Synthesis of Glycosyl Chlorides Using Catalytic Appel Conditions

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Supporting Information

Contents

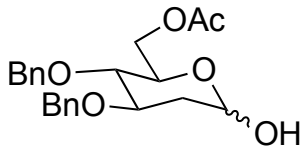
General Experimental

The reagents and solvents used in the following experiments were bought commercially and used without further purification. Dry solvents were obtained using equipment based on Grubb's design[1] and stored in Strauss flask over 4 Å molecular sieves. A Karl Fischer Titrator was used to determine the amount of water in dry solvents. For air-sensitive reactions, solvents were added *via* syringe through rubber septa. Reactions were monitored by thin layer chromatography using silica-coated aluminum plates and the eluents outlined in the respective experiments; spots were detected under 254 nm UV light. Flash column chromatography was performed using silica gel [Davisil, 400–230 mesh (63–40 μm)]. ^{1}H NMR, ^{13}C NMR ^{31}P NMR and 2D NMR were carried out on 300 MHz, 400 MHz, 500 MHz or 600 MHz spectrometers using deuterated chloroform ($CDCl_3$). Chemical shifts are reported in parts per million (ppm), coupling constants (*J*) are reported in Hertz (Hz) and multiplicities are abbreviated as; s (singlet), d (doublet), t (triplet) or m (multiplet) or combinations thereof. Chemical shifts were referenced to the residual proton of TMS for ^{1}H NMR spectra and to the ^{13}C signal of deuterated chloroform ($CDCl_3$) for ^{13}C NMR spectra. For compounds not reported in literature, NMR assignments have been made using COSY, HSQC and HMBC. Mass Spectra were recorded by the University College Dublin, School of Chemistry mass spectrometry service using ESI-MS and GCMS techniques.

Synthesis of Hemiacetals 1 and Acceptor 6

Syntheses of benzyl-protected hemiacetals **1a-c**,[2] benzoyl- and acetyl-protected hemiacetals **1i,l,m-p**,[3,4] 2-deoxy benzyl-protected hemiacetals **1d**, **1e**,[5] 2-deoxy acetyl-protected hemiacetal **1f,**[6] acetal-protected hemiacetal **1j**[7] and **1k**[8] and methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **6**[9] were carried out following literature procedures.

6-*O*-Acetyl-3,4-di-*O*-benzyl-2-deoxy-α/β-D-glucopyranose 1g



Following a literature procedure,[10] 6-*O*-acetyl-3,4-di-*O*-benzyl-D-glucal (462 mg, 1.25 mmol), deionised water (0.045 mL, 2.5 mmol), and $Ph_3P.HBr$ (42.9 mg, 0.125 mmol) in THF (3.1 mL) were stirred at room temperature for 24 h. Purification by column chromatography (100:0 to 95:5, DCM/Et_2O) afforded the hydrolysed product **1g** as a white solid (78 mg, 16%, α/β = 75:25). ESI-HRMS for $C_{22}H_{26}O_6Na^+$ $(M+Na)^+$ calculated: 409.1627; found 409.1647.

α/β

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.40 – 7.26 (m, 10H, Ph), 4.32 (dd, *J* = 12.1, 2.4 Hz, 1H, H-6a), 4.27 (dd, *J* = 11.9, 4.5 Hz, 1H, H-6b). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 171.1 (C=O), 138.5 (C), 138.2 (C), 128.5 (CH), 128.2 (CH), 128.0 (CH), 127.93 (CH), 127.86 (CH), 127.8 (CH), 63.7 (C-6).

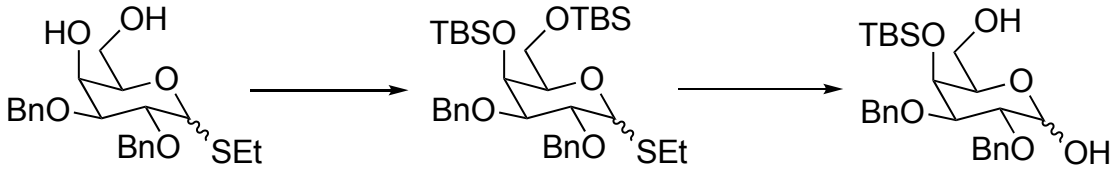
α-OH

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.38 (d, *J* = 3.4 Hz, 1H, H-1), 4.94 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.66 (d, *J* = 10.8 Hz, 2H, 2 x C*H*HPh), 4.62 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.10 – 4.03 (m, 2H, H-3 and H-5), 3.46 (t, *J* = 9.4 Hz, 1H, H-4), 2.95 (t, *J* = 2.6 Hz, 1H, OH), 2.31 (ddd, *J* = 13.1, 4.9, 1.5 Hz, 1H, H-2_{eq}), 2.03 (s, 3H, CH_3), 1.67 (dddd, *J* = 13.2, 11.3, 3.6, 2.0 Hz, 1H, H-2_{ax}). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 92.2 (C-1), 78.0 (C-4), 77.2 (C-3), 75.0 (Ph*C*H_2), 71.9 (Ph*C*H_2), 69.5 (C-5), 35.5 (C-2), 21.0 (CH_3).

β-OH

Selected signals ^{1}H NMR (500 MHz, Chloroform-*d*): δ 4.93 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.78 (ddd, *J* = 9.6, 6.2, 2.0 Hz, 1H, H-1), 3.72 – 3.65 (m, 1H, H-3), 3.52 – 3.48 (m, 1H, H-5), 3.48 – 3.40 (m, 1H, H-4), 2.41 (ddd, *J* = 12.7, 5.0, 2.0 Hz, 1H, H-2_{eq}), 1.58 (ddd, *J* = 12.6, 11.6, 9.6 Hz, 1H, H-2_{ax}). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 94.2 (C-1), 79.3 (C-3), 77.3 (C-4), 73.4 (C-5), 71.6 (Ph*C*H_2), 37.9 (C-2).

2,3-Di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α/β-D-galactopyranose S1



Under a N_2 atmosphere, a solution of ethyl 2,3-di-*O*-benzyl-1-deoxy-1-thiol-α/β-D-galactopyranose[11] (270 mg, 0.667 mmol), TBSCl (404 mg, 2.68 mmol), imidazole (365 g, 5.36 mmol) and DMAP (8 mg, 0.07 mmol) in anhydrous DMF (0.8 mL) was heated to 60 °C for 17 h. The reaction mixture was cooled to room temperature and poured over cold water. The product was extracted with pentane and washed with saturated $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude material was dissolved in 9:1 acetone/water (9 mL) and treated with NBS (176 mg, 0.989 mmol) at 0 °C. The yellow solution went colourless over 30 min, TLC analysis (3:1; cyclohexane/EtOAc) showed complete conversion of the starting material to the hydrolysed product. The reaction was quenched with saturated $NaHCO_3$, acetone was removed under a flow of air and then DCM was added. The organic layer was washed with saturated $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by column chromatography (6:1 to 3:1, DCM/EtOAc) afforded the hydrolysed product **S1** as a syrup (80 mg, 25% yield over two steps, α/β = 60:40).

α/β

^{1}H NMR (300 MHz, Chloroform-*d*): δ 7.40 – 7.27 (m, 10H, Ph), 4.92 – 4.63 (m, 4H, C*H*HPh), 0.024 (s, 3H, $SiCH_3$), 0.018 (s, 3H, $SiCH_3$). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 128.5 (CH), 128.41 (CH), 128.3 (CH), 128.09 (CH), 128.0 (CH), 127.7 (CH), 26.15 ($SiC(CH_3)_3$), 18.62 ($SiC(CH_3)_3$), -3.85 ($SiCH_3$), -4.74 ($SiCH_3$)

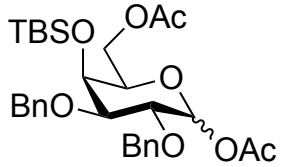
α-OH

^{1}H NMR (300 MHz, Chloroform-*d*): δ 5.27 (d, *J* = 3.4 Hz, 1H, H-1), 4.07 (d, *J* = 1.4 Hz, 1H, H-4), 4.04 – 3.94 (m, 1H, H-5), 3.91 (dd, *J* = 9.8, 3.5 Hz, 1H, H-2), 3.85 – 3.76 (m, 1H, H-6a), 3.77 (dd, *J* = 9.8, 2.6 Hz, 1H, H-3), 3.63 – 3.50 (m, 1H, H-6b), 3.29 (s, 1H, OH), 0.86 (s, 9H, $SiC(CH_3)_3$), 0.04 (s, 3H, $SiCH_3$). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 138.4 (C), 138.2 (C), 128.6 (CH), 128.38 (CH), 128.2 (CH), 128.07 (CH), 91.9 (C-1), 77.8 (C-3), 76.1 (C-2), 73.62 ($PhCH_2$), 73.58 ($PhCH_2$), 72.5 (C-5), 70.2 (C-4), 63.02 (C-6).

β-OH

^{1}H NMR (300 MHz, Chloroform-*d*): δ 4.70 (H-1, cross-peak in HSQC to 97.6 ppm, overlaps with C*H*HPh), 4.04 – 3.94 (m, 1H, H-4), 3.88 – 3.79 (m, 1H, H-6a), 3.66 (dd, *J* = 9.3, 7.0 Hz, 1H, H-2), 3.59 – 3.50 (m, 2H, H-6b, H-5), 3.41 (dd, *J* = 9.2, 2.7 Hz, 1H, H-3), 0.88 (s, 9H, SiC(C*H*$_3$)$_3$), 0.06 (s, 3H, SiCH$_3$). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 138.5 (C), 138.1 (C), 127.85 (CH), 127.78 (CH), 97.6 (C-1), 81.2 (C-3), 80.1 (C-2), 76.4 (C-5), 74.9 (Ph*C*H$_2$), 73.66 (Ph*C*H$_2$), 69.2 (C-4), 62.98 (C-6).

1,6-Di-*O*-acetyl-2,3-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α/β-D-galactopyranose S2



A solution of **S1** (80 mg, 0.17 mmol) in pyridine (0.5 mL) was treated with acetic anhydride (0.06 mL, 0.7 mmol) and DMAP (2 mg, 0.02 mmol) and stirred at room temperature. TLC analysis (9:1; DCM/EtOAc) after 3 h showed complete consumption of starting material. The reaction mixture was diluted with DCM and washed with 1 M HCl, saturated NaHCO$_3$, and brine. The organic layer was dried over MgSO$_4$, filtered and concentrated *in vacuo* to give **S2** a yellow syrup (quantitative, α/β = 60:40).

α/β

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.42 – 7.26 (m, 10H), 4.81 (d, *J* = 11.5 Hz, 1H, C*H*HPh). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 170.7 (C=O), 138.0 (C), 128.50 (CH), 128.4 (CH), 128.11 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 21.0 (CH$_3$).

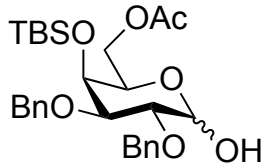
α-OAc

^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.35 (d, *J* = 3.6 Hz, 1H, H-1), 4.73 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 4.71 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.68 (d, J = 11.7 Hz, 1H, C*H*HPh), 4.17 (dd, *J* = 11.1, 7.2 Hz, 1H, H-6a), 4.13 – 4.12 (m, 1H, H-4), 4.10 (dd, *J* = 11.2, 5.9 Hz, 1H, H-6b), 4.05 (dd, *J* = 10.2, 3.5 Hz, 1H, H-2), 3.99 (t, *J* = 6.4 Hz, 1H, H-5), 3.75 (dd, *J* = 10.1, 2.6 Hz, 1H, H-3), 2.07 (s, 6H, 2 x CH$_3$), 0.85 (s, 9H, SiC(C*H*$_3$)$_3$), 0.04 (s, 3H, SiCH$_3$), 0.03 (s, 3H, SiCH$_3$). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 169.7 (C=O), 138.33 (C), 128.53 (CH), 128.3 (CH), 128.2 (CH), 128.09 (CH), 90.9 (C-1), 77.5 (C-3), 74.6 (C-2), 73.8 (Ph*C*H$_2$), 73.4 (Ph*C*H$_2$), 71.6 (C-5), 69.8 (C-4), 63.5 (C-6), 26.09 (SiC(*C*H$_3$)$_3$), 21.3 (CH$_3$), 18.62 (Si*C*(CH$_3$)$_3$), -3.81 (SiCH$_3$), -4.9 (SiCH$_3$).

β-OAc

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.60 (d, *J* = 7.9 Hz, 1H, H-1), 4.75 – 4.71 (m, 2H, 2 x C*H*HPh), 4.73 (d, *J* = 11.2 Hz, 1H, C*H*HPh), 4.22 (dd, *J* = 11.3, 7.1 Hz, 1H, H-6a), 4.16 (dd, *J* = 11.2, 6.0 Hz, 1H, H-6b), 4.08 – 4.02 (m, 1H, H-4), 3.85 (dd, *J* = 9.6, 8.0 Hz, 1H, H-2), 3.71 (ddd, *J* = 6.9, 5.6, 1.0 Hz, 1H, H-5), 3.48 (dd, *J* = 9.7, 2.7 Hz, 1H, H-3), 2.14 (s, 6H, 2 x CH_3), 0.91 (s, 9H, SiC(C*H*$_3$)$_3$), 0.10 (s, 3H, $SiCH_3$), 0.05 (s, 3H, $SiCH_3$). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 169.5 (C=O), 138.32 (C), 127.85 (CH), 127.84 (CH), 94.3 (C-1), 81.4 (C-3), 77.6 (C-2), 75.2 (Ph*C*H$_2$), 73.9 (C-5), 73.7 (Ph*C*H$_2$), 69.0 (C-4), 63.4 (C-6), 26.15 (SiC(*C*H$_3$)$_3$), 21.2 (CH_3), 18.65 (Si*C*(CH$_3$)$_3$), -3.85 ($SiCH_3$), -4.8 ($SiCH_3$).

6-*O*-Acetyl-2,3-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α/β-D-galactopyranose 1h



Following literature procedure,[12] under a N_2 atmosphere, a solution of **S2** (94 mg, 0.17 mmol) in anhydrous DCM (0.9 mL) was treated with TMSI (28 μL, 0.20 mmol) in a Schlenk flask covered with aluminium foil. After stirring at room temperature for 20 min, DIPEA (35 μL, 0.25 mmol) was added followed by deionised water (7 μL, 0.4 mmol). The reaction was stirred at room temperature for 1 h. TLC analysis (98:2; DCM/ether) showed full consumption of starting material. The reaction was diluted with DCM and washed with saturated $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by column chromatography (100:0 to 95:5; DCM/ether) gave the product **1h** as a white solid (66 mg, 75% yield, α/β = 75:25). *m/z* (ESI-HRMS) calc'd for $C_{28}H_{40}O_7SiNa^+$ (M+Na$^+$): 539.2433; found 539.2441.

α/β

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.39 – 7.27 (m, 10H). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 128.06 (CH), 127.73 (CH), 21.0 (CH_3), -4.8 ($SiCH_3$).

α-OH

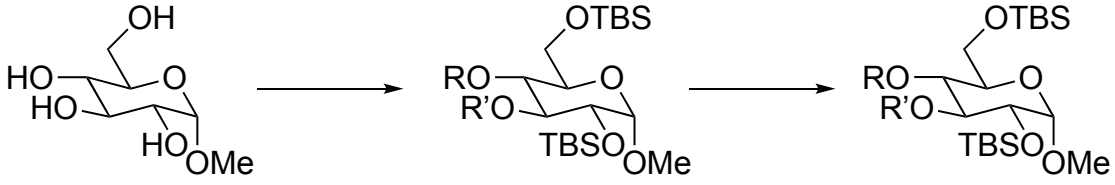
^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.24 (d, *J* = 3.5 Hz, 1H, H-1), 4.80 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.76 (d, *J* = 11.6 Hz, 1H, C*H*HPh), 4.73 (d, *J* = 11.5 Hz, 1H, C*H*HPh), 4.69 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.20 – 4.13 (m, 2H, H-6a, H-6b), 4.12 – 4.08 (m, 2H, H-4, H-5), 3.91 (dd, *J* = 9.8, 3.5 Hz, 1H, H-2), 3.77 (dd, *J* = 9.7, 2.6 Hz, 1H, H-3), 2.07 (s, 3H, CH_3), 0.86 (s, 9H, SiC(C*H*$_3$)$_3$), 0.06 (s, 3H, $SiCH_3$), 0.02 (s, 3H, $SiCH_3$). ^{13}C NMR (126 MHz,

Chloroform-*d*): δ 170.8 (C=O), 138.3 (C), 138.10 (C), 128.6 (CH), 128.4 (CH), 128.2 (CH), 128.08 (CH), 92.0 (C-1), 77.6 (C-3), 76.0 (C-2), 73.66 (Ph*C*H_2), 73.65 (Ph*C*H_2), 70.0 (C-4/5), 69.9 (C-4/5), 63.97 (C-6), 26.13 (SiC(*C*H_3)$_3$), 18.63 (Si*C*(CH_3)$_3$), -3.84 ($SiCH_3$).

β-OH

^{1}H NMR (500 MHz, Chloroform-*d*): δ 4.89 (d, *J* = 11.2 Hz, 1H, C*H*HPh), 4.81 (d, *J* = 11.2 Hz, 1H, C*H*HPh), 4.79 – 4.72 (m, 2H, 2 x C*H*HPh), 4.67 (d, *J* = 7.1 Hz, 1H, H-1), 4.23 (dd, *J* = 11.3, 7.1 Hz, 1H, H-6a), 4.20 – 4.16 (m, 1H, H-6b), 4.03 (dd, *J* = 2.7, 1.2 Hz, 1H, H-4), 3.66 (dd, *J* = 9.5, 7.1 Hz, 1H, H-2), 3.65 – 3.61 (m, 1H, H-5), 3.40 (dd, *J* = 9.5, 2.7 Hz, 1H, H-3), 2.07 (s, 3H, CH_3), 0.88 (s, 9H, SiC(C*H*$_3$)$_3$), 0.07 (s, 3H, $SiCH_3$), 0.04 (s, 3H, $SiCH_3$).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 170.9 (C=O), 138.5 (C), 138.14 (C), 128.5 (CH), 128.3 (CH), 128.09 (CH), 127.9 (CH), 127.78 (CH), 97.7 (C-1), 81.2 (C-3), 80.0 (C-2), 75.0 (Ph*C*H_2), 73.67 (Ph*C*H_2), 73.4 (C-5), 69.2 (C-4), 64.05 (C-6), 26.14 (SiC(*C*H_3)$_3$), 18.65 (Si*C*(CH_3)$_3$), -3.82 ($SiCH_3$).

Methyl 4-acetyl-2,3,6-tri-*O-tert*-butyldimethylsilyl-α-D-glucopyranoside S5 and Methyl 3-acetyl-2,4,6-tri-*O-tert*-butyldimethylsilyl-α-D-glucopyranoside S6



S3: R= H, R'= TBS
S4: R= TBS, R'= H

S5: R= Ac, R'= TBS
S6: R= TBS, R'= Ac

In a flame-dried 25 mL Schlenk flask placed under three cycles of vacuum and nitrogen, methyl α-D-glucopyranose (1.3 g, 6.8 mmol), TBSCl (6.15 g, 40.8 mmol), imidazole (5.55 g, 81.6 mmol) and DMAP (83 mg, 0.68 mmol) were added. The solids were dissolved in dry DMF (8 mL) and stirred at 60 °C for 14 h. The reaction mixture was diluted with pentane and washed with cold water. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to give a colourless syrup. Following purification by column chromatography (100:0 to 96:4, pentane/Et_2O) the products **S3** and **S4** were inseparable and a syrup (3.63 g, quant.) was obtained (^{1}H NMR spectrum of the syrup showed **S3**:**S4** = 40:60). The mixture of **S3** and **S4** (3.6 g, 6.8 mmol) and DMAP (82 mg, 0.67 mmol) were dissolved in anhydrous pyridine (1.1 mL, 14 mmol). The solution was treated with acetic anhydride (1.3 mL, 14 mmol) and stirred at room temperature for 3 h. The reaction mixture was diluted with DCM and washed with 1 M HCl, followed by saturated $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated *in vacuo*. Trituration with pentane/MeOH afforded **S5** as a white

solid (840 mg, 21% yield) and **S6** as a colourless syrup (840 mg, 21%). NMR data were consistent with literature data.[13]

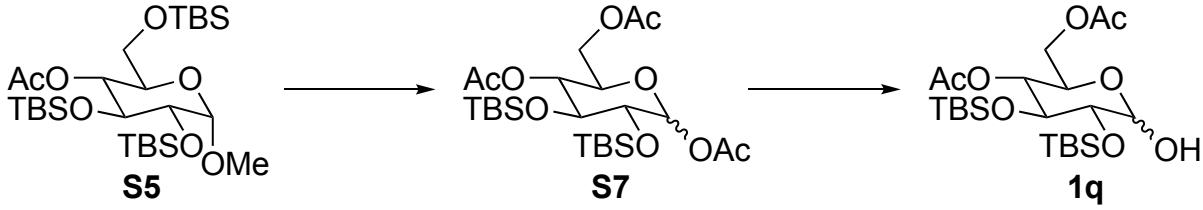
S5

^{1}H NMR (500 MHz, Chloroform-*d*): δ 4.70 (dd, *J* = 10.1, 8.8 Hz, 1H, H-4), 4.66 (d, *J* = 3.4 Hz, 1H, H-1), 3.94 (t, *J* = 8.9 Hz, 1H, H-3), 3.69 – 3.52 (m, 4H, H-2, 5, 6a, 6b), 3.38 (s, 3H, OCH_3), 2.06 (s, 3H, CH_3), 0.92, 0.88, 0.84 (s x 3, 27H, $SiC(CH_3)_3$), 0.10 (s, 6H, 2 x $SiCH_3$), 0.09, 0.06, 0.05, 0.04 (s x 4, 12H, $SiCH_3$).

S6

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.26 (dd, *J* = 9.8, 8.7 Hz, 1H, H-3), 4.60 (d, *J* = 3.6 Hz, 1H, H-1), 3.81 (dd, *J* = 11.3, 2.0 Hz, 1H, H-6a), 3.72 (dd, *J* = 11.3, 5.0 Hz, 1H, H-6b), 3.65 – 3.56 (m, 2H, H-4, H-5), 3.55 (dd, *J* = 9.7, 3.6 Hz, 1H, H-2), 3.38 (s, 3H, OCH_3), 2.06 (s, 3H, CH_3), 0.90, 0.86, 0.84 (s x 3, 27H, $SiC(CH_3)_3$), 0.08, 0.06, 0.06, 0.03 (s x 4, 18H, $SiCH_3$).

4,6-Diacetyl-2,3,-di-*O-tert*-butyldimethylsilyl-α-D-glucopyranoside 1q



Following the literature procedure,[12,14] **S5** (637 mg, 1.10 mmol) was treated with acetic anhydride (6 mL) and conc. H_2SO_4 (a few drops, cat.) was added at 0 °C and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with DCM and washed with water, saturated $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated *in vacuo* to get crude **S7** as a colourless syrup. Under a nitrogen atmosphere, the crude **S7** was dissolved in dry DCM (5.5 mL) and treated with TMSI (0.31 mL, 2.2 mmol) at room temperature. After the brown reaction mixture was stirred at this temperature for 1 h, the solvent was removed and then the residue was re-dissolved in acetone (5.5 mL) and treated with Ag_2CO_3 (334 mg, 1.21 mmol) and water (0.04 mL, 2 mmol). The reaction mixture was stirred at room temperature for 1 h. After purification by column chromatography (R_f = 0.36; 2:1, pentane/Et_2O), the title compound **1q** was obtained as a very thick syrup (100 mg, 18% yield over three steps, α/β = 83:17).

m/z (ESI-HRMS) calc'd for $C_{22}H_{45}O_8Si_2^+$ ($M+H^+$): 493.2647; found 493.2653.

S7

α/β

^{1}H NMR (500 MHz, Chloroform-*d*): δ 2.08 (s, 3H, CH_3). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 25.96 (SiC(*C*H_3)$_3$).

α-OAc

^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.12 (d, *J* = 3.5 Hz, 1H, H-1), 4.95 (dd, *J* = 10.3, 8.9 Hz, 1H, H-4), 4.16 (dd, *J* = 12.4, 4.7 Hz, 1H, H-6a), 3.98 (dd, *J* = 12.4, 2.4 Hz, 1H, H-6b), 3.95 (t, *J* = 8.9 Hz, 1H, H-3), 3.90 (ddd, *J* = 10.2, 4.7, 2.6 Hz, 1H, H-5), 3.75 (dd, *J* = 8.8, 3.6 Hz, 1H, H-2), 2.14 (s, 3H, CH_3), 2.073 (s, 3H, CH_3), 0.869 (s, 9H, SiC(C*H*$_3$)$_3$), 0.861 (s, 9H, SiC(C*H*$_3$)$_3$), 0.12 (s, 3H, $SiCH_3$), 0.104 (s, 3H, $SiCH_3$), 0.094 (s, 3H, $SiCH_3$), 0.087 (s, 3H, $SiCH_3$). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 171.0 (C=O), 169.65 (C=O), 169.54 (C=O), 91.8 (C-1), 72.7 (C-2), 72.0 (C-3), 70.8 (C-4), 70.2 (C-5), 62.4 (C-6), 26.2 (SiC(*C*H_3)$_3$), 21.42 (CH_3), 21.1 (CH_3), 20.95 (CH_3), 18.1 (Si*C*(CH$_3$)$_3$), 18.00 (Si*C*(CH$_3$)$_3$), -2.8 ($SiCH_3$), -3.7 ($SiCH_3$), -4.2 (2 x $SiCH_3$).

β-OAc

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.62 (d, *J* = 5.9 Hz, 1H, H-1), 4.99 – 4.91 (m, 1H, H-4), 4.27 (dd, *J* = 12.2, 5.6 Hz, 1H, H-6a), 4.08 (dd, *J* = 12.1, 3.5 Hz, 1H, H-6b), 3.85 (ddd, *J* = 8.1, 5.6, 3.4 Hz, 1H, H-5), 3.78 (dd, *J* = 6.1, 7.3 Hz, 1H, H-3), 3.67 (t, *J* = 6.0 Hz, 1H, H-2), 2.12 (s, 3H, CH_3), 2.068 (s, 3H, CH_3), 0.879 (s, 9H, SiC(C*H*$_3$)$_3$), 0.874 (s, 9H, SiC(C*H*$_3$)$_3$), 0.16 (s, 3H, $SiCH_3$), 0.101 (s, 3H, $SiCH_3$), 0.097 (s, 3H, $SiCH_3$). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 169.9 (C=O), 169.51 (C=O), 94.4 (C-1), 74.2 (C-3), 73.1 (C-2), 72.8 (C-5), 70.4 (C-4), 63.0 (C-6), 26.01 (SiC(*C*H$_3$)$_3$), 21.5 (CH_3), 21.41 (CH_3), 20.97 (CH_3), 18.2 (Si*C*(CH$_3$)$_3$), 18.02 (Si*C*(CH$_3$)$_3$), -3.1, -3.3, -4.06, -4.15 (4 x $SiCH_3$).

1q

α-OH

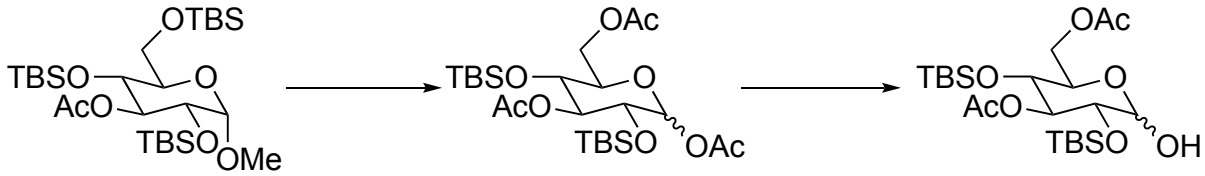
^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.18 (t, *J* = 3.5 Hz, 1H, H-1), 4.87 (dd, *J* = 9.6, 8.0 Hz, 1H, H-4), 4.21 (dd, *J* = 12.2, 5.1 Hz, 1H, H-6a), 4.11 (ddd, *J* = 9.7, 5.1, 2.5 Hz, 1H, H-5), 4.04 (dd, *J* = 12.2, 2.6 Hz, 1H, H-6b), 3.94 (t, *J* = 8.0 Hz, 1H, H-3), 3.69 (dd, *J* = 8.0, 3.4 Hz, 1H, H-2), 3.03 (d, *J* = 3.5 Hz, 1H, OH), 2.09 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 0.94 (s, 9H, SiC(C*H*$_3$)$_3$), 0.86 (s, 9H, SiC(C*H*$_3$)$_3$), 0.14, 0.13, 0.10, 0.09 (s x 4, 12 H, $SiCH_3$). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 171.04 (C=O), 169.85 (C=O), 92.8 (C-1), 73.9 (C-2), 71.8 (C-

3), 70.9 (C-4), 68.8 (C-5), 62.8 (C-6), 26.3 (SiC(CH$_3$)$_3$), 25.9 (SiC(CH$_3$)$_3$), 21.4 (CH$_3$), 21.0 (CH$_3$), 18.3 (SiC(CH$_3$)$_3$), 18.0 (SiC(CH$_3$)$_3$), -3.1, -3.5, -4.2, -4.4 (4 x SiCH$_3$).

β-OH

^{1}H NMR (500 MHz, Chloroform-*d*): δ 4.90 (dd, *J* = 8.6, 5.5 Hz, 1H, H-4), 4.79 (dd, *J* = 8.4, 4.3 Hz, 1H, H-1), 4.19 – 4.13 (m, 2H, H-6a, H-6b), 3.87 (ddd, *J* = 8.9, 5.7, 3.4 Hz, 1H, H-5), 3.76 (t, *J* = 5.8 Hz, 1H, H-3), 3.61 (dd, *J* = 5.9, 4.4 Hz, 1H, H-2), 3.28 (d, *J* = 8.5 Hz, 1H, OH), 2.08 (s, 3H, CH$_3$), 2.07 (s, 3H, CH$_3$), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.89 (s, 9H, SiC(CH_3)$_3$), 0.14, 0.125, 0.119, 0.10 (s x 4, 12H, SiCH$_3$). ^{13}C NMR (126 MHz, Chloroform-*d*) selected signals: δ 97.5 (C-1), 74.7, (C-2) 74.3 (C-3), 71.2 (C-4 and C-5), 63.9 (C-6), 26.2 (SiC(CH$_3$)$_3$) , 21.3 (CH$_3$), -3.8, -4.0 (2 x SiCH$_3$).

3,6-Diacetyl-2,4-di-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranoside 1r



Following the literature procedure,[12,14] **S6** (830 mg, 1.43 mmol) was treated with acetic anhydride (6 mL) and conc. H_2SO_4 (a few drops, cat.) was added at 0 °C and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with DCM and washed with water, saturated $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated *in vacuo* to get crude **S8** as a colourless syrup. Under a nitrogen atmosphere, the crude **S8** was dissolved in dry DCM (7.1 mL) and treated with TMSI (0.41 mL, 2.9 mmol) at room temperature. After the brown reaction mixture was stirred at this temperature for 1 h, the solvent was removed and then the residue was re-dissolved in acetone (7.1 mL) and treated with Ag_2CO_3 (433 mg, 1.57 mmol) and water (0.05 mL, 3 mmol). The reaction mixture was stirred at room temperature for 1 h. After purification by column chromatography (R_f = 0.30; 2:1, pentane/Et_2O), the title compound **1r** was obtained as a very thick syrup (150 mg, 21% yield over three steps, α/β = 67:33).

m/z (ESI-HRMS) calc'd for $C_{22}H_{44}O_8Si_2Na^+$ (M+Na$^+$): 515.2467; found 515.2472.

S8

α/β

^{1}H NMR (500 MHz, Chloroform-*d*): δ 0.046 (s, 3H, SiCH$_3$).

α-OAc

^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.13 (d, *J* = 3.8 Hz, 1H, H-1), 5.29 (t, *J* = 9.4 Hz, 1H, H-3), 4.32 (dd, *J* = 12.2, 2.2 Hz, 1H, H-6a), 4.10 (dd, *J* = 12.1, 4.2 Hz, 1H, H-6b), 3.88 (ddd, *J* = 9.6, 4.1, 2.2 Hz, 1H, H-5), 3.75 (t, *J* = 9.4 Hz, 1H, H-4), 3.73 (dd, *J* = 9.6, 3.9 Hz, 1H, H-2), 2.16 (s, 3H, CH_3), 2.093 (s, 3H, CH_3), 2.092 (s, 3H, CH_3), 0.85 (s, 9H, SiC(CH_3)$_3$), 0.82 (s, 9H, SiC(CH_3)$_3$), 0.054 (s, 3H, $SiCH_3$), 0.053 (s, 3H, $SiCH_3$), 0.04 (s, 3H, $SiCH_3$). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 170.80 (C=O), 169.67 (C=O), 169.59 (C=O), 91.2 (C-1), 75.10 (C-3), 72.3 (C-5), 70.5 (C-2), 68.9 (C-4), 62.82 (C-6), 25.8 (SiC(*C*H_3)$_3$), 25.5 (SiC(*C*H_3)$_3$), 22.0 (CH_3), 21.14 (CH_3), 21.0 (CH_3), 18.0 (Si*C*(CH_3)$_3$), 17.8 (Si*C*(CH_3)$_3$), -3.9, -4.5, -4.8, -5.0 (4 x $SiCH_3$).

β-OAc

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.52 (d, *J* = 7.9 Hz, 1H, H-1), 5.12 (t, *J* = 9.0 Hz, 1H, H-3), 4.35 (dd, *J* = 12.7, 2.6 Hz, 1H, H-6a), 4.07 (dd, *J* = 12.7, 4.9 Hz, 1H, H-6a), 3.71 (t, *J* = 9.1 Hz, 1H, H-4), 3.66 – 3.59 (m, 1H, H-5), 3.63 (dd, *J* = 9.2, 8.0 Hz, 1H, H-2), 2.12 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 0.84 (s, 9H, SiC(CH_3)$_3$), 0.83 (s, 9H, SiC(CH_3)$_3$), 0.10 (s, 3H, $SiCH_3$), 0.07 (s, 3H, $SiCH_3$), 0.02 (s, 3H, $SiCH_3$). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 170.83 (C=O), 169.60 (C=O), 169.1 (C=O), 94.3 (C-1), 77.7 (C-3), 75.10 (C-5), 72.0 (C-2), 69.1 (C-4), 62.85 (C-6), 25.7 (SiC(*C*H_3)$_3$), 25.6 (SiC(*C*H_3)$_3$), 22.2 (CH_3), 21.3 (CH_3), 21.07 (CH_3), 17.97 (Si*C*(CH_3)$_3$), 17.96 (Si*C*(CH_3)$_3$), -3.4, -4.1, -4.4, -4.7 (4 x $SiCH_3$).

1r

α/β

^{1}H NMR (500 MHz, Chloroform-*d*): δ 2.10 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 0.84 (s, 9H, SiC(CH_3)$_3$), 0.04 (s, 3H, $SiCH_3$). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 25.7 (SiC(*C*H_3)$_3$), 21.1 (CH_3).

α-OH

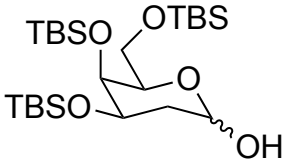
^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.24 (t, *J* = 9.2 Hz, 1H, H-3), 5.12 (dd, *J* = 3.8, 1.8 Hz, 1H, H-1), 4.37 (dd, *J* = 12.0, 2.1 Hz, 1H, H-6a), 4.12 (dd, *J* = 11.9, 4.4 Hz, 1H, H-6b), 4.07 (ddd, *J* = 9.6, 4.4, 2.0 Hz, 1H, H-5), 3.70 (t, *J* = 9.4 Hz, 1H, H-4), 3.65 (dd, *J* = 9.5, 3.6 Hz, 1H, H-2), 3.13 (d, *J* = 1.8 Hz, 1H, OH), 0.87 (s, 9H, SiC(CH_3)$_3$), 0.08, 0.07, 0.03 (s x 3, 9H, $SiCH_3$). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 170.94 (C=O), 169.7 (C=O), 92.9 (C-1), 75.1

(C-3), 72.2 (C-2), 70.2 (C-5), 68.9 (C-4), 63.1 (C-6), 25.6 (SiC(CH$_3$)$_3$), 22.0 (CH$_3$), 18.01 (SiC(CH$_3$)$_3$), 17.9 (SiC(CH$_3$)$_3$), -3.90, -4.43, -4.80, -4.81 (4 x SiCH$_3$).

β-OH

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.06 (t, *J* = 9.2 Hz, 1H, H-3), 4.65 (dd, *J* = 7.5, 5.4 Hz, 1H, H-1), 4.41 (dd, *J* = 12.0, 2.2 Hz, 1H, H-6a), 4.03 (dd, *J* = 12.0, 5.2 Hz, 1H, H-6b), 3.73 – 3.62 (m, 1H, H-4), 3.52 (ddd, *J* = 9.4, 5.1, 2.2 Hz, 1H, H-5), 3.41 (dd, *J* = 9.4, 7.4 Hz, 1H, H-2), 3.17 (dd, *J* = 5.3 Hz, 1H, OH), 0.85 (s, 9H, SiC(CH_3)$_3$), 0.11, 0.06, 0.03 (s x 3, 9H, SiCH$_3$). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.91 (C=O), 169.8 (C=O), 97.5 (C-1), 77.6 (C-3), 74.6 (C-2), 74.5 (C-5), 69.3 (C-4), 63.2 (C-6), 25.8 (SiC(CH$_3$)$_3$), 22.2 (CH$_3$), 18.1 (SiC(CH$_3$)$_3$), 17.97 (SiC(CH$_3$)$_3$), -3.83, -4.62, -4.65 (3 x SiCH$_3$).

3,4,6-Tri-*O*-*tert*-butyldimethylsilyl-2-deoxy-α/β-D-galactopyranose 1s



Following a literature procedure,[15] 3,4,6-tri-*O*-*tert*-butyldimethylsilyl-D-galactal[15] (200 mg, 0.409 mmol), deionised water (0.04 mL, 2.0 mmol), and TsOH.2H$_2$O (7.8 mg, 0.041 mmol) in DCM (1.64 mL) were stirred at room temperature for 4 h. Purification by column chromatography (100:0 to 95:5, DCM/Et$_2$O) afforded the hydrolysed product **1s** as a syrup (130 mg, 63%, α/β = 75:25). ESI-HRMS for $C_{24}H_{54}O_5Si_3Na^+$ $(M+Na)^+$ calculated: 529.3177; found 529.3159.

α/β

^{1}H NMR (500 MHz, Chloroform-*d*): 0.09, 0.08 (s x 2, 6H, SiCH$_3$), 0.06 (s, 6H, 2 x SiCH$_3$).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 26.4 (SiC(CH$_3$)$_3$), 26.3 (SiC(CH$_3$)$_3$), 26.1 (SiC(CH$_3$)$_3$), 18.75 (SiC(CH$_3$)$_3$), 18.69 (SiC(CH$_3$)$_3$), 18.4 (SiC(CH$_3$)$_3$), -3.8 (SiCH$_3$), -4.2 (SiCH$_3$), -4.5 (SiCH$_3$), -4.7 (SiCH$_3$), -5.07 (SiCH$_3$), -5.11 (SiCH$_3$).

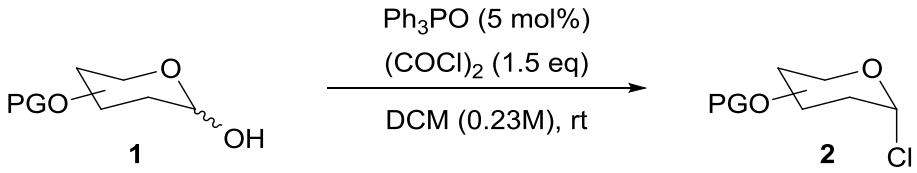
α-OH

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.34 (br s, 1H, H-1), 4.10 (ddd, *J* = 11.7, 4.3, 2.3 Hz, 1H, H-3), 3.88 – 3.83 (m, 2H, H-4 and H-5), 3.69 (dd, *J* = 10.1, 7.0 Hz, 1H, H- 6a), 3.62 (dd, *J* = 10.0, 6.3 Hz, 1H, H-6b), 2.43 (t, *J* = 2.4 Hz, 1H, OH), 2.09 (tdd, *J* = 12.5, 3.6, 2.2 Hz, 1H, H-2a), 1.65 (ddt, *J* = 12.5, 4.4, 1.3 Hz, 1H, H-2b), 0.92, 0.90, 0.89 (s x 3, 27H, SiC(CH_3)$_3$), 0.11, 0.10 (s x 2, 6H, SiCH$_3$). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 92.9 (C-1), 73.1 (C-4 or C-5), 70.4 (C-4 or C-5), 68.0 (C-3), 62.7 (C-6), 33.8 (C-2).

β-OH

^{1}H NMR (500 MHz, Chloroform-*d*): δ 4.74 (ddd, *J* = 9.3, 7.8, 2.5 Hz, 1H, H-1), 3.82 – 3.80 (m, 1H, H-4), 3.75 (dd, *J* = 10.0, 7.6 Hz, 1H, H-6a), 3.71 – 3.65 (m, 2H, H-3 and H-6b), 3.31 (ddd, *J* = 7.7, 5.8, 1.0 Hz, 1H, H-5), 2.92 (d, *J* = 7.8 Hz, 1H, OH), 1.91 (td, *J* = 11.7, 9.4 Hz, 1H, H-2a), 1.86 – 1.80 (m, 1H, H-2b), 0.91 (br s, 18H, SiC(CH_3)$_3$), 0.89 (s, 9H, SiC(CH_3)$_3$), 0.12, 0.10 (s x 2, 6H, $SiCH_3$). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 94.7 (C-1), 76.7 (C-5), 71.5 (C-3), 68.9 (C-4), 62.0 (C-6), 37.5 (C-2).

General Procedure A for synthesis of Glycosyl Chlorides



A 25 mL crimp-top vial charged with a stir-bar, hemiacetal (1 eq) and triphenylphosphine oxide (5 mol%) was placed under three cycles of vacuum and nitrogen. The solids were dissolved in anhydrous DCM (0.23 M), treated with oxalyl chloride (1.5 eq) and left to stir at room temperature. The reactions were monitored by ^{1}H NMR spectroscopy and spectroscopic yields were determined by quantitative ^{1}H NMR spectroscopy using dimethyl sulfone as an internal standard.

Procedure for Slow Addition of hemiacetal and Oxalyl Chloride

A 25 mL Schlenk flask charged with triphenylphosphine oxide (15 mol%) was placed under three cycles of vacuum and nitrogen. The phosphine oxide was dissolved in anhydrous $CHCl_3$ (0.1 M), treated with oxalyl chloride (15 mol%) and stirred till no effervescence was observed. To this mixture was added solutions of the hemiacetal (1 eq) and oxalyl chloride (1 eq) in anhydrous $CHCl_3$ (0.25 M) slowly over a period of 7 h using a syringe pump.

Procedure for Uncatalysed Reactions

A 25 mL crimp-top vial charged with a stir-bar and hemiacetal (1 eq) was placed under three cycles of vacuum and nitrogen. The hemiacetal was dissolved in anhydrous DCM (0.23 M), treated with oxalyl chloride (1.5 eq) and left to stir at room temperature. The reactions were monitored by ^{1}H NMR spectroscopy and spectroscopic yields were determined by quantitative ^{1}H NMR spectroscopy using dimethyl sulfone as an internal standard.

General Procedure B for synthesis of Glycosyl Chlorides

A 25 mL crimp-top vial charged with a stir-bar and hemiacetal (1 eq) was placed under three cycles of vacuum and nitrogen. A stock solution of the chlorotriphenylphosphonium chloride salt in DCM (1.0 eq, 0.23 M) was added to the reaction flask and left to stir at room temperature. The reactions were monitored by ^{1}H NMR spectroscopy and spectroscopic

yields were determined by quantitative ^{1}H NMR spectroscopy using dimethyl sulfone as an internal standard.

Preparation of stock solution of chlorotriphenylphosphonium chloride salt

A flame-dried 25 mL Schlenk flask was charged with triphenylphosphine oxide (1 eq) and a magnetic stirbar. The flask was placed under three cycles of vacuum and nitrogen. A solution of the phosphine oxide in dry DCM (0.23 M) was treated with oxalyl chloride (1.5 eq) and left to stir at room temperature for 15 min. The stock solution was stored in a 25 ml Young's tube under nitrogen (*the Young's tube was flamed-dried and placed under three cycles of vacuum and nitrogen prior to use*).

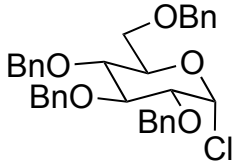
General Procedure C for synthesis of Glycosyl Chlorides

A 25 mL crimp-top vial charged with a stir-bar and hemiacetal (1 eq) was placed under three cycles of vacuum and nitrogen. A stock solution of the chlorotriphenylphosphonium chloride salt in DCM (1.2 eq, 0.28 M) was added to the reaction flask and left to stir at room temperature. The reactions were monitored by ^{1}H NMR spectroscopy and spectroscopic yields were determined by quantitative ^{1}H NMR spectroscopy using dimethyl sulfone as an internal standard.

Preparation of stock solution of chlorotriphenylphosphonium chloride salt

A flame-dried 25 mL Schlenk flask was charged with triphenylphosphine oxide (1 eq) and a magnetic stirbar. The flask was placed under three cycles of vacuum and nitrogen. A solution of the phosphine oxide in dry DCM (0.28 M) was treated with oxalyl chloride (1 eq) and left to stir at room temperature for 15 min. The stock solution was stored in a 25 ml Young's tube under nitrogen (*the Young's tube was flamed-dried and placed under three cycles of vacuum and nitrogen prior to use*).

2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl chloride 2a



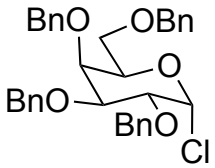
Following the general procedure A, hemiacetal **1a** (114.6 mg, 0.212 mmol) was used. After 2 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to give glycosyl chloride **2a** (93% spectroscopic yield, α/β = 95:5).

Gram scale synthesis

Following the general procedure, hemiacetal **1a** (1.50 g, 2.77 mmol) was used. After 3 h, ^{1}H NMR showed complete consumption of the hemiacetal. After a short quick column (R_f = 0.9, cyclohexane/ethyl acetate; 1:2) the pure glucosyl chloride **2a** was obtained as a cloudy white syrup (1.44 g, 93% yield, α/β = 95:5).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.38–7.25 (m, 18H, Ph), 7.14 (dd, *J* = 7.4, 2.1 Hz, 2H, Ph), 6.07 (d, *J* = 3.7 Hz, 1H, α-H), 5.20 (d, *J* = 7.8 Hz, 0.05H, β-H), 4.97 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 4.83 (d, *J* = 10.7 Hz, 1H, C*H*HPh), 4.82 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 4.75–4.67 (m, 2H, 2 × C*H*HPh), 4.57 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.50 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 4.46 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.08 (dt, *J* = 10.2, 2.3 Hz, 1H, H-5), 4.03 (t, *J* = 9.2 Hz, 1H, H-3), 3.78–3.70 (m, 3H, H-2, H-4, H-6a), 3.64 (dd, *J* = 11.0, 1.9 Hz, 1H, H-6b). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 138.6 (C), 138.1 (C), 137.7 (C), 137.5 (C), 128.7 (CH), 128.52 (CH), 128.50 (CH), 128.2 (CH), 128.15 (CH), 128.07 (CH), 128.05 (CH), 127.97 (CH), 127.91 (CH), 127.90 (CH), 127.8 (CH), 93.6 (C-1), 81.5 (C-3), 79.9 (C-2), 76.5 (C-4), 75.9 (Ph*C*H$_2$), 75.3 (Ph*C*H$_2$), 73.6 (Ph*C*H$_2$), 73.5 (C-5), 73.0 (Ph*C*H$_2$), 67.8 (C-6). NMR data were consistent with literature data.[16,17]

2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl chloride 2b

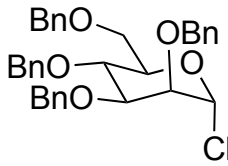


Following the general procedure A, hemiacetal **1b** (114.6 mg, 0.212 mmol) was used. After 16 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to give glycosyl chloride **2b** (72% spectroscopic yield, α/β ≥ 95:5).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.42–7.20 (m, 20H, Ph), 6.14 (d, *J* = 3.8 Hz, 1H, H-1), 4.94 (d, *J* = 11.3 Hz, 1H, C*H*HPh), 4.85 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.78–4.72 (m, 2H, 2 ×

C*H*HPh), 4.71(d, *J* = 11.6 Hz, 1H, C*H*HPh), 4.56 (d, *J* = 11.3 Hz, 1H, C*H*HPh), 4.48 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.40 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.25–4.21 (m, 1H, H-5), 4.21 (dd, *J* = 9.8, 3.8 Hz, 1H, H-2), 4.01–3.99 (m, 1H, H-4), 3.97 (dd, *J* = 9.7, 2.8 Hz, 1H, H-3), 3.55 (dd, *J* = 9.4, 6.9 Hz, 1H, H-6a), 3.53 (dd, *J* = 9.4, 6.1 Hz, 1H, H-6b). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 138.6 (C), 138.4 (C), 137.9 (C), 137.8 (C), 128.53 (CH), 128.51 (CH), 128.4 (CH), 128.3 (CH), 128.05 (CH), 127.99 (CH), 127.97 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 95.1 (C-1), 78.5 (C-3), 76.3 (C-2), 75.1 (Ph*C*H$_2$), 74.5 (C-4), 73.6 (Ph*C*H$_2$), 73.5 (Ph*C*H$_2$), 73.2 (Ph*C*H$_2$), 72.5 (C-5), 68.1 (C-6). NMR data were consistent with literature data.[18]

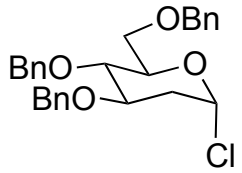
2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl chloride 2c



Following the general procedure A, hemiacetal **1c** (114.6 mg, 0.212 mmol) was used. After 16 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to give glycosyl chloride **2c** (79% spectroscopic yield, α/β ≥ 95:5).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.37–7.22 (m, 18H, Ph), 7.18 (dd, *J* = 7.4, 2.0 Hz, 2H, Ph), 6.10 (d, *J* = 1.7 Hz, 1H, H-1), 4.89 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 4.72 (d, *J* = 12.3 Hz, 1H, C*H*HPh), 4.68 (d, *J* = 12.3 Hz, 1H, C*H*HPh), 4.65 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.64 (d, *J* = 12.1 Hz, 1H, C*H*HPh) 4.59 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.54 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 4.51 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.18 (dd, *J* = 9.4, 3.1 Hz, 1H, H-3), 4.09 (t, *J* = 9.6 Hz, 1H, H-4), 4.03–3.99 (m, 1H, H-5), 3.88 (dd, *J* = 2.9, 1.9 Hz, 1H, H-2), 3.81 (dd, *J* = 11.2, 4.4 Hz, 1H, H-6a), 3.69 (dd, *J* = 11.2, 1.7 Hz, 1H, H-6b). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 138.3 (C), 138.18 (C), 138.17 (C), 137.7 (C), 128.6 (CH), 128.54 (CH), 128.46 (CH), 128.44 (CH), 128.1 (CH), 128.01 (CH), 127.98 (CH), 127.93 (CH), 127.92 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 91.7 (C-1), 78.5 (C-3), 77.9 (C-2), 75.4 (Ph*C*H$_2$), 74.7 (C-5), 74.2 (C-4), 73.5 (Ph*C*H$_2$), 73.0 (Ph*C*H$_2$), 72.6 (Ph*C*H$_2$), 68.4 (C-6). NMR data were consistent with literature data.[19,20]

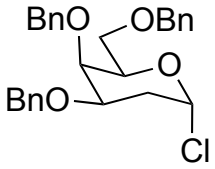
3,4,6-Tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl chloride 2d



Following the general procedure A, hemiacetal **1d** (92.1 mg, 0.212 mmol) was used. After 2 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to give glycosyl chloride **2d** (83% spectroscopic yield, α/β ≥ 95:5).

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.34–7.24 (m, 13H, Ph), 7.20–7.18 (m, 2H, Ph), 6.30 (d, *J* = 3.2 Hz, 1H, H-1), 4.90 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 4.67 (s, 2H, 2 × C*H*HPh), 4.60 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.55 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 4.49 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.16 (ddd, *J* = 11.0, 9.2, 4.8 Hz, 1H, H-3), 4.06 (br d, *J* = 9.8 Hz, 1H, H-5), 3.81 (dd, *J* = 10.9, 3.4 Hz, 1H, H-6a), 3.72 (t, *J* = 9.5 Hz, 1H, H-4), 3.66 (dd, *J* = 10.8, 1.7 Hz, 1H, H-6b), 2.51 (dd, *J* = 13.7, 4.8 Hz, 1H, H-2eq), 2.06 (ddd, *J* = 13.9, 11.2, 3.7 Hz, 1H, H-2ax). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 138.2 (2 × C), 137.8 (C), 128.45 (CH), 128.40 (CH), 128.4 (CH), 127.9 (CH), 127.7 (CH), 92.7 (C-1), 77.3 (C-4), 76.6 (C-3), 75.1 (Ph*C*H$_2$), 73.9 (C-5), 73.5 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 68.0 (C-6), 39.6 (C-2). NMR data were consistent with literature data.[21]

3,4,6-Tri-*O*-benzyl-2-deoxy-α-D-galactopyranosyl chloride 2e

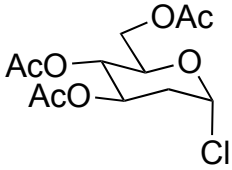


Following the general procedure A, hemiacetal **1e** (92.1 mg, 0.212 mmol) was used. After 2 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to give glycosyl chloride **2e** (73% spectroscopic yield, α/β ≥ 95:5).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.38–7.26 (m, 15H, Ph), 6.36 (d, *J* = 3.3 Hz, 1H, H-1), 4.93 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 4.62 (s, 2H, 2 × C*H*HPh), 4.60 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 4.50 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.43 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.21 (br t, *J* = 6.5 Hz, 1H, H-5), 4.11 (ddd, *J* = 11.7, 4.3, 2.4 Hz, 1H, H-3), 4.00 (br s, 1H, H-4), 3.61 (dd, *J* = 9.4, 7.1 Hz, 1H, H-6a), 3.56 (dd, *J* = 9.4, 5.9 Hz, 1H, H-6b), 2.58 (ddd, *J* = 13.2, 11.8, 3.8 Hz, 1H, H-2ax), 2.25 (dd, *J* = 13.2, 4.4 Hz, 1H, H-2eq). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 138.6 (C), 138.1 (C), 137.9 (C), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.5 (CH), 94.1 (C-1, $^1J_{1CH}$ = 183 Hz, from coupled HSCQ), 74.6 (Ph*C*H$_2$), 74.0 (C-

3), 73.5 (Ph*C*H_2), 73.0 (C-5), 72.8 (C-4), 70.8 (Ph*C*H_2), 68.5 (C-6), 35.5 (C-2). Attempts to obtain HRMS (ESI) resulted in mass spectra for the hydrolysed product **1e**.

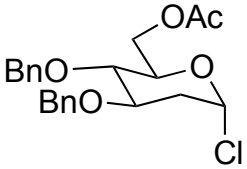
3,4,6-Tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride 2f



Following the general procedure A, hemiacetal **1f** (61.5 mg, 0.212 mmol) was used. After 24 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to give glycosyl chloride **2f** (92% spectroscopic yield, α/β ≥ 95:5).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.25 (d, *J* = 3.5 Hz, 1H, H-1), 5.49 (ddd, *J* = 11.3, 9.6, 5.2 Hz, 1H, H-3), 5.08 (t, *J* = 9.9 Hz, 1H, H-4), 4.35 (dd, *J* = 12.4, 4.3 Hz, 1H, H-6a), 4.30 (ddd, *J* = 10.2, 4.2, 2.0 Hz, 1H, H-5), 4.10 (dd, *J* = 12.4, 2.0 Hz, 1H, H-6b), 2.54 (ddd, *J* = 13.6, 5.2, 1.2 Hz, 1H, H-2eq), 2.20 (ddd, *J* = 13.6, 11.4, 3.9 Hz, 1H, H-2ax), 2.09 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.03 (s, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 170.7 (C=O), 170.1 (C=O), 169.8 (C=O), 90.5 (C-1), 71.0 (C-5), 68.4 (C-4), 68.2 (C-3), 61.6 (C-6), 39.0 (C-2), 21.0 (CH_3), 20.81 (CH_3), 20.80 (CH_3). NMR data were consistent with literature data.[22]

6-*O*-Acetyl,3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl chloride 2g

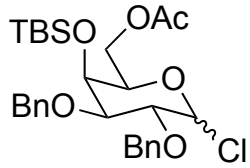


Following the general procedure A, hemiacetal **1g** (20 mg, 0.052 mmol) was used. After 8 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to generate glycosyl chloride **2g** (67% spectroscopic yield, α/β ≥ 95:5).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.42 – 7.27 (m, 10H, Ph), 6.24 (d, *J* = 3.1 Hz, 1H, H-1), 4.94 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.68 (s, 2H, 2 x C*H*HPh), 4.63 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.34 (dd, *J* = 12.2, 4.1 Hz, 1H, H-6a), 4.30 (dd, *J* = 12.2, 2.3 Hz, 1H, H-6b), 4.19 (ddd, *J* = 11.0, 8.9, 4.8 Hz, 1H, H-3), 4.13 (ddd, *J* = 10.0, 3.8, 2.4 Hz, 1H, H-5), 3.54 (dd, *J* = 10.0, 8.9 Hz, 1H, H-4), 2.54 (ddd, *J* = 13.6, 4.8, 1.2 Hz, 1H, H-2a), 2.10 – 2.00 (m, 1H, H-2b), 2.03 (s, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 170.8 (C=O), 138.1 (C), 137.9 (C), 128.6 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 92.0 (C-1, $^1J_{1CH}$ = 185 Hz, from coupled HSQC), 76.9 (C-4), 76.8 (C-3), 75.2 (Ph*C*H_2), 72.4 (C-5), 72.2 (Ph*C*H_2),

62.7 (C-6), 39.6 (C-2), 20.9 (CH_3). Attempts to obtain HRMS (ESI) resulted in mass spectra for the hydrolysed product **1g**.

