Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

A new method for *α*-specific glucosylation and its application to one-pot synthesis of a branched *α*-glucan

Yanxin Zhang,[a] Shihao Zhou,[a] Xiaohan Wang,[a] Han Zhang,[a] Zhongwu Guo*[ab] and Jian Gao*[a]

a. National Glycoengineering Research Center, Shandong Provincial Key Laboratory of Carbohydrate Chemistry and Glycobiology, Shandong University, 72 Binhai Road, Qingdao, Shandong 266237, China

b. Department of Chemistry, University of Florida, 214 Leigh Hall, Gainesville, Florida 32611, United State

* Corresponding author. E-mail: zguo@chem.ufl.edu; E-mail: jgao@sdu.edu.cn

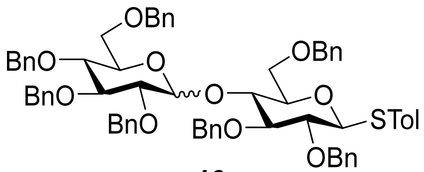
Table of Contents

I. Experimental procedures

General methods: Chemical and materials were purchased from commercial sources and were used as received without further purification unless otherwise noted. Molecular sieve 4Å was flame-dried under high vacuum and cooled under an Argon atmosphere immediately before use. Analytical TLC was carried out on Silica Gel 60Å F254 plates with detection by a UV detector and/or by charring with 15% H_2SO_4 in EtOH (w/v). Mass spectrometry (MS) was performed on a high resolution ESI-TOF MS machine. NMR spectra were recorded on a 500 or 600 MHz machine with chemical shifts reported in ppm (δ) downfield from internal tetramethylsilane (TMS) reference. Signals are described as s (singlet), d (doublet), t (triplet), or m (multiplet), and the coupling constants are reported in Hz.

General procedures for preactivation-based glucosylation: A mixture of donor (0.10 mmol, 1.0 equiv) and freshly activated MS 4Å in anhydrous Et_2O (5 mL) was stirred at room temperature under Argon atmosphere for 1.0 h and then cooled to -78 °C. A solution of AgOTf (25.7 mg, 0.10 mmol, 1.0 equiv) in Et_2O (0.2 mL) was added to the reaction mixture. After stirring for fifteen minutes, *p*-TolSCl (14.5 μL, 0.10 mmol, 1.0 equiv) was added to the reaction mixture through a microsyringe without touching the flask. Fifteen minutes later, a solution of acceptor (0.09 mmol, 0.9 equiv) in Et_2O (0.5 mL), which was precooled to -78 °C, was added to the reaction mixture dropwise. The reaction solution was allowed to warm up to room temperature slowly in 1.5 h and stirred for another 15 min. The reaction mixture was then quenched with Et_3N, diluted with CH_2Cl_2 (50 mL), and filtered. The filtrate was concentrated under vacuum, and the residue purified by silica gel column chromatography to give product.

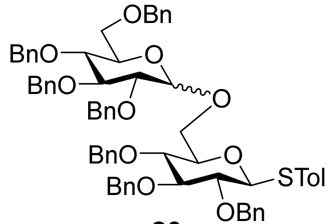
***p*-Tolyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-1-thio-*β*-D-glucopyranoside (19)**



19

Donor **1** reacted with acceptor **5** by the general procedure for glycosylation to give product **19** (86 mg, 89% yield) as syrup after column purification (hexanes/ethyl acetate, 14:1): α/β = 4:1 as determined by integrations of H-1' and SPhCH_3 signals with the stereochemistry determine by $J_{H1',H2'}$ coupling constant. α-**19**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.56 – 7.00 (m, 39H, Ph), 5.64 (d, J = 3.6 Hz, 1H, H-1'), 4.93 – 4.67 (m, 6H, Bn), 4.62 (d, J = 10.2 Hz, 1H, H-1), 4.60 – 4.43 (m, 7H, Bn), 4.31 (d, J = 12.0 Hz, 1H, Bn), 4.09 (t, J = 9.0 Hz, 1H, H-4), 3.95 – 3.83 (m, 2H, H-3', H-6a), 3.82 – 3.72 (m, 3H, H-3, H-5', H-6b), 3.68 – 3.62 (m, 1H, H-4'), 3.60 – 3.48 (m, 4H, H-2, H-2', H-5, H-6a'), 3.44 – 3.31 (m, 1H, H-6b'), 2.32 (s, 3H, PhCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 97.05 (C-1'), 87.34 (C-1), 86.78, 82.02, 80.86, 79.28, 78.70, 77.68, 72.52, 71.00, 69.10, 68.15, 21.15 (PhCH_3). HR ESI-TOF MS (m/z): calcd for $C_{68}H_{74}NO_{10}S$ $[M + NH_4]^+$, 1096.5033; found, 1096.5024.

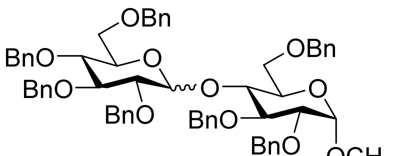
p-Tolyl 2,3,4,6-tetra-O-benzyl-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-1-thio-β-D-glucopyranoside (20)



20

Donor **1** reacted with acceptor **6** by the general procedure for glycosylation to give product **20** (83 mg, 86% yield) as a syrup after column purification (hexanes/ethyl acetate, 14:1): α/β = 5:1 as determined by integrations of H-1' and SPhCH_3 signals with the stereochemistry determine by $J_{H1',H2'}$ coupling constant. α-**20** (G. Wasonga, Y. Zeng, X. Huang, *Sci. China Chem.* **2011**, *54*, 66-73): ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.49 – 7.00 (m, 39H, Ph), 5.04 (d, *J* = 3.6 Hz, 1H, H-1'), 5.01 – 4.71 (m, 8H, Bn), 4.69 – 4.41 (m, 7H, Bn, H-1), 4.00 (t, *J* = 9.6 Hz, 1H, H-3'), 3.90 – 3.87 (m, 1H, H-5'), 3.85 (dd, *J* = 12.0, 4.8 Hz, 1H, H-6a), 3.78 (d, *J* = 12.0 Hz, 1H, H-6b), 3.74 – 3.59 (m, 6H, H-3, H-2', H-4, H-4', H-6a', H-6b'), 3.51 – 3.46 (m, 1H, H-5), 3.26 (t, *J* = 9.0 Hz, 1H, H-2), 2.22 (s, 3H, PhCH_3). HR ESI-TOF MS (*m/z*): calcd for $C_{68}H_{74}NO_{10}S$ [M + NH_4]$^+$, 1096.5033; found, 1096.5046.

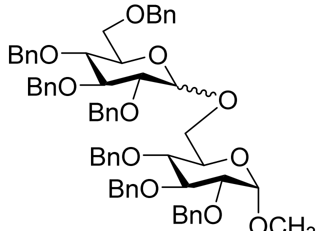
Methyl 2,3,4,6-tetra-O-benzyl-D-glucopyranosyl-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (21)



21

Donor **1** reacted with acceptor **7** by the general procedure for glycosylation to give product **21** (83 mg, 93% yield) as a syrup after column purification (hexanes/ethyl acetate, 13:1): α/β = 3:1 as determined by integrations of H-1' and OCH_3 signals with the stereochemistry determine by $J_{H1',H2'}$ coupling constant. α-**21**: ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.50 – 7.05 (m, 35H, Ph), 5.73 (d, *J* = 3.6 Hz, 1H, H-1'), 5.07 (d, *J* = 11.4 Hz, 1H, Bn), 4.94 – 4.76 (m, 4H, Bn), 4.73 (d, *J* = 12.0 Hz, 1H, Bn), 4.67 – 4.50 (m, 6H, Bn, H-1), 4.48 – 4.38 (m, 2H, Bn), 4.30 (d, *J* = 12.0 Hz, 1H, Bn), 4.14 – 4.05 (m, 2H, H-3, H-4), 3.94 (t, *J* = 9.6 Hz, 1H, H-3'), 3.90 – 3.82 (m, 2H, H-5, H-6a), 3.76 – 3.60 (m, 4H, H-2, H-4', H-5', H-6b), 3.58 – 3.48 (m, 2H, H-2', H-6a'), 3.43 – 3.41 (m, 1H, H-6b'), 3.40 (s, 3H, OCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 97.78 (C-1), 96.65 (C-1'), 82.07, 82.05, 80.21, 79.46, 77.64, 72.27, 70.97, 69.53, 69.02, 68.15, 55.17 (OCH_3). HR ESI-TOF MS (*m/z*): calcd for $C_{62}H_{70}NO_{11}$ [M + NH_4]$^+$, 1004.4949; found, 1004.4943.

Methyl 2,3,4,6-tetra-O-benzyl-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (22)

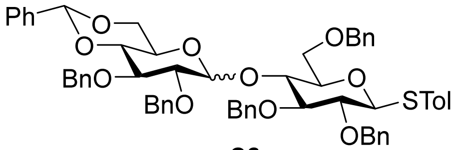


22

Donor **1** reacted with acceptor **8** by the general procedure for glycosylation to give product **22** (80 mg, 90% yield) as a syrup after column purification (hexanes/ethyl acetate, 13:1): α/β = 2:1 as determined by integrations of H-1' and OCH_3 signals with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. α-**22** (G. Wasonga, Y. Zeng, X. Huang, *Sci. China Chem.* **2011**, *54*, 66-73.): ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.37 – 7.10 (m, 35H, Ph), 4.98 (d, *J* = 3.6 Hz, 1H, H-1'), 4.98 – 4.90 (m, 3H, Bn), 4.84 – 4.79 (m, 2H, Bn), 4.77 (d, *J* = 12.0 Hz, 1H, Bn) , 4.71

(d, J = 12.0 Hz, 1H, Bn), 4.68 – 4.63 (m, 3H, Bn), 4.61 – 4.55 (m, 2H, Bn), 4.55 (d, J = 3.6 Hz, 1H, H-1), 4.45 (d, J = 10.8 Hz, 1H, Bn), 4.42 (d, J = 12.0 Hz, 1H, Bn), 4.01 – 3.94 (m, 2H, H-3, H-3'), 3.83 – 3.75 (m, 3H, H-5, H-5', H-6a'), 3.74 – 3.70 (m, 1H, H-6a), 3.69 – 3.61 (m, 3H, H-4, H-4', H-6b'), 3.57 – 3.55 (m, 1H, H-6b), 3.54 (dd, J = 9.6, 3.6 Hz, 1H, H-2'), 3.44 (dd, J = 9.6, 3.6 Hz, 1H, H-2), 3.35 (s, 3H, OCH_3). HR ESI-TOF MS (*m/z*): calcd for $C_{62}H_{70}NO_{11}$ [M + NH$_4$]$^+$, 1004.4949; found, 1004.4947.

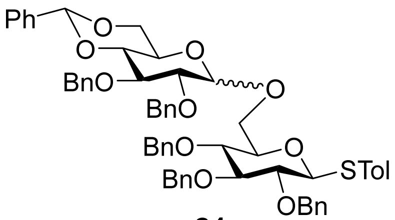
p-Tolyl 4,6-O-benzylidene-2,3-di-O-benzyl-D-glucopyranosyl-(1→4)-2,3,6-tri-O-benzyl-1-thio-β-D-glucopyranoside (23)



23

Donor **2** reacted with acceptor **5** by the general procedure for glycosylation to give product **23** (81 mg, 91% yield) as a syrup after column purification (hexanes/ethyl acetate, 15:1): α/β = 4:1 as determined by integrations of H-1' and SPhCH_3 signals with the stereochemistry determine by $J_{H1',H2'}$ coupling constant. α-**23**: ^{1}H NMR (600 MHz, CDCl$_3$) δ: 7.80 – 6.95 (m, 34H, Ph), 5.67 (d, J = 3.6 Hz, 1H, H-1'), 5.53 (s, 1H, PhC*H*), 4.92 – 4.78 (m, 4H, Bn), 4.74 – 4.66 (m, 3H, Bn), 4.62 – 4.50 (m, 4H, Bn, H-1), 4.16 – 4.10 (m, 2H, H-4, H-6a'), 3.99 (t, J = 9.6 Hz, 1H, H-3'), 3.91 – 3.78 (m, 4H, H-3, H-5, H-6a,6b), 3.64 – 3.55 (m, 3H, H-4', H-5', H-6b'), 3.54 – 3.47 (m, 2H, H-2, H-2'), 2.32 (s, 3H, PhCH_3). ^{13}C NMR (150 MHz, CDCl$_3$) δ: 101.11 (Ph*C*H), 97.49 (C-1'), 87.28 (C-1), 86.91, 82.30, 80.84, 78.75, 78.61, 78.37, 71.62, 68.89, 65.57, 63.30, 21.14 (Ph*C*H$_3$). HR ESI-TOF MS (*m/z*): calcd for $C_{61}H_{66}NO_{10}S$ [M + NH$_4$]$^+$, 1004.4407; found, 1004.4415.

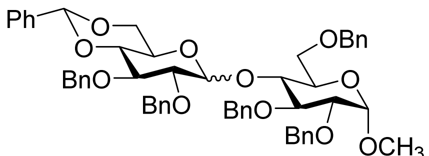
p-Tolyl 4,6-O-benzylidene-2,3-di-O-benzyl-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzyl-1-thio-β-D-glucopyranoside (24)



24

Donor **2** reacted with acceptor **6** by the general procedure for glycosylation to give product **24** (78 mg, 88% yield) as a syrup after column purification (hexanes/ethyl acetate, 15:1): α/β = 5:1 as determined by integrations of H-1' and SPhCH_3 signals with the stereochemistry determine by $J_{H1',H2'}$ coupling constant. α-**24**: ^{1}H NMR (600 MHz, CDCl$_3$) δ: 7.71 – 6.89 (m, 34H, Ph), 5.58 (s, 1H, PhC*H*), 5.05 (d, J = 3.6 Hz, 1H, H-1'), 4.95 – 4.74 (m, 8H, Bn), 4.70 – 4.56 (m, 3H, Bn, H-1), 4.30 (dd, J = 10.2, 4.8 Hz, 1H, H-6a'), 4.04 (t, J = 9.6 Hz, 1H, H-3'), 3.98 – 3.91 (m, 1H, H-5'), 3.87 (dd, J = 12.0, 4.2 Hz, 1H, H-6a), 3.80 (dd, J = 12.0, 1.8 Hz, 1H, H-6b), 3.76 – 3.62 (m, 4H, H-3, H-4', H-5, H-6b'), 3.61 – 3.57 (m, 1H, H-2'), 3.53 – 3.44 (m, 1H, H-4), 3.26 (t, J = 9.6 Hz, 1H, H-2), 2.23 (s, 3H, PhCH_3). ^{13}C NMR (150 MHz, CDCl$_3$) δ: 101.36 (Ph*C*H), 98.26 (C-1'), 88.39 (C-1), 86.65, 82.18, 81.12, 79.56, 78.83, 78.03, 77.40, 69.14, 66.20, 62.61, 21.06 (Ph*C*H$_3$). HR ESI-TOF MS (*m/z*): calcd for $C_{61}H_{66}NO_{10}S$ [M + NH$_4$]$^+$, 1004.4407; found, 1004.4419.

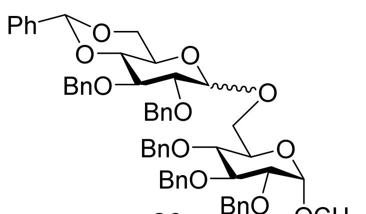
Methyl 4,6-O-benzylidene-2,3-di-O-benzyl-D-glucopyranosyl-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (25)



25

Donor **2** reacted with acceptor **7** by the general procedure for glycosylation to give product **25** (74 mg, 92% yield) as a syrup after column purification (hexanes/ethyl acetate, 15:1): α/β = 3:1 as determined by integrations of H-1' and OCH_3 signals with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. α-**25**: ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.68 – 7.06 (m, 30H, Ph), 5.78 (d, *J* = 3.6 Hz, 1H, H-1'), 5.56 (s, 1H, PhC*H*), 5.07 (d, *J* = 12.0 Hz, 1H, Bn), 4.93 (d, *J* = 11.4 Hz, 1H, Bn), 4.85 – 4.76 (m, 2H, Bn), 4.74 – 4.67 (m, 3H, Bn), 4.65 (d, *J* = 3.6 Hz, 1H, H-1), 4.63 – 4.55 (m, 3H, Bn), 4.24 – 4.10 (m, 3H, H-3, H-4, H-6a'), 4.02 (t, *J* = 9.6 Hz, 1H, H-3'), 3.94 – 3.83 (m, 3H, H-5, H-5', H-6a), 3.73 – 3.67 (m, 1H, H-6b), 3.66 – 3.61 (m, 3H, H-2, H-4', H-6b'), 3.57 – 3.51 (m, 1H, H-2'), 3.41 (s, 3H, OCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 101.12 (Ph*C*H), 97.74 (C-1), 97.19 (C-1'), 82.31, 82.13, 80.26, 78.86, 78.76, 71.61, 69.34, 68.94, 68.79, 63.29, 55.20 (O*C*H_3). HR ESI-TOF MS (*m/z*): calcd for $C_{55}H_{62}NO_{11}$ [M + NH_4]$^+$, 912.4323; found, 912.4343.

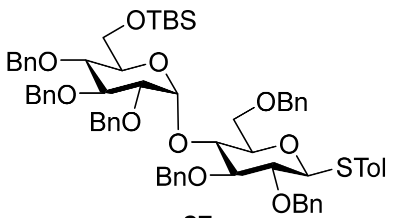
Methyl 4,6-*O*-benzylidene-2,3-di-*O*-benzyl-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (26)



26

Donor **2** reacted with acceptor **8** by the general procedure for glycosylation to give product **26** (72 mg, 90% yield) as a syrup after column purification (hexanes/ethyl acetate, 15:1): α/β = 6:1 as determined by integrations of H-1' and OCH_3 signals with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. α-**26**: ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.50 – 7.15 (m, 30H, Ph), 5.53 (s, 1H, PhC*H*), 4.97 (d, *J* = 10.8 Hz, 1H, Bn), 4.92 (d, *J* = 3.6 Hz, 1H, H-1'), 4.91 – 4.86 (m, 2H, Bn), 4.83 – 4.79 (m, 2H, Bn), 4.75 – 4.65 (m, 3H, Bn), 4.63 (d, *J* = 10.8 Hz, 1H, Bn), 4.59 – 4.55 (m, 2H, H-1, Bn), 4.20 (dd, *J* = 10.2, 4.8 Hz, 1H, H-6a'), 4.02 – 3.96 (m, 2H, H-3, H-3'), 3.91 – 3.86 (m, 1H, H-5'), 3.81 – 3.66 (m, 4H, H-5, H-6a, H-6b, H-6b'), 3.64 – 3.56 (m, 2H, H-4, H-4'), 3.53 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2), 3.43 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2'), 3.34 (s, 3H, OCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 101.27 (Ph*C*H), 98.18 (C-1'), 97.96 (C-1), 82.15, 82.08, 80.03, 79.28, 77.90, 77.70, 70.33, 69.07, 66.32, 62.51, 55.19 (O*C*H_3). HR ESI-TOF MS (*m/z*): calcd for $C_{55}H_{62}NO_{11}$ [M + NH_4]$^+$, 912.4323; found, 912.4340.

***p*-Tolyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-*α*-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-1-thio-*β*-D-glucopyranoside (27)**

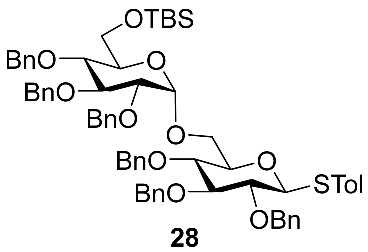


27

Donor **3** reacted with acceptor **5** by the general procedure for glycosylation to give product **27** (88 mg, 89% yield) as a syrup after column purification (hexanes/ethyl acetate, 14:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.54 – 7.50 (m, 2H, Ph), 7.41 – 7.00 (m, 32H, Ph), 5.56 (d, *J* = 3.6 Hz, 1H, H-1'), 4.91 – 4.84 (m, 5H, Bn), 4.80 (d, *J* = 10.8 Hz, 1H, Bn), 4.68 (d, *J* = 10.8 Hz, 1H, Bn), 4.64 (d, *J* = 9.6 Hz, 1H, H-1), 4.62 – 4.56 (m, 4H, Bn), 4.52 (d, *J*

= 12.0 Hz, 1H, Bn), 4.10 (t, J = 9.0 Hz, 1H, H-4), 3.98 – 3.89 (m, 2H, H-3', H-6a), 3.87 – 3.78 (m, 2H, H-3, H-6b), 3.72 (dd, J = 11.4, 3.0 Hz, 1H, H-6a'), 3.70 – 3.61 (m, 3H, H-4', H-5', H-6b'), 3.61 – 3.54 (m, 2H, H-2, H-5), 3.42 (dd, J = 9.6, 3.6 Hz, 1H, H-2'), 2.33 (s, 3H, PhCH_3), 0.89 (s, 9H, *t*Bu), 0.03 (s, 3H, SiCH_3), 0.02 (s, 3H, SiCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 138.71, 138.69, 138.67, 138.50, 138.00, 137.96, 137.69, 132.74, 129.68, 129.61, 128.38, 128.36, 128.29, 128.26, 127.98, 127.86, 127.69, 127.65, 127.58, 127.55, 127.38, 127.35, 127.17, 126.54, 96.57 (C-1'), 87.36 (C-1), 86.84, 81.86, 80.77, 79.85, 78.71, 77.56, 77.25, 77.04, 76.83, 75.67, 75.19, 75.02, 74.19, 73.35, 73.17, 72.44, 72.28, 69.21, 61.86, 25.98, 21.16, 18.35, -5.05, -5.34. HR ESI-TOF MS (*m/z*): calcd for $C_{67}H_{82}NO_{10}SSi$ $[M + NH_4]^+$, 1120.5429; found, 1120.5447.

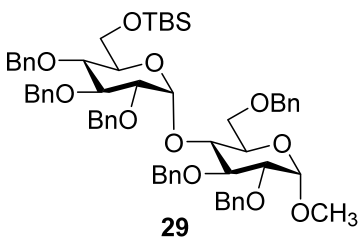
p-Tolyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-*α*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-1-thio-*β*-D-glucopyranoside (28)



28

Donor **3** reacted with acceptor **6** by the general procedure for glycosylation to give product **28** (86 mg, 87% yield) as a syrup after column purification (hexanes/ethyl acetate, 14:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.48 (d, J = 8.4 Hz, 2H, Ph), 7.43 – 7.22 (m, 30H, Ph), 7.09 (d, J = 7.8 Hz, 2H, Ph), 5.05 (d, J = 3.6 Hz, 1H, H-1'), 4.97 (d, J = 10.8 Hz, 1H, Bn), 4.92 (d, J = 11.4 Hz, 1H, Bn), 4.90 – 4.86 (m, 2H, Bn), 4.85 – 4.80 (m, 3H, Bn), 4.78 (d, J = 12.0 Hz, 1H, Bn), 4.74 – 4.67 (m, 3H, Bn), 4.63 (d, J = 10.2 Hz, 1H, Bn), 4.56 (d, J = 9.6 Hz, 1H, H-1), 4.01 (t, J = 9.6 Hz, 1H, H-3'), 3.87 – 3.82 (m, 2H, H-6a, H-6a'), 3.81 – 3.77 (m, 2H, H-6b, H-6b'), 3.77 – 3.73 (m, 1H, H-5'), 3.71 (t, J = 9.6 Hz, 1H, H-4), 3.68 – 3.60 (m, 2H, H-3, H-4'), 3.54 (dd, J = 9.6, 3.6 Hz, 1H, H-2'), 3.49 – 3.45 (m, 1H, H-5), 3.26 (t, J = 9.6 Hz, 1H, H-2), 2.23 (s, 3H, PhCH_3), 0.91 (s, 9H, *t*Bu), 0.08 (s, 3H, SiCH_3), 0.07 (s, 3H, SiCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 138.81, 138.72, 138.56, 138.51, 138.19, 138.07, 137.91, 133.27, 129.76, 129.67, 128.44, 128.43, 128.41, 128.38, 128.37, 128.32, 128.26, 128.14, 127.90, 127.84, 127.76, 127.72, 127.68, 127.59, 127.55, 127.52, 127.48, 97.03 (C-1'), 88.17 (C-1), 86.65, 81.73, 81.08, 80.57, 78.96, 77.58, 77.54, 75.78, 75.63, 75.46, 74.99, 74.95, 72.41, 71.65, 65.74, 62.17, 25.98, 21.08, 18.35, -5.05, -5.32. HR ESI-TOF MS (*m/z*): calcd for $C_{67}H_{82}NO_{10}SSi$ $[M + NH_4]^+$, 1120.5429; found, 1120.5442.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-*α*-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*α*-D-glucopyranoside (29)

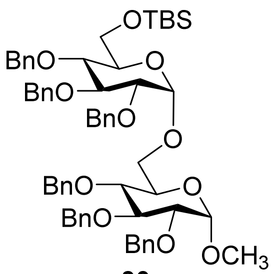


29

Donor **3** reacted with acceptor **7** by the general procedure for glycosylation to give product **29** (86 mg, 94% yield) as a syrup after column purification (hexanes/ethyl acetate, 14:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.52 – 6.97 (m, 30H, Ph), 5.61 (d, J = 3.6 Hz, 1H, H-1'), 5.03 (d, J = 11.4 Hz, 1H, Bn), 4.89 – 4.83 (m, 2H, Bn), 4.83 – 4.76 (m, 2H, Bn), 4.71 (d, J

= 12.0 Hz, 1H, Bn), 4.65 (d, J = 10.8 Hz, 1H, Bn), 4.62 (d, J = 3.6 Hz, 1H, H-1), 4.60 – 4.50 (m, 5H, Bn), 4.08 – 4.05 (m, 2H, H-3, H-4), 3.92 (t, J = 8.4 Hz, 1H, H-3'), 3.88 – 3.83 (m, 2H, H-5', H-6a), 3.69 – 3.57 (m, 6H, H-2', H-4', H-5, H-6b, H-6a',6b'), 3.40 (dd, J = 10.2, 3.6 Hz, 1H, H-2), 3.38 (s, 3H, OCH_3), 0.86 (s, 9H, *t*Bu), -0.01 (s, 6H, SiCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 139.07, 138.78, 138.74, 138.12, 138.03, 138.00, 128.41, 128.34, 128.32, 128.29, 128.22, 128.18, 128.00, 127.90, 127.80, 127.77, 127.58, 127.55, 127.36, 127.23, 127.03, 126.68, 97.74 (C-1), 96.04 (C-1'), 82.07, 81.88, 80.14, 79.95, 77.50, 75.69, 74.97, 74.19, 73.34, 73.16, 73.11, 72.17, 71.98, 69.42, 69.05, 61.84, 55.12, 25.95, 18.31, -5.07, -5.38. HR ESI-TOF MS (*m/z*): calcd for $C_{61}H_{78}NO_{11}Si$ [M + NH_4]$^+$, 1028.5344; found, 1028.5355.

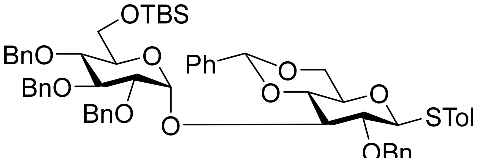
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-*α*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (30)



30

Donor **3** reacted with acceptor **8** by the general procedure for glycosylation to give product **30** (83 mg, 91% yield) as a syrup after column purification (hexanes/ethyl acetate, 14:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.69 – 7.00 (m, 30H, Ph), 5.00 (d, J = 10.2 Hz, 1H, Bn), 4.99 (d, J = 4.2 Hz, 1H, H-1'), 4.98 – 4.89 (m, 3H, Bn), 4.85 (d, J = 10.8 Hz, 1H, Bn), 4.81 (d, J = 10.2 Hz, 1H, Bn), 4.77 – 4.64 (m, 5H, Bn), 4.59 (d, J = 12.0 Hz, 1H, Bn), 4.58 (d, J = 3.6 Hz, 1H, H-1), 4.05 – 3.97 (m, 2H, H-3, H-3'), 3.85 (dd, J = 12.0, 4.8 Hz, 1H, H-6a), 3.83 – 3.72 (m, 4H, H-5', H-6b, H-6a',6b'), 3.72 – 3.67 (m, 2H, H-4', H-5), 3.58 (t, J = 9.6 Hz, 1H, H-4), 3.52 (dd, J = 9.6, 3.6 Hz, 1H, H-2'), 3.46 (dd, J = 9.6, 3.6 Hz, 1H, H-2), 3.38 (s, 3H, OCH_3), 0.90 (s, 9H, *t*Bu), 0.05 (s, 3H, SiCH_3), 0.04 (s, 3H, SiCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 138.85, 138.79, 138.73, 138.58, 138.43, 138.21, 128.43, 128.39, 128.37, 128.35, 128.17, 128.03, 128.00, 127.85, 127.81, 127.69, 127.65, 127.57, 127.56, 127.53, 97.97 (C-1), 97.04 (C-1'), 82.15, 81.71, 80.40, 80.14, 77.80, 77.62, 75.74, 75.63, 75.03, 74.87, 73.42, 72.35, 71.67, 70.47, 65.74, 62.20, 55.14, 25.95, 18.32, -5.10, -5.35. HR ESI-TOF MS (*m/z*): calcd for $C_{61}H_{78}NO_{11}Si$ [M + NH_4]$^+$, 1028.5344; found, 1028.5348.

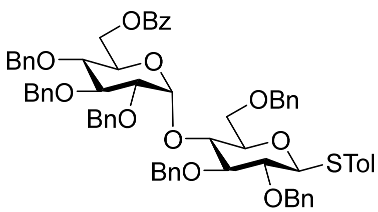
***p*-Tolyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-*α*-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-benzyl-1-thio-*β*-D-glucopyranoside (31)**



31

Donor **3** reacted with acceptor **9** by the general procedure for glycosylation to give product **31** (78 mg, 86% yield) as a syrup after column purification (hexanes/ethyl acetate, 14:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.54 – 6.92 (m, 29H, Ph), 5.59 (d, J = 3.6 Hz, 1H, H-1'), 5.49 (s, 1H, PhCH), 5.02 – 4.95 (m, 2H, Bn), 4.92 (d, J = 10.8 Hz, 1H, Bn), 4.84 (d, J = 10.8 Hz, 1H, Bn), 4.75 (d, J = 10.2 Hz, 1H, H-1), 4.70 (d, J = 9.6 Hz, 1H, Bn), 4.65 – 4.56 (m, 2H, Bn), 4.43 – 4.32 (m, 2H, H-6a, Bn), 4.17 (t, J = 9.6 Hz, 1H, H-3), 4.02 (t, J = 9.6 Hz, 1H, H-3'), 3.95 – 3.91 (m, 1H, H-5'), 3.88 – 3.76 (m, 2H, H-4, H-6b), 3.65 (t, J = 9.6 Hz, 1H, H-4'), 3.58 (t, J = 10.2 Hz, 1H, H-2), 3.55 – 3.51 (m, 1H, H-5), 3.46 – 3.41 (m, 3H, H-2', H-6a',6b'), 2.38 (s, 3H, PhCH_3), 0.83 (s, 9H, *t*Bu), -0.06 (s, 3H, SiCH_3) , -0.07 (s, 3H, SiCH_3). ^{13}C NMR (150 MHz, CDCl$_3$) *δ*: 139.05, 138.79, 138.24, 137.85, 137.32, 136.91, 132.85, 129.88, 129.40, 129.10, 128.80, 128.45, 128.33, 128.23, 128.19, 128.13, 128.07, 127.79, 127.61, 127.54, 127.46, 127.44, 127.37, 126.38, 102.07 (Ph*C*H), 96.03 (C-1'), 88.76 (C-1), 82.22, 81.84, 79.16, 78.92, 77.14, 76.64, 75.84, 75.76, 74.86, 71.42, 70.95, 69.83, 68.87, 61.40, 26.01, 21.18, 18.27, -5.25, -5.47. HR ESI-TOF MS (*m/z*): calcd for $C_{60}H_{74}NO_{10}SSi$ [M + NH$_4$]$^+$, 1028.4803; found, 1028.4832.

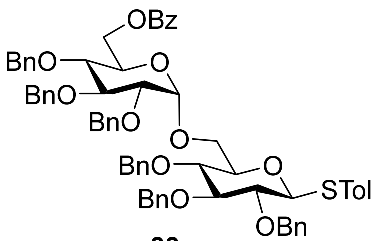
***p*-Tolyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-1-thio-*β*-D-glucopyranoside (32)**



32

Donor **4** reacted with acceptor **5** by the general procedure for glycosylation to give product **32** (87 mg, 88% yield) as a syrup after column purification (hexanes/ethyl acetate, 12:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, CDCl$_3$) *δ*: 8.03 – 7.99 (m, 2H, Ph), 7.60 – 7.03 (m, 37H, Ph), 5.56 (d, *J* = 3.6 Hz, 1H, H-1'), 4.92 – 4.88 (m, 4H, Bn), 4.85 (d, *J* = 10.2 Hz, 1H, Bn), 4.80 (d, *J* = 10.8 Hz, 1H, Bn), 4.64 (d, *J* = 9.6 Hz, 1H, H-1), 4.61 – 4.56 (m, 5H, Bn), 4.52 (d, *J* = 12.0 Hz, 1H, Bn), 4.41 – 4.39 (m, 2H, H-6a',6b'), 4.10 (t, *J* = 9.6 Hz, 1H, H-4), 4.06 – 4.02 (m, 1H, H-5'), 3.99 (t, *J* = 9.6 Hz, 1H, H-3'), 3.89 (dd, *J* = 11.4, 4.2 Hz, 1H, H-6a), 3.82 – 3.78 (m, 2H, H-3, H-6b), 3.62 – 3.55 (m, 2H, H-4', H-5), 3.52 (t, *J* = 9.6 Hz, 1H, H-2), 3.49 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2'), 2.33 (s, 3H, PhCH_3). ^{13}C NMR (150 MHz, CDCl$_3$) *δ*: 166.13, 138.67, 138.37, 138.18, 137.86, 137.83, 137.77, 133.02, 132.75, 129.97, 129.70, 129.68, 129.60, 128.46, 128.43, 128.39, 128.36, 128.32, 128.30, 128.27, 128.23, 128.09, 127.97, 127.95, 127.92, 127.85, 127.72, 127.63, 127.60, 127.51, 127.11, 126.44, 96.64 (C-1'), 87.51 (C-1), 86.57, 81.90, 80.75, 79.68, 78.74, 77.73, 75.76, 75.22, 74.13, 73.36, 73.28, 73.10, 69.64, 68.97, 63.42, 21.16. HR ESI-TOF MS (*m/z*): calcd for $C_{68}H_{72}NO_{11}S$ [M + NH$_4$]$^+$, 1110.4826; found, 1110.4823.

***p*-Tolyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-1-thio-*β*-D-glucopyranoside (33)**

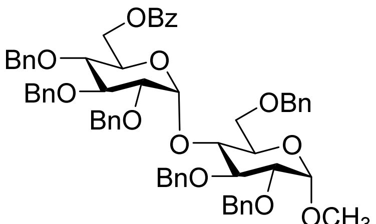


33

Donor **4** reacted with acceptor **6** by the general procedure for glycosylation to give product **33** (86 mg, 87% yield) as a syrup after column purification (hexanes/ethyl acetate, 12:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, CDCl$_3$) *δ*: 8.02 (d, *J* = 7.8 Hz, 2H), 7.60 – 7.17 (m, 35H, Ph), 7.06 (d, *J* = 7.8 Hz, 2H, Ph), 5.03 (d, *J* = 3.0 Hz, 1H, H-1'), 5.02 (d, *J* = 11.4 Hz, 1H, Bn), 4.92 (d, *J* = 10.8 Hz, 1H, Bn), 4.91 – 4.86 (m, 2H, Bn), 4.86 – 4.79 (m, 4H, Bn), 4.74 (d, *J* = 12.0 Hz, 1H, Bn), 4.68 – 4.59 (m, 3H, Bn), 4.57 (d, *J* = 9.6 Hz, 1H, H-1), 4.54 (dd, *J* = 12.6, 1.8 Hz, 1H, H-6a'), 4.47 (dd, *J* = 12.0, 4.2 Hz, 1H, H-6b'), 4.08 – 4.05 (m, 1H, H-5') , 4.05 (t, *J* = 9.0 Hz, 1H, H-3'), 3.85 (dd, *J* = 11.4, 4.8 Hz, 1H, H-6a), 3.76 (dd, *J* = 12.0, 1.8 Hz, 1H, H-6b), 3.71 – 3.61 (m, 3H, H-3, H-

4, H-4'), 3.60 (dd, J = 9.6, 3.6 Hz, 1H, H-2'), 3.50 – 3.46 (m, 1H, H-5), 3.24 (t, J = 9.0 Hz, 1H, H-2), 2.21 (s, 3H, PhCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 166.20, 138.54, 138.52, 138.31, 138.09, 138.03, 137.94, 137.75, 133.02, 132.82, 130.01, 129.96, 129.76, 129.69, 128.49, 128.45, 128.44, 128.39, 128.37, 128.25, 128.16, 127.96, 127.83, 127.81, 127.75, 127.72, 127.66, 127.59, 127.57, 97.06 (C-1'), 88.48 (C-1), 86.62, 81.76, 81.13, 80.30, 78.65, 77.57, 75.89, 75.63, 75.46, 75.13, 75.00, 72.45, 68.92, 66.14, 63.42, 21.05. HR ESI-TOF MS (*m/z*): calcd for $C_{68}H_{72}NO_{11}S$ [M + NH_4]$^+$, 1110.4826; found, 1110.4831.

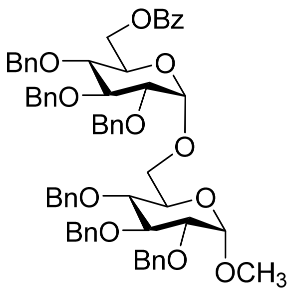
Methyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*α*-D-glucopyranoside (34)



34

Donor **4** reacted with acceptor **7** by the general procedure for glycosylation to give product **34** (81 mg, 90% yield) as a syrup after column purification (hexanes/ethyl acetate, 12:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.01 (d, J = 7.8 Hz, 2H, Ph), 7.58 – 7.18 (m, 33H, Ph), 5.58 (d, J = 3.6 Hz, 1H, H-1'), 5.01 (d, J = 11.4 Hz, 1H, Bn), 4.95 – 4.89 (m, 2H, Bn), 4.86 – 4.79 (m, 2H, Bn), 4.70 (d, J = 12.0 Hz, 1H, Bn), 4.62 (d, J = 3.6 Hz, 1H, H-1), 4.61 – 4.50 (m, 6H, Bn), 4.39 (dd, J = 12.0, 2.4 Hz, 1H, H-6a'), 4.34 (dd, J = 12.0, 4.2 Hz, 1H, H-6b'), 4.09 (t, J = 9.0 Hz, 1H, H-3), 4.04 (t, J = 9.0 Hz, 1H, H-4), 4.02 – 3.96 (m, 2H, H-3', H-5'), 3.90 – 3.83 (m, 2H, H-5, H-6a), 3.67 – 3.63 (m, 1H, H-6b), 3.62 – 3.55 (m, 2H, H-2, H-4'), 3.48 (dd, J = 9.6, 3.6 Hz, 1H, H-2'), 3.39 (s, 3H, OCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 166.10, 139.05, 138.43, 137.96, 137.92, 137.85, 132.99, 130.02, 129.69, 128.45, 128.44, 128.36, 128.34, 128.30, 128.21, 128.18, 128.08, 128.03, 127.94, 127.88, 127.73, 127.69, 127.67, 127.58, 127.55, 127.02, 126.71, 97.79 (C-1), 96.33 (C-1'), 81.92, 81.82, 79.91, 79.78, 77.67, 75.80, 75.19, 74.30, 73.39, 73.36, 73.16, 73.12, 69.56, 68.87, 63.39, 55.18. HR ESI-TOF MS (*m/z*): calcd for $C_{62}H_{68}NO_{12}$ [M + NH_4]$^+$, 1018.4742; found, 1018.4752.

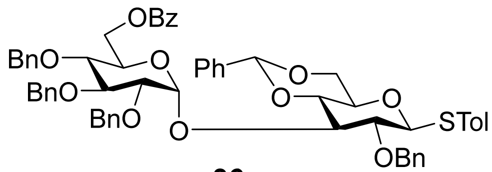
Methyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (35)



35

Donor **4** reacted with acceptor **8** by the general procedure for glycosylation to give product **35** (83 mg, 92% yield) as a syrup after column purification (hexanes/ethyl acetate, 12:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.02 – 7.91 (m, 2H, Ph), 7.59 – 7.20 (m, 33H, Ph), 4.99 (d, J = 4.2 Hz, 1H, H-1'), 4.97 – 4.94 (m, 2H, Bn), 4.94 – 4.90 (m, 2H, Bn), 4.83 – 4.79 (m, 2H, Bn), 4.72 – 4.68 (m, 3H, Bn), 4.63 (d, J = 11.4 Hz, 1H, Bn), 4.60 (d, J = 10.8 Hz, 1H, Bn), 4.58 (d, J = 12.0 Hz, 1H, Bn), 4.56 (d, J = 3.6 Hz, 1H, H-1), 4.50 (dd, J = 12.0, 1.8 Hz, 1H, H-6a'), 4.39 (dd, J = 12.0, 4.2 Hz, 1H, H-6b'), 4.04 – 3.96 (m, 3H, H-3, H-3', H-5'), 3.84 – 3.77 (m, 2H, H-5, H-6a), 3.73 – 3.69 (m, 1H, H-6b), 3.63 – 3.58 (m, 2H, H-4, H-4'), 3.56 (dd, J = 9.6, 3.6 Hz, 1H, H-2'), 3.42 (dd, J = 9.6, 3.6 Hz, 1H, H-2), 3.36 (s, 3H, OCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 166.19, 138.76, 138.46, 138.29, 138.28, 138.11, 137.94, 133.04, 129.91, 129.63, 128.43, 128.41, 128.38, 128.34, 128.21, 128.01, 127.99, 127.93, 127.87, 127.81, 127.73, 127.71, 127.69, 127.61, 127.60, 97.89 (C-1), 96.88 (C-1'), 82.08, 81.69, 80.13, 80.09, 77.79, 77.49, 75.76, 75.74, 75.04, 73.34, 72.46, 70.33, 68.85, 65.99, 63.41, 55.19. HR ESI-TOF MS (*m/z*): calcd for $C_{62}H_{68}NO_{12}$ [M + NH_4]$^+$, 1018.4742; found, 1018.4750.

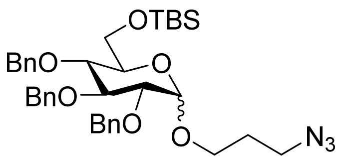
_p_-Tolyl 6-_O_-benzoyl-2,3,4-tri-_O_-benzyl-_α_-D-glucopyranosyl-(1→3)-4,6-_O_-benzylidene-2-_O_-benzyl-1-thio-_β_-D-glucopyranoside (36)



36

Donor **4** reacted with acceptor **9** by the general procedure for glycosylation to give product **36** (80 mg, 89% yield) as a syrup after column purification (hexanes/ethyl acetate, 12:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.93 (d, *J* = 7.2 Hz, 2H, Ph), 7.62 – 6.95 (m, 32H, Ph), 5.61 (d, *J* = 3.6 Hz, 1H, H-1'), 5.48 (s, 1H, PhC*H*), 5.09 – 5.05 (m, 2H, Bn), 4.92 (d, *J* = 10.8 Hz, 1H, Bn), 4.88 (d, *J* = 10.2 Hz, 1H, Bn), 4.74 (d, *J* = 9.6 Hz, 1H, H-1), 4.71 (d, *J* = 10.2 Hz, 1H, Bn), 4.61 (d, *J* = 12.0 Hz, 1H, Bn), 4.52 (d, *J* = 10.8 Hz, 1H, Bn), 4.38 (dd, *J* = 10.2, 4.2 Hz, 1H, H-6a), 4.33 (d, *J* = 12.0 Hz, 1H, Bn), 4.31 – 4.27 (m, 1H, H-5'), 4.21 – 4.16 (m, 2H, H-3, H-6a'), 4.06 (t, *J* = 9.6 Hz, 1H, H-3'), 4.02 (dd, *J* = 12.0, 4.2 Hz, 1H, H-6b'), 3.86 (t, *J* = 9.6 Hz, 1H, H-4), 3.81 (t, *J* = 10.2 Hz, 1H, H-6b), 3.61 (t, *J* = 9.6 Hz, 1H, H-2), 3.57 (t, *J* = 9.6 Hz, 1H, H-4'), 3.54 – 3.47 (m, 2H, H-2', H-5), 2.40 (s, 3H, PhC*H*$_3$). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 166.09, 138.55, 138.32, 138.16, 137.54, 137.09, 136.85, 132.85, 132.82, 129.95, 129.93, 129.72, 129.50, 129.22, 128.66, 128.48, 128.43, 128.34, 128.26, 128.18, 128.11, 128.06, 127.94, 127.74, 127.71, 127.58, 127.51, 126.47, 102.31 (Ph*C*H), 95.88 (C-1'), 89.10 (C-1), 82.07, 81.74, 78.73, 77.58, 76.93, 75.92, 75.88, 75.35, 71.13, 69.88, 68.86, 68.68, 63.00, 21.21. HR ESI-TOF MS (*m/z*): calcd for $C_{61}H_{64}NO_{11}S$ [M + NH_4]$^+$, 1018.4200; found, 1018.4195.

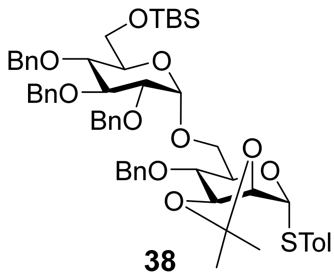
3-Azidopropyl 2,3,4-tri-_O_-benzyl-6-_O_-_tert_-butyldimethylsilyl-_α_-D-glucopyranoside (37)



37

Donor **3** reacted with acceptor **10** by the general procedure for glycosylation to give product **37** (49 mg, 84% yield) as a syrup after column purification (hexanes/ethyl acetate, 12:1): α/β = 12:1 as determined by integrations of H-1 and TBS signals with the stereochemistry determined by $J_{H1,H2}$ coupling constant. α-**37**: ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.46 – 7.17 (m, 15H, Ph), 4.96 (d, *J* = 10.8 Hz, 1H, Bn), 4.88 (d, *J* = 10.8 Hz, 1H, Bn), 4.82 (d, *J* = 10.8 Hz, 1H, Bn), 4.78 (d, *J* = 12.0 Hz, 1H, Bn), 4.72 (d, *J* = 3.6 Hz, 1H, H-1), 4.66 – 4.62 (m, 2H, Bn), 3.97 (t, *J* = 9.6 Hz, 1H, H-3), 3.80 – 3.77 (m, 1H, H-6a), 3.75 – 3.70 (m, 1H, H-5), 3.63 – 3.58 (m, 1H, H-6b), 3.54 (t, *J* = 9.6 Hz, 1H, H-4), 3.50 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2), 3.47 – 3.34 (m, 4H, OC*H*$_2$CH$_2$, C*H*$_2$N$_3$), 1.93 – 1.81 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 0.88 (s, 9H, *t*Bu), 0.04 (s, 3H, SiC*H*$_3$), 0.03 (s, 3H, SiC*H*$_3$). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 138.76, 138.38, 138.30, 128.44, 128.40, 128.33, 128.04, 127.92, 127.88, 127.84, 127.74, 127.62, 96.91 (C-1), 82.03, 80.41, 77.68, 75.80, 75.09, 73.25, 71.75, 64.47, 62.21, 48.38, 28.87, 25.91, 18.30, -5.17, -5.38. HR ESI-TOF MS (*m/z*): calcd for $C_{36}H_{53}N_4O_6Si$ [M + NH_4]$^+$, 665.3734; found, 665.3735.

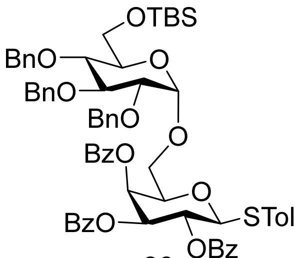
p-Tolyl 2,3,4-tri-O-benzyl-6-O-$tert$-butyldimethylsilyl-α-D-glucopyranosyl-(1→6)-4-O-benzyl-2,3-di-O-isopropylidene-1-thio-α-D-mannopyranoside (38)



38

Donor **3** reacted with acceptor **11** by the general procedure for glycosylation to give product **38** (79 mg, 91% yield) as a syrup after column purification (hexanes/ethyl acetate, 14:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.47 – 7.09 (m, 24H, Ph), 5.71 (s, 1H, H-1), 4.96 (d, J = 11.4 Hz, 1H, Bn), 4.93 (d, J = 10.8 Hz, 1H, Bn), 4.90 (d, J = 10.8 Hz, 1H, Bn), 4.83 (d, J = 3.6 Hz, 1H, H-1'), 4.76 (d, J = 10.8 Hz, 1H, Bn), 4.72 – 4.63 (m, 4H, Bn), 4.42 – 4.35 (m, 3H, H-2, H-3, H-5), 4.01 (t, J = 9.6 Hz, 1H, H-3'), 3.90 (dd, J = 11.4, 5.4 Hz, 1H, H-6a), 3.81 (dd, J = 11.4, 4.2 Hz, 1H, H-6a'), 3.77 (dd, J = 11.4, 1.8 Hz, 1H, H-6b'), 3.76 – 3.68 (m, 2H, H-5', H-4), 3.68 (dd, J = 11.4, 1.8 Hz, 1H, H-6b), 3.59 (t, J = 9.6 Hz, 1H, H-4'), 3.50 (dd, J = 9.6, 3.6 Hz, 1H, H-2'), 2.18 (s, 3H, PhCH_3), 1.46 (s, 3H, CCH_3), 1.39 (s, 3H, CCH_3), 0.90 (s, 9H, tBu), 0.05 (s, 6H, SiCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 138.88, 138.83, 138.72, 138.24, 137.69, 132.28, 130.15, 129.90, 129.05, 128.34, 128.33, 128.24, 128.11, 127.99, 127.79, 127.72, 127.66, 127.54, 127.53, 127.44, 125.31, 109.51 (CH_3CCH_3), 97.36 (C-1'), 84.86 (C-1), 81.84, 80.30, 78.45, 77.66, 76.63, 76.16, 75.64, 74.95, 73.03, 72.33, 71.59, 69.86, 66.67, 62.23, 27.90, 26.55, 25.98, 20.99, 18.34, -5.08, -5.38. HR ESI-TOF MS (m/z): calcd for $C_{56}H_{74}NO_{10}SSi$ [M + NH_4]$^+$, 980.4803; found, 980.4813.

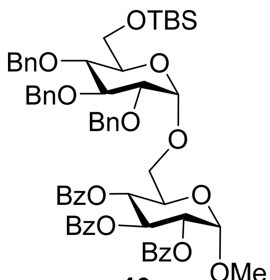
p-Tolyl 2,3,4-tri-O-benzyl-6-O-$tert$-butyldimethylsilyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-1-thio-β-D-galactopyranoside (39)



39

Donor **3** reacted with acceptor **12** by the general procedure for glycosylation to give product **39** (96 mg, 93% yield) as a syrup after column purification (hexanes/ethyl acetate, 15:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.99 (d, J = 8.0 Hz, 2H, Ph), 7.92 (d, J = 8.0 Hz, 2H, Ph), 7.76 (d, J = 8.5 Hz, 2H, Ph), 7.64 – 7.20 (m, 26H, Ph), 7.13 (d, J = 7.5 Hz, 2H, Ph), 5.93 (d, J = 3.0 Hz, 1H, H-4), 5.72 (t, J = 10.0 Hz, 1H, H-2), 5.55 (dd, J = 10.0, 3.5 Hz, 1H, H-3), 4.95 (d, J = 10.5 Hz, 1H, Bn), 4.93 – 4.88 (m, 2H, Bn, H-1), 4.81 (d, J = 11.0 Hz, 1H, Bn), 4.71 (d, J = 3.0 Hz, 1H, H-1'), 4.70 – 4.67 (m, 3H, Bn), 4.22 (t, J = 5.5 Hz, 1H, H-5), 3.98 (t, J = 9.5 Hz, 1H, H-3'), 3.92 – 3.86 (m, 2H, H-6a, H-6a'), 3.84 – 3.78 (m, 2H, H-5', H-6b'), 3.61 (t, J = 9.5 Hz, 1H, H-4'), 3.56 (dd, J = 10.0, 5.0 Hz, 1H, H-6b), 3.46 (dd, J = 10.0, 3.5 Hz, 1H, H-2'), 2.29 (s, 3H, PhCH_3), 0.87 (s, 9H, tBu), 0.01 (s, 6H, SiCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.44, 165.39, 165.19, 138.87, 138.63, 138.54, 138.16, 134.52, 133.44, 133.24, 133.13, 130.02, 129.82, 129.74, 129.67, 129.44, 129.10, 128.89, 128.49, 128.46, 128.44, 128.39, 128.38, 128.31, 128.22, 128.03, 127.96, 127.84, 127.81, 127.76, 127.73, 127.57, 127.53, 97.12 (C-1'), 86.27 (C-1), 81.90, 80.19, 77.47, 76.33, 75.81, 74.97, 73.16, 73.14, 71.86, 68.96, 68.06, 66.48, 62.07, 25.94, 21.24, 18.30, -5.15, -5.41. HR ESI-TOF MS (*m/z*): calcd for $C_{67}H_{76}NO_{13}SSi$ $[M + NH_4]^+$, 1162.4807; found, 1162.4805.

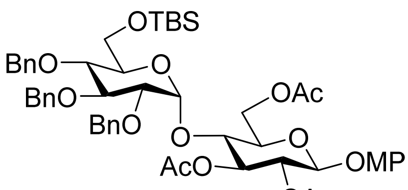
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-*α*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside (40)



40

Donor **3** reacted with acceptor **13** by the general procedure for glycosylation to give product **40** (85 mg, 90% yield) as a syrup after column purification (hexanes/ethyl acetate, 10:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.02 – 7.20 (m, 30H, Ph), 6.16 (t, *J* = 9.5 Hz, 1H, H-3), 5.55 (t, *J* = 10.0 Hz, 1H, H-4), 5.24 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2), 5.23 (d, *J* = 3.5 Hz, 1H, H-1), 4.91 (d, *J* = 10.5 Hz, 1H, Bn), 4.89 (d, *J* = 10.0 Hz, 1H, Bn), 4.79 (d, *J* = 11.0 Hz, 1H, Bn), 4.78 (d, *J* = 12.5 Hz, 1H, Bn), 4.73 (d, *J* = 3.5 Hz, 1H, H-1'), 4.68 – 4.63 (m, 2H, Bn), 4.36 – 4.31 (m, 1H, H-5), 4.00 (t, *J* = 9.5 Hz, 1H, H-3'), 3.87 (dd, *J* = 11.0, 7.0 Hz, 1H, H-6a), 3.78 – 3.66 (m, 3H, H-6a',6b', H-6b), 3.61 – 3.55 (m, 2H, H-4', H-5'), 3.49 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2'), 3.46 (s, 3H, OCH_3), 0.89 (s, 9H, *t*Bu), 0.02 (s, 3H, $SiCH_3$), 0.01 (s, 3H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 165.82, 165.81, 165.24, 138.84, 138.50, 133.30, 133.02, 129.93, 129.91, 129.67, 129.29, 129.12, 129.06, 128.39, 128.38, 128.36, 128.33, 128.30, 128.24, 128.11, 127.81, 127.68, 127.60, 127.53, 127.47, 96.95, 96.71, 81.70, 80.37, 77.53, 75.62, 74.74, 73.07, 72.26, 71.59, 70.65, 69.68, 68.61, 66.37, 61.97, 55.56, 25.94, 18.30, -5.17, -5.41. HR ESI-TOF MS (m/z): calcd for $C_{61}H_{72}NO_{14}Si$ $[M + NH_4]^+$, 1070.4722; found, 1070.4743.

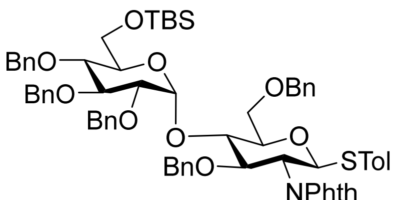
***p*-Methoxyphenyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-*α*-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-*β*-D-glucopyranoside (41)**



41

Donor **3** reacted with acceptor **14** by the general procedure for glycosylation to give product **41** (62 mg, 72% yield) as a syrup after column purification (hexanes/ethyl acetate, 10:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.41 – 6.80 (m, 19H, Ph), 5.36 (t, *J* = 9.5 Hz, 1H, H-3), 5.20 (dd, *J* = 9.5, 7.5 Hz, 1H, H-2), 4.93 (d, *J* = 7.5 Hz, 1H, H-1), 4.88 – 4.83 (m, 2H, Bn), 4.82 (d, *J* = 11.0 Hz, 1H, Bn), 4.76 (d, *J* = 3.5 Hz, 1H, H-1'), 4.75 (d, *J* = 11.5 Hz, 1H, Bn), 4.66 – 4.62 (m, 2H, Bn), 4.59 (dd, *J* = 12.0, 2.0 Hz, 1H, H-6a), 4.31 (dd, *J* = 12.5, 5.0 Hz, 1H, H-6b), 3.93 – 3.86 (m, 2H, H-3', H-4), 3.81 – 3.77 (m, 4H, H-6a', $PhOCH_3$), 3.74 (dd, *J* = 11.5, 2.0 Hz, 1H, H-6b'), 3.70 – 3.64 (m, 2H, H-5, H-5'), 3.56 (t, *J* = 9.5 Hz, 1H, H-4'), 3.40 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2'), 2.08 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 1.94 (s, 3H, $COCH_3$), 0.89 (s, 9H, *t*Bu), 0.04 (s, 3H, $SiCH_3$), 0.02 (s, 3H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 170.13, 170.04, 169.63, 155.69, 150.97, 138.63, 138.41, 138.02, 128.55, 128.43, 128.40, 128.38, 128.21, 128.11, 128.05, 127.78, 127.67, 127.66, 118.70, 114.52, 100.09 (C-1), 99.11 (C-1'), 81.17, 80.44, 77.33, 76.18, 75.77, 74.99, 73.82, 73.60, 73.41, 73.11, 71.64, 62.86, 61.89, 55.65, 25.92, 20.91, 20.78, 20.73, 18.34, -5.23, -5.43. HR ESI-TOF MS (m/z): calcd for $C_{52}H_{70}NO_{15}Si$ $[M + NH_4]^+$, 976.4515; found, 976.4533.

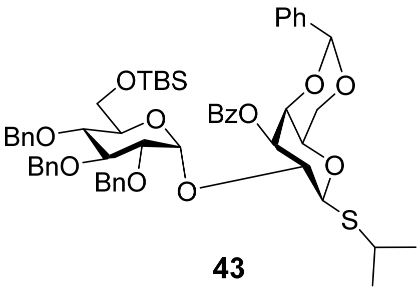
_p_-Tolyl 2,3,4-tri-_O_-benzyl-6-_O_-_tert_-butyldimethylsilyl-_α_-D-glucopyranosyl-(1→4)-2-deoxy-2-phthalimido-3,6-di-_O_-benzyl-1-thio-_β_-D-glucopyranoside (42)



42

Donor **3** reacted with acceptor **15** by the general procedure for glycosylation to give product **42** (90 mg, 88% yield) as a syrup after column purification (hexanes/ethyl acetate, 12:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, CDCl$_3$) *δ*: 7.75 (d, *J* = 6.6 Hz, 1H, Ph), 7.69 – 7.63 (m, 3H, Ph), 7.39 – 7.13 (m, 22H, Ph), 6.98 (d, *J* = 7.8 Hz, 2H, Ph), 6.91 – 6.76 (m, 5H, Ph), 5.45 (d, *J* = 10.2 Hz, 1H, H-1), 5.41 (d, *J* = 3.6 Hz, 1H, H-1'), 4.90 – 4.86 (m, 2H, Bn), 4.83 – 4.77 (m, 2H, Bn), 4.69 (d, *J* = 10.8 Hz, 1H, Bn), 4.65 – 4.56 (m, 4H, Bn), 4.50 (dd, *J* = 10.2, 8.4 Hz, 1H, H-3), 4.37 (d, *J* = 12.0 Hz, 1H, Bn), 4.32 (t, *J* = 10.2 Hz, 1H, H-2), 4.15 (t, *J* = 8.4 Hz, 1H, H-4), 4.05 (dd, *J* = 11.4, 3.6 Hz, 1H, H-6a), 3.98 (t, *J* = 9.6 Hz, 1H, H-3'), 3.87 (dd, *J* = 10.8, 1.2 Hz, 1H, H-6a'), 3.78 – 3.73 (m, 2H, H-5', H-6b), 3.73 – 3.69 (m, 1H, H-5), 3.68 – 3.61 (m, 2H, H-4', H-6b'), 3.47 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2'), 2.28 (s, 3H, PhC*H*$_3$), 0.89 (s, 9H, *t*Bu), 0.02 (s, 3H, SiC*H*$_3$), 0.01 (s, 3H, SiC*H*$_3$). ^{13}C NMR (150 MHz, CDCl$_3$) *δ*: 168.10, 167.35, 138.64, 138.59, 138.54, 138.15, 138.02, 137.89, 133.39, 129.51, 128.40, 128.35, 128.31, 128.26, 128.07, 128.05, 127.98, 127.89, 127.86, 127.66, 127.63, 127.59, 127.57, 127.46, 127.38, 126.94, 97.38 (C-1'), 83.31 (C-1), 81.76, 81.10, 80.16, 79.33, 77.54, 75.70, 75.62, 75.07, 73.93, 73.41, 73.21, 72.47, 69.10, 61.98, 54.58, 25.96, 21.14, 18.33, -5.09, -5.36. HR ESI-TOF MS (*m/z*): calcd for $C_{68}H_{79}N_2O_{11}SSi$ $[M + NH_4]^+$, 1159.5174; found, 1159.5175.

