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Supporting Information

Stereoselective Construction of β-Mannopyranosides by Anomeric *O*-Alkylation: Synthesis of the Trisaccharide Core of *N*-linked Glycans

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Supporting Information

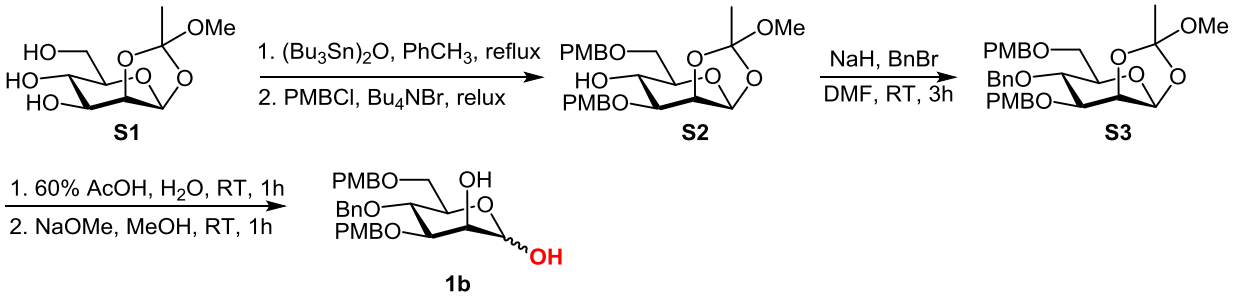
Table of Contents

General Information

Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on either Bruker 600 (^{1}H NMR-600 MHz; ^{13}C NMR 150 MHz) or INOVA 600 (^{1}H NMR-600 MHz; ^{13}C NMR-150 MHz) or Varian VXR-400 (^{1}H NMR 400 MHz; ^{13}C NMR 100 MHz) at ambient temperature with $CDCl_3$ as the solvent unless otherwise stated. Chemical shifts are reported in parts per million relative to residual protic solvent internal standard $CDCl_3$: ^{1}H NMR at δ 7.26, ^{13}C NMR at δ 77.36. Data for ^{1}H NMR are reported as follows: chemical shift, integration, multiplicity (app = apparent, par obsc = partially obscure, ovrlp = overlapping, s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, m = multiplet) and coupling constants in Hertz. All ^{13}C NMR spectra were recorded with complete proton decoupling. Infrared spectra were recorded on a PerkinElmer FT-IR spectrophotometer. High resolution mass spectra (HRMS) were obtained on a Waters Synapt High Definition Mass Spectrometer by electrospray ionization. Optical rotations were measured with Autopol-IV digital polarimeter; concentrations are expressed as g/100 mL.

All reagents and chemicals were purchased from Acros Organics, Sigma Aldrich, Fisher Scientific, Alfa Aesar, and Strem Chemicals and used without further purification. THF, methylene chloride, toluene, and diethyl ether were purified by passing through two packed columns of neutral alumina (Innovative Technology). Anhydrous DMF, and benzene were purchased from Acros Organics and Sigma-Aldrich and used without further drying. All reactions were carried out in oven-dried glassware under an argon atmosphere unless otherwise noted. Analytical thin layer chromatography (TLC) was performed using 0.25 mm silica gel 60-F plates. Preparative TLC plates were purchased from Sorbent Technologies (Cat#: 1617124, Silica G Prep TLC Plates, w/UV254, glass backed, 1000um, 20x20cm). Flash column chromatography was performed using 200-400 mesh silica gel (Scientific Absorbents, Inc.). Yields refer to chromatographically and spectroscopically pure materials, unless otherwise stated.

1. Preparation of lactol donors:



To a solution of known tri-ol **S1**[1] (4.72 g, 20.0 mmol) in benzene (55 mL) was added bis-tributyltin oxide (15 mL, 30 mmol). A dean-stark trap and reflux condenser were attached and the yellow solution was refluxed overnight. The resulting mixture was cooled to room temperature. 4-methoxybenzyl chloride (8.1 mL, 60 mmol) and tetrabutylammonium iodide (7.4g, 20 mmol) were added and the solution was stirred at 90^{o}C for 14 hours without the dean-stark trap. After cooling to room temperature, acetonitrile (200 mL) was added, and the mixture was washed with hexanes (2 X 100 mL), dried (Na_2SO_4), filtered and concentrated. Purification by silica gel column chromatography (hexanes: EtOAc = 10:1 to 1:1) furnished 8.56 g (89% yield) of **S2**.

To a solution of alcohol **S2** (1.26 g, 2.66 mmol) in 3.0 mL *N,N*-dimethylformamide cooled at 0^{o}C was added sodium hydride (215 mg, 5.32 mmol) portion wise. The resulting mixture was stirred at 0^{o}C for 1 hour before benzyl bromide (0.65 mL, 5.32 mmol) was added. The reaction mixture was warmed up and stirred at ambient temperature for 3 h. The resulting mixture was diluted with EtOAc (50 mL), washed with water (4x50 mL), dried over anhydrous sodium sulfate, filtered and concentrated. The resulting crude residue was recrystallized with hexanes-EtOAc to afford orthoester **S3** (1.12g, 75%) which is characterized below:

$[\alpha]_D^{21}$ = 48.5° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 - 7.33 (m, 5H, aromatic), 7.20 - 7.25 (m, 4H, aromatic), 6.83 - 6.88 (m, 4H, aromatic), 5.33 (d, J = 2.57 Hz, 1H, H-1), 4.87 (d, J = 10.64 Hz, 1H, benzylic), 4.67 - 4.75 (m, 2H, benzylic), 4.51 - 4.59 (m, 2H, benzylic), 4.45 - 4.49 (m, 1H, benzylic), 4.35 (dd, J = 2.66, 3.94 Hz, 1H, H-2), 3.87 (t, J = 9.45 Hz, 1H, H-4), 3.79 (d, J = 4.40 Hz, 6H, OCH_3), 3.65 - 3.71 (m, 3H), 3.37 - 3.42 (m, 1H, H-5), 3.28 (s, 3H, orthoester OCH_3), 1.73 (s, 3H, orthoester CH_3)

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 159.5, 138.6, 130.6, 130.2, 130.0, 129.6, 128.7, 128.4, 128.1, 124.3, 114.2, 114.0, 97.9, 78.9, 75.6, 74.6, 74.5, 73.3, 72.3, 69.0, 55.6, 55.6, 50.1, 24.8

FT-IR (thin film): 2910, 1612, 1514, 1455, 1383, 1302, 1247, 1206, 1173, 1010, 1046, cm^{-1}.

ESIHRMS $[C_{32}H_{38}O_9 + Na]^+$ calculated 589.2414, found 589.2413.

S3 (1.12g, 1.98 mmol) was suspended in 60% aq. acetic acid (20 mL) and stirred at RT under Argon for 2 h. A colorless solution formed, which was diluted with EtOAc (100

[1] Liu, L.; Johnstone, K.; Fairweather, J.; Ferro, V. *Aust. J. Chem.* **2009**, *62*, 546.

mL), washed with water (3x100 mL) and saturated aq. $NaHCO_3$ (2x100 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to give colorless oil. This oil was dissolved in MeOH (20 mL) and 5.4 M sodium methoxide solution in methanol (0.35 mL, 1.80 mmol) was added. The mixture was stirred at RT for 2 h. The reaction was neutralized by the addition of Amberlyst IR-120 (H^+), stirred for 30 min, filtered and concentrated. The residue was recrystallized with hexanes-EtOAc to give 4-*O*-benzyl-3,6-di-*O*-(4-methoxybenzyl)-D-mannopyranose **1b** as a white solid that was a mixture of *α*- and *β*-anomers (725 mg, 72 %, *α*/*β* = 2.3/1.0) which are characterized below:

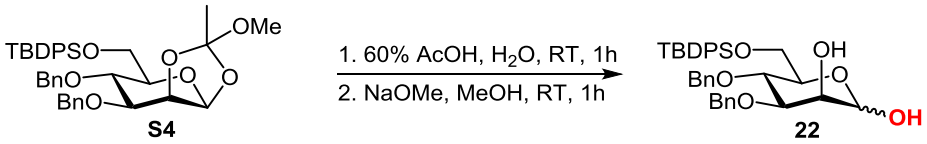
$[\alpha]_D^{21}$ = 20.8° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 - 7.34 (m, 7H, aromatic), 7.24 (d, *J* = 8.62 Hz, 2H, aromatic), 7.14 - 7.18 (m, 3H, aromatic), 6.84 (d, *J* = 8.80 Hz, 3H, aromatic), 6.86 (d, *J* = 8.80 Hz, 3H, aromatic), 5.25 - 5.28 (m, 1H, (H-1) α anomer), 4.78 - 4.84 (m, 1H, benzylic), 4.49 - 4.67 (m, 5H), 4.39 - 4.47 (m, 3H), 4.03 (ddd, *J* = 1.93, 5.96, 9.90 Hz, 1H,), 3.97 - 4.01 (m, 1H, (H-2) α anomer), 3.88 - 3.94 (m, 2H, (H-3) α anomer), 3.74 - 3.82 (m, 8H), 3.58 - 3.72 (m, 5H), 2.62 (d, *J* = 2.57 Hz, 1H, (O1-H) α anomer), 1.91 (br. s., 1H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 159.7, 159.6, 159.5, 138.6, 138.5, 130.3, 130.2, 130.1, 130.1, 129.9, 129.8, 128.6, 128.6, 128.2, 128.2, 128.0, 128.0, 114.2, 114.1, 114.0, 94.6, 94.2, 81.6, 79.7, 75.3, 75.3, 74.9, 74.8, 74.0, 73.4, 73.2, 71.9, 71.6, 71.0, 69.2, 69.2, 68.8, 68.6, 55.6, 55.5

FT-IR (thin film): 3412, 2909, 1612, 1513, 1455, 1365, 1247, 1214, 1066, 1034, 749 cm^{-1}.

ESIHRMS $[C_{29}H_{34}O_8 + Na]^+$ calculated 533.2146, found 533.2148.



Known compound **S4**[2] (276mg, 0.42mmol) was suspended in 60 % aq. acetic acid (4.0 mL) and stirred at RT under Argon for 2 h. A colorless solution formed, which as diluted with EtOAc (20 mL), washed with water (3x20 mL) and saturated aq. $NaHCO_3$ (2x20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated to give colorless oil. This oil was dissolved in MeOH (4.0 mL) and 5.4 M sodium methoxide solution in methanol (75 µL, 0.4 mmol) was added. The mixture was stirred at RT for 2 h. The reaction was neutralized by the addition of Amberlyst IR-120 (H^+), stirred for 30 min, filtered and concentrated. The residue was purified by silica gel column chromatography (hexanes: EtOAc = 5:1 to 2:1) to give desired product 3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-D-mannopyranose **22** as a mixture of *α*- and *β*-anomers (151 mg, 60 %, *α*/*β* = 2/1) which are characterized below:

$[\alpha]_D^{21}$ = -102.5° (*c* = 0.2, $CHCl_3$).

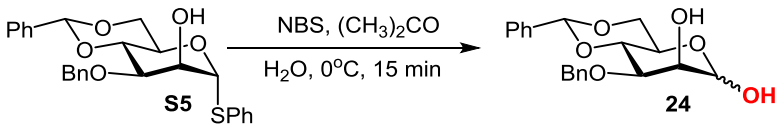
[2] Mayer, T. G.; Schmidt, R. R. *European J. Org. Chem.* **1999**, *1999*, 1153.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 - 7.77 (m, 3H, aromatic), 7.67 - 7.71 (m, 3H, aromatic), 7.27 - 7.44 (m, 23H, aromatic), 7.18 - 7.23 (m, 3H, aromatic), 5.27 - 5.30 (m, 1H, (H-1) α anomer), 4.87 - 4.92 (m, 2H, benzylic), 4.66 - 4.76 (m, 4H), 4.64 (d, *J* = 10.82 Hz, 1H), 4.07 (br. s., 1H, (H-2) α anomer), 3.86 - 4.04 (m, 7H), 3.60 - 3.68 (m, 2H), 3.29 - 3.34 (m, 1H), 2.40 (d, *J* = 3.30 Hz, 2H), 1.07 (s, 5H), 1.06 (s, 9H, $C(CH_3)_3$ α anomer)

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.8, 138.3, 136.3, 136.3, 136.0, 134.2, 133.7, 130.0, 130.0, 129.9, 129.0, 128.9, 128.8, 128.7, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 127.9, 94.4, 94.2, 82.0, 80.0, 76.0, 75.5, 74.4, 73.9, 72.8, 72.5, 72.3, 69.3, 68.9, 63.5, 63.2, 27.2, 27.2, 19.7, 19.7

FT-IR (thin film): 3441, 3073, 3036, 2930, 2859, 1456, 1430, 1103, 740, 700, 504 cm^{-1}.

ESIHRMS $[C_{36}H_{42}O_6Si + Na]^+$ calculated 621.2648, found 621.2668.



To a solution of known compound **S5**[3] (0.9 g, 2.0 mmol) in 30 mL acetone and 2.0 mL water cooled at 0℃ was added *N*-bromosuccinimide (1.1 g, 6.0 mmol). The resulting mixture was stirred at 0°C for 15 minutes. Saturated sodium thiosulfate (50 mL) was added and acetone was removed under reduced pressure. The remaining aqueous mixture was extracted with ethyl acetate (3×50 mL). Combined extracts were washed with brine (50mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The crude residue was purified by flash column chromatography (hexanes: EtOAc = 2:1 to 1:1) to furnish 0.6 g of 3-*O*-benzyl-4,6-*O*-benzylidene-D-mannopyranose **24** as a mixture of *α*- and *β*-anomers (83% yield, *α*/*β* = 1.6/1.0) which are characterized below:

$[\alpha]_D^{21}$ = -61.2° (*c* = 0.2, $CHCl_3$).

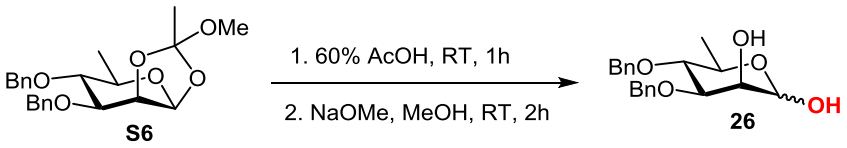
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (ddd, *J* = 1.74, 5.46, 7.29 Hz, 3H, aromatic), 7.28 - 7.41 (m, 13H, aromatic), 5.62 (s, 1H, benzylidene, α anomer), 5.60 (s, 0.6H, benzylidene, β anomer), 5.29 (dd, *J* = 1.47, 3.48 Hz, 1H, (H-1) α anomer), 4.85 - 4.93 (m, 1.6H, benzylic), 4.80 (d, *J* = 11.92 Hz, 0.6H, (H-1) β anomer), 4.70 - 4.77 (m, 1.6H, benzylic), 4.35 (dd, *J* = 5.04, 10.55 Hz, 1H), 4.26 (dd, *J* = 4.77, 10.27 Hz, 1H, (H-3) α anomer), 3.97 - 4.15 (m, 6H), 3.81 - 3.88 (m, 2H), 3.72 (dd, *J* = 3.48, 9.54 Hz, 1H), 3.37 (dt, *J* = 4.95, 9.72 Hz, 1H, (H-5) α anomer), 2.78 - 2.82 (m, 0.6H, (O2-H) β anomer), 2.67 - 2.73 (m, 2H, (O1-H, O2-H) α anomer)

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 138.0, 137.8, 137.7, 129.4, 129.3, 128.9, 128.8, 128.6, 128.6, 128.5, 128.3, 128.3, 128.2, 126.4, 126.4, 101.9, 101.8, 95.1, 94.7, 79.2, 78.7, 77.3, 75.5, 73.5, 70.6, 70.4, 69.2, 68.9, 66.6, 63.8.

FT-IR (thin film): 3412, 2931, 2872, 1457, 1374, 1215, 1094, 754, 698 cm^{-1}.

ESIHRMS $[C_{20}H_{22}O_6 + H]^+$ calculated 359.1495, found 359.1497.

[3] Adero, P. O.; Furukawa, T.; Huang, M.; Mukherjee, D.; Retailleau, P.; Bohé, L.; Crich, D. *J. Am. Chem. Soc.* **2015**, *137*, 10336.



S6[4] (2.31g, 5.78mmol) was suspended in 60 % aq. acetic acid (60 mL) and stirred at RT under Argon for 2 h. A colorless solution formed, which was diluted with EtOAc (100 mL), washed with water (3x100 mL) and saturated aq. $NaHCO_3$ (2x100 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated to give colorless oil. This oil was dissolved in MeOH (60 mL) and 5.4 M sodium methoxide solution in methanol (1.2, 5.78 mmol) was added. The mixture was stirred at RT for 2 h. The reaction was neutralized by the addition of Amberlyst IR-120 (H^+), stirred for 30 min, filtered and concentrated. The residue was recrystallized with hexanes-EtOAc to afford desired product 3,4-di-*O*-benzyl-D-rhamnose **26** as a mixture of *α*- and *β*-anomers (1.18 g, 60 %, *α*/*β* = 1.2/1.0) which are characterized below:

$[\alpha]_D^{21}$ = -4.4° (*c* = 1.0, $CHCl_3$).

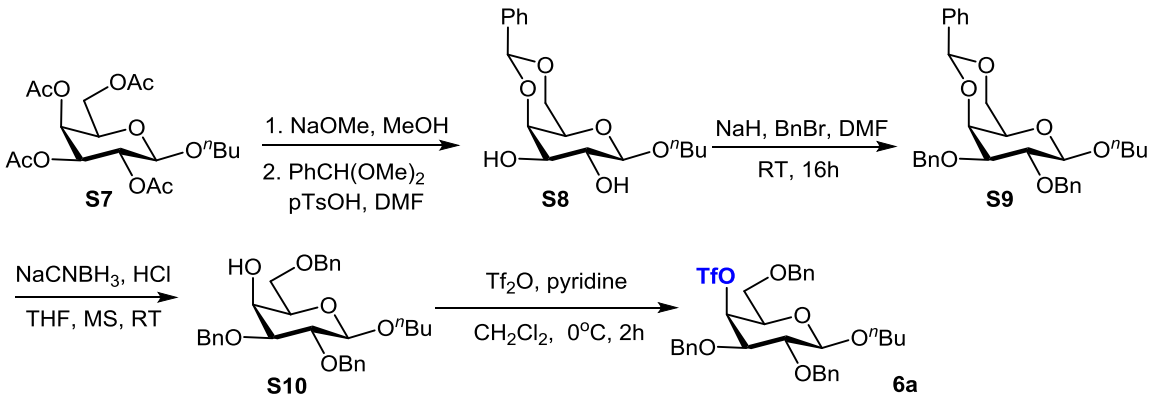
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 - 7.39 (m, 19H, aromatic), 5.23 (s, 1H, (H-1) α anomer), 4.87 - 4.93 (m, 2H, benzylic), 4.62 - 4.75 (m, 7H, benzylic and (H-1) β anomer overlapping), 4.07 (dd, *J* = 1.74, 3.21 Hz, 1H, (H-2) α anomer), 3.96 - 4.03 (m, 2H), 3.91 (dd, *J* = 3.12, 9.17 Hz, 1H, (H-3) α anomer), 3.57 (ddd, *J* = 1.74, 3.16, 9.03 Hz, 1H, (H-4) β anomer), 3.41 - 3.50 (m, 2H), 3.37 (qd, *J* = 6.08, 9.47 Hz, 1H, (H-5) β anomer), 1.35 (d, *J* = 6.05 Hz, 2H, (H-6) β anomer), 1.31 (d, *J* = 6.24 Hz, 3H, (H-6) α anomer)

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.6, 138.4, 138.2, 137.9, 128.9, 128.9, 128.8, 128.7, 128.4, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 94.1, 81.8, 80.2, 79.8, 79.7, 75.7, 75.7, 72.4, 72.3, 72.3, 71.6, 71.6, 69.4, 69.1, 69.1, 67.8, 18.2, 18.2.

FT-IR (thin film): 3405, 3034, 2909, 1497, 1454, 1214, 1092, 748, 698, 668 cm^{-1}.

ESIHRMS $[C_{20}H_{24}O_5 + Na]^+$ calculated 367.1516, found 367.1527.

2. Preparation of sugar-derived triflates:



[4] Palcic, M.; Ripka, J.; Kaur, K.; Shoreibah, M.; Hindsgaul, O.; Pierce, M. *J. Biol. Chem.* **1990**, *265*, 6759.

To a solution of known compound **S7**[5] (9.1 g, 22.2 mmol) in MeOH (100 mL) was added 5.4 M sodium methoxide solution in methanol (4.1 mL, 22.2 mmol). The mixture was stirred at RT for 2 h. The reaction was neutralized by the addition of Amberlyst IR-120 (H^+), stirred for 30 min, filtered and concentrated to afford corresponding tetra-ol. This tetra-ol was azeotroped with toluene (3x50mL) and used for next step without purification. To a solution of this tetra-ol in 40.0 mL *N,N*-dimethylformamide was added *p*-toluenesulfonic acid (210 mg, 1.1 mmol) and benzaldehyde dimethyl acetal (5.0 mL, 33.3 mmol). The resulting solution was stirred at room temperature for 12 hours. The mixture was diluted with EtOAc (200 mL), washed with saturated aq. $NaHCO_3$ (200 mL) then brine (200 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography (hexanes: EtOAc: methanol = 1:1:5%) to afford **S8** (4.6 g, 64 % over 2 steps)

To a solution of **S8** (4.6 g, 14.2 mmol) in *N,N*-dimethylformamide (40 mL) cooled at 0^oC was added sodium hydride (3.6 g, 56.8 mmol) portion wise. The resulting mixture was stirred at 0^oC for 1 hour before benzyl bromide (8.0 mL, 42.6 mmol) was added. The reaction mixture was warmed up and stirred at ambient temperature overnight. The resulting mixture was diluted with EtOAc (200 mL), washed with water (4×100 mL), dried over anhydrous sodium sulfate, filtered and concentrated. The resulting crude residue was recrystallized with hexanes-EtOAc to afford **S9** (4.94 g, 69%).

To a solution of **S9** (4.94 g, 9.8 mmol) in tetrahydrofuran (100mL) was added freshly dried 4Å molecular sieves and sodium cyanoborohydride (3.1 g, 49 mmol). This resulting mixture was cooled to 0^oC and 1N hydrogen chloride in diethyl ether (60 mL) was added. The mixture was warmed up to room temperature and stirred for an hour. The resulting mixture was filtered through a pad of celite, washed sequentially with saturated aq. $NaHCO_3$ (200 mL) and brine (200 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography (toluene: EtOAc: methanol = 20:1:1% to 1:1:1%) to afford **S10** (4.12 g, 83%) which is characterized below:

$[\alpha]_D^{21}$ = 72.7° (*c* = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 - 7.39 (m, 15H, aromatic), 4.92 (d, *J* = 11.00 Hz, 1H, benzylic), 4.70 - 4.75 (m, 3H, benzylic), 4.59 (s, 2H, benzylic), 4.35 (d, *J* = 7.70 Hz, 1H, H-1), 4.02 (br. s., 1H, H-4), 3.96 (td, *J* = 6.44, 9.49 Hz, 1H, $CH_2CH_2CH_2CH_3$), 3.80 (dd, *J* = 6.05, 9.90 Hz, 1H, H-6), 3.73 (dd, *J* = 6.05, 9.90 Hz, 1H, H-6), 3.64 (dd, *J* = 7.79, 9.45 Hz, 1H, H-2), 3.47 - 3.58 (m, 3H), 2.46 - 2.51 (m, 1H, OH), 1.59 - 1.69 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.36 - 1.49 (m, 2H, $CH_2CH_2CH_2CH_3$), 0.93 (t, *J* = 7.34 Hz, 3H, $CH_2CH_2CH_2CH_3$)

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.9, 138.4, 138.3, 128.8, 128.8, 128.7, 128.5, 128.2, 128.2, 128.1, 128.1, 128.0, 104.0, 80.9, 79.3, 75.5, 74.1, 73.5, 72.8, 70.0, 69.6, 67.3, 32.2, 19.6, 14.2

[5] Pilgrim, W.; Murphy, P. V. *J. Org. Chem.* **2010**, *75*, 6747.

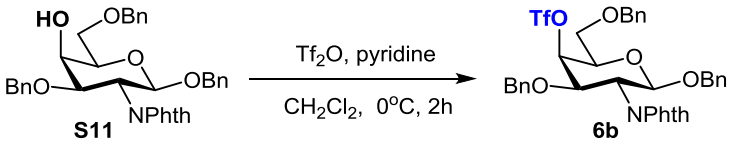
FT-IR (thin film): 3484, 3068, 3030, 2929, 2872, 1738, 1454, 1371, 1215, 1096, 1078, 752 cm^{-1}.

ESIHRMS $[C_{31}H_{38}O_6 + H]^+$ calculated 507.2747, found 507.2749.

To a mixture of alcohol **S10** (2.63 g, 5.20 mmol) and pyridine (4.2 mL, 52 mmol) in 26 mL methylene chloride cooled at 0°C was added triflic anhydride (1.75 mL, 10.4 mmol) dropwise. The resulting mixture was stirred at 0°C for 2 hours and then quenched with ice water. The organic layer was separated and the aqueous layer was extracted with methylene chloride (3×100 mL). The combined organic layer was washed sequentially with saturated copper sulfate (3×100 mL) and water (3×100 mL), dried over anhydrous sodium sulfate, filtered and concentrated. The residue was purified by short silica gel column chromatography with methylene chloride to afford 2.18 g (65%) of the sugar derived triflate **6a** which is characterized below:

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 - 7.48 (m, 6H, aromatic), 7.32 - 7.41 (m, 9H, aromatic), 5.46 (d, *J* = 2.93 Hz, 1H, H-4), 4.96 (dd, *J* = 7.15, 11.19 Hz, 2H, benzylic), 4.81 (d, *J* = 10.82 Hz, 1H, benzylic), 4.65 - 4.74 (m, 2H, benzylic), 4.52 (d, *J* = 11.19 Hz, 1H, benzylic), 4.46 (d, *J* = 7.70 Hz, 1H, H-1), 4.01 (td, *J* = 6.46, 9.44 Hz, 1H, $CH_2CH_2CH_2CH_3$), 3.76 - 3.83 (m, 2H), 3.68 - 3.75 (m, 2H), 3.63 - 3.67 (m, 1H, H-3), 3.60 (td, *J* = 6.95, 9.40 Hz, 1H, $CH_2CH_2CH_2CH_3$), 1.65 - 1.78 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.43 - 1.57 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.01 (t, *J* = 7.34 Hz, 3H, $CH_2CH_2CH_2CH_3$)

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.4, 137.6, 137.4, 128.8, 128.6, 128.4, 128.4, 128.3, 128.3, 128.1, 128.0, 104.1, 82.1, 78.7, 78.1, 75.7, 74.0, 73.2, 71.3, 70.5, 67.4, 32.0, 19.5, 14.1.



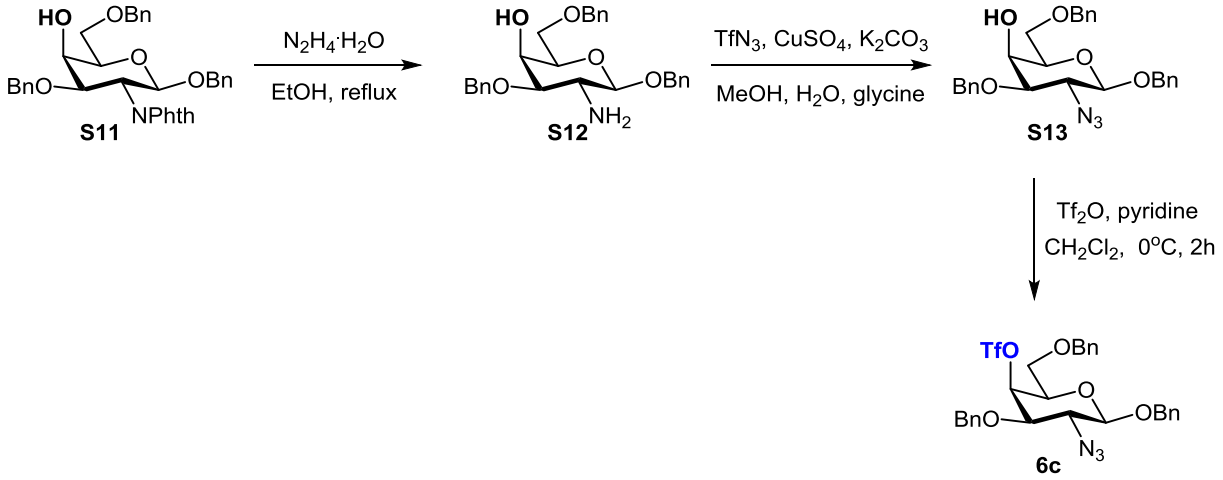
To a solution of known compound **S11**[6] (0.58 g, 1.0 mmol) and pyridine (0.4 mL, 5.0 mmol) in 5.0 mL methylene chloride cooled at 0°C was added triflic anhydride (0.35 mL, 2.0 mmol) dropwise. The resulting mixture was stirred at 0°C for 2 hours and then quenched with ice water. The organic layer was separated and the aqueous layer was extracted with methylene chloride (3×50 mL). The combined organic layer was washed sequentially with saturated copper sulfate (3×50 mL) and water (3×50 mL), dried over anhydrous sodium sulfate, filtered and concentrated. The residue was purified by silica gel column chromatography with methylene chloride to afford 500 mg (69%) of the sugar derived triflate **6b** which is characterized below:

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.34 Hz, 1H, aromatic), 7.73 (t, *J* = 7.43 Hz, 1H, aromatic), 7.68 (t, *J* = 7.43 Hz, 1H, aromatic), 7.47 (d, *J* = 7.15 Hz, 1H, aromatic), 7.39 - 7.44 (m, 4H, aromatic), 7.34 - 7.38 (m, 1H, aromatic), 7.04 - 7.08 (m, 1H, aromatic), 6.94 - 7.03 (m, 7H, aromatic), 6.84 - 6.89 (m, 2H, aromatic), 5.52 (d, *J* =

[6] Westerlind, U.; Hagback, P.; Duk, M.; Norberg, T. *Carbohydr. Res.* **2002**, *337*, 1517.

2.93 Hz, 1H, H-4), 5.11 (d, *J* = 8.44 Hz, 1H, H-1), 4.79 (d, *J* = 12.47 Hz, 1H, benzylic), 4.71 (dd, *J* = 9.54, 11.92 Hz, 2H, benzylic), 4.51 (d, *J* = 11.37 Hz, 1H, benzylic), 4.43 - 4.48 (m, 2H), 4.36 - 4.40 (m, 1H, H-3), 4.22 (d, *J* = 12.47 Hz, 1H, benzylic), 3.97 (dd, *J* = 5.69, 8.44 Hz, 1H, H-5), 3.80 (dd, *J* = 5.50, 9.17 Hz, 1H, H-6), 3.74 (t, *J* = 8.89 Hz, 1H, H-6)

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.1, 167.4, 137.6, 136.9, 136.9, 134.2, 133.9, 131.8, 131.8, 128.9, 128.5, 128.5, 128.5, 128.5, 128.4, 128.1, 128.0, 128.0, 123.8, 123.4, 97.7, 80.8, 74.0, 72.4, 72.2, 71.6, 71.3, 67.3, 52.6.



To a solution of known compound **S11**[6] (1.37 g, 2.36 mmol) in ethanol (50 mL) was added hydrazine hydrate (0.8 mL, 19 mmol). The resulting mixture was refluxed overnight, filtered through a pad of celite, and concentrated. The residue was purified by silica gel column chromatography (hexanes: EtOAc: methanol = 1:1:1%) to afford alcohol **S12** (1.0 g, 94%).

To a mixture of alcohol **S12** (415 mg, 0.92 mmol), methanol (3.0 mL), and water (3.0 mL) was added potassium carbonate (192 mg, 1.4 mmol) and copper sulfate pentahydrate (2.5 mg, 10 µmol). Freshly prepared triflic azide[7] (prepared from 2.0 mmol of triflic anhydride) was then added to this resulting mixture. This mixture was stirred for 24 hours before glycine (700 mg) was added. The resulting mixture was stirred for additional 12 hours, then extracted with dichloromethane (3x50 mL). The organic extracts were combined and washed sequentially with saturated aq. $NaHCO_3$ (50 mL), brine (50 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography (hexanes: EtOAc = 10:1 to 7:1) to give alcohol **S13** (297 mg, 68%) which is characterized below:

$[\alpha]_D^{21}$ = 13.7° (*c* = 1.0, $CHCl_3$).

[7] Vilà, S.; Badosa, E.; Montesinos, E.; Feliu, L.; Planas, M. *European J. Org. Chem.* **2015**, *2015*, 1117.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 - 7.42 (m, 15H, aromatic), 4.94 (d, *J* = 11.92 Hz, 1H, benzylic), 4.65 - 4.74 (m, 3H, benzylic), 4.60 (s, 2H, benzylic), 4.27 (d, *J* = 8.07 Hz, 1H, H-1), 4.00 (dd, *J* = 0.64, 3.21 Hz, 1H, H-4), 3.79 - 3.84 (m, 1H, H-6), 3.70 - 3.78 (m, 2H, H-6 and H-2 overlapping), 3.51 (dt, *J* = 1.01, 5.91 Hz, 1H, H-5), 3.29 (dd, *J* = 3.21, 10.00 Hz, 1H, H-3)

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.2, 137.5, 137.1, 129.0, 128.8, 128.8, 128.6, 128.4, 128.2, 128.2, 128.1, 100.8, 79.6, 74.1, 73.6, 72.4, 71.0, 69.4, 66.0, 63.0

FT-IR (thin film): 3473, 3029, 2931, 2870, 2112, 1454, 1362, 1214, 1070, 749, cm^{-1}.

ESIHRMS $[C_{27}H_{29}N_3O_5 + H]^+$ calculated 476.2185, found 476.2185.

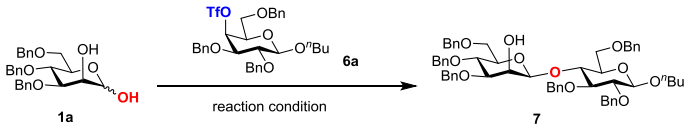
To a solution of alcohol **S13** (190 mg, 0.4 mmol) and pyridine (0.35 mL, 4.0 mmol) in 2.0 mL methylene chloride cooled at 0^{o}C was added triflic anhydride (0.27 mL, 1.6 mmol) dropwise. The resulting mixture was stirred at 0°C for 2 hours and then quenched with ice water. The organic layer was separated and the aqueous layer was extracted with methylene chloride (3×20 mL). The combined organic layer was washed sequentially with saturated copper sulfate (3×20 mL) and water (3×20 mL), dried over anhydrous sodium sulfate, filtered and concentrated. The residue was purified by silica gel column chromatography with methylene chloride to afford 196 mg (81%) of the sugar derived triflate **6c** which is characterized below:

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 - 7.43 (m, 15H, aromatic), 5.34 (d, *J* = 2.93 Hz, 1H, H-4), 4.91 (d, *J* = 11.74 Hz, 1H, benzylic), 4.86 (d, *J* = 11.74 Hz, 1H, benzylic), 4.65 (dd, *J* = 3.30, 11.55 Hz, 2H, benzylic), 4.57 (d, *J* = 11.74 Hz, 1H, benzylic), 4.45 (d, *J* = 11.37 Hz, 1H, benzylic), 4.30 (d, *J* = 8.07 Hz, 1H, H-1), 3.62 - 3.74 (m, 4H), 3.34 (dd, *J* = 2.93, 10.27 Hz, 1H, H-3)

^{13}C NMR (150 MHz, $CDCl_3$) δ 137.5, 136.6, 136.5, 128.9, 128.9, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 100.9, 80.3, 76.4, 74.1, 73.0, 71.6, 71.5, 67.2, 62.8.

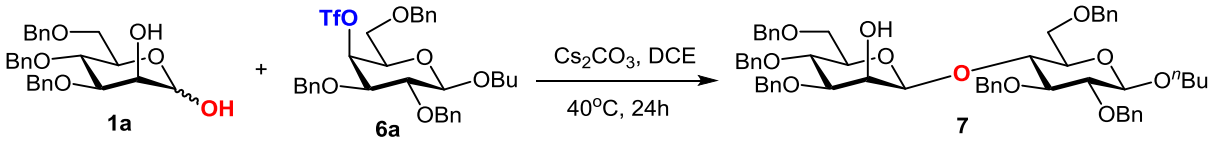
3. General procedure for preparation of *O*-linked *β*-mannopyranosides:

Table. Anomeric O-alkylation of 3,4,6-tri-O-benzyl-D-mannopyranose 1a with D-galactose-derived C4-triflate 6a.[a]



Entry	Reaction condition	Yield,[b] *α*/*β* ratio
1	NaH (2.5 or 3 eq.), 15-C-5 (1.5 eq.), triflate **6a** (1.5 eq.), 1,4-dioxane, RT	trace
2	NaH (2.5 or 3 eq.), 15-C-5 (1.5 eq.), triflate **6a** (1.5 eq.), CH_2Cl_2, RT	trace
3	Cs_2CO_3 (1.5 eq.), triflate **6a** (1.5 eq.), CH_3CN, 40 ^oC	25% (51% BRSM), *β* only
4	Cs_2CO_3 (1.5 eq.), triflate **6a** (1.5 eq.), DMF, 40 ^oC	trace
5	Cs_2CO_3 (1.5 eq.), triflate **6a** (1.5 eq.), 1,4-dioxane, 40 ^oC	24% (30% BRSM), *β* only
6	Cs_2CO_3 (1.5 eq.), triflate **6a** (1.5 eq.), THF, 40 ^oC	30% (47% BRSM), *β* only
7	Cs_2CO_3 (1.5 eq.), triflate **6a** (1.5 eq.), $ClCH_2CH_2Cl$, 40 ^oC	48% (67% BRSM), *β* only
8	Cs_2CO_3 (1.5 eq.), triflate **6a** (1.5 eq.), toluene, 40 ^oC	21% (30% BRSM), *β* only
9	Cs_2CO_3 (1.5 eq.), triflate **6a** (1.5 eq.), $ClCH_2CH_2Cl$/DMF (10/1, v/v), 40 ^oC	23% (54% BRSM), *β* only
10	Cs_2CO_3 (2.5 eq.), triflate **6a** (2.0 eq.), $ClCH_2CH_2Cl$, 40 ^oC	67% (73% BRSM), *β* only
11	Cs_3PO_4 (2.5 eq.), triflate **6a** (2.0 eq.), $ClCH_2CH_2Cl$, 40 ^oC	59% (63% BRSM), *β* only
12	Cs_2CO_3 (2.5 eq.), triflate **6a** (2.0 eq.), $ClCH_2CH_2Cl$, 50 ^oC	64% (70% BRSM), *β* only
13	Cs_2CO_3 (3.0 eq.), triflate **6a** (2.5 eq.), $ClCH_2CH_2Cl$, 40 ^oC	75% (86% BRSM), *β* only
14	Cs_2CO_3 (3.0 eq.), triflate **6a** (2.5 eq.), $ClCH_2CH_2Cl$, 40 ^oC, 40 hours	75% (81% BRSM), *β* only
15	2-Aminoethyl diphenylborinate (0.1 eq.), K_2CO_3 or $^iPr_2NEt$, CH_3CN, 40 ^oC	no desired product

[a] All reactions were performed using 0.1 mmol of 3,4,6-tri-*O*-benzyl-D-mannopyranose **1a** in 1 mL solvent for 24 hours. [b] Isolated yield based on the lactol donor **1a**. Yield calculated based on recovered lactol donor **1a** is reported in the parenthesis. BRSM = based on recovered starting material (donor **1a**).



To a mixture of 3,4,6-tri-*O*-benzyl-D-mannopyranose **1a**[8] (45 mg, 0.1 mmol), sugar-derived triflate acceptor **6a** (160 mg, 0.25 mmol), and cesium carbonate (98 mg, 0.3 mmol) was added 1,2-dichloroethane (1.0 mL). The reaction mixture was stirred at 40℃ for 24 hours. The crude reaction mixture was purified by preparative thin layer chromatography (hexanes: EtOAc: methanol = 2:1:1%) to furnish 70 mg (75% yield) of *β*-mannoside **7** which is characterized below. The *β*-configuration of the mannosidic linkage in **7** was unambiguously assigned by measuring the $J_{(C,H)}$ for the anomeric carbon. For **7**, $J_{(C,H)}$ of mannosidic anomeric carbon was determined to be 157 Hz.

[8] Jonke, S.; Liu, K. g.; Schmidt, R. R. *Chem. Eur. J.* **2006**, *12*, 1274.