6-*O*-Acetyl,2,3-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α/β-D-galactopyranosyl chloride 2h



Following the general procedure A, hemiacetal **1h** (15 mg, 0.029 mmol) was used. After 2 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to give glycosyl chloride **2h** (90% spectroscopic yield, α:β = 91:9).

α-Cl

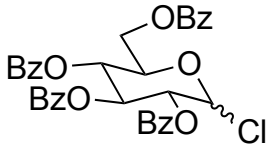
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.40 – 7.27 (m, 10H, Ph), 6.10 (d, *J* = 3.7 Hz, 1H, H-1), 4.82 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 4.75 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.71 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 4.70 (d, *J* = 11.9 Hz, 1H, C*H*HPh) 4.17 – 4.05 (m, 5H, H-6a/b, H-5, H-4, H-2), 3.83 (dd, *J* = 9.9, 2.6 Hz, 1H, H-3), 2.06 (s, 3H, CH_3), 0.83 (s, 9H, SiC(CH_3)$_3$), 0.03 (s, 3H, $SiCH_3$), 0.00 (s, 3H, $SiCH_3$). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 170.7 (C=O), 138.1 (C), 137.7 (C), 128.6 (CH), 128.3 (CH), 128.2 (CH), 128.11 (CH), 128.07 (CH), 127.8 (CH), 95.0 (C-1, $^1J_{1CH}$ = 183 Hz, from coupled HSCQ), 77.0 (C-3), 75.4 (C-2), 74.0 (Ph*C*H$_2$), 73.1 (Ph*C*H$_2$), 72.5 (C-4/5), 69.8 (C-4/5), 63.2 (C-6), 26.0 (SiC(*C*H$_3$)$_3$), 20.9 (CH_3), 18.6 (Si*C*(CH$_3$)$_3$), -3.8 ($SiCH_3$), -5.0 ($SiCH_3$).

β-Cl (tentatively assigned; selected signals)

^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.17 (d, *J* = 8.2 Hz, H-1), 4.89 (d, *J* = 10.4 Hz, 1H, C*H*HPh), 3.64 (t, *J* = 6.3 Hz, 1H), 3.38 (dd, *J* = 9.5, 2.6 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*): δ 90.9 (from HSQC);

Attempts to obtain HRMS (ESI) resulted in mass spectra for the hydrolysed product **1h**.

2,3,4,6-Tetra-*O*-benzoyl-α/β-D-glucopyranosyl chloride 2i



Following the general procedure A, hemiacetal **1i** (126.5 mg, 0.2120 mmol) was used. After 16 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to give glycosyl chloride **2i** (76% spectroscopic yield, α/β = 1:3).

α/β

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.10–7.80 (m, 8H, Ph), 7.58–7.27 (m, 12H, Ph). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 133.9 (C), 133.7 (C), 133.5 (C), 133.4 (C), 130.2 (CH), 130.0 (CH), 129.9 (CH), 129.5 (CH), 128.8 (CH), 128.6 (CH), 128.52 (CH), 128.48 (CH).

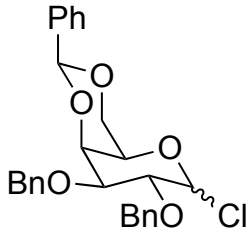
α-Cl

^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.56 (d, *J* = 4.0 Hz, 1H, H-1), 6.27 (t, *J* = 9.9 Hz, 1H, H-3), 5.80 (t, *J* = 10.0 Hz, 1H, H-4), 5.50 (dd, *J* = 10.0, 4.0 Hz, 1H, H-2), 4.76 (ddd, *J* = 10.4, 4.4, 2.8 Hz, 1H, H-5), 4.70–4.65 (m, 1H, H-6a), 4.55–4.49 (m, 1H, H-6b). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.17 (C=O), 165.73 (C=O), 165.54 (C=O), 165.22 (C=O), 90.6 (C-1, $^{1}J_{1CH}$ = 188 Hz, from coupled HSQC), 71.8 (C-2), 71.1 (C-5), 70.0 (C-3), 68.4 (C-4), 62.2 (C-6).

β-Cl

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.92–5.86 (m, 1H, H-3), 5.81 (t, *J* = 9.6 Hz, 1H, H-4), 5.72 (t, *J* = 8.6 Hz, 1H, H-2), 5.67 (d, *J* = 8.3 Hz, 1H, H-1), 4.68 (dd, *J* = 12.4, 3.1 Hz, 1H, H-6a), 4.53 (dd, *J* = 12.3, 5.1 Hz, 1H, H-6b), 4.29 (ddd, *J* = 9.8, 5.0, 3.0 Hz, 1H, H-5). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 166.21 (C=O), 165.75 (C=O), 165.15 (C=O), 164.98 (C=O), 88.1 (C-1, $^{1}J_{1CH}$ = 174 Hz, from coupled HSQC), 76.0 (C-5), 74.1 (C-2), 73.1 (C-3), 68.9 (C-4), 63.0 (C-6). NMR data were consistent with literature data for β-Cl.[23]

2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-galactopyranosyl chloride 2j



Following the general procedure A, hemiacetal **1j** (23 mg, 0.052 mmol) was used. After 7.5 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to generate glycosyl chloride **2j** (77% spectroscopic yield, α/β = 97:3).

α-Cl

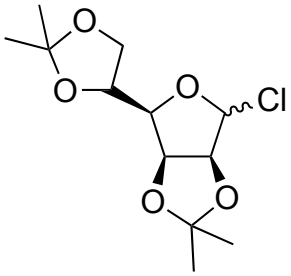
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.55 – 7.27 (m, 15H, Ph), 6.23 (d, *J* = 3.7 Hz, 1H, H-1α), 5.51 (s, 1H, H-7α), 4.84 (d, *J* = 12.2 Hz, 1H, C*H*HPh), 4.83 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.75 (d, *J* = 12.2 Hz, 1H, C*H*HPh), 4.72 (d, *J* = 11.6 Hz, 1H, C*H*HPh), 4.27 – 4.20 (m, 3H, H-2, H-4 and H-6a), 4.08 – 4.00 (m, 2H, H-3 and H-6b), 3.95 (br s, 1H, H-5). ^{13}C

NMR (101 MHz, Chloroform-*d*): δ 138.5 (C), 138.0 (C), 137.6 (C), 129.1 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 128.0 (CH), 127.8 (CH), 126.3 (CH), 101.1 (C-7), 95.4 (C-1), 75.5 (C-3), 75.3 (C-2/4), 74.1 (C-2/4), 73.5 (Ph*C*H_2), 72.5 (Ph*C*H_2), 69.0 (C-6), 65.8 (C-5). NMR data were consistent with literature data.[18,24]

β-Cl (selected signals)

^{1}H NMR (400 MHz, Chloroform-*d*): 5.20 (d, *J* = 8.6 Hz, 0.3H, H-1). NMR data were consistent with literature data.[24]

2,3:5,6-Di-*O*-isopropylidene-α/β-D-mannofuranosyl chloride 2k



Following the general procedure A, hemiacetal **1k** (13 mg, 0.052 mmol), K_2CO_3 (5 eq) and powdered 4Å molecular sieves were used. After 2 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to generate glycosyl chloride **2k** (77% spectroscopic yield, α/β = 93:7).

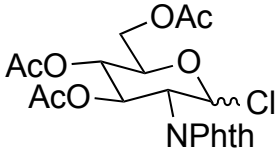
α-Cl

^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.07 (s, 1H, H-1), 4.96 (d, *J* = 5.8 Hz, 1H, H-2), 4.89 (dd, *J* = 5.8, 3.6 Hz, 1H, H-3), 4.44 (ddd, *J* = 7.8, 6.3, 4.4 Hz, 1H, H-5), 4.22 (dd, *J* = 7.7, 3.5 Hz, 1H, H-4), 4.11 (dd, *J* = 8.7, 6.3 Hz, 1H, H-6a), 4.02 (dd, *J* = 8.8, 4.3 Hz, 1H, H-6b), 1.47 (s, 6H, 2 x CH_3), 1.39 (s, 3H, CH_3), 1.34 (s, 3H, CH_3). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 113.4 ($O_2C(CH_3)_2$), 109.6 ($O_2C(CH_3)_2$), 97.8 (C-1, $^1J_{1CH}$ = 191 Hz, from coupled HSQC), 89.3 (C-2), 82.5 (C-4), 78.7 (C-3), 72.5 (C-5), 66.8 (C-6), 27.0 (CH_3), 25.9 (CH_3), 25.3(CH_3), 24.8 (CH_3). NMR data were consistent with literature data.[18]

Selected signals for **β-Cl** (tentatively assigned)

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.63 (d, *J* = 4.0 Hz, 1H, H-1), 4.79 (dd, *J* = 6.2, 4.0 Hz, 1H, CH), 3.81 (dd, *J* = 8.3, 4.4 Hz, 1H, CH), 1.62 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.41 (s, 3H, CH_3). ^{13}C NMR (126 MHz, Chloroform-*d*): 92.0 (C-1, $^1J_{1CH}$ = 180 Hz, from coupled HSQC).

3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-α/β-D-glucopyranosyl chloride 2l



Following the general procedure A, hemiacetal **1l** (92.3 mg, 0.212 mmol) was used. After 16 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to give glycosyl chloride **2l** (92% spectroscopic yield, α/β = 1:2).

α/β

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.88 (m, 2H, Ph), 7.77 (m, 2H, Ph). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 170.6 (C=O), 170.0 (C=O), 169.3 (C=O), 167.4 (C=O), 134.7 (CH), 131.3 (C), 124.0 (CH).

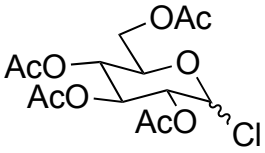
α-Cl

^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.69 (dd, *J* = 11.5, 9.1 Hz, 1H, H-3), 6.24 (d, *J* = 3.7 Hz, 1H, H-1), 5.14 (dd, *J* = 10.2, 9.2 Hz, 1H, H-4), 4.77 (dd, *J* = 11.5, 3.7 Hz, 1H, H-2), 4.48 (ddd, *J* = 10.3, 3.8, 1.9 Hz, 1H, H-5), 4.42 (dd, *J* = 12.5, 4.0 Hz, 1H, H-6a), 4.18 (dd, *J* = 12.5, 1.9 Hz, 1H, H-6b), 2.12 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 1.90 (s, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 91.5 (C-1, $^{1}J_{1CH}$ = 183 Hz, from coupled HSQC), 70.1 (C-5), 69.2 (C-4), 66.9 (C-3), 61.3 (C-6), 55.9 (C-2), 20.83 (CH_3), 20.81 (CH_3), 20.78 (CH_3).

β-Cl

^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.20 (d, *J* = 9.3 Hz, 1H, H-1), 5.79 (dd, *J* = 10.5, 9.2 Hz, 1H, H-3), 5.25 (dd, *J* = 10.2, 9.3 Hz, 1H, H-4), 4.52 (dd, *J* = 10.5, 9.4 Hz, 1H, H-2), 4.34 (dd, *J* = 12.5, 4.7 Hz, 1H, H-6a), 4.21 (dd, *J* = 12.5, 2.1 Hz, 1H, H-6b), 3.99 (ddd, *J* = 10.3, 4.7, 2.2 Hz, 1H, H-5), 2.14 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 1.87 (s, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 85.7 (C-1, $^{1}J_{1CH}$ = 174 Hz, from coupled HSQC), 75.8 (C-5), 70.7 (C-3), 68.3 (C-4), 61.8 (C-6), 57.6 (C-2), 20.9 (CH_3), 20.7 (CH_3), 20.5 (CH_3). NMR data were consistent with literature data for β-Cl.[25,26]

2,3,4,6-Tetra-*O*-acetyl-α/β-D-glucopyranosyl chloride 2o



Following the general procedure B, hemiacetal **1o** (18 mg, 0.052 mmol) was used. After 1 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to generate glycosyl chloride **2o** (92% spectroscopic yield, α/β = 29:71).

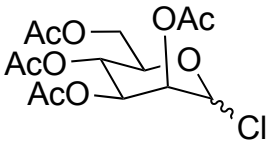
α-Cl

^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.30 (d, *J* = 4.0 Hz, 1H, H-1), 5.56 (t, *J* = 9.8 Hz, 1H, H-3), 5.16 – 5.11 (m, 1H, H-4), 5.02 (dd, *J* = 10.1, 4.0 Hz, 1H, H-2), 4.36 – 4.29 (m, 2H, H-5 and H-6a), 4.16 – 4.11 (m, 1H, H-6b), 2.104 (s, 3H, CH_3), 2.101 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.04 (s, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 170.60 (C=O), 169.9 (C=O), 169.5 (C=O), 90.2 (C-1), 70.8 (C-2), 70.5 (C-5), 69.5 (C-3), 67.5 (C-4), 61.2 (C-6), 20.8 (br, CH_3). NMR data were consistent with literature data.[18,27]

β-Cl

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.32 (d, *J* = 8.2 Hz, 1H, H-1), 5.23 – 5.15 (m, 3H, H-2, H-3 and H-4), 4.27 (dd, *J* = 12.5, 4.8 Hz, 1H, H-6a), 4.17 (dd, *J* = 12.5, 2.3 Hz, 1H, H-6b), 3.83 (ddd, *J* = 9.6, 4.7, 2.2 Hz, 1H, H-5), 2.11 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.02 (s, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 170.66 (C=O), 170.1 (C=O), 169.3 (C=O), 169.1 (C=O), 87.7 (C-1), 75.6 (C-5), 73.5 (C-2/3), 72.9 (C-2/3), 67.7 (C-4), 61.7 (C-6), 20.8, 20.6 (br, CH_3). NMR data were consistent with literature data.[28]

2,3,4,6-Tetra-O-acetyl-α/β-D-mannopyranosyl chloride 2p



Following the general procedure B, hemiacetal **1p** (18 mg, 0.052 mmol) was used. After 1 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to generate glycosyl chloride **2p** (71% spectroscopic yield, α/β = 83:17).

α-Cl

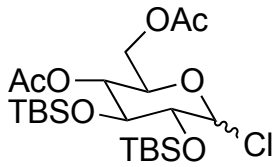
^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.00 (d, *J* = 1.6 Hz, 1H, H-1), 5.61 (dd, *J* = 10.2, 3.4 Hz, 1H, H-3), 5.39 (dd, *J* = 3.4, 1.7 Hz, 1H, H-2), 5.36 (t, *J* = 10.1 Hz, 1H, H-4), 4.32 (dd, *J* = 12.2, 5.0 Hz, 1H, H-6a), 4.30 – 4.25 (m, 1H, H-5), 4.15 (dd, *J* = 12.2, 2.0 Hz, 1H, H-6b),

2.18 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.01 (s, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 170.6, 169.8, 169.71, 169.65 (4 x C=O), 88.9 (C-1), 71.6 (C-2), 71.4 (C-5), 67.8 (C-3), 65.4 (C-4), 61.7 (C-6), 20.9 (CH_3), 20.8 (CH_3), 20.74 (CH_3), 20.68 (CH_3). NMR data were consistent with literature data.[18,27]

β-Cl

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.54 (d, *J* = 1.1 Hz, 1H, H-1), 5.51 (dd, *J* = 3.4, 1.2 Hz, 1H, H-2), 5.28 (t, *J* = 10.0 Hz, 1H, H-4), 5.11 (dd, *J* = 10.0, 3.3 Hz, 1H, H-3), 4.30 – 4.25 (m, 1H, H-6a), 4.18 (dd, *J* = 12.4, 2.5 Hz, 1H, H-6b), 3.80 (ddd, *J* = 9.9, 5.7, 2.5 Hz, 1H, H-5), 2.24 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.01 (s, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*) selected peaks: δ 85.8 (C-1), 76.3 (C-5), 71.1 (C-2), 70.3 (C-3), 65.1 (C-4), 62.3 (C-6). NMR data were consistent with literature data.[29]

4,6-*O*-Diacetyl-2,3-di-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranosyl chloride 2q



Following the general procedure C, hemiacetal **1q** (15 mg, 0.030 mmol) was used. After 4 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to give glycosyl chloride **2q** (90% spectroscopic yield, α:β = 1:1).

α/β

^{1}H NMR (500 MHz, Chloroform-*d*): 2.09, 2.09, 2.08, 2.07 (s x 4, 12H, CH_3), 0.94, 0.901, 0.897, 0.85 (s x 4, 36H, $SiC(CH_3)_3$), 0.135, 0.125, 0.121, 0.118, 0.111, 0.10, 0.09 (s x 7, 24H, $SiCH_3$). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 26.2, 25.9, 25.8, 25.7 (4 x $SiC(CH_3)_3$), 21.3, 21.2, 20.92, 20.88 (4 x CH_3), 18.3, 18.0, 17.9 (3 x $SiC(CH_3)_3$), -3.0, -3.4, -4.1, -4.27, -4.32, -4.38, -4.42, -4.6 (8 x $SiCH_3$).

α-Cl

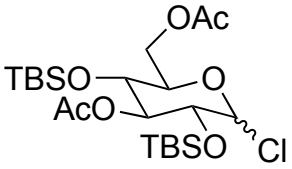
^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.98 (d, *J* = 3.6 Hz, 1H, H-1), 4.96 (dd, *J* = 10.1, 8.9 Hz, 1H, H-4), 4.23 – 4.15 (m, 2H, H-6a, H-5), 4.06 – 4.01 (m, 2H, H-3, H-6b), 3.80 (dd, *J* = 8.8, 3.6 Hz, 1H, H-2). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 170.80 (C=O), 169.6 (C=O), 95.5 (C-1, $^1J_{1CH}$ = 182 Hz, from coupled HSCQ), 74.1 (C-2), 71.6 (C-3), 71.1 (C-5), 70.2 (C-4), 63.2 (C-6).

Attempts to obtain HRMS (ESI) resulted in mass spectra for the hydrolysed product **1q**.

β-Cl

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.71 (dd, *J* = 2.8, 0.9 Hz, 1H, H-1), 5.18 (dd, *J* = 6.6, 5.6 Hz, 1H, H-4), 4.39 (dd, *J* = 11.9, 6.1 Hz, 1H, H-6a), 4.30 (dd, *J* = 11.9, 4.6 Hz, 1H, H-6b), 4.09 (td, *J* = 6.3, 4.6 Hz, 1H, H-5), 3.93 (t, *J* = 2.8 Hz, 1H, H-2), 3.86 (ddd, *J* = 5.5, 2.8, 0.9 Hz, 1H, H-3). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 170.77 (C=O), 169.8 (C=O), 90.9 (C-1, $^1J_{1CH}$ = 182 Hz, from coupled HSCQ), 76.5 (C-2), 73.9 (C-5), 73.2 (C-3), 69.6 (C-4), 62.0 (C-6). W-coupling is noted between H-1 and H-3; NOESY from H-1 shows strong correlation to H-2 and weak correlation to H-3 & H-5; combined data suggest a distorted conformation is adopted by the β-Cl.

3,6-*O*-Diacetyl-2,4-di-*O*-*tert*-butyldimethylsilyl-α/β-D-glucopyranosyl chloride 2r



Following the general procedure C, hemiacetal **1r** (16 mg, 0.032 mmol) was used. After 6 h, ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to give glycosyl chloride **2r** (87% spectroscopic yield, α/β = 88:12).

α/β

^{1}H NMR (500 MHz, Chloroform-*d*): δ 2.10, 2.09 (s x 2, 6H, CH_3), 0.08, 0.06, 0.05, 0.04 (s x 4, 12H, $SiCH_3$).

α-Cl

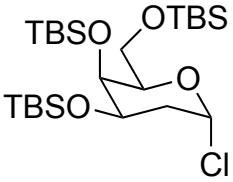
^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.92 (d, *J* = 3.9 Hz, 1H, H-1), 5.33 (t, *J* = 9.3 Hz, 1H, H-3), 4.42 – 4.35 (m, 1H, H-6a), 4.17 – 4.10 (m, 2H, H-6b, H-4/5), 3.78 (dd, *J* = 9.4, 4.0 Hz, 1H, H-2), 3.78 – 3.74 (m, 1H, H-4/5), 0.87 (s, 9H, $SiC(CH_3)_3$), 0.85 (s, 9H, $SiC(CH_3)_3$). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 170.6 (C=O), 169.3 (C=O), 94.5 (C-1, $^1J_{1CH}$ = 182 Hz, from coupled HSCQ), 74.6 (C-3), 72.9 (C-4/5), 71.8 (C-2), 68.4 (C-4/5), 62.4 (C-6), 25.7 ($SiC(CH_3)_3$), 25.4 ($SiC(CH_3)_3$), 21.8 (CH_3), 20.9 (CH_3), 18.0 ($SiC(CH_3)_3$), 17.8 ($SiC(CH_3)_3$), -3.9, -4.4, -4.87, -4.90 (4 x $SiCH_3$).

β-Cl

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.20 (d, *J* = 7.4 Hz, 1H, H-1), 4.99 (dd, *J* = 8.7, 8.0 Hz, 1H, H-3), 4.43 (dd, *J* = 12.1, 2.3 Hz, 1H, H-6a), 4.02 (dd, *J* = 12.1, 5.0 Hz, 1H, H-6b), 3.84 (dd, *J* = 9.6, 8.7 Hz, 1H, H-4), 3.70 (t, *J* = 7.6 Hz, 1H, H-2), 3.63 (ddd, *J* = 9.6, 5.0, 2.2

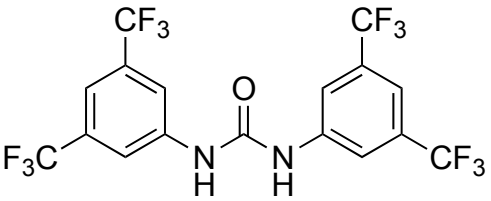
Hz, 1H, H-5). ^{13}C NMR (126 MHz, Chloroform-*d*) selected peaks: δ 91.5 (C-1, $^{1}J_{1CH}$ = 175 Hz, from coupled HSCQ), 78.1 (C-3), 77.4 (C-5), 75.8 (C-2), 68.7 (C-4), 62.7 (C-6). Attempts to obtain HRMS (ESI) resulted in mass spectra for the hydrolysed product **1r**.

3,4,6-Tri-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-galactopyranosyl chloride 2s



Following the general procedure for uncatalysed reactions, hemiacetal **1s** (26 mg, 0.052 mmol) was used. After 8 h ^{1}H NMR spectroscopy showed complete consumption of the hemiacetal to generate glycosyl chloride **2s** (90% spectroscopic yield, α/β ≥ 95:5).
^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.32 (d, *J* = 3.3 Hz, 1H, H-1), 4.24 (ddd, *J* = 11.4, 4.1, 2.3 Hz, 1H, H-3), 3.95 (br s, 1H, H-4), 3.92 (t, *J* = 6.8 Hz, 1H, H-5), 3.72 (dd, *J* = 10.1, 7.5 Hz, 1H, H-6a), 3.63 (dd, *J* = 10.1, 6.1 Hz, 1H, H-6b), 2.47 (ddd, *J* = 13.1, 11.6, 3.7 Hz, 1H, H-2$_{ax}$), 1.93 (ddt, *J* = 13.2, 4.3, 1.3 Hz, 1H, H-2$_{eq}$), 0.92, 0.90, 0.89 (s x 3, 27 H, SiC(C*H*$_3$)$_3$), 0.118 (s, 3H, SiCH$_3$), 0.116 (s, 3H, SiCH$_3$), 0.11, 0.10, 0.07, 0.06 (s x 4, 12H, SiCH$_3$). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 95.1 (C-1, $^{1}J_{1CH}$ = 185 Hz, from coupled HSQC), 75.7 (C-5), 69.7 (C-4), 68.0 (C-3), 61.5 (C-6), 37.9 (C-2), 26.3 (SiC(*C*H$_3$)$_3$), 26.2 (SiC(*C*H$_3$)$_3$), 26.0 (SiC(*C*H$_3$)$_3$), 18.7 (Si*C*(CH$_3$)$_3$), 18.6 (Si*C*(CH$_3$)$_3$), 18.3 (Si*C*(CH$_3$)$_3$), -3.8 (SiCH$_3$), -4.3 (SiCH$_3$), -4.6 (SiCH$_3$), -4.9 (SiCH$_3$), -5.1 (SiCH$_3$), -5.2 (SiCH$_3$). Attempts to obtain HRMS (ESI) resulted in mass spectra for the hydrolysed product **1s**.

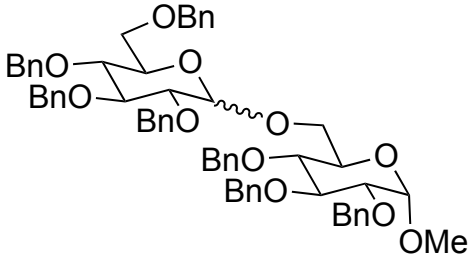
1,3-Bis[3,5-bis(trifluoromethyl)phenyl]urea 8



Following the literature procedure,[30] a flame-dried 25 mL Schlenk flask was placed under three cycles of vacuum and nitrogen, and then was charged with 3,5-bis(trifluoromethyl)aniline (0.341 mL, 2.18 mmol) and anhydrous THF (10 mL). 3,5-Bis(trifluoromethyl)phenyl isocyanate (0.452 mL, 2.62 mmol) was added to the solution and the reaction mixture was left to stir at room temperature for 48 h. The reaction mixture was concentrated *in vacuo* and the crude solid obtained was washed with cold DCM (3 × 10 mL) to give 1,3-bis[3,5-bis(trifluoromethyl)phenyl]urea **8** as a white solid (0.962 g, 91% yield).

^{1}H NMR (300 MHz, Methanol-d_4): δ 8.10 (s, 4H), 7.56 (s, 2H). ^{19}F NMR (282 MHz, Methanol-d_4): δ -64.67. ^{13}C NMR (101 MHz, Methanol-d_4): δ 154.1, 142.5, 133.3 (q, J = 33.2 Hz), 124.8 (q, J = 271.8 Hz), 119.9–119.5 (m), 116.5 (hept, J = 3.2 Hz). NMR data were consistent with literature data.[30]

One-Pot Glycosylation Using Urea Catalyst

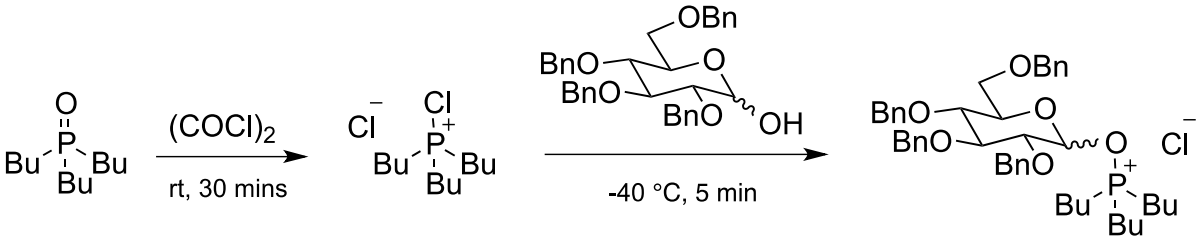


A 25 mL reaction tube charged with a stir-bar, hemiacetal **1a** (54.1 mg, 0.1000 mmol) and triphenylphosphine oxide (1.4 mg, 5.0 μmol) was placed under three cycles of vacuum and nitrogen. The solids were dissolved in anhydrous DCM (0.23 M), treated with oxalyl chloride (13 μml, 0.15 mmol) and left to stir at room temperature. After 2 h, the solvent and excess oxalyl chloride were removed by applying vacuum. Following the literature procedure,[30] acceptor **6** (23.2 mg, 0.0499 mmol), urea catalyst **8** (4.8 mg, 9.9 μmol), tris(trimethoxyphenyl)phosphine **7** (106.5 mg, 0.200 mmol) and K_2CO_3 (22 mg, 0.16 mmol) were added to the reaction tube and placed under three cycles of vacuum and nitrogen. The contents were dissolved in anhydrous DCE (0.5 mL) and stirred at reflux for 12 h. At that point most of the solvent had evaporated from the reaction mixture; additional anhydrous DCE (0.5 mL) was added and the reaction mixture was stirred at reflux for another 12 h. The reaction mixture was purified by column chromatography (R_f = 0.23, pentane/ethyl acetate; 4:1) to give the product **9** as a white solid. (35.2 mg, 71% yield, α/β = 88:12).

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.39–7.18 (m, 33H), 7.16–7.08 (m, 2H), 4.98 (d, J = 3.5 Hz, 1H, H-1), 4.96 (d, J = 10.6 Hz, 1H, C*H*HPh), 4.93 (d, J = 9.7 Hz, 1H, C*H*HPh), 4.91 (d, J = 10.4 Hz, 1H, C*H*HPh), 4.82 (d, J = 11.0 Hz, 1H, C*H*HPh), 4.80 (d, J = 10.8 Hz, 1H, C*H*HPh), 4.77 (d, J = 10.9 Hz, 1H, C*H*HPh), 4.70 (d, J = 12.1 Hz, 1H, C*H*HPh), 4.66 (s, 2H, 2 × C*H*HPh), 4.64 (d, J = 11.3 Hz, 1H, C*H*HPh), 4.57 (d, J = 12.0 Hz, 2H, 2 × C*H*HPh), 4.55 (d, J = 3.2 Hz, 1H, H-1'), 4.45 (d, J = 11.0 Hz, 1H, C*H*HPh), 4.41 (d, J = 12.1 Hz, 1H, C*H*HPh), 3.99 (d, J = 9.5 Hz, 1H, H-3'), 3.94 (d, J = 9.5 Hz, 1H, H-3), 3.85–3.74 (m, 3H, H-6a', H-5, H-5'), 3.71 (d, J = 11.1 Hz, 1H, H-6b'), 3.68–3.59 (m, 3H, H-6a, H-4, H-4'), 3.57–3.53 (m, 1H, H-6b), 3.53 (dd, J = 9.5, 3.6 Hz, 1H, H-2), 3.44 (dd, J = 9.6, 3.6 Hz, 1H, H-2'),

3.35 (s, 3H, OCH_3). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 138.96 (C), 138.95 (C), 138.61 (C), 138.58 (C), 138.56 (C), 138.3 (C), 138.1 (C), 128.54 (CH), 128.46 (CH), 128.44 (CH), 128.41 (CH), 128.14 (CH), 128.14 (CH), 128.11 (CH), 128.01 (CH), 127.97 (CH), 127.87 (CH), 127.84 (CH), 127.77 (CH), 127.75 (CH), 127.71 (CH), 127.68 (CH), 127.66 (CH), 127.63 (CH), 98.1 (C-1'), 97.4 (C-1), 82.3 (C-3'), 81.8 (C-3), 80.3 (C-2'), 80.1 (C-2), 77.9 (C-4/4'), 77.8 (C-4/4'), 75.85 (Ph*C*H_2), 75.6 (Ph*C*H_2), 75.1 (Ph*C*H_2), 75.0 (Ph*C*H_2), 73.55 (Ph*C*H_2), 73.51 (Ph*C*H_2), 72.5 (Ph*C*H_2), 70.5 (C-5'), 70.4 (C-5), 68.6 (C-6), 66.2 (C-6'), 55.3 (OCH_3). NMR data was consistent with literature data.[31]

Mechanistic Studies (alkoxyphosphonium salt 5b)



A 25 mL Schlenk flask was charged with tributylphosphine oxide (40.5 mg, 0.185 mmol) and a magnetic stirbar. Under a nitrogen atmosphere, the flask was heated with a heat gun until the phosphine oxide melted and was then evacuated for 15 minutes. This was repeated another two times. A solution of the phosphine oxide in dry $CDCl_3$ (3.7 mL) was then treated with oxalyl chloride (23.7 μl, 0.277 mmol) and was left to stir at room temperature for 1 h. The reaction mixture was cooled to -40 °C and hemiacetal **1a** (100 mg, 0.185 mmol) was added to the reaction flask. The contents were stirred for 5 mins and an aliquot (0.6 mL) of the reaction mixture was quickly transferred to an NMR tube under nitrogen in a deep Schenk tube at -40 °C. The tube was capped under a positive flow of nitrogen and sealed with Teflon tape. Subsequent NMR experiments were carried out at -10 °C. Hemiacetal **1a**, a small amount of glycosyl chloride **2a**, chlorophosphonium salt **4b** and a small amount of protonated phosphine oxide were present in addition to a species assigned as alkoxyphosphonium salt **5b**. Selected signals attributed to **5b**: ^1H NMR (600 MHz, Chloroform-*d*): δ 5.33 (dd, *J* = 7.2, 7.1 Hz 1H, H-1), 3.87 (br d, *J* = 9.7 Hz, 1H, H4/5), 3.80 (app t, *J* = 9.0 Hz, 1H, H-3), 3.52 (app t, *J* = 8.3 Hz, 1H, H-2), 2.56 (dt, *J* = 20.3, 10.6 Hz, 6H, CH_2), 1.47–1.41 (m, 6H, CH_2), 0.90 (t, *J* = 7.1 Hz, 9H, CH_3). HSQC NMR (600 × 151 MHz, Chloroform-*d*): cross peak at 5.33 (^1H), 100.0 (C-1, $^1J_{1CH}$ = 170 Hz, from coupled HSQC). ^{31}P NMR (243 MHz, Chloroform-*d*): δ 102.4.

Anomerisation Tests

Following the general procedure, hemiacetal **1a** (125 mg, 0.231 mmol) was used and tributylphosphine oxide (1 eq.) was used in place of triphenylphosphine oxide. After 1 h the ^{1}H NMR spectrum showed complete consumption of the hemiacetal (α/β-glycosyl chloride **2a** = 75:25). After a short quick column (R_f = 0.9, cyclohexane/ethyl acetate; 1:2) the pure glucosyl chloride **2a** was obtained as a cloudy white syrup (111 mg, 86% yield, α/β = 87:13). A stock solution of **2a** in anhydrous DCM (0.23 M) was prepared and divided into three reactions **A**, **B** and **C**. Reaction **A** was used as a control, to reaction **B** was added triphenyl phosphine oxide (5 mol%) and to reaction **C** was added triphenyl phosphine oxide (5 mol%) and a drop of conc HCl. At intervals of 1 h, an aliquot was taken from each reaction, solvent was removed and ^{1}H NMR experiments were carried out. There was no significant change in α/β ratio over time under these conditions (**Table 1**).

Anomerisation Test with chlorophosphonium salt/$(COCl)_2$

Following the procedure above the pure glycosyl chloride **2a** was obtained as a cloudy white syrup (α/β = 89.5:10.5). A 25 mL crimp-top vial charged with a stir-bar, pure glycosyl chloride **2a** and triphenylphosphine oxide (5 mol%) was placed under three cycles of vacuum and nitrogen. The solids were dissolved in anhydrous DCM (0.23 M), treated with oxalyl chloride (1.5 eq) and left to stir at room temperature. At intervals of 1 h, an aliquot was taken from the reaction, solvent was removed under inert atmosphere and ^{1}H NMR experiments were carried out using anhydrous $CDCl_3$. There was no significant change in α/β ratio over time under these conditions (**Table 2**).

Table 1. Anomerisation Test

Entry	Time h	A Control α/β	B Ph_3PO α/β	C Ph_3PO, conc HCl α/β
1	0.2	87:13	87:13	87:13
2	1	87:13	87:13	87:13
3	2	87:13	87:13	87:13
4	3	87:13	87:13	87:13
5	3.5	87:13	87:13	88:12

Table 1. Anomerisation Test under CPS, $(COCl)_2$ conditions

Entry	Time	CPS, $(COCl)_2$
	h	α/β
1	1	90:10
2	2	90:10
3	4	90:10

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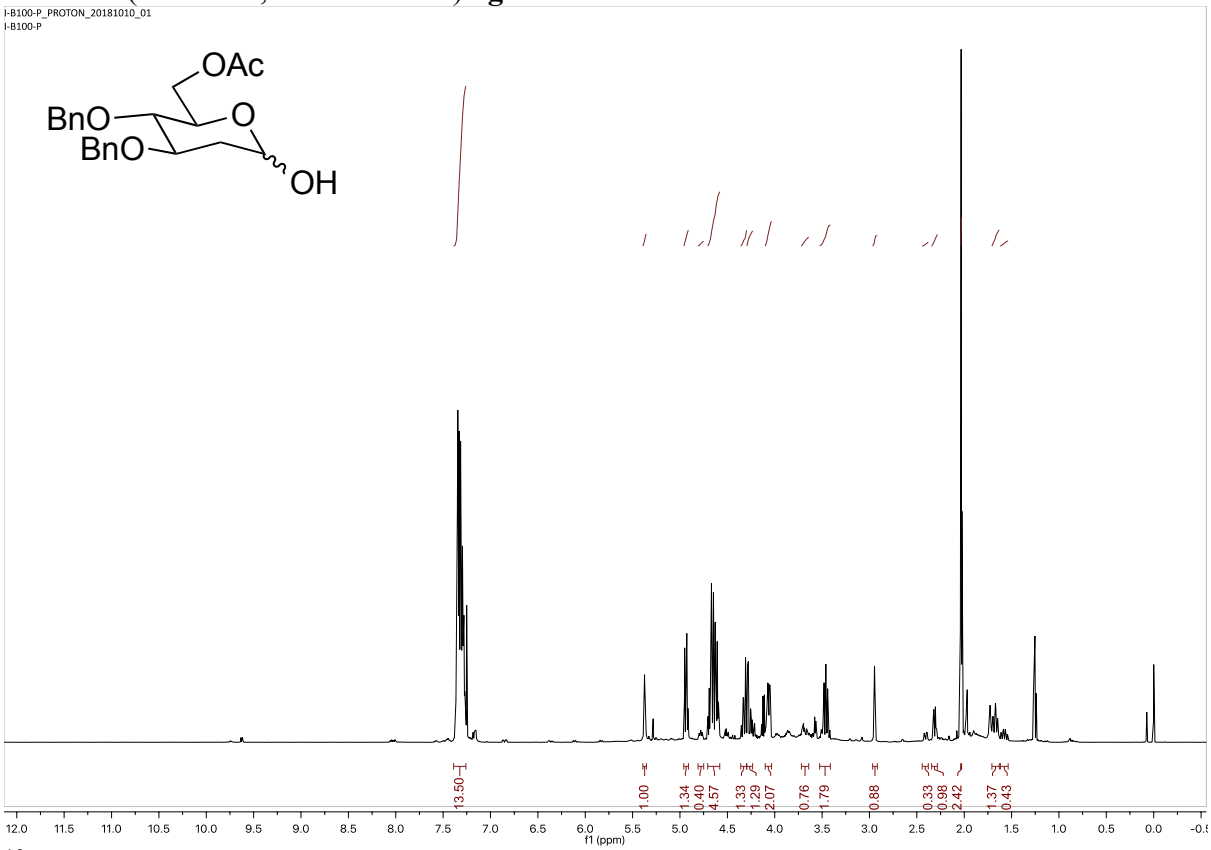
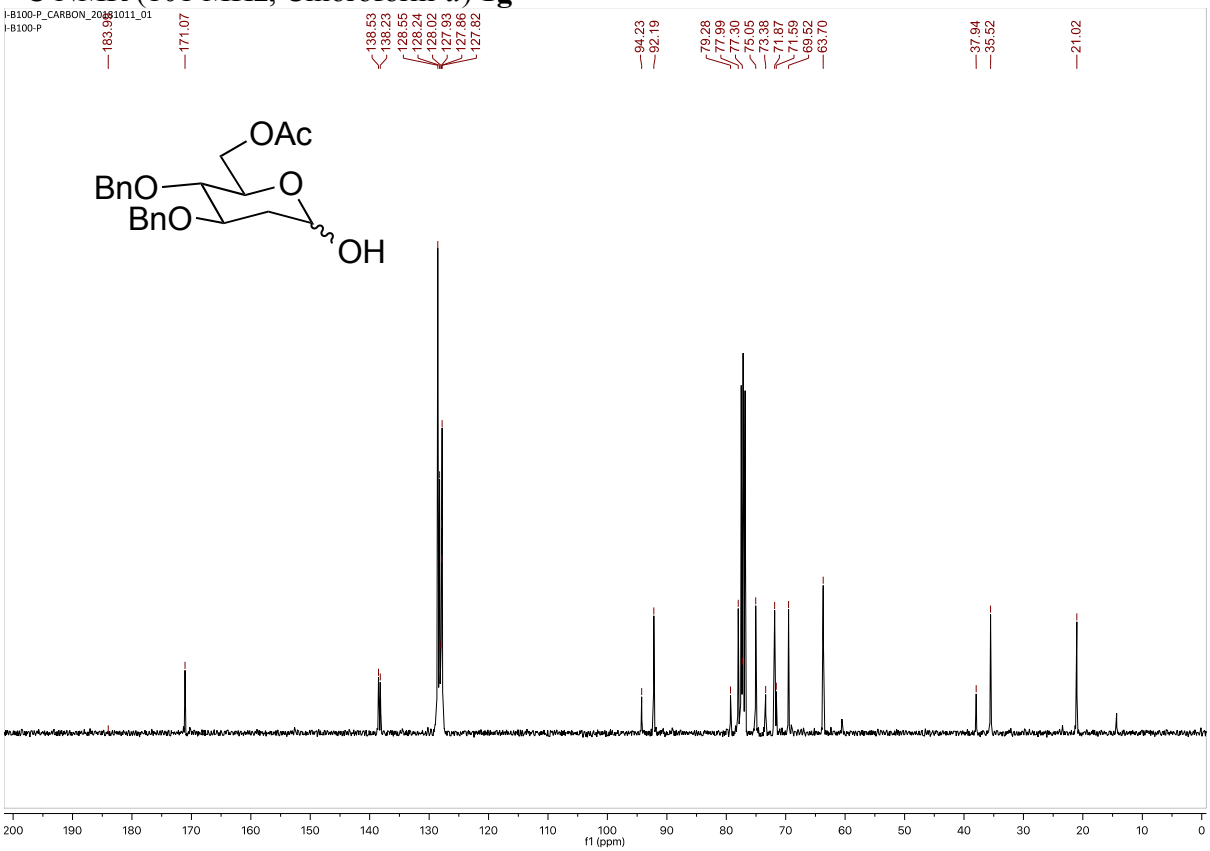
NMR Spectra

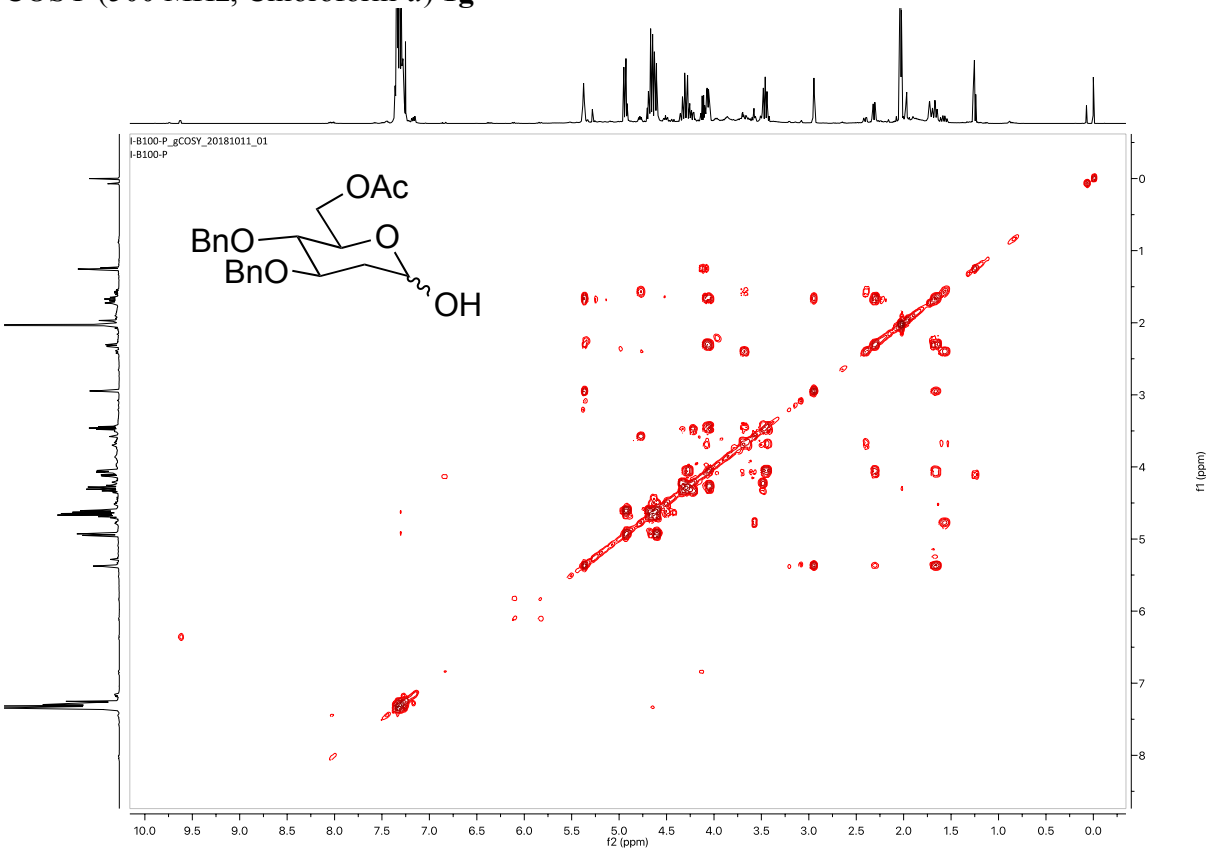
^{1}H NMR (500 MHz, Chloroform-*d*) **1g**



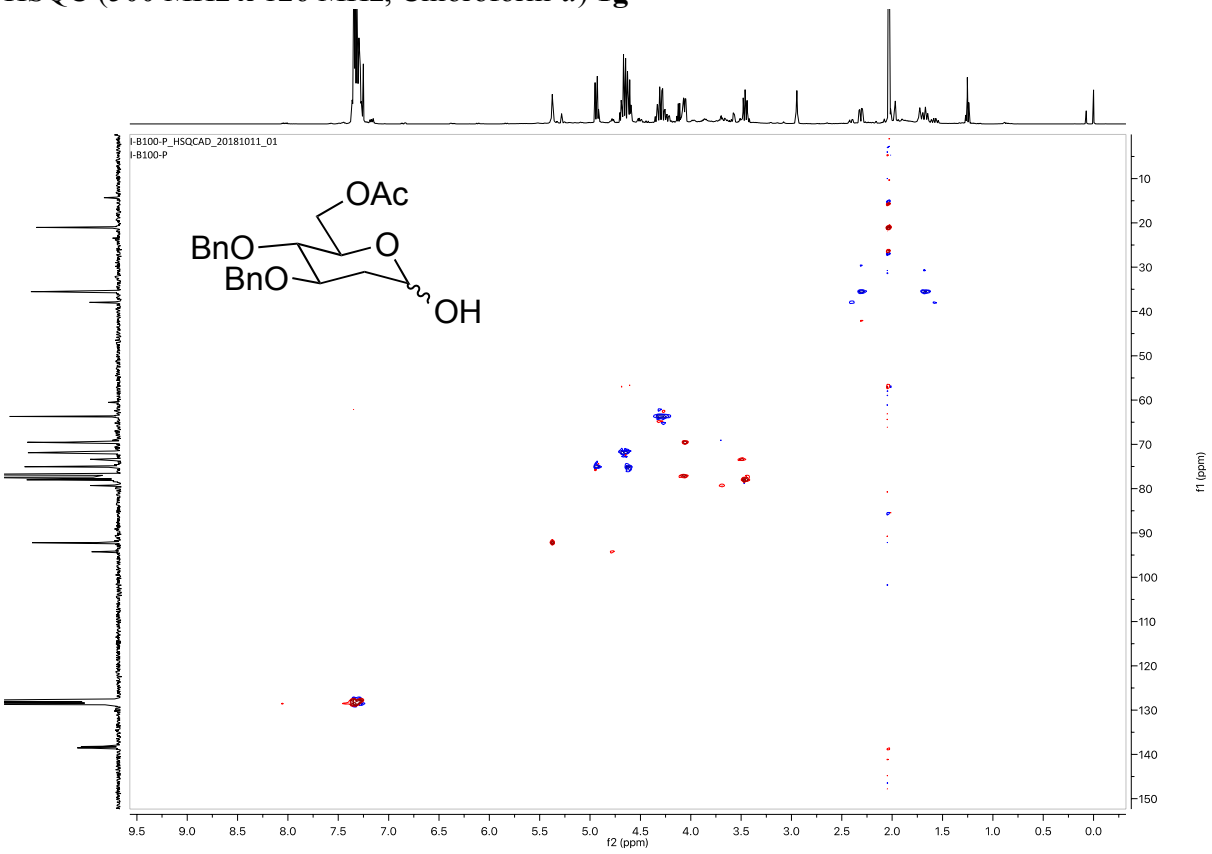
^{13}C NMR (101 MHz, Chloroform-*d*) **1g**



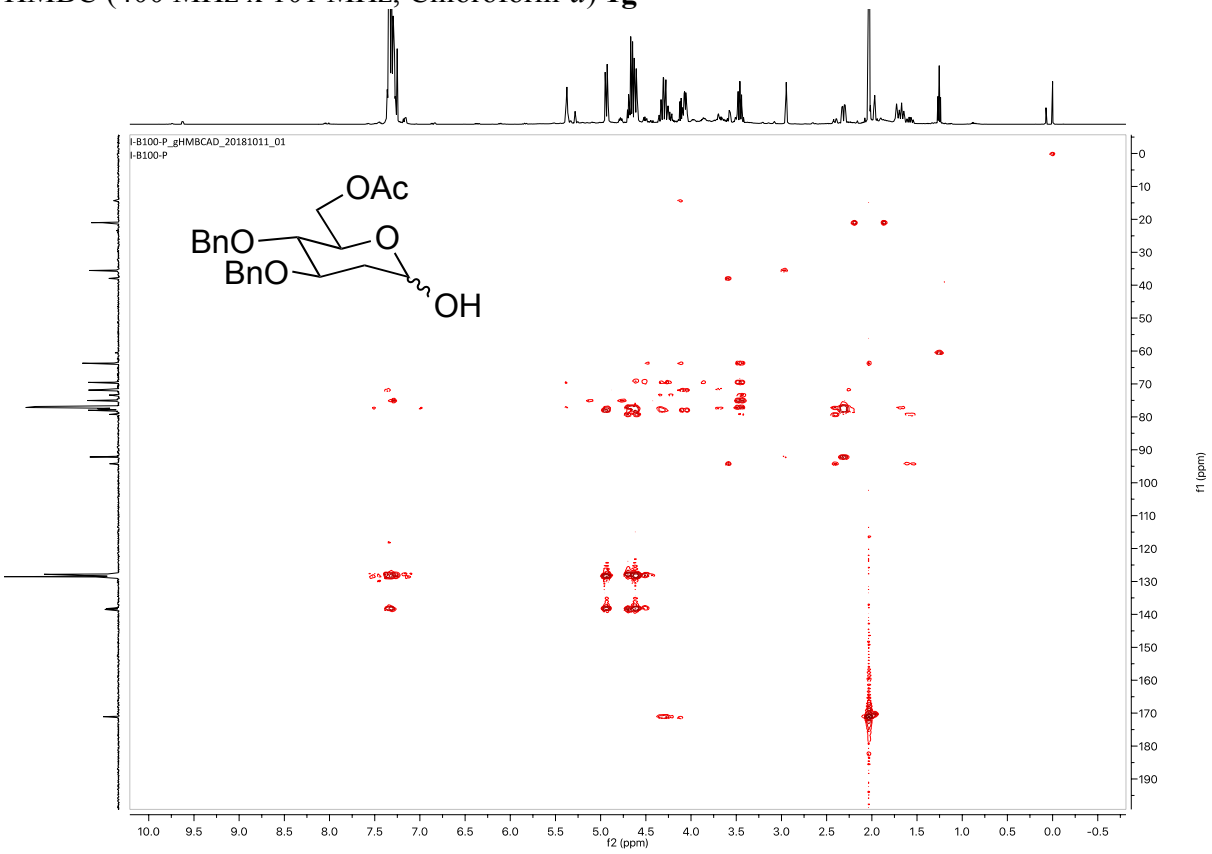
COSY (500 MHz, Chloroform-*d*) **1g**



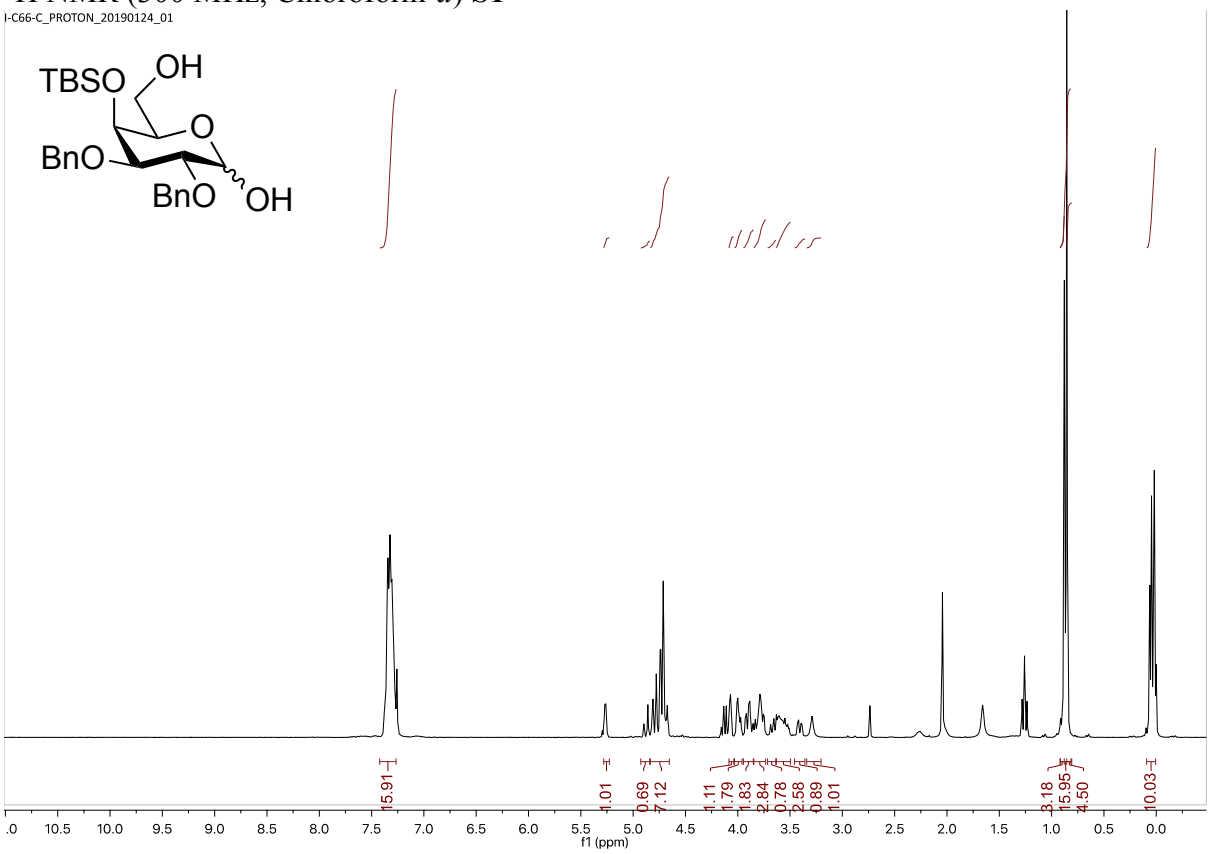
HSQC (500 MHz x 126 MHz, Chloroform-*d*) **1g**



