Supporting Information for

Epimeric and amino disaccharide analogs as probes of an α-(1→6)-mannosyltransferase involved in mycobacterial lipoarabinomannan biosynthesis.

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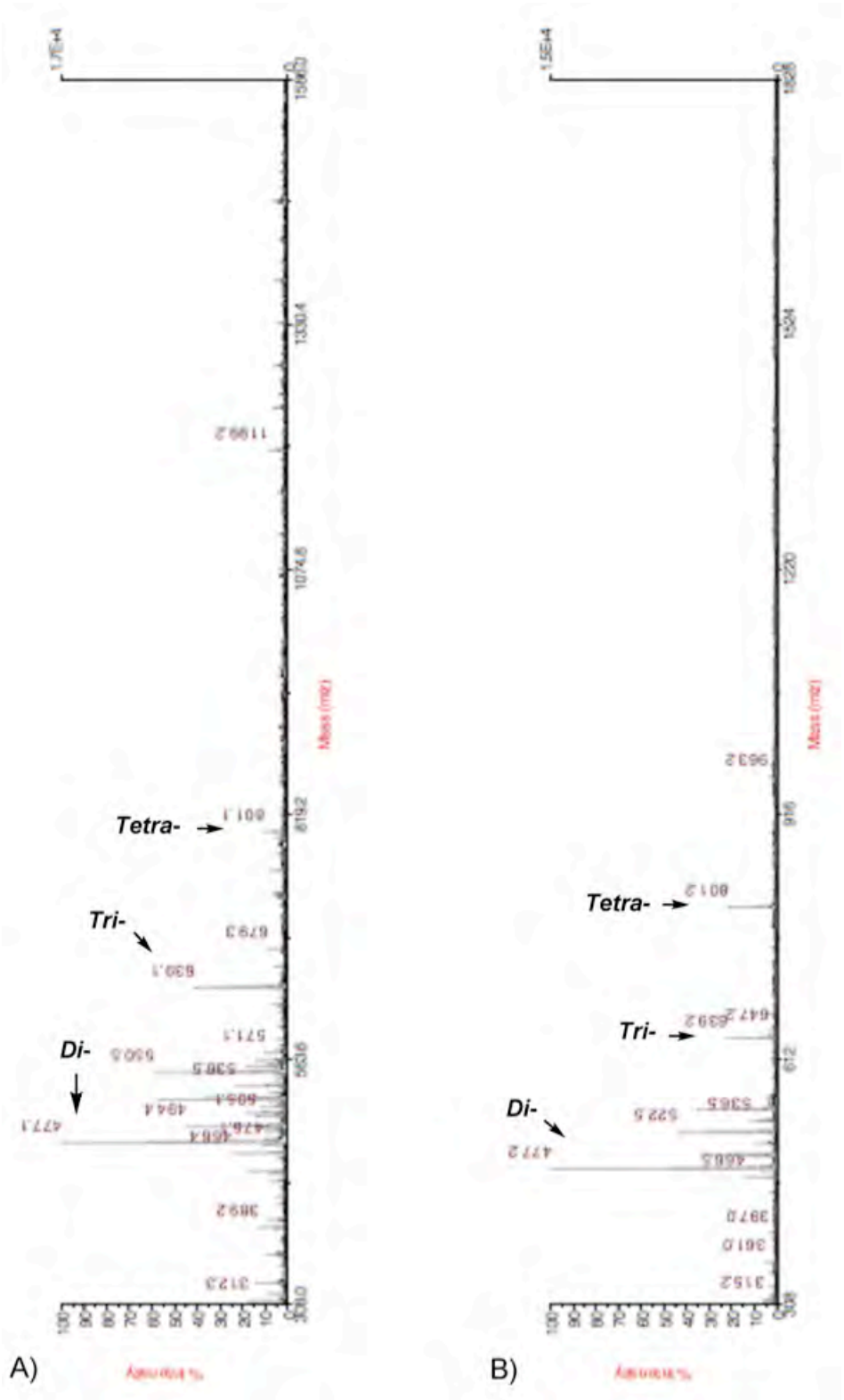
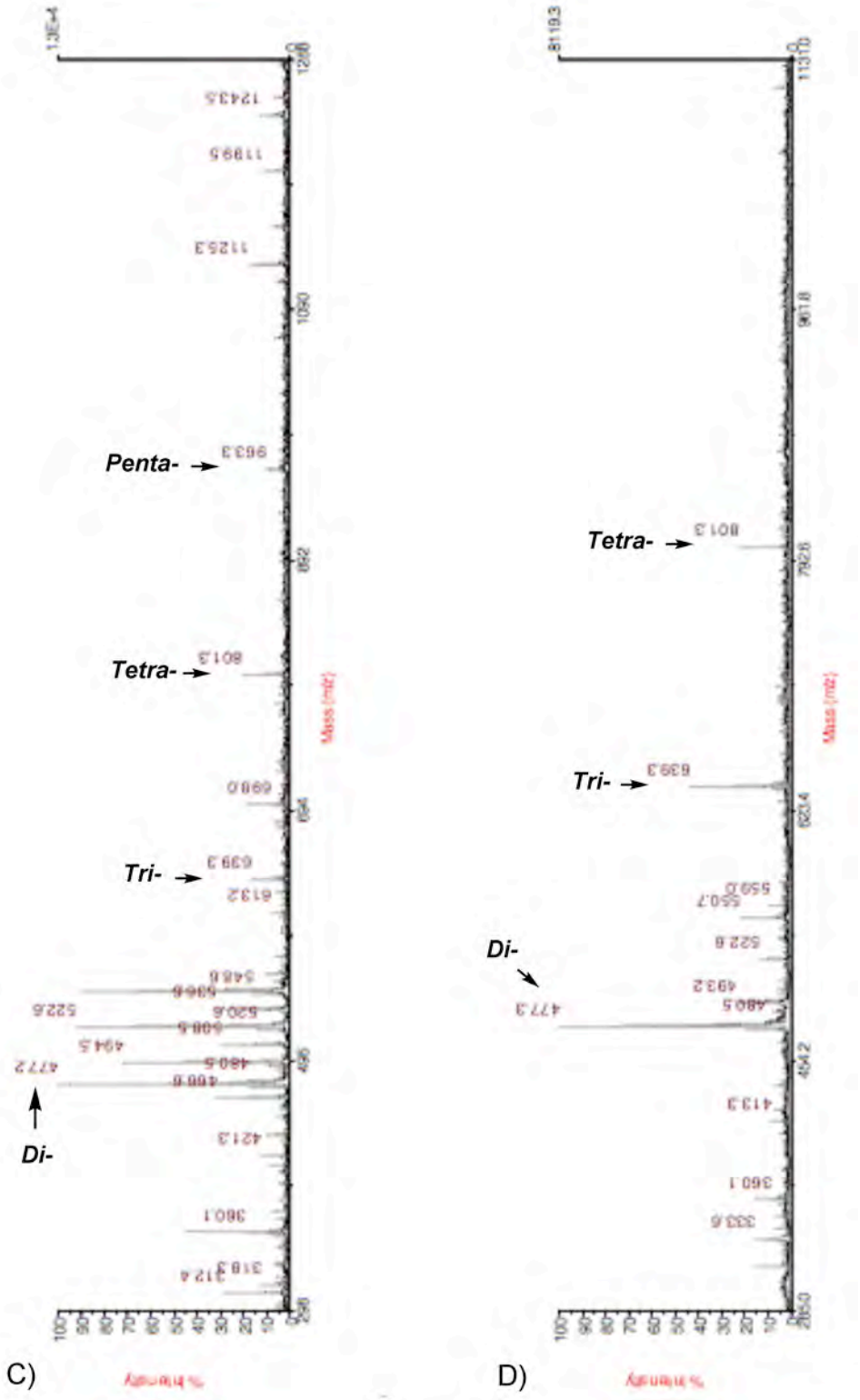
Figure S1. MALDI mass spectra of enzymatic products isolated from incubation mixtures using analogs **3** (A), **5** (B), **7** (C), and **9** (D) at 2 mM concentrations.





C) D)

Phenyl 2-*O*-acetyl-6-*O*-(*tert*-butyldiphenylsilyl)-3,4-*O*-isopropylidene-1-thio-α-D-talopyranoside (13)

Monosaccharide **20** (102 mg, 0.086 mmol) was dissolved in 1:1 CH_2Cl_2–pyridine (4 mL) and acetic anhydride (0.16 mL) was added. The reaction mixture was stirred for 4 h and then diluted with CH_2Cl_2 (25 mL) before being washed with 1 M HCl (3 x 10 mL), satd aq $NaHCO_3$ (10 mL) and H_2O (10 mL). The organic layer was dried ($MgSO_4$), concentrated and the crude product was purified by chromatography (6:1 hexane–EtOAc) to give **13** (98 mg, 89%) as colorless oil: R_f 0.40 (6:1 hexane–EtOAc); $[\alpha]_D$ = +77.0 (*c* 2.8, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.68–7.73 (m, 4H, ArH), 7.50–7.54 (m, 2H, ArH), 7.35–7.45 (m, 6H, ArH), 7.21–7.26 (m, 3H, ArH), 5.45 (d, 1H, *J* = 8.6 Hz, H-1), 5.08 (dd, 1H, *J* = 8.6, 2.9 Hz, H-2), 4.60 (dd, 1H, *J* = 7.6, 2.9 Hz, H-3), 4.39 (dd, 1H, *J* = 7.6, 1.9 Hz, H-4), 3.93 (ddd, 1H, *J* = 6.5, 6.2, 1.9 Hz, H-5), 3.84 (dd, 1H, *J* = 10.4, 6.2 Hz, H-6a), 3.77 (dd, 1H, *J* = 10.4, 6.5 Hz, H-6b), 2.19 (s, 3H, C(O)C*H*$_3$), 1.44 (s, 3H, C(C*H*$_3$)$_2$), 1.33 (s, 3H, C(C*H*$_3$)$_2$), 1.05 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 170.2 (*C*=O), 135.7 (2C, Ar), 135.6 (2C, Ar), 133.5 (Ar), 133.4 (2C, Ar), 132.7 (2C, Ar), 129.6 (2C, Ar), 128.8 (2C, Ar), 127.7 (2C, Ar), 127.6 (3C, Ar), 110.8 (*C*(CH$_3$)$_2$), 83.8 (C-1), 73.7 (C-4), 75.6 (C-3), 71.5 (C-5), 69.1 (C-2), 62.4 (C-6), 26.8 (C(*C*H$_3$)$_3$), 26.1 (C(*C*H$_3$)$_2$), 25.5 (C(*C*H$_3$)$_2$), 21.1 (C(O)*C*H$_3$), 19.2 (*C*(CH$_3$)$_3$). HRMS (ESI) calcd. for (M + Na) $C_{33}H_{40}O_6SiS$: 615.2207. Found: 615.2207.

Octyl 2-*O*-acetyl-3,4-*O*-isopropylidene-α-D-talopyranoside (14)

Octyl talopyranoside **23** (112 mg, 0.18 mmol) was dissolved in THF (5 mL) and 1.0 M tetra-*n*-butylammonium fluoride in THF (0.9 mL, 0.90 mmol) was added and the solution

was stirred at rt overnight. The solvent was evaporated and the residue was purified by chromatography (2:1 hexane–EtOAc) to give **14** (51 mg, 74%) as a colorless oil. R_f 0.11 (2:1 hexane–EtOAc); $[\alpha]_D$ = +87.8 (*c* 1.7, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 4.88–4.95 (m, 2H, H-1, H-2), 4.59 (dd, 1H, *J* = 7.5, 2.5 Hz, H-3), 4.35 (dd, 1H, *J* = 7.5, 1.8 Hz, H-4), 3.70–3.90 (m, 4H, H-5, H-6a, H-6b, octyl OCH_2), 3.45 (dt, 1H, *J* = 9.7, 6.6 Hz, octyl OCH_2), 2.16 (s, 3H, C(O)CH_3), 2.08 (br s, 1H, O*H*), 1.48–1.62 (m, 5H, C(CH_3)$_2$, octyl OCH$_2$CH_2), 1.20–1.39 (m, 13H, C(CH_3)$_2$, octyl CH_2), 0.87 (t, 3H, *J* = 6.7 Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 170.2 (*C*=O), 110.8 (*C*(CH$_3$)$_2$), 97.6 (C-1, $^1J_{C,H}$ = 171.9 Hz), 74.6 (C-4), 72.2 (C-3), 70.5 (C-2), 69.8 (C-5), 68.2 (octyl O*C*H$_2$), 62.2 (C-6), 31.8 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.3(1) (octyl *C*H$_2$), 29.2(6) (octyl *C*H$_2$), 26.0(3) (C(*C*H$_3$)$_2$), 26.0(0) (octyl *C*H$_2$), 25.2 (C(*C*H$_3$)$_2$), 22.6 (octyl *C*H$_2$), 21.1 (C(O)*C*H$_3$), 14.1 (octyl *C*H$_3$). Anal. Calcd for $C_{19}H_{34}O_7$ (422.27): C, 68.22; H, 9.06. Found: C, 68.28; H, 9.06. HRMS (ESI) calcd. for (M + Na) $C_{19}H_{34}O_7$: 397.2197. Found: 397.2198.

_p_-Tolyl 2,3,4-tri-_O_-benzyl-6-_O-tert_-butyldiphenylsilyl-1-thio-β-D-glucopyranoside (15)

Tetraol **24**[1] (1.50 g, 5.24 mmol) and imidazole (0.90 g, 13.1 mmol) were dissolved in DMF (15 mL) and *tert*-butylchlorodiphenylsilane (1.7 mL, 6.55 mmol) was added. The reaction mixture was heated at 45 °C for 5 h and was quenched by the addition of H_2O (2 mL). The mixture was then diluted with EtOAc (60 mL), washed with H_2O (3 x 20 mL), 1M HCl (20 mL) and satd aq $NaHCO_3$ (20 mL). The organic layer was dried ($MgSO_4$), concentrated and the resulting oil was dissolved in DMF (4.5 mL) and BnBr (1.0 mL, 8.6 mmol) was added. The solution was cooled in an ice bath and 60% NaH in mineral oil

(0.30 g, 7.64 mmol) was added portion wise, and the mixture was warmed to rt. After 3 h, the reaction was quenched by the addition of CH_3OH (15 mL), diluted with EtOAc (90 mL), washed with H_2O (3 x 40 mL), brine (40 mL) and dried ($MgSO_4$), filtered and concentrated to pale yellow oil, was purified by chromatography (9:1 hexane–EtOAc) to give **15** (1.43 g, 95%) as a colorless oil: R_f 0.33 (9:1 hexane–EtOAc); $[\alpha]_D$ = –14.4 (*c* 1.8, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.77–7.81 (m, 2H, ArH), 7.70–7.74 (m, 2H, ArH), 7.50–7.54 (m, 2H, ArH), 7.39–7.45 (m, 4H, ArH), 7.24–7.38 (m, 15H, ArH), 7.13–7.17 (m, 2H, ArH), 7.70–7.04 (m, 2H, ArH), 4.85–4.92 (m, 4H, PhC*H*$_2$), 4.74 (d, 1H, *J* = 10.2 Hz, PhC*H*$_2$), 4.70 (d, 1H, *J* = 10.8 Hz, PhC*H*$_2$), 4.63 (d, 1H, *J* = 9.8 Hz, H-1), 4.00 (dd, 1H, *J* = 11.4, 1.8 Hz, H-6a), 3.95 (dd, 1H, *J* = 11.4, 3.7 Hz, H-6b), 3.80 (dd, 1H, *J* = 8.9, 8.9 Hz, H-4), 3.72 (dd, 1H, *J* = 8.9, 8.9 Hz, H-3), 3.53 (dd, 1H, *J* = 9.8, 8.9 Hz, H-2), 3.38 (ddd, 1H, *J* = 8.9, 3.7, 1.8 Hz, H-5), 2.31 (s, 3H, C*H*$_3$), 1.11 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.4 (Ar), 138.3 (Ar), 138.1 (Ar), 137.5 (Ar), 135.9 (2C Ar), 135.7 (2C, Ar), 133.5 (Ar), 133.0 (Ar), 132.4 (2C, Ar), 130.2 (Ar), 129.7, 129.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.7(9), 127.7(5), 127.7(3), 127.6(8) (23 x Ar), 87.8 (C-1), 86.9 (C-3), 80.8 (C-2), 80.0 (C-5), 77.5 (C-4), 76.0 (Ph*C*H$_2$), 75.3 (Ph*C*H$_2$), 75.1 (Ph*C*H$_2$), 62.7 (C-6), 26.9 (C(*C*H$_3$)$_3$), 21.1 (*C*H$_3$), 19.3 (*C*(CH$_3$)$_3$). HRMS (ESI) calcd. for (M + Na) $C_{50}H_{54}O_5SiS$: 817.3354. Found: 817.3356.

Phenyl 6-*O*-*tert*-butyldiphenylsilyl-1-thio-β-D-galactopyranoside (18)

Tetraol **17**[2] (2.68 g, 9.85 mmol) and imidazole (1.68 g, 24.6 mmol) were dissolved in DMF (6 mL) and *tert*-butylchlorodiphenylsilane (3.2 mL, 12.3 mmol) was added. The reaction mixture was heated at 45 °C for 3 h and was quenched by the addition of H_2O

(2 mL). The mixture was then diluted with EtOAc (100 mL), washed with H_2O (3 x 30 mL), 1M HCl (30 mL) and satd aq $NaHCO_3$ (30 mL). The organic layer was dried ($MgSO_4$), concentrated, and the crude product was purified by chromatography (1:1 hexane–EtOAc) to give **18** (4.73 g, 94%) as a colorless oil: R_f 0.35 (1:1 hexane–EtOAc); $[\alpha]_D$ = –19.0 (*c* 1.2, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.67–7.75 (m, 4H, ArH), 7.53–7.57 (m, 2H, ArH), 7.35–7.47 (m, 6H, ArH), 7.23–7.29 (m, 3H, ArH), 4.50 (d, 1H, *J* = 9.7 Hz, H-1), 4.09 (m, 1H, H-4), 3.92–4.00 (m, 2H, H-6a, H-6b), 3.68 (ddd, 1H, *J* = 9.7, 9.7, 1.7 Hz, H-2), 3.55–3.62 (m, 2H, H-3, H-5), 2.96 (d, 1H, *J* = 6.4 Hz, O*H*), 2.94 (d, 1H, *J* = 3.7 Hz, O*H*), 2.73 (d, 1H, *J* = 1.7 Hz, O*H*), 1.07 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 135.7 (2C, Ar), 135.6 (2C, Ar), 132.9 (Ar), 132.7 (Ar), 132.6 (Ar), 132.2 (2C, Ar), 129.9 (2C, Ar), 129.0 (2C, Ar), 127.8 (5C, Ar), 88.6 (C-1), 78.2 (C-5), 75.0 (C-3), 70.0 (C-2), 69.4 (C-4), 63.8 (C-6), 31.8 (octyl *C*H_2), 26.8 (C(*C*H_3)$_3$), 19.2 (*C*(CH$_3$)$_3$). HRMS (ESI) calcd. for (M + Na) $C_{28}H_{34}O_5SiS$: 553.1789. Found: 553.1785.

Phenyl 6-*O*-*tert*-butyldiphenylsilyl-3,4-*O*-isopropylidene-1-thio-β-D-galactopyranoside (19)

Triol **18** (3.37 g, 6.60 mmol), 2,2-dimethoxypropane (6.5 mL, 52.8 mmol), and *p*-TsOH (25 mg) were dissolved in acetone (90 mL) and the mixture was stirred for 2 h. The reaction mixture was neutralized with triethylamine, concentrated, and purified by chromatography (4:1 hexane–EtOAc) to give **19** (3.70 g, quant.) as white foam: R_f 0.30 (4:1 hexane–EtOAc); $[\alpha]_D$ = –2.3 (*c* 1.3, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.69–7.74 (m, 4H, ArH), 7.52–7.56 (m, 2H, ArH), 7.35–7.46 (m, 6H, ArH), 7.24–7.29 (m, 3H, ArH), 4.43 (d, 1H, *J* = 10.3 Hz, H-1), 4.27 (dd, 1H, *J* = 5.5, 2.0 Hz, H-4), 4.07 (dd, 1H, *J*

= 6.9, 5.5 Hz, H-3), 3.89–4.01 (m, 3H, H-5, H-6a, H-6b), 3.55 (dd, 1H, *J* = 10.3, 6.9, 2.3 Hz, H-2), 2.41 (d, 1H, *J* = 2.3 Hz, O*H*), 1.41 (s, 3H, C(CH_3)$_2$), 1.33 (s, 3H, C(CH_3)$_2$), 1.06 (s, 9H, C(CH_3)$_3$; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 135.6(4) (2C, Ar), 135.6(2) (2C, Ar), 133.4 (Ar), 133.3 (Ar), 132.4 (2C, Ar), 132.3 (Ar), 129.7(1) (Ar), 129.7(0) (Ar), 129.0 (2C, Ar), 127.9 (Ar), 127.7 (2C, Ar), 127.6 (2C, Ar), 110.1 (*C*(CH$_3$)$_2$), 88.3 (C-1), 79.0 (C-3), 77.2 (C-5), 73.3 (C-4), 71.6 (C-2), 63.0 (C-6), 28.1 (C(*C*H$_3$)$_2$), 26.8 (C(*C*H$_3$)$_3$), 26.3 (C(*C*H$_3$)$_2$), 19.2 (*C*(CH$_3$)$_3$). HRMS (ESI) calcd. for (M + Na) $C_{31}H_{38}O_5SiS$: 573.2102. Found: 573.2105.

Phenyl 6-*O*-*tert*-butyldiphenylsilyl-3,4-*O*-isopropylidene-1-thio-α-D-talopyranoside (20)

Oxalyl chloride (350 µL, 0.69 mmol) was dissolved in CH_2Cl_2 (3.5 mL) and DMSO (110 µL, 1.52 mmol) was added dropwise at –78 °C. After stirring for 30 min, alcohol **19** (253 mg, 0.46 mmol) in CH_2Cl_2 (3.5 mL) was added dropwise to the mixture over 10 min. After being stirred for 20 min, the solution was then warmed to –60 °C and triethylamine (0.43 mL, 3.1 mmol) was added slowly as the solution warmed to rt over 40 min. The reaction was quenched by the addition H_2O and the organic layer was washed with H_2O (5 mL) and brine (5 mL). The organic layer was dried ($MgSO_4$), concentrated, and the crude ketone intermediate was redissolved in MeOH (17 mL). Sodium borohydride (35 mg, 0.92 mmol) was then added and the mixture was stirred for 20 min before being neutralized with AcOH. The solution was concentrated and the crude product was purified by chromatography (3:1 hexane–EtOAc) to give α-glycoside **20** (135 mg, 53%) and its β-glycoside isomer (23 mg, 9%) as a colorless oils; α-glycoside **20**, R_f 0.32; β-

glycoside, R_f 0.46 (3:1 hexane–EtOAc); Only the α-glycoside was fully characterized: $[\alpha]_D$ = +107.9 (*c* 0.8, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.69–7.74 (m, 4H, ArH), 7.53–7.57 (m, 2H, ArH), 7.34–7.46 (m, 6H, ArH), 7.21–7.29 (m, 3H, ArH), 5.33 (d, 1H, *J* = 7.4 Hz, H-1), 4.55 (dd, 1H, *J* = 7.5, 3.4 Hz, H-3), 4.35 (dd, 1H, *J* = 7.5, 2.0 Hz, H-4), 3.97 (ddd, 1H, *J* = 6.6, 6.0, 2.0 Hz, H-5), 3.85 (dd, 1H, *J* = 10.3, 6.0 Hz, H-6a), 3.80 (dd, 1H, *J* = 10.3, 6.6 Hz, H-6b), 3.75 (ddd, 1H, *J* = 7.4, 7.2, 3.4 Hz, H-2), 2.50 (d, 1H, *J* = 7.2 Hz, O*H*), 1.45 (s, 3H, C(CH_3)$_2$), 1.35 (s, 3H, C(CH_3)$_2$), 1.06 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 135.7 (2C, Ar), 135.6 (2C, Ar), 133.5 (Ar), 133.4 (2C, Ar), 132.6 (2C, Ar), 129.7 (2C, Ar), 128.9 (2C, Ar), 127.7 (Ar), 127.6(4) (2C, Ar), 127.6(0) (2C, Ar), 110.3 (*C*(CH$_3$)$_2$), 87.2 (C-1), 73.3 (2C, C-3, C-4), 70.8 (C-5), 68.3 (C-2), 62.7 (C-6), 26.8 (C(*C*H$_3$)$_3$), 26.0 (C(*C*H$_3$)$_2$), 25.3 (C(*C*H$_3$)$_2$), 19.2 (*C*(CH$_3$)$_3$). HRMS (ESI) calcd. for (M + Na) $C_{31}H_{38}O_5SiS$: 573.2102. Found: 573.2107.

Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-talopyranoside (21) and **phenyl 2,3,4-tri-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-α-D-talopyranoside (22)**

Talopyranoside **20** (20 mg, 0.036 mmol) was dissolved in 4:1 AcOH–H_2O (2 mL) and heated at 50 °C for 1 h. The reaction mixture was then diluted with EtOAc (10 mL) and washed with satd aq $NaHCO_3$ (2 x 5 mL). The organic layer was dried ($MgSO_4$), and concentrated. The crude residue was then dissolved in pyridine (1.5 mL) and acetic anhydride (0.4 mL) and DMAP (small grain) were added. The reaction mixture was stirred for 1 day and then diluted with CH_2Cl_2 (10 mL), before being washed with 0.5 M HCl (3 x 5 mL), water (5 mL) and brine (5 mL). The organic layer was dried ($MgSO_4$), concentrated and the resulting crude mixture was purified by chromatography (2:1

hexane–EtOAc) to give **21** (10 mg, 65%) and **22** (6 mg, 26%) as colorless oils. Data for **21**: R_f 0.27 (2:1, hexane–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.34–7.51 (m, 2H, ArH), 7.30–7.34 (m, 3H, ArH), 5.57 (d, 1H, *J* = 1.2 Hz, H-1), 5.36 (m, 1H, H-4), 5.31 (ddd, 1H, *J* = 3.8, 1.2, 1.2 Hz, H-2), 5.25 (dd, 1H, *J* = 3.8, 3.8 Hz, H-3), 4.77 (app. td, 1H, *J* = 6.4, 1.6 Hz, H-5), 4.15–4.22 (m, 2H, H-6a, H-6b), 2.14 (s, 6H, C(O)CH_3), 2.01 (s, 3H, C(O)CH_3), 2.00 (s, 3H, C(O)CH_3). Data for **22**: R_f 0.52 (2:1, hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.61–7.64 (m, 4H, ArH), 7.34–7.44 (m, 8H, ArH), 7.20–7.24 (m, 3H, ArH), 5.51 (m, 1H, H-4), 5.48 (d, 1H, *J* = 1.3 Hz, H-1), 5.32 (ddd, 1H, *J* = 3.7, 1.3, 1.3 Hz, H-2), 5.27 (dd, 1H, *J* = 3.7, 3.7 Hz, H-3), 4.77 (app. td, 1H, *J* = 6.0, 1.4 Hz, H-5), 3.66–3.75 (m, 2H, H-6a, H-6b), 2.11 (s, 3H, C(O)CH_3), 2.03 (s, 3H, C(O)CH_3), 2.02 (s, 3H, C(O)CH_3), 1.03 (s, 9H, C(CH_3)$_3$).

Octyl 2-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-3,4-*O*-isopropylidene-α-D-talopyranoside (23)

Thioglycoside **13** (31 mg, 0.052 mmol) and powdered 4 Å molecular sieves (50 mg) were dried overnight under vacuum with P_2O_5. Dry CH_2Cl_2 (2 mL) was added and the solution was cooled to 0 °C before the sequential addition of octanol (10 μL, 0.065 mmol), *N*-iodosuccinimide (16 mg, 0.065 mmol) and TMSOTf (3 μL, 0.016 mmol). The mixture was stirred for 1 h at 0 °C and neutralized with triethylamine, before being filtered through Celite and concentrated. The crude residue was purified by chromatography (4:1 hexane–EtOAc) to give **23** (272 mg, 89%) as a colorless oil. R_f 0.38 (4:1 hexane–EtOAc); $[\alpha]_D$ = +35.6 (*c* 0.9, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.68–7.73 (m, 4H, ArH), 7.35–7.45 (m, 6H, ArH), 4.92 (dd, 1H, *J* = 6.2, 2.9 Hz, H-2),

4.86 (d, 1H, *J* = 6.2 Hz, H-1), 4.56 (dd, 1H, *J* = 7.6, 2.9 Hz, H-3), 4.32 (dd, 1H, *J* = 7.6, 1.7 Hz, H-4), 3.79–3.89 (m, 3H, H-5, H-6a, H-6b), 3.75 (dt, 1H, *J* = 9.7, 6.7 Hz, octyl OC*H*$_2$), 3.39 (dt, 1H, *J* = 9.7, 6.9 Hz, octyl OC*H*$_2$), 2.16 (s, 3H, C(O)C*H*$_3$), 1.50–1.60 (m, 2H, octyl OCH$_2$C*H*$_2$), 1.44 (s, 3H, C(C*H*$_3$)$_2$), 1.20–1.34 (m, 13H, C(C*H*$_3$)$_2$, octyl C*H*$_2$), 1.06 (s, 9H, C(C*H*$_3$)$_3$), 0.88 (t, 3H, *J* = 6.9 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 170.3 (*C*=O), 135.7 (2 x Ar), 135.6 (2 x Ar), 135.5 (2 x Ar), 127.6(1) (2 x Ar), 127.5(8) (4 x Ar), 110.5 (isopropylidene *C*), 97.4 (C-1), 74.1 (C-4), 72.3 (C-3), 70.9 (C-2), 70.7 (C-5), 67.9 (octyl O*C*H$_2$), 62.6 (C-6), 31.8 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 26.8 (C(*C*H$_3$)$_3$), 26.1 (C(*C*H$_3$)$_2$), 26.0 (octyl *C*H$_2$), 25.3 (C(*C*H$_3$)$_2$), 22.6 (octyl *C*H$_2$), 21.1 (C(O)*C*H$_3$), 19.2 (*C*(CH$_3$)$_3$), 14.1 (octyl *C*H$_3$). HRMS (ESI) calcd. for (M + Na) $C_{35}H_{52}O_7Si$: 635.3375. Found: 635.3374.

Octyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (26)

Thioglycoside **11**[3] (4.12 g, 4.9 mmol), alcohol **10**[4] (2.30 g, 4.1 mmol), and powdered 4 Å molecular sieves (2.5 g) were dried overnight under vacuum with P_2O_5. Dry CH_2Cl_2 (100 mL) was added and the reaction mixture was cooled to 0 °C before the addition of *N*-iodosuccinimide (1.5 g, 6.2 mmol) and TMSOTf (0.22 mL, 1.2 mmol). The mixture was stirred for 1 h at 0 °C and neutralized with triethylamine, before being filtered through Celite and concentrated. The crude residue was purified by chromatography (6:1 hexane–EtOAc) to give **26** (4.45 g, 85%) as a pale yellow oil. R_f 0.26 (6:1 hexane–EtOAc); $[\alpha]_D$ = –30.2 (*c* 3.0, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.13–8.17 (m, 2H, ArH), 7.83–7.91 (m, 4H, ArH), 7.72–7.76 (m, 2H, ArH), 7.56–7.61 (m, 3H, ArH), 7.51–

7.55 (m, 1H, ArH), 7.18–7.46 (m, 26H, ArH), 7.13–7.17 (m, 2H, ArH), 6.18 (dd, 1H, *J* = 10.2, 10.2 Hz, H-4′), 5.88 (dd, 1H, *J* = 10.2, 3.3 Hz, H-3′), 5.77 (dd, 1H, *J* = 3.3, 1.8 Hz, H-2′), 5.23 (d, 1H, *J* = 1.8 Hz, H-1′), 5.02 (d, 1H, *J* = 11.4 Hz, PhC*H*$_2$), 4.84 (d, 1H, *J* = 1.8 Hz, H-1), 4.75 (d, 1H, *J* = 12.0 Hz, PhC*H*$_2$), 4.71 (d, 1H, *J* = 12.0 Hz, PhC*H*$_2$), 4.69 (d, 1H, *J* = 11.4 Hz, PhC*H*$_2$), 4.65 (s, 2H, PhC*H*$_2$), 4.22 (ddd, 1H, *J* = 10.2, 3.0, 3.0 Hz, H-5′), 3.92–3.98 (m, 3H, H-3, H-4, H-6a), 3.83–3.89 (m, 2H, H-5, H-6b), 3.83 (d, 2H, *J* = 3.0 Hz, H-6a′, H-6b′), 3.80 (dd, 1H, *J* = 2.4, 1.8 Hz, H-2), 3.76 (dt, 1H, *J* = 9.6, 6.6 Hz, octyl OC*H*$_2$), 3.42 (dt, 1H, *J* = 9.6, 6.6 Hz, octyl OC*H*$_2$), 1.54–1.63 (m, 2H, octyl OCH$_2$C*H*$_2$), 1.18–1.40 (m, 10H, octyl C*H*$_2$), 1.07 (s, 9H, C(C*H*$_3$)$_3$), 0.84 (t, 3H, *J* = 6.6 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 165.4 (*C*=O), 165.3 (*C*=O), 165.2 (*C*=O), 138.5 (Ar), 138.5 (Ar), 138.5 (Ar), 135.8 (2C, Ar), 135.8 (2C, Ar), 133.1 (Ar), 133.0 (Ar), 132.8 (Ar), 130.0 (Ar), 129.8, 129.7(0), 129.6(7), 129.6, 129.5(2), 129.4(9), 129.4(6), 128.5, 128.3(7), 128.3(3), 128.3(0), 128.2(6), 128.1(7), 127.8(4), 127.8(2), 127.7, 127.6, 127.5, 127.4(7) (37C, Ar), 97.7(1) (C-1′/C-1, $^1J_{C,H}$ = 172.3 Hz), 97.6(6) (C-1′/C-1, $^1J_{C,H}$ = 168.8 Hz), 80.6 (C-3), 75.0 (Ph*C*H$_2$), 74.9(4) (C-2), 74.9(0) (C-4), 72.6 (Ph*C*H$_2$), 72.1 (Ph*C*H$_2$), 71.4 (C-5), 71.2 (C-5′), 70.8 (C-2′), 70.7 (C-3′), 67.8 (octyl O*C*H$_2$), 66.8(7) (C-6), 66.8(1) (C-4′), 62.5 (C-6′), 31.8 (octyl *C*H$_2$), 29.5 (2C, octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 26.7 (C(*C*H$_3$)$_3$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 19.2 (*C*(CH$_3$)$_3$), 14.1 (octyl *C*H$_3$). HRMS (ESI) calcd. for (M + Na) $C_{78}H_{86}O_{14}Si$: 1297.5679. Found: 1297.5683.

Octyl 2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (27)

Silylated disaccharide **26** (4.0 g, 3.1 mmol) was dissolved in THF (25 mL) and 70% HF·pyridine (2 mL) and pyridine (5 mL) were added and the solution was stirred overnight. The crude product was then diluted with CH_2Cl_2 (150 mL), washed with H_2O (50 mL), 1 M HCl (2 x 50 mL), and satd aq $NaHCO_3$ (50 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated and the residue was purified by chromatography to give **27** as a colorless oil (2.2 g, 66%): R_f 0.34 (3:1 hexane–EtOAc); $[\alpha]_D$ = –28.3 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.09–8.13 (m, 2H, ArH), 7.93–7.97 (m, 2H, ArH), 7.78–7.83 (m, 2H, ArH), 7.59–7.64 (m, 1H, ArH), 7.47–7.56 (m, 3H, ArH), 7.20–7.44 (m, 20H, ArH), 6.00 (dd, 1H, *J* = 10.2, 3.6 Hz, H-3′), 5.81 (dd, 1H, *J* = 10.2, 10.2 Hz, H-4′), 5.74 (dd, 1H, *J* = 3.6, 1.8 Hz, H-2′), 5.21 (d, 1H, *J* = 1.8 Hz, H-1′), 5.04 (d, 1H, *J* = 10.6 Hz, PhC*H*$_2$), 4.82 (d, 1H, *J* = 1.8 Hz, H-1), 4.77 (d, 1H, *J* = 12.6 Hz, PhC*H*$_2$), 4.72 (d, 1H, *J* = 12.6 Hz, PhC*H*$_2$), 4.69 (d, 1H, *J* = 11.6 Hz, PhC*H*$_2$), 4.65 (s, 2H, PhC*H*$_2$), 4.11 (ddd, 1H, *J* = 10.2, 3.6, 3.0 Hz, H-5′), 3.92–3.98 (m, 3H, H-3, H-4, H-6a), 3.82–3.89 (m, 2H, H-5, H-6b), 3.79 (dd, 1H, *J* = 2.4, 1.8 Hz, H-2), 3.71–3.80 (m, 2H, H-6a′, octyl OC*H*$_2$), 3.66 (ddd, 1H, *J* = 12.6, 6.0, 3.6 Hz, H-6b′), 3.40 (dt, 1H, *J* = 9.6, 6.6 Hz, octyl OC*H*$_2$), 2.59 (dd, 1H, *J* = 8.4, 6.0 Hz, O*H*), 1.52–1.64 (m, 2H, octyl OCH$_2$C*H*$_2$), 1.18–1.40 (m, 10H, octyl C*H*$_2$), 0.85 (t, 3H, *J* = 7.2 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 166.5 (*C*=O), 165.3 (*C*=O), 165.2 (*C*=O), 138.4(9) (Ar), 138.4(8) (Ar), 138.4(2) (Ar), 133.6 (Ar), 133.4 (Ar), 133.0 (Ar), 129.9(3), 129.8(8), 129.7, 129.5, 129.3, 128.9, 128.6, 128.5, 128.4, 128.3(4), 128.2(9), 128.2, 127.8, 127.7, 127.6, 127.5 (30C, Ar), 97.8 (C-1′/C-1), 97.7 (C-1′/C-1), 80.5 (C-3), 75.0 (Ph*C*H$_2$), 74.9 (C-2/C-4), 74.8 (C-2/C-4), 72.7 (Ph*C*H$_2$), 72.1 (Ph*C*H$_2$), 71.2 (C-5), 70.8 (C-5′), 70.6 (C-2′), 69.6 (C-3′), 67.8 (octyl O*C*H$_2$), 67.5 (C-4′), 67.2 (C-6), 61.3 (C-6′), 31.8 (octyl *C*H$_2$), 29.5 (2C, octyl

CH_2), 29.3 (octyl *C*H_2), 26.2 (octyl *C*H_2), 22.7 (octyl *C*H_2), 14.1 (octyl *C*H_3). HRMS (ESI) calcd. for (M + Na) $C_{62}H_{68}O_{14}$: 1059.4501. Found: 1059.4488.

Octyl 2,3,4-tri-*O*-benzoyl-6-*O*-*p*-toluenesulfonyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (28)

Disaccharide **27** (155 mg, 0.15 mmol) was dissolved in pyridine (2 mL) and the solution was cooled to 0 °C in an ice bath followed by the addition of *p*-toluenesulfonyl chloride (58 mg, 0.30 mmol). The reaction mixture was stirred overnight and then was diluted with CH_2Cl_2 (25 mL), washed with 1 M HCl (3 x 10 mL), satd aq $NaHCO_3$ (10 mL) and H_2O (10 mL). The organic layer was dried ($MgSO_4$), concentrated and the crude product was then purified by chromatography (3:1 hexane–EtOAc) to give **28** as a colorless oil (162 mg, 91%): R_f 0.36 (3:1 hexane–EtOAc); $[\alpha]_D$ = –22.9 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.06–8.09 (m, 2H, ArH), 7.82–7.86 (m, 2H, ArH), 7.77–7.81 (m, 2H, ArH), 7.72–7.76 (m, 2H, ArH), 7.59–7.64 (m, 1H, ArH), 7.46–7.54 (m, 3H, ArH), 7.18–7.44 (m, 20H, ArH), 7.13–7.17 (m, 2H, ArH), 5.84 (dd, 1H, *J* = 10.0, 2.9 Hz, H-3′), 5.81 (dd, 1H, *J* = 10.0, 10.0 Hz, H-4′), 5.68 (dd, 1H, *J* = 2.9, 2.0 Hz, H-2′), 5.12 (d, 1H, *J* = 2.0 Hz, H-1′), 5.02 (d, 1H, *J* = 11.3 Hz, PhC*H*$_2$), 4.84 (d, 1H, *J* = 1.9 Hz, H-1), 4.77 (d, 1H, *J* = 12.5 Hz, PhC*H*$_2$), 4.73 (d, 1H, *J* = 12.5 Hz, PhC*H*$_2$), 4.68 (d, 1H, *J* = 11.3 Hz, PhC*H*$_2$), 4.65 (s, 2H, PhC*H*$_2$), 4.37 (ddd, 1H, *J* = 10.0, 4.9, 2.4 Hz, H-5′), 4.27 (dd, 1H, *J* = 11.0, 2.4 Hz, H-6a′), 4.16 (dd, 1H, *J* = 11.0, 4.9 Hz, H-6b′), 3.91–3.98 (m, 2H, H-3, H-4), 3.89 (dd, 1H, *J* = 11.1, 5.9 Hz, H-6a), 3.80–3.87 (m, 2H, H-5, H-6b), 3.80 (dd, 1H, *J* = 2.0, 1.9 Hz, H-2), 3.74 (dt, 1H, *J* = 9.7, 6.7 Hz, octyl OC*H*$_2$), 3.40 (dt, 1H, *J* = 9.7, 6.5 Hz, octyl OC*H*$_2$), 2.30 (s, 3H, tosyl C*H*$_3$), 1.52–1.62 (m, 2H, octyl OCH_2CH_2), 1.18–1.40

(m, 10H, octyl CH_2), 0.84 (t, 3H, J = 6.9 Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 165.2 (*C*=O), 165.1(7) (*C*=O), 165.0(8) (*C*=O), 144.5 (Ar), 138.4(9) (Ar), 138.4(7) (Ar), 138.4(5) (Ar), 133.4 (Ar), 133.3 (Ar), 133.0 (Ar), 132.7 (Ar), 130.0, 129.7, 129.6, 129.4, 129.2, 129.0, 128.6, 128.4, 128.3(4), 128.2(8), 128.2(0), 128.1, 127.9(2), 127.8(6), 127.7, 127.5(3), 127.5(1) (34C, Ar), 97.7 (C-1), 97.5 (C-1′), 80.4 (C-3), 75.1 (Ph*C*H_2), 74.8 (2C, C-2, C-4), 72.7 (Ph*C*H_2), 72.1 (Ph*C*H_2), 71.3 (C-5), 70.3 (C-2′), 69.8 (C-3′), 68.6 (C-5′), 68.0 (C-6′), 67.8 (octyl O*C*H_2), 67.3 (C-6), 66.9 (C-4′), 31.8 (octyl *C*H_2), 29.5 (2C, octyl *C*H_2), 29.3 (octyl *C*H_2), 26.2 (octyl *C*H_2), 22.7 (octyl *C*H_2), 21.5 (tosyl *C*H_3), 14.1 (octyl *C*H_3). HRMS (ESI) calcd. for (M + Na) $C_{69}H_{74}O_{16}S$: 1213.4590. Found: 1213.4593.