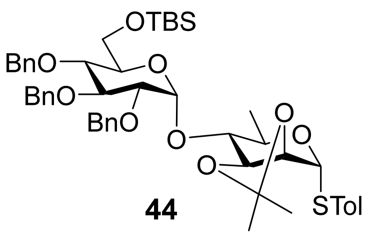
Isopropyl 2,3,4-tri-_O_-benzyl-6-_O_-_tert_-butyldimethylsilyl-_α_-D-glucopyranosyl-(1→2)-3-_O_-benzoyl-4,6-_O_-benzylidene-1-thio-_β_-D-galactopyranoside (43)



43

Donor **3** reacted with acceptor **16** by the general procedure for glycosylation to give product **43** (76 mg, 86% yield) as a syrup after column purification (hexanes/ethyl acetate, 12:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, CDCl$_3$) *δ*: 8.02 – 7.98 (m, 2H, Ph), 7.53 – 7.17 (m, 21H, Ph), 7.00 – 6.90 (m, 2H, Ph), 5.75 (d, *J* = 3.6 Hz, 1H, H-1'), 5.48 (s, 1H, PhC*H*), 5.34 (dd, *J* = 9.6, 3.6 Hz, 1H, H-3), 4.92 (d, *J* = 12.0 Hz, 1H, Bn), 4.84 (d, *J* = 10.8 Hz, 1H, Bn), 4.74 (d, *J* = 9.0 Hz, 1H, H-1), 4.70 – 4.62 (m, 3H, Bn), 4.49 (d, *J* = 3.6 Hz, 1H, H-4), 4.45 (t, *J* = 9.6 Hz, 1H, H-2), 4.43 (d, *J* = 10.8 Hz, 1H, Bn), 4.35 (dd, *J* = 12.6, 1.2 Hz, 1H, H-6a), 4.03 (dd, *J* = 12.6, 1.8 Hz, 1H, H-6b), 3.81 (t, *J* = 9.6 Hz, 1H, H-3'), 3.73 – 3.69 (m, 1H, H-5'), 3.60 – 3.57 (m, 1H, H-5), 3.50 (dd, *J* = 11.4, 1.8 Hz, 1H, H-6a'), 3.46 (t, *J* = 9.6 Hz, 1H, H-4'), 3.44 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2'), 3.42 – 3.33 (m, 1H, SC*H*), 3.31 (dd, *J* = 11.4, 3.6 Hz, 1H, H-6b'), 1.37 (d, *J* = 6.6 Hz, 3H, CHC*H*$_3$), 1.31 (d, *J* = 6.6 Hz, 3H, CHC*H*$_3$), 0.80 (s, 9H, *t*Bu), -0.06 (s, 3H, SiC*H*$_3$), -0.07 (s, 3H, SiCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 166.16, 138.88, 138.81, 138.27, 137.86, 133.14, 129.95, 129.84, 128.84, 128.29, 128.25, 128.08, 128.05, 128.02, 127.94, 127.56, 127.44, 127.13, 127.08, 126.23, 100.85 (Ph*C*H), 96.08 (C-1'), 84.03 (C-1), 81.18, 80.11, 77.10, 75.62, 74.73, 74.15, 73.77, 73.13, 71.54, 69.89, 69.32, 69.15, 61.80, 34.43, 25.88, 24.48, 23.67, 18.26, -5.22, -5.41. HR ESI-TOF MS (*m/z*): calcd for $C_{56}H_{72}NO_{11}SSi$ $[M + NH_4]^+$, 994.4595; found, 994.4603.

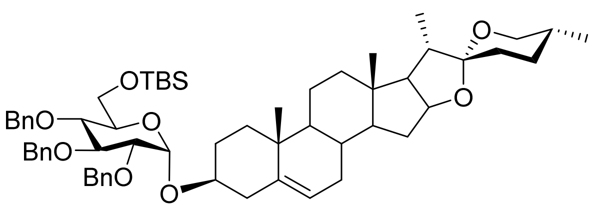
_p_-Tolyl 2,3,4-tri-_O_-benzyl-6-_O_-_tert_-butyldimethylsilyl-_α_-D-glucopyranosyl-(1→4)-6-deoxy-2,3-di-_O_-isopropylidene-1-thio-_α_-D-mannopyranoside (44)



44

Donor **3** reacted with acceptor **17** by the general procedure for glycosylation to give product **44** (69 mg, 89% yield) as a syrup after column purification (hexanes/ethyl acetate, 12:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.45 – 7.26 (m, 17H, Ph), 7.13 (d, *J* = 7.8 Hz, 2H, Ph), 5.67 (d, *J* = 3.0 Hz, 1H, H-1'), 5.66 (s, 1H, H-1), 4.98 (d, *J* = 10.8 Hz, 1H, Bn), 4.88 (d, *J* = 11.4 Hz, 1H, Bn), 4.86 – 4.79 (m, 2H, Bn), 4.74 (d, *J* = 11.4 Hz, 1H, Bn), 4.67 (d, *J* = 10.8 Hz, 1H, Bn), 4.36 (dd, *J* = 7.2, 5.4 Hz, 1H, H-3), 4.32 (d, *J* = 5.4 Hz, 1H, H-2), 4.23 (dq, *J* = 9.6, 6.0 Hz, 1H, H-5), 3.93 (t, *J* = 9.6 Hz, 1H, H-3'), 3.84 (dd, *J* = 11.4, 4.2 Hz, 1H, H-6a'), 3.75 (dd, *J* = 11.4, 1.8 Hz, 1H, H-6b'), 3.70 – 3.63 (m, 2H, H-5', H-4), 3.57 (t, *J* = 9.6 Hz, 1H, H-4'), 3.54 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2'), 2.33 (s, 3H, PhCH_3), 1.54 (s, 3H, CCH_3), 1.37 (s, 3H, CCH_3), 1.21 (d, *J* = 6.0 Hz, 3H, H-6), 0.87 (s, 9H, *t*Bu), 0.03 (s, 3H, SiCH_3), 0.02 (s, 3H, SiCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 138.81, 138.46, 138.12, 137.84, 132.56, 129.80, 129.57, 128.41, 128.40, 128.15, 128.07, 128.04, 127.78, 127.74, 127.61, 109.45 (CH_3*C*CH_3), 95.15 (C-1'), 84.14 (C-1), 81.71, 80.13, 78.56, 77.66, 77.42, 76.80, 75.85, 75.20, 72.97, 72.12, 65.58, 62.14, 28.00, 26.59, 25.94, 21.14, 18.36, 18.35, -5.15, -5.40. HR ESI-TOF MS (*m/z*): calcd for $C_{49}H_{68}NO_9SSi$ $[M + NH_4]^+$, 874.4384; found, 874.4390.

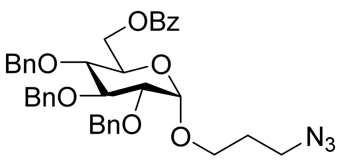
Diosgenyl 2,3,4-tri-_O_-benzyl-6-_O_-_tert_-butyldimethylsilyl-_α_-D-glucopyranoside (45)



45

Donor **3** reacted with acceptor **18** by the general procedure for glycosylation to give product **45** (80 mg, 92% yield) as a syrup after column purification (hexanes/ethyl acetate, 25:1) with the stereochemistry determined by $J_{H1,H2}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.40 – 7.13 (m, 15H, Ph), 5.35 – 5.31 (m, 1H), 5.01 (d, *J* = 10.8 Hz, 1H, Bn), 4.92 (d, *J* = 3.6 Hz, 1H, H-1), 4.90 (d, *J* = 10.8 Hz, 1H, Bn), 4.83 (d, *J* = 10.8 Hz, 1H, Bn), 4.78 (d, *J* = 12.0 Hz, 1H, Bn), 4.69 – 4.63 (m, 2H, Bn), 4.42 (q, *J* = 7.2 Hz, 1H), 4.03 (t, *J* = 9.6 Hz, 1H), 3.82 – 3.72 (m, 3H), 3.54 – 3.47 (m, 4H), 3.39 (t, *J* = 11.4 Hz, 1H), 2.48 – 2.41 (m, 1H), 2.31 – 2.25 (m, 1H), 2.05 – 1.42 (m, 15H), 1.35 – 0.92 (m, 13H), 0.89 (s, 9H, *t*Bu), 0.83 – 0.78 (m, 6H), 0.05 (s, 3H, SiCH_3), 0.04 (s, 3H, SiCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 140.83, 138.90, 138.43, 138.33, 129.02, 128.44, 128.40, 128.22, 128.10, 128.06, 127.98, 127.82, 127.74, 127.59, 125.29, 121.44, 109.27, 93.96 (C-1), 82.12, 80.83, 80.24, 78.03, 77.26, 77.05, 76.83, 75.80, 75.64, 75.11, 73.07, 71.64, 66.84, 62.46, 62.11, 56.52, 50.04, 41.61, 40.27, 39.79, 37.05, 36.95, 32.08, 31.86, 31.44, 31.40, 30.31, 28.81, 27.25, 25.98, 21.48, 20.86, 19.46, 18.33, 17.16, 16.31, 14.56, -5.11, -5.34. HR ESI-TOF MS (*m/z*): calcd for $C_{60}H_{88}NO_8Si$ [M + NH_4]$^+$, 978.6279; found, 978.6285.

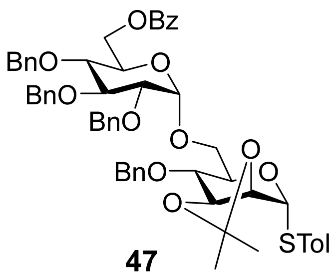
3-Azidopropyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (46)



46

Donor **4** reacted with acceptor **10** by the general procedure for glycosylation to give product **46** (50 mg, 87% yield) as a syrup after column purification (hexanes/ethyl acetate, 9:1) with the stereochemistry determined by $J_{H1,H2}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 8.02 – 7.98 (m, 2H, Ph), 7.58 – 7.22 (m, 18H, Ph), 5.02 (d, *J* = 10.8 Hz, 1H, Bn), 4.92 (d, *J* = 10.8 Hz, 1H, Bn), 4.85 (d, *J* = 10.8 Hz, 1H, Bn), 4.80 (d, *J* = 12.0 Hz, 1H, Bn), 4.73 (d, *J* = 3.6 Hz, 1H, H-1), 4.65 (d, *J* = 12.0 Hz, 1H, Bn), 4.62 (d, *J* = 10.8 Hz, 1H, Bn), 4.55 (dd, *J* = 12.0, 2.4 Hz, 1H, H-6a), 4.47 (dd, *J* = 12.0, 4.8 Hz, 1H, H-6b), 4.04 (t, *J* = 9.6 Hz, 1H, H-3), 3.97 – 3.92 (m, 1H, H-5), 3.79 – 3.72 (m, 1H, OCH_2CH_2), 3.61 (t, *J* = 9.6 Hz, 1H, H-4), 3.58 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2), 3.49 – 3.33 (m, 3H, CH_2N_3, OCH_2CH_2), 1.97 – 1.83 (m, 2H, $CH_2CH_2CH_2$). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 166.19, 138.50, 138.11, 137.68, 133.09, 129.84, 129.63, 128.51, 128.49, 128.38, 128.13, 128.08, 127.98, 127.95, 127.77, 97.00 (C-1), 81.99, 80.25, 77.62, 75.91, 75.27, 73.34, 69.01, 64.79, 63.43, 48.26, 28.82. HR ESI-TOF MS (*m/z*): calcd for $C_{37}H_{43}N_4O_7$ [M + NH_4]$^+$, 655.3132; found, 655.3134.

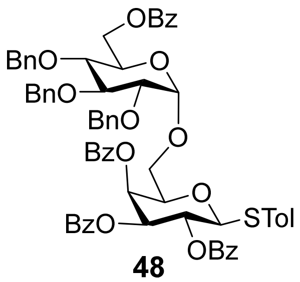
***p*-Tolyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl-(1→6)-4-*O*-benzyl-2,3-di-*O*-isopropylidene-1-thio-*α*-D-mannopyranoside (47)**



47

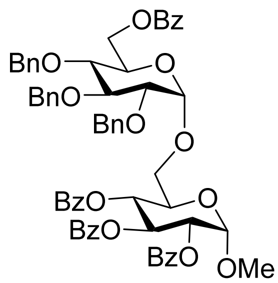
Donor **4** reacted with acceptor **11** by the general procedure for glycosylation to give product **47** (77 mg, 90% yield) as a syrup after column purification (hexanes/ethyl acetate, 10:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 8.00 (d, *J* = 8.4 Hz, 2H, Ph), 7.59 – 6.99 (m, 27H, Ph), 5.71 (s, 1H, H-1), 5.00 – 4.91 (m, 3H, Bn), 4.82 (d, *J* = 3.6 Hz, 1H, H-1'), 4.78 (d, *J* = 10.2 Hz, 1H, Bn), 4.69 (s, 2H, Bn), 4.65 – 4.61 (m, 2H, Bn), 4.50 (dd, *J* = 12.0, 2.4 Hz, 1H, H-6a'), 4.46 (dd, *J* = 12.0, 4.2 Hz, 1H, H-6b'), 4.43 – 4.34 (m, 3H, H-2, H-3, H-5), 4.03 (t, *J* = 9.6 Hz, 1H, H-3'), 4.02 – 3.97 (m, 1H , H-5'), 3.91 (dd, *J* = 11.4, 5.4 Hz, 1H, H-6a), 3.72 (dd, *J* = 10.2, 6.6 Hz, 1H, H-4), 3.67 – 3.61 (m, 2H, H-4', H-6b), 3.55 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2'), 2.17 (s, 3H, $PhCH_3$), 1.47 (s, 3H, CCH_3), 1.39 (s, 3H, CCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 166.22, 138.57, 138.46, 138.12, 138.02, 137.80, 133.58, 133.01, 132.33, 130.15, 129.95, 129.92, 129.91, 129.66, 128.45, 128.43, 128.41, 128.35, 128.31, 128.17, 128.00, 127.97, 127.86, 127.83, 127.80, 127.74, 127.71, 127.58, 109.56 (CH_3CCH_3), 97.40 (C-1'), 84.88 (C-1), 81.82, 80.03, 78.43, 77.58, 76.59, 76.05, 75.78, 75.19, 73.02, 72.40, 69.76, 68.85, 67.01, 63.43, 27.92, 26.55, 21.00. HR ESI-TOF MS (*m/z*): calcd for $C_{57}H_{64}NO_{11}S$ [M + NH_4]$^+$, 970.4200; found, 970.4224.

***p*-Tolyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-*β*-D-galactopyranoside (48)**


48

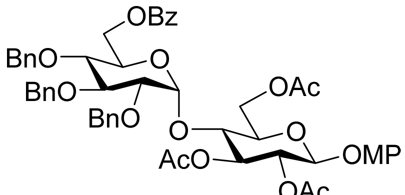
Donor **4** reacted with acceptor **12** by the general procedure for glycosylation to give product **48** (95 mg, 94% yield) as a syrup after column purification (hexanes/ethyl acetate, 10:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.06 (d, *J* = 7.5 Hz, 2H, Ph), 8.02 (d, *J* = 8.0 Hz, 2H, Ph), 7.89 (d, *J* = 8.5 Hz, 2H, Ph), 7.89 (d, *J* = 8.5 Hz, 2H, Ph), 7.63 – 7.11 (m, 31H, Ph), 7.13 (d, *J* = 7.5 Hz, 2H, Ph), 5.96 (d, *J* = 3.5 Hz, 1H, H-4), 5.76 (t, *J* = 10.0 Hz, 1H, H-2), 5.59 (dd, *J* = 10.0, 3.5 Hz, 1H, H-3), 5.02 (d, *J* = 10.5 Hz, 1H, Bn), 4.96 (d, *J* = 8.0 Hz, 1H, H-1), 4.94 (d, *J* = 9.5 Hz, 1H, Bn), 4.85 (d, *J* = 9.5 Hz, 1H, Bn), 4.74 (d, *J* = 3.5 Hz, 1H, H-1'), 4.71 (s, 2H, Bn), 4.67 (d, *J* = 10.5 Hz, 1H, Bn), 4.60 (dd, *J* = 12.0, 3.5 Hz, 1H, H-6a'), 4.56 (dd, *J* = 12.0, 4.0 Hz, 1H, H-6b'), 4.28 (t, *J* = 6.0 Hz, 1H, H-5), 4.21 – 4.17 (m, 1H, H-5'), 4.06 (t, *J* = 9.5 Hz, 1H, H-3'), 3.96 (dd, *J* = 9.5, 6.0 Hz, 1H, H-6a), 3.65 (t, *J* = 9.5 Hz, 1H, H-4'), 3.62 – 3.57 (m, 2H, H-2', H-6b), 2.30 (s, 3H, PhC*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 166.24, 165.49, 165.43, 165.21, 138.63, 138.62, 137.97, 137.85, 134.52, 133.50, 133.28, 133.18, 133.08, 130.00, 129.90, 129.84, 129.75, 129.74, 129.73, 129.43, 128.95, 128.87, 128.52, 128.49, 128.42, 128.27, 128.25, 128.06, 127.98, 127.84, 127.74, 127.57, 97.13 (C-1'), 86.43 (C-1), 81.96, 80.01, 77.50, 76.27, 75.94, 75.22, 73.24, 73.14, 69.27, 68.96, 68.07, 66.95, 63.46, 21.26. HR ESI-TOF MS (*m/z*): calcd for $C_{68}H_{66}NO_{14}S$ $[M + NH_4]^+$, 1152.4204; found, 1152.4208.

Methyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside (49)


49

Donor **4** reacted with acceptor **13** by the general procedure for glycosylation to give product **49** (86 mg, 92% yield) as a syrup after column purification (hexanes/ethyl acetate, 8:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.06 – 7.21 (m, 35H, Ph), 6.17 (t, *J* = 10.0 Hz, 1H, H-3), 5.52 (t, *J* = 10.0 Hz, 1H, H-4), 5.26 (d, *J* = 3.5 Hz, 1H, H-1), 5.19 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2), 5.00 (d, *J* = 11.0 Hz, 1H, Bn), 4.95 (d, *J* = 11.0 Hz, 1H, Bn), 4.85 (d, *J* = 11.0 Hz, 1H, Bn), 4.81 (d, *J* = 12.5 Hz, 1H, Bn), 4.76 (d, *J* = 3.5 Hz, 1H, H-1'), 4.68 (d, *J* = 12.5 Hz, 1H, Bn), 4.64 (d, *J* = 11.0 Hz, 1H, Bn), 4.51 (d, *J* = 12.0 Hz, 1H, H-6a'), 4.38 – 4.30 (m, 2H, H-5, H-6b'), 4.12 – 4.05 (m, 2H, H-3', H-5'), 3.90 (dd, *J* = 11.0, 6.5 Hz, 1H, H-6a), 3.61 – 3.55 (m, 3H, H-2', H-4', H-6b), 3.49 (s, 3H, OC*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 166.13, 165.80, 165.74, 165.23, 138.62, 138.31, 138.06, 133.39, 133.32, 133.06, 133.02, 130.02, 129.94, 129.90, 129.69, 129.29, 129.14, 128.98, 128.49, 128.46, 128.43, 128.41, 128.27, 128.15, 127.92, 127.90, 127.85, 127.77, 127.69, 96.88, 96.82, 81.73, 80.28, 77.64, 75.77, 74.94, 73.15, 72.19, 70.62, 69.55, 68.98, 68.59, 66.58, 63.43, 55.64. HR ESI-TOF MS (m/z): calcd for $C_{62}H_{62}NO_{15}$ $[M + NH_4]^+$, 1060.4119; found, 1060.4149.

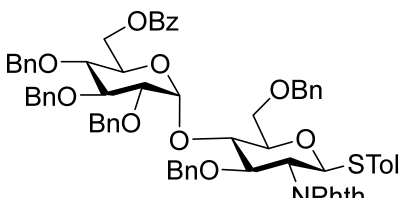
***p*-Methoxyphenyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-*β*-D-glucopyranoside (50)**



50

Donor **4** reacted with acceptor **14** by the general procedure for glycosylation to give product **50** (64 mg, 75% yield) as a syrup after column purification (hexanes/ethyl acetate, 8:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.04 – 6.79 (m, 24H, Ph), 5.38 (t, *J* = 9.5 Hz, 1H, H-3), 5.18 (dd, *J* = 9.5, 8.0 Hz, 1H, H-2), 4.93 (d, *J* = 7.5 Hz, 1H, H-1), 4.91 (d, *J* = 11.0 Hz, 1H, Bn), 4.88 (d, *J* = 11.0 Hz, 1H, Bn), 4.84 (d, *J* = 10.5 Hz, 1H, Bn), 4.82 (d, *J* = 3.5 Hz, 1H, H-1'), 4.76 (d, *J* = 12.0 Hz, 1H, Bn), 4.66 (d, *J* = 12.0 Hz, 1H, Bn), 4.62 – 4.57 (m, 2H, Bn, H-6a), 4.54 (dd, *J* = 12.0, 2.0 Hz, 1H, H-6a'), 4.42 (dd, *J* = 12.0, 4.5 Hz, 1H, H-6b'), 4.28 (dd, *J* = 12.0, 5.0 Hz, 1H, H-6b), 4.05 – 4.00 (m, 1H, H-5'), 3.97 (t, *J* = 9.5 Hz, 1H, H-3'), 3.89 (t, *J* = 9.5 Hz, 1H, H-4), 3.78 (s, 3H, PhOC*H*₃), 3.72 – 3.67 (m, 1H, H-5), 3.57 (t, *J* = 9.5 Hz, 1H, H-4'), 3.49 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2'), 2.09 (s, 3H, COCH_3), 1.99 (s, 3H, COCH_3), 1.95 (s, 3H, COCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 170.13, 170.05, 169.57, 166.08, 155.72, 150.92, 138.36, 137.82, 137.66, 133.10, 129.84, 129.66, 128.64, 128.51, 128.45, 128.40, 128.23, 128.19, 128.11, 128.00, 127.90, 127.82, 118.73, 114.53, 100.03 (C-1), 98.73 (C-1'), 81.23, 80.33, 77.48, 76.34, 75.86, 75.12, 73.86, 73.50, 73.37, 71.56, 70.42, 63.38, 62.56, 55.65, 20.93, 20.77, 20.72. HR ESI-TOF MS (m/z): calcd for $C_{53}H_{56}O_{16}Na$ $[M + Na]^+$, 971.3466; found, 971.3496.

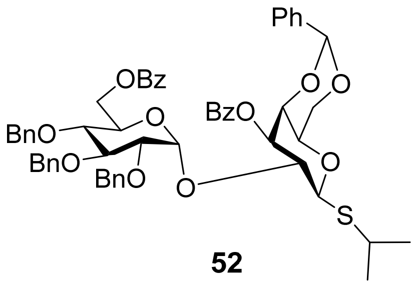
***p*-Tolyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl-(1→4)-2-deoxy-2-phthalimido-3,6-di-*O*-benzyl-1-thio-*β*-D-glucopyranoside (51)**



51

Donor **4** reacted with acceptor **15** by the general procedure for glycosylation to give product **51** (86 mg, 84% yield) as a syrup after column purification (hexanes/ethyl acetate, 11:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 8.12 – 8.05 (m, 1H, Ph), 8.02 – 7.95 (m, 2H, Ph), 7.76 – 7.12 (m, 28H, Ph), 7.02 – 6.71 (m, 7H, Ph), 5.41 (d, *J* = 10.2 Hz, 1H, H-1), 5.36 (d, *J* = 3.6 Hz, 1H, H-1'), 4.98 – 4.87 (m, 2H, Bn), 4.80 – 4.74 (m, 2H, Bn), 4.63 – 4.58 (m, 3H, Bn), 4.54 – 4.51 (m, 2H, Bn), 4.48 (dd, *J* = 10.2, 9.0 Hz, 1H, H-3), 4.44 (dd, *J* = 12.0, 2.4 Hz, 1H, H-6a'), 4.39 (dd, *J* = 12.0, 4.8 Hz, 1H, H-6b'), 4.33 (d, *J* = 12.0 Hz, 1H, Bn), 4.28 (t, *J* = 10.2 Hz, 1H, H-2), 4.13 (t, *J* = 9.6 Hz, 1H, H-4), 4.11 – 4.08 (m, 1H, H-5'), 4.02 – 3.98 (m, 2H, H-3', H-6a), 3.75 (dd, *J* = 11.4, 1.8 Hz, 1H, H-6b), 3.69 – 3.63 (m, 1H, H-5), 3.57 (t, *J* = 9.6 Hz, 1H, H-4'), 3.51 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2'), 2.27 (s, 3H, PhCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 166.11, 138.27, 138.23, 138.16, 138.05, 137.82, 137.73, 133.64, 133.38, 133.03, 130.15, 129.90, 129.63, 129.51, 128.86, 128.47, 128.44, 128.39, 128.36, 128.23, 128.04, 127.88, 127.86, 127.72, 127.70, 127.66, 127.46, 127.43, 126.90, 126.26, 97.30 (C-1'), 83.45 (C-1), 81.71, 80.76, 79.99, 79.30, 77.70, 76.44, 75.75, 75.20, 73.94, 73.26, 73.25, 69.79, 68.76, 63.49, 54.53, 21.13. HR ESI-TOF MS (*m/z*): calcd for $C_{69}H_{69}N_2O_{12}S$ $[M + NH_4]^+$, 1149.4571; found, 1149.4579.

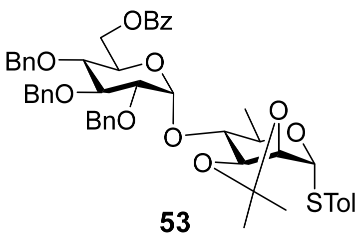
Isopropyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl-(1→2)-3-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-*β*-D-galactopyranoside (52)



52

Donor **4** reacted with acceptor **16** by the general procedure for glycosylation to give product **52** (74 mg, 85% yield) as a syrup after column purification (hexanes/ethyl acetate, 10:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^1H NMR (600 MHz, $CDCl_3$) δ: 7.99 (d, *J* = 7.8 Hz, 2H, Ph), 7.91 (d, *J* = 7.8 Hz, 2H, Ph), 7.51 – 7.44 (m, 4H, Ph), 7.43 – 7.39 (m, 2H, Ph), 7.36 – 7.14 (m, 18H, Ph), 6.91 – 6.87 (m, 2H, Ph), 5.80 (d, *J* = 3.6 Hz, 1H, H-1'), 5.50 (s, 1H, PhC*H*), 5.40 (dd, *J* = 9.6, 3.6 Hz, 1H, H-3), 4.95 (d, *J* = 11.4 Hz, 1H, Bn), 4.90 (d, *J* = 10.8 Hz, 1H, Bn), 4.76 (d, *J* = 9.0 Hz, 1H, H-1), 4.71 – 4.65 (m, 3H, Bn), 4.49 (d, *J* = 4.2 Hz, 1H, H-4), 4.46 (t, *J* = 9.6 Hz, 1H, H-2), 4.37 – 4.30 (m, 2H, H-6a, Bn), 4.23 (d, *J* = 12.0 Hz, 1H, H-6a'), 4.06 – 4.02 (m, 1H, H-6b), 4.01 – 3.97 (m, 1H, H-5'), 3.90 – 3.85 (m, 2H, H-3', H-6b'), 3.61 – 3.58 (m, 1H, H-5), 3.52 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2'), 3.48 (t, *J* = 9.6 Hz, 1H, H-4'), 3.39 – 3.33 (m, 1H, SC*H*), 1.34 (d, *J* = 6.6 Hz, 3H, CHCH_3), 1.29 (d, *J* = 6.6 Hz, 3H, CHCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 166.17, 166.12, 138.50, 138.06, 137.99, 137.70, 133.38, 132.91, 129.78, 129.73, 129.69, 129.51, 128.91, 128.41, 128.35, 128.30, 128.17, 128.10, 128.09, 127.92, 127.67, 127.62, 127.42, 127.38, 126.17, 100.95 (Ph*C*H), 95.99 (C-1'), 83.89 (C-1), 81.14, 79.88, 77.21, 75.78, 74.55, 74.48, 73.87, 73.13, 70.42, 69.37, 69.13, 68.88, 63.26, 34.57, 24.33, 23.68. HR ESI-TOF MS (*m/z*): calcd for $C_{57}H_{62}NO_{12}S$ $[M + NH_4]^+$, 984.3993; found, 984.4005.

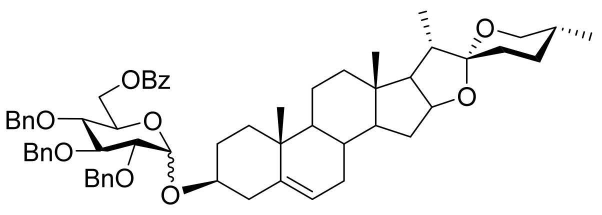
***p*-Tolyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl-(1→4)-6-deoxy-2,3-di-*O*-isopropylidene-1-thio-*α*-D-mannopyranoside (53)**



53

Donor **4** reacted with acceptor **17** by the general procedure for glycosylation to give product **53** (66 mg, 87% yield) as a syrup after column purification (hexanes/ethyl acetate, 14:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^1H NMR (600 MHz, $CDCl_3$) δ: 8.00 (d, *J* = 7.8 Hz, 2H, Ph), 7.57 – 7.04 (m, 22H, Ph), 5.67 (d, *J* = 4.2 Hz, 1H, H-1'), 5.66 (s, 1H, H-1), 5.04 (d, *J* = 10.2 Hz, 1H, Bn), 4.92 (d, *J* = 10.8 Hz, 1H, Bn), 4.88 – 4.82 (m, 2H, Bn), 4.75 (d, *J* = 11.4 Hz, 1H, Bn), 4.61 (d, *J* = 10.8 Hz, 1H, Bn), 4.51 (dd, *J* = 12.0, 2.4 Hz, 1H, H-6a'), 4.46 (dd, *J* = 12.0, 4.8 Hz, 1H, H-6b'), 4.35 (t, *J* = 6.0 Hz, 1H, H-3), 4.31 (d, *J* = 5.4 Hz, 1H, H-2), 4.28 – 4.21 (m, 1H, H-5), 4.08 – 4.03 (m, 1H, H-5'), 4.01 (t, *J* = 9.6 Hz, 1H, H-3'), 3.70 – 3.57 (m, 3H, H-2', H-4, H-4'), 2.34 (s, 3H, PhCH_3), 1.44 (s, 3H, CCH_3), 1.34 (s, 3H, CCH_3), 1.26 (d, *J* = 6.0 Hz, 3H, H-6). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 166.25, 138.53, 137.95, 137.94, 137.68, 133.05, 132.64, 129.85, 129.79, 129.71, 129.65, 129.46, 128.49, 128.38, 128.19, 128.08, 127.99, 127.90, 127.77, 109.53 (CH_3CCH_3), 95.29 (C-1'), 84.18 (C-1), 81.75, 79.90, 78.35, 78.33, 77.72, 76.69, 75.94, 75.33, 73.05, 69.36, 65.39, 63.73, 27.93, 26.48, 21.17, 18.37. HR ESI-TOF MS (*m/z*): calcd for $C_{50}H_{58}NO_{10}S$ $[M + NH_4]^+$, 864.3781; found, 864.3783.

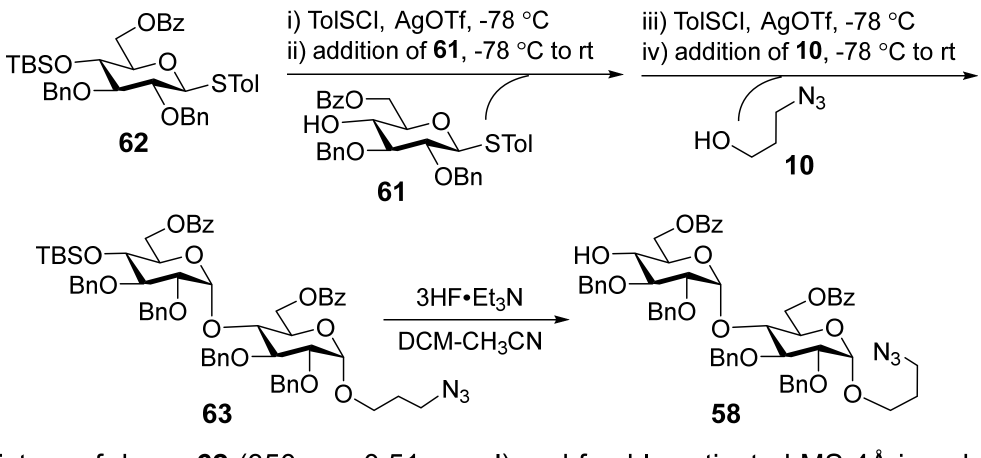
Diosgenyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (54)



54

Donor **4** reacted with acceptor **18** by the general procedure for glycosylation to give product **54** (80 mg, 93% yield) as a syrup after column purification (hexanes/ethyl acetate, 15:1): α/β = 10:1 as determined by integrations of H-1 and C*H*$_3$ signals with the stereochemistry determine by $J_{H1,H2}$ coupling constant. α-**54**: ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 8.00 – 7.97 (m, 2H, Ph), 7.56 – 7.52 (m, 1H, Ph), 7.42 – 7.19 (m, 17H, Ph), 5.23 (d, *J* = 5.4 Hz, 1H), 5.04 (d, *J* = 10.8 Hz, 1H, Bn), 4.92 (d, *J* = 11.4 Hz, 1H, Bn), 4.91 (d, *J* = 3.6 Hz, 1H, H-1), 4.84 (d, *J* = 10.8 Hz, 1H, Bn), 4.78 (d, *J* = 12.0 Hz, 1H, Bn), 4.67 (d, *J* = 12.0 Hz, 1H, Bn), 4.61 (d, *J* = 10.8 Hz, 1H, Bn), 4.56 – 4.52 (m, 1H, H-6a), 4.48 – 4.40 (m, 2H, H-6b, H-4), 4.12 – 4.05 (m, 2H, H-3, H-5), 3.58 – 3.53 (m, 2H, H-2), 3.50 – 3.44 (m, 2H), 3.39 (t, *J* = 10.8 Hz, 1H), 2.50 – 2.40 (m, 1H), 2.33 – 2.28 (m, 1H), 2.03 – 1.40 (m, 15H), 1.35 – 0.75 (m, 19H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 166.26, 140.59, 138.63, 138.10, 137.72, 132.97, 129.85, 129.71, 128.52, 128.47, 128.43, 128.41, 128.37, 128.32, 128.20, 128.15, 128.11, 128.07, 128.00, 127.97, 127.94, 127.72, 121.53, 109.27, 94.38 (C-1), 82.07, 80.80, 80.05, 77.98, 76.58, 75.89, 75.28, 73.13, 68.85, 66.84, 63.77, 62.09, 56.52, 49.99, 41.59, 40.26, 39.86, 39.76, 37.00, 36.89, 32.10, 31.85, 31.41, 31.38, 30.30, 28.80, 27.39, 20.82, 19.38, 19.35, 17.15, 16.29, 14.55. HR ESI-TOF MS (*m/z*): calcd for $C_{61}H_{78}NO_9$ $[M + NH_4]^+$, 968.5677; found, 968.5682.

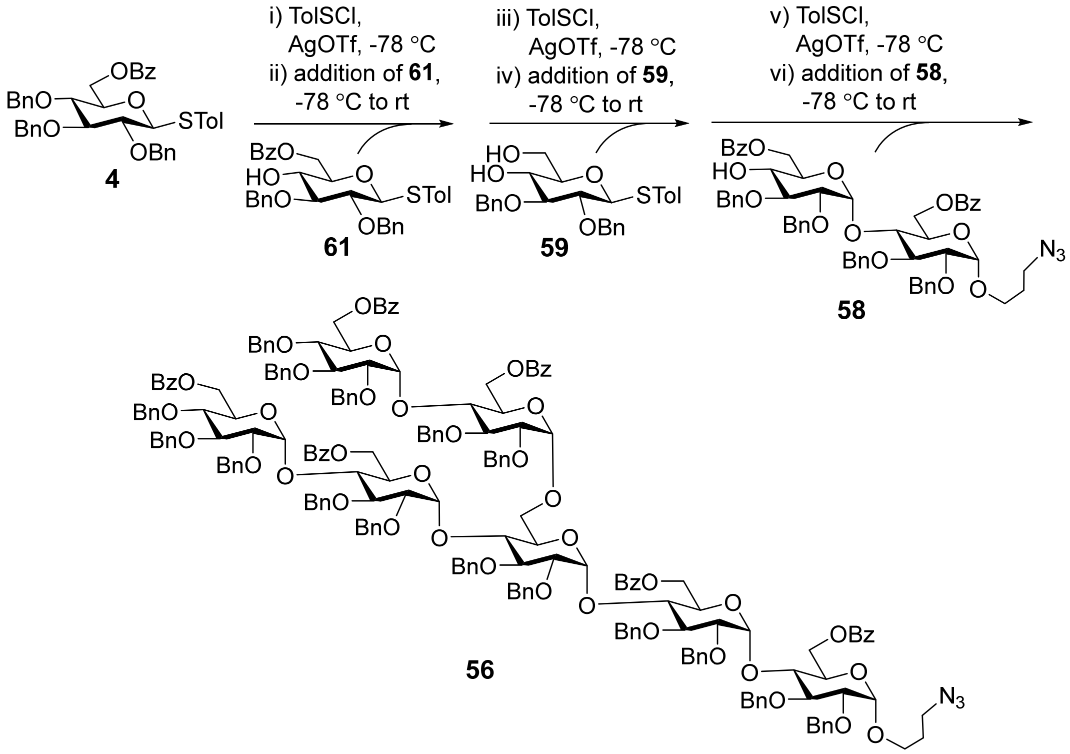
3-Azidopropyl 6-*O*-benzoyl-2,3-di-*O*-benzyl-*α*-D-glucopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-*α*-D-glucopyranoside (58)



After the mixture of donor **62** (350 mg, 0.51 mmol) and freshly activated MS 4Å in anhydrous diethyl ether (20 mL) was stirred at room temperature for 1.0 h and then cooled to -78 °C, a solution of AgOTf (132 mg, 0.51 mmol) in diethyl ether (1.5 mL) was added. The mixture was stirred for 15 min, and *p*-

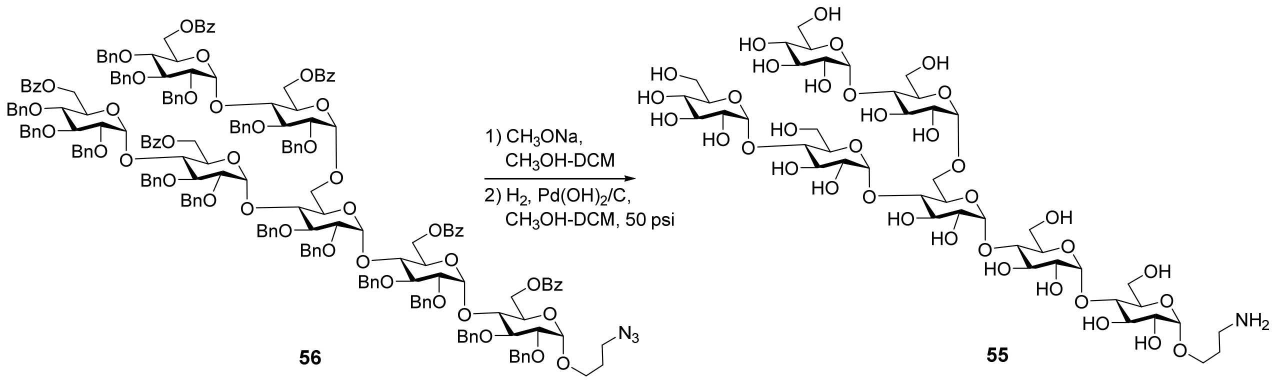
TolSCl (74 μL, 0.51 mmol) was added through a microsyringe without touching the flask. Fifteen minutes later, a solution of acceptor **61** (262 mg, 0.46 mmol) in anhydrous diethyl ether (2.0 mL), which was precooled to -78 °C, was added. The reaction was warmed up to room temperature slowly in 1.5 h and stirred for another 15 min, before it was cooled to -78 °C again. Next, the AgOTf (118 mg, 0.46 mmol) in anhydrous diethyl ether (1.0 mL), *p*-TolSCl (66 μL, 0.46 mmol), and precooled **10** (46 mg, 0.46 mmol) were added sequentially. The reaction mixture was warmed up to room temperature slowly and stirred for another 15 min before it was quenched with Et_3N, diluted with CH_2Cl_2, and filtered. The filtrate was concentrated under vacuum, and the residue purified by flash silica gel column chromatography (hexanes/ethyl acetate, 8:1) to provide **63**. To the solution of **63** in acetonitrile/CH_2Cl_2 (V/V, 1:3, 4 mL) was added triethylamine trihydrofluoride (1 mL). The reaction solution was stirred at room temperature for overnight. The mixture was diluted with ethyl acetate (20 mL) and washed with saturated aq. $NaHCO_3$ solution and brine, the organic layer was dried with Na_2SO_4 and concentrated. Purification of the residue on a silica gel column (hexanes/ethyl acetate, 7:1) provided product **58** (279 mg, 61% for three steps) as a syrup. ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 8.08 – 7.96 (m, 4H, Ph), 7.60 – 7.51 (m, 2H, Ph), 7.47 – 7.37 (m, 4H, Ph), 7.31 – 7.15 (m, 20H, Ph), 5.71 (d, *J* = 3.6 Hz, 1H, H-1'), 5.02 (d, *J* = 11.4 Hz, 1H, Bn), 4.89 (d, *J* = 10.8 Hz, 1H, Bn), 4.82 – 4.75 (m, 2H, Bn), 4.72 (d, *J* = 3.6 Hz, 1H, H-1), 4.71 (dd, *J* = 12.0, 2.4 Hz, 1H, H-6a), 4.65 (d, *J* = 12.0 Hz, 1H, Bn), 4.61 (d, *J* = 12.0 Hz, 1H, Bn), 4.58 (dd, *J* = 12.0, 3.6 Hz, 1H, H-6a'), 4.55 – 4.52 (m, 3H, Bn, H-6b), 4.28 (dd, *J* = 12.0, 2.4 Hz, 1H, H-6b'), 4.10 (t, *J* = 9.0 Hz, 1H, H-3'), 4.09 – 4.05 (m, 1H, H-5), 4.00 (dd, *J* = 9.6, 8.4 Hz, 1H, H-4), 3.90 – 3.87 (m, 1H, H-5'), 3.86 (t, *J* = 9.6 Hz, 1H, H-3), 3.77 – 3.71 (m, 1H, OCH_2CH_2), 3.58 (dd, *J* = 9.0, 3.6 Hz, 1H, H-2), 3.51 (t, *J* = 9.6 Hz, 1H, H-4'), 3.47 – 3.38 (m, 4H, H-2', OCH_2CH_2, N_3CH_2), 2.77 (s, 1H, O*H*), 1.94 – 1.87 (m, 2H, $CH_2CH_2CH_2$). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 166.87, 166.15, 138.83, 138.40, 137.83, 137.76, 133.25, 133.15, 129.82, 129.71, 129.67, 129.64, 128.51, 128.48, 128.34, 128.32, 128.31, 128.25, 128.02, 128.00, 127.97, 127.83, 127.65, 127.58, 127.13, 126.57, 97.12 (C-1'), 96.58 (C-1), 81.46, 80.86, 80.41, 78.91, 75.60, 74.17, 73.60, 73.37, 73.22, 71.12, 70.20, 68.39, 64.89, 63.79, 63.42, 48.25, 28.78. HR ESI-TOF MS (m/z): calcd for $C_{57}H_{59}N_3O_{13}Na$ $[M + Na]^+$, 1016.3946; found, 1016.3933.

3-Azidopropyl 4,6-di-*O*-[6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-*α*-D-glucopyranosyl]-2,3-di-*O*-benzyl-*α*-D-glucopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-O-benzyl-*α*-D-glucopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-*α*-D-glucopyranoside (56)



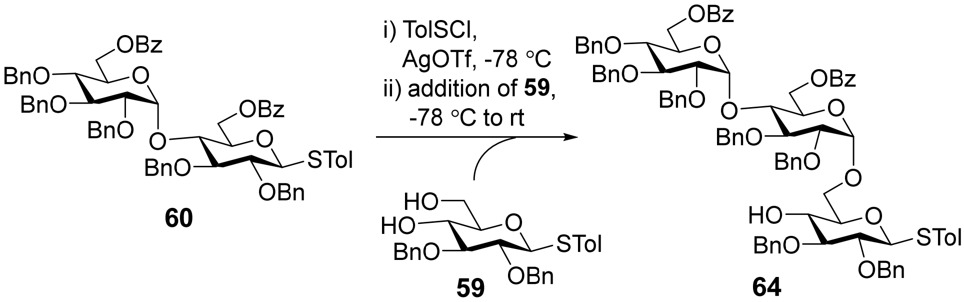
After the mixture of donor **4** (128 mg, 194 μmol) and freshly activated MS 4Å in anhydrous diethyl ether (10 mL) was stirred at room temperature for 1.0 h and then cooled to -78 °C, a solution of AgOTf (50 mg, 194 μmol) in diethyl ether (0.5 mL) was added. The mixture was stirred for 15 min, and *p*-TolSCl (28 μL, 194 μmol) was added through a microsyringe without touching the flask. Fifteen minutes later, a solution of precooled acceptor **61** (100 mg, 176 μmol) in anhydrous diethyl ether (1.5 mL) was added. The reaction was warmed up to room temperature slowly in 1.5 h and stirred for another 15 min, before it was cooled to -78 °C. Next, the AgOTf (45 mg, 176 μmol) in anhydrous diethyl ether (0.5 mL), *p*-TolSCl (25 μL, 176 μmol), and precooled **59** (37 mg, 80 μmol) were added sequentially. The reaction mixture was warmed up to room temperature slowly in 1.5 h and stirred for another 15 min before it was cooled to -78 °C again. Then, the AgOTf (21 mg, 80 μmol) in anhydrous diethyl ether (0.2 mL), *p*-TolSCl (12 μL, 80 μmol), and precooled **58** (79 mg, 80 μmol) were added in the same sequence. The reaction was warmed up to room temperature slowly and stirred for another 15 min before it was quenched with Et_3N, diluted with CH_2Cl_2, and filtered. The filtrate was concentrated under vacuum, and the residue purified by flash silica gel column chromatography (hexanes/ethyl acetate, 8:1) to provide **56** (143 mg, 54% yield for one-pot three step reactions) as a white syrup. ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 8.16 – 8.09 (m, 3H, Ph), 8.08 – 7.99 (m, 4H, Ph), 7.95 – 7.89 (m, 4H, Ph), 7.58 – 6.85 (m, 99H, Ph), 5.86 (d, *J* = 3.6 Hz, 1H, H-1^A), 5.68 (d, *J* = 3.6 Hz, 1H, H-1^B), 5.62 (d, *J* = 3.6 Hz, 1H, H-1^C), 5.59 (d, *J* = 3.6 Hz, 1H, H-1^D), 5.36 (d, *J* = 3.0 Hz, 1H, H-1^E), 5.29 (d, *J* = 3.6 Hz, 1H, H-1^F), 5.17 (d, *J* = 10.8 Hz, 1H, Bn), 5.05 – 4.97 (m, 2H), 4.90 – 4.79 (m, 7H), 4.78 – 4.74 (m, 3H), 4.72 (d, *J* = 3.6 Hz, 1H, H-1^G), 4.70 – 4.65 (m, 4H), 4.65 – 4.58 (m, 4H), 4.58 – 4.43 (m, 13H), 4.41 – 4.29 (m, 5H), 4.26 – 4.19 (m, 4H), 4.19 – 4.03 (m, 10H), 4.02 – 3.88 (m, 8H), 3.80 (d, *J* = 10.2 Hz, 1H), 3.75 – 3.69 (m, 1H), 3.65 (t, *J* = 9.6 Hz, 1H), 3.62 – 3.57 (m, 3H), 3.57 – 3.35 (m, 10H), 3.16 (dd, *J* = 9.6, 3.6 Hz, 1H), 1.93 – 1.81 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 166.12, 166.04, 165.96, 165.86, 165.73, 139.17, 138.89, 138.73, 138.63, 138.40, 138.15, 137.94, 137.90, 137.89, 137.82, 137.71, 137.68, 137.57, 133.45, 133.30, 133.18, 133.04, 132.88, 132.84, 130.04, 129.97, 129.95, 129.91, 129.84, 129.81, 129.76, 129.73, 129.70, 129.66, 129.64, 129.62, 129.58, 128.66, 128.54, 128.52, 128.49, 128.45, 128.40, 128.38, 128.34, 128.32, 128.31, 128.27, 128.25, 128.22, 128.18, 128.15, 128.08, 128.04, 128.00, 127.98, 127.95, 127.94, 127.92, 127.85, 127.75, 127.74, 127.71, 127.67, 127.53, 127.50, 127.48, 127.42, 127.37, 127.25, 127.23, 127.20, 127.16, 127.03, 126.85, 126.81, 126.72, 126.68, 126.50, 126.26, 96.96 (C-1^D), 96.93 (C-1^A), 96.90 (C-1^B), 96.71 (C-1^E), 96.63 (C-1^G), 96.54 (C-1^C), 96.25 (C-1^F), 81.88, 81.62, 81.34, 81.21, 80.85, 80.31, 80.19, 79.91, 79.64, 79.35, 79.05, 78.88, 78.26, 77.63, 77.57, 75.75, 75.63, 75.33, 74.96, 74.90, 74.77, 74.40, 73.85, 73.72, 73.57, 73.34, 73.26, 72.49, 72.30, 72.24, 71.95, 69.97, 69.80, 69.44, 69.38, 68.62, 67.87, 64.89, 63.98, 63.86, 63.61, 63.31, 63.03, 62.97, 48.28, 28.81. HR ESI-TOF MS (m/z): calcd for $C_{199}H_{201}N_4O_{42}$ $[M + NH_4]^+$, 3318.3715; found, 3318.3709.

3-Aminopropyl 4,6-di-*O*-[*α*-D-glucopyranosyl-(1→4)-*α*-D-glucopyranosyl]-*α*-D-glucopyranosyl-(1→4)-*α*-D-glucopyranosyl-(1→4)-*α*-D-glucopyranoside (55)



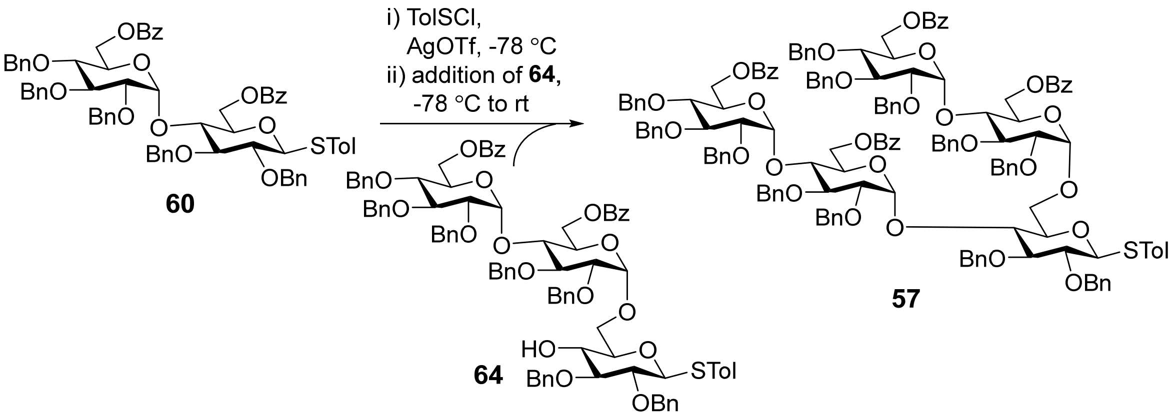
To a solution of **56** (50 mg, 15 μmol) in CH_3OH/CH_2Cl_2 (V/V, 3:1, 10 mL) was added sodium methoxide (1 mL, 1.0 M in methanol). The reaction mixture was stirred at room temperature for 3 hours and then neutralized by Amberlite® IR120 hydrogen form. The resin was removed by filtration and the filtrate was concentrated under vacuum. The residue was dissolved in a mixed solvent of CH_3OH/CH_2Cl_2 (V/V, 9:1, 10 mL), and a catalytic amount of 20 wt% $Pd(OH)_2/C$ was added. The reaction mixture was stirred for 36 h under H_2 atmosphere in 50 psi. The progress of the reaction was monitored by MALDI-TOF mass spectrometer. Upon completion, the reaction mixture was filtrated and the filtrate was purified on a Sephadex G-25 gel column with H_2O as the eluent to produce the synthetic target **55** (16 mg, 85% over two steps) as a white foam. ^{1}H NMR (600 MHz, D_2O) δ: 5.23 (d, J = 4.2 Hz, 1H, H-1^A), 5.21 (d, J = 3.6 Hz, 1H, H-1^B), 5.18 (d, J = 4.2 Hz, 1H, H-1^C), 5.16 (d, J = 3.6 Hz, 1H, H-1^D), 5.14 (d, J = 3.6 Hz, 1H, H-1^E), 4.78 (d, J = 3.6 Hz, 1H, H-1^F), 4.75 (d, J = 4.2 Hz, 1H, H-1^G), 3.87 – 3.37 (m, 42H), 3.25 – 3.21 (m, 2H), 3.04 – 2.92 (m, 2H), 1.87 – 1.78 (m, 2H). ^{13}C NMR (150 MHz, D_2O) δ: 99.86 (C-1^E), 99.81 (C-1^C), 99.75 (C-1^D), 99.56 (C-1^B), 99.32 (C-1^A), 98.37 (C-1^F), 98.00 (C-1^G), 78.59, 77.65, 77.24, 76.64, 76.54, 73.37, 73.23, 73.20, 73.11, 72.88, 72.79, 72.71, 72.59, 71.69, 71.56, 71.52, 71.26, 71.23, 71.20, 71.17, 71.00, 70.77, 70.23, 70.22, 70.12, 69.16, 69.15, 67.32, 65.75, 60.53, 60.43, 60.36, 60.34, 60.32, 60.23, 37.67, 26.37. HR ESI-TOF MS (m/z): calcd for $C_{45}H_{80}NO_{36}$ $[M + H]^+$, 1210.4460, found, 1210.4484.

***p*-Tolyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-*α*-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzyl-1-thio-*β*-D-glucopyranoside (64)**



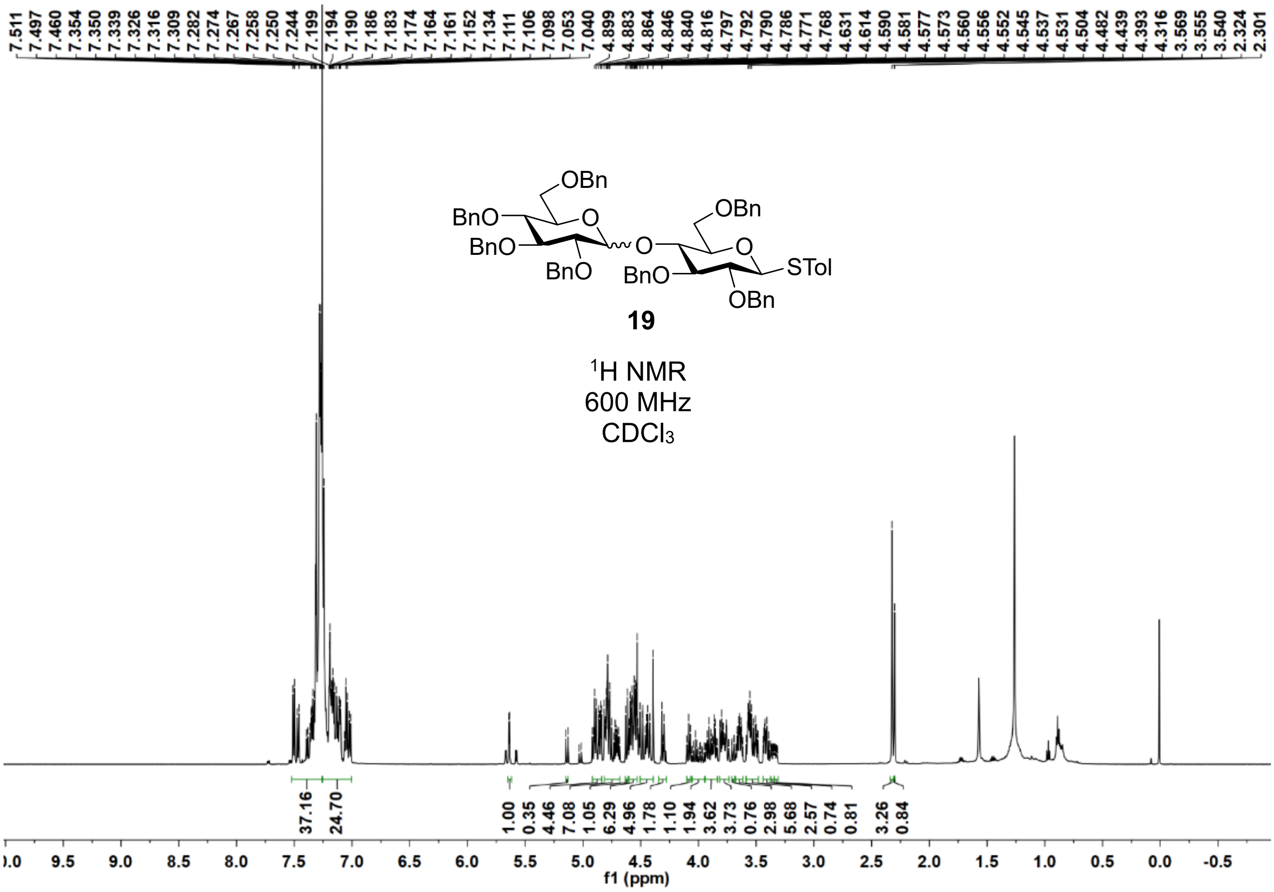
Donor **60** (300 mg, 0.27 mmol) reacted with acceptor **59** (115 mg, 0.25 mmol) by the general procedure for glycosylation to give product **64** (286 mg, 80%) as a syrup after column purification (hexanes/ethyl acetate, 6:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 8.04 (d, *J* = 8.4 Hz, 2H, Ph), 7.97 (d, *J* = 8.4 Hz, 2H, Ph), 7.57 – 6.96 (m, 45H, Ph), 5.60 (d, *J* = 3.6 Hz, 1H, H-1''), 5.01 (d, *J* = 11.4 Hz, 1H, Bn), 4.87 (d, *J* = 3.0 Hz, 1H, H-1'), 4.93 – 4.80 (m, 6H, Bn), 4.76 (d, *J* = 10.8 Hz, 1H, Bn), 4.72 – 4.52 (m, 9H, H-1, H-6a',6b', Bn), 4.39 (dd, *J* = 12.0, 1.8 Hz, 1H, H-6a''), 4.33 (dd, *J* = 12.0, 3.6 Hz, 1H, H-6b''), 4.20 – 4.04 (m, 2H, H-3', H-5'), 4.04 – 3.94 (m, 4H, H-3'', H-4', H-5'', H-6a), 3.73 (t, *J* = 9.6 Hz, 1H, H-4), 3.62 – 3.57 (m, 3H, H-2', H-4'', H-6b), 3.54 (t, *J* = 9.0 Hz, 1H, H-3), 3.51 – 3.46 (m, 2H, H-5, H-2''), 3.33 (t, *J* = 9.6 Hz, 1H, H-2), 3.06 – 2.98 (m, 1H, O*H*), 2.25 (s, 3H, PhC*H*$_3$). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 166.13, 165.96, 138.95, 138.60, 138.34, 138.06, 137.87, 137.80, 137.77, 133.13, 132.95, 132.64, 129.92, 129.88, 129.78, 129.76, 129.72, 129.66, 128.55, 128.52, 128.51, 128.47, 128.44, 128.41, 128.36, 128.33, 128.31, 128.25, 128.18, 127.96, 127.92, 127.85, 127.81, 127.78, 127.68, 127.57, 127.52, 127.03, 126.56, 97.35 (C-1''), 97.01 (C-1'), 88.28 (C-1), 86.12, 81.70, 81.29, 80.28, 80.16, 79.48, 77.63, 77.26, 75.74, 75.49, 75.35, 75.02, 74.62, 74.31, 73.44, 72.94, 72.13, 70.04, 68.41, 68.07, 63.82, 63.25, 21.10. HR ESI-TOF MS (m/z): calcd for $C_{88}H_{92}NO_{17}S$ [M + NH_4]$^+$, 1466.6086; found, 1466.6102.

