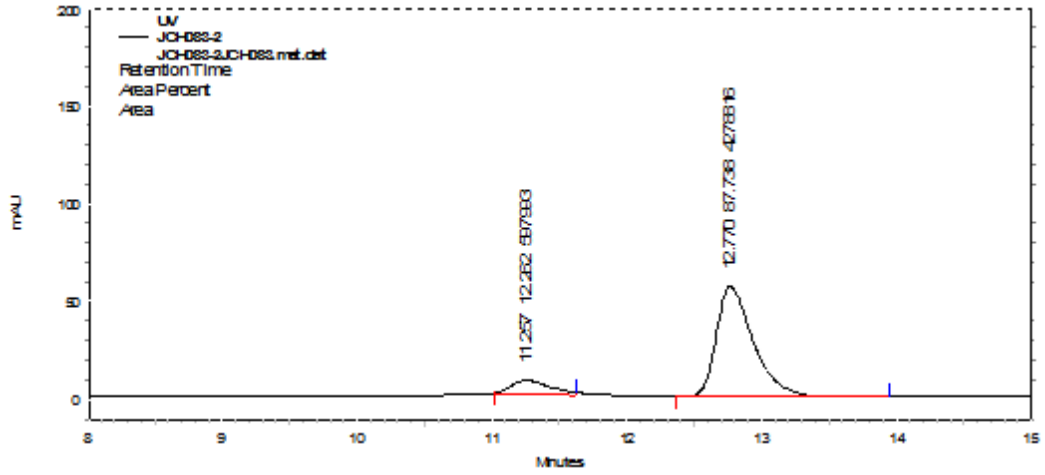
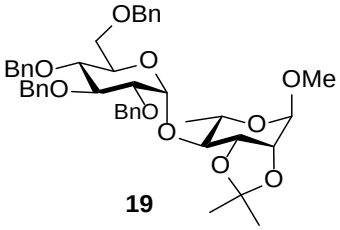


Figure S14-2. HPLC chromatogram for crude product **6** obtained from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.3 Methyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (19)



19

α-Anomer of disaccharide **19**[13] was (78 mg, 70%) synthesized from donor **2** (100 mg, mmol) and acceptor **16** (46 mg, 0.23 mmol) according to one-pot *in situ* adduct transformation and glycosylation procedure (Table 2, entry 1 in article). For α-anomer of **19**, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 – 7.23 (m, 18H, Ar*H*), 7.19 – 7.15 (m, 2H, Ar*H*), 4.97 (d, *J* = 3.5 Hz, 1H, H-1′), 4.95(d, *J* = 10.09 Hz, 1H) 4.88 – 4.81 (m, 3H, including H-1), 4.79 (d, *J* = 11.6 Hz, 1H), 4.70 (d, *J* = 11.7 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.53 (d, *J* = 10.7 Hz, 1H), 4.49 (d, *J* = 12.1 Hz, 1H), 4.12 – 4.08 (m, 1H), 4.08 – 4.04 (m, 2H), 3.98 (t, *J* = 9.4 Hz, 1H), 3.82 – 3.71 (m , 3H), 3.67 – 3.62 (m, 1H), 3.59 (dd, *J* = 9.8, 3.6 Hz, 1H), 3.33 (m, 4H), 1.43 (s, 3H, isopropylidene-C*H*$_3$), 1.31 (d, *J* = 6.3 Hz, 3H, C*H*$_3$), 1.25 (s, 3H, isopropylidene-C*H*$_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.8, 138.4, 138.0, 137.9, 128.4, 128.4, 128.3, 128.3, 128.2, 127.9, 127.9, 127.9, 127.8, 127.6, 127.6, 127.5, 108.9, 98.3 (C-1′, $J_{CH'}$ = 167.9 Hz,), 97.8 (C-1, J_{CH} = 167.4 Hz), 82.2, 80.9, 79.9, 77.9, 76.8, 75.9, 75.5, 75.1, 74.2, 73.5, 70.3, 68.0, 64.7, 54.6, 28.1, 26.3, 17.4; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{44}H_{52}NaO_{10}^+$, 763.3453; found 763.3450. The α/β ratio of **19** was

determined to be 19:1 by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 23/7. Retention time for β anomer standard sample of **19** obtained from low concentration glycosylation = 11.8 min (Figure S15-1).[7,14] For **19** obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention for α anomer = 17.0 min; β anomer = 12.1 min (Figure S15-2).

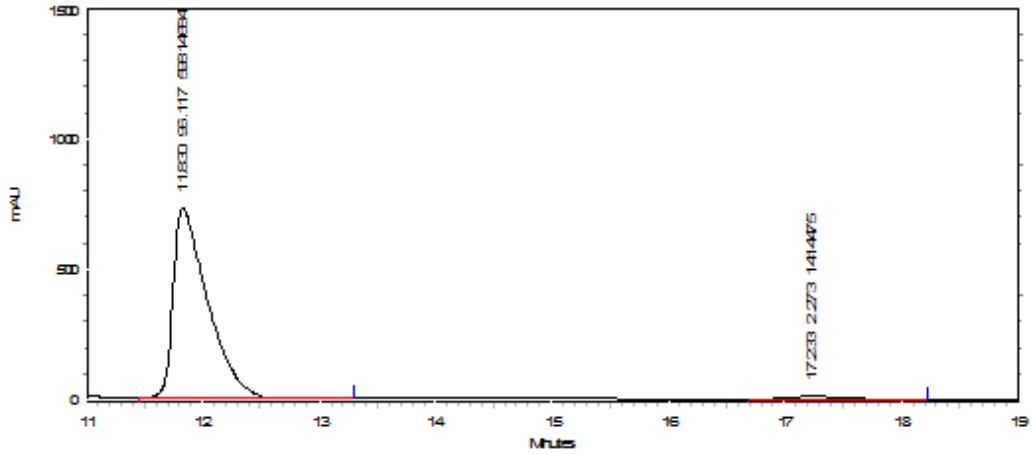


Figure S15-1. HPLC chromatogram for β-anomer of disaccharide **19**.

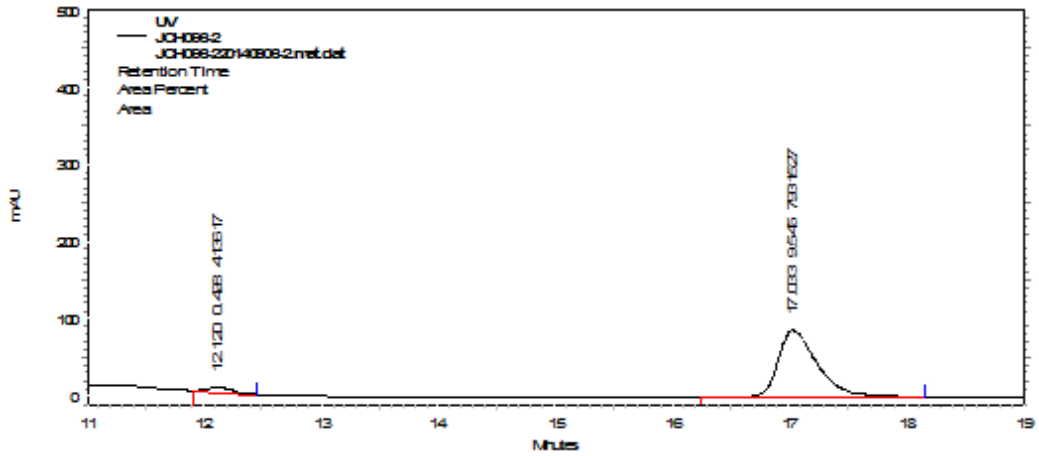
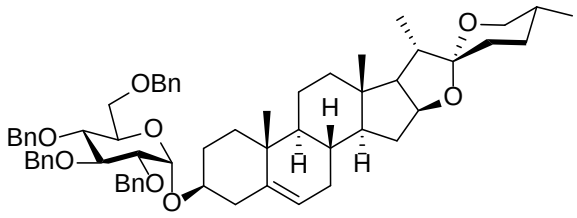


Figure S15-2. HPLC chromatogram for crude product **19** obtained from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.4 Diosgeninyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (20)



20

Diogeninyl α-glucoside **20** was (75 mg, 60%) synthesized from glycosylation of diosgenine acceptor **17** (94 mg, 0.225 mmol) with Glc donor **2** (100 mg, 0.15 mmol) using one-pot *in situ* adduct transformation and glycosylation procedure (Table 2, entry 2 in article). For α-glucoside **20**, R_f 0.54 (hexanes/EtOAc 3/1); $[\alpha]_D^{35}$ +150 (c 0.08, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 – 7.25 (m, 18H, Ar-H), 7.13 (dd, *J* = 2.0, 7.5 Hz, 2H, Ar-H), 5.28 (d, *J* = 5.0 Hz, 1H), 5.00 (d, *J* = 11.0 Hz, 1H), 4.93 (d, *J* = 3.5 Hz, 1H, H-1), 4.82 (dd, *J* = 8.0, 10.5 Hz, 2H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.47 (d, *J* = 6.5 Hz, 1H), 4.44 (d, *J* = 8.0 Hz, 1H), 4.41 (q, J = 15.5 Hz, 1H), 3.99 (t, *J* = 9.5 Hz, 1H), 3.87 (d, *J* = 10.5 Hz, 1H), 3.73 (dd, *J* = 4.0, 11.0 Hz, 1H), 3.64 – 3.61 (m, 2H), 3.55 (dd, *J* = 4.0, 10.0 Hz, 1H), 3.48 – 3.43 (m, 2H), 3.37 (t, *J* = 10.5 Hz, 1H), 2.42 (t, *J* = 11.0 Hz, 1H) , 2.28 (dd, *J* = 3.0, 13.0 Hz, 1H), 2.00 – 1.95 (m, 2H), 1.88 – 1.84 (m, 3H), 1.79 – 1.72 (m, 2H), 1.68 – 1.60 (m, 5H), 1.54 – 1.50 (m, 3H), 1.48 – 1.42 (m, 2H), 1.31 – 1.27 (m, 2H), 1.20 – 1.07 (m, 3H), 1.04 – 1.01 (m, 4H), 0.97 (d, *J* = 7.0 Hz, 3H), 0.93 (dd, *J* = 5.0, 11.5 Hz, 1H), 0.78 (t, *J* = 3.5 Hz, 6H); 13C NMR (125 MHz, CDCl3): δ 140.95, 139.04, 138.35, 138.33, 138.05, 128.49, 128.46, 128.45, 128.41, 128.22, 128.05, 127.99, 127.93, 127.89, 127.84, 127.78, 127.71, 127.63, 127.61, 121.51, 109.36, 94.74, 82.20, 80.91, 80.03, 77.97, 76.57, 75.75, 75.21, 73.51, 73.17, 70.15, 68.69, 66.93, 62.20, 56.61, 50.12, 41.70, 40.36, 39.95, 39.87, 37.16, 37.02, 32.17, 31.94, 31.52, 31.48, 30.39, 29.78, 28.89, 27.57, 20.94, 19.50, 17.22, 16.37, 14.61; HRMS-ESI (*m/z*): [M + Na]+ calcd for C61H76NaO8+, 959.5438; found, 959.5437.

The α/β ratio of **20** was determined to be 14/1 by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 85/15. Retention time of β anomer standard of **20** = 5.4

min (Figure S16-1).[7] For **20** obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention time of α anomer = 6.1 min (Figure S16-2).

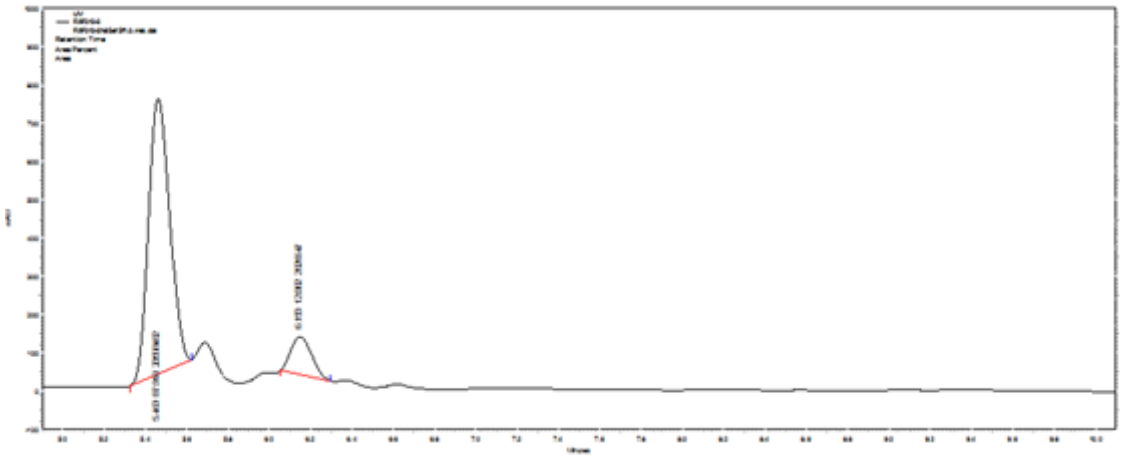


Figure S16-1. HPLC chromatogram of β-anomer of **20**.

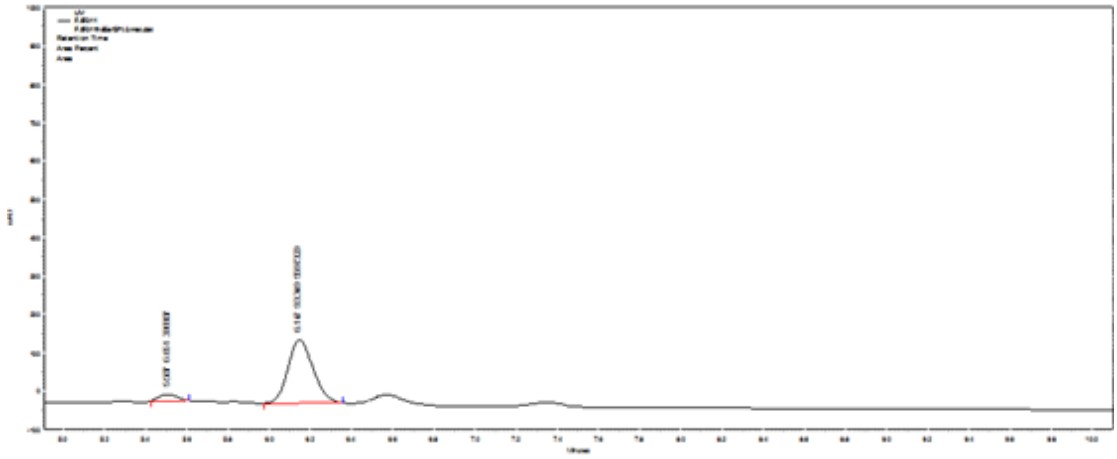
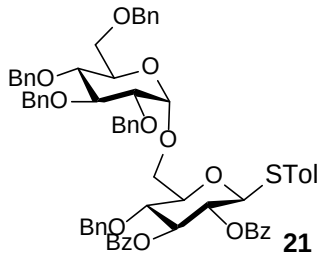


Figure S16-2. HPLC chromatogram for crude **20** obtained from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.5 *p*-Tolyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzoyl- 4-*O*-benzyl-thio-β-D-glucopyranoside (21)



21

α-Anomer of disaccharide **21** was (101 mg, 68%) synthesized from Glc **2** (100 mg, 0.15 mmol) and thioglucoside acceptor **18** (132 mg, 0.23 mmol) using one-pot *in situ* adduct transformation and glycosylation procedure (Table 2, entry 3 in article). For α-anomer of **21**, R_f 0.35 (hexanes/EtOAc 3/1); $[\alpha]_D^{35}$ +49.8 (*c* 0.610, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.52 – 7.46 (m, *J* = 13.7, 7.4 Hz, 2H), 7.40 – 7.24 (m, 25H), 7.15 – 7.12 (m, 2H), 7.11 – 7.08 (m, 2H), 7.06 – 7.03 (m, 4H), 5.65 (t, *J* = 9.4 Hz, 1H), 5.29 (t, *J* = 9.7 Hz, 1H), 5.11 (d, *J* = 3.5 Hz, 1H, H-1′), 5.01 (d, *J* = 10.9 Hz, 1H), 4.86 (d, *J* = 10.9 Hz, 1H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.80 (d, *J* = 10.0 Hz, 1H), 4.73 – 4.68 (m, 2H), 4.65 (d, *J* = 12.2 Hz, 1H), 4.54 – 4.49 (m, 4H), 4.02 (t, *J* = 9.3 Hz, 1H), 3.92 – 3.87 (m, 4H), 3.75 – 3.66 (m, 4H), 3.62 (dd, *J* = 9.6, 3.5 Hz, 1H, H-2′), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6, 165.2, 138.8, 138.5, 138.4, 138.2, 138.0, 137.3, 134.0, 133.1, 133.0, 129.83, 129.77, 129.75, 129.5, 129.4, 128.5, 128.4, 128.29, 128.27, 128.19, 128.17, 127.91, 127.90, 127.84, 127.79, 127.71, 127.70, 127.63, 127.55, 97.1 (C-1′, J_{CH} = 168.8), 86.6, 81.9, 80.3, 79.6, 77.7, 76.3, 75.7, 75.6, 75.1, 74.6, 73.4, 72.9, 71.0, 70.3, 68.6, 65.2, 21.1 (*C*H_3); HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{68}H_{66}NaO_{12}S^+$, 1129.4167; found, 1129.4162.

The α/β ratio of **21** was 9:1 determined by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc gradient from 4/1 to 11/9. Retention time of β anomer of **21** (from low concentration glycosylation) = 15.1 min (Figure S17-1). For disaccharide **21** obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention time for α anomer = 17.4 min; β anomer = 15.1 min (Figure S17-2). β-Anomer of disaccharide **21** was synthesized from donor **2** and acceptor **18** using the low concentration glycosylation.[7]

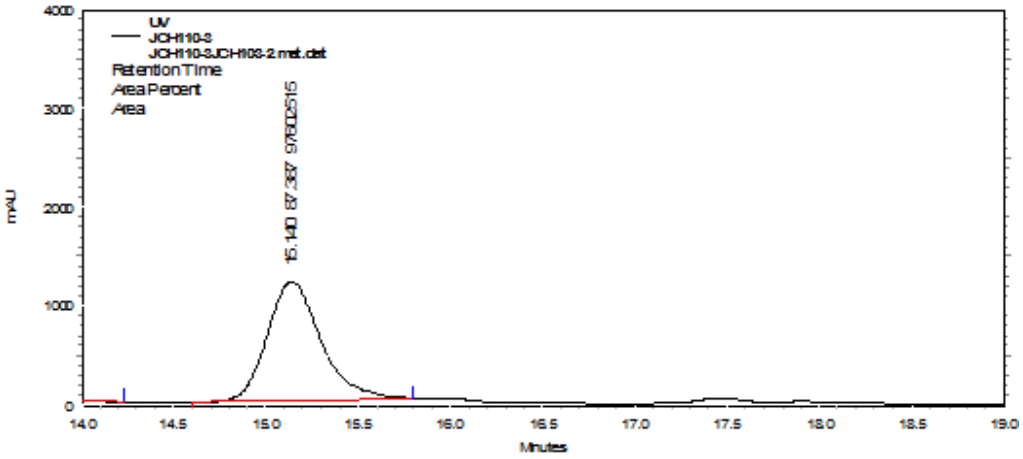


Figure S17-1. HPLC chromatogram for β-anomer of **21**.

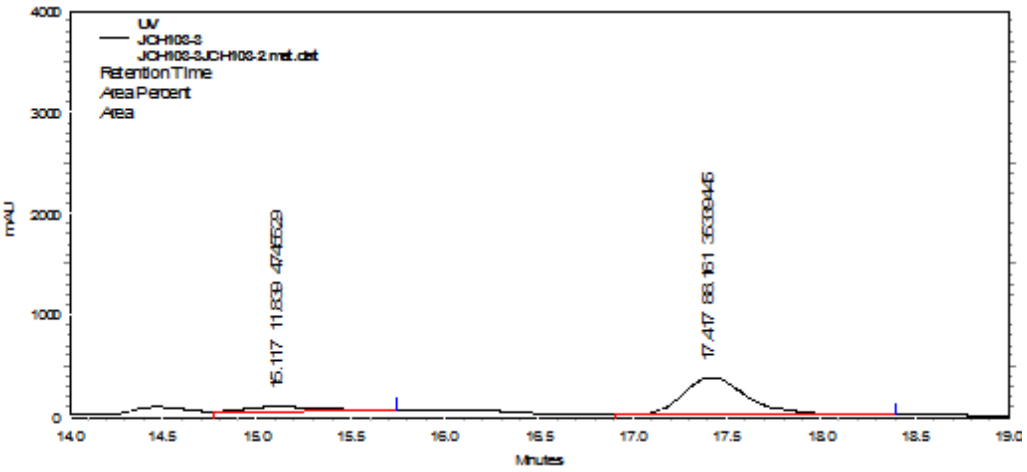
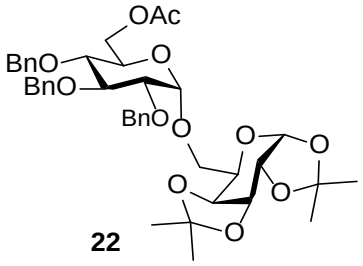


Figure S17-2. HPLC chromatogram for crude product **21** obtained from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.6 6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-1,2:3,4-*O*-diisopropylidene-α-D-galactopyranose (22)



22

α-Anomer of disaccharide **22**[15] was (41 mg, 70%) synthesized from glycosylation of galactosyl acceptor **15** (31 mg, 0.12 mmol with glucosyl donor **9** (50 mg, 0.08 mmol) using one-pot *in situ* adduct transformation and glycosylation procedure (Table 2, entries 4 and 5 in article).

For α-anomer of **22**, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.24 (m, 15H, Ar*H*), 5.52 (d, *J* = 5.0 Hz, 1H, H-1), 5.00 (d, *J* = 10.8 Hz, 1H), 4.94 (d, *J* = 3.6 Hz, 1H, H-1′), 4.86 (d, *J* = 10.9 Hz, 1H), 4.81 (d, *J* = 10.8 Hz, 1H), 4.72 (q, *J* = 11.9 Hz, 2H), 4.60 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.56 (d, *J* = 10.9 Hz, 1H), 4.35 – 4.29 (m, 3H), 4.23 (dd, *J* = 12.0, 2.1 Hz, 1H), 4.06 – 3.99 (m, 2H), 3.94 (ddd, *J* = 10.1, 4.1, 2.1 Hz, 1H), 3.80-3.70 (m, 2H), 3.55 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.49 (dd, *J* = 9.9, 9.1 Hz, 1H), 2.02 (s, 3H, COC*H*$_3$), 1.54 (s, 3H, isopropylidene-C*H*$_3$), 1.45 (s, 3H, isopropylidene-C*H*$_3$), 1.33 (s, 3H, isopropylidene-C*H*$_3$), 1.31 (s, 3H, isopropylidene-C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.8 (C=O), 138.7, 138.1, 137.9, 128.41, 128.37, 128.36, 128.1, 127.9, 127.83, 127.78, 127.75, 127.6, 109.2, 108.6, 97.0 (C-1′, $J_{CH'}$ = 168.0 Hz), 96.3 (C-1, J_{CH} = 178.4 Hz), 81.8, 79.8, 77.2, 75.6, 74.8, 72.4, 70.9, 70.6, 70.6, 68.6, 66.6, 65.9, 63.1, 26.1, 26.0, 24.9, 24.6, 20.8 (*C*H$_3$CO); HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{41}H_{50}NaO_{12}^+$, 757.3195; found, 757.3197.

The α/β ratio of **22** was determined to be >19/1 by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 3/1 gradient to 7/3. Retention time for β anomer of **22** obtained from low concentration glycosylation = 13.4 (Figure S18-1). For sample obtained from one-pot *in situ* adduct transformation and glycosylation procedure using DIEA, retention time for α anomer of **22** = 12.7 min and no β anomer of **22** detected at 13.4 min (Figure S18-2). For sample obtained from one-pot *in situ* adduct transformation and glycosylation procedure using LTD, retention time for α anomer of **22** (with LTD as the base) = 12.3 min and β anomer of **22** = 13.6 min (Figure S18-3). β-Anomer of disaccharide **22**[15] was (92 mg, 74%) synthesized from **9** and **15** according to low concentration glycosylation procedure.[7]

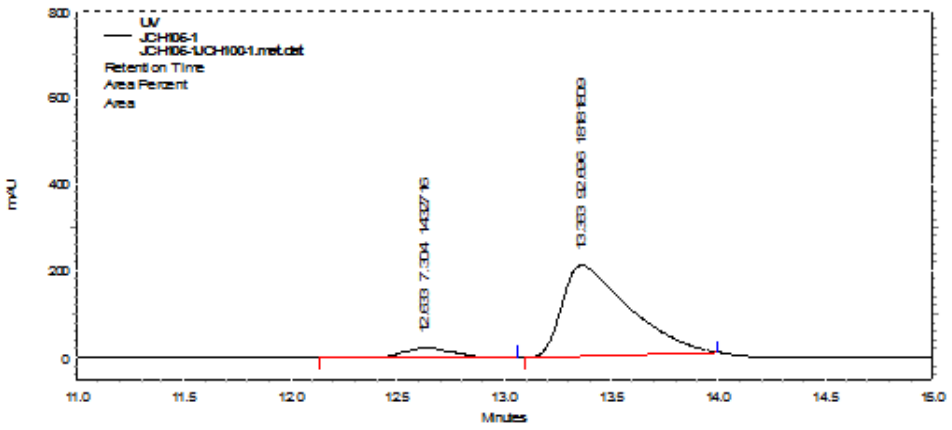


Figure S18-1. HPLC chromatogram of β-anomer standard **22**.

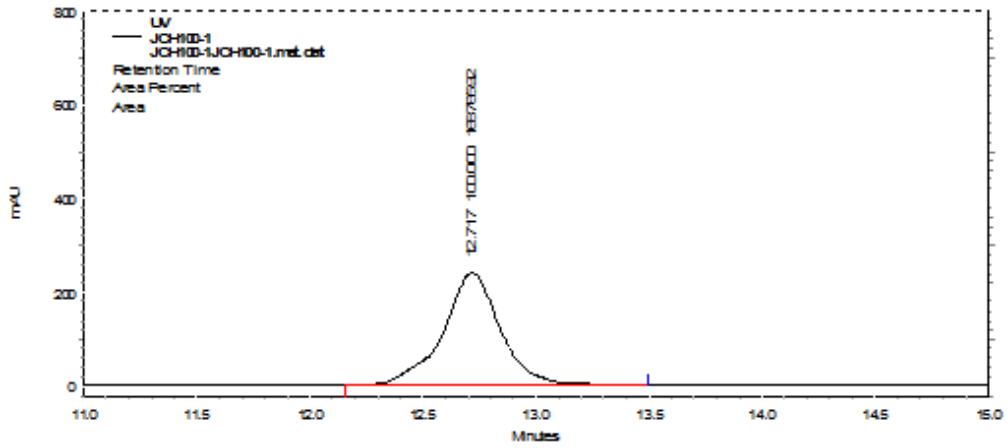


Figure 18-2. HPLC chromatogram for crude disaccharide product **22** obtained from one-pot *in situ* adduct transformation and glycosylation procedure with DIEA.

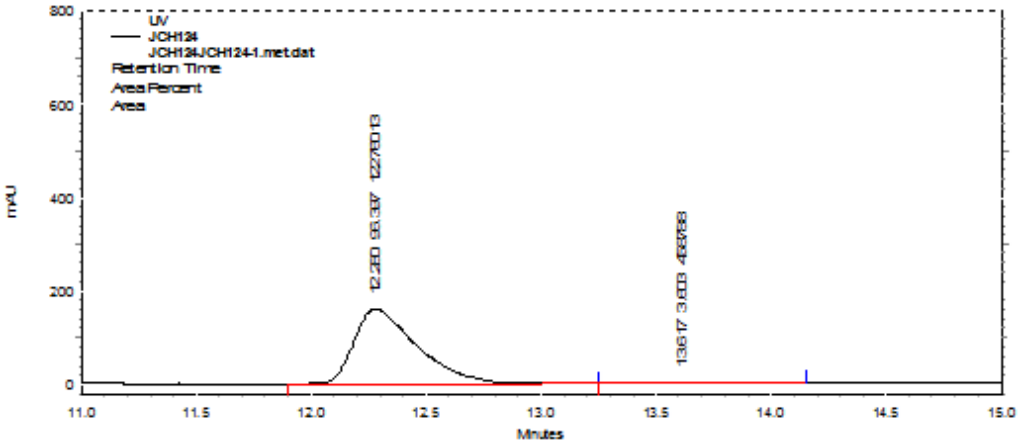
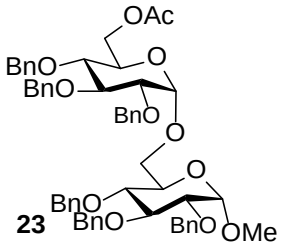


Figure S18-3. Partial HPLC chromatogram for crude disaccharide product **22** obtained from one-pot *in situ* adduct transformation and glycosylation procedure with LTD.

2.5.7 Methyl 6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (23)



23

α-Anomer of disaccharide **23**[5] was (1.1 g, 70%) prepared from glucosyl acceptor **4** (1.2 g, 2.51 mmol) with thioglucoside donor **9** (1.0 g, 1.67 mmol) using one-pot *in situ* adduct transformation and glycosylation procedure (Table 2, entry 6 in article). For α-anomer of **23**, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 – 7.23 (m, 30H, Ar*H*), 4.98 (d, *J* = 1.4 Hz, 1H), 4.96 – 4.94 (m, 2H, including H-1′), 4.93 (d, *J* = 11.4 Hz, 1H), 4.87 (d, *J* = 11.0 Hz, 1H), 4.81 (d, *J* = 10.8 Hz, 1H), 4.78 (d, *J* = 10.9 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.67 – 4.62 (m, 3H), 4.60 – 4.52 (m, 3H, including H-1), 4.19 (d, *J* = 3.1 Hz, 2H), 3.98 (td, *J* = 9.2, 6.2 Hz, 2H), 3.85 (dt, *J* = 10.1, 3.0 Hz, 1H), 3.82 – 3.76 (m, 2H), 3.70 (d, *J* = 10.4 Hz, 1H), 3.64 (t, *J* = 9.4 Hz, 1H), 3.51 (dd, *J* = 9.6, 3.4 Hz, 1H, H-2′), 3.48 – 3.42 (m, 2H, including H-2), 3.36 (s, 3H, OC*H*$_3$), 1.96 (s, 3H,COC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6 (C=O), 138.7, 138.5, 138.3, 138.2, 138.1, 138.0, 128.4 128.3, 128.3, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 97.9 (C-1, J_{CH} = 168.5 Hz), 97.0 (C-1′, $J_{CH'}$ = 167.1 Hz), 82.1, 81.5, 80.1, 79.9, 77.7, 77.1, 75.7, 75.5, 74.9, 74.8, 73.3, 72.3, 70.3, 68.7, 66.0, 63.0, 55.1 (O*C*H$_3$), 20.76 (CO*C*H$_3$). HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{57}H_{62}NaO_{12}^+$, 961.4134; found, 961.4135.

The α/β ratio of **23** was determined to be >19/1 by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc/CH_2Cl_2 7/2/1 gradient to 6/3/1. Retention time for β anomer standard **23** obtained from low concentration glycosylation = 11.9 min (Figure S19-1). For **23** obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention time of α anomer = 15.0 min; β anomer = 12.2 min (Figure S19-2). β-Anomer of disaccharide **23**[5] was synthesized from Glc acceptor **4** with Glc donor **9** according to low concentration glycosylation procedure.[7]

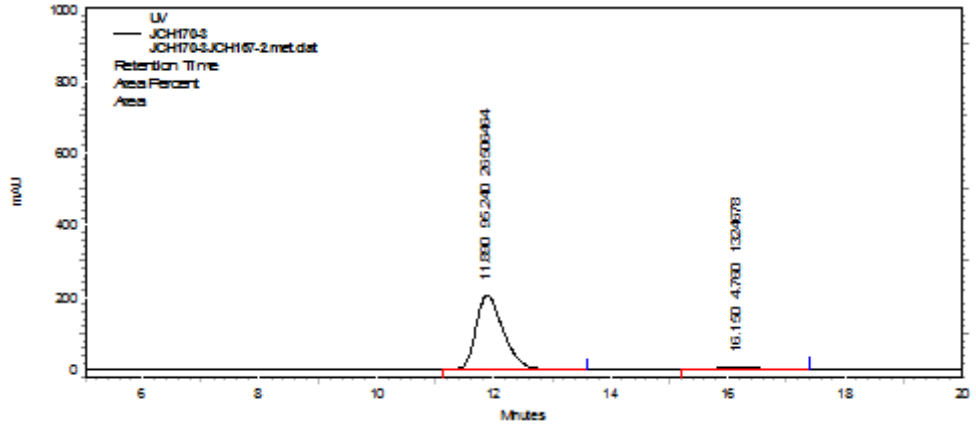


Figure S19-1. HPLC chromatogram of β-anomer of **23**.

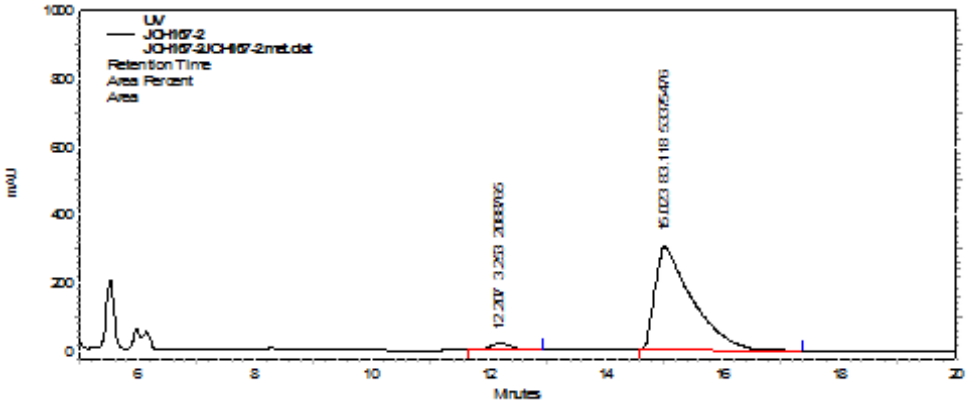
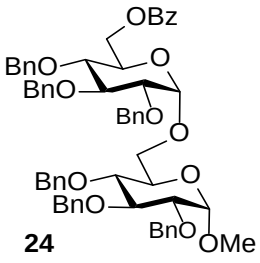


Figure S19-2. HPLC chromatogram for crude **23** obtained from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.8 Methyl 6-*O*-Benzoyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (24)

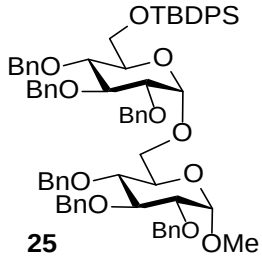


24

α-Anomer of disaccharide **24** was (75 mg, 60%) synthesized from glucoside acceptor **4** (105 mg, 0.225 mmol) with thioglucoside donor **10** (100 mg, 0.125 mmol) using one-pot *in situ* adduct transformation and glycosylation procedure (Table 2, entry 7 in article). The resulting mixture

was dried (over $MgSO_4$), filtered, and concentrated for flash chromatography purification over silica gel (Elution: hexanes/EtOAc 1/0 to 7/1) to furnish the glycosylation product. For α-disaccharide **24**, R_f 0.34 (hexanes/EtOAc 3/1); $[\alpha]_D^{35}$ +59.75 (*c* 0.569, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.88 (m, 2H, Ar-H), 7.45 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.32 – 7.22 (m, 13H, Ar-H), 7.20 – 7.15 (m, 19H, Ar-H), 4.90 (d, *J* = 3.2 Hz, 1H), 4.87 (t, *J* = 2.8 Hz, 2H), 4.84 (d, *J* = 5.6 Hz, 1H), 4.82 (d, *J* = 5.2 Hz, 1H), 4.72 (dd, *J* = 3.2, 10.8 Hz, 2H), 4.59 (t, *J* = 13.6 Hz, 4H), 4.53 (s, 1H), 4.50 (d, *J* = 2.0 Hz, 1H), 4.47 (d, *J* = 3.2 Hz, 1H), 4.42 (dd, *J* = 2.0, 12.0 Hz, 1H), 4.30 (dd, *J* = 4.4, 12.0 Hz, 1H), 3.96 – 3.88 (m, 3H), 3.75 – 3.69 (m, 2H), 3.62 (d, *J* = 10.0 Hz, 1H), 3.54 – 3.45 (m, 3H), 3.32 (dd, J = 3.6, 9.6 Hz, 1H), 3.27 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2 (C=O), 138.9, 138.6, 138.38, 138.37, 138.2, 138.0, 133.1, 130.0, 129.7, 128.47, 128.46, 128.41, 128.39, 128.2, 128.04, 128.03, 127.97, 127.90, 127.84, 127.78, 127.75, 127.72, 127.65, 127.63, 98.0 ($^1J_{CH}$ = 165.4 Hz), 97.0 ($^1J_{CH}$ = 168.4 Hz), 82.2, 81.8, 80.24, 80.20, 77.9, 77.6, 75.8, 75.1, 73.4, 72.5, 70.4, 68.9, 66.1, 63.5, 55.2; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{62}H_{64}NaO_{12}^+$, 1023.4290; found, 1023.4332. The α:β ratio of the product was estimated by ^1H NMR spectroscopy.

2.5.9 Methyl 6-*O*-*tert*-Butyl-diphenylsilyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (25)



25

α-Anomer of disaccharide **25** was (80 mg, 55%) synthesized from glucosyl acceptor **4** (87 mg, 0.188 mmol) with thioglucoside donor **11** (100 mg, 0.125 mmol) using one-pot *in situ* adduct transformation and glycosylation procedure (Table 2, entry 8 in article). For α-disaccharide **25**, R_f 0.42 (hexanes/EtOAc 3/1); $[\alpha]_D^{28}$ +52.1 (*c* 2.07, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.63 (m, 4H, Ar-H), 7.38 – 7.23 (m, 34H, Ar-H), 7.15 – 7.12 (m, 2H, Ar-H), 5.01 (t, *J* = 3.6 Hz, 1H; H-1′), 4.95 – 4.87 (m, 4H), 4.83 – 4.77 (m, 2H), 4.71 – 4.53 (m, 7H; including H-1),

4.02 – 3.95 (m, 2H), 3.82 – 3.64 (m, 9H), 3.57 – 3.52 (m, 1H), 3.44 – 3.40 (m, 1H), 3.35 (s, 3H; CH_3), 1.02 (s, 9H; *t*butyl-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.8, 138.64, 138.57, 138.4, 138.3, 135.9, 135.7, 133.7, 133.4, 129.62, 129.58, 128.5, 128.43, 128.41, 128.35, 128.2, 128.06, 128.03, 127.9, 127.8, 127.73, 127.69, 127.66, 127.60, 127.57, 98.02 ($^1J_{CH}$ = 168.5 Hz), 97.00 ($^1J_{CH}$ = 167.1 Hz), 82.2, 81.9, 80.5, 80.2, 77.84, 77.79, 75.75, 75.7, 75.1, 75.0, 73.4, 72.4, 71.7, 70.6, 65.7, 63.0, 55.2, 26.9, 19.4; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{71}H_{78}NaO_{11}Si^+$, 1157.5206; found, 1157.5227.

The α/β ratio of **25** was determined to be 10/1 by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 80/20. Retention time of β anomer standard of **25** = 7.6 min (Figure S20-1). For **25** obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention time of α anomer = 8.2 min (Figure S20-2).

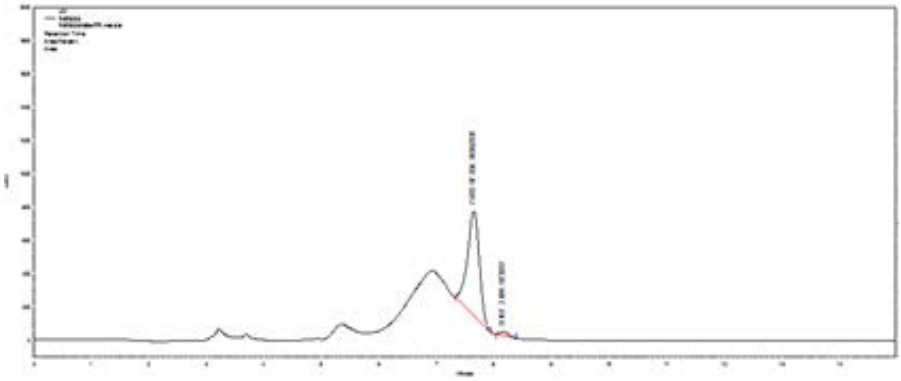


Figure S20-1. HPLC chromatogram of β-anomer of **25**.

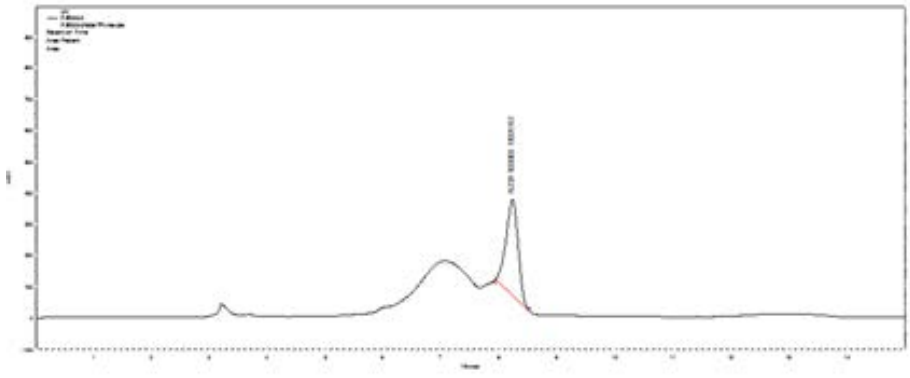
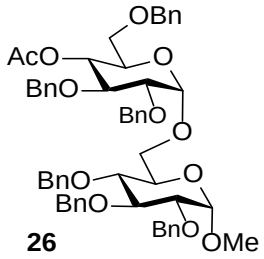


Figure S20-2. HPLC chromatogram for crude **25** obtained from one-pot *in situ* adduct transformation and glycosylation procedure.

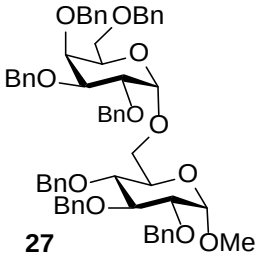
2.5.10 Methyl 4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (26)



26

α-Anomer of disaccharide **26** was (1.02 g, 65%) synthesized from acceptor **4** (1.17 g, 2.51 mmol) with donor **12** (1.0 g, 1.67 mmol) using one-pot *in situ* adduct transformation and glycosylation procedure (Table 2, entry 9 in article). For α-disaccharide **26**, R_f 0.16 (hexanes/EtOAc 3/1); $[\alpha]_D^{35}$ +76.2 (*c* 0.315, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 – 7.22 (m, 30H, Ar-H), 5.02 (d, *J* = 10.0 Hz, 1H) , 4.99 (d, *J* = 5.0 Hz, 1H) , 4.95 (d, *J* = 3.5 Hz, 2H, including H-1′), 4.92 (d, *J* = 10.5 Hz, 1H), 4.82 (t, *J* = 11.5 Hz, 2H) , 4.71 (d, *J* = 12.5 Hz, 1H) , 4.66 (d, *J* = 5.0 Hz, 2H) , 4.63 (d, *J* = 8.0 Hz, 1H) , 4.59 (d, *J* = 1.5 Hz, 1H) , 4.57 (d, *J* = 3.0 Hz, 1H; H-1) , 4.45 (q, *J* = 12.0 Hz, 2H) , 3.99 (t, *J* = 9.0 Hz, 1H) , 3.87 (t, *J* = 12.5 Hz, 1H) , 3.84 – 3.77 (m, 3H), 3.71 (d, *J* = 11.5 Hz, 1H) , 3.65 (t, *J* = 9.5 Hz, 1H) , 3.56 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.45 (dd, *J* = 3.5, 9.5 Hz, 1H), 3.41 (dd, *J* = 3.0, 11.0 Hz, 1H), 3.37 (d, *J* = 5.0 Hz, 1H) , 3.35 (s, 3H, CH_3) , 1.80 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.7 (C=O), 138.9, 138.7, 138.5, 138.3, 138.2, 137.9, 128.51, 128.47, 128.46, 128.36, 128.34, 128.11, 128.07, 128.03, 127.94, 127.91, 127.77, 127.76, 127.73, 127.69, 127.65, 127.58, 98.1 (C-1, $^1J_{CH}$ = 165.0 Hz), 97.2 (C-1′, $^1J_{CH}$ = 168.6 Hz), 82.22 80.3, 79.7, 78.6, 77.9, 75.8, 75.1, 74.9, 73.6, 73.5, 72.6, 70.5, 70.4, 68.94, 68.89, 66.3, 55.2, 20.9. HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{57}H_{62}NaO_{12}^+$, 961.4133; found, 961.4150. The α:β ratio of **26** was 12:1 as estimated by ^{1}H NMR spectroscopy.