Octyl 6-azido-2,3,4-tri-*O*-benzoyl-6-deoxy-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (29)

Tosylated disaccharide **28** (136 mg, 0.12 mmol) was dissolved in DMF (2 mL) and sodium azide (68 mg, 1.0 mmol) was added and the solution was heated under reflux for 6 h. The crude solution was then diluted with EtOAc (25 mL) and washed with H_2O (10 mL). The organic phase was dried (Na_2SO_4), filtered, concentrated and the residue was purified by chromatography (6:1 hexane–EtOAc) to give **29** as a colorless oil (119 mg, 98%): R_f 0.31 (6:1 hexane–EtOAc); $[\alpha]_D$ = +3.5 (*c* 1.3, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.10–8.14 (m, 2H, ArH), 7.90–7.95 (m, 2H, ArH), 7.78–7.83 (m, 2H, ArH), 7.60–7.65 (m, 1H, ArH), 7.48–7.55 (m, 3H, ArH), 7.18–7.45 (m, 20H, ArH), 5.89 (dd, 1H, J = 9.9, 3.2 Hz, H-3′), 5.84 (dd, 1H, J = 9.9, 9.9 Hz, H-4′), 5.73 (dd, 1H, J = 3.2, 1.8 Hz, H-2′), 5.20 (d, 1H, J = 1.8 Hz, H-1′), 5.03 (d, 1H, J = 11.3 Hz, PhCH_2), 4.83 (d, 1H, J

= 1.7 Hz, H-1), 4.76 (d, 1H, *J* = 11.2 Hz, PhC*H*$_2$), 4.71 (d, 1H, *J* = 11.3 Hz, PhC*H*$_2$), 4.69 (d, 1H, *J* = 11.2 Hz, PhC*H*$_2$), 4.64 (s, 2H, PhC*H*$_2$), 4.33 (ddd, 1H, *J* = 9.9, 6.5, 3.2 Hz, H-5′), 3.95–4.04 (m, 3H, H-3, H-4, H-6a), 3.90 (dd, 1H, *J* = 11.1, 1.7 Hz, H-6b), 3.84–3.89 (m, 1H, H-5), 3.79 (dd, 1H, *J* = 2.2, 1.7 Hz, H-2), 3.74 (dt, 1H, *J* = 9.7, 6.9 Hz, octyl OC*H*$_2$), 3.38–3.48 (m, 3H, H-6a′, H-6b′, octyl OC*H*$_2$), 1.53–1.64 (m, 2H, octyl OCH$_2$C*H*$_2$), 1.18–1.40 (m, 10H, octyl C*H*$_2$), 0.85 (t, 3H, *J* = 6.9 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 165.6 (*C*=O), 165.2 (*C*=O), 165.1 (*C*=O), 138.4(9) (2C, Ar), 138.4(5) (Ar), 133.4(4) (Ar), 133.4(1) (Ar), 133.0 (Ar), 129.9 (Ar), 129.8, 129.7, 129.5, 129.2, 129.0, 128.6, 128.4(4), 128.4(1), 128.3(5), 128.2(9), 128.2, 127.9, 127.8, 127.7, 127.6, 127.5(4), 127.5(3) (29C, Ar), 97.7 (C-1), 97.6 (C-1′), 80.5 (C-3), 75.1 (Ph*C*H$_2$), 74.9 (C-2/C-4), 74.8 (C-2/C-4), 72.7 (Ph*C*H$_2$), 72.1 (Ph*C*H$_2$), 71.3 (C-5), 70.4 (C-2′/C-5′), 70.1 (C-2′/C-5′), 69.7 (C-3′), 68.0 (C-4′), 67.8 (octyl O*C*H$_2$), 67.3 (C-6), 51.2 (C-6′), 31.8 (octyl *C*H$_2$), 29.5 (2C, octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). HRMS (ESI) calcd. for (M + Na) $C_{62}H_{67}N_3O_{13}$: 1084.4566. Found: 1084.4569. FTIR: 2102.3 cm^{-1}.

Octyl 2,3,4-tri-*O*-benzoyl-6-deoxy-6-trifluoroacetamido-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (30)

Azide **29** (50 mg, 0.047 mmol) was dissolved in pyridine (3 mL) and 20% $Pd(OH)_2$–C (10 mg) was added. The mixture was stirred for 4.5 h under a H_2 atmosphere and the catalyst was separated by filtration through a short pad of Celite. The filtrate was concentrated and the residue was redissolved in pyridine (2 mL) before trifluoroacetic anhydride (16 µL, 0.11 mmol) was added dropwise at 0 °C. The mixture was slowly

warmed to rt and stirred overnight. The solution was then diluted with EtOAc (25 mL), washed with H_2O (10 mL) and satd aq $NaHCO_3$ (10 mL). The organic layer was dried (Na_2SO_4), concentrated and the resulting crude product was then redissolved in MeOH (6 mL) and 20% $Pd(OH)_2$–C (10 mg) was added. The mixture was stirred overnight under a H_2 atmosphere and the catalyst was separated by filtration through a short pad of Celite. The filtrate was concentrated and the residue purified by chromatography (15:1 CH_2Cl_2–MeOH) to give **30** as a clear glass (28 mg, 68%): R_f 0.35 (15:1 CH_2Cl_2–MeOH); $[\alpha]_D$ = –29.3 (*c* 0.2, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.02–8.07 (m, 2H, ArH), 7.93–7.98 (m, 2H, ArH), 7.78–7.82 (m, 2H, ArH), 7.60–7.65 (m, 1H, ArH), 7.46–7.55 (m, 3H, ArH), 7.36–7.45 (m, 3H, ArH), 7.23–7.27 (m, 3H, ArH, C(O)N*H*), 5.96 (dd, 1H, *J* = 10.1, 3.4 Hz, H-3′), 5.75 (dd, 1H, *J* = 3.4, 1.8 Hz, H-2′), 5.70 (dd, 1H, *J* = 10.1, 10.1 Hz, H-4′), 5.25 (d, 1H, *J* = 1.8 Hz, H-1′), 4.87 (d, 1H, *J* = 1.3 Hz, H-1), 4.41 (ddd, 1H, *J* = 10.1, 4.9, 2.7 Hz, H-5′), 4.10 (dd, 1H, *J* = 11.4, 4.5 Hz, H-6a), 3.92–3.98 (m, 3H, H-6a′, H-2, H-4), 3.92 (dd, 1H, *J* = 11.4, 1.9 Hz, H-6b), 3.85 (dd, 1H, *J* = 9.9, 3.0 Hz, H-3), 3.79 (dd, 1H, *J* = 9.9, 3.0, 1.9 Hz, H-5), 3.73 (dt, 1H, *J* = 9.7, 6.7 Hz, octyl OC*H*$_2$), 3.41–3.50 (m, 2H, H-6b′, octyl OC*H*$_2$), 3.03 (br s, 2H, *OH*), 1.83 (br s, 1H, *OH*), 1.54–1.64 (m, 2H, octyl OCH_2CH_2), 1.18–1.42 (m, 10H, octyl C*H*$_2$), 0.86 (t, 3H, *J* = 6.9 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 166.5 (*C*=O), 165.6 (*C*=O), 165.4 (*C*=O), 157.5 (CF_3C=O, $^2J_{C=O,F}$ = 37.1 Hz), 133.8 (Ar), 133.7(7) (Ar), 133.4 (Ar), 129.9 (2C, Ar), 129.8 (2C, Ar), 129.7 (2C, Ar), 129.0 (Ar), 128.8 (Ar), 128.7 (2C, Ar), 128.6 (2C, Ar), 128.4 (2C, Ar), 128.3(5) (Ar), 116.0 (*C*F$_3$, ^1J = 287.4 Hz), 99.9 (C-1), 97.7 (C-1′), 72.3 (C-3), 71.1 (C-5), 71.0 (C-2), 70.5 (C-2′), 69.4 (C-3′), 68.7 (C-4), 68.1 (octyl O*C*H$_2$), 67.8(3) (C-4′), 67.8(1) (C-5′), 67.8 (C-6), 39.7 (C-6′), 31.8 (octyl *C*H$_2$), 29.4 (2C, octyl

CH_2), 29.3 (octyl *C*H_2), 26.2 (octyl *C*H_2), 22.6 (octyl *C*H_2), 14.1 (octyl *C*H_3); ^{19}F NMR (376.1 MHz, $CDCl_3$) δ_F –76.2 (s, 3F). HRMS (ESI) calcd. for (M + Na) $C_{43}H_{50}NO_{14}F_3$: 884.3076. Found: 884.3078.

Octyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (31)

Thioglycoside **15** (110 mg, 0.14 mmol), alcohol **10**[4] (65 mg, 0.12 mmol), and powdered 4 Å molecular sieves (100 mg) were dried overnight under vacuum with P_2O_5. Dry CH_2Cl_2 (4 mL) was added and the solution was cooled to 0 °C before the addition of *N*-iodosuccinimide (41 mg, 0.17 mmol) and TMSOTf (6 μL, 0.035 mmol). The mixture was stirred for 1 h at 0 °C and neutralized with triethylamine, before being filtered through Celite and concentrated. The crude product was partially purified by chromatography (9:1 hexane–EtOAc) to give the desired disaccharide as a mixture of α and β isomers (5:1). The silylated disaccharide mixture was then dissolved in THF (2 mL) and and 1.0 M tetra-*n*-butylammonium fluoride in THF (0.31 mL, 0.31 mmol) was added and the solution was stirred at rt overnight. The solvent was evaporated and the residue was purified by chromatography (3:1 hexane–EtOAc) to give **31** (59 mg, 50%) as a colorless oil. R_f 0.32 (3:1 hexane–EtOAc); $[\alpha]_D$ = +33.5 (*c* 1.2, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.18–7.40 (m, 30H, ArH), 5.11 (d, 1H, *J* = 3.5 Hz, H-1′), 4.92 (d, 1H, *J* = 11.0 Hz, PhC*H*$_2$), 4.88 (d, 1H, *J* = 11.1 Hz, PhC*H*$_2$), 4.87 (d, 1H, *J* = 11.2 Hz, PhC*H*$_2$), 4.81 (d, 1H, *J* = 1.7 Hz, H-1), 4.75 (d, 1H, *J* = 11.0 Hz, PhC*H*$_2$), 4.62–4.72 (m, 7H, PhC*H*$_2$), 4.55 (d, 1H, *J* = 11.6 Hz, PhC*H*$_2$), 4.05 (dd, 1H, *J* = 9.6, 9.6 Hz, H-4), 4.00 (dd, 1H, *J* = 9.2, 9.2 Hz, H-3′), 3.92 (dd, 1H, *J* = 9.6, 3.2 Hz, H-3), 3.75–3.89 (m, 6H, H-5′, H-6a′, H-

2, H-5, H-6a, H-6b), 3.62–3.72 (m, 2H, H-6b′, octyl OC*H*$_2$), 3.51 (dd, 1H, *J* = 9.2, 9.2 Hz, H-4′), 3.47 (dd, 1H, *J* = 9.2, 3.5 Hz, H-2′), 3.33 (dt, 1H, *J* = 9.6, 6.7 Hz, octyl OC*H*$_2$), 1.72 (dd, 1H, *J* = 7.7, 4.9 Hz, O*H*), 1.46–1.54 (m, 2H, octyl OCH$_2$C*H*$_2$), 1.20–1.34 (m, 10H, octyl C*H*$_2$), 0.87 (t, 3H, *J* = 6.9 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.9 (Ar), 138.8 (Ar), 138.7 (Ar), 138.4(2) (Ar), 138.4(0) (Ar), 138.3 (Ar), 128.4, 128.3, 128.2(9), 128.2(8), 128.2(2), 128.1(9), 128.0, 127.9(2), 127.9(1), 127.7, 127.6(3), 127.6(1), 127.5(3), 127.5(1), 127.5(0), 127.4(7) (30C, Ar), 97.8 (C-1), 96.3 (C-1′), 81.6 (C-3′), 80.4 (C-2′), 80.3 (C-3), 77.5 (C-4′), 75.5 (PhCH$_2$), 75.3 (C-2), 75.1(4) (PhCH$_2$), 75.1(0) (C-4), 74.9 (PhCH$_2$), 72.9 (PhCH$_2$), 72.6 (PhCH$_2$), 72.2 (PhCH$_2$), 72.0 (C-5′/C-5), 70.8 (C-5′/C-5), 67.7 (octyl OCH$_2$), 65.8 (C-6), 62.0 (C-6′), 31.8 (octyl CH$_2$), 29.4 (2C, octyl CH$_2$), 29.2 (octyl CH$_2$), 26.2 (octyl CH$_2$), 22.7 (octyl CH$_2$), 14.1 (octyl CH$_3$). HRMS (ESI) calcd. for (M + Na) $C_{62}H_{74}O_{11}$: 1017.5123. Found: 1017.5126.

Octyl 2,3,4-tri-*O*-benzyl-6-*O*-*p*-toluenesulfonyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (32)

Disaccharide **31** (126 mg, 0.13 mmol) was dissolved in pyridine (3 mL) and the solution was cooled to 0°C in an ice bath followed by the addition of *p*-toluenesulfonyl chloride (49 mg, 0.25 mmol). The reaction mixture was stirred overnight and then the mixture was diluted with CH_2Cl_2 (25 mL), washed with 1 M HCl (3 x 10 mL), satd aq $NaHCO_3$ (10 mL), and H_2O (10 mL). The organic layer was dried ($MgSO_4$), concentrated and the crude product was then purified by chromatography (6:1 hexane–EtOAc) to give **31** (129 mg, 89%) as a colorless oil: R_f 0.27 (6:1 hexane–EtOAc); $[\alpha]_D$ = +43.1 (*c* 1.3, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.75–7.79 (m, 2H, ArH), 7.20–7.38 (m, 30H,

ArH), 7.12–7.16 (m, 2H, ArH), 5.02 (d, 1H, *J* = 3.4 Hz, H-1′), 4.92 (d, 1H, *J* = 11.0 Hz, PhC*H*$_2$), 4.90 (d, 1H, *J* = 11.2 Hz, PhC*H*$_2$), 4.83 (d, 1H, *J* = 10.8 Hz, PhC*H*$_2$), 4.79 (d, 1H, *J* = 1.8 Hz, H-1), 4.70 (d, 1H, *J* = 11.0 Hz, PhC*H*$_2$), 4.61–4.69 (m, 6H, PhC*H*$_2$), 4.55 (d, 1H, *J* = 11.8 Hz, PhC*H*$_2$), 4.42 (d, 1H, *J* = 10.8 Hz, PhC*H*$_2$), 4.23 (dd, 1H, *J* = 10.6, 3.6 Hz, H-6a), 4.18 (dd, 1H, *J* = 10.6, 2.1 Hz, H-6b), 3.88–4.03 (m, 4H, H-3′, H-5′, H-3, H-5), 3.79 (dd, 1H, *J* = 3.1, 1.8 Hz, H-2), 3.74–3.80 (m, 2H, H-6a′, H-6b′, H-4), 3.64 (dt, 1H, *J* = 9.7, 6.8 Hz, octyl OC*H*$_2$), 3.48 (dd, 1H, *J* = 10.1, 9.0 Hz, H-4′), 3.45 (dd, 1H, *J* = 9.6, 3.4 Hz, H-2′), 3.32 (dt, 1H, *J* = 9.7, 6.6 Hz, octyl OC*H*$_2$), 2.38 (s, 3H, tosyl CH_3), 1.44–1.54 (m, 2H, octyl OCH_2C*H*$_2$), 1.20–1.34 (m, 10H, octyl C*H*$_2$), 0.87 (t, 3H, *J* = 6.9 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 144.7 (Ar), 138.7 (Ar), 138.6(9) (Ar), 138.6(4) (Ar), 138.3(4) (Ar), 138.2(7) (Ar), 138.1 (Ar), 133.0 (Ar), 129.8, 128.4, 128.3(1), 128.3(0), 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6(3), 127.6(0), 127.5(4), 127.5(1), 127.4(9) (34C, Ar), 97.8 (C-1), 96.4 (C-1′), 81.5 (C-3′), 80.5 (C-3), 79.9 (C-2′), 76.8 (C-4′), 75.4 (Ph*C*H$_2$), 75.3 (C-2), 75.0(8) (C-5′), 75.0(6) (Ph*C*H$_2$), 74.8 (Ph*C*H$_2$), 72.9 (Ph*C*H$_2$), 72.5 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 71.8 (C-4), 68.6(2) (C-6), 68.5(6) (C-5), 67.7 (octyl O*C*H$_2$), 66.1 (C-6′), 31.8 (octyl *C*H$_2$), 29.4(5) (octyl *C*H$_2$), 29.4(2) (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 21.6 (tosyl *C*H$_3$), 14.1 (octyl *C*H$_3$). HRMS (ESI) calcd. for (M + Na) $C_{69}H_{80}O_{13}S$: 1171.5212. Found: 1171.5210.

Octyl 6-amino-2,3,4-tri-*O*-benzyl-6-deoxy-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (33)

Tosylated disaccharide **32** (100 mg, 0.093 mmol) was dissolved in DMF (2 mL) and sodium azide (54 mg, 0.84 mmol) was added and the solution was heated under reflux

for 6 h. The crude product was then diluted with EtOAc (25 mL) and washed with H_2O (10 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated and the residue was purified by chromatography (6:1 hexane–EtOAc) to give **33** as a colorless oil (76 mg, 85%): R_f 0.36 (6:1 hexane–EtOAc); $[\alpha]_D$ = +58.6 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.18–7.38 (m, 30H, ArH), 5.14 (d, 1H, *J* = 3.4 Hz, H-1′), 4.94 (d, 1H, *J* = 10.9 Hz, PhC*H*$_2$), 4.91 (d, 1H, *J* = 11.1 Hz, PhC*H*$_2$), 4.90 (d, 1H, *J* = 11.2 Hz, PhC*H*$_2$), 4.81 (d, 1H, *J* = 1.7 Hz, H-1), 4.73 (d, 1H, *J* = 10.9 Hz, PhC*H*$_2$), 4.70 (d, 1H, *J* = 10.9 Hz, PhC*H*$_2$), 4.62–4.70 (m, 5H, PhC*H*$_2$), 4.57 (d, 1H, *J* = 11.1 Hz, PhC*H*$_2$), 4.56 (d, 1H, *J* = 11.8 Hz, PhC*H*$_2$), 4.06 (dd, 1H, *J* = 9.6, 9.6 Hz, H-3), 3.98 (dd, 1H, *J* = 9.4, 9.4 Hz, H-3′), 3.86–3.95 (m, 3H, H-5′, H-4, H-6a), 3.84 (dd, 1H, *J* = 11.7, 1.5 Hz, H-6b), 3.77–3.82 (m, 2H, H-2, H-5), 3.65 (dt, 1H, *J* = 9.7, 6.8 Hz, octyl OC*H*$_2$), 3.51 (dd, 1H, *J* = 9.4, 3.4 Hz, H-2′), 3.42–3.48 (m, 2H, H-4′, H-6a′), 3.30–3.36 (m, 2H, H-6b′, octyl OC*H*$_2$), 1.45–1.53 (m, 2H, octyl OCH$_2$C*H*$_2$), 1.20–1.34 (m, 10H, octyl C*H*$_2$), 0.87 (t, 3H, *J* = 6.9 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.7(7) (Ar), 138.7(3) (Ar), 138.6(8) (Ar), 138.4 (Ar), 138.3 (Ar), 138.2 (Ar), 128.4, 128.3(1), 128.2(6), 128.2(2), 128.1, 128.0, 127.9(7), 127.9(4), 127.8, 127.7, 127.6(1), 127.5(8), 127.5(1), 127.4(8) (30C, Ar), 97.8 (C-1), 96.3 (C-1′), 81.4 (C-3′), 80.4 (C-4), 80.2 (C-2′), 78.3 (C-4′), 75.5 (Ph*C*H$_2$), 75.3 (C-2), 75.1(4) (Ph*C*H$_2$), 75.1(2) (C-3), 75.0 (Ph*C*H$_2$), 72.8 (Ph*C*H$_2$), 72.5 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 71.9 (C-5), 69.9 (C-5′), 67.6 (octyl O*C*H$_2$), 66.0 (C-6), 51.4 (C-6′), 31.8 (octyl *C*H$_2$), 29.4 (2C, octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). HRMS (ESI) calcd. for (M + Na) $C_{62}H_{73}N_3O_{10}$: 1042.5188. Found: 1042.5188. FTIR: 2099.9 cm^{-1}.

Octyl 6-deoxy-6-trifluoroacetamido-α-D-glucopyranosyl-(1→6)-α-D-mannopyranoside (34)

Azide **33** (67 mg, 0.066 mmol) was dissolved in pyridine (3 mL) and 20% $Pd(OH)_2$–C (17 mg) was added. The mixture was stirred overnight under a H_2 atmosphere and the catalyst was separated by filtration through a short pad of Celite. The filtrate was concentrated and the residue was redissolved in pyridine (2 mL) before trifluoroacetic anhydride (20 μL, 0.13 mmol) was added dropwise at 0 °C. The mixture was slowly warmed to rt and stirred overnight. The solution was then diluted with EtOAc (25 mL), washed with H_2O (10 mL) and satd aq $NaHCO_3$ (10 mL). The organic layer was dried (Na_2SO_4), concentrated and the resulting crude product was then redissolved in MeOH (6 mL) and 20% $Pd(OH)_2$–C (15 mg) was added. The mixture was stirred overnight under a H_2 atmosphere and the catalyst was separated by filtration through a short pad of Celite. The filtrate was concentrated and the residue purified by chromatography (8:1 CH_2Cl_2–MeOH) to give **34** as a clear glass (26 mg, 72%): R_f 0.24 (8:1 CH_2Cl_2–MeOH); $[\alpha]_D$ = +74.4 (*c* 0.4, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ_H 4.82 (d, 1H, *J* = 3.7 Hz, H-1′), 4.71 (d, 1H, *J* = 1.5, 1.8 Hz, H-1), 3.96 (dd, 1H, *J* = 10.7, 4.0 Hz, H-6a), 3.74–3.80 (m, 3H, H-5′, H-2, H-4), 3.60–3.73 (m, 5H, H-3′, H-6a′, H-3, H-5, octyl OCH_2), 3.58 (dd, 1H, *J* = 10.7, 2.2 Hz, H-6b), 3.48 (dd, 1H, *J* = 14.0, 7.8 Hz, H-6b′), 3.40 (dt, 1H, *J* = 9.7, 6.4 Hz, octyl OCH_2), 3.37 (dd, 1H, *J* = 9.7, 3.7 Hz, H-2′), 3.12 (dd, 1H, *J* = 9.9, 8.9 Hz, H-4′), 1.52–1.62 (m, 2H, octyl OCH_2CH_2), 1.24–1.42 (m, 10H, octyl CH_2), 0.89 (t, 3H, *J* = 6.9 Hz, octyl CH_3); ^{13}C NMR (125 MHz, CD_3OD) δ_C 159.3 (CF_3C=O, $^2J_{C=O,F}$ = 37.1 Hz), 117.6 (CF_3, ^1J = 285.9 Hz),101.8 (C-1), 99.7 (C-1′), 75.0 (C-3′), 73.8 (C-2′), 73.6 (C-4′), 72.8(3) (C-3), 72.8(2) (C-5), 72.2 (C-2), 71.1 (C-5′), 68.8 (octyl OCH_2), 68.3 (C-

4), 67.1 (C-6), 42.1 (C-6′), 33.0 (octyl CH_2), 30.6 (octyl CH_2), 30.5 (octyl CH_2), 30.4 (octyl CH_2), 27.4 (octyl CH_2), 23.7 (octyl CH_2), 14.4 (octyl CH_3); ^{19}F NMR (376.1 MHz, $CDCl_3$) δ_F –77.5 (s, 3F). HRMS (ESI) calcd. for (M + Na) $C_{22}H_{38}NO_{11}F_3$: 572.2289. Found: 572.2286.

Octyl 2,3,4,-tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-2-*O*-acetyl-3,4-*O*-isopropylidene-α-D-talopyranoside (35)

Thioglycoside **11**[5] (186 mg, 0.20 mmol), alcohol **14** (55 mg, 0.15 mmol), and powdered 4 Å molecular sieves (100 mg) were dried overnight under vacuum with P_2O_5. Dry CH_2Cl_2 (4 mL) was added and the solution was cooled to 0 °C before the addition of *N*-iodosuccinimide (53 mg, 0.23 mmol) and TMSOTf (8 µL, 0.045 mmol). The mixture was stirred for 1 h at 0 °C and neutralized with triethylamine, before being filtered through Celite and concentrated. The crude product was purified by chromatography (4:1 hexane–EtOAc) to give **35** as a colorless oil (144 mg, 90%): R_f 0.21 (4:1 hexane–EtOAc); $[\alpha]_D$ = –47.1 (*c* 0.3, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.11–8.16 (m, 2H, ArH), 7.83–7.94 (m, 4H, ArH), 7.70–7.75 (m, 2H, ArH), 7.51–7.62 (m, 3H, ArH), 7.25–7.46 (m, 12H, ArH), 7.12–7.17 (m, 2H, ArH), 6.20 (dd, 1H, *J* = 10.2, 10.2 Hz, H-4′), 5.82 (dd, 1H, *J* = 10.2, 3.3 Hz, H-3′), 5.73 (dd, 1H, *J* = 3.3, 1.8 Hz, H-2′), 5.16 (d, 1H, *J* = 1.8 Hz, H-1′), 5.01 (dd, 1H, *J* = 5.7, 3.0 Hz, H-2), 4.91 (d, 1H, *J* = 5.7 Hz, H-1), 4.64 (dd, 1H, *J* = 7.8, 3.0 Hz, H-3), 4.41 (dd, 1H, *J* = 7.8, 1.8 Hz, H-4), 4.20–4.25 (m, 1H, H-5′), 4.02–4.07 (m, 1H, H-5), 3.82–3.97 (m, 4H, H-6a′, H-6b′, H-6a, octyl OCH_2), 3.76 (dd, 1H, *J* = 10.2, 6.0 Hz, H-6b), 3.46 (dd, 1H, *J* = 9.6, 6.6 Hz, octyl OCH_2), 2.05 (s, 3H, C(O)CH_3), 1.54–1.64 (m, 2H, octyl CH_2), 1.48 (s, 3H, C(CH_3)$_2$), 1.36 (s, 3H, C(CH_3)$_2$), 1.10–1.34

(m, 10H, octyl C*H*$_2$), 1.08 (s, 9H, C(C*H*$_3$)$_3$), 0.80 (t, 3H, *J* = 7.2 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 170.2 (*C*=O), 165.5 (*C*=O), 165.4 (*C*=O), 165.2 (*C*=O), 135.8 (2C, Ar), 135.5 (2C, Ar), 133.3 (Ar), 133.1(1) (Ar), 133.0(7) (Ar), 133.0(0) (Ar), 129.9(9) (2C, Ar), 129.8 (2C, Ar), 129.7(3) (2C, Ar), 129.7(0) (2C, Ar), 129.6 (Ar), 129.5 (Ar), 129.4 (Ar), 129.3 (Ar), 128.5 (2C, Ar), 128.3 (2C, Ar), 128.2 (2C, Ar), 127.6 (2C, Ar), 127.5 (2C, Ar), 110.8 (*C*(CH$_3$)$_2$), 97.5 (C-1, $^1J_{C,H}$ = 173.0 Hz), 97.3 (C-1′, $^1J_{C,H}$ = 172.2 Hz), 74.0 (C-4), 72.3 (C-3), 71.4 (C-5′), 70.7 (C-2, C-3′), 70.5 (C-2′), 68.3 (C-5), 68.1 (octyl O*C*H$_2$), 66.5 (C-4′), 66.0 (C-6), 62.4 (C-6′), 31.8 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 26.7 (C(*C*H$_3$)$_3$), 26.1(0) (C(*C*H$_3$)$_2$), 26.0(7) (octyl *C*H$_2$), 25.3 (C(*C*H$_3$)$_2$), 22.6 (octyl *C*H$_2$), 21.1 (C(O)*C*H$_3$), 19.2 (*C*(CH$_3$)$_3$), 14.0 (octyl *C*H$_3$). HRMS (ESI) calcd. for (M + Na) $C_{62}H_{74}O_{15}Si$: 1109.4689. Found: 1109.4695.

Octyl 2,3,4,-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2-*O*-acetyl-3,4-*O*-isopropylidene-α-D-talopyranoside (36)

Disaccharide **35** (137 mg, 0.13 mmol) was dissolved in THF (4 mL) and then 70% HF·pyridine (0.2 mL) and pyridine (1 mL) were added. After stirring overnight, the crude product was then diluted with CH_2Cl_2 (50 mL), washed with H_2O (15 mL), 1 M HCl (2 x 15 mL), and satd aq $NaHCO_3$ (15 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated, and the residue was purified by chromatography to give **36** as a colorless oil (82 mg, 77%): R_f 0.55 (1:1 hexane–EtOAc); $[\alpha]_D$ = –42.0 (*c* 0.3, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.08–8.12 (m, 2H, ArH), 7.94–7.98 (m, 2H, ArH), 7.79–7.84 (m, 2H, ArH), 7.59–7.64 (m, 1H, ArH), 7.46–7.60 (m, 3H, ArH), 7.36–7.45 (m, 3H, ArH), 7.23–7.28 (m, 2H, ArH), 5.93 (dd, 1H, *J* = 10.1, 3.4 Hz, H-3′), 5.80 (dd, 1H, *J* = 10.1,

10.1 Hz, H-4′), 5.67 (dd, 1H, *J* = 3.4, 1.7 Hz, H-2′), 5.15 (d, 1H, *J* = 1.7 Hz, H-1′), 4.98 (dd, 1H, *J* = 6.2, 2.9 Hz, H-2), 4.90 (d, 1H, *J* = 6.2 Hz, H-1), 4.62 (dd, 1H, *J* = 7.6, 2.9 Hz, H-3), 4.39 (dd, 1H, *J* = 7.6, 1.8 Hz, H-4), 4.18 (ddd, 1H, *J* = 10.1, 3.9, 2.2 Hz, H-5′), 4.05 (ddd, 1H, *J* = 7.0, 4.9, 1.8 Hz, H-5), 3.92 (dd, 1H, *J* = 10.4, 7.0 Hz, H-6a), 3.74–3.91 (m, 4H, H-6a′, H-6b′, H-6b, octyl OCH_2), 3.46 (dt, 1H, *J* = 9.7, 6.7 Hz, octyl OCH_2), 2.75 (dd, 1H, *J* = 8.4, 5.7 Hz, O*H*), 2.16 (s, 3H, C(O)CH_3), 1.57–1.65 (m, 2H, octyl CH_2), 1.51 (s, 3H, C(CH_3)$_2$), 1.34 (s, 3H, C(CH_3)$_2$), 1.14–1.54 (m, 10H, octyl CH_2), 0.83 (t, 3H, *J* = 6.8 Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 170.2 (*C*=O), 166.4 (*C*=O), 165.4 (*C*=O), 165.3 (*C*=O), 133.6 (Ar), 133.5 (Ar), 133.1 (Ar), 129.9(1) (2C, Ar), 129.8(6) (2C, Ar), 129.7 (2C, Ar), 129.3 (Ar), 129.2 (Ar), 128.8 (Ar), 128.6 (2C, Ar), 128.5 (2C, Ar), 128.3 (2C, Ar), 110.9 (*C*(CH$_3$)$_2$), 97.6 (C-1′/C-1), 97.5 (C-1′/C-1), 74.3 (C-4), 72.4 (C-3), 71.1 (C-5′), 70.6 (C-2′), 70.5 (C-2), 69.6 (C-3′), 68.7 (C-5), 68.3 (octyl O*C*H$_2$), 67.3 (C-4′), 66.7 (C-6), 61.5 (C-6′), 31.8 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 26.0(9) (C(*C*H$_3$)$_2$), 26.0(7) (octyl *C*H$_2$), 25.3 (C(*C*H$_3$)$_2$), 22.6 (octyl *C*H$_2$), 21.1 (C(O)*C*H$_3$), 14.0 (octyl *C*H$_3$). HRMS (ESI) calcd. for (M + Na) $C_{46}H_{56}O_{15}$: 871.3511. Found: 871.3508.

Octyl 6-azido-2,3,4,-tri-*O*-benzoyl-6-deoxy-α-D-mannopyranosyl-(1→6)-2-*O*-acetyl-3,4-*O*-isopropylidene-α-D-talopyranoside (37)

Disaccharide **36** (86 mg, 0.10 mmol) was dissolved in pyridine (1 mL) and the solution was cooled to 0 °C in an ice bath followed by the addition of *p*-toluenesulfonyl chloride (50 mg, 0.25 mmol). The reaction mixture was stirred overnight and then diluted with CH_2Cl_2 (25 mL), washed with 1 M HCl (3 x 10 mL), satd aq $NaHCO_3$ (10 mL), and H_2O

(10 mL). The organic layer was dried ($MgSO_4$) and concentrated to colorless oil. The crude intermediate was dissolved in DMF (2 mL) and sodium azide (65 mg, 1.0 mmol) was added and the solution was heated under reflux for 4 h. The crude product was then diluted with EtOAc (25 mL) and washed with H_2O (10 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated and the residue purified by chromatography (3:1 hexane–EtOAc) to give **37** as a colorless oil (74 mg, 84%): R_f 0.27 (3:1 hexane–EtOAc); $[\alpha]_D$ = –11.3 (*c* 0.8, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.08–8.14 (m, 2H, ArH), 7.91–7.96 (m, 2H, ArH), 7.78–7.83 (m, 2H, ArH), 7.59–7.65 (m, 1H, ArH), 7.47–7.55 (m, 3H, ArH), 7.35–7.45 (m, 3H, ArH), 7.23–7.29 (m, 2H, ArH), 5.82–5.88 (m, 2H, H-3′, H-4′), 5.68 (dd, 1H, *J* = 2.8, 1.7 Hz, H-2′), 5.12 (d, 1H, *J* = 1.7 Hz, H-1′), 4.99 (dd, 1H, *J* = 6.2, 2.8 Hz, H-2), 4.93 (d, 1H, *J* = 6.2 Hz, H-1), 4.64 (dd, 1H, *J* = 7.6, 2.8 Hz, H-3), 4.40 (dd, 1H, *J* = 7.6, 1.8 Hz, H-4), 4.36 (ddd, 1H, *J* = 10.1, 6.4, 2.6 Hz, H-5′), 4.06 (ddd, 1H, *J* = 7.6, 7.2, 5.1 Hz, H-5), 3.99 (dd, 1H, *J* = 10.2, 7.2 Hz, H-6a), 3.88 (dt, 1H, *J* = 9.8, 6.5 Hz, octyl OC*H*$_2$), 3.79 (dd, 1H, *J* = 10.2, 5.1 Hz, H-6b), 3.47–3.56 (m, 2H, H-6a′, octyl OC*H*$_2$), 3.44 (dd, 1H, *J* = 13.3, 2.6 Hz, H-6b′), 2.17 (s, 3H, C(O)C*H*$_3$), 1.57–1.66 (m, 2H, octyl C*H*$_2$), 1.54 (s, 3H, C(C*H*$_3$)$_2$), 1.36 (s, 3H, C(C*H*$_3$)$_2$), 1.12–1.38 (m, 10H, octyl C*H*$_2$), 0.82 (t, 3H, *J* = 6.8 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 170.2 (*C*=O), 165.6 (*C*=O), 165.4 (*C*=O), 165.2 (*C*=O), 133.5 (2C, Ar), 133.1 (Ar), 129.9 (2C, Ar), 129.8 (2C, Ar), 129.7 (2C, Ar), 129.3 (Ar), 129.1 (Ar), 128.8 (Ar), 128.6 (2C, Ar), 128.5 (2C, Ar), 128.3 (2C, Ar), 111.0 (*C*(CH$_3$)$_2$), 97.6 (C-1), 97.2 (C-1′), 74.1 (C-4), 72.4 (C-3), 70.8 (C-2), 70.4 (C-5′), 70.2 (C-2′), 69.7 (C-5), 68.3 (C-3′), 68.2 (octyl O*C*H$_2$), 67.9 (C-4′), 66.4 (C-6), 51.3 (C-6′), 31.8 (octyl *C*H$_2$), 29.6 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 26.1 (octyl *C*H$_2$), 26.0 (C(*C*H$_3$)$_2$), 25.4 (C(*C*H$_3$)$_2$), 22.6 (octyl *C*H$_2$), 21.1 (C(O)*C*H$_3$), 14.0

(octyl *C*H_3). HRMS (ESI) calcd. for (M + Na) $C_{46}H_{55}N_3O_{14}$: 896.3576. Found: 896.3573. FTIR: 2102.6 cm^{-1}.

Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (38)

Thioglycoside **12**[5] (39 mg, 0.056 mmol), alcohol **16**[6] (25 mg, 0.045 mmol), and powdered 4 Å molecular sieves (75 mg) were dried overnight under vacuum with P_2O_5. Dry CH_2Cl_2 (3 mL) was added and the solution was cooled to 0 °C before the addition of *N*-iodosuccinimide (16 mg, 0.068 mmol) and TMSOTf (2 μL, 0.014 mmol). The mixture was stirred for 1 h at 0 °C and neutralized with triethylamine, before being filtered through Celite and concentrated. The crude product was purified by chromatography (4:1 hexane–EtOAc) to give **38** (47 mg, 92%) as a pale yellow oil. R_f 0.26 (4:1 hexane–EtOAc); $[\alpha]_D$ = +16.4 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.04–8.12 (m, 4H, ArH), 7.90–7.94 (m, 2H, ArH), 7.82–7.87 (m, 2H, ArH), 7.49–7.63 (m, 3H, ArH), 7.25–7.47 (m, 24H, ArH), 6.09 (dd, 1H, *J* = 10.1, 10.1 Hz, H-4′), 5.90 (dd, 1H, *J* = 10.1, 3.3 Hz, H-3′), 5.75 (dd, 1H, *J* = 3.3, 1.8 Hz, H-2′), 5.18 (d, 1H, *J* = 1.8 Hz, H-1′), 5.05 (d, 1H, *J* = 11.0 Hz, PhC*H*$_2$), 5.04 (d, 1H, *J* = 11.7 Hz, PhC*H*$_2$), 4.85 (d, 1H, *J* = 11.0 Hz, PhC*H*$_2$), 4.79 (d, 1H, *J* = 11.7 Hz, PhC*H*$_2$), 4.79 (d, 1H, *J* = 3.7 Hz, H-1), 4.72 (d, 1H, *J* = 11.7 Hz, PhC*H*$_2$), 4.69 (d, 1H, *J* = 11.7 Hz, PhC*H*$_2$), 4.65 (dd, 1H, *J* = 12.1, 2.4 Hz, H-6a′), 4.43 (ddd, 1H, *J* = 10.1, 4.4, 2.4 Hz, H-5′), 4.37 (dd, 1H, *J* = 12.1, 4.4 Hz, H-6b′), 4.07 (dd, 1H, *J* = 9.2, 9.2 Hz, H-3), 3.97 (dd, 1H, *J* = 11.0, 5.1 Hz, H-6a), 3.92 (ddd, 1H, *J* = 9.0, 5.1, 1.5 Hz, H-5), 3.83 (dd, 1H, *J* = 11.0, 1.5 Hz, H-6b), 3.73 (dt, 1H, *J* = 9.8, 7.0 Hz, octyl OC*H*$_2$), 3.59 (dd, 1H, *J* = 9.2, 3.7 Hz, H-2), 3.56 (dd, 1H, *J* = 9.2, 9.0 Hz, H-4),

3.47 (dt, 1H, J = 9.8, 6.6 Hz, octyl OCH_2), 1.64–1.76 (m, 2H, octyl OCH$_2$CH_2), 1.18–1.46 (m, 10H, octyl CH_2), 0.86 (t, 3H, J = 7.0 Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 166.1 (Ar), 165.5 (Ar), 165.3 (Ar), 165.2 (Ar), 138.9 (Ar), 138.4 (Ar), 138.3 (Ar), 133.4, 133.1, 133.0(2), 130.0(0), 129.8(5), 129.8(0), 129.7(5), 129.7(3), 129.4, 129.2, 129.1, 128.6, 128.4(8), 128.4(3), 128.4(1), 128.3(6), 128.2(7), 127.9(8), 127.9(2), 127.8, 127.7(7), 127.7(0), 127.5 (35C, Ar), 97.8 (C-1′, $^1J_{C,H}$ = 174.6 Hz), 96.5 (C-1), 82.1 (C-3), 80.5 (C-2), 77.9 (C-4), 75.6 (PhCH$_2$), 75.1 (PhCH$_2$), 73.1 (PhCH$_2$), 70.3, 70.0 (C-2′, C-3′), 69.9 (C-5), 68.9 (C-5′), 68.3 (octyl OCH$_2$), 66.9 (C-4′), 66.7 (C-6), 62.7 (C-6′), 31.9 (octyl CH$_2$), 29.5(2) (octyl CH$_2$), 29.4(8) (octyl CH$_2$), 29.3 (octyl CH$_2$), 26.3 (octyl CH$_2$), 22.7 (octyl CH$_2$), 14.1 (octyl CH$_3$). HRMS (ESI) calcd. for (M + Na) $C_{69}H_{72}O_{15}$: 1163.4763. Found: 1163.4766.

