Supporting Information

Ionic Catch and Release Oligosaccharide Synthesis (ICROS)

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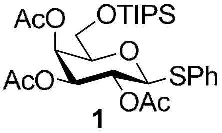
Content

Experimental Procedures:

General glycosylation reactions:

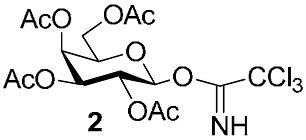
Experimental Procedures

General. Chemicals were purchased from Aldrich and Fluka and used without further purification. Preactivated molecular sieves kept in an oven at 150 °C were activated in a standard Microwave (800 W) for 3 minutes (3 x 1 minute) and cooled under vacuum. Dry solvents were obtained by distillation using standard procedures or by passage through a column of anhydrous alumina using equipment from Anhydrous Engineering (University of Bristol) based on the Grubbs' design. Reactions requiring anhydrous conditions were performed under nitrogen; glassware and needles were either flame dried immediately prior to use or placed in an oven (150 °C) for at least 2 hours and allowed to cool either in a desiccators or under reduced pressure; liquid reagents, solutions or solvents were added *via* syringe or cannula through rubber septa; solid reagents were added *via* Schlenk type adapters. Reactions were monitored by TLC on Kieselgel 60 F254 (Merck) and by MALDI-TOF in case with Itag compounds. Detection was by examination under UV light (254 nm) and by charring with 10% sulfuric acid in ethanol. Flash column chromatography was performed using silica gel [Merck, 230−400 mesh (40−63 µm)]. Extracts were concentrated under reduced pressure using both a Büchi rotary evaporator (bath temperatures up to 40 °C) at a pressure of either 15 mmHg (diaphragm pump) or 0.1 mmHg (oil pump), as appropriate, and a high vacuum line at room temperature. ^{1}H NMR and ^{13}C NMR spectra were measured in the solvent stated at 400 or 500 Hz using Varian *INOVA* instruments. Chemical shifts are quoted in parts per million from $SiMe_4$ and coupling constants (*J*) given in Hertz. Multiplicities are abbreviated as: b (broad), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or combinations thereof. Positive ion Matrix Assisted Laser Desorption Ionization Time-Of-Flight (MALDI-TOF) mass spectra were recorded using an HP-MALDI instrument using gentisic acid matrix. Elemental analysis was performed by the University of Bristol Microanalysis Service.



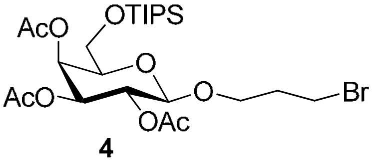
1

***Phenyl 2,3,4-tri-O-acetyl-6-O-triisopropylsilyl-1-thio-β-D-galactopyranoside* (1)** Synthesized following reported procedures. Spectroscopic data in agreement with reported literature.[1]



2

***2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl trichloroacetimidate* (2)** Synthesized following reported procedures. Spectroscopic data in agreement with reported literature. [2]



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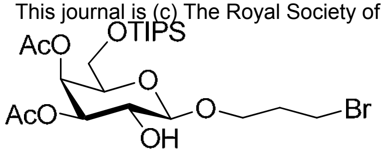
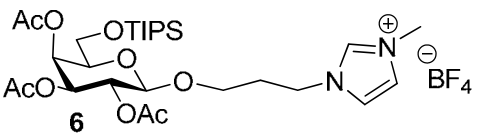


5

3-bromopropyl 2,3,4-tri-O-acetyl-6-O-triisopropylsilyl-β-D-galactopyranoside (**4**) **and** ***3-bromopropyl 3,4-di-O-acetyl-6-O-triisopropylsilyl-β-D-galactopyranoside*** (**5**). To a solution of **1** (300 mg, 0.541 mmol) in dry CH_2Cl_2 (15mL) was added activated 4 Å molecular sieves, *N*-iodosuccinimide (243 mg, 0.443 mmol, 2 equiv.), 3-bromopropanol (196 μL, 2.2 mmol), and TMSOTf (49 μL, 0.27 mmol) After stirring at -78 ºC and warming to -40 ° C over a 2 hour period the reaction mixture was quenched with triethylamine (3 mL). The reaction mixture was then filtered, concentrated *in vacuo*, and the residue purified by silica gel flash column chromatography, with 9:1 hexanes/ethyl acetate as the eluent, to afford **5** as a colourless oil (130 mg, 41%) and **6** as a colourless oil (121 mg, 41%).

Compound **4**: ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) : δ = 5.52 (d, 1H, $J_{4,3}$ = 3.5 Hz, H-4), 5.19 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 10.5 Hz, H-2), 5.05 (dd, 1H, $J_{3,4}$ = 3.0 Hz, $J_{3,2}$ = 10.5 Hz, H-3), 4.48 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.05-3.98 (m, 1H, $OC\underline{H}_2$), 3.84-3.74 (2H, m, $OC\underline{H}_2$, H-6a), 3.66 (dd, 1H, $J_{6b,5}$ = 4.5 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6b), 3.58-3.53 (m, 1H, H-5), 3.51-3.48 (m, 2H, $C\underline{H}_2Br$),2.23-1.99 (m, 11H in which 2.11 (s, 3H, $C\underline{H}_3$ *Ac*), 2.06 (s, 3H, $C\underline{H}_3$ *Ac*), 1.97 (s, 3H, $C\underline{H}_3$ *Ac*), $OCH_2C\underline{H}_2$) 1.11-0.97 (m, 21H, *TIPS*) ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) : δ = 170.1, 169.9, 169.6 (CO), 101.5 (C-1), 73.6 (C-5), 71.2 (C-3), 69.2 (C-2), 67.2 ($O\underline{C}H_2$), 67.0 (C-4), 60.9 (C-6), 32.2 ($OCH_2\underline{C}H_2$), 30.2 ($\underline{C}H_2Br$), 20.8 ($\underline{C}H_3$ *Ac*), 20.7 ($\underline{C}H_3$ *Ac*), 20.6 ($\underline{C}H_3$ *Ac*), 17.83, 11.8 (*TIPS*). ESI-HRMS for $C_{24}H_{43}BrNaO_9Si^+$ (MNa^+) calcd: 605.1752, found: 605.1760.

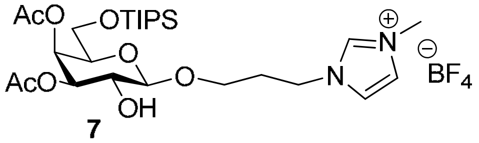
Compound **5**: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) : δ = 5.51 (d, 1H, $J_{4,3}$= 3.5 Hz, H-4), 4.97 (dd, 1H, $J_{3,4}$ = 3.5 Hz, $J_{3,2}$ = 10.5 Hz, H-3), 4.38 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.07 (dt, 1H, *J* = 5.5 Hz, 10.0 Hz, $OC\underline{H}_2$), 3.83-3.70 (m, 5H, H-5, H-2, H-6a, H-6b, $OC\underline{H}_2$), 3.56-3.51 (m, 2H, $C\underline{H}_2Br$), 2.23-2.04 (m, 8H, $OCH_2C\underline{H}_2$ and in which 2.11 (s, 3H, $C\underline{H}_3$ *Ac*), 2.06 (s, 3H, $C\underline{H}_3$ *Ac*), 1.11-1.00 (m, 21H, *TIPS*); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) : δ = 170.50, 170.05 (CO), 103.5 (C-1), 73.9 (C-2), 73.0 (C-3), 69.6 (C-5), 68.1 ($O\underline{C}H_2$), 67.4 (C-4), 61.2 (C-6), 32.6 ($OCH_2\underline{C}H_2$), 30.2 ($\underline{C}H_2Br$), 20.9 ($\underline{C}H_3$ *Ac*), 20.8 ($\underline{C}H_3$ *Ac*), 18.0 (*TIPS*), 11.9 (*TIPS*). ESI-HRMS for $C_{22}H_{41}BrNaO_8Si^+$ (MNa^+) calcd: 563.1652, found: 563.1656.



6

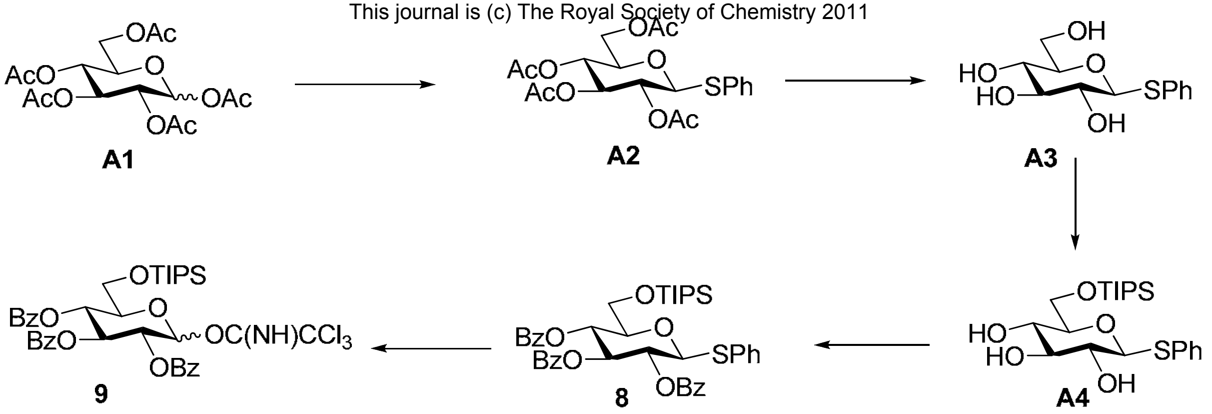
3-(3-Methylimidazolium)-1-propyl 2,3,4-tri-O-acetyl-6-O-triisopropylsilyl-β-D-galactopyranoside tetrafluoroborate (**6**). To a solution of **4** (230 mg, 0.424 mmol, 1eq) in MeCN (5 mL) was added *N*-methylimidazole (122 μL) and the mixture was refluxed for 18 hours, before a further *N*-methylimidazole

(122 µL) was added and the mixture was refluxed for a further 24 hours. To the reaction mixture was added KBF$_4$ (60 mg) and the reaction mixture was stirred for 24 hours. The reaction mixture was filtered, concentrated *in vacuo*, dried under high vacuum and washed with diethyl ether (3 x 15 mL) with sonication. Decantation of the ether phase followed by drying under vacuum afforded **6** as a light brown oil (258 mg, 90%). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) : δ = 10.3 (s, 1H, NC$\underline{\mathrm{H}}$N), 7.39 (t, 1H, J = 2.0 Hz, NC$\underline{\mathrm{H}}$CHN), 7.35 (t, 1H, J = 2.0 Hz, NCHC$\underline{\mathrm{H}}$N), 5.50 (dd, 1H, $J_{4,5}$ = 0.5 Hz, $J_{4,3}$ = 3.0 Hz, H-4), 5.08 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 10.5 Hz, H-2), 5.03 (dd, 4.99 (m, 1H, $J_{3,4}$ = 3.0 Hz, $J_{3,2}$ = 10.5 Hz, H-3), 4.52-4.36 (m, 3H, in which d at 4.46 (1H, $J_{1,2}$ = 8.0 Hz, H-1, C$\underline{\mathrm{H}}_2$N), 4.09 (s, 3H, C$\underline{\mathrm{H}}_3$N), 3.95-3.89 (m, 1H, OC$\underline{\mathrm{H}}_2$), 3.81-3.70 (m, 3H, H-6a, H-6b, OC$\underline{\mathrm{H}}_2$), 3.68-3.62 (m, 1H, H-5), 2.29-2.20 (m, 2H, OCH$_2$C$\underline{\mathrm{H}}_2$), 2.13 (s, 3H, C$\underline{\mathrm{H}}_3$ *Ac*), 2.06 (s, 3H, C$\underline{\mathrm{H}}_3$ *Ac*), 1.97 (s, 3H, C$\underline{\mathrm{H}}_3$ *Ac*), 1.04-0.99 (s, 21H, *TIPS*). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) : δ = 169.9, 169.8, 169.7 (CO), 137.8 (N$\underline{\mathrm{C}}$HN), 122.8 (N$\underline{\mathrm{C}}$HCHN), 122.6 (NCH$\underline{\mathrm{C}}$HN), 101.1 (C-1), 73.6 (C-2), 70.9 (C-3), 69.1 (C-5), 66.8 (C-4), 65.9 (O$\underline{\mathrm{C}}$H$_2$), 60.7 (C-6), 47.3 ($\underline{\mathrm{C}}$H$_2$N), 36.7 ($\underline{\mathrm{C}}$H$_3$-N), 30.3 (OCH$_2\underline{\mathrm{C}}$H$_2$), 21.0 ($\underline{\mathrm{C}}$H$_3$ *Ac*), 20.7 ($\underline{\mathrm{C}}$H$_3$ *Ac*), 20.6 ($\underline{\mathrm{C}}$H$_3$ *Ac*), 17.8, 11.7 (*TIPS*). ESI-HRMS for $C_{28}H_{49}N_2O_9Si^+$ (M$^+$), calcd: 585.3202, found: 585.3198.



7

***3-(3-Methylimidazolium)-1-propyl 3,4-di-O-acetyl-6-O-triisopropylsilyl-β-D-galactopyranoside tetrafluoroborate* (7)**. To a solution of **5** (300 mg, 0.554 mmol) in MeCN (5 mL) was added N-methylimidazole (159 µL, 2 mmol) and the mixture was refluxed for 18 hours after which the reaction was complete. To the reaction mixture was added KBF$_4$ (84 mg, 0.67 mmol) and the reaction mixture was stirred for 24 hours. The reaction mixture was filtered, concentrated *in vacuo*, dried under high vacuum and washed with diethyl ether (3 x 15 mL) with sonication. Decantation of the ether phase followed by drying under vacuum afforded **10** as a light brown oil (252 mg, 84 %). ^{1}H NMR (CD$_3$OD, 400 MHz, ppm) : δ = 8.98 (1H, s, NC$\underline{\mathrm{H}}$N), 7.69, 7.60 (2H, NC$\underline{\mathrm{H}}$C$\underline{\mathrm{H}}$N), 5.48 (d, 1H, $J_{4,3}$ = 3.5 Hz, H-4), 4.92 (dd, 1H, $J_{3,4}$ = 3.5 Hz, $J_{3,2}$ = 10.0 Hz, H-3), 4.47 (d, 1H, $J_{1,2}$ = 8.0, H-1) 4.42 (m, 2H, C$\underline{\mathrm{H}}_2$N), 3.96 (s, 3H, C$\underline{\mathrm{H}}_3$N), 3.88 (m, 1H, H-5), 3.82-3.80 (m, 1H, H-6a), 3.70-3.69 (m, 1H, H-6b), 3.60-3.55 (m, 3H, H-2, OC$\underline{\mathrm{H}}_2$), 2.21 (m, 2H, OCH$_2$C$\underline{\mathrm{H}}_2$), 2.11 (s, 3H, C$\underline{\mathrm{H}}_3$ *Ac*), 2.01 (s, 3H, C$\underline{\mathrm{H}}_3$ *Ac*), 1.06 (s 21H, *TIPS*); ^{13}C NMR (CD$_3$OD, 100 MHz, ppm) : δ = 172.2, 171.9 (CO), 138.4 (N$\underline{\mathrm{C}}$HN), 124.9 (N$\underline{\mathrm{C}}$H), 123.9 (N$\underline{\mathrm{C}}$H), 104.4 (C-1), 75.0 (C-3), 74.3 (C-5), 70.1 (C-2), 68.8 (C-4), 66.8 (O$\underline{\mathrm{C}}$H$_2$), 62.2 (C-6), 47.9 ($\underline{\mathrm{C}}$H$_2$N), 36.8 ($\underline{\mathrm{C}}$H$_3$N), 31.0 (OCH$_2\underline{\mathrm{C}}$H$_2$), 21.0 ($\underline{\mathrm{C}}$H$_3$ *Ac*), 20.92 ($\underline{\mathrm{C}}$H$_3$ *Ac*), 18.5, 13.1 (*TIPS*). ESI-HRMS for $C_{26}H_{47}N_2O_8Si^+$ (M$^+$), calcd: 543.3096, found: 543.3121.

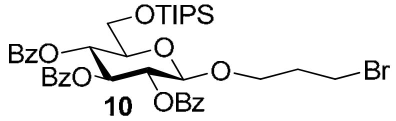


***Phenyl 2,3,4-tri-O-benzoyl-1-thio-6-O-triisopropylsilyl -β-D-glucopyranoside* (8)**. To a solution of 1,2,3,4,6-*O*-acetyl-D-glucopyranose **A1** (3.12 g, 0.008 mol) in CH_2Cl_2 (60 mL) was added ZnI_2 (7.6 g, 0.023 mol) and TMSSPh (4.5 mL, 0.024 mol). The mixture was then left stirring at room temperature for 2 h. After filtration on celite, the mixture was diluted in DCM (20 mL) and washed with HCl 0.1 M (200 mL), sat $NaHCO_3$ (2 x 200 mL), sat brine (2 x 100 mL) and H_2O (2 x 250 mL). The organic layer was then dried over $MgSO_4$, filtered and concentrated under vacuum to give 3.14 g (89%) of clean **A2** as observed by NMR. 2.0 g (4.545 mmol) of **A2** were dissolved in a mixture of MeOH/Et_3N/H_2O (1/8/1, 50 mL) and left stirring overnight at room temperature. The solution was then co-evaporated with toluene and dried under vacuum to afford **A3** (1.5 g) of sufficient purity to be taken into the following step without further purification. The **A3** mixture was dissolved in DMF (20 mL) and imidazole (544 mg, 1.5 eq) and triisopropylsilyl chloride (1.6 mL, 1.5 eq) were added. The resulting mixture was left stirring at room temperature for 24h until TLC showed completion of the reaction. The solvent was then evaporated under high pressure and the residue dissolved in EtOAc (100 mL) and washed with water (100 mL). The aqueous layer was then extracted with EtOAc (4 x 100 mL). The collected organic layer was dried over $MgSO_4$ and then evaporated under vacuum to give **A4**, which was dissolved in pyridine (50 mL) and BzCl (1.8 mL) and DMAP (61 mg) were added. The solution was stirred overnight. The reaction mixture was then quenched with MeOH at 0 °C. Co-evaporation of the solvent with toluene followed by crystallisation in EtOH gave **8** (2 g) as a white solid, column chromatography of the filtered fraction (petroleum ether/Et_2O : 10/0- 9/1) gave another 1.0 g of **8**. Overall, 3.0 g of **8** were obtained in 90 % yield from 3 steps starting from **A2**. Rf = 0.4 (95/5 : petrolium ether/EtOAc). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) : δ = 8.01-7.98 (m, 2H, Ph), 7.95-7.92 (m, 2H, Ph), 7.84-7.82 (m, 2H, Ph), 7.57-7.51 (m, 4H, Ph), 7.46-7.36 (m, 5H, Ph), 7.34-7.26 (m, 5H, Ph), 5.91 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3), 5.57 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4), 5.50 (dd, 1H, $J_{2,3}$ = 9.5 Hz, $J_{2,1}$ = 10.0 Hz, H-2), 5.08 (d, 1H, $J_{1,2}$ = 10.0 Hz, H-1), 3.98-3.93 (m, 3H, H-6a, H-6b, H-5), 1.15-1.02 (m, 21H, *TIPS*). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ = 165.9, 165.1 (CO), 133.2, 133.1, 132.6, 132.5 (C_q, Ph), 129.8, 129.7, 129.6, 129.3, 129.2, 128.9, 128.8, 128.4, 128.3, 128.2 , 128.0 ($\underline{C}$H, Ph), 86.4 (C-1), 79.9 (C-5), 74.6 (C-3), 70.7 (C-2), 69.2 (C-4), 63.0 (C-6), 17.9, 11.9 (*TIPS*). HRMS-ESI for $C_{42}H_{48}NaO_8SSi$ (MNa^+) calcd: 763.2764, found: 763.2731.

2,3,4-tri-O-Benzoyl-6-O-triisopropylsilyl-β-D-glucopyranoside trichloroacetimidate (**9**)

Method A with K_2CO_3: A solution of thioglycoside **8** (700 mg, 0.94 mmol), NBS (204 mg, 1.13 mmol) in acetone (20 mL) was stirred at room temperature for 30 min. The reaction was quenched dropwise with $NaHCO_3$ at 0 °C and the acetone was removed under vacuum. CH_2Cl_2 (150 mL) was added to the residue and the organic layer was washed with sat $Na_2S_2O_3$ (2 x 40 mL), H_2O (2x50 mL), dried with $MgSO_4$, filtered, and concentrated. The residue was co-evaporated with toluene and dried under vacuum overnight. To the crude mixture, CH_2Cl_2 (8 mL), K_2CO_3 (780 mg, 5.64 mmol) and CCl_3CN (940 µL, 9.4 mmol) were added and the reaction was stirred for 21 h. The mixture was concentrated under vacuum and purified by silica gel chromatography (toluene) to yield 300 mg (47 %) of **9** as an α/β: 1/1 mixture.

Method B with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene): A solution of thioglycoside **8** (1.76 g, 2.38 mmol), NBS (513 mg, 2.85 mmol) in acetone (50 mL) was stirred at room temperature for 30 min. The reaction was quenched dropwise with $NaHCO_3$ at 0 °C and the acetone was removed under vacuum. CH_2Cl_2 (150 mL) was added to the residue and the organic layer was washed with sat $Na_2S_2O_3$ (2 x 40 mL), H_2O (2x50 mL), dried with $MgSO_4$, filtered, and concentrated. The residue was co-evaporated with toluene and dried under vacuum overnight. To the crude residue, CH_2Cl_2 (25 mL), DBU (460 µL, 0.97 mmol) and CCl_3CN (2.4 mL, 23.8 mmol), were added and the reaction was stirred for 1 h. The mixture was concentrated under vacuum and purified by silica gel chromatography to afford 1.36 g (72 %) of **9** as the α isomer. $R_f = 0.5$ (Toluene). ^{1}HNMR ($CDCl_3$, 400 MHz, ppm) : δ = 8.71 (N$\underline{H}$, α), 8.60 (N$\underline{H}$, β), 8.00-7.89 (m, 13H, Ph), 7.56-7.27 (m, 17H, Ph), 6.87 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1α), 6.26 (t, 1H, $J_{3,2} = J_{3,4}$ = 10.0 Hz, H-3α), 6.26 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1β), 5.96 (t, 1H, $J_{3,2} = J_{3,4}$ = 10.0 Hz, H-3β) 5.81-5.75 [m, 3H, in which dd at 5.79 (1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 10.0 Hz, H-2β), H-4α, H-4β], 5.58 (dd, 1H, $J_{2,1}$ = 4.0 Hz, $J_{2,3}$ = 10.0 Hz, H-2α), 4.41 (ddd, 1H, $J_{5,6a}$ = 3.5 Hz, $J_{5,6b}$ = 4.0 Hz, $J_{5,4}$ = 10.0 Hz, H-5α), 4.11 (ddd, 1H, $J_{5,6a}$ =2.0 Hz, $J_{5,6b}$ = 4.5 Hz, $J_{5,4}$ = 10.0 Hz, H-5β), 4.05 (dd, 1H, $J_{6a,5}$ = 2.5 Hz, H-6a β), 4.00-3.93 (m, 3H, H-6a α, H-6b α ,H-6b β), 1.11-1.01 (m, 42H, *TIPS*). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) : δ = 165.7, 165.4, 154.0, 164.8, 164.8 (CO), 160., 160.5 (CO), 133.4, 133.2, 133.1 (C_q, Ph), 129.9, 129.8, 129.7, 129.2, 129.1, 129.0, 128.9, 128.7, 128.4, 128.3, 128.20, 125.7 ($\underline{C}$H, Ph), 95.7 (C-1β), 93.3 (C-1α), 90.9, 90.4 ($\underline{C}Cl_3$ α and β), 78.0 (C-5β), 73.8 (C-5α), 73.0 (C-3β), 71.0(C-2α), 70.9 (C-2β), 70.5 (C-3α), 62.4 (C-6β), 62.4 (C-6α), 68.7, 68.6 (C-4 α and β), 17.8, 11.9 (*TIPS*). HRMS-ESI for $C_{38}H_{44}Cl_3NNaO_9Si$ (MNa^+), calcd: 814.1761, found: 814.1743.

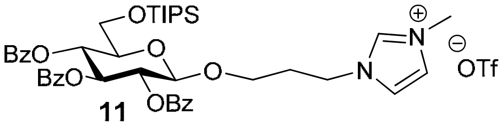


10

3-Bromopropyl 2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranoside (10)

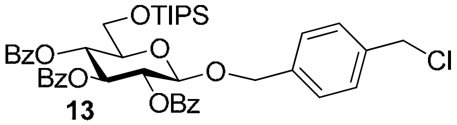
Method A: trichloroacetimidate donor. To a solution of **9** (600 mg, 0.76 mmol) in CH_2Cl_2 (6 mL), 3-bromopropan-1-ol (96 µL, 0.99 mmol) and 4 Å molecular sieves (2 g) were added. The mixture was stirred for 30 minutes at room temperature before cooling to -40 °C. TMSOTf (10% solution in CH_2Cl_2, 150 µL, 0.052 mmol, 0.1 eq) was then added and the reaction was kept at -40 °C for another 1 h. After quenching with Et_3N (50 µL), the mixture was concentrated under vacuum and the residue purified by silica gel chromatography using toluene as the eluant to give 480 mg (83%) of **10**.

Method B: Thiophenyl donor. To a solution of **8** (200 mg, 0.268 mmol) in CH_2Cl_2 (1.2 mL), 3-bromopropan-1-ol (48 µL, 0.496 mmol), 2,6-di-*tert*butyl-4-methyl-pyridine (55 mg, 0.268 mmol) and 4 Å molecular sieves were added and the mixture was stirred for 30 minutes at room temperature before cooling to 0 °C. Tf_2O/Me_2S_2 (1M solution in CH_2Cl_2 0.4 mL, 0.4 mmol) was then added and the reaction was kept at 0 °C for another 2 h before being quenched with Et_3N (100 µL). The mixture was concentrated under vacuum and the residue was purified by flash chromatography using toluene as the eluant to give 120 mg (58%) of **10**. R_f = 0.28 (Toluene). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) : δ = 7.99-7.97 (m, 2H, Ph), 7.94-7.92 (m, 2H, Ph), 7.85-7.83 (m, 2H, Ph) 7.54-7.49 (m, 2H, Ph), 7.45-7.39 (m, 5H, Ph), 7.31-7.25 (m, 2H, Ph), 5.87 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3), 5.56 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4), 5.47 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 4.83 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.04 (dt, 1H, J= 5.0 Hz, J= 10.0 Hz, $C\underline{H}_2O$), 3.95-3.87 (m, 3H, H-6a, H-6b, H-5), 3.73 (ddd, 1H, ^3J= 5.0, 8.0 Hz, ^2J= 10.0 Hz, $C\underline{H}_2O$), 3.39-3.35 (m, 2H, $C\underline{H}_2Br$), 2.19-1.97 (m, 2H, $OCH_2C\underline{H}_2$), 1.07-1.01 (m, 21H, *TIPS*). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) : δ = 165.9, 165.2, 165.1 (CO), 133.2, 133.2, 133.1, (C_q, Ph), 129.8, 129.7, 129.3, 129.2, 129.0, 128.4, 128.2, 128.2 ($\underline{C}H$, Ph), 101.3 (C-1), 75.6 (C-5), 73.3 (C-3), 72.1 (C-2), 69.5 (C-4), 67.2 ($O\underline{C}H_2$), 62.8 (C-6), 32.2 ($OCH_2\underline{C}H_2$), 30.1 ($\underline{C}H_2Br$). 17.9, 11.9 (*TIPS*). ESI-HRMS (MNa+) for $C_{39}H_{49}BrNaO_9Si^+$ calcd. : 791.2221; found : 791.2229.