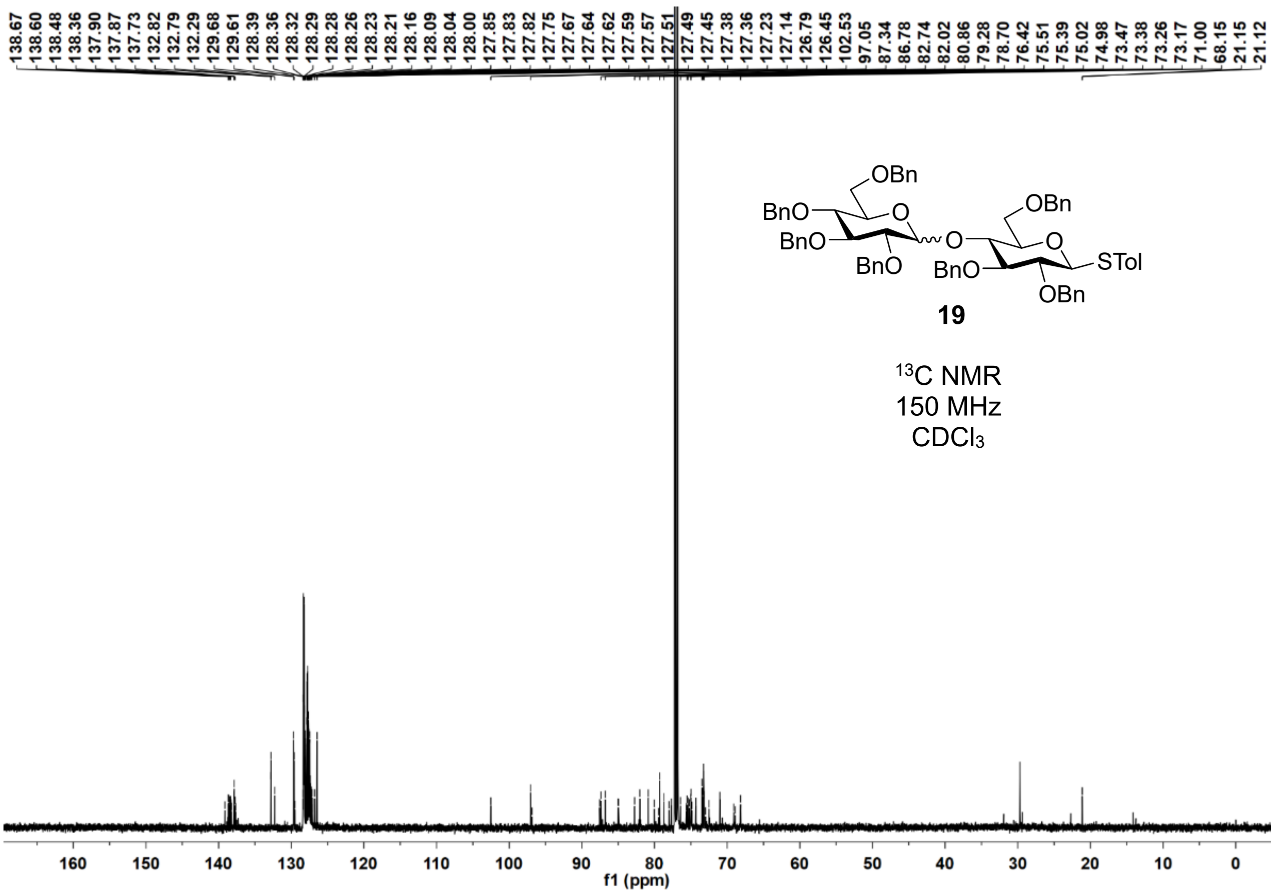
***p*-Tolyl 4,6-di-*O*-[6-O-benzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-*α*-D-glucopyranosyl]-2,3-di-*O*-benzyl-1-thio-*β*-D-glucopyranoside (57)**

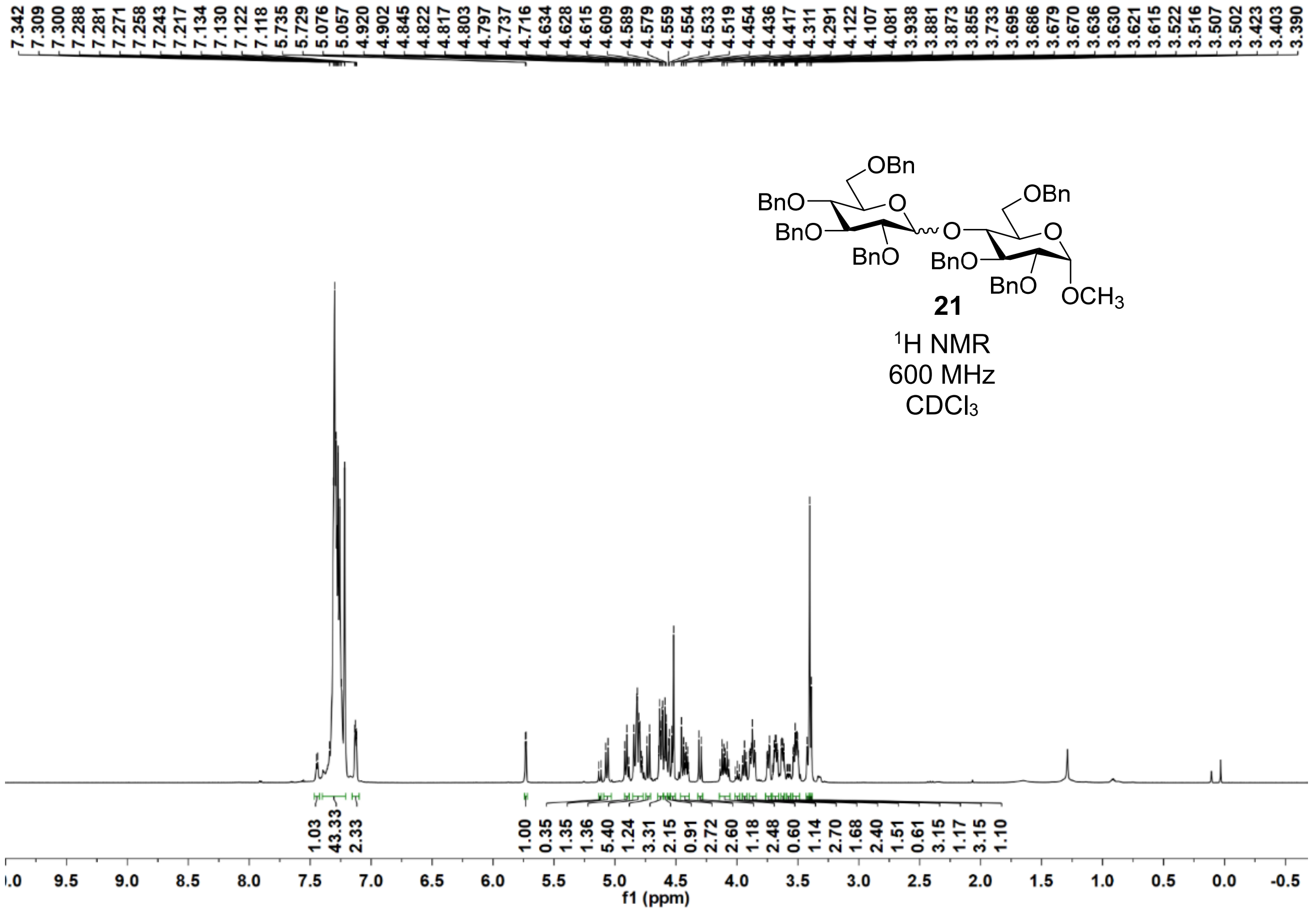


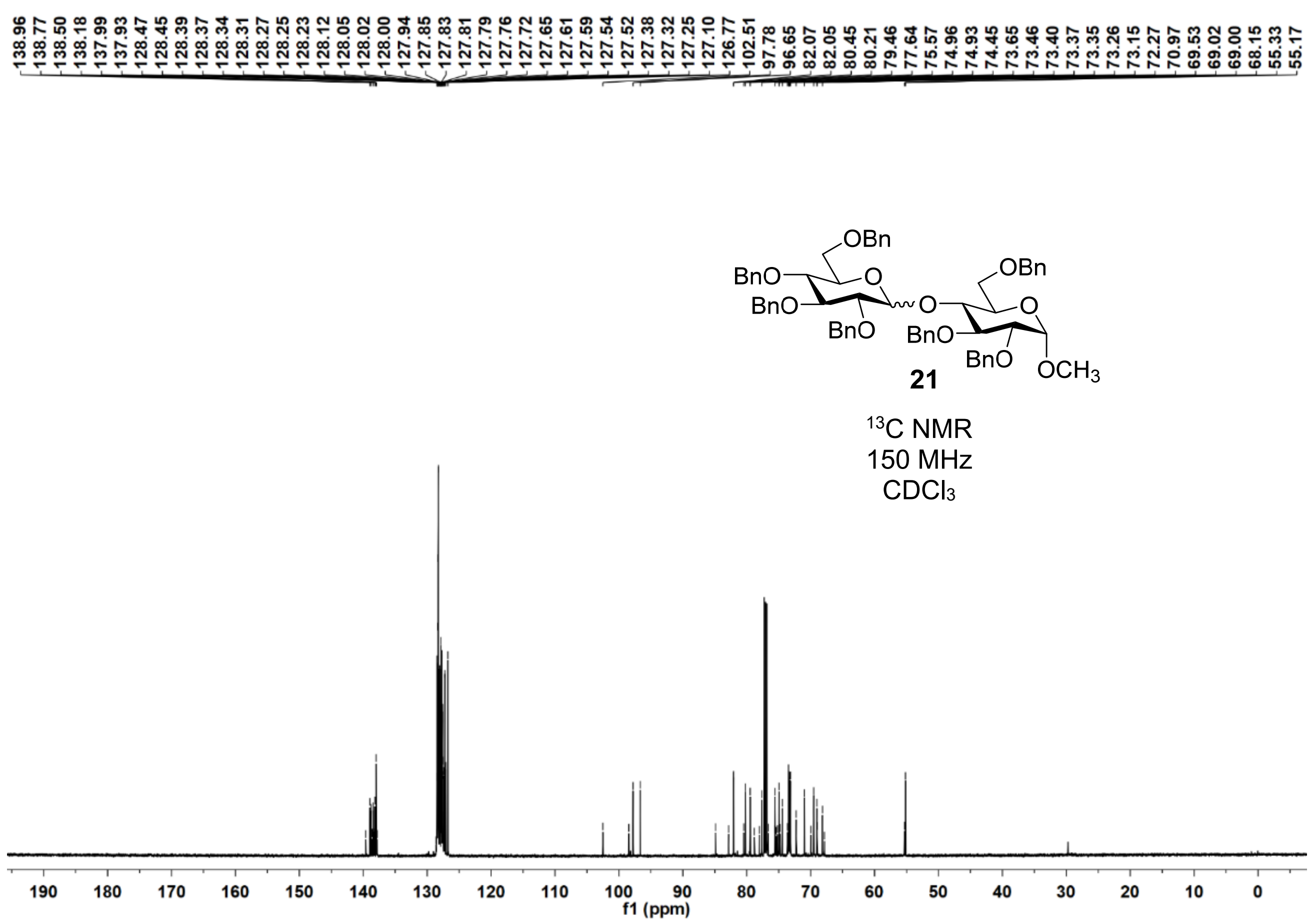
Donor **60** (180 mg, 0.16 mmol) reacted with acceptor **64** (214 mg, 0.15 mmol) by the general procedure for glycosylation to give product **57** (316 mg, 88%) as a syrup after column purification (hexanes/ethyl acetate, 8:1) with the stereochemistry determined by $J_{H1',H2'}$ coupling constant. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.05 (d, J = 7.8 Hz, 2H, Ph), 8.01 (d, J = 7.8 Hz, 2H, Ph), 7.94 (d, J = 8.4 Hz, 4H, Ph), 7.53 – 6.91 (m, 76H, Ph), 5.63 (d, J = 3.6 Hz, 1H, H-1^{A}), 5.58 (d, J = 3.6 Hz, 1H, H-1^{B}), 5.36 (d, J = 3.0 Hz, 1H, H-1^{C}), 5.24 (d, J = 3.0 Hz, 1H, H-1^{D}), 5.09 (d, J = 11.4 Hz, 1H, Bn), 4.95 (d, J = 11.4 Hz, 1H, Bn), 4.90 – 4.64 (m, 13H, Bn), 4.68 – 4.44 (m, 12H, H-1^{E}, Bn), 4.42 – 4.16 (m, 8H), 4.15 – 3.83 (m, 11H), 3.69 (t, J = 8.4 Hz, 1H), 3.60 (t, J = 9.6 Hz, 1H, H-3^{E}), 3.58 – 3.52 (m, 3H), 3.52 – 3.39 (m, 3H), 3.23 (t, J = 9.6 Hz, 1H, H-2^{E}), 2.23 (s, 3H, PhCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 166.03, 165.95, 165.90, 165.89, 138.92, 138.68, 138.39, 138.31, 138.06, 137.89, 137.86, 137.85, 137.82, 137.72, 137.71, 137.54, 133.16, 133.03, 132.94, 132.88, 132.76, 130.89, 130.11, 129.96, 129.93, 129.89, 129.78, 129.73, 129.70, 129.66, 129.66, 129.62, 128.81, 128.46, 128.41, 128.38, 128.36, 128.30, 128.26, 128.22, 128.20, 128.13, 128.08, 128.05, 127.99, 127.93, 127.88, 127.85, 127.78, 127.68, 127.64, 127.61, 127.55, 127.51, 127.47, 127.45, 127.35, 127.08, 127.00, 126.96, 126.86, 126.50, 126.38, 97.56 (C-1^{B}), 97.14 (C-1^{A}), 96.78 (C-1^{C}), 96.21 (C-1^{D}), 88.33 (C-1^{E}), 85.54, 81.77, 81.64, 81.19, 80.84, 80.54, 80.27, 79.84, 79.43, 79.31, 78.36, 77.55, 75.70, 75.66, 75.29, 75.22, 75.05, 74.91, 74.19, 73.88, 73.38, 73.15, 72.56, 72.51, 70.04, 69.92, 69.53, 68.33, 65.60, 65.55, 63.79, 63.72, 63.17, 21.10. HR ESI-TOF MS (m/z): calcd for $C_{149}H_{150}NO_{29}S$ $[M + NH_4]^+$, 2449.0014; found, 2449.0010.

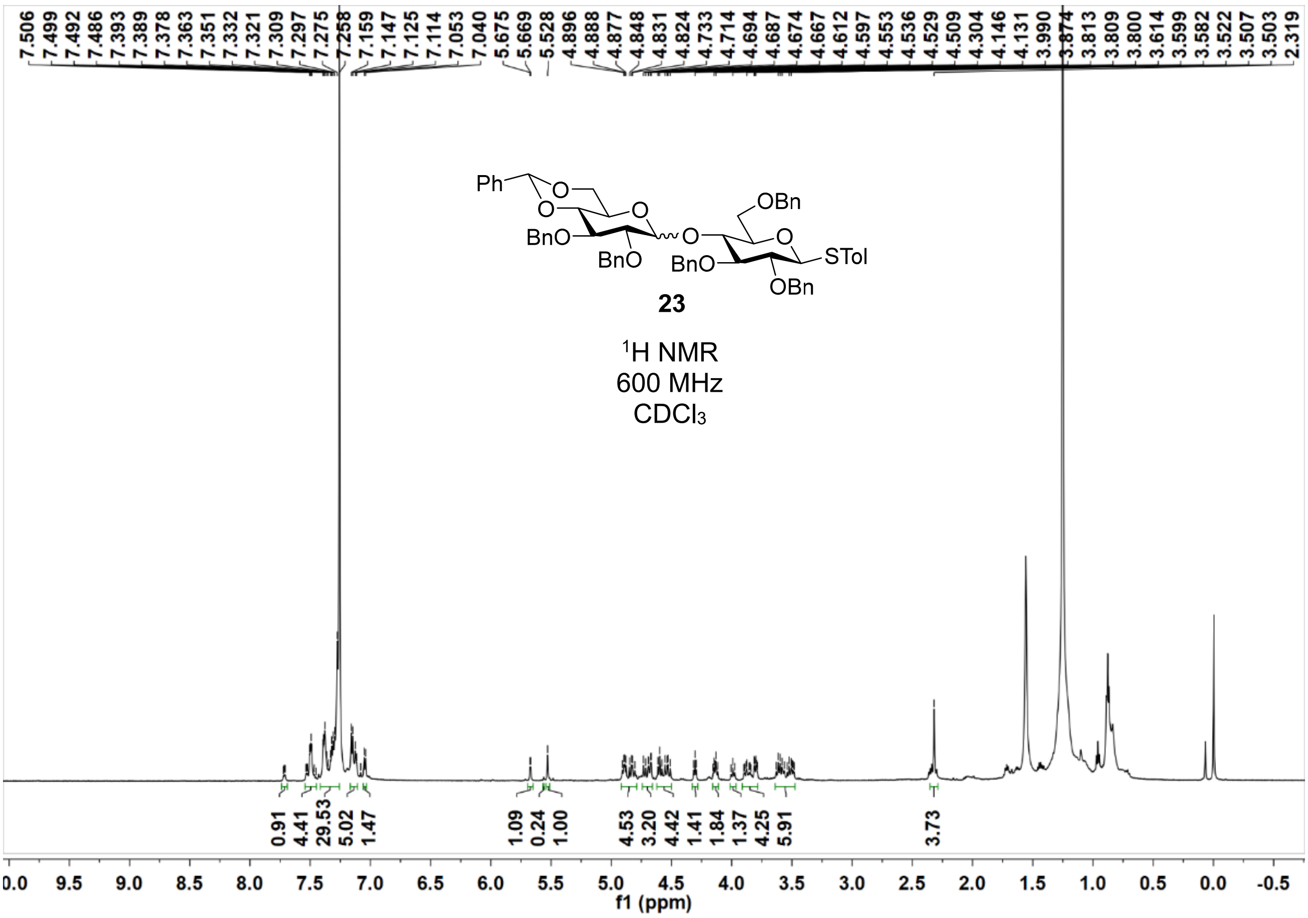
II. NMR spectra of synthetic intermediates and final products

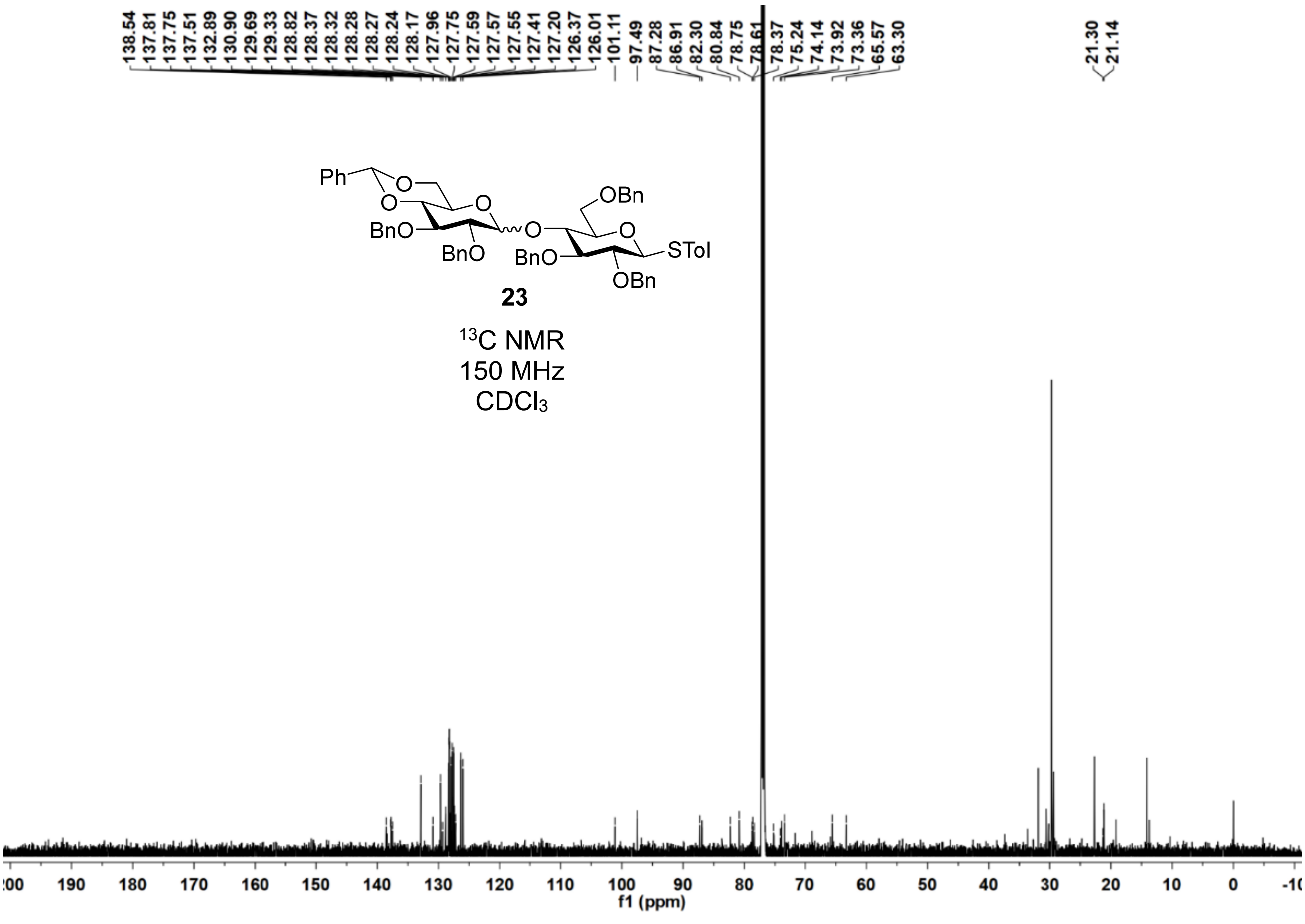


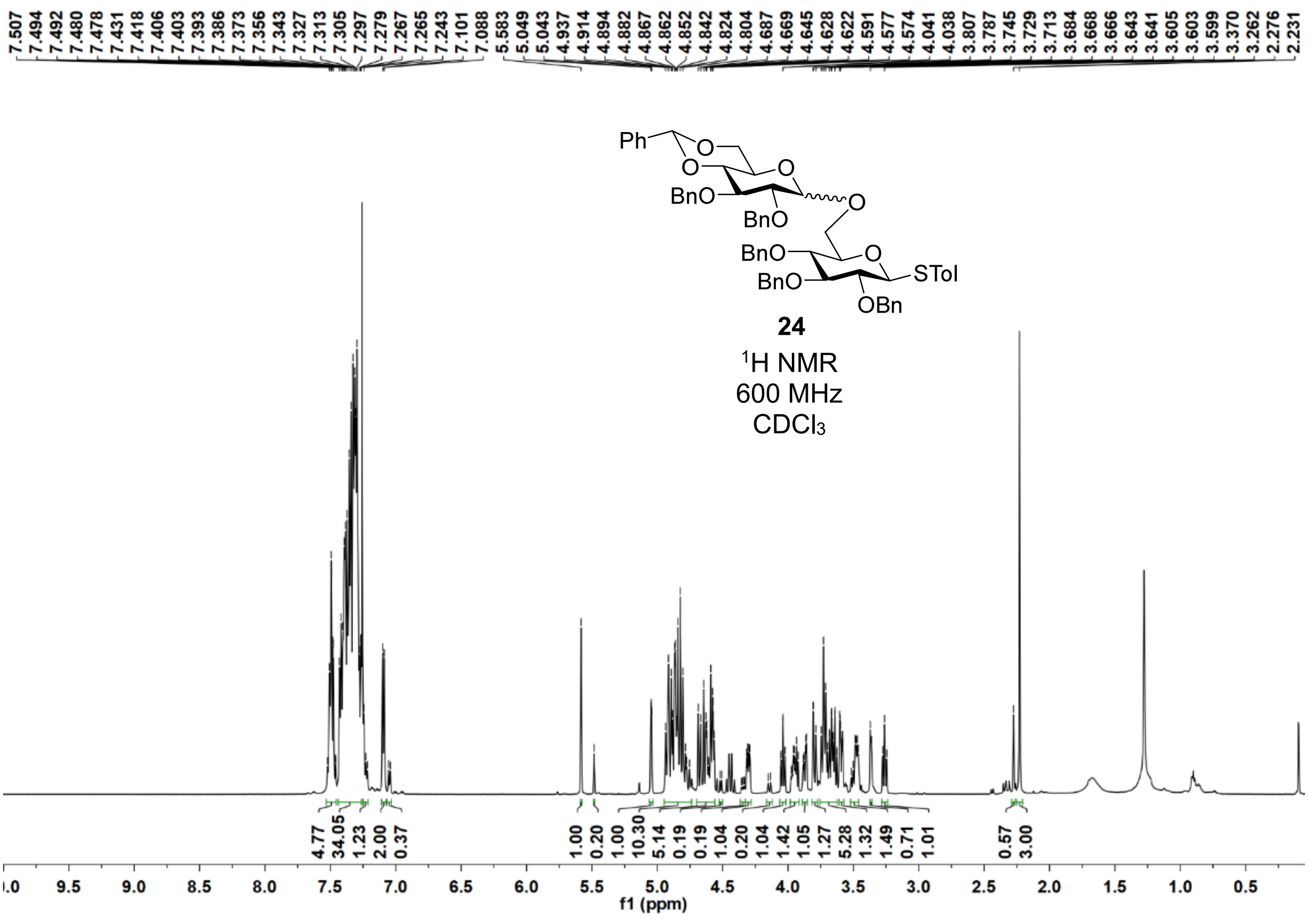



7.342 7.309 7.300 7.288 7.281 7.271 7.258 7.243 7.217 7.134 7.130 7.122 7.118 5.735 5.729 5.076 5.057 4.920 4.902 4.845 4.822 4.817 4.803 4.797 4.737 4.716 4.634 4.628 4.615 4.609 4.589 4.579 4.559 4.554 4.533 4.519 4.454 4.436 4.417 4.311 4.291 4.122 4.107 4.081 3.938 3.881 3.873 3.855 3.733 3.695 3.686 3.679 3.670 3.636 3.630 3.621 3.615 3.522 3.516 3.507 3.502 3.423 3.403 3.390
OBn
BnO
O
BnO
BnO
O
OBn
O
BnO
BnO
OCH3
21
1H NMR
600 MHz
CDCl3
1.03 43.33 2.33 1.00 0.35 1.35 1.36 5.40 1.24 3.31 2.15 0.91 2.72 2.60 1.18 2.48 0.60 1.14 2.70 1.68 2.40 1.51 0.61 3.15 1.17 3.15 1.10
f1 (ppm)

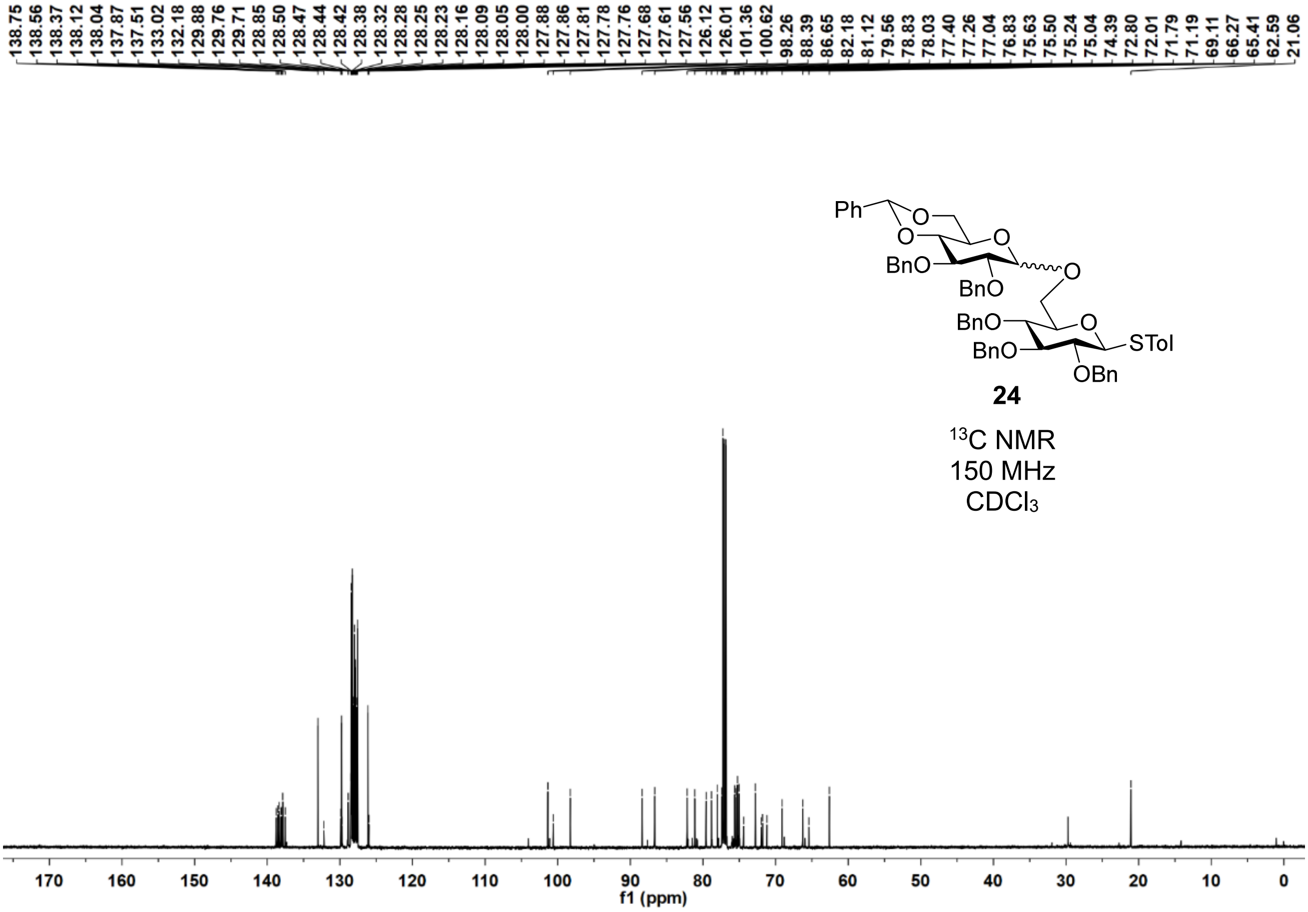

138.96 138.77 138.50 138.18 137.99 137.93 128.47 128.45 128.39 128.37 128.34 128.31 128.27 128.25 128.23 128.12 128.05 128.02 128.00 127.94 127.85 127.83 127.81 127.79 127.76 127.72 127.65 127.61 127.59 127.54 127.52 127.38 127.32 127.25 127.10 126.77 102.51 97.78 96.65 82.07 82.05 80.45 80.21 79.46 77.64 75.57 74.96 74.93 74.45 73.65 73.46 73.40 73.37 73.35 73.26 73.15 72.27 70.97 69.53 69.02 69.00 68.15 55.33 55.17
OBn
BnO
O
BnO
BnO
O
OBn
O
BnO
BnO
OCH3
21
13C NMR
150 MHz
CDCl3
f1 (ppm)


Ph
O
O
O
BnO
BnO
O
OBn
O
BnO
STol
OBn
23
1H NMR
600 MHz
CDCl3
f1 (ppm)

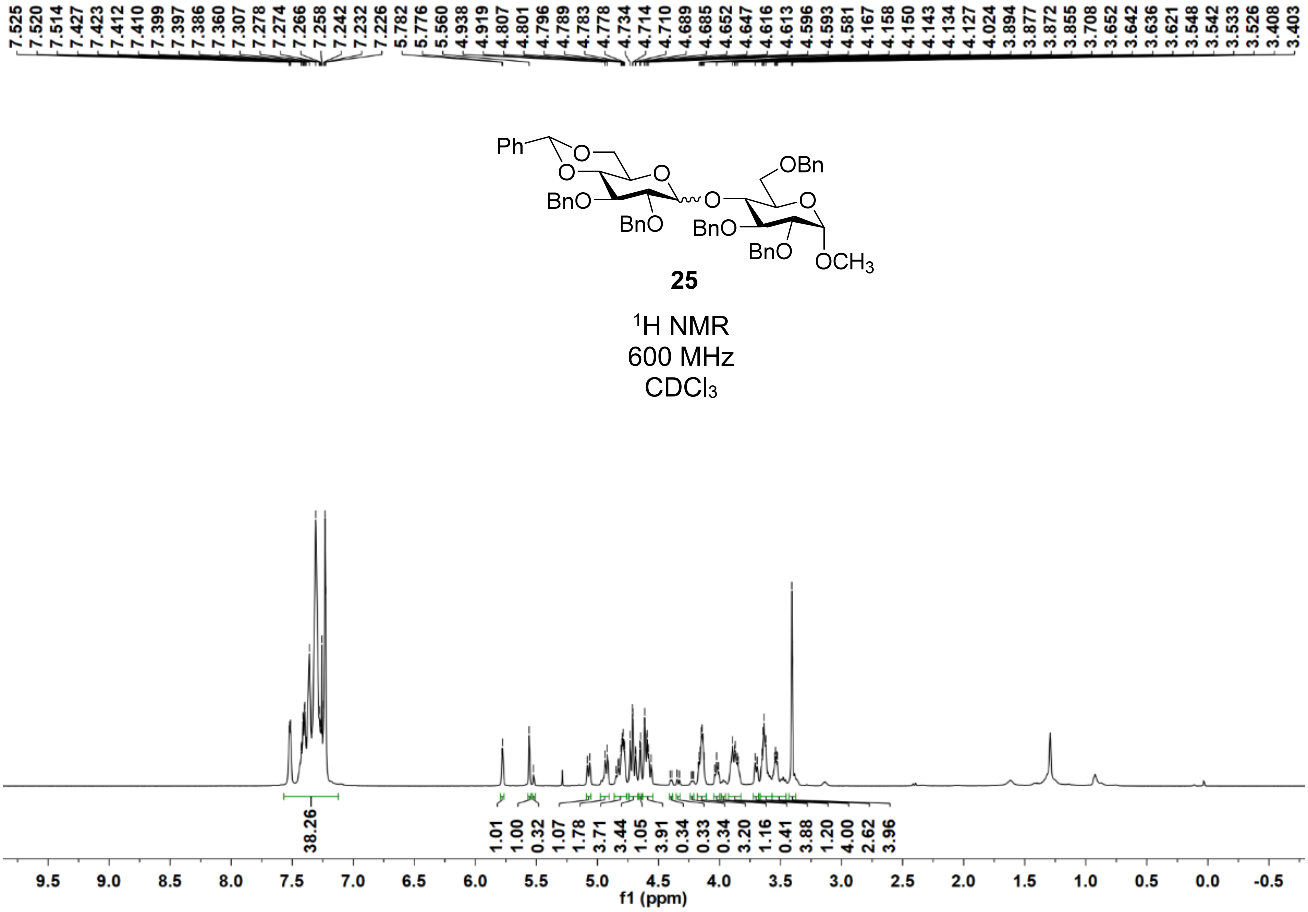

Ph
O
O
O
BnO
BnO
O
OBn
O
BnO
STol
OBn
23
13C NMR
150 MHz
CDCl3
f1 (ppm)

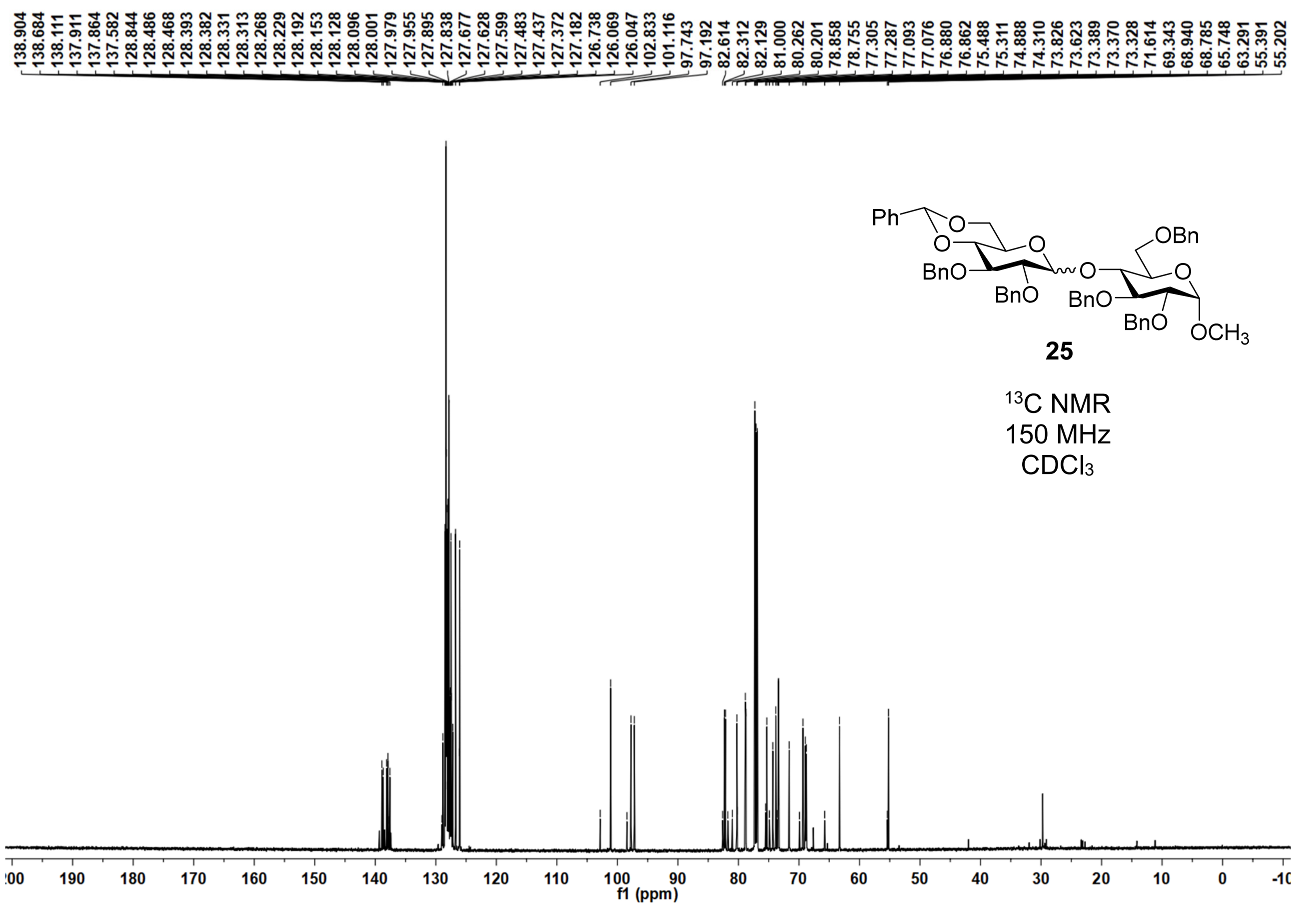


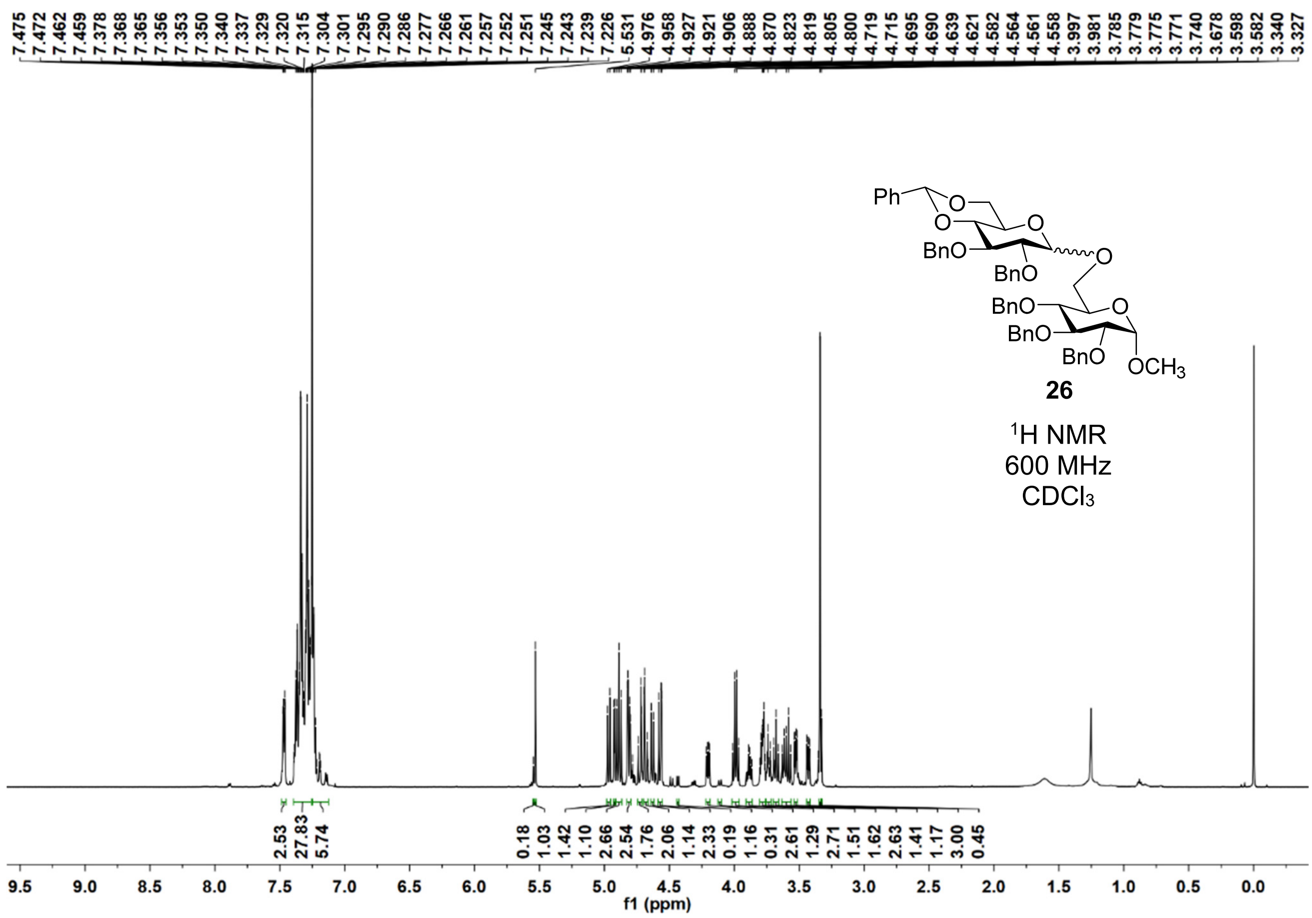
24
1H NMR
600 MHz
CDCl3
f1 (ppm)

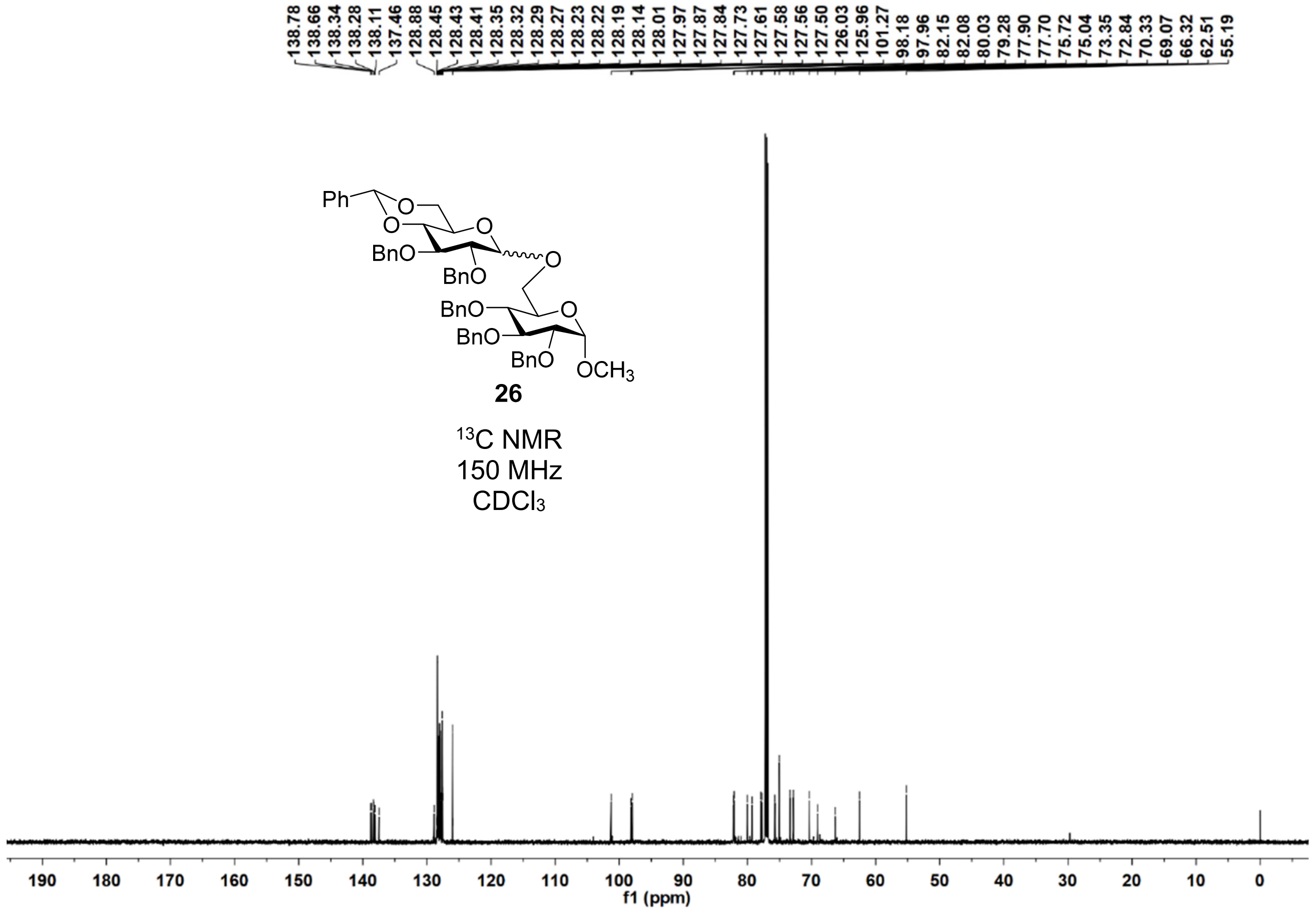


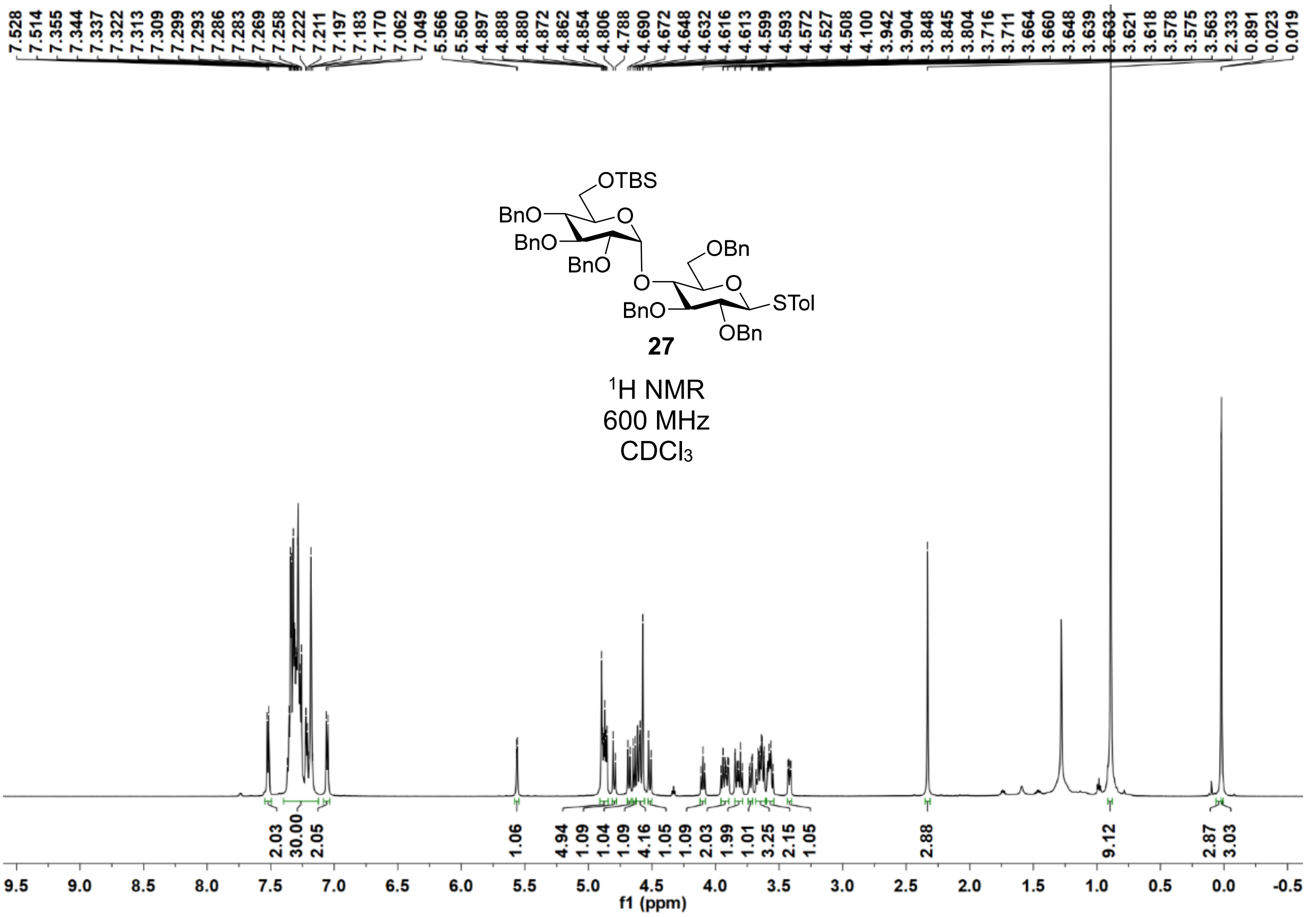
24
13C NMR
150 MHz
CDCl3
f1 (ppm)

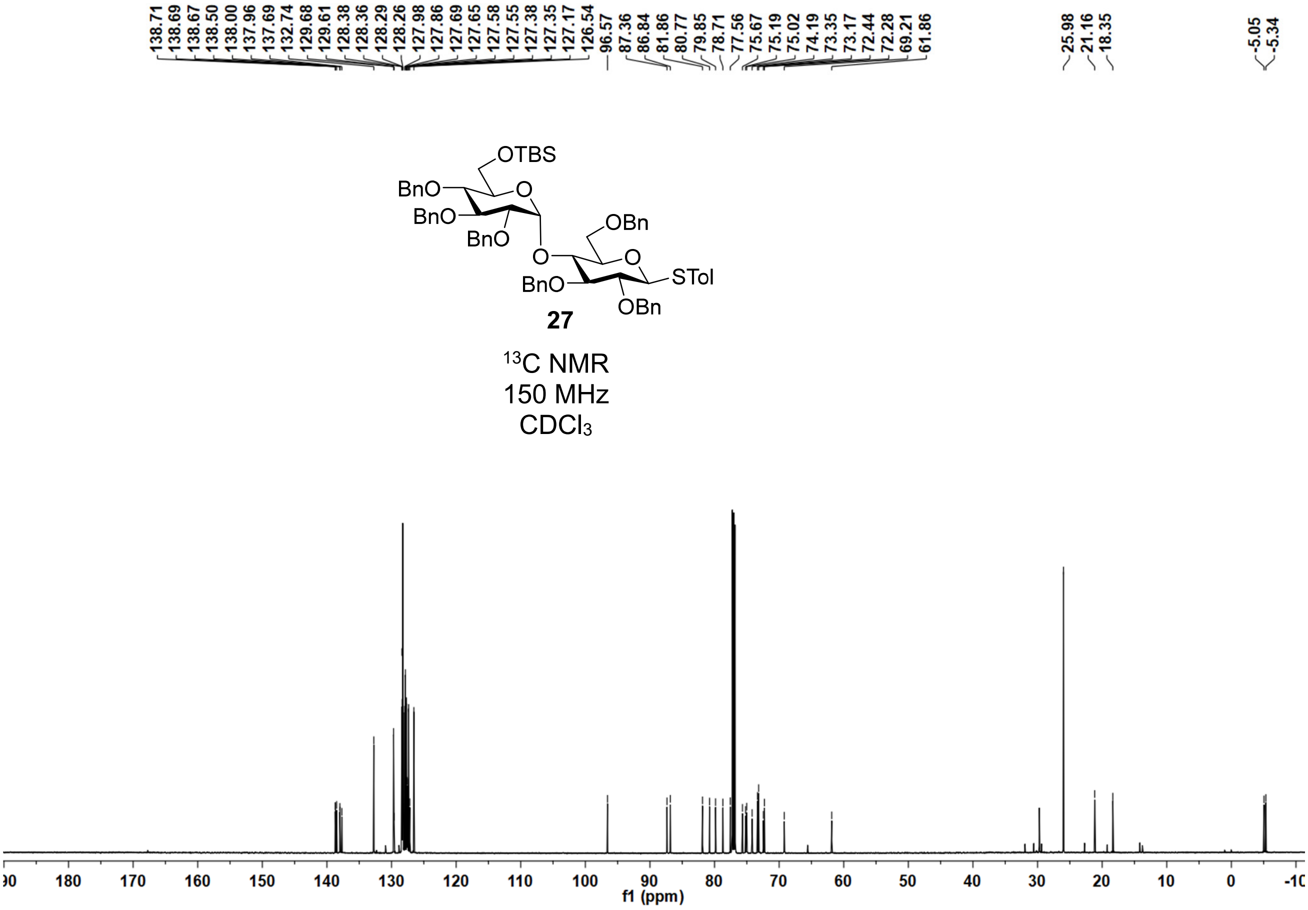

7.525 7.520 7.514 7.427 7.423 7.412 7.410 7.399 7.397 7.386 7.360 7.307 7.278 7.274 7.266 7.258 7.242 7.232 7.226 5.782 5.776 5.560 4.938 4.919 4.807 4.801 4.796 4.789 4.783 4.778 4.734 4.714 4.710 4.689 4.685 4.652 4.647 4.616 4.613 4.596 4.593 4.581 4.167 4.158 4.150 4.143 4.134 4.127 4.024 3.894 3.877 3.872 3.855 3.708 3.652 3.642 3.636 3.621 3.548 3.542 3.533 3.526 3.408 3.403
Ph
O
O
O
BnO
BnO
O
OBn
O
BnO
BnO
OCH3
25
1H NMR
600 MHz
CDCl3
38.26
1.01 1.00 0.32 1.07 1.78 3.71 3.44 1.05 3.91 0.34 0.33 0.34 3.20 1.16 0.41 3.88 1.20 4.00 2.62 3.96
9.5 9.0 8.5 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 0.0 -0.5
f1 (ppm)

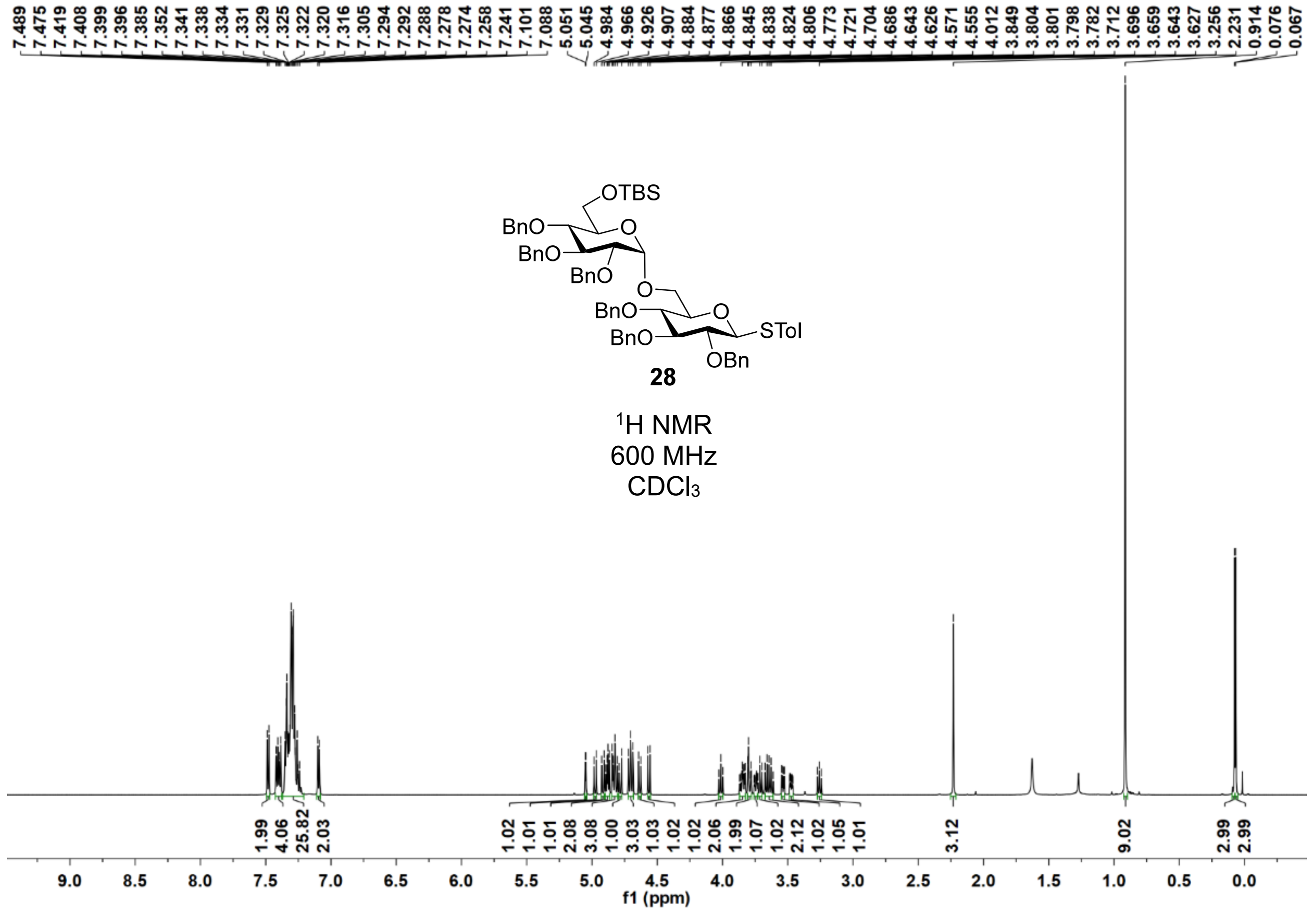

138.904 138.684 138.111 137.911 137.864 137.582 128.844 128.486 128.468 128.393 128.382 128.331 128.313 128.268 128.229 128.192 128.153 128.128 128.096 128.001 127.979 127.955 127.895 127.838 127.677 127.628 127.599 127.483 127.437 127.372 127.182 126.738 126.069 126.047 102.833 101.116 97.743 97.192 82.614 82.312 82.129 81.000 80.262 80.201 78.858 78.755 77.305 77.287 77.093 77.076 76.880 76.862 75.488 75.311 74.888 74.310 73.826 73.623 73.389 73.370 73.328 71.614 69.343 68.940 68.785 65.748 63.291 55.391 55.202
Ph
O
O
O
BnO
BnO
O
OBn
O
BnO
BnO
OCH3
25
13C NMR
150 MHz
CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

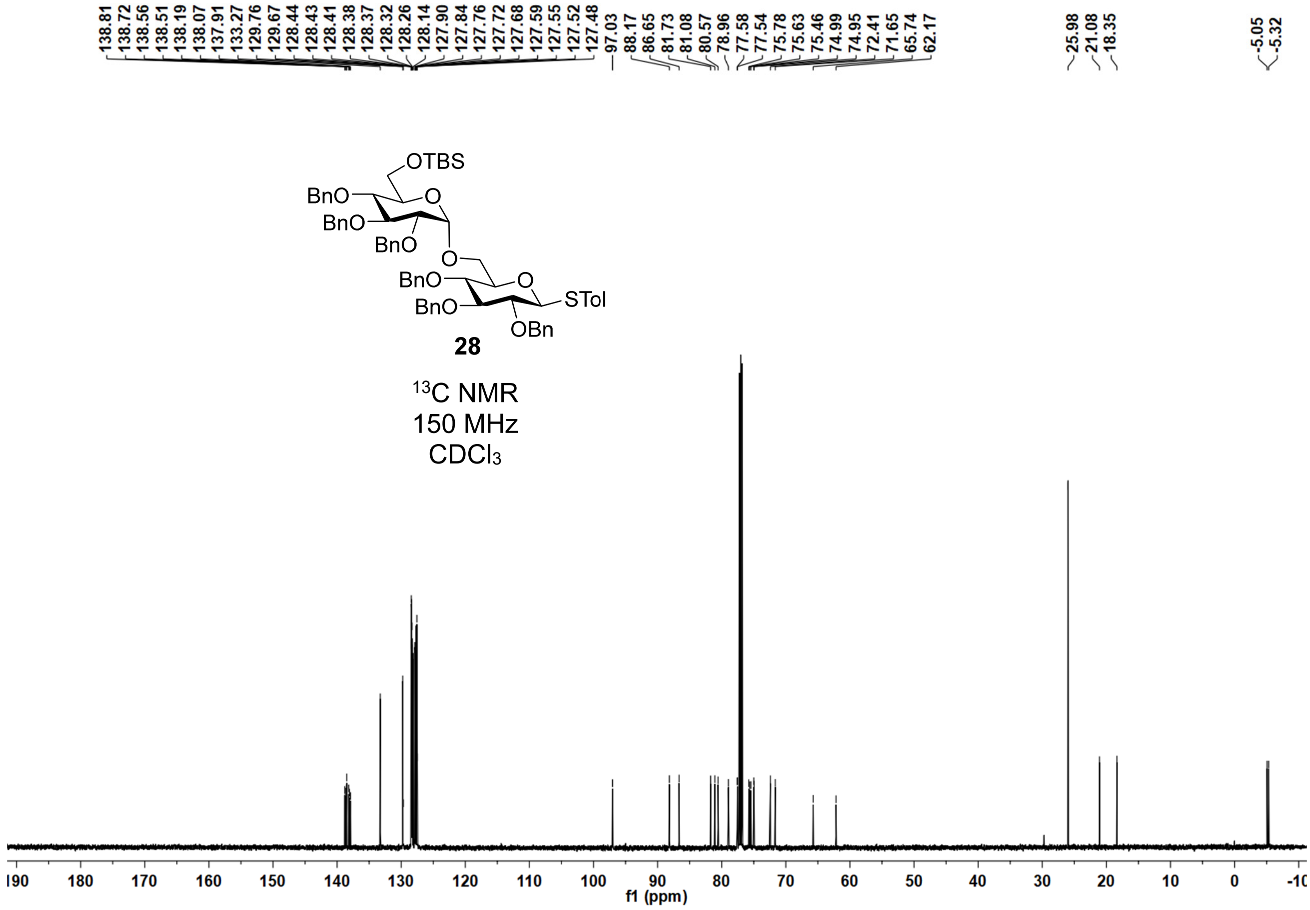

7.475 7.472 7.462 7.459 7.378 7.368 7.365 7.356 7.353 7.350 7.340 7.337 7.329 7.320 7.315 7.304 7.301 7.295 7.290 7.286 7.277 7.266 7.261 7.257 7.252 7.251 7.245 7.243 7.239 7.226 5.531 4.976 4.958 4.927 4.921 4.906 4.888 4.870 4.823 4.819 4.805 4.800 4.719 4.715 4.695 4.690 4.639 4.621 4.582 4.564 4.561 4.558 3.997 3.981 3.785 3.779 3.775 3.771 3.740 3.678 3.598 3.582 3.340 3.327
Ph
O
O
O
BnO
BnO
O
BnO
BnO
O
BnO
OCH3
26
1H NMR
600 MHz
CDCl3
2.53 27.83 5.74 0.18 1.03 1.42 1.10 2.66 2.54 1.76 2.06 1.14 2.33 0.19 1.16 0.31 2.61 1.29 2.71 1.51 1.62 2.63 1.41 1.17 3.00 0.45
9.5 9.0 8.5 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 0.0
f1 (ppm)

