Supporting Information

for

The Isothiocyanato Moiety. An Ideal Protecting Group for Stereoselective Sialic Acid Glycoside Synthesis and Subsequent Diversification**

General Experimental: All reagents and solvents were purchased from commercial suppliers and were used without further purification unless otherwise specified. All reactions were performed in an atmosphere of dry argon. All organic extracts were dried over sodium sulfate and concentrated under vacuum. Chromatographic purifications were carried out over silica gel, Sephadex G-10, Sephadex C-25 and Dowex 50WX8-100 sodium ion exchange resin. Analytical thin-layer chromatography was performed with pre-coated glass backed plates (w/UV 254) and visualized by UV irradiation (254 nm) or by staining with 25% H_2SO_4 in EtOH or ceric ammonium molybdate solution. Specific rotations were obtained using a digital polarimeter (Autopol III) in the solvent specified. High resolution mass spectra were recorded with an electrospray source coupled to a time-of-flight mass analyzer (Waters). ^{1}H, ^{13}C, ^{19}F and 2D NMR spectra were recorded at 600 MHz (Agilent). Stereochemical assignments of coupled sialosides are based on $^{3}J_{C1\text{-}H3ax}$ values[1]. Ammonical methanol was prepared by using ammonium hydroxide solution (28% in water) and methanol in 1:9 ratio.

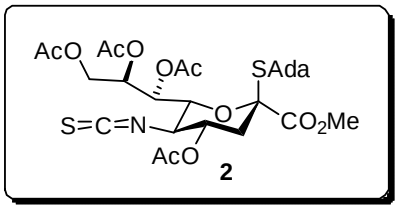
General Coupling Protocol: A solution of donor (0.15 mmol), acceptor (0.18 mmol), and activated 4 Å acid-washed powdered molecular sieves (300 mg, 2.0 g/mmol) in anhydrous CH_2Cl_2:MeCN (2:1, 2 mL) was stirred for 0.5 h under Ar, and then cooled to -78 ^{o}C followed by addition of NIS (42 mg, 0.18 mmol) and TfOH (2 μL, 0.02 mmol). The reaction mixture was stirred at -78 ^{o}C for 5 h and then quenched with DIPEA (7 μL). The mixture was diluted with CH_2Cl_2, filtered through Celite, washed with 20% aqueous $Na_2S_2O_3$ solution, dried over Na_2SO_4,

and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with EtOAc: hexanes systems to afford the desired coupled products.

Acid washed molecular sieves: 4 Å molecular sieves (30 g) were soaked in 2 *N* HCl (80 mL) for 12 h. The mixture was concentrated under reduced pressure, and then slurried with water (100 mL). The slurry was filtered and washed with water (200 mL). The resulting solid was dried at 254 ^{o}C for 24 h to give acid-washed molecular sieves (28 g), which were directly used for glycosylation.

General Protocol for Amide Formation from Isothiocyanates [2]: To the required 9-fluorenylmethyl (Fm) thioester (0.03 mmol) at room temperature was added a piperidine (0.21 mmol) in DMF (500 μL). The reaction mixture was stirred for 15 min, then diluted with $CHCl_3$ (3 mL). The resulting solution was washed with 1*N* HCl aq. (3 mL) and brine (3 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was dried under high vacuum, and dissolved in dry CH_2Cl_2 (0.5 mL) before addition of the isothiocyanate (0.02 mmol). The reaction mixture was stirred for 36 h at room temperature before the volatiles were removed *in vacuo*. The residue was purified by column chromatography on silica gel eluting with EtOAc: hexanes systems to afford the corresponding amides.

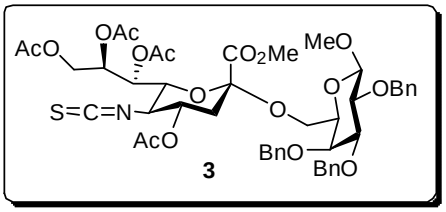
Methyl (1-Adamantanyl 4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-2-thio-D-*glycero*-β-D-*galacto*-non-2-ulopyranosid)onate (2):



To a stirred solution of **1** (1.5 g, 2.8 mmol) in MeOH (8 mL) was added 2M HCl in diethyl ether (8 mL) at 0 ^{o}C. The resulting solution was stirred at room temperature for 3.5 h., and then concentrated under reduced pressure. Without further purification the residue was dissolved in MeCN (8 mL) and H_2O (16 mL), and $NaHCO_3$ (2.3 g, 27 mmol) added. To the vigorously stirred mixture at room temperature was slowly added *O*-phenyl chlorothionoformate (0.8 g, 4.8 mmol) in MeCN (8 mL) through a dropping funnel, after which stirring was continued for 1.0 h

at room temperature. The resulting mixture was extracted with EtOAc (100 mL x 3), and the combined extracts were washed with brine and then dried over Na_2SO_4 and concentrated. The crude was treated with acetic anhydride (15 mL) and pyridine (12 mL), stirred at room temperature for 6 h, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with EtOAc/DCM (1/5) to give the desired isothiocyanate (1.0 g, 59%) as a off-white compound with spectral data consistent with those reported in the literature.[3]

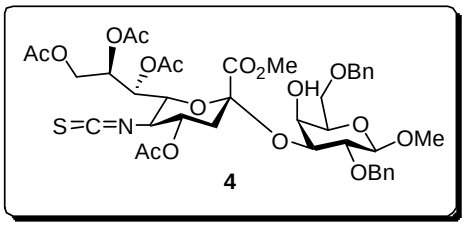
Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→6)-2,3,4-tri-*O*-benzyl-β-D-galactopyranoside (3):



3

Compound **3** was prepared according to general glycosylation procedure using donor **2 (**50 mg, 0.08 mmol) and acceptor **8** (43 mg, 0.09 mmol) in CH_2Cl_2/CH_3CN (1.2 mL, 2:1) at -78 ^oC. After chromatographic purification (gradient elution of EtOAc /Hexanes 2% to 20%) compound **3 (**57 mg, 80%) was obtained as a white foam. $[\alpha]^{20}_D$ = -10.3 (*c* =1, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ: 7.35-7.22 (m, 15H), 5.45 (d, *J* = 9.2 Hz, 1H), 5.33 (m, 1H), 4.94 (d, *J* = 11.7 Hz, 1H), 4.92-4.89 (m, 1H), 4.87 (d, *J* = 11.0 Hz, 1H), 4.75-4.68 (m, 3H), 4.62 (d, *J* = 11.7 Hz, 1H), 4.28-4.26 (m, 2H), 4.15 (dd, *J* = 12.8, 4.4 Hz, 1H), 4.01 (d, *J* = 10.6 Hz, 1H), 3.88-3.85 (m, 1H), 3.82 (d, *J* = 2.6 Hz, 1H), 3.77 (t, *J* = 9.5 Hz, 1H), 3.63 (s, 3H), 3.58 (t, *J* = 10.3 Hz, 1H), 3.55 (s, 3H), 3.52-3.48 (m, 3H), 2.67 (dd, *J* =13.2, 4.8 Hz, 1H), 2.15 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.05 (s, 3H), 1.75 (t, *J* = 12.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 170.7, 169.6, 169.5, 169.4, 167.2 ($^3J_{C\text{-}H}$ = 6.7 Hz), 140.2, 138.8, 138.5, 128.3, 128.2, 128.1, 128.0, 127.6, 127.5, 127.4, 127.3, 104.9, 98.5, 81.9, 79.5, 75.1, 74.2, 73.4, 72.9, 72.6, 71.8, 69.7, 67.9, 67.6, 63.0, 61.7, 57.0, 56.3, 52.9, 37.2, 20.9, 20.8, 20.7, 20.6; ESIHRMS calcd for $C_{47}H_{55}O_{17}NSNa$ ($[M + Na]^+$) 960.3088, found 960.3089.

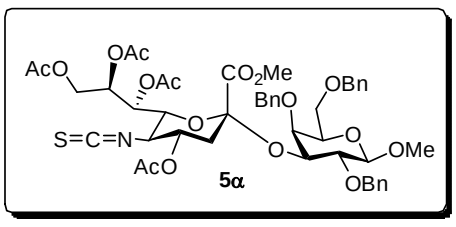
Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-2,4-di-*O*-benzyl-β-D-galactopyranoside (4):



4

Compound **4** was prepared according to general glycosylation procedure using donor **2 (**30 mg, 0.05 mmol) and acceptor **9** (21 mg, 0.06 mmol) in CH_2Cl_2/CH_3CN (0.6 mL, 2:1) at -78 ^oC. After chromatographic purification (gradient elution of EtOAc /Hexanes 2% to 20%), compound **4 (**30 mg, 79%) was obtained as a white foam. $[\alpha]^{20}_D$ = -11.9 (*c* = 1.1, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ: 7.35-7.27 (m, 10H), 5.43 (d, *J* = 8.8 Hz, 1H), 5.38 (m, 1H), 4.91 (m, 1H), 4.79 (d, *J* = 11.7 Hz, 1H), 4.64 (d, *J* = 11.7 Hz, 1H), 4.58-4.56 (m, 1H), 4.32 (d, *J* = 7.7 Hz, 1H), 4.25 (dd, *J* = 2.2, 12.8 Hz, 1H), 4.04 (dd, *J* = 9.2, 4.7 Hz, 1H), 4.02 (d, *J* = 4.0 Hz, 1H), 3.97 (dd, *J* = 10.6, 1.5 Hz, 1H), 3.80 (s, 3H), 3.78 (d, *J* = 5.9 Hz, 1H), 3.75-3.71 (m, 2H), 3.59 (t, *J* = 5.9 Hz, 1H), 3.55 (m, 4H), 3.51-3.48 (m, 2H), 2.65 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.11 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.93 (s, 3H), 1.78 (t, *J* = 12.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 170.6, 169.8, 169.3, 169.2, 167.9 ($^3J_{C\text{-}H}$ = 7.5 Hz), 140.3, 138.9, 138.0, 128.36, 128.1, 127.7, 127.4, 104.6, 97.7, 77.3, 75.8, 74.8, 73.5, 72.6, 71.9, 69.7, 69.2, 68.2, 67.9, 67.6, 61.8, 56.9, 56.2, 53.2, 36.3, 29.5, 20.8, 20.7, 20.3; ESIHRMS calcd for $C_{40}H_{49}O_{17}NSNa$ ($[M + Na]^+$) 870.2618, found 870.2619.

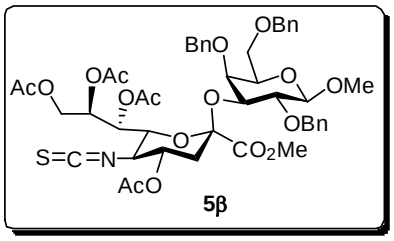
Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (5α):



5α

Compound **5** was prepared according to general glycosylation procedure using donor **2 (**300 mg, 0.5 mmol) and acceptor **10** (260 mg, 0. 6 mmol) in CH_2Cl_2/CH_3CN (6 mL, 2:1) at -78 ^oC. After chromatographic purification (gradient elution of EtOAc /Hexanes 2% to 20%), compound **5 (**380 mg, 87%) was obtained as a white foam. $[\alpha]^{20}_D$ = -23.0 (*c* =0.9, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ: 7.35-7.22 (m, 15H), 5.43-5.39 (m, 2H), 4.95 (dt, *J* = 10.3, 4.7 Hz, 1H), 4.84 (d, *J* = 11.7 Hz, 1H), 4.80 (d, *J* = 11.4 Hz, 1H), 4.64 (d, *J* = 11.4 Hz, 1H), 4.50 (d, *J* = 11.7 Hz, 1H), 4.44 (d, *J* = 11.4 Hz, 1H), 4.38 (d, *J* = 11.7 Hz, 1H), 4.30-4.26 (m, 2H), 3.99 (dd, *J* = 12.8, 3.7 Hz, 1H), 3.85 (d, *J* = 10.3 Hz, 1H), 3.74 (s, 3H), 3.68 (d, *J* = 2.6 Hz, 1H), 3.67-3.57 (m, 3H), 3.54 (m, 4H), 3.50 (t, *J* = 10.3 Hz, 1H), 2.58 (dd, *J* = 4.8, 13.6 Hz, 1H), 2.13 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 1.90 (s, 3H), 1.85 (t, *J* = 12.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 170.6, 169.6, 169.3, 169.2, 167.5 ($^3J_{C\text{-}H}$ = 7.0 Hz), 140.3, 139.0, 138.7, 137.9, 128.4, 128.1, 128.0, 127.8, 127.7, 127.6, 127.4, 127.2, 104.9, 98.77, 77.5,76.3, 76.2, 74.8, 73.5, 73.0, 71.6, 69.9, 68.4, 68.0, 67.5, 61.5, 57.0, 56.3, 53.0, 43.3, 35.5, 21.0, 20.8, 20.7, 20.3; ESIHRMS calcd for $C_{47}H_{55}O_{17}NSNa$ ($[M + Na]^+$) 960.3088, found 960.3090.

Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-D-*glycero*- β-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (5β):

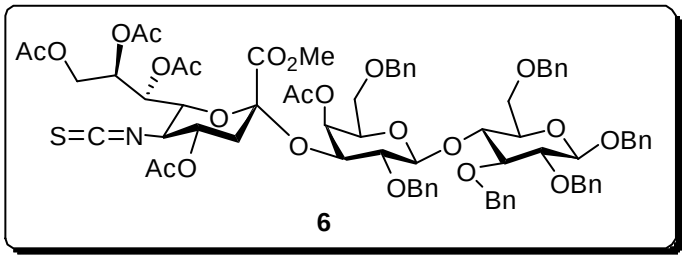


5β

Application of the general coupling protocol to donor **2** (30 mg, 0.05 mmol) and acceptor **10** (21 mg, 0.06 mmol) in neat dichloromethane at -30 ^oC gave the compound **5β (**9 mg, 20%) as a white foam after chromatography on silica gel eluting with EtOAc /Hexanes (2% to 20%). $[\alpha]^{20}_D$ = -12.5 (*c* =0.8, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ: 7.34-7.30 (m, 15H), 5.40 (m, 1H), 5.23 (m, 1H), 5.20 (m, 1H), 4.83 (d, *J* = 11.4 Hz, 1H), 4.77-4.74 (m, 2H), 4.64 (d, *J* = 11.4 Hz, 1H), 4.60 (d, *J* = 11.7 Hz, 1H), 4.55-4.48 (m, 2H), 4.26 (d, *J* = 7.7 Hz, 1H), 4.19 (m, 1H), 4.08-4.01 (m, 2H), 3.80-3.78 (m, 2H), 3.73-3.70 (m, 2H), 3.66-3.64 (m, 2H), 3.48 (s, 3H), 3.35 (s, 3H), 2.77 (dd, *J* = 4.8, 13.6 Hz, 1H), 2.12 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.73 (t, *J* =

11.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 170.5, 170.1, 169.3, 169.3, 166.4, 140.9, 138.4, 138.1, 128.6, 128.3, 128.0, 127.8, 127.6, 107.9, 105.0, 99.0, 73.4, 71.5, 69.9, 69.5, 69.4, 68.9, 67.7, 62.2, 61.6, 56.9, 56.6, 54.2, 52.6, 52.5, 36.6, 29.6, 20.9, 20.8, 20.7, 20.5 (C-1, $^3J_{C\text{-}1,H\text{-}ax}$ = 1.0 Hz); ESIHRMS calcd for $C_{47}H_{55}O_{17}NSNa$ ($[M + Na]^+$) 960.3088, found 960.3089.

Benzyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(2→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (6):

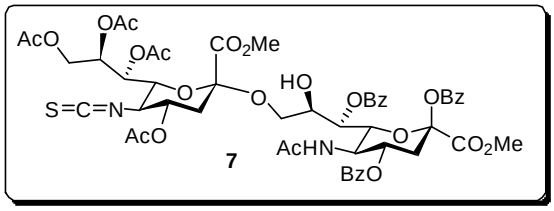


6

Compound **6** was prepared according to general glycosylation procedure using donor **2 (**30 mg, 0.05 mmol) and acceptor **11** (49.6 mg, 0.06 mmol) in CH_2Cl_2/CH_3CN (0.6 mL, 2:1) at -78 ^oC. The crude was dissolved in pyridine (1 mL) was treated with acetic anhydride (0.8 mL) then stirred overnight at room temperature. The reaction mixture was concentrated under reduced pressure. After chromatographic purification (gradient elution of EtOAc /Hexanes 2% to 20%) compound **6 (**34.8 mg, 55%) was obtained as a white foam. $[\alpha]^{25}_D$ = -21.3 (*c* = 0.3, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.38-7.14 (m, 30H; Ar-H), 5.58 (m, 1H), 5.44 (dd, *J* = 9.2, 1.8 Hz, 1H), 5.06 (d, *J* = 3.3 Hz, 1H), 5.01 (td, *J* = 9.9, 4.4 Hz, 1H), 4.96-4.85 (m, 4H), 4.75-4.67 (m, 3H), 4.62 (dd, *J* = 11.7, 2.7 Hz, 2H), 4.53 (d, *J* = 12.1 Hz, 1H), 4.43 (m, 2H), 4.36 (d, *J* = 11.7 Hz, 1H), 4.31 (dd, *J* = 9.9, 3.6 Hz, 1H), 4.26 (dd, *J* = 12.8, 2.2 Hz, 1H), 4.20 (d, *J* = 12.1 Hz, 1H), 4.07 (dd, *J* = 12.4, 4.0 Hz, 1H), 3.97 (t, *J* = 9.5 Hz, 1H), 3.84 (s, 3H), 3.77 (t, *J* = 9.9 Hz, 1H), 3.71 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.65 (dd, *J* = 11.0, 5.1 Hz, 1H), 3.60 (t, *J* = 6.9 Hz, 1H), 3.52 (m, 2H), 3.43 (m, 2H), 3.29 (m, 3H), 2.67 (dd, *J* = 12.8, 4.7 Hz, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.73 (s, 3H), 1.64 (t, *J* = 12.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 170.6, 169.7, 169.6, 169.2, 169.1, 167.2 ($^3J_{C\text{-}H}$ = 6.5 Hz), 140.1, 139.2, 139.1, 138.6,

138.5, 138.0, 137.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.6, 127.6, 127.5, 127.4, 127.3, 127.2, 127.2, 127.1, 127.1, 102.3, 102.0, 97.3, 82.7, 81.8, 79.1, 76.3, 75.0, 74.9, 74.7, 74.0, 73.2, 72.9, 71.5, 70.8, 70.0, 68.7, 68.6, 67.7, 67.5, 67.4, 61.7, 60.0, 56.2, 53.2, 36.8, 21.1, 20.8, 20.7, 20.6, 20.1; ESIHRMS calcd for $C_{75}H_{83}O_{23}NSNa$ ($[M + Na]^+$) 1420.4983, found 1420.4974.

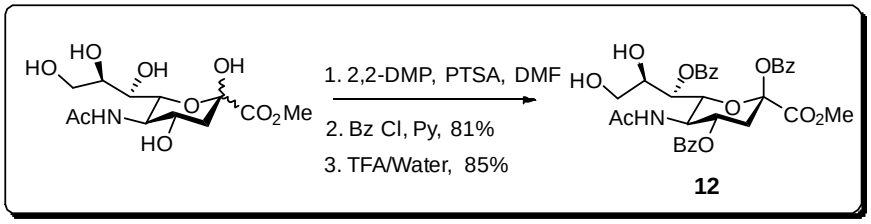
Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy--5-isothiocyanato-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-α(2→9)-[(5-acetamido-2,4,7-tri-*O*-benzoyl-3,5-dideoxy-2-α-D-*glycero*-D-*galacto*-2-nonulopyranose)onate] (7):



7

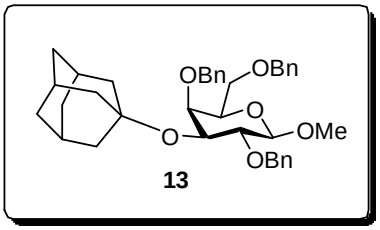
Compound **7** was prepared according to general glycosylation procedure using donor **2 (**30 mg, 0.05 mmol) and acceptor **12** (49.6 mg, 0.06 mmol) in CH_2Cl_2/CH_3CN (0.6 mL, 2:1) at -68 ^oC. After chromatographic purification (gradient elution of EtOAc /Hexanes 2% to 20%) compound **7 (**35 mg, 58%) was obtained as a white foam. $[\alpha]^{20}_D$ = -10.6 (*c* = 0.5, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ: 8.10 (dd, *J* = 7.7, 3.7 Hz, 4H), 7.95 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.53-7.44 (m, 5H), 7.37 (t, *J* = 7.7 Hz, 2H), 5.73 (td, *J* = 10.6, 4.7 Hz, 1H), 5.60 (d, *J* = 9.5 Hz, 1H), 5.39 (m, 2H), 5.16 (m, 1H), 4.82 (td, *J* = 9.9, 4.4 Hz, 1H), 4.57 (dd, *J* = 10.6, 1.5 Hz, 1H), 4.26 (m, 2H), 4.10 (dd, *J* = 12.5, 2.2 Hz, 1H), 4.00 (dd, *J* = 10.6, 1.5 Hz, 1H), 3.92 (dd, *J* = 12.8, 2.2 Hz, 1H), 3.83 (s, 3H), 3.68 (m, 4H), 3.46 (m, 2H), 2.88 (dd, *J* = 13.2, 5.1 Hz, 1H), 2.49 (dd, *J* = 13.2, 4.7 Hz, 1H), 2.17 (t, *J* =11.4 Hz, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.84 (s, 3H), 1.57 (t, *J* =12.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 170.8, 170.1, 169.8, 169.5, 169.4, 169.3, 167.4 ($^3J_{C\text{-}H}$ = 6.5 Hz), 166.3, 165.4, 164.6, 139.9, 134.0, 133.4, 133.1, 130.0, 130.0, 129.8, 129.2, 128.7, 128.8, 128.8, 98.54, 97.8, 71.9, 69.6, 69.5, 69.5, 68.3, 67.9, 67.8, 66.9, 61.7, 60.0, 56.2, 53.2, 52.9, 49.3, 37.1, 36.7, 29.6, 23.2, 21.0, 20.8, 20.4; ESIHRMS calcd for $C_{52}H_{56}O_{23}N_2SNa$ ($[M + Na]^+$) 1131.2860, found 1131.2892.

Methyl (5-acetamido-2,4,6-tri-*O*-benzoyl-3,5-dideoxy-D-β-*glycero*-D-*galacto*-2-nonulopyranose)onate (12):



A stirred solution of methyl ester of *N*-acetylneuraminic acid[4] (1.5 g, 4.64 mmol) in anhydrous dimethylformamide (15 mL) was treated with 2,2-dimethoxypropane (1.2 g, 11.5 mmol) and p-toluenesulfonic acid (15 mg) at room temperature. The resulting reaction mixture was stirred at 80 ºC for 2 h. The solvent was evaporated under reduced pressure, taken up in pyridine (14 mL) and treated at 0 ºC with benzoyl chloride (3.9 g, 27.7 mmol). After stirring for 1 h at 0 ºC, the volatiles were removed under reduced pressure and the residue was dissolved in dichloromethane (10 mL) and was washed with 0.1 N HCl (10 mL), saturated aqueous $NaHCO_3$ (2 x 5 mL), and brine (5 mL). The organic layer was concentrated to afford a yellow form which was treated with TFA (2.3 mL, 80 %) at room temperature for 10 min. The resulted compound was extracted into dichloromethane (10 mL) and was washed with saturated aqueous $NaHCO_3$ (10 mL), water (10 mL) and brine (5 mL). The organic layer was concentrated to afford a yellow oil that was purified by chromatography on silica gel (EtOAc/Hexanes 5% to 80%) to afford **12**[5] (480 mg, 85%) as a white foam. $[\alpha]_D^{26}$= -71 (*c* = 0.4, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.10 (m, 4H), 7.95 (d, *J* = 7.3 Hz, 2H), 7.59 (m, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.47 (m, 4H), 7.38 (t, *J* = 7.7 Hz, 2H), 5.64 (m, 2H), 5.27 (d, *J* = 8.8 Hz, 1H), 4.48 (m, 2H), 4.09 (d, *J* = 7.7 Hz, 1H), 3.85 (s, 3H), 3.65 (m, 1H), 3.51 (m, 1H), 2.91 (dd, *J* = 13.2, 4.4 Hz, 1H), 2.28 (t, *J* =11.7 Hz, 1H), 1.79 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 170.1, 166.9, 166.7 ($^3J_{C\text{-}H}$ = 0 Hz), 166.6, 164.9, 129.7, 129.4, 129.0, 128.7, 128.5, 128.4, 98.0, 72.7, 69.4, 69.3, 69.2, 62.5, 53.3, 49.5, 37.0, 23.0; ESIHRMS calcd for $C_{33}H_{33}O_{12}N$ ($[M + Na]^+$) 658.1901, found 658.1888.

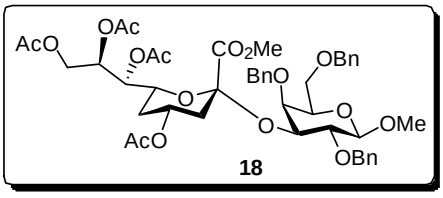
Methyl 3-*O*-(1-adamantyl)-2,4,6-tri-*O*-benzyl-*β*-D-galactopyranoside (13):



13

Application of the general coupling protocol to donor **2** (30 mg, 0.05 mmol) and acceptor **10** (21 mg, 0.06 mmol) in neat dichloromethane at -30 ^{o}C gave the 1-adamanantyl ether **13** (7 mg, 27%) yield as an oil solid after chromatography on silica gel eluting with EtOAc /Hexanes (2% to 20%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.40-7.26 (m, 15H), 4.57 (d, *J* = 11.7 Hz, 1H), 4.76 (dd, *J* = 10.7, 2.3 Hz, 2H), 4.63 (d, *J* = 11.7 Hz, 1H), 4.43 (dd, *J* = 12.2, 7.2 Hz, 2H), 4.25 (d, *J* = 7.8 Hz, 1H), 3.78 (m, 1H), 3.65-3.56 (m, 5H), 3.50 (s, 3H), 2.11 (m, 3H), 1.85-1.82 (d, *J* = 11.7 Hz, 3H), 1.76-1.73 (d, *J* = 11.7 Hz, 3H), 1.63-1.54 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 128.3, 128.2, 128.2, 127.9, 127.7, 127.3, 105.2, 73.8, 73.5, 72.5, 69.1, 57.0, 42.6, 36.3, 30.5; ESIHRMS calcd for $C_{38}H_{46}O_6Na$ ($[M + Na]^+$) 621.3192, found 621.3195.

Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy--α-D-*gluco*-2-nonulopyranosyl)onate]-(2→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (18):

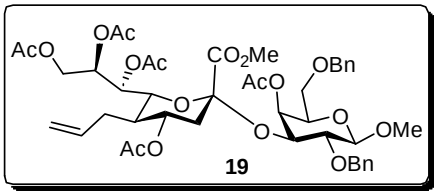


18

To a solution of **5** (50 mg, 0.05 mmol) in anhydrous toluene (1.5 mL) under Ar was added tris(trimethylsilylsilane) (65 mg, 0.26 mmol) followed by azoisobutyronitrile (1 mg, 0.006 mmol) at room temperature. The resulting reaction mixture was stirred at 85 ºC for 1 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography eluting with 30% EtOAc in hexanes to give the title compound **18** (36 mg, 78%) as a yellow foam. $[\alpha]_D^{25}$= -7.4 (*c* = 2.3, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 6.9 Hz, 2H), 7.34-7.20 (m, 13H), 5.44 (m, 1H), 5.17 (dd, *J* = 8.4, 2.2 Hz, 1H), 4.91 (d, *J* = 11.7 Hz, 1H), 4.82 (m, 2H), 4.71 (d, *J* = 11.3 Hz , 1H), 4.52 (d, *J* = 11.7 Hz, 1H), 4.48 (d, *J* = 11.3 Hz, 1H), 4.41 (d, *J* = 11.7 Hz, 1H), 4.32 (d, *J* = 7.7 Hz, 1H), 4.29 (dd, *J* = 12.8, 2.5 Hz, 1H), 4.05 (m,

2H), 3.94 (dt, *J* = 12.1, 1.8 Hz, 1H), 3.73 (d, *J* = 2.5 Hz, 1H), 3.68 (s, 3H), 3.67-3.57 (m, 4H), 3.54 (s, 3H), 2.50 (dd, *J* = 11.7, 4.4 Hz, 1H), 2.10 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H), 1.92 (s, 3H), 1.89 (m, 1H), 1.80 (t, *J* = 12.4 Hz, 1H), 1.24 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 170.4, 169.9, 169.8, 169.6, 168.3, 139.2, 138.9, 138.1, 128.3, 128.0, 127.9, 127.8, 127.7, 127.2, 127.0, 104.9, 99.5, 77.6, 76.6, 75.8, 74.8, 73.4, 73.2, 70.6, 69.4, 68.8, 68.4, 67.1, 61.7, 60.0, 57.0, 52.6, 36.1, 32.0, 21.0, 20.9, 20.6, 20.4; ESIHRMS calcd for $C_{46}H_{56}O_{17}Na$ ($[M + Na]^+$) 903.3415, found 903.3432.

Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-5-*C*-allyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (19):

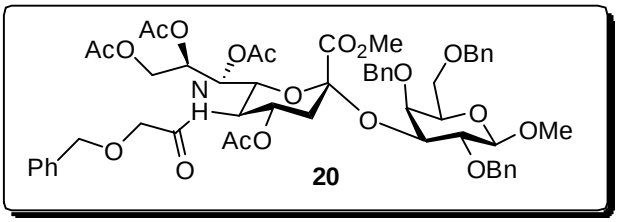


19

Acetic anhydride (1.0 mL) added to a solution of **4** (60 mg, 0.07 mmol) in pyridine (1.5 mL) at 0 ºC and the resulting reaction mixture stirred for 4 h. The reaction mixture was concentrated under reduced pressure and was purified by chromatography to give a pentaacetate which was taken forward to the next step without further characterization. To a solution of this pentaacetate (62 mg) in anhydrous benzene (1.0 mL) under Ar was added allyltris(trimethylsilylsilane) (502 mg, 1.74 mmol) followed by azoisobutyronitrile (11.4 mg, 0.04 mmol) at room temperature. The resulting reaction mixture was stirred at 80 ºC for 12 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography eluting with 30% EtOAc in hexanes to give the title compound **19** (27 mg, 45%) as yellow foam. $[\alpha]_D^{25}$= -2.2 (*c*= 0.7, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 7.7 Hz, 2H), 7.32-7.20 (m, 8H), 5.62 (m, 1H), 5.57 (m, 1H), 5.42 (d, *J* = 8.4 Hz, 1H), 5.05 (d, *J* = 3.3 Hz, 1H), 5.02 (m, 2H), 4.86 (td, *J* = 11.4, 4.7 Hz, 1H), 4.80 (m, 2H), 4.52 (d, *J* = 11.7 Hz, 1H), 4.45 (d, *J* = 12.1 Hz, 1H), 4.44 (d, *J* = 8.4 Hz, 1H), 4.38 (dd, *J* = 9.4, 2.9 Hz, 1H), 4.30 (dd, *J* = 12.4, 1.8 Hz, 1H), 4.10 (dd, *J* = 12.8, 4.0 Hz, 1H), 3.80 (m, 3H), 3.67 (d, *J* = 11.0 Hz, 1H), 3.56 (s, 3H), 3.53-3.41 (m, 4H), 2.57 (dd, *J* = 12.1, 4.4 Hz, 1H), 2.22 (dd, *J* = 14.3, 3.6 Hz, 1H), 2.10 (s, 3H), 2.08 (m, 1H), 2.03

(s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.76 (s, 3H), 1.59 (t, *J* = 12.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 170.6, 170.0, 170.0, 169.8, 169.7, 168.2, 139.6, 138.0, 133.2, 128.2, 127.9, 127.6, 127.5, 127.1, 126.9, 117.7, 104.5, 97.0, 78.1, 74.3, 73.4, 72.7, 72.0, 72.0, 69.3, 69.2, 68.7, 68.5, 68.0, 62.1, 57.3, 52.7, 38.9, 37.6, 30.3, 21.2, 20.9, 20.8, 20.7, 20.3; ESIHRMS calcd for $C_{44}H_{56}O_{18}Na$ ($[M + Na]^+$) 895.3364, found 895.3358.

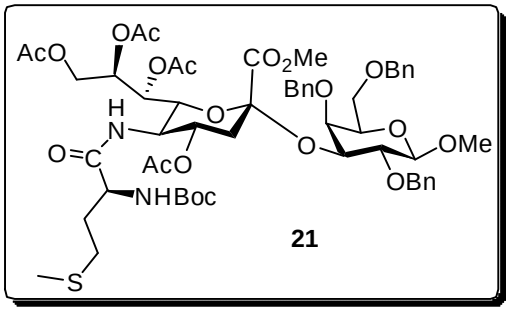
Methyl [methyl (4,7,8,9-tri-*O*-acetyl-5-(benzyloxyacetamido)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (20):



20

Compound **20** was prepared according to general protocol for amide formation using isothiocyanate **5 (**0.03 g, 0.05 mmol) and Fm thioester **30** (49.6 mg, 0.06 mmol) in CH_2Cl_2 (0.5 mL) at 40 ^{o}C. After chromatographic purification (gradient elution of EtOAc/Hexanes 4% to 40%) compound **20 (**20 mg, 61%) was obtained as a white foam. $[\alpha]^{20}_{D}$ = -5.3 (*c* = 0.3, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.40-7.19 (m, 20H), 6.31 (d, *J* = 10.3 Hz, 1H), 5.47 (m, 1H), 5.29 (dd, *J* = 8.8, 2.2 Hz, 1H), 4.89 (dt, *J* = 11.7, 4.7 Hz, 1H), 4.86 (d, *J* = 11.7 Hz, 1H), 4.82 (d, *J* = 12.1 Hz, 1H), 4.72 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.53 (d, *J* = 11.7 Hz, 1H), 4.49 (d, *J* = 11.7 Hz, 2H), 4.42 (d, *J* = 11.7 Hz, 1H), 4.34 (d, *J* = 7.3 Hz, 1H), 4.28 (dd, *J* = 12.4, 2.5 Hz, 1H), 4.10 (m, 2H), 3.95 (dd, *J* = 12.4, 4.7 Hz, 1H), 3.92-3.81 (m, 4H), 3.70 (s, 3H), 3.68-3.59 (m, 4H), 3.53 (s, 3H), 2.52 (dd, *J* = 13.1, 4.7 Hz, 1H), 2.12 (s, 3H), 2.05 (t, *J* = 13.1, 1H), 1.98 (s, 3H), 1.95 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 170.4, 170.3, 170.2, 169.8, 169.7, 168.2, 139.1, 138.1, 136.7, 128.8-126.9, 104.8, 98.8, 77.6, 76.3, 76.2, 74.8, 74.6, 73.5, 73.4, 73.0, 72.1, 69.1, 68.6, 68.5, 67.0, 62.0, 57.1, 52.8, 48.4, 36.7, 29.6, 21.1, 20.7, 20.7, 20.6; ESIHRMS calcd for $C_{55}H_{65}NO_{19}Na$ ($[M + Na]^+$) 1066.4049, found 1066.4042.

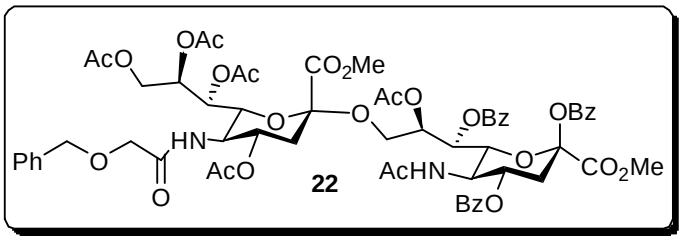
Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-(L-methioninamido)-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (21):



21

Compound **21** was prepared according to general amide formation procedure using isothiocyanate **5 (**30 mg, 0.02 mmol) and 9-fluorenylmethyl thioester of *N*-*tert*-Butoxycarbonyl-L-methionine[2a] (12 mg, 0.06 mmol) in CH_2Cl_2 (0.5 mL) at 40 ^oC. After chromatographic purification (gradient elution of EtOAc /Hexanes 10% to 90%) compound **21 (**18 mg, 52%) was obtained as a white foam. $[\alpha]^{25}_D$ = -13.8 (*c* = 0.5, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ: 7.38 (d, *J* = 7.3 Hz, 2H), 7.34-7.19 (m, 15H), 6.10 (d, *J* = 9.5 Hz, 1H), 5.46 (m, 1H), 5.17 (d, *J* = 8.4 Hz, 1H), 5.06 (d, *J* = 5.8 Hz, 1H), 4.90-4.84 (m, 2H), 4.82 (d, *J* = 11.7 Hz, 1H), 4.71 (d, *J* = 11.7 Hz, 1H), 4.48 (d, *J* = 11.7 Hz, 2H), 4.42 (d, *J* = 11.7 Hz, 1H), 4.34 (d, *J* = 7.3 Hz, 1H), 4.22 (d, *J* = 12.1 Hz, 1H), 4.14 (q, *J* = 7.3 Hz, 1H), 4.08 (dd, *J* = 9.9, 2.5 Hz, 1H), 4.04-3.94 (m, 2H), 3.90 (d, *J* = 7.3 Hz, 1H), 3.73 (d, *J* = 11.3 Hz, 1H), 3.72 (s, 3H), 3.70-3.63 (m, 2H), 3.64-3.58 (m, 3H), 3.53 (s, 3H), 2.53 (dd, *J* = 13.2, 4.7 Hz, 1H), 2.10 (s, 6H), 2.03 (t, *J* = 8.4 Hz, 1H), 2.00 (s, 3H), 1.96 (s, 3H), 1.90 (s, 3H), 1.80 (m, 1H), 1.47 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 171.7, 170.4, 170.2, 169.9, 169.6, 168.1, 156.1, 139.2, 138.1, 128.3, 128.0, 127.9, 127.7, 127.6, 127.6, 127.6, 127.1, 127.0, 104.9, 98.5, 80.5, 77.63, 76.3, 76.2, 74.8, 74.6, 73.4, 73.0, 72.1, 68.8, 68.6, 68.4, 67.2, 62.1, 60.0, 57.0, 52.7, 53.6, 48.8, 36.5, 30.1, 29.6, 28.3, 21.0, 20.8, 20.7, 20.6, 15.0; ESIHRMS calcd for $C_{56}H_{74}O_{20}N_2SNa$ ($[M + Na]^+$) 1149.4453, found 1149.4462.

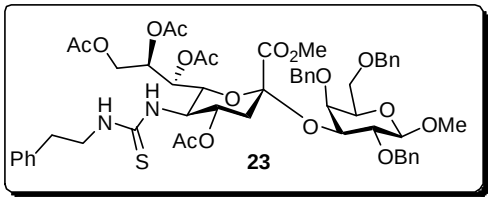
Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-5-(benzyloxyacetamido)-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-α(2→9)-[5-acetamido-8-*O*-acetyl-2,4,7-tri-*O*-benzoyl-3-deoxy-2-α-D-*glycero*-D-*galacto*-nonulopyranosel)onate] (22):



22

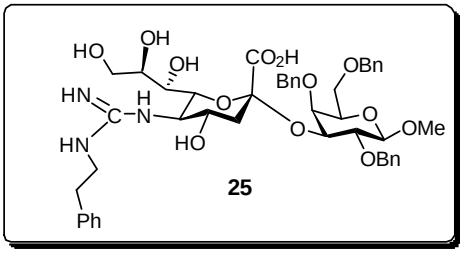
Acetic anhydride (0.8 mL) added to a solution of compound **7** (24 g, 0.02 mmol) in pyridine (1.0 mL) at 0 ºC and the resulting reaction mixture stirred for 4 h. The reaction mixture was concentrated under reduced pressure and was purified by chromatography to give a pentaacetate which was taken forward to the next step without further characterization. Compound **22** was prepared according to general amide formation procedure using isothiocyanate **7-Ac** (24 mg) and Fm thioester **30** (12 mg, 0.06 mmol) in CH_2Cl_2 (0.5 mL) at 40 ^oC. After chromatographic purification (gradient elution of EtOAc/Hexanes 10% to 90%), compound **22 (**12 mg, 46%) was obtained as a white foam. $[\alpha]^{25}_D$ = -13.3 (*c* = 0.6, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 7.7 Hz, 2H), 8.13 (d, *J* = 7.7 Hz, 2H), 7.95 (d, *J* = 7.7 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.54-7.45 (m, 5H), 7.40-7.30 (m, 7H), 6.22 (d, *J* = 10.3 Hz, 1H), 5.97 (dt, *J* = 10.6, 4.7 Hz, 1H), 5.78 (d, *J* = 8.8 Hz, 1H), 5.66 (d, *J* = 8.4 Hz, 1H), 5.32 (m, 1H), 5.21 (dd, d, *J* = 8.4, 1.8 Hz, 1H), 4.93 (m, 1H), 4.75 (dt, *J* = 10.2, 4.4 Hz, 1H), 4.64 (d, *J* = 10.6 Hz, 1H), 4.55 (d, *J* = 11.7 Hz, 1H), 4.50 (d, *J* = 11.7 Hz, 1H), 4.06-3.96 (m, 2H), 3.93-3.85 (m, 4H), 3.84-3.80 (m, 5H), 3.71 (s, 3H), 3.67 (dd, *J* = 12.8, 4.7 Hz, 1H), 3.57 (dd, *J* = 11.3, 2.9 Hz, 1H), 2.91 (dd, *J* = 13.5, 5.1 Hz, 1H), 2.46 (dd, *J* = 13.2, 4.7 Hz, 1H), 2.18 (t, *J* = 13.2 Hz, 1H), 2.07 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H), 1.93 (s, 3H), 1.84 (t, *J* =12.8 Hz, 1H), 1.71 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 170.6, 170.3, 170.3, 170.1, 169.7, 169.7, 169.1, 167.8, 166.6, 166.0, 165.4, 163.5, 136.7, 133.8, 133.3, 130.1, 130.0, 129.7, 129.3, 129.3, 128.7, 128.6, 128.5, 128.4, 128.2, 128.0, 98.3, 97.8, 73.4, 72.2, 70.9, 69.6, 69.1, 68.9, 68.5, 67.9, 67.8, 66.6, 62.4, 61.7, 60.0, 53.0, 52.7, 50.8, 48.2, 37.5, 36.5, 23.5, 21.0, 20.7, 20.7, 20.4; ESIHRMS calcd for $C_{62}H_{68}N_2O_{26}Na$ ($[M + Na]^+$) 1279.3928, found 1279.3939.

Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-5-(*N*'-(2-phenylethyl)thioureido)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-[2,4,6-tri-*O*-benzyl-β-D-galactopyranoside] (23):



To a solution of isothiocyanate **5** (65 mg, 0.06 mmol) in anhydrous DCM (1.8 mL) under Ar was added 2-phenylethylamine (10 mg, 0.8 mmol) at room temperature. The resulting reaction mixture was stirred at room temperature for 1 h, then quenched with 1N HCl and washed with water (2 mL), and brine (2.0 mL). The solvent was evaporated under reduced pressure to give the title compound **23** (72 mg, 90%) as yellow foam. $[\alpha]_D^{25}$= -9.4 (*c* = 0.4, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 7.3 Hz, 3H), 7.36-7.19 (m, 17H), 6.24 (br s, 1H), 5.40 (td, *J* = 7.7, 2.2 Hz, 1H), 5.27 (m, 1H), 4.95 (br s, 1H), 4.89 (d, *J* = 11.3 Hz, 1H), 4.84 (d, *J* = 12.1 Hz, 1H), 4.72 (d, *J* = 11.7 Hz, 1H), 4.50 (t, *J* = 11.7 Hz, 2H), 4.43 (d, *J* = 11.7 Hz, 2H), 4.34 (d, *J* = 7.7 Hz, 1H), 4.12 (d, *J* = 8.8 Hz, 1H), 3.98 (dd, *J* = 12.4, 6.2 Hz 1H), 3.89 (m, 1H), 3.70 (d, *J* = 2.2 Hz, 1H), 3.68 (s, 3H), 3.67-3.59 (m, 4H), 3.54 (s, 3H), 2.85 (m, 2H), 2.46 (dd, *J* = 13.2, 4.0 Hz, 1H), 2.14 (m, 1H), 2.09 (s, 3H), 1.96 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 171.2, 170.4, 170.4, 170.1, 169.9, 168.2, 139.2, 138.1, 128.7, 128.3, 127.9, 127.8, 127.7, 127.6, 127.6, 127.1, 127.1, 126.6, 104.6, 98.9, 77.5, 76.4, 76.2, 74.8, 74.6, 73.4, 73.0, 72.5, 70.0, 69.6, 68.6, 67.5, 62.1, 60.0, 57.1, 54.5, 52.7, 36.0, 34.9, 21.3, 21.1, 20.9, 20.7; ESIHRMS calcd for $C_{55}H_{66}O_{17}N_2SNa$ ($[M + Na]^+$) 1081.3938, found 1081.3980.

Methyl [5-(*N*'-(2-phenylthyl)guanidino)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulo-pyranosylonate]-(2→3)-[2,4,6-tri-*O*-benzyl-β-D-galactopyranoside] (25):

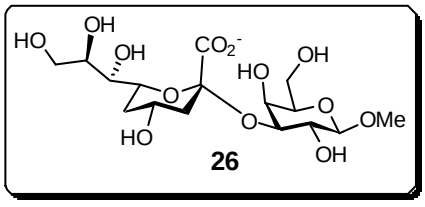


25

To a solution of thiourea **23** (83 mg, 0.07 mmol) in anhydrous dichloromethane (2.0 mL) under Ar was added DMAP (1 mg, 0.008 mmol) followed by DIPEA (50 mg, 0.38 mmol) at room temperature. The resulting reaction mixture was treated with methyl iodide (33 mg, 0.23 mmol) drop wise and stirred at room temperature for 30 h, then quenched with 0.1N HCl (2.0 mL) and was washed with water (2.0 mL), and brine (2.0 mL). The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography eluting with 30%

EtOAc in hexanes to give the isothiourea **24**[6] (57 mg, 56%) as a colorless liquid, which was taken forward to the next step without further characterization. A stirred solution of compound **24** (33 mg, 0.03 mmol) in anhydrous dimethylformamide (1.5 mL) was transferred into a glass tube and cooled to -33 °C. Dry gaseous ammonia was then passed into the reaction for for 5min ,after which the reaction mixture was stirred at 0 °C for 5 min to enable evaporation of excess ammonia. The glass tube was sealed and the reaction was stirred at 130 °C for 36 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography (eluent: gradient elution of 5-60% ammonical methanol in EtOAc) to give the title compound **25** (11 mg, 49%) as a colorless oil. $[\alpha]_D^{25}$= -10.1 (*c* 0.7, dichloromethane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.46 (d, *J* = 7.3 Hz, 3H), 7.36-7.16 (m, 17H), 5.00 (d, *J* = 11.3 Hz, 1H), 4.84 (d, *J* = 11.3 Hz, 1H), 4.75 (d, *J* = 11.3 Hz, 1H), 4.60 (br s, 1H), 4.56 (d, *J* = 11.7 Hz, 1H), 4.39 (d, *J* = 11.7 Hz, 1H), 4.35-4.29 (m, 2H), 4.25 (d, *J* = 7.7 Hz, 1H), 3.96 (d, *J* = 2.2 Hz, 1H), 3.93 (m, 1H), 3.78 (dd, *J* = 11.3, 2.5 Hz, 2H), 3.65-3.60 (m, 2H), 3.60-3.54 (m, 2H), 3.54 (t, *J* = 7.7 Hz, 1H), 3.49 (m, 4H), 3.42 (m, 1H), 3.39-3.34 (m, 2H), 3.30 (m, 1H), 2.89 (dd, *J* = 12.4, 4.7 Hz, 1H), 2.81 (m, 2H), 1.79 (t, *J* = 12.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 173.3, 157.4, 139.1, 138.6, 137.9, 137.8, 128.4, 128.2, 128.2, 128.0, 127.9, 127.8, 127.7, 127.5, 127.2, 127.1, 127.0, 126.32, 104.5, 100.1, 78.1, 75.8, 75.1, 74.9, 74.7, 73.2, 72.8, 72.6, 71.8, 69.1, 68.9, 62.8, 60.0, 55.9, 48.0, 42.8, 40.5, 34.5; ESIHRMS calcd for $C_{46}H_{58}O_{13}N_3$ ($[M + H]^+$) 860.3970, found 860.3945.

Methyl [Sodium (3,5-dideoxy-α-D-*gluco*-2-nonulopyranosyl)onate]-(2→3)-[β-D-galactopyranoside] (26):

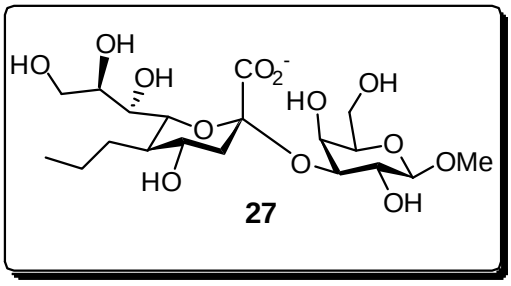


26

Sodium methoxide (3 mg, 0.05 mmol) was added to a solution of compound **18** (26 mg, 0.03 mmol) in MeOH (1.0 mL). After stirring for 1 h at room temperature, the mixture was diluted with MeOH (1 mL) and 2N NaOH (0.2 mL) and refluxed at 70 °C, for 2 h. The solution was neutralized with Amberlyst-15, filtered through small plug of Celite, and the filter plug washed

with MeOH (2 mL). The combined filtrates were concentrated under reduced pressure to furnish a residue, which was taken up in phosphate buffer (*p*H =7, 1.0 mL) treated with 5% Pd on carbon (30 mg), and stirred at room temperature for 15 h under 1 atm of H_2. The reaction mixture was filtered through Celite, and the filtrate was concentrated in vacuo. The residue was purified by chromatography on a Sephadex G-10 column (eluent: water) and then by chromatography on Dowex 50 WX8-100 sodium ion exchanger eluting with water. The resulting solution was frozen in a dry-ice/acetone bath, and then lyophilized to give compound **26** (11.5 mg, 91%) as a white foam. $[\alpha]^{20}_{D}$ = -12.3 (*c* = 0.7, H_2O); ^{1}H NMR (600 MHz, D_2O) δ: 4.17 (d, *J* = 8.1 Hz, 1H), 3.86 (dd, *J* = 9.5, 2.9 Hz, 1H), 3.72 (d, *J* = 2.9 Hz, 1H), 3.69-3.63 (m, 3H), 3.61 (d, *J* = 12.1 Hz, 1H), 3.57-3.50 (m, 2H), 3.48-3.41 (m, 2H), 3.37 (br s, 1H), 3.36 (s, 3H), 3.31 (t, *J* = 9.5 Hz, 1H), 2.46 (dd, *J* = 11.7, 3.6 Hz, 1H), 1.62 (d, *J* = 9.9 Hz, 1H), 1.33 (t, *J* = 11.7 Hz, 1H), 1.30 (d, *J* = 12.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 174.3, 103.4, 100.0, 75.4, 74.8, 72.1, 71.2, 71.0, 69.0, 67.4, 65.3, 62.3, 60.8, 56.8, 40.2, 33.9; ESIHRMS calcd for $C_{16}H_{27}O_{13}$ ($[M - H]^-$) 427.1452, found 427.1461.

Methyl [sodium (3,5-dideoxy-5-*C*-propyp-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-β-D-galactopyranoside (27):

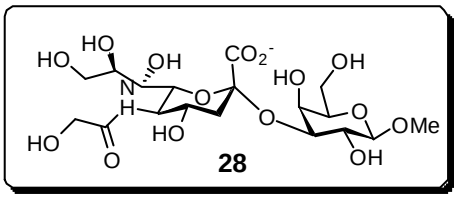


27

Sodium methoxide (1.7 mg, 0.03 mmol) was added to a solution of compound **19** (14 mg, 0.02 mmol) in MeOH (0.5 mL). After 30 min of stirring at room temperature, the mixture was diluted with MeOH (1 mL) and 2N NaOH (0.2 mL) and refluxed at 70 °C, for 2h. The solution was neutralized with amberlyst-15 and filtered through small plug of celite and was washed with MeOH (2 mL). The solution was then concentrated under reduced pressure to furnish a crude residue. The solution of the deacetylated product in phosphate buffer (*p*H =7, 0.5 mL) with suspended 5% Pd on carbon (17 mg) was stirred at room temperature for 8 h under H2 atmosphere. The whole mixture was filtered through celite, and the filtrate was concentrated in

vacuo. The residue was purified through a Sephadex G-10 column and passed through Dowex 50 WX8-100 sodium ion exchanger both using water as eluent. The resulting solution was frozen in a dry-ice/acetone bath, and then lyophilized to get compound **27** (7 mg, 93%) as a white foam. $[\alpha]^{20}_{D}$ = -18.2 (*c* = 0.5, H_2O); ^{1}H NMR (600 MHz, D_2O) *δ*: 4.19 (d, *J* = 8.1 Hz, 1H), 3.89 (dd, *J* = 9.9, 3.3 Hz, 1H), 3.73 (d, *J* = 2.9 Hz, 1H), 3.72-3.68 (m, 2H), 3.55 (m, 4H), 3.49 (dd, *J* = 8.4, 4.0 Hz, 2H), 3.47-3.42 (m, 2H), 3.38 (s, 3H), 3.33 (t, *J* = 8.1 Hz, 1H), 2.47 (dd, *J* = 12.1, 4.4 Hz, 1H), 1.43 (t, *J* = 11.7 Hz, 1H), 1.31 (m, 1H), 1.24 (m, 1H), 1.16 (m, 1H), 1.01 (m, 1H), 0.69 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 174.5, 103.4, 99.4, 75.3, 74.8, 73.7, 72.3, 69.0, 68.4, 67.8, 67.3, 62.5, 60.8, 60.0, 56.8, 41.4 , 27.3 , 17.6 , 13.9; ESIHRMS calcd for $C_{19}H_{33}O_{13}$ ($[M - H]^-$) 469.1921, found 469.1907.

