Electronic Supplementary Information

Visible-Light-Promoted 3,5-Dimethoxyphenyl Glycoside Activation and Glycosylation

Yafei Cao,[‡a] Minmin Zhou,[‡b] Run-Ze Mao,[a] You Zou,[a] Feng Xia,[a] Da-Ke Liu,[a] Jianhui Liu,[b] Qin Li,[a] De-Cai Xiong,*[ac] and Xin-Shan Ye*[a]

[a]*State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences, Peking University, Xue Yuan Road No. 38, Beijing 100191, China.*
[b]*School of Chemical Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China.*
[c]*State Key Laboratory of Pharmaceutical Biotechnology, Nanjing University, Nanjing 210023, Jiangsu, China.*

[‡]*These authors contributed equally to this work.*

**E-mail: xinshan@bjmu.edu.cn; decai@bjmu.edu.cn.*

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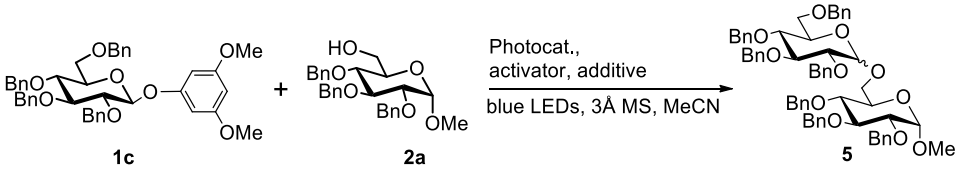
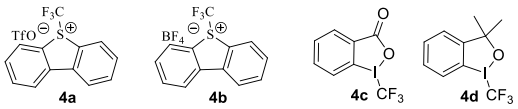
1 General information

All chemicals were purchased as reagent grade and used without further purification except noted. All solvents were purified before use. CH_2Cl_2, CH_3CN, and pyridine were refluxed over CaH_2 and distilled. Methanol was distilled from magnesium. DMF was stirred with CaH_2 and distilled under reduced pressure. Toluene was refluxed over sodium and distilled. Ether was distilled with potassium and sodium. Reactions were performed in oven-dried glassware with freshly distilled solvents under an argon atmosphere except noted. Thin-layer chromatography (TLC) was performed on silica gel-coated aluminum plates (60 F_{254}, E. Merck). Compounds were visualized by UV light (254 nm) and charring with a solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (24.00 g, 19.4 mmol) and $Ce(NH_4)_2(NO_3)_6$ (0.50 g, 0.9 mmol) in sulfuric acid (5%, 500 mL) or $KMnO_4$ (1.5 g, 19.4 mmol) and K_2CO_3 (10 g, 19.4 mmol) in aqueous NaOH (5%, 2.5 mL) and water (150 mL). Column chromatography was performed on silica gel (200-300 mesh). ^1H NMR spectra were recorded with the Avance III-400 or III-600 (Bruker) and the chemical shifts were referenced to the peak of solvent or TMS (0 ppm). ^{13}C NMR spectra were recorded using the same NMR spectrometers and the chemical shifts were reported relative to solvent or TMS (0 ppm). Assignments of resonances in ^1H and ^{13}C NMR spectra were done using ^1H-^1H COSY, HSQC and HMBC experiments. The following standard abbreviations are used to indicate multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets and br = broad. Optical rotations were obtained on a Hanon P850 Automatic Polarimeter. HRMS experiments were performed on a Waters Xevo G2 Q-TOF spectrometer or a Bruker APEX IV FTMS instrument.

2 Optimization of reaction conditions

Table S1 Preliminary optimization of *O*-glycosylation conditions[a]