Octyl 2-*O*-acetyl-3,4-*O*-isopropylidene-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl-(1→6)-2,3,4,-tri-*O*-benzyl-α-D-talopyranoside (39)

Thioglycoside **13** (39 mg, 0.065 mmol), alcohol **10**[4] (33 mg, 0.057 mmol), and powdered 4 Å molecular sieves (75 mg) were dried overnight under vacuum with P_2O_5. Dry CH_2Cl_2 (3 mL) was added and the solution was cooled to 0 °C before the addition of *N*-iodosuccinimide (20 mg, 0.23 mmol) and TMSOTf (4 μL, 0.020 mmol). The mixture was stirred for 1 h at 0 °C and neutralized with triethylamine, before being filtered through Celite and concentrated. The crude product was purified by chromatography (6:1 hexane–EtOAc) to give **39** as a colorless oil (54 mg, 81%): R_f 0.22 (6:1 hexane–EtOAc); $[\alpha]_D$ = +33.6 (*c* 0.8, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.68–7.74 (m, 4H, ArH), 7.22–7.42 (m, 21H, ArH), 5.12 (d, 1H, J = 6.2, H-1′), 4.99 (dd, 1H, J = 6.2, 3.1 Hz, H-2′),

4.86 (d, 1H, J = 10.7 Hz, PhCH_2), 4.79 (d, 1H, J = 1.8 Hz, H-1), 4.72 (d, 1H, J = 12.4 Hz, PhCH_2), 4.68 (d, 1H, J = 12.4 Hz, PhCH_2), 4.63 (s, 2H, PhCH_2), 4.58 (dd, 1H, J = 7.6, 3.1 Hz, H-3′), 4.56 (d, 1H, J = 10.7 Hz, PhCH_2), 4.38 (dd, 1H, J = 7.6, 1.9 Hz, H-4′), 3.79–3.96 (m, 7H, H-5′, H-6a′, H6b′, H-3, H-4, H6a, H-6b), 3.75 (dd, 1H, J = 3.1, 1.8 Hz, H-2), 3.70 (ddd, 1H, J = 9.6, 5.8, 1.5 Hz, H-5), 3.60 (dt, 1H, J = 9.7, 6.7 Hz, octyl OCH_2), 3.31 (dt, 1H, J = 9.7, 6.5 Hz, octyl OCH_2), 2.04 (s, 3H, C(O)CH_3), 1.42–1.53 (m, 5H, octyl CH_2, C(CH_3)$_2$), 1.21–1.34 (m, 13H, octyl CH_2, C(CH_3)$_2$), 1.06 (s, 9H, C(CH_3)$_3$), 0.89 (t, 3H, J = 7.2 Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 170.4 (*C*=O), 138.7 (Ar), 138.5 (Ar), 135.7 (2C, Ar), 135.6 (2C, Ar), 133.5(3) (Ar), 133.4(6) (Ar), 129.5(9) (Ar), 129.5(8) (Ar), 128.3(3), 128.2(9), 128.0, 127.8, 127.6, 127.5(9), 127.5(5), 127.5(1), 127.4 (20C, Ar), 110.4 (*C*(CH$_3$)$_2$), 97.6(2) (C-1, $^1J_{C,H}$ = 167.0 Hz), 97.6(0) (C-1′, $^1J_{C,H}$ = 175.8 Hz), 80.3 (C-3), 75.3 (C-2), 75.1(7) (C-4), 75.1(6) (Ph*C*H$_2$), 73.9 (C-4′), 72.7 (Ph*C*H$_2$), 72.2 (C-3′), 72.1 (Ph*C*H$_2$), 71.7 (C-5), 70.8 (C-2′), 70.3 (C-5′), 67.4 (octyl OCH$_2$), 66.3 (C-6), 62.4 (C-6′), 31.8 (octyl *C*H$_2$), 29.4 (2C, octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.8 (C(*C*H$_3$)$_3$), 26.2 (octyl *C*H$_2$), 26.1 (C(*C*H$_3$)$_2$), 25.3 (C(*C*H$_3$)$_2$), 22.7 (octyl *C*H$_2$), 20.9 (C(O)*C*H$_3$), 19.2 (*C*(CH$_3$)$_3$), 14.1 (octyl *C*H$_3$). HRMS (ESI) calcd. for (M + Na) $C_{62}H_{80}O_{12}Si$: 1067.5311. Found: 1067.5315.

Octyl 2,3,4-tri-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-glucopyranosyl-(1→6)-2-*O*-acetyl-3,4-*O*-isopropylidene-α-D-talopyranoside (40)

Thioglycoside **15** (143 mg, 0.18 mmol), alcohol **14** (53 mg, 0.14 mmol), and powdered 4 Å molecular sieves (150 mg) were dried overnight under vacuum with P_2O_5. Dry CH_2Cl_2 (5 mL) was added and the solution was cooled to 0 °C before the addition of *N*-

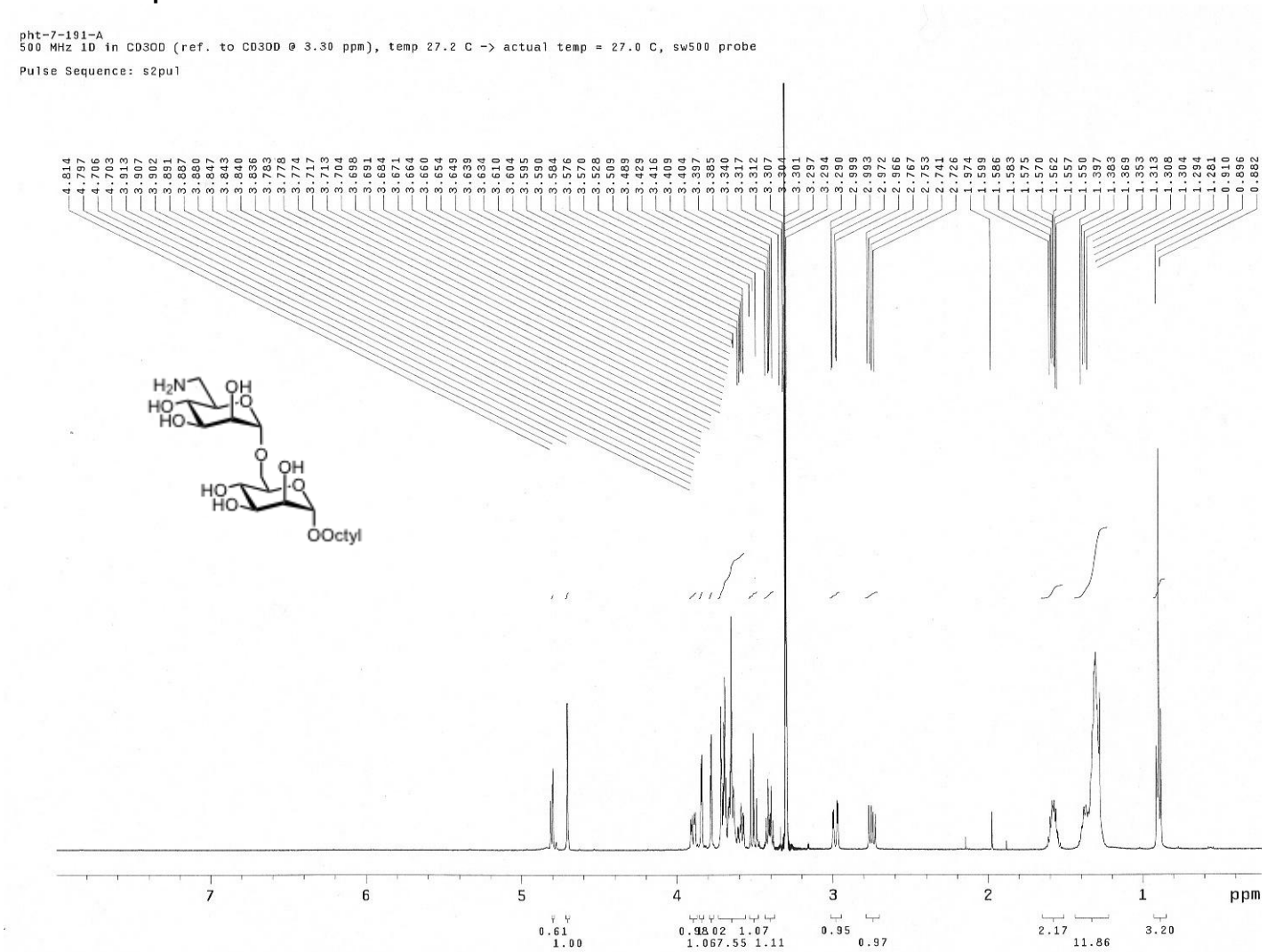
iodosuccinimide (50 mg, 0.21 mmol) and TMSOTf (8 μL, 0.042 mmol). The mixture was stirred for 1 h at 0 °C and neutralized with triethylamine, before being filtered through Celite and concentrated. The crude product was purified by chromatography (4:1 hexane–EtOAc) to give the α glycoside (97 mg, 66%, R_f 0.31, 4:1 hexane–EtOAc) and β-glycoside (32 mg, 22%, R_f 0.38, 4:1 hexane–EtOAc) isomers, both as a colorless oils. Only the α isomer **40** was fully characterized. $[\alpha]_D$ = +40.1 (*c* 1.8, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.65–7.73 (m, 4H, ArH), 7.24–7.44 (m, 19H, ArH), 7.16–7.19 (m, 2H, ArH), 4.96 (d, 1H, *J* = 10.8 Hz, PhC*H*$_2$), 4.90–3.94 (m, 3H, PhC*H*$_2$, H-1′, H-2), 4.84 (d, 1H, *J* = 6.4 Hz, H-1), 4.81 (d, 1H, *J* = 10.8 Hz, PhC*H*$_2$), 4.78 (d, 1H, *J* = 11.9 Hz, PhC*H*$_2$), 4.74 (d, 1H, *J* = 11.9 Hz, PhC*H*$_2$), 4.66 (d, 1H, *J* = 11.1 Hz, PhC*H*$_2$), 4.57 (dd, 1H, *J* = 7.6, 2.8 Hz, H-3), 4.39 (dd, 1H, *J* = 7.6, 1.7 Hz, H-4), 4.01 (dd, 1H, *J* = 9.4, 9.4 Hz, H-3′), 3.90–3.98 (m, 2H, H-6a′, H-5), 3.87 (dd, 1H, *J* = 11.3, 1.6 Hz, H-6b′), 3.78–3.83 (m, 1H, H-5′), 3.69–3.78 (m, 3H, H-4′, H-6a, octyl OC*H*$_2$), 3.61 (dd, 1H, *J* = 10.0, 6.5 Hz, H-6b), 3.57 (dd, 1H, *J* = 9.4, 3.6 Hz, H-2′), 3.35 (dt, 1H, *J* = 9.8, 6.6 Hz, octyl OC*H*$_2$), 2.15 (s, 3H, C(O)C*H*$_3$), 1.42–1.52 (m, 5H, octyl C*H*$_2$, C(C*H*$_3$)$_2$), 1.31 (s, 3H, C(C*H*$_3$)$_2$), 1.15–1.30 (m, 10H, octyl C*H*$_2$), 1.06 (s, 9H, *t*-Bu), 0.85 (t, 3H, *J* = 7.0 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 170.2 (*C*=O), 138.8 (Ar), 138.6 (Ar), 138.5 (Ar), 135.8 (2C, Ar), 135.6 (2C, Ar), 133.7 (Ar), 133.3 (Ar), 129.5(5), 129.5(1), 128.4, 128.3, 128.1, 127.7, 127.6(3), 127.6(0), 127.5, 127.4 (21C, Ar), 110.6 (*C*(CH$_3$)$_2$), 97.4 (C-1, $^1J_{C,H}$ = 172.3 Hz), 96.9 (C-1′), 82.2 (C-3′), 80.4 (C-2′), 77.7 (C-4′), 75.9 (Ph*C*H$_2$), 74.9 (Ph*C*H$_2$), 74.2 (C-4), 75.2 (C-4), 72.8 (Ph*C*H$_2$), 72.4 (C-3), 71.5 (C-5′), 71.0 (C-2), 68.5 (C-5), 68.0 (octyl O*C*H$_2$), 65.7 (C-6), 62.8 (C-6′), 31.8 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 26.8 (C(*C*H$_3$)$_3$), 26.2 (C(*C*H$_3$)$_2$), 26.0 (octyl *C*H$_2$), 25.5

($C(CH_3)_2$), 22.6 (octyl CH_2), 21.1 ($C(O)CH_3$), 19.3 ($C(CH_3)_3$), 14.1 (octyl CH_3). HRMS (ESI) calcd. for (M + Na) $C_{62}H_{80}O_{12}Si$: 1067.5311. Found: 1067.5312.

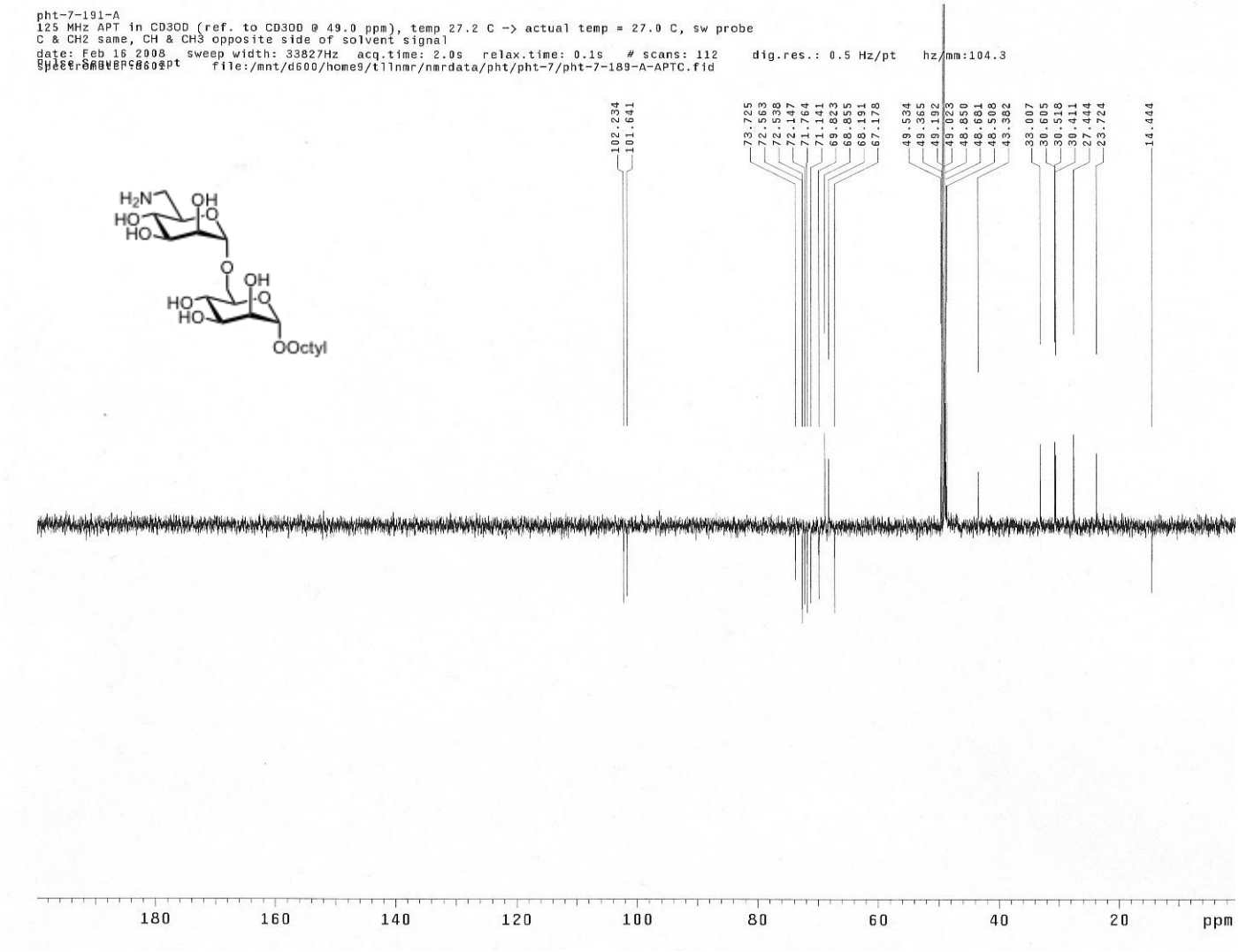
References

1. J. Broddefalk, K.-E. Bergquist and J. Kihlberg, *Tetrahedron*, 1998, **54**, 12047–12070.
2. J. Ohlsson and G. Magnusson, *Carbohydr. Res.*, 2000, **329**, 49-55.
3. A. Watts and S. J. Williams, *Org. Biomol. Chem.*, 2005, 1982–1992.
4. V. Subramaniam, S. S. Gurcha, G. S. Besra and T. L. Lowary, *Biorg. Med. Chem.*, 2005, **13**, 1083–1094.
5. P. H. Tam and T. L. Lowary, *Carbohydr. Res.*, 2007, **342**, 1741–1772.
6. C. Wing, J. C. Errey, B. Mukhopadhyay, J. S. Blanchard and R. A. Field, *Org. Biomol. Chem.*, 2006, **4**, 3945–3950.

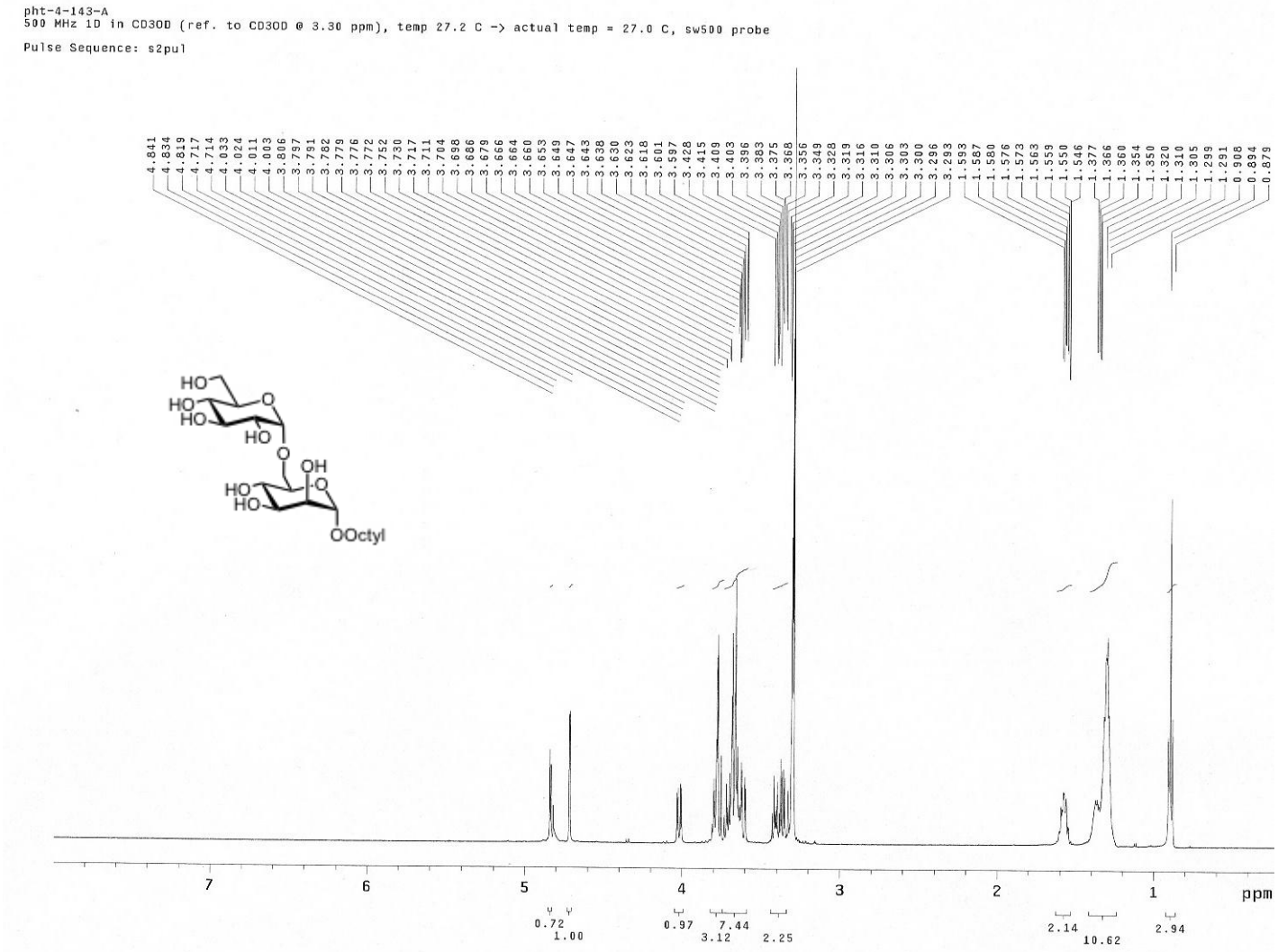
^{1}H NMR spectrum of **2**



^{13}C NMR spectrum of **2**



^{1}H NMR spectrum of **3**



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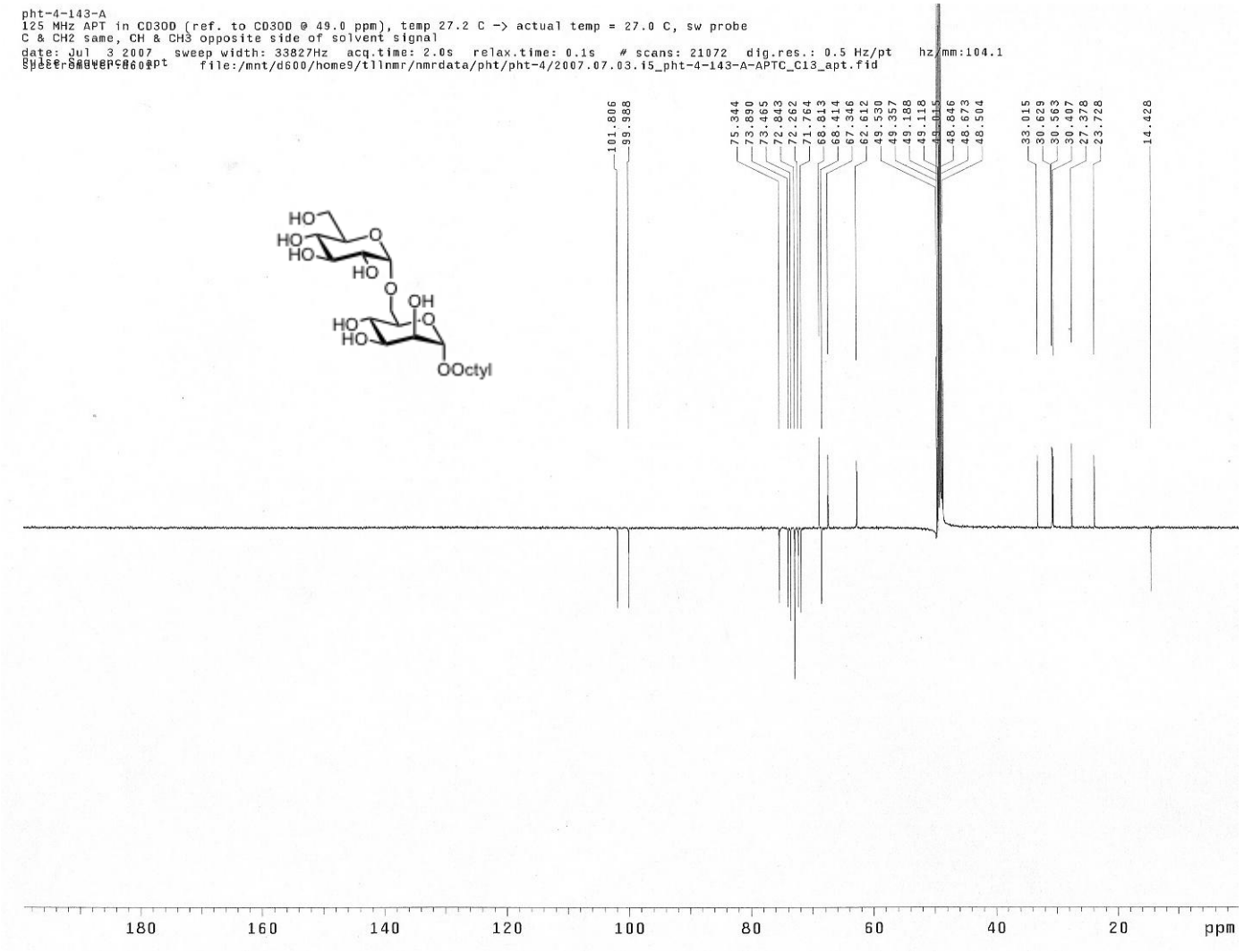
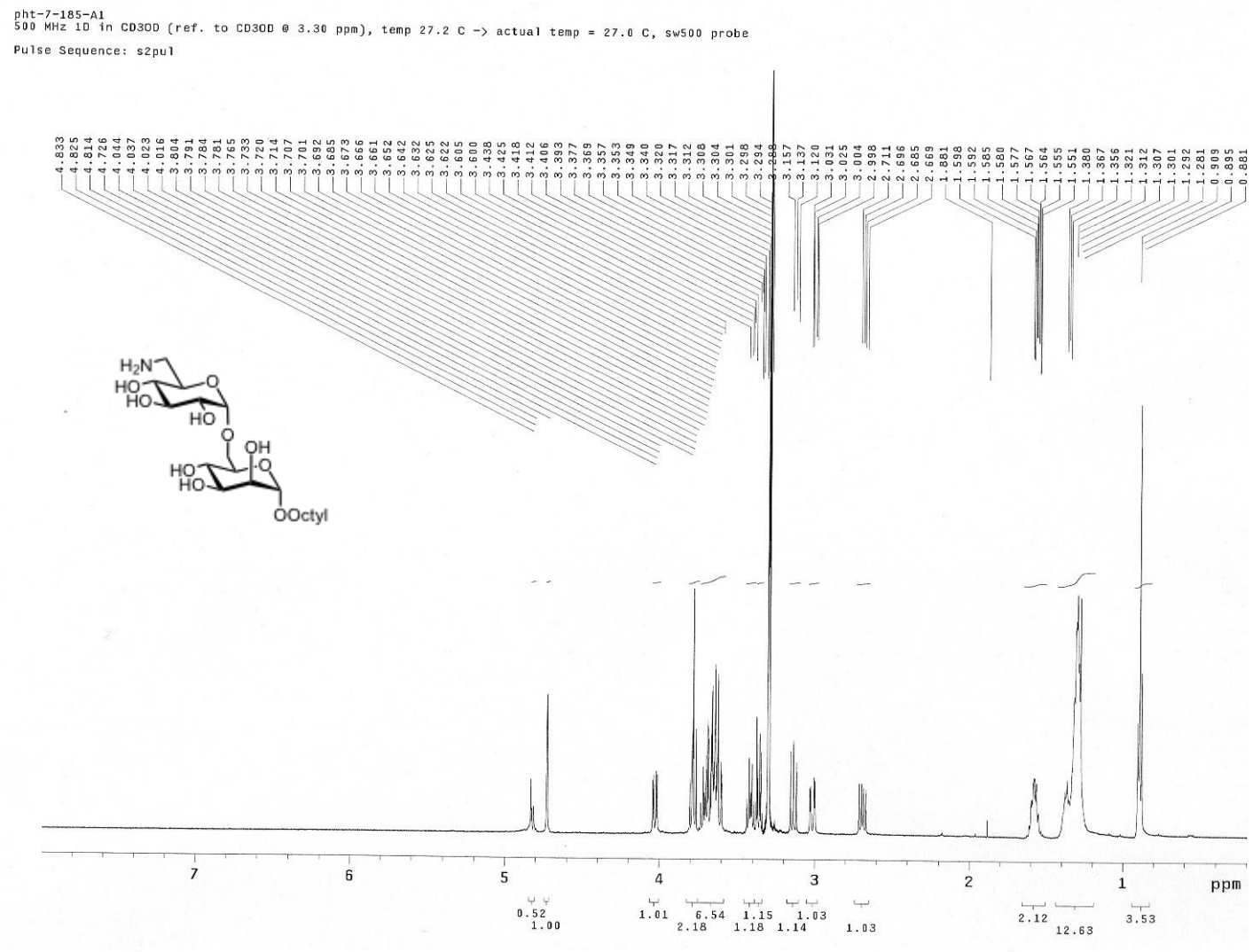
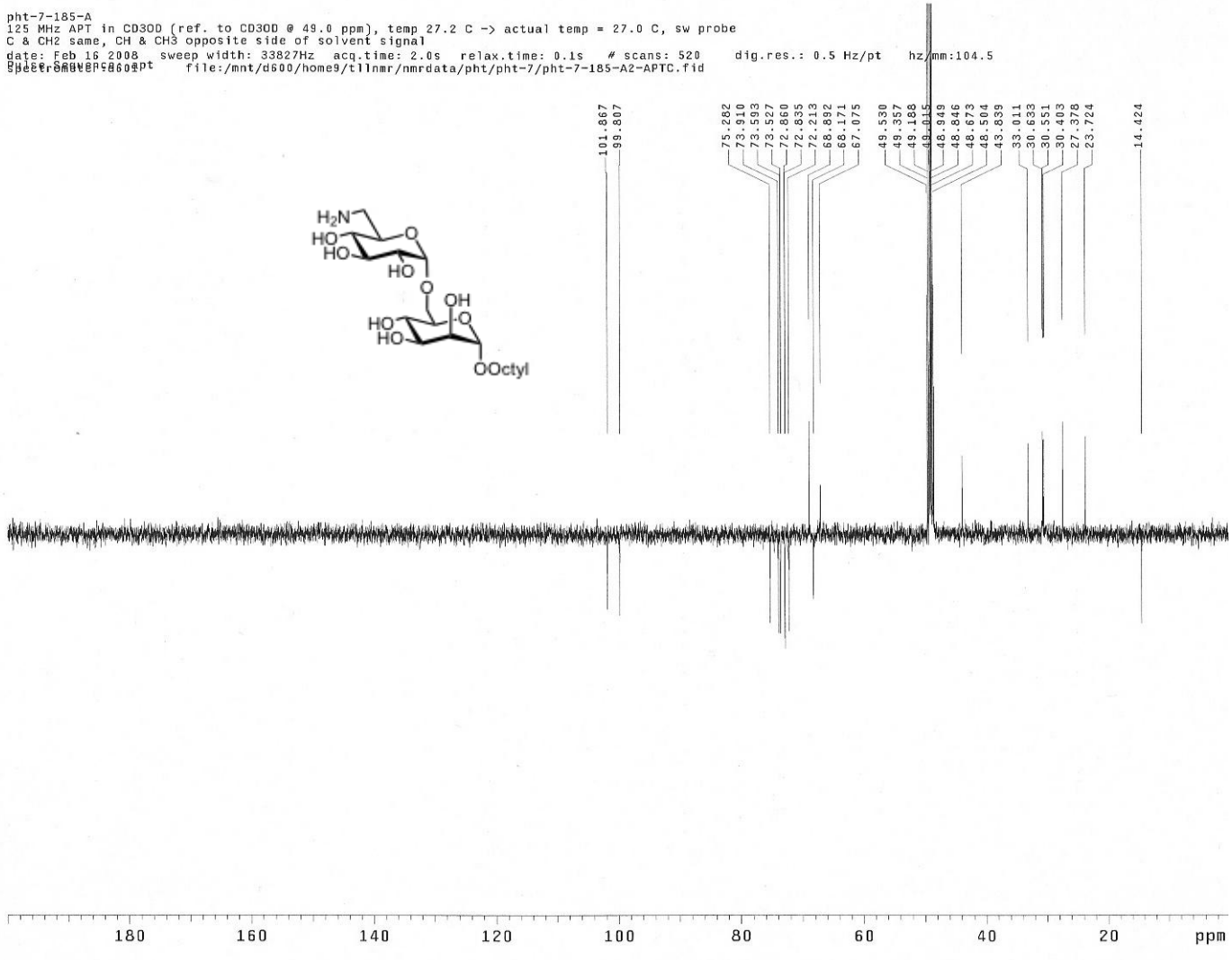


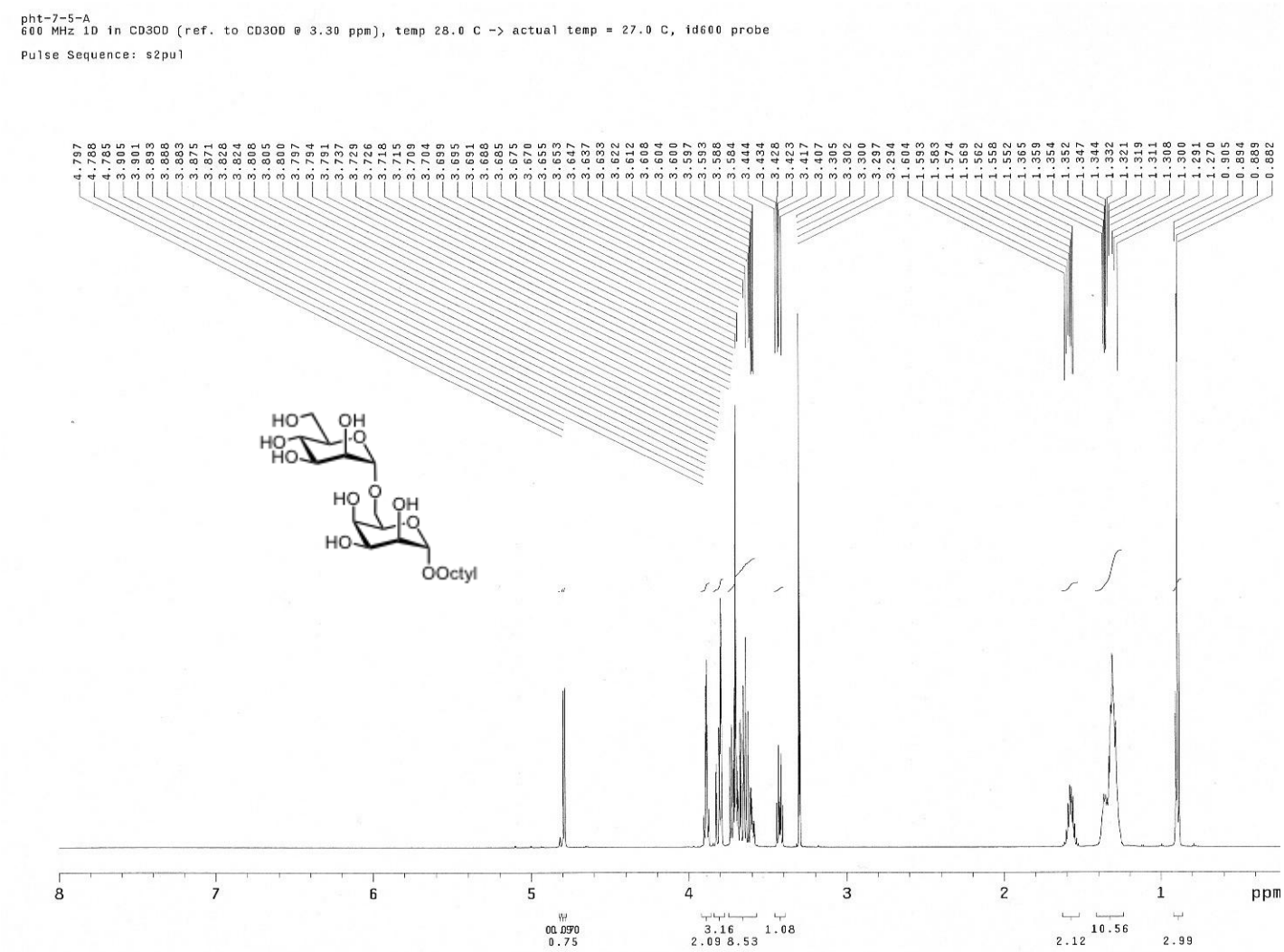
^{1}H NMR spectrum of **4**



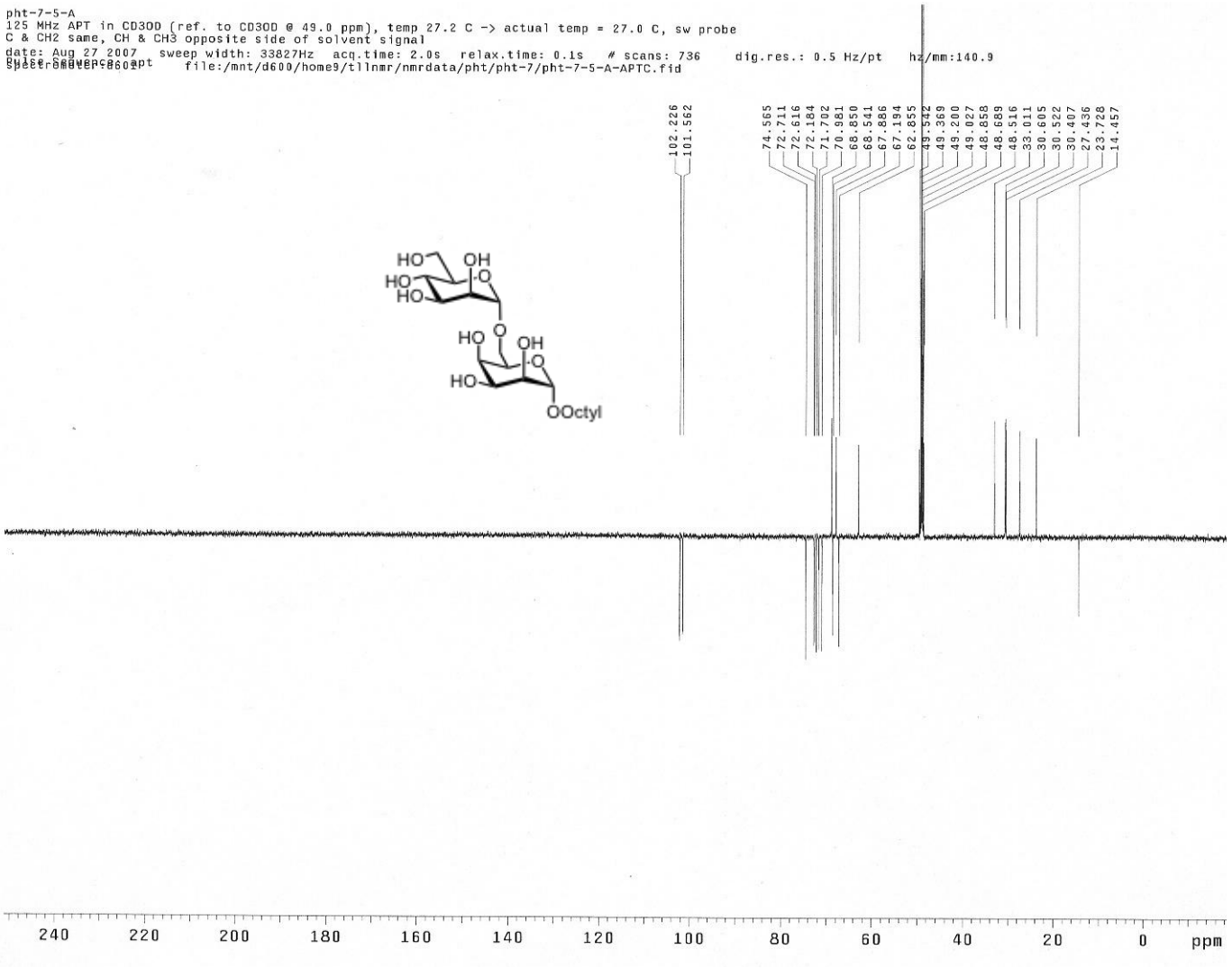
^{13}C NMR spectrum of **4**



^{1}H NMR spectrum of **5**



^{13}C NMR spectrum of **5**



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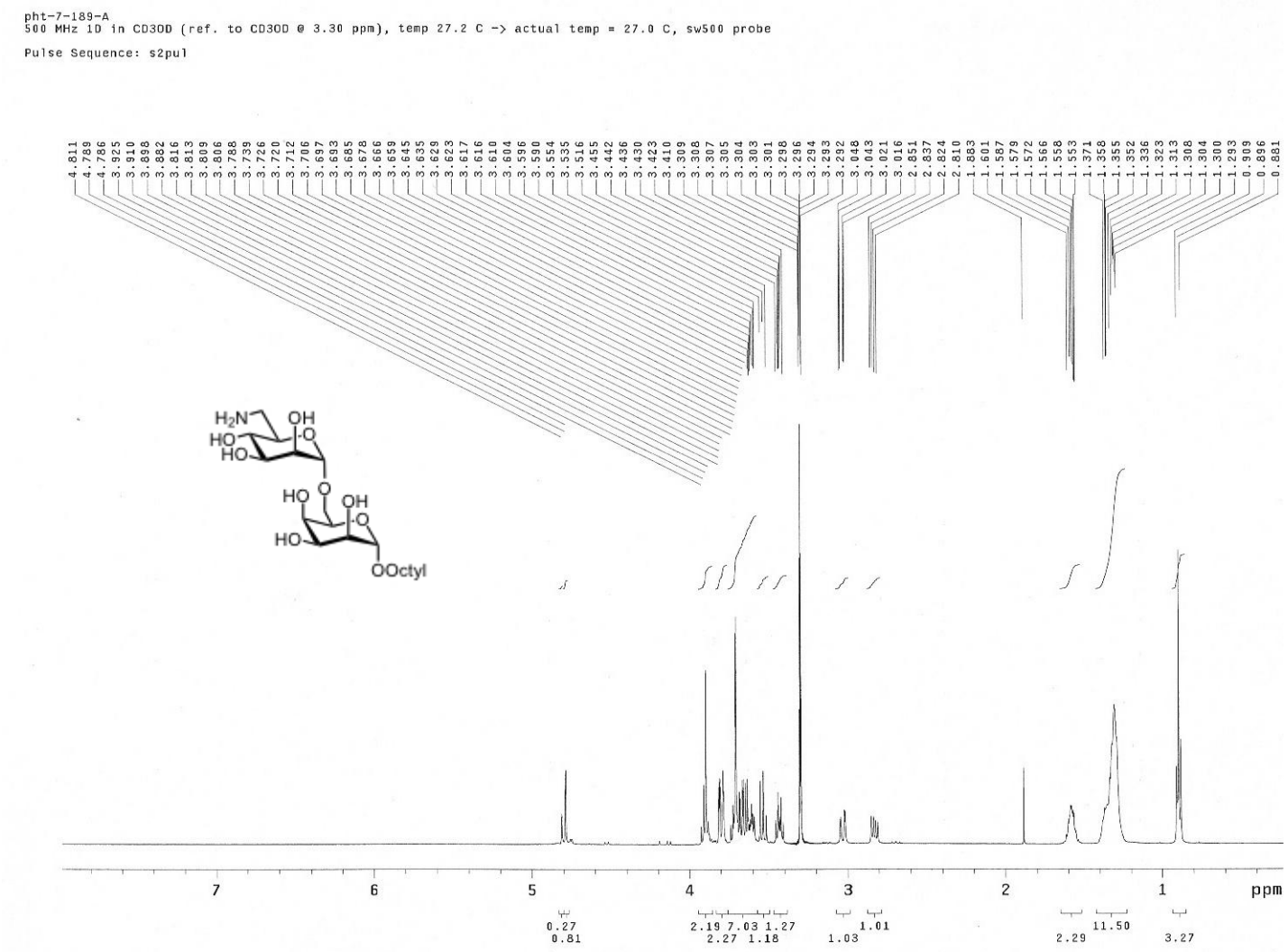