2.5.11 Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (27)



27

α-Anomer of disaccharide **27**[16] (54.4 mg, 69%) was synthesized from donor **13** (50 mg, 0.08 mmol) and acceptor **4** (56 mg, 0.12 mmol) using one-pot *in situ* adduct transformation and glycosylation procedure (Table 2, entry 10 in article). For α-anomer of **27**, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.17 (m, 35H, Ar-H), 4.99 (d, *J* = 3.5 Hz, 1H, H-1), 4.95 (d, *J* = 8.7 Hz, 1H), 4.93 (d, *J* = 9.2 Hz, 1H), 4.84 (d, *J* = 11.0 Hz, 1H), 4.80 (d, *J* = 4.8 Hz, 1H, H-1′), 4.78 (d, *J* = 5.9 Hz, 1H), 4.72 – 4.67 (m, 4H), 4.60 – 4.56 (m, 2H), 4.54 (d, *J* = 4.2 Hz, 1H), 4.53 (d, *J* = 3.5 Hz, 1H, H-1), 4.42 (d, *J* = 11.8 Hz, 1H), 4.36 (d, *J* = 11.8 Hz, 1H), 4.03 (dd, *J* = 3.5, 9.5 Hz, 1H), 3.99 – 3.93 (m, 2H), 3.93 – 3.88 (m, 2H), 3.82 – 3.70 (m, 3H), 3.59 (t, *J* = 9.3 Hz, 1H), 3.54 – 3.46 (m,2H), 3.41 (dd, *J* = 3.6, 9.6 Hz, 1H, H-2′), 3.29 (s, 3H, OC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.9, 138.8, 138.71, 138.67, 138.4, 138.2, 138.1, 128.4, 128.32, 128.30, 128.25, 128.20, 128.15, 128.14, 128.09, 128.07, 128.01, 128.00, 127.93, 127.91, 127.8, 127.7, 127.60, 127.58, 127.5, 127.4, 127.3, 97.90 (C-1, $^{1}J_{CH}$ =168.3 Hz), 97.85 (C-1′, $^{1}J_{CH}$ =168.3 Hz), 82.0, 80.2, 78.2, 78.0, 76.51, 75.6, 75.1, 75.0, 74.7, 73.3, 73.3, 72.8, 72.5, 70.3, 69.4, 68.9, 66.4, 55.0 (O*C*H$_3$). The α/β ratio of **27** was determined to be >19/1 by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 4/1 to 7/3. Retention time for β anomer of **27** = 15.1 min (Figure S21-1). For **27** obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention time for α anomer = 13.4 min; no β anomer was detected at 15.1 min (Figure S21-2). β-Anomer of disaccharide **27**[16] was synthesized from **13** and **4** using low concentration glycosylation procedure.[7]

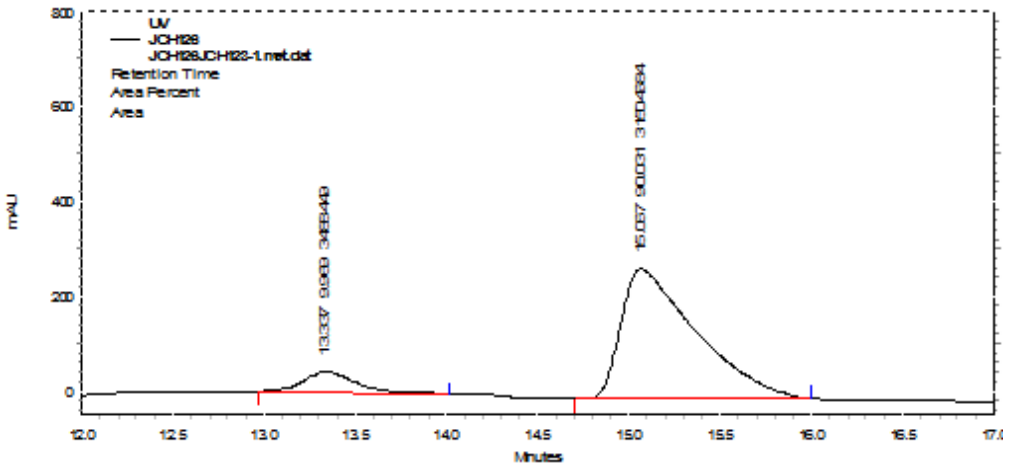


Figure S21-1. HPLC chromatogram of β-anomer of **27**.

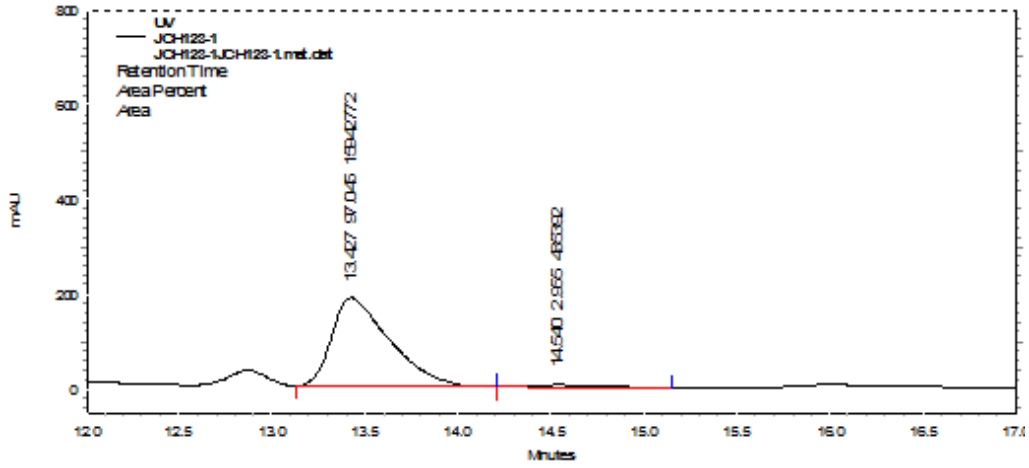
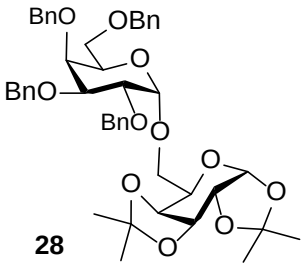


Figure S21-2. HPLC chromatogram for crude product **27** from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.12 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactose (28)



28

α-Anomer of disaccharide **28**[17] was (135 mg, 63%, 13:1 α:β) synthesized from acceptor **15** (117 mg, 0.45 mmol) and donor **13** (200 mg, 0.30 mmol) with the one-pot *in situ* adduct transformation and glycosylation procedure (Table 2, entry 11 in main text). For α-anomer of **28**,

R_f 0.28 (hexanes/EtOAc 3/1); $[\alpha]_D^{35}$ +48.0 (*c* 0.248, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.83 – 7.78 (m, 3H, Ar-H), 7.75 – 7.72 (m, 1H, Ar-H), 7.50 – 7.44 (m, 3H, Ar-H), 7.39 – 7.38 (m, 2H, Ar-H), 7.35 – 7.22 (m, 11H, Ar-H), 5.52 (d, *J* = 4.8 Hz, 1H, H-1), 5.03 (d, *J* = 3.6 Hz, 1H, H-1′), 4.97 (dd, *J* = 4.8, 12.0 Hz, 2H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.78 (s, 2H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.57 (dd, *J* = 2.4, 8.0 Hz, 1H), 4.49 (d, *J* = 12.8 Hz, 1H), 4.43 (d, *J* = 12.8 Hz, 2H), 4.34 – 4.29 (m, 2H), 4.12 (dd, *J* = 1.6, 10.8 Hz, 1H), 4.07 – 4.01 (m, 3H), 3.83 – 3.73 (m, 2H), 3.62 – 3.52 (m, 2H), 1.50 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.30 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.79, 138.77, 138.1, 136.5, 133. 5, 132.9, 128.4, 128.30, 128.23, 128.17, 128.0, 127.94, 127.85, 127.8, 127.7, 127.54, 127.53, 126.03, 126.00, 125.8, 125.7, 109.2, 108.6, 97.6 (C-1, $^1J_{CH}$ = 168.5 Hz), 96.4 (C-1′, $^1J_{CH}$ = 176.2 Hz), 79.0, 76.5, 75.1, 74.9, 73.4, 73.1, 72.7, 70.9, 70.71, 70.67, 69.2, 68.7, 66.4, 65.9, 26.2, 26.1, 24.5, 24.6.

The α/β ratio of **28** was determined to be 10/1 by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 75/25. Retention time of β anomer of **28** = 9.7 min (Figure S22-1). For **28** obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention time of α anomer = 7.9 min (Figure S22-2).

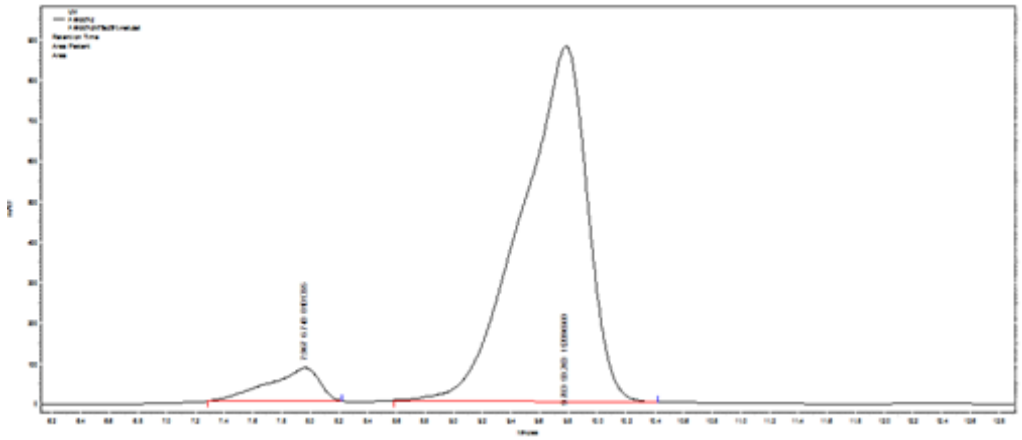


Figure S22-1. HPLC chromatogram of β-anomer of **28**.

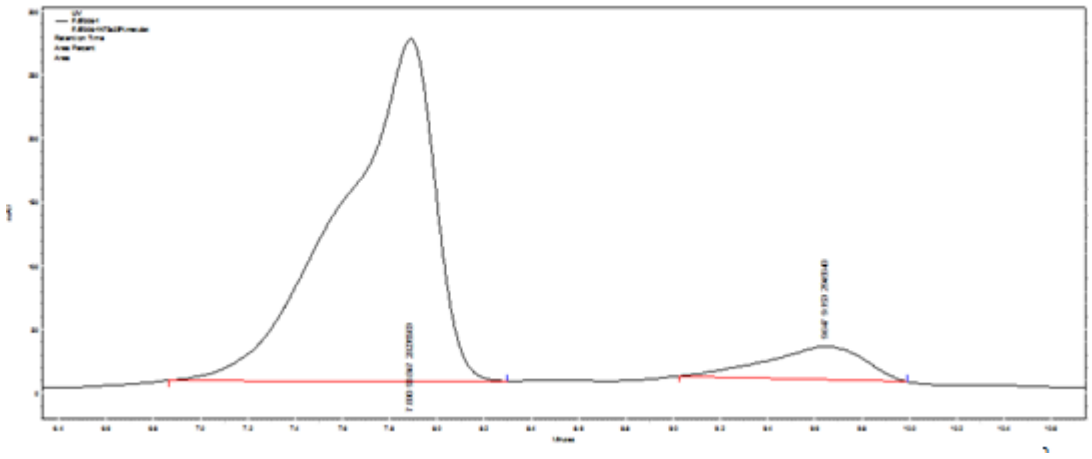
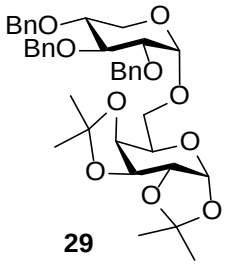


Figure S22-2. HPLC chromatogram for crude **28** obtained from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.13 2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (29)



29

α-Anomer of disaccharide **29**[18] was (45 mg, 75%) synthesized from the reaction of acceptor **15** (36 mg, 0.14 mmol) with xylosyl donor **14** (50 mg, 0.09 mmol) using one-pot *in situ* adduct transformation and glycosylation procedure (Table 2, entry 12 in main text). For α-anomer of disaccharide **29**, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.26 (m, 15H), 5.53 (d, *J* = 5.0 Hz, 1H, H-1), 4.92 (d, *J* = 10.9 Hz, 1H), 4.89 – 4.86 (m, 2H, including H-1′), 4.75 – 4.70 (m, 3H), 4.64 – 4.59 (m, 2H), 4.36 (dd, *J* = 7.9, 1.8 Hz, 1H), 4.31 (dd, *J* = 5.0, 2.3 Hz, 1H), 4.07 – 4.03 (m, 1H), 3.93 – 3.87 (m, 1H), 3.77 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.71 (dd, *J* = 10.2, 7.7 Hz, 1H), 3.62-3.55 (m, 3H), 3.46 (dd, *J* = 3.6, 9.5 Hz, 1H), 1.54 (s, 3H, isopropylidene-*C*H_3), 1.45 (s, 3H, isopropylidene-*C*H_3), 1.33 (s, 3H, isopropylidene-*C*H_3), 1.31 (s, 3H, isopropylidene-*C*H_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.0, 138.4, 138.3, 128.39, 128.37, 128.30, 128.27, 128.25, 128.17, 127.94, 127.91, 127.80, 127.78, 127.75, 127.71, 127.6, 127.48, 127.46, 127.43, 109.1,

108.6, 97.2 (C-1′, $^{1}J_{CH'}$ = 167.6 Hz), 96.3 (C-1,$^{1}J_{CH}$ = 178.6 Hz), 81.2, 79.6, 78.0, 75.6, 73.4, 72.5, 70.8, 70.7, 70.6, 66.3, 65. 8, 60.0, 26.1, 26.0, 24.9, 24.6.

The α/β ratio of **29** was determined by HPLC analysis (Elution: hexanes/EtOAc 4/1 gradient to 7/3). Retention time of β anomer of **29** = 16.4 min (Figure S23-1). For **29** obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention time for α anomer = 12.1 min and β anomer = 16.6 min, thus α/β = 5/1 (Figure S23-2). β-Anomer of disaccharide **29** was synthesized from **14** and **15** according to the low concentration glycosylation procedure.

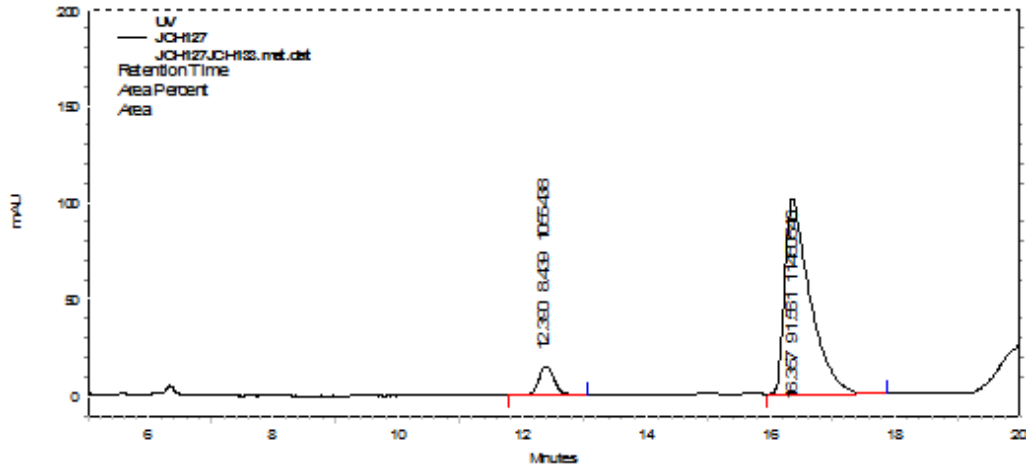


Figure S23-1. HPLC chromatogram of β-anomer **29**.

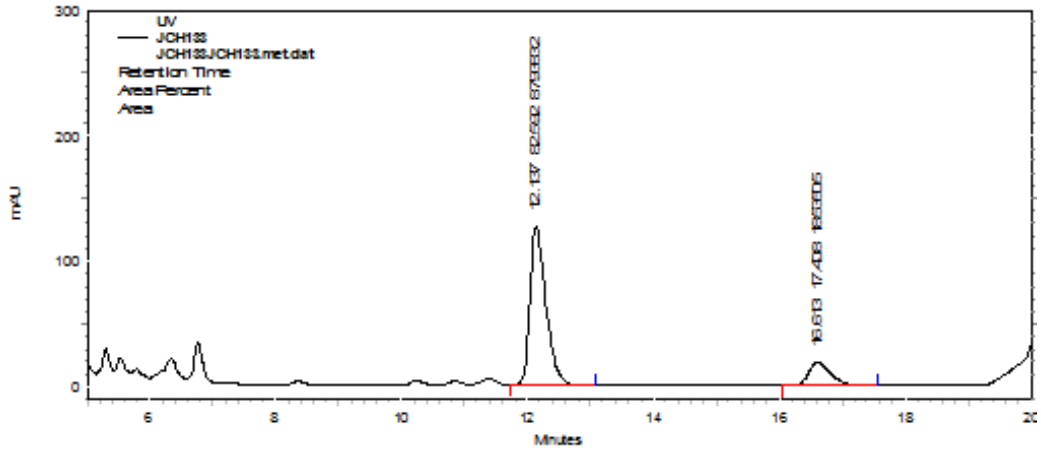
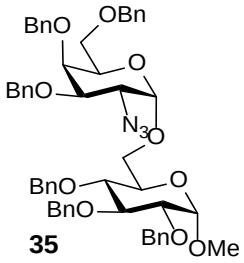


Figure S23-2. Partial HPLC chromatogram of crude product **29** from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.14 Methyl 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→6)-2,3,4- tri-*O*-benzyl-α-D-glucopyranoside (35)



35

α-Anomer of disaccharide **35** was (102 mg, 65%) synthesized from glucosyl acceptor **4** (121 mg, 0.26 mmol) with 2-azido-2-deoxythiogalactoside donor **30** (100 mg, 0.17 mmol) using one-pot *in situ* adduct transformation and glycosylation procedure (Table 3, entry 1 in article). For α-anomer of disaccharide **35**, R_f 0.4 (hexanes/EtOAc 2.5/1); $[\alpha]_D^{25}$ +60.4 (*c* 0.345, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.43 – 7.20 (m, 30H), 5.01 – 4.96 (m, 2H, including H-1′), 4.90 – 4.84 (m, 2H), 4.83 – 4.75 (m, 2H), 4.72 (d, *J* = 10.8 Hz, 1H), 4.65 (d, *J* = 10.7 Hz, 2H), 4.60 – 4.50 (m, 3H, including H-1), 4.44 (d, *J* = 11.8 Hz, 1H, OC*H*Ph), 4.37 (d, *J* = 11.1 Hz, 1H, OC*H*Ph), 4.03 – 3.96 (m, 2H), 3.96 – 3.91 (m, 1H), 3.91 – 3.86 (m, 1H), 3.85 – 3.73 (m, 3H), 3.69 (d, *J* = 11.1 Hz, 1H, H-6), 3.59 – 3.48 (m, 4H), 3.33 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.7, 138.2, 138.2, 138.1, 137. 8, 137.4, 128.5, 128.4, 128.3, 128.2, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 98.5 (C-1′, $J_{CH'}$ = 171.0 Hz), 97.8 (C-1, J_{CH} = 166.9 Hz), 81.9, 80.0, 77.8, 76.5, 75.7, 74.9, 74.7, 73.4, 73.3, 71.9, 69.9, 69.6, 68.5, 66.6, 59.8, 55.0; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{55}H_{59}N_3NaO_{10}^+$, 944.4093; found, 944.4097.

The α/β ratio of **35** was determined by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 3/1. For β anomer standard of **35**, retention time = 12.4 min (Figure S24-1). For **35** obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention time of α anomer = 10.2 min and β anomer = 12.8 min, thus α/β ratio >19/1 (Figure S24-2). β-Aonmer of disaccharide **35**[19] was synthesized from **30** and **4** using the low concentration glycosylation procedure.[7]

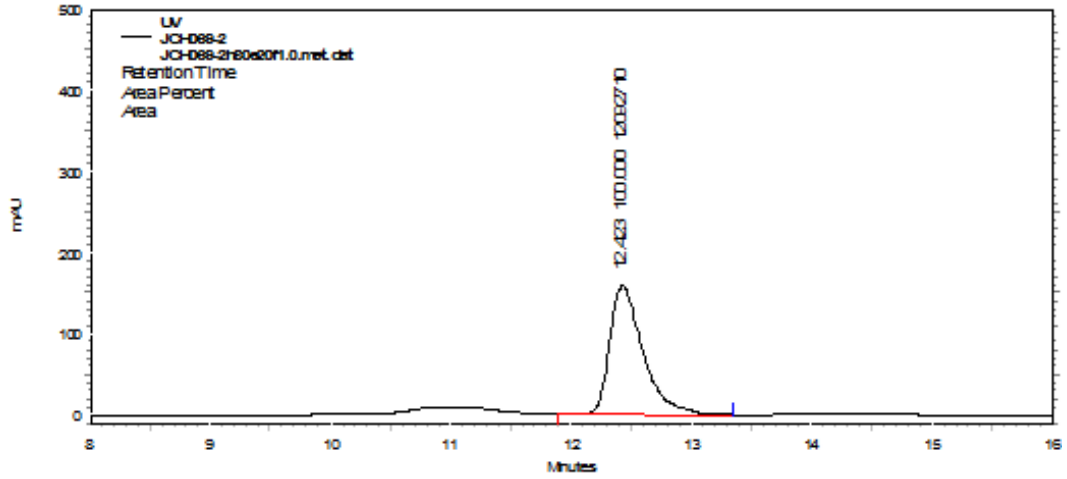


Figure S24-1. HPLC chromatogram of β anomer of **35**.

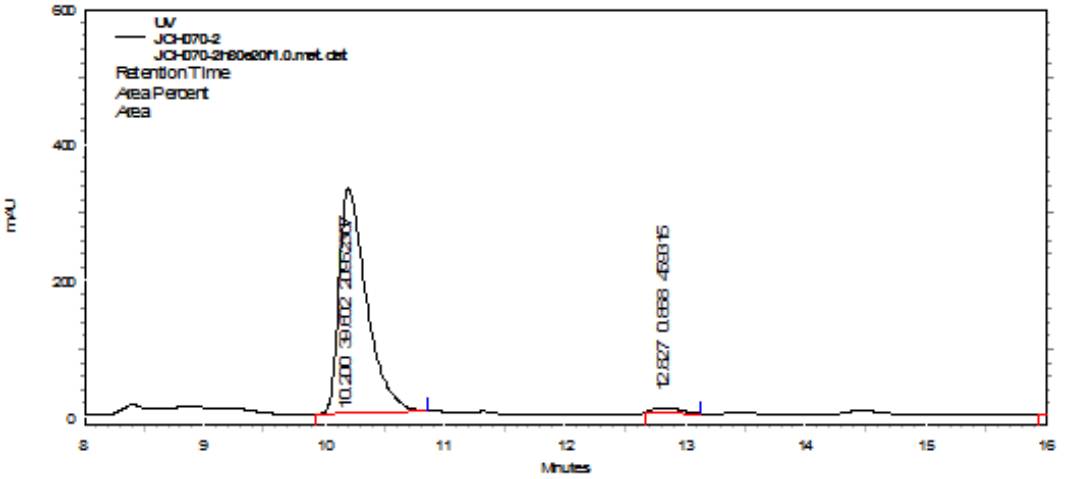
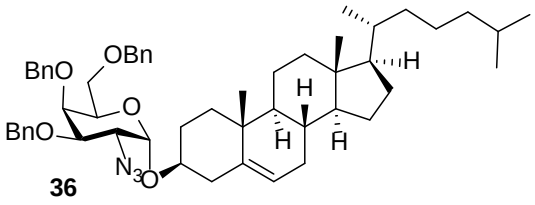


Figure S24-2. HPLC chromatogram for crude product **35** from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.15 Cholesteryl 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranoside (36)



36

α-Anomer of cholesteryl galactoside **36** was (55 mg, 54%) synthesized from cholesterol **33** (70 mg, 0.18 mmol) and $GalN_3$ donor **30** (70 mg, 0.12 mmol) according to one-pot *in situ* adduct transformation and glycosylation procedure (Table 3, entry 2 in article) and was obtained as a white amorphous solid upon column chromatography purification (Elution: hexanes/EtOAc/

CH_2Cl_2 30/1/1 to 26/1/1). For α-anomer of **36**, R_f 0.7 (hexanes/EtOAc 5/1); $[\alpha]_D^{35}$ +51.0 (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 – 7.22 (m, 15H), 5.28 (d, *J* = 5.0 Hz, 1H), 5.05 (d, *J* = 3.6 Hz, 1H, H-1′), 4.88 (d, *J* = 11.3 Hz, 1H), 4.72 (q, *J* = 11.3 Hz, 2H), 4.53 (d, *J* = 11.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.43 (d, *J* = 11.7 Hz, 2H), 4.10 – 4.03 (m, 2H), 3.98 (dd, *J* = 2.6, 10.7 Hz, 1H), 3.79 (dd, *J* = 3.6, 10.7 Hz, 1H, H-2), 3.63 – 3.53 (m, 2H), 3.51 – 3.43 (m, 1H), 2.41 – 2.28 (m, 2H), 2.06 – 1.89 (m, 3H), 1.90 – 1.78 (m, 2H), 1.63 – 0.84 (m, 33H), 0.68 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.6, 138.4, 137.9, 137.7, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.8, 127.7, 127.6, 121.9, 96.8 (C-1, $J_{CH'}$ = 168.5 Hz), 78.2, 77.4, 74.8, 73.6, 73.5, 72.2, 69.6, 68.8, 59.7 (C-2′), 56.8, 56.1, 50.1, 42.3, 40.0, 39.8, 39.5, 37.0, 36.7, 36.2, 35.8, 31.9, 31.9, 28.2, 28.0, 27.9, 24.3, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 11.9. HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{54}H_{73}N_3NaO_5^+$, 866.5442; found, 866.5443.

The α/β ratio of **32** was determined to be >19/1 by HPLC analysis (Table 3, Entry 2). HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 24/1 gradient to 19/1. For β anomer standard of **36** obtained from low concentration glycosylation, retention time = 23.4 min (Figure S25-1). For **36** obtained from one-pot *in situ* adduct transformation and glycosylation, retention time of α anomer = 12.5 min and no β anomer was detected at 23.4 min (Figure S25-2). β-Anomer of cholesteryl galactoside **36** was synthesized from cholesterol **33** and donor **30** based on the low concentration glycosylation procedure.[7]

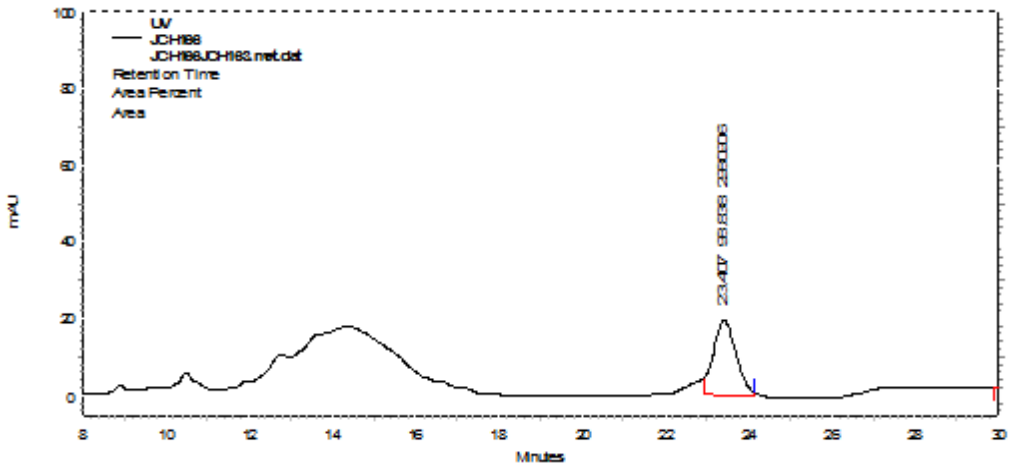


Figure S25-1. HPLC chromatogram of β anomer standard **36**.

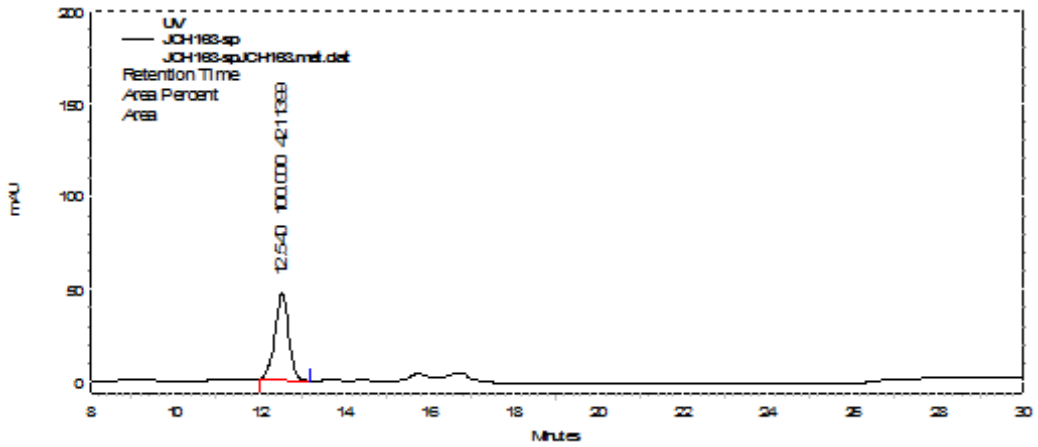
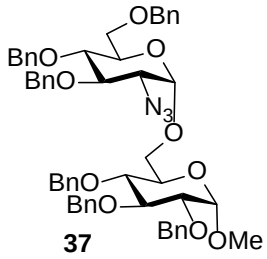


Figure S25-2. HPLC chromatogram for crude product **36** from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.16 Methyl 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-2,3,4- tri-*O*-benzyl-α-D-glucopyranoside (37)



37

α-Anomer of disaccharide **37** was (30 mg, 55%) synthesized from glucosyl acceptor **4** (28 mg, 0.06 mmol) and 2-azido-2-deoxythioglucoside donor **31** (70 mg, 0.12 mmol) according to one-pot *in situ* adduct transformation and glycosylation procedure with 2-azido-2-deoxythioglucoside donor (Table 3, entry 3 in main text). For α-anomer **37**, R_f 0.3 (hexanes/EtOAc 2.5/1); $[\alpha]_D^{25}$ +46.8 (*c* 0.513, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.24 (m, 28H, Ar*H*), 7.15 – 7.17 (m, 2H, Ar*H*), 5.00 (d, *J* = 3.5 Hz, 1H, H-1′), 4.98 (d, *J* = 10.8 Hz, 1H), 4.94 (d, *J* = 11.2 Hz, 1H, benzyl-H), 4.85 (d, *J* = 3.0 Hz, 2H), 4.81 – 4.78 (m, 2H), 4.77 (d, *J* = 2.7 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H, benzyl-H), 4.61 – 4.55 (m, 3H, including H-1), 4.48 (d, *J* = 11.0 Hz, 1H, benzyl-H), 4.42 (d, *J* = 12.1 Hz, 1H, benzyl-H), 4.00 (t, *J* = 9.3 Hz, 1H, H-3), 3.92 (dd, *J* = 8.6, 10.2 Hz, 1H, H-3′), 3.82 (dd, *J* = 4.5, 11.3 Hz, 1H, H-6), 3.79 – 3.72 (m, 2H), 3.72 – 3.66 (m, 2H), 3.63 (dd, *J* = 3.3, 10.8 Hz, 1H, H-6′), 3.59 – 3.51 (m, 3H), 3.37 (s, 3H, OC*H*$_3$), 3.33 (dd, *J* = 3.5, 10.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.7, 138.3, 138.1,

138.0, 137.9, 137.8, 128.43, 128.38, 128.37, 128.35, 128.14, 128.10, 128.05, 128.03, 127.96, 127.87, 127.85, 127.82, 127.76, 127.71, 127.69, 127.65, 127.63, 127.61, 127.60, 98.2 (C-1′, $J_{CH'}$ = 171.3 Hz), 97.9 (C-1, J_{CH} = 167.4 Hz), 82.0, 80.1, 79.8, 78.2, 77.7, 75.8, 75.2, 74.9, 735, 73.4, 70.7, 69.9, 68.1, 66.4, 63.5, 55.2 (O*C*H$_3$). HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{55}H_{59}N_3NaO_{10}^+$, 944.4093; found, 944.4094.

The α/β ratio of **37** was determined to be 9/1 by HPLC analysis (Table 3, Entry 4). HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 77/23. For β anomer standard of **37**, retention time = 9.5 min (Figure S27-1). For **37** obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention time of α anomer = 12.0 min; β anomer = 9.6 min (Figure S27-2). β-Anomer of disaccharide **37**[18] was synthesized from **31** and **4** according to the low concentration glycosylation procedure.[7]

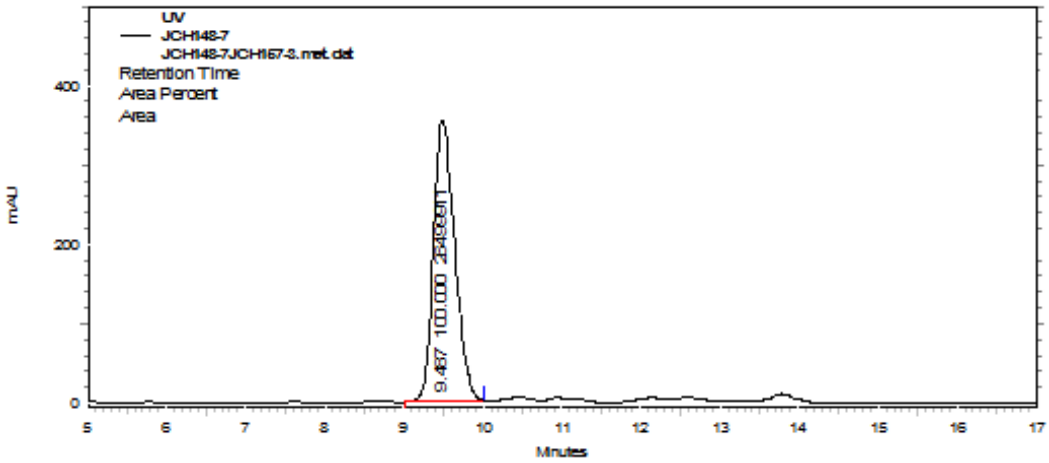


Figure S27-1. HPLC chromatogram of β-anomer of **37**.

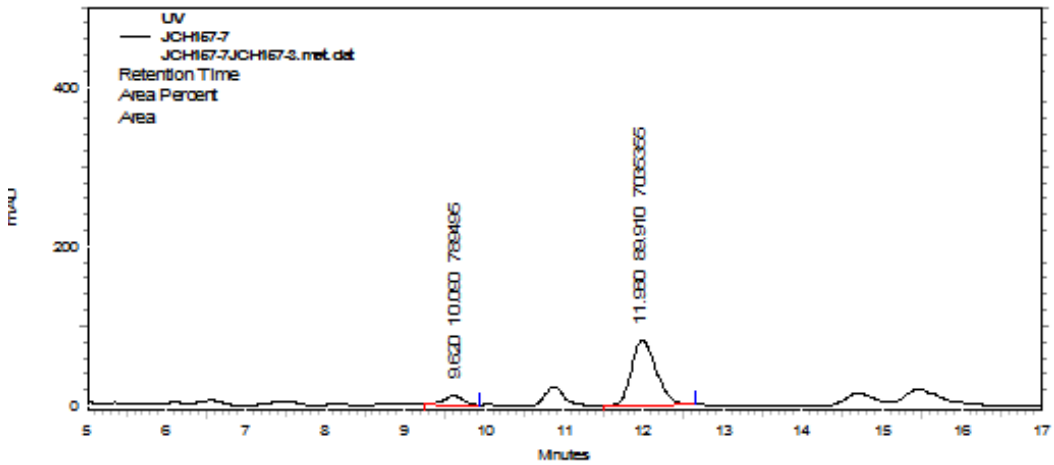
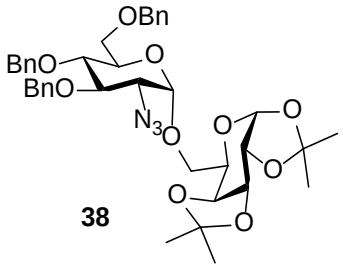


Figure S27-2. HPLC chromatogram for crude product **37** from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.17 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (38)



38

α-Anomer of disaccharide **38** was (27 mg, 84%) synthesized from galactosyl acceptor **15** (12 mg, 0.045 mmol) with 2-azido-2-deoxythioglucoside donor **31** (50 mg, 0.09 mmol) according to one-pot *in situ* adduct transformation and glycosylation procedure (Table 3, entry 4 in article). For α-anomer of **38**, R_f 0.2 (hexanes/EtOAc 3/1); $[\alpha]_D^{25}$ +37.4 (*c* 0.643, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.23 (m, 13H, Ar*H*), 7.18 – 7.13 (m, 2H, Ar*H*), 5.51 (d, *J* = 5.0 Hz, 1H, H-1), 4.99 (d, *J* = 3.5 Hz, 1H, H-1′), 4.86 (s, 2H), 4.79 (d, *J* = 10.9 Hz, 1H, OC*H*Ph), 4.66 – 4.59 (m, 2H), 4.52 (d, *J* = 10.8 Hz, 1H, OC*H*Ph), 4.48 (d, *J* = 12.1 Hz, 1H, OC*H*Ph), 4.34 – 4.29 (m, 2H), 4.03 – 3.97 (m, 2H, including H-3′), 3.90 – 3.86 (m, 1H), 3.82 (dd, *J* = 10.3, 6.4 Hz, 1H), 3.80 – 3.73 (m, 2H), 3.71 (dd, *J* = 8.7, 5.0 Hz, 1H), 3.66 (dd, *J* = 10.8, 1.8 Hz, 1H), 3.33 (dd, *J* = 10.3, 3.5 Hz, 1H, H-2′), 1.53 (s, 3H, isopropylidene-C*H*$_3$), 1.43 (s, 3H, isopropylidene-C*H*$_3$), 1.34 (s, 3H, isopropylidene-C*H*$_3$), 1.33 (s, 3H, isopropylidene-C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.0, 137.8, 128.40, 128.36, 128.35, 128.0, 127.9, 127.81, 127.77, 127.71, 127.68, 109.2, 108.6, 98.2 (C-1′, $J_{CH'}$ = 170.0 Hz), 96.2 (C-1, J_{CH} = 178.8 Hz), 79.9, 78.2, 75.2, 74.9, 73.5, 70.8, 70.7, 70.61, 70.55, 68.1, 66.8, 66.2, 63.4 (C-2′), 26.1, 25.94, 24.92, 24.4. HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{39}H_{47}N_3NaO_{10}^+$, 740.3154; found, 740.3155.

The α/β ratio of **38** was determined by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 17/3 gradeint to 7/3. For β anomer standard of **38**, retention time = 19.8 min (Figure S26-1)**.** For **38** obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention time for α anomer = 17.5 min and β anomer = 20.2 min, thus

α/β ratio: > 15/1 (Figure S26-2). β-Anomer of disaccharide **38**[19] was synthesized from **31**and **15** according to the low concentration glycosylation procedure.[7]

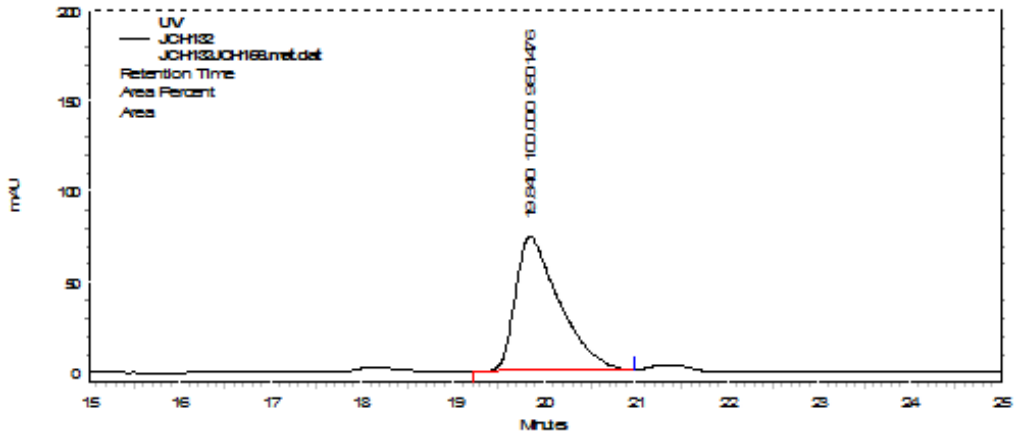


Figure S26-1. HPLC chromatogram of β-anomer of **38**.

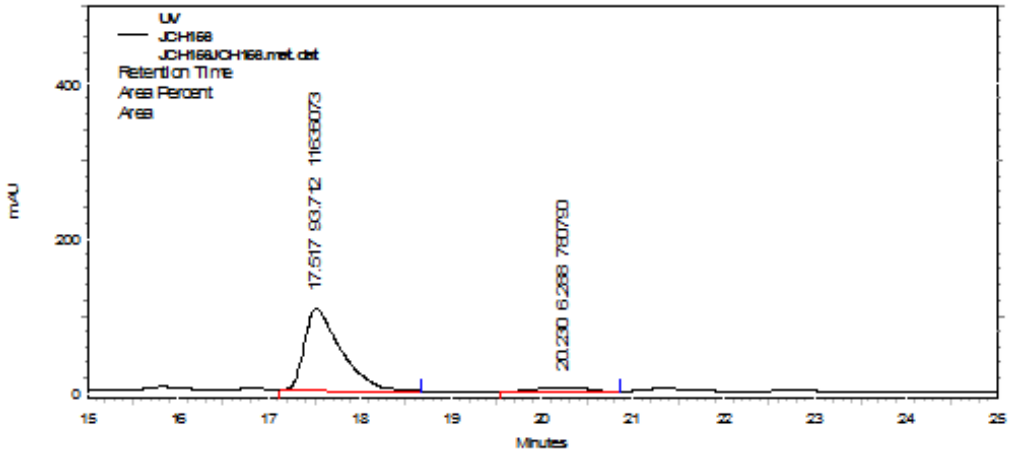
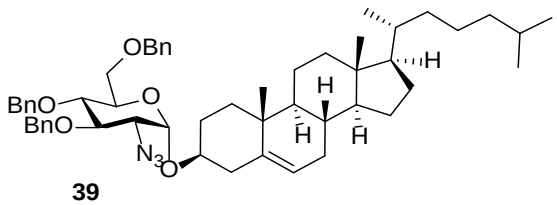


Figure S26-2. HPLC chromatogram for crude product **38** obtained from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.18 Cholesteryl 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranoside (39).



39

α-Anomer of cholesteryl 2-azido-2-deoxyglucoside **39** was (39 mg, 54%) synthesized as a white greasy solid from reaction of cholesterol **33** (33 mg, 0.085 mmol) with 2-azido-2-

deoxythioglucoside donor **31** (100 mg, 0.17 mmol) according to one-pot *in situ* adduct transformation and glycosylation procedure (Table 3, entry 5 in article). For α-anomer **39**, R_f 0.6 (hexanes/EtOAc 5/1); $[\alpha]_D^{35}$ +22.0 (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.25 (m, 13H), 7.17 – 7.14 (m, 2H), 5.30 (d, *J* = 4.7 Hz, 1H), 5.08 (d, *J* = 3.5 Hz, 1H, H-1′), 4.88 (q, *J* = 10.7 Hz, 2H), 4.81 (d, *J* = 10.8 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.53 – 4.46 (m, 2H), 4.06 – 4.00 (m, 1H, H-3′), 3.97 – 3.91 (m, 1H), 3.80 – 3.75 (m, 1H), 3.73 – 3.68 (m, 1H), 3.68 – 3.63 (m, 1H), 3.55 – 3.46 (m, 1H), 3.30 (dd, *J* = 10.3, 3.5 Hz, 1H, H-2′), 2.40 – 2.30 (m, 2H), 2.04 – 1.91 (m, 3H), 1.90 – 1.78 (m, 2H), 1.62 – 1.31 (m, 13H), 1.20 – 1.02 (m, 9H), 0.95 – 0.84 (m, 11H)., 0.68 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.5, 138.04, 137.95, 137.8, 128.434, 128.425, 128.36, 128.0, 127.9, 127.82, 127.80, 127.7, 122.0, 96.3 (C-1′, $J_{CH'}$ = 168.0 Hz), 80.2, 78.4, 78.2, 75.3, 75.1, 73.5, 70.7, 68.4, 63.3, 56.8, 56.2, 50.1, 42.3, 40.0, 39.8, 39.5, 37.0, 36.7, 36.2, 35.8, 31.93, 31.87, 28.2, 28.0, 27.8, 24.3, 23.82, 22.81, 22.6, 21.0, 19.4, 18.7, 11.9; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{54}H_{73}N_3NaO_5^+$, 866.5442; found, 866.5433.

The α/β ratio of **39** was determined to be >19/1 by HPLC analysis. HPLC conditions: flow rate 1.0 mL/min; elution: hexanes/EtOAc 24/1 gradient to 19/1. For β anomer standard of **39**, retention time = 13.6 min (Figure S28-1). For **39** obtained from one-pot *in situ* adduct transformation and glycosylation procedure, retention time of α anomer = 22.3 min and no β anomer was detected at 13.6 min (Figure S28-2). β-Anomer of cholesteryl 2-azido-2-deoxy glucoside **39** was obtained from the donor **31** and the cholesterol acceptor **33** using the low concentration glycosylation procedure.

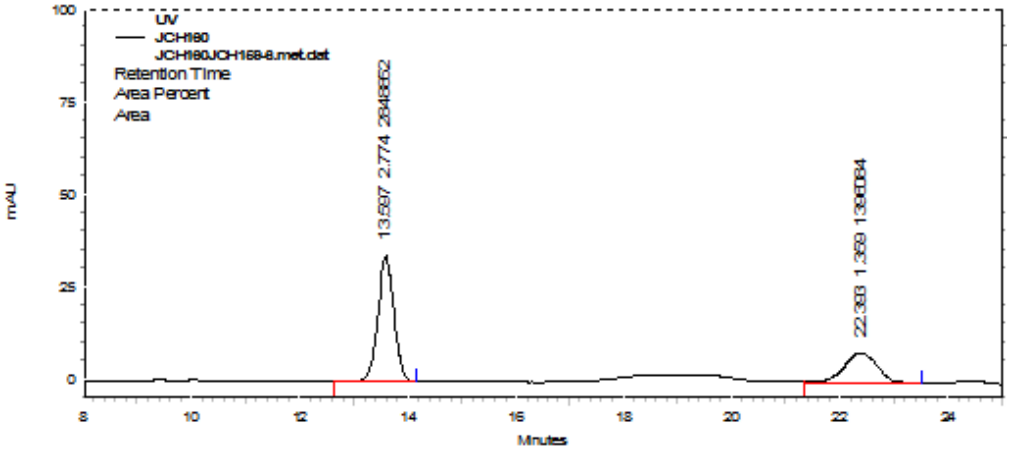


Figure S28-1. HPLC chromatogram of β-anomer of **39**.

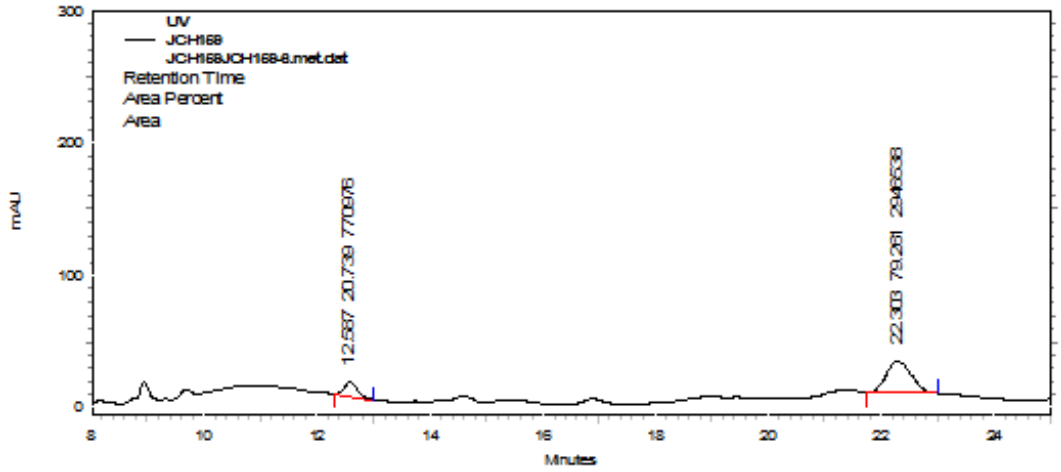
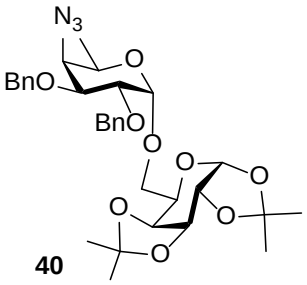


Figure S28-2. HPLC chromatogram of crude product **39** obtained from one-pot *in situ* adduct transformation and glycosylation procedure.