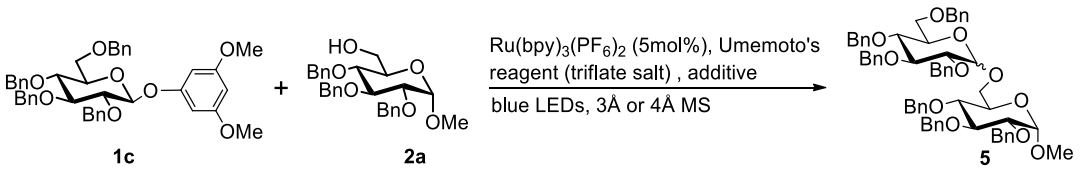




Entry	Donor/ Acceptor	Activator (equiv.)	Photocat. (equiv.)	Vis (h)	Additive (equiv.)	Yield
1	1.5/1.0	**4a** (3.0)	$Ru(bpy)_3PF_6$ (5%)	12 h	-	62%
2	1.5/1.0	**4b** (3.0)	$Ru(bpy)_3PF_6$ (5%)	12 h	-	43%
3	1.5/1.0	CBr_4 (3.0)	$Ru(bpy)_3PF_6$ (5%)	12 h	-	not found
4	1.5/1.0	Cl_3CBr (3.0)	$Ru(bpy)_3PF_6$ (5%)	12 h	-	trace
5	1.5/1.0	O_2 (1 atm)	$Ru(bpy)_3PF_6$ (5%)	12 h	-	not found
6	1.5/1.0	**4a** (3.0)	$Ir(bpy)_3$ (5%)	12 h	-	40%
7	1.5/1.0	**4c** (3.0)	$Ru(bpy)_3PF_6$ (5%)	12 h	-	not found
8	1.5/1.0	**4d** (3.0)	$Ru(bpy)_3PF_6$ (5%)	12 h	-	trace

[a]General conditions: 0.03 mmol of **1c**, 0.02 mmol of **2a** (1.0 equiv.), photocat. (5 mol%), activator, 3 Å MS, 2.0 mL of MeCN under the irradiation of blue LEDs (28 W). Yield was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S2 Optimization of *O*-glycosylation conditions[a]

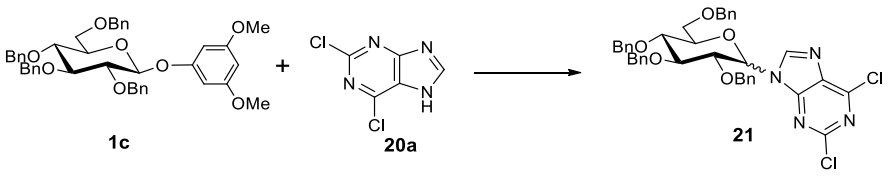


Entry	Donor/ Acceptor	Umemoto's reagent (triflate salt) (equiv.)	Solvent (0.01 M)	Vis (h)	Additive (equiv.)	Temp. (°C)	Yield[b]
1	1.5/1.0	3.0	MeCN	12	TTBP (1.5)	rt	50%
2	1.5/1.0	3.0	MeCN	12	$Cu(OTf)_2$ (1.5)	rt	12%
3	1.5/1.0	3.0	MeCN	12	CuI (1.5)	rt	trace
4	1.5/1.0	3.0	MeCN	12	DIPEA (1.5)	rt	26%
5	1.5/1.0	3.0	MeCN	12	DTBMP (1.5)	rt	21%
6	1.5/1.0	3.0	MeCN	12	HFIP (1.5)	rt	57%
7	1.5/1.0	3.0	MeCN[c]	12	-	rt	72%

8	1.5/1.0	4.5	MeCN	12	-	rt	52%
9	1.5/1.0	3.0	MeCN[c]	12	no Ar	rt	46%
10	1.5/1.0	3.0	MeCN	12	no Ar	rt	32%
11	1.5/1.0	3.0	MeCN	12	-	-30	90%
12	1.5/1.0	3.0	DCM	12	-	-30	27%
13	1.5/1.0	3.0	THF	12	-	-30	not found
14	1.5/1.0	3.0	DCE	12	-	-30	30%
15	1.5/1.0	3.0	1,4-dioxane	12	-	-30	trace
16	1.5/1.0	3.0	DMF	12	-	-30	not found
17	1.5/1.0	3.0	DMSO	12	-	-30	5%
18	1.1/1.0	2.2	MeCN	12	-	-30	63%
19	1.3/1.0	2.6	MeCN	12	-	-30	80%
20	1.5/1.0	3.0	MeCN[c]	12	-	-30	57%
21	1.5/1.0	3.0	MeCN	12	-	-50	90%
22	1.5/1.0	3.0	MeCN	4	-	-30	78%
23	1.5/1.0	3.0	MeCN	8	-	-30	85%
24	1.5/1.0	3.0	MeCN	24	-	-30	78%
25	1.5/1.0	2.0	MeCN	12	-	-30	93%
26	1.5/1.0	1.5	MeCN	12	-	-30	95%
27	1.5/1.0	4.5	MeCN	12	-	-30	54%

[a]General conditions: **1c**, 0.02 mmol of **2a** (1.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (5 mol%), Umemoto's reagent (triflate salt), 3 Å (for MeCN) or 4 Å (for other solvents) MS, under the irradiation of blue LEDs (28 W). [b]Yield was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]0.005 M.