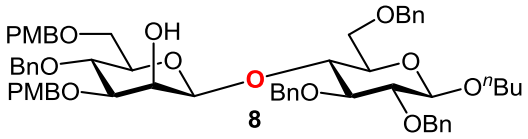
$[\alpha]_D^{21}$ = -8.3° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 - 7.35 (m, 23H, aromatic), 7.20 - 7.26 (m, 5H, aromatic), 7.18 (dd, *J* = 1.74, 7.61 Hz, 2H, aromatic), 4.91 - 4.98 (m, 2H, benzylic), 4.82 - 4.89 (m, 2H, benzylic), 4.71 (d, *J* = 11.00 Hz, 1H, benzylic), 4.62 - 4.67 (m, 2H, benzylic and H-1' overlapping), 4.41 - 4.58 (m, 6H), 4.39 (d, *J* = 7.89 Hz, 1H, H-1), 3.92 - 4.00 (m, 3H), 3.84 (t, *J* = 9.54 Hz, 1H, H-4'), 3.73 - 3.80 (m, 2H, H-6), 3.69 (t, *J* = 9.17 Hz, 1H, H-3), 3.52 - 3.64 (m, 3H), 3.46 - 3.51 (m, 1H, H-5), 3.44 (dd, *J* = 7.89, 9.17 Hz, 1H, H-2), 3.35 (dd, *J* = 3.03, 9.26 Hz, 1H, H-3'), 3.26 (ddd, *J* = 2.20, 4.54, 9.77 Hz, 1H, H-5'), 2.64 - 2.68 (m, 1H, OH), 1.59 - 1.71 (m, 3H, $CH_2CH_2CH_2CH_3$), 1.38 - 1.50 (m, 2H, $CH_2CH_2CH_2CH_3$), 0.95 (t, *J* = 7.43 Hz, 3H, $CH_2CH_2CH_2CH_3$)

^{13}C NMR (150 MHz, $CDCl_3$) δ 139.1, 138.7, 138.6, 138.4, 138.2, 128.7, 128.7, 128.7, 128.6, 128.5, 128.4, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.7, 127.7, 104.0, 100.2, 83.5, 82.4, 81.8, 76.1, 75.9, 75.6, 75.5, 75.2, 74.6, 74.2, 73.8, 73.6, 71.4, 70.1, 69.4, 69.3, 68.0, 32.2, 19.6, 14.2.

FT-IR (thin film): 3446, 3065, 3029, 2867, 1496, 1453, 1362, 1090, 1057, 734 cm^{-1}.

ESIHRMS $[C_{58}H_{66}O_{11} + Na]^+$ calculated 961.4497, found 961.4510.



8

β-Mannoside **8** was prepared from 4-*O*-benzyl 3,6-di-*O*-(4-methoxybenzyl)-D-mannopyranose **1b** and sugar-derived triflate acceptor **6a** following the general procedure. The crude reaction mixture was purified by preparative thin layer chromatography (hexanes: EtOAc: methanol = 2:1:1%) to furnish 75 mg (75% yield) of *β*-mannoside **8** which is characterized below. For **8**, $J_{(C,H)}$ of mannosidic anomeric carbon was determined to be 160 Hz.

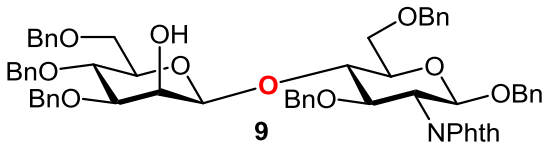
$[\alpha]_D^{21}$ = 3.8° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 - 7.36 (m, 15H, aromatic), 7.14 - 7.26 (m, 9H, aromatic), 6.77 - 6.84 (m, 4H, aromatic), 4.94 (dd, *J* = 10.91, 16.78 Hz, 2H, benzylic), 4.86 (d, *J* = 11.00 Hz, 1H, benzylic), 4.80 (d, *J* = 10.82 Hz, 1H, benzylic), 4.70 (d, *J* = 10.82 Hz, 1H, benzylic), 4.61 - 4.65 (m, 2H, benzylic and 1H' overlapping), 4.54 (d, *J* = 12.29 Hz, 1H), 4.45 - 4.51 (m, 2H), 4.43 (d, *J* = 8.44 Hz, 1H), 4.32 - 4.41 (m, 4H), 3.92 - 3.98 (m, 3H), 3.74 - 3.82 (m, 8H), 3.68 (t, *J* = 9.08 Hz, 1H, H-3), 3.51 - 3.60 (m, 3H), 3.46 - 3.50 (m, 1H, H-5), 3.43 (dd, *J* = 7.79, 9.08 Hz, 1H, H-2), 3.33 (dd, *J* = 3.03, 9.26 Hz, 1H, H-3'), 3.24 (ddd, *J* = 2.11, 4.40, 9.81 Hz, 1H, H-5'), 2.62 - 2.69 (m, 1H, OH), 1.60 - 1.72 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.37 - 1.51 (m, 2H, $CH_2CH_2CH_2CH_3$), 0.94 (t, *J* = 7.43 Hz, 3H, $CH_2CH_2CH_2CH_3$)

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 159.3, 139.1, 138.7, 138.7, 138.4, 130.8, 130.3, 129.7, 129.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.3, 128.1, 128.0, 128.0, 127.9, 127.7, 114.1, 114.0, 104.0, 100.3, 83.5, 82.4, 81.5, 76.2, 75.9, 75.6, 75.4, 75.2, 74.7, 74.2, 73.8, 73.3, 71.1, 70.1, 69.4, 69.0, 68.0, 55.6, 55.5, 32.2, 19.6, 14.2

FT-IR (thin film): 3462, 3030, 2867, 1612, 1513, 1454, 1362, 1246, 1089, 1055, 820, 735, 697 cm^{-1}.

ESIHRMS [$C_{60}H_{70}O_{13}$ + Na]$^+$ calculated 1021.4668, found 1021.4740.



9

β-Mannoside **9** was prepared from 3,4,6-tri-*O*-benzyl-D-mannopyranose **1a** and sugar-derived triflate acceptor **6b** following the general procedure. The crude reaction mixture was purified by preparative thin layer chromatography (hexanes: EtOAc: methanol = 2:1:1%) to furnish 69 mg (68% yield) of *β*-mannoside **9** which is characterized below. For **9**, $J_{(C,H)}$ of mannosidic anomeric carbon was determined to be 160 Hz.

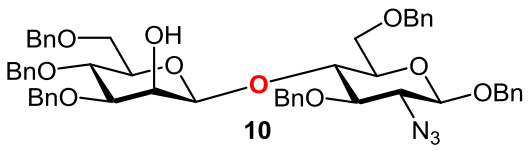
[α]$_D^{21}$ = 25.7° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 - 7.58 7.26 (br. t, 4H, aromatic) - 7.40 (m, 13H, aromatic), 7.16 - 7.25 (m, 7H, aromatic), 7.00 - 7.10 (m, 5H, aromatic), 6.94 - 6.99 (m, 2H, aromatic), 6.73 - 6.82 (m, 3H, aromatic), 5.13 (d, *J* = 8.44 Hz, 1H, H-1), 4.77 - 4.90 (m, 3H, benzylic), 4.65 - 4.72 (m, 2H, benzylic and H-1' overlapping), 4.58 - 4.63 (m, 1H, benzylic), 4.42 - 4.54 (m, 7H, benzylic), 4.38 (dd, *J* = 8.62, 10.64 Hz, 1H, H-3), 4.24 (dd, *J* = 8.62, 10.64 Hz, 1H, H-2), 4.09 (dd, *J* = 8.62, 9.72 Hz, 1H, H-4), 4.02 (d, *J* = 2.93 Hz, 1H, H-2'), 3.81 - 3.88 (m, 2H), 3.74 - 3.79 (m, 1H, H-6), 3.67 - 3.72 (m, 1H, H-5), 3.58 - 3.66 (m, 2H), 3.40 (dd, *J* = 3.12, 9.17 Hz, 1H, H-3'), 3.28 - 3.33 (m, 1H, H-5'), 2.52 (br. s., 1H, OH)

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.8, 138.6, 138.5, 138.2, 138.2, 137.6, 133.9, 133.8, 128.9, 128.8, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.2, 128.2, 128.1, 128.0, 127.9, 127.7, 127.3, 123.5, 100.8, 97.9, 82.0, 78.6, 78.2, 75.7, 75.4, 75.1, 74.8, 74.3, 73.9, 73.7, 71.6, 71.2, 69.2, 69.0, 68.3, 56.1

FT-IR (thin film): 3492, 3030, 2867, 1775, 1712, 1496, 1453, 1388, 1074, 737, 698 cm^{-1}.

ESIHRMS [$C_{62}H_{61}NO_{12}$ +H]$^+$ calculated 1012.4272, found 1012.4243.



10

β-Mannoside **10** was prepared from 3,4,6-tri-*O*-benzyl-D-mannopyranose **1a** and sugar-derived triflate acceptor **6c** following the general procedure. The crude reaction mixture was purified by preparative thin layer chromatography (hexanes: EtOAc = 2:1) to furnish 62 mg (68% yield) of *β*-mannoside **10** which is characterized below. For **10**, $J_{(C,H)}$ of mannosidic anomeric carbon was determined to be 159 Hz.

[α]$_D^{21}$ = -27.9° (*c* = 1.0, $CHCl_3$).

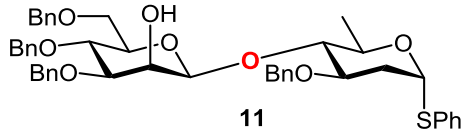
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 - 7.43 (m, 6H, aromatic), 7.27 - 7.35 (m, 20H, aromatic), 7.22 - 7.26 (m, 2H, aromatic), 7.17 - 7.22 (m, 2H, aromatic), 5.02 (d, *J* = 11.00 Hz, 1H, benzylic), 4.94 (d, *J* = 11.92 Hz, 1H, benzylic), 4.84 (dd, *J* = 10.91, 17.15

Hz, 2H, benzylic), 4.57 - 4.72 (m, 4H, benzylic and H-1' overlapping), 4.49 - 4.55 (m, 3H, benzylic), 4.41 - 4.47 (m, 2H, benzylic), 4.30 - 4.36 (d, 1H, H-1), 3.96 - 4.03 (m, 2H), 3.84 (t, *J* = 9.45 Hz, 1H, H-4'), 3.71 - 3.81 (m, 2H), 3.62 - 3.68 (m, 1H), 3.57 (dd, *J* = 4.95, 10.82 Hz, 1H), 3.41 - 3.50 (m, 3H), 3.38 (dd, *J* = 3.12, 9.17 Hz, 1H, H-3'), 3.29 (ddd, *J* = 1.83, 4.91, 9.77 Hz, 1H, H-5'), 2.53 (d, *J* = 2.75 Hz, 1H, OH)

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.6, 138.5, 138.1, 137.1, 128.9, 128.8, 128.8, 128.8, 128.7, 128.6, 128.6, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 128.0, 127.8, 101.0, 100.2, 81.9, 77.6, 77.1, 76.2, 75.9, 75.4, 75.4, 74.9, 74.3, 73.8, 73.7, 71.6, 71.3, 69.3, 68.9, 68.1, 66.5

FT-IR (thin film): 3451, 3030, 2867, 2109, 1731, 1496, 1453, 1362, 1058, 735, 697 cm^{-1}.

ESIHRMS [$C_{54}H_{57}N_3O_{10}$ +H]$^+$ calculated 908.4122, found 908.4146.



11

β-Mannoside **11** was prepared from 3,4,6-tri-*O*-benzyl-D-mannopyranose **1a** and sugar-derived triflate acceptor **6d**[9] following the general procedure, except using 2.0 equivalents of triflate **6d** and 2.5 equivalents of cesium carbonate. The crude reaction mixture was purified by preparative thin layer chromatography (hexanes: EtOAc = 2:1) to furnish 63 mg (83% yield) of *β*-mannoside **11** which is characterized below. For **11**, $J_{(C,H)}$ of mannosidic anomeric carbon was determined to be 159 Hz.

$[\alpha]_D^{21}$ = 66.6° (*c* = 1.0, $CHCl_3$).

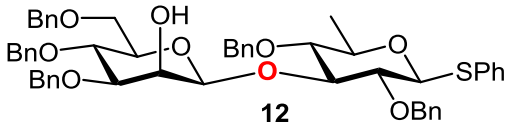
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 - 7.47 (m, 2H, aromatic), 7.38 - 7.41 (m, 2H, aromatic), 7.26 - 7.37 (m, 18H, aromatic), 7.20 - 7.26 (m, 3H, aromatic), 5.57 (dd, *J* = 2.02, 5.50 Hz, 1H, H-1), 4.90 (d, *J* = 10.82 Hz, 1H, benzylic), 4.75 (dd, *J* = 7.34, 11.74 Hz, 2H, benzylic), 4.62 - 4.69 (m, 3H, benzylic and H-1' overlapping), 4.53 - 4.59 (m, 2H, benzylic), 4.48 - 4.52 (m, 1H, benzylic), 4.26 (qd, *J* = 6.24, 8.99 Hz, 1H, H-5), 4.09 (br. s., 1H, H-2'), 3.98 (ddd, *J* = 4.68, 7.98, 10.82 Hz, 1H, H-3), 3.92 (t, *J* = 9.45 Hz, 1H, H-4'), 3.65 - 3.73 (m, 2H, H-6'), 3.50 - 3.57 (m, 2H), 3.36 (ddd, *J* = 2.11, 4.59, 9.81 Hz, 1H, H-5'), 2.69 (br. s., 1H, OH), 2.42 (ddd, *J* = 2.20, 4.72, 13.62 Hz, 1H, H-2), 2.10 (ddd, *J* = 5.59, 10.87, 13.62 Hz, 1H, H-2), 1.31 (d, *J* = 6.42 Hz, 3H, H-6).

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.7, 138.6, 138.6, 138.2, 135.3, 131.5, 129.2, 128.8, 128.7, 128.7, 128.6, 128.4, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.4, 100.2, 83.6, 82.6, 81.9, 76.1, 75.9, 75.5, 74.3, 73.8, 72.1, 71.7, 69.4, 68.7, 68.3, 36.4, 18.5.

FT-IR (thin film): 3454, 3065, 3029, 2869, 1731, 1583, 1496, 1453, 1364, 1067, 738 cm^{-1}.

ESIHRMS [$C_{46}H_{50}O_8S$ + Na]$^+$ calculated 785.3119, found 785.3150.

[9] Zhu, D.; Baryal, K. N.; Adhikari, S.; Zhu, J. *J. Am. Chem. Soc.* **2014**, *136*, 3172.



12

β-Mannoside **12** was prepared from 3,4,6-tri-*O*-benzyl-D-mannopyranose **1a** and sugar-derived triflate acceptor **6e**[9] following the general procedure, except using 2.0 equivalents of triflate **6e** and 2.5 equivalents of cesium carbonate. The crude reaction mixture was purified by preparative thin layer chromatography (hexanes: EtOAc = 2:1) to furnish 73 mg (84% yield) of *β*-mannoside **12** which is characterized below. For **12**, $J_{(C,H)}$ of mannosidic anomeric carbon was determined to be 160 Hz.

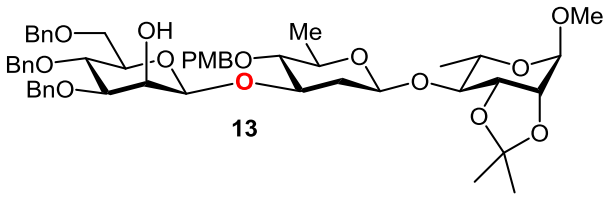
$[\alpha]_D^{21}$ = 20.5° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 - 7.56 (m, 2H, aromatic), 7.27 - 7.37 (m, 18H, aromatic), 7.16 - 7.26 (m, 10H, aromatic), 5.14 (d, *J* = 11.00 Hz, 1H, benzylic), 5.08 (d, *J* = 10.45 Hz, 1H, benzylic), 4.79 - 4.86 (m, 2H, benzylic and H-1' overlapping), 4.46 - 4.64 (m, 6H, benzylic), 4.41 (s, 2H, benzylic), 3.92 - 3.99 (m, 2H), 3.83 (t, *J* = 9.54 Hz, 1H, H-4'), 3.66 (dd, *J* = 1.74, 10.91 Hz, 1H, H-6'), 3.57 (dd, *J* = 4.95, 11.00 Hz, 1H, H-6'), 3.52 (t, *J* = 9.45 Hz, 1H, H-2), 3.35 - 3.42 (m, 1H, H-5), 3.25 - 3.32 (m, 2H), 3.19 - 3.25 (m, 1H, H-4), 1.35 (d, *J* = 6.05 Hz, 3H, H-6)

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.9, 138.8, 138.5, 138.2, 138.2, 134.1, 132.0, 129.3, 129.0, 128.9, 128.7, 128.6, 128.5, 128.5, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 101.1, 87.7, 84.3, 82.3, 82.0, 81.8, 75.9, 75.7, 75.7, 75.6, 75.3, 74.6, 73.7, 71.7, 69.4, 68.7, 18.7

FT-IR (thin film): 3470, 3030, 2926, 2867, 1732, 1496, 1453, 1090, 1027, 736, 697 cm^{-1}.

ESIHRMS $[C_{53}H_{56}O_9S + H]^+$ calculated 869.3723, found 869.3716.



13

β-Mannoside **13** was prepared from 3,4,6-tri-*O*-benzyl-D-mannopyranose **1a** and sugar-derived triflate acceptor **6f**[9] following the general procedure, except using 2.0 equivalents of triflate **6f** and 2.5 equivalents of cesium carbonate. The crude reaction mixture was purified by preparative thin layer chromatography (hexanes: EtOAc = 2:1) to furnish 84 mg (93% yield) of *β*-mannoside **13** which is characterized below. For **13**, $J_{(C,H)}$ of mannosidic anomeric carbon was determined to be 157 Hz.

$[\alpha]_D^{21}$ = 13° (*c* = 0.2, $CHCl_3$).

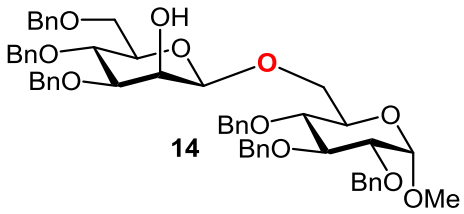
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 - 7.41 (m, 2H, aromatic), 7.27 - 7.36 (m, 12H, aromatic), 7.21 - 7.26 (m, 3H, aromatic), 6.74 - 6.78 (m, 2H, aromatic), 4.95 (d, *J* = 10.45 Hz, 1H, benzylic), 4.90 (d, *J* = 10.82 Hz, 1H, benzylic), 4.87 (dd, *J* = 1.65, 9.72 Hz, 1H, H-1'), 4.85 (s, 1H, H-1), 4.78 (d, *J* = 11.74 Hz, 1H, benzylic), 4.67 (d, *J* = 11.74 Hz, 1H, benzylic), 4.56 - 4.63 (m, 4H), 4.51 - 4.54 (m, 1H), 4.04 - 4.15 (m, 4H), 3.96 (t, *J* = 9.45 Hz, 1H, H-4), 3.74 - 3.81 (m, 2H), 3.72 (s, 3H), 3.55 - 3.66 (m, 3H), 3.40 - 3.44 (m, 1H, H-3), 3.36 (s, 3H, OCH_3), 3.29 (qd, *J* = 6.14, 9.28 Hz, 1H, H-5'), 3.10 (t, *J* = 8.99

Hz, 1H, H-4'), 2.28 (ddd, *J* = 1.56, 5.23, 12.10 Hz, 1H, H-2'), 1.49 (m, 4H, CH_3 and H-2' overlapping), 1.33 (s, 3H, CH_3), 1.31 (d, *J* = 6.24 Hz, 3H, H-6'), 1.27 (d, *J* = 6.05 Hz, 3H, H-6)

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 138.8, 138.6, 138.2, 131.1, 130.2, 128.8, 128.7, 128.7, 128.5, 128.2, 128.2, 128.1, 128.0, 127.8, 114.0, 109.6, 98.2, 98.0, 96.6, 82.3, 82.0, 78.9, 77.8, 76.9, 76.4, 76.0, 75.6, 74.6, 74.5, 73.8, 71.7, 71.5, 69.5, 69.0, 64.6, 55.6, 55.1, 36.9, 28.1, 26.8, 18.6, 17.8

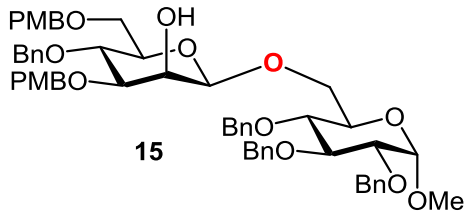
FT-IR (thin film): 3476, 2932, 1615, 1513, 1454, 1371, 1246, 1090, 741 cm^{-1}.

ESIHRMS [$C_{51}H_{64}O_{14}$ + Na]$^+$ calculated 923.4188, found 923.4231.



14

β-Mannoside **14** was prepared from 3,4,6-tri-*O*-benzyl-D-mannopyranose **1a** and sugar-derived triflate acceptor **6g** following the general procedure, except using 1.5 equivalents of triflate **6g** and 1.5 equivalents of cesium carbonate. The crude reaction mixture was purified by preparative thin layer chromatography (hexanes: EtOAc: methanol = 2:1:1%) to furnish 83 mg (93% yield) of *β*-mannoside **14** whose spectroscopic data match with the date reported in the literature.[10]



15

β-Mannoside **15** was prepared from 4-*O*-benzyl-3,6-di-*O*-(4-methoxybenzyl)-D-mannopyranose **1b** and sugar-derived triflate acceptor **6g** following the procedure described for preparation of **14**. The crude reaction mixture was purified by preparative thin layer chromatography (hexanes: EtOAc: methanol = 2:1:1%) to furnish 87 mg (91% yield) of *β*-mannoside **15** which is characterized below. For **15**, $J_{(C,H)}$ of mannosidic anomeric carbon was determined to be 159 Hz.

$[\alpha]_D^{21}$ = 121.5° (*c* = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 - 7.39 (m, 16H, aromatic), 7.21 - 7.25 (m, 6H, aromatic), 7.18 (dd, *J* = 1.56, 7.79 Hz, 2H, aromatic), 6.80 - 6.86 (m, 4H, aromatic), 5.00 (d, *J* = 11.00 Hz, 1H, benzylic), 4.85 (dd, *J* = 8.62, 11.00 Hz, 2H, benzylic), 4.76 - 4.82 (m, 2H, benzylic), 4.64 - 4.69 (m, 2H, benzylic), 4.43 - 4.61 (m, 6H), 4.14 - 4.17 (m, 1H), 4.11 (dd, *J* = 1.93, 10.91 Hz, 1H), 3.99 (t, *J* = 9.26 Hz, 1H, H-3), 3.91 (d, *J* = 2.93 Hz, 1H, H-2'), 3.75 - 3.81 (m, 8H), 3.62 - 3.71 (m, 2H, H-6'), 3.57 (dd, *J* = 5.41, 10.91 Hz, 1H, H-6), 3.51 (dd, *J* = 3.58, 9.63 Hz, 1H, H-2), 3.42 - 3.47 (m, 2H, H-4 and H-3' overlapping), 3.34 (s, 3H, OCH_3), 3.30 - 3.34 (m, 1H, H-5')

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 159.5, 139.1, 138.6, 138.6, 138.4, 130.6, 130.3, 129.8, 129.8, 128.8, 128.7, 128.7, 128.5, 128.4, 128.3, 128.3, 128.1, 128.0,

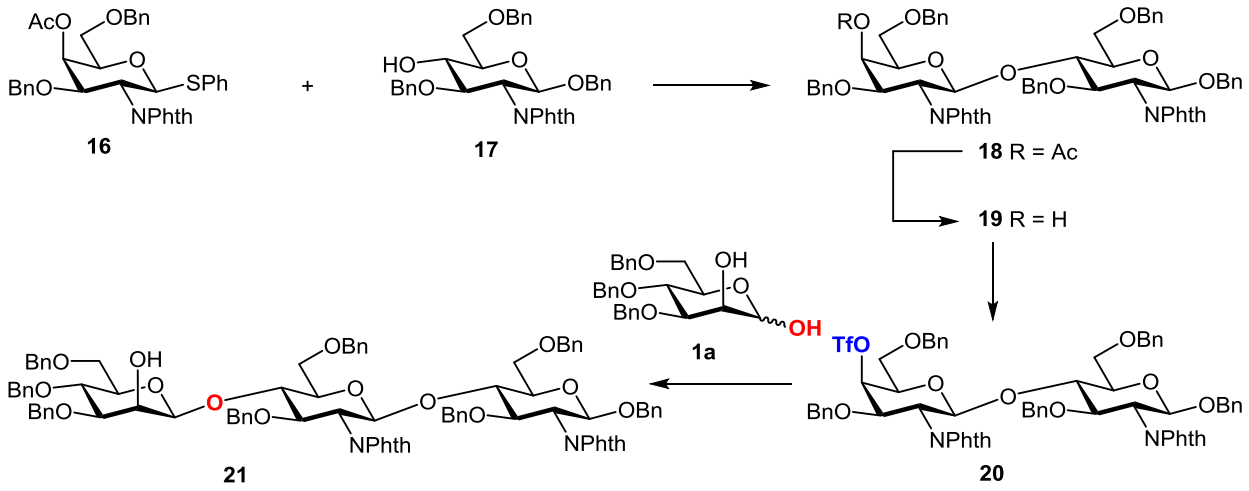
[10] Chayajarus, K.; Chambers, D. J.; Chughtai, M. J.; Fairbanks, A. J. *Org. Lett.* **2004**, *6*, 3797.

128.0, 114.2, 114.0, 100.2, 98.2, 82.5, 81.3, 80.1, 77.9, 76.1, 75.7, 75.5, 75.1, 74.5, 73.7, 73.4, 71.3, 70.1, 69.1, 68.6, 68.4, 55.6, 55.6, 55.5

FT-IR (thin film): 3494, 3033, 2925, 2859, 1612, 1513, 1454, 1367, 1305, 1247, 1094, 1070, 738, 698 cm^{-1}.

ESIHRMS $[C_{57}H_{64}O_{13}+H]^+$ calculated 957.4425, found 957.4373.

4. Synthesis of the trisaccharide core of the *N*-linked glycans via anomeric *O*-alkylation:



To a mixture of **16**[11] (174 mg, 0.3 mmol), **17**[12] (243 mg, 0.39 mmol), activated 4Å molecular sieves (200 mg), and NIS (170 mg) was added dichloromethane (15 mL). The solution was cooled to -20℃ and added triflic acid (13 µL) dropwise. The resulting solution was stirred at this temperature for an hour before filtering through celite. The filtrate was quenched with aqueous $NaHCO_3$ and sequentially washed with aqueous $Na_2S_2O_3$ and brine solution. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by silica gel chromatography (hexanes: EtOAc : CH_2Cl_2 = 5:1:1) to give disaccharide **18** (320 mg, 97%) which is characterized below:

$[\alpha]_D^{21}$ = 20° (*c* = 0.1, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.15 Hz, 1H, aromatic), 7.63 - 7.77 (m, 6H, aromatic), 7.26 - 7.38 (m, 10H, aromatic), 6.83 - 7.07 (m, 16H, aromatic), 5.61 (d, *J* = 2.57 Hz, 1H, H-4'), 5.33 (d, *J* = 8.25 Hz, 1H, H-1'), 4.96 (d, *J* = 8.25 Hz, 1H, H-1), 4.87 (d, *J* = 12.10 Hz, 1H, benzylic), 4.69 (d, *J* = 12.47 Hz, 1H, benzylic), 4.58 (d, *J* = 12.29 Hz, 1H, benzylic), 4.32 - 4.53 (m, 6H), 4.12 - 4.30 (m, 4H), 3.66 (dt, *J* = 0.73, 6.69 Hz, 1H, H-5'), 3.48 - 3.53 (m, 1H), 3.31 - 3.47 (m, 4H), 2.02 (s, 3H, CH_3)

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[11] Sawada, T.; Fujii, S.; Nakano, H.; Ohtake, S.; Kimata, K.; Habuchi, O. *Carbohydr. Res.* **2005**, *340*, 1983.

[12] Dinkelaar, J.; Duivenvoorden, B. A.; Wennekes, T.; Overkleeft, H. S.; Boot, R. G.; Aerts, J. M.; Codée, J. D.; van der Marel, G. A. *European J. Org. Chem.* **2010**, *2010*, 2565.

^{13}C NMR (150 MHz, $CDCl_3$) d 170.6, 168.7, 168.0, 139.1, 138.8, 138.1, 137.8, 137.5, 134.4, 134.2, 133.9, 132.1, 132.0, 131.9, 128.8, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 127.9, 127.9, 127.8, 127.7, 127.6, 127.3, 123.9, 123.5, 97.8, 97.5, 77.2, 76.3, 74.9, 74.4, 73.9, 73.1, 73.0, 72.3, 71.4, 70.8, 68.4, 67.7, 66.0, 56.0, 54.0, 21.2, 1.4

FT-IR (thin film): 3031, 2925, 2867, 1775, 1744, 1713, 1453, 1387, 1074, 721, 698 cm^{-1}.

ESILRMS $[C_{27}H_{29}N_3O_5 + Na]^+$ calculated 1115.39, found 1115.80.

To a solution of **18** (320 mg, 0.29 mmol), methanol (10 mL), and THF (10 mL) was added a 0.5M solution of NaOMe in MeOH until a pH of 10 was reached. The mixture was stirred at RT for 7 hours. The reaction was neutralized by the addition of Amberlyst IR-120 (H^+), stirred for 30 min, filtered and concentrated. The residue was purified by silica gel column chromatography (hexanes: EtOAc: CH_2Cl_2 = 3:1:1) to give alcohol **19** (221 mg, 72%) which is characterized below:

$[\alpha]_D^{21}$ = 16.8° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.34 Hz, 1H, aromatic), 7.61 - 7.79 (m, 6H, aromatic), 7.27 - 7.39 (m, 10H, aromatic), 7.22 - 7.26 (m, 1H, aromatic), 6.95 - 7.07 (m, 12H, aromatic), 6.82 - 6.86 (m, 3H, aromatic), 5.29 (d, *J* = 8.25 Hz, 1H, H-1'), 4.94 - 4.99 (m, 1H, H-1), 4.86 (d, *J* = 12.29 Hz, 1H, benzylic), 4.69 (d, *J* = 12.47 Hz, 1H, benzylic), 4.63 (d, *J* = 12.47 Hz, 1H, benzylic), 4.40 - 4.56 (m, 6H, 5 benzylic and H-2' overlapping), 4.37 (d, *J* = 12.29 Hz, 1H, benzylic), 4.32 (d, *J* = 12.29 Hz, 1H, benzylic), 4.27 (dd, *J* = 3.30, 11.00 Hz, 1H, H-3'), 4.13 - 4.20 (m, 4H), 3.75 (dd, *J* = 6.79, 9.72 Hz, 1H, H-6'), 3.63 (dd, *J* = 5.23, 9.63 Hz, 1H, H-6'), 3.50 - 3.57 (m, 2H, H-5 and H-5' ovrlapping), 3.42 (dd, *J* = 4.13, 10.91 Hz, 1H, H-4), 3.31 - 3.36 (m, 1H, H-3), 2.58 (s, 1H, OH)

^{13}C NMR (150 MHz, $CDCl_3$) d 168.9, 168.1, 139.0, 138.8, 138.4, 137.6, 137.5, 134.4, 134.2, 133.8, 133.8, 132.1, 132.0, 131.9, 128.8, 128.6, 128.5, 128.4, 128.4, 128.1, 128.1, 128.0, 128.0, 127.8, 127.8, 127.6, 127.5, 127.2, 124.0, 123.4, 97.7, 97.4, 77.0, 76.2, 75.1, 74.9, 74.6, 73.9, 73.3, 72.9, 71.4, 70.8, 69.0, 65.6, 56.0, 53.4

FT-IR (thin film): 3478, 3029, 2872, 1774, 1710, 1457, 1386, 1070, 748, 720, 697 cm^{-1}.

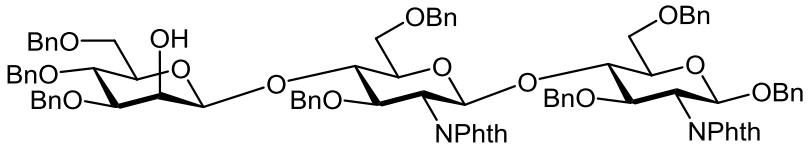
ESILRMS $[C_{27}H_{29}N_3O_5 + Na]^+$ calculated 1073.38, found 1073.60.

To a solution of alcohol **19** (525 mg, 0.5 mmol) and pyridine (0.8 mL, 20 mmol) in 2.5 mL methylene chloride cooled at 0^{o}C was added triflic anhydride (0.34 mL, 2.0 mmol) dropwise. The resulting mixture was stirred at 0°C for 3 hours and then quenched with ice water. The organic layer was separated and the aqueous layer was extracted with methylene chloride (3×50 mL). The combined organic layer was washed sequentially with saturated copper sulfate (3x50 mL) and water (3x50 mL), dried over anhydrous magnesium sulfate, filtered and concentrated. The residue was purified by silica gel column chromatography with methylene chloride to afford 540 mg (90%) of the sugar derived triflate **20** which is characterized below:

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.34 Hz, 1H, aromatic), 7.76 (dt, *J* = 0.92, 7.43 Hz, 1H, aromatic), 7.71 (dt, *J* = 0.92, 7.43 Hz, 1H, aromatic), 7.61 - 7.68 (m,

3H, aromatic), 7.37 - 7.42 (m, 2H, aromatic), 7.32 - 7.36 (m, 3H, aromatic), 7.26 - 7.29 (m, 5H, aromatic), 7.22 - 7.26 (m, 1H, aromatic), 6.88 - 7.06 (m, 16H, aromatic), 5.46 (d, J = 2.20 Hz, 1H, H-4'), 5.28 (d, J = 7.70 Hz, 1H, H-1'), 4.93 - 4.98 (m, 1H, H-1), 4.80 (d, J = 12.10 Hz, 1H, benzylic), 4.70 (t, J = 12.38 Hz, 2H, benzylic), 4.52 (d, J = 11.19 Hz, 1H, benzylic), 4.29 - 4.47 (m, 7H), 4.12 - 4.22 (m, 4H), 3.61 (dd, J = 5.50, 8.99 Hz, 1H, H-5'), 3.54 (dd, J = 5.32, 8.99 Hz, 1H, H-6'), 3.49 (d, J = 9.90 Hz, 1H, H-4), 3.39 - 3.44 (m, 1H, H-6'), 3.28 - 3.36 (m, 2H, H-3 and H-5 overlapping)

^{13}C NMR (150 MHz, $CDCl_3$) d 168.6, 167.4, 138.8, 138.7, 137.6, 137.4, 136.9, 134.5, 134.2, 134.0, 131.9, 131.7, 128.9, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.5, 127.3, 124.1, 123.5, 97.7, 97.4, 80.6, 76.8, 76.5, 74.7, 74.6, 74.0, 72.9, 72.5, 72.2, 71.2, 70.9, 68.3, 66.8, 56.0, 53.3



21

β-Mannoside **21** was prepared from 3,4,6-tri-*O*-benzyl-D-mannopyranose **1a** (50 mg, 0.11 mmol), sugar-derived triflate acceptor **20** (325 mg, 0.275 mmol), and Cs_2CO_3 (108 mg, 0.33 mmol) following the general procedure. The crude reaction mixture was purified by preparative thin layer chromatography (hexanes: EtOAc = 1:1) followed by another preparative thin layer chromatography (hexanes: EtOAc: CH_2Cl_2 = 2:1:1) to furnish 117 mg (72% yield) of β-mannoside **21** which is characterized below. For **21**, $J_{(C,H)}$ of mannosidic anomeric carbon was determined to be 159 Hz.

$[\alpha]_D^{21}$ = 8.0° (c = 0.2, $CHCl_3$).

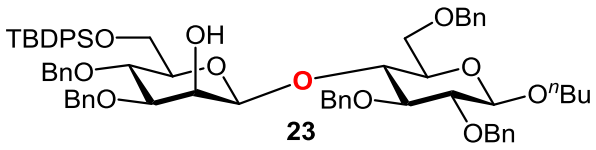
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, J = 6.97 Hz, 1H, aromatic), 7.59 - 7.75 (m, 5H, aromatic), 7.26 - 7.35 (m, 16H, aromatic), 7.12 - 7.23 (m, 8H, aromatic), 7.01 - 7.05 (m, 1H aromatic), 6.91 - 7.00 (m, 8H, aromatic), 6.70 - 6.83 (m, 6H, aromatic), 5.27 (d, J = 8.44 Hz, 1H, H-1'), 4.90 - 4.95 (m, 2H, H-1 and benzylic overlapping), 4.77 - 4.85 (m, 2H, benzylic), 4.59 - 4.70 (m, 3H, benzylic and H-1' overlapping), 4.43 - 4.57 (m, 9H), 4.33 - 4.43 (m, 4H), 4.14 - 4.27 (m, 3H), 4.06 - 4.13 (m, 2H), 4.01 (d, J = 2.93 Hz, 1H, H-2"), 3.84 (t, J = 9.44 Hz, 1H, H-4"), 3.62 - 3.70 (m, 3H), 3.57 - 3.63 (m, 2H, H-6"), 3.53 – 3.57 (m, 1H), 3.34 – 3.42 (m, 3H), 3.25 - 3.31 (m, 2H)

^{13}C NMR (150 MHz, $CDCl_3$) d 167.9, 139.0, 138.9, 138.7, 138.6, 138.6, 138.2, 138.2, 137.5, 128.8, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.3, 127.2, 100.7, 97.4, 97.2, 82.0, 78.9, 78.2, 76.6, 75.8, 75.7, 75.4, 75.2, 74.8, 74.8, 74.6, 74.3, 73.7, 73.6, 72.9, 71.7, 70.8, 69.3, 68.4, 68.3, 56.9, 56.0

FT-IR (thin film): 3483, 3030, 2867, 1775, 1713, 1496, 1453, 1387, 1074, 740, 721, 698 cm^{-1}.

ESILRMS $[C_{54}H_{57}N_3O_{10}+Na]^+$ calculated 1505.57, found 1506.10.

5. Anomeric *O*-alkylation of various D-mannopyranose type donors.



23

β-Mannoside **23** was prepared from 3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-D-mannopyranose **22** and sugar-derived triflate acceptor **6a** following the general procedure, except using 2.0 equivalents of triflate **6a** and 2.5 equivalents of cesium carbonate. The crude reaction mixture was purified by preparative thin layer chromatography (hexanes: EtOAc = 5:1) to furnish 43 mg (40% yield) of *β*-mannoside **23** which is characterized below. For **23**, $J_{(C,H)}$ of mannosidic anomeric carbon was determined to be 160 Hz.

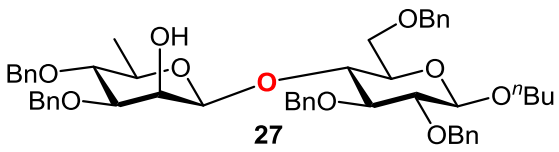
$[\alpha]_D^{21}$ = 126.2° (*c* = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 – 7.73 (m, 2H, aromatic), 7.61 – 7.67 (m, 2H, aromatic), 7.27 – 7.42 (m, 20H, aromatic), 7.20 – 7.26 (m, 4H, aromatic), 7.09 – 7.17 (m, 7H, aromatic), 4.92 (d, *J* = 10.9 Hz, 1H, benzylic), 4.87 (dd, *J* = 11.2, 6.2 Hz, 2H, benzylic), 4.79 (d, *J* = 11.6 Hz, 1H, benzylic), 4.69 (d, *J* = 10.9 Hz, 1H, benzylic), 4.52 – 4.64 (m, 5H), 4.47 (d, *J* = 11.9 Hz, 1H), 4.38 (d, *J* = 7.8 Hz, 1H, H-1), 3.91–4.01 (m, 4H), 3.63 – 3.80 (m, 5H), 3.48 – 3.56 (m, 2H), 3.45 (dd, *J* = 9.1, 7.8 Hz, 1H, H-2), 3.35 (dd, *J* = 9.2, 3.0 Hz, 1H, H-3'), 3.09 (ddd, *J* = 9.7, 4.2, 1.8 Hz, 1H, H-5'), 2.54 (s, 1H, OH), 1.64 (dp, *J* = 8.5, 6.7 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.34 – 1.51 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.01 (s, 9H, $C(CH_3)_3$), 0.94 (t, *J* = 7.4 Hz, 3H, $CH_2CH_2CH_2CH_3$).

^{13}C NMR (150 MHz, $CDCl_3$) δ 139.0, 138.7, 138.5, 138.3, 136.2, 136.0, 133.8, 133.5, 129.9, 129.9, 128.7, 128.7, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.6, 104.0, 99.9, 82.7, 82.5, 81.9, 76.9, 75.8, 75.5, 75.1, 74.9, 74.6, 73.9, 73.7, 71.4, 70.1, 69.4, 68.2, 63.1, 32.2, 27.2, 19.7, 19.6, 14.2

FT-IR (thin film): 3452, 3033, 2929, 2861, 1499, 1457, 1363, 1112, 1057, 738, 698 cm^{-1}.