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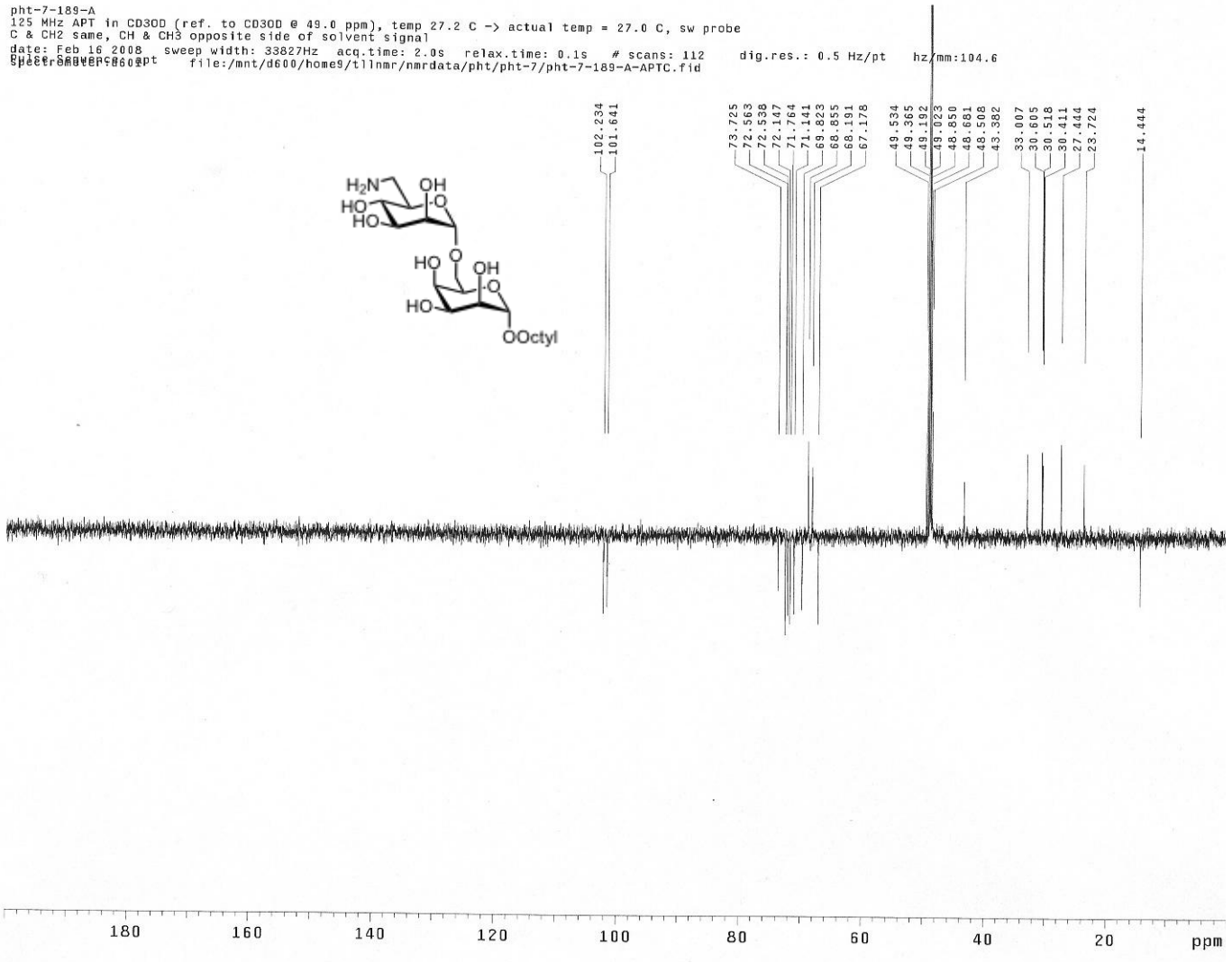
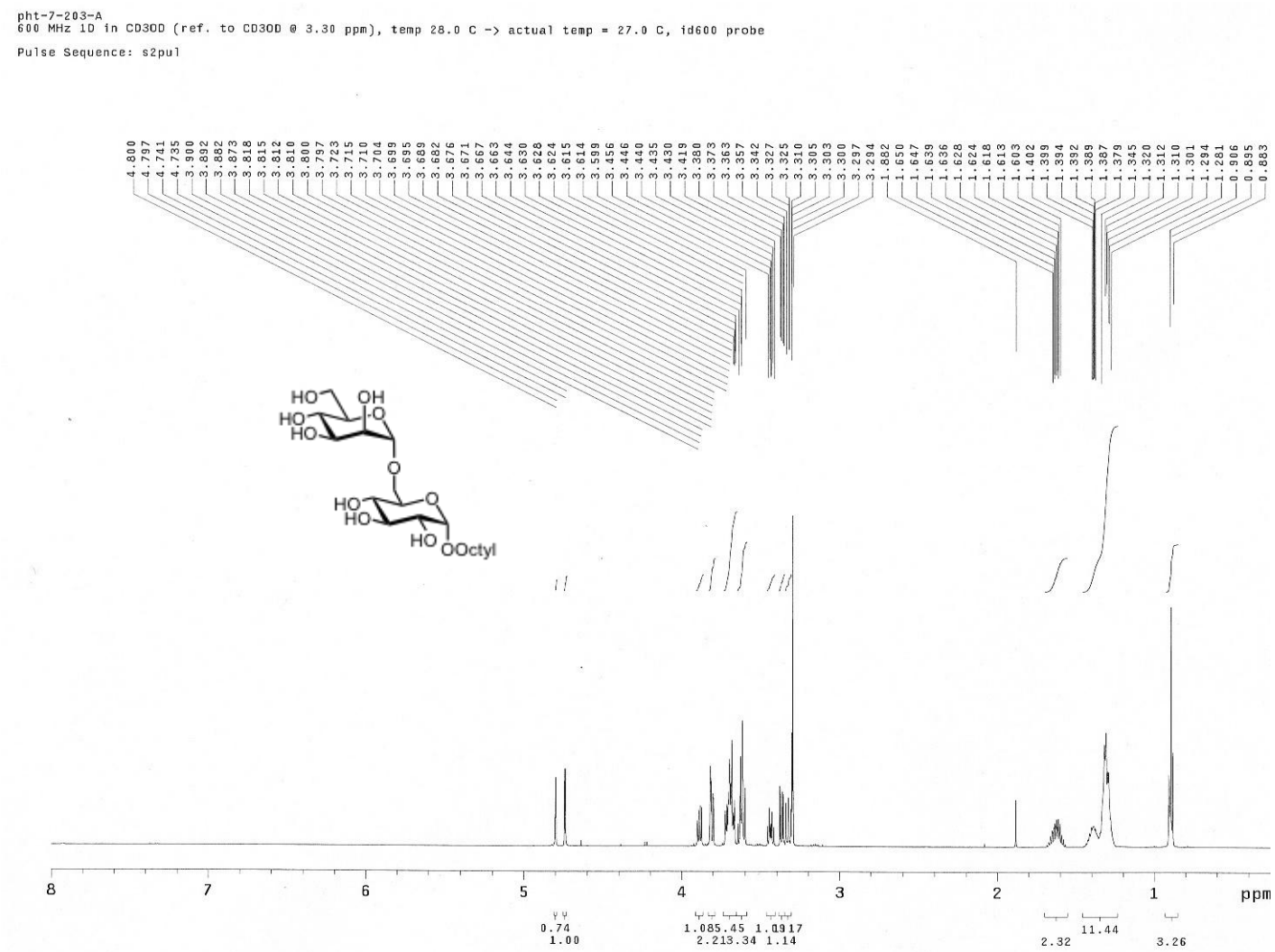
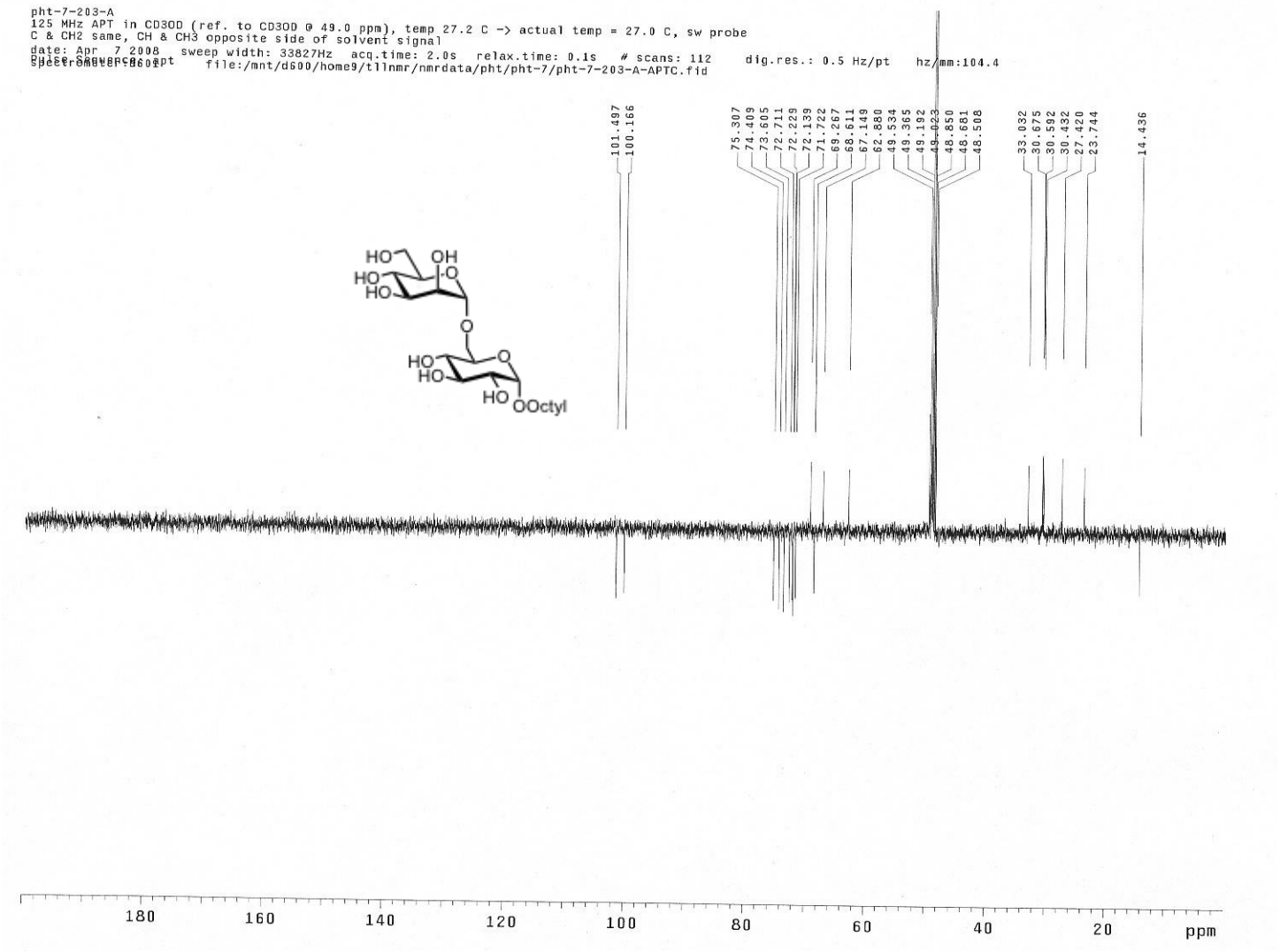


^{1}H NMR spectrum of **7**



^{13}C NMR spectrum of **7**



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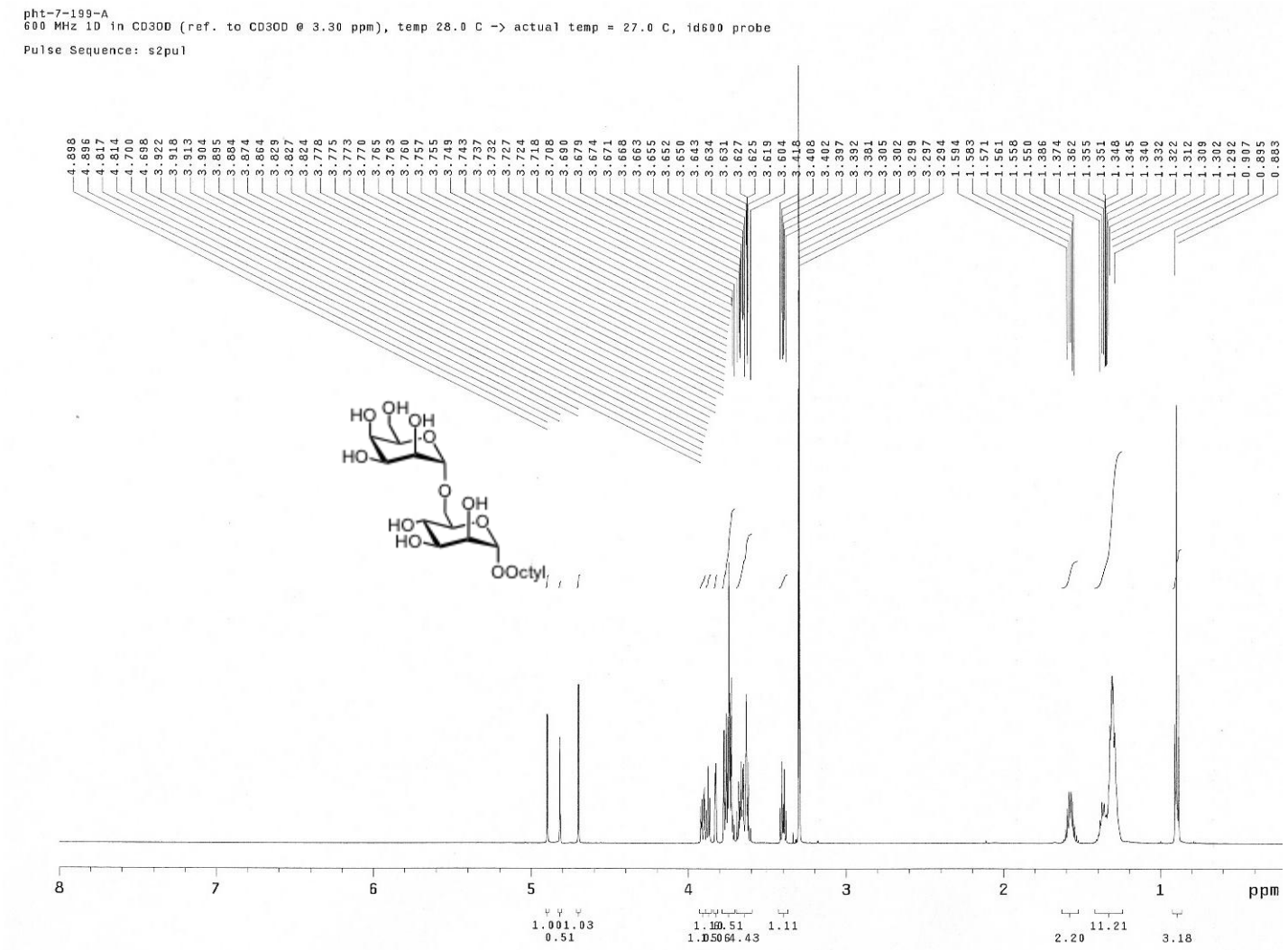

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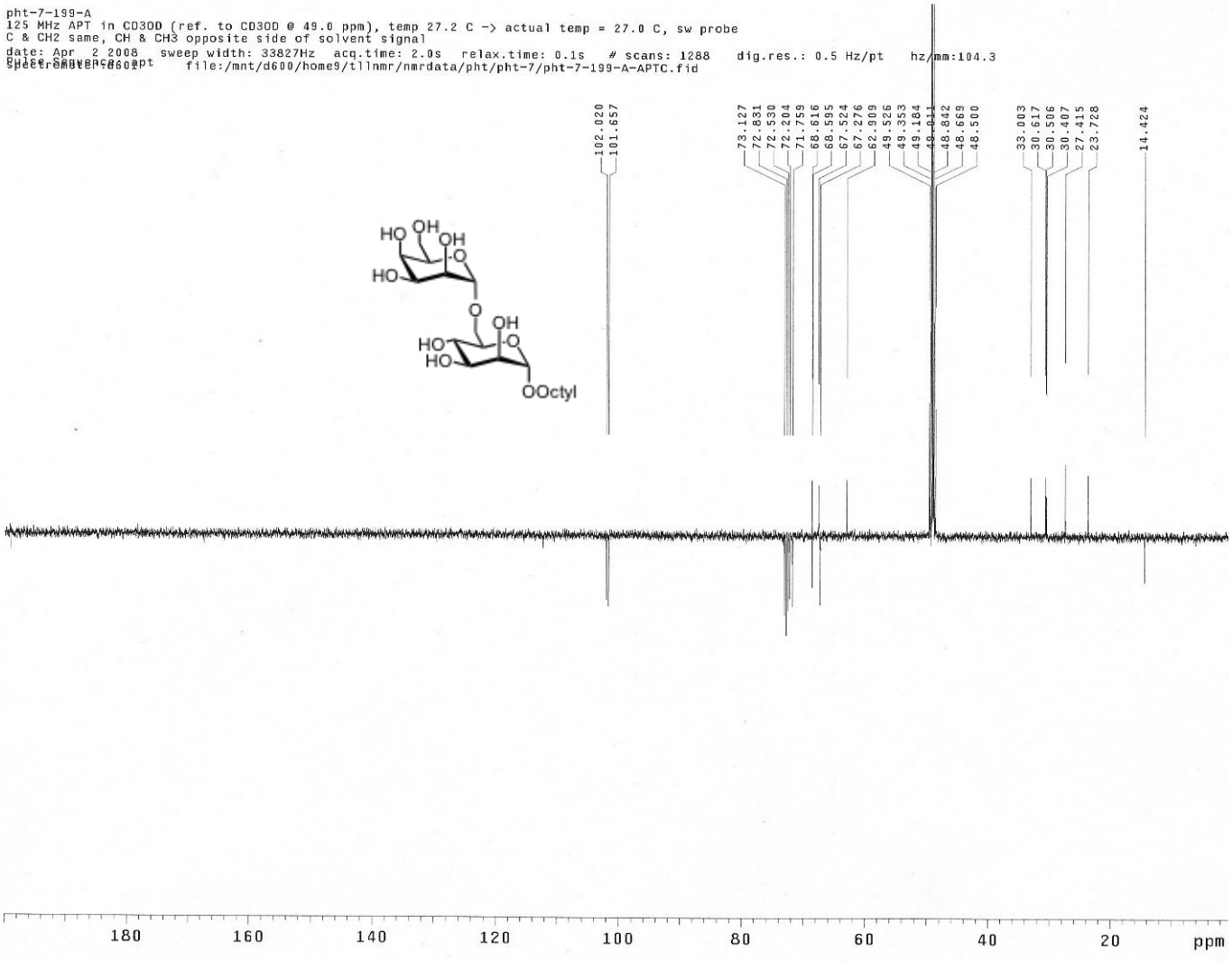
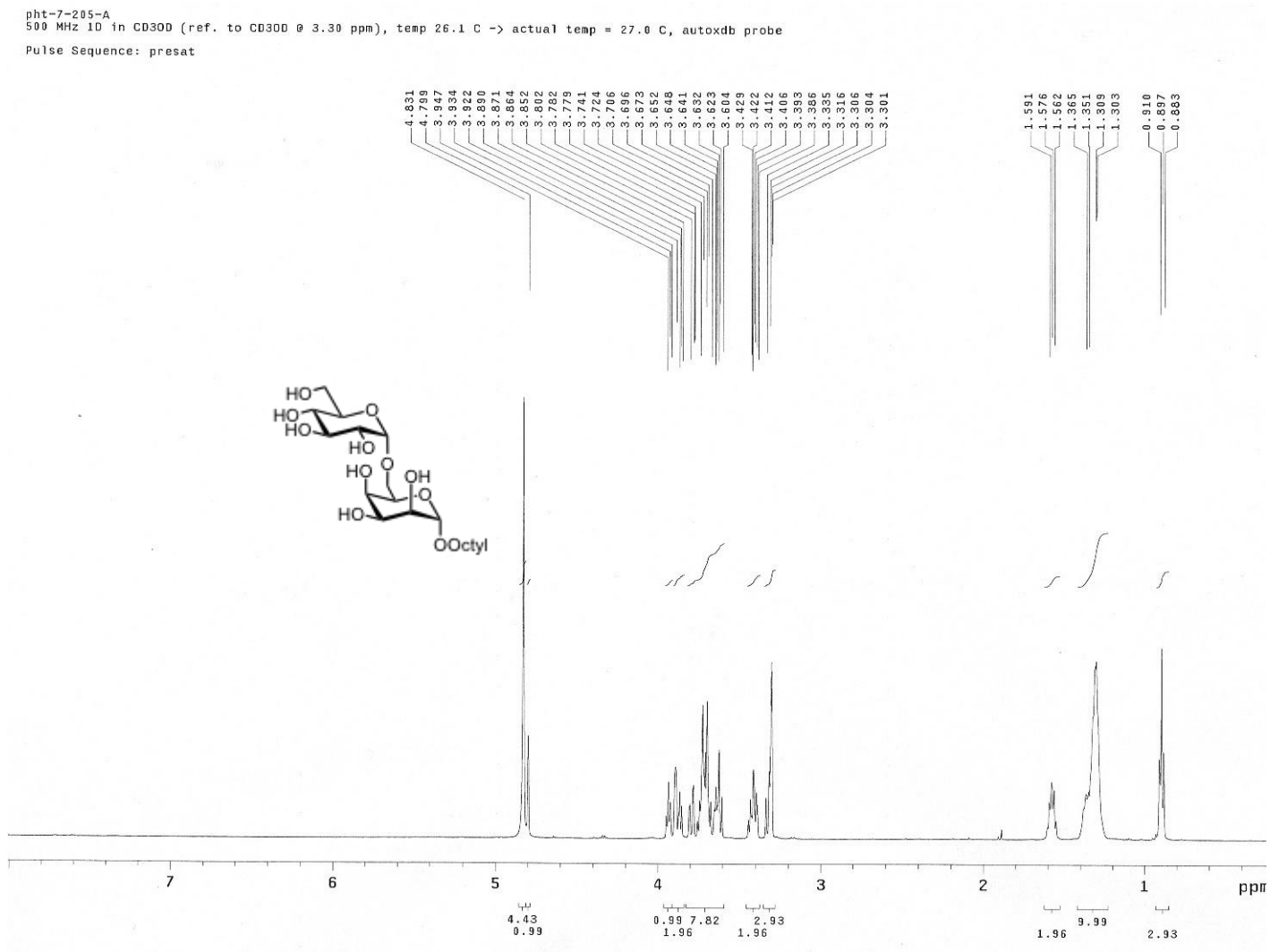
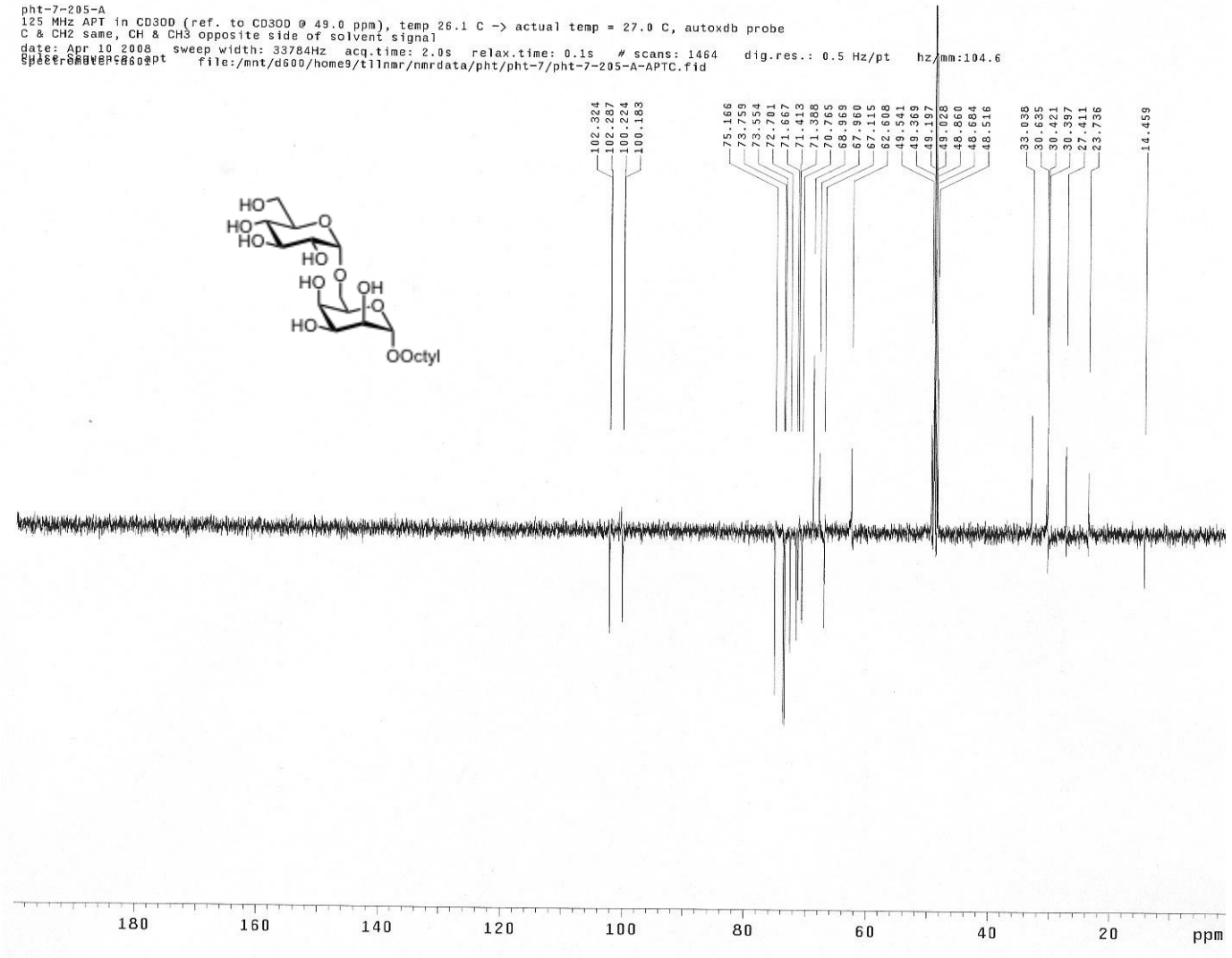