Table S3 Screening of the *N*-glycosylation conditions with 2,6-dichloropurine[a]

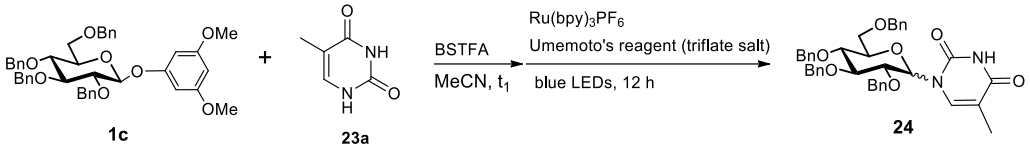


Entry	Vis (h)	Additive (equiv.)	Temp. (°C)	Yield[b]
1	12	-	rt	50%
2	12	NaOAc (1.5)	rt	69%

3	12	Li_2CO_3 (1.5)	rt	74%
4	12	KOH (1.5)	rt	85%
5	6	KOH (1.5)	rt	30%
6	24	KOH (1.5)	rt	78%
7	36	KOH (1.5)	rt	81%
8	12	KOH (1.5)	-30	58%
9	12	KOH (1.5)	40	83%

[a]General conditions: 0.03 mmol of donor **1c** (1.5 equiv.), 2,6-dichloropurine (1.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (5 mol%), Umemoto's reagent (triflate salt) (3.0 equiv.), 3 Å MS (200 mg), MeCN (2.0 mL) under the irradiation of blue LEDs (28 W) for 12 h. [b]Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S4 Screening of the *N*-glycosylation conditions with thymine[a]



Entry	t_1 (h)	Vis (h)	Additive	Yield[b]
1[c]	-	12	KOH	not found
2	0.5	12	-	58%
3	5	12	-	56%
4	12	12	-	52%
5	0.5	12	NaOH	60%
6[d]	0.5	12	-	90%

[a]General conditions: 0.02 mmol of thymine (1.0 equiv.), BSTFA (3.0 equiv.) in MeCN (2.0 mL), stirred at room temperature, then addition of **1c** (1.5 equiv), $Ru(bpy)_3(PF_6)_2$ (5 mol%), Umemoto's reagent (triflate salt) (3.0 equiv.), under the irradiation of blue LEDs (28 W). [b]Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]Without the activation by BSTFA. [d]0.02 mmol of **1c** (1.0 equiv.), thymine (3.0 equiv.), BSTFA (9.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (5 mol%), Umemoto's reagent (triflate salt) (2.0 equiv.).

3 Glycosylation procedures

General procedure A for *O*-glycosylations:

A mixture of glycosyl donor (0.03 mmol, 1.5 equiv.), acceptor (0.02 mmol, 1.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.001 mmol, 5 mol%) and Umemoto's reagent (0.03 mmol, 1.5 equiv.) was dissolved in dry MeCN (2.0 mL) containing freshly activated 3 Å molecular sieves (200 mg). The mixture was stirred under argon for 0.5 h. Subsequently, the reaction mixture was cooled to -30 °C and irradiated by blue LEDs (28W) for 12 h. After which, it was filtered through Celite. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel to give the product. The α/β ratio was determined by ^{1}H NMR.

General procedure B for *N*-glycosylation of purine:

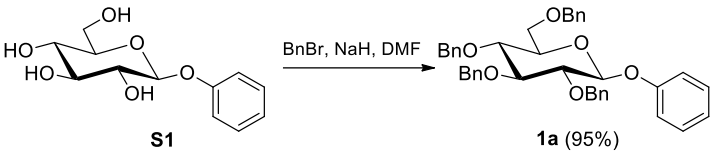
A mixture of glycosyl donor (0.03 mmol, 1.5 equiv.), purine (0.02 mmol, 1.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.001 mmol, 5 mol%), Umemoto's reagent (0.06 mmol, 3.0 equiv.) and KOH (0.03 mmol, 1.5 equiv.) was dissolved in dry MeCN (2.0 mL) containing freshly activated 3 Å molecular sieves (200 mg). The mixture was stirred under argon for 0.5 h. Subsequently, the reaction mixture was irradiated by blue LEDs (28 W) for 12 h. After which, it was filtered through Celite. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel to give the product. The α/β ratio was determined by ^{1}H NMR.