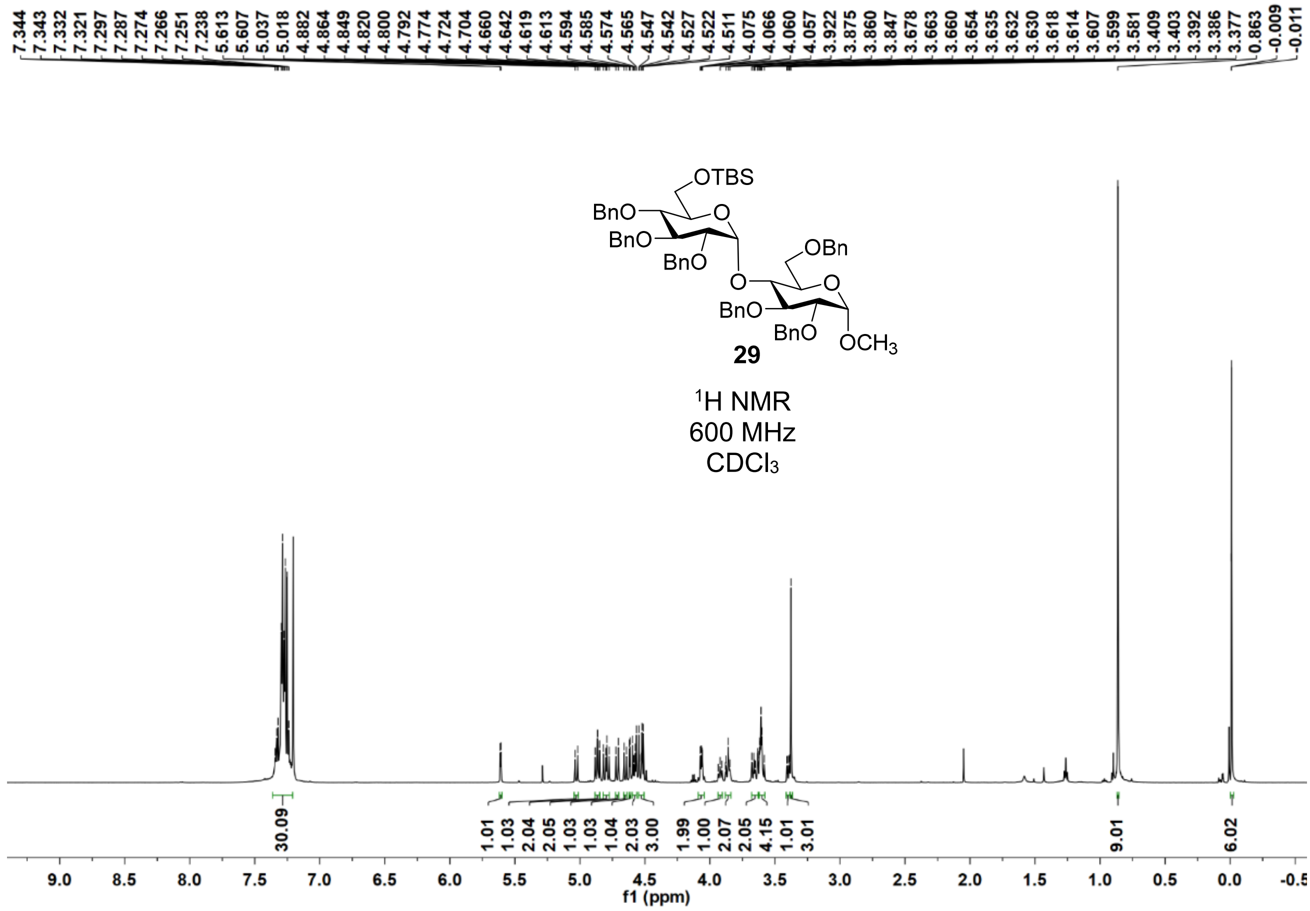

138.78 138.66 138.34 138.28 138.11 137.46 128.88 128.45 128.43 128.41 128.35 128.32 128.29 128.27 128.23 128.22 128.19 128.14 128.01 127.97 127.87 127.84 127.73 127.61 127.58 127.56 127.50 126.03 125.96 101.27 98.18 97.96 82.15 82.08 80.03 79.28 77.90 77.70 75.72 75.04 73.35 72.84 70.33 69.07 66.32 62.51 55.19
Ph
O
O
O
BnO
BnO
O
BnO
BnO
O
BnO
OCH3
26
13C NMR
150 MHz
CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

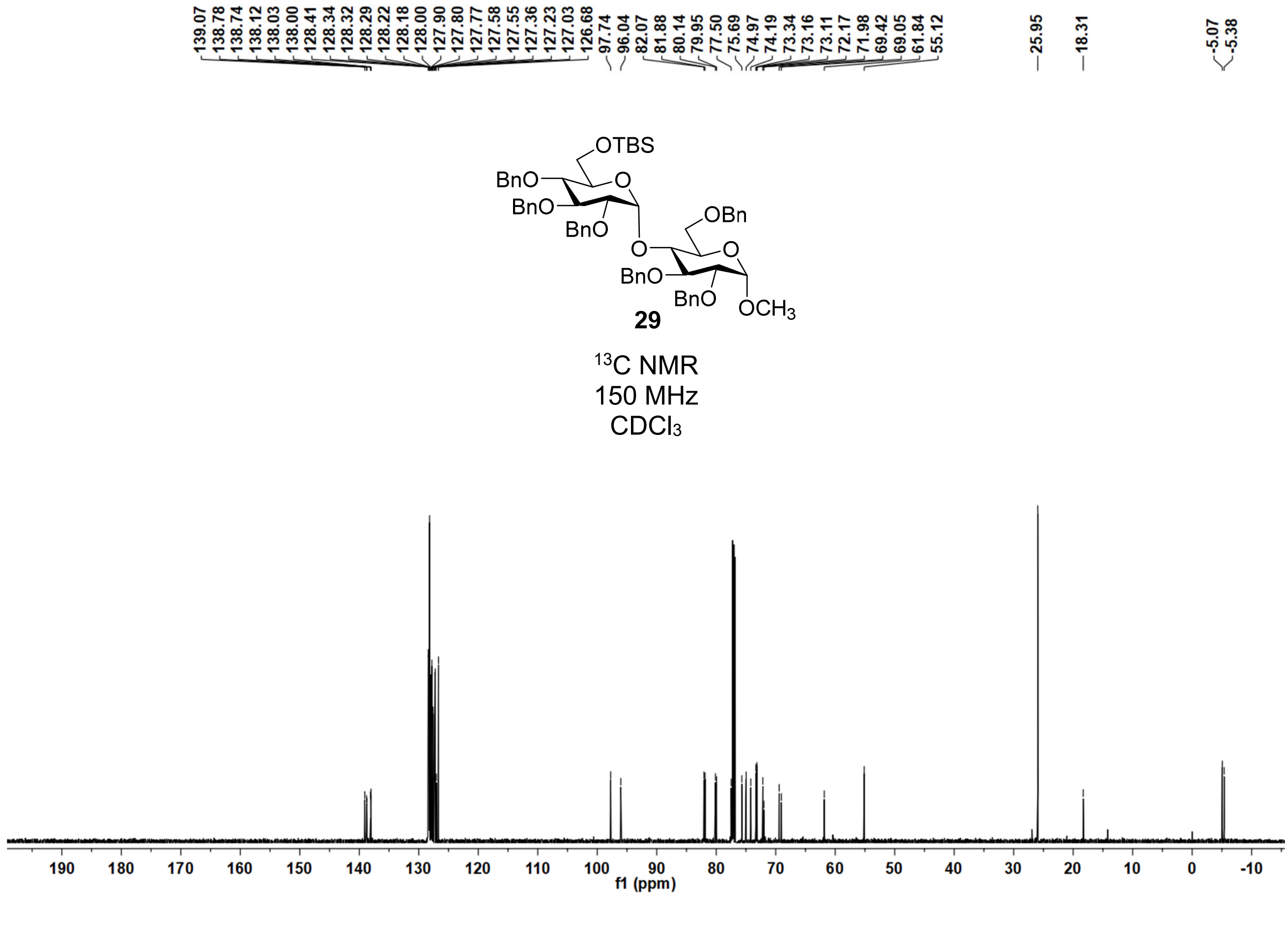

7.528 7.514 7.355 7.344 7.337 7.322 7.313 7.309 7.299 7.293 7.286 7.283 7.269 7.258 7.222 7.211 7.197 7.183 7.170 7.062 7.049 5.566 5.560 4.897 4.888 4.880 4.872 4.862 4.854 4.806 4.788 4.690 4.672 4.648 4.632 4.616 4.613 4.599 4.593 4.572 4.527 4.508 4.100 3.942 3.904 3.848 3.845 3.804 3.716 3.711 3.664 3.660 3.648 3.639 3.633 3.621 3.618 3.578 3.575 3.563 2.333 0.891 0.023 0.019
OTBS
BnO
BnO
BnO
O
O
OBn
O
BnO
STol
OBn
27
^{1}H NMR
600 MHz
$CDCl_3$
2.03 30.00 2.05 1.06 4.94 1.09 1.04 1.09 4.16 1.05 1.09 2.03 1.99 1.01 3.25 2.15 1.05 2.88 9.12 2.87 3.03
9.5 9.0 8.5 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 0.0 -0.5
f1 (ppm)

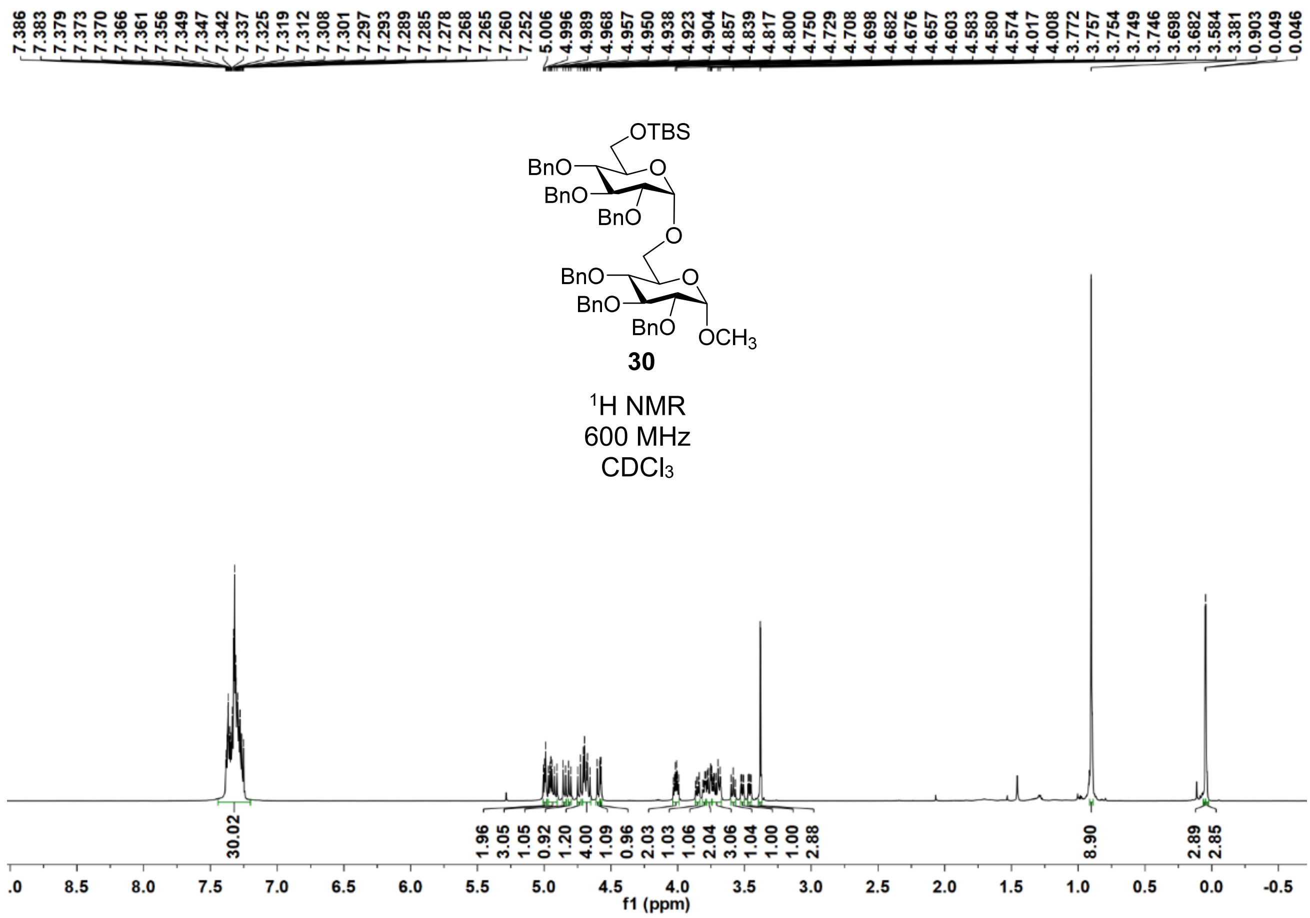

138.71 138.69 138.67 138.50 138.00 137.96 137.69 132.74 129.68 129.61 128.38 128.36 128.29 128.26 127.98 127.86 127.69 127.65 127.58 127.55 127.38 127.35 127.17 126.54 96.57 87.36 86.84 81.86 80.77 79.85 78.71 77.56 75.67 75.19 75.02 74.19 73.35 73.17 72.44 72.28 69.21 61.86 25.98 21.16 18.35 -5.05 -5.34
OTBS
BnO
BnO
BnO
O
O
OBn
O
BnO
STol
OBn
27
^{13}C NMR
150 MHz
$CDCl_3$
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

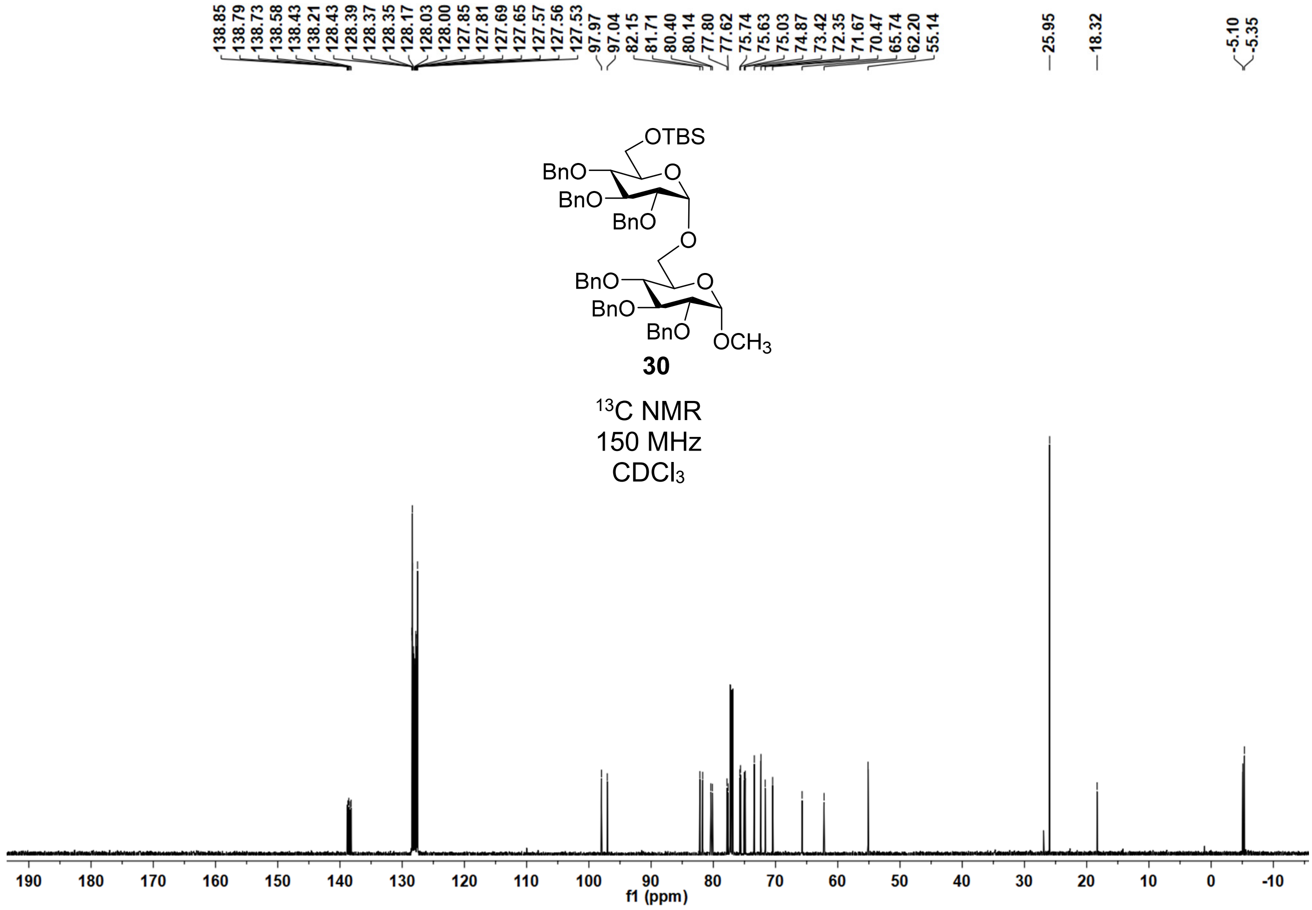

7.489 7.475 7.419 7.408 7.399 7.396 7.385 7.352 7.341 7.338 7.334 7.331 7.329 7.325 7.322 7.320 7.316 7.305 7.294 7.292 7.288 7.278 7.274 7.258 7.241 7.101 7.088 5.051 5.045 4.984 4.966 4.926 4.907 4.884 4.877 4.866 4.845 4.838 4.824 4.806 4.773 4.721 4.704 4.686 4.643 4.626 4.571 4.555 4.012 3.849 3.804 3.801 3.798 3.782 3.712 3.696 3.659 3.643 3.627 3.256 2.231 0.914 0.076 0.067
OTBS
BnO
O
BnO
BnO
O
BnO
O
BnO
STol
OBn
28
^{1}H NMR
600 MHz
$CDCl_3$
1.99 4.06 25.82 2.03 1.02 1.01 1.01 2.08 3.08 1.00 3.03 1.03 1.02 1.02 2.06 1.99 1.07 1.02 2.12 1.02 1.05 1.01 3.12 9.02 2.99 2.99
9.0 8.5 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 0.0
f1 (ppm)

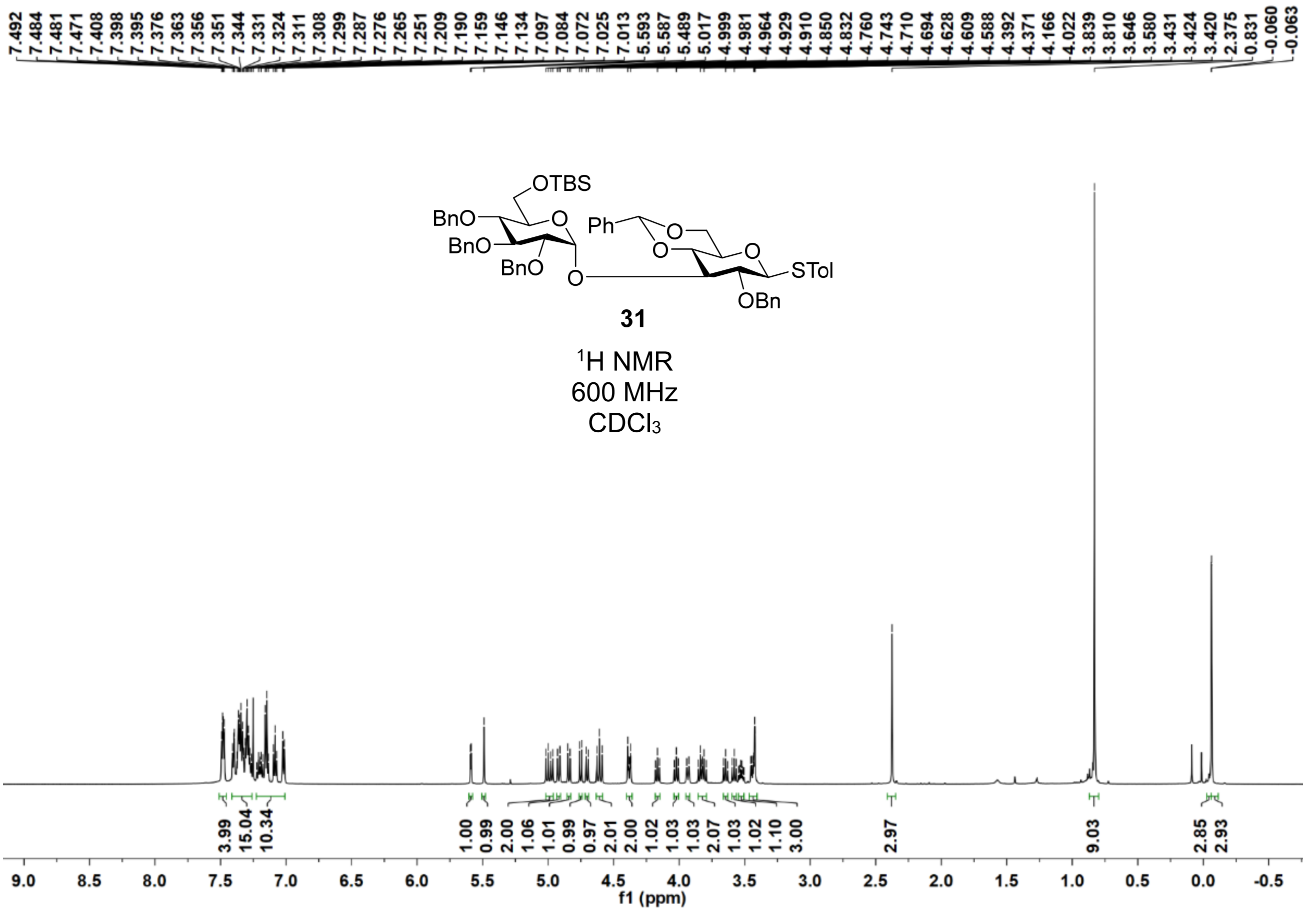

138.81 138.72 138.56 138.51 138.19 138.07 137.91 133.27 129.76 129.67 128.44 128.43 128.41 128.38 128.37 128.32 128.26 128.14 127.90 127.84 127.76 127.72 127.68 127.59 127.55 127.52 127.48 97.03 88.17 86.65 81.73 81.08 80.57 78.96 77.58 77.54 75.78 75.63 75.46 74.99 74.95 72.41 71.65 65.74 62.17 25.98 21.08 18.35 -5.05 -5.32
OTBS
BnO
O
BnO
BnO
O
BnO
O
BnO
STol
OBn
28
^{13}C NMR
150 MHz
$CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

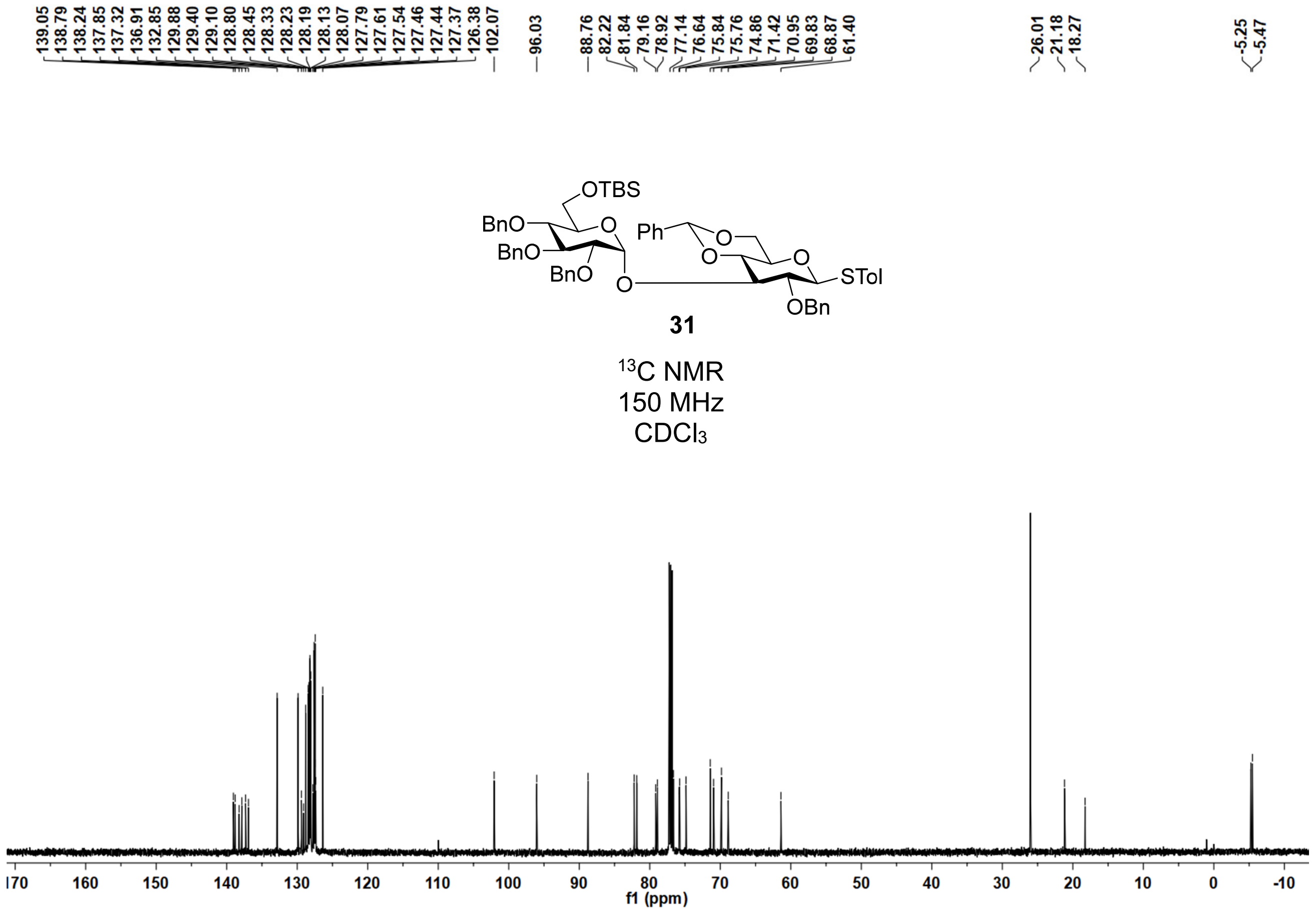

7.344 7.343 7.332 7.321 7.297 7.287 7.274 7.266 7.251 7.238 5.613 5.607 5.037 5.018 4.882 4.864 4.849 4.820 4.800 4.792 4.774 4.724 4.704 4.660 4.642 4.619 4.613 4.594 4.585 4.574 4.565 4.547 4.542 4.527 4.522 4.511 4.075 4.066 4.060 4.057 3.922 3.875 3.860 3.847 3.678 3.663 3.660 3.654 3.635 3.632 3.630 3.618 3.614 3.607 3.599 3.581 3.409 3.403 3.392 3.386 3.377 0.863 -0.009 -0.011
OTBS
BnO
BnO
BnO
O
OBn
BnO
BnO
OCH3
29
1H NMR
600 MHz
CDCl3
30.09
1.01 1.03 2.04 2.05 1.03 1.03 1.04 2.03 3.00 1.99 1.00 2.07 2.05 4.15 1.01 3.01
9.01
6.02
f1 (ppm)

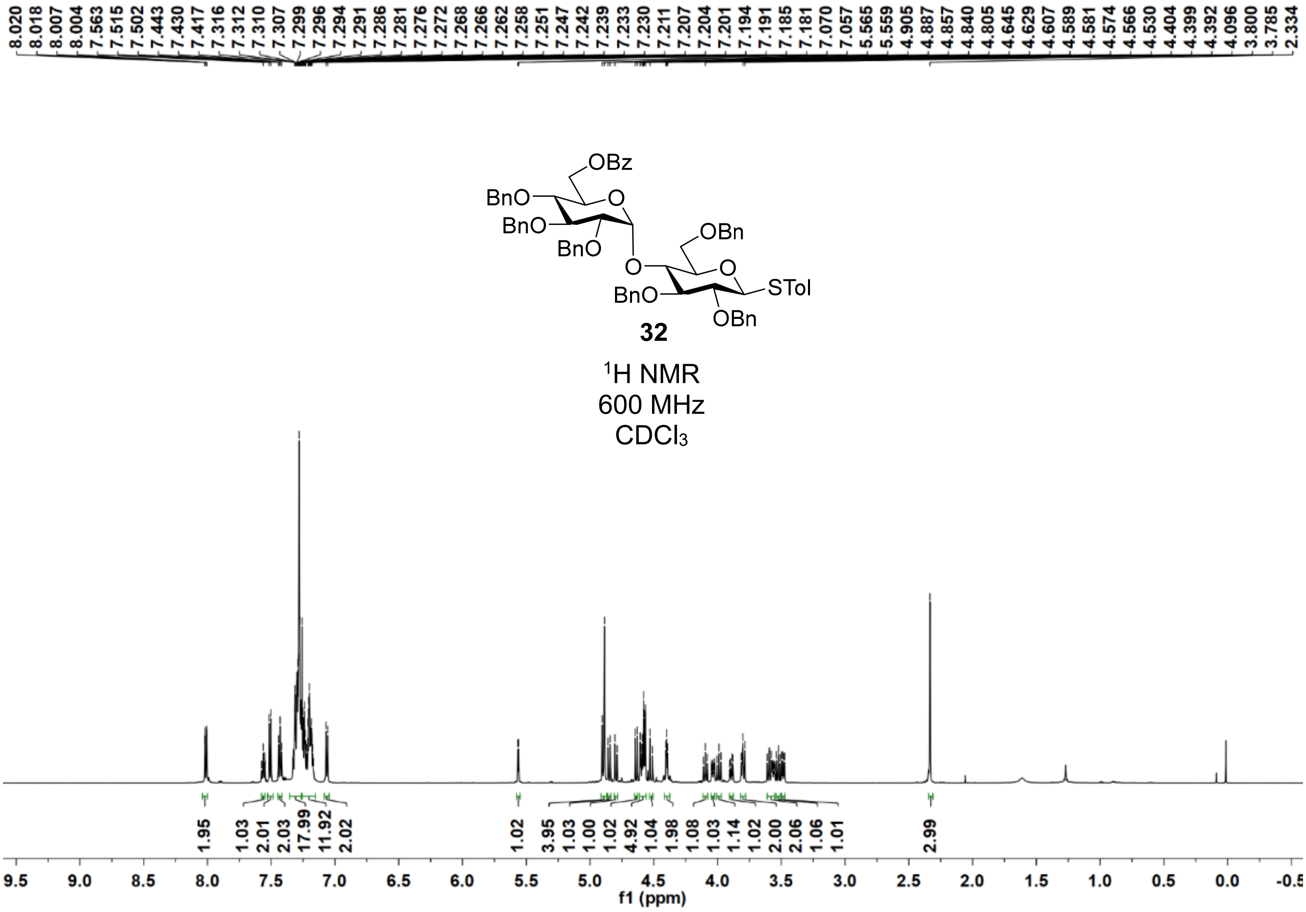

139.07 138.78 138.74 138.12 138.03 138.00 128.41 128.34 128.32 128.29 128.22 128.18 128.00 127.90 127.80 127.77 127.58 127.55 127.36 127.23 127.03 126.68 97.74 96.04 82.07 81.88 80.14 79.95 77.50 75.69 74.97 74.19 73.34 73.16 73.11 72.17 71.98 69.42 69.05 61.84 55.12 25.95 18.31 -5.07 -5.38
OTBS
BnO
BnO
BnO
O
OBn
BnO
BnO
OCH3
29
13C NMR
150 MHz
CDCl3
f1 (ppm)

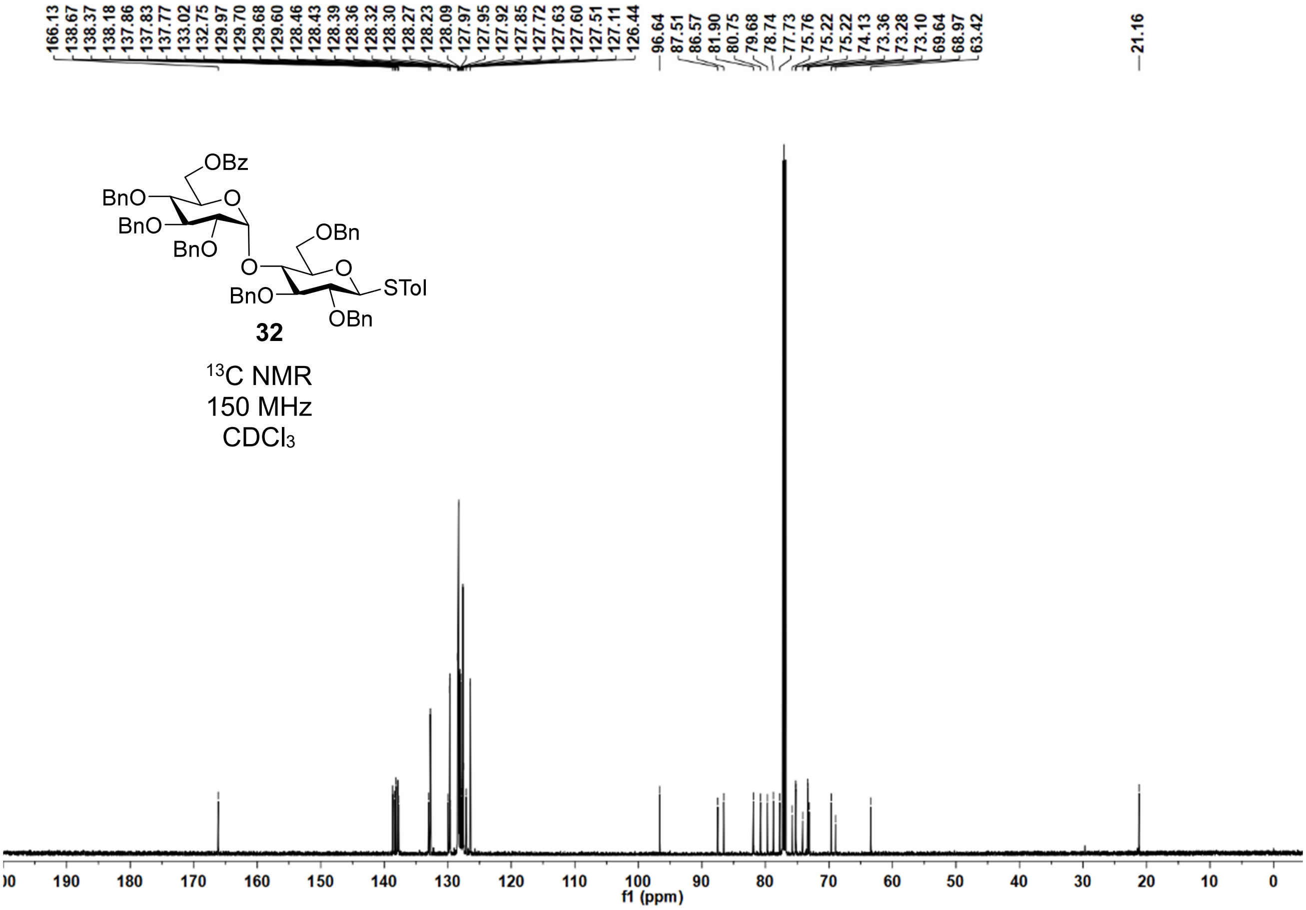

OTBS
BnO
BnO
BnO
O
BnO
BnO
BnO
OCH3
30
1H NMR
600 MHz
CDCl3
f1 (ppm)

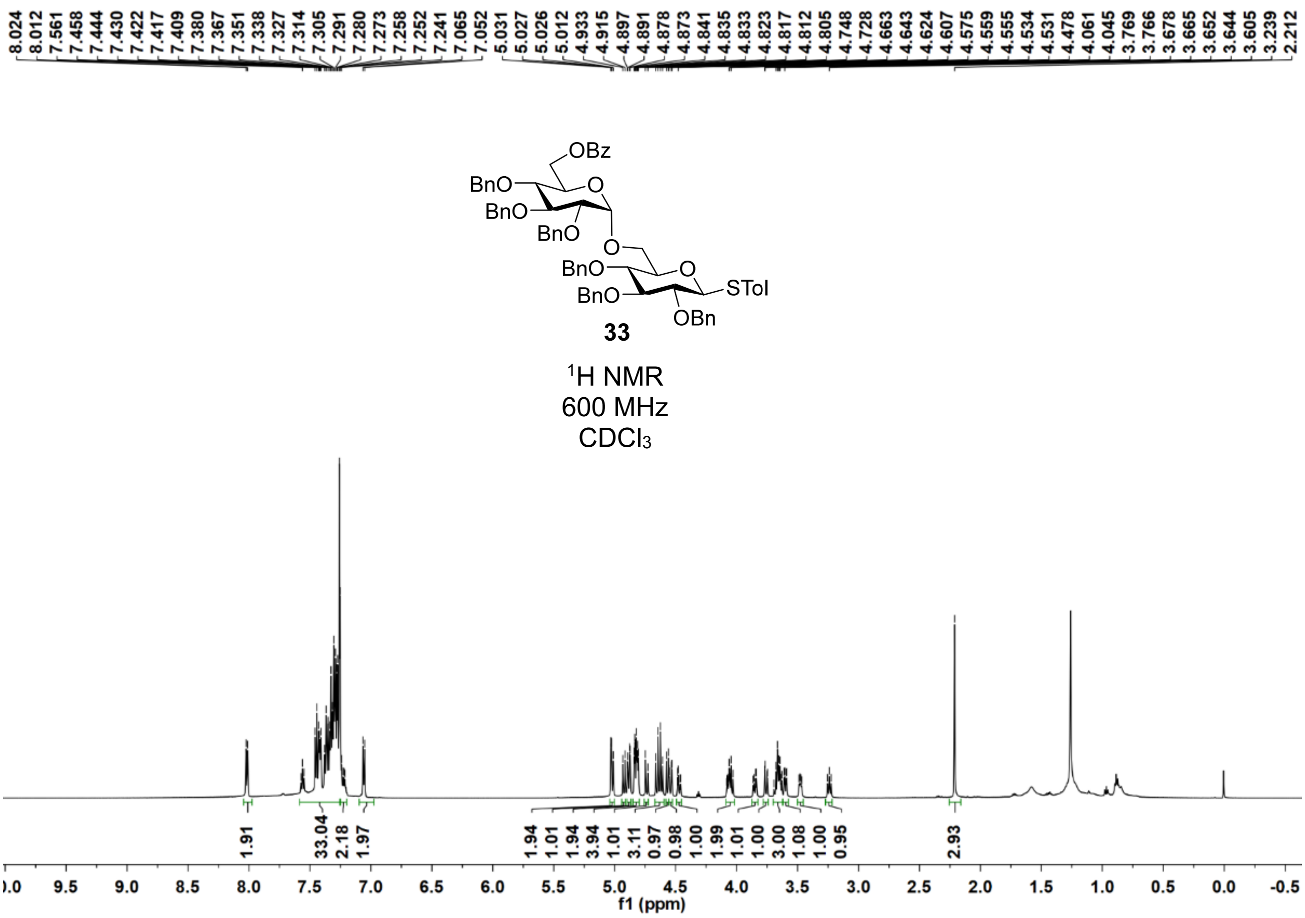

OTBS
BnO
BnO
BnO
O
BnO
BnO
BnO
OCH3
30
13C NMR
150 MHz
CDCl3
f1 (ppm)

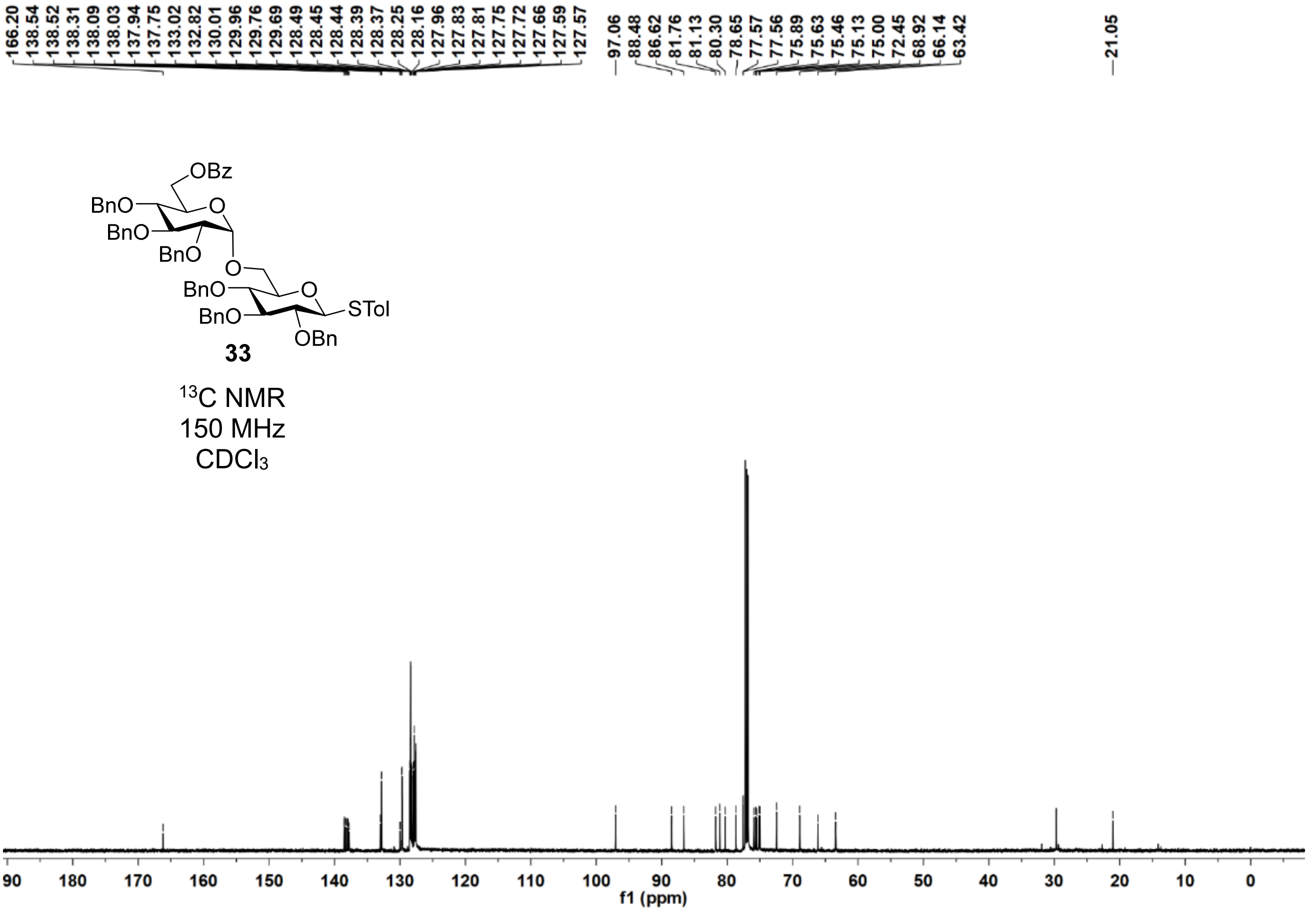

7.492 7.484 7.481 7.471 7.408 7.398 7.395 7.376 7.363 7.356 7.351 7.344 7.331 7.324 7.311 7.308 7.299 7.287 7.276 7.265 7.251 7.209 7.190 7.159 7.146 7.134 7.097 7.084 7.072 7.025 7.013 5.593 5.587 5.489 5.017 4.999 4.981 4.964 4.929 4.910 4.850 4.832 4.760 4.743 4.710 4.694 4.628 4.609 4.588 4.392 4.371 4.166 4.022 3.839 3.810 3.646 3.580 3.431 3.424 3.420 2.375 0.831 -0.060 -0.063
OTBS
BnO
BnO
BnO
O
Ph
O
O
O
STol
OBn
31
^{1}H NMR
600 MHz
CDCl3
3.99 15.04 10.34 1.00 0.99 2.00 1.06 1.01 0.99 0.97 2.01 2.00 1.02 1.03 1.03 2.07 1.03 1.02 1.10 3.00 2.97 9.03 2.85 2.93
9.0 8.5 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 0.0 -0.5
f1 (ppm)

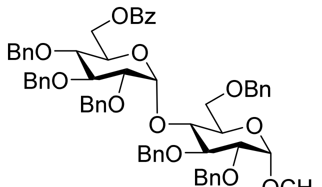

139.05 138.79 138.24 137.85 137.32 136.91 132.85 129.88 129.40 129.10 128.80 128.45 128.33 128.23 128.19 128.13 128.07 127.79 127.61 127.54 127.46 127.44 127.37 126.38 102.07 96.03 88.76 82.22 81.84 79.16 78.92 77.14 76.64 75.84 75.76 74.86 71.42 70.95 69.83 68.87 61.40 26.01 21.18 18.27 -5.25 -5.47
OTBS
BnO
BnO
BnO
O
Ph
O
O
O
STol
OBn
31
^{13}C NMR
150 MHz
CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.020 8.018 8.007 8.004 7.563 7.515 7.502 7.443 7.430 7.417 7.316 7.312 7.310 7.307 7.299 7.296 7.294 7.291 7.286 7.281 7.276 7.272 7.268 7.266 7.262 7.258 7.251 7.247 7.242 7.239 7.233 7.230 7.211 7.207 7.204 7.201 7.194 7.191 7.185 7.181 7.070 7.057 5.565 5.559 4.905 4.887 4.857 4.840 4.805 4.645 4.629 4.607 4.589 4.581 4.574 4.566 4.530 4.404 4.399 4.392 4.096 3.800 3.785 2.334
OBz
BnO
BnO
BnO
O
OBn
O
BnO
STol
OBn
32
^{1}H NMR
600 MHz
CDCl3
1.95 1.03 2.01 2.03 17.99 11.92 2.02 1.02 3.95 1.03 1.00 1.02 4.92 1.04 1.98 1.08 1.03 1.14 1.02 2.00 2.06 1.06 1.01 2.99
f1 (ppm)


166.13 138.67 138.37 138.18 137.86 137.83 137.77 133.02 132.75 129.97 129.70 129.68 129.60 128.46 128.43 128.39 128.36 128.32 128.30 128.27 128.23 128.09 127.97 127.95 127.92 127.85 127.72 127.63 127.60 127.51 127.11 126.44 96.64 87.51 86.57 81.90 80.75 79.68 78.74 77.73 75.76 75.22 75.22 74.13 73.36 73.28 73.10 69.64 68.97 63.42 21.16
OBz
BnO
BnO
BnO
O
OBn
O
BnO
STol
OBn
32
^{13}C NMR
150 MHz
CDCl3
f1 (ppm)

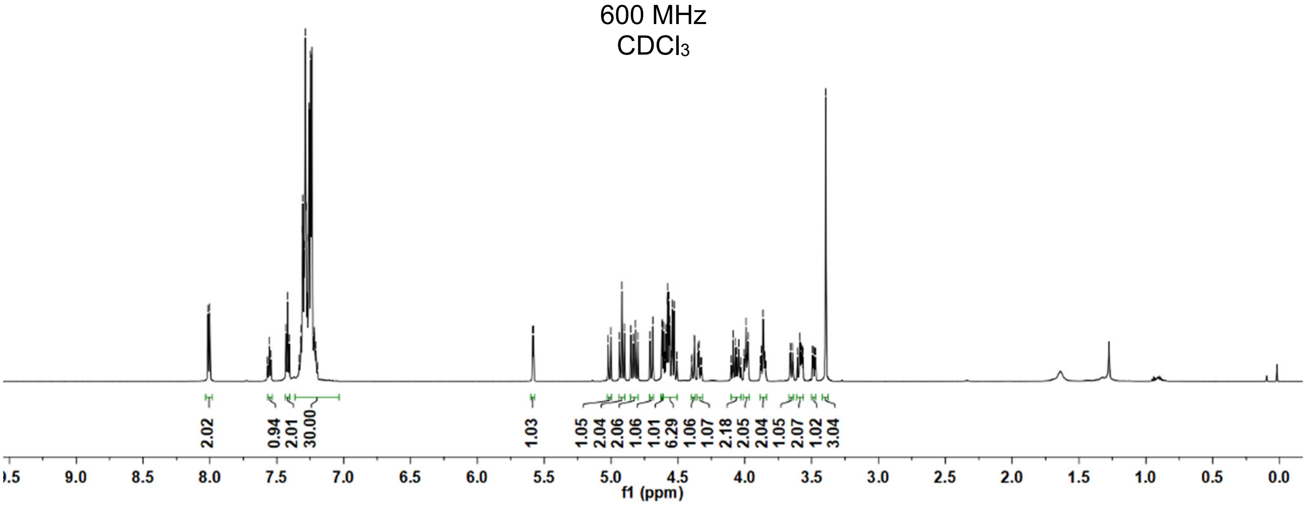

8.024 8.012 7.561 7.458 7.444 7.430 7.422 7.417 7.409 7.380 7.367 7.351 7.338 7.327 7.314 7.305 7.291 7.280 7.273 7.258 7.252 7.241 7.065 7.052 5.031 5.027 5.026 5.012 4.933 4.915 4.897 4.891 4.878 4.873 4.841 4.835 4.833 4.823 4.817 4.812 4.805 4.748 4.728 4.663 4.643 4.624 4.607 4.575 4.559 4.555 4.534 4.531 4.478 4.061 4.045 3.769 3.766 3.678 3.665 3.652 3.644 3.605 3.239 2.212
OBz
BnO
BnO
BnO
O
BnO
BnO
STol
OBn
33
^{1}H NMR
600 MHz
$CDCl_3$
1.91 33.04 2.18 1.97 1.94 1.01 1.94 3.94 1.01 3.11 0.97 0.98 1.00 1.99 1.01 1.00 3.00 1.08 1.00 0.95 2.93
f1 (ppm)

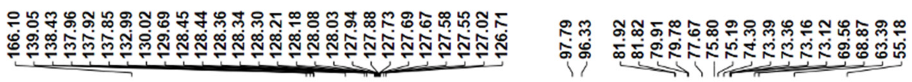

166.20 138.54 138.52 138.31 138.09 138.03 137.94 137.75 133.02 132.82 130.01 129.96 129.76 129.69 128.49 128.45 128.44 128.39 128.37 128.25 128.16 127.96 127.83 127.81 127.75 127.72 127.66 127.59 127.57 97.06 88.48 86.62 81.76 81.13 80.30 78.65 77.57 77.56 75.89 75.63 75.46 75.13 75.00 72.45 68.92 66.14 63.42 21.05
OBz
BnO
BnO
BnO
O
BnO
BnO
STol
OBn
33
^{13}C NMR
150 MHz
$CDCl_3$
f1 (ppm)

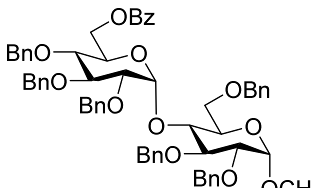


34

^{1}H NMR
600 MHz
$CDCl_3$

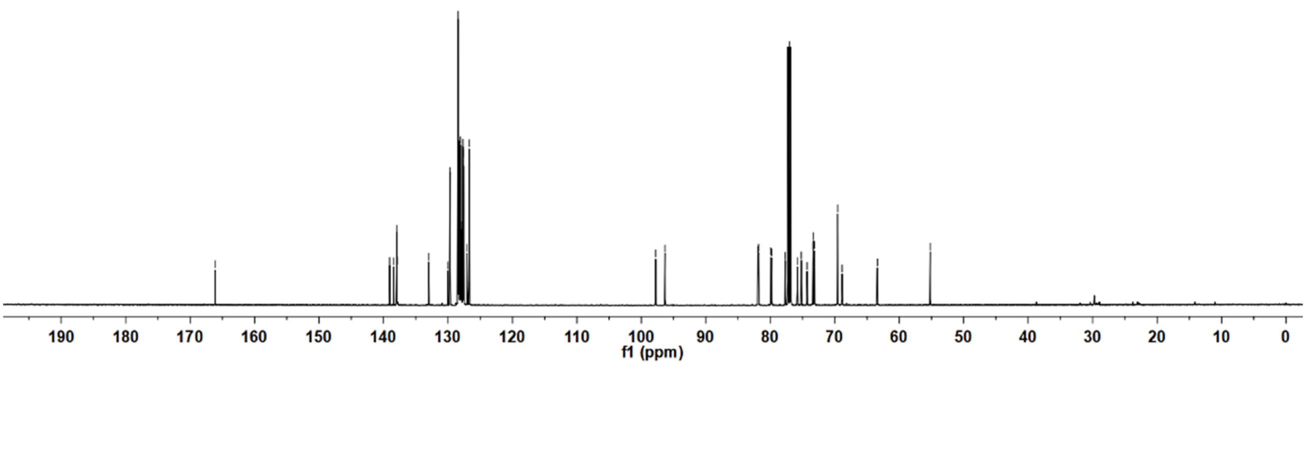


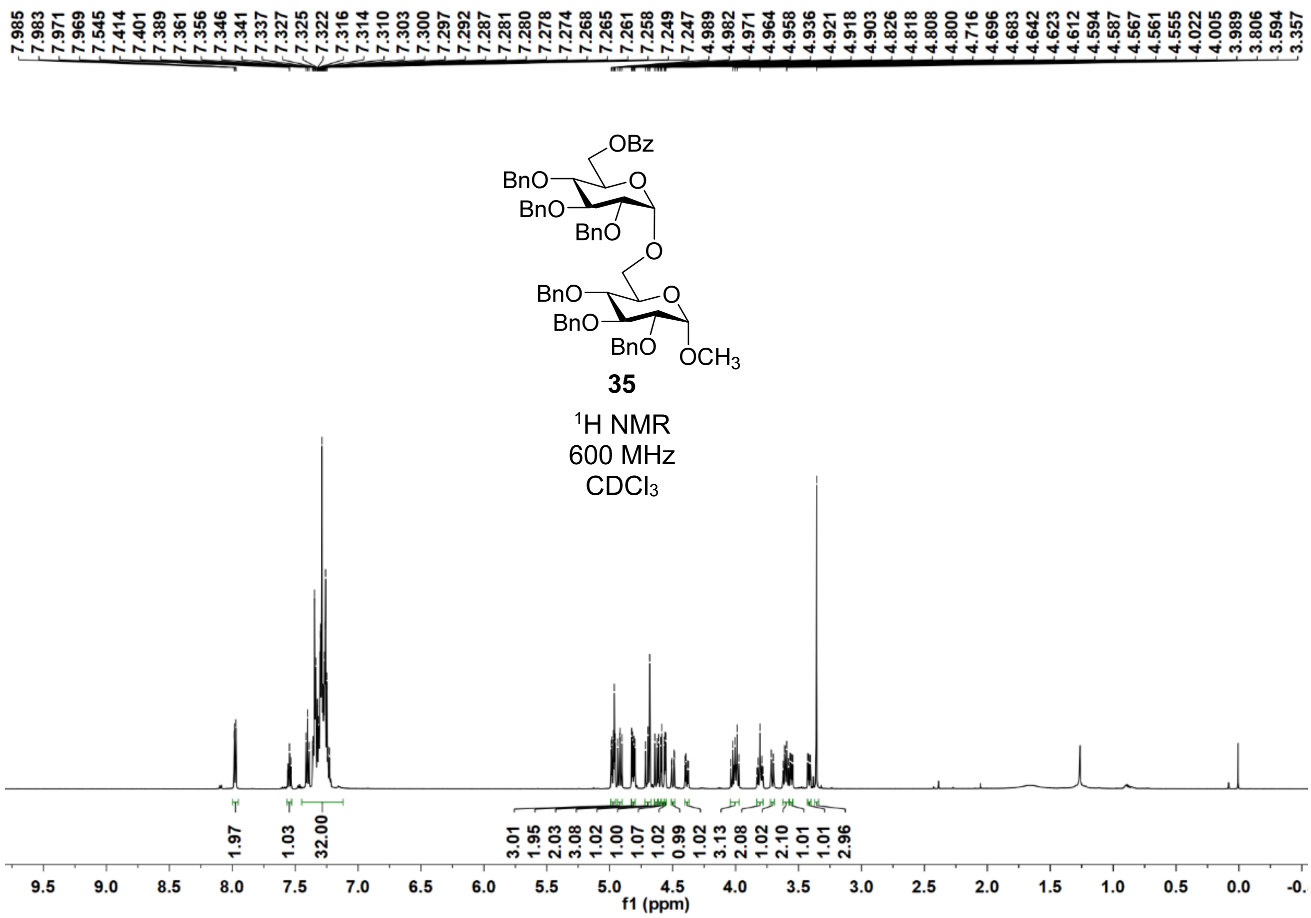


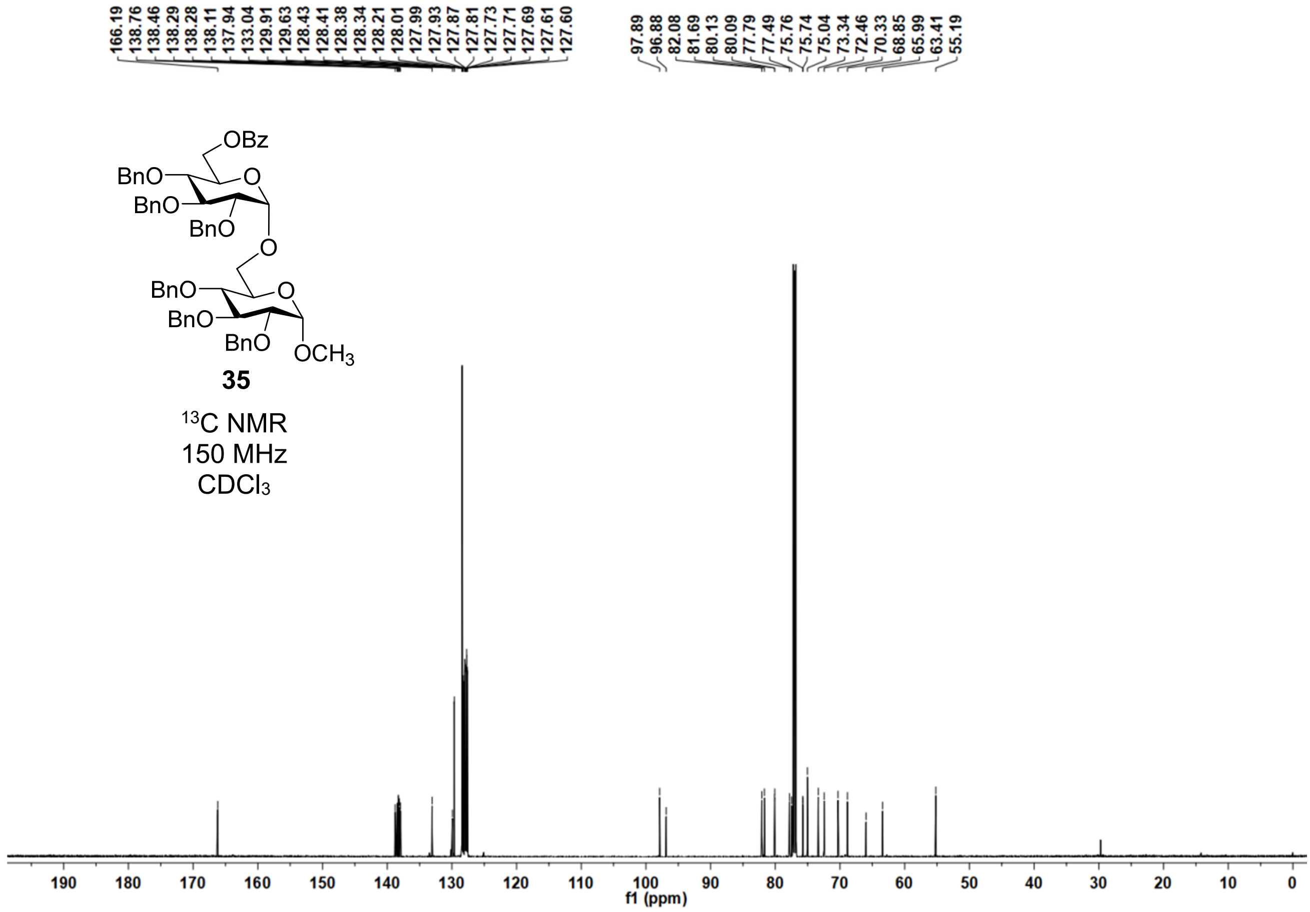


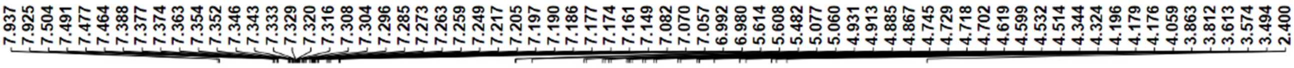
34

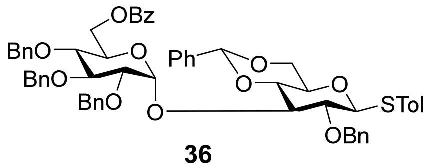
^{13}C NMR
150 MHz
$CDCl_3$




7.985
7.983
7.971
7.969
7.545
7.414
7.401
7.389
7.361
7.356
7.346
7.341
7.337
7.327
7.325
7.322
7.316
7.314
7.310
7.303
7.300
7.297
7.292
7.287
7.281
7.280
7.278
7.274
7.268
7.265
7.261
7.258
7.249
7.247
4.989
4.982
4.971
4.964
4.958
4.936
4.921
4.918
4.903
4.826
4.818
4.808
4.800
4.716
4.696
4.683
4.642
4.623
4.612
4.594
4.587
4.567
4.561
4.555
4.022
4.005
3.989
3.806
3.594
3.357
OBz
BnO
O
BnO
BnO
O
BnO
O
BnO
BnO
OCH_3
35
^{1}H NMR
600 MHz
$CDCl_3$
1.97
1.03
32.00
3.01
1.95
2.03
3.08
1.02
1.00
1.07
1.02
0.99
1.02
3.13
2.08
1.02
2.10
1.01
1.01
2.96
9.5 9.0 8.5 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 0.0 -0.
f1 (ppm)