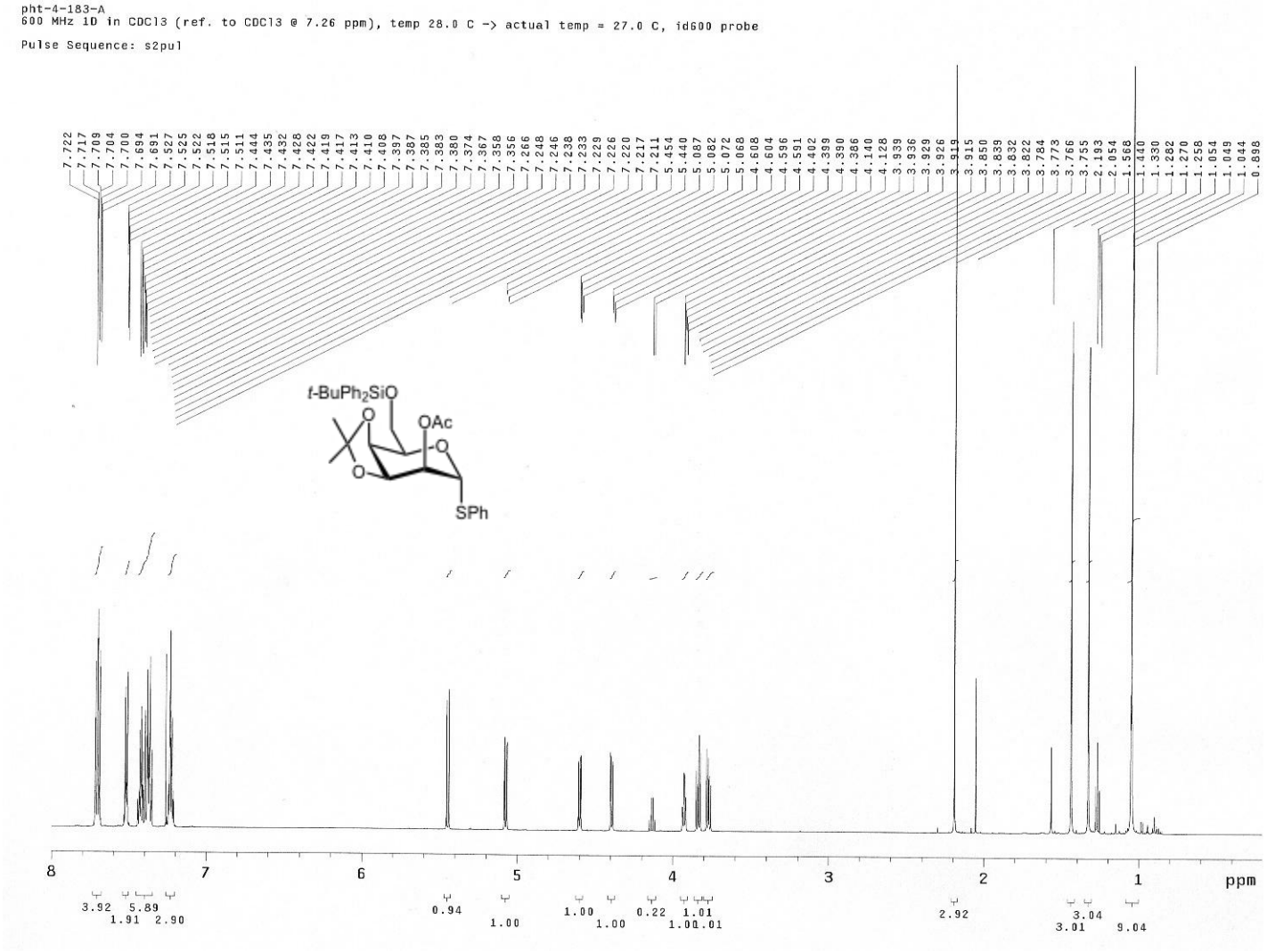
^{1}H NMR spectrum of **9**



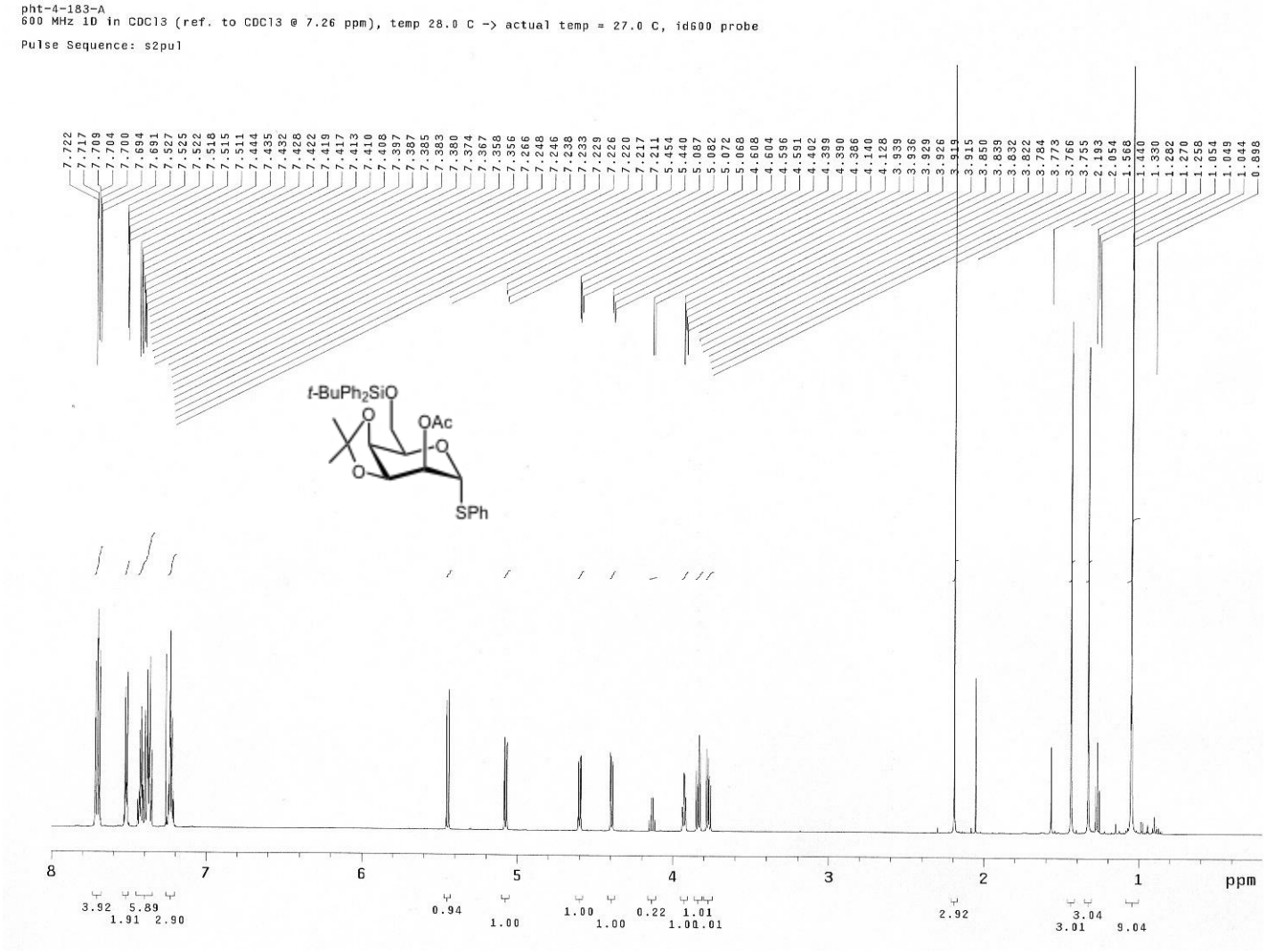
^{13}C NMR spectrum of **9**



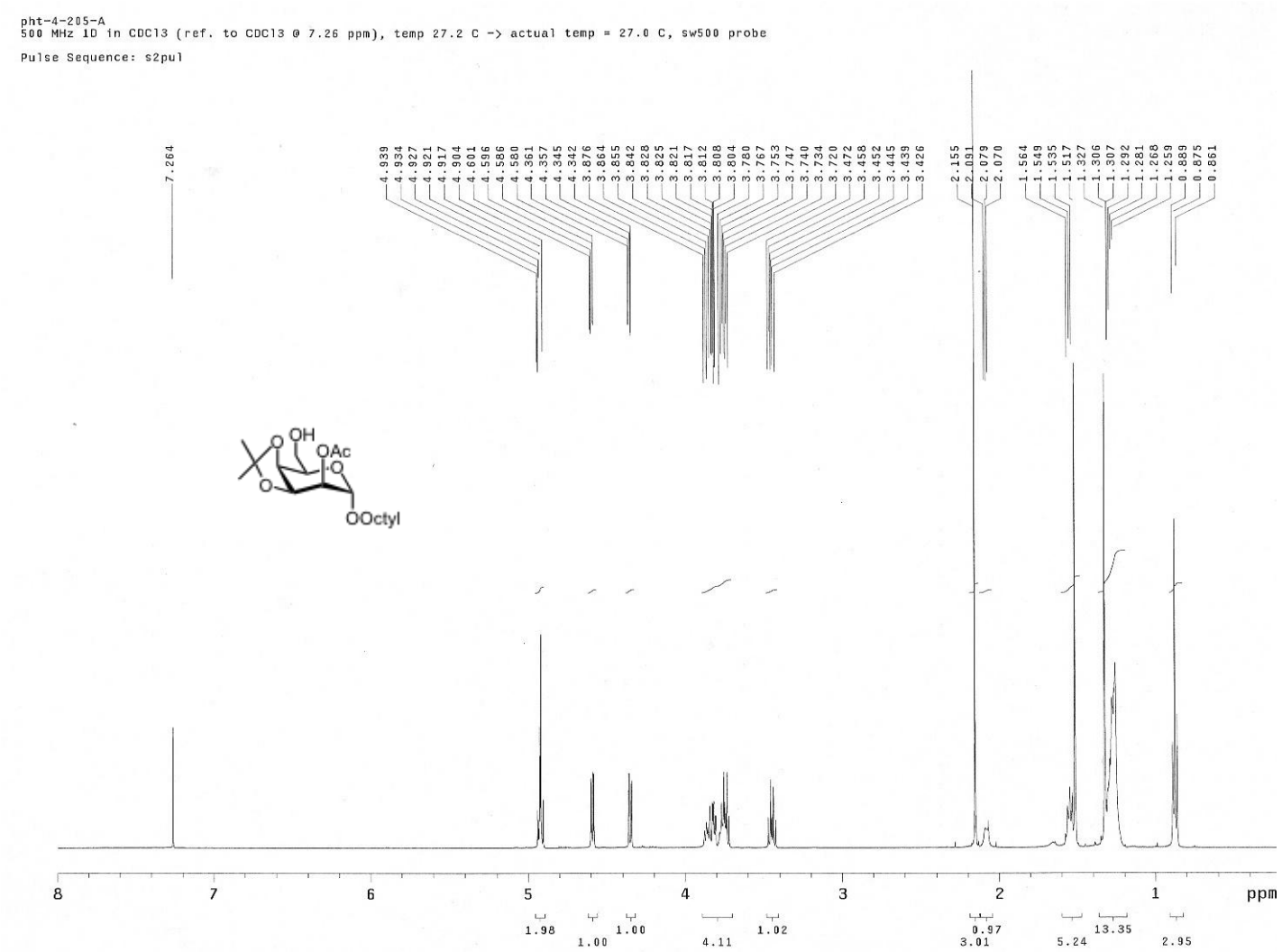
^{1}H NMR spectrum of **13**



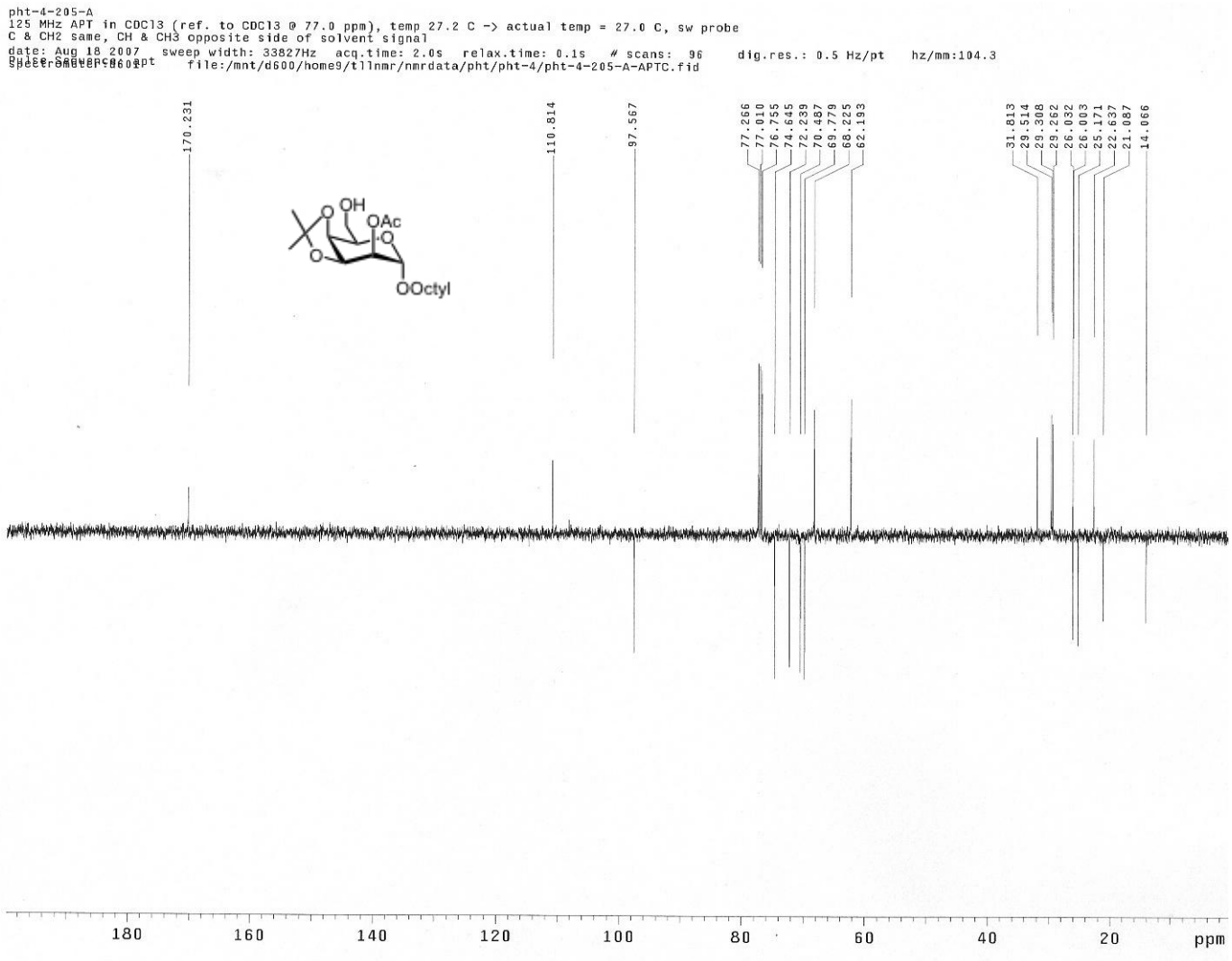
^{13}C NMR spectrum of **13**



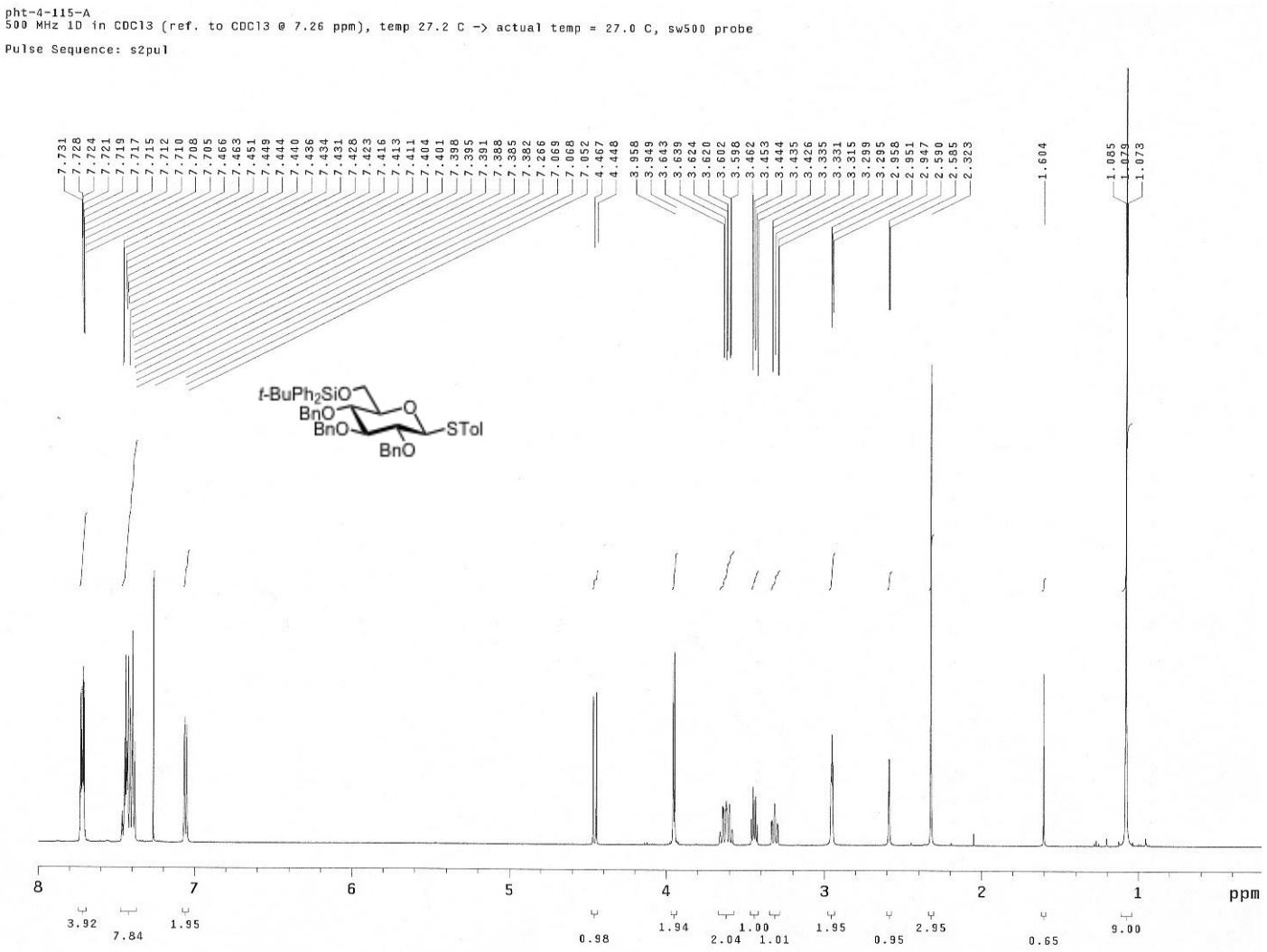
^{1}H NMR spectrum of **14**



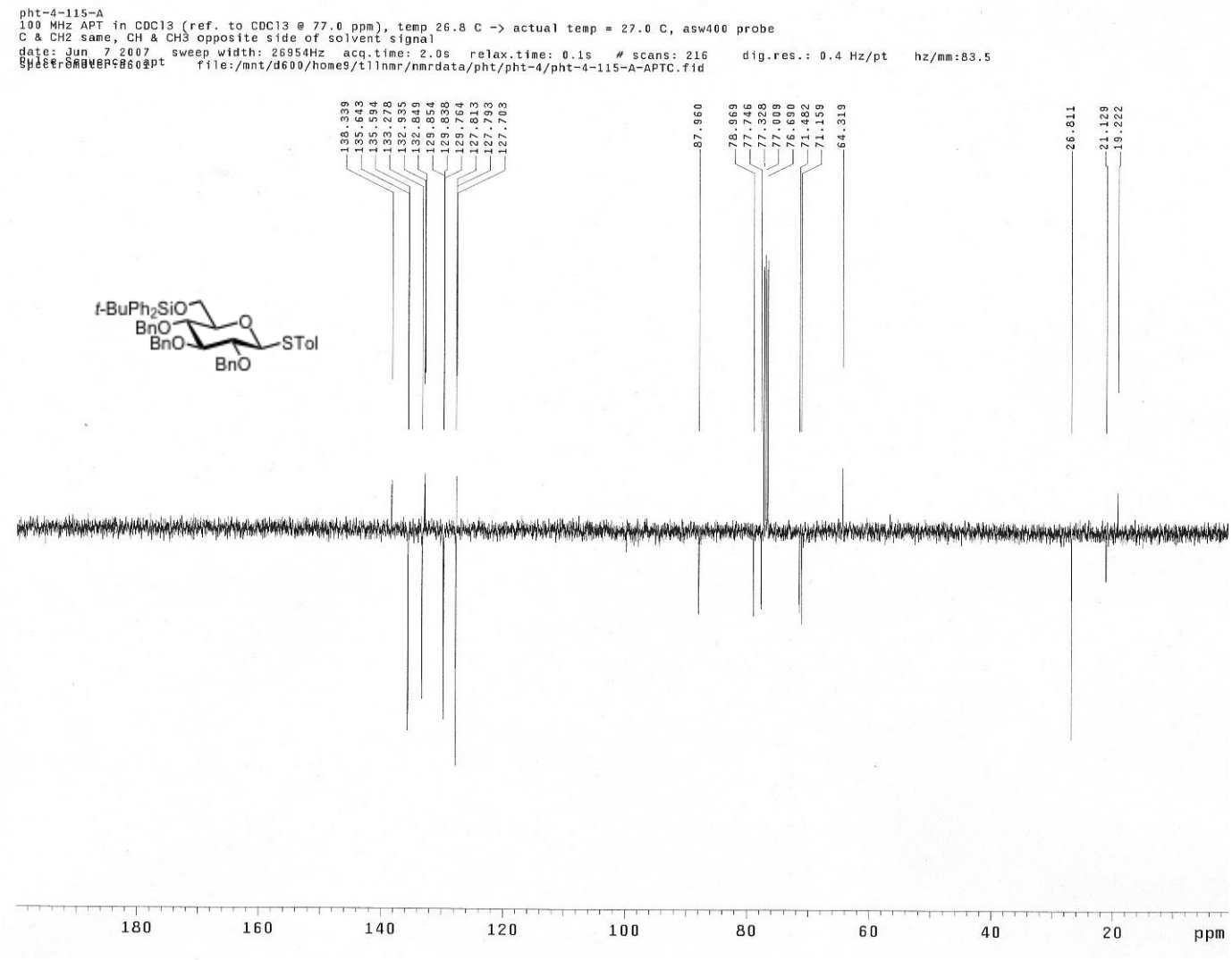
^{13}C NMR spectrum of **14**



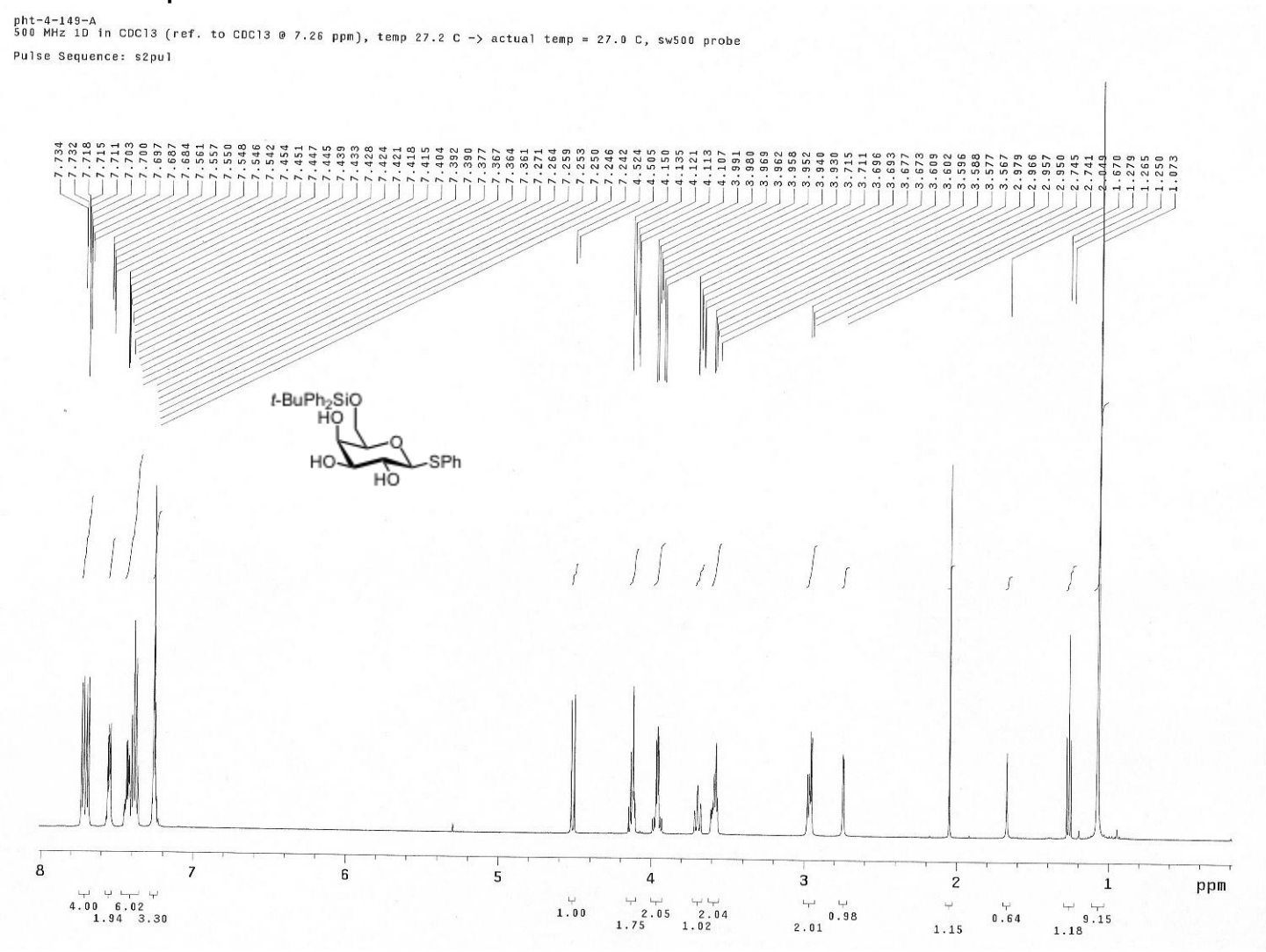
^{1}H NMR spectrum of **15**



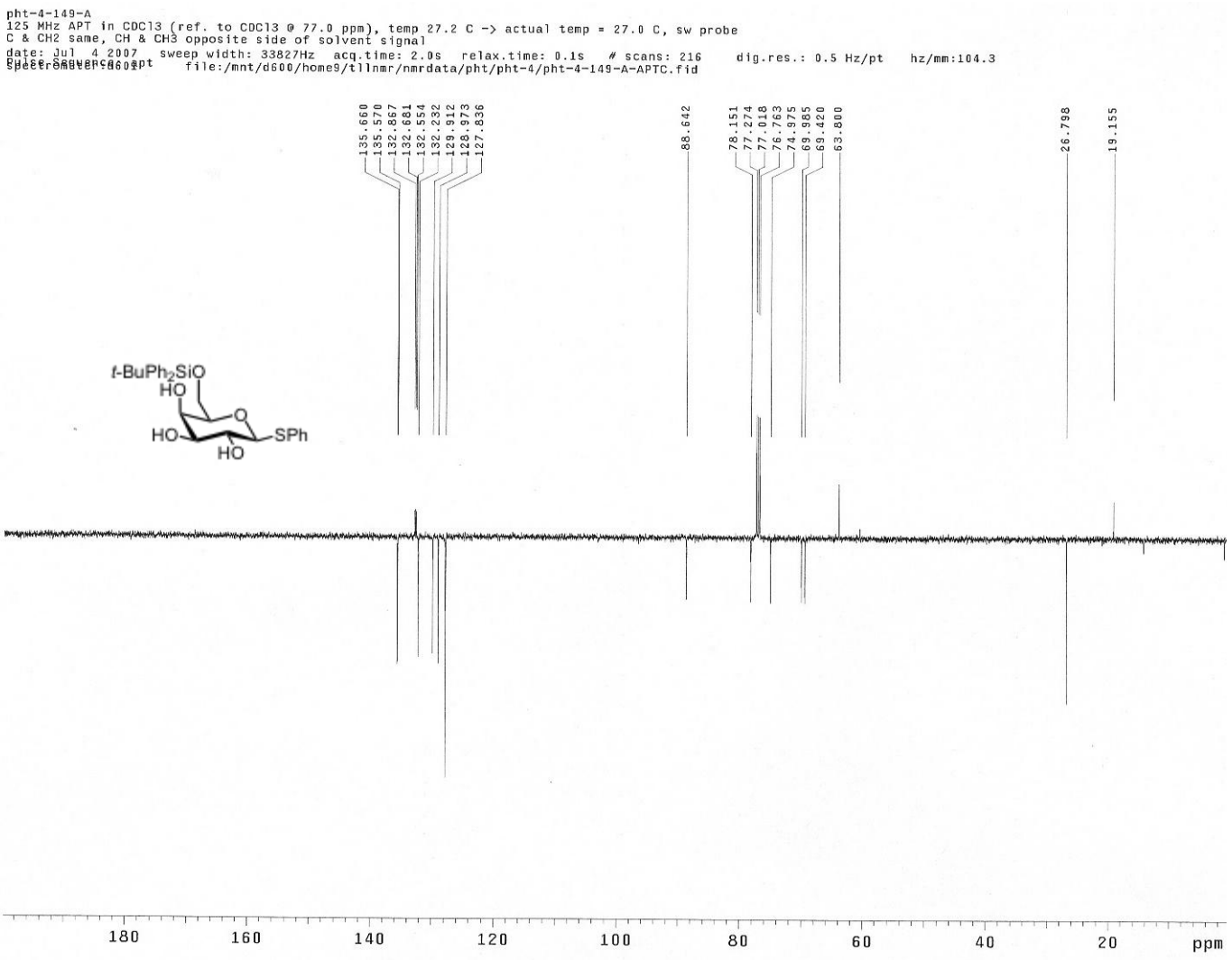
^{13}C NMR spectrum of **15**



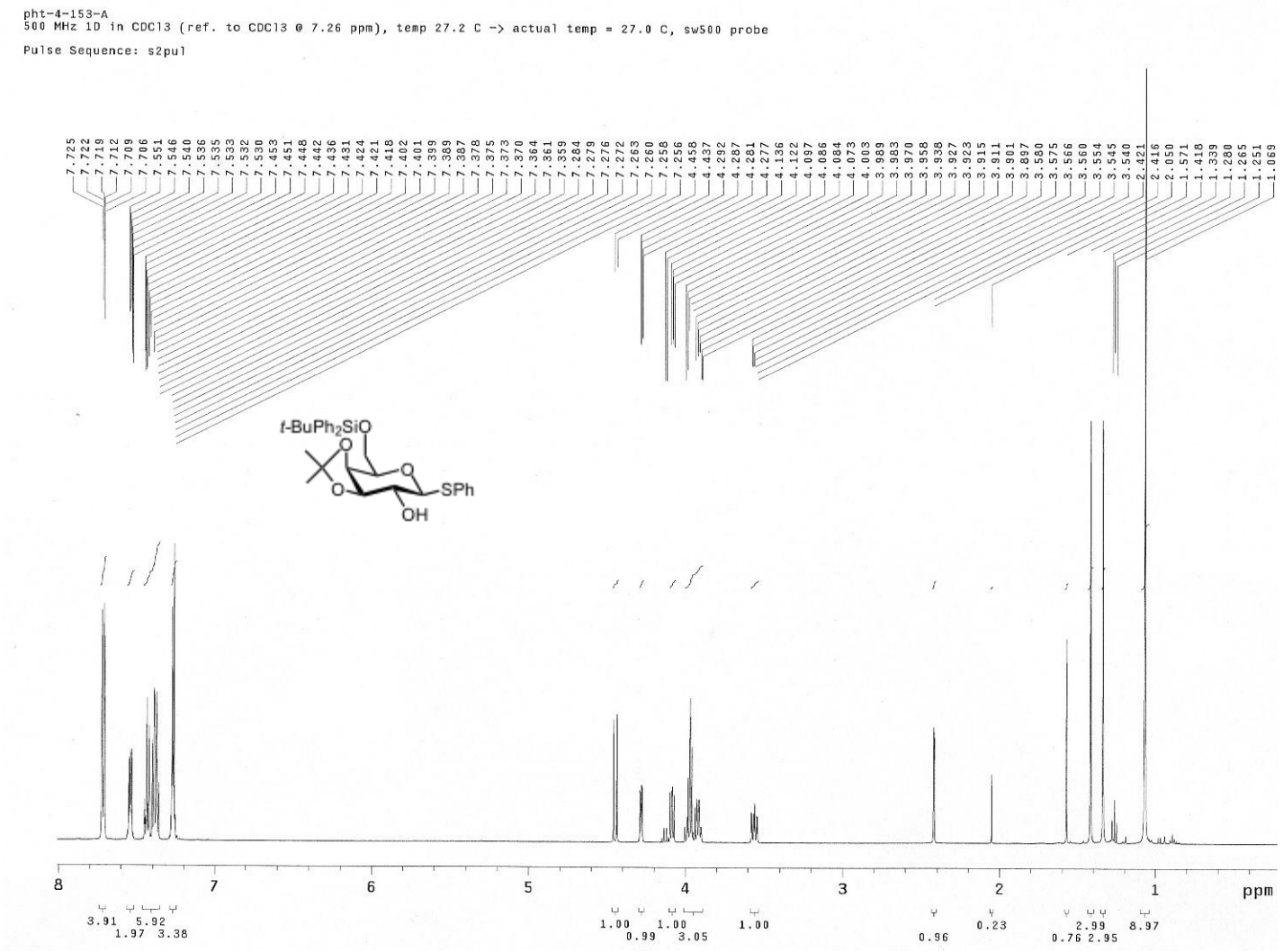
^{1}H NMR spectrum of **18**



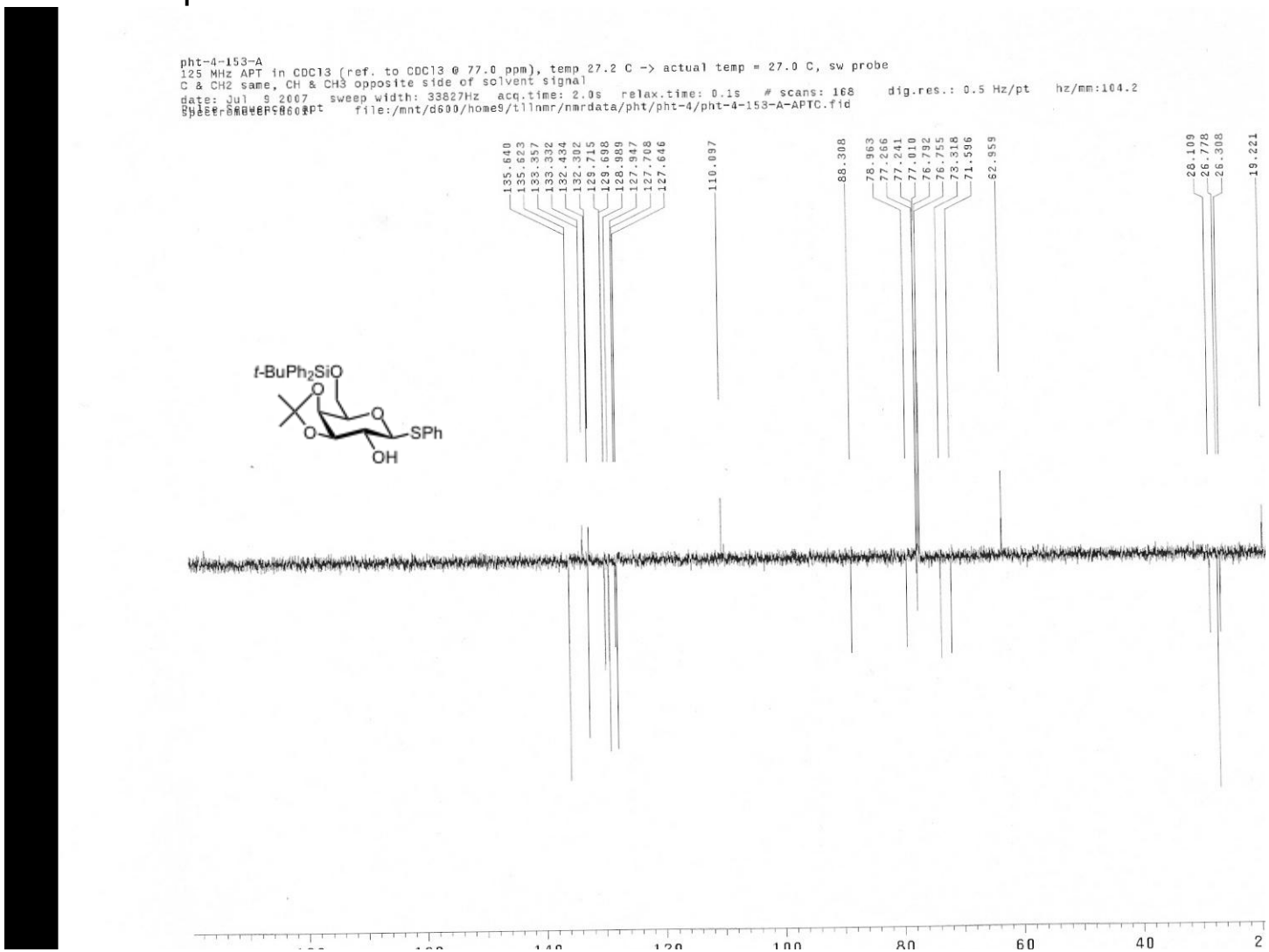
^{13}C NMR spectrum of **18**



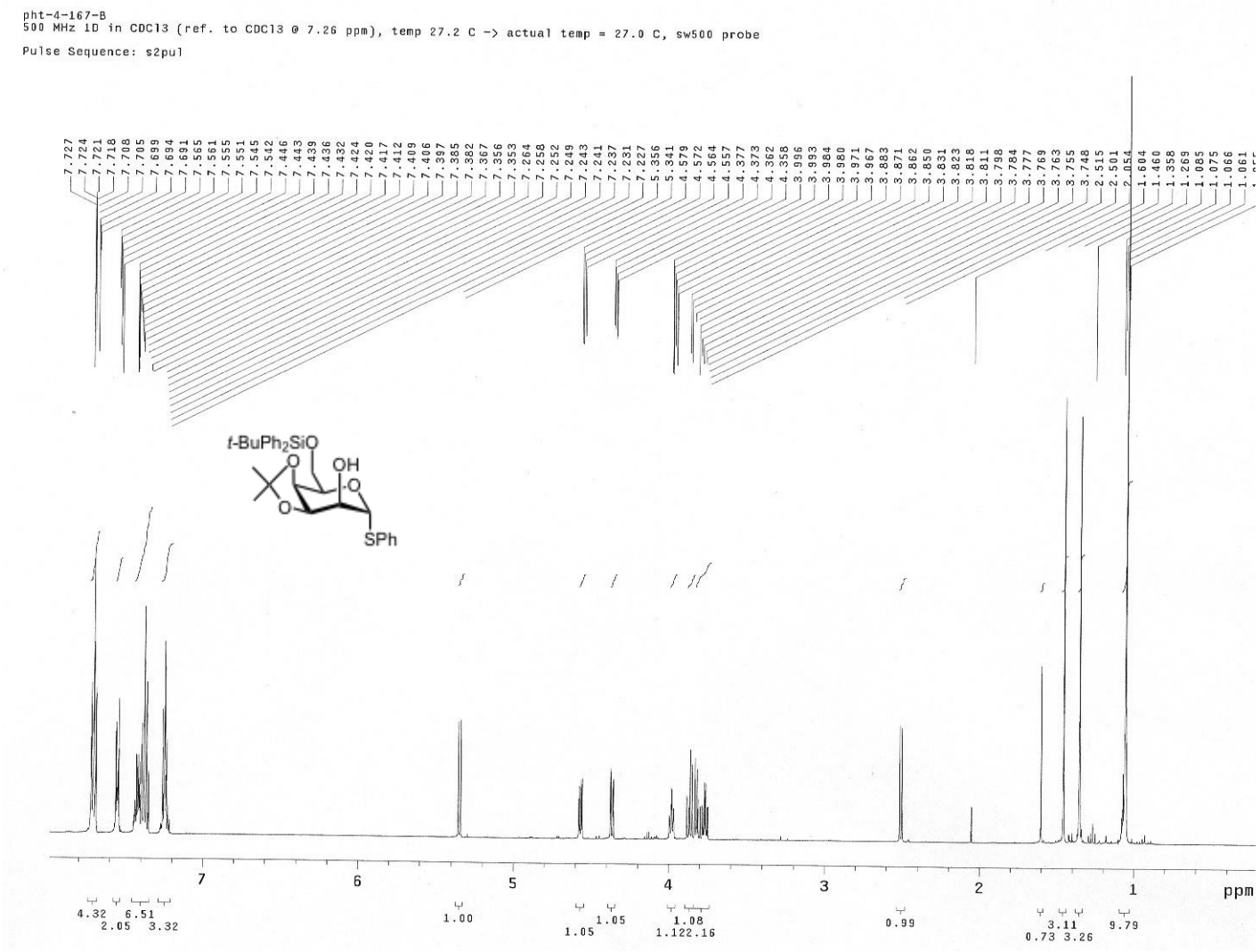
^{1}H NMR spectrum of **19**



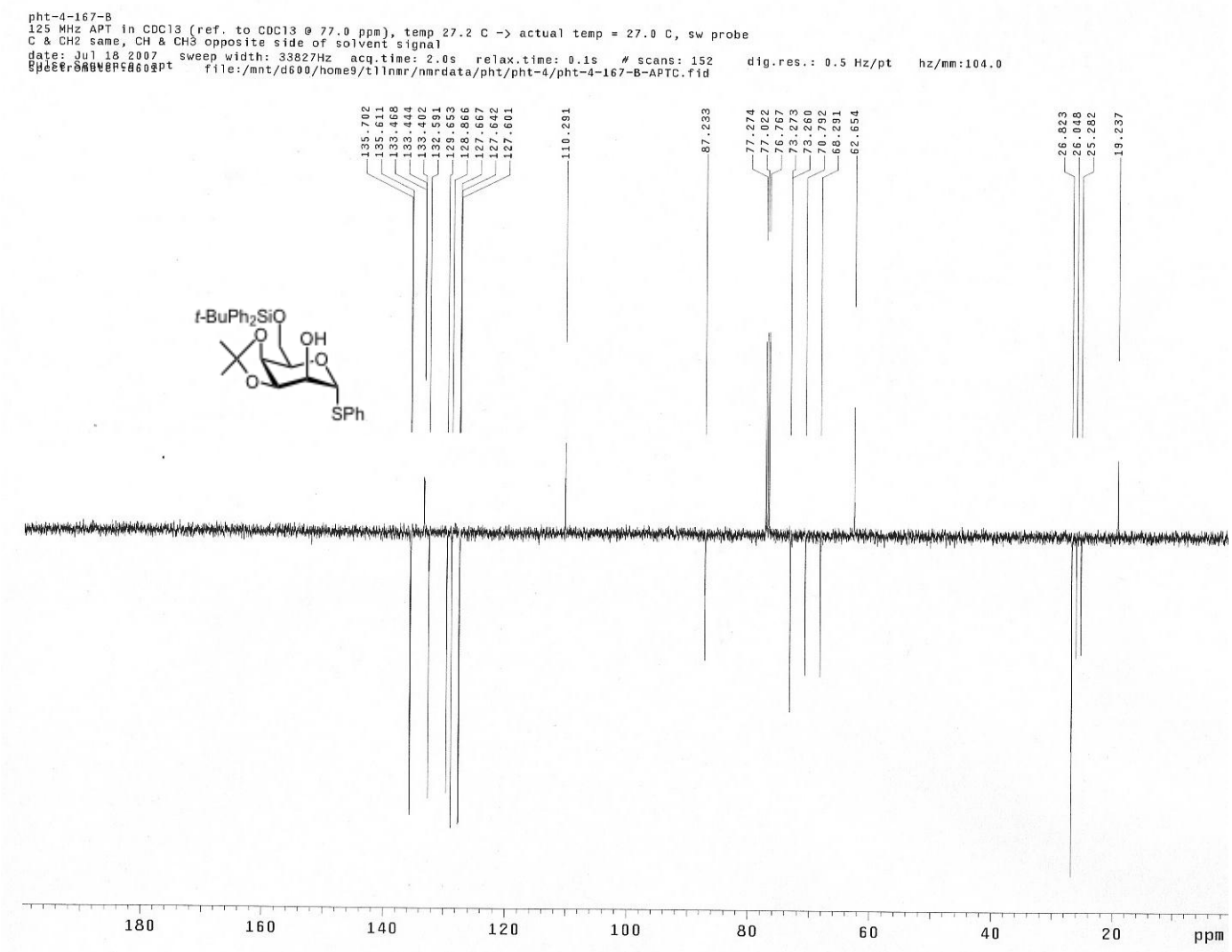
^{13}C NMR spectrum of **19**