11

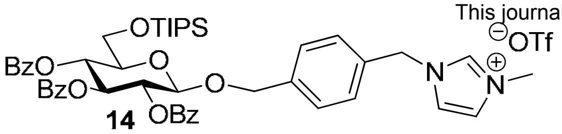
3-(3-Methylimidazolium)-1-propyl 2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranoside trifluoromethanesulfonate **(11)** To a solution of **10** (160 mg, 0.21 mmol) in acetonitrile (20mL) was added 1-methylimidazole (68 µL, 0.84 mmol) and potassium trifluoromethanesulfonate (158 mg, 0.84 mmol) and the mixture was refluxed over night. After filtration of the salts, the solution was evaporated under reduced pressure and the residue redissolved in CH_2Cl_2 and washed with H_20 (5mL) to remove the excess of imidazole from the product. The aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL). The collected organic fractions were dried with Na_2SO_4, concentrated and dried under vacuum. The residue was washed with *n*-hexane (3x 5 mL) and Et_2O (3x 5 mL) to give 160 mg (83%) of **11**. ^{1}HNMR ($CDCl_3$, 400 MHz, ppm) : δ = 9.13 (s, 1H, $NC\underline{H}N$), 7.97-7.16 (m, 17H, 15H (Ph) + 2H (imidazolium), 5.86 (t, 1H, $J_{3,4} = J_{3,2} = 9.5$ Hz, H-3), 5.60 (t, 1H, $J_{4,3} = J_{4,5} = 9.5$ Hz, H-4), 5.38 (dd, 1H, $J_{2,1} = 8.0$ Hz, $J_{2,3} = 9.5$ Hz, H-2), 4.80 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.31-4.25 (m, 2H, $C\underline{H}_2N$), 3.97-3.87 (m, 7H in which s at 3.93, $C\underline{H}_3N$, H-5, H-6a, H-6b, $OC\underline{H}_2$), 3.42-3.31 (m, 1H, $OC\underline{H}_2$), 2.19-2.15 (m, 2H, $OCH_2C\underline{H}_2$), 1.08-0.95 (m, 21H, *TIPS*). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) : δ = 165.8, 165.4, 165.1 (CO), 137.0 ($N\underline{C}HN$), 133.7, 133.3, (C_q, Ph), 129.7, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 125.3, 122.9, 122.8 ($\underline{C}H$,*aromatic*), 100.9 (C-1), 75.5 (C-5), 73.0 (C-3), 72.2 (C-2), 69.1 (C-4), 65.7 ($O\underline{C}H_2$), 62.5 (C-6), 47.2 ($\underline{C}H_2N$), 36.4 ($\underline{C}H_3N$), 29.9 ($OCH_2\underline{C}H_2$), 17.8, 11.9 (*TIPS*). ^{19}F NMR ($CDCl_3$, 400 MHz, ppm): δ = -80.3 (TfO^-). HRMS-ESI for $C_{43}H_{55}N_2O_9Si^+$ (M^+), calcd: 771.3665, found: 771.3671.



13

***4-(Chloromethyl)benzyl 2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranoside* (13)**

To a solution of **9** (210 mg, 0.25 mmol) in CH_2Cl_2 (2 mL), 4-chloromethyl benzyl alcohol **12** (79 mg, 0.50 mmol) and 4 Å molecular sieves (500 mg) were added. The mixture was stirred for 30 minutes at room temperature before cooling to -40 °C. TMSOTf (4 µL, 0.02 mmol) was then added and the reaction was kept at -40°C for another 1h. After quenching with Et_3N (20 µL), the mixture was concentrated under vacuum and the residue purified by silica gel chromatography using toluene as the eluant to give 187 mg (94%) of **13**. R_f = 0.3 (Toluene), ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) : δ = 7.95-7.90 (m, 4H, Ph), 7.84-7.82 (m, 2H, Ph), 7.57-7.49 (m, 2H, Ph), 7.45-7.35 (m, 5H, Ph), 7.30-7.26 (m, 4H, Ph), 7.22 (s, 4H, $ClCH_2Ph$), 5.82 (t, 1H, $J_{3,4} = J_{3,2} = 9.5$ Hz, H-3), 5.56 (dd, 1H, $J_{2,1} = 8.0$ Hz, $J_{2,3} = 9.5$ Hz, H-2), 5.54 (t, 1H, $J_{4,3} = J_{4,5} = 9.5$ Hz, H-4), 4.92 (d, 1H, $J = 12.5$ Hz, $OC\underline{H}_2$), 4.81 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.73 (d, 1H, $J = 12.5$ Hz, $OC\underline{H}_2$), 4.55 (bs, 2H, $ClC\underline{H}_2$), 3.96 (bs, 2H, H-6a, H-6b), 3.85 (dt, 1H, $J_{5,6a} = J_{5,6b} = 3.5$ Hz, $J_{5,4} = 9.5$ Hz, H-5), 1.09-1.04 (m, 21H, *TIPS*). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) : δ = 165.8, 165.1 (CO), 137.1, 137.0 (C_q, Ph), 133.2, 133.1, 133.0, 129.9, 129.8, 129.7, 129.4, 129.2, 129.0, 128.6, 128.3, 128.2, 128.1 ($\underline{C}H$, *aromatic*), 99.2 (C-1), 75.7 (C-5), 73.3 (C-3), 72.0 (C-2), 69.7 (C-4), 69.7 ($O\underline{C}H_2$), 63.0 (C-6), 45.9 ($\underline{C}H_2Cl$), 17.9, 12.0 (*TIPS*). ESI-HRMS (MNa^+) for $C_{44}H_{51}ClNaO_9Si^+$ calcd: 809.2889; found: 809.2907.



14

4-(1-Methyl-3-methyleneimidazolium)-benzyl 2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranoside trifluoromethanesulfonate **(14)**. To a solution of **13** (181 mg, 0.238 mmol) in CH_3CN (5 mL), 1-methyl imidazole (153 µL, 1.922 mmol), potassium trifluoromethylsulfonate (358 mg, 1.904 mmol) were added and the mixture was refluxed for 24 h before being cooled to room temperature. TLC showed completion of the reaction. The solvent was then evaporated to dryness followed by addition of a mixture of H_2O/CH_2Cl_2 (5 mL/15 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL) and EtOAc (2 x 15 mL). The combined organic layer was then dried over Na_2SO_4, filtered and evaporated. The dried residue was washed 3 times with a mixture 1/1 of *n*-hexane/EtOAc to give **14 (**200 mg, 89%) as a yellow foam. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) : δ = 9.20 (s, 1H, NC$\underline{H}$N), 7.94-7.91 (m, 4H, Ph), 7.84-7.82 (m, 2H, Ph), 7.57-7.51 (m, 2H, Ph), 7.45-7.36 (m, 5H, Ph), 7.31-7.23 (m, 7H, Ph), 7.17 (t, 1H, J = 1.5 Hz, NC$\underline{H}$CHN), 5.86 (t, 1H, $J_{3,4}$ = $J_{3,2}$ = 9.5 Hz, H-3), 5.59 (t, 1H, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, H-4), 5.55 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 5.31 (bs, 2H, C$\underline{H_2}$N), 4.95 (d, 1H, J = 12.0 Hz, OC$\underline{H_2}$), 4.87 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.70 (d, 1H, J = 12.0 Hz, OC$\underline{H_2}$), 3.99-3.96 (m, 2H, H-6a, H-6b), 3.93 (s, 3H, NC$\underline{H_3}$), 3.93-3.88 (m, 1H, H-5), 1.09-1.03 (m, 21H, *TIPS*). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) : δ = 165.8, 165.2, 165.1 (CO), 138.6, 137.0 (C_q, Ph), 133.4, 133.3, 133.2, 132.1, 129.7, 129.6, 129.2, 129.1, 129.0, 128.9, 128.7, 128.4, 128.3, 128.2, ($\underline{C}$H, *aromatic*), 123.5, 121.8 ($\underline{C}$H, *imidazolium*), 99.7 (C-1), 75.6 (C-5), 73.2 (C-3), 72.0 (C-2), 69.7 (O$\underline{C}H_2$), 69.4 (C-4), 62.7 (C-6), 53.1 ($\underline{C}H_2$N), 36.4 (N$\underline{C}H_3$), 17.8, 11.9 (*TIPS*). ESI-HRMS (M^+) for $C_{48}H_{57}N_2O_9Si^+$ calcd: 833.3828; found: 833.3828.

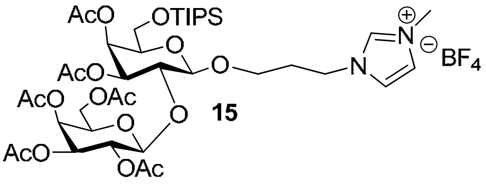
General OTIPS deproctection of ITagged saccharides.

Method A: To a solution of 6-OTIPS protected compounds **11**, **14**, **20** and **22** (1 mmol) in CH_2Cl_2 (10 mL) was added HCl (1.25 M in MeOH, 20 eq) and left stirring at room temperature for 18 h. MALDI-TOF analysis showed completion of the reaction. The mixture was co-evaporated with toluene. CH_2Cl_2 was added to the residue and washed with H_2O (2x2 mL), dried over Na_2SO_4, filtered, concentrated under reduced pressure and dried under vacuum for 2 h. The dried residue was washed twice with Et_2O to give products **19**, **21**, **23** and **25**.

General glycosylation reactions.

Method B: Trichloroactimidate donor. To a solution of acceptor (1 mmol) and donor (2 mmol) in 5-20 mL of CH_2Cl_2, 4 Å molecular sieves (MS) were added and the mixture was left stirring for 30 minutes at room temperature before cooling to 0 °C. TMSOTf (0.3 mmol) was added at 0 °C. The reaction was left to warm to room temperature overnight. MALDI-TOF analysis showed completion of the reaction. The mixture was then filtered, concentrated under reduced pressure and dried under vacuum. The obtained oil was then washed twice with *n*-hexane and *n*-hexane/Et_2O 1:1 to give the coupling product.

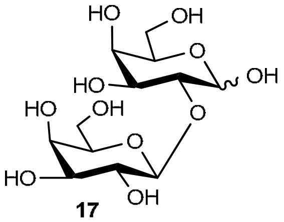
Method C: Thiophenyl glycoside donor. To a solution of acceptor (1 mmol) and donor (3 mmol) in 5-20 mL of CH_2Cl_2, 4 A° MS were added and the mixture was left stirring for 30 minutes at room temperature before cooling to 0°C. Tf_2O/Me_2S_2 (1M solution in CH_2Cl_2, 4.5 mL, 4.5 mmol) was then added at 0°C and the reaction was left to warm to room temperature overnight. MALDI-TOF analysis showed completion of the reaction. The mixture was then filtered and the solvent concentrated under reduced pressure. The dried residue was washed with H_2O (10 mL) and the aqueous layer was then extracted twice with abundant quantity of CH_2Cl_2 (2x50 mL). The organic fractions were evaporated and dried under high vacuum. The dried residue was washed three times with a mixture of 1/1 : n-hexane/Et_2O to give the coupling product. Note: Some of the ITag-product will be partially soluble in the water phase. The water fractions must be wash carefully with DCM to ensure most of the product is recovered.



15

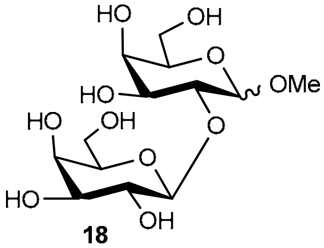
3-(3-Methylimidazolium)-1-propyl 3,4-di-O-acetyl-2-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-6-O-(triisopropyl)silyl-β-D-galactopyranoside tetrafluoroborate **(15)**

Following general glycosylation ***Method B:*** from **7** (30 mg, 0.06 mmol) to give **15** (43.4 mg, 90%). ^{1}HNMR ($CDCl_3$, 400 MHz, ppm) : δ_H = 9.20 (s, 1H, NC$\underline{H}$N), 7.73, 7.38 (2s, 2H, 2 x NC-H), 5.46-5.45 (m, 1H, H-4^B), 5.38 (d, 1H, $J_{4,3}$ = 3.0 Hz, H-4^A), 5.09 (dd, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 10.5 Hz, H-2^B), 5.01 (dd, 1H, $J_{3,4}$ = 3.0 Hz, $J_{3,2}$ = 10.5 Hz, H-3^A), 4.98 (dd, 1H, $J_{3,4}$ = 3.0 Hz, $J_{3,2}$ = 10.5 Hz, H-3^B), 4.73 (1H, d, $J_{1,2}$ = 8.0 Hz, H-1^B), 4.54-4.46 (m, 3H, H-5^A, $OCH_2CH_2C\underline{H_2}$,), 4.34 (1H, d, $J_{1,2}$ = 8.0 Hz, H-1^A), 4.30-4.27 (m, 1H, H-6a^B), 4.10-4.07 (m, 2H, $OC\underline{H_2}CH_2CH_2$), 4.06 (s, 3H, $C\underline{H_3}N$), 4.01-3.99 (m, 2H, H-5^B, H-6b^B), 3.90 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 10.5 Hz, H-2^A), 3.79-3.77 (m, 1H, H-6a^A), 3.73-3.71 (m, 1H, H-6b^A), 2.23-2.18 (m, 2H, $OCH_2C\underline{H_2}CH_2$), 2.19 (s, 3H, $C\underline{H}_3$ *Ac*), 2.15 (s, 3H, $C\underline{H}_3$ *Ac*), 2.06 (s, 3H, $C\underline{H}_3$ *Ac*), 2.03 (s, 3H, $C\underline{H}_3$ *Ac*), 1.97 (s, 3H, $C\underline{H}_3$ *Ac*), 1.95 (s, 3H, $C\underline{H}_3$ *Ac*), 2.01 (3H, s), 1.01 (21H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) : δ = 167-164 (6xCO), 138.0 (N$\underline{C}$HN), 124.96 (N$\underline{C}$-H), 123.98 (N$\underline{C}$-H), 100.8 (C-1^A), 101.2 (C-1^B), 73.5 (C-5^A), 70.8 (C-3^A), 70.2 (C-3^B), 75.2 (C-2^A), 68.2 (C-2^B), 67.3 (C-4^B), 66.9 (C-4^A), 65.8 (C-5^B), 60.3 (C-6^B), 61.5 ($O\underline{C}H_2$), 60.7 (C-6^A), 45.5 ($\underline{C}H_2N$), 36.3 ($N\underline{C}H_3$), 29.8 $OCH_2\underline{C}H_2$), 17.5, 11.6 (*TIPS*). HRMS:(ESI$^+$) Found M$^+$ 873.4053, $C_{26}H_{47}O_8N_2Si^+$ requires 873.4047.



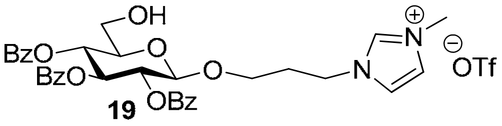
17

2-O-(α/β-D-galactopyranosyl)-β-D-galactopyranose* (17)**. Following g*eneral OTIPS removal* ***Method A to remove TIPS group from **15** (10 mg, 0.01 mmol). The resulting product was then dissolved in CH_2Cl_2 (1 mL) and NH_3 (2M solution in MeOH, 10 mL) were added. The the solution was heated at 60 °C for 24h. MALDI-TOF showed completion of the reaction. The mixture was co-evaporated with toluene and the dried residue washed with CH_2Cl_2 (3 x 2 mL) to afford **16** that was taken to the next step without further purification. The dried mixture was then redissolved in H_2O (5 mL) and HCl (50 μL, 1M) was added. The mixture was left stirring at reflux for 8 h. TLC showed completion of the reaction. The reaction mixture was then co-evaporated with toluene and the dried residue was purified over reverse phase C-18 column chromatography with a gradiet of H_2O/MeOH: 9/1-1/1 to give (3 mg, 77%) of **17** as α/β (5/1) mixture. NMR and MS data in agreement with reported literature.[4]



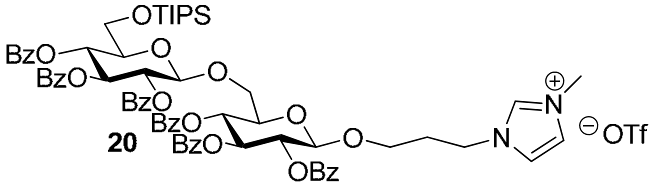
18

Methyl 2-O-(α/β-D-galactopyranosyl)-β-D-galactopyranoside* (18)**. Following g*eneral OTIPS removal* ***Method A to remove TIPS group from **15** (14 mg, 0.02 mmol). The resulting product was then dissolved in CH_2Cl_2 (1 mL) and NH_3 (2M in MeOH, 10 mL) were added. The the solution was heated at 60 °C for 24h. MALDI-TOF showed completion of the reaction. The mixture was co-evaporated with toluene and the dried residue washed with CH_2Cl_2 (3 x 2 mL) to afford **16** that was taken to the next step without further purification. The dried mixture was then redissolved in CH_2Cl_2 (10 mL) and HCl (1.25 M in MeOH, 10 eq) was added. The mixture was left stirring at reflux for 8 h. TLC showed completion of the reaction. The reaction mixture was then co-evaporated with toluene and the dried residue was purified over reverse phase C-18 column chromatography with a gradiet of H_2O/MeOH: 9/1-1/1 to give **18** (4.7 mg, 82%) as α/β (9/1) mixture. NMR and MS data in agreement with reported literature.[5]



19

3-(3-Methylimidazolium)-1-propyl 4,6-O-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside trifluoromethanesulfonate **(19).** Following g*eneral OTIPS removal* ***Method A***. From **11** (220 mg, 0.29 mmol) to give **19** (180 mg, 94%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) : δ = 9.06 (s, 1H, NC$\underline{H}$N), 7.95-7.25 (m, 17H, 15 H (Ph) + 2H (imidazole), 5.89 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3), 5.46 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4), 5.36 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 4.85 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1),4.35 (t, 2H, J = 6.5 Hz, CH_2N), 3.87 (bd, 1H, J = 12.0 Hz, H-6a) , 3.83-3.70 (m, 3H, H-6b, H-5, OC$\underline{H_2}$), 3.42-3.31 (m, 1H, OC$\underline{H_2}$), 2.71 (bs, 1H, O$\underline{H}$), 2.11-2.00 (m, 2H, $OCH_2C\underline{H_2}$). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) : δ = 165.9, 165.6, 165. (CO), 137.1 (N$\underline{C}$HN), 133.6, 133.4, (C_q, Ph), 129.9, 129.7, 129.6, 129.0, 128.8, 128.5, 128.4, 128.3, 128.2, 125.3, 123.4, 122.6 ($\underline{C}$H, *aromatic*), 100.6 (C-1), 74.6 (C-5), 72.8 (C-3), 71.9 (C-2), 69.5 (C-4), 65.8 (C-6), 60.5 (O$\underline{C}H_2$), 47.0 ($\underline{C}H_2N$), 36.4 (N$\underline{C}H_3$), 29.9 ($OCH_2\underline{C}H_2$). ^{19}F NMR ($CDCl_3$, 400 MHz, ppm): δ = -78.43 (TfO$^-$). HRMS-ESI for $C_{34}H_{35}N_2O_9^+$ (M^+), calcd: 615.2336, found: 615.2337.



20

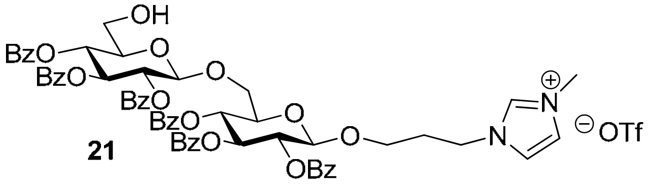
3-(3-Methylimidazolium)-propyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranosyl)- β-D-glucopyranoside trifluoromethanesulfonate **(20)**.

Following general glycosylation ***Method B***. From 19 (140 mg, 0.23 mmol) to give **20** (236 mg, 94%)

Following general glycosylation ***Method C***. From **19** (30 mg, 0.05 mmol) to give **20** (41 mg, 76%)

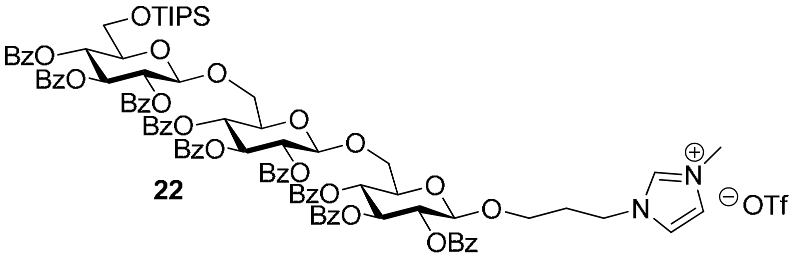
^{1}HNMR ($CDCl_3$, 400 MHz, ppm) : δ = 9.09 (s, 1H, NC$\underline{H}$N), 8.08-7.23 (m, 32H, 30H (Ph) + 2H (imidazole), 5.91 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3^A) 5.76 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3^B), 5.54 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4^A), 5.44 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2^A), 5.30 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4^B), 5.01 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2^B), 4.89 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^A), 4.70 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^B), 4.32-4.25 (m, 1H, C$\underline{H_2}$N), 4.19-4.14 (m, 2H, C$\underline{H_2}$N + H-6a^B), 4.02 (s, 3H, C$\underline{H_3}$N), 4.01-3.97 (m, 1H, H-5^B), 3.88-3.82 (m, 3H, H-5^A, 2xH-6^A), 3.75 (dd, 1H, $J_{6b,5}$ = 5.5 Hz, $J_{6b,6a}$ = 12.0 Hz, H-6b^B), 3.64-3.58 (m, 1H, OC$\underline{H_2}$), 3.50-3.45 (m, 1H, OC$\underline{H_2}$), 1.98-1.92 (bs, 2H, $OCH_2C\underline{H_2}$), 0.98-0.91 (m, 21H, *TIPS*). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) : δ = 165.7, 165.4, 165.3, 165.0, 164.9 (CO), 137.0 (N$\underline{C}$HN), 133.7, 133.6, 133.6, 133.5, 133.5, 133.4, 133.3, 133.2 (C_q, Ph), 130.0, 129.9, 129.8, 129.8, 129.7, 129.7, 129.6, 129.6, 129.0, 128.9, 129.9, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 125.3, 125.2 ($\underline{C}$H, *aromatic*), 101.8 (C-1^A), 100.3 (C-1^B), 75.6 (C-5^A), 72.9 (C-5^B) 72.8 (C-3^A), 72.7 (C-3^B), 72.2 (C-2^A), 71.7

(C-2^B), 69.2 (C-4^A), 69.1 (C-4^B), 67.8 (C-6^B), 64.7 ($O\underline{C}H_2$), 64.4 (C-6^A), 46.6 ($\underline{C}H_2N$), 36.3 ($N\underline{C}H_3$), 29.6 $OCH_2\underline{C}H_2$), 17.8, 11.7 (*TIPS*). HRMS-ESI for $C_{70}H_{77}N_2O_{17}Si^+$ (M^+), calcd: 1245.5034, found: 1245.4986.



21

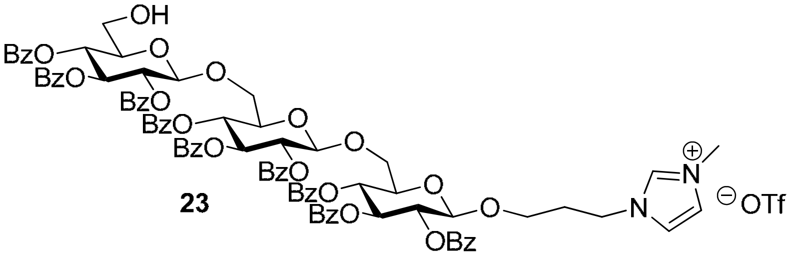
3-(3-Methylimidazolium)-propyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranoside trifluoromethanesulfonate* (21).** Following g*eneral OTIPS removal* ***Method A. From **20** (220 mg, 0.18 mmol) to give **21** (194 mg, 97%). ^{1}HNMR ($CDCl_3$, 400 MHz, ppm) : δ = 9.06 (s, 1H, $NC\underline{H}N$), 8.05-7.19 (m, 32H, 30H (Ph) + 2H (imidazole), 5.98 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3^A) 5.73 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3^B), 5.43 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4^A), 5.41 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2^A), 5.30 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4^B), 5.06 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2^B), 4.87 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^A), 4.71 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^B), 4.36-4.16 (m, 3H, $C\underline{H_2}N$+H-6), 4.02 (s, 3H, $C\underline{H_3}N$), 3.96-3.56 (m, 9H, 3xH-6, H-5^A, H-5^B, $OC\underline{H_2}$), 3.88-3.82 (m, 3H, H-5^A, 2xH-6^A), 3.75 (dd, 1H, $J_{6b,5}$ = 5.5 Hz, $J_{6b,6a}$ = 12.0 Hz, H-6b^B), 3.64-3.58 (m, 1H, $OC\underline{H_2}$), 3.50-3.45 (m, 1H, $OC\underline{H_2}$), 1.98-1.92 (bs, 2H, $OCH_2C\underline{H_2}$), 0.98-0.91 (m, 21H, *TIPS*). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) : δ = 165.7, 165.4, 165.3, 165.0, 164.9 (CO), 137.0 ($N\underline{C}HN$), 133.7, 133.6, 133.6, 133.5, 133.5, 133.4, 133.3, 133.2 (C_q, Ph), 130.0, 129.9, 129.8, 129.8, 129.7, 129.7, 129.6, 129.6, 129.0, 128.9, 129.9, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 125.3, 125.2 ($\underline{C}H$, aromatic), 101.8 (C-1^A), 100.3 (C-1^B), 75.6 (C-5^A), 72.9 (C-5^B) 72.8 (C-3^A), 72.7 (C-3^B), 72.2 (C-2^A), 71.7 (C-2^B), 69.2 (C-4^A), 69.1 (C-4^B), 67.8 (C-6^B), 64.7 ($O\underline{C}H_2$), 64.4 (C-6^A), 46.6 ($\underline{C}H_2N$), 36.3 ($N\underline{C}H_3$), 29.6 $OCH_2\underline{C}H_2$), 17.8, 11.7 (*TIPS*). HRMS-ESI for $C_{61}H_{57}N_2O_{17}^+$ (M^+), calcd: 1089.3673, found: 1089.3652.