ESIHRMS $[C_{67}H_{78}O_{11}Si + H]^+$ calculated 1087.5392, found 1089.5453.



27

β-Mannoside **27** was prepared from 3,4-di-*O*-benzyl-D-rhamnose **26** and sugar-derived triflate acceptor **6a** following the general procedure, except using 2.0 equivalents of triflate **6a** and 2.5 equivalents of cesium carbonate. The crude reaction mixture was purified by preparative thin layer chromatography (hexanes: EtOAc = 5:1) to furnish 25 mg (30% yield) of *β*-mannoside **27** which is characterized below. For **27**, $J_{(C,H)}$ of mannosidic anomeric carbon was determined to be 157 Hz.

$[\alpha]_D^{21}$ = 152.8° (*c* = 0.2, $CHCl_3$).

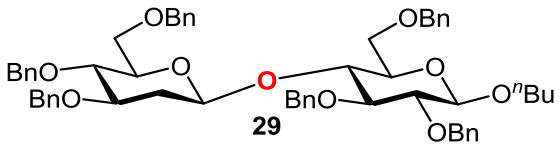
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 - 7.35 (m, 23H, aromatic), 7.25 (d, *J* = 6.97 Hz, 2H, aromatic), 4.84 - 4.95 (m, 4H,), 4.70 (d, *J* = 11.00 Hz, 1H), 4.61 - 4.67 (m, 2H), 4.58 (d, *J* = 10.82 Hz, 1H), 4.54 (dd, *J* = 3.85, 11.92 Hz, 2H), 4.44 (d, *J* = 11.92 Hz, 1H),

4.38 (d, *J* = 7.89 Hz, 1H, H-1), 3.88 - 3.99 (m, 3H), 3.71 - 3.80 (m, 2H, H-6), 3.66 (t, *J* = 9.08 Hz, 1H, H-3), 3.54 (td, *J* = 6.88, 9.54 Hz, 1H), 3.40 - 3.48 (m, 3H), 3.31 (dd, *J* = 3.12, 9.17 Hz, 1H, H-3'), 3.15 (qd, *J* = 6.11, 9.35 Hz, 1H, H-5'), 2.62 (d, *J* = 2.57 Hz, 1H, OH), 1.60 - 1.70 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.38 - 1.48 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.22 (d, *J* = 6.05 Hz, 3H, H-6'), 0.93 (t, *J* = 7.43 Hz, 3H, $CH_2CH_2CH_2CH_3$)

^{13}C NMR (150 MHz, $CDCl_3$) δ 139.0, 138.7, 138.7, 138.4, 138.3, 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 104.1, 100.1, 83.8, 82.4, 81.6, 79.7, 76.1, 75.8, 75.8, 75.2, 74.7, 73.8, 72.1, 71.4, 70.2, 69.4, 68.0, 32.2, 19.6, 18.2, 14.2

FT-IR (thin film): 3478, 3030, 2934, 2872, 1499, 1456, 1365, 1094, 1068, 741, 697 cm^{-1}.

ESIHRMS $[C_{51}H_{60}O_{10}+H]^+$ calculated 833.4265, found 833.4256.



29

β-Mannoside **29** was prepared from 3,4,6-tri-*O*-benzyl-2-deoxy-D-glucose **28** and sugar-derived triflate acceptor **6a** following the general procedure, except using 2.0 equivalents of triflate **6a** and 2.5 equivalents of cesium carbonate. The crude reaction mixture was purified by preparative thin layer chromatography (hexanes: EtOAc = 5:1) to furnish 59 mg (64% yield) of *β*-mannoside **29** which is characterized below:

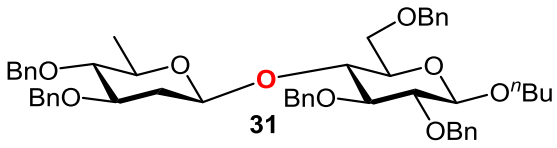
$[\alpha]_D^{21}$ = 23.9° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 - 7.35 (m, 22H, aromatic), 7.16 - 7.26 (m, 8H, aromatic), 5.00 (d, *J* = 11.19 Hz, 1H, benzylic), 4.90 (d, *J* = 10.82 Hz, 1H, benzylic), 4.79 - 4.87 (m, 2H, benzylic), 4.68 (d, *J* = 10.82 Hz, 1H, benzylic), 4.60 - 4.66 (m, 2H, benzylic and H-1' overlapping), 4.50 - 4.57 (m, 3H, benzylic), 4.38 - 4.49 (m, 3H, benzylic), 4.35 – 4.39 (d, 1H, H-1), 3.95 (td, *J* = 6.49, 9.40 Hz, 1H, $CH_2CH_2CH_2CH_3$), 3.86 (t, *J* = 9.35 Hz, 1H, H-4), 3.74 (dd, *J* = 2.11, 10.91 Hz, 1H, H-6), 3.68 (dd, *J* = 4.22, 11.00 Hz, 1H, H-6), 3.56 - 3.64 (m, 3H), 3.38 - 3.56 (m, 5H), 3.25 (td, *J* = 3.07, 9.26 Hz, 1H, H-5'), 2.25 (ddd, *J* = 1.83, 4.58, 12.47 Hz, 1H, H-2'), 1.61 - 1.70 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.50 - 1.57 (m, 1H, H-2'), 1.37 - 1.49 (m, 2H, $CH_2CH_2CH_2CH_3$), 0.94 (t, *J* = 7.43 Hz, 3H, $CH_2CH_2CH_2CH_3$)

^{13}C NMR (150 MHz, $CDCl_3$) δ 139.5, 138.8, 138.8, 138.7, 138.7, 138.5, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.3, 128.0, 128.0, 127.9, 127.9, 127.9, 127.7, 127.5, 104.0, 100.3, 83.6, 82.3, 79.6, 78.3, 76.6, 75.6, 75.5, 75.3, 74.9, 73.8, 73.6, 71.7, 70.1, 69.4, 69.2, 37.2, 32.2, 19.7, 14.2.

FT-IR (thin film): 3030, 2927, 2865, 1732, 1496, 1453, 1361, 1089, 1056, 734, 697 cm^{-1}.

ESIHRMS $[C_{58}H_{66}O_{10}+Na]^+$ calculated 945.4548, found 945.4581.



31

β-Mannoside **31** was prepared from 3,4-di-*O*-benzyl-D-olivose **30** and sugar-derived triflate acceptor **6a** following the general procedure, except using 2.0 equivalents of triflate **6a** and 2.5 equivalents of cesium carbonate. The crude reaction mixture was purified by preparative thin layer chromatography (hexanes: EtOAc = 5:1) to furnish 12 mg (15% yield) of *β*-mannoside **31** which is characterized below:

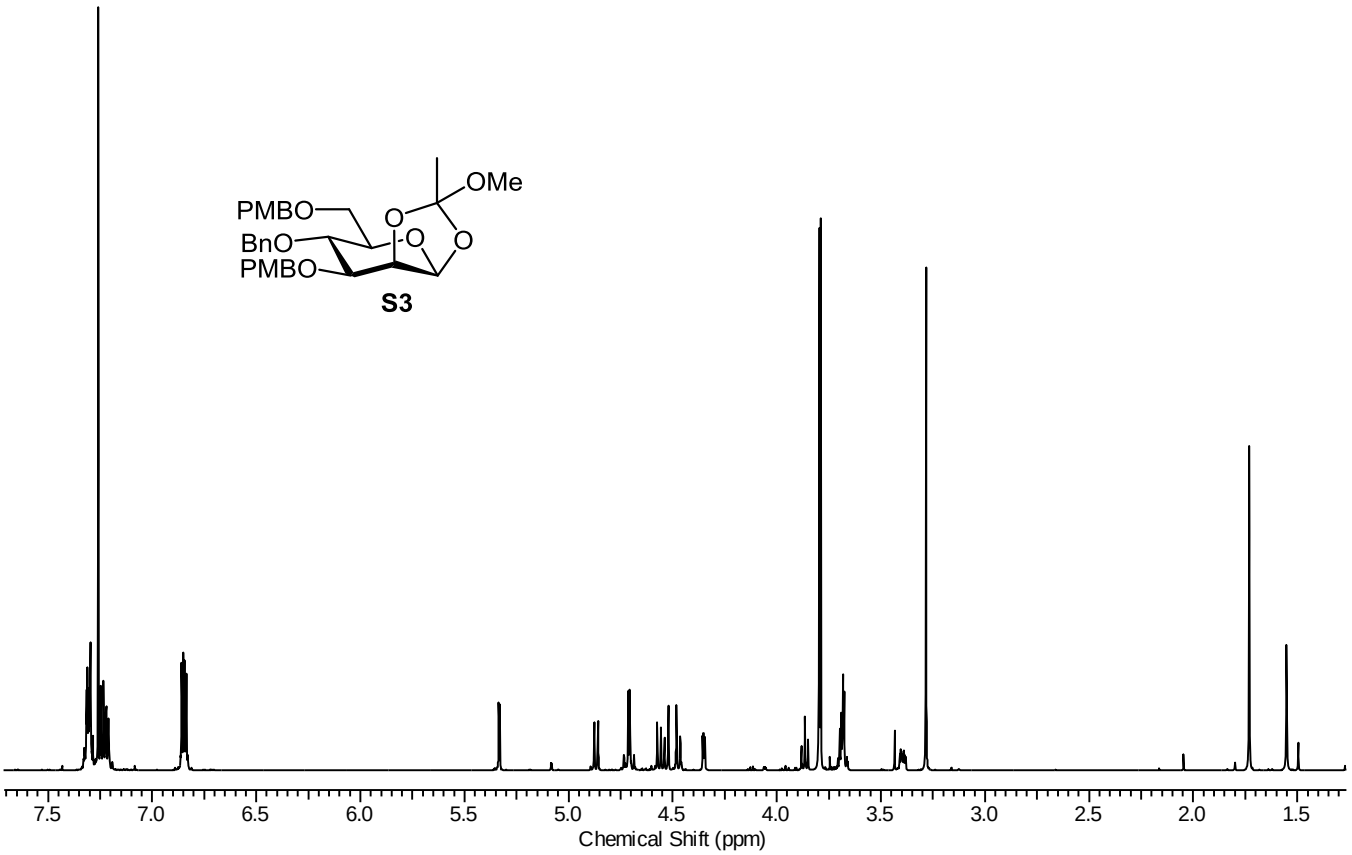
$[\alpha]_D^{21}$ = 135.3° (*c* = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 - 7.37 (m, 23H, aromatic), 7.22 - 7.26 (m, 2H, aromatic), 4.94 (d, *J* = 10.64 Hz, 1H, benzylic), 4.90 (d, *J* = 10.82 Hz, 2H, benzylic), 4.81 (d, *J* = 10.82 Hz, 1H, benzylic), 4.58 - 4.71 (m, 4H, benzylic and H-1' overlapping), 4.50 - 4.57 (m, 2H, benzylic), 4.43 - 4.48 (m, 1H, benzylic), 4.37 (d, *J* = 7.89 Hz, 1H, H-1), 3.95 (td, *J* = 6.51, 9.54 Hz, 1H, $CH_2CH_2CH_2CH_3$), 3.84 (t, *J* = 9.35 Hz, 1H, H-4), 3.73 (dd, *J* = 2.11, 10.91 Hz, 1H, H-6), 3.68 (dd, *J* = 4.22, 10.82 Hz, 1H, H-6), 3.51 - 3.61 (m, 2H), 3.38 - 3.48 (m, 3H), 3.19 (qd, *J* = 6.07, 9.31 Hz, 1H, H-5'), 3.06 (t, *J* = 8.99 Hz, 1H, H-4'), 2.25 (ddd, *J* = 2.02, 4.95, 12.47 Hz, 1H, H-2'), 1.59 - 1.69 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.36 - 1.53 (m, 3H, $CH_2CH_2CH_2CH_3$ and H-2' overlapping), 1.21 (d, *J* = 6.05 Hz, 3H, H-6'), 0.93 (t, *J* = 7.43 Hz, 3H, $CH_2CH_2CH_2CH_3$)

^{13}C NMR (150 MHz, $CDCl_3$) δ 139.3, 138.8, 138.8, 138.7, 138.5, 128.7, 128.7, 128.7, 128.5, 128.5, 128.4, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.7, 104.0, 100.1, 84.0, 83.8, 82.3, 79.4, 76.6, 75.7, 75.6, 75.3, 75.0, 73.8, 71.8, 71.6, 70.1, 69.2, 37.5, 32.2, 19.6, 18.5, 14.2

FT-IR (thin film): 3028, 2958, 2934, 2870, 1496, 1453, 1363, 1094, 1073, 735, 697 cm^{-1}.