Methyl [sodium (3-dideoxy-5-(glyceramido)-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-β-D-galactopyranoside (28):

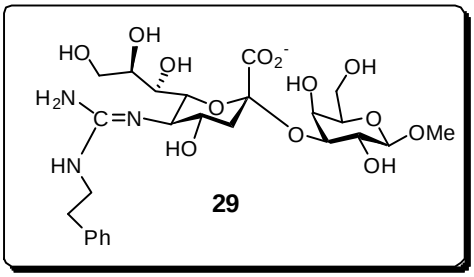


28

Sodium methoxide (1.6 mg, 0.02 mmol) was added to a solution of compound **20** (16 mg, 0.015 mmol) in MeOH (0.5 mL). After 30 min of stirring at room temperature, the mixture was diluted with MeOH (1 mL) and 2N NaOH (0.2 mL) and refluxed at 70 °C, for 2h. The solution was neutralized with amberlyst-15 and filtered through small plug of celite and was washed with MeOH (2 mL). The solution was then concentrated under reduced pressure to furnish a crude residue. The solution of the deacetylated product in phosphate buffer (*p*H =7, 0.5 mL) with suspended 5% Pd on carbon (30 mg) was stirred at room temperature for 20h under H_2 atmosphere. The whole mixture was filtered through celite, and the filtrate was concentrated in vacuo. The residue was purified through a Sephadex G-10 column and passed through a Dowex 50 WX8-100 sodium ion exchanger both using water as eluent. The resulting solution was frozen in a dry-ice/acetone bath, and then lyophilized to get compound **28** (7 mg, 91%) as a white foam. $[\alpha]^{25}_{D}$ = +0.4 (*c* = 0.5, H_2O); ^{1}H NMR (600 MHz, D_2O) *δ*: 4.18 (d, *J* = 8.1 Hz, 1H), 3.91 (s, 2H), 3.89 (dd, *J* = 9.9, 3.3 Hz, 1H), 3.74 (d, *J* = 2.9 Hz, 1H), 3.72 (d, *J* = 10.2 Hz, 1H),

3.67 (m, 2H), 3.59 (dd, *J* = 11.3, 4.4 Hz, 1H), 3.63-3.50 (m, 3H), 3.47 (m, 1H), 3.43 (dd, 1H), 3.38 (d, *J* = 9.2 Hz, 1H), 3.36 (s, 3H), 3.33 (t, *J* = 8.1 Hz, 1H), 2.57 (dd, *J* = 12.1, 4.4 Hz, 1H), 1.60 (t, *J* = 12.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 175.6, 173.7, 103.8, 99.6, 75.7, 74.8, 72.4, 71.7, 69.0, 67.9, 67.8, 67.3, 62.3, 60.8, 60.8, 56.8, 51.2, 39.5; ESIHRMS calcd for $C_{18}H_{30}O_{15}N$ ([M - H]$^-$) 500.1615, found 500.1633.

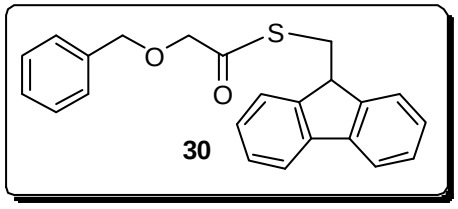
Methyl [sodium (3-dideoxy-5-(*N*'-(2-phenylethyl)guanidino)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)-β-D-galactopyranoside (29):



29

The solution of **26** (15 mg, 0.02 mmol) in methanol (1 mL) was treated with 5% Pd on carbon (30 mg) was stirred at room temperature for 10 h under 1 atm of H_2. The mixture was filtered through Celite, and the filtrate was concentrated in vacuo. The residue was purified through a Sephadex C-25 column and passed through a Dowex 50 WX8-100 sodium ion exchanger both using water as eluent. The resulting solution was frozen in a dry-ice/acetone bath, and then lyophilized to get compound **29** (5.2 mg, 52%) as white foam. $[\alpha]^{20}_D$ = -10.7 (*c* = 0.1, H_2O); ^{1}H NMR (600 MHz, D_2O) *δ*: 7.21 (t, *J* = 7.3 Hz, 2H), 7.13 (m, 3H), 4.19 (d, *J* = 7.7 Hz, 1H), 3.89 (dd, *J* = 9.9, 2.9 Hz, 1H), 3.76-3.70 (m, 2H), 3.68 (dd, *J* = 12.1, 2.5 Hz, 1H), 3.60-3.51 (m, 3H), 3.50-3.43 (m, 4H), 3.38 (s, 3H), 3.37-3.30 (m, 3H), 3.21 (t, *J* = 9.2 Hz, 1H), 2.72 (dt, *J* = 6.6, 1.8 Hz, 2H), 2.57 (dd, *J* = 12.4, 4.7 Hz, 1H), 1.55 (t, *J* = 12.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 173.4, 156.4, 138.4, 128.8, 128.7, 126.9, 103.4, 99.4, 75.6, 74.7, 72.5, 71.9, 69.0, 68.4, 68.1, 67.1, 62.3, 60.8, 56.9, 54.3 , 42.6, 39.8, 34.2; ESIHRMS calcd for $C_{25}H_{40}O_{13}N_3$ ([M - H]$^-$) 588.2405, found 588.2422.

***S*-(9-Fluorenylmethyl) benzyloxythioacetate (30):**



30

To a ~2.0 M solution of 2-(benzyloxy)acetic acid (60 mg, 0.36 mmol), 9-fluorenylmethylthiol[2a] (100 mg, 0.47 mmol) and DMAP (5mg, 0.04 mmol) in CH_2Cl_2 (1 mL), was added a solution of DCC (82 mg, 0.39 mmol) in CH_2Cl_2 (0.4 mL) at 0 ºC**.** The suspension was stirred for 1 h at 0 ºC and overnight at room temperature. The suspension was filtered to remove the resulting white solid which was washed with CH_2Cl_2 (2 mL**)** repeatedly. The filtrate was concentrated and purified by chromatography over silica gel to give the title thioester (30) as a colorless oil (128 mg, 98%). $\alpha]_D^{26}$= +30.0 (*c* = 1.2, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.76 (d, *J* = 7.7 Hz, 2H), 7.69 (d, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.39-7.29 (m, 7H), 4.48 (s, 2H), 4.22 (t, *J* = 5.9 Hz, 1H), 4.10 (s, 2H), 3.59 (d, *J* = 5.9 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 199.7, 145.4, 141.2, 136.8, 128.5, 128.1, 128.1, 127.7, 127.2, 124.7, 119.9, 74.7, 73.7, 46.7, 31.1; ESIHRMS calcd for $C_{23}H_{20}O_2SNa$ ($[M + Na]^+$) 383.1082, found 383.1073.

Competition reaction:

A solution of isothiocyanate donor **2** (42 mg, 0.06 mmol), *N*-acetyl-5-*N*,4-*O*-oxazolidinone-protected adamantanyl thiosialoside donor **16**[7] (41 mg, 0.06 mmol), acceptor **10** (30.4 mg, 0.06 mmol) and activated 4 Å acid-washed powdered molecular sieves (150 mg) in anhydrous CH_2Cl_2:MeCN (2:1, 0.5 mL) was stirred for 0.5 h under Ar, and then cooled to -78 ^{o}C followed by addition of NIS (7 mg, 0.06 mmol) and TfOH (1 μL, 0.01 mmol). The reaction mixture was stirred at -78 ^{o}C for 5 h and then quenched with DIPEA (10 μL). The mixture was diluted with CH_2Cl_2, filtered through Celite, washed with 20% aqueous $Na_2S_2O_3$ solution, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with EtOAc: hexanes systems to afford the coupled products, **17 (**31 mg, 51%)[7] and compound **5** (2 mg, 3%) and the unreacted donors **2** (31 mg, 74%) and **16** (7 mg, 17%).

References:

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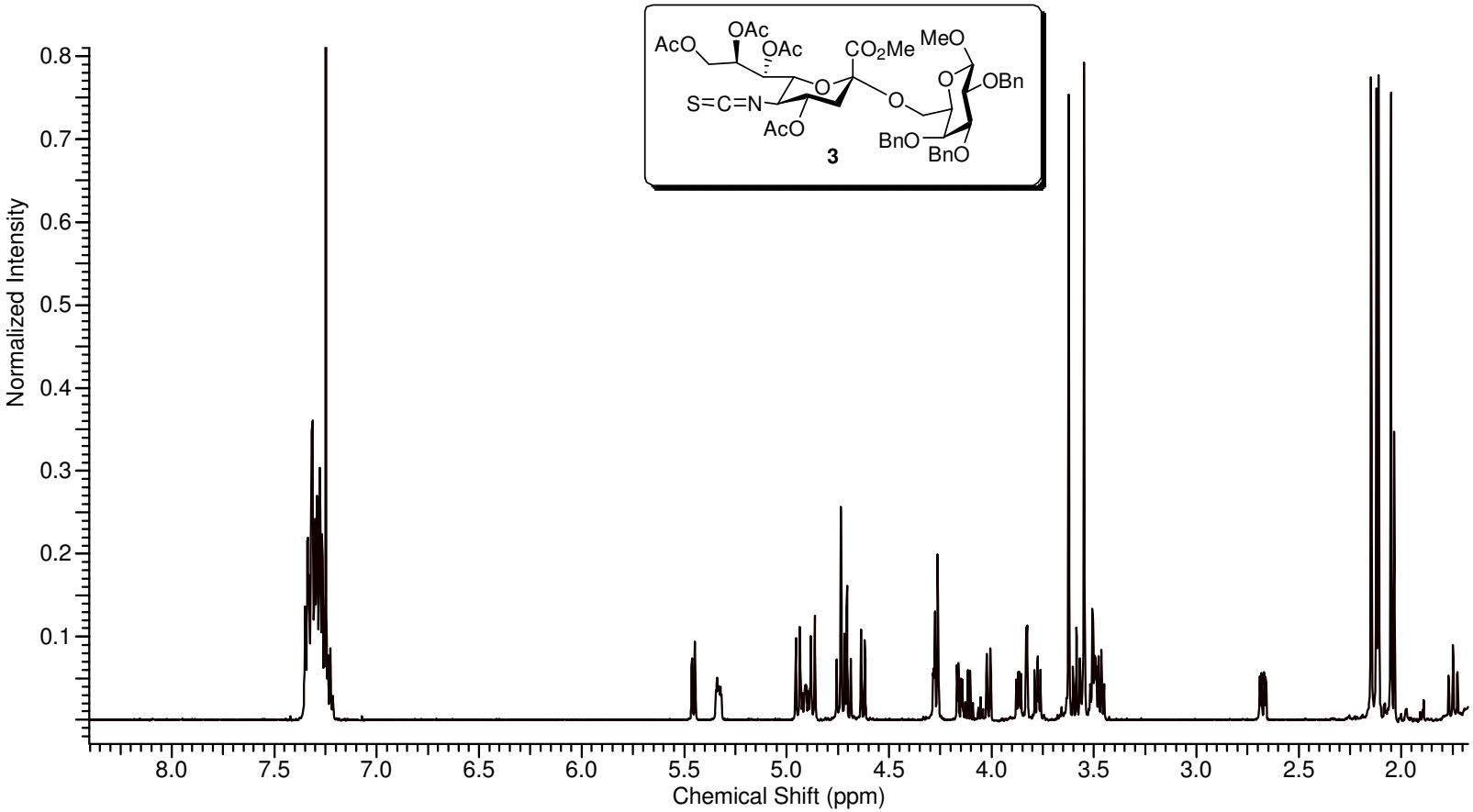
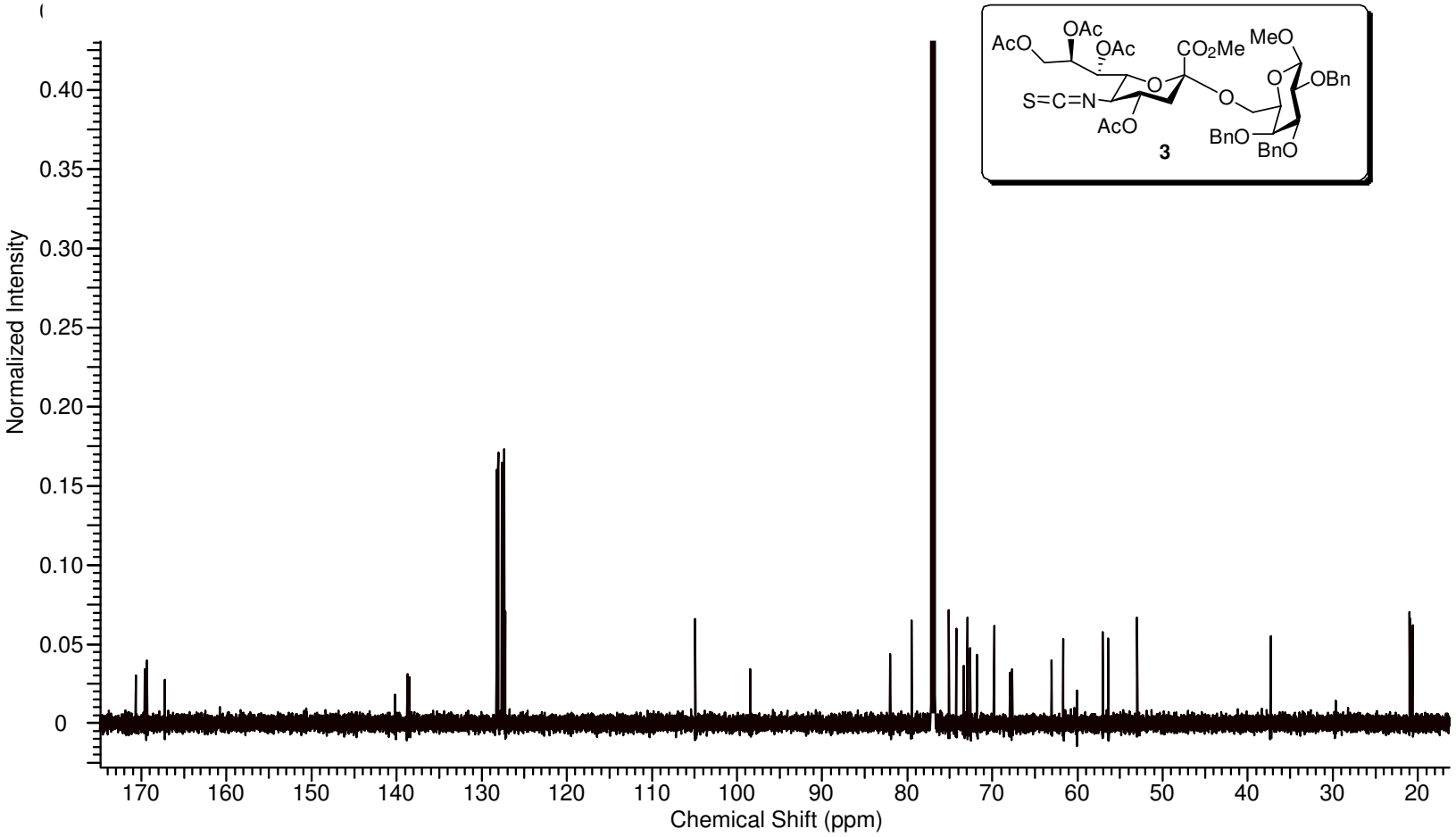
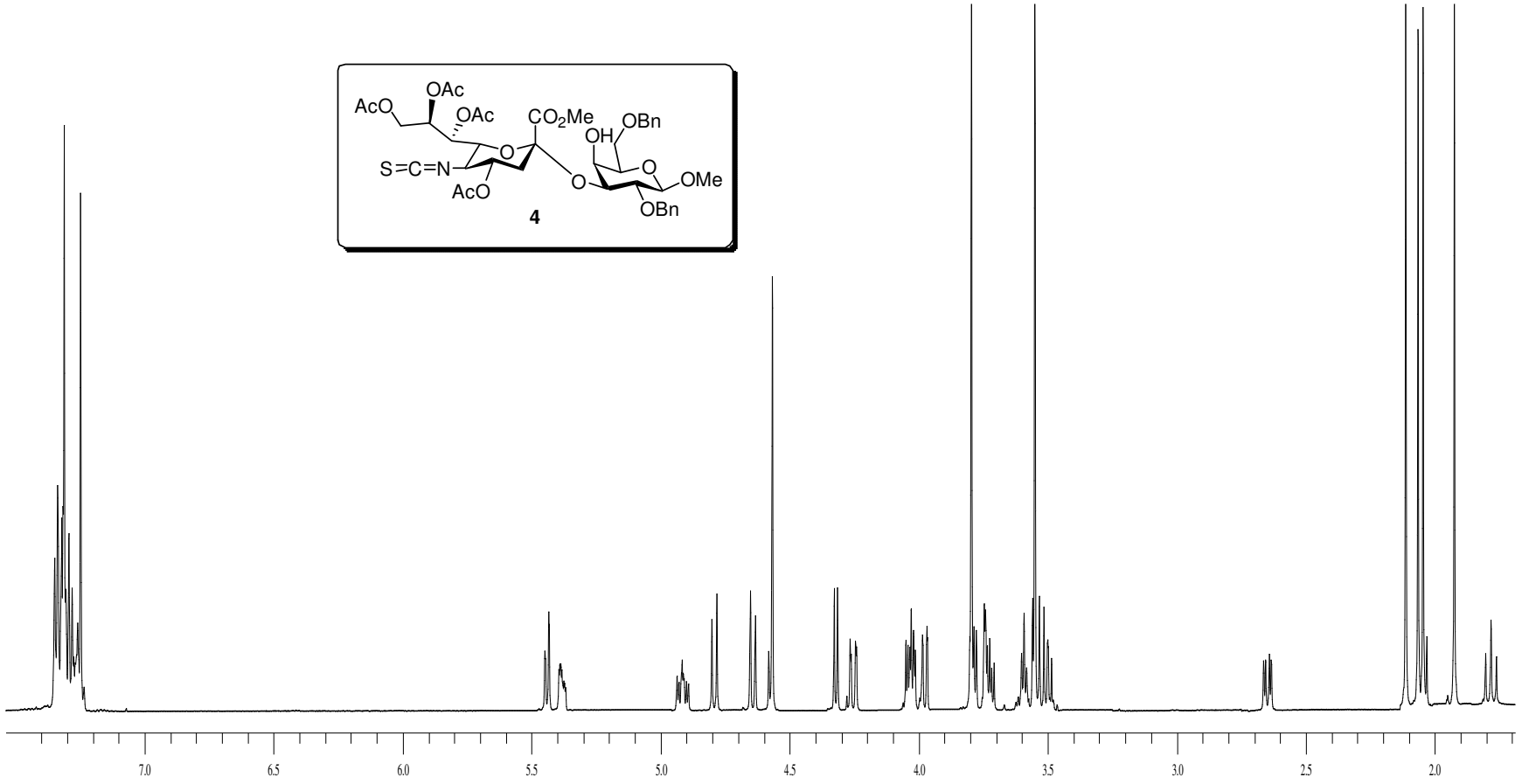
^{1}H NMR (600 MHz, $CDCl_3$) Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→6)-2,3,4-tri-*O*-benzyl-β-D-galactopyranoside (3):



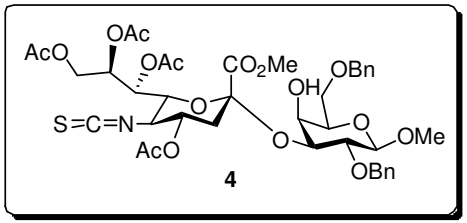
^{13}C NMR (151 MHz, $CDCl_3$) Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→6)-2,3,4-tri-*O*-benzyl-β-D-galactopyranoside (3):



^{1}H NMR (600 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-2,4-di-*O*-benzyl-β-D-galactopyranoside (4):

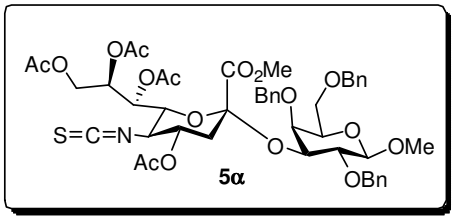


^{13}C NMR (151 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-2,4-di-*O*-benzyl-β-D-galactopyranoside (4):

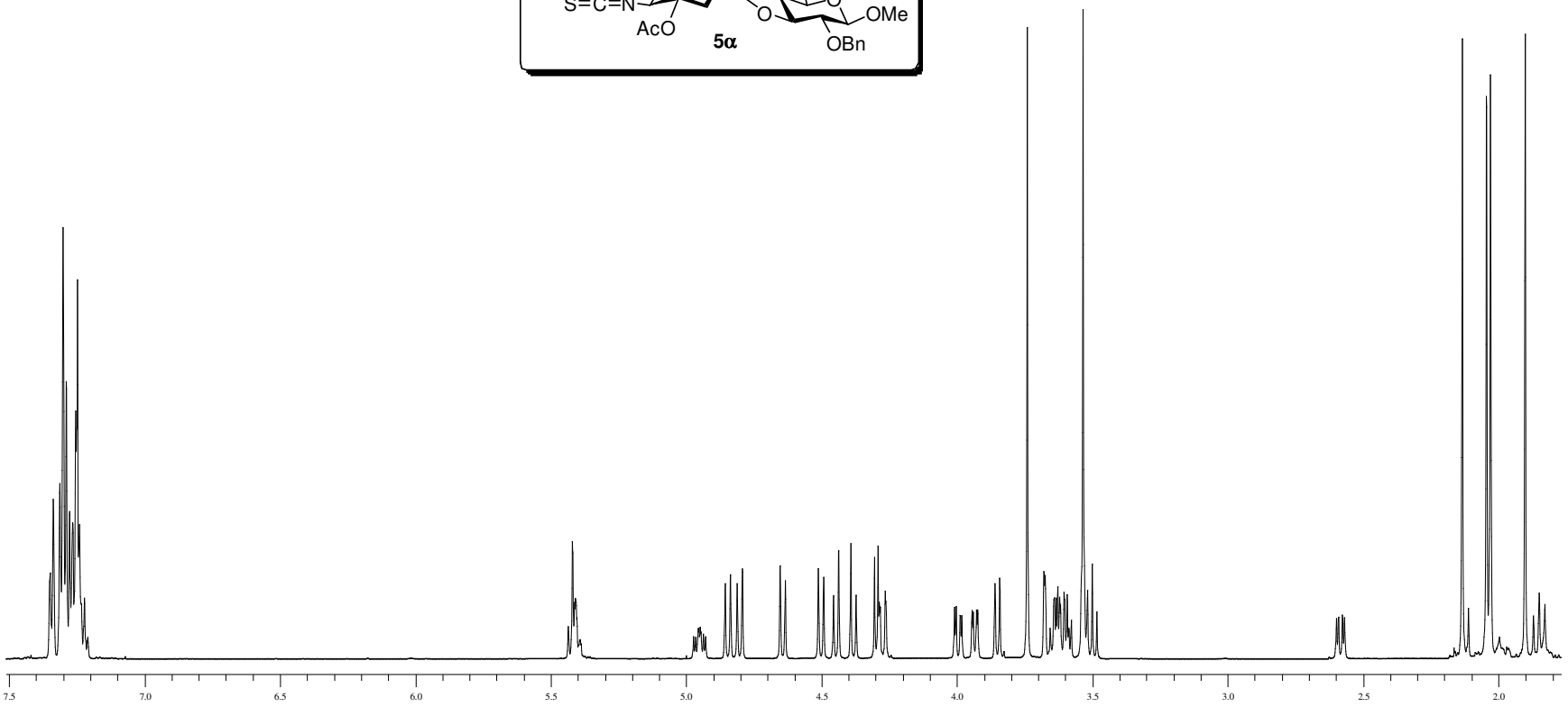


4

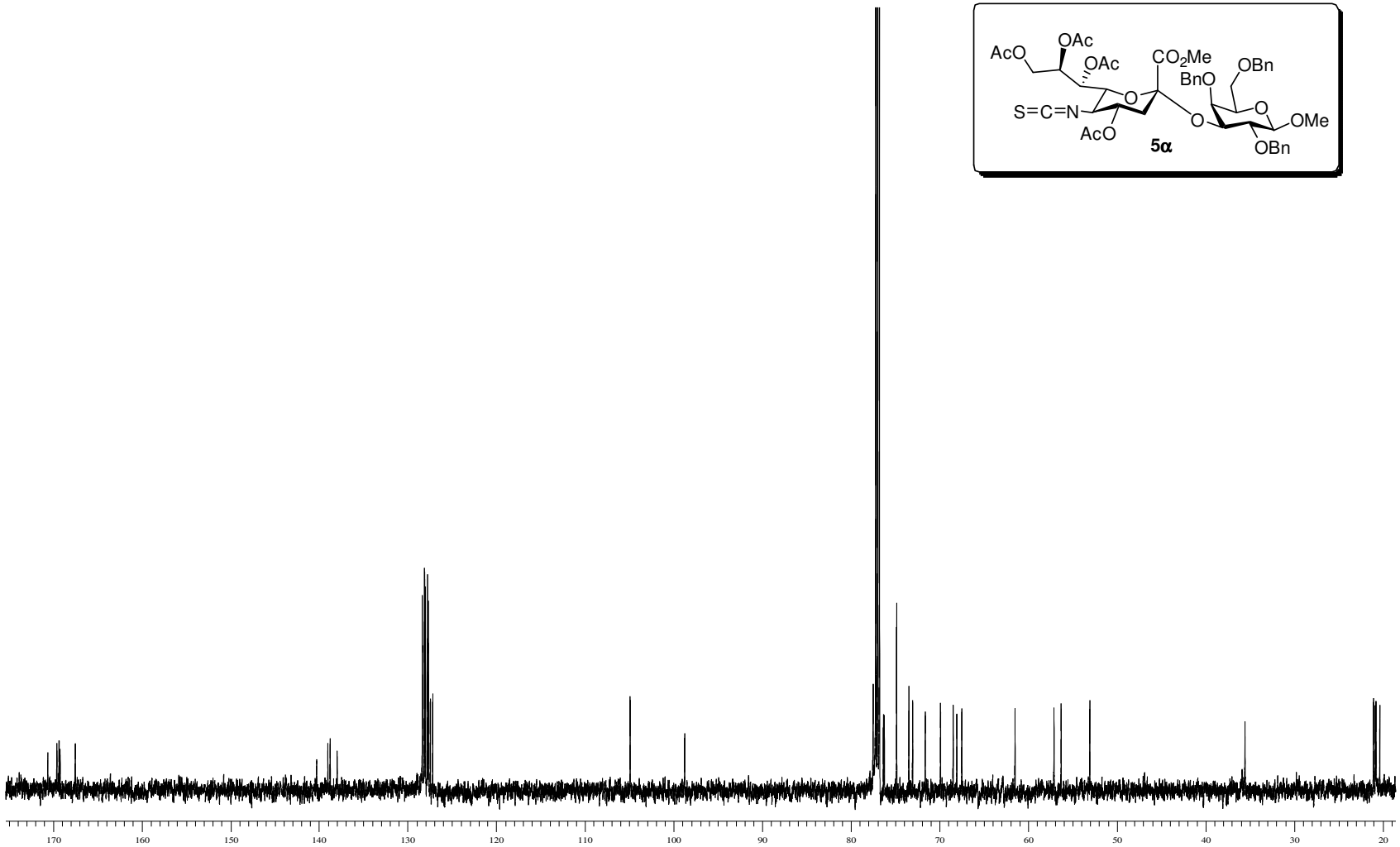
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (5α):