22

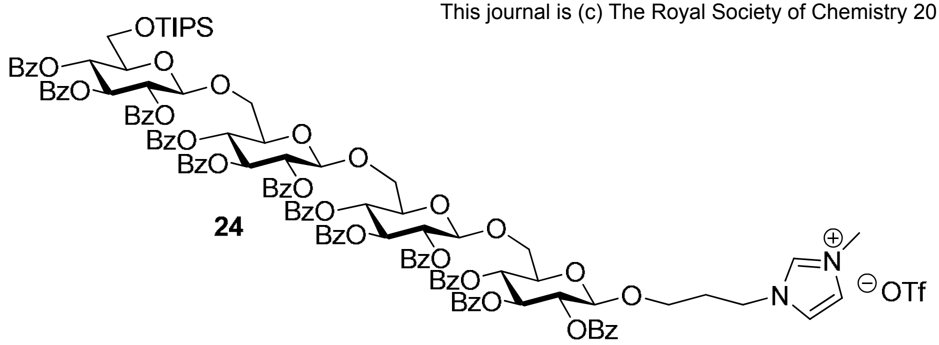
3-(3-Methylimidazolium)-propyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside trifluoromethanesulfonate* (22)** *Following general glycosylation* ***Method B. From **21** (240 mg, 0.22 mmol) to give **22** (172 mg, 94%). ^{1}HNMR ($CDCl_3$, 500 MHz, ppm) : δ = 9.19 (s, 1H, $NC\underline{H}N$), 8.09-7.18 (m, 47H, 45H (Ph) + 2H (imidazole), 5.95 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3), 5.89 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3), 5.87 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3), 5.67 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4), 5.49 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 5.31 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4), 5.28 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 5.23 (t, 1H, $J_{4,3}$ =

$J_{4,5}$ = 9.5 Hz, H-4), 5.12 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 4.91 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.88 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.78 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^B), 4.48-4.23 (m, 2H, $C\underline{H}_2N$), 4.14-3.62 (m, 14H in which a singulet at 4.07 (3H, $C\underline{H}_3N$), 3xH-5, 6xH-6, $C\underline{H}_2O$), 2.19-2.14 (m, 2H, $OCH_2C\underline{H}_2$), 1.05-0.91 (m, 21H, *TIPS*). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) : 165.8, 165.5, 165.4, 165.3, 165.2, 165.1, 165.1, 165.0, (CO), 137.1 ($N\underline{C}HN$), 133.6, 133.5, 133.4, 133.3, 133.2, 133.1 (C_q, Ph), 130.0, 129.9, 129.8, 129.7, 129.7, 129.6, 129.5,129.2, 129.1, 129.0, 128.9, 129.9, 128.8, 128.6, 128.4, 128.4, 128.2, 128.2, 128.1, 123.8, 123. ($\underline{C}H$, *aromatic*), 102.2, 101.9, 100.3 (3 x C-1), 76.1, 73.2, 73.0, 72.4, 72.3, 72.2, 71.8, 71.6, 69.7, 69.5, 69.2, 68.2, 64.6, 62.8, 46.5 ($\underline{C}H_2N$), 36.4 ($N\underline{C}H_3$), 29.8 ($OCH_2\underline{C}H_2$), 17.8, 11.7 (TIPS). HRMS-ESI for $C_{97}H_{99}N_2O_{25}Si^+$ (M^+), calcd : 1719.6325, found: 1719.6301.



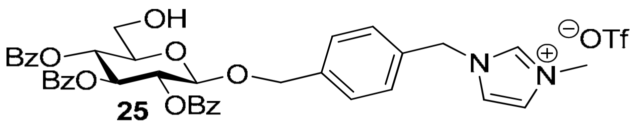
23

***3-(3-Methylimidazolium)-propyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside trifluoromethanesulfonate* (23).** *Following general OTIPS removal.* From **22** (228 mg, 0.13 mmol) to give **23** (200 mg, 97%). ^{1}HNMR ($CDCl_3$, 400 MHz, ppm) : δ = 9.14 (s, 1H, $NC\underline{H}N$), 8.02-7.24 (m, 47H, 45H (Ph) + 2H (imidazole), 5.90 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3), 5.89 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3), 5.74 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3), 5.44 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4), 5.41 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4), 5.33 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4), 5.30 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 5.27 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 4.97 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 4.85 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.84 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.74 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1) 4.52-4.39 (m, 2H), 4.14-3.62 (m, 14H in which s at 4.07 (3H, $C\underline{H}_3N$), 2.12 (bs, 2H, $OCH_2C\underline{H}_2$). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) : δ = 165.8, 165.7, 165.5, 165.5, 165.4, 165.0, 165.0, 164.9, 164.8 (CO), 137.8 ($N\underline{C}HN$), 133.6, 133.4, 133.3, 133.3, 133.2, 133.1, 133.0 (C_q, Ph), 129.9, 129.8, 129.8, 129.7, 129.6, 129.6, 129.5,129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 12.8.3, 128.2, 128.1, 123.7, 123.10 ($\underline{C}H$, aromatic), 101.6, 101.0, 100.3 (3xC-1), 77.2, 74.7, 72.9, 72.8, 72.4, 72.3, 71.8, 71.7, 71.6, 69.3, 69.1, 68.7, 67.4, 65.5, 60.7, 47.3 ($\underline{C}H_2N$), 37.1 ($N\underline{C}H_3$), 29.6 ($OCH_2\underline{C}H_2$). HRMS-ESI for $C_{88}H_{79}N_2O_{25}$ (M^+), calcul: 1563.4964, found: 1563.4966.



24

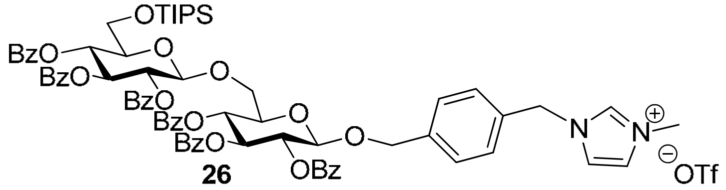
3-(3-Methylimidazolium)-propyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranosyl)- β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside trifluoromethanesulfonate **(24).** *Following general glycosylation* ***Method B.*** From **23** (60 mg, 0.04 mmol) to give **24** (85 mg, 88%). ^{1}HNMR ($CDCl_3$, 500 MHz) : 9.13 (s, 1H, NC<u>H</u>N), 8.02-7.24 (m, 62H, 60 H (Ph) + 2H (imidazole), 5.94 (t, 1H, J = 9.5 Hz), 5.88 (t, 1H, J = 9.5 Hz,), 5.87 (t, 1H, J= 9.5 Hz), 5.84 (t, 1H, J= 9.5 Hz), 5.67 (t, 1H, J= 9.5 Hz), 5.49 (t, 1H, J= 9.5 Hz), 5.45 (dd, 1H, J = 8.0, 9.5 Hz) 5.39 (dd, 1H, J = 8.0, 9.5 Hz), 5.24 (dd, 1H, J = 8.0, 9.5 Hz), 5.19-5.11 (m, 3H), 5.04 (d, J = 8.0 Hz) 5.03 (d, J = 8.0 Hz), 5.75 (d, J = 8.0 Hz), 5.44 (d, J = 8.0 Hz), 4.94-4.42 (m, 1H), 4.32-4.30 (m, 2H), 4.15 (t, 2H, J = 9.0 Hz, C<u>H</u>$_2$N), 4.04 (s, 3H, C<u>H</u>$_3$N), 4.00-3.95 (m, 2H), 3.84-3.63 (m, 9H), 3.52-3.48 (m, 1H), 2.11 (bs, 2H, OCH$_2$C<u>H</u>$_2$), 0.88-0.81 (m, 21H, *TIPS*). ^{13}C NMR ($CDCl_3$, 125 MHz) : 165.8, 165.7, 165.6, 165.5, 165.5, 165.4, 165.3, 165.2, 165.0, 164.9, 164.7 (CO), 137.2 (N<u>C</u>HN), 133.5, 133.4, 133.3, 133.2, 133.1, 133.1, 133.0, 132.9, 132.8, 132.7 (C_q, Ph), 130.1, 130.0, 129.9, 129.8, 129.8, 129.8, 129.7, 129.7, 129.6, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 12.8.3, 128.2, 128.1, 123.8, 123.7 (<u>C</u>H $_{aromatic}$), 102.9, 102.3, 101.9, 100.2 (4 x C-1), 76.3, 73.7, 72.9, 72.8, 72.6, 72.5, 72.3, 72.1, 72.0, 71.8, 71.7, 71.6, 71.1, 71.0, 70.4, 70.2, 69.9, 69.8, 69.6, 69.3, 64.7, 63.0, 46.9 (<u>C</u>H$_2$N), 36.6 (N<u>C</u>H$_3$), 29.0 (OCH$_2$<u>C</u>H$_2$), 17.9, 11.7 (*TIPS*). HRMS-ESI for $C_{88}H_{79}N_2O_{25}$ (M^+), calcd: 2193.76155, found: 2193.76154. Elemental analysis ($C_{125}H_{121}F_3N_2O_{36}SSi$): (%) Calculated: C, 64.04; H, 5.20; N, 1.19 S, 1.37; Found: C, 64.13; H, 5.32; N, 1.28; S, 1.42.



25

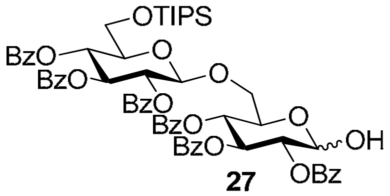
***4-(1-Methyl-3-methyleneimidazolium)benzyl 2,3,4-tri-O-benzoyl-6-β-D-glucopyranoside trifluoromethanesulfonate* (25)**

Following ***Method A*** for TIPS deprotection: from **14** (186 mg, 0.19 mmol) to give **25** (150 mg, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) : δ = 9.09 (s, 1H, NC<u>H</u>N), 7.95-7.94 (m, 4H, Ph), 7.85-7.83 (m, 2H, Ph), 7.56-7.52 (m, 2H, Ph), 7.46-7.38 (m, 5H, Ph), 7.31-7.26 (m, 8H, Ph + 2H imidazolium), 5.84 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3), 5.54 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 5.52 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4), 5.29 (bs, 2H, C<u>H</u>$_2$N), 4.95 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.93 (d, 1H, J = 12.0 Hz, OC<u>H</u>$_2$), 4.73 (d, 1H, J = 12.0 Hz, OC<u>H</u>$_2$), 3.89-3.84 (m, 6H, H-6a, H-5 + 3.89 s, CH_3N), 3.75 (bd, 1H J = 11.0 Hz, H-6b). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) : δ = 166.0, 165.7, 165.2 (CO), 138.4, 136.6 (C_q, Ph), 133.7, 133.5, 133.3, 132.4, 129.9, 129.7, 129.6, 129.0, 128.9, 128.8, 128.6, 128.5, 128.3 (CH, *aromatic*), 123.7, 122.1 (CH, *imidazolium*), 100.3 (C-1), 74.6 (C-5), 72.8 (C-3), 71.9 (C-2), 70.7 (OCH_2), 69.4 (C-4), 61.2 (C-6), 53.1 (CH_2N), 36.5 (NCH_3). ESI-HRMS (M^+) for $C_{39}H_{37}N_2O_9^+$ calcd: 677.2494; found: 677.2493.



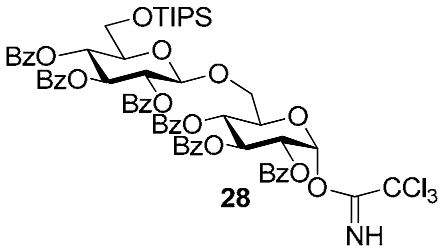
26

***4-(1-Methyl-3-methyleneimidazolium)-benzyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranosyl)-β-D-glucopyranoside trifluoromethanesulfonate* (26).** *Following general Glycosylation **Method B**:* From **25** (58 mg, 0.09 mmol) to give **26** (100 mg, 98%). ^{1}HNMR ($CDCl_3$, 500 MHz, ppm) : δ = 9.26 (s, 1H, NCHN), 7.93-7.86 (m, 8H, Ph), 7.81-7.80 (m, 2H, Ph), 7.77-7.75 (m, 2H, Ph), 7.55-7.49 (m, 4H, Ph), 7.45-7.35 (m, 12H, Ph), 7.29-7.24 (m, 4H, Ph), 7.21 (t, 1H, J = 1.5 Hz, NCHCHN), 7.19 (d, 2H J = 8.5 Hz, CH, OCH_2*Ph*), 7.13 (t, 1H, J = 1.5 Hz, NCHCHN), 7.09 (d, 2H J = 8.5 Hz, CH, OCH_2*Ph*), 5.85 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3^A) 5.79 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3^B), 5.56 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4^A), 5.50 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2^A), 5.43 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2^B), 5.34 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4^B), 5.31 (bs, 2H, CH_2N), 4.93 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^A), 4.68 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^B), 4.50 (d, 1H, J = 13.0 Hz, OCH_2), 4.28 (d, 1H, J = 13.0 Hz, OCH_2), 4.12 (dd, $J_{6a,5}$ = 1.5 Hz, $J_{6a,6b}$ = 10.5 Hz, H-6a^A), 4.03 (dt, $J_{5,6a} = J_{5,6b}$ = 2.0 Hz, $J_{5,4}$ = 9.5 Hz, H-5^B), 3.93 (s, 3H, CH_3N), 3.89-3.83 (m, 3H, H-5^A, H-6a^B, H-6b^B), 3.81 (dd, 1H, $J_{6b,5}$ = 8.0 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6b^A), 0.95-0.88 (m, 21H, *TIPS*).^{13}C NMR ($CDCl_3$, 125 MHz, ppm) : δ = 165.9, 165.6, 165.3, 165.2, 165.1, 165.0, (CO), 138.4, 137.2, 133.5, 133.4, 133.3, 133.2, 133.1, 133.0, 131.9, 129.8, 129.7, 129.6, 129.5, 129.2, 129.1, 129.0, 128.9, 129.8, 128.7, 128.6, 128.4, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 123.4, 121.7 (CH, *aromatic*), 101.2 (C-1^A), 99.4 (C-1^B), 75.4 (C-5^A), 73.7 (C-5^B) 73.3 (C-3^A), 72.8 (C-3^B), 72.2 (C-2^A), 71.8 (C-2^B), 69.8 (C-4^B), 69.6 (OCH_2), 69.2 (C-4^A), 68.7 (C-6^A), 62.5 (C-6^B), 53.2 (CH_2N), 36.5 (NCH_3), 17.7, 11.7 (*TIPS*). ESI-HRMS for $C_{75}H_{79}N_2O_{17}Si^+$ (M^+) calcd: 1307.5143; found: 1307.5142. Elemental analysis ($C_{76}H_{79}F_3N_2O_{20}SSi$): (%) Calculated: C, 62.62; H, 5.46; N, 1.92; S, 2.20; Found: C, 62.77; H, 5.56; N, 1.98; S, 2.32.



27

2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranosyl)-β-D-glucopyranose **(27).** To a solution of **26** (60 mg, 0.05 mmol) in HCOOH/EtOH (0.3 mL/6 mL) was added black Pd/C and the mixture was stirred under hydrogen atmosphere for 2 days. The obtained residue was filtered through celite and purified over silica gel column chromatography with a gradient from 9/1 to7/3 (n-hexane/EtOAc) to give **26 (**33 mg, 70%) as α/β (3.3/1) mixture. R_f = 0.3 (*n*-hexane/EtOAc: 7/3). ($CDCl_3$, 500 MHz, ppm) : δ = 7.97-7.16 (m, 39 H, Ph), 6.02 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3^{A} α), 5.81 (1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3^{B} α), 5.79 (t, 0.3H , $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3^{A} β), 5.73 (t, 0.3H , $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3^{B} β), 5.48 (t, 0.3H , $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4^{B} β), 5.45 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4^{B} α), 5.37 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2^{B} α), 5.37 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2^{B} β), 5.26 (t, 0.3H , $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4^{A} β), 5.23 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1^{A} α), 5.22 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4^{A} α 1H, 5.13 (dd, 1H, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2^{A} β), 5.02 (dd, 1H, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, H-2^{A} α), 4.88 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^{B} β), 4.85 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^{B} α), 7.45 (d, 0.3 H, J1,2 = 8.0 Hz, H-1^{A} β), 4.38 (brt, 1H, J = 9.0 Hz, H-5^{A} α), 4.07-4.03 (m, 0.3H, H-5^{A} β) 3.99 (brd, 0.3H, $J_{6a,6b}$ = 11.5 Hz, H-6a^{A} β), 3.97 (brd, 1H, $J_{6a,6b}$ = 11.5 Hz, H-6a^{A} α), 3.89-3.86 (m, 0.3 H, , H-5^{B} β), 3.84-3.77 (m, 3.6H, H-6a^{B}, H-6b^{B}, H-5^{B} α, H-6a^{B}, H-6b^{B} β), 3.72 (dd, 0.3 H, $J_{6b,5}$ = 7.5 Hz, $J_{6b,6a}$ = 11.5 Hz, H-6b^{A} β), 3.68 (dd, 0.3 H, $J_{6b,5}$ = 8.5 Hz, $J_{6b,6a}$ = 11.5 Hz, H-6b^{A} α), 0.95-0.88 (m, 27.3 H, *TIPS*). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) : δ = 166.2, 165.8, 165.7, 165.4, 165.3, 165.1 (CO), 133.5, 133.4, 133.3, 133.2, 133.1, 133.0, 129.9, 129.8, 129.7, 129.7, 129.6, 129.2, 129.1, 129.0. 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.2 ($\underline{C}$H, *aromatic*), 102.0 (C-1^{B} α), 101.7 (C-1^{B} β), 95.6 (C-1^{A} β), 90.1 (C-1^{A} α), 75.6 (C-5^{B} α), 75.5 (C-5^{B} β) , 74.1, 73.8, 72.9, 72.4, 72.3, 70.0, 69.7, 69.5, 69.4, 69.3, 68.9, 65.8, 62.9, 62.8, 17.8, 11.9 (*TIPS*) HRMS-ESI for $C_{63}H_{66}NaO_{17}Si^+$ (MNa^+) calcd: 1145.3967; found: 1145.3961.



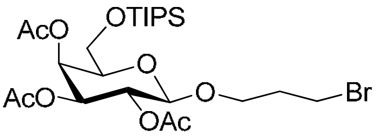
28

2,3,4-tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-6-O-triisopropylsilyl-β-D-glucopyranosyl)-β-D-glucopyranosyl trichloroacetimidate **(28).** To a solution of hemiacetal **27** (30 mg, 0.03 mmol) in dry CH_2Cl_2

(1 mL) was respectively added trichloroacetonitrile (27 µL, 10 eq), DBU (4 µL, 1 eq) and the solution was stirred for 10 h at room temperature. After evaporation of the solvent, the residue was purified by flash chromatography (8/2 : n-hexane/EtOAc) to give **28** (28 mg, 83%). $R_f = 0.6$ (7/3:n-hexane/EtOAc). ^{1}HNMR ($CDCl_3$, 500 MHz, ppm) : δ = 8.19 (s, 1H, N$\underline{H}$), 7.99-7.72 (m, 10H, Ph), 7.46-7.11 (m, 20H, Ph), 6.59 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1^A), 6.09 (t, 1H, $J_{3,4} = J_{3,2}$ = 10.0 Hz, H-3^A), 5.75 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, H-3^B), 5.45-5.42 (m, 2H, H-4^A, H-4^B), 5.38 (dd, 1H, 2,1 = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2^B), 5.33 (dd, 1H, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, H-2^A), 4.86 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^B), 4.40-4.36 (m, 1H, H-5^B) 4.04 (brd, 1H, $J_{6a,6b}$ = 10.5 Hz, H-6a^B), 3.83-3.71 (m, 4H, H-5^A, H-6a^A, H-6b^A, H-6b^B), 0.94-0.81 (m, 21H, *TIPS*).^{13}C NMR ($CDCl_3$, 125 MHz, ppm) : δ = 165.9, 165.6, 165.3, 165.2, 165.1, 165.0, 164.3 (CO), 160.2 (C=NH), 133.5, 133.4, 133.3, 133.2, 133.0, 132.9 (C_{quart} Ph), 130.0, 129.9, 129.9 129.8, 129.7, 129.7, 129.6, 129.5, 129.3, 128.9, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1 ($\underline{C}$H, *aromatic*), 100.8 (C-1^B), 92.8 (C-1^A), 75.5 (C-5^A), 73.3 (C-3^B), 72.0 (C-5^B), 71.9 (C-2^B), , 70.7 (C-2^A) 70.1 (C-3^A), 69.5 (C-4^A) 68.7 (C-4^B), 67.4 (C-6^A), 62.7 (C-6^B), 17.8, 11.8 (*TIPS*). ESI-HRMS for $C_{65}H_{66}Cl_3NNaO_{17}Si^+$ (MNa^+) calcd: 1288.0363; found: 1288.0359.