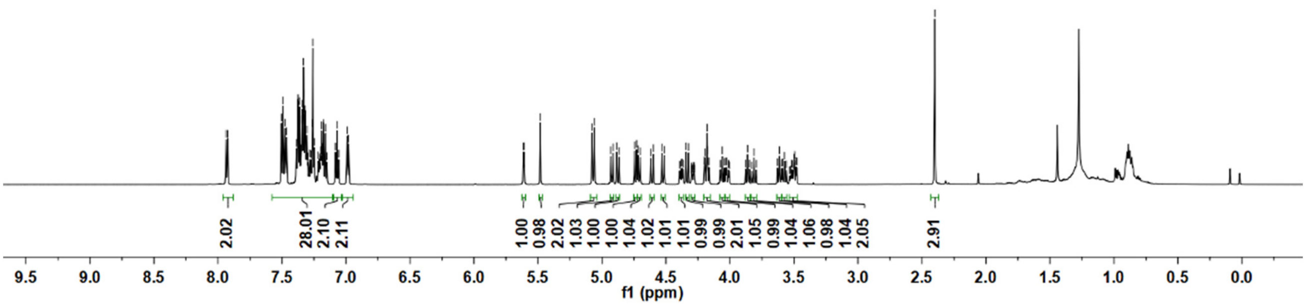

166.19
138.76
138.46
138.29
138.28
138.11
137.94
133.04
129.91
129.63
128.43
128.41
128.38
128.34
128.21
128.01
127.99
127.93
127.87
127.81
127.73
127.71
127.69
127.61
127.60
97.89
96.88
82.08
81.69
80.13
80.09
77.79
77.49
75.76
75.74
75.04
73.34
72.46
70.33
68.85
65.99
63.41
55.19
OBz
BnO
O
BnO
BnO
O
BnO
O
BnO
BnO
OCH_3
35
^{13}C NMR
150 MHz
$CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

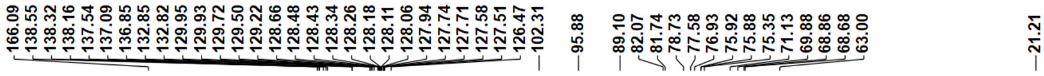


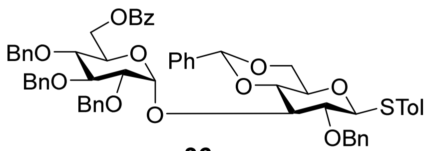


36

^{1}H NMR
600 MHz
$CDCl_3$

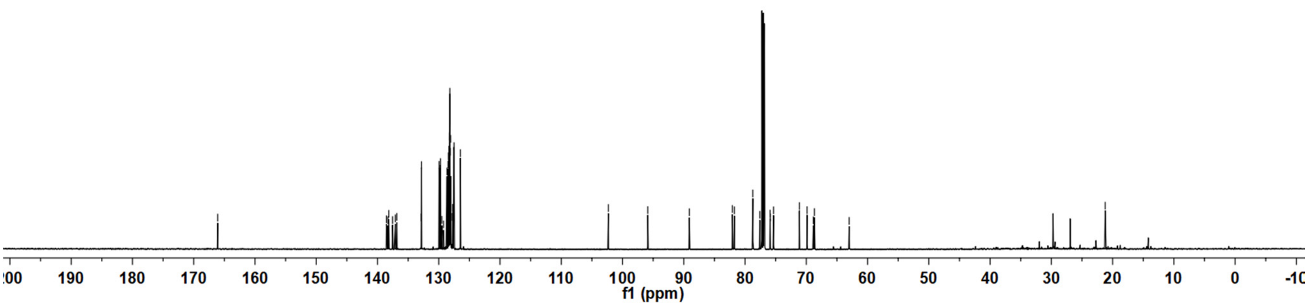


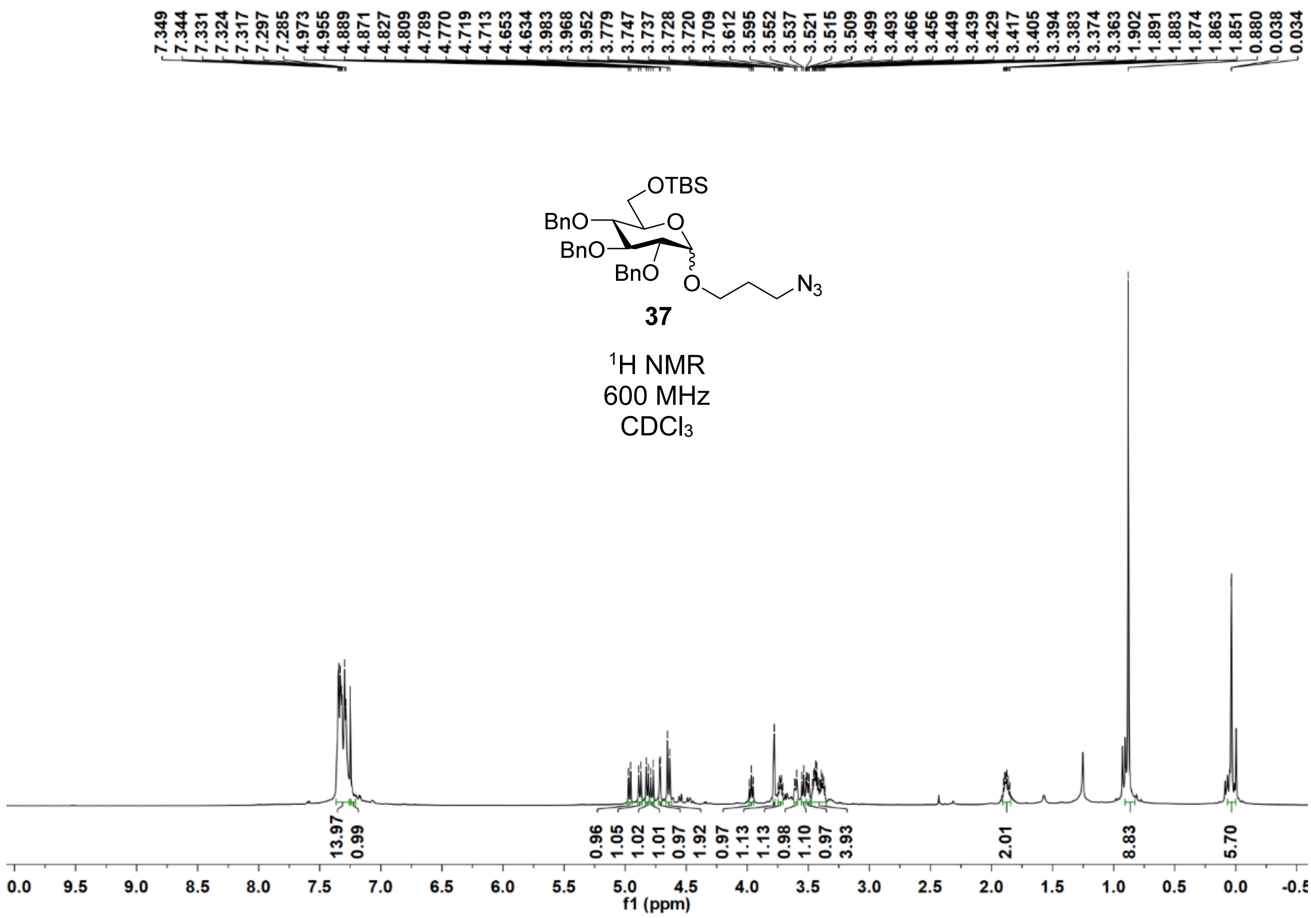




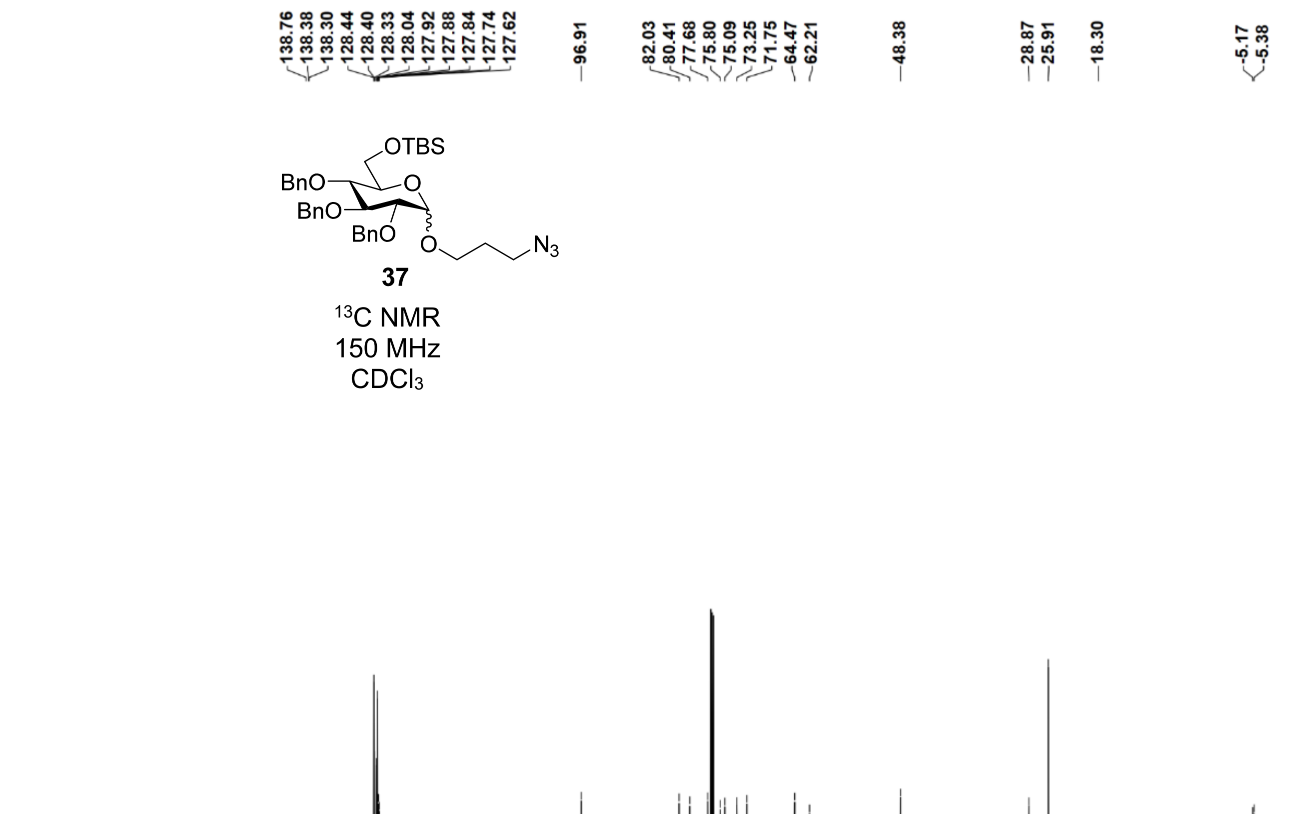
36

^{13}C NMR
150 MHz
$CDCl_3$

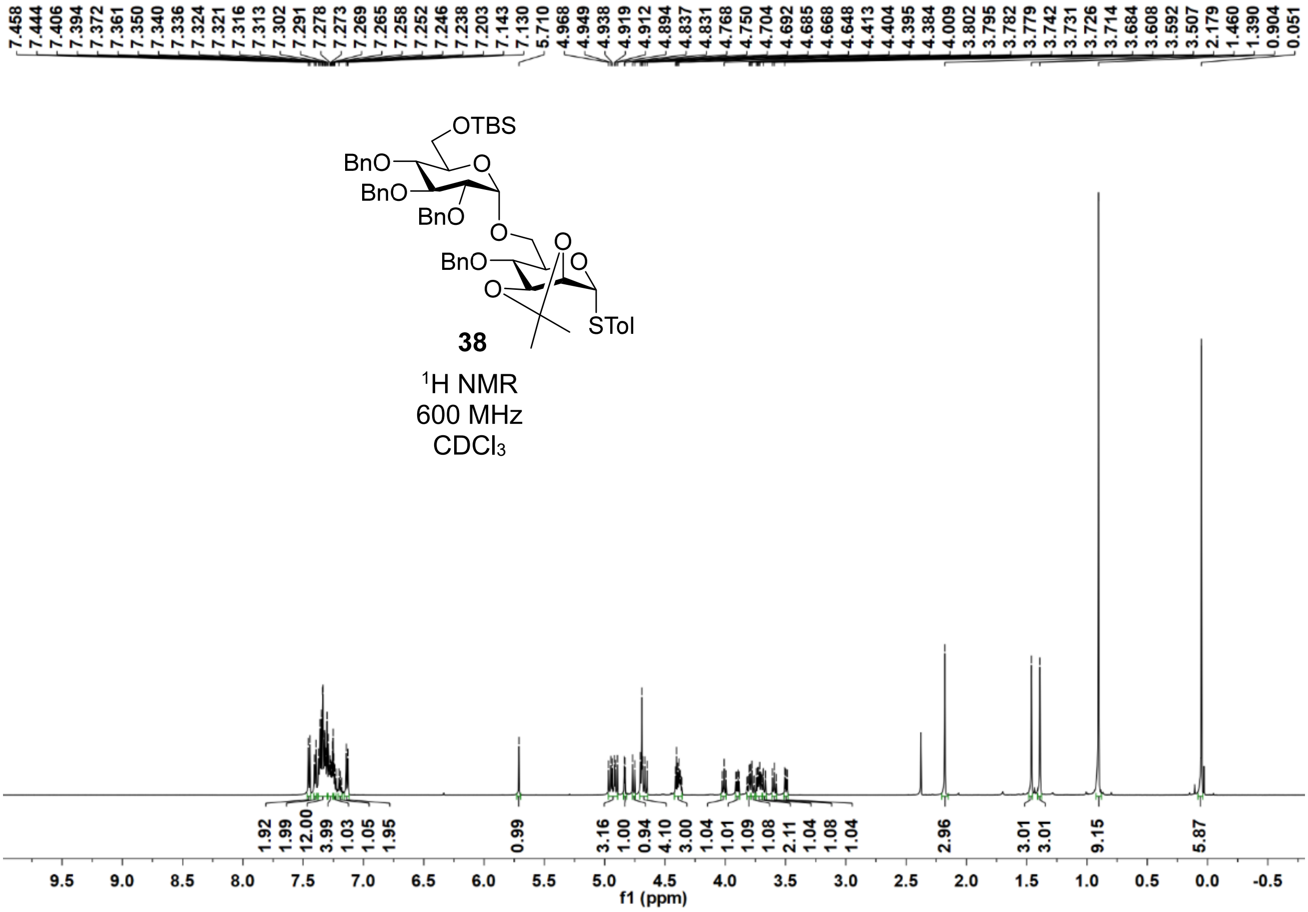


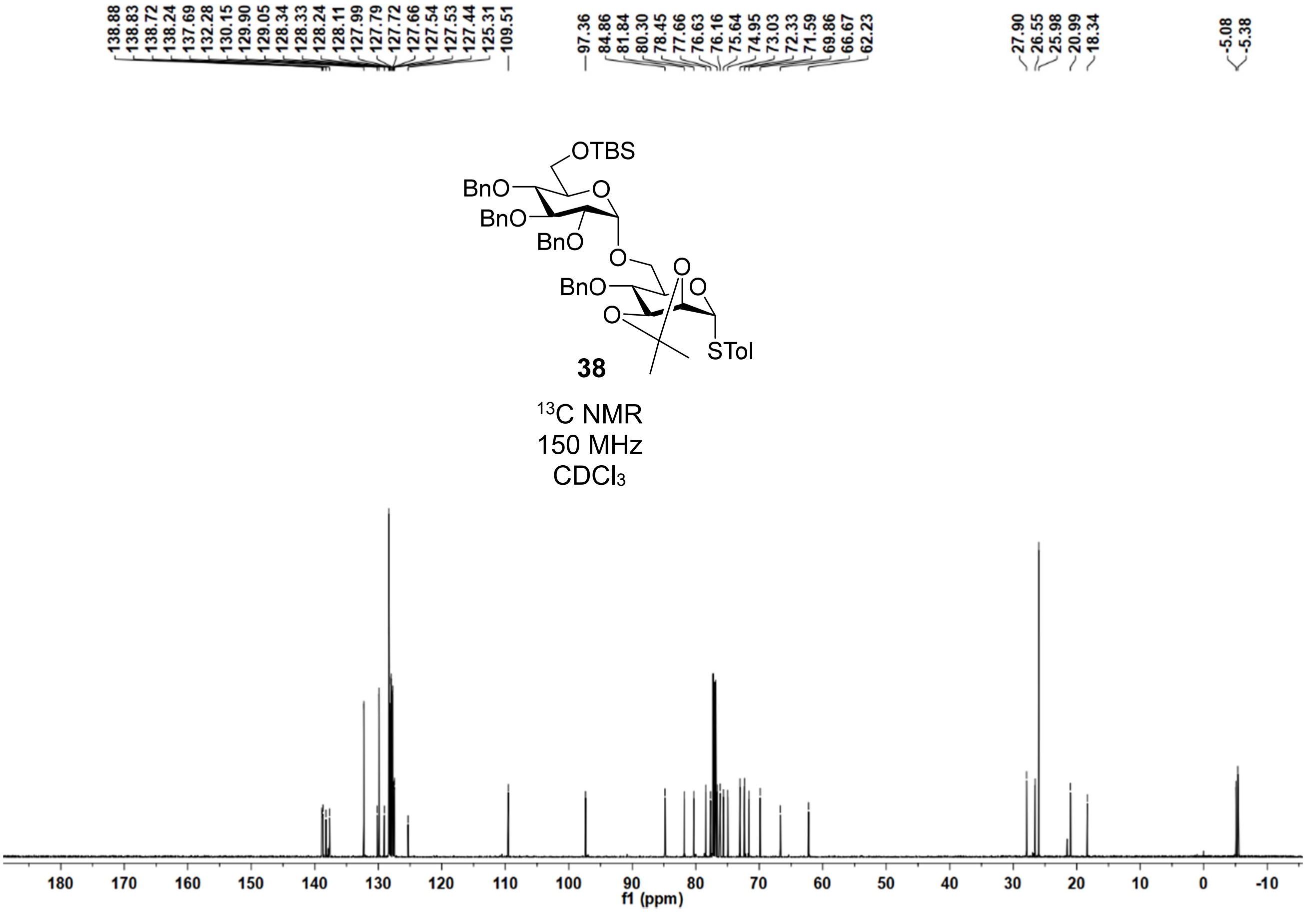


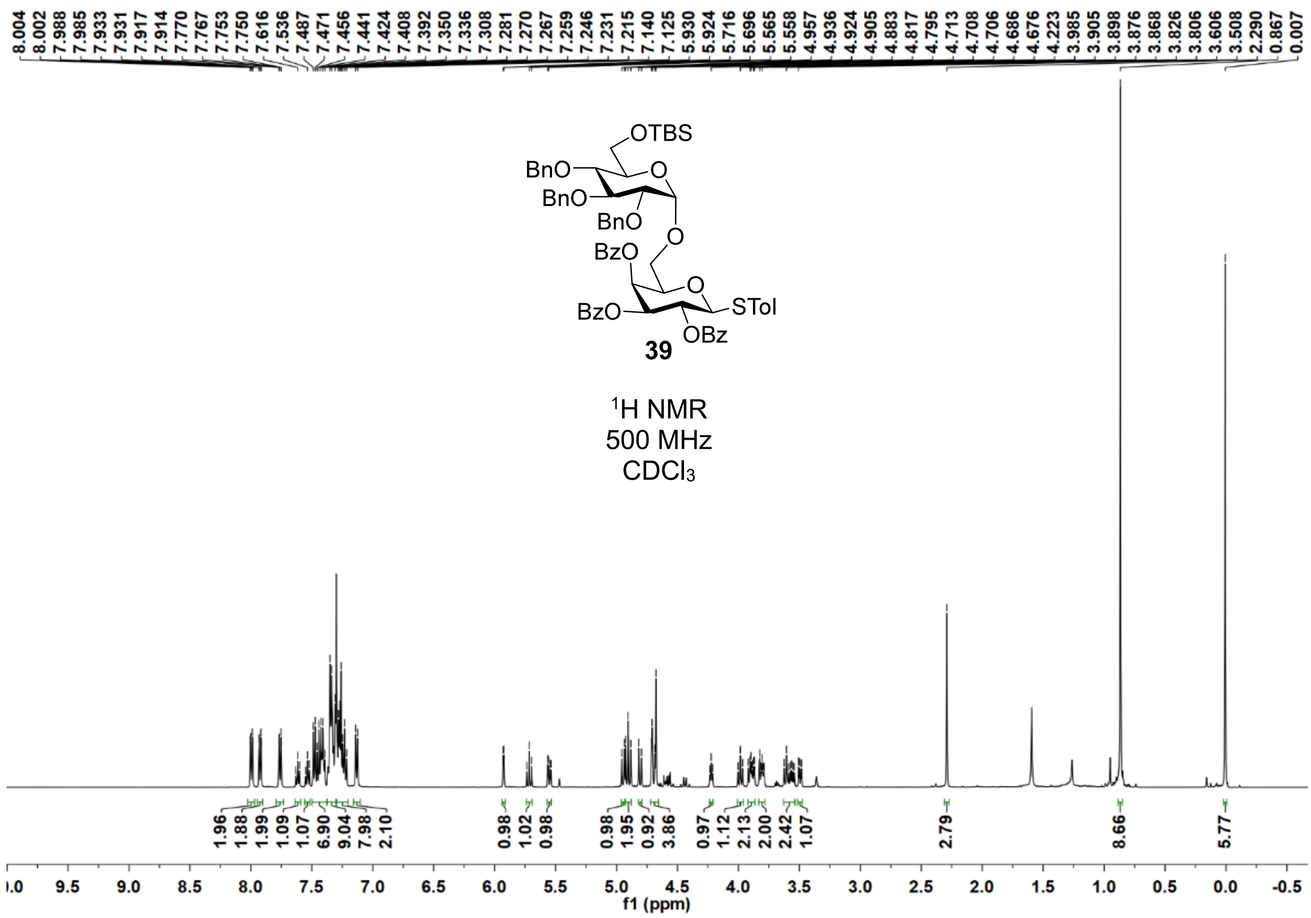
7.349 7.344 7.331 7.324 7.317 7.297 7.285 4.973 4.955 4.889 4.871 4.827 4.809 4.789 4.770 4.719 4.713 4.653 4.634 3.983 3.968 3.952 3.779 3.747 3.737 3.728 3.720 3.709 3.612 3.595 3.552 3.537 3.521 3.515 3.509 3.499 3.493 3.466 3.456 3.449 3.439 3.429 3.417 3.405 3.394 3.383 3.374 3.363 1.902 1.891 1.883 1.874 1.863 1.851 0.880 0.038 0.034
OTBS
BnO
BnO
BnO
O
O
N3
37
1H NMR
600 MHz
CDCl3
13.97 0.99 0.96 1.05 1.02 1.01 0.97 1.92 0.97 1.13 1.13 0.98 1.10 0.97 3.93 2.01 8.83 5.70
f1 (ppm)

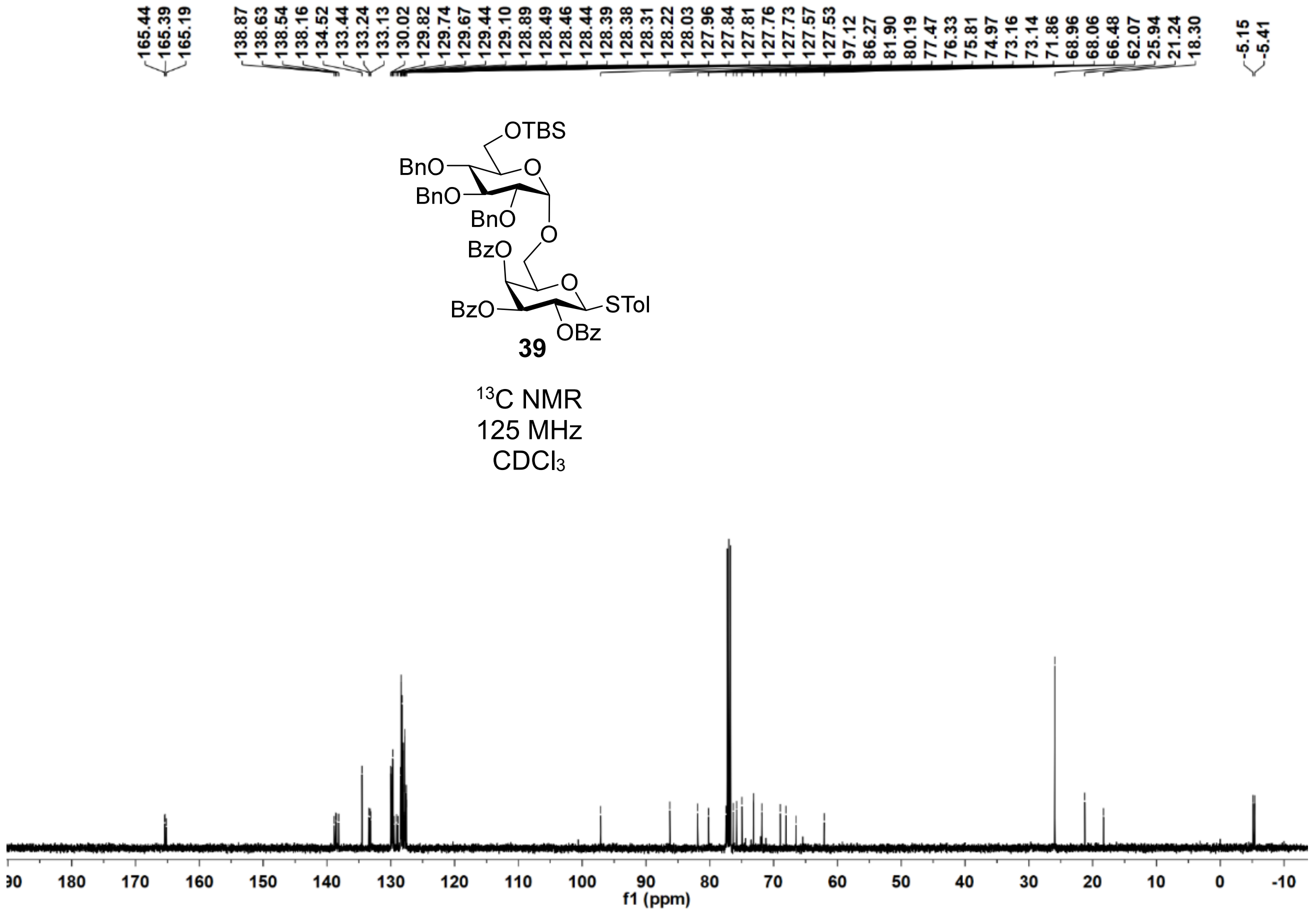


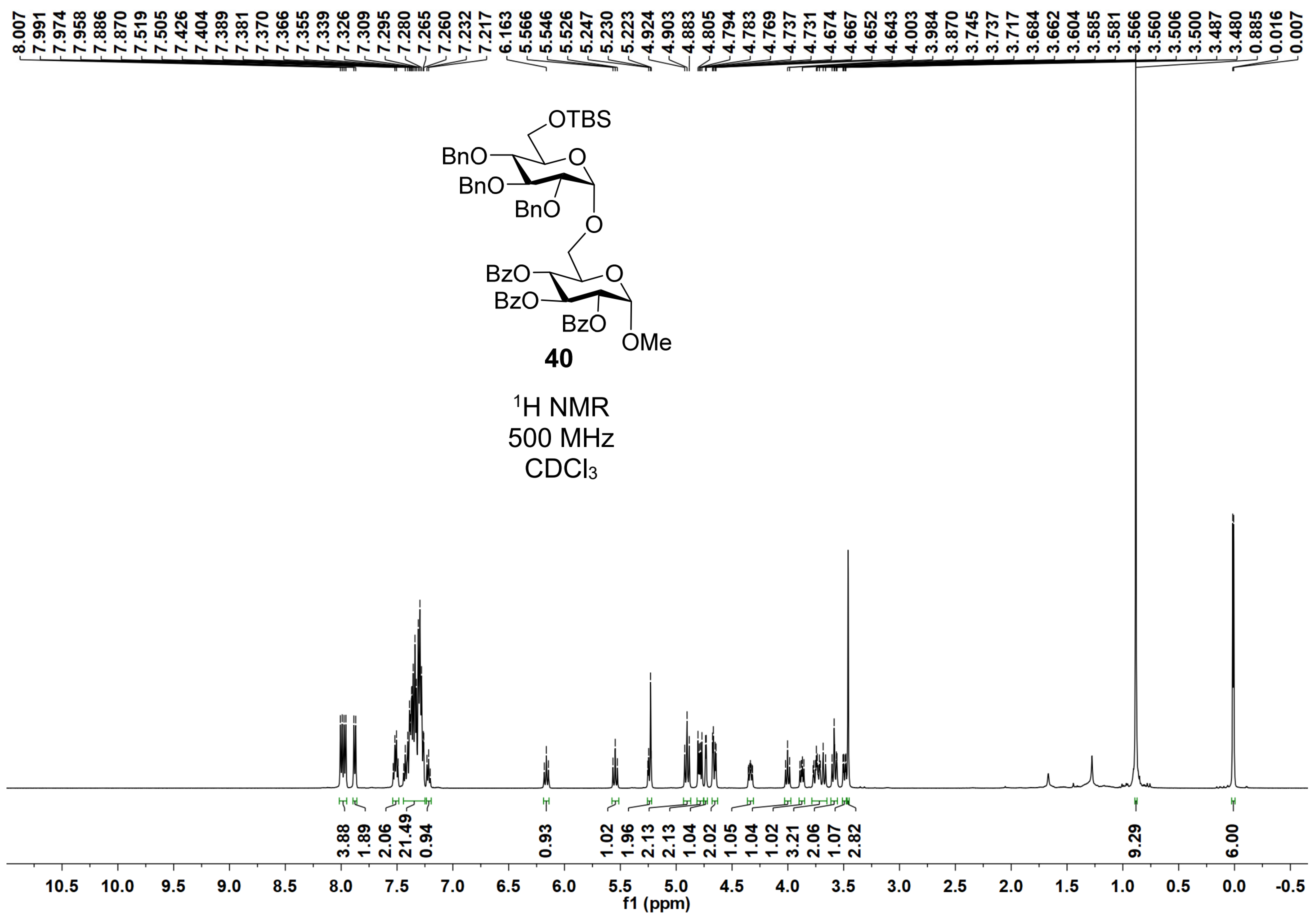
138.76 138.38 138.30 128.44 128.40 128.33 128.04 127.92 127.88 127.84 127.74 127.62 96.91 82.03 80.41 77.68 75.80 75.09 73.25 71.75 64.47 62.21 48.38 28.87 25.91 18.30 -5.17 -5.38
OTBS
BnO
BnO
BnO
O
O
N3
37
13C NMR
150 MHz
CDCl3
f1 (ppm)

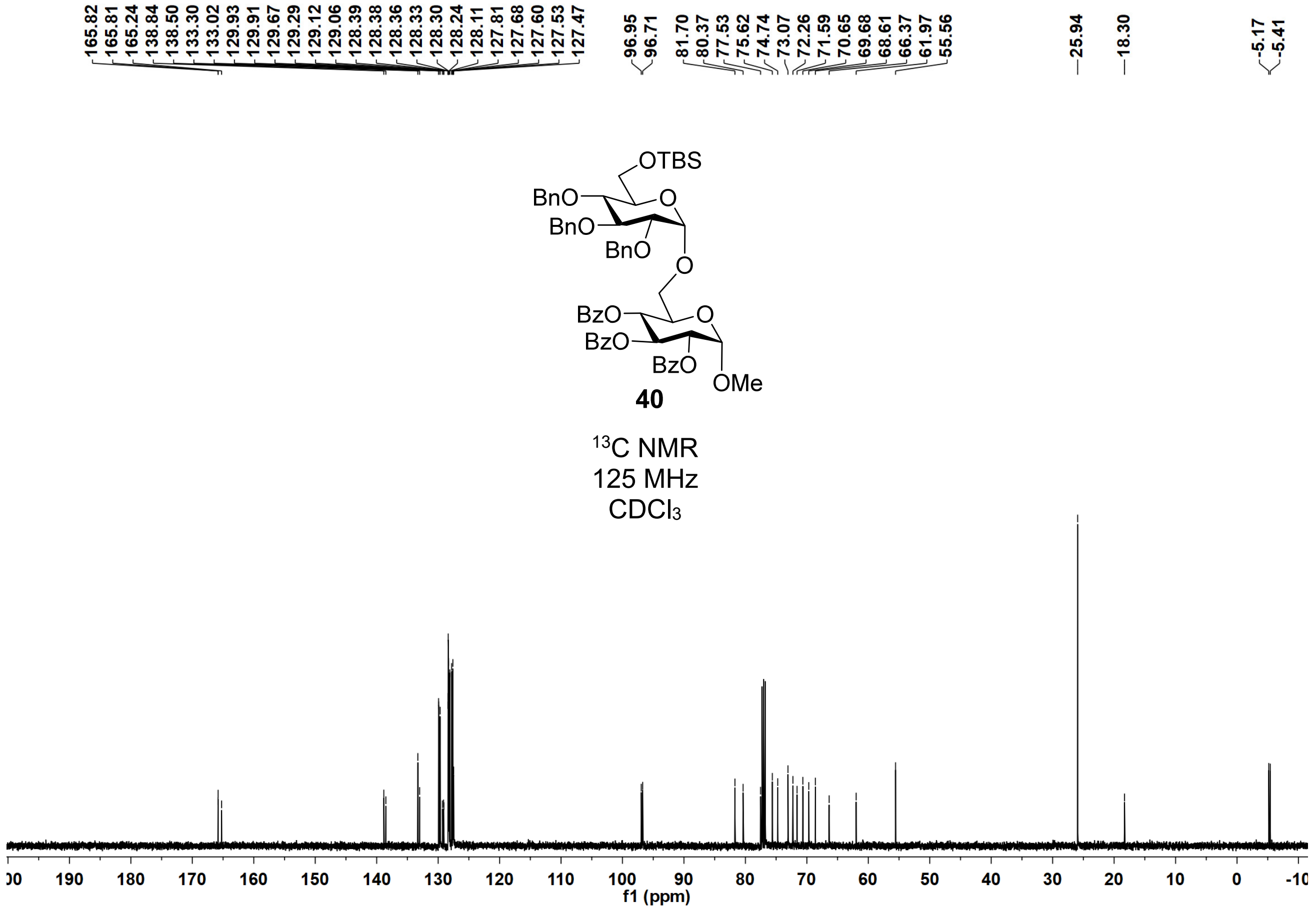

7.458 7.444 7.406 7.394 7.372 7.361 7.350 7.340 7.336 7.324 7.321 7.316 7.313 7.302 7.291 7.278 7.273 7.269 7.265 7.258 7.252 7.246 7.238 7.203 7.143 7.130 5.710 4.968 4.949 4.938 4.919 4.912 4.894 4.837 4.831 4.768 4.750 4.704 4.692 4.685 4.668 4.648 4.413 4.404 4.395 4.384 4.009 3.802 3.795 3.782 3.779 3.742 3.731 3.726 3.714 3.684 3.608 3.592 3.507 2.179 1.460 1.390 0.904 0.051
OTBS
BnO
BnO
BnO
O
O
BnO
O
O
O
STol
38
1H NMR
600 MHz
CDCl3
1.92 1.99 12.00 3.99 1.03 1.05 1.95 0.99 3.16 1.00 0.94 4.10 3.00 1.04 1.01 1.09 1.08 2.11 1.04 1.08 1.04 2.96 3.01 3.01 9.15 5.87
9.5 9.0 8.5 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 0.0 -0.5
f1 (ppm)

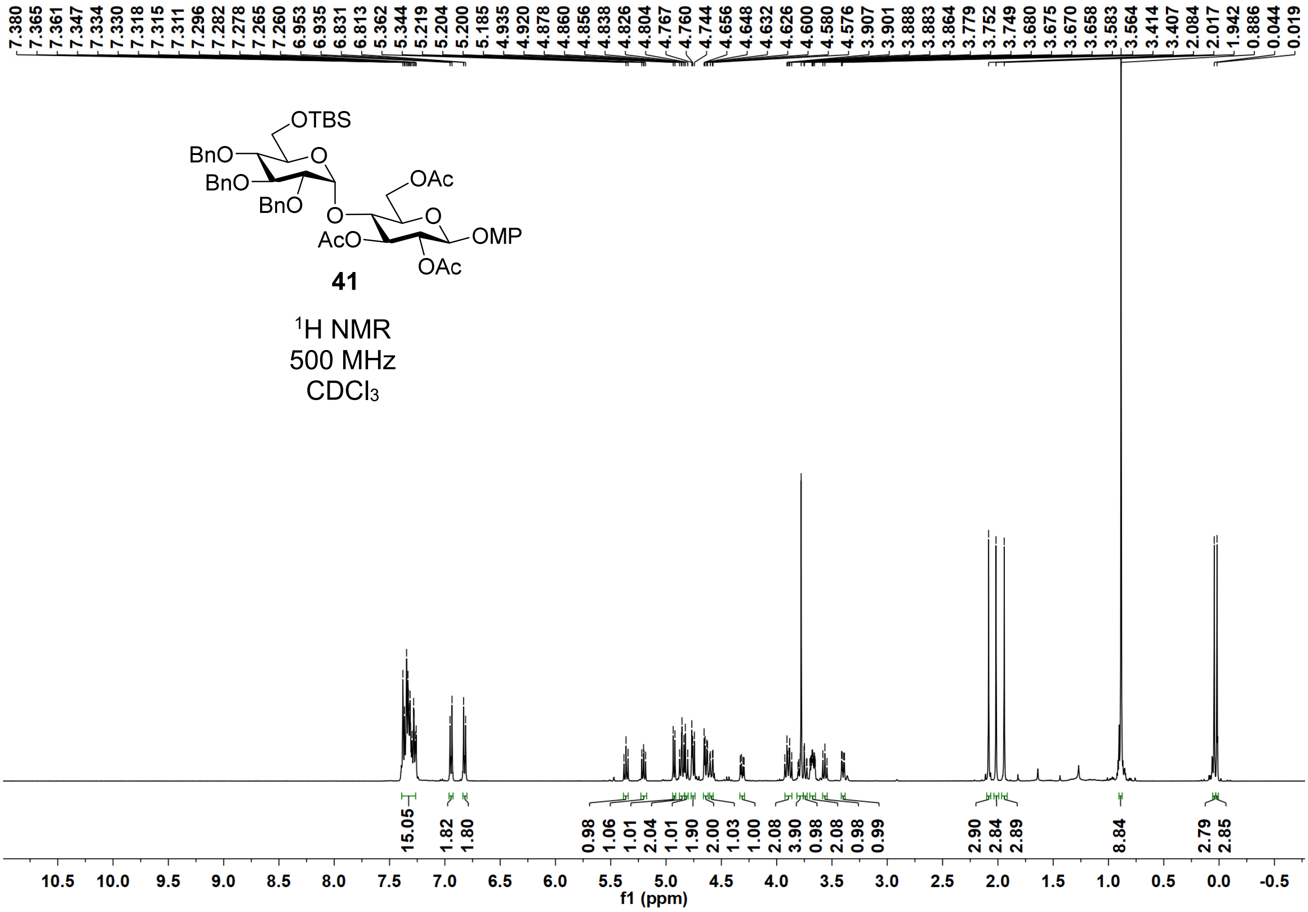

138.88 138.83 138.72 138.24 137.69 132.28 130.15 129.90 129.05 128.34 128.33 128.24 128.11 127.99 127.79 127.72 127.66 127.54 127.53 127.44 125.31 109.51 97.36 84.86 81.84 80.30 78.45 77.66 76.63 76.16 75.64 74.95 73.03 72.33 71.59 69.86 66.67 62.23 27.90 26.55 25.98 20.99 18.34 -5.08 -5.38
OTBS
BnO
BnO
BnO
O
O
BnO
O
O
O
STol
38
13C NMR
150 MHz
CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

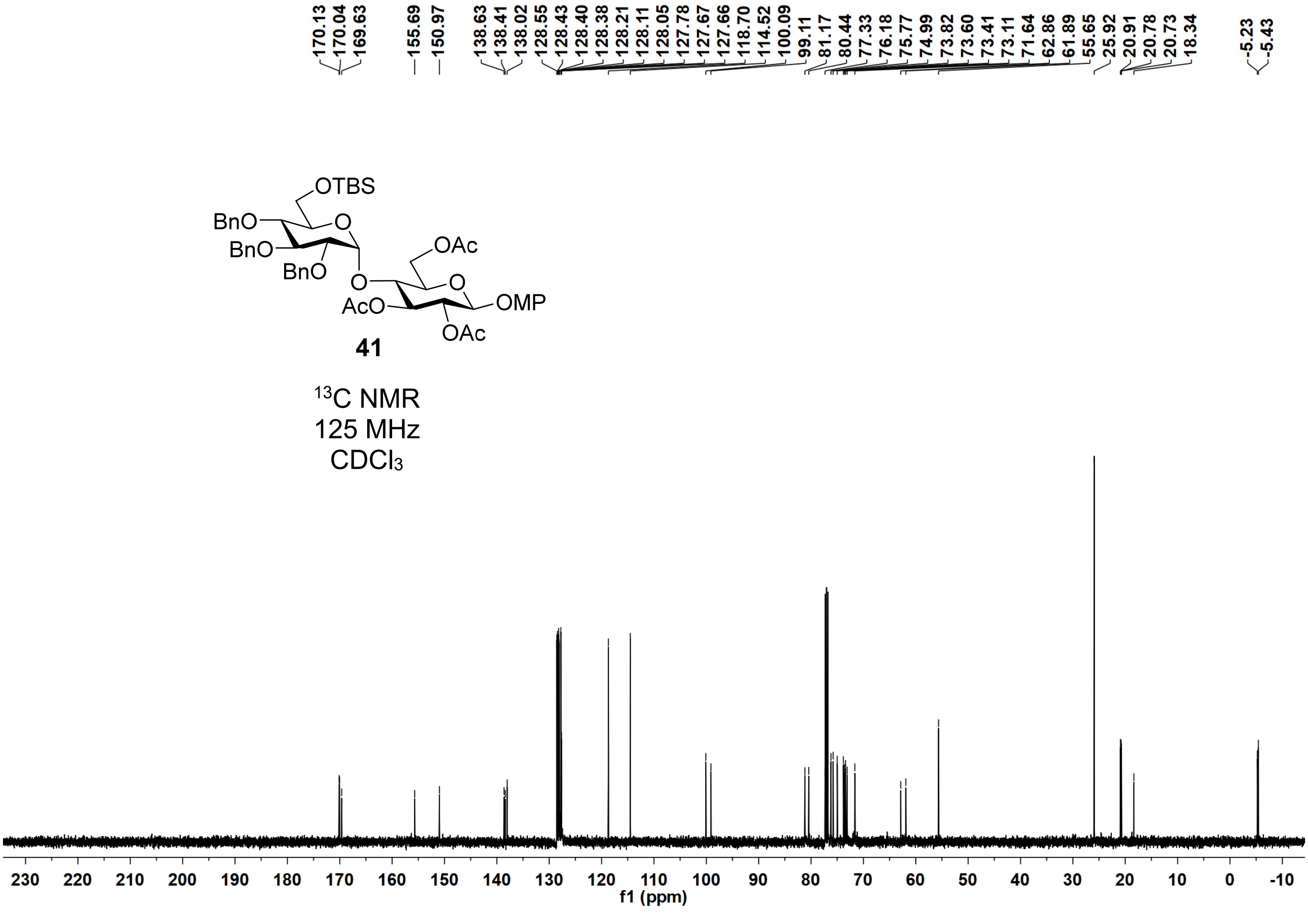

8.004 8.002 7.988 7.985 7.933 7.931 7.917 7.914 7.770 7.767 7.753 7.750 7.616 7.536 7.487 7.471 7.456 7.441 7.424 7.408 7.392 7.350 7.336 7.308 7.281 7.270 7.267 7.259 7.246 7.231 7.215 7.140 7.125 5.930 5.924 5.716 5.696 5.565 5.558 4.957 4.936 4.924 4.905 4.883 4.817 4.795 4.713 4.708 4.706 4.686 4.676 4.223 3.985 3.905 3.898 3.876 3.868 3.826 3.806 3.606 3.508 2.290 0.867 0.007
OTBS
BnO
BnO
BnO
O
O
BzO
O
STol
BzO
OBz
39
1H NMR
500 MHz
CDCl3
1.96 1.88 1.99 1.09 1.07 6.90 9.04 7.98 2.10 0.98 1.02 0.98 0.98 1.95 0.92 3.86 0.97 1.12 2.13 2.00 2.42 1.07 2.79 8.66 5.77
9.5 9.0 8.5 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 0.0 -0.5
f1 (ppm)

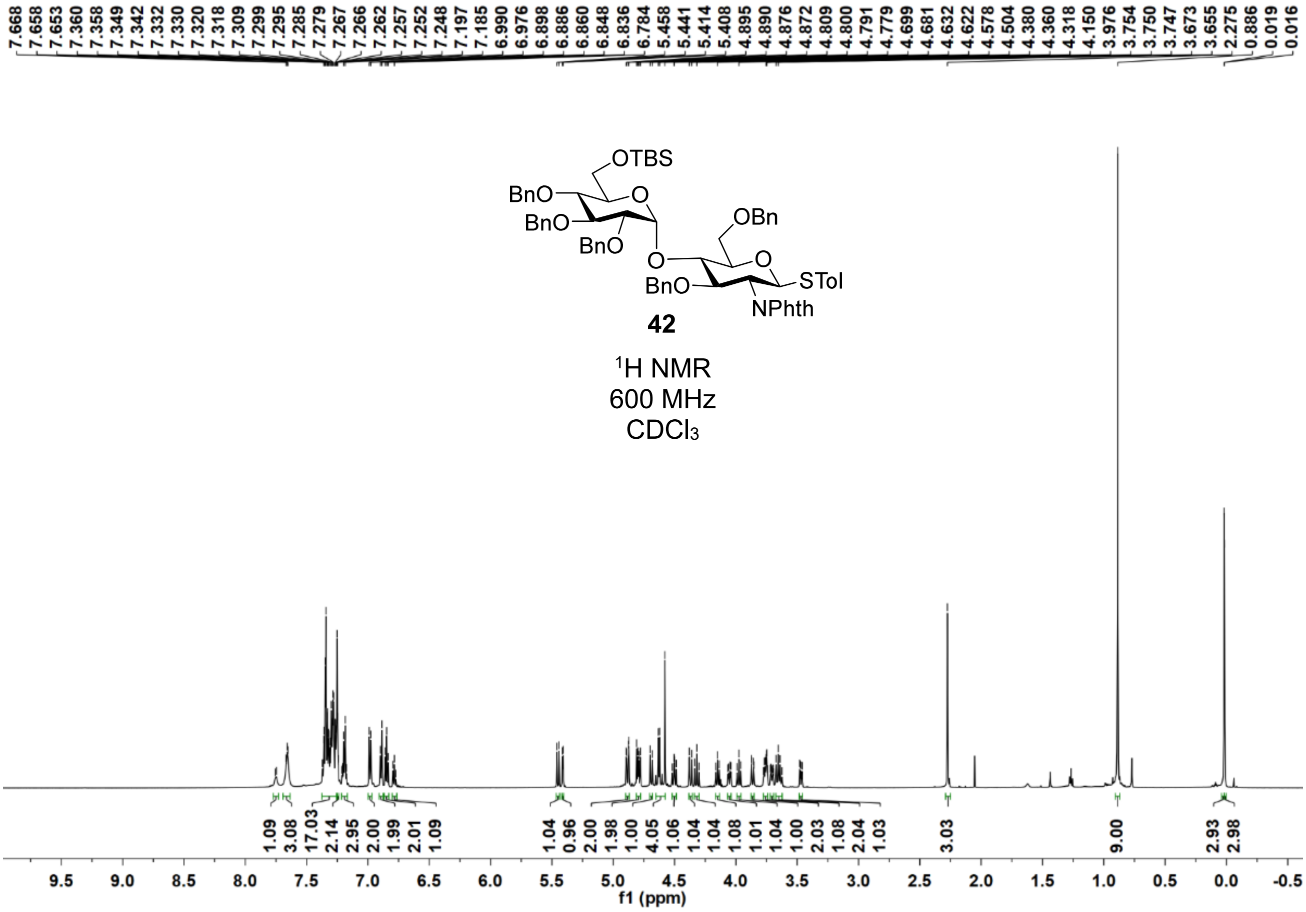

165.44 165.39 165.19 138.87 138.63 138.54 138.16 134.52 133.44 133.24 133.13 130.02 129.82 129.74 129.67 129.44 129.10 128.89 128.49 128.46 128.44 128.39 128.38 128.31 128.22 128.03 127.96 127.84 127.81 127.76 127.73 127.57 127.53 97.12 86.27 81.90 80.19 77.47 76.33 75.81 74.97 73.16 73.14 71.86 68.96 68.06 66.48 62.07 25.94 21.24 18.30 -5.15 -5.41
OTBS
BnO
BnO
BnO
O
O
BzO
O
STol
BzO
OBz
39
13C NMR
125 MHz
CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

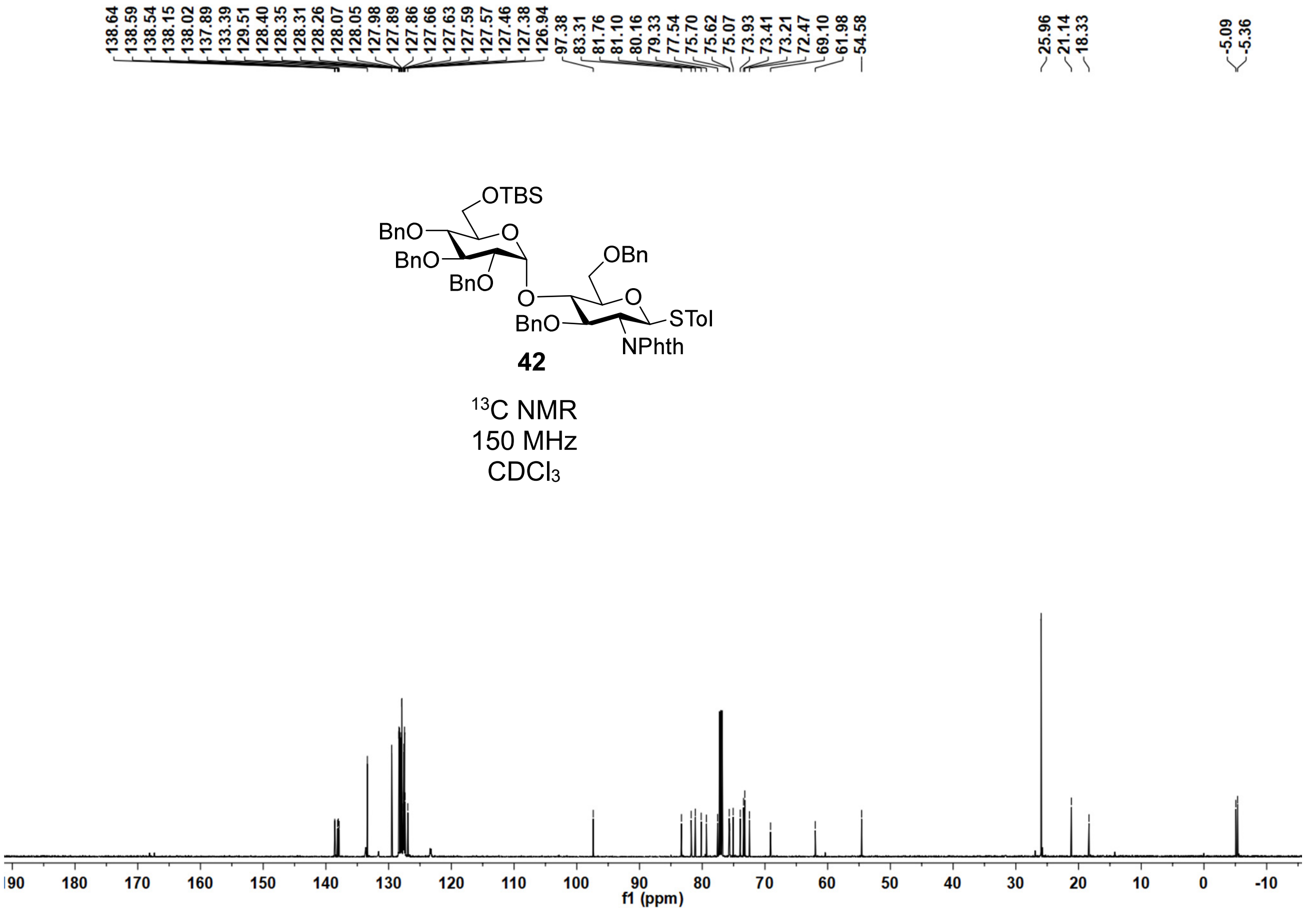

8.007 7.991 7.974 7.958 7.886 7.870 7.519 7.505 7.426 7.404 7.389 7.381 7.370 7.366 7.355 7.339 7.326 7.309 7.295 7.280 7.265 7.260 7.232 7.217 6.163 5.566 5.546 5.526 5.247 5.230 5.223 4.924 4.903 4.883 4.805 4.794 4.783 4.769 4.737 4.731 4.674 4.667 4.652 4.643 4.003 3.984 3.870 3.745 3.737 3.717 3.684 3.662 3.604 3.585 3.581 3.566 3.560 3.506 3.500 3.487 3.480 0.885 0.016 0.007
OTBS
BnO
BnO
BnO
O
BzO
BzO
BzO
OMe
40
^{1}H NMR
500 MHz
$CDCl_3$
3.88 1.89 2.06 21.49 0.94 0.93 1.02 1.96 2.13 2.13 1.04 2.02 1.05 1.04 1.02 3.21 2.06 1.07 2.82 9.29 6.00
10.5 10.0 9.5 9.0 8.5 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 0.0 -0.5
f1 (ppm)

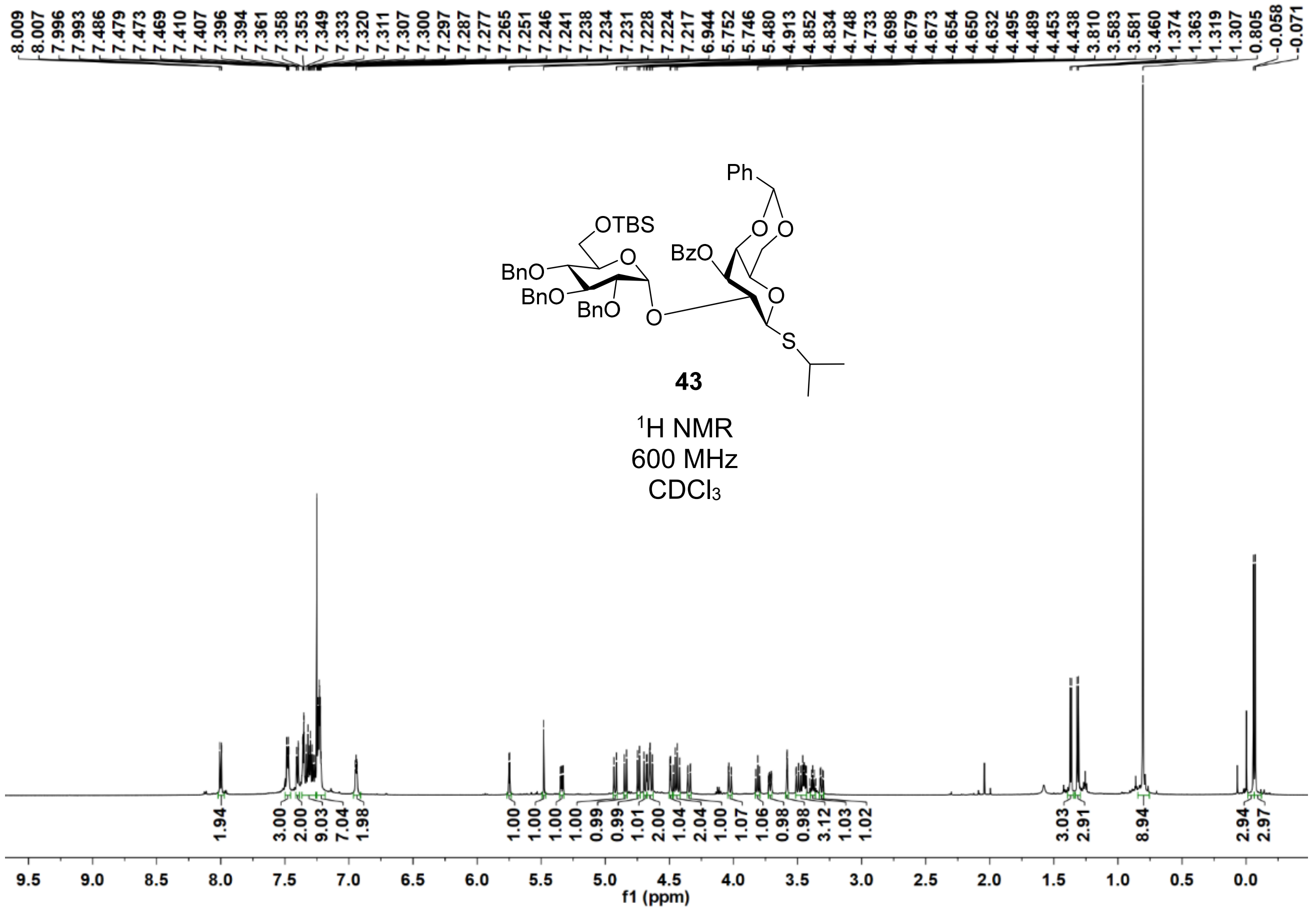

165.82 165.81 165.24 138.84 138.50 133.30 133.02 129.93 129.91 129.67 129.29 129.12 129.06 128.39 128.38 128.36 128.33 128.30 128.24 128.11 127.81 127.68 127.60 127.53 127.47 96.95 96.71 81.70 80.37 77.53 75.62 74.74 73.07 72.26 71.59 70.65 69.68 68.61 66.37 61.97 55.56 25.94 18.30 -5.17 -5.41
OTBS
BnO
BnO
BnO
O
BzO
BzO
BzO
OMe
40
^{13}C NMR
125 MHz
$CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