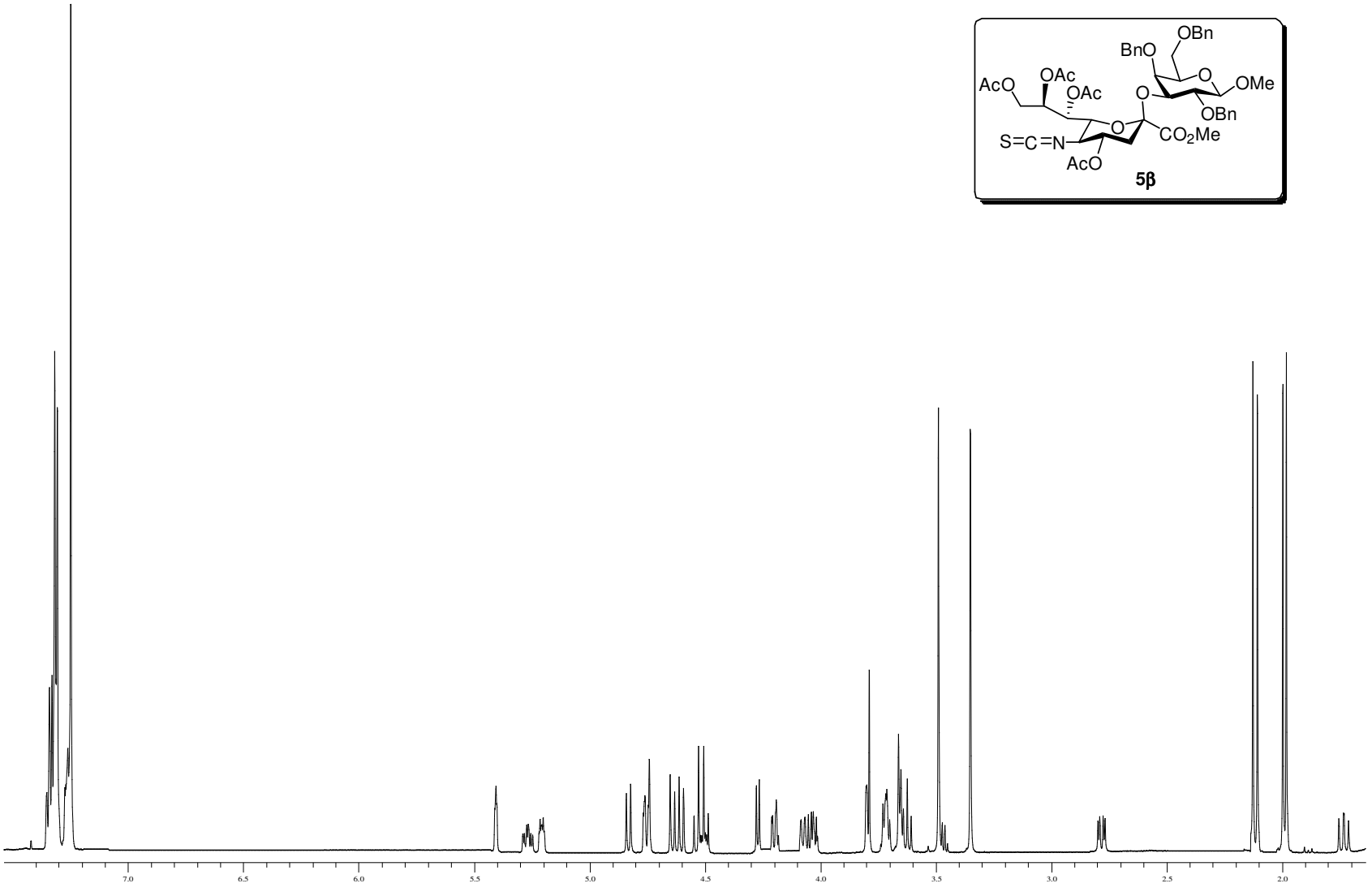
5α



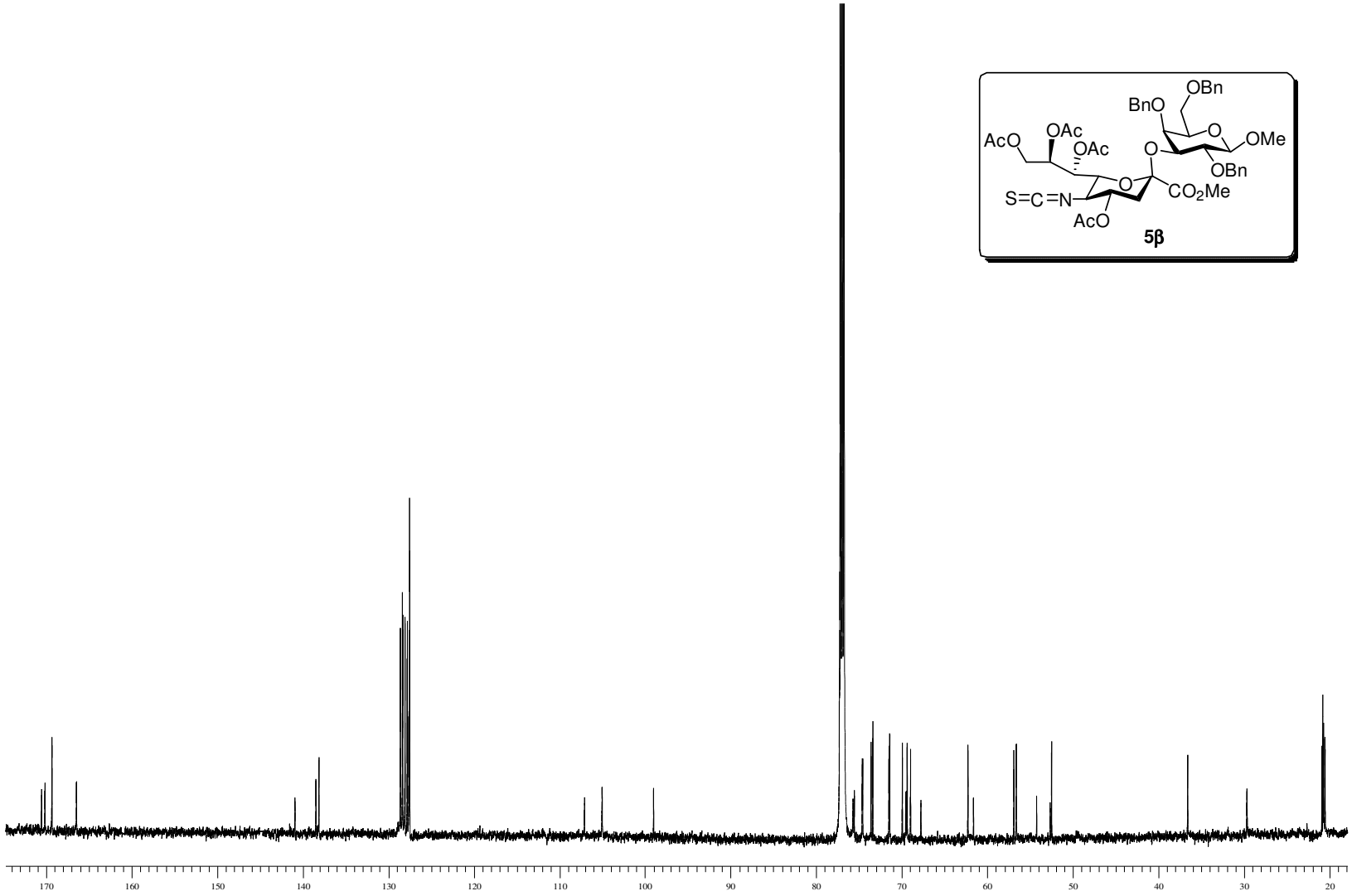
^{13}C NMR (151 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (5α):



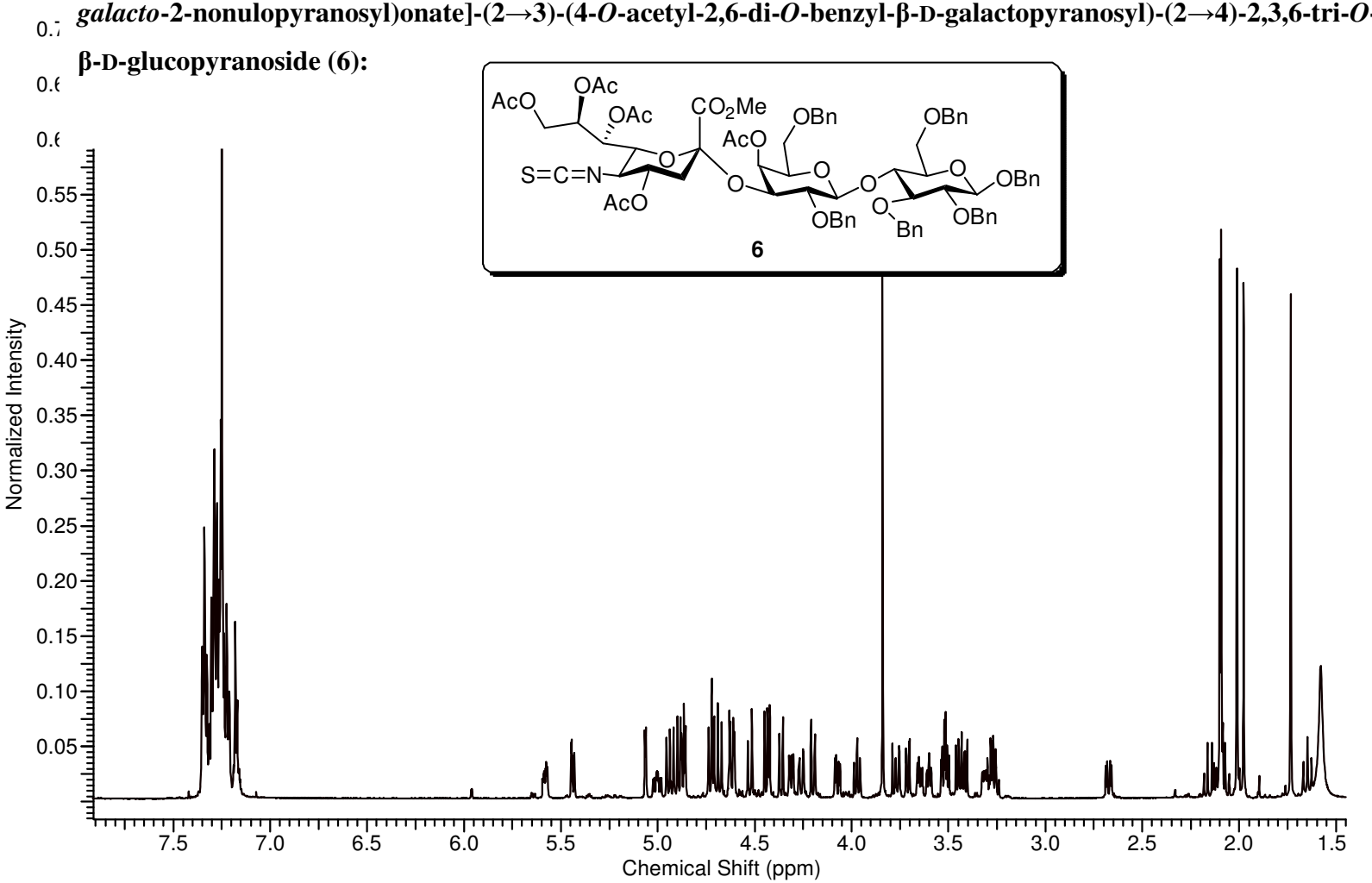
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-D-*glycero*- β-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (5β):



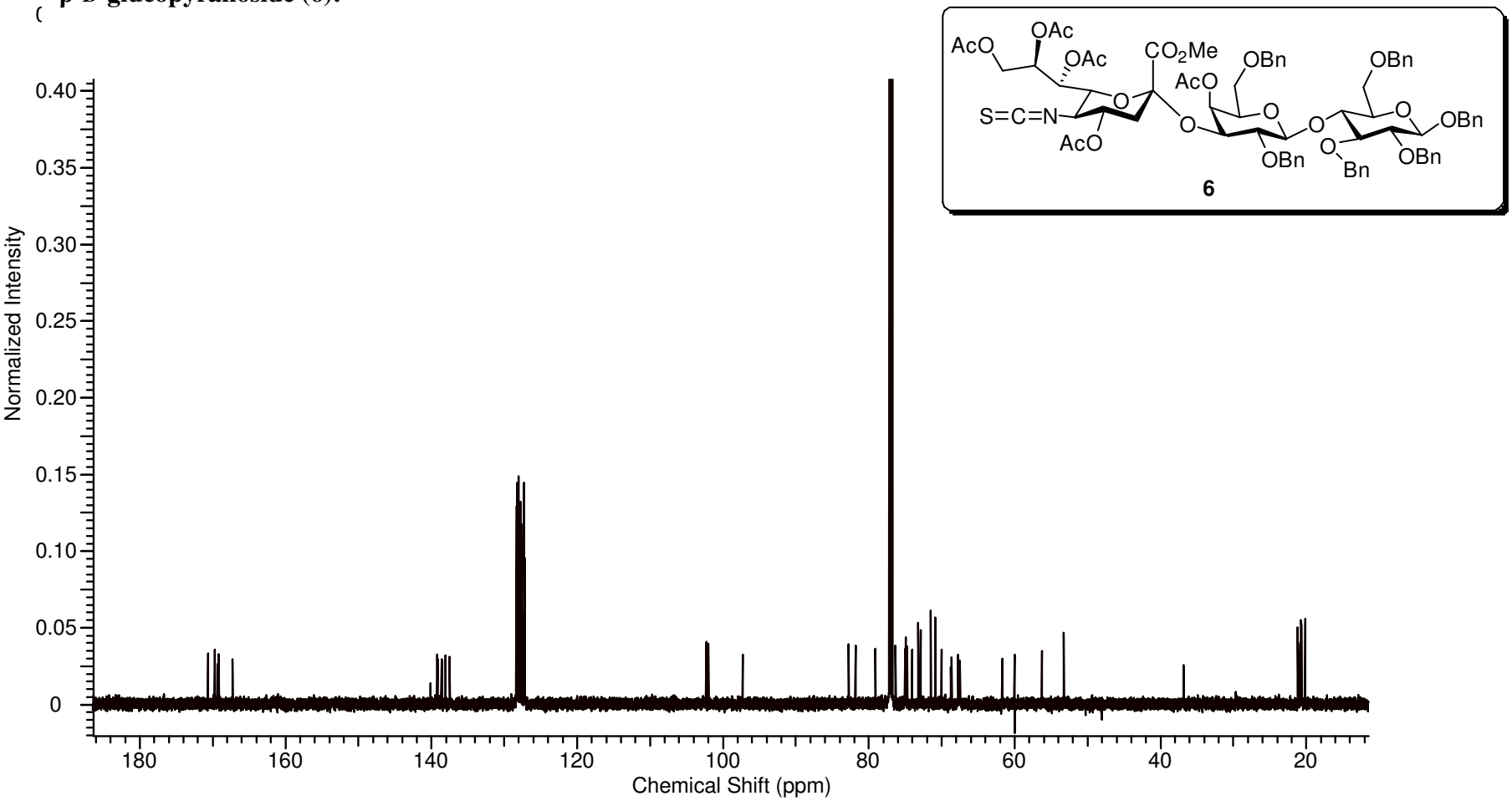
^{13}C NMR (600 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-D-*glycero*- β-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (5β):



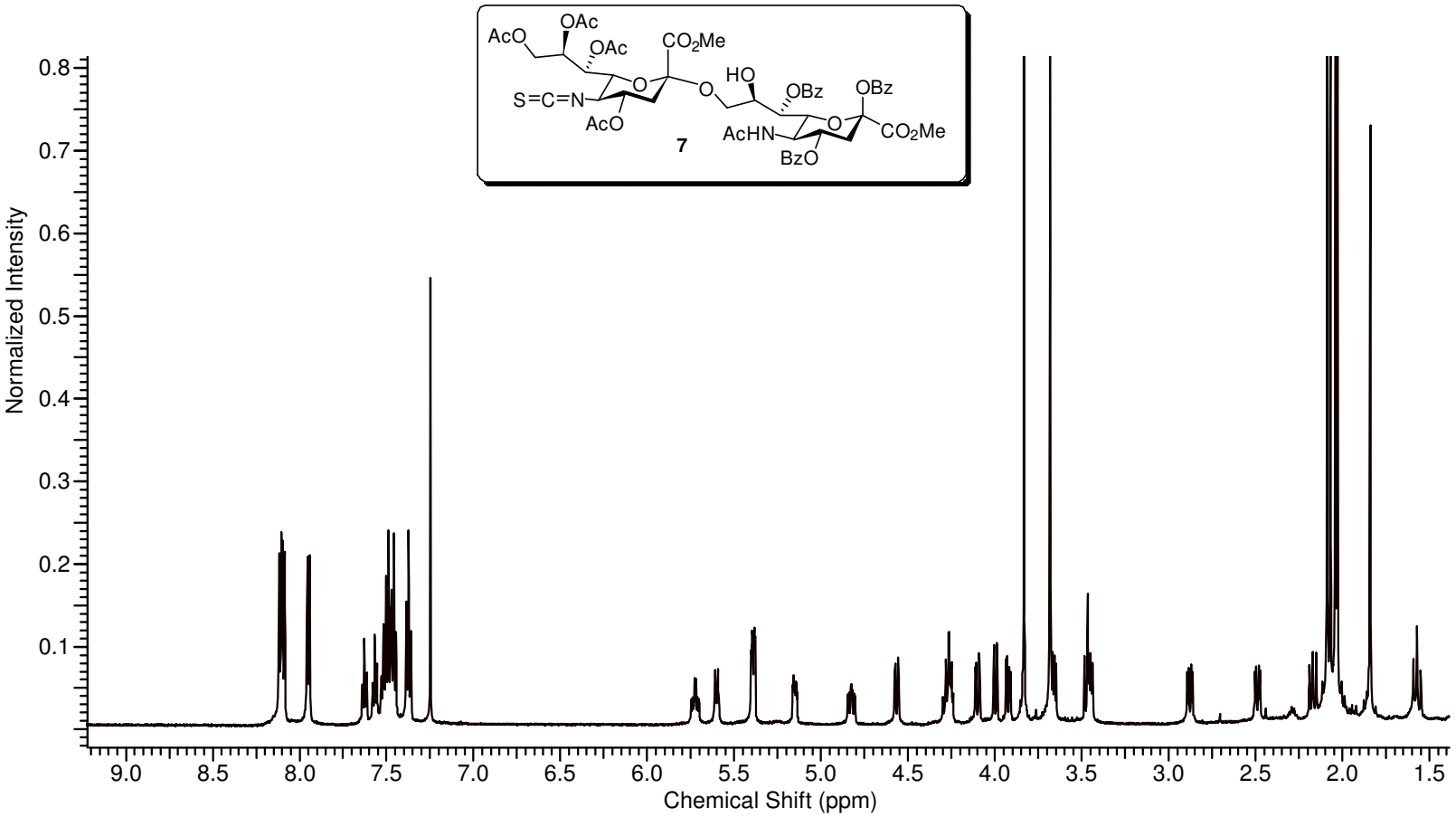
^{1}H NMR (600 MHz, $CDCl_3$) of Benzyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(2→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (6):



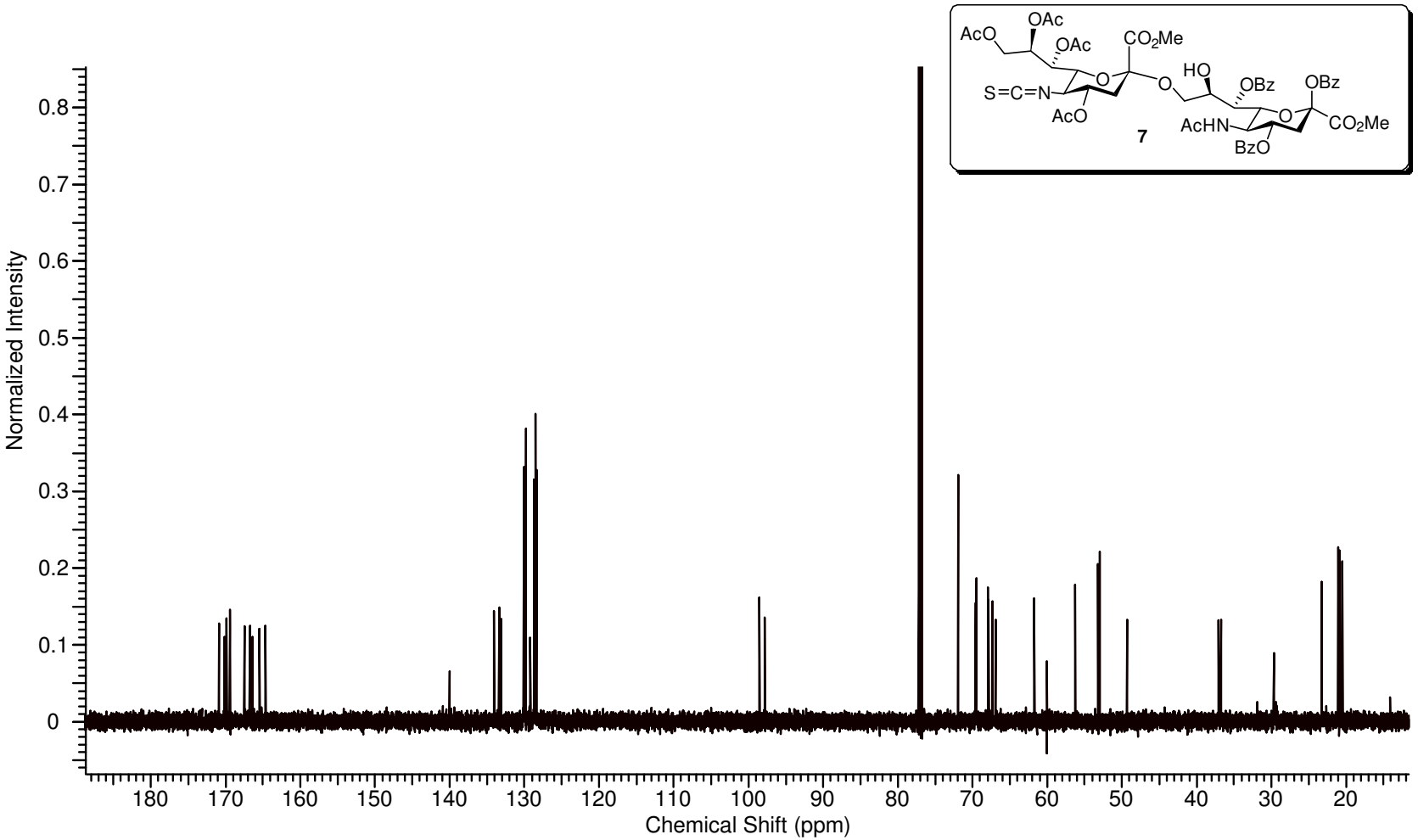
^{13}C NMR (151 MHz, $CDCl_3$) of Benzyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-isothiocyanato-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(2→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (6):



