Supporting Information

1,2-*Trans* and regioselective glycosylation of multihydroxy sugars via a concise pattern of $BF_3 \cdot Et_2O$ in THF

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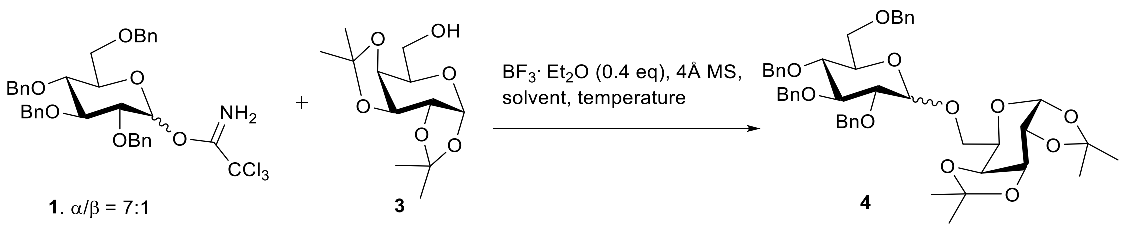
Table of contents

1. General information

All reactions were carried out with regular solvents in glassware, unless otherwise specified. The chemicals were reagent grade as supplied. Powdered molecular sieves (4Å MS) were dried with heating gun under vacuum for 10 min prior to use. Spots on TLC were visualized by UV light (254 nm) or by heating with a solution with 5% H_2SO_4 in ethanol. Flash column chromatography was performed on regular silica gel (200 ~ 300 mesh), unless otherwise noted. Optical rotations were measured with Anton paar MCP 500. High resolution mass spectra (HRMS) were recorded on Thermo scientific Q Exactive HF Orbitrap-FTMS spectrometer using electrospray ionization (ESI) positive ion mode. ^{1}H NMR, ^{13}C NMR, HSQC, COSY, and NOESY spectra were recorded on 300 MHz, 400 MHz, 500 MHz, or 600 MHz spectrometers in $CDCl_3$, CD_3OD, or THF-*d8*. The anomeric product ratios were analyzed through integration of ^{1}H NMR signals. Chemical shifts are reported in parts per million (ppm). All coupling constants are absolute values and are expressed in hertz. The description of the signals includes the following: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, br = broad, and m = multiplet.

2. Reaction discovery and optimization

Table S1. Reaction discovery and optimization

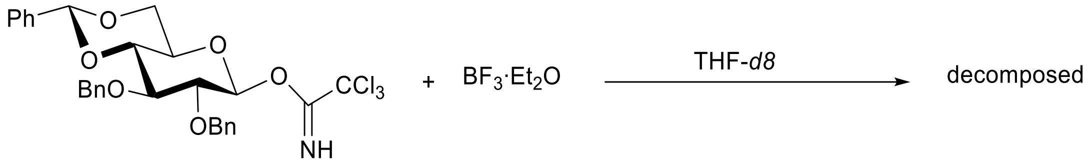


Entry	Solvent	$BF_3 \cdot Et_2O$ (eq)	Temperature	β/α[a]	Yield[b]
1	THF	0.1 eq	–50 °C	β only	79%
2	THF	0.2 eq	–50 °C	β only	88%
3	THF	0.4 eq	–50 °C	β only	91%
4	THF	1.0 eq	–50 °C	> 20:1	94%
5	THF	2.0 eq	–50 °C	> 20:1	90%
6	THF	4.0 eq	–50 °C	19:1	86%
7	THF	0.4 eq	10 °C	7:1	60%[c]
8	THF	0.4 eq	0 °C	9:1	61%
9	THF	0.4 eq	–25 °C	β only	70%
10	MTBE	0.4 eq	–25 °C	12:1	53%
11	ether	0.4 eq	–25 °C	3:1	66%
12	2-methyl-THF	0.4 eq	–25 °C	17:1	69%
13	toluene	0.4 eq	–25 °C	6:1	68%
14	MTBE	0.4 eq	–50 °C	β only	75%
15	ether	0.4 eq	–50 °C	20:1	71%
16	2-methyl-THF	0.4 eq	–50 °C	> 20:1	91%
17	toluene	0.4 eq	–50 °C	6:1	58%
18	2, 5-dimethyl THF	0.4 eq	–50 °C	β only	91%
19	DCE	0.4 eq	–50 °C	8:1	80%
20	CH_2Cl_2	0.4 eq	–50 °C	5.1:1	70%
21	$PhCF_3$	0.4 eq	–50 °C	8.5:1	81%
22	THF/CH_2Cl_2 = 1:1	0.4 eq	–50 °C	β only	84%
23	THF (5 eq) in CH_2Cl_2	0.4 eq	–50 °C	5:1	80%

[a]Determined by ^1H NMR. [b]Isolated by chromatography. [c]The formation of glycosyl fluoride reduces the yield, a phenomenon that is also observed when involving hindered acceptors.

3. NMR studies

3.1. Variable-temperature NMR studies



8β

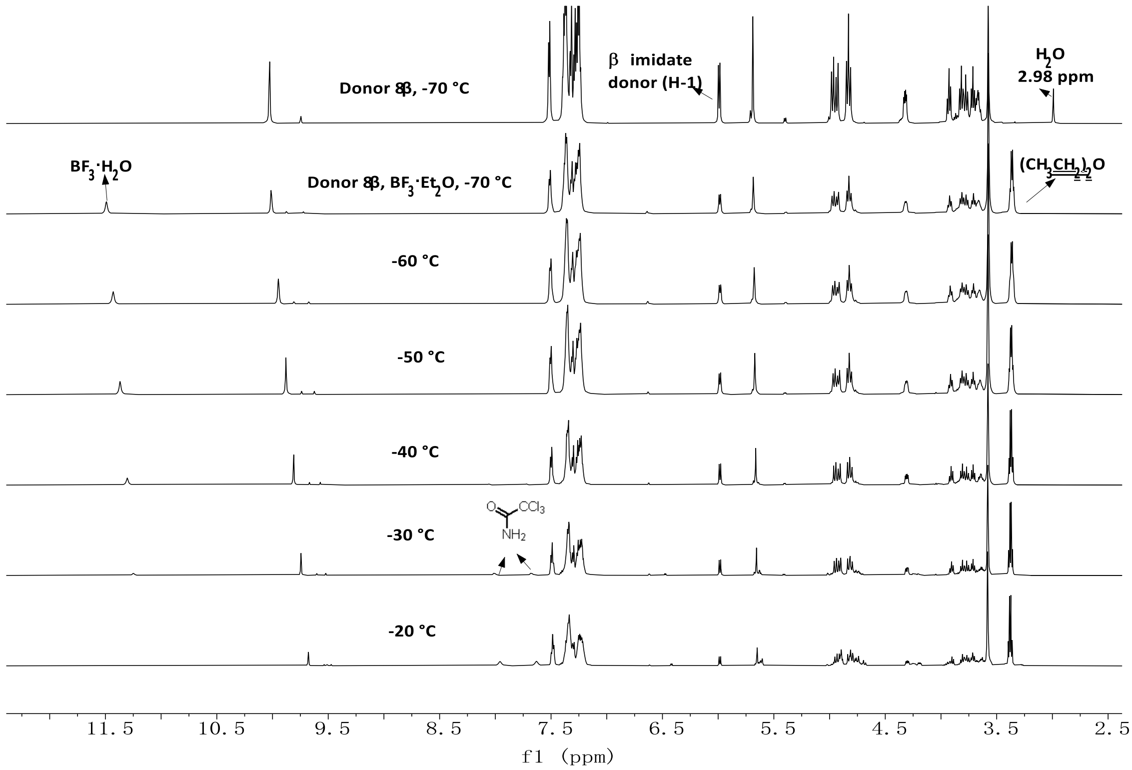


Fig. S1. Variable-temperature ^1H NMR studies on donor **8β** with $BF_3·Et_2O$ (1 eq)

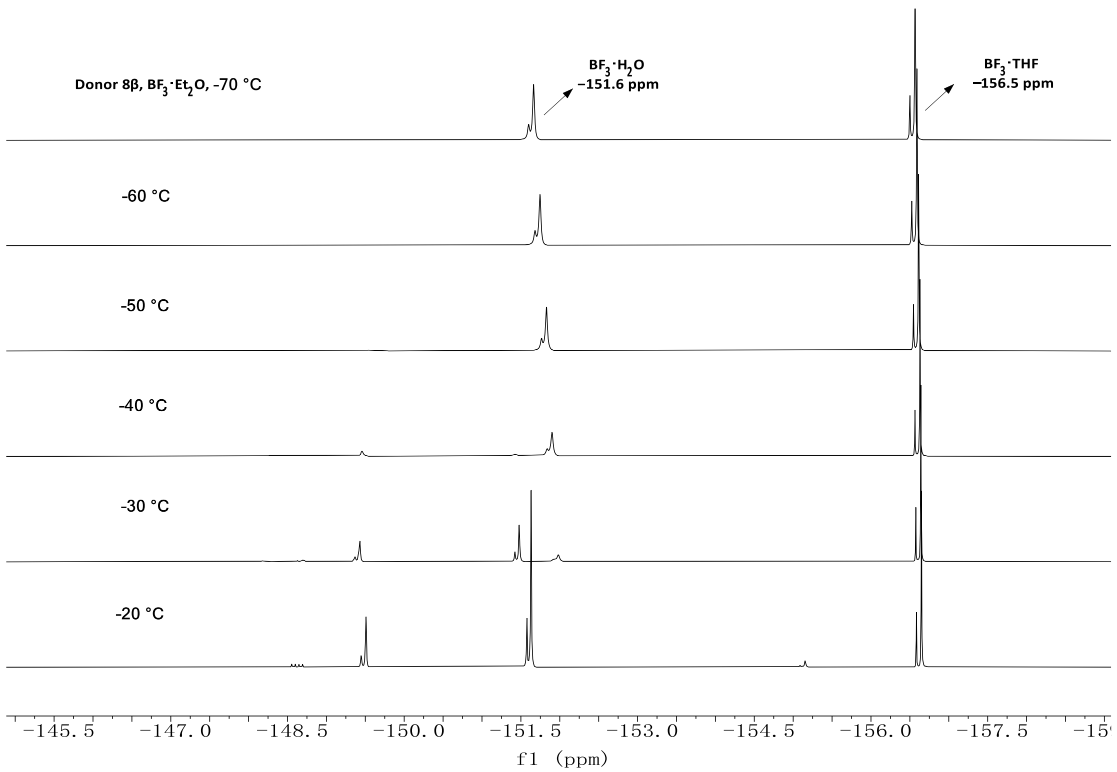


Fig. S2. Variable-temperature ^{19}F NMR studies on donor **8β** with $BF_3\cdot Et_2O$ (1 eq)

Operation: A solution of pure donor **8β** (0.03 mmol) in THF-*d*8 (0.5 mL) was added to an NMR tube, and its ^1H NMR spectrum (600 MHz, THF-*d*8) was recorded at –70 °C. After the tube was cooled to –78 °C by dry ice-acetone bath, $BF_3\cdot Et_2O$ (0.03 mmol) in THF-*d*8 (0.05 mL) was added via a syringe. Their ^1H NMR spectra (600 MHz, THF-*d8*) (**Fig. S1**) and ^{19}F NMR spectra (282 MHz, THF-*d8*) (**Fig. S2**) were collected from −70 °C to −20 °C gradually as the showed temperature interval.

Observation and discussion: In the ^1H NMR spectra (**Fig. S1**), the H_2O peak at 2.98 ppm disappeared after the addition of $BF_3\cdot Et_2O$. Meanwhile, a new peak at 11.48 ppm appeared. Donor **8β** remained intact until the temperature rose to –30 °C, at which temperature the peak at 11.48 ppm disappeared. No isomerization from β-donor to α-donor was observed during the process.

In the ^{19}F NMR spectra (**Fig. S2**), two sets of two singlets were observed at −151.6 ppm and −156.5 ppm after the addition of $BF_3\cdot Et_2O$. The one at −156.5 ppm was assigned to $BF_3\cdot THF$ after comparing the ^{19}F NMR spectrum of the commercially available $BF_3\cdot THF$ in THF-*d8* (**Fig. S5**). The other one at −151.6 ppm corresponds to the significantly downfield-shifted δ_H of 11.48 ppm originally from H_2O in the ^1H NMR spectrum.

3.2. $BF_3 \cdot H_2O$ determination

$$BF_3 \cdot Et_2O + H_2O + \text{THF-}d8 \xrightarrow{-70\ °C} BF_3 \cdot \text{THF-}d8 + BF_3 \cdot x(H_2O) + Et_2O$$

As all the signals in ^{19}F NMR spectra presented as sets of two singlets corresponding to ^{10}B and ^{11}B were observed in a relatively narrow range, we supposed only transformation of BF_3 could occur in the system. Thus, we can deduce the content of fluoroboron species according to the ratio of the integration of signals.

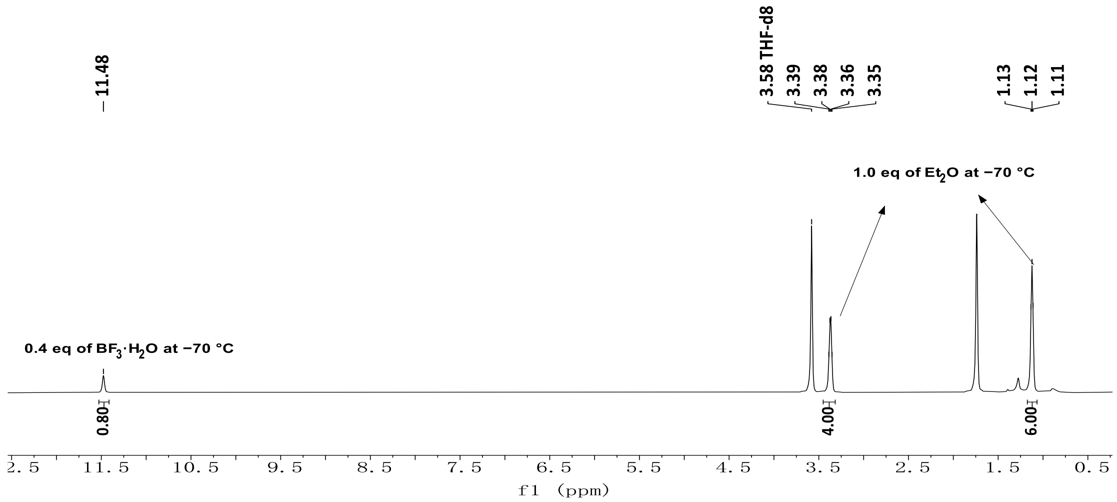


Fig. S3. ^1H NMR spectrum of THF-*d8* at −70 °C after the addition of $BF_3 \cdot Et_2O$

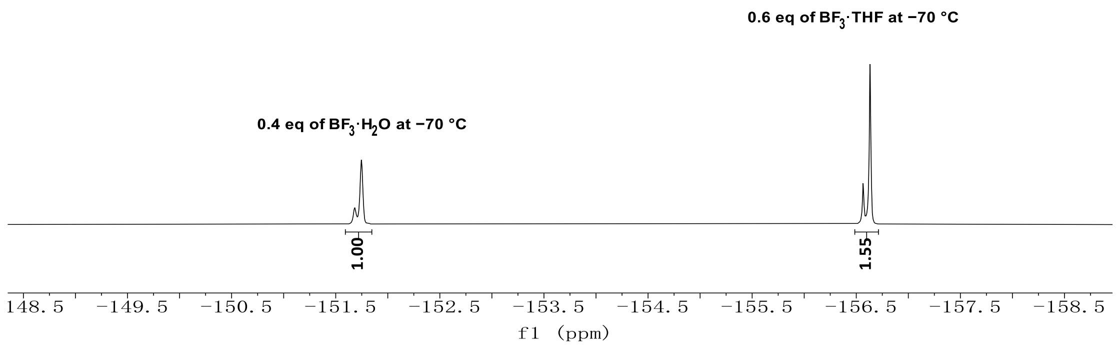


Fig. S4. ^{19}F NMR spectrum of THF-*d8* at −70 °C after the addition of $BF_3 \cdot Et_2O$

Operation: THF-*d8* (0.5 mL) in an NMR tube was cooled to −78 °C by dry ice-acetone bath, then $BF_3 \cdot Et_2O$ (0.06 mmol) in THF-*d*8 (0.1 mL) was added via a syringe. ^1H NMR spectrum (600 MHz, THF-*d*8) (**Fig. S3)** and ^{19}F NMR spectrum (282 MHz, THF-*d8*) (**Fig. S4.)** were collected at −70°C.

Observation and discussion: In the ^{1}H NMR spectrum (**Fig. S3**), signals at 3.37 (q, J = 7.1 Hz, 2H, CH_2) ppm and 1.12 (t, J = 6.9 Hz, 3H, CH_3) ppm belong to the free Et_2O without the observable signal of $BF_3{\cdot}Et_2O$, indicating the instant and complete release of Et_2O from $BF_3{\cdot}Et_2O$ in THF-*d8*. The peak at 11.48 ppm were assigned to species relevant to H_2O and BF_3 complex [i.e., $BF_3{\cdot}X$ (H_2O)][1]. Since the ratio of the amount of Et_2O and $BF_3{\cdot}x(H_2O)$ is x to 0.40 according to the integration, we can infer $BF_3{\cdot}x(H_2O)$ accounts for (40/x) % of the total BF_3; In the ^{19}F NMR spectrum (**Fig. S4**), the presence of singlet at −151.6 ppm corresponds to the appearance of 11.48 ppm along with disappearing of H_2O at 2.98 ppm was concluded, indicating the presence of $BF_3{\cdot}x$ (H_2O) (**Fig. S1**, **Fig. S2**). The spectrum shows the fluoroboron species consist of 39% $BF_3{\cdot}x$ (H_2O) and 61% BF_3·THF, supporting x = 1 and the presence of $BF_3{\cdot}H_2O$.

	chemical shift	peak integration		species
^{1}H NMR	11.48 ppm	0.8 eq		$BF_3{\cdot}H_2O/BF_3{\cdot}2H_2O/BF_3OH$
	3.37 ppm	4.0 eq		$(CH_3\underline{CH_2})_2O$
	1.12 ppm	6.0 eq		$(\underline{CH_3}CH_2)_2O$
^{19}F NMR	151.6 ppm	1	=	$BF_3{\cdot}H_2O$
	156.5 ppm	1.55		BF_3·THF

3.3. BF_3·THF determination

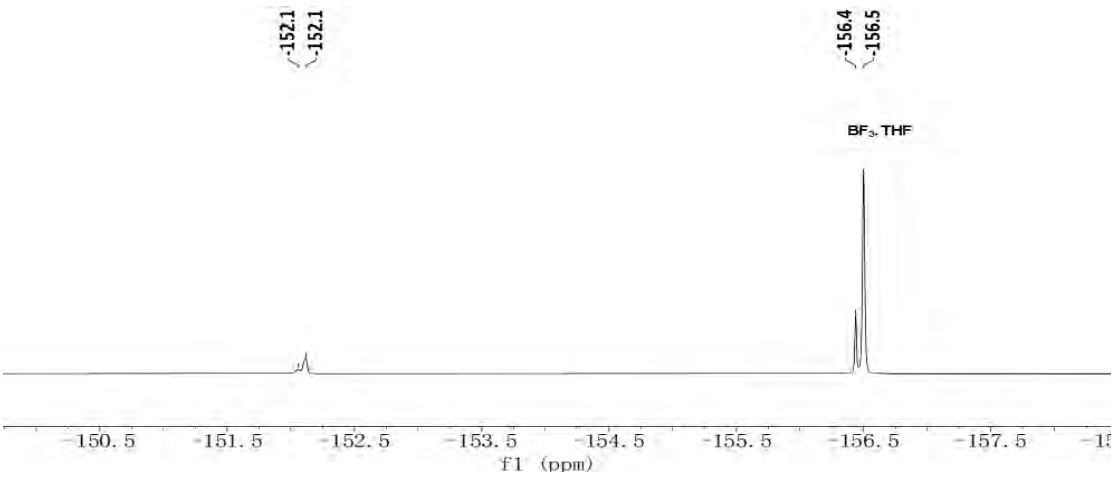


Fig. S5. ^{19}F NMR spectrum of BF_3.THF in THF-*d8* at rt

Operation:THF-*d8* (0.5 mL) was added to an NMR tube, commercially available BF_3·THF (0.48 mmol) in THF-*d8* (0.1 mL) was added via a syringe. ^{19}F NMR spectrum (282 MHz, THF-*d8*) was collected at rt.

Observation and discussion: The singlet at −156.5 ppm was assigned to the BF_3·THF.

3.4. BF_3·MeOH determination

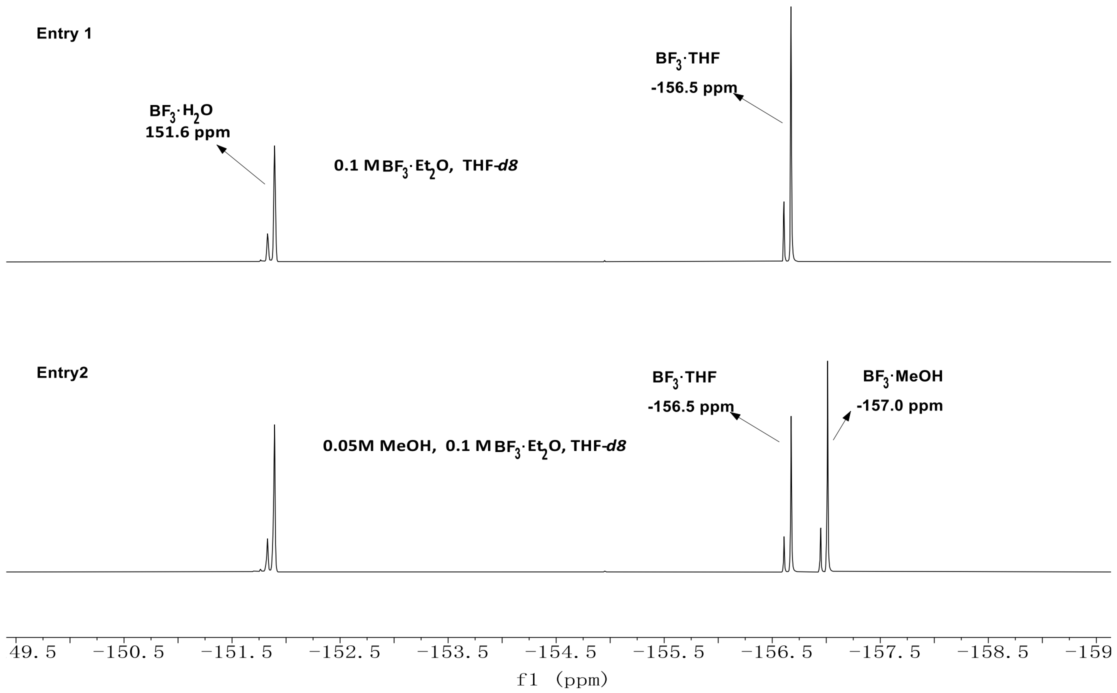


Fig. S6. ^{19}F NMR spectra of BF_3 with or without MeOH in THF-d_8 at −50 °C

Operation: Entry 1: THF-*d8* (0.5 mL) in an NMR tube was cooled to −78 °C by dry ice-acetone bath, then $BF_3·Et_2O$ (0.06 mmol) in THF-*d*8 (0.1 mL) was added via a syringe. ^{19}F NMR spectrum (282 MHz, THF-*d*8) was collected at −50°C.

Entry 2: THF-*d8* (0.5 mL) and MeOH (0.03 mmol) in THF-*d8* (0.05 mL) were added into an NMR tube, the tube was cooled to −78 °C by dry ice-acetone bath, then $BF_3·Et_2O$ (0.06 mmol) in THF-d_8 (0.05 mL) was added via a syringe. ^{19}F NMR spectrum (282 MHz, THF-*d*8) was collected at −50°C.

Observation and discussion: The peak at 157.0 ppm was assigned to BF_3·MeOH. BF_3·H_2O, BF_3·THF, and BF_3·MeOH coexisted in **Fig. S6**.

4. DFT calculations

All calculation were performed with the Gaussian 16 package.[2] Geometry optimizations were performed with M06-2X and the 6-31G** basis set with the PCM (THF) solvation model. Frequency analysis was conducted at the same level to obtain thermal energy corrections under 223 K and standard atmosphere pressure. The single-point energy calculations were performed at the M06-2X/6-311+G**/PCM(THF) level of theory with the optimized structure. The conformations of 4,6-*O*-methylene-pyranosides were determined by literature results and conformation search utilized the molclus program combined with the xTB method.[3, 4] The calculated structures are represented with the CYLview software.[5]

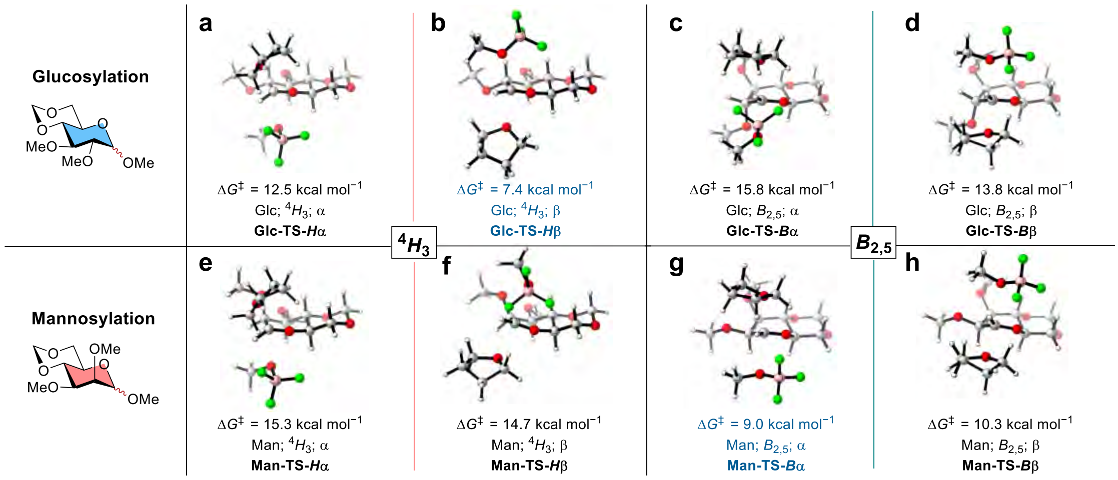


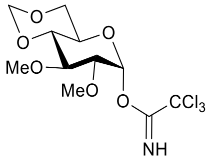
Fig. S7. Calculated (M06-2X) transition states for the nucleophilic attack of $[BF_3OMe]^-$ to 4,6-*O*-methylidene protected oxocarbenium-solvent complex, leading to the formation of the α- and β-glycosides in each case. **a–h**, Transition states with the $^4H_3$ or $B_{2,5}$ conformation for the formation of glycoside: **a**, α-glucoside ($^4H_3$); **b**, β-glucoside ($^4H_3$); **c**, α-glucoside ($B_{2,5}$); **d**, β-glucoside ($B_{2,5}$); **e**, α-mannoside ($^4H_3$); **f**, β-mannoside ($^4H_3$); **g**, α-mannoside ($B_{2,5}$); **h**, β-mannoside ($B_{2,5}$).

Table S2. Electronic energies (M06-2X/6-311+G**/PCM(THF)) and thermochemical corrections (M06-2X/6-31G**/PCM(THF)) for the oxocarbenium-solvent complexes and corresponding transition state structures with conformations $^4H_3$ and $B_{2,5}$ for reaction with methanol.

Formation		α-Glucoside		β-Glucoside		α-Mannoside		β-Mannoside	
Conformation		$^4H_3$	$B_{2,5}$	$^4H_3$	$B_{2,5}$	$^4H_3$	$B_{2,5}$	$^4H_3$	$B_{2,5}$
Starting Material	E_e (a.u.)	-1400.092083	-1400.093061	-1400.086595	-1400.088621	-1400.090427	-1400.084514	-1400.091389	-1400.086938
	G_{corr} (223 K) (a.u.)	0.392436	0.393218	0.391148	0.393068	0.391781	0.392672	0.392717	0.394037
	G_{223} (a.u.)	-1399.699647	-1399.699843	-1399.695447	-1399.695553	-1399.698646	-1399.691842	-1399.698672	-1399.692901
Transition State	E_e (a.u.)	-1400.069826	-1400.066038	-1400.076614	-1400.068484	-1400.065767	-1400.075118	-1400.063359	-1400.073365
	G_{corr} (223 K) (a.u.)	0.389869	0.391369	0.388499	0.390541	0.391530	0.390774	0.388094	0.391125

G_{223} (a.u.)	-1399.679957	-1399.674669	-1399.688115	-1399.677943	-1399.674237	-1399.684344	-1399.675265	-1399.682240

Cartesian coordinates (Å) and energies of the optimized structures



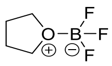
E_e = -2315.320448 a.u.

G_{corr} (223 K) = 0.253589 a.u.

G_{223}^{o} = -2315.066859 a.u.

C	-1.88201100	1.11547700	0.14649200
C	-0.63112500	1.05520300	-0.73025400
C	0.02637500	-0.32957100	-0.71184800
C	-1.98524000	-1.36625800	-0.10016500
C	-2.76938000	-0.06070300	-0.22414200
H	0.81049200	-0.38853600	-1.46803200
H	-0.93177200	1.25866000	-1.76863000
H	-1.57610300	1.03252100	1.20087000
H	-1.65693100	-1.49012500	0.93876700
H	-3.09019200	0.06008600	-1.27401100
C	-2.90496300	-2.51867200	-0.47368000
H	-2.42910700	-3.48576000	-0.30508600
H	-3.18669300	-2.43478000	-1.53452900
O	-0.86688200	-1.35501700	-0.97992200
O	0.56042300	-0.57033300	0.60030400
O	0.32659600	1.98372500	-0.28969700
O	-2.49615600	2.35809500	-0.10127200
O	-3.90917800	-0.13812700	0.61324600
O	-4.05213200	-2.45260700	0.35982300
C	-4.71659900	-1.22552100	0.22950200
H	-5.57137100	-1.24669700	0.90405300
H	-5.04161500	-1.08678700	-0.81576100
C	-3.21240400	2.87813200	1.00655000
H	-3.61198500	3.84504500	0.69764300
H	-4.03403700	2.21748700	1.29723500
H	-2.54592600	3.02410400	1.86594900

C	0.45418300	3.12575700	-1.11799300
H	-0.49857500	3.65887200	-1.19084100
H	1.20270200	3.76983300	-0.65481900
H	0.79622800	2.84659200	-2.12316700
C	1.73923300	-0.08074800	1.03667100
N	1.78162800	0.49280200	2.15198400
H	2.73412300	0.71634100	2.43476600
C	2.97709700	-0.41094600	0.14652000
Cl	2.79253500	-2.02355200	-0.58663900
Cl	4.46557500	-0.41022600	1.12633300
Cl	3.15877200	0.81935100	-1.13581500



E_e = -557.015019 a.u.

G_{corr} (223 K) = 0.110127 a.u.

G_{223}^o = -556.904892 a.u.

C	-0.89540000	-1.17575500	-0.42315600
O	-0.11495600	0.06009300	-0.56031100
C	-0.91291700	1.21937000	-0.14250700
C	-2.32880500	0.67745700	-0.05280100
C	-2.09668600	-0.76424800	0.40789300
H	-1.16453100	-1.48348000	-1.43448600
H	-0.24681900	-1.91886700	0.03687900
H	-0.53087500	1.53858000	0.82903200
H	-0.75668000	1.99694100	-0.88743900
H	-2.93361900	1.25894000	0.64373100
H	-2.80992900	0.69474400	-1.03435500
H	-1.83939000	-0.78843800	1.47035800
H	-2.95300500	-1.41639300	0.23402300
B	1.34978900	0.00692700	0.06569600
F	1.96204800	-1.02204800	-0.59154600
F	1.86339100	1.24563100	-0.19404900
F	1.15327100	-0.23895500	1.40333800

MeOH

E_e = -115.709083 a.u.

G_{corr} (223 K) = 0.035847 a.u.

G_{223}^{o} = -115.673236 a.u.

C	-0.04709300	0.65931500	0.00000000
H	-1.09003500	0.98161000	0.00000000
H	0.43955300	1.07630600	0.89006300
H	0.43955300	1.07630600	-0.89006300
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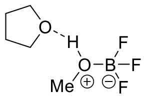
H	0.87022700	-1.04886400	0.00000000



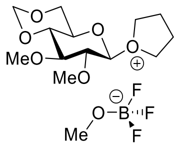
E_e = -672.742494 a.u.

G_{corr} (223 K) = 0.160567 a.u.

G_{223}^{o} = -672.581927 a.u.

C	1.99078900	1.83003900	-0.21568800
H	3.04696100	1.57840000	-0.29766500
H	1.74649600	2.65218500	-0.88630600
H	1.74392800	2.08149800	0.81706800
O	1.25040400	0.67202700	-0.63351100
H	0.21248100	0.83989400	-0.62865000
B	1.56326000	-0.63990100	0.12954400
F	1.42963000	-0.36191100	1.47786000
F	0.59605800	-1.51617200	-0.32109900
F	2.84191500	-0.99770800	-0.20740100
C	-1.86239200	-0.09254000	-1.27789000
O	-1.19000700	0.95063700	-0.52385500
C	-1.59979300	0.90609700	0.86928700
C	-2.82151100	-0.00200900	0.89052700
C	-2.49814300	-0.99428700	-0.22959800
H	-2.60637500	0.38991100	-1.91784500
H	-1.11223600	-0.59500900	-1.89029900
H	-0.77079600	0.49076900	1.45189700

H	-1.79876500	1.93072200	1.18719200
H	-2.95765500	-0.47830100	1.86237900
H	-3.72367400	0.56816100	0.65077900
H	-1.76453600	-1.72797400	0.11160800
H	-3.37744000	-1.51375800	-0.61301200



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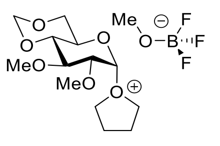
G_{corr} (223 K) = 0.392436 a.u.

G_{223}^{o} = -1399.699647 a.u.

C	-1.65663200	-0.81258500	-0.70865300
C	-0.26828600	-1.46856400	-0.77893000
C	0.71072300	-0.59790600	-0.00203400
C	-0.90177800	0.32519200	1.37478500
C	-1.99377800	-0.54140600	0.74995400
H	-0.33672400	-2.46939500	-0.32348900
H	-1.60338400	0.14655600	-1.24615300
H	-0.81124600	1.26502000	0.82074600
H	-2.04047400	-1.50459400	1.29007600
O	0.33452600	-0.38931000	1.31854800
C	-1.26372000	0.60405900	2.82254400
H	-0.57128100	1.31386900	3.27730000
H	-1.25508000	-0.33473500	3.39832900
O	-3.23276400	0.12986600	0.87317700
O	-2.55566100	1.19282200	2.83868700
C	-3.51343900	0.36949100	2.23234700
H	-4.46616800	0.89503200	2.27643600
H	-3.56876300	-0.59470200	2.76657400
O	-2.56845200	-1.69212400	-1.31921700
O	0.20781100	-1.54034400	-2.09522300
C	-0.01401500	-2.79149100	-2.72749400
H	0.49811900	-3.59706600	-2.18448900

H	-1.08136900	-3.01800600	-2.78885300
H	0.40760100	-2.71413200	-3.72988300
C	-3.61523300	-1.03260200	-2.01428000
H	-4.21132200	-0.41291500	-1.33858600
H	-3.21022300	-0.40478000	-2.81812600
H	-4.24388800	-1.81023100	-2.44988900
H	0.89846500	0.32593400	-0.55173000
O	2.01554700	-1.24317100	0.06790200
C	3.13971600	-0.27388600	0.34630100
C	2.14384200	-2.44934300	0.94387400
C	4.11750100	-1.12203700	1.12617300
H	3.45414400	0.07693600	-0.63233200
H	2.68742700	0.54001600	0.91534200
C	3.20693900	-2.04357600	1.94355600
H	1.16213600	-2.63711700	1.37117000
H	2.45157900	-3.24743800	0.26942300
H	4.75160600	-0.49558000	1.75429300
H	4.75211900	-1.70205900	0.45184800
H	2.74813000	-1.49608200	2.77046600
H	3.72831500	-2.91651700	2.33683200
O	-0.14048300	2.22661500	-1.13220500
F	1.28526700	2.29519600	0.67608900
F	2.16558400	1.86222200	-1.39546200
F	1.43764100	3.97466300	-0.89548800
C	-0.32291100	2.22692800	-2.52552800
H	0.06078300	3.14848800	-2.98333900
H	0.18029500	1.37283200	-2.99958300
H	-1.39399100	2.15982900	-2.74600600
B	1.18380300	2.61872600	-0.69633400



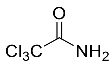
E_e = -1400.086595 a.u.

G_{corr} (223 K) = 0.391148 a.u.

G_{223}^{o} = -1399.695447 a.u.

C	-0.21858200	-0.80977300	1.50328500
C	0.44276900	0.47431800	1.00047500
C	1.03598000	0.35421400	-0.40530800
C	-0.31741200	-1.54622100	-0.85033600
C	-1.14554900	-1.29096600	0.40314100
H	-0.35284000	1.22379100	0.89372300
H	0.55213600	-1.57239700	1.70554700
H	0.43108000	-2.31709800	-0.61637800
H	-1.89544900	-0.51268200	0.19689100
O	0.32967900	-0.35515100	-1.30712300
C	-1.22908900	-2.05823800	-1.95643500
H	-0.66100400	-2.34882900	-2.84211700
H	-1.94600700	-1.26934500	-2.21351400
O	-1.77441100	-2.51433500	0.75037200
O	-1.88317200	-3.22035700	-1.46608400
C	-2.61084800	-2.93908600	-0.30035700
H	-3.08388200	-3.86689200	0.01855600
H	-3.36160500	-2.15931900	-0.50737400
O	-0.89197100	-0.46757700	2.68835900
O	1.44641900	0.90533800	1.88363800
C	1.04546200	1.96883400	2.73814900
H	1.89262400	2.18054300	3.39161100
H	0.80377200	2.86552000	2.15567400
H	0.17845700	1.67593200	3.33503700
C	-1.05342900	-1.54532200	3.59508800
H	-0.07864700	-1.96072000	3.88242600
H	-1.54192100	-1.13870400	4.48138900
H	-1.67032900	-2.33970200	3.16696800
H	1.28459700	1.32296500	-0.83814100
C	2.87736000	-1.12263100	-1.45127800
C	3.56162300	0.49571400	0.23533100
C	4.38066000	-1.14220100	-1.29118200

H	2.55067200	-0.57336900	-2.33517400
H	2.39171900	-2.09405500	-1.39788100
C	4.67005300	0.26679500	-0.77402300
H	3.77668900	0.11958600	1.23254800
H	3.18979500	1.51571800	0.29651600
H	4.67894900	-1.89778200	-0.56046200
H	4.86760000	-1.35745000	-2.24266600
H	5.64860100	0.35631600	-0.30167000
H	4.60528100	0.99321700	-1.58786900
O	2.43046500	-0.35531000	-0.25817700
O	-0.71155900	2.47066400	-1.13368400
F	-2.26944100	0.86382900	-1.73123300
F	-2.35381200	1.73637500	0.38499000
F	-2.98987800	3.02183900	-1.39586600
C	-0.41946500	3.67057000	-0.46996000
H	0.66930200	3.80311100	-0.42025900
H	-0.84544600	4.54091300	-0.98664800
H	-0.81115000	3.67057900	0.55813500
B	-2.08712200	2.03590600	-0.98076400

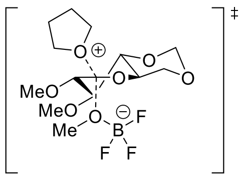


E_e = -1587.970380 a.u.

G_{corr} (223 K) = 0.022872 a.u.

G_{223}^{o} = -1587.947508 a.u.

C	1.25849500	0.53567300	-0.03290400
O	1.46297400	1.72783500	-0.04413500
N	2.19827800	-0.42148500	-0.02941800
H	3.16594900	-0.13521500	-0.03098700
H	1.98347700	-1.40655700	-0.02639300
C	-0.21049100	-0.02000300	-0.00190200
Cl	-1.36046000	1.31142300	-0.09999300
Cl	-0.45696900	-1.13037300	-1.37842700
Cl	-0.44899400	-0.91190500	1.52696300



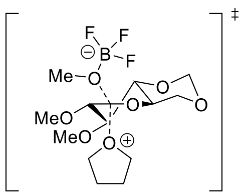
E_e = -1400.069826 a.u.

G_{corr} (223 K) = 0.389869 a.u.

G_{223}^{o} = -1399.679957 a.u.

C	1.77669900	0.00102400	0.91616200
C	0.37419000	0.00684000	1.53284100
C	-0.71952600	0.14942200	0.50084700
C	0.69938000	-0.53058200	-1.26010100
C	1.72171300	-0.99373700	-0.23201500
H	0.23565300	-0.99099000	1.97942100
H	2.01419400	1.00355200	0.53594600
H	0.98035400	0.45043600	-1.64536400
H	1.44060900	-1.98408300	0.17140700
O	-0.61925500	-0.34911800	-0.68601100
C	0.62238000	-1.52963700	-2.39934100
H	-0.02684900	-1.16277600	-3.19530700
H	0.25213900	-2.50244300	-2.03847000
O	2.95940100	-1.10323500	-0.90239700
O	1.93341200	-1.65071600	-2.92698300
C	2.85992000	-2.04260600	-1.95116300
H	3.83538000	-2.09029600	-2.43149400
H	2.57417200	-3.02204700	-1.53279000
O	2.66075300	-0.39648400	1.93064500
O	0.19222200	1.00378800	2.49089700
C	0.28349300	0.53532900	3.83050000
H	-0.49883000	-0.20614500	4.03316800
H	1.26645200	0.09615900	4.02124900
H	0.13380900	1.40197800	4.47406300
C	3.96389400	0.15306600	1.79889300
H	4.43390800	-0.16106700	0.86294800
H	3.92649000	1.24862800	1.83642900

H	4.54624000	-0.21520000	2.64390400
H	-1.53215100	0.84301500	0.67004600
O	-2.05047500	-1.21415500	1.28011100
C	-3.38282400	-0.81141200	0.85280100
C	-1.78409900	-2.55971000	0.83059700
C	-4.03332400	-2.07508600	0.30411700
H	-3.89018800	-0.38352000	1.71830300
H	-3.27345900	-0.04473600	0.07680500
C	-2.82569300	-2.84039900	-0.24152200
H	-0.75283500	-2.59785900	0.46525600
H	-1.88100500	-3.22854700	1.69068200
H	-4.78080000	-1.84790200	-0.45672300
H	-4.51158900	-2.64083000	1.10830900
H	-2.50494500	-2.41331200	-1.19661200
H	-3.00851400	-3.90752400	-0.37230200
O	0.07086900	2.25047600	-0.35243500
F	-0.63482700	1.69190300	-2.49604200
F	-2.22395200	2.07674600	-0.88038600
F	-1.01723800	3.82222000	-1.73813600
C	0.22701600	3.30208200	0.57606900
H	0.46563000	4.23909900	0.06404400
H	-0.68475200	3.45359300	1.17017500
H	1.03521800	3.04702700	1.26576800
B	-0.95698300	2.47719100	-1.38210000



E_e = -1400.076614 a.u.

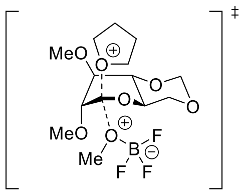
G_{corr} (223 K) = 0.388499 a.u.

G_{223}^{o} = -1399.688115 a.u.

C	0.07914900	0.75053600	1.47995700
C	-0.24217800	-0.65842400	0.97791600

C	-0.59400200	-0.69477400	-0.48921300
C	0.24882600	1.47054900	-0.88633200
C	0.99546500	1.37424400	0.43814900
H	0.69780000	-1.22848900	1.04189200
H	-0.85334400	1.32885800	1.56675400
H	-0.64620700	2.08539000	-0.74497200
H	1.89138200	0.74536900	0.31822400
O	-0.22984900	0.17658400	-1.34227200
C	1.13606400	2.11188100	-1.94367300
H	0.59251600	2.27713800	-2.87516900
H	2.01262000	1.48220800	-2.12473100
O	1.35670700	2.69519100	0.79300500
O	1.50379600	3.38325500	-1.42694800
C	2.17946300	3.26157100	-0.20374800
H	2.43666900	4.26634400	0.12689000
H	3.07929600	2.63919100	-0.33115100
O	0.69988100	0.59999500	2.72884200
O	-1.26900200	-1.28625700	1.68881200
C	-0.81210300	-2.13644300	2.73588400
H	-1.70457800	-2.54439900	3.21056600
H	-0.20810900	-2.95799400	2.33423900
H	-0.22493500	-1.57311000	3.46442500
C	0.51785200	1.70383400	3.60318300
H	-0.54903500	1.87395800	3.79439700
H	1.01189100	1.44376500	4.53967500
H	0.96192000	2.61429300	3.19287300
H	-1.11804500	-1.55119200	-0.89510000
C	-3.08007300	1.08600800	-1.18193700
C	-3.67515500	-0.77886700	0.13479900
C	-4.54209900	0.73853600	-1.45303600
H	-2.45604500	0.91284800	-2.06766700
H	-2.93743900	2.11576400	-0.84191600
C	-4.58384900	-0.74477900	-1.08454000
H	-4.20345800	-0.47733600	1.04600800

H	-3.19250600	-1.73950900	0.31411200
H	-5.19729100	1.31111100	-0.79050100
H	-4.82750500	0.94255200	-2.48586600
H	-5.58807700	-1.11053100	-0.86548200
H	-4.15841700	-1.35096300	-1.89070100
O	-2.64458300	0.19694200	-0.13503300
O	1.05114500	-2.31675700	-1.06396000
F	2.42942800	-0.57826100	-1.68539800
F	2.66975300	-1.45901700	0.41228400
F	3.35774700	-2.66783100	-1.40496300
C	0.85969400	-3.53375600	-0.38479200
H	-0.21519900	-3.70311200	-0.23961500
H	1.26675600	-4.37629500	-0.95540100
H	1.34468500	-3.52462100	0.60098200
B	2.40104100	-1.76951600	-0.94706900



E_e = -1400.066038 a.u.

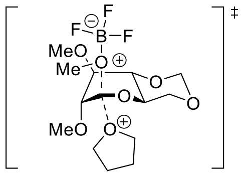
G_{corr} (223 K) = 0.391369 a.u.

$G_{223}{}^{o}$ = -1399.674669 a.u.

C	-1.78445700	0.01439300	1.25849600
C	-0.27822100	-0.34377300	1.34455100
C	0.44016100	-0.15696400	0.02064900
C	-1.43639300	-1.13500600	-0.95065600
C	-2.28666100	-0.12434600	-0.17840300
H	1.39399900	0.33549800	-0.07576900
H	-2.31436500	-0.74530900	1.85650900
H	-1.38533500	-2.09415300	-0.43109600
H	-2.19957500	0.85446200	-0.67697900
O	-0.08812600	-0.59647000	-1.04665700
O	-3.62326700	-0.58297500	-0.19540000

C	-1.98885200	-1.28602500	-2.36013200
H	-1.47294200	-2.06852000	-2.91692700
H	-1.88693300	-0.32946100	-2.89496300
O	-3.34856800	-1.66076800	-2.23991500
C	-4.08676400	-0.71047300	-1.52039000
H	-4.03098800	0.26846600	-2.02419700
H	-5.11328600	-1.06829300	-1.46808600
C	2.72265500	-2.24664700	1.29278600
H	2.70331500	-1.48447200	2.08538500
O	-1.96981900	1.28935400	1.80376000
C	-3.33348400	1.66187700	1.91241600
H	-3.35850600	2.60647400	2.45528500
H	-3.79555700	1.79584500	0.92831100
H	-3.90157900	0.90342400	2.46594300
O	2.28364500	-1.72389300	0.06237300
H	3.74985700	-2.62169600	1.20943700
H	2.06786700	-3.07000200	1.58786600
B	3.23989200	-0.82072900	-0.56836800
F	3.45339800	0.29716700	0.28826700
F	4.45501400	-1.43571900	-0.83899400
F	2.63912200	-0.33876700	-1.74418800
C	0.57547000	2.38380700	-1.50491200
O	-0.14417800	2.07605600	-0.29972400
C	0.32155700	3.02185000	0.67219700
C	1.83272700	3.07871000	0.45502200
C	1.98395600	2.82295700	-1.06199100
H	0.57764100	1.48762400	-2.12966200
H	0.04217600	3.18548900	-2.02869800
H	-0.14817200	3.99299700	0.46567300
H	-0.00182000	2.67492900	1.65307000
H	2.25315000	4.03455300	0.77173800
H	2.33329300	2.28234200	1.01201900
H	2.29730000	3.71752400	-1.60295200
H	2.70886900	2.02864600	-1.24436400

H	0.20481500	0.28982400	2.09892500
O	-0.13941800	-1.71492900	1.63771100
C	-0.18643000	-1.98779500	3.03084100
H	-1.12812000	-1.64767500	3.47756500
H	-0.10891000	-3.06928800	3.13687900
H	0.65280500	-1.50609600	3.54513000



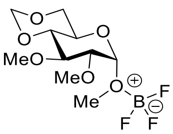
E_e = -1400.068484 a.u.

G_{corr} (223 K) = 0.390541 a.u.

$G_{223}{}^{o}$ = -1399.677943 a.u.

C	1.30226400	-1.30324600	-0.88133500
C	-0.24535300	-1.16594800	-0.93090600
C	-0.77364900	-0.02908600	-0.05358100
C	0.91545300	-0.54571000	1.46022700
C	1.90648400	-0.54650000	0.29625600
H	1.50607600	-2.37088000	-0.68889900
H	0.57644600	-1.56171700	1.68974400
H	2.11353400	0.49468400	0.01437200
O	-0.22639900	0.24842400	1.06907800
C	1.55408200	0.12581300	2.66744800
H	0.91827500	0.05899200	3.55133100
H	1.73555100	1.17931800	2.41620700
O	2.76239900	-0.55832300	2.95134500
O	3.08221000	-1.20421900	0.74100700
O	1.79733200	-0.93359500	-2.13867800
C	3.63089200	-0.53329900	1.85035600
H	4.53390300	-1.07001100	2.13706900
H	3.85708000	0.50977200	1.57508500
C	3.19350400	-1.12561800	-2.27793900
H	3.43126800	-0.94726300	-3.32681700

H	3.76188600	-0.42861200	-1.65328400
H	3.47860000	-2.15021100	-2.00502200
H	-1.46965700	0.71518600	-0.41317600
O	-2.54514800	-0.84948200	0.73151200
C	-3.09460200	0.14583200	1.62229600
C	-3.49772000	-1.16290100	-0.30767700
C	-4.59787100	0.08215800	1.39498500
H	-2.77805100	-0.10642700	2.63520800
H	-2.68715900	1.13066500	1.35432200
C	-4.66502100	-0.19882600	-0.10784000
H	-3.00835500	-1.04879200	-1.28061700
H	-3.78741300	-2.21021000	-0.18529200
H	-5.09857000	1.00656900	1.68582400
H	-5.03131300	-0.74704200	1.96119900
H	-4.49614200	0.72454800	-0.67054200
H	-5.61388800	-0.63001400	-0.42944900
O	0.43867400	1.49647800	-1.33194400
F	-1.01187900	2.76369700	0.02588400
F	1.21192500	2.52781000	0.58295800
F	0.59488400	3.84742900	-1.19204800
C	-0.13790700	1.59280700	-2.61234900
H	0.31076300	0.82892200	-3.25320900
H	-1.22972900	1.43232600	-2.58285500
H	0.04164600	2.58104400	-3.04485500
B	0.30873300	2.68806700	-0.47767800
H	-0.52111300	-0.92319900	-1.96524000
O	-0.85177200	-2.36606100	-0.51267000
C	-0.86715200	-3.33925200	-1.54440700
H	0.14233300	-3.56097000	-1.91134700
H	-1.30004900	-4.24296200	-1.11682100
H	-1.48274300	-2.99758000	-2.38609700



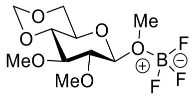
E_e = -1167.685080 a.u.

G_{corr} (223 K) = 0.277682 a.u.

G_{223}^o = -1167.407398 a.u.

C	-1.43400500	0.78534600	0.24759900
C	-0.41395100	1.45705600	-0.68103700
C	0.88605100	0.64708300	-0.80500300
C	-0.25586400	-1.33727900	-0.32263500
C	-1.61100800	-0.64180100	-0.25165900
H	-0.82980800	1.41721800	-1.69999700
H	-1.05052200	0.76784900	1.28104600
H	0.17952800	-1.37599900	0.68035200
H	-2.05279900	-0.60079800	-1.26251500
O	0.61716700	-0.64463400	-1.21342000
C	-0.45017500	-2.75959800	-0.81756200
H	0.48503600	-3.31895600	-0.77044700
H	-0.82097800	-2.74920700	-1.85375300
O	-2.45125900	-1.39652500	0.60222600
O	-1.38154500	-3.39539600	0.04614900
C	-2.59890000	-2.70439900	0.09705600
H	-3.24908500	-3.24272900	0.78503200
H	-3.04438800	-2.65516600	-0.91101200
O	-2.61981200	1.53533900	0.17251100
O	-0.14735800	2.78728200	-0.32828900
C	-0.88139900	3.74492300	-1.07944700
H	-0.62979800	3.67583700	-2.14480800
H	-1.95623700	3.60244700	-0.94578400
H	-0.58713700	4.72581600	-0.70547200
C	-3.42584100	1.46260500	1.33807900
H	-3.76455800	0.44038500	1.52621600
H	-2.87398800	1.82714300	2.21379600
H	-4.28664600	2.10941500	1.16499400
H	1.55555700	1.10562000	-1.53515000
O	1.63892400	0.52361600	0.44919200
F	2.45123800	-1.74795000	0.49912700

F	3.40617300	-0.26672500	-0.97675500
F	3.80874200	-0.08411300	1.26565600
C	1.87095100	1.73753000	1.21348400
H	2.50585500	1.44501000	2.04161900
H	2.36374100	2.47832800	0.58223400
H	0.91455300	2.11622900	1.56008400
B	2.95644200	-0.50112000	0.28822200



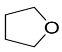
E_e = -1167.688443 a.u.

G_{corr} (223 K) = 0.277503 a.u.

G_{223}^{o} = -1167.410940 a.u.

C	-1.06777900	1.21418600	0.21958500
C	0.42973200	0.88728300	0.16263200
C	0.71578600	-0.44108900	0.87265900
C	-1.44672400	-1.22228100	0.60427400
C	-1.84861400	-0.00868000	-0.23351400
H	0.72385700	0.80448100	-0.89138100
H	-1.33749200	1.45148000	1.26176700
H	-1.66781900	-1.01392300	1.66287600
H	-1.60016000	-0.21582500	-1.28871500
O	-0.06909400	-1.49906100	0.42597300
C	-2.26773700	-2.42007000	0.15070800
H	-2.09823600	-3.28982800	0.78677200
H	-1.99913700	-2.67221000	-0.88615300
O	-3.24222900	0.19707600	-0.09642900
O	-3.64017400	-2.07384600	0.24935800
C	-3.94540700	-0.94569500	-0.52443300
H	-5.00643200	-0.73926800	-0.39249800
H	-3.70917500	-1.14375500	-1.58335000
O	-1.28622200	2.32787600	-0.61220600
O	1.20399600	1.84640900	0.83839700
C	1.65357700	2.92771000	0.03076100

H	2.33853300	3.50930900	0.64935800
H	2.18978200	2.54898600	-0.84452700
H	0.81789900	3.55461000	-0.28846500
C	-2.34376400	3.17188500	-0.18589400
H	-2.13992800	3.57354700	0.81500100
H	-2.39259400	3.99727000	-0.89719500
H	-3.29901200	2.64026900	-0.17354500
H	0.60347100	-0.29454000	1.95745300
O	2.07045600	-0.86546300	0.66798500
F	1.70697500	-1.14560600	-1.66575600
F	3.21266900	0.43412600	-0.96527800
F	3.71108800	-1.78678300	-0.74018900
C	3.00061300	-0.51692700	1.72571800
H	2.63116000	-0.95485500	2.65213800
H	3.94618500	-0.97060300	1.44099500
H	3.07362700	0.56688000	1.79208900
B	2.73538500	-0.84190200	-0.83024200



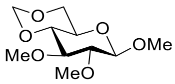
E_e = -232.409965 a.u.

G_{corr} (223 K) = 0.098220 a.u.

G_{223}^{o} = -232.311745 a.u.

C	-1.16060000	-0.42582700	-0.13689400
O	0.00000400	-1.24578900	-0.00009300
C	1.16056300	-0.42584100	0.13701500
C	0.72709500	0.98976500	-0.23787500
C	-0.72705400	0.98981100	0.23781600
H	-1.51307100	-0.46319300	-1.17682400
H	-1.95070400	-0.82103900	0.50849600
H	1.51277100	-0.46311600	1.17704300
H	1.95082300	-0.82111700	-0.50814100
H	1.34356700	1.75768800	0.23280100
H	0.76941400	1.12587700	-1.32311100
H	-0.76934800	1.12606400	1.32303400

H	-1.34351900	1.75770200	-0.23292200



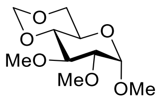
E_e = -843.099212 a.u.

G_{corr} (223 K) = 0.265358 a.u.

G_{223}^{o} = -842.833854 a.u.

C	0.05085400	1.18111900	0.20448000
C	1.26779900	0.32509600	-0.17222200
C	1.08452100	-1.14300900	0.22684400
C	-1.23598900	-0.96359600	0.25597100
C	-1.21699400	0.48030100	-0.24368400
H	1.39181400	0.36628500	-1.26488400
H	0.02832000	1.29478000	1.30157700
H	-1.20520000	-0.95536900	1.35765100
H	-1.23943100	0.46467600	-1.34737500
H	1.07741400	-1.22043800	1.33133800
C	-2.53875100	-1.60896900	-0.19220200
H	-2.65788300	-2.60966400	0.22602700
H	-2.55358100	-1.67408500	-1.29108500
O	-0.13587100	-1.66531600	-0.27572900
O	2.12699500	-1.87277600	-0.30815600
O	-2.35968600	1.15350400	0.25047300
O	0.08373500	2.44225600	-0.41760200
O	2.39507800	0.85360900	0.49037700
O	-3.61543900	-0.81362400	0.28019600
C	-3.52642300	0.50569600	-0.18926900
H	-4.37451300	1.05203200	0.22159000
H	-3.55327100	0.50870400	-1.29251800
C	3.58166800	0.84905600	-0.28424700
H	3.85360700	-0.16488000	-0.59022600
H	3.46509200	1.47791800	-1.17700000
H	4.37028800	1.26671000	0.34353300
C	0.90902200	3.41036700	0.20354800
H	0.76941500	3.40578300	1.29186100

H	1.96910700	3.24635800	-0.01098800
H	0.60397200	4.38163900	-0.19028100
C	2.19447900	-3.20132500	0.18999400
H	1.30065000	-3.76810900	-0.08409500
H	3.07354200	-3.66308000	-0.25854800
H	2.30103800	-3.19889300	1.28168000



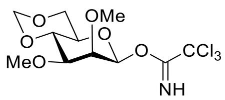
E_e = -843.100876 a.u.

G_{corr} (223 K) = 0.265524 a.u.

$G_{223}{}^{o}$ = -842.835352 a.u.

C	0.30679500	1.09173900	0.13860800
C	1.36575100	0.24277700	-0.57318900
C	1.08472900	-1.26519800	-0.43541900
C	-1.20301400	-0.88309300	-0.08259000
C	-1.06559500	0.62127800	-0.29841900
H	1.32313300	0.48155200	-1.64921000
H	0.40645500	0.94790600	1.22467500
H	-1.08195300	-1.09744200	0.98768100
H	-1.18635400	0.83487100	-1.37529000
C	-2.59850100	-1.30390700	-0.51598200
H	-2.79246100	-2.35412000	-0.29104300
H	-2.71261500	-1.14102900	-1.59888500
O	-0.23239100	-1.57405700	-0.84732200
O	-2.07992900	1.28218100	0.43560500
O	0.44891600	2.45070600	-0.20356000
O	2.61388200	0.60950900	-0.04233600
O	-3.53901000	-0.52743300	0.21149100
C	-3.34429300	0.84674100	0.00376300
H	-4.08913200	1.37149300	0.60083600
H	-3.46470900	1.07925600	-1.06840500
C	3.71296400	-0.03114300	-0.65657100
H	3.77830100	-1.08627300	-0.36373900

H	3.65217500	0.03495900	-1.75116100
H	4.61320500	0.48305200	-0.31839000
C	1.16844800	3.21642200	0.74511000
H	0.66806200	3.19887300	1.72198600
H	2.19306400	2.85104900	0.85905500
H	1.18505500	4.24296500	0.37528900
H	1.72252800	-1.85139200	-1.11222300
O	1.32535300	-1.61711700	0.88921800
C	1.22074400	-3.01320400	1.11716300
H	1.90529400	-3.56376800	0.45922800
H	1.49740500	-3.18834900	2.15638300
H	0.19980700	-3.36837800	0.94359600



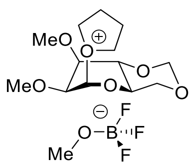
E_e = -2315.329520 a.u.

G_{corr} (223 K) = 0.252835 a.u.

G_{223}^o = -2315.076685 a.u.

C	2.49544500	0.98710200	-0.62205800
C	1.02091300	1.25377300	-0.24873600
C	0.19687600	0.00844300	-0.56769200
C	1.97550600	-1.42293600	-0.23324900
C	2.92809200	-0.27128300	0.10396200
H	2.57494800	0.81456100	-1.70907300
H	2.02770900	-1.61259100	-1.31761300
H	2.88429300	-0.07875800	1.18760400
C	2.45168900	-2.66653700	0.50194400
H	1.86961500	-3.54593200	0.22261200
H	2.36460800	-2.50499400	1.58706400
O	0.65342100	-1.10755200	0.15299000
O	3.33697000	2.04395900	-0.23307200
O	4.23743800	-0.65137200	-0.27507800
O	3.80111400	-2.90735500	0.13314900
C	4.62159300	-1.80720000	0.42623100

H	5.63001200	-2.06227400	0.10284900
H	4.59484800	-1.60317400	1.51024200
C	3.31556500	3.14119900	-1.12418800
H	4.04735000	3.86264400	-0.75954700
H	3.58981000	2.82916900	-2.13974100
H	2.33115900	3.62639900	-1.15760800
H	0.21532400	-0.20765200	-1.64529100
O	0.89724300	1.50490700	1.12897100
O	-1.12691100	0.25628500	-0.15831800
H	0.61625100	2.08879000	-0.83889800
C	0.89277200	2.87754000	1.47389000
H	0.10503100	3.41487800	0.92958900
H	0.68329100	2.93282200	2.54293000
H	1.86100800	3.34534200	1.27089600
C	-2.07249100	-0.56023100	-0.65693000
C	-3.42107500	-0.16865400	-0.01420600
N	-1.84585600	-1.46412400	-1.49722700
H	-2.68968700	-1.96735700	-1.76240900
Cl	-3.76306700	1.54036200	-0.38663300
Cl	-3.29808800	-0.38865100	1.74750600
Cl	-4.73932200	-1.17649200	-0.64122400



E_e = -1400.084514 a.u.

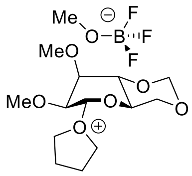
G_{corr} (223 K) = 0.392672 a.u.

G_{223}^o = -1399.691842 a.u.

C	1.80955900	0.94913100	-0.83793300
C	0.28190900	0.74799600	-0.95745700
C	-0.28852300	-0.06149000	0.19255300
C	1.52517100	-1.50879800	-0.30572900
C	2.40403400	-0.27056700	-0.12863900
H	-1.37344900	-0.07204800	0.19362000

H	2.25232100	1.00833900	-1.84482100
H	1.43706600	-1.74270000	-1.37381000
H	2.46540800	-0.03729900	0.94802000
O	0.22028400	-1.32012200	0.25020100
O	3.69105400	-0.56625100	-0.63665600
C	2.19021300	-2.67786700	0.40834000
H	1.65186600	-3.61074000	0.23723400
H	2.21990500	-2.46950800	1.48920700
O	3.49854300	-2.82874200	-0.11460800
C	4.25422800	-1.66125800	0.04928600
H	4.33700400	-1.41534400	1.12155100
H	5.23495300	-1.84290400	-0.38715000
C	-2.71564200	-0.15257200	-2.57688200
H	-2.59548000	0.88770200	-2.24261900
O	2.03472100	2.14372900	-0.13453300
C	3.39890400	2.53096300	-0.12557900
H	3.44937700	3.50216800	0.36633100
H	4.01928000	1.81153900	0.42020400
H	3.78231100	2.61794700	-1.15025500
O	-2.36619900	-1.06234800	-1.56686800
O	-0.45022500	1.92771100	-1.10045700
C	-0.15819700	2.61435500	-2.30685100
H	-0.28936400	1.94884700	-3.16961100
H	-0.86565100	3.43981000	-2.37711000
H	0.86343800	3.00904200	-2.29508400
H	0.09027600	0.08644800	-1.81916600
H	-3.75632800	-0.28543700	-2.90459900
H	-2.06686900	-0.31462600	-3.44568600
B	-3.28355200	-1.09018000	-0.44820700
F	-3.49220400	0.23657700	0.03792000
F	-4.52221300	-1.64144300	-0.77817500
F	-2.67890700	-1.82025800	0.59436000
C	-0.62435200	-0.17754200	2.64657100
O	0.08623800	0.56514600	1.56510800

C	-0.31090300	1.98244000	1.79693000
C	-1.79695900	1.89501700	2.09270800
C	-1.98102500	0.51553600	2.77024800
H	-0.66419600	-1.21671200	2.33057800
H	0.02034500	-0.05774000	3.51677500
H	0.28739600	2.26935600	2.66307300
H	-0.01477100	2.54388900	0.91823300
H	-2.10702900	2.72444700	2.72918100
H	-2.36973900	1.92506900	1.16411200
H	-2.25550500	0.60171100	3.82207700
H	-2.74072600	-0.05926200	2.24093200



E_e = -1400.086938 a.u.

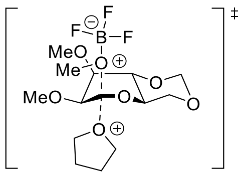
G_{corr} (223 K) = 0.394037 a.u.

G_{223}^{o} = -1399.692901 a.u.

C	1.74786500	1.55239900	0.10809000
C	0.35131200	1.92201700	-0.45447000
C	-0.50317700	0.66562000	-0.40367200
C	1.32050500	-0.33934100	-1.54109200
C	2.08750100	0.11694900	-0.30161000
H	0.45828800	2.22189900	-1.50957500
H	2.51081400	2.23190700	-0.30431000
H	1.59719800	0.28005300	-2.40487000
H	1.77074600	-0.54406400	0.52117000
O	-0.08439800	-0.28243800	-1.31117500
C	1.69393800	-1.79383900	-1.80002700
H	1.24681400	-2.16763100	-2.72254900
H	1.33887700	-2.39361600	-0.95006000
O	3.10559600	-1.86509000	-1.94783800
O	3.47277600	-0.03305900	-0.55505300

O	1.66932000	1.68469600	1.50617200
O	-0.30575000	2.91183600	0.27798800
C	3.76481900	-1.38966500	-0.80779200
H	4.83526000	-1.45843500	-0.99698300
H	3.47636700	-1.99062900	0.07121800
C	2.91569000	1.48640300	2.14752800
H	2.76073500	1.68352200	3.20857300
H	3.28109200	0.46047800	2.01980800
H	3.67236200	2.17688400	1.75182500
C	0.37716100	4.15387300	0.28161200
H	-0.27902700	4.87223700	0.77244500
H	1.31650300	4.08102500	0.83894400
H	-0.60300300	0.25434900	0.60278300
O	-1.88346900	1.00230000	-0.83652800
C	-2.61223800	-0.01303100	-1.67391700
C	-2.79156500	1.54118900	0.22585000
C	-4.04397600	0.43403000	-1.49262200
H	-2.20672000	0.09446300	-2.67585600
H	-2.39059900	-0.98977900	-1.24503700
C	-4.10452300	0.81703300	-0.01117700
H	-2.31947600	1.32158900	1.18118000
H	-2.82053900	2.61201700	0.04112600
H	-4.72941800	-0.37653700	-1.74306300
H	-4.26346100	1.29287200	-2.13223700
H	-4.14185500	-0.07886000	0.60787600
H	-4.95080000	1.46403200	0.22165500
O	0.09062900	-1.81787900	1.29608600
F	-2.15882500	-1.14209900	1.05225900
F	-1.26139600	-2.72352600	-0.34791700
F	-1.71027100	-3.23866200	1.84765900
C	0.26352900	-1.38176700	2.61974100
H	1.31454100	-1.11120600	2.77355700
H	-0.34710300	-0.49295300	2.84133700
H	-0.00504800	-2.16390700	3.34075300

B	-1.24954900	-2.25305600	0.96987700
H	0.58095000	4.49000200	-0.74296500



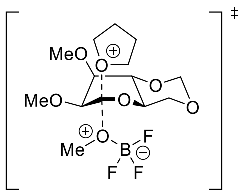
E_e = -1400.073365 a.u.

G_{corr} (223 K) = 0.391125 a.u.

G_{223}^{o} = -1399.682240 a.u.

C	1.23805200	1.48869900	-0.72166900
C	-0.31970300	1.36776800	-0.66315200
C	-0.80079700	0.04683700	-0.11971200
C	0.89733500	-0.91825200	-1.37890900
C	1.86697400	0.09699900	-0.77284100
H	-0.67066100	1.38450500	-1.70914600
H	1.49836600	1.99257300	-1.66797500
H	0.53802100	-0.59404500	-2.36292100
H	2.08904100	-0.23267600	0.25294300
O	-0.22217300	-1.04241100	-0.47779400
C	1.58332000	-2.27415000	-1.47246000
H	0.96308700	-3.00516800	-1.99314800
H	1.79845500	-2.62257400	-0.45457300
O	2.77019500	-2.09789500	-2.22855800
O	3.03203200	0.11971600	-1.57897200
O	1.66126000	2.26561800	0.35946600
O	-0.94624700	2.36551200	0.07938300
C	3.62073400	-1.15895300	-1.62727800
H	4.51013200	-1.08000900	-2.25045700
H	3.87629400	-1.48440700	-0.60576100
C	3.05014900	2.53721300	0.33167400
H	3.24760400	3.24415400	1.13753600
H	3.64322200	1.63024100	0.49230700
H	3.34550600	2.98135400	-0.62853000

C	-0.87127700	3.64175400	-0.53730600
H	-1.43842800	4.32632900	0.09242000
H	0.16627600	3.98175600	-0.60316300
H	-1.44817400	-0.02979900	0.74461000
O	-2.46293100	-0.13885300	-1.26998500
C	-2.96770400	-1.48831700	-1.07655900
C	-3.52106400	0.82361400	-1.01364900
C	-4.48017500	-1.33861200	-0.99177800
H	-2.61848200	-2.09740500	-1.91119700
H	-2.54553900	-1.87730500	-0.14226100
C	-4.62302600	0.03129900	-0.32516000
H	-3.09715000	1.62938900	-0.41184900
H	-3.84558200	1.21770800	-1.98148100
H	-4.93510400	-2.14878500	-0.42066600
H	-4.92055500	-1.32380900	-1.99263700
H	-4.42510900	-0.04403500	0.74849300
H	-5.60477700	0.48452900	-0.46778200
O	0.50801400	0.16352700	1.94973800
F	-0.99144300	-1.64726400	2.10541700
F	1.24038700	-2.00001700	1.63770300
F	0.58084000	-1.36845700	3.74508600
C	-0.02974200	1.14160500	2.80593800
H	0.24267600	2.12384900	2.41607700
H	-1.12909400	1.08019000	2.85376600
H	0.35442400	1.02283100	3.82499900
B	0.33534500	-1.21933900	2.37941000
H	-1.31888300	3.61219600	-1.53957800



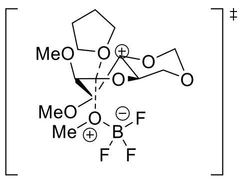
E_e = -1400.075118 a.u.

G_{corr} (223 K) = 0.390774 a.u.

G_{223}^{o} = -1399.684344 a.u.

C	-1.79944300	0.34751200	1.03846900
C	-0.27676100	0.61378900	1.20376900
C	0.52025400	0.27953800	-0.02049500
C	-0.76148900	-1.63585400	-0.14192000
C	-2.01079300	-0.77047800	0.01252500
H	1.43577000	0.79548000	-0.27864000
H	-2.19409200	-0.00450200	2.00472000
H	-0.42388700	-2.04999700	0.81380000
H	-2.21125300	-0.29253500	-0.96132500
O	0.29847800	-0.80513700	-0.65436200
O	-3.08342600	-1.60728500	0.39279400
C	-1.02393100	-2.75525800	-1.13381600
H	-0.17871000	-3.44238600	-1.17093400
H	-1.20019100	-2.32839300	-2.13273900
O	-2.16225100	-3.46316400	-0.67586000
C	-3.28025800	-2.62590700	-0.56371800
H	-3.50707500	-2.16877000	-1.54123900
H	-4.11041900	-3.23625500	-0.21303100
C	2.97631000	0.24516500	1.91754100
H	3.33728600	0.96431200	1.16592200
O	-2.42135600	1.54626500	0.67019400
C	-3.83607600	1.46419800	0.71929600
H	-4.21808900	2.45986700	0.49517900
H	-4.22495700	0.75063000	-0.01582900
H	-4.17270200	1.15724100	1.71802300
O	2.21731600	-0.78280700	1.32905600
O	0.06103800	1.91148200	1.57621200
C	-0.39811800	2.24897700	2.87698800
H	-0.02847800	1.52696900	3.61609100
H	0.00244100	3.23635700	3.10287100
H	-1.49185500	2.28237500	2.90658300
H	0.09916000	-0.11479400	1.94289200
H	3.84927600	-0.15638000	2.44357200

H	2.34917600	0.78789200	2.63340200
B	2.90065500	-1.50918900	0.25424100
F	3.01163100	-0.65966900	-0.87793000
F	4.17841800	-1.90228500	0.65010100
F	2.11345100	-2.62426000	-0.05895700
C	0.46145200	1.42991700	-2.59511500
O	-0.41179000	1.57301800	-1.45948300
C	-0.42444300	2.98840800	-1.19008900
C	1.04373600	3.39873900	-1.29745400
C	1.61585700	2.41853500	-2.35136300
H	0.77233100	0.38550400	-2.65117200
H	-0.11060100	1.68398100	-3.49364000
H	-1.03458300	3.46777800	-1.96597100
H	-0.87761000	3.13003400	-0.21292300
H	1.15464400	4.44418100	-1.58846600
H	1.53171100	3.26160100	-0.32847400
H	1.89572500	2.92303500	-3.27721600
H	2.50035400	1.89598000	-1.97770900



E_e = -1400.065767 a.u.

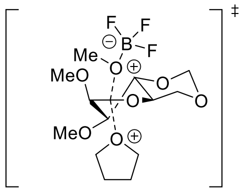
G_{corr} (223 K) = 0.391530 a.u.

G_{223}^{o} = -1399.674237 a.u.

C	1.75934500	-0.21114900	0.97273100
C	0.33917300	-0.26550100	1.56209100
C	-0.71249800	0.21112600	0.54425100
C	0.76011100	-0.15878800	-1.28239500
C	1.68156200	-0.94110800	-0.35517200
H	0.27301300	0.39799800	2.43150600
H	2.03672000	0.83593500	0.79552100
H	1.15913800	0.84629800	-1.43611900

H	1.29329900	-1.95861300	-0.18024800
H	-1.50950200	0.88607100	0.82300700
O	-0.55945000	0.04780900	-0.72642200
C	0.64464300	-0.87713200	-2.61554600
H	0.06790300	-0.29139600	-3.33273300
H	0.17152900	-1.86291600	-2.48090600
O	1.96100100	-1.01357700	-3.12415700
O	2.93519400	-1.01963000	-1.00313500
O	2.61876200	-0.82292300	1.89416600
O	0.09721800	-1.59995600	1.92697600
O	-2.22392500	-1.17500500	0.77592500
C	-3.44472400	-0.53596700	0.32054000
C	-1.99541700	-2.38937400	0.02681600
C	-4.15803700	-1.58886100	-0.51604800
H	-3.99631900	-0.21341700	1.20512900
H	-3.17573800	0.34156300	-0.28067700
C	-2.97770900	-2.34000300	-1.13497500
H	-0.94719300	-2.40958300	-0.27777500
H	-2.18020700	-3.23174100	0.70023500
H	-4.82332900	-1.14041900	-1.25475600
H	-4.74201700	-2.25489500	0.12519300
H	-2.55381000	-1.75858700	-1.96010000
H	-3.23618700	-3.33431900	-1.50116100
C	2.80071000	-1.69716800	-2.23182200
H	3.78872900	-1.73895700	-2.68662900
H	2.40476400	-2.70965100	-2.04686700
C	3.93123000	-0.28318600	1.87643200
H	3.91822800	0.78444700	2.13105700
H	4.50264500	-0.82331400	2.63211200
H	4.40235600	-0.41336400	0.89796000
C	-0.58315600	-1.74757200	3.16320200
H	0.01062600	-1.31855700	3.97833800
H	-1.57050100	-1.27693000	3.13052800
H	-0.70051100	-2.81922900	3.32634000

O	0.28018800	2.34960500	0.47049800
F	-0.19637300	2.56380900	-1.78673900
F	-1.93779200	2.61734600	-0.28703800
F	-0.49465300	4.38878700	-0.42818500
C	0.31658500	2.96013300	1.73945600
H	1.14464800	2.53432300	2.31808000
H	0.47284500	4.03832000	1.64873800
H	-0.61808300	2.79691000	2.29806500
B	-0.59529600	3.00425200	-0.52287000



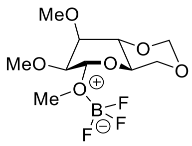
E_e = -1400.063359 a.u.

G_{corr} (223 K) = 0.388094 a.u.

G_{223}^{o} = -1399.675265 a.u.

C	-1.45279900	-1.68228800	0.08272300
C	-0.10112200	-1.38418300	0.76869700
C	0.66421900	-0.24623200	0.12119400
C	-1.03448900	0.19951800	-1.46214700
C	-1.99441100	-0.35706100	-0.41318600
H	-1.27639000	-2.34016900	-0.78316300
H	-0.92531900	-0.50100300	-2.29597400
H	-2.04687100	0.35264100	0.42982600
O	0.28322800	0.40346300	-0.89593400
C	-1.56908700	1.54004000	-1.95206500
H	-0.95492700	1.95619200	-2.75091900
H	-1.59703600	2.24494200	-1.11325400
O	-3.25261000	-0.50201200	-1.03431400
O	-2.86238500	1.28144900	-2.47875500
C	-3.71455300	0.74729800	-1.50443800
H	-4.68129200	0.57350900	-1.97372900
H	-3.80117300	1.44437100	-0.65564300

O	-2.27585900	-2.30868500	1.02465400
C	-3.22732100	-3.19799400	0.45651400
H	-2.72572000	-3.99997900	-0.09945400
H	-3.78076800	-3.63257300	1.28916500
H	-3.91537700	-2.67144400	-0.20916400
H	1.55719500	0.14256800	0.59899000
C	2.82946300	-0.60515400	-1.88202000
C	3.12169100	-2.18944700	-0.15853500
C	4.27911100	-1.06591500	-1.89588000
H	2.74139800	0.41121800	-1.47615100
H	2.32995200	-0.64990300	-2.85150300
C	4.46068000	-1.51537200	-0.44460500
H	3.12886900	-3.24983700	-0.42980000
H	2.81099700	-2.09684400	0.88853000
H	4.40516800	-1.91090400	-2.57902700
H	4.96245500	-0.26863200	-2.19124600
H	5.30247800	-2.19297700	-0.29660800
H	4.59460900	-0.64510900	0.20476000
O	2.15349800	-1.52222000	-0.99304500
O	-0.17000100	1.78951500	1.31721100
F	2.06766600	2.09312500	0.60935900
F	0.36611400	3.15392700	-0.49543800
F	0.97309600	3.83824800	1.60797800
C	-0.37185300	1.84115600	2.70983100
H	0.52884100	1.54099100	3.26445900
H	-0.64837400	2.84973700	3.03430900
H	-1.17067300	1.14356000	2.97070000
B	0.80481300	2.73670700	0.76954300
H	0.55090200	-2.26380200	0.68337100
O	-0.25320300	-1.00372400	2.10468400
C	-0.06016700	-2.05932300	3.03674200
H	0.96231000	-2.45168700	2.97242400
H	-0.21535100	-1.62488600	4.02439500
H	-0.77936400	-2.86375100	2.86693800



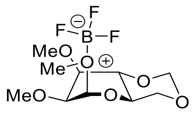
E_e = -1167.677736 a.u.

G_{corr} (223 K) = 0.276735 a.u.

G_{223}^{o} = -1167.401001 a.u.

C	1.46463900	1.21512600	-0.03735600
C	0.00090800	1.15154500	-0.52099200
C	-0.80965100	0.10403500	0.24942700
C	1.03146100	-1.25992200	-0.31125800
C	2.03313600	-0.20027100	0.13410600
H	-1.14374400	0.51730900	1.20314200
H	2.06228000	1.73112800	-0.80571100
H	0.81684800	-1.17623000	-1.38400200
H	2.18836000	-0.35742600	1.21553900
O	-0.13343900	-1.07852900	0.47841800
O	3.25143800	-0.37001800	-0.56180400
C	1.64285700	-2.62647300	-0.04766900
H	1.02121500	-3.43659900	-0.43049500
H	1.78933100	-2.76177400	1.03448000
O	2.88339600	-2.67068600	-0.73868300
C	3.75868800	-1.66200700	-0.31282000
H	3.95510900	-1.77033800	0.76737100
H	4.67667300	-1.76455000	-0.88942800
C	-2.60160200	0.60328400	-1.50076400
H	-2.93022400	1.53562800	-1.04919200
O	1.48136100	1.94089800	1.16502200
C	2.78982900	2.33188700	1.53596600
H	2.70730300	2.88590500	2.47078600
H	3.44657300	1.46588400	1.68802100
H	3.23464600	2.97608800	0.76577100
O	-2.03328000	-0.26743600	-0.48583200
O	-0.68917800	2.35546300	-0.35829300

C	-0.12966500	3.43516200	-1.08334400
H	0.00093300	3.17301900	-2.14166000
H	-0.83038200	4.26550000	-1.00182700
H	0.83508000	3.73494800	-0.65958300
H	0.04497700	0.86846200	-1.58479300
H	-3.43754300	0.03608900	-1.90327000
H	-1.86398000	0.77794900	-2.27966000
B	-3.22057000	-0.85961000	0.47424400
F	-3.91148800	0.25319700	0.87183700
F	-3.92197100	-1.67810800	-0.36129100
F	-2.57060700	-1.49005300	1.48844300



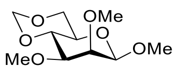
E_e = -1167.684748 a.u.

G_{corr} (223 K) = 0.278999 a.u.

G_{223}^{o} = -1167.405749 a.u.

C	0.17867400	1.67520800	0.05071700
C	-0.80742300	1.26841800	-1.06846600
C	-1.00101400	-0.24785600	-1.10022900
C	1.38156200	-0.21520800	-1.10460800
C	1.23589700	0.57520300	0.19625800
H	-0.32167700	1.49823600	-2.03133900
H	0.70009000	2.60059400	-0.24453200
H	1.67448500	0.47744700	-1.90531200
H	0.92034300	-0.11915800	0.99054000
O	0.16775200	-0.87957200	-1.46060900
C	2.48909400	-1.24785500	-0.93514400
H	2.69777900	-1.76353400	-1.87381600
H	2.19149000	-1.97781000	-0.17318500
O	3.67015300	-0.55776200	-0.55071800
O	2.49392700	1.14837200	0.51081500
O	-0.55803500	1.89020500	1.22673600
O	-2.04888700	1.90461000	-1.01114500

C	3.47543500	0.14622600	0.64367100
H	4.41228000	0.64621500	0.88569400
H	3.17942700	-0.55029900	1.44611300
C	0.22594700	2.43227200	2.27498800
H	-0.45047700	2.63495800	3.10532900
H	1.00411900	1.73318400	2.60073500
H	0.70685400	3.36670900	1.95674700
C	-1.95446300	3.31339600	-1.13425300
H	-2.97346800	3.69171700	-1.21097200
H	-1.46948600	3.75224600	-0.25593500
H	-1.79381100	-0.54462500	-1.79207400
O	-1.39352000	-0.76365800	0.22657400
F	-1.44133800	-2.94900100	-0.75646700
F	0.21240700	-2.44392100	0.77154600
F	-1.93694300	-2.73149400	1.46212000
C	-2.68356800	-0.27703100	0.69633700
H	-2.58039200	0.78104300	0.90947700
H	-3.43368400	-0.45628600	-0.07746800
H	-2.90903200	-0.84780700	1.58925800
B	-1.11152700	-2.37337900	0.43508100
H	-1.39629500	3.58961100	-2.03830500



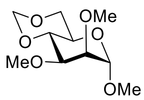
E_e = -843.097216 a.u.

G_{corr} (223 K) = 0.265208 a.u.

G_{223}^{o} = -842.832008 a.u.

C	0.05486200	1.20745100	-0.60732900
C	-1.29576200	0.54615800	-0.26146600
C	-1.22874300	-0.95106400	-0.58622000
C	1.06784000	-1.04977000	-0.25554900
C	1.15241000	0.43623100	0.09861400
H	0.20910700	1.13638100	-1.69866700
H	1.21974700	-1.15652900	-1.34257800
H	1.00878700	0.55054800	1.18507500

C	2.19440300	-1.77534200	0.46454900
H	2.24784700	-2.82562300	0.17329300
H	2.03345500	-1.71095200	1.55151600
O	-0.17917200	-1.57952300	0.13046800
O	2.43130400	0.91526700	-0.27774100
O	0.13485600	2.54527100	-0.19235300
O	3.42256400	-1.16405300	0.09913300
C	3.42923000	0.20487600	0.40965800
H	4.39097800	0.60299500	0.08817400
H	3.29135900	0.33829600	1.49638300
C	-0.85506600	3.38020000	-0.75125700
H	-0.91472500	3.25804300	-1.84154000
H	-1.84380400	3.18330800	-0.31749300
H	-0.57147300	4.40849500	-0.52420500
O	-1.53392400	0.77743700	1.10367600
H	-2.09787300	0.98238400	-0.87600100
C	-2.90028500	0.86675200	1.46599800
H	-2.92854000	1.21134400	2.50082100
H	-3.42263100	1.59908500	0.83478300
H	-3.40470800	-0.09873400	1.38359300
H	-1.03423400	-1.08232000	-1.67021500
O	-2.42457400	-1.54202400	-0.23301300
C	-2.51063100	-2.90675200	-0.61676900
H	-1.78505200	-3.51495600	-0.07109800
H	-3.52137000	-3.23781100	-0.38009000
H	-2.33485600	-3.01539700	-1.69450200



E_e = -843.101268 a.u.

G_{corr} (223 K) = 0.265704 a.u.

G_{223}^o = -842.835564 a.u.

C	0.51292800	-0.90623000	-0.64526300
C	1.53538800	0.04217200	0.01027300

C	0.97135700	1.46739000	0.11329600
C	-1.24140200	0.69569200	0.11022000
C	-0.80100800	-0.76710700	0.09478500
H	0.37536300	-0.58997700	-1.69232200
H	-1.38548300	1.02761200	-0.92723500
H	-0.65407600	-1.10769400	1.13277900
C	-2.56959000	0.78743000	0.84542200
H	-2.98369300	1.79654400	0.80421000
H	-2.42623000	0.50043300	1.89857500
O	-0.27841200	1.49884800	0.76644600
O	-1.81770600	-1.53289200	-0.52813900
O	0.90105300	-2.25468700	-0.58381500
O	-3.49257800	-0.08290700	0.20797400
C	-3.02005500	-1.40463900	0.18567800
H	-3.76896900	-2.00552700	-0.32908000
H	-2.87232000	-1.76130500	1.21960500
C	2.13602500	-2.52407700	-1.20927600
H	2.17577700	-2.09717500	-2.22076900
H	2.97952500	-2.13339400	-0.62560700
H	2.23045200	-3.60851600	-1.27750800
H	1.62068500	2.09890400	0.73587100
O	0.90051700	1.96310600	-1.18914000
C	0.47386100	3.31471100	-1.24881900
H	1.12627200	3.95356700	-0.64054100
H	0.53517700	3.62179800	-2.29247200
H	-0.55621400	3.42079500	-0.89412800
O	1.82872600	-0.46970000	1.28826500
H	2.44553600	0.09345500	-0.60523900
C	3.09255400	-0.07695600	1.78369600
H	3.22834800	-0.57423800	2.74445000
H	3.89500800	-0.38686600	1.10086200
H	3.16170300	1.00713300	1.93574500

5. Experimental section

5.1. Synthesis of acceptors

Acceptors	Name	Reference
3	1:2,3:4-Di-*O*-isopropylidene-D-galactopyranose	6
61a	Methyl 2,3,6-tri-benzyl-α-D-glucopyranoside	7
61b	Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside	8
61c	Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside	8
61d	Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside	7
61e	Methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside	9
61g	Phenylmethyl N-(5-hydroxypentyl)-N-(phenylmethyl)carbamate	10
66a	Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside	7
66b	Methyl 2,3-di-*O*-benzoyl-α-D-glucopyranoside	11
66c	Methyl 4,6-*O*-benzylidene-α-D-mannopyranoside	10
66d	Methyl 2,6-di-*O*-benzyl-α-D-galactopyranoside	12
66e	6-*O*-Tert-butyldimethylsilyl-D-glucal	13
66f	Methyl 6-*O*-tert-butyldiphenylsilyl-α-D-glucopyranoside	13
66g	Methyl 6-*O*-triphenylmethyl-α-D-glucopyranoside	9
66h	Methyl 6-deoxy-α-D-glucopyranoside	8
66i	Methyl 6-*O*-tert-butyldiphenylsilyl-α-D-galactopyranoside	13
66j	4-Methylphenyl-6-*O*-triisopropylsilyl-1-thio-β-D-galactopyranoside	13
66k	4-Methoxyphenyl-6-*O*-tert-butyldiphenylsilyl-α-D-mannopyranoside	13
66l	4-Methoxyphenyl-α-L-rhamnopyranoside	14

5.2. General preparation of trichloroimidate donors

General procedure A: To a solution of hemiacetal (1.0 mmol, 1.0 eq) in dry CH_2Cl_2 (8 mL) were added $NCCCl_3$ (1.5 mmol, 1.5 eq) and DBU (0.15 mmol, 0.15 eq) successively at 0 °C. After stirred at rt for 1 h, the mixture was concentrated under vacuum, and then purified by silica gel column chromatography (PE/EA = 20:1 ~ 10:1) to give the donor.

General procedure B: To a solution of hemiacetal (1.0 mmol, 1 eq) in dry CH_2Cl_2 (8 mL) were added $NCCCl_3$ (20 mmol, 20 eq) and DBU (0.15 mmol, 0.15 eq) successively at 0 °C. After stirred at rt for 1 h, the mixture was concentrated under vacuum, and then purified by silica gel column chromatography (PE/EA = 20:1 ~ 10:1) to give the donor.

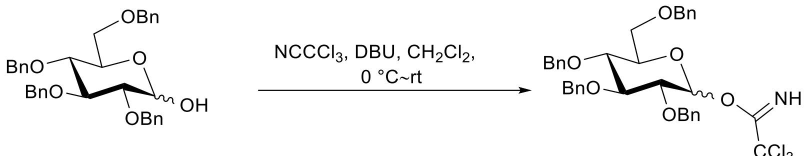
General procedure C: To a solution of hemiacetal (1.0 mmol, 1.0 eq) in dry CH_2Cl_2 (8 mL) were added $NCCCl_3$ (1.5 mol, 1.5 eq) and Cs_2CO_3 (0.10 mmol, 0.10 eq) successively at 0 °C. After stirred at rt for 1 h, the mixture was filtered, and the filtrate was concentrated under vacuum to give the donor, which was used in the next step without further purification.

General procedure D: To a solution of hemiacetal (1.0 mmol, 1.0 eq) in dry CH_2Cl_2 (8 mL) were added $NCCCl_3$ (5.0 mmol, 5.0 eq) and K_2CO_3 (5.0 mmol, 5.0 eq) successively at 0 °C. After stirred at rt for 1 h, the mixture was concentrated under vacuum, and then purified by silica gel column chromatography (PE/EA = 20:1 ~ 10:1) to give the donor.

Notification: Silica gel utilized to purify the trichloroimidate donors was all neutralized by petroleum ether/triethylamine (20:1, *v*/*v*).

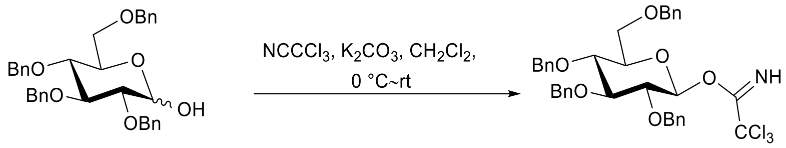
5.3. Synthesis of donor 1, 2, 5 ~ 18, 33 ~ 46

2,3,4,6-Tetra-*O*-benzyl-D-glucopyranosyl trichloroacetimidate (1)



S1 — **1** (α/β = 7:1)

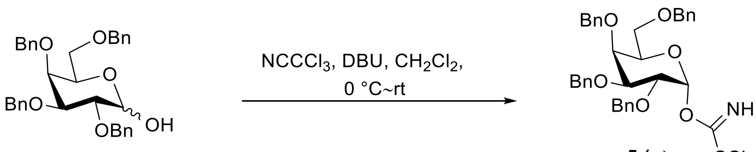
According to **general procedure A**, commercially available **S1** (2.1 g, 3.7 mmol) was treated with $NCCCl_3$ (1.2 mL, 7.4 mmol) and DBU (80 μL, 0.6 mmol) in dry CH_2Cl_2 (25 mL) to give donor **1** (2.2 g, 87%, α/β = 7:1) as a syrup. The spectroscopic data were in accordance with the literature.[15]



S1 — **2** (β)

According to **general procedure D**, commercially available **S1** (1.0 g, 1.9 mmol) was treated with $NCCCl_3$ (1.0 mL, 9.5 mmol) and K_2CO_3 (1.3 g, 9.5 mmol) in dry CH_2Cl_2 (15 mL) to give donor **2** (0.90 g, 71%, β/α = 4:1) as a white solid. The spectroscopic data were in accordance with the literature.[15]

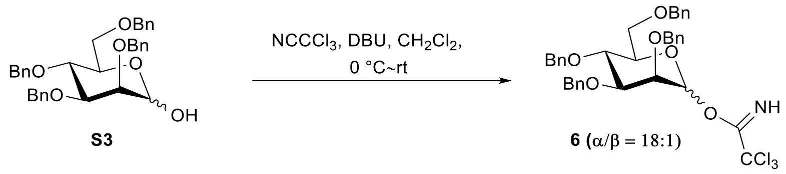
2,3,4,6-Tetra-*O*-benzyl-D-galacopyranosyl trichloroacetimidate (5)



S2 — **5** (α)

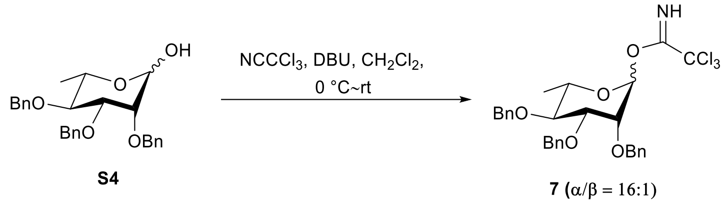
According to **general procedure A**, **S2** (2.6 g, 5.0 mmol) was treated with $NCCCl_3$ (1.6 mL, 10 mmol) and DBU (110 μL, 0.80 mmol) in dry CH_2Cl_2 (15 mL) to give donor **5** (2.5 g, 86%, α) as a yellow oil. The spectroscopic data were in accordance with the literature.[16]

2,3,4,6-Tetra-*O*-benzyl-D-mannopyranosyl trichloroacetimidate (6)



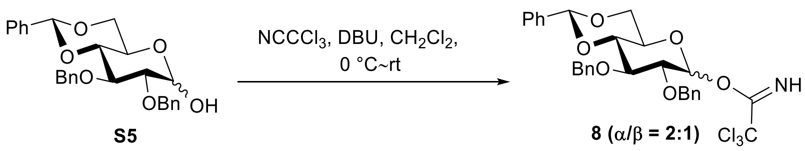
According to **general procedure A**, **S3** (2.0 g, 3.8 mmol) was treated with $NCCCl_3$ (1.2 mL, 7.4 mmol) and DBU (80 µL, 0.60 mmol) in dry CH_2Cl_2 (15 mL) to give donor **6** (1.9 g, 75%, α/β = 18:1) as a yellow oil. The spectroscopic data were in accordance with the literature.[17]

2,3,4,6-Tetra-*O*-benzyl-L-rhamnopyranosyl trichloroacetimidate (7)



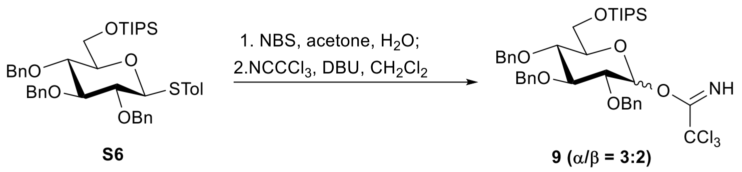
According to **general procedure A**, **S4**[18] (1.0 g, 1.9 mmol) was treated with $NCCCl_3$ (0.60 mL, 3.7 mmol) and DBU (40 µL, 0.30 mmol) in dry CH_2Cl_2 (10 mL) to give donor **7** (1.2 g, 90%, α/β = 16:1) as a colorless oil. The spectroscopic data were in accordance with the literature.[18]

2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranosyl trichloroacetimidate (8)



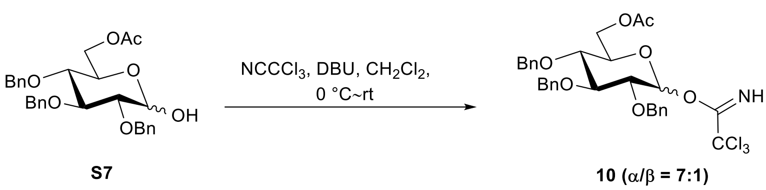
According to **general procedure A**, **S5**[19] (0.85 g, 1.9 mmol) was treated with $NCCCl_3$ (0.60 mL, 3.7 mmol) and DBU (40 µL, 0.30 mmol) in dry CH_2Cl_2 (10 mL) to give donor **8** (1.1 g, 83%, α/β = 2:1) as a white solid. For the β isomer of donor **8**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.73 (s, 1H), 7.51–7.48 (m, 2H), 7.40–7.27 (m, 13H), 5.93 (d, *J* = 7.6 Hz, 1H), 5.59 (s, 1H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.89 (d, *J* = 10.6 Hz, 1H), 4.81 (d, *J* = 10.7 Hz, 1H), 4.79 (d, *J* = 11.4 Hz, 1H), 4.42 (dd, *J* = 10.5, 4.9 Hz, 1H), 3.92–3.74 (m, 4H), 3.66–3.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 138.3, 137.8, 137.2, 129.1, 128.39, 128.36, 128.3, 128.03, 127.98, 127.86, 127.7, 126.1, 101.3, 98.2, 90.8, 81.1, 80.9, 80.7, 75.3, 75.0, 68.7, 66.7; For the α isomer of donor **8**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.52–7.48 (m, 2H), 7.41–7.34(m, 5H), 7.33–7.27 (m, 8H), 6.43 (d, *J* = 3.7 Hz, 1H), 5.58 (s, 1H), 4.94 (d, *J* = 11.3 Hz, 1H), 4.85 (d, *J* = 11.3 Hz, 1H), 4.81–4.70 (m, 2H), 4.32 (dd, *J* = 10.3, 4.9 Hz, 1H), 4.12 (t, *J* = 9.3 Hz, 1H), 4.08–3.99 (m, 1H), 3.81–3.67 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 138.5, 137.9, 137.1, 129.0, 128.4, 128.33, 128.30, 128.0, 127.8, 127.7, 127.6, 126.0, 101.3, 94.7, 91.1, 81.5, 78.6, 78.0, 75.3, 73.4, 68.8, 65.1.

2, 3, 4-Tri-*O*-benzyl-6-*O*-triisopropylsilyl-D-glucopyranosyl trichloroacetimidate (9)



To a solution of **S6**[20] (500 mg, 1.8 mmol) in acetone/H_2O (10 mL, 9:1, *v*/*v*) was added NBS (1.0 g, 5.4 mmol). After stirred at rt for 1 h, the mixture was quenched by saturated aq. $Na_2S_2O_3$ and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 10:1) to give hemiacetal (400 mg, 89%). According to **general procedure A**, the hemiacetal (400 mg, 0.66 mol) was treated with $NCCCl_3$ (0.20 mL, 1.2 mmol) and DBU (13 μL, 0.10 mmol) in dry CH_2Cl_2 (6 mL) to give donor **9** (0.32 g, 77%, α/β = 3:2) as a yellow oil. For the β isomer of donor **9** : ^1H NMR (300 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.36–7.32 (m, 15H), 5.83 (d, *J* = 7.6 Hz, 1H), 4.98 (d, *J* = 10.7 Hz, 1H), 4.93–4.89 (m, 2H), 4.87 (d, *J* = 4.6 Hz, 1H), 4.82–4.76 (m, 2H), 4.04–4.02 (m, 2H), 3.89 (t, *J* = 9.1 Hz, 1H), 3.79 (t, *J* = 8.7 Hz, 1H), 3.72 (t, *J* = 8.2 Hz, 1H), 3.53–3.45 (m, 1H), 1.14–1.05 (m, 21H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 138.5, 138.3, 128.5, 128.4, 128.0, 127.7, 98.2, 91.1, 84.5, 81.3, 76.9, 76.4, 75.9, 75.1, 75.0, 61.8, 18.03, 17.98, 12.0; For the α isomer of donor **9**:^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.41–7.30 (m, 15H), 6.59 (d, *J* = 3.4 Hz, 1H), 4.98 (d, *J* = 10.6 Hz, 1H), 4.95–4.83 (m, 2H), 4.82–4.70 (m, 3H), 4.12 (t, *J* = 9.3 Hz, 1H), 4.05–3.97 (m, 2H), 3.96–3.91 (m, 1H), 3.82 (t, *J* = 9.6 Hz, 1H), 3.75 (dd, *J* = 9.5, 3.3 Hz, 1H), 1.16–1.07 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 138.7, 138.63, 138.59, 138.4, 138.1, 128.54, 128.49, 128.45, 128.39, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.67, 127.65, 127.6, 94.4, 91.4, 81.4, 79.9, 76.8, 75.8, 75.4, 74.6, 72.9, 62.2, 18.1, 18.0, 12.0.

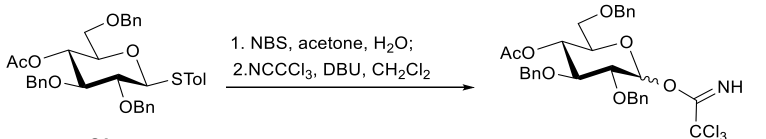
2,3,4-Tri-*O*-benzyl-6-*O*-acetyl-D-glucopyranosyl trichloroacetimidate (10)



According to **general procedure A**, **S7**[20] (0.51 g, 1.0 mmol) was treated with $NCCCl_3$ (0.15 mL, 1.5 mmol) and DBU (23 μL, 0.015 mmol) in dry CH_2Cl_2 (10 mL) to give donor **10** (1.1 g, 83%, α/β = 7:1) as a yellow oil. For the β isomer of donor **10**: ^1H NMR (300

MHz, $CDCl_3$) δ 8.72 (s, 1H), 5.84 (d, *J* = 7.3 Hz, 1H), 2.05 (s, 3H); For the α isomer of donor **10**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.39–7.30 (m, 15H), 6.49 (d, *J* = 3.5 Hz, 1H), 5.02 (d, *J* = 10.8 Hz, 1H), 4.92 (d, *J* = 10.7 Hz, 1H), 4.87 (d, *J* = 10.8 Hz, 1H), 4.78 (d, *J* = 11.6 Hz, 1H), 4.71 (d, *J* = 11.7 Hz, 1H), 4.61 (d, *J* = 10.8 Hz, 1H), 4.29 (m, 2H), 4.15–4.03 (m, 2H), 3.78 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.63 (dd, *J* = 10.2, 9.0 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 161.1, 138.3, 137.8, 137.6, 128.7, 128.6, 128.2, 128.0, 127.9, 127.8, 98.2, 91.2, 84.6, 81.4, 80.8, 79.3, 79.1, 76.4, 75.8, 75.6, 75.3, 74.9, 74.8, 73.7, 72.9, 71.4, 62.8, 62.6, 20.9, 20.8.

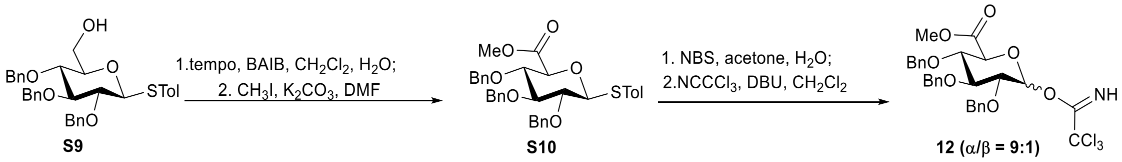
2,3,6-Tri-*O*-benzyl-4-*O*-acetyl-D-glucopyranosyl trichloroacetimidate (11)



S8 **11 (α/β = 9:1)**

To a solution of **S8**[20] (800 mg, 1.3 mmol) in acetone/H_2O (10 mL, 9:1, *v*/*v*) was added NBS (700 mg, 4.0 mmol). After stirred at rt for 1 h, the mixture was quenched by saturated aq. $Na_2S_2O_3$ and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 5:1) to give hemiacetal (600 mg, 92%). According to **general procedure A**, the hemiacetal (600 mg, 1.2 mmol) was treated with $NCCCl_3$ (0.18 mL, 1.8 mmol) and DBU (27 µL, 0.020 mmol) in dry CH_2Cl_2 (10 mL) to give donor **11** (0.62 g, 80%, α/β = 9:1) as a yellow oil. For the β isomer of donor **11**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 5.87 (d, *J* = 7.8 Hz, 1H), 1.86 (s, 3H); For the α isomer of donor **11**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.37–7.29 (m, 15H), 6.53 (d, *J* = 3.4 Hz, 1H), 5.21 (t, *J* = 9.9 Hz, 1H), 4.90 (d, *J* = 11.6 Hz, 1H), 4.77 (d, *J* = 11.7 Hz, 1H), 4.73 (s, 1H), 4.69 (d, *J* = 11.4 Hz, 1H), 4.54 (d, *J* = 12.1 Hz, 1H), 4.49 (d, *J* = 11.9 Hz, 1H), 4.10–4.05 (m, 1H), 4.02 (t, *J* = 9.5 Hz, 1H), 3.84 (dd, *J* = 9.6, 3.3 Hz, 1H), 3.57 (dd, *J* = 11.0, 2.9 Hz, 1H), 3.50 (dd, *J* = 11.0, 4.4 Hz, 1H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 161.1, 138.3, 137.8, 137.7, 128.6, 128.44, 128.41, 128.35, 128.3, 128.2, 128.1, 127.99, 127.97, 127.9, 127.84, 127.76, 127.69, 127.66, 94.1, 91.2, 79.1, 78.3, 75.1, 73.5, 73.0, 71.7, 69.6, 68.5, 20.9.

2,3,4-Tri-*O*-benzyl-D-glucuronic acid methyl ester trichloroacetimidate (12)

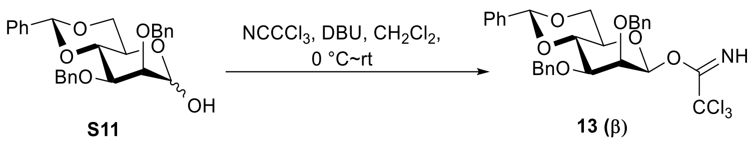


S9 **S10** **12 (α/β = 9:1)**

To a solution of **S9**[20] (600 mg, 1.1 mmol) in CH_2Cl_2/H_2O (12 mL, 2:1, *v*/*v*) were added 2,2,6,6-tetramethyl-1-oxylpiperidine (tempo) (34 mg, 0.20 mmol) and iodobenzene diacetate (BAIB) (860 mg, 2.7 mmol) successively. After stirred at rt for 3 h, the mixture was quenched by saturated aq. $Na_2S_2O_3$, and extracted with EA (3 x 15 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was used without further purification. To a solution of the residue above in DMF (10 mL) were added K_2CO_3 (720 mg, 5.5 mmol) and CH_3I (0.20 mL, 3.3 mmol). After stirred at rt for 2 h, the mixture was extracted with EA (3 x 15 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 10:1) to provide **S10** (580 mg, 92%) as a syrup. $[\alpha]_D^{21}$ = –2.9 (c = 1.0 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.52–7.47 (m, 2H), 7.45–7.32 (m, 13H), 7.28–7.24 (m, 2H), 7.14–7.10 (m, 2H), 4.92–4.81 (m, 3H), 4.77 (d, *J* = 10.8 Hz, 1H), 4.72 (d, *J* = 10.2 Hz, 1H), 4.66 (d, *J* = 9.7 Hz, 1H), 4.64 (d, *J* = 10.8 Hz, 1H), 3.90 (d, *J* = 9.6 Hz, 1H), 3.81 (t, *J* = 9.2 Hz, 1H), 3.74–3.67 (m, 4H), 3.49 (dd, *J* = 9.7, 8.6 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 138.2, 137.9, 137.7, 132.9, 129.8, 129.2, 128.51, 128.48, 128.46, 128.2, 128.02, 127.95, 127.9, 127.8, 88.6, 85.9, 80.3, 79.3, 78.0, 75.9, 75.5, 75.2, 52.5, 21.2; HRMS (ESI) calcd for $C_{35}H_{36}O_6SNa$ $[M+Na]^+$ 607.2125, found 607.2123.

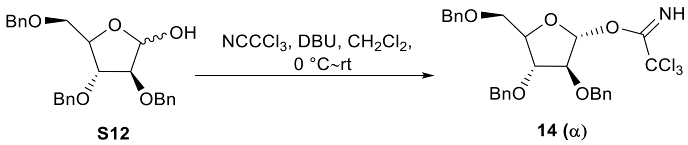
To a solution of **S10** (0.50 g, 0.86 mmol) in acetone/H_2O (10 mL, 9:1, *v*/*v*) was added NBS (1.0 g, 5.4 mmol). After stirred at rt for 1 h, the mixture was quenched by saturated aq. $Na_2S_2O_3$ and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 4:1) to give hemiacetal (0.32 g, 78%). According to **general procedure A**, the hemiacetal (300 mg, 0.60 mmol) was treated with $NCCCl_3$ (95 μL, 0.090 mmol) and DBU (14 μL, 0.010 mmol) in dry CH_2Cl_2 (5 mL) to give donor **12** (0.32 g, 82%, α/β = 9:1) as a yellow oil. For the β isomer of donor **12**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 5.92 (m, 1H), 3.71 (s, 3H); For the α isomer of donor **12**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.34–7.28 (m, 13H), 7.24–7.22 (m, 2H), 6.50 (d, *J* = 3.5 Hz, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.73 (d, *J* = 11.7 Hz, 1H), 4.68 (d, *J* = 11.7 Hz, 1H), 4.59 (d, *J* = 10.8 Hz, 1H), 4.41 (d, *J* = 10.1 Hz, 1H), 4.06 (t, *J* = 9.3 Hz, 1H), 3.89–3.80 (m, 2H), 3.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 161.1, 138.3, 137.7, 137.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 94.0, 91.0, 80.7, 78.9, 78.8, 75.8, 75.5, 73.1, 72.5, 52.6.

2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl trichloroacetimidate (13)



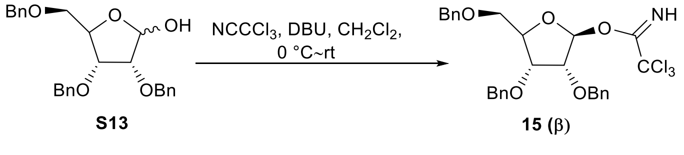
According to **general procedure A**, **S11**[19] (210 mg, 0.40 mmol) was treated with $NCCCl_3$ (67 µL, 0.60 mmol) and DBU (10 µL, 0.060 mmol) in dry CH_2Cl_2 (10 mL) to give donor **13** (0.18 g, 68%, β) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.53–7.49 (m, 2H), 7.43–7.40 (m, 2H), 7.39–7.32 (m, 6H), 7.32–7.25 (m, 5H), 6.27 (d, *J* = 1.8 Hz, 1H), 5.66 (s, 1H), 4.86–4.82 (m, 1H), 4.82–4.76 (m, 2H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.37–4.28 (m, 2H), 4.03–3.96 (m, 2H), 3.90 (d, *J* = 1.9 Hz, 1H), 3.89–3.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 138.2, 137.7, 137.4, 129.0, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 126.0, 101.5, 96.5, 90.8, 78.4, 75.2, 75.2, 73.6, 73.3, 68.5, 66.9. The spectroscopic data were in accordance with the literature.[21]

2,3,5-Tri-*O*-benzyl-α-D-arabifuanosyl trichloroacetimidate (14)



According to **general procedure A**, **S12**[22] (2.0 g, 4.8 mmol) was treated with $NCCCl_3$ (700 µL, 7.1 mmol) and DBU (110 µL, 0.070mmol) in dry CH_2Cl_2 (25 mL) to give donor **14** (2.5 g, 93%, α) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.43–7.36 (m, 10H), 7.35–7.30 (m, 5H), 6.43 (s, 1H), 4.76 (d, *J* = 11.9 Hz, 1H), 4.66–4.59 (m, 3H), 4.59–4.56 (m, 2H), 4.52 (q, *J* = 5.0 Hz, 1H), 4.33 (d, *J* = 2.3 Hz, 1H), 4.13 (dd, *J* = 5.7, 2.3 Hz, 1H), 3.74–3.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 138.0, 137.7, 137.3, 128.7, 128.54, 128.50, 128.4, 128.2, 128.04, 128.00, 127.9, 127.8, 127.73, 127.70, 104.4, 91.3, 86.6, 83.8, 83.5, 73.5, 72.2, 72.1, 69.4.

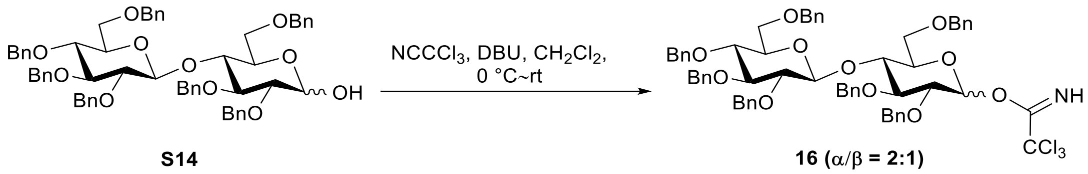
2,3,5-Tri-*O*-benzyl-β-D-ribofuanosyl trichloroacetimidate (15)



According to **general procedure A**, **S13**[22] (1.0 g, 2.4 mmol) was treated with $NCCCl_3$ (350 µL, 3.5 mmol) and DBU (54 µL, 0.030 mmol) in dry CH_2Cl_2 (16 mL) to give donor **15** (1.2 g, 90%, β) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.48–7.33 (m, 15H), 6.40 (s, 1H), 4.85 (d, *J* = 12.0 Hz, 1H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.66–4.59 (m, 3H), 4.58–4.53 (m, 1H), 4.50 (d, *J* = 11.7 Hz, 1H), 4.20 (dd, *J* = 7.4, 4.4 Hz, 1H), 4.14 (d, *J* = 4.6 Hz, 1H), 3.77 (dd, *J* = 11.0, 3.6 Hz, 1H), 3.68 (dd, *J* = 11.0, 5.1 Hz, 1H); ^{13}C NMR

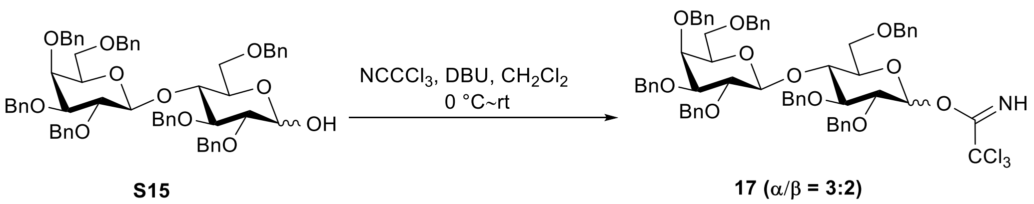
(100 MHz, $CDCl_3$) δ 160.8, 138.2, 137.5, 128.52, 128.46, 128.4, 128.2, 128.04, 128.02, 127.98, 127.7, 127.6, 103.5, 91.1, 82.2, 78.5, 77.3, 73.3, 72.6, 72.2, 70.2.