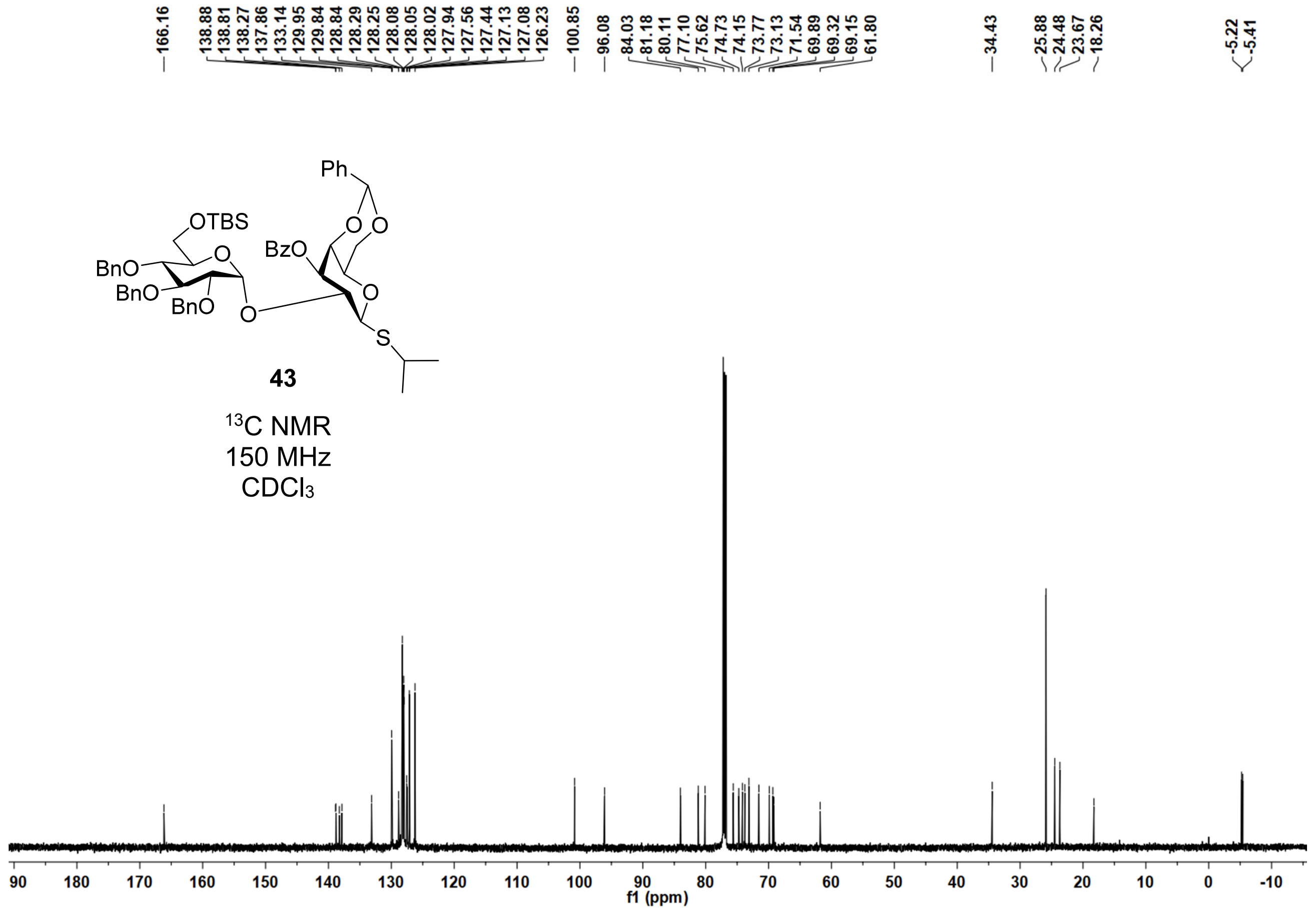

7.380 7.365 7.361 7.347 7.334 7.330 7.318 7.315 7.311 7.296 7.282 7.278 7.265 7.260 6.953 6.935 6.831 6.813 5.362 5.344 5.219 5.204 5.200 5.185 4.935 4.920 4.878 4.860 4.856 4.838 4.826 4.804 4.767 4.760 4.744 4.656 4.648 4.632 4.626 4.600 4.580 4.576 3.907 3.901 3.888 3.883 3.864 3.779 3.752 3.749 3.680 3.675 3.670 3.658 3.583 3.564 3.414 3.407 2.084 2.017 1.942 0.886 0.044 0.019
OTBS
BnO
BnO
BnO
O
OAc
AcO
OMP
OAc
41
¹H NMR
500 MHz
CDCl₃
15.05 1.82 1.80 0.98 1.06 1.01 2.04 1.01 1.90 2.00 1.03 1.00 2.08 3.90 0.98 2.08 0.98 0.99 2.90 2.84 2.89 8.84 2.79 2.85
10.5 10.0 9.5 9.0 8.5 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 0.0 -0.5
f1 (ppm)

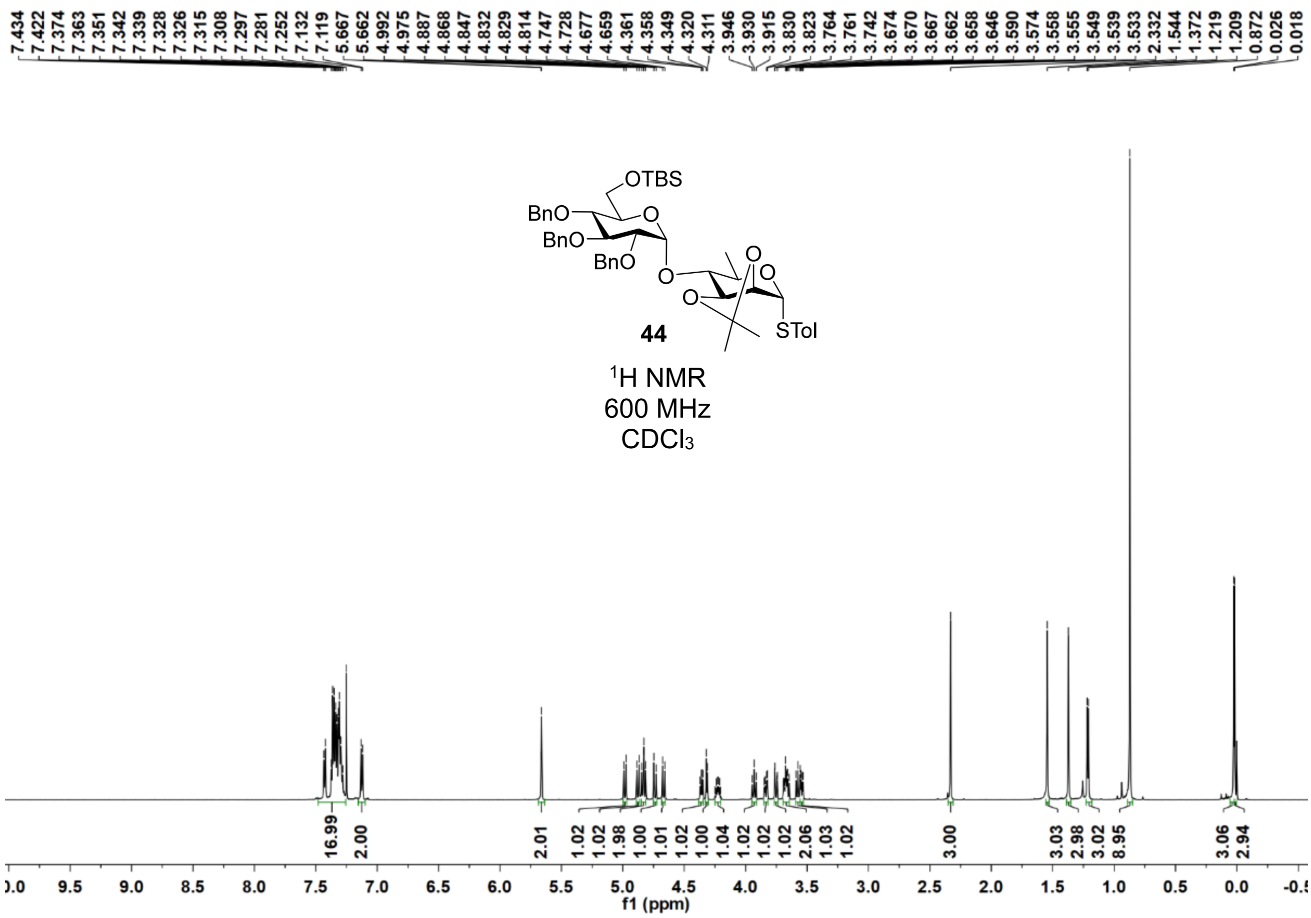

170.13 170.04 169.63 155.69 150.97 138.63 138.41 138.02 128.55 128.43 128.40 128.38 128.21 128.11 128.05 127.78 127.67 127.66 118.70 114.52 100.09 99.11 81.17 80.44 77.33 76.18 75.77 74.99 73.82 73.60 73.41 73.11 71.64 62.86 61.89 55.65 25.92 20.91 20.78 20.73 18.34 -5.23 -5.43
OTBS
BnO
BnO
BnO
O
OAc
AcO
OMP
OAc
41
¹³C NMR
125 MHz
CDCl₃
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

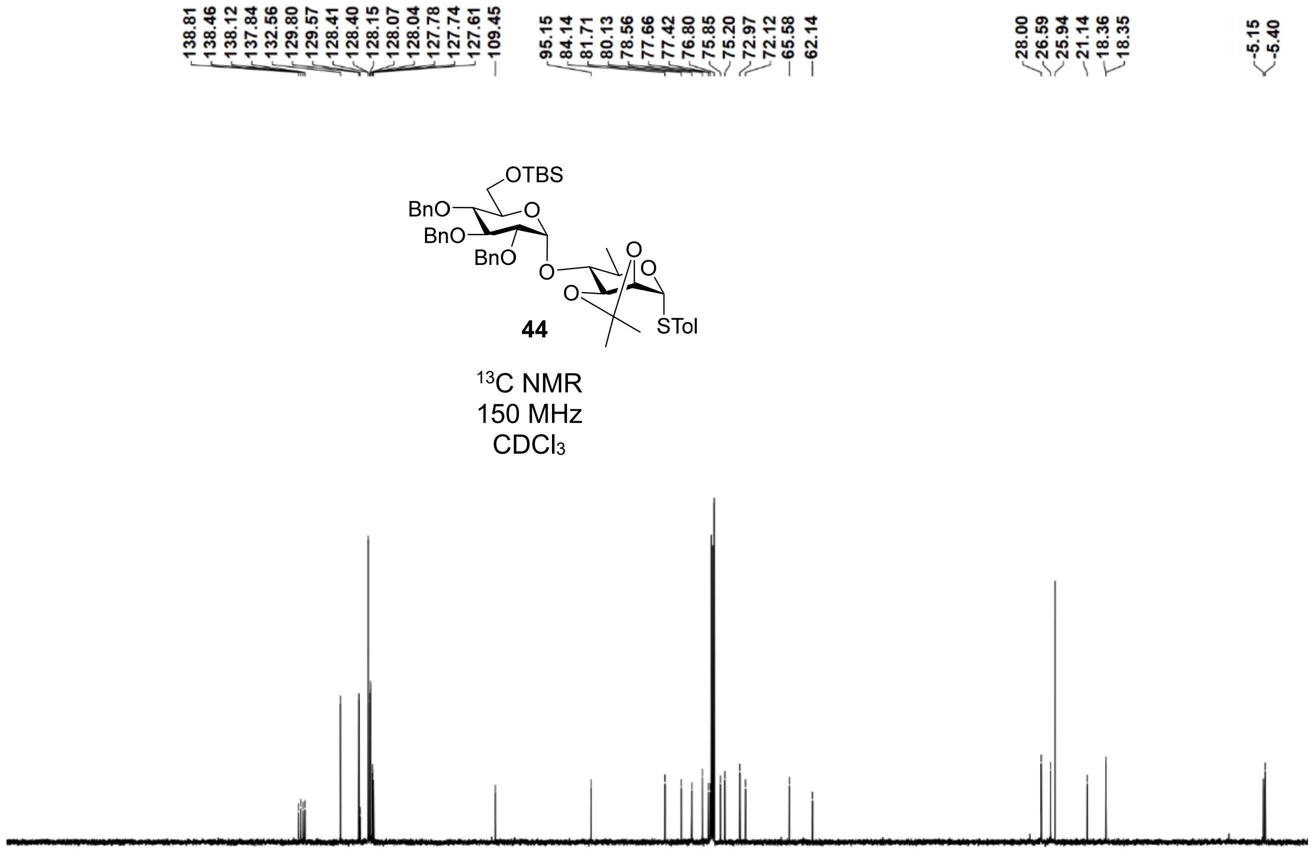

7.668 7.658 7.653 7.360 7.358 7.349 7.342 7.332 7.330 7.320 7.318 7.309 7.299 7.295 7.285 7.279 7.267 7.266 7.262 7.257 7.252 7.248 7.197 7.185 6.990 6.976 6.898 6.886 6.860 6.848 6.836 6.784 5.458 5.441 5.414 5.408 4.895 4.890 4.876 4.872 4.809 4.800 4.791 4.779 4.699 4.681 4.632 4.622 4.578 4.504 4.380 4.360 4.318 4.150 3.976 3.754 3.750 3.747 3.673 3.655 2.275 0.886 0.019 0.016
OTBS
BnO
BnO
BnO
O
OBn
O
BnO
STol
NPhth
42
1H NMR
600 MHz
CDCl3
1.09 3.08 17.03 2.14 2.95 2.00 1.99 2.01 1.09 1.04 0.96 2.00 1.98 1.00 4.05 1.06 1.04 1.04 1.08 1.01 1.04 1.00 2.03 1.08 2.04 1.03 3.03 9.00 2.93 2.98
f1 (ppm)

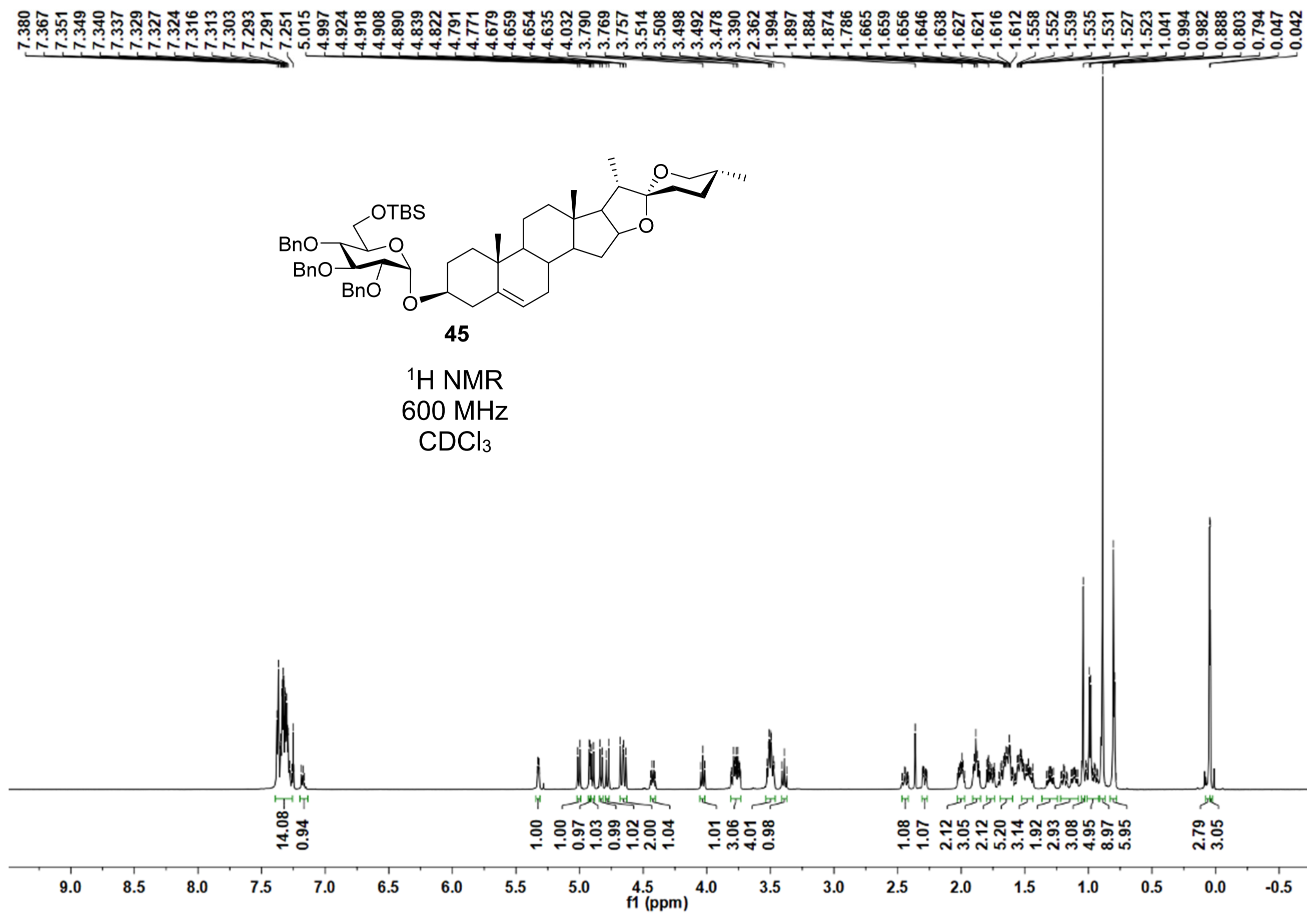

138.64 138.59 138.54 138.15 138.02 137.89 133.39 129.51 128.40 128.35 128.31 128.26 128.07 128.05 127.98 127.89 127.86 127.66 127.63 127.59 127.57 127.46 127.38 126.94 97.38 83.31 81.76 81.10 80.16 79.33 77.54 75.70 75.62 75.07 73.93 73.41 73.21 72.47 69.10 61.98 54.58 25.96 21.14 18.33 -5.09 -5.36
OTBS
BnO
BnO
BnO
O
OBn
O
BnO
STol
NPhth
42
13C NMR
150 MHz
CDCl3
f1 (ppm)

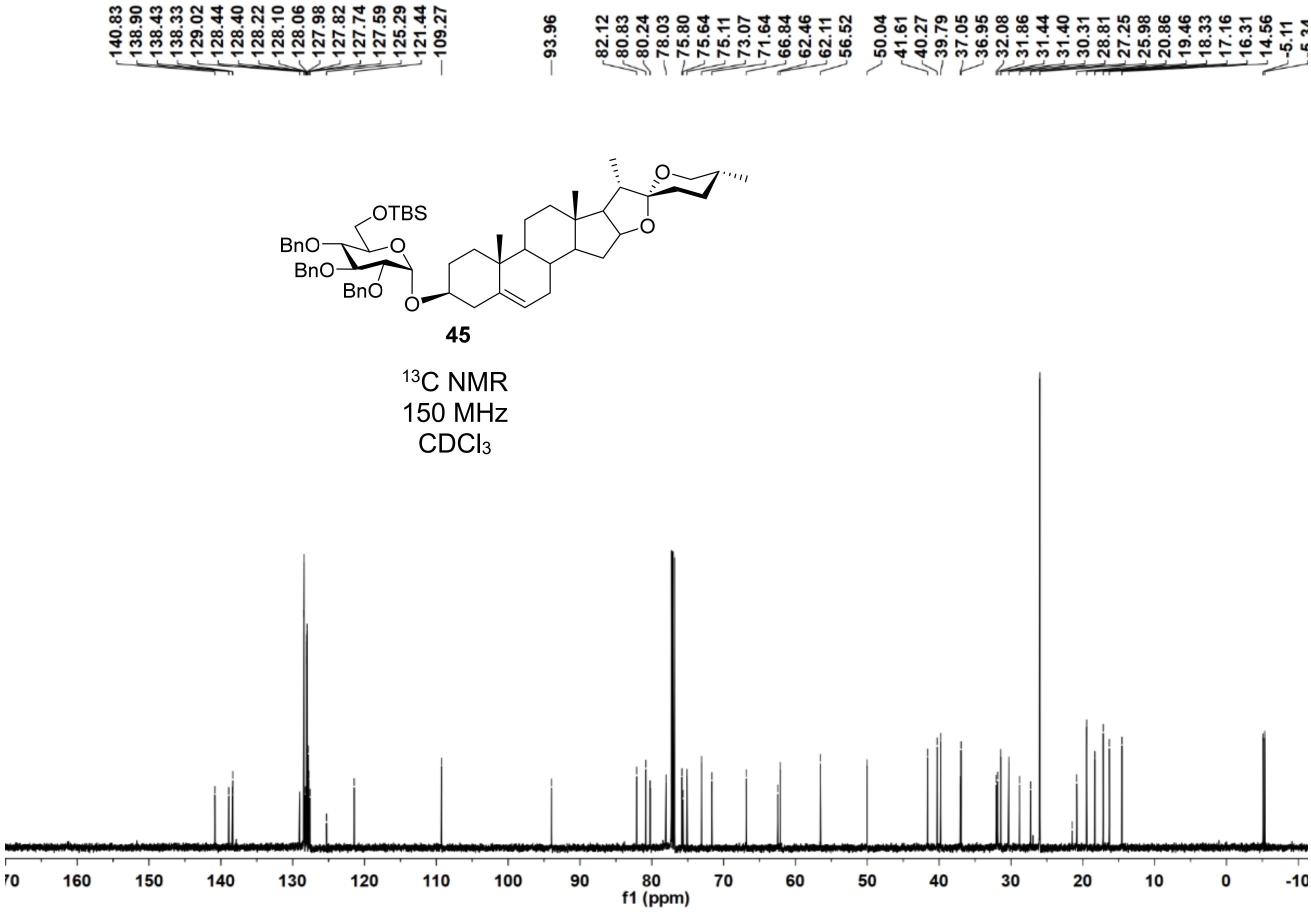

8.009 8.007 7.996 7.993 7.486 7.479 7.473 7.469 7.410 7.407 7.396 7.394 7.361 7.358 7.353 7.349 7.333 7.320 7.311 7.307 7.300 7.297 7.287 7.277 7.265 7.251 7.246 7.241 7.238 7.234 7.231 7.228 7.224 7.217 6.944 5.752 5.746 5.480 4.913 4.852 4.834 4.748 4.733 4.698 4.679 4.673 4.654 4.650 4.632 4.495 4.489 4.453 4.438 3.810 3.583 3.581 3.460 1.374 1.363 1.319 1.307 0.805 -0.058 -0.071
Ph
OTBS
BnO
BnO
BnO
BzO
O
S
43
1H NMR
600 MHz
CDCl3
1.94 3.00 2.00 9.03 7.04 1.98 1.00 1.00 1.00 1.00 0.99 0.99 1.01 2.00 1.04 2.04 1.00 1.07 1.06 0.98 0.98 3.12 1.03 1.02 3.03 2.91 8.94 2.94 2.97
f1 (ppm)

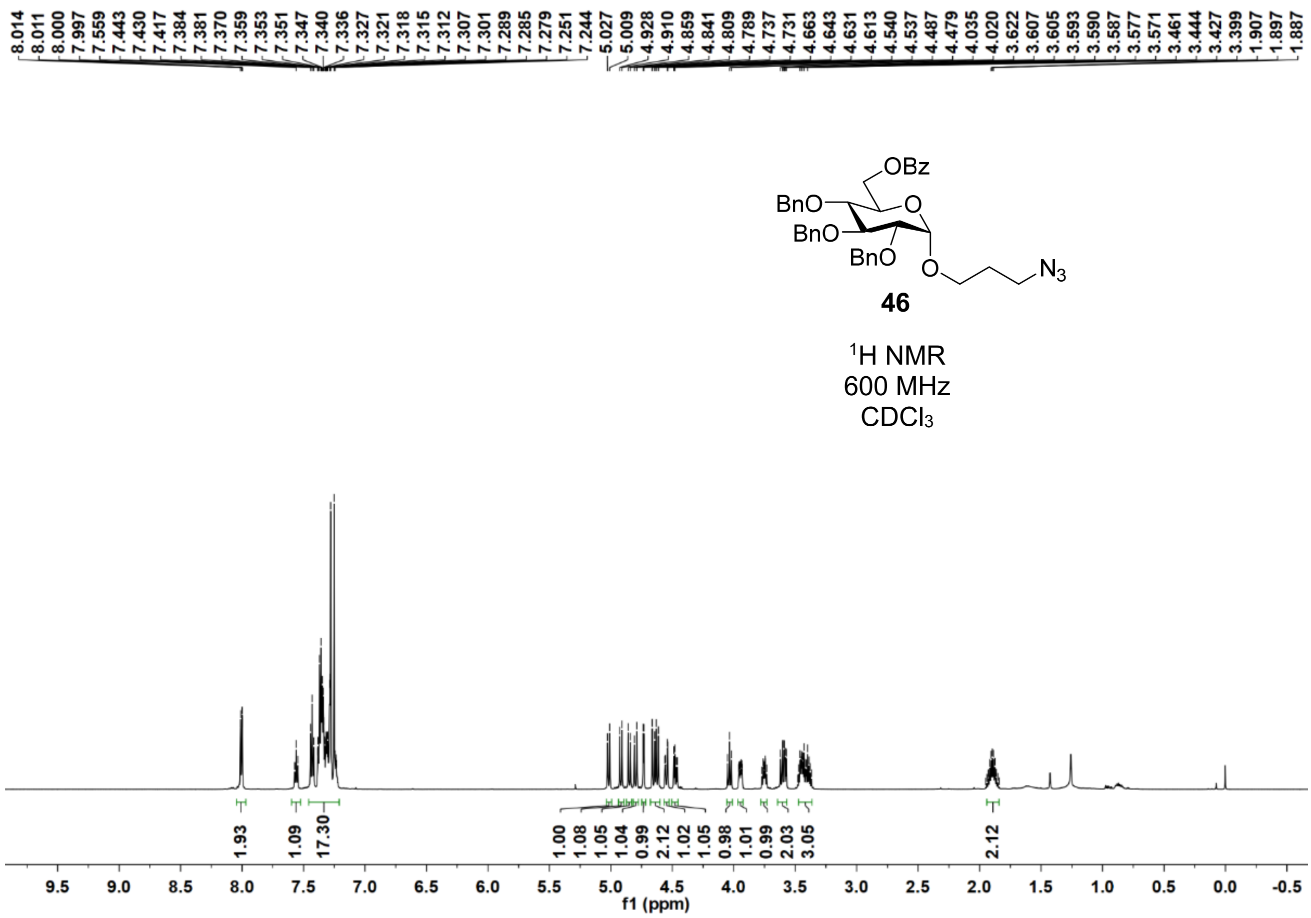

166.16 138.88 138.81 138.27 137.86 133.14 129.95 129.84 128.84 128.29 128.25 128.08 128.05 128.02 127.94 127.56 127.44 127.13 127.08 126.23 100.85 96.08 84.03 81.18 80.11 77.10 75.62 74.73 74.15 73.77 73.13 71.54 69.89 69.32 69.15 61.80 34.43 25.88 24.48 23.67 18.26 -5.22 -5.41
Ph
OTBS
BnO
BnO
BnO
BzO
O
S
43
13C NMR
150 MHz
CDCl3
f1 (ppm)

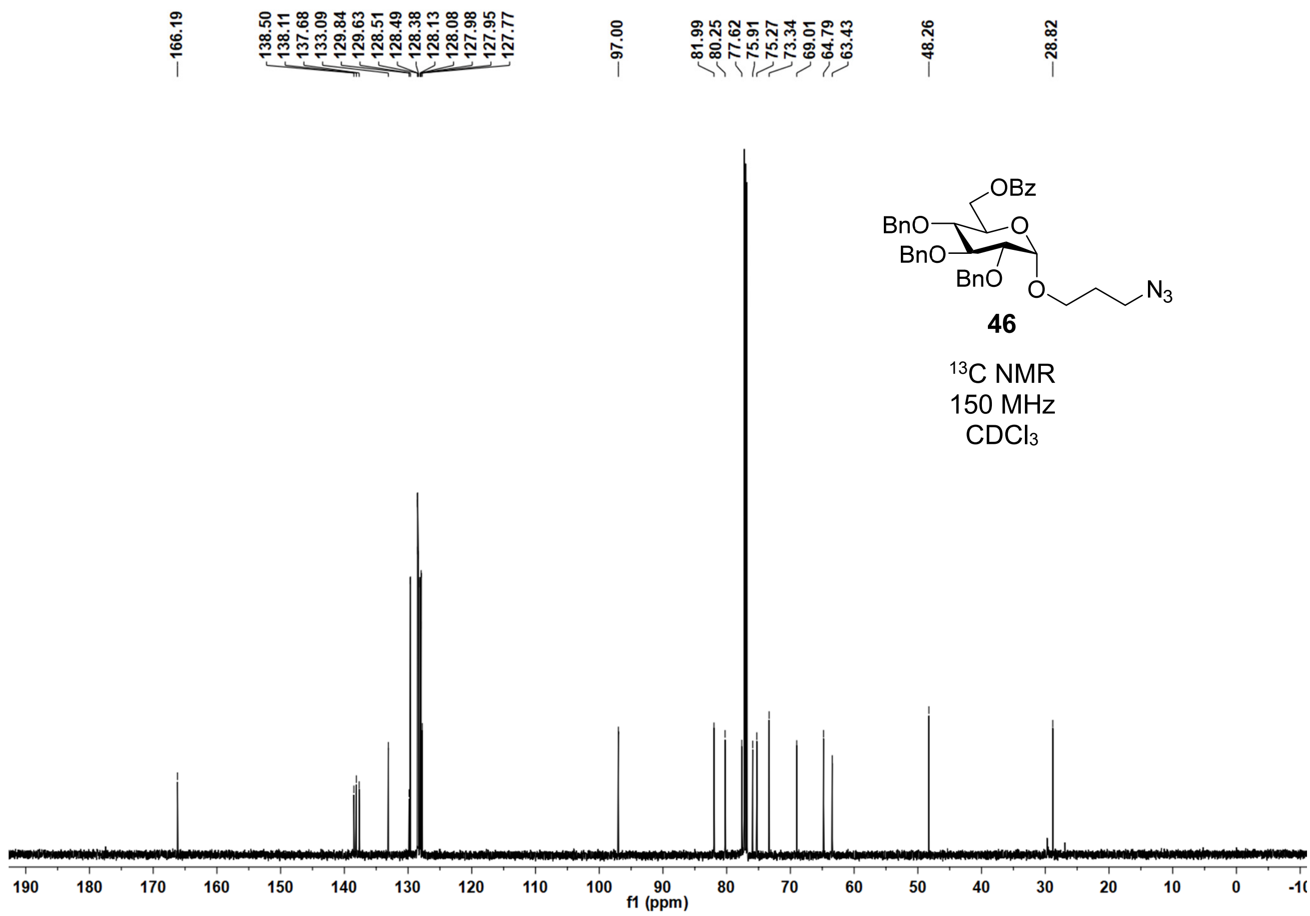

7.434 7.422 7.374 7.363 7.351 7.342 7.339 7.328 7.326 7.315 7.308 7.297 7.281 7.252 7.132 7.119 5.667 5.662 4.992 4.975 4.887 4.868 4.847 4.832 4.829 4.814 4.747 4.728 4.677 4.659 4.361 4.358 4.349 4.320 4.311 3.946 3.930 3.915 3.830 3.823 3.764 3.761 3.742 3.674 3.670 3.667 3.662 3.658 3.646 3.590 3.574 3.558 3.555 3.549 3.539 3.533 2.332 1.544 1.372 1.219 1.209 0.872 0.026 0.018
OTBS
BnO
BnO
BnO
O
O
O
O
O
STol
44
^{1}H NMR
600 MHz
$CDCl_3$
16.99 2.00 2.01 1.02 1.02 1.98 1.00 1.01 1.02 1.00 1.04 1.02 1.02 1.02 2.06 1.03 1.02 3.00 3.03 2.98 3.02 8.95 3.06 2.94
f1 (ppm)

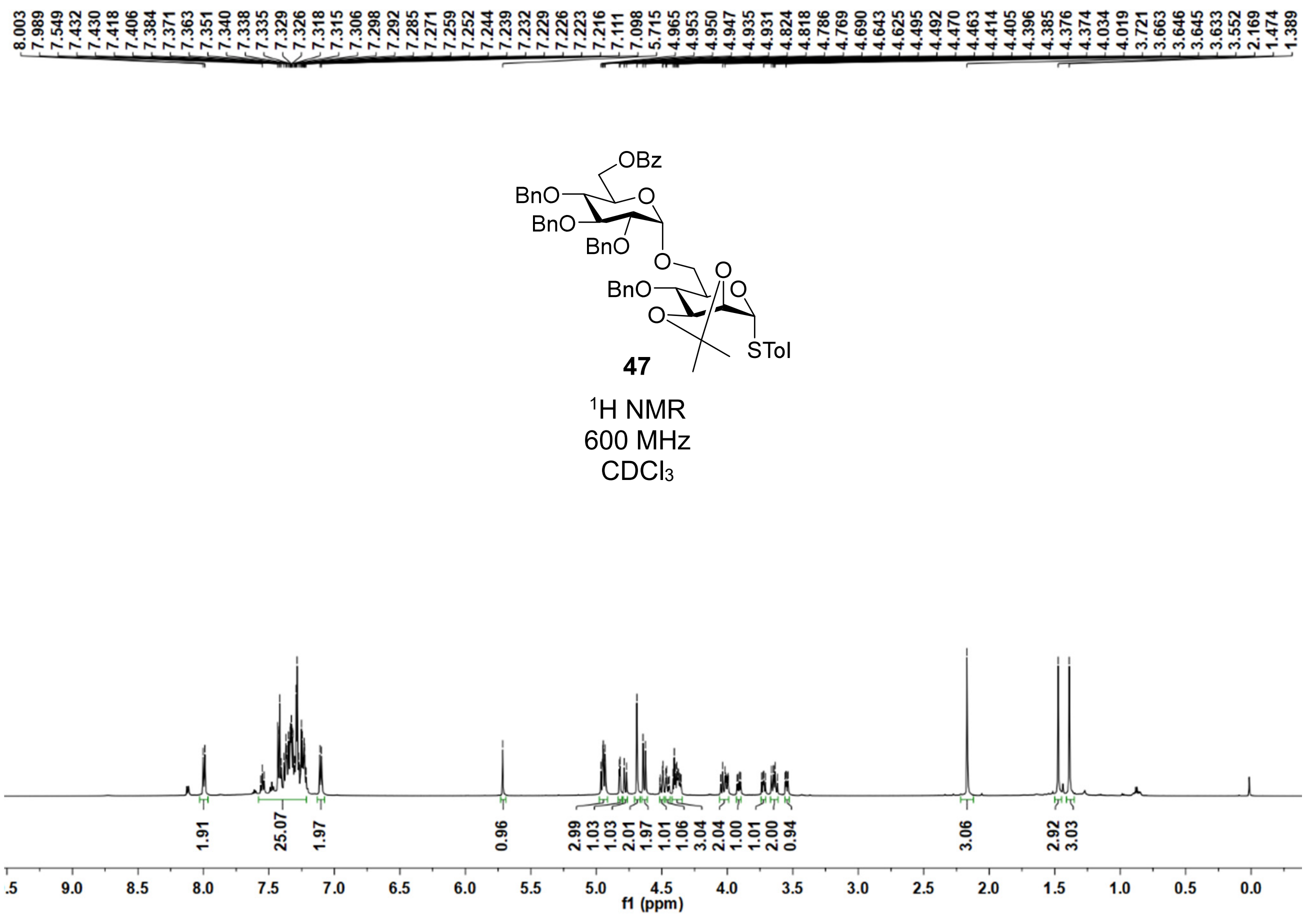

138.81 138.46 138.12 137.84 132.56 129.80 129.57 128.41 128.40 128.15 128.07 128.04 127.78 127.74 127.61 109.45 95.15 84.14 81.71 80.13 78.56 77.66 77.42 76.80 75.85 75.20 72.97 72.12 65.58 62.14 28.00 26.59 25.94 21.14 18.36 18.35 -5.15 -5.40
OTBS
BnO
BnO
BnO
O
O
O
O
O
STol
44
^{13}C NMR
150 MHz
$CDCl_3$
f1 (ppm)

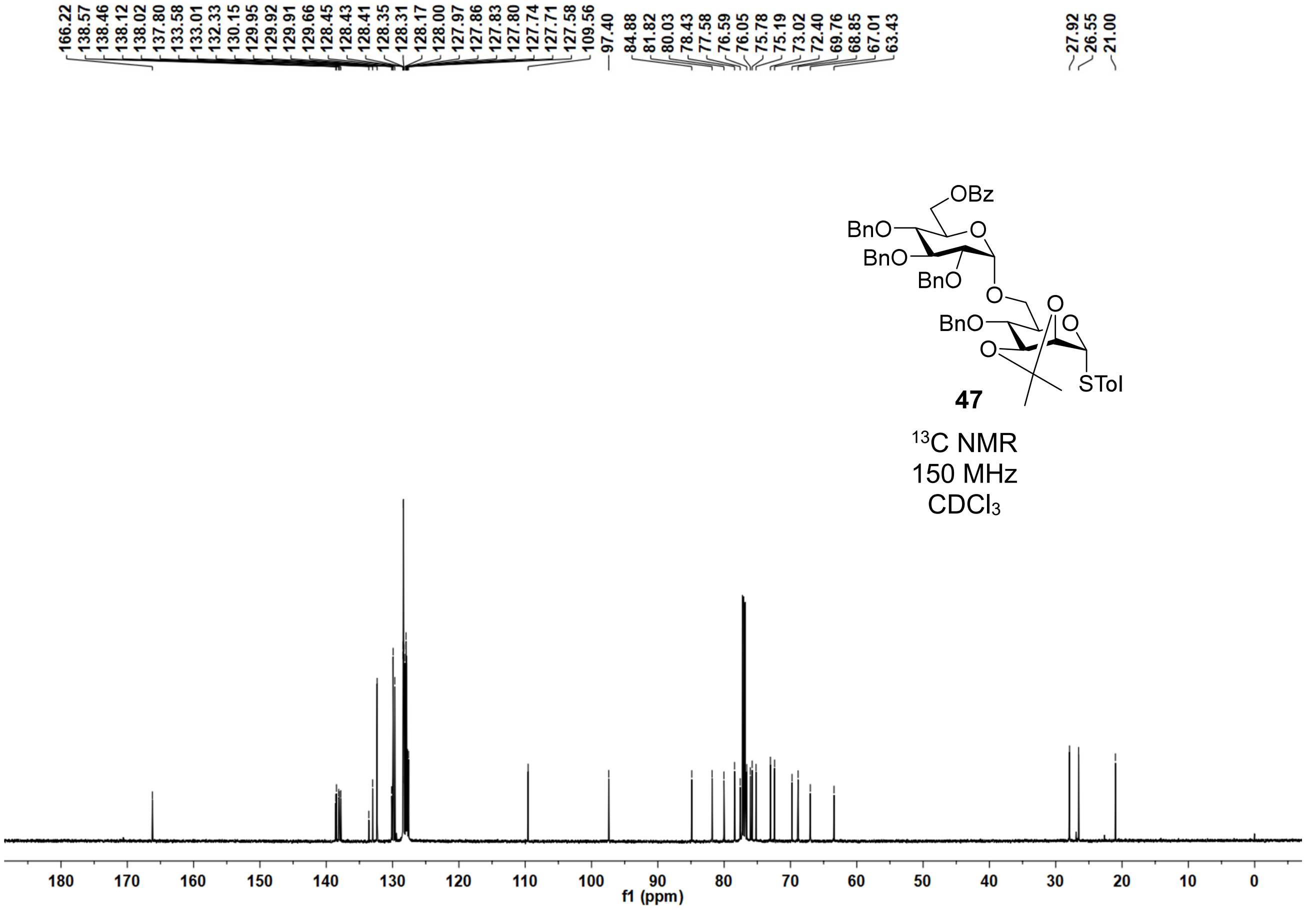

7.380 7.367 7.351 7.349 7.340 7.337 7.329 7.327 7.324 7.316 7.313 7.303 7.293 7.291 7.251 5.015 4.997 4.924 4.918 4.908 4.890 4.839 4.822 4.791 4.771 4.679 4.659 4.654 4.635 4.032 3.790 3.769 3.757 3.514 3.508 3.498 3.492 3.478 3.390 2.362 1.994 1.897 1.884 1.874 1.786 1.665 1.659 1.656 1.646 1.638 1.627 1.621 1.616 1.612 1.558 1.552 1.539 1.535 1.531 1.527 1.523 1.041 0.994 0.982 0.888 0.803 0.794 0.047 0.042
OTBS
BnO
BnO
BnO
O
O
O
O
45
1H NMR
600 MHz
CDCl3
14.08 0.94 1.00 1.00 0.97 1.03 0.99 1.02 2.00 1.04 1.01 3.06 4.01 0.98 1.08 1.07 2.12 3.05 2.12 5.20 3.14 1.92 2.93 3.08 4.95 8.97 5.95 2.79 3.05
9.0 8.5 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 0.0 -0.5
f1 (ppm)

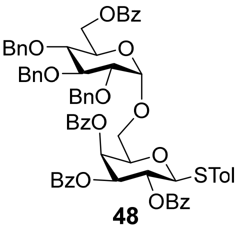

140.83 138.90 138.43 138.33 129.02 128.44 128.40 128.22 128.10 128.06 127.98 127.82 127.74 127.59 125.29 121.44 109.27 93.96 82.12 80.83 80.24 78.03 75.80 75.64 75.11 73.07 71.64 66.84 62.46 62.11 56.52 50.04 41.61 40.27 39.79 37.05 36.95 32.08 31.86 31.44 31.40 30.31 28.81 27.25 25.98 20.86 19.46 18.33 17.16 16.31 14.56 -5.11
OTBS
BnO
BnO
BnO
O
O
O
O
45
13C NMR
150 MHz
CDCl3
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.014 8.011 8.000 7.997 7.559 7.443 7.430 7.417 7.384 7.381 7.370 7.359 7.353 7.351 7.347 7.340 7.336 7.327 7.321 7.318 7.315 7.312 7.307 7.301 7.289 7.285 7.279 7.251 7.244 5.027 5.009 4.928 4.910 4.859 4.841 4.809 4.789 4.737 4.731 4.663 4.643 4.631 4.613 4.540 4.537 4.487 4.479 4.035 4.020 3.622 3.607 3.605 3.593 3.590 3.587 3.577 3.571 3.461 3.444 3.427 3.399 1.907 1.897 1.887
OBz
BnO
O
BnO
BnO
O
N3
46
1H NMR
600 MHz
CDCl3
1.93 1.09 17.30 1.00 1.08 1.05 1.04 0.99 2.12 1.02 1.05 0.98 1.01 0.99 2.03 3.05 2.12
f1 (ppm)


166.19
138.50 138.11 137.68 133.09 129.84 129.63 128.51 128.49 128.38 128.13 128.08 127.98 127.95 127.77
97.00
81.99 80.25 77.62 75.91 75.27 73.34 69.01 64.79 63.43
48.26
28.82
OBz
BnO
O
BnO
BnO
O
N3
46
13C NMR
150 MHz
CDCl3
f1 (ppm)

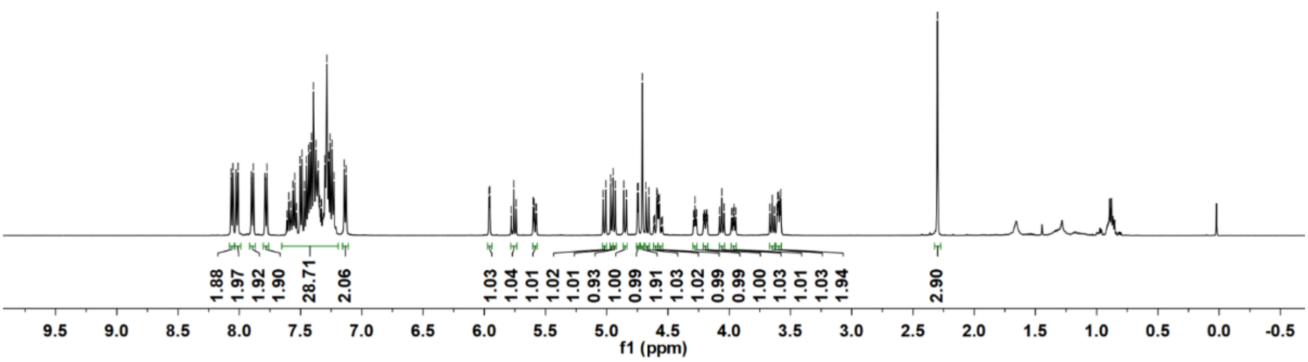

8.003 7.989 7.549 7.432 7.430 7.418 7.406 7.384 7.371 7.363 7.351 7.340 7.338 7.335 7.329 7.326 7.318 7.315 7.306 7.298 7.292 7.285 7.271 7.259 7.252 7.244 7.239 7.232 7.229 7.226 7.223 7.216 7.111 7.098 5.715 4.965 4.953 4.950 4.947 4.947 4.935 4.931 4.824 4.818 4.786 4.769 4.690 4.643 4.625 4.495 4.492 4.470 4.463 4.414 4.405 4.396 4.385 4.376 4.374 4.034 4.019 3.721 3.663 3.646 3.645 3.633 3.552 2.169 1.474 1.389
OBz
BnO
BnO
BnO
O
O
BnO
O
O
O
STol
47
1H NMR
600 MHz
CDCl3
1.91 25.07 1.97 0.96 2.99 1.03 1.03 2.01 1.97 1.01 1.06 3.04 2.04 1.00 1.01 2.00 0.94 3.06 2.92 3.03
f1 (ppm)

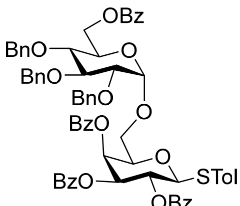

166.22 138.57 138.46 138.12 138.02 137.80 133.58 133.01 132.33 130.15 129.95 129.92 129.91 129.66 128.45 128.43 128.41 128.35 128.31 128.17 128.00 127.97 127.86 127.83 127.80 127.74 127.71 127.58 109.56 97.40 84.88 81.82 80.03 78.43 77.58 76.59 76.05 75.78 75.19 73.02 72.40 69.76 68.85 67.01 63.43 27.92 26.55 21.00
OBz
BnO
BnO
BnO
O
O
BnO
O
O
O
STol
47
13C NMR
150 MHz
CDCl3
f1 (ppm)