References

(1) Broddefalk, J.; Forsgren, M.; Sethson, I.; Kihlberg, J. *J. Org. Chem.* 1999, **64**, 8948.
(2) Schmidt, R. R.; Stumpp, M. *Liebigs Ann. Der Chemie* 1983, 1249.
(3) Joosten, J. A. F.; Loimaranta, V.; Appeldoorn, C. C. M.; Haataja, S.; El Maate, F. A.; Liskamp, R. M. J.; Finne, J.; Pieters, R. J. *J. Med. Chem.* 2004, **47**, 6499.
(4) Fontana, J. D.; Duarte, J. H.; Iacomini, M.; Gorin, P. A. J. *Carbohydr. Res.* 1982, **108**, 221.
(5) Gorin, P. A. J. *Carbohydr. Res.* 1982, **101**, 13.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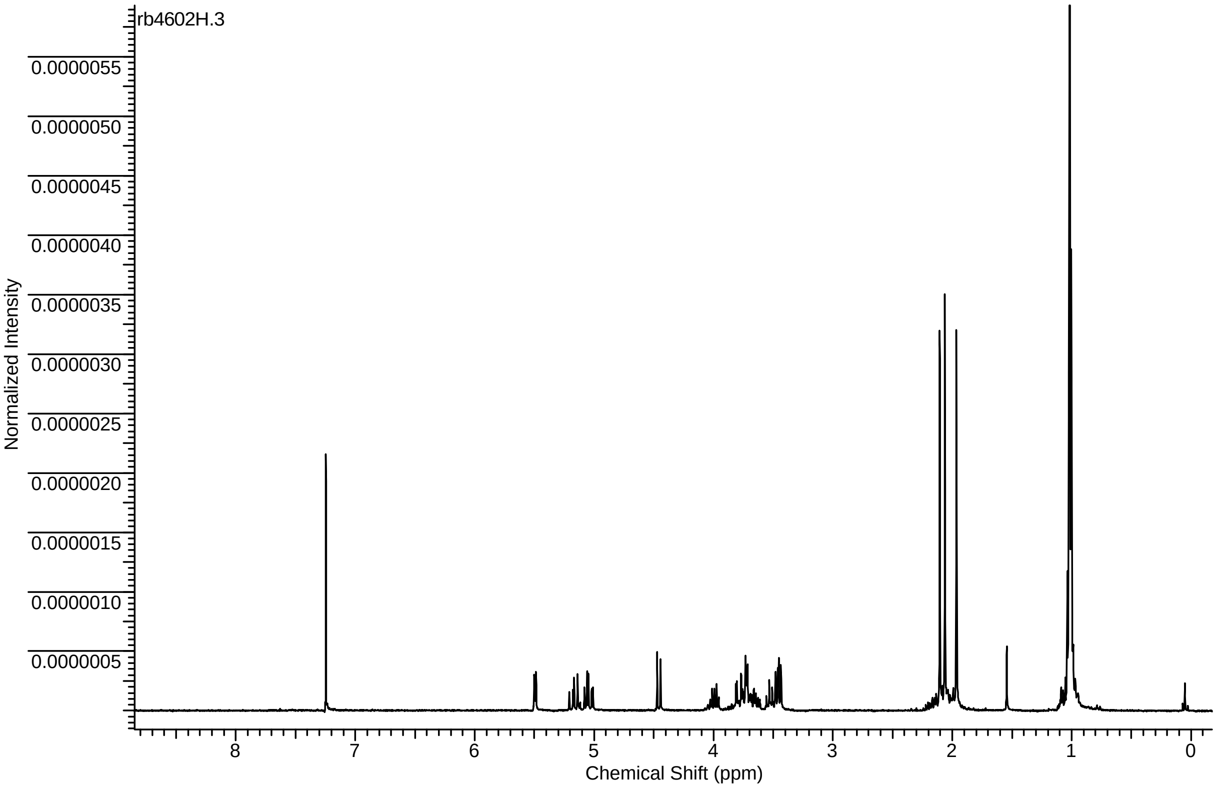
4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4
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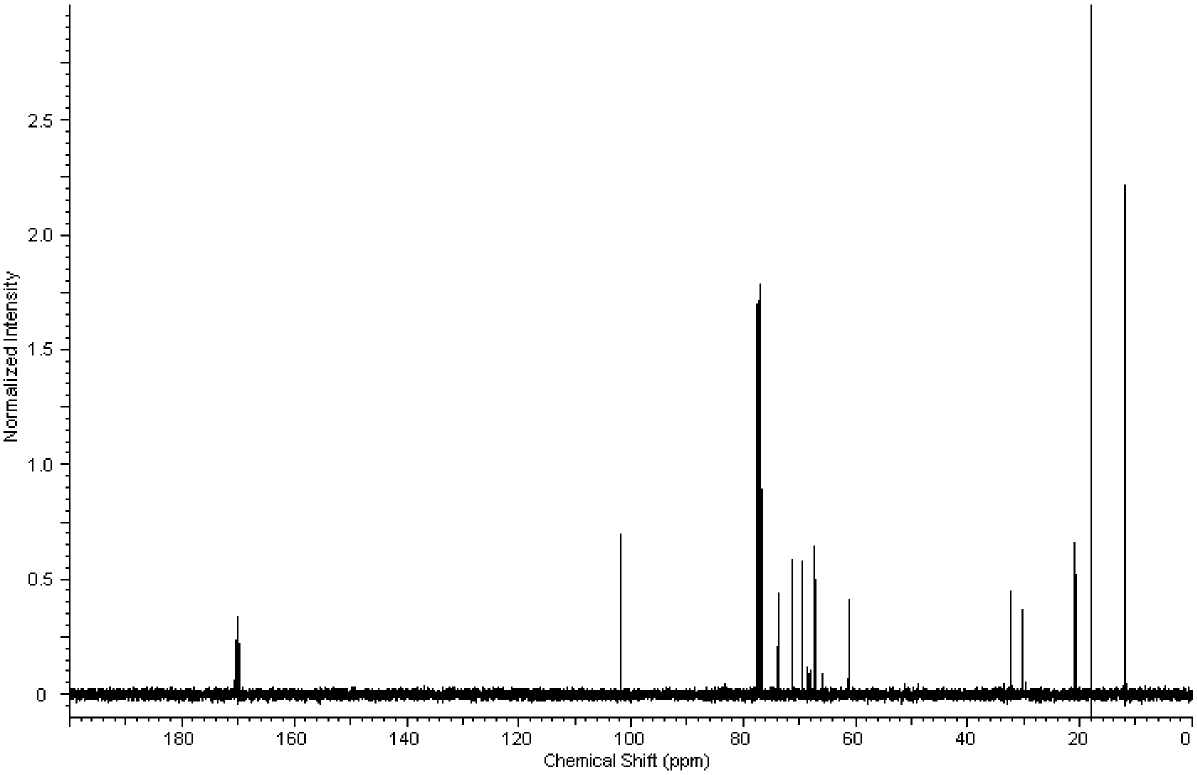
Chemical Shift (ppm)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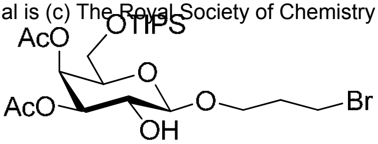
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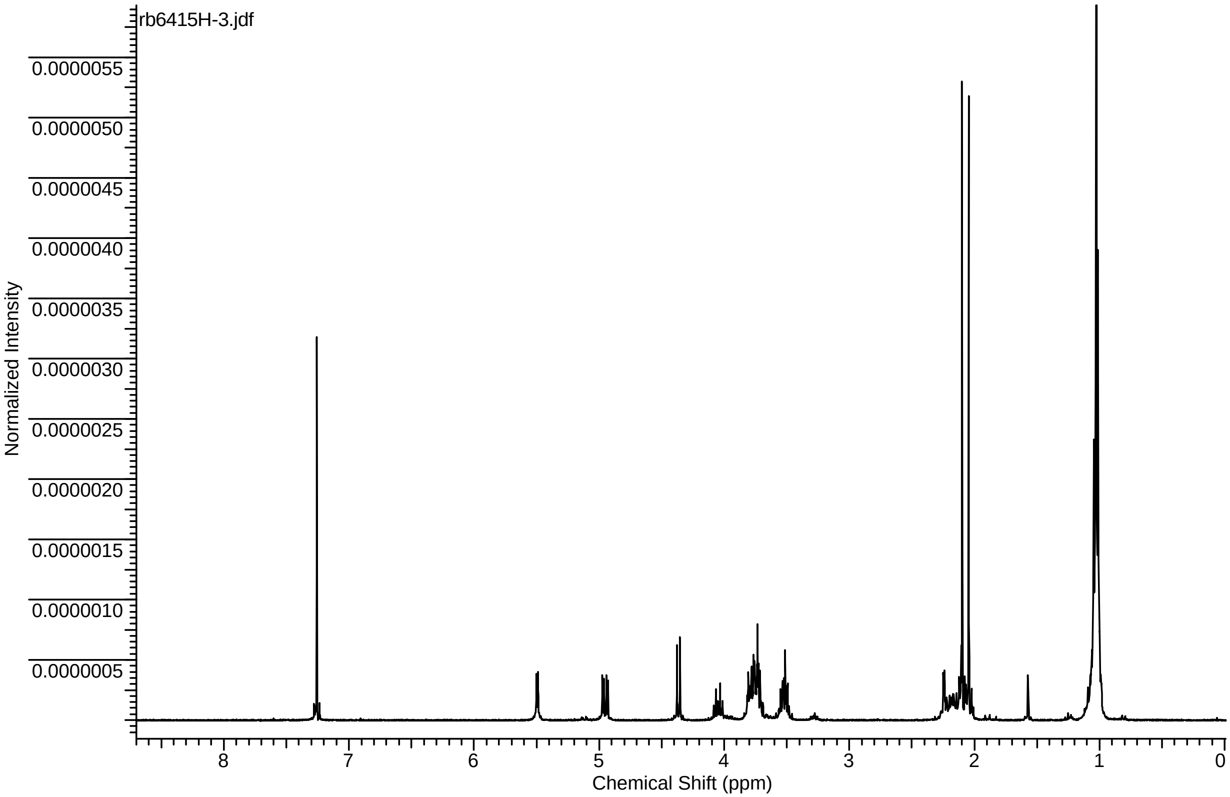
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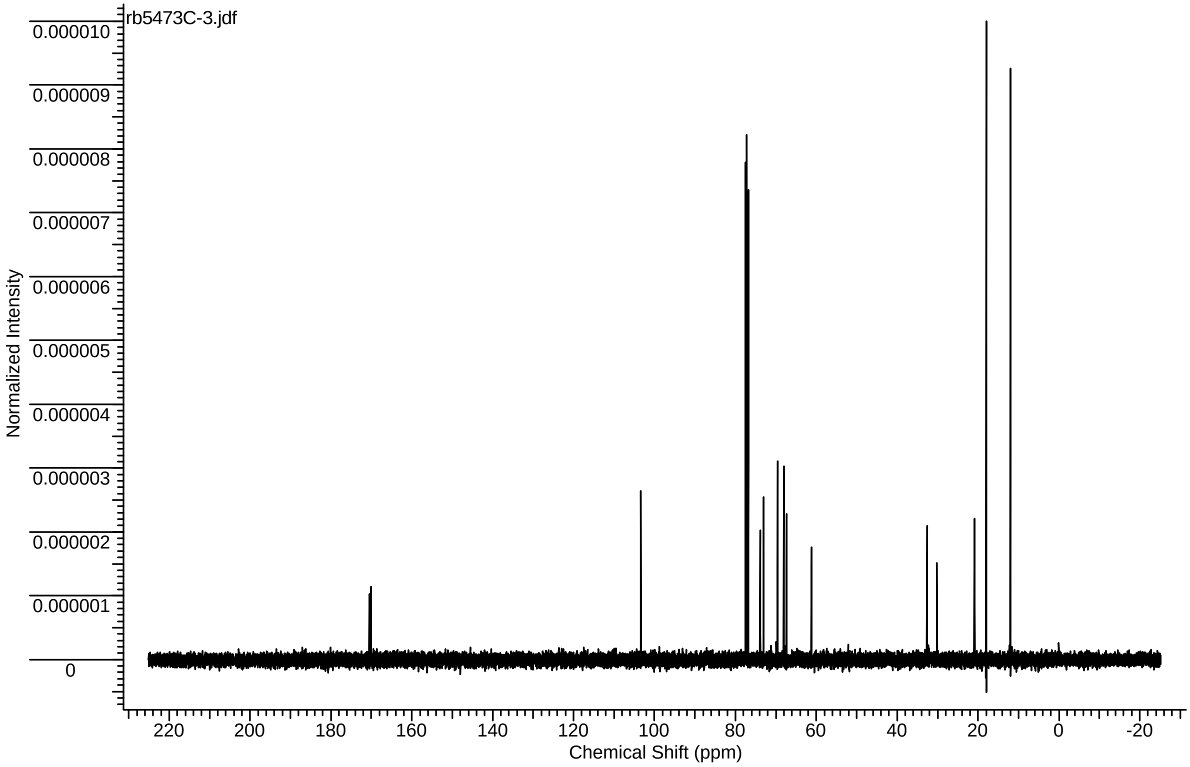
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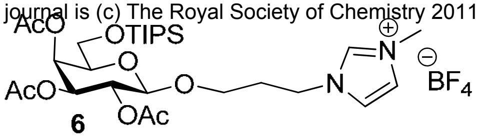
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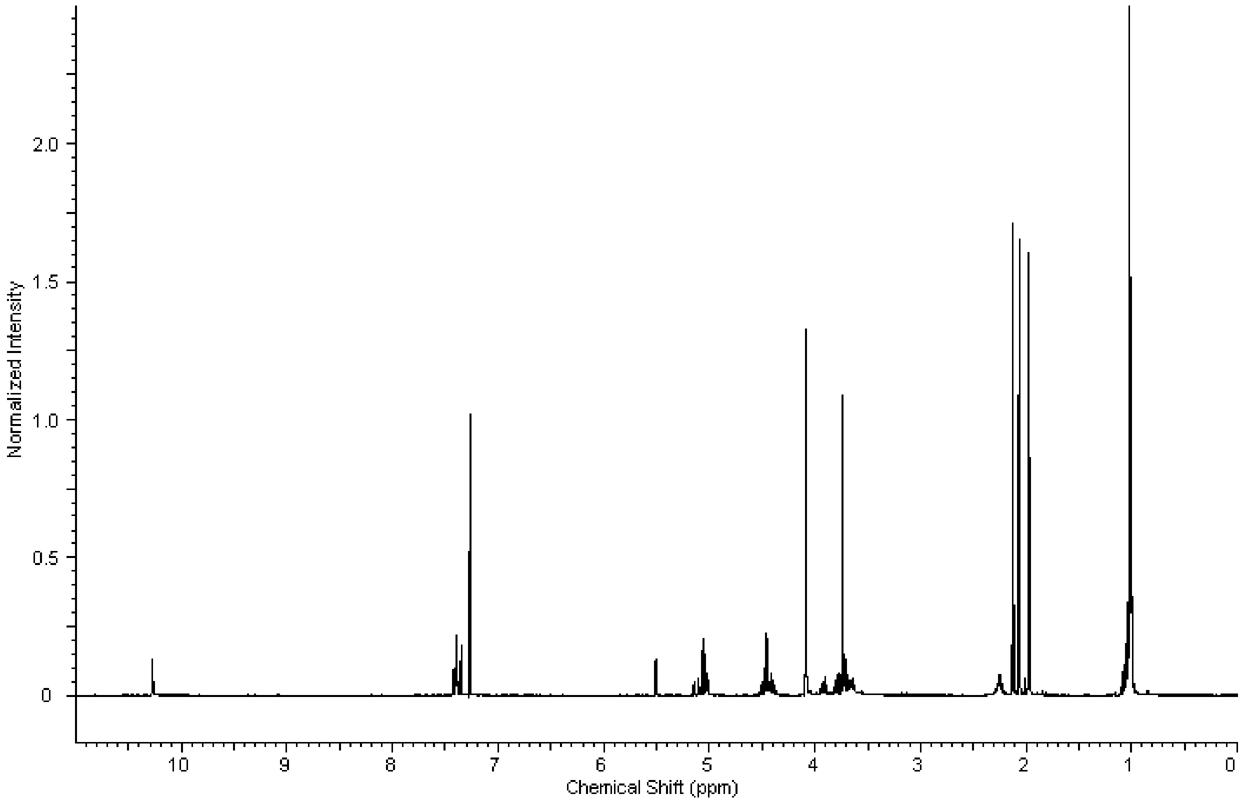
6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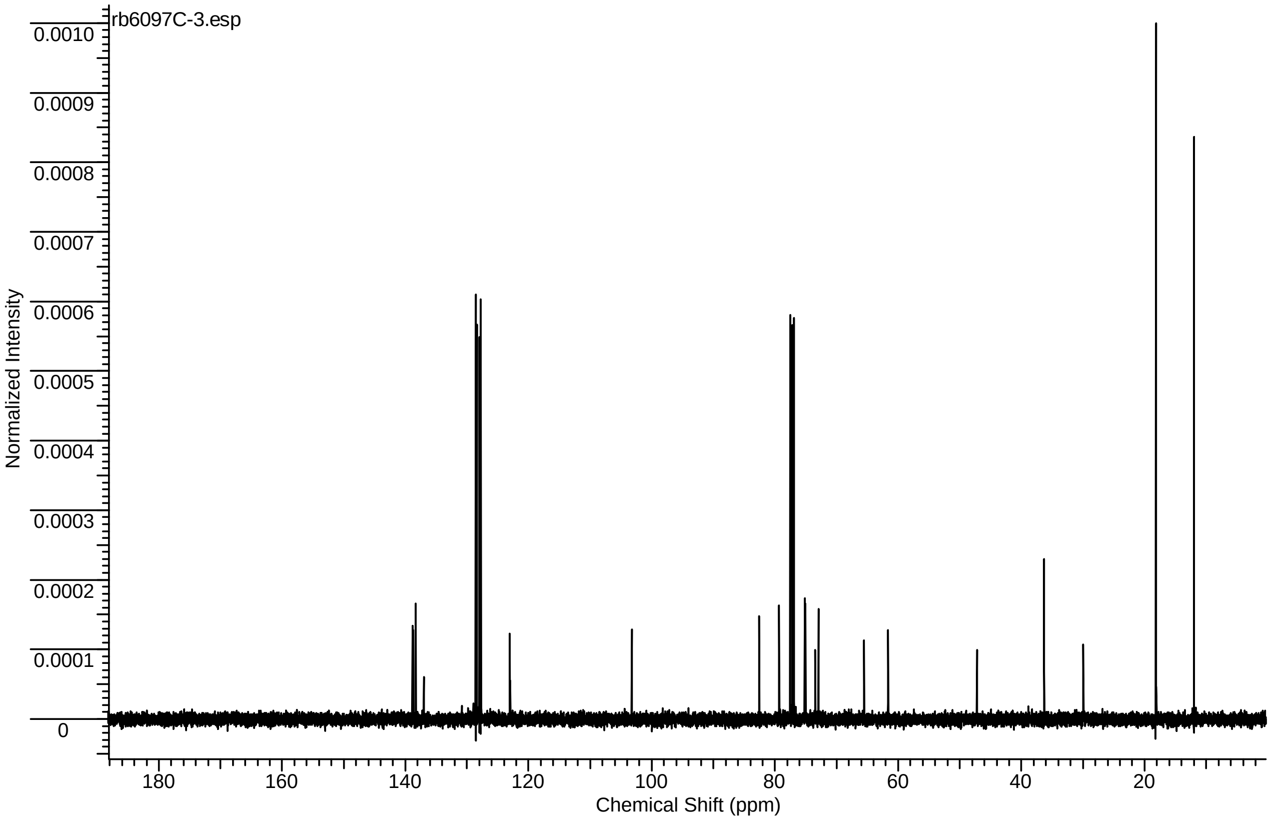
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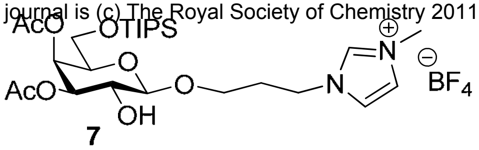
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N
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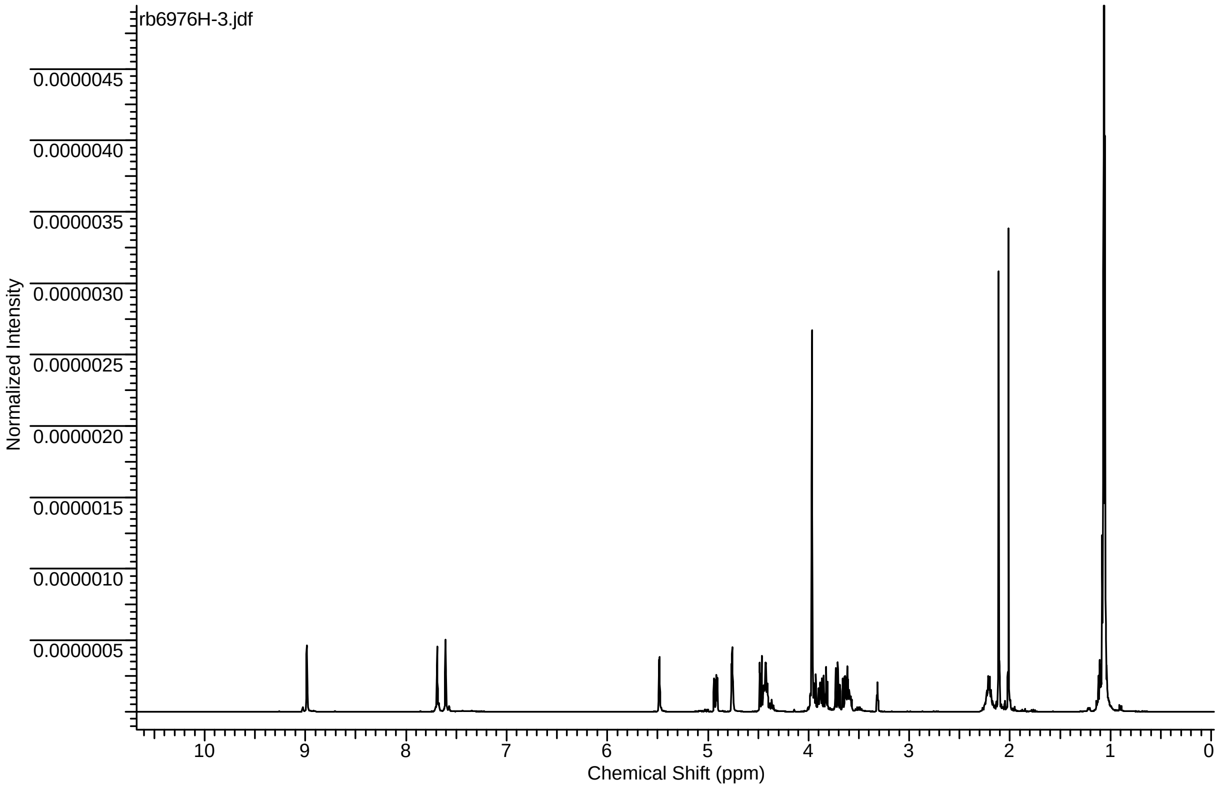
7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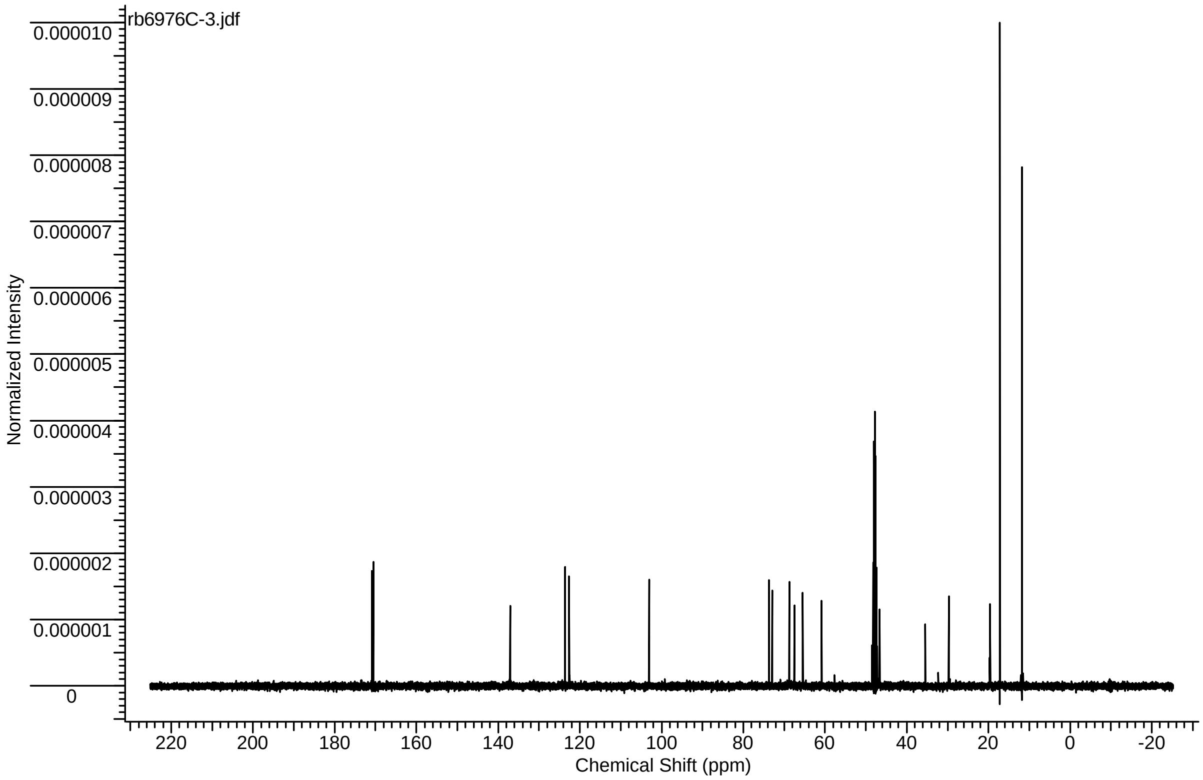
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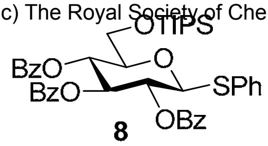
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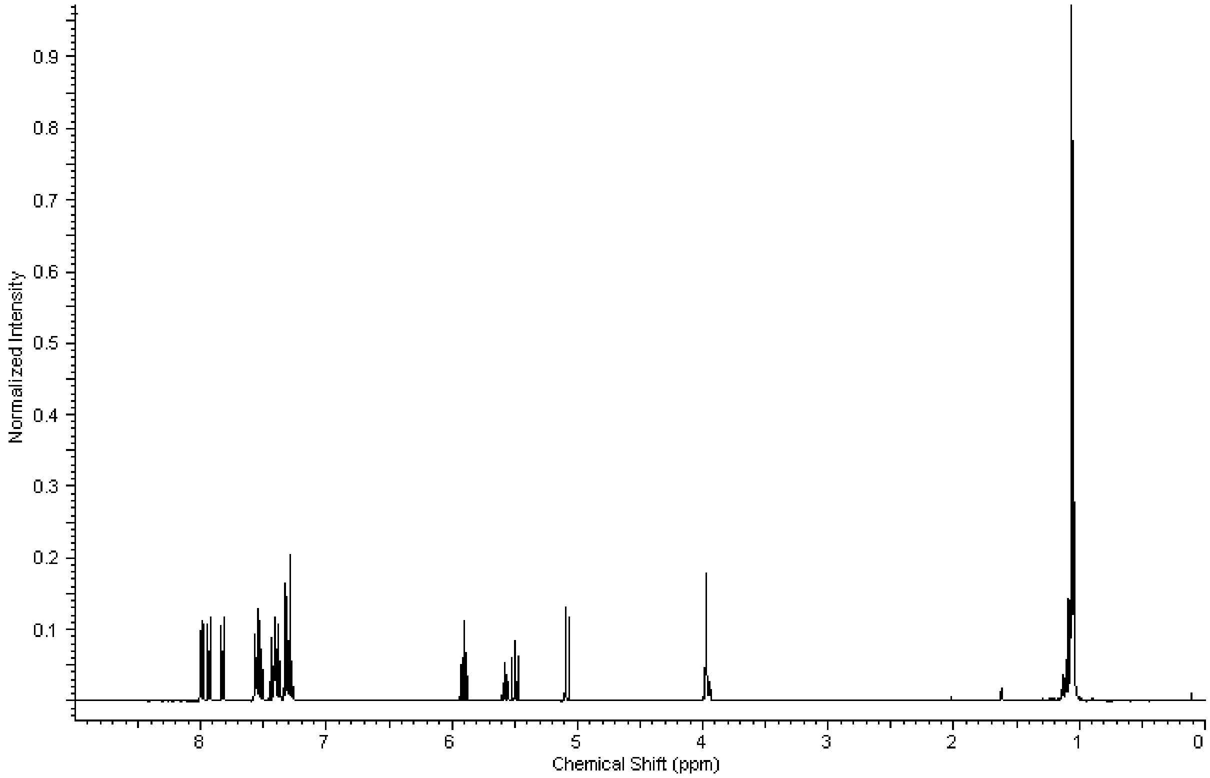
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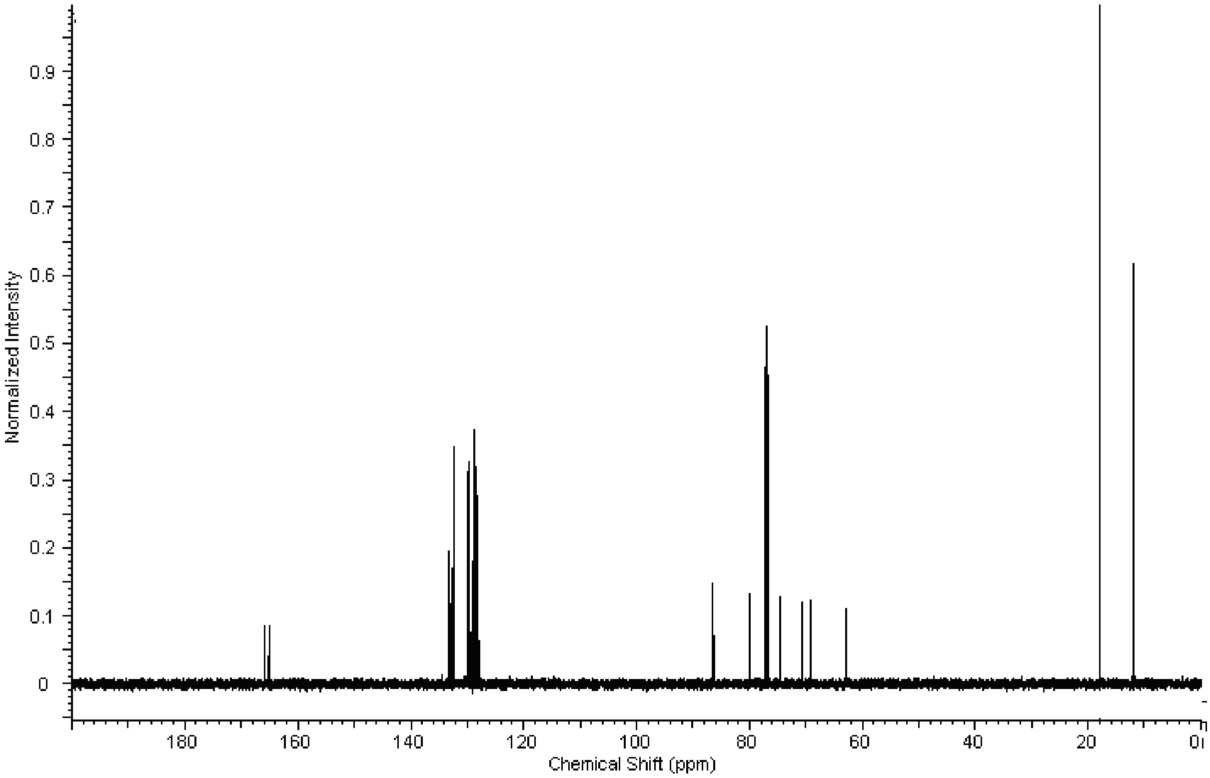
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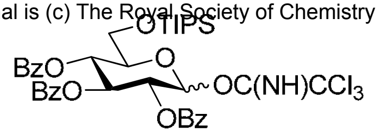
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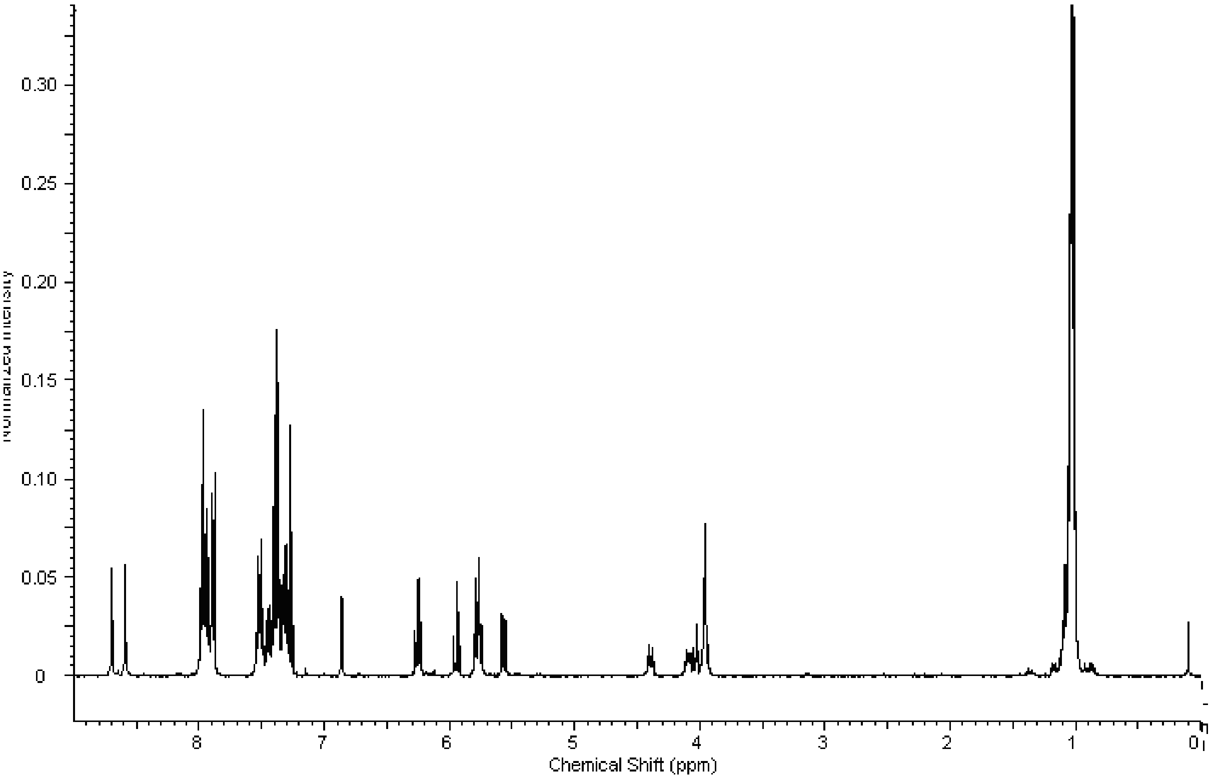
OBz