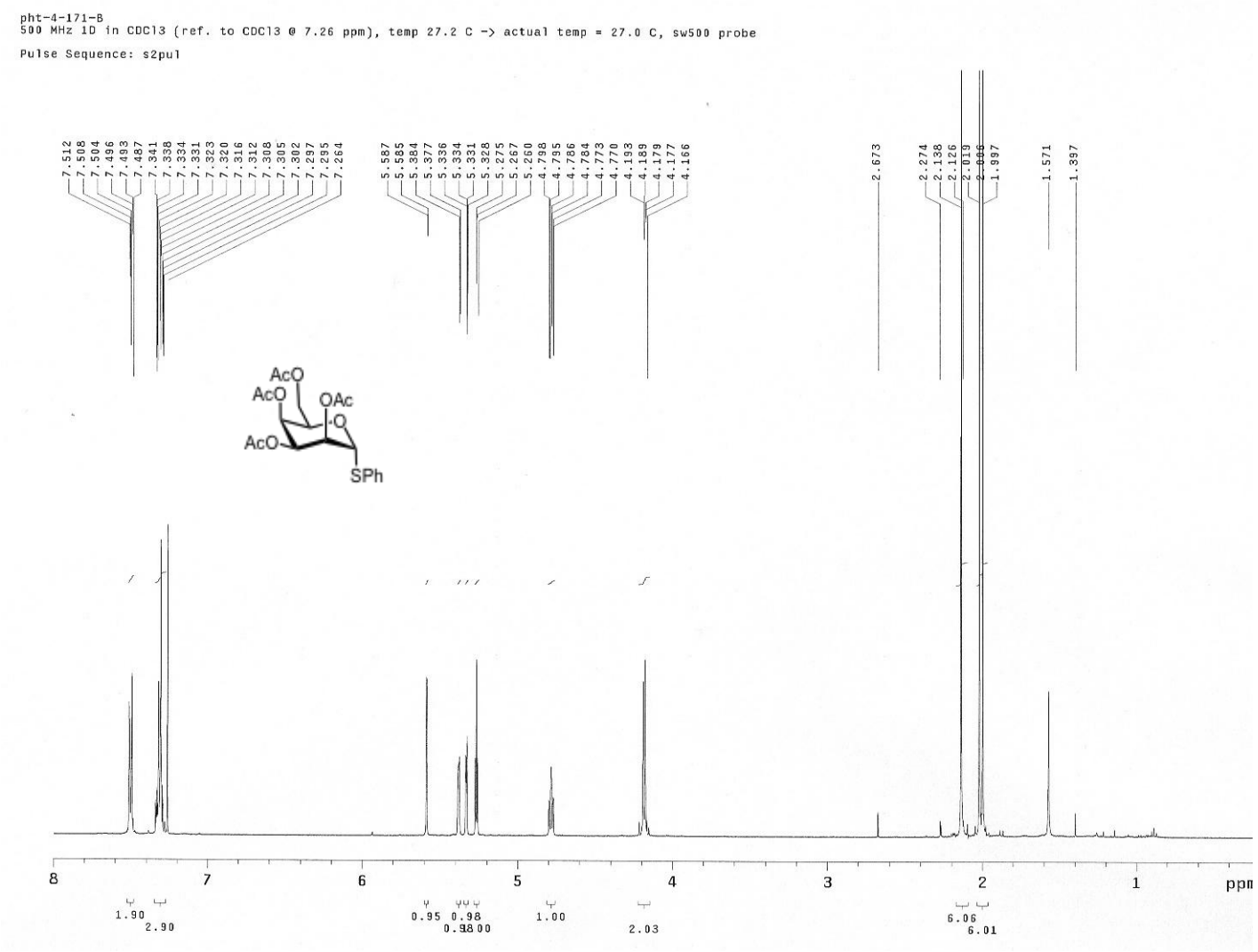
^{1}H NMR spectrum of **20**



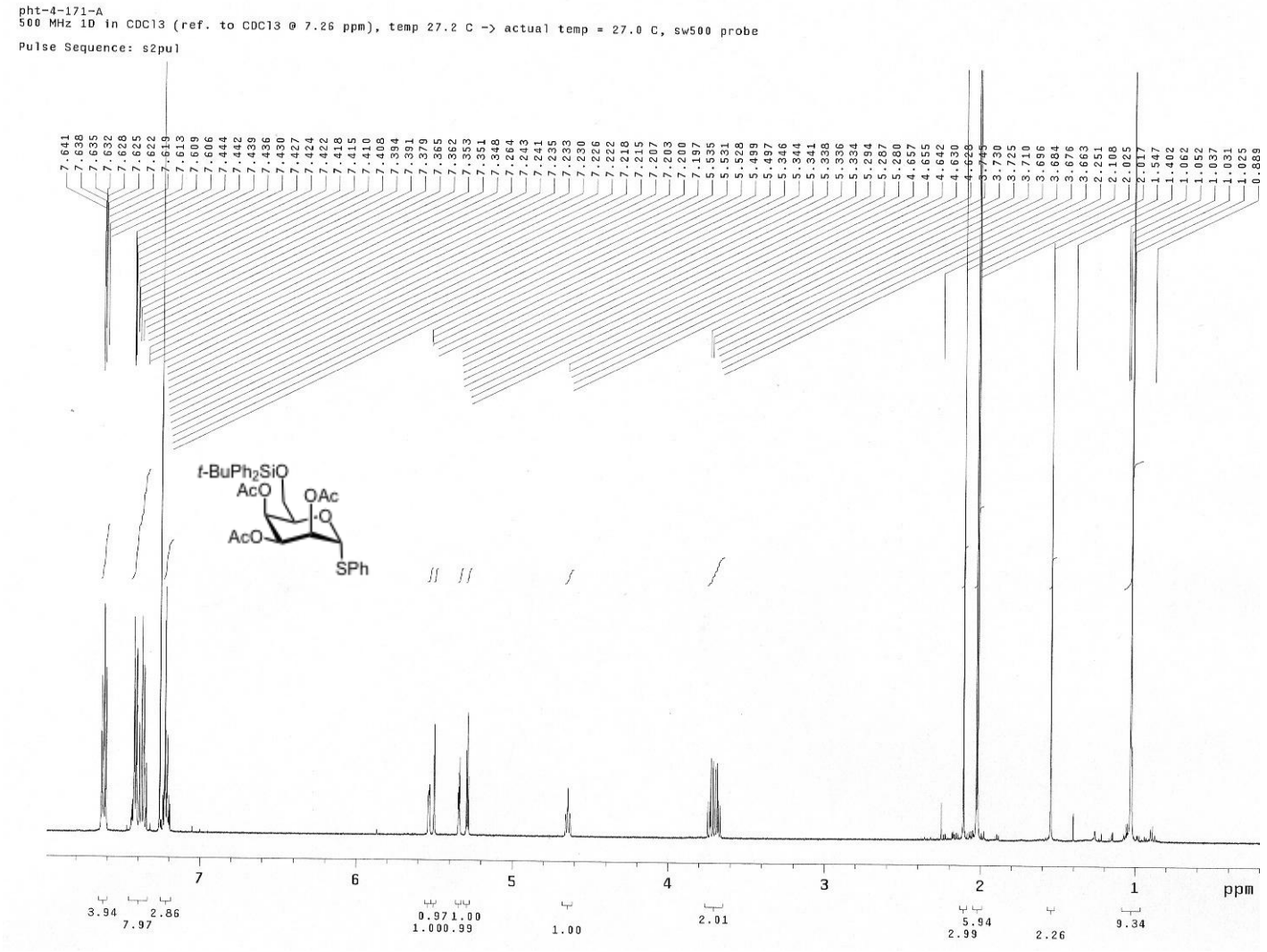
^{13}C NMR spectrum of **20**



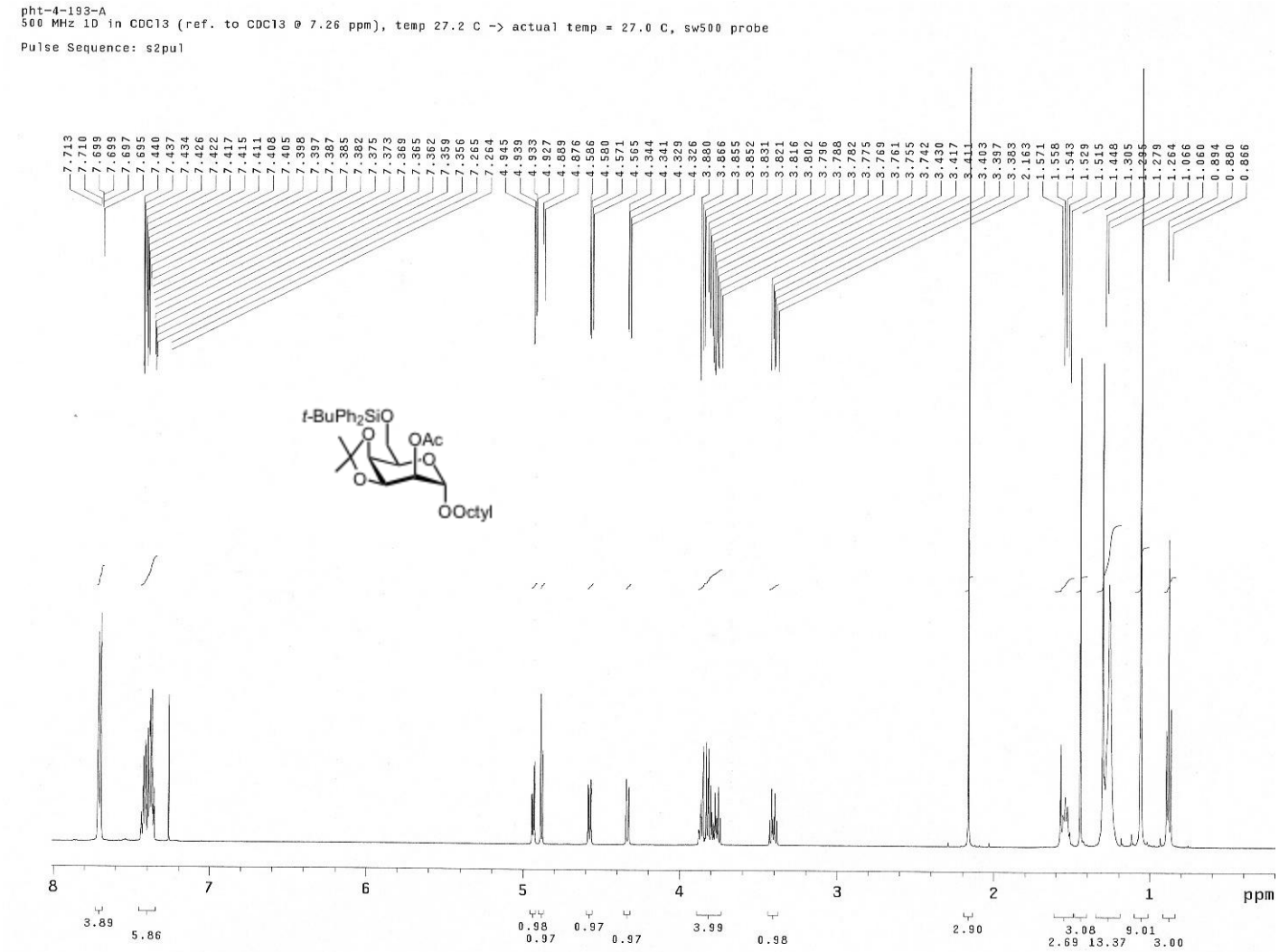
^{1}H NMR spectrum of **21**



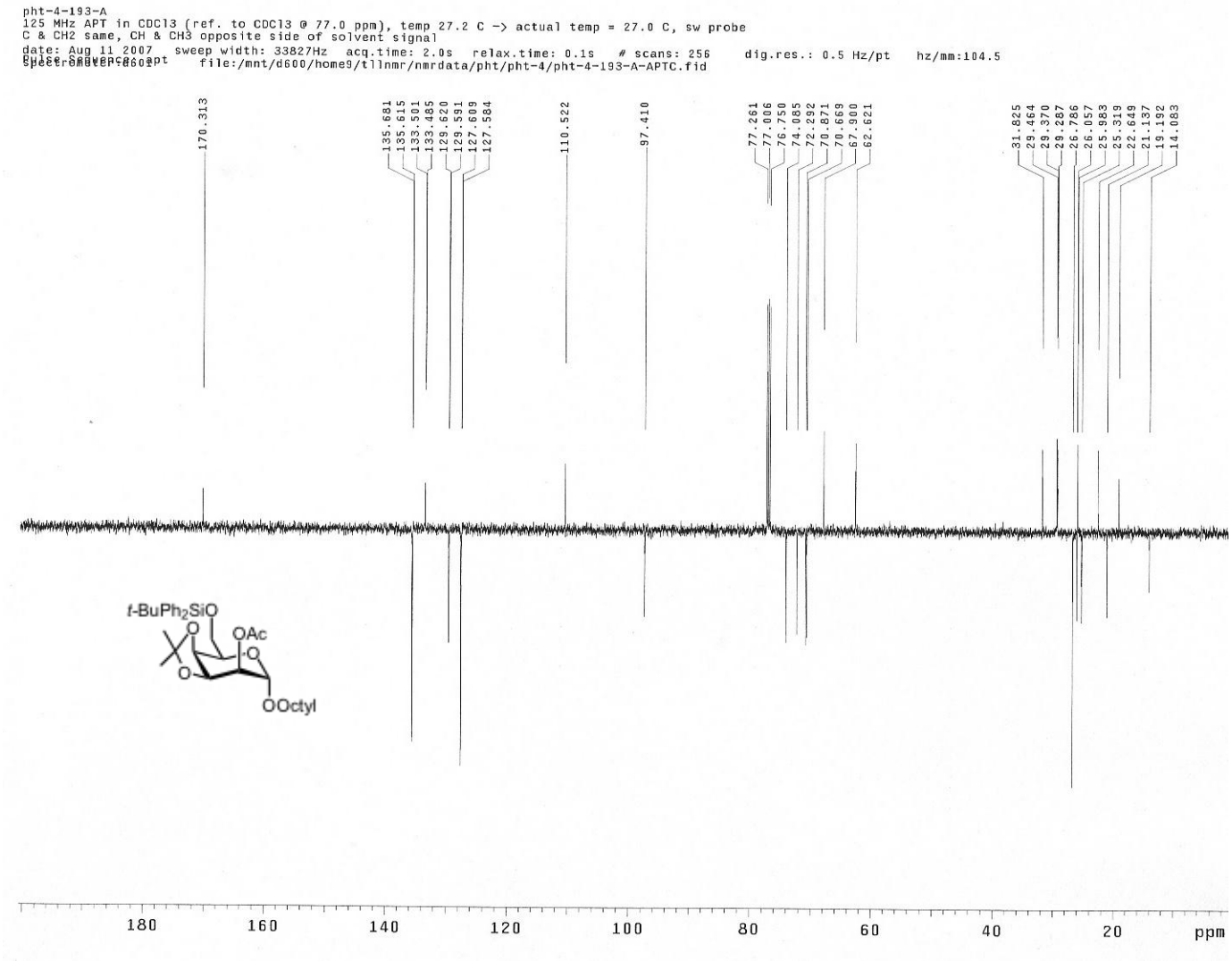
^{1}H NMR spectrum of **22**



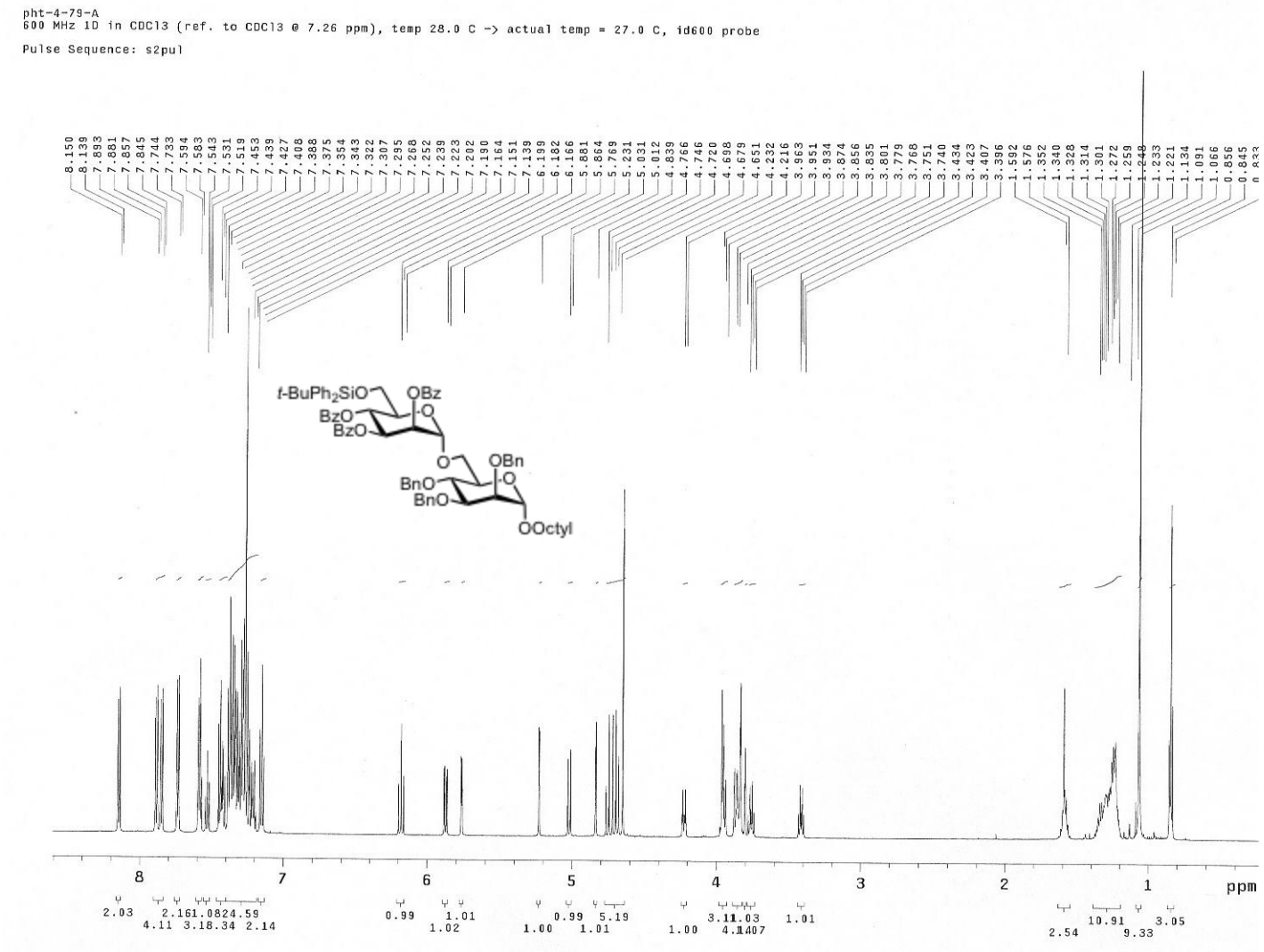
^{1}H NMR spectrum of **23**



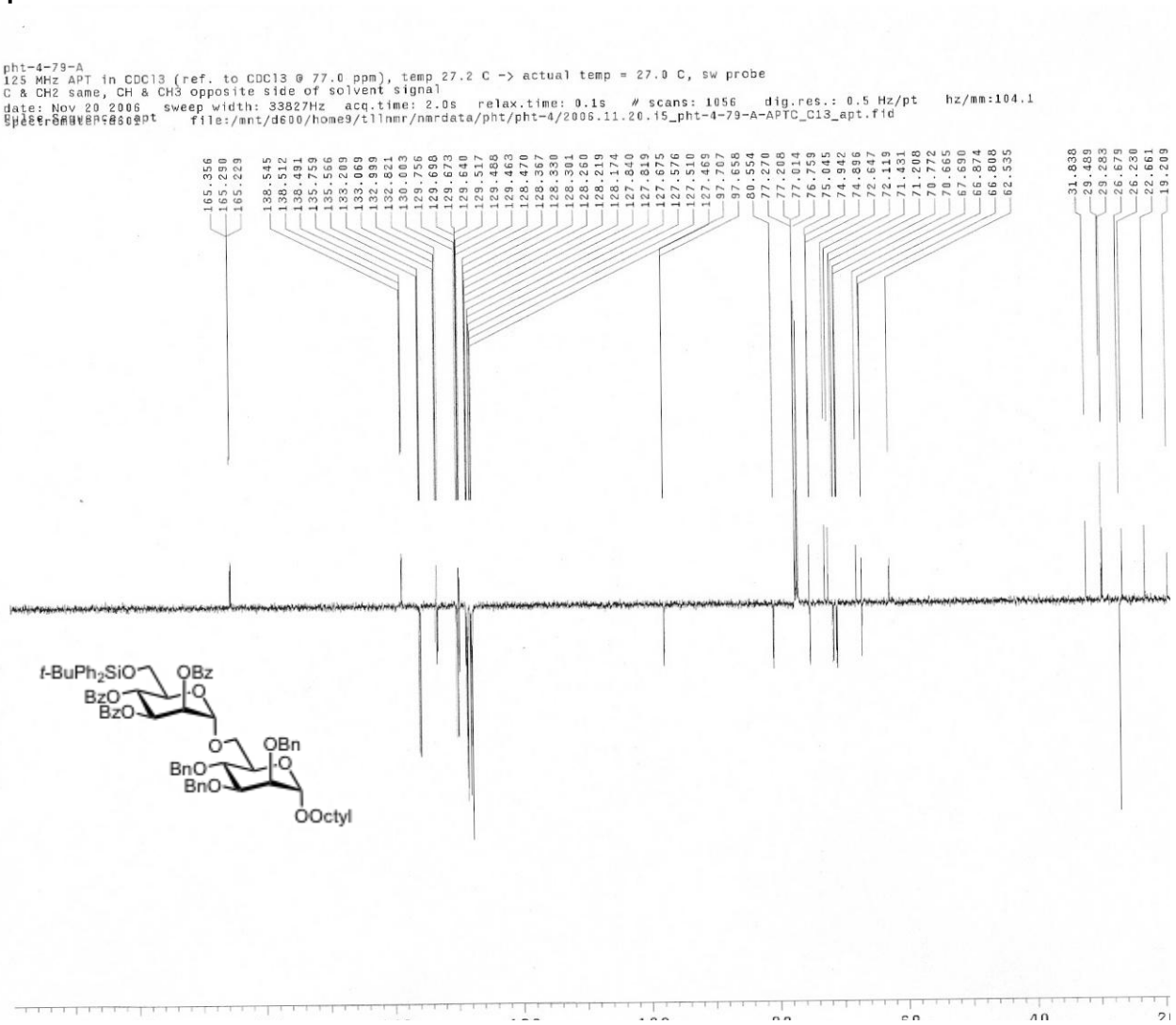
^{13}C NMR spectrum of **23**



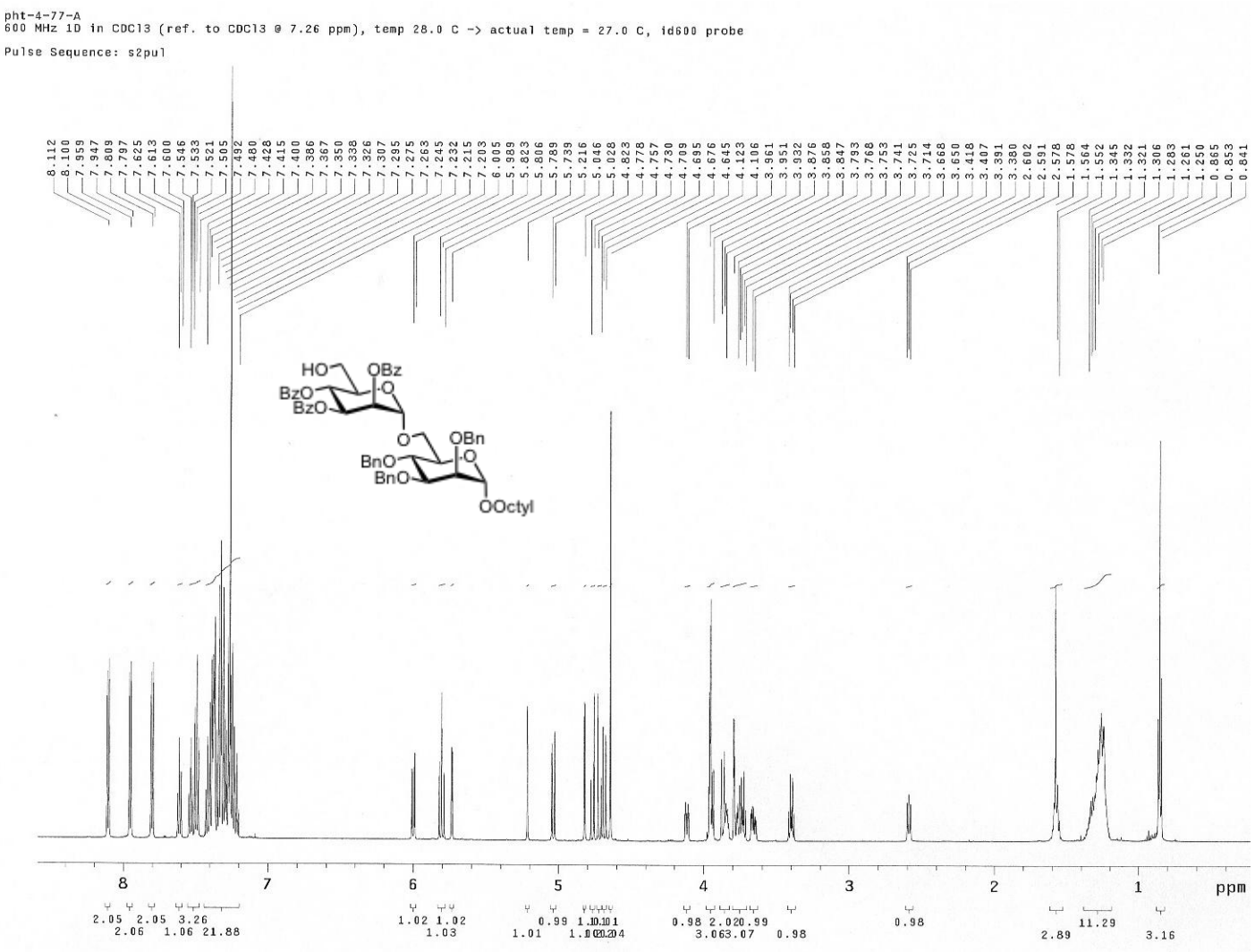
^{1}H NMR spectrum of **26**



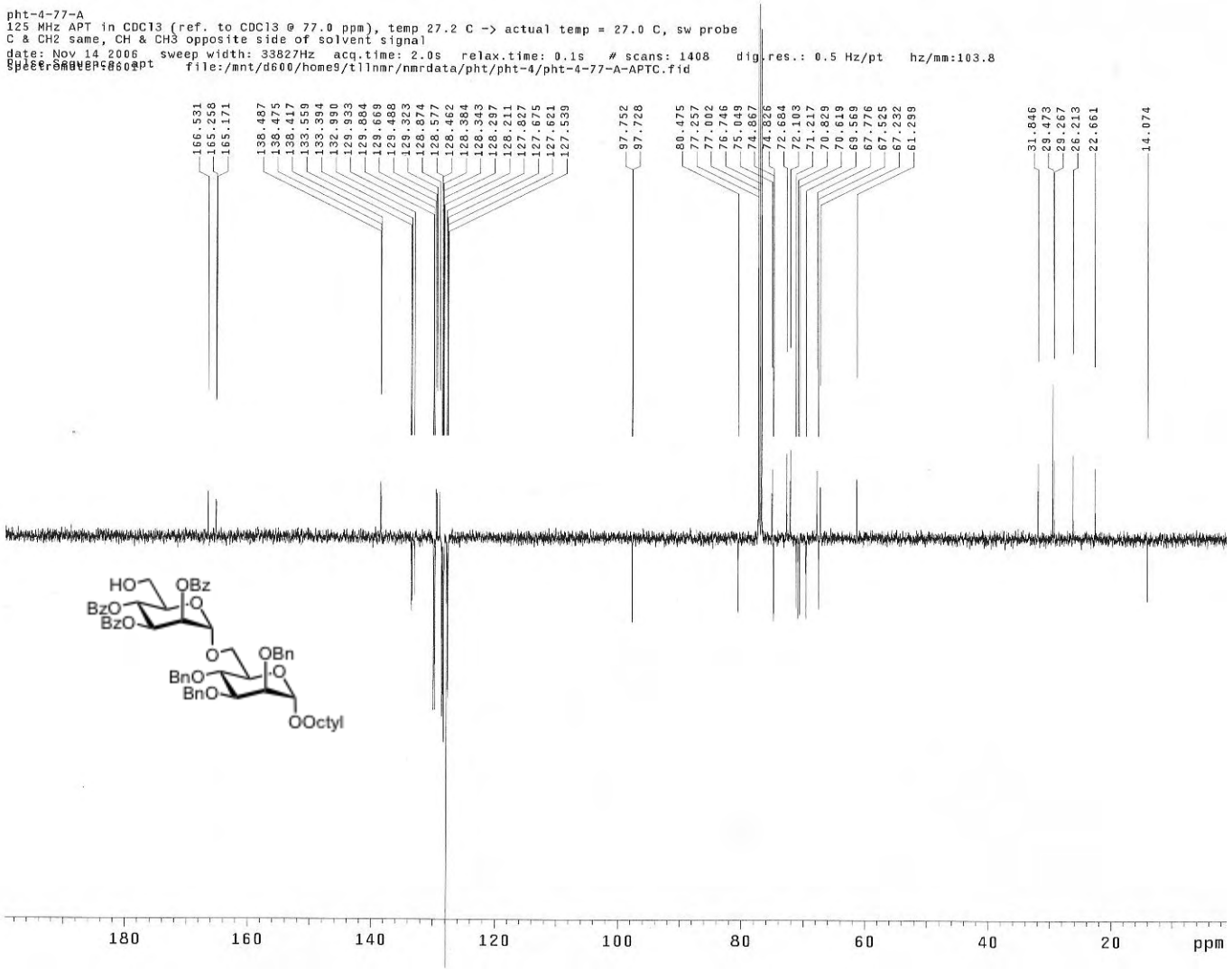
^{13}C NMR spectrum of **26**



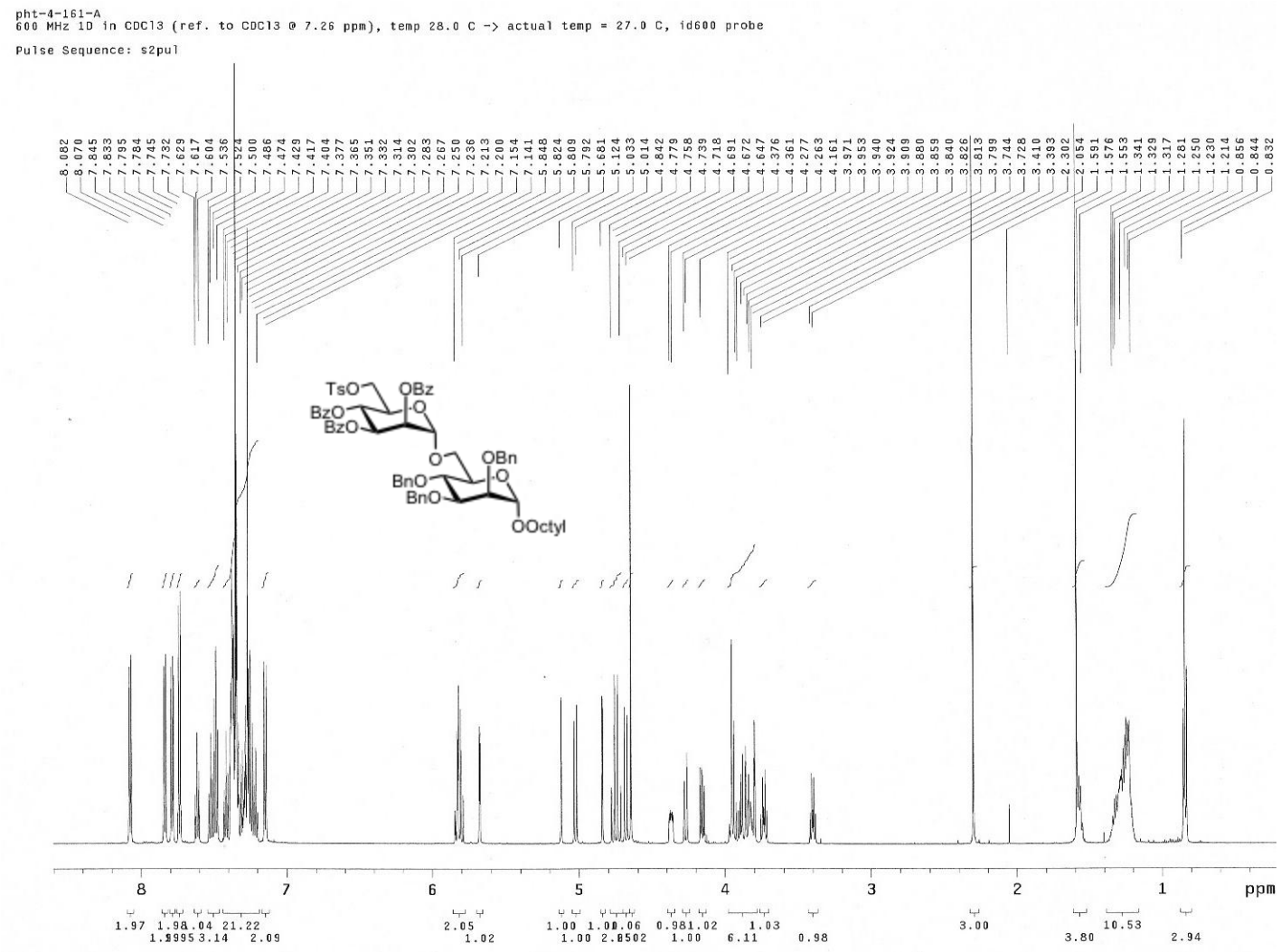
^{1}H NMR spectrum of **27**



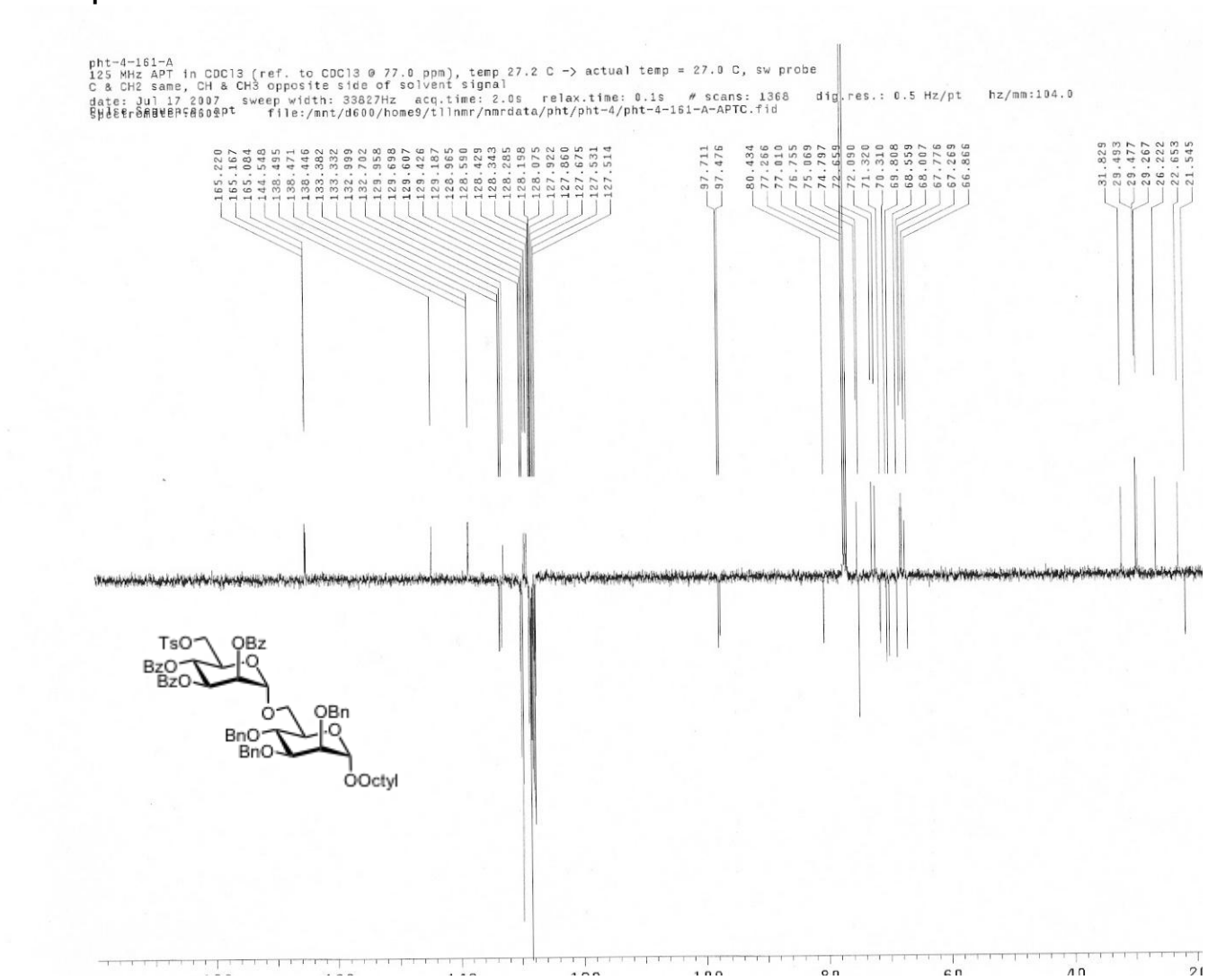
^{13}C NMR spectrum of **27**



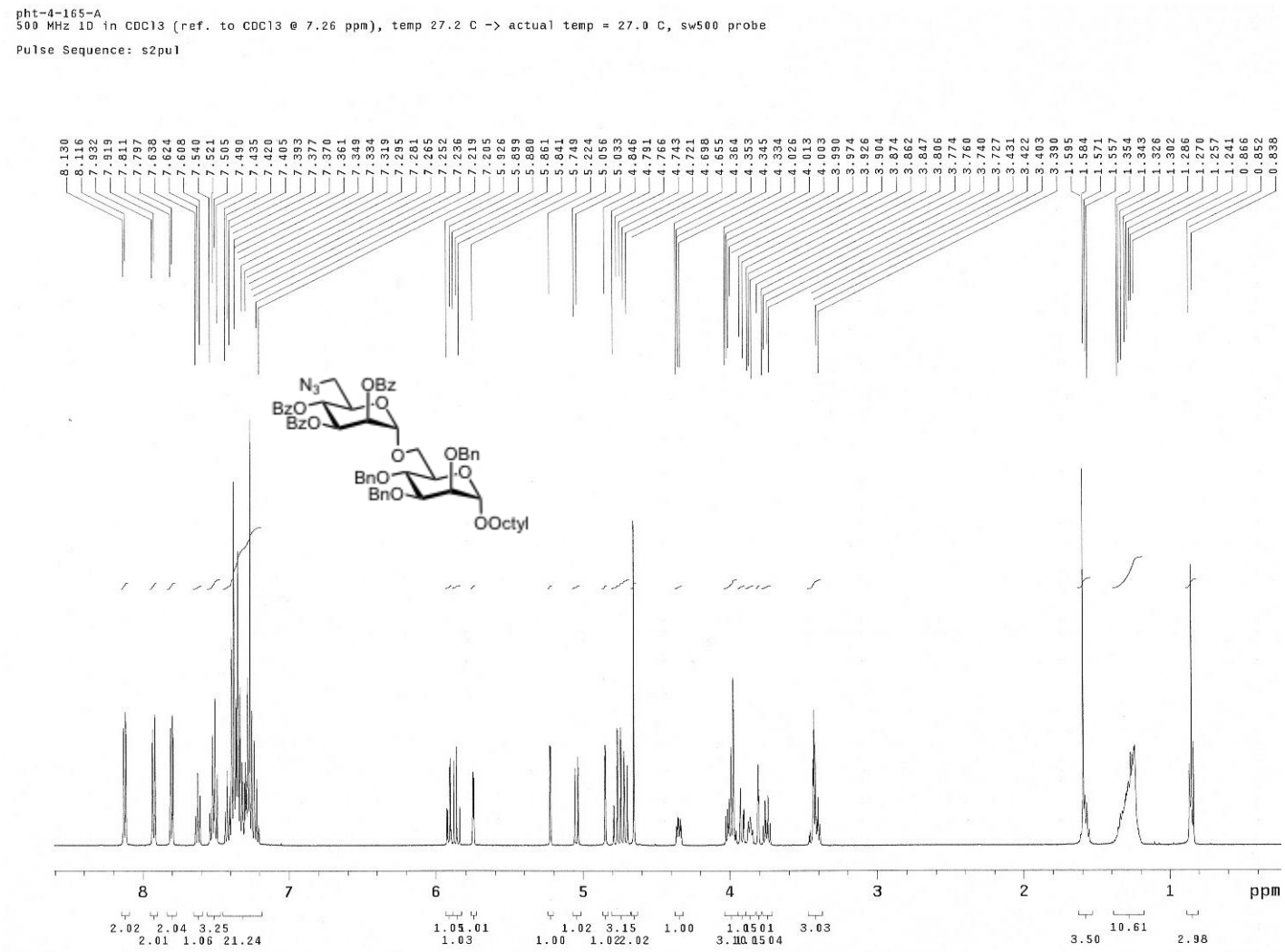
^{1}H NMR spectrum of **28**



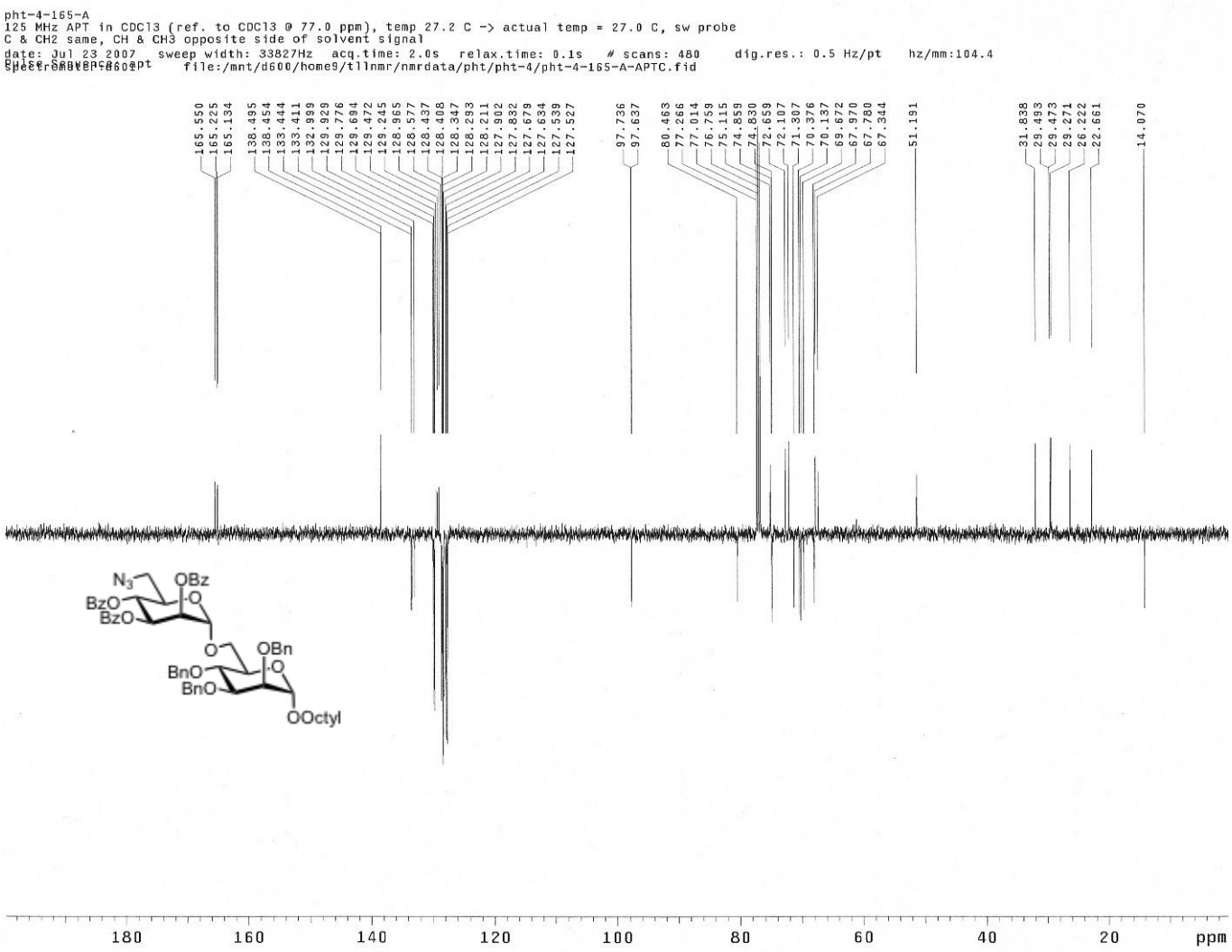
^{13}C NMR spectrum of **28**