2.5.19 4-Azido-2,3-di-*O*-benzyl-4,6-dideoxy-α-D-fucopyranosyl-(1→6)-1,2:3,4-di- *O*-isopropylidene-α-D-galactopyranose (40)

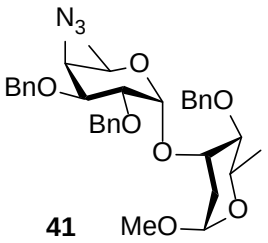


40

α-Anomer of disaccharide **40** (53 mg, α only, 76%) was synthesized from reaction of galactosyl acceptor **15** (41 mg, 0.158 mmol) with D-Fuc4N$_3$ donor **32** (50 mg, 0.105 mmol) using the one-pot *in situ* adduct transformation and glycosylation procedure (Table 3, entry 6 in article). For α-anomer of **40**, R_f 0.48 (Hexanes/EtOAc = 2/1); $[\alpha]_D^{35}$ +3.32 (*c* 2.85, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 – 7.27 (m, 10H, Ar*H*), 5.52 (d, *J* = 5.0 Hz, 1H, H-1), 4.87 (d, *J* = 3.5 Hz, 1H, H-1'), 4.83 (d, *J* = 11.5 Hz, 1H, benzyl-H), 4.76 (d, *J* = 11.5, 1H, benzyl-H), 4.74(d, *J* = 11.5, 1H, benzyl-H), 4.70 (d, *J* = 11.5, 1H, benzyl-H), 4.58 (dd, *J* = 8.0, 2.5 Hz, 1H), 4.31 (dd, *J* = 2.4 Hz, 1H), 4.28 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.07 – 3.99 (m, 3H), 3.84 (dd, *J* = 10.0, 3.5 Hz, 1H), 3.73 (d, *J* = 3.5, 2H), 3.72 (d, *J* = 3.6, 1H), 1.51 (s, 3H, C*H*$_3$), 1.44 (s, 3H, C*H*$_3$), 1.33 (s, 3H, C*H*$_3$), 1.31 (s, 3H, C*H*$_3$), 1.22 (d, *J* = 6.4 Hz, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.5, 138.3, 128.4, 128.3, 127.7, 127.7, 127.6, 109.3, 109.3, 108.53, 108.5, 97.4 (C-1), 96.3 (C-1'), 78.0, 75.9,

73.1, 72.9, 71.0, 70.7, 70.6, 66.7, 66.2, 65.0, 64.5, 26.1, 26.0, 24.9, 24.6, 17.3; HRMS (ESI): calcd for $C_{32}H_{41}N_3O_9Na^+$ $[M + Na]^+$ requires 634.2735, found 634.2757 *m/z*. The α-anomer of disaccharide **40** was obtained as the only anomer and HPLC analysis was not performed for this reaction.

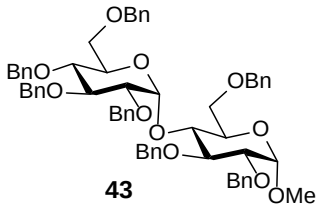
2.5.20 Methyl 4-Azido-2,3-di-*O*-benzyl-4,6-dideoxy-α-D-fucopyranosyl-(1→3)- 4-*O*-benzyl-2,6-dideoxy-α-D-*ribo*-hexopyranoside (41)



41

Disaccharide **41** (71 mg, 70%, α only) was synthesized from glycosylation of methyl α-digitoside acceptor **34** (40.6 mg, 0.161 mmol) with 4-azido-4-deoxy-1-thio-D-fucopyranosyl donor **32** (91.8 mg, 0.193 mmol) according to one-pot *in situ* adduct transformation and glycosylation procedure (Table 3, entry 7 in article). For **41**, R_f 0.30 (Hexanes/EtOAc = 5/1); $[\alpha]_D^{35}$ +75.10 (*c* 1.75, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (t, *J* = 8.5 Hz, 4H, Ar*H*), 7.34 – 7.22 (m, 11H, Ar*H*), 5.11 (d, *J* = 3.0 Hz, 1H, H-1′), 4.83 (d, *J* = 12 Hz, 1H), 4.80 (d, *J* =12 Hz, 1H), 4.71 (d, *J* = 11.5 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 2.5 Hz, 1H, H-1), 4.590 (dd, *J* = 7.0, 12.0 Hz, 2H), 3.91 (dd, *J* = 6.5, 13.5 Hz, 1H), 3.87 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.55 (d, *J* = 2.5 Hz, 1H,), 3.21 (s, 3H, O*CH*$_3$), 3.18 (dd, *J* = 2.5, 8.5 Hz, 1H), 2.24 (dd, *J* = 2.0, 15.0 Hz, 1H, H-2$_{eq}$), 1.72 (dt, *J* = 4.0, 15.0 Hz, 1H, H-2$_{ax}$), 1.27 (d, *J* = 6.5 Hz, 1H, C*H*$_3$), 1.04 (d, *J* = 6.5 Hz, 1H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 138.4, 138.3, 128.3, 128.2, 128.1, 127.6, 127.6, 127.5, 127.3, 127.2, 127.2, 97.2 (C-1), 93.8 (C-1′), 79.9, 77.4, 76.1, 73.0, 71.8, 71.4, 67.34, 65.1, 64.4, 63.3, 54.9, 31.3, 17.97, 17.2; HRMS (ESI): calcd for $C_{34}H_{41}N_3O_7Na^+$ $[M + Na]^+$ requires 626.2837, found 626.2864 *m/z*. The α-anomer of disaccharide **41** was obtained as the only anomer and no HPLC analysis was performed for this reaction.

2.5.21 Methyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (43)

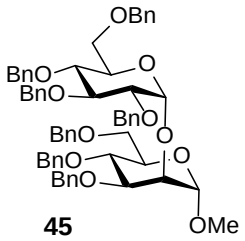


43

Mixture of thioglucoside donor **2** (100 mg, 0.15 mmol) and flame-dried molecular sieve (4Å, 300 mg) was suspended in dried CH_2Cl_2 (3 mL) such that the final concentration of **2** was 50 mM. Then, NFM (60 μL, 0.6 mmol) was added to the mixture. The resulting mixture was stirred at room temperature for 10 min and at 0 °C for additional 20-30 min. Subsequently, NIS (50.6 mg, 0.225 mmol) and TMSOTf (27 μL, 0.15 mmol) were added, and the reaction progress was monitored by TLC. Upon activation of glycosyl donor and formation of imidinium ion intermediate (by TLC examination), acceptor **42** (104.5 mg, 0.225 mmol) was added. The mixture was stirred at 0 °C. Upon completion of the glycosylation reaction (~24 h), the reaction was quenched by addition of Et_3N. Workup procedure: $NaHCO_3$ and $Na_2S_2O_3$(s) were added to the mixture, followed by stirring until the deep red color of the reacting solution changed to pale yellow. The resulting mixture was dried (over $MgSO_4$), filtered, and concentrated for flash chromatography purification over silica gel (Elution: hexanes/EtOAc 7:1) to furnish the glycosylation product. The disaccharide **43** (106 mg, 0.11 mmol, 70%, α:β 16:1 from NMR) was obtained as a glassy solid and no β-anomer was isolated in the reaction.[11] For α-anomer of **43**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.18 (m, 33H, Ar-H), 7.11 – 7.08 (m, 2H, Ar-H), 5.69 (d, *J* = 3.6 Hz, 1H, H-1′), 5.02 (d, *J* = 11.6 Hz, 1H), 4.87 (d, *J* = 10.8 Hz, 1H), 4.81 – 4.75 (m, 4H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 3.6 Hz, 1H), 4.57 (d, *J* = 1.2 Hz, 1H, H-1), 4.54 (s, 1H), 4.52 (d, *J* = 3.6 Hz, 1H), 4.49 (d, *J* = 2.8 Hz, 2H), 4.42 (d, *J* = 10.8 Hz, 1H), 4.27 (d, *J* = 12.0 Hz, 1H), 4.12 – 4.01 (m, 2H), 3.93 – 3.81 (m, 3H), 3.73 – 3.64 (m, 3H), 3.59 (dd, *J* = 3.6, 8.8 Hz, 1H), 3.49 (dd, *J* = 3.6, 10.0 Hz, 2H), 3.40 (d, *J* = 1.6 Hz, 1H), 3.37 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 138.8, 138.6, 138.2, 138.1, 138.04, 138.00, 128.5, 128.37, 128.35, 128.30, 128.27, 128.25, 128.1, 128.0, 127.87, 127.86, 127.75, 127.67, 127.61, 127.5, 127.4, 127.3, 127.1,

126.8, 97.8 ($^1J_{CH}$ = 166.2 Hz), 96.70 ($^1J_{CH}$ = 168.4 Hz), 82.10, 82.08, 80.3, 79.5, 77.7, 75.6, 75.0, 74.5, 73.5, 73.4, 73.3, 73.2, 72.4, 71.0, 69.6, 69.1, 68.3, 55.2.

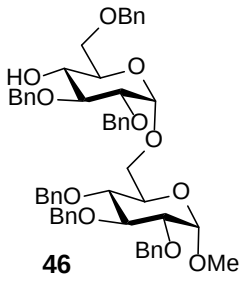
2.5.22 Methyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (45)



Mixture of donor **2** (100 mg, 0.15 mmol) and flame-dried molecular sieve (4Å) (0.3 mg) was suspended in dried CH_2Cl_2 (3 mL). Then, NFM (120 μL, 1.2 mmol) was added to the mixture. The resulting mixture was stirred at room temperature for 10 min and at -20 °C for additional 20-30 min. Subsequently, NIS (50.6 mg, 0.225 mmol) and TMSOTf (27 μL, 0.15 mmol) were added, and the reaction progress was monitored by TLC. Upon activation of glycosyl donor and formation of imidinium ion adduct (by TLC examination), acceptor **40** (104.5 mg, 0.225 mmol) was added. The mixture was stirred at -20 °C. Upon completion of the glycosylation reaction (~24 h), the reaction was quenched by addition of $NaHCO_3$. Workup procedure: $NaHCO_3$ and $Na_2S_2O_3$(s) were added to the mixture, followed by stirring until the deep red color of the reacting solution changed to pale yellow. The resulting mixture was dried (over $MgSO_4$), filtered, and concentrated for flash chromatography purification over silica gel (Elution: hexanes/EtOAc 1/0 to 5/1) to furnish the glycosylation product. Disaccharide **41** (91 mg, 61%, α:β >19:1 from NMR) was obtained after chromatography purification (Elution: hexanes/EtOAc 5:1). For α-anomer **45**, R_f 0.28 (hexanes/EtOAc 3/1); $[\alpha]_D^{17}$ +90.0 (*c* 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.20 (m, 25H, Ar-H), 7.17 – 7.10 (m, 10H, Ar-H), 5.48 (d, *J* = 3.6 Hz, 1H, anomeric proton), 4.90 (d, *J* = 10.8 Hz, 1H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.78 (d, *J* = 11.6 Hz, 1H), 4.75 (d, *J* = 2.4 Hz, 1H, anomeric proton), 4.70 (d, *J* = 10.8 Hz, 1H), 4.66 (s, 1H), 4.63 (d, *J* = 2.8 Hz, 1H), 4.60 (s, 1H), 4.54 – 4.42 (m, 4H), 4.34 (d, *J* = 10.8 Hz, 1H), 4.20 (t, *J* = 2.0 Hz, 1H), 4.03 (q, *J* = 19.2 Hz, 2H), 3.94 – 3.87 (m, 2H), 3.83 – 3.79 (m, 1H), 3.75 – 3.65 (m, 4H), 3.60 (t, *J* = 9.2 Hz, 1H), 3.54 (dd, *J* = 3.6, 9.6 Hz, 1H), 3.30 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 138.7,

138.6, 138.4, 138.2, 138.0, 128.5, 128.43, 128.37, 128.32, 128.31, 128.29, 128.1, 128.04, 127.96, 127.85, 127.81, 127.76, 127.70, 127.62, 127.50, 127.48, 127.4, 127.2, 100.1 ($^1J_{CH}$ = 168.9 Hz), 97.2 ($^1J_{CH}$ = 169.8 Hz), 81.5, 80.6, 79.7, 77.5, 75.6, 75.1, 75.0, 74.9, 73.5, 73.45, 73.1, 72.7, 72.3, 71.2, 70.7, 69.4, 68.6, 54.7; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{62}H_{66}NaO_{11}^+$, 1009.4503; found, 1009.4548. The α:β ratio of **40** was >19:1 based on the estimation from ^{1}H NMR spectroscopy.

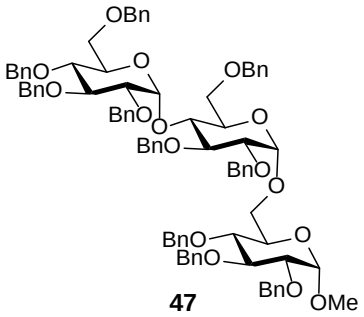
2.5.23 Methyl 2,3,6-Tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (46).



46

For α-disaccharide **46**, R_f 0.43 (hexanes/EtOAc/CH_2Cl_2 2/1/1); $[\alpha]_D^{30}$ +55.34 (*c* 1.012, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.20 (m, 30H, Ar-H), 4.98-4.94 (m, 3H, including one aromatic proton), 4.92 (dd, *J* = 2.0, 11.0 Hz, 1H), 4.82 (dd, *J* = 2.5, 11.0 Hz, 1H), 4.73 – 4.63 (m, 5H), 4.55 – 4.52 (m, 3H, including one aromatic proton), 4.48 (d, *J* = 12.0 Hz, 1H) , 3.99 (td, *J* = 2.5, 9.0 Hz, 1H), 3.84 – 3.73 (m, 5H), 3.70 (d, *J* = 11.5 Hz, 1H) , 3.66 (dd, *J* = 3.5, 9.5 Hz, 1H), 3.62 – 3.57 (m, 3H), 3.51 (dt, *J* = 9.5, 2.5 Hz, 1H), 3.43 (dt, *J* = 9.5, 2.5 Hz, 1H), 3.34 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8, 138.7, 138.4, 138.3, 138.1, 138.0, 128.5, 128.38, 128.36, 128.33, 128.31, 128.30, 128.04, 127.95, 127.8, 127.7, 127.63, 127.56, 98.0 ($^1J_{CH}$ = 166.4 Hz), 97.2 ($^1J_{CH}$ = 168.1 Hz), 82.1, 80.6, 80.1, 79.6, 77.8, 75.8, 75.7, 75.6, 75.1, 75.01, 74.96, 73. 5, 73.43, 73.37, 73.33, 73.30, 72.14, 72.10, 72.07, 70.6, 70.3, 70.1, 69.5, 66.1, 55.1; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{55}H_{60}NaO_{11}^+$, 919.4028; found, 919.4041.

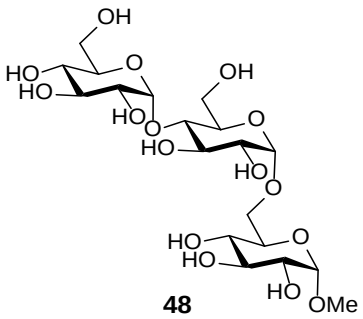
2.5.24 Methyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (47):



47

Trisaccharide **47** was (48 mg, 60%) synthesized from glycosylation of disaccharide **46** (100 mg, 0.12 mmol) with donor **2** (109 mg, 0.17 mmol) according to the glycosylation protocol for preparation of **43**. The trisaccharide **47** was obtained as a white glassy solid by flash chromatography purification (Elution: hexanes/EtOAc 7/1 to 5/1) and no other anomer was obtained. For trisaccharide **47**, R_f 0.19 (hexanes/EtOAc 3/1); $[\alpha]_D^{30}$ +71.6 (*c* 0.475, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.33 -7.19 (m, 43H, Ar-H), 7.14 – 7.10 (m, 7H Ar-H), 5.68 (d, *J* = 3.5 Hz, 1H, anomeric proton), 4.99-4.92 (m, 4H, including one aromatic proton), 4.86-4.73 (m, 5H), 4.70-4.67 (m, 2H), 4.61-4.41 (m, 10H, including one aromatic proton), 4.27 (dd, *J* = 3.0, 12.0 Hz, 1H), 4.07-3.97 (m, 3H), 3.90-3.87 (m, 2H), 3.81-3.79 (m, 3H), 3.74-3.70 (m, 2H), 3.66-3.56 (m, 4H), 3.48-3.42 (m, 3H), 3.38-3.35 (m, 4H, including CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.1, 138.9, 138.8, 138.6, 138.4, 138.3, 138.24, 138.19, 138.16, 138.0, 128.5, 128.44, 128.38, 128.34, 128.29, 128.25, 128.19, 128.03, 127.99, 127.93, 127.87, 127.85, 127.83, 127.74, 127.65, 127.60, 127.58, 127.52, 127.48, 127.38, 127.29, 127.0, 126.9, 98.0 ($^1J_{CH}$ = 165.5 Hz), 96.8 ($^1J_{CH}$ = 172.3 Hz), 96.8 ($^1J_{CH}$ = 168.6 Hz), 82.2, 82.1, 81.7, 80.2, 80.1, 79.5, 77.8, 77.7, 75.8, 75.5, 75.1, 75.0, 74.1, 73.5, 73.4, 73.2, 73.1, 72.9, 72.3, 71.0, 70.5, 69.9, 69.2, 68.3, 65.9, 55.3. HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{89}H_{94}NaO_{16}^+$, 1441.6434; found, 1441.6431.

2.5.25 Methyl D-Glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→6)-α-D-glucopyranoside (48).



48

Protected trisaccharide **47** (147 mg, 0.10 mmol) dissolved in 4:1:0.5 MeOH/EtOAc/AcOH solvent mixture was treated with Pd/C (100 mg) under H_2 (1 atm). The reaction mixture was stirred at RT for 2 days and then filter (over celite) to remove Pd/C. The resulting filtrate was concentrated and purified by FPLC (Elution: 1:1 MeOH:H_2O, flow rate 0.5 mL/min) to obtain the trisaccharide **48** as a white glassy solid (30 mg, 56%). For **48**, R_f 0.09 (CH_2Cl_2/MeOH/H_2O 2/1/0.05); $[\alpha]_D^{35}$ +28.8 (*c* 0.35, MeOH); ^{1}H NMR (500 MHz, CD_3OD): δ 5.15 (d, *J* = 4.0 Hz, 1H, anomeric H), 4.85 (d, *J* = 4.0 Hz, 1H, anomeric H overlap with residual H_2O signals), 4.67 (d, *J* = 4.0 Hz, 1H, reducing end H-1), 3.92 – 3.88 (m, 2H), 3.86 – 3.64 (m, 8H), 3.61 (td, *J* = 3.0, 9.5 Hz, 2H), 3.54 (t, *J* = 9.5 Hz, 1H), 3.47 – 3.43 (m, 2H), 3.42 (s, 3H, CH_3), 3.41 (m, 1H), 3.35 (dd, *J* = 10.0, 11.5 Hz, 1H), 3.27 (t, *J* = 9.0 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD): δ 103.0 ($^1J_{CH}$ 172.5 Hz), 101.5 ($^1J_{CH}$ 171.3 Hz), 100.0 ($^1J_{CH}$ 168.85 Hz), 81.8, 75.4, 75.2, 75.1, 74.9, 74.4, 73.5, 72.3, 72.1, 72.0, 71.6, 67.8, 62.9, 62.1, 56.0 (O*C*H_3); HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{19}H_{34}NaO_{16}^+$, 541.1739; found, 541.1745.

3 Reference

S1. B. Ghosh, Y. H. Lai, Y. Y. Shih, T. K. Pradhan, C. H. Lin, K. K. T. Mong, *Chem. Asian J.* 2013, **8**, 3191-3199 (donor **1**).

S2. Z. Zhang, I.-R. Ollmann, X.-S. Ye, R. Wishnat, T. Baasov, C.-H. Wong, *J. Am. Chem. Soc.*, 1999, **121**, 734-753 (donors **2 ,10**).

S3. A.-M. David, N.A.H. Ruthven, R.M. Ronald, *Chem. Phys. Lipids*, 1987, **43**, 113-127 (acceptor **3**).

S4. C.-R. Shie, Z.-H. Tzeng, S.-S. Kulkarni, B.-J. Uang, C.-Y. Hsu, S.-C. Hung, *Angew. Chem. Int. Ed*. 2005, **44**, 1665-1668 (acceptors **4**, **42**).

S5 C. McDonnell, O. Lopez, P. Murphy, J. G. F. Bolanos, R. Hazell, M. Bols, *J. Am. Chem. Soc.*

2004, **126**, 12374-12385 (donor **9**, α-disaccharide **23**).

S6. M. M. Matin, M. Ibrahim, *J. Appl. Sci. Res.* 2010, **6**, 1527-1532 (Acceptor **12**).

S7. C.-S. Chao, Y.-F. Yen, W.-C. Hung, K.-K. T. Mong, *Adv. Synth. Catal*. 2011, **353**, 879-884 (acceptor **18**).

S8. K.-K. T. Mong, Y.-F. Yen, W.-C. Hung, Y. H. Lai, J. H. Chen, *Eur. J. Org. Chem.* 2012, 3009-3017 (donor **30**).

S9. A. B. Ingle, C. S. Chao, W. C. Hung, K. K. T. Mong, *Org. Lett.* 2013, **15**, 5290-5293 (donor **31**).

S10. C. Li, Y. Sun, J.; Zhang, Z. Zhao, G. Yu, H. Guan, *Carbohydr. Res.* 2013, **376**, 15-23 (precursor substrate **32a** for **32**).

S11 J.-H. Chen, J.-H. Ruei, K.-K. T. Mong, *Eur. J. Org. Chem.* 2014, 1827-1831 (precursor substrate **34a** for **34**).

S12. H. W. He, X. M. Zhu, *Org. Lett.* 2014, **16**, 3102-3105 (α-disaccharide **6**, **23**).

S13. S.-R. Lu, Y.-H. Lai, J.-H. Chen, C.-Y. Liu, K.-K. T. Mong, *Angew. Chem. Int. Ed.* 2011, **50**, 7315-7320 (α-disaccharide **19**).

S14. Nagai, H.; Sasaki, K.; Matsumura, S.; Toshima, K. *Carbohydr. Res.* 2005, **340**, 337-353 (β-disaccharide 16).

S15. S. Valerio, A. Iadonisi, M. Adinolfi, A. Ravida, *J. Org. Chem.* 2007, **72**, 6097 (α/β-disaccharide **22**).

S16. Nguyen, H. M.; Chen, Y. N.; Duron, S. G.; Gin, D. Y. *J. Am. Chem. Soc.* 2001, **123**, 8766 (**27**).

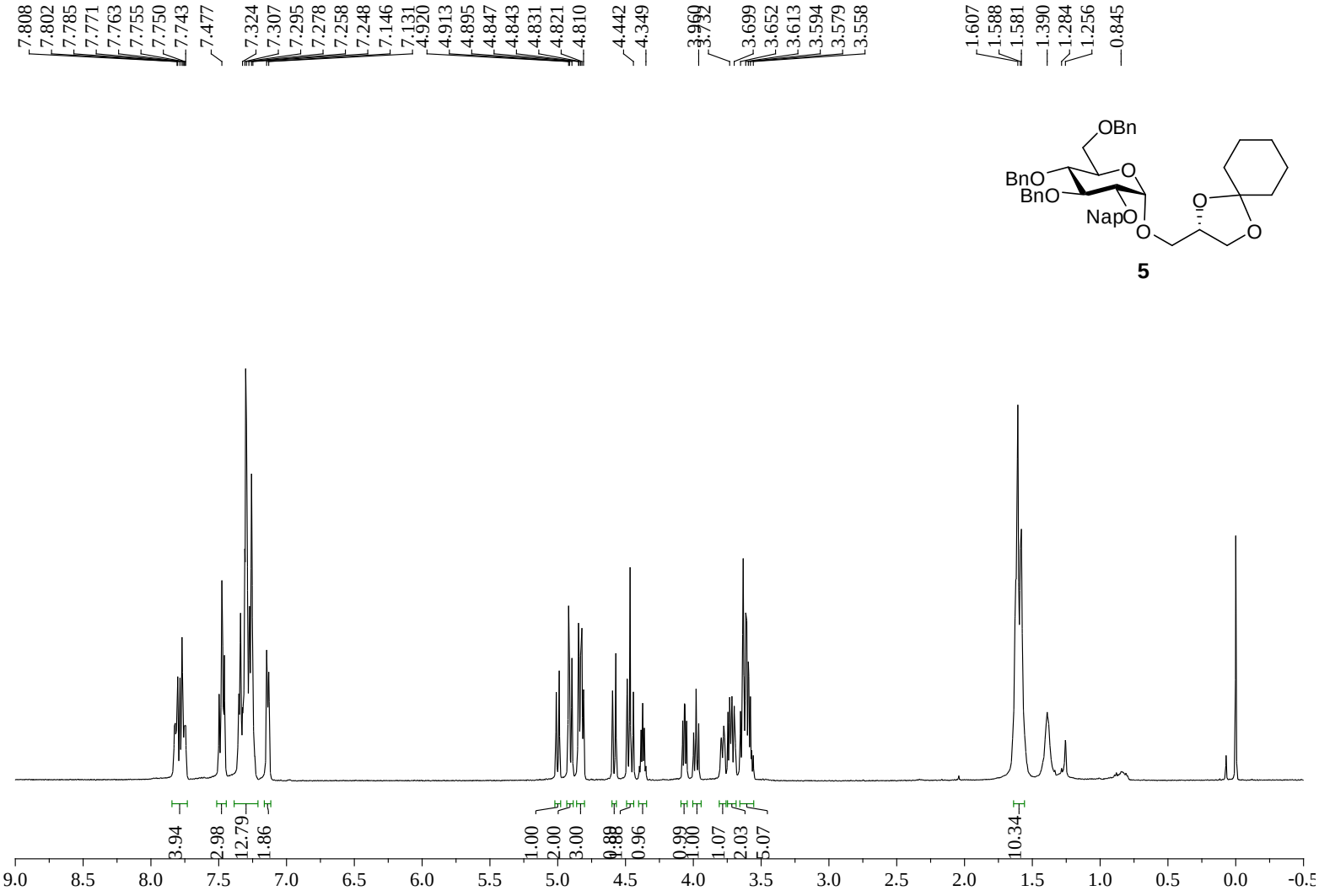
S17. A. Chu, S. H. Nguyen, J. A. Sisel, A. Minciunescu, and C. S. Bennett, *Org. Lett.* 2013, **15**, 2566 (α-disaccharide **28**).

S18. P. Wang, P. Haldar, Y. Wang, H. Hu, *J. Org. Chem.* 2007, **72**, 5870-5873 (α-disaccharide **29**).

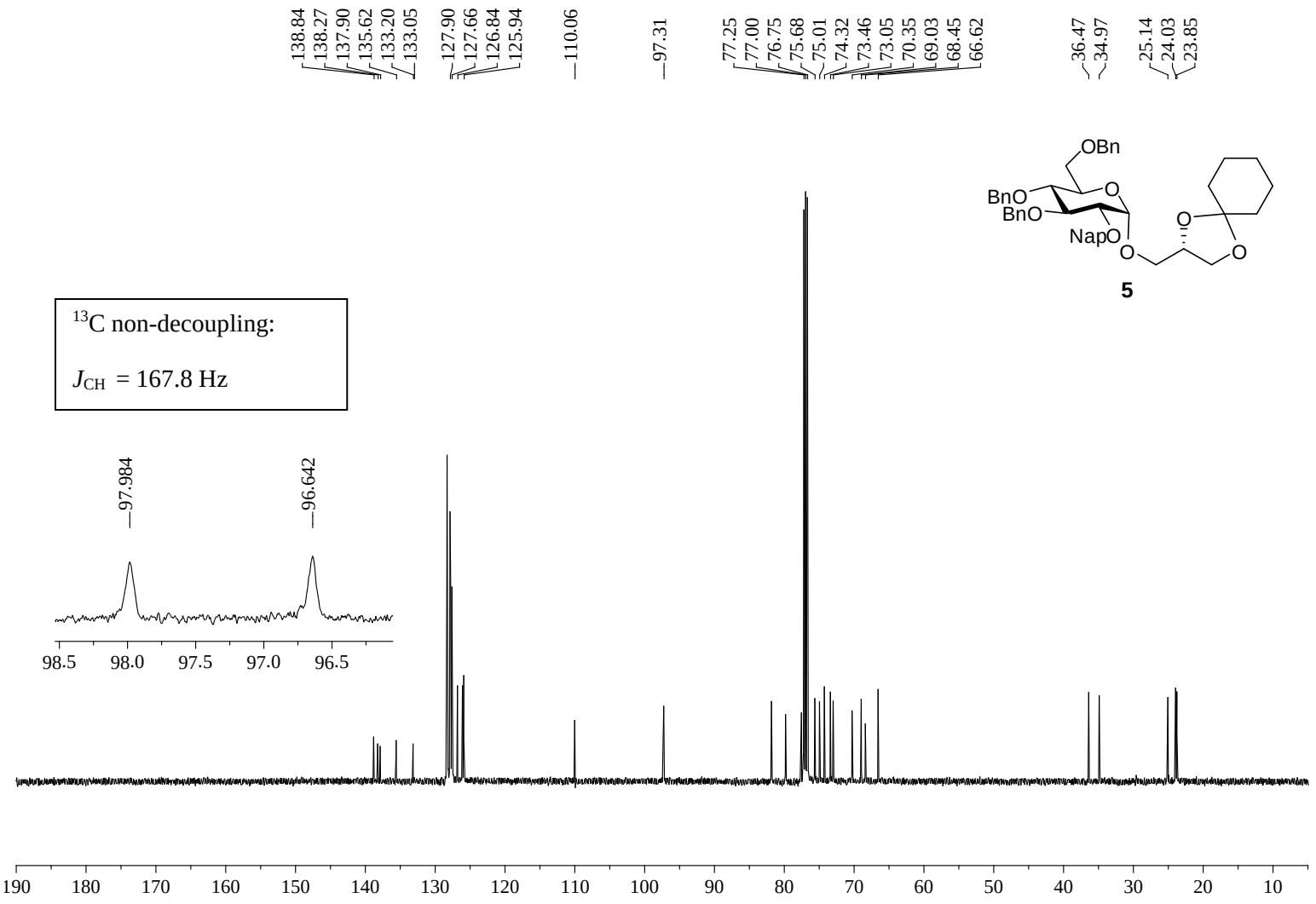
S19. T. Tsuda, S. Nakamura, S. Hashimoto, *Tetrahedron* 2004, **60**, 10711-10737 (β-anomer of disaccharides **35**, **37**, **38**).

4 NMR spectra

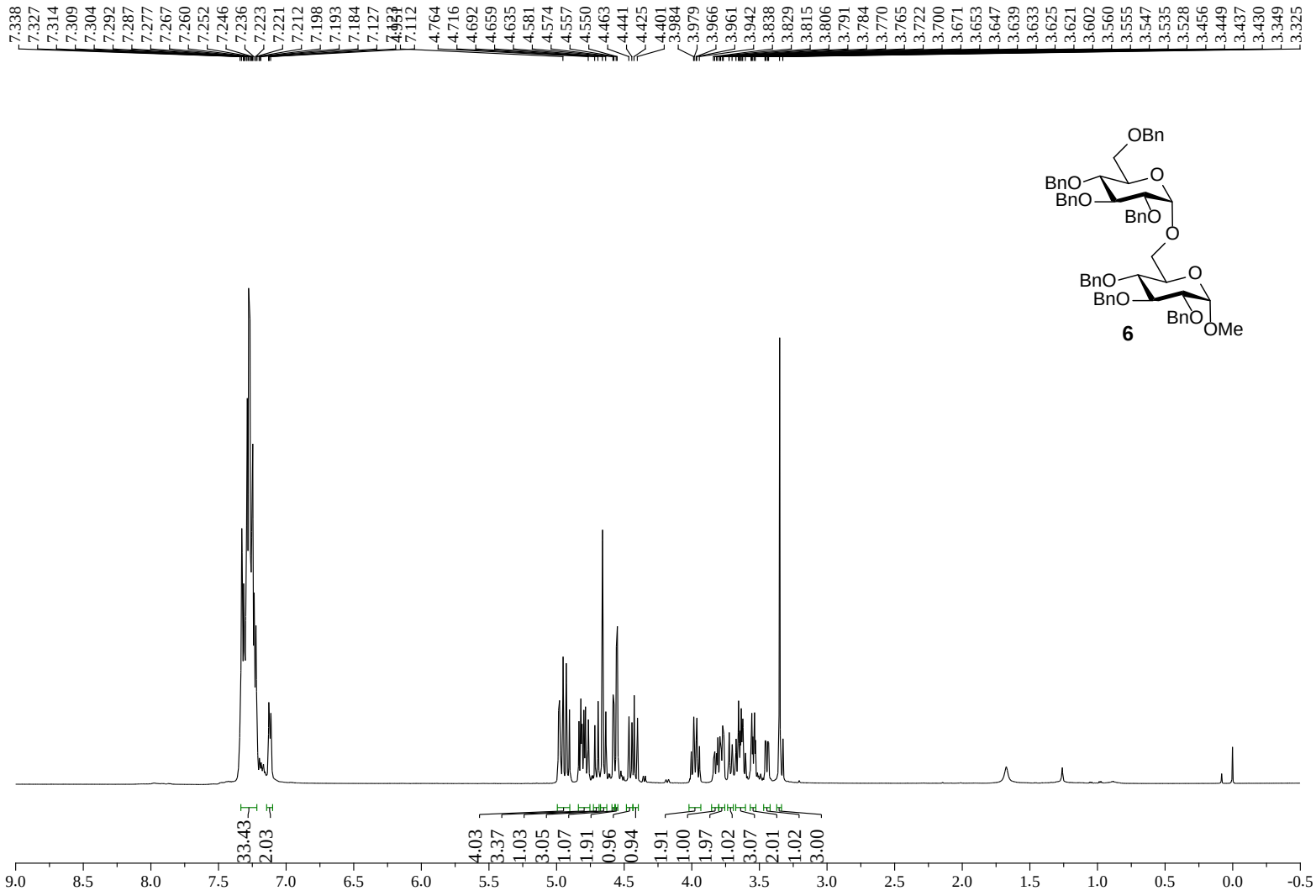
^{1}H NMR of 3-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(2-naphthylmethyl)-α-D-glucopyranosyl]-1,2-*O*-cyclohexylidene-*sn*-glycerol (5)



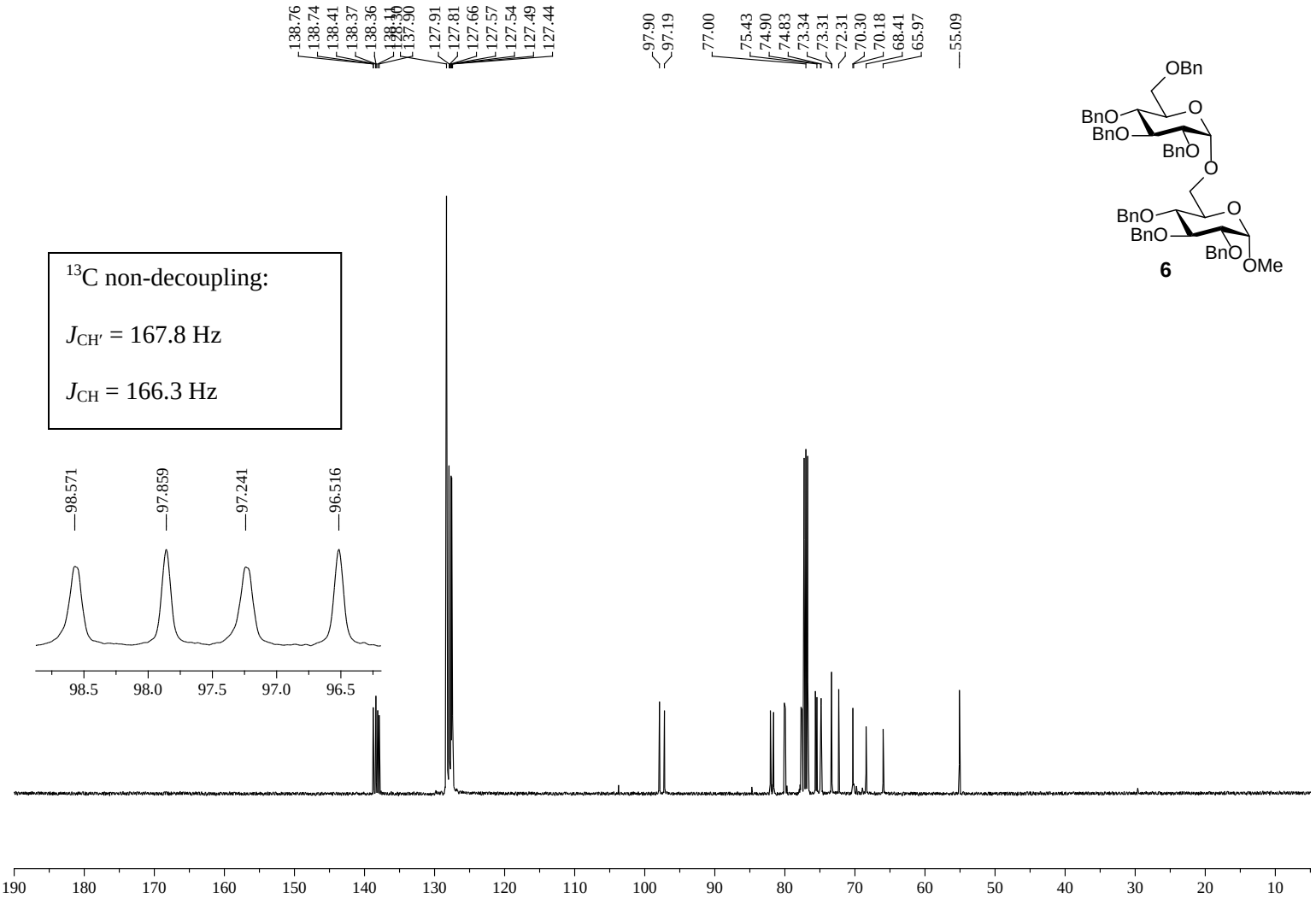
^{13}C NMR of 3-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(2-naphthylmethyl)-α-D-glucopyranosyl]-1,2-*O*-cyclohexylidene-*sn*-glycerol (5)



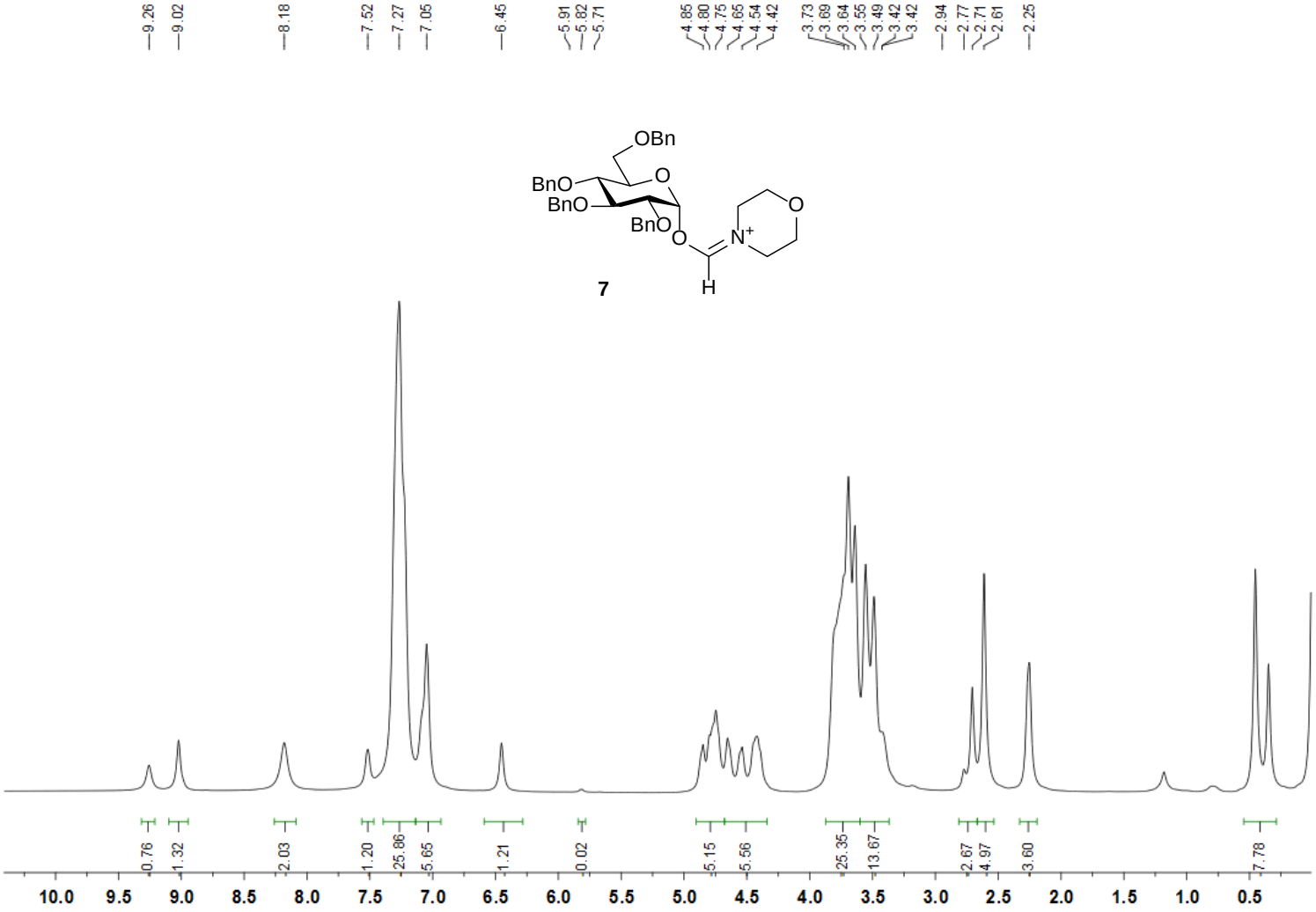
^{1}H NMR of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*- benzyl-α-D-glucopyranoside (6)



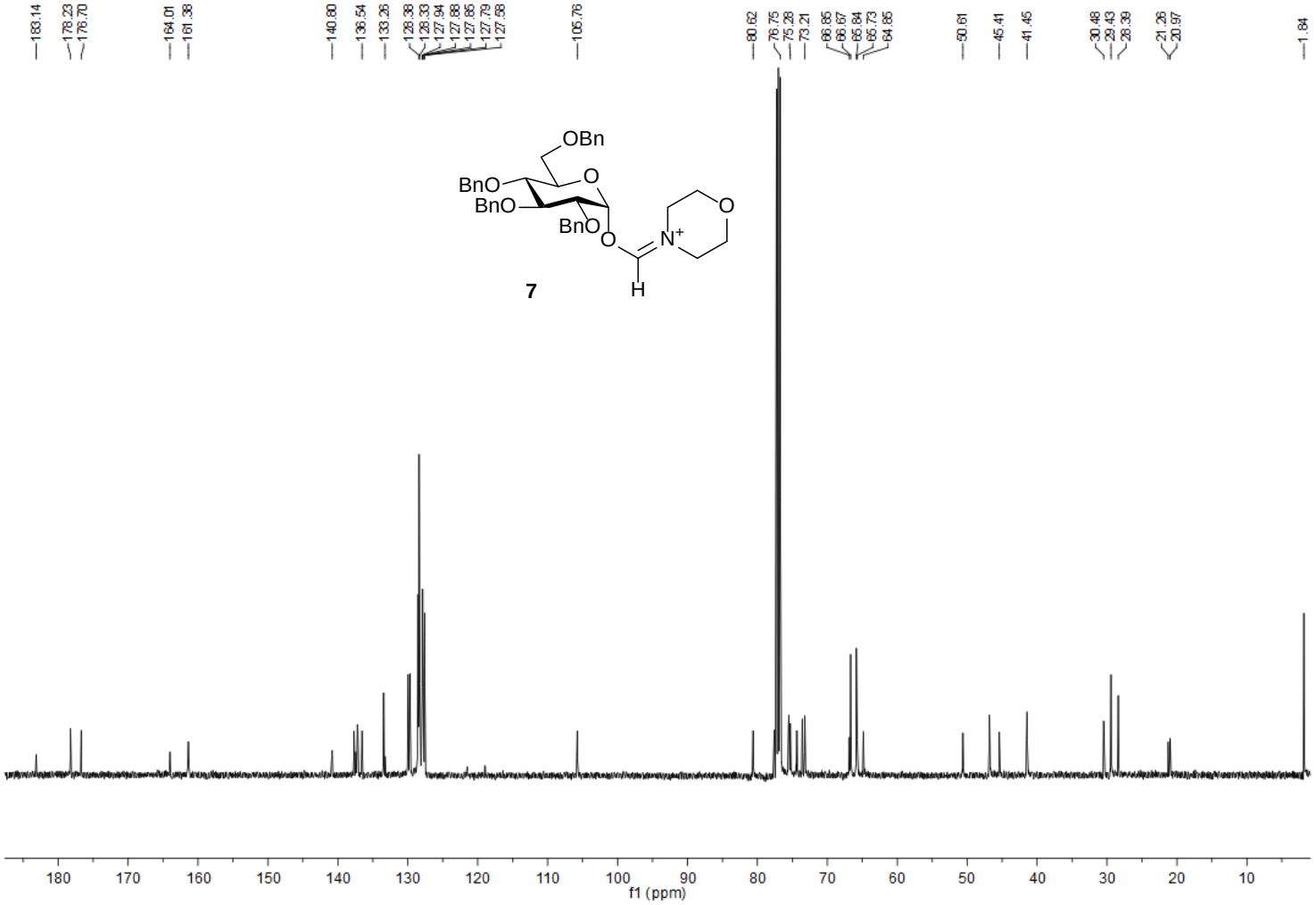
^{13}C NMR of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (6)