ESIHRMS $[C_{51}H_{60}O_9 + Na]^+$ calculated 839.4130, found 839.4165.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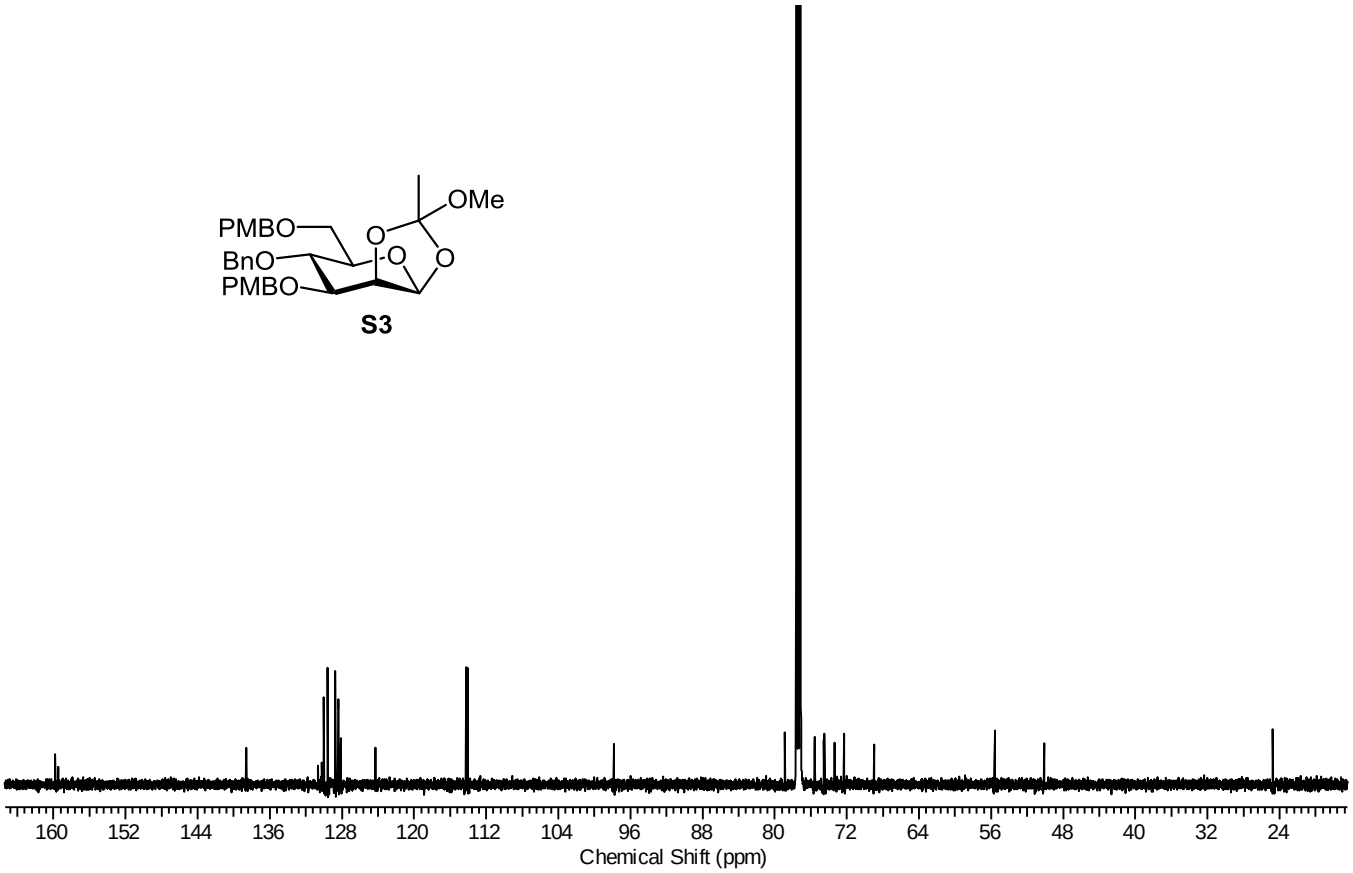
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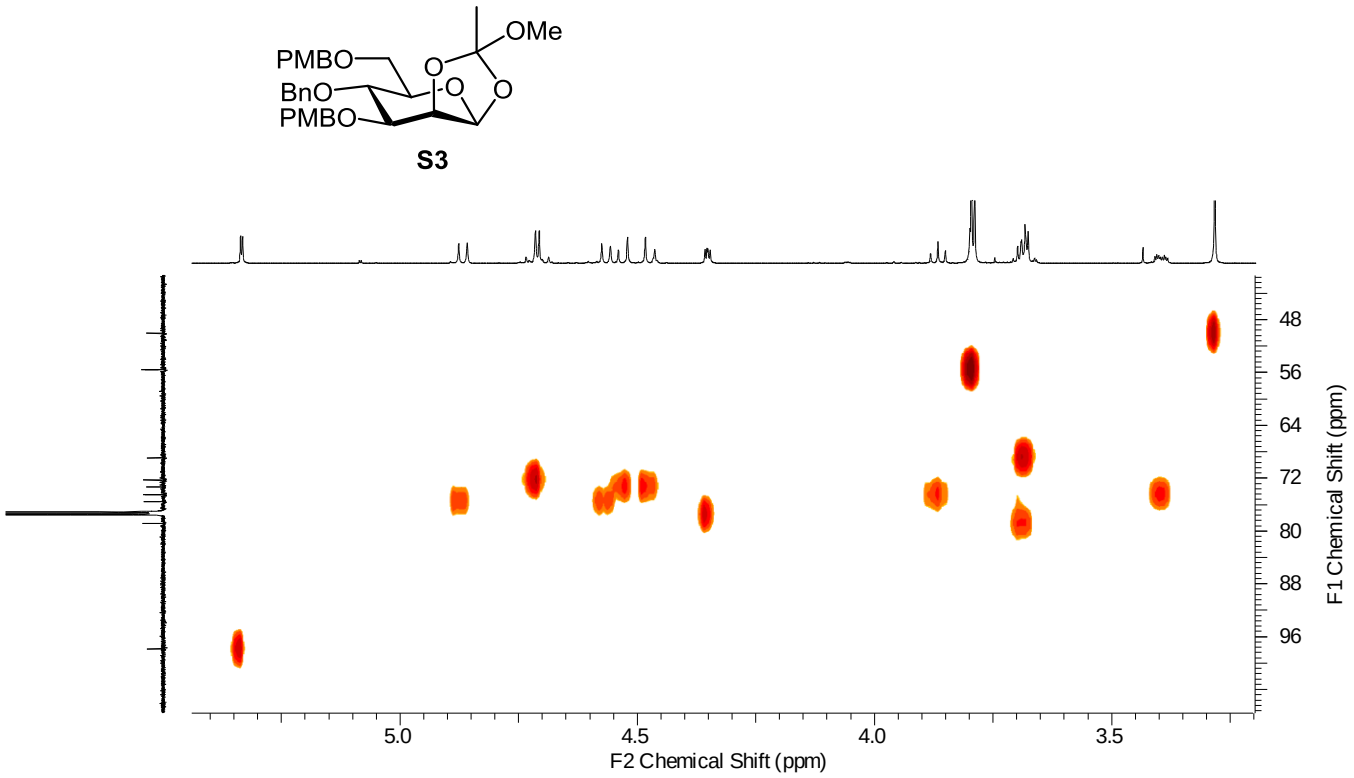
Chemical Shift (ppm)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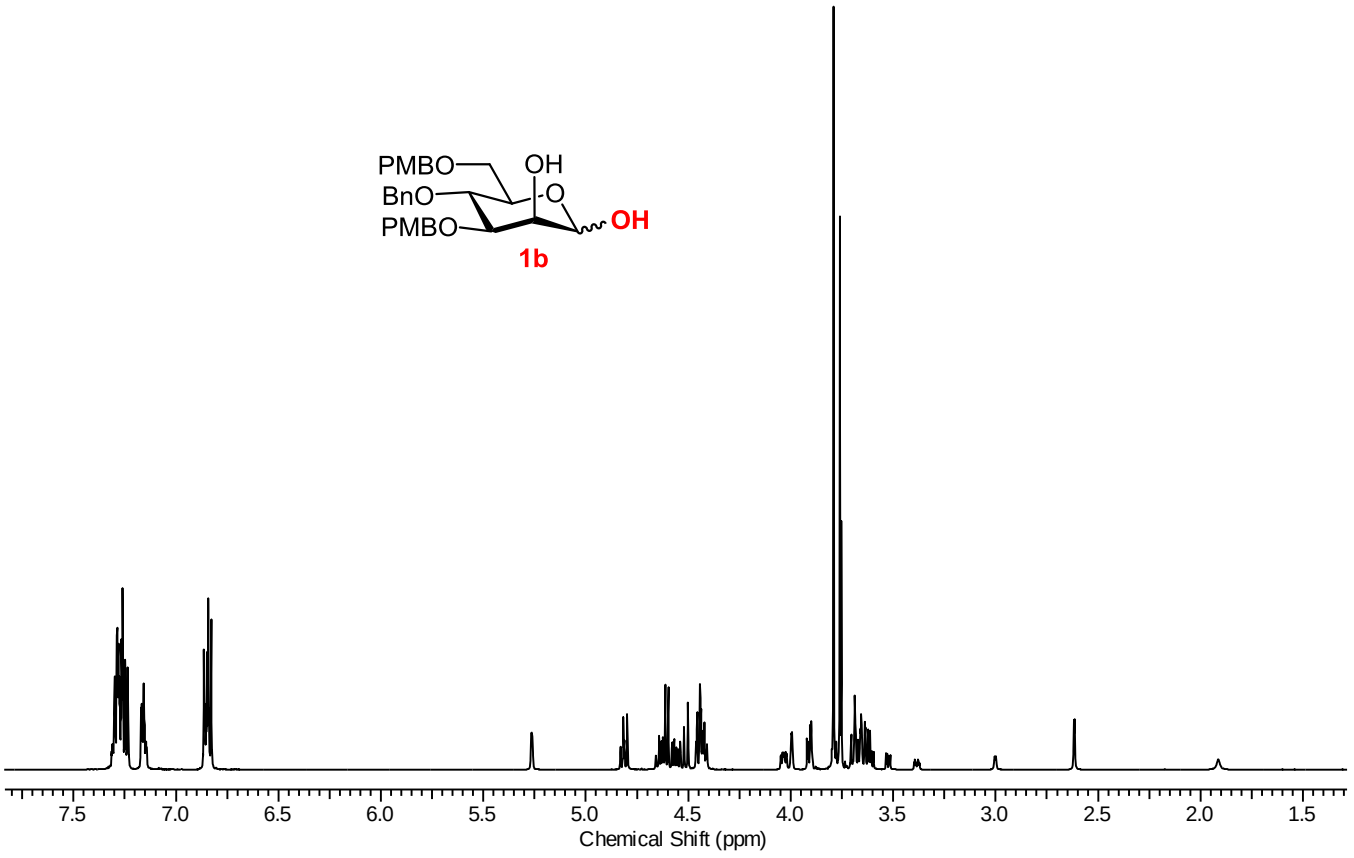
F2 Chemical Shift (ppm)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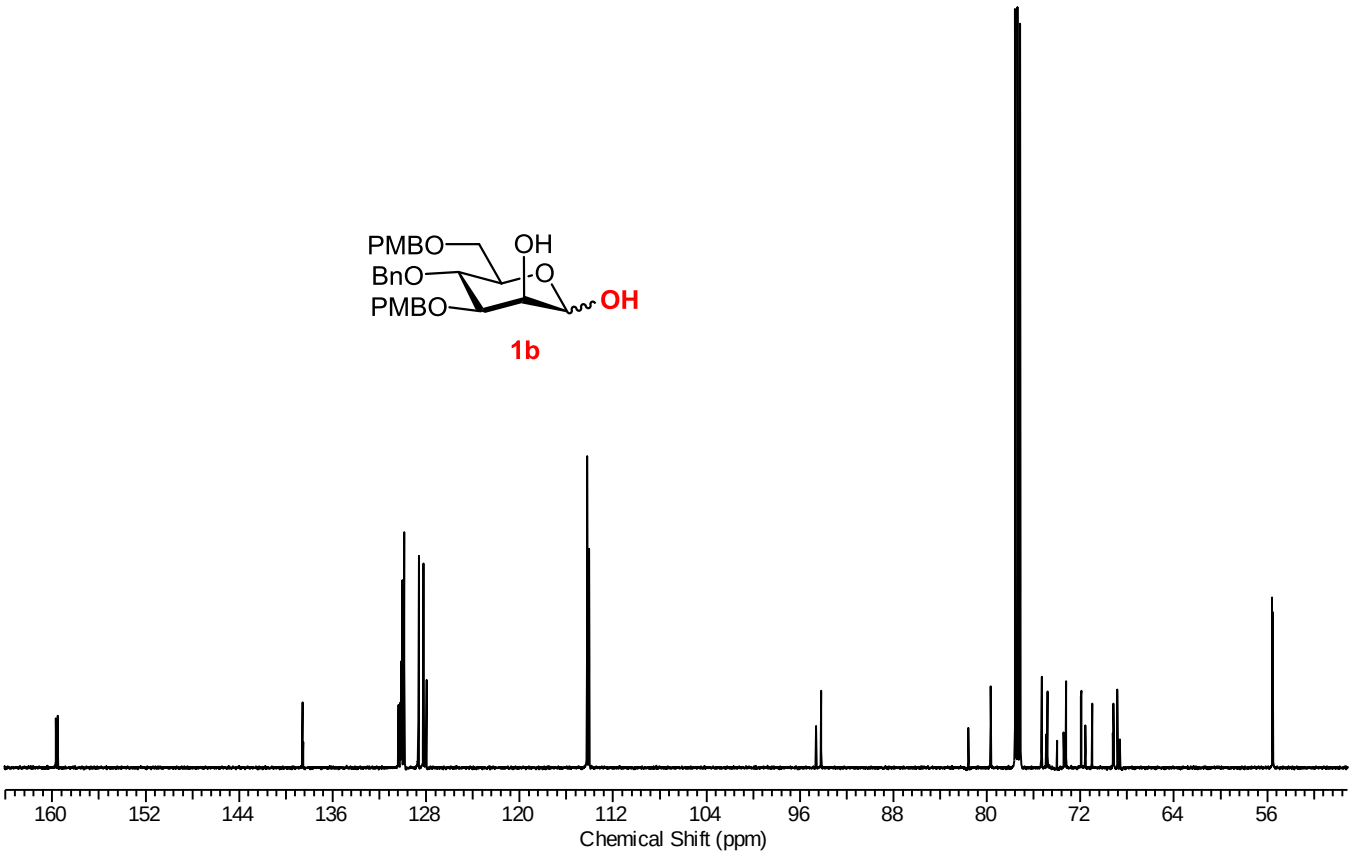
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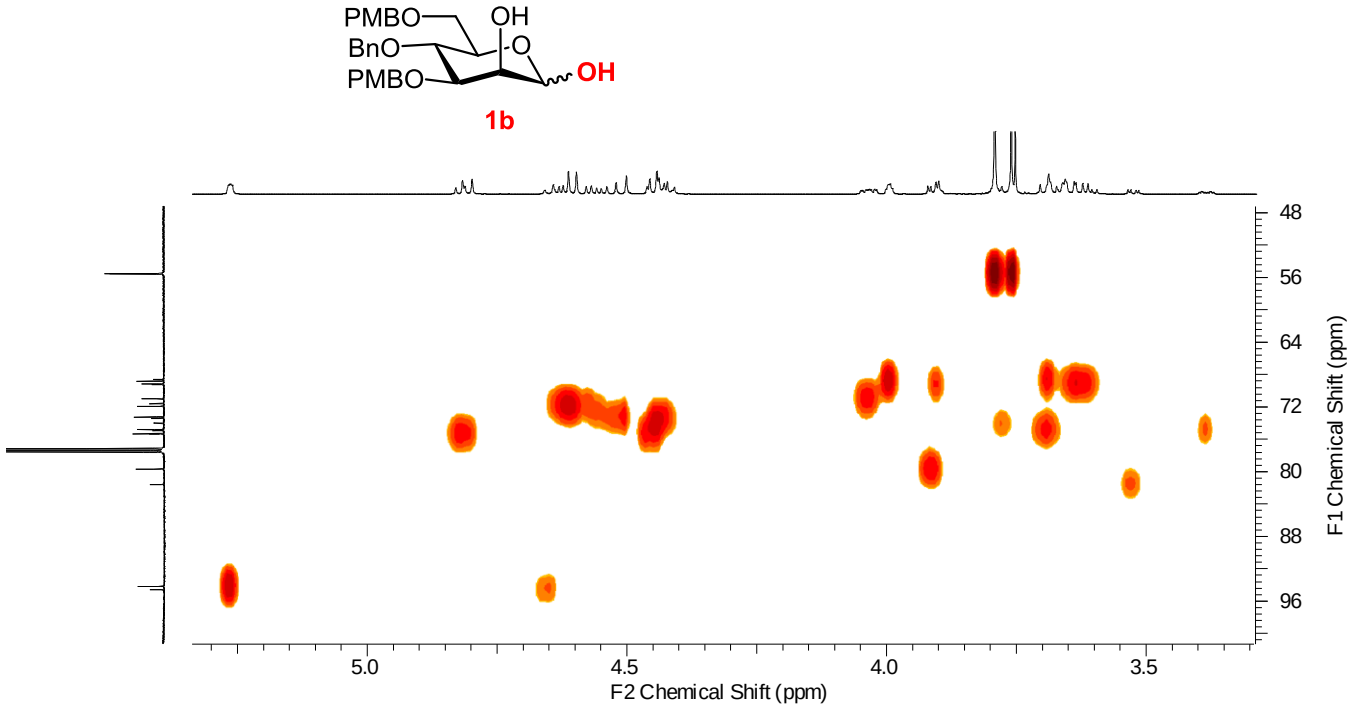
Chemical Shift (ppm)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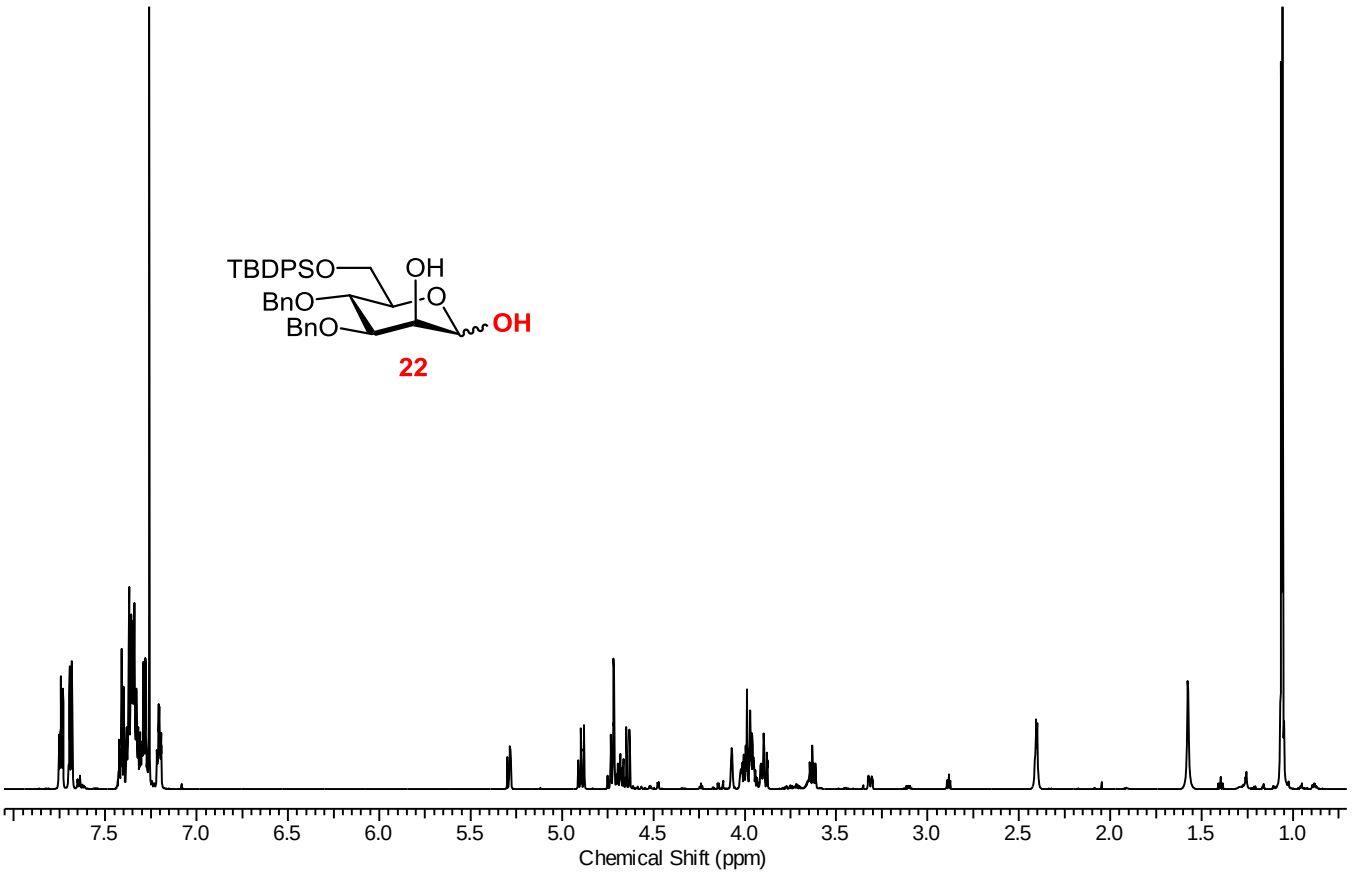
F2 Chemical Shift (ppm)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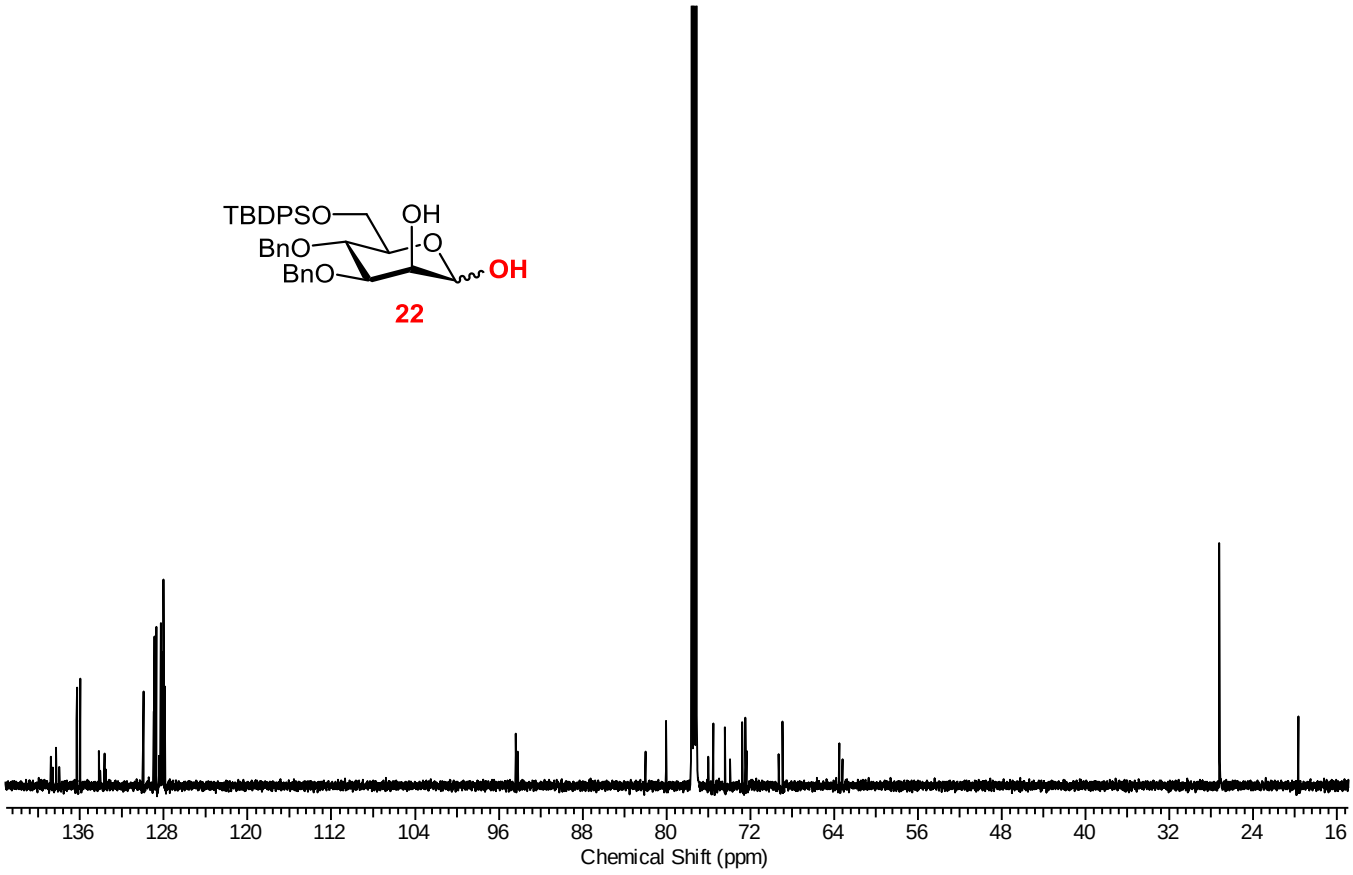
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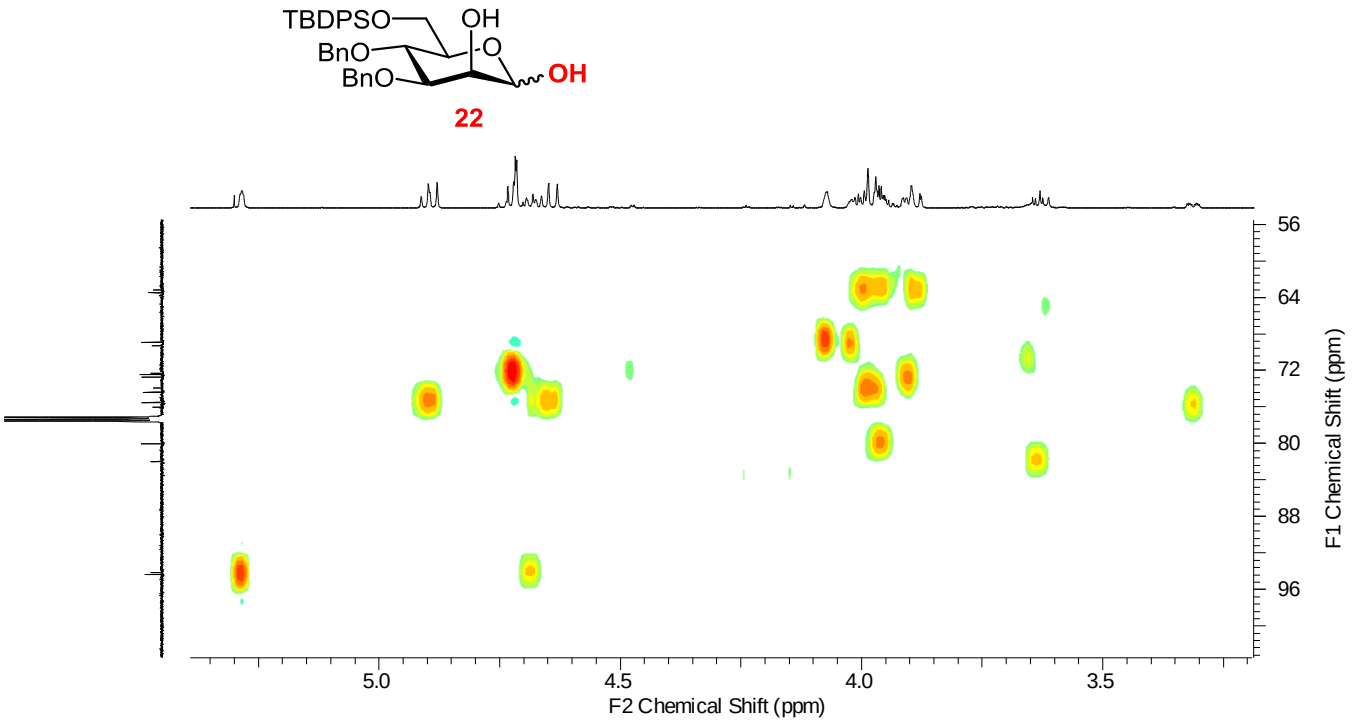
Chemical Shift (ppm)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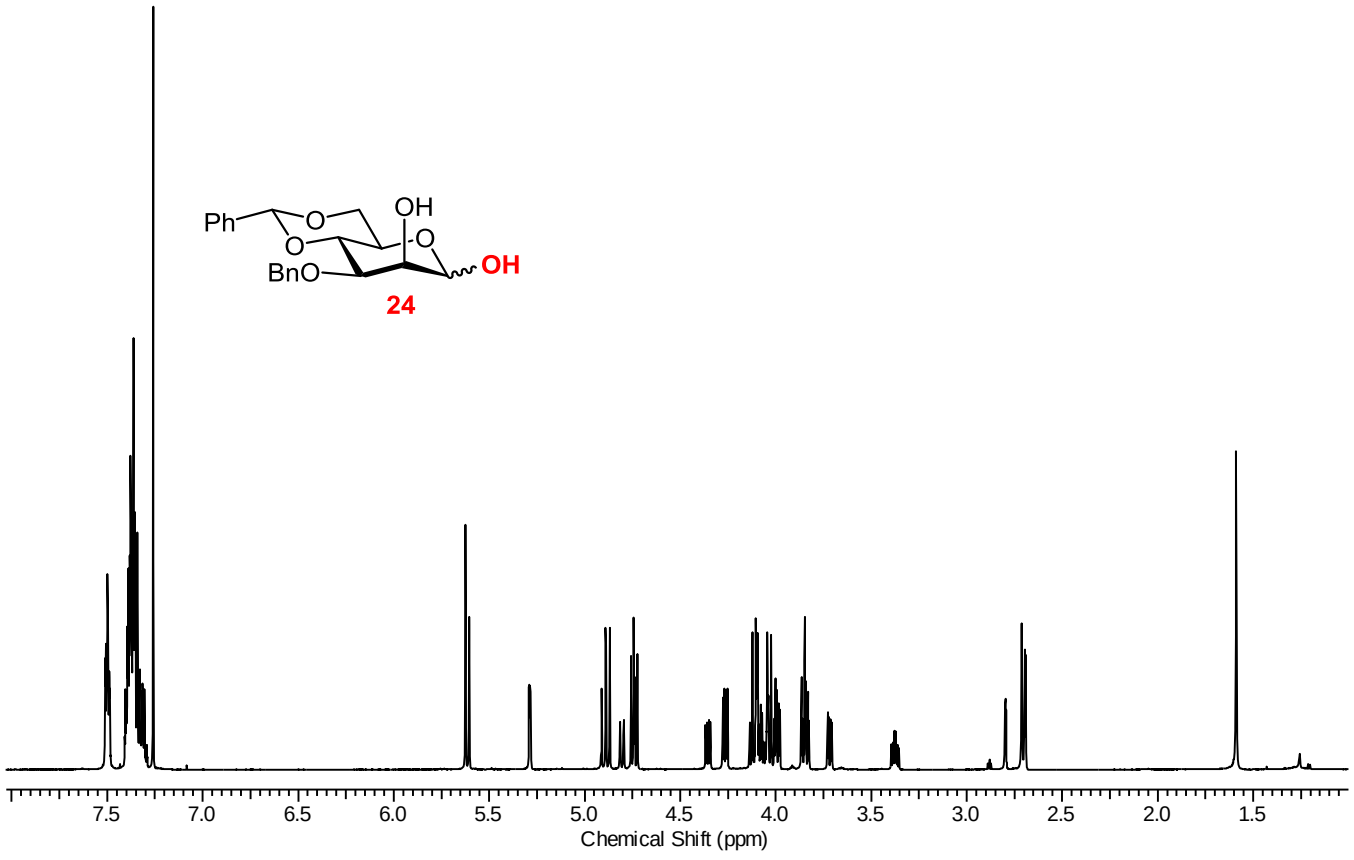
F2 Chemical Shift (ppm)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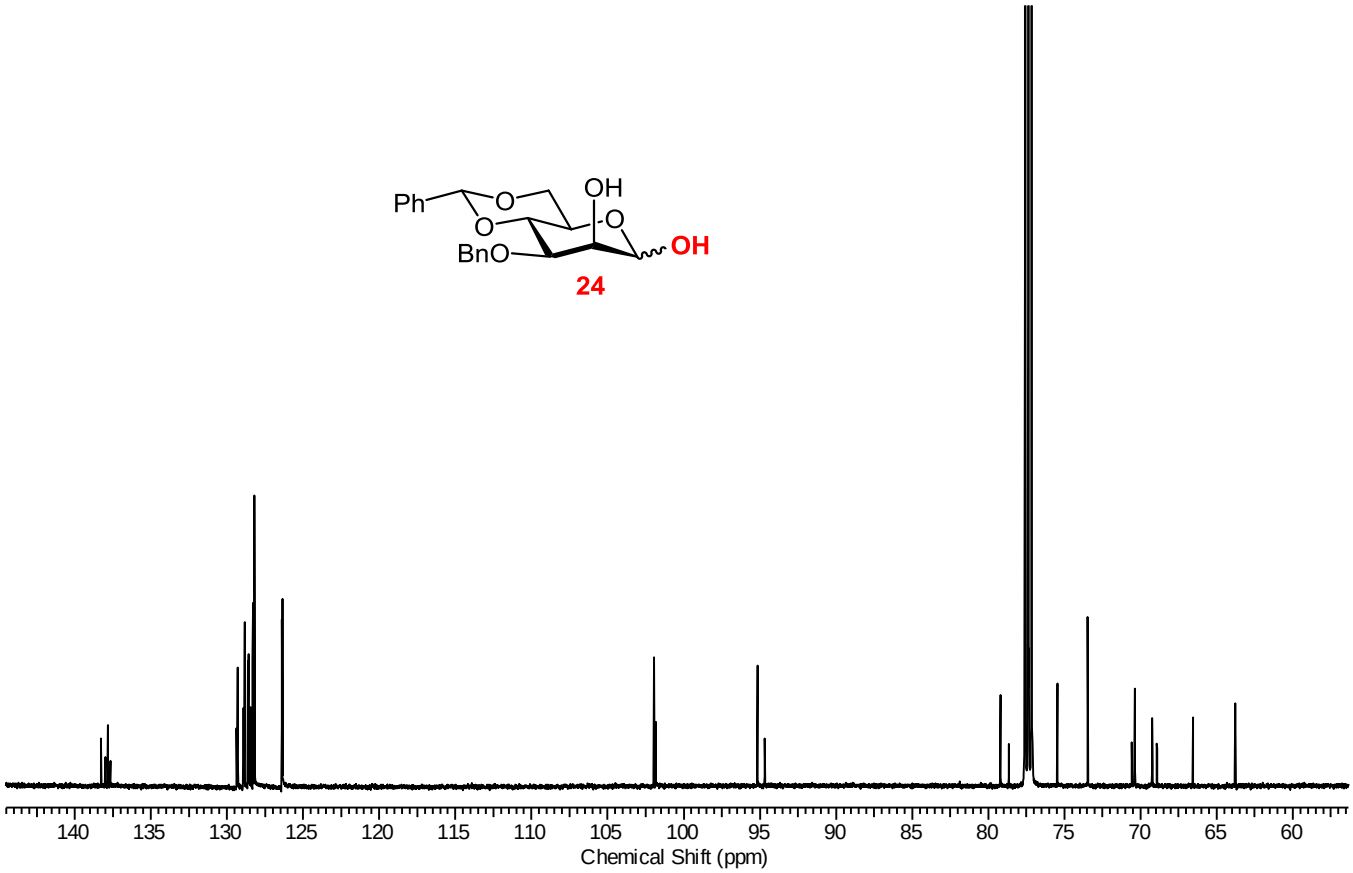
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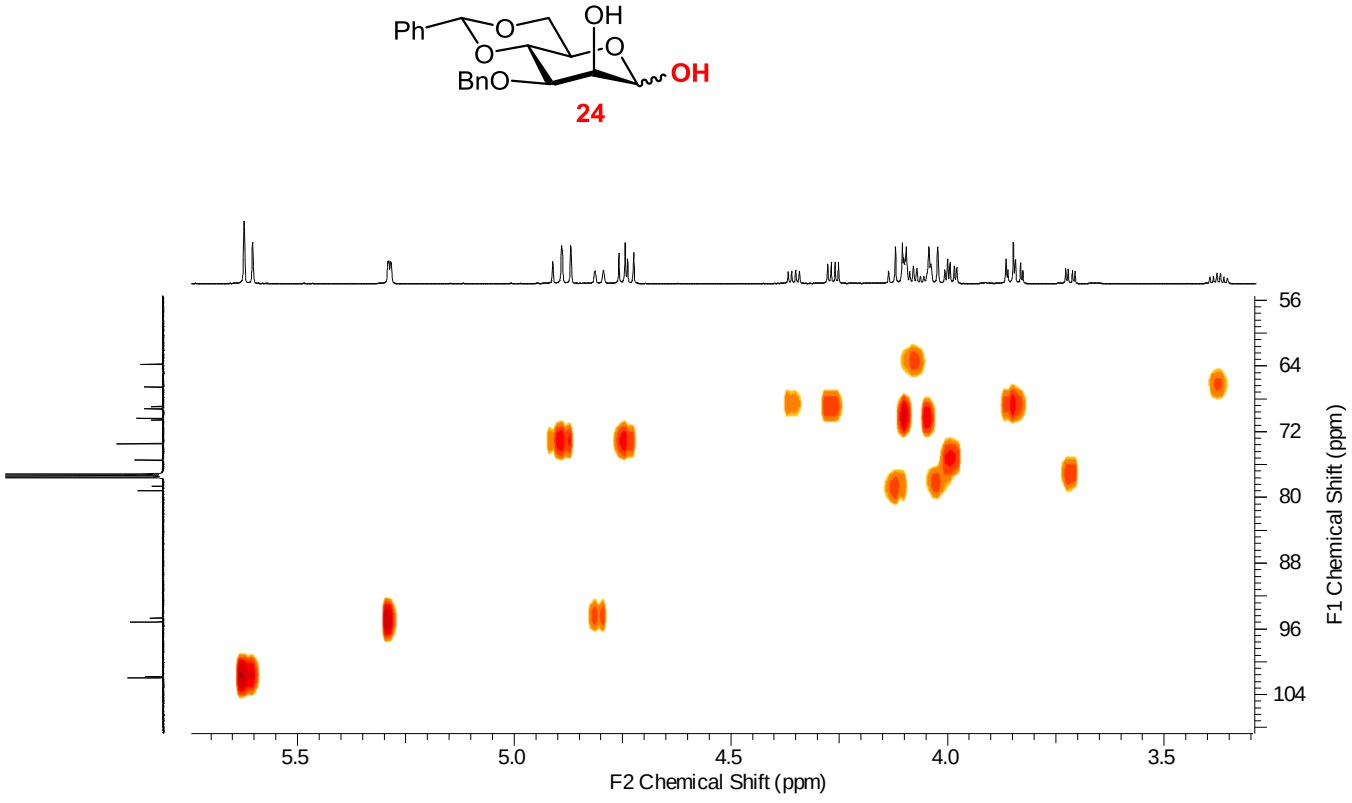
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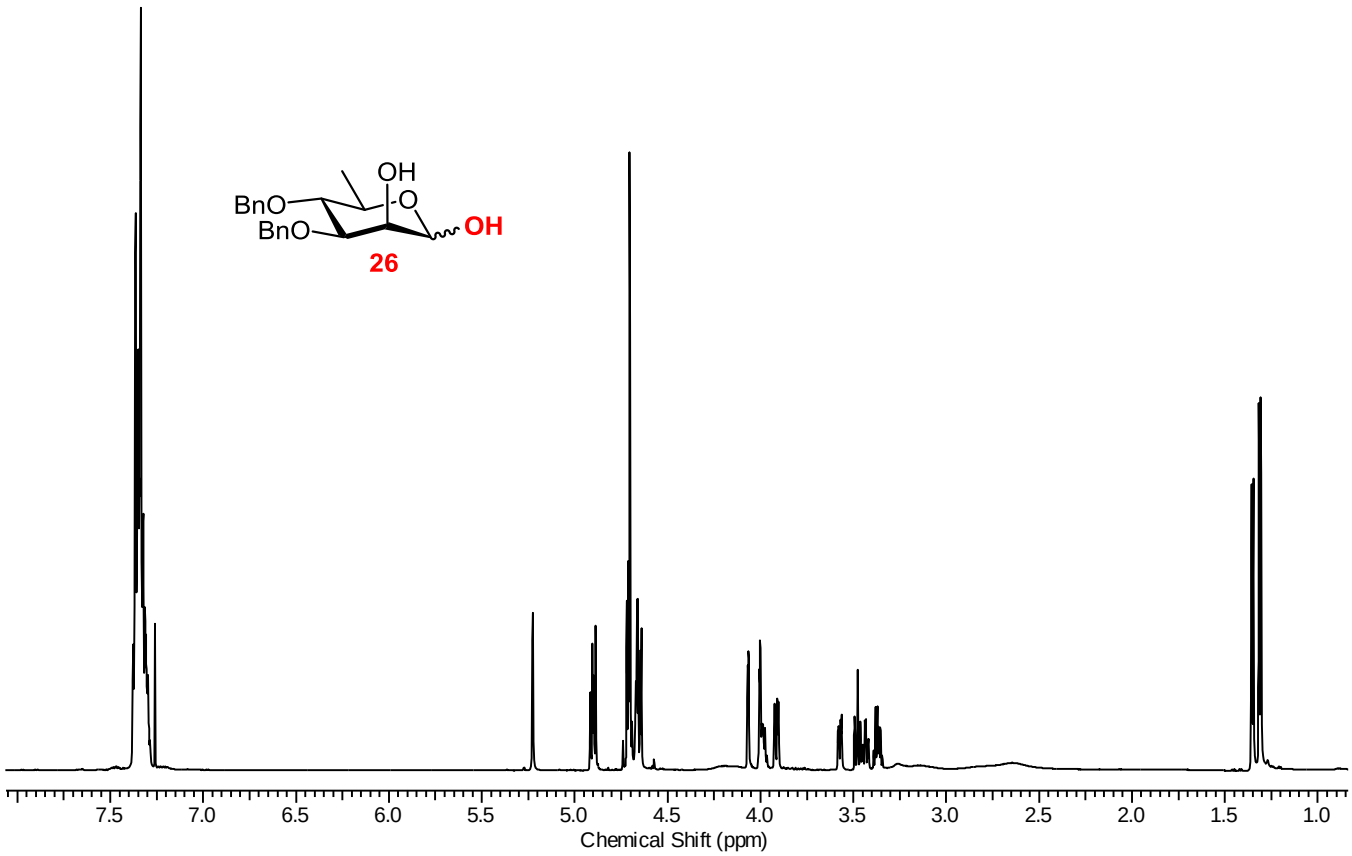
F2 Chemical Shift (ppm)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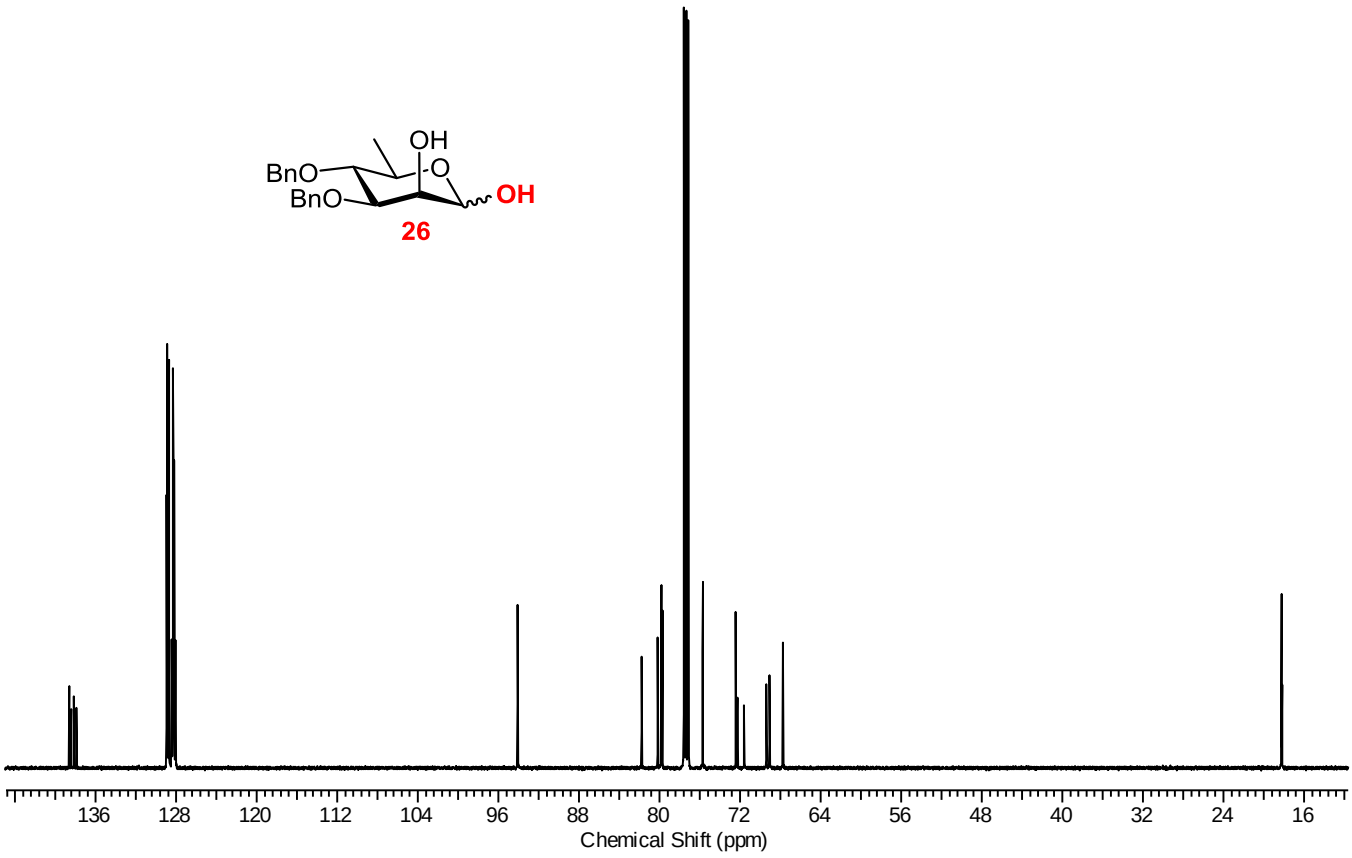
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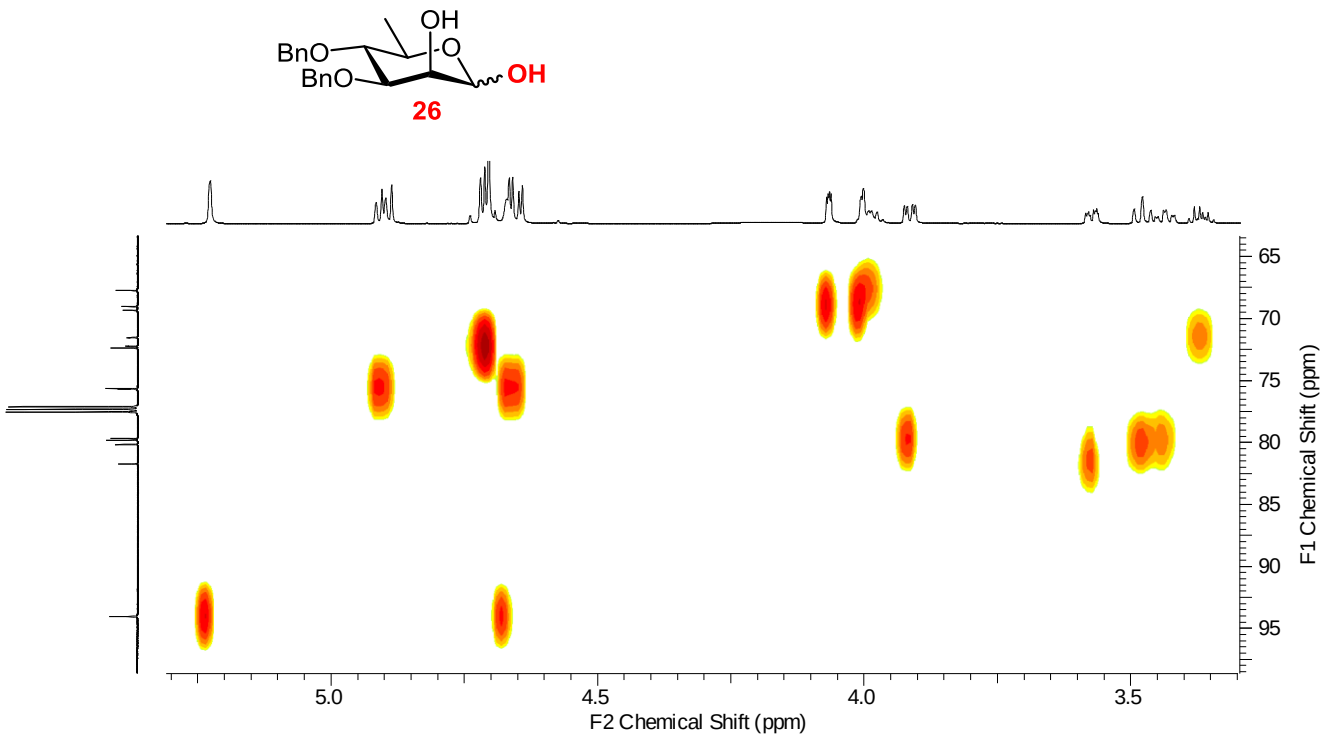
Chemical Shift (ppm)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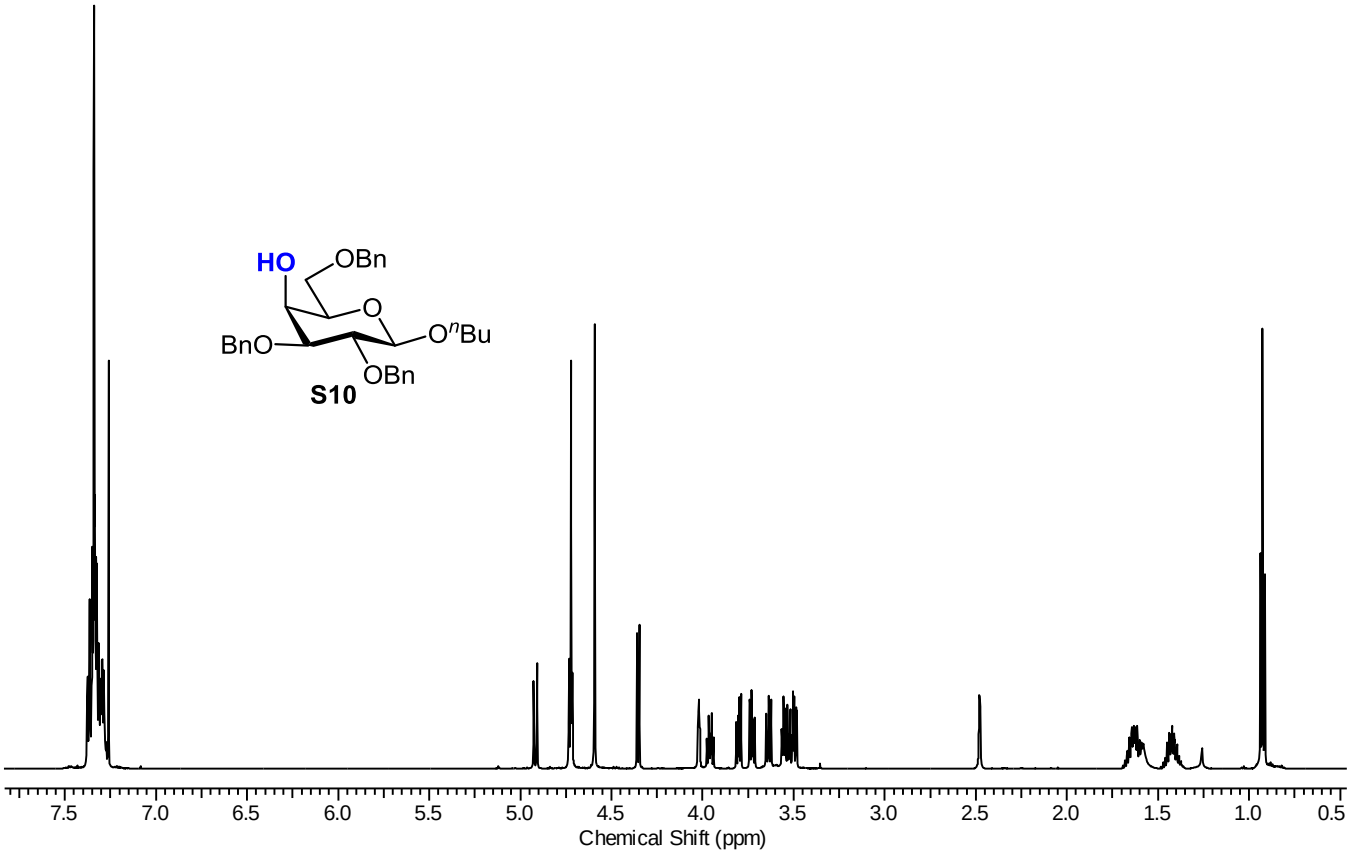
F2 Chemical Shift (ppm)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BnO
O^{n}Bu
OBn
S10
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1.5
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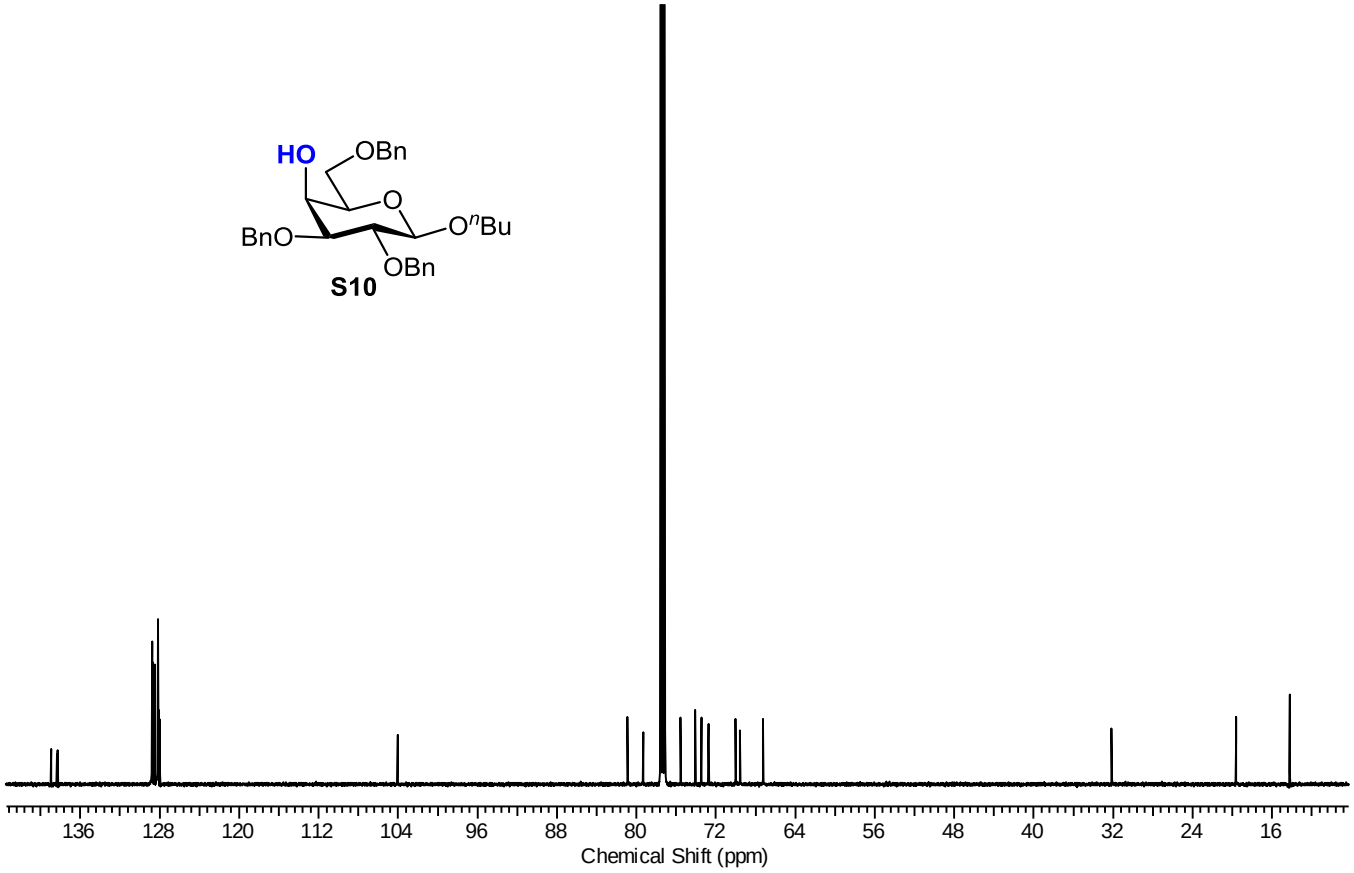
Chemical Shift (ppm)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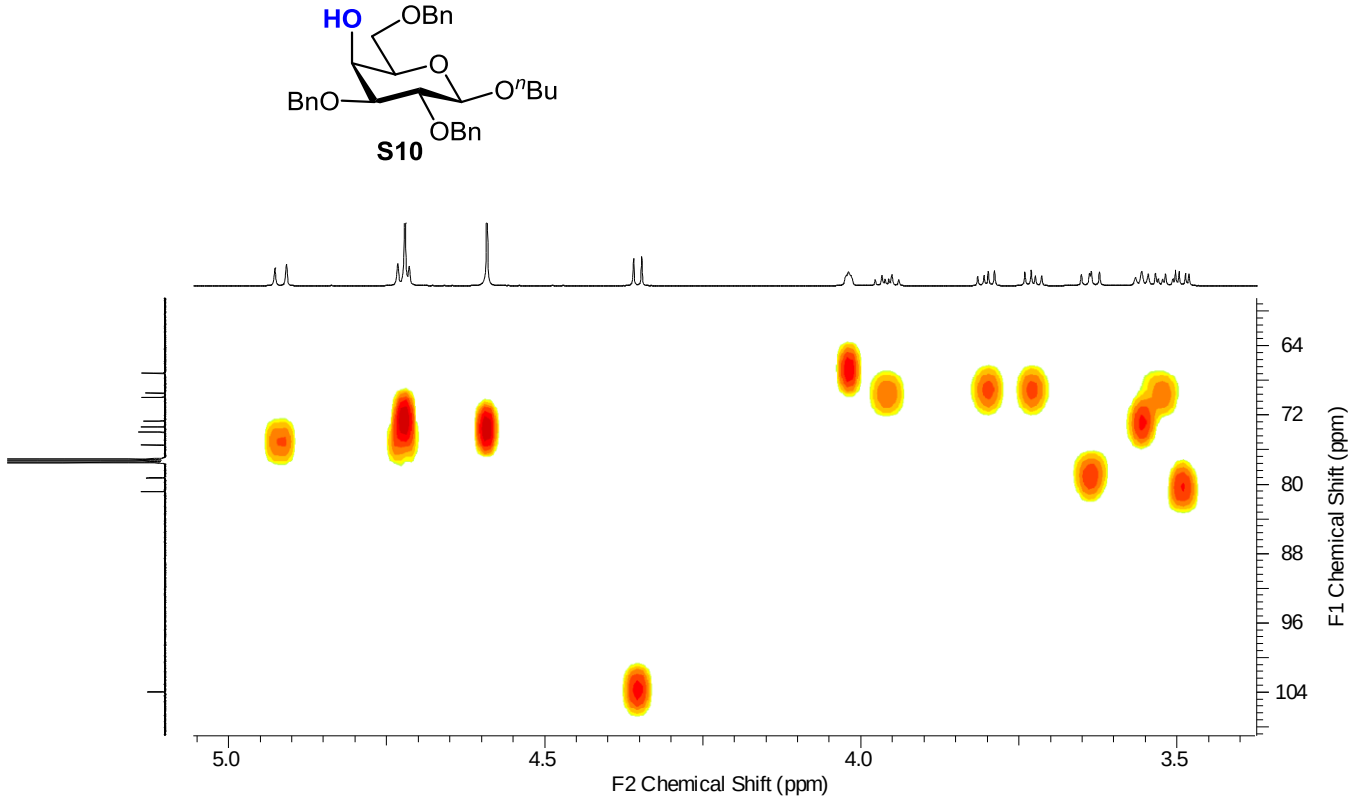
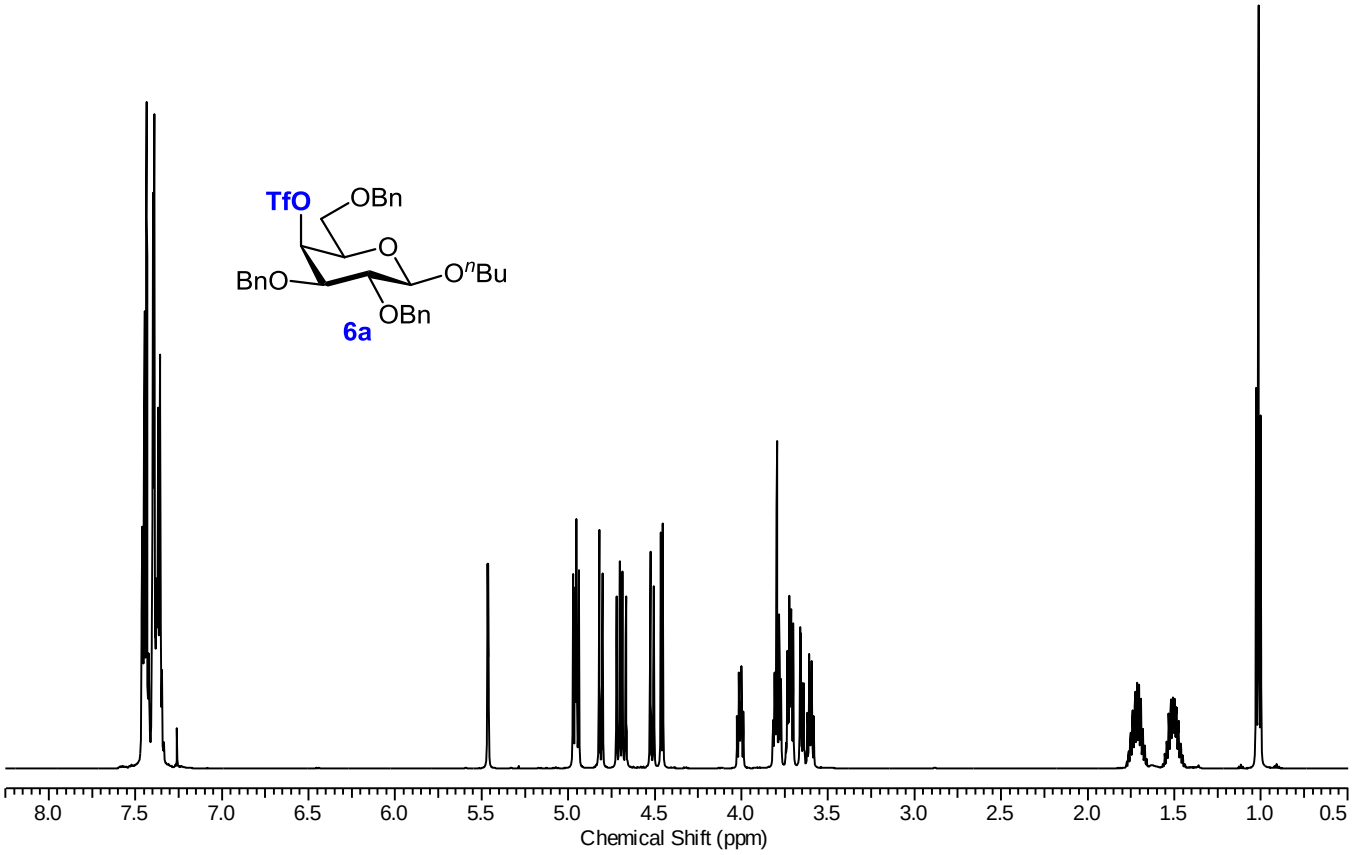
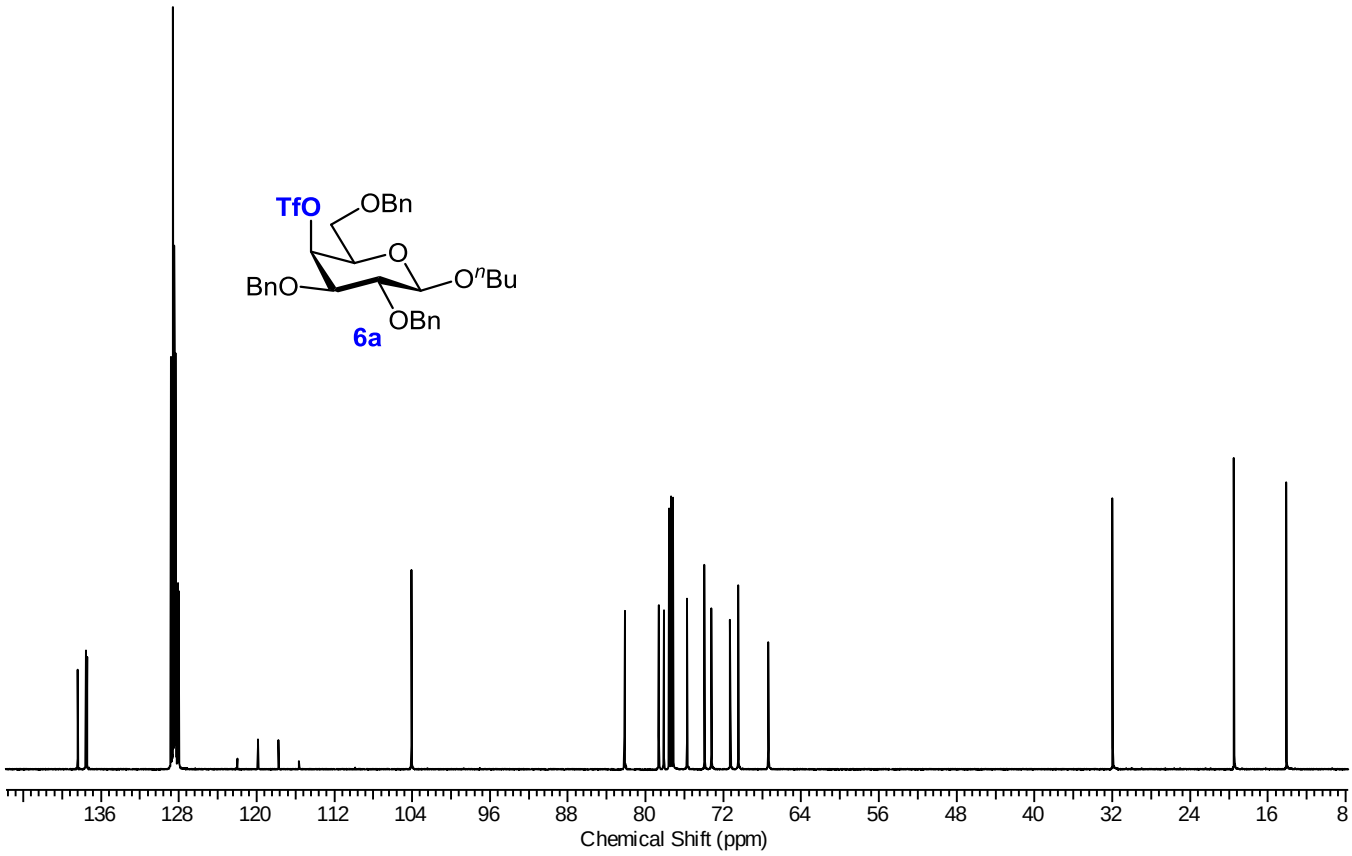
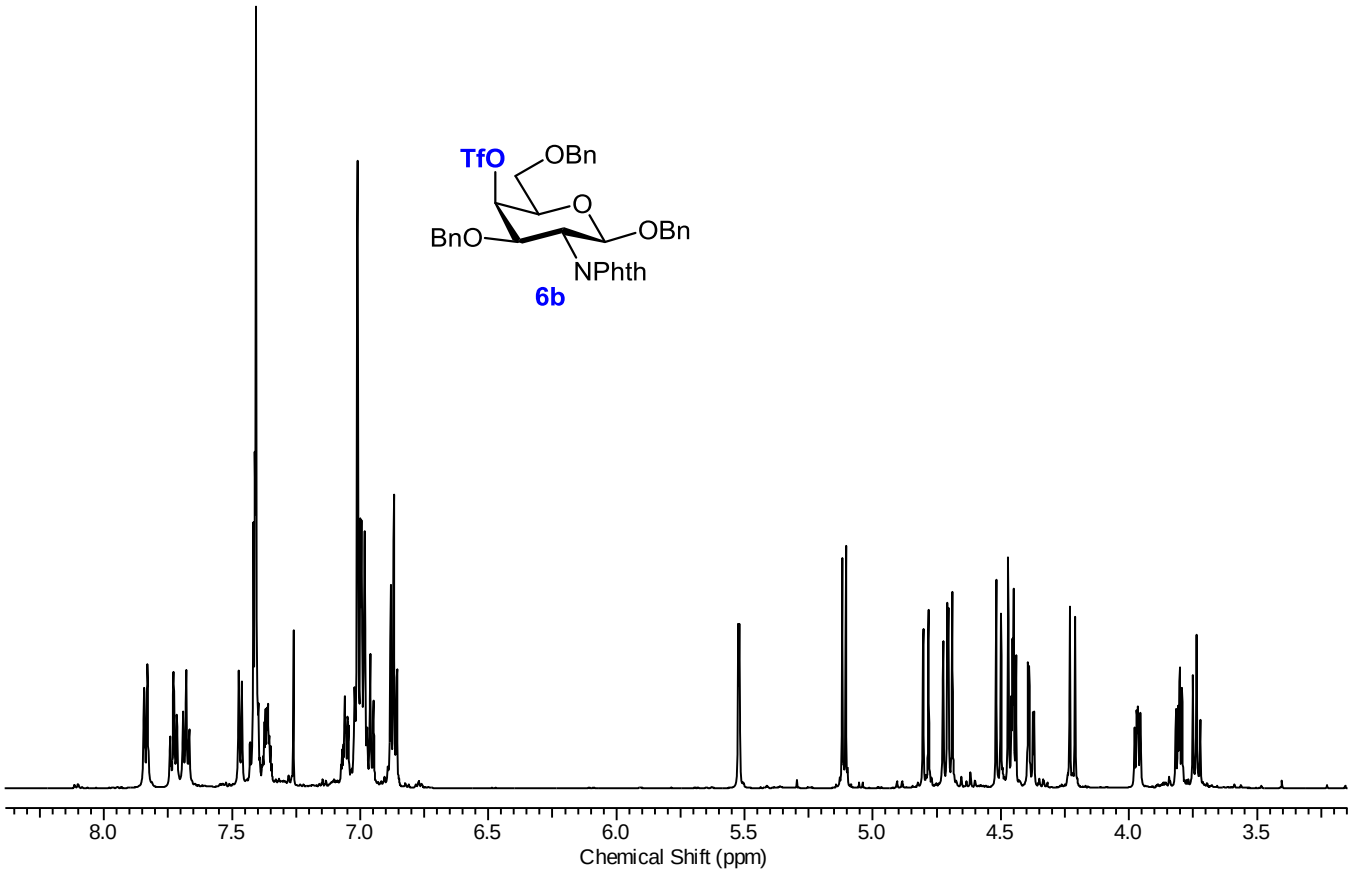
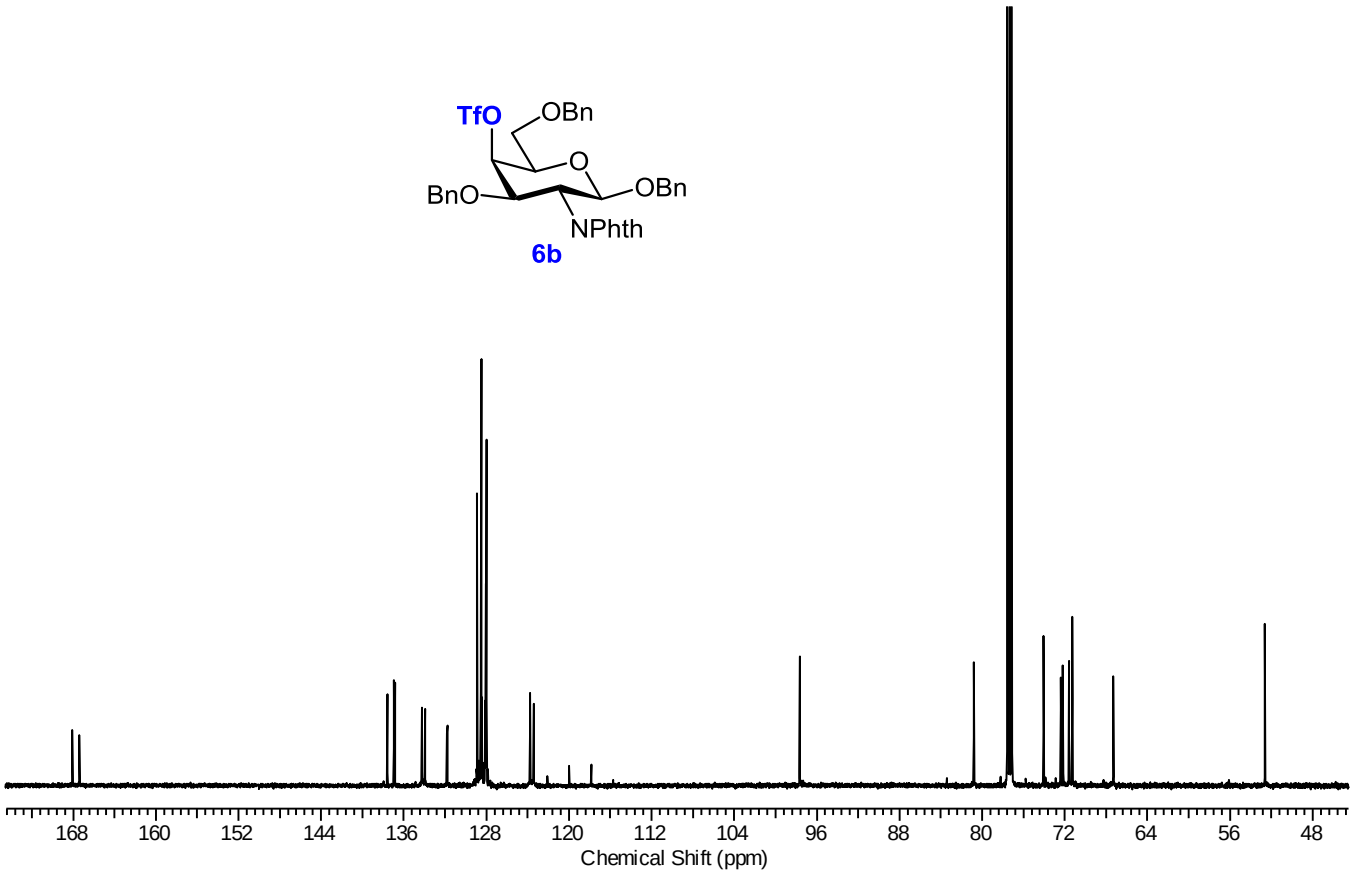
24
16
Chemical Shift (ppm)