9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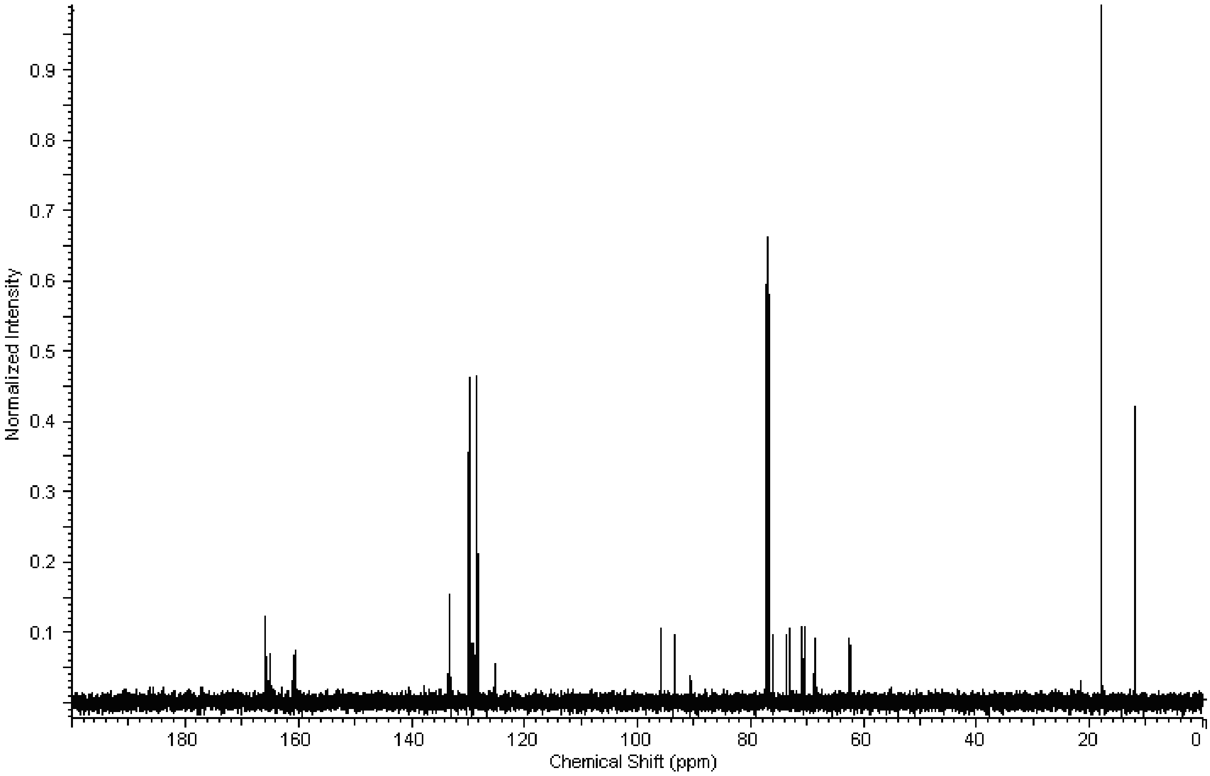
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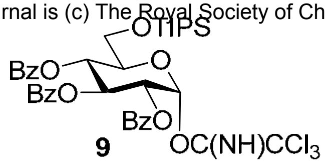
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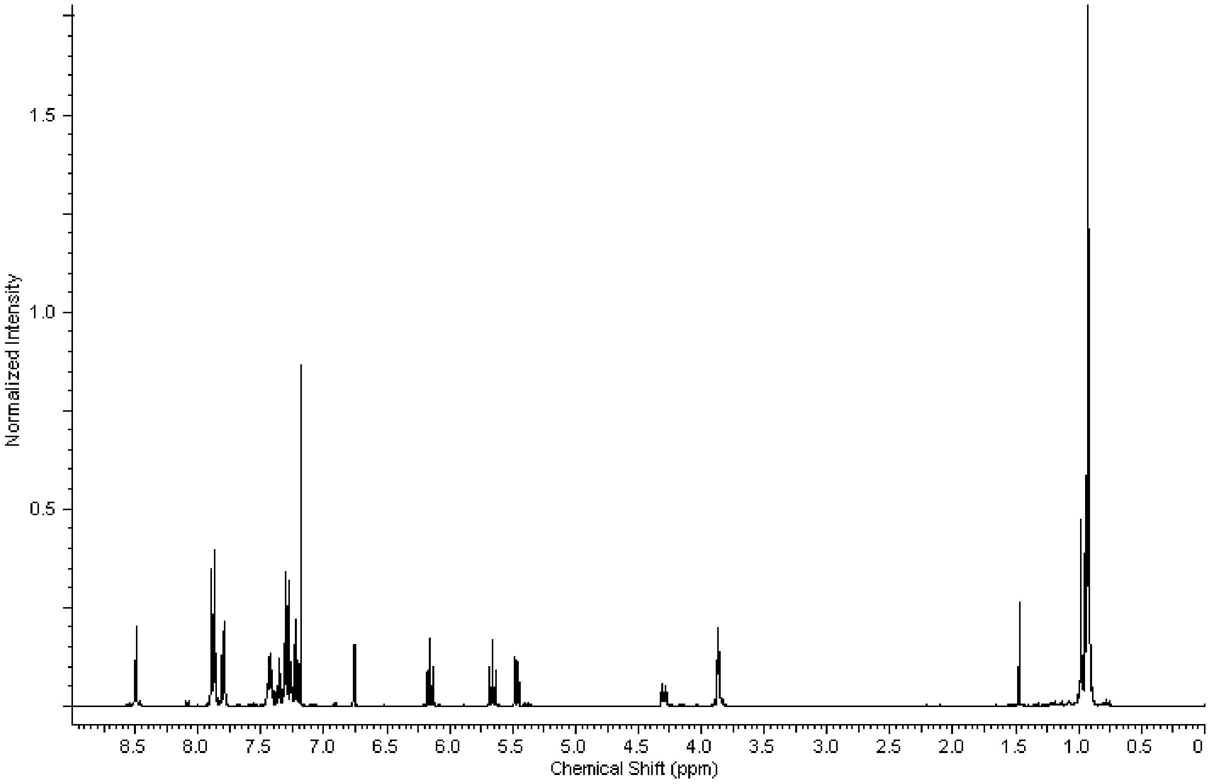
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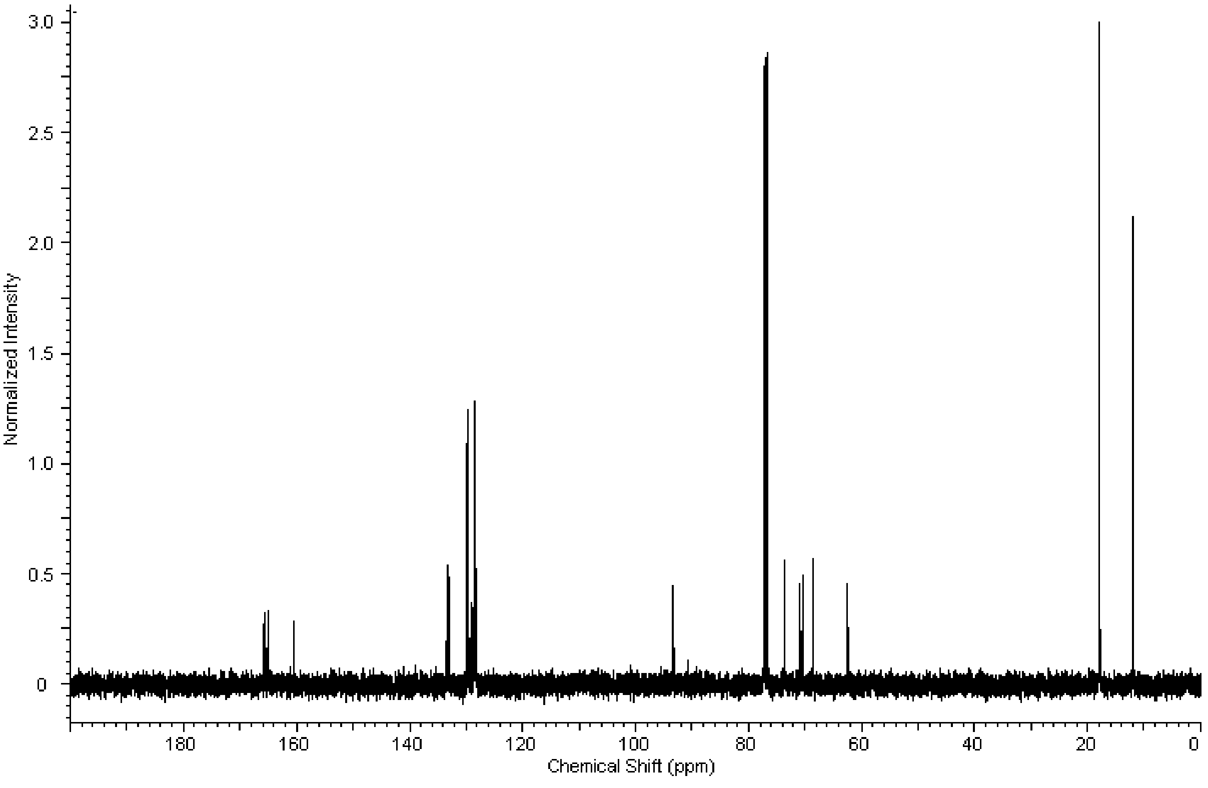
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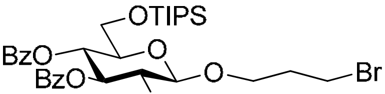
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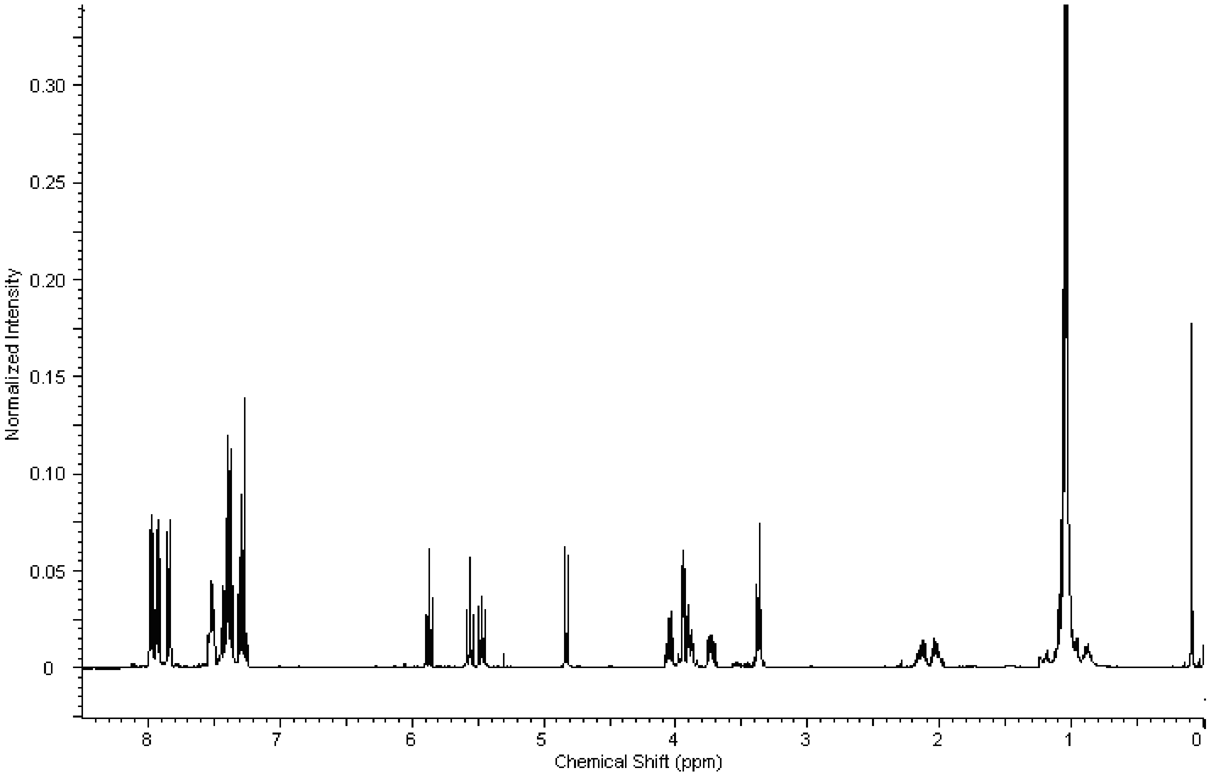
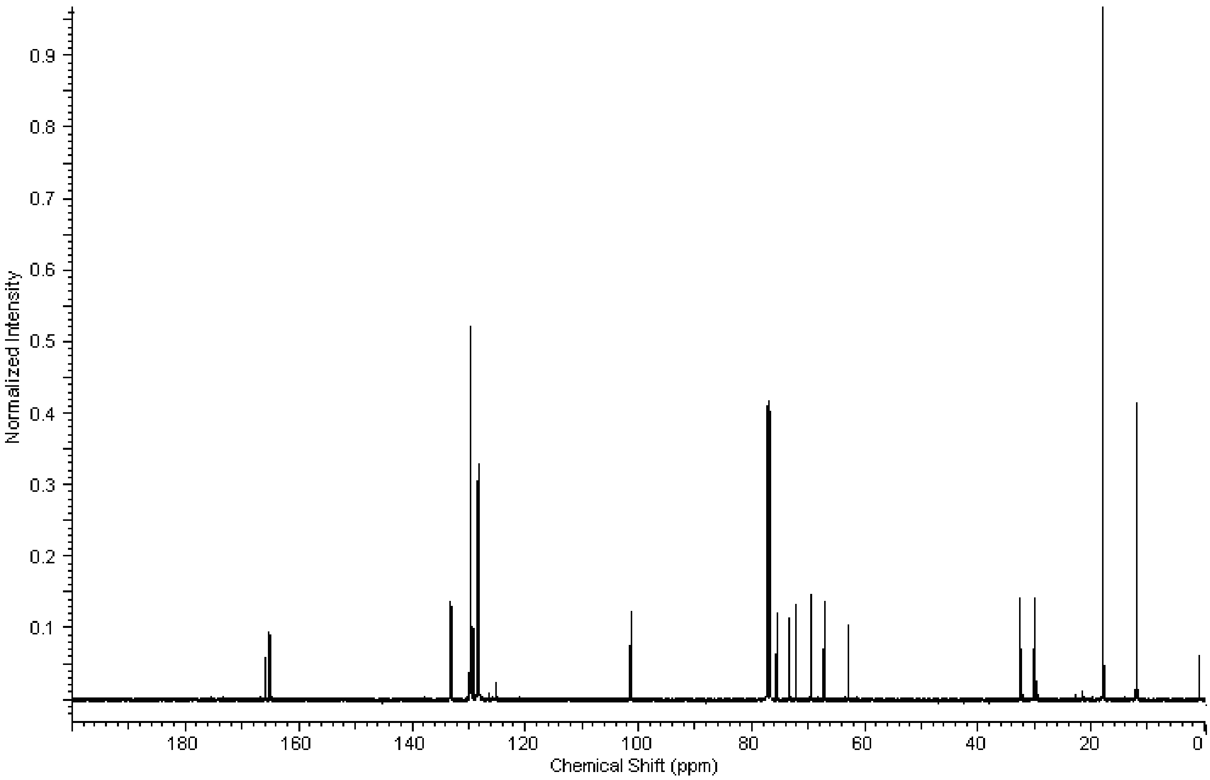
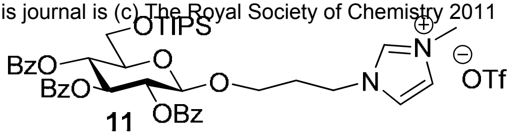
Br