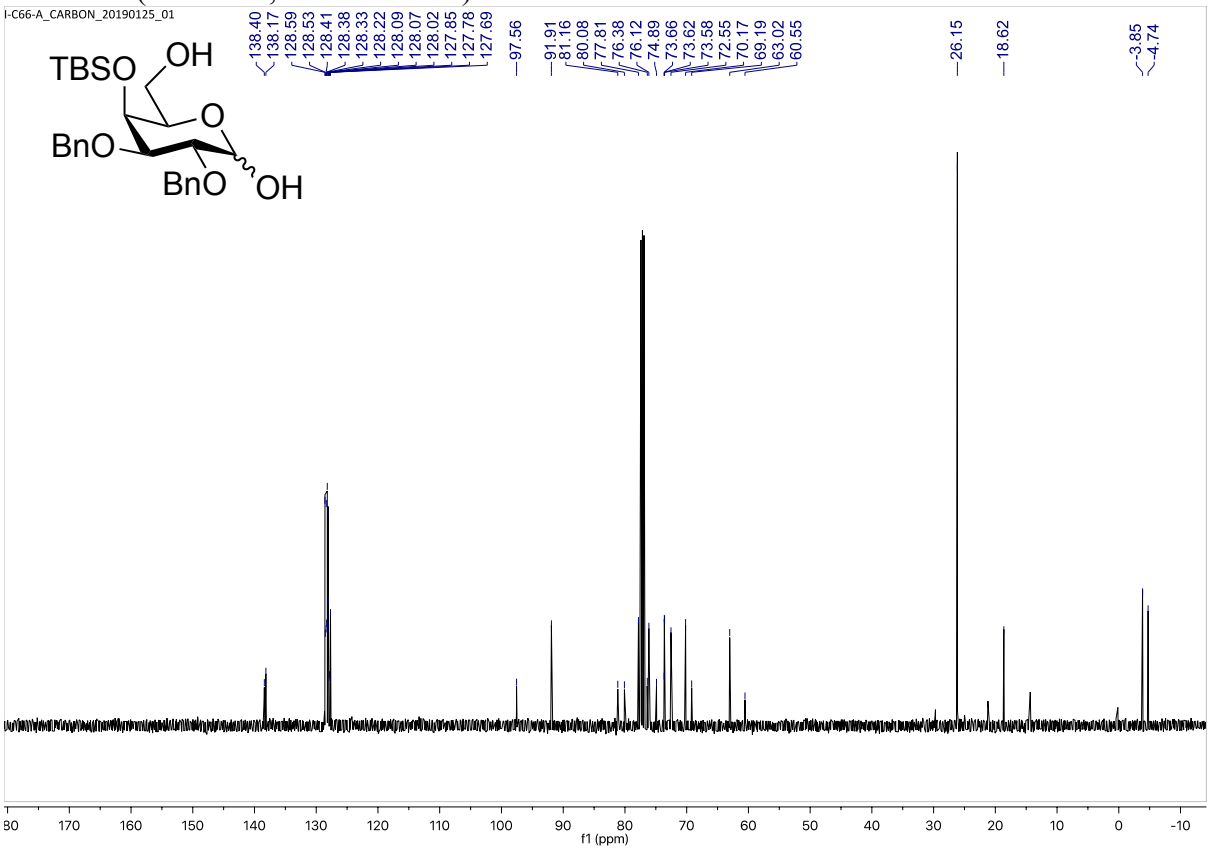
HMBC (400 MHz x 101 MHz, Chloroform-*d*) **1g**



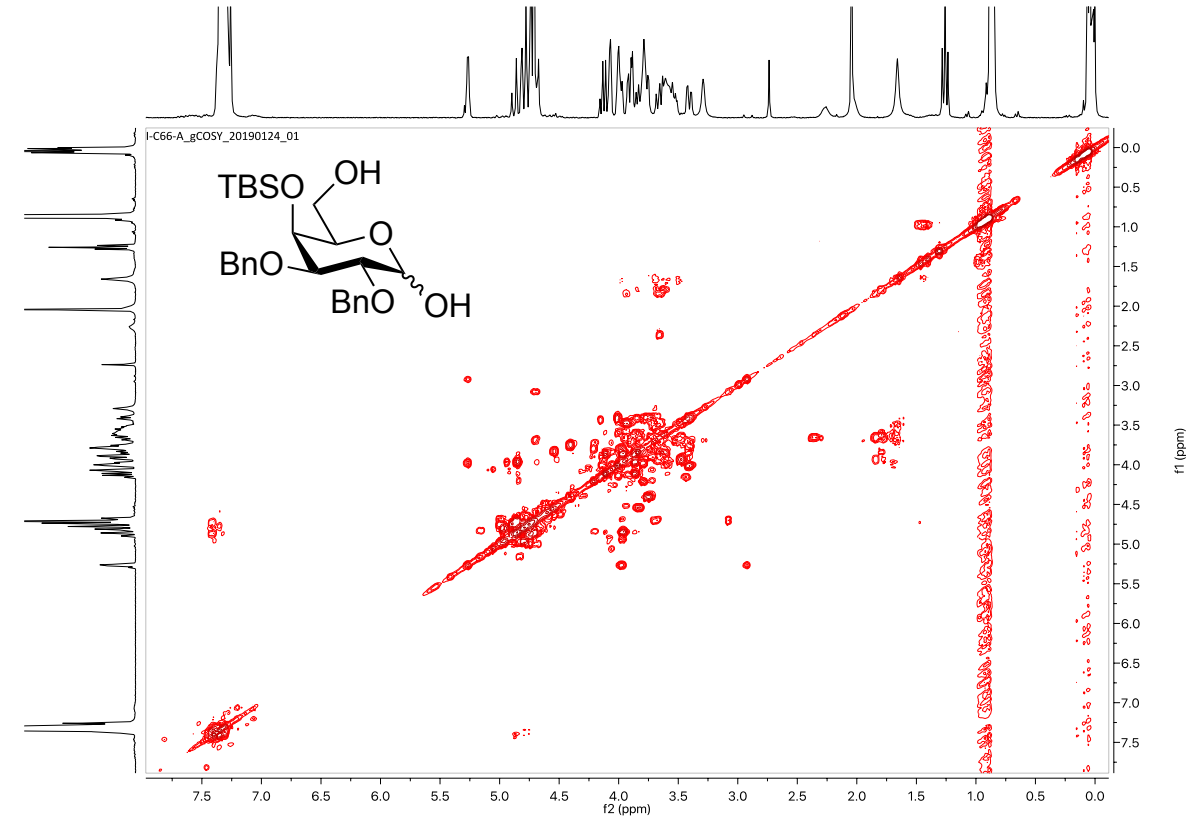
^{1}H NMR (300 MHz, Chloroform-*d*) **S1**



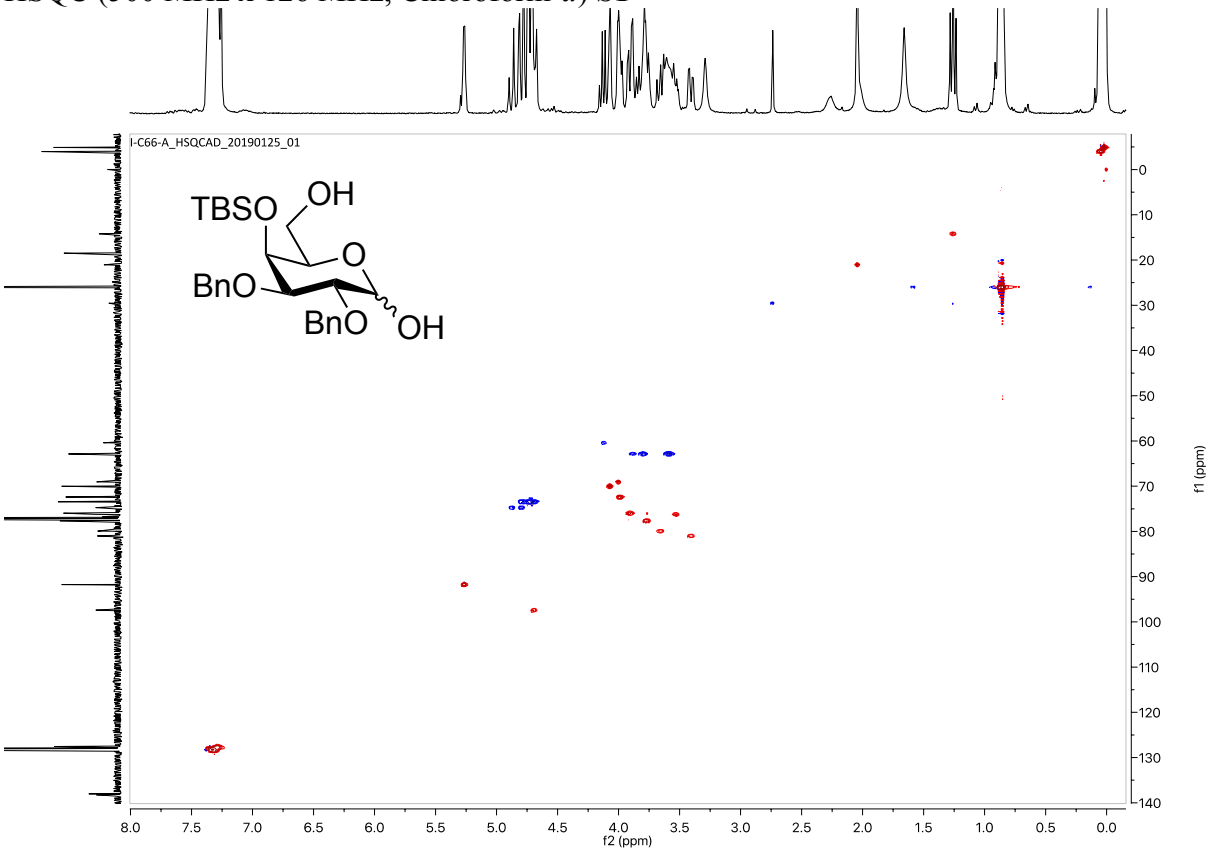
^{13}C NMR (126 MHz, Chloroform-*d*) **S1**



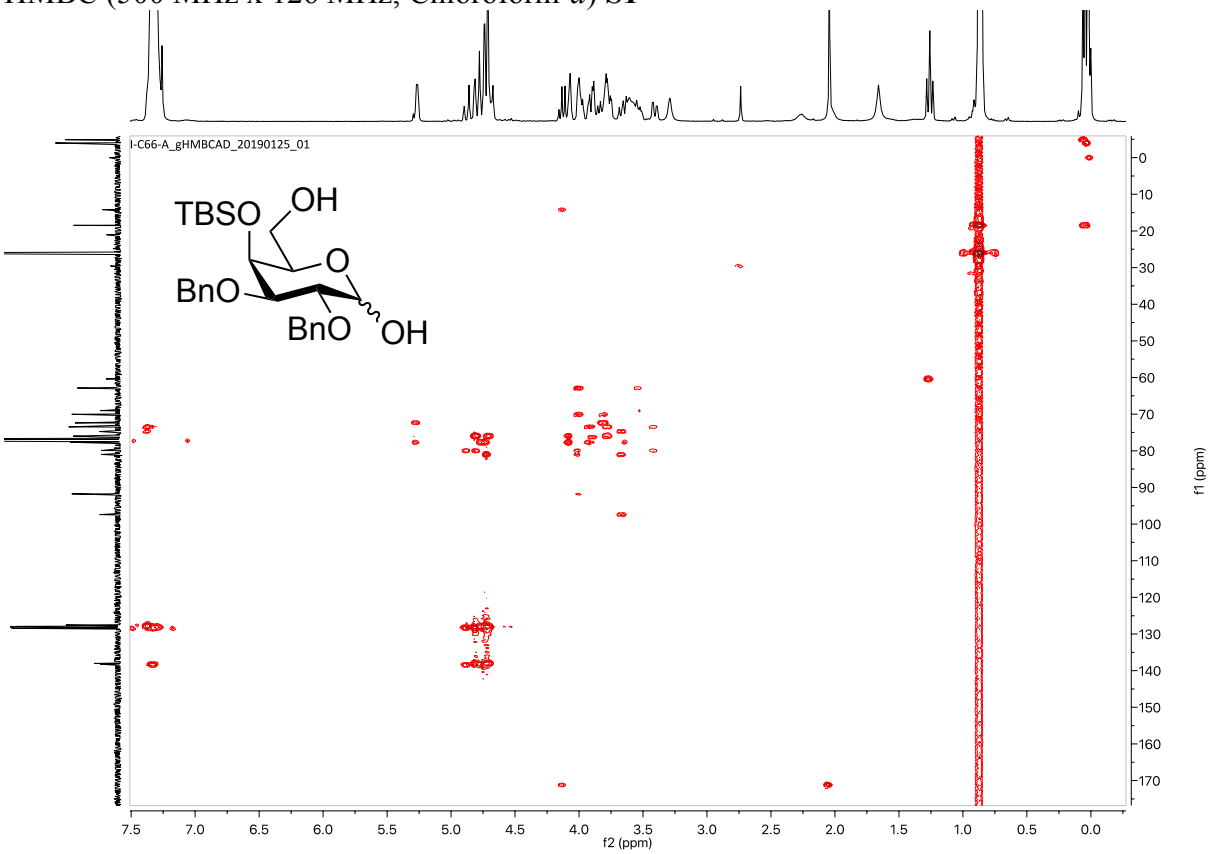
COSY (500 MHz, Chloroform-*d*) **S1**



HSQC (500 MHz x 126 MHz, Chloroform-*d*) **S1**



HMBC (500 MHz x 126 MHz, Chloroform-*d*) **S1**



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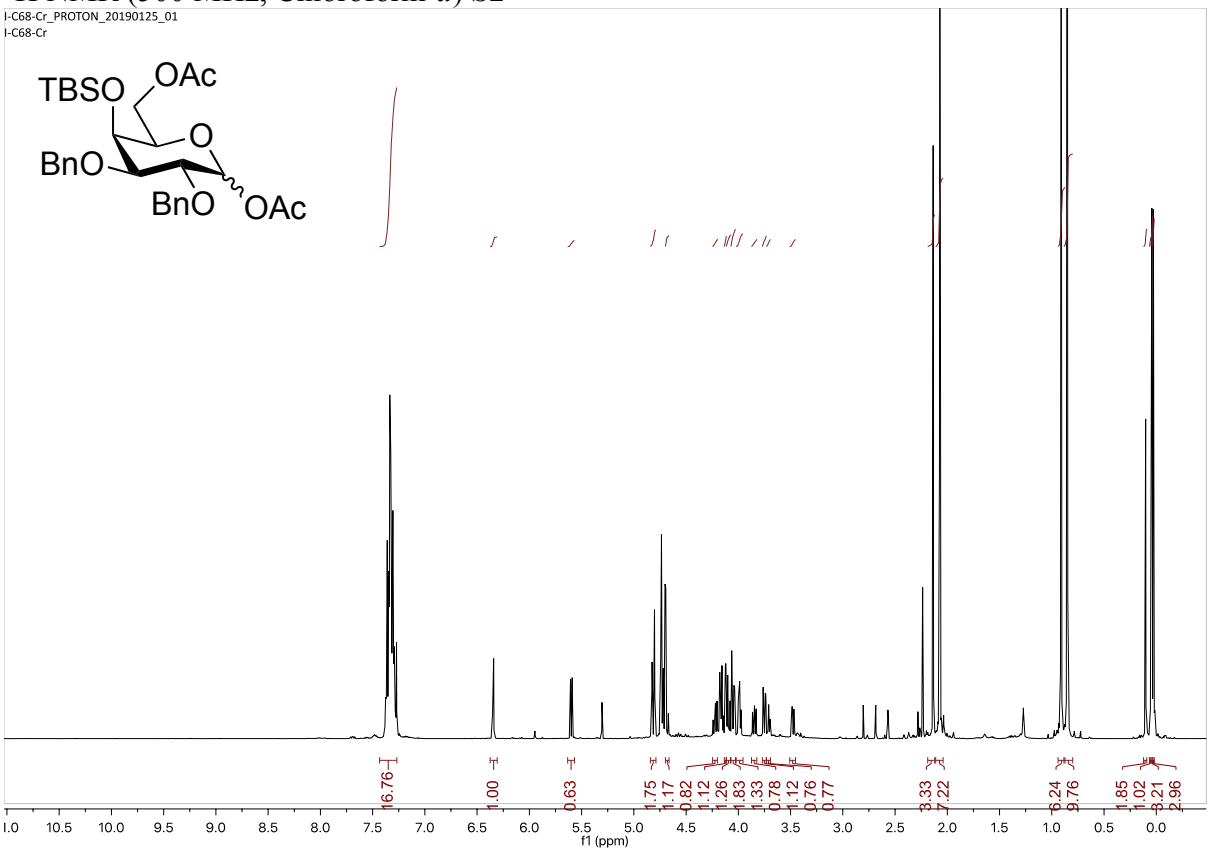
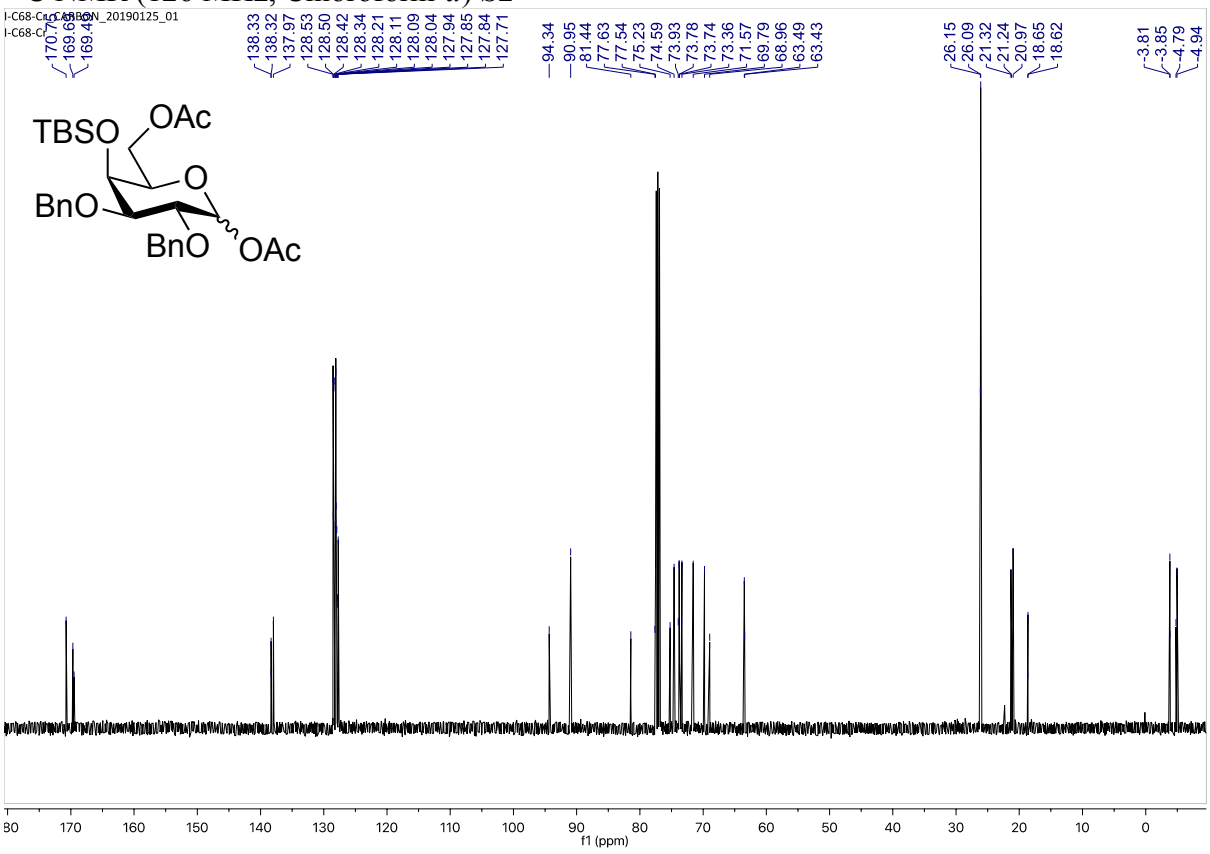
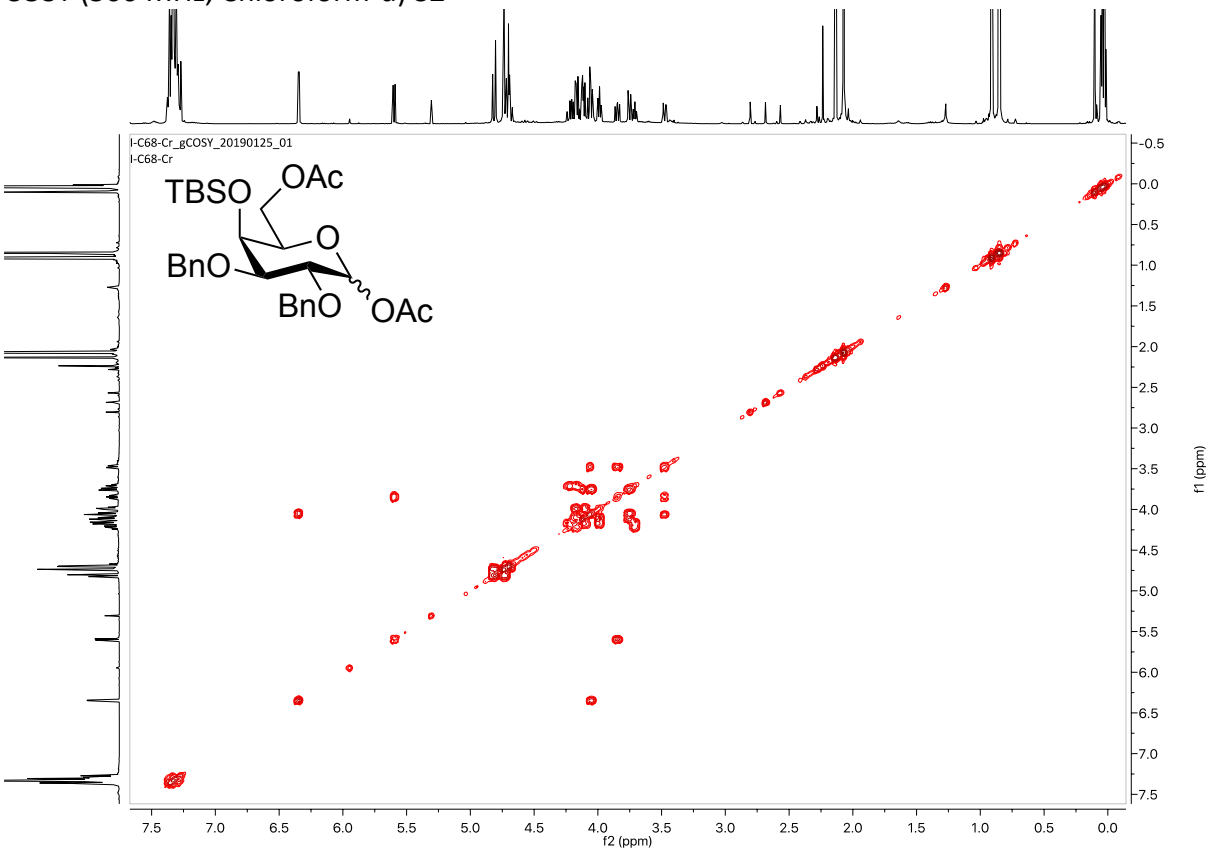


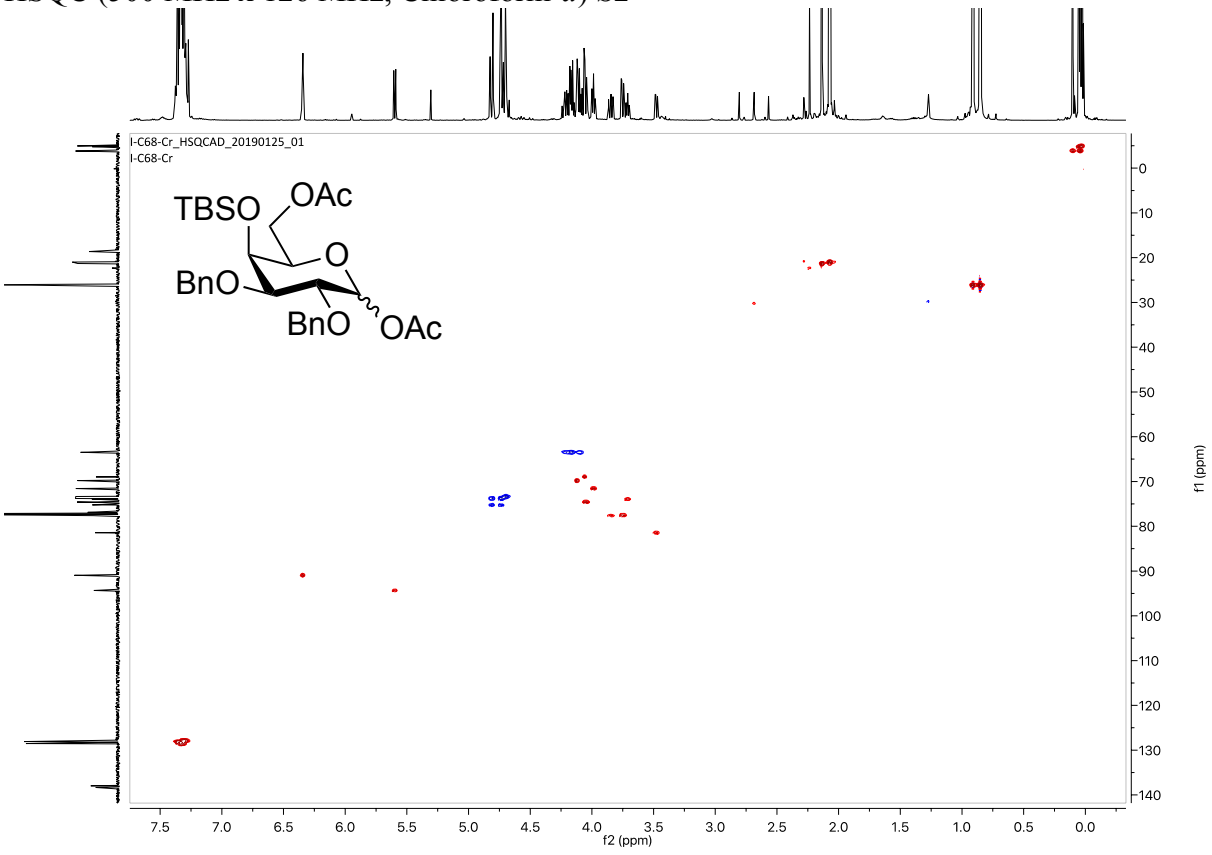
^{13}C NMR (126 MHz, Chloroform-*d*) **S2**



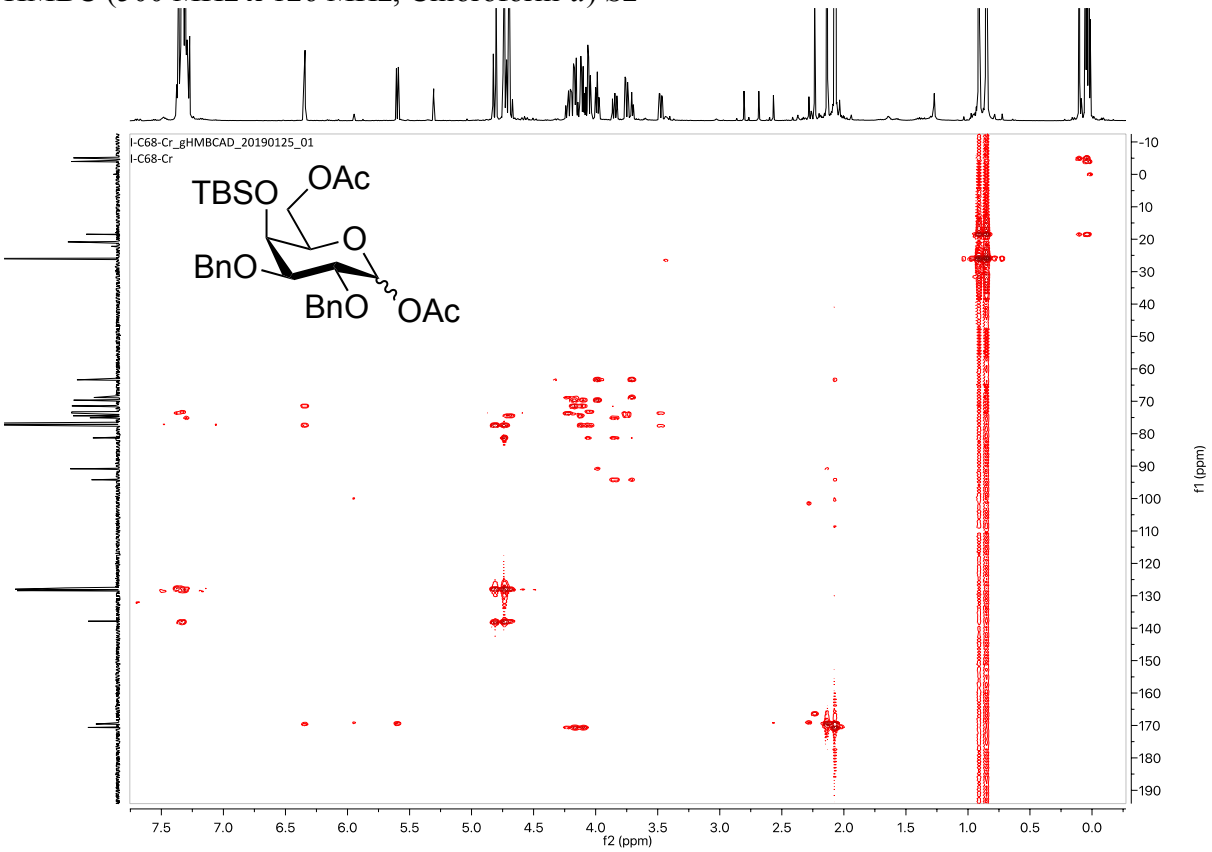
COSY (500 MHz, Chloroform-d) **S2**



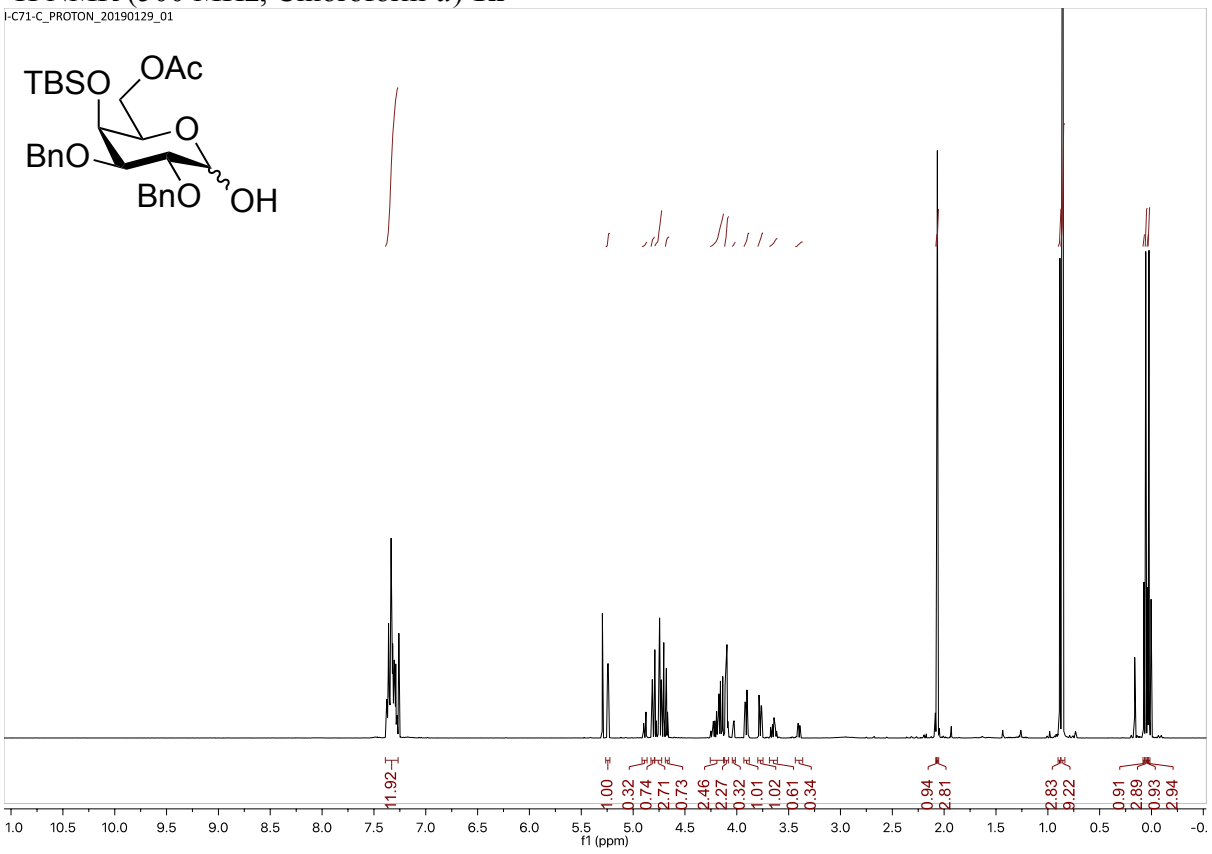
HSQC (500 MHz x 126 MHz, Chloroform-*d*) **S2**



HMBC (500 MHz x 126 MHz, Chloroform-*d*) **S2**



^{1}H NMR (500 MHz, Chloroform-*d*) **1h**



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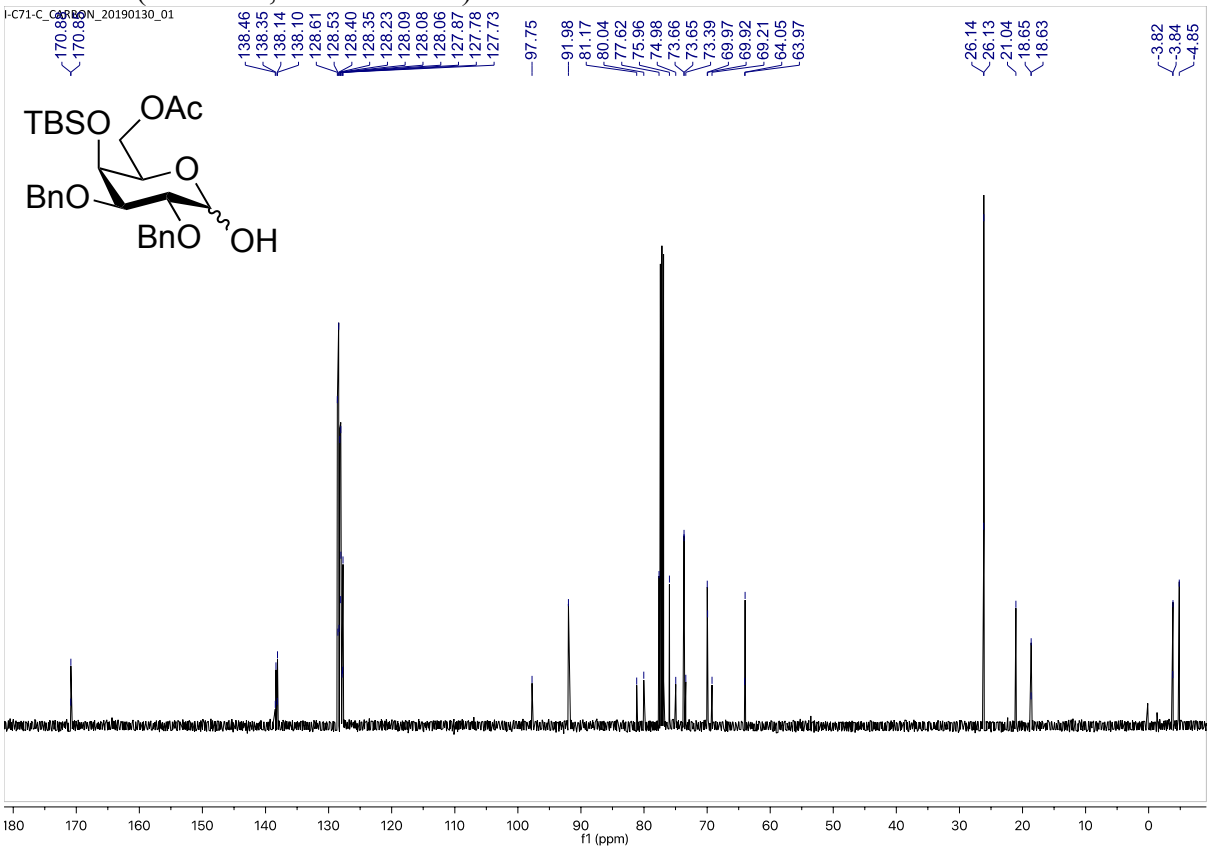
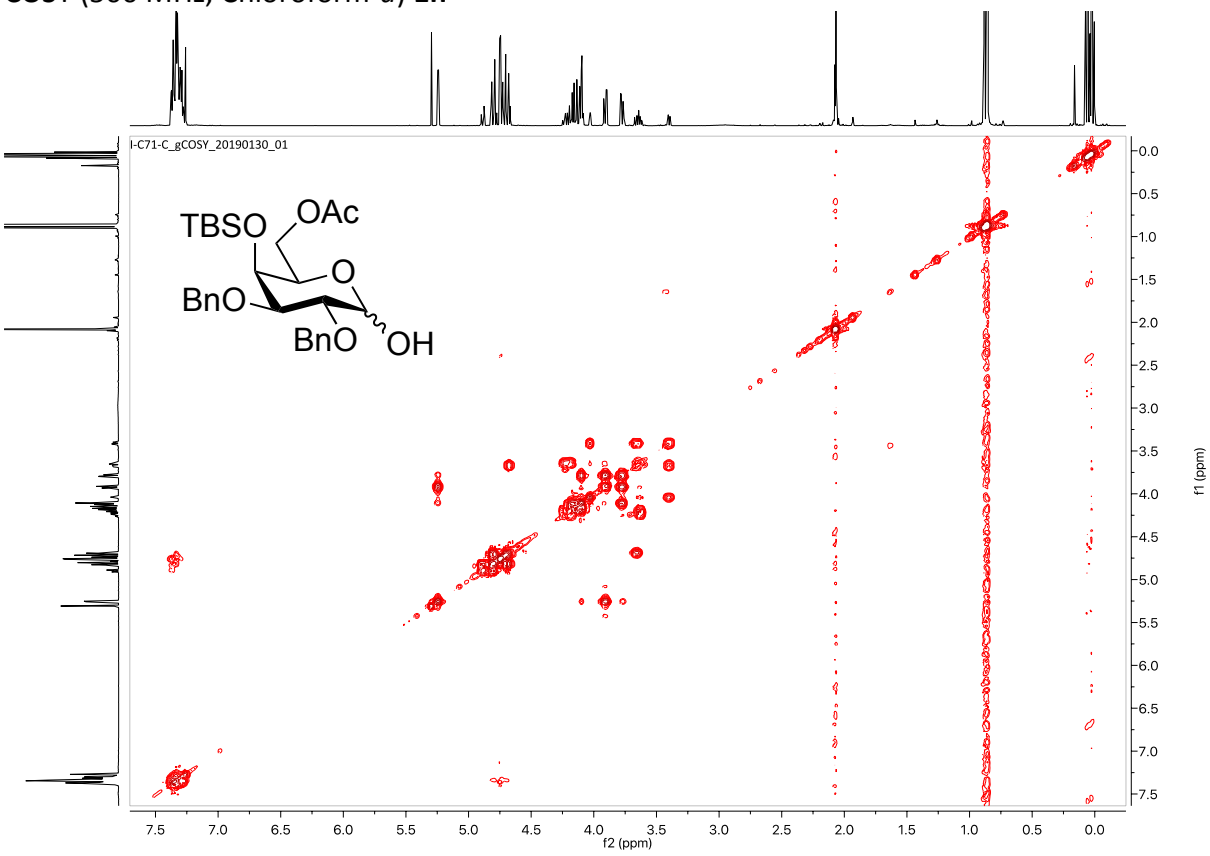
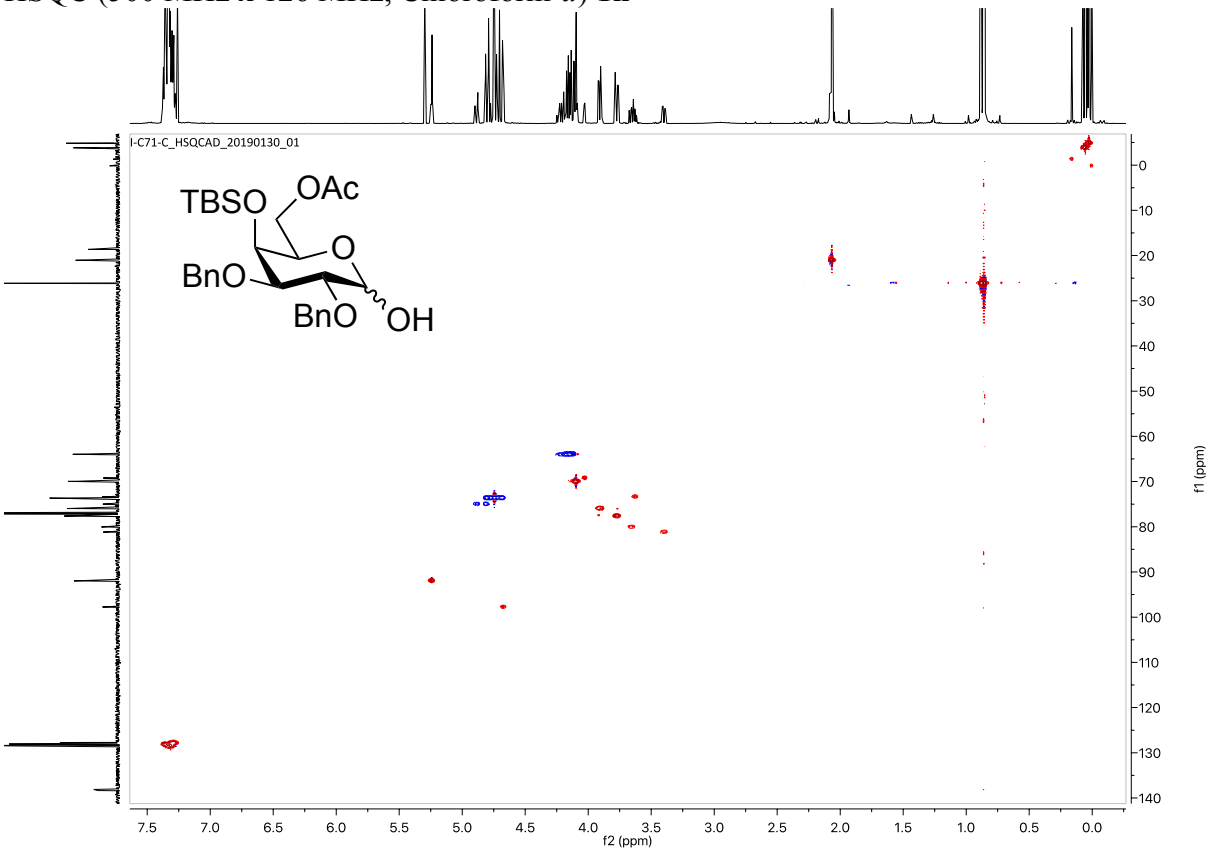


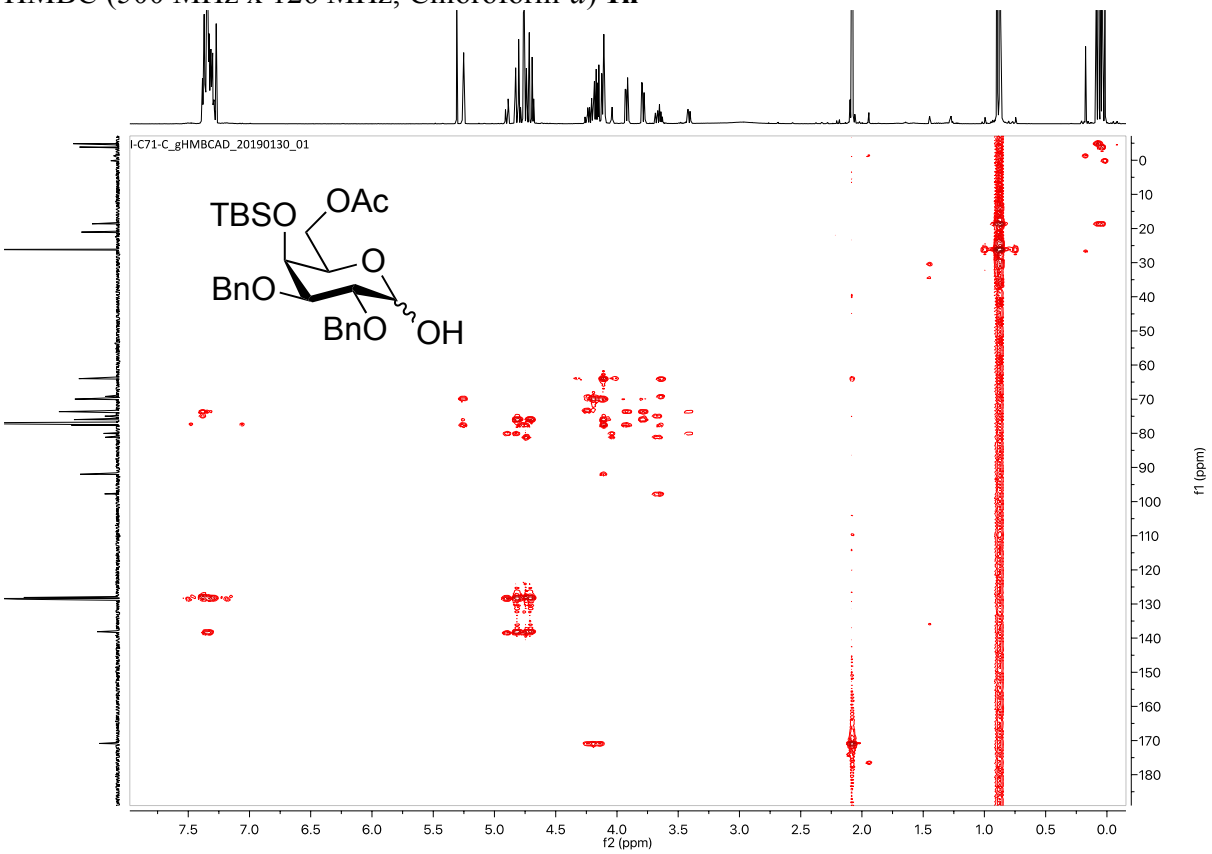
COSY (500 MHz, Chloroform-*d*) **1h**



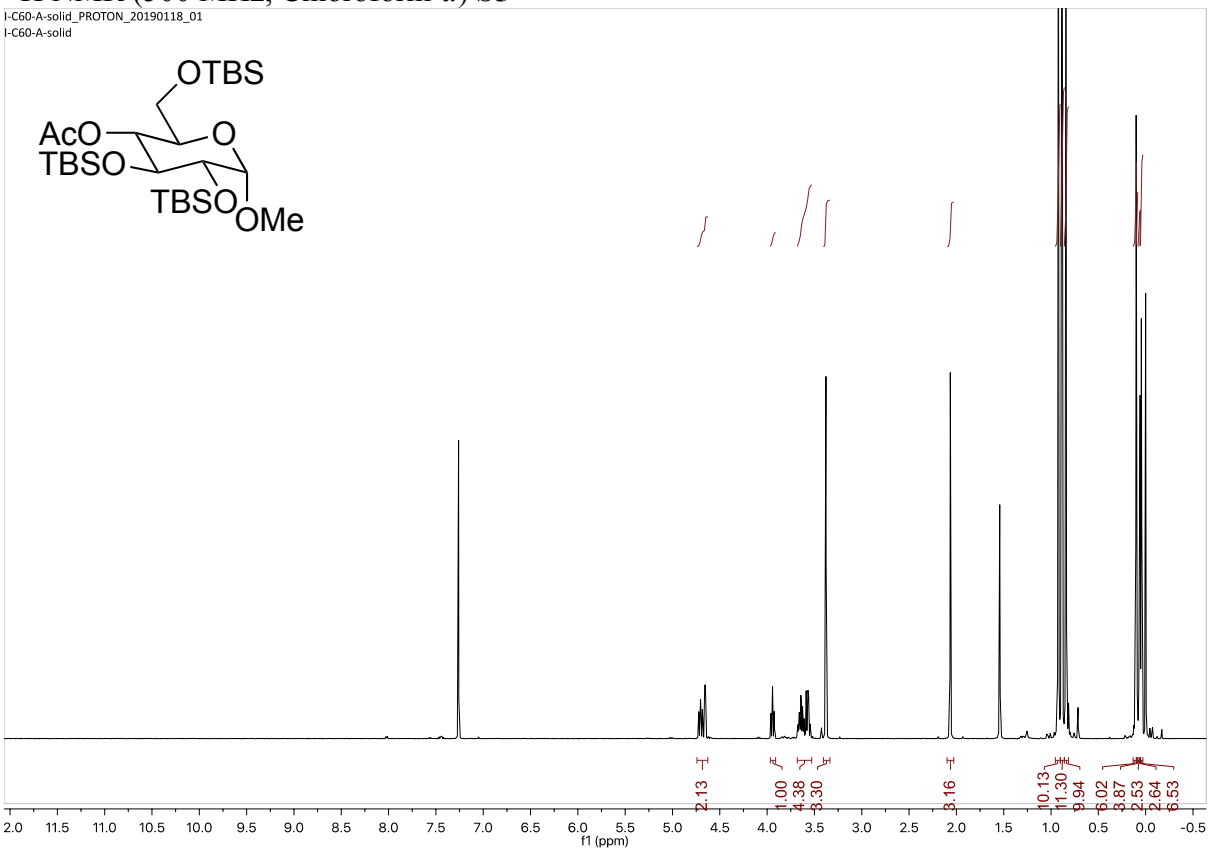
HSQC (500 MHz x 126 MHz, Chloroform-*d*) **1h**



HMBC (500 MHz x 126 MHz, Chloroform-*d*) **1h**



^{1}H NMR (500 MHz, Chloroform-*d*) **S5**



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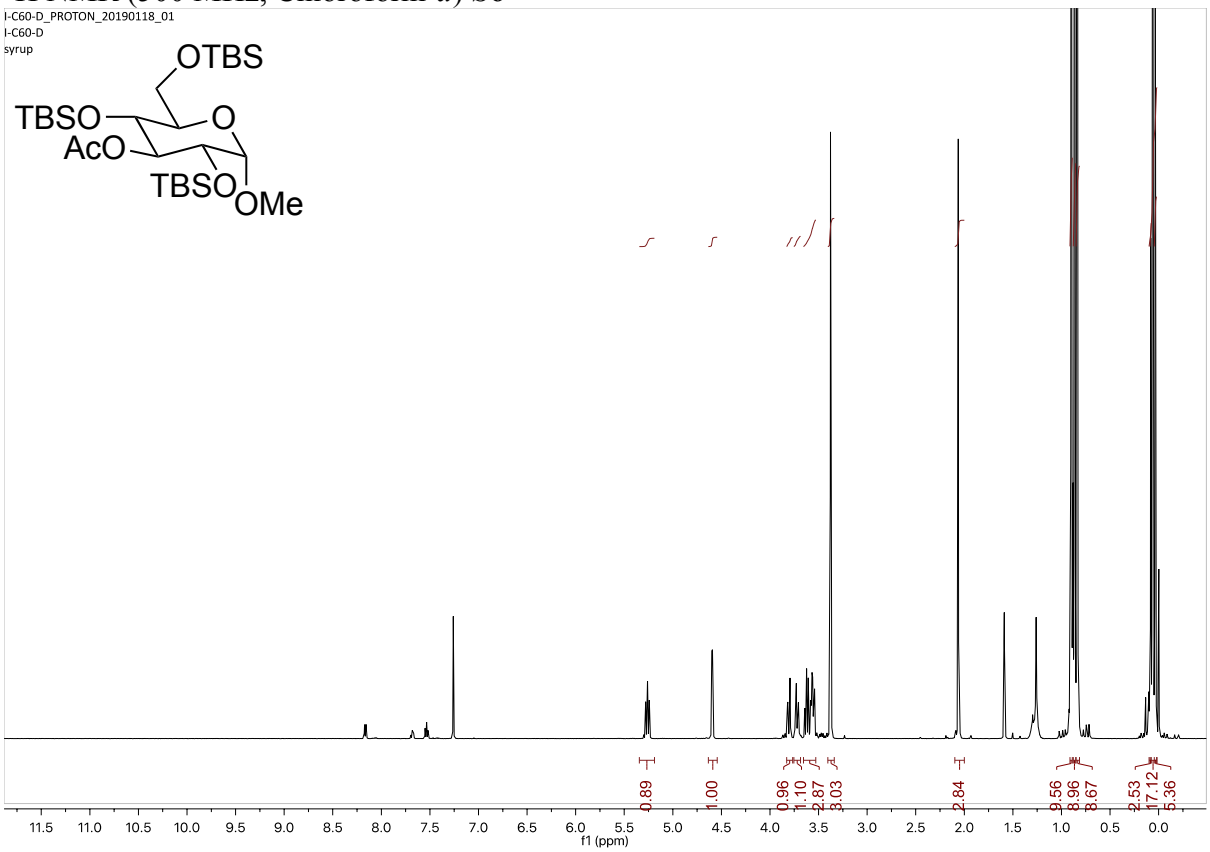
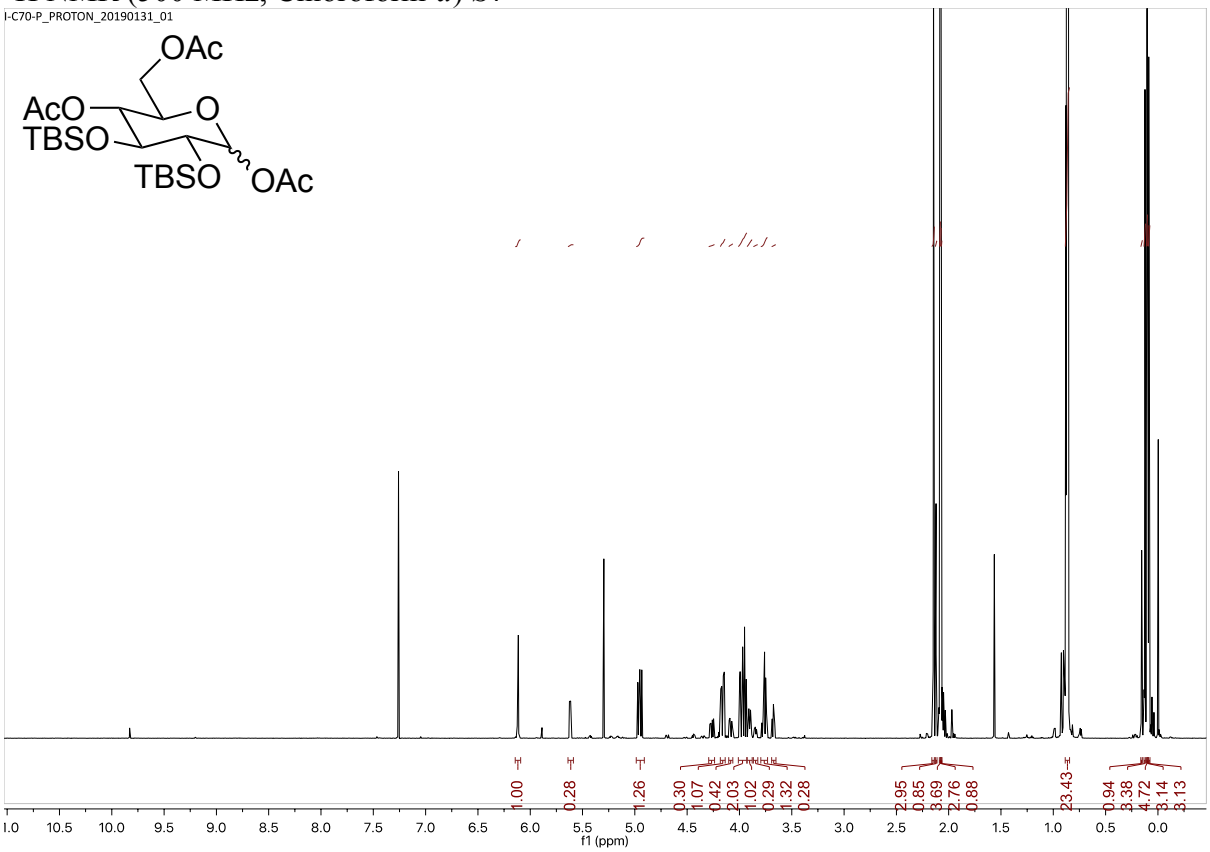
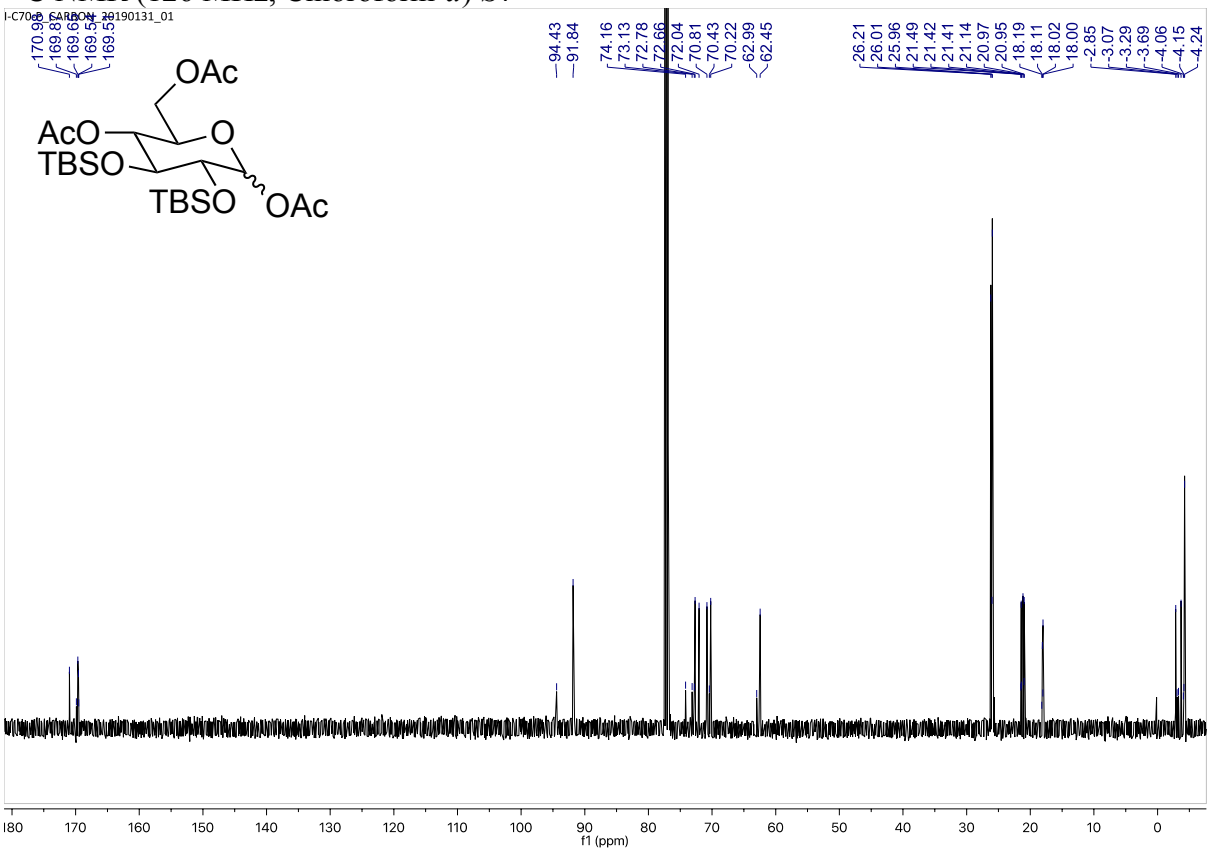