48

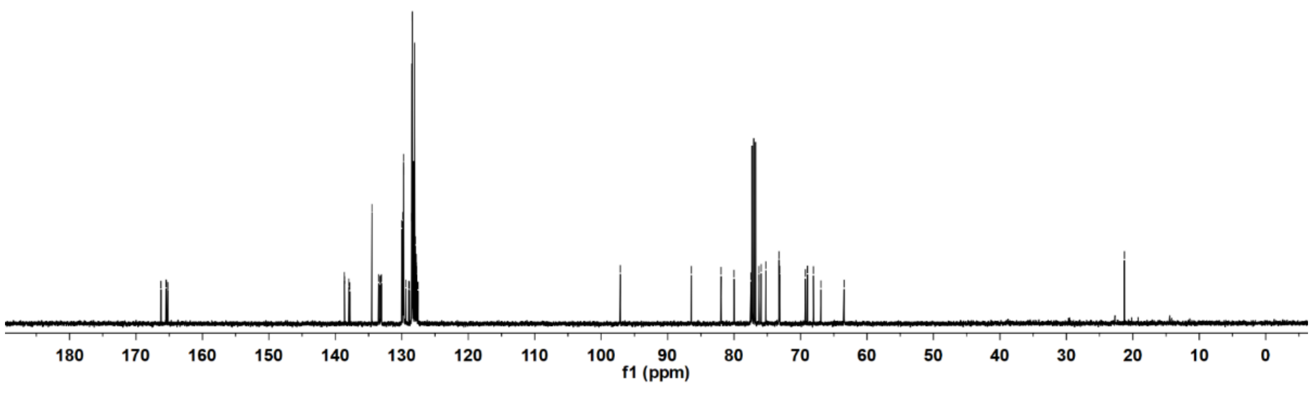
^{1}H NMR
500 MHz
$CDCl_3$

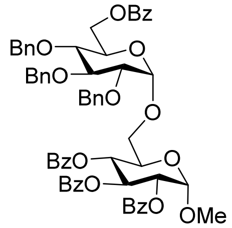




48

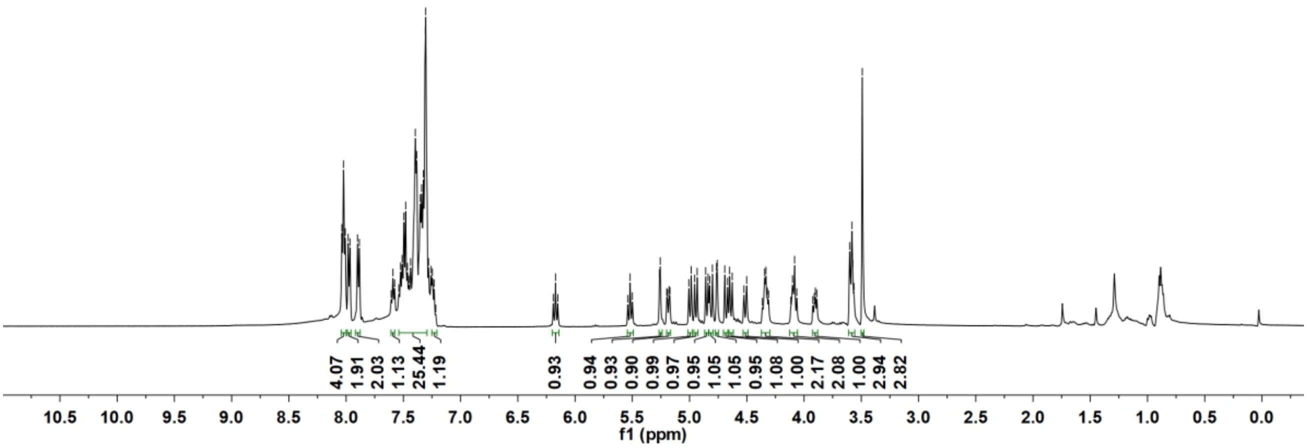
^{13}C NMR
125 MHz
$CDCl_3$

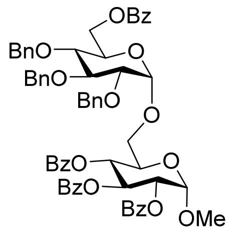




49

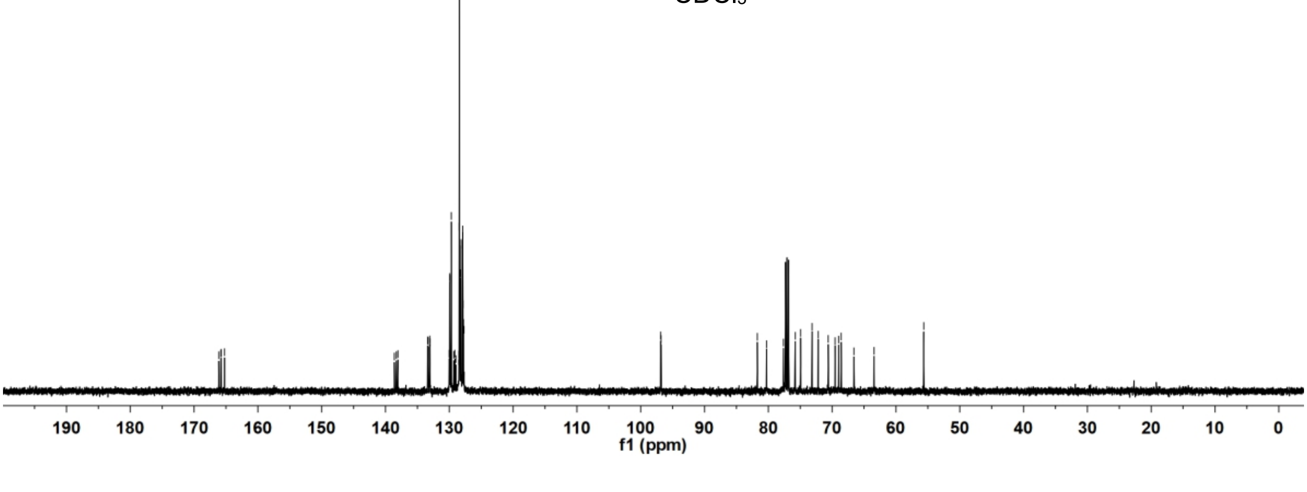
^{1}H NMR
500 MHz
$CDCl_3$

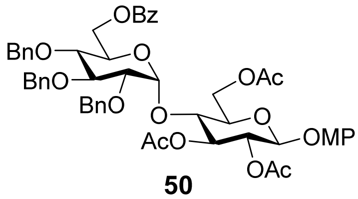




49

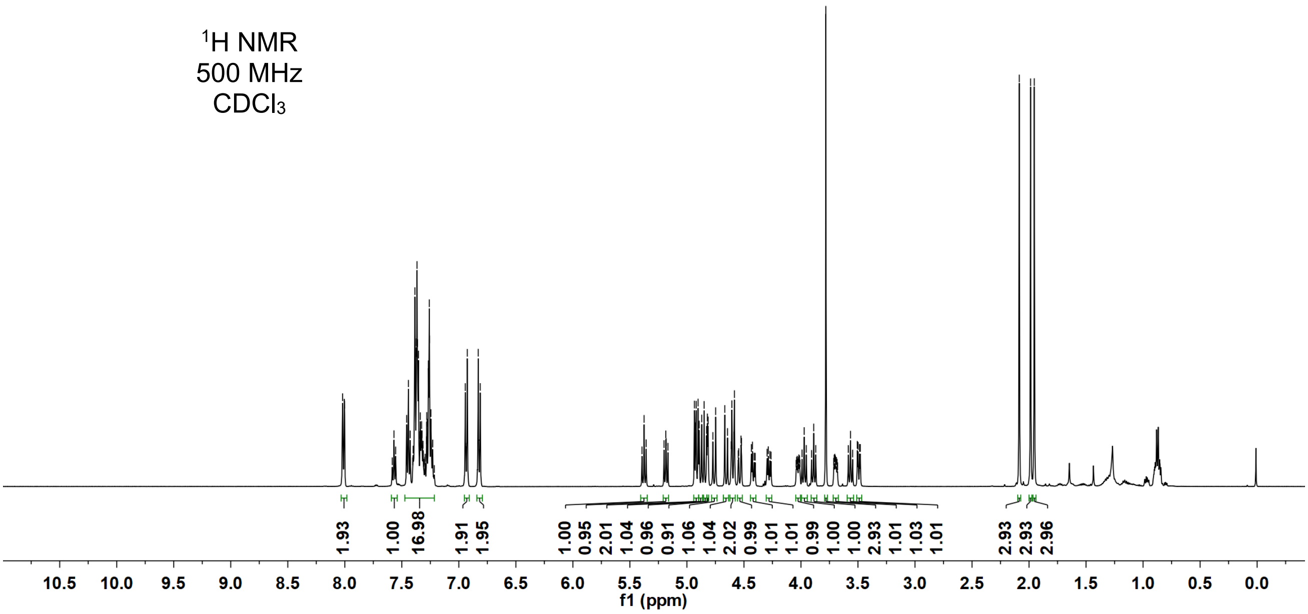
^{13}C NMR
125 MHz
$CDCl_3$

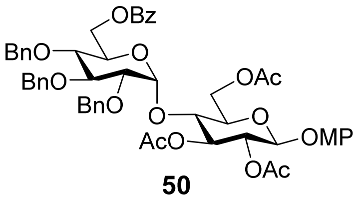




50

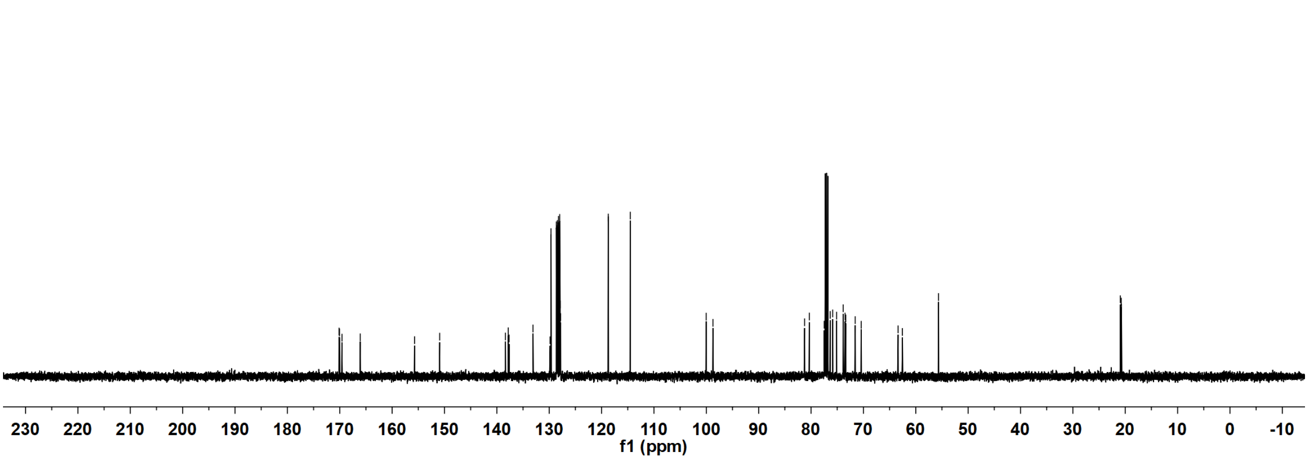
^{1}H NMR
500 MHz
$CDCl_3$

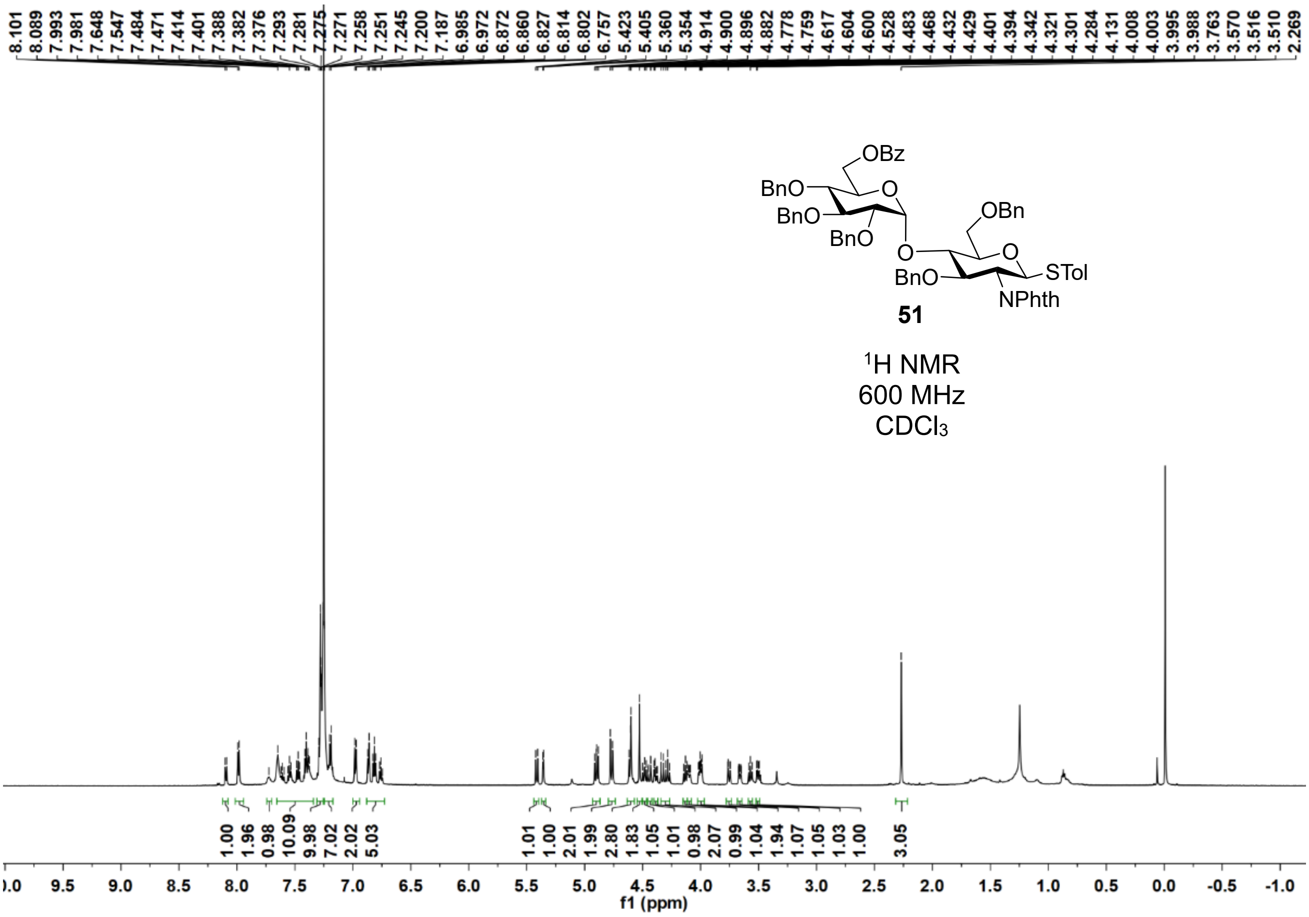


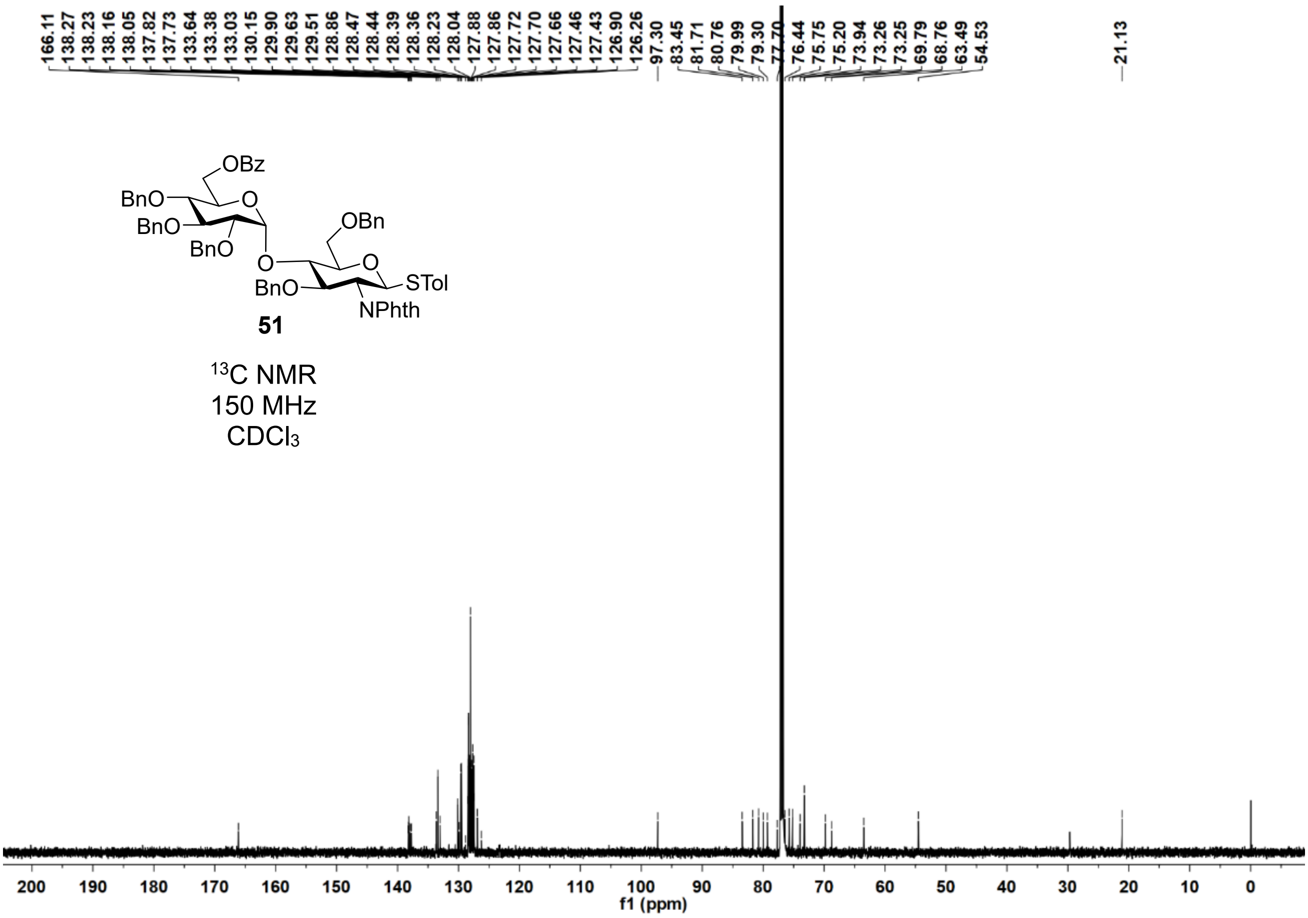


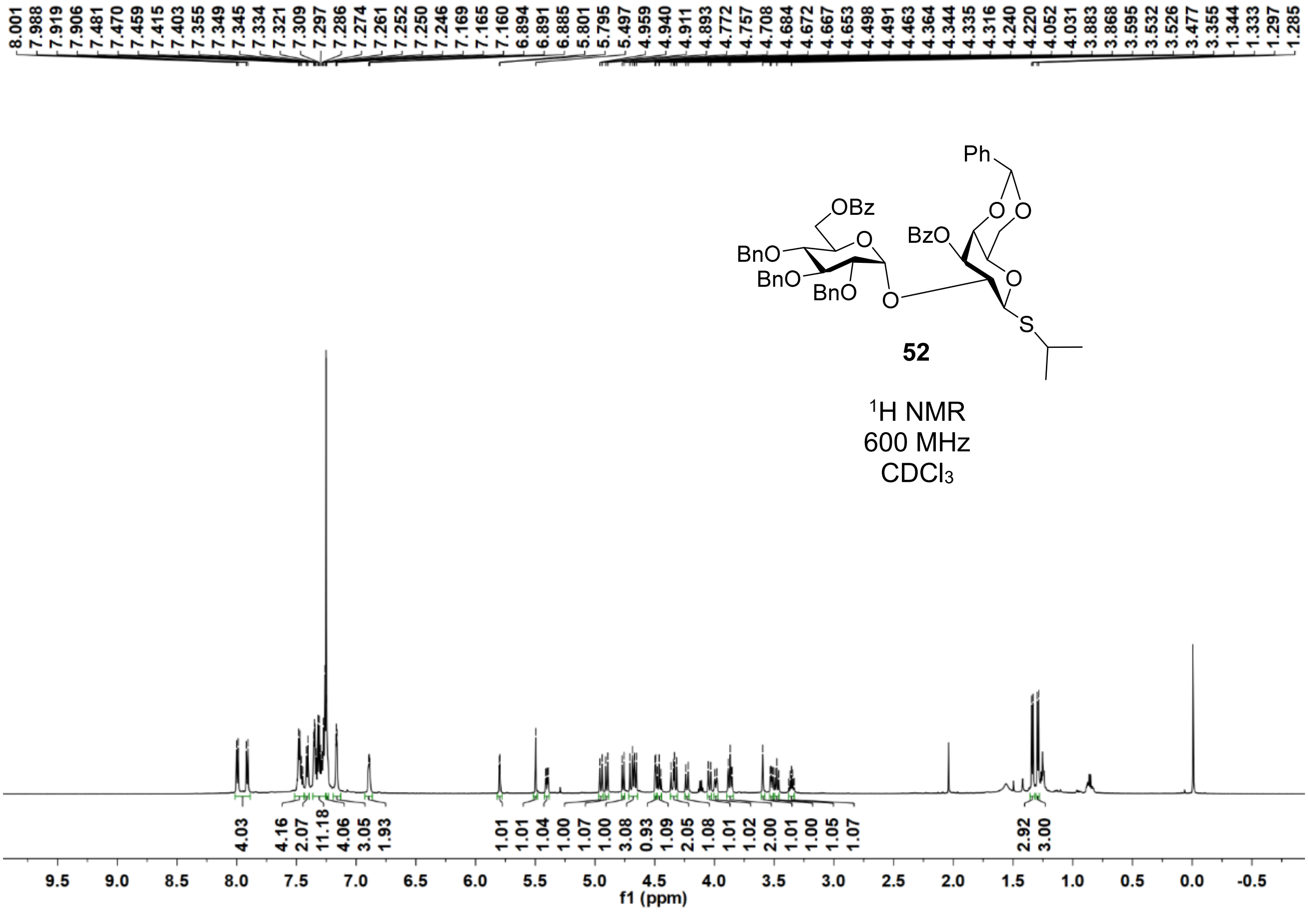
50

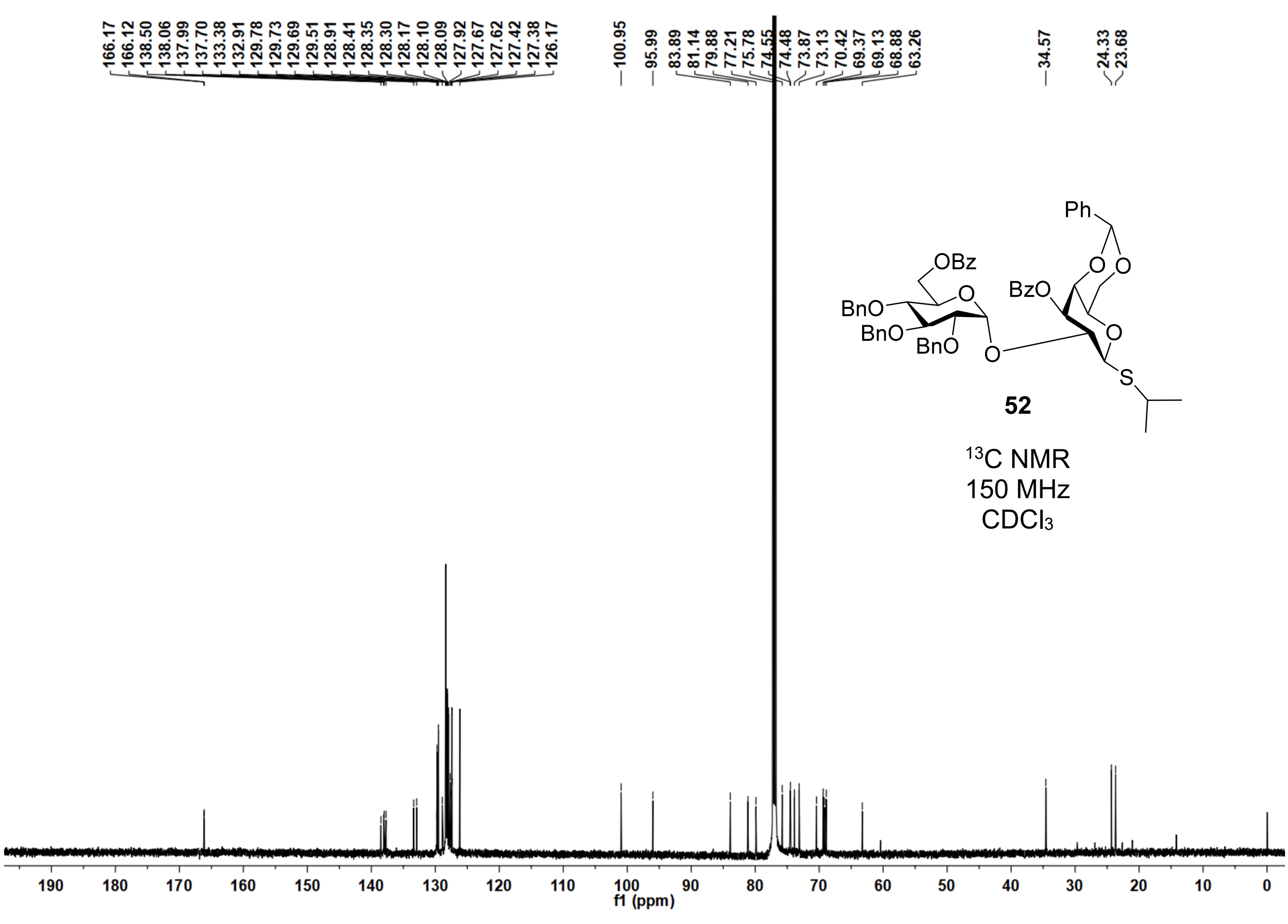
^{13}C NMR
125 MHz
$CDCl_3$

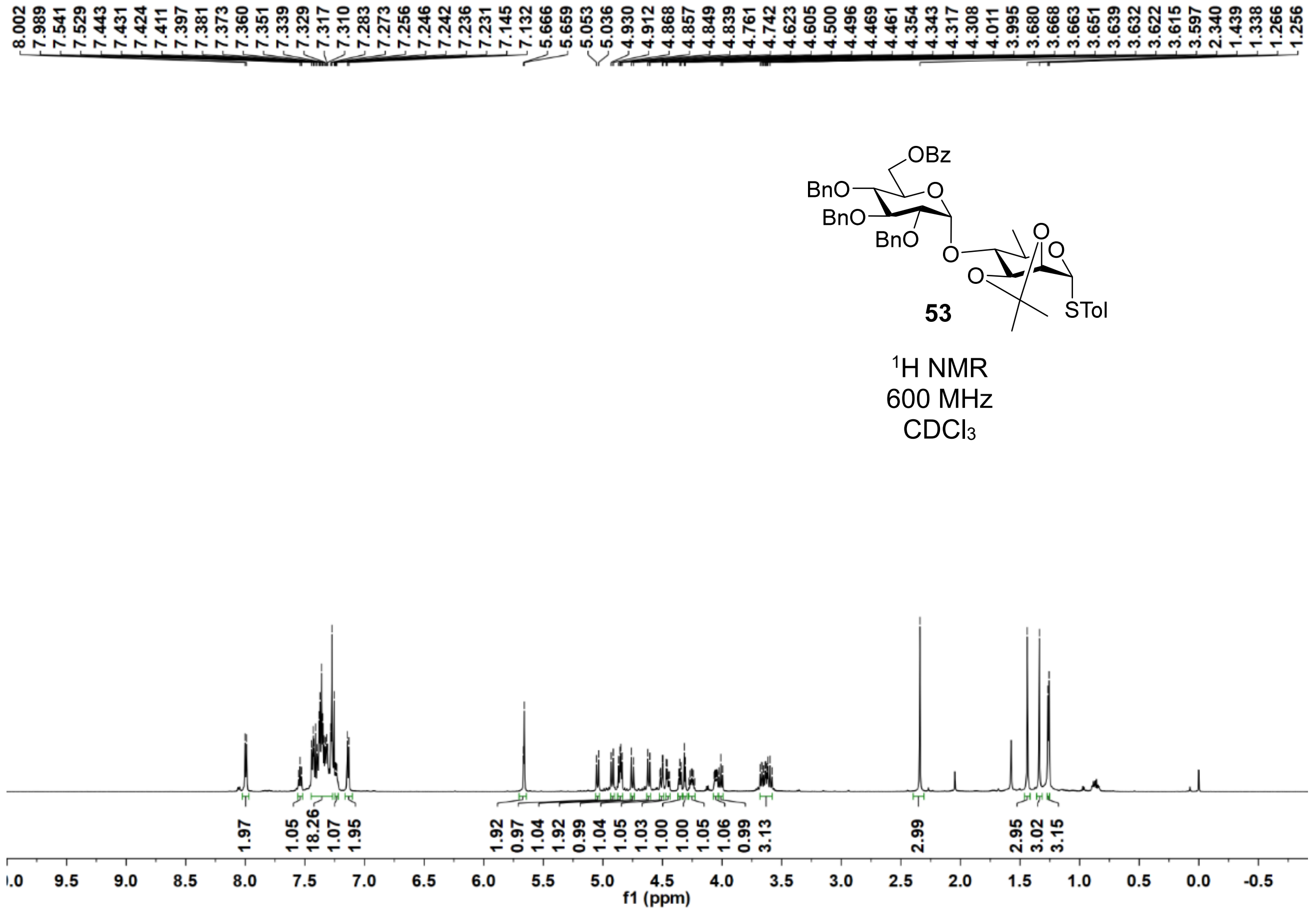


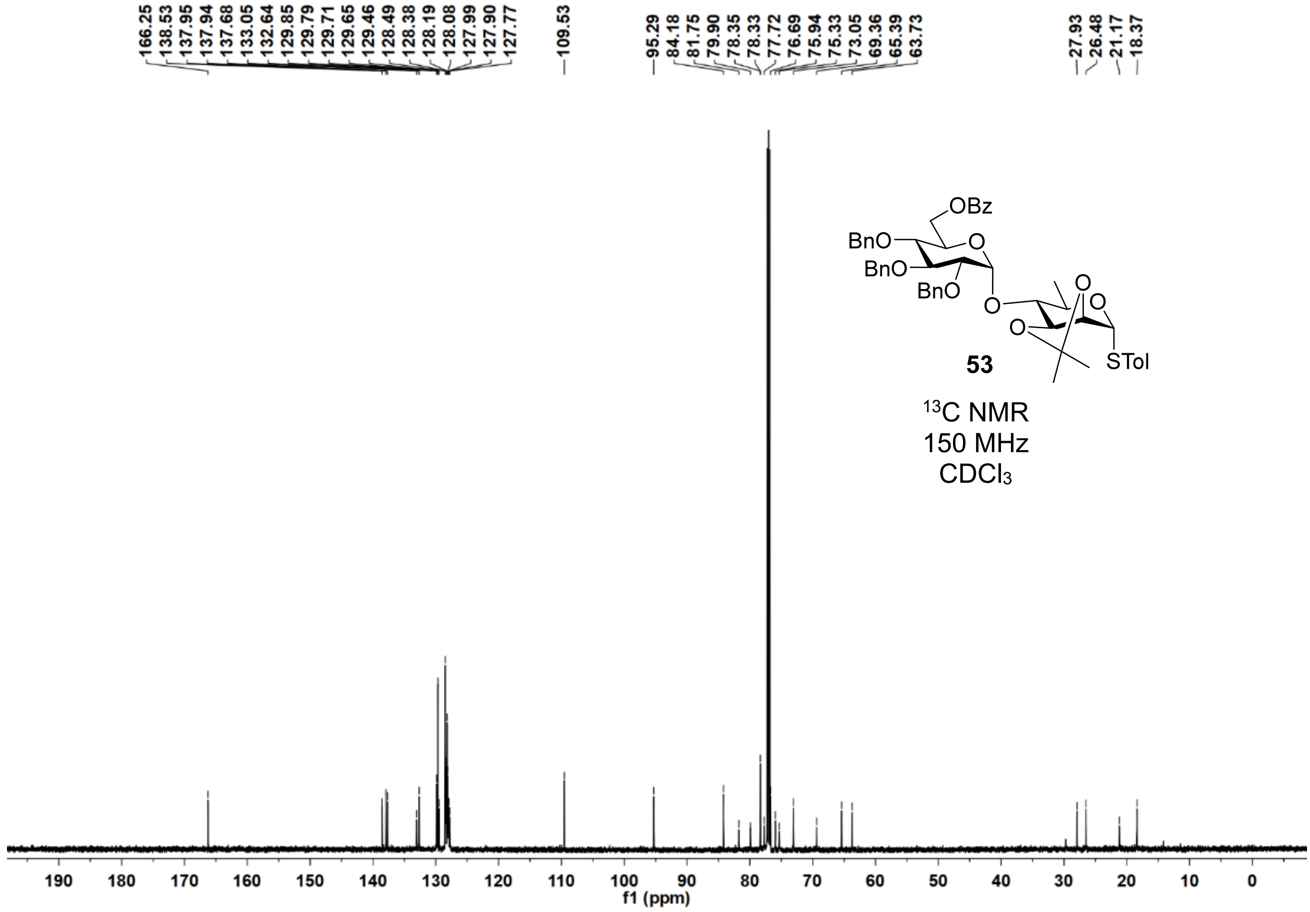

8.101
8.089
7.993
7.981
7.648
7.547
7.484
7.471
7.414
7.401
7.388
7.382
7.376
7.293
7.281
7.275
7.271
7.258
7.251
7.245
7.200
7.187
6.985
6.972
6.872
6.860
6.827
6.814
6.802
6.757
5.423
5.405
5.360
5.354
4.914
4.900
4.896
4.882
4.778
4.759
4.617
4.604
4.600
4.528
4.483
4.468
4.432
4.429
4.401
4.394
4.342
4.321
4.301
4.284
4.131
4.008
4.003
3.995
3.988
3.763
3.570
3.516
3.510
2.269
OBz
BnO
O
BnO
BnO
OBn
O
O
BnO
STol
NPhth
51
1H NMR
600 MHz
CDCl3
1.00
1.96
0.98
10.09
9.98
7.02
2.02
5.03
1.01
1.00
2.01
1.99
2.80
1.83
1.05
1.01
0.98
2.07
0.99
1.04
1.94
1.07
1.05
1.03
1.00
3.05
f1 (ppm)

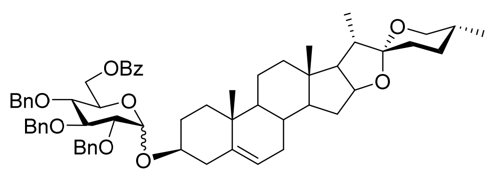

166.11
138.27
138.23
138.16
138.05
137.82
137.73
133.64
133.38
133.03
130.15
129.90
129.63
129.51
128.86
128.47
128.44
128.39
128.36
128.23
128.04
127.88
127.86
127.72
127.70
127.66
127.46
127.43
126.90
126.26
97.30
83.45
81.71
80.76
79.99
79.30
77.70
76.44
75.75
75.20
73.94
73.26
73.25
69.79
68.76
63.49
54.53
21.13
OBz
BnO
O
BnO
BnO
OBn
O
O
BnO
STol
NPhth
51
13C NMR
150 MHz
CDCl3
f1 (ppm)


8.001 7.988 7.919 7.906 7.481 7.470 7.459 7.415 7.403 7.355 7.349 7.345 7.334 7.321 7.309 7.297 7.286 7.274 7.261 7.252 7.250 7.246 7.169 7.165 7.160 6.894 6.891 6.885 5.801 5.795 5.497 4.959 4.940 4.911 4.893 4.772 4.757 4.708 4.684 4.672 4.667 4.653 4.498 4.491 4.463 4.364 4.344 4.335 4.316 4.240 4.220 4.052 4.031 3.883 3.868 3.595 3.532 3.526 3.477 3.355 1.344 1.333 1.297 1.285
Ph
OBz
BnO
BnO
BnO
BzO
O
S
52
^{1}H NMR
600 MHz
$CDCl_3$
4.03 4.16 2.07 11.18 4.06 3.05 1.93 1.01 1.01 1.04 1.00 1.07 1.00 3.08 0.93 1.09 2.05 1.08 1.01 1.02 2.00 1.01 1.00 1.05 1.07 2.92 3.00
f1 (ppm)


166.17 166.12 138.50 138.06 137.99 137.70 133.38 132.91 129.78 129.73 129.69 129.51 128.91 128.41 128.35 128.30 128.17 128.10 128.09 127.92 127.67 127.62 127.42 127.38 126.17 100.95 95.99 83.89 81.14 79.88 77.21 75.78 74.55 74.48 73.87 73.13 70.42 69.37 69.13 68.88 63.26 34.57 24.33 23.68
Ph
OBz
BnO
BnO
BnO
BzO
O
S
52
^{13}C NMR
150 MHz
$CDCl_3$
f1 (ppm)

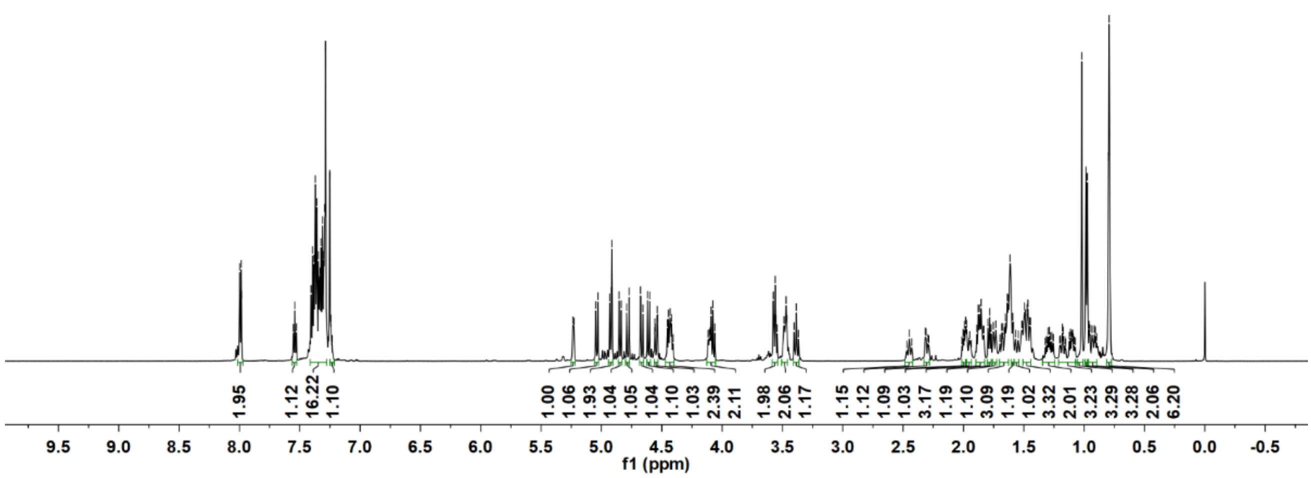

8.002 7.989 7.541 7.529 7.443 7.431 7.424 7.411 7.397 7.381 7.373 7.360 7.351 7.339 7.329 7.317 7.310 7.283 7.273 7.256 7.246 7.242 7.236 7.231 7.145 7.132 5.666 5.659 5.053 5.036 4.930 4.912 4.868 4.857 4.849 4.839 4.761 4.742 4.623 4.605 4.500 4.496 4.469 4.461 4.354 4.343 4.317 4.308 4.011 3.995 3.680 3.668 3.663 3.651 3.639 3.632 3.622 3.615 3.597 2.340 1.439 1.338 1.266 1.256
OBz
BnO
BnO
BnO
O
O
O
O
STol
53
1H NMR
600 MHz
CDCl3
1.97 1.05 18.26 1.07 1.95 1.92 0.97 1.04 1.92 0.99 1.04 1.05 1.03 1.00 1.00 1.05 1.06 0.99 3.13 2.99 2.95 3.02 3.15
f1 (ppm)

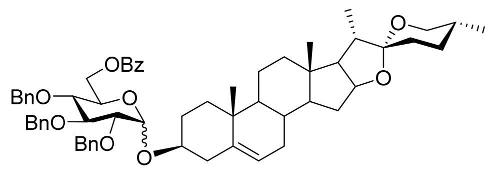

166.25 138.53 137.95 137.94 137.68 133.05 132.64 129.85 129.79 129.71 129.65 129.46 128.49 128.38 128.19 128.08 127.99 127.90 127.77 109.53 95.29 84.18 81.75 79.90 78.35 78.33 77.72 76.69 75.94 75.33 73.05 69.36 65.39 63.73 27.93 26.48 21.17 18.37
OBz
BnO
BnO
BnO
O
O
O
O
STol
53
13C NMR
150 MHz
CDCl3
f1 (ppm)



54

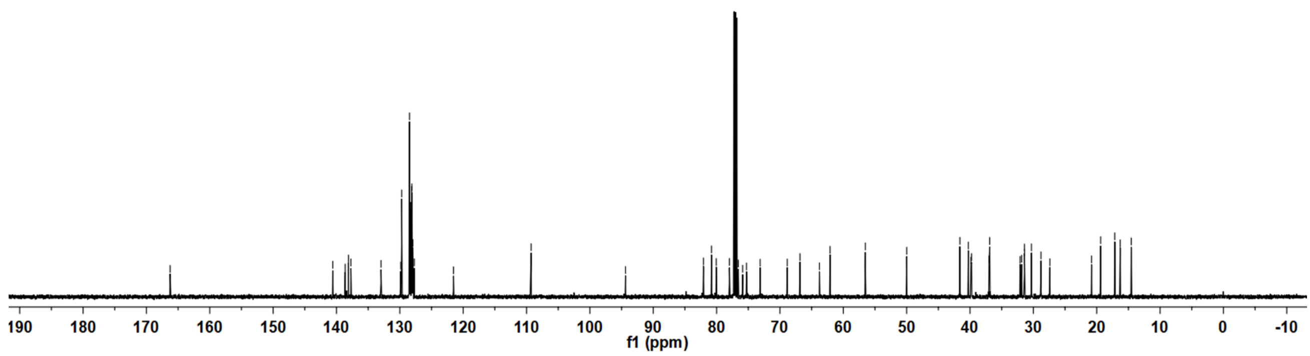
^{1}H NMR
600 MHz
$CDCl_3$

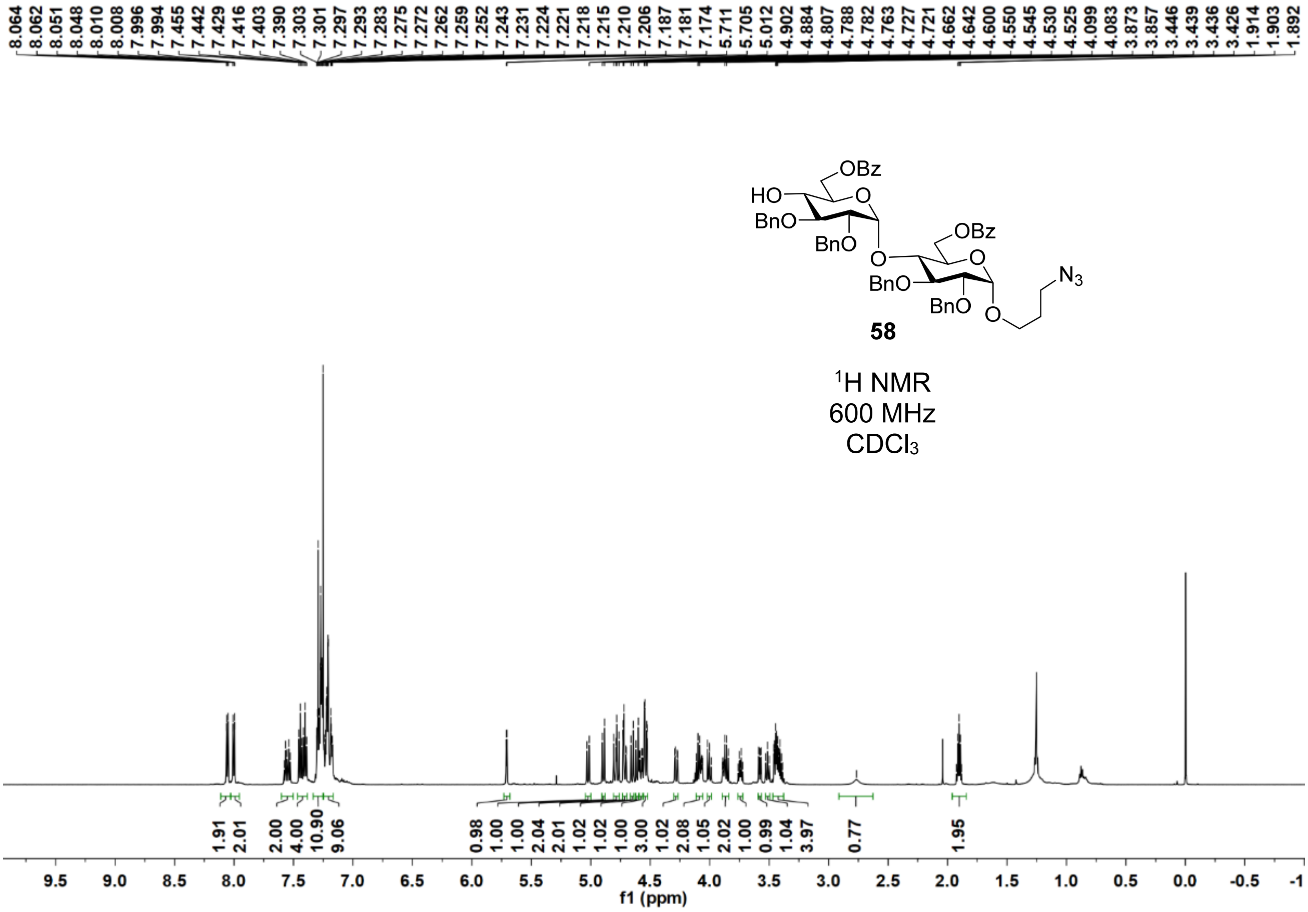


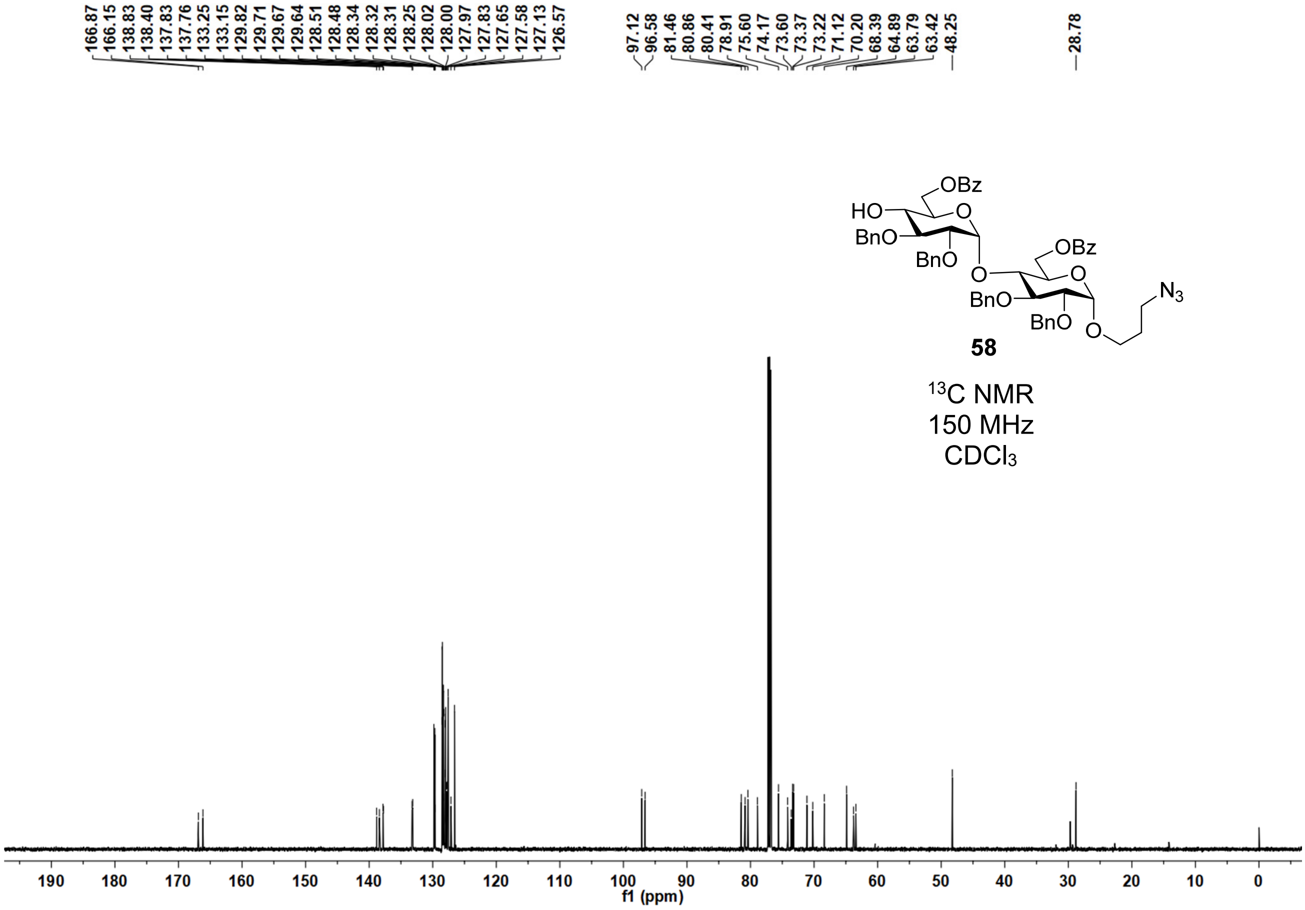


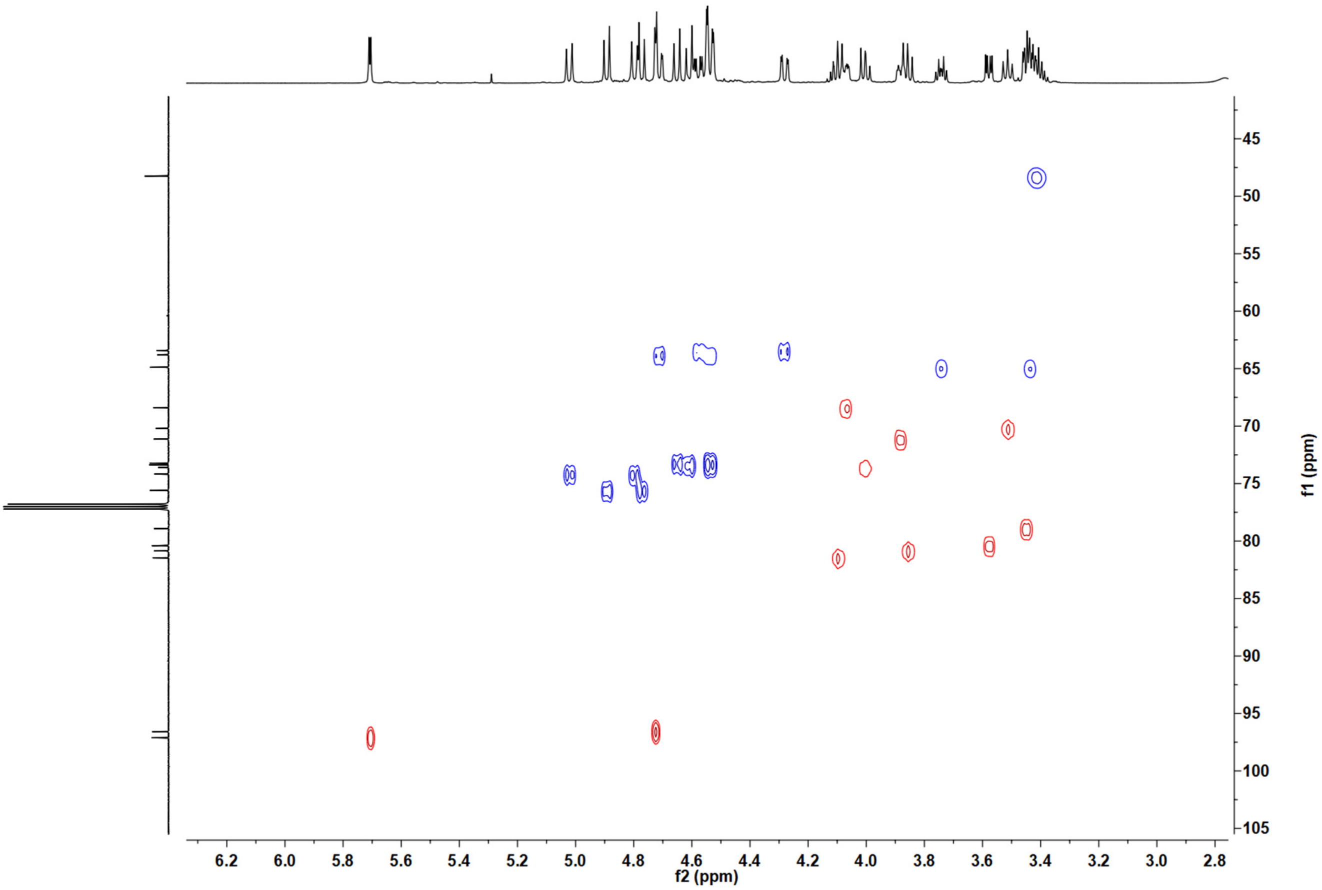
54

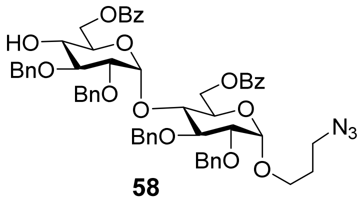
^{13}C NMR
150 MHz
$CDCl_3$




8.064 8.062 8.051 8.048 8.010 8.008 7.996 7.994 7.455 7.442 7.429 7.416 7.403 7.390 7.303 7.301 7.297 7.293 7.283 7.275 7.272 7.262 7.259 7.252 7.243 7.231 7.224 7.221 7.218 7.215 7.210 7.206 7.187 7.181 7.174 5.711 5.705 5.012 4.902 4.884 4.807 4.788 4.782 4.763 4.727 4.721 4.662 4.642 4.600 4.550 4.545 4.530 4.525 4.099 4.083 3.873 3.857 3.446 3.439 3.436 3.426 1.914 1.903 1.892
OBz
HO
O
BnO
BnO
O
OBz
O
N3
BnO
BnO
O
58
1H NMR
600 MHz
CDCl3
1.91 2.01 2.00 4.00 10.90 9.06 0.98 1.00 1.00 2.04 2.01 1.02 1.02 1.00 3.00 1.02 2.08 1.05 2.02 1.00 0.99 1.04 3.97 0.77 1.95
9.5 9.0 8.5 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 0.0 -0.5 -1
f1 (ppm)

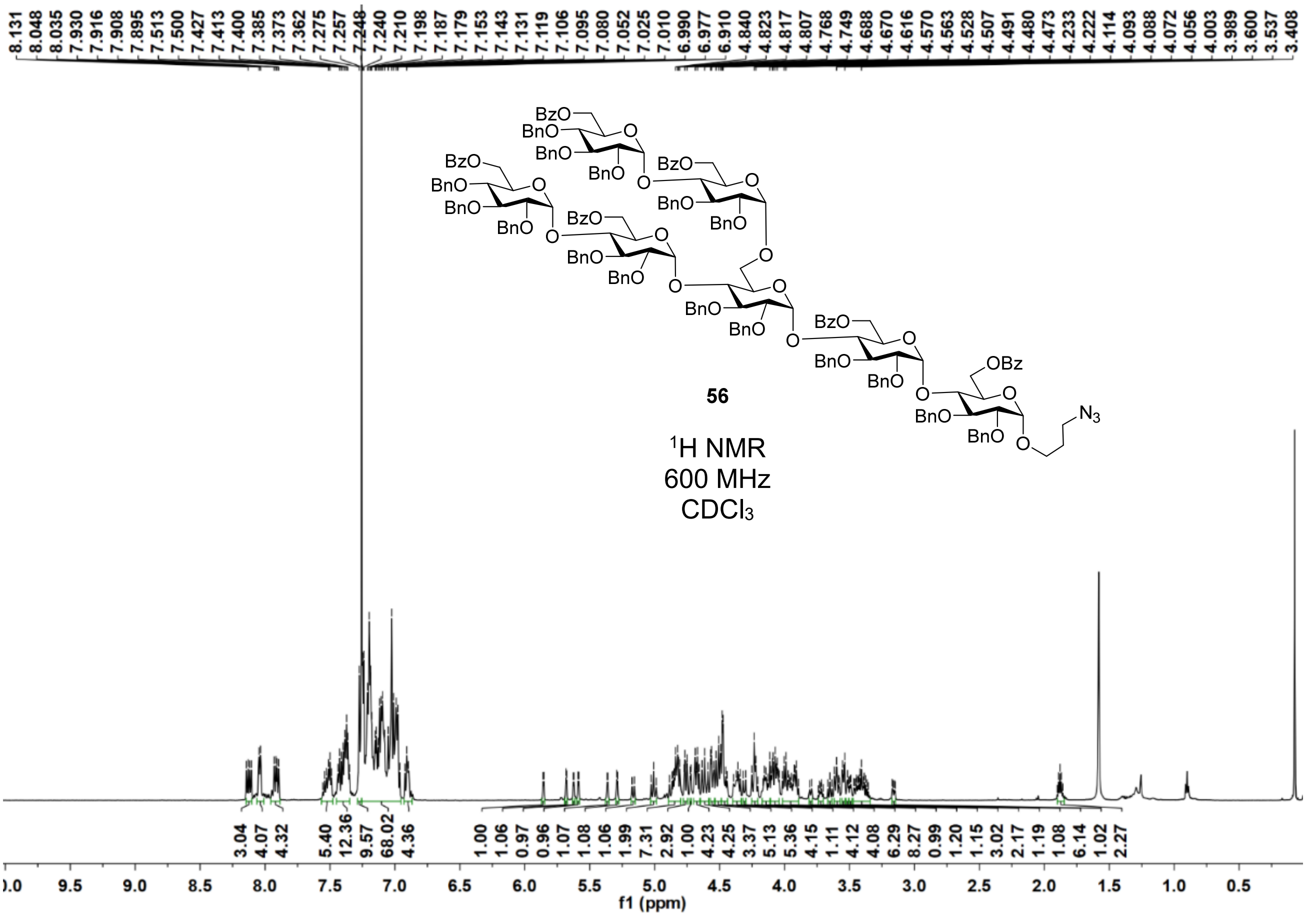

166.87 166.15 138.83 138.40 137.83 137.76 133.25 133.15 129.82 129.71 129.67 129.64 128.51 128.48 128.34 128.32 128.31 128.25 128.02 128.00 127.97 127.83 127.65 127.58 127.13 126.57
97.12 96.58 81.46 80.86 80.41 78.91 75.60 74.17 73.60 73.37 73.22 71.12 70.20 68.39 64.89 63.79 63.42 48.25
28.78
OBz
HO
O
BnO
BnO
O
OBz
O
N3
BnO
BnO
O
58
13C NMR
150 MHz
CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

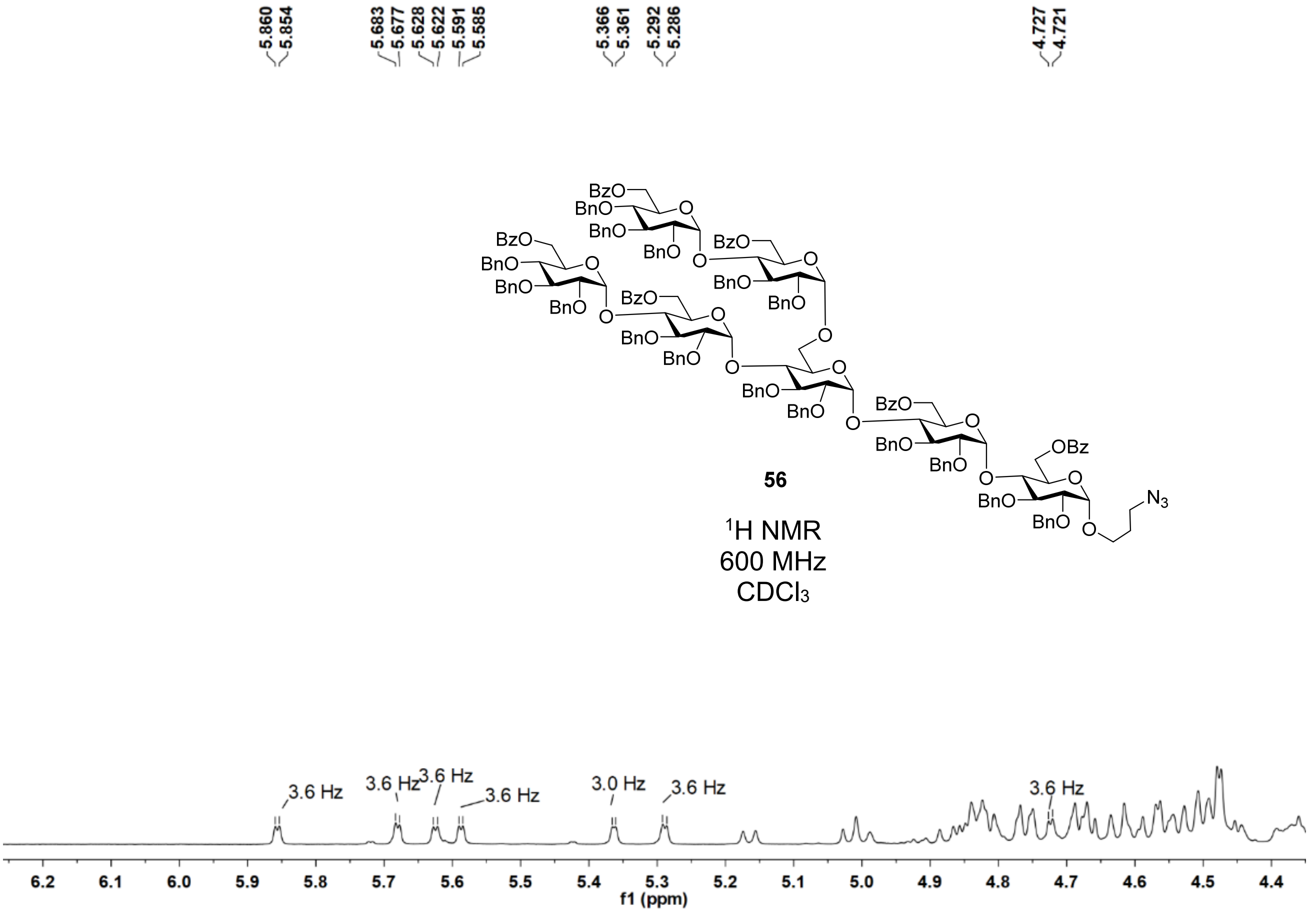


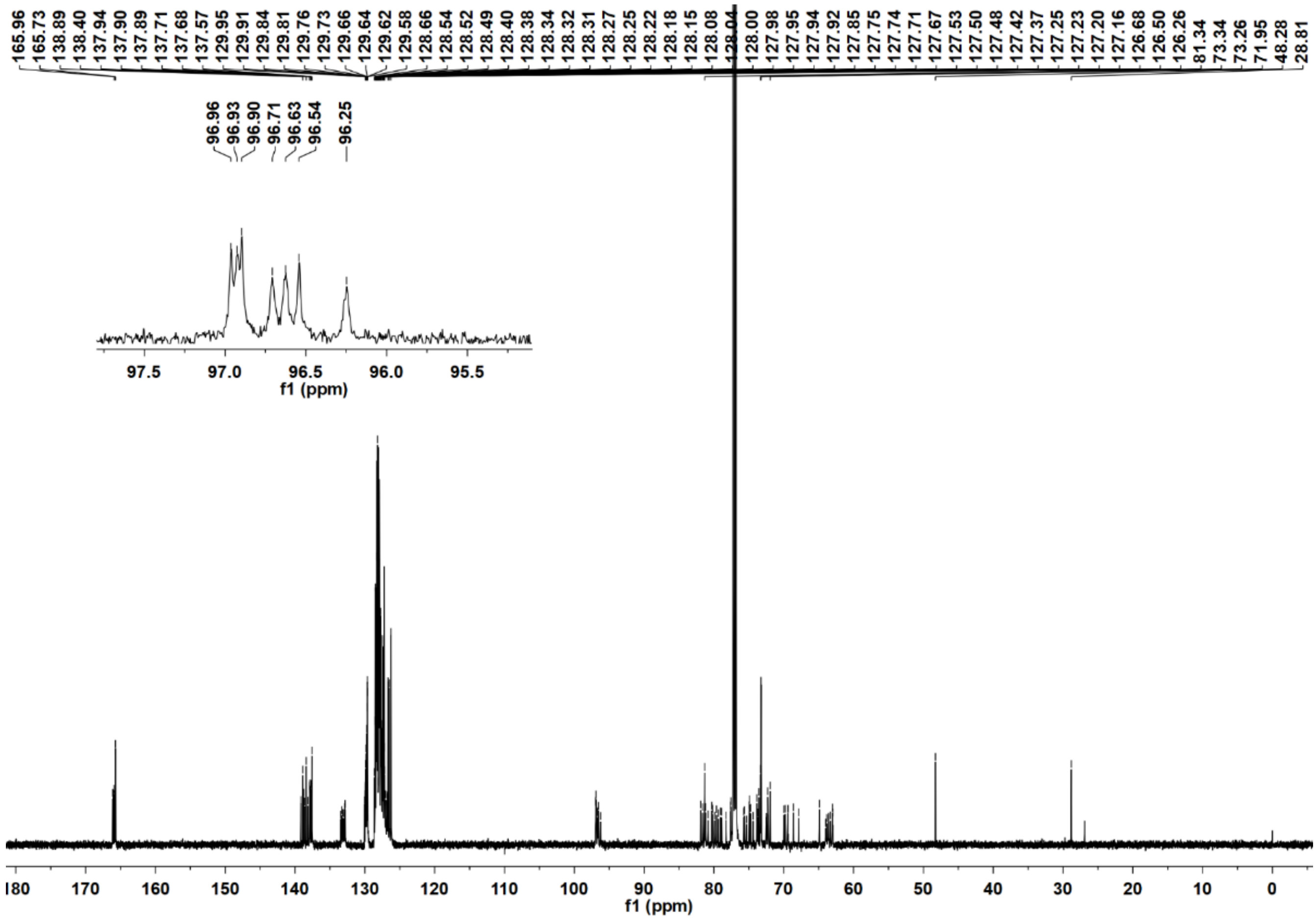


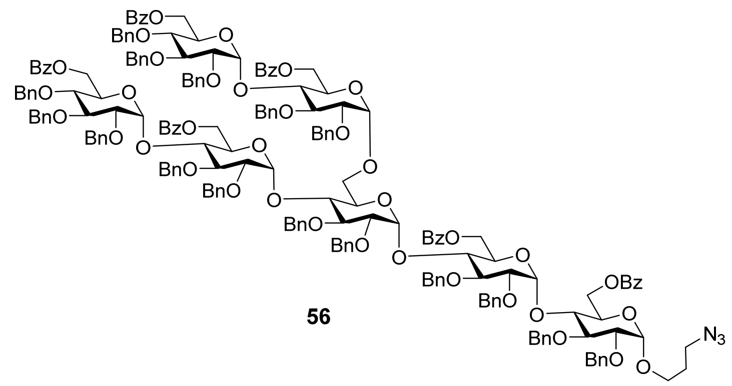
58

^{1}H- ^{13}C HSQC
600/150 MHz
$CDCl_3$


56
^{1}H NMR
600 MHz
CDCl$_3$
f1 (ppm)

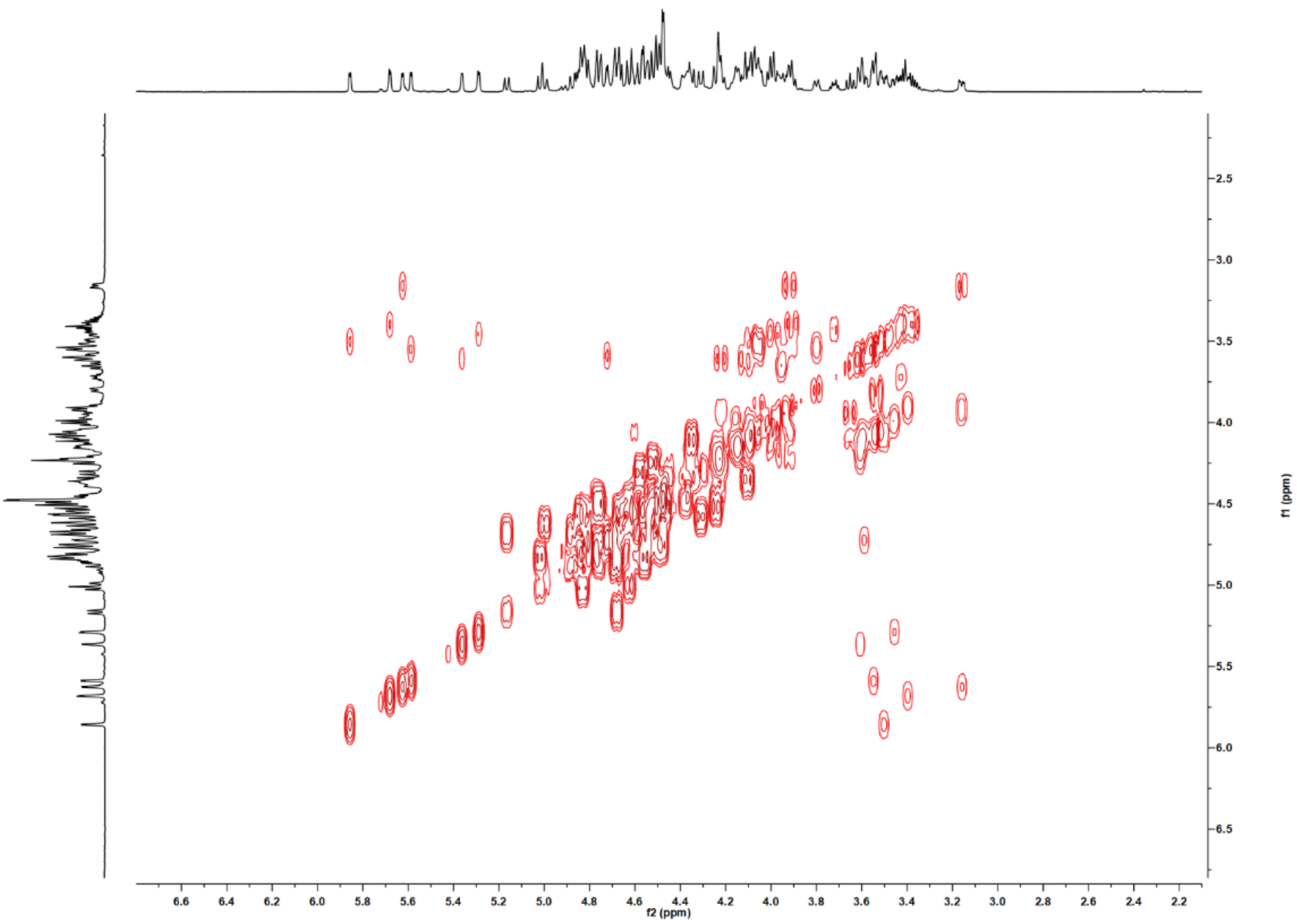

56
^{1}H NMR
600 MHz
CDCl$_3$
3.6 Hz
3.6 Hz
3.6 Hz
3.6 Hz
3.0 Hz
3.6 Hz
3.6 Hz
f1 (ppm)