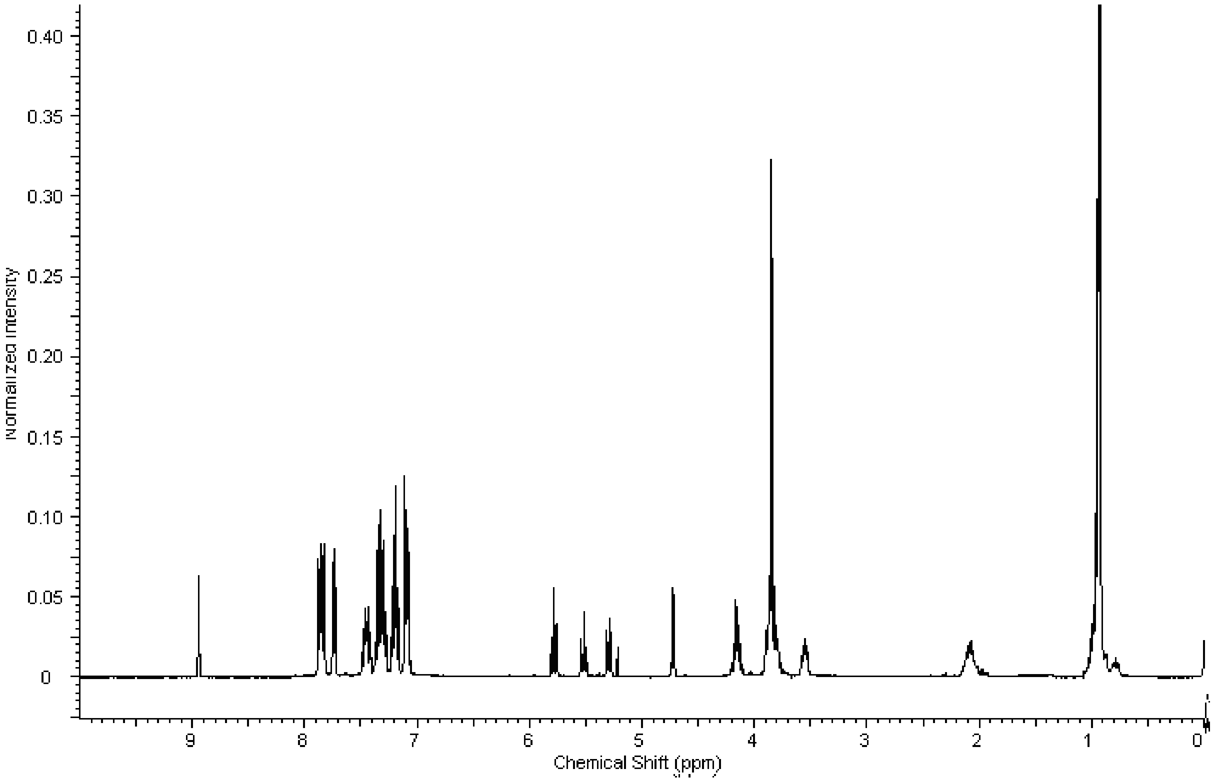
10

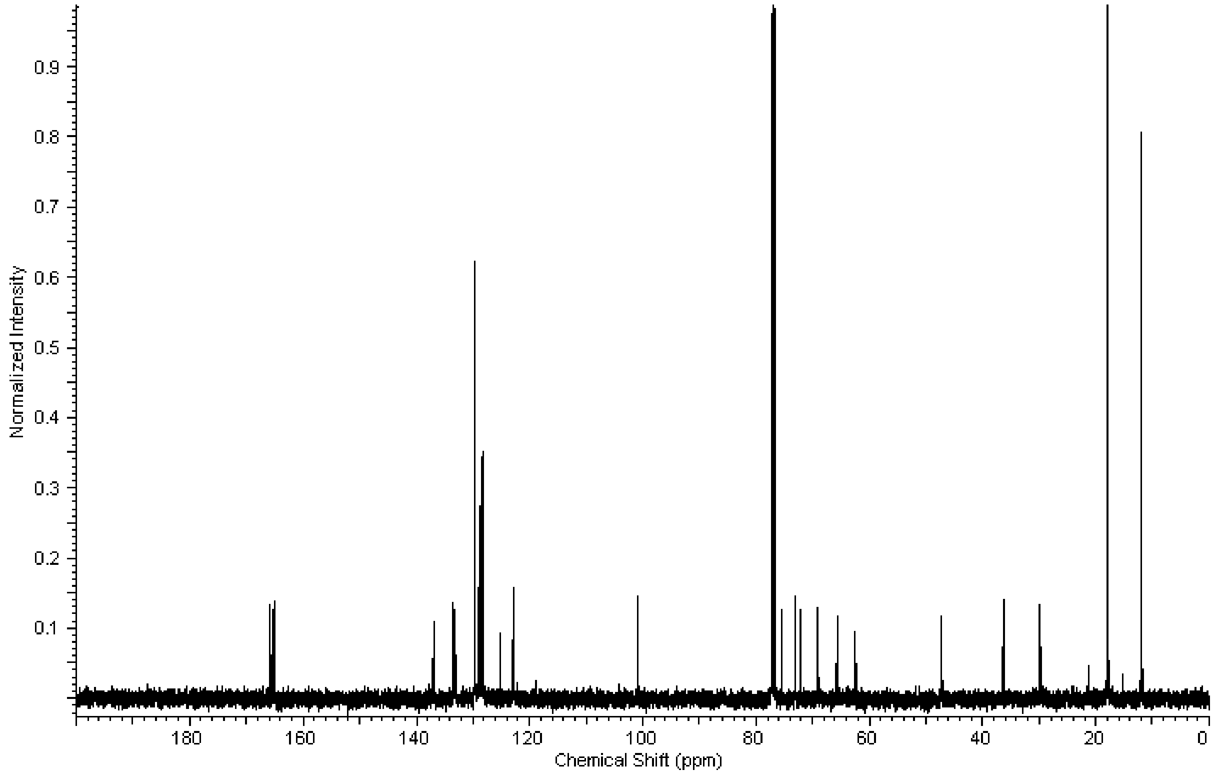

Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

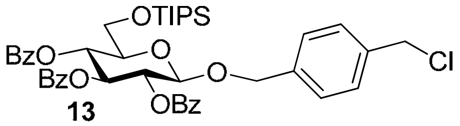

Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


OTIPS
BzO
BzO
O
O
OBz
N
N
⊕
⊖
OTf

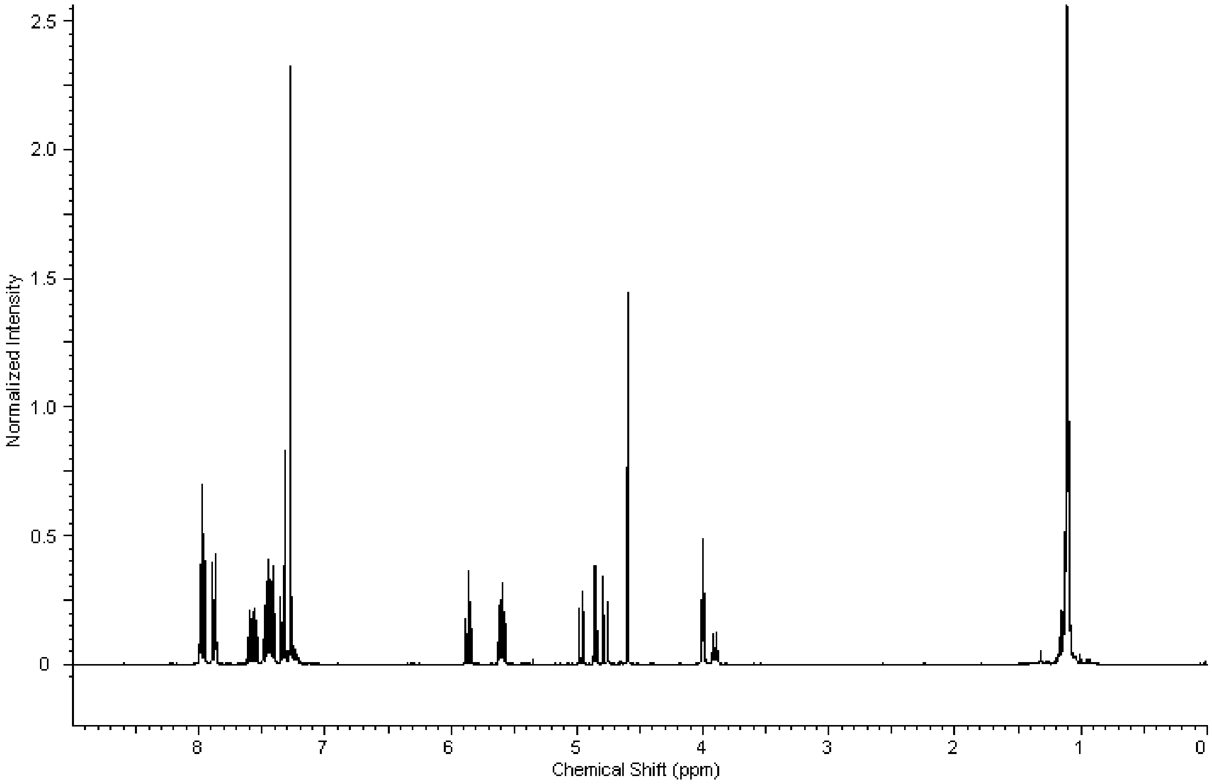
11

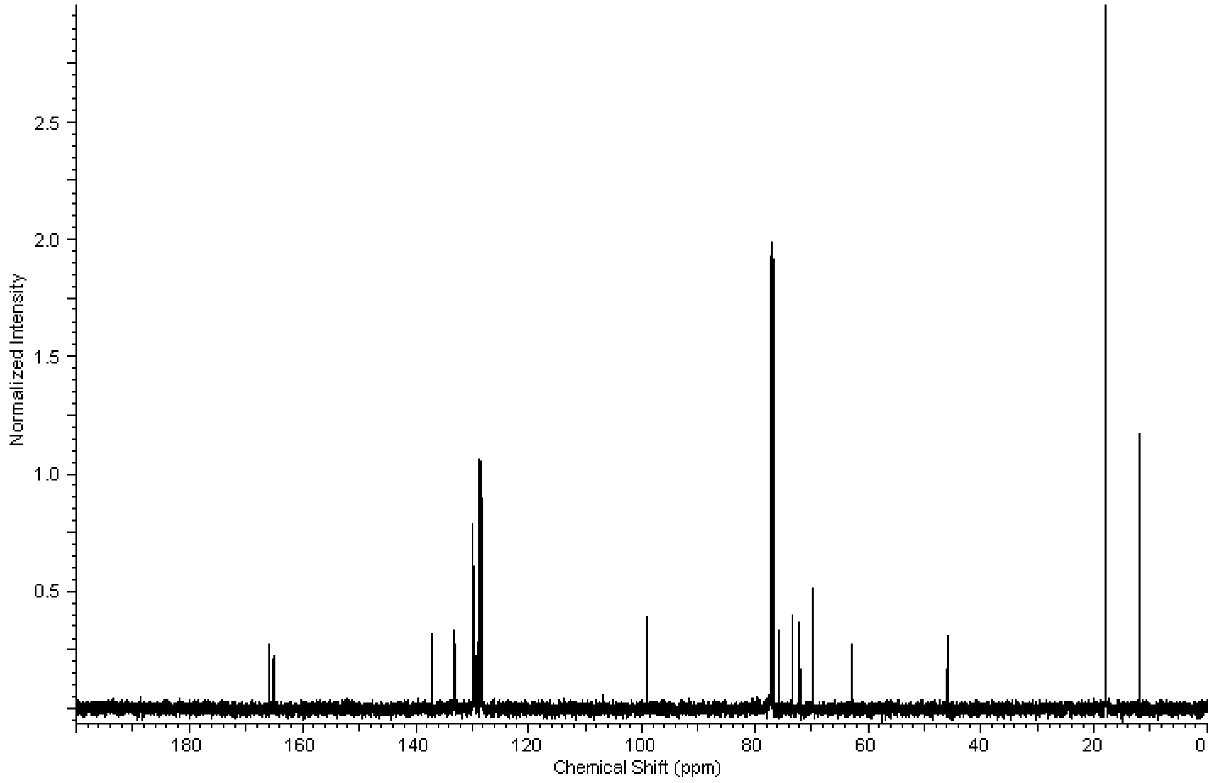

Normalized Intensity
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

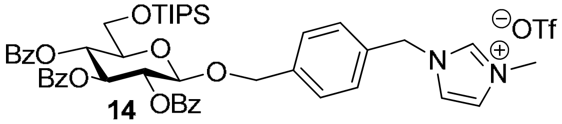

Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


OTIPS
BzO
BzO
O
O
OBz
Cl

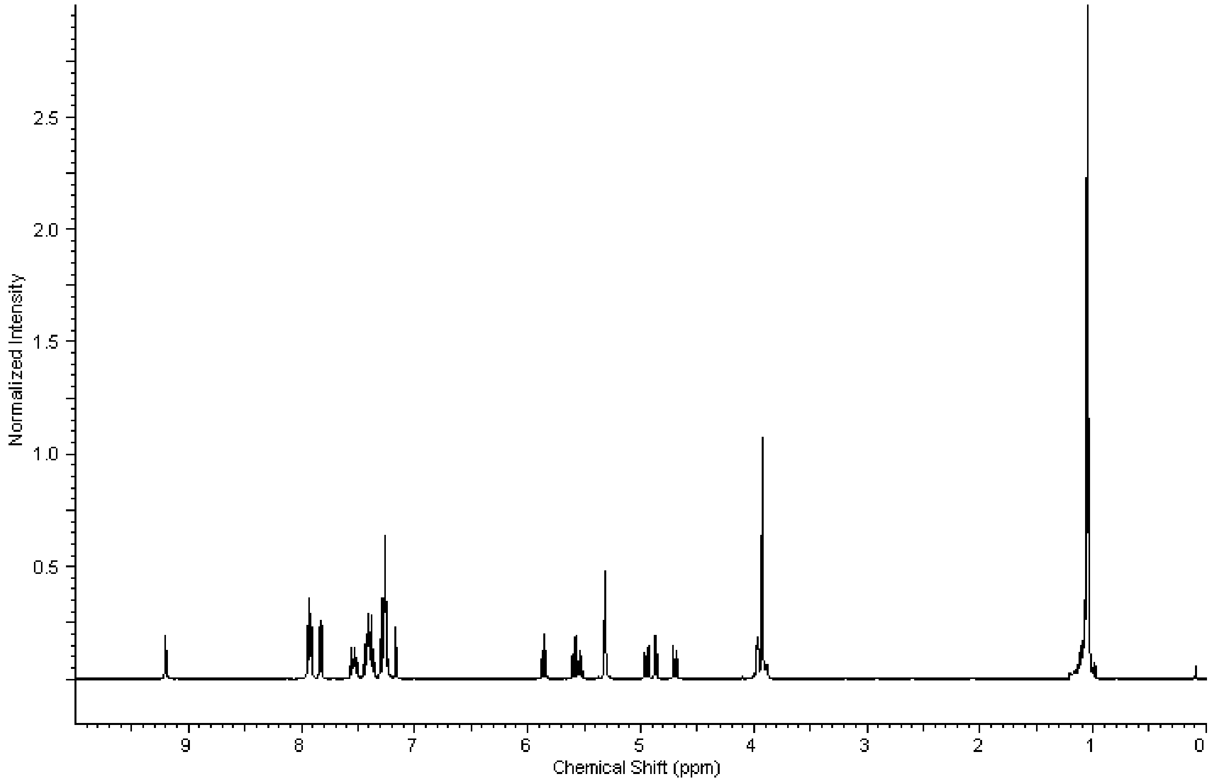
13

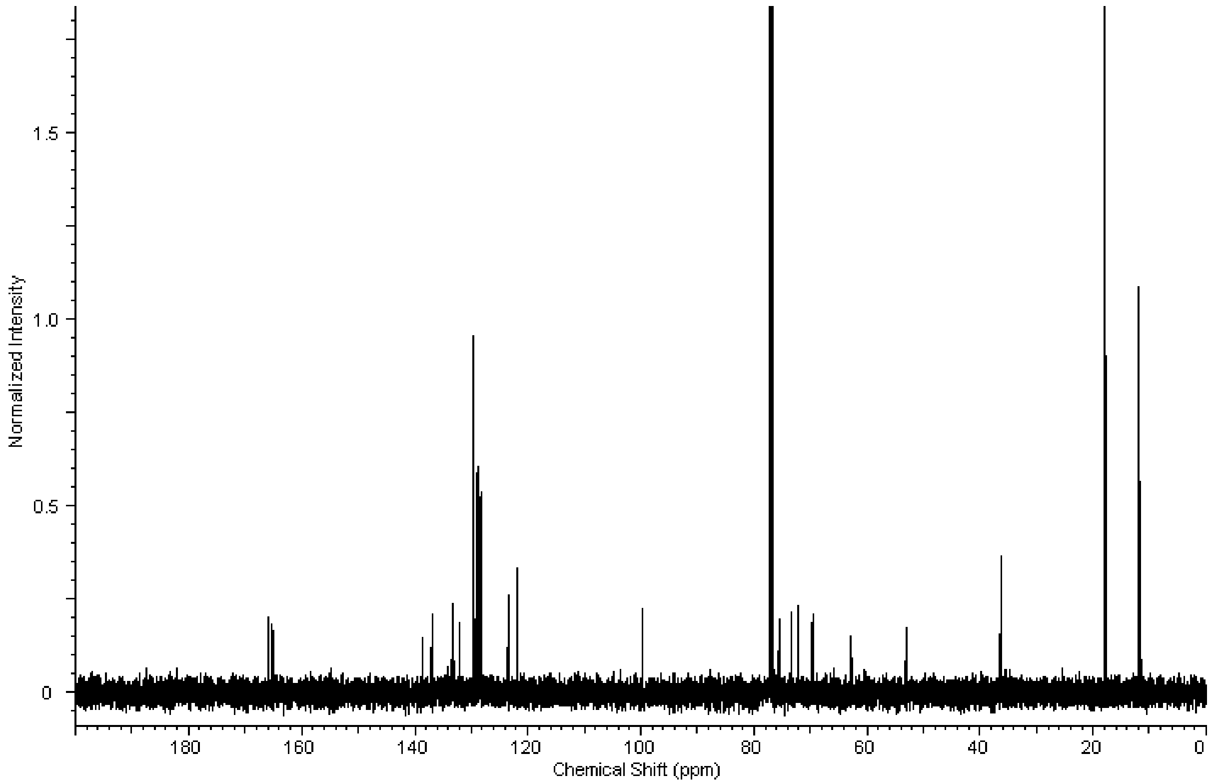

Normalized Intensity
2.5
2.0
1.5
1.0
0.5
0
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

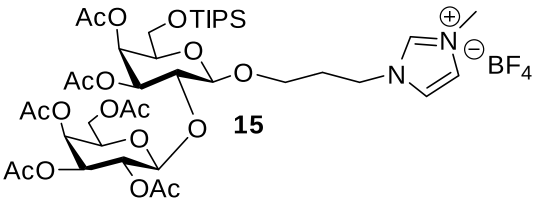

Normalized Intensity
2.5
2.0
1.5
1.0
0.5
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


OTIPS
BzO
BzO
O
OBz
O
N
N
⊕
⊖OTf

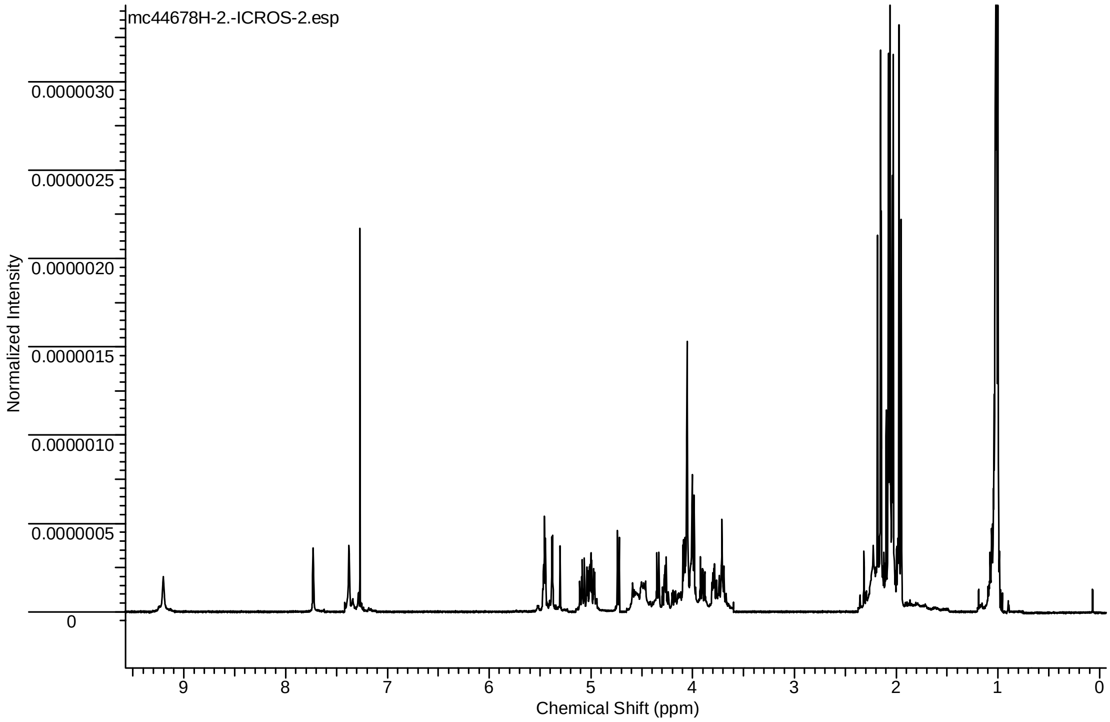
14

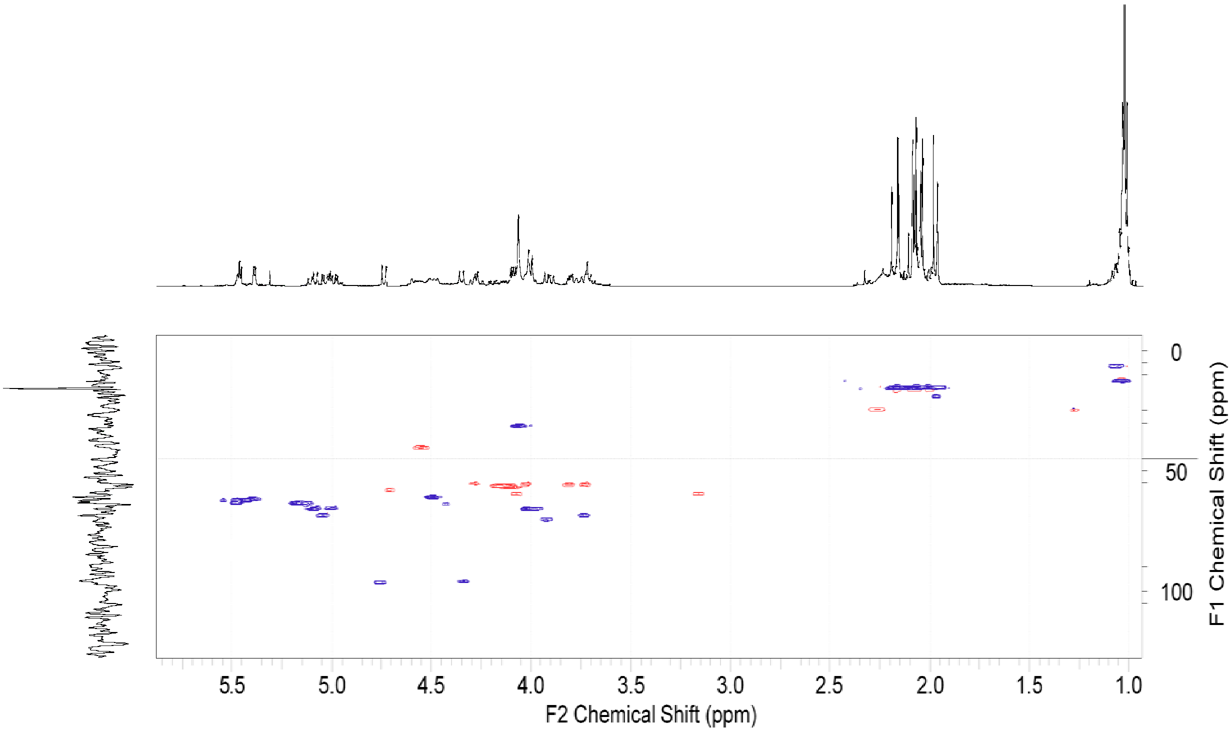

Normalized Intensity
2.5
2.0
1.5
1.0
0.5
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

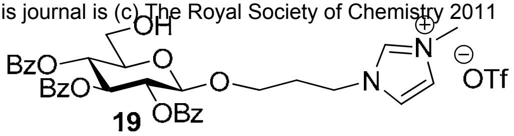

Normalized Intensity
1.5
1.0
0.5
0
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


AcO
OTIPS
O
AcO
O
N
N
BF4
AcO
OAc
O
O
AcO
OAc

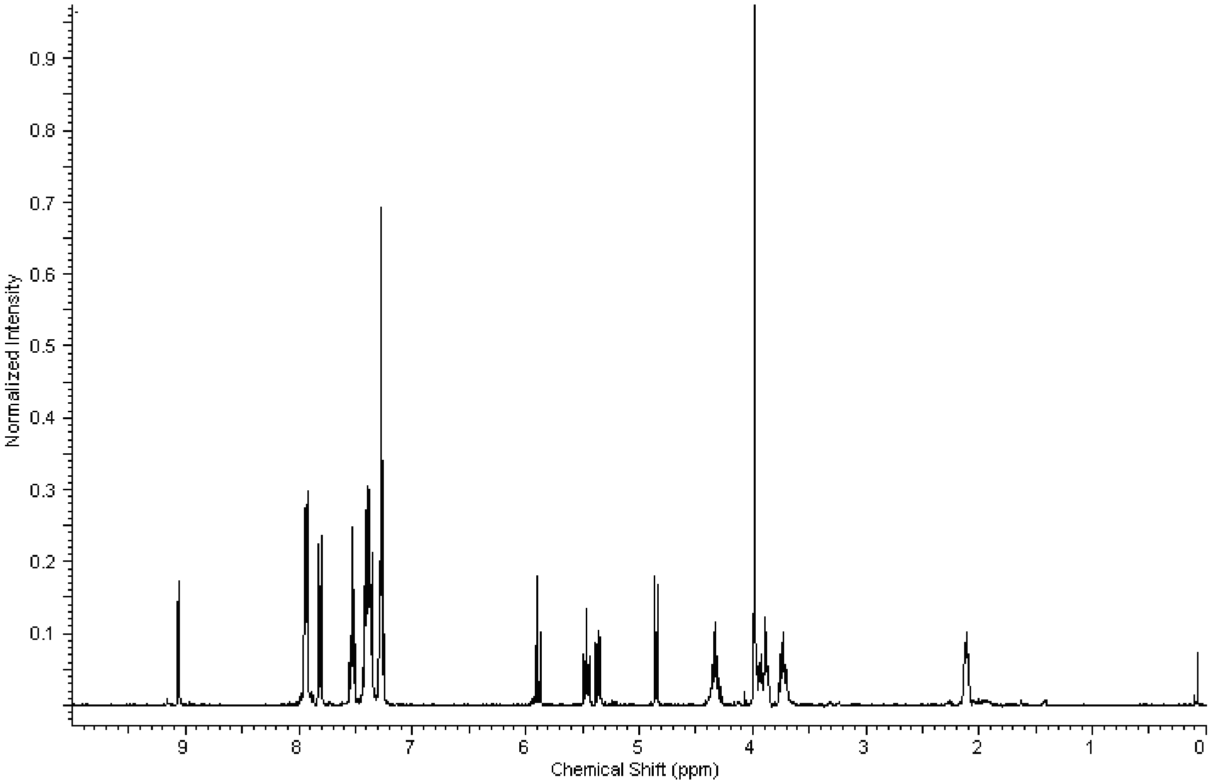
15

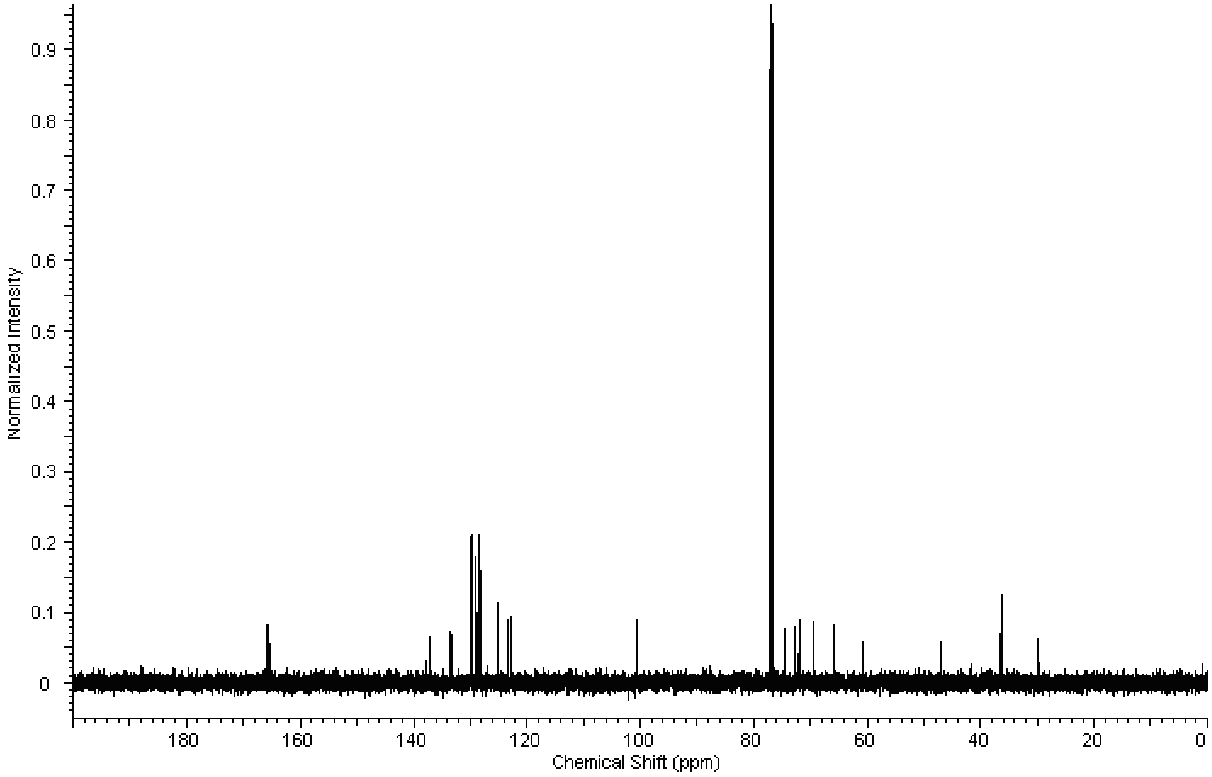

mc44678H-2.-ICROS-2.esp
Normalized Intensity
0.0000030
0.0000025
0.0000020
0.0000015
0.0000010
0.0000005
0
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

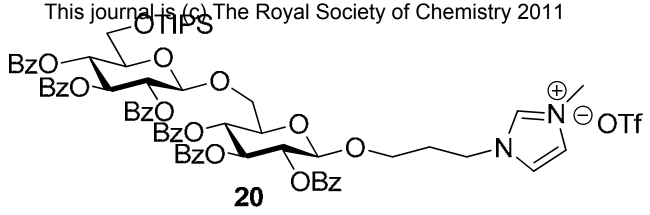

0
50
100
F1 Chemical Shift (ppm)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
F2 Chemical Shift (ppm)