2,3,4,6-*O*-Benzyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-glucopyranosyl trichloroacetimidate (16)



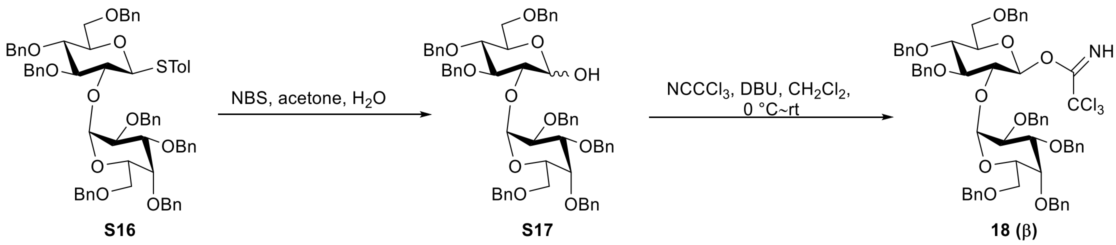
According to **general procedure A**, **S14**[23] (1.2 g, 1.2 mmol) was treated with $NCCCl_3$ (180 µL,1.8 mmol), DBU (28 µL, 0.020 mmol) in dry CH_2Cl_2 (16 mL) to give donor **16** (1.1 g, 80%, α/β = 2:1) as a yellow oil. For the β isomer of donor **16**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.44–7.19 (m, 35H), 5.84 (d, *J* = 7.5 Hz, 1H), 5.14 (d, *J* = 11.4 Hz, 1H), 4.93 (d, *J* = 10.9 Hz, 1H), 4.89 (d, *J* = 10.7 Hz, 1H), 4.87–4.82 (m, 3H), 4.82–4.78 (m, 2H), 4.78–4.73 (m, 1H), 4.67–4.57 (m, 3H), 4.51 (d, *J* = 12.1 Hz, 1H), 4.45 (s, 2H), 4.21 (t, *J* = 9.2 Hz, 1H), 3.91 (dd, *J* = 11.3, 3.4 Hz, 1H), 3.78–3.70 (m, 4H), 3.67 (t, *J* = 9.3 Hz, 1H), 3.64–3.55 (m, 3H), 3.44 (t, *J* = 8.4 Hz, 1H), 3.40–3.35 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 139.1, 138.6, 138.5, 138.35, 138.27, 138.1, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.74, 127.68, 127.6, 127.4, 127.3, 102.4, 98.3, 84.9, 82.71, 82.66, 80.2, 78.0, 75.9, 75.7, 75.10, 75.07, 75.02, 74.9, 73.3, 73.2, 68.9, 67.5; For the α isomer of donor **16**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.46–7.21 (m, 35H), 6.49 (d, *J* = 3.5 Hz, 1H), 5.14 (d, *J* = 11.3 Hz, 1H), 4.94 (d, *J* = 10.9 Hz, 1H), 4.88 (d, *J* = 6.3 Hz, 1H), 4.87–4.80 (m, 4H), 4.79–4.74 (m, 2H), 4.64–4.59 (m, 2H), 4.50–4.45 (m, 3H), 4.42 (d, *J* = 11.9 Hz, 1H), 4.19 (t, *J* = 9.6 Hz, 1H), 4.02 (t, *J* = 9.3 Hz, 1H), 3.99–3.92 (m, 2H), 3.79–3.73 (m, 2H), 3.69 (t, *J* = 9.3 Hz, 1H), 3.64 (dd, *J* = 11.0, 4.5 Hz, 1H), 3.57–3.51 (m, 2H), 3.43 (t, *J* = 8.4 Hz, 1H), 3.40–3.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 139.3, 138.6, 138.5, 138.4, 138.3, 138.2, 137.8, 128.6, 128.53, 128.47, 128.43, 128.35, 128.33, 128.32, 128.3, 128.1, 128.0, 127.91, 127.85, 127.74, 127.71, 127.64, 127.58, 127.4, 127.2, 102.6, 94.5, 91.4, 84.9, 82.6, 79.6, 78.3, 78.0, 75.9, 75.7, 75.21, 75.19, 74.9, 73.4, 73.2, 73.2, 69.0, 67.4.

2,3,4,6-*O*-Benzyl-β-D-galacopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-D-glucopyranosyl trichloroacetimidate (17)



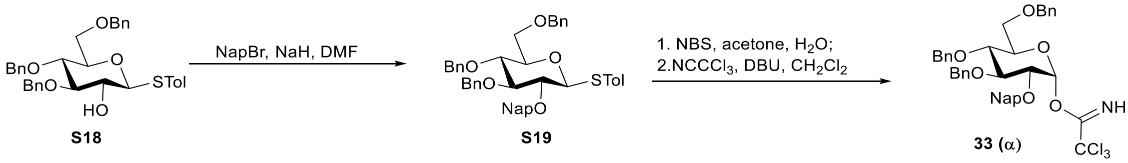
According to **general procedure A**, **S15**[23] (1.1 g, 1.0 mmol) was treated with $NCCCl_3$ (0.15 mL, 1.5 mmol) and DBU (23 µL, 0.02 mmol) in dry CH_2Cl_2 (15 mL) to give donor **17** (0.91 g, 78%, α/β = 3:2) as yellow oil. For the β isomer of donor **17**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.40–7.13 (m, 35H), 5.80–5.75 (m, 1H), 5.06 (d, *J* = 10.8 Hz, 1H), 5.97 (d, *J* = 11.4 Hz, 1H), 4.87 (d, *J* = 10.7 Hz, 1H), 4.83–4.74 (m, 3H), 4.74–4.66 (m, 3H), 4.56 (d, *J* = 12.2 Hz, 1H), 4.56 (d, *J* = 11.5 Hz, 1H), 4.46 (d, *J* = 7.7 Hz, 1H), 4.44 (d, *J* = 12.1 Hz, 1H), 4.35 (d, *J* = 11.8 Hz, 1H), 4.25 (d, *J* = 11.8 Hz, 1H), 4.09 (t, *J* = 9.4 Hz, 1H), 3.91 (d, *J* = 2.9 Hz, 1H), 3.85 (dd, *J* = 11.3, 3.6 Hz, 1H), 3.73–3.65 (m, 1H), 3.76–3.69 (m, 3H), 3.61–3.53 (m, 2H), 3.40 (dd, *J* = 9.7, 2.9 Hz, 1H), 3.38–3.34(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 139.05, 138.97, 138.7, 138.5, 138.3, 138.2, 138.1, 128.42, 128.39, 128.34, 128.29, 128.27, 128.2, 128.1, 128.0, 127.94, 127.91, 127.85, 127.76, 127.74, 127.72, 127.69, 127.6, 127.51, 127.45, 127.4, 127.2, 102.7, 98.3, 91.0, 82.9, 82.5, 80.3, 79.9, 76.0, 75.9, 75.4, 75.3, 75.1, 74.7, 73.7, 73.4, 73.1, 72.6, 68.2, 67.6. For the α isomer of donor **17**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.41–7.10 (m, 35H), 6.44 (d, *J* = 3.5 Hz, 1H), 5.05 (d, *J* = 10.6 Hz, 1H), 5.01 (d, *J* = 11.4 Hz, 1H), 4.84 (d, *J* = 11.1 Hz, 1H), 4.79–4.75 (m, 3H), 4.74–4.70 (m, 3H), 4.59 (d, *J* = 11.5 Hz, 1H), 4.54 (d, *J* = 12.1 Hz, 1H), 4.41–4.31 (m, 3H), 4.28 (d, *J* = 11.8 Hz, 1H), 4.13–4.07 (m, 1H), 3.98–3.88 (m, 4H), 3.78 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.71 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.59 (t, *J* = 8.4 Hz, 1H), 3.53–3.49 (m, 1H), 3.42–3.34 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 139.2, 139.1, 138.8, 138.6, 138.3, 138.2, 138.1, 128.4, 128.35, 128.33, 128.23, 128.21, 127.96, 127.91, 127.85, 127.8, 127.74, 127.71, 127.61, 127.59, 127.6, 127.5, 127.45, 127.38, 127.1, 102.9, 94.6, 91.5, 82.5, 79.9, 79.7, 78.4, 75.8, 75.5, 75.2, 74.7, 73.7, 73.5, 73.22, 73.19, 73.14, 73.12, 72.6, 68.2, 67.5.

2,3,4,6-*O*-Benzyl-α-D-galacopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl trichloroacetimidate (18)



To a solution of **S16**[23] (400 mg, 0.60 mmol) in acetone/H_2O (7 mL, 6:1, *v/v*) was added NBS (520 mg, 3.0 mmol) at 0 °C. After stirred for 1 h, the mixture was quenched by saturated aq. $Na_2S_2O_3$ and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 6:1) to give **S17** (310 mg, 86%). According to **general procedure A**, **S17** (300 mg, 1.9 mmol) was treated with $NCCCl_3$ (0.60 mL, 3.7 mmol) and DBU (40 µL, 0.30 mmol) in dry CH_2Cl_2 (5 mL) to give donor **18** (280 mg, 72%, β) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.45–7.31 (m, 30H), 7.26–7.22 (m, 3H), 7.21–7.17 (m, 2H), 6.07 (d, *J* = 7.7 Hz, 1H), 5.65 (d, *J* = 3.6 Hz, 1H), 5.01 (d, *J* = 11.5 Hz, 1H), 4.93 (d, *J* = 11.3 Hz, 1H), 4.84–4.78 (m, 4H), 4.74–4.70 (m, 2H), 4.68 (d, *J* = 9.8 Hz, 1H), 4.65 (d, *J* = 10.6 Hz, 1H), 4.61 (d, *J* = 12.2 Hz, 1H), 4.56 (d, *J* = 11.3 Hz, 1H), 4.40–4.30 (m, 3H), 4.19 (t, *J* = 8.3 Hz, 1H), 4.12 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.94 (dd, *J* = 10.2, 2.8 Hz, 1H), 3.90 (t, *J* = 8.9 Hz, 1H), 3.86–3.79 (m, 3H), 3.75–3.72 (m, 2H), 3.55 (dd, *J* = 9.5, 6.3 Hz, 1H), 3.35 (dd, *J* = 9.5, 6.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 138.8, 138.6, 138.5, 138.31, 138.27, 138.1, 137.9, 128.52, 128.48, 128.46, 128.44, 128.41, 128.36, 128.31, 128.27, 128.15, 128.03, 128.00, 127.92, 127.90, 127.8, 127.71, 127.67, 127.64, 127.59, 127.54, 127.50, 127.48, 127.4, 98.7, 95.9, 90.9, 83.3, 78.6, 78.0, 76.2, 75.9, 75.7, 75.1, 74.9, 73.43, 73.40, 73.1, 72.9, 69.1, 69.0, 68.2.

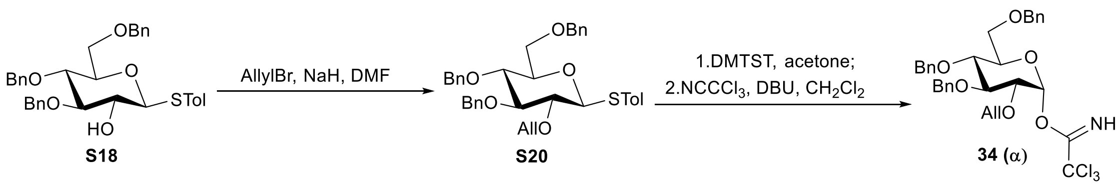
3,4,6-*O*-Benzyl-2-*O*-(naphthaleneyl-2-methyl)-α-D-glucopyranosyl trichloroacetimidate (33)



To a solution of **S18**[24] (200 mg, 0.36 mmol) in DMF (2 mL) were added NaH (30 mg, 0.72 mmol), NapBr (100 μL, 0.54 mmol) successively. After stirred at rt for 1 h, the mixture was quenched by water, and extracted with EA (3 x 20 mL). the combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 15:1) to give **S19** (0.21 g, 93%) as a colorless oil. $[\alpha]^{22}_{D}$ = +11.7 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.82 (m, 4H), 7.61 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.59–7.56 (m, 2H), 7.54–7.51 (m, 2H), 7.42–7.39 (m, 4H), 7.38–7.32 (m, 9H), 7.28–7.24 (m, 2H), 7.11–7.07 (m, 2H), 5.12 (d, *J* = 10.5 Hz, 1H), 4.97 (d, *J* = 11.0 Hz, 1H), 4.95–4.91 (m, 2H), 4.89 (d, *J* = 10.9 Hz, 1H), 4.71 (d, *J* = 9.7 Hz, 1H), 4.69–4.65 (m, 2H), 4.60 (d, *J* = 11.9 Hz, 1H), 3.86 (dd, *J* = 10.9, 2.0 Hz, 1H), 3.82–3.76 (m, 2H), 3.72 (t, *J* = 9.3 Hz, 1H), 3.60 (dd, *J* = 9.8, 8.6 Hz, 1H), 3.58–3.53 (m, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.4, 138.1, 137.8, 135.7, 135.6, 133.4, 133.1, 132.7, 129.8, 129.7, 128.52, 128.50, 128.4, 128.2, 128.04, 128.02, 127.9, 127.8, 127.7, 127.6, 127.0, 126.3, 126.1, 126.0, 87.8, 86.8, 80.9, 79.1, 77.9, 75.9, 75.5, 75.1, 73.5, 69.1, 21.2; HRMS (ESI) calcd for $C_{45}H_{48}O_5NS$ $[M+NH_4]^+$ 714.3248, found 714.3243.

To a solution of **S19** (210 mg, 0.34 mmol) in acetone/H_2O (9 mL, 9:1, *v*/*v*) was added NBS (180 mg, 1.0 mmol). After stirred at rt for 1 h, the mixture was quenched by saturated aq. $Na_2S_2O_3$ and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 8:1) to give hemiacetal (170 mg, 95%). According to **general procedure A**, the hemiacetal (170 mg, 0.34 mol) was treated with $NCCCl_3$ (45 µL, 0.51 mmol) and DBU (6.0 µL, 0.050 mmol) in dry CH_2Cl_2 (4 mL) to give donor **33** (0.17 g, 81%, α) as a syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.85 (dd, J = 6.2, 3.4 Hz, 1H), 7.82–7.78 (m, 2H), 7.76 (dd, J = 6.2, 3.3 Hz, 1H), 7.51–7.48 (m, 2H), 7.47–7.43 (m, 1H), 7.33 (m, 13H), 7.20–7.17 (m, 2H), 6.60 (d, J = 3.4 Hz, 1H), 5.02 (d, J = 11.0 Hz, 1H), 4.93 (d, J = 11.8 Hz, 1H), 4.90 (br, 1H), 4.88 (d, J = 3.7 Hz, 1H), 4.86 (d, J = 6.3 Hz, 1H), 4.63 (d, J = 12.1 Hz, 1H), 4.55 (d, J = 10.6 Hz, 1H), 4.49 (d, J = 12.1 Hz, 1H), 4.11 (t, J = 9.3 Hz, 1H), 4.05-4.01 (m, 1H), 3.86 (dd, J = 5.9, 3.7 Hz, 1H), 3.84–3.82 (m, 1H), 3.80 (d, J = 3.6 Hz, 1H), 3.70 (dd, J = 10.9, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 138.7, 138.1, 137.9, 135.5, 133.3, 133.1, 128.50, 128.46, 128.4, 128.21, 128.17, 128.1, 128.03, 127.99, 127.96, 127.9, 127.8, 127.75, 127.68, 126.5, 126.2, 126.0, 125.7, 94.5, 91.4, 81.4, 79.4, 76.9, 75.7, 75.4, 73.5, 73.2, 73.0, 68.1.

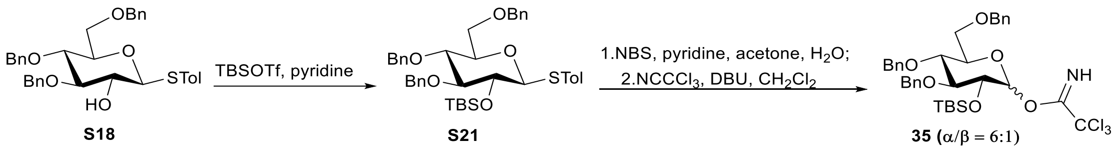
3,4,6-*O*-Benzyl-2-*O*-allyl-α-D-glucopyranosyl trichloroacetimidate (34)



To a solution of **S18** (400 mg, 0.70 mmol) in DMF (6 mL) were added NaH (60 mg, 5.4 mmol) and AllylBr (93 µL, 1.0 mmol) successively. After stirred at rt for 1 h, the mixture was quenched by water, and extracted with EA (3 x 20 mL). the combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 12:1) to give **S20** (0.39 g, 91%) as a colorless oil. $[\alpha]_D^{20}$ = −10.5 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.49 (m, 2H), 7.38–7.30 (m, 13H), 7.25–7.21 (m, 2H), 7.08–7.05 (m, 2H), 6.07–5.97 (m, 1H), 5.36–5.30 (m, 1H), 5.24–5.20 (m, 1H), 4.93 (d, J = 10.8 Hz, 1H), 4.88–4.83 (m, 2H), 4.64–4.54 (m, 4H), 4.45–4.39 (m, 1H), 4.30–4.25 (m, 1H), 3.81 (dd, J = 10.9, 2.0 Hz, 1H), 3.74 (dd, J = 10.9, 4.6 Hz, 1H), 3.68 (t, J = 8.7 Hz, 1H), 3.62 (t, J = 9.2 Hz, 1H), 3.52–3.48 (m, 1H), 3.38 (dd, J = 9.7, 8.4 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 138.3, 138.1, 137.7, 134.7, 132.7, 129.8, 129.6, 128.49, 128.46, 128.4, 128.0, 127.8, 127.8, 127.7, 127.6, 117.4, 87.6, 86.7, 80.6, 79.1, 77.7, 75.9, 75.1, 74.2, 73.4, 69.1, 21.1; HRMS (ESI) calcd for $C_{37}H_{44}O_5NS$ $[M+NH_4]^+$ 614.2935, found 614.2931.

To a solution of **S20** (390 mg, 0.66 mmol) in acetone (5 mL) was added $MeSSMe_2OTf$ (DMTST) (0.20 g, 2.3 mmol). After stirred at rt for 20 min, the mixture was quenched by water, and extracted with EA (3 x 8 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 8:1) to give hemiacetal (0.28 g, 87%). According to **general procedure A**, the hemiacetal (280 mg, 0.57 mmol) was treated with $NCCCl_3$ (90 µL, 0.85 mmol) and DBU (12 µL, 0.08 mmol) in dry CH_2Cl_2 (5 mL) to give donor **34** (300 mg, 83%, α) as a syrup. ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.41–7.30 (m, 13H), 7.20–7.17 (m, 2H), 6.56 (d, *J* = 3.4 Hz, 1H), 5.91 (m, 1H), 5.33 (dd, *J* = 17.3, 1.8 Hz, 1H), 5.20 (dd, *J* = 10.5 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.89 (d, *J* = 10.6 Hz, 1H), 4.85 (d, *J* = 10.8 Hz, 1H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.55 (d, *J* = 10.7 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.22–4.19 (m, 2H), 4.07–3.98 (m, 2H), 3.85–3.79 (m, 2H), 3.71 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 138.7, 138.1, 137.9, 134.5, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 117.3, 94.5, 91.3, 81.4, 79.2, 76.8, 75.7, 75.4, 73.5, 73.2, 72.0, 68.1.

3,4,6-*O*-Benzyl-2-*O*-tert-butyldimethylsilyl-D-glucopyranosyl trichloroacetimidate (35)

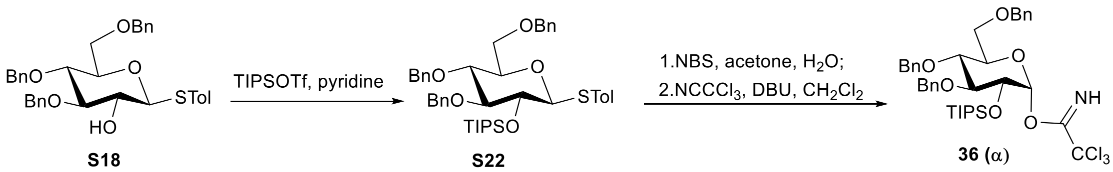


S18 S21 35 (α/β = 6:1)

To a solution of **S18** (400 mg, 0.70 mmol) in CH_2Cl_2 (6 mL) were added pyridine (0.30 mL, 2.8 mmol) and TBSOTf (0.54 mL, 1.4 mmol) successively. After stirred at rt for 1 h, the mixture was concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 12:1) to give **S21** (450 mg, 93%) as a colorless oil. $[\alpha]^{20}_D$= −19.6 (c = 1.0 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.50–7.45 (m, 2H), 7.38–7.30 (m, 9H), 7.30–7.24 (m, 4H), 7.12–7.05 (m, 4H), 5.00 (d, *J* = 11.8 Hz, 1H), 4.87 (d, *J* = 11.8 Hz, 1H), 4.73 (d, *J* = 10.7 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.59–4.56 (m, 2H), 4.54 (d, *J* = 6.8 Hz, 1H), 3.79 (dd, *J* = 10.9, 2.0 Hz, 1H), 3.75–3.65 (m, 3H), 3.57–3.48 (m, 2H), 2.33 (s, 3H), 0.96 (s, 9H), 0.26 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.3, 137.9, 137.2, 131.8, 131.4, 129.6, 128.39, 128.36, 128.2, 127.9, 127.84, 127.79, 127.6, 127.1, 126.7, 90.2, 87.1, 79.0, 78.7, 75.1, 74.9, 73.8, 73.5, 69.1, 26.2, 25.7, 21.1, 18.3, -3.4, -3.8; HRMS (ESI) calcd for $C_{40}H_{54}O_5NSSi$ $[M+NH_4]^+$ 688.3486, found 688.3492.

To a solution of **S21** (400 mg, 0.60 mmol) in acetone/H_2O (9 mL, 9:1, *v*/*v*) were added pyridine (96 µL, 1.2 mmol) and NBS (520 mg, 3.0 mmol) at 0 °C successively. After stirred for 1 h, the mixture was quenched by saturated aq. $Na_2S_2O_3$ and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 8:1) to give hemiacetal (200 mg, 89%). According to **general procedure B**, the hemiacetal (300 mg, 0.50 mmol) was treated with $NCCCl_3$ (1.0 mL, 10 mmol) and DBU (8.0 μL, 0.050 mmol) in dry CH_2Cl_2 (2 mL) to give donor **35** (300 mg, 60%, α/β = 6:1) as a syrup. For the β isomer of donor **35**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 2.6 Hz, 1H), 7.39–7.27 (m, 13H), 7.15–7.12 (m, 2H), 5.78 (dd, *J* = 7.2, 3.1 Hz, 1H), 4.95 (dd, *J* = 11.6, 2.6 Hz, 1H), 4.89 (dd, *J* = 11.7, 2.7 Hz, 1H), 4.76 (dd, *J* = 10.8, 2.6 Hz, 1H), 4.65 (dd, *J* = 12.3, 2.5 Hz, 1H), 4.63–4.56 (m, 2H), 3.96–3.91 (m, 1H), 3.87–3.81 (m, 1H), 3.78–3.75 (m, 2H), 3.72–3.63(m, 2H), 0.92–0.89 (m, 9H), 0.19–0.16 (m, 3H), 0.11–0.08 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 138.6, 138.2, 137.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 127.3, 127.0, 99.2, 91.2, 85.6, 77.7, 75.8, 75.0, 74.8, 73.4, 73.2, 68.3, 25.9, 18.0, −4.0, −4.4; For the α isomer of donor **35:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.41–7.28 (m, 13H), 7.14–7.10 (m, 2H), 6.39 (d, *J* = 2.6 Hz, 1H), 4.97 (d, *J* = 11.3 Hz, 1H), 4.88 (d, *J* = 11.3 Hz, 1H), 4.83 (d, *J* = 10.6 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 10.7 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.04–4.00 (m, 1H), 4.00–3.94 (m, 2H), 3.86–3.82 (m, 1H), 3.82–3.76 (m, 1H), 3.70 (dd, *J* = 10.9, 2.0 Hz, 1H), 0.90 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 138.8, 138.0, 137.9, 128.4, 128.3, 128.1, 127.8, 127.5, 127.4, 96.4, 91.4, 82.2, 76.9, 75.6, 75.3, 73.6, 73.2, 72.9, 68.0, 25.7, 17.9, −4.6, −4.8.

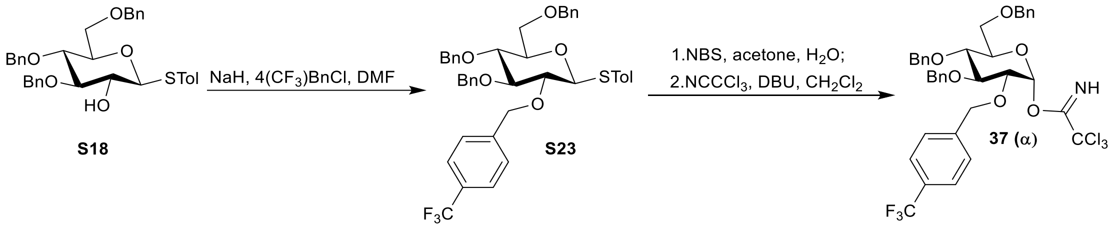
3,4,6-*O*-Benzyl-2-*O*-triisopropylsilyl-α-D-glucopyranosyl trichloroacetimidate (36)



To a solution of **S18** (310 mg, 0.54 mmol) in CH_2Cl_2 (6 mL) were added pyridine (210 μL, 2.2 mmol) and TIPSOTf (290 μL, 1.1 mmol) successively. After stirred at rt for 12 h, the mixture was concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 10:1) to give **S22**[20] (0.32 g, 83%) as a colorless oil. To a solution of **S22** (300 mg, 0.40 mmol) in acetone/H_2O (6 mL, 9:1, *v*/*v*) was added NBS (220 mg, 1.3 mmol). After stirred at rt for 1 h, the mixture was quenched by saturated aq. $Na_2S_2O_3$ and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 12:1) to give hemiacetal (240 mg, 93%). According to **General Procedure B**, the hemiacetal (240 mg, 0.41 mmol) was treated with $NCCCl_3$ (0.80 mL, 8.0 mmol) and DBU (8.0 μL, 0.040 mmol) in dry CH_2Cl_2

(10 mL) to give donor **36** (210 mg, 71%, α) as a syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.40–7.27 (m, 13H), 7.10–7.05 (m, 2H), 6.39 (d, *J* = 3.4 Hz, 1H), 4.99 (d, *J* = 11.6 Hz, 1H), 4.94 (d, *J* = 11.7 Hz, 1H), 4.81 (d, *J* = 10.5 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.53 (d, *J* = 10.6 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.13 (dd, *J* = 9.4, 3.4 Hz, 1H), 4.04–3.97 (m, 2H), 3.85–3.77 (m, 2H), 3.70 (dd, *J* = 10.9, 2.0 Hz, 1H), 1.12–1.04 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 138.9, 138.0, 137.9, 128.5, 128.43, 128.37, 128.2, 128.1, 128.0, 127.8, 127.2, 96.6, 91.4, 82.6, 77.4, 75.5, 75.2, 73.6, 73.2, 72.9, 68.1, 18.1, 18.0, 12.6.

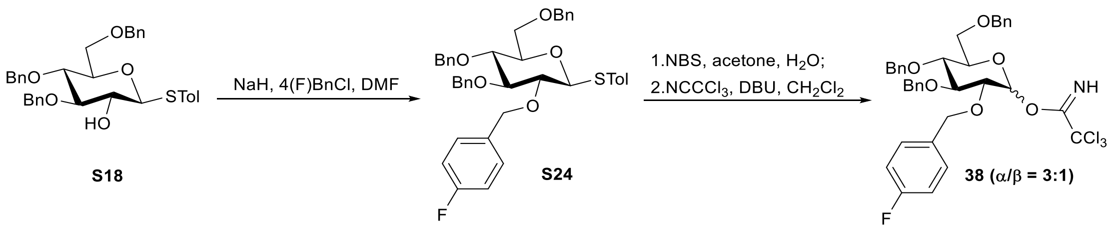
3,4,6-*O*-Benzyl-2-*O*-[4-trifluoromethyl-benzyl]-α-D-glucopyranosyl trichloroacetimidate (37)



To a solution of **S18** (210 mg, 0.37 mmol) in DMF (3 mL) were added NaH (37 mg, 1.4 mmol) and 4-(trifluoromethyl)benzyl bromide (92 µL, 0.74 mmol) successively. After stirred at rt for 4 h, the mixture was quenched by water, and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 8:1) to give **S23** (240 mg, 92%) as a white solid. $[\alpha]_D^{20}$ = +0.7 (c = 2.0 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66–7.60 (m, 2H), 7.55–7.50 (m, 4H), 7.45–7.38 (m, 4H), 7.38–7.22 (m, 11H), 7.13–7.03 (m, 2H), 5.01–4.89 (m, 2H), 4.88–4.78 (m, 3H), 4.68 (d, *J* = 5.4 Hz, 1H), 4.66–4.63 (m, 2H), 4.59 (d, *J* = 11.9 Hz, 1H), 3.90–3.64 (m, 4H), 3.61–3.45 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 138.3, 138.0, 137.9, 132.7, 129.8, 129.6, 128.52, 128.50, 128.4, 128.01, 127.99, 127.9, 127.8, 127.74, 127.70, 127.6, 125.4, 125.31, 125.28, 87.6, 86.8, 81.0, 79.2, 77.9, 75.9, 75.1, 74.4, 73.5, 69.0, 21.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.4; HRMS (ESI) calcd for $C_{42}H_{45}O_5NF_3S$ $[M+NH_4]^+$ 732.2965, found 732.2966.

To a solution of **S23** (42 mg, 0.058 mmol) in acetone/H_2O (2 mL, 9:1, *v*/*v*) were added NBS (37 mg, 0.18 mmol). After stirred at 0°C for 5 mins, the mixture was quenched by saturated aq. $Na_2S_2O_3$ and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 6:1) to give hemiacetal (35 mg, 96%). According to **general procedure A,** the hemiacetal (35 mg, 0.06 mmol) was treated with $NCCCl_3$ (18 μL, 0.18 mmol) and DBU (1.2 μL, 0.010 mmol) in dry CH_2Cl_2 (2 mL) to give donor **37** (39 mg, 90%, α) as a colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.56–7.51 (m, 2H), 7.42–7.38 (m, 2H), 7.35–7.26 (m, 13H), 7.21–7.11 (m, 2H), 6.57 (d, *J* = 3.4 Hz, 1H), 4.93–4.83 (m, 3H), 4.80 (d, *J* = 12.4 Hz, 1H), 4.72 (d, *J* = 12.4 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 10.6 Hz, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 4.06 (t, *J* = 9.4 Hz, 1H), 4.03–3.95 (m, 1H), 3.86–3.79 (m, 1H), 3.79–3.73 (m, 2H), 3.67 (dd, *J* = 10.9, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 138.5, 138.0, 137.8, 128.5, 128.44, 128.37, 128.1, 128.0, 127.92, 127.88, 127.8, 127.7, 127.4, 125.4, 125.33, 125.29, 94.2, 91.2, 81.3, 79.6, 76.9, 75.7, 75.4, 73.5, 73.2, 72.1, 67.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.5.

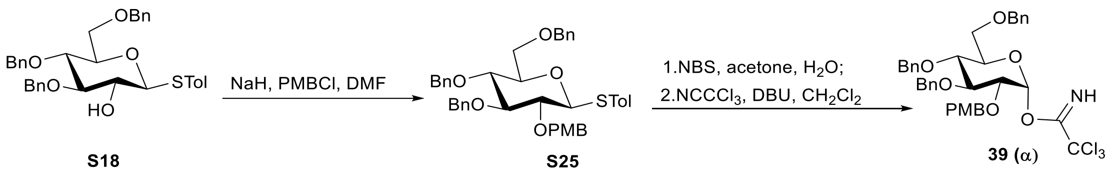
3,4,6-*O*-Benzyl-2-*O*-[4-fluoro-benzyl]-D-glucopyranosyl trichloroacetimidate (38)



To a solution of **S18** (200 mg, 0.37 mmol) in DMF (3 mL) were added NaH (37 mg, 1.4 mmol) and 4-fluorobenzyl chloride (140 mg, 0.74 mmol) successively. After stirred at rt for 4 h, the mixture was quenched by water, and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 10:1) to give **S24** (230 mg, 92%) as a colorless syrup. $[\alpha]_D^{20}$ = −6.2 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.42 (m, 2H), 7.37–7.25 (m, 15H), 7.21–7.16 (m, 2H), 7.06–6.95 (m, 4H), 4.88–4.78 (m, 4H), 4.68 (d, *J* = 10.2 Hz, 1H), 4.62–4.47 (m, 4H), 3.78 (dd, *J* = 10.9, 2.0 Hz, 1H), 3.75–3.70 (m, 1H), 3.70–3.60 (m, 2H), 3.51–3.42 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 161.3, 138.4, 138.3, 138.0, 137.8, 134.0, 133.9, 132.7, 130.1, 130.0, 129.73, 129.71, 128.51, 128.47, 128.4, 128.0, 127.9, 127.8, 127.73, 127.70, 127.6, 115.4, 115.2, 87.7, 86.8, 80.7, 79.1, 77.9, 75.8, 75.1, 74.6, 73.5, 69.0, 21.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.5; HRMS (ESI) calcd for $C_{41}H_{45}F_3NO_5S$ $[M+NH_4]^+$ 682.2997, found 682.2997.

To a solution of **S24** (210 mg, 0.31 mmol) in acetone/H_2O (3 mL, 9:1, *v*/*v*) was added NBS (110 mg, 0.63 mmol). After stirred at 0°C for 10 mins, the mixture was quenched by saturated aq. $Na_2S_2O_3$ and extracted with EA (3 x 20 mL). the combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 8:1) to give hemiacetal (140 mg, 83%). According to **general procedure A,** the hemiacetal (44 mg, 0.079 mmol) was treated with $NCCCl_3$ (24 µL, 0.24 mmol) and DBU (1.5 µL, 0.012 mmol) in dry CH_2Cl_2 (2 mL) to give donor **38** (48 mg, 86%, α/β = 3:1) as a colorless syrup. For the β isomer of donor **38**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 5.82 (d, *J* = 7.1 Hz, 1H); For the α isomer of donor **38**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.38–7.30 (m, 15H), 7.19–7.17 (m, 2H), 7.02–6.98 (m, 2H), 6.55 (d, *J* = 3.5 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.89–4.87 (m, 1H), 4.87–4.84 (m, 1H), 4.76–4.72 (m, 1H), 4.71–4.65 (m, 1H), 4.64–4.62 (m, 1H), 4.58 (d, *J* = 6.1 Hz, 1H), 4.53 (d, *J* = 12.4 Hz, 1H), 4.06 (t, *J* = 9.4 Hz, 1H), 4.03–3.99 (m, 1H), 3.80–3.75 (m, 3H), 3.71–3.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 138.6, 138.0, 137.8, 133.8, 129.4, 129.3, 128.5, 128.43, 128.40, 128.1, 128.0, 127.9, 115.4, 115.1, 94.3, 81.3, 79.3, 76.8, 75.7, 75.4, 73.5, 73.2, 72.2, 68.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ −114.5, −114.7.

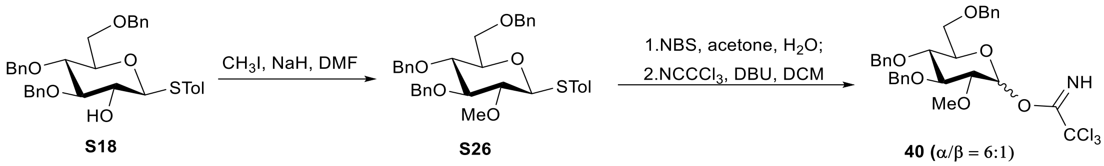
3,4,6-*O*-Benzyl-2-*O*-[4-methoxyl-benzyl]-α-D-glucopyranosyl trichloroacetimidate (39)



To a solution of **S18** (210 mg, 0.37 mmol) in DMF (3 mL) were added NaH (37 mg, 1.4 mmol) and 4–methoxybenzyl chloride (100 µL, 0.74 mmol) at 0 °C successively. After stirred at rt for 4 h, the mixture was quenched by water, and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 12:1) to give **S25** (220 mg, 92%) as a white solid. $[\alpha]_D^{20}$ = –46.4 (c = 1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.53–7.47 (m, 2H), 7.38–7.25 (m, 15H), 7.20–7.17 (m, 2H), 7.06–7.00 (m, 2H), 6.88–6.83 (m, 2H), 4.91 (dd, *J* = 10.9, 1.7 Hz, 1H), 4.88–4.77 (m, 3H), 4.66 (dd, *J* = 9.9, 1.7 Hz, 1H), 4.65–4.57 (m, 3H), 4.53 (dd, *J* = 11.9, 1.4 Hz, 1H), 3.79 (s, 3H), 3.78–3.59 (m, 4H), 3.51–3.43 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 138.6, 138.4, 138.1, 137.7, 132.7, 130.4, 130.0, 129.9, 129.7, 128.50, 128.47, 128.4, 128.0, 127.85, 127.79, 127.7, 127.6, 113.9, 87.8, 86.8, 80.6, 79.1, 77.9, 75.8, 75.10, 75.08, 73.5, 69.1, 55.3, 21.2; HRMS (ESI) calcd for $C_{42}H_{44}O_6SNa$ $[M+Na]^+$ 699.2751, found 699.2743.

To a solution of **S25** (140 mg, 0.21 mmol) in acetone/H_2O (3 mL, 9:1, *v*/*v*) was added NBS (110 mg, 0.63 mmol). After stirred at 0 °C for 10 mins, the mixture was quenched by saturated aq. $Na_2S_2O_3$ and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 6:1) to give hemiacetal (98 mg, 81%). According to **general procedure A**, the hemiacetal (140 mg, 0.27 mmol) was treated with $NCCCl_3$ (81 µL, 0.81 mmol) and DBU (6.0 µL, 0.040 mmol) in dry CH_2Cl_2 (5 mL) to give donor **39** (160 mg, 83%, α) as a colorless syrup; ^1H NMR (300 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.44–7.26 (m, 15H), 7.25–7.12 (m, 2H), 6.94–6.80 (m, 2H), 6.53 (d, *J* = 3.5 Hz, 1H), 5.07–4.92 (m, 1H), 4.92–4.80 (m, 2H), 4.78–4.46 (m, 5H), 4.14–3.97 (m, 2H), 3.94–3.63 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 159.3, 138.7, 138.1, 137.9, 130.1, 129.4, 128.48, 128.45, 128.43, 128.39, 128.1, 128.03, 128.00, 127.9, 127.8, 127.6, 113.8, 94.5, 81.4, 79.0, 75.6, 75.4, 73.5, 73.1, 72.5, 68.0, 55.3.

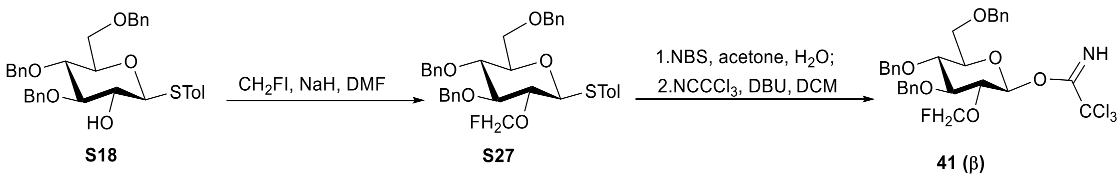
2-*O*-Methyl-3,4,6-*O*-benzyl-D-glucopyranosyl trichloroacetimidate (40)



To a solution of **S18** (400 mg, 0.72 mmol) in DMF (6 mL) were added NaH (60 mg, 1.4 mmol) and CH_3I (85 µL, 1.4 mmol) at 0 °C successively. After stirred at rt for 4 h, the mixture was quenched by water, and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 10:1) to give **S26** (350 mg, 85%) as a syrup. $[\alpha]_D^{20}$ = −14.4 (c = 0.8 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.53–7.49 (m, 2H), 7.38–7.30 (m, 13H), 7.25–7.20 (m, 2H), 7.08–7.04 (m, 2H), 4.92 (d, *J* = 10.8 Hz, 1H), 4.88–4.82 (m, 2H), 4.64–4.58 (m, 2H), 4.57–4.50 (m, 2H), 3.80 (dd, *J* = 10.9, 2.0 Hz, 1H), 3.73 (dd, *J* = 10.9, 4.6 Hz, 1H), 3.66 (s, 3H), 3.65–3.57 (m, 2H), 3.50 (s, 1H), 3.20 (dd, *J* = 9.7, 8.4 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.41, 138.35, 138.1, 137.7, 132.8, 129.64, 129.57, 128.5, 128.4, 128.03, 127.96, 127.8, 127.7, 127.6, 87.4, 86.8, 82.7, 79.0, 77.6, 75.8, 75.1, 73.4, 69.1, 61.0, 21.1; HRMS (ESI) calcd for $C_{35}H_{38}O_5SNa$ $[M+Na]^+$ 593.2332, found 593.2332.

To a solution of **S26** (300 mg, 0.51 mmol) in acetone/H_2O (5 mL, 9:1, *v*/*v*) was added NBS (300 mg, 1.6 mmol). After stirred at rt for 1 h, the mixture was quenched by saturated aq. $Na_2S_2O_3$ and extracted with EA (3 x 20 mL), the combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 6:1) to give hemiacetal (210 mg, 86%). According to **general procedure A**, the hemiacetal (200 mg, 0.40 mol) was treated with $NCCCl_3$ (64 µL, 0.60 mmol) and DBU (9.5 µL, 0.060 mmol) in dry CH_2Cl_2 (7 mL) to give donor **40** (230 mg, 88%, α/β = 6:1) as a syrup; For the β isomer of donor **40**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.70 (s, 1H), 5.72 (d, *J* = 8.0 Hz); For the α isomer of donor **40**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.43–7.30 (m, 13H), 7.21–7.16 (m, 2H), 6.61 (d, *J* = 3.4 Hz, 1H), 4.98 (d, *J* = 11.0 Hz, 1H), 4.88 (d, *J* = 10.6 Hz, 1H), 4.84 (d, *J* = 10.9 Hz, 1H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.55 (d, *J* = 10.6 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.05–3.96 (m, 2H), 3.86–3.75 (m, 2H), 3.73–3.67 (m, 1H), 3.61–3.53 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5, 138.8, 138.1, 137.9, 128.4, 128.1, 128.0, 127.91, 127.86, 127.8, 127.7, 94.0, 91.3, 81.8, 81.4, 76.7, 75.5, 75.4, 73.5, 73.1, 68.0, 59.0.

2-*O*-Fluoromethyl-3,4,6-*O*-benzyl-β-D-glucopyranosyl trichloroacetimidate (41)

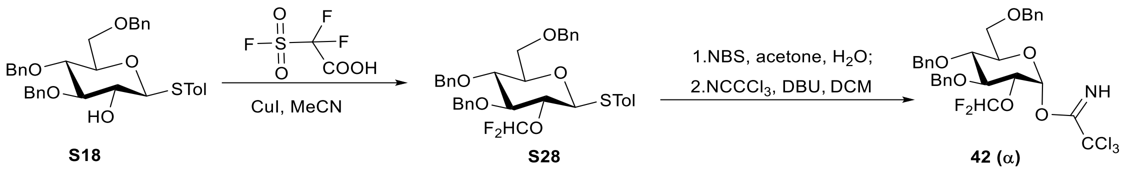


To a solution of **S18** (400 mg, 0.72 mmol) in DMF (6 mL) were added NaH (60 mg, 1.4 mmol) and CH_2FI (85 μL, 1.4 mmol) successively. After stirred at rt for 4 h, the mixture was quenched by water, and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 12:1) to give **S27** (350 mg, 85%) as a syrup. $[\alpha]^{20}_{D}$ = −7.6 (c = 0.5 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55–7.49 (m, 2H), 7.42–7.32 (m, 13H), 7.28-7.24 (m, 2H), 7.11–7.05 (m, 2H), 5.58 (dd, *J* = 23.9, 2.9 Hz, 1H), 5.40 (dd, *J* = 25.7, 2.9 Hz, 1H), 4.97 (d, *J* = 10.4 Hz, 1H), 4.88 (d, *J* = 10.9 Hz, 1H), 4.83 (d, *J* = 10.4 Hz, 1H), 4.67–4.55 (m, 4H), 3.83 (dd, *J* = 11.0, 2.1 Hz, 1H), 3.79–3.64 (m, 4H), 3.57–3.52 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 138.10, 138.06, 138.0, 132.9, 129.8, 129.0, 128.5, 128.40, 128.45, 128.36, 127.90, 127.88, 127.69, 127.61, 127.6, 104.1 (d, *J* = 217 Hz), 86.81, 86.78, 85.5, 80.9, 79.2, 77.6, 76.1, 75.1, 73.5, 69.0, 21.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ −146.0; HRMS (ESI) calcd for $C_{35}H_{41}FNO_5S^+$ $[M+NH_4]^+$ 606.2684, found 606.2689.

To a solution of **S27** (300 mg, 0.50 mmol) in acetone/H_2O (5 mL, 9:1, *v*/*v*) was added NBS (300 mg, 1.6 mmol). After stirred at rt for 1 h, the mixture was quenched by saturated $Na_2S_2O_3$ and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then the organic layer was concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 8:1) to give hemiacetal (210 mg, 86%). According to **general procedure A**, the hemiacetal (200 mg, 0.40 mol) was treated with $NCCCl_3$ (64 μL, 0.60 mmol) and DBU (9.0 μL, 0.060 mmol) in dry CH_2Cl_2 (7 mL) to give donor **41** (230 mg, 88%, β) as a syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.43–7.38 (m, 2H), 7.36-7.31 (m, 11H), 7.24–7.16 (m, 2H), 5.77 (d, *J* = 8.0 Hz, 1H), 5.58–5.50 (m, 1H), 5.38–5.32 (m, 1H), 5.00 (d, *J* =

10.6 Hz, 1H), 4.86 (d, *J* = 11.0 Hz, 1H), 4.80 (d, *J* = 10.6 Hz, 1H), 4.63 (d, *J* = 12.2 Hz, 1H), 4.61–4.53 (m, 2H), 3.95 (t, *J* = 8.5 Hz, 1H), 3.80–3.75 (m, 4H), 3.69–3.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 138.13, 138.05, 138.0, 128.43, 128.42, 128.37, 128.3, 128.0, 127.7, 103.7 (d, *J* = 217 Hz), 97.2, 90.8, 83.3, 81.1, 77.0, 76.0, 75.7, 75.1, 73.4, 68.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ −147.6.

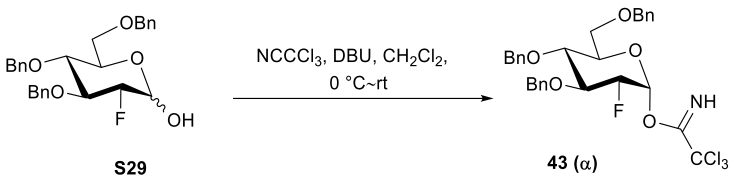
2-*O*-Difluoromethyl-3,4,6-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate (42)



To a solution of **S18** (400 mg, 0.72 mmol) in MeCN (8 mL) were added CuI (27 mg, 0.14 mmol) and difluoro(fluorosulfonyl)acetic acid (110 μL, 1.0 mmol) successively. After stirred at 60 °C for 6 h, the mixture was extracted with EA (3 x 15 mL). The combined organic layer was washed with brine and dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 10:1) to give **S29** (180 mg, 41%) as a syrup. $[\alpha]_D^{20}$ = −7.3 (c = 0.5 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.48 (m, 2H), 7.39–7.31 (m, 13H), 7.26–7.21 (m, 2H), 7.09–7.04 (m, 2H), 6.39 (t, *J* = 75.9 Hz, 1H), 4.94–4.81 (m, 3H), 4.66–4.61 (m, 2H), 4.60–4.54 (m, 2H), 3.83–3.77 (m, 2H), 3.76–3.69 (m, 2H), 3.66 (t, *J* = 9.0 Hz, 1H), 3.53–3.51 (m, 1H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 138.2, 137.8, 137.6, 133.5, 129.8, 128.5, 128.4, 128.1, 128.0, 127.9, 127.7, 117.9, 85.8, 84.7, 79.2, 77.6, 77.3, 76.1, 75.1, 73.4, 68.7, 21.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ −78.2; HRMS (ESI) calcd for $C_{35}H_{40}F_2O_5NS^+$ $[M+NH_4]^+$ 624.2590, found 624.2590.

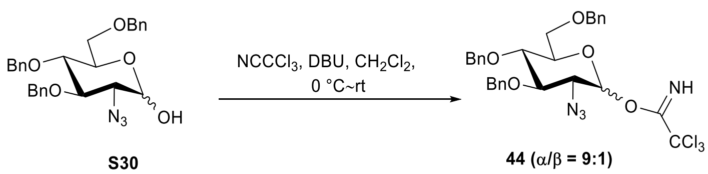
To a solution of **S28** (180 mg, 0.30 mmol) in acetone/H_2O (3 mL, 9:1, *v*/*v*) was added NBS (160 mg, 0.90 mmol). After stirred at rt for 1 h, the mixture was quenched by saturated aq. $Na_2S_2O_3$, and extracted with EA (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 8:1) to give hemiacetal (140 mg, 94%). According to **general procedure A**, the hemiacetal (120 mg, 0.24 mmol) was treated with $NCCCl_3$ (36 µL, 0.36 mmol) and DBU (5.0 µL, 0.040 mmol) in dry CH_2Cl_2 (7 mL) to give donor **42** (140 mg, 90%, α) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.38–7.31 (m, 13H), 7.20–7.16 (m, 2H), 6.53 (d, *J* = 3.5 Hz, 1H), 6.34 (dd, *J* = 75.2, 73.0 Hz, 1H), 4.91–4.82 (m, 3H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 10.6 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.38 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.09 (t, *J* = 9.3 Hz, 1H), 4.03–3.99 (m, 1H), 3.89 (dd, *J* = 10.1, 9.0 Hz, 1H), 3.83 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.71 (dd, *J* = 11.0, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 138.0, 137.8, 137.8, 128.5, 128.4, 128.13, 128.08, 128.0, 127.9, 127.8, 118.6, 116.0, 113.4(t, J = 264 Hz), 94.7, 91.0, 79.7, 77.0, 76.9, 75.8, 75.4, 73.7, 73.5, 73.2, 67.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ −81.1, −81.7, −81.8, −82.4.

2-Deoxy-2-fluoro-3,4,6-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate (43)



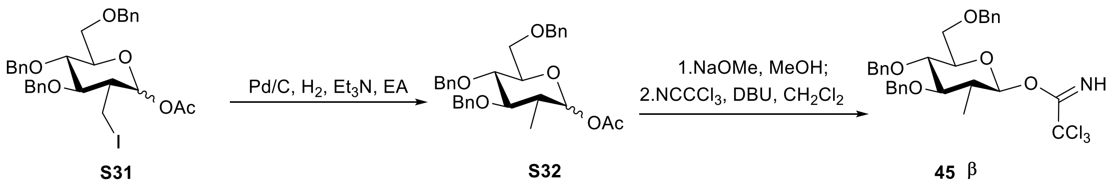
According to **general procedure A**, **S29**[15] (450 mg, 1.0 mmol) was treated with $NCCCl_3$ (0.15 mL, 1.5 mmol) and DBU (22 μL, 0.20 mmol) in dry CH_2Cl_2 (8 mL) to give donor **43** (480 mg, 81%, α) as a yellow oil. The spectroscopic data were in accordance with the literature.[15]

2-Deoxy-2-azide-3,4,6-*O*-benzyl-D-glucopyranosyl trichloroacetimidate (44)



According to **general procedure A**, **S30**[25] (1.0 g, 2.1 mmol) was treated with $NCCCl_3$ (0.32 mL, 3.2 mmol) and DBU (48 μL, 0.32 mmol) in dry CH_2Cl_2 (15 mL) to give donor **44** (1.05 g, 80%, α/β = 9:1) as a yellow oil. For the β isomer of donor **44**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 5.66 (d, J = 8.4 Hz, 1H); For the α isomer of donor **44**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.42–7.32 (m, 13H), 7.23–7.18 (m, 2H), 6.48 (d, J = 3.5 Hz, 1H), 4.98 (d, J = 10.7 Hz, 1H), 4.94 (s, 1H), 4.86 (d, J = 10.7 Hz, 1H), 4.65 (d, J = 11.9 Hz, 1H), 4.61 (d, J = 10.7 Hz, 1H), 4.51 (d, J = 12.0 Hz, 1H), 4.10–4.01 (m, 2H), 3.93 (d, J = 9.5 Hz, 1H), 3.84 (dd, J = 11.1, 3.1 Hz, 1H), 3.79–3.68 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 137.73, 137.68, 128.6, 128.5, 128.1, 128.0, 127.9, 95.0, 90.9, 80.1, 77.7, 75.6, 75.3, 73.6, 67.8, 63.1.

2-Deoxy-2-methyl-3,4,6-*O*-benzyl-β-D-glucopyranosyl trichloroacetimidate (45)

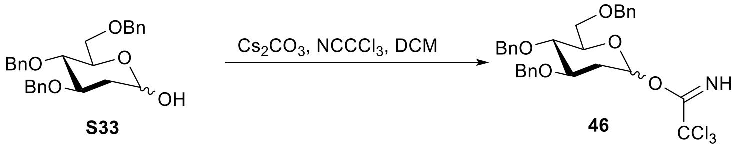


To a solution of **S31**[26] (2.0 g, 3.2 mmol) in EA (20 mL) were added Pd/C (0.5 g, wetted with ca. 55% Water) and Et_3N (0.50 mL, 3.9 mmol). After stirred under H_2 at 60 °C for

6 h, the mixture was filtered, and the filtrate was concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 8:1) to give **S32** (1.5 g, 94%) as a colorless oil. For the β isomer of **S32:** $[\alpha]_D^{23}$ = +17.1 (c = 1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.31 (m, 13H), 7.22–7.18 (m, 2H), 5.44 (d, *J* = 9.2 Hz, 1H), 4.94 (d, *J* = 11.0 Hz, 1H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.73–4.66(m, 2H), 4.60 (d, *J* = 10.8 Hz, 1H), 4.54 (d, *J* = 12.1 Hz, 1H), 3.83–3.74 (m, 3H), 3.61–3.57 (m, 1H), 3.34 (dd, *J* = 10.7, 8.8 Hz, 1H), 2.16 (s, 3H), 2.01–1.94 (m, 1H), 1.03 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 138.3, 138.1, 138.0, 128.49, 128.46, 128.4, 128.0, 127.92, 127.87, 127.83, 127.79, 127.7, 95.8, 84.7, 78.7, 75.8, 75.4, 74.8, 73.59, 73.56, 68.4, 41.6, 21.1, 12.2; HRMS (ESI) calcd for $C_{30}H_{38}O_6N$ $[M+NH_4]^+$ 508.2694 , found 508.2697; For the α isomer of **S32**: $[\alpha]_D^{21}$ = +49.1 (c = 1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39–7.31 (m, 13H), 7.23–7.19 (m, 2H), 6.14 (d, *J* = 3.3 Hz, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.86 (d, *J* = 10.7 Hz, 1H), 4.73–4.66 (m, 2H), 4.59 (d, *J* = 10.7 Hz, 1H), 4.54 (d, *J* = 12.1 Hz, 1H), 3.92–3.87 (m, 1H), 3.85–3.79 (m, 2H), 3.72–3.62 (m, 2H), 2.12 (s, 4H), 1.04 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 138.4, 138.1, 138.0, 128.5, 128.4, 128.3, 128.03, 127.95, 127.9, 127.8, 127.7, 94.5, 82.2, 78.8, 75.5, 75.0, 73.6, 68.4, 40.1, 21.0, 12.3; HRMS (ESI) calcd for $C_{30}H_{38}O_6N$ $[M+NH_4]^+$ 508.2694, found 508.2697.

To a solution of **S32** (1.5 g, 3.0 mmol) in MeOH (15 mL) was added NaOMe (33 mg, 0.60 mmol). After stirred at rt for 1 h, the mixture was neutralized by resin (H^+). Collected the filtrate and then concentrated under vacuum. The residue was purified by silica gel column chromatography (PE/EA = 6:1) to give hemiacetal (1.2 g, 88%). According to **general procedure A**, the hemiacetal (600 mg, 1.3 mmol) was treated with $NCCCl_3$ (210 μL, 2.0 mmol) and DBU (40 μL, 0.020 mmol) in dry CH_2Cl_2 (8 mL) to give donor **45** (β) as a syrup, which was used in the next step without further purification due to its liability. ^1H NMR (300 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.38–7.30 (m, 13H), 7.25–7.21 (m, 2H), 5.57 (d, *J* = 9.0 Hz, 1H), 4.93 (d, *J* = 11.0 Hz, 1H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.71 (d, *J* = 7.3 Hz, 1H), 4.68 (m, 1H), 4.64 (d, *J* = 10.6 Hz, 1H), 4.59 (d, *J* = 12.2 Hz, 1H), 3.80 (d, *J* = 3.1 Hz, 1H), 3.75 (d, *J* = 9.0 Hz, 1H), 3.67 (d, *J* = 3.0 Hz, 1H), 3.50–3.44 (m, 1H), 3.37 (dd, *J* = 10.6, 8.6 Hz, 1H), 2.10 (m, 1H), 1.11 (d, *J* = 6.5 Hz, 3H).

2-Deoxyl-3,4,6-*O*-benzyl-D-glucopyranosyl trichloroacetimidate (46)



According to **general procedure C**, **S33**[27] (400 mg, 0.90 mmol) was treated with $NCCCl_3$ (0.14 mL, 1.4 mmol) and Cs_2CO_3 (60 mg, 0.020 mmol) in dry CH_2Cl_2 (8 mL) to give donor **46**, which was used in the next step without further purification.

5.4. General procedure for glycosylation

General procedure E: Procedure for glycosylation

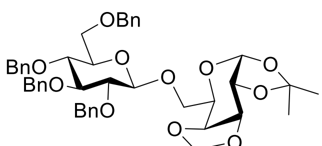
To a solution of trichloroimidate donor (1.2 eq, 30 mM) and acceptor (1.0 eq) in dry THF was added freshly activated 4Å molecular sieves (0.5 g/mmol). After cooled to −50 °C under N_2, $BF_3{\cdot}Et_2O$ (0.4 eq) in THF was added. After kept stirring for 3 h, the mixture was quenched with Et_3N, filtered, and then concentrated under vacuum. The residue was purified by column chromatograph on silica gel to give the corresponding product.

General Procedure F: Procedure for glycosylation

To a solution of trichloroimidate donor (1.0 eq, 30 mM) and acceptor (1.0 eq) in dry THF was added freshly activated 4Å molecular sieves (0.5 g/mmol). After cooled to −60 °C under N_2, $BF_3{\cdot}Et_2O$ (0.4 eq) in THF was added. After kept stirring for 3 h, the mixture was quenched with Et_3N, filtered, and then concentrated under vacuum. The residue was purified by column chromatograph on silica gel to give the corresponding product.

5.5. Substrate scope

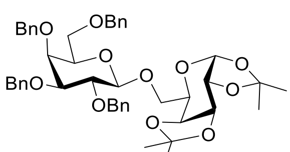
2,3,4,6-*O*-benzyl-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (4)



4

According to **general procedure E**, donor **8** (44 mg, 0.064 mmol) and acceptor **3** (14 mg, 0.054 mmol) was treated with $BF_3{\cdot}Et_2O$ (3.0 µL, 0.022 mmol) in dry THF (2 mL). to give product **4** (38 mg, 91%, β) as a yellow oil. The spectroscopic data were in accordance with the literature.[28]

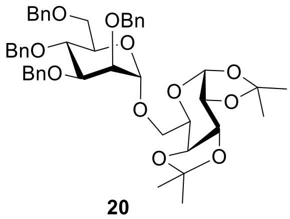
2,3,4,6-*O*-benzyl-β-D-galactopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (19)



19

According to **general procedure E**, donor **8** (44 mg, 0.064 mmol) and acceptor **3** (14 mg, 0.054 mmol) was treated with $BF_3 \cdot Et_2O$ (2.7 μL, 0.022 mmol) in dry THF (2 mL). to give product **19** (40 mg, 95%, β/α = 13:1) as a yellow oil. The spectroscopic data were in accordance with the literature.[29]

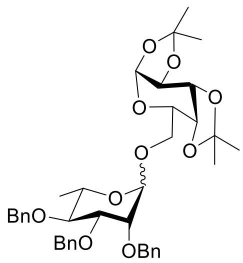
2,3,4,6-*O*-benzyl-α-D-mannopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (20)



20

According to **general procedure E**, donor **8** (44 mg, 0.064 mmol) and acceptor **3** (14 mg, 0.054 mmol) was treated with $BF_3 \cdot Et_2O$ (2.7 μL, 0.022 mmol) in dry THF (2 mL) to give product **20** (32 mg, 92%, α) as a yellow oil. The spectroscopic data were in accordance with the literature.[30]

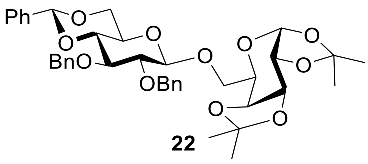
2,3,4,6-*O*-benzyl-L-rhamnopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (21)



21

According to **general procedure E**, donor **8** (37 mg, 0.064 mmol) and acceptor **3** (14 mg, 0.054 mmol) and $BF_3 \cdot Et_2O$ (2.7 μL, 0.022 mmol) in dry THF (2 mL) to give product **21** (33 mg, 91%, α/β = 10:1) as a yellow oil. The spectroscopic data were in accordance with the literature.[31]

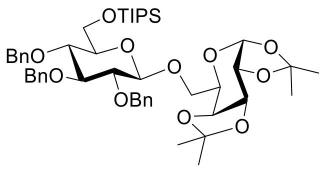
2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (22)



22

According to **general procedure E**, donor **8** (33 mg, 0.055 mmol) and acceptor **3** (12 mg, 0.046 mmol) was treated with $BF_3 \cdot Et_2O$ (2.4 μL, 0.018 mmol) in dry THF (3 mL) to give product **22** (31 mg, 98%, β) as a white solid. $[\alpha]_D^{21}$ = −37.1 (c = 1.0 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.50–7.27 (m, 15H), 5.58 (d, *J* = 5.0 Hz, 1H), 5.56 (s, 1H), 5.02 (d, *J* = 11.0 Hz, 1H), 4.90 (d, *J* = 11.4 Hz, 1H), 4.81 (d, *J* = 11.4 Hz, 1H), 4.75 (d, *J* = 11.1 Hz, 1H), 4.63–4.56 (m, 2H), 4.38–4.30 (m, 2H), 4.24 (d, *J* = 7.9 Hz, 1H), 4.14–4.05 (m, 2H), 3.82–3.70 (m, 2H), 3.67 (t, *J* = 9.0 Hz, 1H), 3.48 (t, *J* = 8.2 Hz, 1H), 3.41 (dd, *J* = 9.9, 5.1 Hz, 1H), 1.51 (s, 3H), 1.46 (s, 3H), 1.32 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 138.5, 137.3, 128.9, 128.6, 128.29, 128.26, 128.2, 128.1, 127.61, 127.58, 126.0, 109.5, 108.6, 105.0, 101.1, 96.4, 81.5, 81.4, 80.7, 75.2, 74.9, 71.4, 70.8, 70.4, 70.1, 68.8, 67.2, 66.0, 26.1, 26.0, 25.0, 24.5; HRMS (ESI) calcd for$C_{39}H_{46}O_{11}Na^+$ [M+Na]$^+$ 713.2932, found 713.2935.

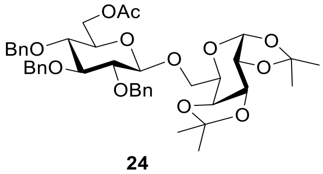
2,3,4-tri-*O*-benzyl-6-*O*-triisopropylsilyl-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (23)



23

According to **general procedure E**, donor **9** (52 mg, 0.070 mmol) and acceptor **3** (15 mg, 0.058 mmol) was treated with $BF_3{\cdot}Et_2O$ (3.0 μL, 0.023 mmol) in dry THF (3 mL) to give product **23** (48 mg, 99%, β) as a yellow oil. $[\alpha]_D^{21}$ = −25.9 (c = 1.0 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.44–7.40 (m, 2H), 7.34–7.26 (m, 13H), 5.57 (d, *J* = 5.0 Hz, 1H), 5.04 (d, *J* = 11.1 Hz, 1H), 4.94 (d, *J* = 10.8 Hz, 1H), 4.85 (d, *J* = 10.7 Hz, 1H), 4.80 (d, *J* = 10.8 Hz, 1H), 4.71 (d, *J* = 11.1 Hz, 1H),4.69 (d, *J* = 10.7 Hz, 1H), 4.58 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.44 (d, *J* = 7.7 Hz, 1H), 4.32 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.23 (d, *J* = 8.0 Hz, 1H), 4.11–4.01 (m, 2H), 4.00–3.89 (m, 2H), 3.74–3.60 (m, 3H), 3.43 (t, *J* = 8.2 Hz, 1H), 3.28 (dd, *J* = 7.3, 2.6 Hz, 1H), 1.50 (s, 3H), 1.45 (s, 3H), 1.32 (s, 3H), 1.32 (s, 3H) 1.10–1.05 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 138.7, 138.5, 128.5, 128.4, 128.3, 128.0, 127.8, 127.6, 127.5, 109.3, 108.6, 103.9, 96.4, 84.6, 82.1, 77.5, 77.4, 77.1, 76.6, 75.9, 75.8, 75.0, 74.5, 71.3, 70.7, 70.5, 68.7, 67.1, 62.4, 26.1, 26.0, 25.0, 24.5, 18.0, 12.0; HRMS (ESI) calcd for $C_{48}H_{72}O_{11}NSi$ [M+NH$_4$]$^+$ 866.4869, found 866.4875.

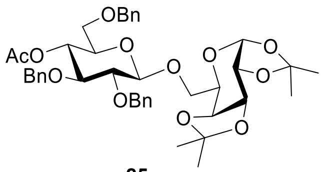
2,3,4-tri-*O*-benzyl-6-*O*-acetyl-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (24)



24

According to **general procedure E**, donor **10** (59 mg, 0.092 mmol) and acceptor **3** (20 mg, 0.077 mmol) was treated with $BF_3 \cdot Et_2O$ (4.0 µL, 0.030 mmol) in dry THF (3 mL) to give product **24** (55 mg, 99%, β) as a yellow oil. $[\alpha]_D^{21}$ = −19.1 (c = 1.0 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.45–7.40 (m, 2H), 7.37–7.25 (m, 13H), 5.57 (d, *J* = 5.2 Hz, 1H), 5.07 (d, *J* = 11.2 Hz, 1H), 4.99 (d, *J* = 10.7 Hz, 1H), 4.85 (d, *J* = 10.7 Hz, 1H), 4.78 (d, *J* = 10.8 Hz, 1H), 4.72 (d, *J* = 11.0 Hz, 1H), 4.60 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.53 (d, *J* = 10.7 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.35–4.20 (m, 4H), 4.15–4.06 (m, 2H), 3.78–3.64 (m, 2H), 3.57–3.42 (m, 3H), 2.04 (s, 3H), 1.49 (s, 3H), 1.46 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 138.6, 138.5, 137.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 109.5, 108.6, 104.5, 96.4, 84.5, 81.5, 77.3, 75.7, 75.1, 74.4, 72.8, 71.4, 70.8, 70.4, 70.0, 67.3, 63.2, 26.04, 26.01, 25.0, 24.4, 21.0; HRMS (ESI) calcd for $C_{41}H_{54}O_{12}N$ $[M+NH_4]^+$ 752.3641, found 752.3647.

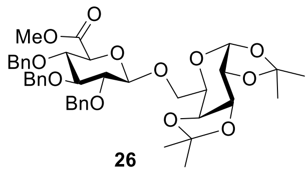
2,3,6-tri-*O*-benzyl-4-*O*-acetyl-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (25)



25

According to **general procedure E**, donor **11** (30 mg, 0.046 mmol) and acceptor **3** (10 mg, 0.038 mmol) was treated with $BF_3 \cdot Et_2O$ (4.0 µL, 0.030 mmol) in dry THF (2 mL) to give product **25** (28 mg, 99%, β) as a yellow oil. $[\alpha]_D^{21}$ = −27.5 (c = 1.0 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.44–7.40 (m, 2H), 7.34–7.27 (m, 11H), 7.25–7.22 (m, 2H), 5.58 (d, *J* = 5.0 Hz, 1H), 5.05 (d, *J* = 11.1 Hz, 1H), 5.00–4.94 (m, 1H), 4.84 (d, *J* = 11.6 Hz, 1H), 4.70 (d, *J* = 11.1 Hz, 1H), 4.62–4.57 (m, 2H), 4.50 (s, 2H), 4.49 (d, *J* = 7.5 Hz, 1H), 4.33 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.24 (dd, *J* = 7.9, 1.8 Hz, 1H), 4.16 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.11–4.07 (m, 1H), 3.75 (dd, *J* = 10.5, 7.3 Hz, 1H), 3.62–3.55 (m, 1H), 3.55–3.47 (m, 4H), 1.81 (s, 3H), 1.51 (s, 3H), 1.45 (s, 3H), 1.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 138.52, 138.49, 137.9, 128.7, 128.4, 128.33, 128.25, 127.92, 127.88, 127.7, 127.60, 127.58, 109.4, 108.6, 104.3, 96.4, 81.5, 81.4, 75.1, 74.5, 73.7, 73.3, 71.4, 70.9, 70.8, 70.5, 70.0, 69.6, 67.5, 26.1, 26.0, 25.0, 24.4, 20.8; HRMS (ESI) calcd for $C_{41}H_{54}O_{12}N$ $[M+NH_4]^+$ 752.3641 , found 752.3647.

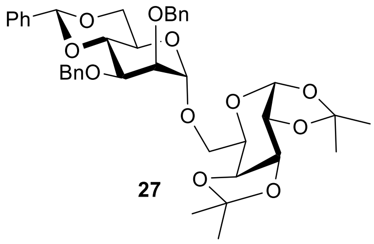
2,3,4-tri-*O*-benzyl-β-D-glucuronic acid methyl ester-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (26)



26

According to **general procedure E**, donor **12** (28 mg, 0.046 mmol) and acceptor **3** (10 mg, 0.040 mmol) was treated with $BF_3 \cdot Et_2O$ (2.1 μL, 0.020 mmol) in dry THF (2 mL) to give product **26** (25 mg, 91%, β) as a yellow oil. $[\alpha]_D^{21}$ = −30.7 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.41 (m, 2H), 7.36–7.28 (m, 11H), 7.25–7.21 (m, 2H), 5.59 (d, *J* = 5.0 Hz, 1H), 5.06 (d, *J* = 11.1 Hz, 1H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.82–4.78 (m, 2H), 4.73 (d, *J* = 11.1 Hz, 1H), 4.62 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.58 (d, *J* = 10.8 Hz, 1H), 4.54 (d, *J* = 7.6 Hz, 1H), 4.34 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.24 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.15 (dd, *J* = 10.6, 3.3 Hz, 1H), 4.09 (dd, *J* = 7.8, 2.3 Hz, 1H), 3.92 (d, *J* = 9.7 Hz, 1H), 3.81 (t, *J* = 9.3 Hz, 1H), 3.74 (s, 4H), 3.67 (t, *J* = 9.0 Hz, 1H), 3.52 (dd, *J* = 9.1, 7.7 Hz, 1H), 1.51 (s, 3H), 1.48 (s, 3H), 1.34 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 138.5, 137.8, 128.7, 128.4, 128.3, 128.0, 127.9, 109.5, 108.6, 104.7, 96.4, 83.7, 81.0, 79.3, 75.8, 75.1, 74.4, 71.4, 70.8, 70.4, 70.2, 67.4, 52.5, 26.06, 25.99, 25.0, 24.4; HRMS (ESI) calcd for $C_{40}H_{48}O_{12}Na$ $[M+Na]^+$ 743.3038, found 743.3043.

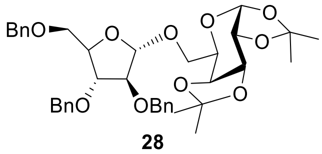
2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (27)



27

According to **general procedure E**, donor **13** (33 mg, 0.055 mmol) and acceptor **3** (12 mg, 0.046 mmol) was treated with $BF_3 \cdot Et_2O$ (2.4 μL, 0.018 mmol) in dry THF (3 mL) to give product **22**[30] (23 mg, 75%, α) as a yellow oil. $[\alpha]_D^{21}$ = −8.0 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.52 (m, 2H), 7.43–7.35 (m, 9H), 7.35–7.29 (m, 4H), 5.67 (s, 1H), 5.56 (d, *J* = 5.0 Hz, 1H), 4.97 (d, *J* = 1.5 Hz, 1H), 4.86–4.82 (m, 2H), 4.79 (d, *J* = 12.3 Hz, 1H), 4.68–4.63 (m, 2H), 4.36 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.31–4.25 (m, 2H), 4.21 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.03-3.98 (m, 2H), 3.93–3.87 (m, 3H), 3.80 (dd, *J* = 10.7, 6.8 Hz, 1H), 3.72 (dd, *J* = 10.8, 6.5 Hz, 1H), 1.55 (s, 3H), 1.47 (s, 3H), 1.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.1, 137.7, 128.8, 128.4, 128.3, 128.2, 128.1, 127.8, 127.51, 127.46, 126.1, 109.4, 108.7, 101.4, 99.0, 96.4, 79.1, 76.4, 76.3, 73.4, 73.1, 70.9, 70.7, 70.6, 68.8, 65.8, 65.4, 64.4, 26.2, 26.0, 25.0, 24.6; HRMS (ESI) calcd for$C_{39}H_{46}O_{11}Na^+$ $[M+Na]^+$ 713.2932, found 713.2935.

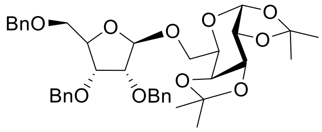
2,3,5-tri-*O*-benzyl-α-D-arabifuanosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (28)



28

According to **general procedure E**, donor **14** (57 mg, 0.10 mmol) and acceptor **3** (22 mg, 0.080 mmol) was treated with $BF_3·Et_2O$ (4.1 µL, 0.030 mmol) in dry THF (3 mL) to give product **28** (55 mg, 98%, α) as a yellow oil. $[\alpha]_D^{21}$ = −0.4 (c = 1.0 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36–7.22 (m, 15H), 5.54 (d, *J* = 5.0 Hz, 1H), 5.17 (d, *J* = 1.3 Hz, 1H), 4.65–4.59 (m, 2H), 4.58–4.54 (m, 2H), 4.52 (d, *J* = 6.9 Hz, 1H), 4.48 (d, *J* = 11.8 Hz, 1H) 4.46 (d, *J* = 11.9 Hz, 1H), 4.32 (dd, *J* = 5.1, 2.4 Hz, 1H), 4.29 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.24–4.18 (m, 1H), 4.08–4.02 (m, 2H), 3.95 (dd, *J* = 7.0, 3.4 Hz, 1H), 3.84 (dd, *J* = 10.5, 6.4 Hz, 1H), 3.75 (dd, *J* = 10.5, 7.7 Hz, 1H), 3.64 (dd, *J* = 10.8, 3.7 Hz, 1H), 3.58 (dd, *J* = 10.8, 5.1 Hz, 1H), 1.50 (s, 3H), 1.45 (s, 3H), 1.32 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 137.9, 137.7, 128.43, 128.35, 128.0, 127.9, 127.82, 127.79, 127.7, 127.6, 109.3, 108.6, 106.3, 96.4, 88.1, 83.5, 80.6, 73.4, 72.2, 71.8, 70.9, 70.7, 69.6, 65.8, 65.5, 26.1, 26.0, 25.0, 24.6; HRMS (ESI) calcd for $C_{38}H_{50}O_{10}N$ $[M+NH_4]^+$ 680.3429, found 680.3435.

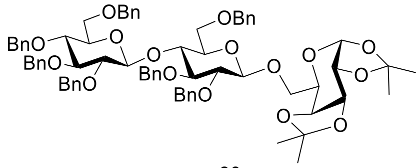
2,3,5-tri-*O*-benzyl-β-D-ribofuanosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (29)



29

According to **general procedure E**, donor **15** (49 mg, 0.088 mmol) and acceptor **3** (19 mg, 0.073 mmol) was treated with $BF_3·Et_2O$ (3.7 µL, 0.029 mmol) in dry THF (3 mL) to give product **29**[32] (46 mg, 95%, β) as a yellow oil. $[\alpha]_D^{21}$ = −9.6 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.38–7.30 (m, 13H), 5.56 (d, *J* = 5.0 Hz, 1H), 5.18 (s, 1H), 4.75 (d, *J* = 12.1 Hz, 1H), 4.65 (d, *J* = 12.2 Hz, 1H), 4.60 (d, *J* = 11.9 Hz, 1H), 4.58–4.55 (m, 3H), 4.46 (d, *J* = 11.9 Hz, 1H), 4.39–4.35 (m, 1H), 4.32 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.07 (dd, *J* = 7.3, 4.6 Hz, 1H), 4.03 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.00–3.97 (m, 1H), 3.91–3.85 (m, 2H), 3.69–3.55 (m, 3H), 1.54 (s, 3H), 1.45 (s, 3H), 1.36 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 138.0, 137.9, 128.4, 128.3, 128.0, 127.9, 127.7, 127.54, 127.48, 109.3, 108.5, 105.4, 96.3, 80.4, 79.4, 78.3, 73.1, 72.3, 72.1, 71.3, 71.2, 70.6, 70.5, 67.6, 66.6, 26.1, 26.0, 25.0, 24.4; HRMS (ESI) calcd for $C_{38}H_{50}O_{10}N$ $[M+NH_4]^+$ 680.3429, found 680.3435.

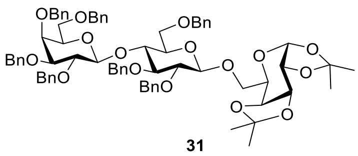
2,3,4,6-*O*-benzyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (30)



30

According to **general procedure E**, donor **16** (51 mg, 0.046 mmol) and acceptor **3** (10 mg, 0.038 mmol) was treated with $BF_3·Et_2O$ (2.0 µL, 0.015 mmol) in dry THF (3 mL) to give product **30** (44 mg, 93%, β) as a yellow oil. $[\alpha]_D^{21}$ = −2.1 (c = 0.9 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.40 (m, 4H), 7.35–7.28 (m, 25H), 7.25–7.20 (m, 6H), 5.61 (d, *J* = 5.0 Hz, 1H), 5.09 (d, *J* = 11.4 Hz, 1H), 5.02 (d, *J* = 11.3 Hz, 1H), 4.92 (d, *J* = 10.9 Hz, 1H), 4.86–4.79 (m, 4H), 4.77 (d, *J* = 11.6 Hz, 1H), 4.73 (d, *J* = 11.0 Hz, 1H), 4.63–4.60 (m, 2H), 4.57 (s, 1H), 4.52 (d, *J* = 7.8 Hz, 1H), 4.49–4.45 (m, 2H), 4.43 (s, 2H), 4.36 (dd, *J* = 5.1, 2.4 Hz, 1H), 4.28 (dd, *J* = 7.9, 1.8 Hz, 1H), 4.19–4.15 (m, 1H), 4.14–4.10 (m, 1H), 4.06 (t, *J* = 9.3 Hz, 1H), 3.86 (dd, *J* = 10.9, 3.7 Hz, 1H), 3.79–3.74 (m, 1H), 3.73–3.71 (m, 1H), 3.71–3.64 (m, 2H), 3.64–3.61 (m, 1H), 3.60–3.57 (m, 1H), 3.55 (t, *J* = 8.4 Hz, 1H), 3.50–3.45 (m, 1H), 3.43–3.39 (m, 1H), 3.38–3.30 (m, 2H), 1.54 (s, 3H), 1.50 (s, 3H), 1.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 138.8, 138.6, 138.5, 138.3, 138.1, 128.6, 128.43, 128.37, 128.3, 128.2, 128.04, 127.96, 127.89, 127.85, 127.7, 127.6, 127.4, 127.1, 109.4, 108.6, 104.3, 102.4, 96.4, 84.9, 82.7, 82.6, 81.1, 78.0, 76.5, 75.7, 75.0, 74.8, 74.5, 73.3, 71.4, 70.8, 70.5, 69.4, 68.9, 68.0, 67.3, 26.1, 26.0, 25.1, 24.5; HRMS (ESI) calcd for $C_{73}H_{82}O_{16}Na^+$ $[M+Na]^+$ 1237.5495, found 1237.5493.

2,3,4,6-*O*-benzyl-β-D-galacopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (31)

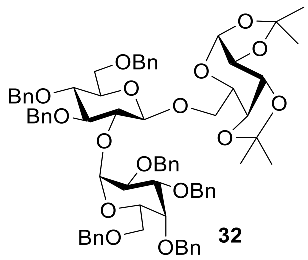


31

According to **general procedure E**, donor **17** (52 mg, 0.046 mmol) and acceptor **3** (10 mg, 0.038 mmol) was treated with $BF_3·Et_2O$ (2.0 µL, 0.015 mmol) in dry THF (3 mL) to give product **31** (40 mg, 85%, β) was obtained as a yellow oil. $[\alpha]_D^{21}$ = −12.3 (c = 1.1 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.39–7.28 (m, 26H), 7.26-7.23 (m, 5H), 7.20–7.16 (m, 2H), 5.60 (d, *J* = 5.0 Hz, 1H), 5.05–4.97 (m, 3H), 4.84 (d, *J* = 11.2 Hz, 1H), 4.80–4.71 (m, 5H), 4.62–4.58 (m, 2H), 4.55 (d, *J* = 6.7 Hz, 1H), 4.47 (d, *J* = 7.7 Hz, 1H), 4.44 (d, *J* = 7.7 Hz, 1H), 4.40 (d, *J* = 8.1 Hz, 1H), 4.38–4.33 (m, 2H), 4.29–4.24 (m, 2H), 4.19–4.08 (m, 2H), 4.01–3.93 (m, 2H), 3.86–3.80 (m, 1H), 3.77 (d, *J* = 2.2 Hz, 1H), 3.76–3.68 (m, 2H), 3.61–3.52 (m, 2H), 3.47–3.40 (m, 2H), 3.39–3.32 (m, 3H), 1.53

(s, 3H), 1.49 (s, 3H), 1.35 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 139.2, 139.1, 138.9, 138.8, 138.5, 138.3, 138.1, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 127.1, 109.4, 108.7, 104.3, 102.8, 96.4, 82.7, 82.5, 81.2, 80.0, 76.6, 75.4, 75.3, 75.1, 74.7, 74.6, 73.6, 73.4, 73.1, 72.9, 72.6, 71.4, 70.8, 70.5, 69.5, 68.1, 67.3, 26.1, 26.0, 25.1, 24.5; HRMS (ESI) calcd for $C_{73}H_{82}O_{16}Na^+$ $[M+Na]^+$ 1237.5495, found 1237.5493.

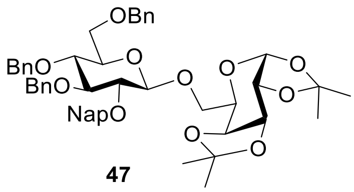
2,3,4,6-*O*-benzyl-α-D-galacopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (32)



32

According to **general procedure E**, donor **18** (41 mg, 0.037 mmol) and acceptor **3** (8 mg, 0.03 mmol) was treated with $BF_3 \cdot Et_2O$ (1.6 µL, 0.012 mmol) in dry THF (2 mL) to give product **32** (28 mg, 78%, β) as a yellow oil. $[\alpha]_D^{21}$ = +16.9 (c = 0.8 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.45 (m, 2H), 7.41–7.37 (m, 5H), 7.37–7.29 (m, 14H), 7.28–7.25 (m, 7H), 7.22–7.19 (m, 2H), 7.19–7.15 (m, 3H), 7.14–7.10 (m, 2H), 5.89 (d, *J* = 3.6 Hz, 1H), 5.44 (d, *J* = 5.0 Hz, 1H), 4.95 (d, *J* = 7.7 Hz, 1H), 4.92 (d, *J* = 5.5 Hz, 1H), 4.90 (d, *J* = 9.8 Hz, 1H), 4.86 (d, *J* = 11.9 Hz, 1H), 4.78–4.74 (m, 2H), 4.71 (d, *J* = 5.6 Hz, 1H), 4.69–4.64 (m, 2H), 4.62–4.57 (m, 2H), 4.56–4.52 (m, 3H), 4.34 (d, *J* = 11.8 Hz, 1H), 4.29-4.24 (m, 4H), 4.20 (dd, *J* = 10.3, 3.1 Hz, 1H), 4.14 (dd, *J* = 10.2, 3.6 Hz, 1H), 4.09–4.06 (m, 1H), 3.91–3.85 (m, 2H), 3.75–3.68 (m, 4H), 3.68–3.63 (m, 2H), 3.52 (dd, *J* = 9.6, 6.3 Hz, 1H), 3.48–3.45 (m, 1H), 3.33 (dd, *J* = 9.6, 6.7 Hz, 1H), 1.51 (s, 3H), 1.45 (s, 3H), 1.33 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 139.1, 139.0, 138.7, 138.4, 138.1, 138.0, 132.5, 129.8, 128.4, 128.33, 128.29, 128.24, 128.16, 128.13, 128.09, 128.0, 127.9, 127.8, 127.7, 127.5, 127.38, 127.35, 127.33, 127.26, 127.24, 109.3, 108.7, 104.0, 96.1, 94.9, 83.7, 81.5, 78.6, 78.0, 77.2, 76.9, 75.9, 75.6, 74.91, 74.88, 74.7, 73.8, 73.6, 73.1, 72.8, 72.0, 71.6, 70.9, 70.3, 69.4, 69.1, 68.6, 67.4, 26.1, 26.0, 25.0, 24.5; HRMS (ESI) calcd for $C_{73}H_{82}O_{16}Na^+$ $[M+Na]^+$ 1237.5495, found 1237.5495

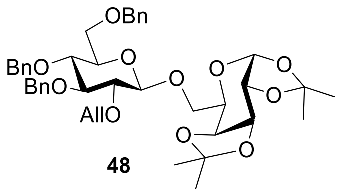
3,4,6-*O*-benzyl-2-*O*-(naphthaleneyl-2-methyl)-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (47)



47

According to **general procedure E**, donor **33** (51 mg, 0.07 mmol) and acceptor **3** (15 mg, 0.058 mmol) was treated with $BF_3·Et_2O$ (3.0 μL, 0.023 mmol) in dry THF (3 mL) to give product **47** (46 mg, 96%, β) as a colorless oil. $[\alpha]_D^{21}$ = −15.6 (c = 1.0 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.83–7.78 (m, 1H), 7.76–7.70 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.46–7.42 (m, 2H), 7.34–7.25(m, 13H), 7.15–7.11 (m, 2H), 5.61 (d, *J* = 4.9 Hz, 1H), 5.22 (d, *J* = 11.2 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.88 (d, *J* = 11.2 Hz, 1H), 4.83–4.76 (m, 2H), 4.65–4.58 (m, 2H), 4.56–4.46 (m, 3H), 4.34 (dd, *J* = 5.1, 2.4 Hz, 1H), 4.25 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.20 (dd, *J* = 10.3, 3.1 Hz, 1H), 4.16–4.10 (m, 1H), 3.79–3.69 (m, 3H), 3.67–3.58 (m, 2H), 3.54 (d, *J* = 7.9 Hz, 1H), 3.45 (d, *J* = 8.4 Hz, 1H), 1.52 (s, 3H), 1.46 (s, 3H), 1.32 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 138.2, 136.2, 133.4, 133.0, 128.4, 128.0, 127.9, 127.8, 127.65, 127.56, 127.5, 127.0, 125.8, 125.7, 109.4, 108.6, 104.5, 96.4, 84.5, 81.6, 77.7, 75.7, 75.0, 74.8, 74.5, 73.5, 71.5, 70.8, 70.5, 69.9, 68.8, 67.5, 26.1, 26.0, 25.1, 24.5; HRMS (ESI) calcd for $C_{50}H_{60}O_{11}N$ $[M+NH_4]^+$ 850.4161, found 850.4167.

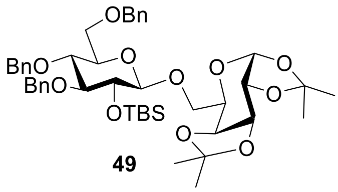
3,4,6-*O*-benzyl-2-*O*-allyl-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (48)



48

According to **general procedure E**, donor **34** (44 mg, 0.069 mmol) and acceptor **3** (15 mg, 0.058 mmol) was treated with $BF_3·Et_2O$ (3.0 μL, 0.023 mmol) in dry THF (3 mL) to give product **48** (38 mg, 90%, β) as a colorless oil. $[\alpha]_D^{20}$ = −27.3 (c = 1.0 in $CHCl_3$);^1H NMR (300 MHz, $CDCl_3$) δ 7.38-7.28 (m,13H), 7.19–7.15 (m, 2H), 6.06–5.93 (m, 1H), 5.57 (d, *J* = 5.0 Hz, 1H), 5.35 (dd, *J* = 17.2, 1.8 Hz, 1H), 5.18 (dd, *J* = 10.3, 1.8 Hz, 1H), 4.99 (d, *J* = 10.8 Hz, 1H), 4.84 (d, *J* = 10.8 Hz, 1H), 4.79 (d, *J* = 10.8 Hz, 1H), 4.66–4.59 (m, 2H), 4.58–4.50 (m, 3H), 4.41 (d, *J* = 7.8 Hz, 1H), 4.33 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.29–4.20 (m, 2H), 4.15 (dd, *J* = 10.7, 3.7 Hz, 1H), 4.08–4.03 (m, 1H), 3.77–3.67 (m, 3H), 3.66–3.57 (m, 2H), 3.46 (d, *J* = 2.0 Hz, 1H), 3.42–3.33 (m, 1H), 1.54 (s, 3H), 1.47 (s, 3H), 1.35 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 138.19, 138.15, 135.4, 128.4, 128.1, 128.0, 127.9, 127.7, 127.6, 117.2, 109.4, 108.6, 104.3, 96.4, 84.6, 81.5, 77.6, 75.8, 75.0, 74.7, 73.5, 73.4, 71.4, 70.7, 70.5, 69.7, 68.8, 67.4, 26.03, 25.99, 25.1, 24.4; HRMS (ESI) calcd for $C_{42}H_{56}O_{11}N$ $[M+NH_4]^+$ 750.3848, found 750.3854.

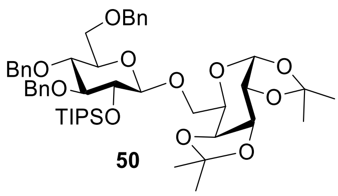
3,4,6-*O*-benzyl-2-*O*-tert-butyldimethylsilyl-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (49)



49

According to general procedure E, donor **35** (52 mg, 0.074 mmol) and acceptor **3** (16 mg, 0.061 mmol) was treated with $BF_3{\cdot}Et_2O$ (3.0 µL, 0.025 mmol) in dry THF (3 mL) to give product **49** (40 mg, 80%, β) as a colorless oil. $[\alpha]_D^{20}$ = −36.6 (c = 1.2 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.38–7.25 (m, 13H), 7.13–7.07 (m, 2H), 5.54 (d, *J* = 5.0 Hz, 1H), 4.94 (d, *J* = 11.4 Hz, 1H), 4.88 (d, *J* = 11.4 Hz, 1H), 4.77 (d, *J* = 10.7 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.62–4.50 (m, 3H), 4.36–4.27 (m, 3H), 4.15 (dd, *J* = 9.9, 5.1 Hz, 1H), 4.08–4.04 (m, 1H), 3.79–3.71 (m, 2H), 3.70–3.62 (m, 2H), 3.59 (t, *J* = 7.8 Hz, 1H), 3.56–3.50 (m, 1H), 3.50–3.44 (m, 1H), 1.55 (s, 3H), 1.46 (s, 3H), 1.35 (s, 3H), 1.35 (s, 3H), 0.92 (s, 9H), 0.17 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.2, 138.1, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 127.2, 109.2, 108.5, 103.8, 96.3, 86.0, 78.2, 75.6, 75.00, 74.96, 74.9, 73.6, 71.4, 70.7, 70.6, 70.5, 68.9, 68.7, 66.9, 26.1, 26.04, 26.01, 25.0, 24.5, 18.2, −3.9, −4.4; HRMS (ESI) calcd for $C_{45}H_{66}O_{11}NSi$ $[M+NH_4]^+$ 824.4400, found 824.4406.

3,4,6-*O*-Benzyl-2-*O*-triisopropylsilyl-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (50)

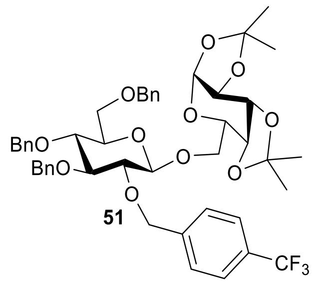


50

According to **general procedure E**, donor **36** (45 mg, 0.060 mmol) and acceptor **3** (13 mg, 0.050 mmol) was treated with $BF_3{\cdot}Et_2O$ (2.5 µL, 0.020 mmol) in dry THF (3 mL) to give product **50** (34 mg, 80%, β) as a yellow oil. $[\alpha]_D^{20}$ = −28.4 (c = 0.9 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39–7.26 (m, 13H), 7.13–7.08 (m, 2H), 5.52 (d, *J* = 5.0 Hz, 1H), 4.93 (d, *J* = 11.4 Hz, 1H), 4.88 (d, *J* = 11.4 Hz, 1H), 4.74 (d, *J* = 10.8 Hz, 1H), 4.62 (d, *J* = 10.2 Hz, 1H), 4.60–4.50 (m, 3H), 4.33–4.28 (m, 3H), 4.17–4.12 (m, 1H), 4.05–4.02 (m, 1H), 3.82–3.72 (m, 3H), 3.65 (d, *J* = 9.4 Hz, 1H), 3.61 (dd, *J* = 10.0, 6.4 Hz, 1H), 3.55 (t, *J* = 8.7 Hz, 1H), 3.50–3.46 (m, 1H), 1.53 (s, 3H), 1.45 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 1.27–

1.19 (m, 3H), 1.12–1.06 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.0, 138.2, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.2, 127.1, 109.2, 108.5, 103.7, 96.3, 86.6, 78.2, 75.6, 75.2, 74.7, 73.6, 71.5, 70.8, 70.5, 68.8, 68.6, 67.0, 26.0, 25.0, 24.6, 18.3, 13.2; HRMS (ESI) calcd for $C_{48}H_{72}O_{11}NSi$ $[M+NH_4]^+$ 866.4869, found 866.4876.

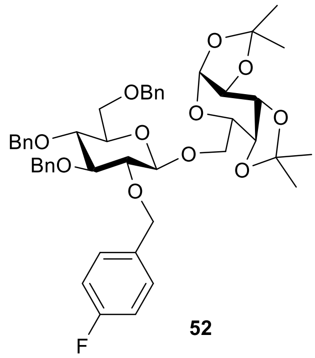
3,4,6-*O*-Benzyl-2-*O*-4-[4-trifluoromethyl-benzyl]-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (51)



51

According to **General Procedure E**, donor **37** (40 mg, 0.060 mmol) and acceptor **3** (13 mg, 0.060 mmol) was treated with $BF_3 \cdot Et_2O$ (3.0 µL, 0.020 mmol) in dry THF (3 mL) to give product **51** (43 mg, 95%, β) as a yellow oil. $[\alpha]_D^{20}$ = –21.4 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 4H), 7.39–7.28 (m, 13H), 7.19–7.12 (m, 2H), 5.58 (d, *J* = 5.0 Hz, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 4.94 (d, *J* = 11.0 Hz, 1H), 4.88–4.75 (m, 3H), 4.72–4.59 (m, 2H), 4.55 (d, *J* = 12.2 Hz, 1H), 4.53 (d, *J* = 10.7 Hz, 1H), 4.48 (d, *J* = 7.8 Hz, 1H), 4.35 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.25 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.20 (dd, *J* = 10.7, 2.9 Hz, 1H), 4.12–4.08 (m, 1H), 3.78–3.69 (m, 3H), 3.69–3.60 (m, 2H), 3.49–3.43 (m, 2H), 1.51 (s, 3H), 1.48 (s, 3H), 1.34 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 138.6, 138.1, 128.5, 128.43, 128.40, 128.0, 127.9, 127.8, 127.72, 127.69, 127.67, 125.12, 125.08, 125.0, 109.5, 108.6, 104.4, 96.4, 84.5, 81.5, 77.7, 75.7, 75.1, 74.7, 73.5, 73.2, 71.5, 70.8, 70.4, 70.1, 68.6, 67.5, 26.03, 26.00, 25.0, 24.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.4; HRMS (ESI) calcd for $C_{47}H_{53}F_3O_{11}Na$ $[M+Na]^+$ 873.3432, found 873.3429.

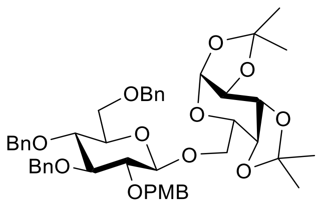
3,4,6-*O*-Benzyl-2-*O*-4-[4-fluoro-benzyl]-β-D–glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (52)



52

According to **General Procedure E**, donor **38** (40 mg, 0.050 mmol) and acceptor **3** (13 mg, 0.060 mmol) was treated with $BF_3 \cdot Et_2O$ (3.0 µL, 0.020 mmol) in dry THF (3 mL) to give product **52** (43 mg, 95%, β) as a yellow oil. $[\alpha]_D^{20}$ = −18.8 (c = 2.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41–7.26 (m, 15H), 7.16–7.09 (m, 2H), 6.97–6.90 (m, 2H), 5.57 (d, *J* = 5.0 Hz, 1H), 5.00 (d, *J* = 11.1 Hz, 1H), 4.92 (d, *J* = 11.0 Hz, 1H), 4.80 (d, *J* = 10.8 Hz, 1H), 4.79 (d, *J* = 11.0 Hz, 1H), 4.68 (d, *J* = 11.1 Hz, 1H), 4.64–4.58 (m, 2H), 4.56–4.46 (m, 2H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.33 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.23 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.17 (dd, *J* = 10.7, 3.1 Hz, 1H), 4.09 (dd, *J* = 7.7, 2.5 Hz, 1H), 3.74–3.67 (m, 3H), 3.65–3.57 (m, 2H), 3.47–3.37 (m, 2H), 1.49 (s, 3H), 1.46 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 138.1, 134.4, 130.6, 130.5, 128.4, 128.0, 127.9, 127.78, 127.76, 127.7, 127.6, 115.1, 114.9, 109.5, 108.6, 104.4, 96.4, 84.5, 81.3, 77.7, 75.7, 75.0, 74.7, 73.53, 73.48, 71.5, 70.8, 70.5, 70.0, 68.7, 67.5, 26.05, 26.02, 25.1, 24.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ −115.2; HRMS (ESI) calcd for $C_{46}H_{53}FO_{11}Na$ $[M+Na]^+$ 823.3464, found 823.3459.

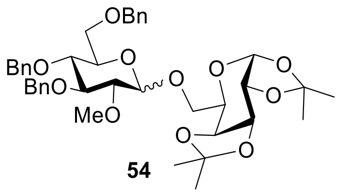
3,4,6-*O*-Benzyl-2-*O*-4-[4-methoxyl-benzyl]-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (53)



53

According to **General Procedure E**, donor **39** (40 mg, 0.060 mmol) and acceptor **3** (13 mg, 0.060 mmol) was treated with $BF_3{\cdot}Et_2O$ (3.0 µL, 0.020 mmol) in dry THF (3 mL) to give product **53** (42 mg, 90%, β) as a yellow oil. $[\alpha]_D^{20}$ = +20.5 (c = 1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.29 (m, 15H), 7.19–7.13 (m, 2H), 6.87–6.81 (m, 2H), 5.61 (d, *J* = 5.0 Hz, 1H), 5.00 (d, *J* = 10.7 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.83 (d, *J* = 10.7 Hz, 1H), 4.79 (d, *J* = 10.9 Hz, 1H), 4.69 (d, *J* = 10.8 Hz, 1H), 4.65 (d, *J* = 12.2 Hz, 1H), 4.63 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.56 (d, *J* = 12.2 Hz, 1H), 4.52 (d, *J* = 10.7 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.36 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.29 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.20 (dd, *J* = 10.6, 3.5 Hz, 1H), 4.14–4.11 (m, 1H), 3.82 (s, 3H), 3.79–3.71 (m, 3H), 3.66–3.61 (m, 2H), 3.51–3.42 (m, 2H), 1.54 (s, 3H), 1.49 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 138.8, 138.2, 130.9, 130.4, 128.44, 128.40, 128.38, 128.37, 128.0, 127.90, 127.89, 127.86, 127.7, 127.64, 127.56, 113.6, 109.4, 108.6, 104.5, 96.4, 84.6, 81.2, 77.7, 75.7, 75.0, 74.7, 74.0, 73.5, 71.5, 70.8, 70.5, 69.8, 68.8, 67.4, 55.3, 26.1, 26.0, 25.1, 24.5; HRMS (ESI) calcd for $C_{47}H_{56}O_{12}Na$ $[M+Na]^+$ 835.3664, found 835.3654.

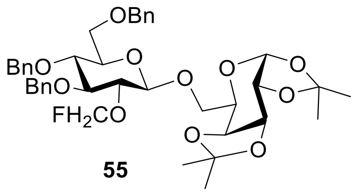
2-*O*-Methyl-3,4,6-*O*-benzyl-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (54)



54

According to **general procedure E**, donor **40** (50 mg, 0.083 mmol) and acceptor **3** (18 mg, 0.069 mmol) was treated with $BF_3{\cdot}Et_2O$ (3.5 µL, 0.028 mmol) in dry THF (2.5 mL) to give product **54** (42 mg, 87%, β/α > 20:1) as a yellow oil. For the β isomer of product **54:** $[\alpha]^{20}_{D}$ = −46.2 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.28 (m, 13H), 7.21–7.17 (m, 2H), 5.58 (d, *J* = 5.0 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.85 (d, *J* = 10.8 Hz, 1H), 4.80 (d, *J* = 11.0 Hz, 1H), 4.67–4.61 (m, 2H), 4.59–4.53 (m, 2H), 4.40 (d, *J* = 7.8 Hz, 1H), 4.34 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.28 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.15 (dd, *J* = 10.8, 3.7 Hz, 1H), 4.09–4.06 (m, 1H), 3.78–3.69 (m, 3H), 3.66 (s, 3H), 3.64–3.56 (m, 2H), 3.47–3.43 (m, 1H), 3.23–3.17 (m, 1H), 1.55 (s, 3H), 1.48 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.23, 138.19, 128.41, 128.38, 128.1, 128.0, 127.9, 127.7, 127.6, 109.4, 108.6, 104.3, 96.4, 84.7, 84.2, 77.5, 75.5, 75.0, 74.7, 73.5, 71.4, 70.7, 70.5, 69.7, 68.8, 67.6, 60.5, 26.0, 25.1, 24.4; HRMS (ESI) calcd for $C_{40}H_{54}O_{11}N^{+}$ $[M+NH_4]^{+}$ 724.3691, found 724.3690; For the α isomer of product **54**:^{1}H NMR (300 MHz, $CDCl_3$) δ 5.55 (d, *J* = 5.4 Hz, 1H), 5.13 (d, *J* = 3.6 Hz, 1H).

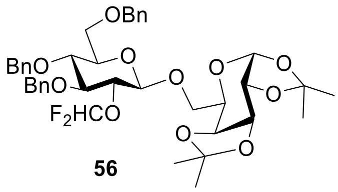
2-*O*-Monofluoromethyl-3,4,6-*O*-benzyl-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (55)



55

According to **general procedure E**, donor **41** (52 mg, 0.083 mmol) and acceptor **3** (18 mg, 0.069 mmol) was treated with $BF_3{\cdot}Et_2O$ (3.5 µL, 0.023 mmol) in dry THF (2.5 mL) to give product **55** (41 mg, 81%, β) as a yellow oil. $[\alpha]^{20}_{D}$ = −20.3 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.40 (m, 2H), 7.36–7.29 (m, 11H), 7.20–7.16 (m, 2H), 5.60 (dd, *J* = 55.5, 3.0 Hz, 1H), 5.56 (d, *J* = 5.0 Hz, 1H), 5.46 (dd, *J* = 48.8, 3.0 Hz, 1H), 5.05 (d, *J* = 10.6 Hz, 1H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.75 (d, *J* = 10.5 Hz, 1H), 4.65–4.61 (m, 2H), 4.54 (d, *J* = 12.2 Hz, 1H), 4.53 (d, *J* = 10.9 Hz, 1H), 4.47–4.43 (m, 1H), 4.34 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.23 (dd, *J* = 8.0, 1.9 Hz, 1H), 4.15 (dd, *J* = 11.1, 2.8 Hz, 1H), 4.04–3.99 (m, 1H), 3.77–3.61 (m, 6H), 3.49–3.45 (m, 1H), 1.55 (s, 3H), 1.47 (s, 3H), 1.35 (m, 3H), 1.35 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 128.4, 127.95, 127.87, 127.7, 109.5, 108.7, 102.2, 96.3, 82.6, 77.3, 75.8, 75.1, 74.8, 73.5, 71.2, 70.8, 70.5, 69.8, 68.4, 67.4, 26.0, 25.9, 25.0, 24.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -149.9; HRMS (ESI) calcd for $C_{40}H_{49}FO_{11}Na^+$ $[M+Na]^+$ 747.3151, found 747.3150.

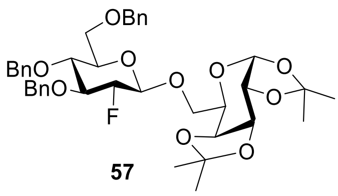
2-*O*-Difluoromethyl-3,4,6-*O*-benzyl-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (56)



56

According to **general procedure E**, donor **42** (48 mg, 0.074 mmol) and acceptor **3** (16 mg, 0.061 mmol) was treated with $BF_3 \cdot Et_2O$ (3.0 µL, 0.026 mmol) in dry THF (2.5 mL) to give product **56** (41 mg, 90%, β) as a yellow oil. $[\alpha]_D^{20}$ = −24.8 (c = 0.7 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.30 (m, 13H), 7.20–7.13 (m, 2H), 6.64 (dd, *J* = 83.6, 72.5 Hz, 1H), 5.56 (d, *J* = 5.0 Hz, 1H), 5.00 (d, *J* = 10.4 Hz, 1H), 4.84 (d, *J* = 10.8 Hz, 1H), 4.76 (d, *J* = 10.5 Hz, 1H), 4.65–4.60 (m, 2H), 4.56–4.50 (m, 3H), 4.34 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.24 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.13 (dd, *J* = 10.8, 3.4 Hz, 1H), 4.05–4.00 (m, 1H), 3.83 (t, *J* = 8.0 Hz, 1H), 3.77–3.69 (m, 4H), 3.65 (d, *J* = 8.8, 1H), 3.51–3.44 (m, 1H), 1.55 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.02, 137.97, 137.9, 128.45, 128.41, 128.0, 127.89, 127.87, 127.86, 127.7, 120.1, 117.6, 115.0, 109.5, 108.7, 102.3, 96.3, 82.6, 78.8, 77.3, 75.8, 75.1, 74.8, 73.5, 71.2, 70.8, 70.5, 69.8, 68.4, 67.4, 26.0, 25.9, 25.0, 24.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ −81.2, −81.8, −83.1, −83.7; HRMS (ESI) calcd for $C_{40}H_{48}F_2O_{11}Na^+$ $[M+Na]^+$ 765.3057, found 765.3059.

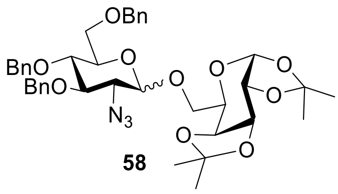
2-Fluoro-3,4,6-*O*-benzyl-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (57)



57

According to **general procedure E**, donor **43** (33 mg, 0.055 mmol) and acceptor **3** (12 mg, 0.046 mmol) was treated with $BF_3 \cdot Et_2O$ (2.3 µL, 0.018 mmol) in dry THF (2 mL) to give product **57** (25.6 mg, 80%, β) as a yellow oil. $[\alpha]_D^{21}$ = −30.8 (c = 1.0 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.29 (m, 13H), 7.21–7.16 (m, 2H), 5.57 (d, *J* = 5.0 Hz, 1H), 4.93 (d, *J* = 11.1 Hz, 1H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.76 (d, *J* = 11.2 Hz, 1H), 4.67–4.60 (m, 3H), 4.57–4.51 (m, 2H), 4.47–4.28 (m, 3H), 4.12–4.04 (m, 2H), 3.87–3.78 (m, 2H), 3.76–3.64 (m, 3H), 3.52–3.47 (m, 1H), 1.57 (s, 3H), 1.47 (s, 3H), 1.36 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.1, 138.0, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 109.3, 108.7, 100.7, 100.4, 96.3, 94.4, 91.9, 83.5, 83.3, 75.1, 74.92, 74.85, 74.8, 73.5, 71.2, 70.6, 70.5, 68.5, 68.4, 67.4, 26.1, 26.0, 25.0, 24.4; HRMS (ESI) calcd for $C_{39}H_{51}O_{10}NF$ $[M+NH_4]^+$ 712.3492, found 712.3498.

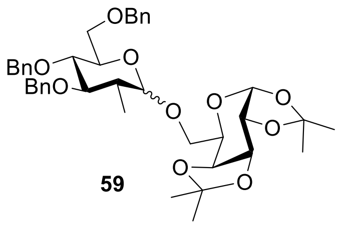
2-Deoxy-2-azide-3,4,6-*O*-benzyl-β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (58)



58

According to **general procedure E**, donor **40** (31 mg, 0.05 mmol) and acceptor **3** (11 mg, 0.042 mmol) was treated with $BF_3 \cdot Et_2O$ (2.0 µL, 0.017 mmol) in dry THF (2 mL) to give product **58** (28 mg, 92%, β/α = 9:1) as a white solid. For the β isomer for product **58**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.27 (m, 13H), 7.18–7.12 (m, 2H), 5.55 (d, *J* = 5.0 Hz, 1H), 4.89 (d, *J* = 10.8 Hz, 1H), 4.79 (d, *J* = 10.7 Hz, 1H), 4.78 (d, *J* = 10.7 Hz, 1H), 4.65–4.39 (m, 5H), 4.32 (dd, *J* = 5.1, 2.4 Hz, 1H), 4.28 (dd, *J* = 7.9, 1.5 Hz, 1H), 4.11–4.02 (m, 2H), 3.83–3.69 (m, 3H), 3.68–3.60 (m, 1H), 3.48–3.31 (m, 3H), 1.54 (s, 3H), 1.45 (s, 3H), 1.33 (m, 3H), 1.33 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 138.04, 137.98, 128.5, 128.43, 128.40, 128.1, 128.0, 127.9, 127.8, 127.7, 109.3, 108.7, 102.5, 96.3, 83.1, 77.7, 75.5, 75.0, 73.6, 71.2, 70.7, 70.5, 68.8, 68.5, 67.6, 66.4, 26.04, 25.99, 25.0, 24.4; HRMS (ESI) calcd for $C_{39}H_{47}O_{10}N_3Na$ $[M+Na]^+$ 740.3154, found 740.3153; For the α isomer of product **58**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.52 (d, *J* = 5.0 Hz, 1H), 4.99 (d, *J* = 3.5 Hz, 1H).

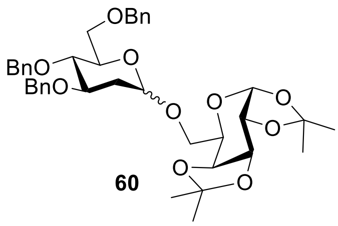
2-Deoxy-2-methyl-3,4,6-*O*-benzyl-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (59)



59

According to **general procedure E**, donor **45** (55 mg, 0.092 mmol) and acceptor **3** (20 mg, 0.077 mmol) was treated with $BF_3 \cdot Et_2O$ (4.0 µL, 0.03 mmol) in dry THF (3 mL) to give product **59** (47 mg, 89%, β/α = 2:1) as a yellow oil. For the β isomer of product **59**: $[\alpha]^{20}_{D}$ = −38.6 (c = 0.8 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.29 (m, 13H), 7.24–7.20 (m, 2H), 5.57 (d, *J* = 5.0 Hz, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.71–4.65 (m, 2H), 4.64–4.57 (m, 3H), 4.33 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.30–4.24 (m, 2H), 4.09–4.02 (m, 2H), 3.82–3.71 (m, 3H), 3.64 (dd, *J* = 9.7, 8.8 Hz, 1H), 3.50–3.46 (m, 1H), 1.86–1.80 (m, 1H), 1.56 (s, 3H), 1.48 (s, 3H), 1.36 (s, 3H), 1.36 (s, 3H), 1.13 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 138.3, 128.45, 128.36, 127.9, 127.7, 127.6, 109.3, 108.6, 105.1, 96.3, 85.4, 79.3, 75.3, 75.1, 74.7, 73.5, 71.4, 70.7, 70.5, 69.1, 68.8, 68.2, 42.8, 26.1, 26.0, 25.0, 24.3, 12.7; HRMS (ESI) calcd for $C_{40}H_{54}O_{10}N$ $[M+NH_4]^+$ 708.3742, found 708.3750. For the α isomer of product **59**: $[\alpha]_D^{20}$ = +38.1 (c = 0.5 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.29 (m, 15H), 7.21–7.17 (m, 2H), 5.56 (d, *J* = 5.0 Hz, 1H), 4.90 (d, *J* = 10.9 Hz, 1H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.78 (d, *J* = 3.4 Hz, 1H), 4.70 (d, *J* = 6.6 Hz, 1H), 4.67 (d, *J* = 5.5 Hz, 1H), 4.63 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.55 (d, *J* = 6.6 Hz, 1H), 4.53 (d, *J* = 7.9 Hz, 1H), 4.34 (dd, *J* = 5.1, 2.3 Hz, 1H), 4.26 (dd, *J* = 8.0, 1.9 Hz, 1H), 4.01–3.97 (m, 1H), 3.89–3.84 (m, 1H), 3.84–3.79 (m, 2H), 3.72–3.63 (m, 4H), 2.00–1.94 (m, 1H), 1.57 (s, 3H), 1.47 (s, 3H), 1.36 (s, 3H), 1.36 (s, 3H), 1.11 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 138.4, 138.1, 128.43, 128.37, 128.0, 127.9, 127.6, 109.3, 109.2, 108.5, 101.1, 96.3, 82.6, 79.4, 75.4, 74.8, 73.5, 71.2, 71.0, 70.7, 70.6, 68.7, 65.9, 65.8, 41.3, 26.2, 26.0, 25.0, 24.4, 12.6; HRMS (ESI) calcd for $C_{40}H_{54}O_{10}N$ $[M+NH_4]^+$ 708.3742, found 708.3750.

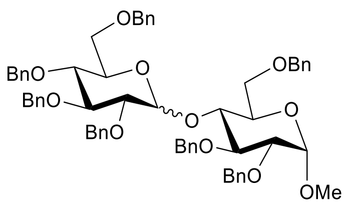
2-Deoxy-3,4,6-*O*-benzyl-D-gulcopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranose (60)



60

According to **general procedure E**, donor **46** (48 mg, 0.083 mmol) and acceptor **3** (18 mg, 0.069 mmol) was treated with $BF_3 \cdot Et_2O$ (3.6 µL, 0.027 mmol) in dry THF (3 mL) to give product **60** (43 mg, 94%, β/α = 1:2) as a white solid. The spectroscopic data were in accordance with the literature.[33, 34]

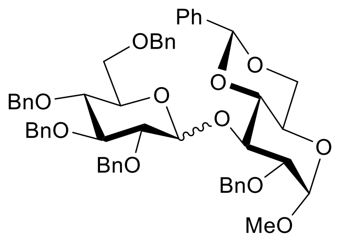
Methyl [2,3,4,6-*O*-benzyl-D-glucopyranosyl]-(1→4)-2,3,6-tri-benzyl-α-D-glucopyranoside (62a)



62a

According to **general procedure E**, donor **1** (32 mg, 0.047 mmol) and acceptor **61a** (18 mg, 0.039 mmol) was treated with $BF_3 \cdot Et_2O$ (2.0 µL, 0.016 mmol) in dry THF (2 mL) to give product **62a** (26 mg, 70%, β/α = 20:1) as a yellow oil. The spectroscopic data were in accordance with the literature.[35]

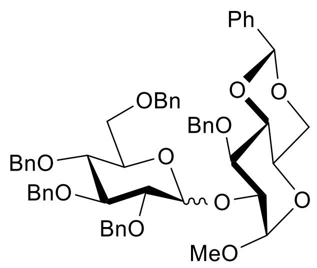
Methyl [2,3,4,6-O-benzyl-D-glucopyranosyl]-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (62b)



62b

According to **general procedure E**, donor **1** (40 mg, 0.058 mmol) and acceptor **61b** (18 mg, 0.048 mmol) was treated with BF_3·Et_2O (2.5 µL, 0.020mmol) in dry THF (3 mL) to give product **62b** (40 mg, 93%, β/α = 7:1) as a white solid. The spectroscopic data were in accordance with the literature.[35]

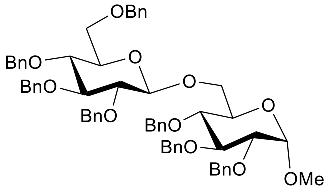
Methyl [2,3,4,6-*O*-benzyl-D-glucopyranosyl]-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (62c)



62c

According to **general procedure E**, donor **1** (48 mg, 0.083 mmol) and acceptor **61c** (18 mg, 0.069 mmol) was treated with BF_3·Et_2O (3.6 µL, 0.027 mmol) in dry THF (3 mL) to give product **62c** (36 mg, 83%, β/α = 6:1) as a white solid. The spectroscopic data were in accordance with the literature.[35]

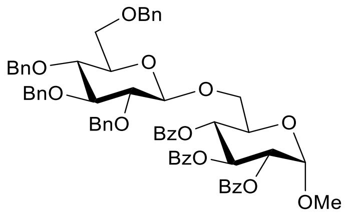
Methyl [2,3,4,6-*O*-benzyl-β-D-glucopyranosyl]-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (62d)



62d

According to **general procedure E**, donor **1** (44 mg, 0.065 mmol) and acceptor **61d** (25 mg, 0.054 mmol) was treated with BF_3·Et_2O (2.7 µL, 0.022 mmol) in dry THF (2 mL) to give product **62d** (45 mg, 85%, β) as a white solid. The spectroscopic data were in accordance with the literature.[11]

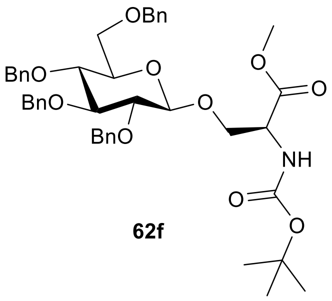
Methyl [(2,3,4,6-*O*-benzyl-β-D-glucopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (62e)



62e

According to **general procedure E**, donor **1** (41 mg, 0.049 mmol) and acceptor **61e** (25 mg, 0.060 mmol) was treated with $BF_3{\cdot}Et_2O$ (2.5 µL, 0.020 mmol) in dry THF (3 mL) to give product **62e** (47 mg, 93%, β) as a white solid. The spectroscopic data were in accordance with the literature.[36]

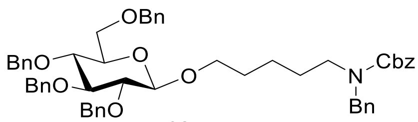
N-Boc-L-serine methyl ester 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (62f)



62f

According to **general procedure E**, donor **1** (56 mg, 0.08 mmol) and acceptor **61f** (15 mg, 0.068 mmol) was treated with $BF_3{\cdot}Et_2O$ (3.5 µL, 0.027 mmol) in dry THF (7 mL) to give product **62f** (55 mg, 99%, β) as a colorless oil. The spectroscopic data were in accordance with the literature.[11]

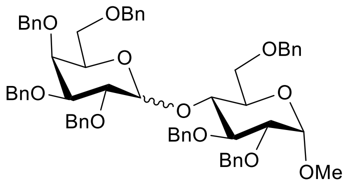
Penthyl N-benzyl (Cbz) 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (62g)



62g

According to **general procedure E**, donor **1** (62 mg, 0.090 mmol) and acceptor **61g** (25 mg, 0.076 mmol) was treated with $BF_3{\cdot}Et_2O$ (4.0 µL, 0.03 mmol) in dry THF (7 mL) to give product **62g** (59 mg, 91%, β) as a colorless oil. $[\alpha]^{20}_{D}$ = +3.0 (c = 1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.29 (m, 27H), 7.23–7.18 (m, 3H), 5.25–5.18 (m, 2H), 5.00–4.94 (m, 2H), 4.87 (d, *J* = 12.8 Hz, 1H), 4.84 (d, *J* = 12.9 Hz, 1H), 4.76 (d, *J* = 11.1 Hz, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 4.62–4.56 (m, 2H), 4.55–4.49 (m, 2H), 4.44–4.37 (m, 1H), 4.01–3.90 (m, 1H), 3.79 (dd, J = 10.8, 2.0 Hz, 1H), 3.72 (dd, J = 11.4, 4.1 Hz, 1H), 3.69–3.60 (m, 2H), 3.58–3.45 (m, 3H), 3.33–3.18 (m, 2H), 1.70–1.51 (m, 4H), 1.45–1.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 156.2, 138.6, 138.5, 138.2, 138.1, 138.0, 128.6, 128.5, 128.45, 128.43, 128.41, 128.04, 127.99, 127.94, 127.89, 127.8, 127.70, 127.66, 127.2, 103.7, 84.7, 82.3, 77.9, 75.7, 75.1, 74.9, 74.8, 73.5, 69.9, 69.0, 67.2, 50.6, 50.3, 47.2, 46.2, 29.5, 28.0, 27.6, 23.4; HRMS (ESI) calcd for $C_{54}H_{63}O_8N_2$ $[M+NH_4]^+$ 867.4579, found 867.4589.