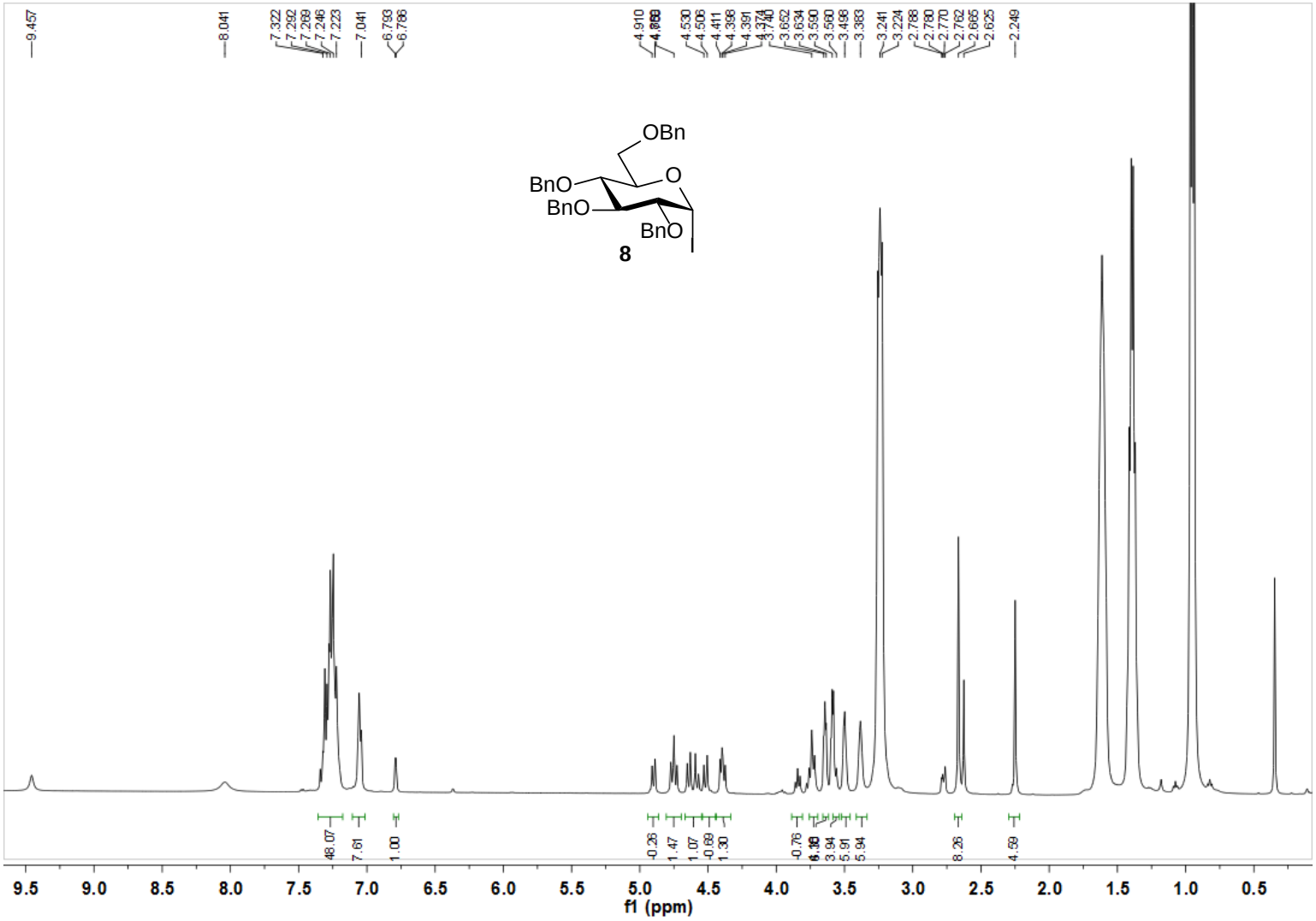
Crude ^{1}H NMR of D-glucopyranosyl imidinium ion (7) at -20 ^{o}C



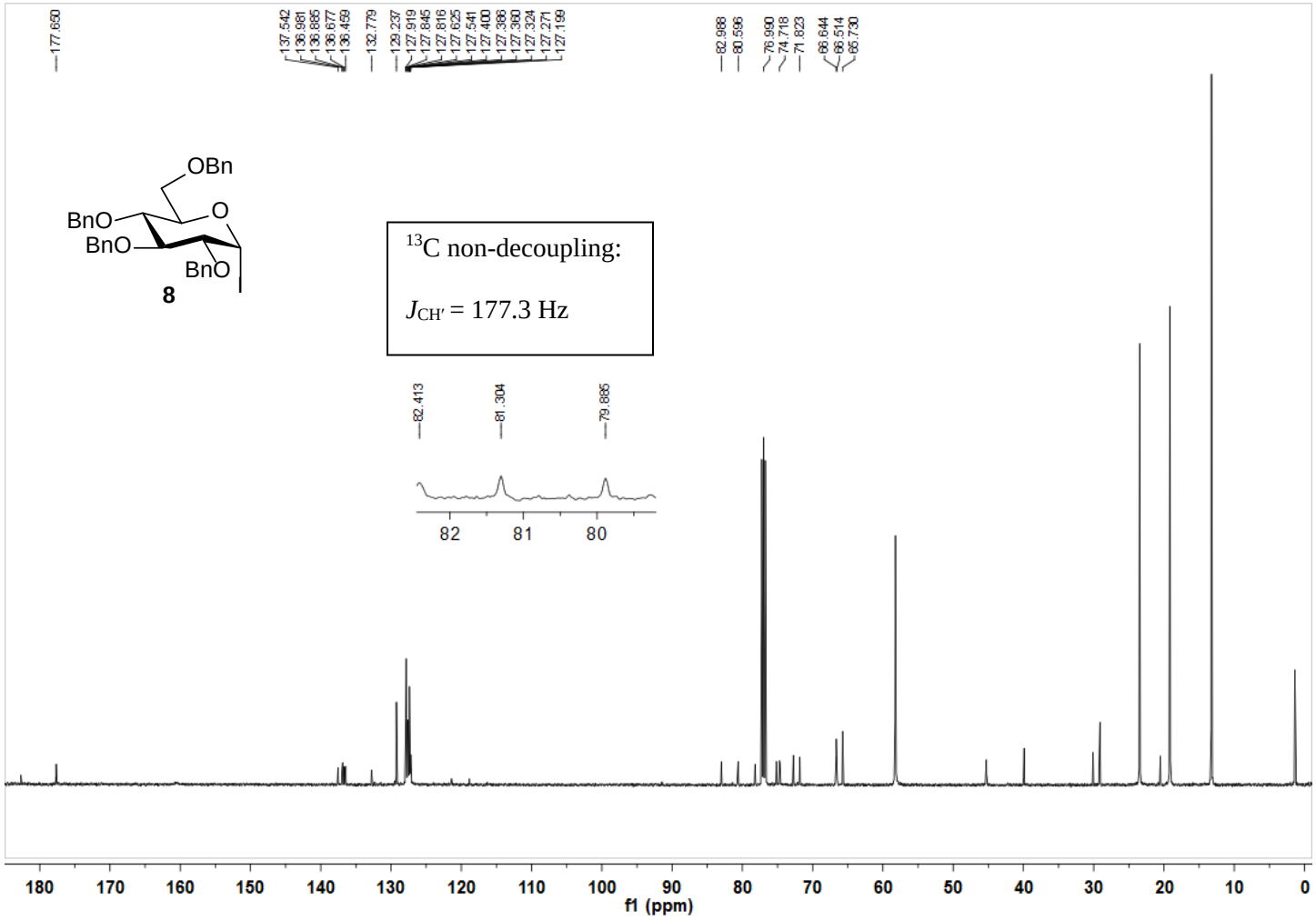
Crude ^{1}H NMR of D-glucopyranosyl imidinium ion (7) at -20 ^{o}C



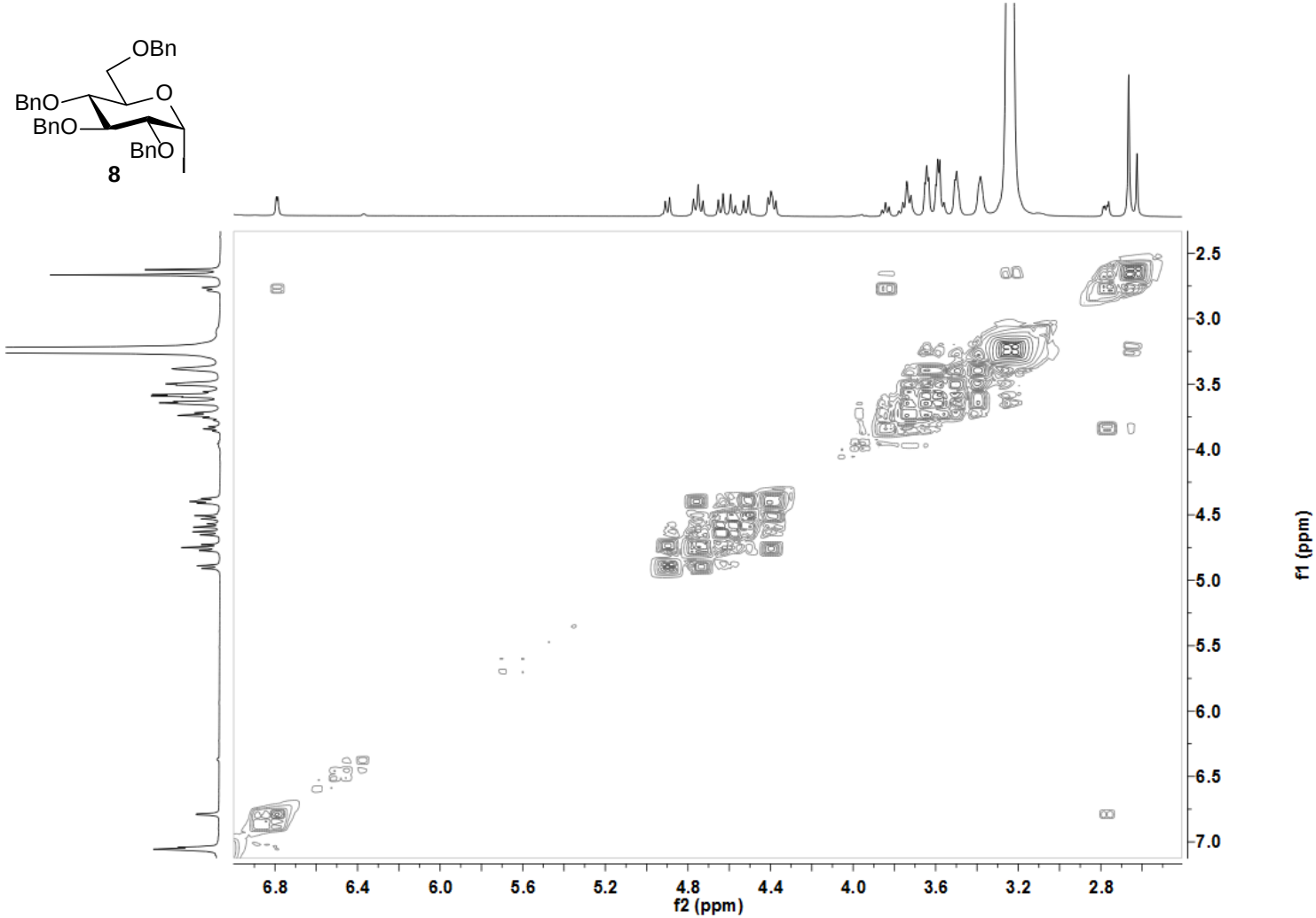
Crude ^{1}H NMR of α-D-glucopyranosyl iodide (8) at 0 °C



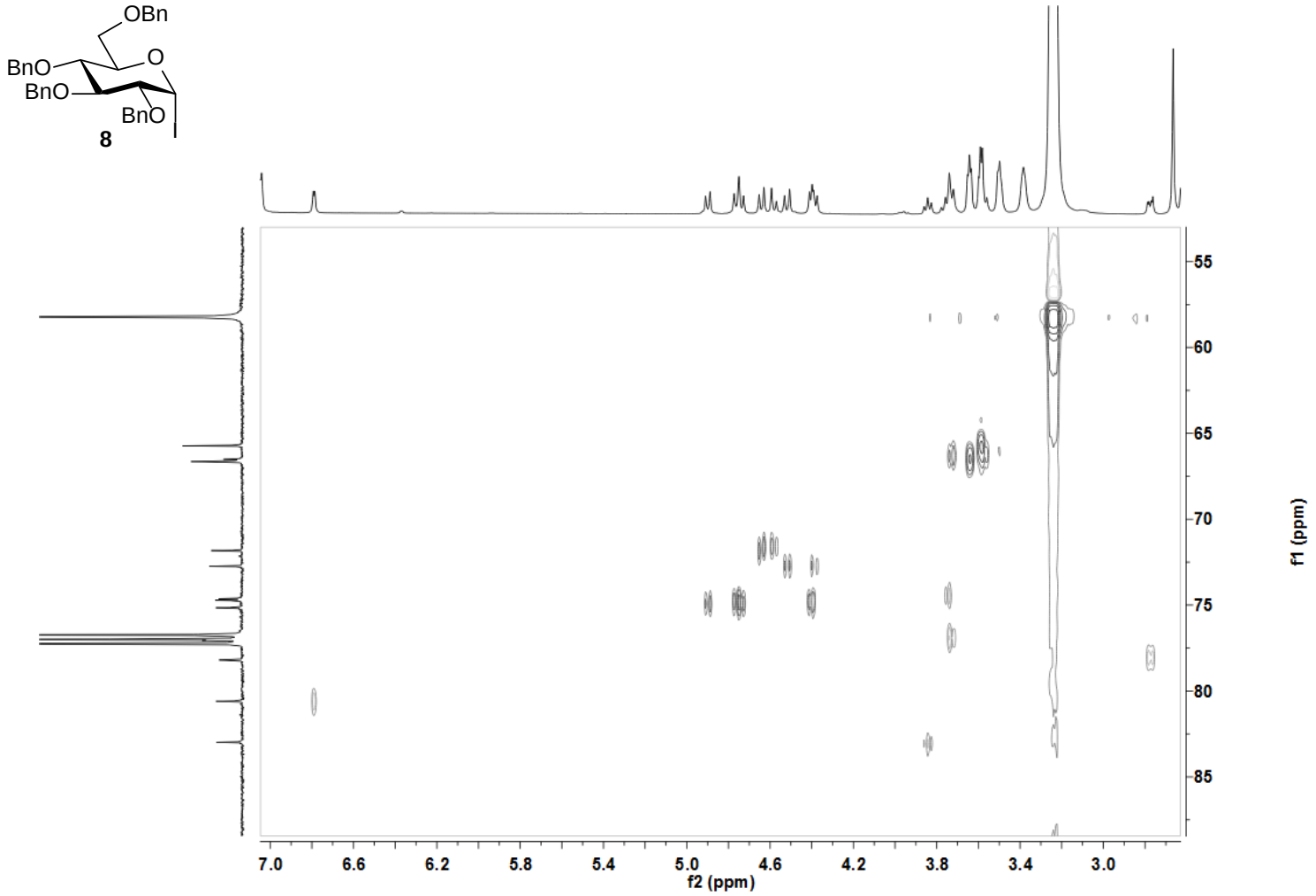
Crude ^{13}C NMR of α-D-glucopyranosyl iodide (8) at 0 °C



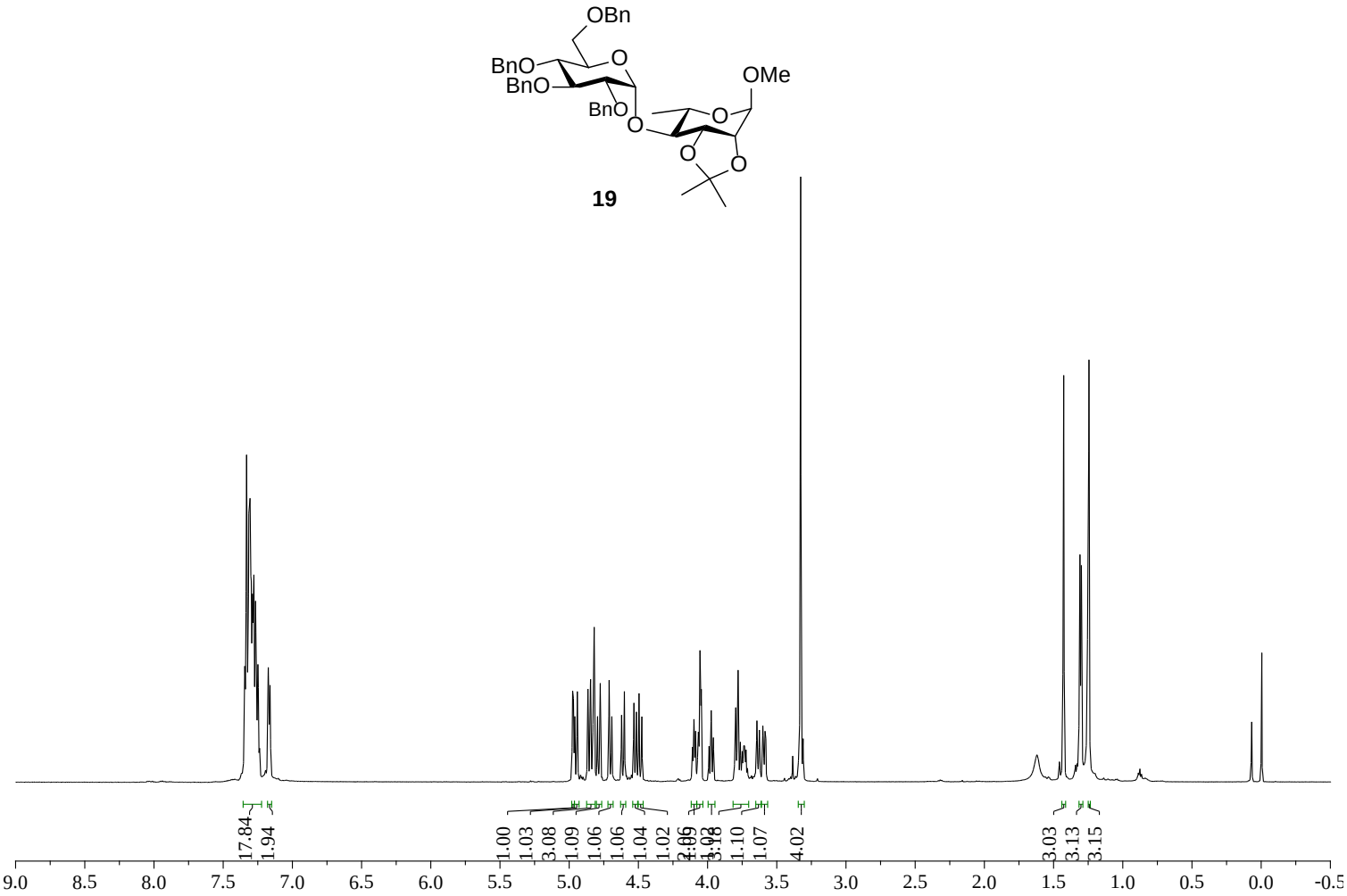
Crude COSY NMR of α-D-glucopyranosyl iodide (8) at 0 ºC



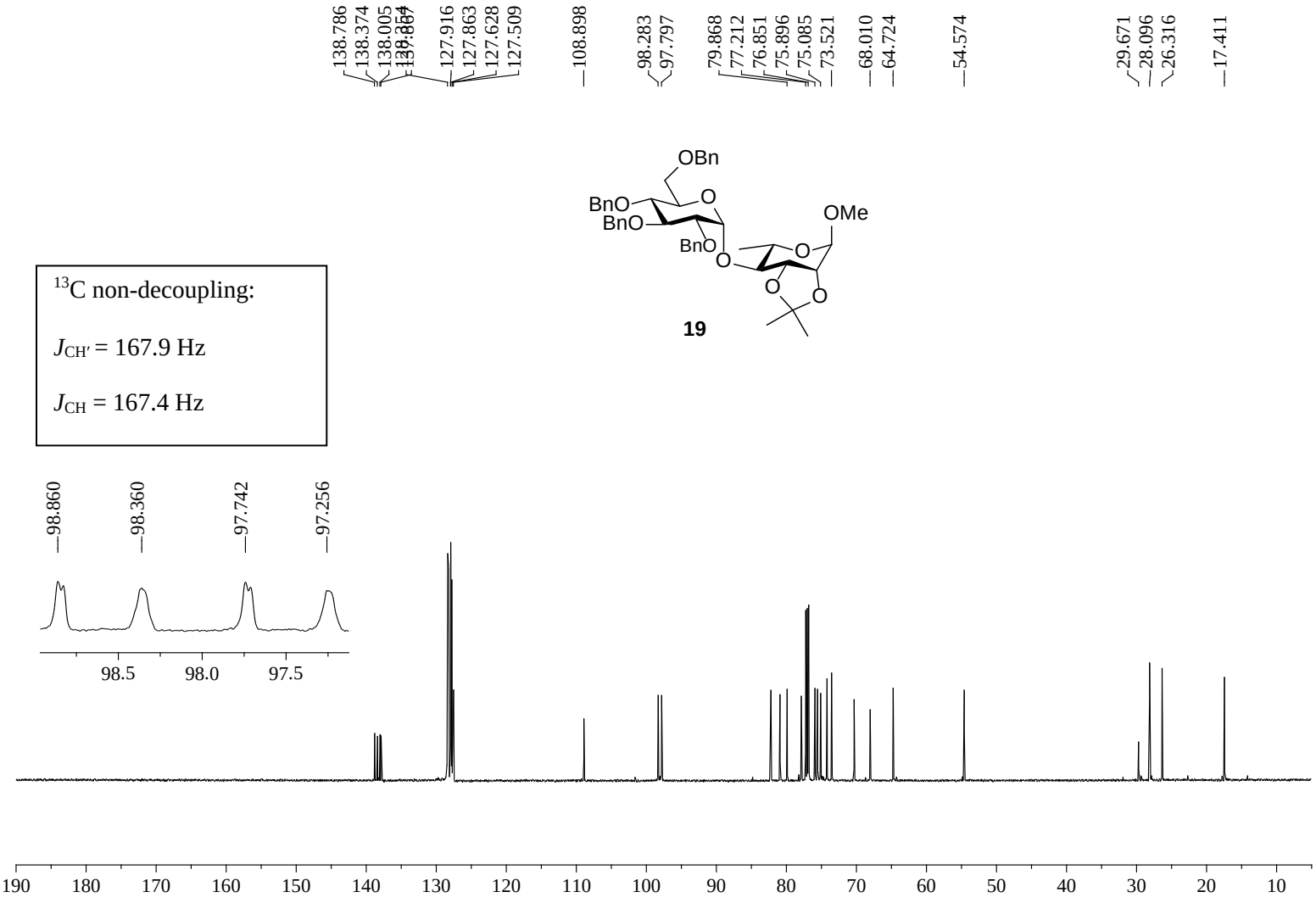
Crude HSQC NMR of α-D-glucopyranosyl iodide (8) at 0 ºC



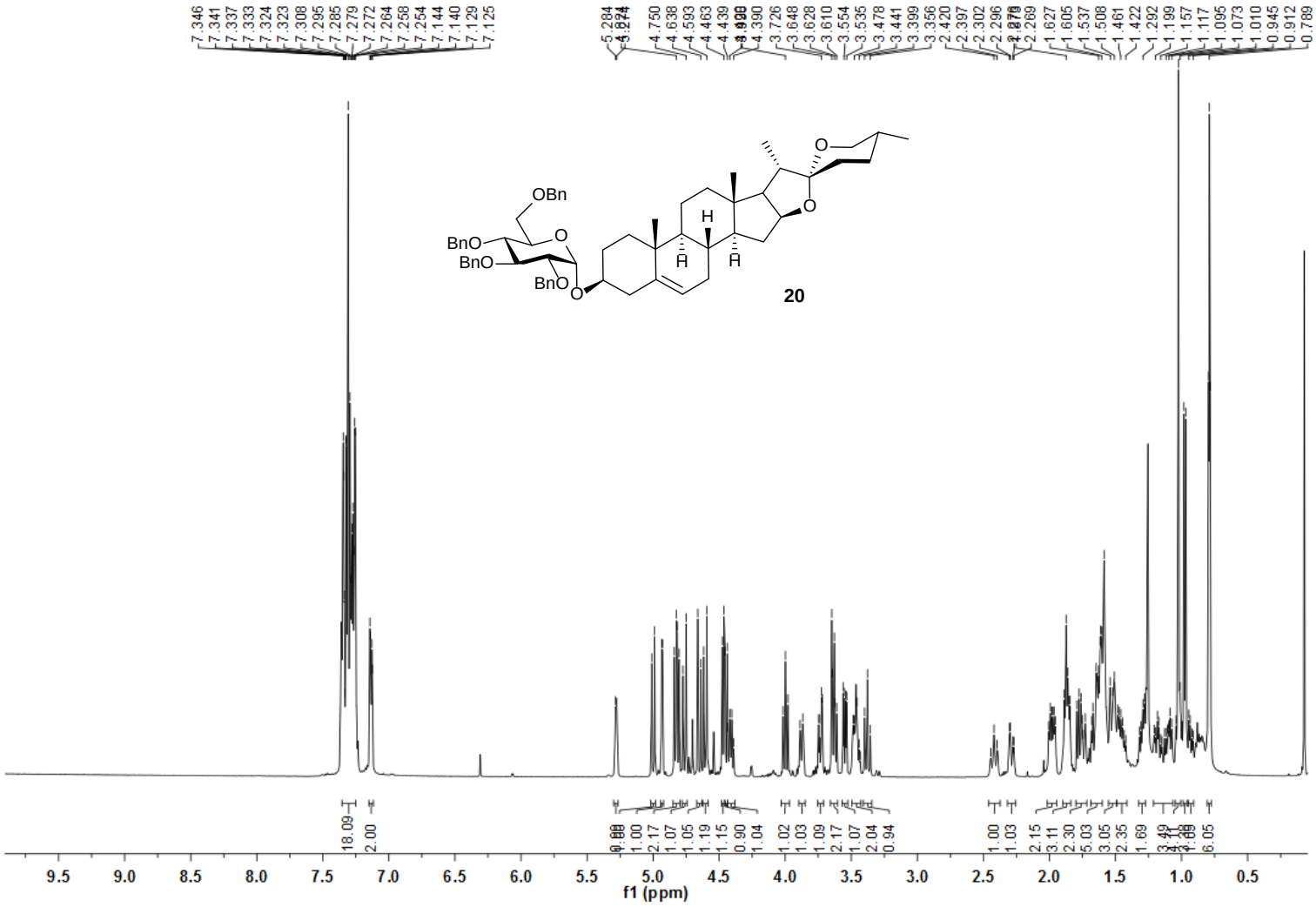
^{1}H NMR of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (19)



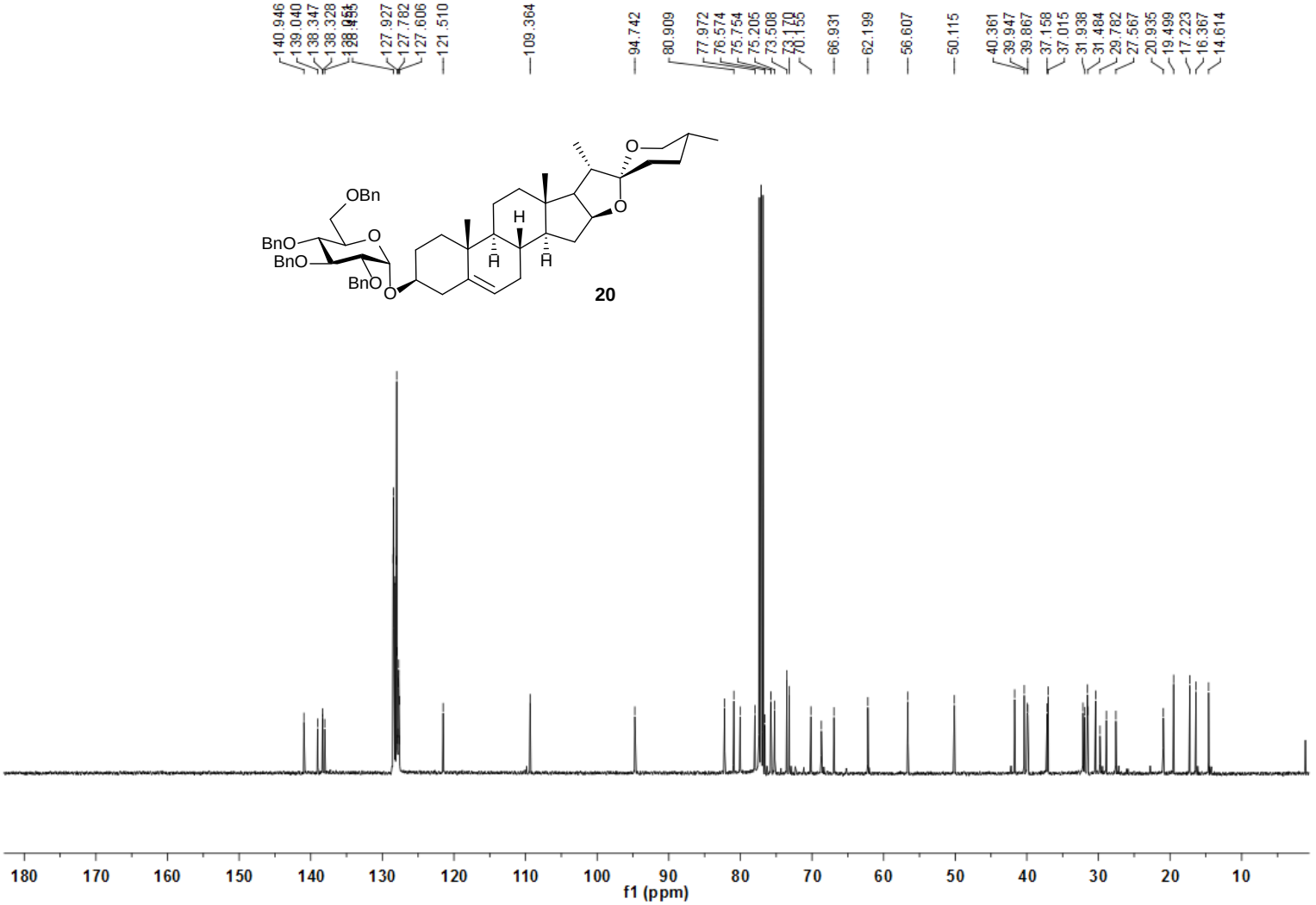
^{13}C NMR of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-*O*- isopropylidene-α-L-rhamnopyranoside (19)



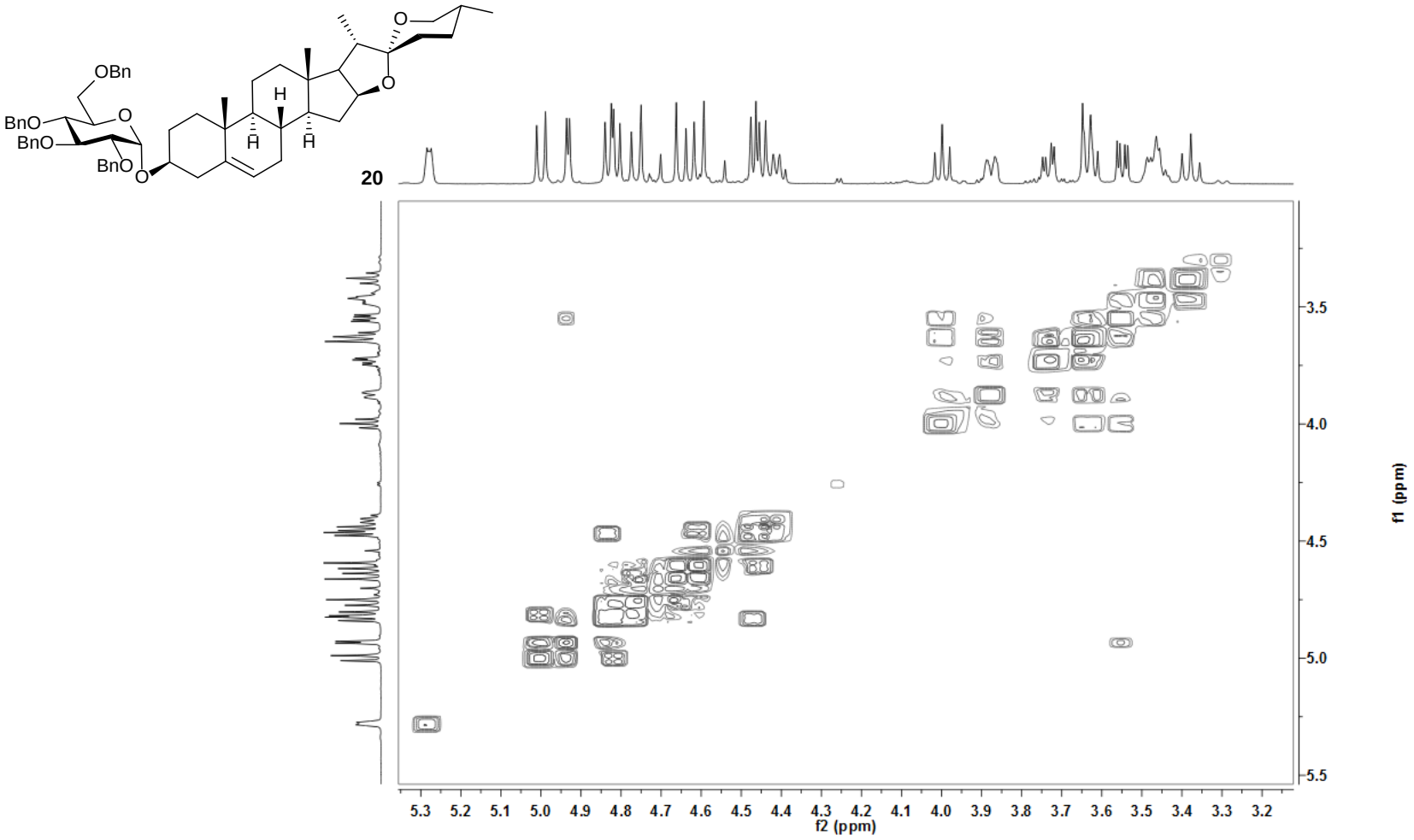
^{1}H NMR of diosgeninyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (20)



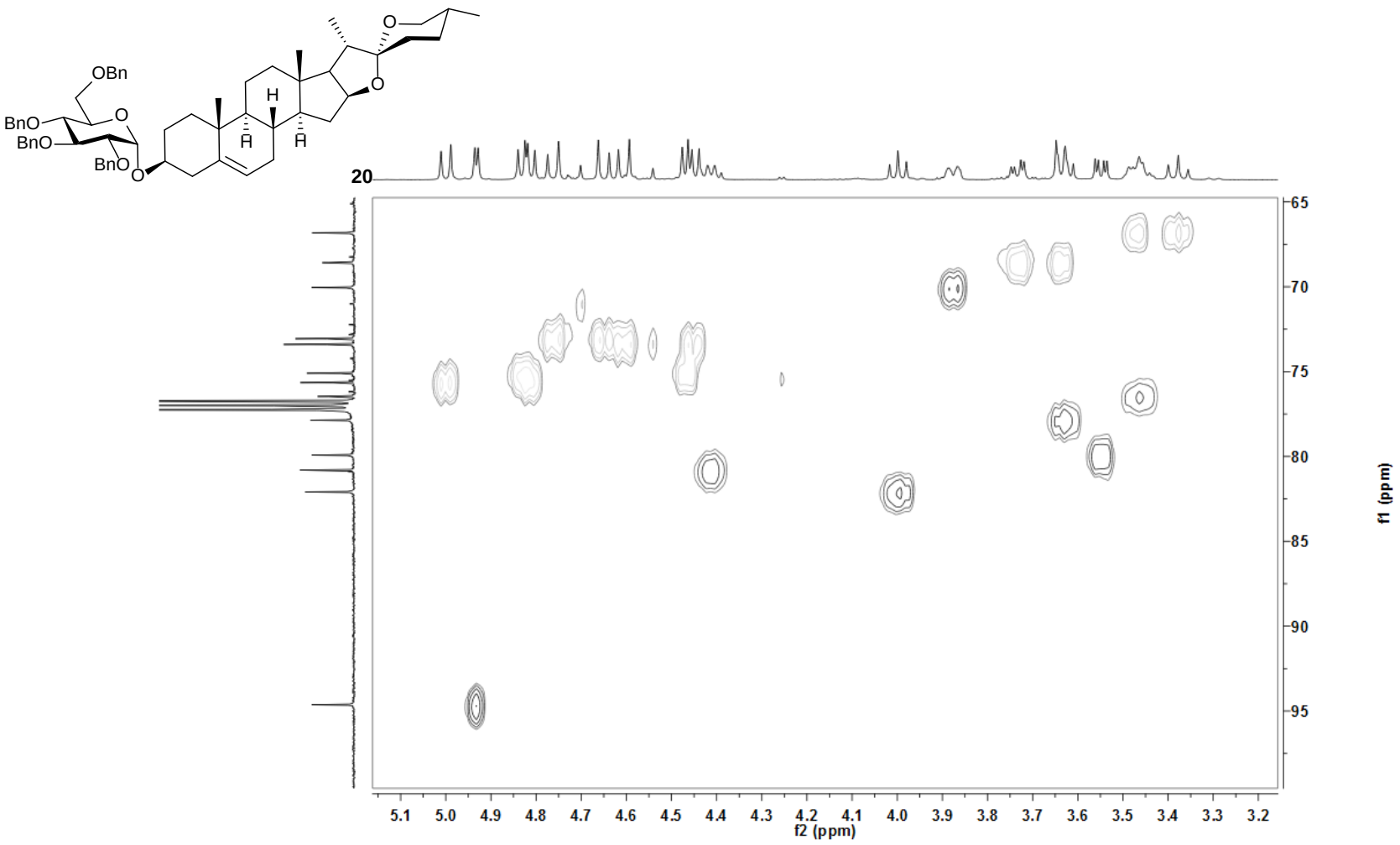
^{13}C NMR of diosgeninyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (20)



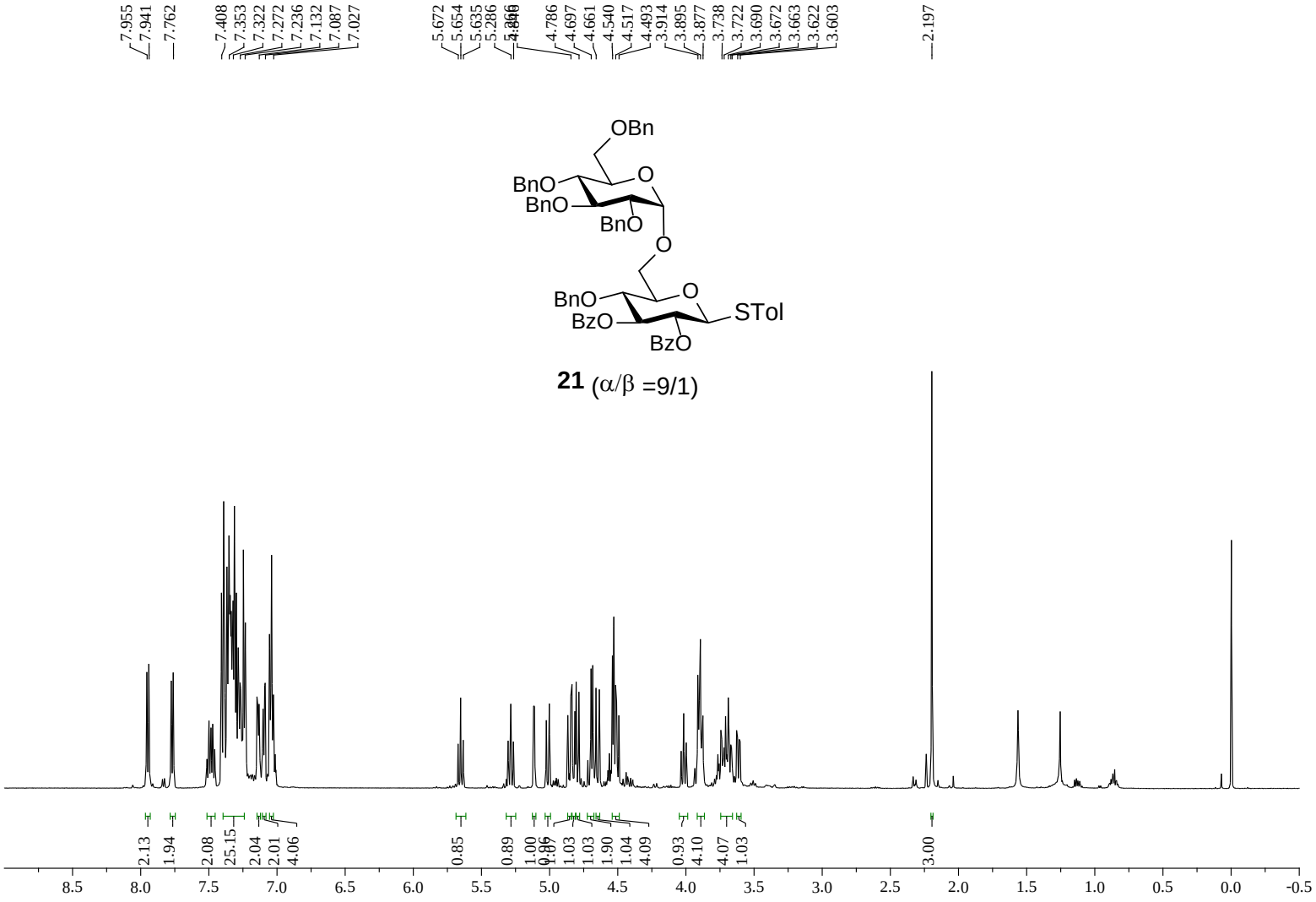
COSY NMR of diosgeninyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (20)



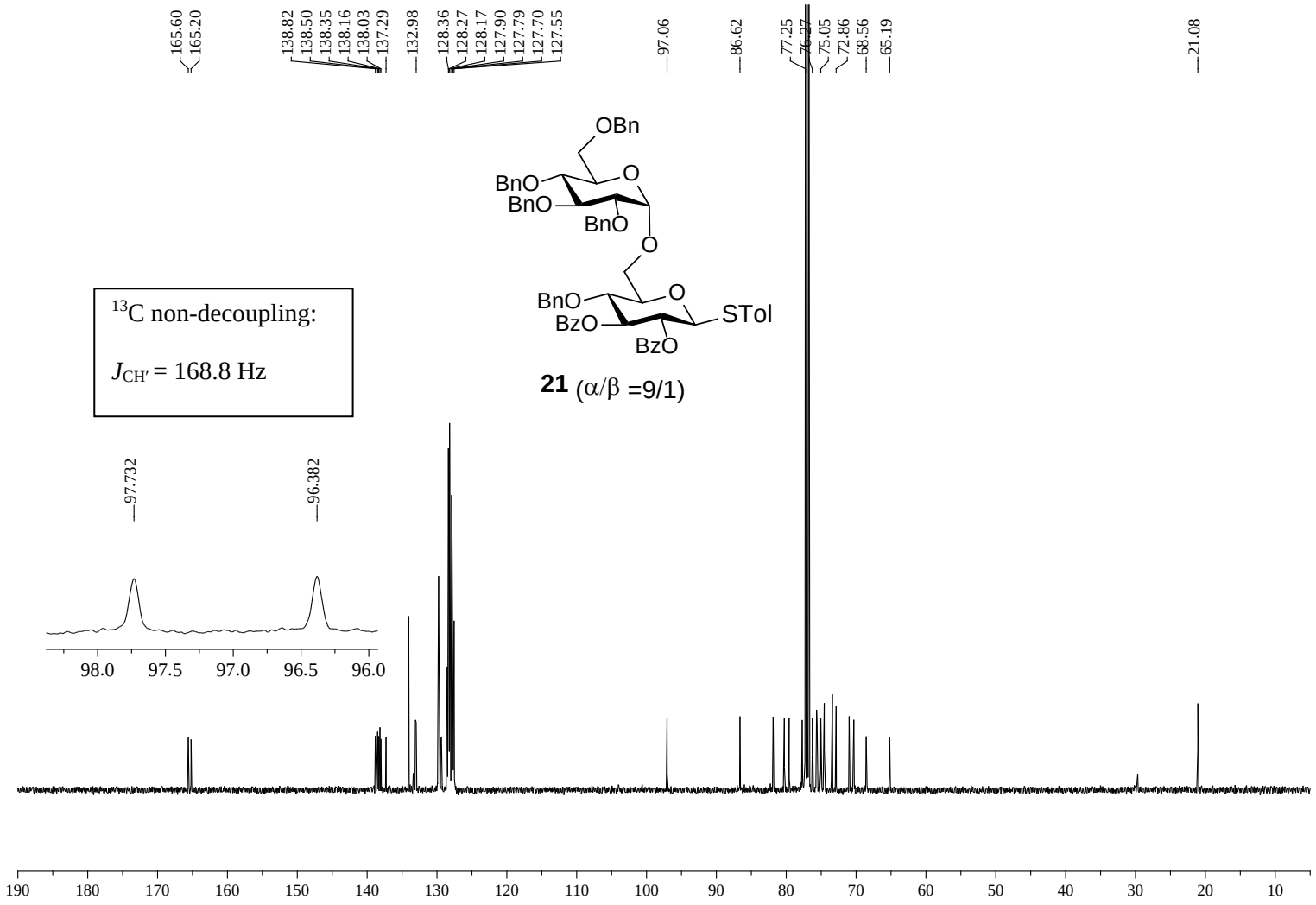
HSQC NMR of diosgeninyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (20)