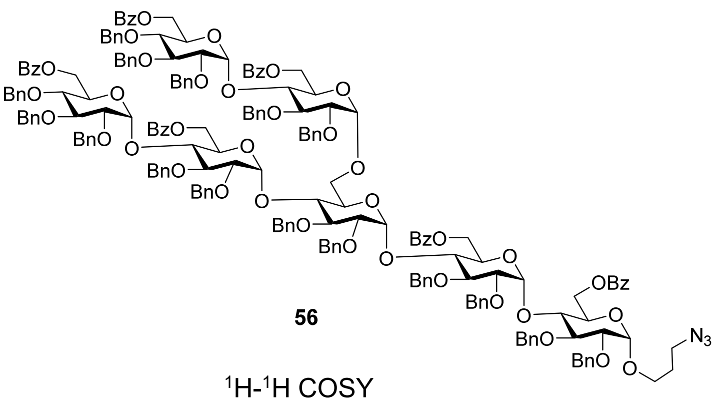




56

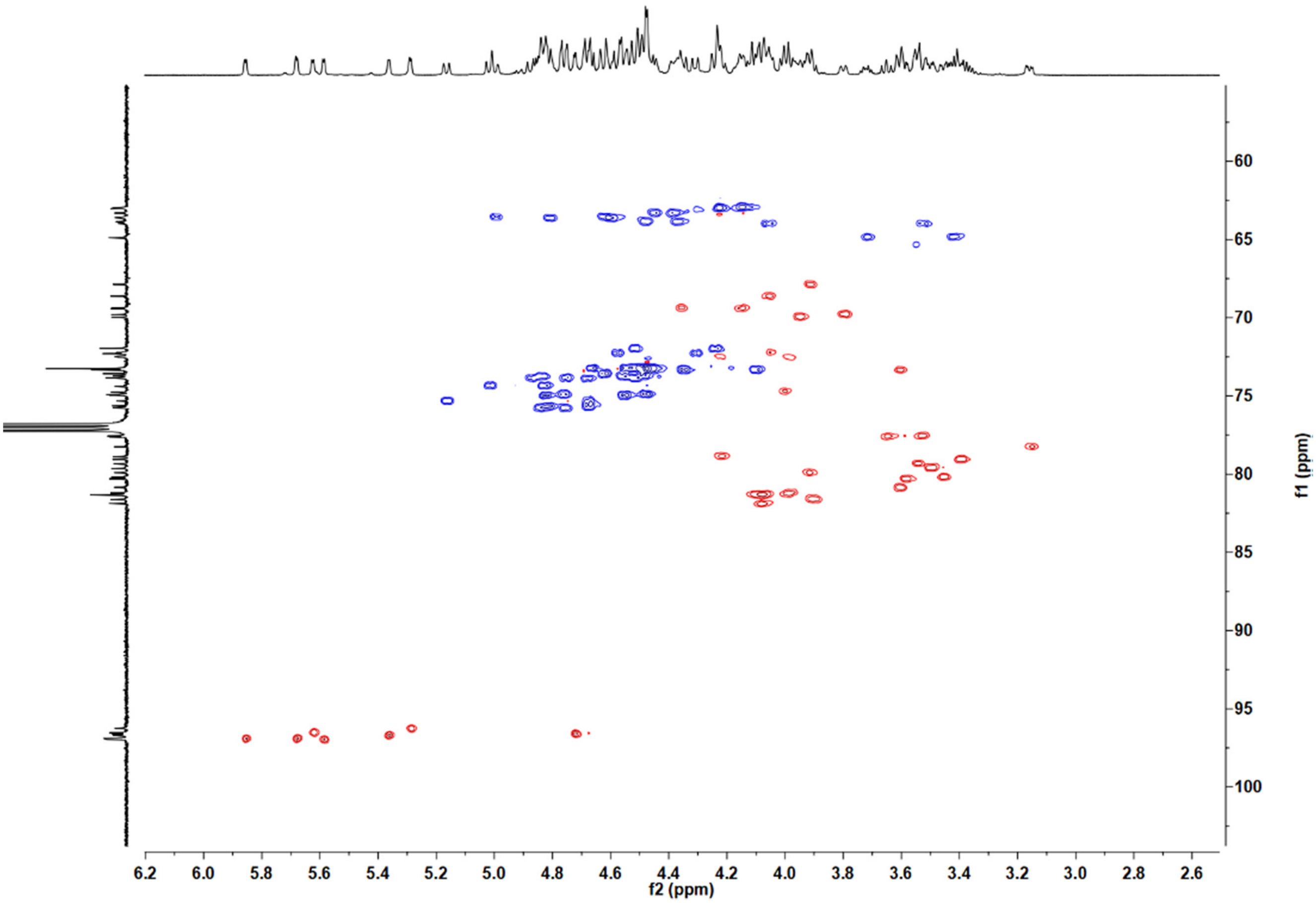
^{13}C NMR
150 MHz
$CDCl_3$

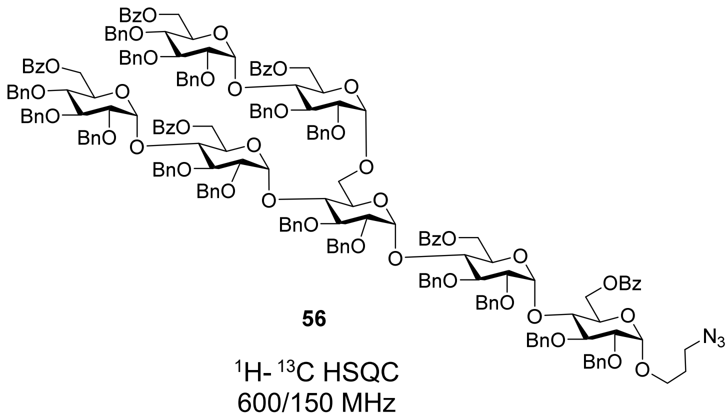




56

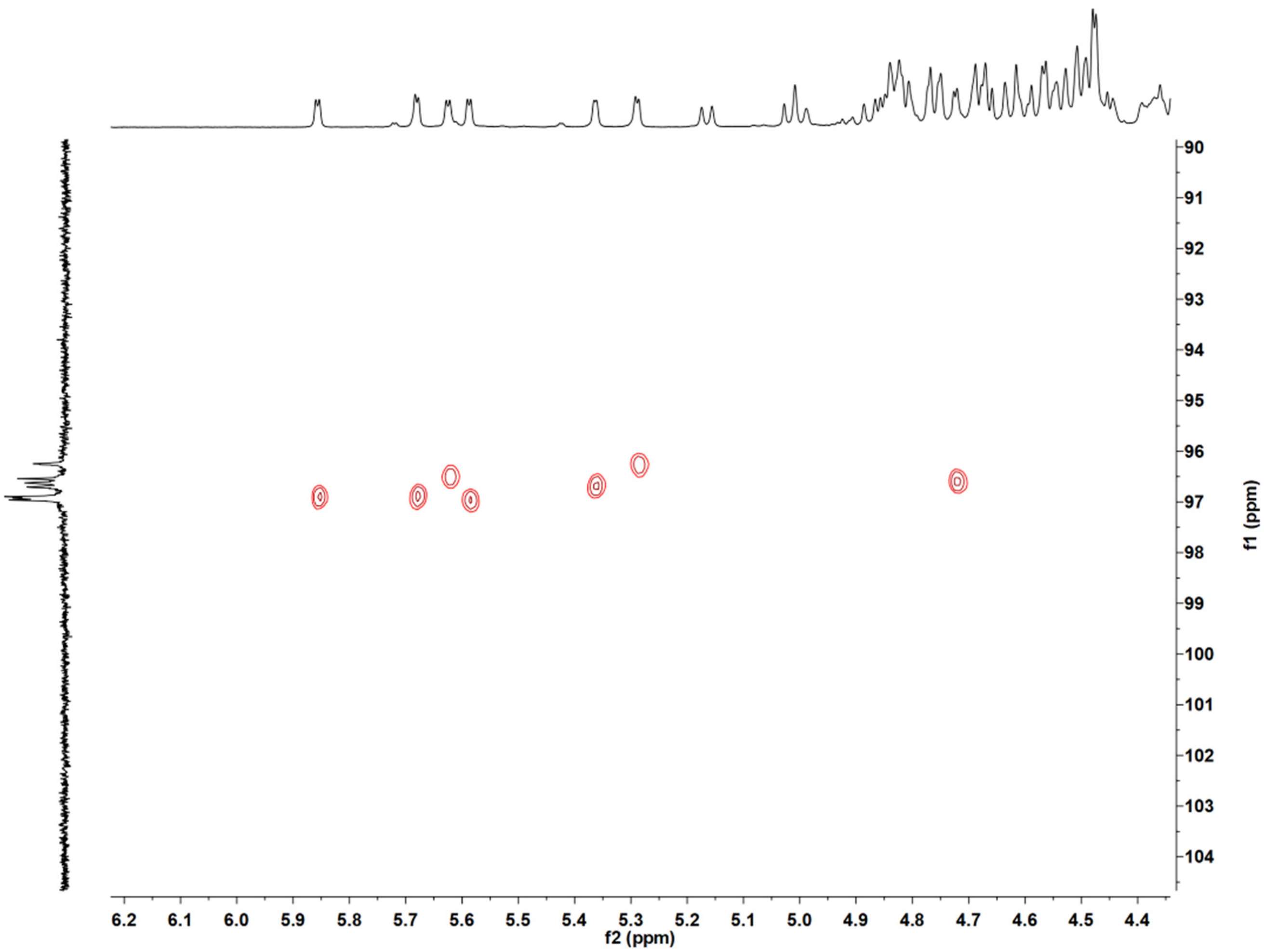
^{1}H-^{1}H COSY
600 MHz
$CDCl_3$

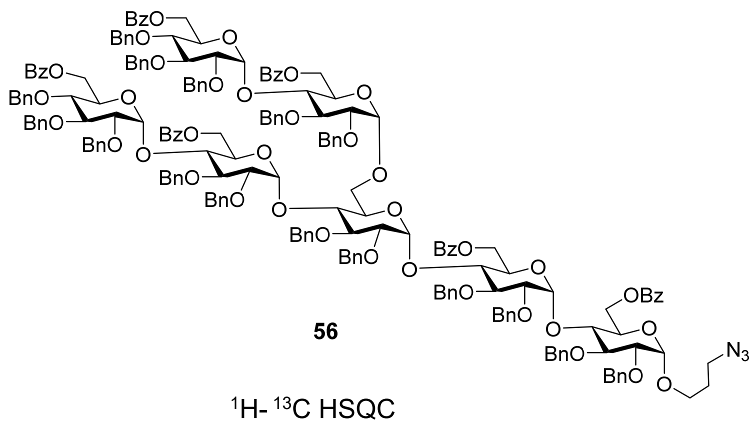




56

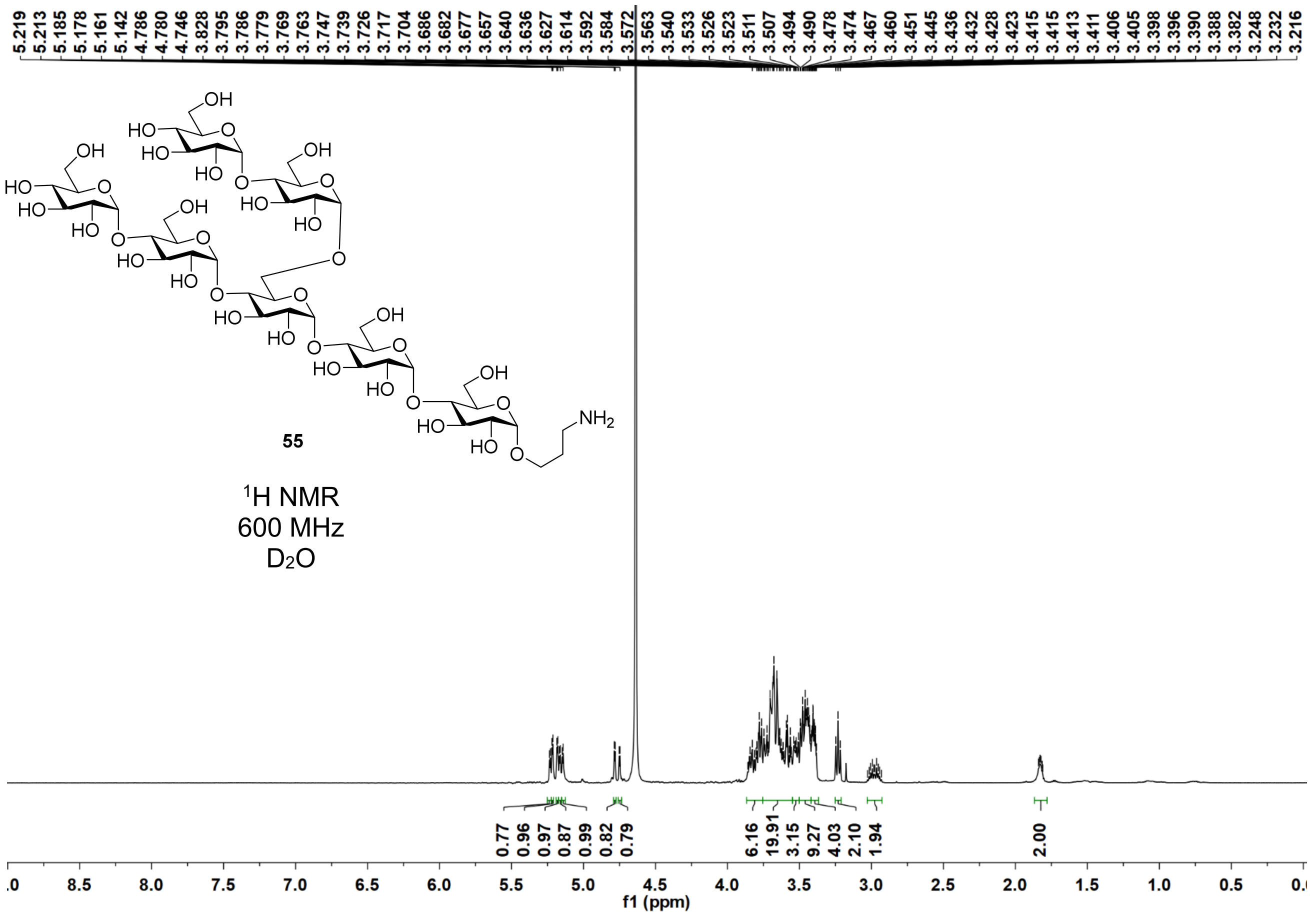
^{1}H- ^{13}C HSQC
600/150 MHz
$CDCl_3$

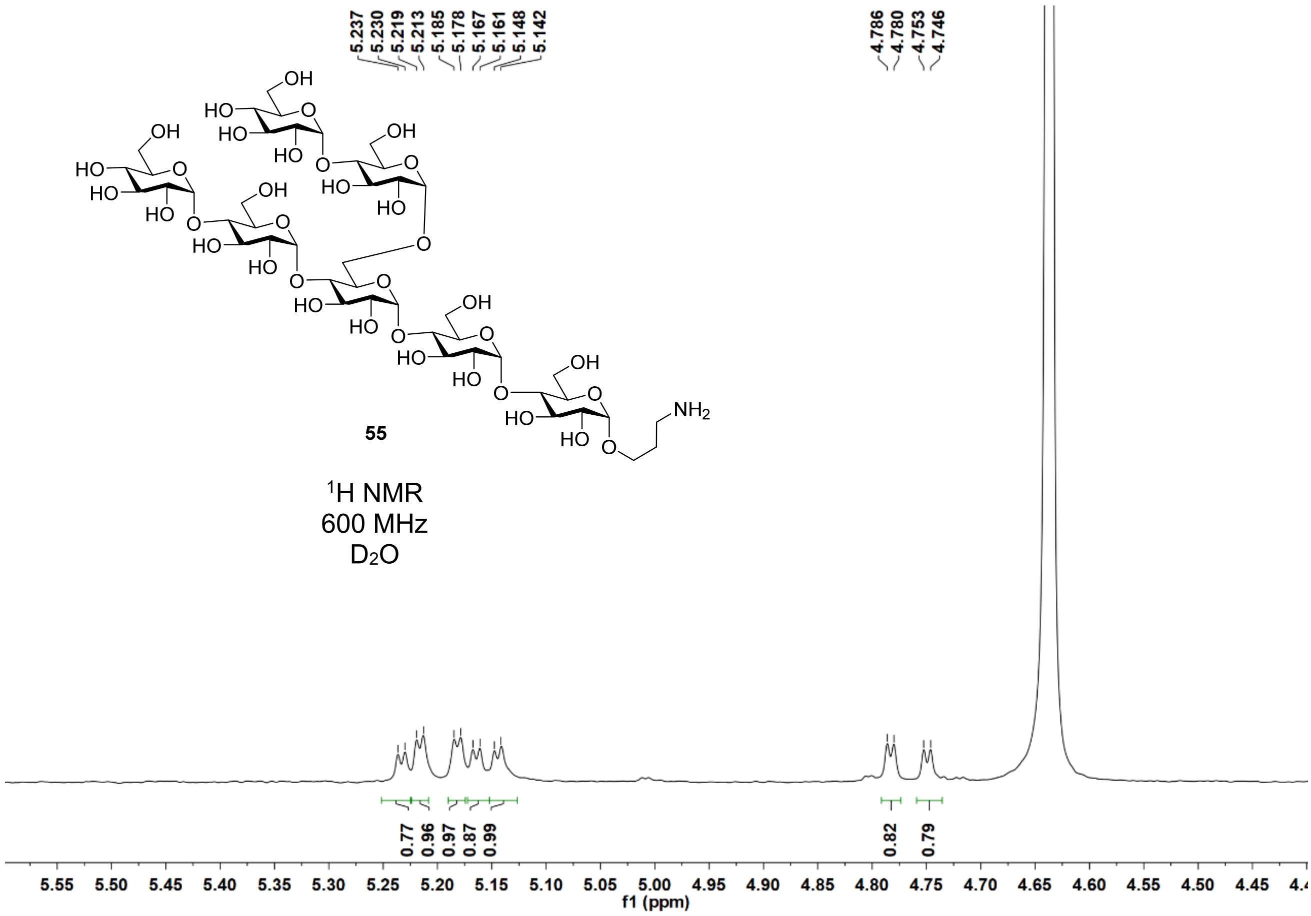


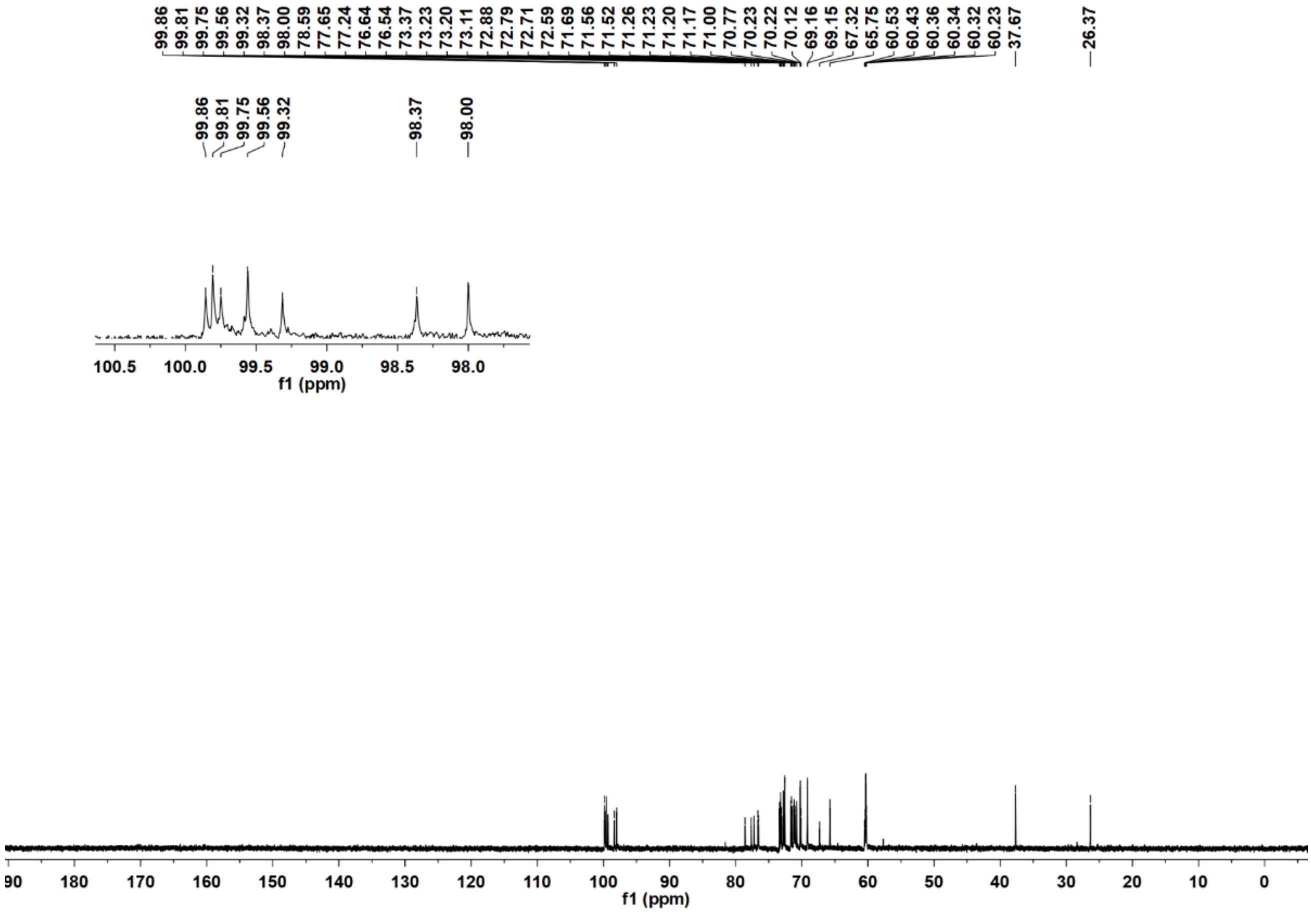


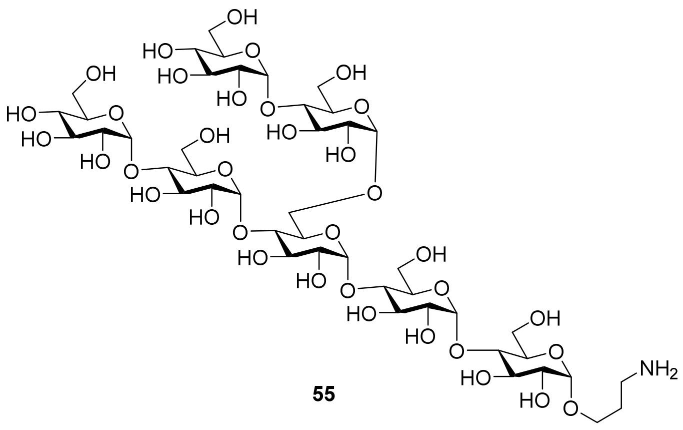
56

^{1}H- ^{13}C HSQC
600/150 MHz
$CDCl_3$


5.219 5.213 5.185 5.178 5.161 5.142 4.786 4.780 4.746 3.828 3.795 3.786 3.779 3.769 3.763 3.747 3.739 3.726 3.717 3.704 3.686 3.682 3.677 3.657 3.640 3.636 3.627 3.614 3.592 3.584 3.572 3.563 3.540 3.533 3.526 3.523 3.511 3.507 3.494 3.490 3.478 3.474 3.467 3.460 3.451 3.445 3.436 3.432 3.428 3.423 3.415 3.415 3.413 3.411 3.406 3.405 3.398 3.396 3.390 3.388 3.382 3.248 3.232 3.216
55
^{1}H NMR
600 MHz
D_2O
0.77 0.96 0.97 0.87 0.99 0.82 0.79 6.16 19.91 3.15 9.27 4.03 2.10 1.94 2.00
f1 (ppm)

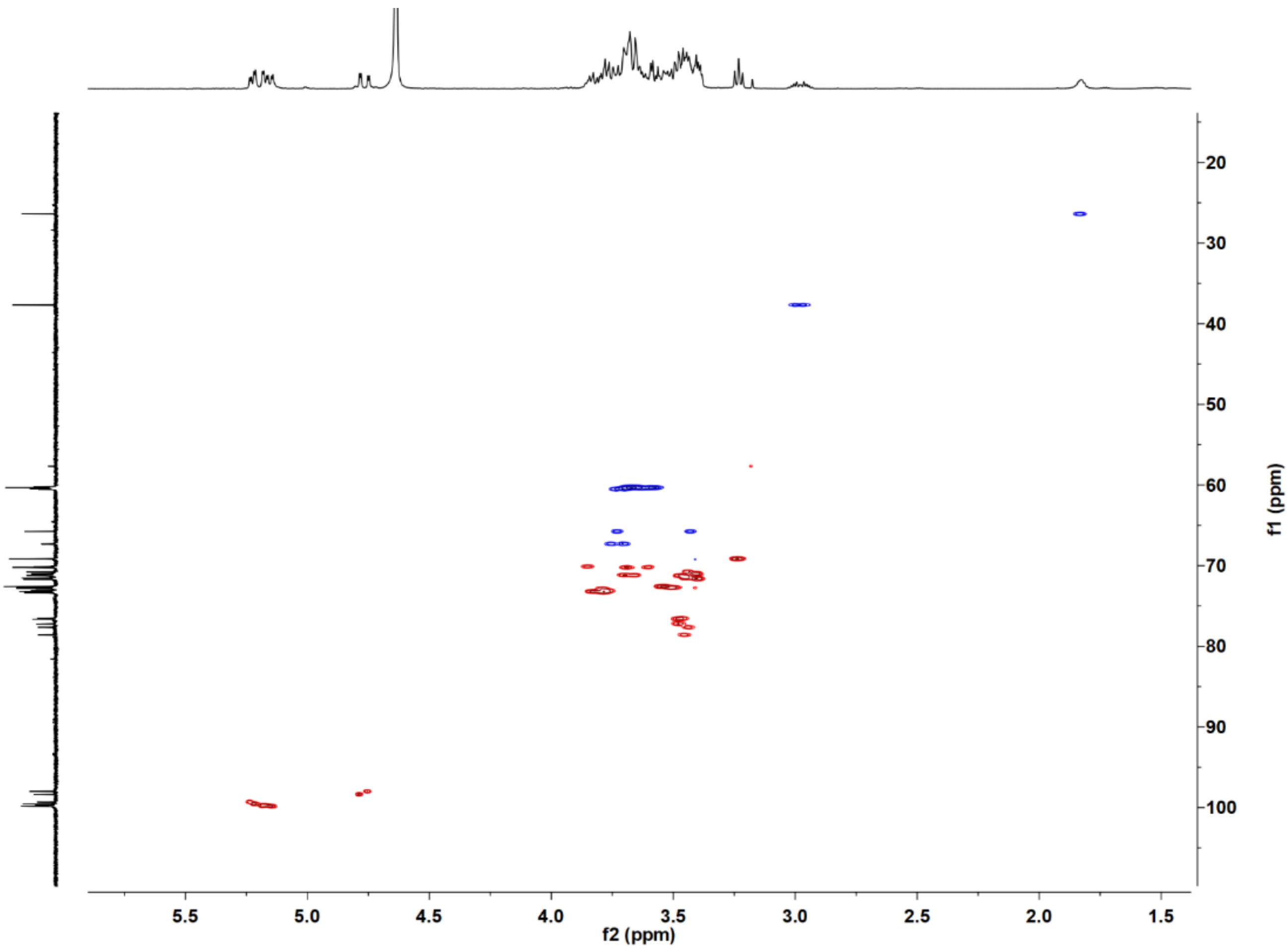

5.237 5.230 5.219 5.213 5.185 5.178 5.167 5.161 5.148 5.142
4.786 4.780 4.753 4.746
55
^{1}H NMR
600 MHz
D_2O
0.77 0.96 0.97 0.87 0.99 0.82 0.79
f1 (ppm)

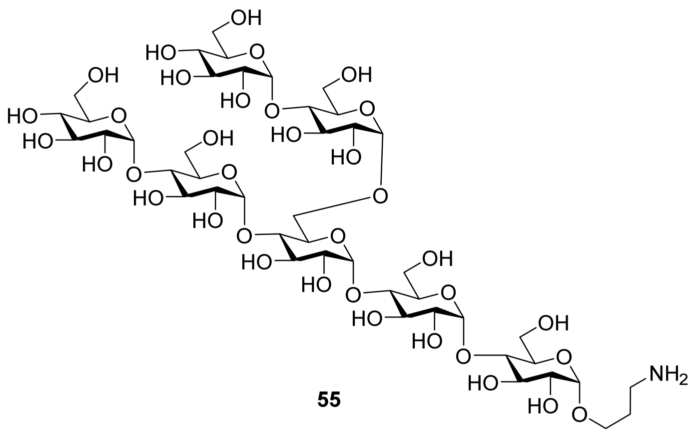




55

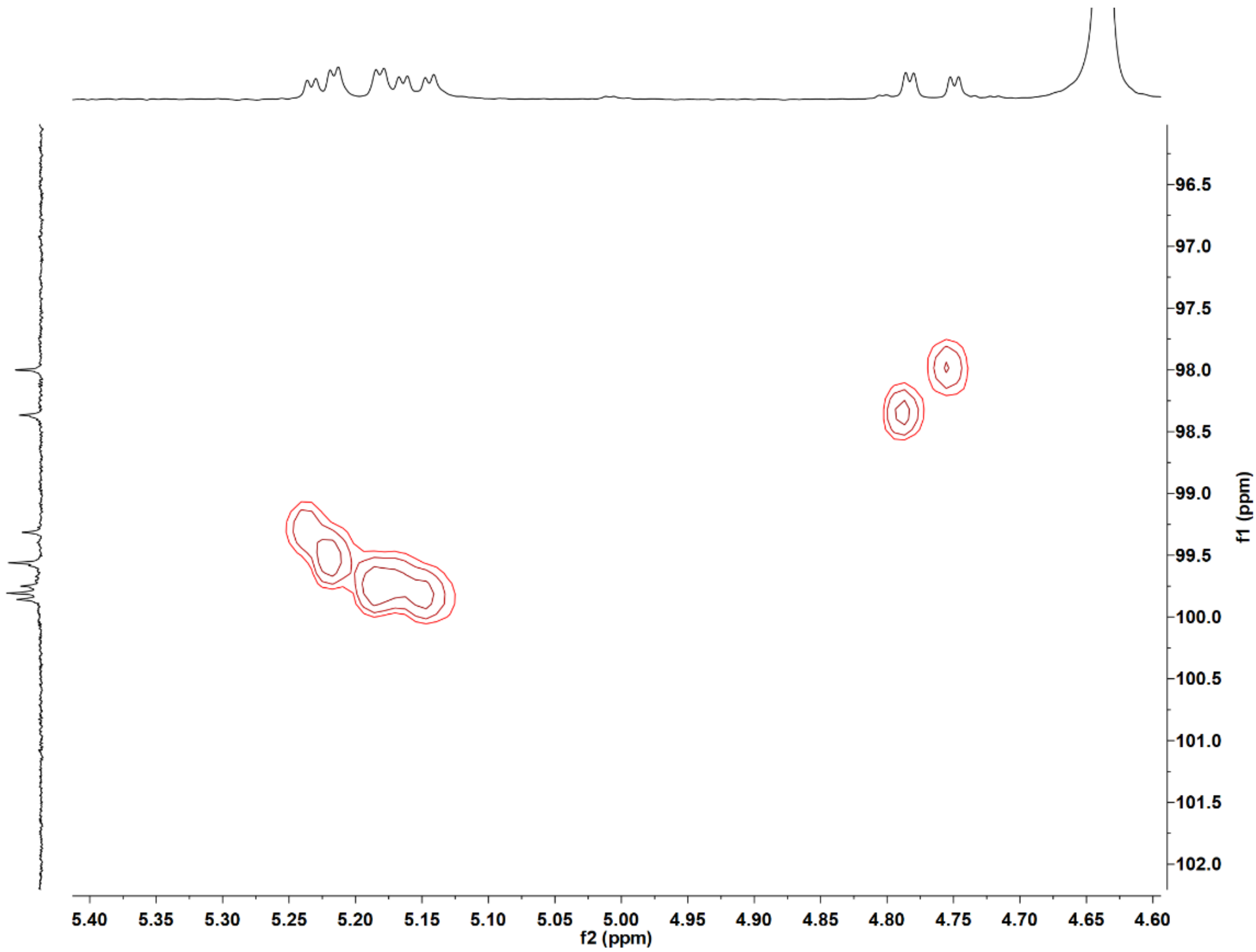
^{13}C NMR
150 MHz
D_2O

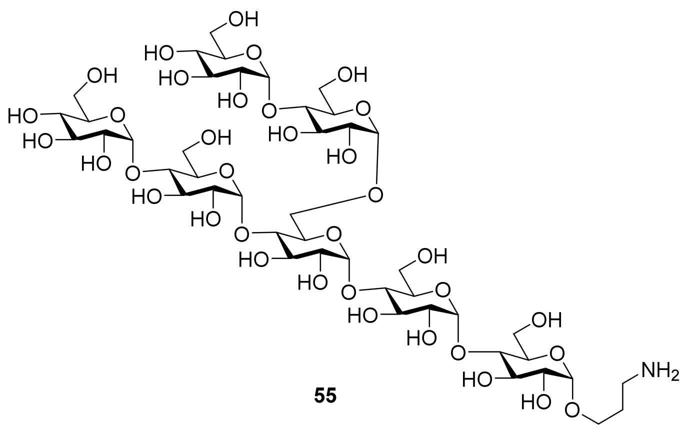




55

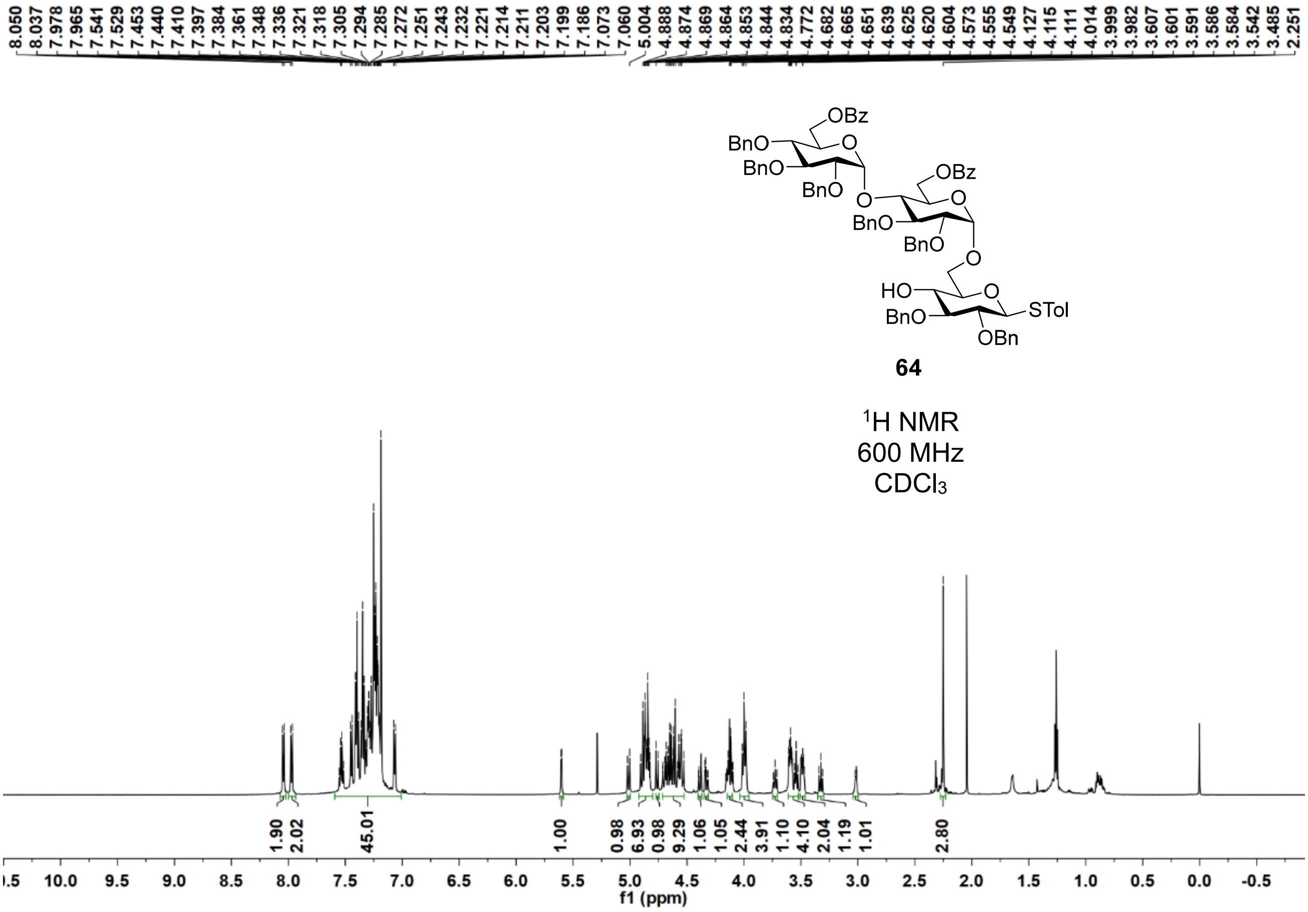
^{1}H- ^{13}C HSQC
600/150 MHz
D_2O



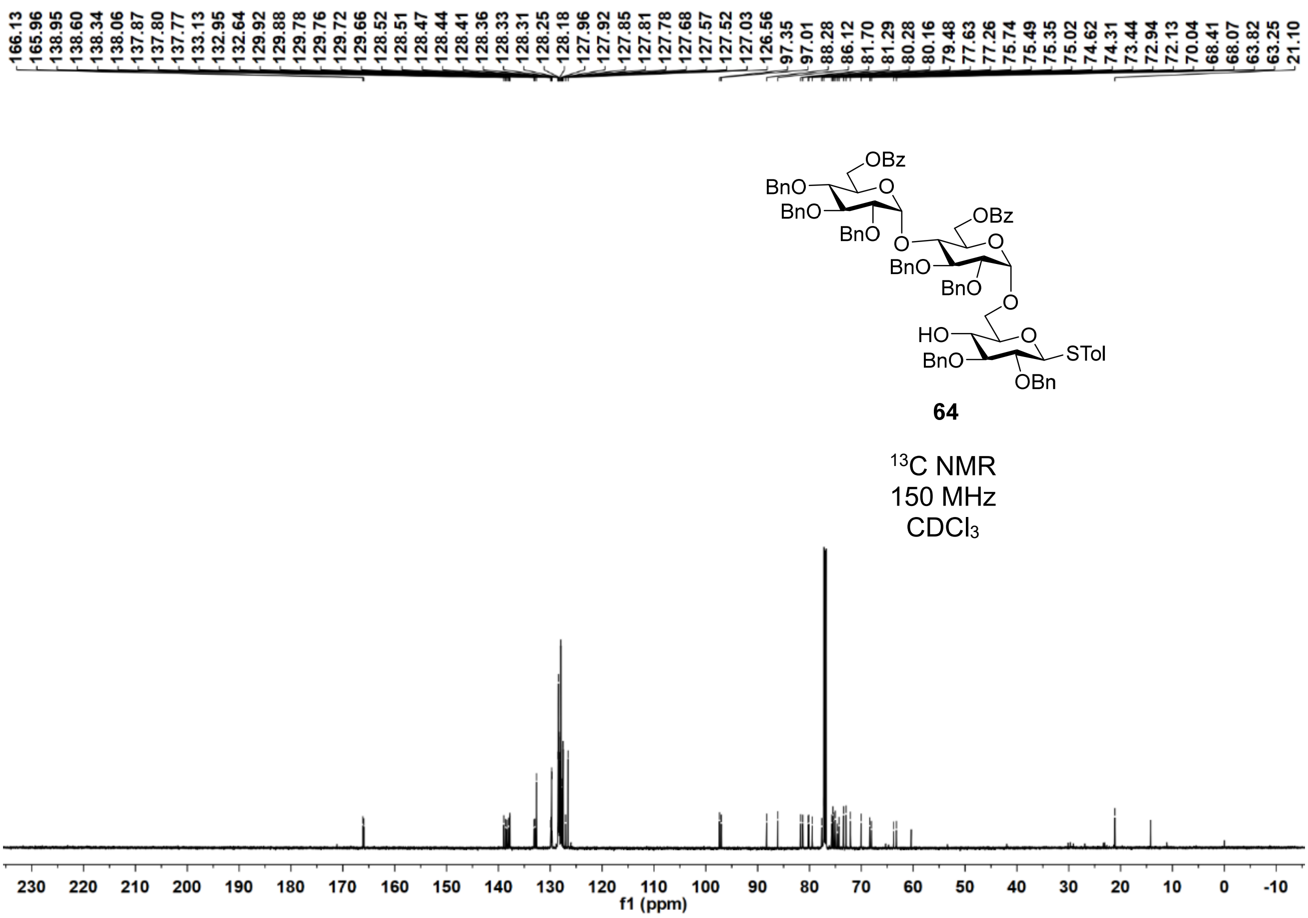


55

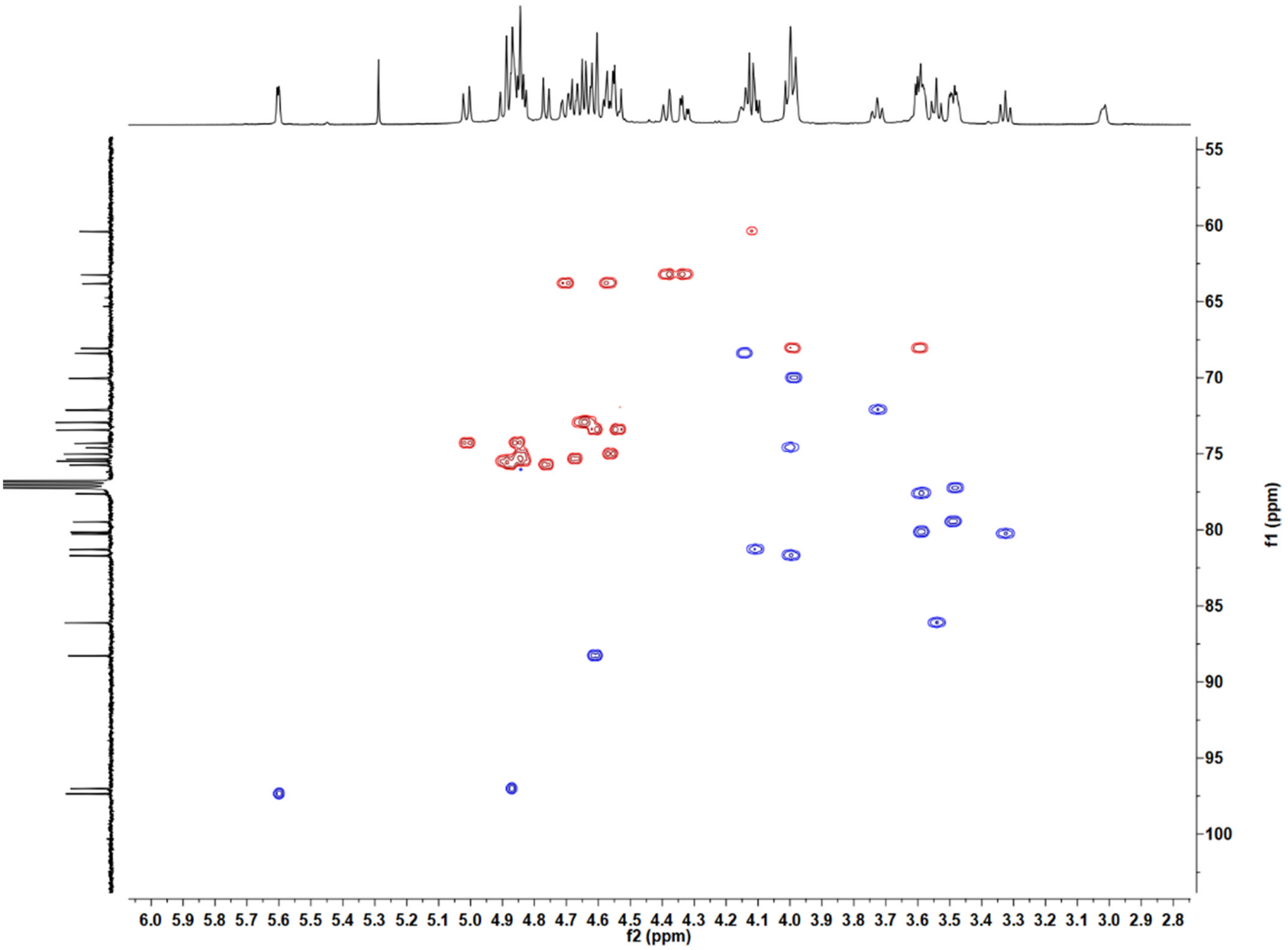
^{1}H- ^{13}C HSQC
600/150 MHz
D_2O

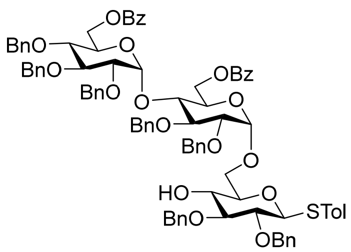


8.050 8.037 7.978 7.965 7.541 7.529 7.453 7.440 7.410 7.397 7.384 7.361 7.348 7.336 7.321 7.318 7.305 7.294 7.285 7.272 7.251 7.243 7.232 7.221 7.214 7.211 7.203 7.199 7.186 7.073 7.060 5.004 4.888 4.874 4.869 4.864 4.853 4.844 4.834 4.772 4.682 4.665 4.651 4.639 4.625 4.620 4.604 4.573 4.555 4.549 4.127 4.115 4.111 4.014 3.999 3.982 3.607 3.601 3.591 3.586 3.584 3.542 3.485 2.251
BnO
OBz
BnO
BnO
OBz
BnO
BnO
HO
BnO
STol
OBn
64
^{1}H NMR
600 MHz
$CDCl_3$
1.90 2.02 45.01 1.00 0.98 6.93 0.98 9.29 1.06 1.05 2.44 3.91 1.10 4.10 2.04 1.19 1.01 2.80
f1 (ppm)



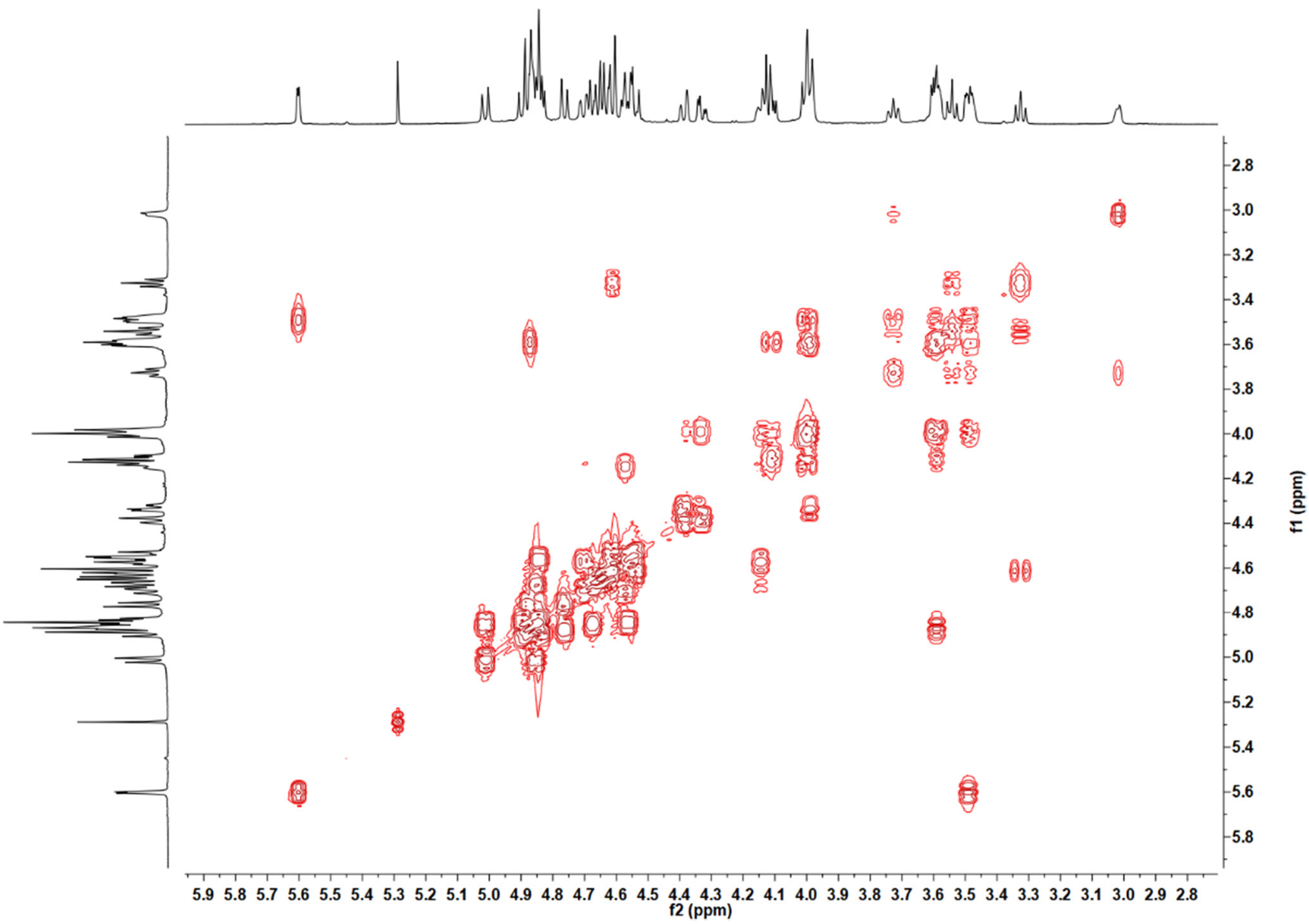
166.13 165.96 138.95 138.60 138.34 138.06 137.87 137.80 137.77 133.13 132.95 132.64 129.92 129.88 129.78 129.76 129.72 129.66 128.52 128.51 128.47 128.44 128.41 128.36 128.33 128.31 128.25 128.18 127.96 127.92 127.85 127.81 127.78 127.68 127.57 127.52 127.03 126.56 97.35 97.01 88.28 86.12 81.70 81.29 80.28 80.16 79.48 77.63 77.26 75.74 75.49 75.35 75.02 74.62 74.31 73.44 72.94 72.13 70.04 68.41 68.07 63.82 63.25 21.10
BnO
OBz
BnO
BnO
OBz
BnO
BnO
HO
BnO
STol
OBn
64
^{13}C NMR
150 MHz
$CDCl_3$
f1 (ppm)

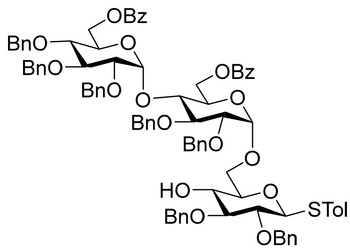




64

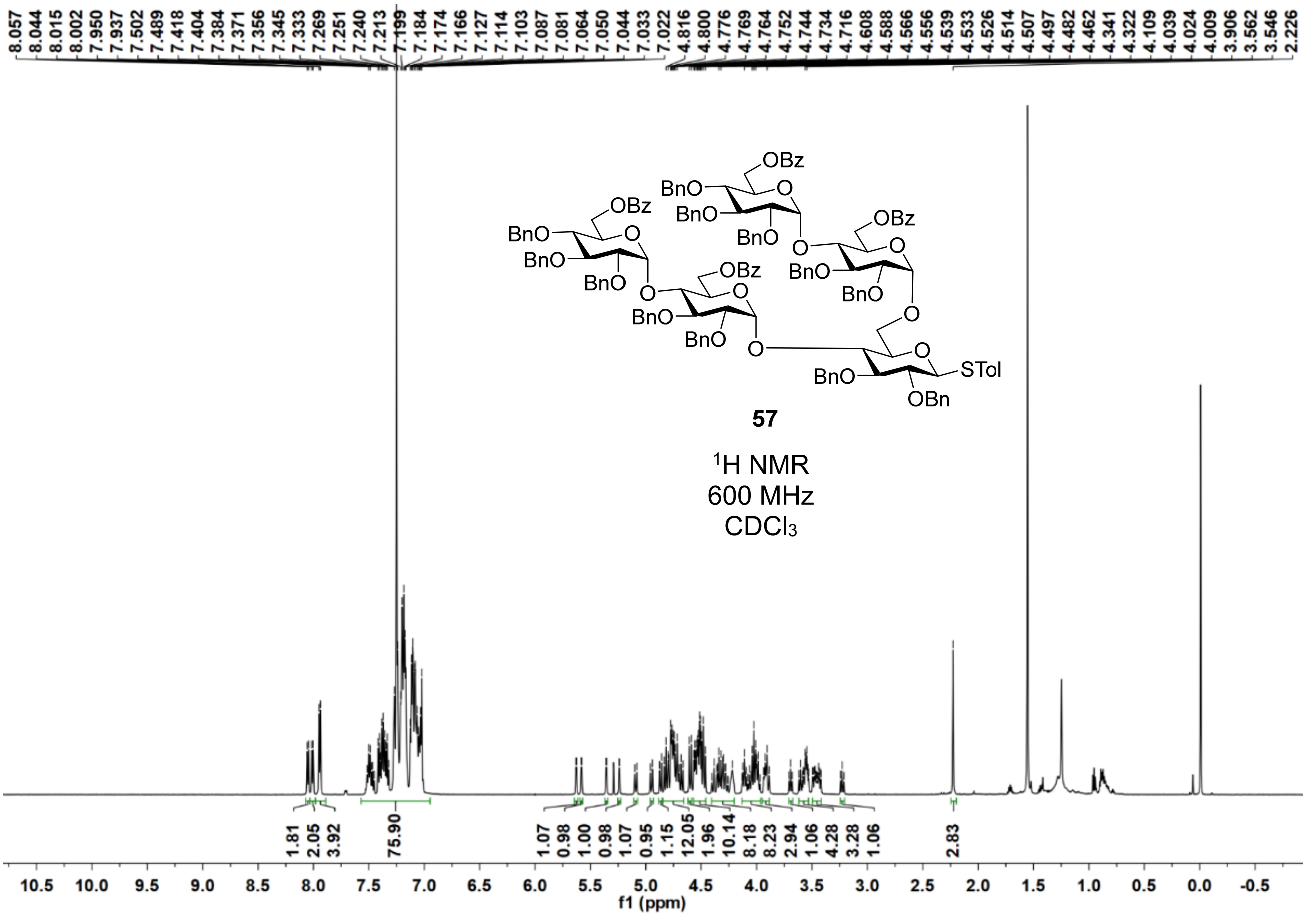
^{1}H- ^{13}C HSQC
600/150 MHz
$CDCl_3$

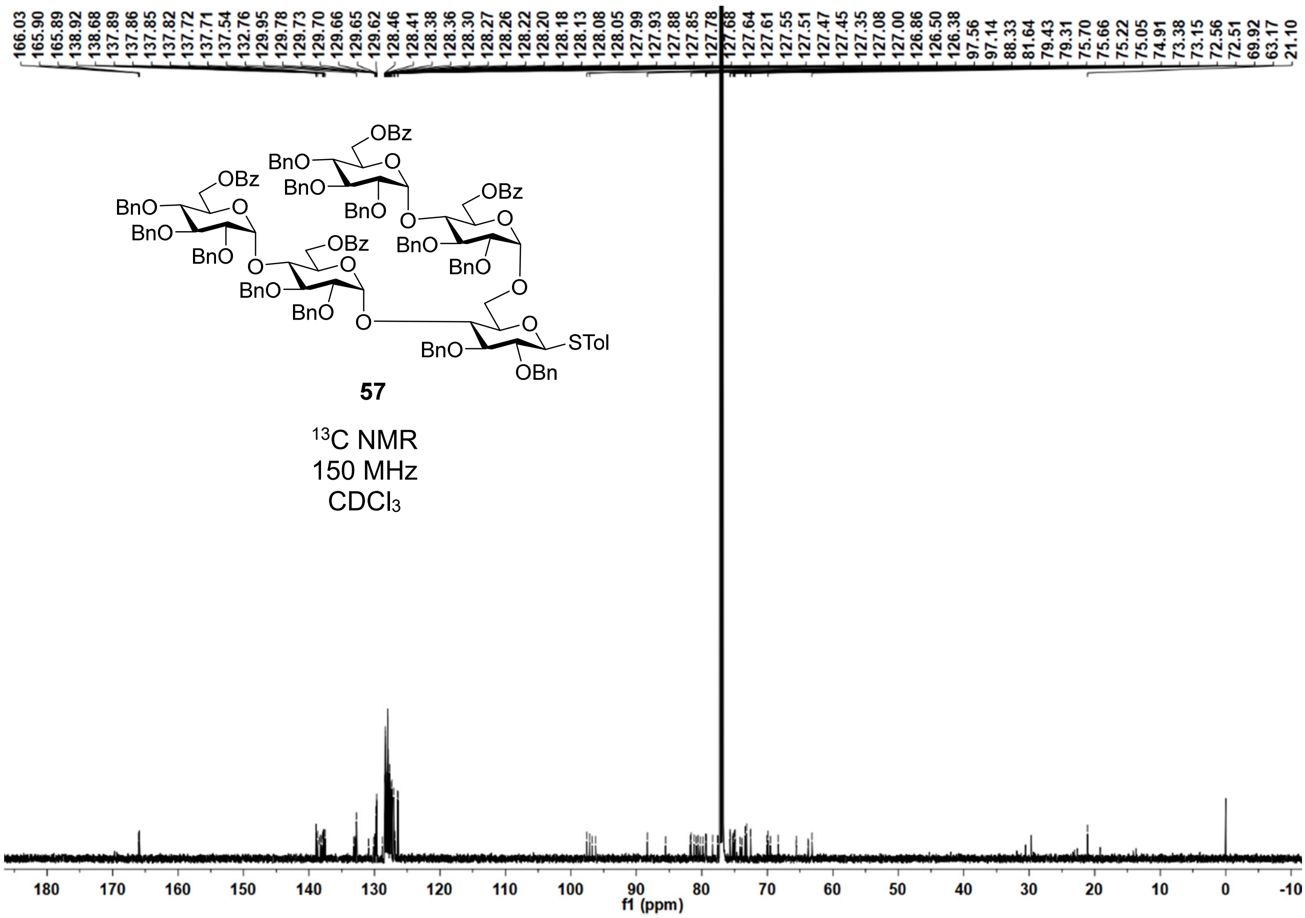


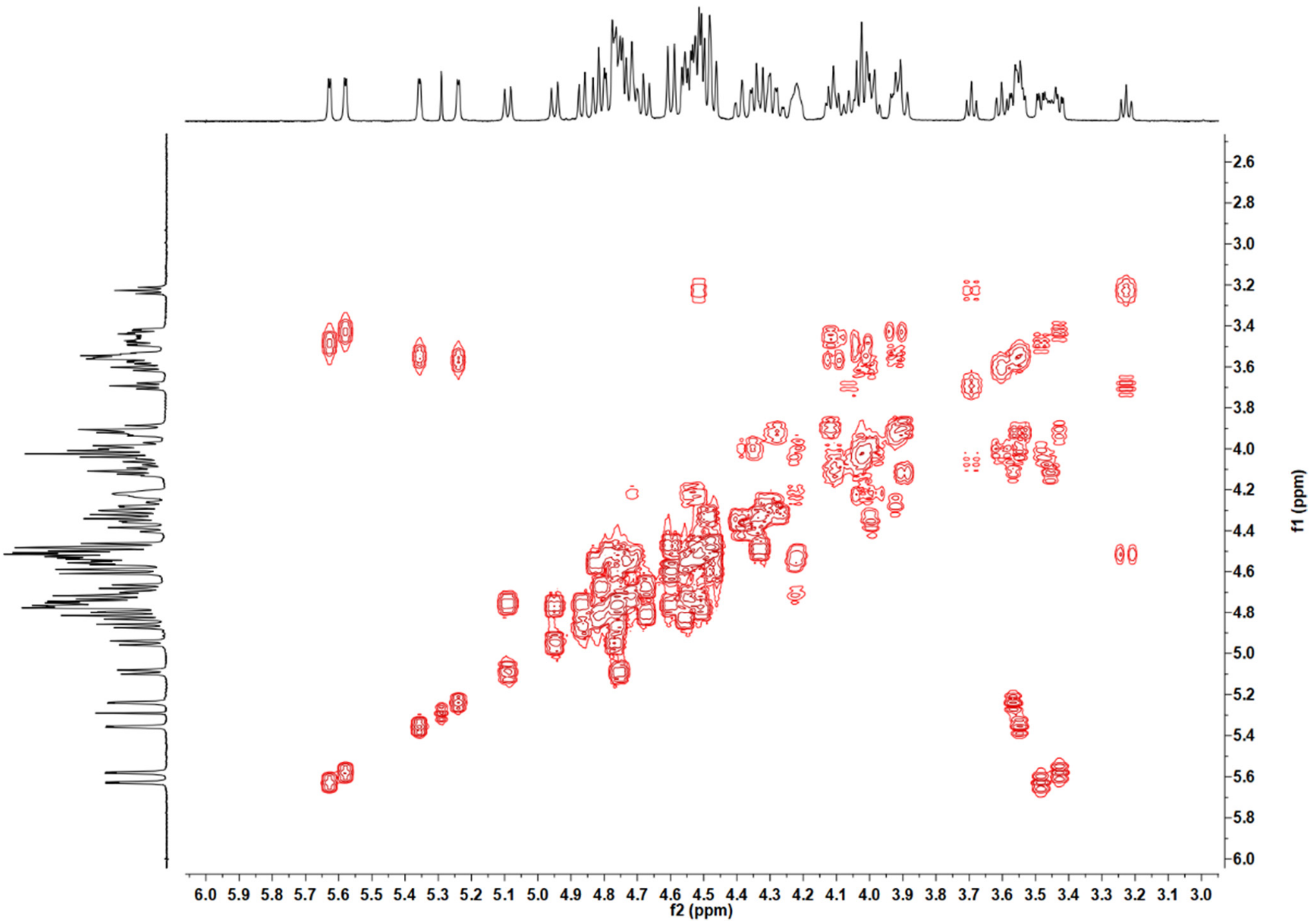


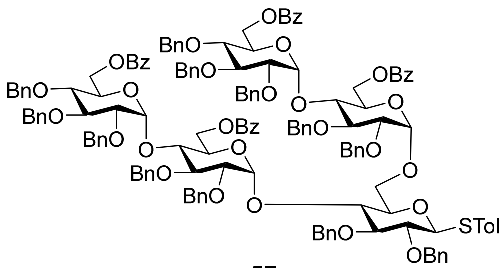
64

^{1}H-^{1}H COSY
600 MHz
$CDCl_3$


8.057 8.044 8.015 8.002 7.950 7.937 7.502 7.489 7.418 7.404 7.384 7.371 7.356 7.345 7.333 7.269 7.251 7.240 7.213 7.199 7.184 7.174 7.166 7.127 7.114 7.103 7.087 7.081 7.064 7.050 7.044 7.033 7.022 4.816 4.800 4.776 4.769 4.764 4.752 4.744 4.734 4.716 4.608 4.588 4.566 4.556 4.539 4.533 4.526 4.514 4.507 4.497 4.482 4.462 4.341 4.322 4.109 4.039 4.024 4.009 3.906 3.562 3.546 2.226
OBz
BnO
BnO
BnO
STol
OBn
57
^{1}H NMR
600 MHz
$CDCl_3$
1.81 2.05 3.92 75.90 1.07 0.98 1.00 0.98 1.07 0.95 1.15 12.05 1.96 10.14 8.18 8.23 2.94 1.06 4.28 3.28 1.06 2.83
10.5 10.0 9.5 9.0 8.5 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 0.0 -0.5
f1 (ppm)

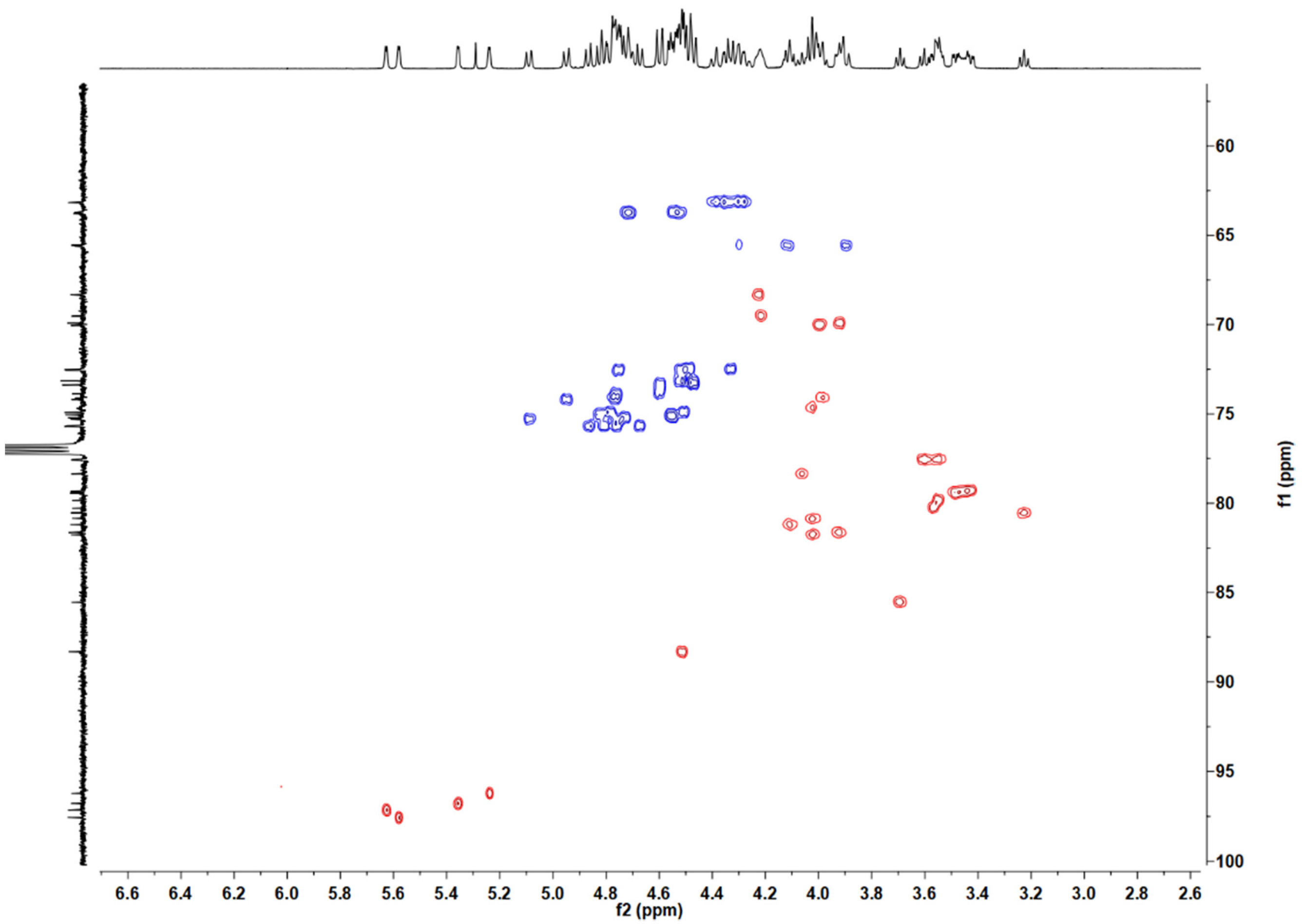

166.03 165.90 165.89 138.92 138.68 137.89 137.86 137.85 137.82 137.72 137.71 137.54 132.76 129.95 129.78 129.73 129.70 129.66 129.65 129.62 128.46 128.41 128.38 128.36 128.30 128.27 128.26 128.22 128.20 128.18 128.13 128.08 128.05 127.99 127.93 127.88 127.85 127.78 127.68 127.61 127.55 127.51 127.47 127.45 127.35 127.08 127.00 126.86 126.50 126.38 97.56 97.14 88.33 81.64 79.43 79.31 75.70 75.66 75.22 75.05 74.91 73.38 73.15 72.56 72.51 69.92 63.17 21.10
OBz
BnO
BnO
BnO
STol
OBn
57
^{13}C NMR
150 MHz
$CDCl_3$
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

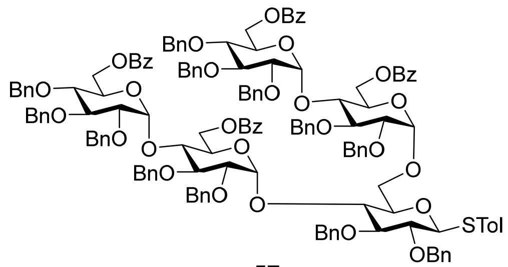




57

^{1}H-^{1}H COSY
600 MHz
$CDCl_3$





57

^{1}H- ^{13}C HSQC
600/150 MHz
$CDCl_3$