OH
BzO
BzO
O
O
OBz
N
N
⊕
⊖
OTf

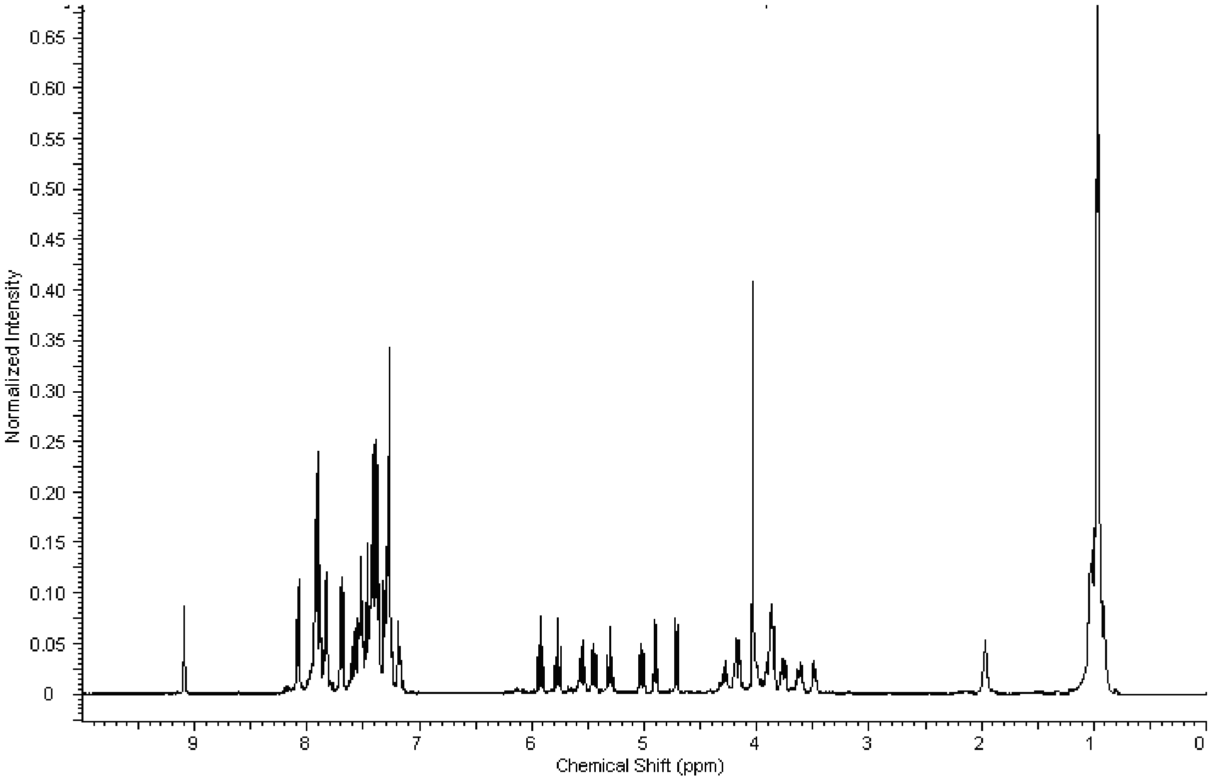
19

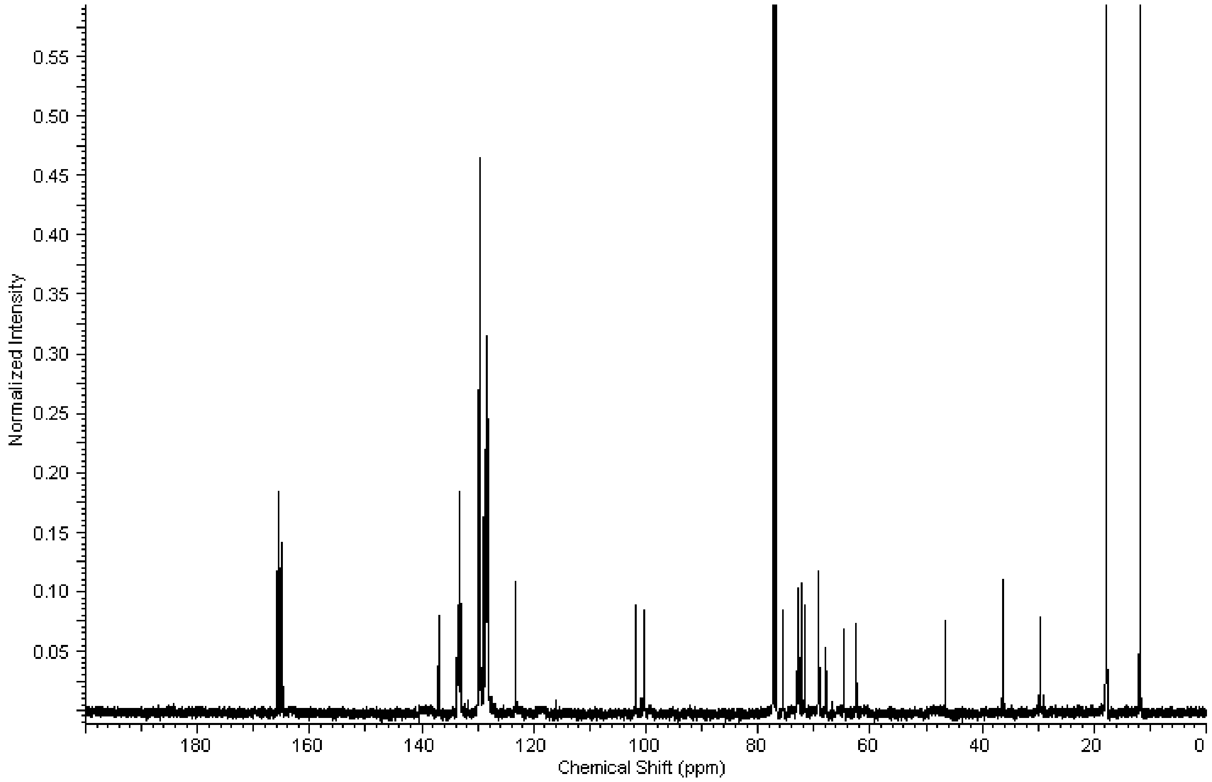

Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

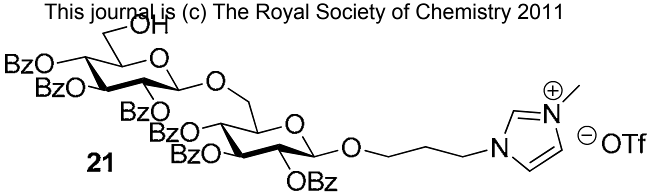

Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


OTIPS
BzO
BzO
BzO
BzO
BzO
OBz
O
N
OTf

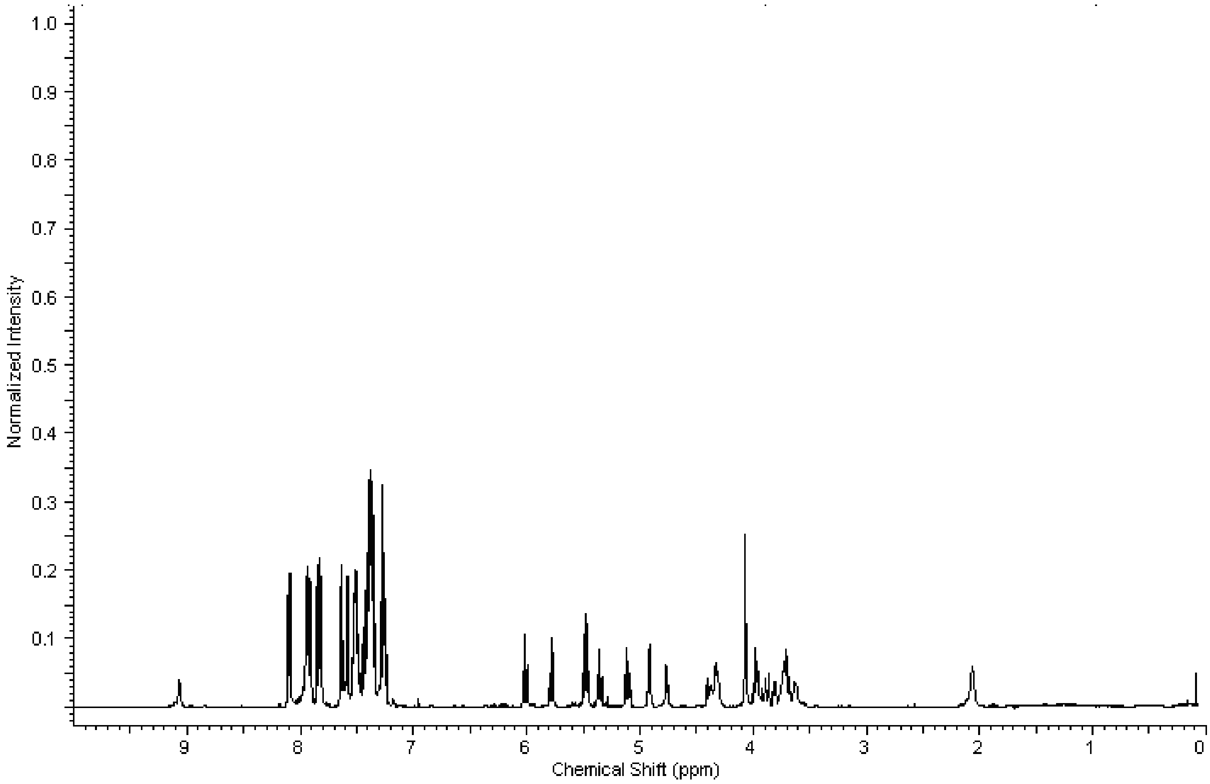
20

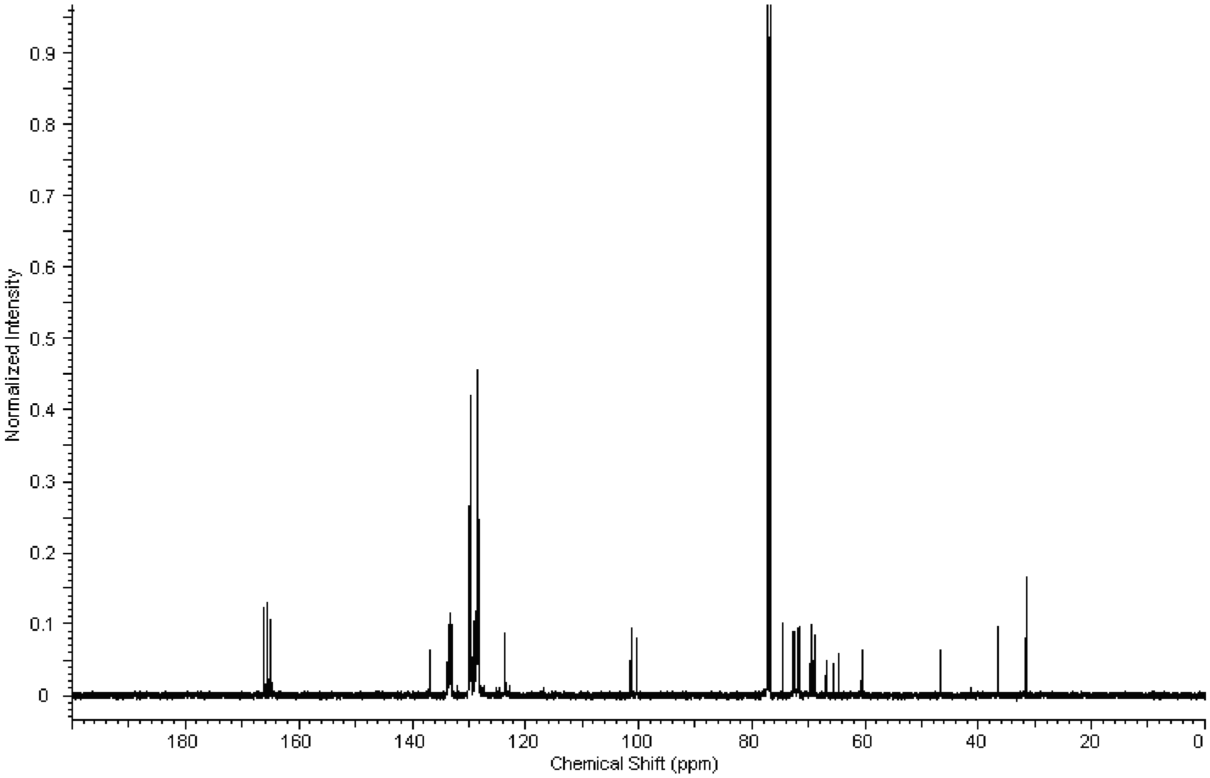

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

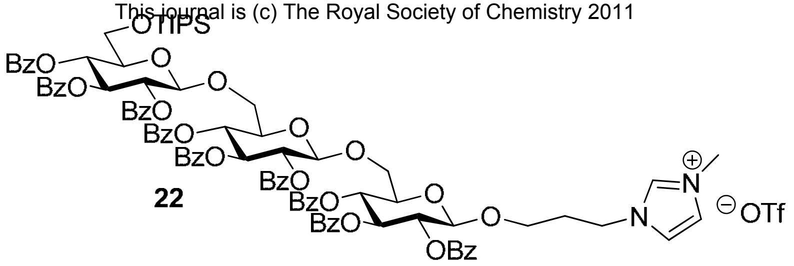

Normalized Intensity
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


OH
BzO
BzO
O
O
BzO
BzO
BzO
O
O
OBz
N
N
⊕
⊖OTf

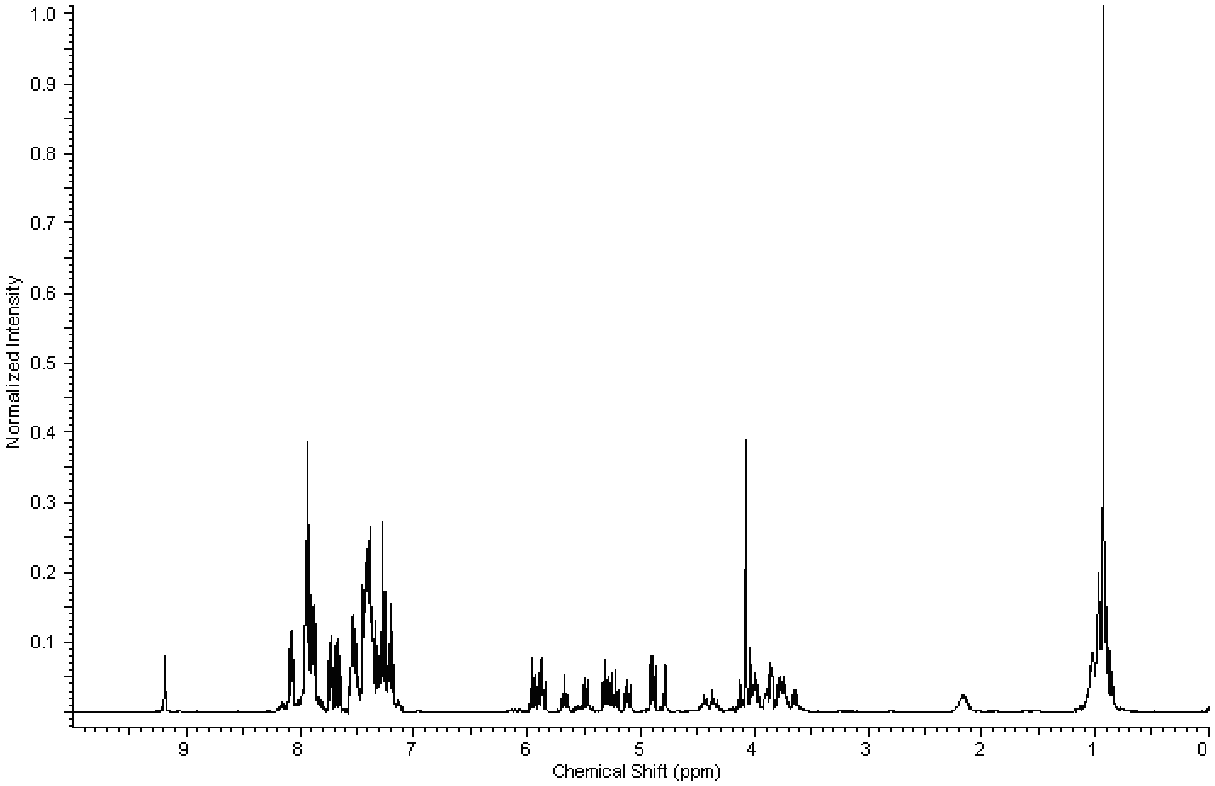
21

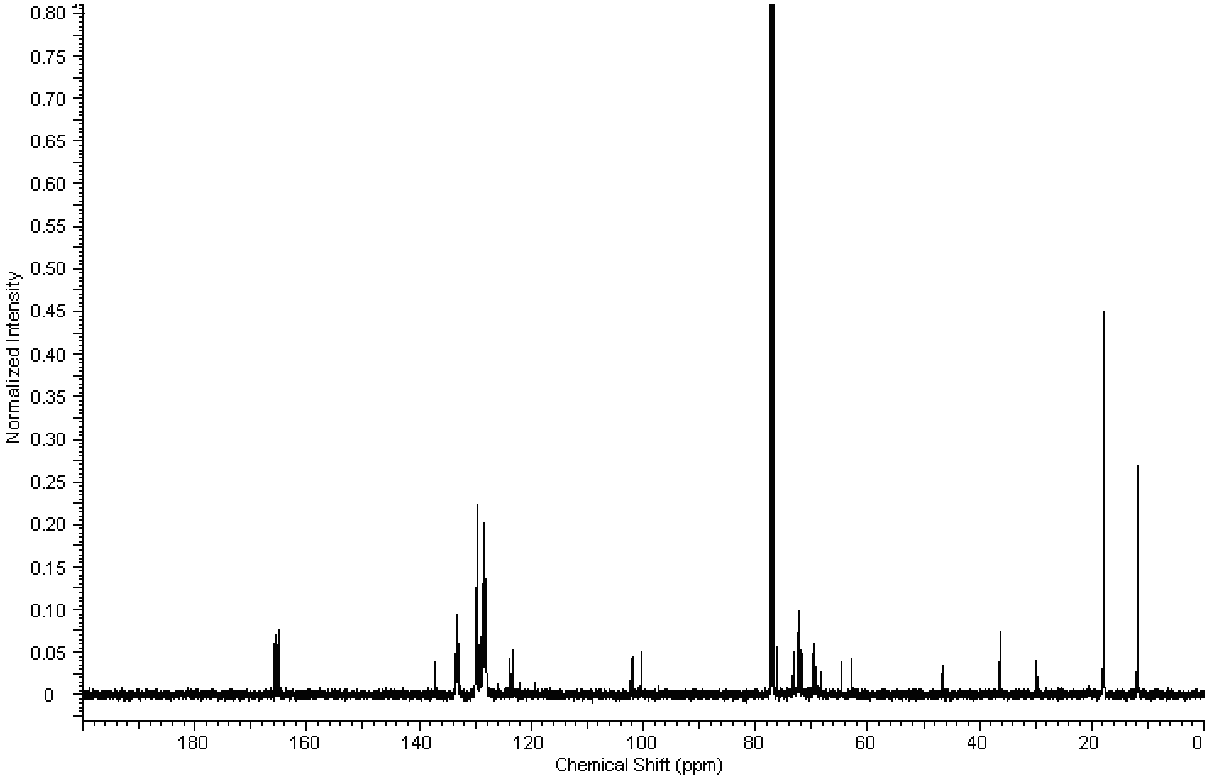

Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

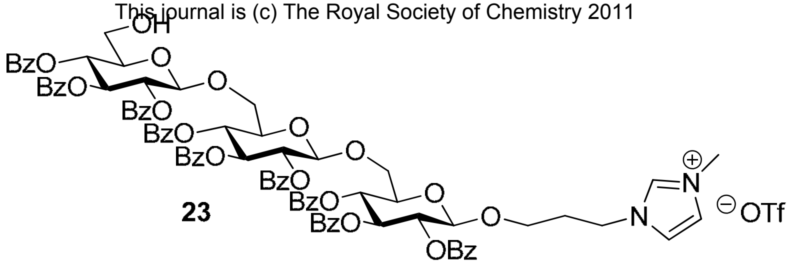

Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


OTIPS
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
OBz
O
N
N
⊕
⊖OTf

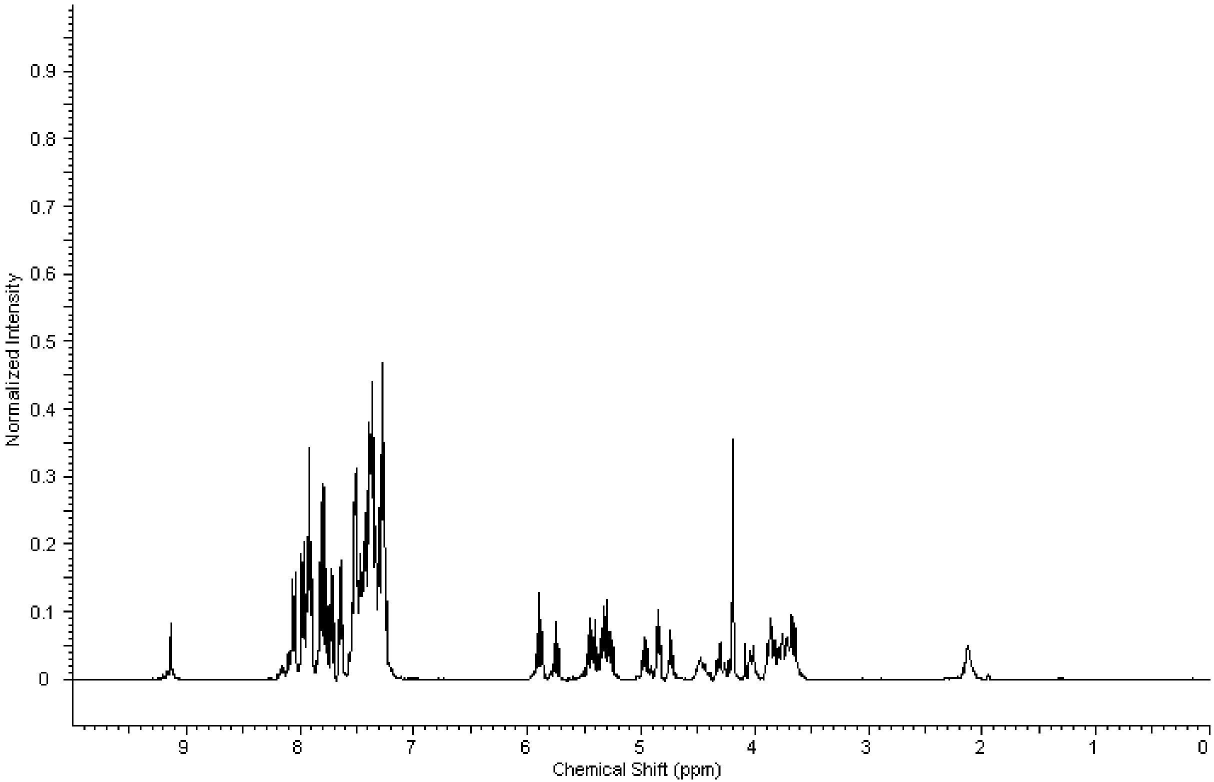
22

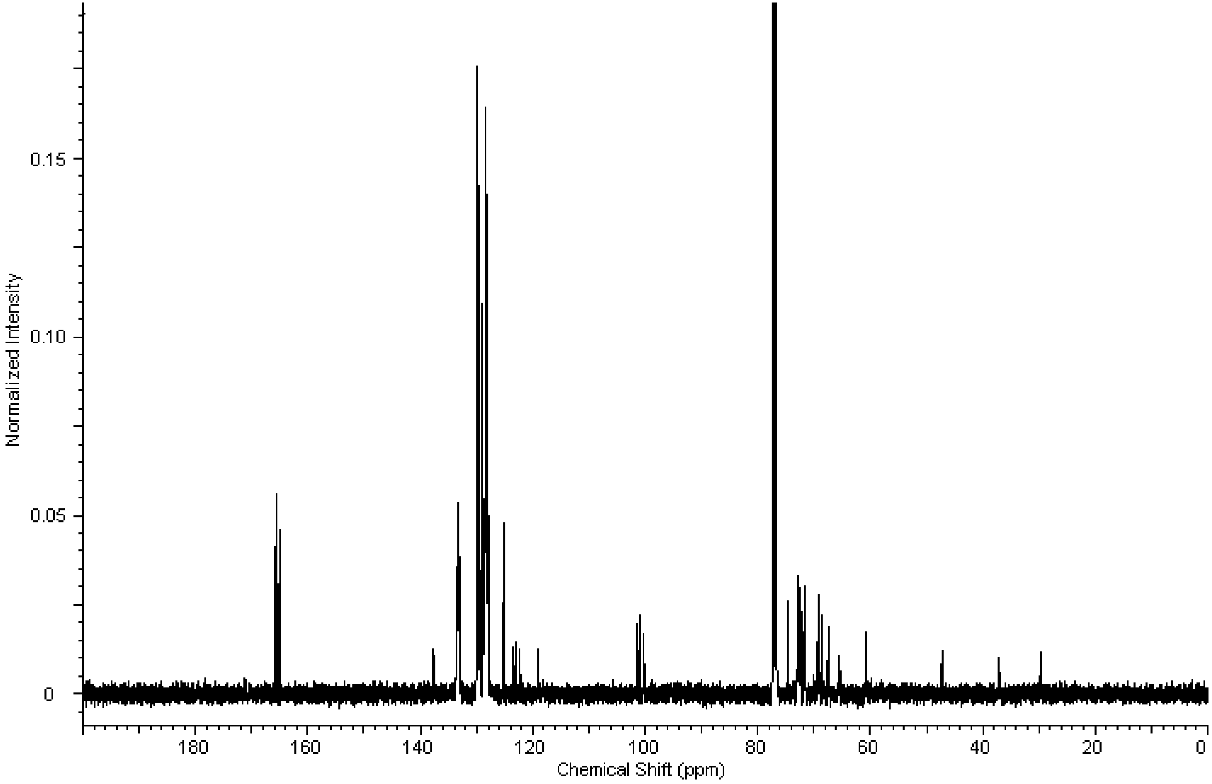

Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

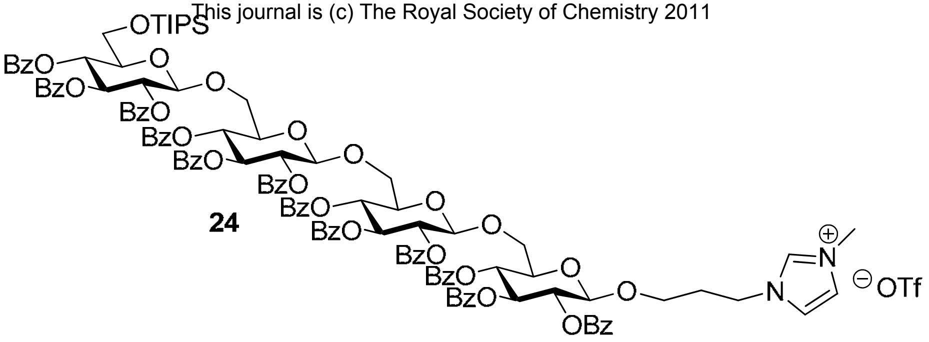

Normalized Intensity
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


BzO
BzO
BzO
OH
O
O
BzO
BzO
BzO
O
O
BzO
BzO
OBz
O
O
N
N
⊕
⊖OTf

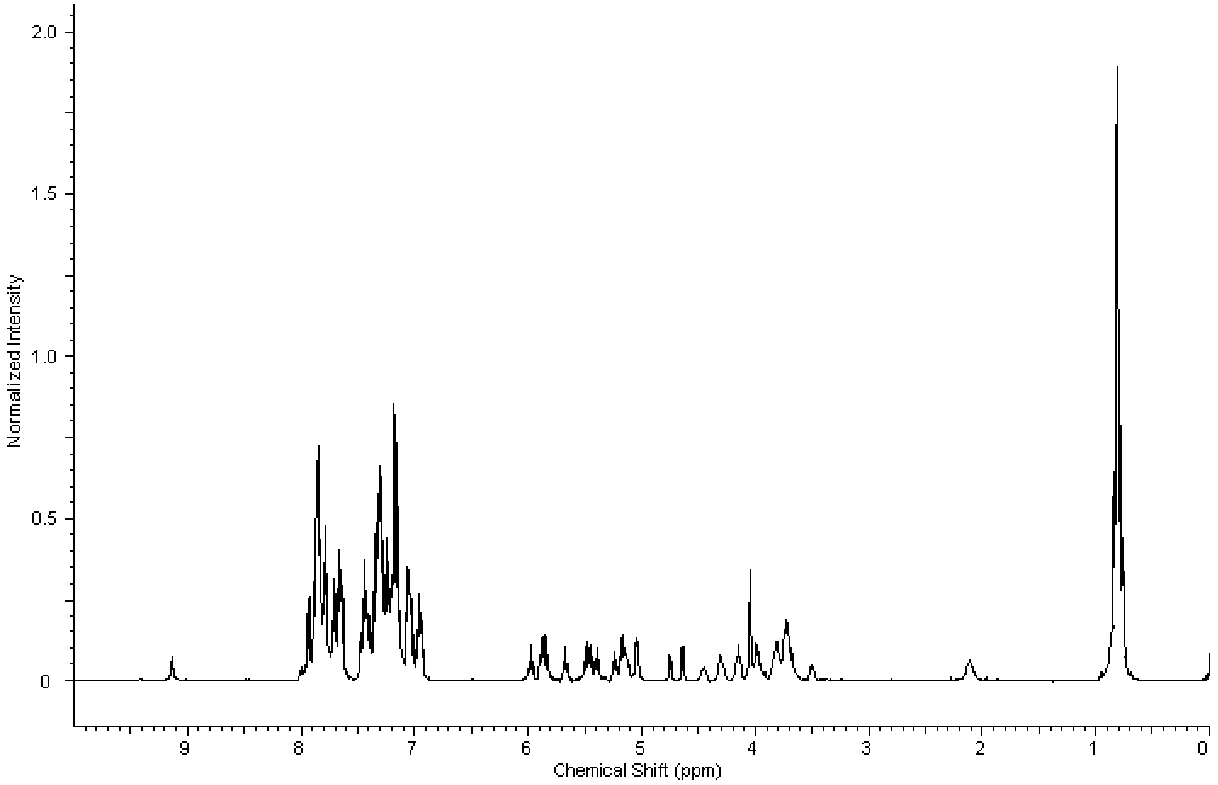
23

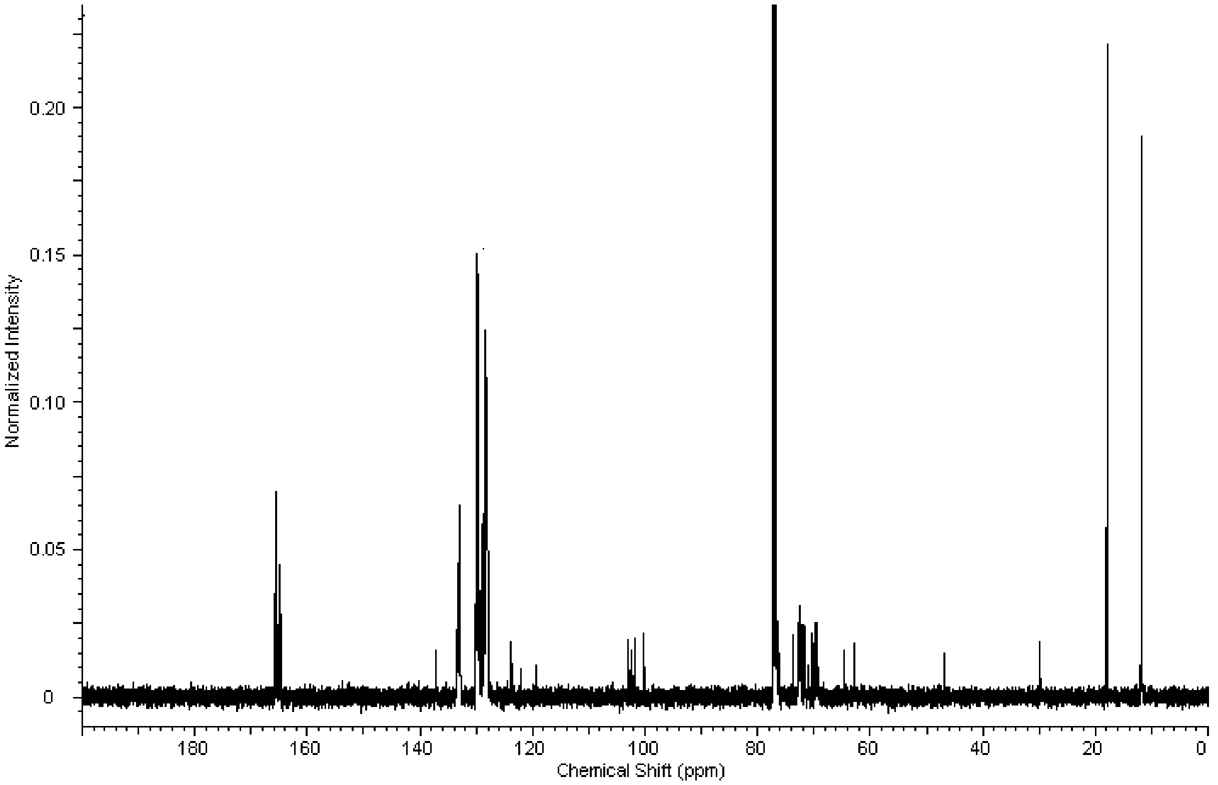

Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

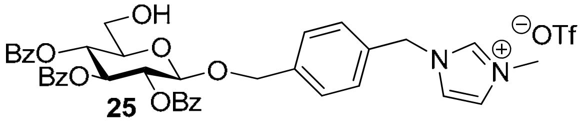

Normalized Intensity
0.15
0.10
0.05
0
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