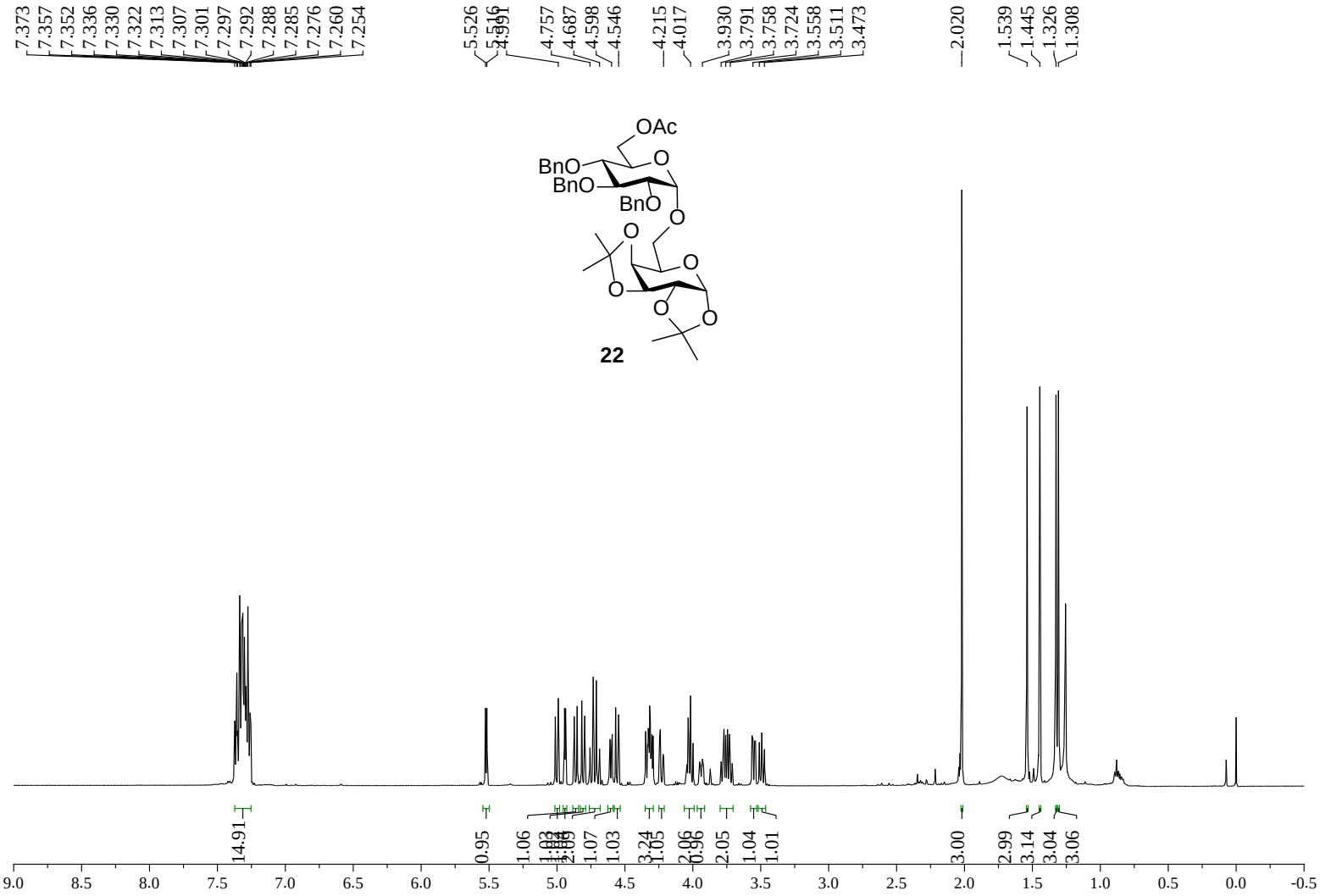
^{1}H NMR of *p*-tolyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzoyl-4-*O*-benzyl-1-thio-β-D-glucopyranoside (21)



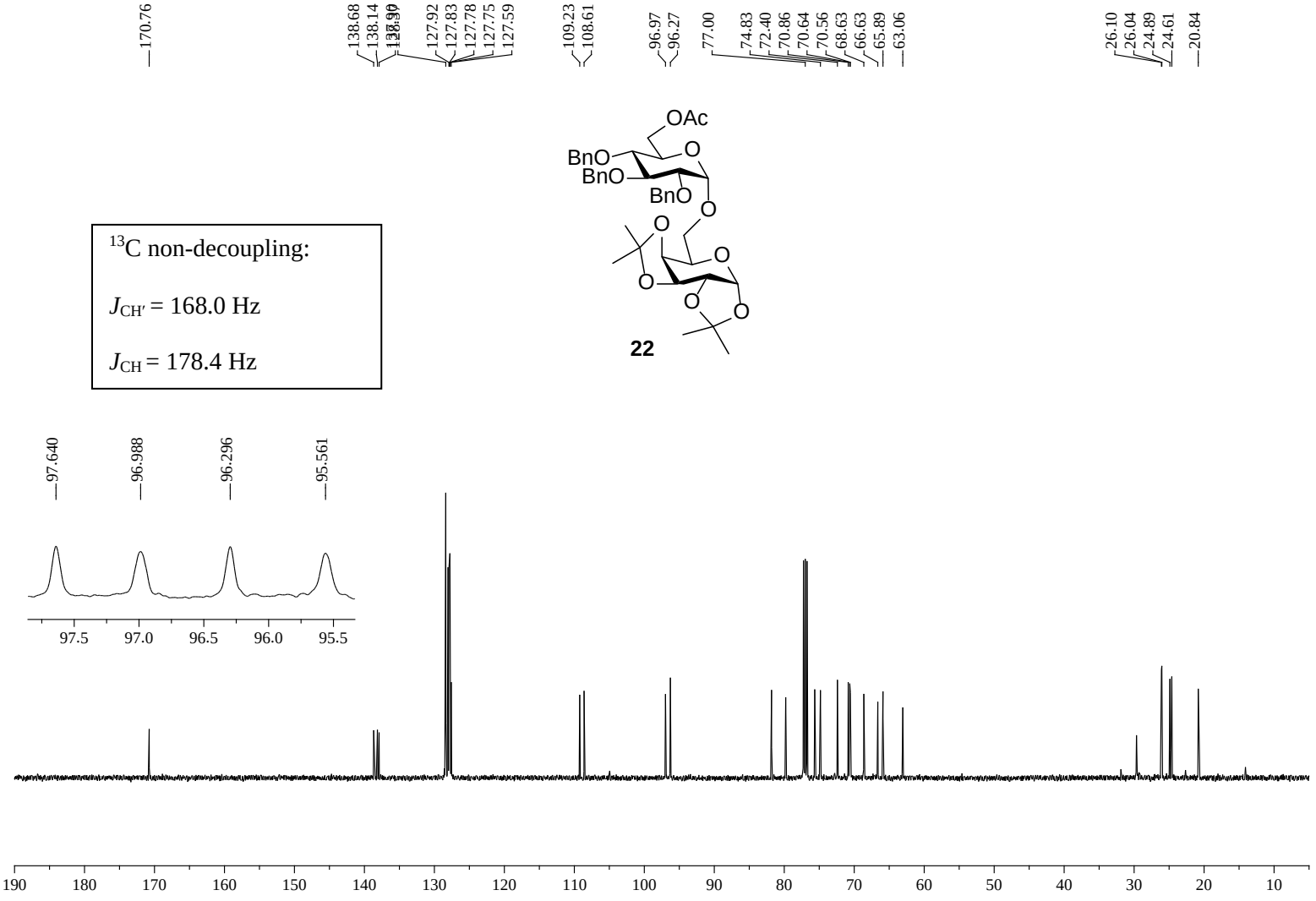
^{13}C NMR of *p*-tolyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzoyl-4-*O*-benzyl-1-thio-β-D-glucopyranoside (21)



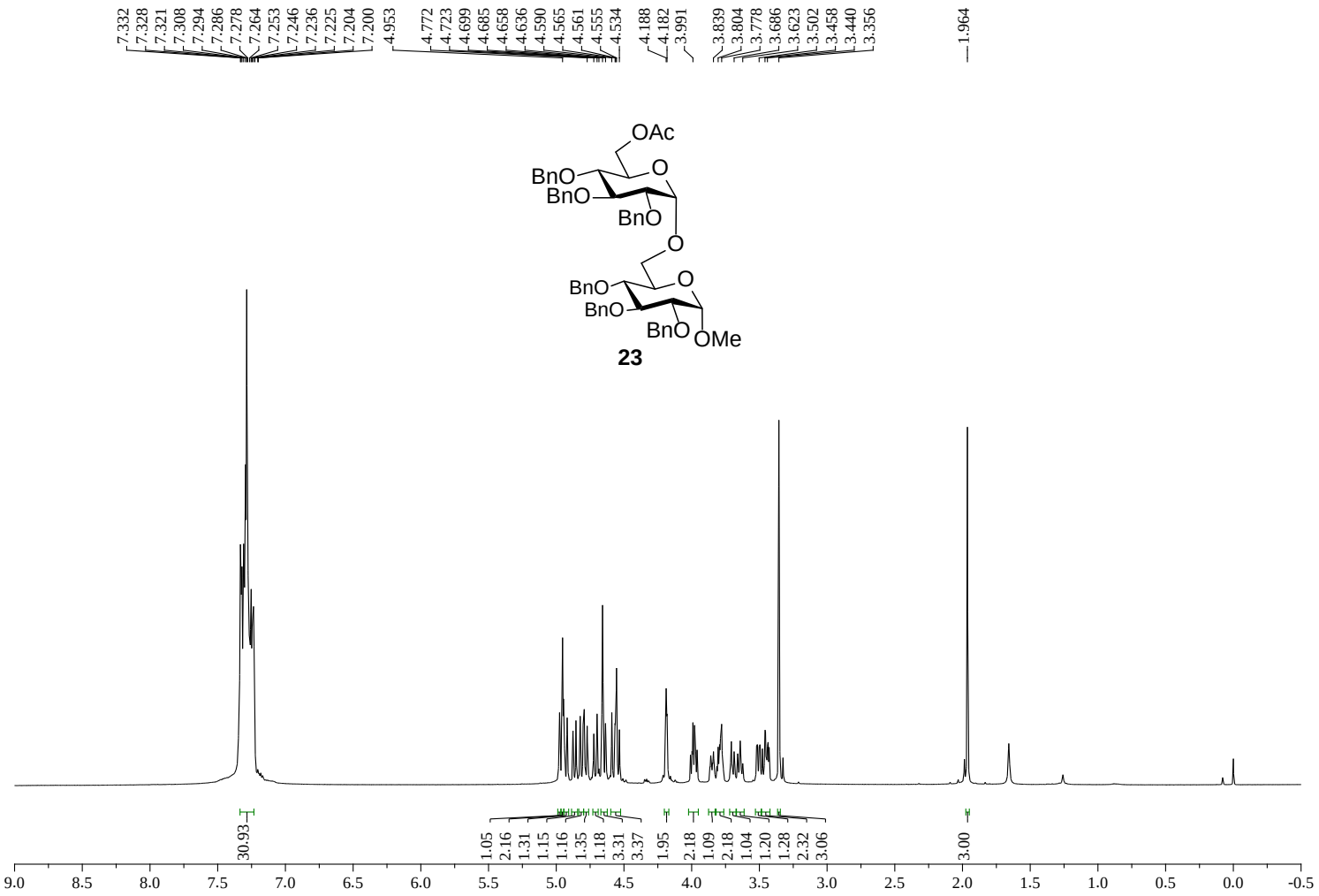
^{1}H NMR of 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (22)



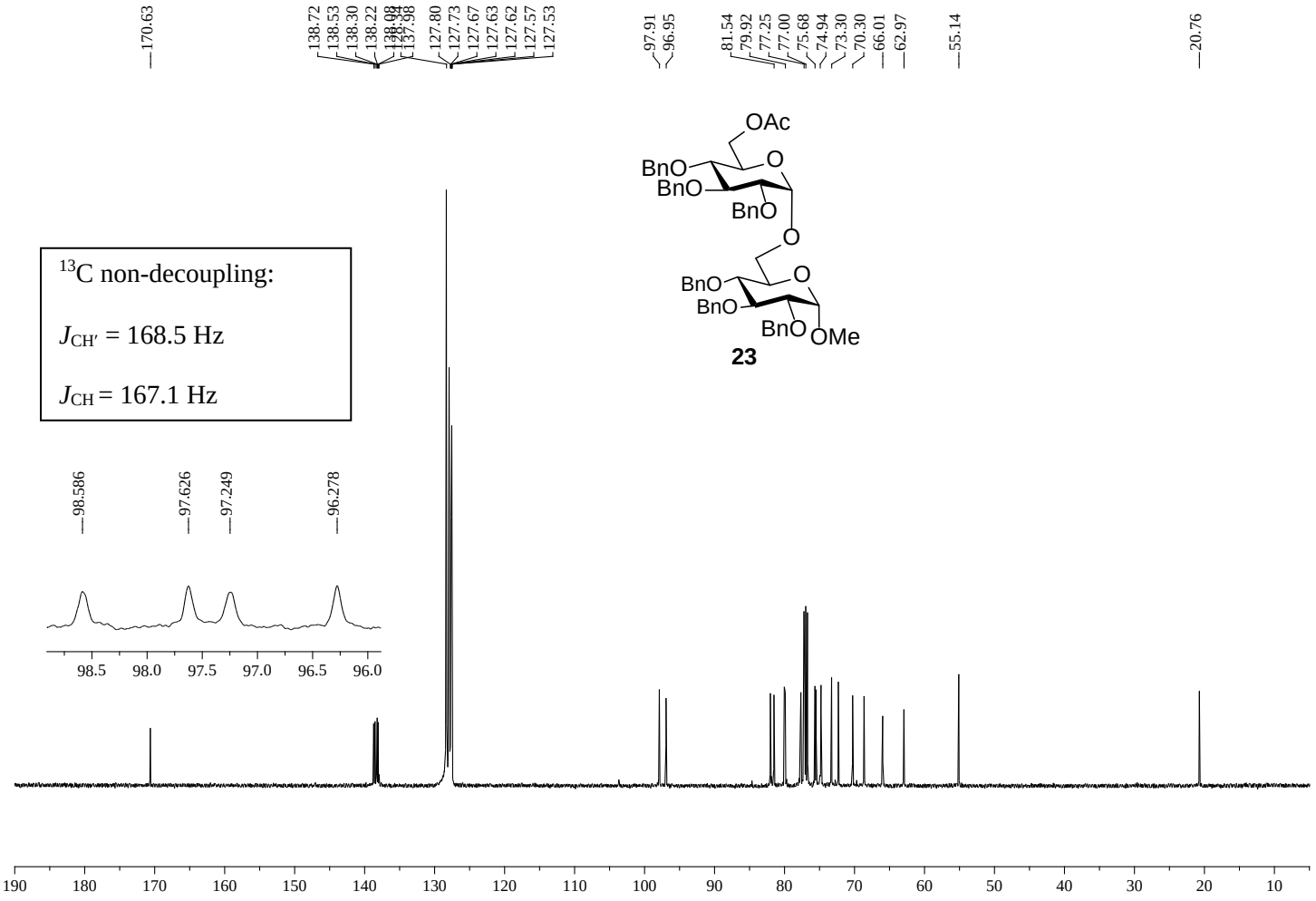
^{13}C NMR of 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-1,2:3,4-*O*-diisopropylidene-α-D-galactopyranose (22)



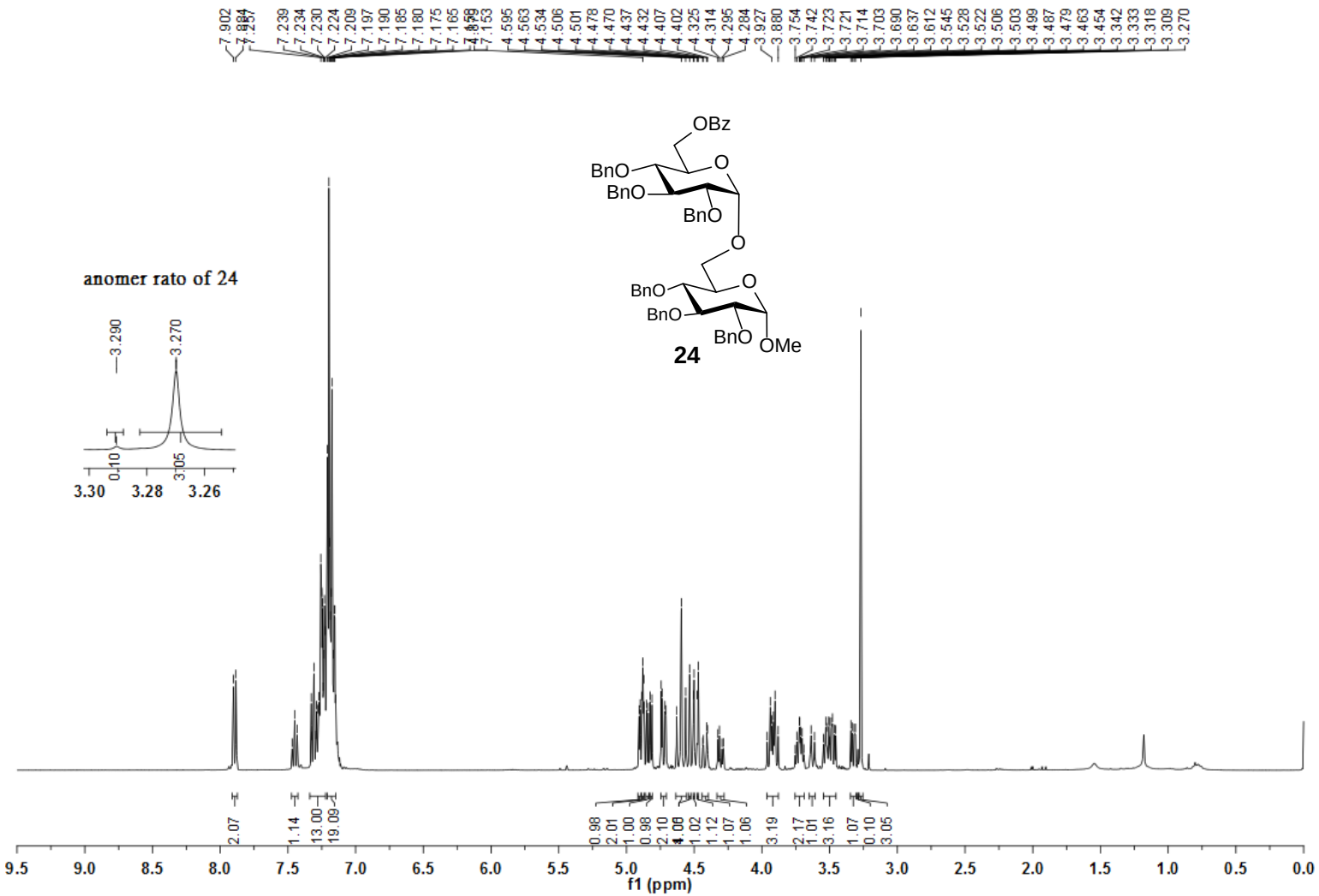
^{1}H NMR of methyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (23)



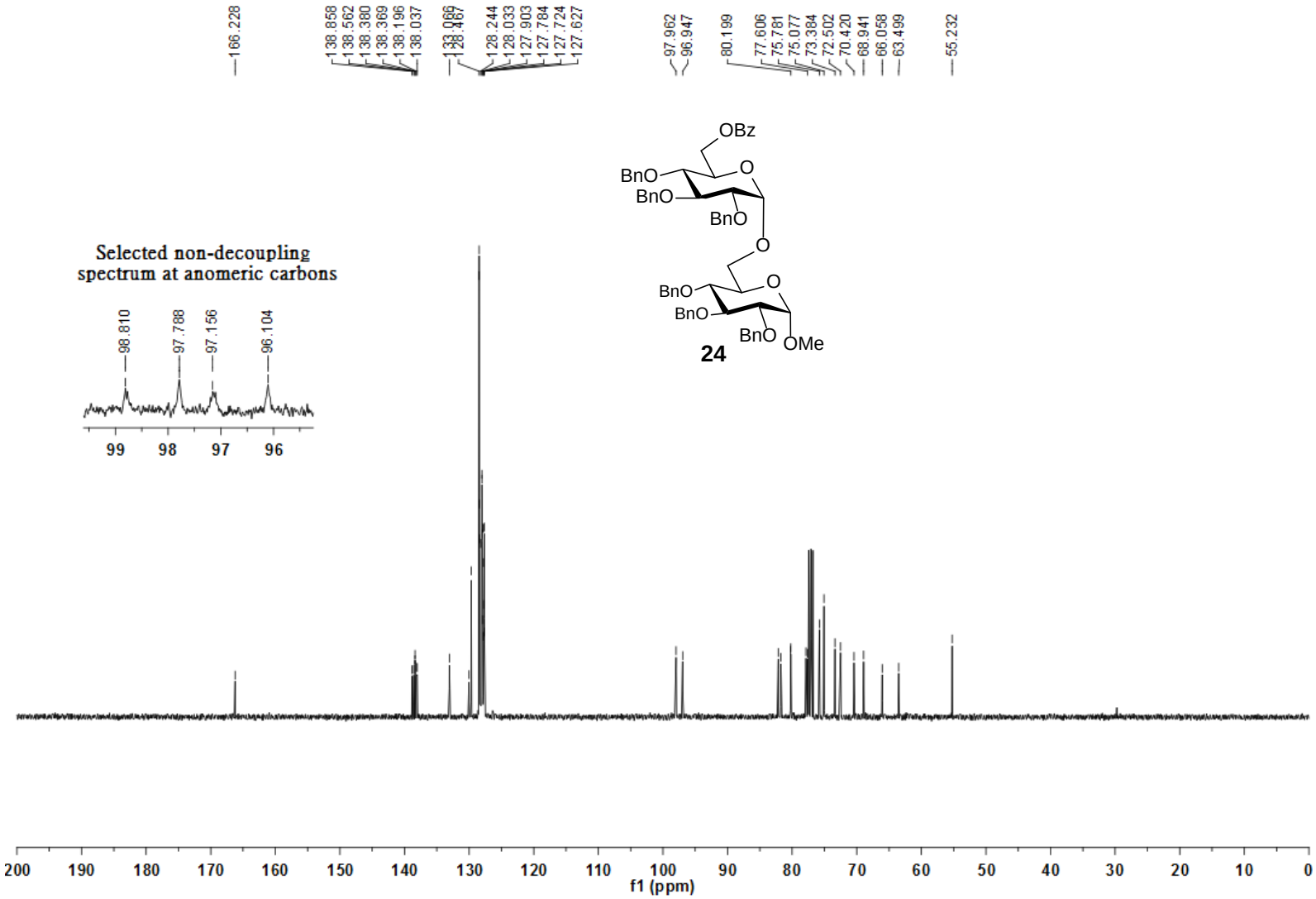
^{13}C NMR of methyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (23)



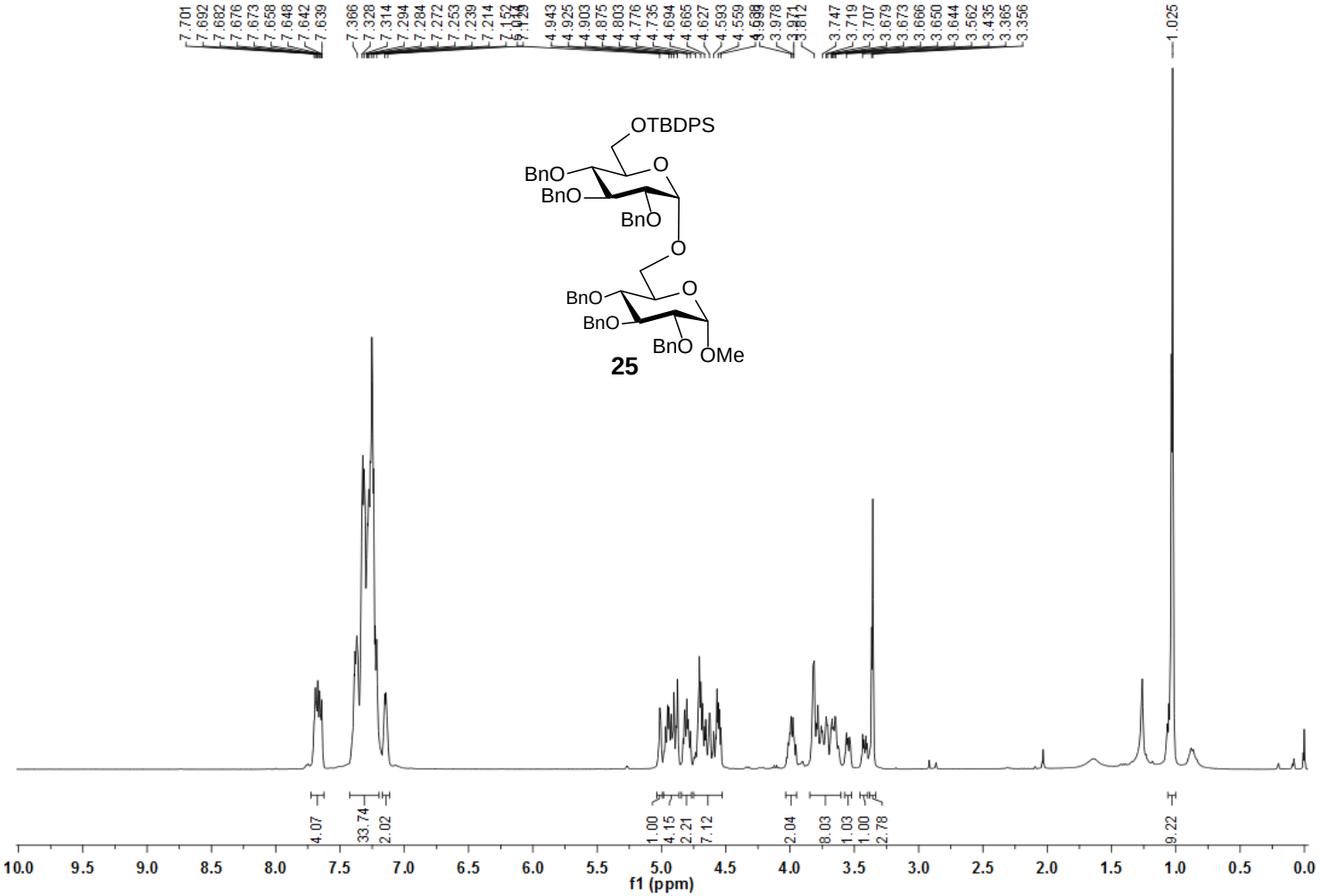
^{1}H NMR of methyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*- benzyl-α-D-glucopyranoside (24)



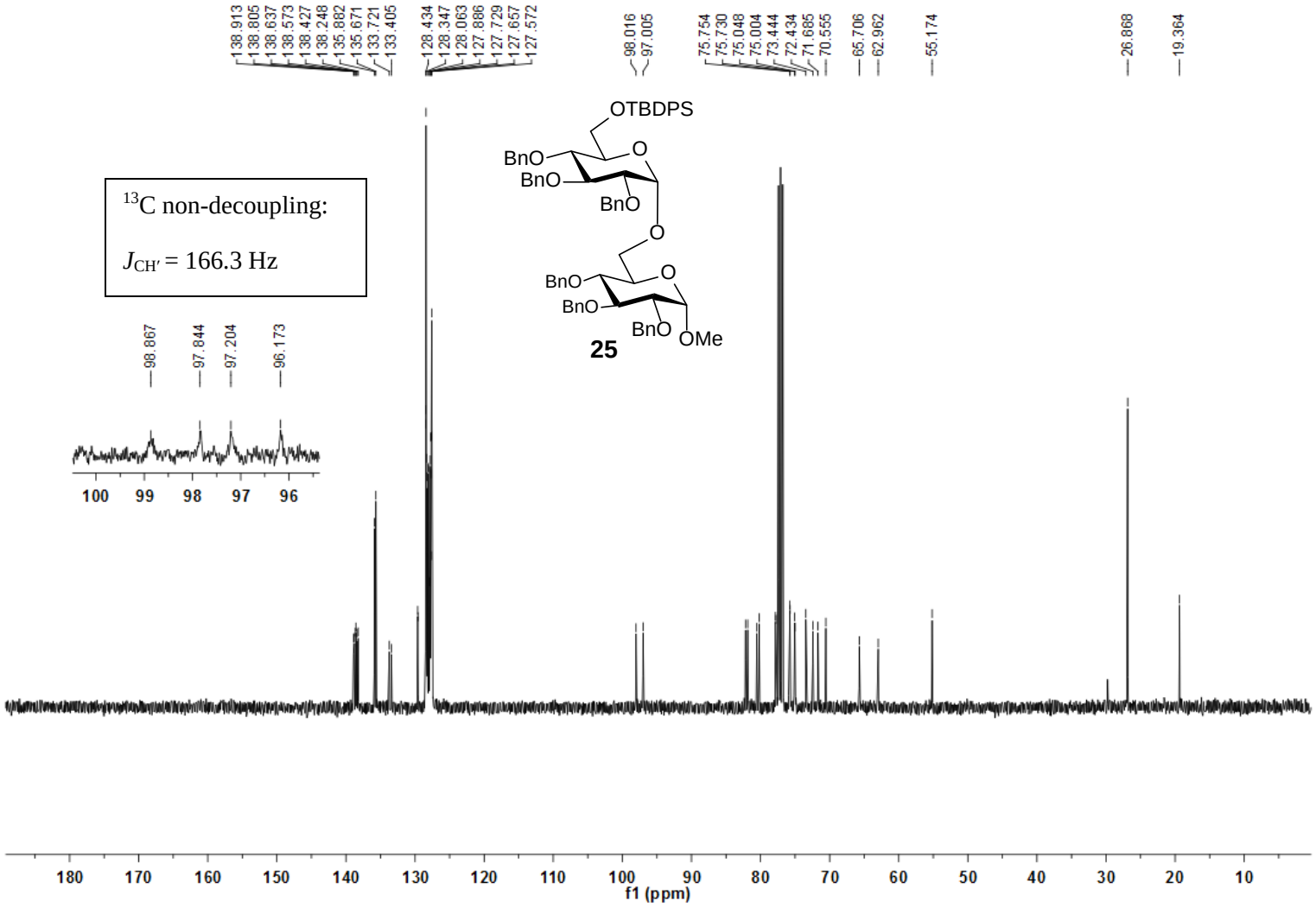
^{13}C NMR of methyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*- benzyl-α-D-glucopyranoside (24)



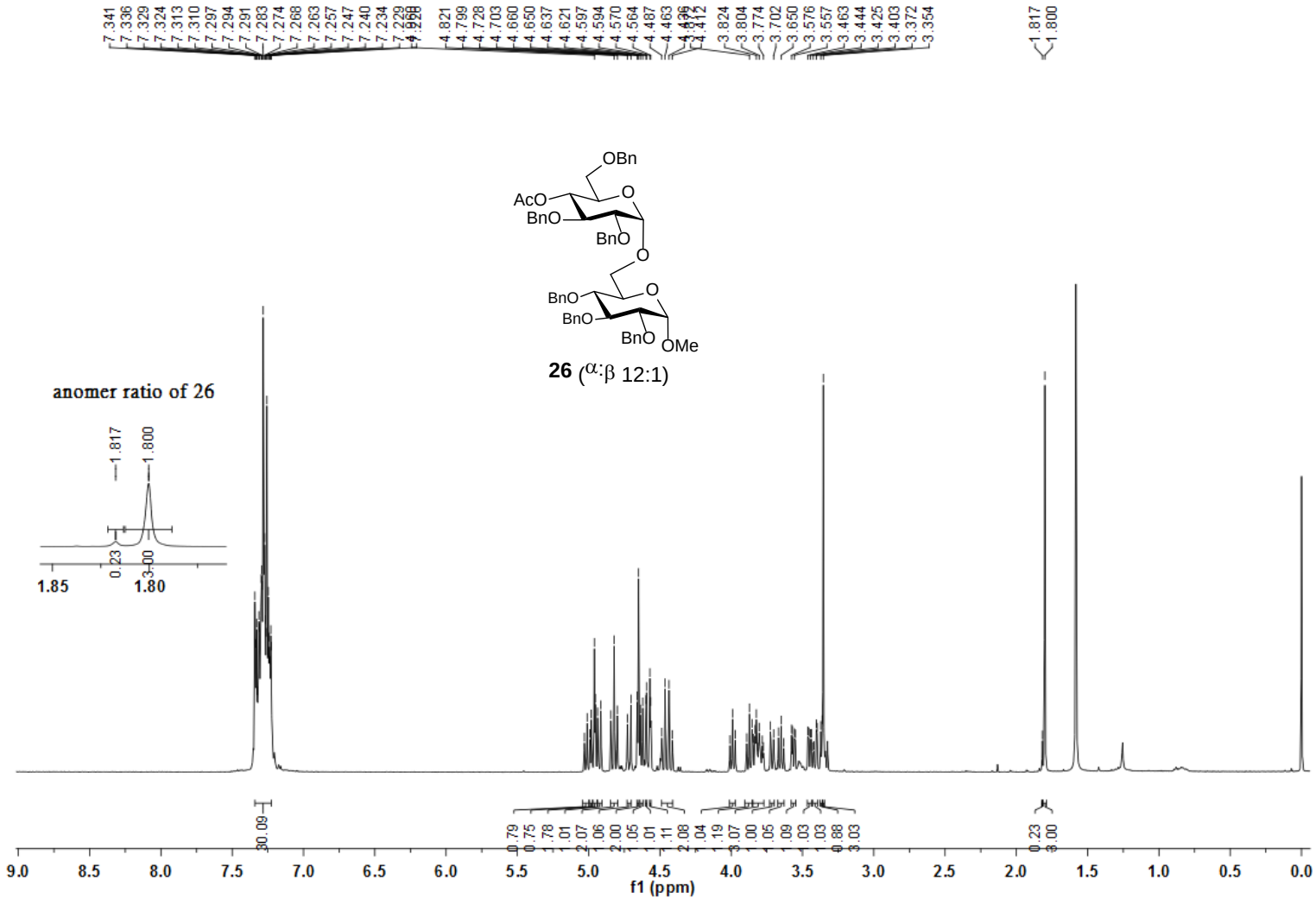
^{1}H NMR of methyl 2,3,4-tri-*O*-benzyl-6-*O*-(*tert*butyldiphenylsilyl)-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside 25



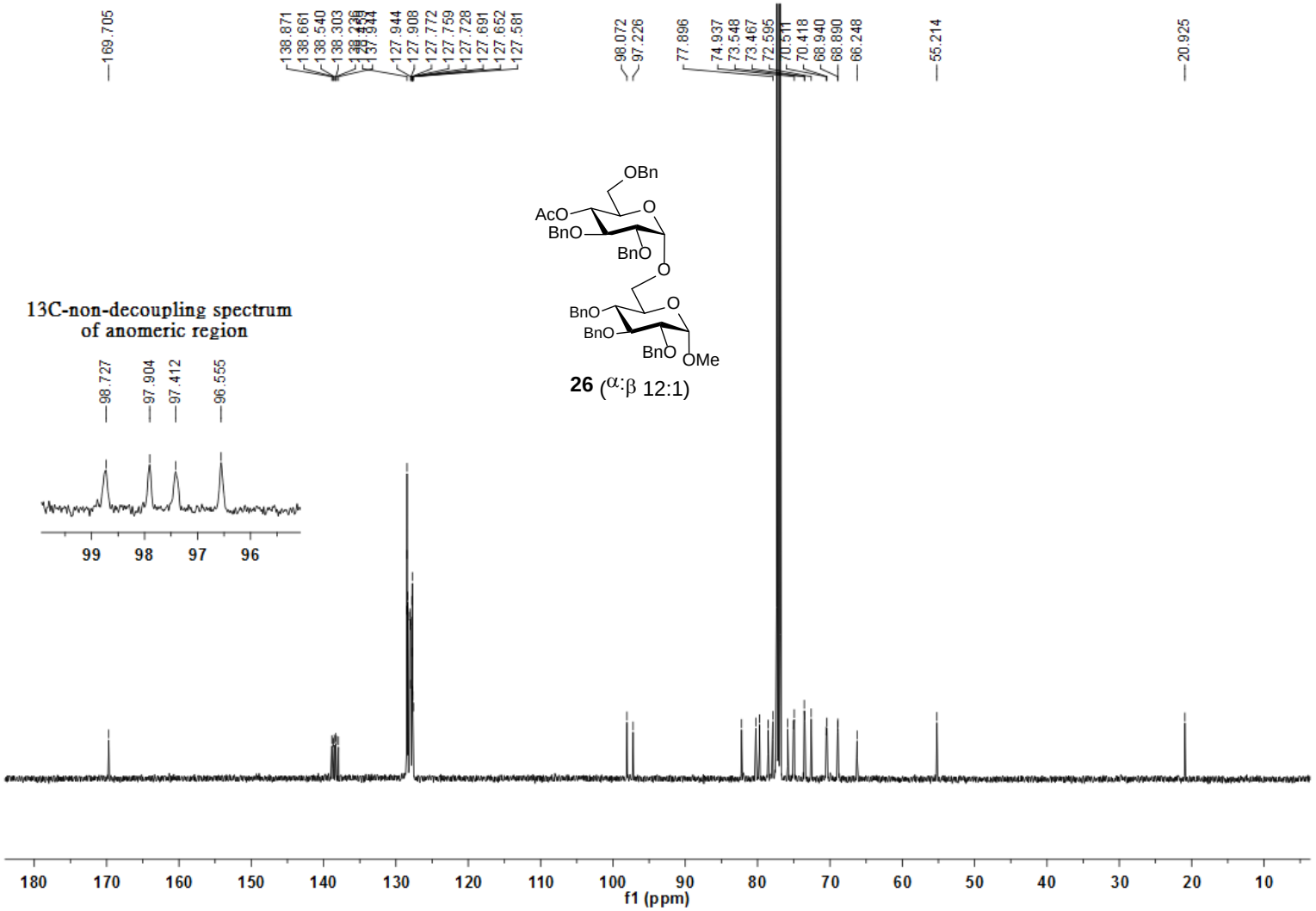
^{13}C NMR of methyl 2,3,4-tri-*O*-benzyl-6-*O*-(*tert*butyldiphenylsilyl)-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside 25



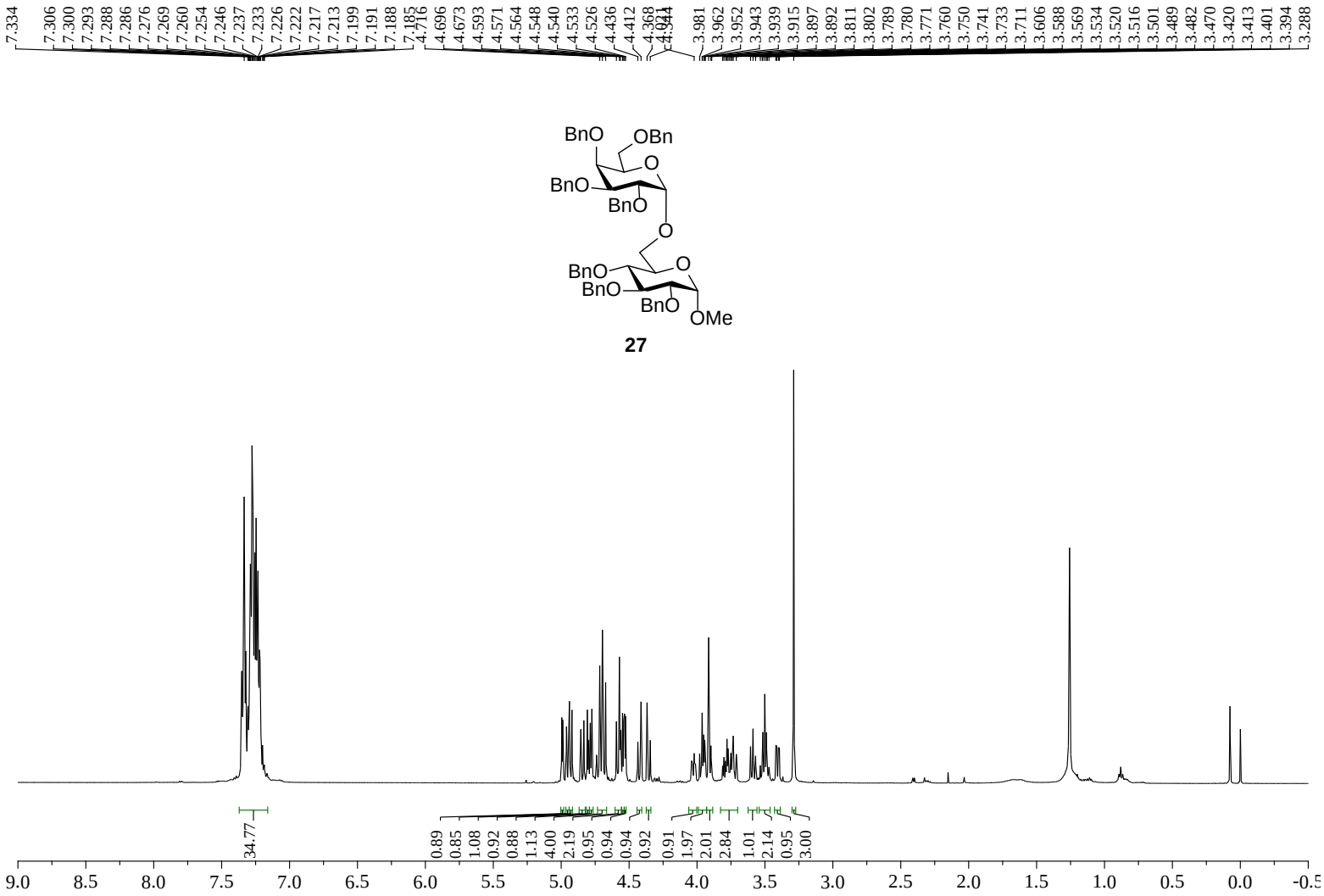
^{1}H NMR of methyl 4-*O*-acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*- benzyl-α-D-glucopyranoside 26



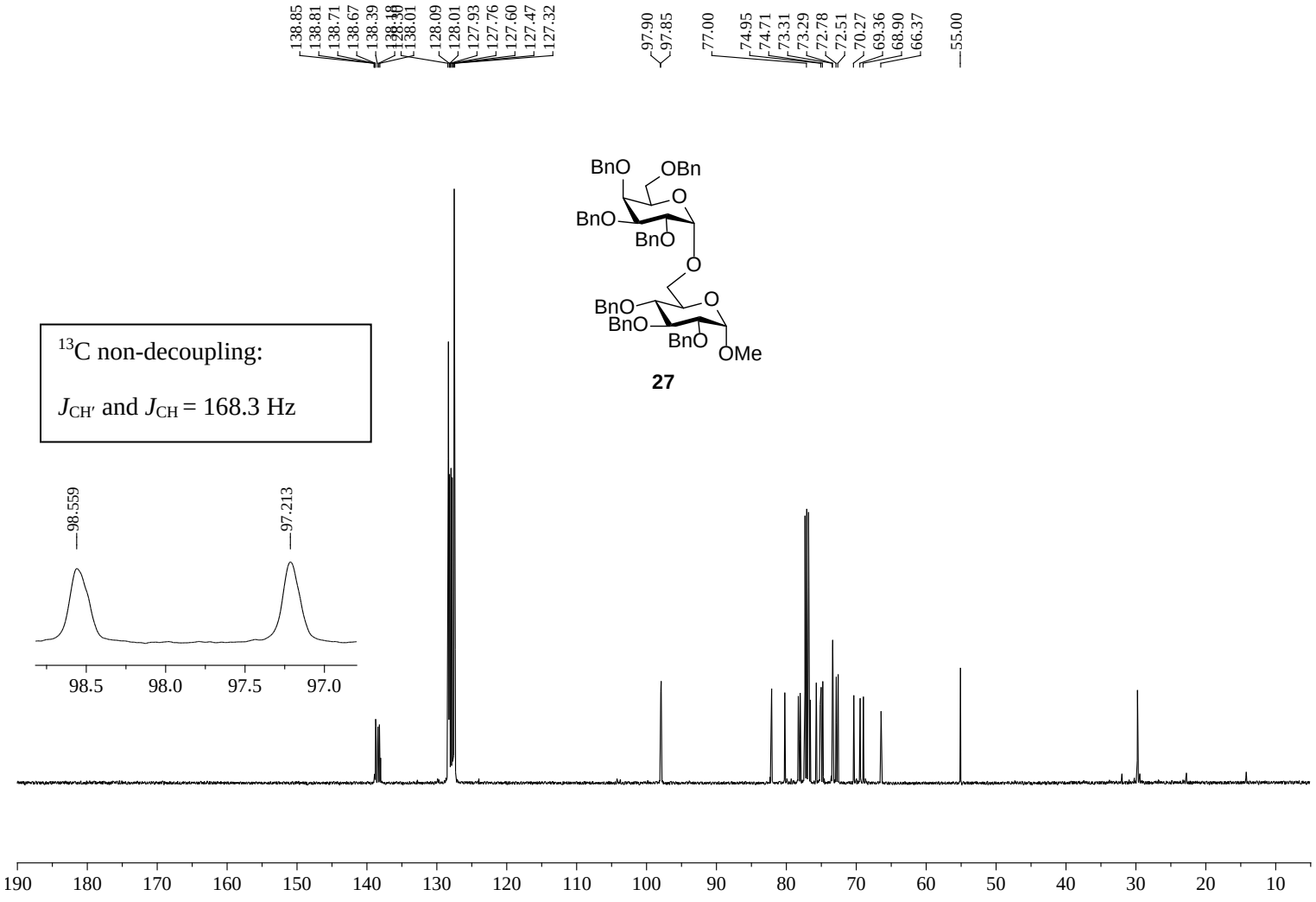
^{13}C NMR of methyl 4-*O*-acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside 26



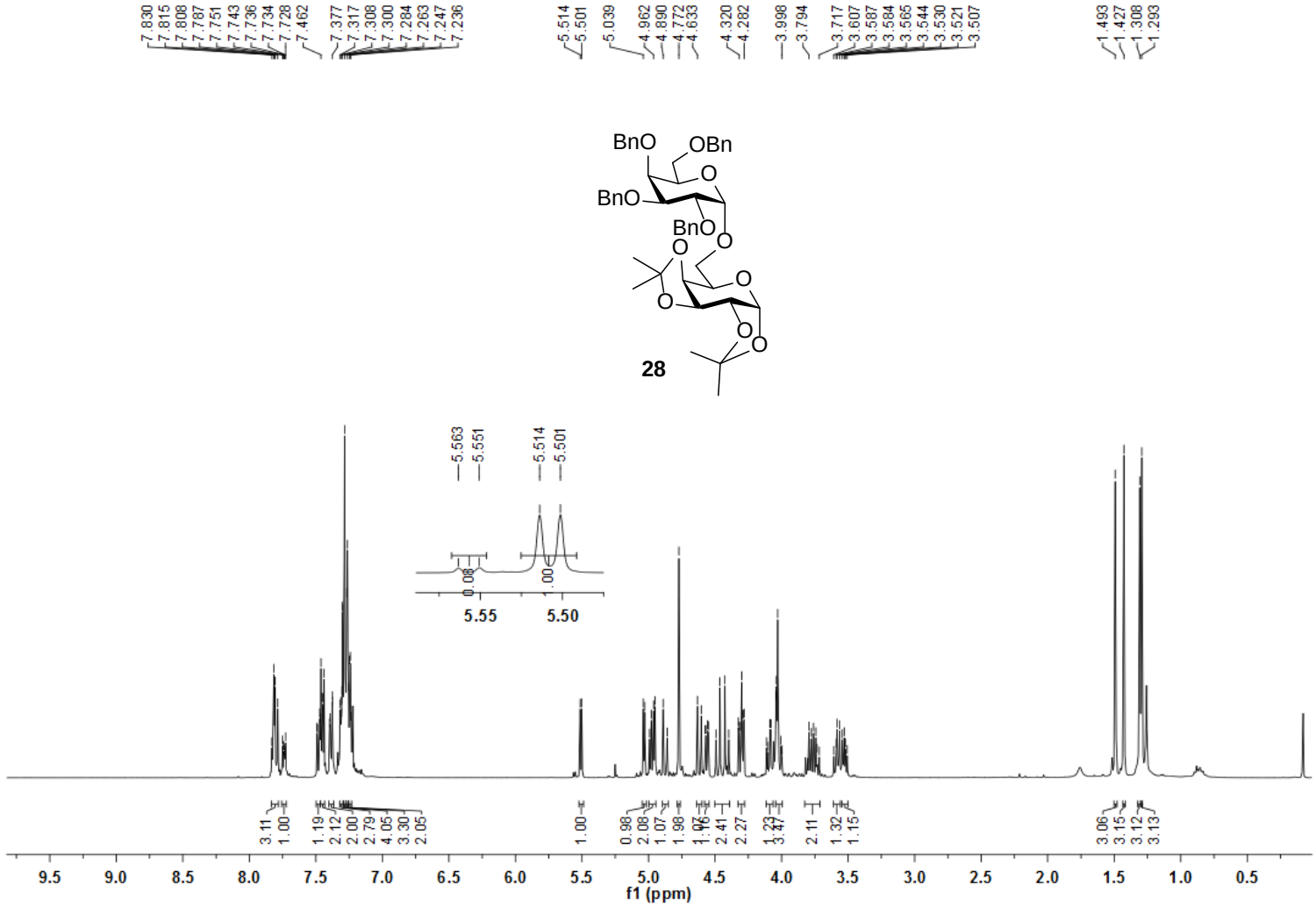
^{1}H NMR of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→6)-2,3,4- tri-*O*-benzyl-α-D-glucopyranoside (27)