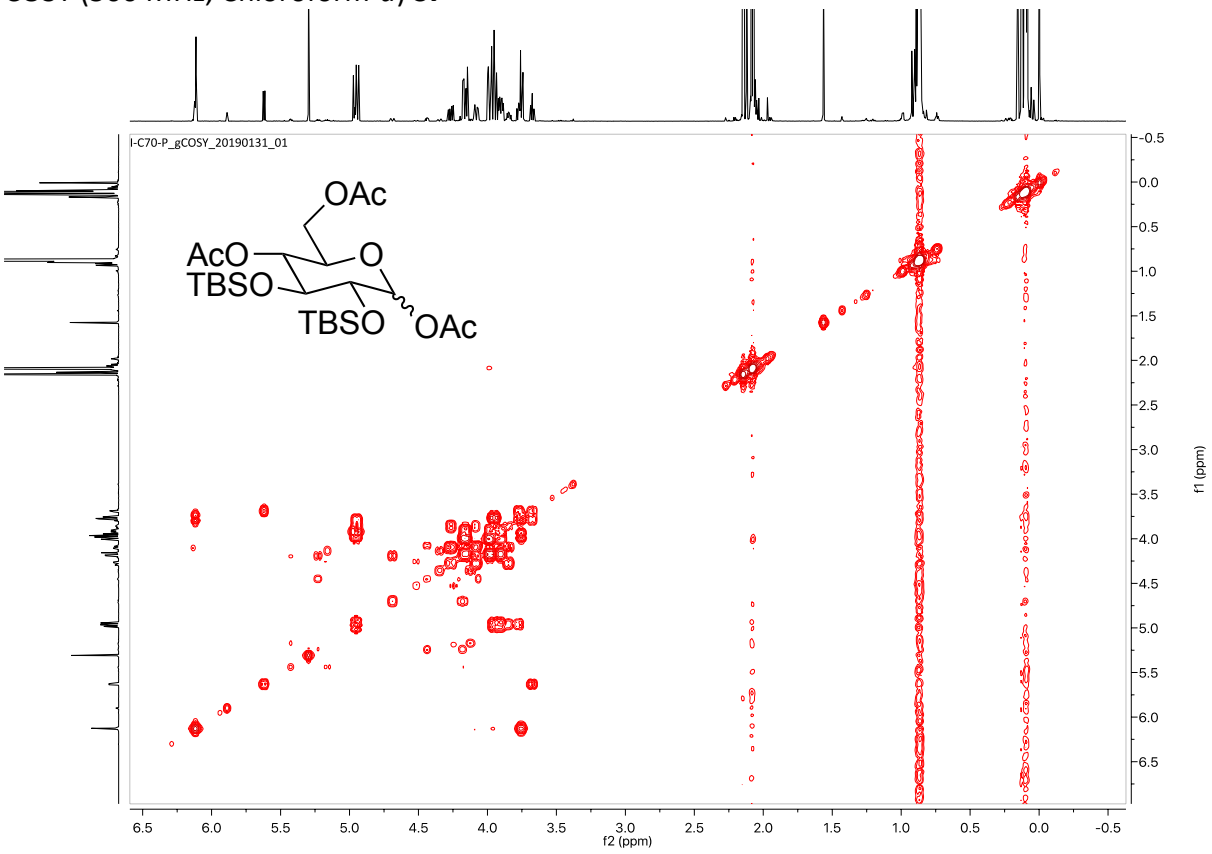
^{1}H NMR (500 MHz, Chloroform-*d*) **S7**



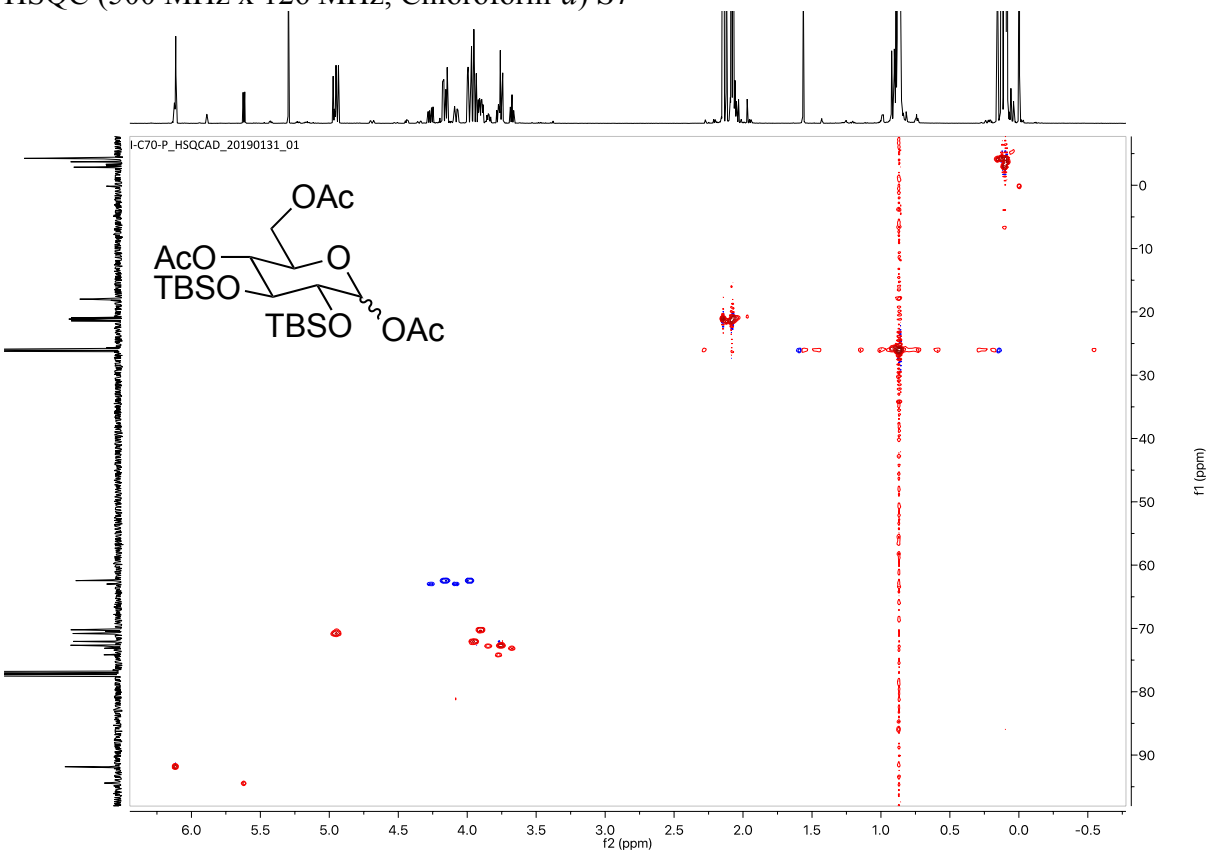
^{13}C NMR (126 MHz, Chloroform-*d*) **S7**



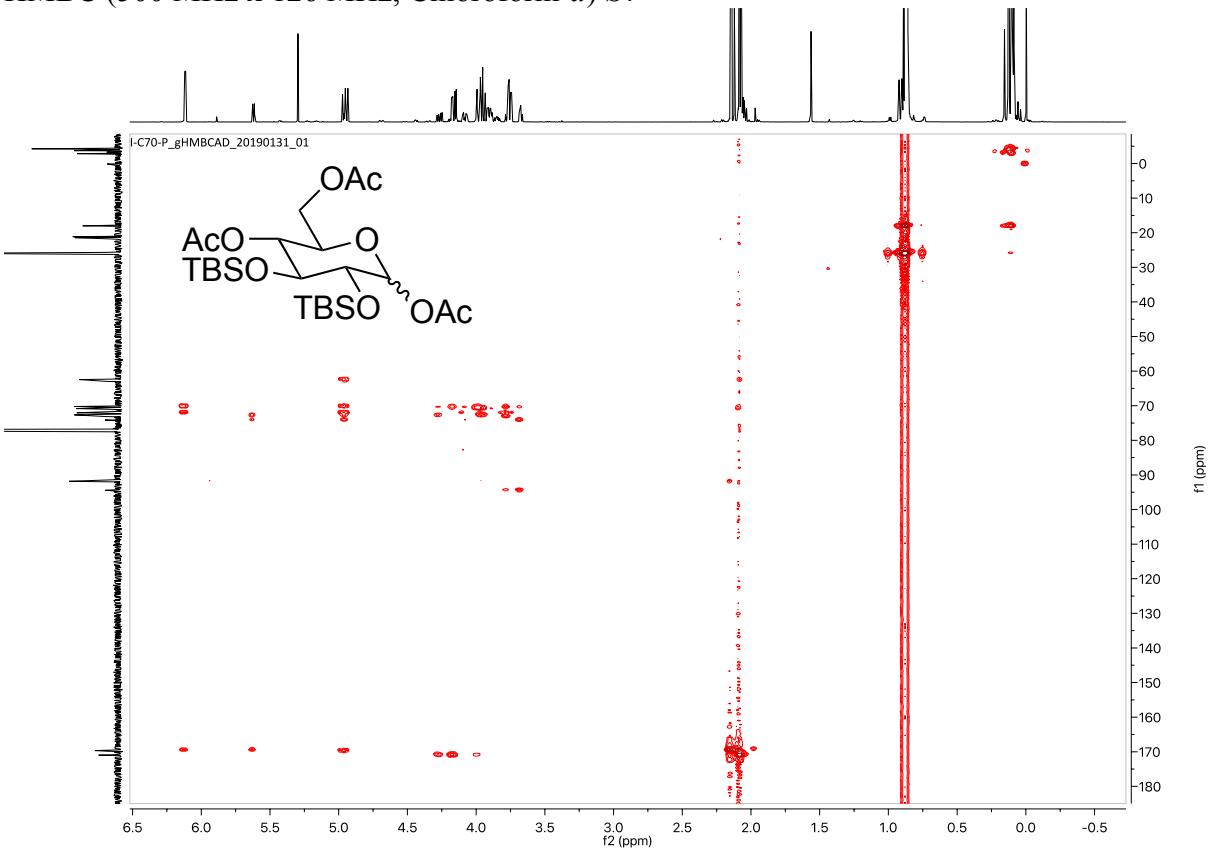
COSY (500 MHz, Chloroform-*d*) **S7**



HSQC (500 MHz x 126 MHz, Chloroform-*d*) **S7**



HMBC (500 MHz x 126 MHz, Chloroform-*d*) **S7**



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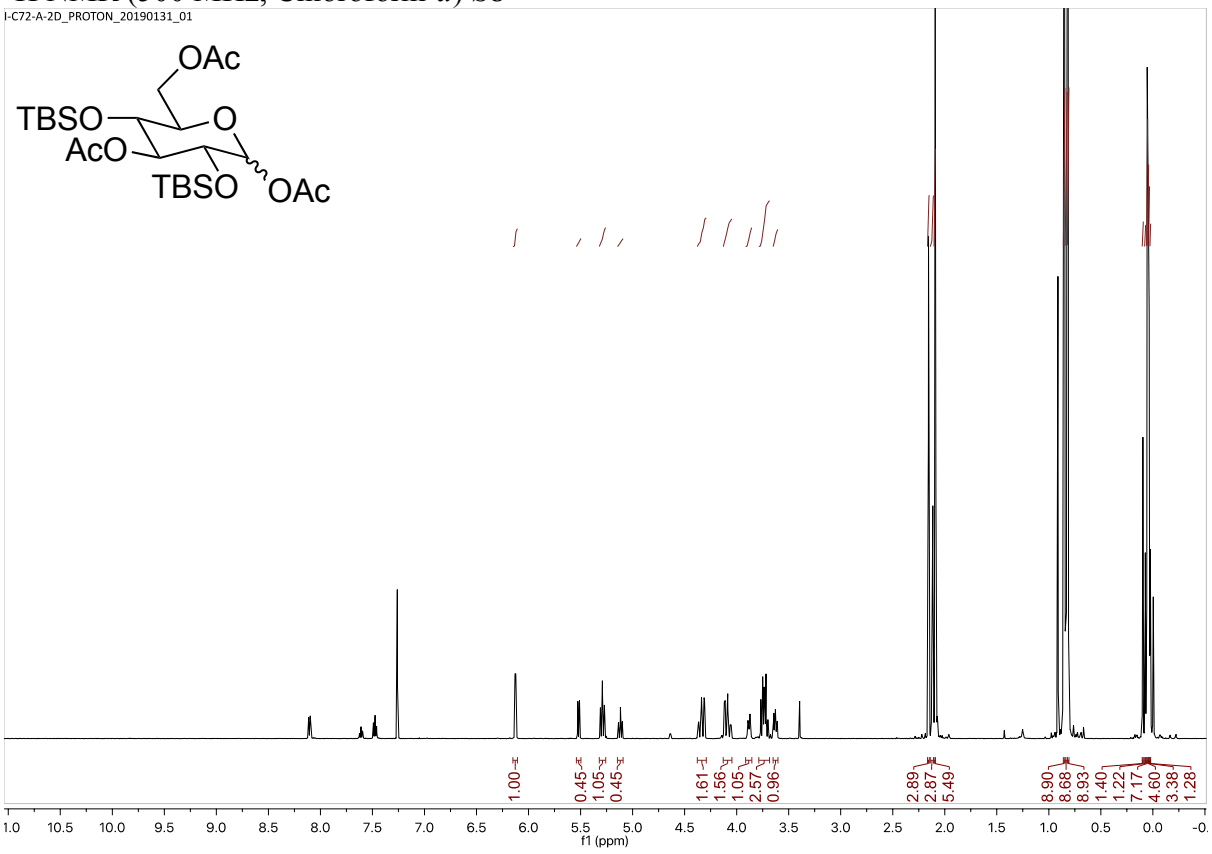
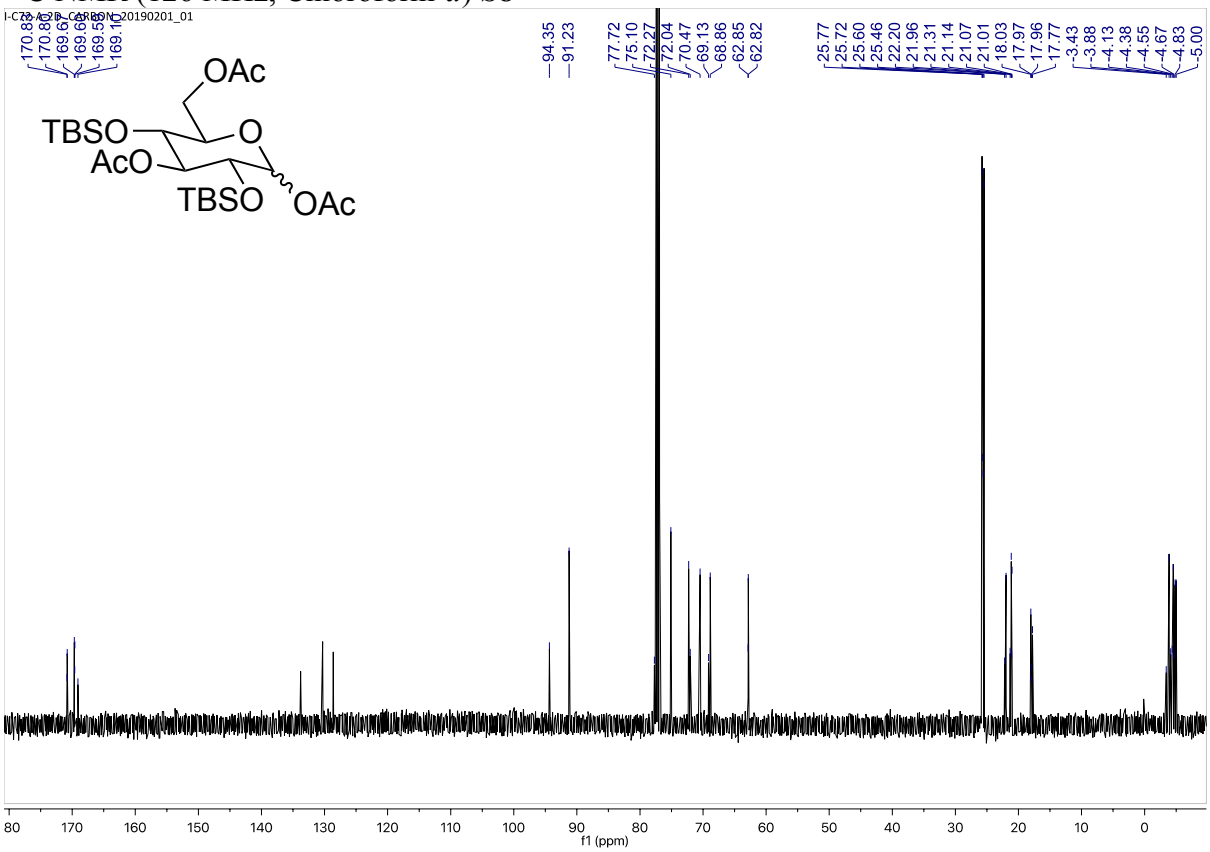
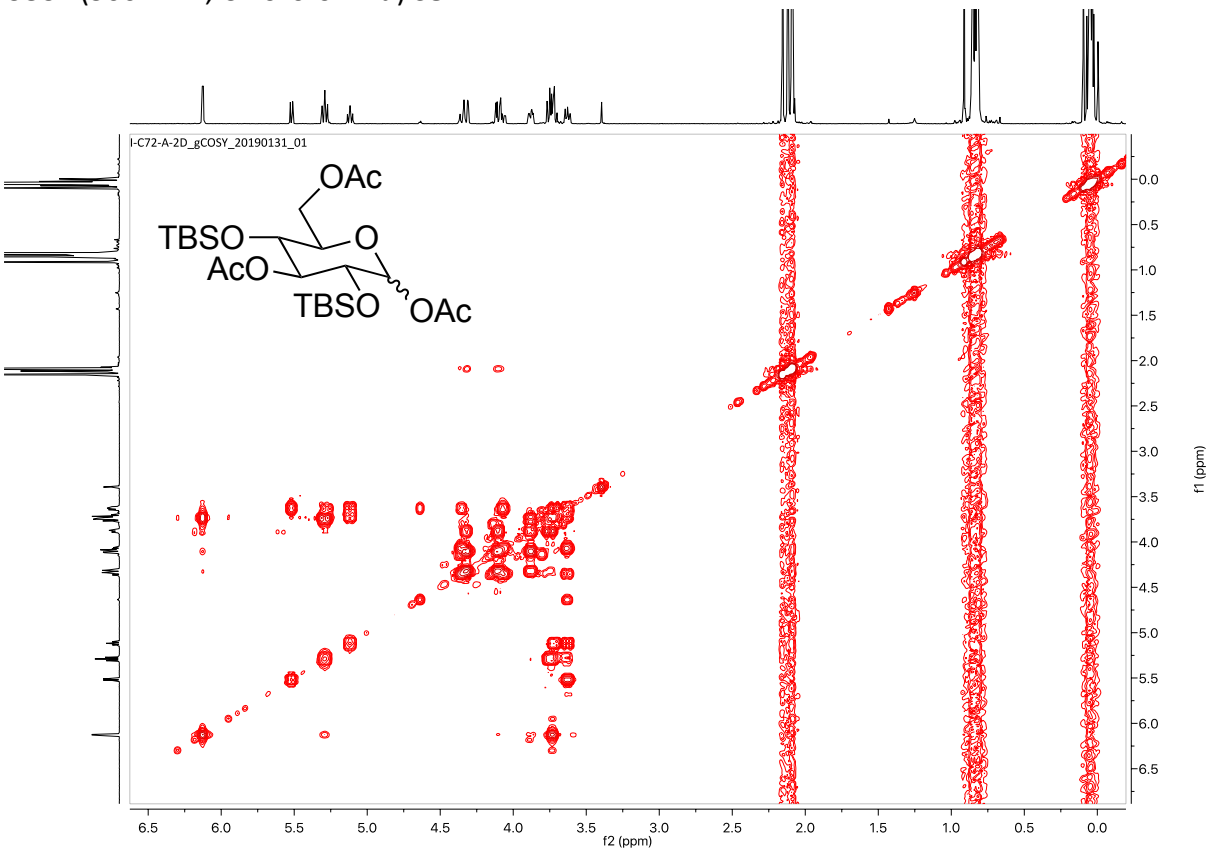


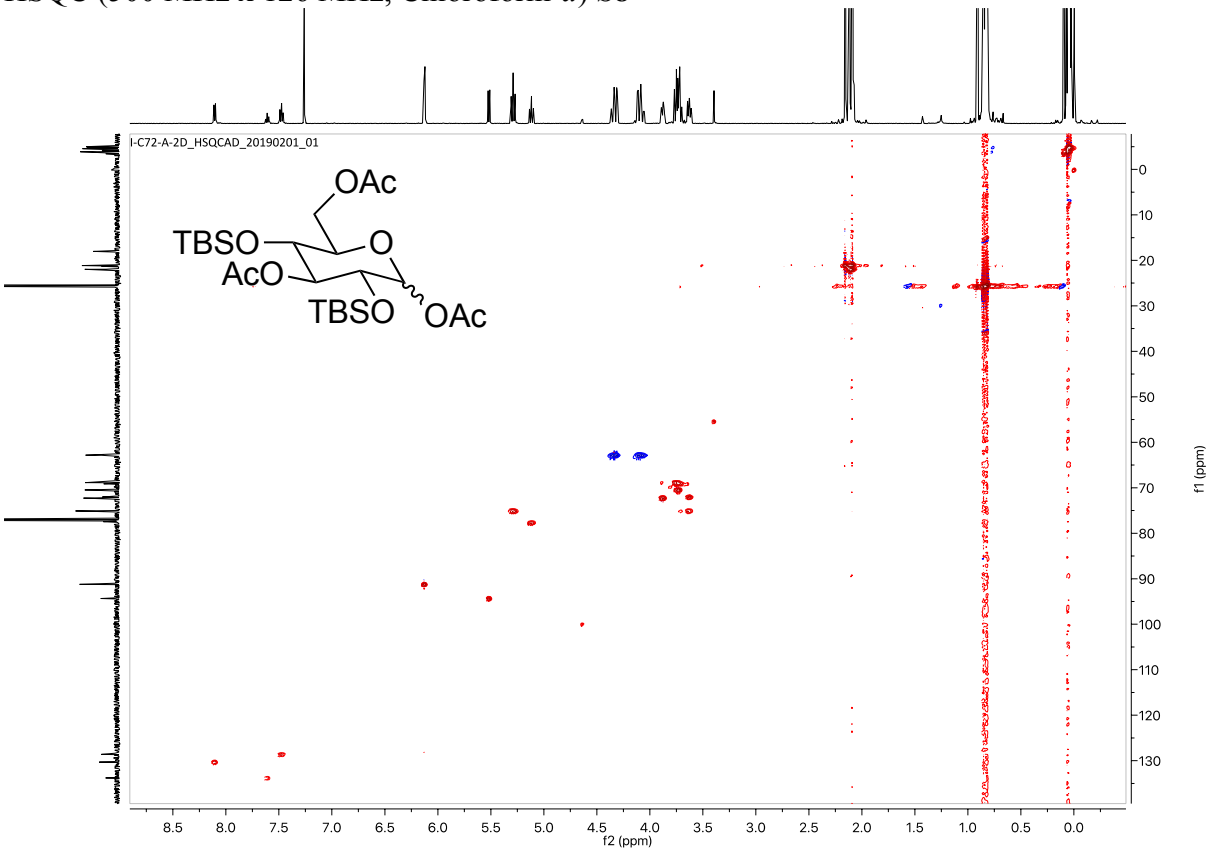
^{13}C NMR (126 MHz, Chloroform-*d*) **S8**



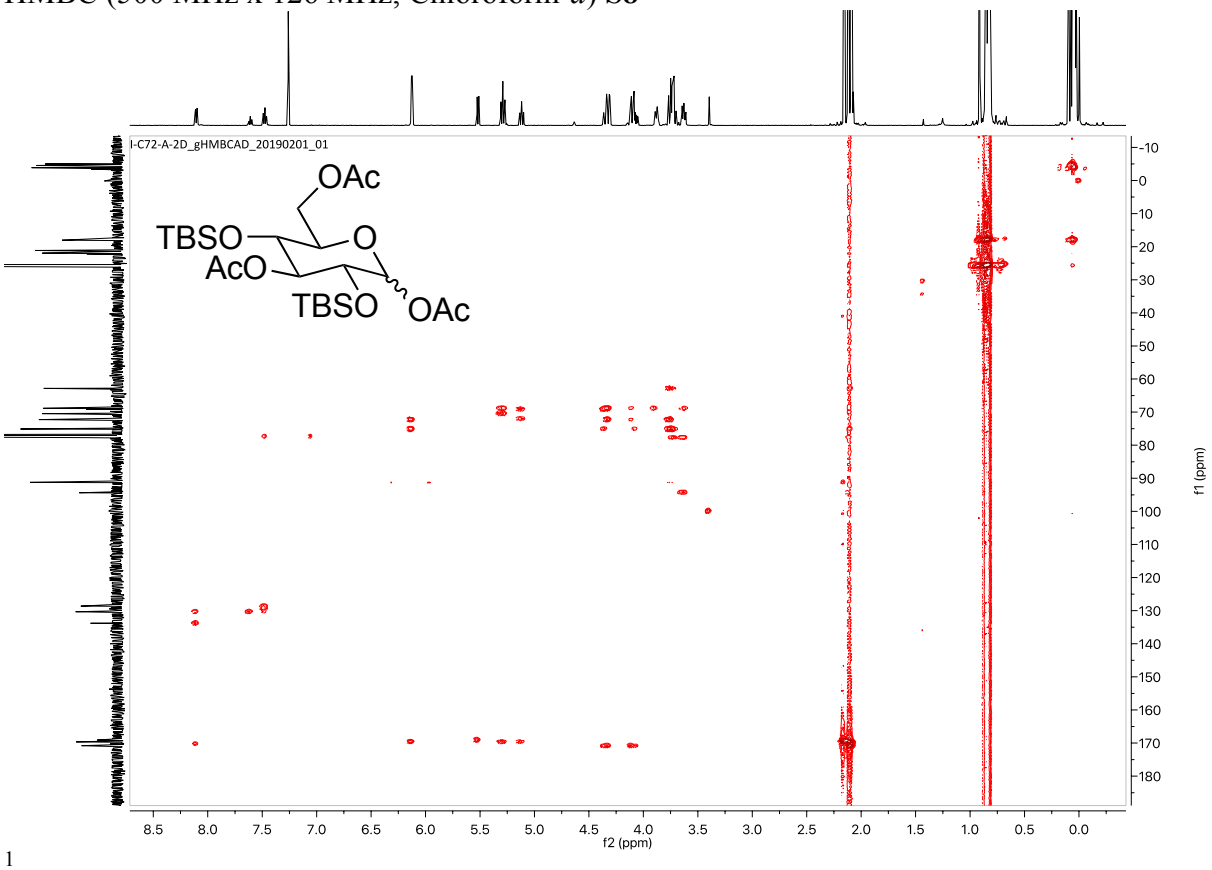
COSY (500 MHz, Chloroform-*d*) **S8**



HSQC (500 MHz x 126 MHz, Chloroform-*d*) **S8**



HMBC (500 MHz x 126 MHz, Chloroform-*d*) **S8**



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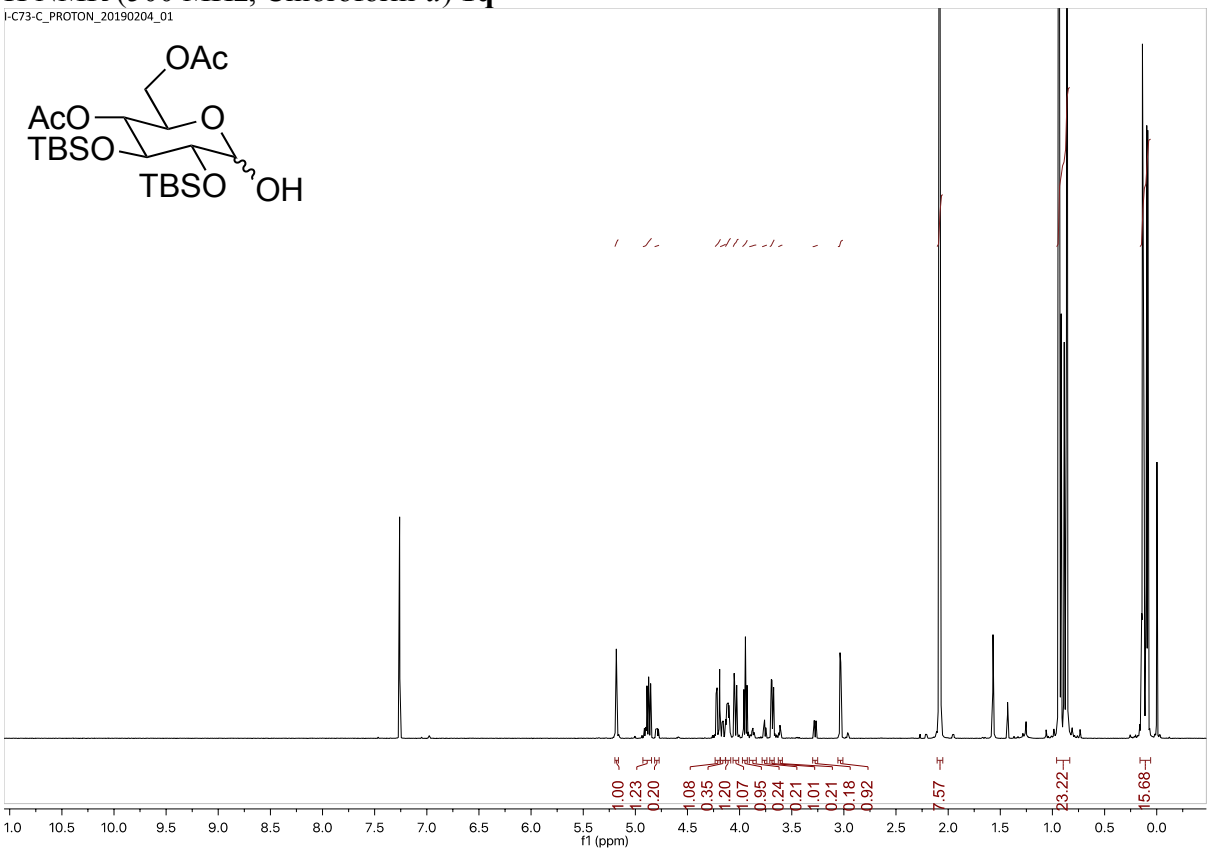
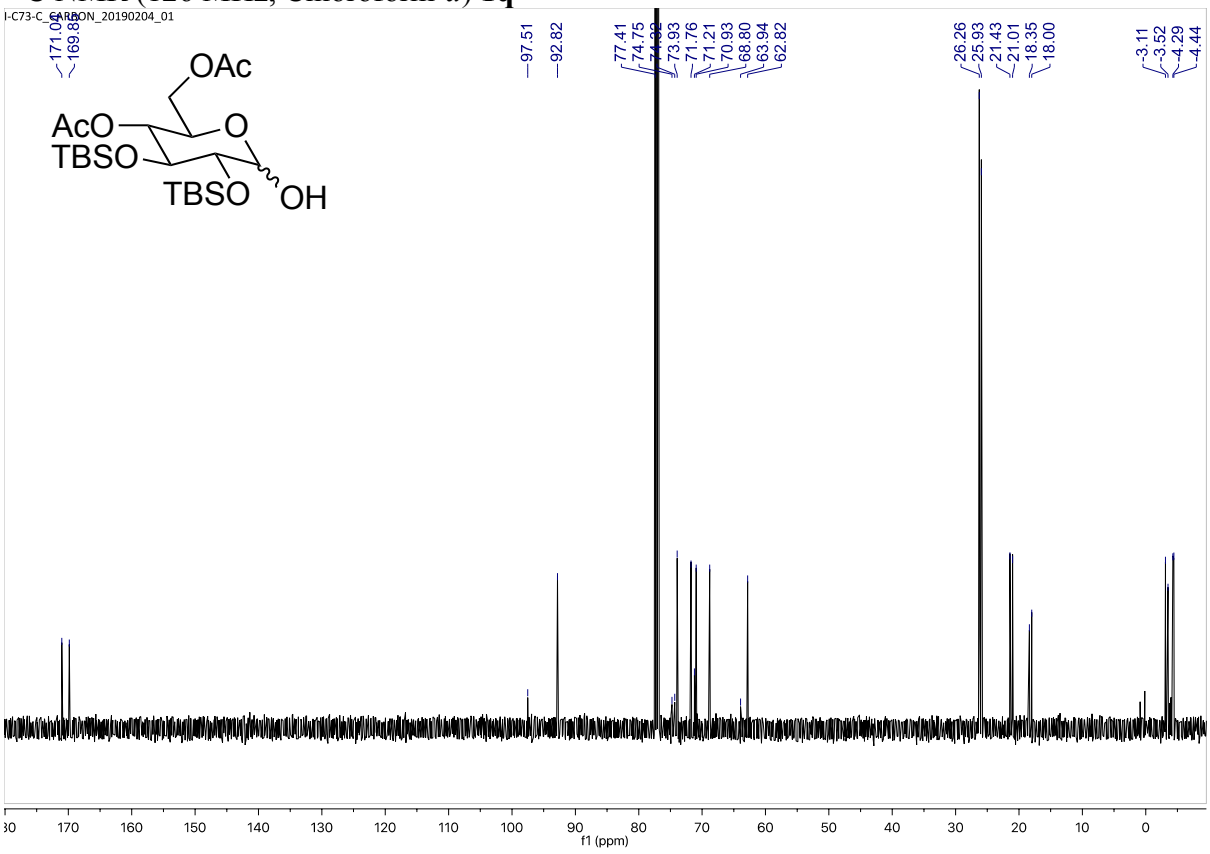
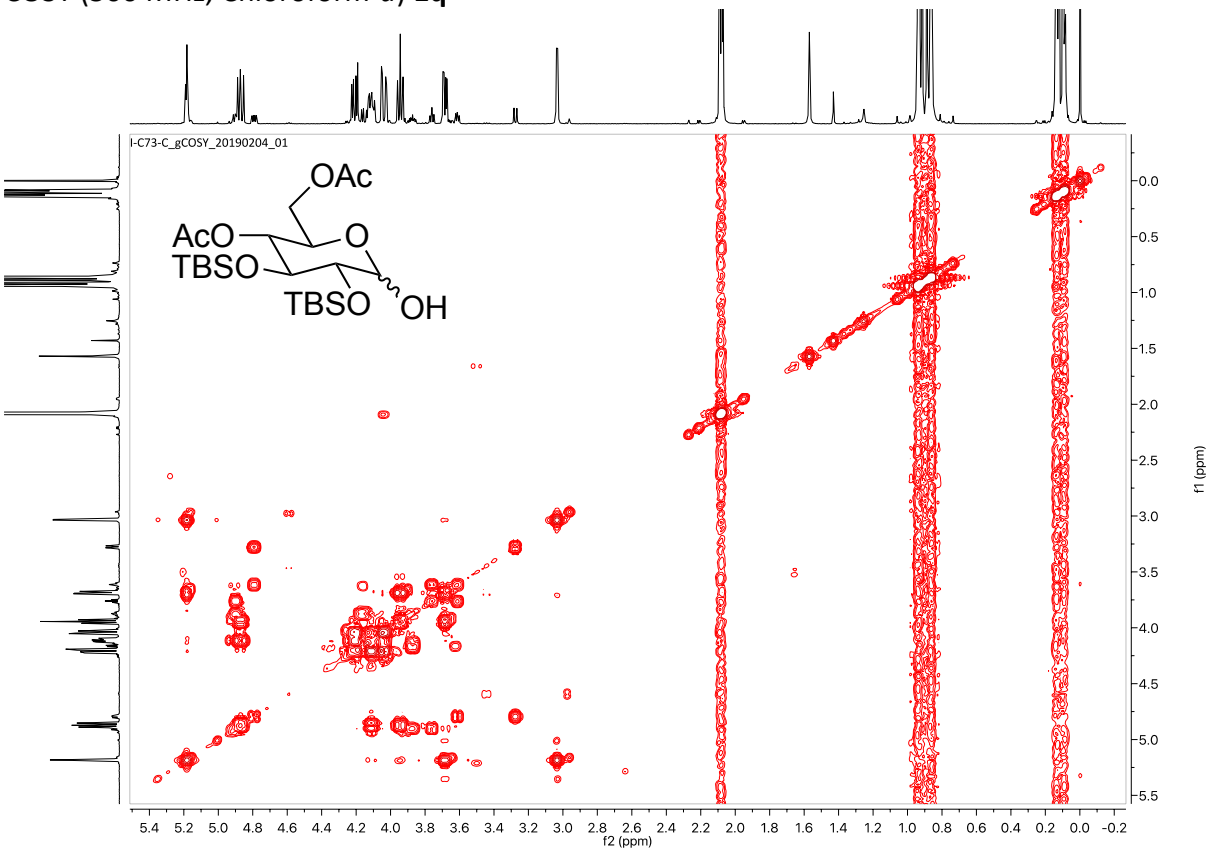
H NMR (500 MHz, Chloroform-*d*) **1q**



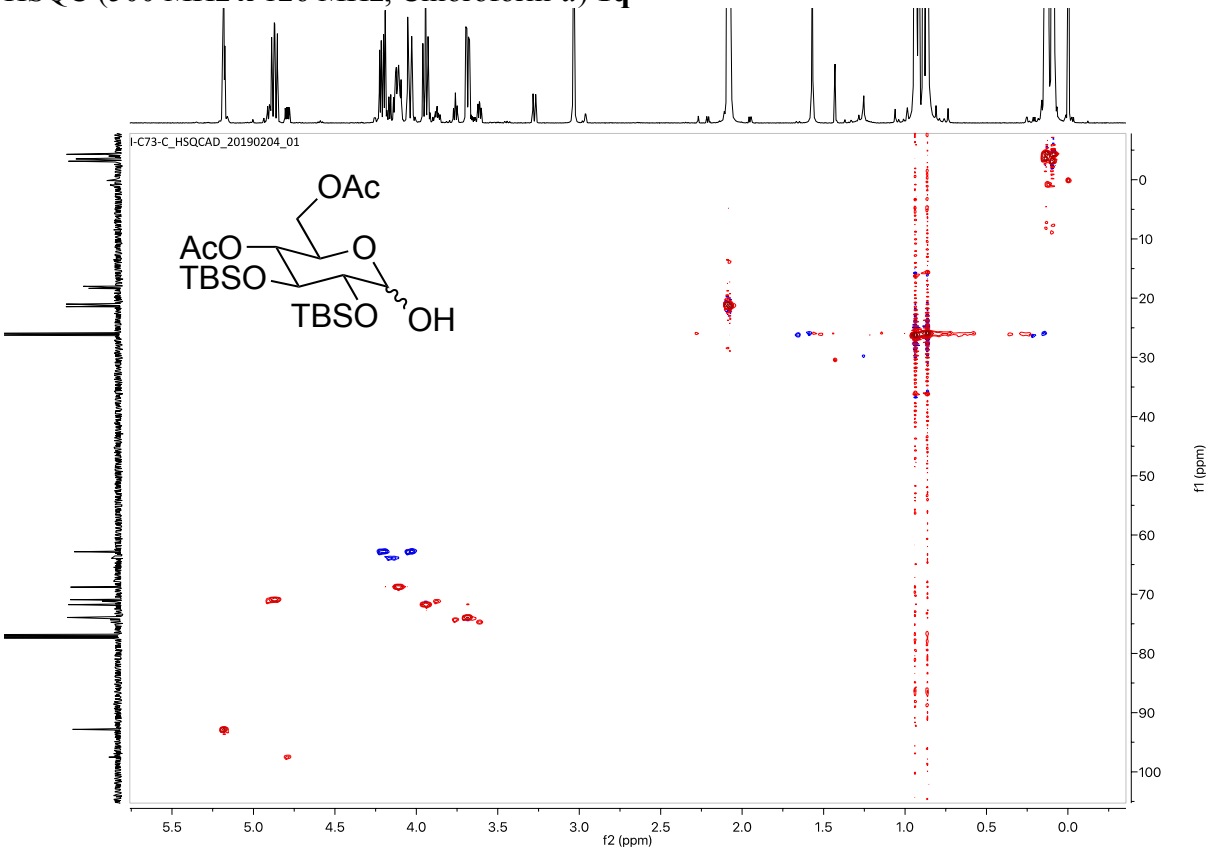
^{13}C NMR (126 MHz, Chloroform-*d*) **1q**



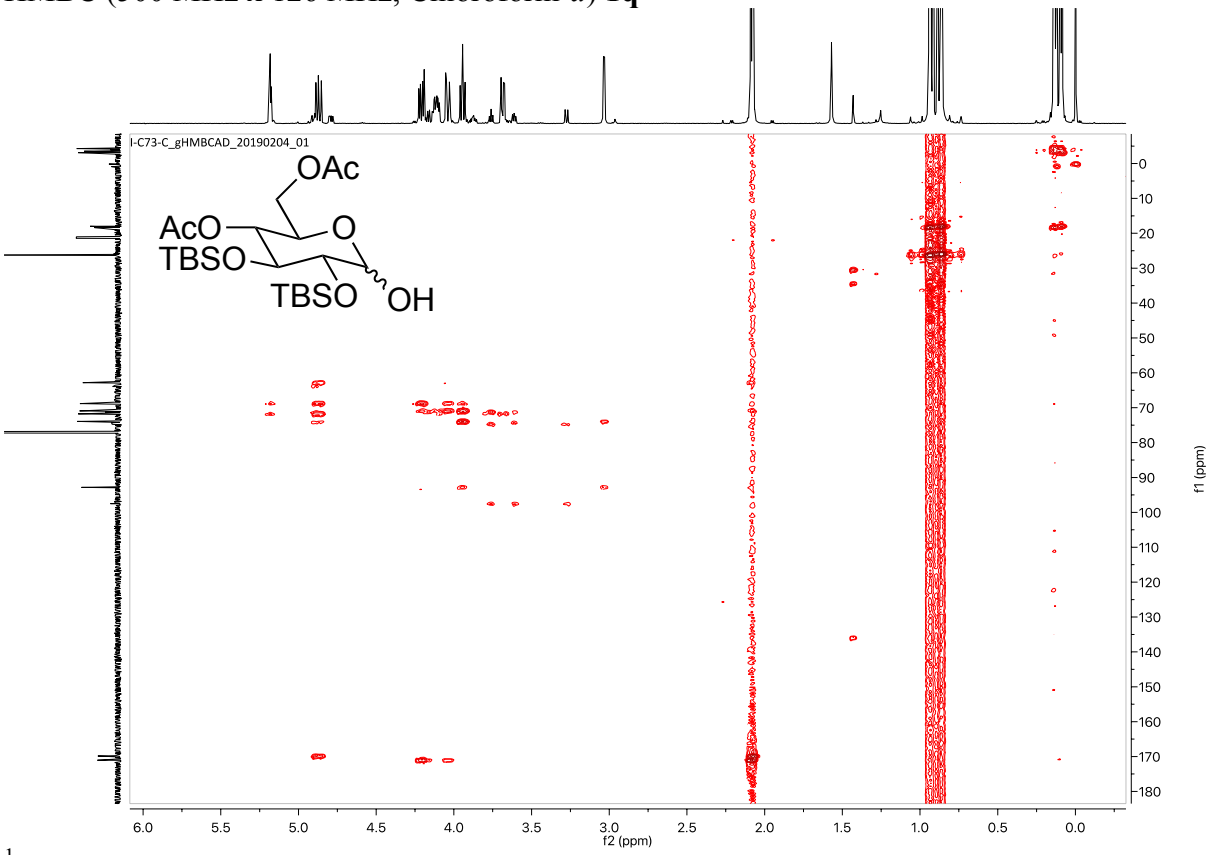
COSY (500 MHz, Chloroform-*d*) **1q**



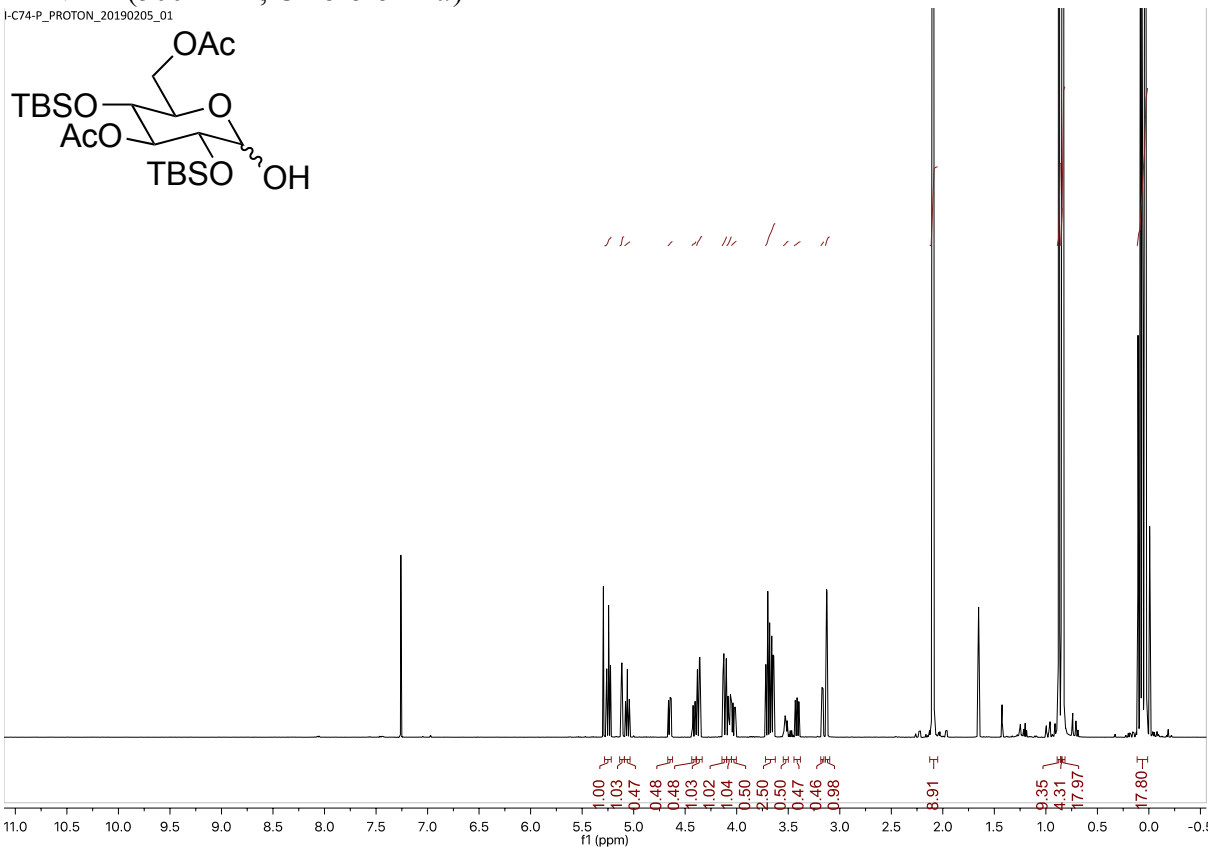
HSQC (500 MHz x 126 MHz, Chloroform-*d*) **1q**



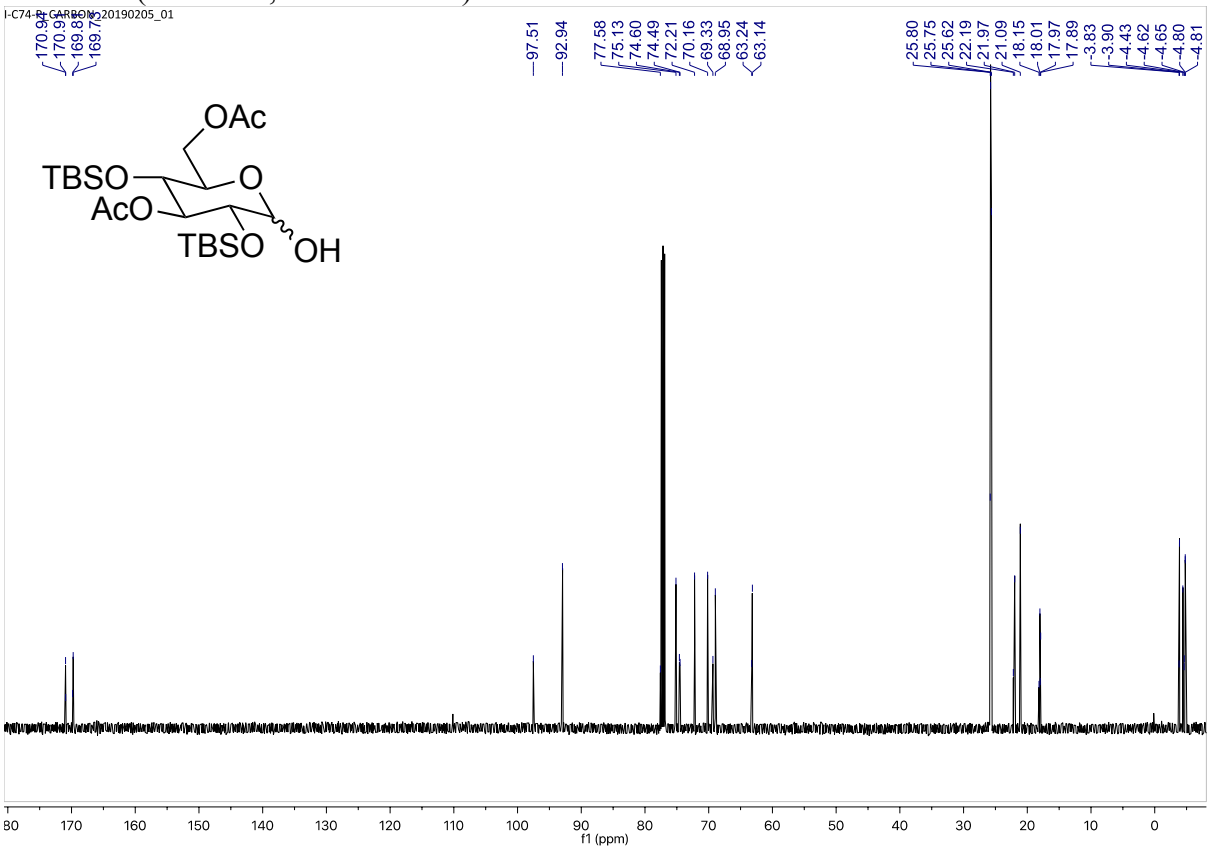
HMBC (500 MHz x 126 MHz, Chloroform-*d*) **1q**



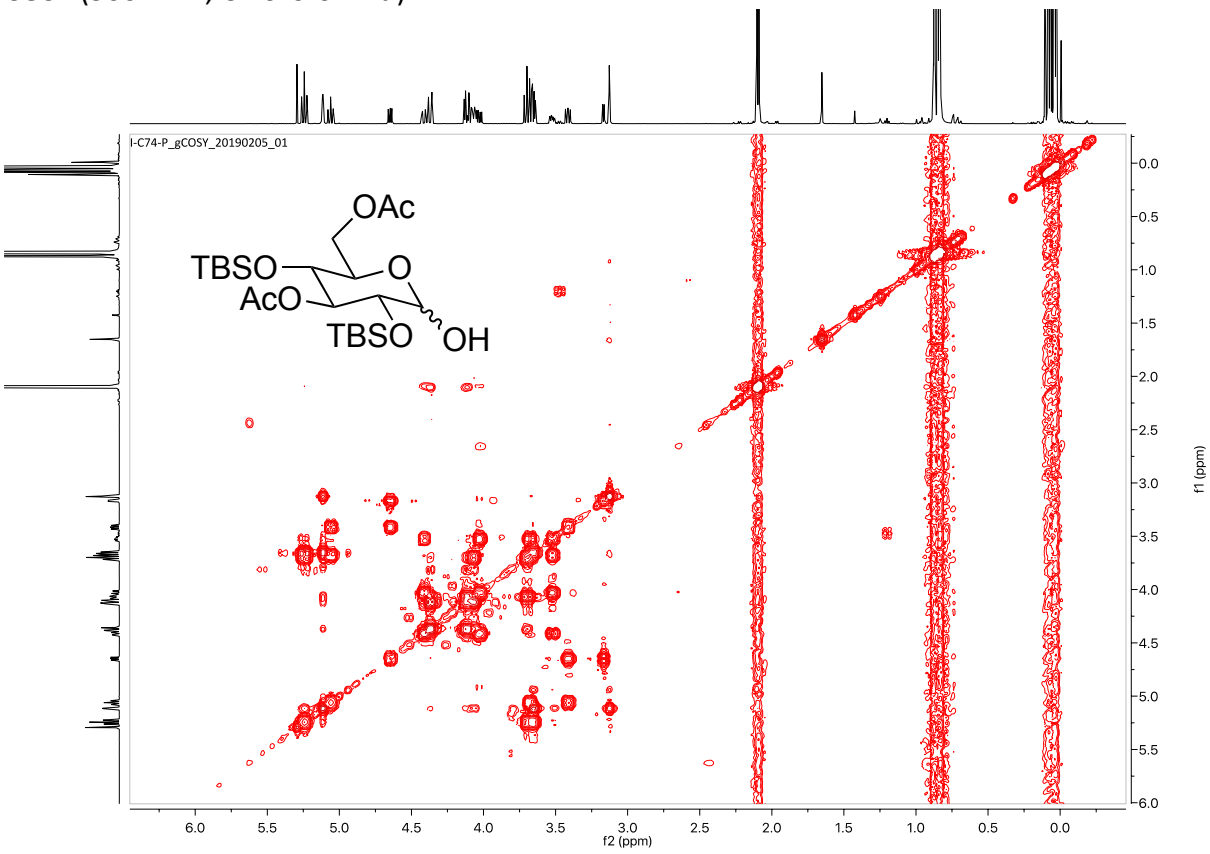
^{1}H NMR (500 MHz, Chloroform-*d*) **1r**