General procedure C for *N*-glycosylation of pyrimidine:

To a suspension of pyrimidine (0.06 mmol, 3.0 equiv.) in dry MeCN (2.0 mL), bis(trimethylsilyl)trifluoroacetamide (BSTFA, 0.18 mmol, 9.0 equiv.) was added at room temperature under argon. After stirring for 0.5 h, glycosyl donor (0.02 mmol, 1.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.001 mmol, 5 mol%), Umemoto's reagent (0.04 mmol, 2.0 equiv.) were added. The mixture was irradiated by blue LEDs (28 W) for 12 h. After which, it was filtered through Celite. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel to give the product. The α/β ratio was determined by ^{1}H NMR.

4 Preparation of glycosyl donors

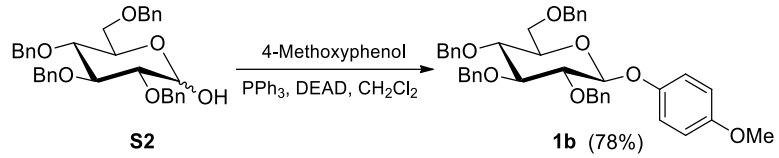
Phenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (1a)



S1 **1a** (95%)

To a solution of phenyl β-D-glucopyranoside (**S1**) (1.00 g, 3.91 mmol) in DMF (20 mL), sodium hydride (60% in mineral oil, 0.938 g, 23.5 mmol) was added portionwise at 0 °C under argon. The mixture was stirred for 0.5 h. Benzyl bromide (2.79 mL, 31.25 mmol) was added dropwise. After stirring for 18 h at room temperature, it was quenched by the addition of MeOH (5 mL) and concentrated in vacuo. The residue was diluted with CH_2Cl_2 and washed with water (3 x 100 mL) and saturated aqueous NaCl solution. The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 15:1) to yield product **1a** (2.29 g, 95%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 20H), 7.21 – 7.16 (m, 2H), 7.11 – 7.02 (m, 3H), 5.05 (d, *J* = 10.9 Hz, 1H), 5.02 – 4.99 (m, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.88 – 4.79 (m, 3H), 4.62 – 4.55 (m, 2H), 4.53 (d, *J* = 12.1 Hz, 1H), 3.80 (dd, *J* = 10.8, 1.6 Hz, 1H), 3.77 – 3.64 (m, 4H), 3.64 – 3.58 (m, 1H). The ^{1}H NMR data coincide with the previous report.[1]

4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (1b)

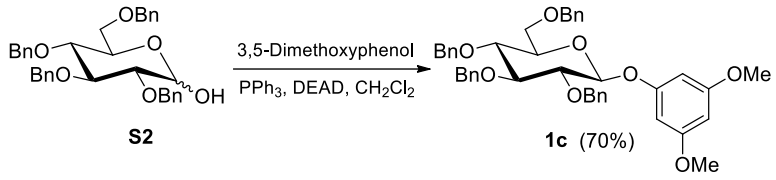


S2 **1b** (78%)

To a solution of 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranose (**S2**) (1.00 g, 1.85 mmol), 4-methoxyphenol (0.344 g, 2.78 mmol) and PPh_3 (0.27 g, 1.85 mmol) in dry CH_2Cl_2 (10 mL), diethyl azodicarboxylate (DEAD, 0.291 mL, 1.85 mmol) was added at 0 °C under argon. The mixture was allowed rising to room temperature slowly. After stirring for 12 h, the reaction mixture was concentrated in vacuo. The residue was diluted with CH_2Cl_2 and washed with water (3 x 100 mL) and saturated aqueous NaCl solution. The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 15:1) to yield product **1b** (0.933 g, 78%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.13 (m, 18H), 7.10 (d, *J* = 7.3 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.72 (d, *J* = 8.9 Hz, 2H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.87 (d, *J* = 10.9 Hz, 1H), 4.84 – 4.69 (m, 4H),