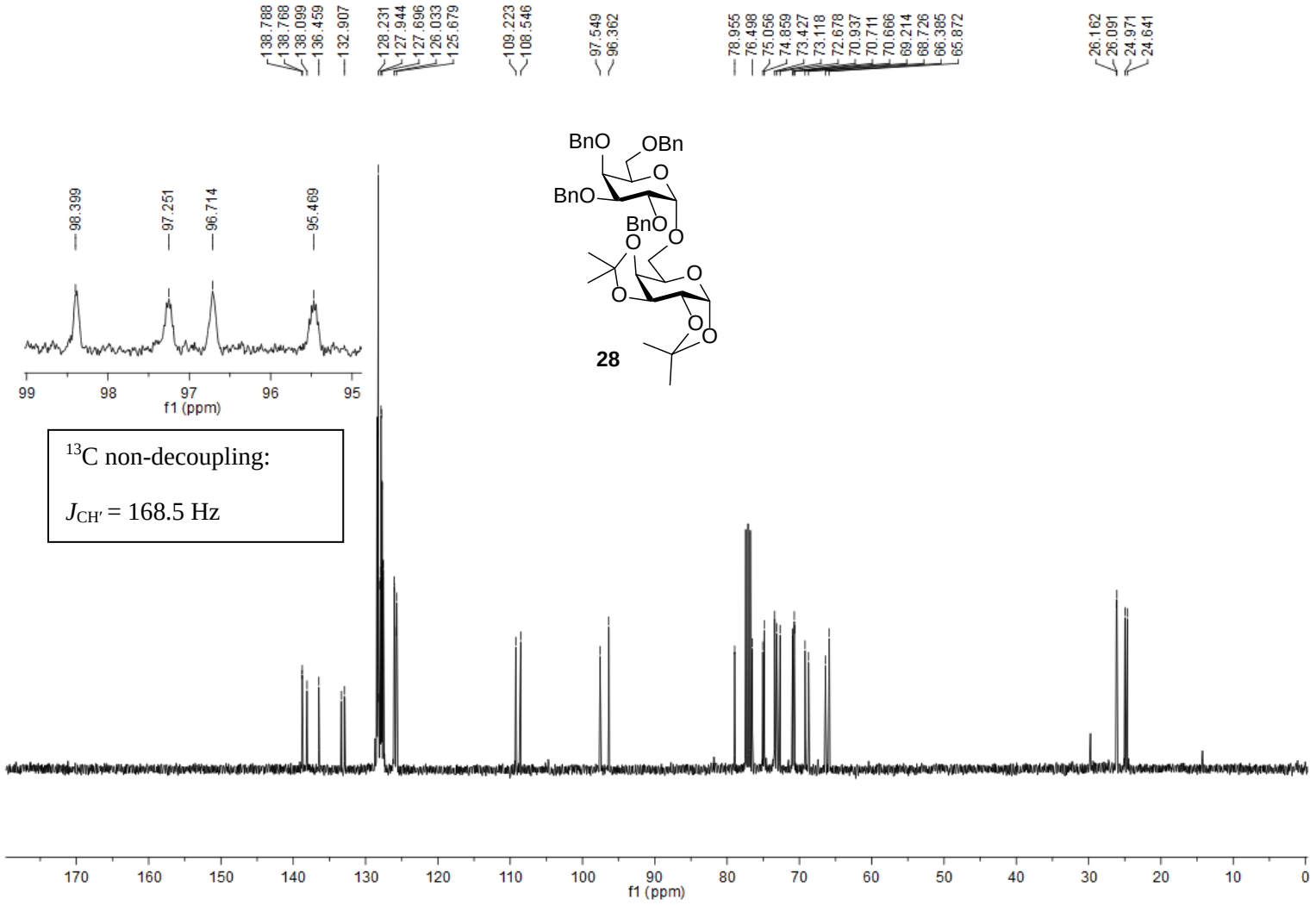
^{13}C NMR of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (27)



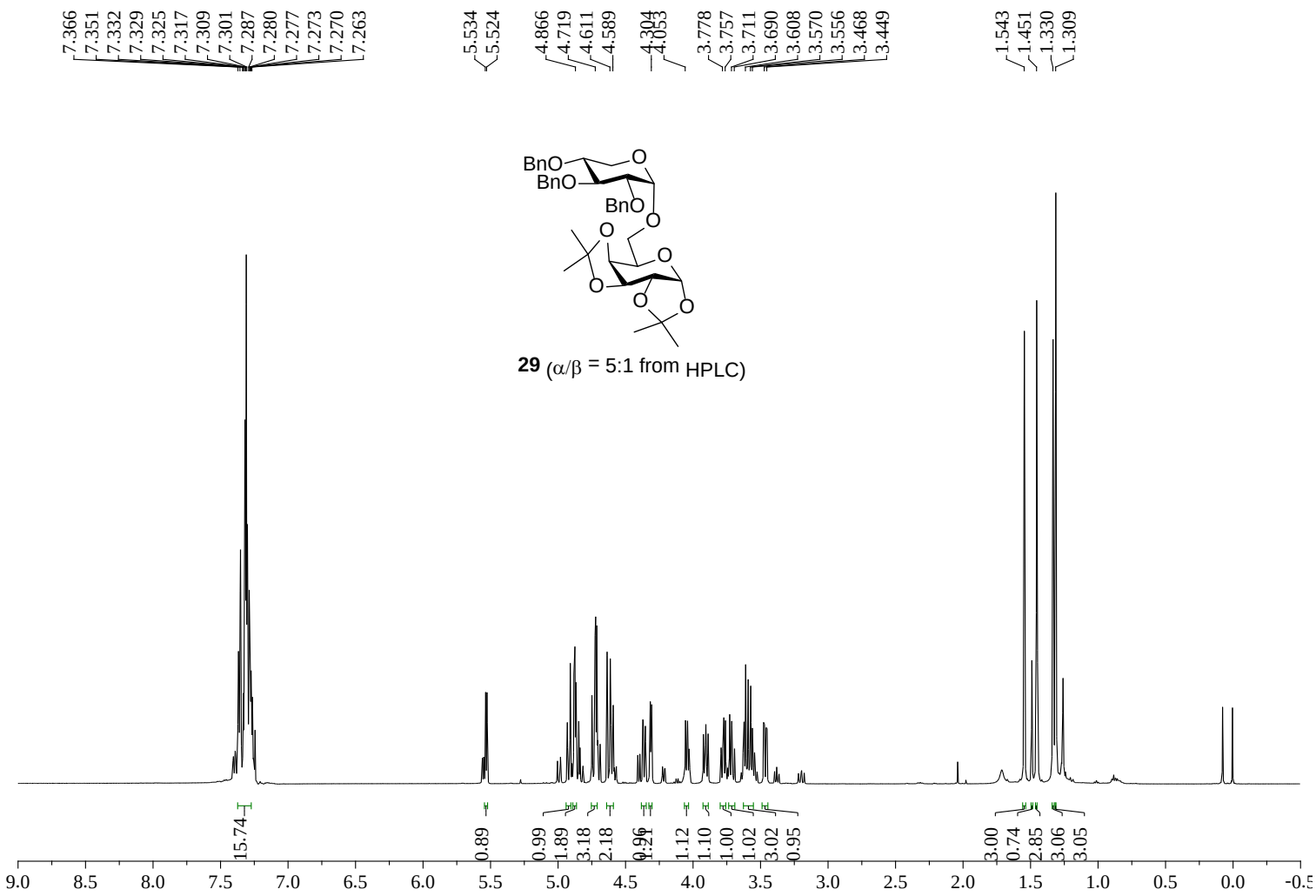
^{1}H NMR of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (28)



^{13}C NMR of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→6)-1,2:3,4- di-*O*-isopropylidene-α-D-galactopyranose (28)

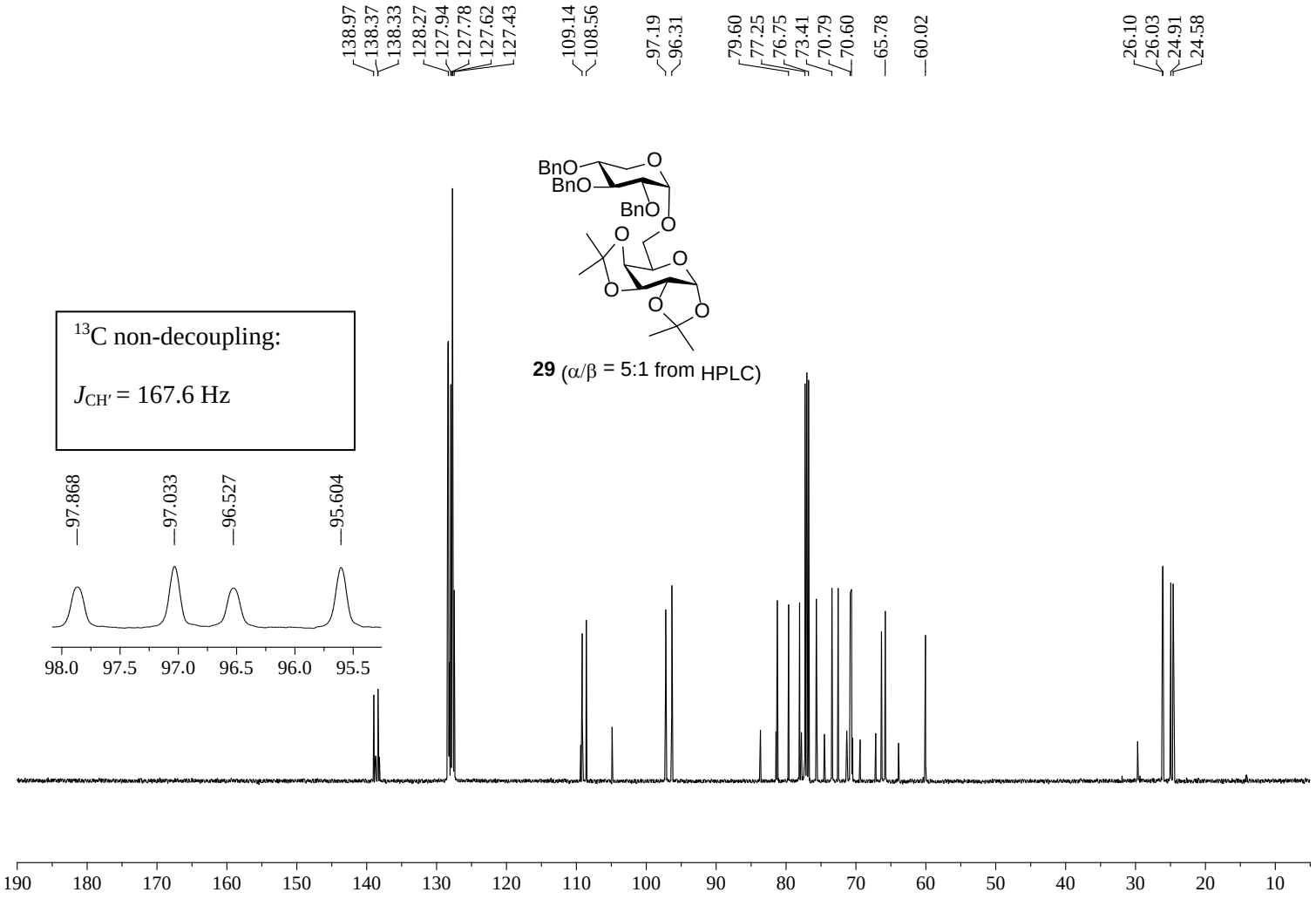


^{1}H NMR of 2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl-(1→6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranoside (29)

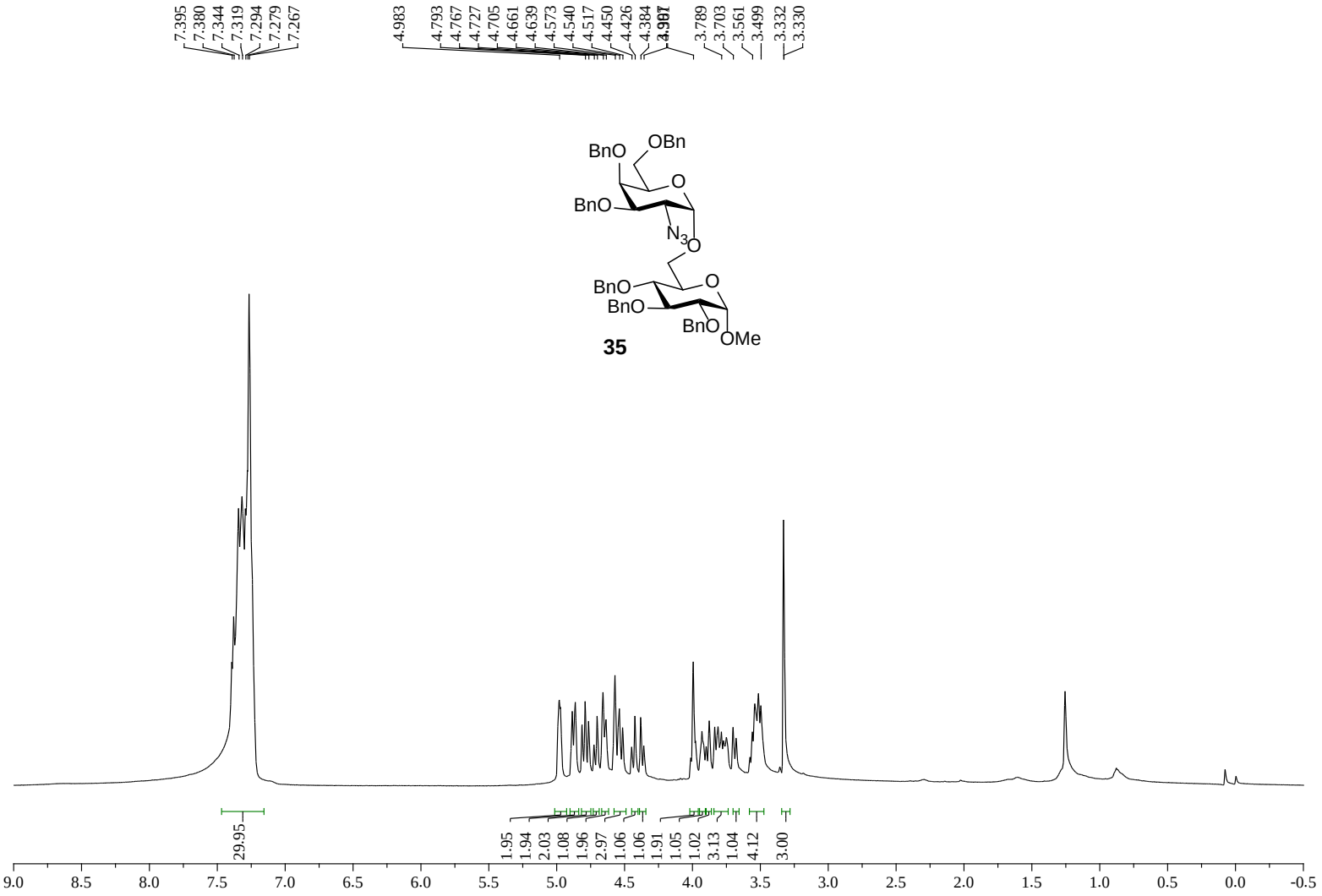


29 (α/β = 5:1 from HPLC)

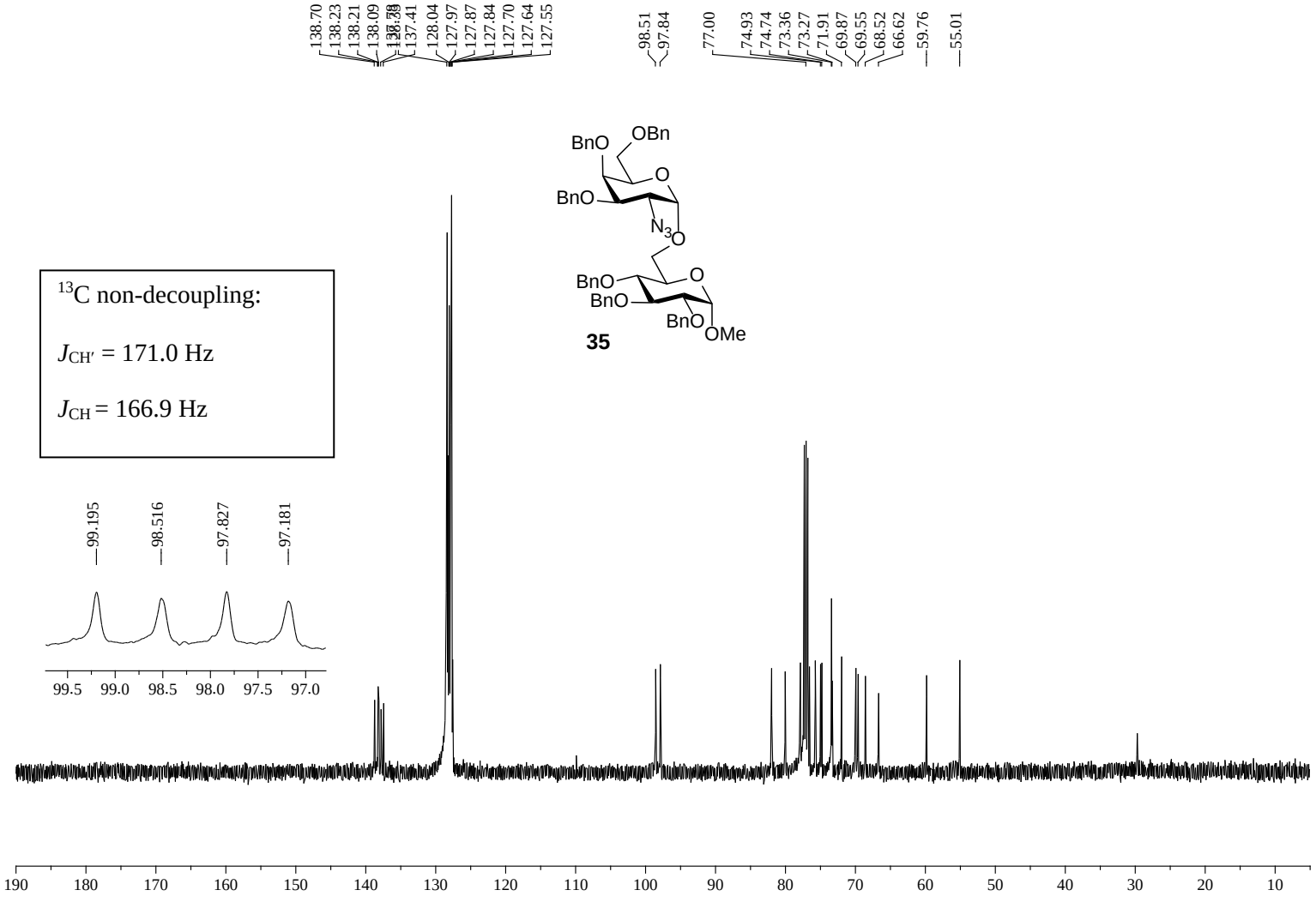
^{13}C NMR of 2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl-(1→6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranoside (29)



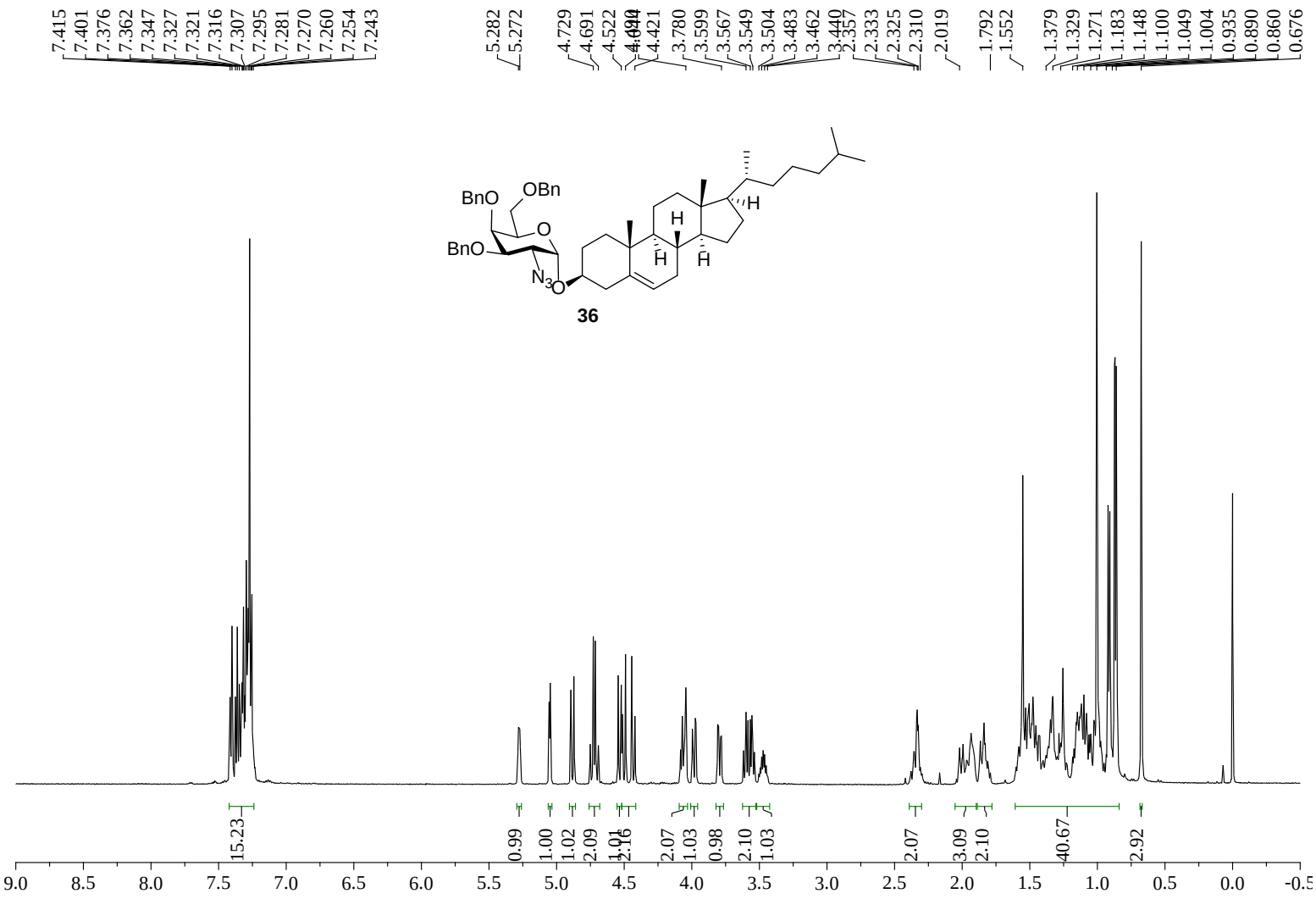
^{1}H NMR of methyl 6-*O*-2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (35)



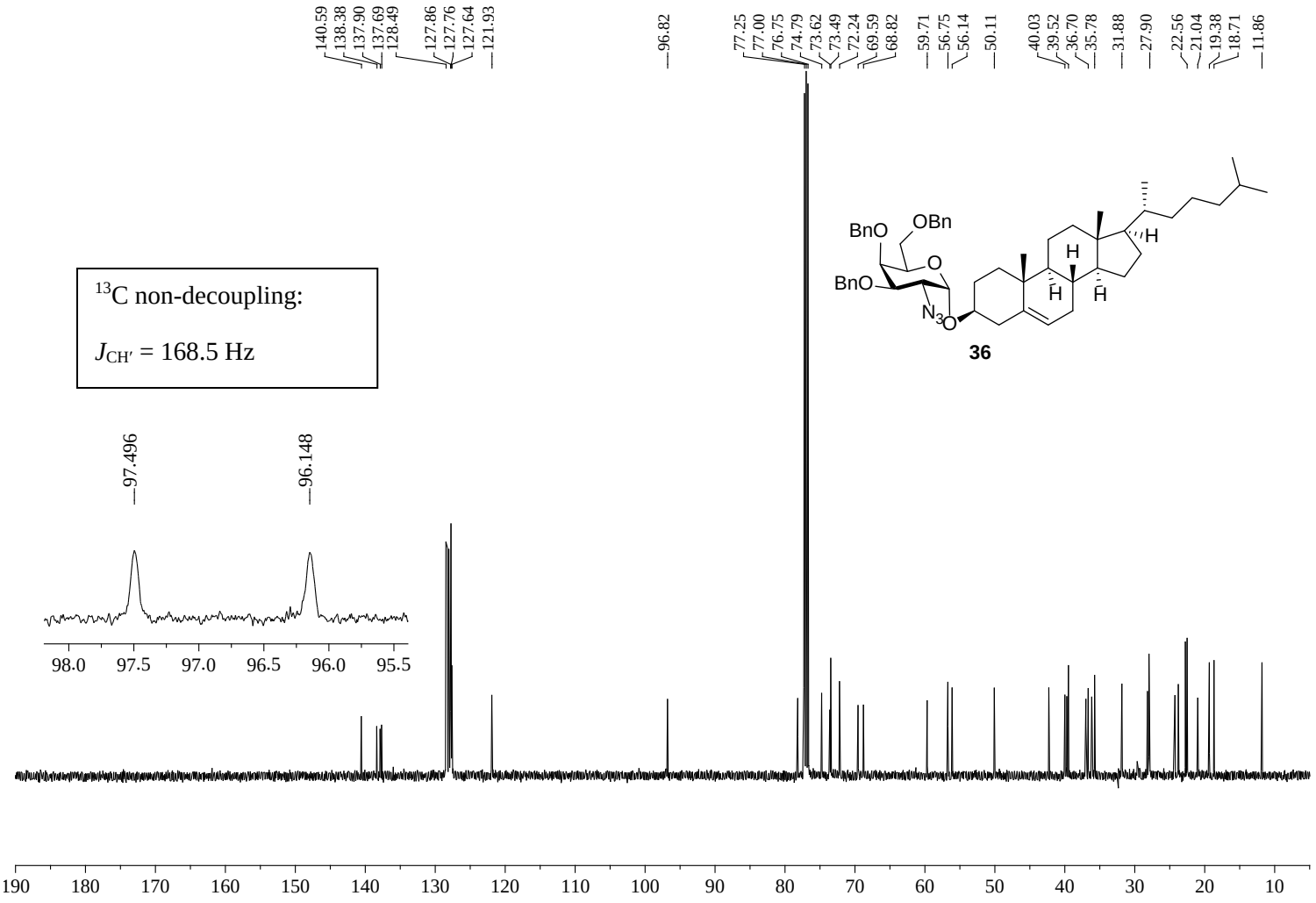
^{13}C NMR of methyl 6-*O*-2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (35)



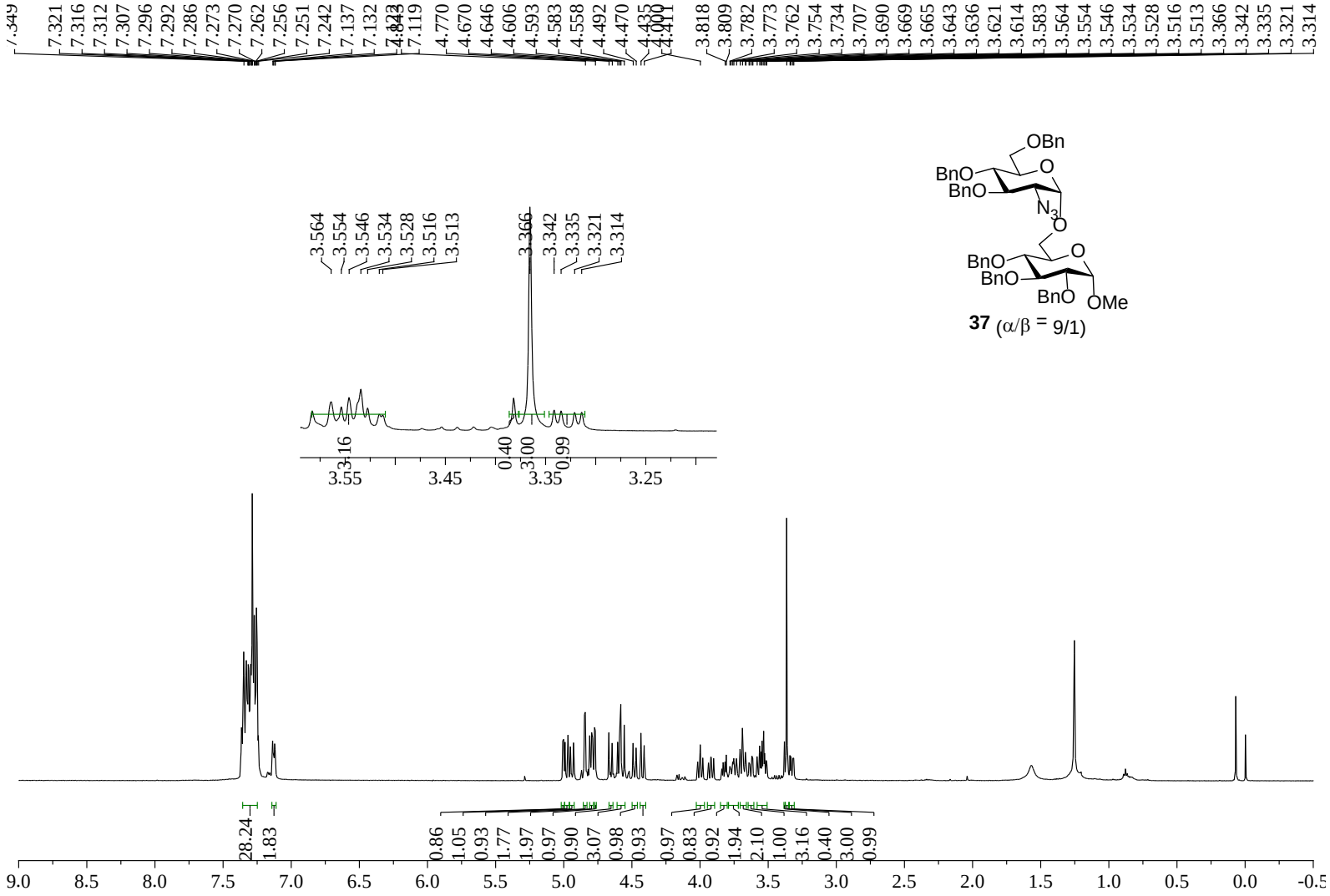
^{1}H NMR of cholesteryl-2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranoside (36)



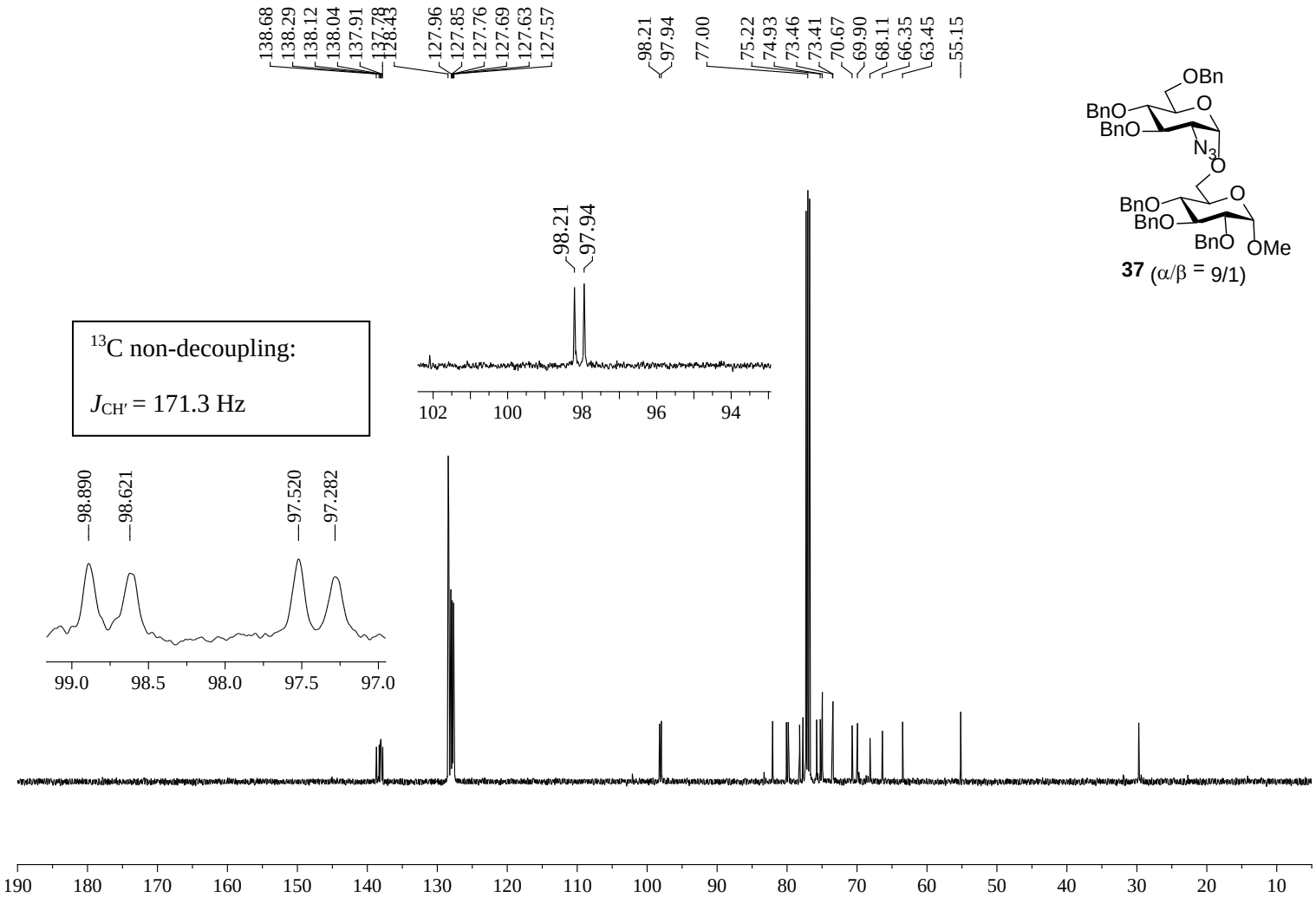
^{13}C NMR of cholesteryl-2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranoside (36)



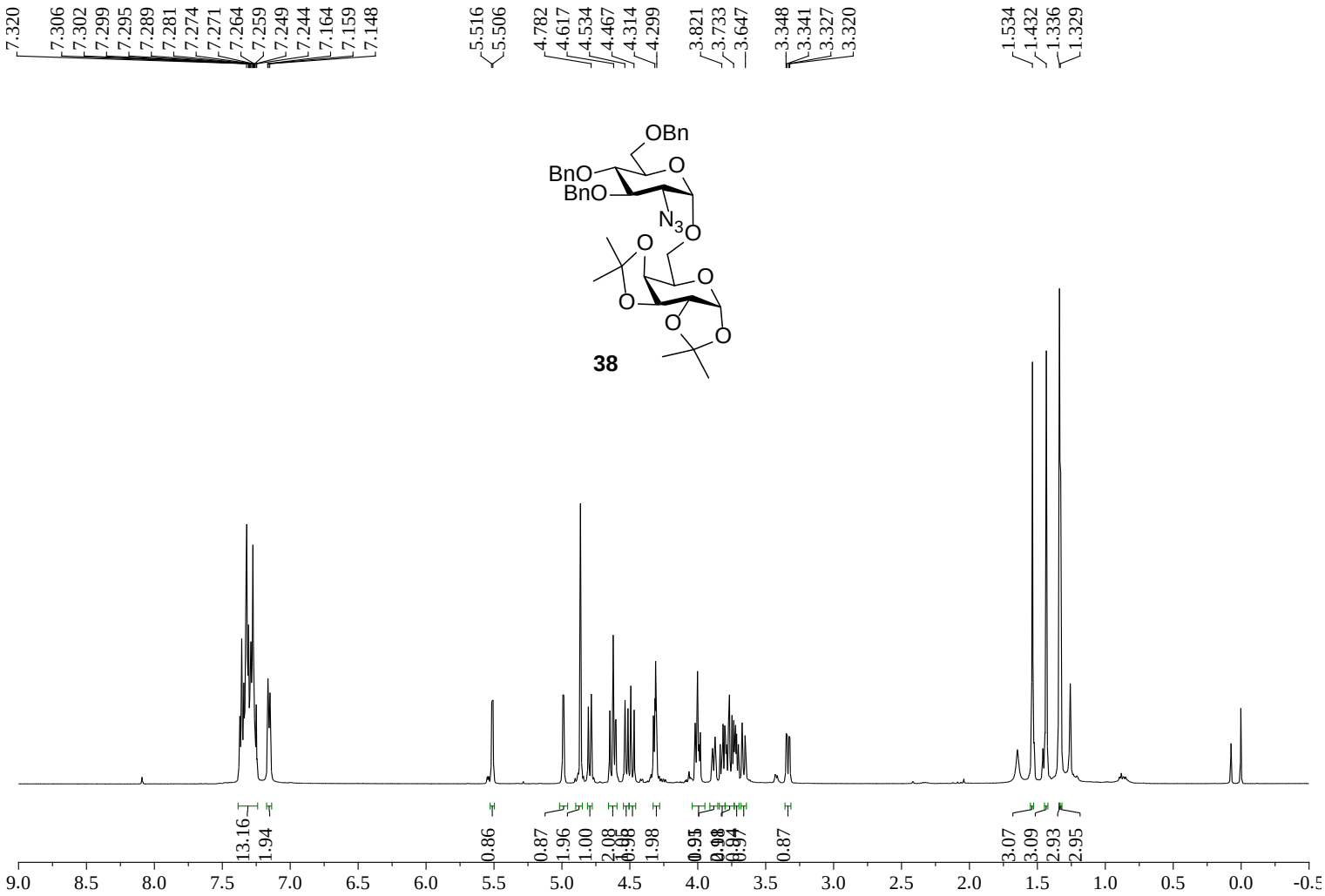
^{1}H NMR of methyl 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (37)



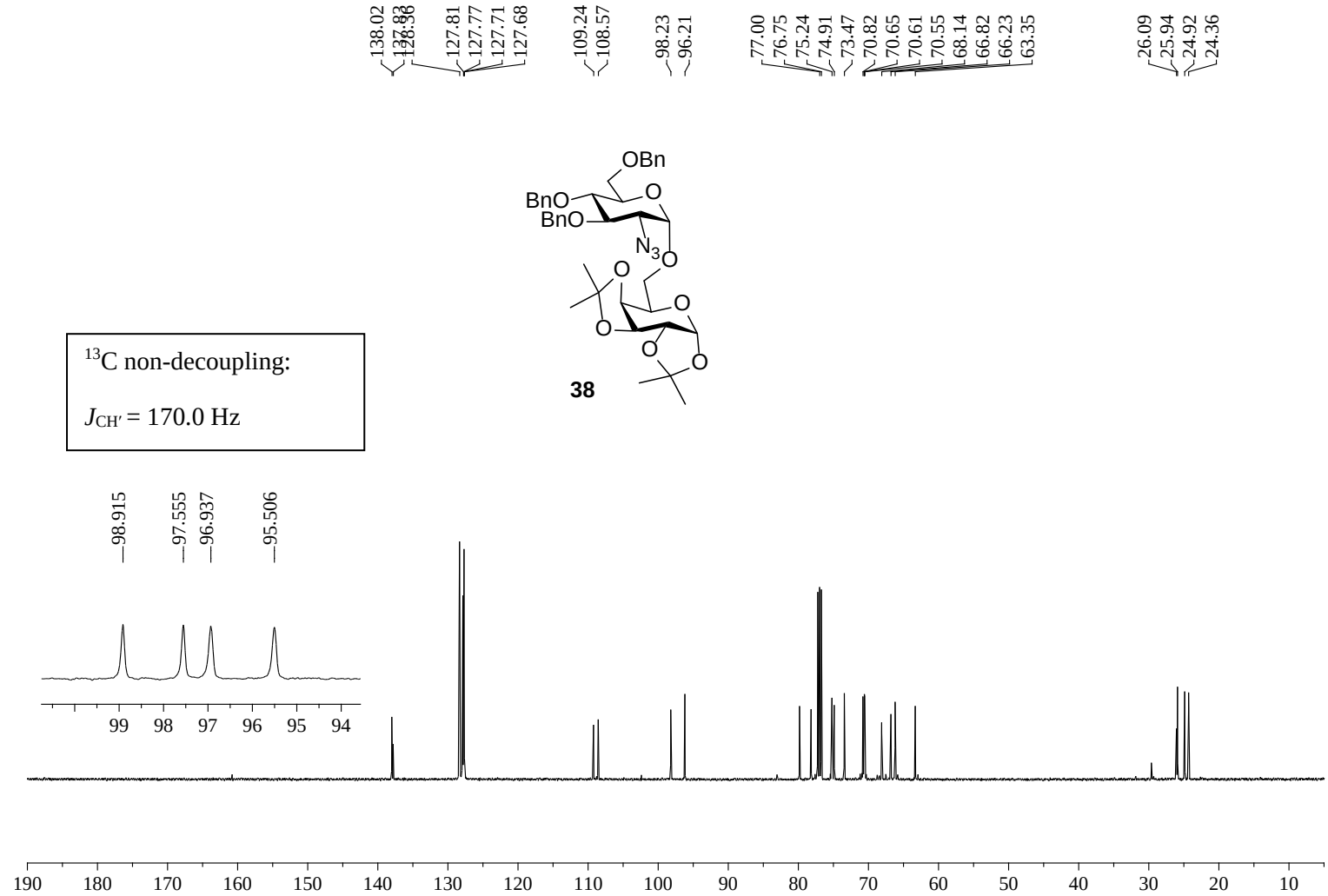
^{13}C NMR of methyl 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (37)



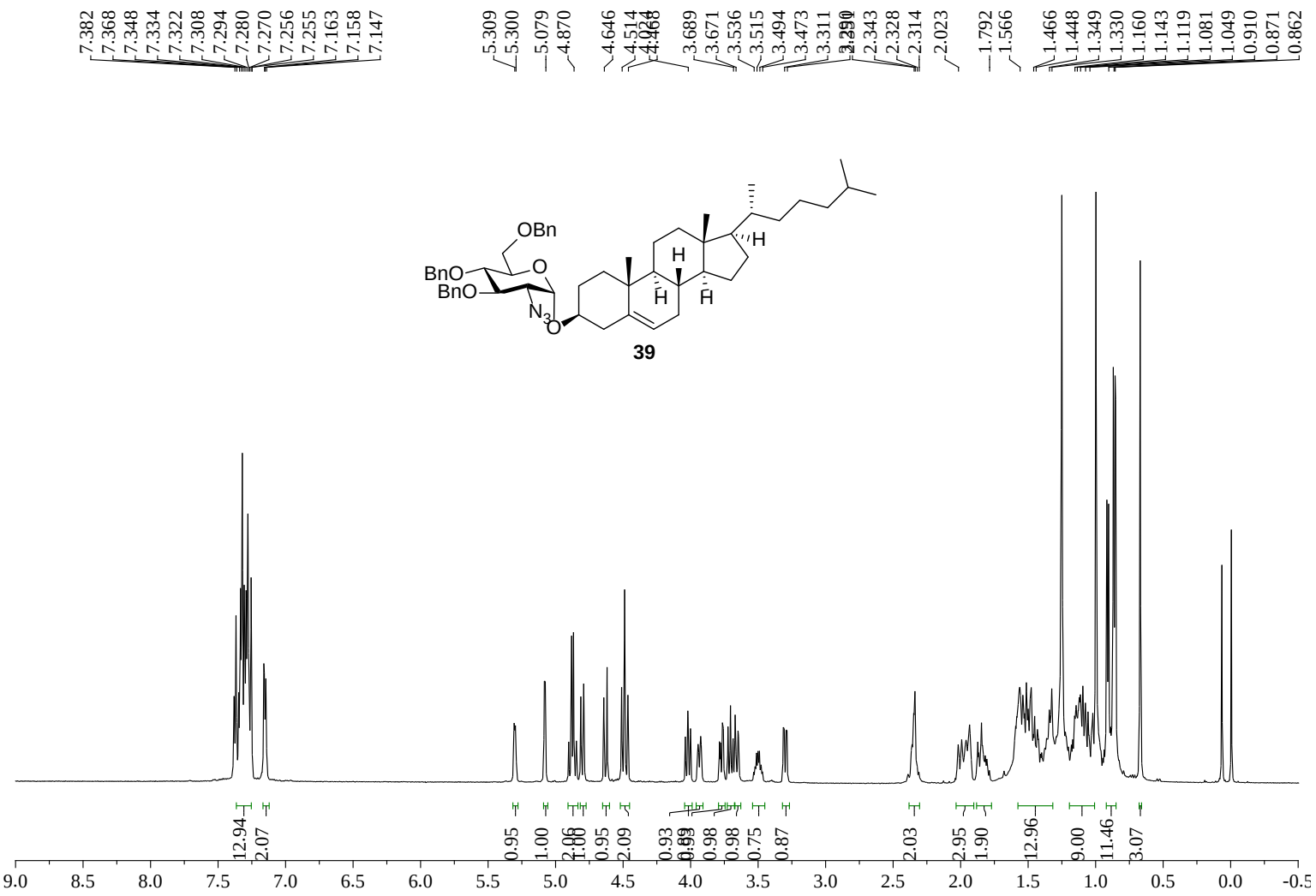
^{1}H NMR of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (38)