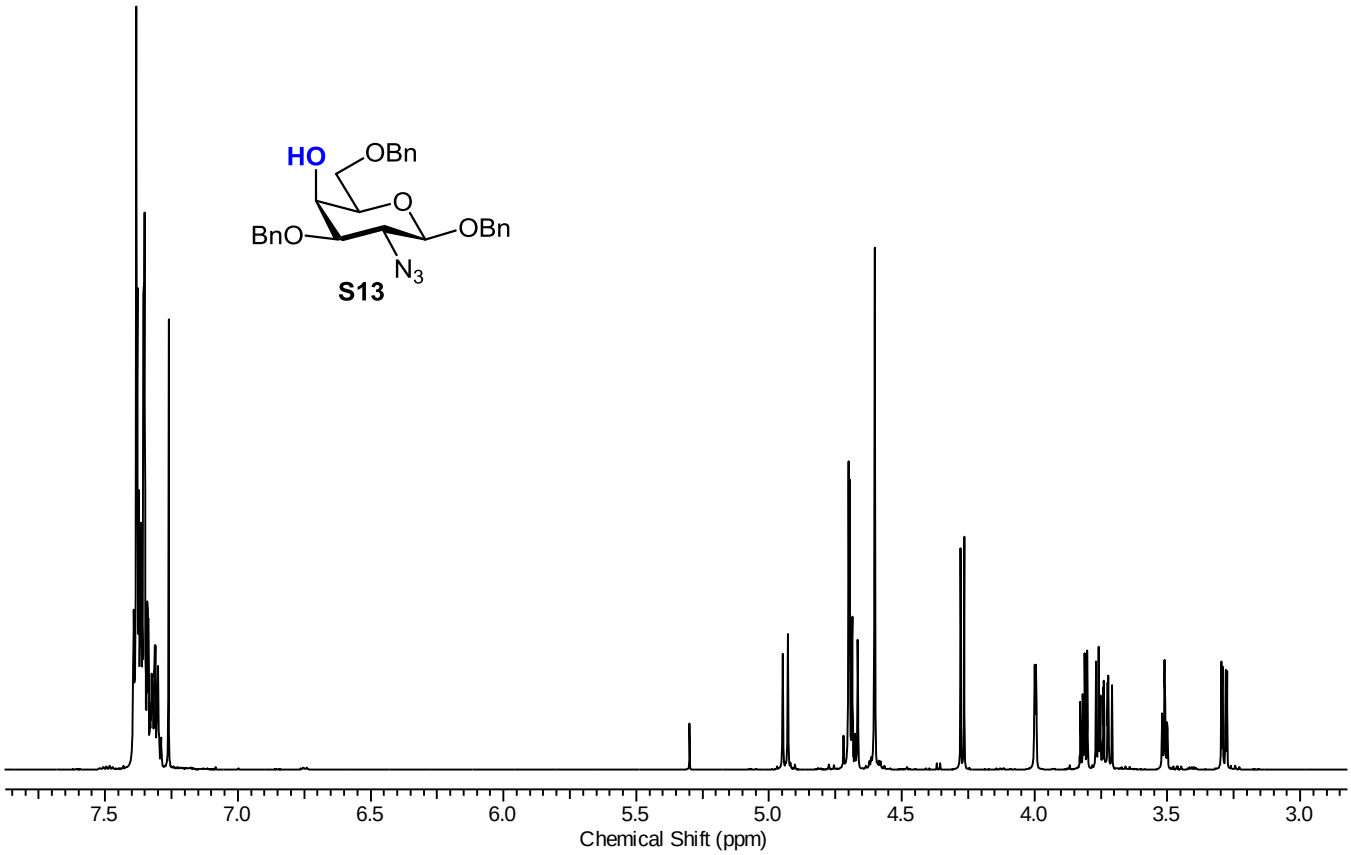

HO
OBn
O
O^{n}Bu
BnO
OBn
S10
5.0
4.5
4.0
3.5
F2 Chemical Shift (ppm)
64
72
80
88
96
104
F1 Chemical Shift (ppm)

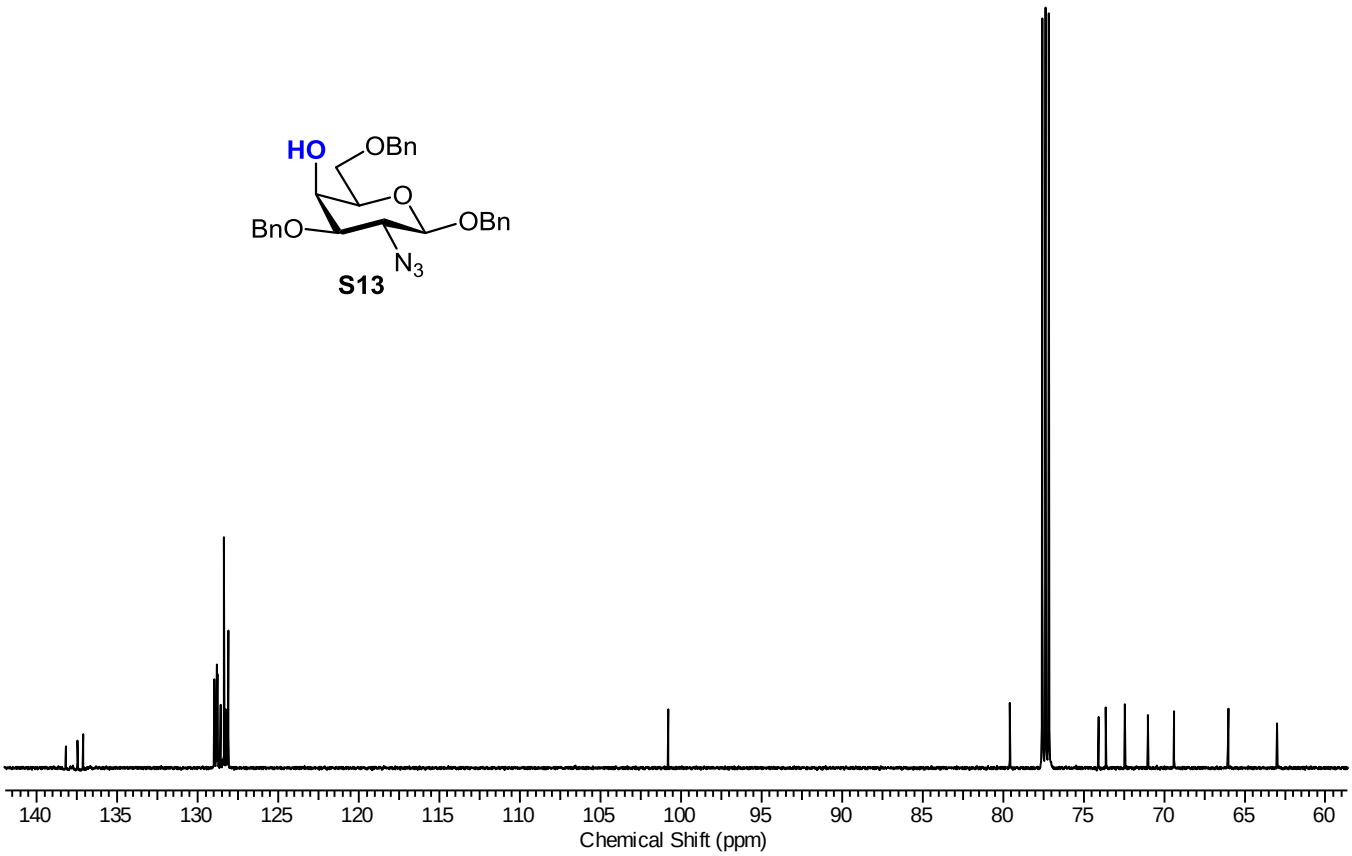

TfO
OBn
O
BnO
O^{n}Bu
OBn
6a
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

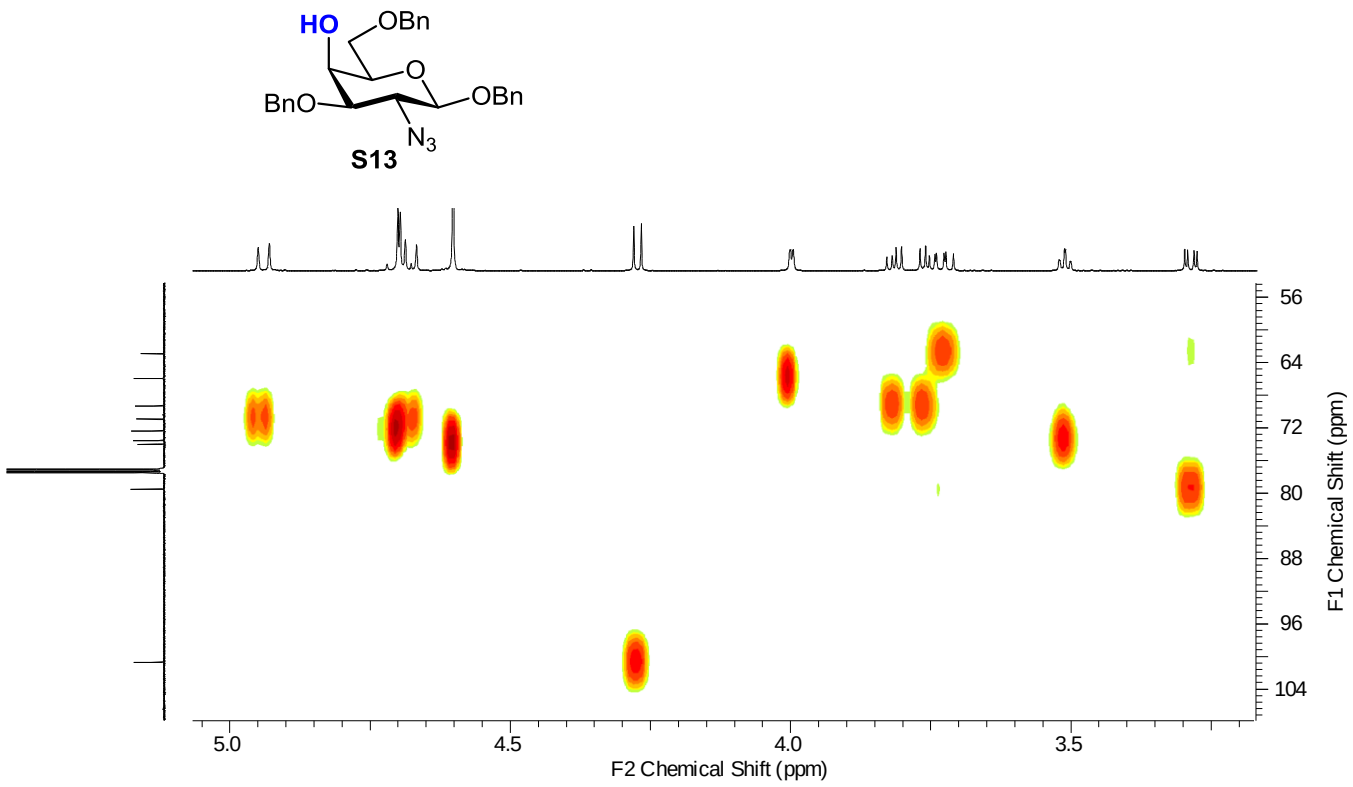

TfO
OBn
O
BnO
O^{n}Bu
OBn
6a
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

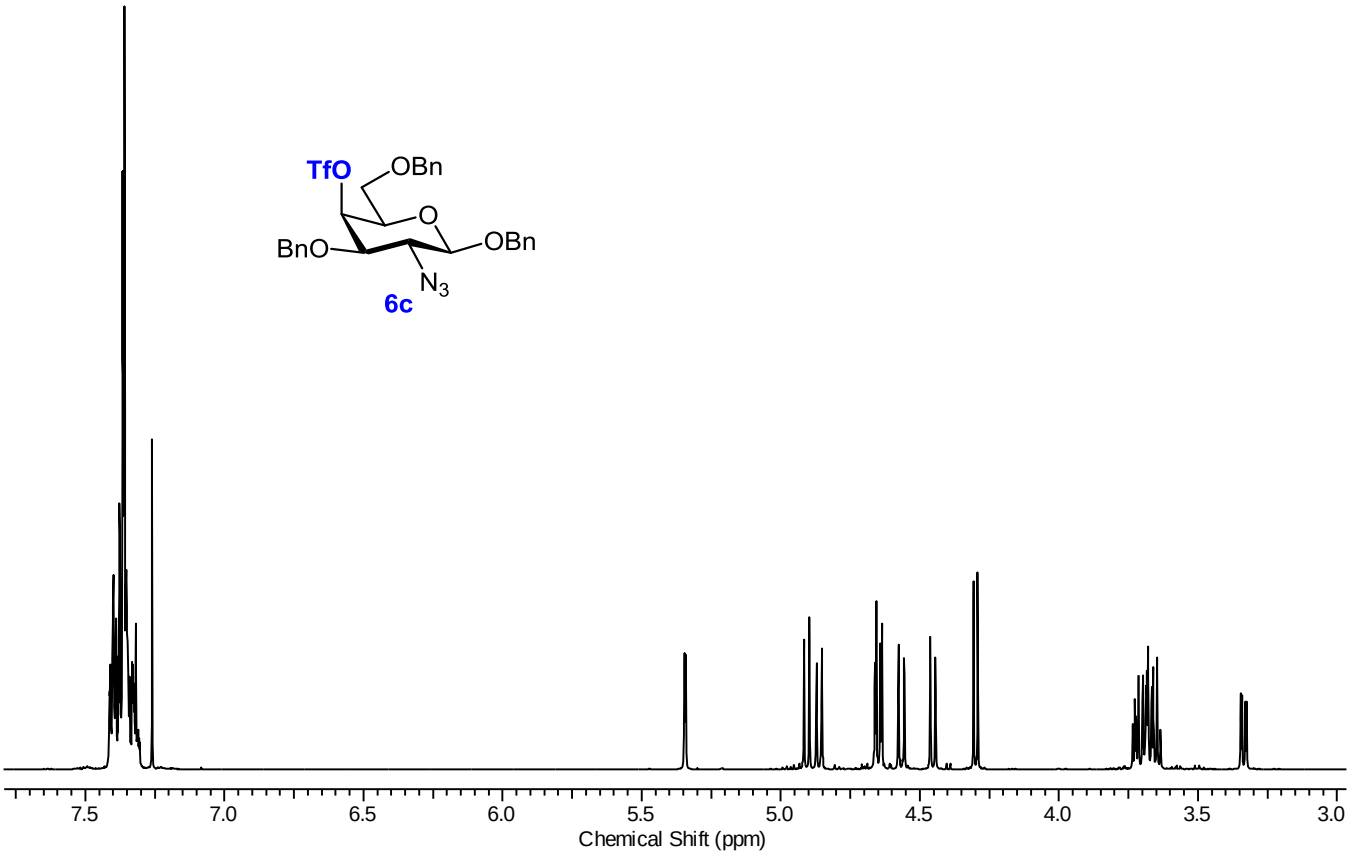

TfO
OBn
O
BnO
OBn
NPhth
6b
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
Chemical Shift (ppm)

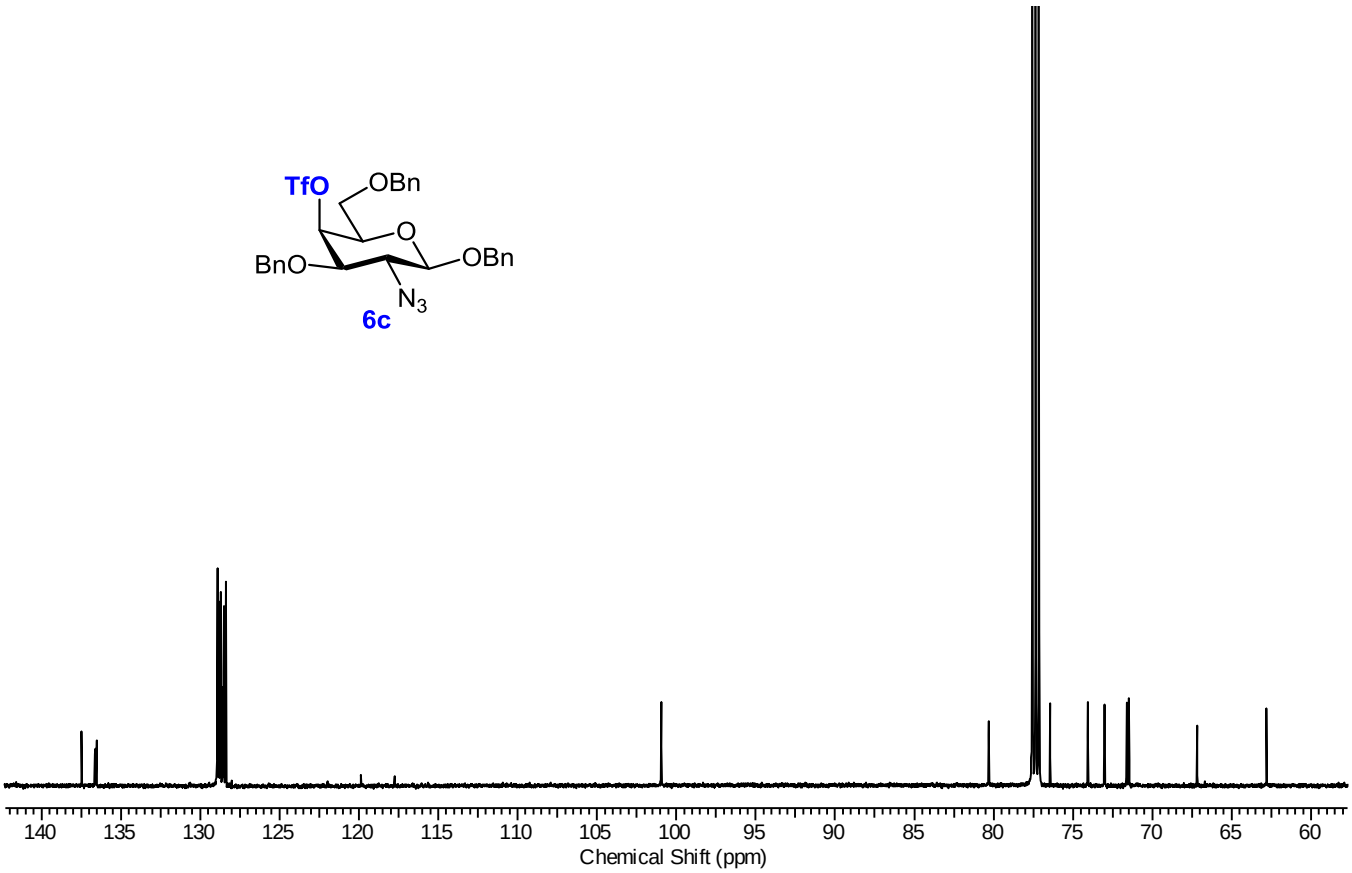

TfO
OBn
O
BnO
OBn
NPhth
6b
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
Chemical Shift (ppm)

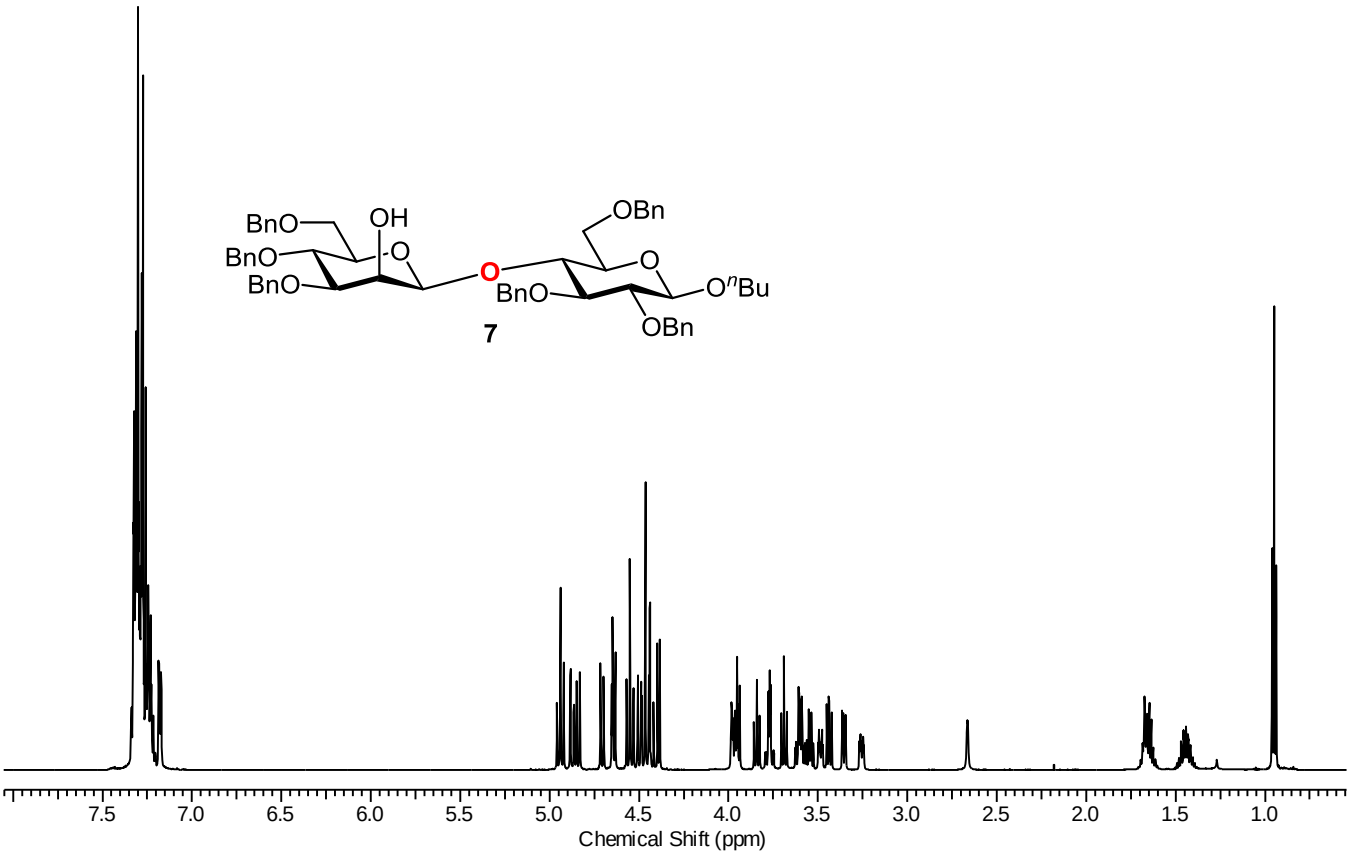

HO
OBn
O
BnO
OBn
N3
S13
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
Chemical Shift (ppm)

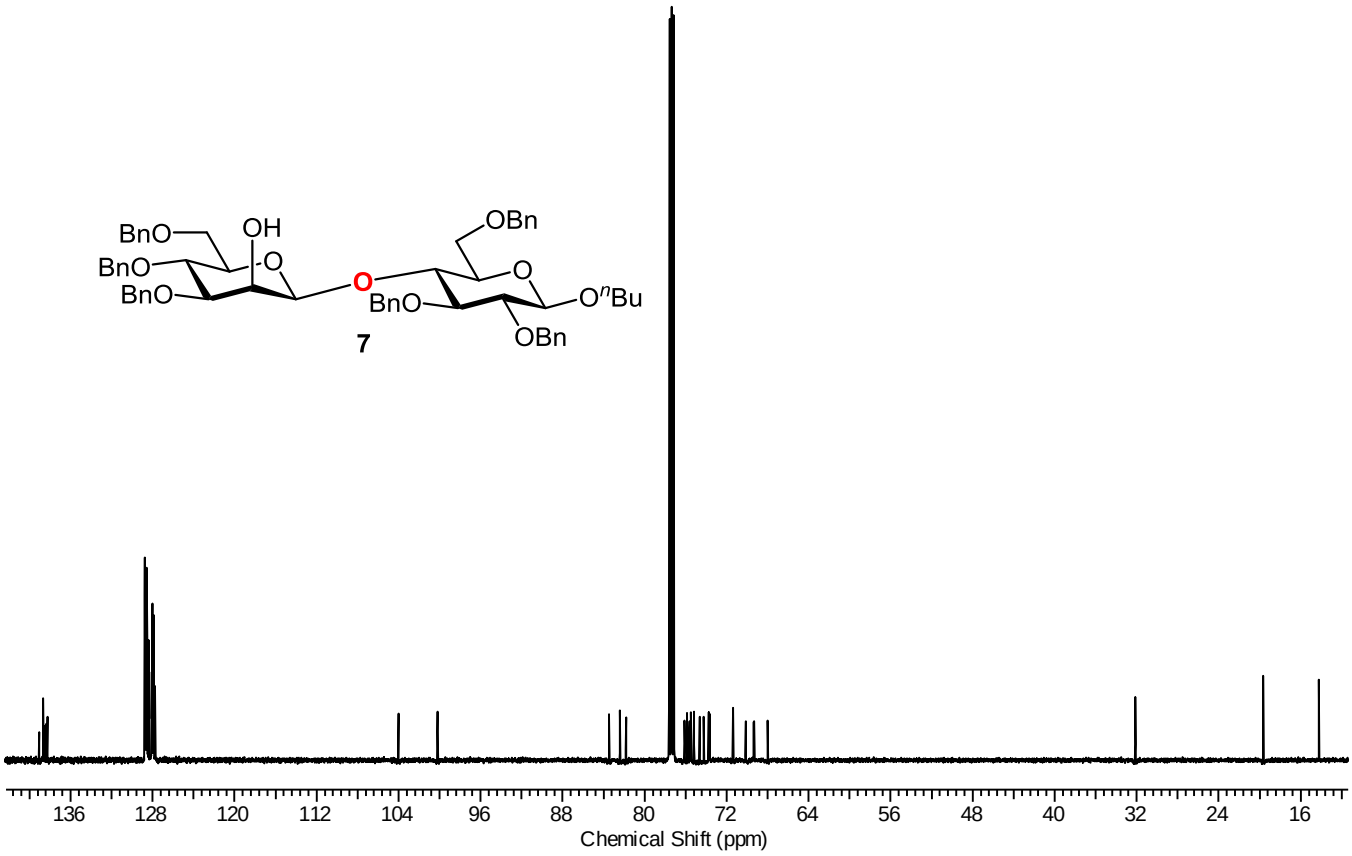

HO
OBn
O
BnO
OBn
N3
S13
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
Chemical Shift (ppm)

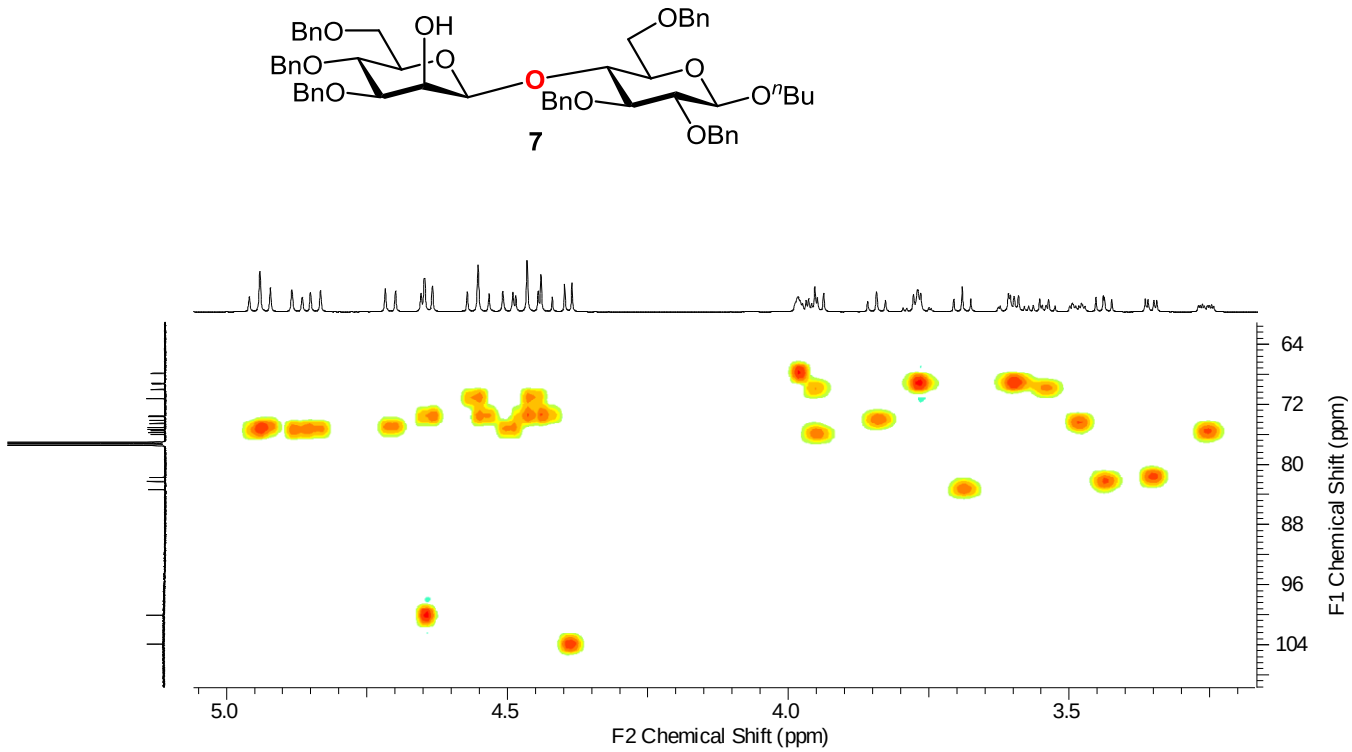

HO
OBn
O
BnO
OBn
N3
S13
56
64
72
80
88
96
104
F1 Chemical Shift (ppm)
5.0
4.5
4.0
3.5
F2 Chemical Shift (ppm)

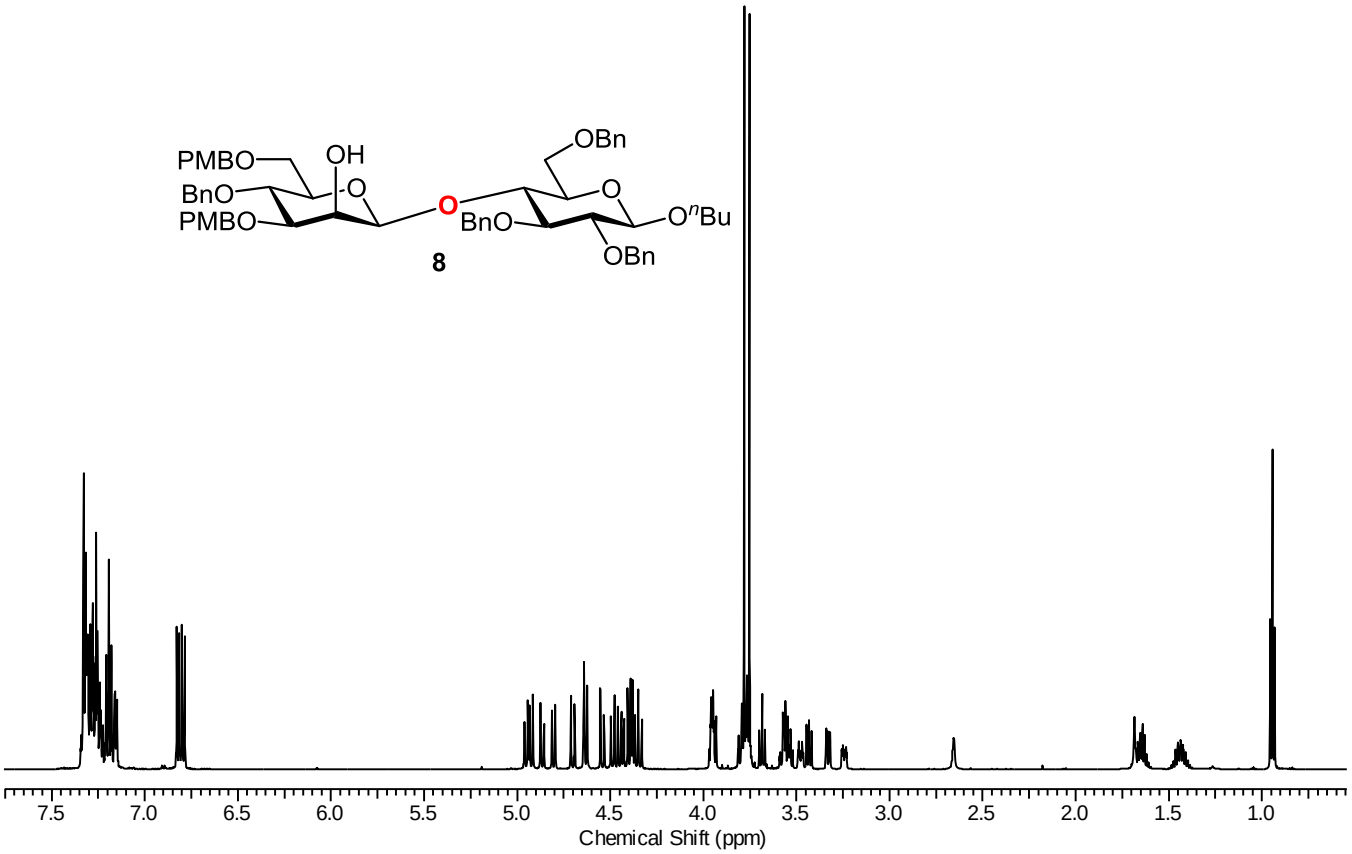

TfO
OBn
O
BnO
OBn
N3
6c
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
Chemical Shift (ppm)