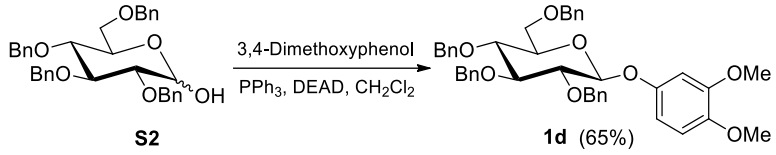
4.55 – 4.41 (m, 3H), 3.74 – 3.53 (m, 8H), 3.53 – 3.45 (m, 1H). The ^{1}H NMR data coincide with the previous report.[2]

3,5-Dimethoxyphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (1c)



It was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 15:1) to yield product **1c** (0.876 g, 70%) as a white solid, following the same procedure for the synthesis of **1b**. $[\alpha]^{25}_{D}$ = -12.0 (c = 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.16 (m, 18H), 7.13 – 7.06 (m, 2H), 6.20 (d, *J* = 2.1 Hz, 2H), 6.10 (t, *J* = 2.1 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.90 (dd, *J* = 5.4, 2.1 Hz, 1H), 4.87 (d, *J* = 10.9 Hz, 1H), 4.80 – 4.70 (m, 3H), 4.53 – 4.46 (m, 2H), 4.43 (d, *J* = 12.0 Hz, 1H), 3.75 – 3.49 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.51, 159.34, 138.61, 138.38, 138.17, 138.13, 128.55, 128.54, 128.52, 128.45, 128.35, 128.07, 128.02, 127.96, 127.89, 127.80, 127.72, 101.80, 95.79, 95.18, 84.80, 82.09, 77.81, 77.37, 75.91, 75.28, 75.18, 75.16, 73.68, 69.01, 55.45. ESI-HRMS calculated for $C_{42}H_{48}NO_8$ $[M+NH_4]^+$ 694.3380, found 694.3383.

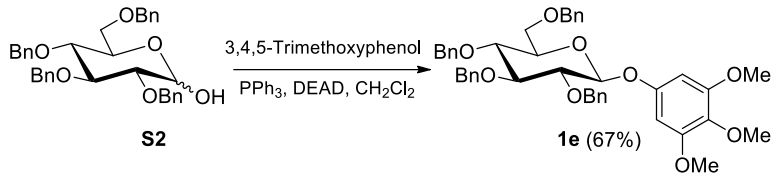
3,4-Dimethoxyphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (1d)



It was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 15:1) to yield product **1d** (0.814 g, 65%) as a white solid, following the same procedure for the synthesis of **1b**. $[\alpha]^{25}_{D}$ = -60.0 (c = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 25H), 7.24 – 7.19 (m, 2H), 6.76 (d, *J* = 8.7 Hz, 1H), 6.71 (d, *J* = 2.7 Hz, 1H), 6.67 (dd, *J* = 8.7, 2.7 Hz, 1H), 5.07 (d, *J* = 11.0 Hz, 1H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.93 – 4.89 (m, 1H), 4.89 – 4.82 (m, 3H), 4.62 – 4.52 (m, 3H), 3.86 (s, 3H), 3.83 – 3.58 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.96, 149.61, 144.94, 138.53, 138.37, 138.12, 138.04, 128.45, 128.43, 128.37, 128.18, 127.98, 127.91, 127.85, 127.79, 127.70, 127.64, 111.72, 108.21, 102.93, 102.89, 84.78, 82.19, 77.88, 75.80, 75.16, 75.07, 73.55,

69.07, 56.34, 55.82. ESI-HRMS calculated for $C_{42}H_{48}NO_8$ $[M+NH_4]^+$ 694.3380, found 694.3378.