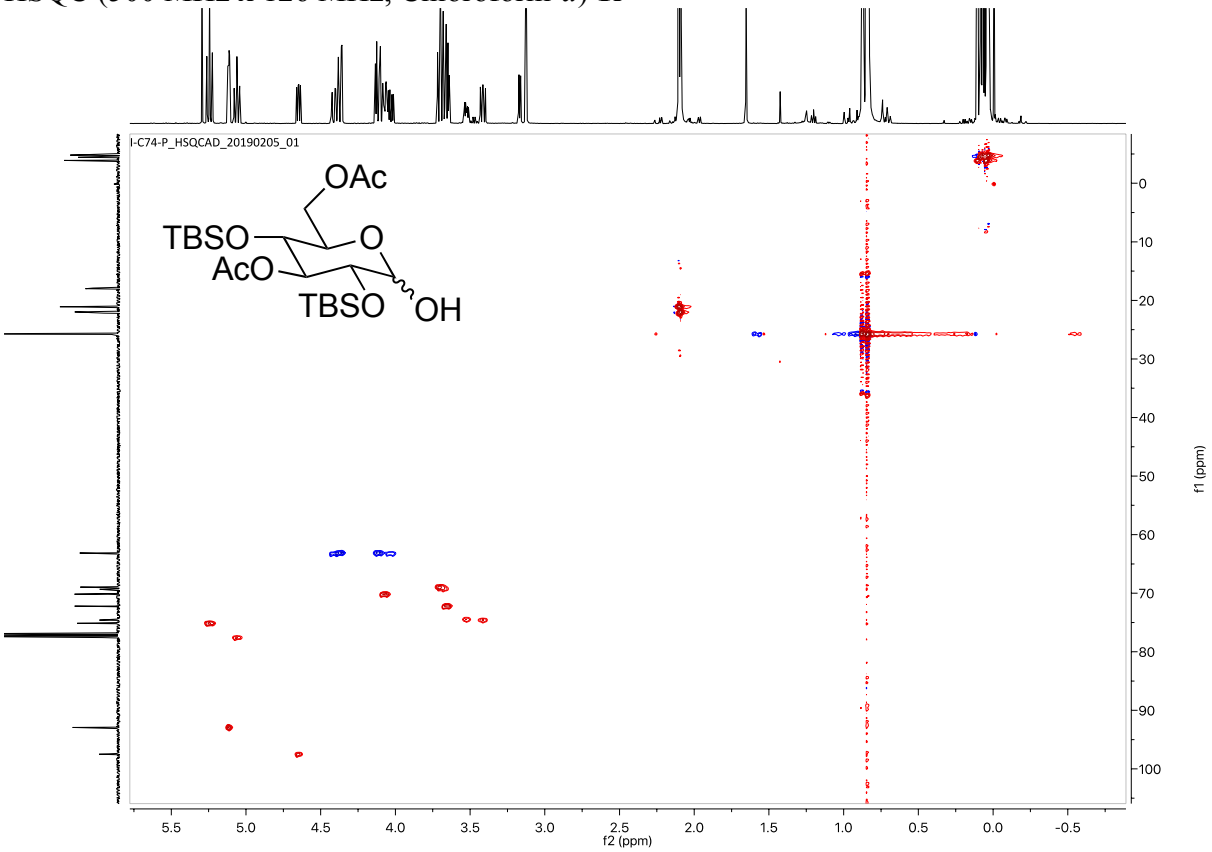
^{13}C NMR (126 MHz, Chloroform-*d*) **1r**



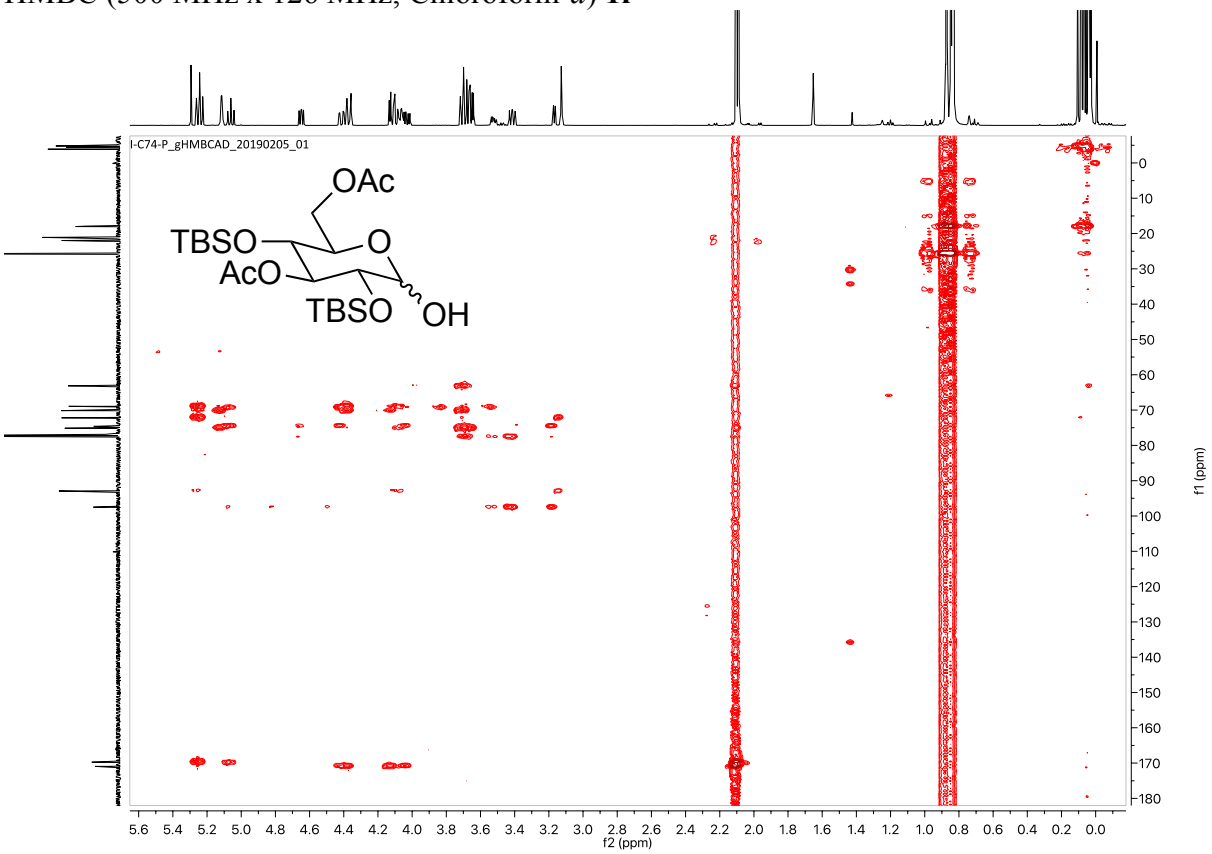
COSY (500 MHz, Chloroform-*d*) **1r**



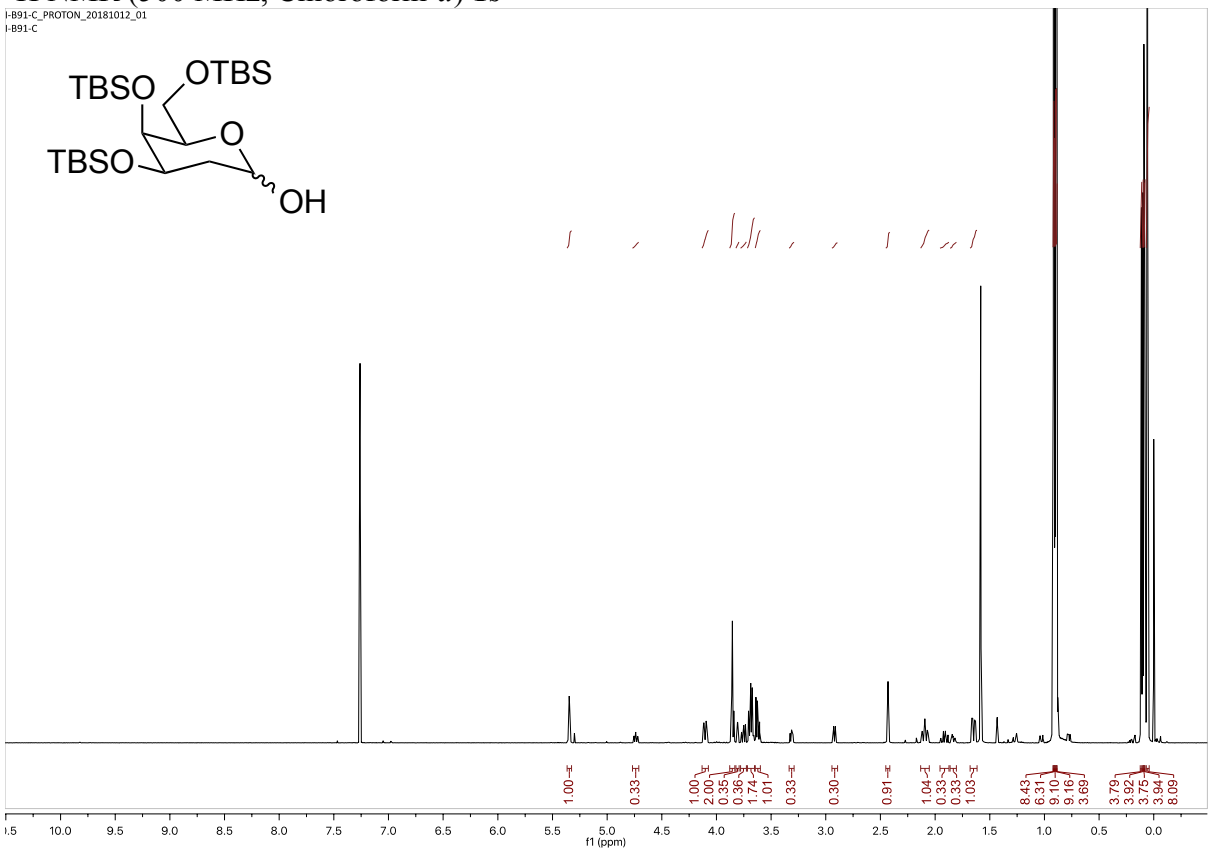
HSQC (500 MHz x 126 MHz, Chloroform-*d*) **1r**



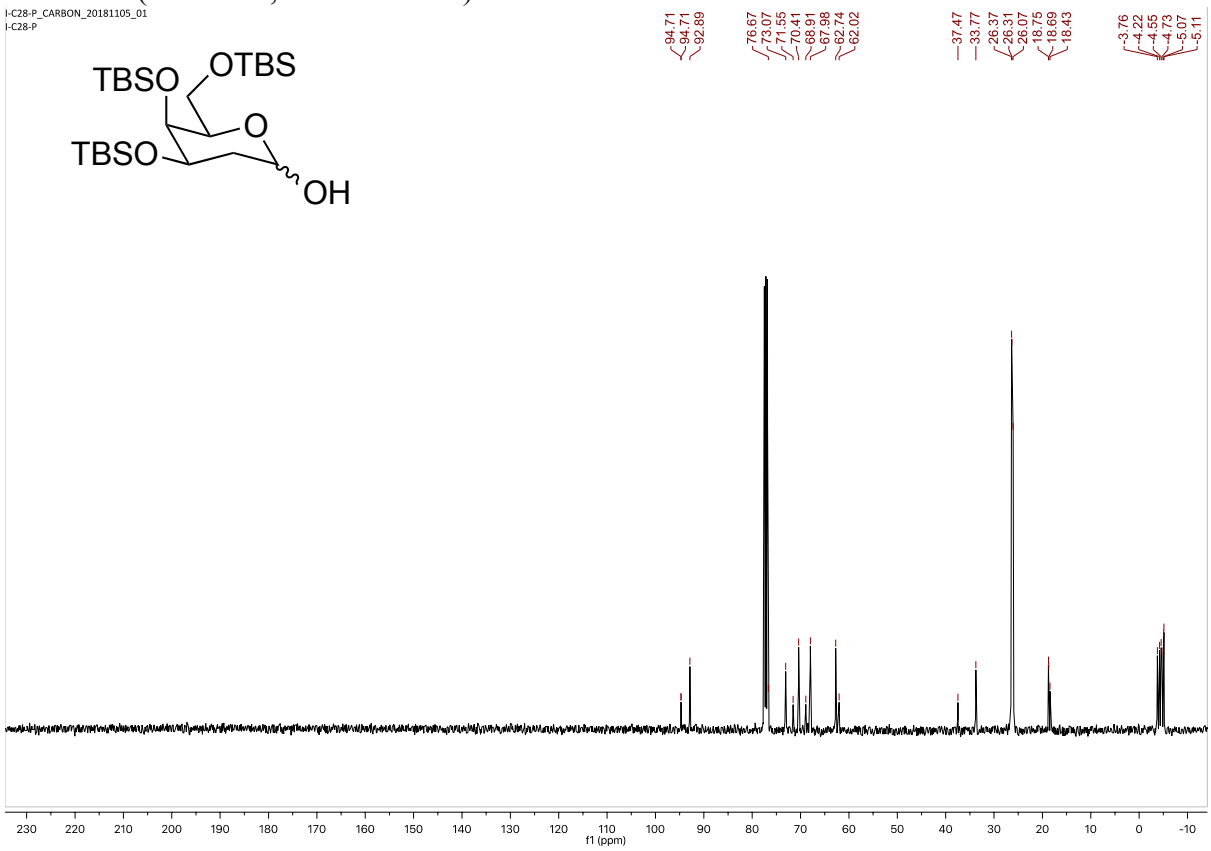
HMBC (500 MHz x 126 MHz, Chloroform-*d*) **1r**



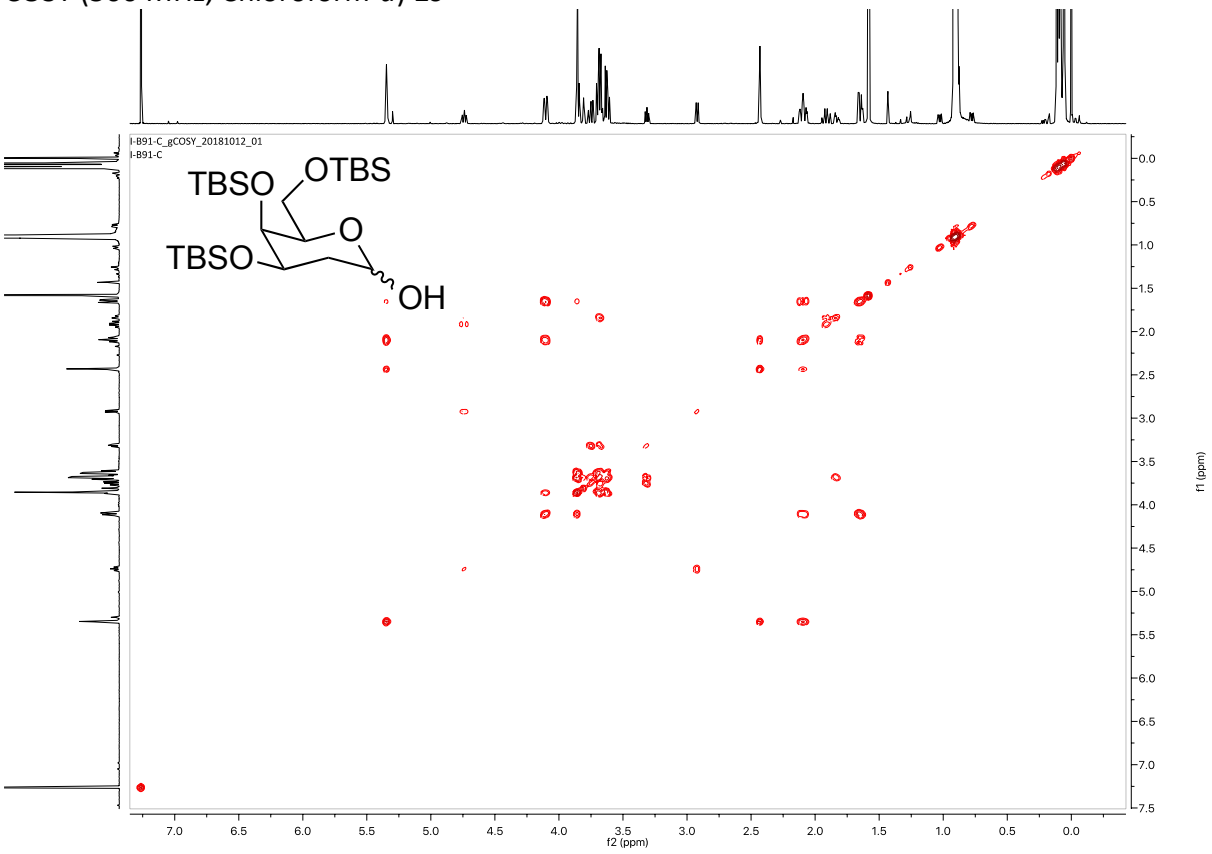
^{1}H NMR (500 MHz, Chloroform-*d*) **1s**



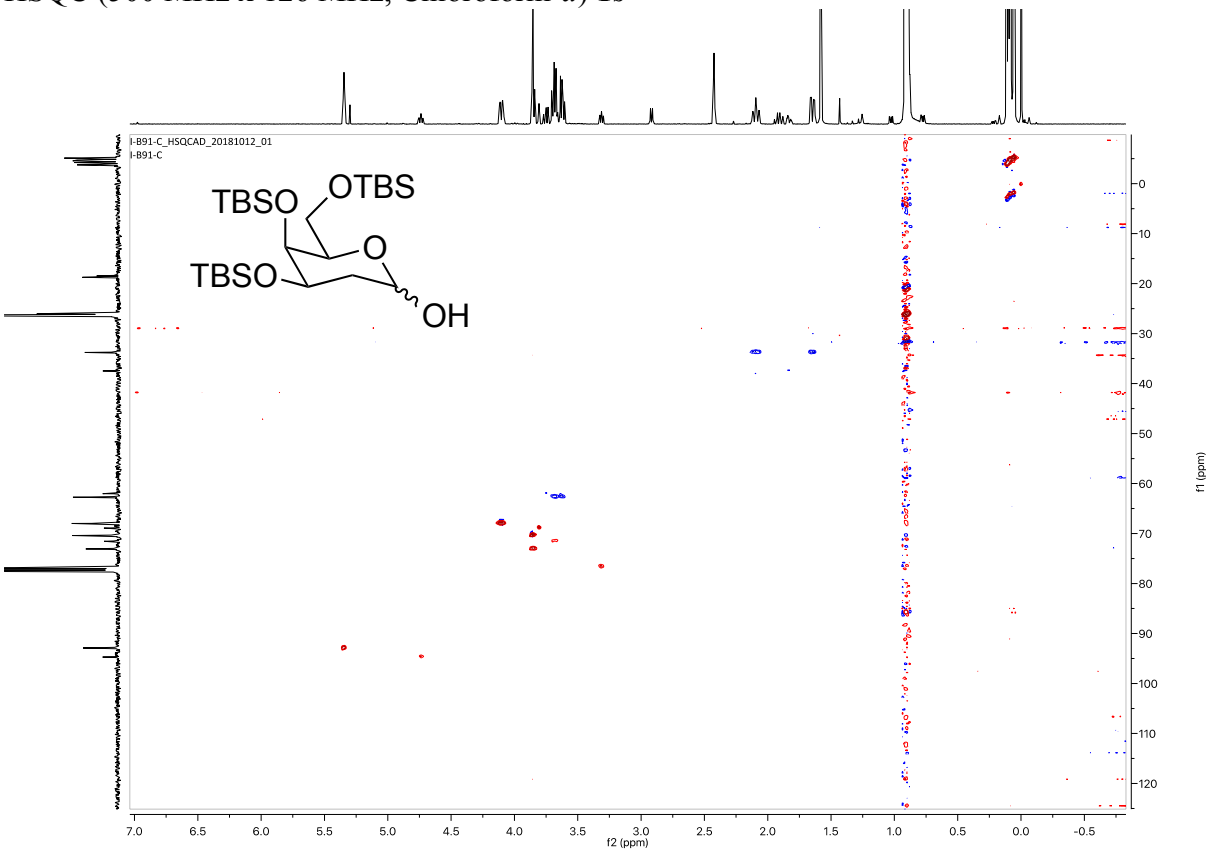
^{13}C NMR (101 MHz, Chloroform-*d*) **1s**



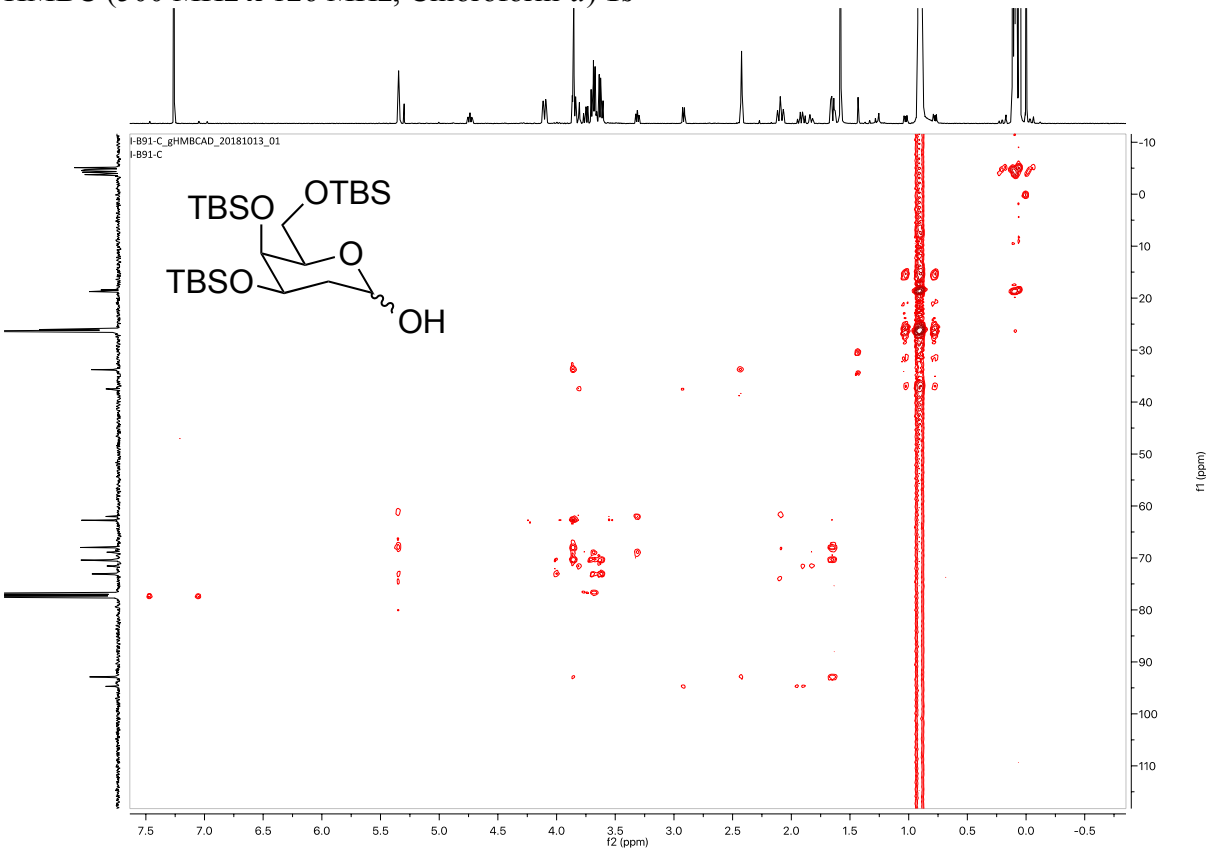
COSY (500 MHz, Chloroform-*d*) **1s**



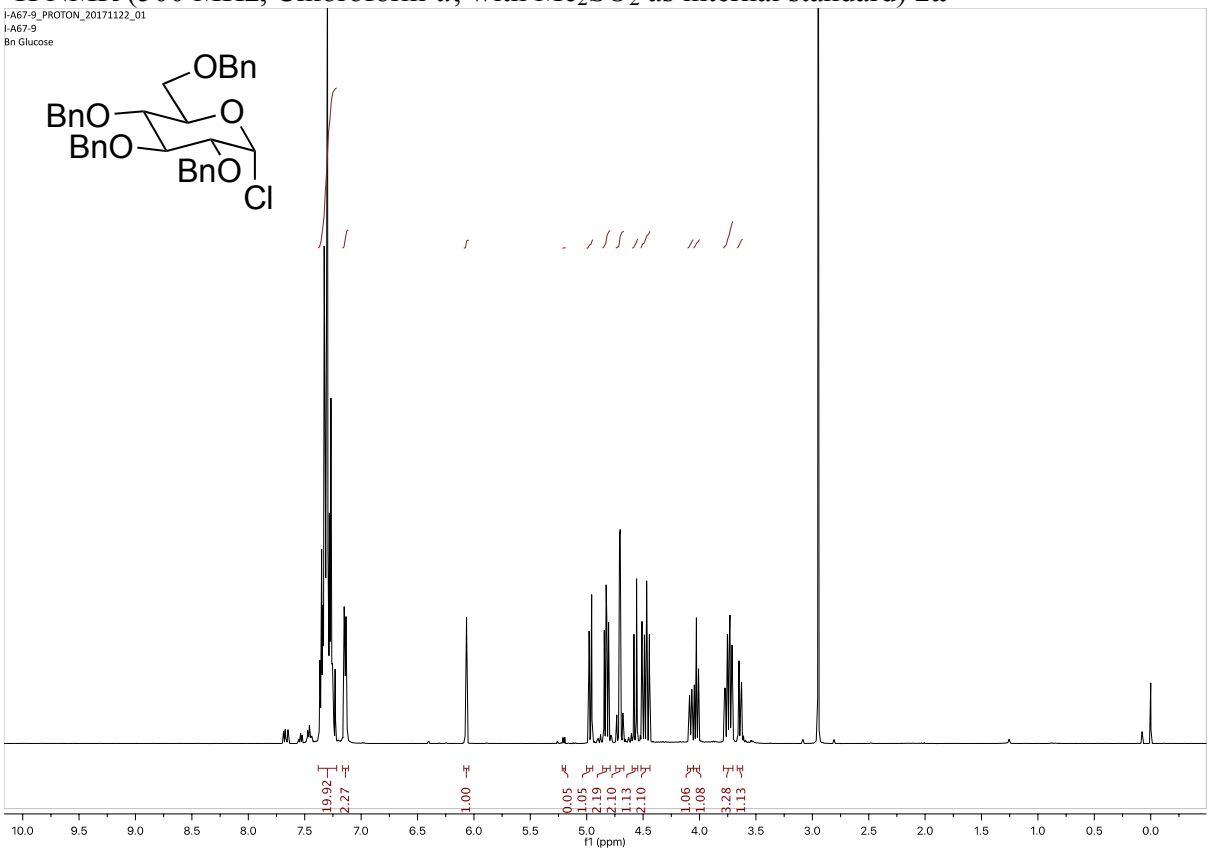
HSQC (500 MHz x 126 MHz, Chloroform-*d*) **1s**



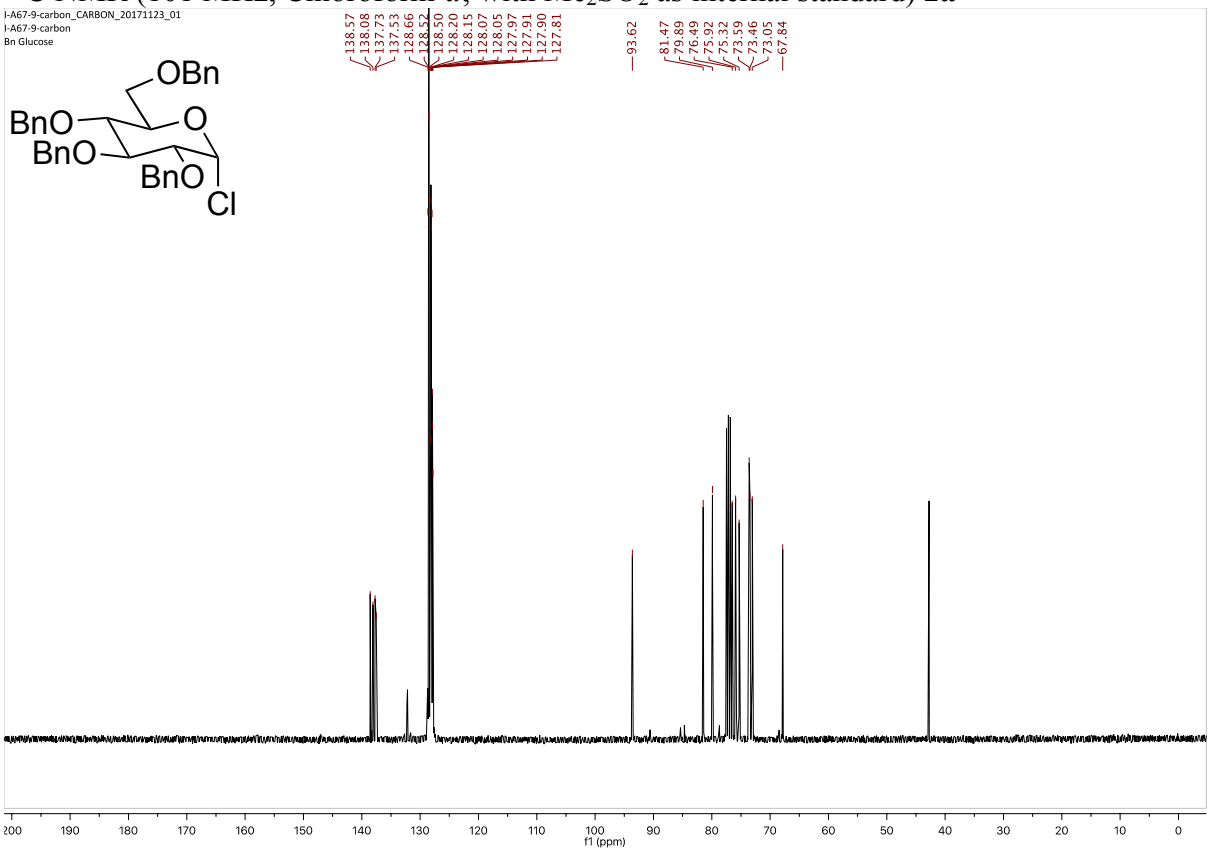
HMBC (500 MHz x 126 MHz, Chloroform-*d*) **1s**



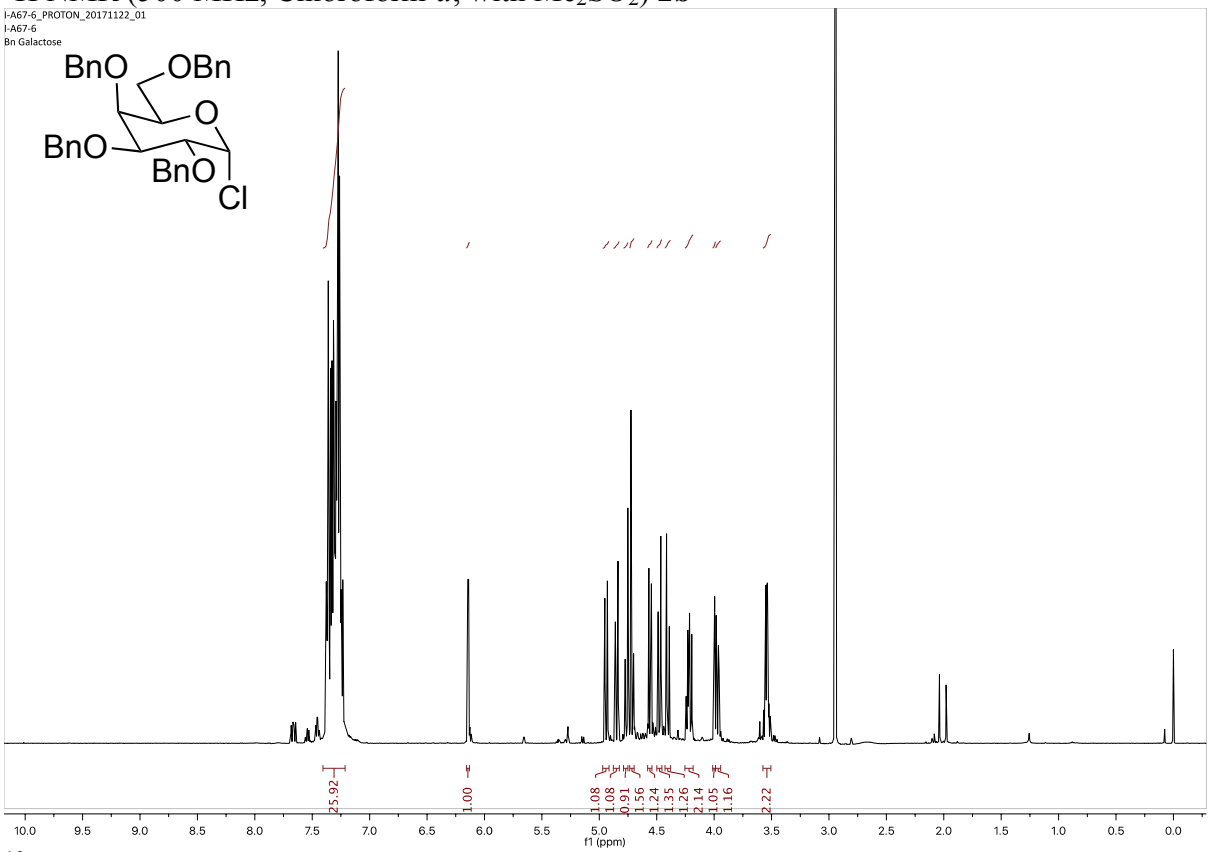
^{1}H NMR (500 MHz, Chloroform-*d*; with Me_2SO_2 as internal standard) **2a**



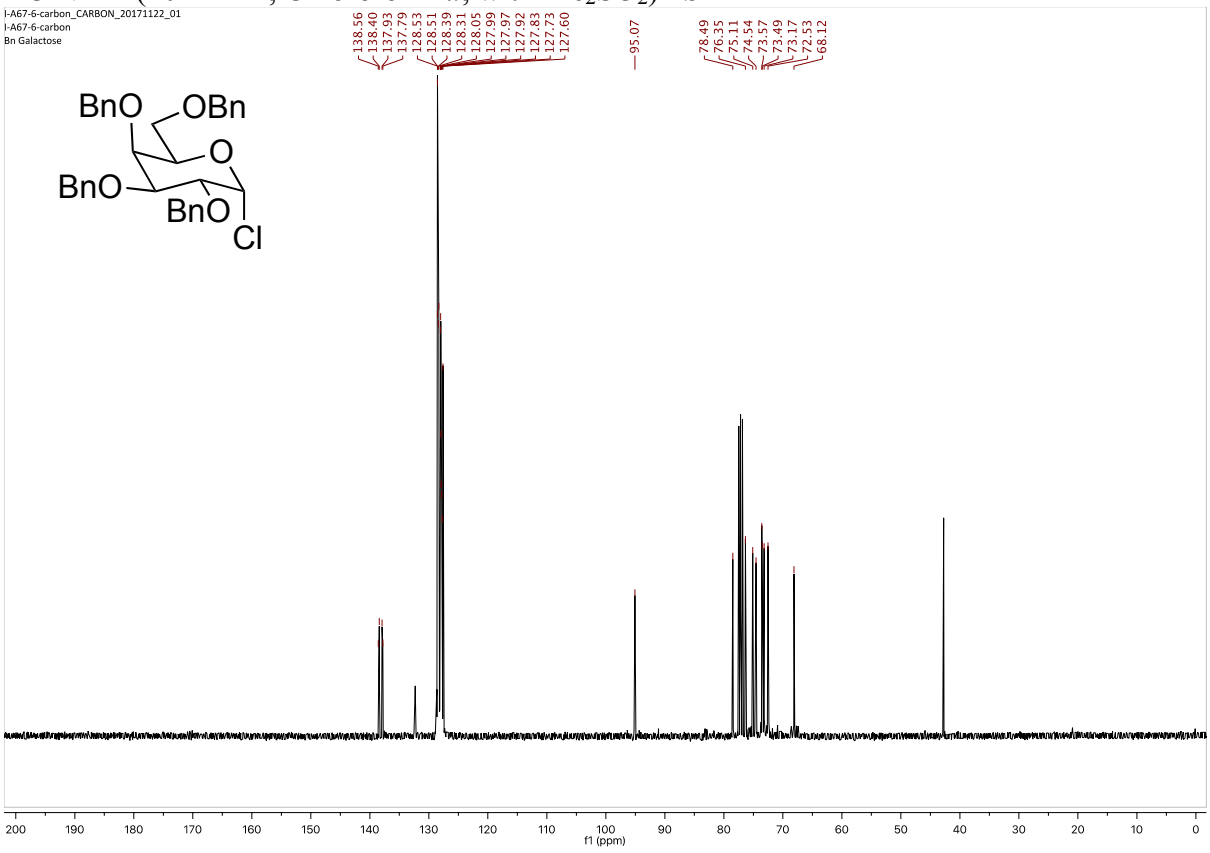
^{13}C NMR (101 MHz, Chloroform-*d*; with Me_2SO_2 as internal standard) **2a**



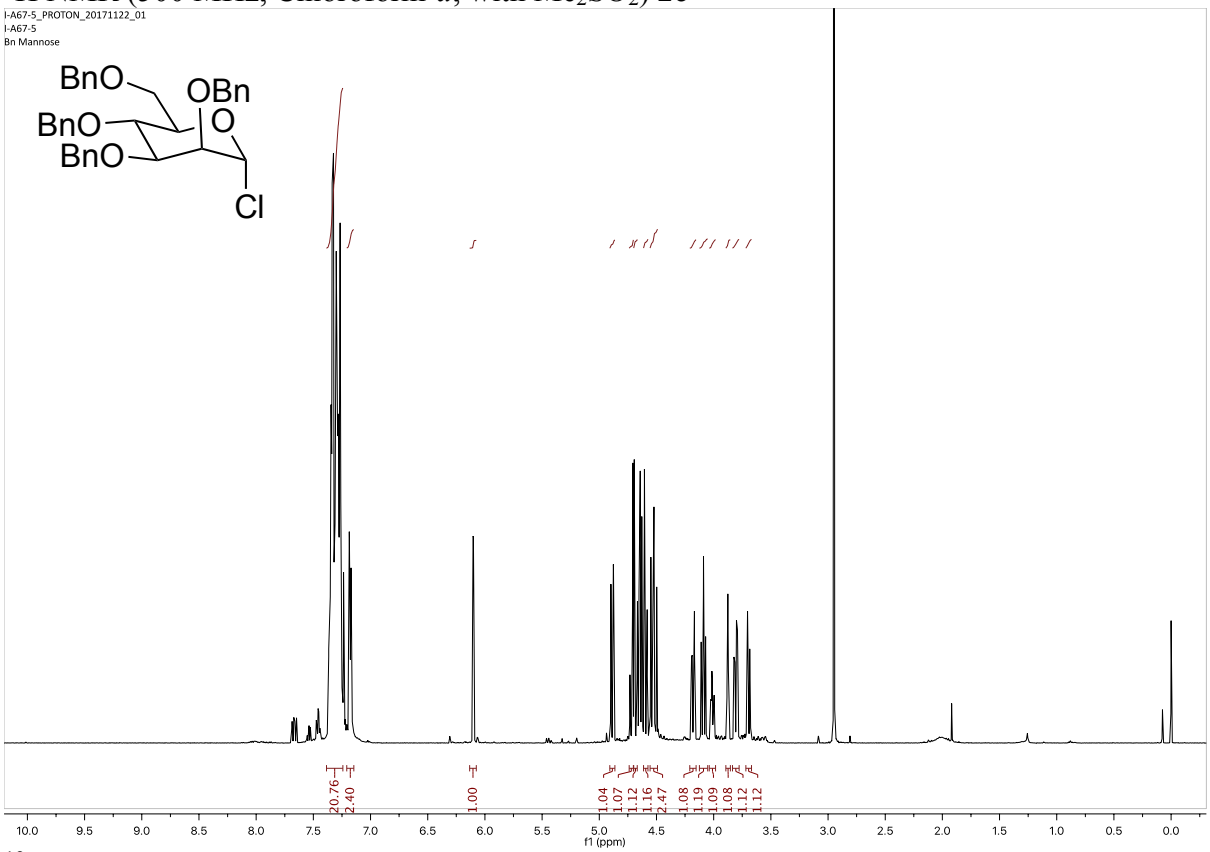
^{1}H NMR (500 MHz, Chloroform-*d*, with Me_2SO_2) **2b**



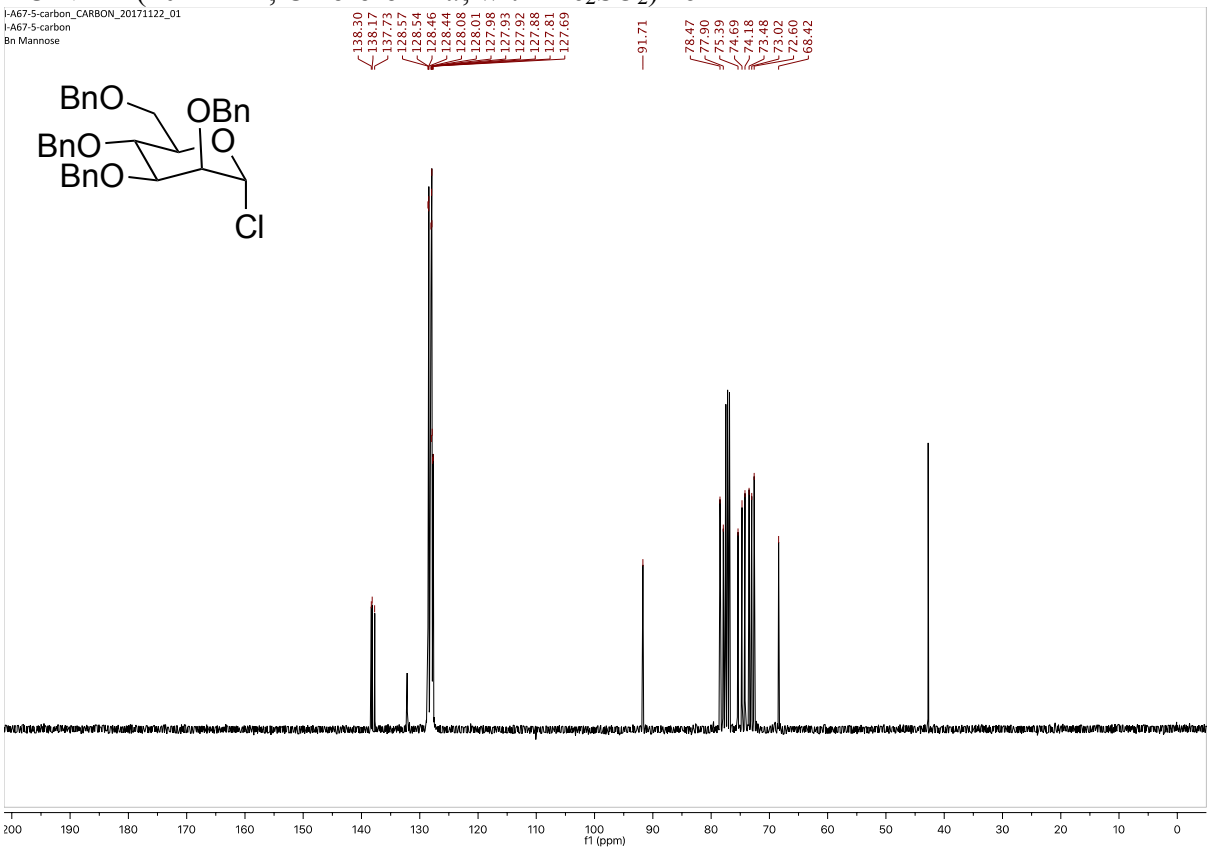
^{13}C NMR (101 MHz, Chloroform-*d*, with Me_2SO_2) **2b**



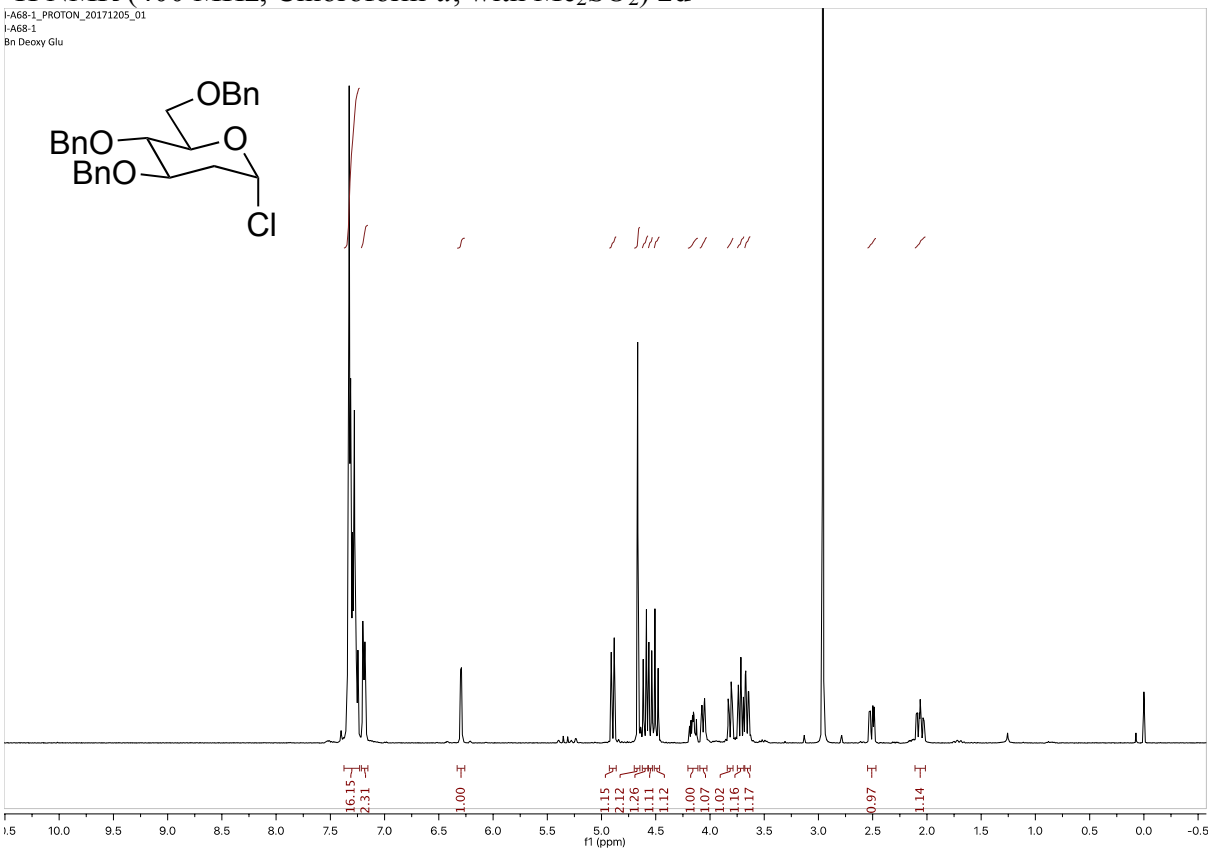
^{1}H NMR (500 MHz, Chloroform-*d*, with Me_2SO_2) **2c**



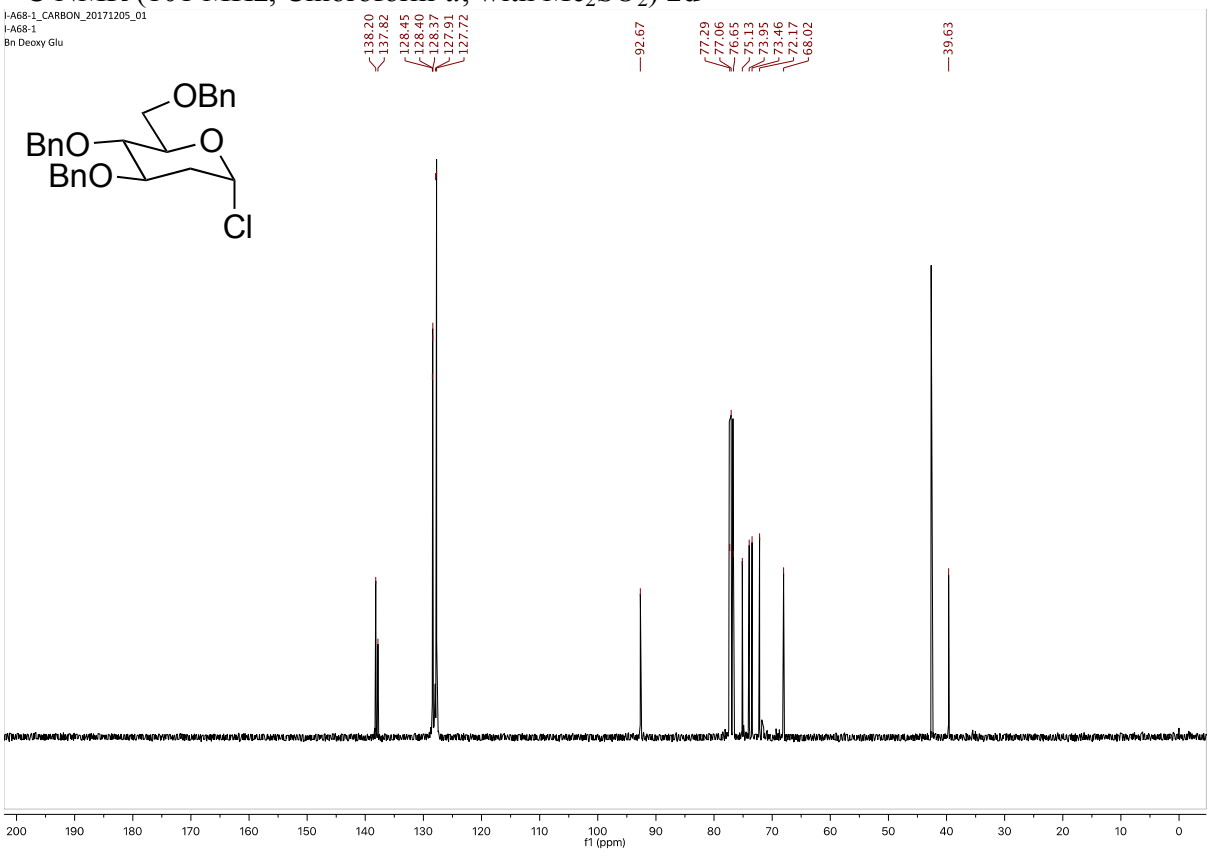
^{13}C NMR (101 MHz, Chloroform-*d*, with Me_2SO_2) **2c**



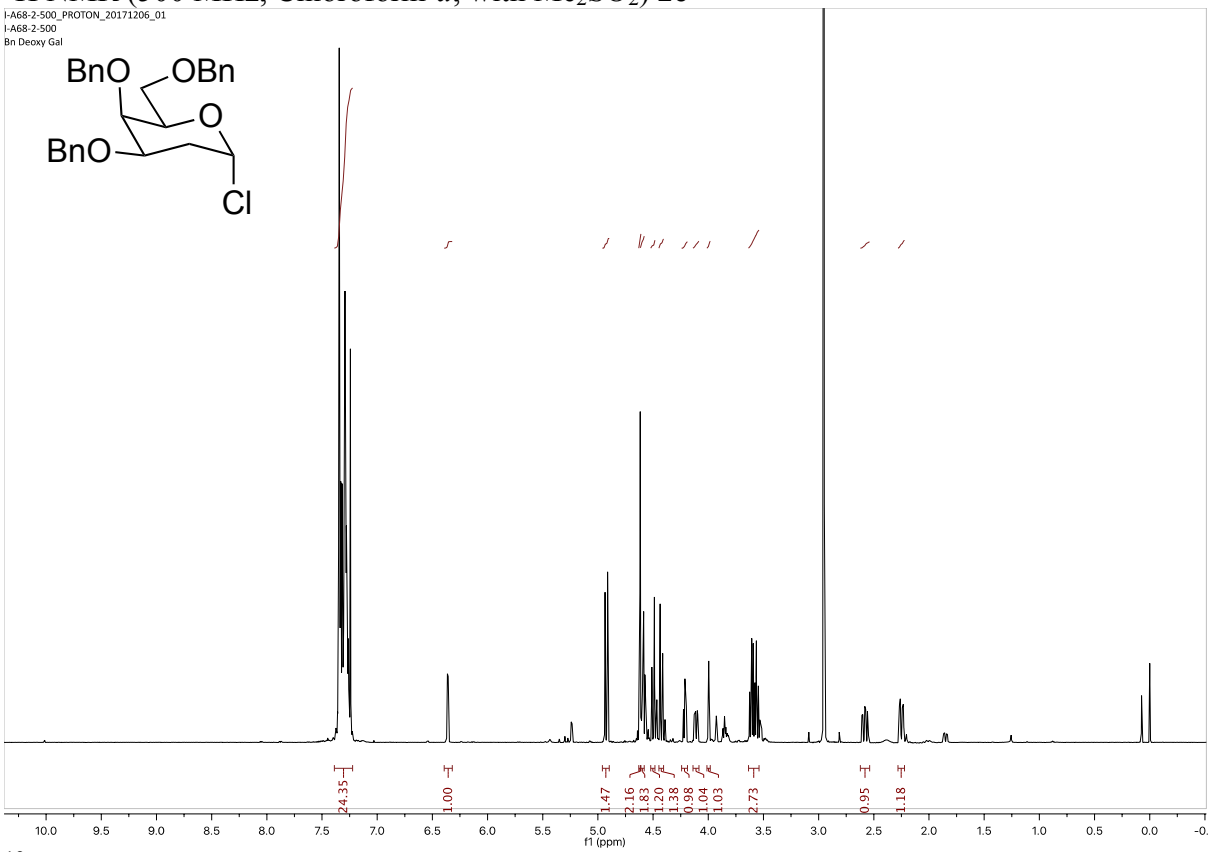
^{1}H NMR (400 MHz, Chloroform-*d*, with Me_2SO_2) **2d**



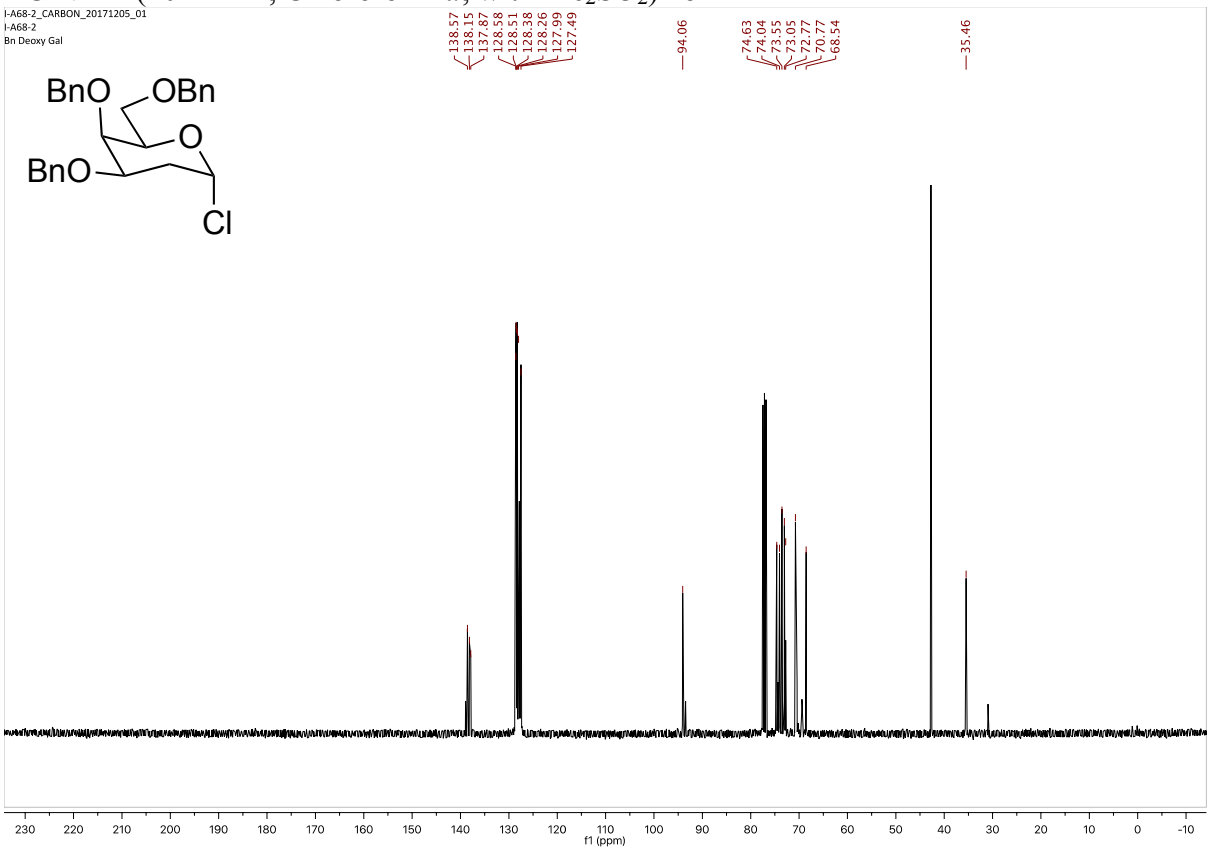
^{13}C NMR (101 MHz, Chloroform-*d*, with Me_2SO_2) **2d**