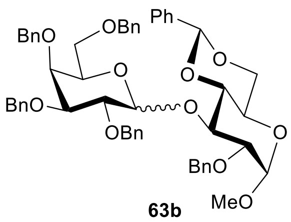
Methyl [2,3,4,6-*O*-benzyl-D-galacopyranosyl]-(1→6)-2,3,6-tri-benzyl-α-D-glucopyranoside (63a)



63a

According to **general procedure E**, donor **5** (44 mg, 0.065 mmol) and acceptor **61a** (25 mg, 0.054 mmol) was treated with $BF_3 \cdot Et_2O$ (2.7 µL, 0.022 mmol) in dry THF (2 mL) to give product **63a** (37 mg, 70%, β/α = 4:1) as a colorless oil. The spectroscopic data were in accordance with the literature.[29]

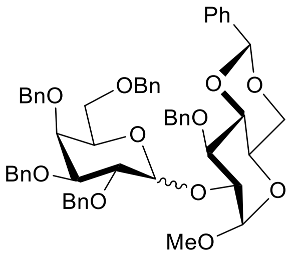
Methyl [2,3,4,6-*O*-benzyl-D-galacopyranosyl]-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (63b)



63b

According to **general procedure E**, donor **5** (33 mg, 0.05 mmol) and acceptor **61b** (15 mg, 0.04 mmol) was treated with $BF_3 \cdot Et_2O$ (2.0 µL, 0.016 mmol) in dry THF (1.5 mL) to give product **63b** (27 mg, 73%, β/α = 3:1) as a white solid. The spectroscopic data were in accordance with the literature.[37]

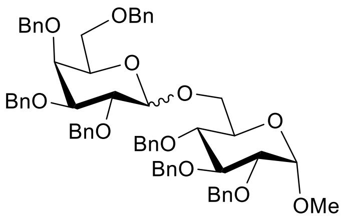
Methyl [2,3,4,6-*O*-benzyl-D-galacopyranosyl]-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (63c)



63c

According to **general procedure E**, donor **6** (36 mg, 0.052 mmol) and acceptor **61c** (20 mg, 0.043 mmol) was treated with $BF_3 \cdot Et_2O$ (2.2 µL, 0.017 mmol) in dry THF (2 mL) to give product **63c** (32 mg, 74%, β/α = 10:1) as a white solid. The spectroscopic data were in accordance with the literature.[38]

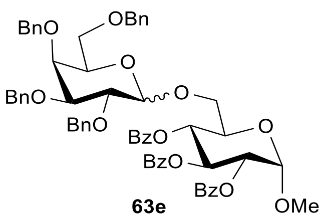
Methyl [2,3,4,6-*O*-benzyl-D-galactopyranosyl]-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (63d)



63d

According to **general procedure E**, donor **5** (53 mg, 0.078 mmol) and acceptor **61d** (30 mg, 0.065 mmol) was treated with $BF_3 \cdot Et_2O$ (3.3 µL, 0.026 mmol) in dry THF (3 mL) to give product **63d** (51 mg, 80%, β/α = 6:1) as a colorless oil. The spectroscopic data were in accordance with the literature.[29]

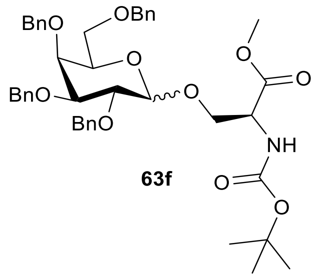
Methyl [2,3,4,6-*O*-benzyl-D-galacopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (63e)



63e

According to **general procedure E**, donor **5** (62 mg, 0.09 mmol) and acceptor **61e** (25 mg, 0.076 mmol) was treated with $BF_3 \cdot Et_2O$ (4.0 µL, 0.03 mmol) in dry THF (7 mL) to give product **63e** (59 mg, 97%, β/α = 13:1) as a colorless oil. The spectroscopic data were in accordance with the literature.[39]

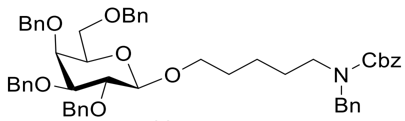
N-Boc-L-serine methyl ester 2,3,4,6-tetra-*O*-benzyl-D-galacopyranoside (63f)



63f

According to **general procedure E**, donor **6** (49 mg, 0.071 mmol) and acceptor **61f** (13 mg, 0.059 mmol) was treated with $BF_3 \cdot Et_2O$ (3.0 μL, 0.024 mmol) in dry THF (2 mL) to give product **63f** (32 mg, 74%, β/α = 16:1) as a white solid. The spectroscopic data were in accordance with the literature.[40]

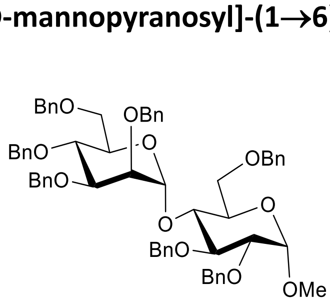
Penthyl N-benzyl (Cbz)2,3,4,6-tetra-*O*-benzyl-β-D-galacopyranoside (63g)



63g

According to **general procedure E**, donor **5** (62 mg, 0.09 mmol) and acceptor **61g** (25 mg, 0.076 mmol) was treated with $BF_3 \cdot Et_2O$ (4.0 μL, 0.030 mmol) in dry THF (7 mL) to give product **63g** (64 mg, 99%, β) as a colorless oil. $[\alpha]_D^{20}$ = −2.4 (c = 1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.29 (m, 29H), 7.23–7.16 (m, 1H), 5.23–5.18 (m, 2H), 4.98 (d, *J* = 11.6 Hz, 1H), 4.92 (dd, *J* = 12.9, 4.3 Hz, 1H), 4.81–4.73 (m, 3H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.53–4.47 (m, 3H), 4.45 (d, *J* = 11.8 Hz, 1H), 4.35 (d, *J* = 7.3 Hz, 1H), 3.97–3.87 (m, 2H), 3.84 (dd, *J* = 9.8, 7.7 Hz, 1H), 3.65–3.60 (m, 2H), 3.58–3.53 (m, 2H), 3.52–3.42 (m, 1H), 3.32–3.17 (m, 2H), 1.68–1.50 (m, 4H), 1.41–1.30 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 156.2, 138.8, 138.7, 138.6, 137.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.95, 127.86, 127.6, 127.3, 104.0, 82.2, 79.6, 75.2, 74.5, 73.6, 73.5, 73.4, 73.0, 69.8, 68.9, 67.2, 50.6, 50.2, 47.2, 46.3, 29.5, 28.0, 27.6, 23.4; **HRMS** (ESI) calcd for $C_{54}H_{63}O_8N_2$ $[M+NH_4]^+$ 867.4579, found 867.4588.

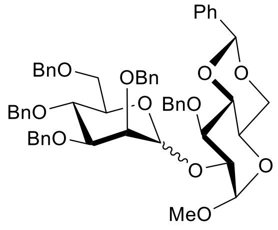
Methyl [2,3,4,6-*O*-benzyl-α-D-mannopyranosyl]-(1→6)-2,3,6-tri-benzyl-α-D-glucopyranoside (64a)



64a

According to **general procedure E**, donor **6** (36 mg, 0.052 mmol) and acceptor **61a** (20 mg, 0.043 mmol) was treated with $BF_3·Et_2O$ (2.0 µL, 0.017 mmol) in dry THF (2 mL) to give product **64a** (14 mg, 30%, α) as a colorless oil. The spectroscopic data were in accordance with the literature.[41]

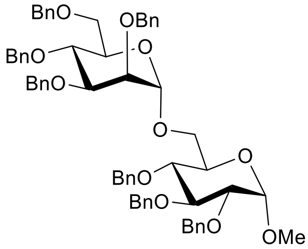
Methyl [2,3,4,6-*O*-benzyl-D-mannopyranosyl]-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (64c)



64c

According to **general procedure E**, donor **6** (44 mg, 0.064 mmol) and acceptor **61c** (20 mg, 0.054 mmol) was treated with $BF_3·Et_2O$ (2.7 µL, 0.022 mmol) in dry THF (2 mL) to give product **64c** (40 mg, 83%, α/β = 20:1) as a white solid. The spectroscopic data were in accordance with the literature.[41]

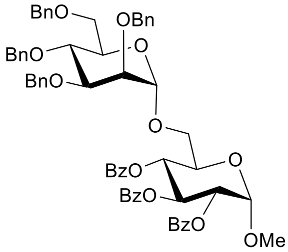
Methyl [2,3,4,6-*O*-benzyl-α-D-mannopyranosyl]-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (64d)



64d

According to **general procedure E**, donor **6** (44 mg, 0.065 mmol) and acceptor **61d** (25 mg, 0.054 mmol) was treated with $BF_3·Et_2O$ (2.7 µL, 0.022 mmol) in dry THF (2 mL) to give product **64d** (39 mg, 74%, α) as a white solid. The spectroscopic data were in accordance with the literature.[41]

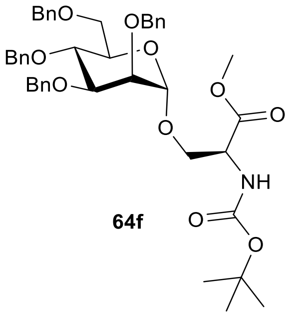
Methyl [2,3,4,6-*O*-benzyl-α-D-mannopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (64e)



64e

According to **general procedure E**, donor **6** (62 mg, 0.090 mmol) and acceptor **61e** (25 mg, 0.076 mmol) was treated with $BF_3·Et_2O$ (4.0 µL, 0.030 mmol) in dry THF (7 mL) to give product **64e** (59 mg, 91%, α) as a colorless oil. The spectroscopic data were in accordance with the literature.[42]

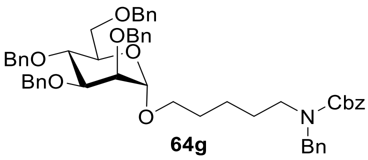
N-Boc-L-serine methyl ester 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (64f)



64f

According to **general procedure E**, donor **6** (48 mg, 0.071 mmol) and acceptor **61f** (13 mg, 0.059 mmol) was treated with $BF_3·Et_2O$ (3.0 µL, 0.024 mmol) in dry THF (2 mL) to give product **64f** (42 mg, 97%, α) as a colorless oil. $[\alpha]_D^{20}$= +14.5 (c = 0.7 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.25 (m, 18H), 7.21–7.15 (m, 2H), 5.38 (d, *J* = 8.9 Hz, 1H), 4.84 (d, *J* = 10.8 Hz, 1H), 4.80 (d, *J* = 2.0 Hz, 1H), 4.73 (d, *J* = 12.4 Hz, 1H), 4.68 (d, *J* = 1.8 Hz, 1H), 4.67–4.64 (m, 1H), 4.64–4.58 (m, 2H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 10.8 Hz, 1H), 4.49–4.45 (m, 1H), 3.99 (t, *J* = 9.3 Hz, 1H), 3.88–3.83 (m, 2H), 3.80 (dd, *J* = 9.2, 3.1 Hz, 1H), 3.75 (q, *J* = 5.6, 5.1 Hz, 1H), 3.72–3.67 (m, 3H), 3.67 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 155.4, 138.39, 13837, 138.3, 138.2, 128.39, 128.35, 128.3, 128.0, 127.80, 127.78, 127.65, 127.64, 127.5, 99.0 ($^1J_{C\text{-}H}$ = 172.0 Hz, α-Man), 79.7, 75.0, 74.8, 74.7, 73.4, 72.7, 72.4, 69.0, 68.7, 53.9, 52.4, 28.3; HRMS (ESI) calcd for $C_{43}H_{55}O_{10}N_2$ $[M+NH_4]^+$ 759.3851, found 759.3849.

Penthyl N-benzyl (Cbz) 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (64g)

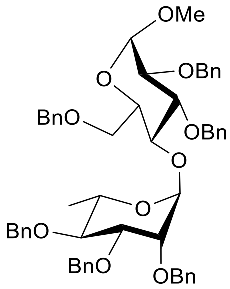


64g

According to **general procedure E**, donor **6** (62 mg, 0.090 mmol) and acceptor **61g** (25 mg, 0.076 mmol) was treated with $BF_3·Et_2O$ (4.0 µL, 0.030 mmol) in dry THF (7 mL) to give product **64g** (63 mg, 97%, β) as a yellow oil. $[\alpha]_D^{20}$ = +19.1 (c = 0.8 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.28 (m, 27H), 7.23–7.17 (m, 3H), 5.23–5.17 (m, 2H), 4.91 (d, *J* = 10.8 Hz, 1H), 4.87 (s, 1H), 4.80 (d, *J* = 12.5 Hz, 1H), 4.75 (d, *J* = 12.5 Hz, 1H), 4.69 (d, *J* = 12.1 Hz, 1H), 4.66 (s, 2H), 4.61–4.52 (m, 3H), 4.51 (d, *J* = 3.8 Hz, 1H), 4.02 (t, *J* = 9.4 Hz, 1H), 3.92 (dd, *J* = 9.8, 3.1 Hz, 1H), 3.84–3.73 (m, 4H), 3.69–3.60 (m, 1H), 3.38–3.17 (m, 3H), 1.61–1.47 (m, 4H), 1.30–1.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

156.7, 156.2, 138.6, 138.4, 137.9, 128.6, 128.5, 128.37, 128.36, 128.33, 128.16, 128.1, 128.0, 127.85, 127.81, 127.65, 127.61, 127.56, 127.5, 127.3, 127.2, 97.9 ($^1J_{C\text{–}H}$ = 171.5 Hz, α-Man), 80.3, 75.2, 75.0, 74.8, 73.4, 72.6, 72.2, 71.8, 69.3, 67.4, 67.2, 50.5, 50.2, 47.1, 46.1, 29.2, 27.9, 27.5, 23.4; HRMS (ESI) calcd for $C_{54}H_{63}O_8N_2$ $[M+NH_4]^+$ 867.4579, found 867.4586.

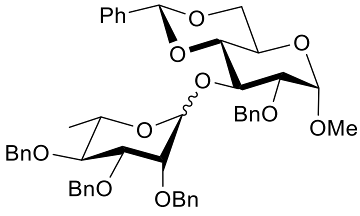
Methyl [2,3,4,6-*O*-benzyl-α-L-rhamnopyranosyl]-(1→4)-2,3,6-tri-benzyl-α-D-glucopyranoside (65a)



65a

According to **general procedure E**, donor **7** (38 mg, 0.065 mmol) and acceptor **61a** (25 mg, 0.054 mmol) was treated with $BF_3{\cdot}Et_2O$ (2.7 µL, 0.022 mmol) in dry THF (2 mL) to give product **65a** (19 mg, 33 %, α) as a colorless oil. $[\alpha]_D^{20}$= −11.2 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.40 (m, 2H), 7.39–7.28 (m, 28H), 5.08 (s, 1H), 5.00 (d, *J* = 10.3 Hz, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.78 (d, *J* = 12.1 Hz, 1H), 4.77 (d, *J* = 10.3 Hz, 1H), 4.66–4.57 (m, 6H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 12.1 Hz, 1H), 3.96 (dd, *J* = 9.6, 6.1 Hz, 1H), 3.87–3.78 (m, 3H), 3.71 (t, *J* = 2.4 Hz, 1H), 3.69–3.53 (m, 2H), 3.49–3.45 (m, 1H), 3.39 (s, 3H), 1.09 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.7, 138.6, 138.4, 138.1, 137.9, 128.5, 128.41, 128.38, 128.30, 128.17, 128.24, 128.17, 128.0, 127.9, 127.8, 127.7, 127.63, 127.56, 127.53, 127.49, 127.42, 127.39, 127.1, 98.2 ($^1J_{C\text{-}H}$ = 172.0 Hz, α-Rha), 97.9, 80.7, 80.5, 80.0, 79.8, 75.6, 75.2, 75.1, 75.0, 73.7, 73.5, 73.5, 72.5, 72.1, 70.0, 68.9, 68.7, 55.3, 17.9; HRMS (ESI) calcd for $C_{55}H_{58}O_{13}N$ $[M+NH_4]^+$ 940.3903, found 940.3912.

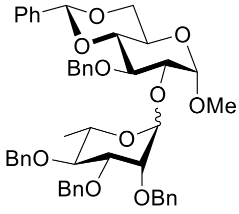
Methyl [2,3,4,6-*O*-benzyl-L-rhamnopyranosyl]-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (65b)



65b

According to **general procedure E**, donor **7** (37 mg, 0.065 mmol) and acceptor **61b** (20 mg, 0.054 mmol) was treated with $BF_3 \cdot Et_2O$ (2.7 μL, 0.022 mmol) in dry THF (7 mL) to give product **65b** (19 mg, 45%, α/β = 2:1) as a white solid. The spectroscopic data were in accordance with the literature.[43, 44]

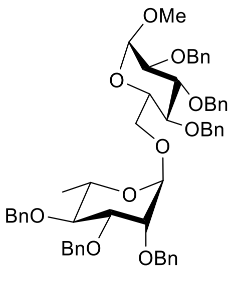
Methyl [2,3,4,6-*O*-benzyl-L-rhamnopyranosyl]-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (65c)



65c

According to **general procedure E**, donor **7** (47 mg, 0.08 mmol) and acceptor**61c** (25 mg, 0.067 mmol) was treated with $BF_3 \cdot Et_2O$ (3.0 μL, 0.027 mmol) in dry THF (3 mL) to give product **65c** (39 mg, 73%, α/β = 20:1) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52–7.47 (m, 2H), 7.43–7.25 (m, 23H), 5.59 (s, 1H), 5.12 (d, *J* = 1.7 Hz, 1H), 4.97 (d, *J* = 10.8 Hz, 1H), 4.87 (d, *J* = 11.7 Hz, 1H), 4.82 (d, *J* = 3.6 Hz, 1H), 4.69–4.61 (m, 4H), 4.57 (s, 2H), 4.35–4.29 (m, 1H), 3.97 (t, *J* = 9.3 Hz, 1H), 3.91 (dd, *J* = 9.1, 3.1 Hz, 1H), 3.88 (dd, *J* = 3.2, 1.7 Hz, 1H), 3.86–3.80 (m, 2H), 3.72–3.78 (m, 2H), 3.67 (d, *J* = 9.2 Hz, 1H), 3.64 (t, *J* = 9.2 Hz, 1H), 3.42 (s, 3H), 1.36 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.75, 138.70, 138.5, 138.3, 137.3, 129.0, 128.4, 128.35, 128.31, 128.25, 128.18, 127.7, 127.61, 127.58, 127.52, 127.50, 126.0, 101.3, 100.7, 99.9 ($^1J_{C–H}$ = 173 Hz, α-Rha), 82.3, 80.3, 80.0, 79.1, 78.0, 75.5, 75.4, 75.0, 72.7, 72.2, 69.1, 68.7, 62.2, 55.2, 18.1; HRMS (ESI) calcd for $C_{48}H_{52}O_{10}Na$ $[M+Na]^+$ 811.3453, found 811.3451.

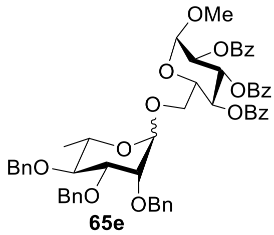
Methyl [2,3,4,6-*O*-benzyl-α-L-rhamnopyranosyl]-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (65d)



65d

According to **general procedure E**, donor **7** (39 mg, 0.067 mmol) and acceptor **61d** (26 mg, 0.056 mmol) was treated with $BF_3 \cdot Et_2O$ (2.8 μL, 0.020 mmol) in dry THF (2 mL) to give product **65d** (43 mg, 88%, α) as a yellow oil. The spectroscopic data were in accordance with the literature.[31]

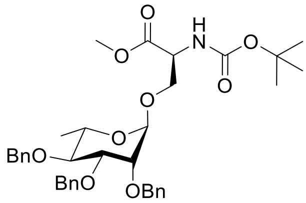
Methyl [2,3,4,6-*O*-benzyl-L-rhamopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (65e)



65e

According to **general procedure E**, donor **7** (34 mg, 0.060 mmol) and acceptor **61e** (25 mg, 0.050 mmol) was treated with $BF_3 \cdot Et_2O$ (2.5 µL, 0.020 mmol) in dry THF (2 mL) to give product **65e** (38 mg, 85%, α/β = 17:1) as a white solid. For the α isomer of product **65e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (m, 2H), 7.97–7.93 (m, 2H), 7.91–7.87 (m, 2H), 7.57–7.50 (m, 2H), 7.49–7.31 (m, 22H), 6.14 (t, *J* = 9.9 Hz, 1H), 5.56 (t, *J* = 9.9 Hz, 1H), 5.27 (dd, *J* = 10.2, 3.6 Hz, 1H), 5.18 (d, *J* = 3.6 Hz, 1H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.81–4.73 (m, 3H), 4.68–4.58 (s, 3H), 4.18–4.12 (m, 1H), 3.93–3.75 (m, 3H), 3.75–3.52 (m, 3H), 3.38 (s, 3H), 1.25 (d, *J* = 5.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 165.3, 133.5, 133.1, 130.0, 129.8, 129.7, 129.1, 128.91, 128.51, 128.45, 128.35, 128.0, 127.9, 127.7, 127.6, 127.5, 98.7, 96.9 ($^1J_{C–H}$ = 174.6 Hz, α-Rha), 79.5, 75.4, 74.8, 72.7, 72.0, 71.9, 70.5, 69.3, 68.8, 68.2, 65.8, 55.5, 17.9; HRMS (ESI) calcd for $C_{55}H_{58}O_{13}N$ $[M+NH_4]^+$ 940.3903 , found 940.3912; For the β isomer of product **65e:** ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.19 (t, *J* = 9.9 Hz, 1H), 5.65 (t, *J* = 9.9 Hz, 1H), 3.48 (s, 3H).

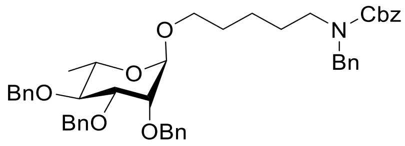
N-Boc-L-serine methyl ester 2,3,4,6-tetra-*O*-benzyl-α-L-rhamnopyranoside (65f)



65f

According to **general procedure E**, donor **7** (63 mg, 0.11 mmol) and acceptor **61f** (20 mg, 0.090 mmol) was treated with $BF_3 \cdot Et_2O$ (4.6 µL, 0.036 mmol) in dry THF (4 mL) to give product **65f** (54 mg, 93%, α) as a yellow oil. $[\alpha]_D^{20}$ = −21.4 (c = 1.0 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.26 (m, 15H), 5.24 (d, *J* = 8.8 Hz, 1H), 4.92 (d, *J* = 11.1 Hz, 1H), 4.75 (d, *J* = 12.4 Hz, 1H), 4.71–4.66 (m, 2H), 4.65–4.60 (m, 2H), 4.58 (d, *J* = 11.6 Hz, 1H), 4.51–4.44 (m, 1H), 4.03 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.71 (s, 3H), 3.70–3.65 (m, 2H), 3.62–3.44 (m, 3H), 1.47 (s, 9H), 1.30 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 155.4, 138.8, 138.5, 138.3, 128.4, 128.3, 127.94, 127.88, 127.85, 127.73, 127.67, 127.6, 98.2 ($^1J_{C–H}$ = 170 Hz, α-Rha), 80.2, 79.8, 75.2, 75.0, 72.9, 72.5, 68.6, 67.5, 53.7, 52.5, 28.4, 18.0; HRMS (ESI) calcd for $C_{36}H_{49}O_9N_2$ $[M+NH_4]^+$ 653.3433, found 653.3439.

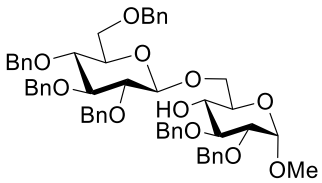
Penthyl N-benzyl (Cbz) 2,3,4,6-tetra-*O*-benzyl-α-L-rhamnopyranoside (65g)



65g

According to **general procedure E**, donor **7** (53 mg, 0.090 mmol) and acceptor **61g** (25 mg, 0.076 mmol) was treated with $BF_3 \cdot Et_2O$ (4.0 μL, 0.030 mmol) in dry THF (4 mL) to give product **65g** (53 mg, 93%, α) was obtained as a yellow oil. $[\alpha]^{20}_{D}$ = −6.3 (c = 1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.48–7.29 (m, 24H), 7.20 (d, *J* = 7.1 Hz, 1H), 5.24–5.17 (m, 2H), 4.97 (d, *J* = 10.7 Hz, 1H), 4.80 (d, *J* = 12.5 Hz, 1H), 4.77–4.72 (m, 2H), 4.69–4.65 (m, 3H), 4.55–4.49 (m, 2H), 3.87 (dd, *J* = 9.0, 2.9 Hz, 1H), 3.79 (s, 1H), 3.71–3.55 (m, 3H), 3.35–3.19 (m, 3H), 1.58–1.43 (m, 4H), 1.36 (d, *J* = 5.7 Hz, 3H), 1.30–1.18 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 156.2, 138.7, 138.5, 138.0, 128.6, 128.5, 128.40, 128.36, 128.2, 128.1, 128.0, 127.91, 127.86, 127.7, 127.62, 127.58, 127.5, 127.3, 98.0 ($^1J_{C–H}$ = 170 Hz, α-Rha), 80.6, 80.3, 75.5, 75.2, 72.9, 72.2, 68.0, 67.2, 50.6, 50.3, 47.2, 46.2, 29.2, 28.0, 27.6, 23.4, 18.1; HRMS (ESI) calcd for $C_{47}H_{57}O_7N_2$ $[M+NH_4]^+$ 761.4160, found 761.4154.

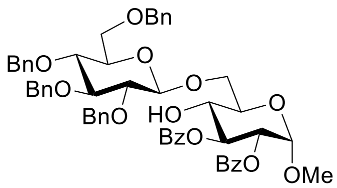
Methyl [2,3,4,6-*O*-benzyl-β-D-glucopyranosyl]-(1→6)-2,3-di-*O*-benzyl-4-hydroxyl-α-D-glucopyranoside (67a)



67a

According to **general procedure F**, donor **1** (50 mg, 0.069 mmol) and acceptor **66a** (15 mg, 0.058 mmol) was treated with $BF_3 \cdot Et_2O$ (3.0 μL, 0.023 mmol) in dry THF (2.5 mL) to give product **67a** (45 mg, 83%, β) as a yellow oil. The spectroscopic data were in accordance with the literature.[11]

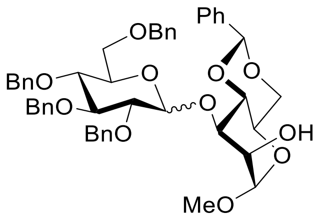
Methyl [2,3,4,6-*O*-benzyl-β-D-glucopyranosyl]-(1→6)-2,3-di-*O*-benzoyl-4-hydroxyl-α-D-glucopyranoside (67b)



67b

According to **general procedure F**, donor **1** (50 mg, 0.069 mmol) and acceptor **66b** (15 mg, 0.058 mmol) was treated with $BF_3{\cdot}Et_2O$ (3.0 µL, 0.023 mmol) in dry THF (2.5 mL) to give product **67b** (45 mg, 98%, β) as a yellow oil. The spectroscopic data were in accordance with the literature.[35]

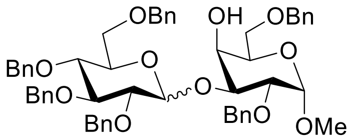
Methyl [2,3,4,6-*O*-benzyl-D-glucopyranosyl]-(1→3)-4,6-*O*-benzylidene-2-hydroxyl-α-D-mannopyranoside (67c)



67c

According to **general procedure F**, donor **1** (50 mg, 0.069 mmol) and acceptor **66c** (15 mg, 0.058 mmol) was treated with $BF_3{\cdot}Et_2O$ (3.0 µL, 0.023 mmol) in dry THF (2.5 mL) to give product **67c** (45 mg, 97%, β/α = 9:1) as a white solid. For the β isomer of product **67c:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.45 (m, 2H), 7.41–7.29 (m, 21H), 7.22–7.17 (m, 2H), 5.60 (s, 1H), 4.95–4.79 (m, 6H), 4.75–4.64 (m, 1H), 4.62–4.48 (m, 3H), 4.35–4.28 (m, 2H), 4.22–4.10 (m, 2H), 3.94–3.88 (m, 2H), 3.78–3.54 (m, 5H), 3.43 (s, 3H), 3.41–3.37 (m, 1H). 3.19 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ, 138.4, 138.1, 138.01, 137.99, 137.5, 129.0, 128.54, 128.48, 128.46, 128.44, 128.41, 128.2, 128.12, 128.07, 128.04, 128.01, 127.88, 127.8, 127.73, 127.71, 127.5, 126.4, 126.3, 102.0, 101.3, 100.1, 85.1, 81.7, 77.8, 77.3, 77.1, 75.6, 75.4, 75.2, 75.0, 73.58, 69.3, 68.95, 68.5, 63.5, 55.1; For the α isomer of product **67c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (s, 1H), 5.51 (d, *J* = 3.7 Hz, 1H), 5.02 (d, *J* = 10.9 Hz, 1H), 4.43 (d, *J* = 12.1 Hz, 1H), 4.03 (t, *J* = 9.3 Hz, 1H), 3.42 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.0, 137.8, 137.7, 137.4, 129.3, 128.3, 128.1,127.9, 127.64, 127.58, 102.3, 101.4, 97.1, 81.4, 79.0, 78.8, 77.5, 75.3, 73.63, 73.4, 71.3, 71.1, 70.7, 69.04, 68.7, 63.4, 60.5, 55.0; HRMS (ESI) calcd for $C_{48}H_{52}O_{11}Na$ $[M+Na]^+$ 827.3402, found 827.3401.

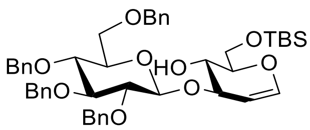
Methyl [2,3,4,6-*O*-benzyl-D-glucopyranosyl]-(1→3)-2,6-di-*O*-benzyl-4-hydroxyl-α-D-galactopyranoside (67d)



67d

According to **general procedure E**, donor **1** (50 mg, 0.069 mmol) and acceptor **66d** (15 mg, 0.058 mmol) was treated with $BF_3 \cdot Et_2O$ (3.0 µL, 0.023 mmol) in dry THF (2.5 mL) to give product **67d** (45 mg, 99%, β/α = 10:1) as a white solid. For the β isomer of product **67d:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.27 (m, 27H), 7.26–7.15 (m, 3H), 5.08 (d, *J* = 11.4 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.88–4.82 (m, 2H), 4.81–4.69 (m, 3H), 4.67–4.45 (m, 8H), 4.18–4.11 (m, 2H), 4.03–3.92 (m, 2H), 3.72–3.61 (m, 5H), 3.61–3.55 (m, 1H), 3.53–3.47 (m, 1H), 3.39 (s, 3H), 2.93 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.51, 138.46, 138.3, 138.2, 138.0, 137.9, 128.6, 128.46, 128.43, 128.39, 128.38, 128.34, 128.30, 128.2, 128.14, 128.08, 128.04, 127.97, 127.92, 127.88, 127.86, 127.84, 127.74, 127.70, 127.65, 127.63, 127.55, 103.4, 98.3, 84.7, 81.9, 78.0, 77.6, 75.9, 75.7, 75.0, 74.6, 74.4, 73.53, 73.45, 69.9, 69.2, 68.7, 68.4, 55.3; For the α isomer of product **67d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.36 (d, *J* = 12.1 Hz, 1H), 3.85 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.41 (s, 3H), 3.20–3.11 (m, 1H); HRMS (ESI) calcd for $C_{55}H_{60}O_{11}Na$ $[M+Na]^+$ 919.4028, found 919.4032.

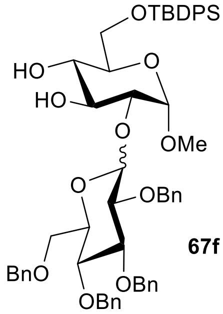
[2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl]-(1→3)-6-*O*-(tert-butyldimethylsilyl)-4-hydroxyl-D-glucal (67e)



67e

According to **general procedure F**, donor **1** (40 mg, 0.058 mmol) and acceptor **66e** (15 mg, 0.058 mmol) was treated with $BF_3 \cdot Et_2O$ (3.0 µL, 0.007 mmol) in dry THF (2.5 mL) to give product **67e** (35 mg, 78%, β) as a colorless syrup. $[\alpha]_D^{20}$ = +10.2 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.26 (m, 18H), 7.17–7.11 (m, 2H), 6.40 (dd, *J* = 6.0, 1.7 Hz, 1H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.93 (d, *J* = 10.9 Hz, 1H), 4.80 (d, *J* = 11.0 Hz, 1H), 4.78 (d, *J* = 11.0 Hz, 1H), 4.73 (d, *J* = 10.9 Hz, 1H), 4.67–4.62 (m, 2H), 4.57–4.45 (m, 4H), 4.24–4.18 (m, 1H), 4.02 (dd, *J* = 11.4, 1.8 Hz, 1H), 3.93 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.85–3.73 (m, 2H), 3.71–3.62 (m, 2H), 3.62–3.55 (m, 1H), 3.54–3.47 (m, 1H), 3.47–3.38 (m, 2H), 0.91 (s, 9H), 0.09 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 138.5, 138.4, 137.8, 137.6, 128.60, 128.56, 128.5, 128.3, 128.21, 128.19, 128.1, 128.04, 127.95, 127.9, 104.0, 100.4, 84.7, 83.0, 82.2, 78.8, 78.1, 76.0, 75.2, 75.1, 74.3, 73.7, 69.3, 67.7, 62.7, 26.2, 18.7, −5.0, −5.1; HRMS (ESI) calcd for $C_{46}H_{62}O_9NSi$ $[M+NH_4]^+$ 800.4188, found 800.4184.

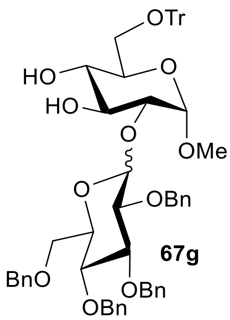
Methyl [2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl]-(1→2)-6-*O*-(*tert*-butyldiphenylsilyl)-3,4-di-hydroxyl-α-D-glucopyranoside (67f)



67f

According to **general procedure F**, donor **1** (40 mg, 0.058 mmol) and acceptor **66f** (25 mg, 0.058 mmol) was treated with $BF_3·Et_2O$ (3.0 μL, 0.023 mmol) in dry THF (3 mL) to give product **66f** (53 mg, 97%, β/α = 7:1) as a colorless syrup. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76–7.72 (m, 4H), 7.48–7.41 (m, 6H), 7.37–7.31 (m, 18H), 7.25–7.18 (m, 2H), 4.97 (d, *J* = 11.0 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.93 (d, *J* = 3.6 Hz, 1H), 4.89–4.86 (m, 2H), 4.85 (d, *J* = 6.3 Hz, 1H), 4.71 (d, *J* = 7.8 Hz, 1H), 4.64–4.57 (m, 2H), 4.55 (d, *J* = 12.1 Hz, 1H), 3.98–3.88 (m, 3H), 3.75–3.68 (m, 4H), 3.64–3.56 (m, 4H), 3.55–3.49 (m, 1H), 3.39 (s, 3H), 3.11 (s, 1H), 2.78 (s, 1H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 138.1, 137.98, 137.97, 135.7, 135.72, 135.69, 133.19, 133.16, 129.82, 129.80, 129.76, 128.6, 128.5, 128.4, 128.1, 128.02, 127.98, 127.92, 127.87, 127.81, 127.78, 127.76, 127.75, 127.7, 104.0, 99.3, 85.0, 82.1, 81.3, 77.9, 75.7, 75., 75.1, 74.7, 73.5, 72.6, 71.8, 70.5, 69.1, 64.4, 55.1, 26.9, 19.3; HRMS (ESI) calcd for $C_{57}H_{66}O_{11}SiNa$ $[M+Na]^+$ 977.4267, found 977.4260.

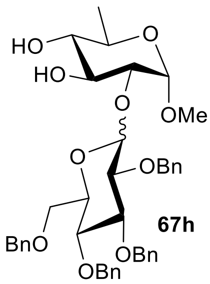
Methyl [2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl]-(1→2)-6-*O*-triphenylmethyl-3,4-di-hydroxyl-α-D-glucopyranoside (67g)



67g

According to **general procedure F**, donor **1** (40 mg, 0.058 mmol) and acceptor **66g** (25 mg, 0.058 mmol) was treated with $BF_3·Et_2O$ (3.0 μL, 0.023 mmol) in dry THF (3 mL) to give product **67g** (48 mg, 87%, β/α = 9:1) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.43 (m, 6H), 7.33–7.26 (m, 24H), 7.25–7.21 (m, 3H), 7.19–7.14 (m, 2H), 4.95–4.89 (m, 3H), 4.84 (d, *J* = 2.2 Hz, 1H), 4.83–4.79 (m, 2H), 4.66 (d, *J* = 7.6 Hz, 1H), 4.60–4.53 (m, 2H), 4.51 (d, *J* = 12.1 Hz, 1H), 3.91–3.86 (m, 1H), 3.74–3.63 (m, 4H), 3.60–3.53 (m, 4H), 3.52–3.45 (m, 1H), 3.39 (s, 3H), 3.37–3.31 (m, 2H), 2.96 (d, *J* = 2.5 Hz, 1H), 2.43 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 138.4, 138.1, 137.99, 137.97, 128.7, 128.6, 128.5, 128.4, 128.03, 127.95, 127.91, 127.88, 127.8, 127.7, 127.1, 104.1, 99.3, 86.9, 85.0, 82.0, 81.3, 77.9, 75.7, 75.2, 75.1, 74.7, 69.6, 69.1, 63.8, 55.2; HRMS (ESI) calcd for $C_{60}H_{66}O_{11}N$ $[M+NH_4]^+$ 976.4630, found 976.4633.

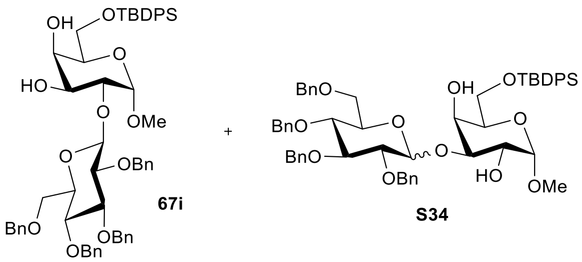
Methyl [2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl]-(1→2)-6-deoxy-3,4-di-hydroxyl-α-D-glucopyranoside (67h)



67h

According to **general procedure F**, donor **1** (40 mg, 0.058 mmol) and acceptor **66h** (11 mg, 0.058 mmol) was treated with $BF_3{\cdot}Et_2O$ (3.0 μL, 0.023 mmol) in dry THF (3 mL) to give product **67h** (42 mg, 93%, β/α = 17:1) as a colorless syrup. For the β isomer of product **67h**:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.30 (m, 18H), 7.24–7.18 (m, 2H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.93 (d, *J* = 11.1 Hz, 1H), 4.90–4.82 (m, 4H), 4.73 (d, *J* = 7.9 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.59 (d, *J* = 11.0 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 3.87 (t, *J* = 9.3 Hz, 1H), 3.75–3.64 (m, 4H), 3.63–3.56 (m, 3H), 3.54–3.48 (m, 1H), 3.39 (s, 3H), 3.24–3.15 (m, 1H), 2.54 (br, 1H), 1.80 (br, 1H), 1.31 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.2, 138.1, 138.0, 128.6, 128.54, 128.51, 128.1, 128.02, 128.00, 127.95, 127.93, 127.91, 127.84, 127.81, 103.7, 99.6, 85.1, 82.2, 81.5, 78.1, 75.9, 75.8, 75.3, 75.1, 74.8, 73.6, 72.5, 69.2, 66.8, 55.3, 17.7; HRMS (ESI) calcd for $C_{41}H_{52}O_{10}N$ $[M+NH_4]^+$ 718.3586, found 718.3586. For the α isomer of product **67h**:^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (t, *J* = 4.8 Hz, 1H), 3.43 (s, 3H).

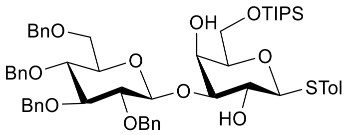
Methyl [2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl]-(1→2)-6-*O*-(tert-butyldiphenylsilyl)-3,4-di-hydroxyl-α-D-galactopyranoside (67i)



67i S34

According to **general procedure F**, donor **1** (58 mg, 0.069 mmol) and acceptor **66i** (25 mg, 0.058 mmol) was treated with $BF_3·Et_2O$ (3.0 μL, 0.023 mmol) in dry THF (3 mL) to give product **67i** and **S34** (49 mg, 90%, **67i**/**S34** = 7:1) as a colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71–7.66 (m, 4H), 7.44–7.37 (m, 6H), 7.35–7.28 (m, 18H), 7.20–7.15 (m, 2H), 4.96–4.88 (m, 3H), 4.87–4.82 (m, 2H), 4.82–4.78 (m, 1H), 4.61–4.58 (m, 1H), 4.58–4.55 (m, 2H), 4.54–4.52 (m, 1H), 4.14–4.08 (m, 1H), 4.02–3.96 (m, 1H), 3.93–3.90 (m, 1H), 3.89–3.86 (m, 1H), 3.85–3.80 (m, 2H), 3.70–3.63 (m, 3H), 3.63–3.58 (m, 2H), 3.49–3.43 (m, 1H), 3.33 (s, 3H), 2.94 (d, *J* = 3.7 Hz, 1H), 2.62 (d, *J* = 2.1 Hz, 1H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 138.10, 138.06, 138.0, 135.7, 135.6, 133.3, 133.1, 129.8, 128.6, 128.45, 128.41, 128.0, 127.93, 127.89, 127.84, 127.77, 127.73, 127.69, 127.67, 104.9, 99.7, 85.1, 82.0, 79.7, 77.9, 75.7, 75.2, 75.0, 74.9, 73.5, 69.5, 69.4, 69.0, 63.2, 55.3, 26.8, 19.2; ^{13}C NMR (100 MHz, $CDCl_3$) of **S34**: δ 104.1, 99.5; HRMS (ESI) calcd for $C_{57}H_{70}O_{11}SiN$ $[M+NH_4]^+$ 972.4713, found 972.4713.

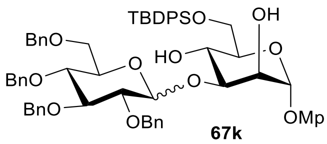
***p*–Methylphenyl-[2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl]-(1→3)-6-*O*-triisopropylsilyl-2,4-hydroxyl-1-thio-α-D-galactopyranoside (67j)**



67j

According to **general procedure F**, donor **1** (40 mg, 0.058 mmol) and acceptor **66j** (26 mg, 0.058 mmol) was treated with $BF_3·Et_2O$ (3.0 μL, 0.023 mmol) in dry THF (2.5 mL) to give product **67j** (41 mg, 74%, β) as a colorless syrup. $[\alpha]^{20}_{D}$ = +0.55 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.44 (m, 2H), 7.38–7.26 (m, 18H), 7.18–7.12 (m, 2H), 7.12–7.08 (m, 2H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.92 (d, *J* = 11.0 Hz, 1H), 4.82–4.78 (m, 2H), 4.73 (d, *J* = 10.9 Hz, 1H), 4.69 (d, *J* = 7.8 Hz, 1H), 4.57 (d, *J* = 12.2 Hz, 1H), 4.52 (d, *J* = 10.8 Hz, 1H), 4.50–4.45 (m, 2H), 4.18 (d, *J* = 3.1 Hz, 1H), 3.99 (dd, *J* = 10.0, 6.3 Hz, 1H), 3.92 (dd, *J* = 10.0, 5.4 Hz, 1H), 3.83 (t, *J* = 9.3 Hz, 1H), 3.70–3.58 (m, 5H), 3.56–3.48 (m, 2H), 3.47–3.41 (m, 1H), 2.83 (br, 1H), 2.61(br, 1H) 2.33 (s, 3H), 1.08–1.03 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.1, 138.00, 138.96, 137.9, 132.9, 129.7, 128.7, 128.5, 128.43, 128.39, 128.0, 127.9, 127.8, 127.74, 127.71, 103.7, 89.0, 84.7, 84.3, 81.7, 78.8, 77.5, 75.7, 75.1, 75.0, 74.8, 73.5, 68.7, 68.5, 68.1, 62.6, 21.2, 18.02, 18.00, 11.9; HRMS (ESI) calcd for $C_{56}H_{76}O_{10}SSiN$ [M+NH4]+ 982.4954, found: 982.4956.

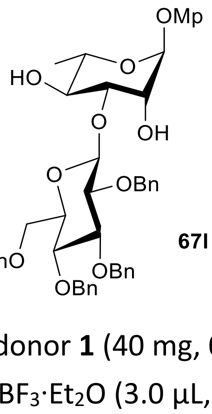
***p*–Methylphenyl-[2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl]-(1→3)-6-*O*-(tert-butyldiphenylsilyl)-2,4-di-hydroxyl-α-D-mannopyranoside (67k)**



67k

According to **general procedure F**, donor **1** (40 mg, 0.058 mmol) and acceptor **66k** (30 mg, 0.058 mmol) was treated with $BF_3 \cdot Et_2O$ (3.0 μL, 0.023 mmol) in dry THF (3 mL) to give product **67k** (48 mg, 80%, β/α = 7:1) as a colorless syrup. For the β isomer of product **67k**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.75–7.66 (m, 4H), 7.36–7.28 (m, 20H), 7.26–7.11 (m, 6H), 7.07–6.99 (m, 2H), 6.80–6.71 (m, 2H), 5.43 (d, *J* = 1.7 Hz, 1H), 4.97–4.90 (m, 2H), 4.88–4.78 (m, 3H), 4.59 (d, *J* = 7.9 Hz, 1H), 4.54–4.45 (m, 3H), 4.21–4.11 (m, 1H), 4.06–3.98 (m, 2H), 3.98–3.90 (m, 3H), 3.90–3.81 (m, 1H), 3.73 (s, 3H), 3.72–3.65 (m, 2H), 3.58–3.51 (m, 3H), 1.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 150.4, 138.4, 138.0, 137.8, 137.6, 135.9, 135.8, 133.9, 133.8, 129.6, 128.8, 128.7, 128.62, 128.59, 128.57, 128.5, 128.4, 128.3, 128.23, 128.20, 128.17, 128.12, 128.08, 128.04, 128.02, 127.93, 127.90, 127.70, 127.65, 127.6, 118.0, 114.7, 103.4, 98.6, 84.9, 83.5, 81.8, 77.9, 76.0, 75.5, 75.3, 74.7, 73.7, 73.4, 70.2, 68.9, 65.9, 63.6, 55.7, 26.9; **HRMS** (ESI) calcd for $C_{63}H_{74}O_{12}SiN$ [M+NH4]+ 1064.4975, found 1064.4967.

***p*-Methylphenyl-[2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl]-(1→3)-6-deoxy-di-2,4-hydroxyl-α-D-mannopyranoside (67l)**



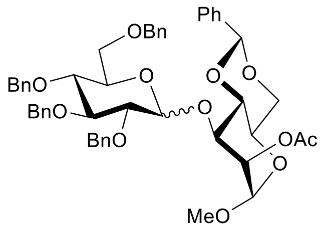
67l

According to **general procedure F**, donor **1** (40 mg, 0.058 mmol) and acceptor **66l** (16 mg, 0.058 mmol) was treated with $BF_3 \cdot Et_2O$ (3.0 μL, 0.023 mmol) in dry THF (3 mL) to give product **67l** (39 mg, 78%, β) as a white solid. $[\alpha]_D^{20}$ = −18.8 (c = 1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41–7.25 (m, 18H), 7.23–7.12 (m, 2H), 7.02–6.92 (m, 2H), 6.85–6.78 (m, 2H), 5.39 (d, *J* = 1.7 Hz, 1H), 4.94–4.89 (m, 1H), 4.89–4.80 (m, 4H), 4.70 (d, *J* = 7.8 Hz, 1H), 4.58–4.48 (m, 3H), 4.26–4.21 (m, 1H), 3.98 (dd, *J* = 9.2, 3.3 Hz, 1H), 3.83–3.75 (m, 4H), 3.73–3.67 (m, 2H), 3.67–3.58 (m, 3H), 3.58–3.50 (m, 2H), 2.95 (br, 1H), 2.48 (br, 1H), 1.24 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 150.3, 138.4, 138.0, 137.9, 128.7, 128.61, 128.60, 128.56, 128.3, 128.2, 128.1, 128.04, 127.98, 127.9, 117.7, 114.7, 103.5, 98.5, 85.1, 82.4, 82.0, 77.9, 75.9, 75.5, 75.2, 74.8, 73.7, 71.7, 70.1, 68.9, 68.3, 55.8, 17.8; HRMS (ESI) calcd for $C_{47}H_{52}O_{13}Na$ $[M+Na]^+$ 815.3402, found 815.3398.

5.6. General Procedure for acetylation of glycosylation products

General procedure G: To a solution of glycosylation products in dry pyridine was added Ac_2O and DMAP successively. After stirred at rt for 2 h, the mixture was concentrated under vacuum, and then purified by silica gel column chromatography (PE/EA = 4:1 ~ 2:1) to give acetylated products.

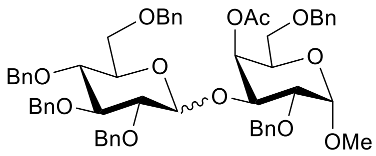
Methyl [2,3,4,6-*O*-benzyl-D-glucopyranosyl]-(1→3)-4,6-*O*-benzylidene-2-*O*-actyl-α-D-mannopyranoside (S35)



S35

According to **general procedure G**, **67c** (40 mg, 0.050 mmol) was treated with Ac_2O (24 µL, 0.25 mmol) and DMAP (3.0 mg, 0.024 mmol) in dry pyridine (2 mL) to give acetylated product **S35** (38 mg, 90%) as a white solid. For the β isomer of product **S35**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.48 (m, 2H), 7.39–7.29 (m, 18H), 7.27–7.14 (m, 5H), 5.62 (s, 1H), 5.39 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.89–4.72 (m, 5H), 4.61–4.47 (m, 5H), 4.32–4.27 (m, 1H), 4.24–4.12 (m, 1H), 3.95–3.85 (m, 2H), 3.75–3.59 (m, 3H), 3.59–3.52 (m, 1H), 3.51–3.46 (m, 1H), 3.41 (s, 3H), 3.39–3.35 (m, 1H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.27, 138.6, 138.5, 138.4, 138.23, 137.5, 129.1, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.5, 127.3, 127.2, 126.3, 102.1, 101.1, 99.5, 84.8, 81.9, 77.9, 77.6, 75.3, 75.1, 74.9, 74.3, 73.5, 72.5, 69.9, 68.8, 68.6, 63.8, 55.2, 21.0; For the α isomer of product **S35**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.43 (m, 2H), 6.99–6.97 (m, 2H), 5.54 (s, 1H), 5.41 (d, *J* = 4.1 Hz, 1H), 5.29 (dd, *J* = 3.6, 1.6 Hz, 1H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.43 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.42(s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.32, 163.21, 138.9, 138.20, 138.1, 137.3, 129.4, 126.4, 102.4, 99.6, 97.6, 81.2, 79.1, 78.8, 75.4, 74.7, 73.4, 72.1, 71.3, 70.8, 70.7, 63.7, 55.2, 21.1; HRMS (ESI) calcd for $C_{50}H_{58}O_{12}SiN$ $[M+NH_4]^+$ 864.3954, found 864.3962.

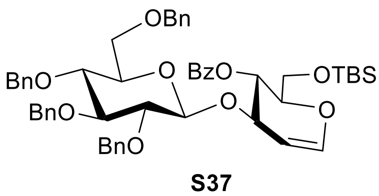
Methyl [2,3,4,6-*O*-benzyl-D-glucopyranosyl]-(1→3)-2,6-di-*O*-benzyl-4-*O*-actyl-α-D-galactopyranoside (S36)



S36

According to **general procedure G**, **67d** (48 mg, 0.054 mmol) was treated with Ac_2O (25 µL, 0.27 mmol) and DMAP (3.0 mg, 0.024 mmol) in dry pyridine (2 mL) to give acetylated product **S36** (44 mg, 87%) as a syrup. For the β isomer of product **S36**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.28 (m, 28H), 7.22–7.17 (m, 2H), 5.57–5.55 (m, 1H), 5.00 (d, *J* = 11.3 Hz, 1H), 4.96 (d, *J* = 11.1 Hz, 1H), 4.88 (d, *J* = 7.7 Hz, 1H), 4.85–4.81 (m, 2H), 4.79 (d, *J* = 11.3 Hz, 1H), 4.74 (d, *J* = 11.8 Hz, 1H), 4.70 (d, *J* = 12.2 Hz, 1H), 4.67 (d, *J* = 3.6 Hz, 1H), 4.62–4.55 (m, 3H), 4.51–4.45 (m, 2H), 4.35 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.12–4.08 (m, 1H), 3.92 (dd, *J* = 10.0, 3.7 Hz, 1H), 3.80–3.73 (m, 2H), 3.73–3.67 (m, 1H), 3.64 (t, *J* = 8.8 Hz, 1H), 3.55 (dd, *J* = 10.1, 5.0 Hz, 1H), 3.53–3.48 (m, 1H), 3.47–3.42 (m, 2H), 3.40 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 138.8, 138.7, 138.5, 138.25, 138.19, 137.9, 128.40, 128.35, 128.3, 128.23, 128.17, 128.1, 127.9, 127.83, 127.77, 127.73, 127.71, 127.64, 127.56, 127.5, 103.1, 98.4, 84.6, 82.7, 77.8, 75.5, 75.0, 74.8, 74.7, 73.61, 73.60, 73.3, 72.6, 71.6, 69.2, 68.6, 68.2, 55.4, 21.0; For the α isomer of product **S36**:^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (d, *J* = 3.3 Hz, 1H), 5.31 (d, *J* = 3.4 Hz, 1H), 1.84(s, 3H); HRMS (ESI) calcd for $C_{57}H_{62}O_{12}Na$ $[M+Na]^+$ 961.4133, found 961.4133.

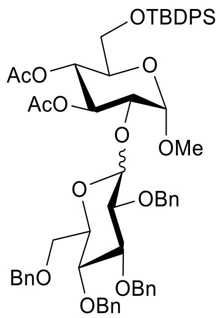
[2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl]-(1→3)-6-*O*-(tert-butyldimethylsilyl)-4-*O*-benzoyl-D-glucal (S37)



S37

To a solution of **67e** (30 mg, 0.037mmol) in dry pyridine (1 mL) was added BzCl (30 µL, 0.18 mmol) and DMAP (3.0 mg, 0.024 mmol) successively. After stirred at rt for 3 h, the mixture was concentrated under vacuum, and then purified by silica gel column chromatography to give benzoylated products **S37** (25 mg, 77%) as a colorless syrup. $[\alpha]_D^{20}$ = −20.5 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–8.00 (m, 2H), 7.56–7.50 (m, 1H), 7.43–7.36 (m, 2H), 7.36–7.27 (m, 10H), 7.27–7.18 (m, 8H), 7.17–7.10 (m, 2H), 6.51 (dd, J = 6.3, 1.1 Hz, 1H), 5.59 (t, J = 4.7 Hz, 1H), 4.96–4.91 (m, 2H), 4.89 (d, J = 10.9 Hz, 1H), 4.80–4.74 (m, 2H), 4.69 (d, J = 10.9 Hz, 1H), 4.56 (d, J = 7.8 Hz, 1H), 4.55–4.48 (m, 2H), 4.41 (d, J = 12.0 Hz, 1H), 4.38–4.33 (m, 1H), 4.32–4.26 (m, 1H), 4.00 (dd, J = 11.8, 7.6 Hz, 1H), 3.86 (dd, J = 11.8, 2.9 Hz, 1H), 3.66–3.54 (m, 4H), 3.47–3.42 (m, 2H), 0.86 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 144.9, 138.7, 138.41, 138.36, 138.2, 133.1, 130.0, 129.8, 128.41, 128.39, 128.3, 128.2, 128.0, 127.8, 127.7, 127.64, 127.59, 127.5, 102.7, 98.6, 84.7, 82.2, 77.79, 77.77, 75.7, 75.00, 74.98, 74.96, 73.5, 71.6, 69.6, 69.0, 62.0, 25.9, 18.4, –5.2, –5.3; HRMS (ESI) calcd for $C_{53}H_{62}O_{10}SiNa$ $[M+Na]^+$ 909.4004, found 909.3996.

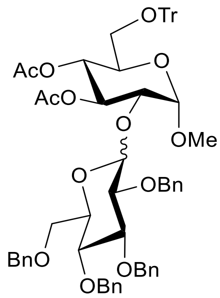
Methyl [2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl]-(1→2)-6-*O*-(tert-butyldiphenylsilyl)-3,4-di-*O*-actyl-α-D-glucopyranoside (S38)



S38

According to **general procedure G**, **67f** (60 mg, 0.063 mmol) was treated with Ac_2O (40 μL, 0.44 mmol) and DMAP (3.0 mg, 0.024 mmol) in dry pyridine (2 mL) to give acetylated product **S38** (58 mg, 87%) was obtained as a colorless syrup. For the β isomer of product **S38**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.61 (m, 4H), 7.46–7.27 (m, 16H), 7.27–7.19 (m, 8H), 7.19–7.07 (m, 2H), 5.51 (t, J = 9.7 Hz, 1H), 5.05 (d, J = 3.6 Hz, 1H), 5.03–4.94 (m, 1H), 4.94–4.84 (m, 2H), 4.84–4.80 (m, 1H), 4.80–4.73 (m, 2H), 4.69–4.58 (m, 2H), 4.58–4.53 (m, 1H), 4.53–4.50 (m, 1H), 4.49 (d, J = 7.7 Hz, 1H), 3.95–3.85 (m, 1H), 3.85–3.77 (m, 1H), 3.71–3.67 (m, 3H), 3.63–3.52 (m, 2H), 3.52–3.46 (m, 2H), 3.44 (s, 3H), 1.84 (s, 3H), 1.71 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 169.9, 138.6, 138.1, 135.79, 135.78, 135.7, 133.3, 133.2, 129.84, 129.81, 128.6, 128.53, 128.50, 128.4, 128.3, 128.12, 128.09, 127.92, 127.89, 127.85, 127.83, 127.82, 127.79, 127.77, 127.7, 127.55, 127.47, 105.1, 99.2, 84.8, 81.7, 77.9, 77.7, 75.8, 75.1, 74.8, 74.6, 73.6, 72.1, 69.8, 69.6, 69.1, 63.0, 55.3, 26.9, 20.7, 19.3; HRMS (ESI) calcd for $C_{61}H_{74}O_{13}SiN$ $[M+NH_4]^+$ 1056.4924, found 1056.4925.

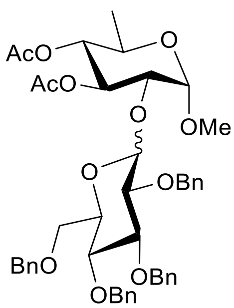
Methyl [2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl]-(1→2)-6-*O*-triphenylmethyl-3,4-di-*O*-actyl-α-D-glucopyranoside (S39)



S39

According to **general procedure G**, **67g** (20 mg, 0.021 mmol) was treated with Ac_2O (40 µL, 0.44 mmol) and DMAP (3.0 mg, 0.024 mmol) in dry pyridine (2 mL) to give acetylated product **S39** (18 mg, 82%) as a white solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.49–7.42 (m, 6H), 7.38–7.25 (m, 20H), 7.25–7.12 (m, 9H), 5.48 (t, *J* = 9.6 Hz, 1H), 5.09 (d, *J* = 3.5 Hz, 1H), 5.01 (t, *J* = 9.7 Hz, 1H), 4.90 (d, *J* = 10.9 Hz, 1H), 4.87–4.73 (m, 3H), 4.69–4.58 (m, 2H), 4.58–4.44 (m, 3H), 3.99–3.90 (m, 1H), 3.85 (dd, *J* = 10.1, 3.7 Hz, 1H), 3.77–3.64 (m, 2H), 3.64–3.55 (m, 2H), 3.55–3.48 (m, 2H), 3.47 (s, 3H), 3.21 (dd, *J* = 10.3, 2.2 Hz, 1H), 3.10 (dd, *J* = 10.3, 5.2 Hz, 1H), 1.70 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.7, 143.8, 138.7, 138.19, 138.17, 128.9, 128.6, 128.55, 128.50, 128.44, 128.35, 128.3, 128.13, 128.09, 128.06, 127.92, 127.90, 127.87, 127.8, 127.7, 127.6, 127.5, 127.1, 105.1, 99.3, 86.7, 84.8, 81.8, 78.0, 77.8, 77.4, 75.8, 75.1, 74.9, 74.6, 73.6, 72.1, 69.8, 69.2, 68.5, 62.4, 55.4, 20.74, 20.65; HRMS (ESI) calcd for $C_{64}H_{66}O_{13}SiNa$ $[M+Na]^+$ 1065.4396, found 1065.4388.

Methyl [2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl]-(1→2)-6-deoxy-3,4-di-*O*-actyl-α-D-glucopyranoside (S40)

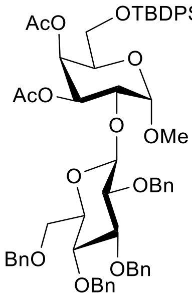


S40

According to **general procedure G**, **67h** (20 mg, 0.028 mmol) was treated with Ac_2O (30 µL, 0.33 mmol) and DMAP (3.0 mg, 0.024 mmol) in dry pyridine (2 mL) to give acetylated product **S40** (19 mg, 87%) as a colorless syrup. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.26 (m, 13H), 7.26–7.22 (m, 5H), 7.18–7.13 (m, 2H), 5.49 (t, *J* = 9.7 Hz, 1H), 4.97 (d, *J* = 3.5 Hz, 1H), 4.89 (d, *J* = 10.9 Hz, 1H), 4.86–4.76 (m, 3H), 4.70 (d, *J* = 9.6 Hz, 1H), 4.68–4.62 (m, 1H), 4.58 (d, *J* = 12.1 Hz, 1H), 4.53 (d, *J* = 7.3 Hz, 1H), 4.51–4.44 (m, 2H), 3.94–3.87 (m, 1H), 3.79 (dd, *J* = 10.1, 3.6 Hz, 1H), 3.70–3.65 (m, 2H), 3.64–3.54 (m, 2H), 3.51–3.42 (m, 2H), 3.41 (s, 3H), 2.01 (s, 3H), 1.71 (s, 3H), 1.18 (d, *J* = 6.2 Hz, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 170.4, 170.2, 155.1, 150.1, 138.6, 138.5, 138.3, 138.1, 128.4, 128.4, 128.3, 128.3, 128.0, 128.0, 127.8, 127.7, 127.5, 127.5, 127.5, 117.8, 114.6, 104.5, 96.4, 84.6, 81.7, 77.7, 75.6, 75.1, 75.0, 74.5, 74.5, 73.5, 72.6, 72.3, 68.8, 67.2, 55.7, 21.1, 20.8, 17.6; HRMS (ESI) calcd for $C_{45}H_{52}O_{12}Na$ $[M+Na]^+$ 807.3351, found 807.3344.

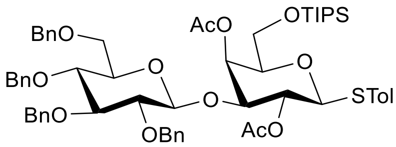
Methyl [2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl]-(1→2)-6-*O*-(tert-butyldiphenylsilyl)-3,4-di-*O*-actyl-α-D-galactopyranoside (S41)



S41

According to **general procedure G**, **67i** (45 mg, 0.063 mmol) was treated with Ac_2O (30 μL, 0.33 mmol) and DMAP (3.0 mg, 0.024 mmol) in dry pyridine (2 mL) to give acetylated product **S41** (38 mg, 78%) as a colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69–7.59 (m, 4H), 7.48–7.31 (m, 8H), 7.30–7.19 (m, 16H), 7.19–7.12 (m, 2H), 5.56 (d, *J* = 3.5 Hz, 1H), 5.40 (dd, *J* = 10.7, 3.4 Hz, 1H), 5.07 (d, *J* = 3.5 Hz, 1H), 4.93–4.85 (m, 2H), 4.83–4.75 (m, 2H), 4.75–4.64 (m, 1H), 4.59–4.51 (m, 2H), 4.51–4.42 (m, 2H), 4.08 (t, *J* = 6.8 Hz, 1H), 3.98 (dd, *J* = 10.6, 3.6 Hz, 1H), 3.74–3.42 (m, 8H), 3.38 (s, 3H), 1.99 (s, 3H), 1.66 (s, 3H), 1.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.1, 138.53, 138.52, 138.1, 138.0, 135.7, 135.6, 133.1, 133.0, 129.84, 129.80, 128.44, 128.41, 128.34, 128.30, 128.1, 128.03, 127.97, 127.84, 127.83, 127.79, 127.78, 127.74, 127.73, 127.59, 127.56, 127.51, 127.47, 105.3, 99.8, 84.6, 81.6, 77.6, 75.8, 75.7, 75.0, 74.7, 74.3, 73.5, 69.21, 69.16, 68.6, 68.4, 61.8, 55.5, 26.7, 20.7, 20.5, 19.1; HRMS (ESI) calcd for $C_{61}H_{70}O_{13}SiNa$ $[M+Na]^+$ 1061.4478, found 1061.4478.

***p*–Methylphenyl-[2,3,4,6-*O*-benzyl-β-D-glucopyranosyl]-(1→3)-6-*O*-triisopropylsilyl-2, 4-*O*-actyl-1-thio-α-D-galactopyranoside (S42)**

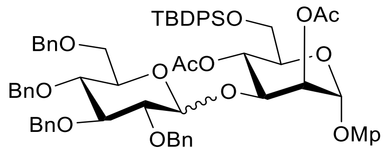


S42

According to general procedure G, **67g** (60 mg, 0.028 mmol) was treated with Ac_2O (30 μL, 0.33 mmol) and DMAP (3.0 mg, 0.024 mmol) in dry pyridine (2 mL) to give acetylated product **S** (54 mg, 83%) as a colorless syrup. $[\alpha]_D^{20}$ = +38.7 (c = 1.0 in $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.37 (m, 2H), 7.37–7.29 (m, 6H), 7.29–7.20 (m, 12H), 7.18–7.12 (m, 2H), 7.11–7.04 (m, 2H), 5.57 (d, *J* = 3.3 Hz, 1H), 5.38 (t, *J* = 9.9 Hz, 1H), 4.86 (d, *J* = 11.1 Hz, 1H), 4.80–4.71 (m, 3H), 4.65–4.59 (m, 2H), 4.58–4.49 (m, 4H), 3.98 (dd, *J* = 9.8, 3.4 Hz, 1H), 3.79–3.70 (m, 3H), 3.70–3.62 (m, 2H), 3.60–3.49 (m, 2H), 3.48–3.41 (m, 1H), 3.39–3.32 (m, 1H), 2.33 (s, 3H), 2.07 (s, 3H), 1.96 (s, 3H), 1.08–1.00 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 138.7, 138.5, 138.4, 138.1, 137.6, 131.8, 130.8, 129.7, 128.52, 128.50, 128.41, 128.37, 128.3, 128.2, 127.9, 127.68, 127.67, 127.64, 127.580, 104.1, 88.0, 84.6, 82.0, 79.1, 77.9, 77.5, 75.6, 75.3, 75.2, 74.7, 73.5, 70.5, 69.7, 69.3, 62.7, 21.3, 21.1, 21.0, 18.1, 11.9; HRMS (ESI) calcd for $C_{60}H_{80}O_{12}SiN$ $[M+NH_4]^+$ 1066.5165, found 1066.5164.

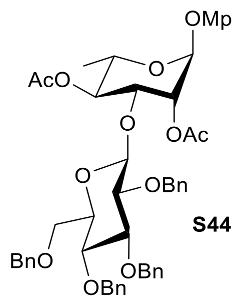
_p_–Methylphenyl-[2,3,4,6-tetra-_O_-benzyl-D-glucopyranosyl]-(1→3)-6-_O_-(tert-butyldiphenylsilyl)-2,4-di-_O_-actyl-α-D-mannopyranoside (S43)



S43

According to **general procedure G**, **67k** (20 mg, 0.028 mmol) was treated with Ac_2O (40 μL, 0.44 mmol) and DMAP (3.0 mg, 0.024 mmol) in dry pyridine (2 mL) to give acetylated product **S43** (31 mg, 74%) as a colorless syrup. For the β isomer of product **S43**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71–7.61 (m, 4H), 7.47–7.08 (m, 26H), 7.08–6.95 (m, 2H), 6.84–6.68 (m, 2H), 5.52–5.34 (m, 3H), 5.01–4.62 (m, 5H), 4.65–4.36 (m, 5H), 4.05–3.95 (m, 1H), 3.86–3.61 (m, 9H), 3.55–3.28 (m, 2H), 1.91 (s, 3H), 1.79 (s, 3H), 1.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 169.8, 155.3, 150.2, 138.62, 138.59, 138.2, 138.1, 135.8, 135.6, 133.4, 133.3, 129.64, 129.61, 128.4, 128.3, 127.95, 127.91, 127.8, 127.7, 127.65, 127.61, 127.57, 127.5, 127.4, 118.3, 114.6, 100.1, 96.6, 84.5, 81.9, 77.7, 75.6, 75.0, 74.9, 74.2, 73.4, 72.4, 72.2, 68.9, 68.8, 66.6, 63.0, 55.7, 26.7, 20.8, 20.6, 19.3. HRMS (ESI) calcd for $C_{67}H_{78}O_{14}SiN$ $[M+NH_4]^+$ 1148.5186, found 1148.5183.

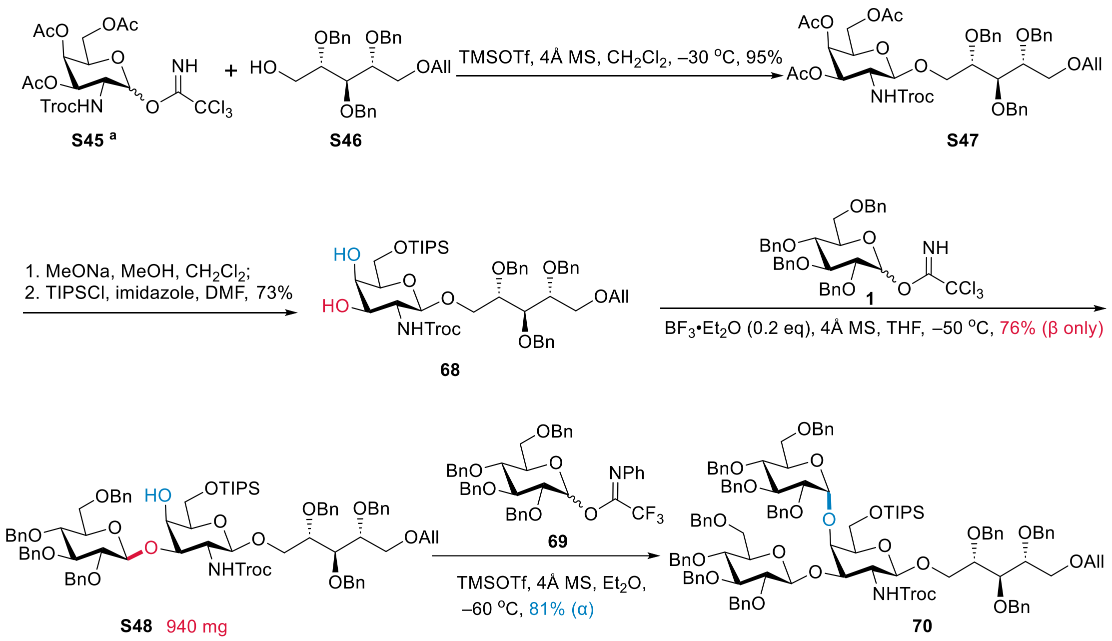
_p_–Methylphenyl-[2,3,4,6-tetra-_O_-benzyl-β-D-glucopyranosyl]-(1→3)-6-deoxy-2,4-di-_O_-actyl-α-D-mannopyranoside (S44)



S44

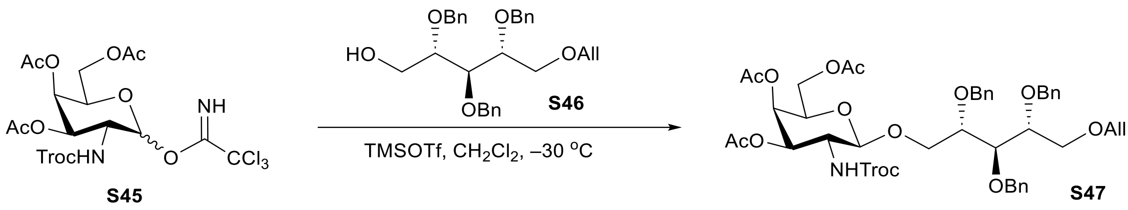
According to **general procedure G**, **67l** (20 mg, 0.025 mmol) was treated with Ac_2O (40 μL, 0.44 mmol) and DMAP (3.0 mg, 0.024 mmol) in dry pyridine (3 mL) to give acetylated product **S44** (20 mg, 91%) as a white solid. $[\alpha]^{20}_{D}$ = −6.1 (c = 1.0 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.39–7.32 (m, 4H), 7.31–7.25 (m, 11H), 7.24–7.20 (m, 3H), 7.20–7.13 (m, 2H), 6.97–6.90 (m, 2H), 6.83–6.76 (m, 2H), 5.46 (dd, *J* = 3.5, 1.9 Hz, 1H), 5.42 (d, *J* = 1.8 Hz, 1H), 5.27 (t, *J* = 9.9 Hz, 1H), 4.91–4.82 (m, 2H), 4.79 (d, *J* = 10.8 Hz, 1H), 4.77 (d, *J* = 11.0 Hz, 1H), 4.65 (d, *J* = 11.5 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 4.60–4.51 (m, 3H), 4.39 (dd, *J* = 10.0, 3.5 Hz, 1H), 4.01–3.88 (m, 1H), 3.76 (s, 3H), 3.73–3.69 (m, 2H), 3.64–3.58 (m, 2H), 3.53–3.38 (m, 2H), 2.14 (s, 3H), 1.86 (s, 3H), 1.18 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 170.2, 155.1, 150.1, 138.6, 138.5, 138.3, 138.1, 128.42, 128.38, 128.31, 128.26, 128.01, 127.96, 127.8, 127.7, 127.54, 127.52, 127.51, 117.8, 114.6, 104.5, 96.4, 84.6, 81.7, 77.7, 75.6, 75.1, 75.0, 74.53, 74.49, 73.5, 72.6, 72.3, 68.8, 67.2, 55.7, 21.1, 20.8, 17.6; HRMS (ESI) calcd for $C_{51}H_{56}O_{13}Na$ $[M+Na]^+$ 899.3613, found 899.3610.

5.7. Gram scale synthesis of protected oligosaccharide antigen 70 related to *Enterococcus faecalis*



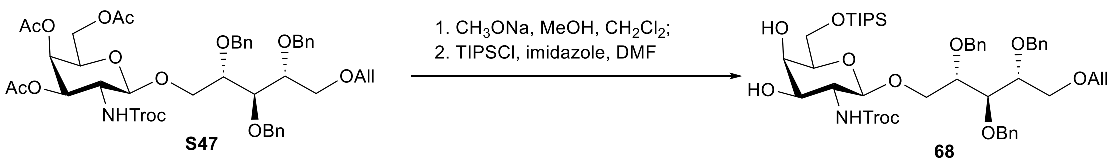
[a]Although glycosylation with 2-azido galactose and $BF_3\cdot Et_2O$/THF is advisable, we cannot obtain 2-azido galactose at a fair price or from compliant reagents. Hence, we prepared **S45** bearing the neighboring participating Troc, and adopted the conventional glycosylation conditions of TMSOTf in CH_2Cl_2.

[(3,4,6-Tri-*O*-acetyl-2-deoxy–[(2,2,2-trichloroethoxy)carbonyl]amino-β-D-galactopyranosyl)]-(1→1)-2,3,4-tri-*O*-benzyl-5-allyl-D-ribitol (S47)



To a solution of **S45**[45] (1.3 g, 2.0 mmol) and **S46**[46] (740 mg, 1.6 mmol) in dry CH_2Cl_2 (20 mL) was added freshly activated 4Å molecular sieves (0.5 g/mmol), the reaction was cooled to –30 ℃ under N_2, TMSOTf (30 μL, 0.16 mmol) was added. After kept stirring for 1.5 h, the mixture was quenched with Et_3N, which was filtered and concentrated under vacuum. The residue was purified by column chromatograph (PE/EA = 3:1) to give product **S47** (1.45 g, 95%) as a colorless syrup. $[\alpha]_D^{20}$ = −19.6 (c =2.0 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.29 (m, 15H), 6.03–5.84 (m, 1H), 5.35–5.26 (m, 2H), 5.24–5.16 (m, 1H), 5.08 (d, *J* = 9.1 Hz, 1H), 4.87–4.74 (m, 3H), 4.71–4.60 (m, 5H), 4.49–4.29 (m, 2H), 4.21–4.05 (m, 3H), 4.04–3.99 (m, 2H), 3.99–3.80 (m, 5H), 3.80–3.60 (m, 3H), 2.14 (s, 3H), 2.06 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.3, 154.2, 138.6, 138.34, 138.31, 134.8, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 117.1, 101.3, 95.6, 78.6, 78.5, 78.0, 74.3, 74.0, 72.5, 72.4, 72.3, 70.5, 70.0, 68.8, 66.6, 61.3, 52.7, 20.7, 20.6; HRMS (ESI) $C_{44}H_{56}Cl_3N_2O_{14}$ $[M+NH_4]^+$ 941.2792, found 941.2791.

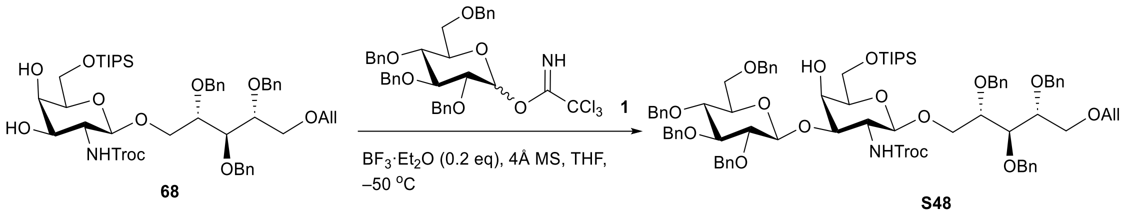
[6-*O*-Triisopropylsilyl-3,4-di-hydroxyl-2-deoxy-2-[(2,2,2-trichloroethoxy)carbonyl]amino-β-D-galactopyranosyl)]-(1→1)-2,3,4-tri-*O*-benzyl-5-allyl-D-ribitol (68)



To a solution of **S47** (1.1 g, 1.2 mmol) in CH_2Cl_2 (10 mL) and MeOH (10 mL) was added CH_3ONa (13 mg, 0.24 mmol). After kept stirring for 5 h, the mixture was neutralized by cation exchange resin (H^+), which was filtered and concentrated under vacuum to obtain crude intermediate product. The intermediate product is dissolved in DMF (20 mL), imidazole (244 mg, 3.6 mmol) and TIPSCl (510 μL, 2.4 mmol) were added into this solution successively. After kept stirring for 10 h, diluted by EA, washed by water (20 mL X 3) and brine. The organic phase was dried with anhydrous Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatograph on silica gel to give product **68** (0.84 g, 76%) as a colorless syrup. $[\alpha]_D^{20}$ = –13.9 (c = 2.0 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.29 (m, 15H), 6.00–5.84 (m, 2H), 5.34–5.24 (m, 1H), 5.22–5.17 (m, 1H), 4.91–4.77 (m, 2H), 4.72 (d, *J* = 11.1 Hz, 1H), 4.69–4.60 (m, 4H), 4.45

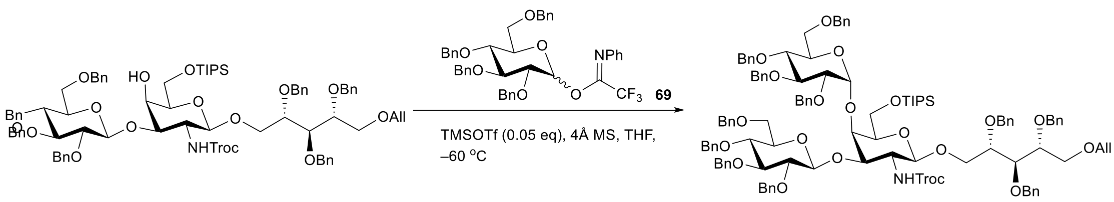
(d, J = 12.1 Hz, 1H), 4.15–4.04 (m, 2H), 4.04–3.97 (m, 4H), 3.97–3.83 (m, 4H), 3.81–3.68 (m, 3H), 3.61–3.53 (m, 1H), 3.35–3.23 (m, 2H), 2.90 (br, 1H), 1.16–1.02 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7, 138.4, 138.1, 134.8, 128.46, 128.49, 128.43, 128.39, 128.2, 128.0, 127.87, 127.85, 127.8, 116.9, 101.2, 95.4, 78.74, 78.67, 77.7, 74.7, 74.2, 72.8, 72.4, 72.3, 70.1, 68.4, 67.6, 62.5, 55.9, 18.0, 17.9, 11.9; HRMS (ESI) calcd for $C_{47}H_{67}Cl_3NO_{11}Si$ $[M+H]^+$ 954.3543, found 954.3537.

[(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→3)-[(2,3,4-tri-*O*-benzyl-6-*O*-acetyl-α-D-glucopyranosyl)-(1→4)]-6-*O*-(triisopropylsilyl)-2-deoxy-2-[(2,2,2-trichloroethoxy)carbonyl]amino-β-D-galactopyranosyl]-(1→1)-2,3,4-tri-*O*-benzyl-5-allyl-D-ribitol (S48)



To a solution of **68** (800 mg, 0.84 mmol) and **1** (690 mg,1.0 mmol) in dry THF (40 mL) was added freshly activated 4Å molecular sieves (0.5 g/mmol), the reaction was cooled to –50 °C under N_2, $BF_3{\cdot}Et_2O$ (21 µL, 0.17 mmol) was added. After kept stirring for 12 h, the mixture was quenched with Et_3N, which was filtered and concentrated under vacuum. The residue was purified by column chromatograph on silica gel to give the product **S48** (0.94 g, 76%, β only) as a colorless syrup. $[\alpha]^{20}_{D}$ = +5.4 (c = 2.0 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.29 (m, 29H), 7.28–7.22 (m, 4H), 7.21–7.15 (m, 2H), 6.01–5.78 (m, 2H), 5.34–5.24 (m, 1H), 5.24–5.15 (m, 1H), 4.97–4.88 (m, 2H), 4.87–4.77 (m, 3H), 4.76–4.58 (m, 8H), 4.57–4.46 (m, 3H), 4.40–4.05 (m, 5H), 4.05–3.91 (m, 4H), 3.90–3.77 (m, 4H), 3.76–3.60 (m, 6H), 3.59–3.42 (m, 4H), 2.97 (br, 1H) 1.16–1.04 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 138.9, 138.62, 138.59, 138.4, 138.0, 137.9, 135.0, 128.5, 128.38, 128.4, 128.35, 128.30, 128.27, 128.10, 128.05, 128.0, 127.92, 127.89, 127.83, 127.76, 127.74, 127.70, 127.62, 127.59, 127.54, 127.49, 127.4, 116.8, 103.7, 100.3, 95.5, 84.5, 81.7, 78.8, 78.7, 78.2, 75.7, 75.1, 74.8, 74.5, 74.0, 73.8, 73.6, 72.4, 72.22, 72.21, 70.3, 68.7, 68.5, 62.0, 54.4, 53.4, 18.03, 18.01, 11.9; HRMS (ESI) calcd for $C_{81}H_{100}Cl_3NO_{16}SiNa$ $[M+Na]^+$ 1498.5769, found 1498.5775.

[(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→3)-[(2,3,4-tri-*O*-benzyl-6-*O*-acetyl-α-D-glucopyranosyl)-(1→4)]-6-*O*-(triisopropylsilyl)-2-deoxy-2-[(2,2,2-trichloroethoxy)carbonyl]amino-β-D-galactopyranosyl]-(1→1)-2,3,4-tri-*O*-benzyl-5-allyl-D-ribitol (70)

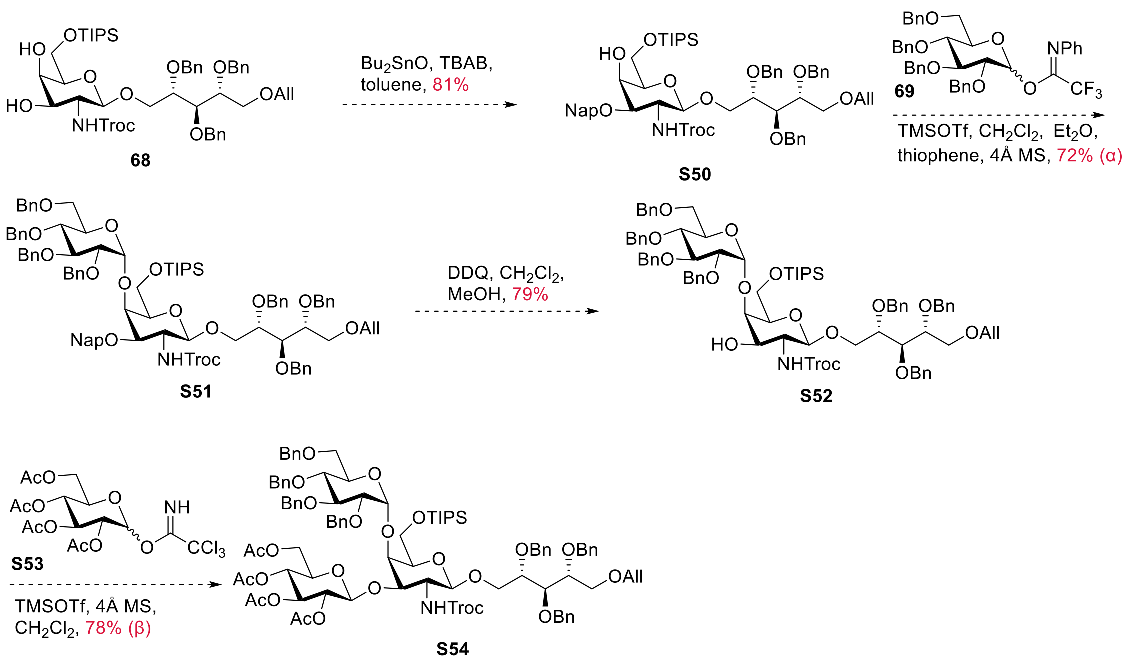


S48 70

To a solution of **S48** (50 mg, 0.034 mmol) and **69**[47] (37 mg, 0.051 mmol) in dry Et_2O (4.0 mL) was added freshly activated 4Å molecular sieves (0.5 g/mmol), the reaction was cooled to –60 °C under N_2, TMSOTf (17 μL, 2.1 μmol, 20 μL diluted in 1.0 mL anhydrous CH_2Cl_2) was added. After kept stirring for 10 h, the mixture was quenched with Et_3N, which was filtered and concentrated under vacuum. The residue was purified by column chromatograph on silica gel to give product **70** (55 mg, 81%) as a colorless syrup. $[\alpha]_D^{20}$ = +29.7 (c = 1.5 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.25 (m, 27H), 7.24–7.07 (m, 28H), 5.92–5.82 (m, 1H), 5.43 (d, *J* = 3.2 Hz, 1H), 5.26–5.21 (m, 1H), 5.13 (dd, *J* = 10.4, 1.7 Hz, 1H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.86–4.78 (m, 4H), 4.78–4.71 (m, 2H), 4.69–4.56 (m, 10H), 4.54–4.47 (m, 4H), 4.47–4.38 (m, 4H), 4.31 (d, *J* = 3.0 Hz, 1H), 4.25–4.17 (m, 2H), 4.15–4.08 (m, 2H), 4.02 (t, *J* = 9.3 Hz, 1H), 3.96–3.91 (m, 4H), 3.88 (br, 1H), 3.85–3.72 (m, 5H), 3.71–3.60 (m, 5H), 3.60–3.43 (m, 5H), 3.43–3.25 (m, 3H), 1.01–0.93 (m, 21H); ^{13}C N MR (100 MHz, $CDCl_3$) δ 154.0, 139.4, 139.1, 139.0, 138.83, 138.75, 138.73, 138.68, 138.4, 138.3, 138.2, 135.1, 128.55, 128.52, 128.4, 128.41, 128.36, 128.32, 128.28, 128.1, 128.03, 128.01, 127.95, 127.91, 127.87, 127.74, 127.70, 127.64, 127.57, 127.5, 127.3, 116.8, 104.9, 100.1, 97.1, 95.8, 84.5, 83.1, 82.2, 80.8, 78.8, 78.3, 77.9, 77.8, 77.4, 76.3, 75.7, 75.6, 75.1, 75.0, 74.9, 74.1, 73.9, 73.5, 72.9, 72.5, 72.3, 72.2, 70.8, 70.5, 69.4, 68.8, 63.2, 55.3, 18.15, 18.13, 12.0. HRMS (ESI) calcd for $C_{115}H_{138}Cl_3N_2O_{21}Si$ $[M+NH_4]^+$ 2015.8621, found 2015.8618.

5.8. E factor comparison between the present and conventional strategies starting with the same diol 68

To simply the calculations and demonstrate the comparison in a more intuitive way, we envisioned a conventional synthetic procedure in **Scheme S1** starting with the same diol **68**. The first step would be the Sn-mediated Nap protection of 3-OH on **68**. However, we failed to accomplish such a selective protection despite many attempts. As an alternative, we referred to those literatures regarding the conversion of analogous substrates, and adopted their reported yields to estimate the E factor for the conventional procedure.[48-50] These estimated yields are marked in red in Scheme S1.



Scheme S1. Conventional procedure

the E factor (EF) is calculated as follows:

$$\mathrm{EF} = \frac{\sum_i M_i(1 + \mathrm{EF}'_i) - P}{P}$$

If materials *i* do not need to be synthesized beforehand, EF'_i is equal to zero.

Here, $\Sigma_i\ M_i$ is the total mass of all materials with M_i being mass of the individual material, and *P* is the mass of product. EF represents for the E factor and EF' represents for that of prior step. Donors **1**, **69**, **S53**, and diol **68** are regarded as starting material to simply the calculation of E factors.

The simple E-factor (sEF) contains only the reagents and starting materials used for synthesis. The complete E-factor (cEF) contains all material used for the synthesis.

Unless otherwise in the original report, the following assumptions were made for synthetic procedures:

- Silica gel for chromatography was used as 20 g per g of crude product
- Solvents for chromatography were used as 500 mL per gram of crude product
- PE/EA = 5:1 was used as eluent for separation of these compound
- The glycosylation was quenched with 5 eq. of Et_3N relative to the promoter
- Solvents for dilution were used as two times the volume of the initial solution
- Anhydrous salts for drying of extracts were used as 20 mg per mL of extract volume
- Aqueous solutions for washing were used in equal volume to the extract volume
- Molecular sieve was added as 50 mg per mL of solvent

Table S3. Mass of waste and product at conversion of compound 68 to S48 (our strategy)

Reagents and organic compounds		Inorganics, salts and quenchers		Solvents	
Compound **68**	800 mg	4Å MS	0.42 g	THF	35.5 g (40 mL)
Donor **1**	690 mg	Et_3N	85 mg (120 µL)	PE for chromatography	404 g (621 mL)
$BF_3 \cdot Et_2O$	24 mg (21 µL)	Silica gel for chromatography	29.8 g	EA for chromatography	112 g (124 mL)
Product	0.94 g				

$$\mathrm{sEF}^1 = \frac{(0.8 + 0.69 + 0.024 - 0.94)\ \mathrm{g}}{0.94\ \mathrm{g}} = 0.61$$

$$\mathrm{cEF}^1 = \frac{(0.8 + 0.69 + 0.085 + 0.42 + 0.024 + 29.8 + 35.5 + 404 + 112 - 0.94)\ \mathrm{g}}{0.94\ \mathrm{g}} = 620$$

Table S4. Mass of waste and product at conversion of compound S48 to 70 (our strategy)

Reagents and organic compounds		Inorganics, salts and quenchers		Solvents	
Compound **S48**	50 mg	4Å MS	17 mg	Et_2O	2.8 g (4.0 mL)
Donor **69**	37 mg	Et_3N	1 mg (1.5 µL)	PE for chromatography	23.6 g (36.2 mL)
TMSOTf	0.47 mg (0.38 µL)	Silica gel for chromatography	1.7 g	EA for chromatography	6.5 g (7.2 mL)
Product	55 mg				

$$\mathrm{sEF}^2 = \frac{(50 + 50 \times 0.61 + 37 + 0.47 - 55)\ \mathrm{mg}}{55\ \mathrm{mg}} = 1.14$$

$$\mathrm{cEF}^2 = \frac{\begin{pmatrix} 50 + 50 \times 620 + 37 + 1 + 17 + 0.47 + \\ 1700 + 2800 + 23600 + 6500 - 55 \end{pmatrix} \mathrm{mg}}{55\ \mathrm{mg}} = 1193$$

Table S5. Mass of waste and product at conversion of compound 68 to S50[48] (conventional procedure)

Reagents and organic compounds	Inorganics, salts and quenchers	Solvents

Compound **68**	1000 mg	KF for washing	2.2 g	Toluene	25 g (28.7 mL)
NapBr	255 mg	NaCl for washing	3.1 g	EA for extraction	10 g (11.4 mL)
Bu_2SnO	352 mg	$MgSO_4$ for drying	0.8 g	H_2O for washing	33 g (33 mL)
TBAB	456 mg	Silica gel for chromatography	25.1 g	Toluene for chromatography	438 g (502 mL)
				EA for chromatography	113 g (125 mL)
Product	929 mg				

$$sEF^1 = \frac{(1 + 0.255 + 0.352 + 0.456 - 0.929)\ \mathrm{g}}{0.929\ \mathrm{g}} = 1.22$$

$$cEF^1 = \frac{\begin{pmatrix} 1 + 0.255 + 0.352 + 0.456 + 2.2 + 3.1 + 0.8 + \\ 25.1 + 25 + 10 + 33 + 438 + 113 - 0.929 \end{pmatrix}\ \mathrm{g}}{0.929\ \mathrm{g}} = 701$$

Table S6. Mass of waste and product at conversion of compound S50 to S51[49] (conventional procedure)

Reagents and organic compounds		Inorganics, salts and quenchers		Solvents	
Compound **S50**	500 mg	4Å MS	170 mg	CH_2Cl_2	4 g (3 mL)
Donor **69**	520 mg	Pyridine	190 mg (200 μL)	Et_2O	4.3 g (6 mL)
TMSOTf	16 mg (14 μL)	$NaHCO_3$ for washing	6.4 g	CH_2Cl_2 for dilution	24 g (18 mL)
Thiophene	410 mg	Na_2SO_4 for drying	0.54 g	H_2O for washing	23 g (23 mL)
		Silica gel for chromatography	28.6 g	PE for chromatography	387 g (595 mL)
				EA for chromatography	107 g (119 mL)
Product	570 mg				

$$\mathrm{sEF}^2 = \frac{(500 + 500 * 1.22 + 520 + 410 + 16 - 570)\ \mathrm{mg}}{570\ \mathrm{mg}} = 2.61$$

$$\mathrm{cEF}^2 = \frac{\begin{pmatrix} 500 + 500 \times 701 + 520 + 190 + 410 + 170 + \\ 16 + 6400 + 540 + 28600 + 4000 + 4300 + \\ 24000 + 23000 + 387000 + 107000 - 570 \end{pmatrix} \mathrm{mg}}{570\ \mathrm{mg}} = 1643$$

Table S7. Mass of waste and product at conversion of compound S51 to S52[48] (conventional procedure)

Reagents and organic compounds		Inorganics, salts and quenchers		Solvents	
Compound **S51**	500 mg	$NaHCO_3$ for washing	8.8 g	CH_2Cl_2	13 g (10 mL)
DDQ	420 mg	$MgSO_4$ for dryness	0.75 g	isobutanol	2 g (2.5 mL)
		Silica gel for chromatography	18.4 g	CH_2Cl_2 for extraction	33 g (25 mL)
				H_2O for washing	32 g (32 mL)
				Toluene for chromatography	301 g (345 mL)
				EA for chromatography	104 g (115 mL)
Product	400mg				

$$\mathrm{sEF}^3 = \frac{(0.5 + 0.5 * 2.61 + 0.42 - 0.4)\ \mathrm{g}}{0.4\ \mathrm{g}} = 4.56$$

$$\mathrm{cEF}^3 = \frac{\begin{pmatrix} 0.5 + 0.5 \times 1643 + 0.42 + 8.8 + 32 + 0.75 + \\ 18.4 + 13 + 2 + 33 + 301 + 104 - 0.4 \end{pmatrix} \mathrm{g}}{0.4\ \mathrm{g}} = 3337$$

Table S8. Mass of waste and product at conversion of compound S52 to S54[48] (conventional procedure)

Reagents and organic compounds	Inorganics, salts and quenchers	Solvents

Compound **S52**	100 mg	4Å MS	95 mg	CH_2Cl_2	2.5 g (1.9 mL)
Donor **S53**	50 mg	Et_3N	1 mg (1.4 µL)	Toluene for chromatography	545 g (625 mL)
TMSOTf	0.45 mg (0.4 µL)	Silica gel for chromatography	3 g	EA for chromatography	112 g (124 mL)
Product	96 mg				

$$\mathrm{sEF}^4 = \frac{(100 + 100 * 4.56 + 50 + 0.45 - 96)\ \mathrm{mg}}{96\ \mathrm{mg}} = 5.32$$

$$\mathrm{cEF}^4 = \frac{\begin{pmatrix} 100 + 100 \times 3337 + 50 + 1 + 95 + 0.45 + \\ 3000 + 2500 + 54500 + 11200 - 96 \end{pmatrix}\ \mathrm{mg}}{96\ \mathrm{mg}} = 4219$$

sEF(conventional): sEF(greener) = 4.7: 1

cEF(conventional): cEF(greener) = 3.5: 1

6. Reference

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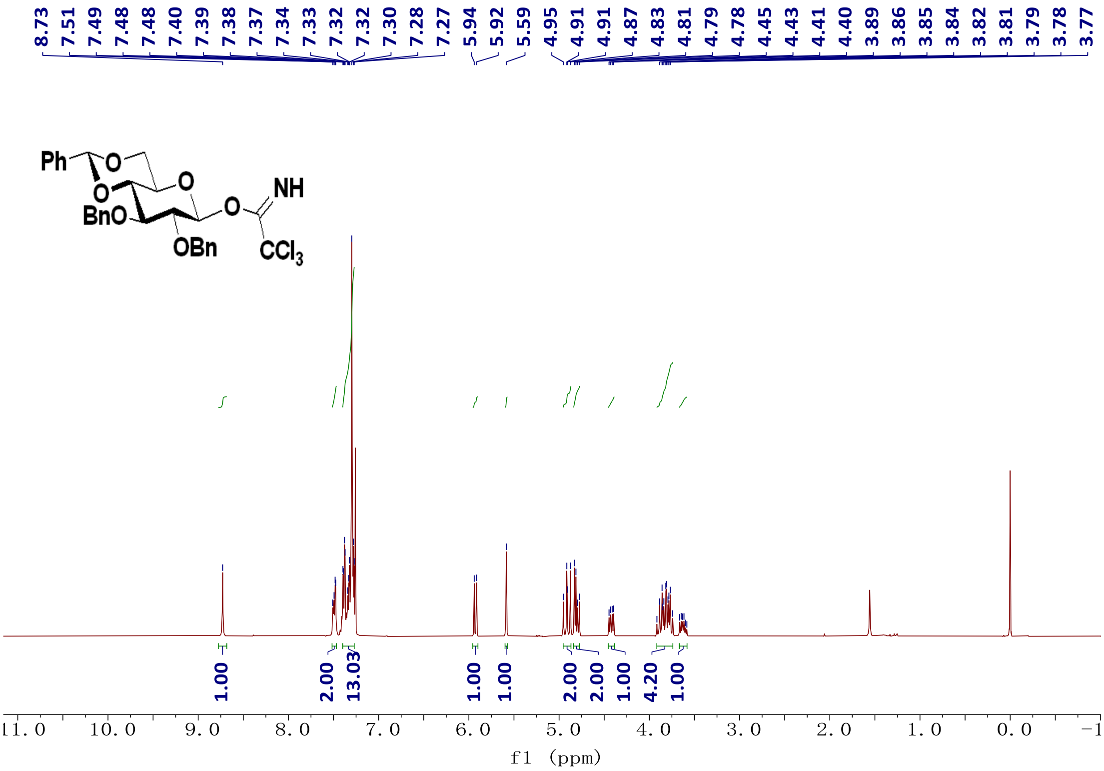
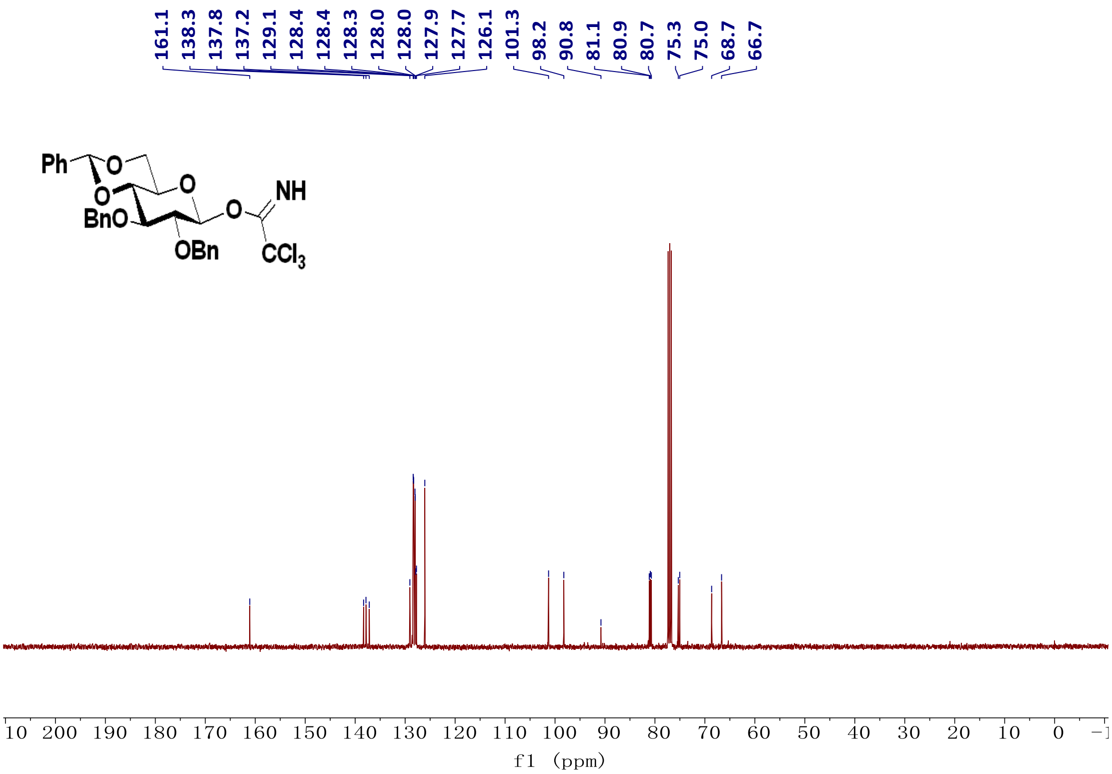
7. NMR spectra



^{1}H NMR of **8 (β)** (300 MHz, $CDCl_3$)



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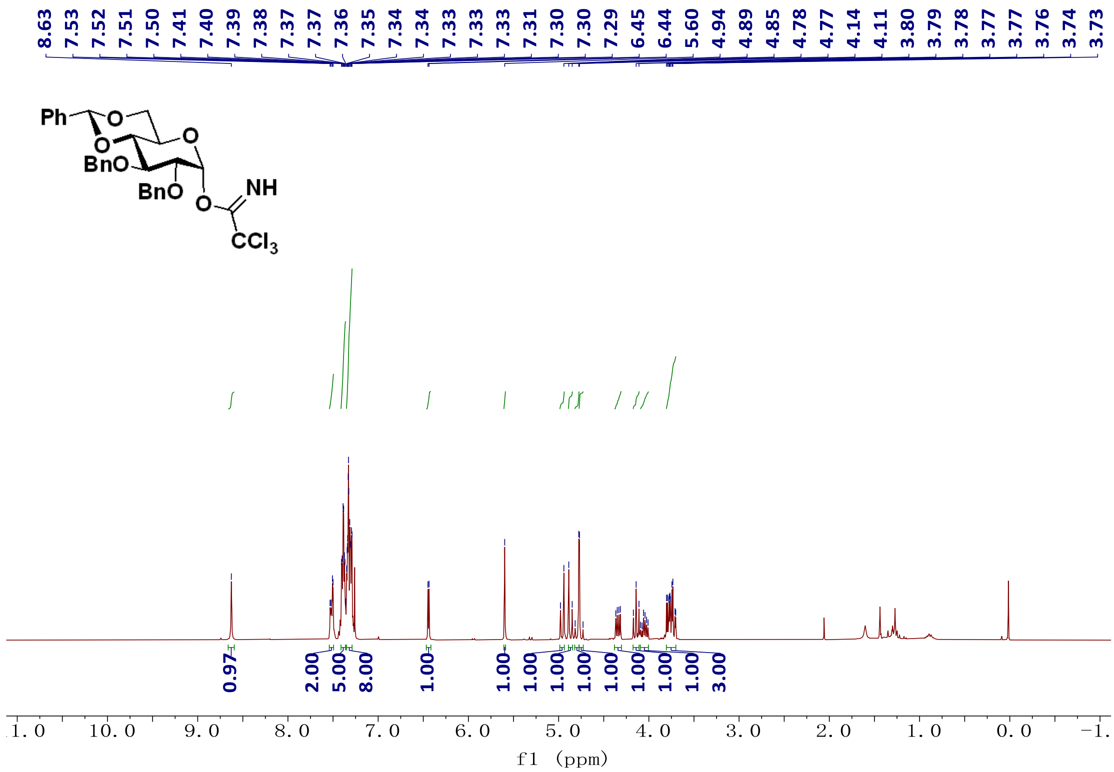

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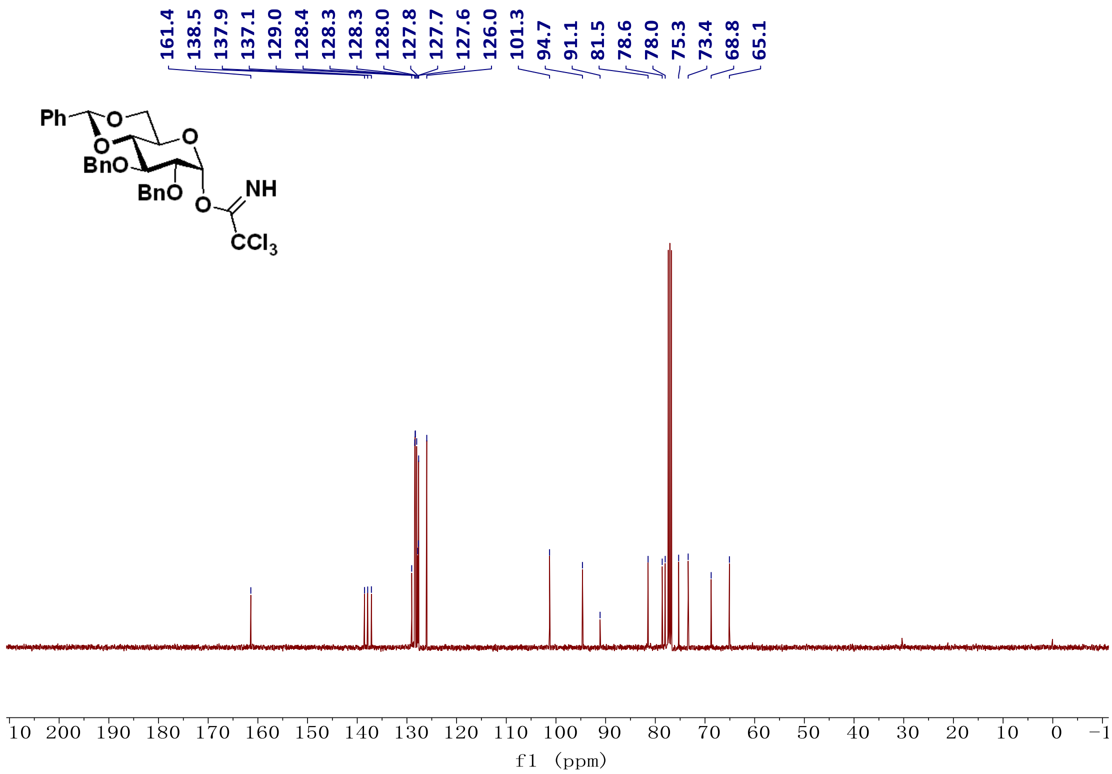

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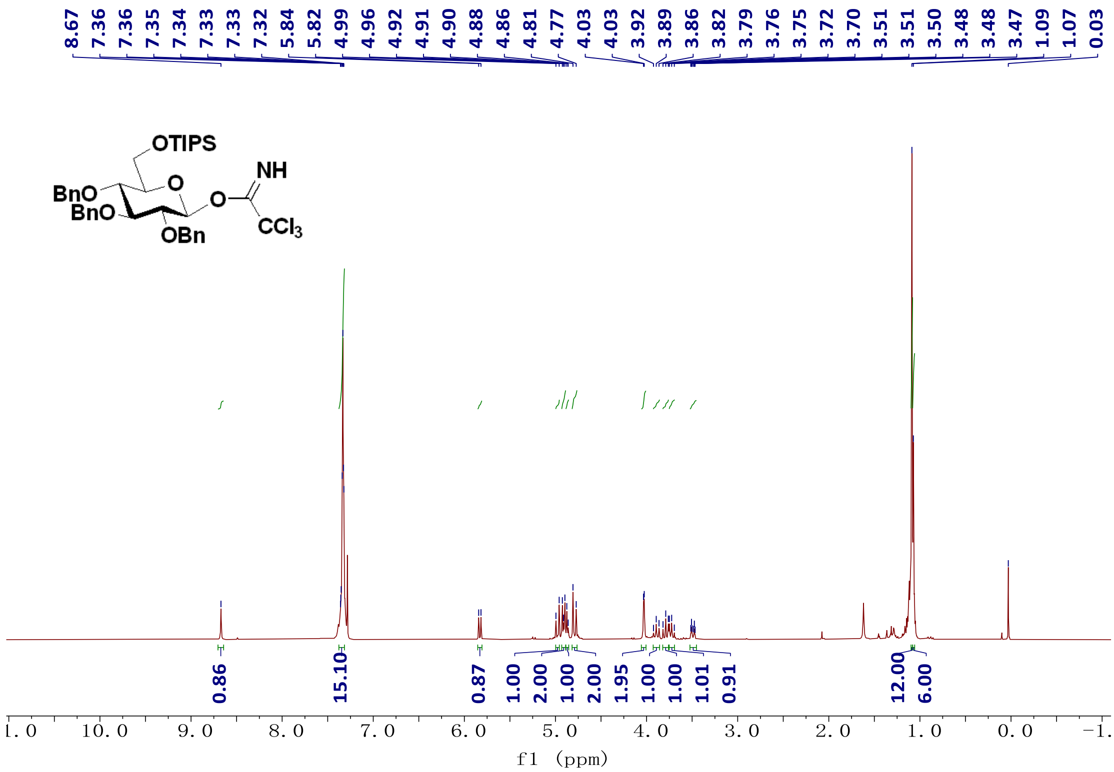
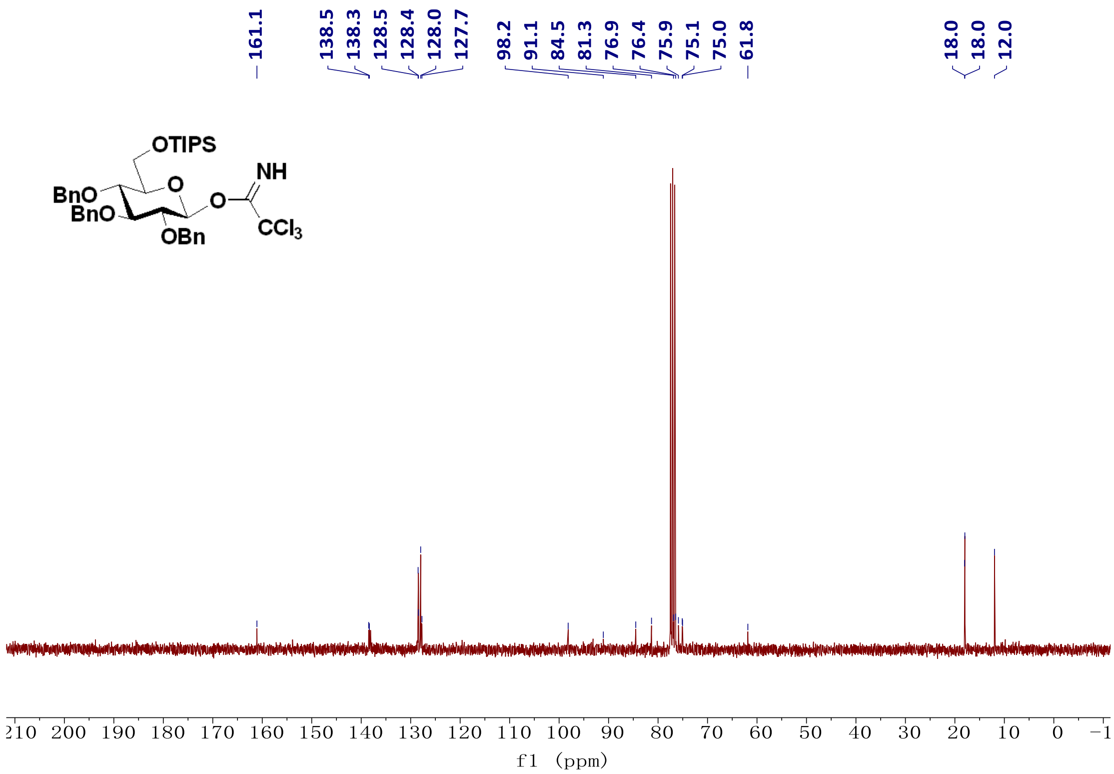


^{1}H NMR of **9 (β)** (300 MHz, $CDCl_3$)



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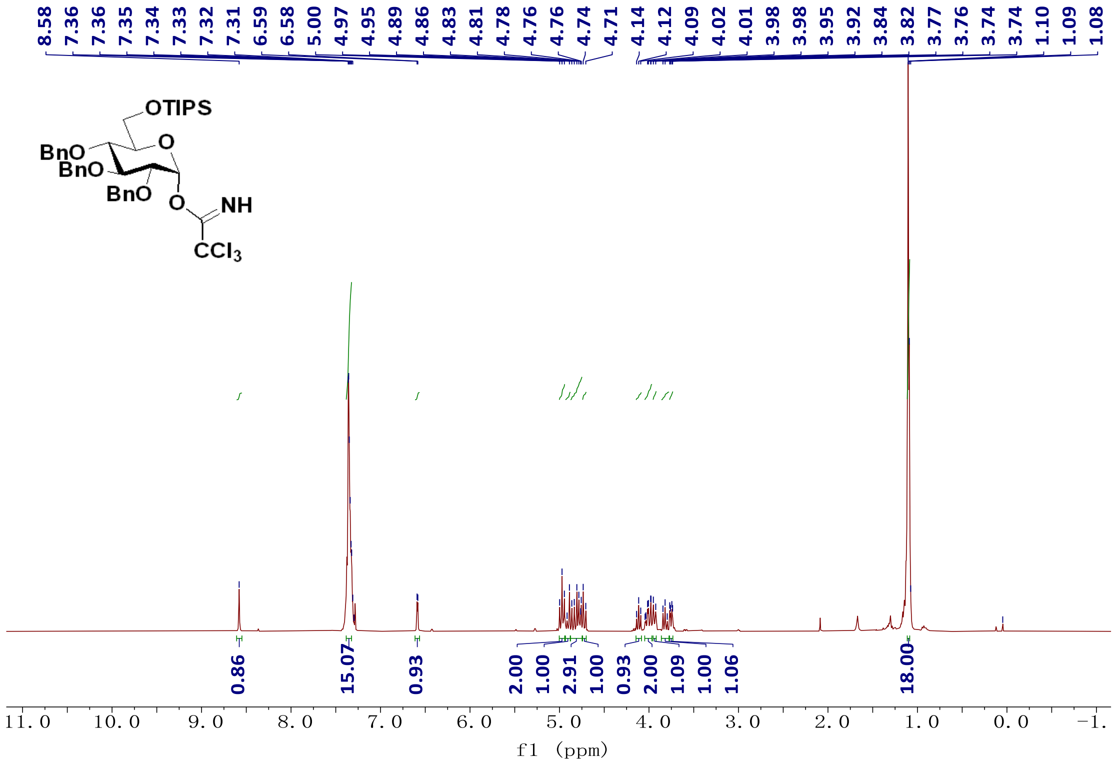