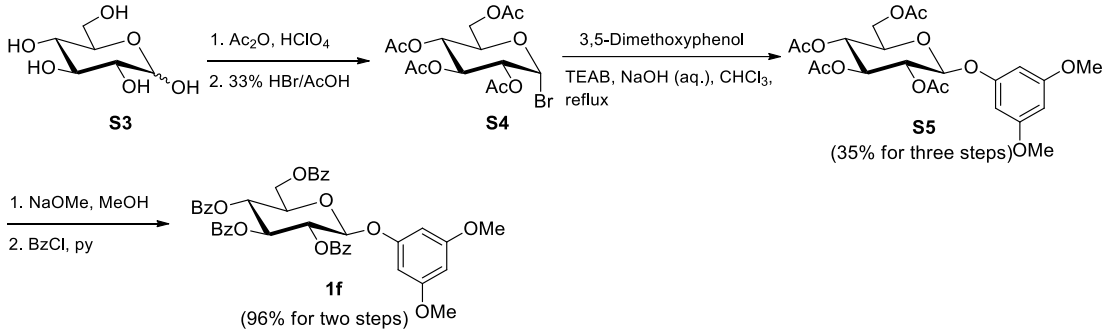
3,4,5-Trimethoxyphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (1e)



S2 **1e** (67%)

It was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 15:1) to yield product **1e** (0.876 g, 67%) as a white solid, following the same procedure for the synthesis of **1b**. $[\alpha]^{25}_D$ = -12.0 (c = 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.18 (m, 18H), 7.11 (d, *J* = 5.3 Hz, 2H), 6.27 (s, 2H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.90 – 4.81 (m, 2H), 4.81 – 4.71 (m, 3H), 4.51 – 4.39 (m, 3H), 3.81 – 3.45 (m, 17H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.15, 153.63, 138.49, 138.37, 137.99, 137.97, 133.82, 128.50, 128.49, 128.47, 128.44, 128.18, 128.00, 127.96, 127.92, 127.85, 127.78, 102.66, 95.21, 84.81, 82.18, 77.92, 77.36, 75.85, 75.23, 75.12, 73.63, 69.20, 61.02, 55.99. ESI-HRMS calculated for $C_{43}H_{50}NO_9$ $[M+NH_4]^+$ 724.3486, found 724.3491.

3,5-Dimethoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (1f)



S3 **S4** **S5** (35% for three steps) **1f** (96% for two steps)

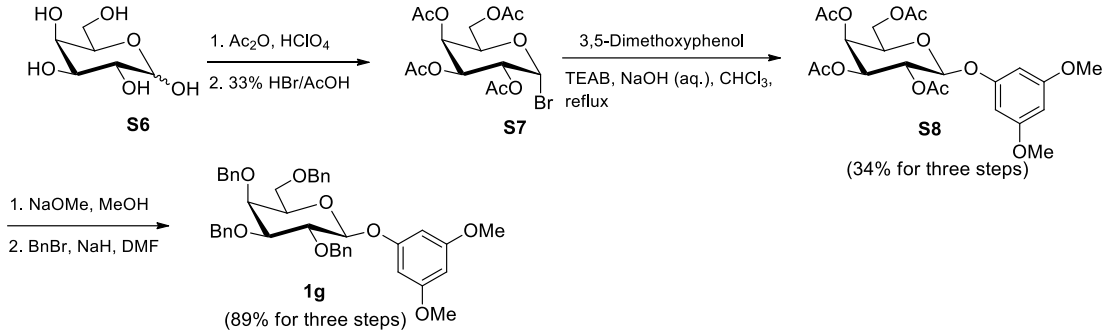
To a mixed solution of $HClO_4$ (70% in water, 24 μL) and Ac_2O (8 mL), D-glucose (2.00 g, 11.1 mmol) was added portionwise over 10 min at 0 °C. After the mixture was stirred for 1 h, 33% HBr/AcOH (9.5 mL) was added. After stirring for 2 h at room temperature, the mixture was diluted with CH_2Cl_2 and washed with water (3 x 100 mL), saturated aqueous $NaHCO_3$ solution (3 x 100 mL) and saturated aqueous NaCl solution. The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed in vacuo and the crude product **S4** was afforded without further purification.