OTIPS
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
O
BzO
BzO
BzO
O
O
OBz
N
N
⊕
⊖OTf

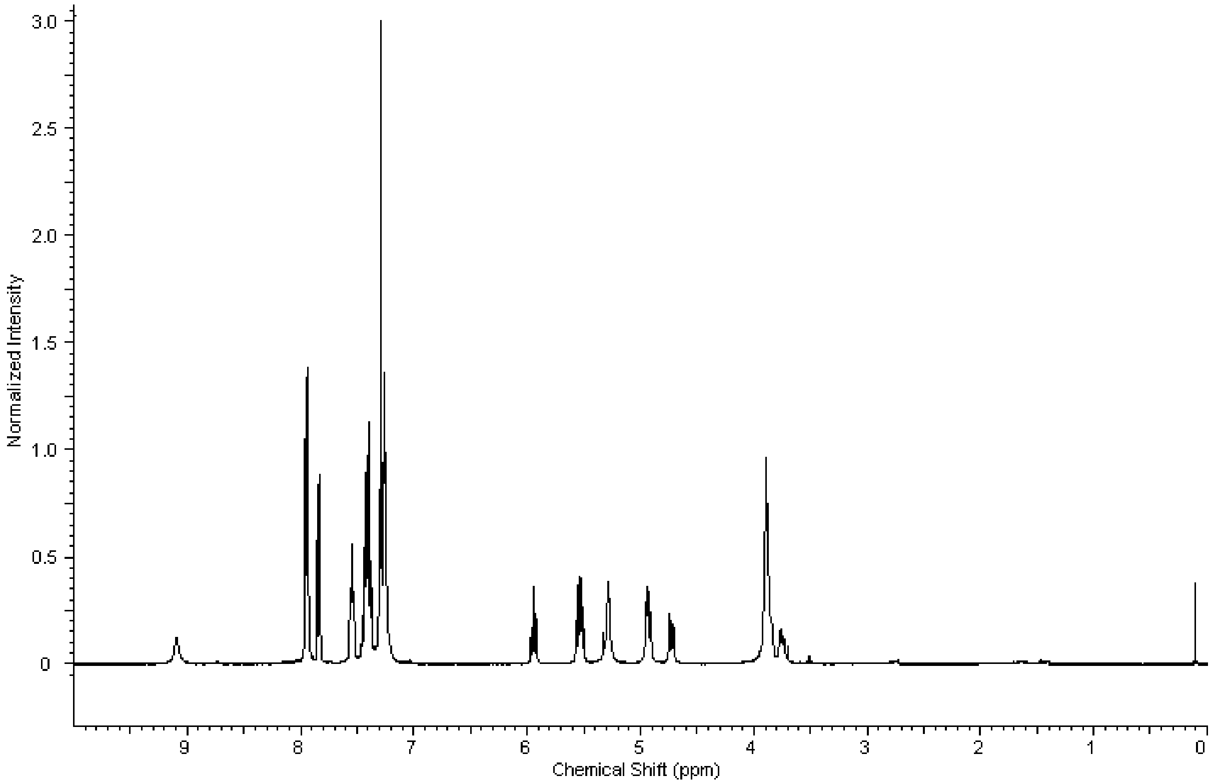
24

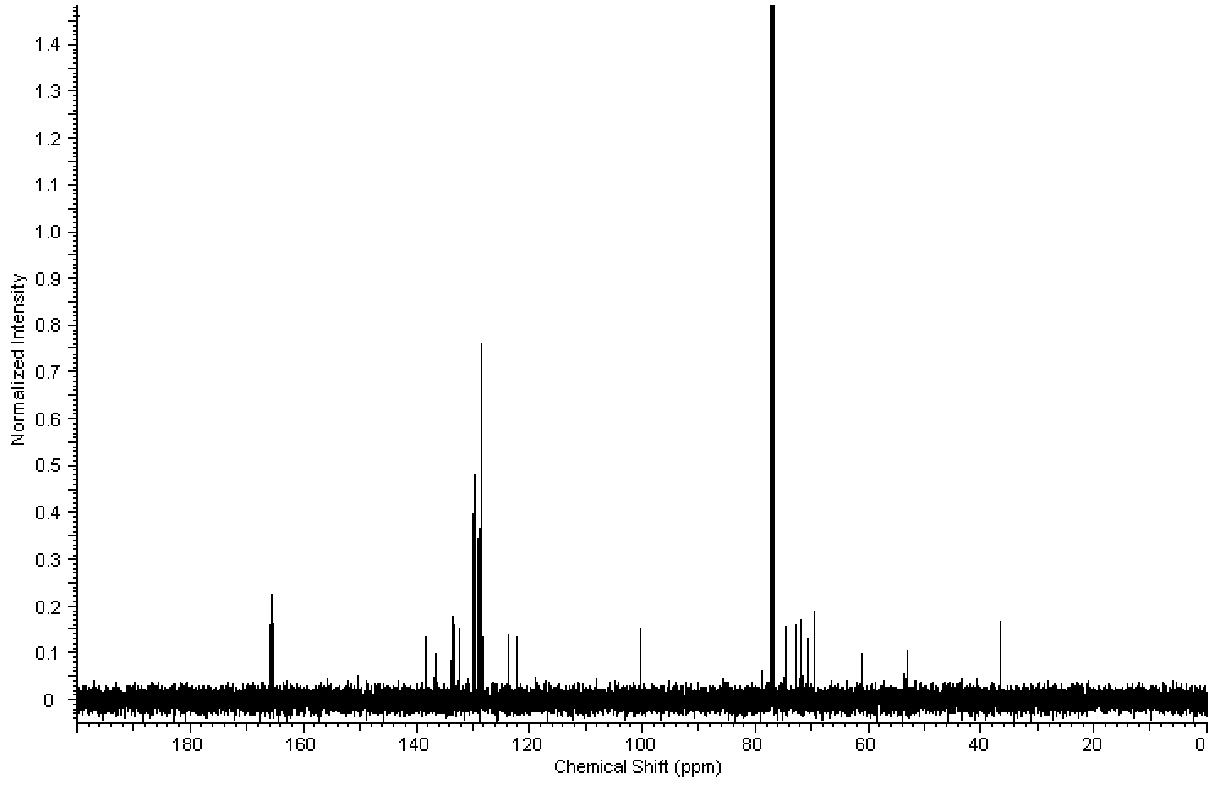

Normalized Intensity
2.0
1.5
1.0
0.5
0
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

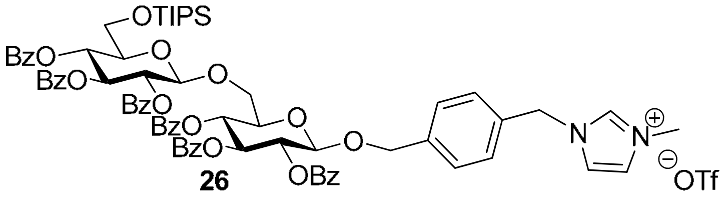

Normalized Intensity
0.20
0.15
0.10
0.05
0
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


OH
BzO
BzO
O
O
OBz
N
N
⊕
⊖OTf

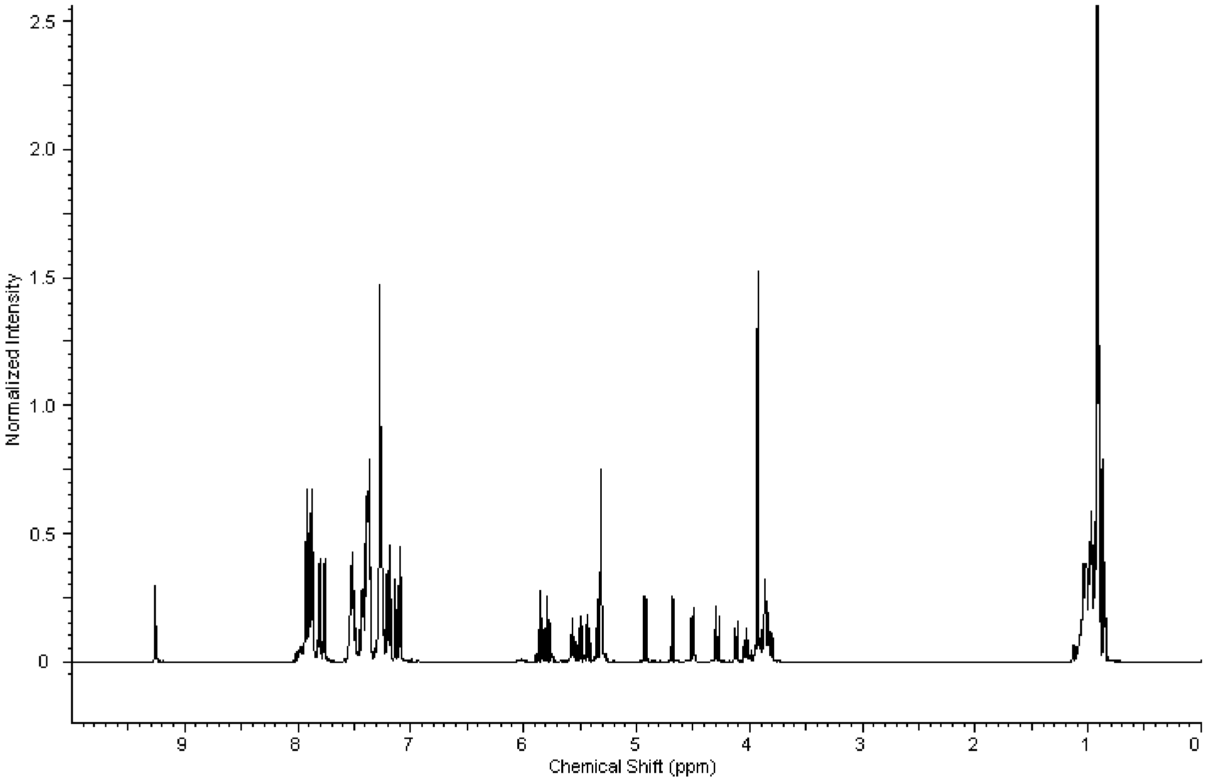
25

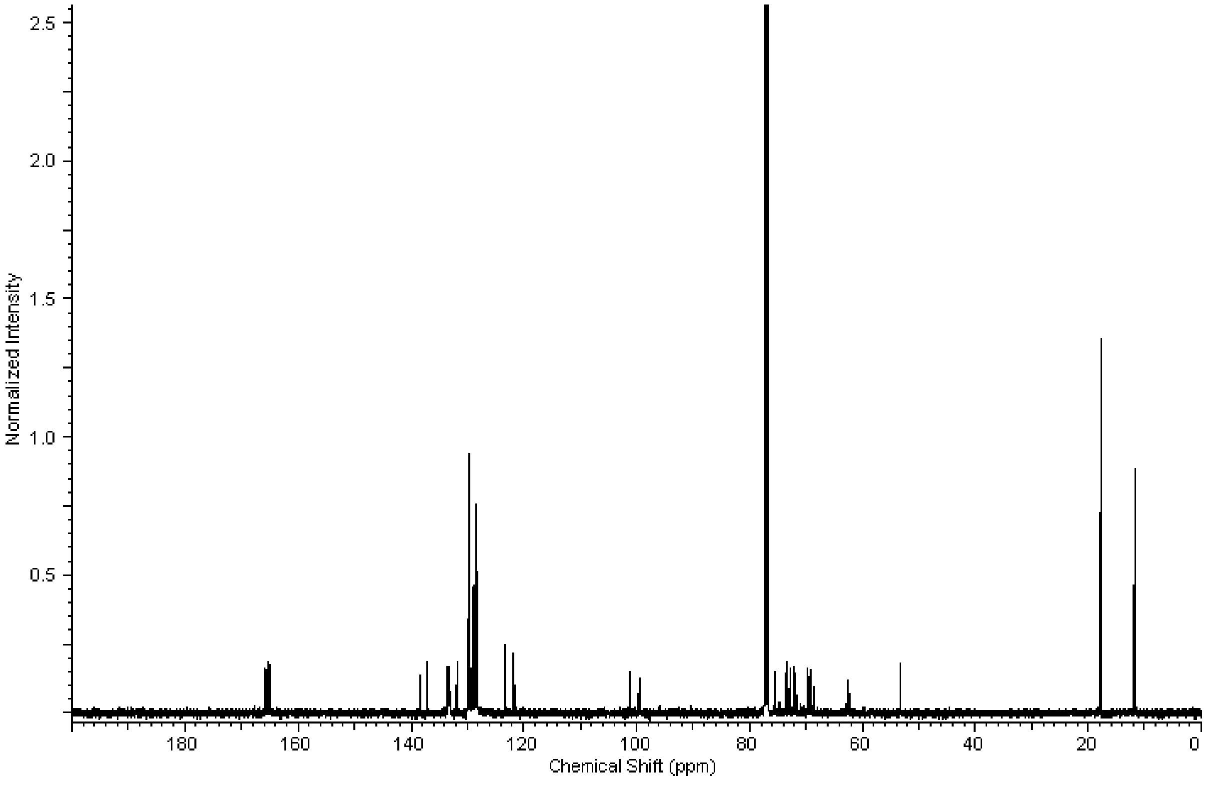

Normalized Intensity
3.0
2.5
2.0
1.5
1.0
0.5
0
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

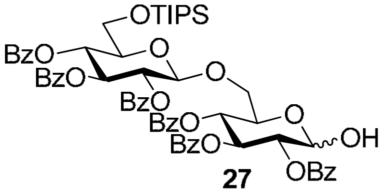

Normalized Intensity
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


OTIPS
BzO
BzO
BzO
O
O
BzO
BzO
O
OBz
O
N
N
⊕
⊖
OTf

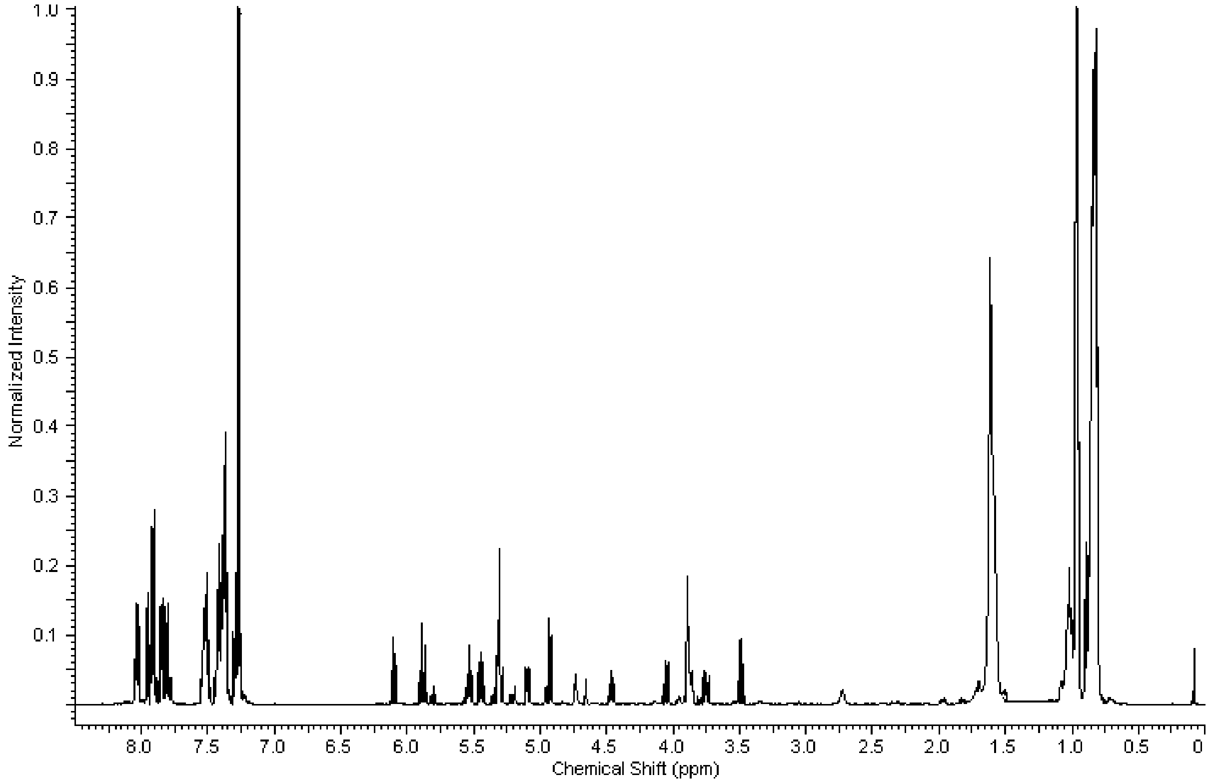
26

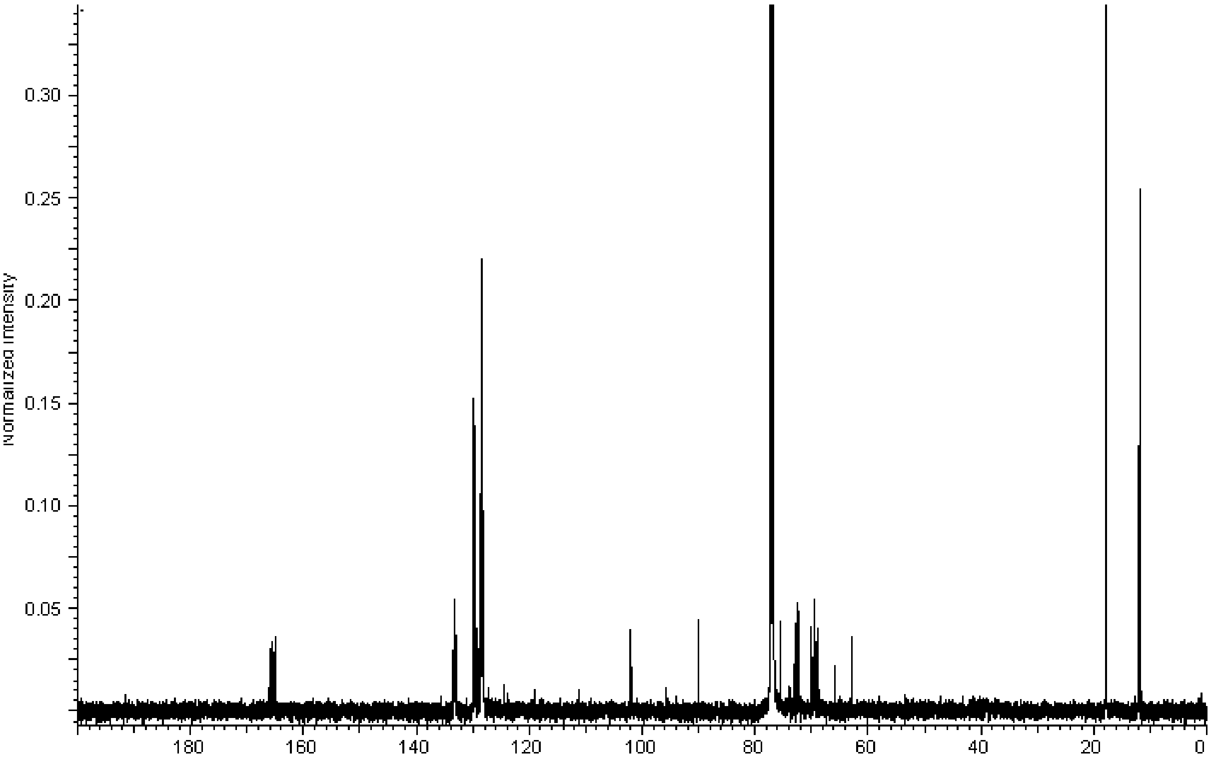

Normalized Intensity
2.5
2.0
1.5
1.0
0.5
0
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

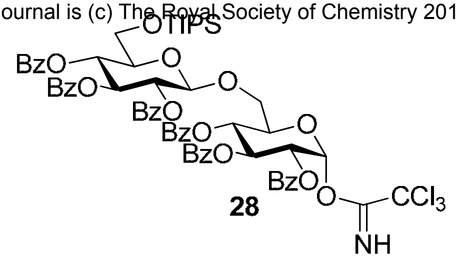

Normalized Intensity
2.5
2.0
1.5
1.0
0.5
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


OTIPS
BzO
O
BzO
O
BzO
BzO
O
BzO
OH
OBz

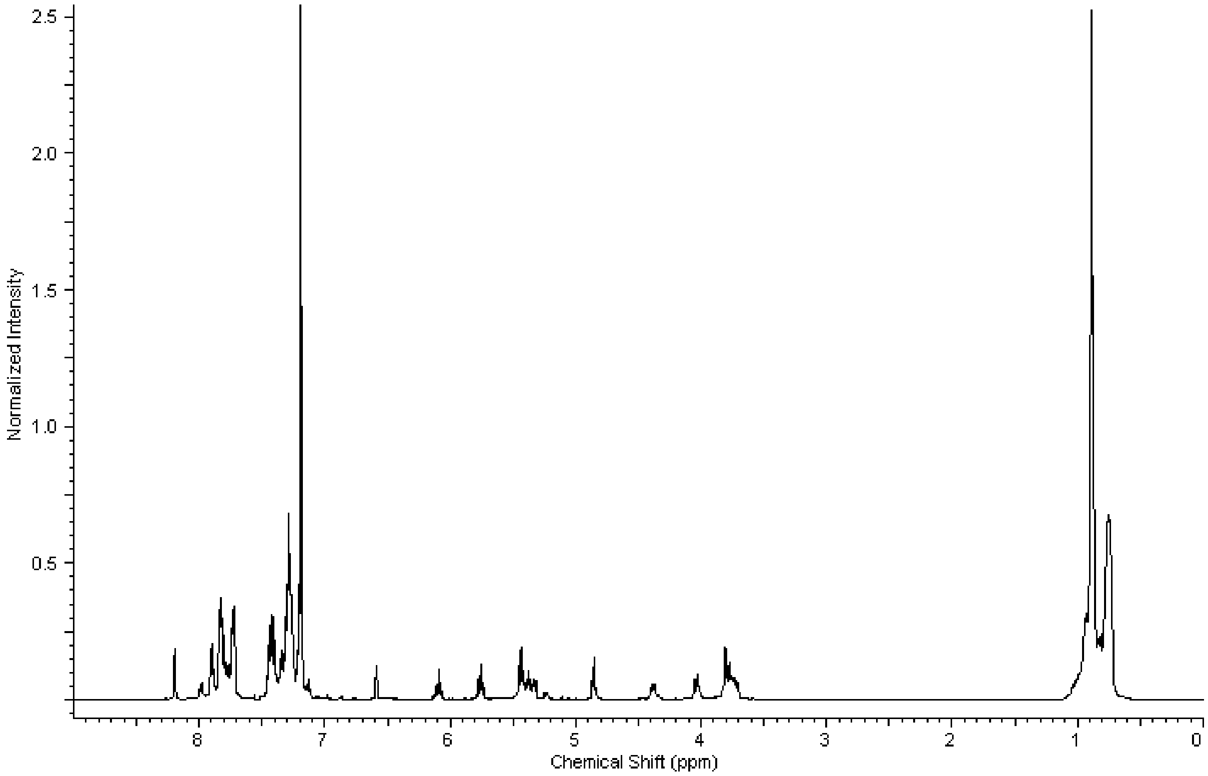
27

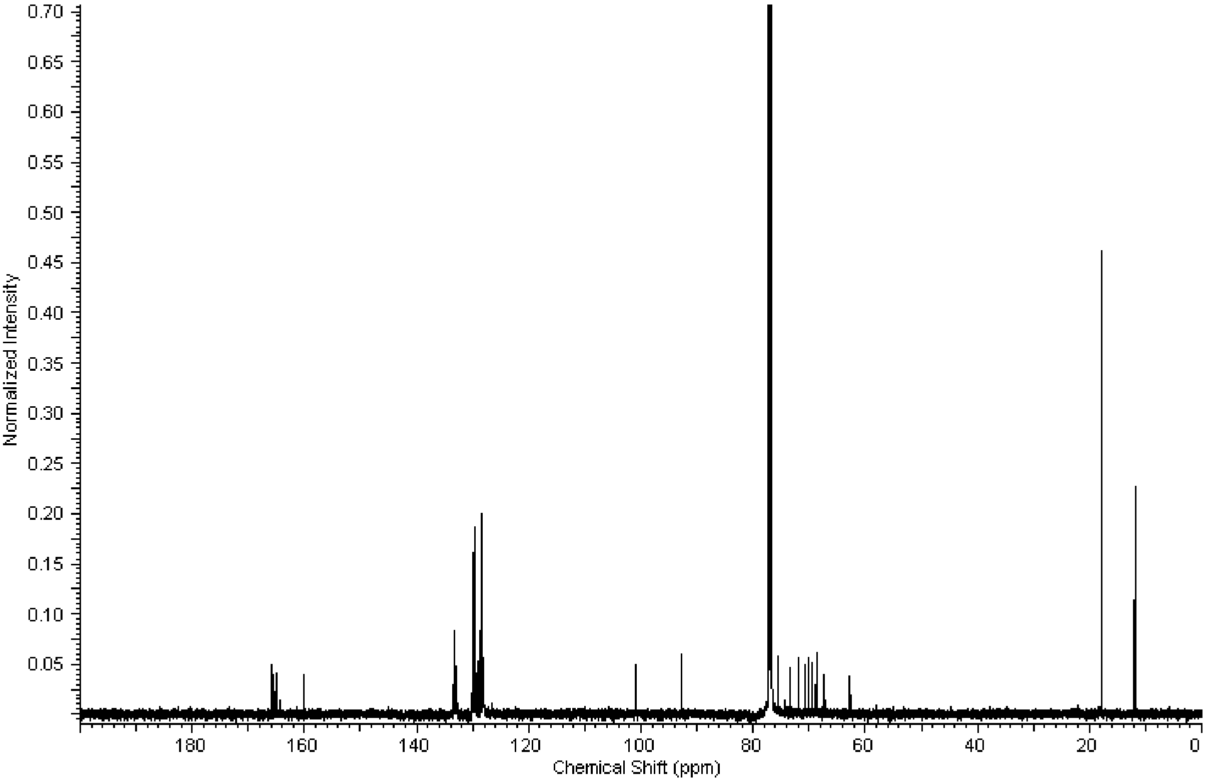

Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


OTIPS
BzO
BzO
BzO
O
O
BzO
BzO
O
BzO
O
CCl3
NH

28


Normalized Intensity
2.5
2.0
1.5
1.0
0.5
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


Normalized Intensity
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)