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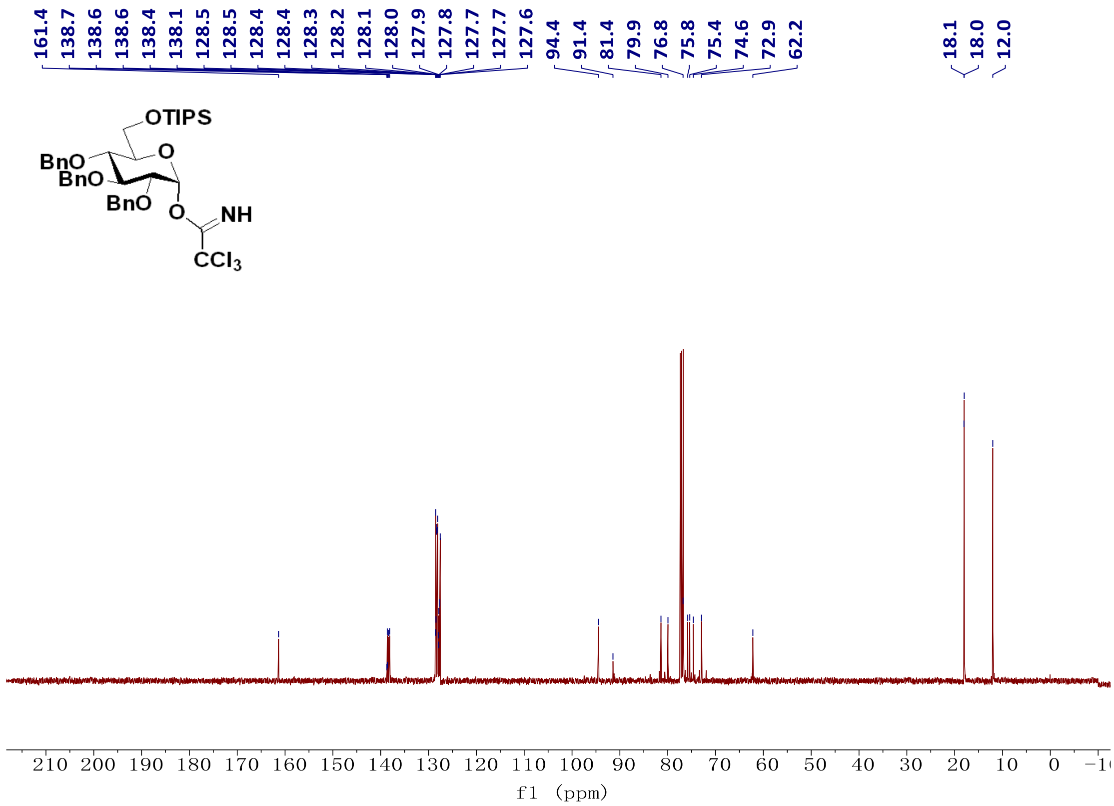

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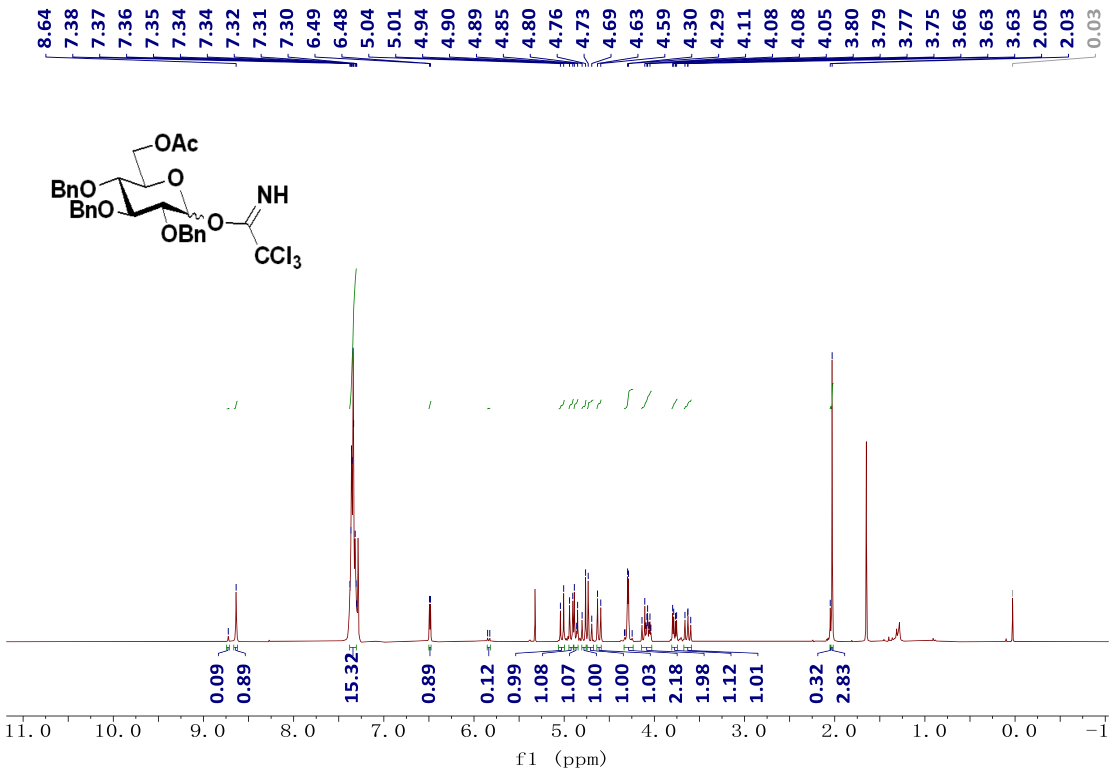
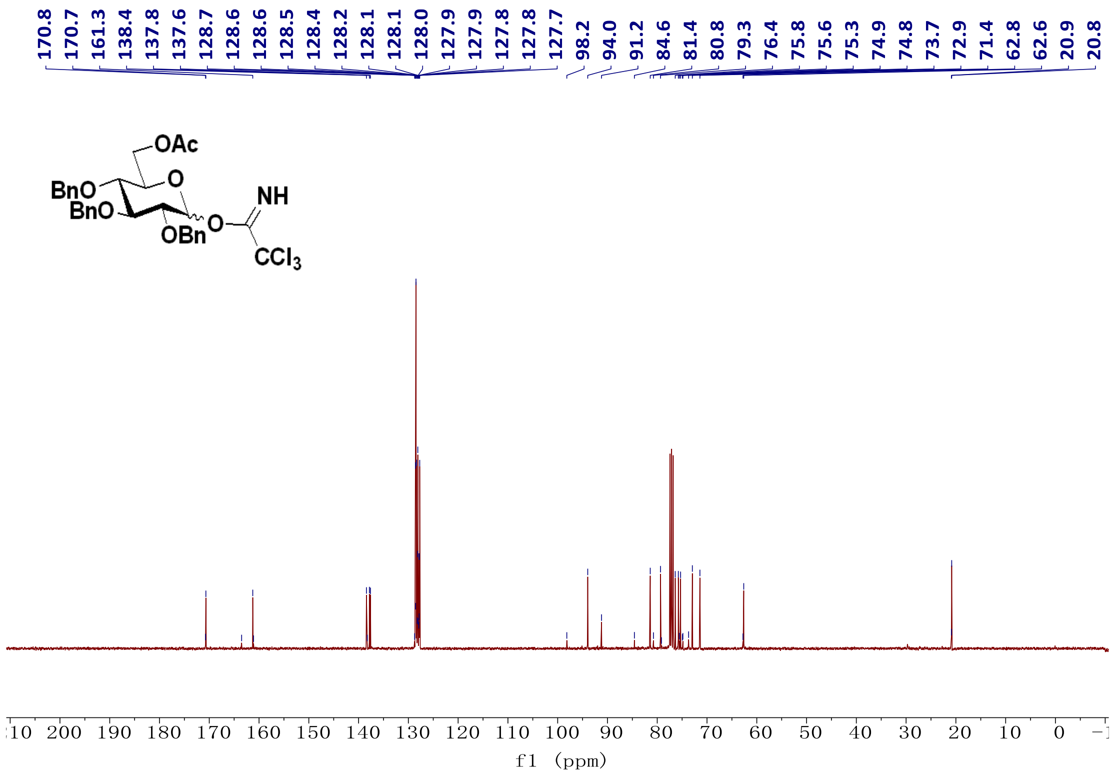


^{1}H NMR of **10** (300 MHz, $CDCl_3$)



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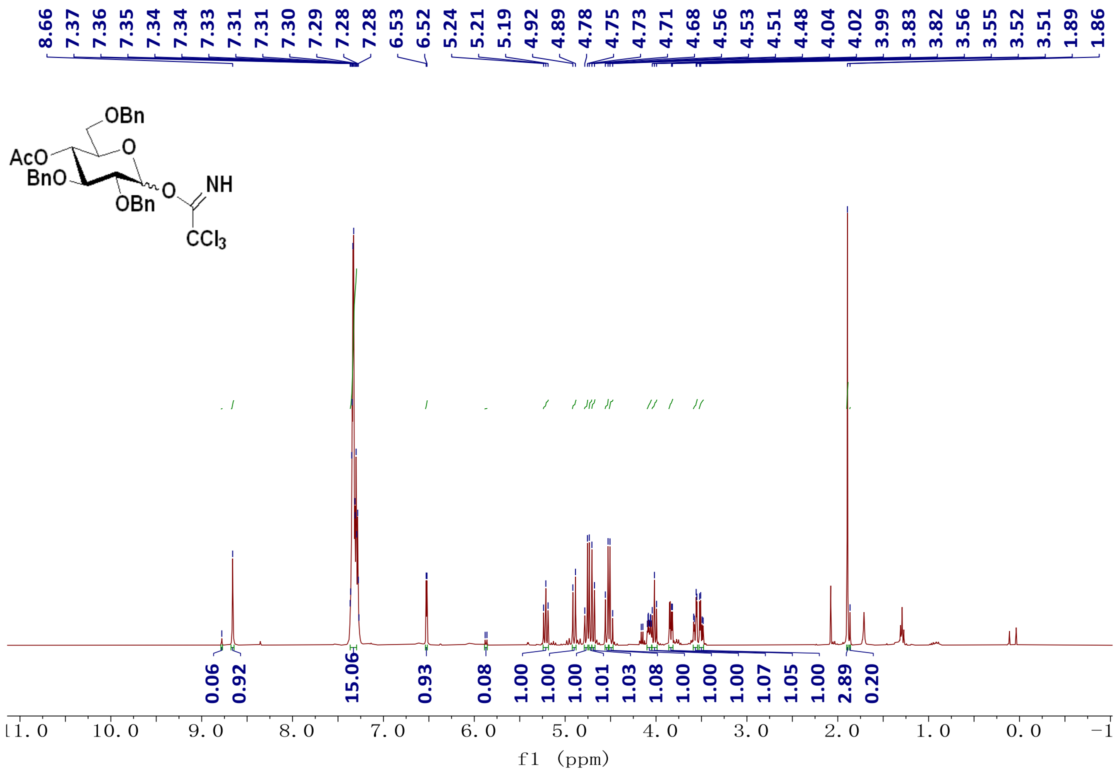

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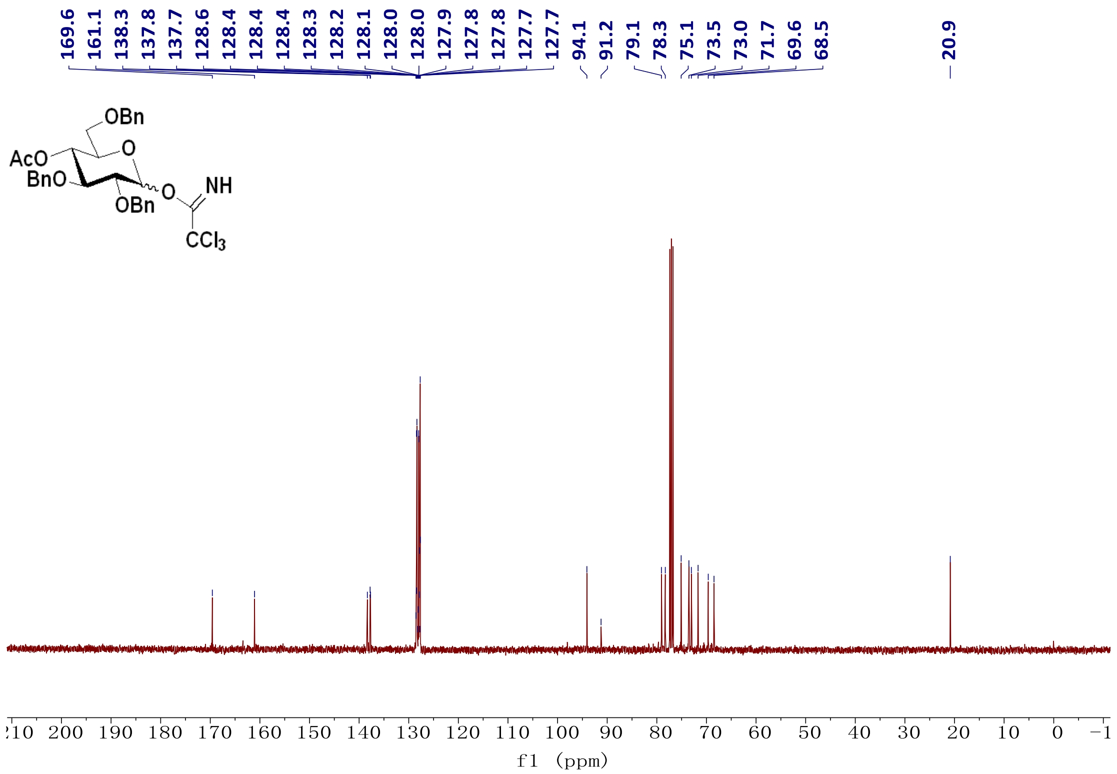
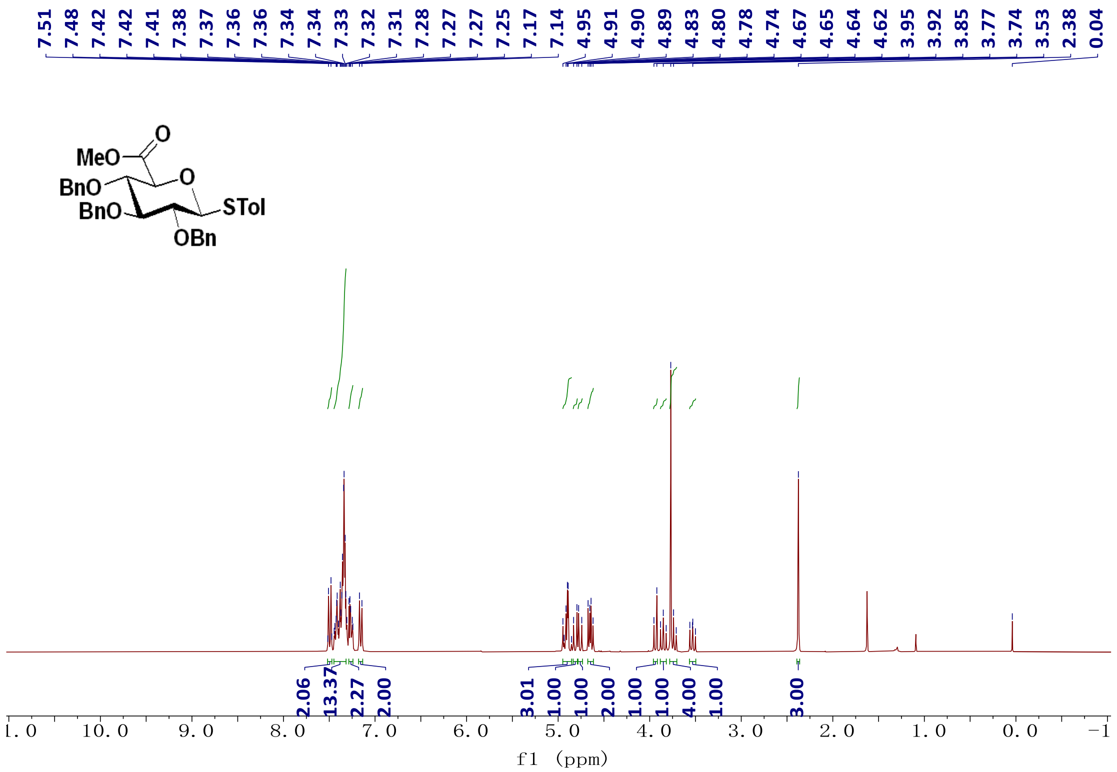


^{13}C NMR of **11** (100 MHz, $CDCl_3$)



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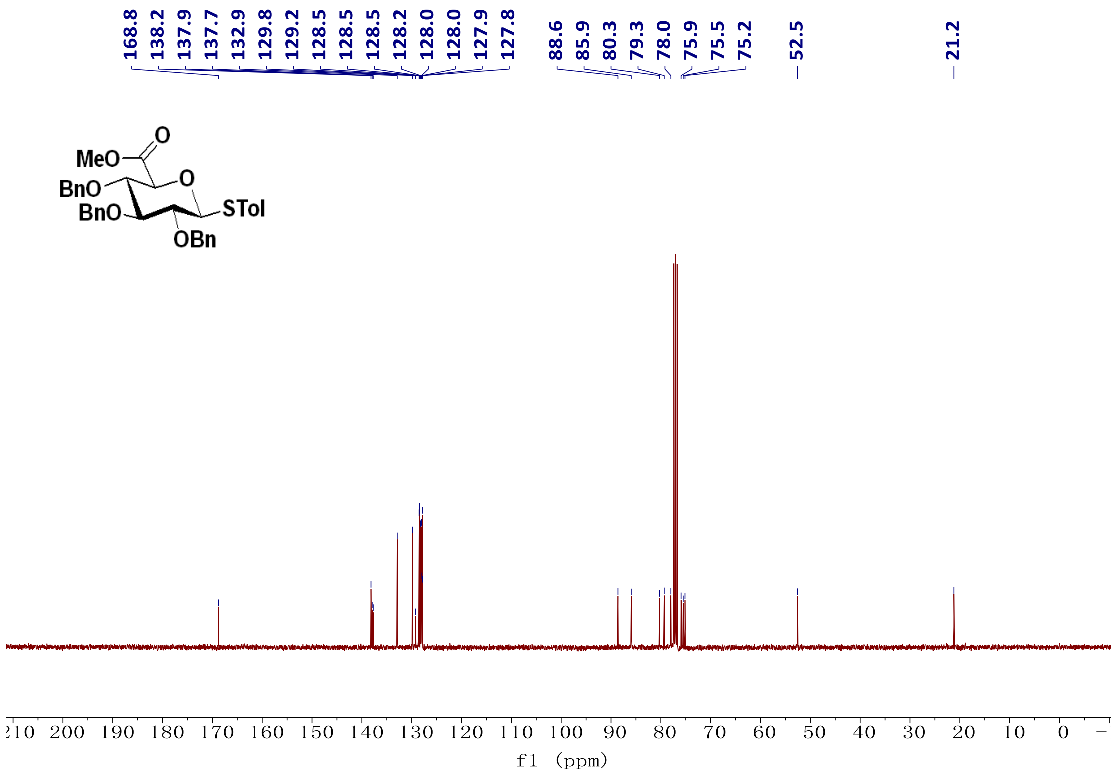

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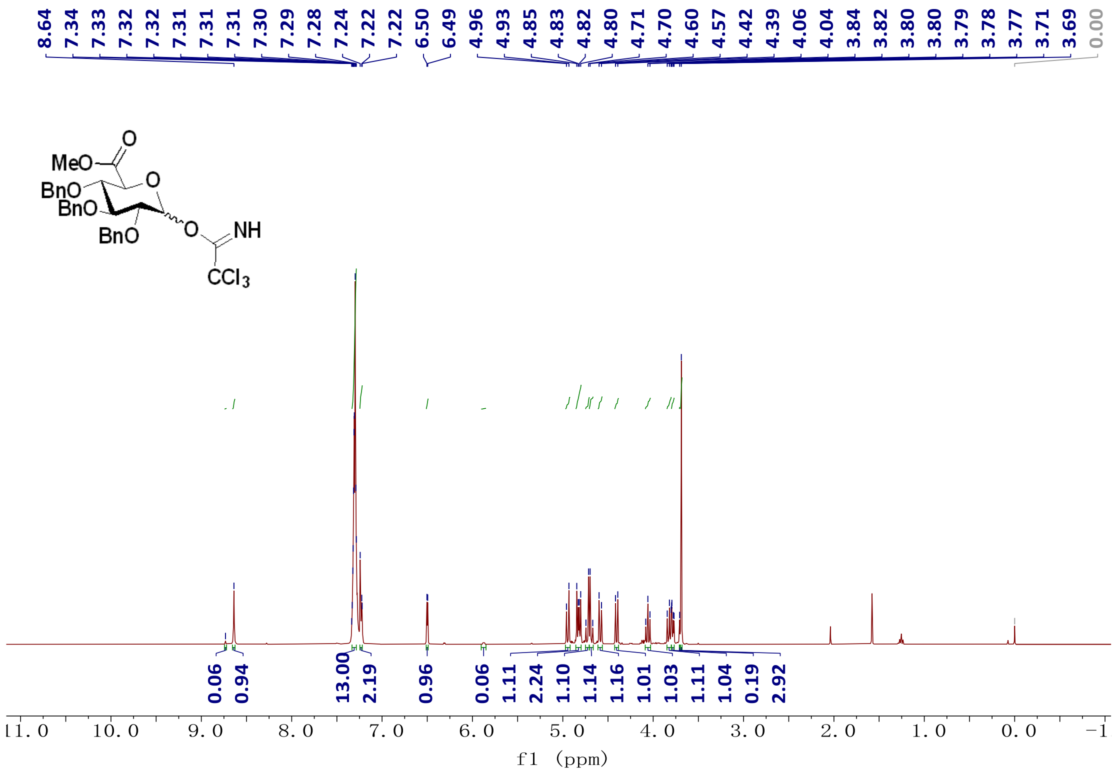

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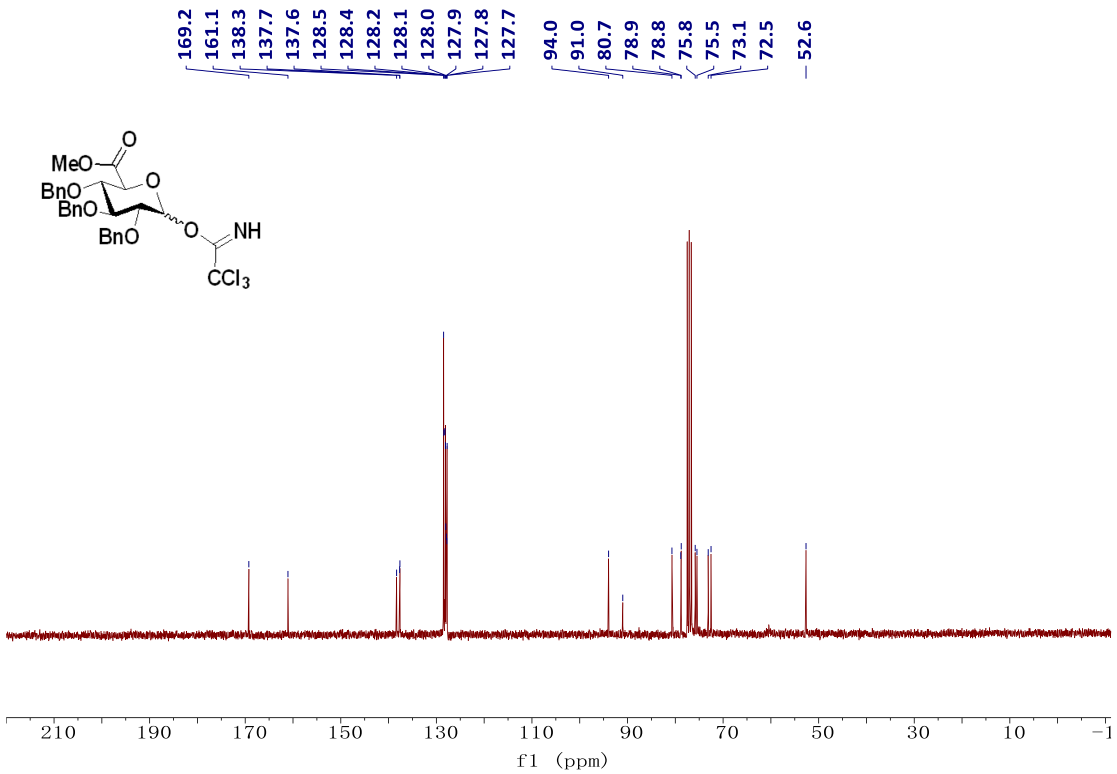
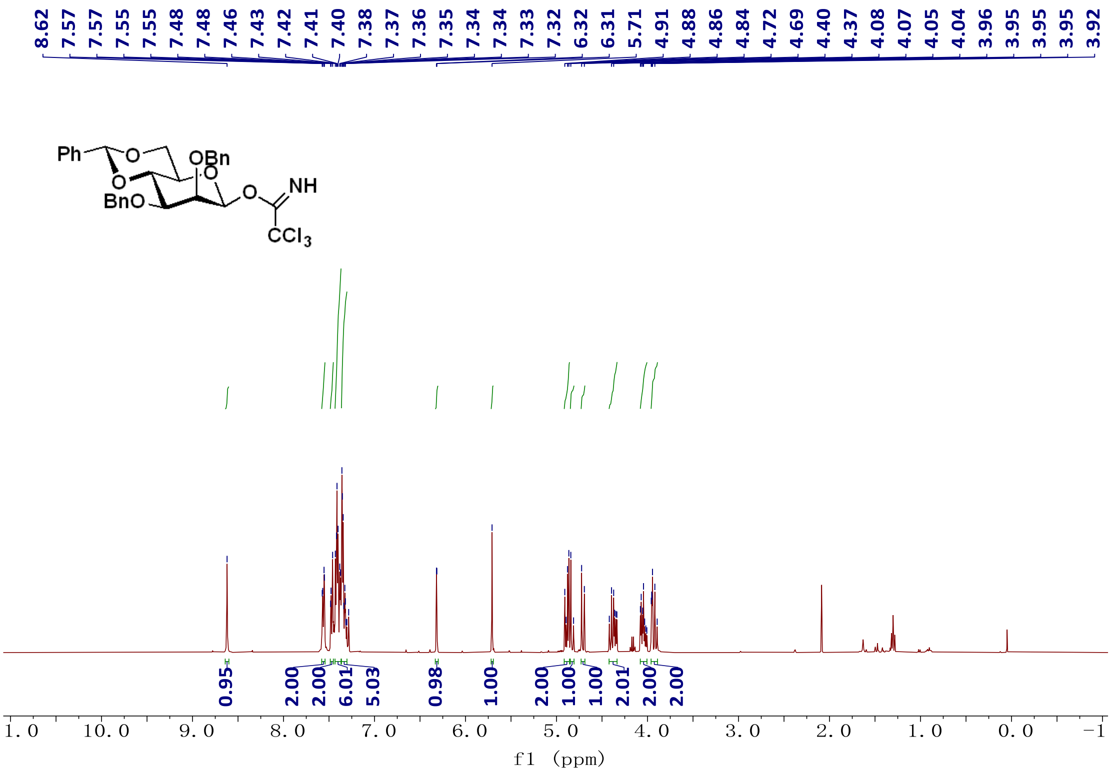


^{13}C NMR of **12** (75 MHz, $CDCl_3$)



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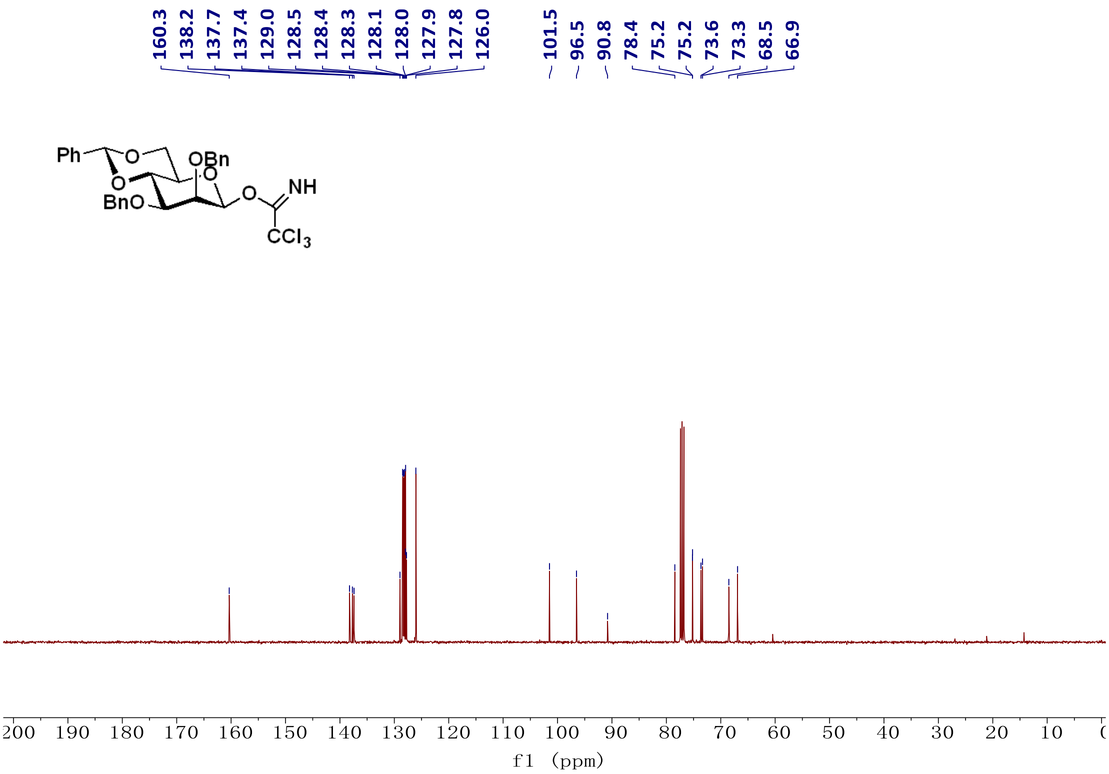
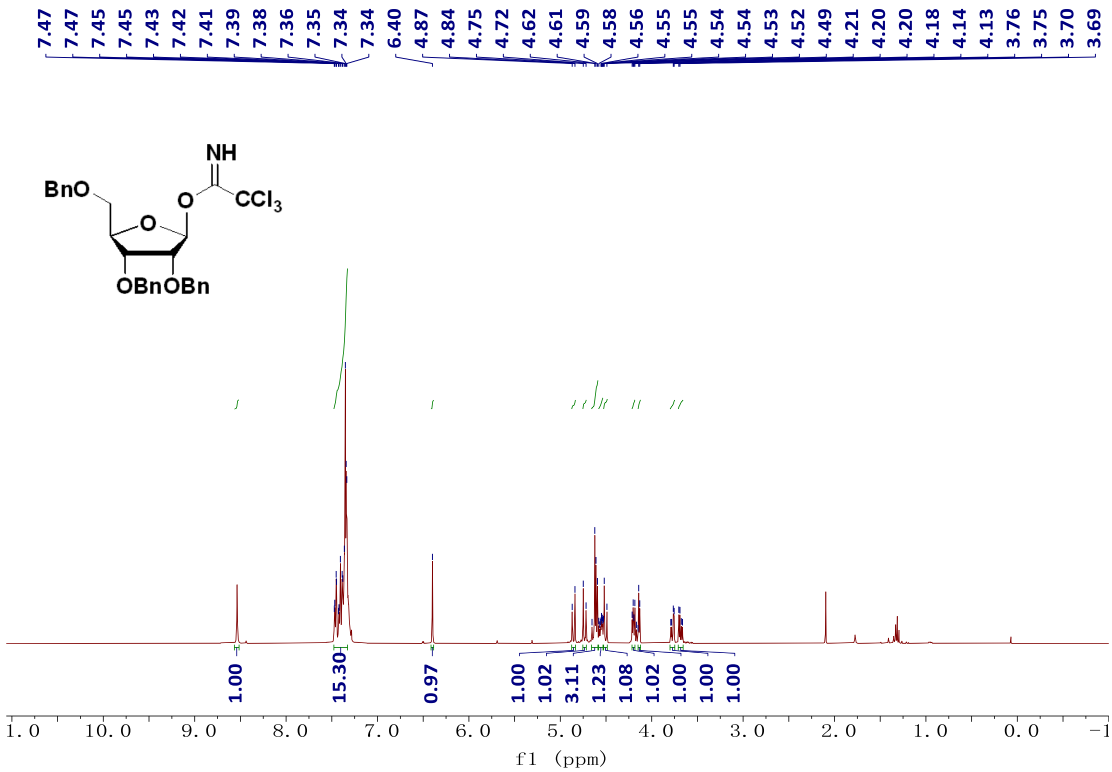
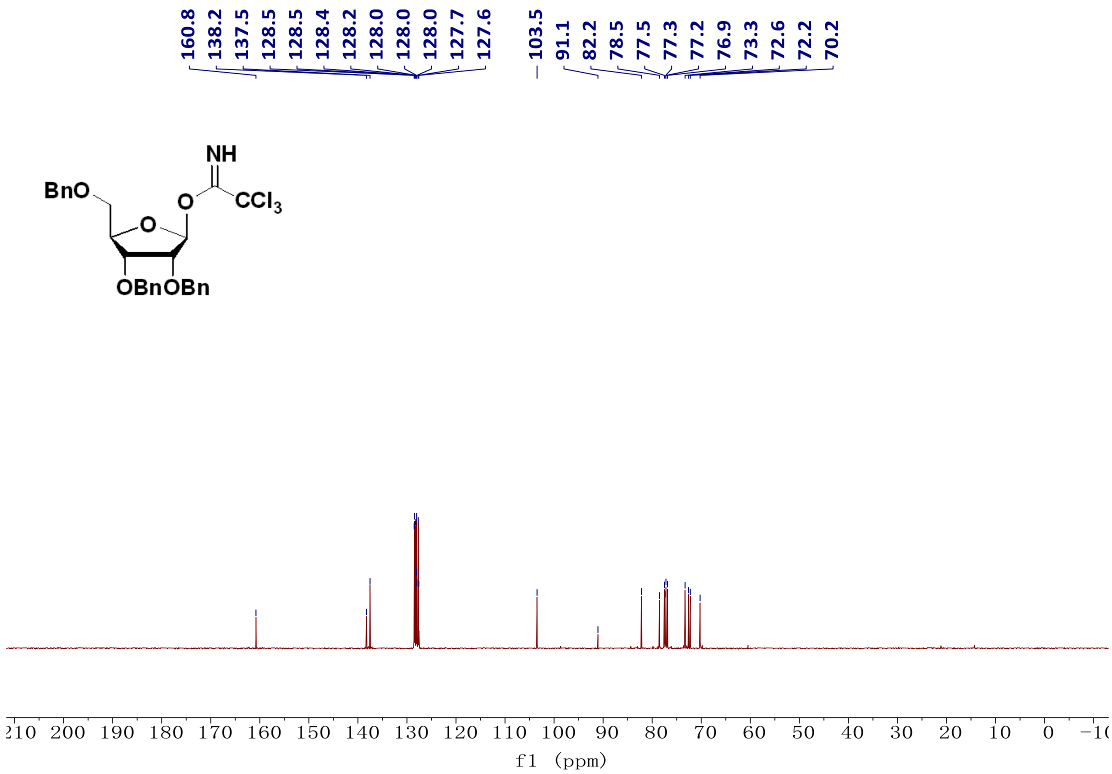


^{13}C NMR of **13** (100 MHz, $CDCl_3$)



^{1}H NMR of **14** (400 MHz, $CDCl_3$)



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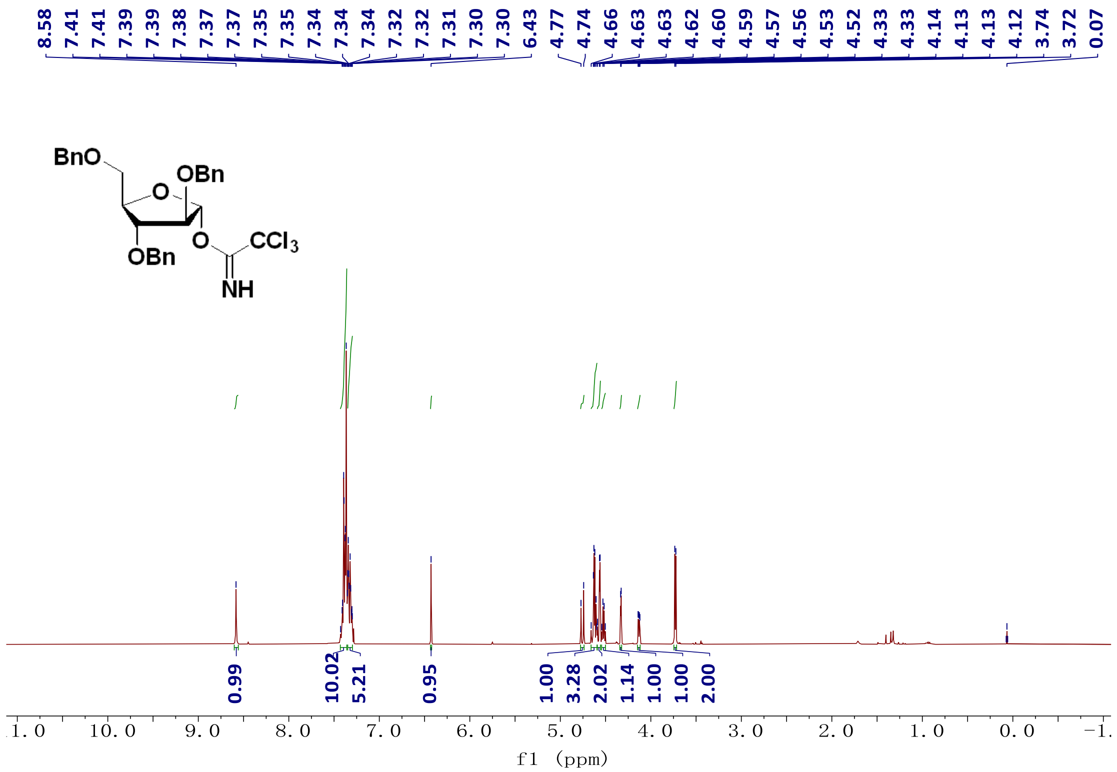
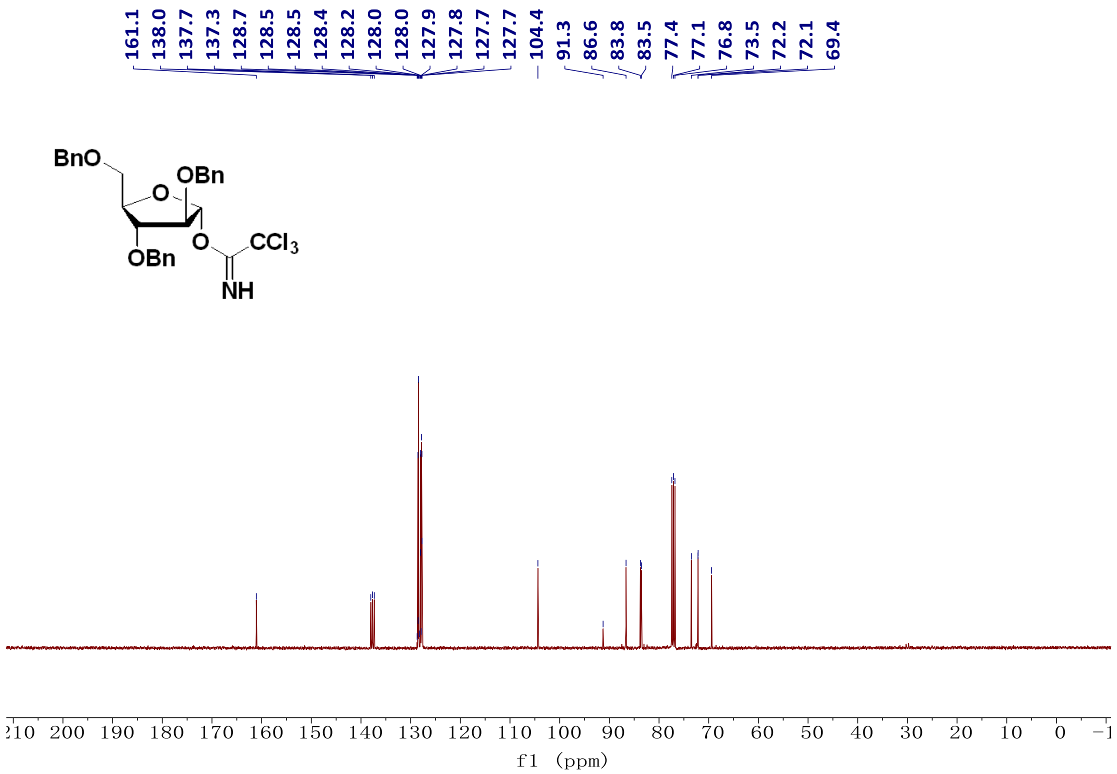


^{1}H NMR of **15** (400 MHz, $CDCl_3$)



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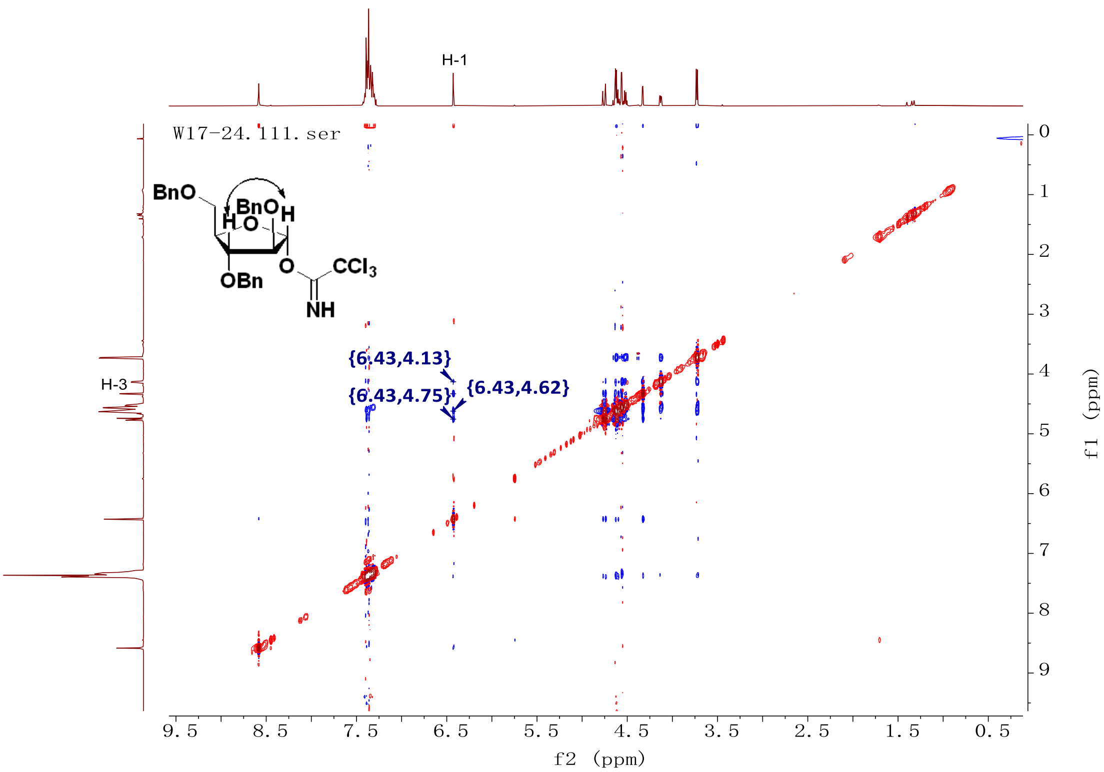
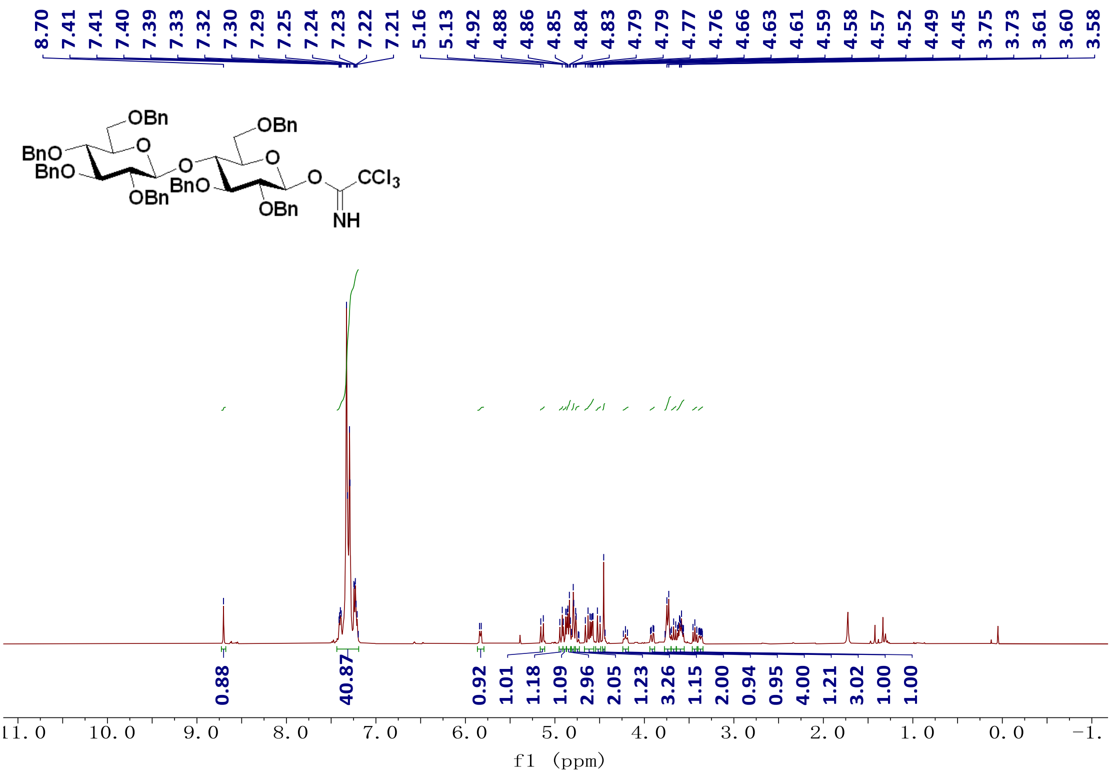
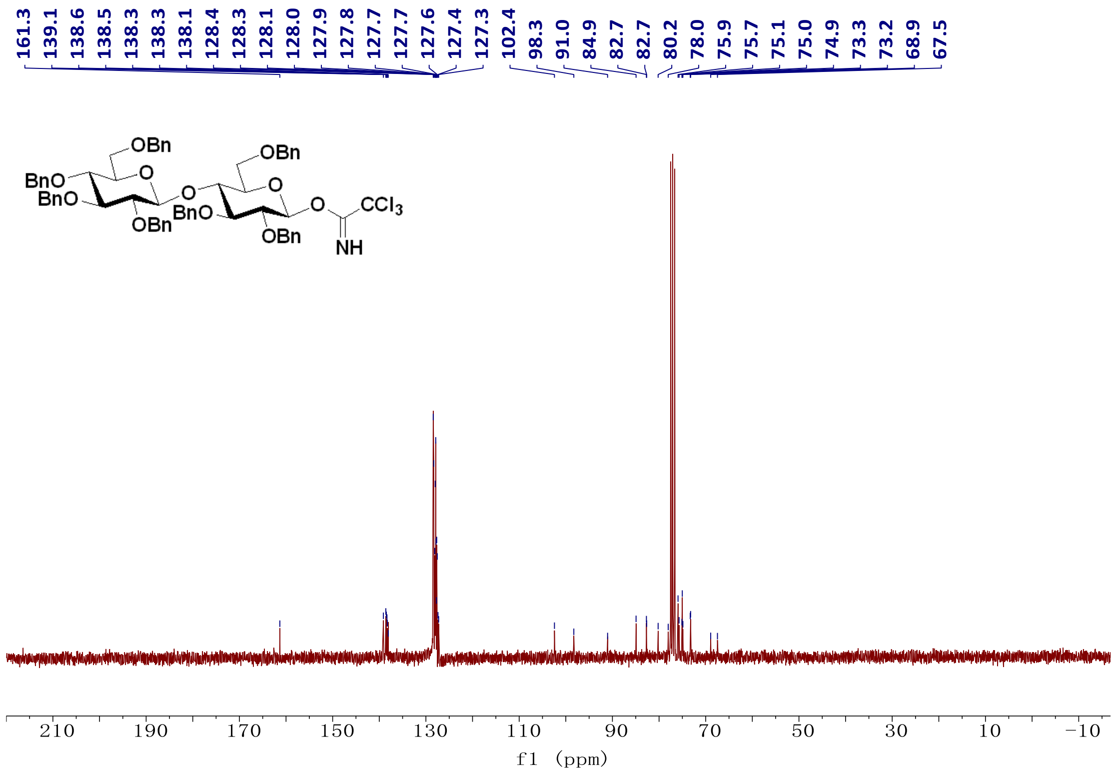


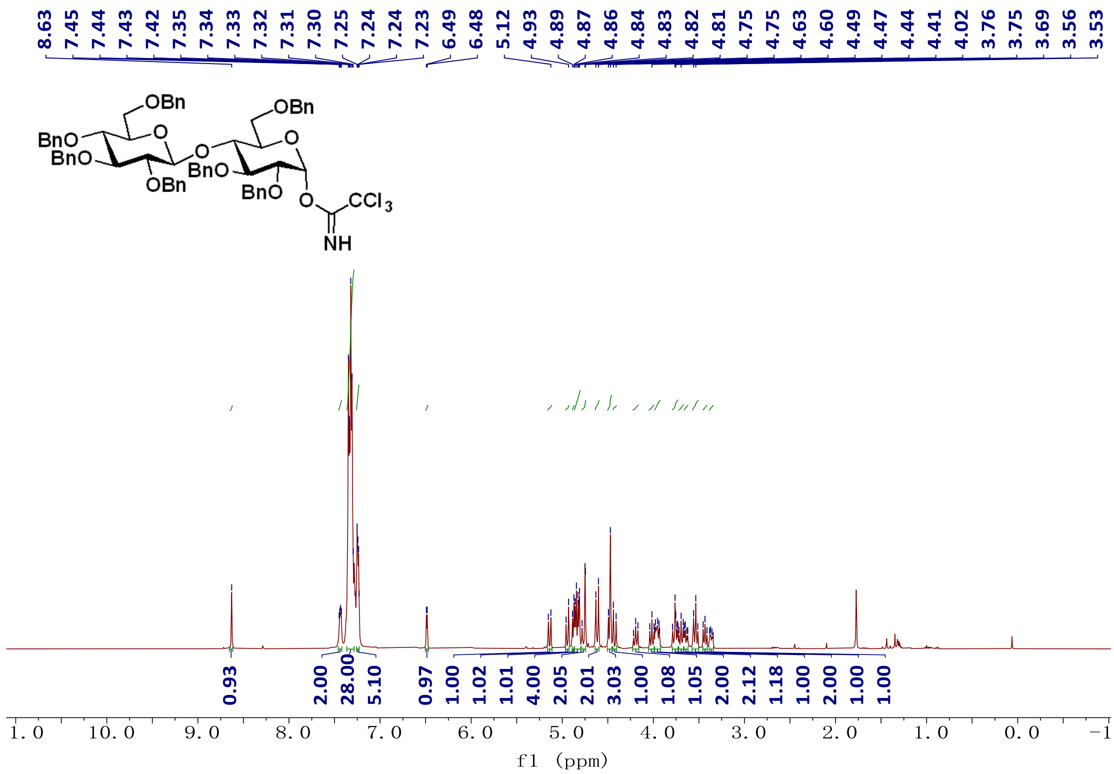
NOESY of **15**



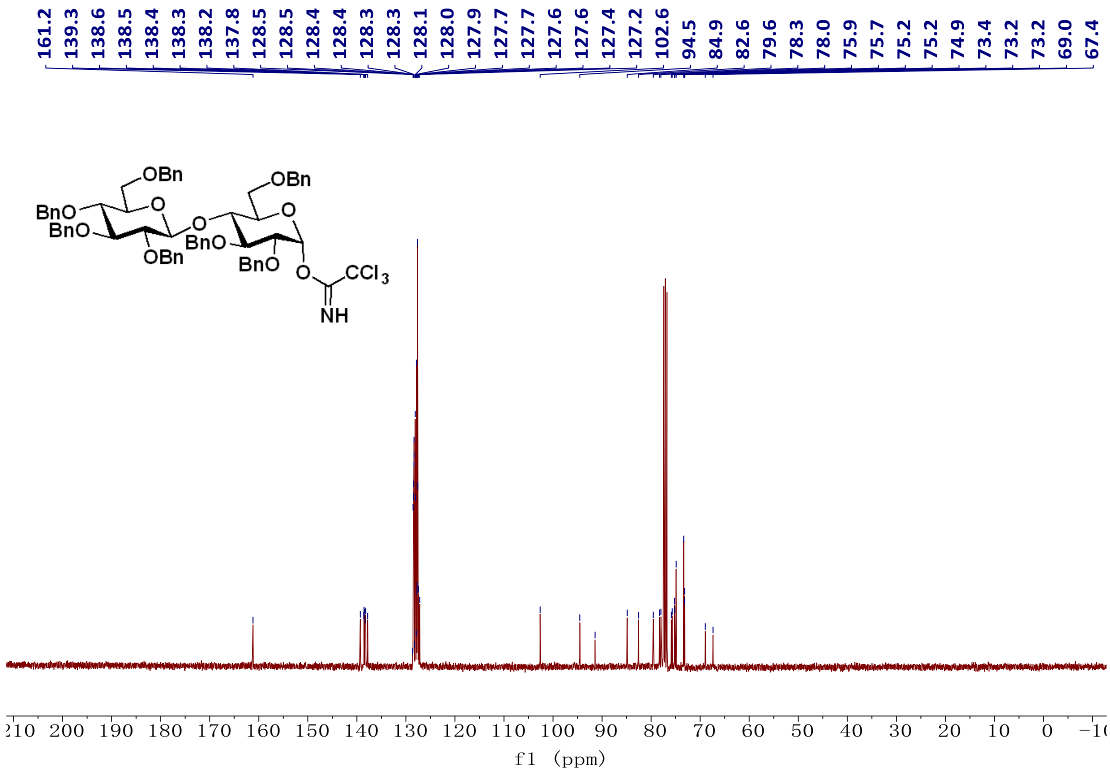
^{1}H NMR of **16 (β)** (400 MHz, $CDCl_3$)



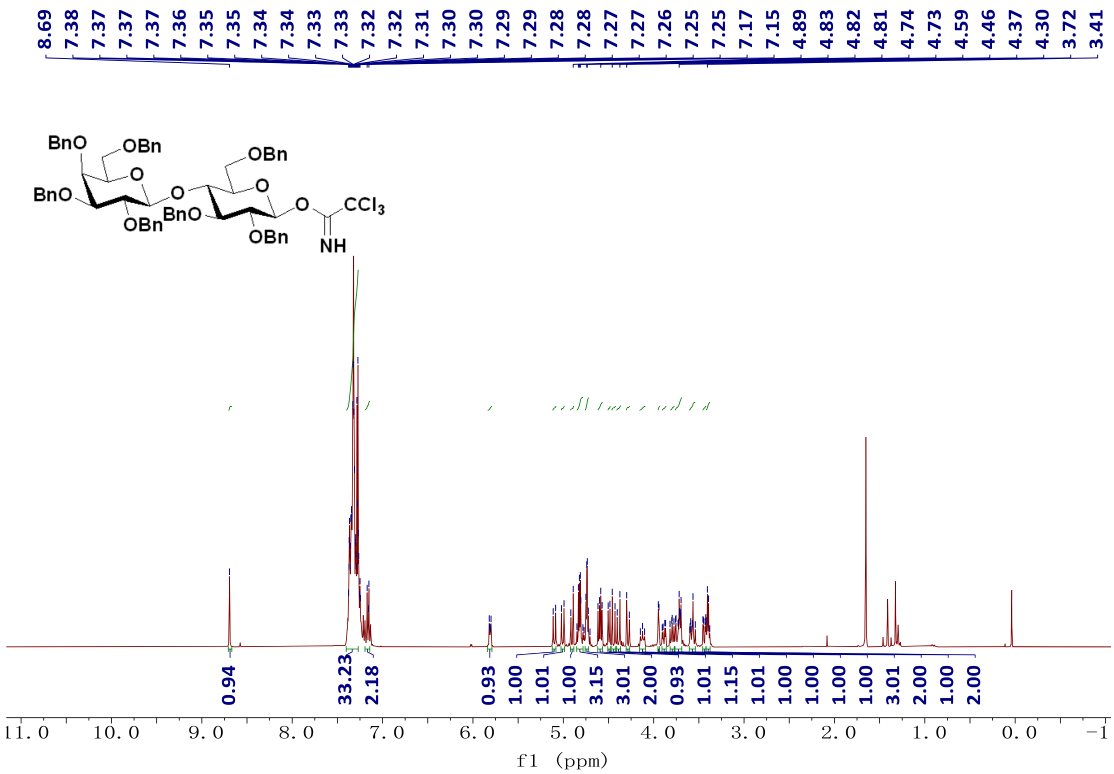
^{13}C NMR of **16 (β)** (75 MHz, $CDCl_3$)



^{1}H NMR of **16 (α)** (400 MHz, $CDCl_3$)



^{13}C NMR of **16 (α)** (100 MHz, $CDCl_3$)



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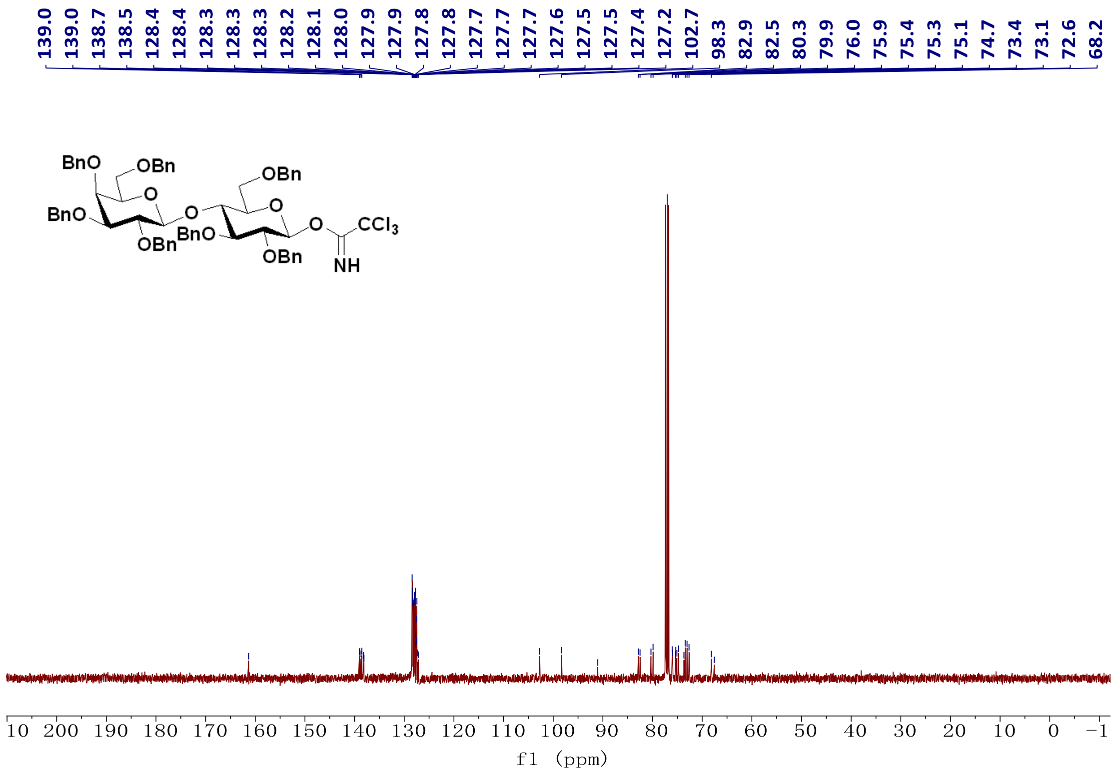

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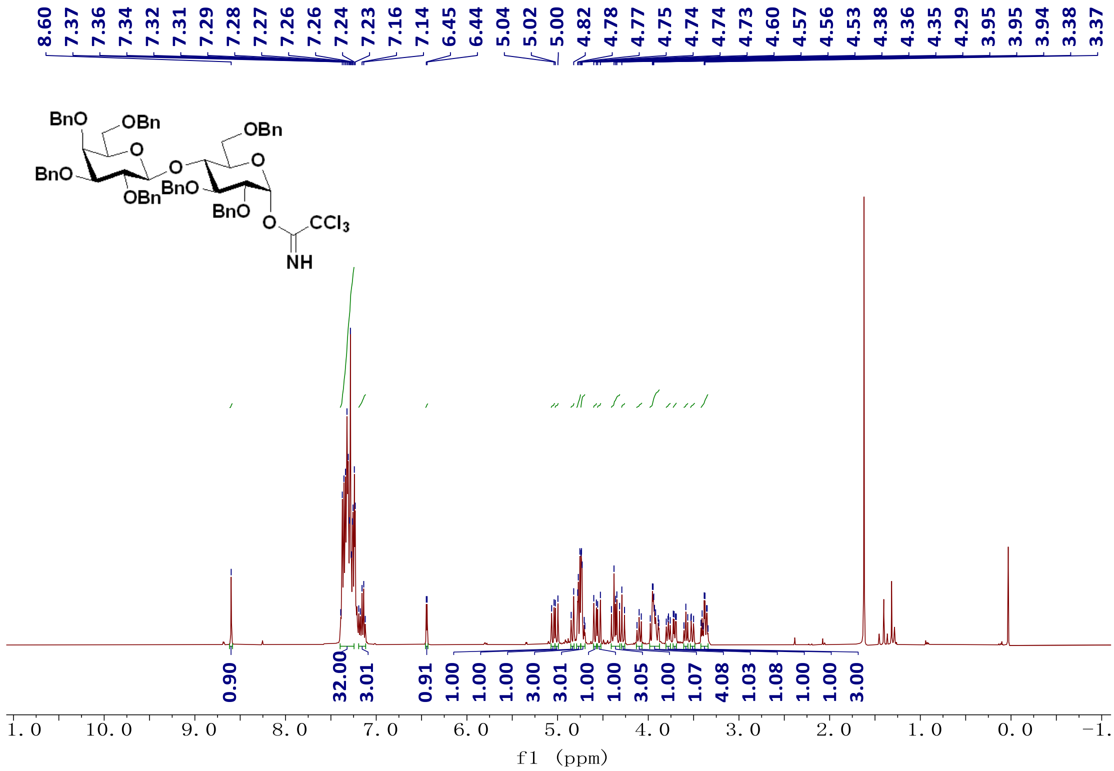

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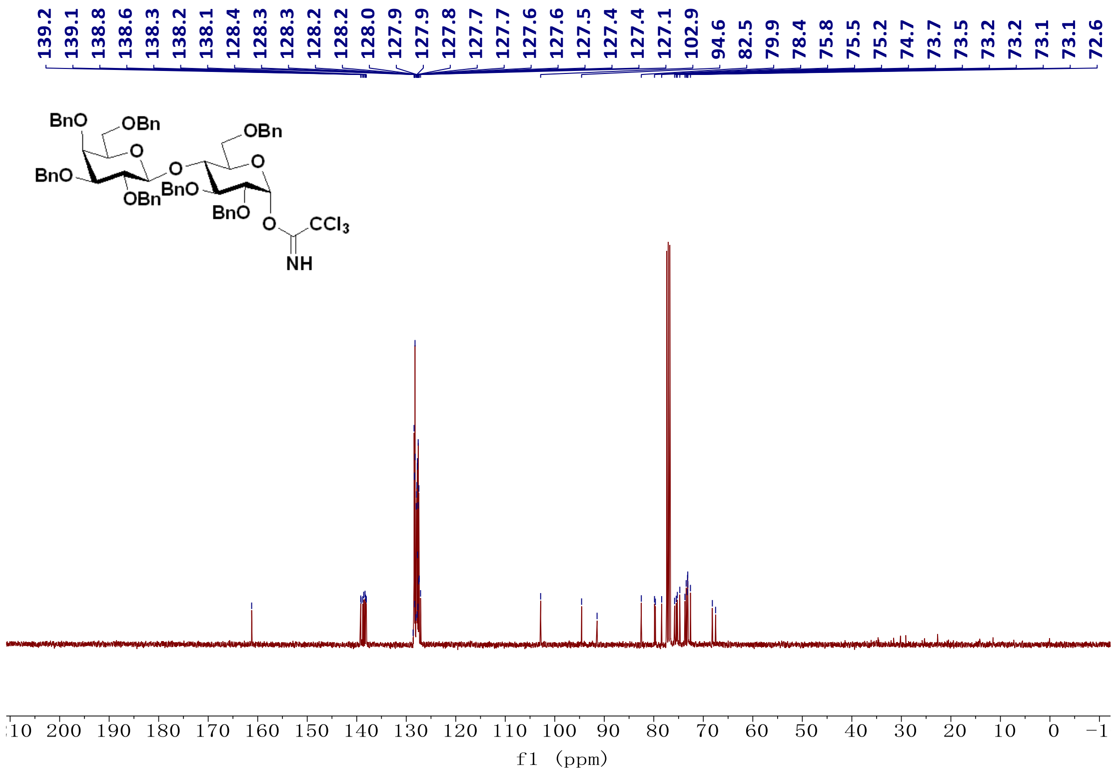

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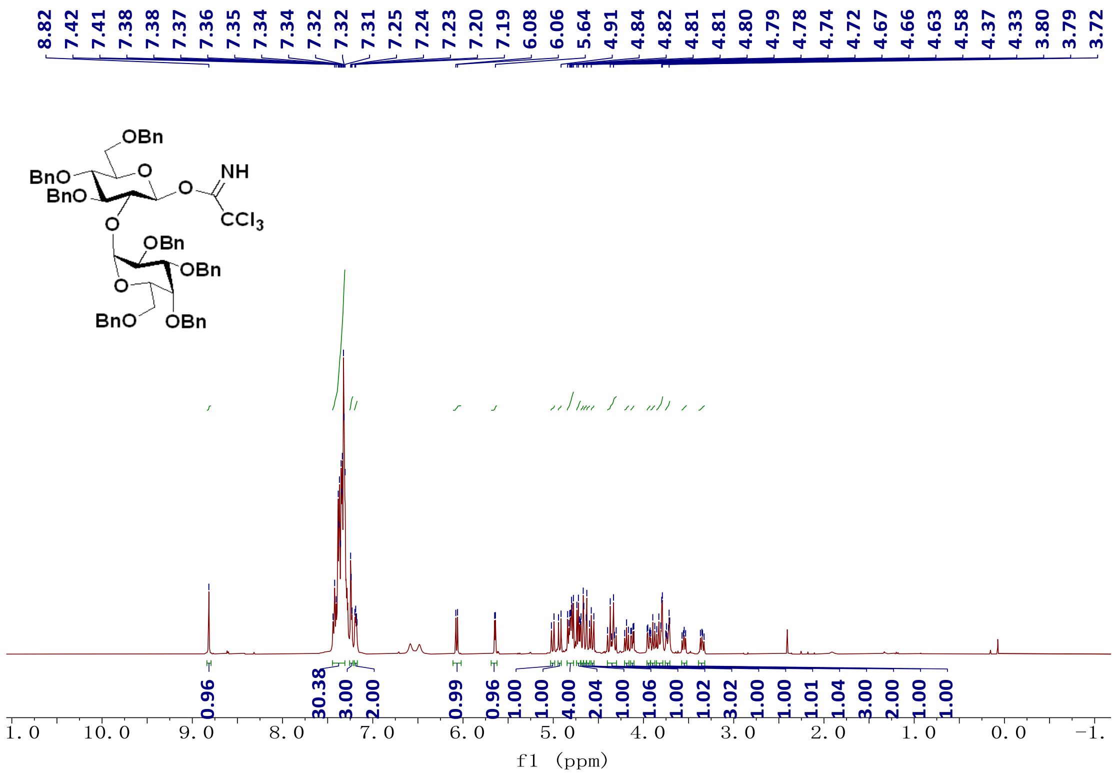

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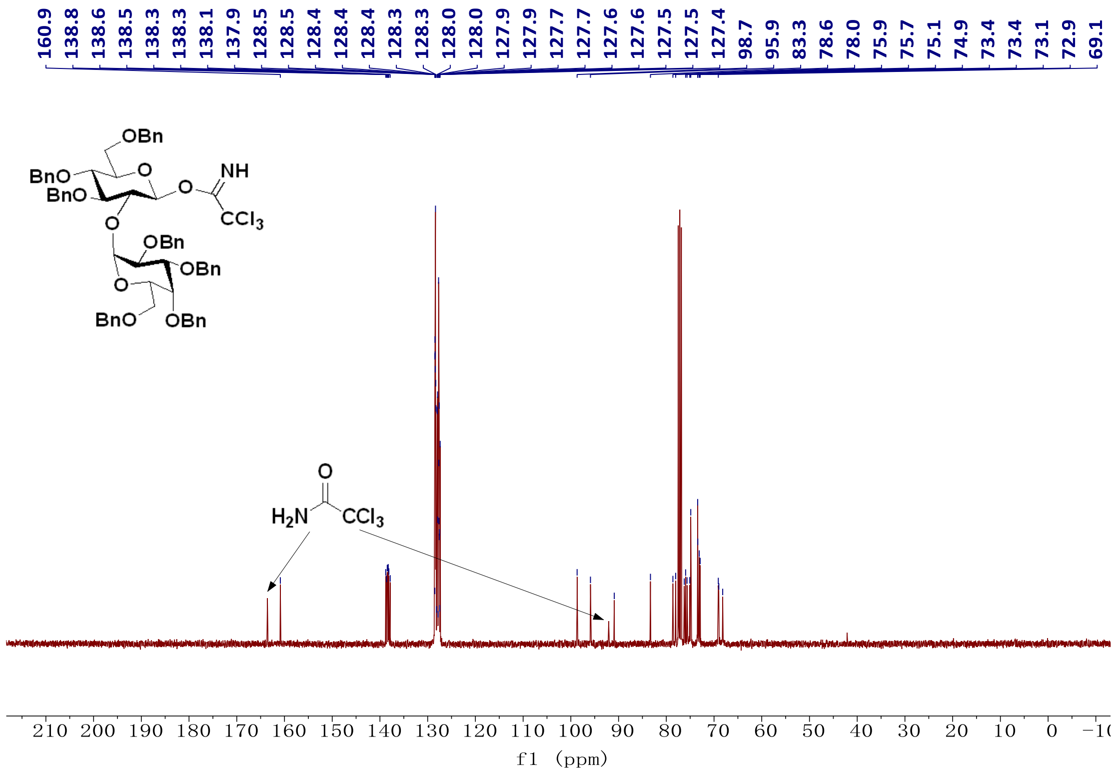

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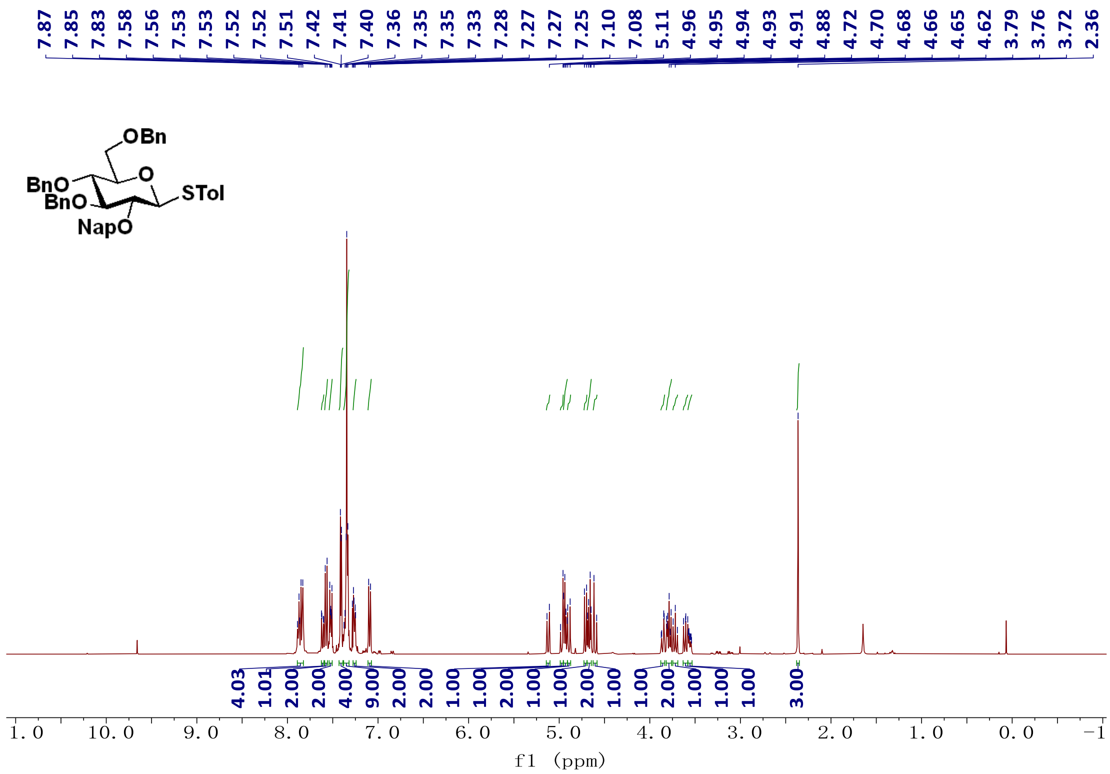

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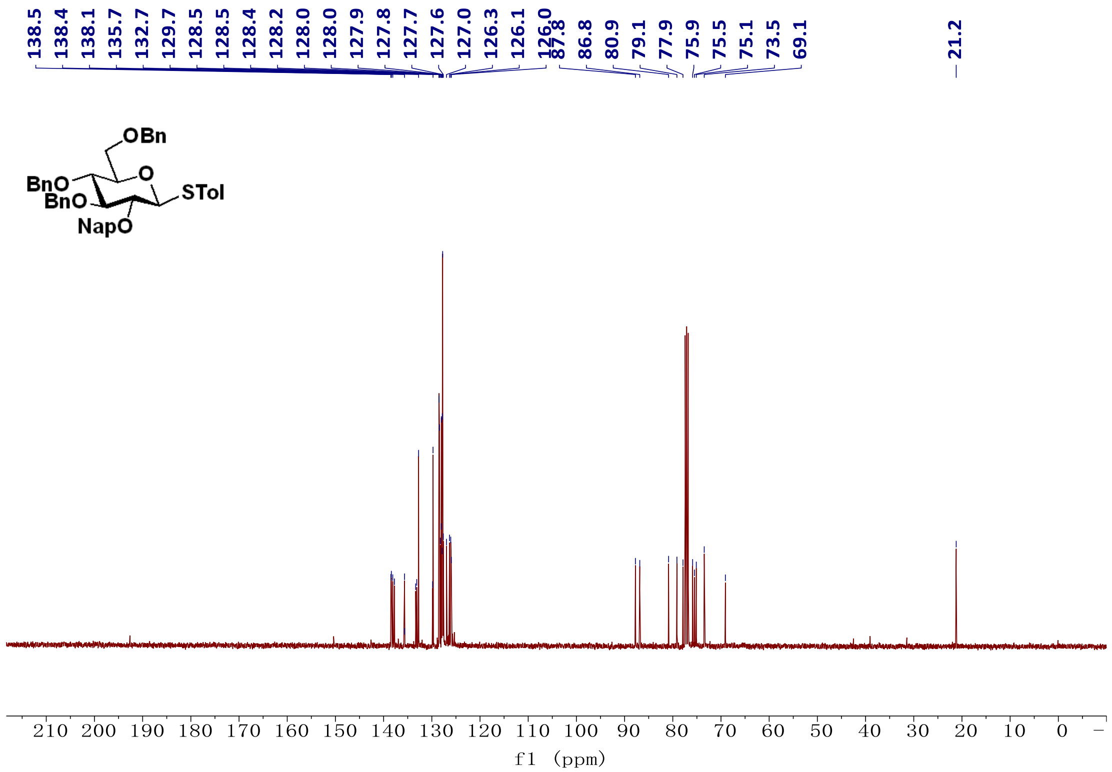

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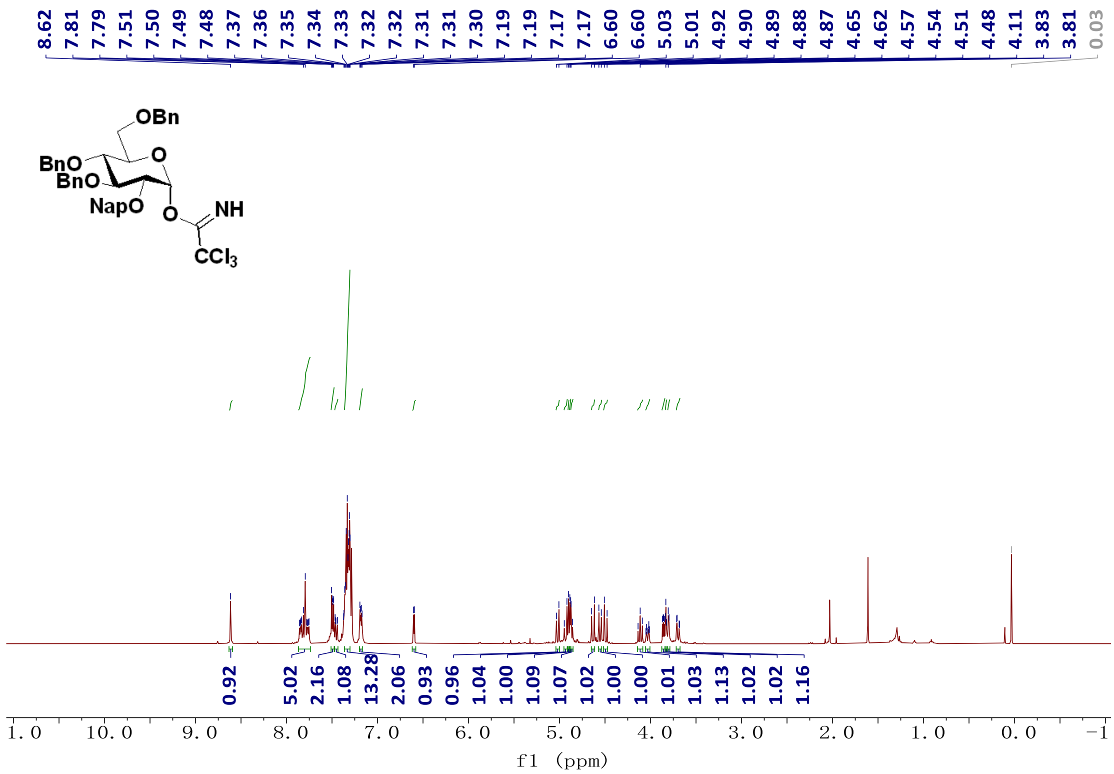

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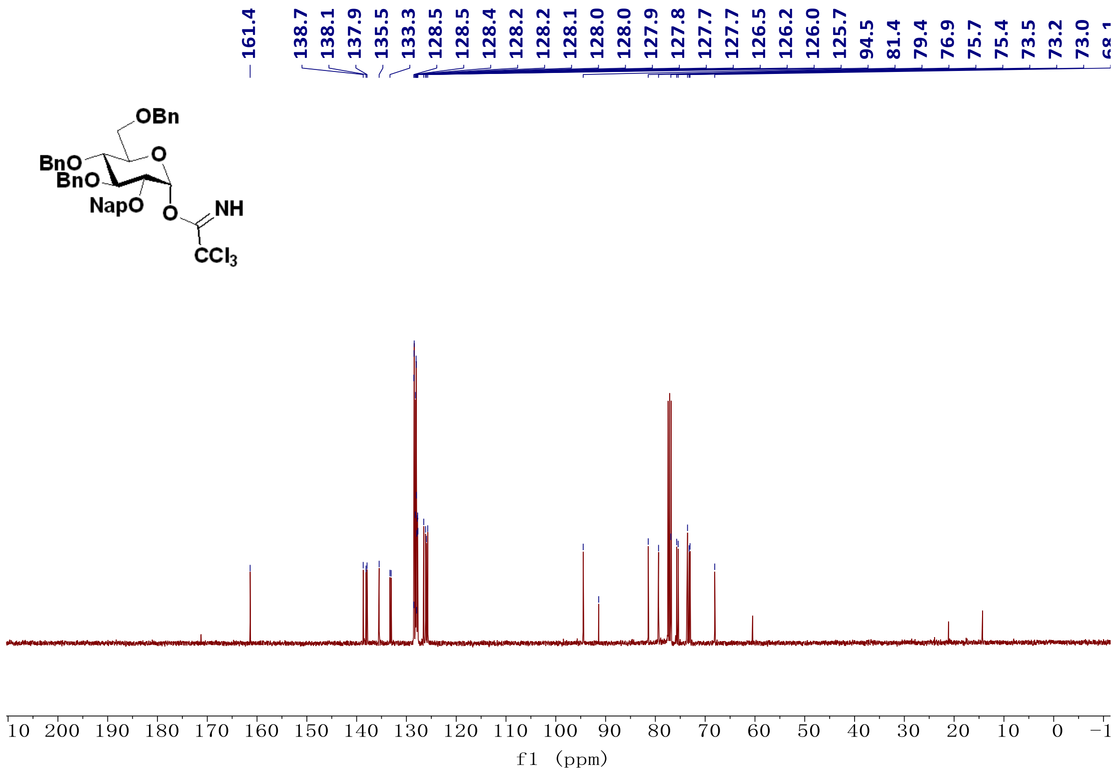

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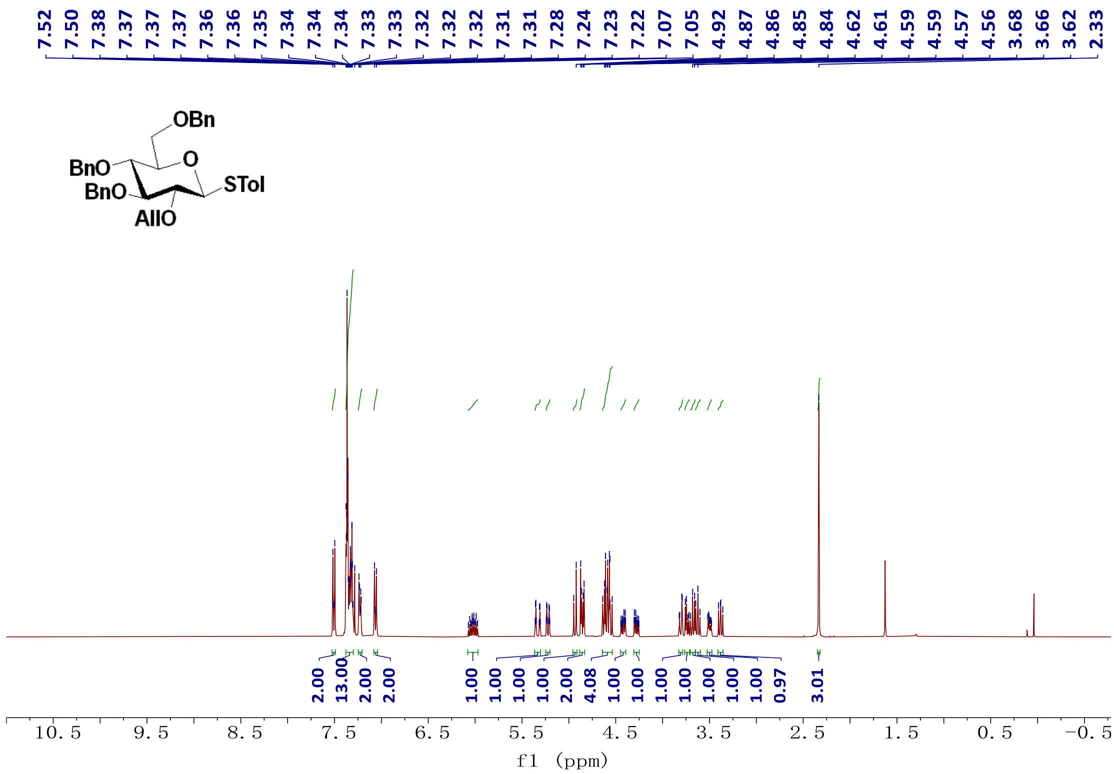

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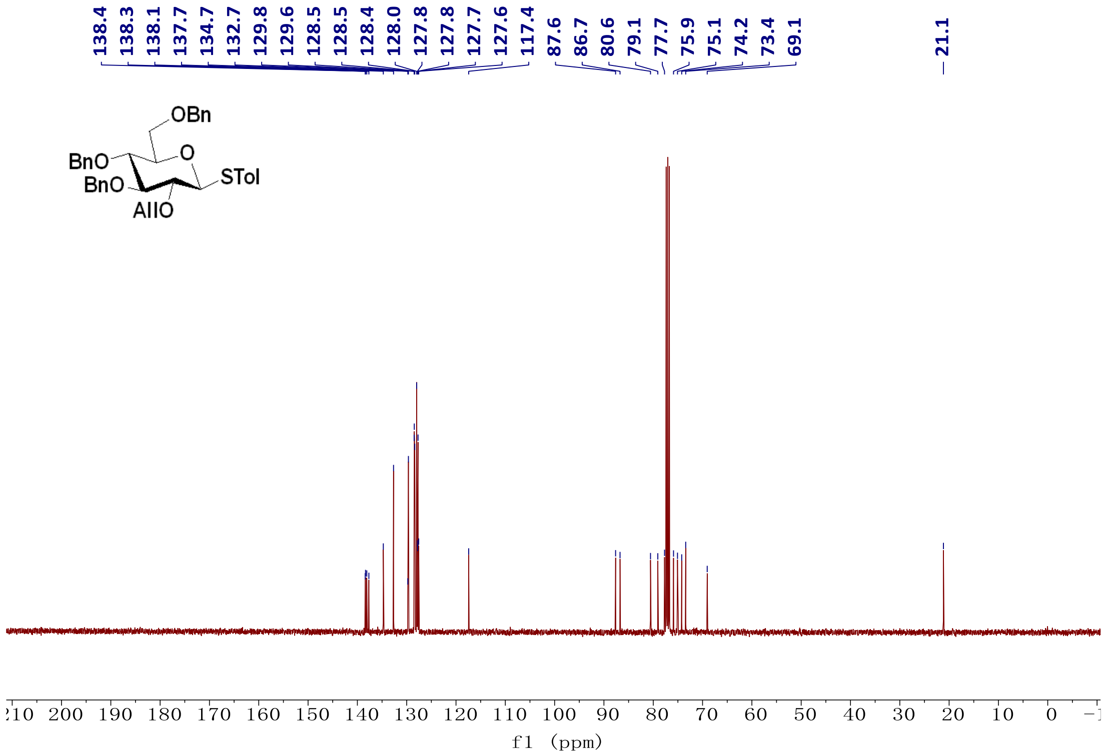

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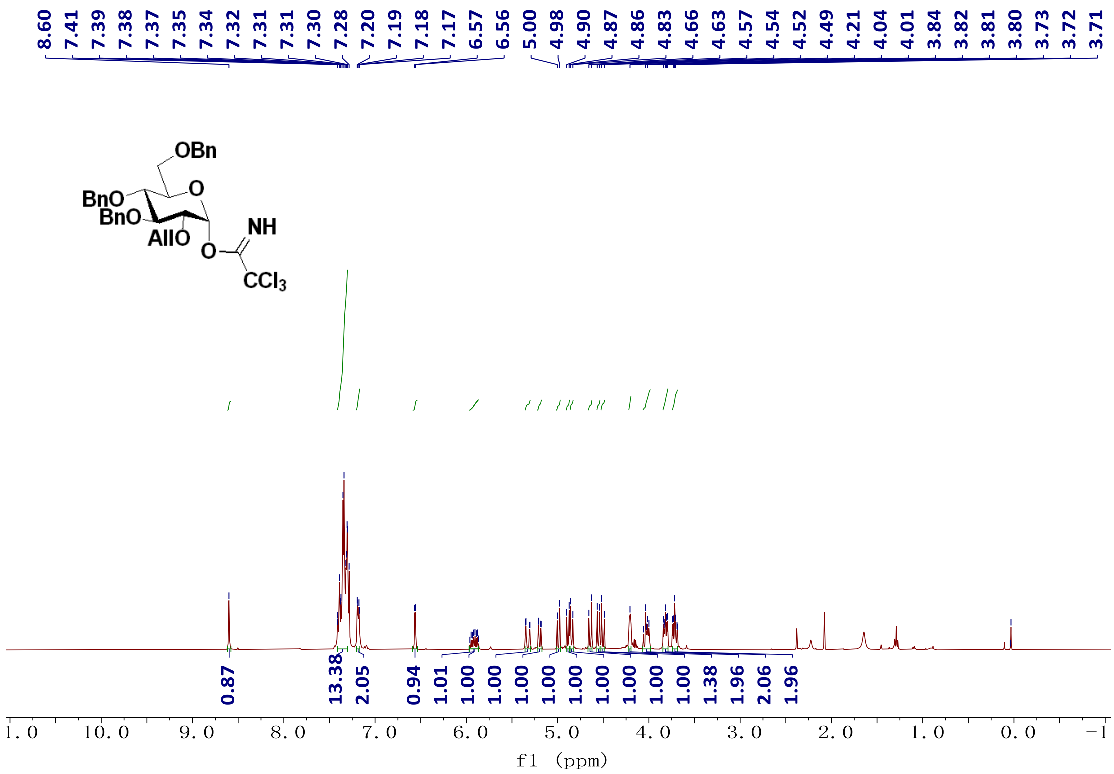

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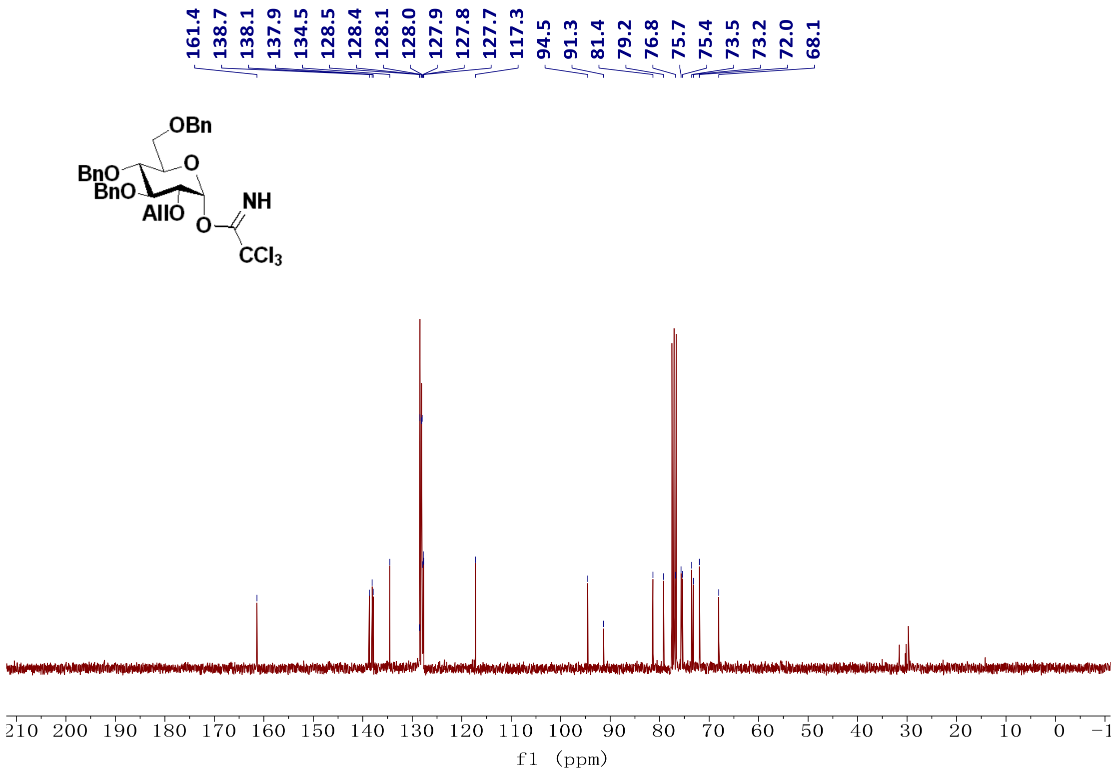

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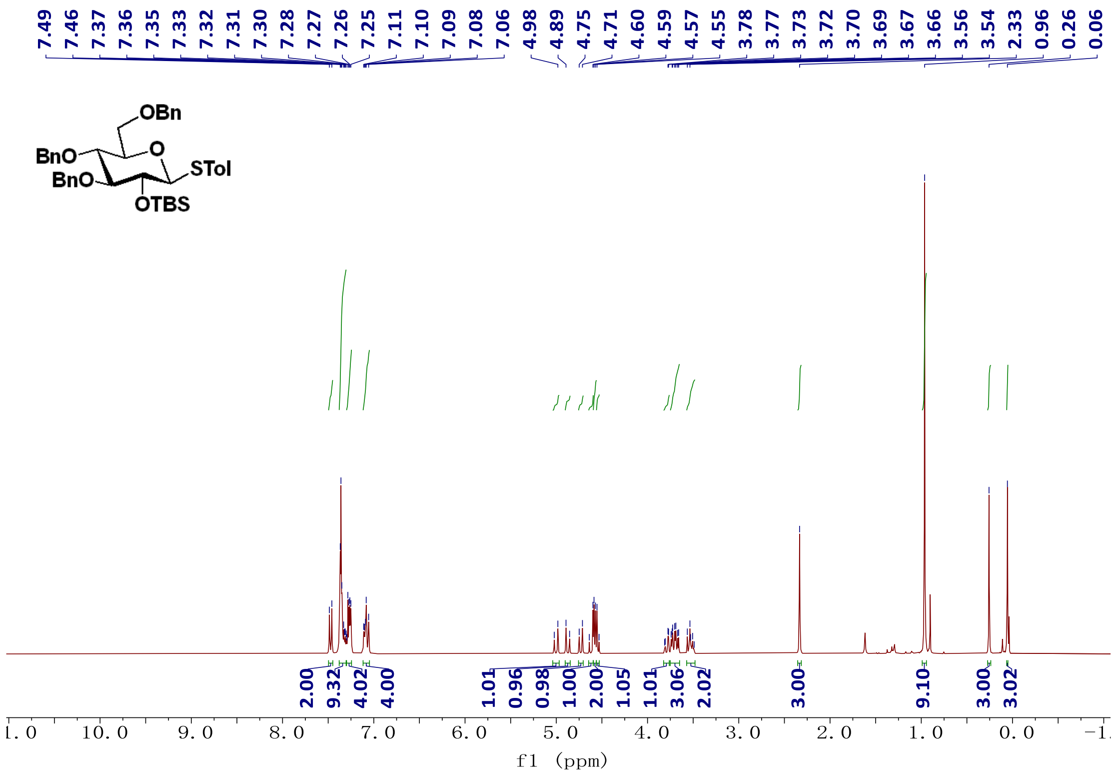

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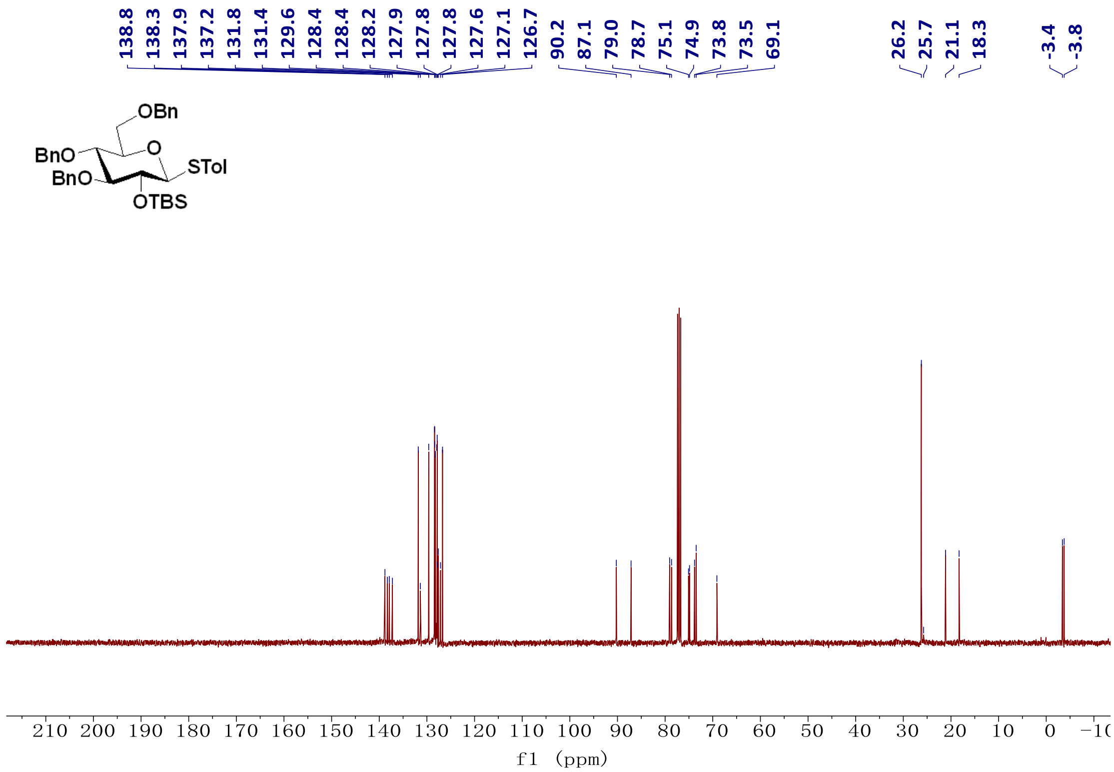

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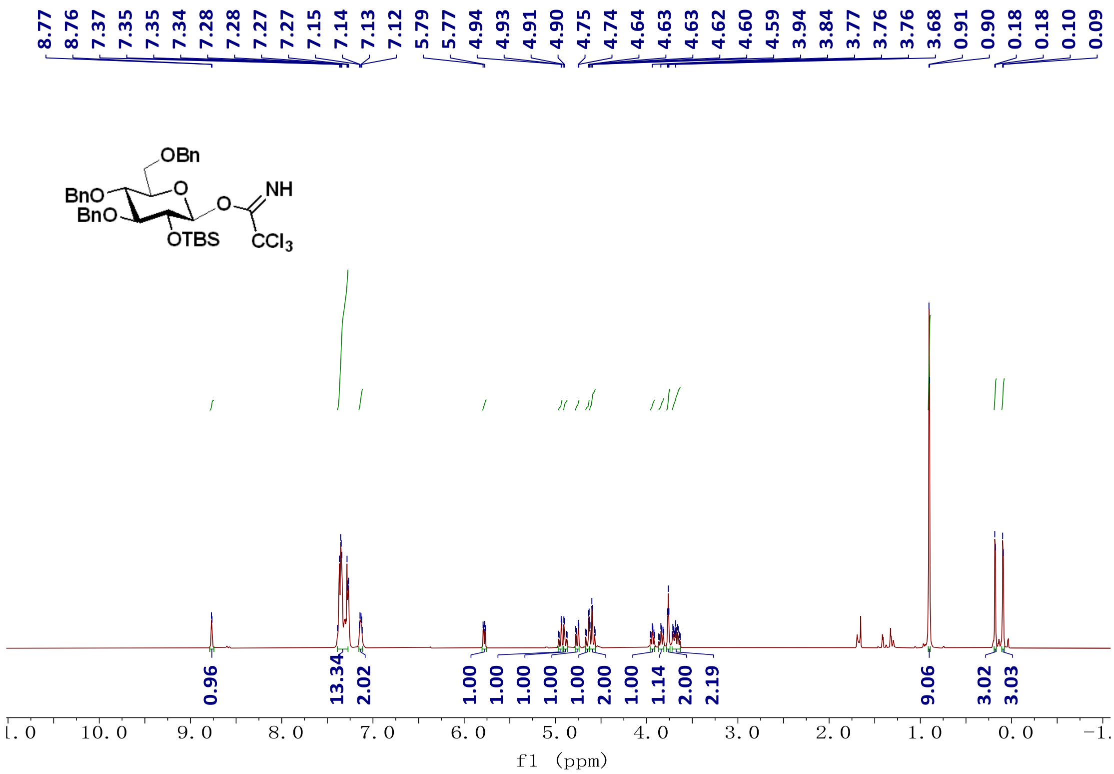
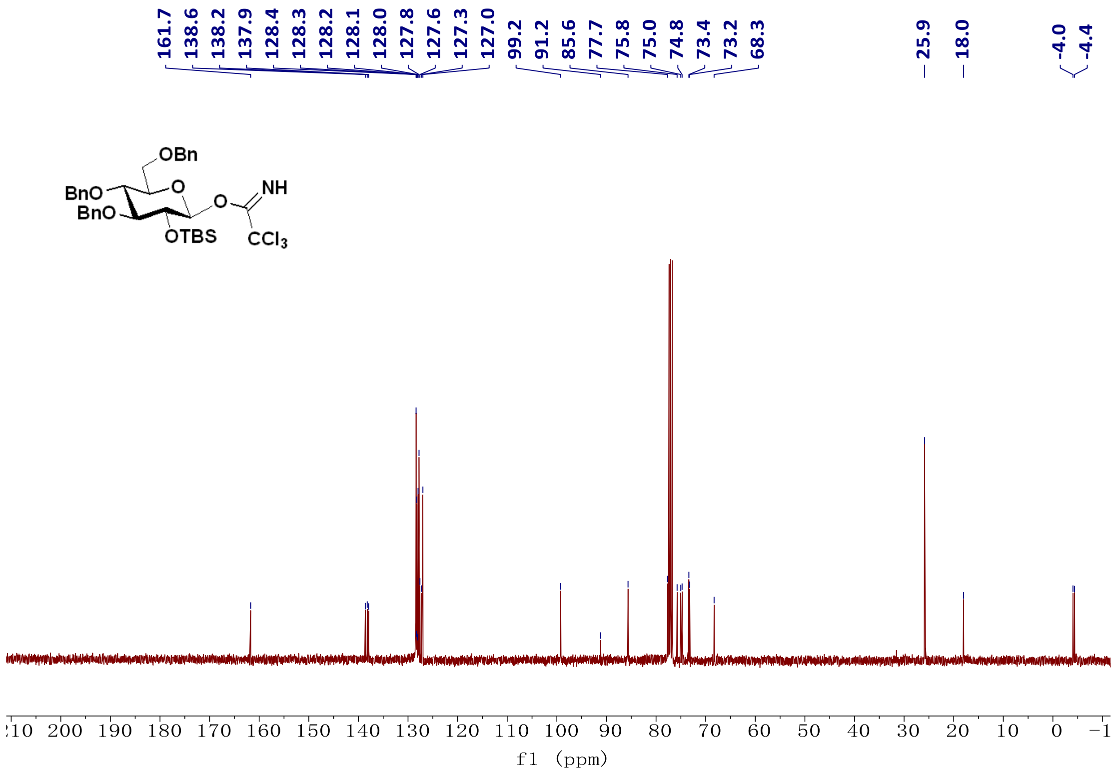
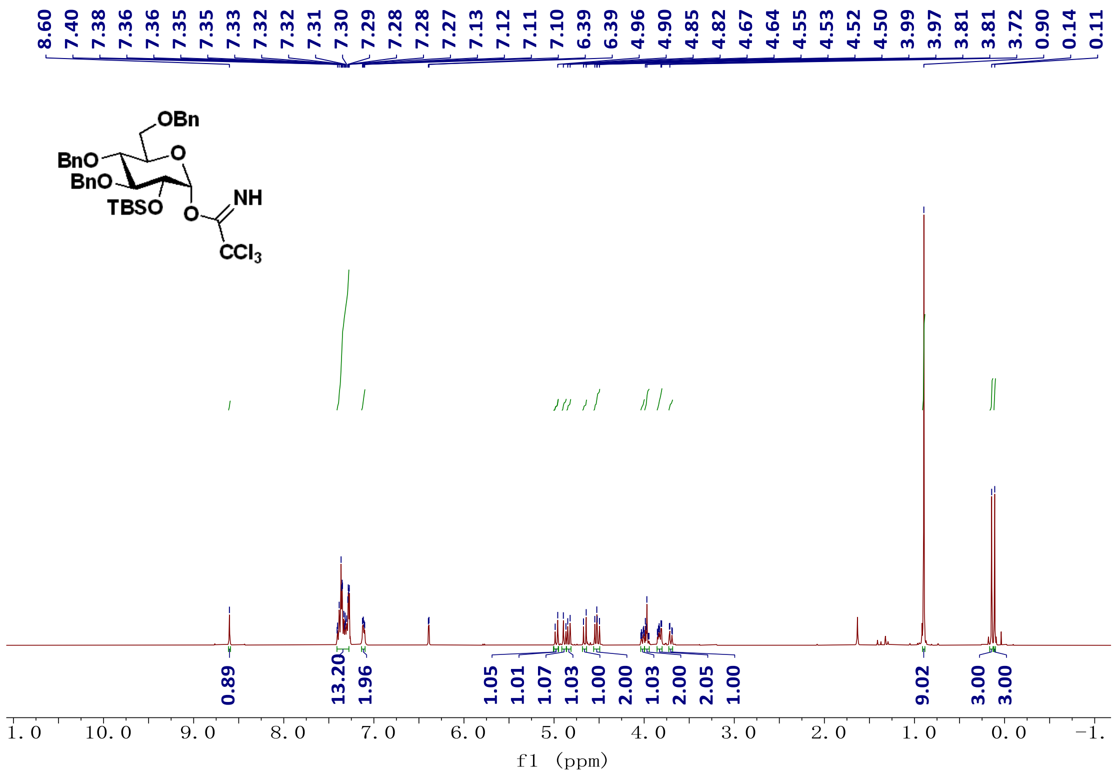


^{1}H NMR of **35 (β)** (400 MHz, $CDCl_3$)



^{13}C NMR of 35 (β) (100 MHz, CDCl$_3$)



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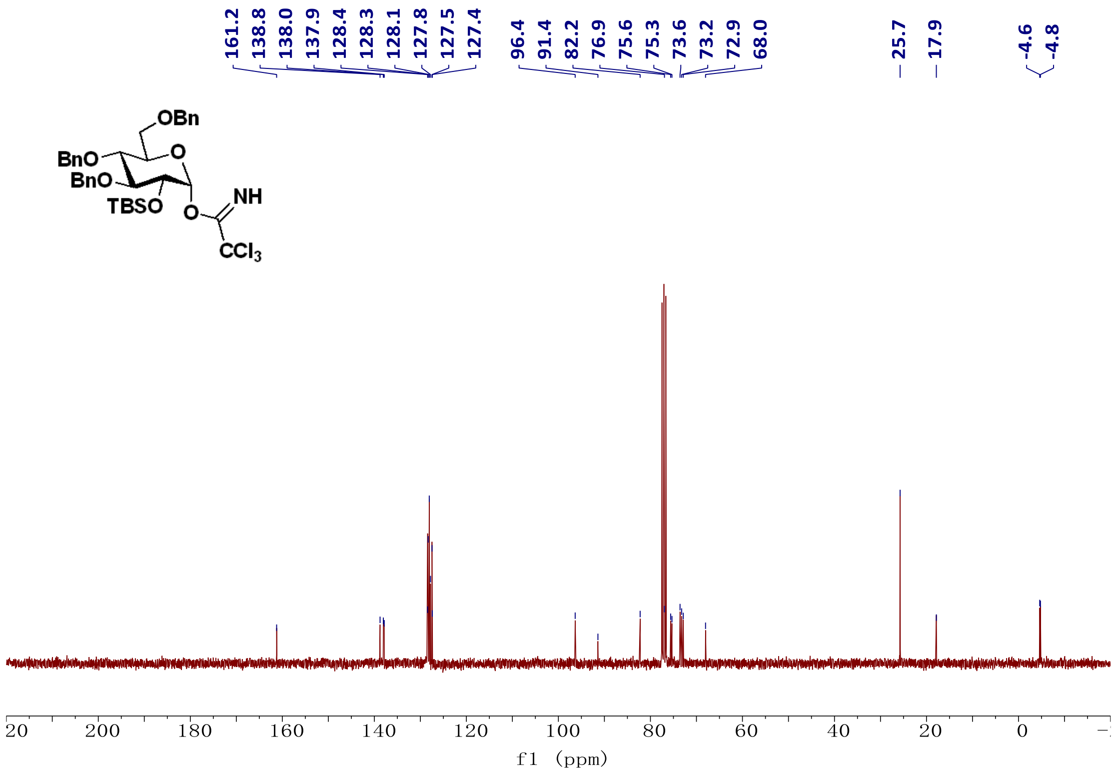

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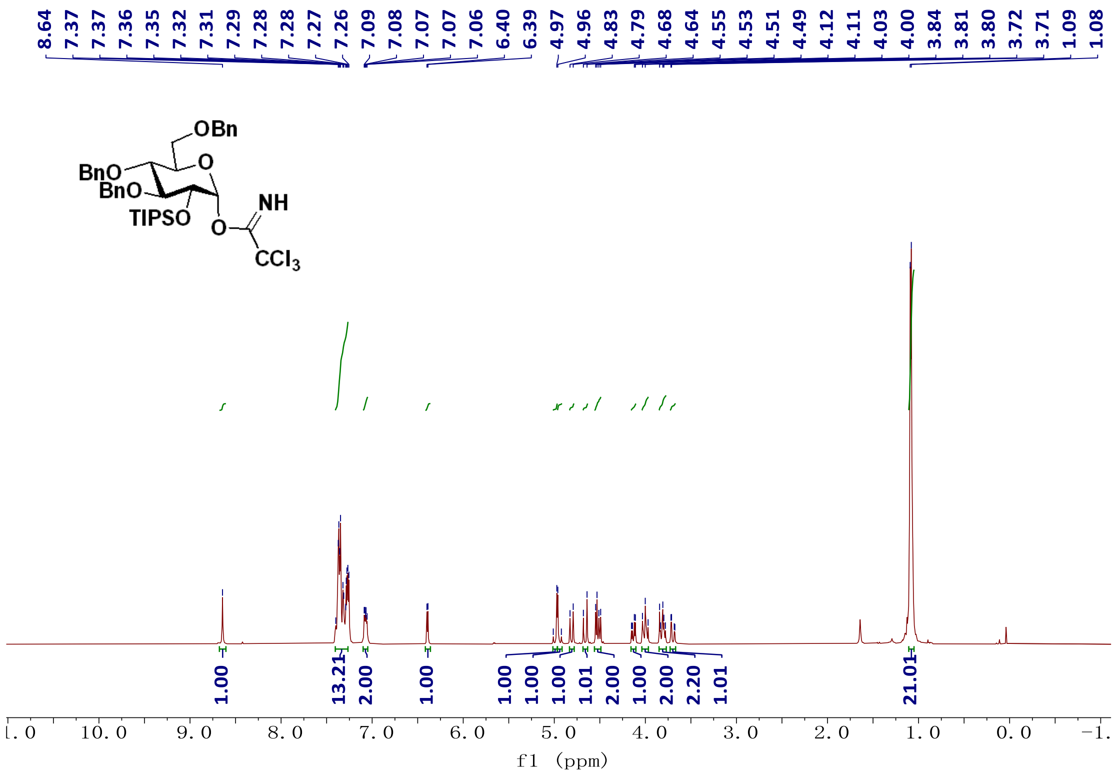

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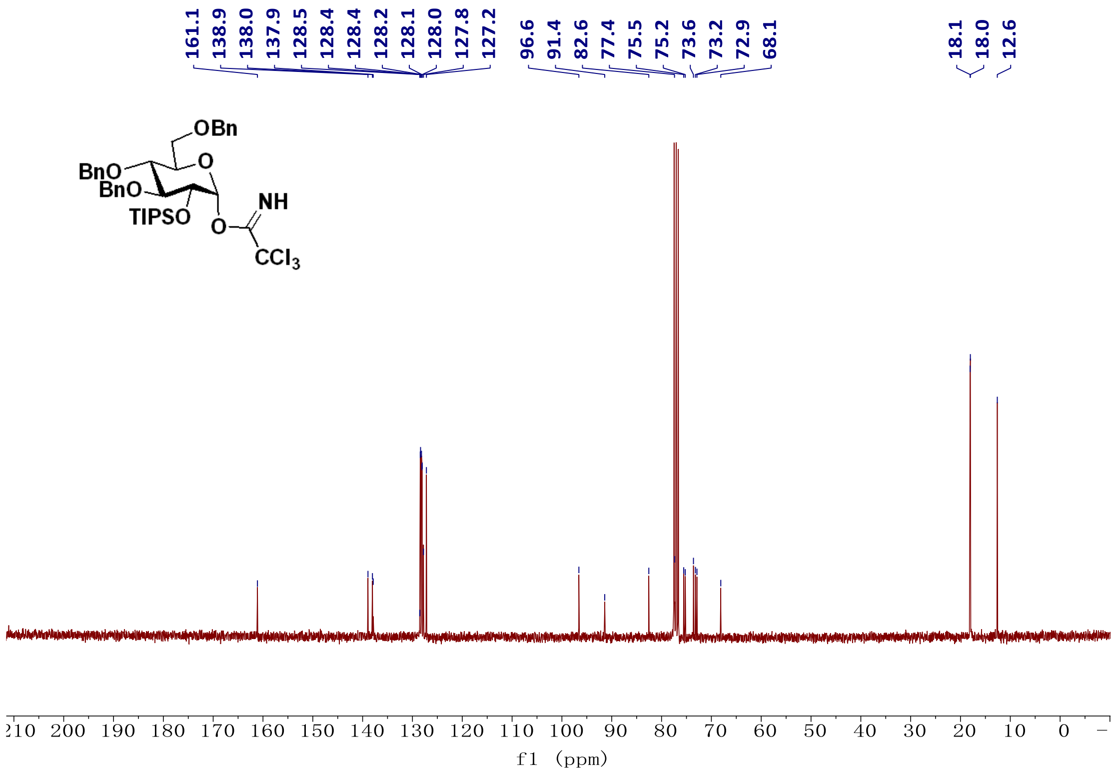

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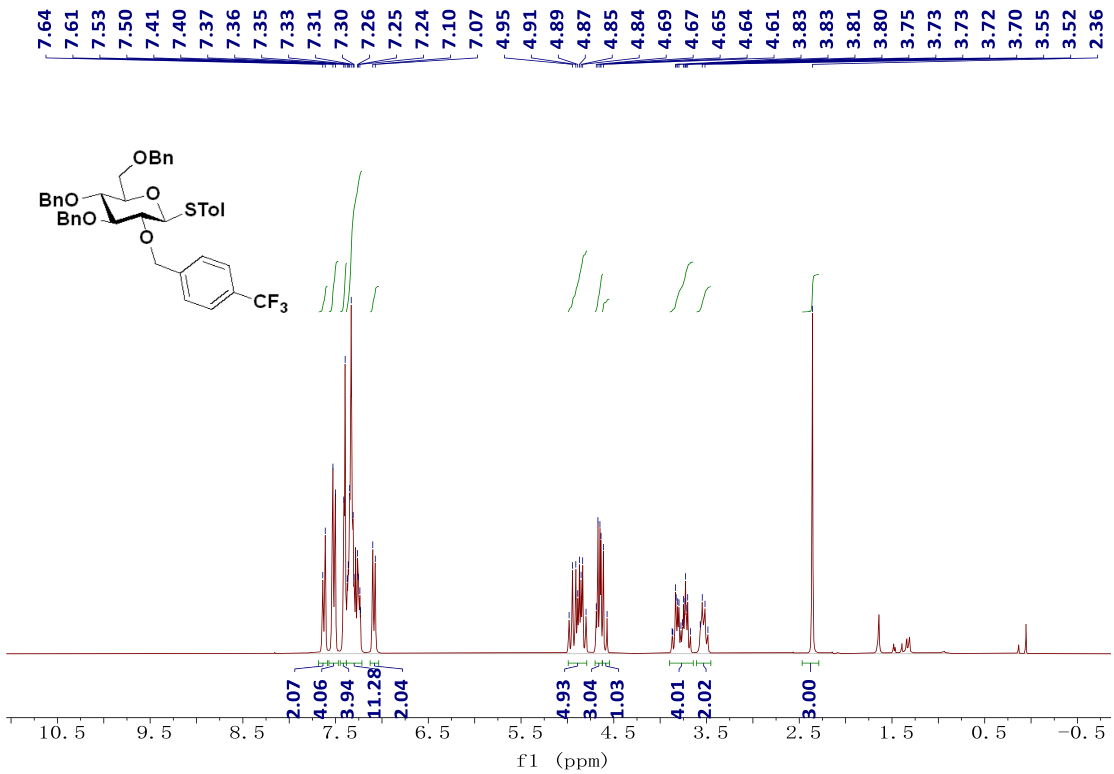

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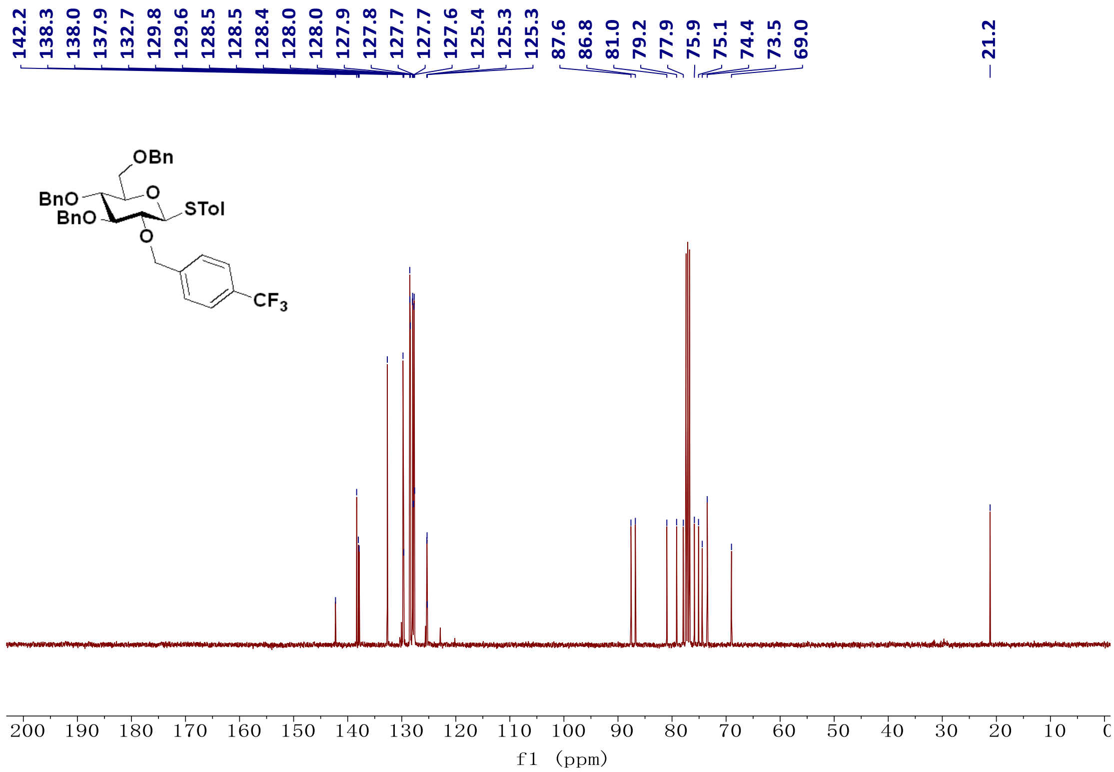