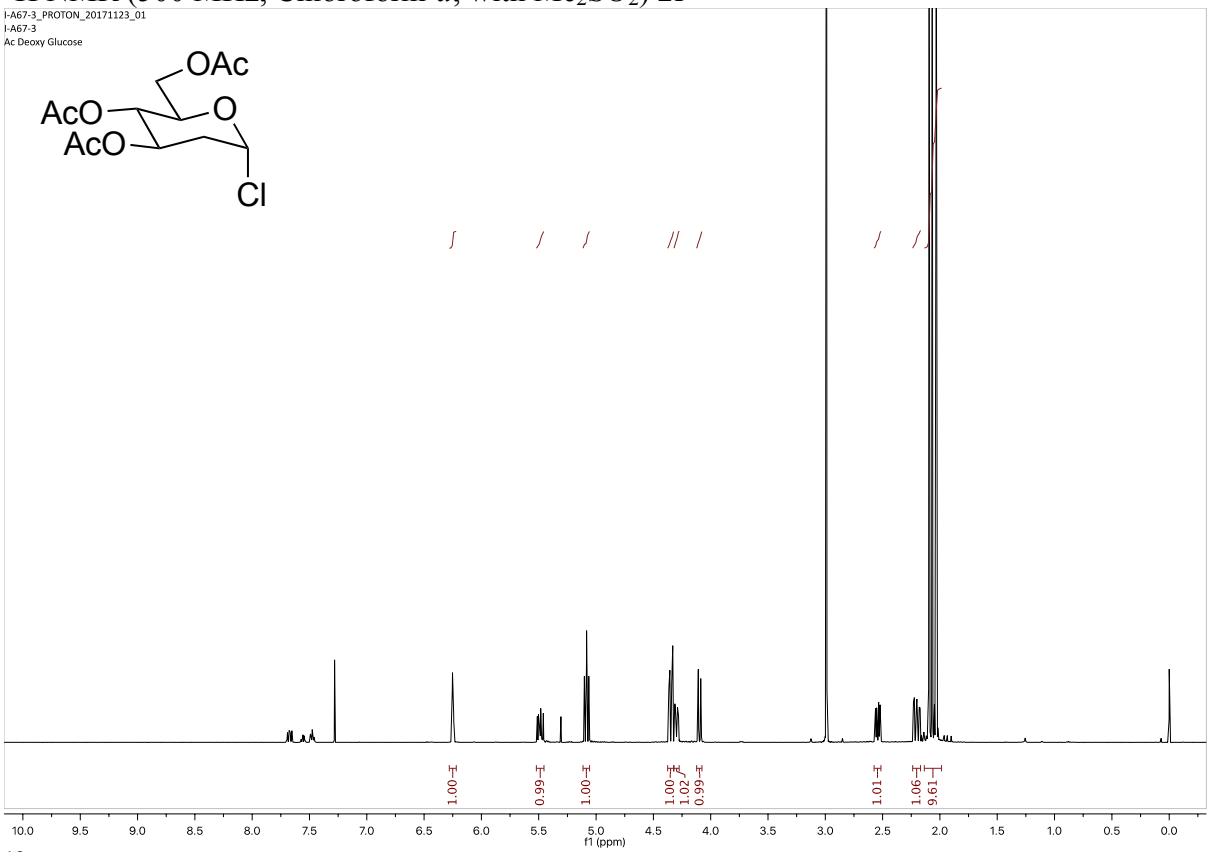
^{1}H NMR (500 MHz, Chloroform-*d*, with Me_2SO_2) **2e**



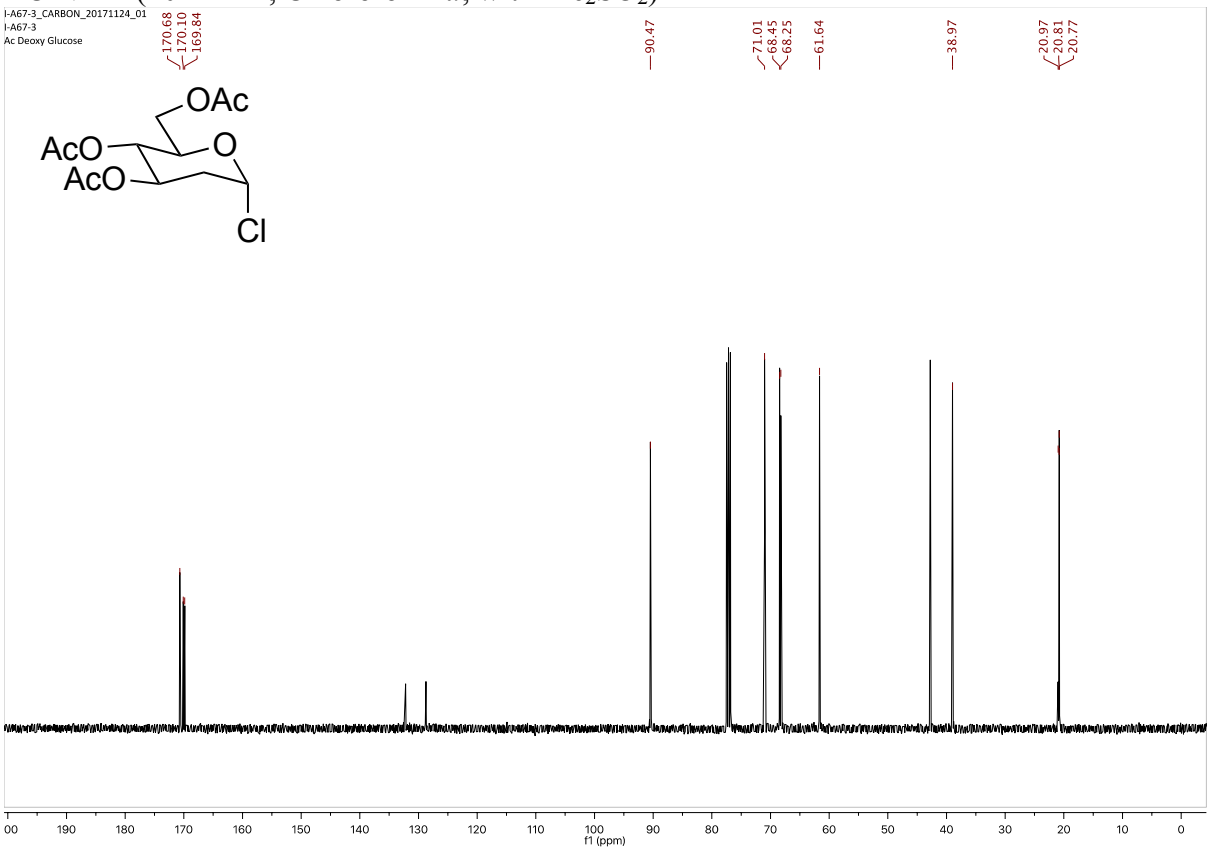
^{13}C NMR (101 MHz, Chloroform-*d*, with Me_2SO_2) **2e**



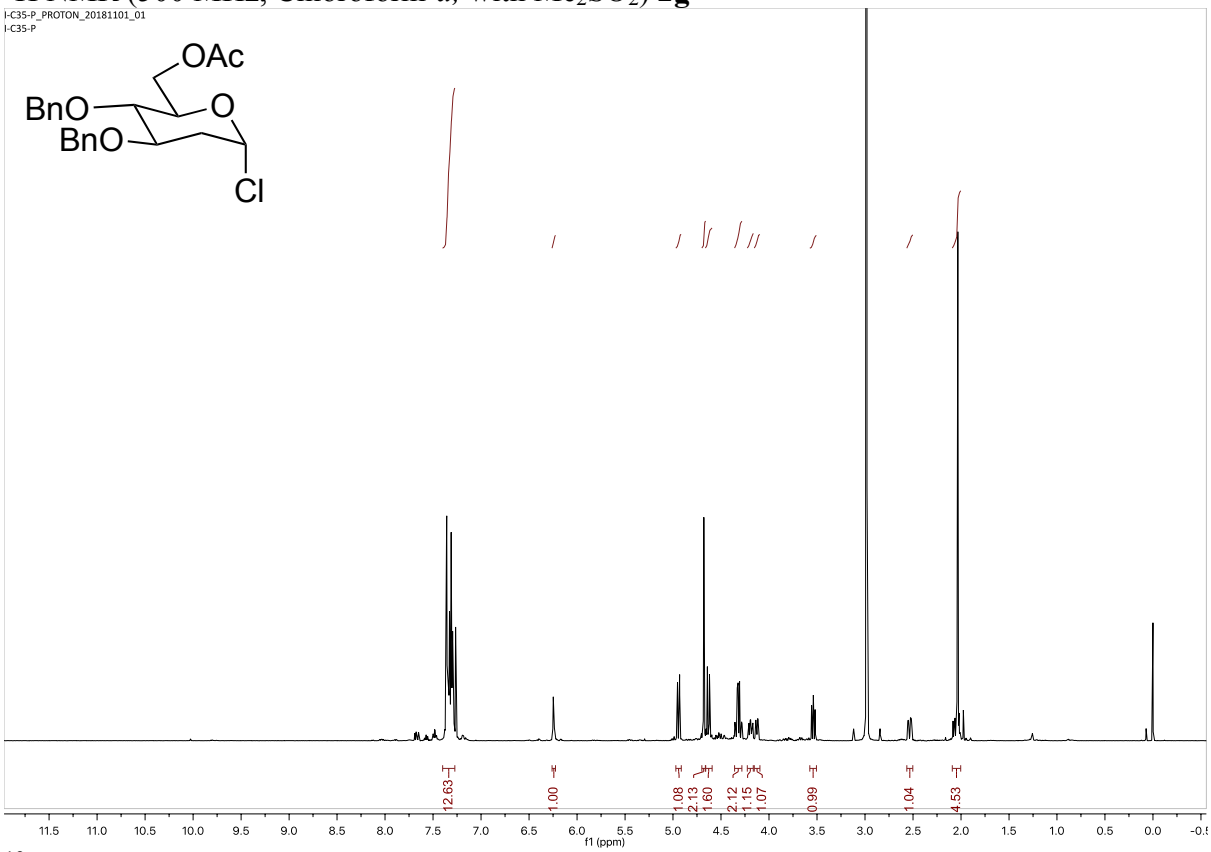
^{1}H NMR (500 MHz, Chloroform-*d*, with Me_2SO_2) **2f**



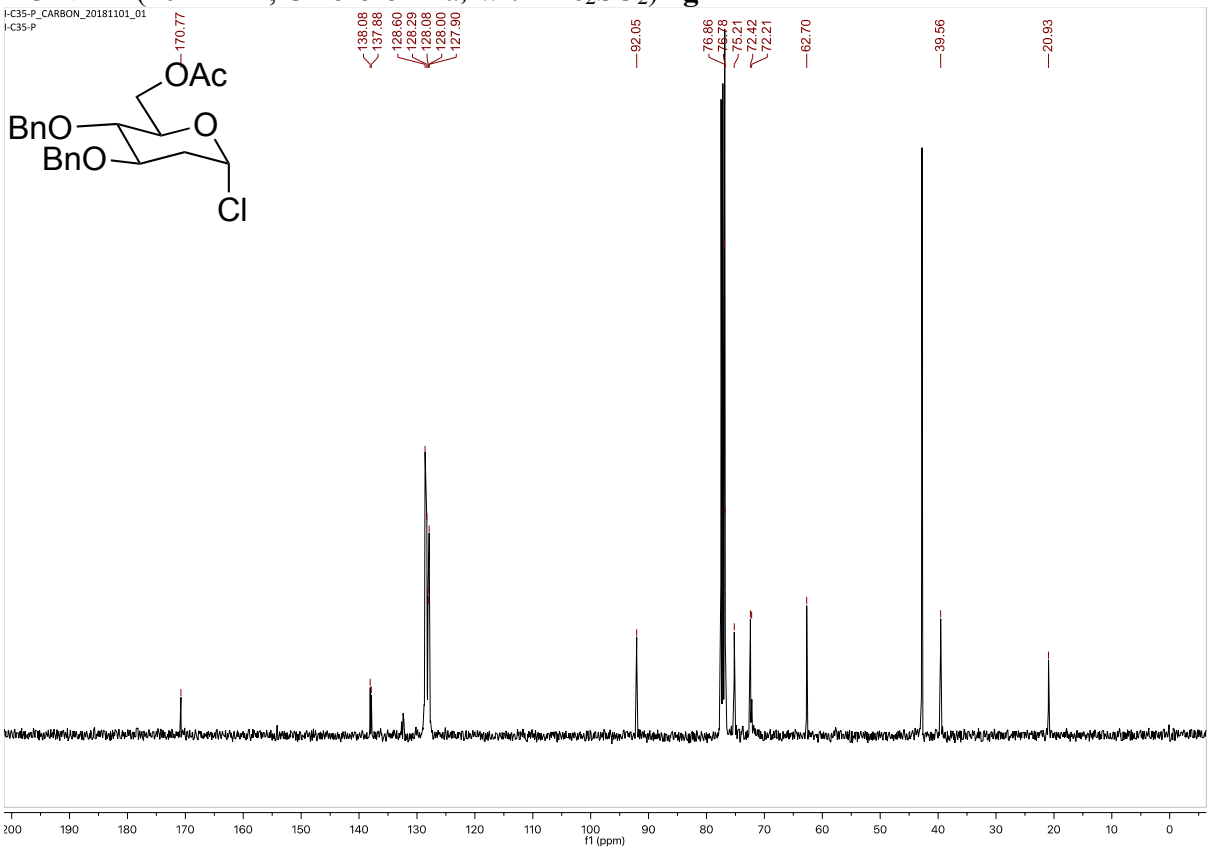
^{13}C NMR (101 MHz, Chloroform-*d*, with Me_2SO_2) **2f**



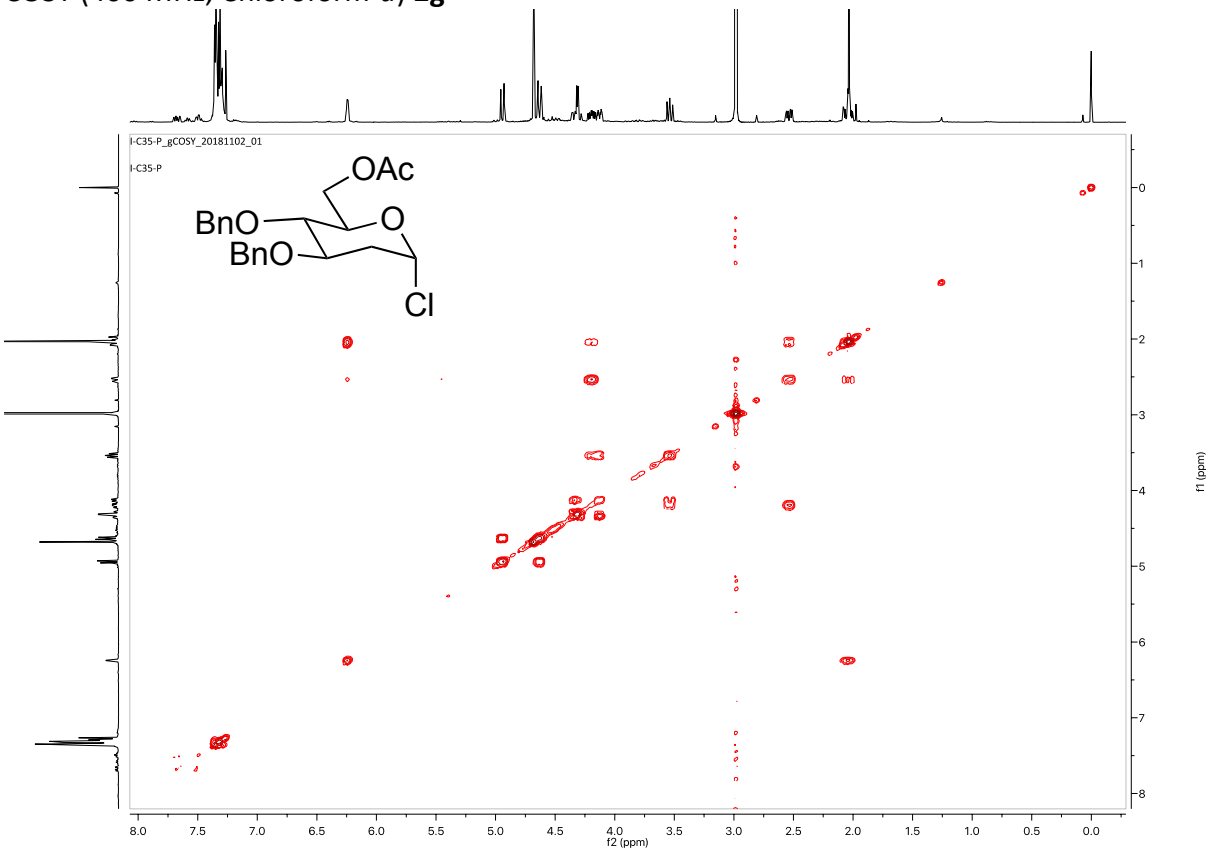
^{1}H NMR (500 MHz, Chloroform-*d,* with Me_2SO_2) **2g**



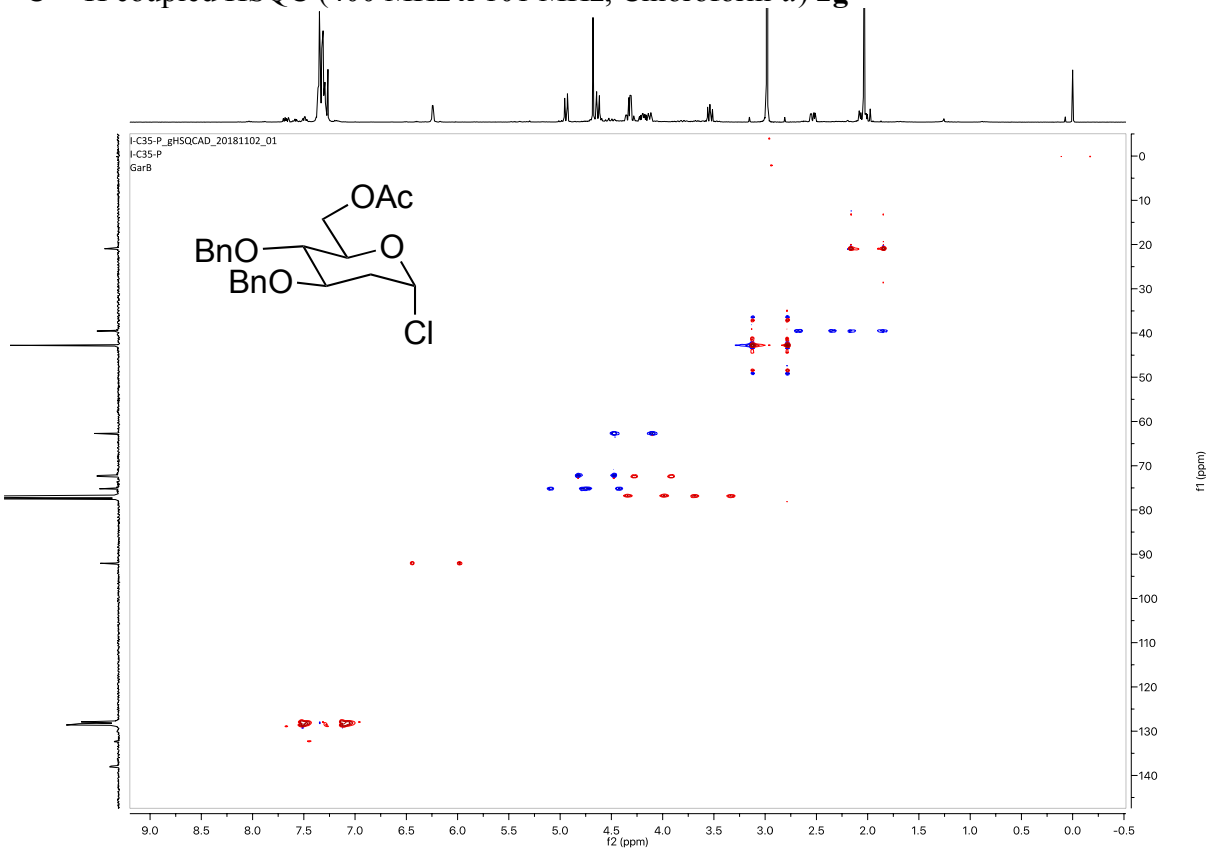
^{13}C NMR (101 MHz, Chloroform-*d,* with Me_2SO_2) **2g**



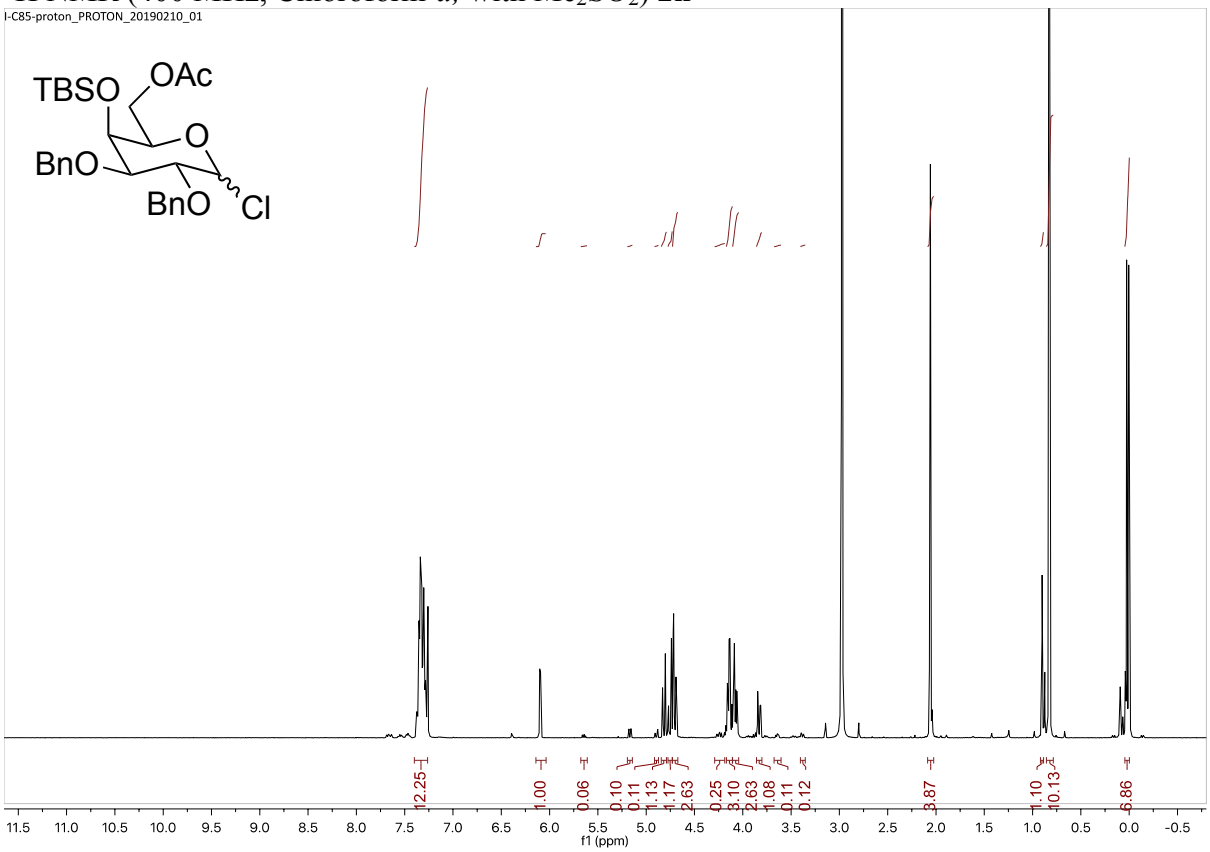
COSY (400 MHz, Chloroform-*d*) **2g**



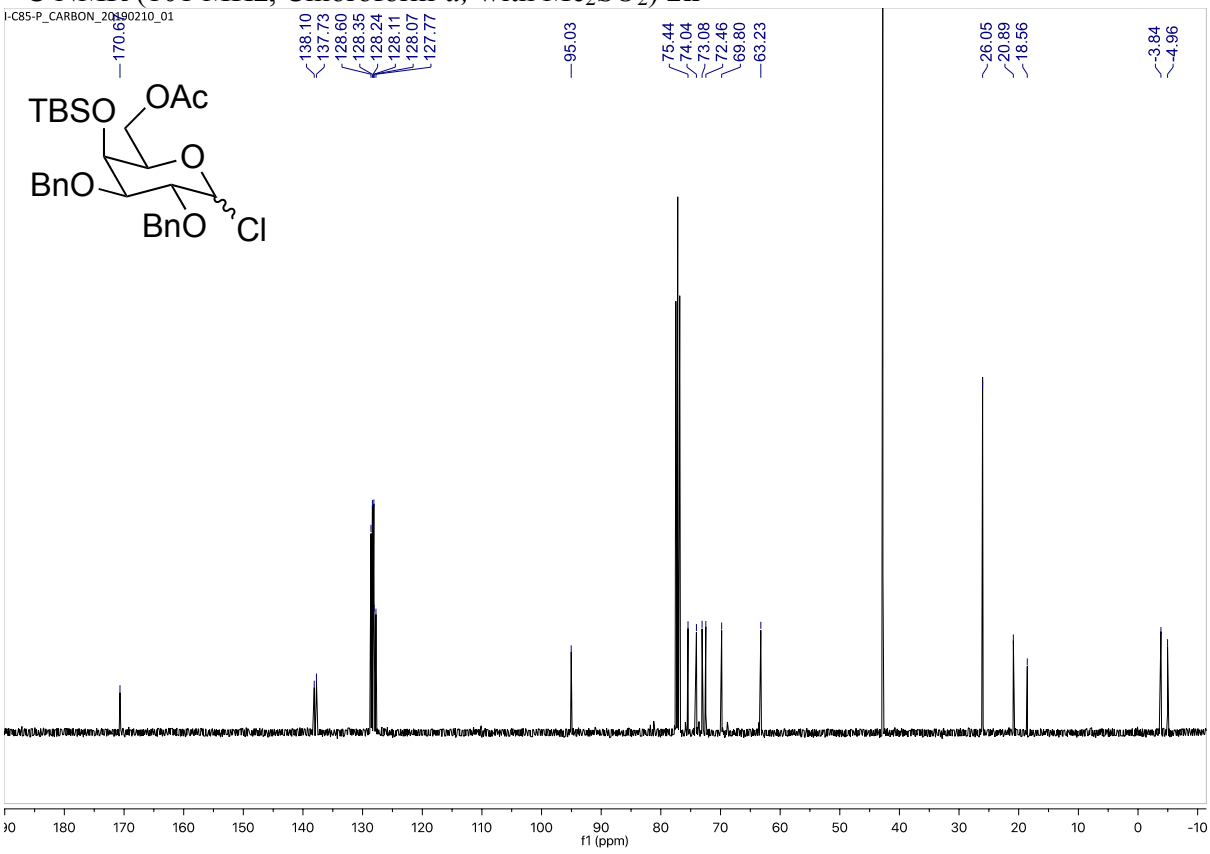
^{13}C - ^{1}H coupled HSQC (400 MHz x 101 MHz, Chloroform-*d*) **2g**



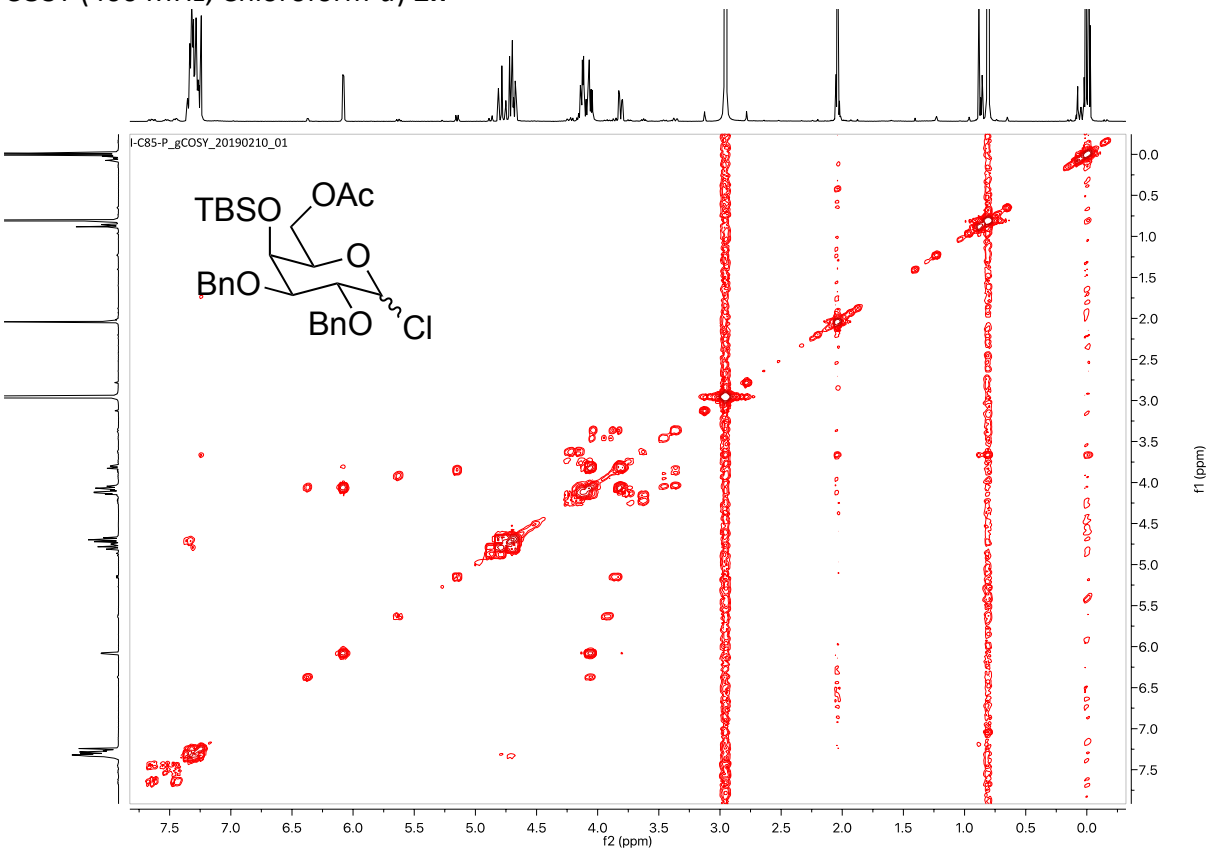
^{1}H NMR (400 MHz, Chloroform-*d,* with Me_2SO_2) **2h**



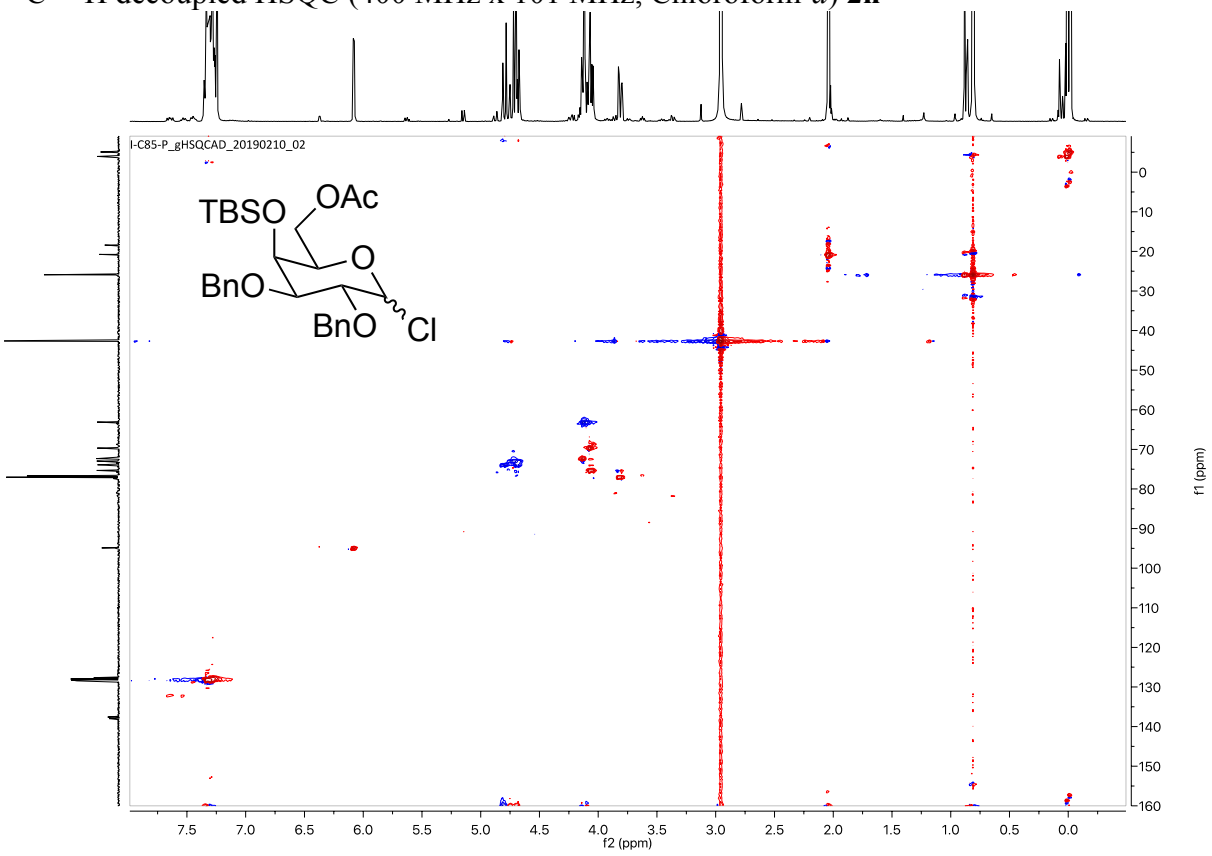
^{13}C NMR (101 MHz, Chloroform-*d,* with Me_2SO_2) **2h**



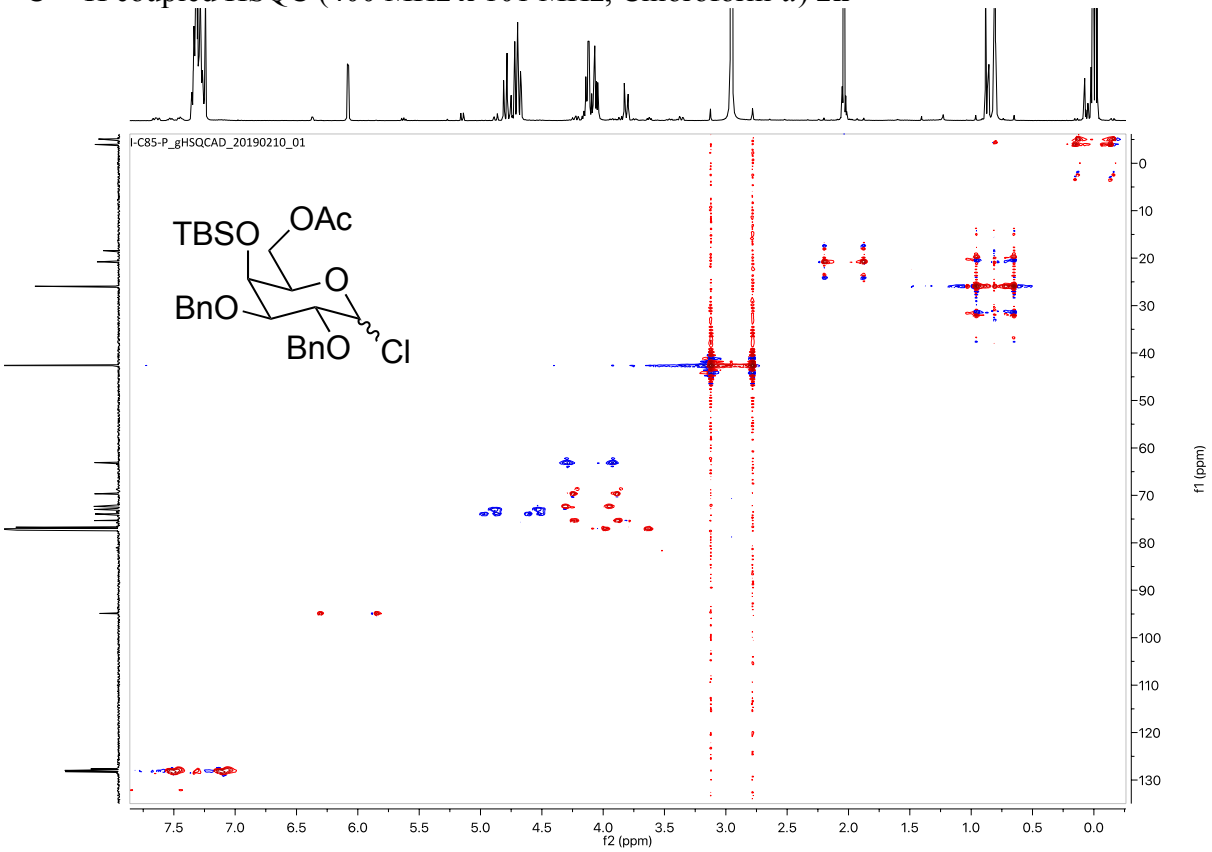
COSY (400 MHz, Chloroform-*d*) **2h**



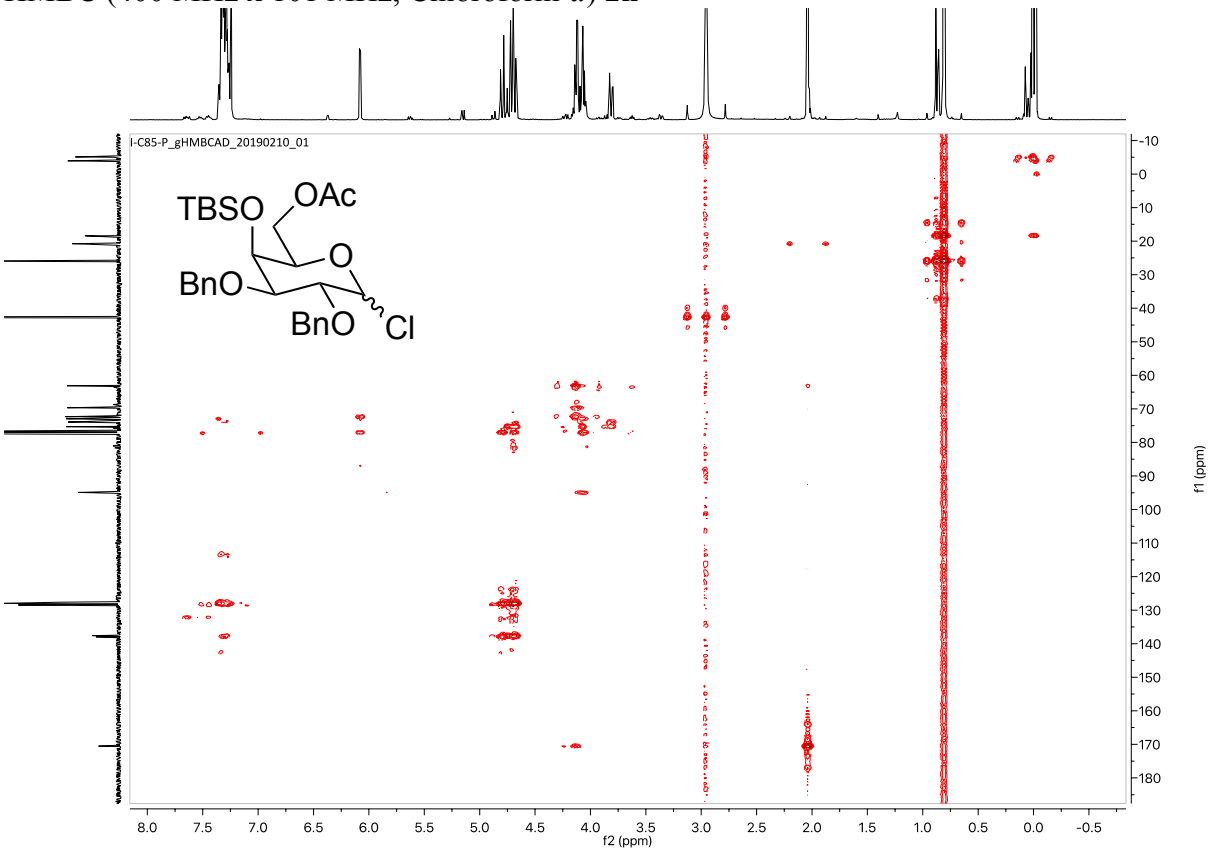
^{13}C - ^{1}H decoupled HSQC (400 MHz x 101 MHz, Chloroform-*d*) **2h**



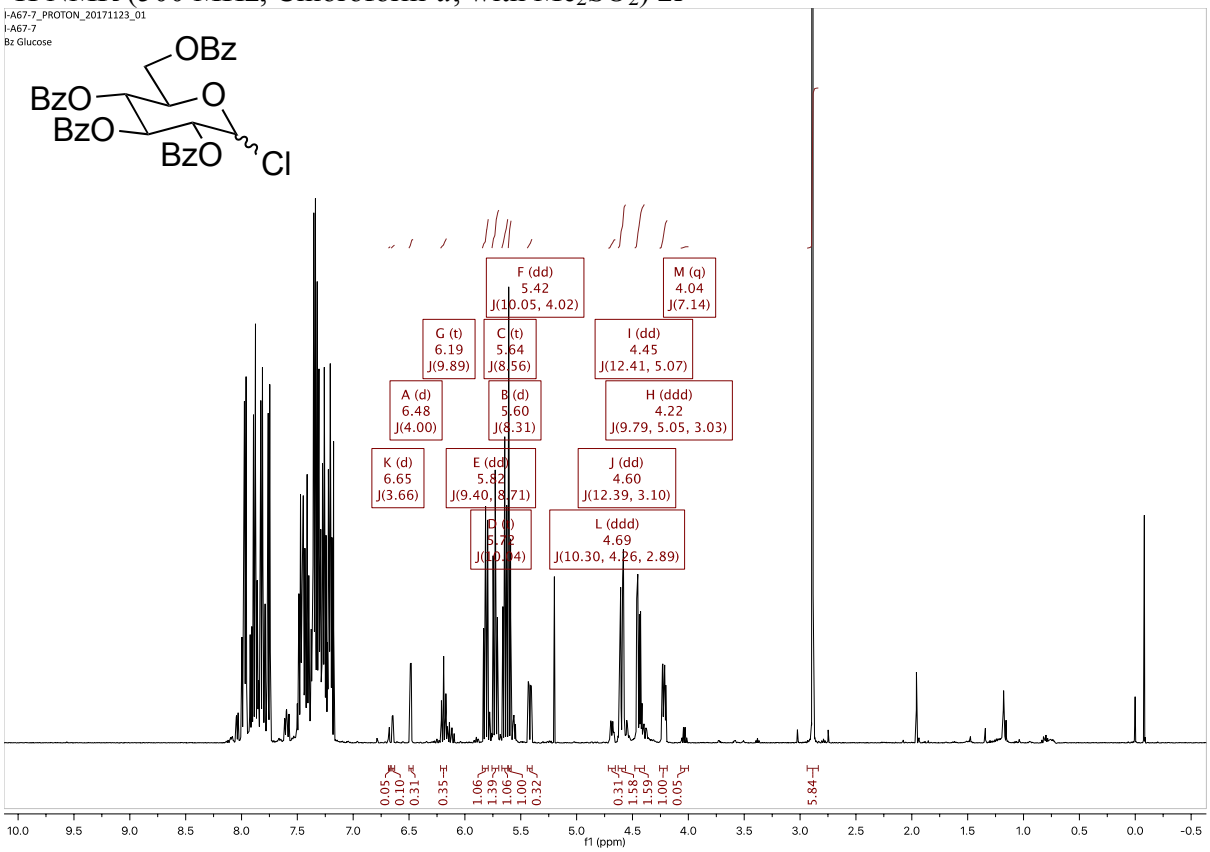
^{13}C - ^{1}H coupled HSQC (400 MHz x 101 MHz, Chloroform-*d*) **2h**



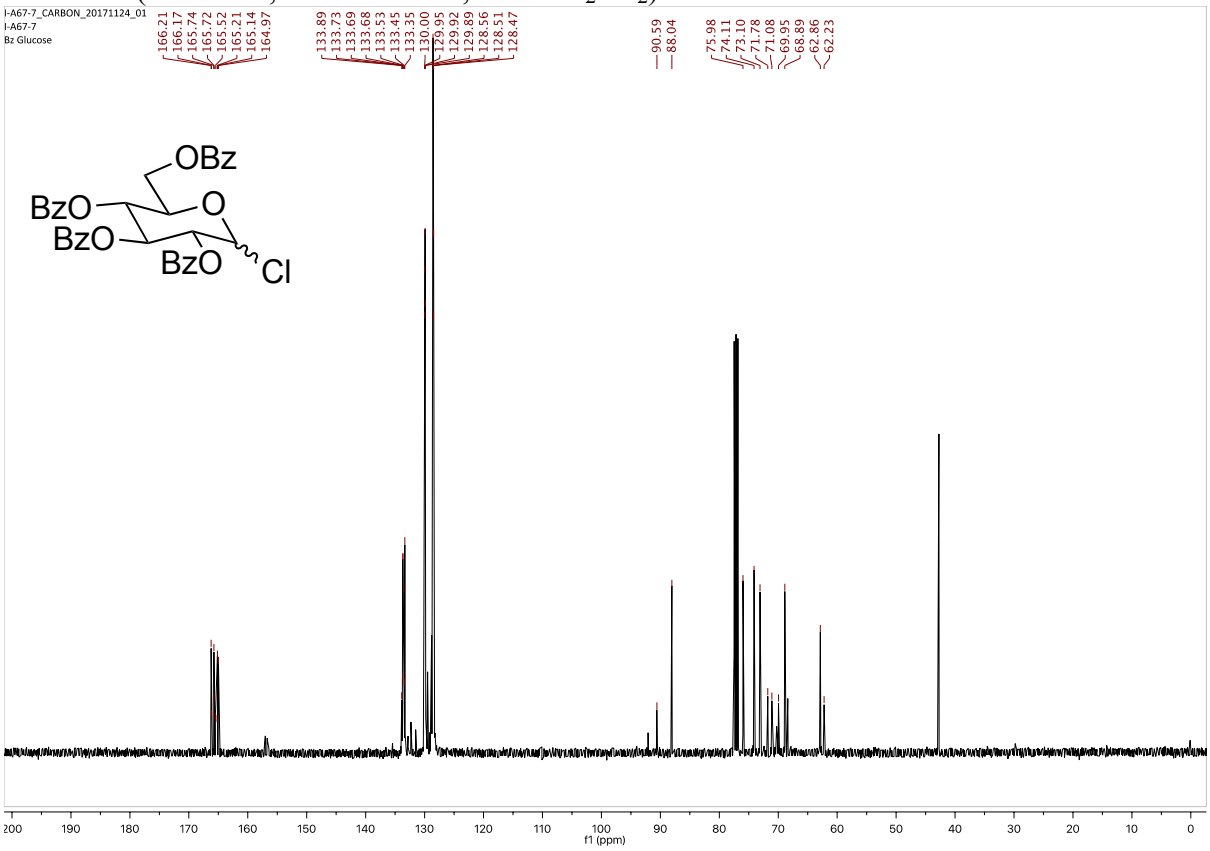
HMBC (400 MHz x 101 MHz, Chloroform-*d*) **2h**



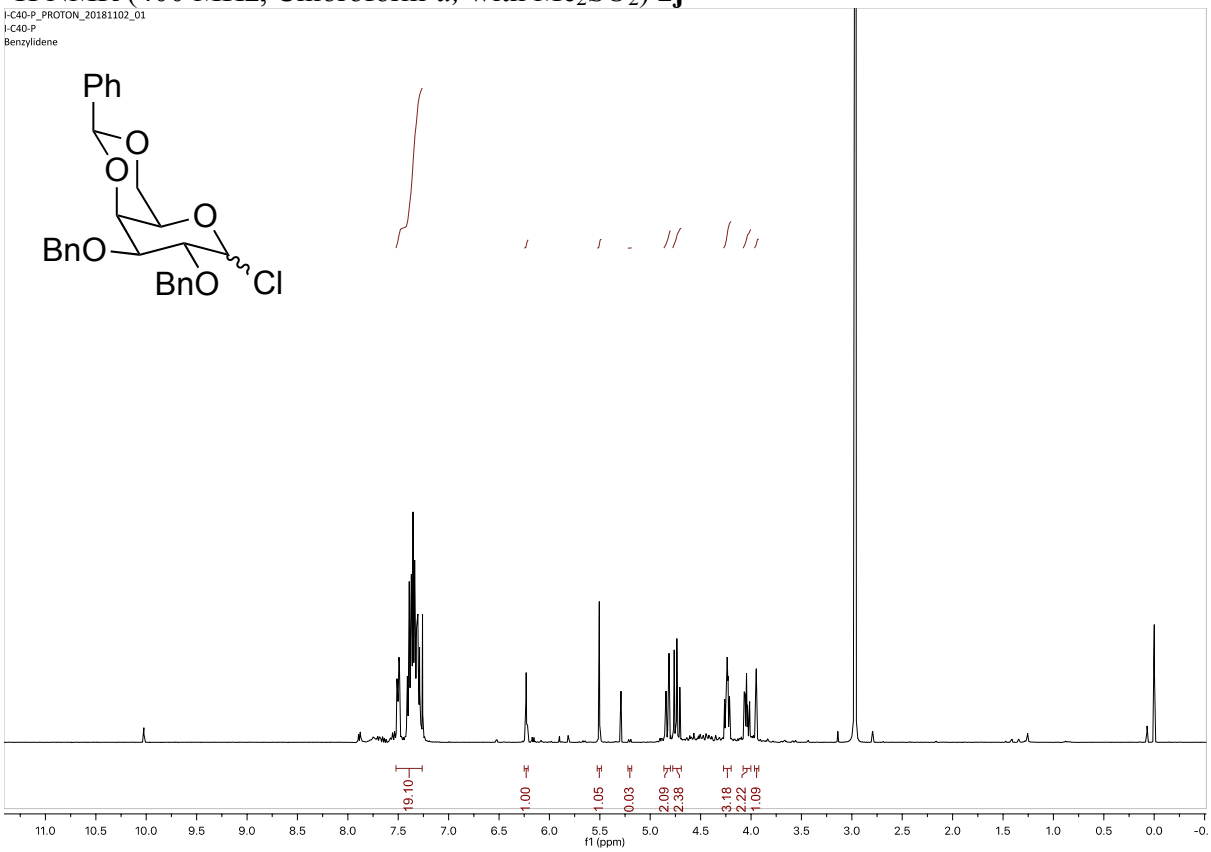
^{1}H NMR (500 MHz, Chloroform-*d*, with Me_2SO_2) **2i**



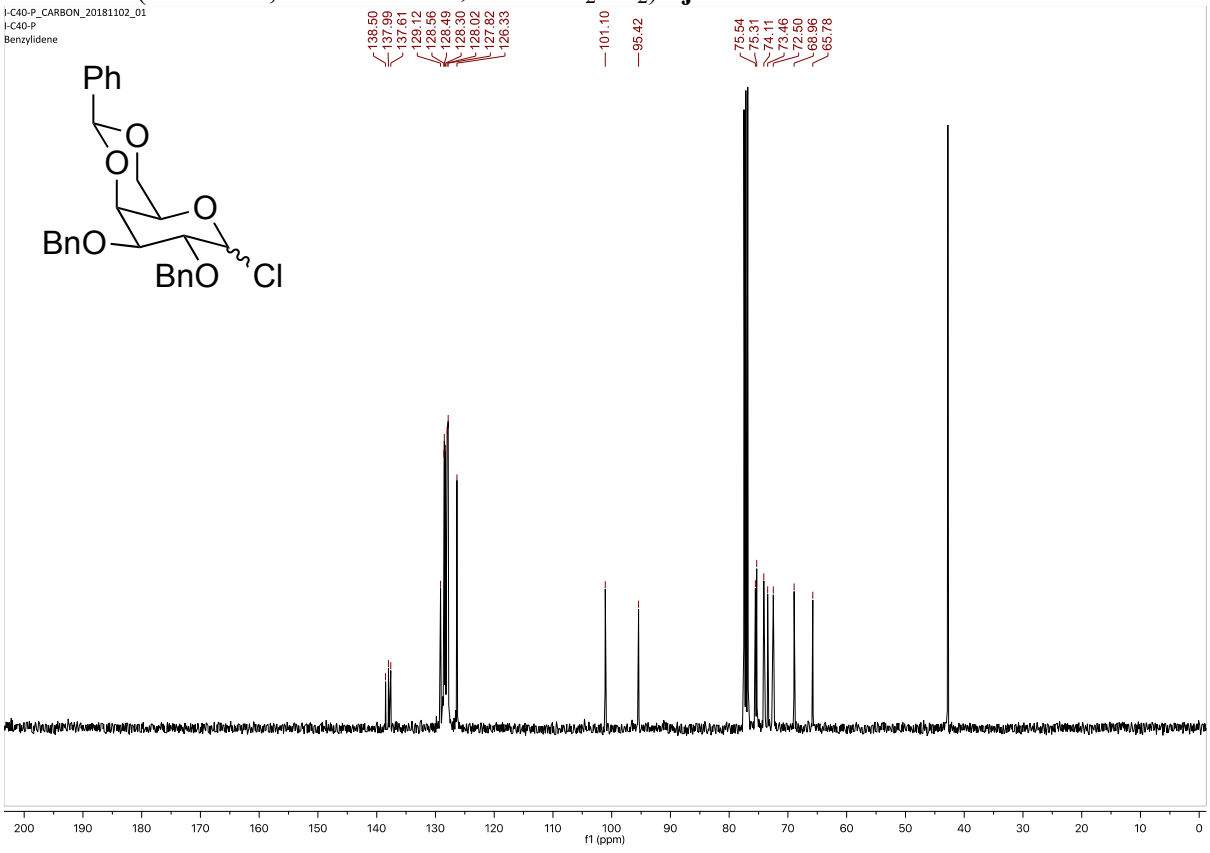
^{13}C NMR (101 MHz, Chloroform-*d*, with Me_2SO_2) **2i**