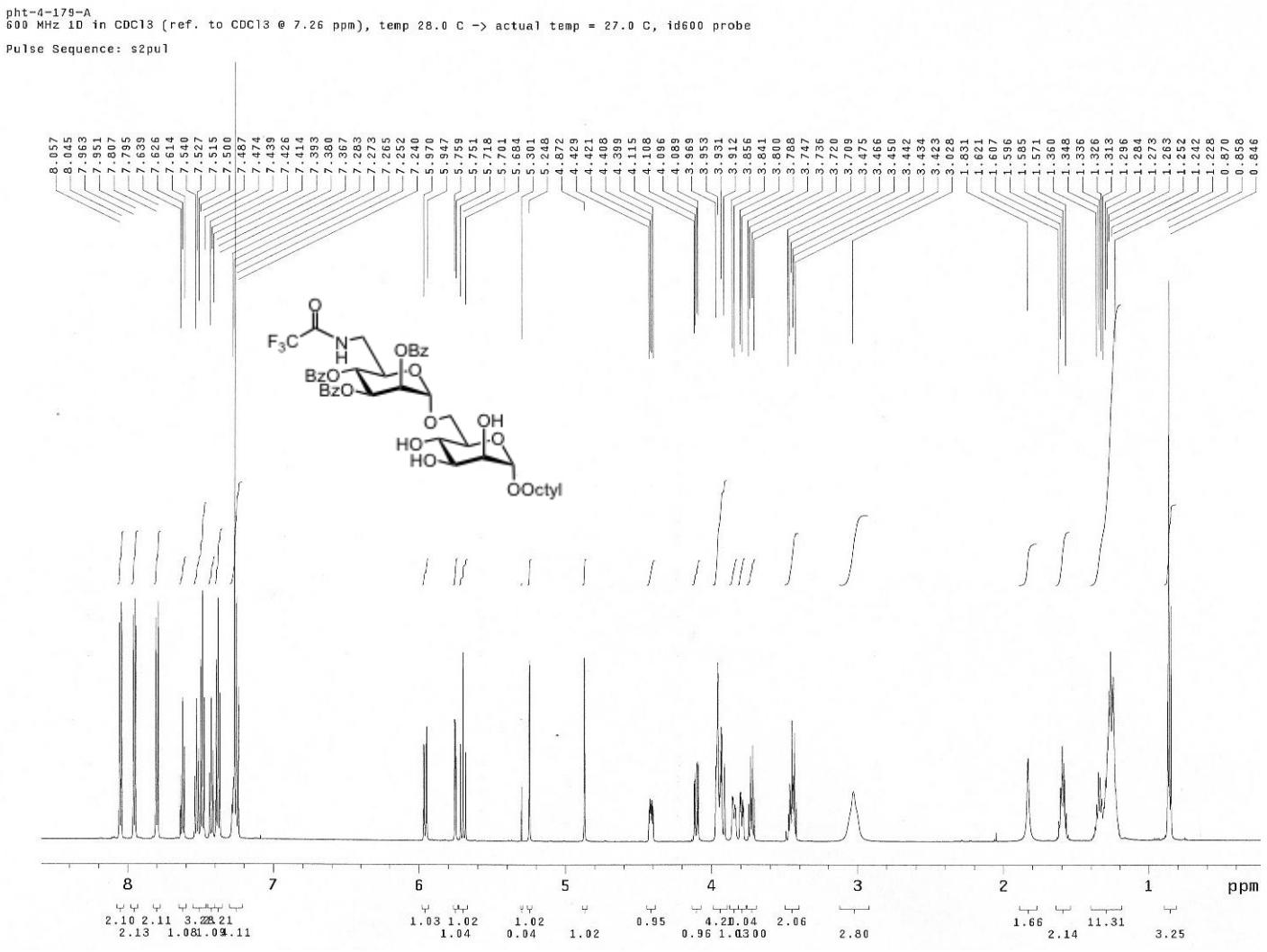
^{1}H NMR spectrum of **29**



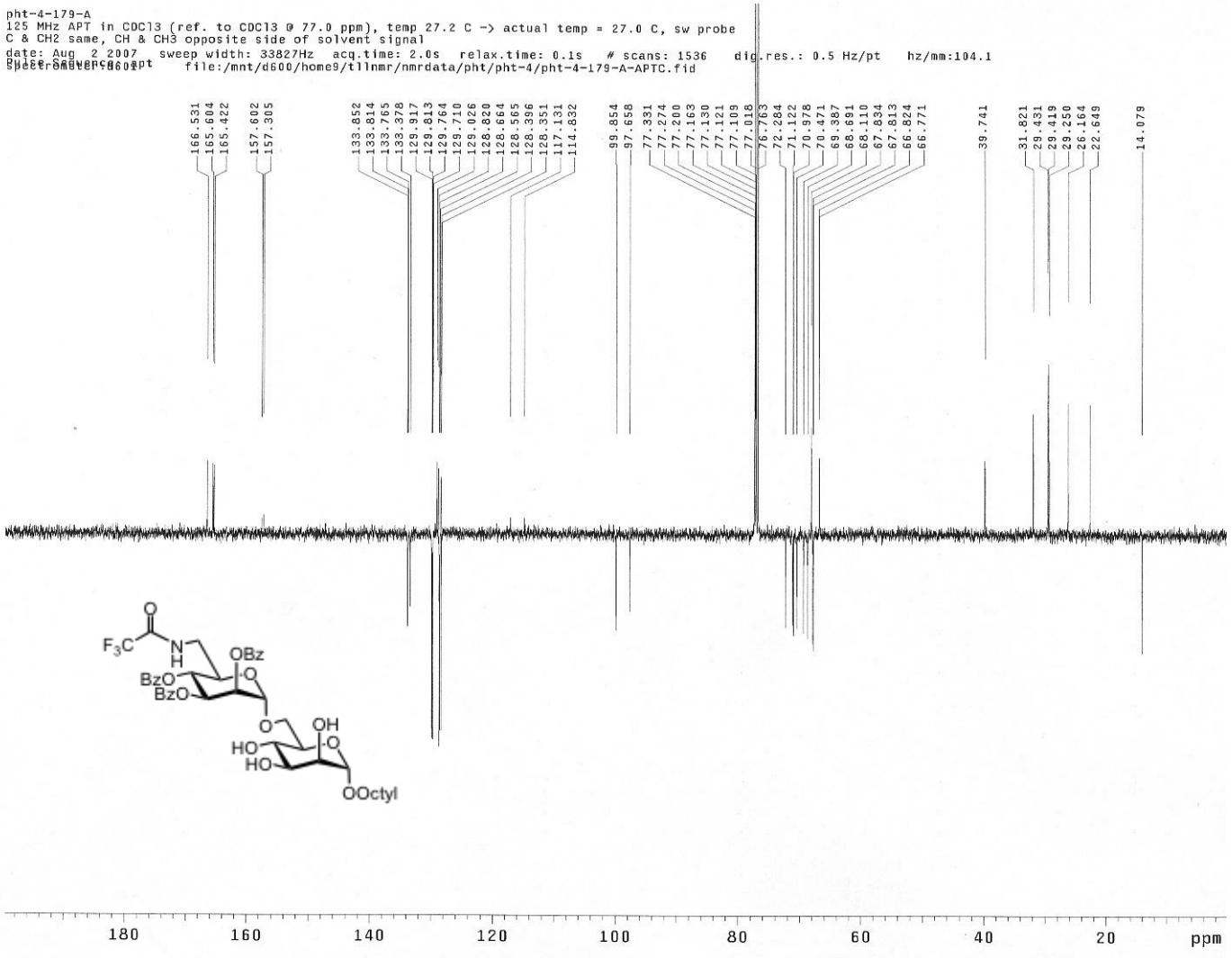
^{13}C NMR spectrum of **29**



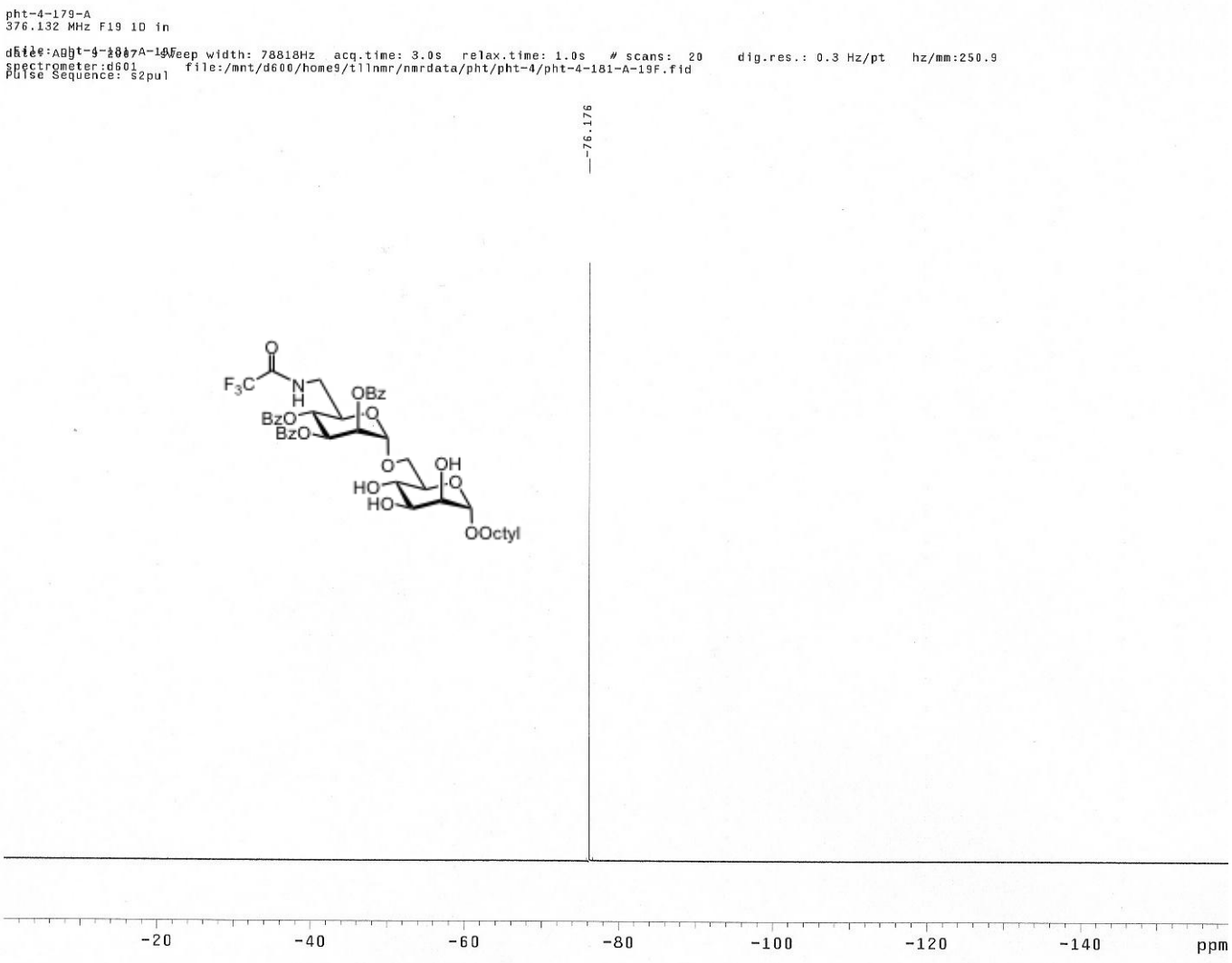
^{1}H NMR spectrum of **30**



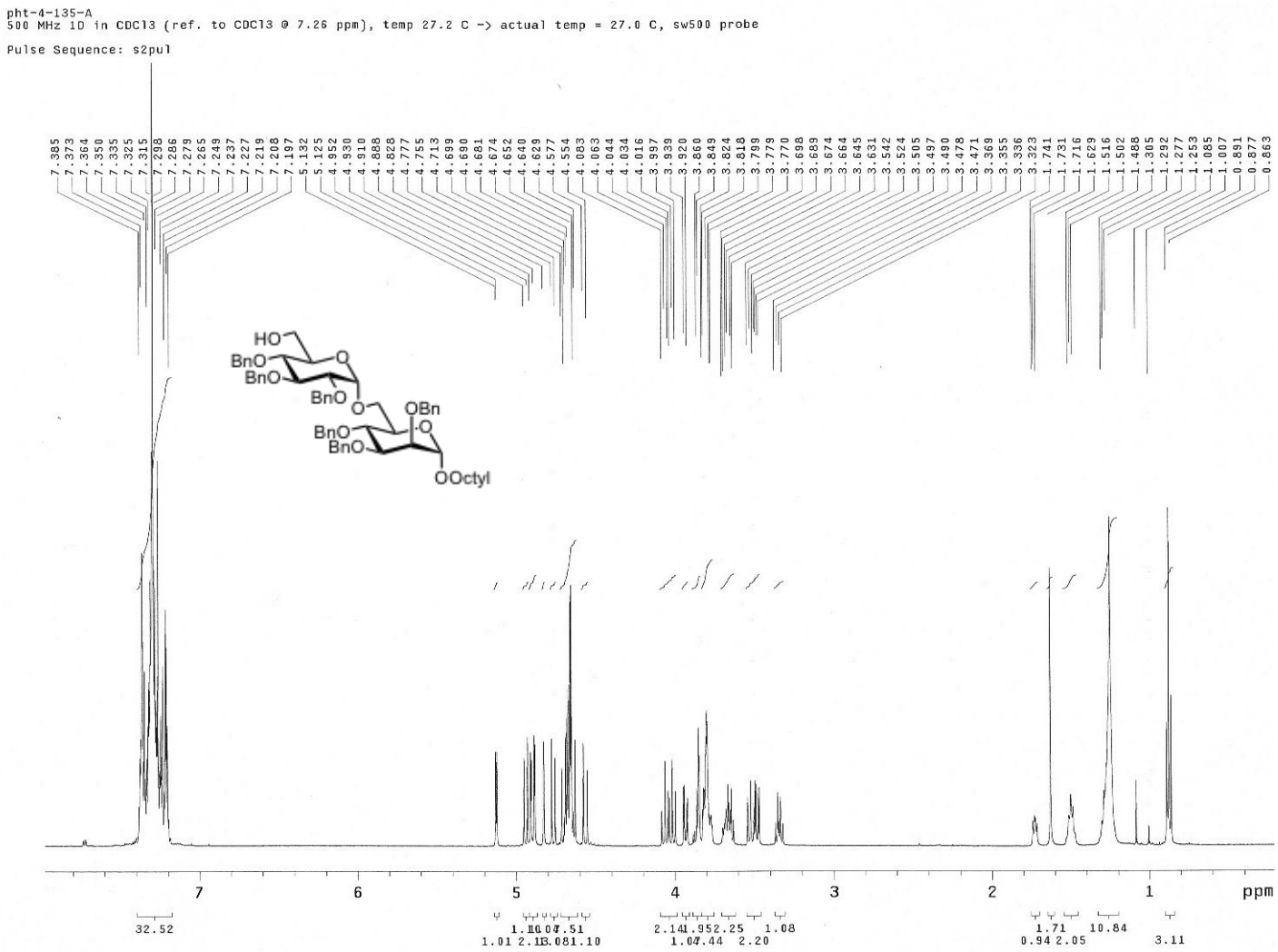
^{13}C NMR spectrum of **30**



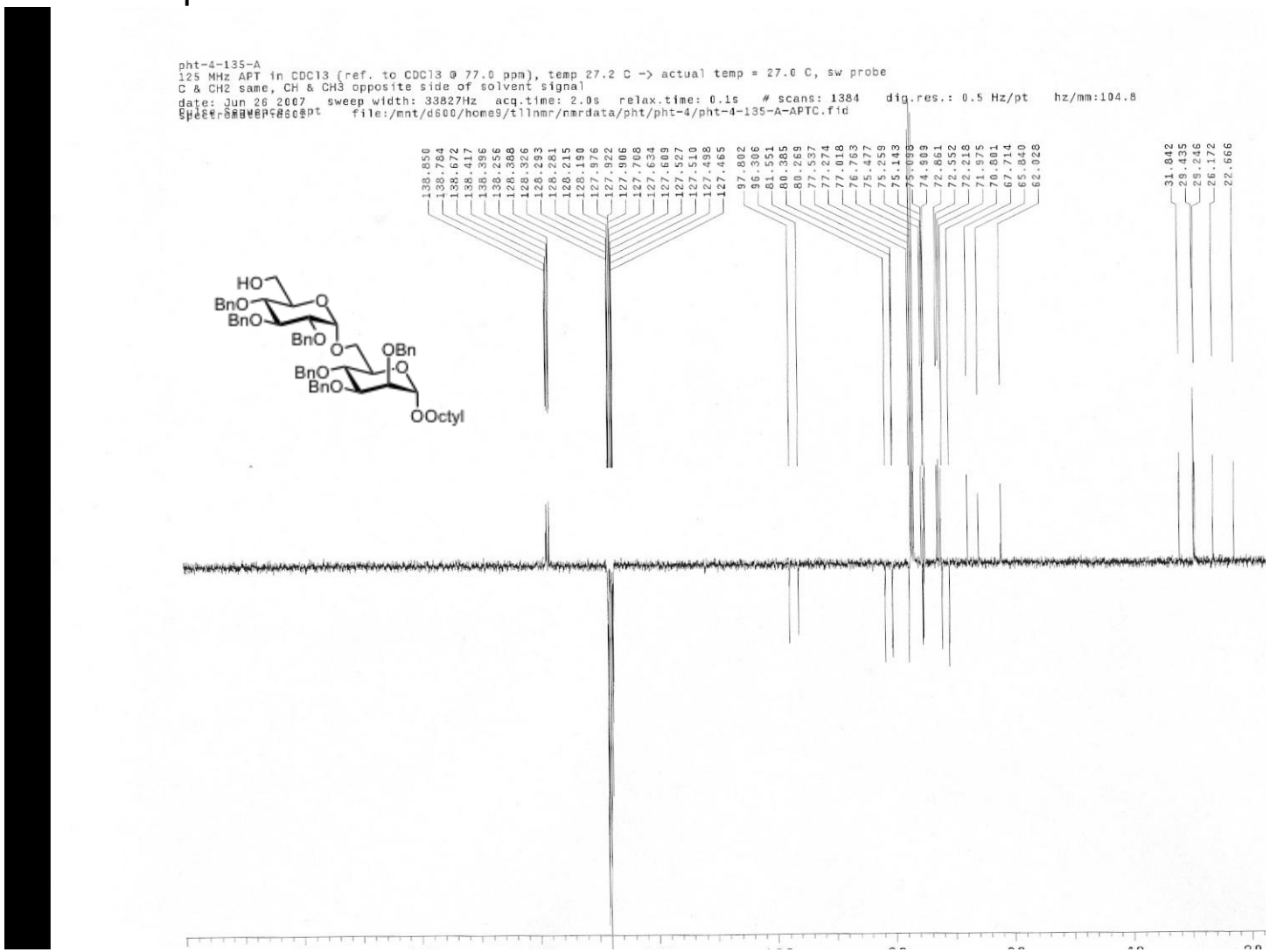
^{19}F NMR spectrum of **30**



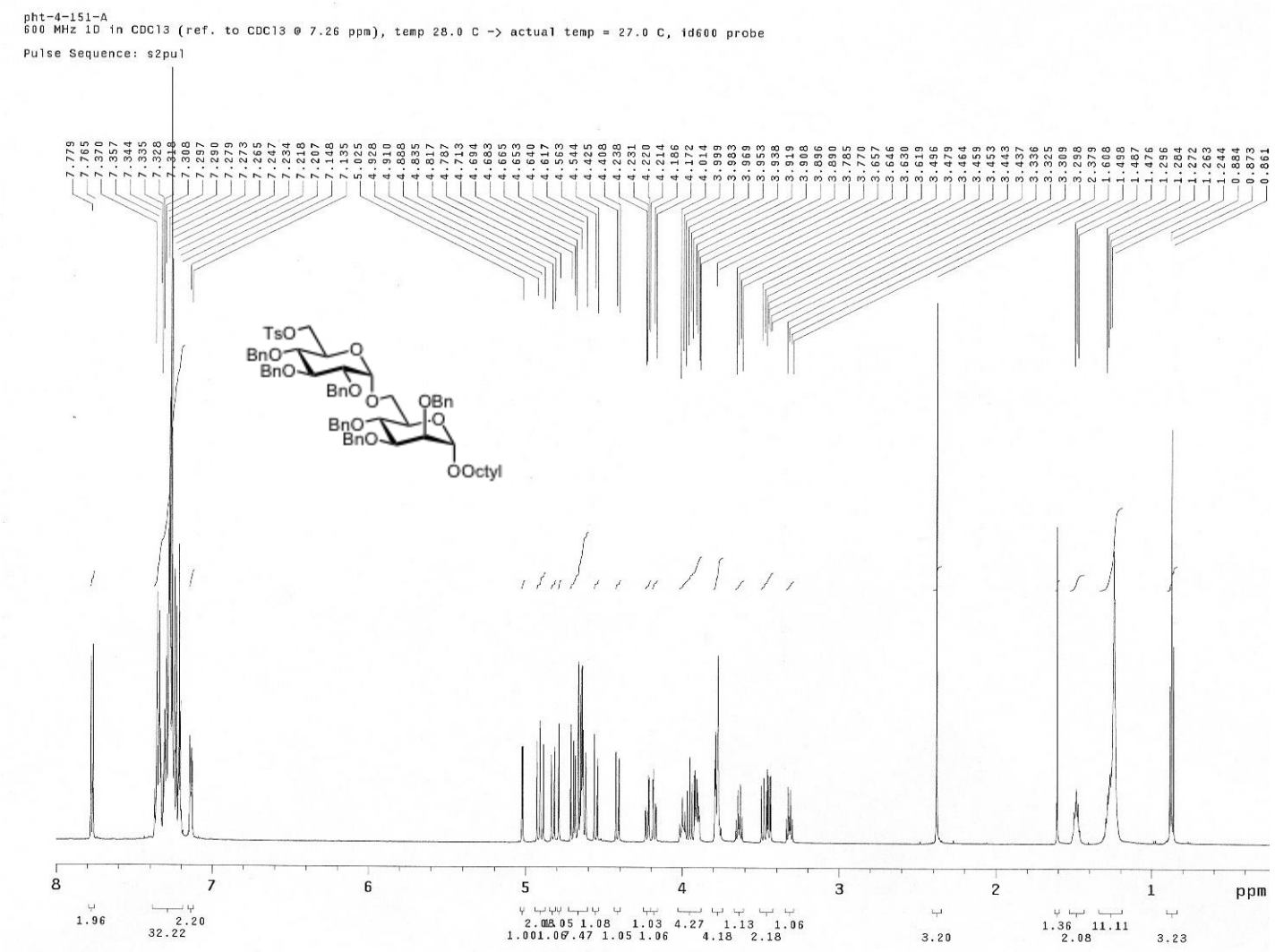
^{1}H NMR spectrum of **31**



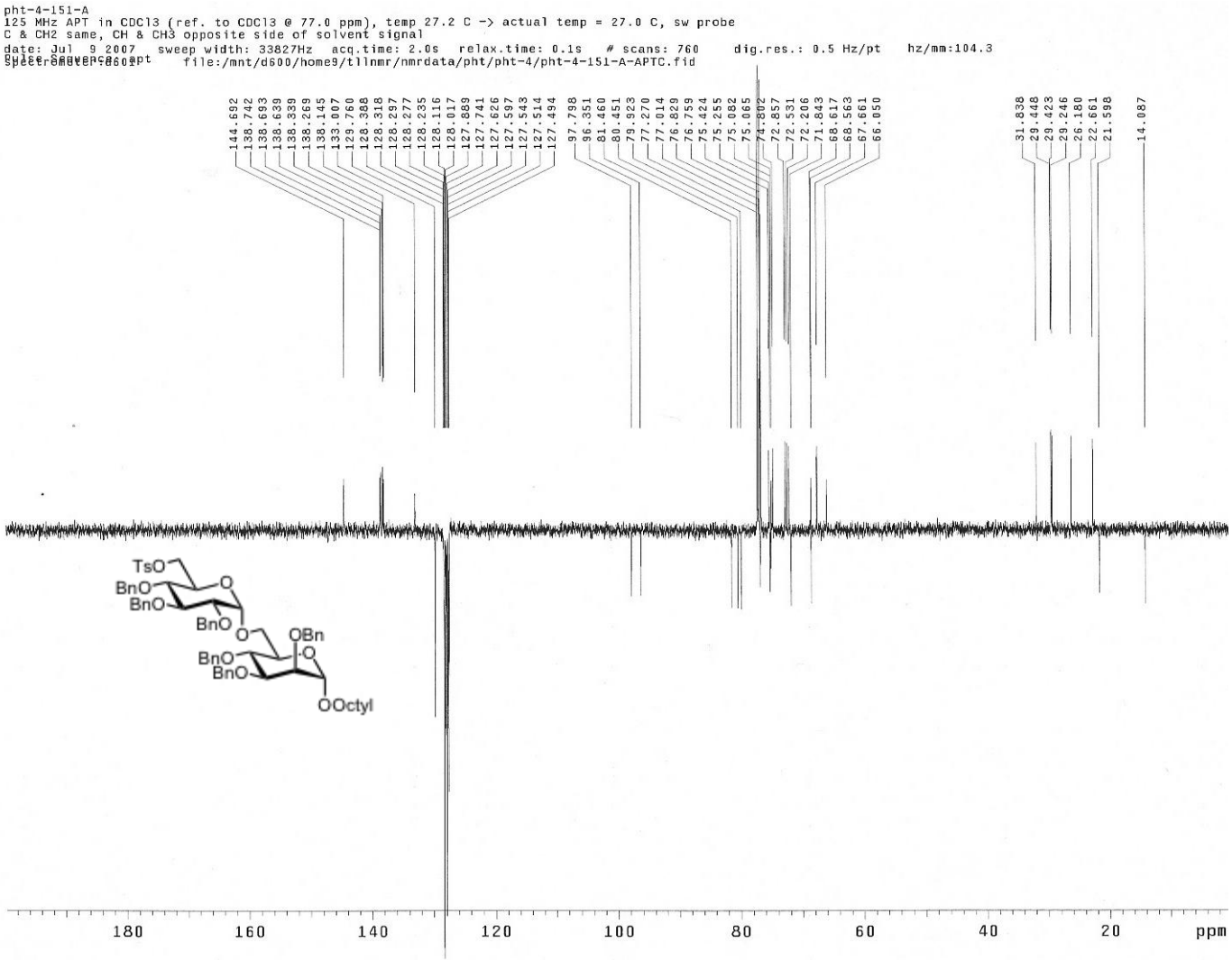
^{13}C NMR spectrum of **31**



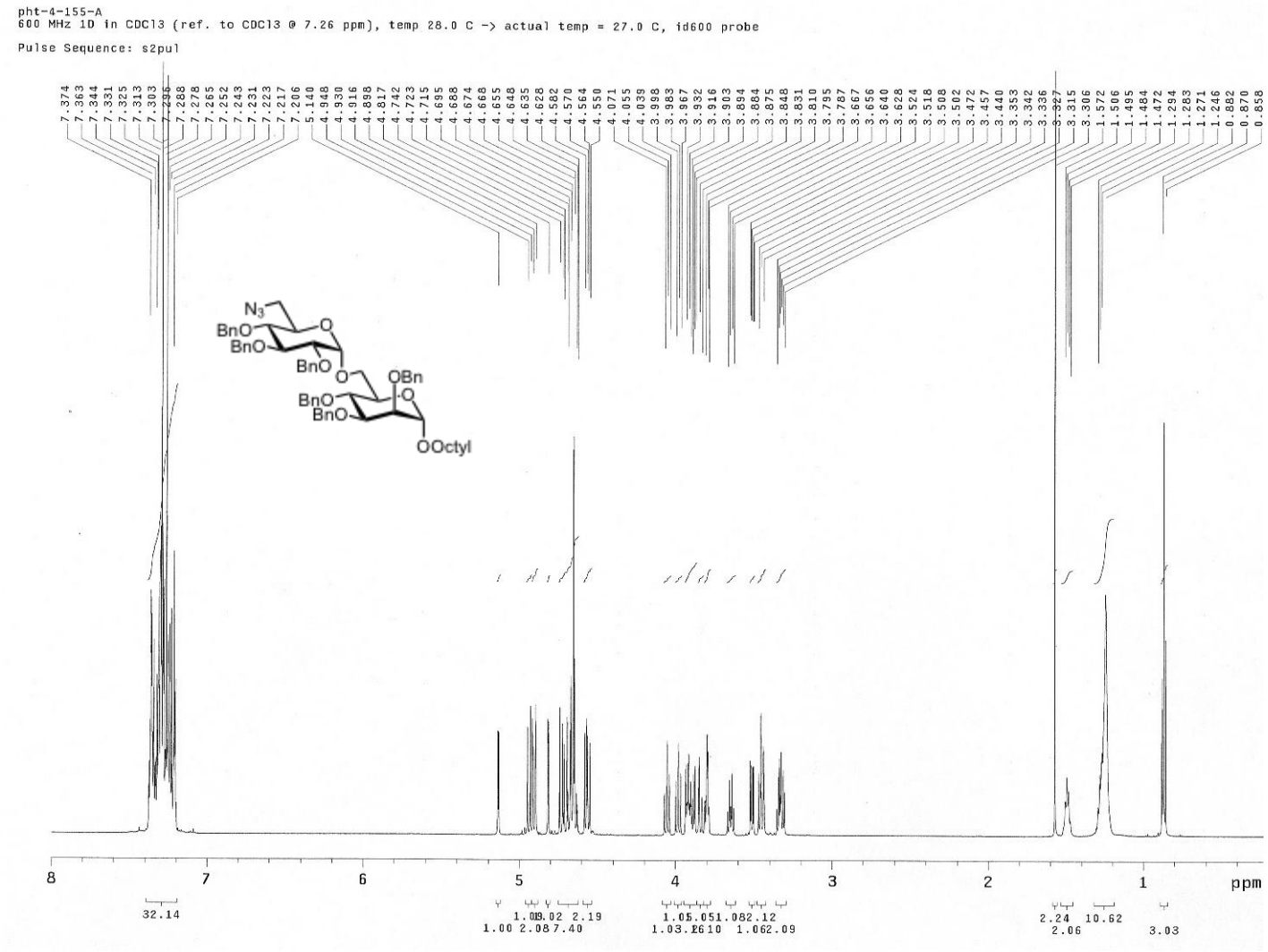
^{1}H NMR spectrum of **32**



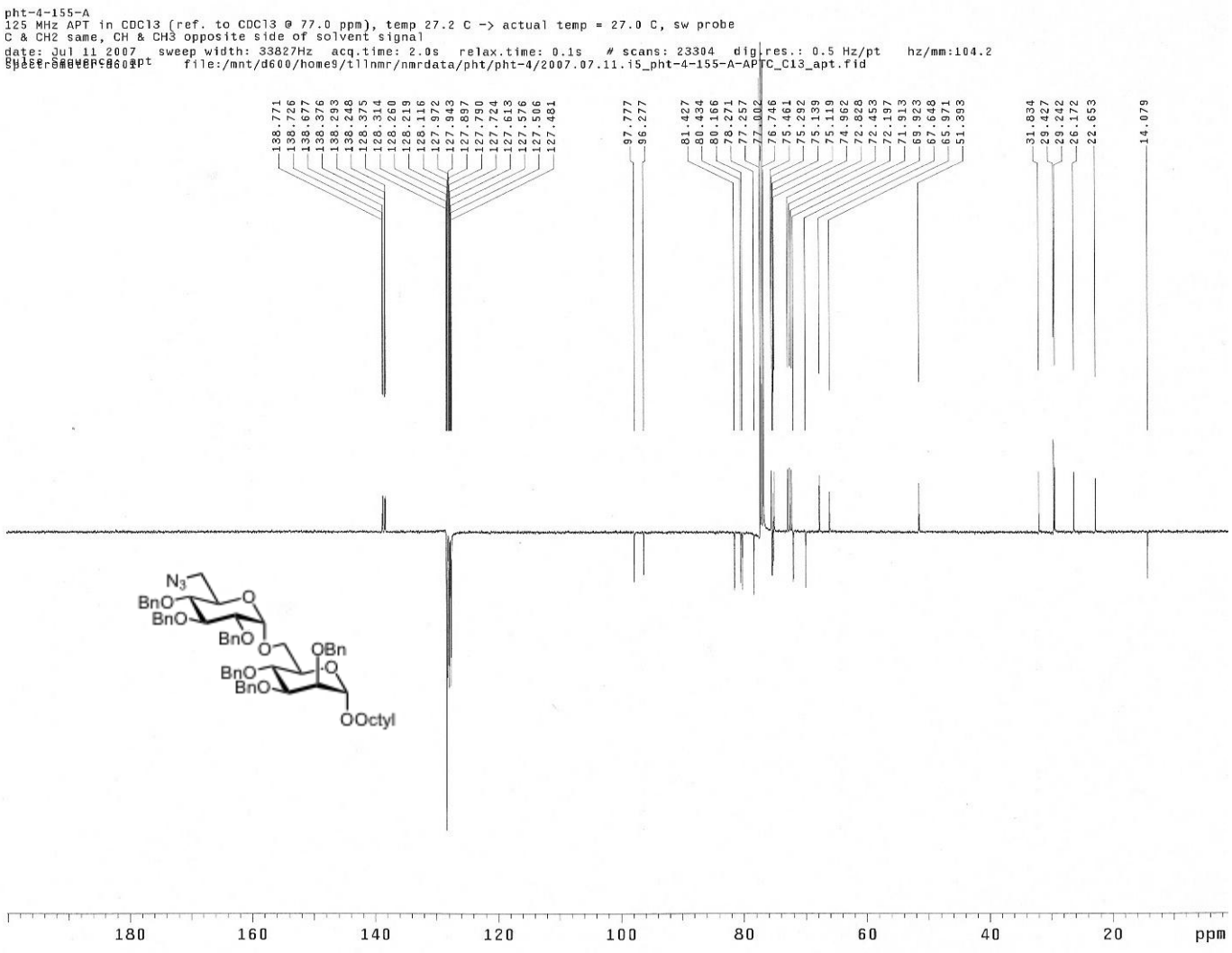
^{13}C NMR spectrum of **32**



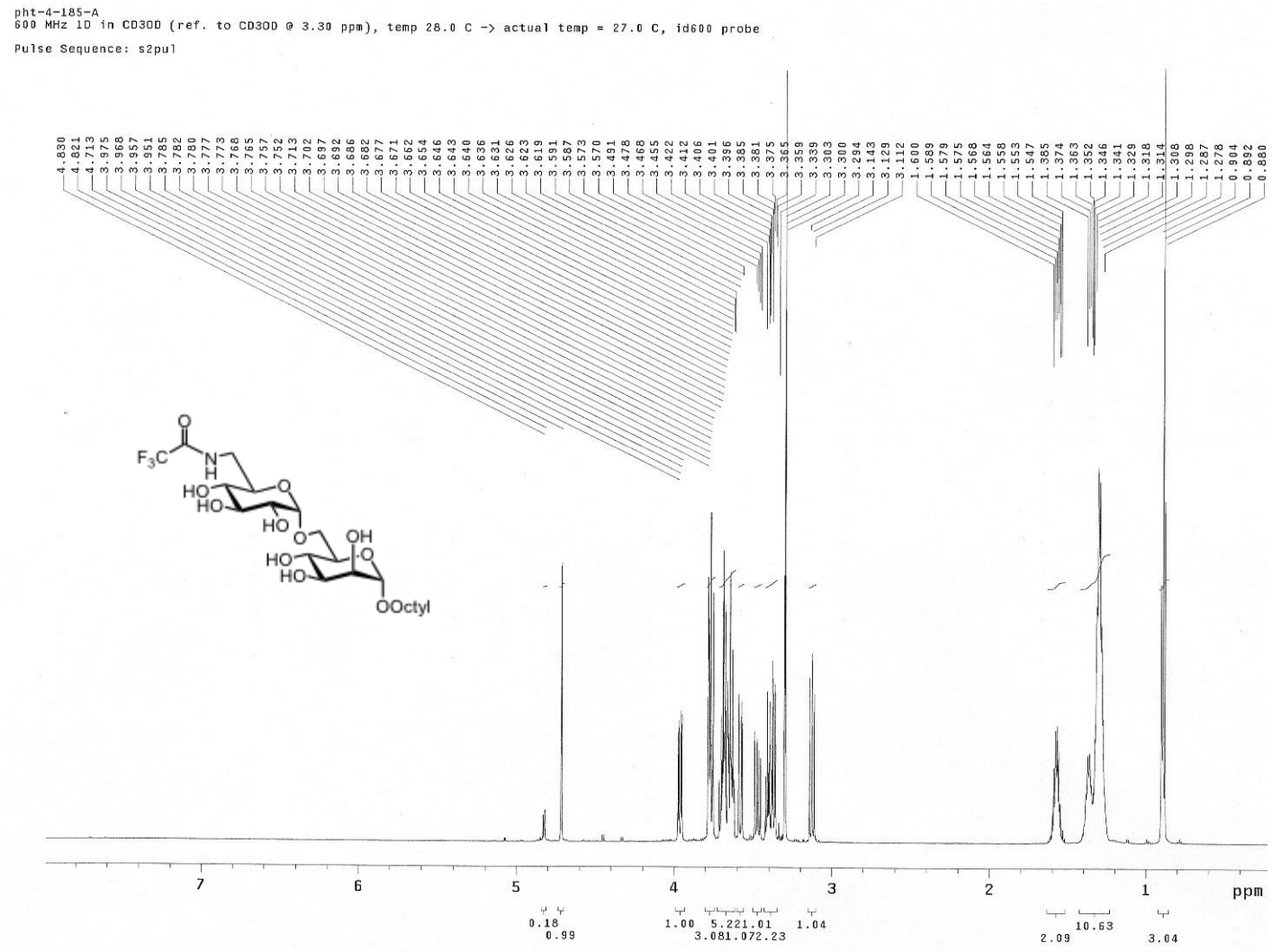
^{1}H NMR spectrum of **33**



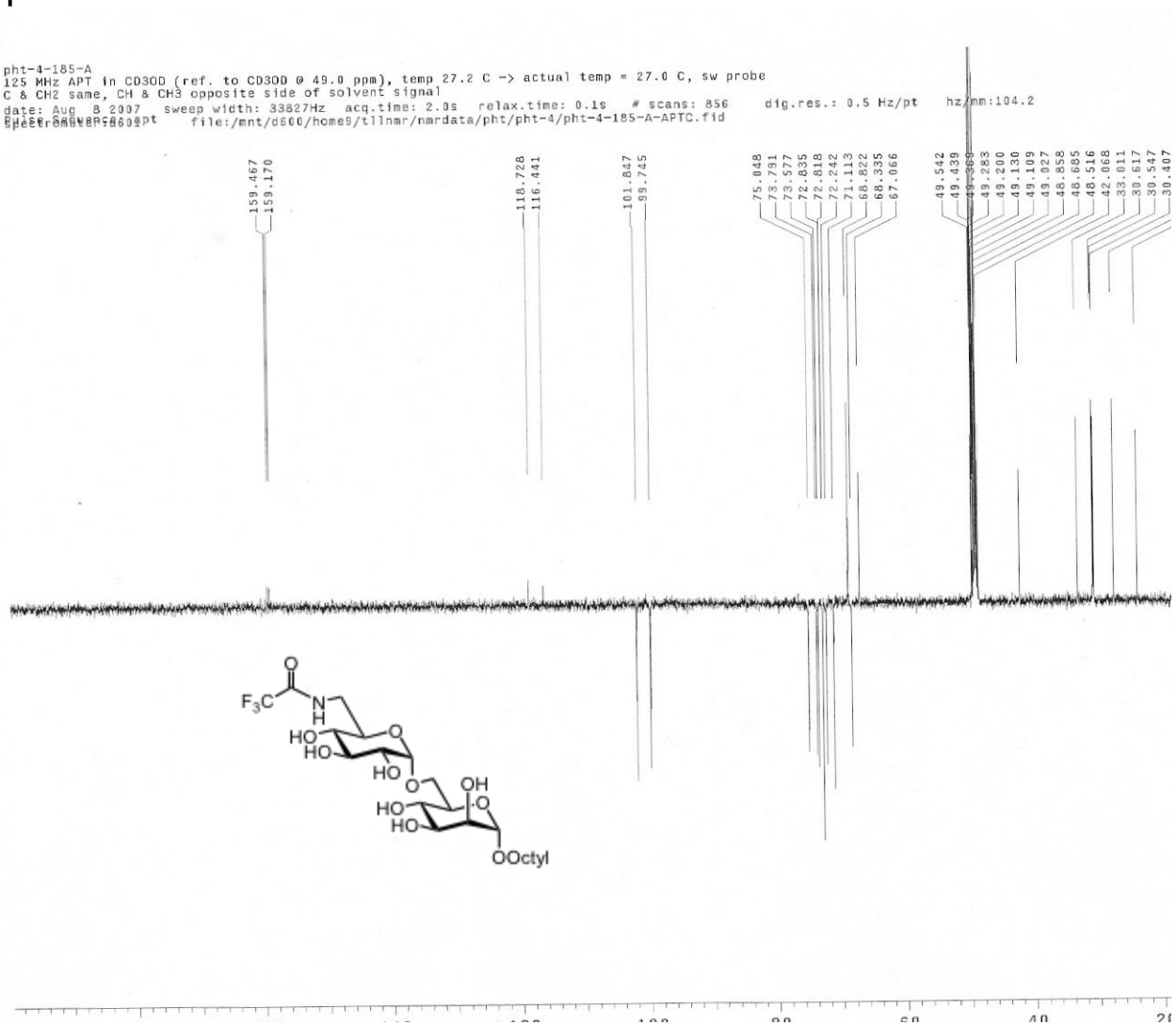
^{13}C NMR spectrum of **33**



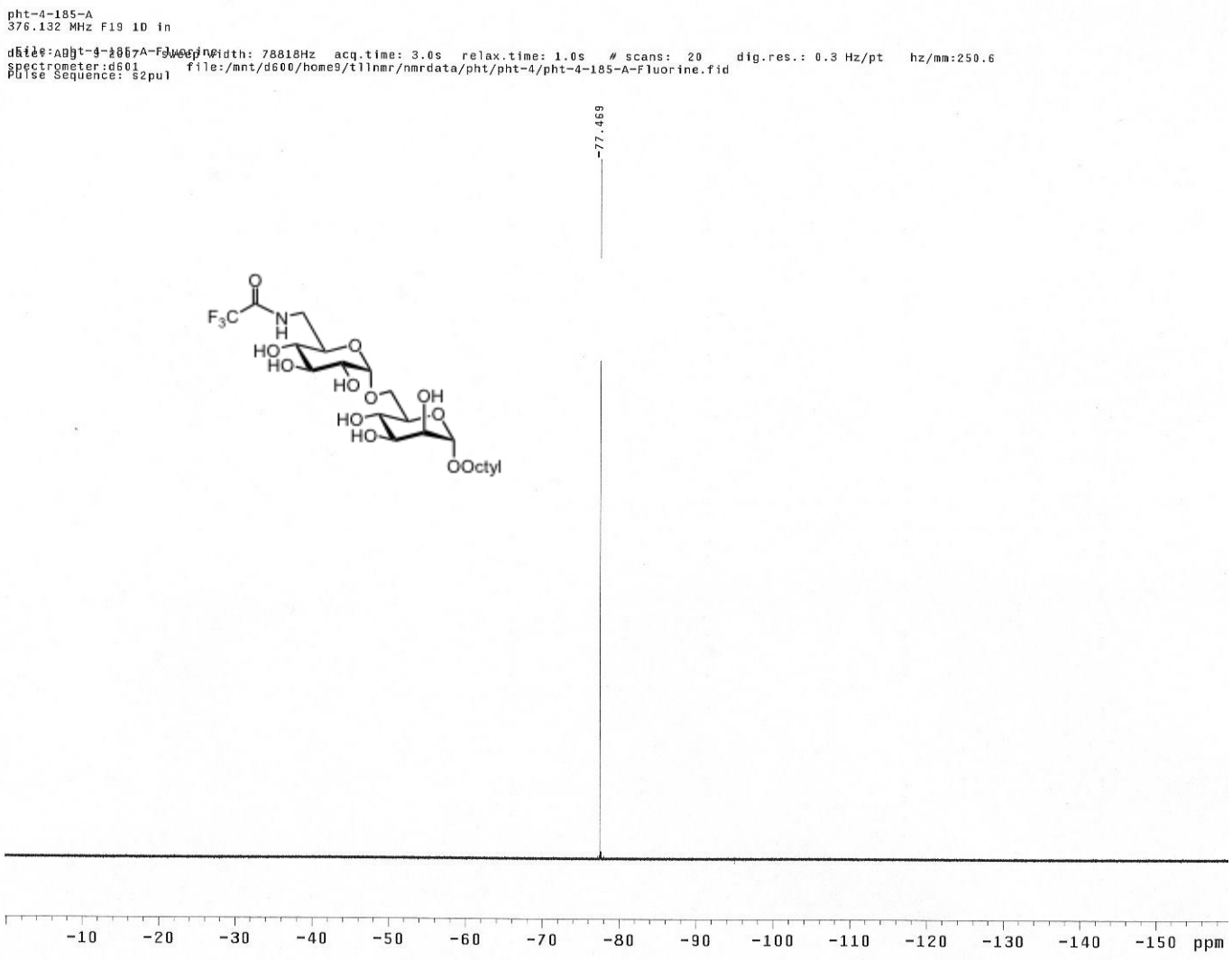
^{1}H NMR spectrum of **34**