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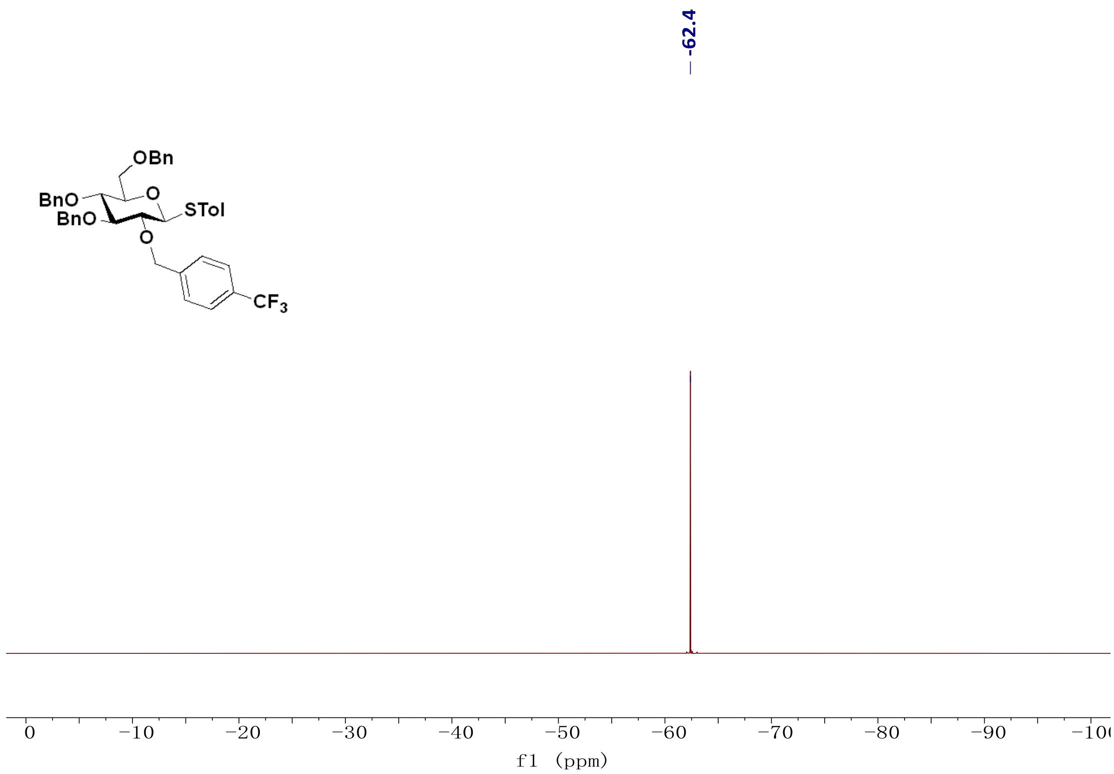
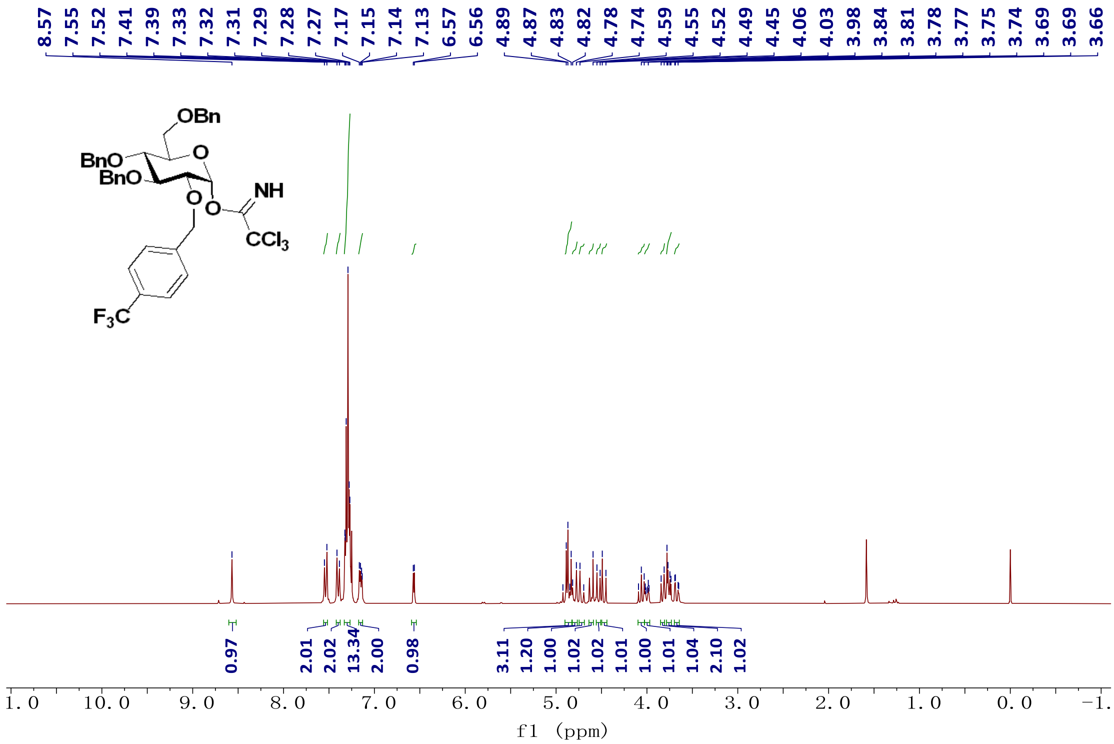
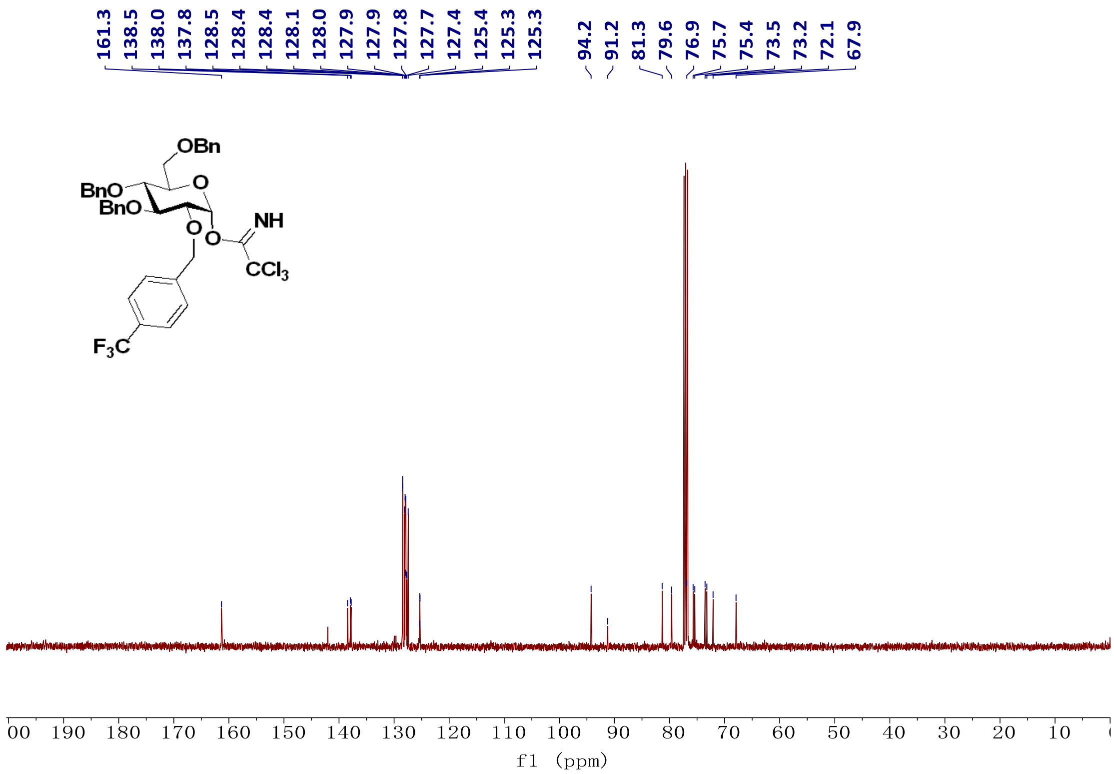


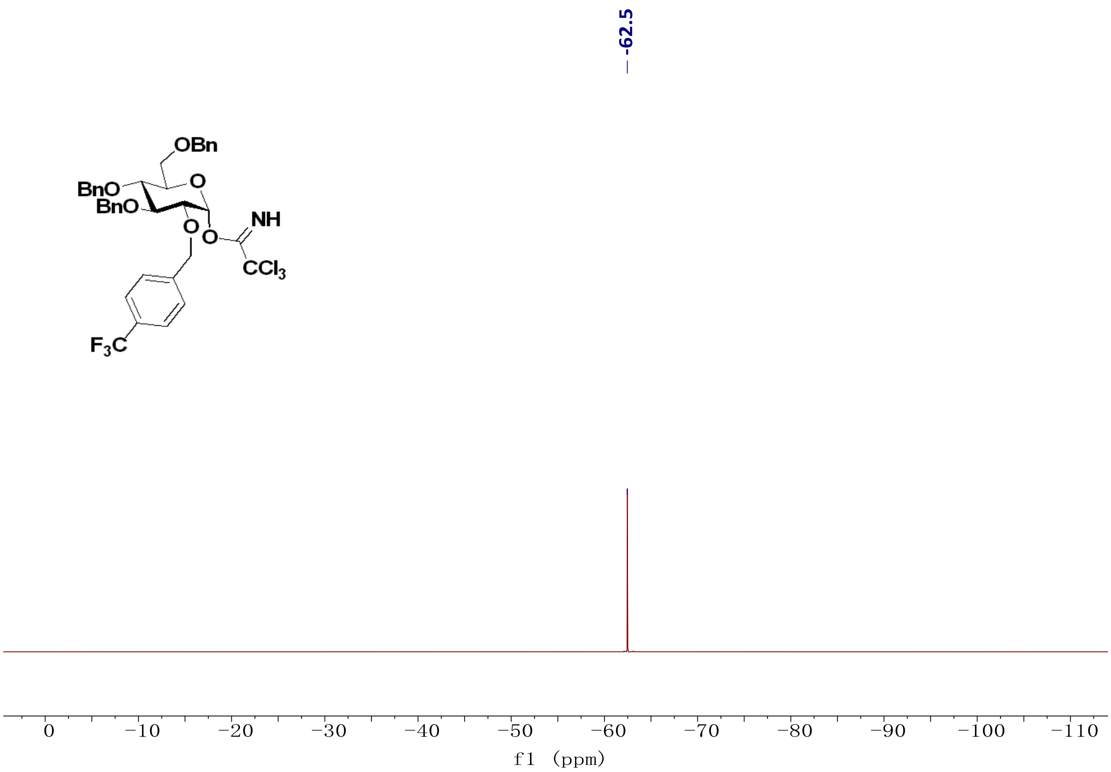
^{19}F NMR of **S23** (282 MHz, $CDCl_3$)



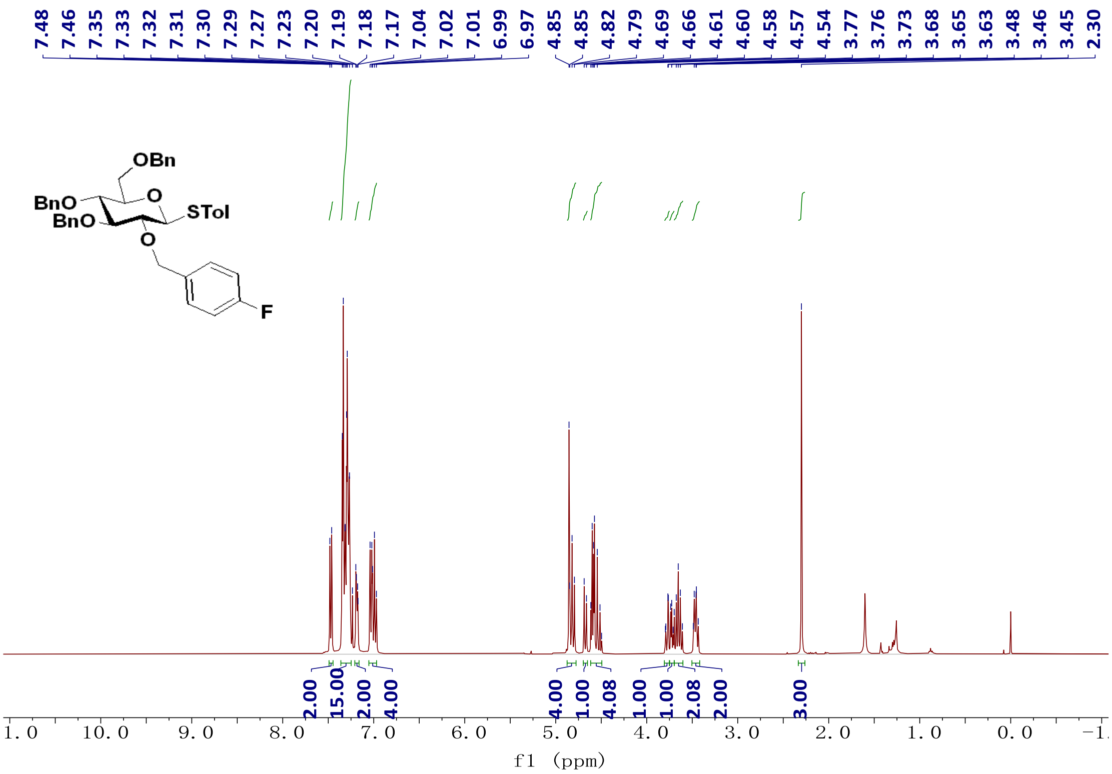
[1]H NMR of **37** (300 MHz, $CDCl_3$)



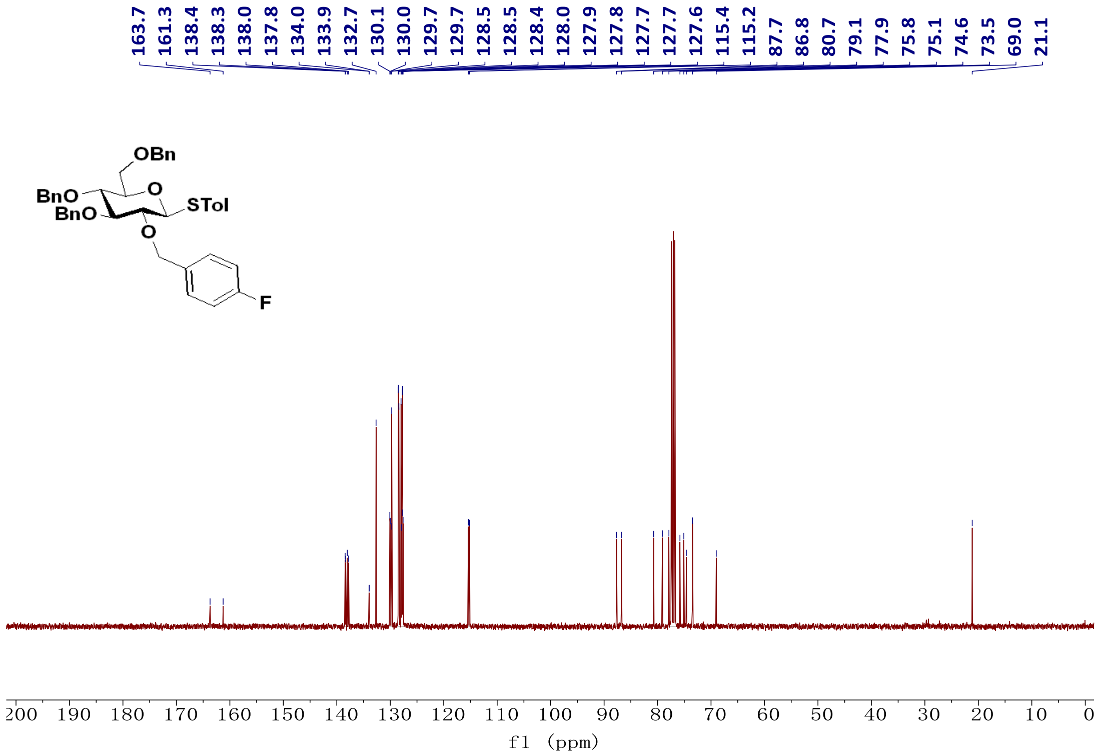
[13]C NMR of **37** (100 MHz, $CDCl_3$)



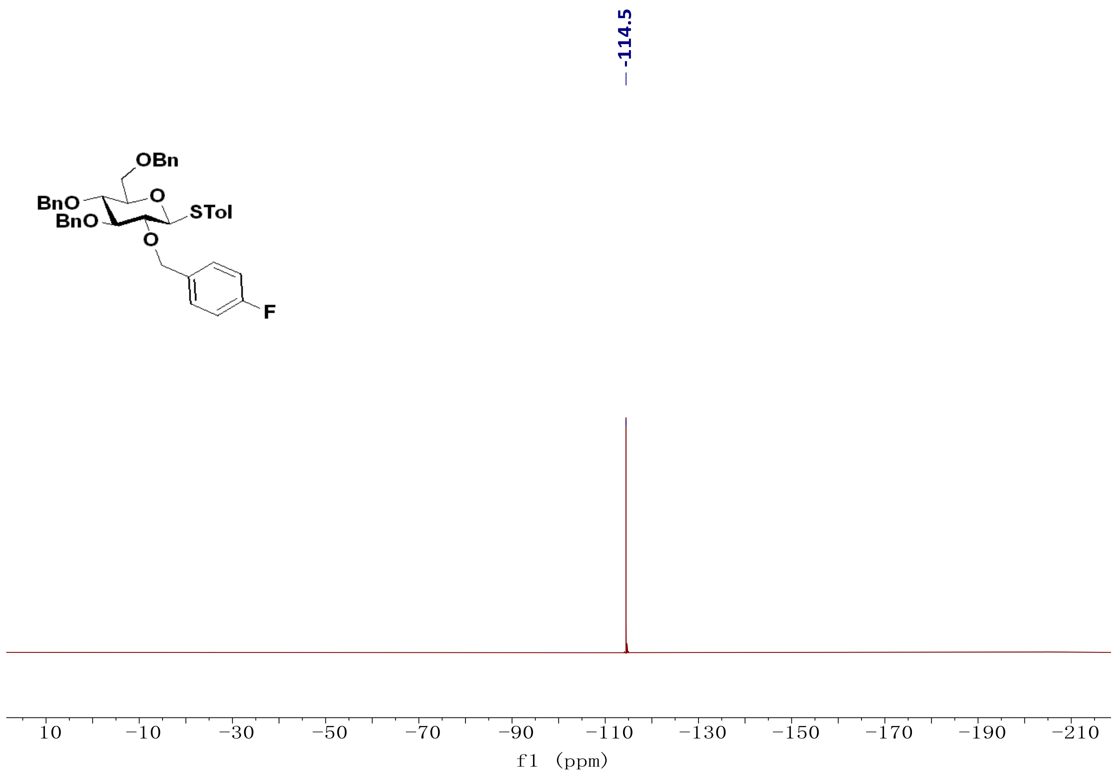
^{19}F NMR of **37** (282 MHz, $CDCl_3$)



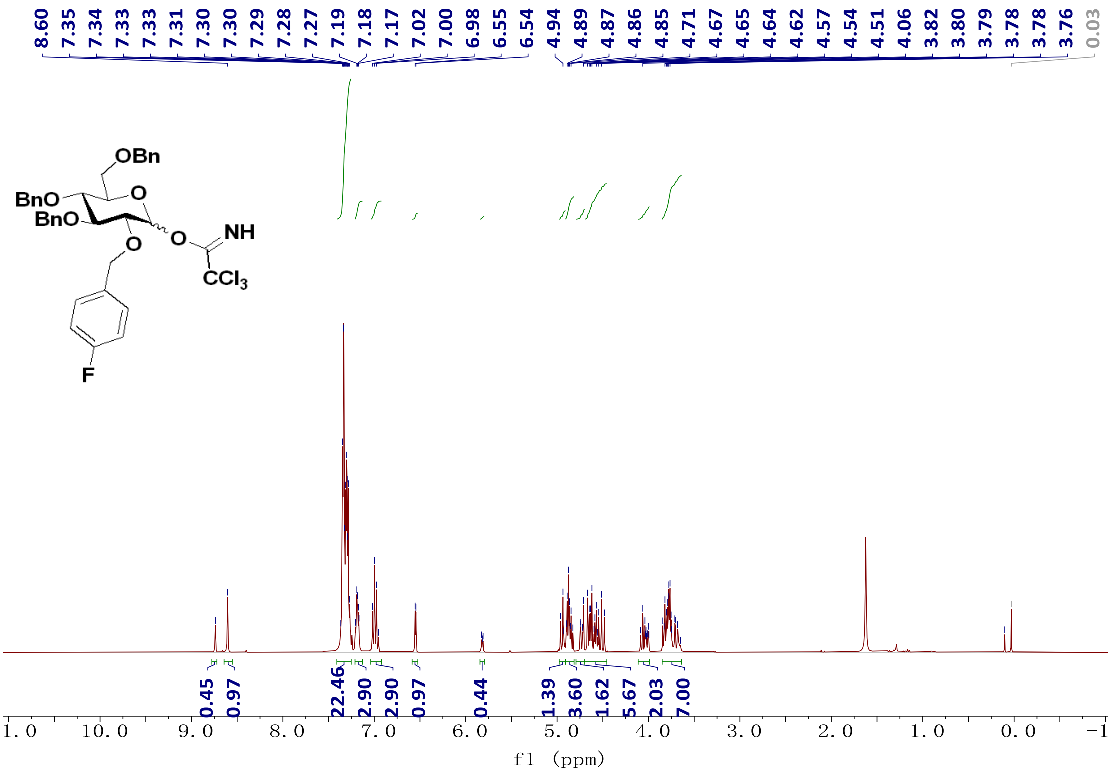
^{1}H NMR of **S24** (400 MHz, $CDCl_3$)



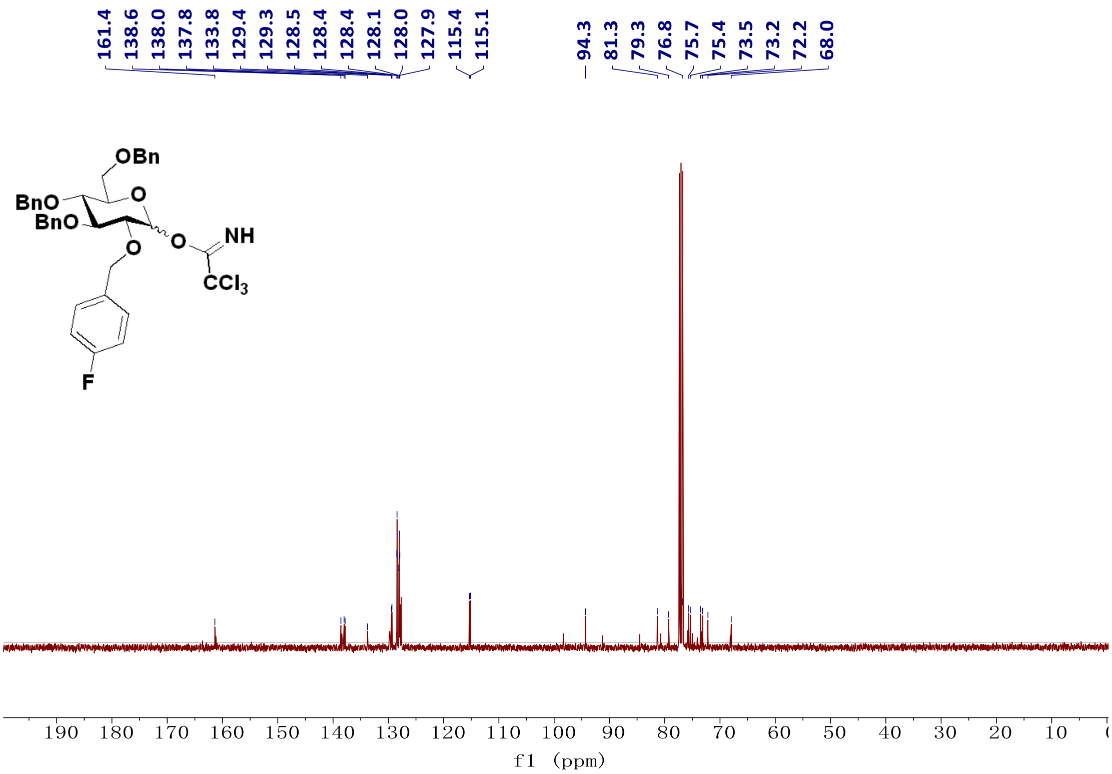
^{13}C NMR of **S24** (100 MHz, $CDCl_3$)



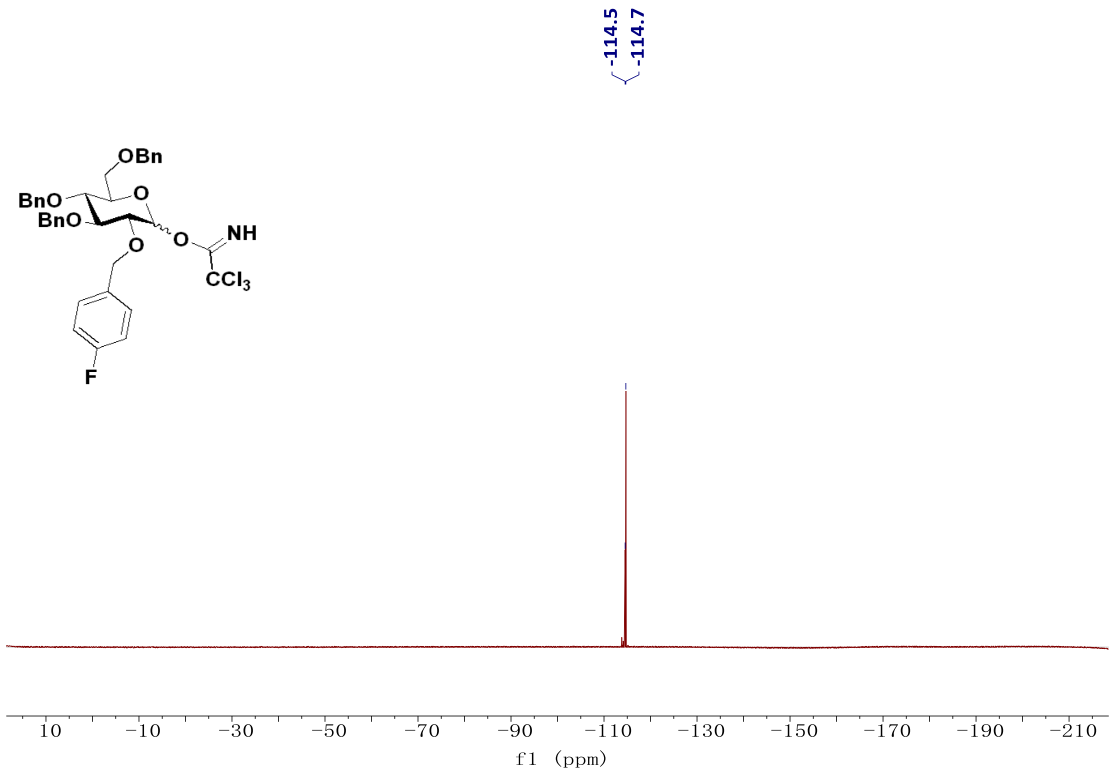
^{19}F NMR of **S24** (282 MHz, $CDCl_3$)



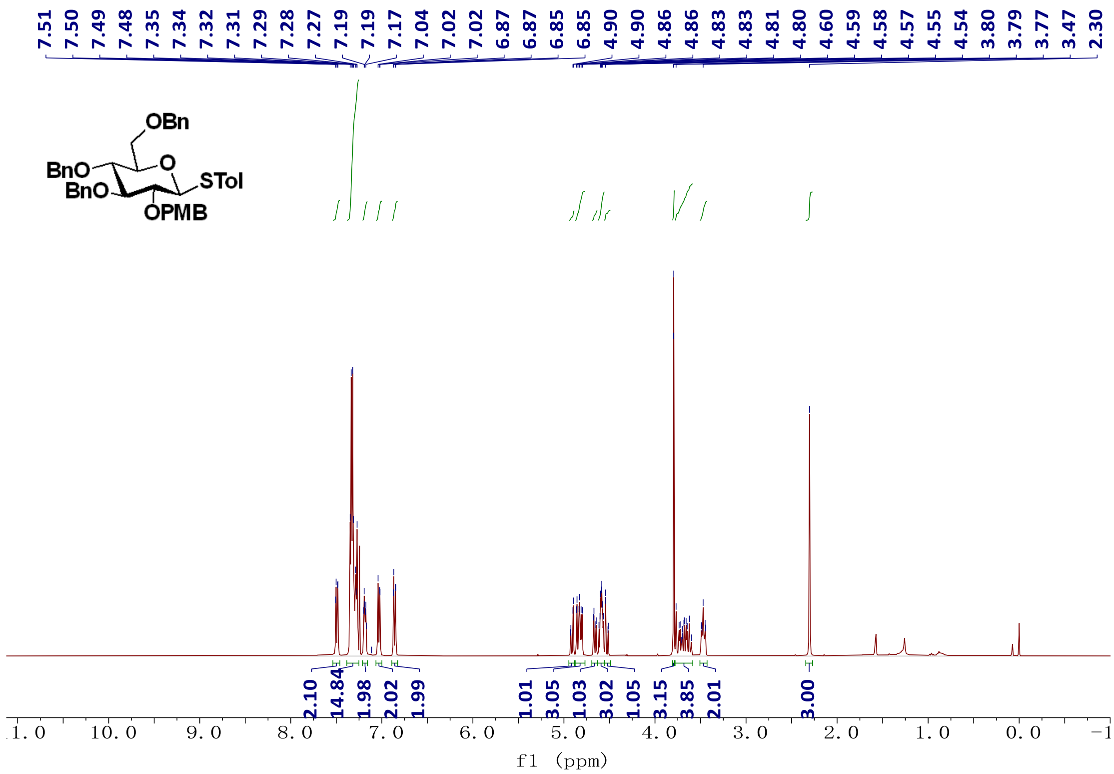
^{1}H NMR of **38** (400 MHz, $CDCl_3$)



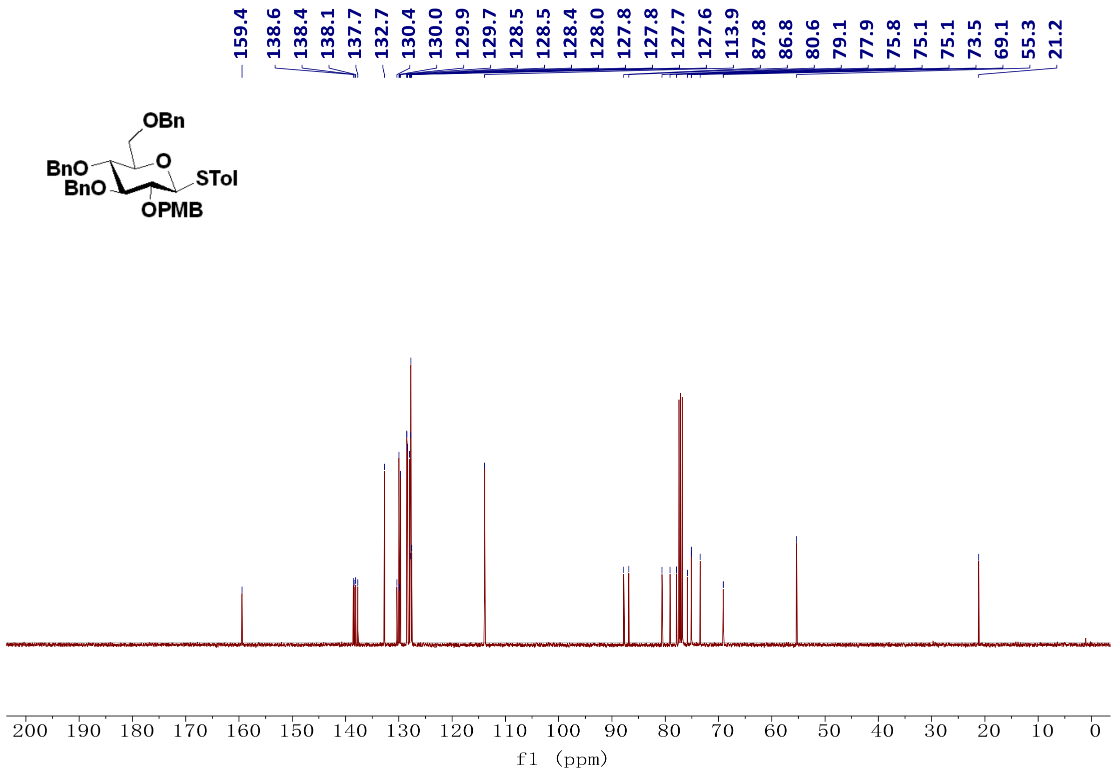
^{13}C NMR of **38** (100 MHz, $CDCl_3$)



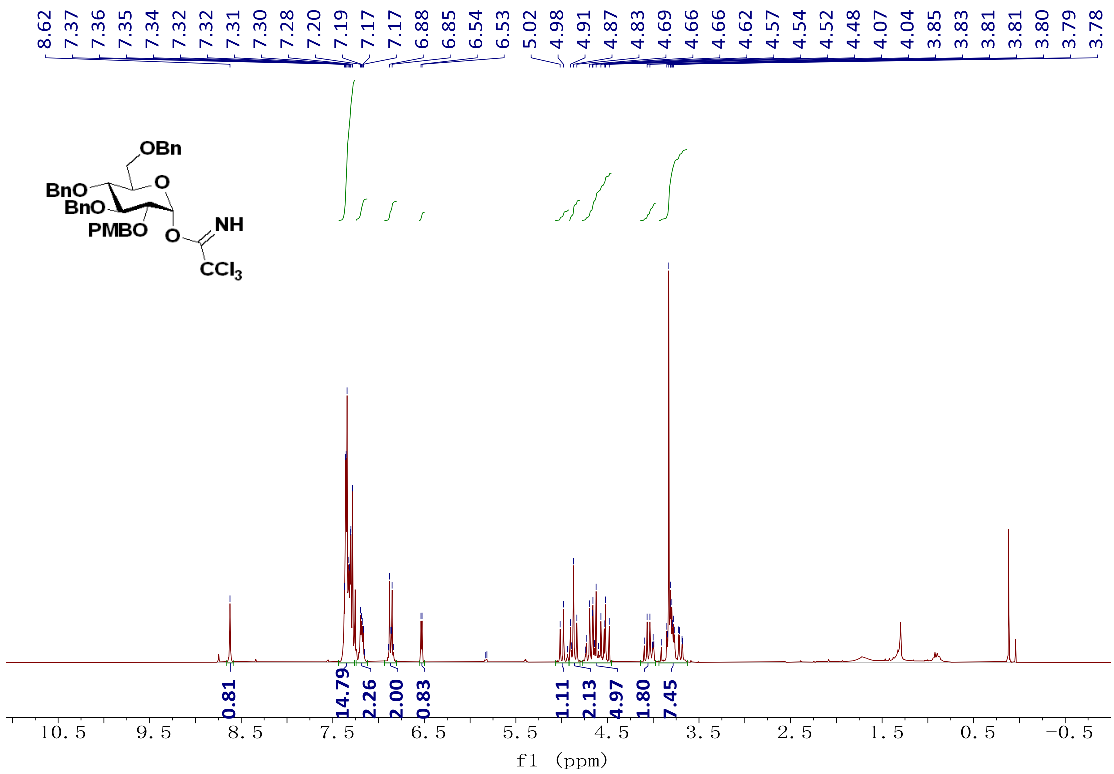
^{19}F NMR of **38** (282 MHz, $CDCl_3$)



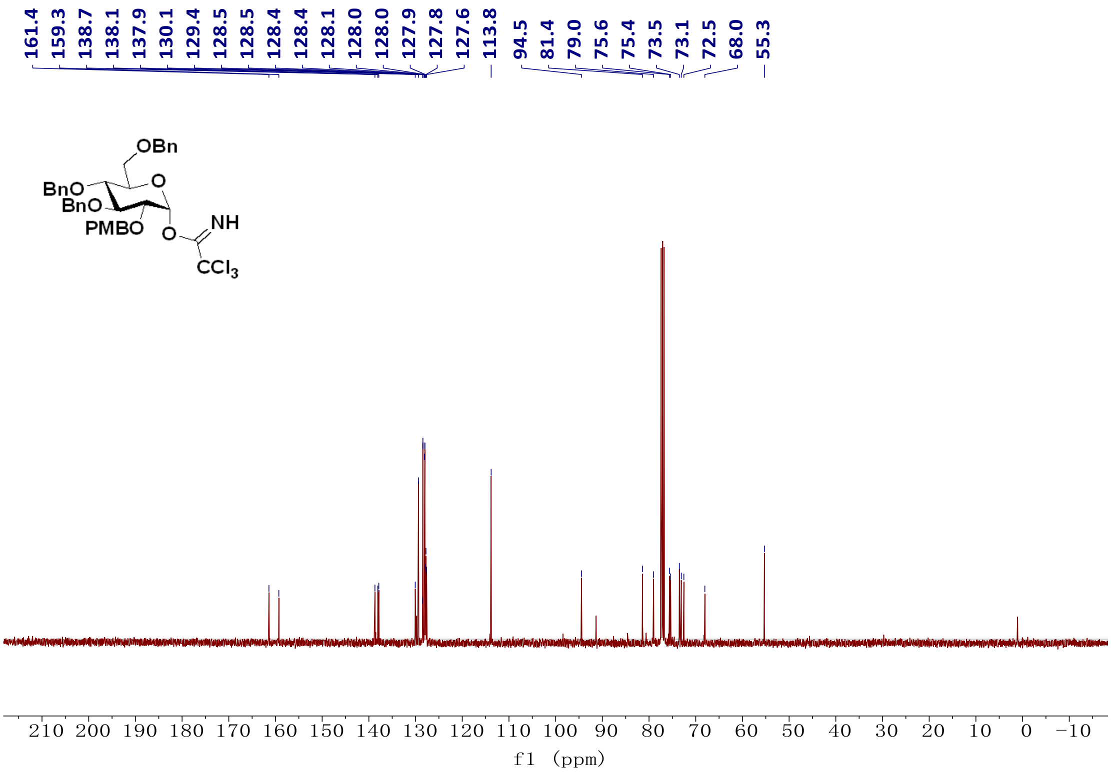
^{1}H NMR of **S25** (400 MHz, $CDCl_3$)



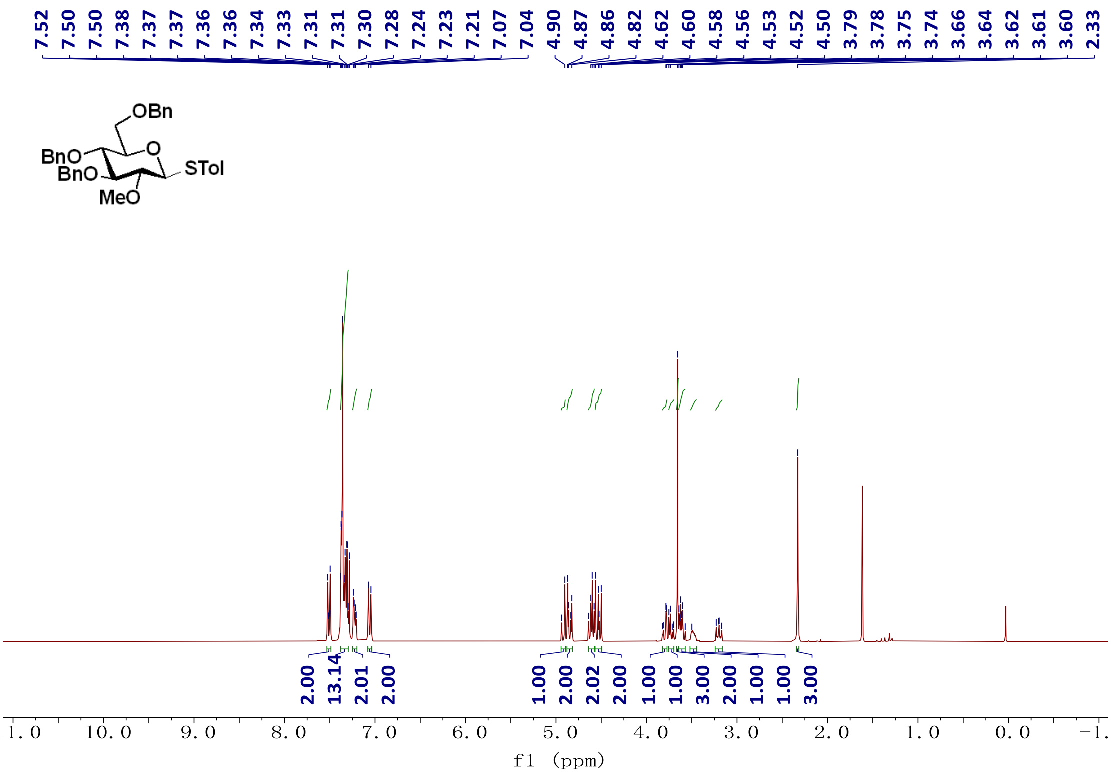
^{13}C NMR of **S25** (100 MHz, $CDCl_3$)



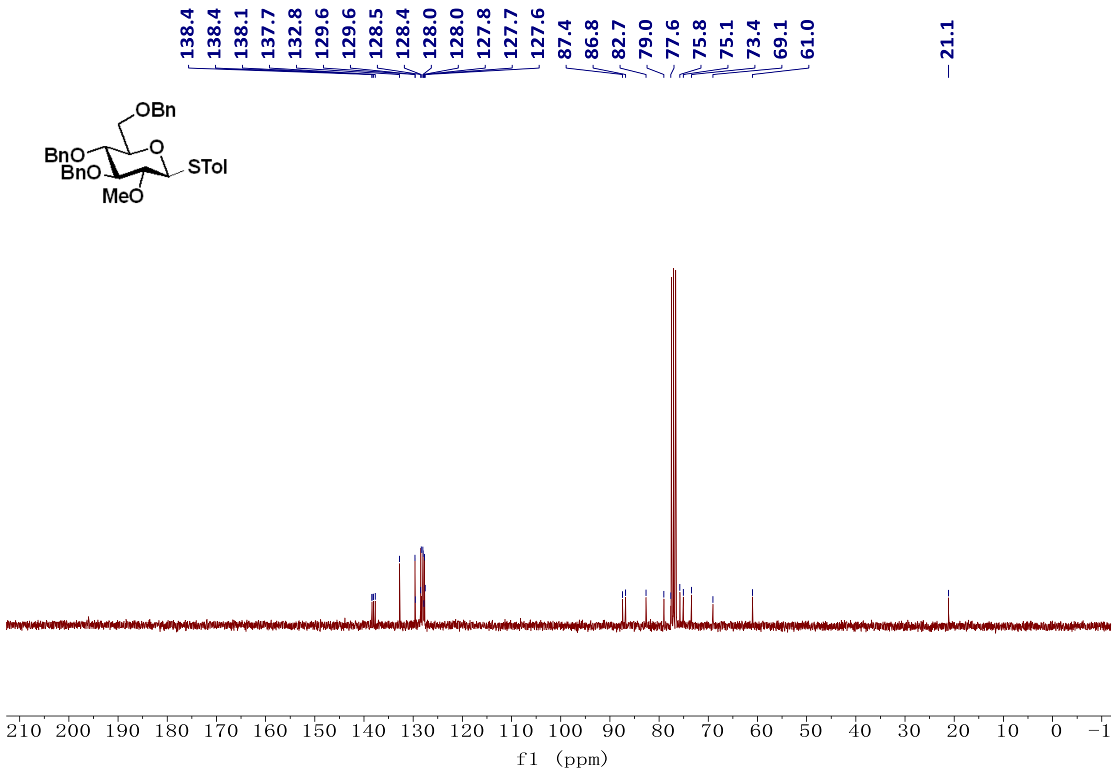
^{1}H NMR of **39** (400 MHz, $CDCl_3$)



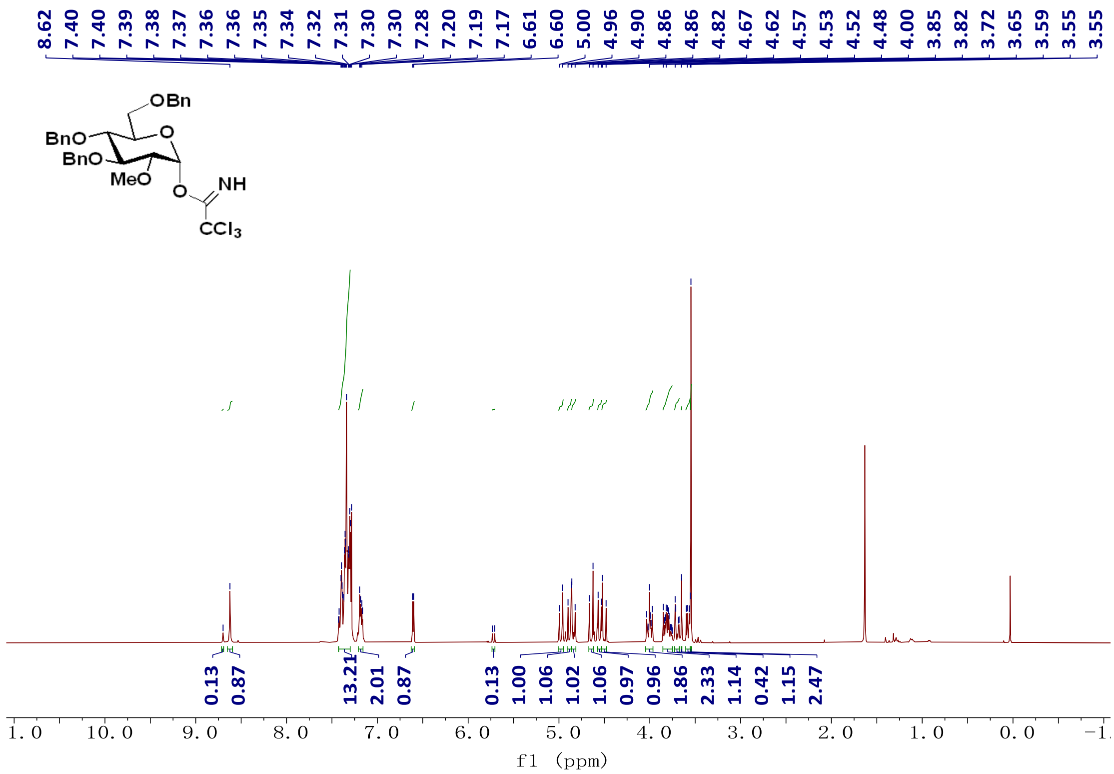
^{13}C NMR of **39** (100 MHz, $CDCl_3$)



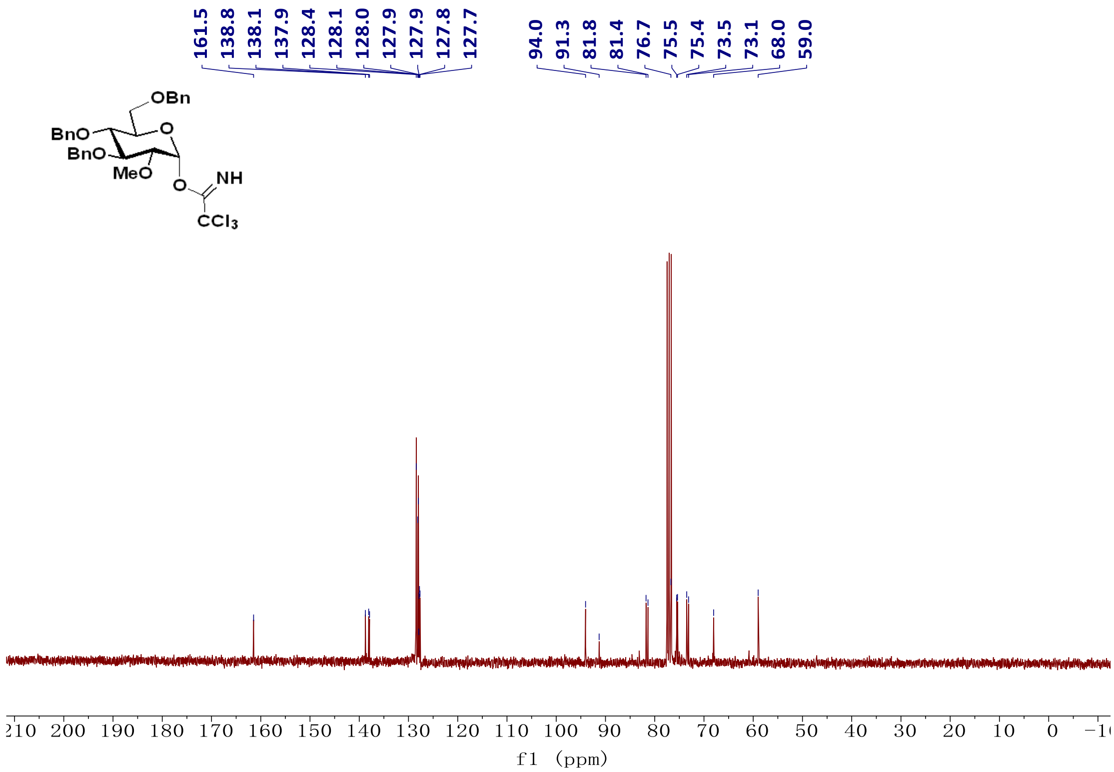
^{1}H NMR of **S26** (300 MHz, $CDCl_3$)



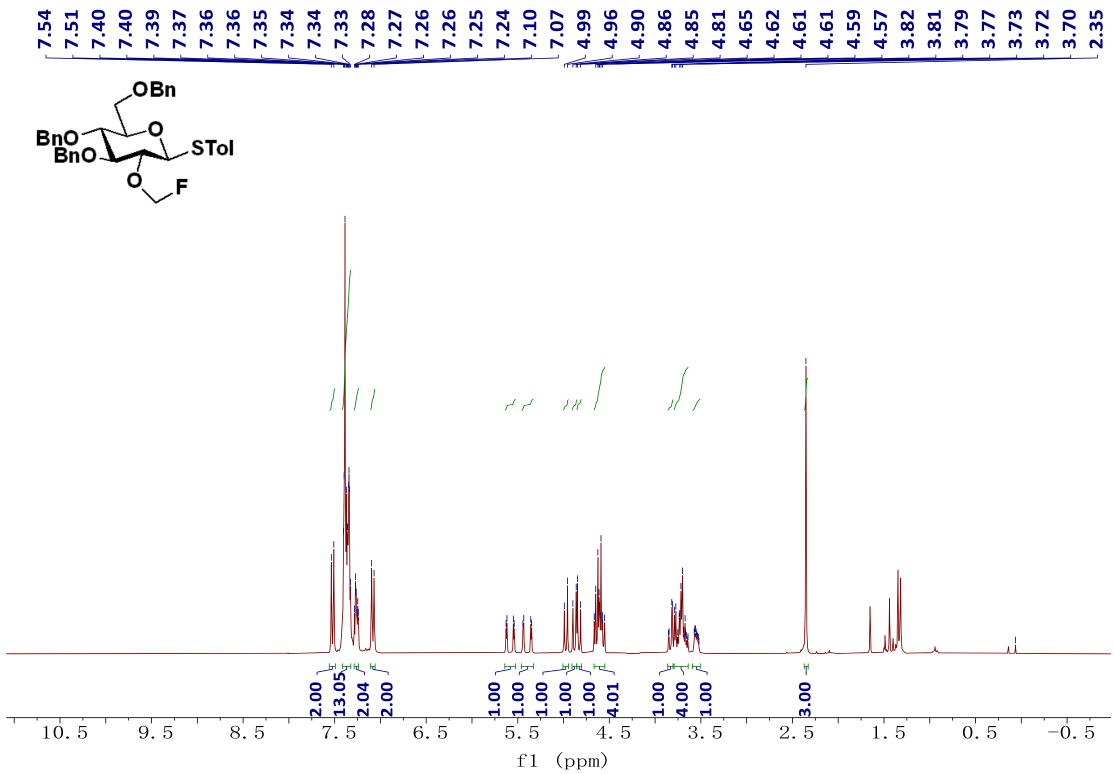
^{13}C NMR of **S26** (75 MHz, $CDCl_3$)



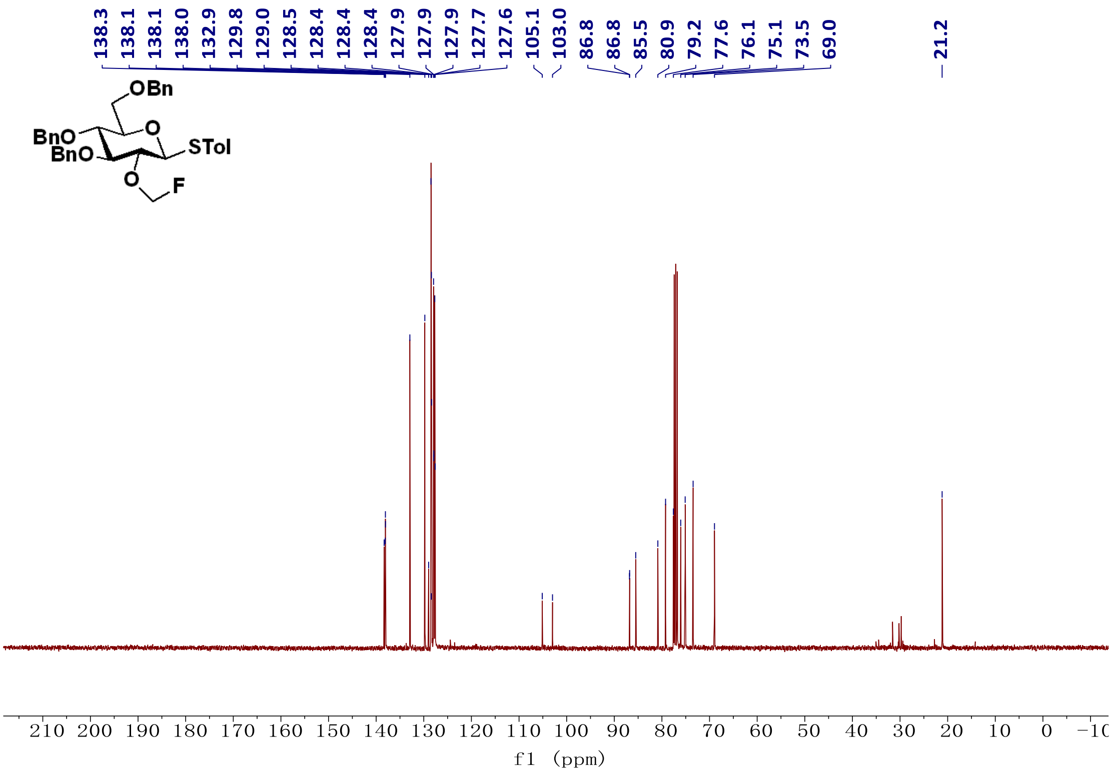
^{1}H NMR of **40** (300 MHz, $CDCl_3$)



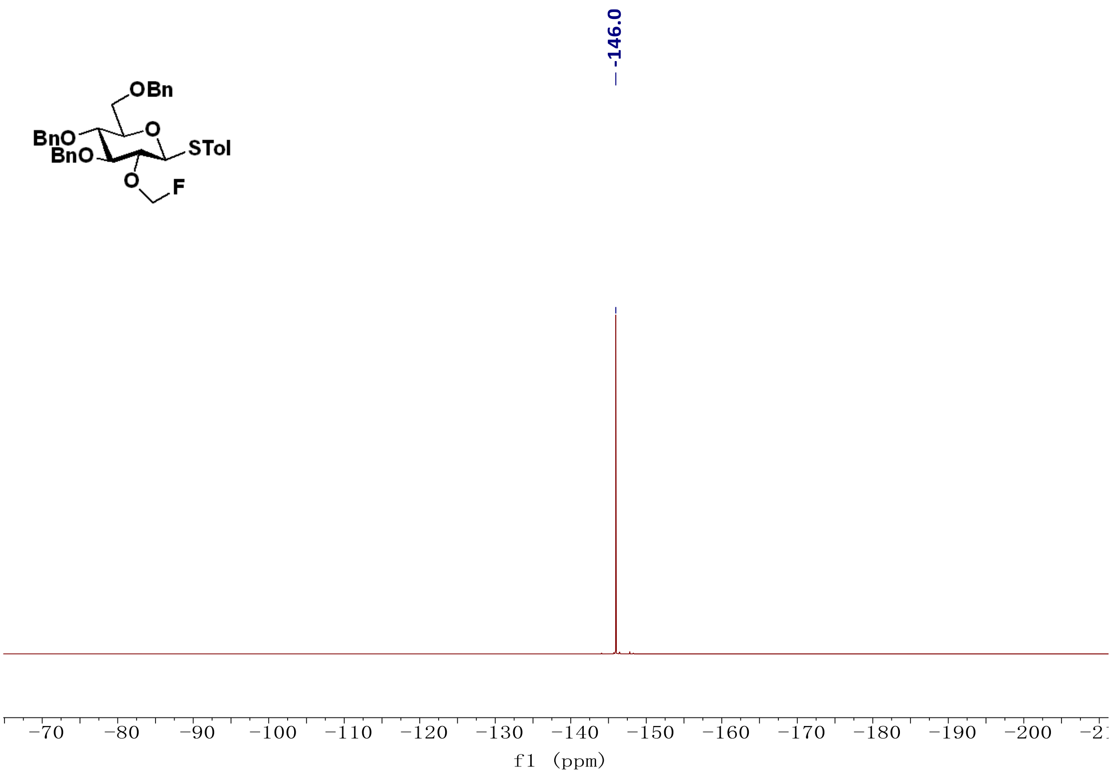
^{13}C NMR of **40** (75 MHz, $CDCl_3$)



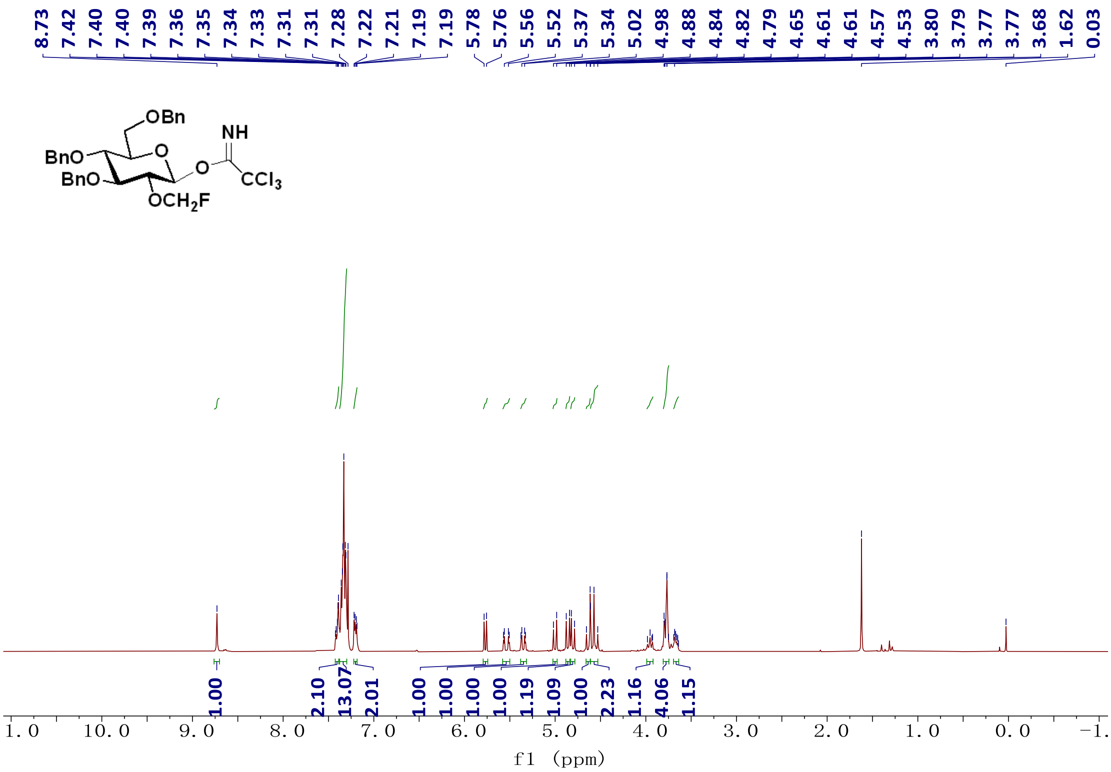
^{1}H NMR of **S27** (300 MHz, $CDCl_3$)



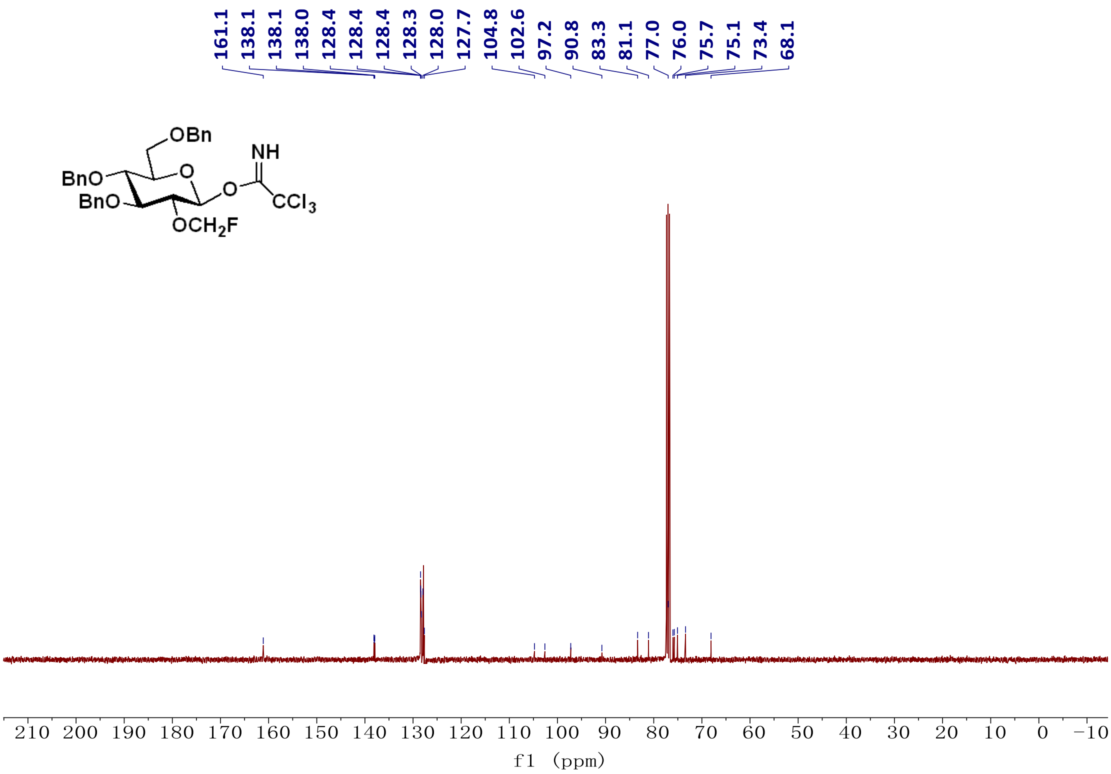
^{13}C NMR of **S27** (100 MHz, $CDCl_3$)



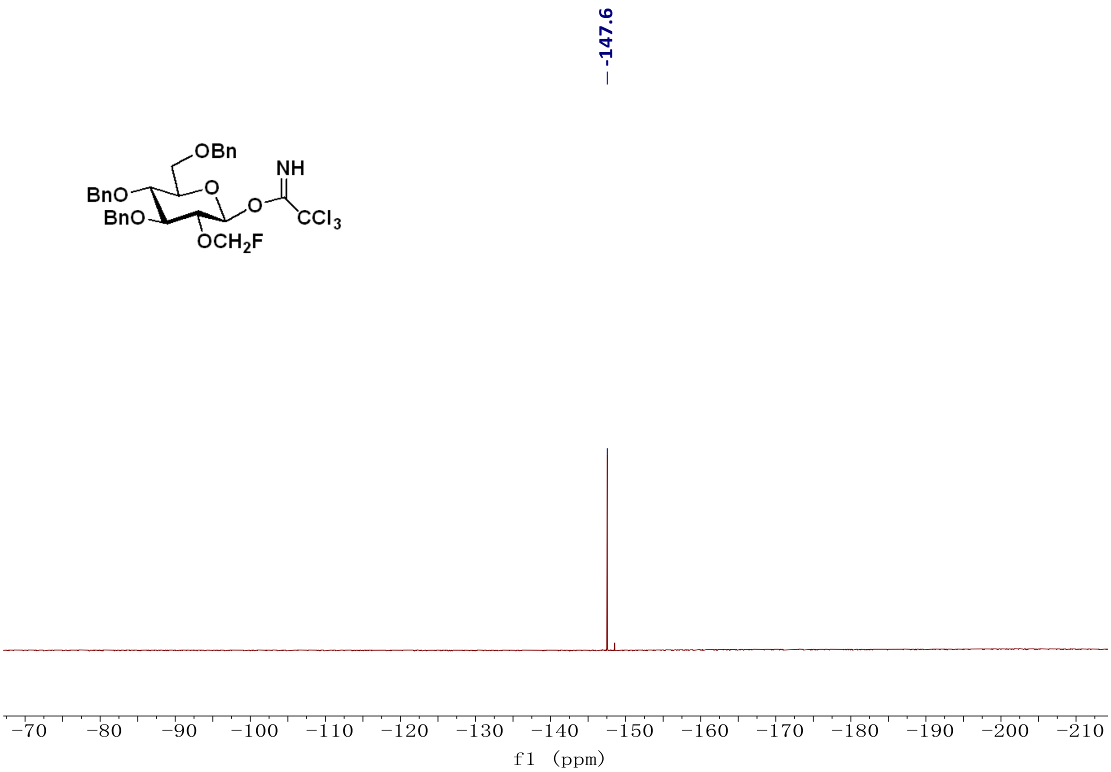
^{19}F NMR of **S27** (282 MHz, $CDCl_3$)



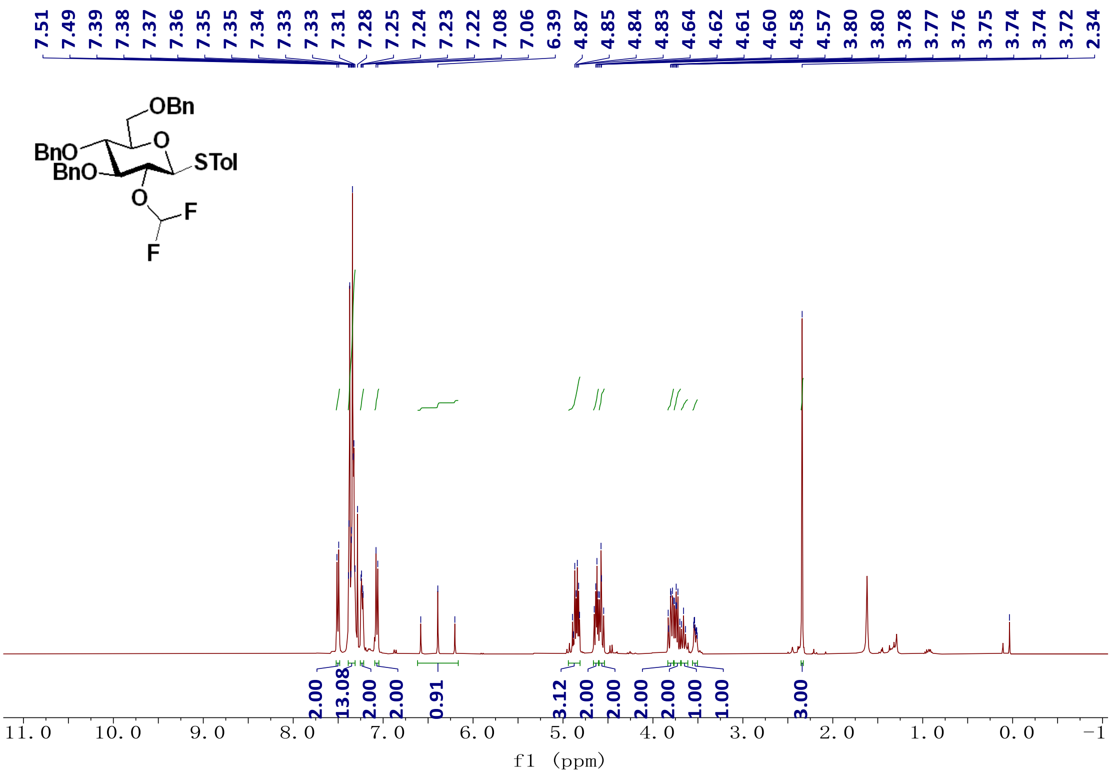
^{1}H NMR of **41** (300 MHz, $CDCl_3$)



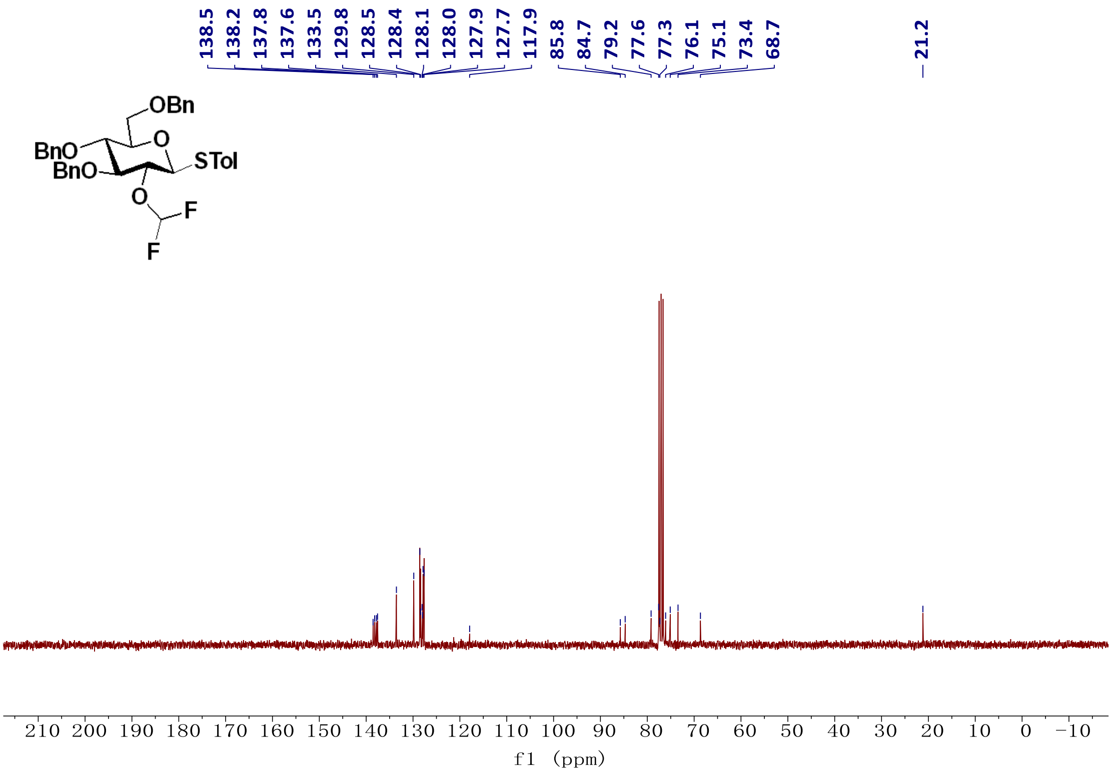
^{13}C NMR of **41** (100 MHz, $CDCl_3$)



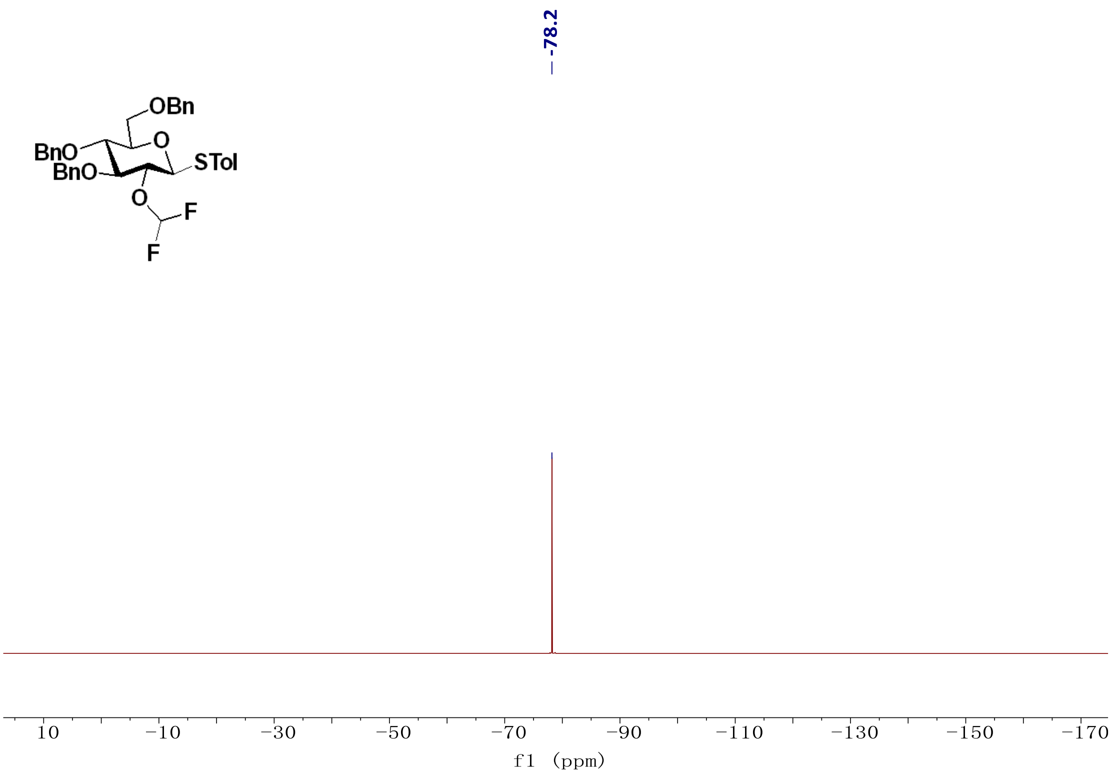
^{19}F NMR of **41** (282 MHz, $CDCl_3$)



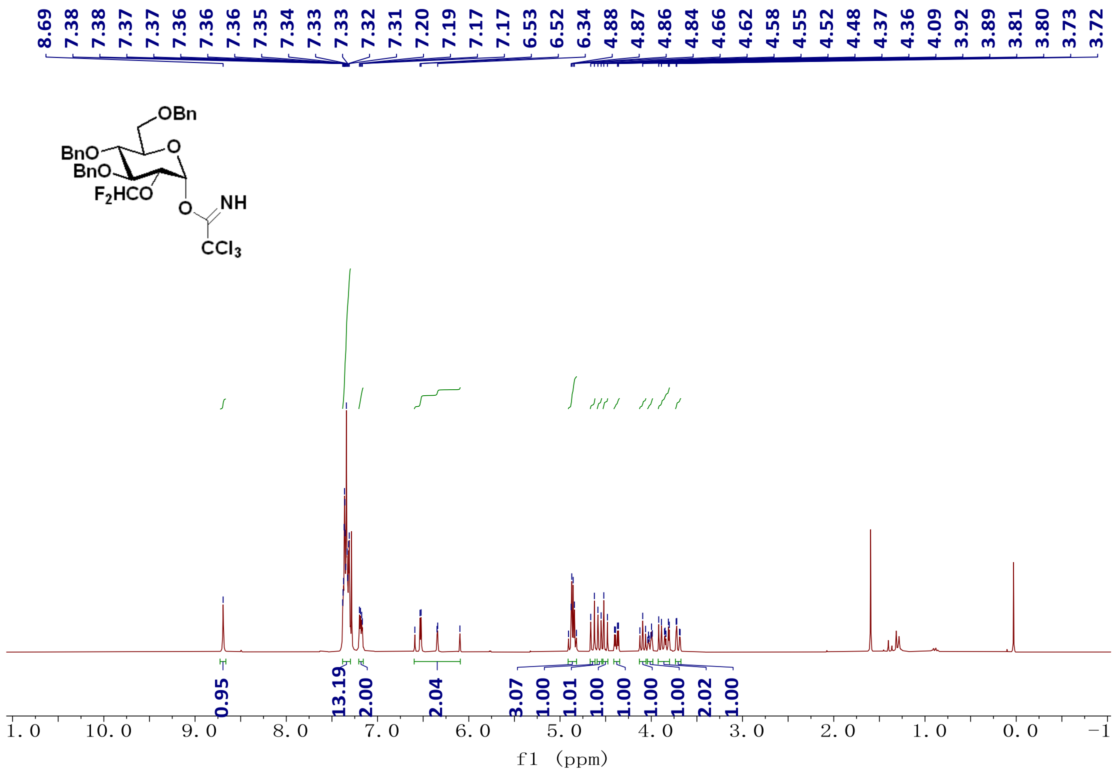
^{1}H NMR of **S28** (400 MHz, $CDCl_3$)



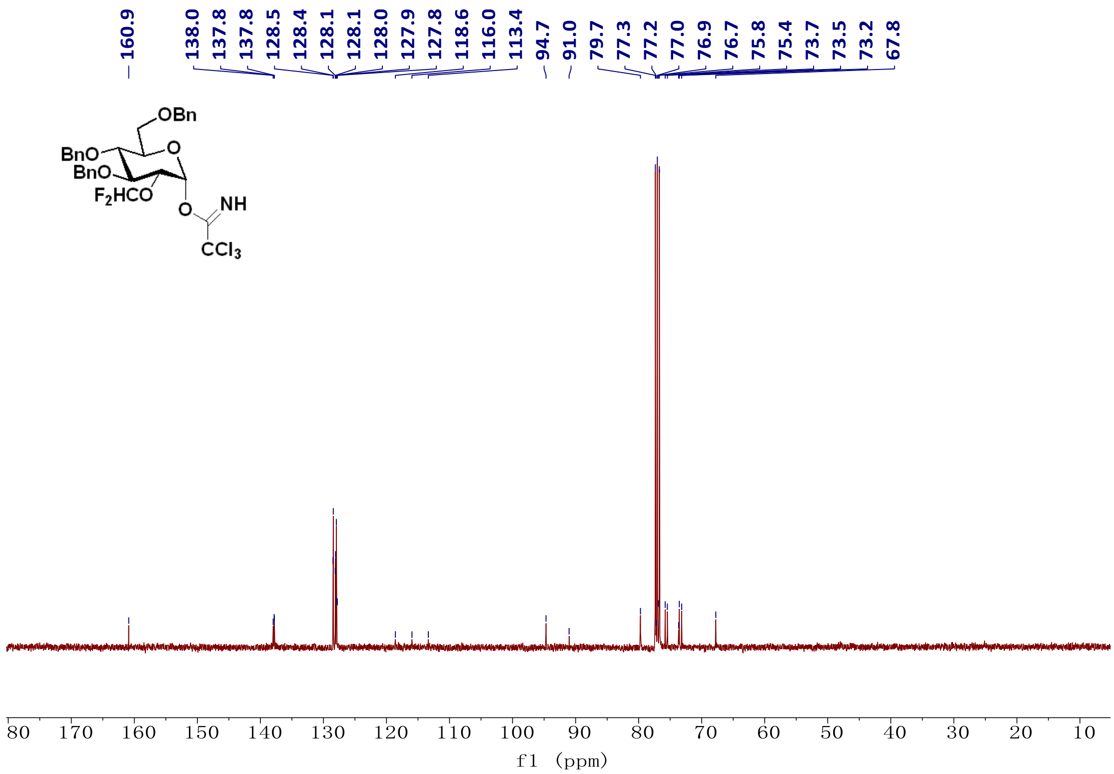
^{13}C NMR of **S28 (**75 MHz, $CDCl_3$)



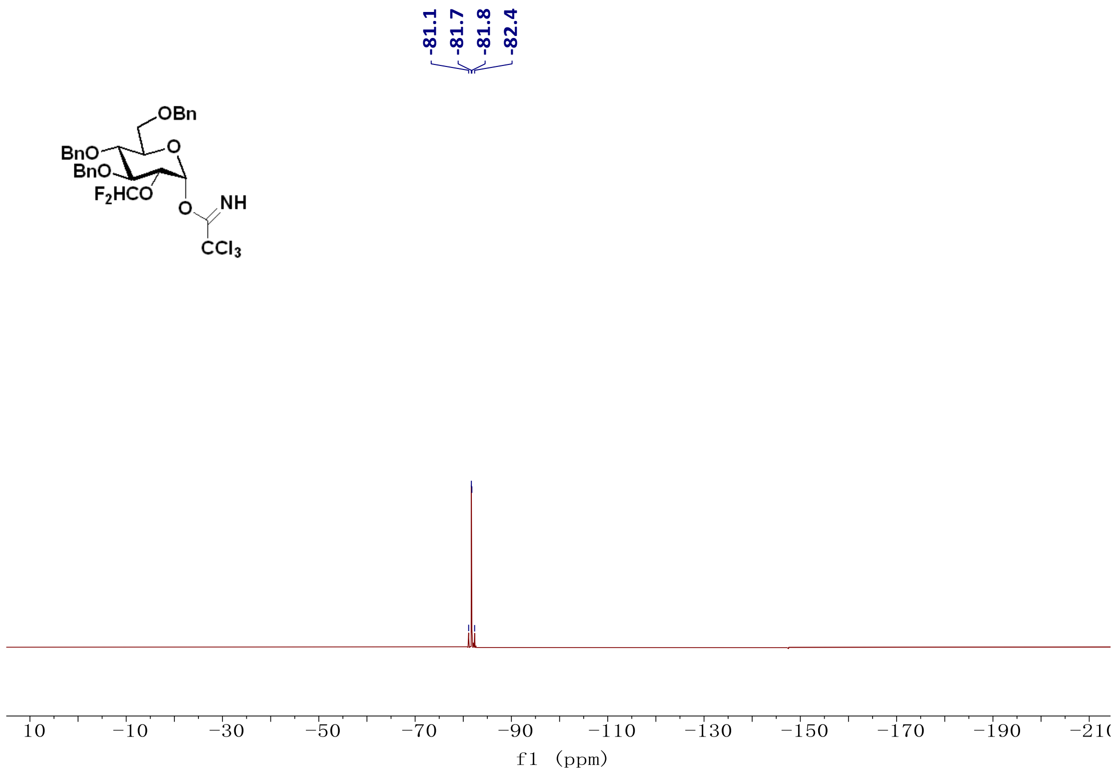
^{19}F NMR of **S28** (282 MHz, $CDCl_3$)



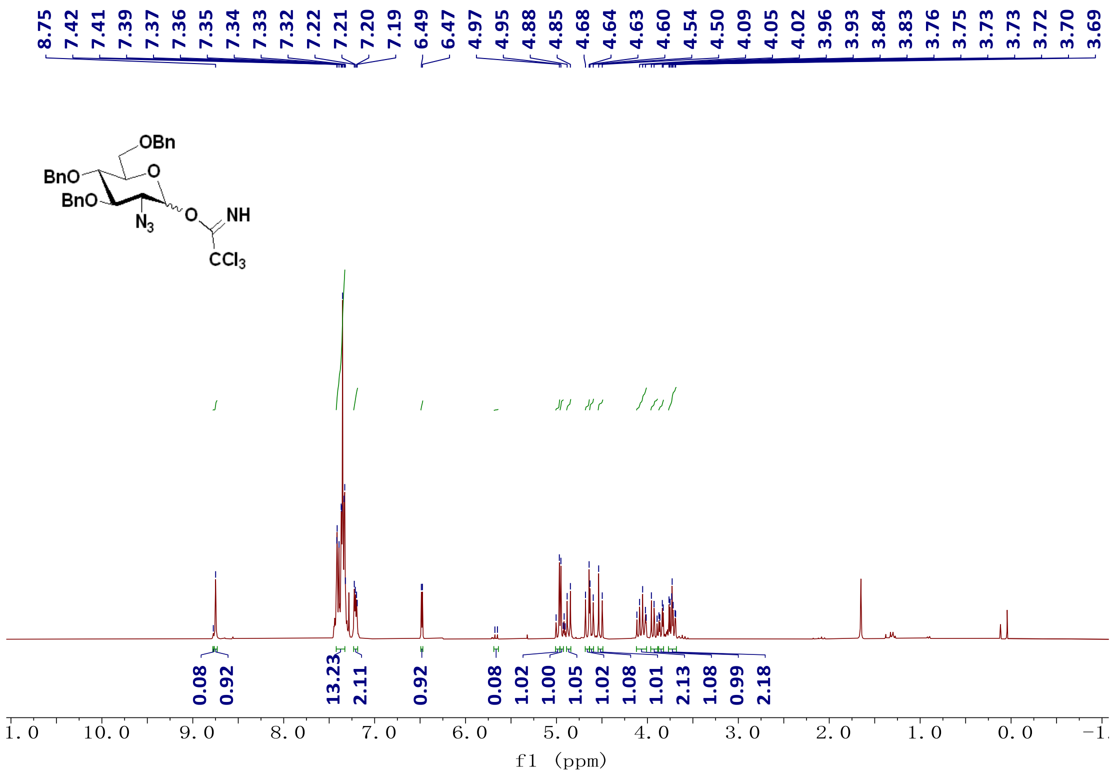
^{1}H NMR of **42** (300 MHz, $CDCl_3$)



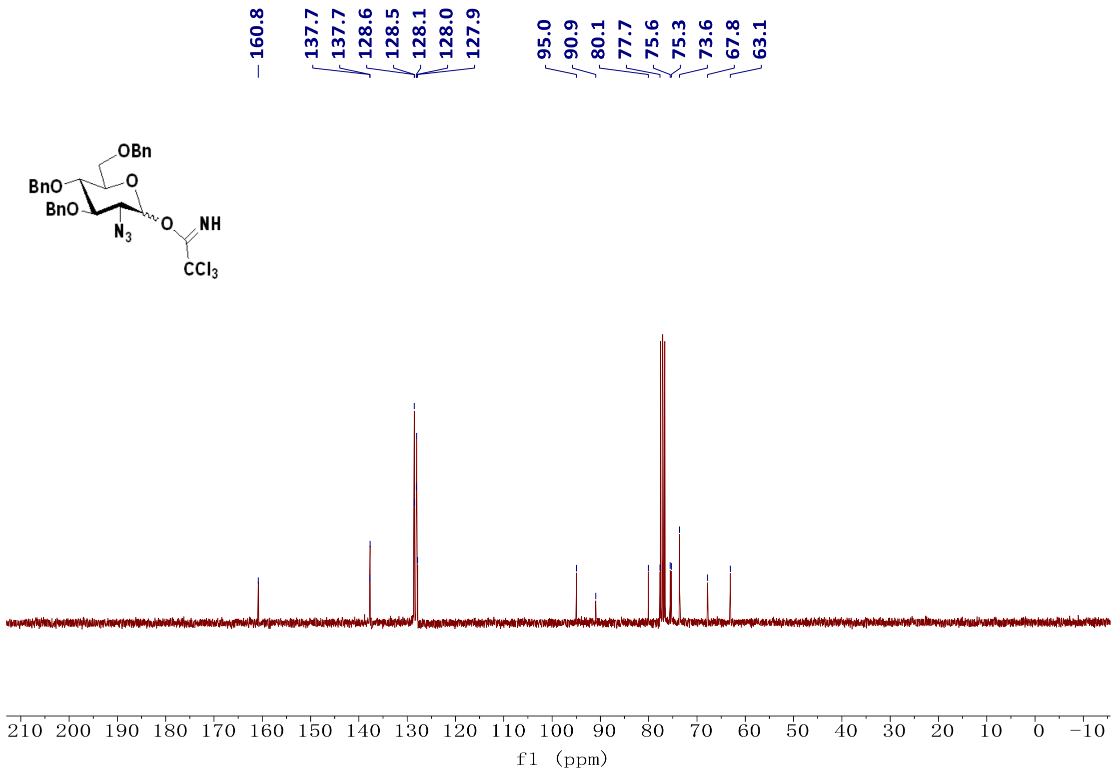
^{13}C NMR of **42** (100 MHz, $CDCl_3$)



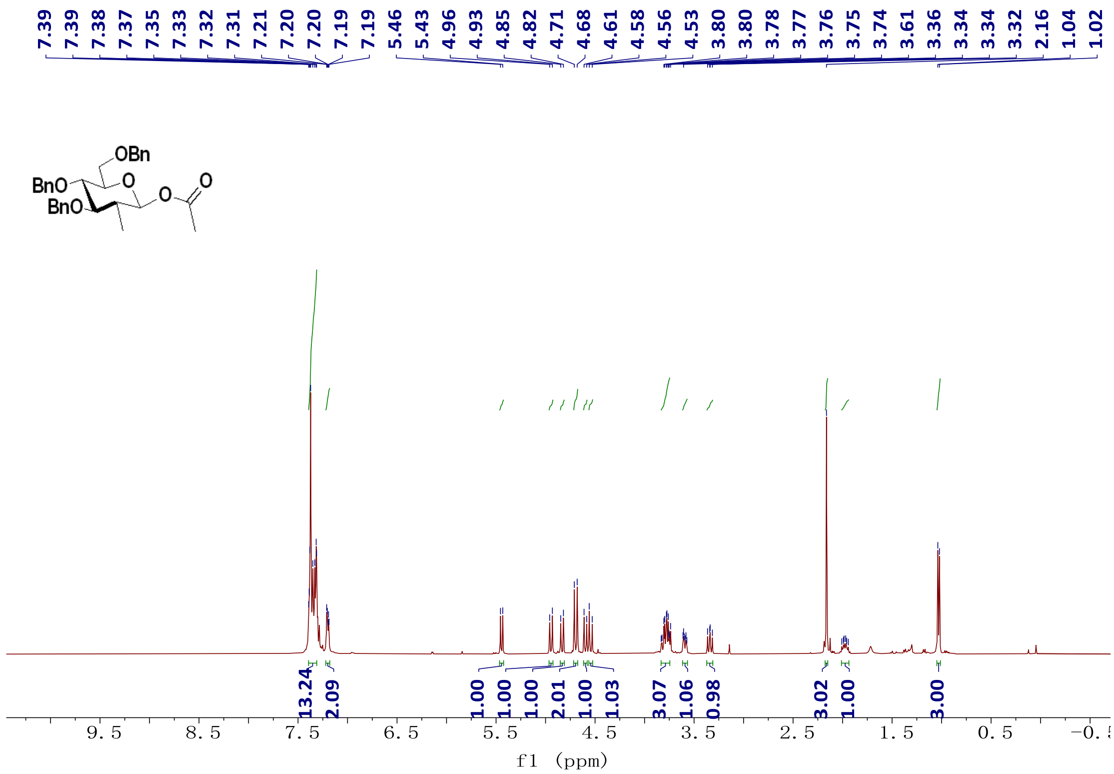
^{19}F NMR of **42** (282 MHz, $CDCl_3$)



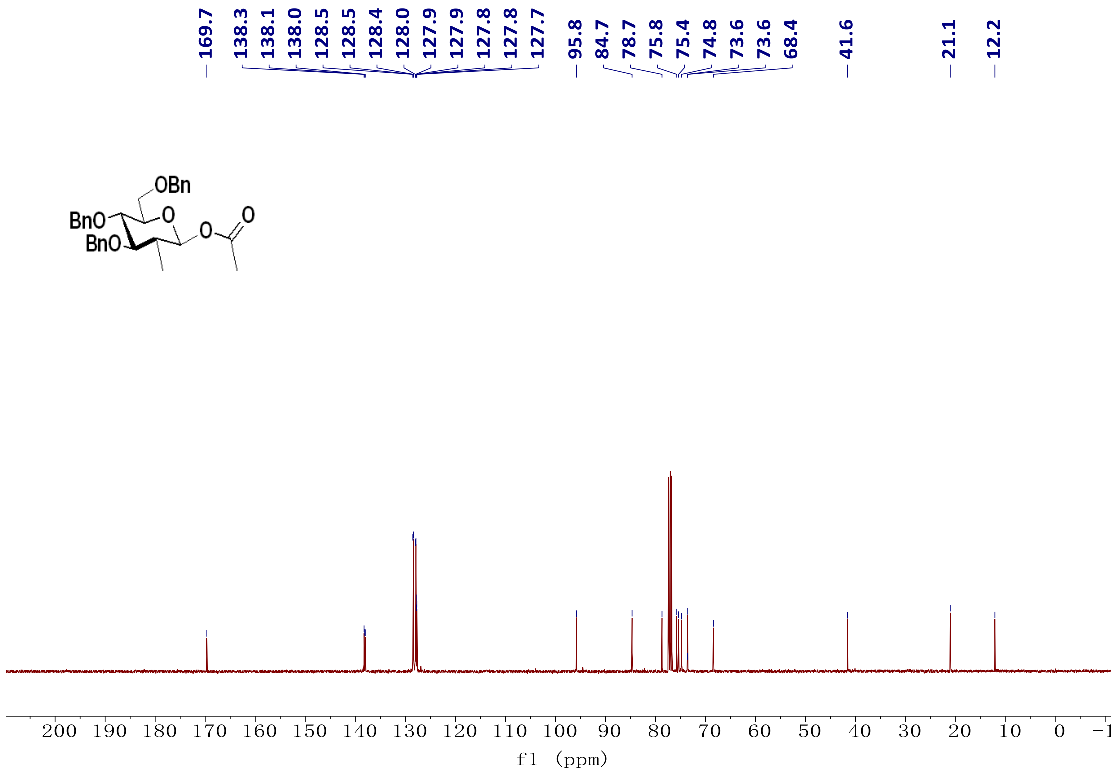
^{1}H NMR of **44** (400 MHz, $CDCl_3$)



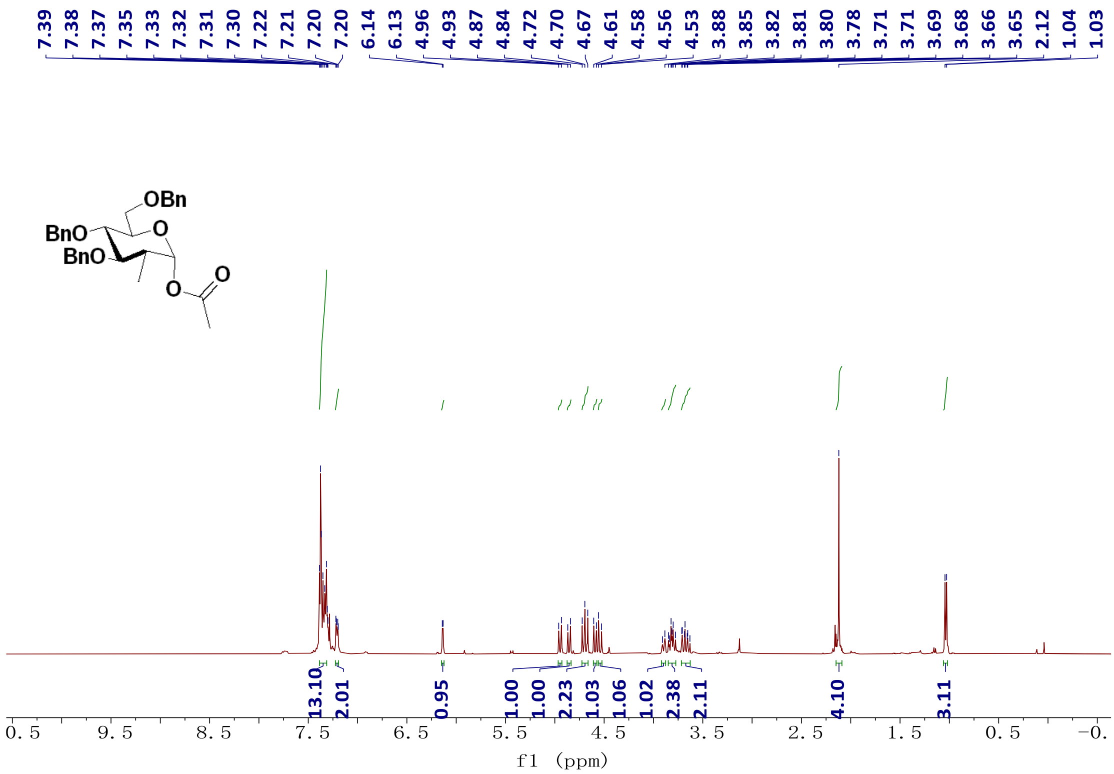
^{13}C NMR of **44** (75 MHz, $CDCl_3$)



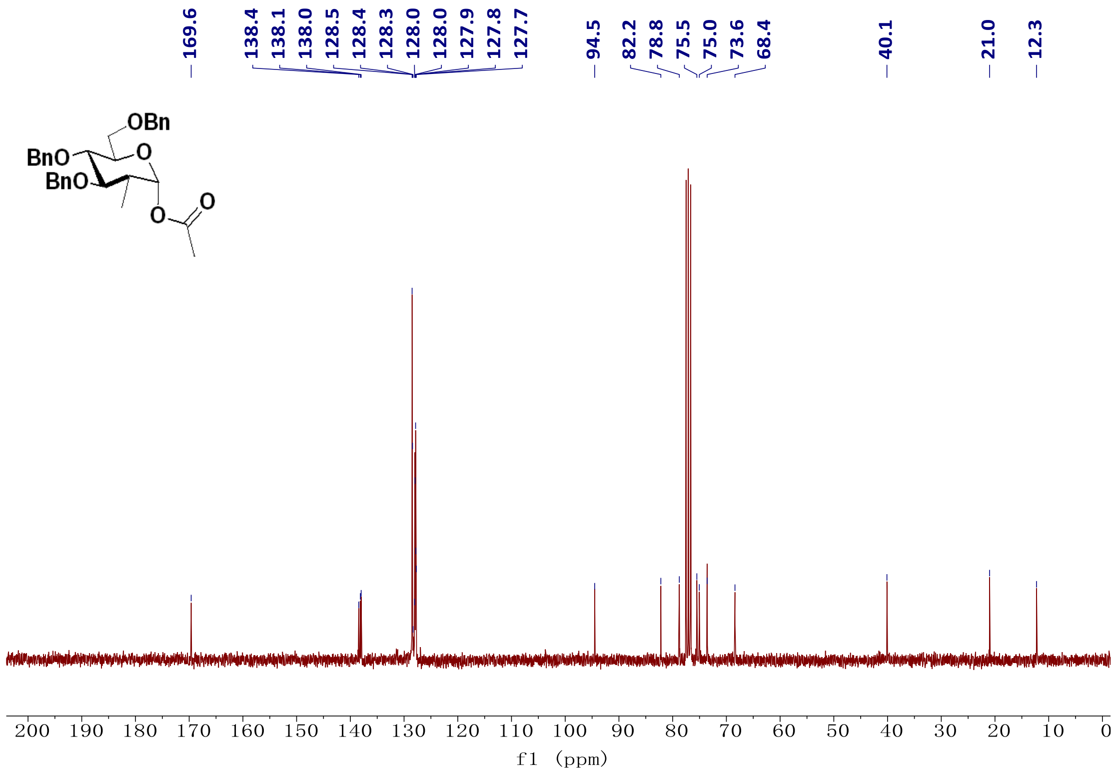
^{1}H NMR of **S32 (β)** (400 MHz, $CDCl_3$)



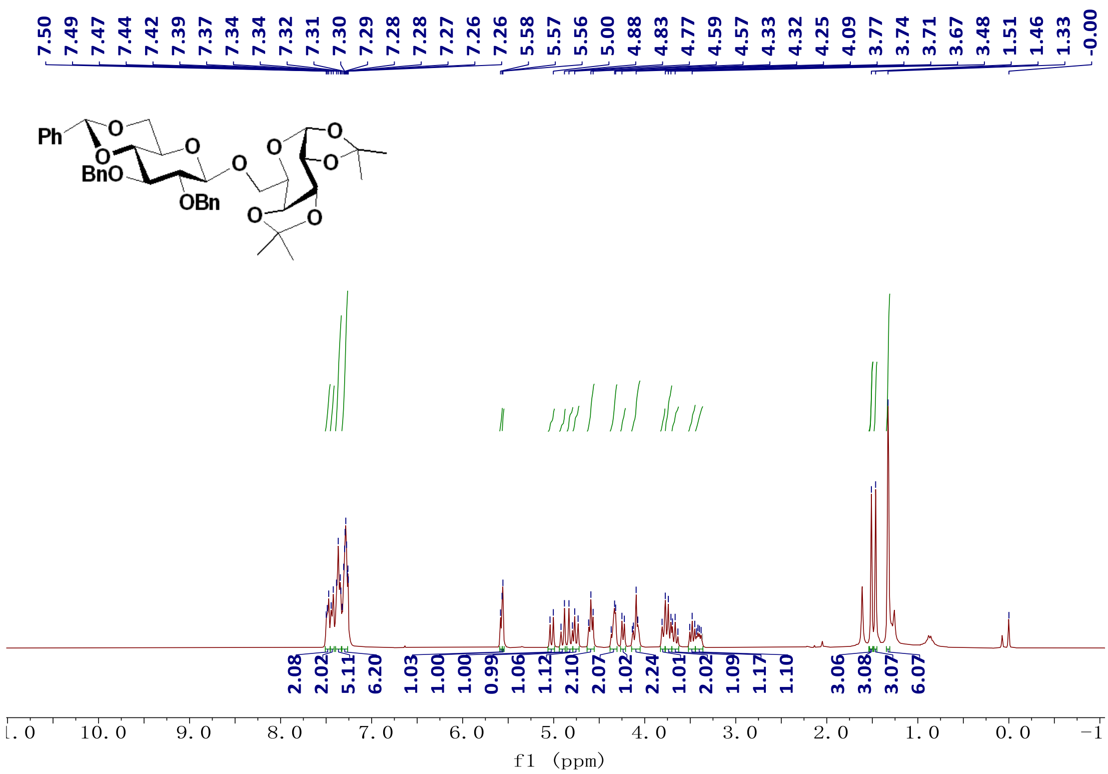
^{13}C NMR of **S32 (β)** (75 MHz, $CDCl_3$)



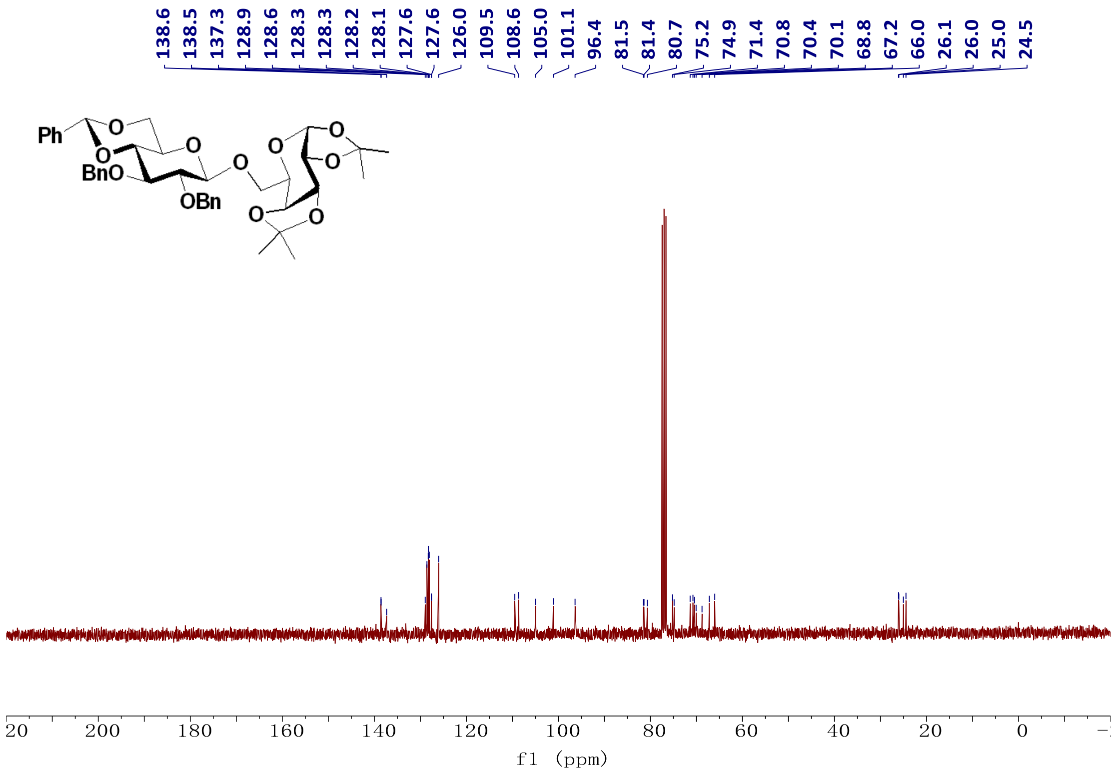
^{1}H NMR of **S32 (α)** (400 MHz, $CDCl_3$)



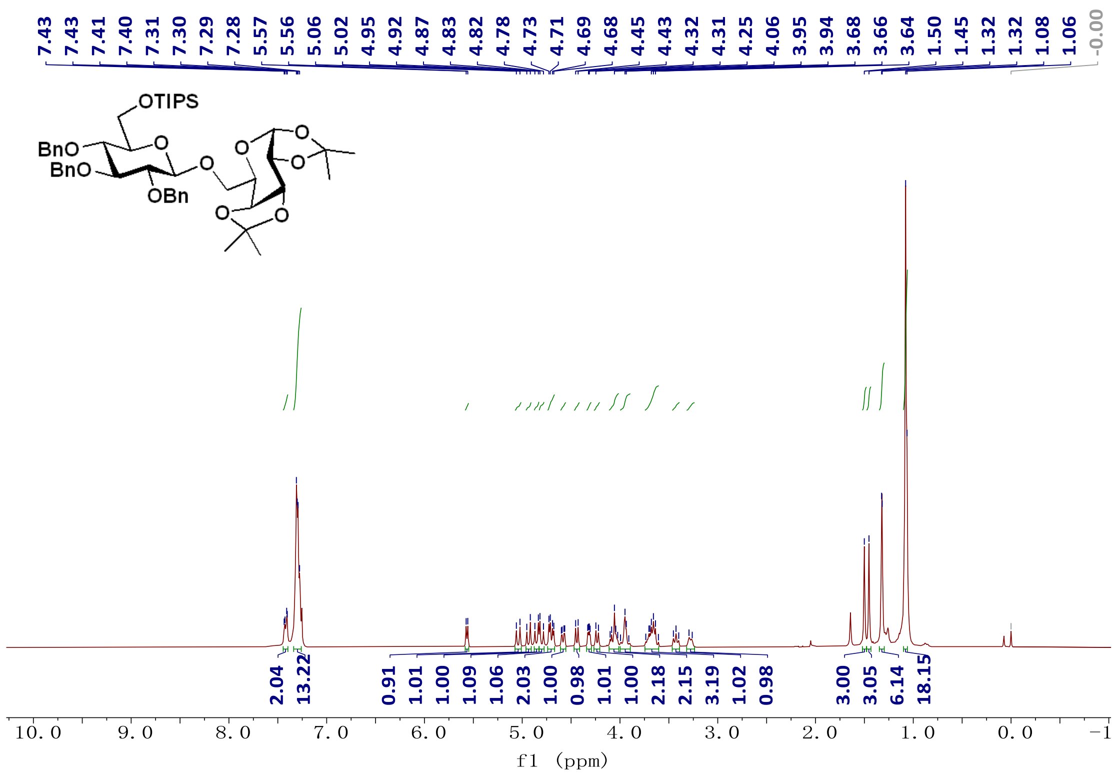
^{13}C NMR of **S32 (α)** (75 MHz, $CDCl_3$)



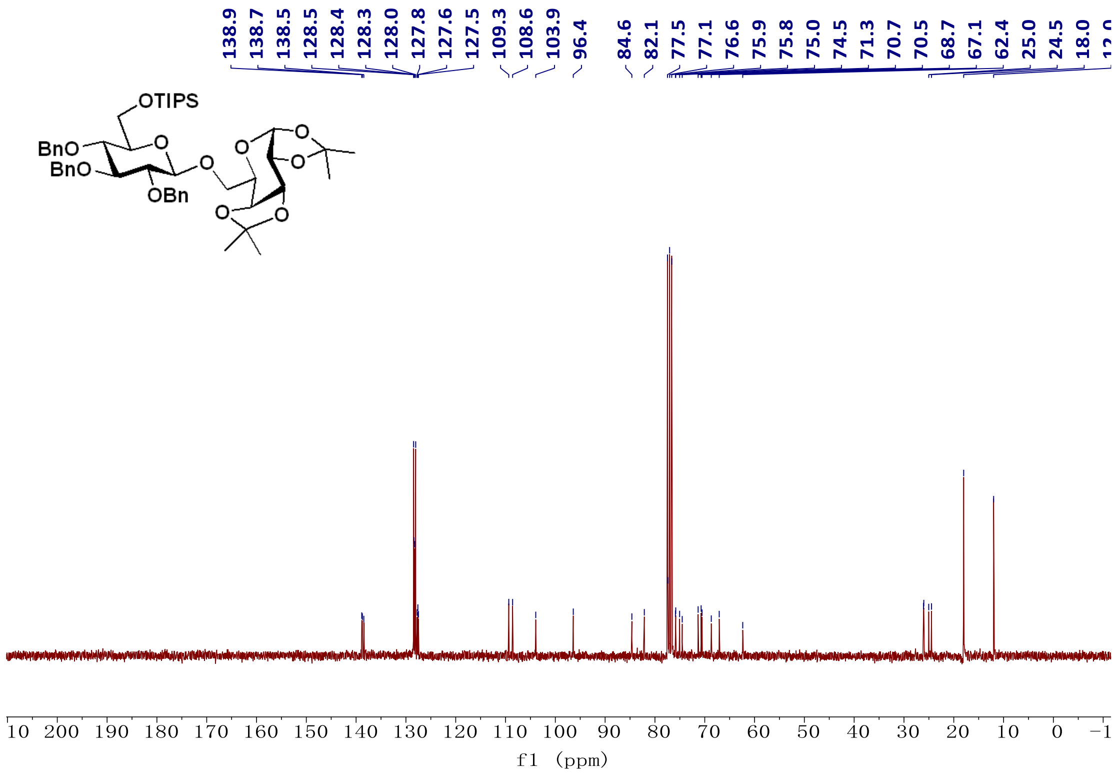
^{1}H NMR of **22** (300 MHz, $CDCl_3$)



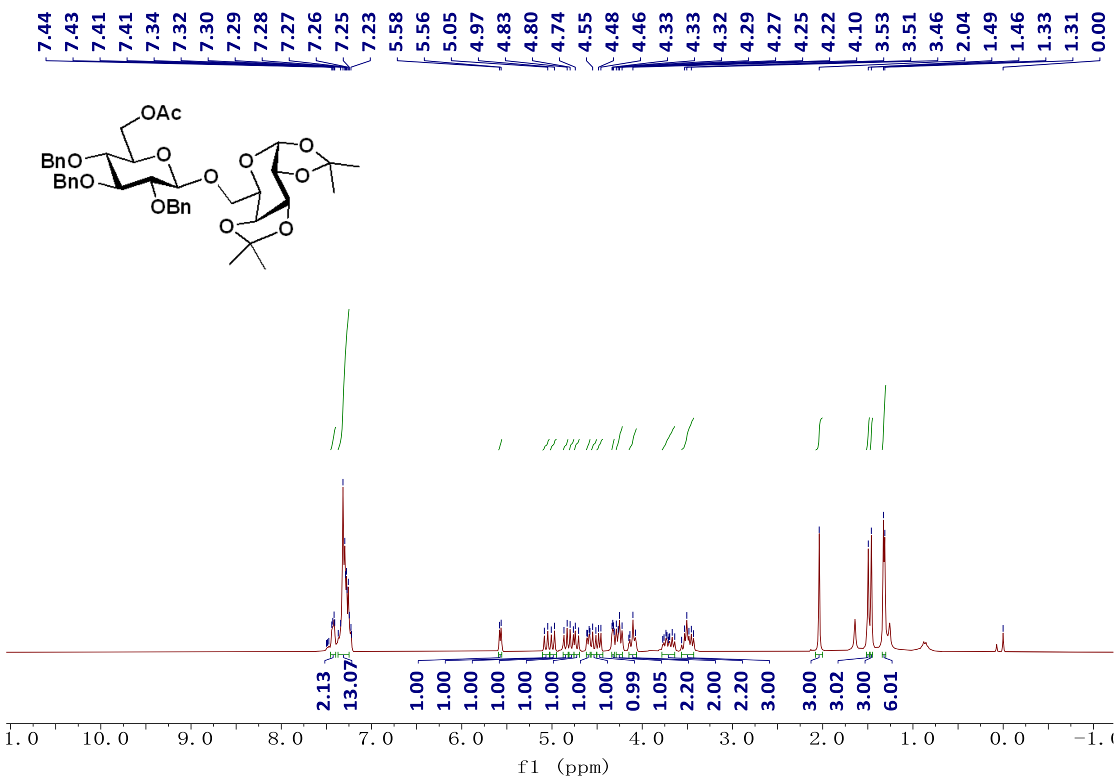
^{13}C NMR of **22** (75 MHz, $CDCl_3$)



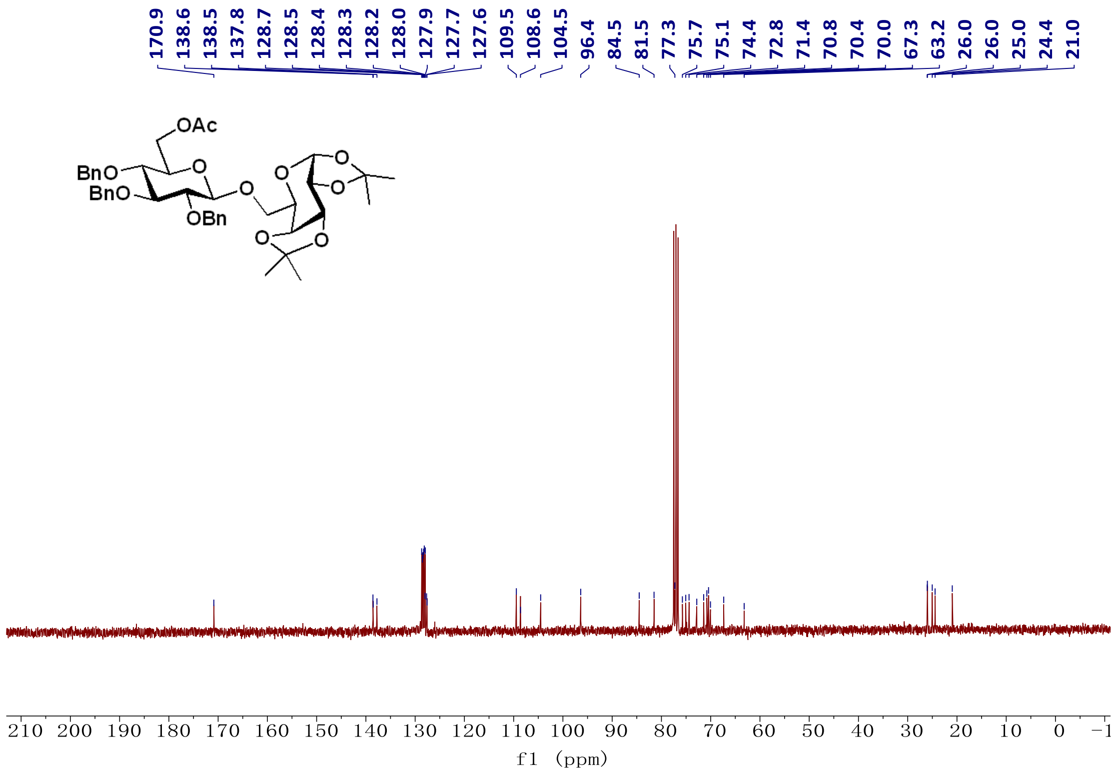
^{1}H NMR of **23** (300 MHz, $CDCl_3$)



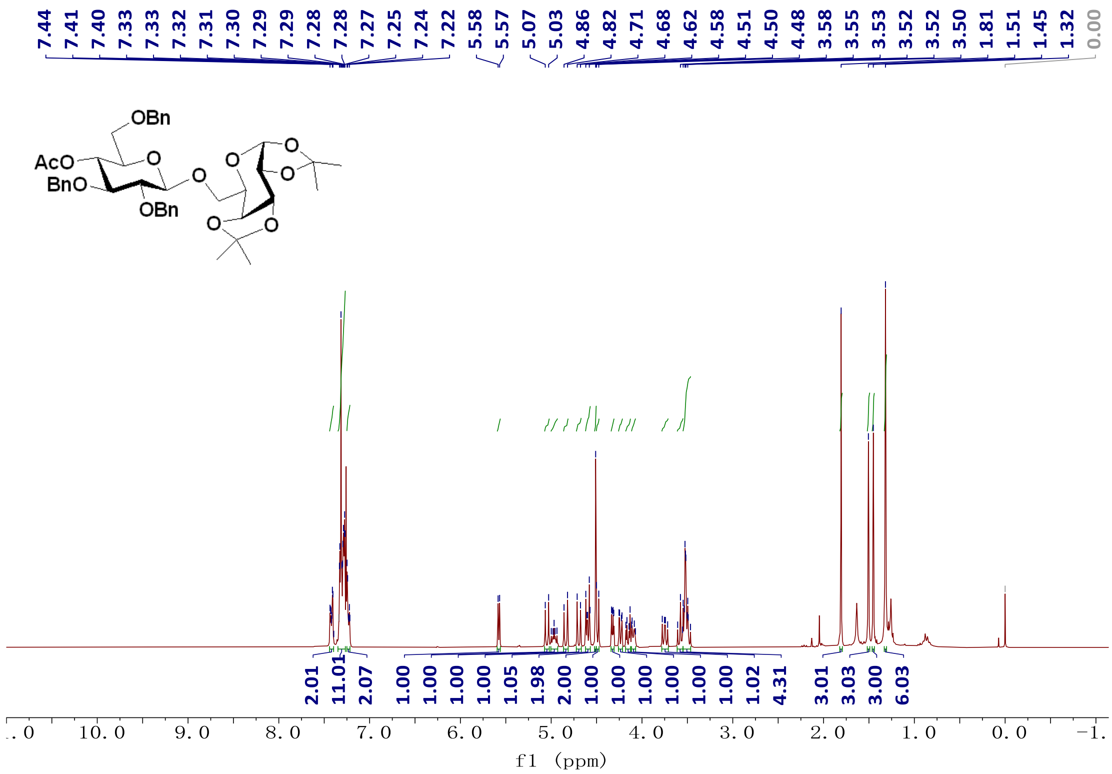
^{13}C NMR of **23** (75 MHz, $CDCl_3$)