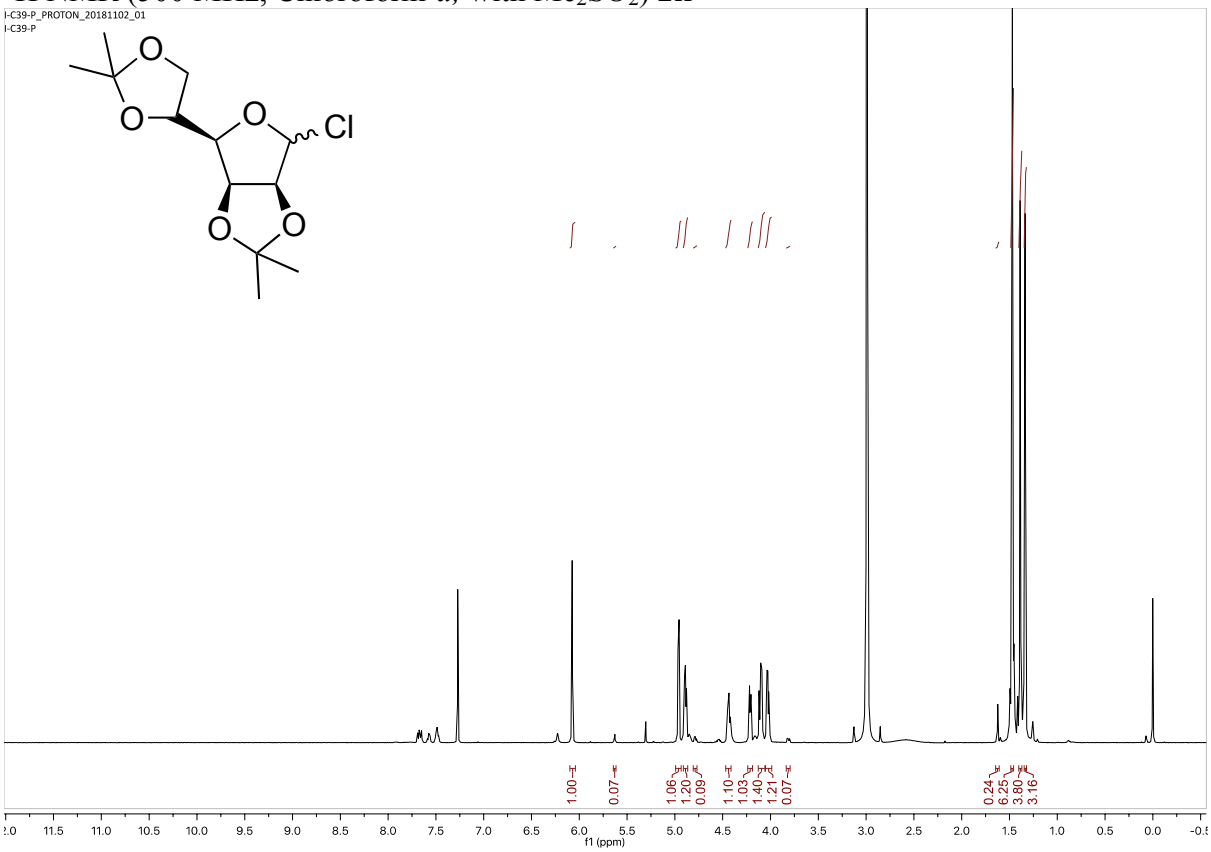
^{1}H NMR (400 MHz, Chloroform-*d,* with Me_2SO_2) **2j**



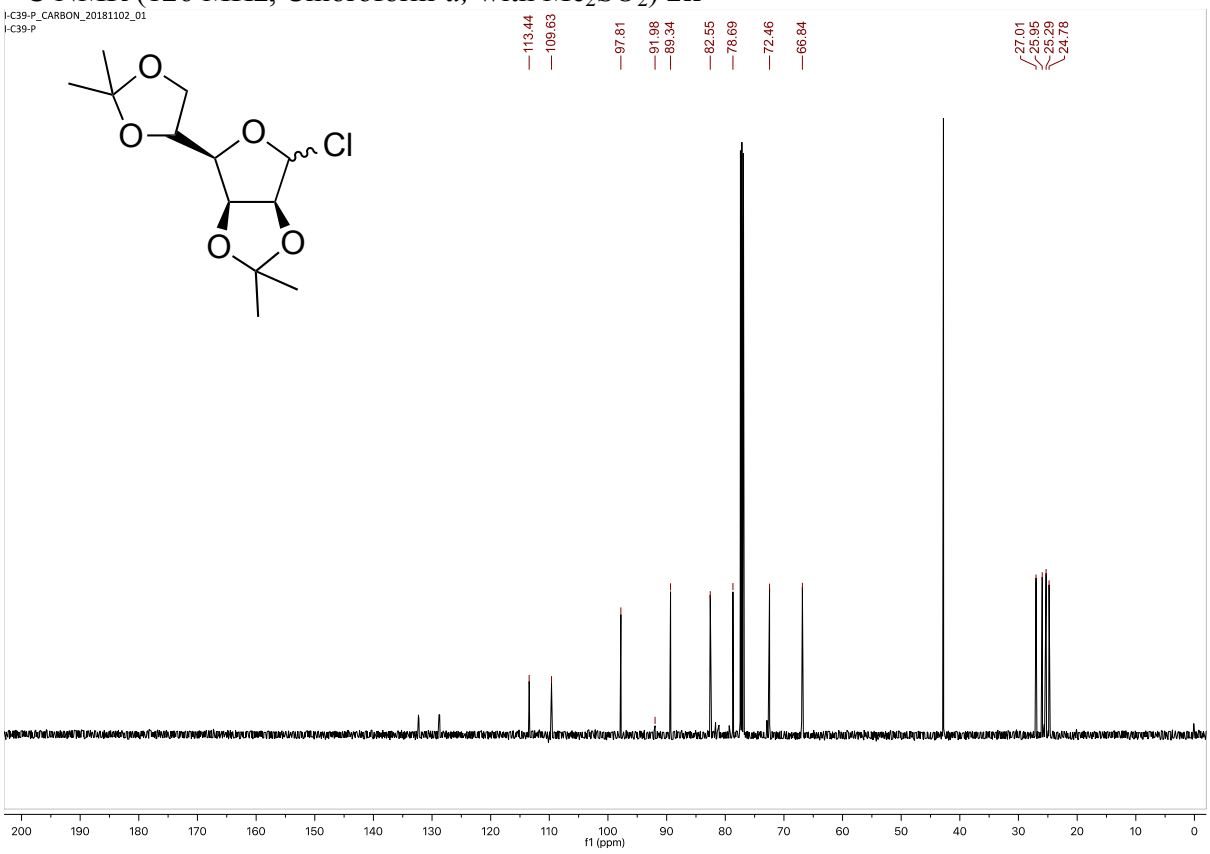
^{13}C NMR (101 MHz, Chloroform-*d,* with Me_2SO_2) **2j**



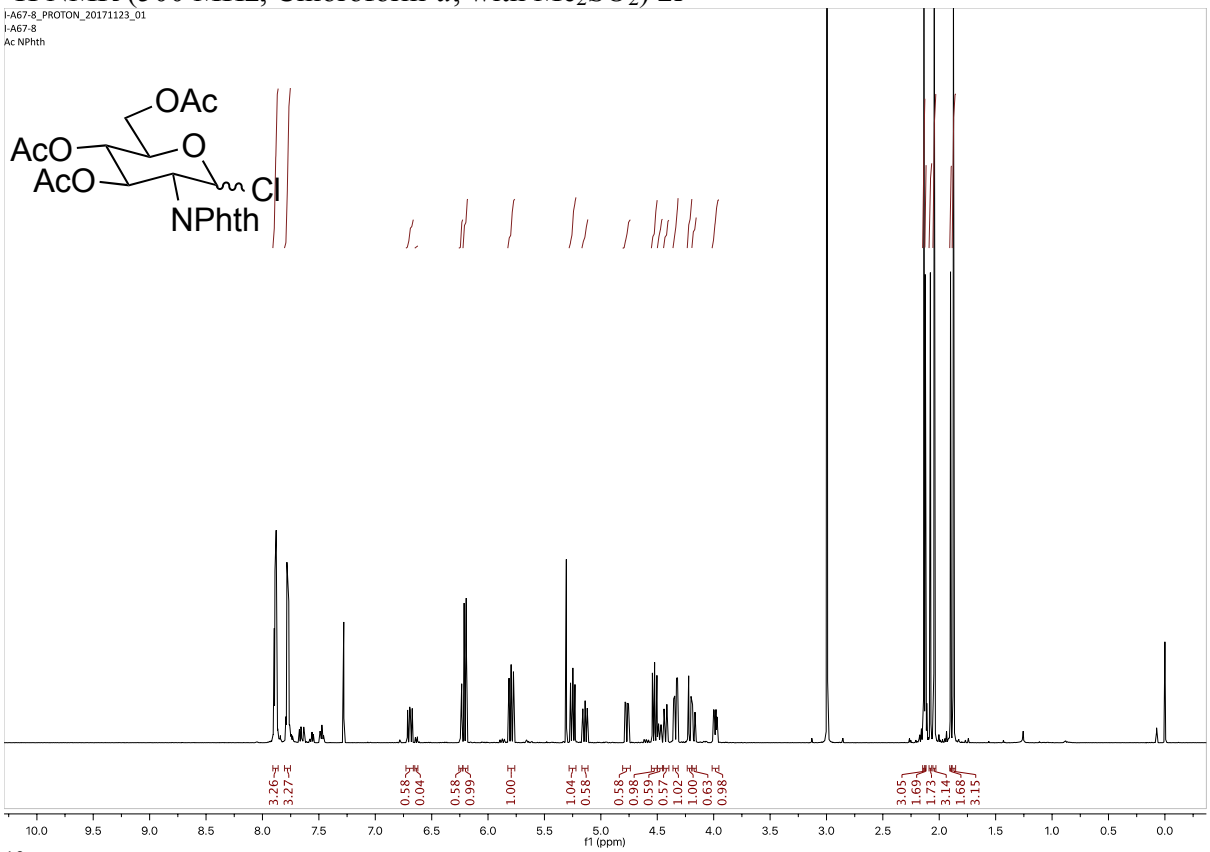
^{1}H NMR (500 MHz, Chloroform-*d,* with Me_2SO_2) **2k**



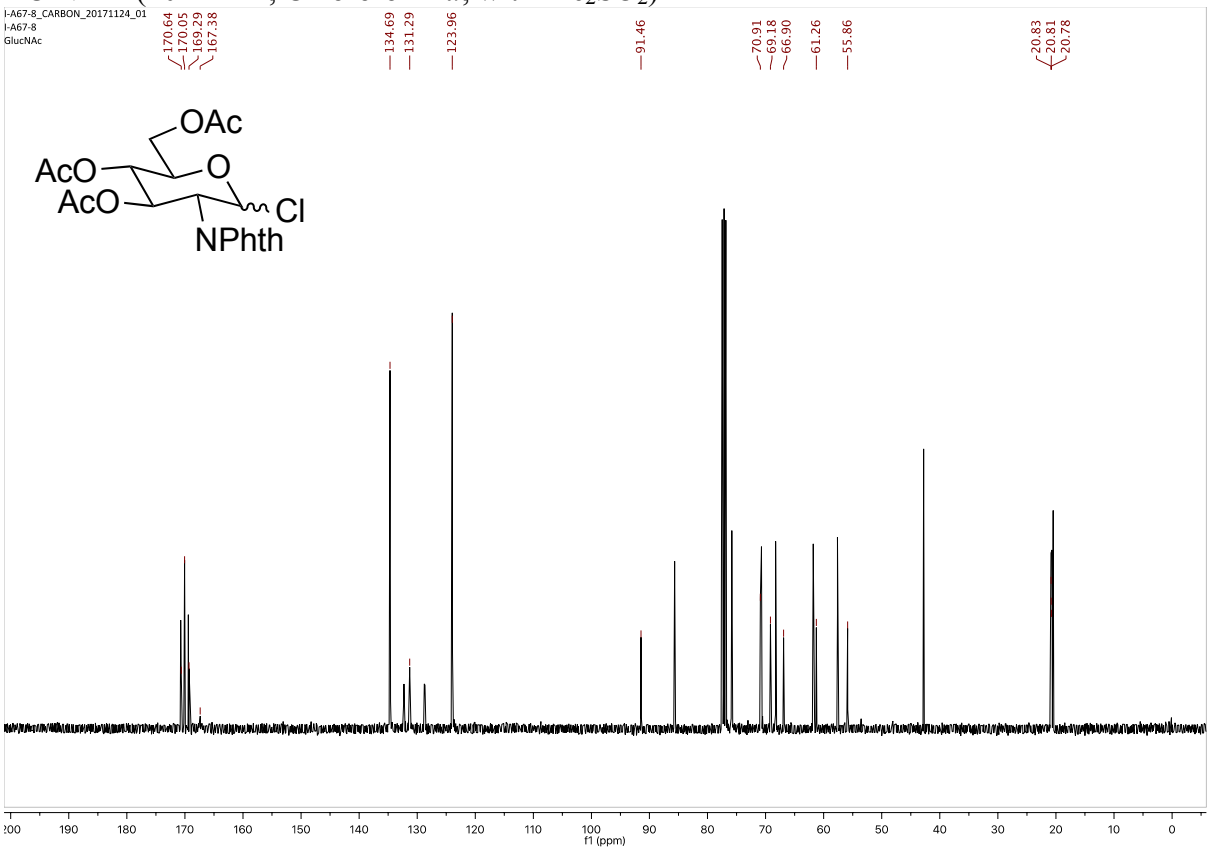
^{13}C NMR (126 MHz, Chloroform-*d,* with Me_2SO_2) **2k**



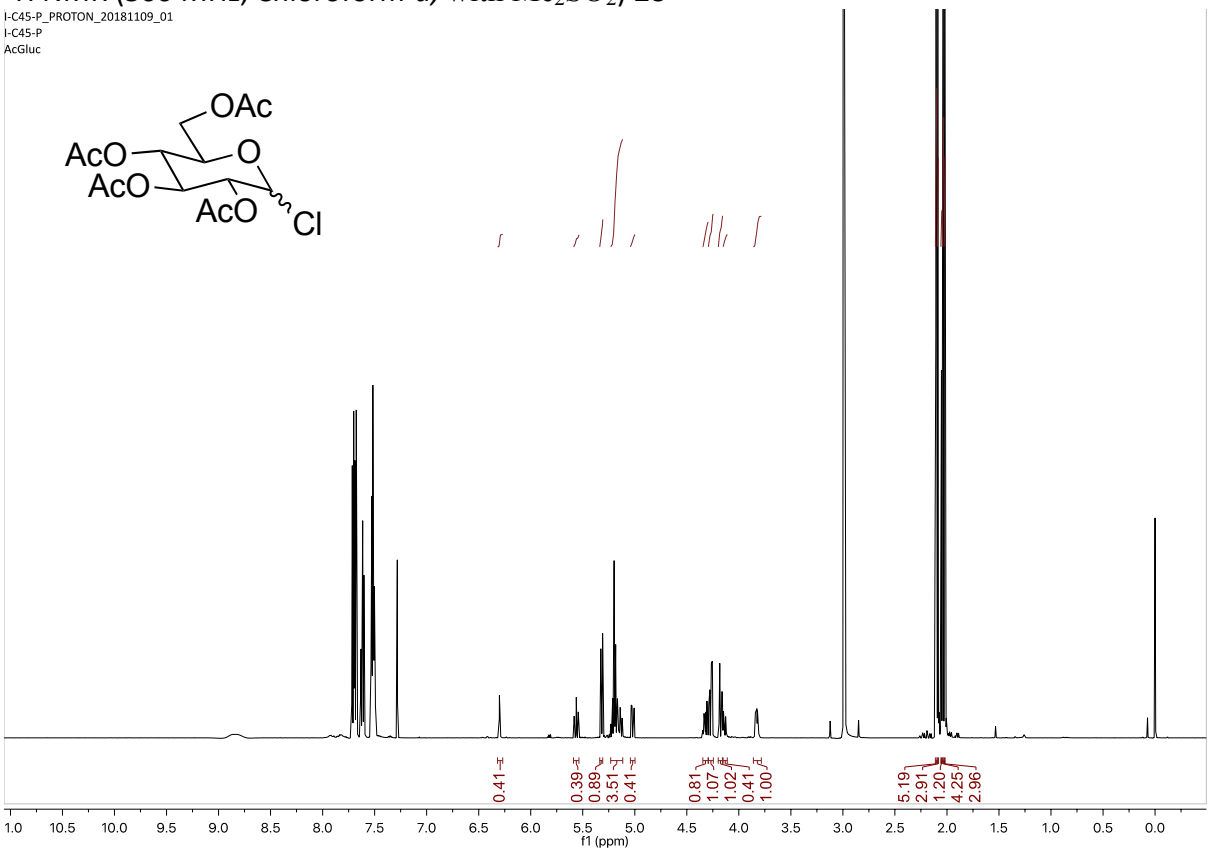
^{1}H NMR (500 MHz, Chloroform-*d*, with Me_2SO_2) **2l**



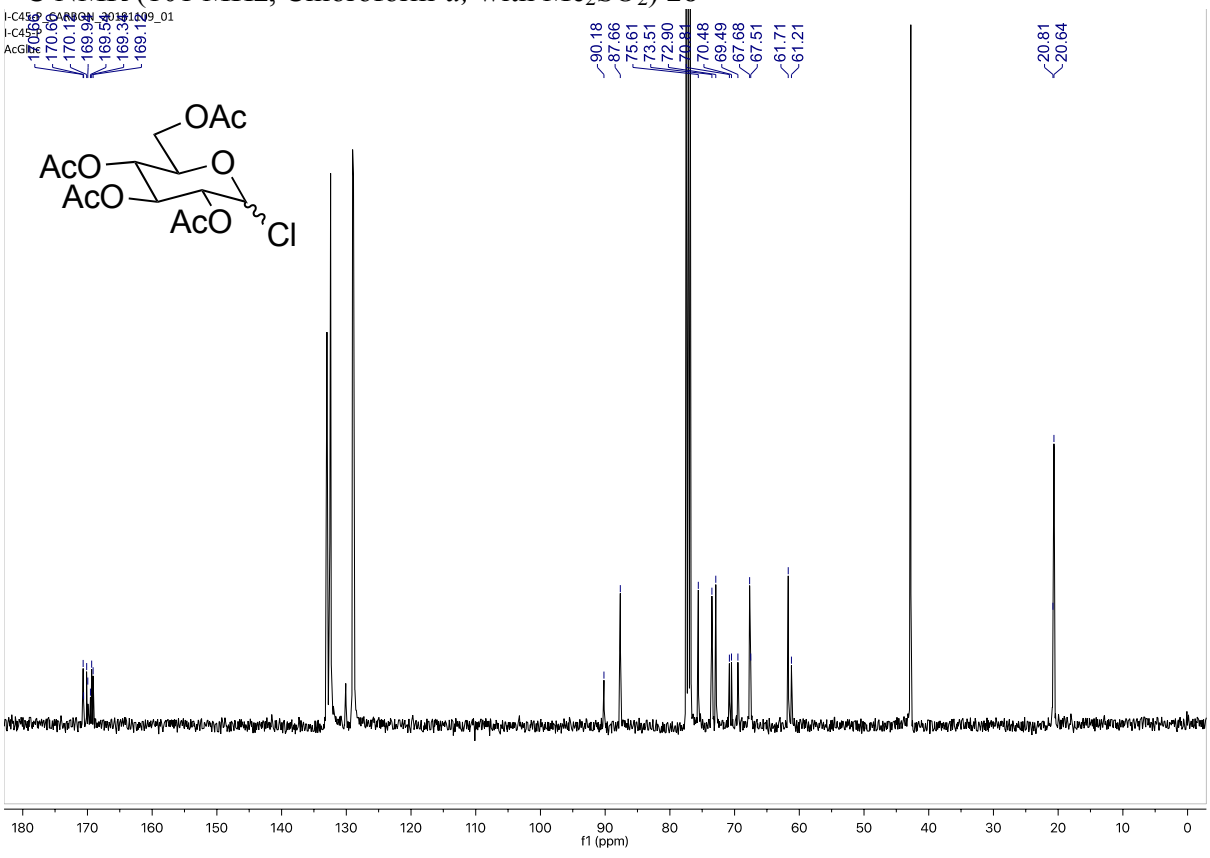
^{13}C NMR (101 MHz, Chloroform-*d*, with Me_2SO_2) **2l**



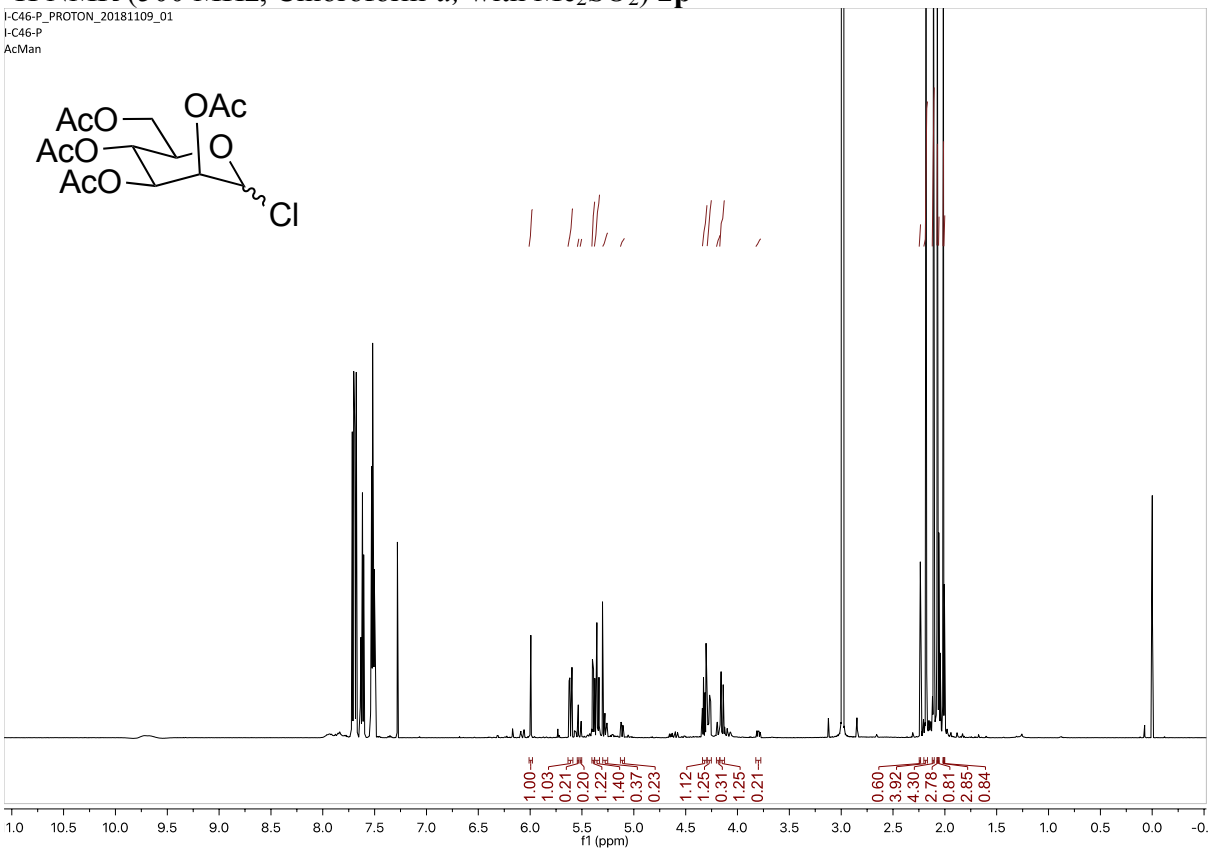
^{1}H NMR (500 MHz, Chloroform-*d*, with Me_2SO_2) **2o**



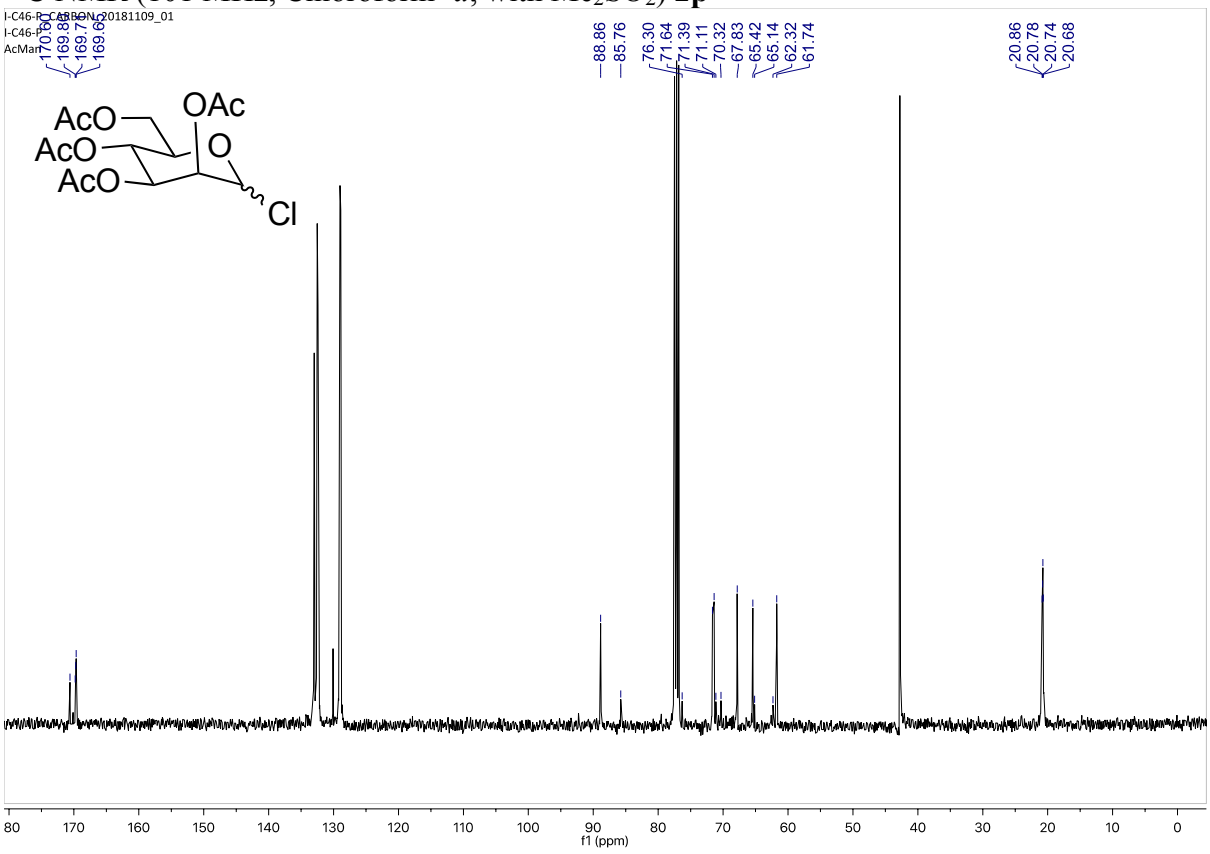
^{13}C NMR (101 MHz, Chloroform-*d*, with Me_2SO_2) **2o**



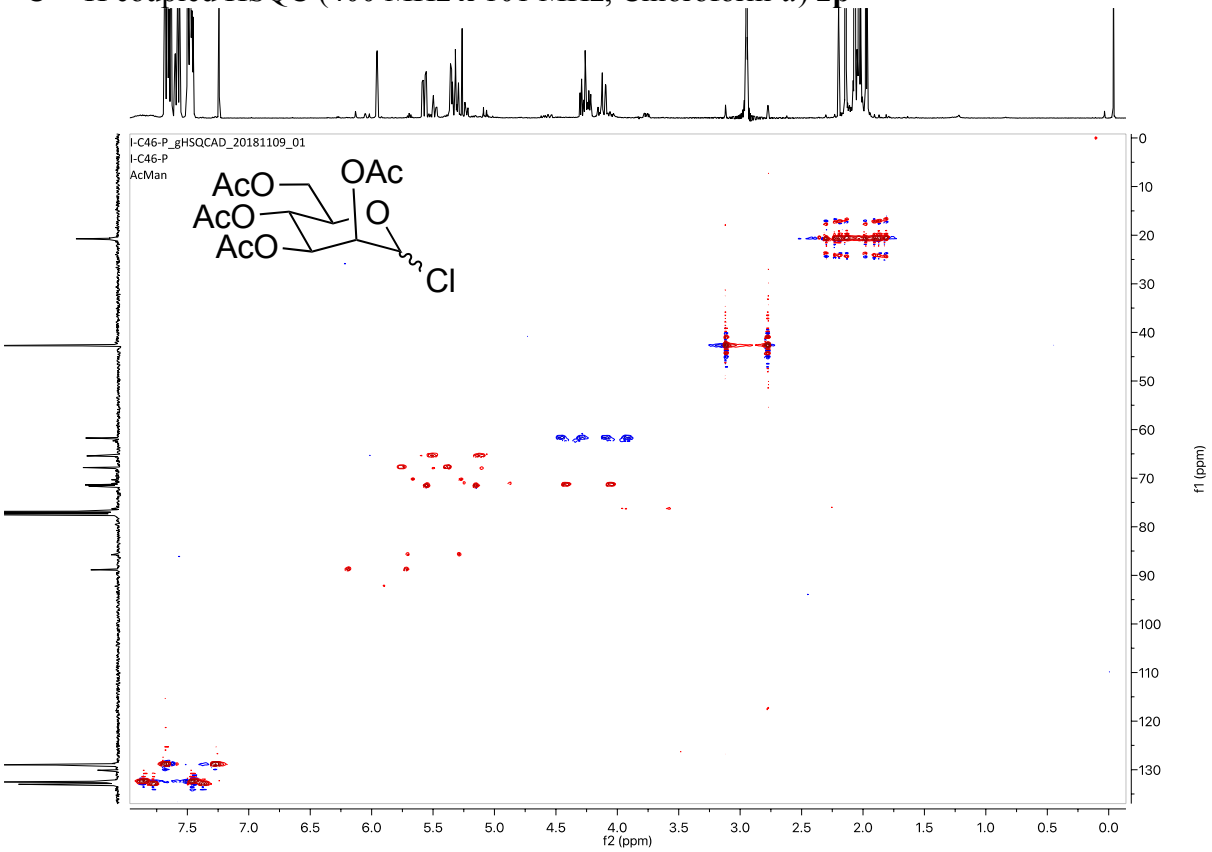
^{1}H NMR (500 MHz, Chloroform-*d,* with Me_2SO_2) **2p**



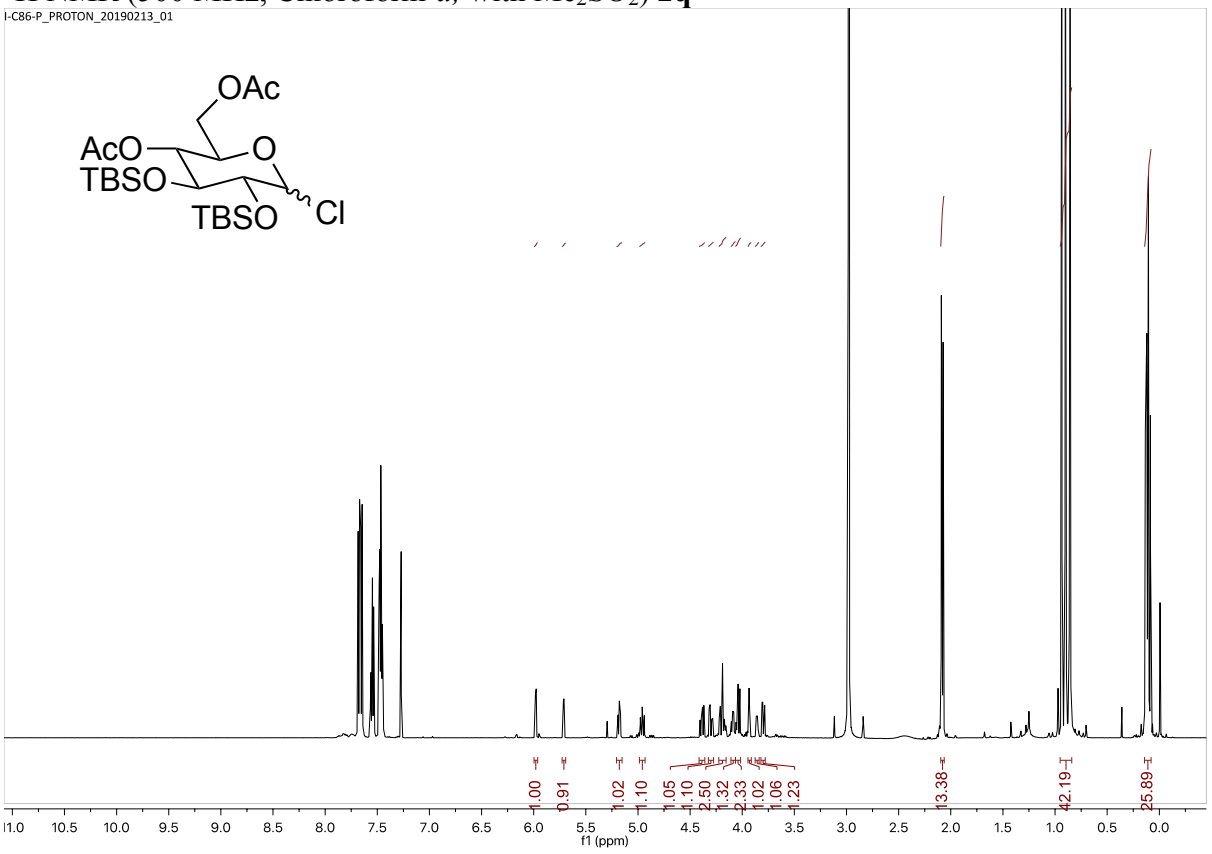
^{13}C NMR (101 MHz, Chloroform- *d*, with Me_2SO_2) **2p**



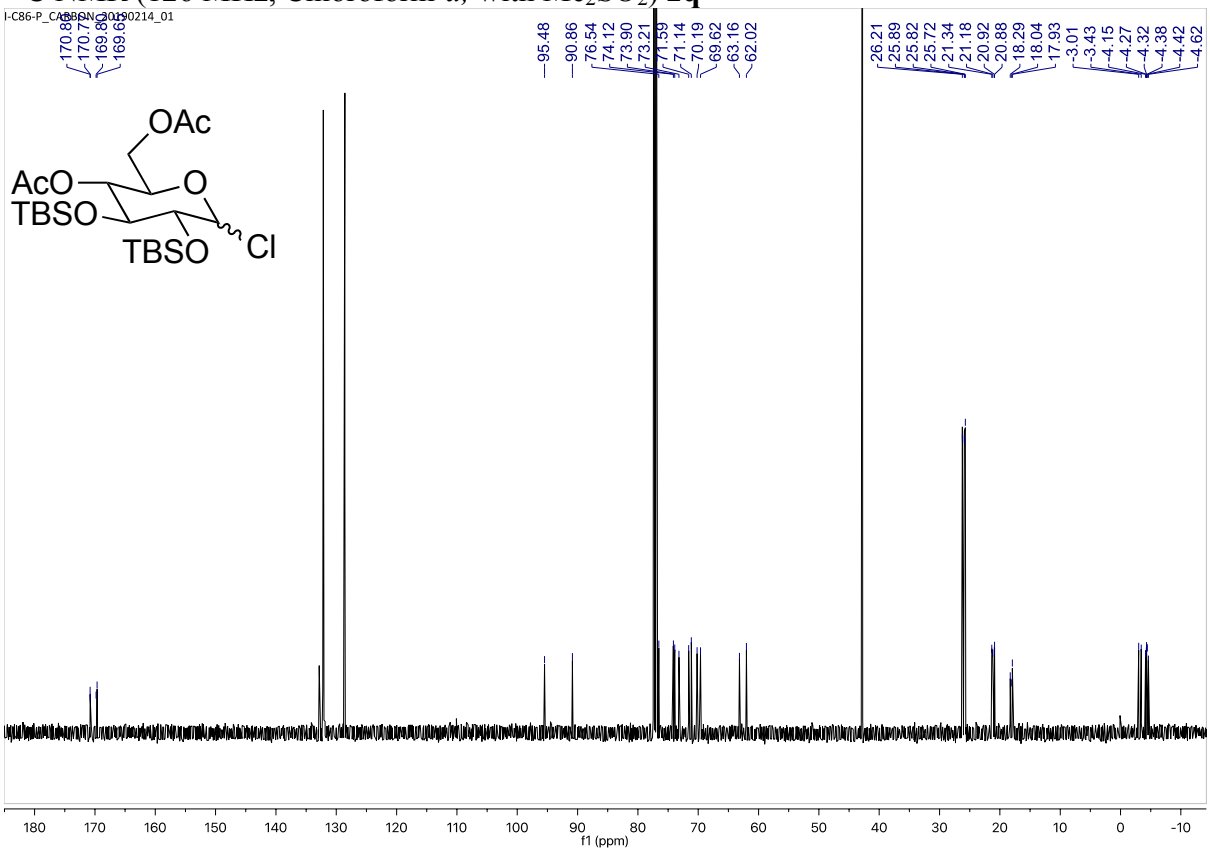
^{13}C - ^{1}H coupled HSQC (400 MHz x 101 MHz, Chloroform-*d*) **2p**



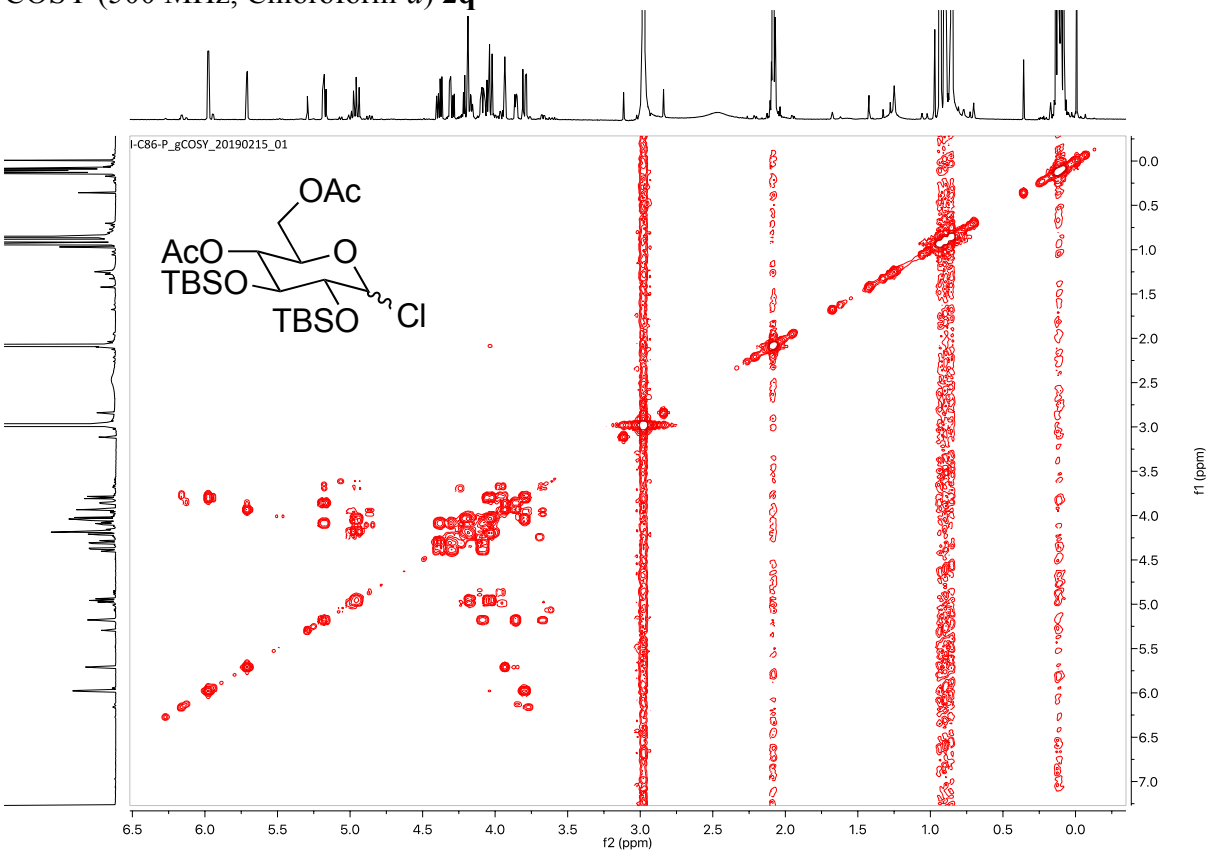
^{1}H NMR (500 MHz, Chloroform-*d,* with Me_2SO_2) **2q**



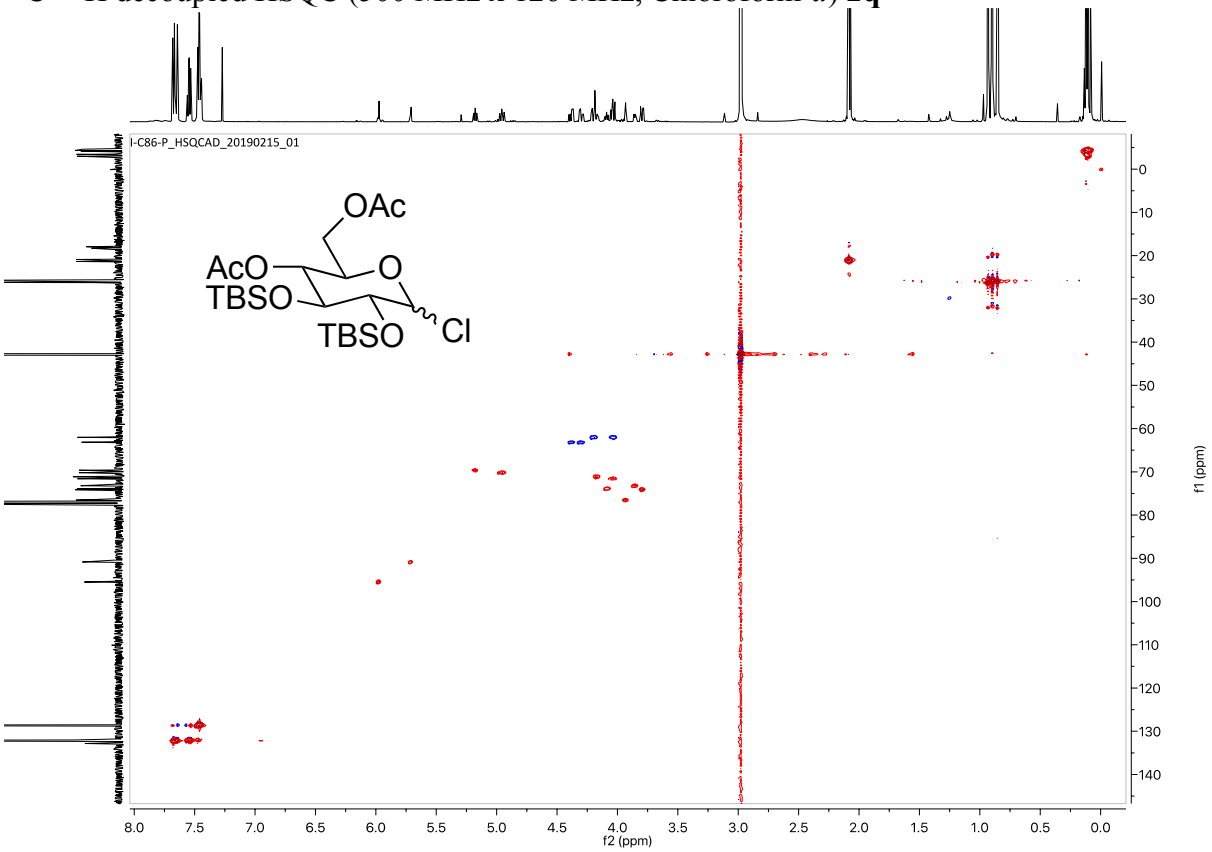
^{13}C NMR (126 MHz, Chloroform-*d,* with Me_2SO_2) **2q**



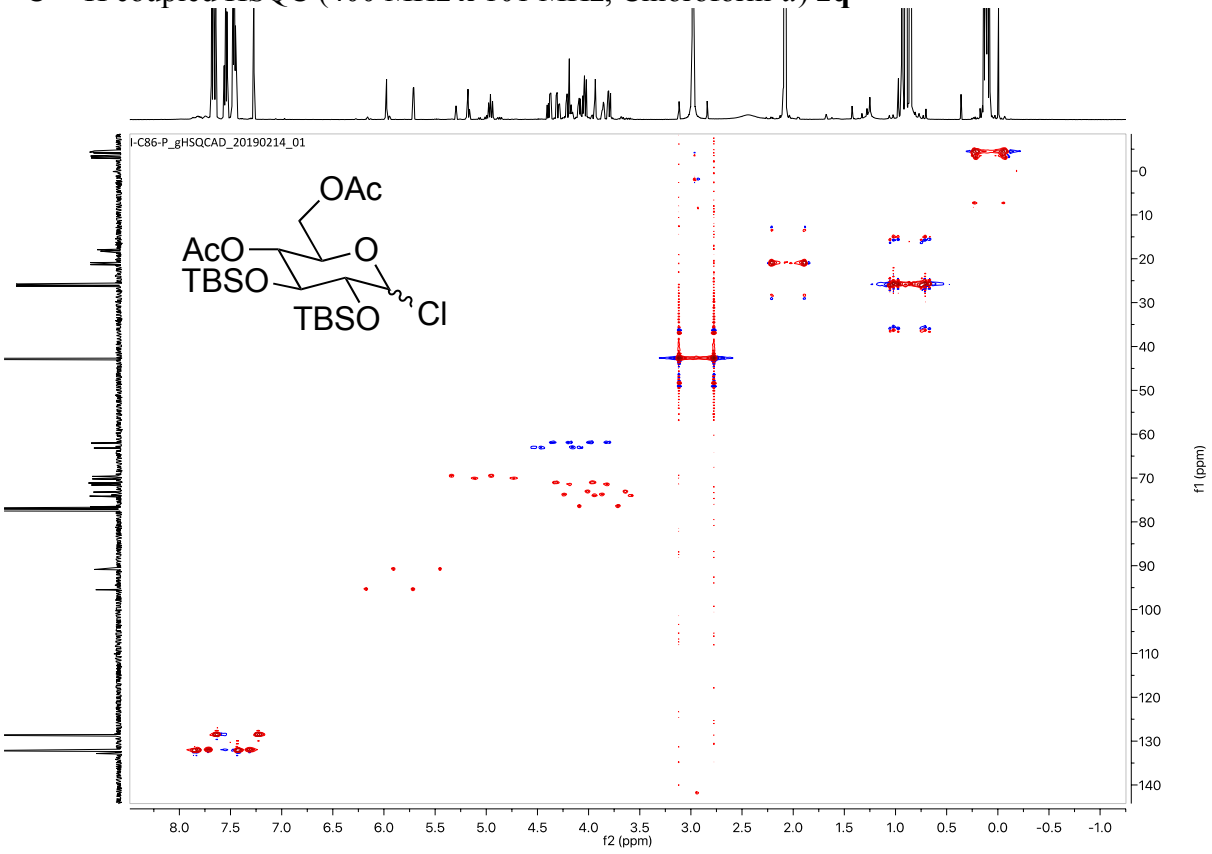
COSY (500 MHz, Chloroform-*d*) **2q**



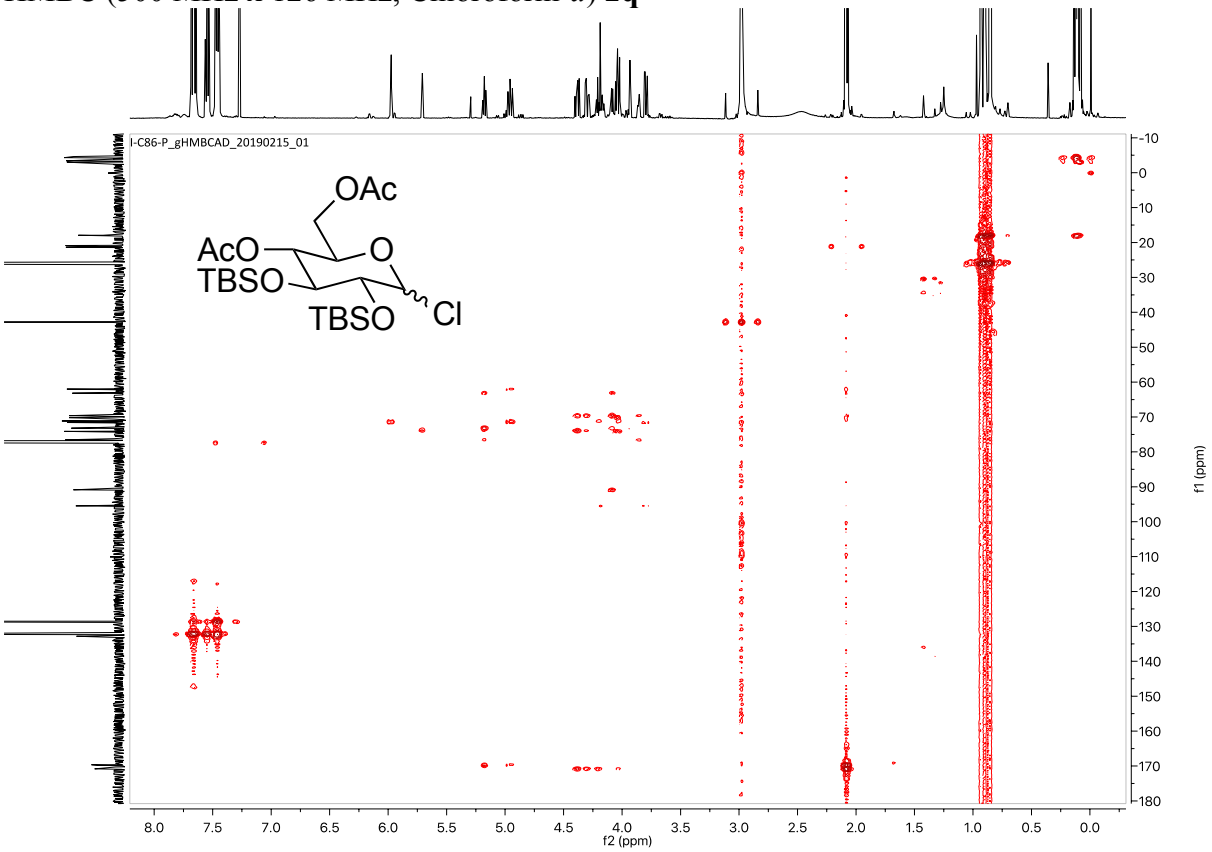
^{13}C - ^{1}H decoupled HSQC (500 MHz x 126 MHz, Chloroform-*d*) **2q**



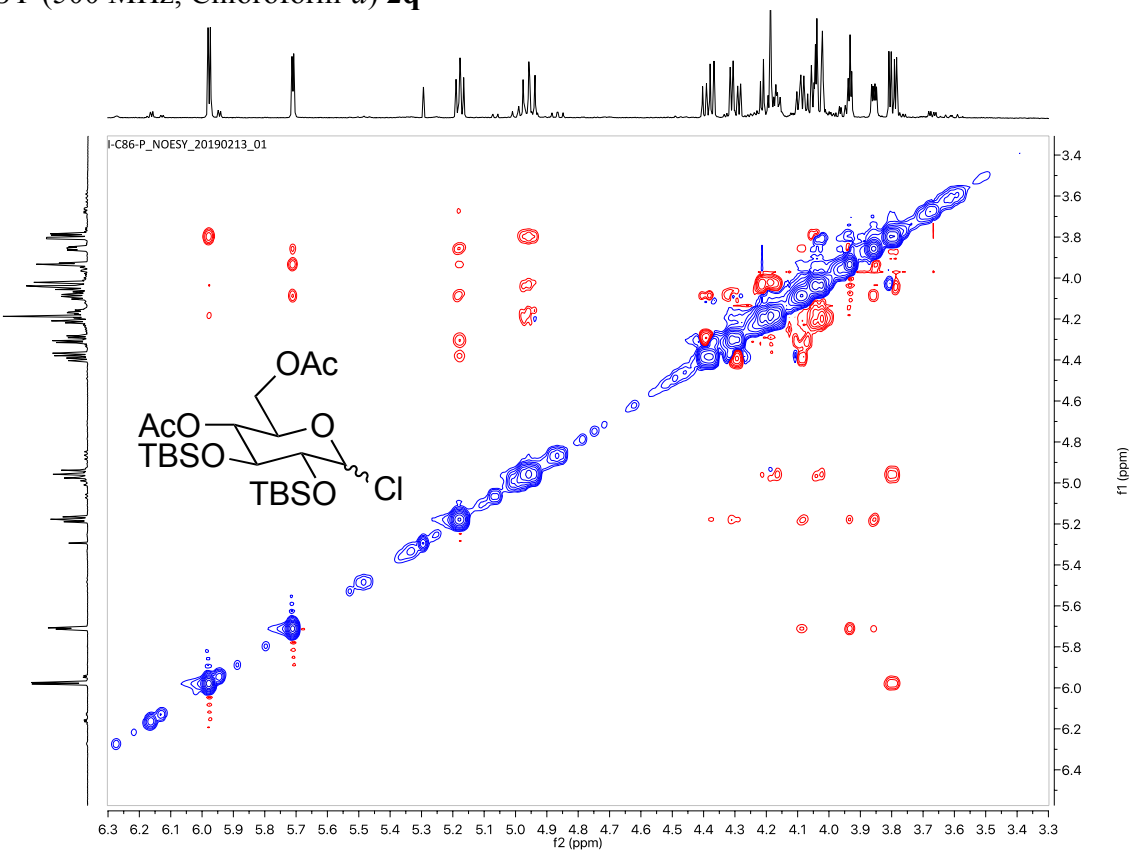
^{13}C - ^{1}H coupled HSQC (400 MHz x 101 MHz, Chloroform-*d*) **2q**



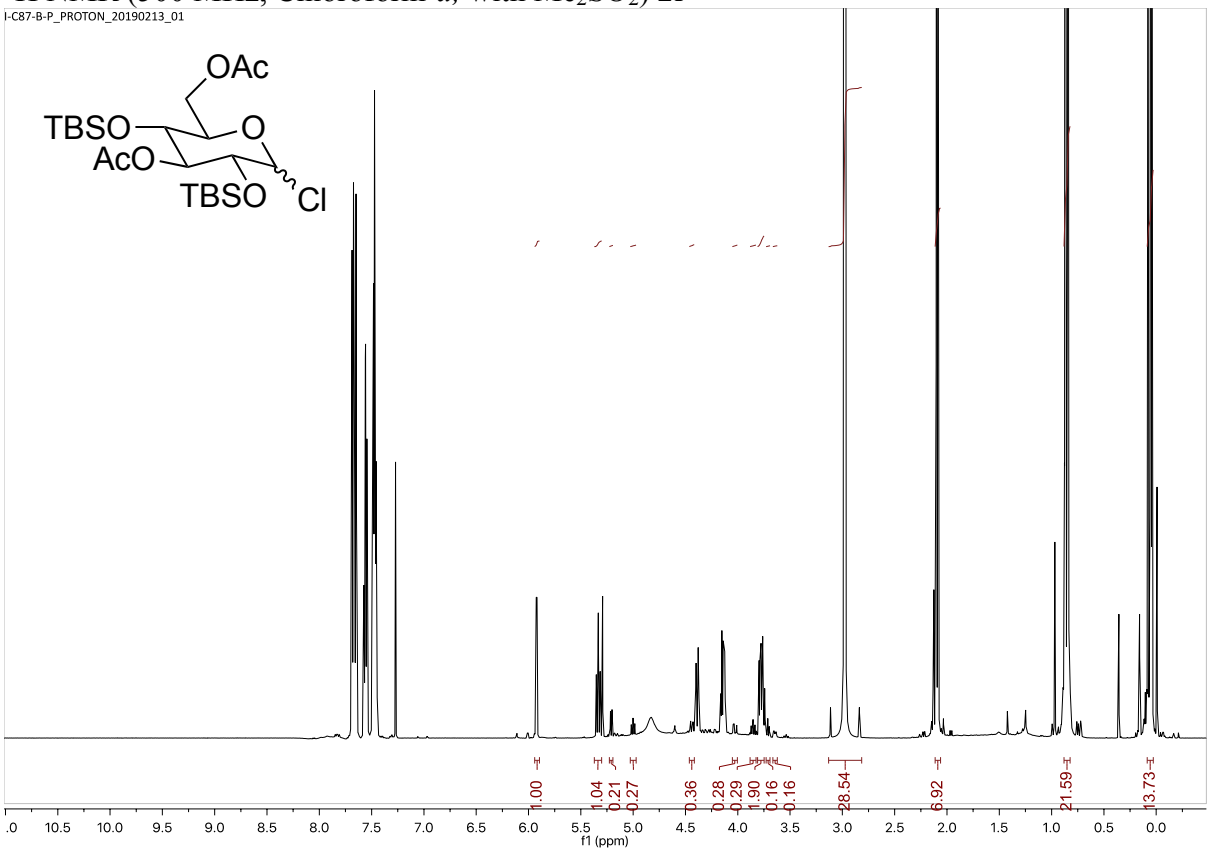
HMBC (500 MHz x 126 MHz, Chloroform-*d*) **2q**