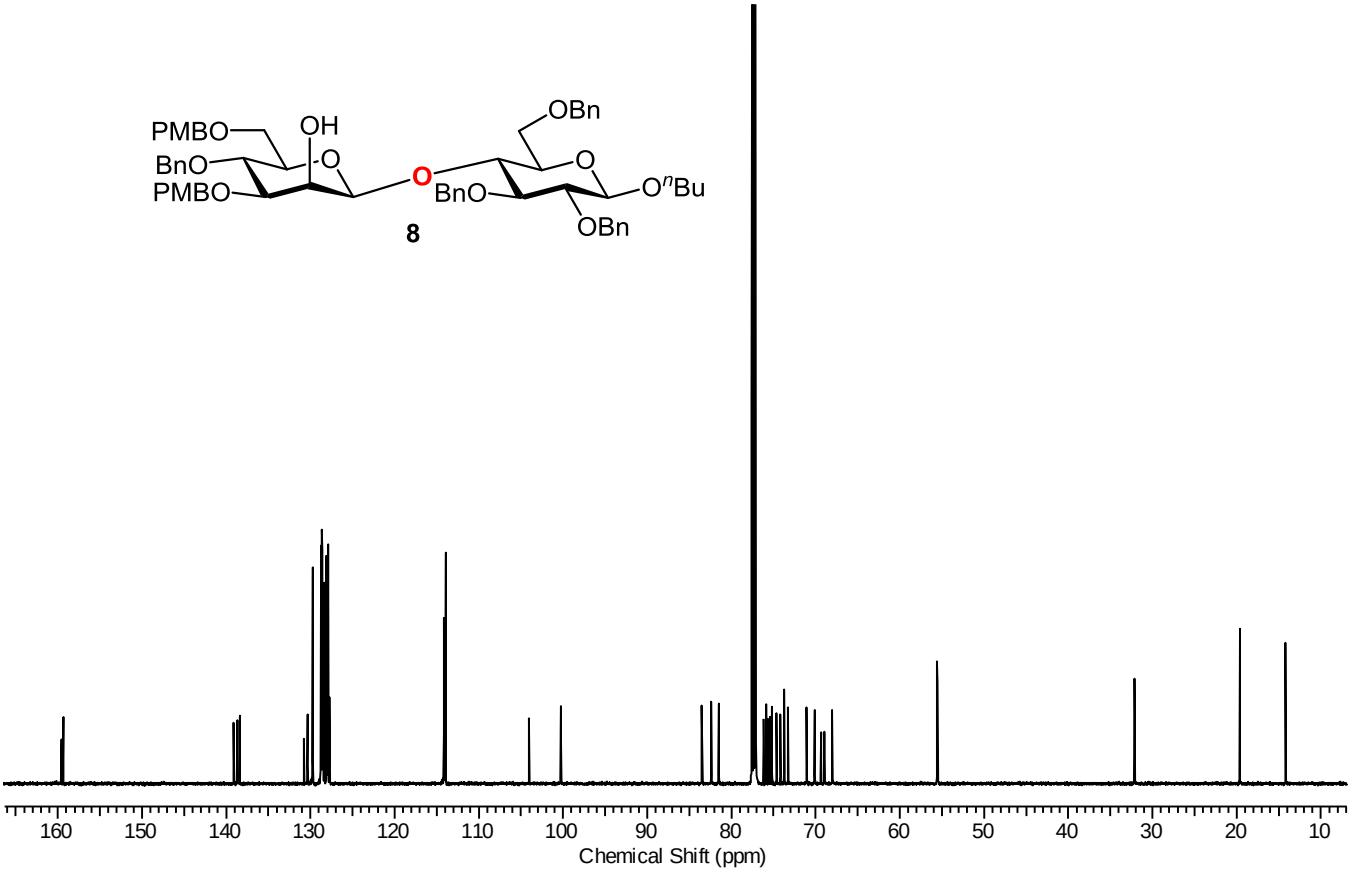

TfO
OBn
O
BnO
OBn
N3
6c
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60
Chemical Shift (ppm)

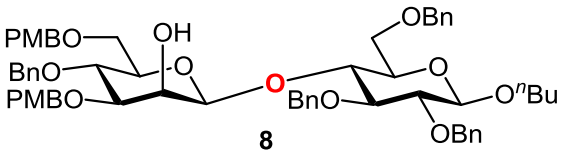

BnO
OH
BnO
O
BnO
O
OBn
O
BnO
O^{n}Bu
OBn
7
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
Chemical Shift (ppm)


BnO
OH
BnO
O
BnO
O
OBn
O
BnO
O^{n}Bu
OBn
7
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)

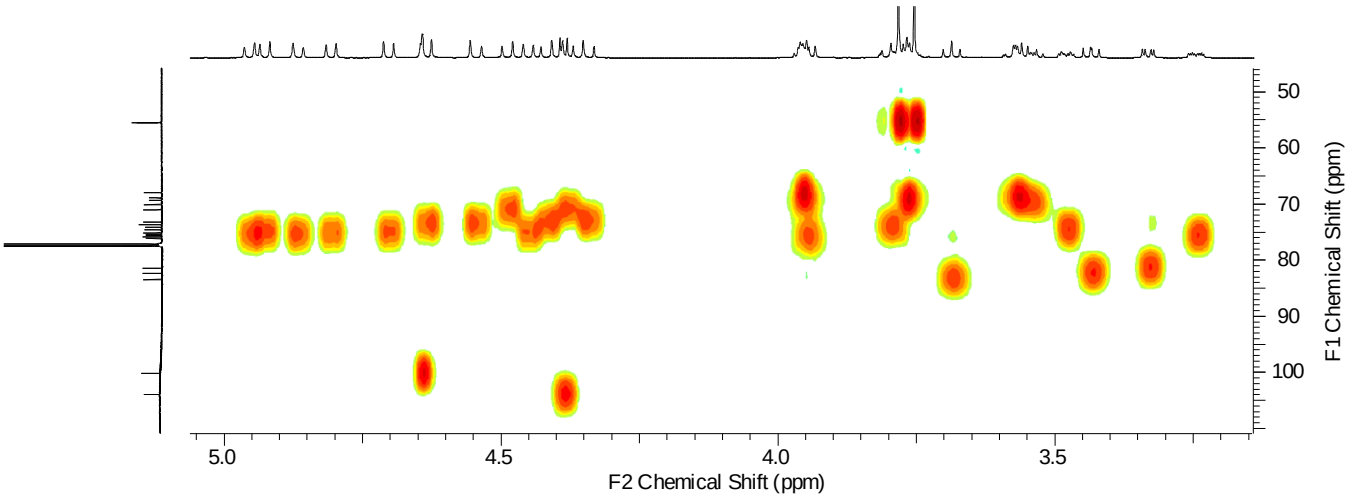

BnO
OH
BnO
O
BnO
O
OBn
O
BnO
O^{n}Bu
OBn
7
64
72
80
88
96
104
F1 Chemical Shift (ppm)
5.0
4.5
4.0
3.5
F2 Chemical Shift (ppm)

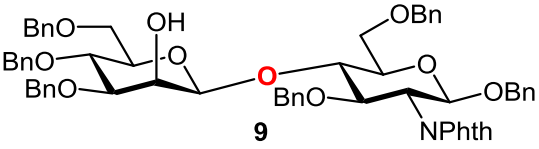

PMBO
OH
BnO
PMBO
O
OBn
O
BnO
O^{n}Bu
OBn
8
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)


PMBO
OH
BnO
PMBO
O
OBn
O
BnO
O^{n}Bu
OBn
8
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)


PMBO
OH
BnO
PMBO
O
O
BnO
OBn
O
O^{n}Bu
OBn

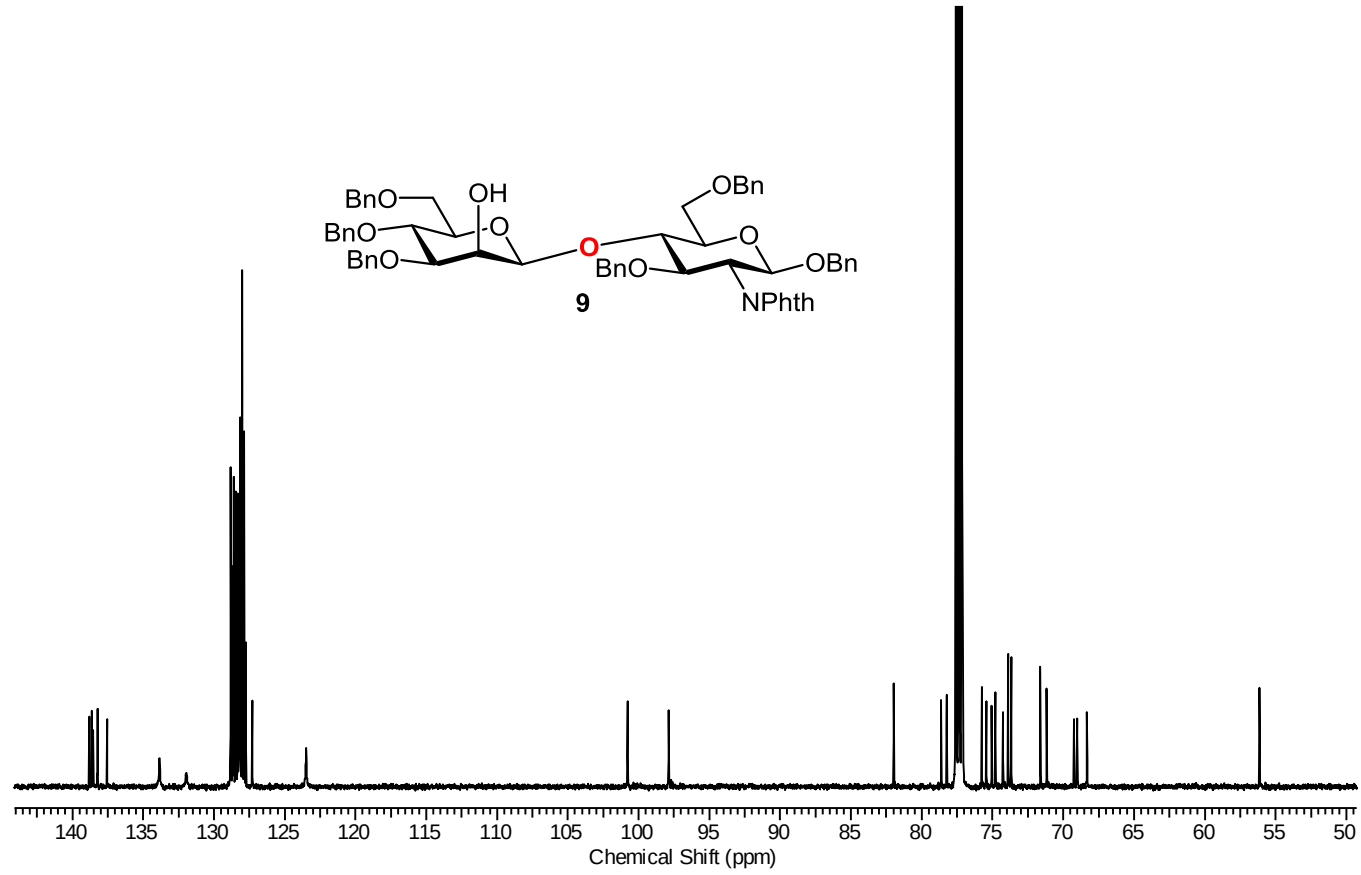
8

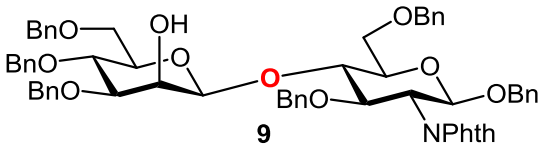

50
60
70
80
90
100
F1 Chemical Shift (ppm)
5.0
4.5
4.0
3.5
F2 Chemical Shift (ppm)

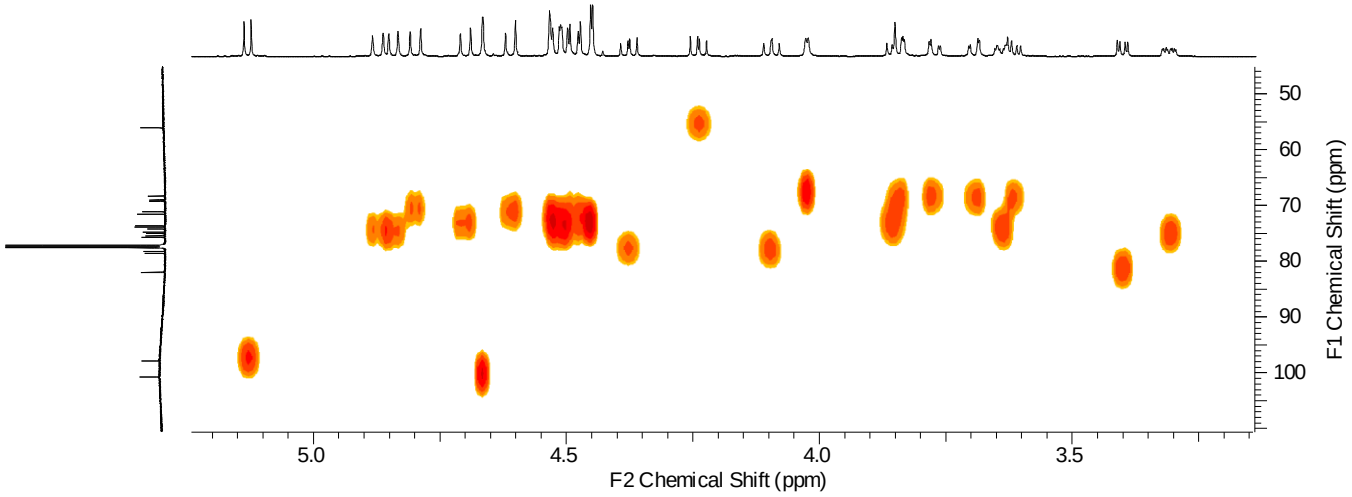

BnO
OH
BnO
BnO
O
O
BnO
OBn
O
OBn
NPhth

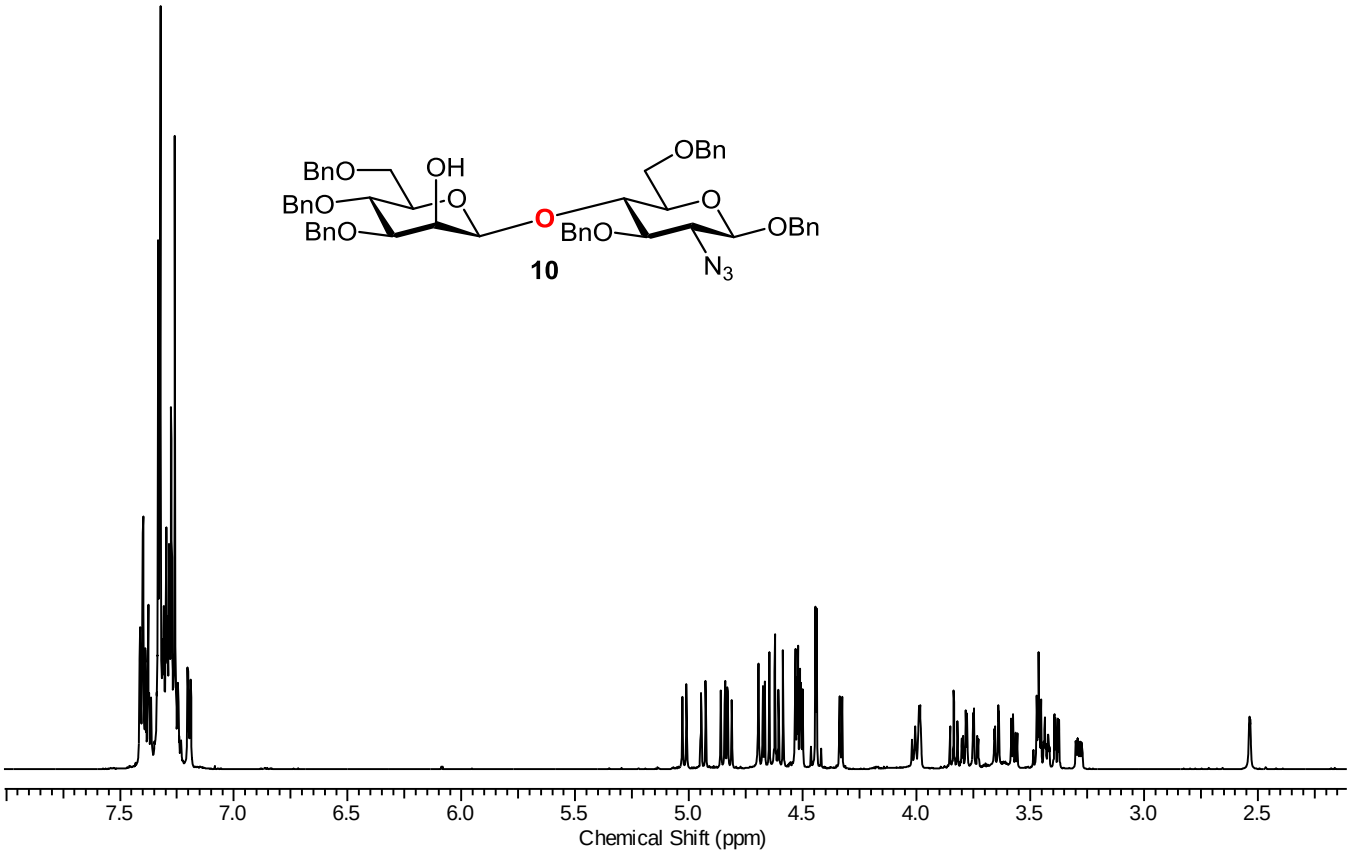
9

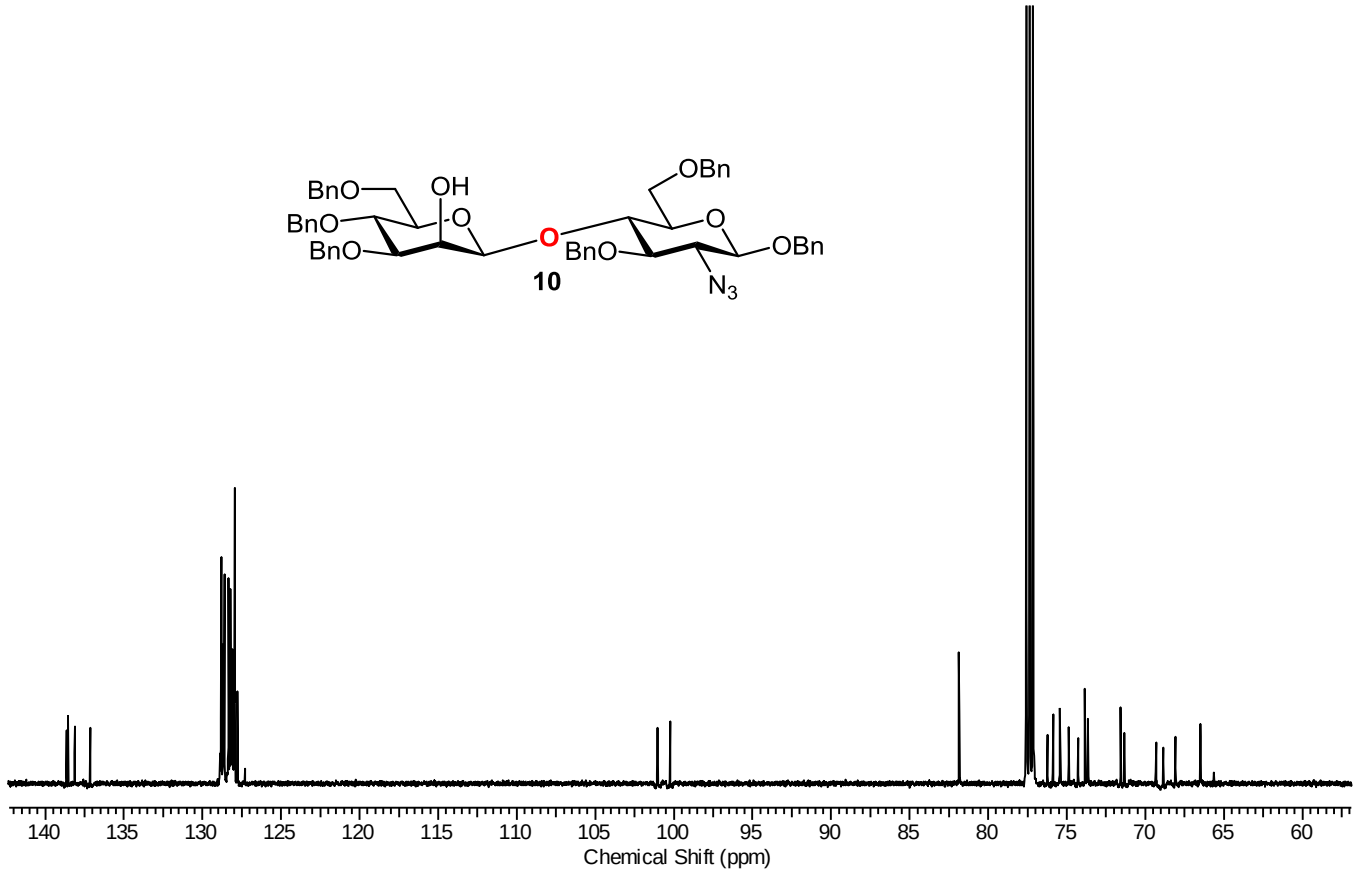
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)

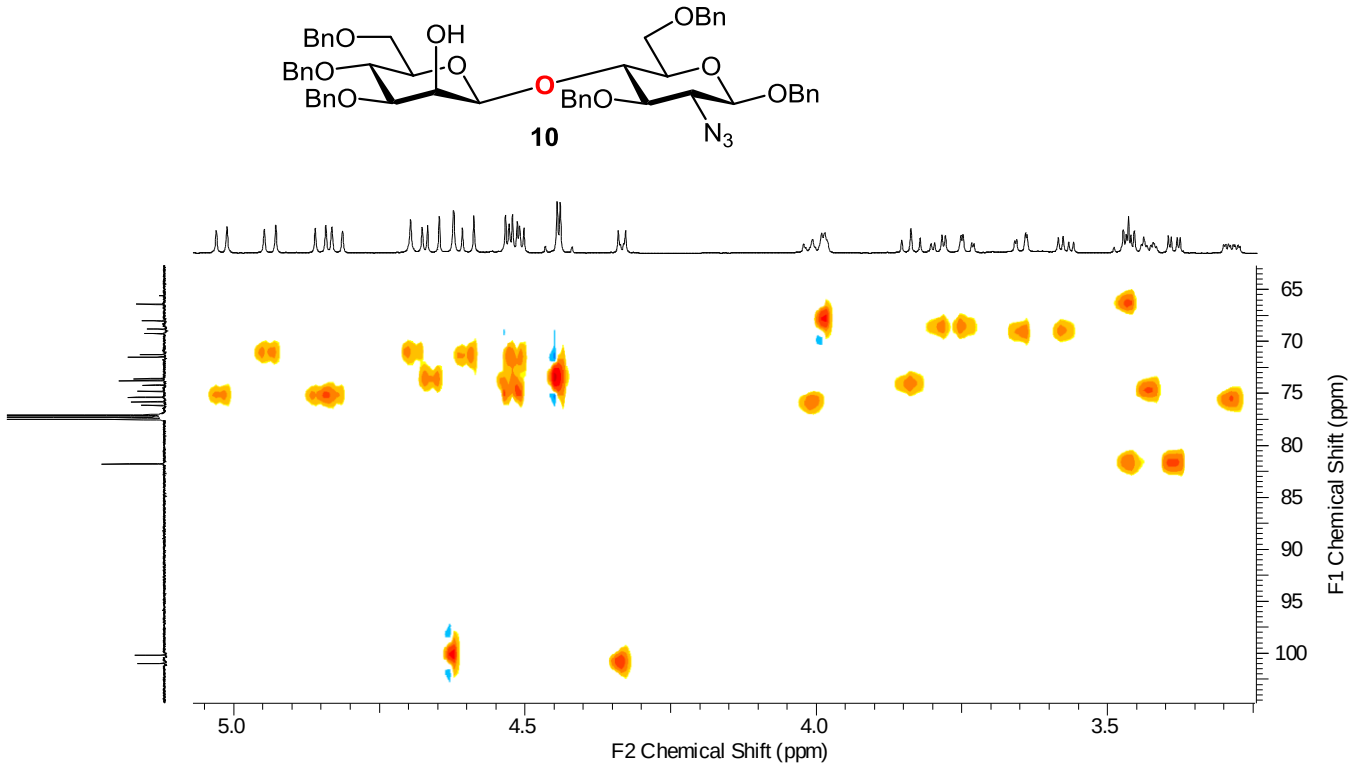

BnO
OH
BnO
O
BnO
O
OBn
BnO
O
OBn
NPhth
9
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
Chemical Shift (ppm)

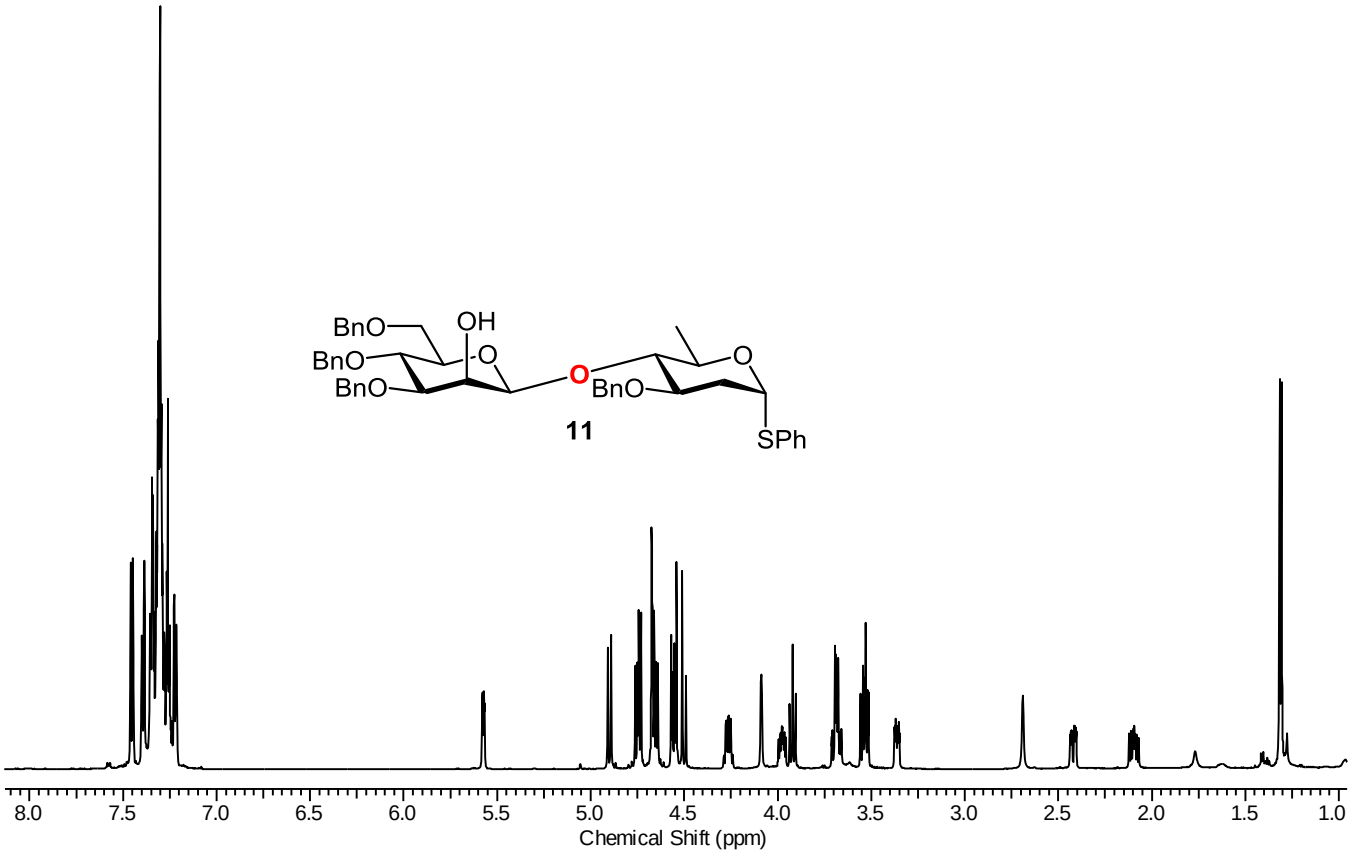

BnO
OH
BnO
O
BnO
O
OBn
BnO
O
OBn
NPhth
9

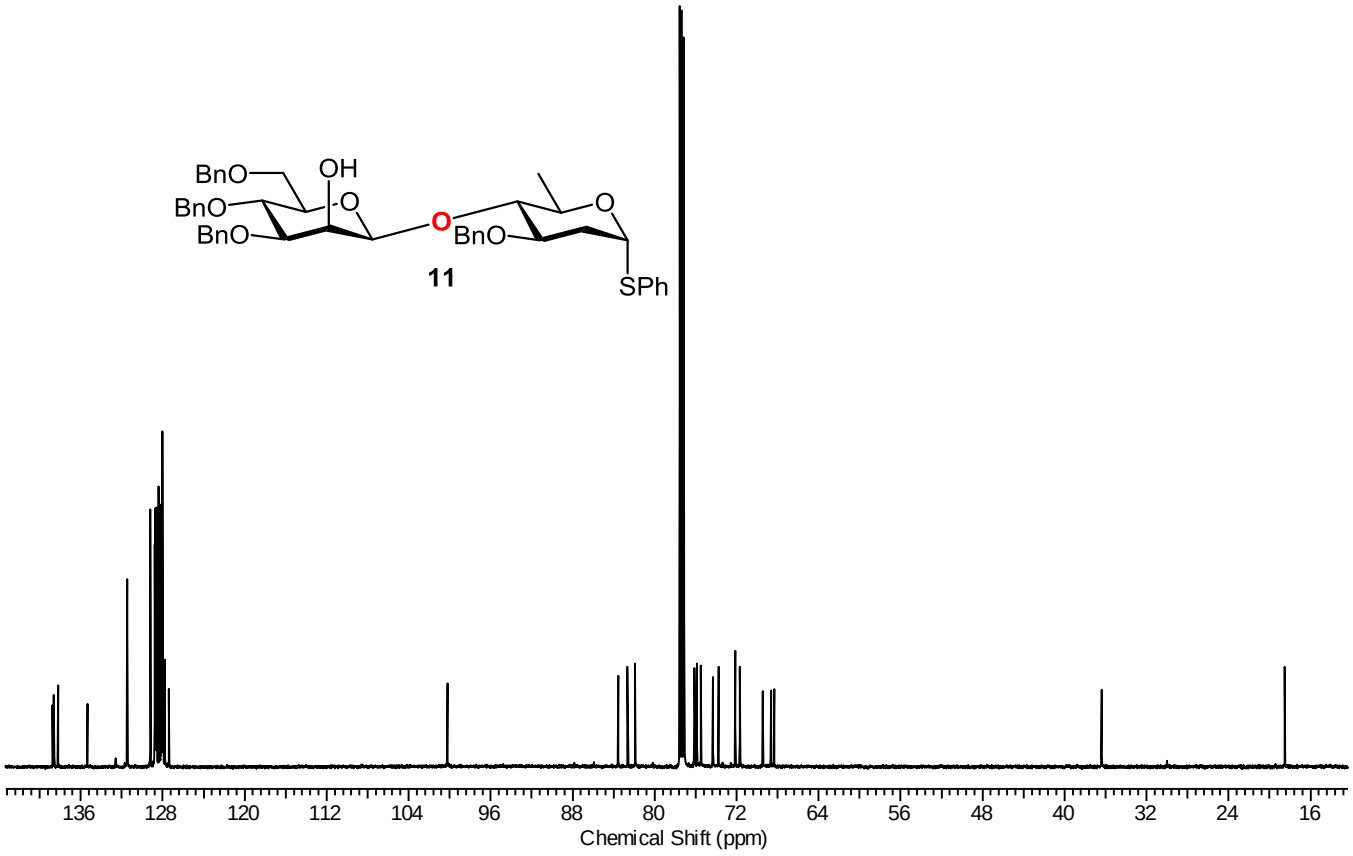

5.0
4.5
4.0
3.5
F2 Chemical Shift (ppm)
50
60
70
80
90
100
F1 Chemical Shift (ppm)

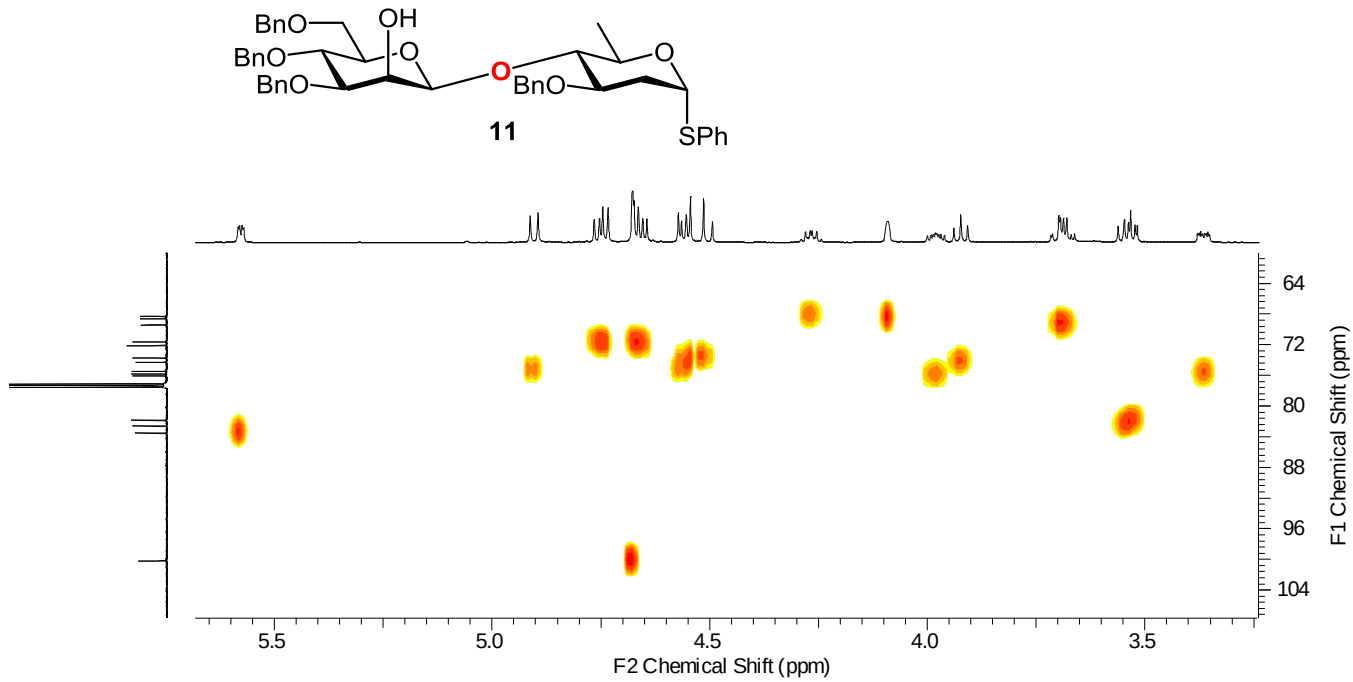

BnO
OH
BnO
O
BnO
O
BnO
OBn
O
OBn
N3
10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
Chemical Shift (ppm)

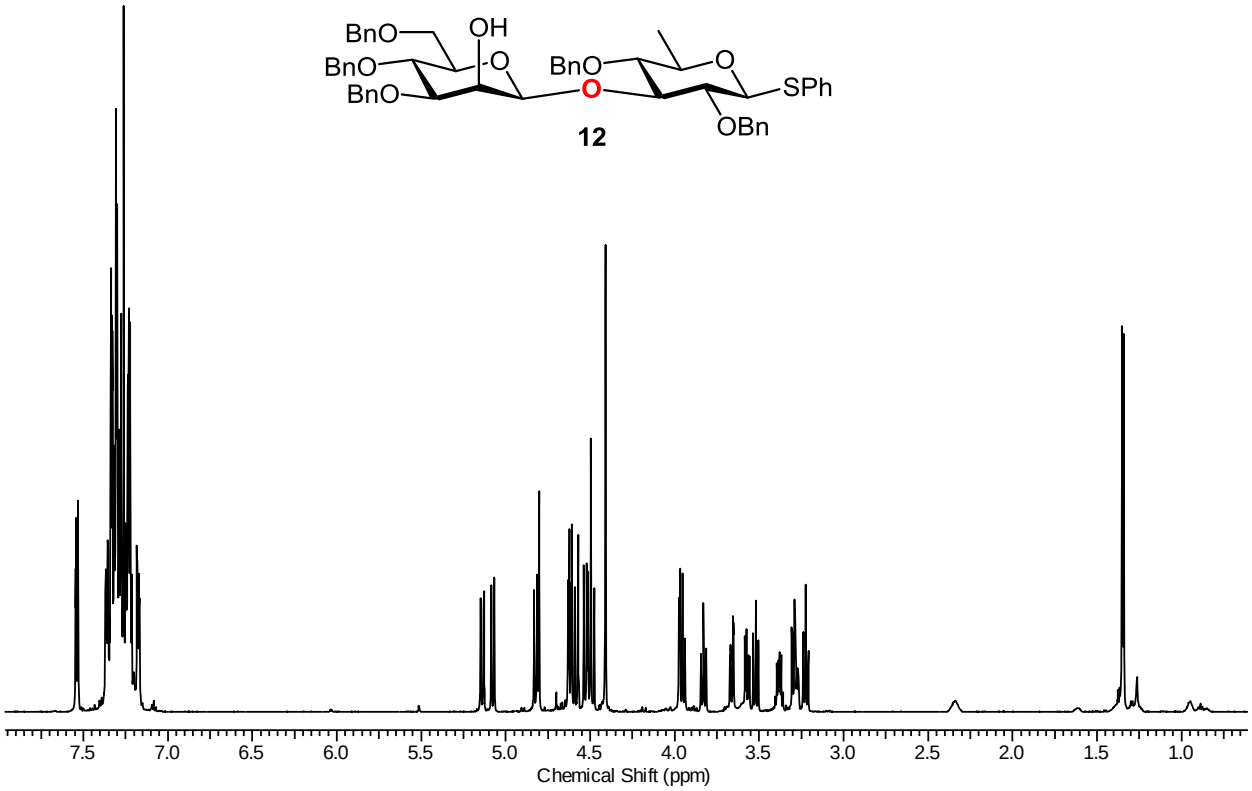

BnO
OH
BnO
O
BnO
O
BnO
OBn
O
OBn
N3
10
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
Chemical Shift (ppm)

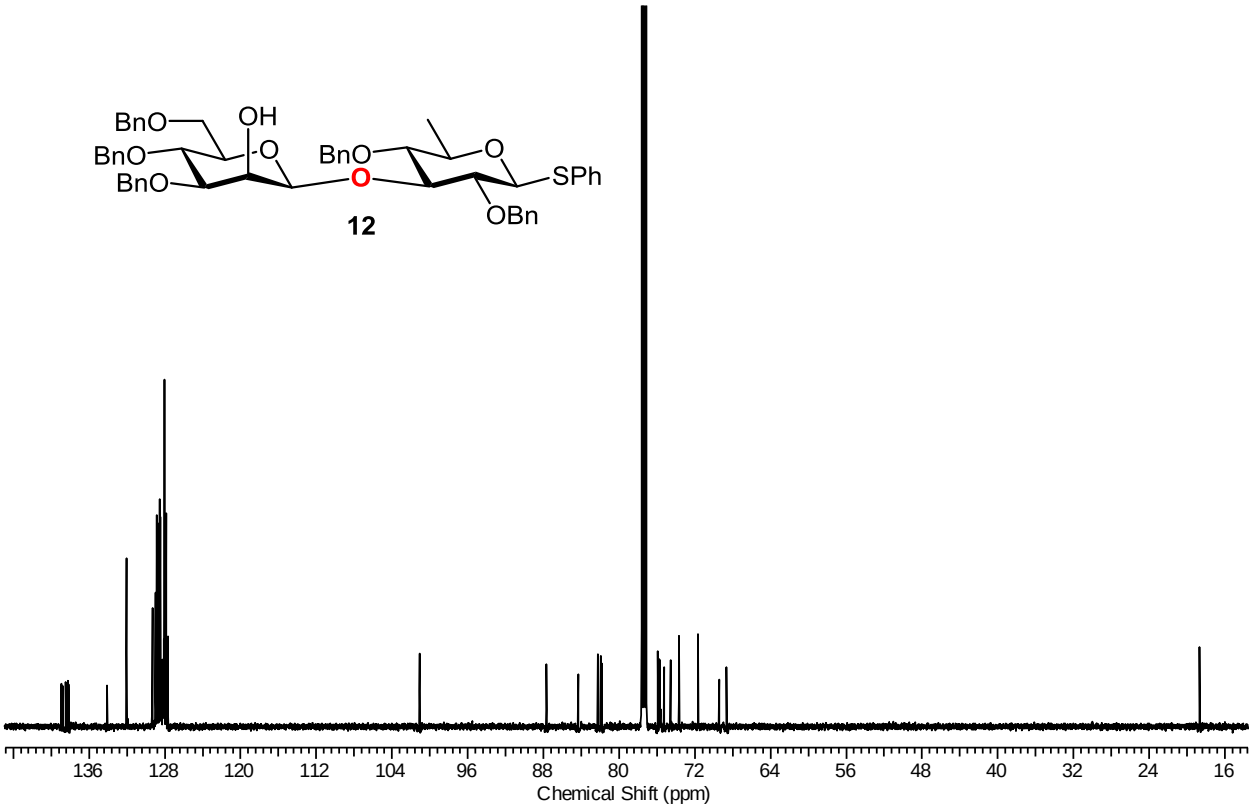

BnO
OH
BnO
O
BnO
O
BnO
OBn
BnO
OBn
N3
10
65
70
75
80
85
90
95
100
F1 Chemical Shift (ppm)
5.0
4.5
4.0
3.5
F2 Chemical Shift (ppm)