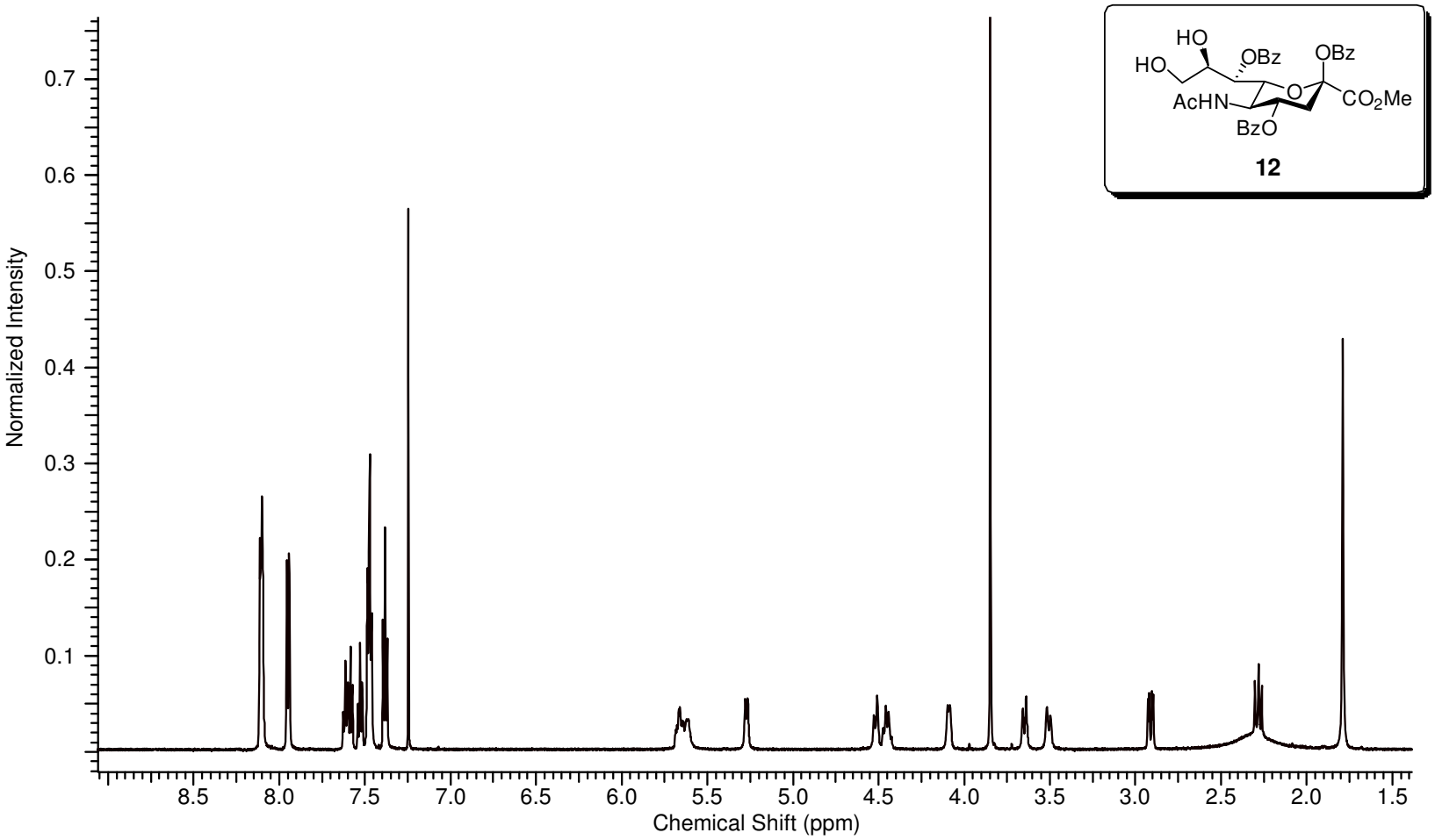
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy--5-isothiocyanato-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-α(2→9)-[(5-acetamido-2,4,7-tri-*O*-benzoyl-3,5-dideoxy-2-α-D-*glycero*-D-*galacto*-2-nonulopyranose)onate] (7):



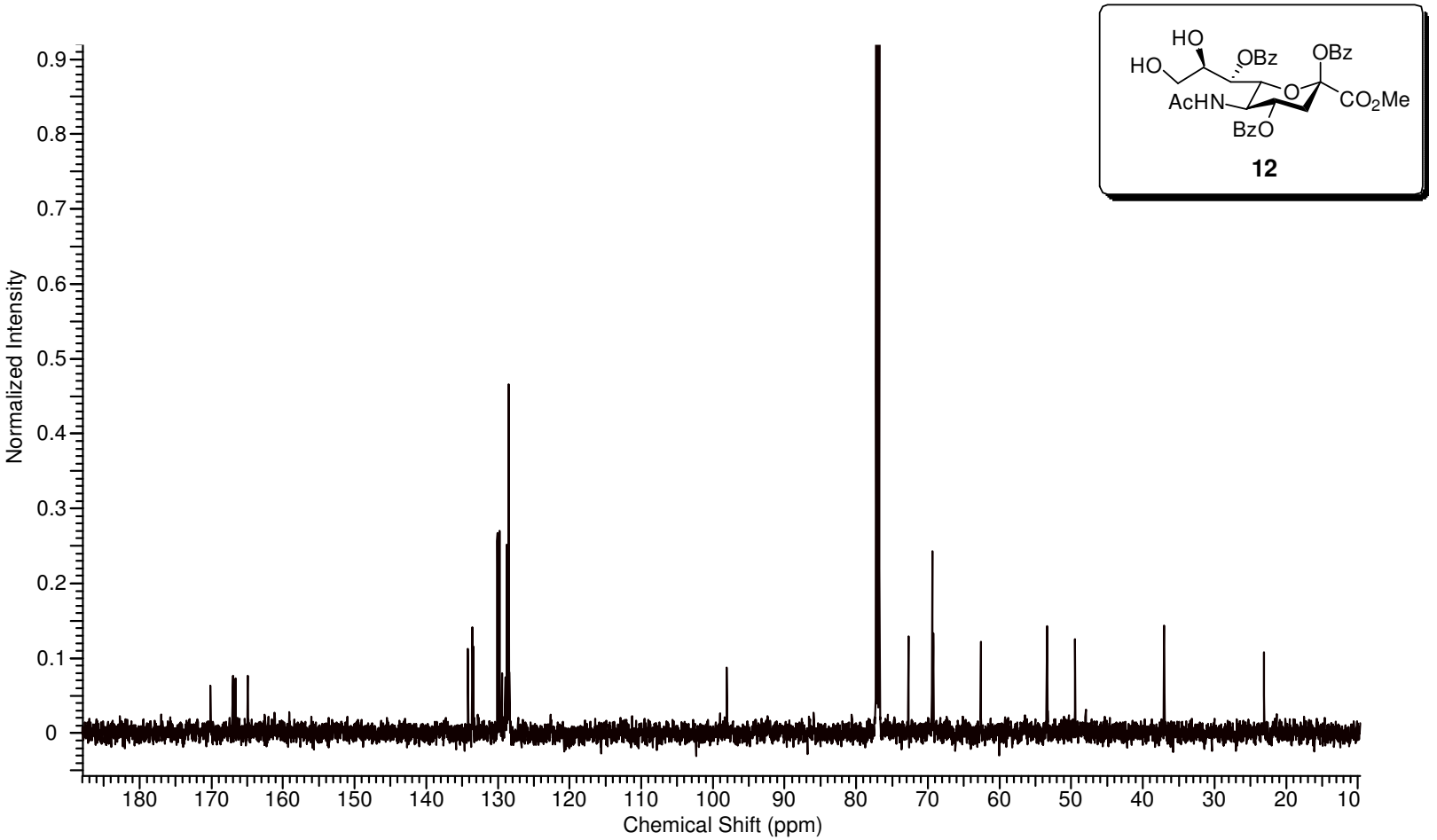
^{13}C NMR (151 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy--5-isothiocyanato-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-α(2→9)-[(5-acetamido-2,4,7-tri-*O*-benzoyl-3,5-dideoxy-2-α-D-*glycero*-D-*galacto*-2-nonulopyranose)onate] (7):



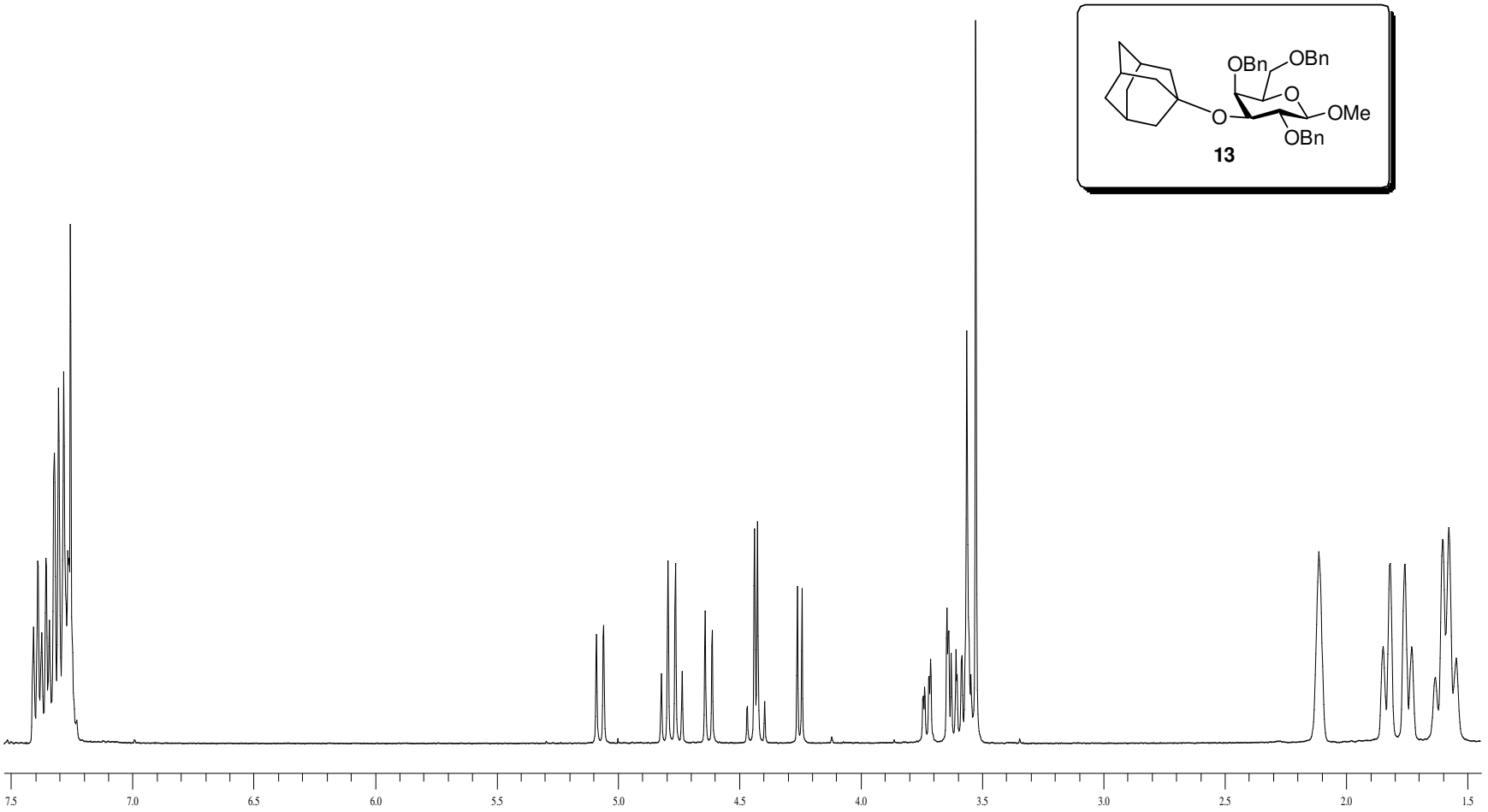
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl (5-acetamido-2,4,6-tri-*O*-benzoyl-3,5-dideoxy-D-β-*glycero*-D-*galacto*-2-nonulopyranose)onate (12):



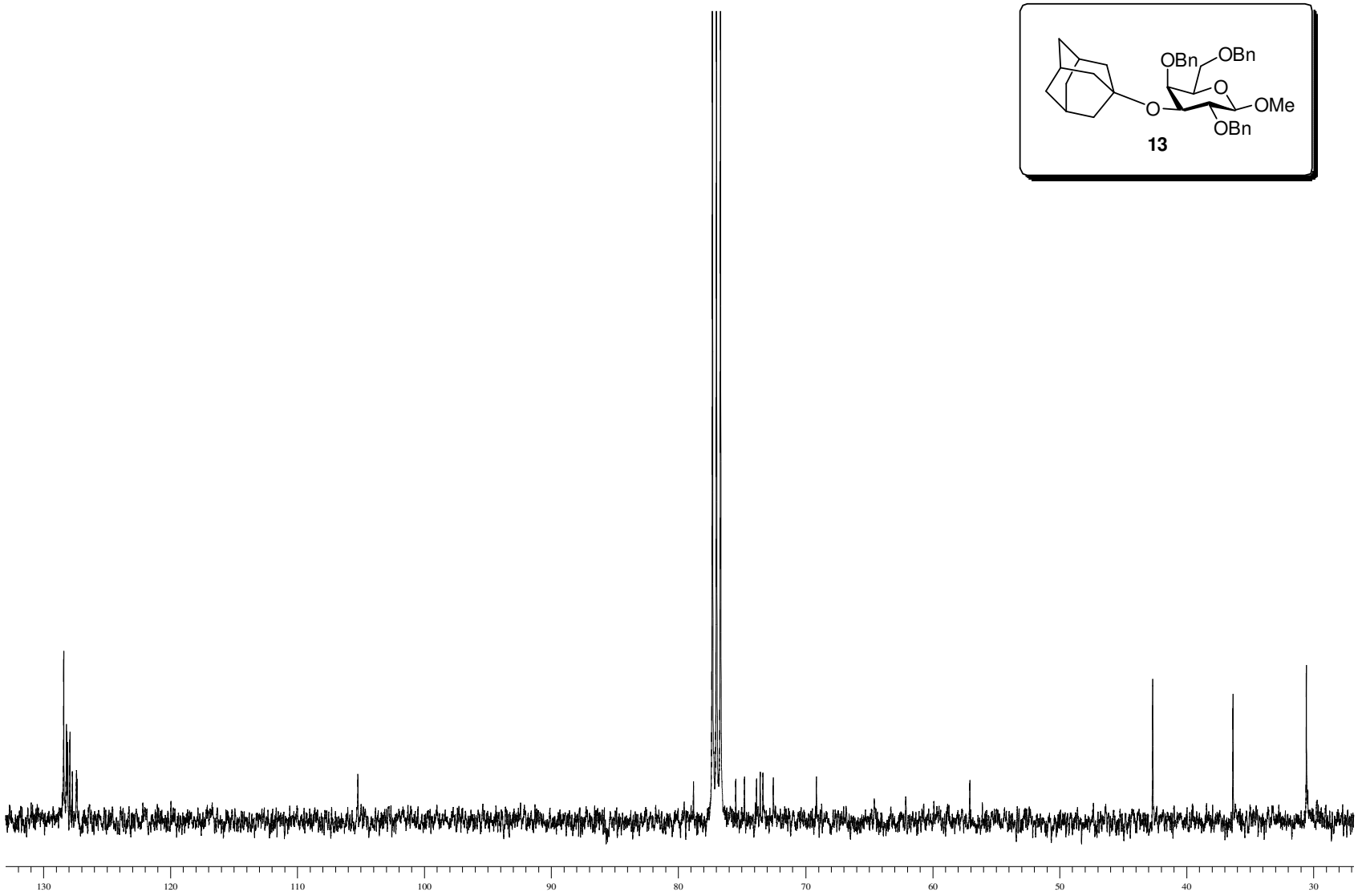
^{13}C NMR (151 MHz, $CDCl_3$) of Methyl (5-acetamido-2,4,6-tri-*O*-benzoyl-3,5-dideoxy-D-β-*glycero*-D-*galacto*-2-nonulopyranose)onate (12):



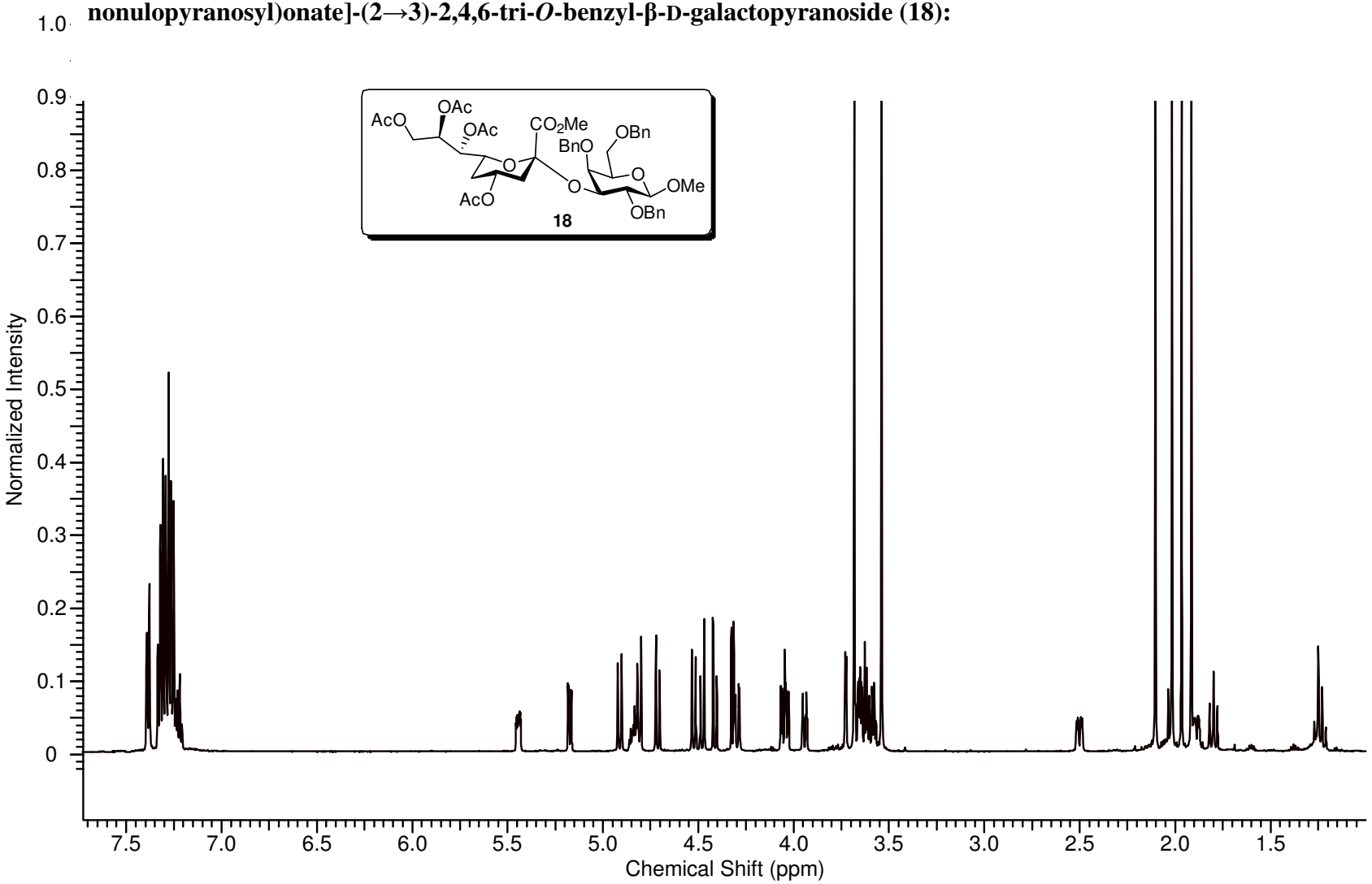
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl 3-*O*-(1-adamantyl)-2,4,6-tri-*O*-benzyl-*β*-D-galactopyranoside (13):



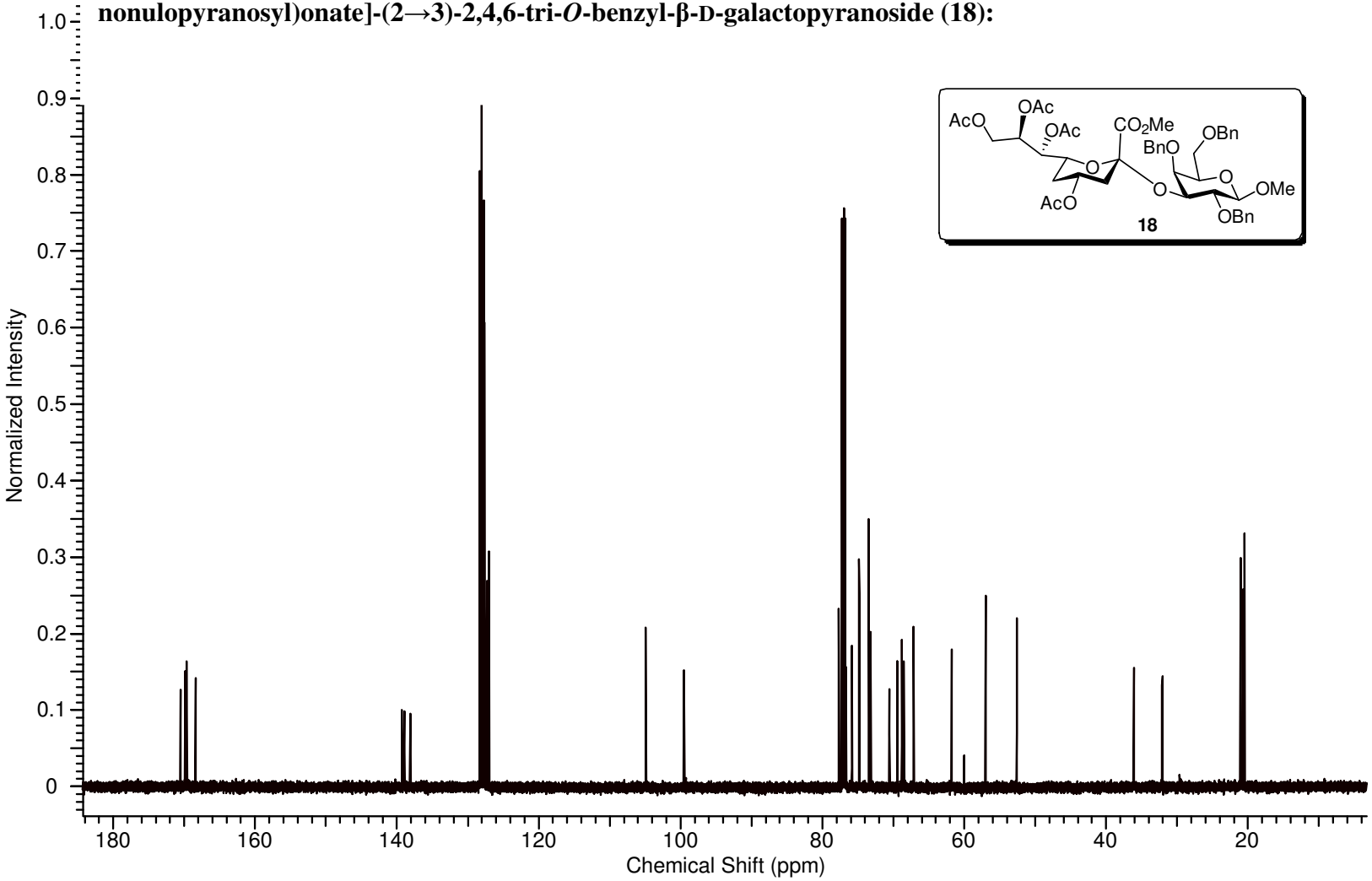
^{13}C NMR (600 MHz, $CDCl_3$) of Methyl 3-*O*-(1-adamantyl)-2,4,6-tri-*O*-benzyl-*β*-D-galactopyranoside (13):



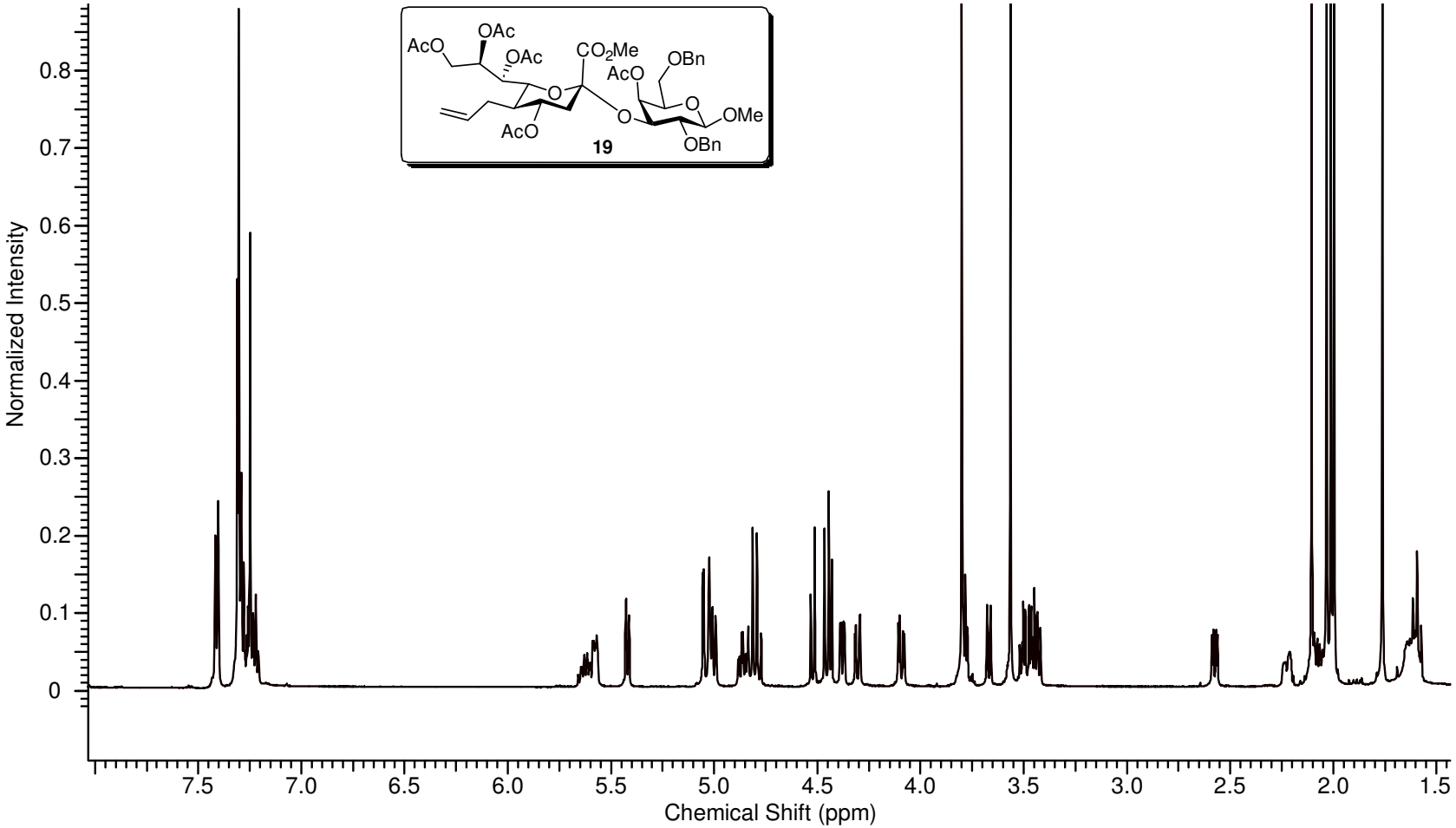
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy--α-D-*gluco*-2-nonulopyranosyl)onate]-(2→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (18):