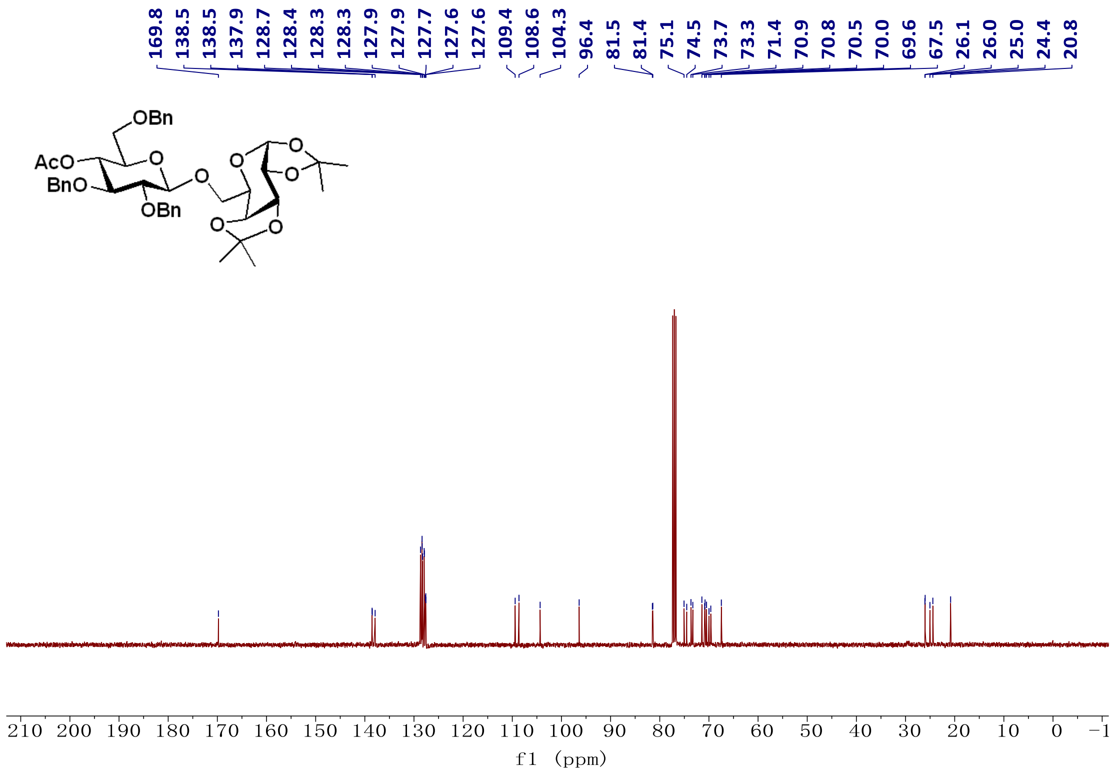
^{1}H NMR of **24** (300 MHz, $CDCl_3$)



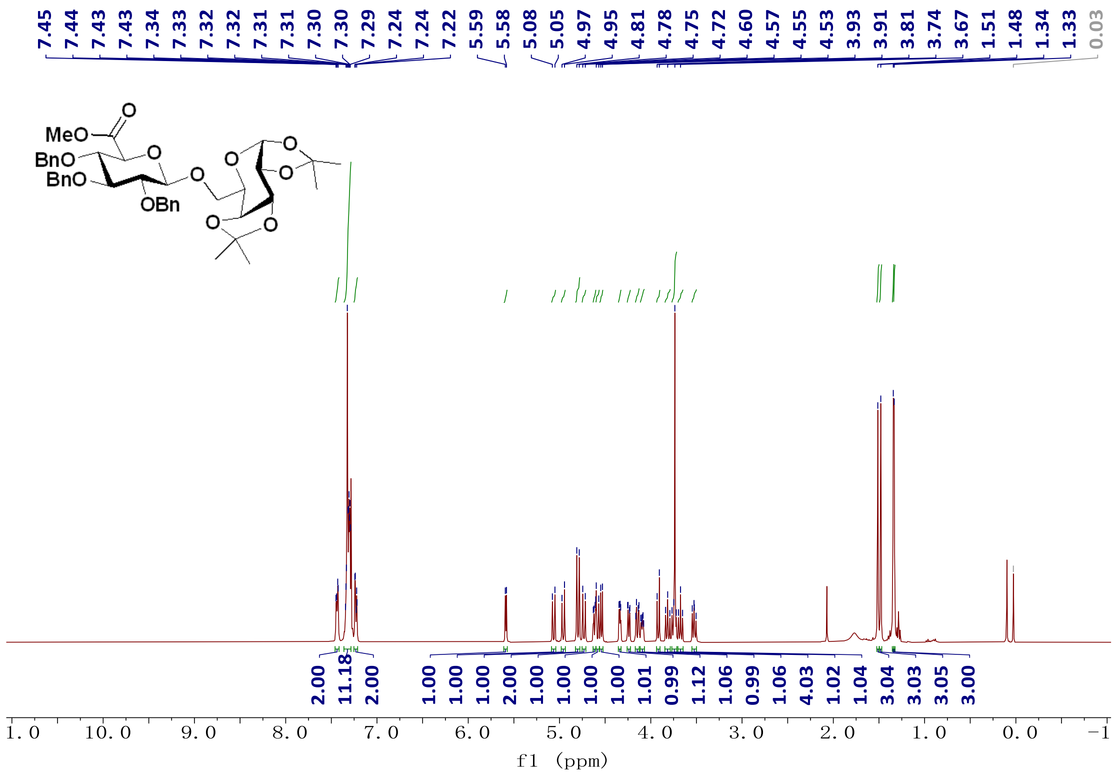
^{13}C NMR of **24** (75 MHz, $CDCl_3$)



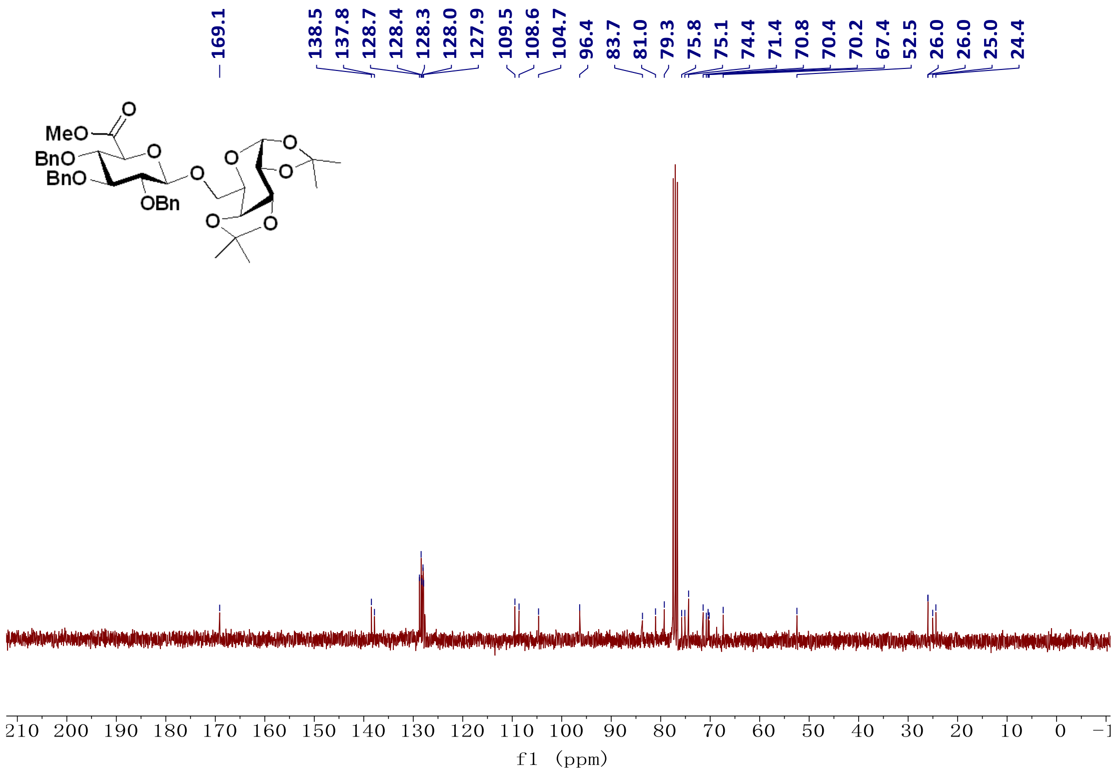
^{1}H NMR of **25** (300 MHz, $CDCl_3$)



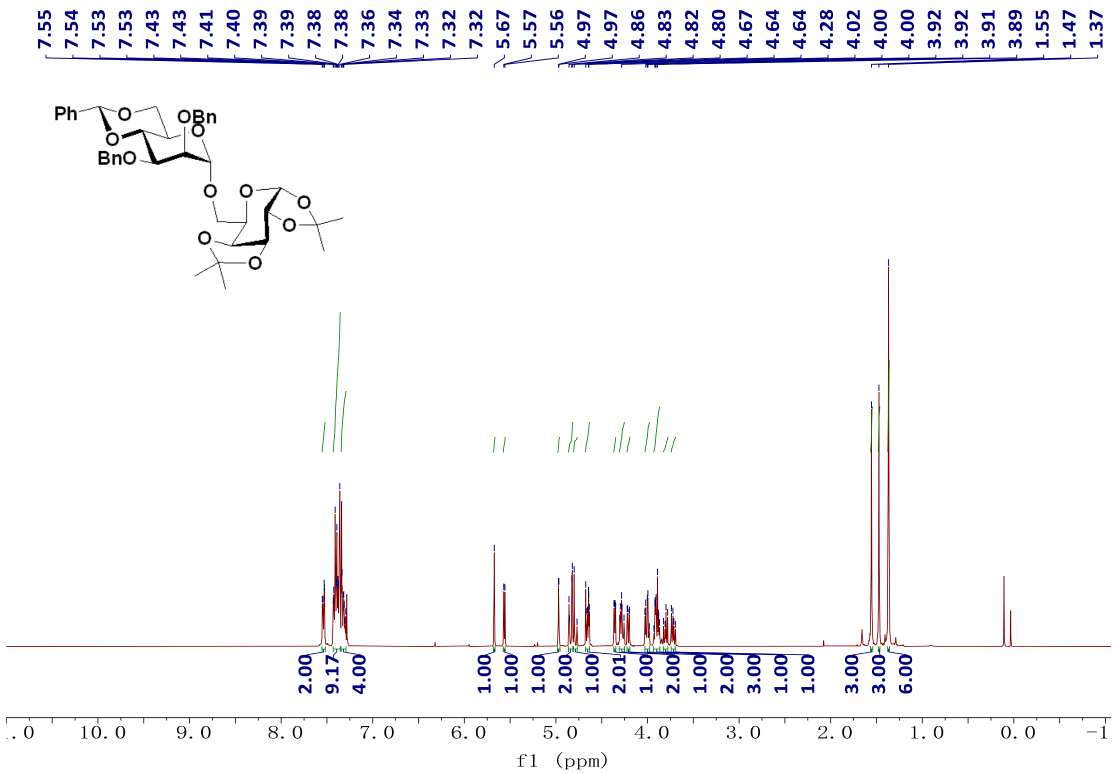
^{13}C NMR of **25** (100 MHz, $CDCl_3$)



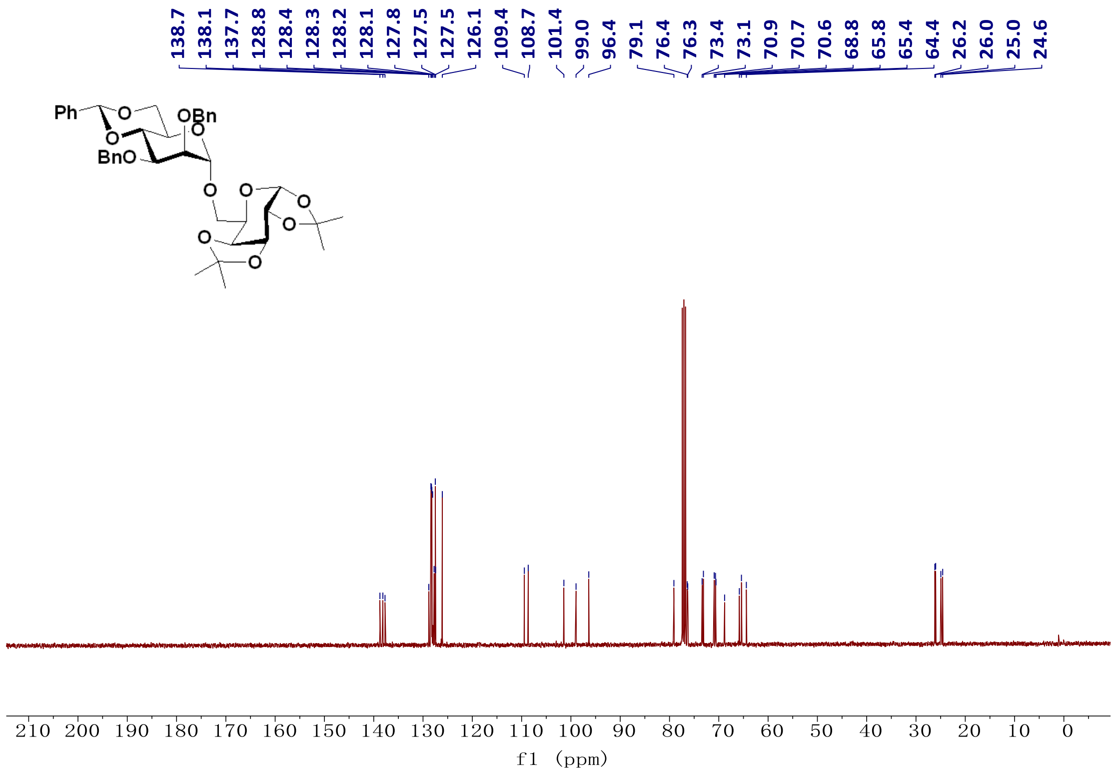
^{1}H NMR of **26** (400 MHz, $CDCl_3$)



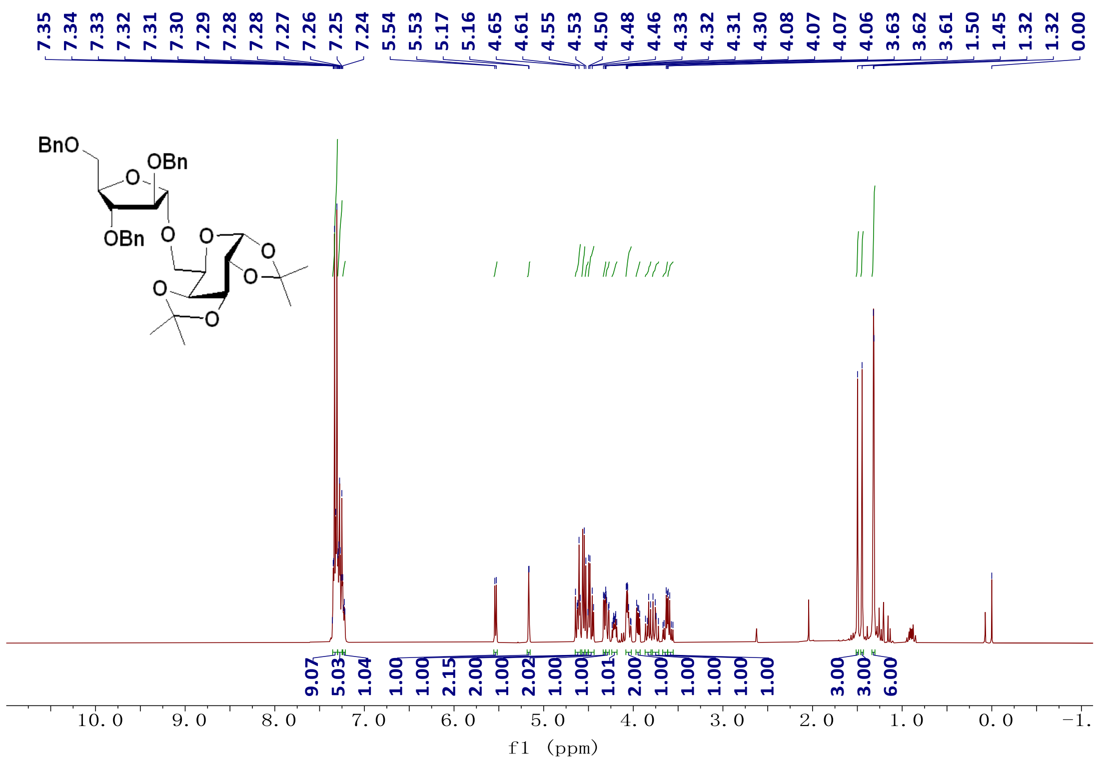
^{13}C NMR of **26** (75 MHz, $CDCl_3$)



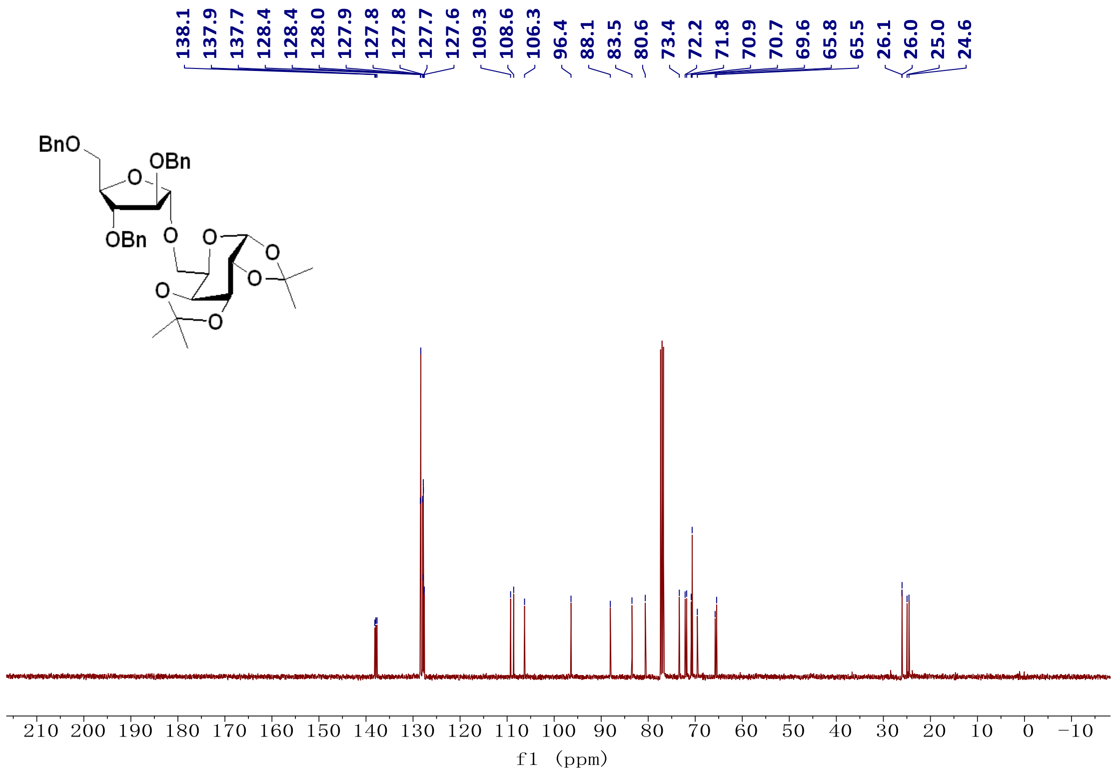
^{1}H NMR of **27** (300 MHz, $CDCl_3$)



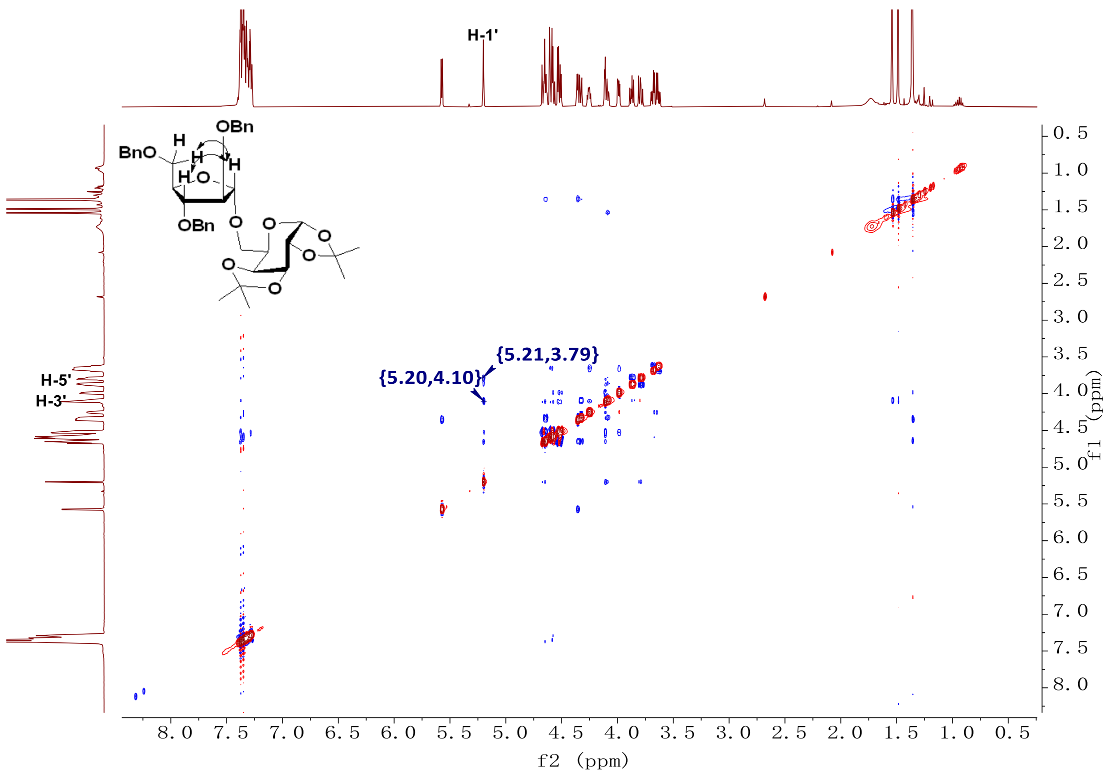
^{13}C NMR of **27** (100 MHz, $CDCl_3$)



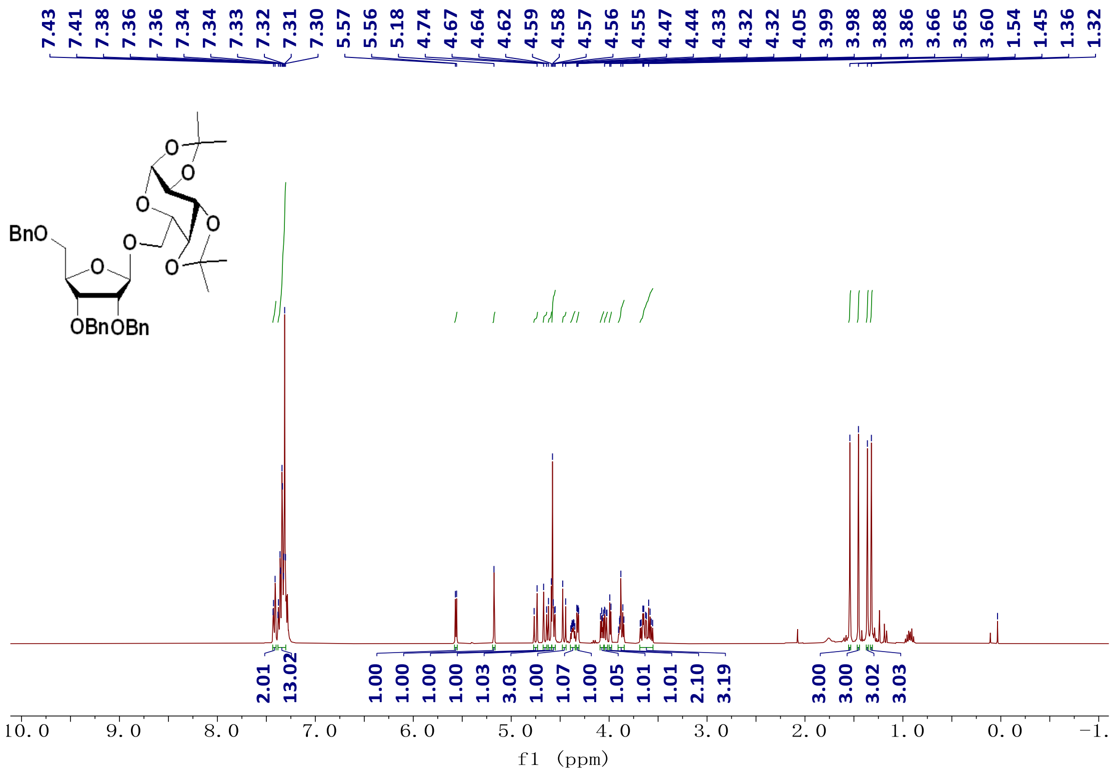
^{1}H NMR of **28** (300 MHz, $CDCl_3$)



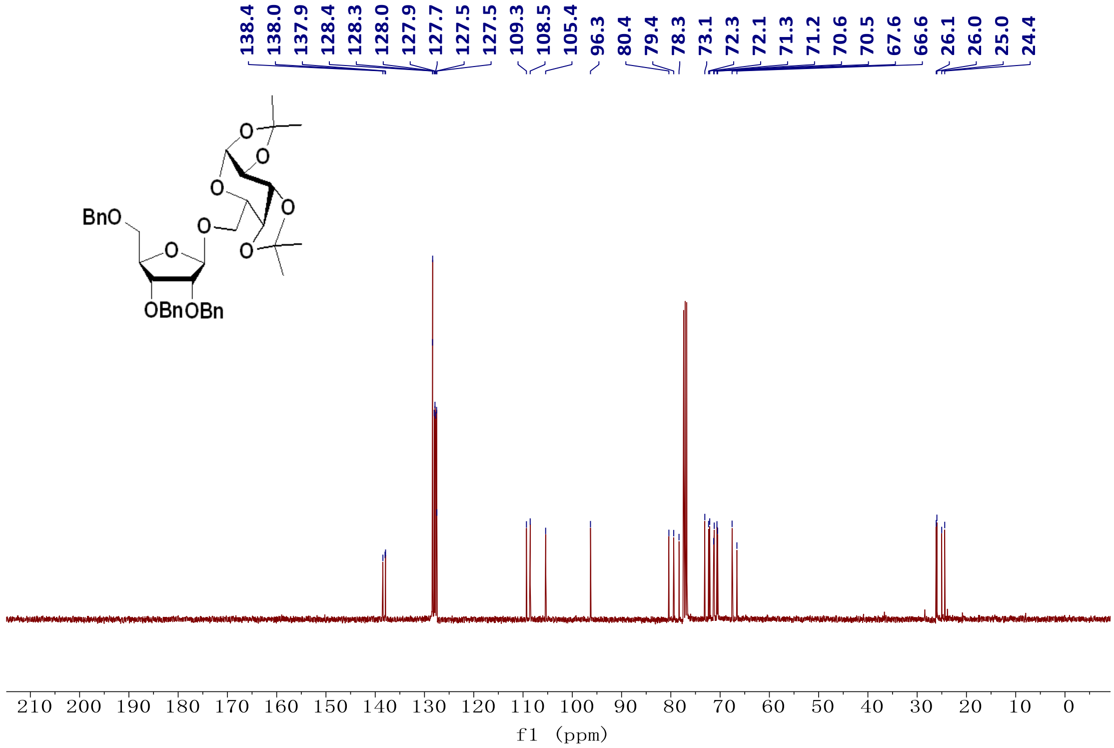
^{13}C NMR of **28** (100 MHz, $CDCl_3$)



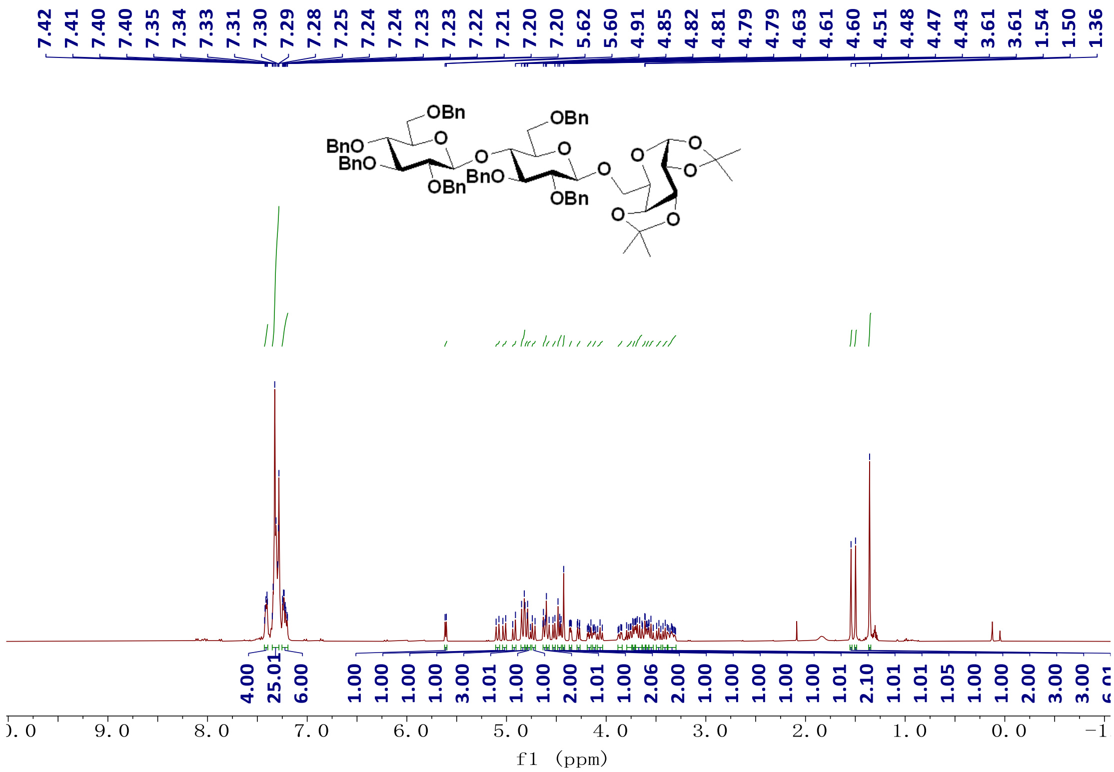
NOESY of **28**



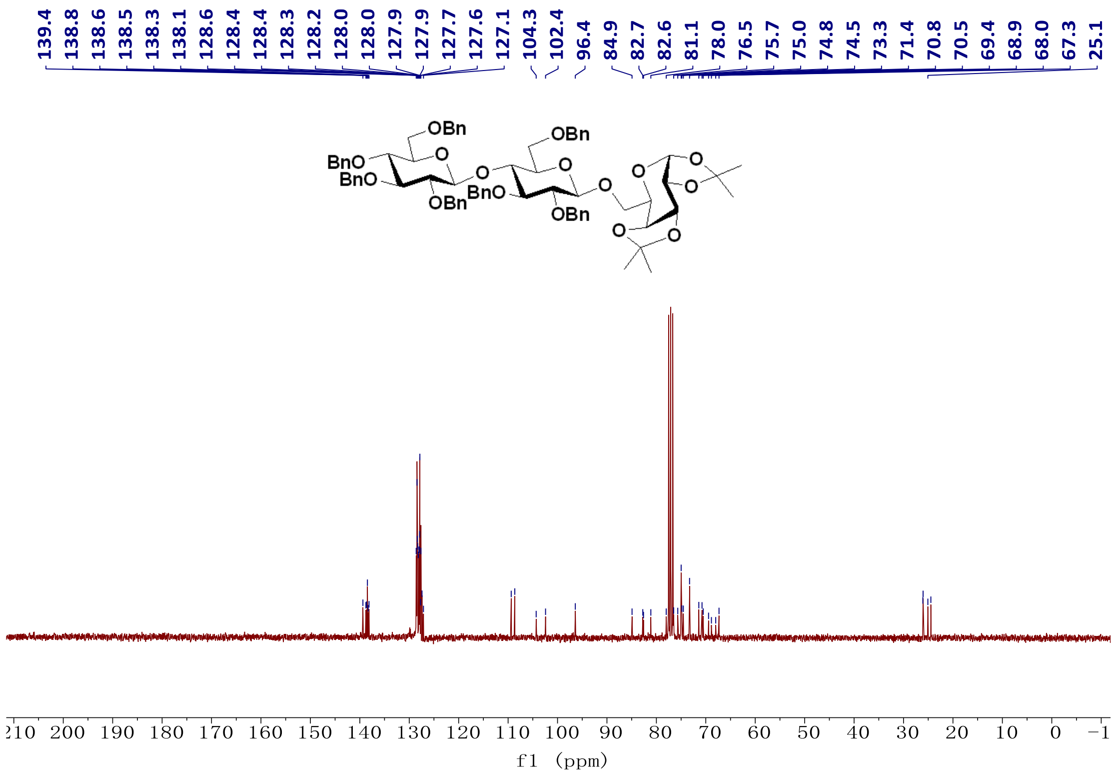
^{1}H NMR of **29** (400 MHz, $CDCl_3$)



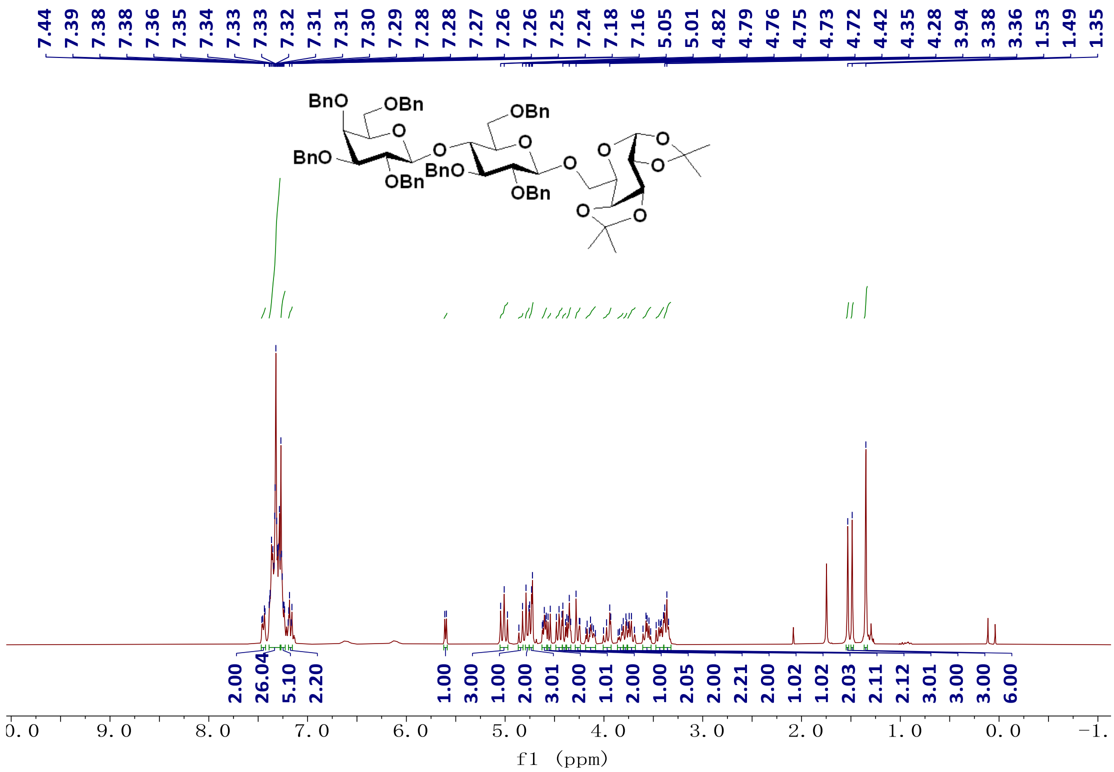
^{13}C NMR of **29** (100 MHz, $CDCl_3$)



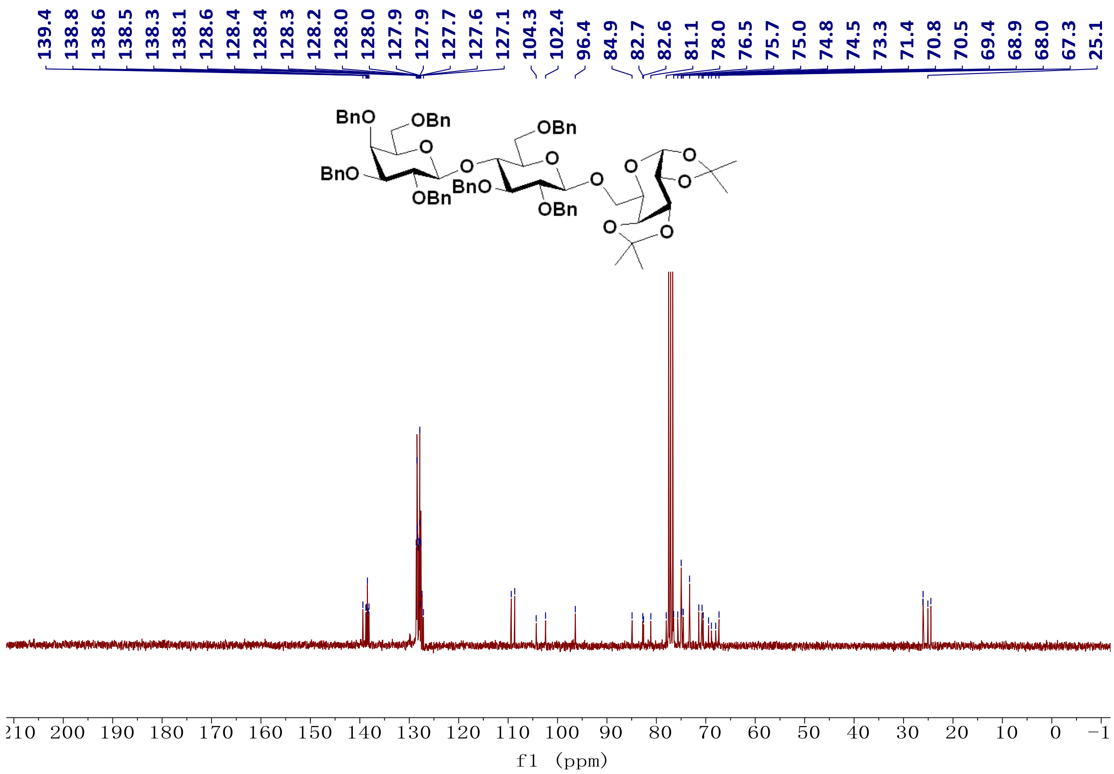
^{1}H NMR of **30** (400 MHz, $CDCl_3$)



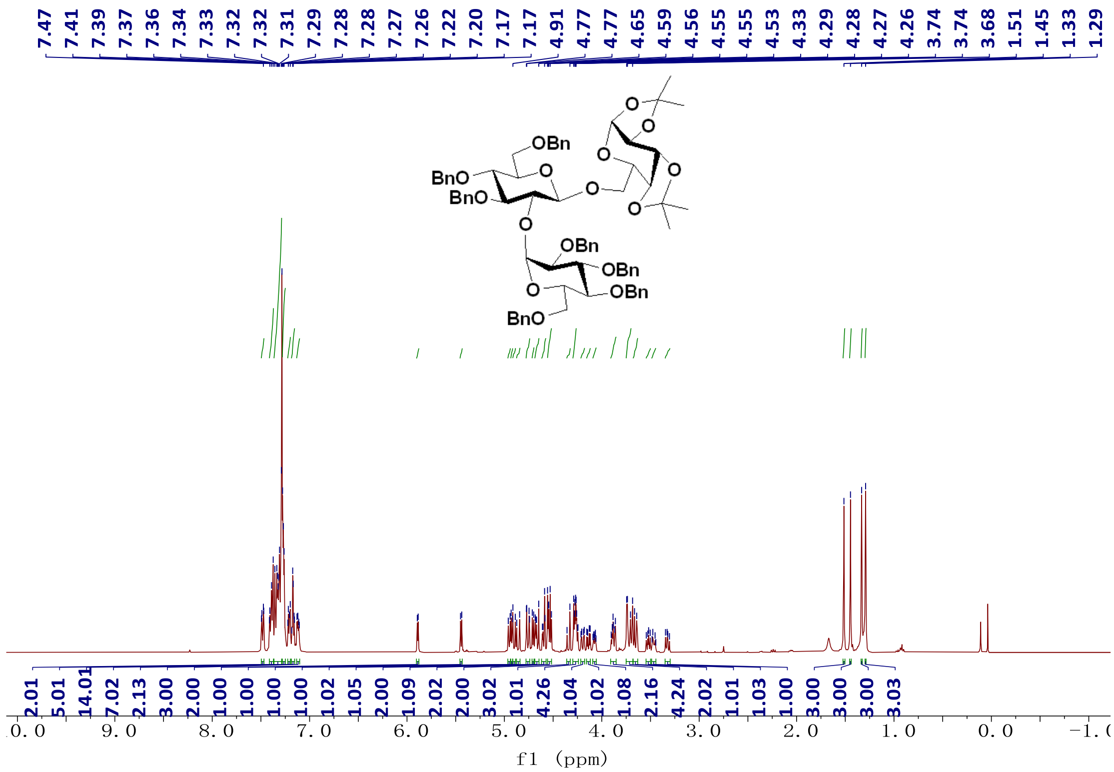
^{13}C NMR of **30** (75 MHz, $CDCl_3$)



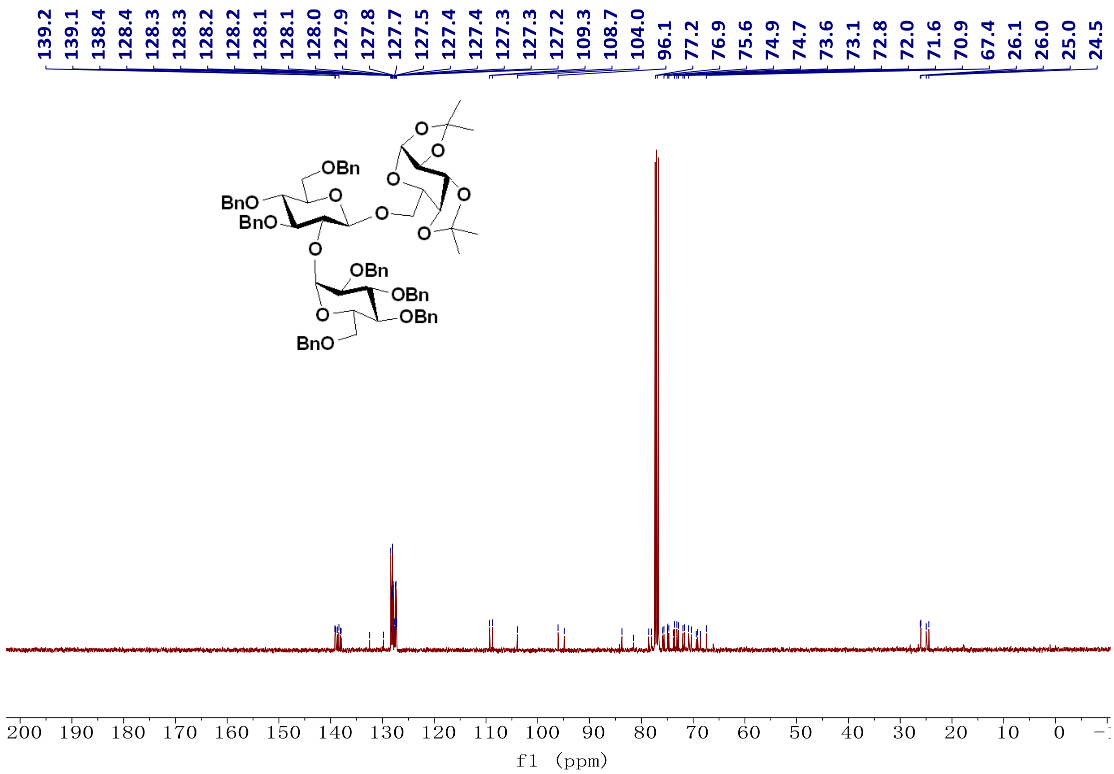
[1]H NMR of **31** (300 MHz, $CDCl_3$)



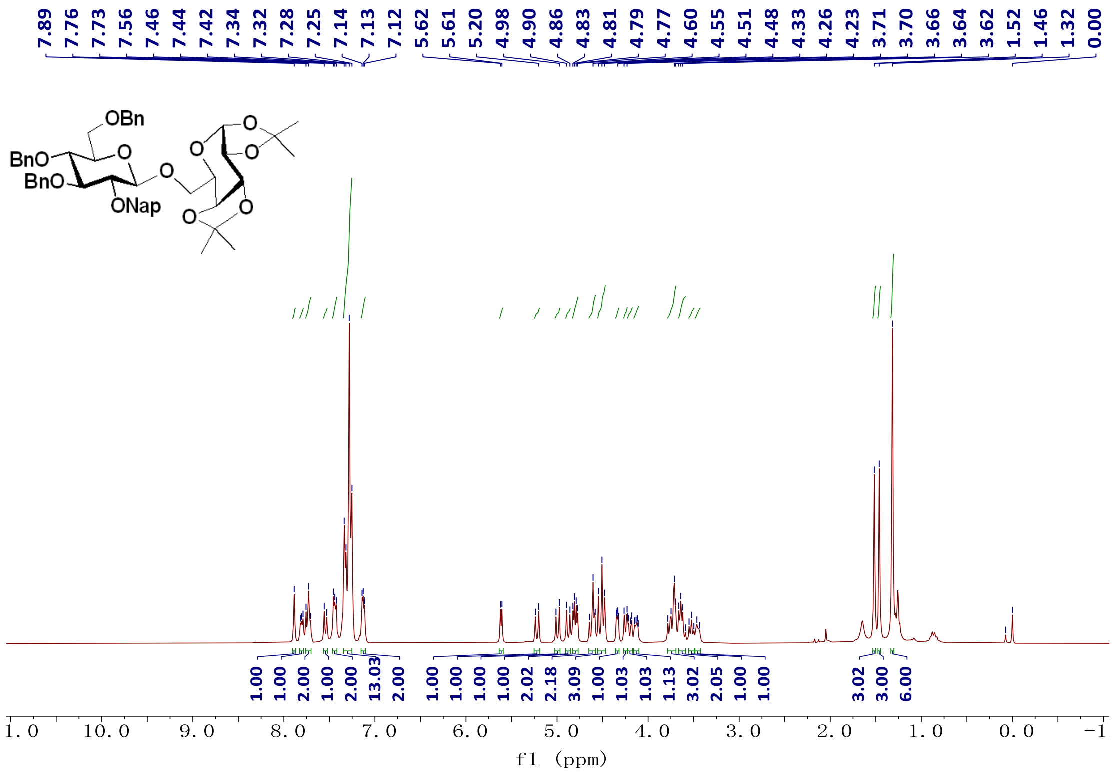
[13]C NMR of **31** (75 MHz, $CDCl_3$)



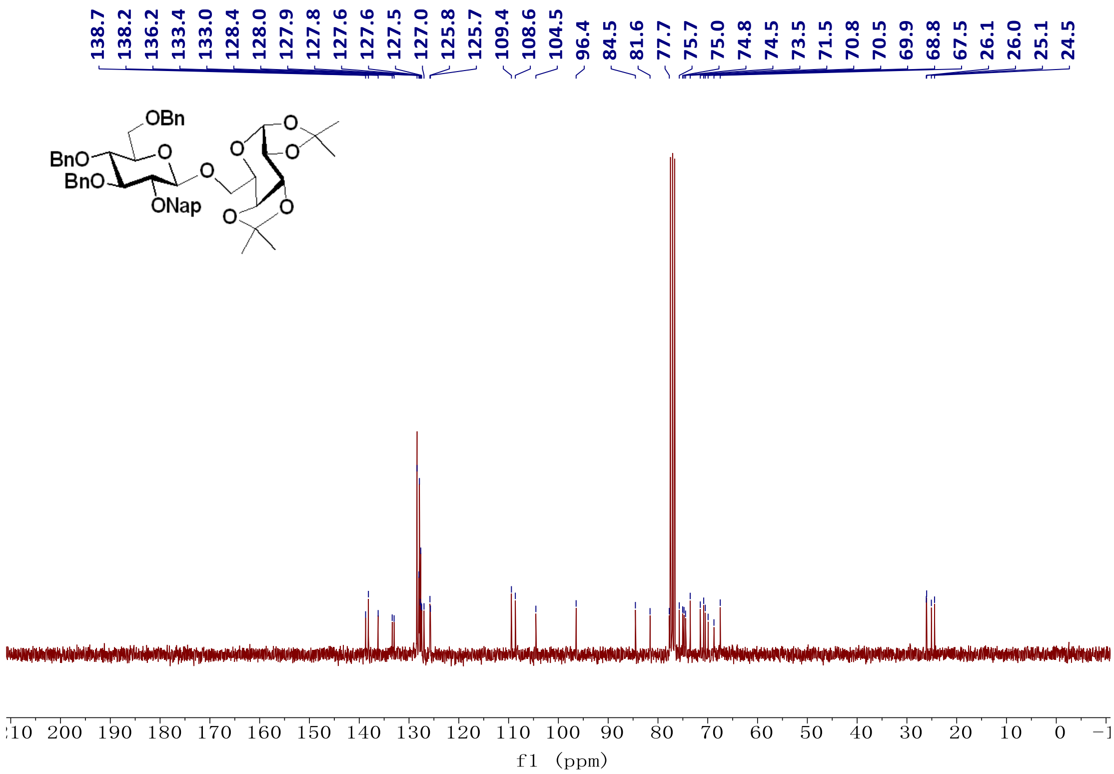
^{1}H NMR of **32** (400 MHz, $CDCl_3$)



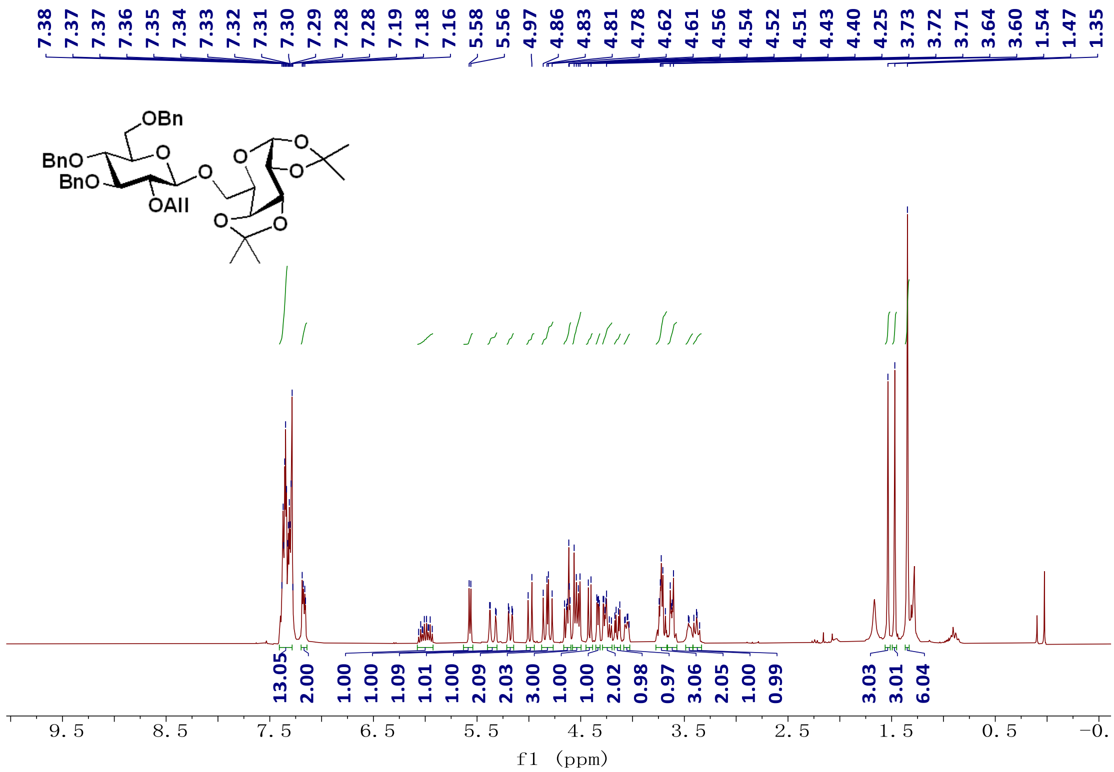
^{13}C NMR of **32** (100 MHz, $CDCl_3$)



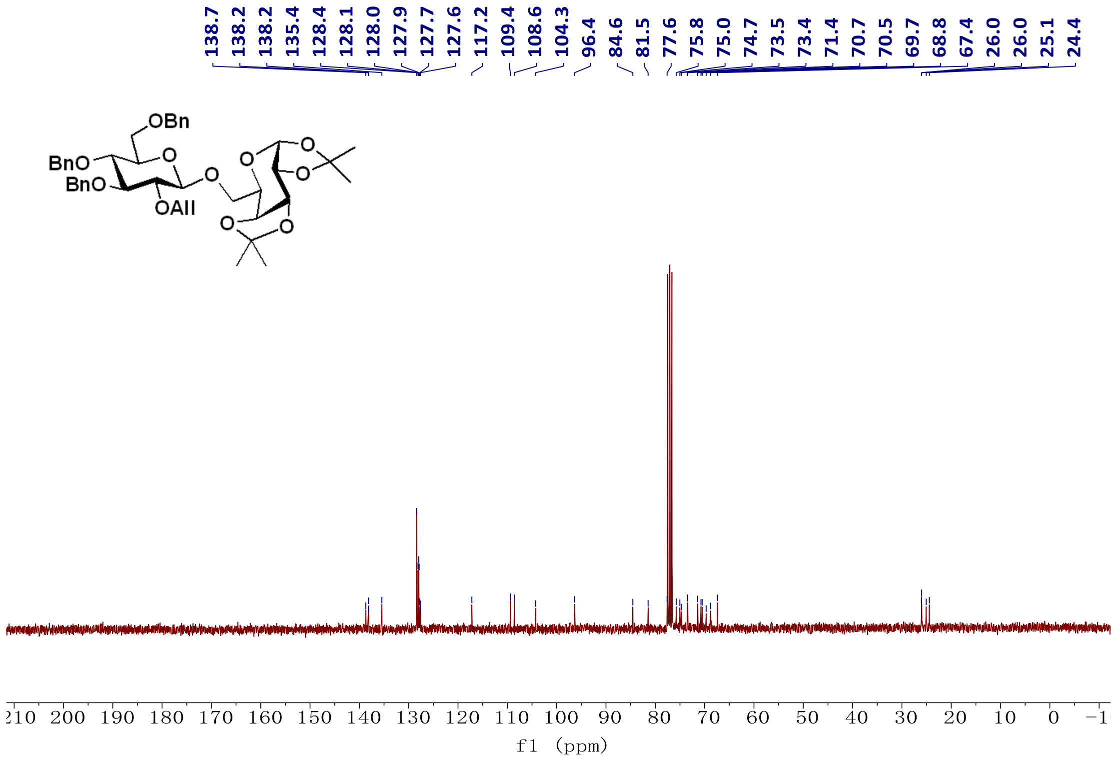
^{1}H NMR of **47** (300 MHz, $CDCl_3$)



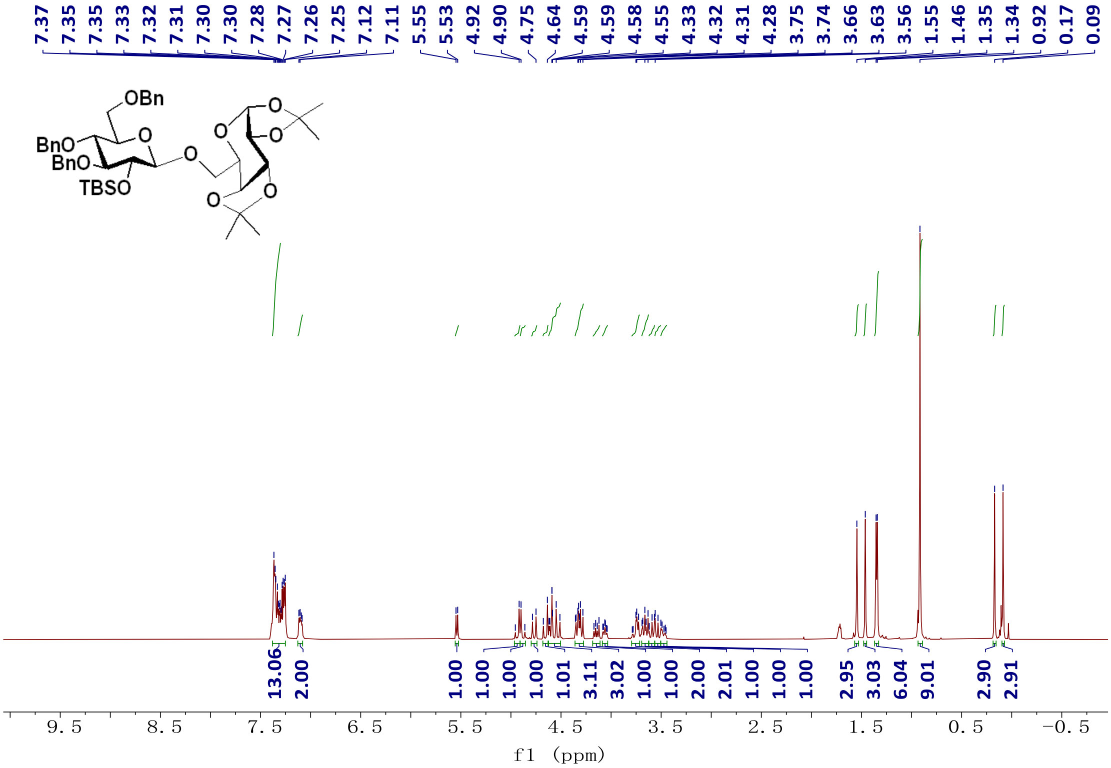
^{13}C NMR of **47** (75 MHz, $CDCl_3$)



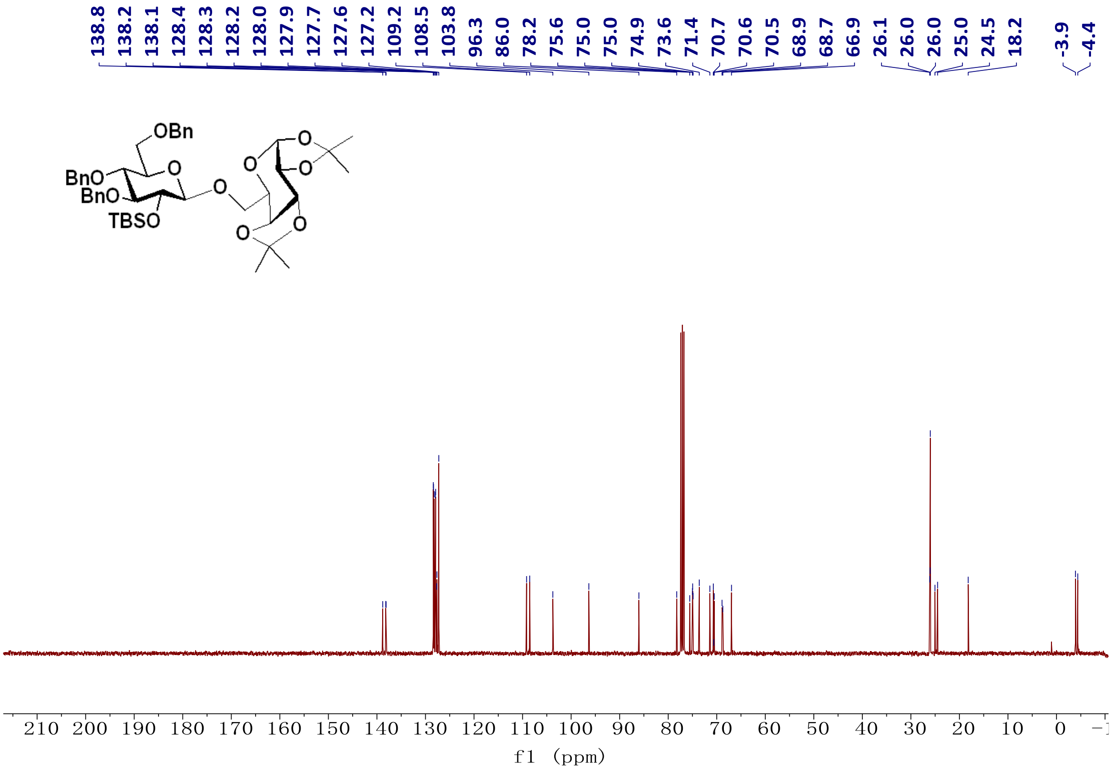
^{1}H NMR of **48** (300 MHz, $CDCl_3$)



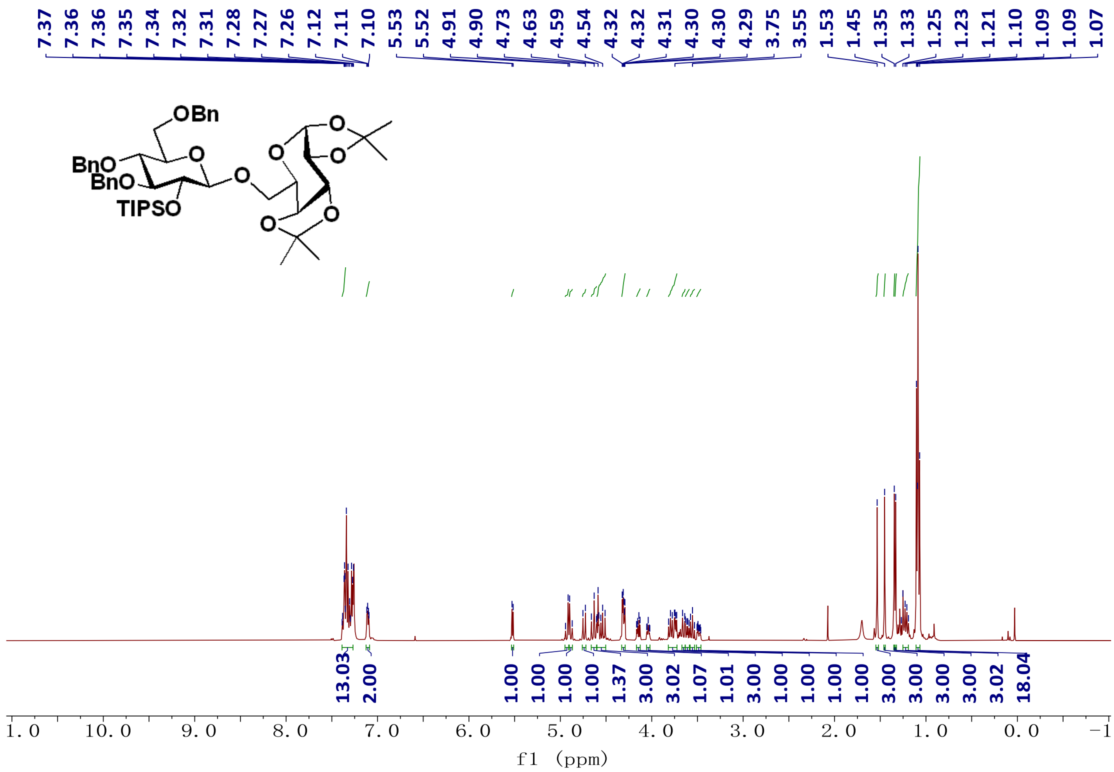
^{13}C NMR of **48** (75 MHz, $CDCl_3$)



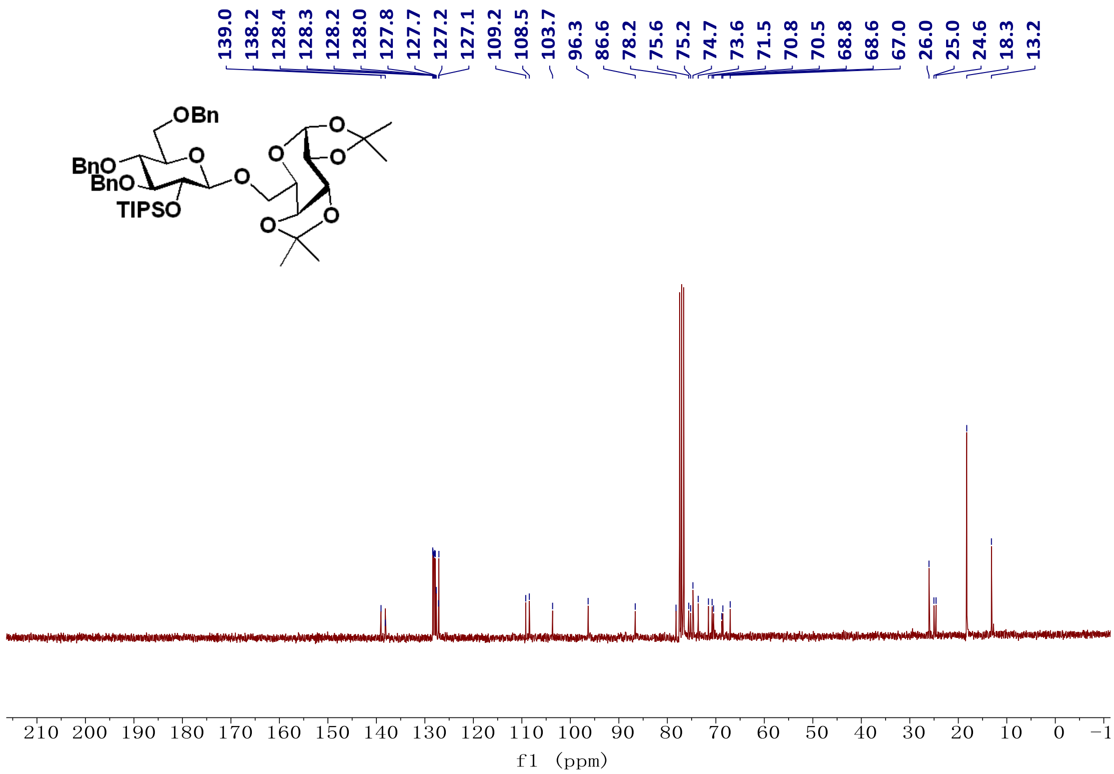
^{1}H NMR of **49** (300 MHz, $CDCl_3$)



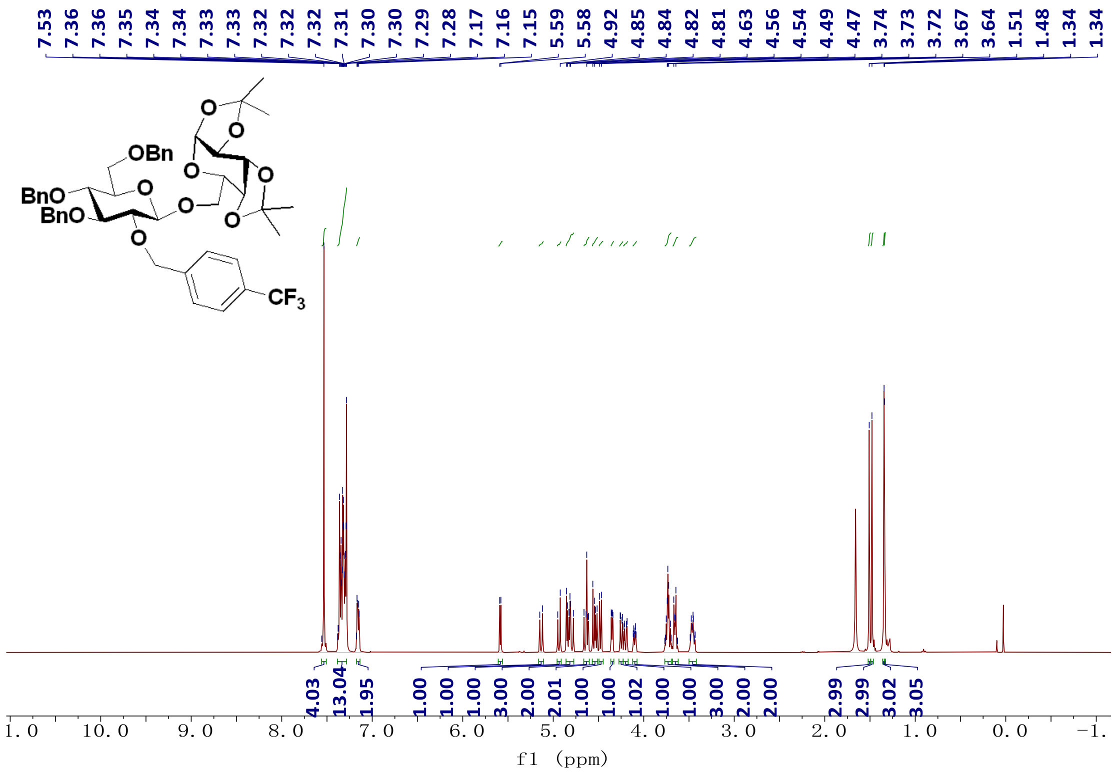
^{13}C NMR of **49** (100 MHz, $CDCl_3$)



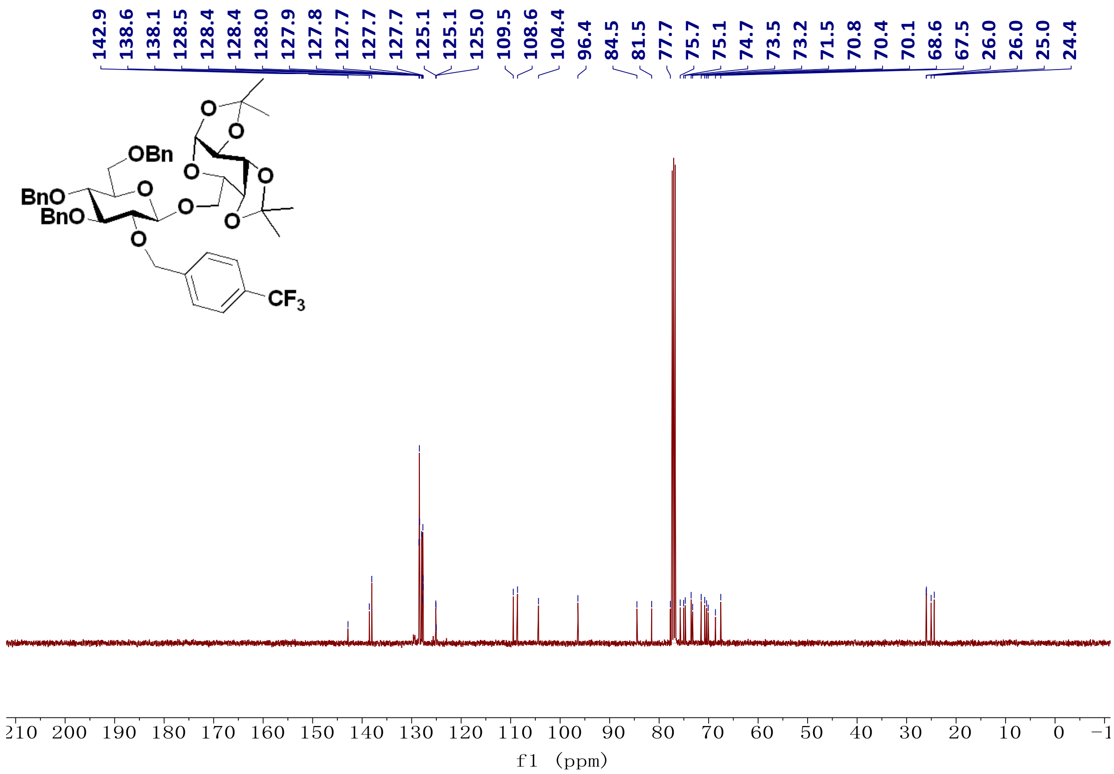
^{1}H NMR of **50** (400 MHz, $CDCl_3$)



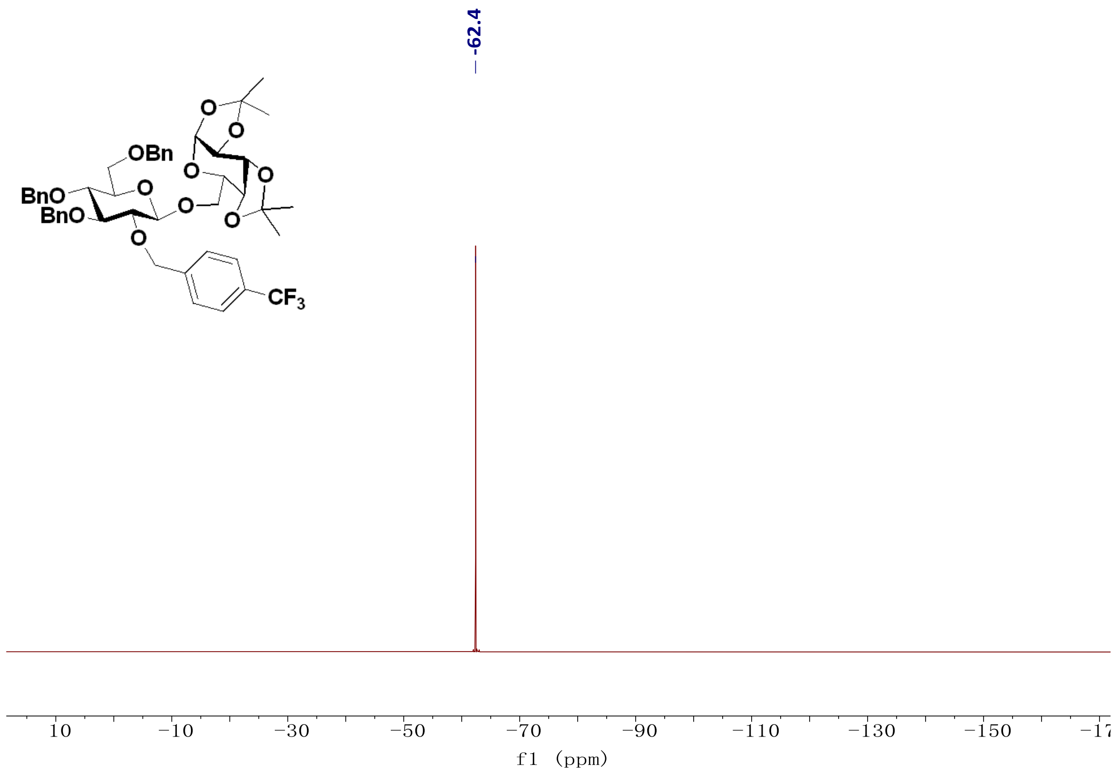
^{13}C NMR of **50** (75 MHz, $CDCl_3$)



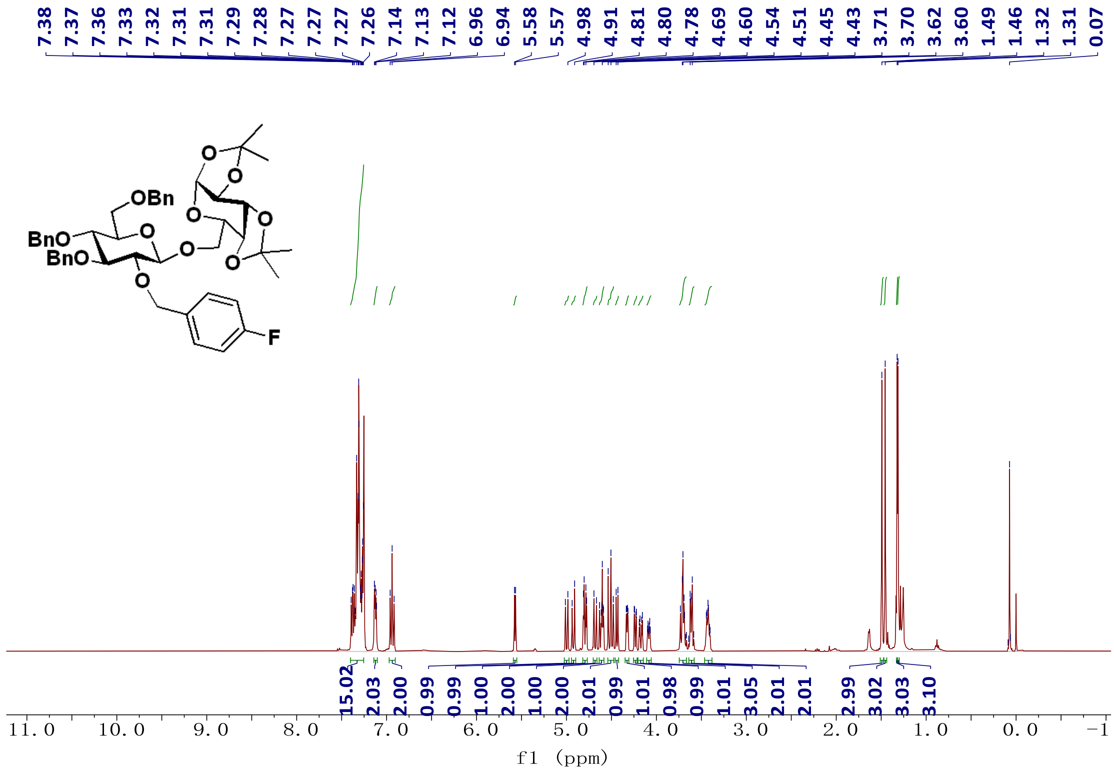
^{1}H NMR of **51** (400 MHz, $CDCl_3$)



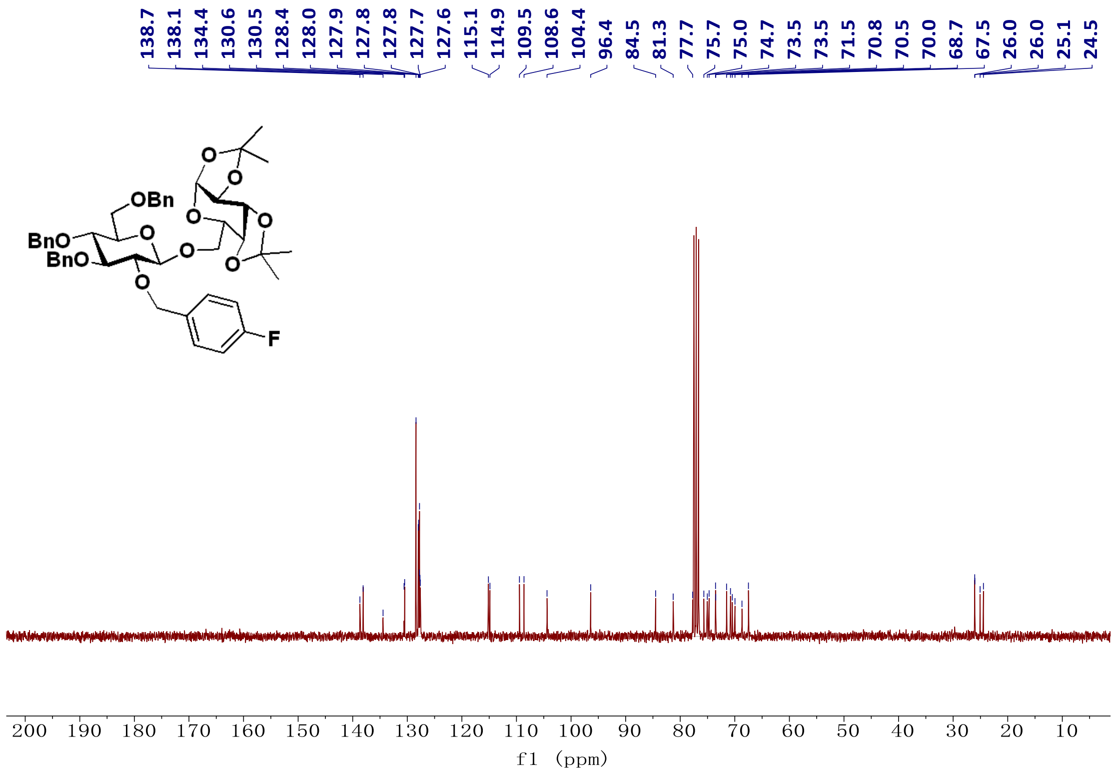
^{13}C NMR of **51** (100 MHz, $CDCl_3$)



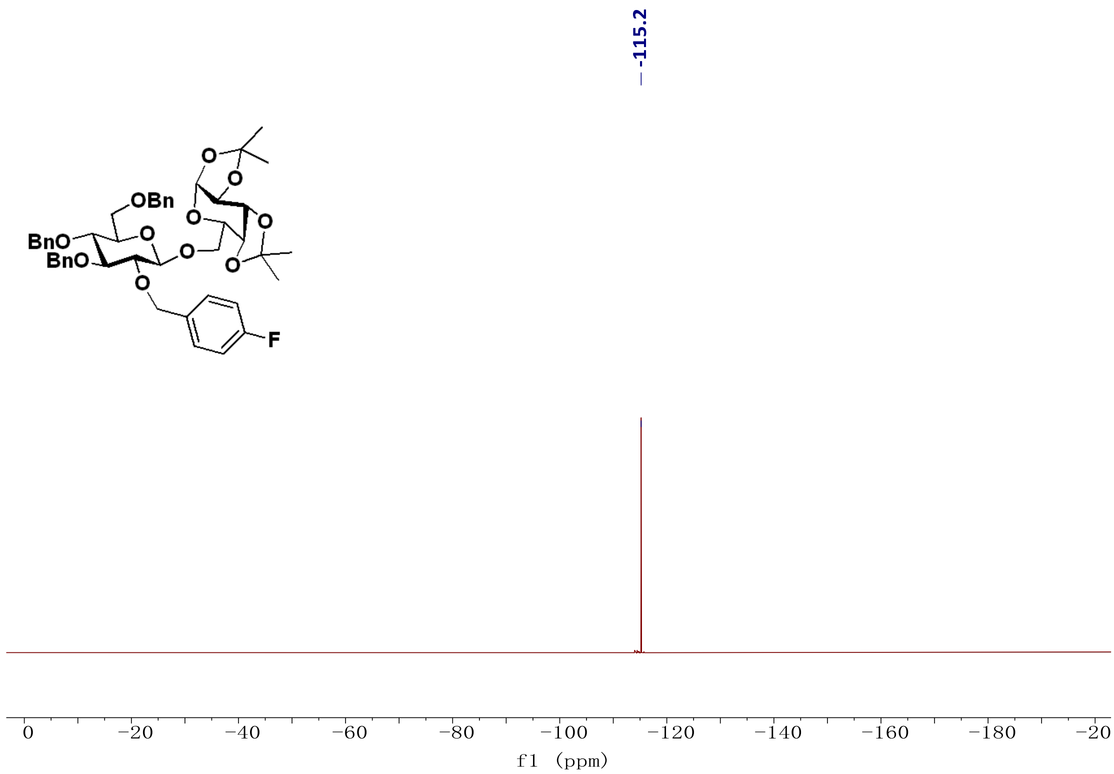
^{19}F NMR of **51** (282 MHz, $CDCl_3$)



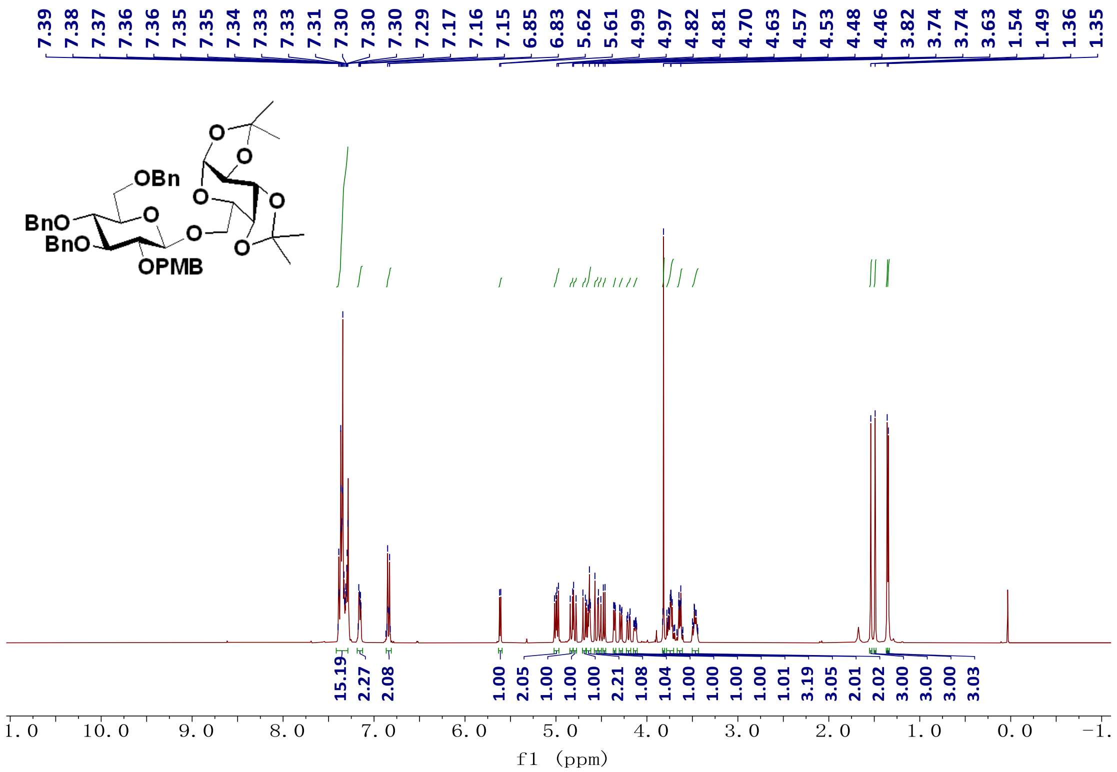
^{1}H NMR of **52** (400 MHz, $CDCl_3$)



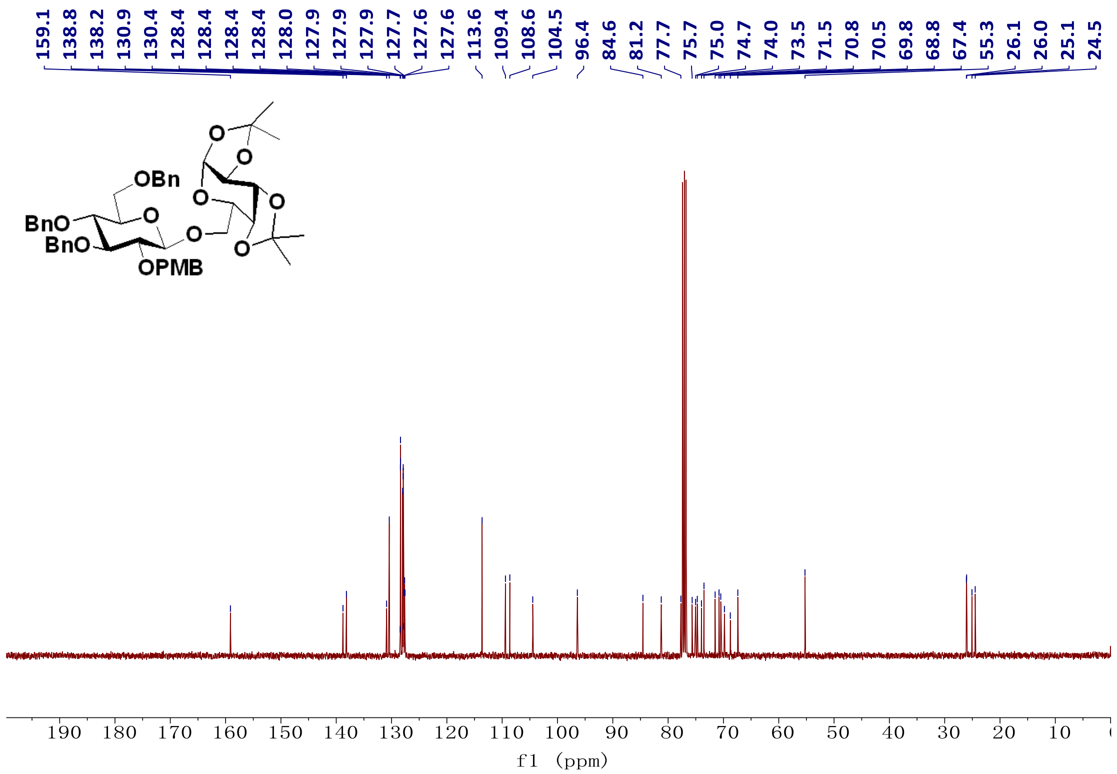
^{13}C NMR of **52** (100 MHz, $CDCl_3$)



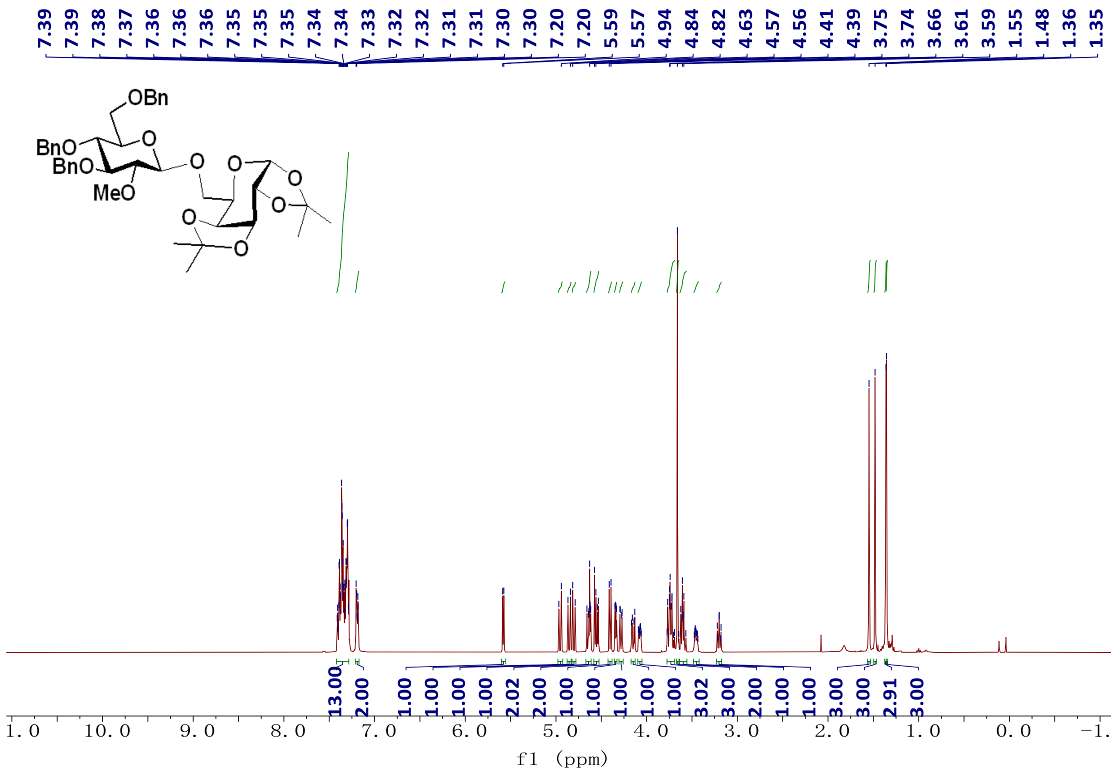
^{19}F NMR of **52** (282 MHz, $CDCl_3$)



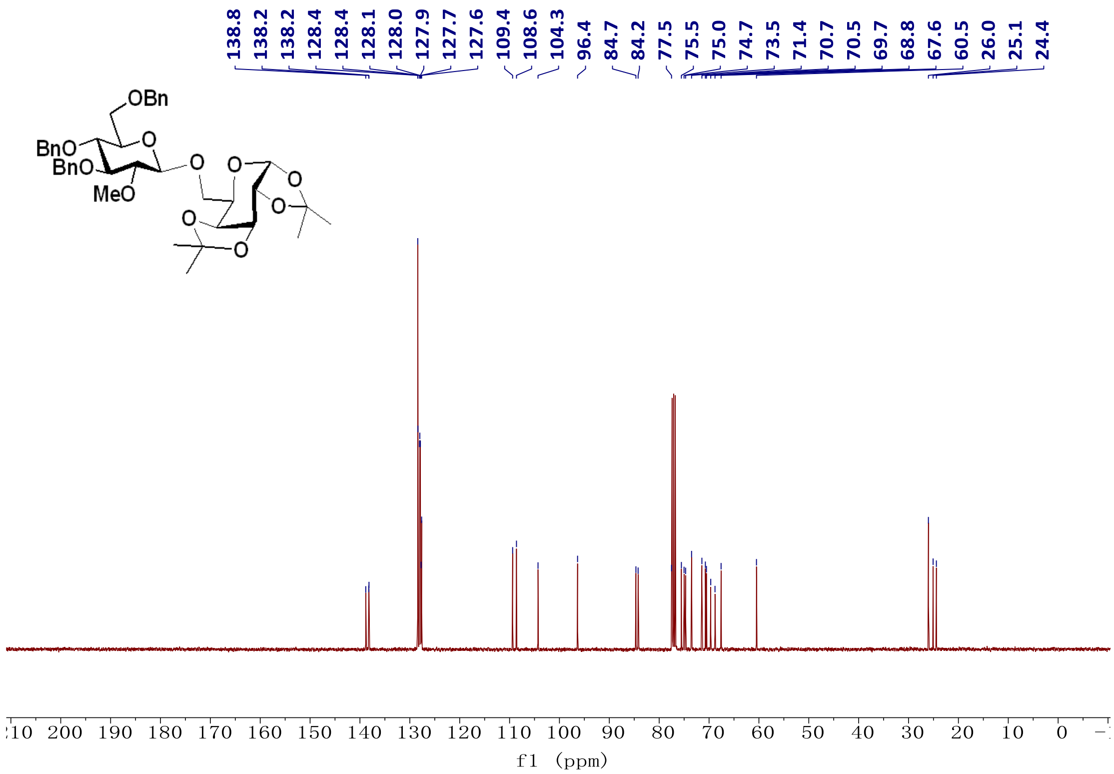
^{1}H NMR of **53** (400 MHz, $CDCl_3$)



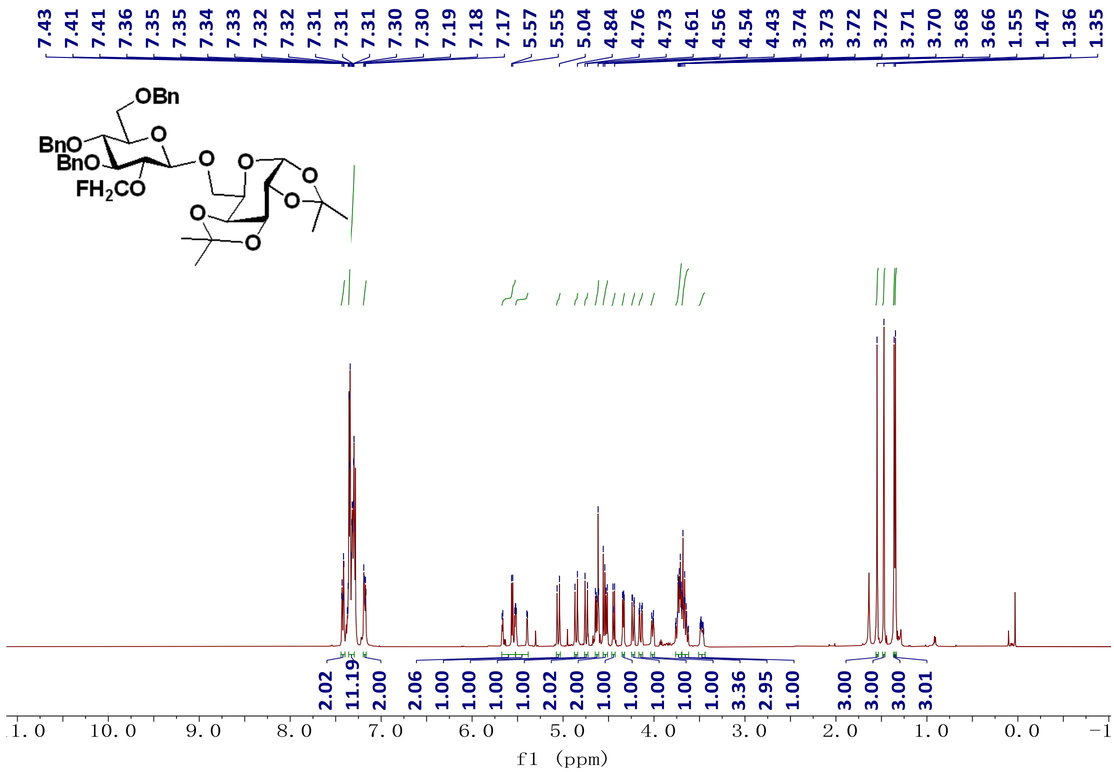
^{13}C NMR of **53** (100 MHz, $CDCl_3$)



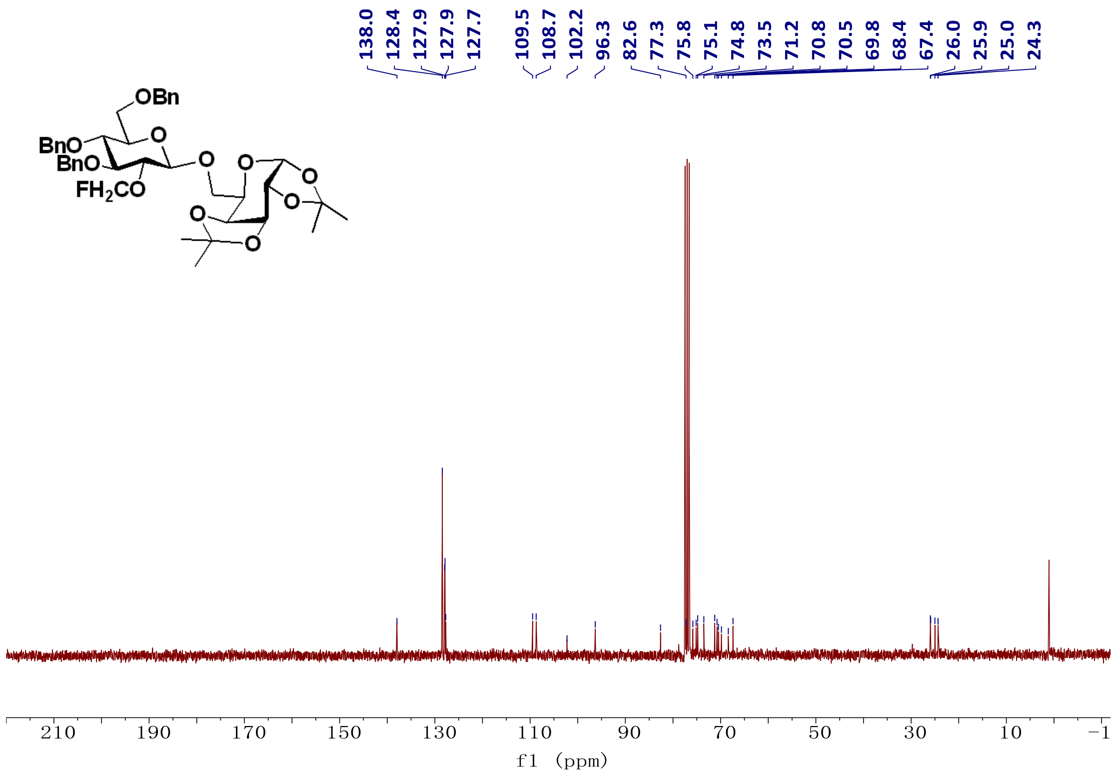
^{1}H NMR of **54** (400 MHz, $CDCl_3$)



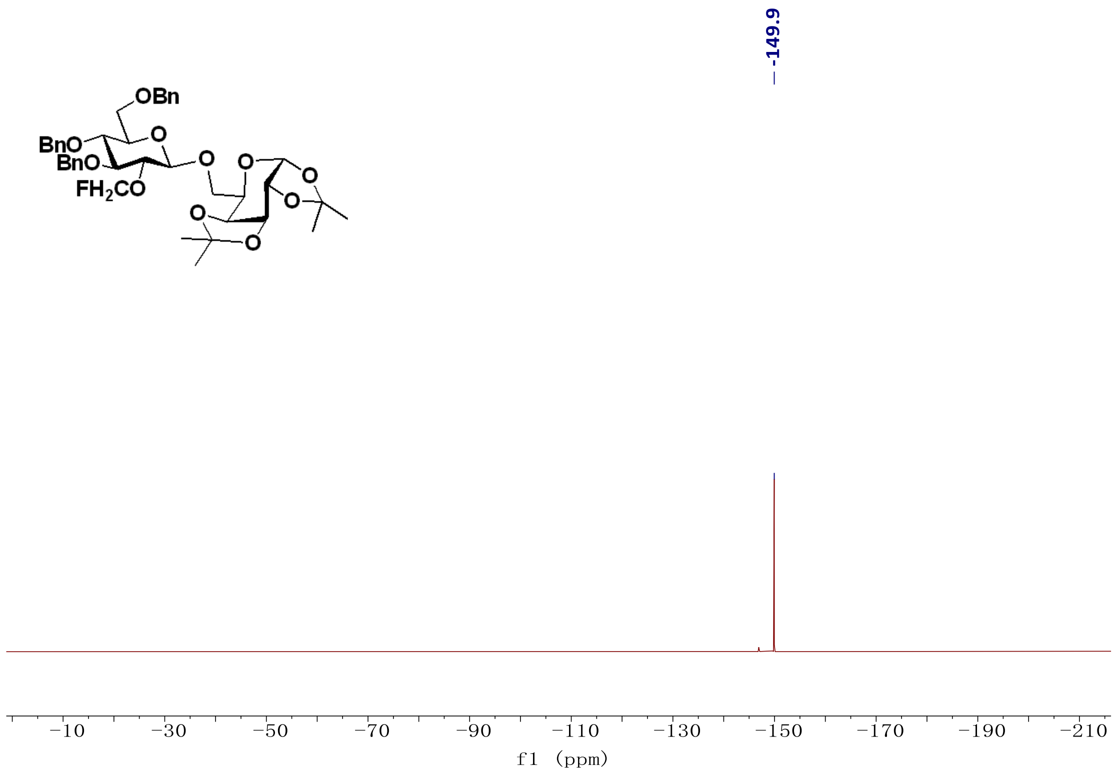
^{13}C NMR of **54** (100 MHz, $CDCl_3$)



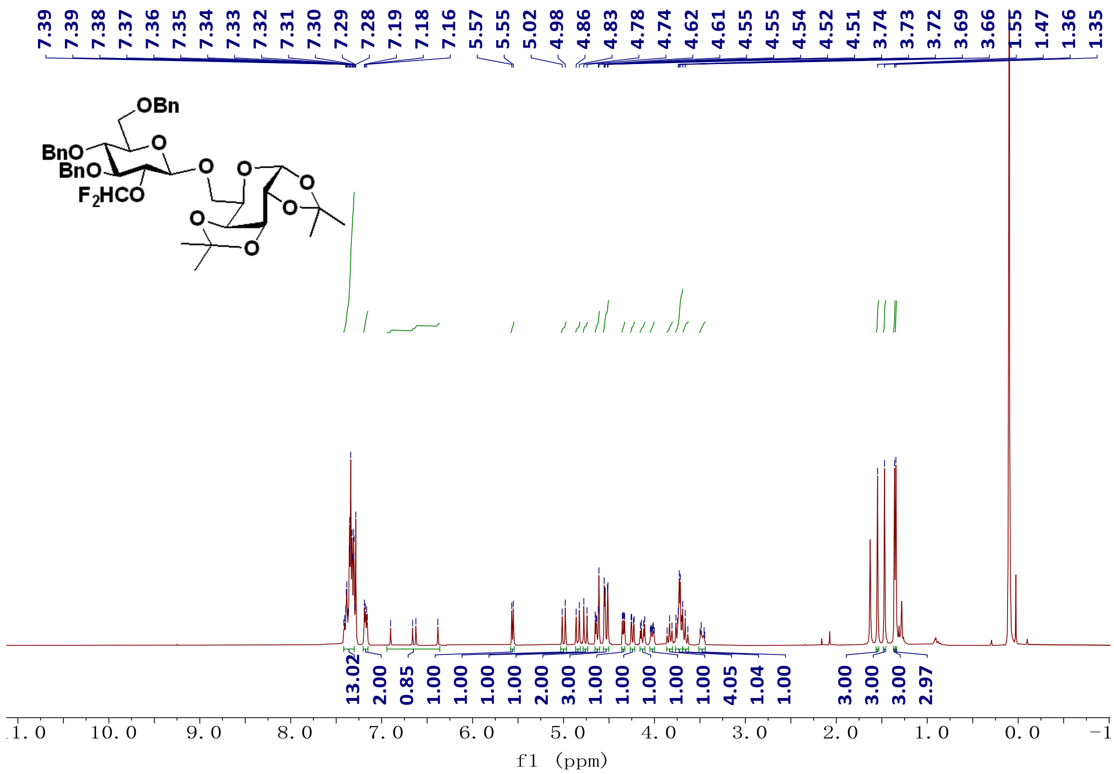
^{1}H NMR of **55** (400 MHz, $CDCl_3$)



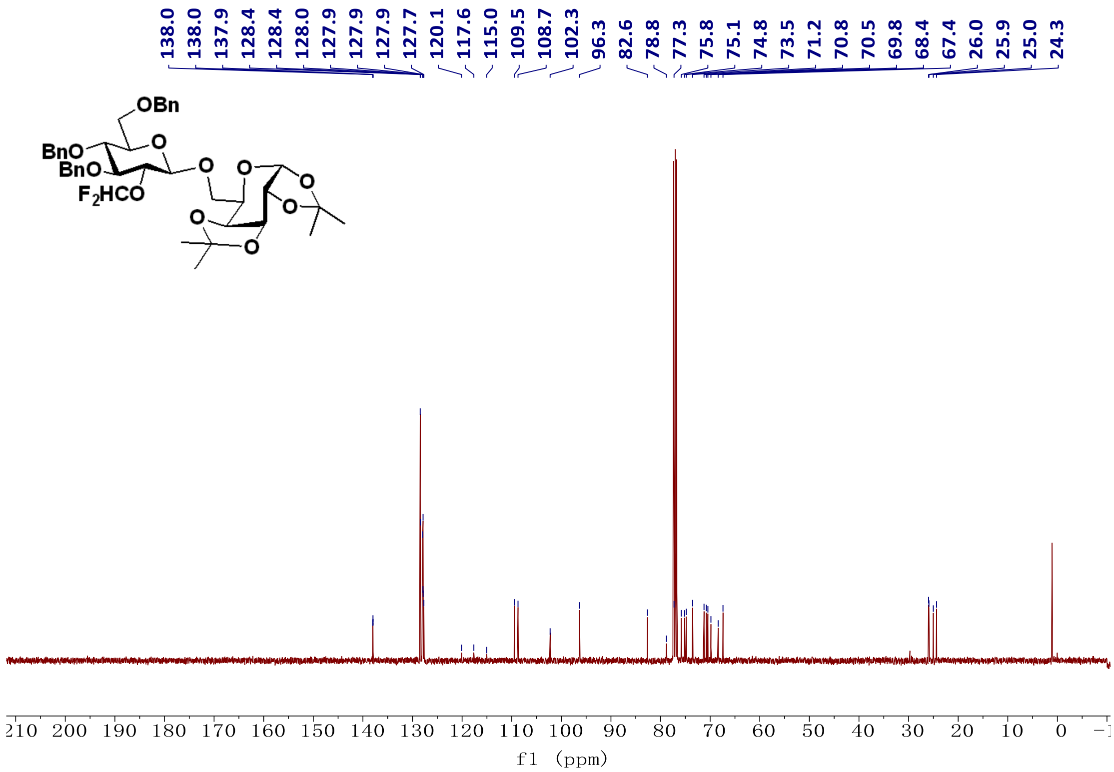
^{13}C NMR of **55** (75 MHz, $CDCl_3$)



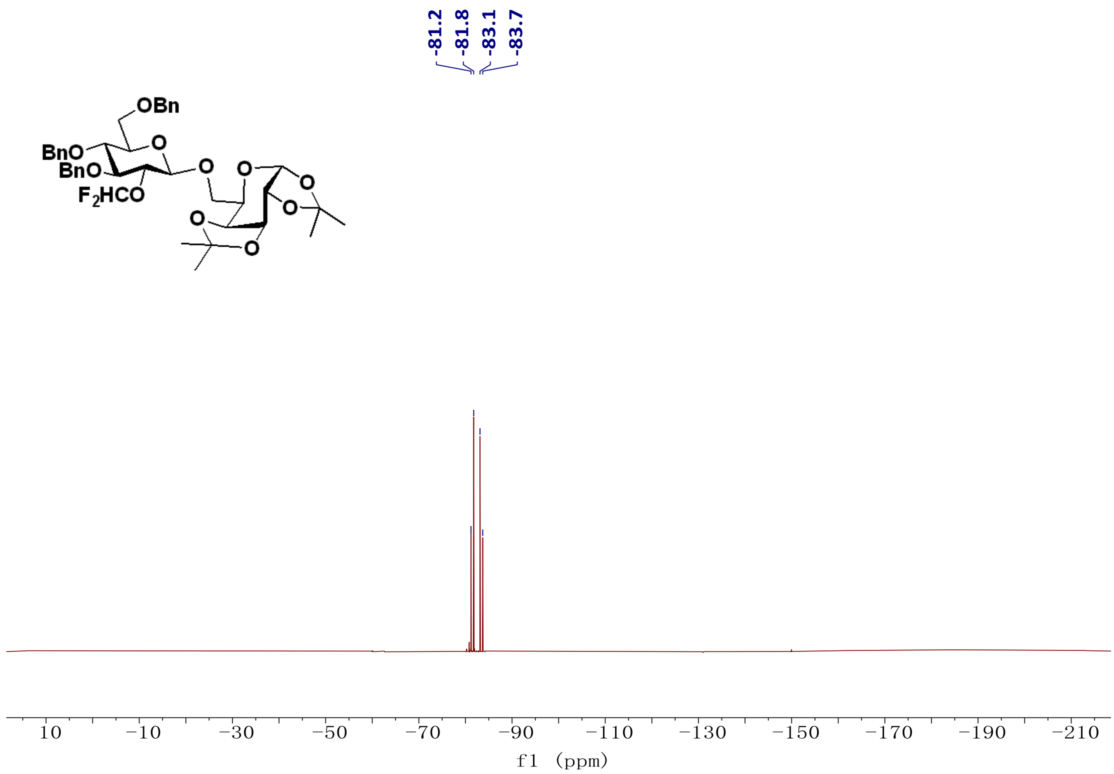
^{19}F NMR of **55** (282 MHz, $CDCl_3$)



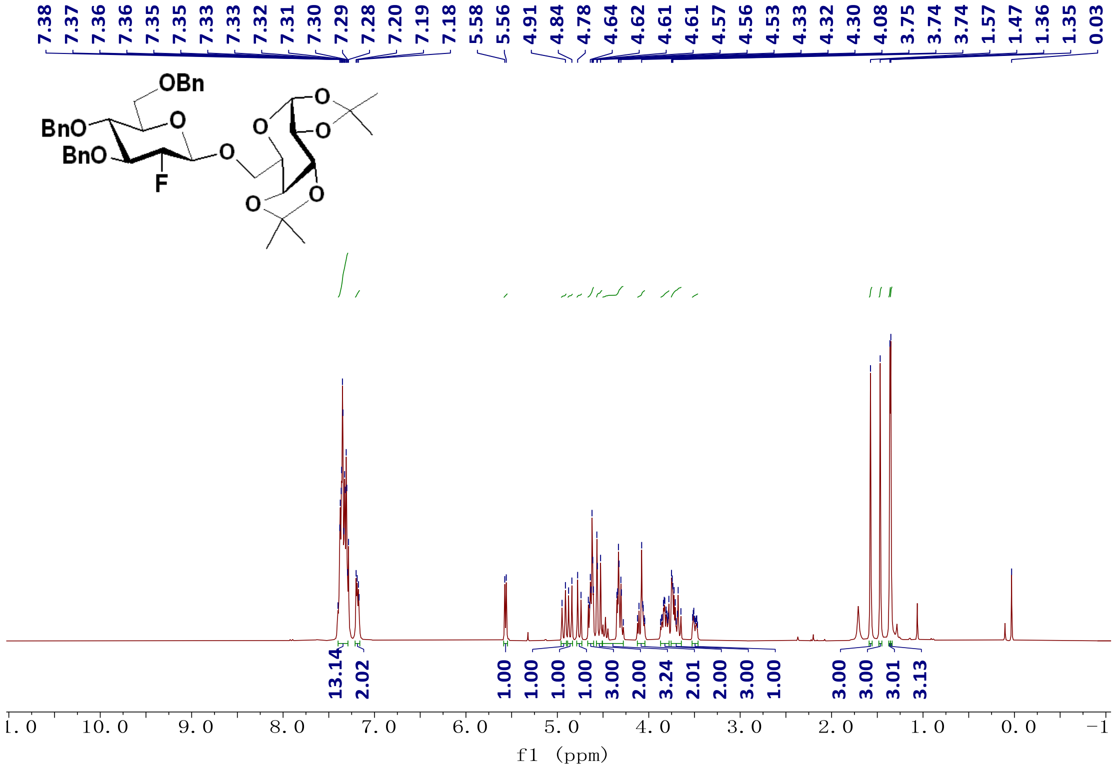
^{1}H NMR of **56** (300 MHz, $CDCl_3$)



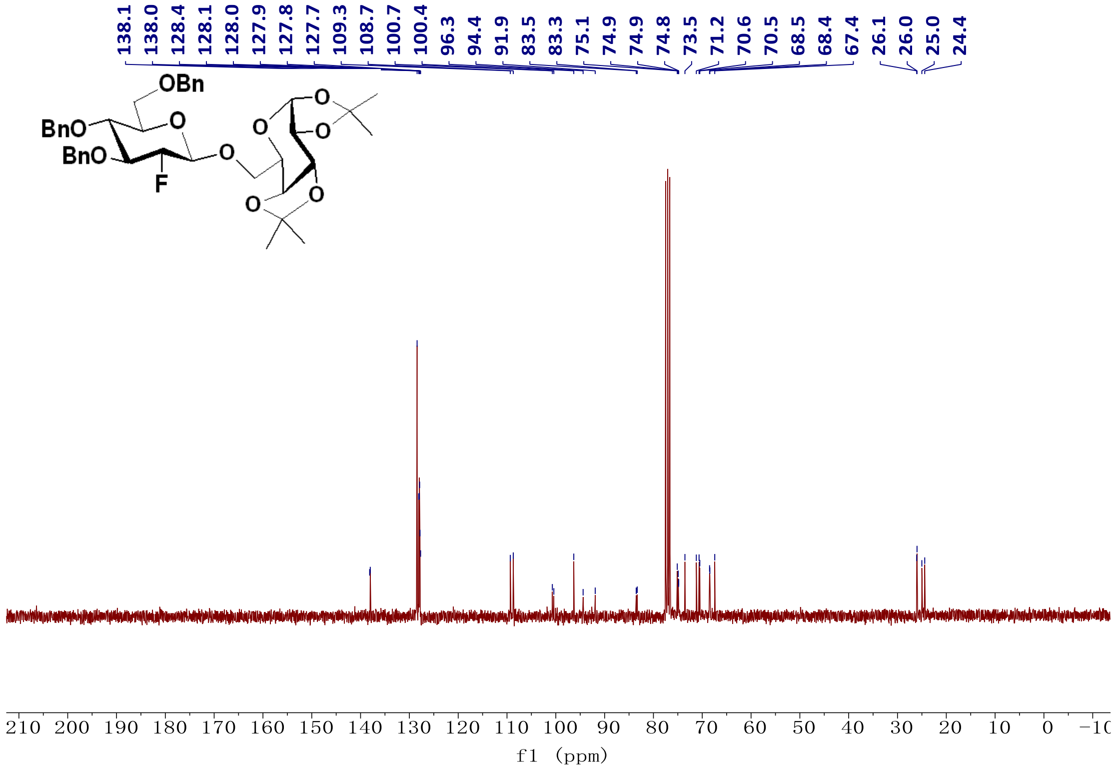
^{13}C NMR of **56** (100 MHz, $CDCl_3$)



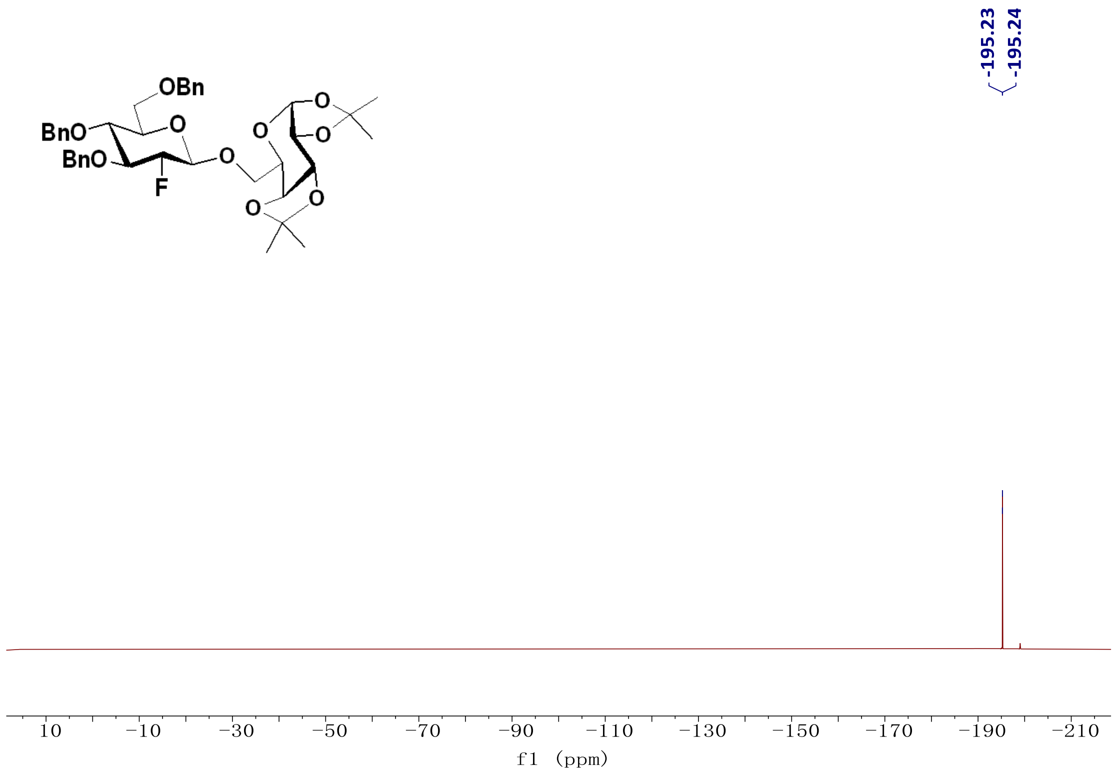
^{19}F NMR of **56** (282 MHz, $CDCl_3$)