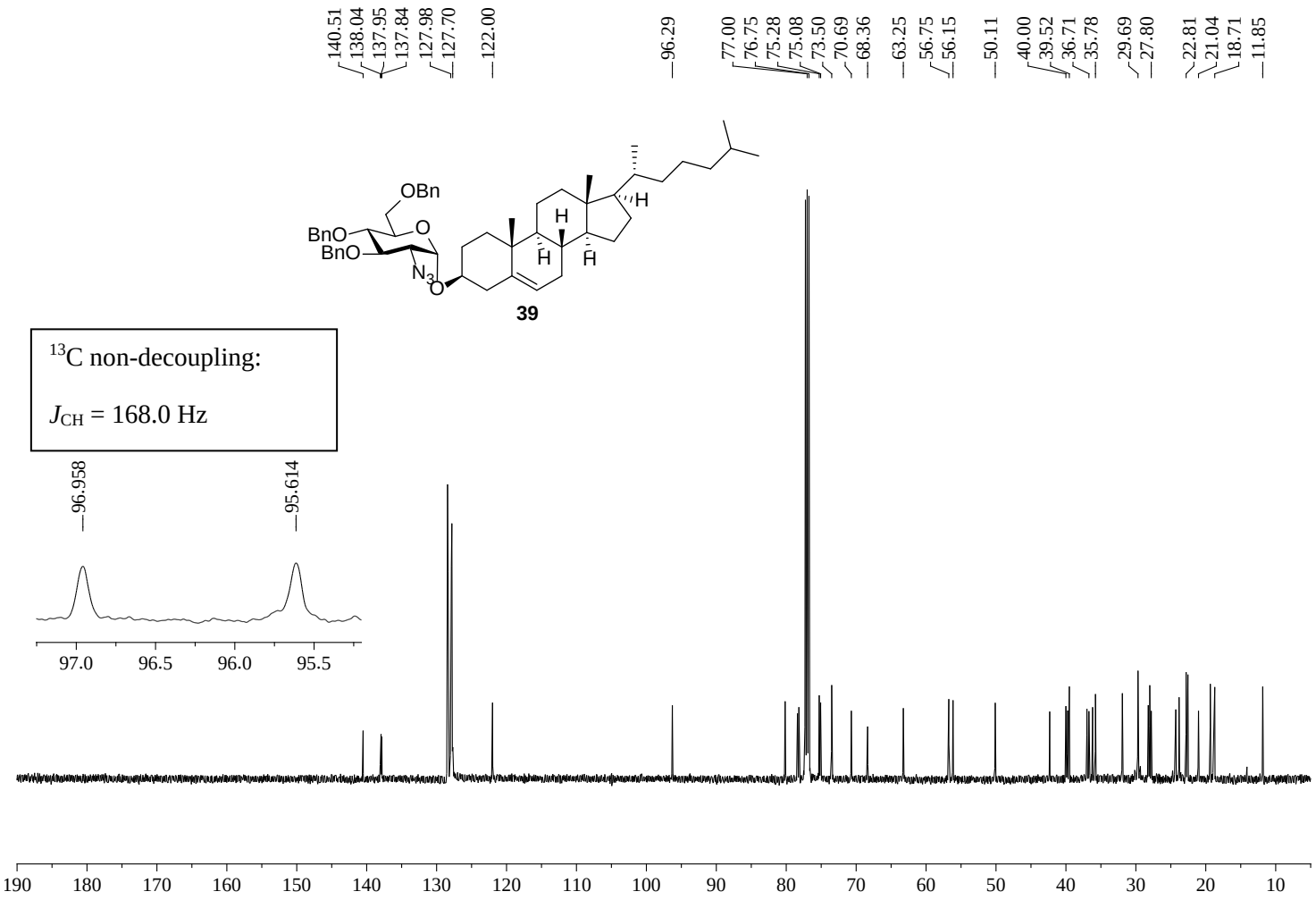
^{13}C NMR of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside 38



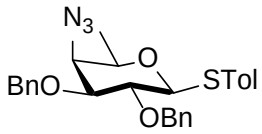
^{1}H NMR of cholesteryl-2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranoside (39)



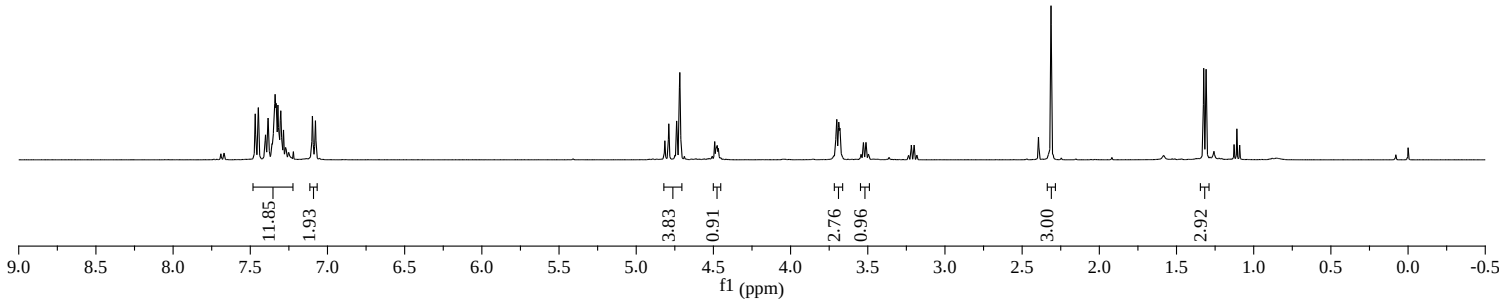
^{13}C NMR of cholesteryl-2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranoside (39)



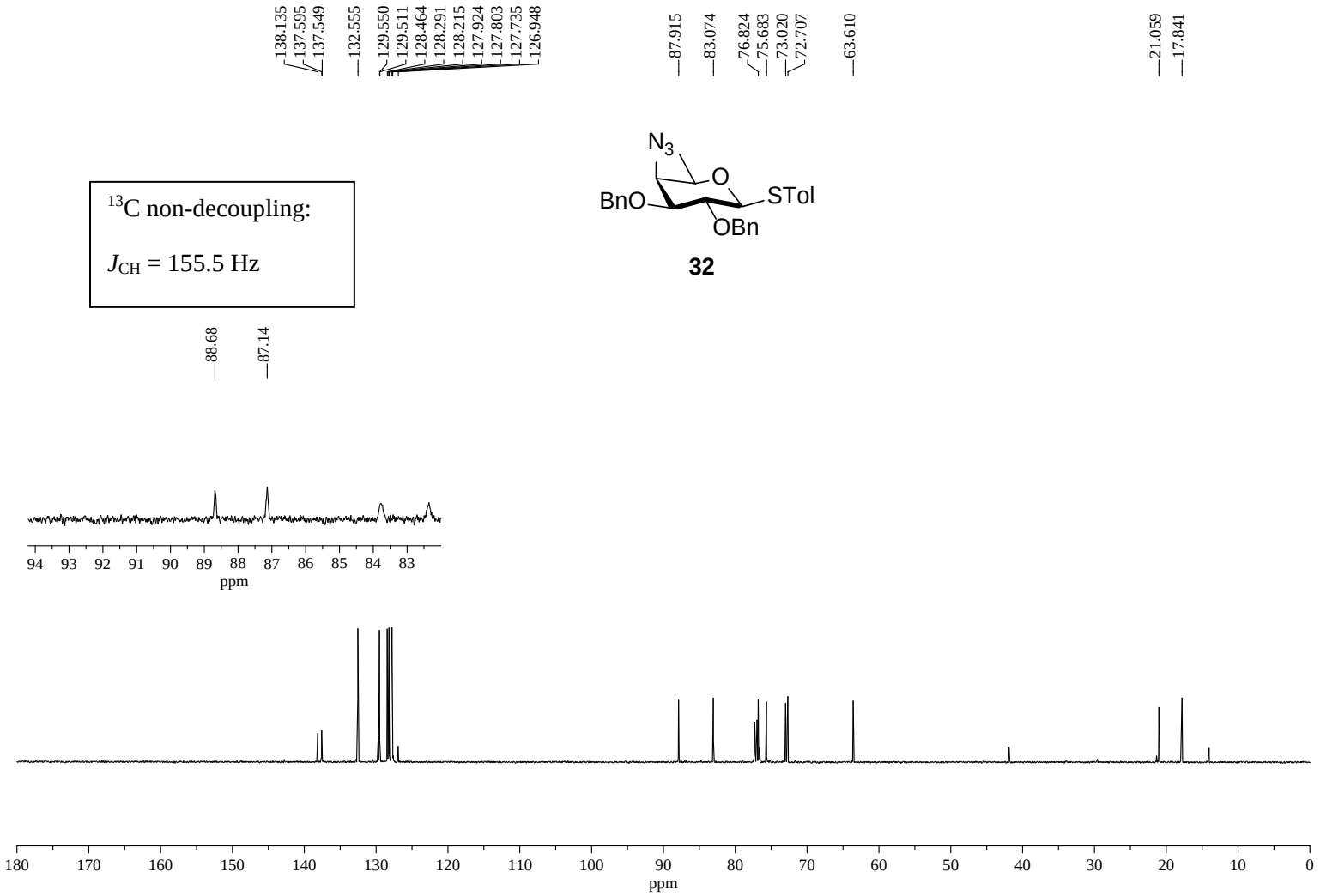
^{1}H NMR spectrum of D-Fuc4N_3 thioglycosyl building block (32)



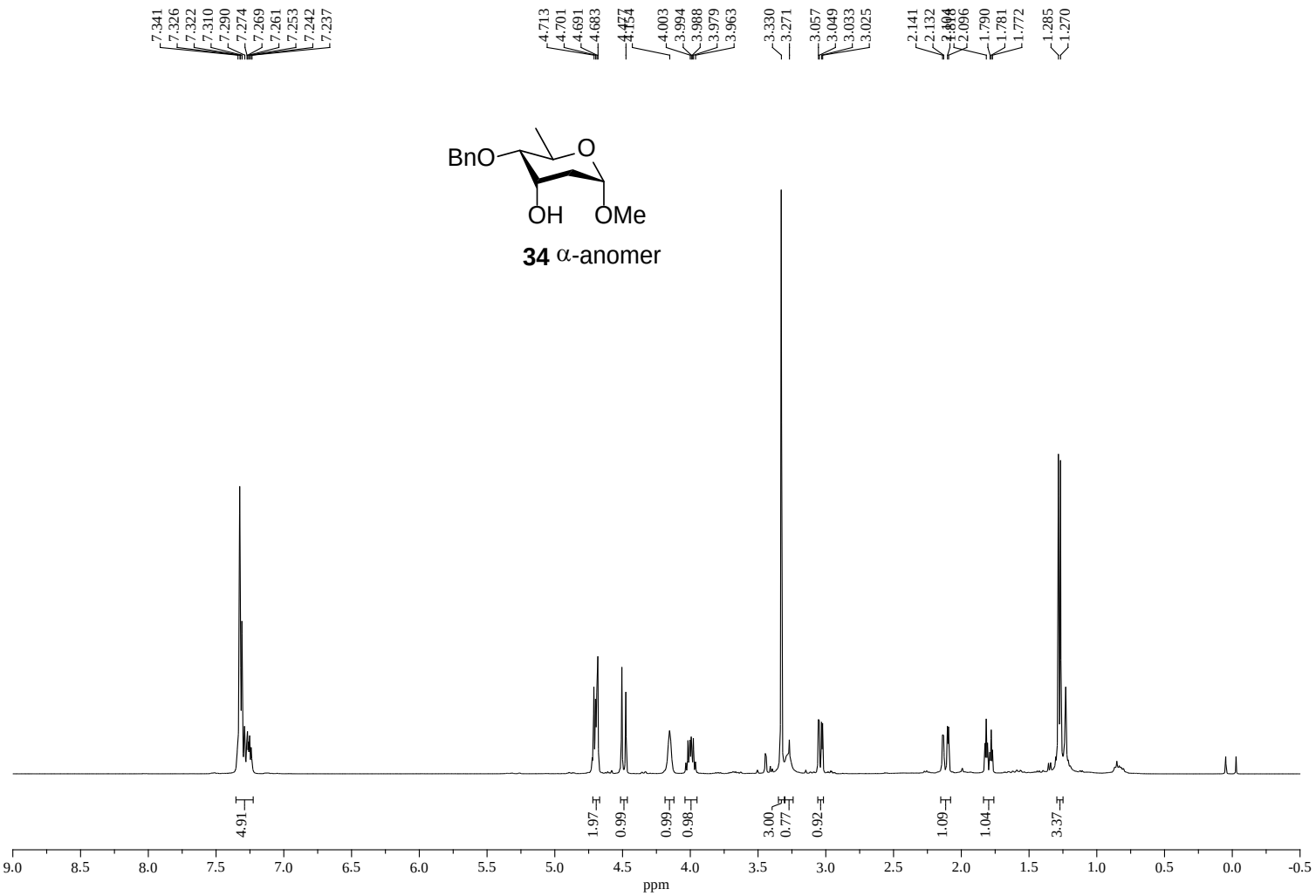
32



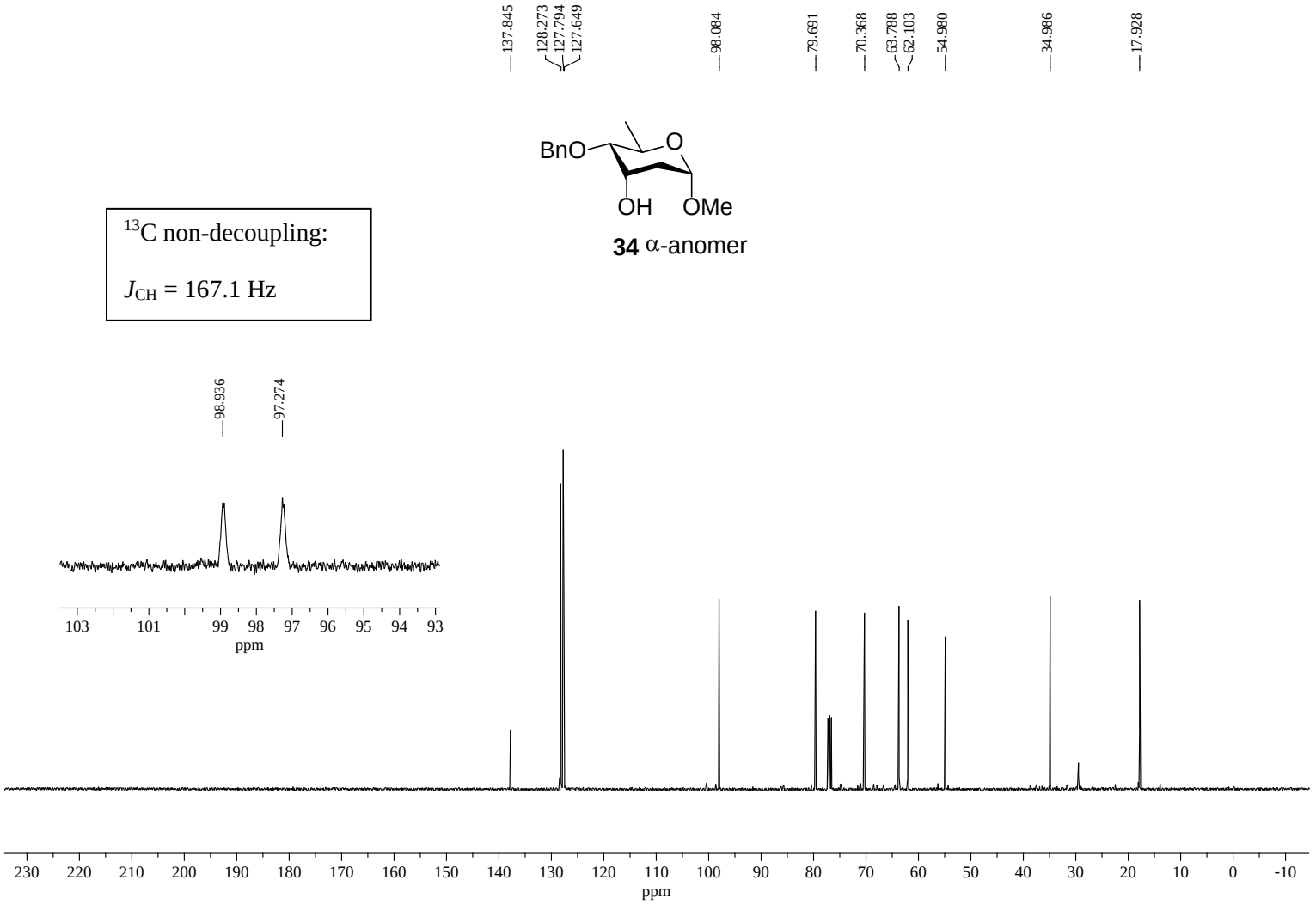
^{13}C NMR spectrum of D-Fuc4N$_3$ thioglycosyl building block (32)



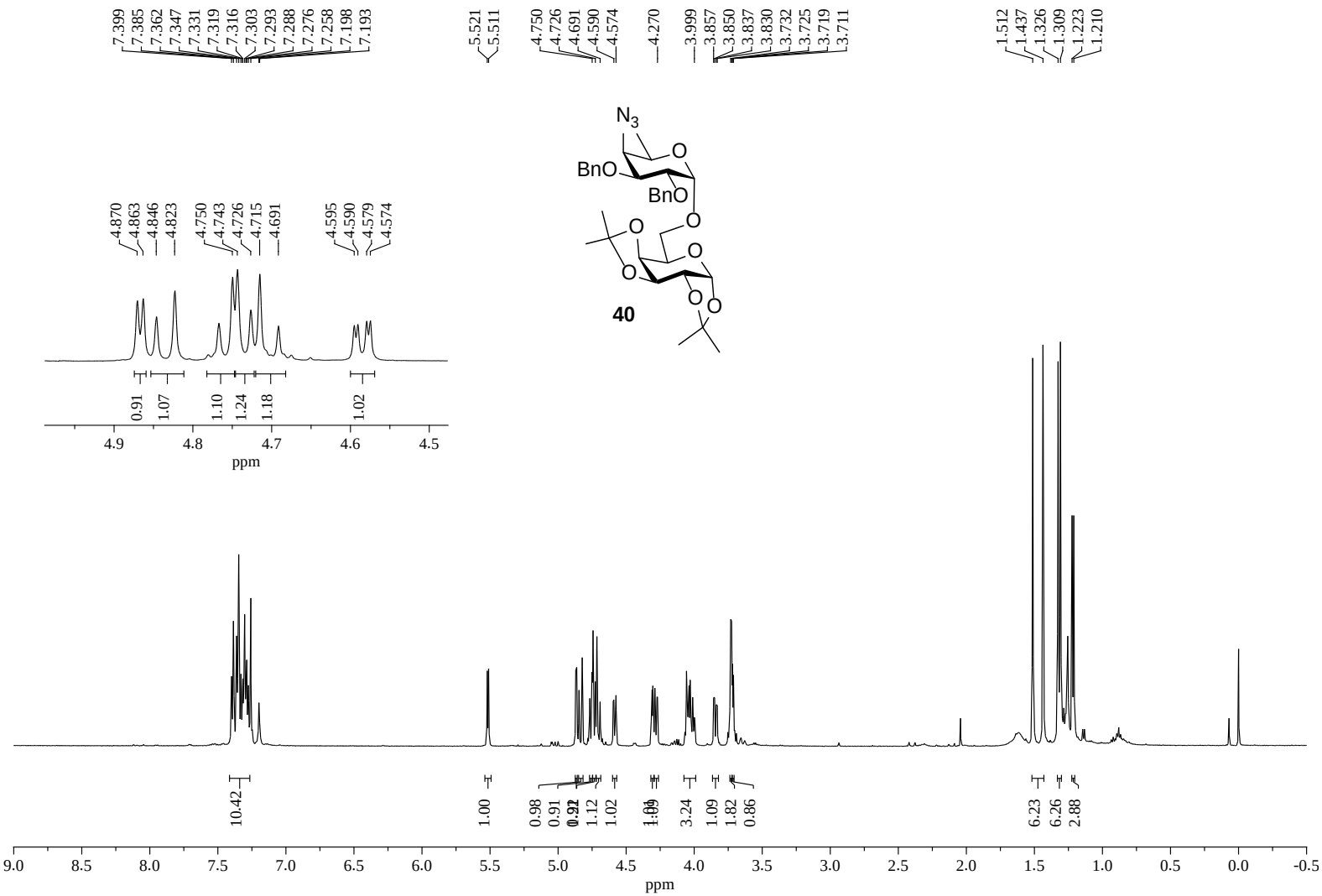
^{1}H NMR spectrum of α-anomer of 2,6-dideoxy acceptor (34)



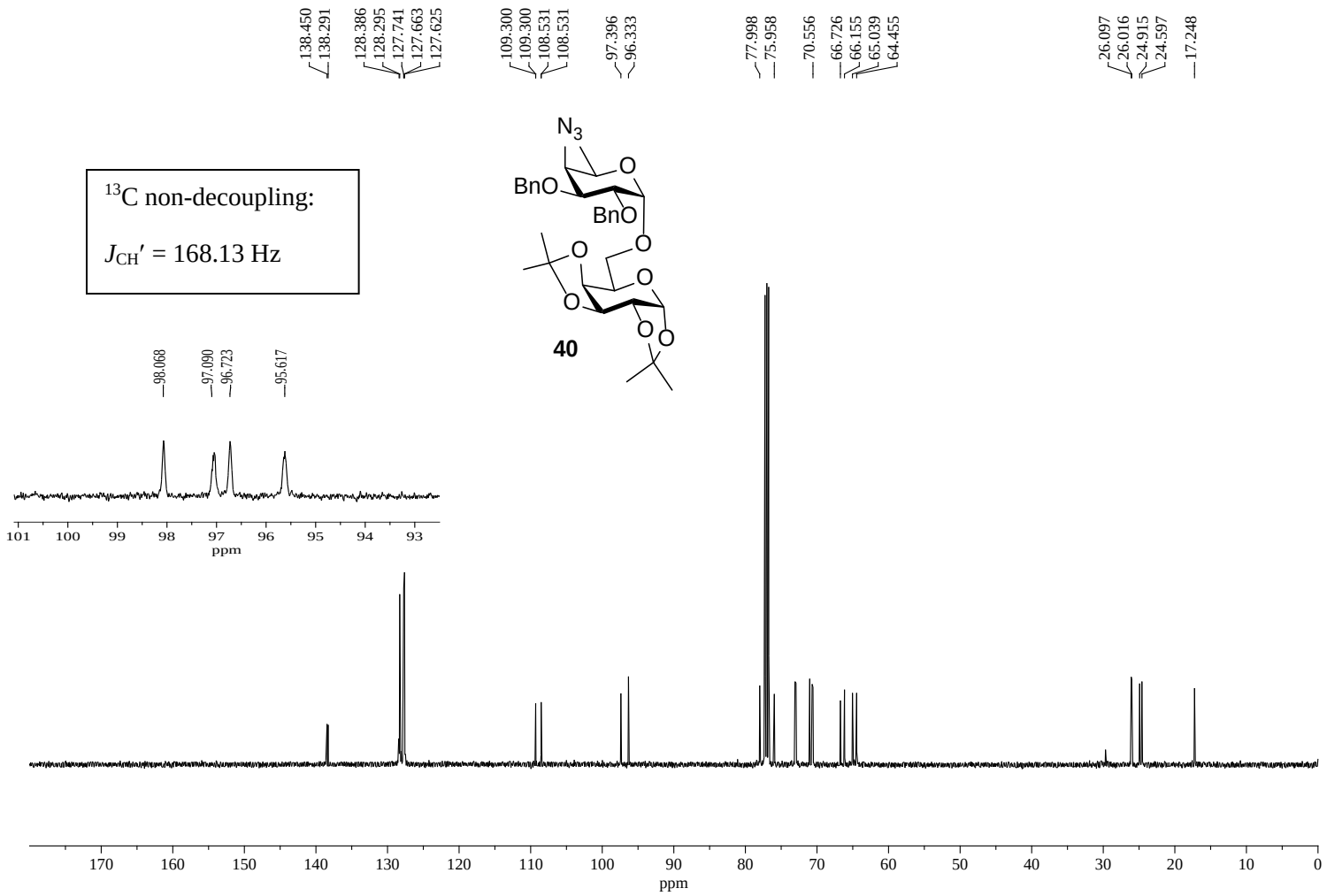
^{13}C NMR spectrum of α-anomer of 2,6-dideoxy acceptor (34)



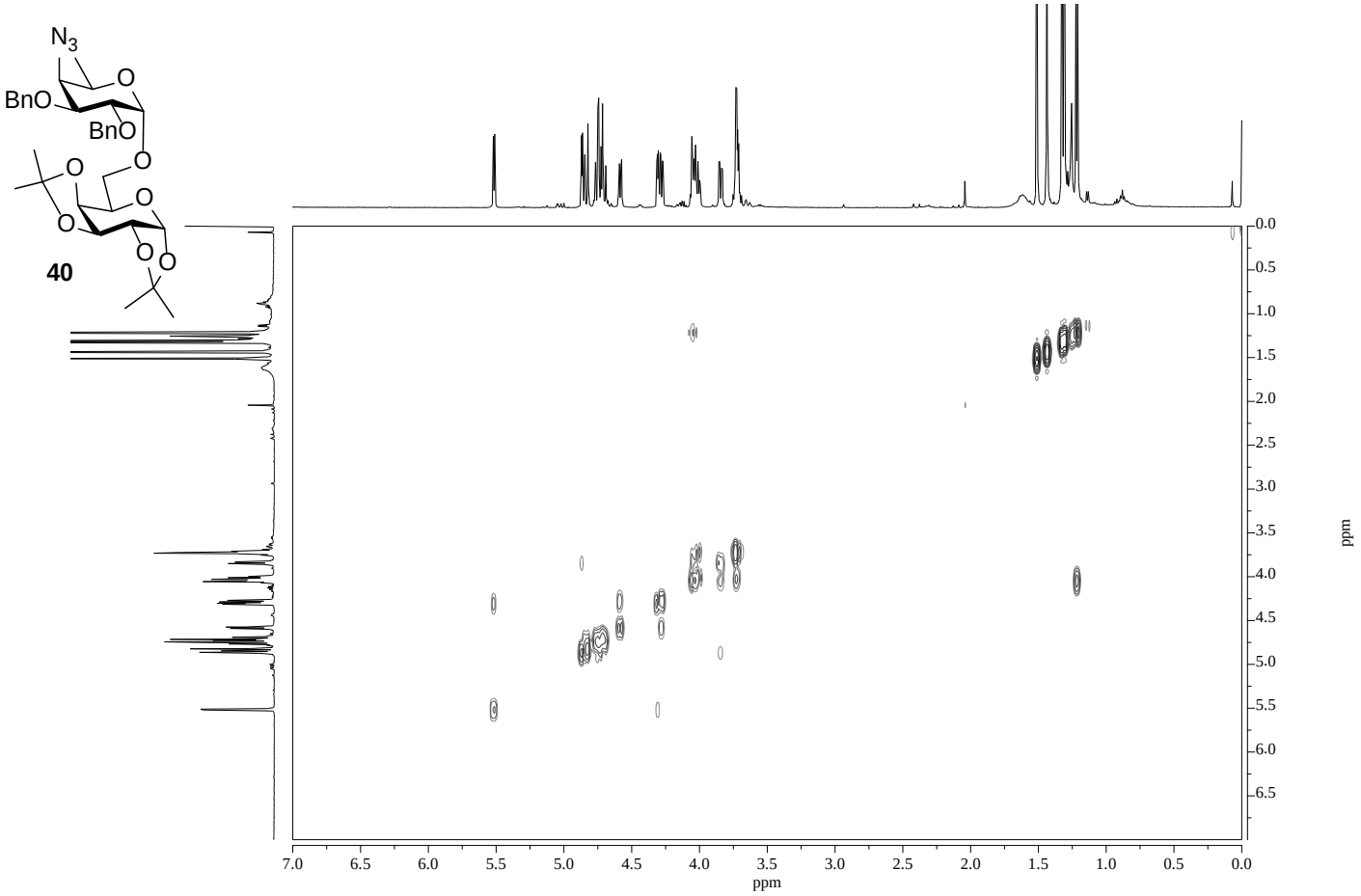
^{1}H NMR spectrum of 4-azido-2,3-di-*O*-benzyl-4,6-dideoxy-α-D-fucopyranosyl-(1→6)-1,2:3,4-di- *O*-isopropylidene-α-D-galactopyranose (40)



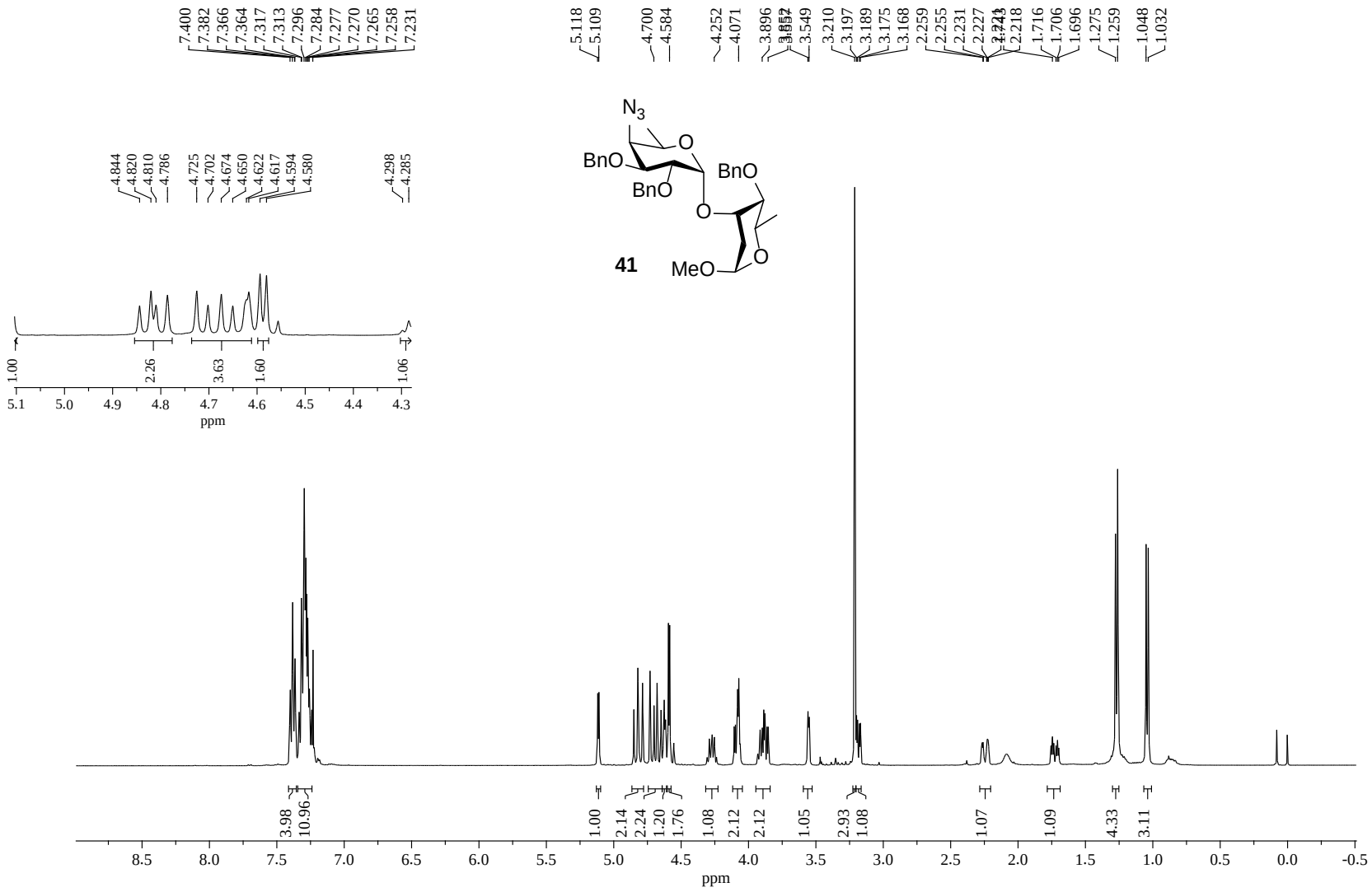
^{13}C NMR spectrum of 4-azido-2,3-di-*O*-benzyl-4,6-dideoxy-α-D-fucopyranosyl-(1→6)-1,2:3,4-di- *O*-isopropylidene-α-D-galactopyranose (40)



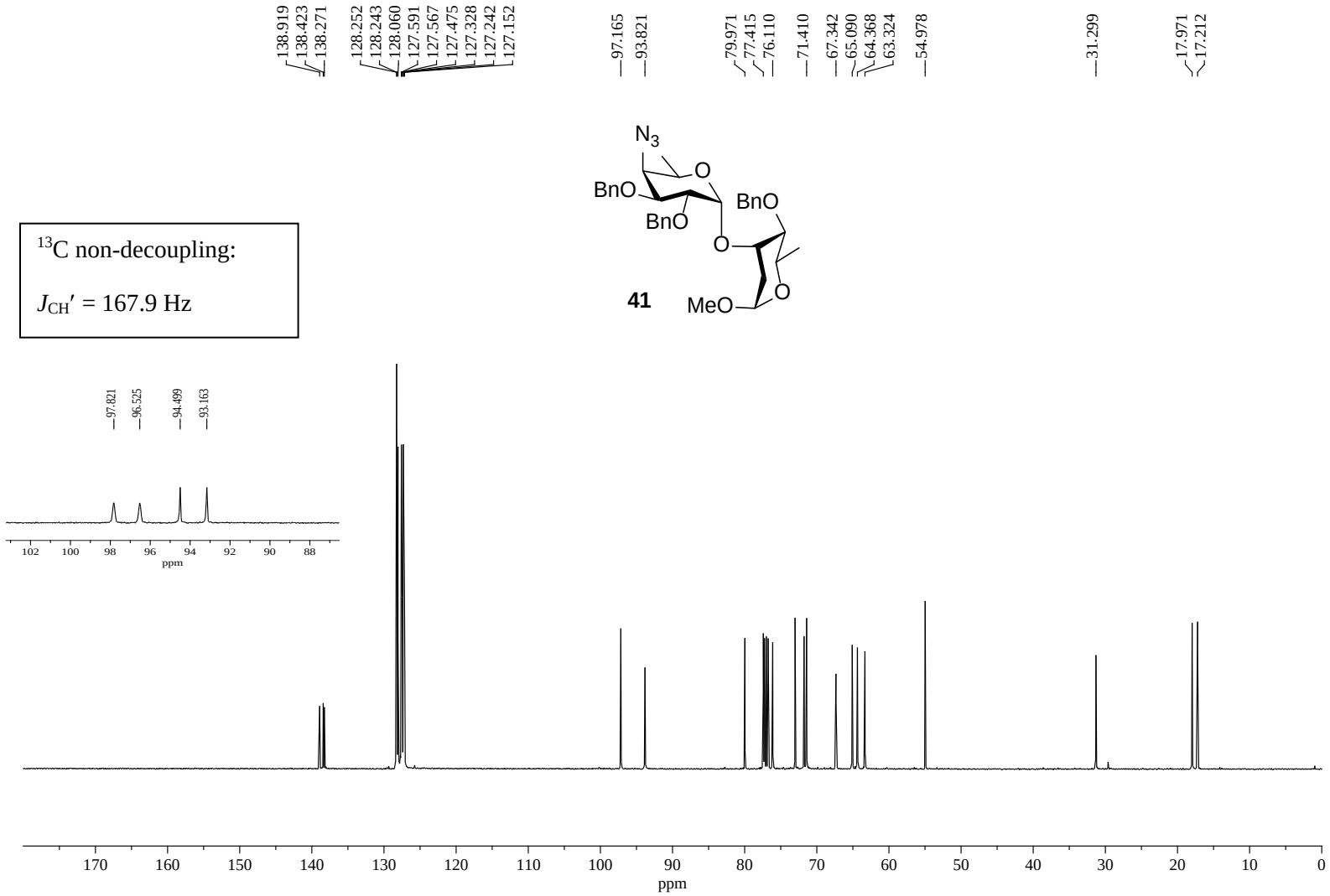
COSY NMR spectrum of 4-azido-2,3-di-*O*-benzyl-4,6-dideoxy-α-D-fucopyranosyl-(1→6)-1,2:3,4-di- *O*-isopropylidene-α-D-galactopyranose (40)



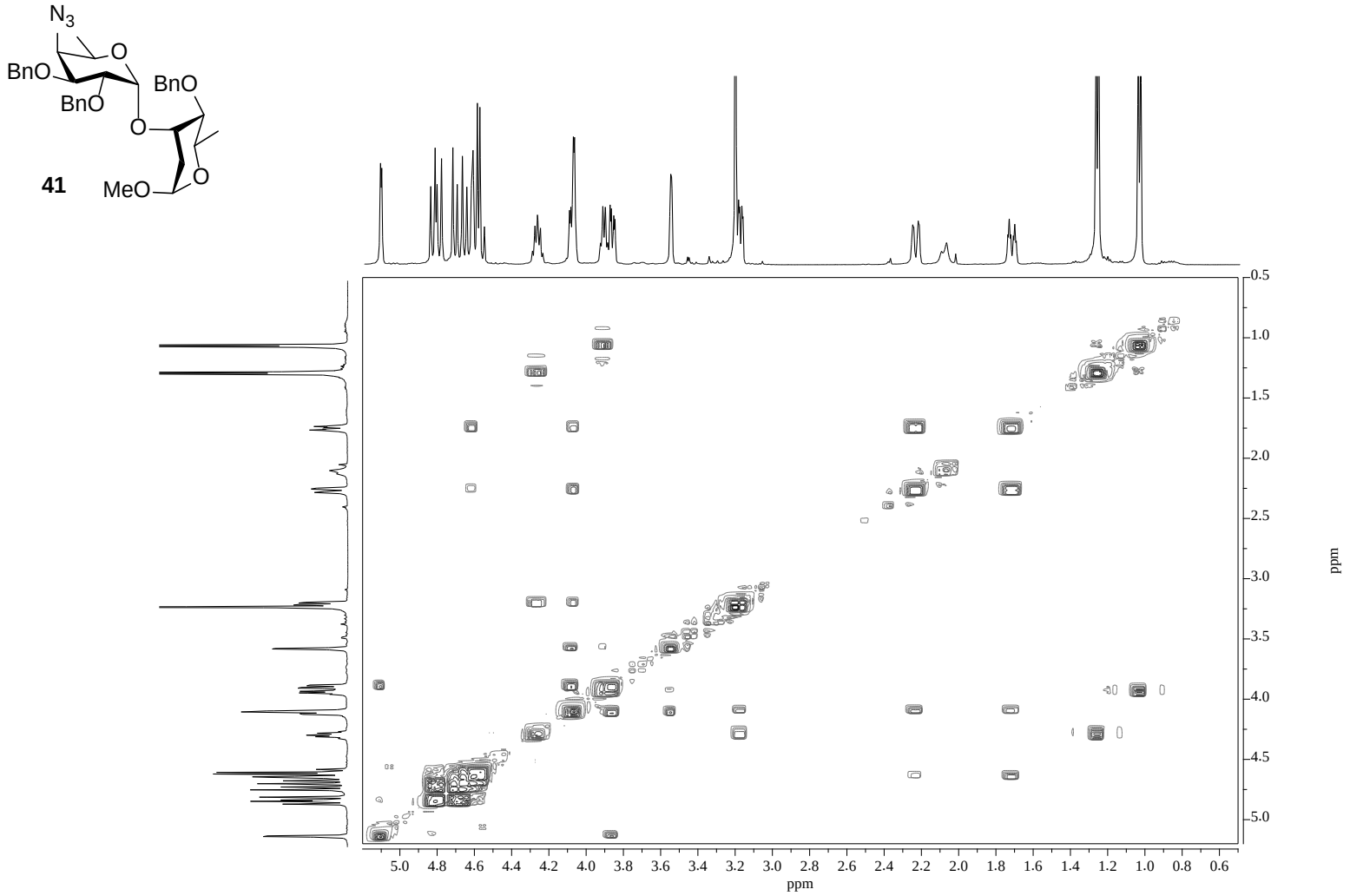
^{1}H NMR spectrum of methyl 4-azido-2,3-di-*O*-benzyl-4,6-dideoxy-α-D-fucopyranosyl-(1→3)- 4-*O*-benzyl-2,6-dideoxy-α-D-*ribo*-hexopyranoside (41)



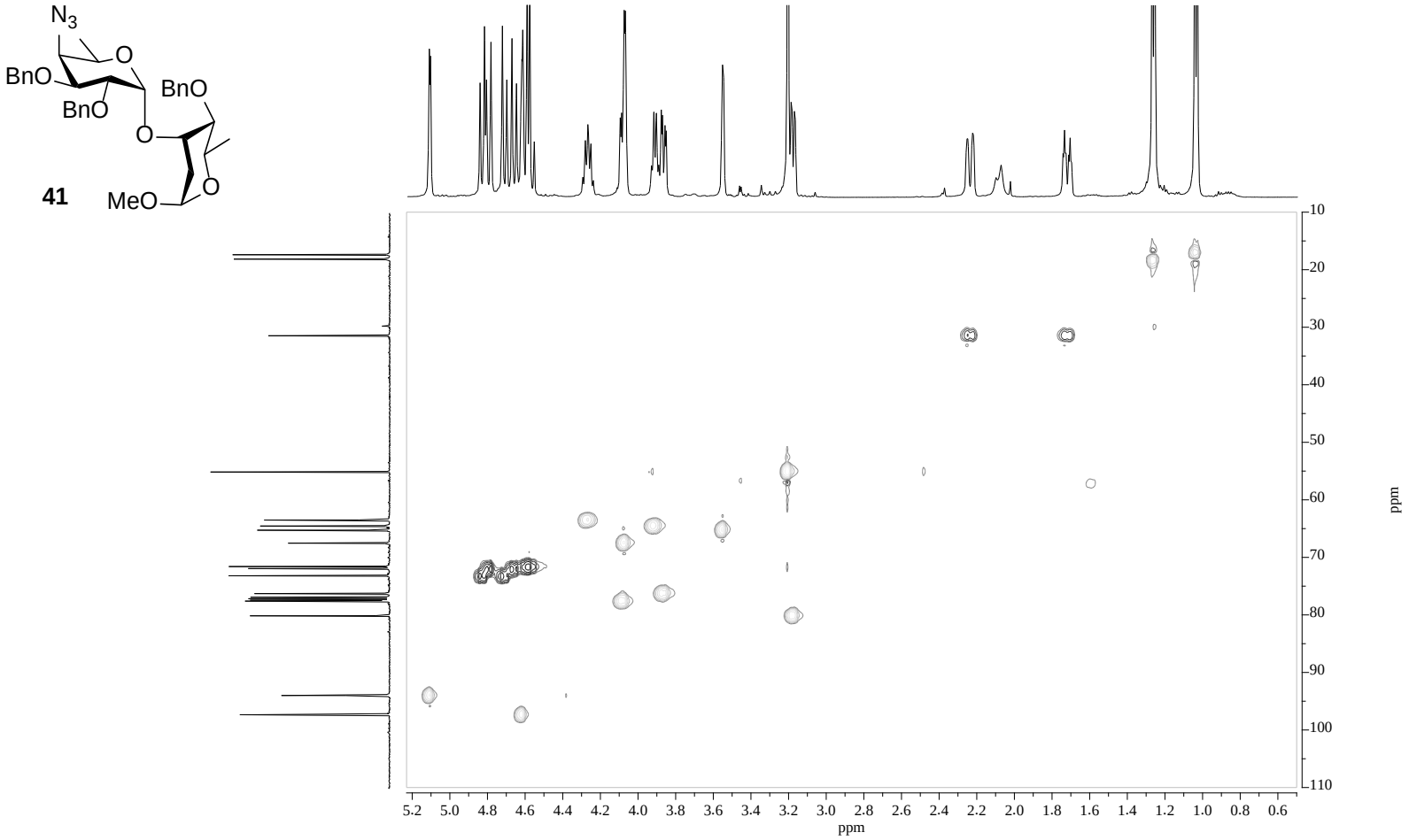
^{13}C NMR spectrum of methyl 4-azido-2,3-di-*O*-benzyl-4,6-dideoxy-α-D-fucopyranosyl-(1→3)- 4-*O*-benzyl-2,6-dideoxy-α-D-*ribo*-hexopyranoside (41)



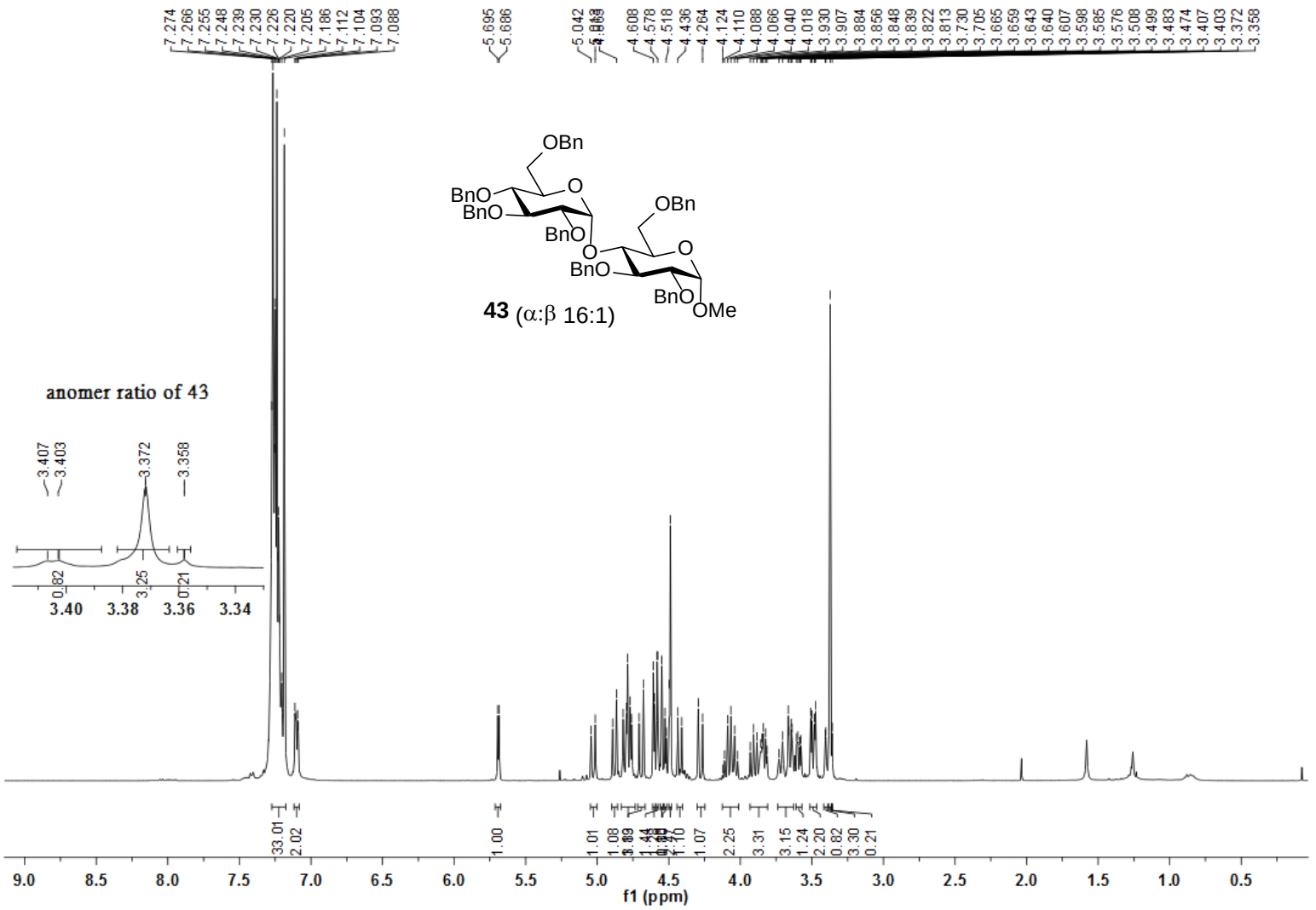
COSY NMR spectrum of methyl 4-azido-2,3-di-*O*-benzyl-4,6-dideoxy-α-D-fucopyranosyl-(1→3)- 4-*O*-benzyl-2,6-dideoxy-α-D-*ribo*-hexopyranoside (41)