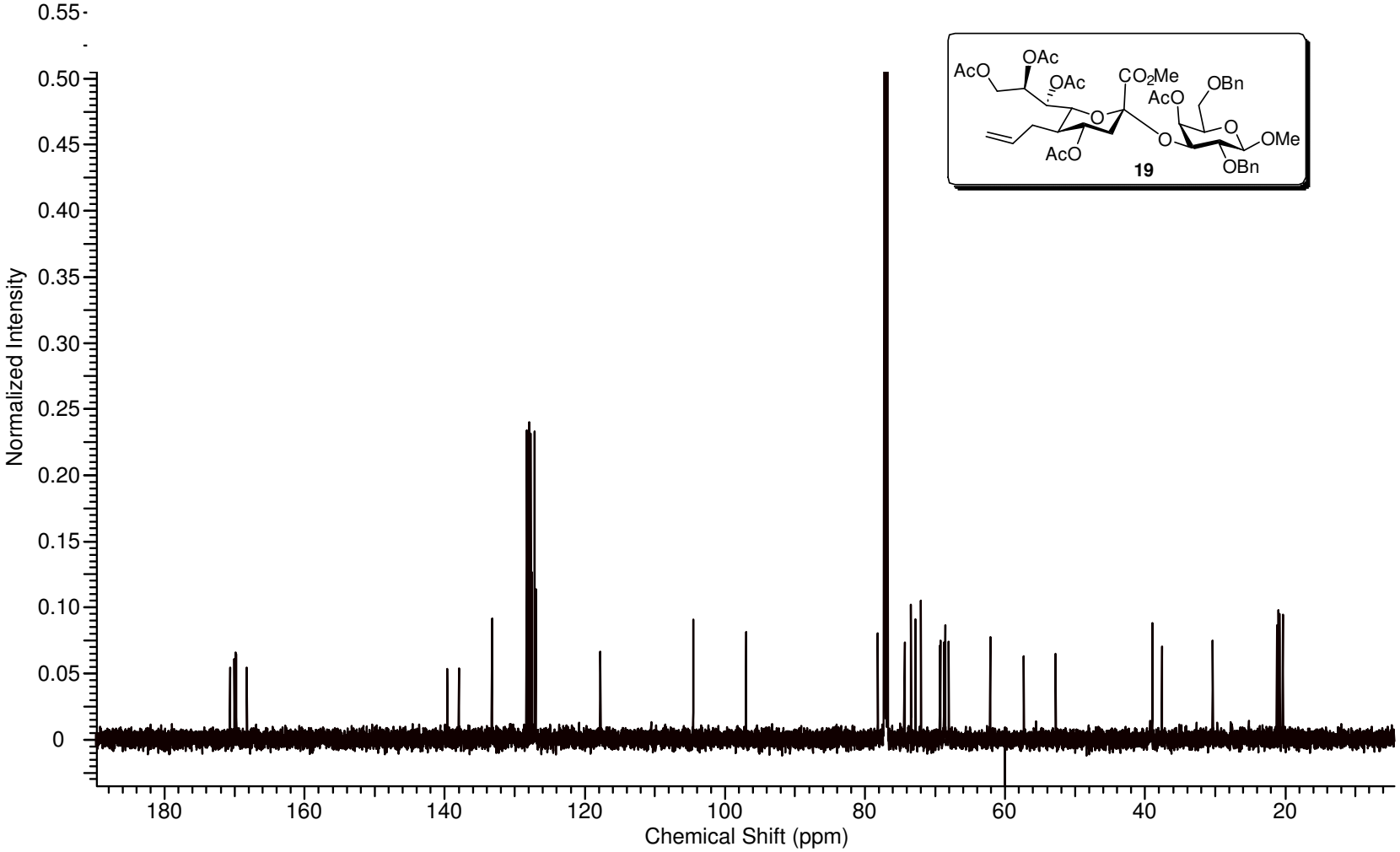
^{13}C NMR (151 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy--α-D-*gluco*-2-nonulopyranosyl)onate]-(2→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (18):



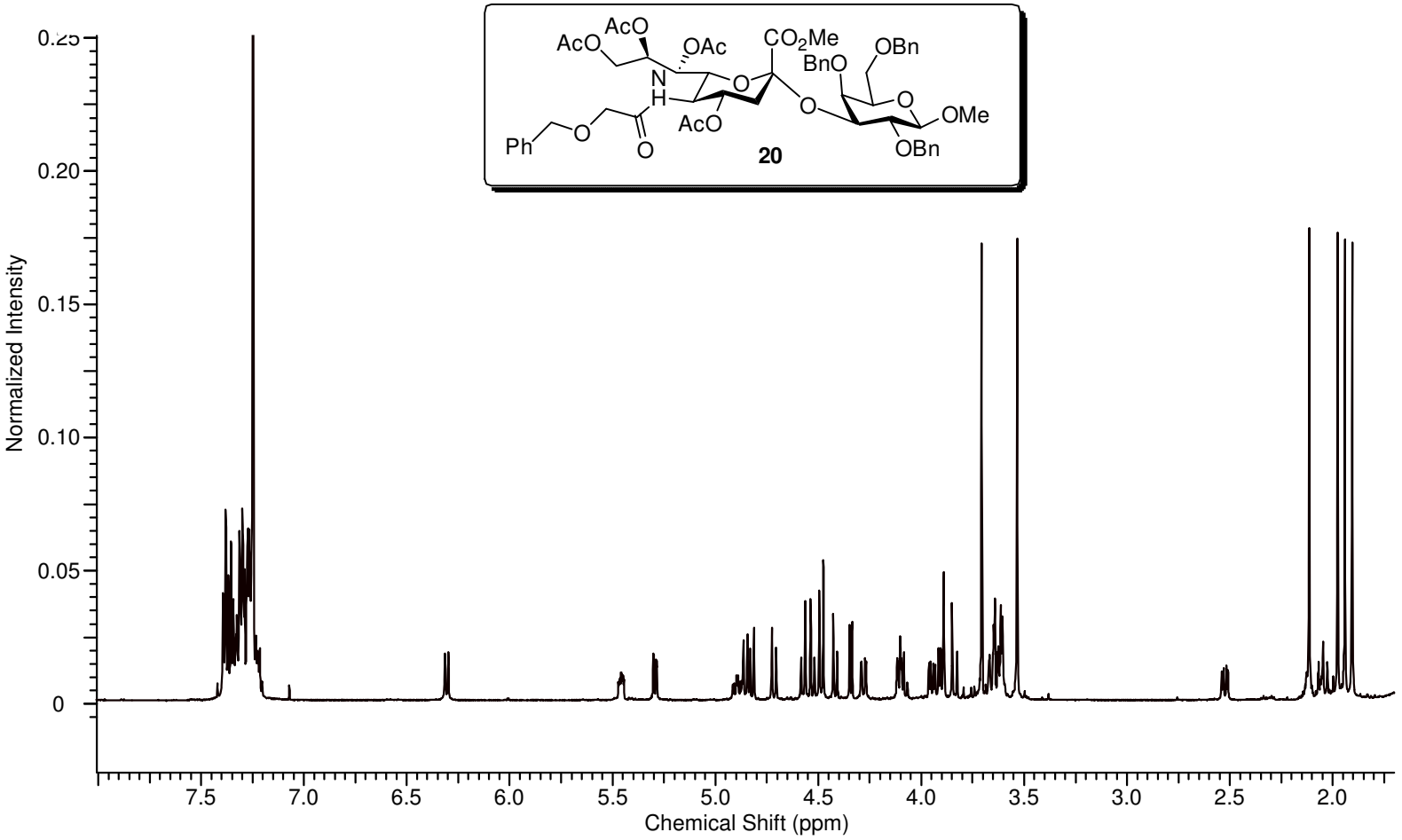
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-5-*C*-allyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (19):



^{13}C NMR (151 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-5-*C*-allyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (19):

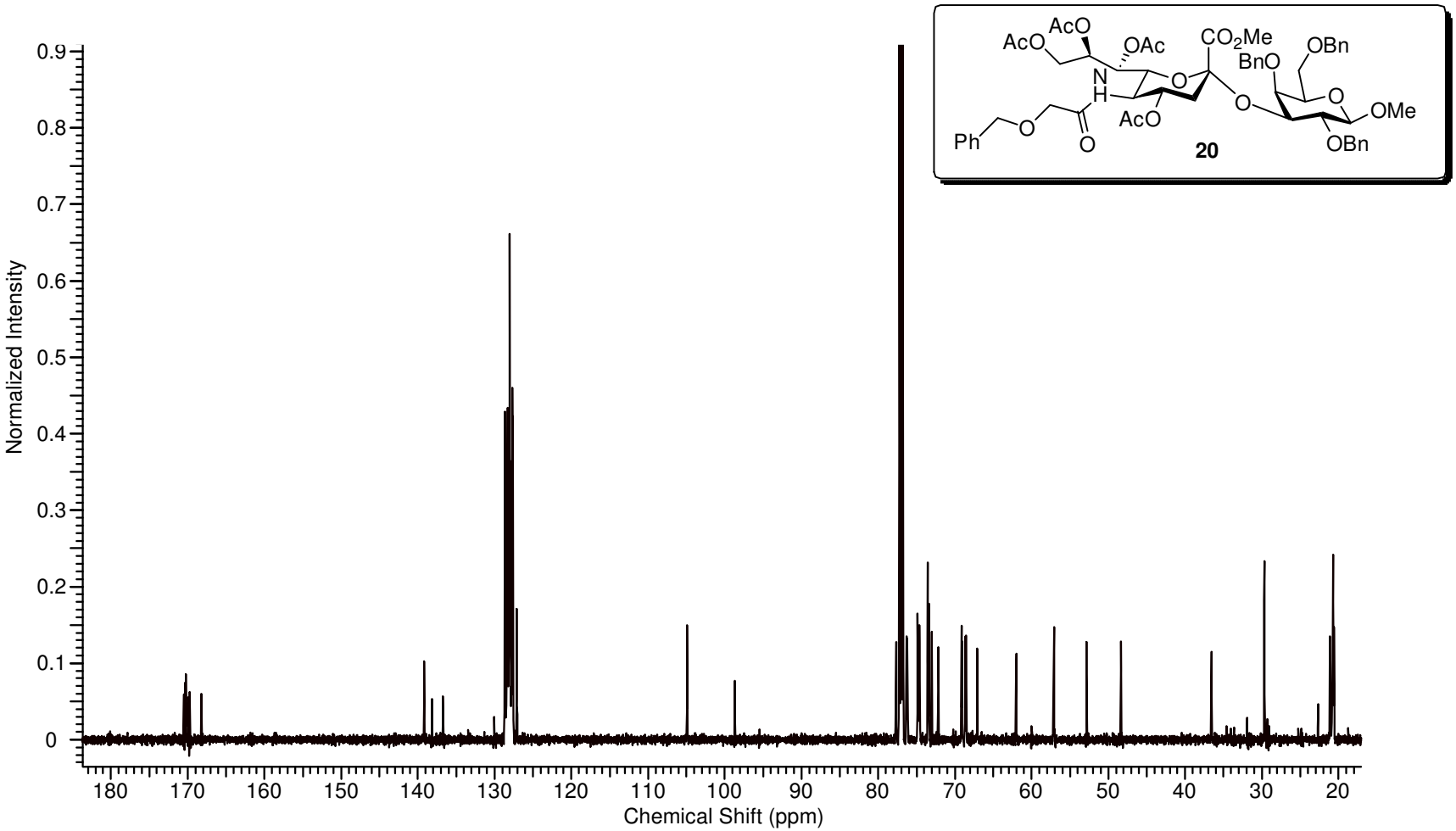


^{1}H NMR (600 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tri-*O*-acetyl-5-(benzyloxyacetamido)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (20):

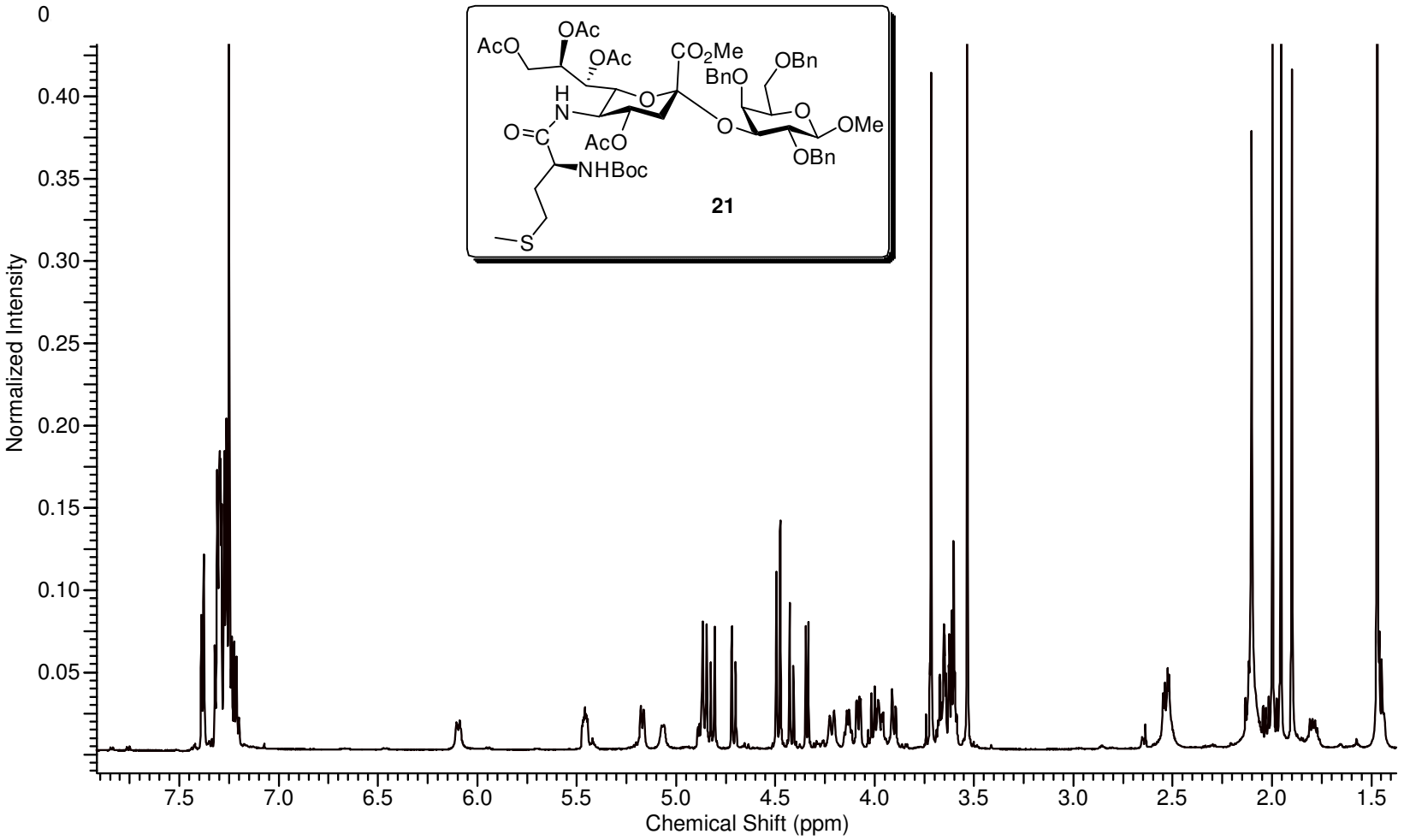


^{13}C NMR (151 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tri-*O*-acetyl-5-(benzyloxyacetamido)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (20):

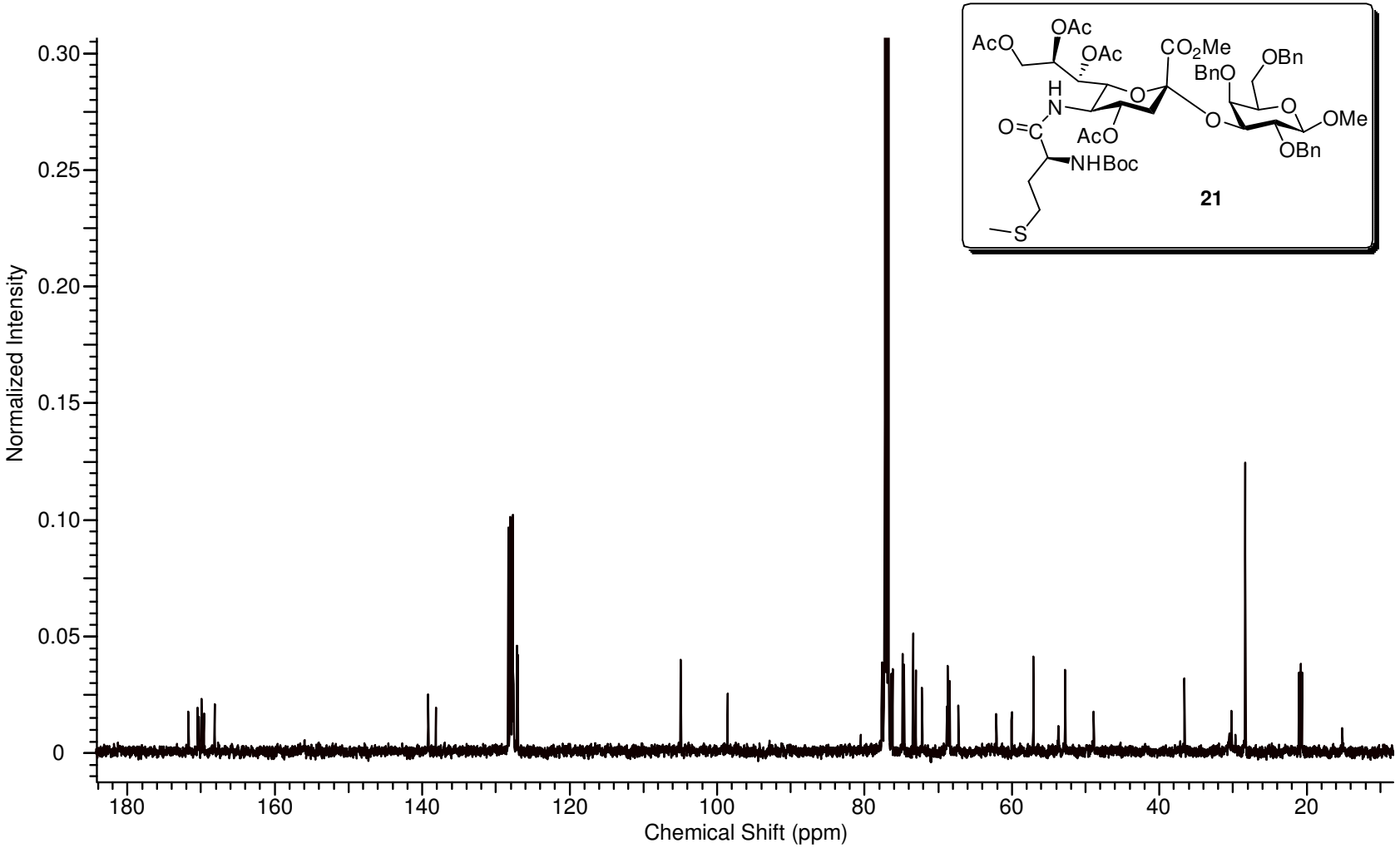
1.



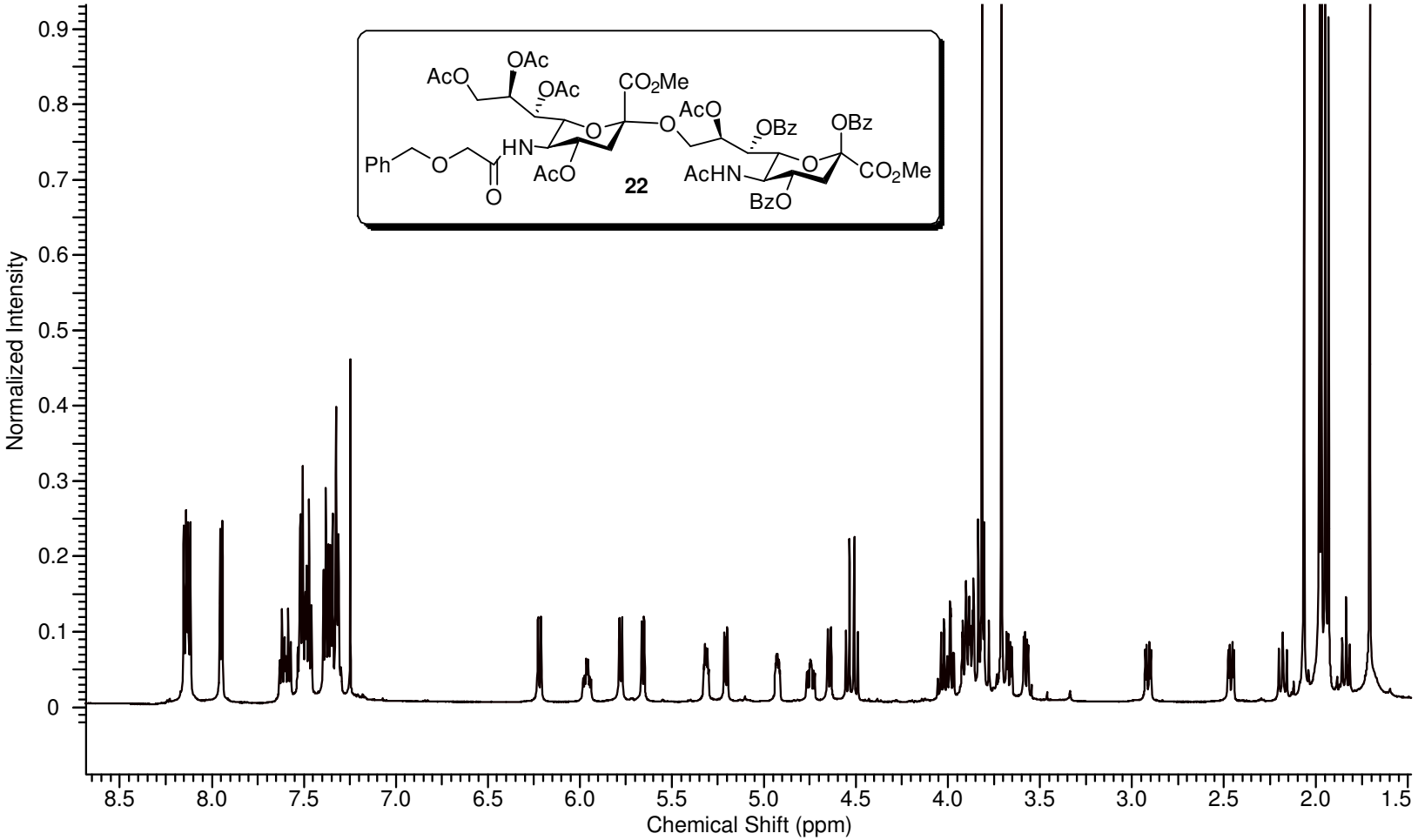
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-(L-methioninamido)-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (21):



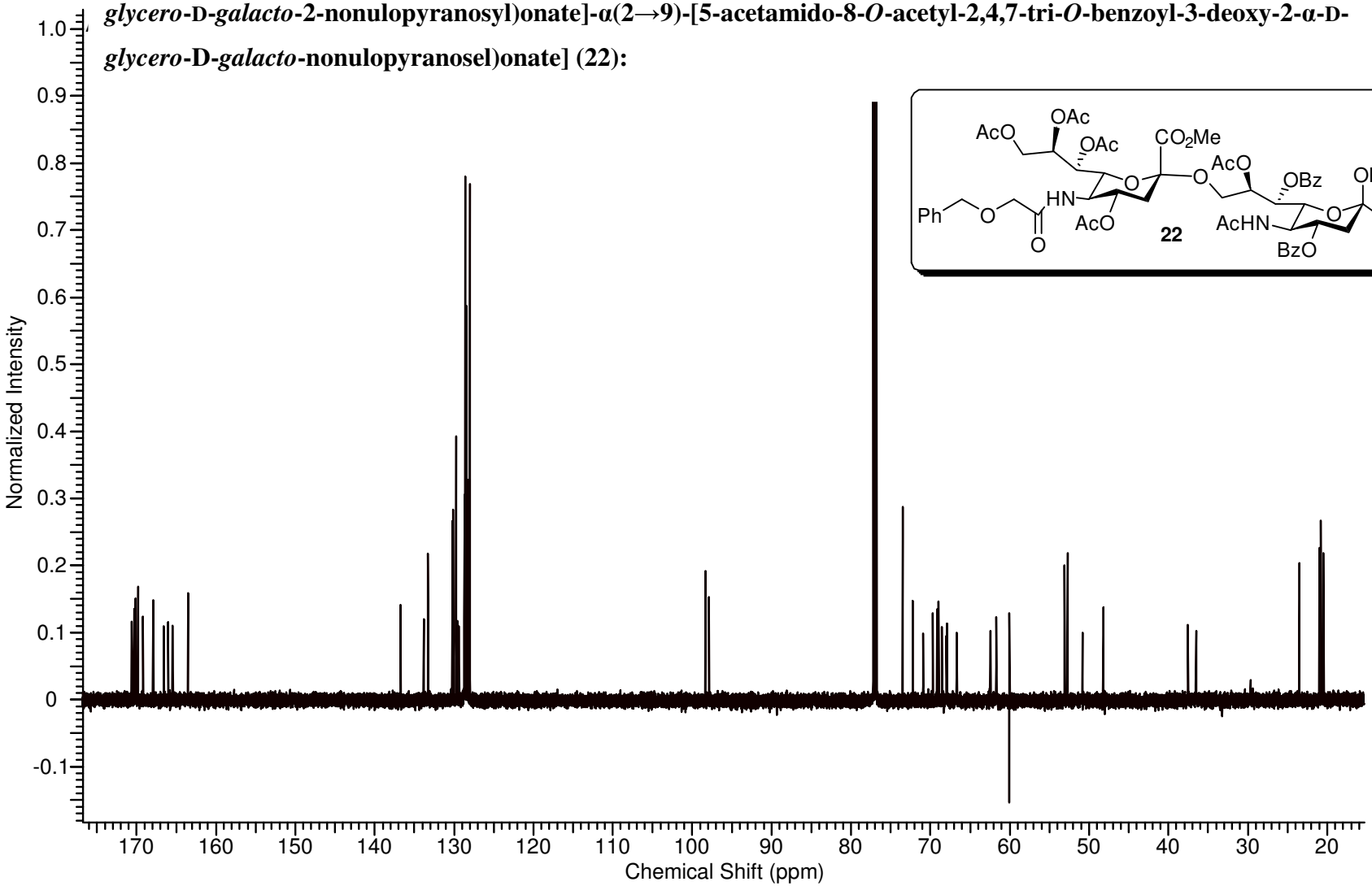
^{13}C NMR (151 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-(L-methioninamido)-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (21):