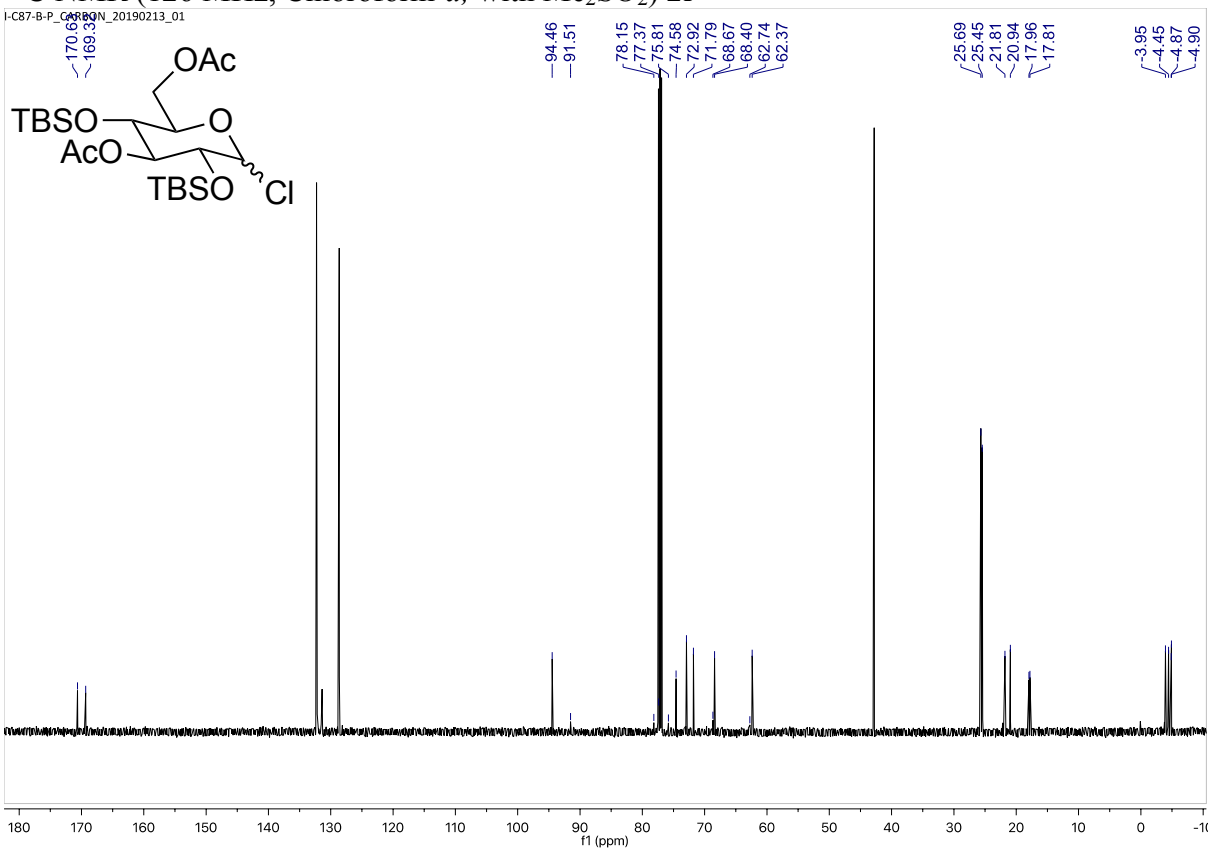
NOESY (500 MHz, Chloroform-*d*) **2q**



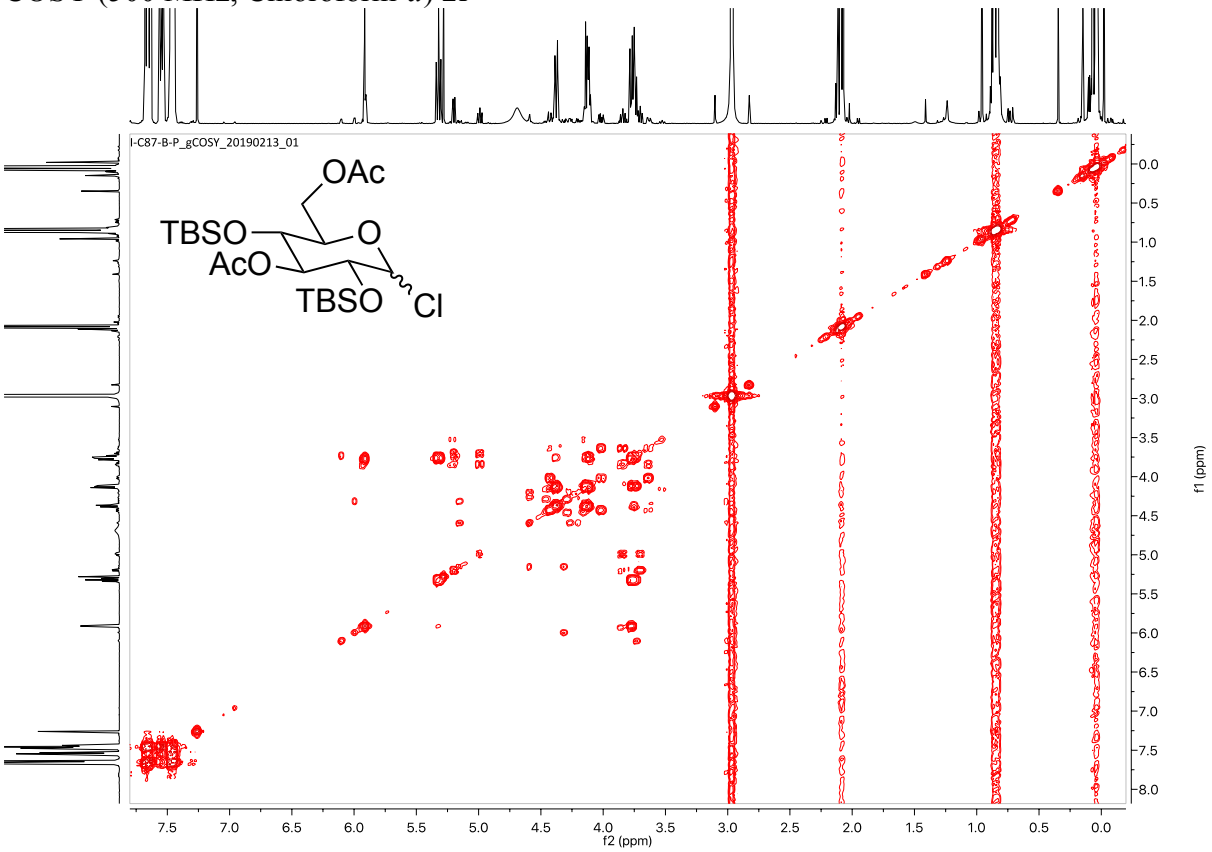
^{1}H NMR (500 MHz, Chloroform-*d,* with Me_2SO_2) **2r**



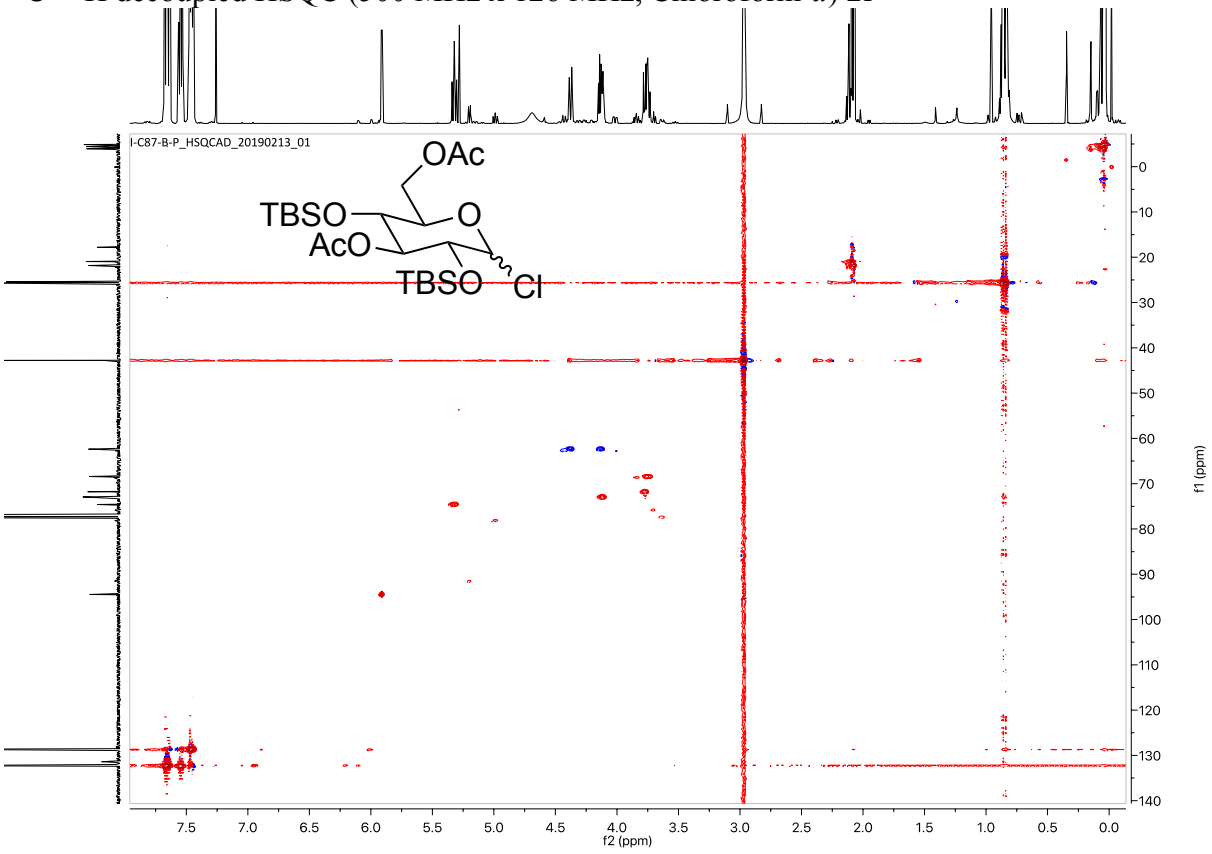
^{13}C NMR (126 MHz, Chloroform-*d,* with Me_2SO_2) **2r**



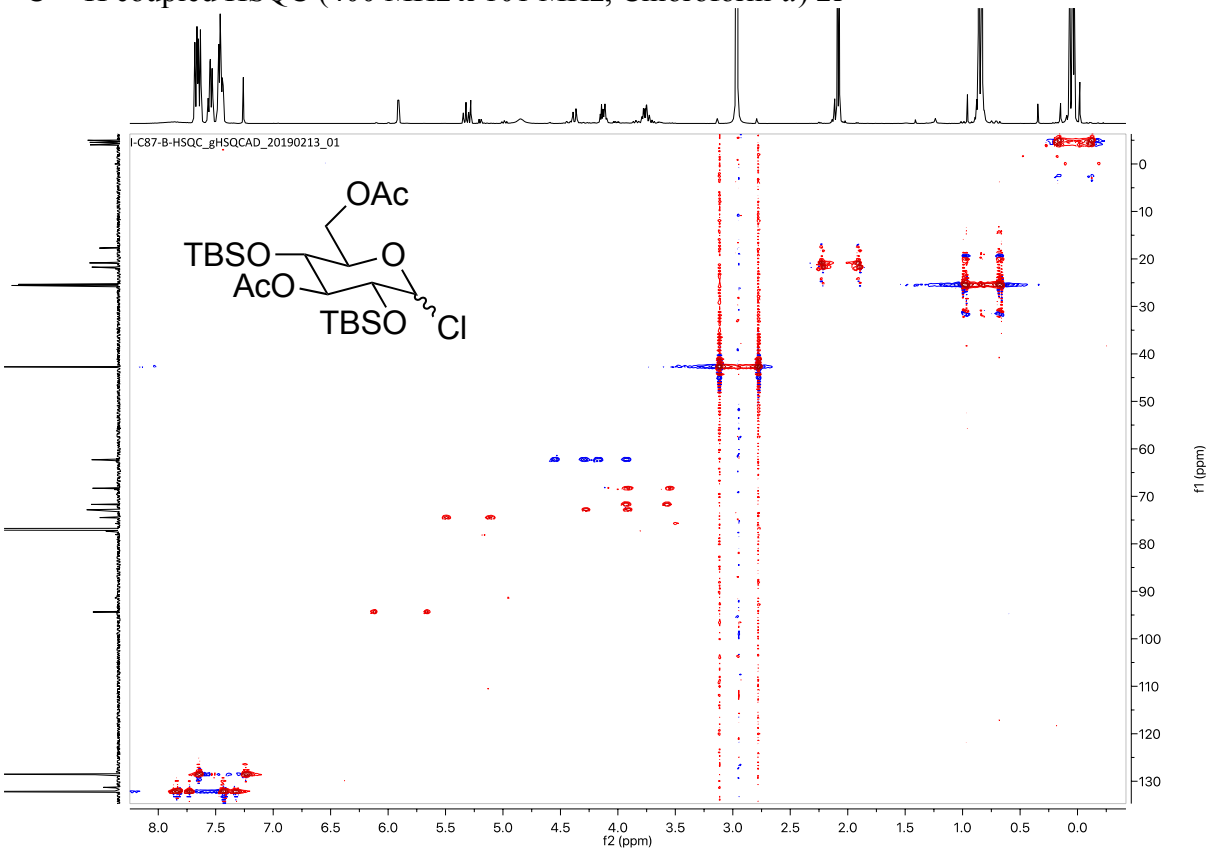
COSY (500 MHz, Chloroform-*d*) **2r**



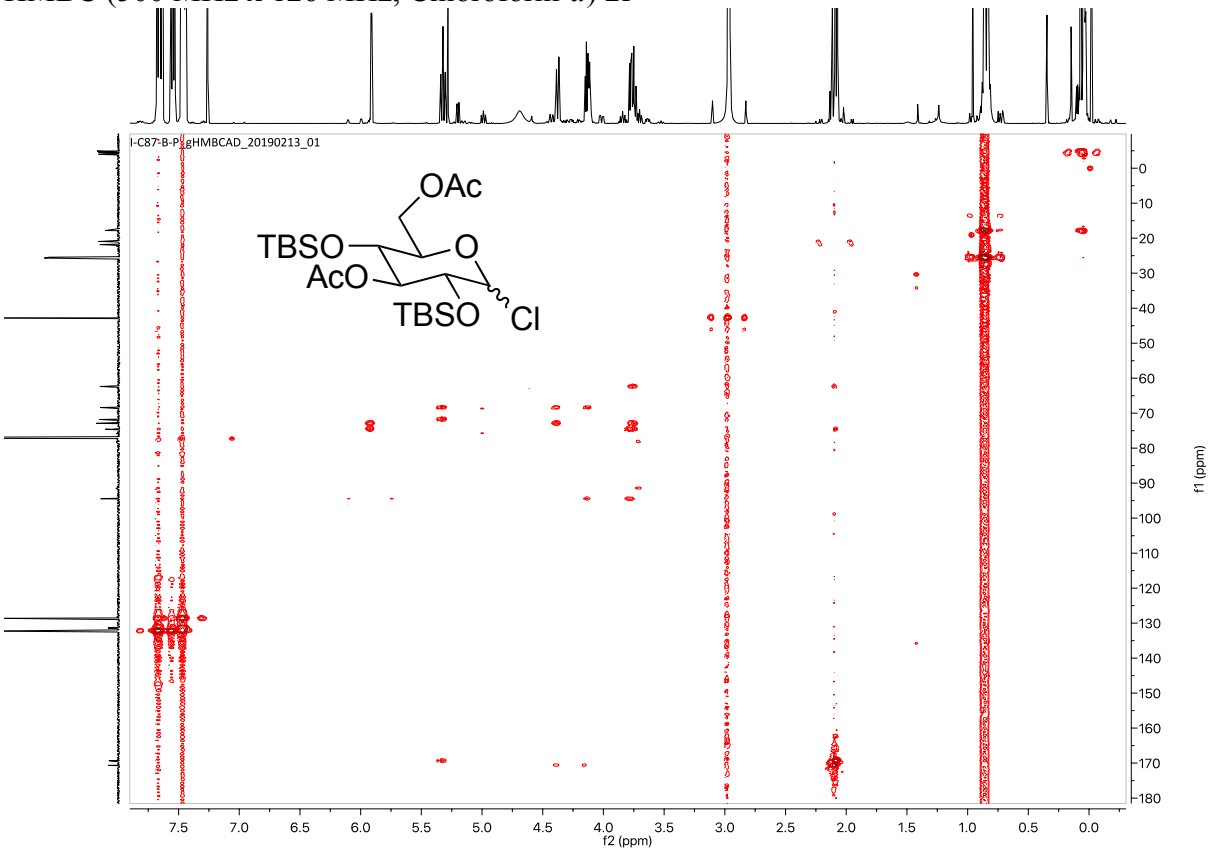
^{13}C - ^{1}H decoupled HSQC (500 MHz x 126 MHz, Chloroform-*d*) **2r**



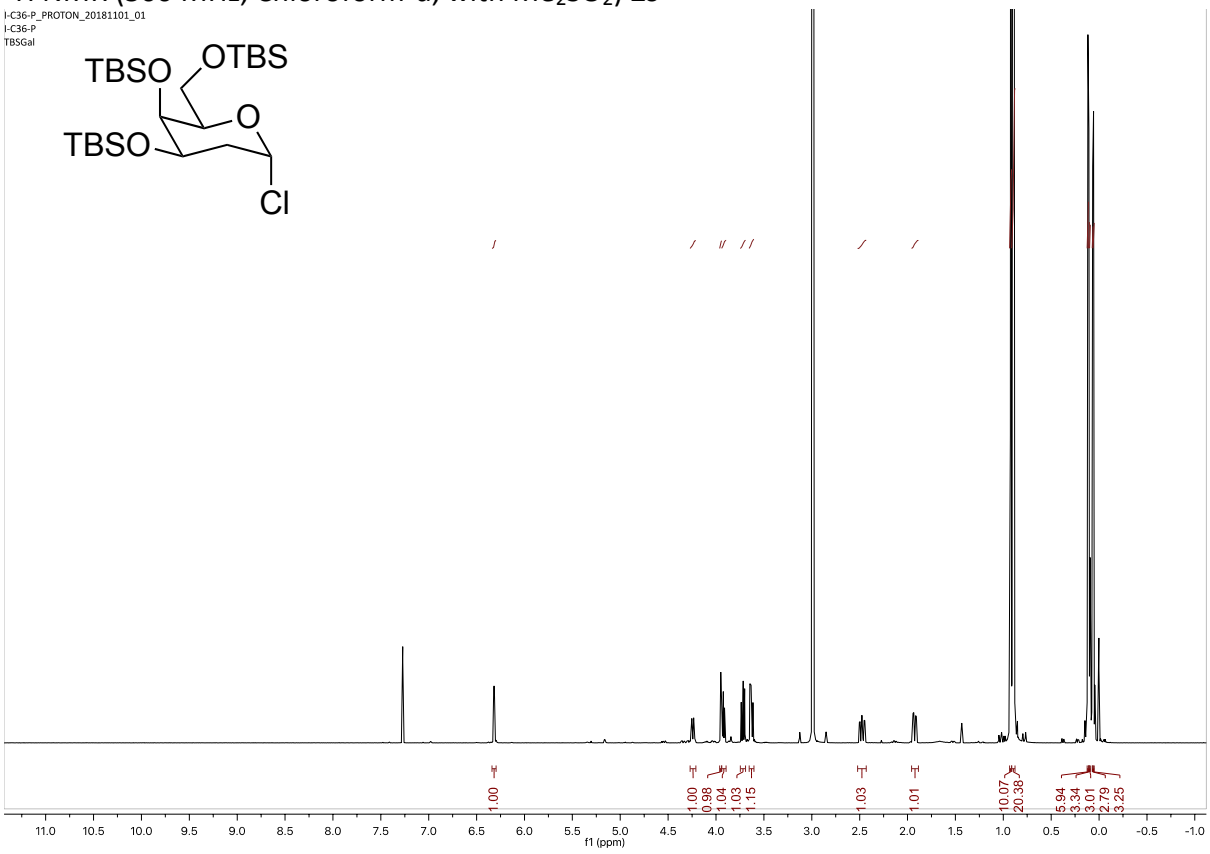
^{13}C - ^{1}H coupled HSQC (400 MHz x 101 MHz, Chloroform-*d*) **2r**



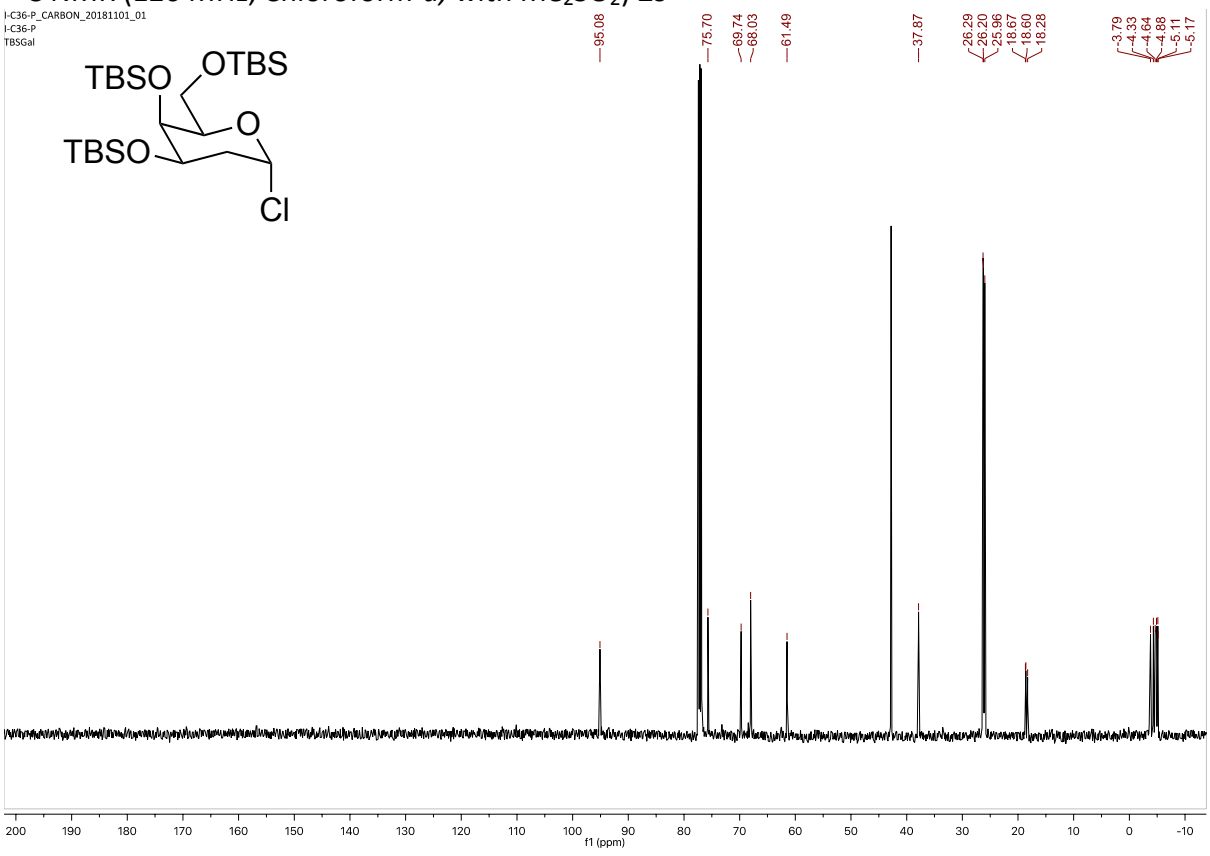
HMBC (500 MHz x 126 MHz, Chloroform-*d*) **2r**



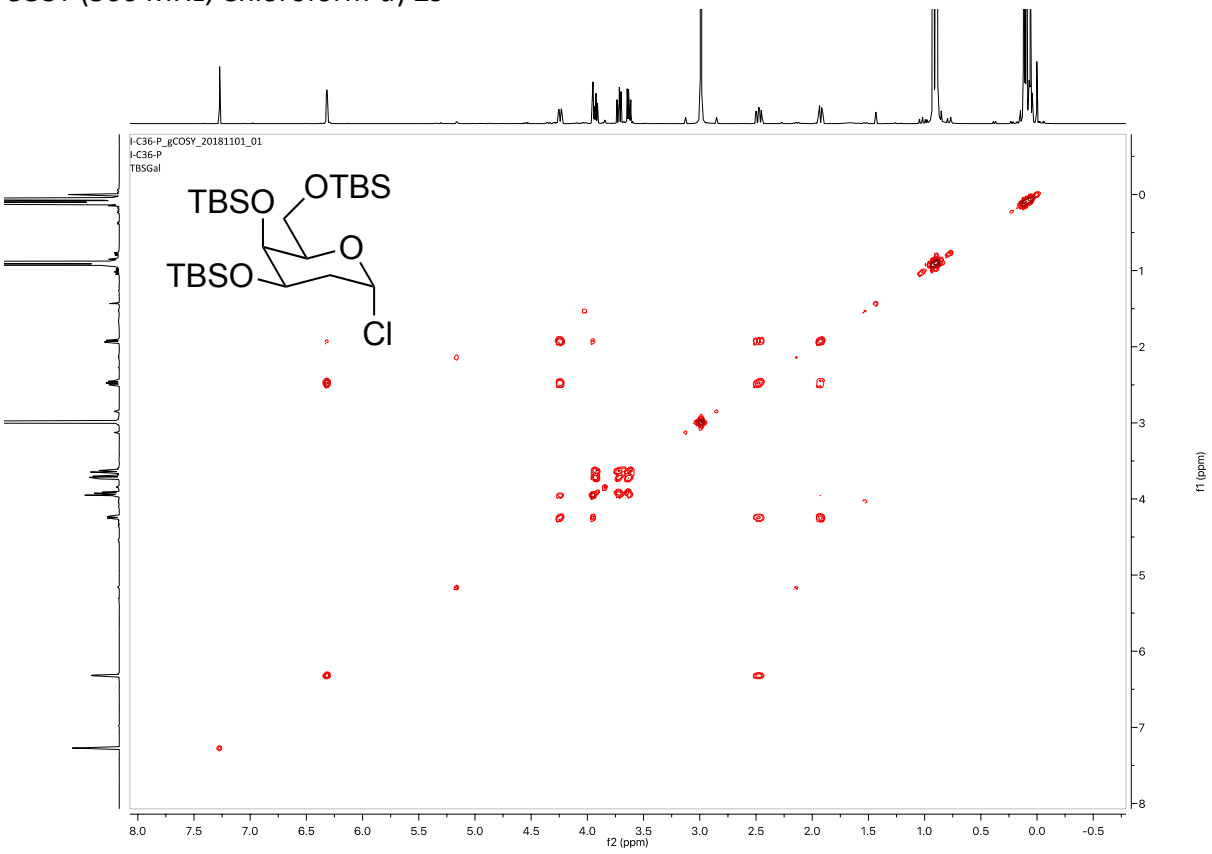
^{1}H NMR (500 MHz, Chloroform-d, with Me_2SO_2) **2s**



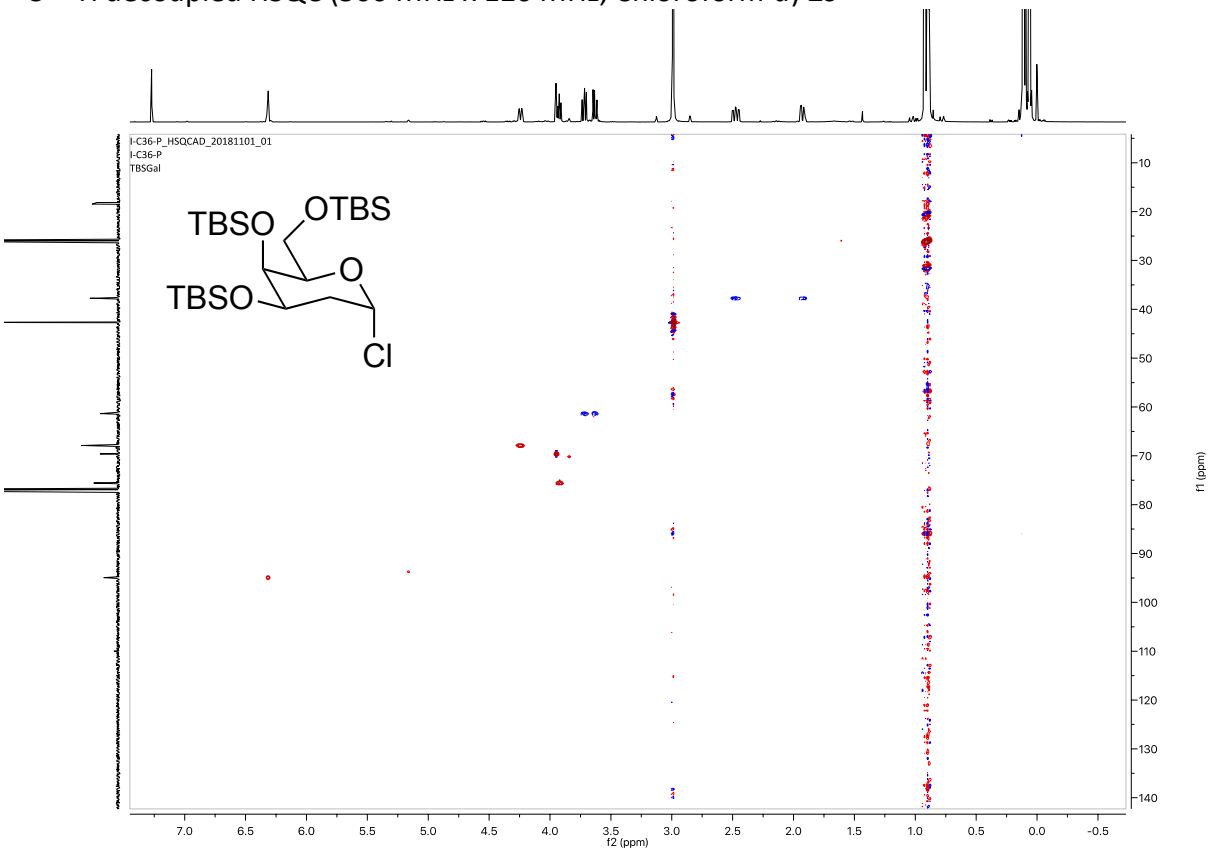
^{13}C NMR (126 MHz, Chloroform-*d,* with Me_2SO_2) **2s**



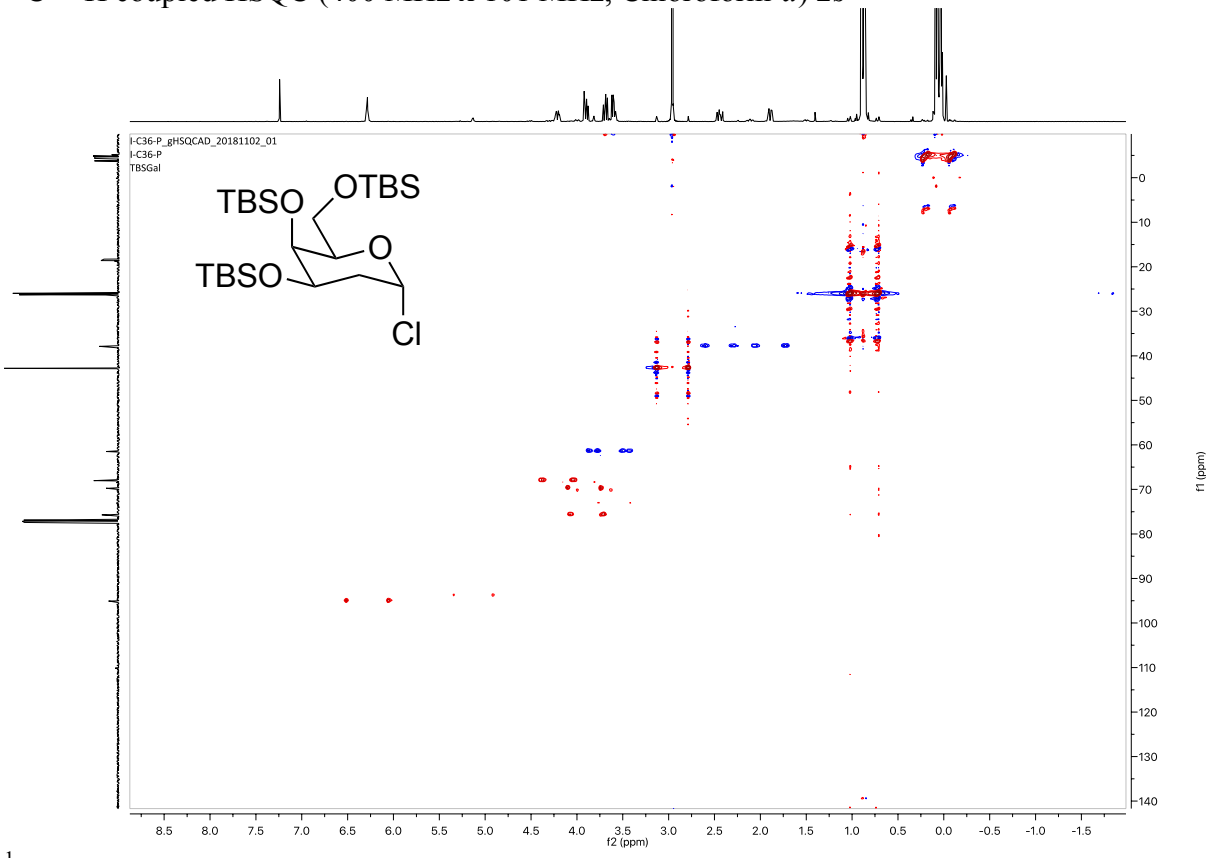
COSY (500 MHz, Chloroform-*d*) **2s**



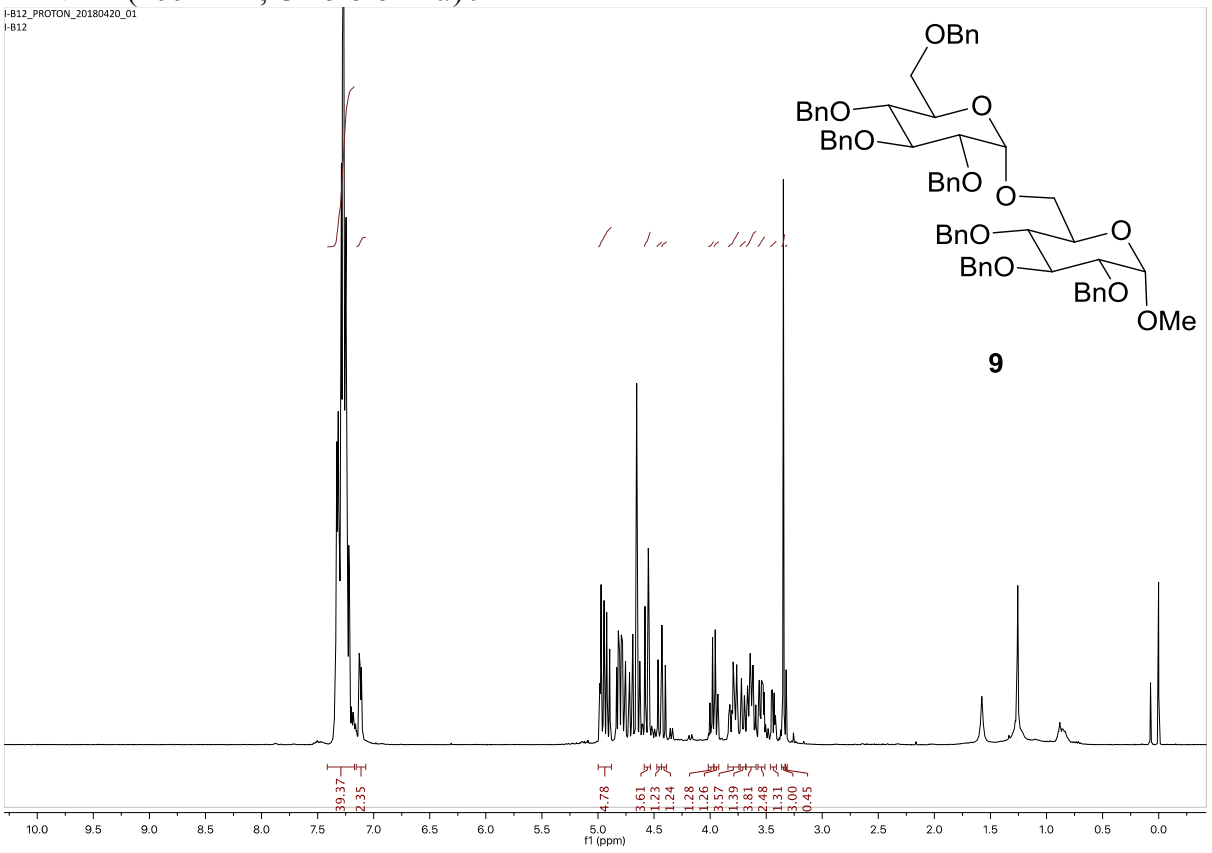
^{13}C - ^{1}H decoupled HSQC (500 MHz x 126 MHz, Chloroform-*d*) **2s**



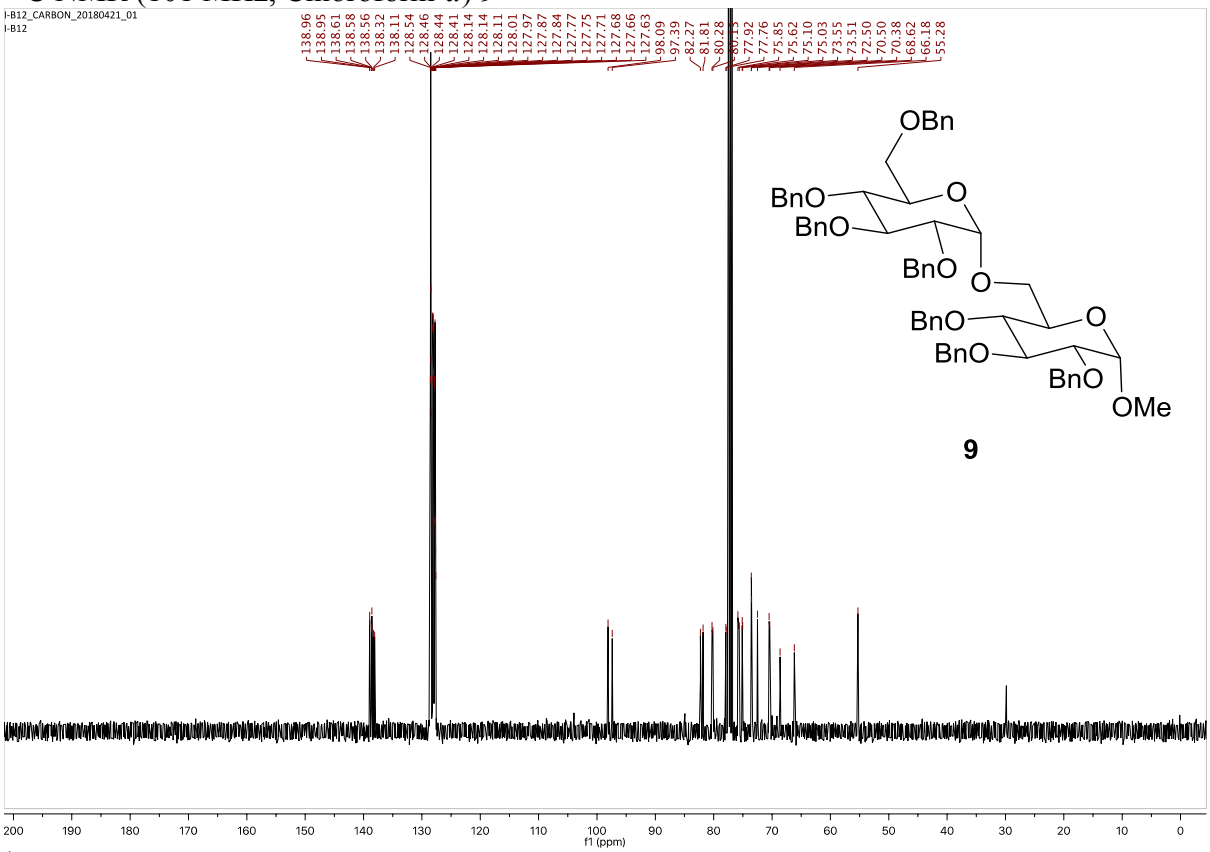
^{13}C - ^{1}H coupled HSQC (400 MHz x 101 MHz, Chloroform-*d*) **2s**



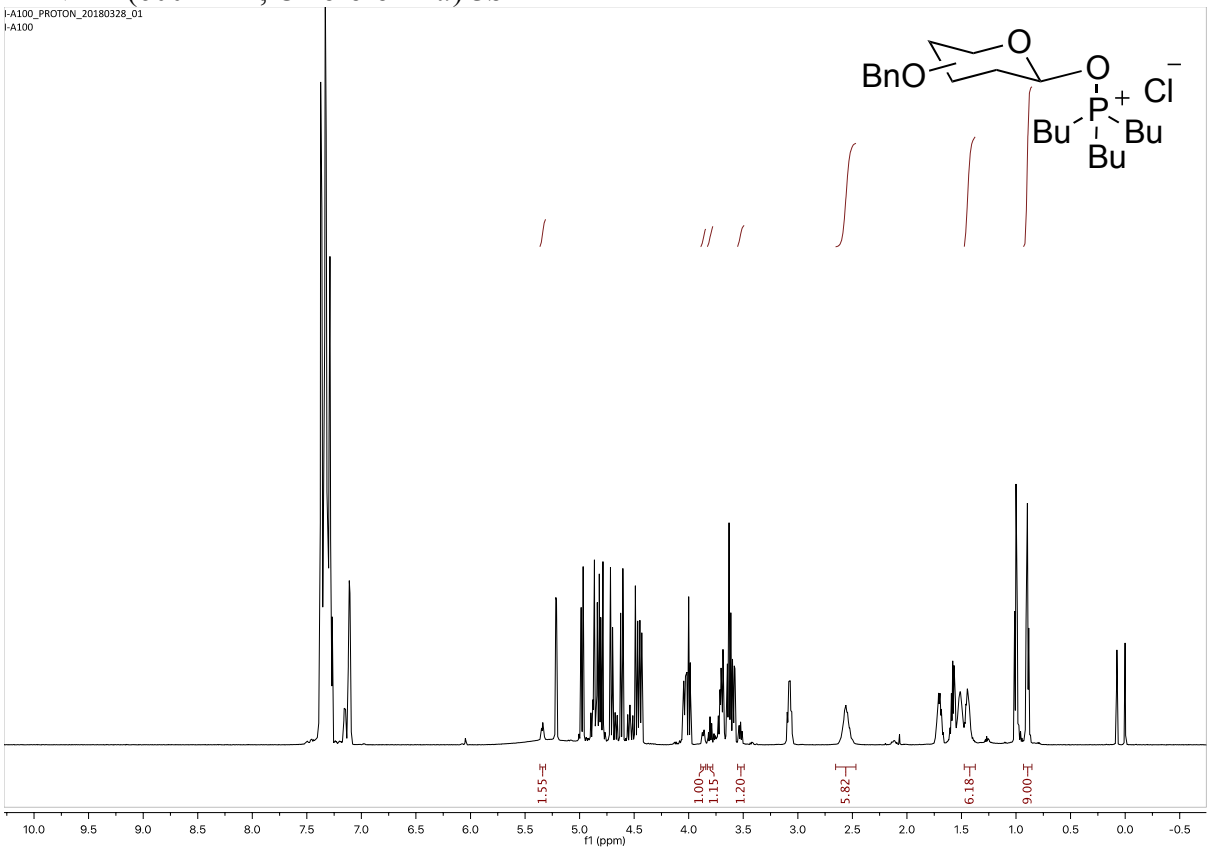
^{1}H NMR (400 MHz, Chloroform-*d*) **9**



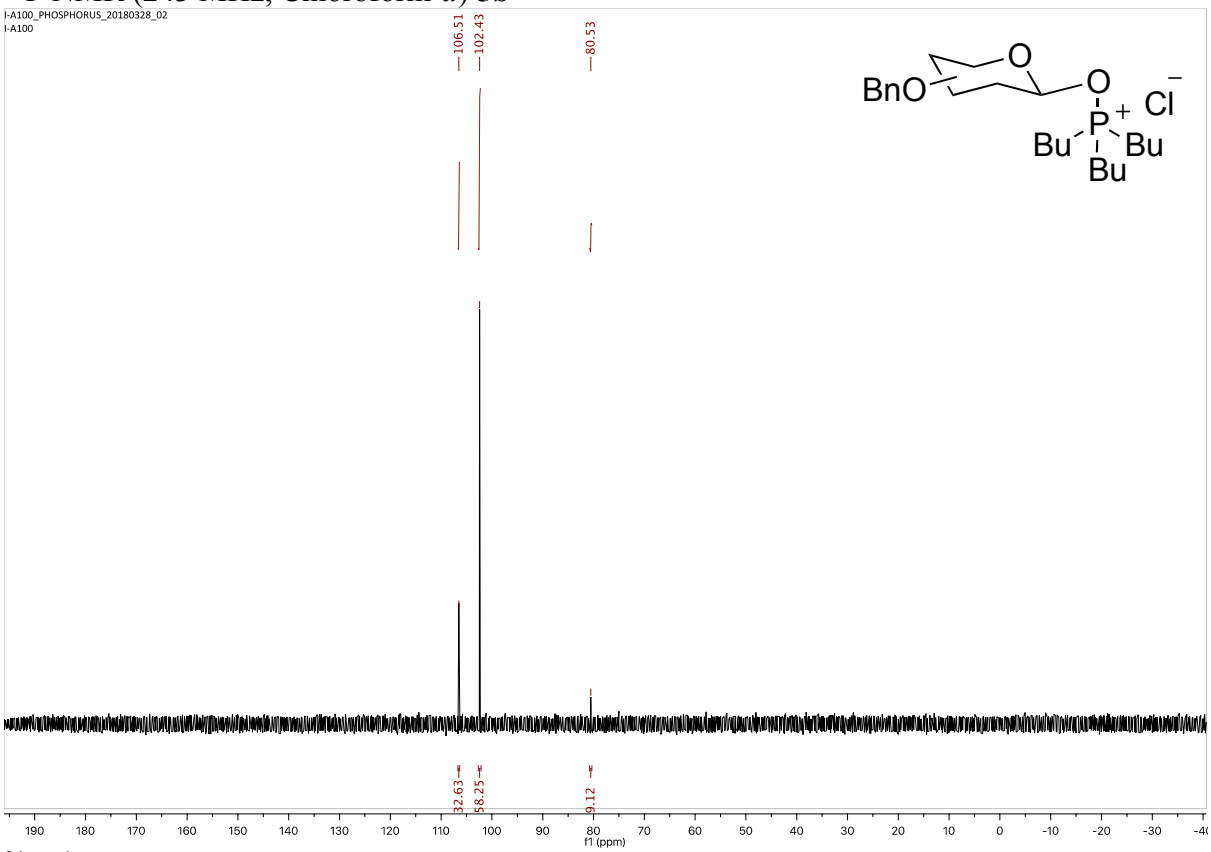
^{13}C NMR (101 MHz, Chloroform-*d*) **9**



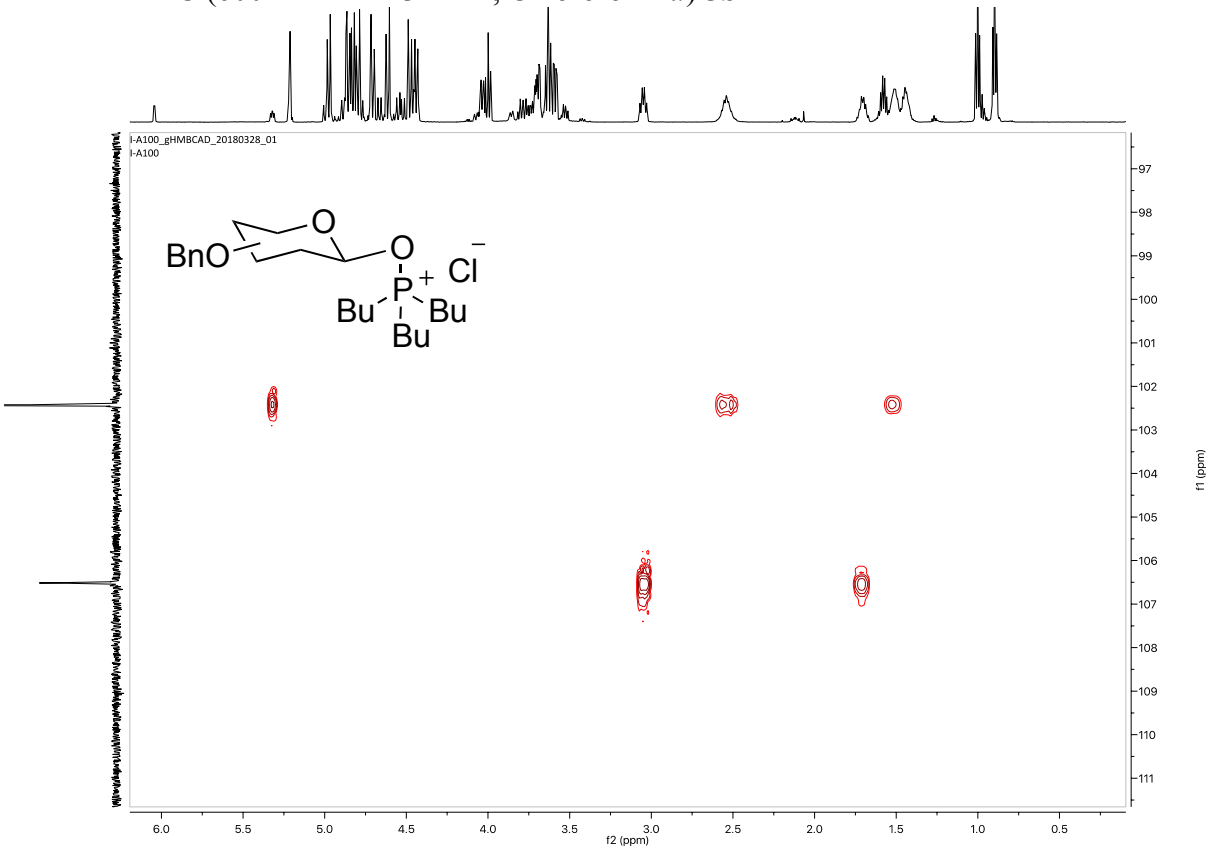
^{1}H NMR (600 MHz, Chloroform-*d*) **5b**



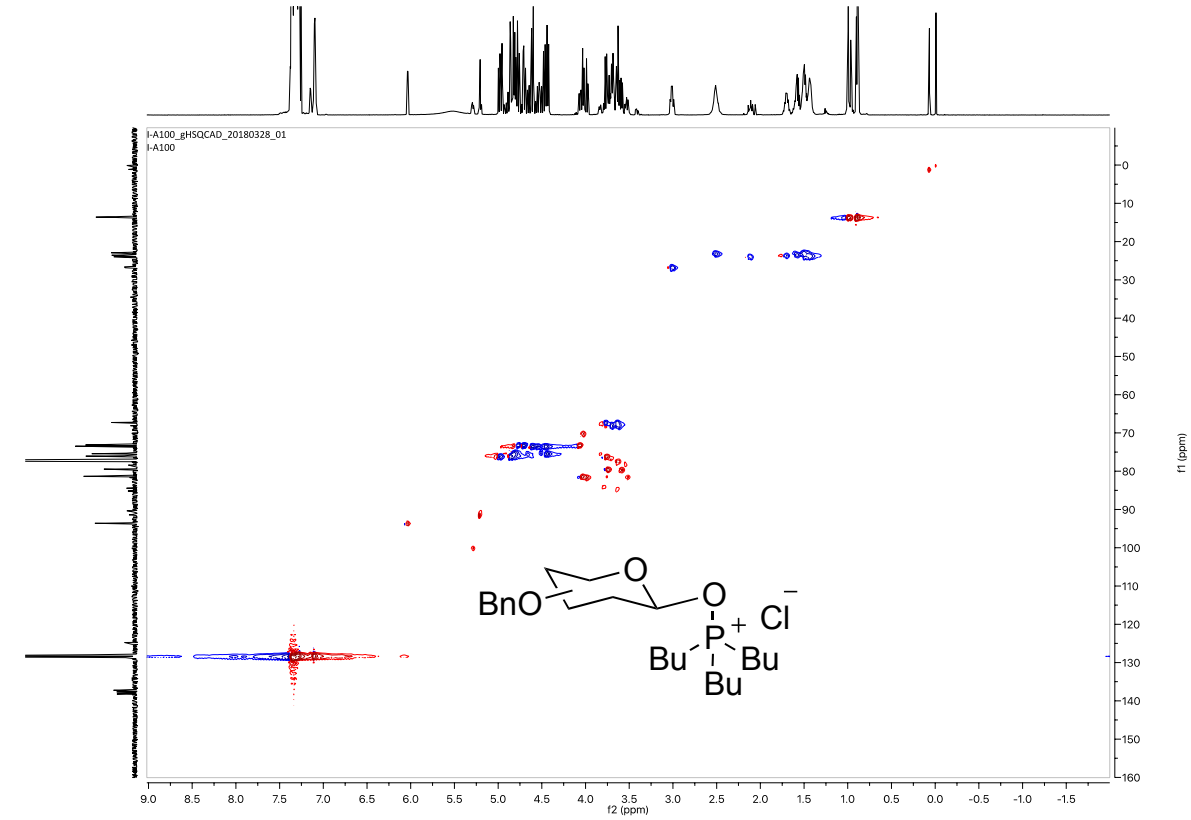
^{31}P NMR (243 MHz, Chloroform-*d*) **5b**



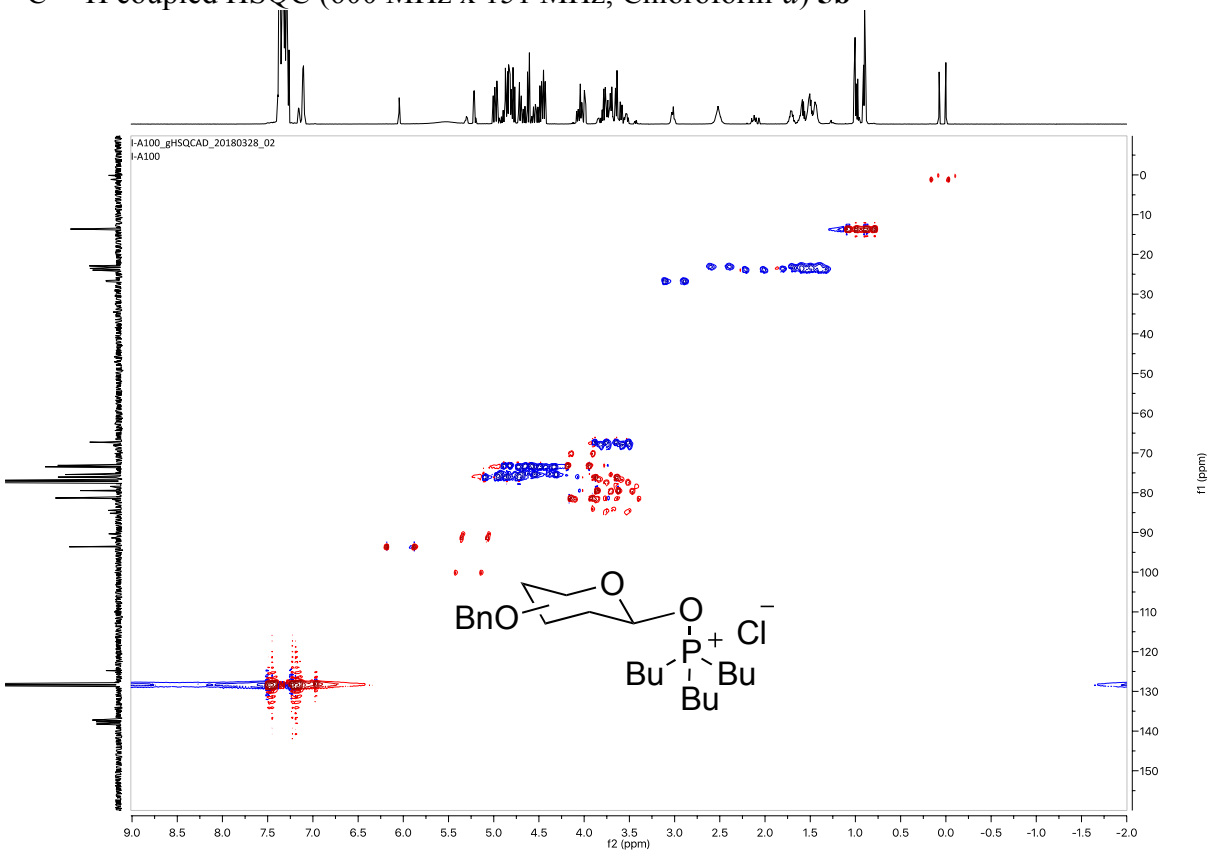
^{31}P- ^{1}H HMBC (600 MHz x 243 MHz, Chloroform-*d*) **5b**



^{13}C - ^{1}H decoupled HSQC (600 MHz x 151 MHz, Chloroform-*d*) **5b**



^{13}C - ^{1}H coupled HSQC (600 MHz x 151 MHz, Chloroform-*d*) **5b**



COSY (600 MHz, Chloroform-*d*) **5b**