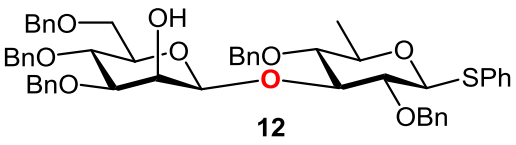

BnO
OH
BnO
O
BnO
O
BnO
SPh
11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)


BnO
OH
BnO
O
BnO
O
BnO
O
BnO
SPh
11
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)

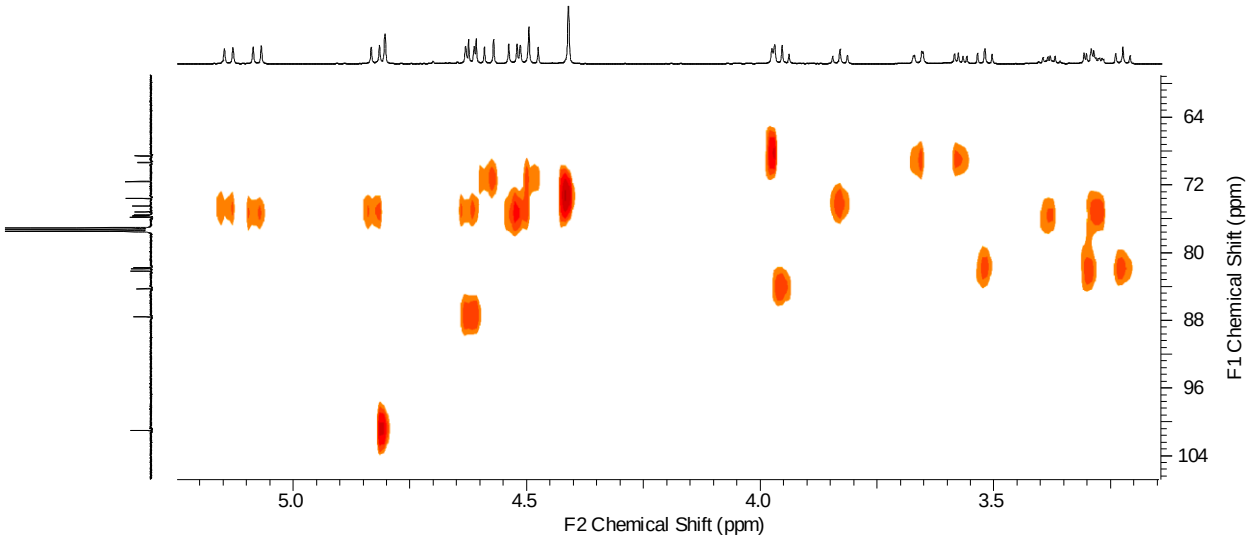

BnO
OH
BnO
O
BnO
O
BnO
O
BnO
SPh
11
64
72
80
88
96
104
F1 Chemical Shift (ppm)
5.5
5.0
4.5
4.0
3.5
F2 Chemical Shift (ppm)

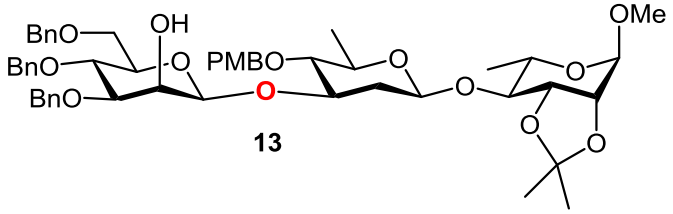

BnO
OH
BnO
O
BnO
BnO
O
O
SPh
OBn
12
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)


BnO
OH
BnO
O
BnO
BnO
O
O
SPh
OBn
12
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)


BnO
OH
BnO
O
BnO
BnO
O
O
SPh
OBn

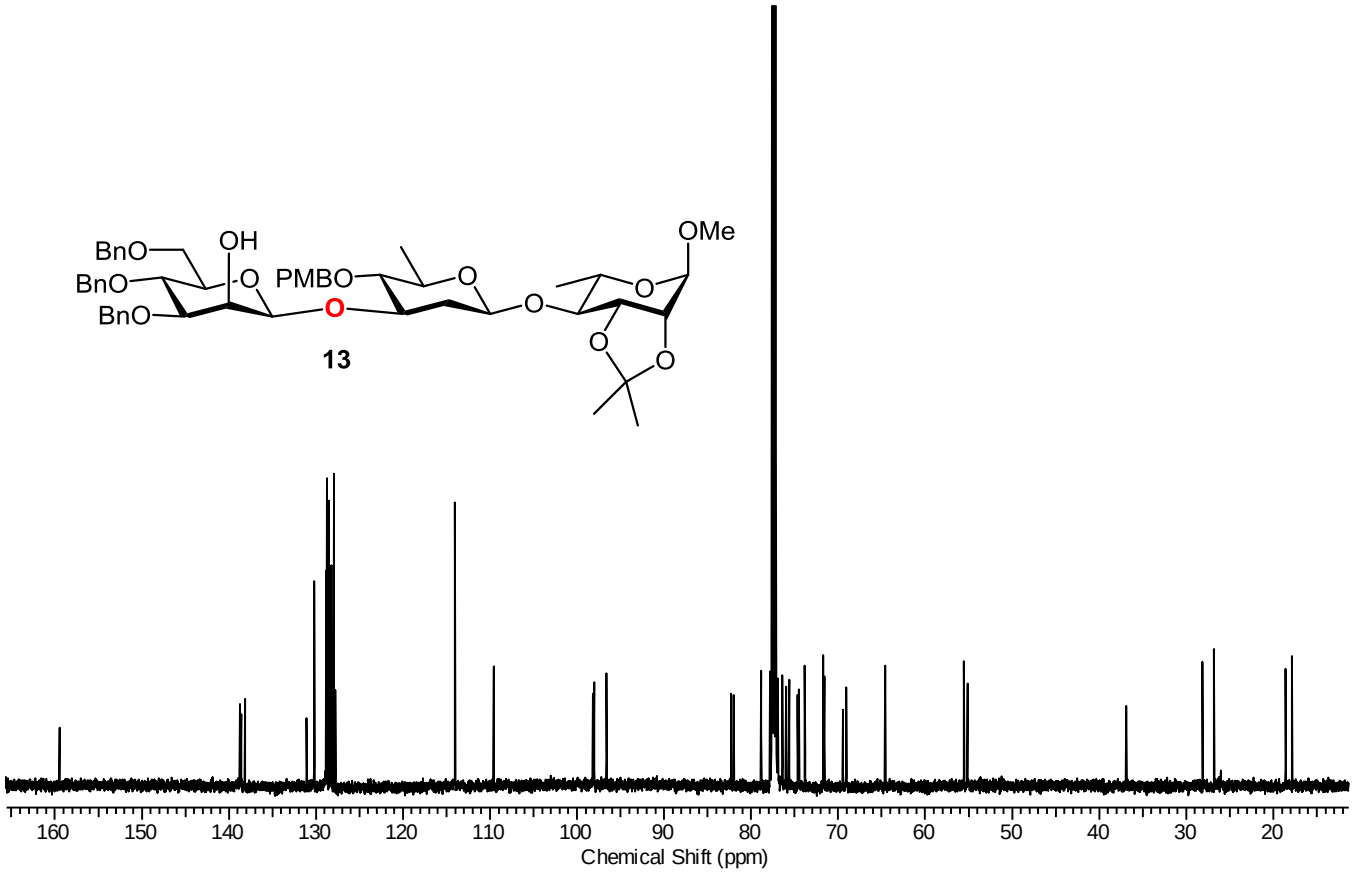
12

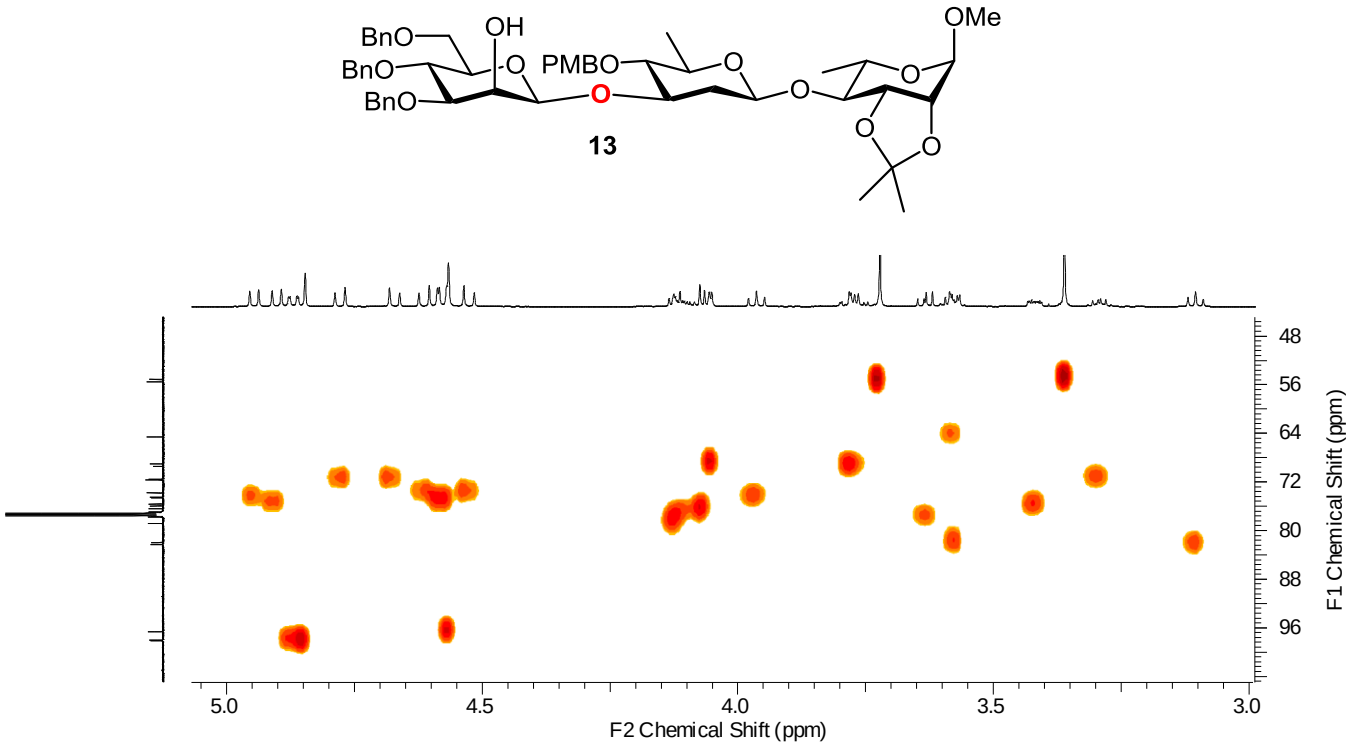

64
72
80
88
96
104
F1 Chemical Shift (ppm)
5.0
4.5
4.0
3.5
F2 Chemical Shift (ppm)

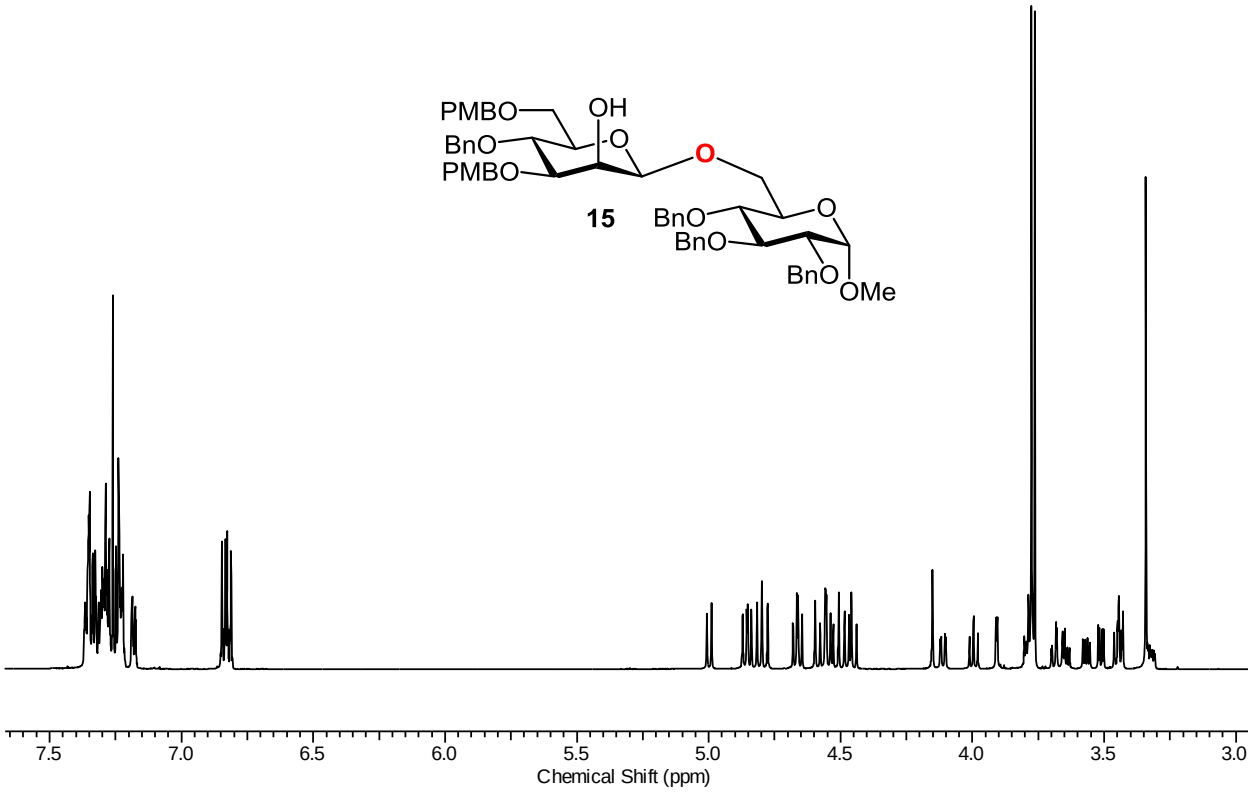

BnO
OH
BnO
O
PMBO
BnO
O
O
O
OMe
O
O

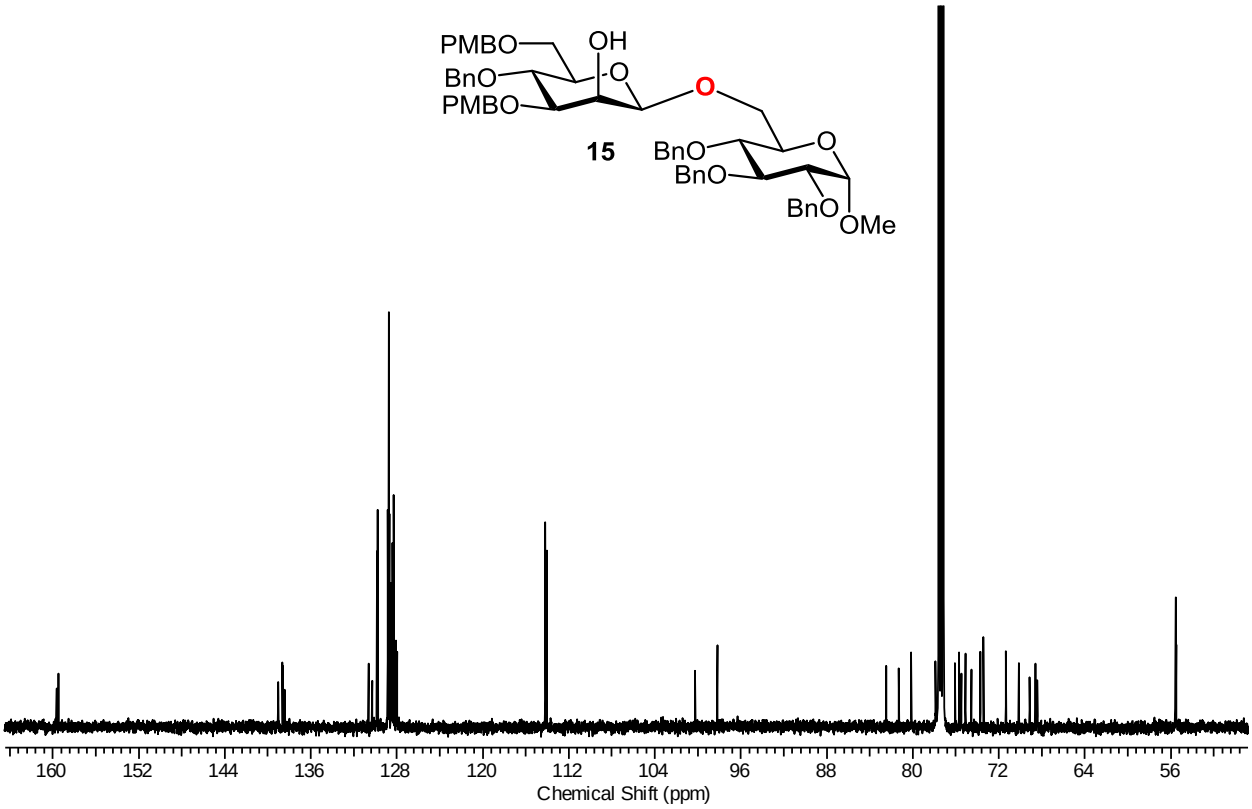
13

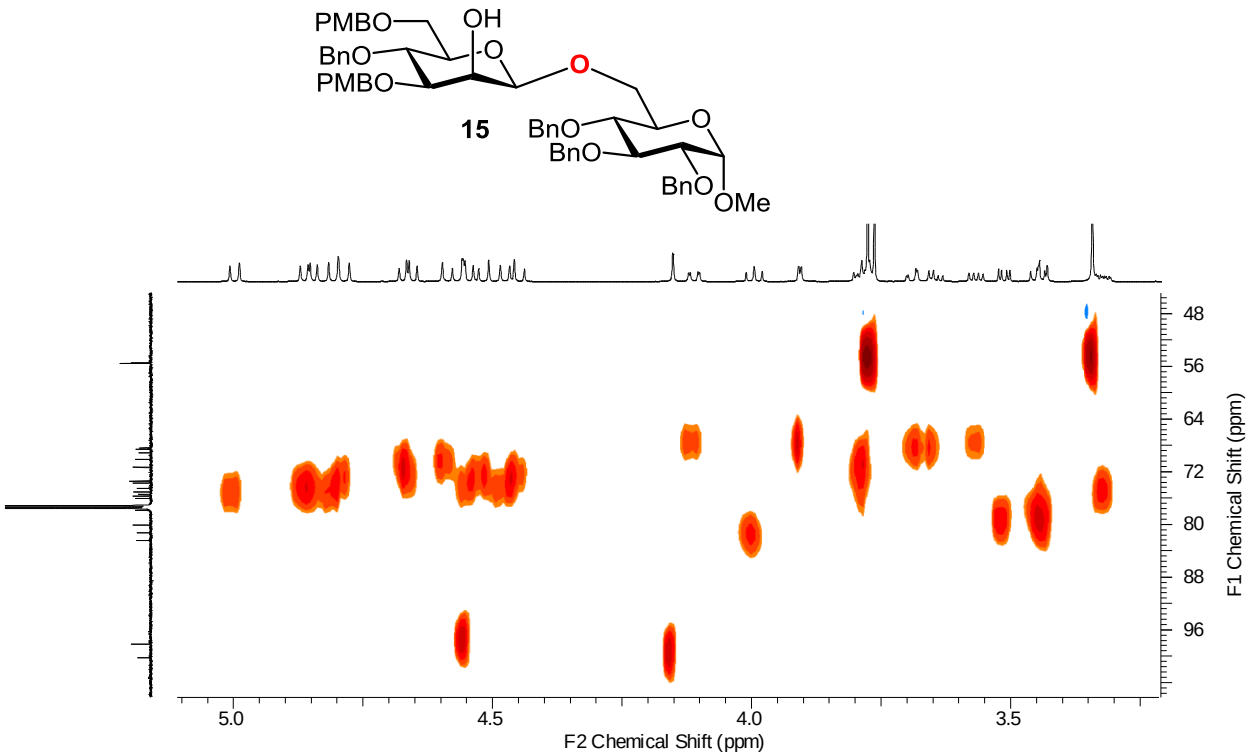
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

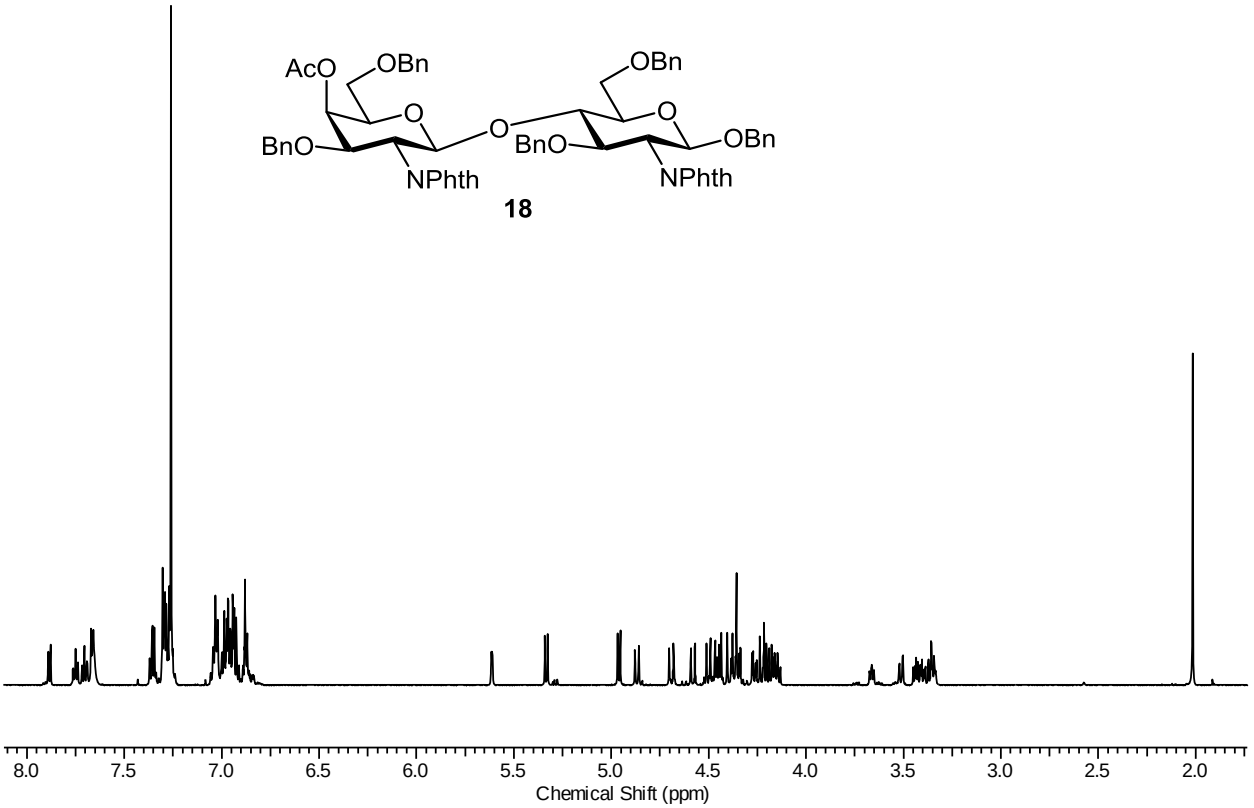

BnO
BnO
BnO
OH
O
PMBO
O
O
O
O
O
O
OMe
13
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
Chemical Shift (ppm)

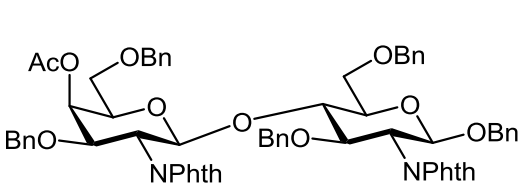

BnO
BnO
BnO
OH
O
PMBO
O
O
O
O
O
O
OMe
13
5.0
4.5
4.0
3.5
3.0
F2 Chemical Shift (ppm)
48
56
64
72
80
88
96
F1 Chemical Shift (ppm)


PMBO
OH
BnO
O
PMBO
O
15
BnO
O
BnO
BnO
OMe
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
Chemical Shift (ppm)


PMBO
OH
BnO
O
PMBO
O
15
BnO
O
BnO
BnO
OMe
160
152
144
136
128
120
112
104
96
88
80
72
64
56
Chemical Shift (ppm)

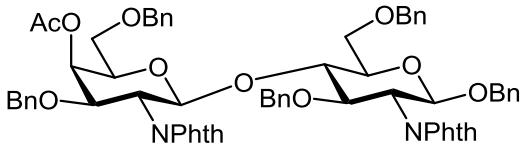

PMBO
OH
BnO
PMBO
O
15
BnO
BnO
O
BnO
OMe
48
56
64
72
80
88
96
F1 Chemical Shift (ppm)
5.0
4.5
4.0
3.5
F2 Chemical Shift (ppm)


AcO
OBn
O
BnO
O
NPhth
OBn
O
BnO
OBn
NPhth
18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)

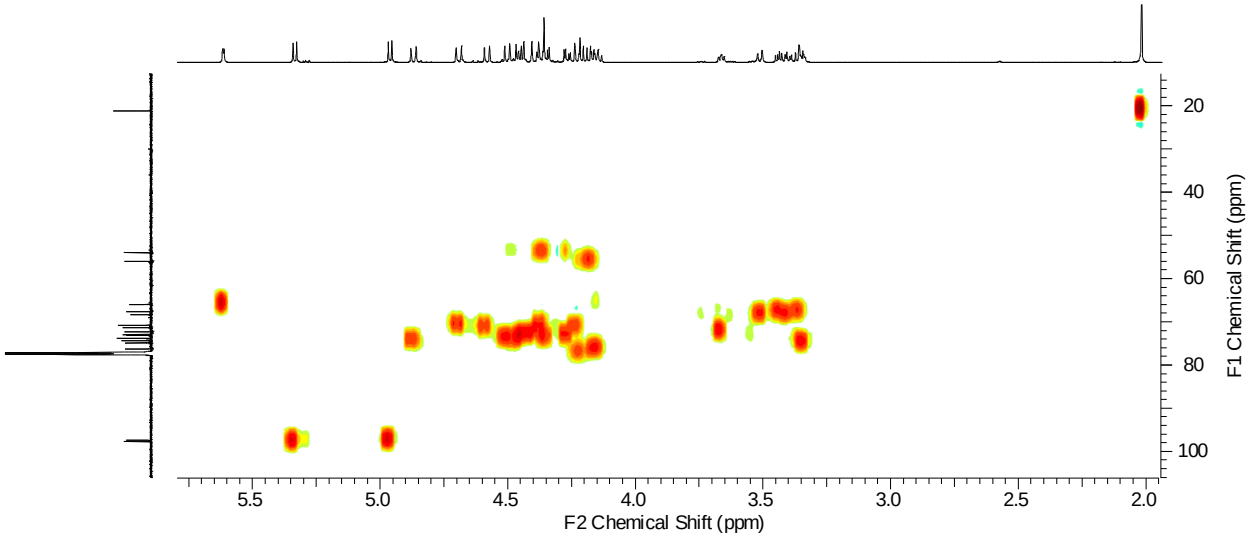

AcO
OBn
O
BnO
NPhth
O
OBn
O
BnO
OBn
NPhth

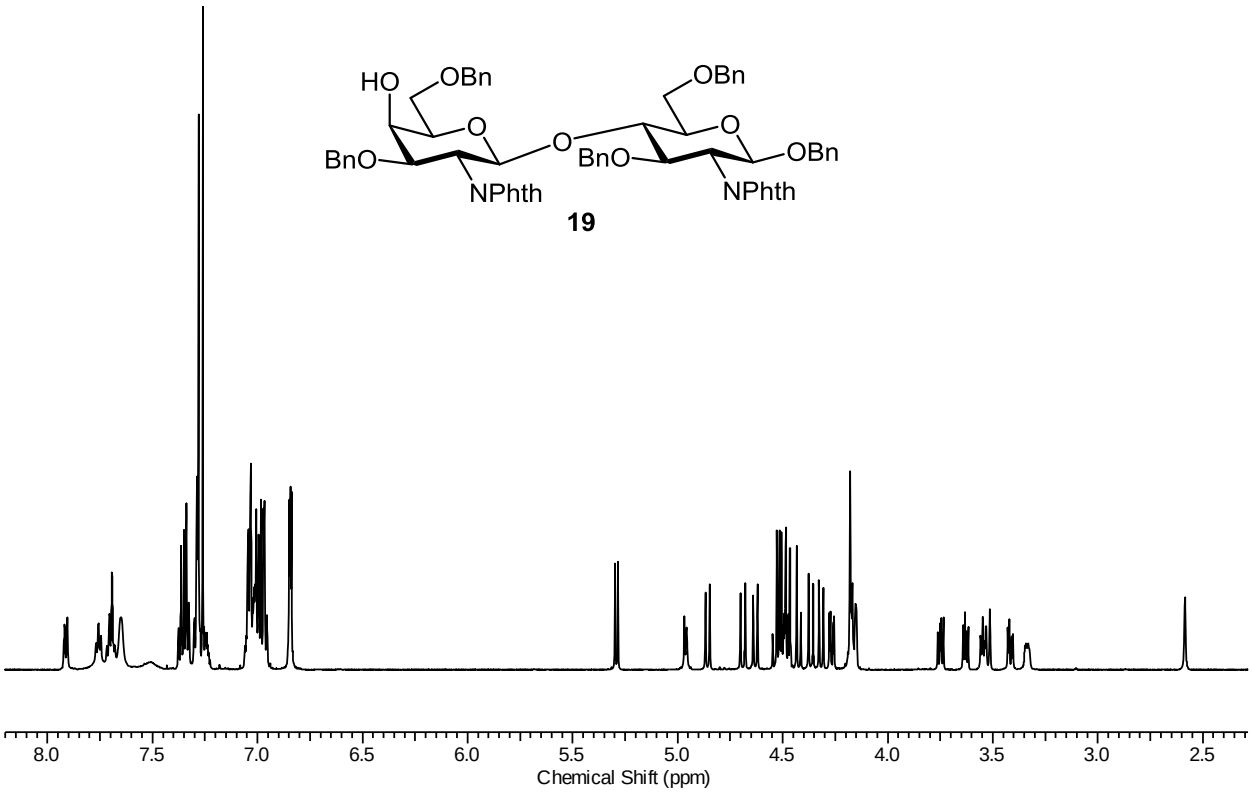
18

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

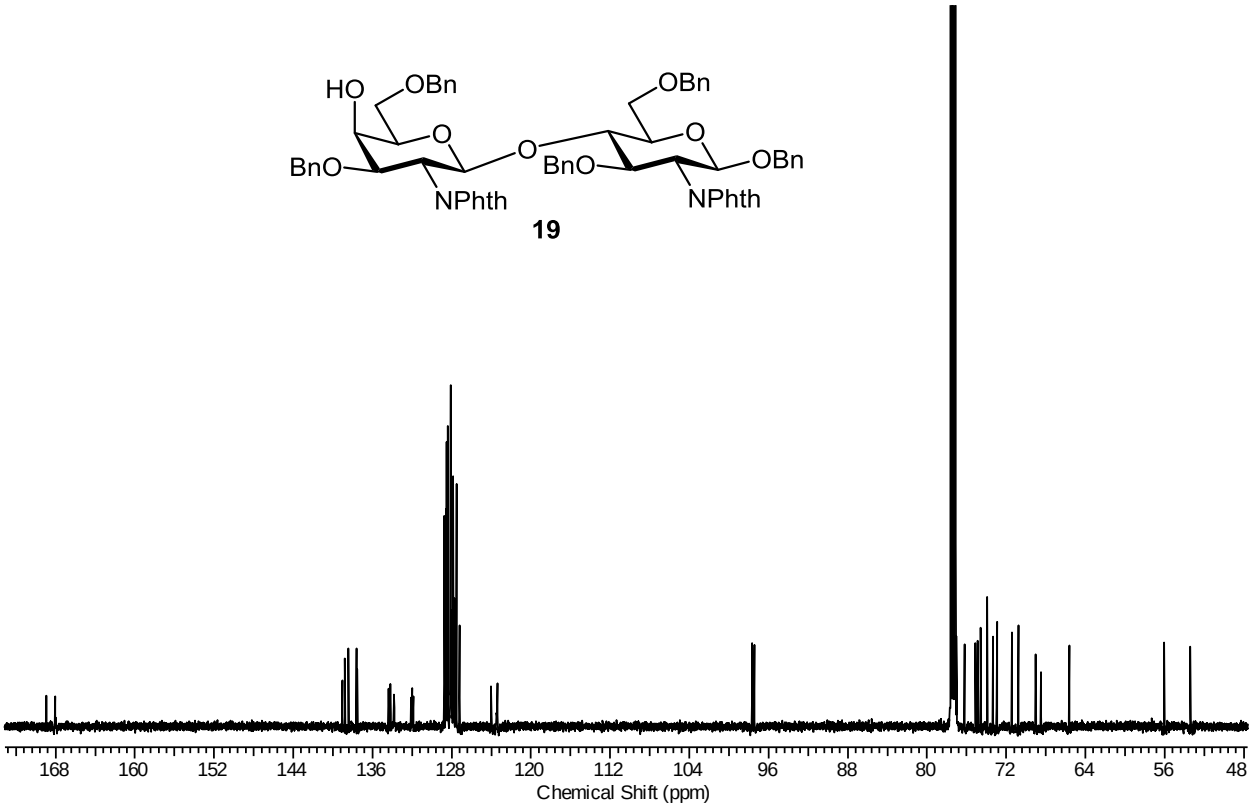

AcO
OBn
O
BnO
NPhth
O
OBn
O
BnO
OBn
NPhth

18

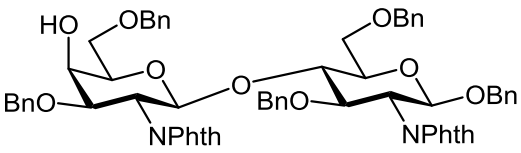

20
40
60
80
100
F1 Chemical Shift (ppm)
5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
F2 Chemical Shift (ppm)


HO
OBn
O
BnO
NPhth
O
OBn
O
BnO
OBn
NPhth
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
Chemical Shift (ppm)

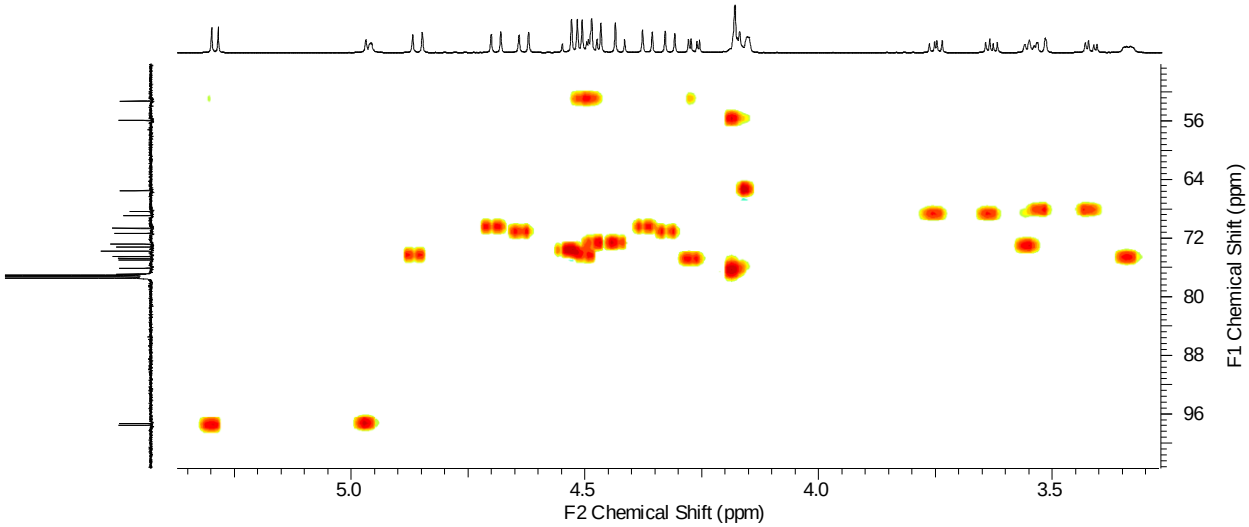
19

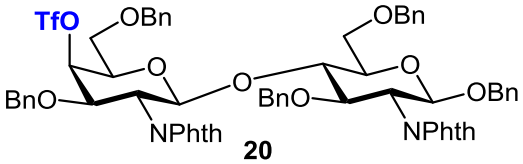

HO
OBn
O
BnO
NPhth
O
OBn
O
BnO
OBn
NPhth
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
Chemical Shift (ppm)

19


HO
OBn
O
BnO
NPhth
O
OBn
O
BnO
OBn
NPhth

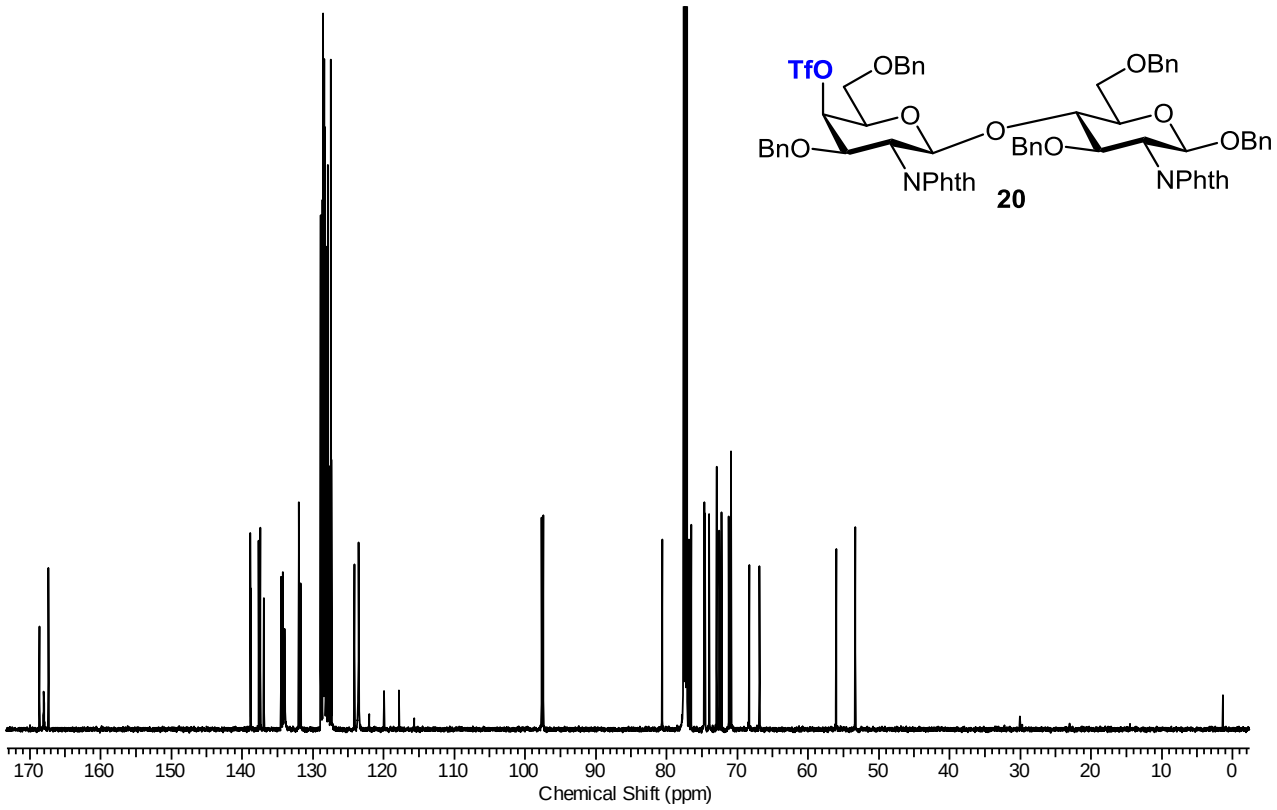
19


56
64
72
80
88
96
F1 Chemical Shift (ppm)
5.0
4.5
4.0
3.5
F2 Chemical Shift (ppm)