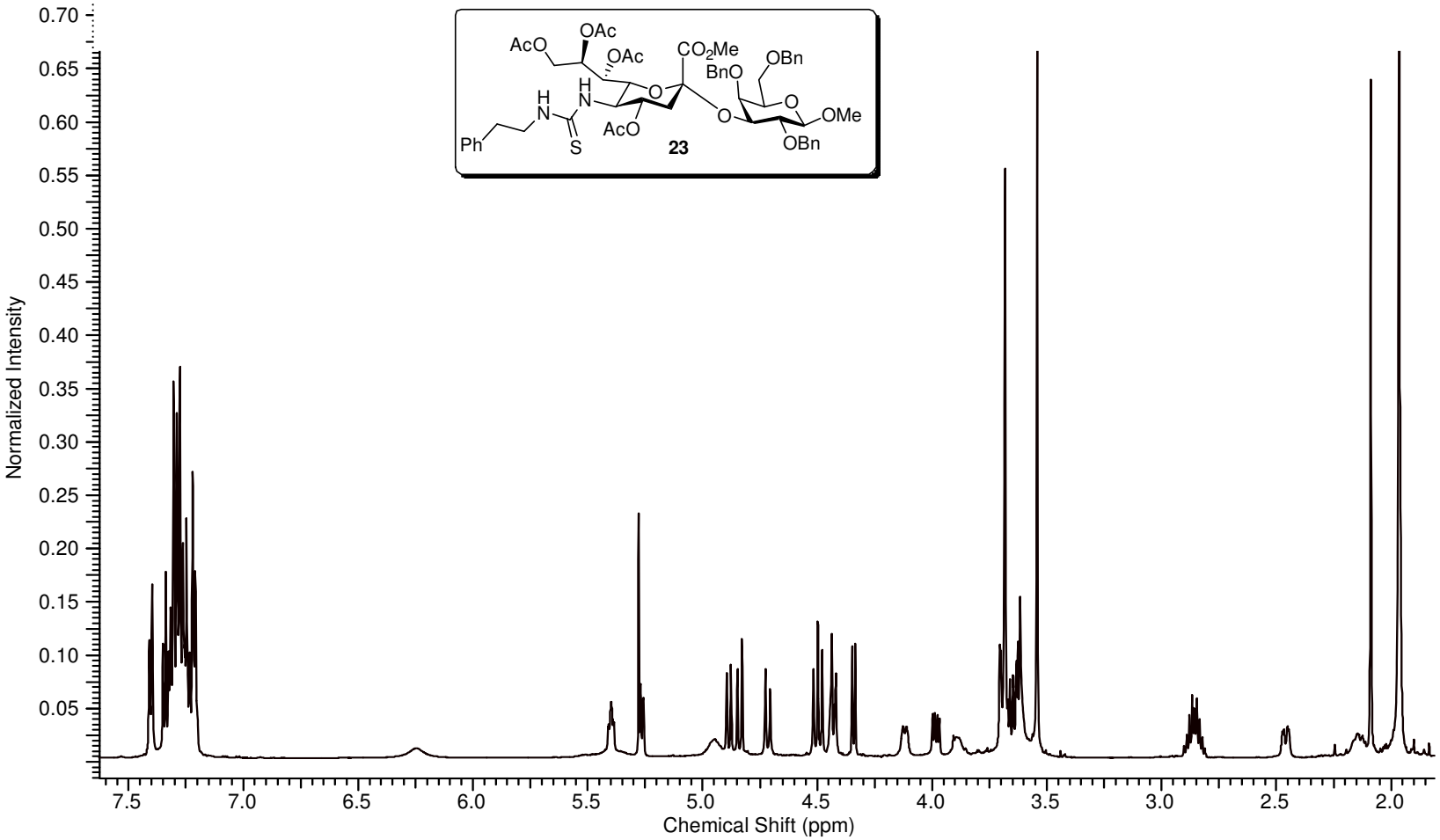
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-5-(benzyloxyacetamido)-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-α(2→9)-[5-acetamido-8-*O*-acetyl-2,4,7-tri-*O*-benzoyl-3-deoxy-2-α-D-*glycero*-D-*galacto*-nonulopyranosel)onate] (22):



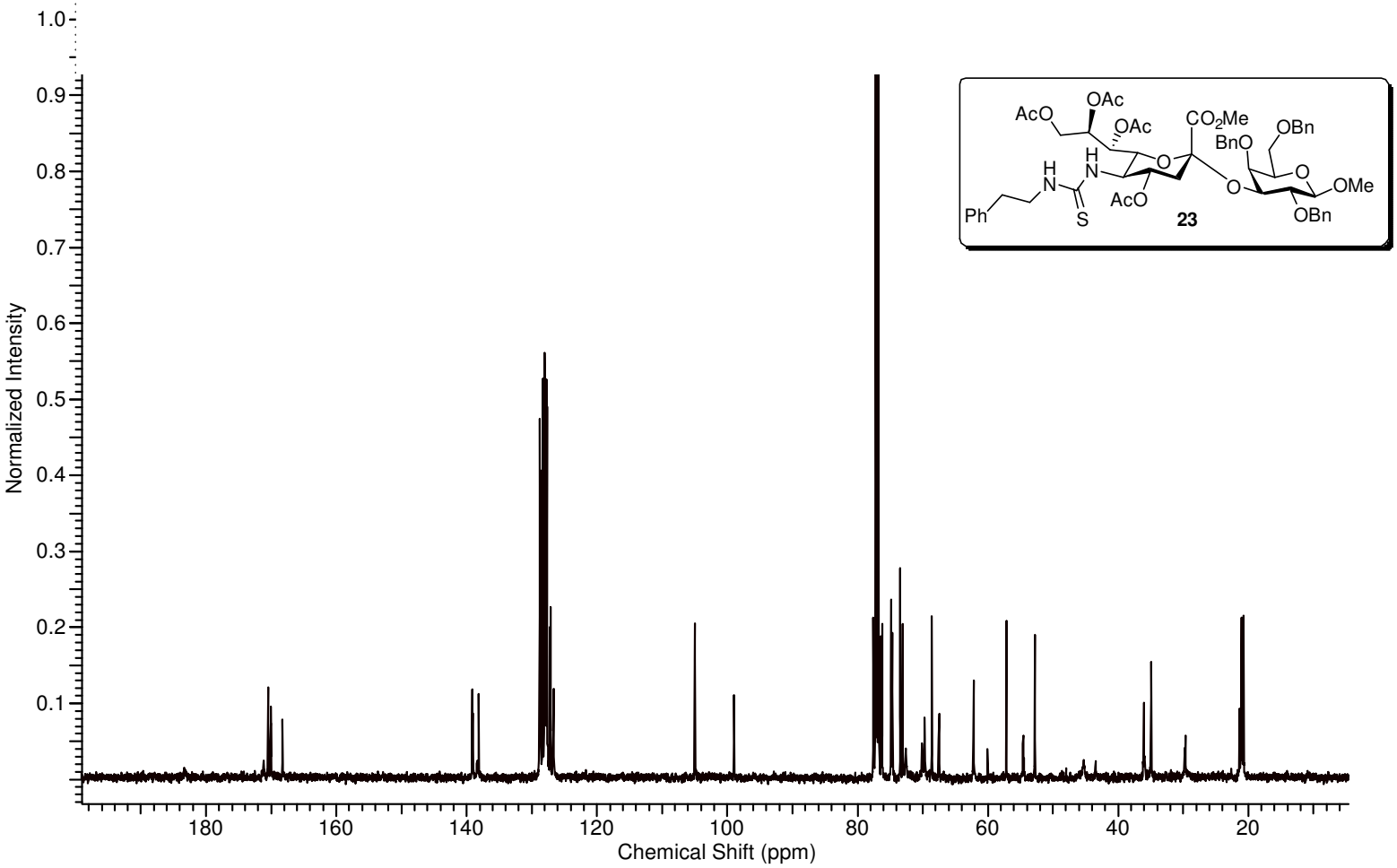
^{13}C NMR (151 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-5-(benzyloxyacetamido)-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-α(2→9)-[5-acetamido-8-*O*-acetyl-2,4,7-tri-*O*-benzoyl-3-deoxy-2-α-D-*glycero*-D-*galacto*-nonulopyranosel)onate] (22):



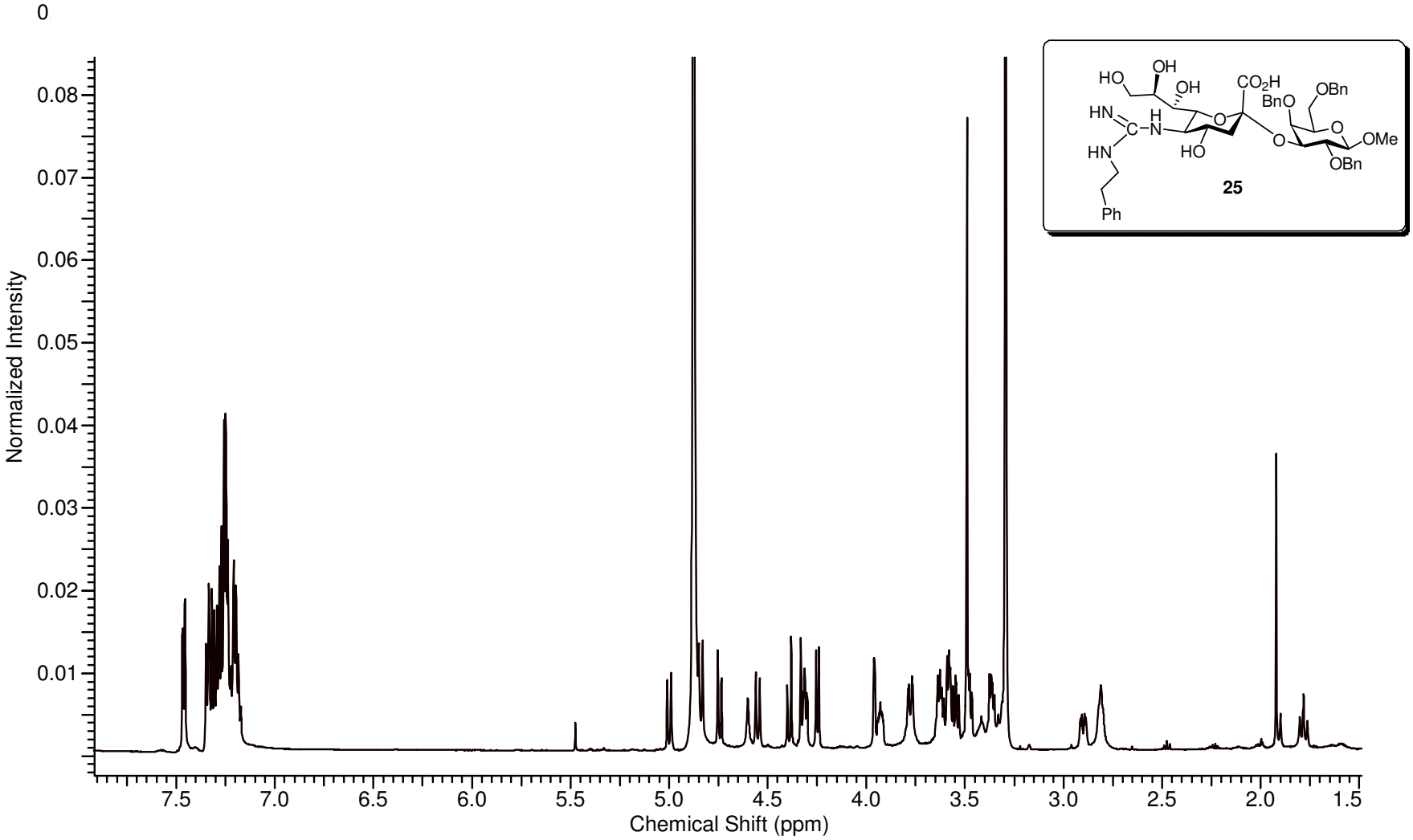
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-5-(*N*'-(2-phenylethyl)thioureido)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-[2,4,6-tri-*O*-benzyl-β-D-galactopyranoside] (23):



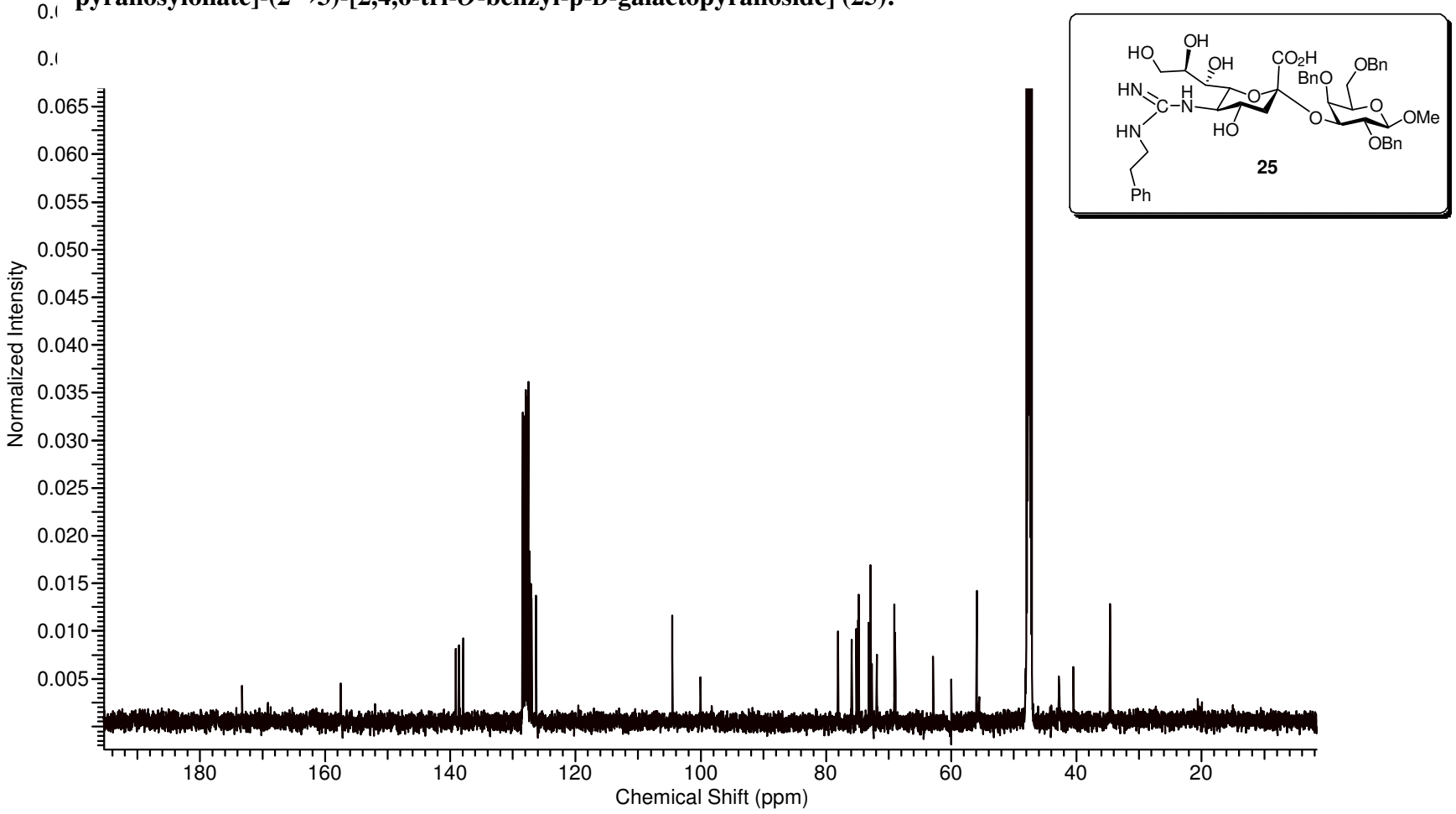
^{13} C NMR (151 MHz, $CDCl_3$) of Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-5-(*N*'-(2-phenylethyl)thioureido)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-[2,4,6-tri-*O*-benzyl-β-D-galactopyranoside] (23):



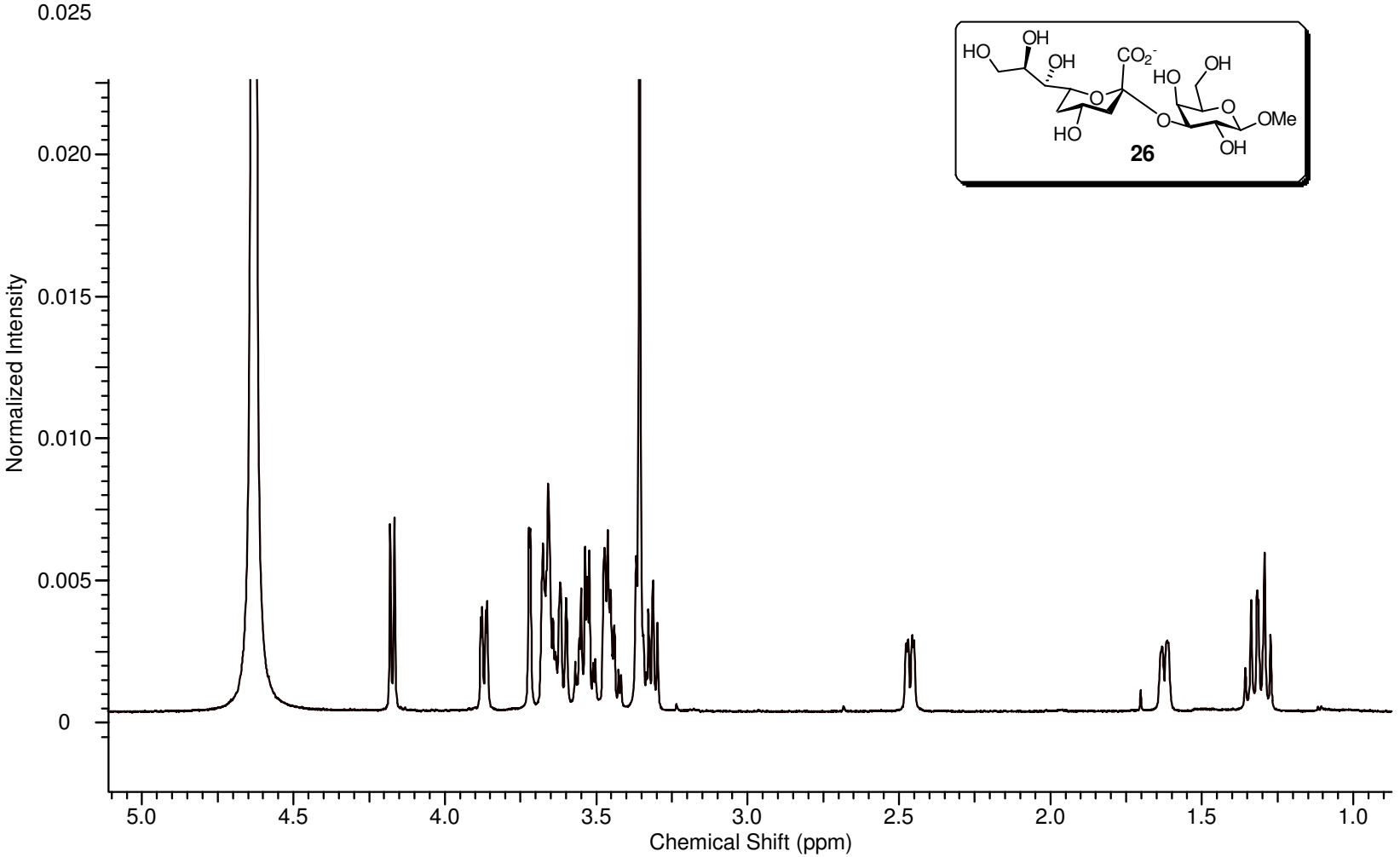
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl [5-(*N*'-(2-phenylthyl)guanidino)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulo-pyranosylonate]-(2→3)-[2,4,6-tri-*O*-benzyl-β-D-galactopyranoside] (25):



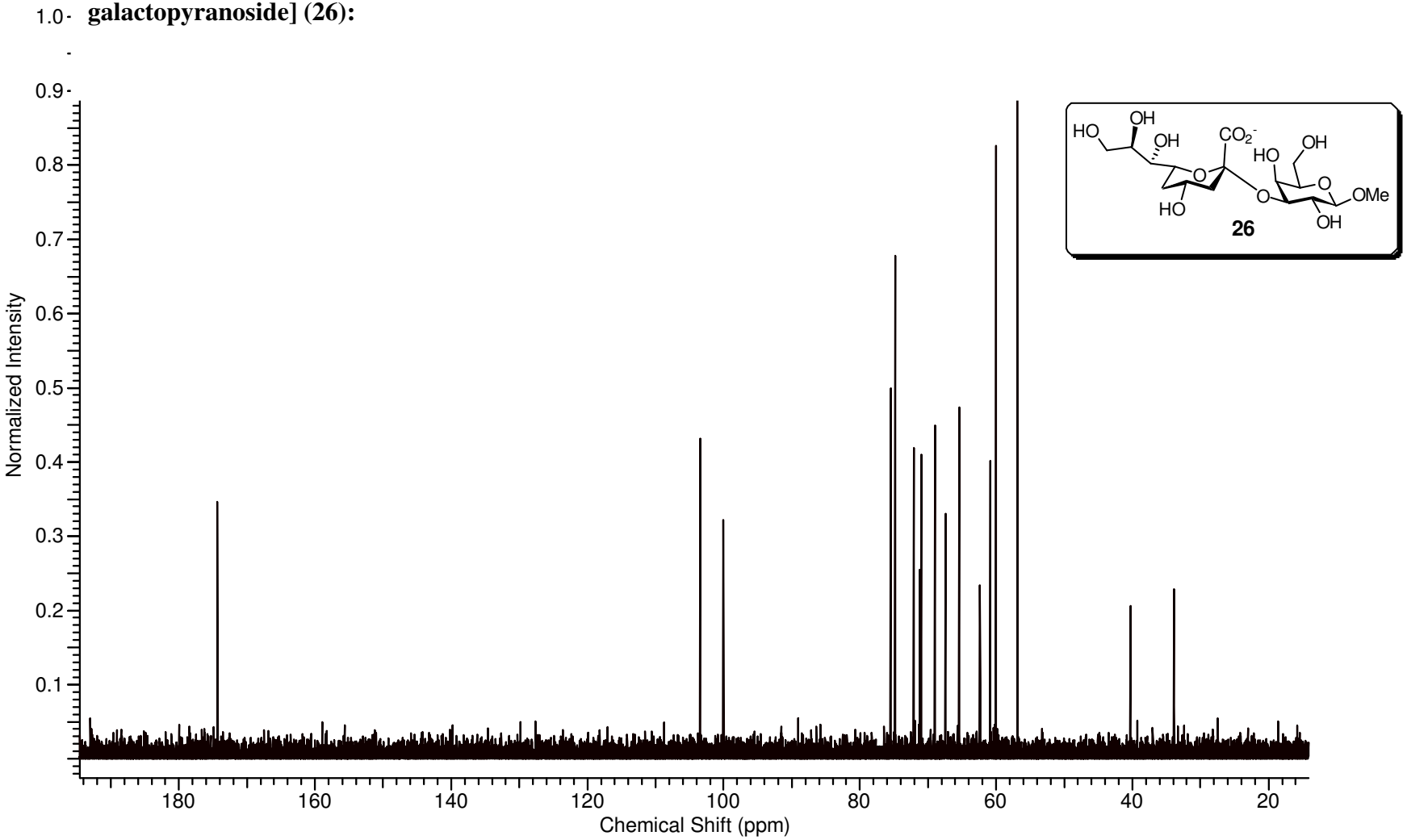
^{13}C NMR (151 MHz, $CDCl_3$) of Methyl [5-(*N*'-(2-phenylthyl)guanidino)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulo-pyranosylonate]-(2→3)-[2,4,6-tri-*O*-benzyl-β-D-galactopyranoside] (25):



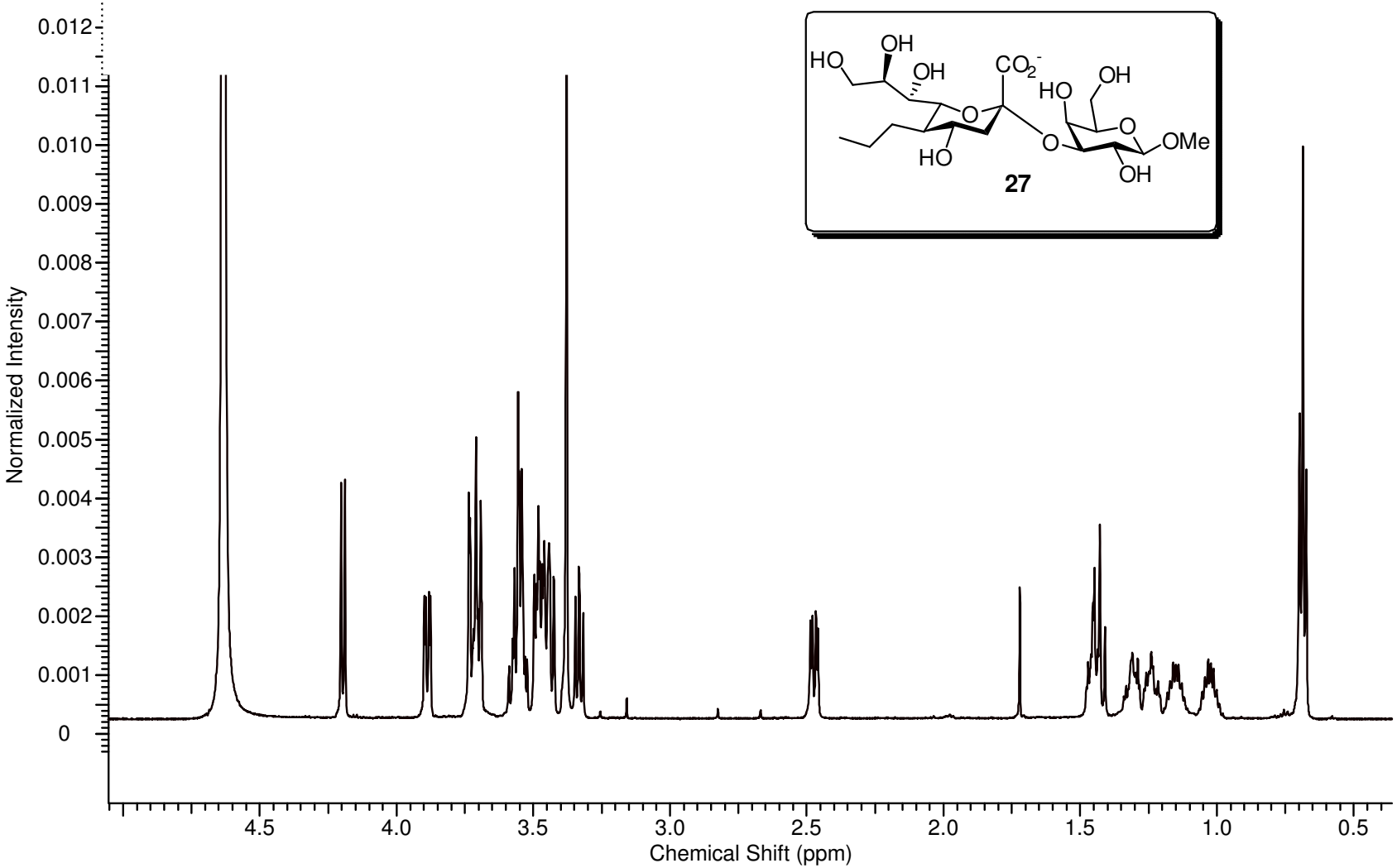
^{1}H NMR (600 MHz, D_2O) of Methyl [Sodium (3,5-dideoxy-α-D-*gluco*-2-nonulopyranosyl)onate]-(2→3)-[β-D-galactopyranoside] (26):