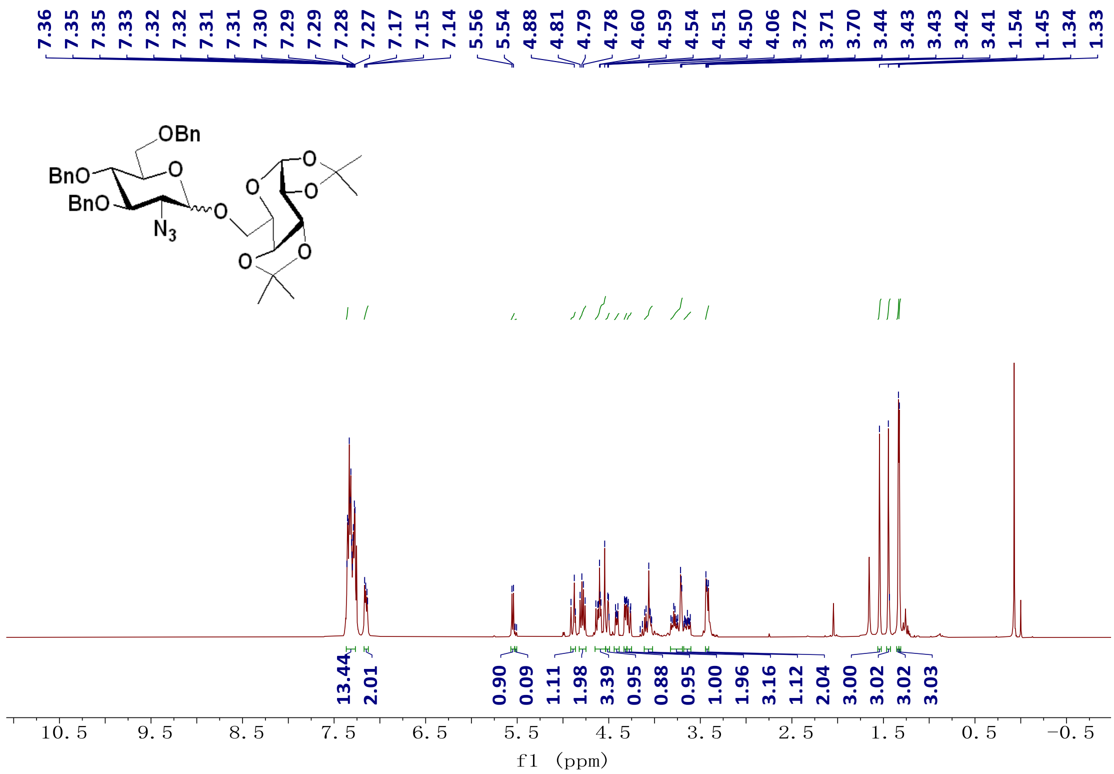
^{1}H NMR of **57** (300 MHz, $CDCl_3$)



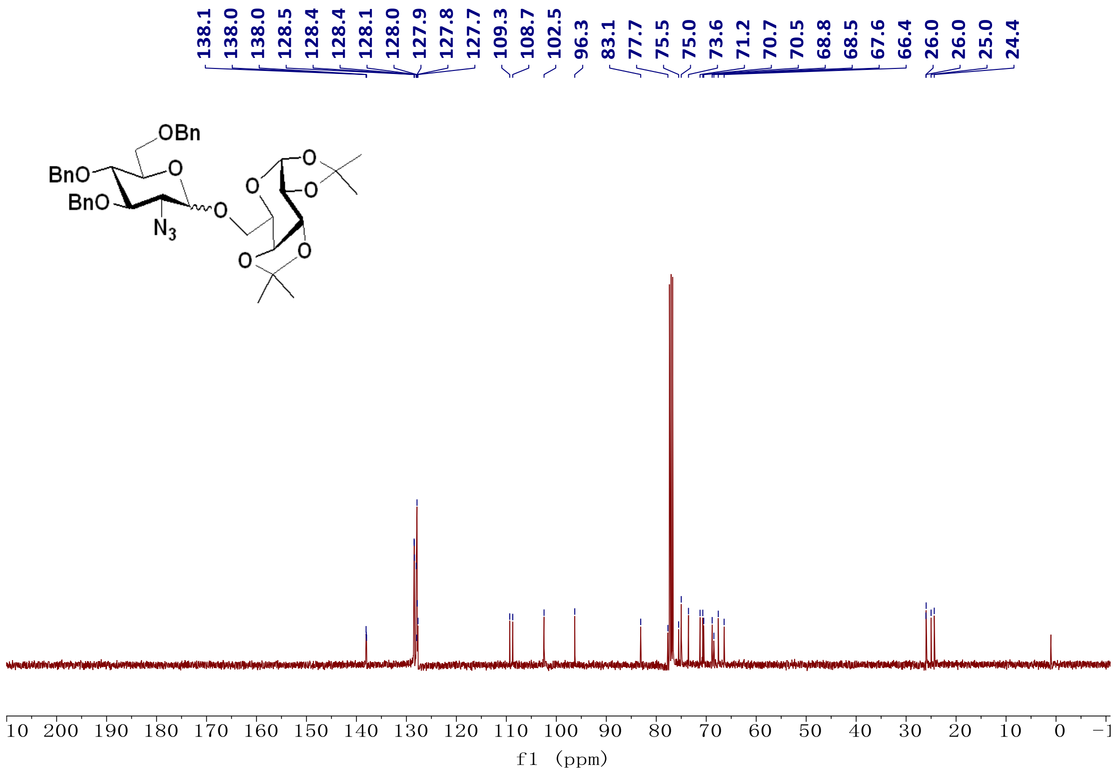
^{13}C NMR of **57** (75 MHz, $CDCl_3$)



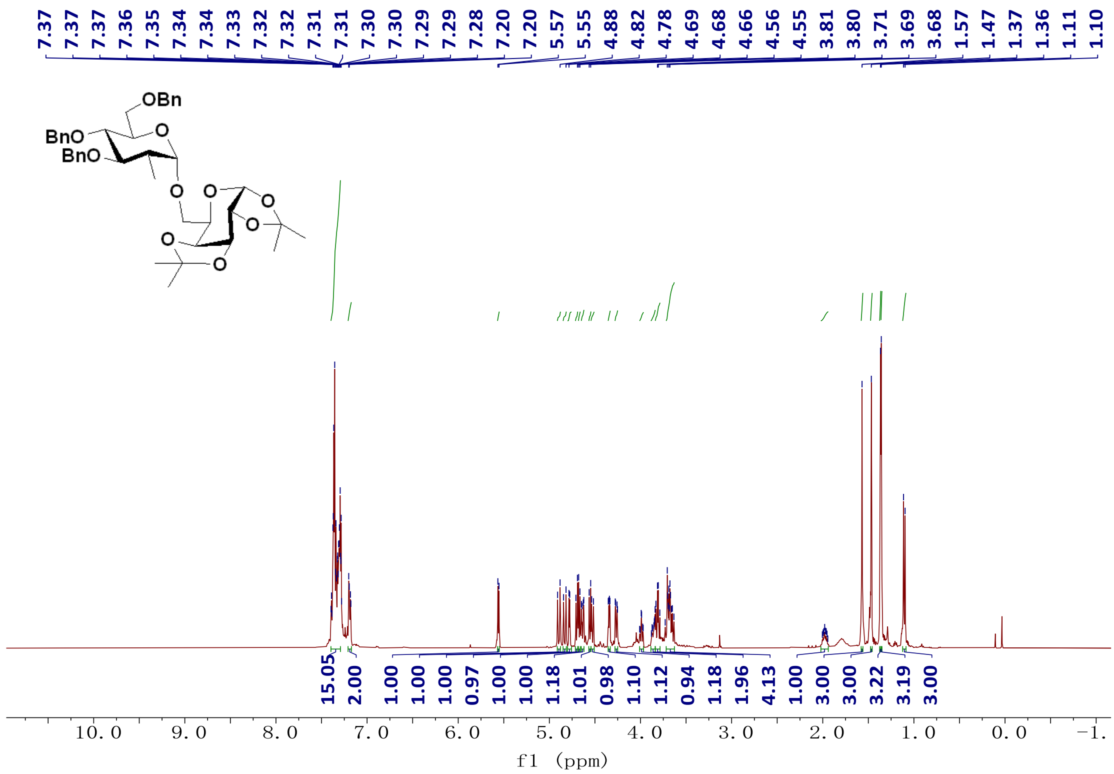
^{19}F NMR of **57** (282 MHz, $CDCl_3$)



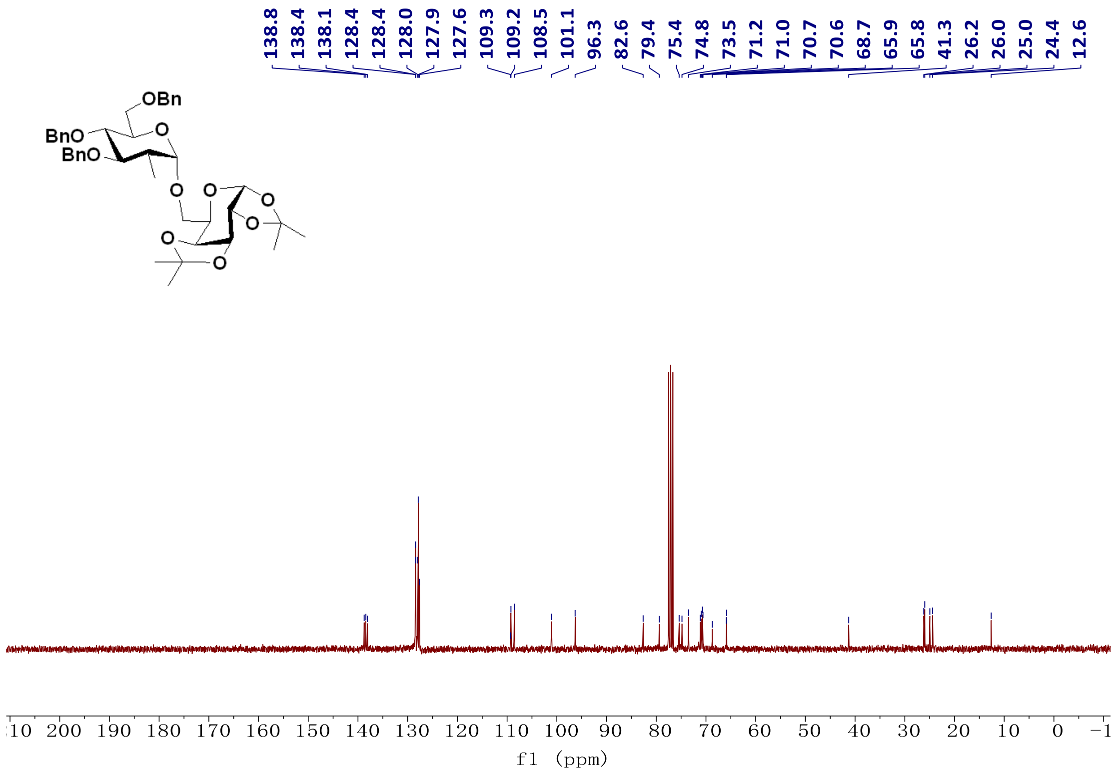
^{1}H NMR of **58** (300 MHz, $CDCl_3$)



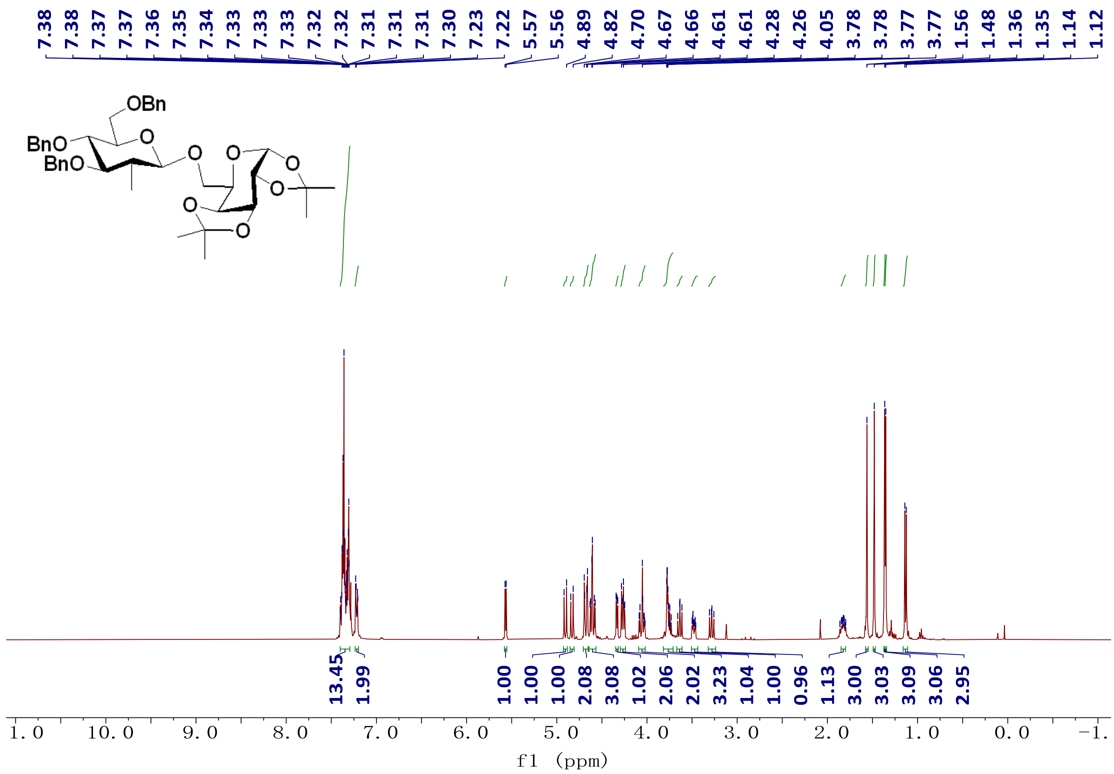
^{13}C NMR of **58** (100 MHz, $CDCl_3$)



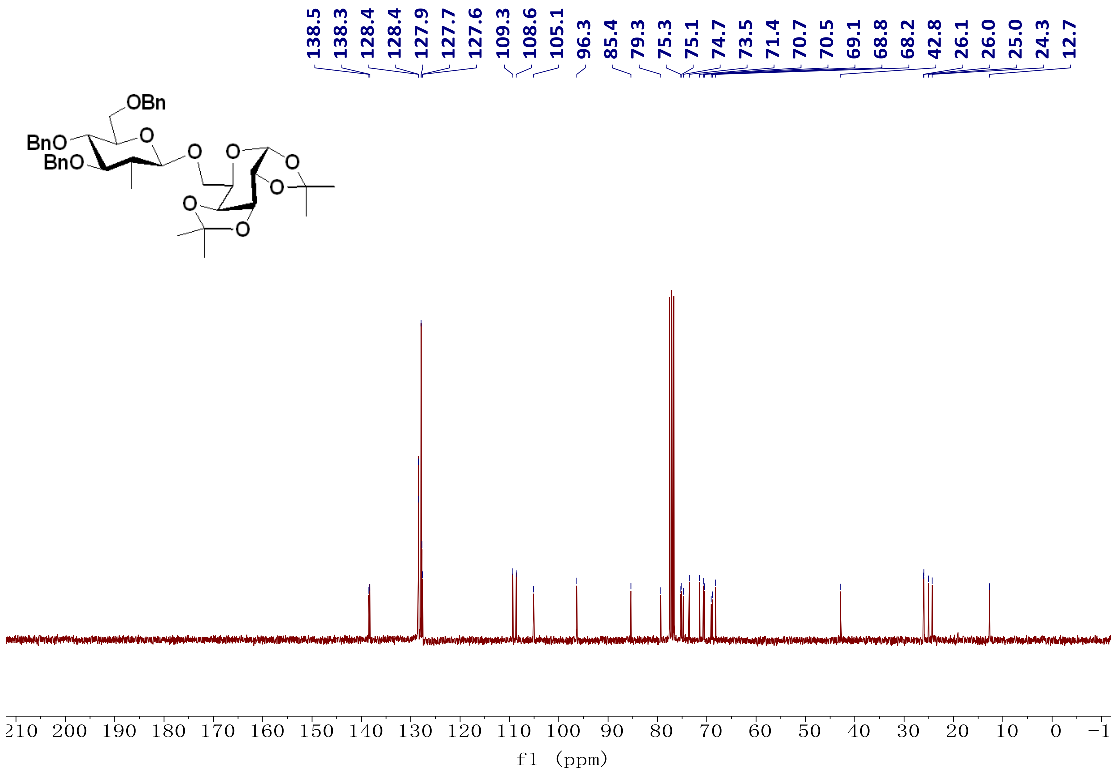
^{1}H NMR of **59 (α)** (400 MHz, $CDCl_3$)



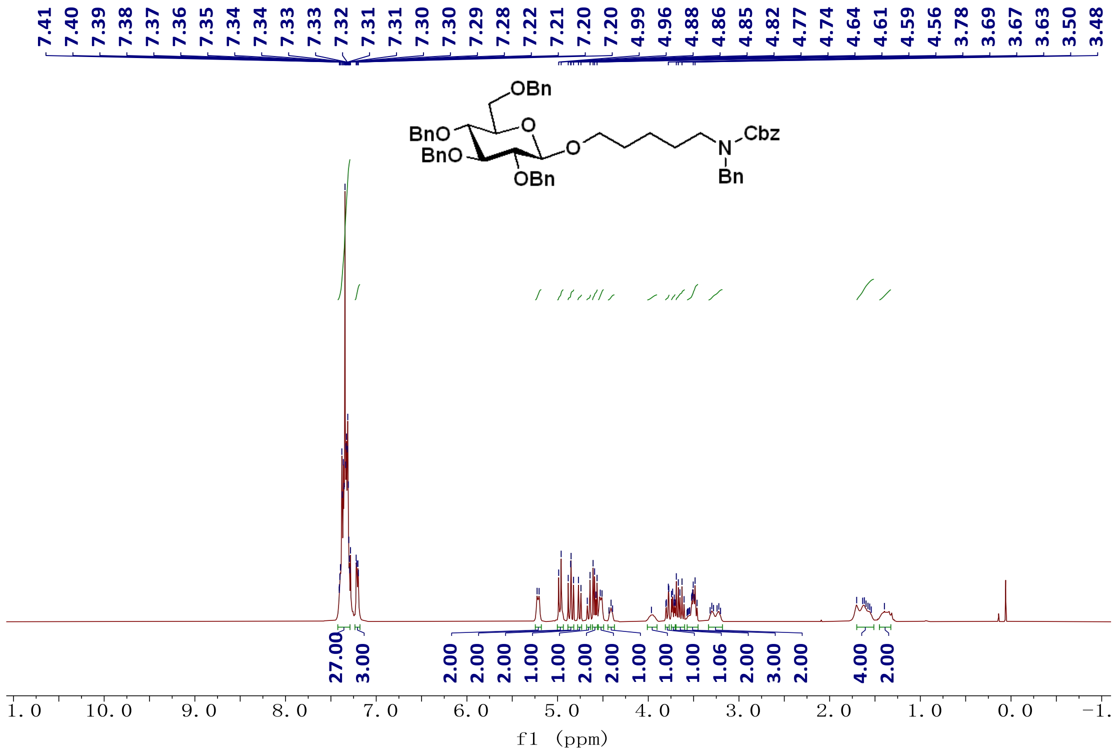
^{13}C NMR **59 (α)** (75 MHz, CDCl$_3$)



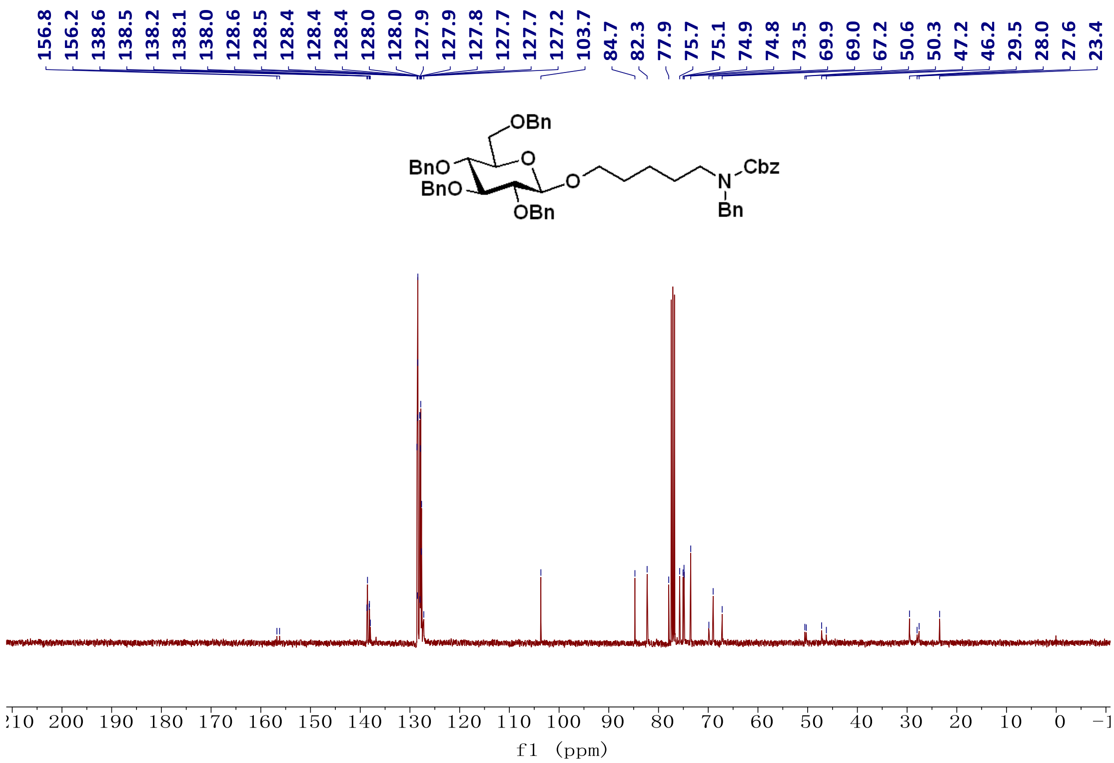
^{1}H NMR of **59 (β)** (400 MHz, CDCl$_3$)



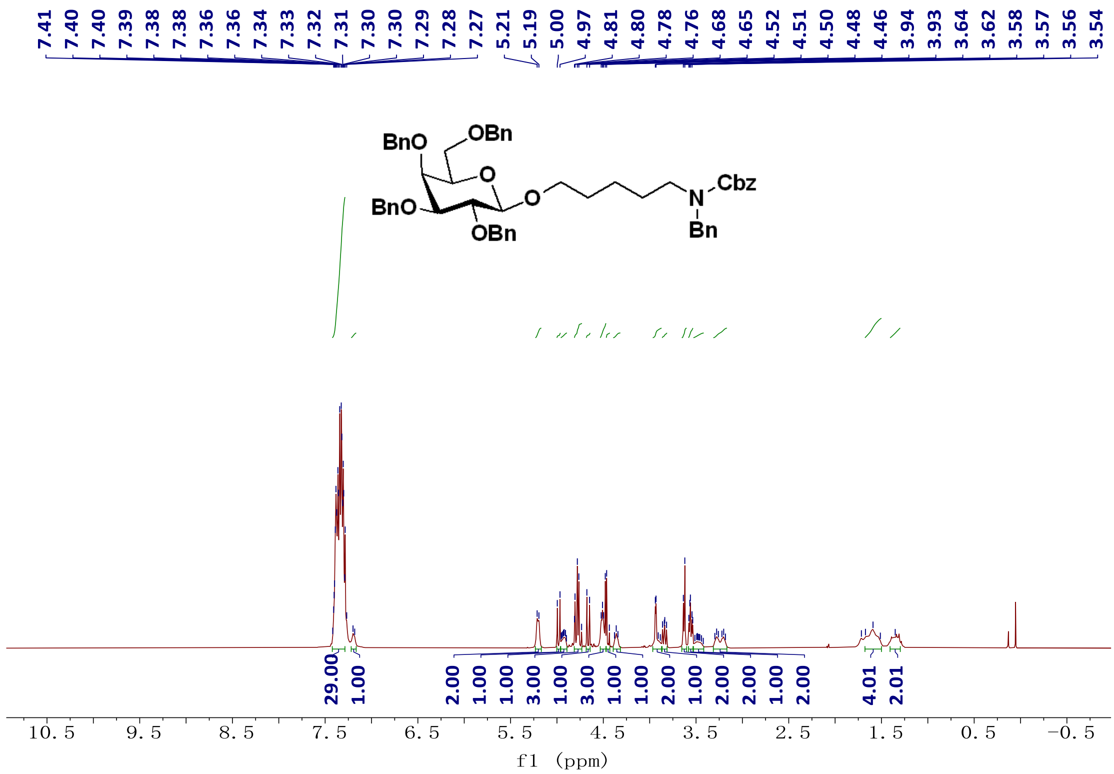
^{13}C NMR **59 (β)** (75 MHz, $CDCl_3$)



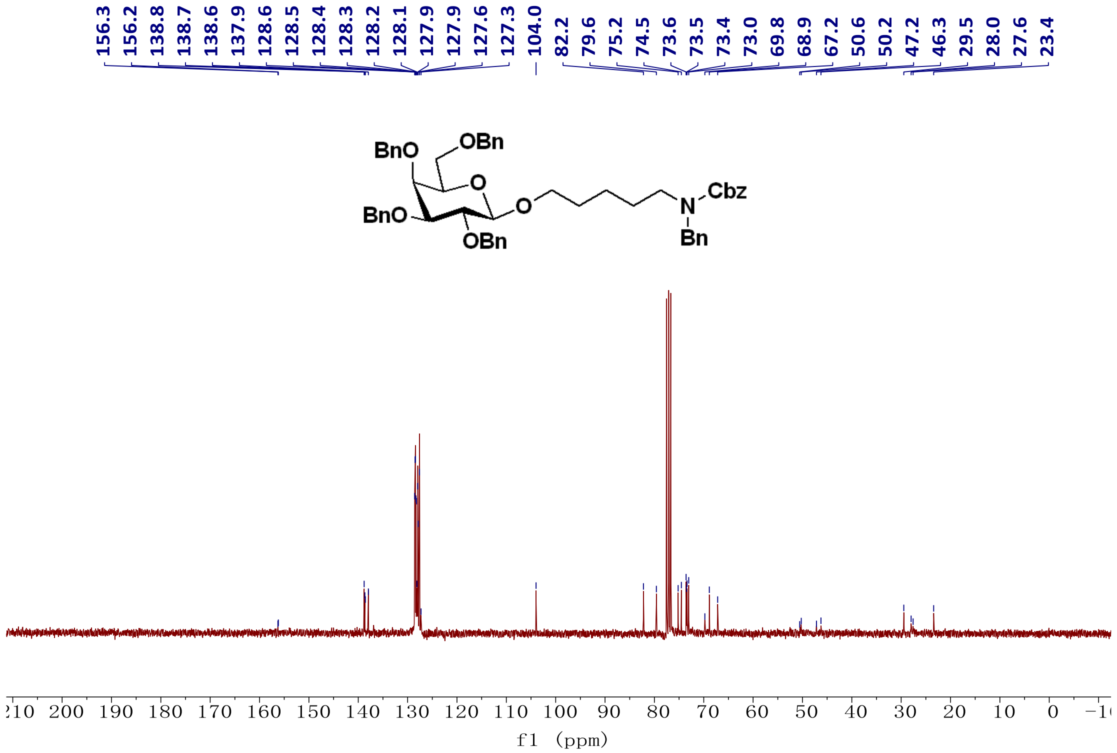
^{1}H NMR **62g** (400 MHz, $CDCl_3$)



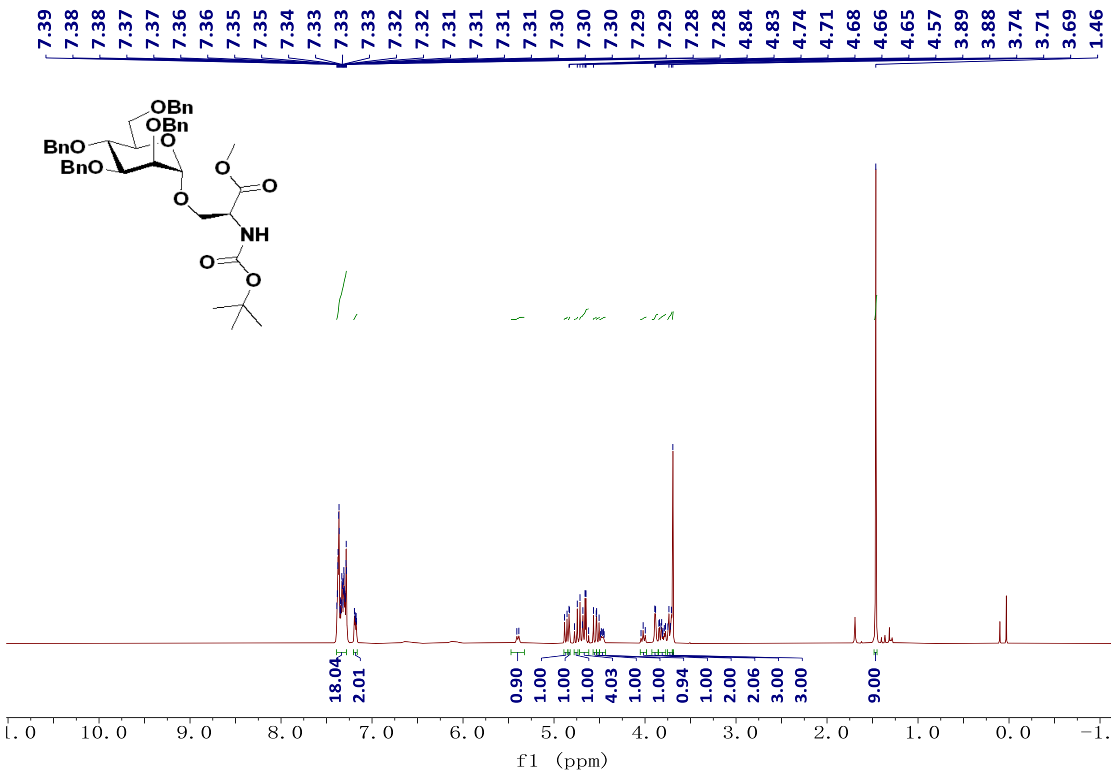
^{13}C NMR of **62g** (100 MHz, $CDCl_3$)



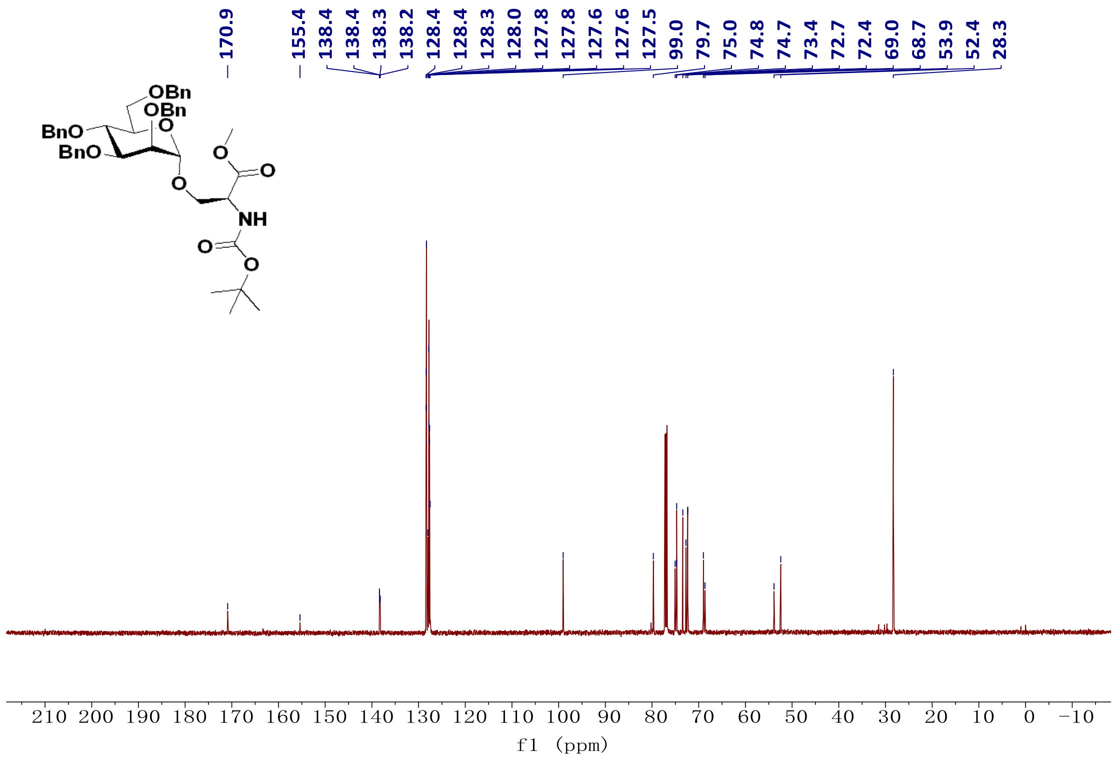
^{1}H NMR **63g** (400 MHz, $CDCl_3$)



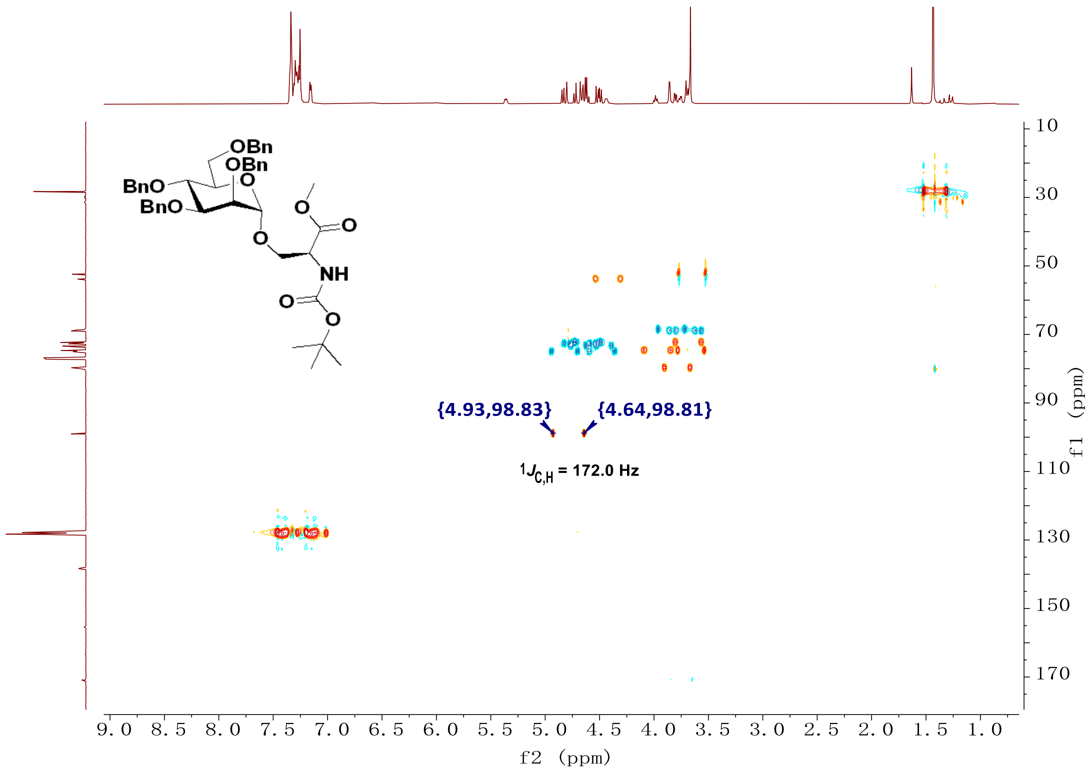
^{13}C NMR of **63g** (100 MHz, $CDCl_3$)



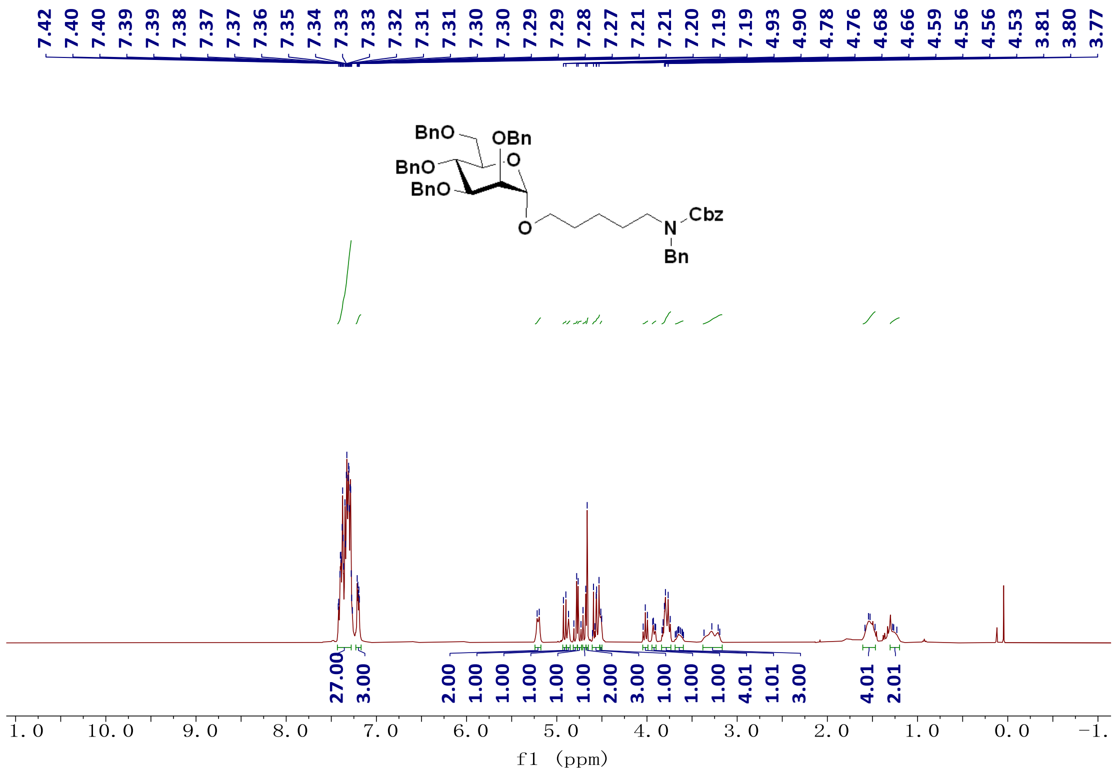
^{1}H NMR **64f** (400 MHz, $CDCl_3$)



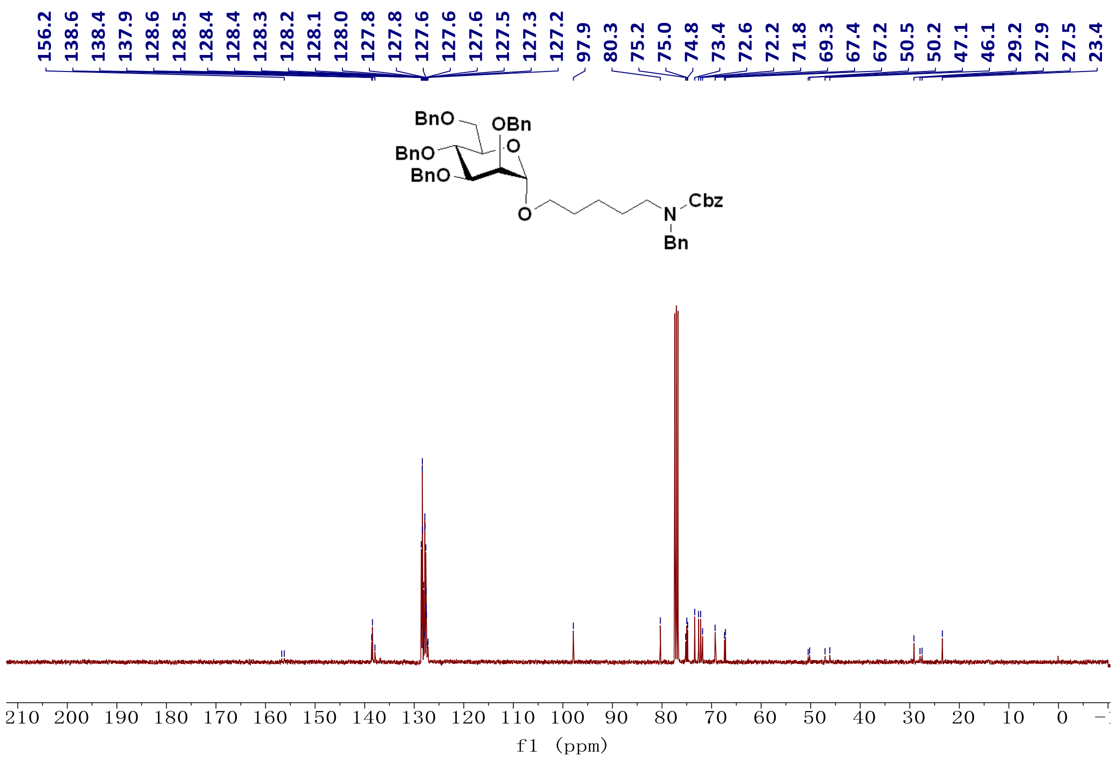
^{13}C NMR of **64f** (150 MHz, $CDCl_3$)



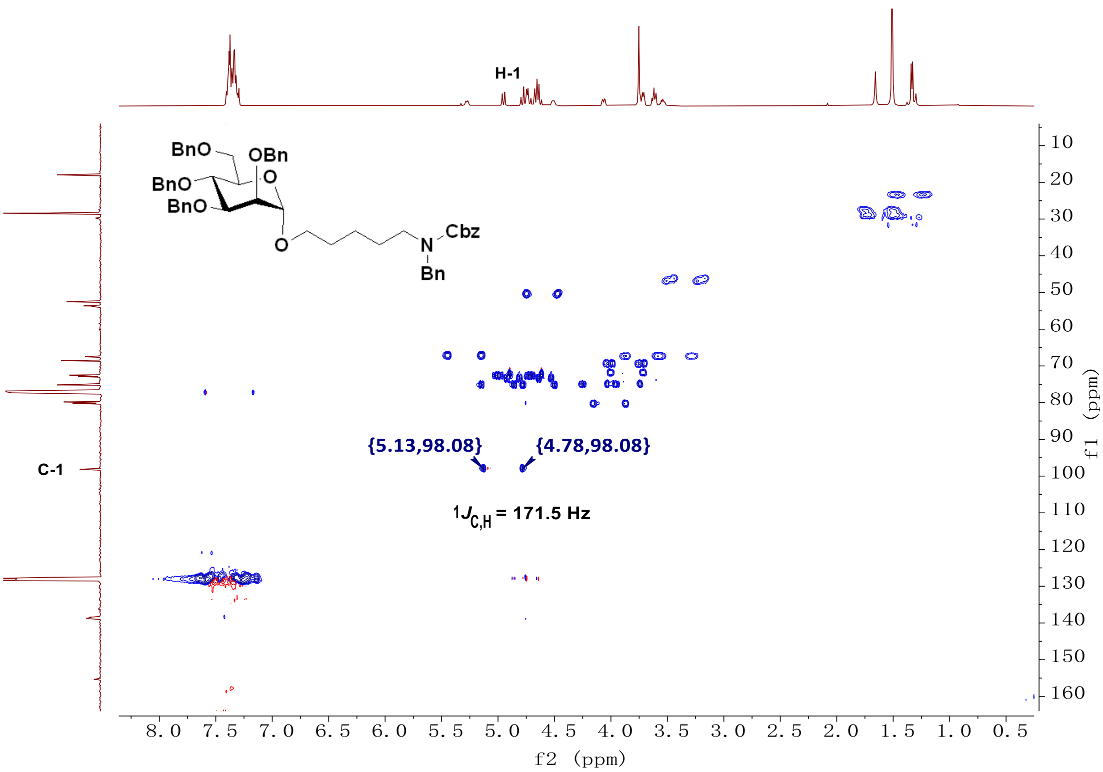
HSQC of **64f**



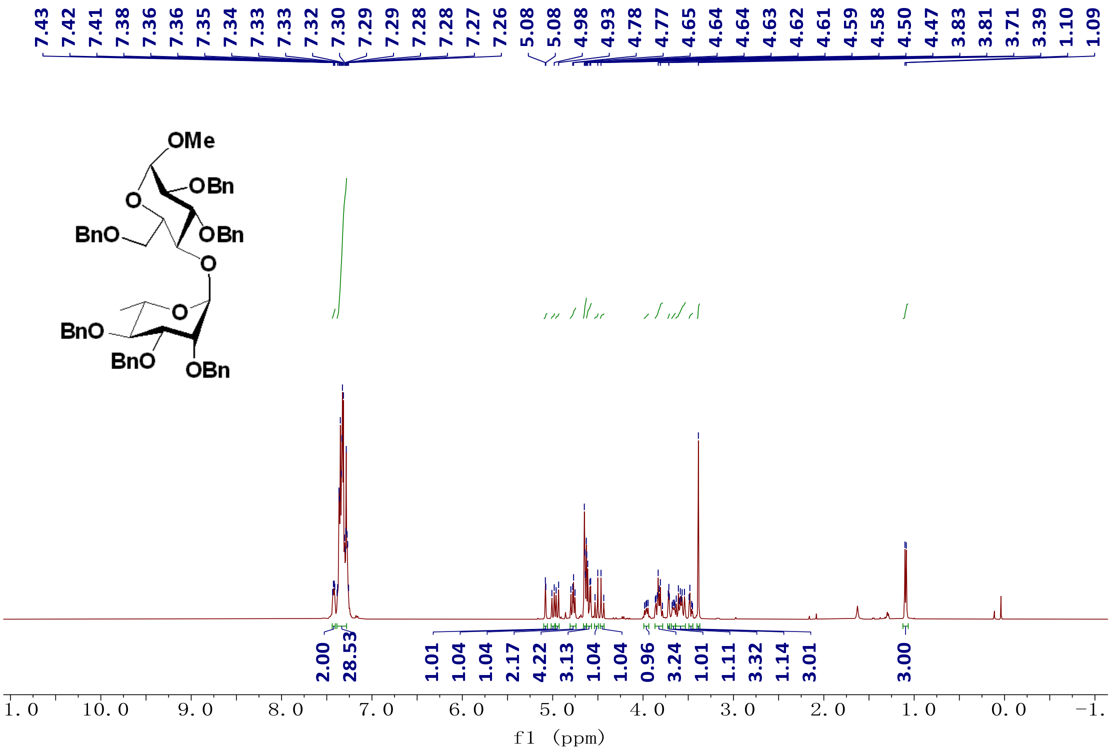
^{1}H NMR **64g** (400 MHz, $CDCl_3$)



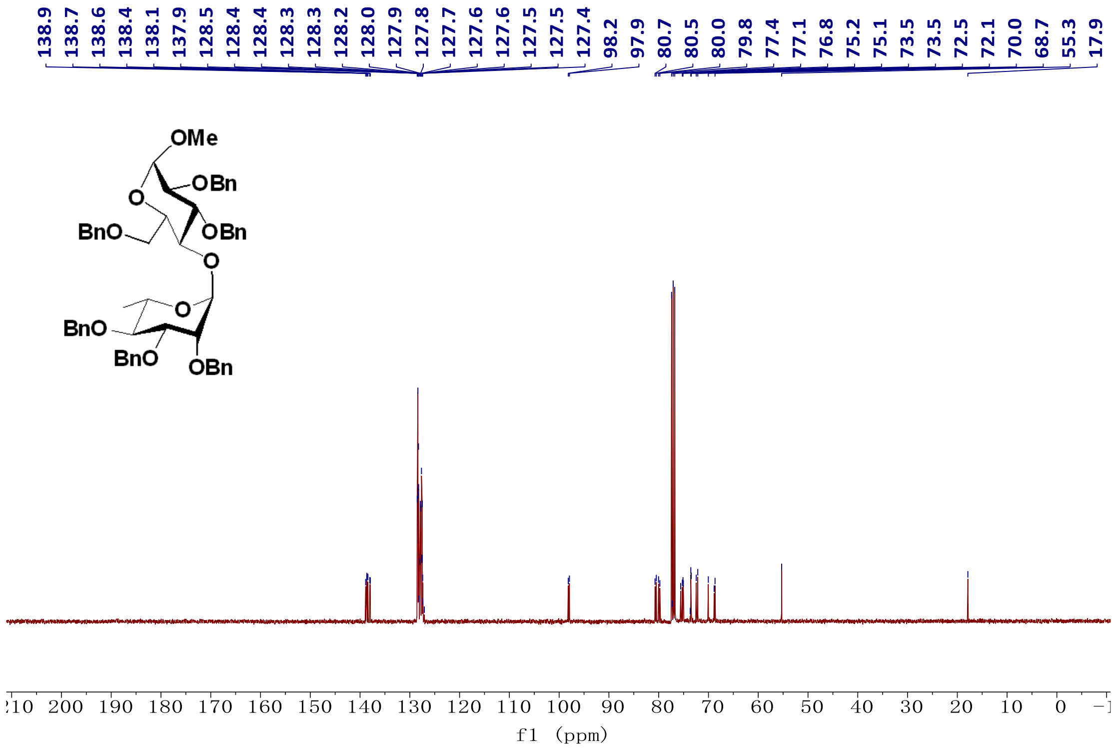
^{13}C NMR of **64g** (100 MHz, $CDCl_3$)



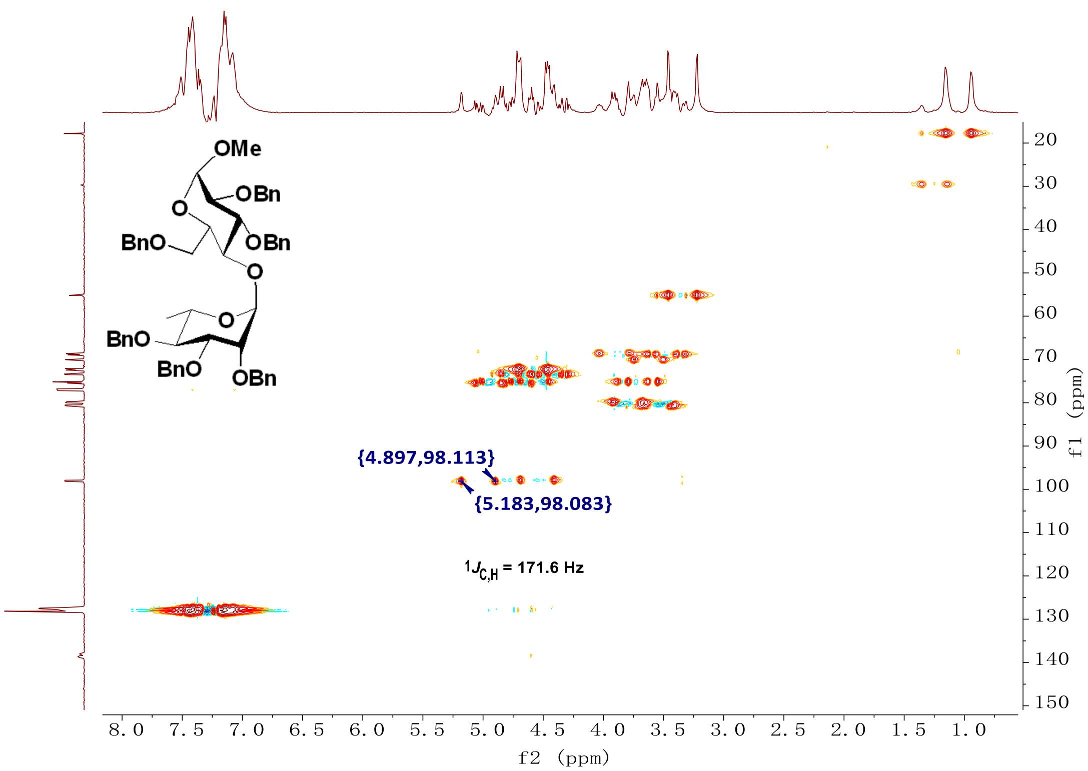
HSQC of **64g**



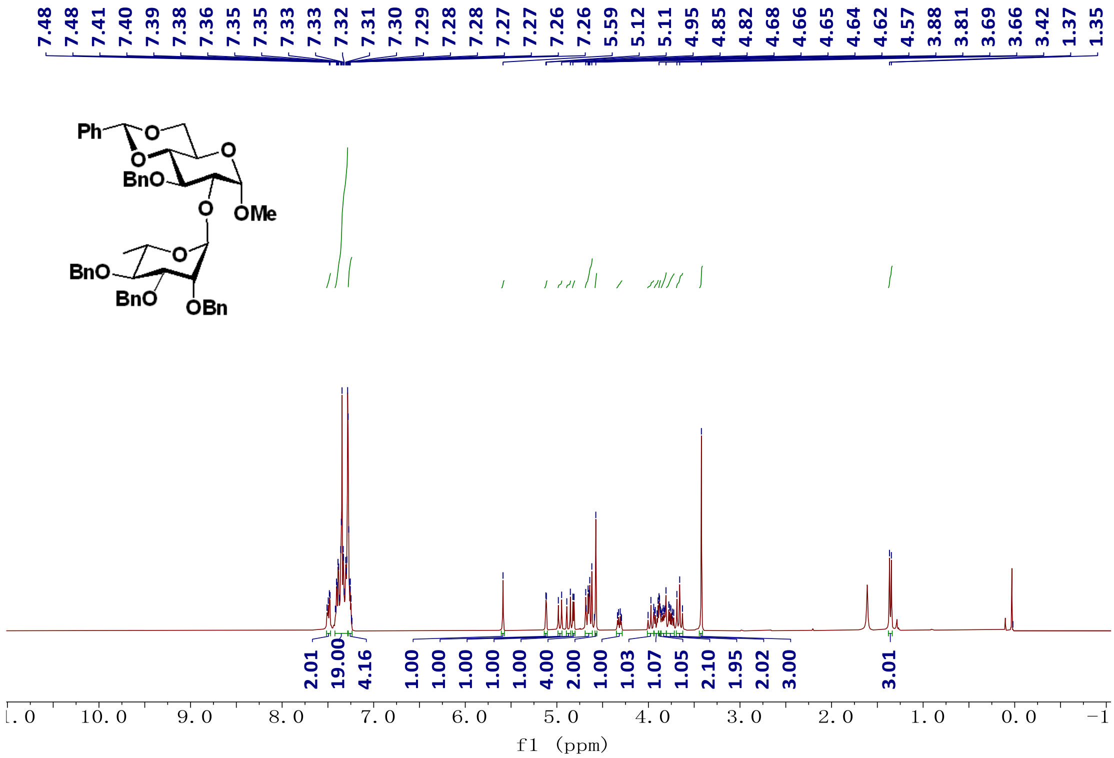
^{1}H NMR of **65a** (400 MHz, $CDCl_3$)



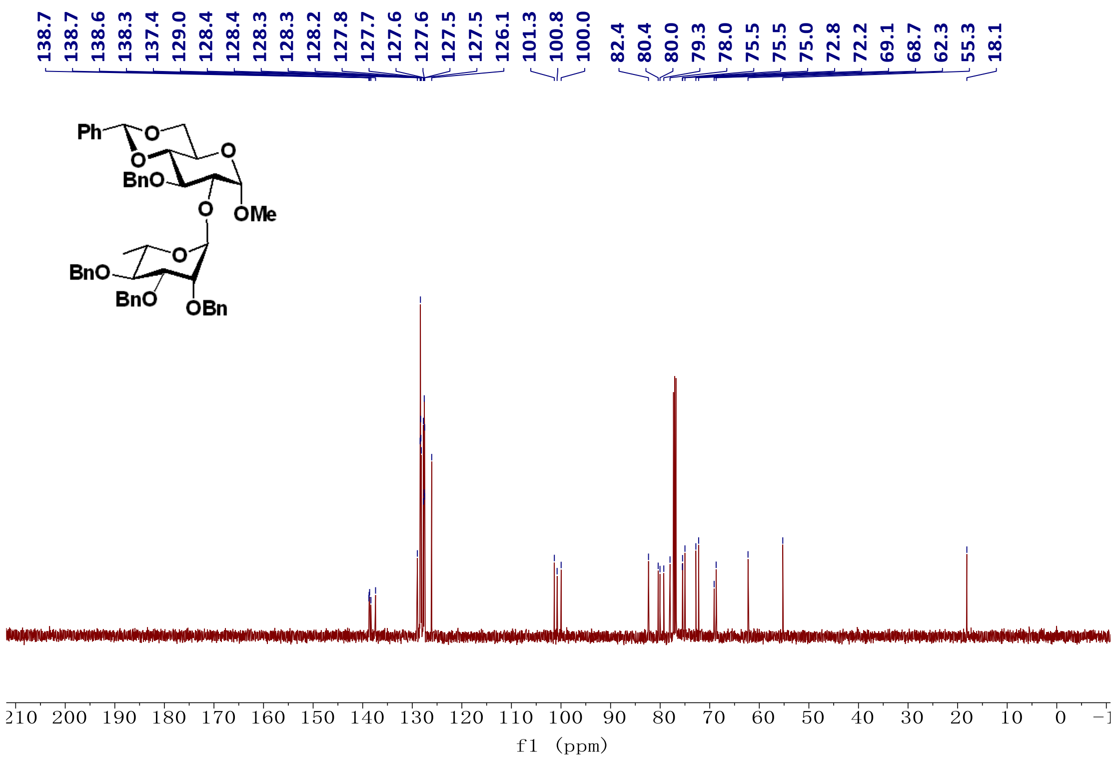
^{13}C NMR of **65a** (100 MHz, $CDCl_3$)



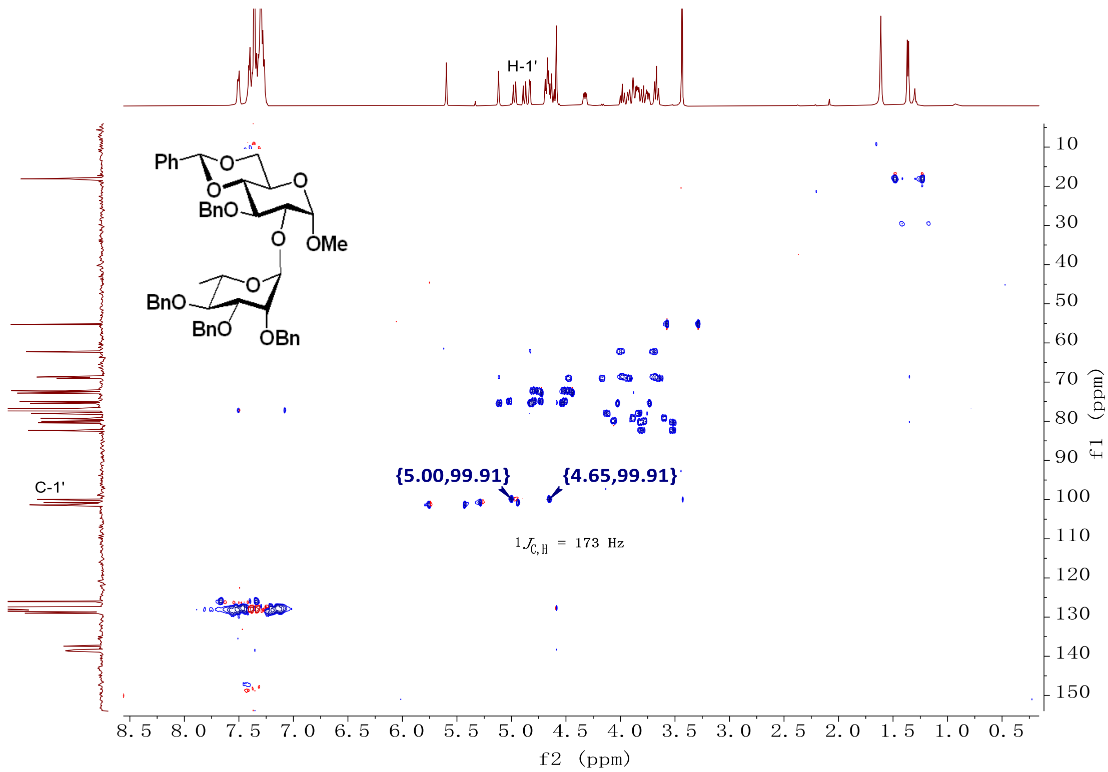
HSQC of **65a**



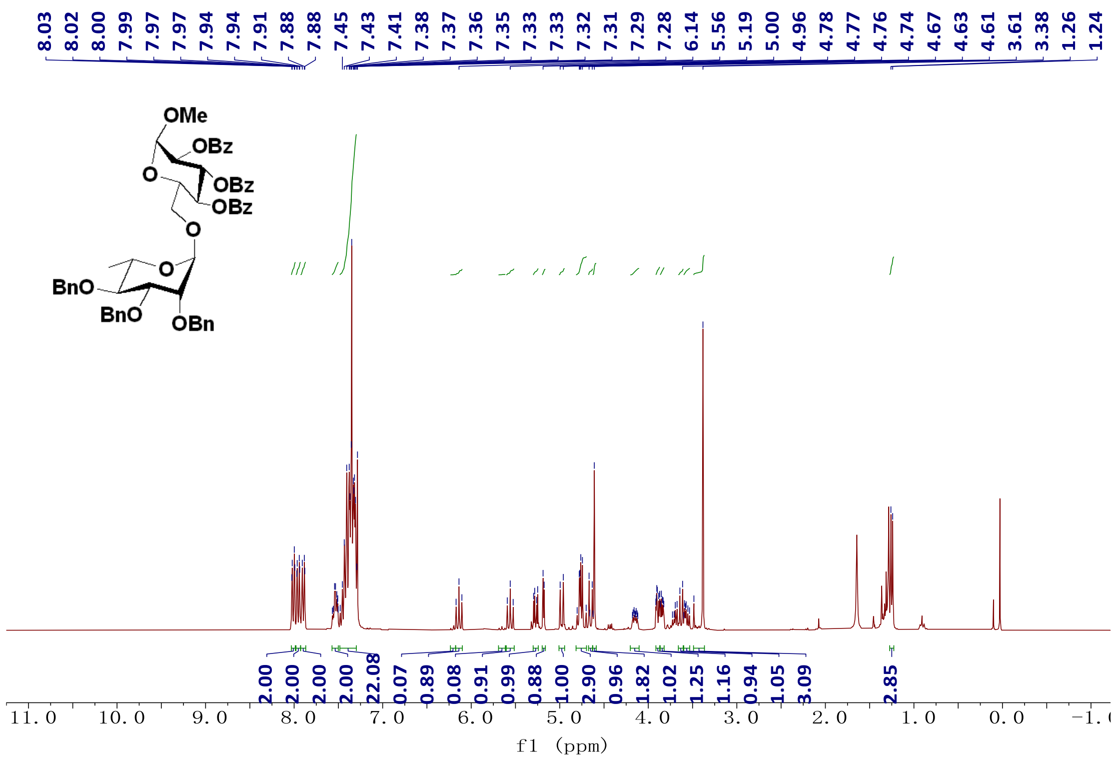
^{1}H NMR of **65c** (300 MHz, $CDCl_3$)



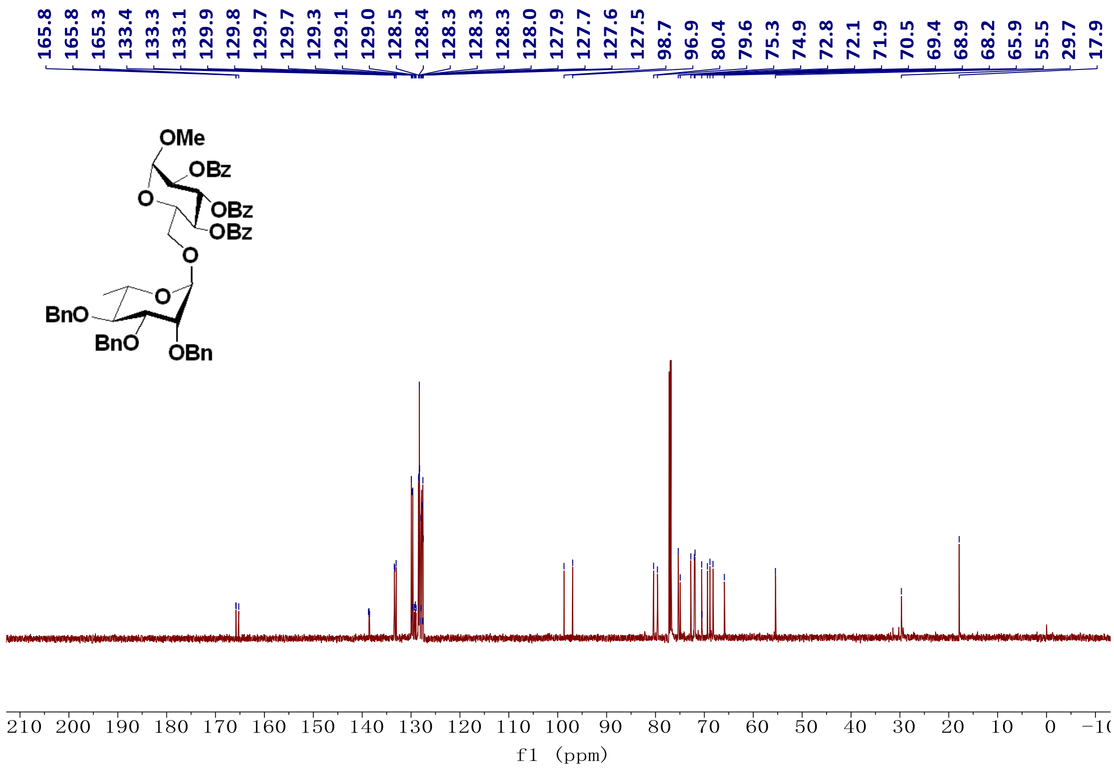
^{13}C NMR of **65c** (125 MHz, $CDCl_3$)



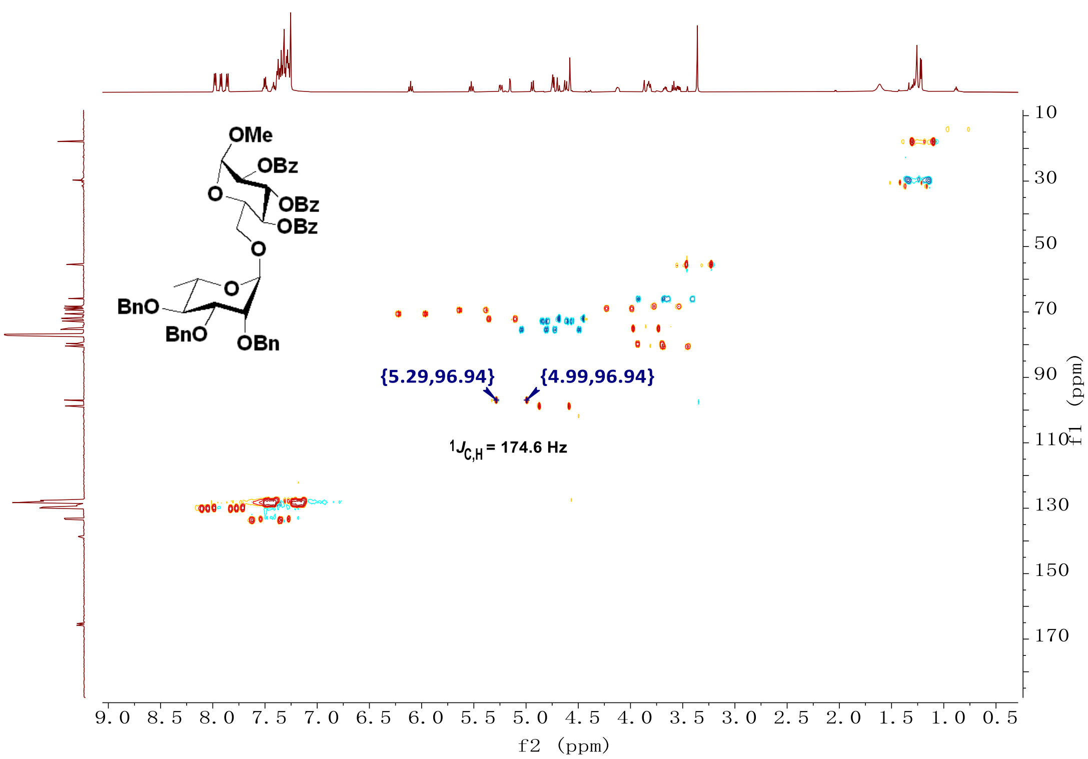
HSQC of **65c**



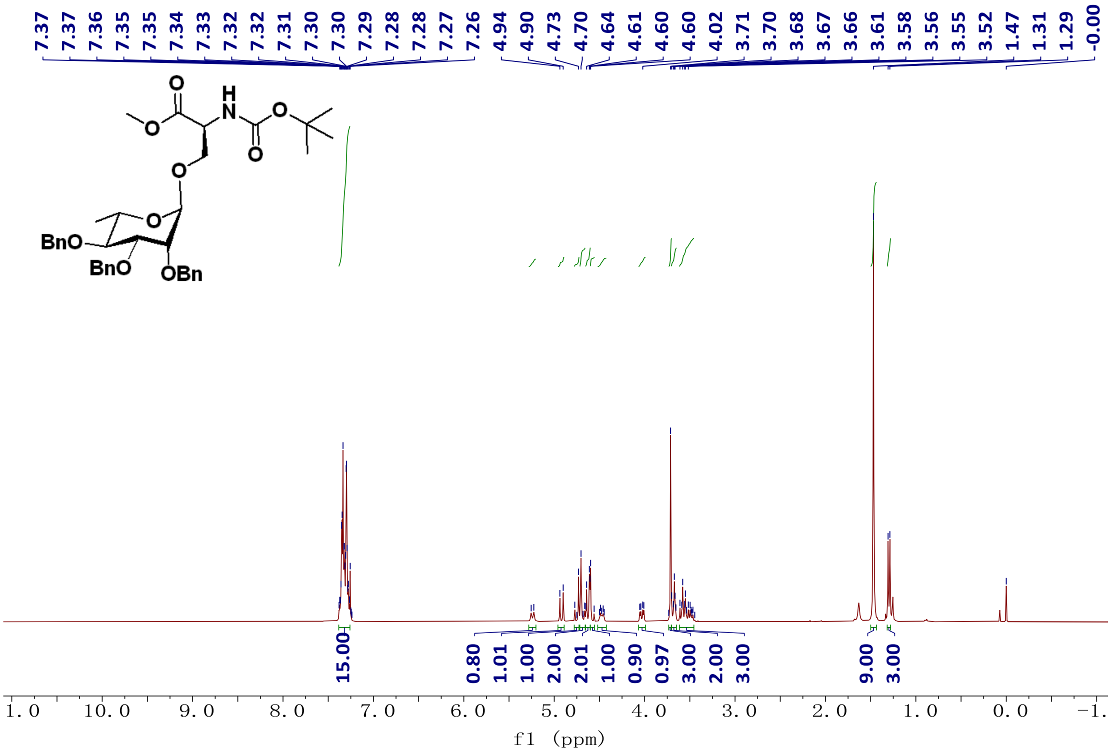
^{1}H NMR of **65e** (300 MHz, $CDCl_3$)



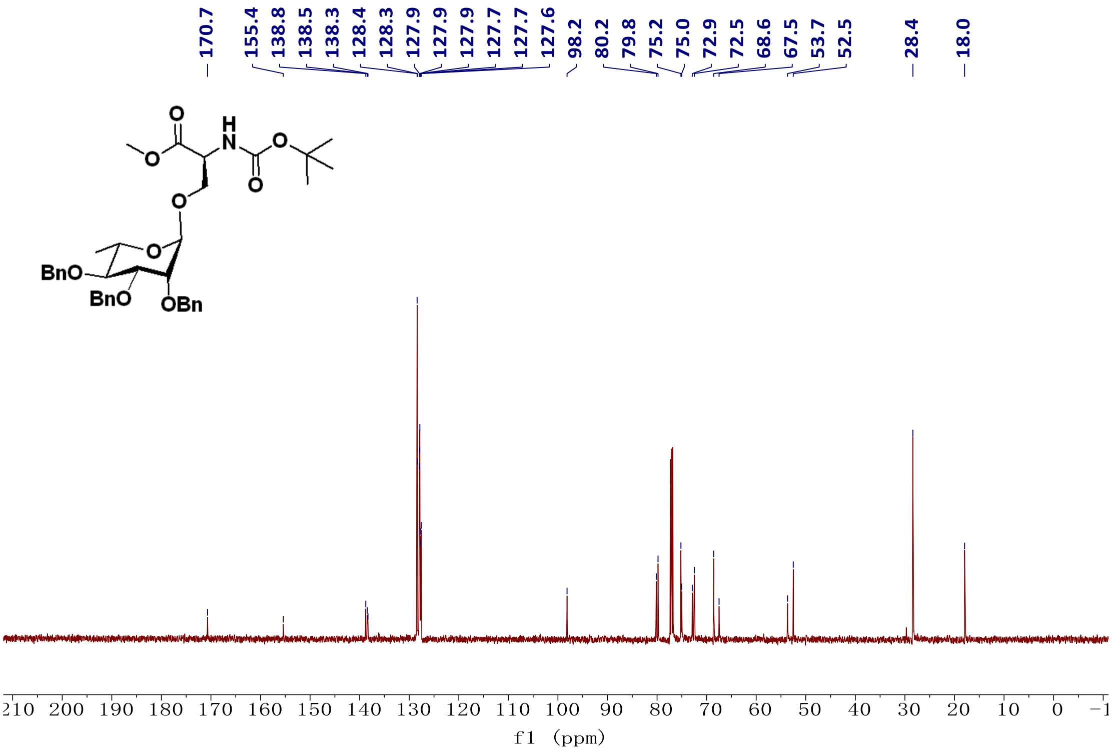
^{13}C NMR of **65e** (150 MHz, $CDCl_3$)



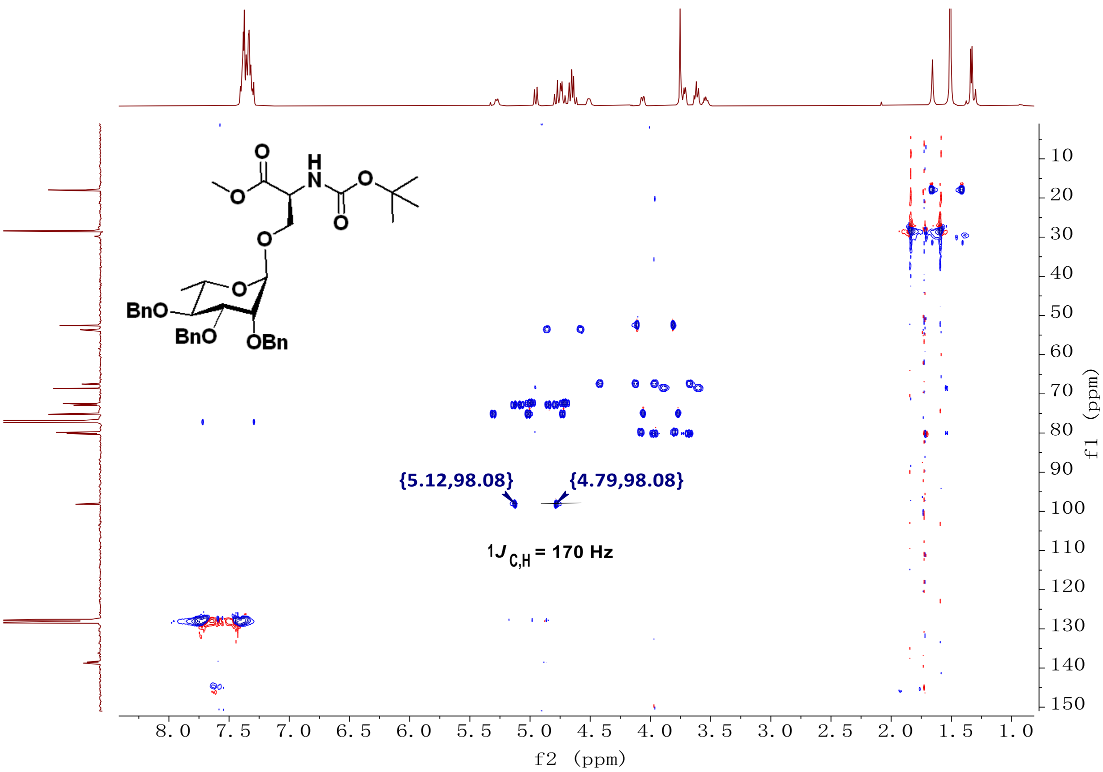
HSQC of **65e**



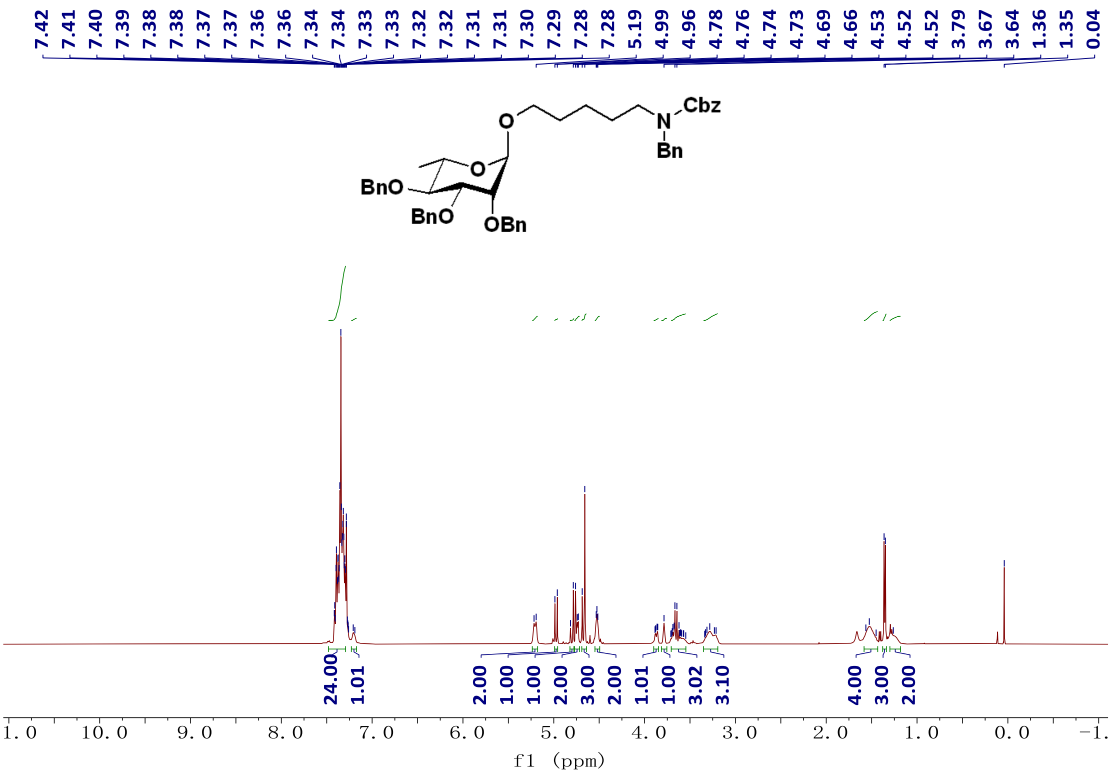
[1]H NMR of **65f** (500 MHz, $CDCl_3$)



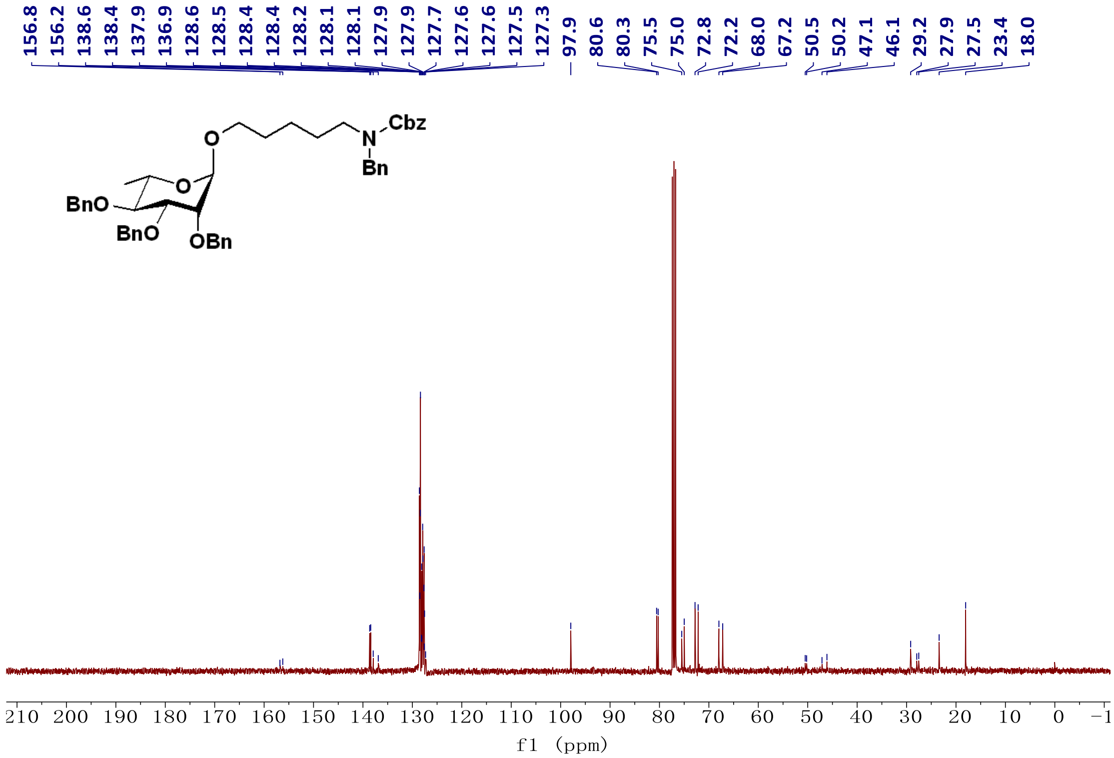
[13]C NMR of **65f** (125 MHz, $CDCl_3$)



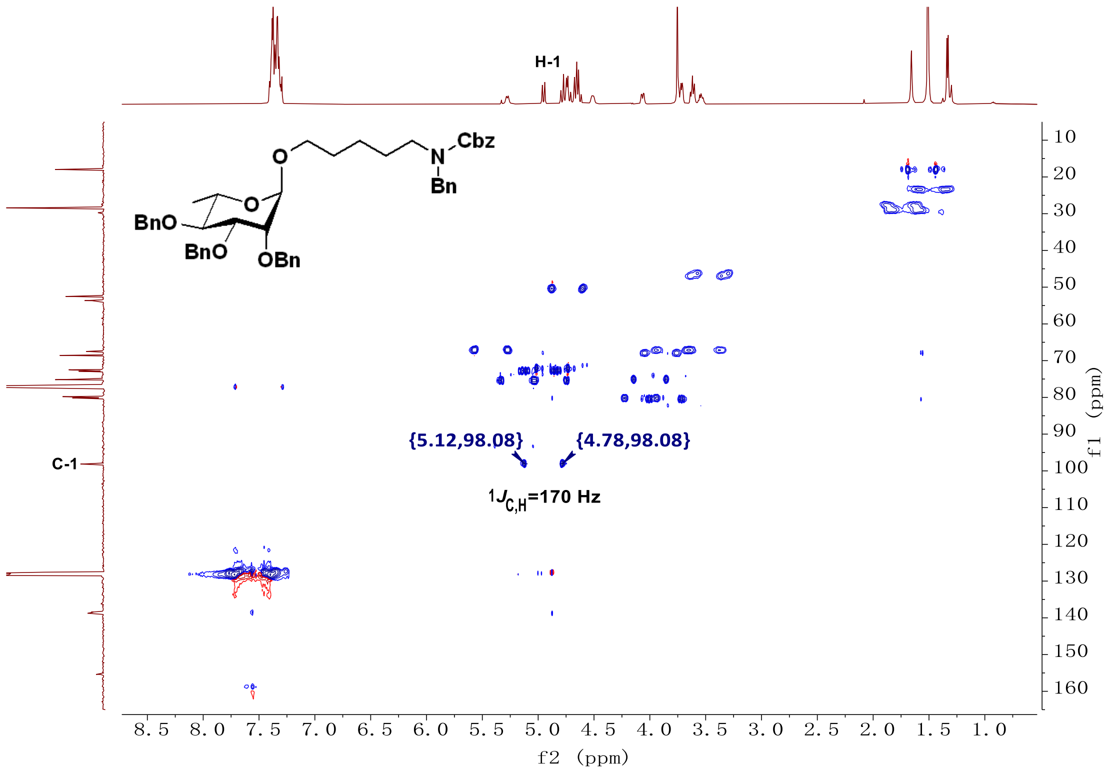
HSQC of **65f**



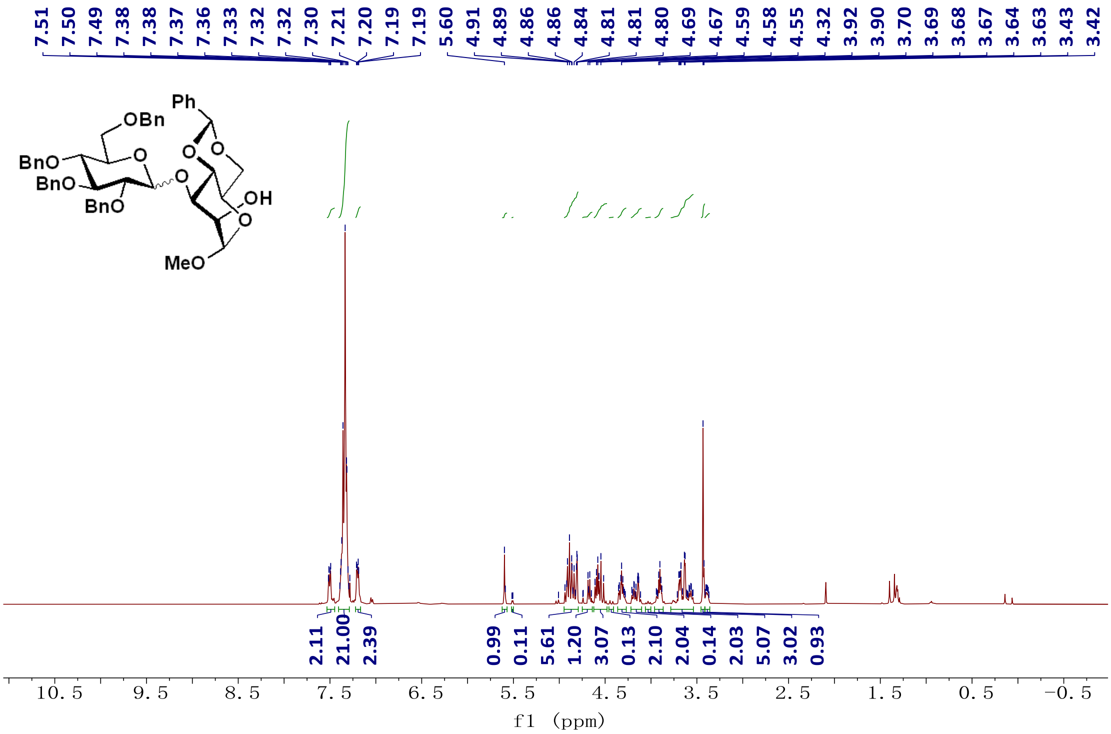
^{1}H NMR of **65g** (400 MHz, $CDCl_3$)



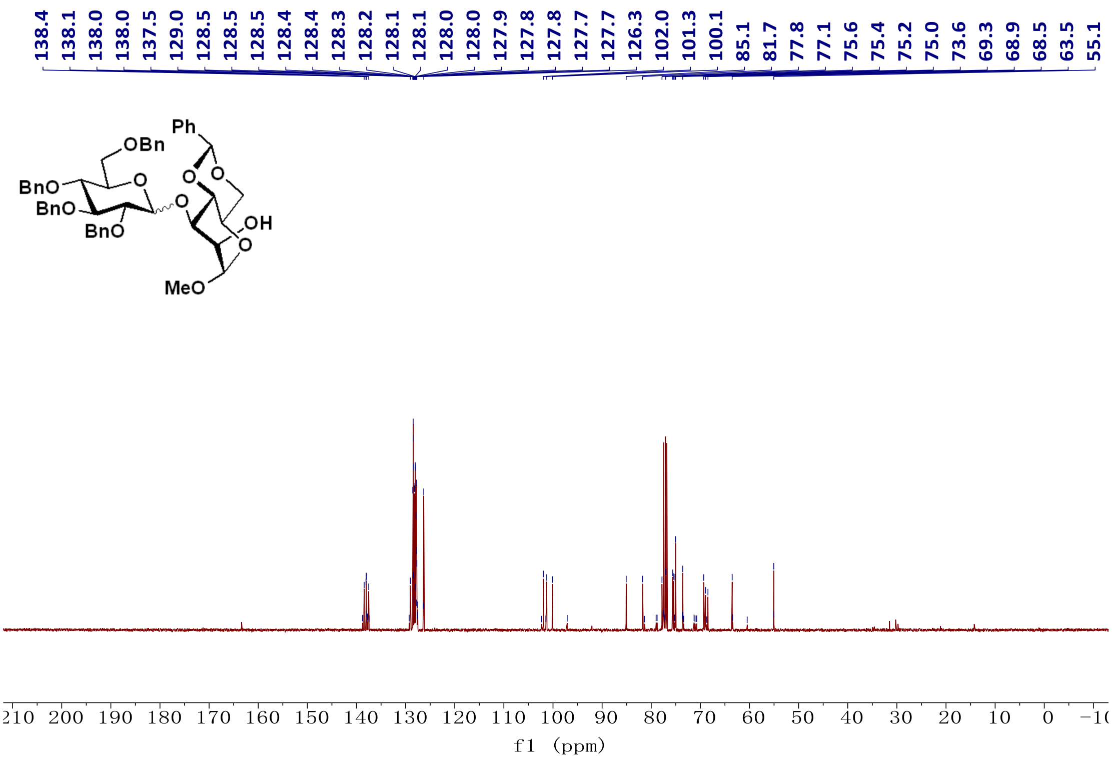
^{13}C NMR of **65g** (125 MHz, $CDCl_3$)



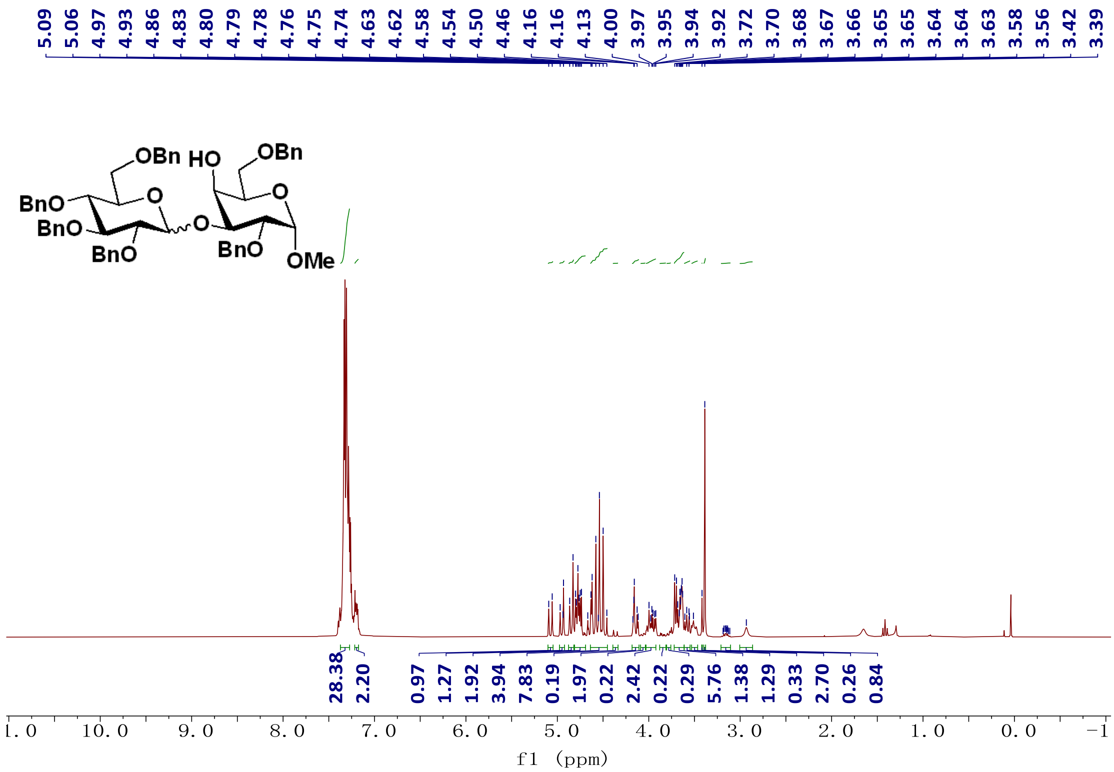
HSQC of **65g**



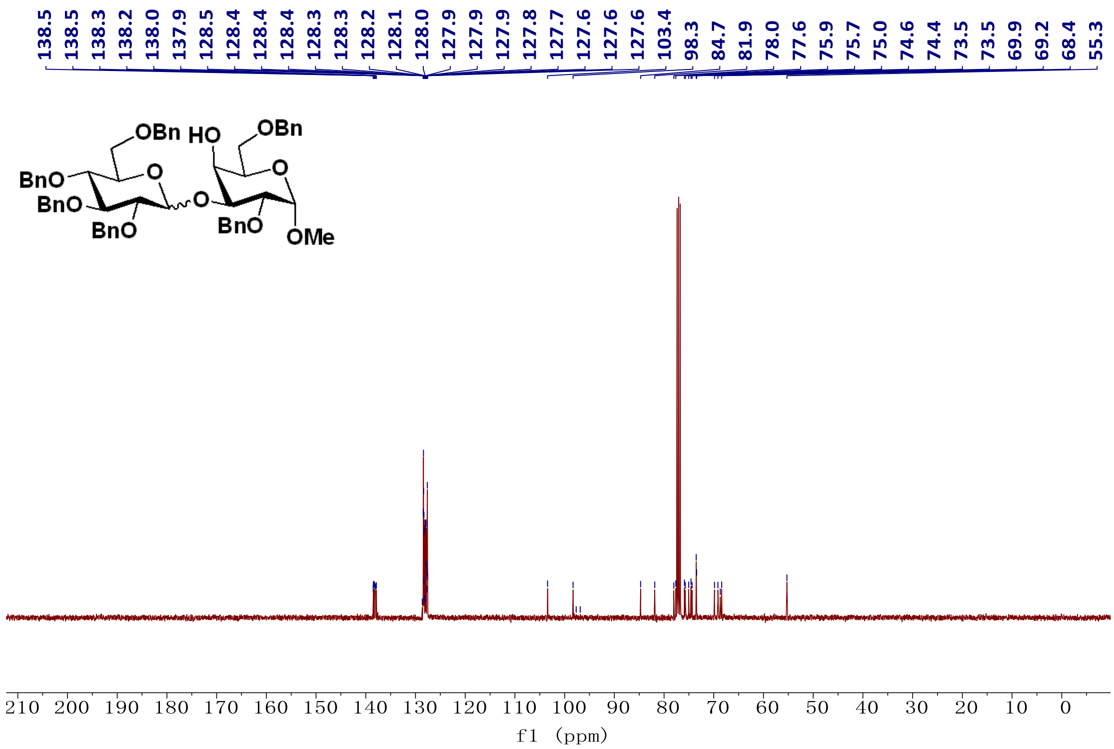
^{1}H NMR of **67c** (400 MHz, $CDCl_3$)



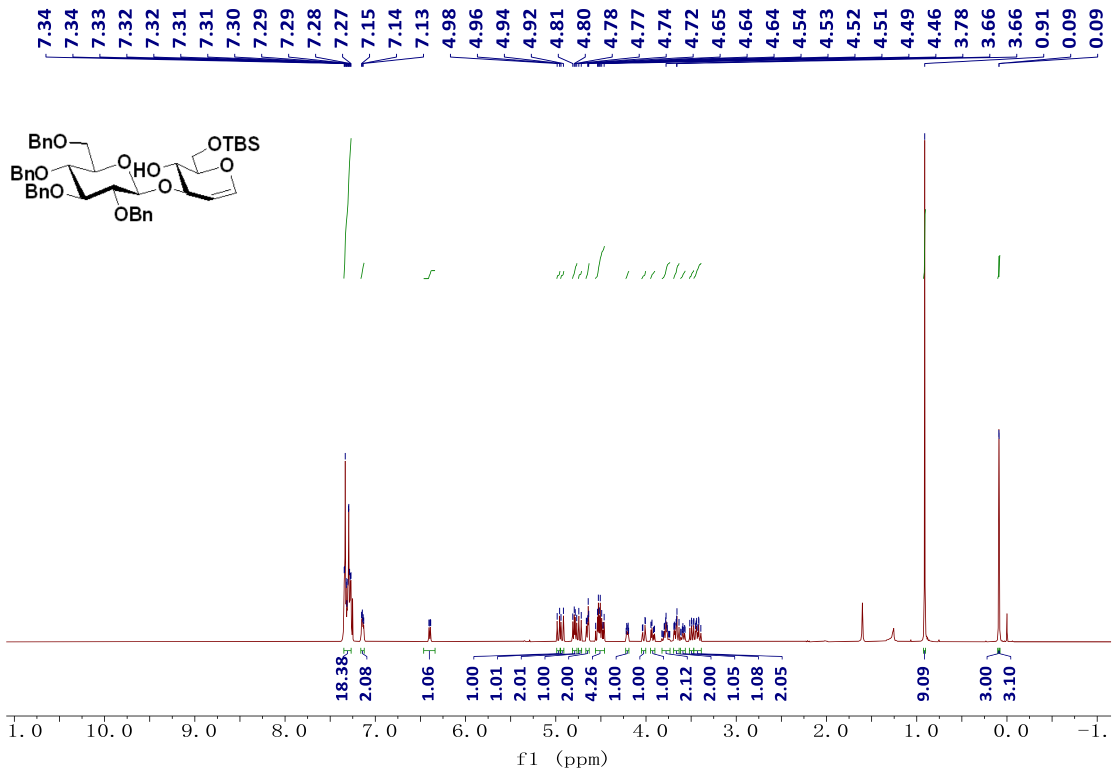
^{13}C NMR of **67c** (100 MHz, $CDCl_3$)



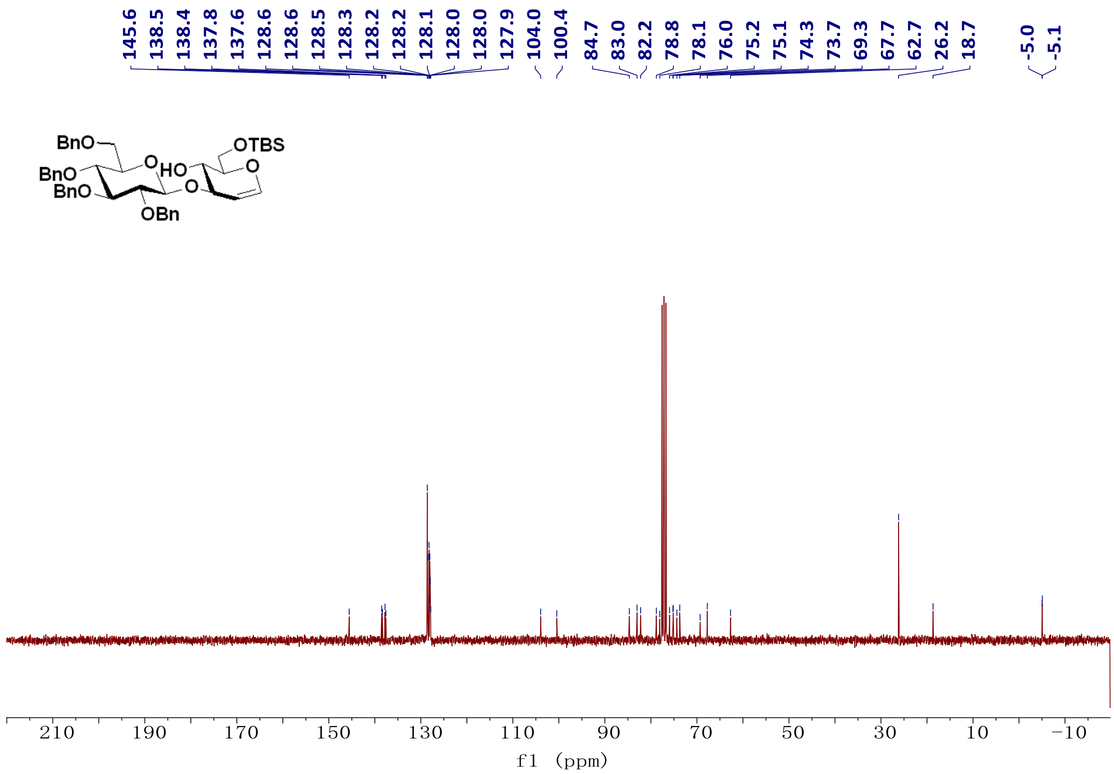
^{1}H NMR of **67d** (300 MHz, $CDCl_3$)



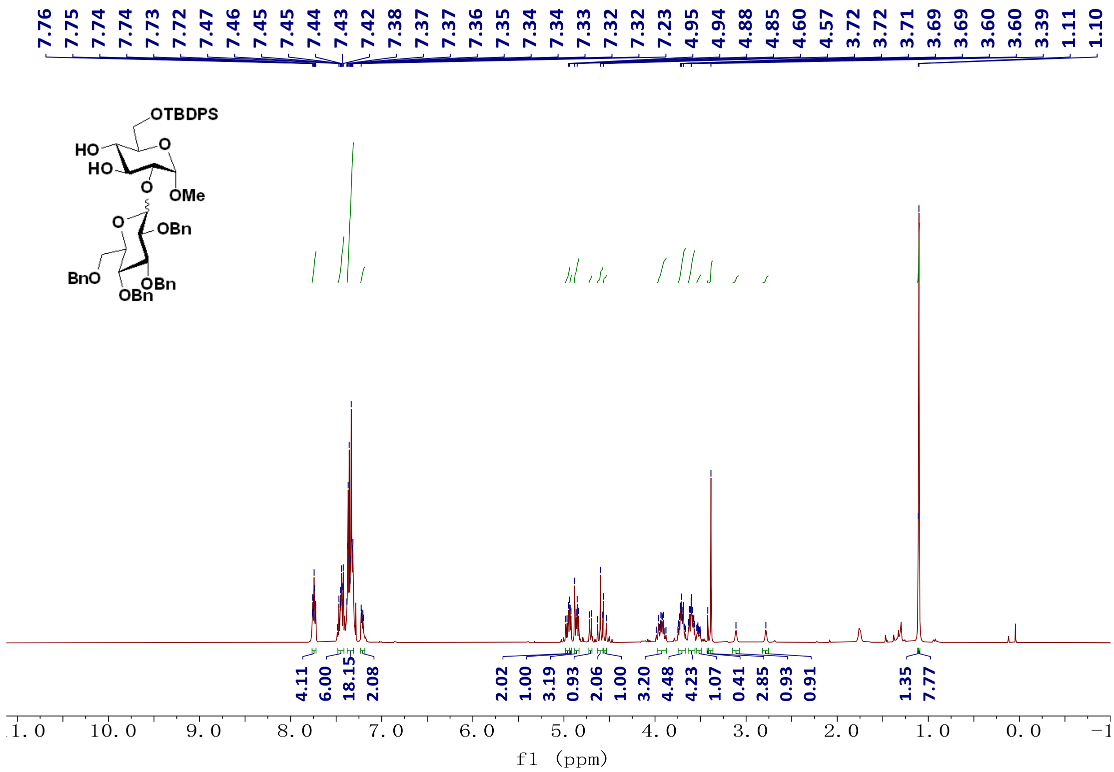
^{13}C NMR of **67d** (100 MHz, $CDCl_3$)



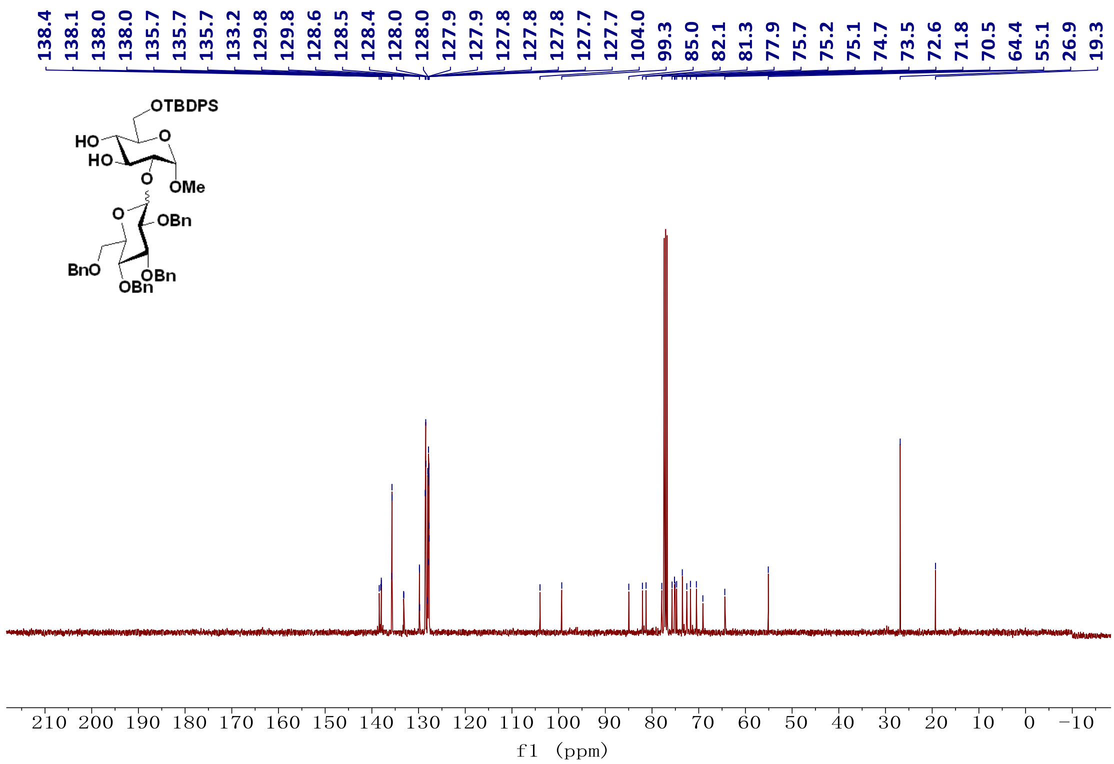
^{1}H NMR of **67e** (400 MHz, $CDCl_3$)



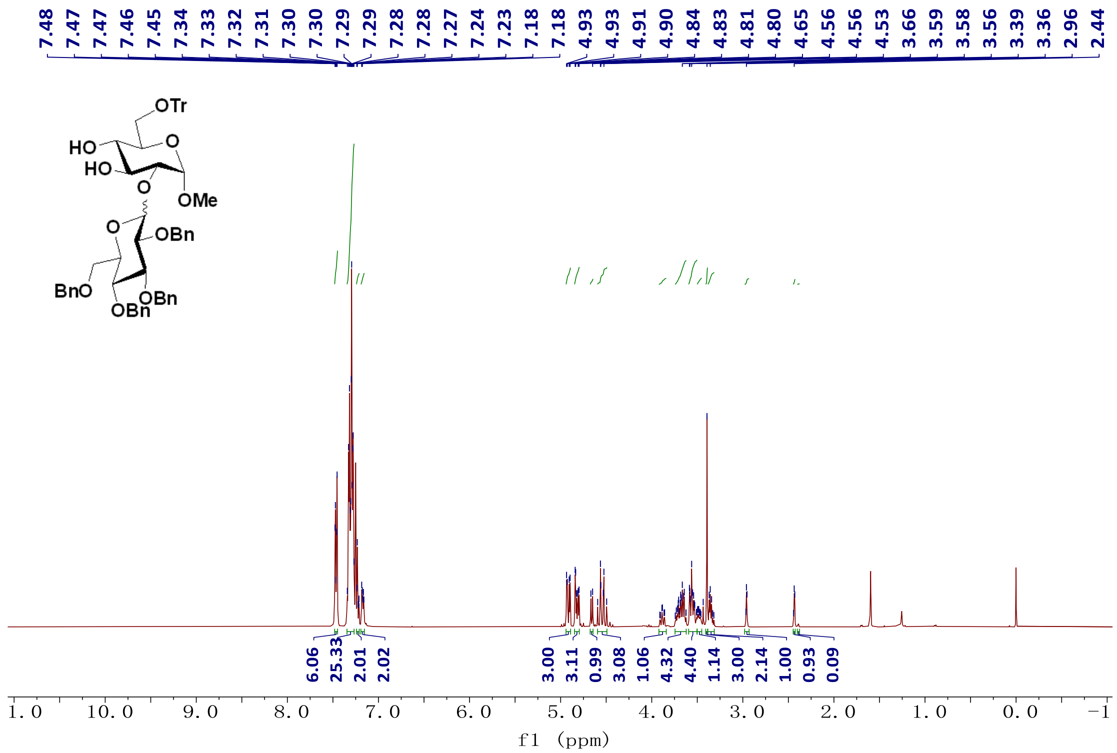
^{13}C NMR of **67e** (75 MHz, $CDCl_3$)



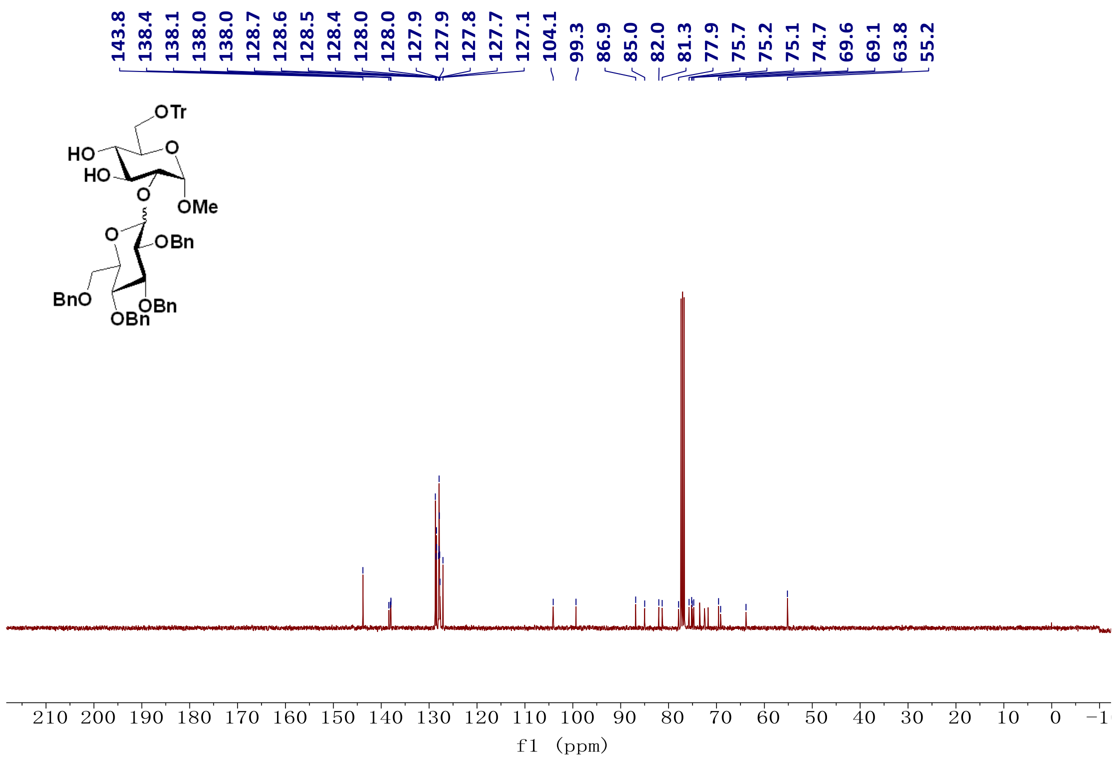
^{1}H NMR of **67f** (400 MHz, $CDCl_3$)



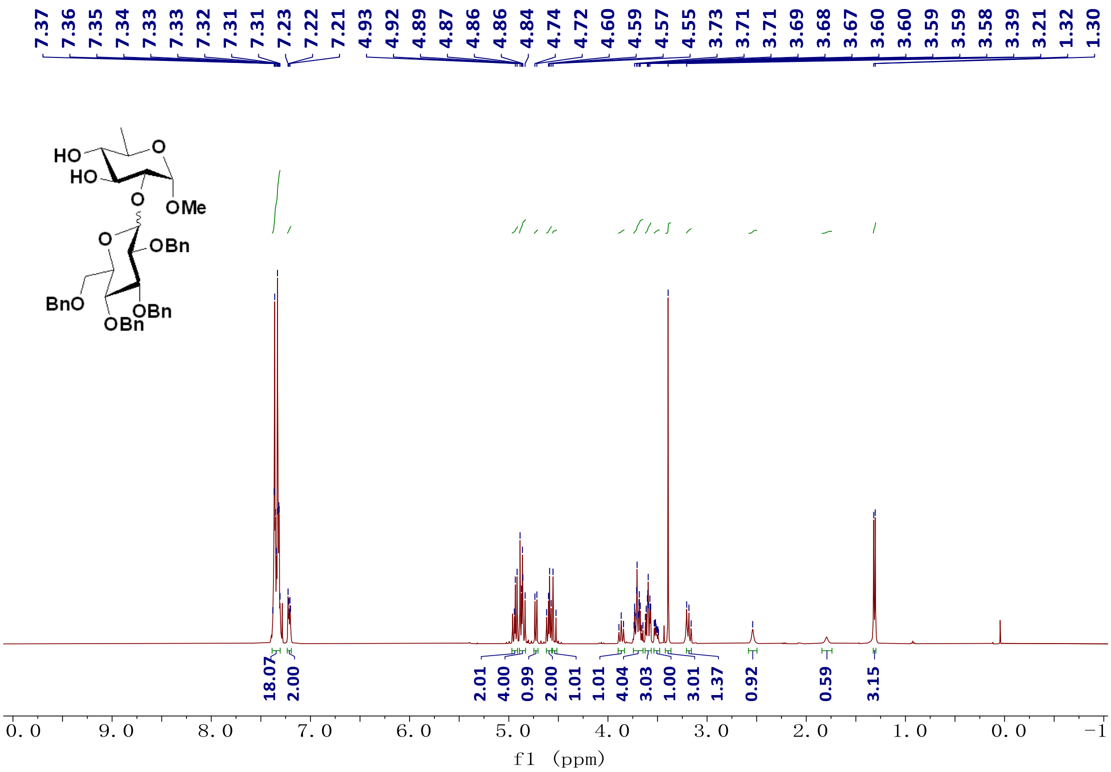
^{13}C NMR of **67f** (75 MHz, $CDCl_3$)



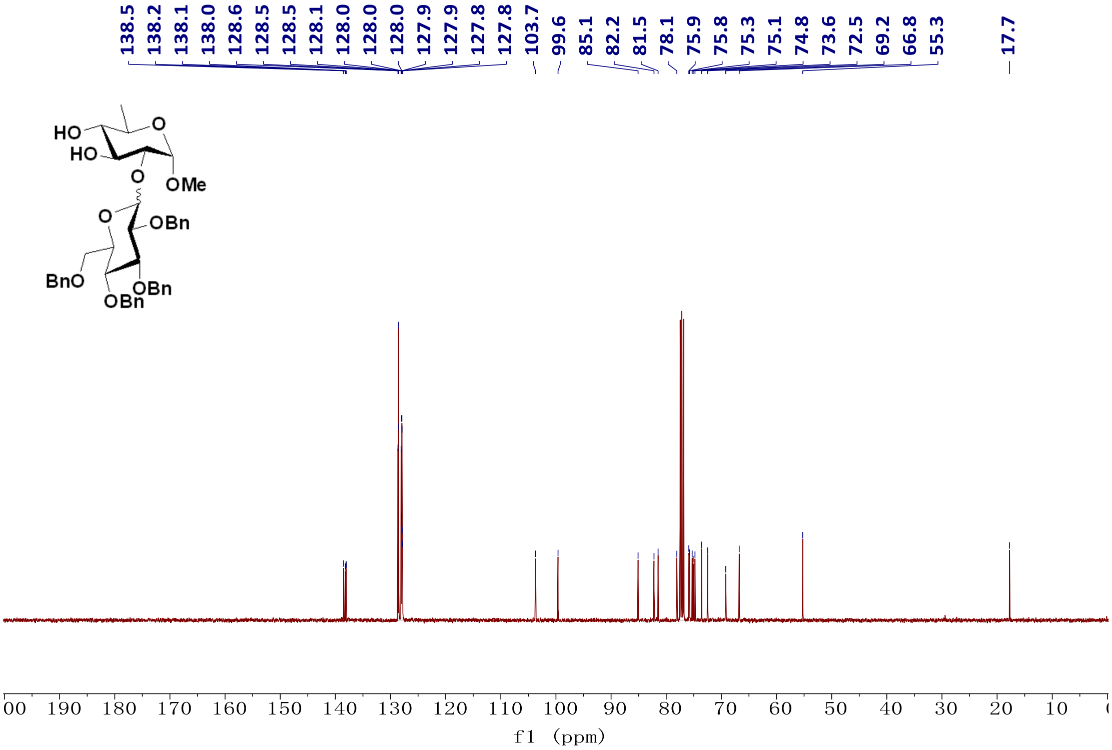
^{1}H NMR of **67g** (400 MHz, $CDCl_3$)