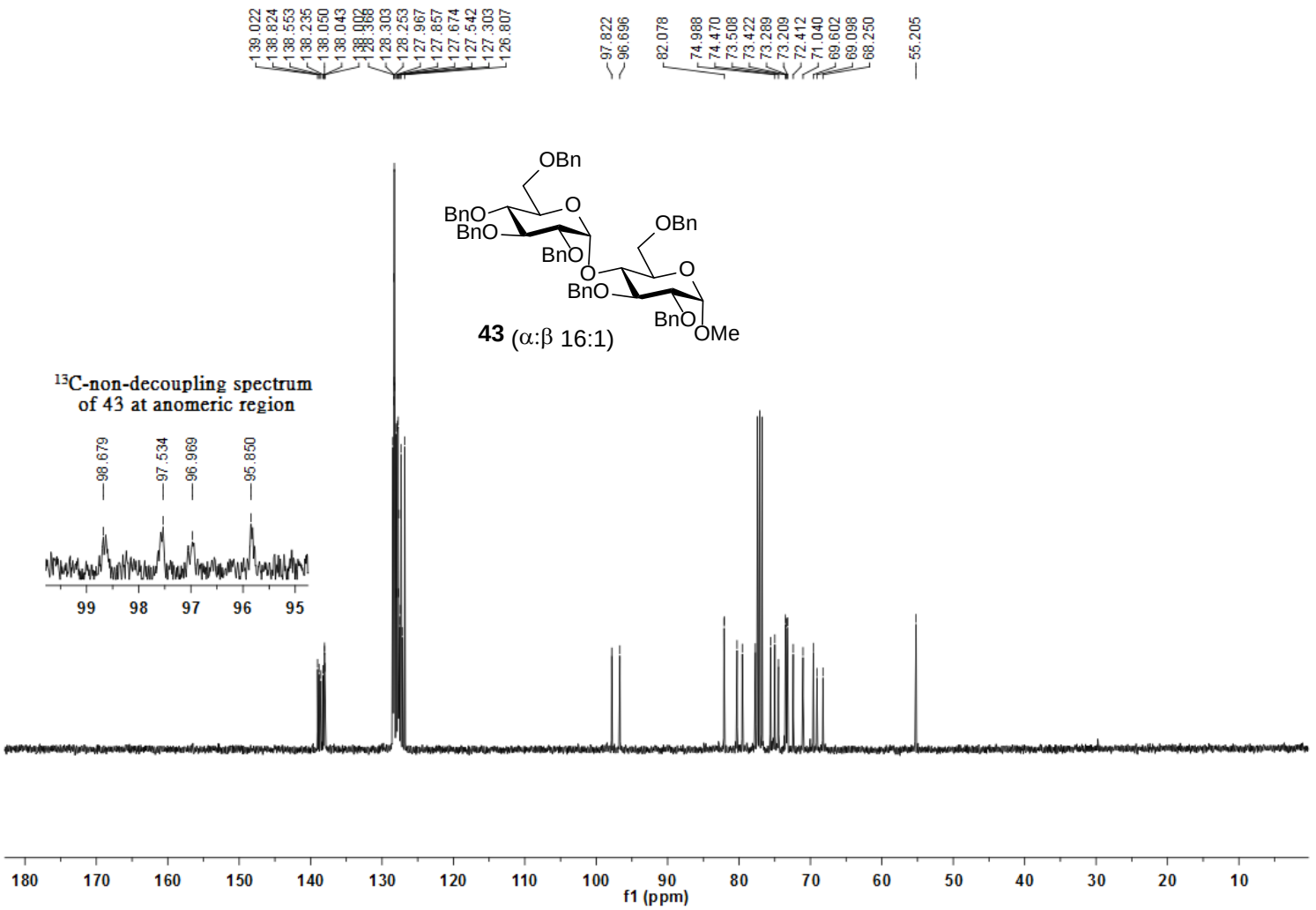
HSQC NMR spectrum of methyl 4-azido-2,3-di-*O*-benzyl-4,6-dideoxy-α-D-fucopyranosyl-(1→3)- 4-*O*-benzyl-2,6-dideoxy-α-D-*ribo*-hexopyranoside (41)



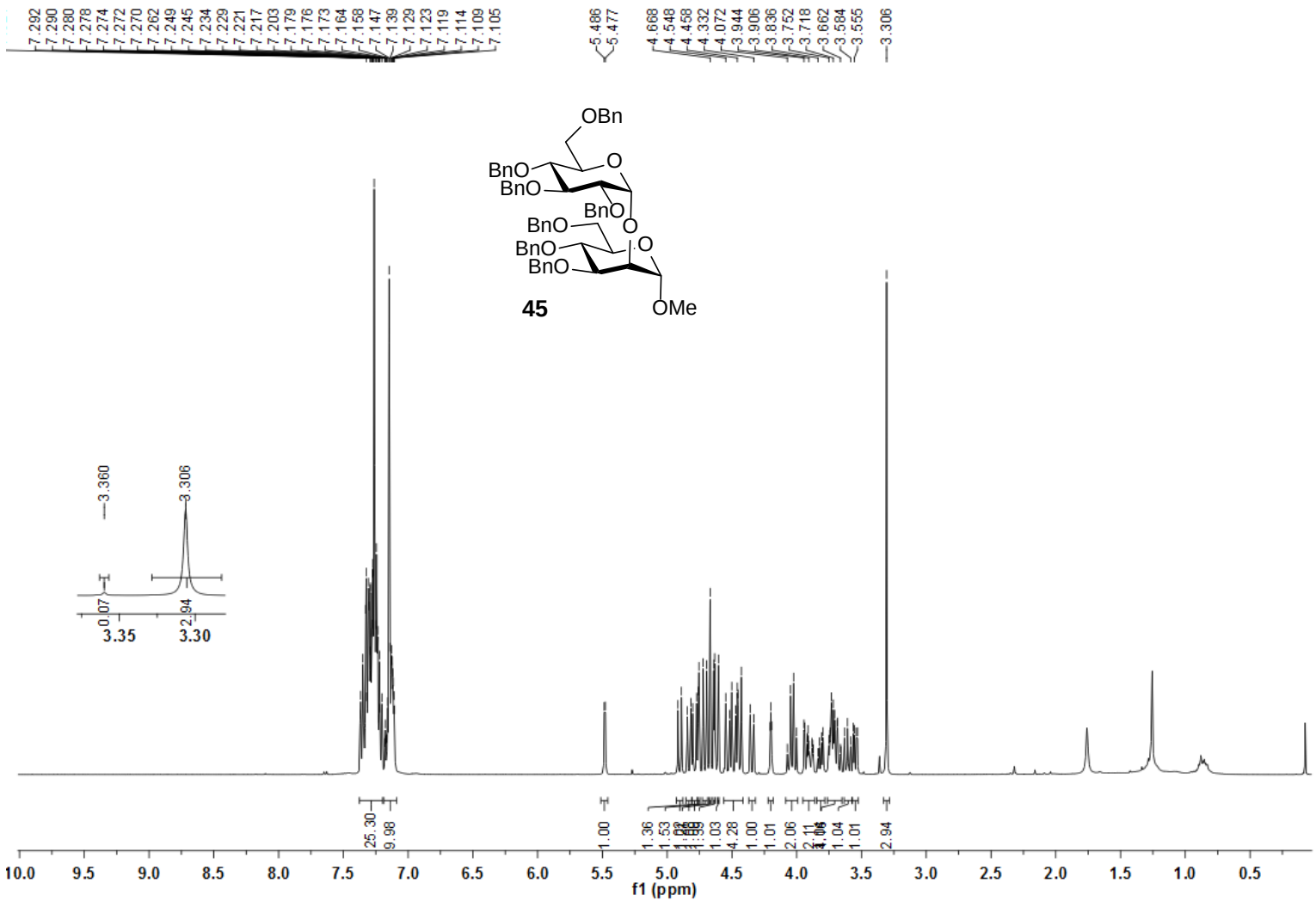
^{1}H NMR spectrum of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (43)



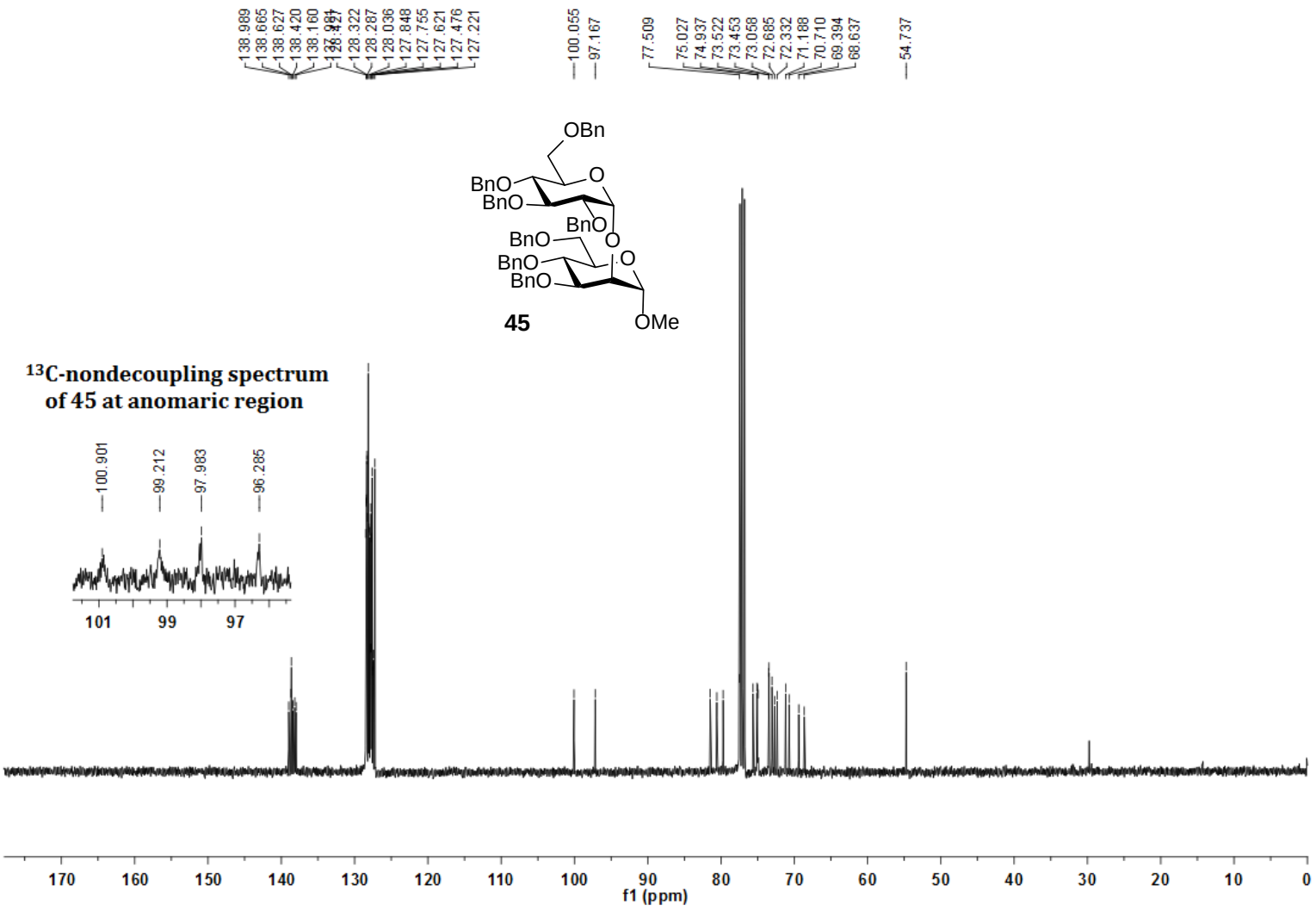
^{13}C NMR spectrum of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (43)



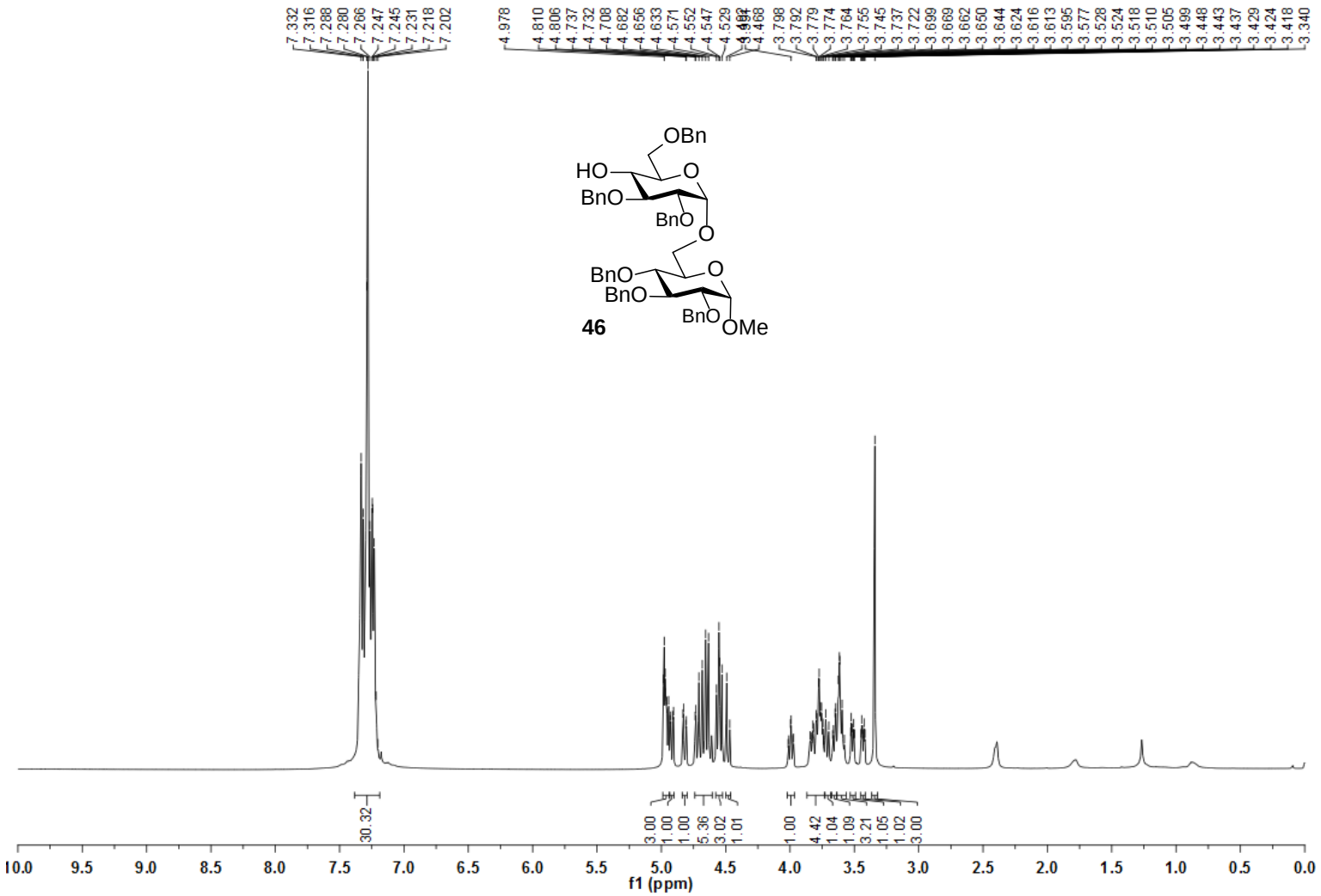
^{1}H NMR spectrum of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (45)



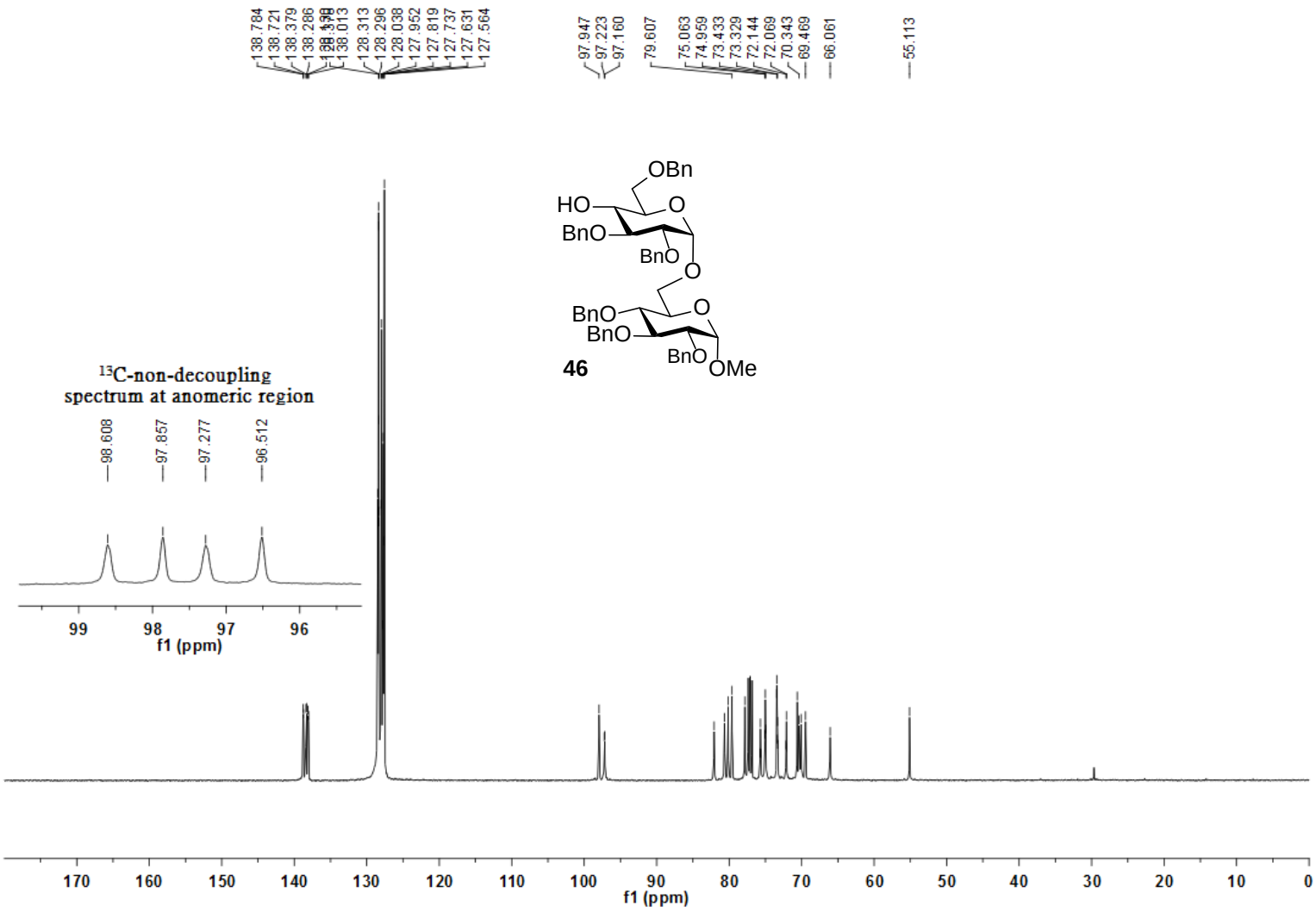
^{13}C NMR spectrum of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (45)



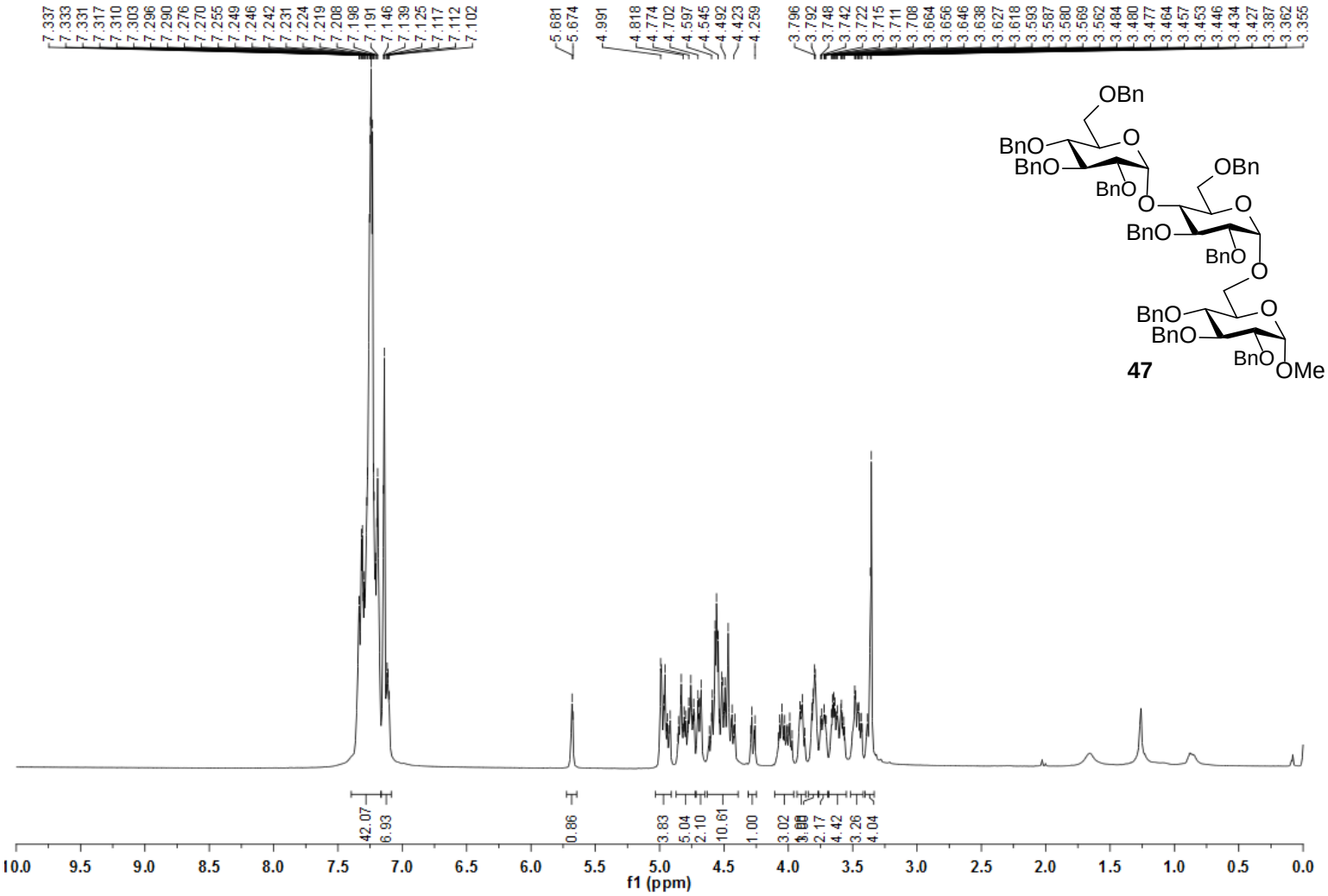
^{1}H NMR spectrum of methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (46)



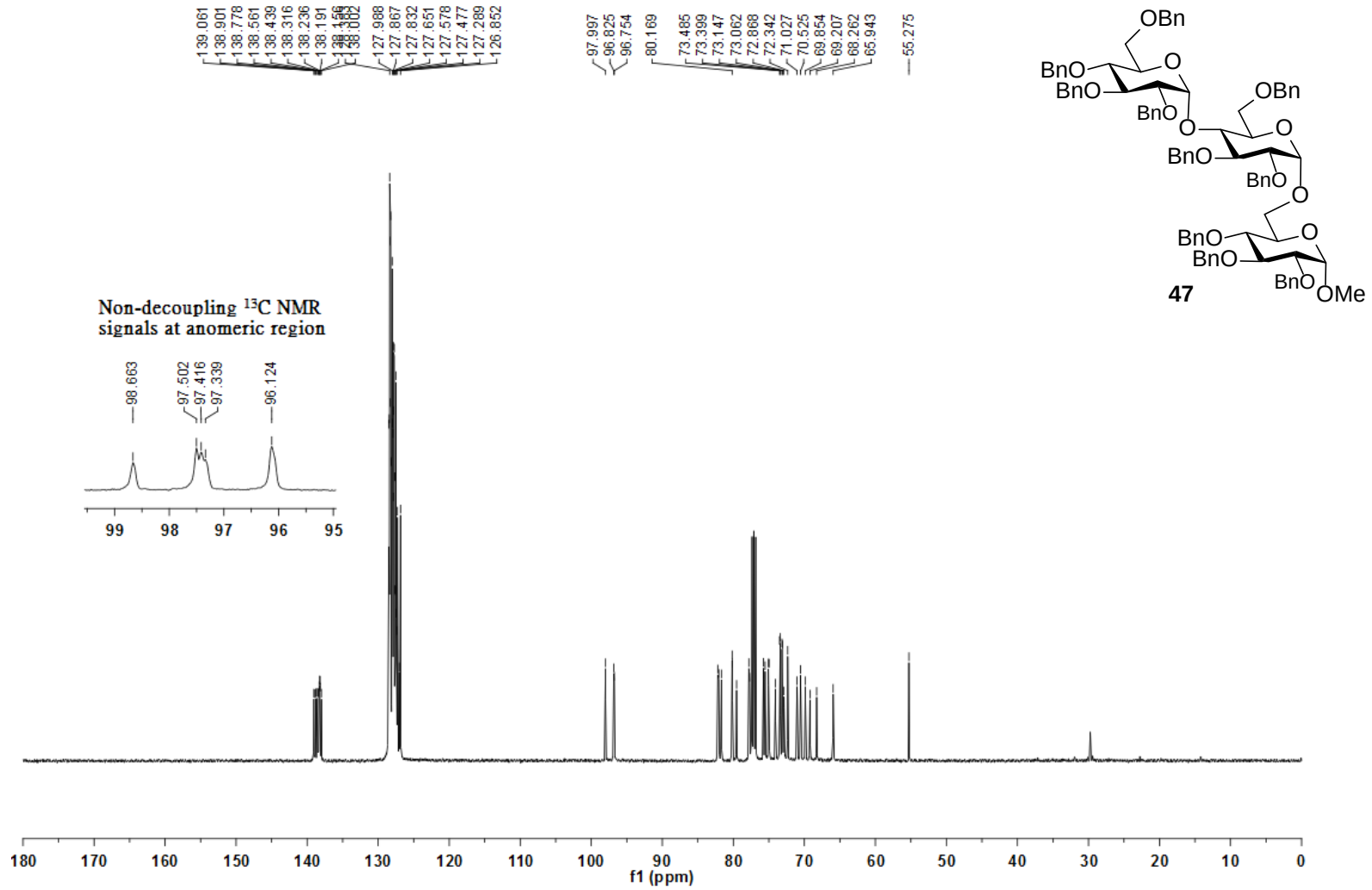
^{13}C NMR spectrum of methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (46)



^{1}H NMR spectrum of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (47)

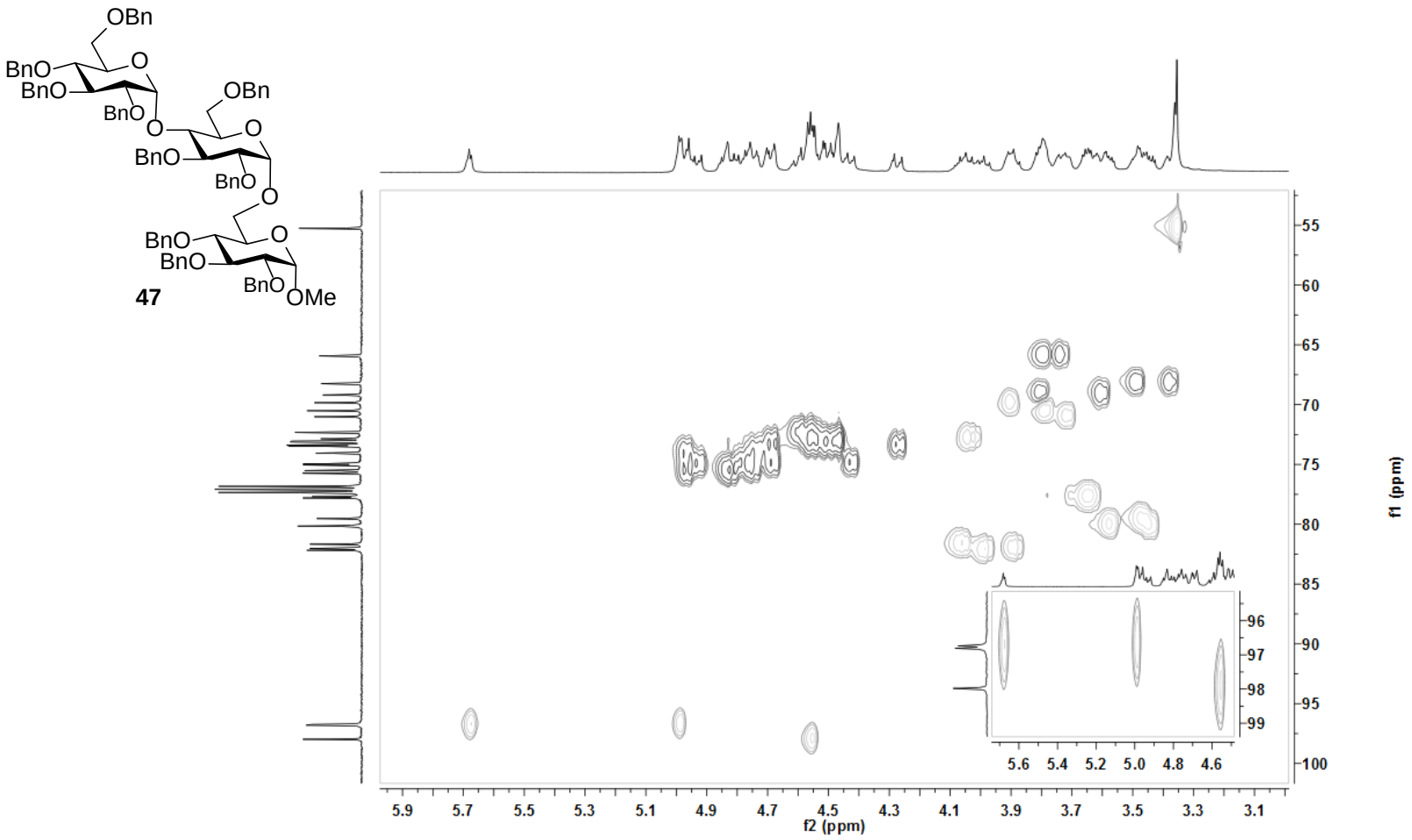


^{13}C NMR spectrum of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)- 2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (47)

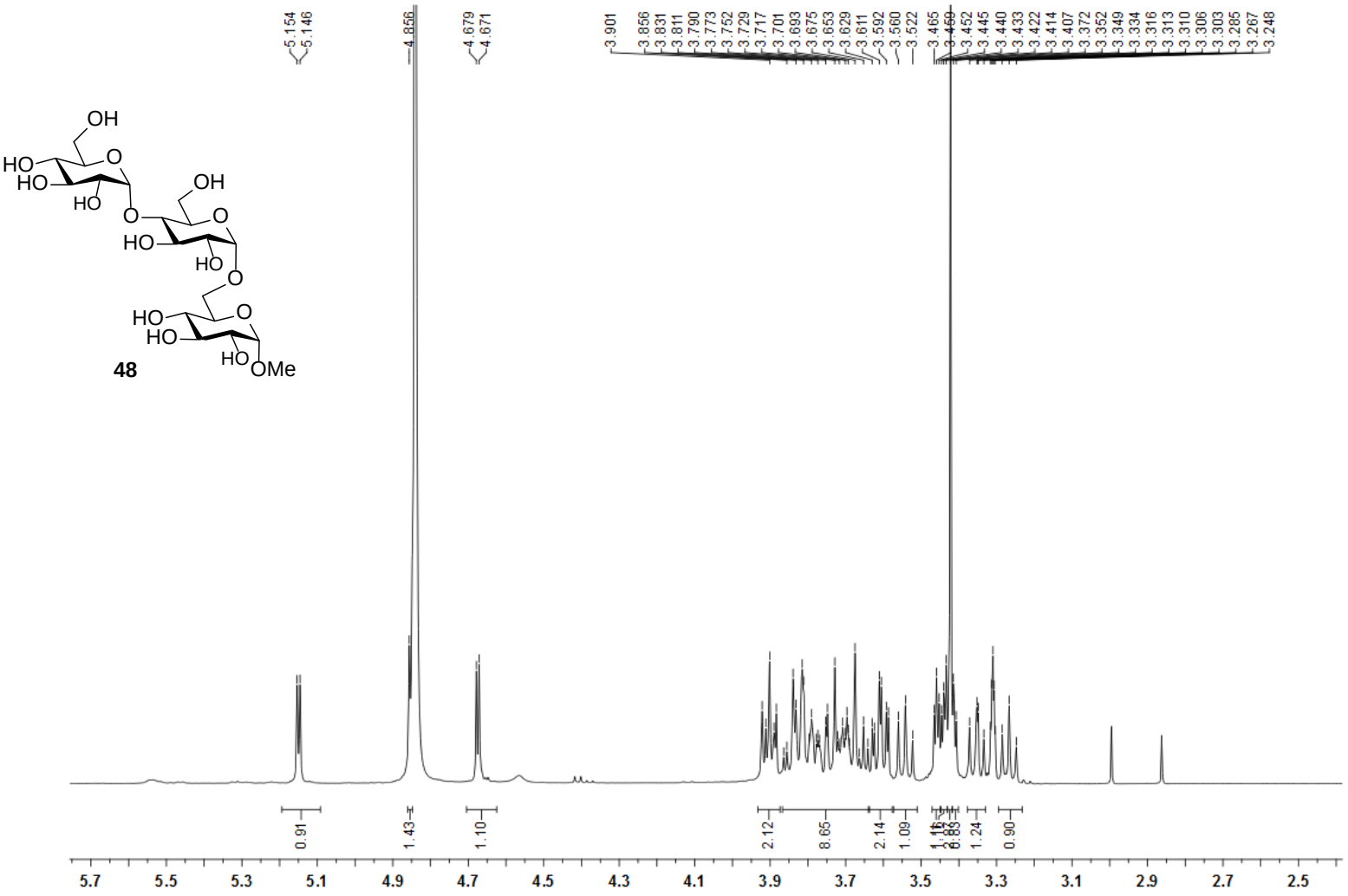


47

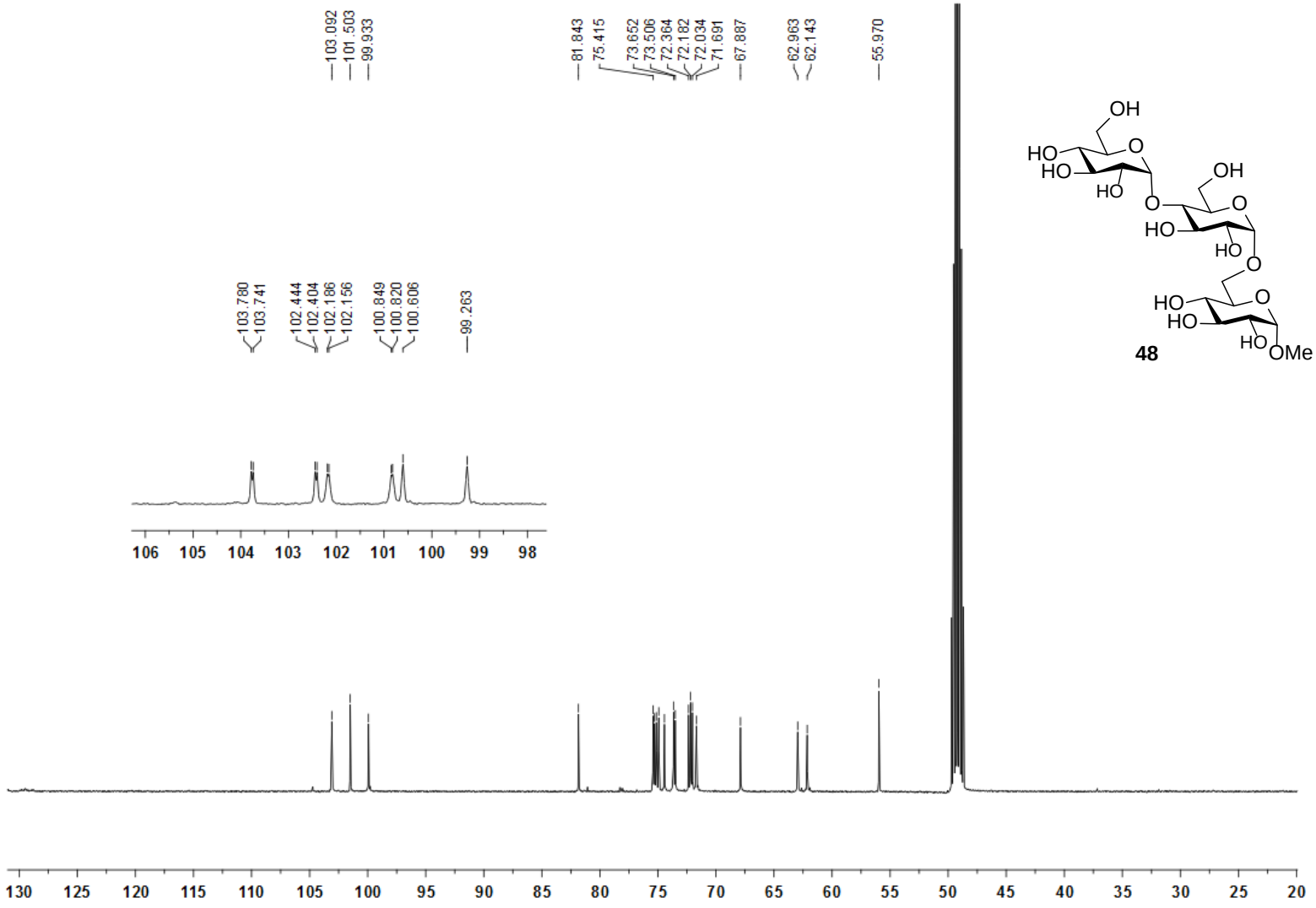
HSQC NMR spectrum of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)- 2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (47)



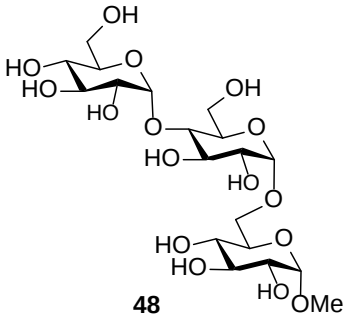
^{1}H NMR spectrum of methyl α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→6)-α-D-glucopyranoside (48)



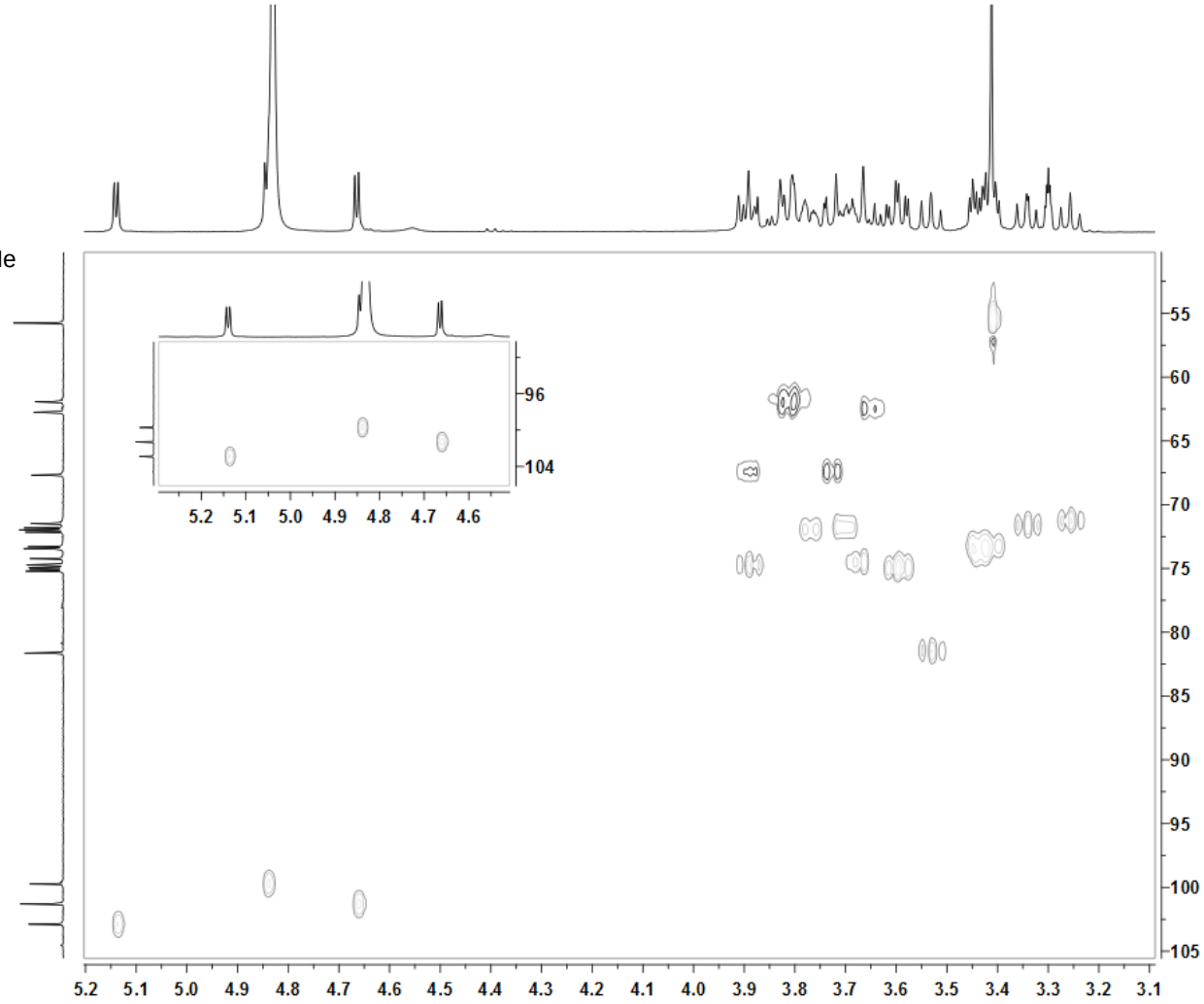
^{13}C NMR spectrum of methyl α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→6)-α-D-glucopyranoside (48)



HSQC NMR spectrum of methyl α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→6)-α-D-glucopyranoside (48)



48



High resolution mass spectrometry of glucosyl chloride 10′

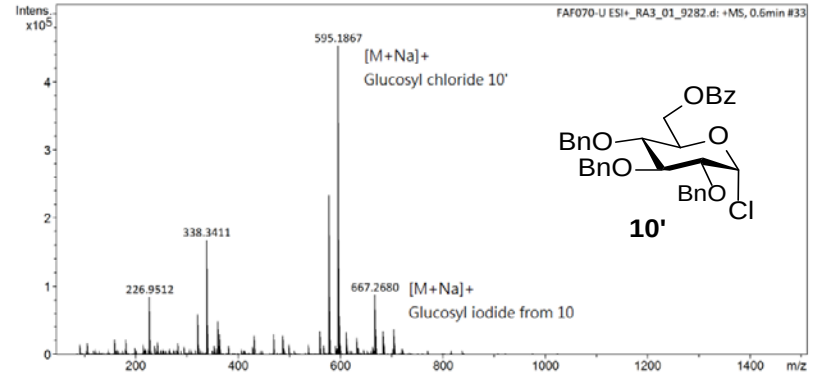
Display Report

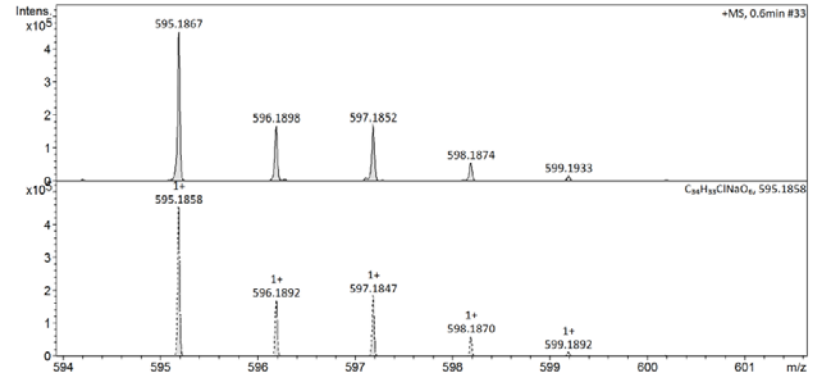
Analysis Info

Analysis Name	D:\Data\nctu service\data\2016\20160329\FAF070-U ESI+_RA3_01_9282.d	Acquisition Date	3/29/2016 11:39:40 AM
Method	Small molecule.m	Operator	NCTU
Sample Name	FAF070-U ESI+	Instrument	impact HD 1819696.00164
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C





FAF070-U ESI+_RA3_01_9282.d

High resolution mass spectrometry of glucosyl chloride 12′