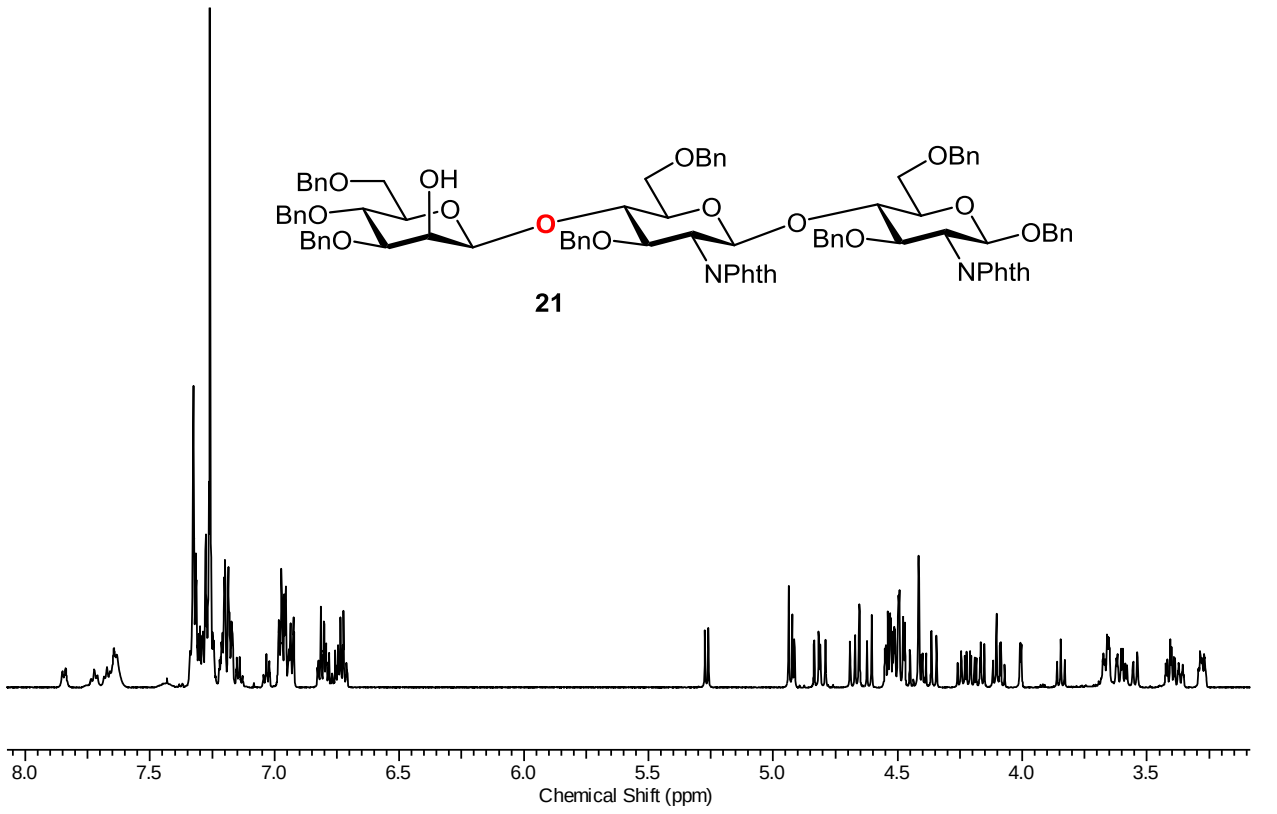

TfO
OBn
O
BnO
NPhth
O
OBn
O
BnO
OBn
NPhth

20

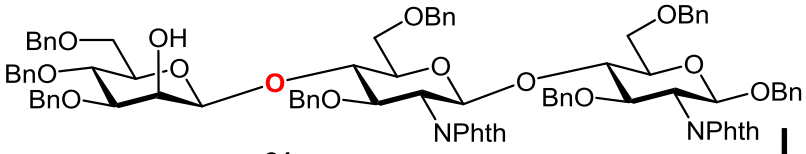
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
Chemical Shift (ppm)


TfO
OBn
O
BnO
NPhth
OBn
O
O
BnO
OBn
NPhth
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

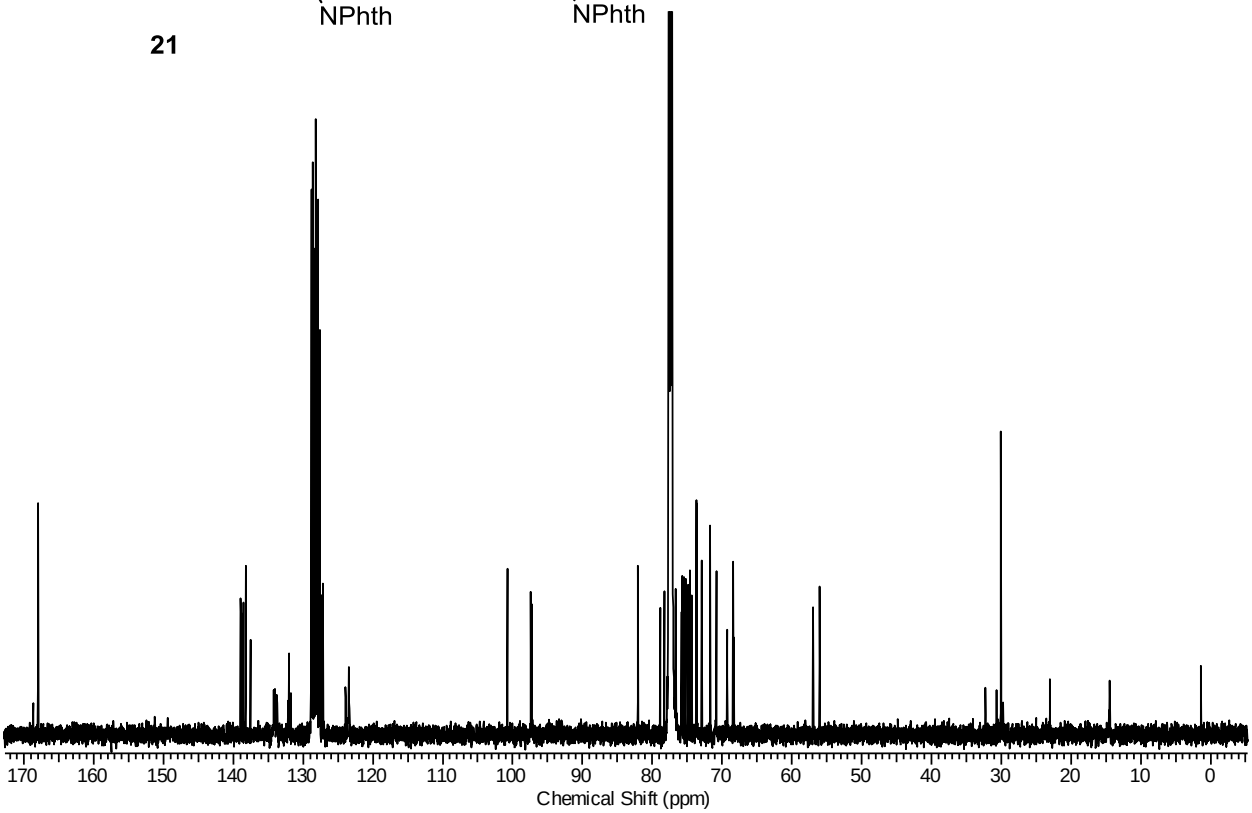
20

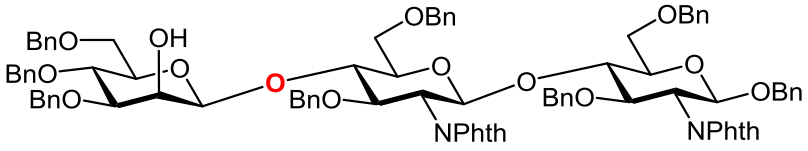

BnO
OH
BnO
O
BnO
O
OBn
O
BnO
NPhth
O
OBn
O
BnO
OBn
NPhth
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5
Chemical Shift (ppm)

21

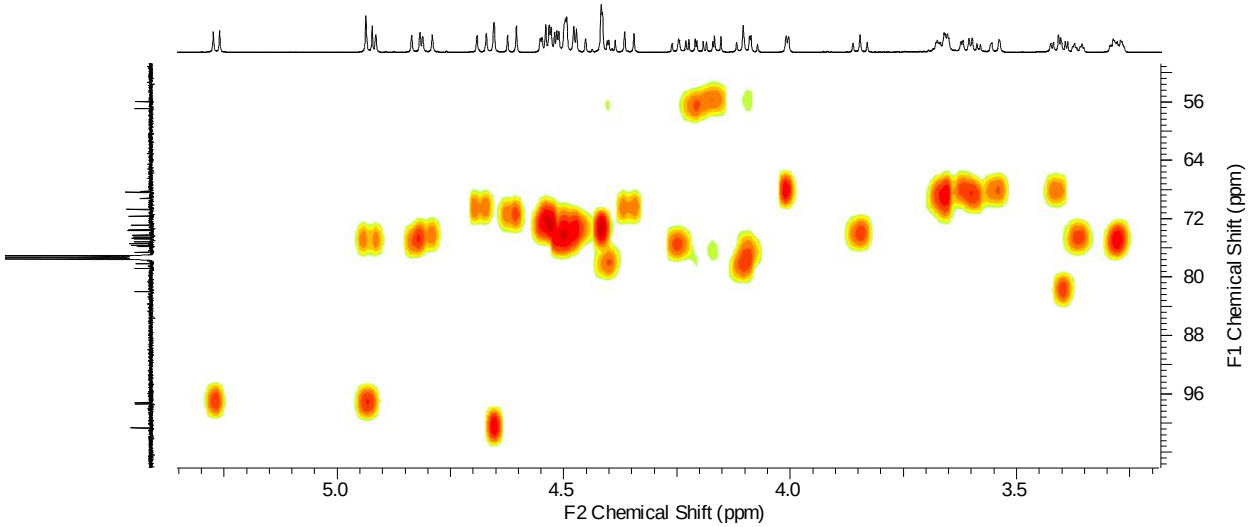

BnO
OH
BnO
O
BnO
O
OBn
O
BnO
NPhth
O
OBn
O
BnO
NPhth
OBn

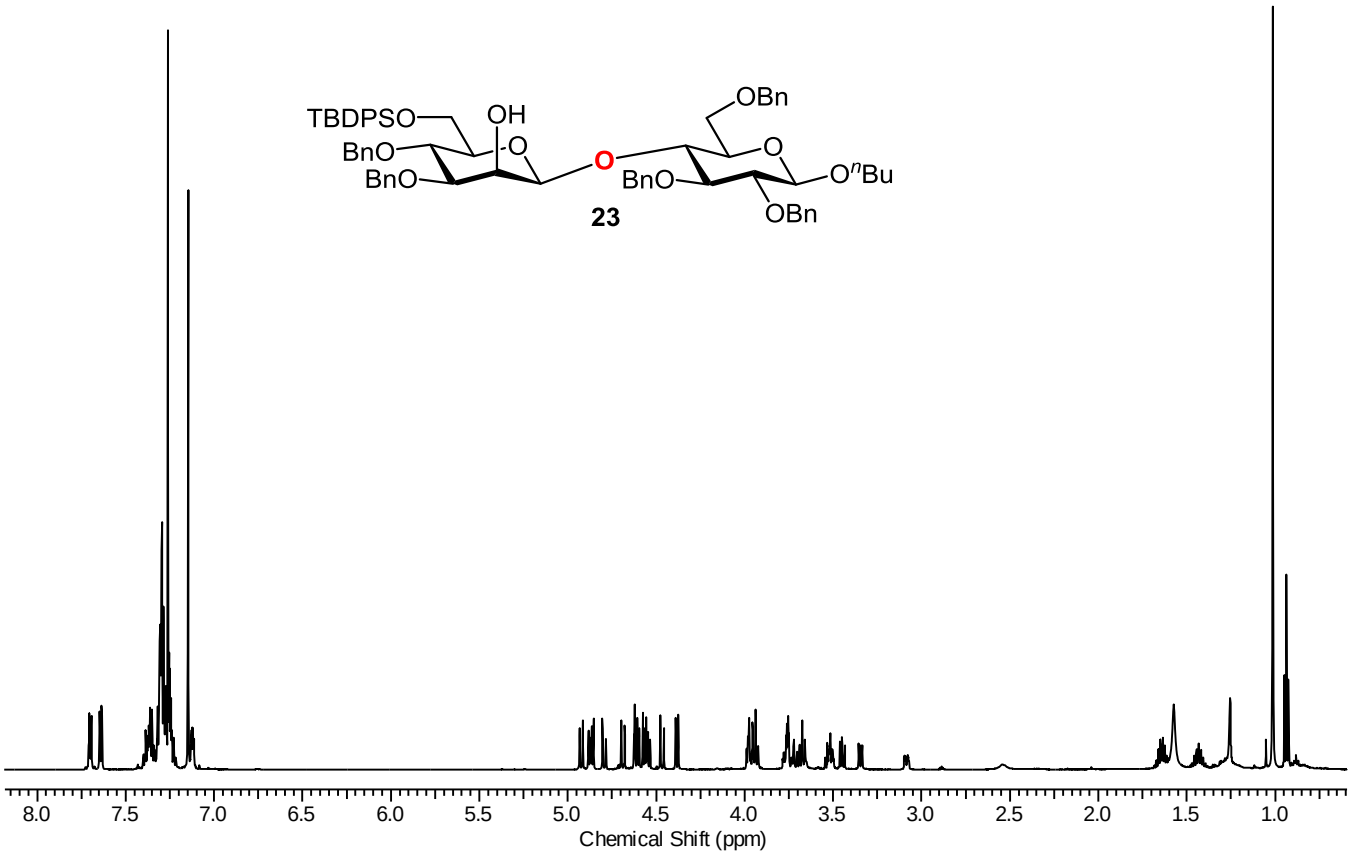
21

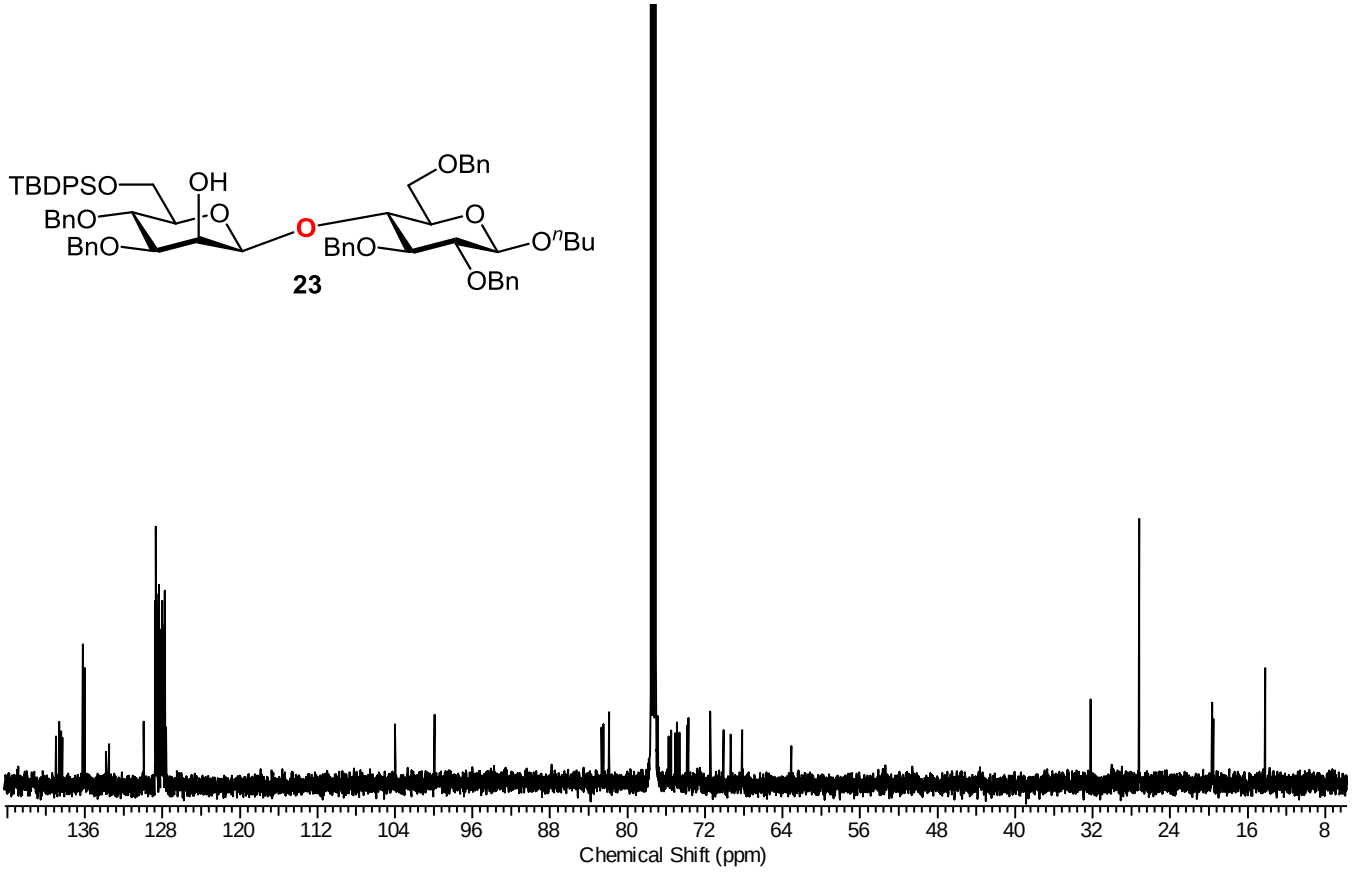

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

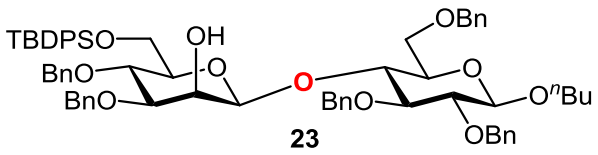

BnO
OH
BnO
O
BnO
O
OBn
O
BnO
NPhth
O
OBn
O
BnO
NPhth
OBn

21

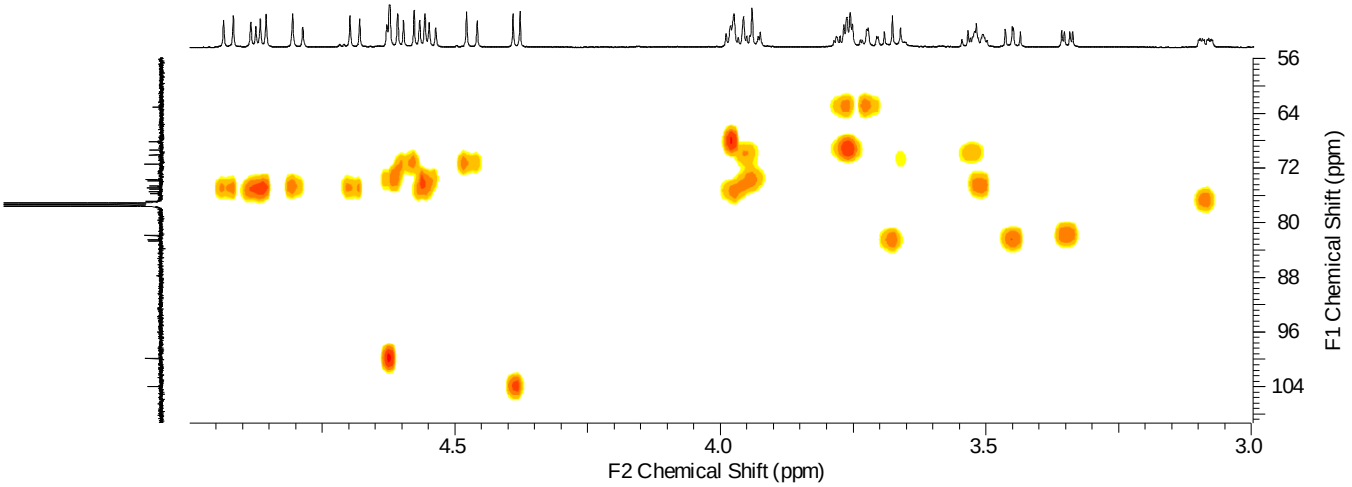

56
64
72
80
88
96
F1 Chemical Shift (ppm)
5.0
4.5
4.0
3.5
F2 Chemical Shift (ppm)

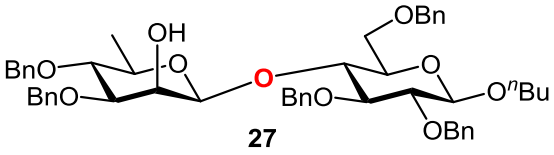

TBDPSO
OH
BnO
BnO
O
OBn
O
BnO
O^{n}Bu
OBn
23
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)


TBDPSO
OH
BnO
BnO
O
OBn
O
BnO
O^{n}Bu
OBn
23
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


TBDPSO
OH
BnO
BnO
O
OBn
O
BnO
O^{n}Bu
OBn

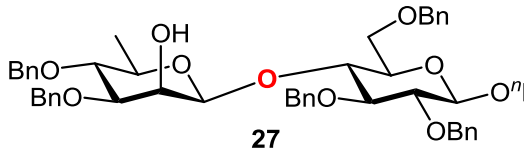
23


56
64
72
80
88
96
104
F1 Chemical Shift (ppm)
4.5
4.0
3.5
3.0
F2 Chemical Shift (ppm)


OH
BnO
BnO
O
OBn
O
BnO
O^{n}Bu
OBn

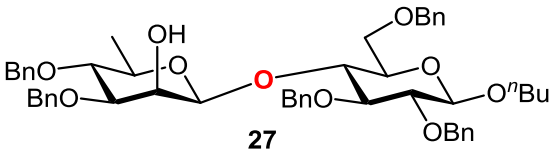
27

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

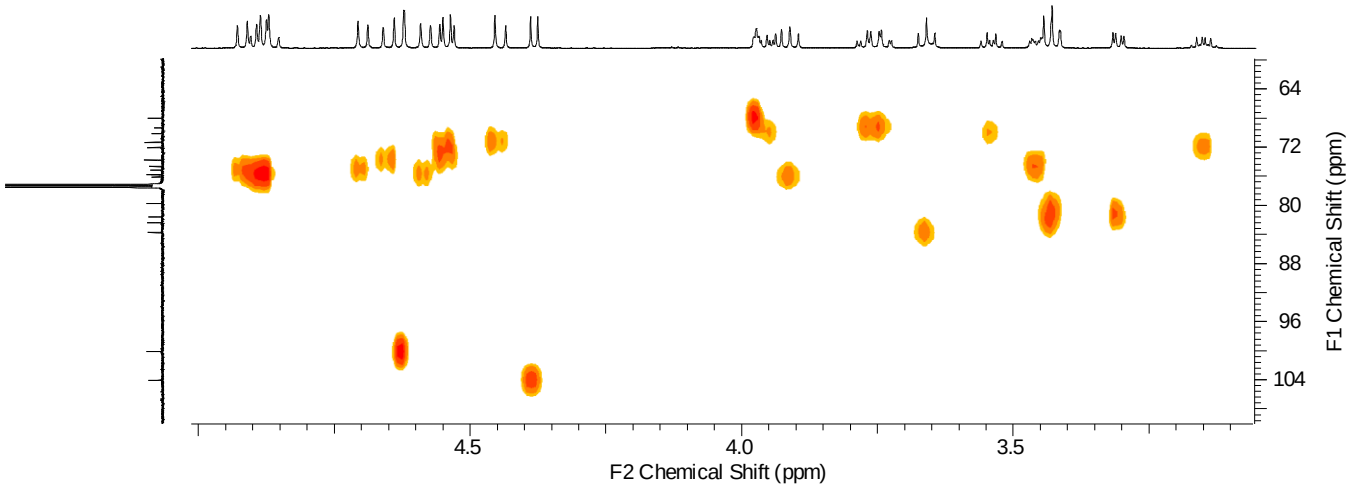

OH
BnO
BnO
O
OBn
BnO
O
O^{n}Bu
OBn

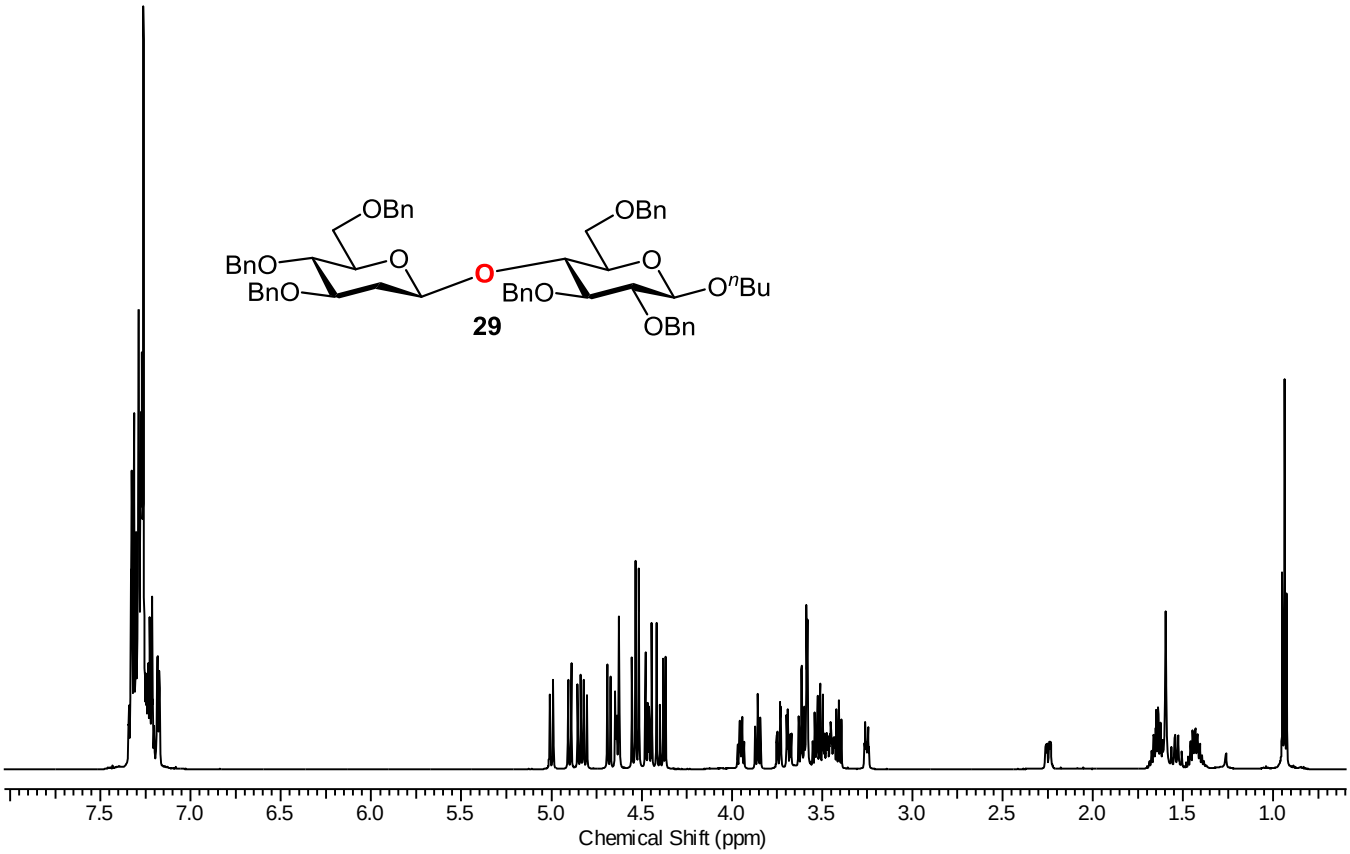
27

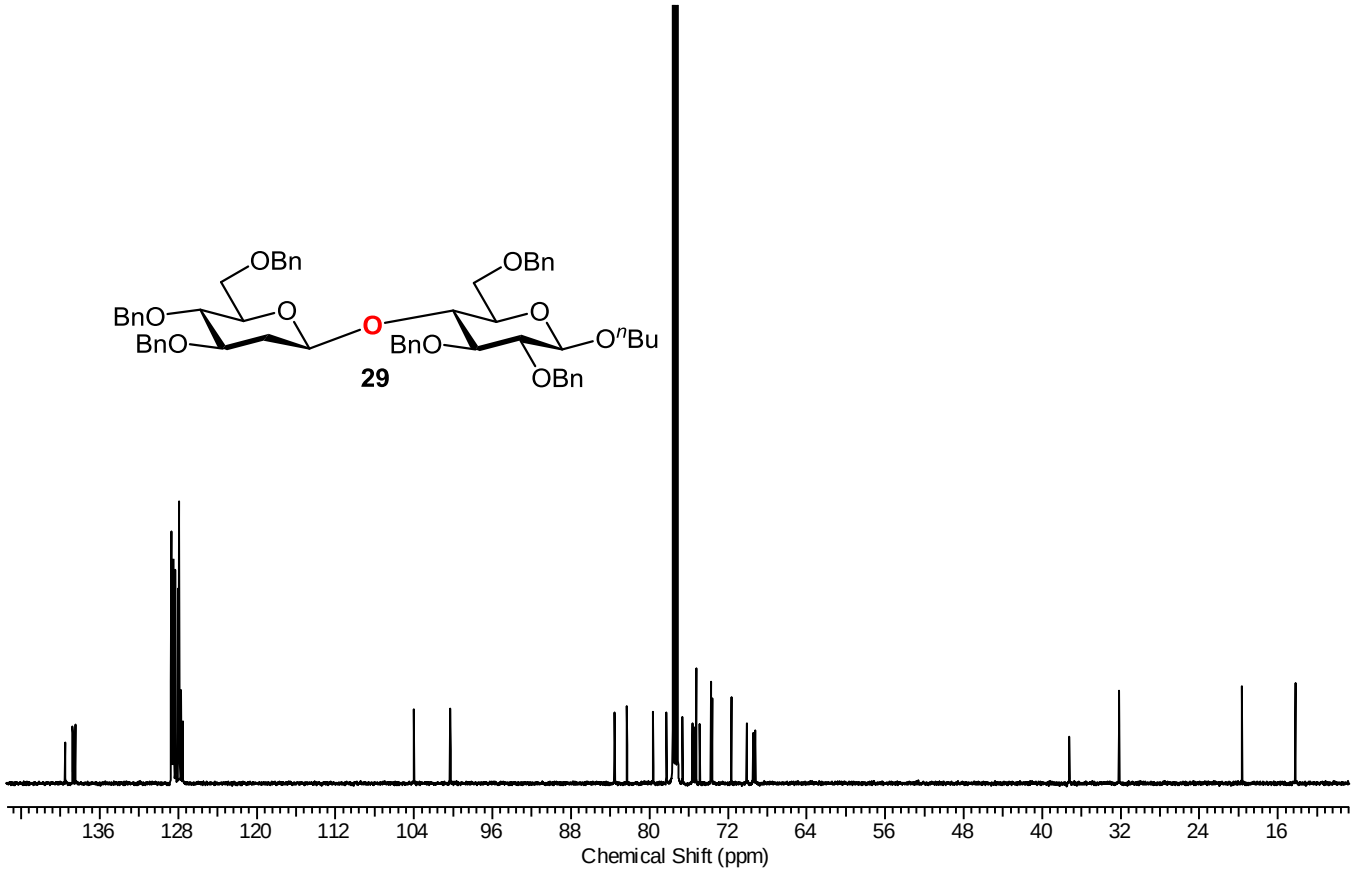
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

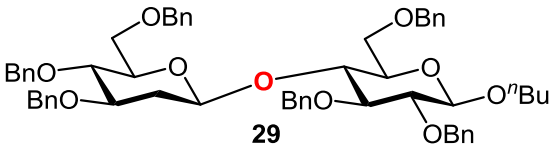

OH
BnO
BnO
O
OBn
BnO
O
O^{n}Bu
OBn

27

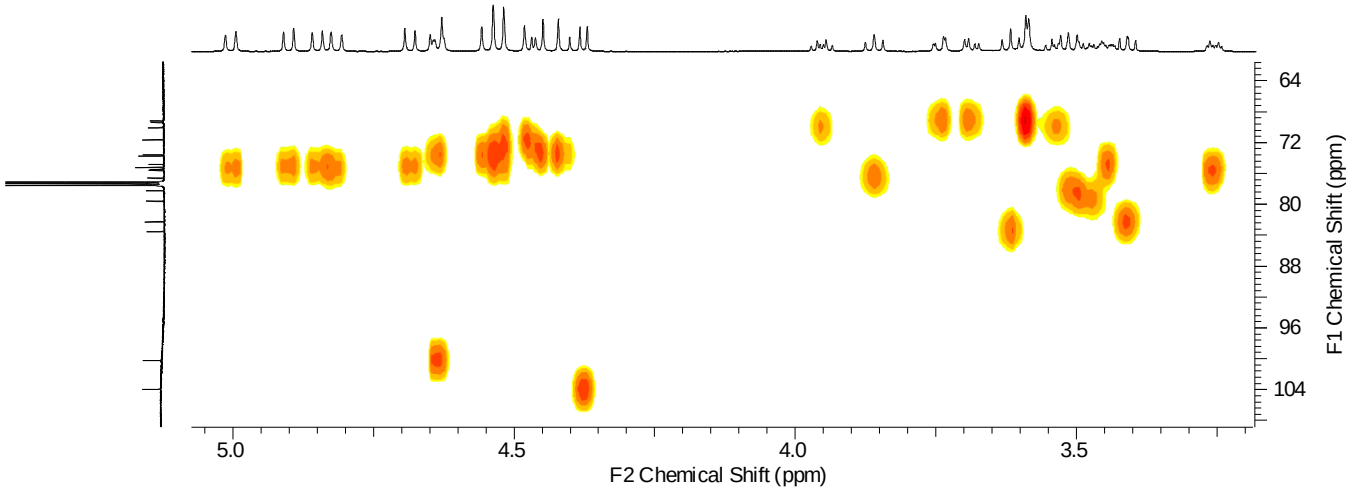

64
72
80
88
96
104
F1 Chemical Shift (ppm)
4.5
4.0
3.5
F2 Chemical Shift (ppm)

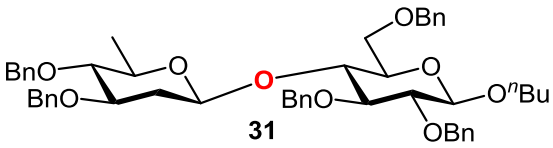

OBn
BnO
O
BnO
O
OBn
O
BnO
O^{n}Bu
OBn
29
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)


OBn
BnO
O
BnO
O
OBn
O
BnO
O^{n}Bu
OBn
29
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)


OBn
OBn
BnO
O
O
BnO
BnO
O^{n}Bu
OBn

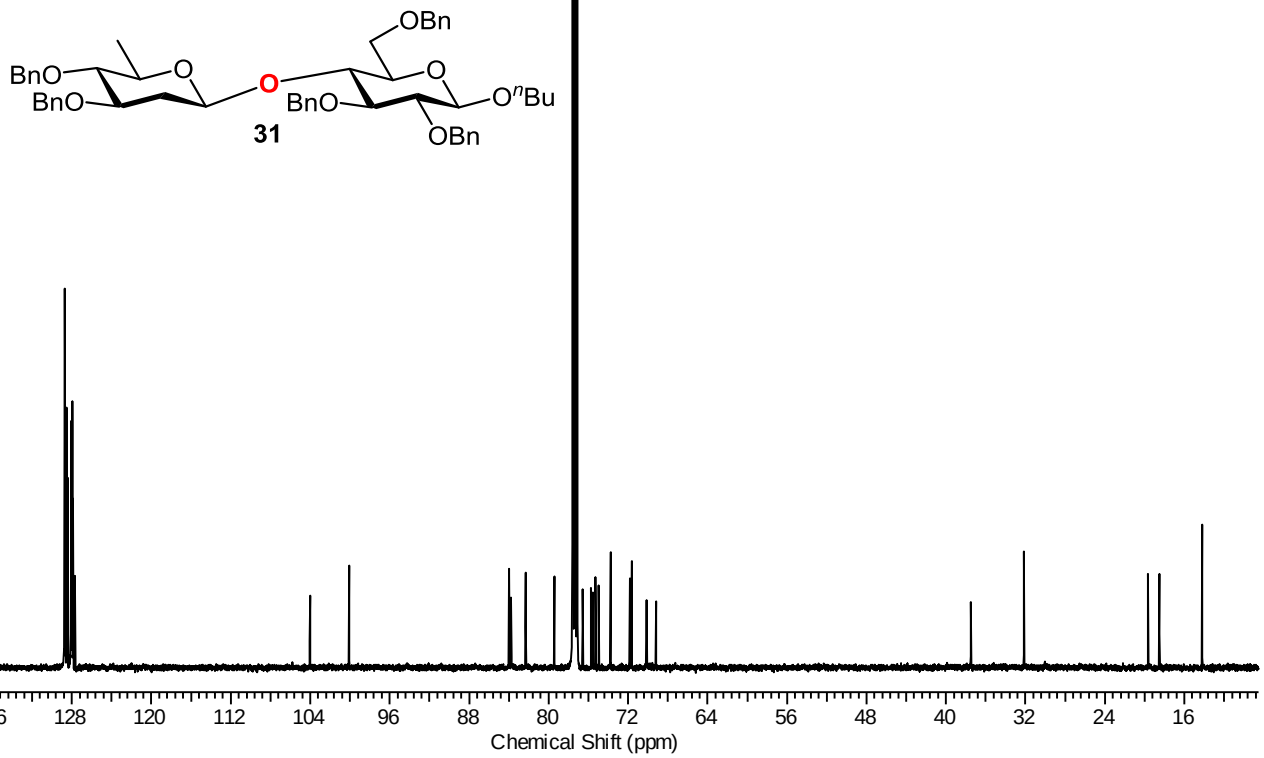
29

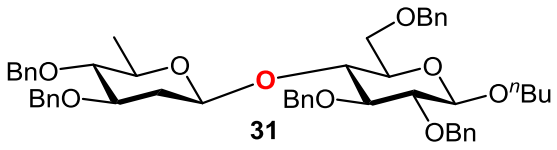

64
72
80
88
96
104
F1 Chemical Shift (ppm)
5.0
4.5
4.0
3.5
F2 Chemical Shift (ppm)

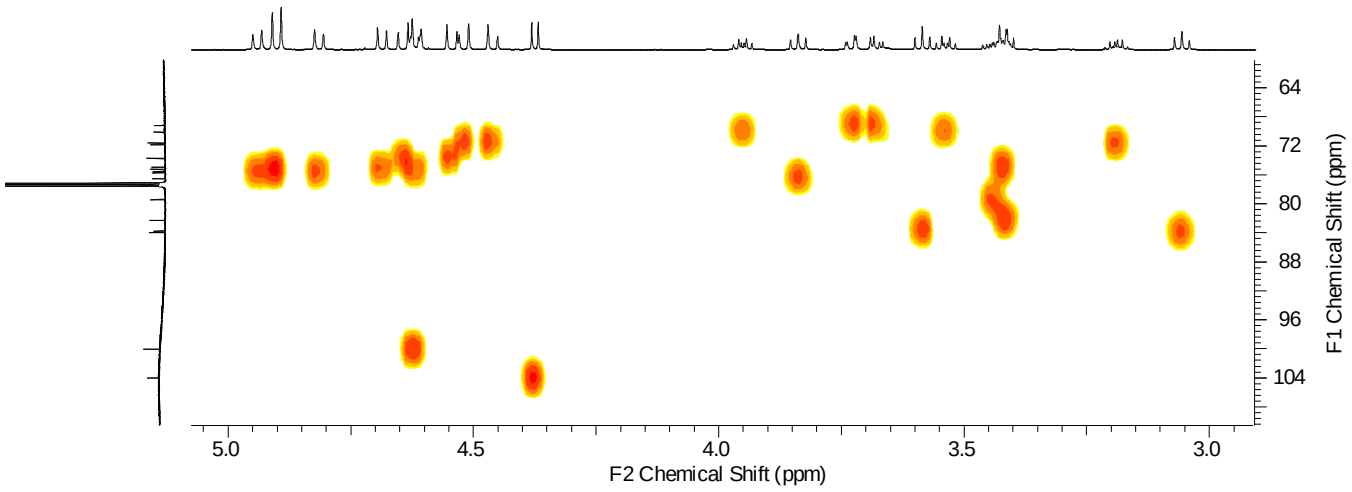

OBn
BnO
O
O
BnO
BnO
O
O^{n}Bu
OBn

31

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


OBn
BnO
O
BnO
O
O
BnO
O^{n}Bu
OBn
31
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)


OBn
BnO
O
BnO
O
O
BnO
O^{n}Bu
OBn
31


64
72
80
88
96
104
F1 Chemical Shift (ppm)
5.0
4.5
4.0
3.5
3.0
F2 Chemical Shift (ppm)