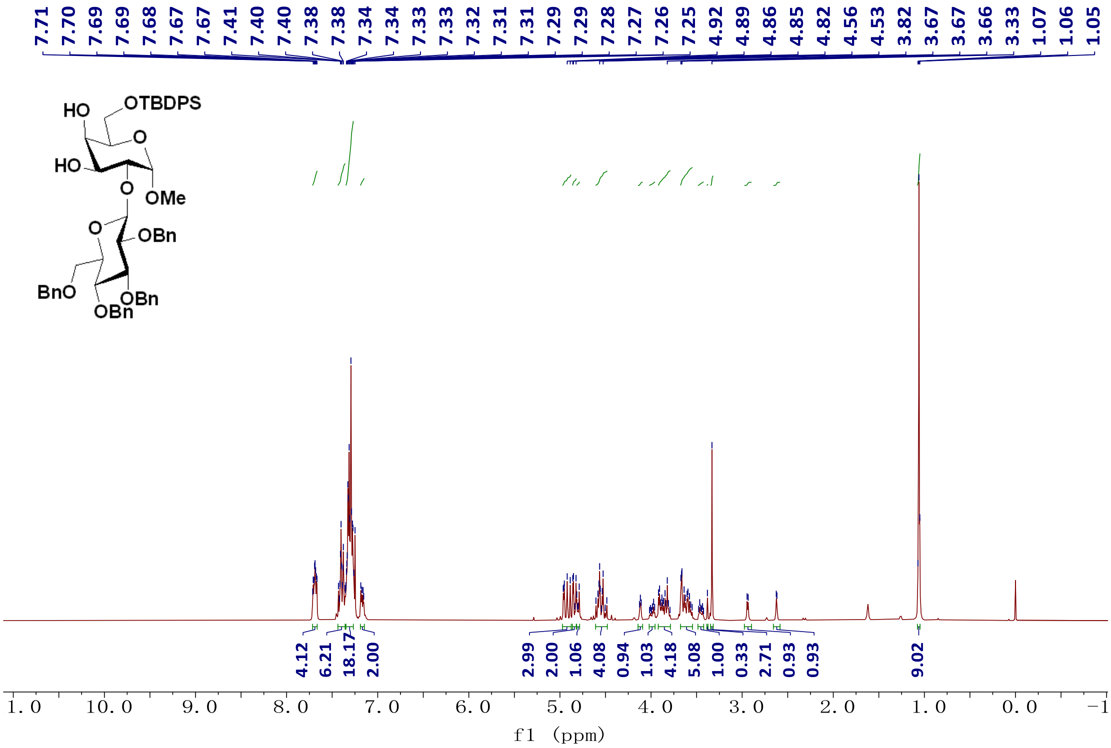
^{13}C NMR of **67g** (100 MHz, $CDCl_3$)



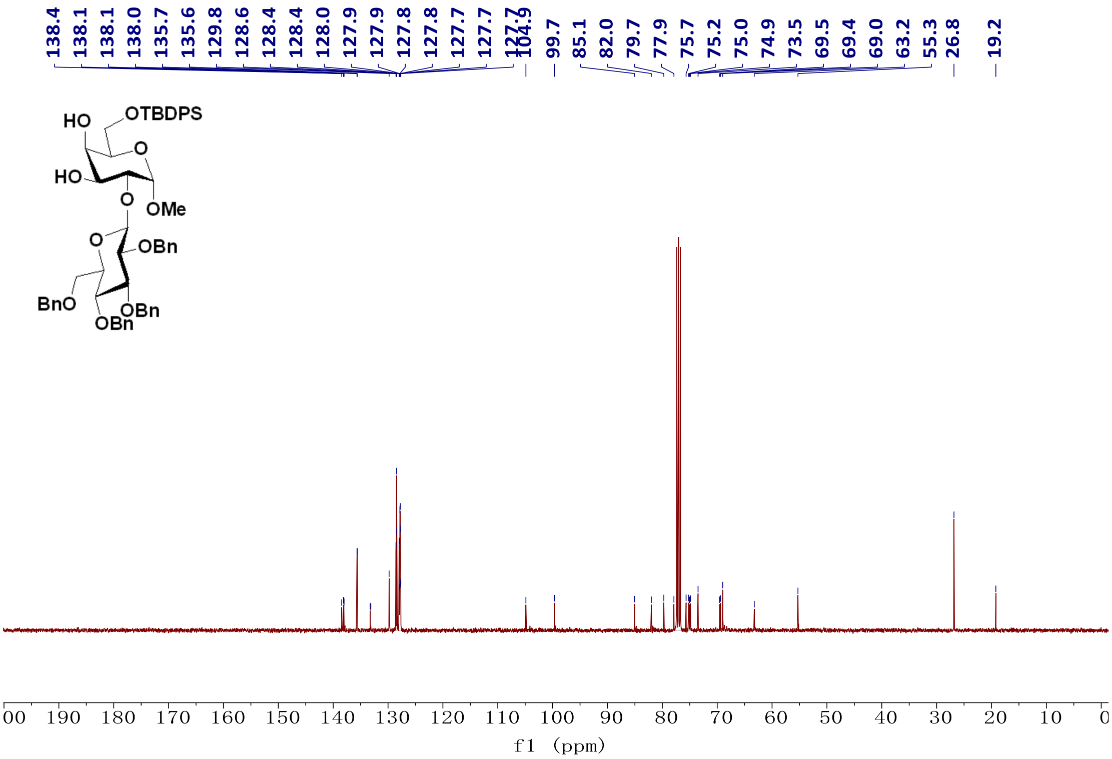
^{1}H NMR of **67h** (400 MHz, $CDCl_3$)



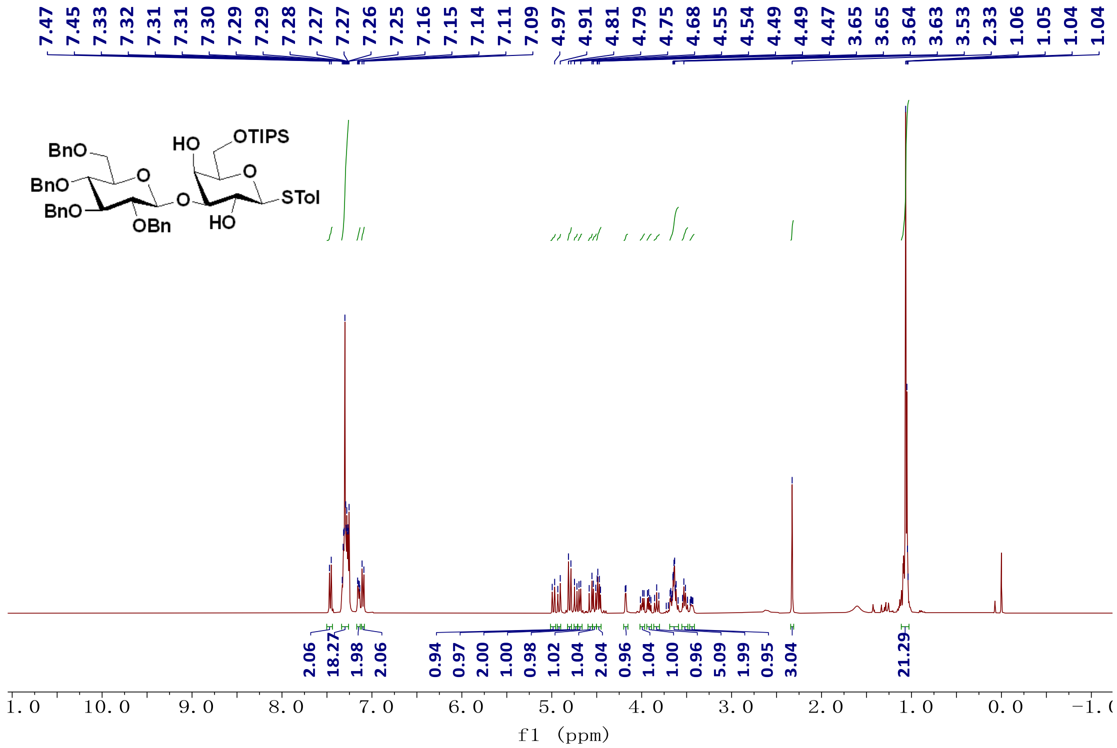
^{13}C NMR of **67h** (100 MHz, $CDCl_3$)



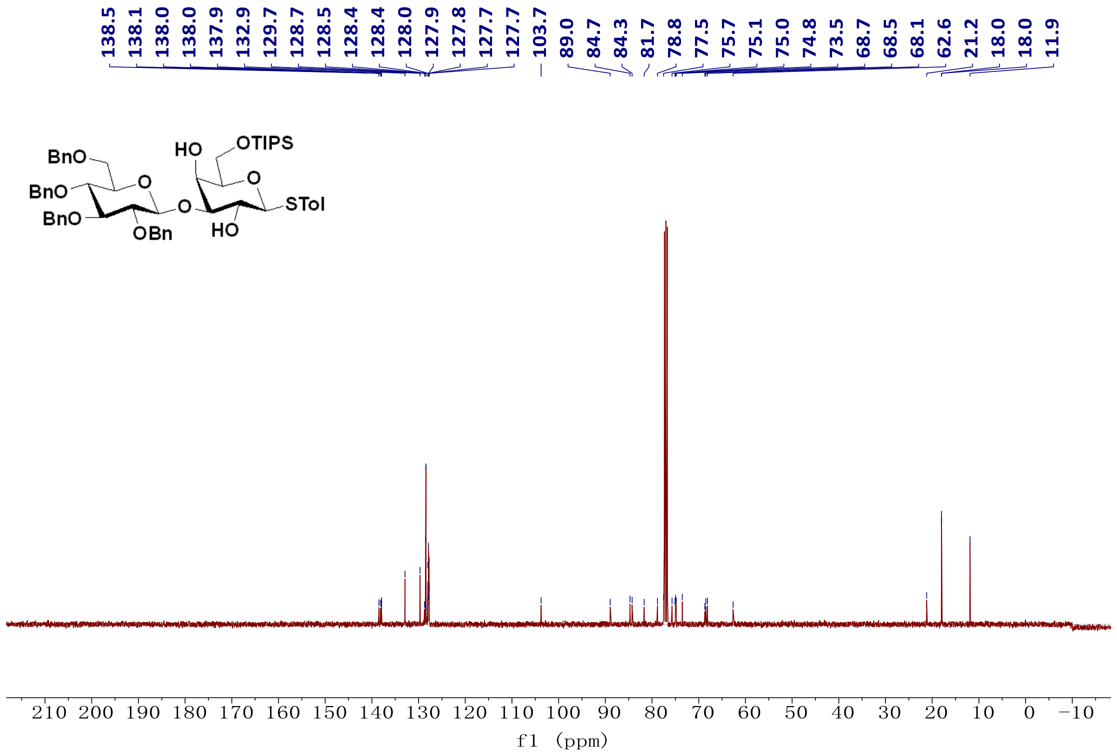
^{1}H NMR of **67i** (400 MHz, $CDCl_3$)



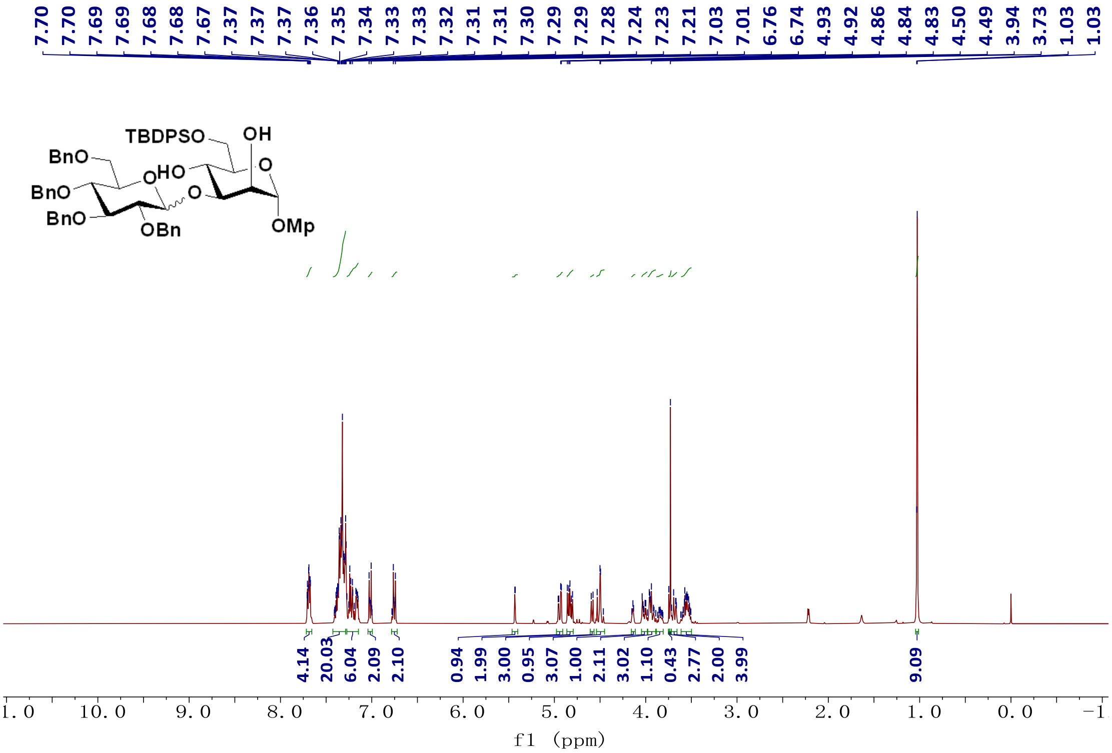
^{13}C NMR of **67i** (100 MHz, $CDCl_3$)



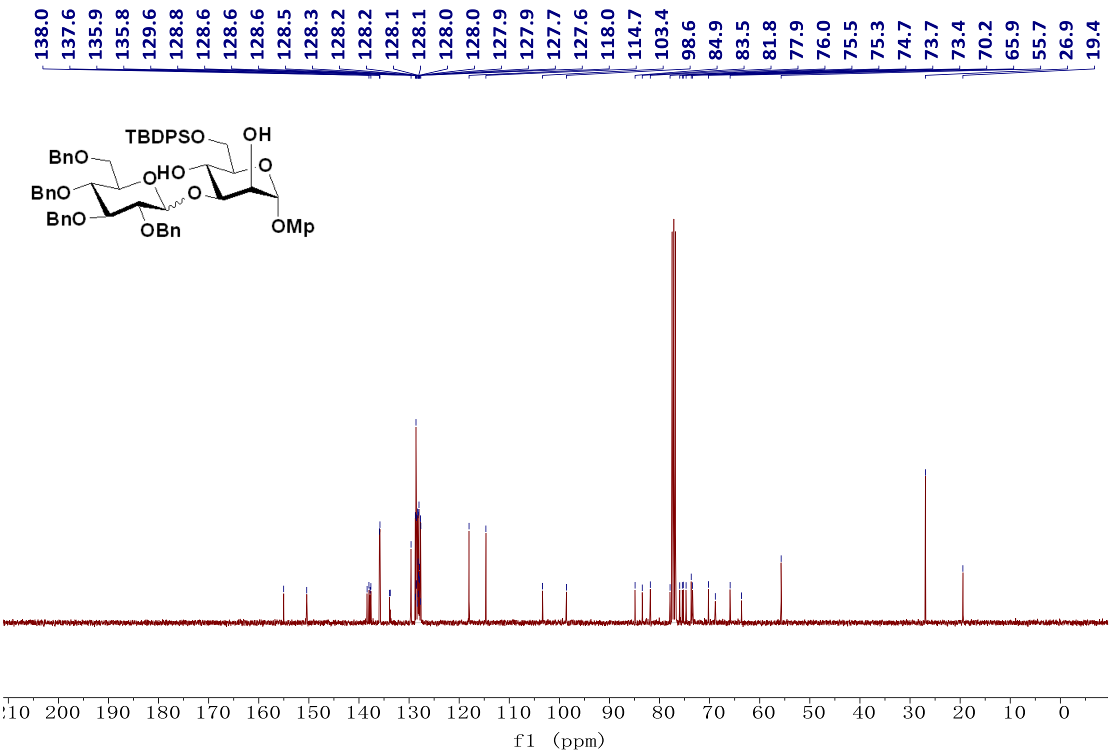
^{1}H NMR of **67j** (400 MHz, $CDCl_3$)



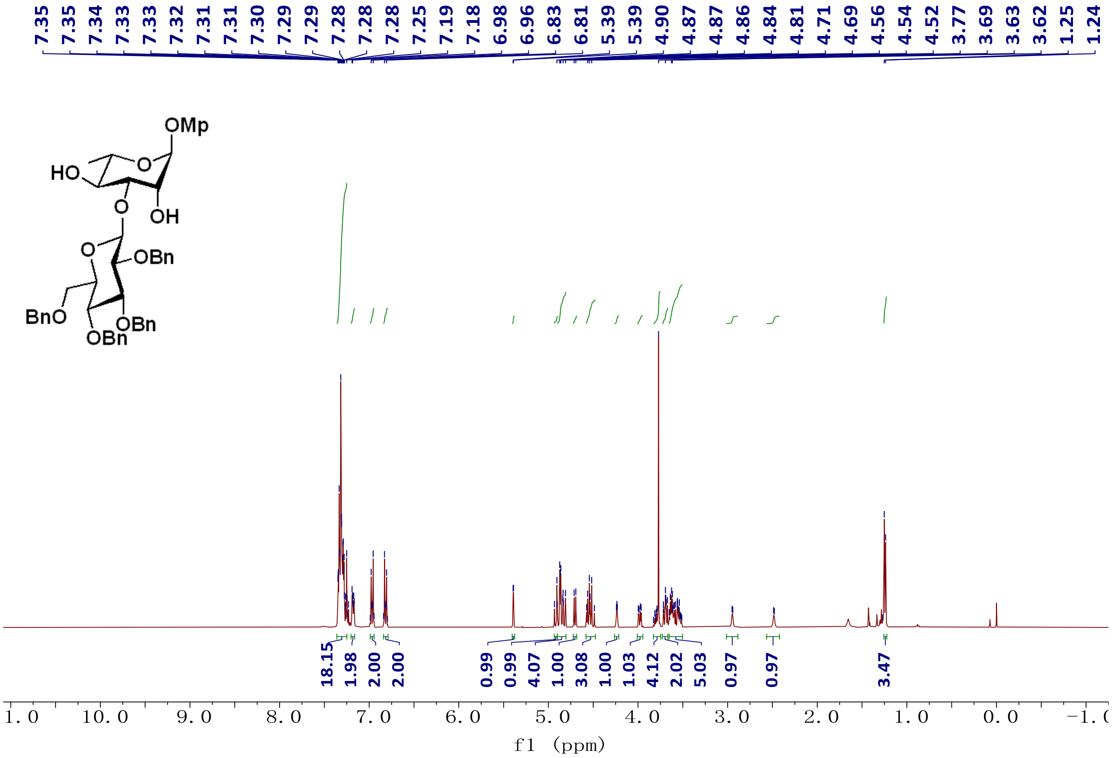
^{13}C NMR of **67j** (100 MHz, $CDCl_3$)



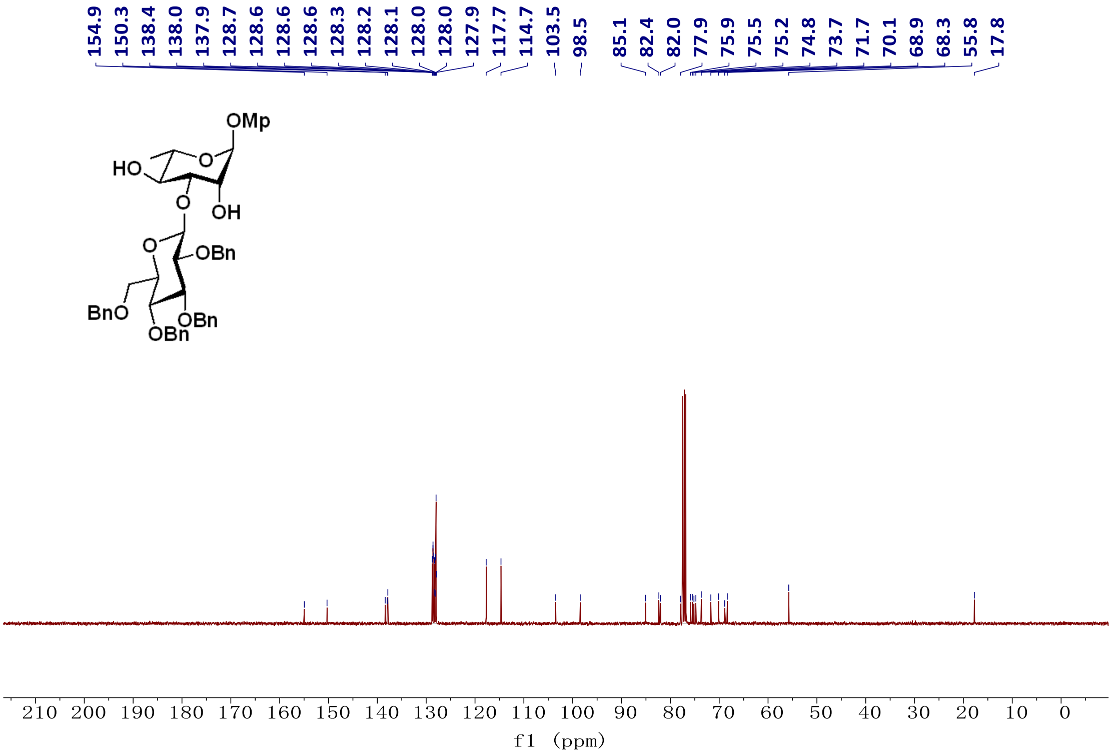
^1H NMR of **67k** (400 MHz, $CDCl_3$)



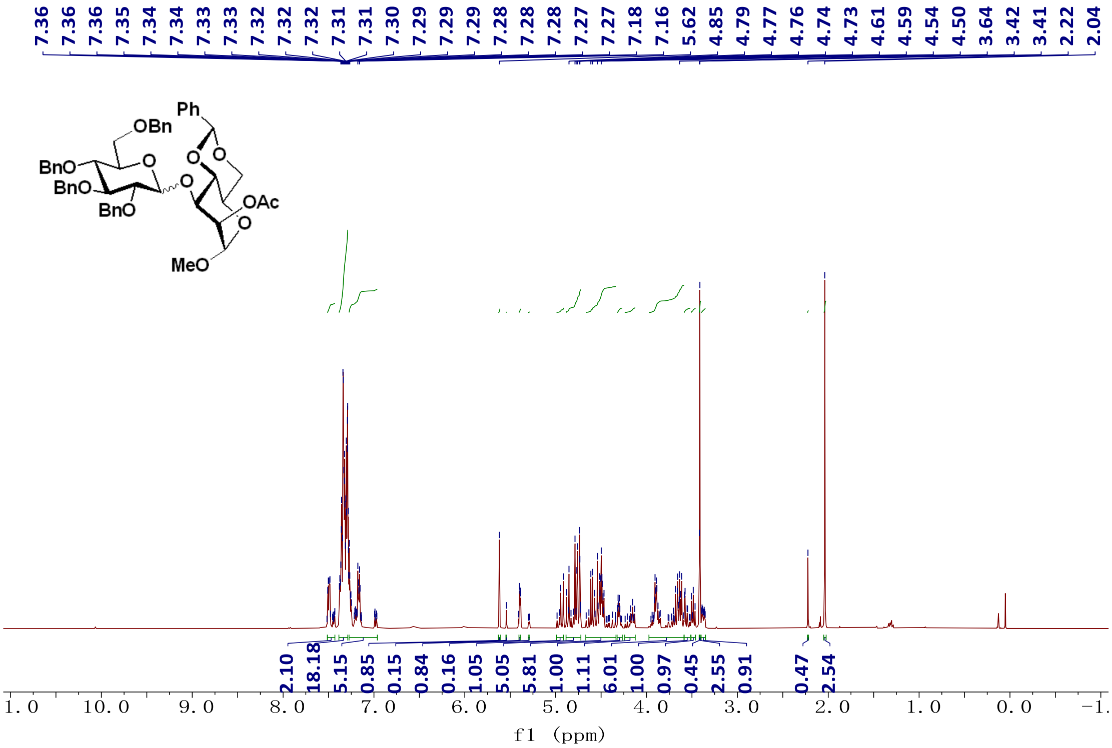
^{13}C NMR of **67k** (100 MHz, $CDCl_3$)



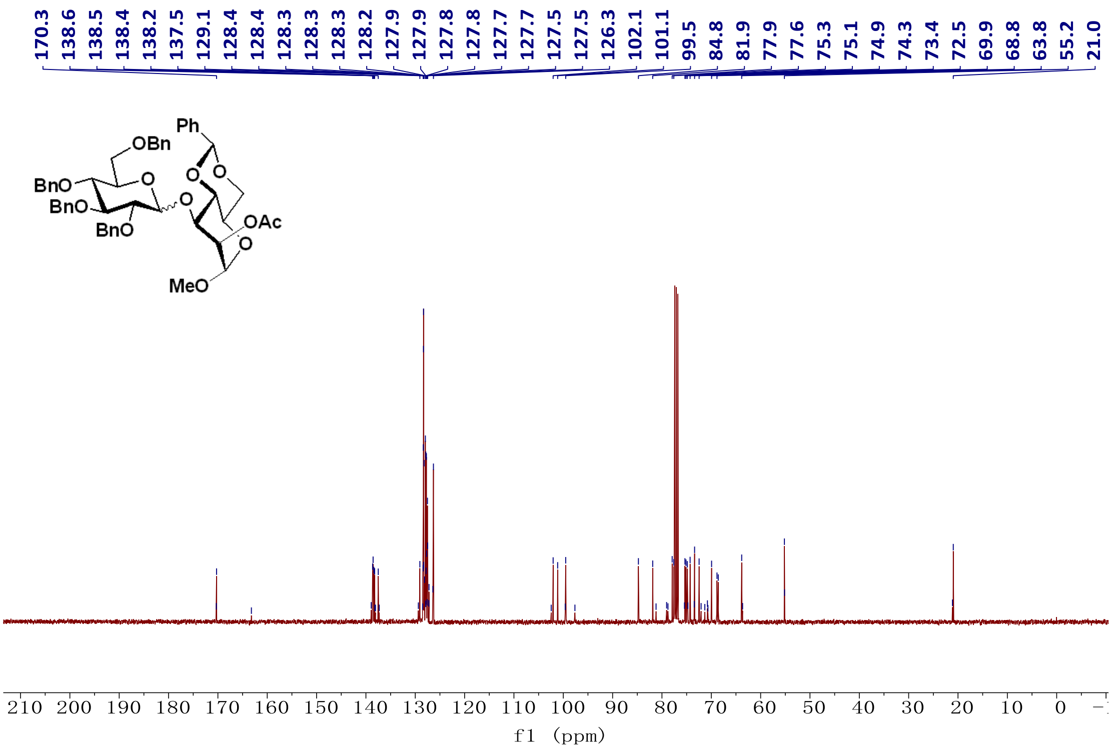
^{1}H NMR of **67l** (400 MHz, $CDCl_3$)



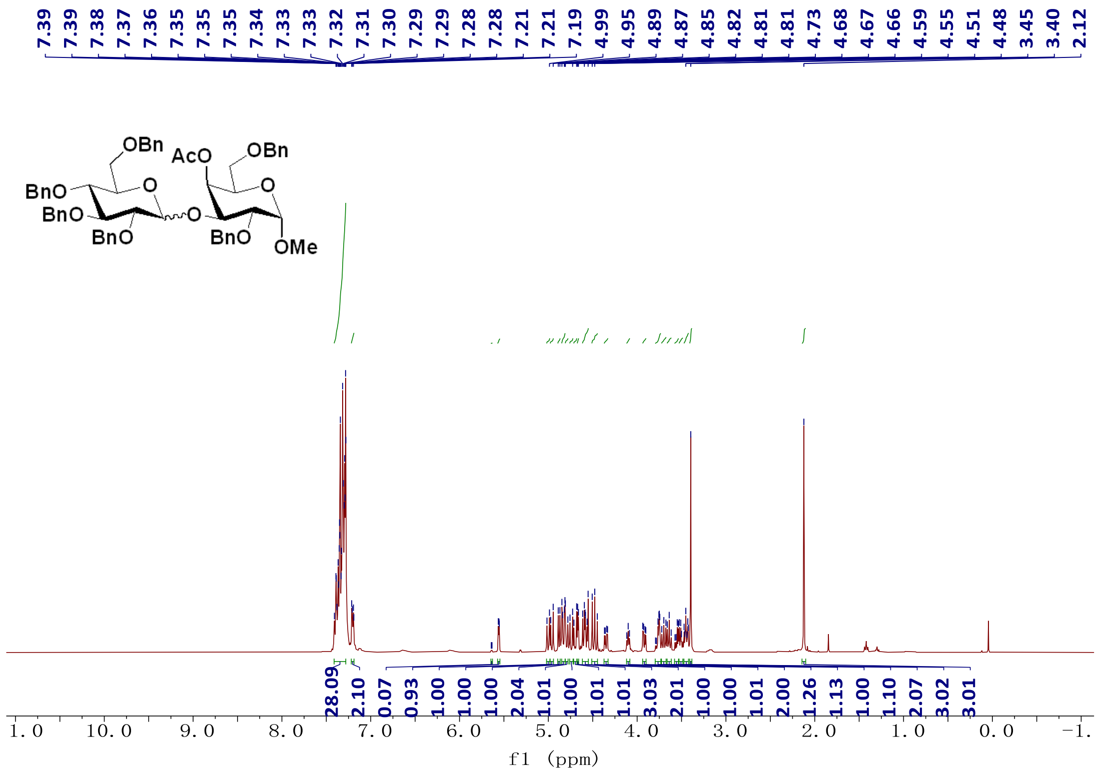
^{13}C NMR of **67l** (100 MHz, $CDCl_3$)



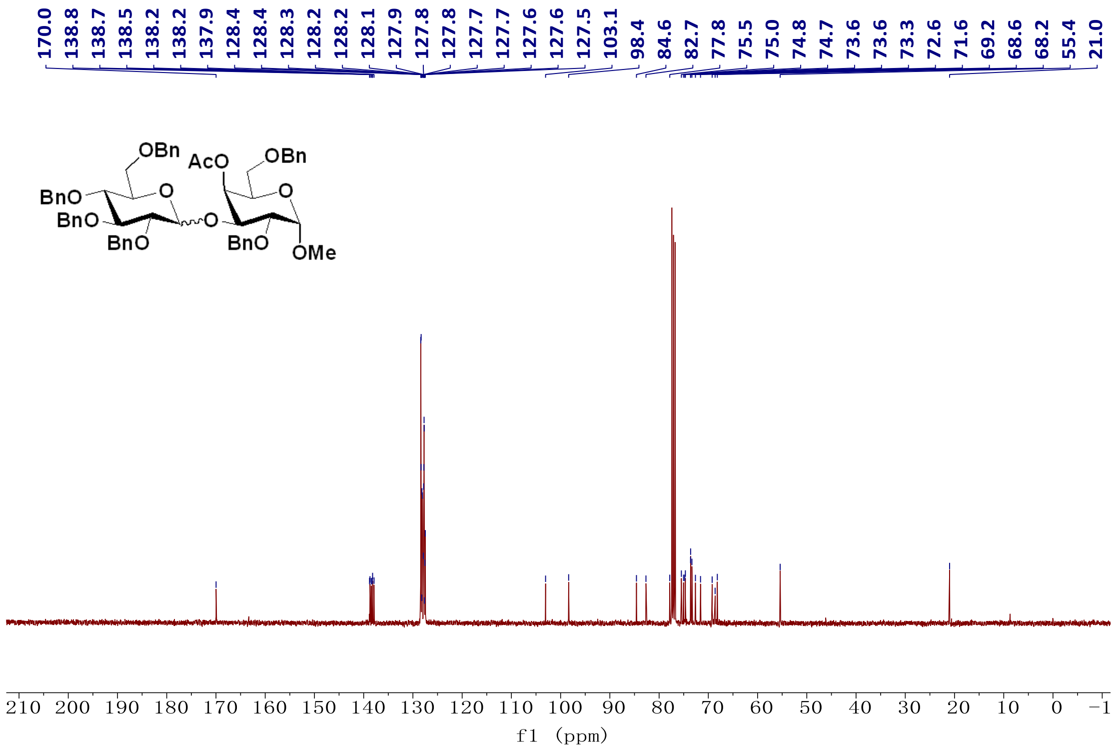
^{1}H NMR of **S35** (400 MHz, $CDCl_3$)



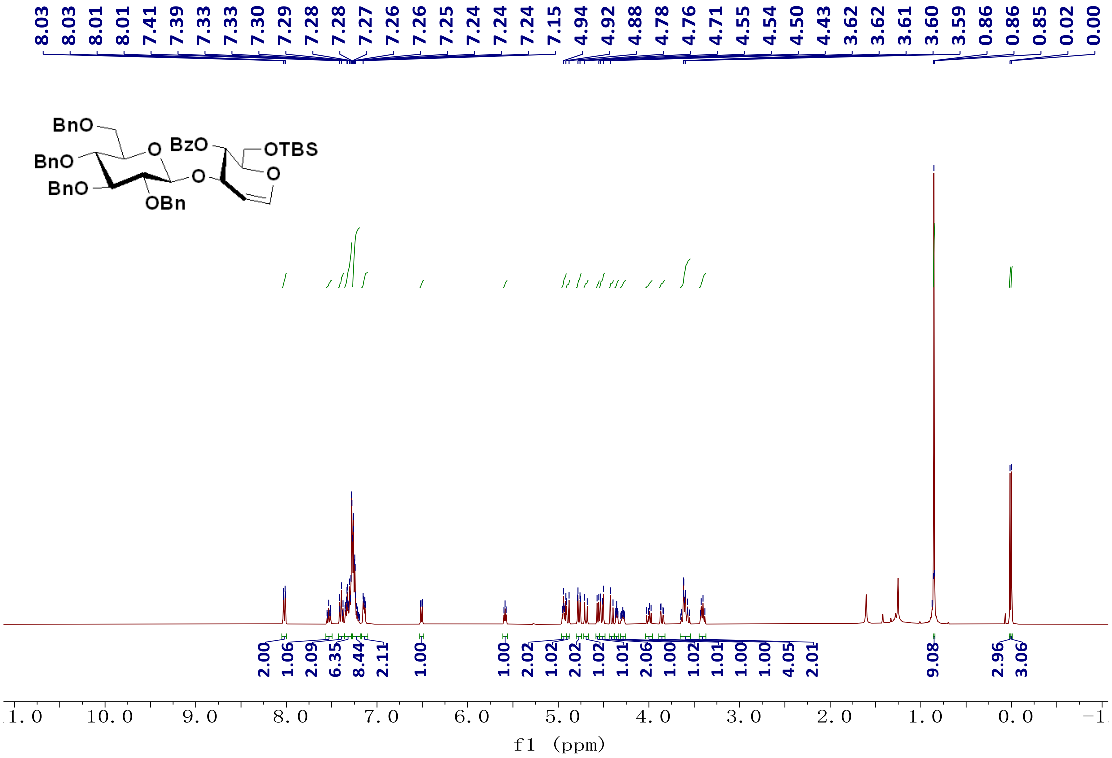
^{13}C NMR of **S35** (100 MHz, $CDCl_3$)



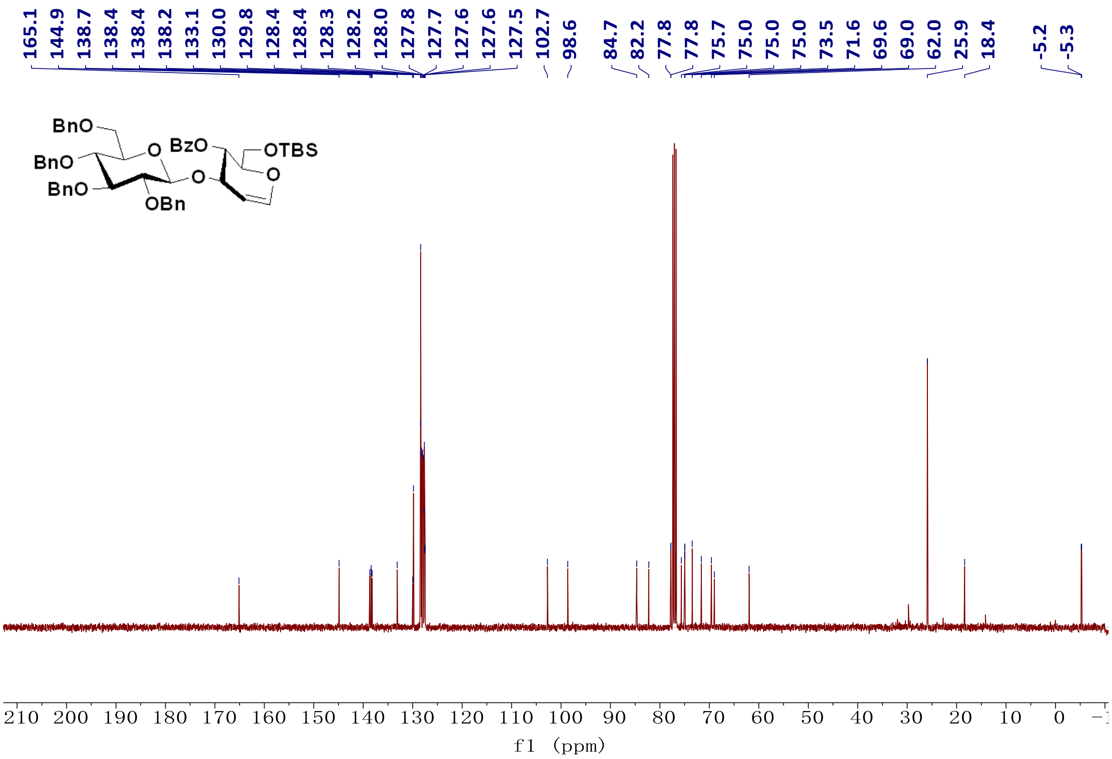
^{1}H NMR of **S36** (400 MHz, $CDCl_3$)



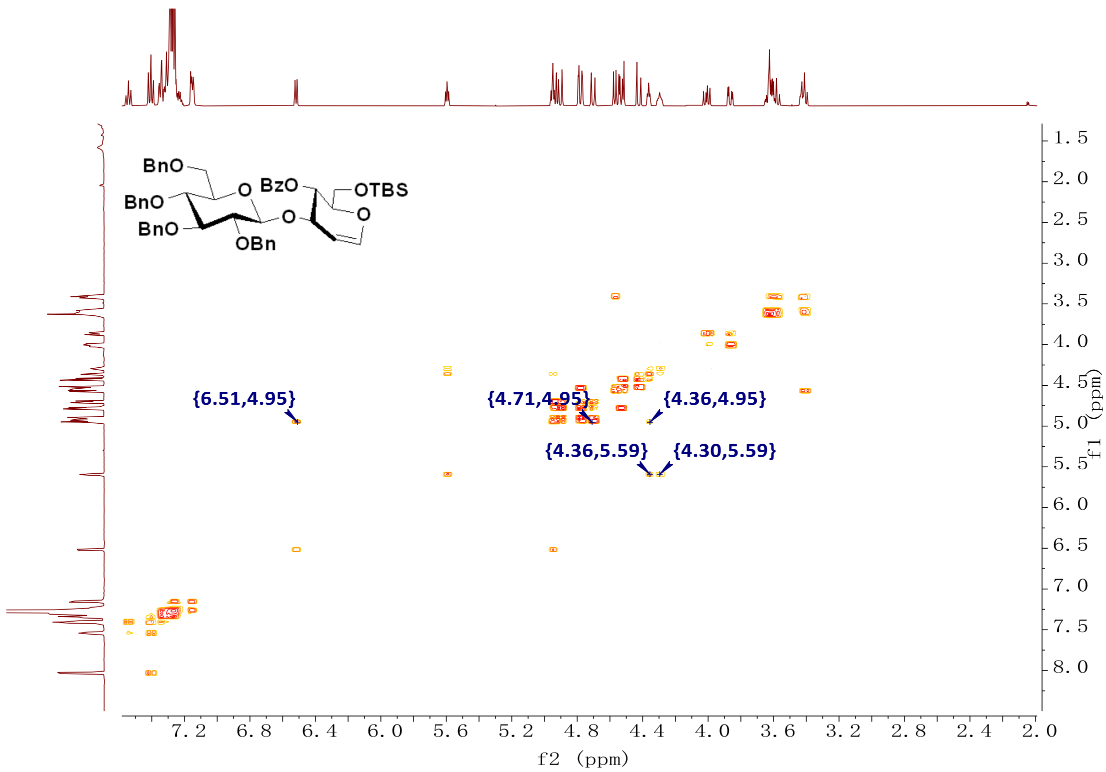
^{13}C NMR of **S36** (100 MHz, $CDCl_3$)



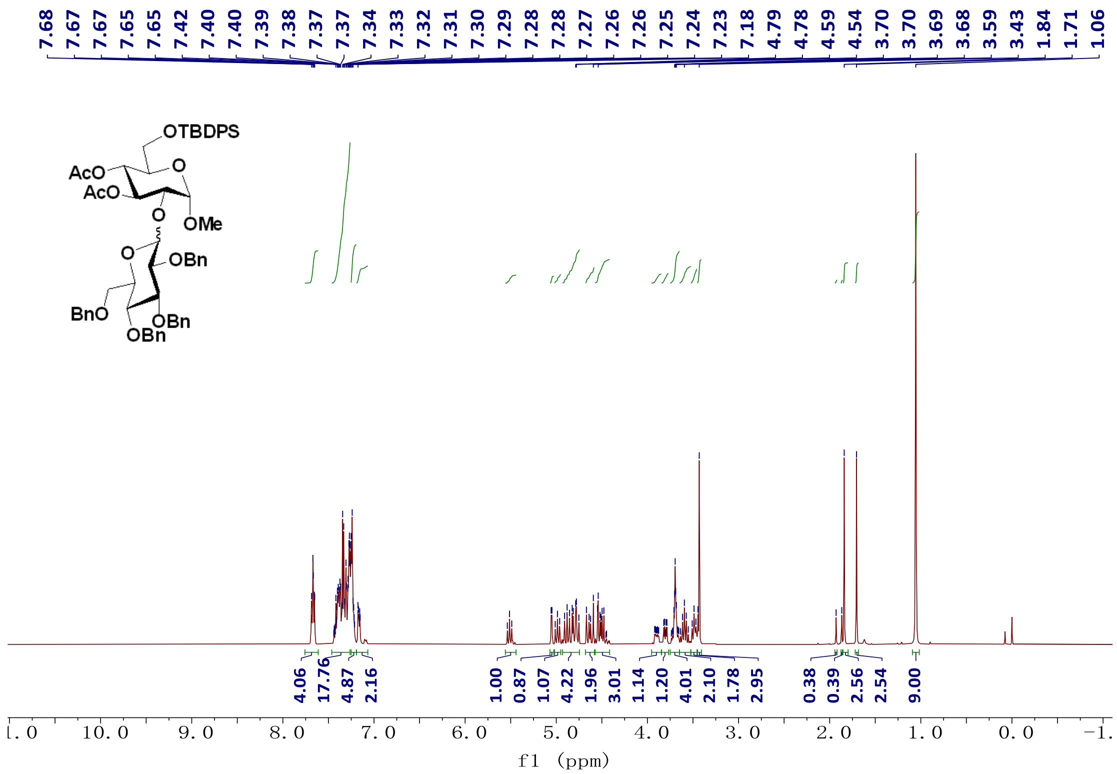
^{1}H NMR of S37 (400 MHz, $CDCl_3$)



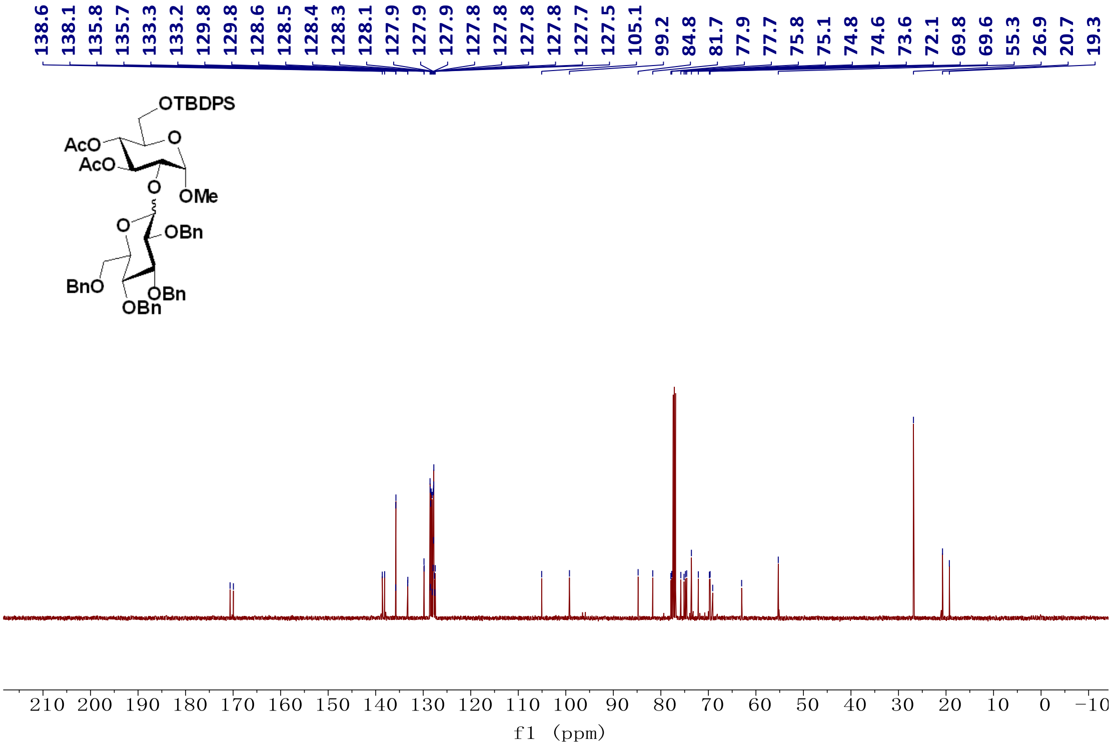
^{13}C NMR of S37 (100 MHz, $CDCl_3$)



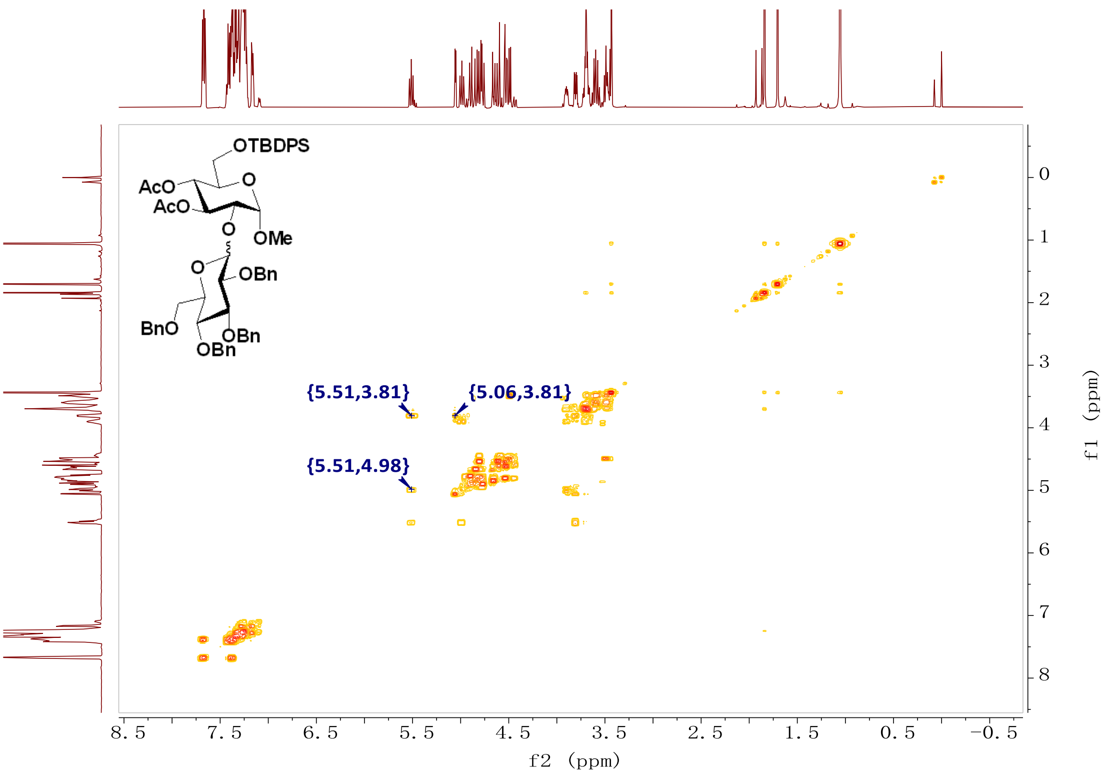
H, H-COSY of **S37**



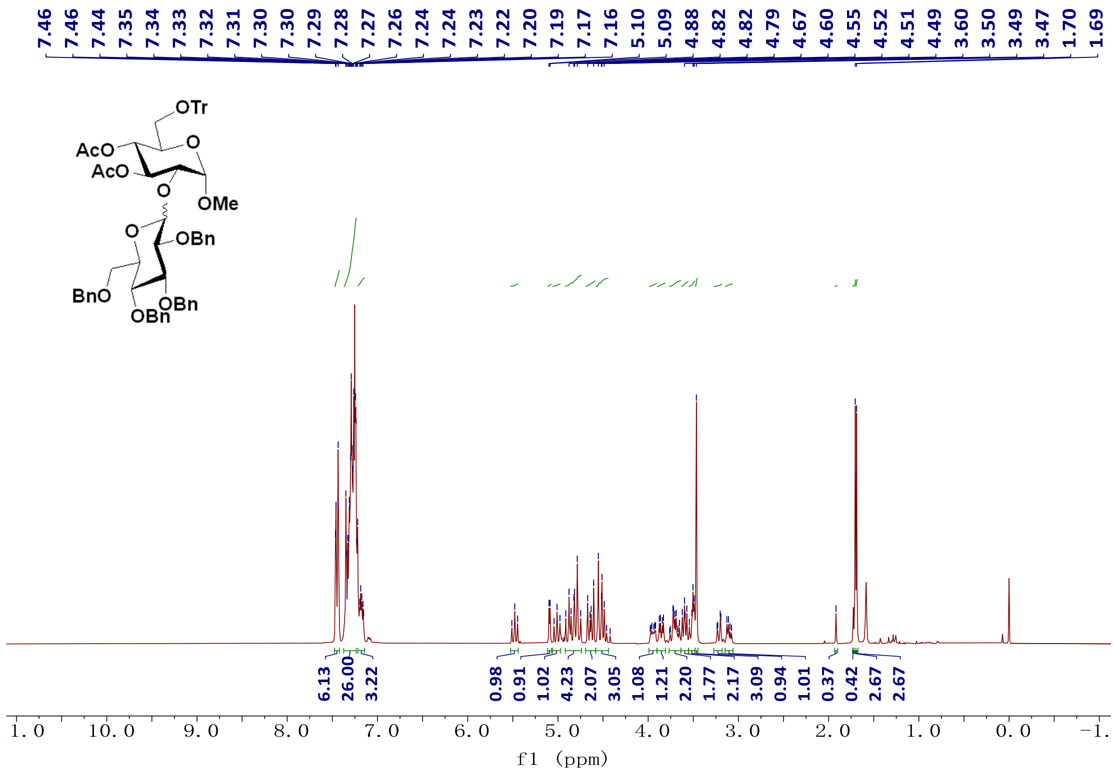
^{1}H NMR of **S38** (400 MHz, $CDCl_3$)



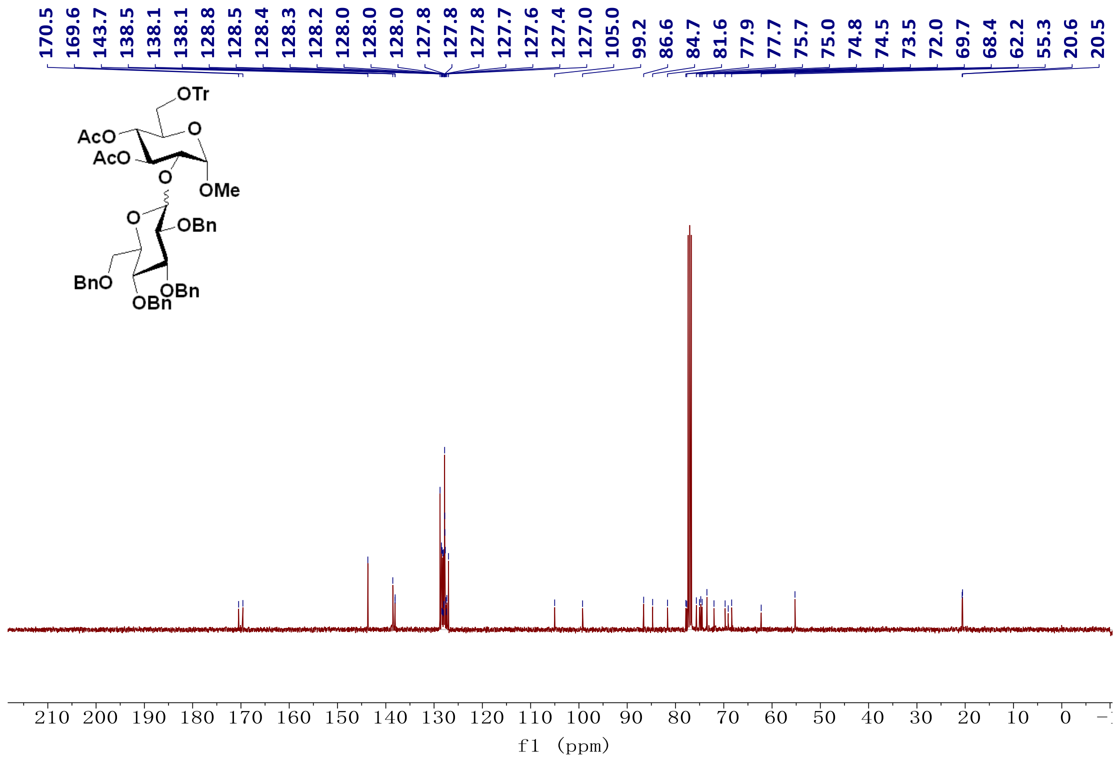
^{13}C NMR of **S38** (126 MHz, $CDCl_3$)



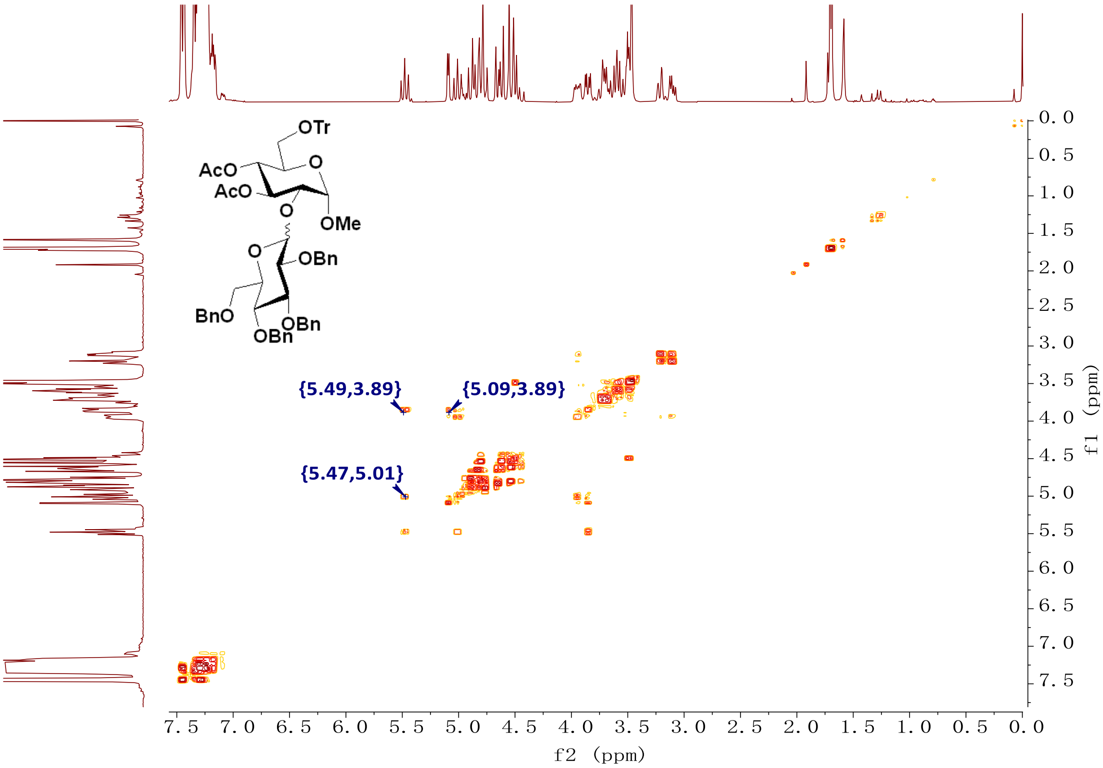
H, H-COSY of **S38**



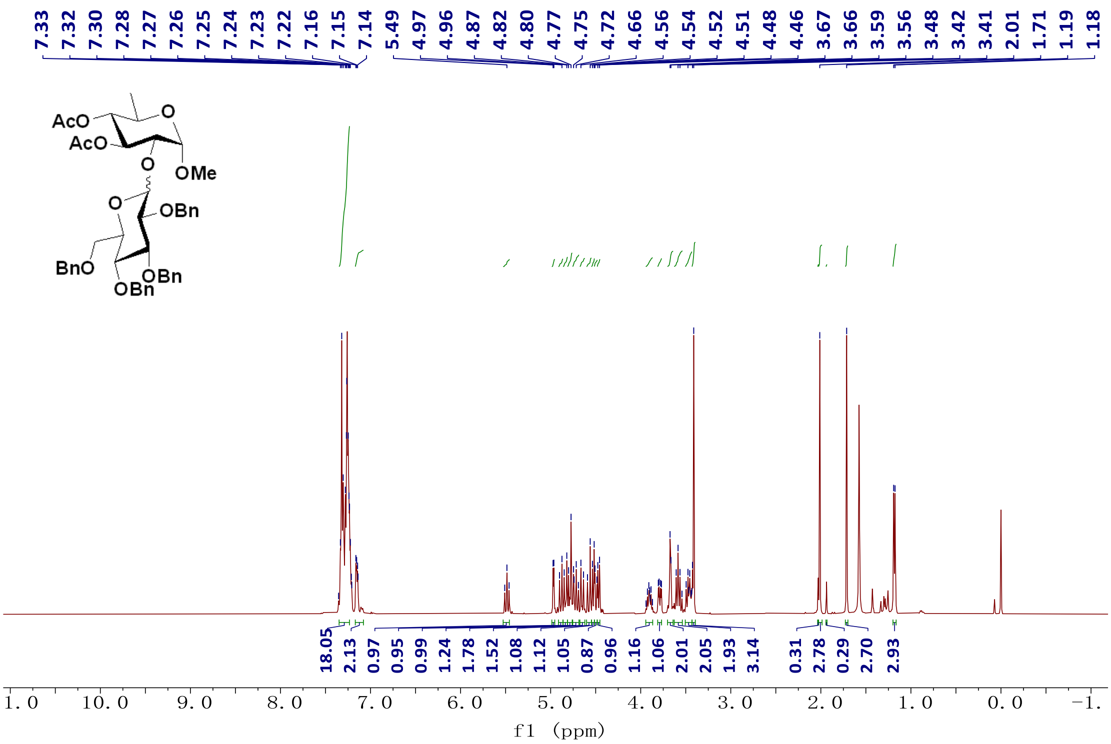
^{1}H NMR of **S39** (300 MHz, $CDCl_3$)



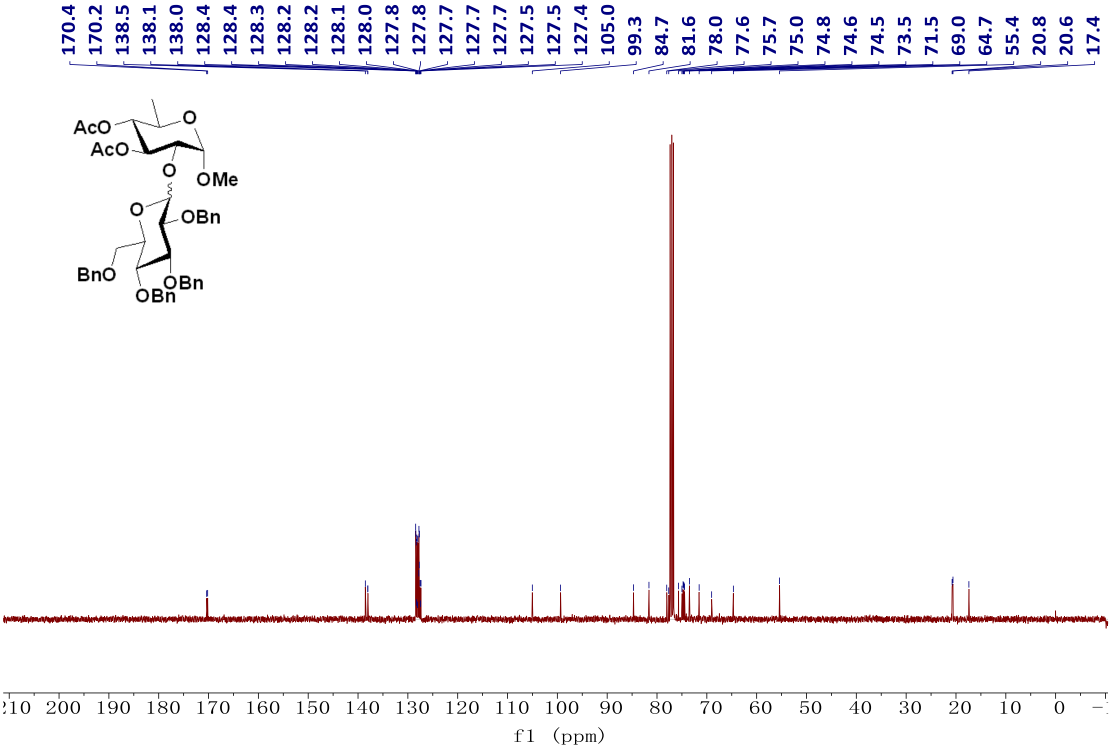
^{13}C NMR of **S39** (100 MHz, $CDCl_3$)



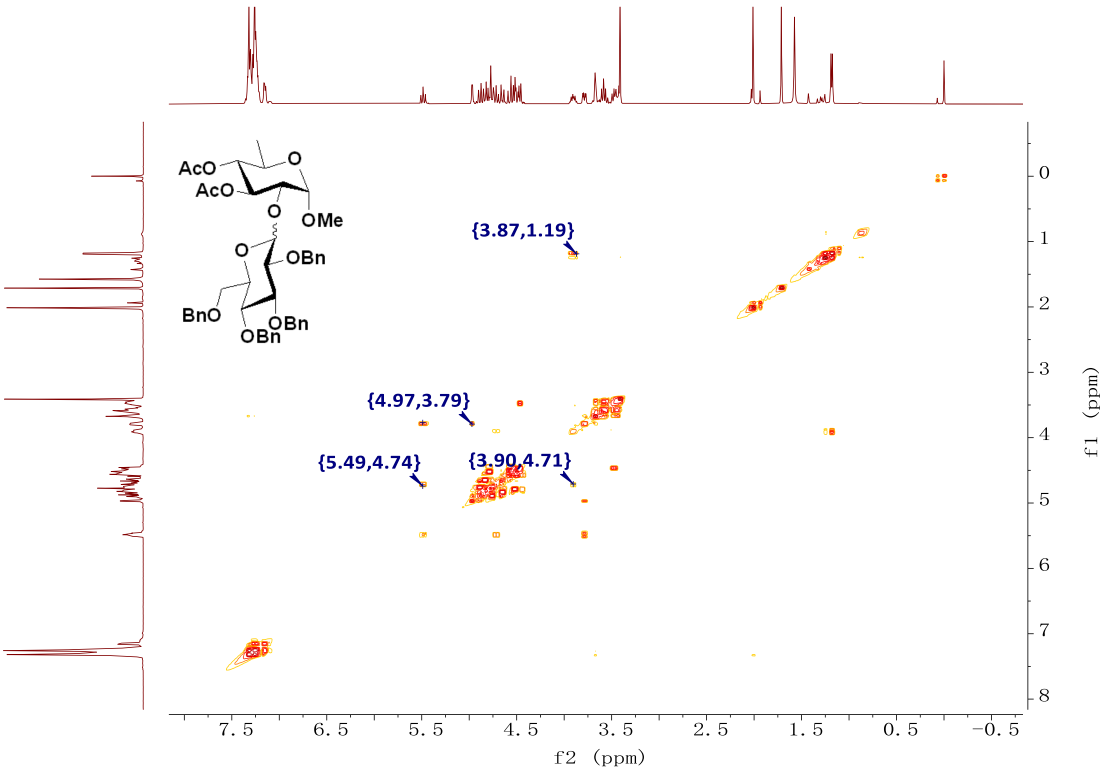
H, H-COSY of **S39**



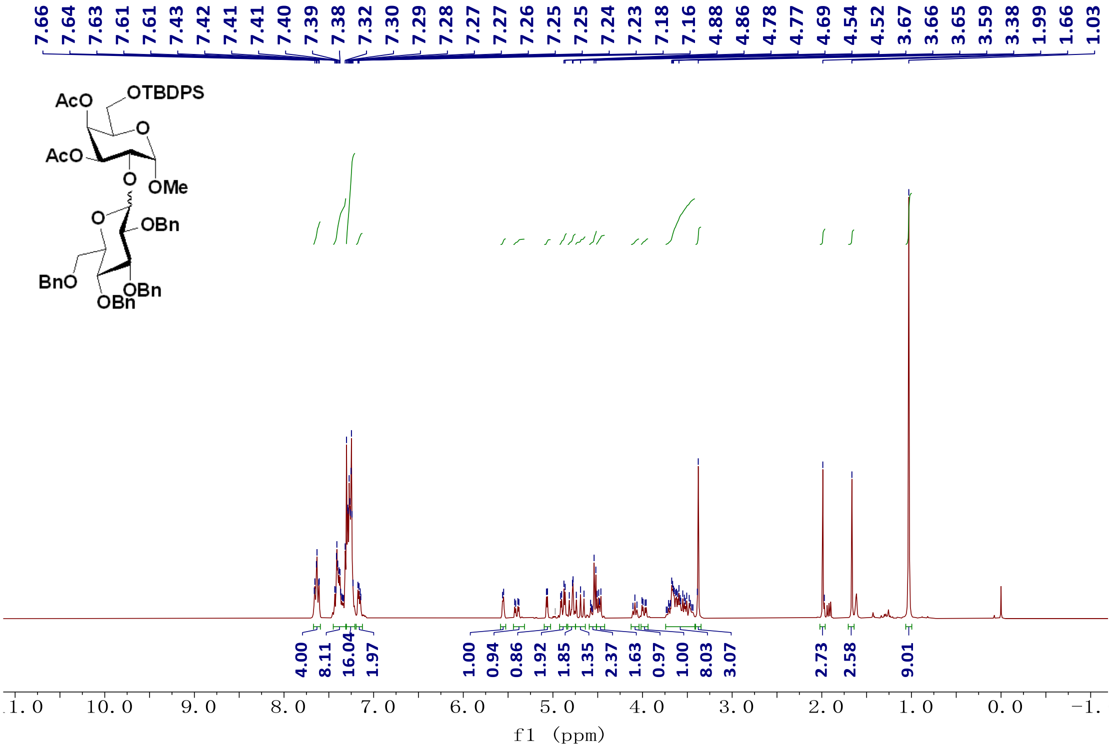
[1]H NMR of **S40** (400 MHz, $CDCl_3$)



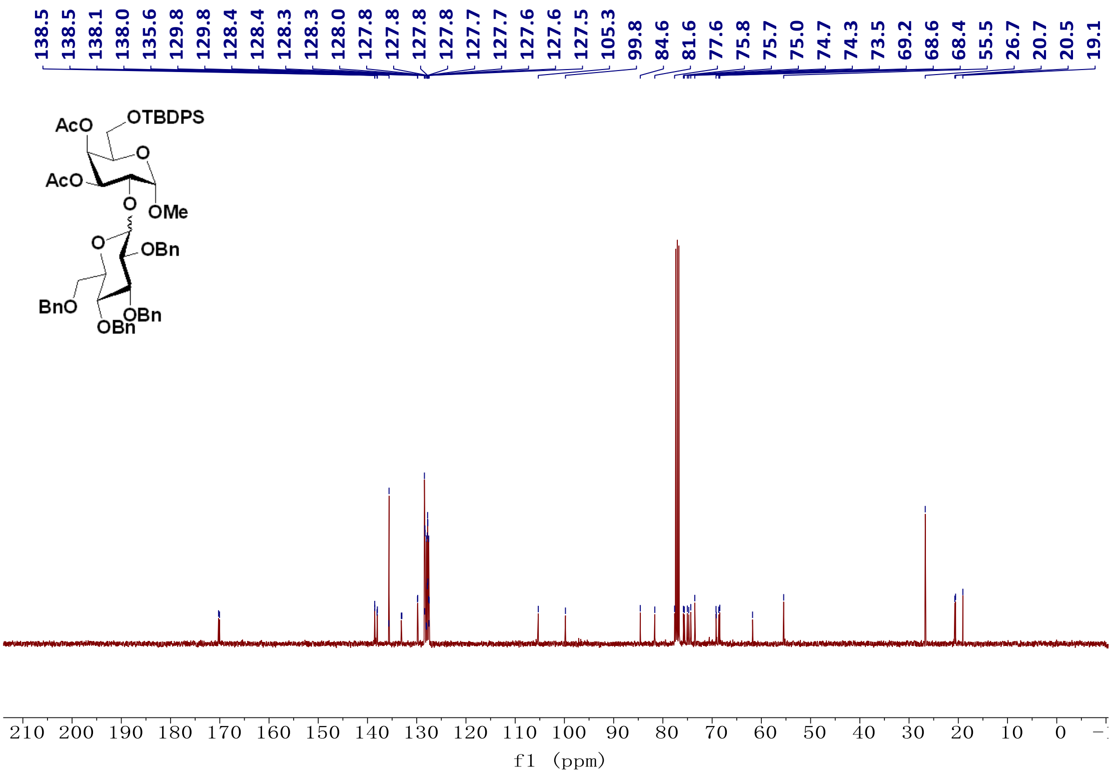
^{13}C NMR of S40 (100 MHz, CDCl$_3$)



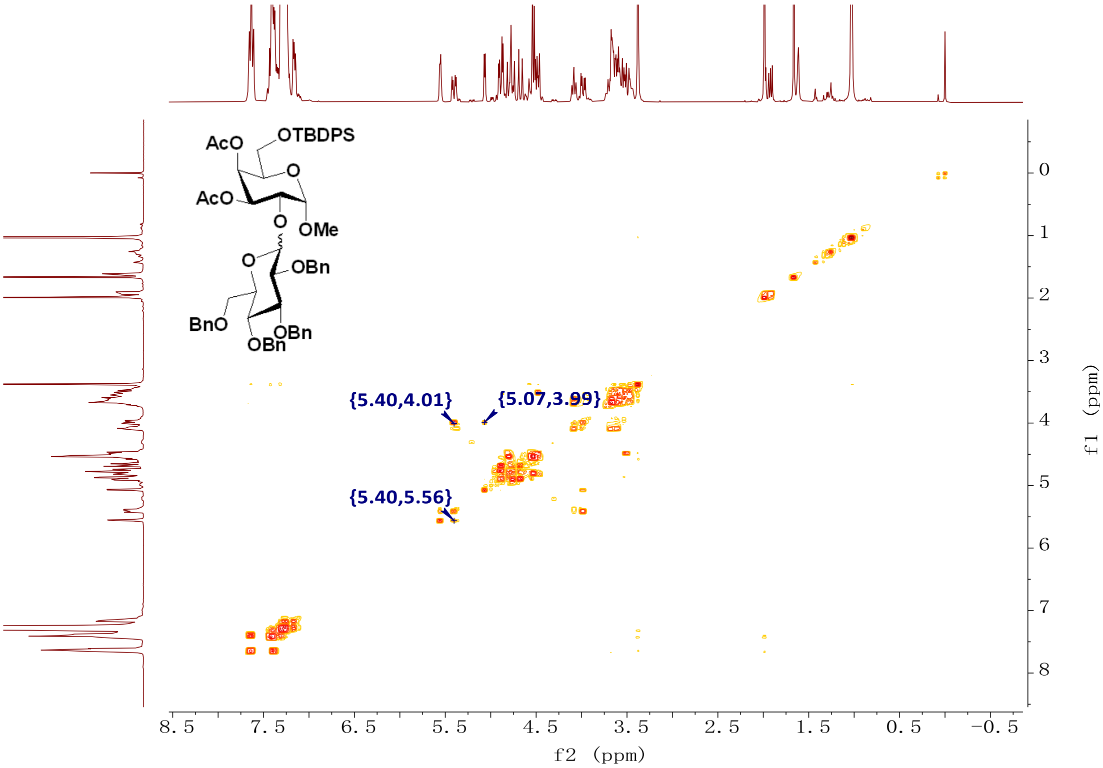
H, H-COSY of **S40**



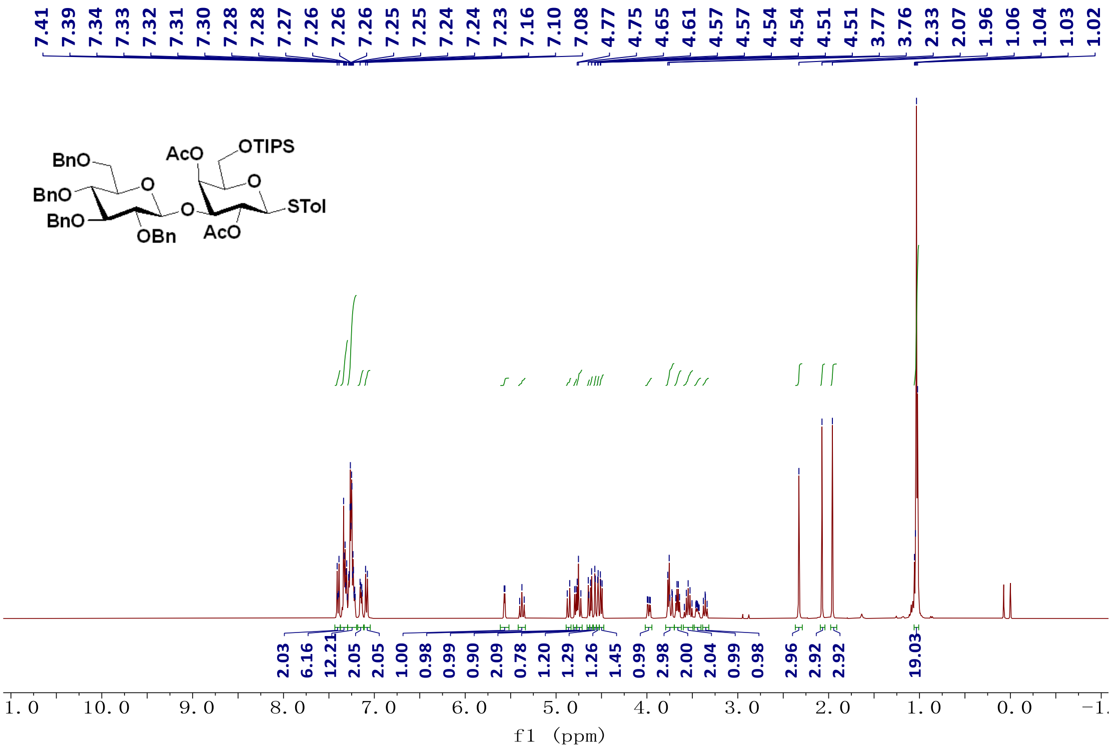
^{1}H NMR of **S41** (300 MHz, $CDCl_3$)



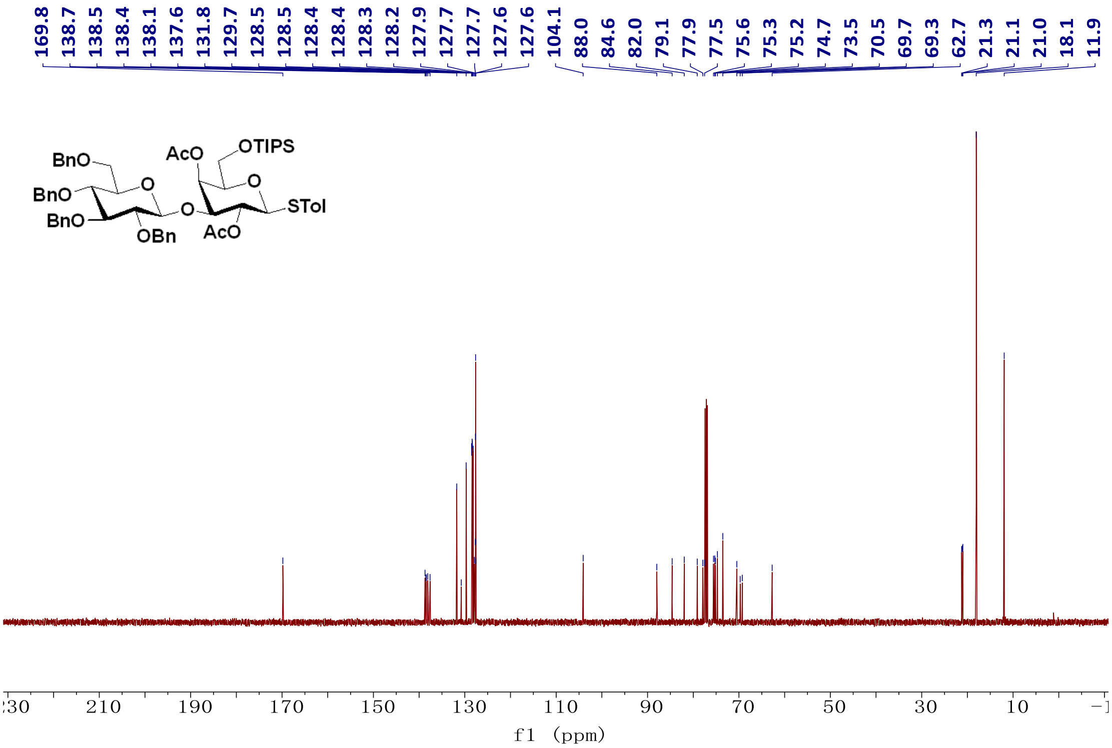
^{13}C NMR of **S41** (100 MHz, $CDCl_3$)



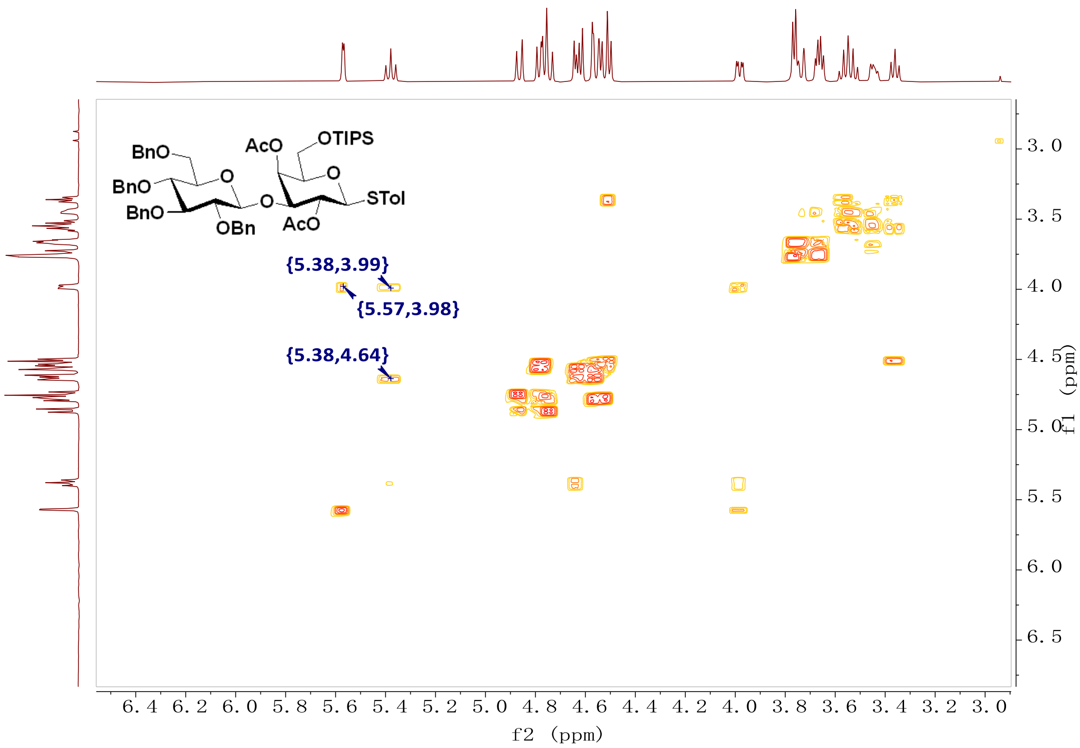
H, H-COSY of **S41**



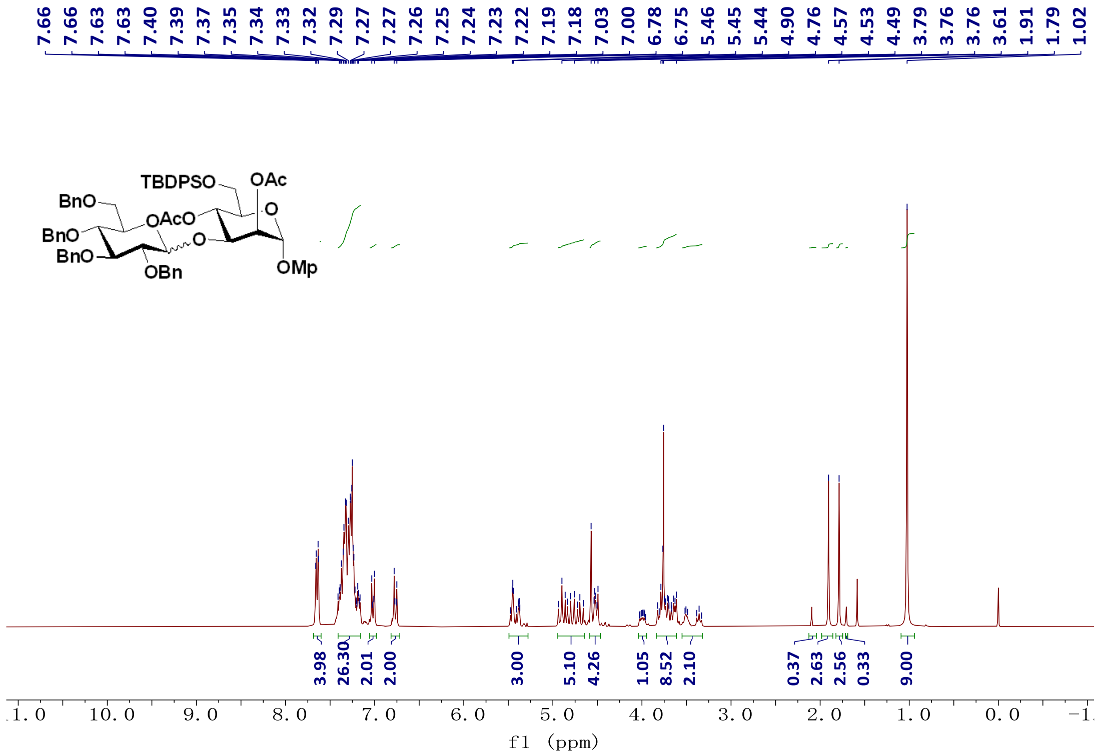
^{1}H NMR of **S42** (400 MHz, $CDCl_3$)



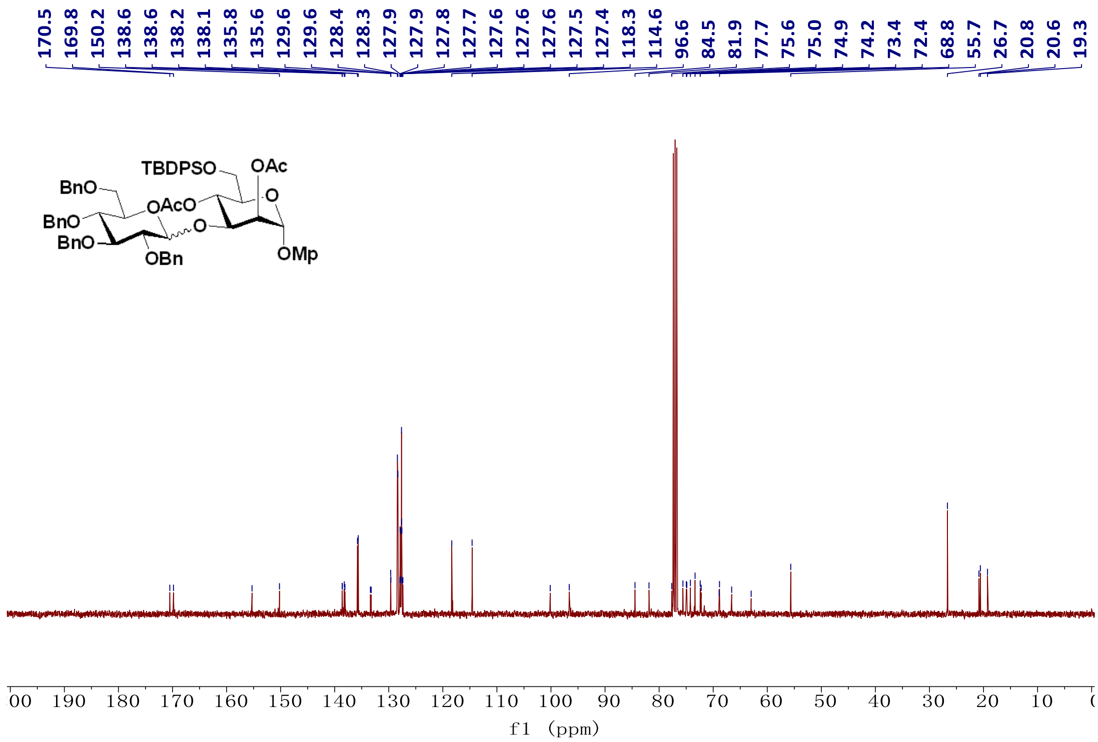
^{13}C NMR of **S42** (100 MHz, $CDCl_3$)



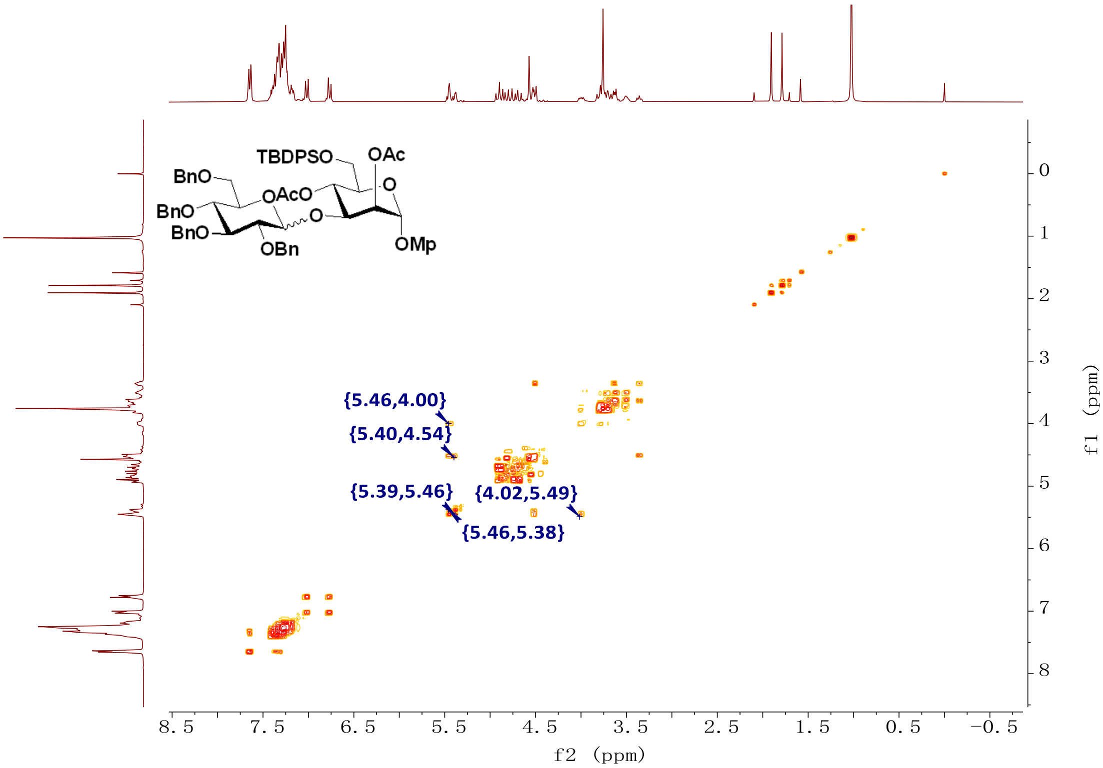
H, H-COSY of **S42**



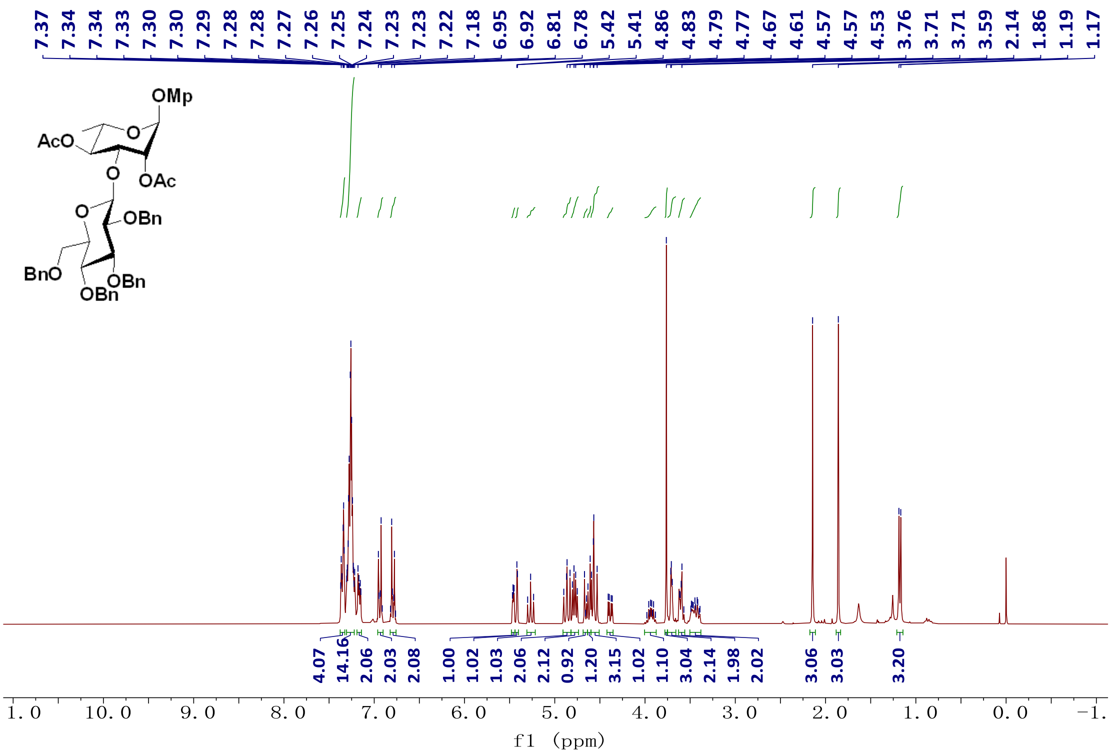
^{1}H NMR of **S43** (300 MHz, $CDCl_3$)



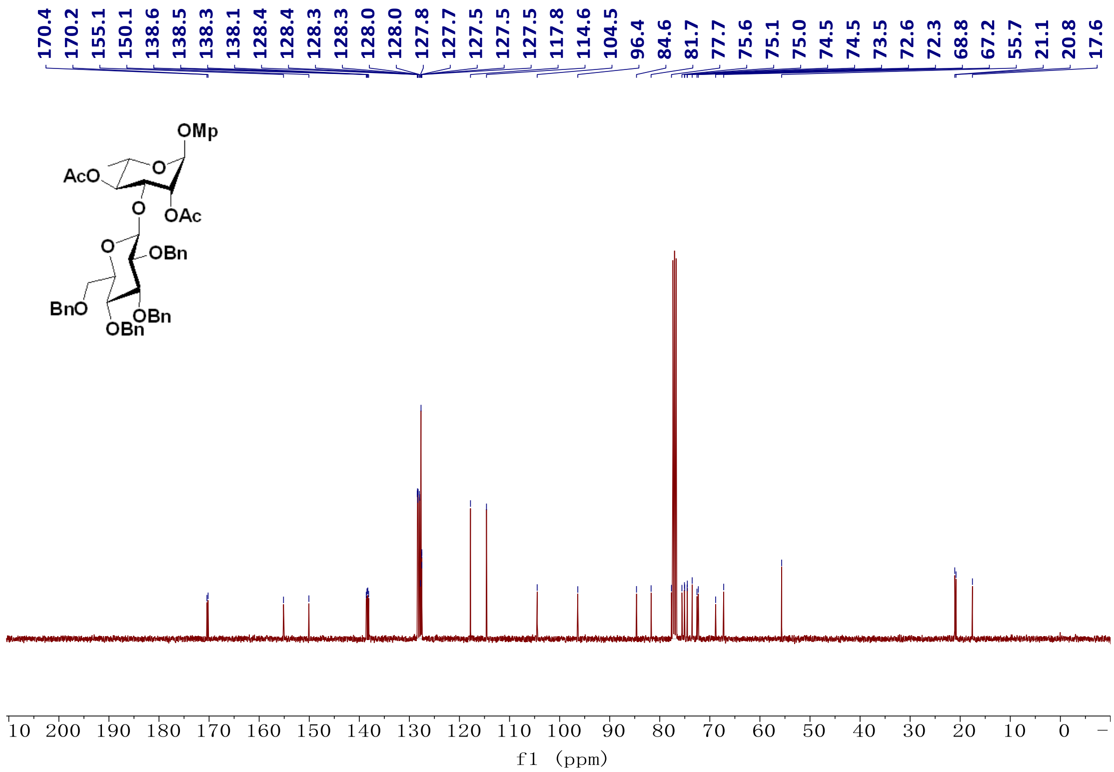
^{13}C NMR of **S43** (100 MHz, $CDCl_3$)



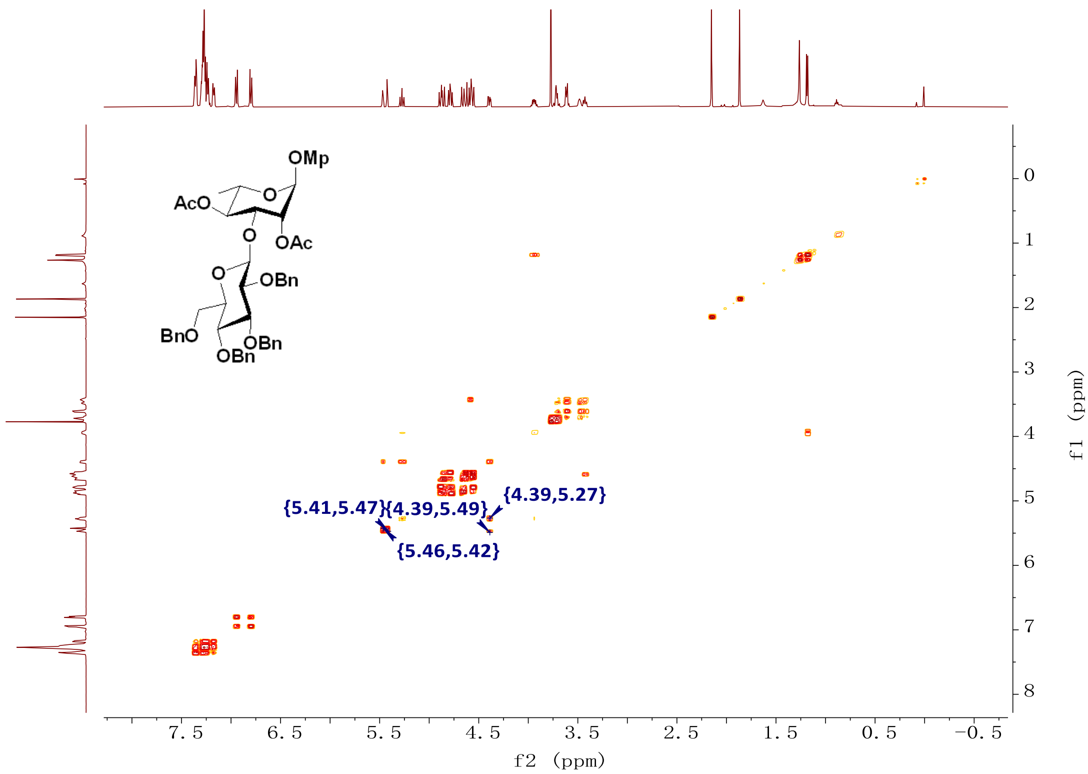
H, H-COSY of **S43**



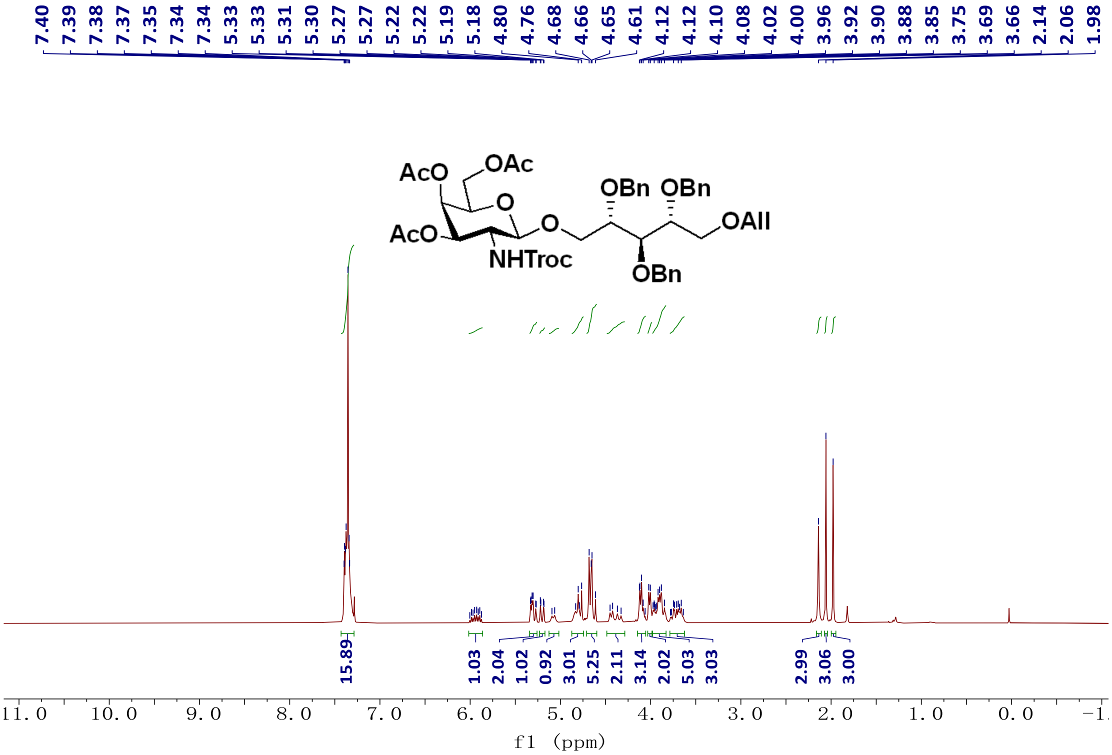
^{1}H NMR of **S44** (300 MHz, $CDCl_3$)



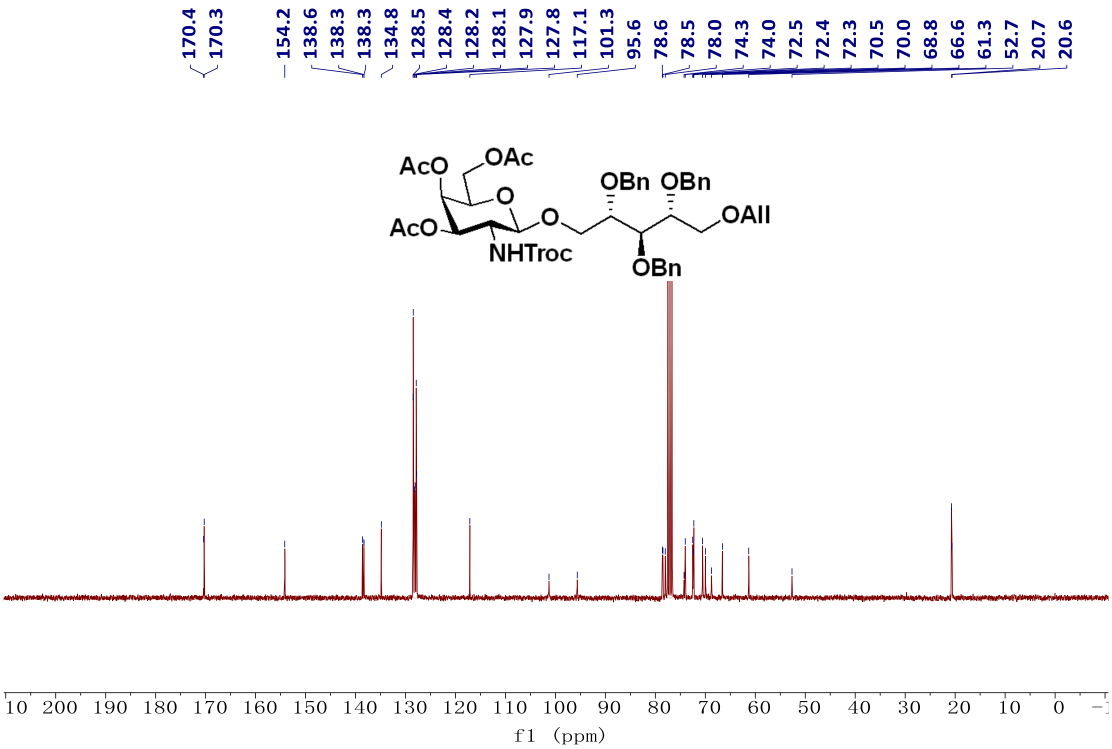
^{13}C NMR of **S44** (100 MHz, $CDCl_3$)



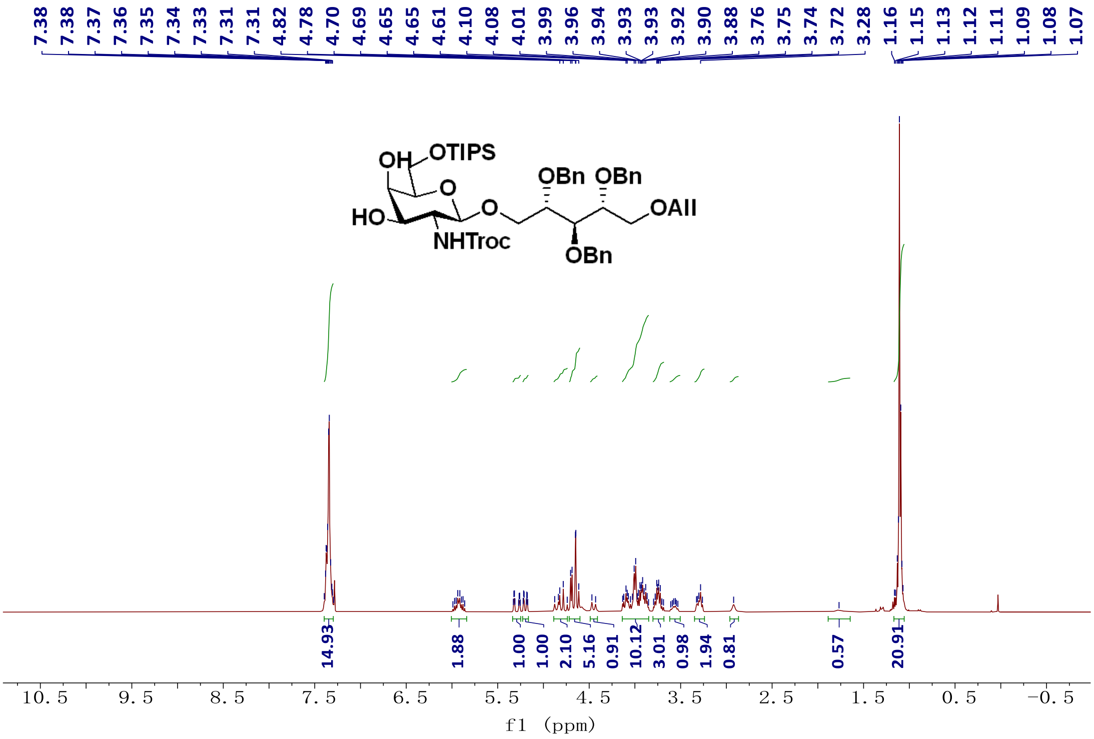
H, H-COSY of **S44**



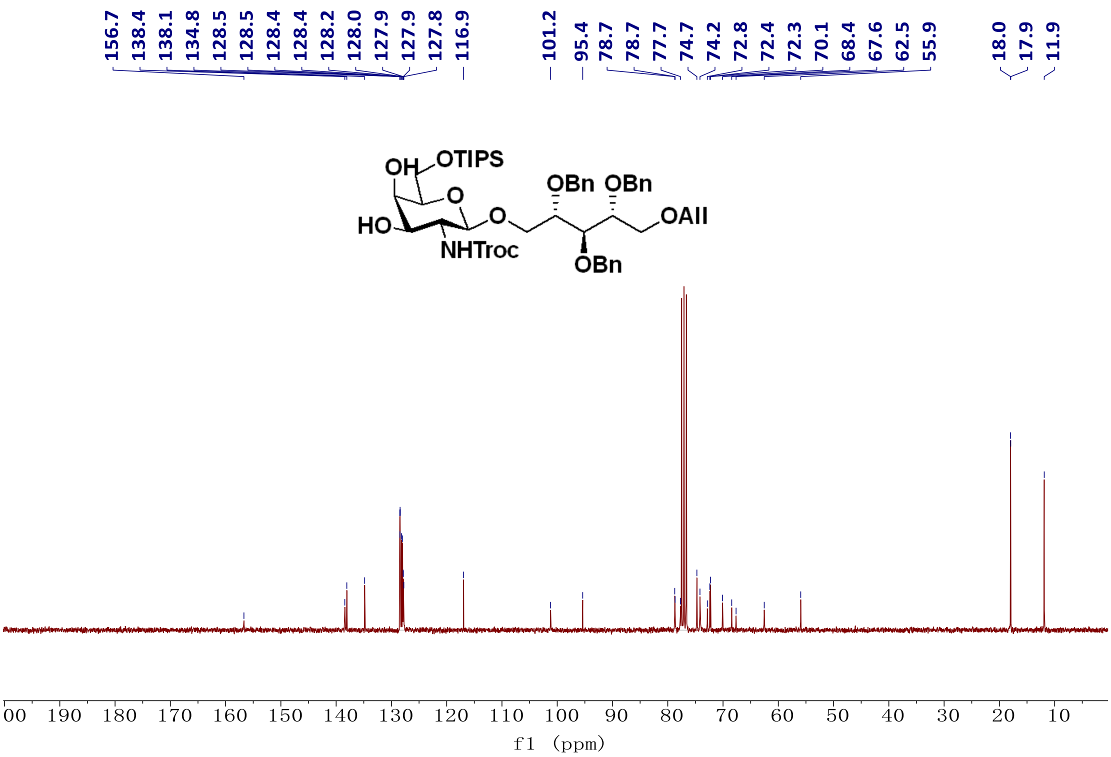
^{1}H NMR of **S47** (300 MHz, $CDCl_3$)



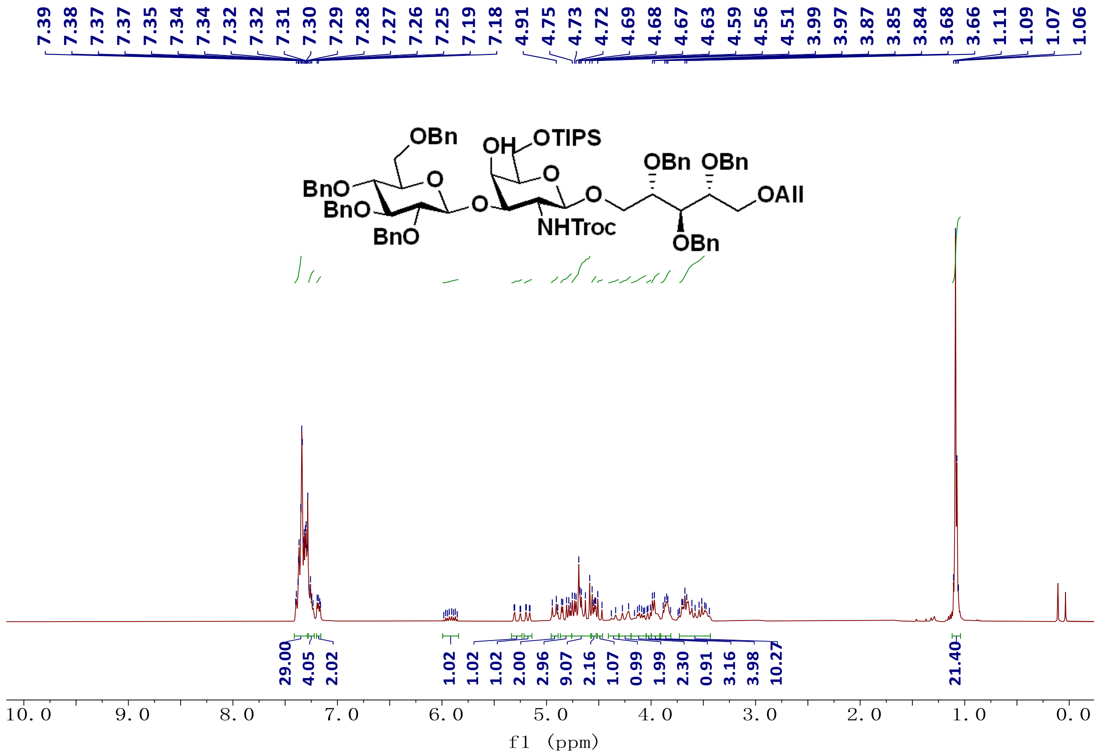
^{13}C NMR of **S47** (75 MHz, $CDCl_3$)



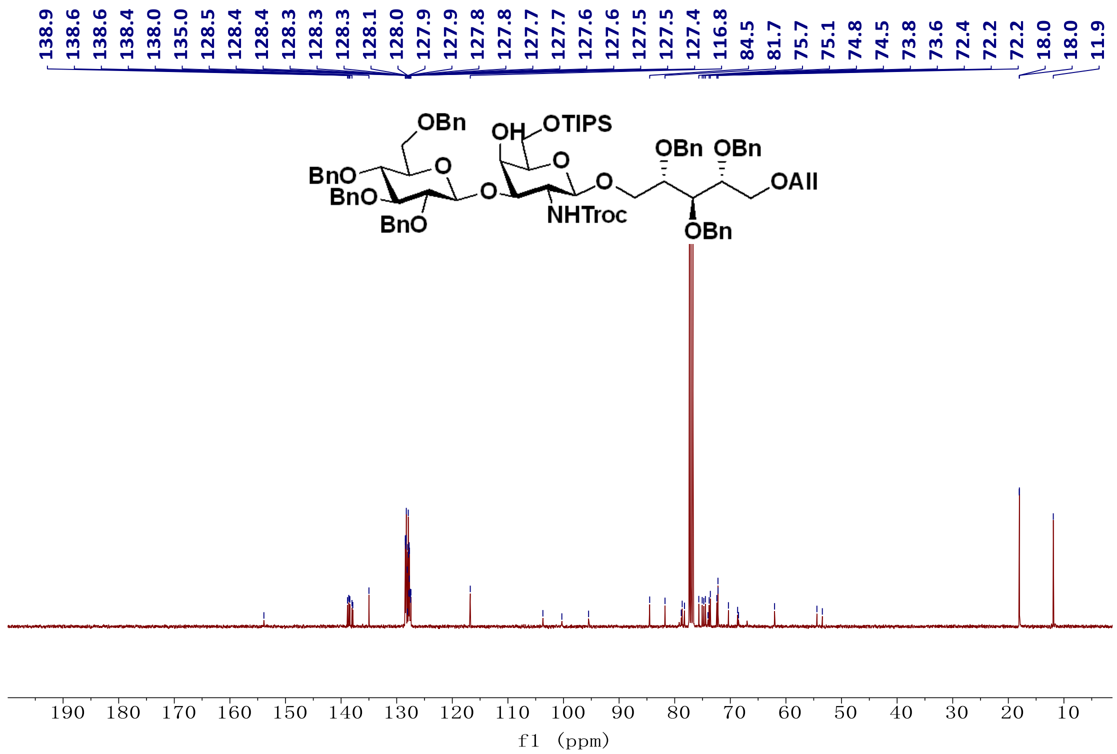
[1]H NMR of **68** (300 MHz, $CDCl_3$)



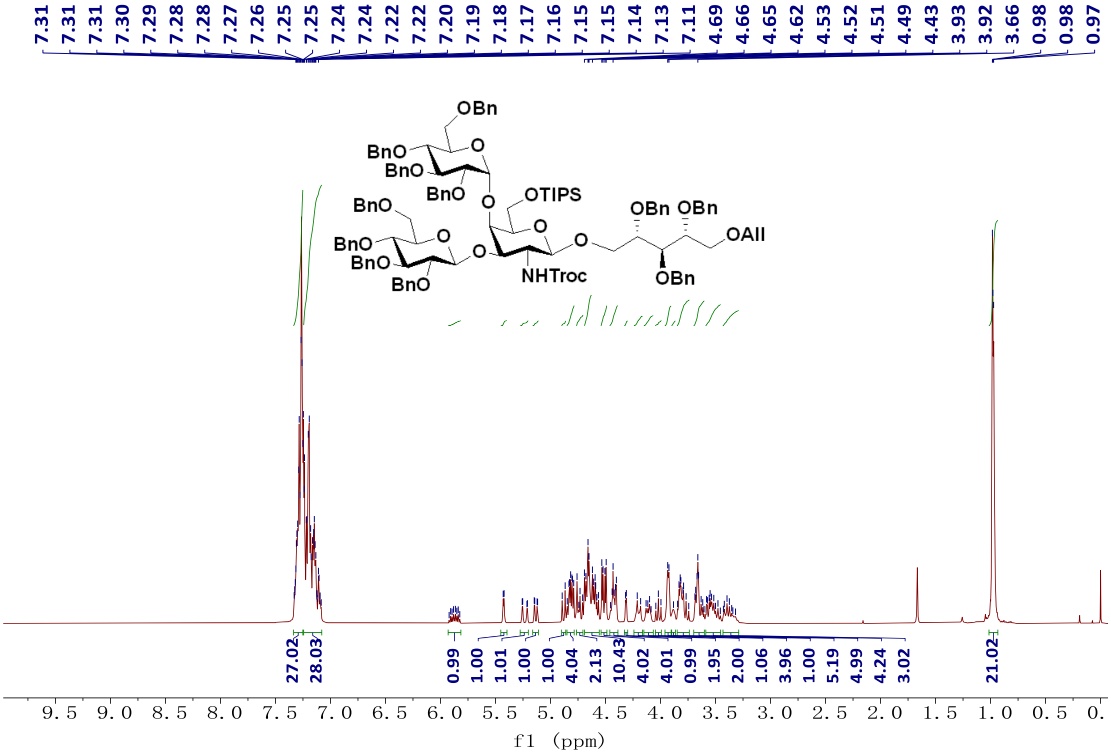
[13]C NMR of **68** (75 MHz, $CDCl_3$)



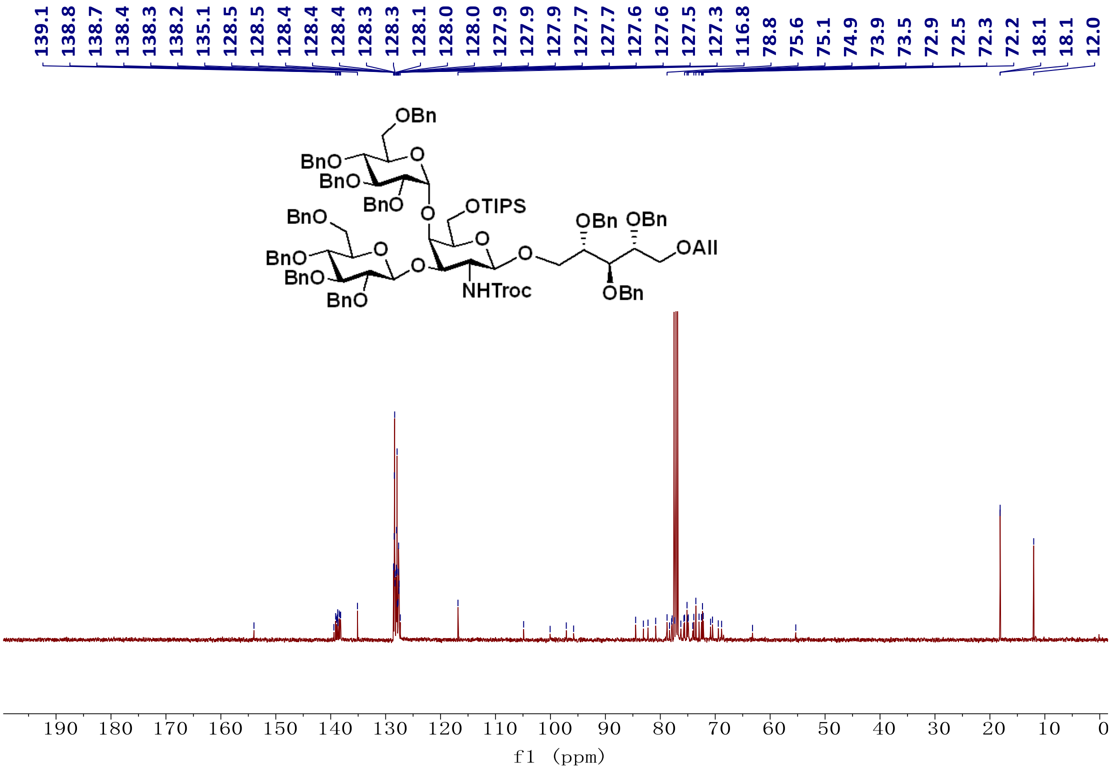
^{1}H NMR of **S48** (300 MHz, $CDCl_3$)



^{13}C NMR of **S48** (75 MHz, $CDCl_3$)



^{1}H NMR of **70** (400 MHz, $CDCl_3$)



^{13}C NMR of **70** (100 MHz, $CDCl_3$)