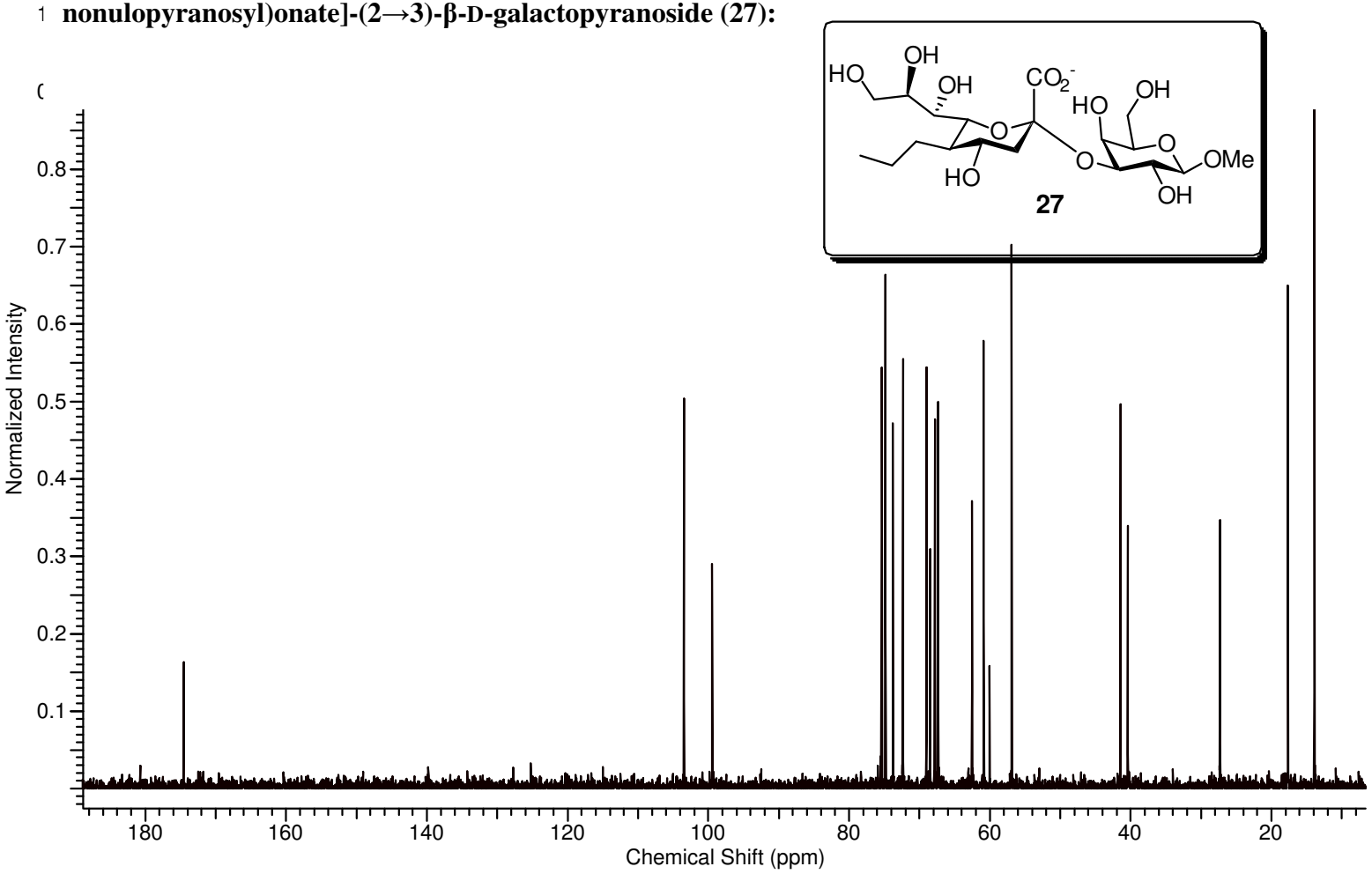
^{13}C NMR (151 MHz, D_2O) of Methyl [Sodium (3,5-dideoxy-α-D-*gluco*-2-nonulopyranosyl)onate]-(2→3)-[β-D-galactopyranoside] (26):



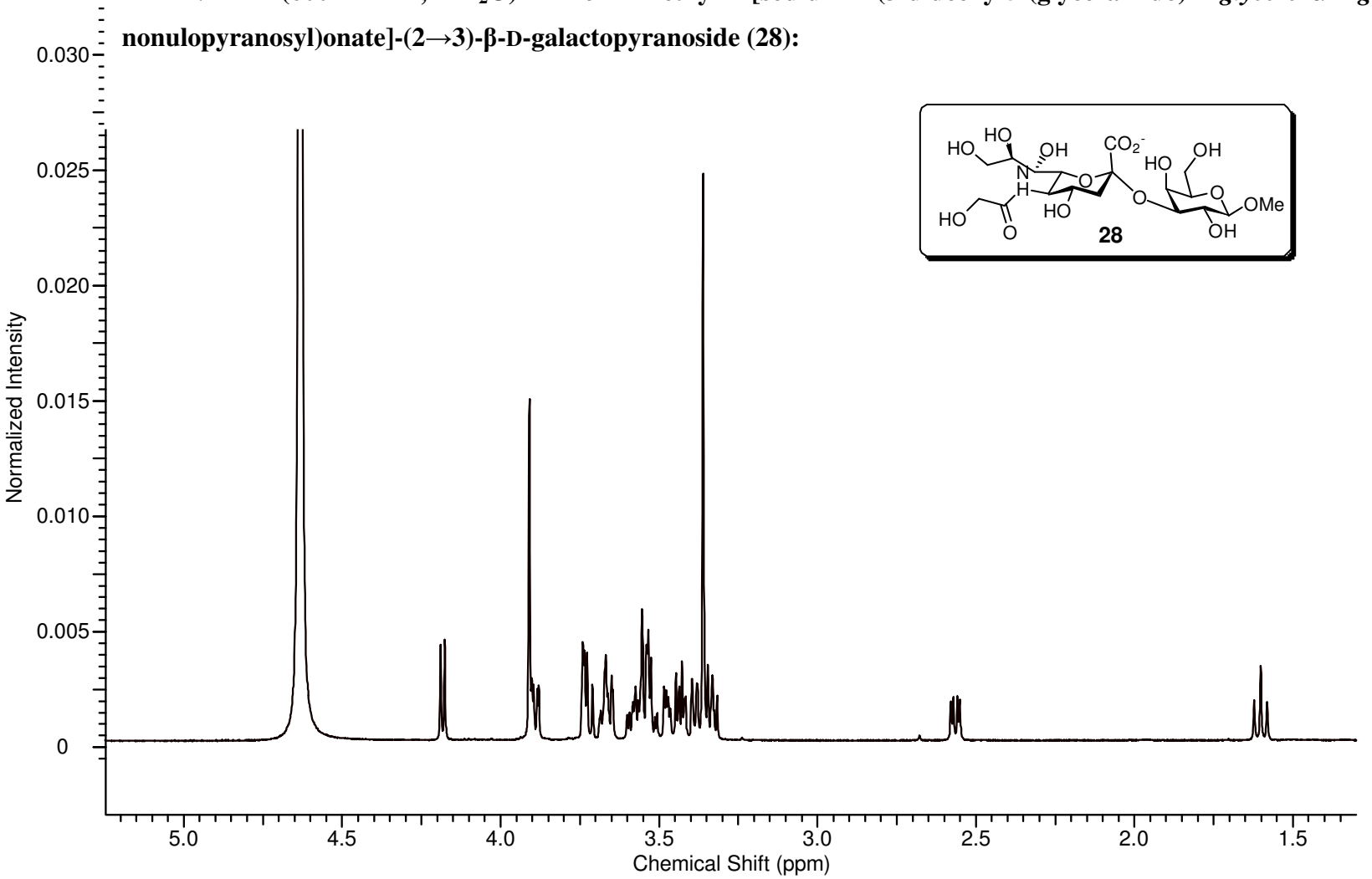
^{1}H NMR (600 MHz, D_2O) of Methyl [sodium (3,5-dideoxy-5-*C*-propyp-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-β-D-galactopyranoside (27):



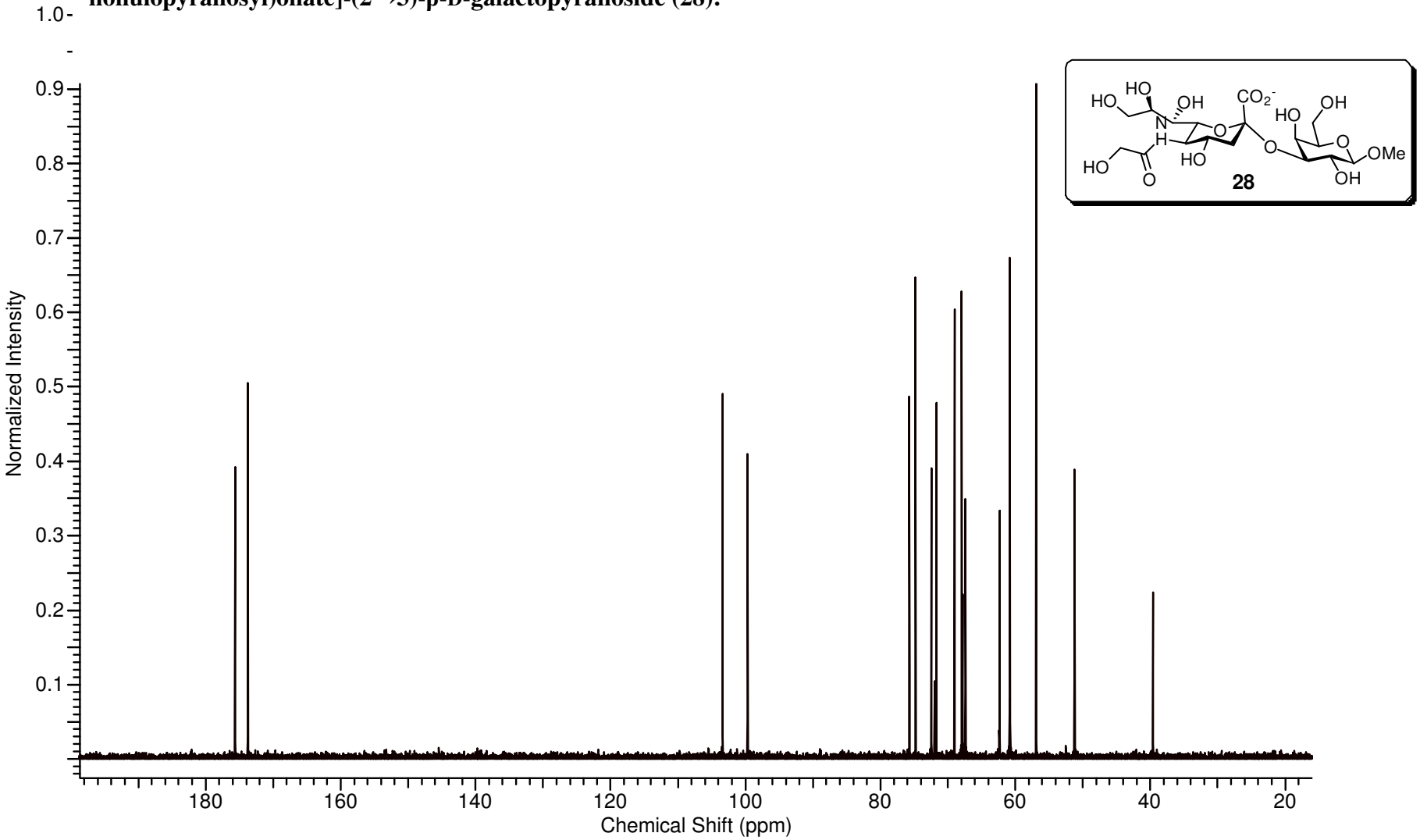
^{13}C NMR (151 MHz, D_2O) of Methyl [sodium (3,5-dideoxy-5-*C*-propyp-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-β-D-galactopyranoside (27):



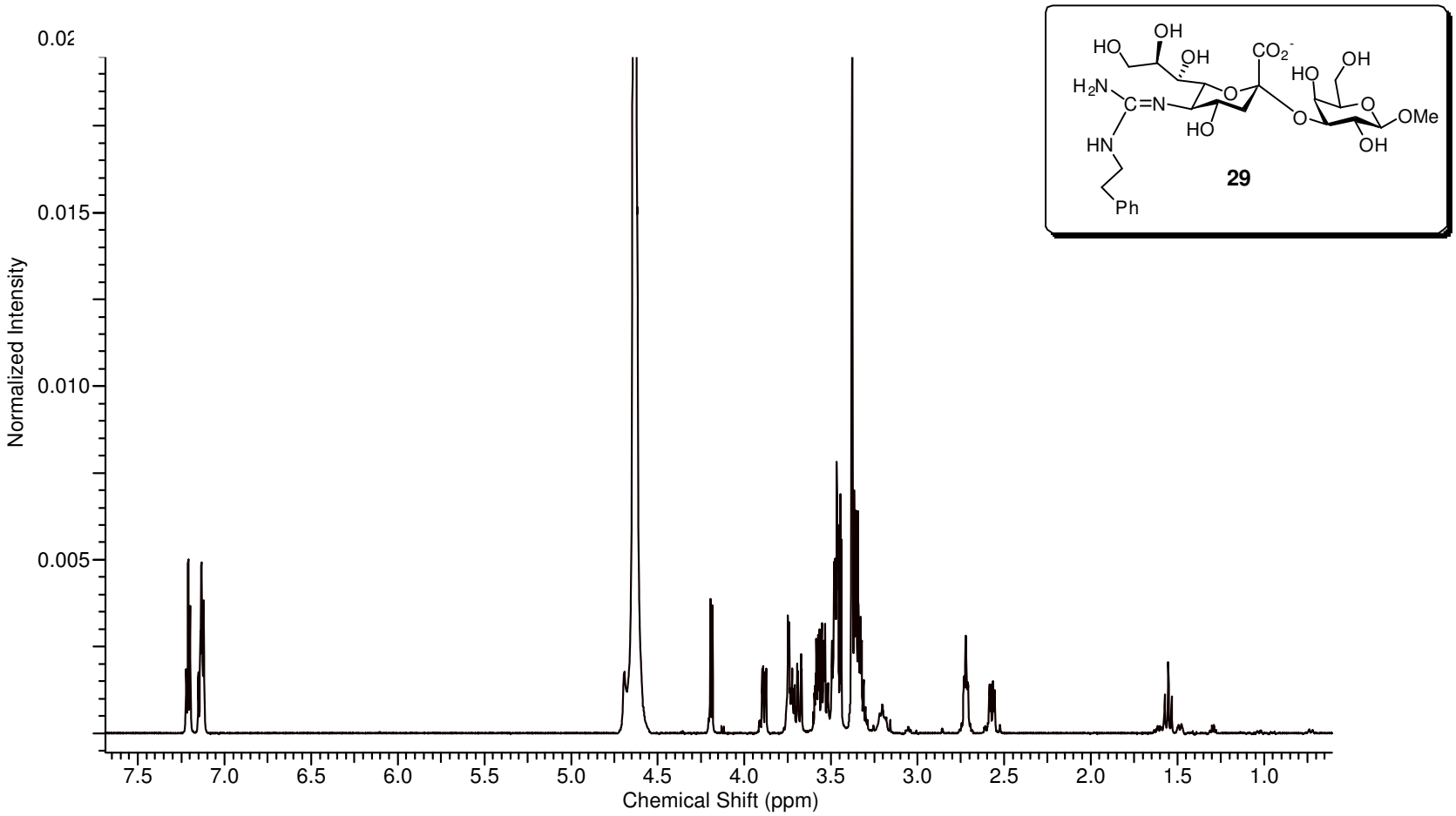
^{1}H NMR (600 MHz, D_2O) of Methyl [sodium (3-dideoxy-5-(glyceramido)-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-β-D-galactopyranoside (28):



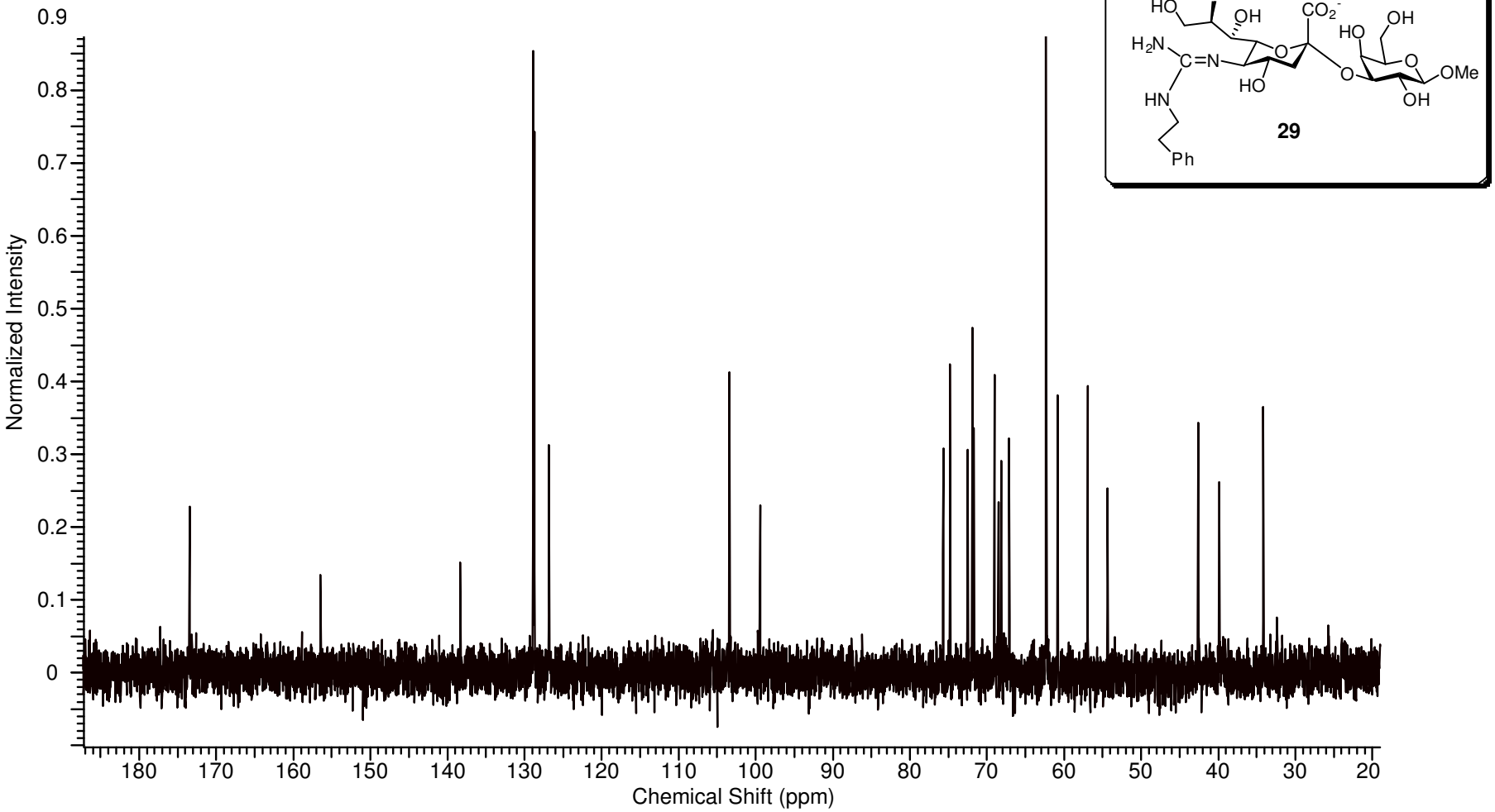
^{13}C NMR (151 MHz, D_2O) of Methyl [sodium (3-dideoxy-5-(glyceramido)-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-β-D-galactopyranoside (28):



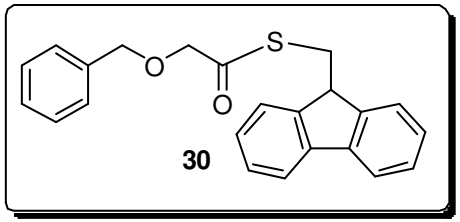
^{1}H NMR (600 MHz, D_2O) of Methyl [sodium (3-dideoxy-5-(*N*'-(2-phenylethyl)guanidino)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)-β-D-galactopyranoside (29):

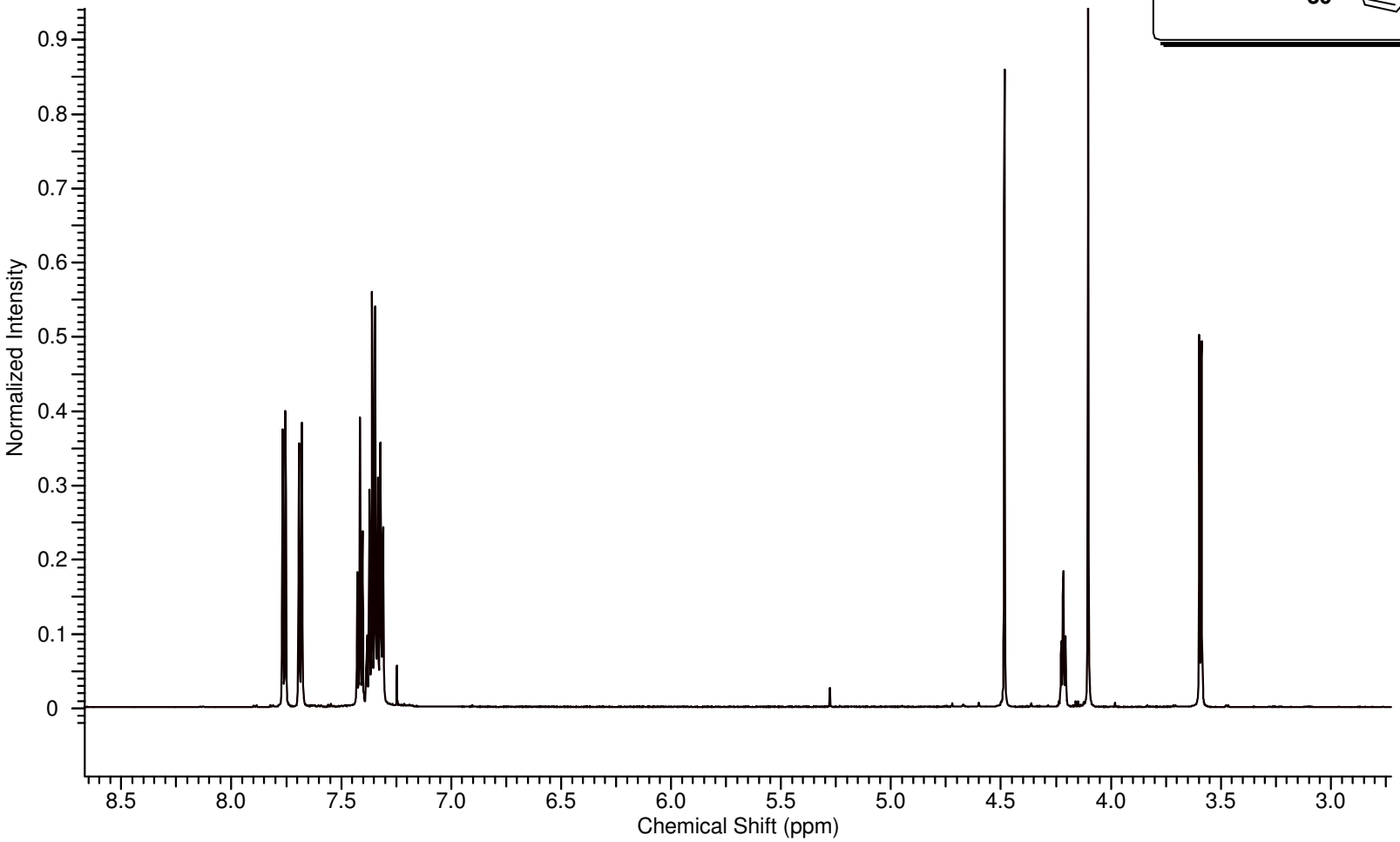


^{13}C NMR (151 MHz, D_2O) of Methyl [sodium (3-dideoxy-5-(*N*'-(2-phenylethyl)guanidino)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)-β-D-galactopyranoside (29):



^{1}HNMR (600 MHz, $CDCl_3$) of (9-Fluorenylmethyl) benzyloxythioaceate (30):





^{13}CNMR (151 MHz, $CDCl_3$) of *S*-(9-Fluorenylmethyl) benzyloxythioaceate (30):