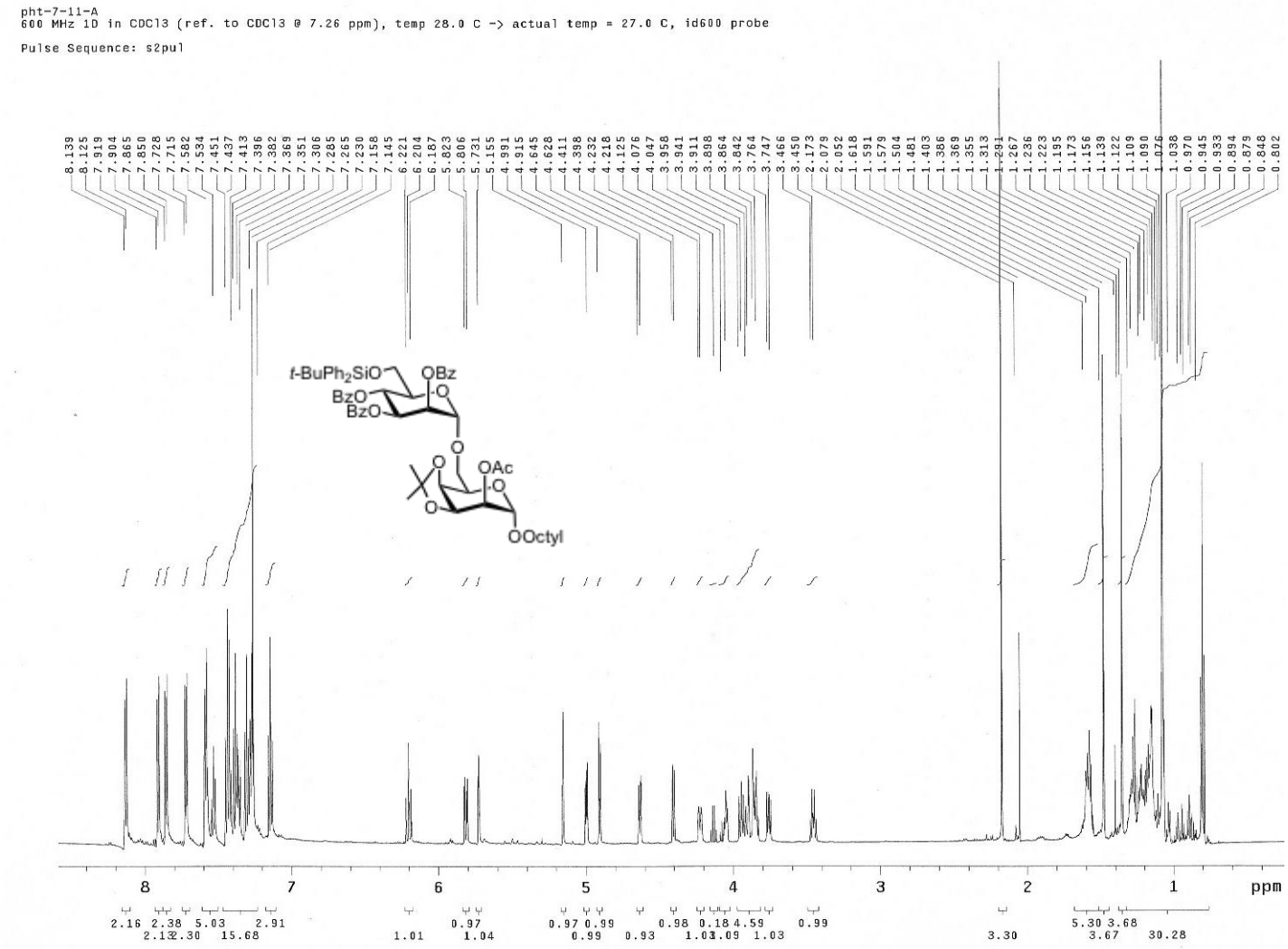
^{13}C NMR spectrum of **34**



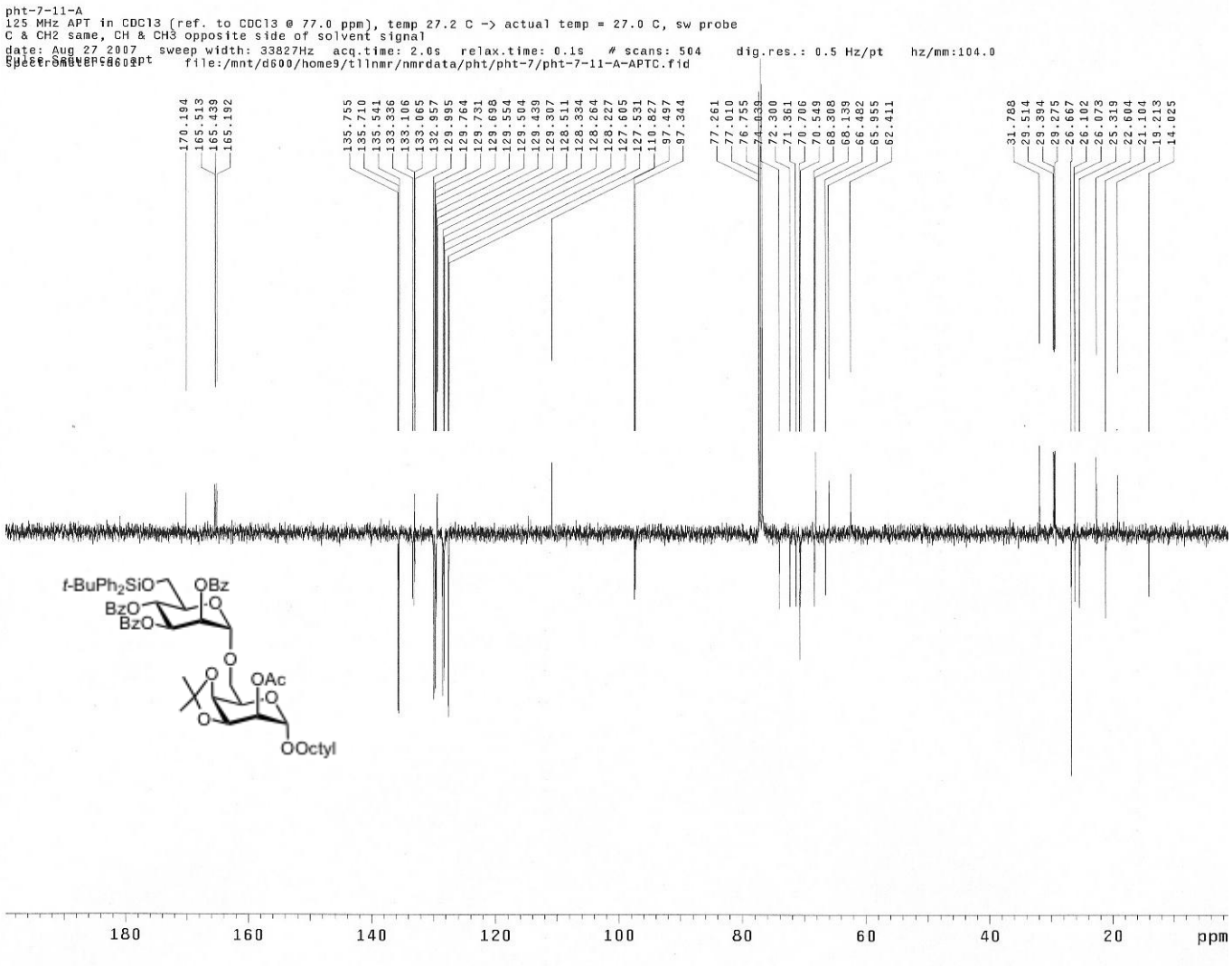
^{19}F NMR spectrum of **34**



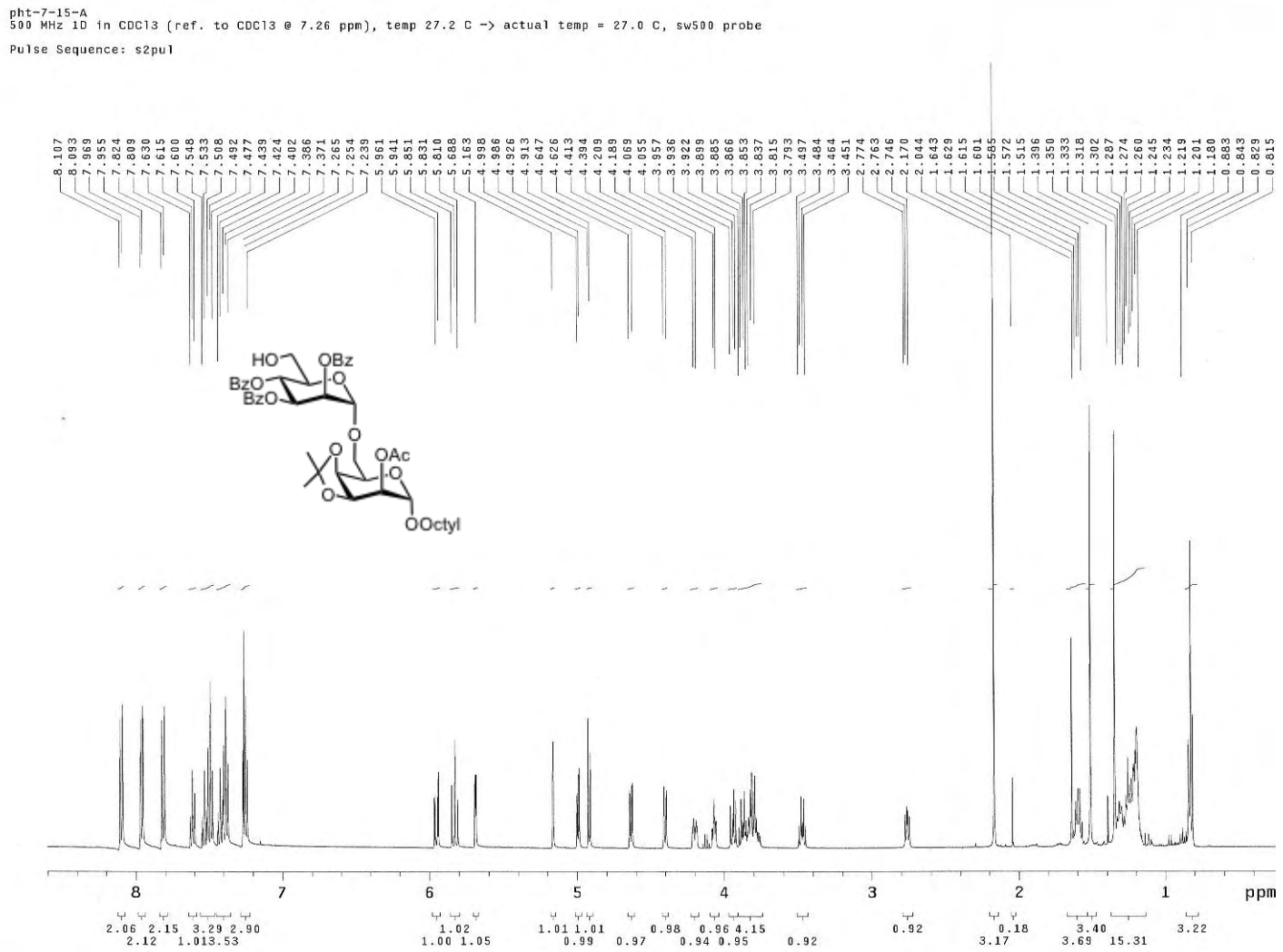
^{1}H NMR spectrum of **35**



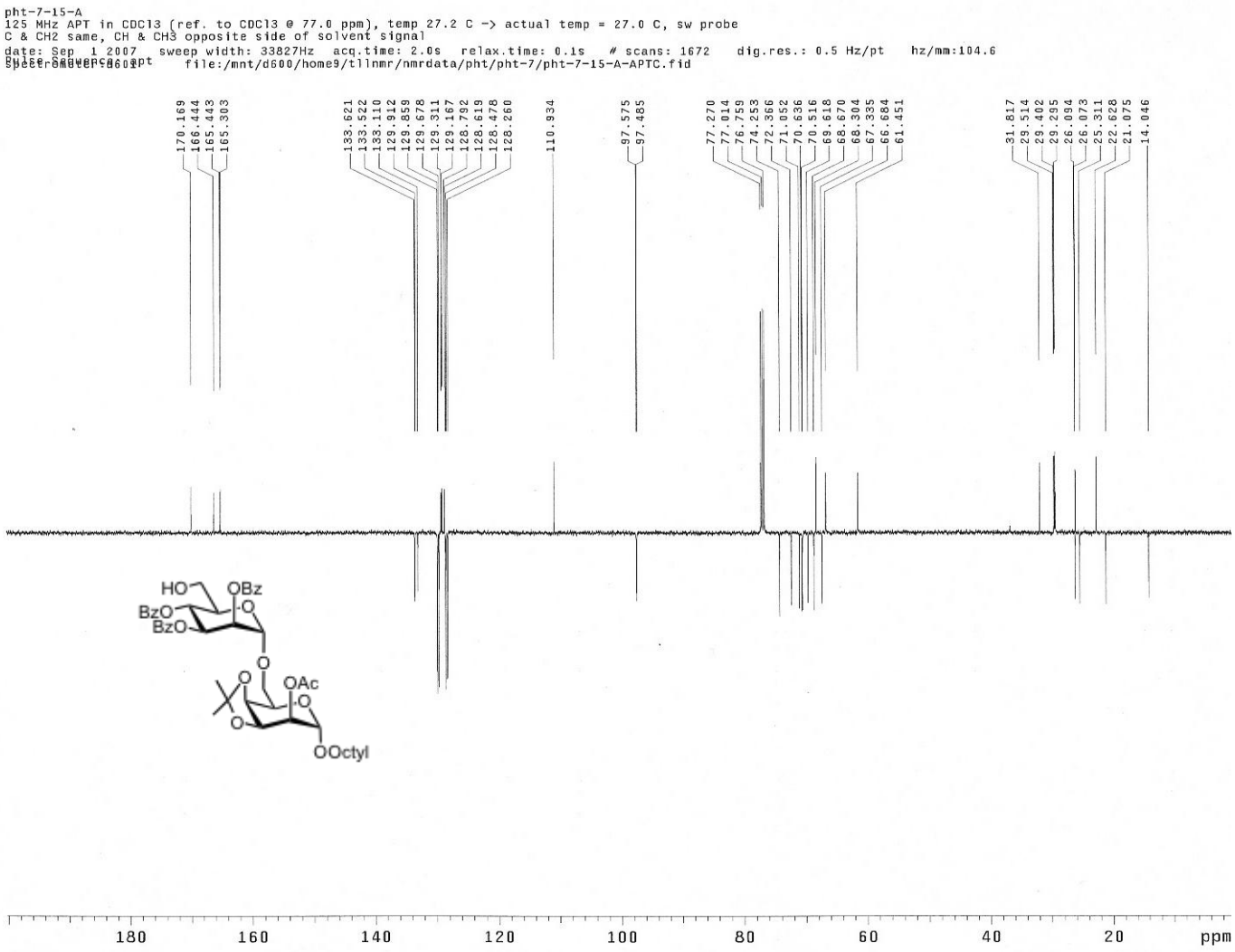
^{13}C NMR spectrum of **35**



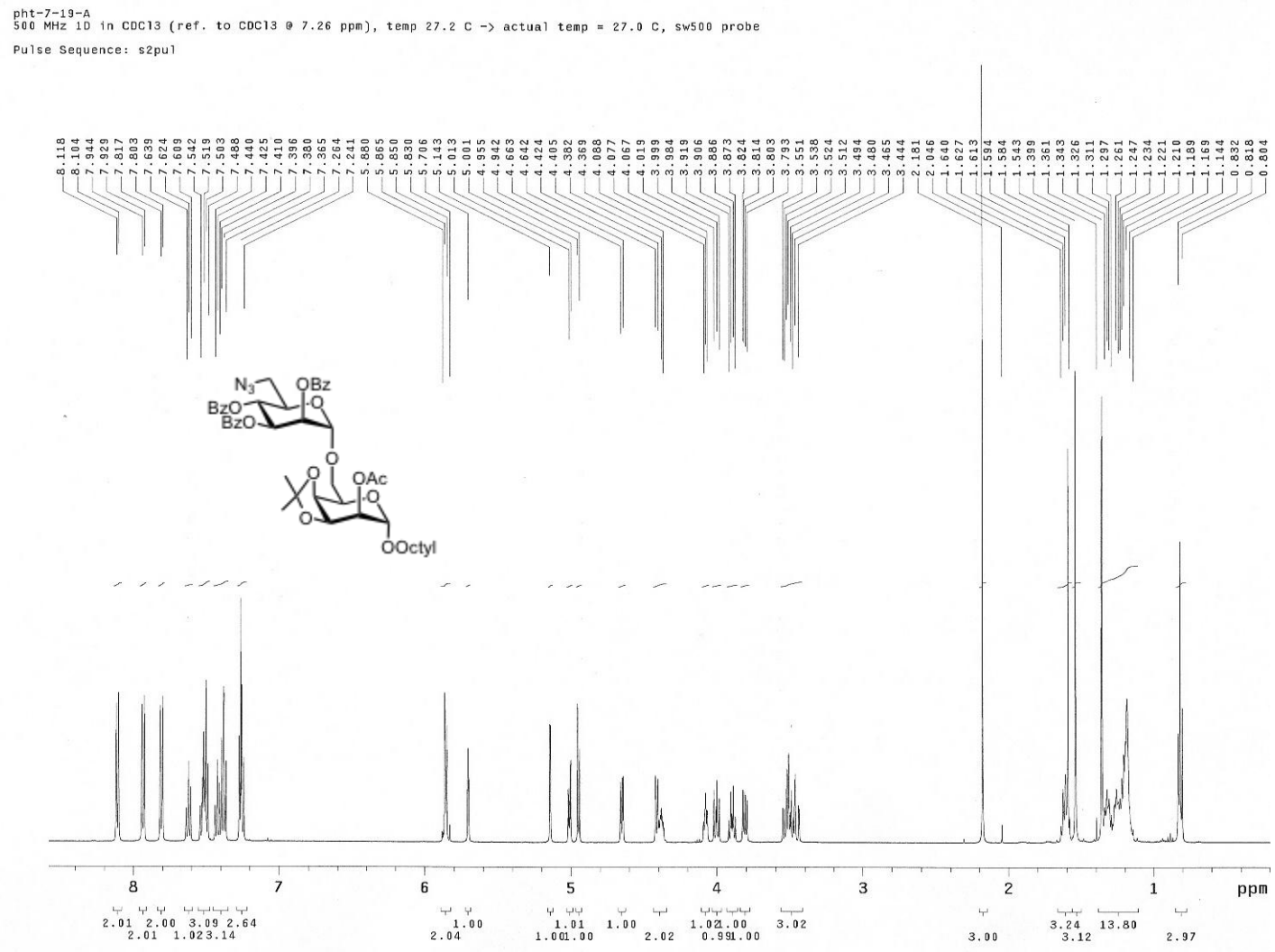
^{1}H NMR spectrum of **36**



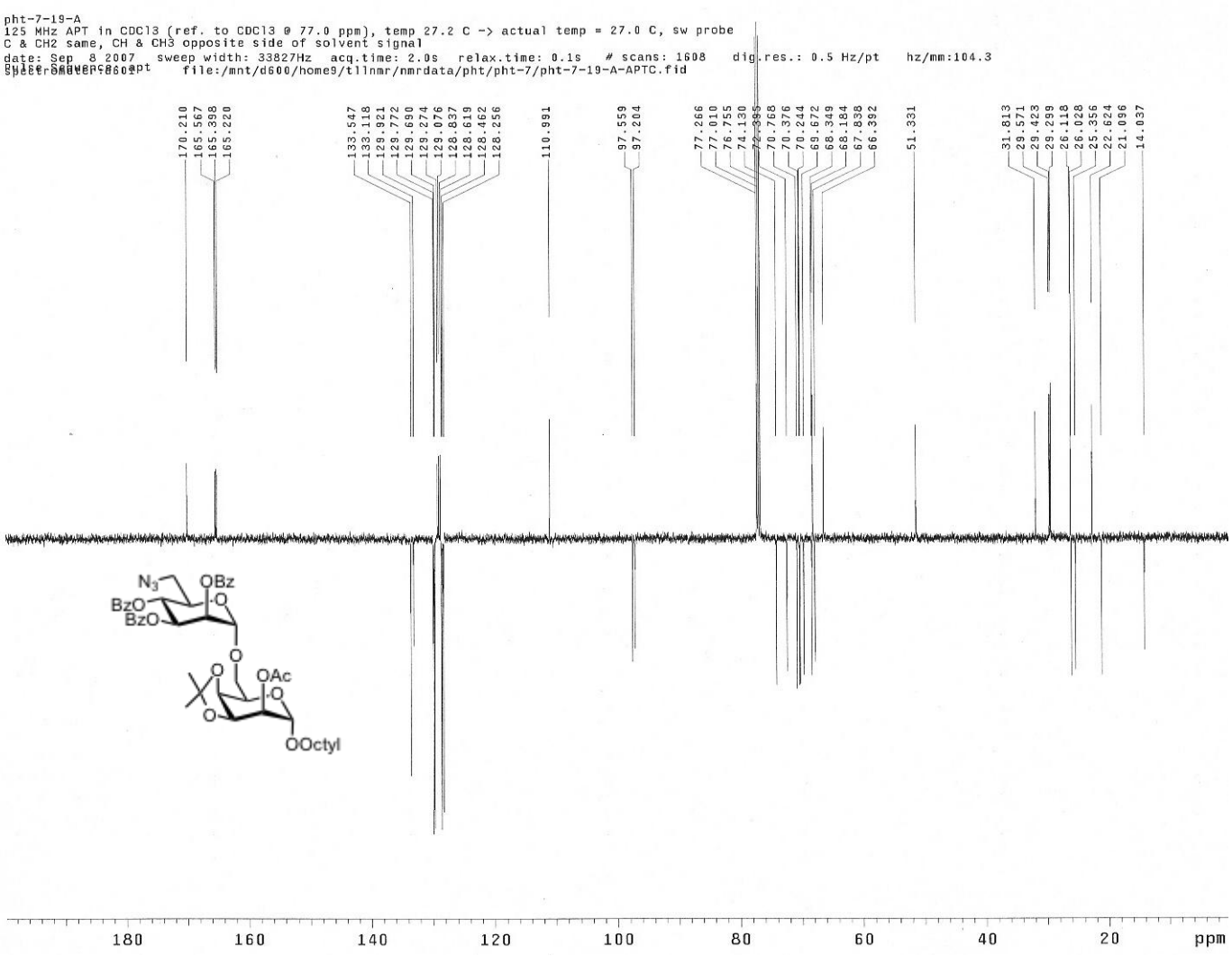
^{13}C NMR spectrum of **36**



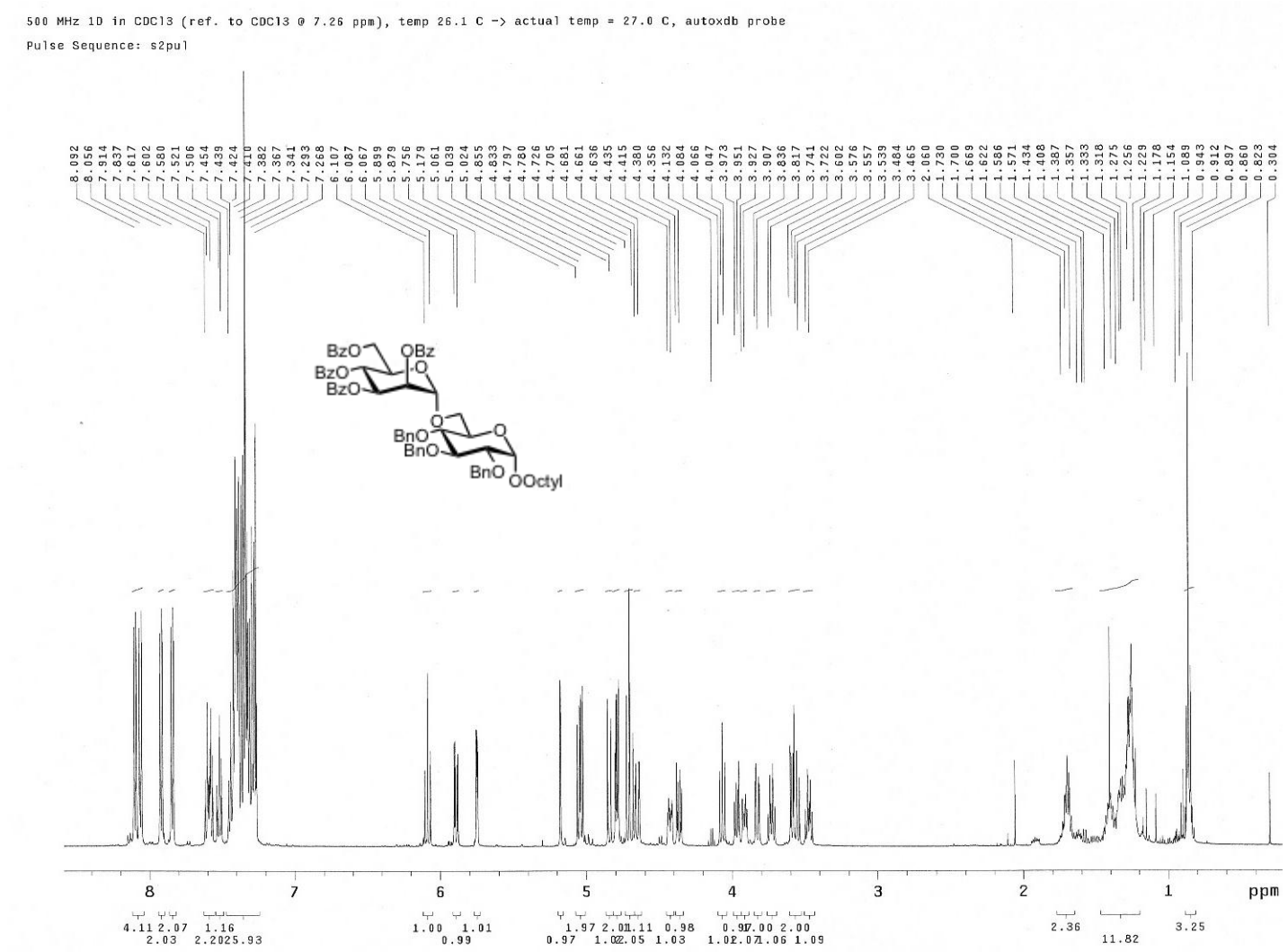
^{1}H NMR spectrum of **37**



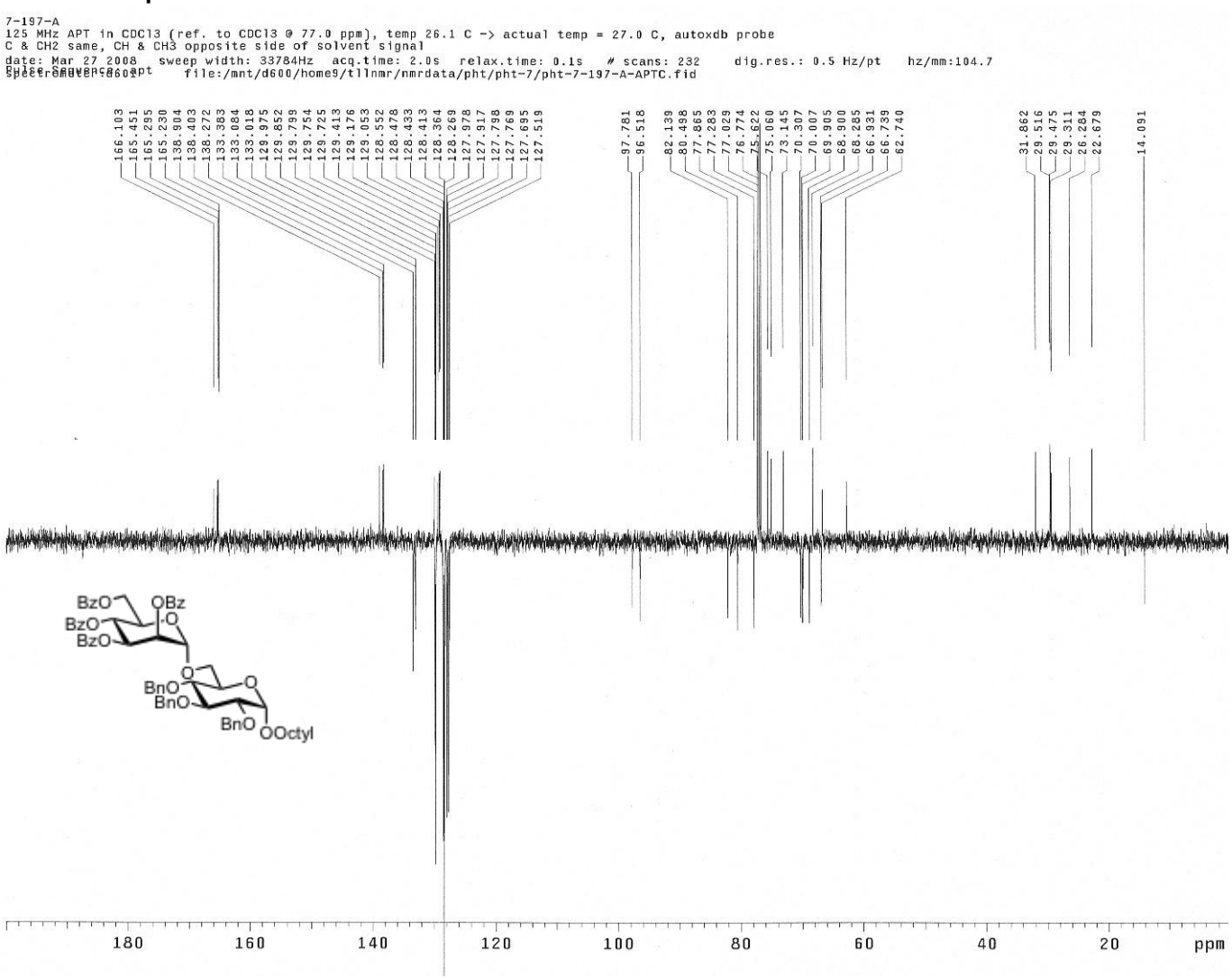
^{13}C NMR spectrum of **37**



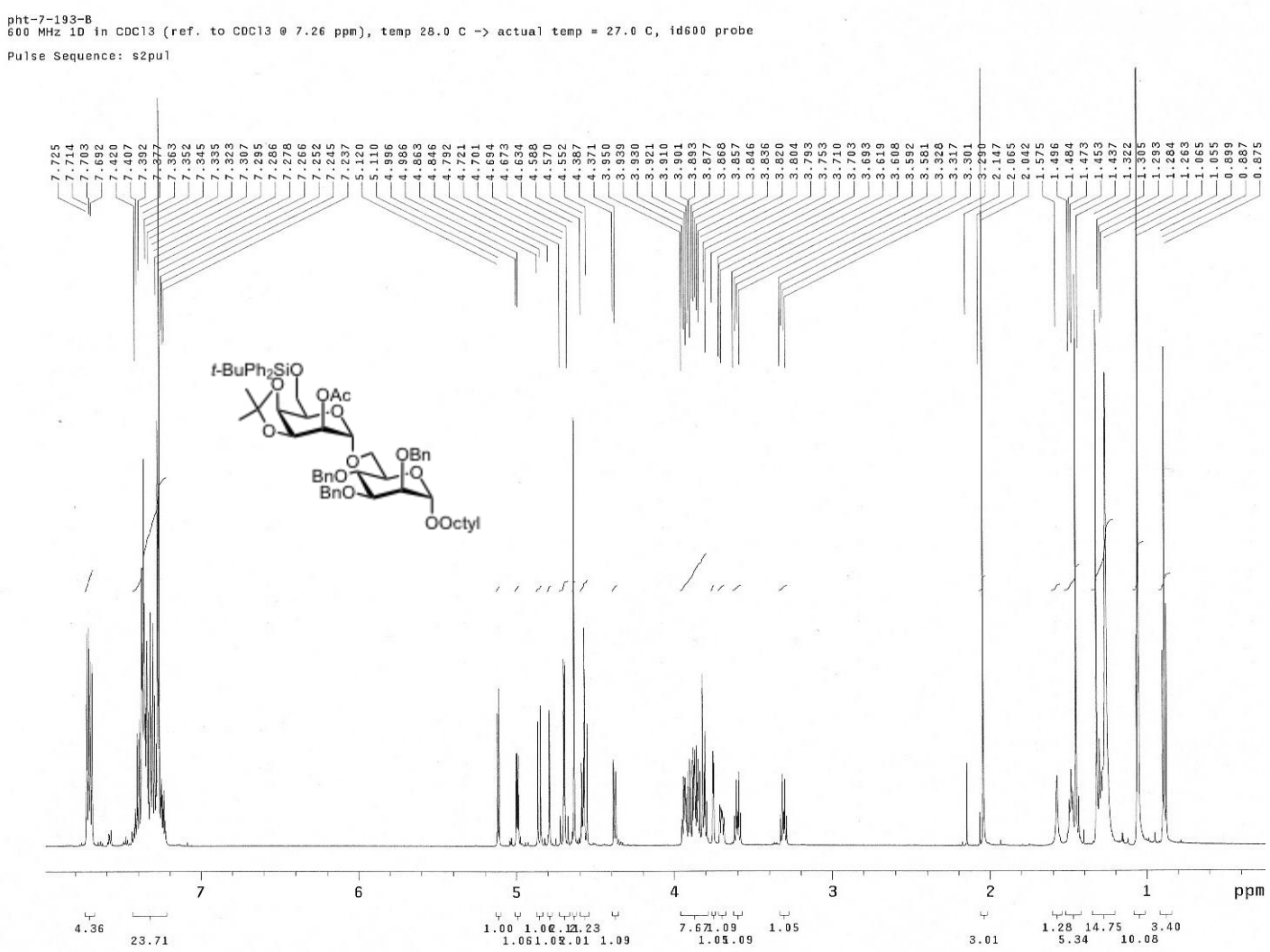
^{1}H NMR spectrum of **38**



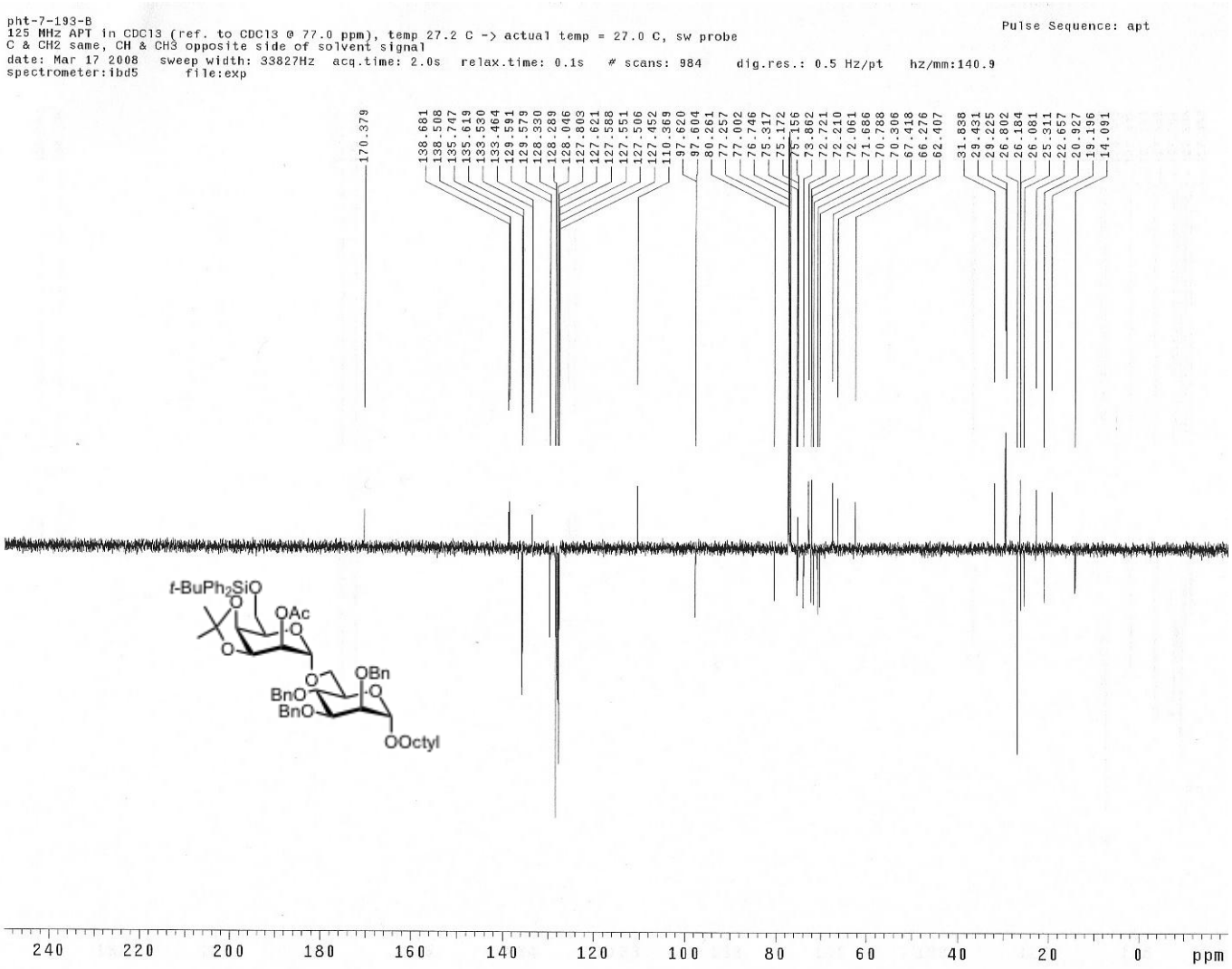
^{13}C NMR spectrum of **38**



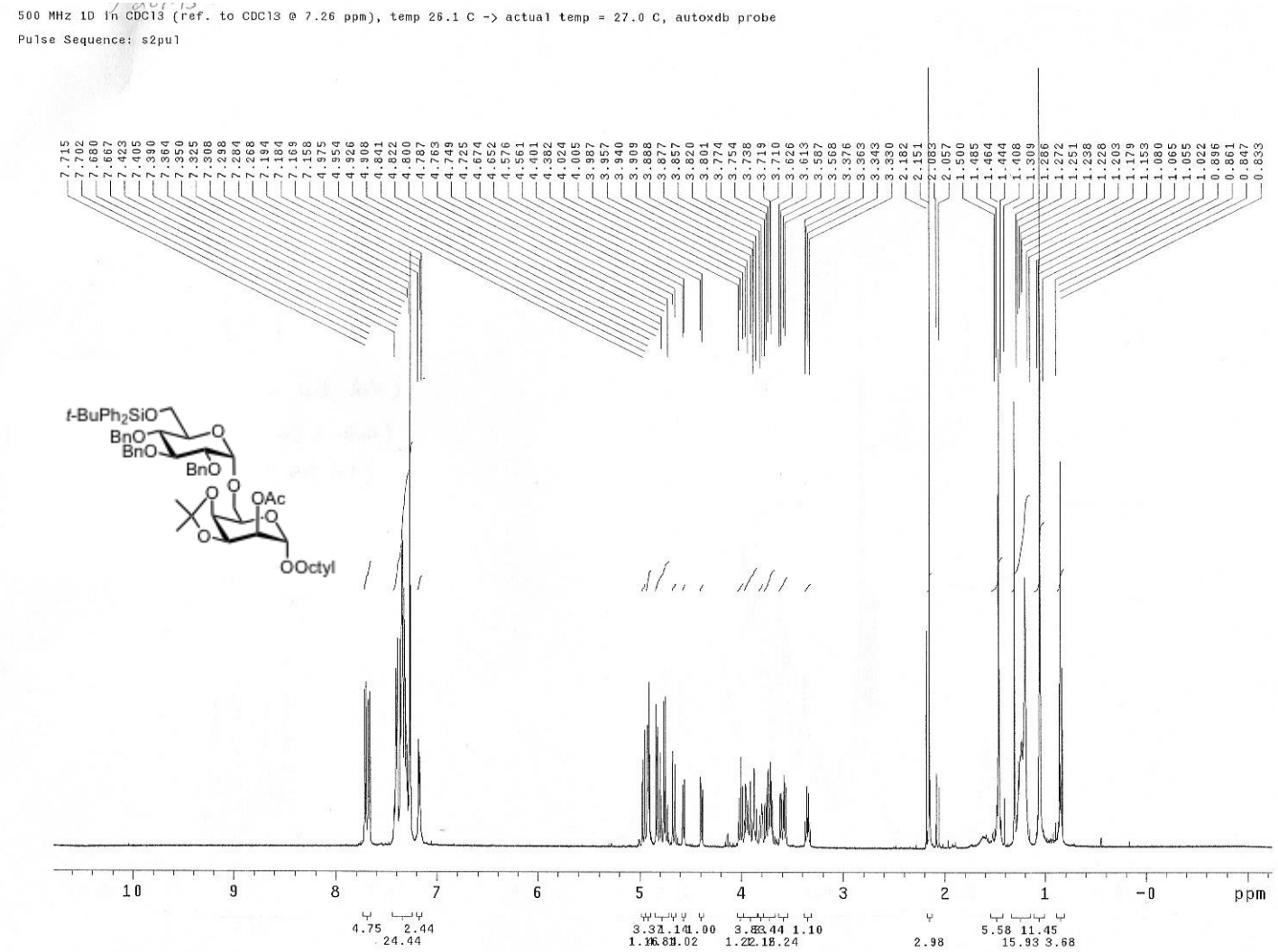
^{1}H NMR spectrum of **39**



^{13}C NMR spectrum of **39**



^{1}H NMR spectrum of **40**



^{13}C NMR spectrum of **40**