The above crude product and tetraethylammonium bromide (TEAB, 0.179 g, 0.556 mmol) were dissolved in $CHCl_3$ (30 mL). A solution of 3,5-dimethoxyphenol (2.57 g, 16.7 mmol, dissolved in 21.2 mL of 1.25 M aqueous NaOH) was added. The mixture was refluxed overnight. The organic layer was washed with water (2 x 100 mL), saturated aqueous NH_4Cl solution (100 mL) and saturated aqueous NaCl solution. The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 3:1) to yield product **S5** (1.88 g, 35%, over three steps) as a white solid. $[\alpha]^{25}_D$ = -25.2 (c = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 – 6.15 (m, 3H), 5.34 – 5.22 (m, 2H), 5.14 (t, *J* = 9.2 Hz, 1H), 5.07 (d, *J* = 7.2 Hz, 1H), 4.27 (dd, *J* = 12.1, 5.5 Hz, 1H), 4.17 (d, *J* = 12.1 Hz, 1H), 3.90 – 3.82 (m, 1H), 3.76 (s, 6H), 2.08 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.73, 170.31, 169.53, 169.44, 161.57, 158.66, 98.89, 95.82, 95.13, 77.36, 72.87, 72.20, 71.22, 68.47, 62.13, 55.54, 20.76, 20.72. ESI-HRMS calculated for $C_{22}H_{29}O_{12}$ $[M+H]^+$ 485.1659, found 485.1663.

To a suspension of **S5** (1.50 g, 3.10 mmol) in MeOH (10 mL), 30% NaOMe/MeOH was added dropwise for maintaining the pH at 9-10. When TLC indicated the compound **S5** was disappeared completely, the mixture was neutralized by the addition of Amberlyst (R) 15 and filtered. The filtrate was evaporated in vacuo and the crude product was afforded without further purification. The above crude product was dissolved in pyridine (20 mL). BzCl (2.15 mL, 18.6 mmol) was added dropwise at 0 °C. After stirring overnight, the solvent was removed in vacuo. The residue was diluted with CH_2Cl_2 and washed with water (3 x 100 mL), saturated aqueous $NaHCO_3$ solution (2 x 100 mL) and saturated aqueous NaCl solution. The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 4:1) to yield product **1f** (2.18 g, 96%, over two steps) as a white solid. $[\alpha]^{25}_D$ = -116 (c = 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.99 – 7.90 (m, 4H), 7.89 – 7.83 (m, 2H), 7.57 – 7.25 (m, 12H), 6.21 (d, *J* = 2.1 Hz, 2H), 6.14 (t, *J* = 2.1 Hz, 1H), 6.00 (t, *J* = 9.5 Hz, 1H), 5.80 (dd, *J* = 9.5, 7.8 Hz, 1H), 5.73 (t, *J* = 9.6 Hz, 1H), 5.44 (d, *J* = 7.7 Hz, 1H), 4.69 (dd, *J* = 12.1, 2.7 Hz, 1H), 4.51 (dd, *J* = 12.1, 6.4 Hz, 1H), 4.36 (ddd, *J* = 9.2, 6.3, 2.6 Hz, 1H), 3.62 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.25, 165.85, 165.34, 165.22, 161.52, 158.82, 133.65, 133.45, 133.43, 133.20, 129.98, 129.95, 129.93, 129.90, 129.61, 129.20,

128.84, 128.77, 128.56, 128.50, 128.44, 99.59, 95.98, 95.50, 77.37, 72.90, 72.80, 71.80, 69.63, 63.44, 55.41. ESI-HRMS calculated for $C_{42}H_{37}O_{12}$ $[M+H]^+$ 733.2285, found 733.2280.

3,5-Dimethoxyphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside (1g)



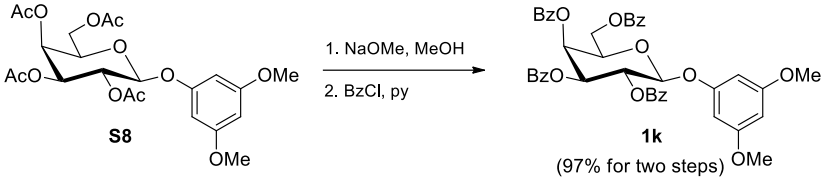
It was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 3:1) to yield product **S8** (1.83 g, 34%, over three steps) as a colorless syrup, following the same procedure for the synthesis of **S5**. $[\alpha]^{25}_{D}$ = -3.68 (c = 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (s, 3H), 5.49 – 5.40 (m, 2H), 5.09 (dd, *J* = 10.4, 3.4 Hz, 1H), 5.02 (d, *J* = 8.0 Hz, 1H), 4.23 – 4.12 (m, 2H), 4.04 (t, *J* = 6.5 Hz, 1H), 3.74 (s, 6H), 2.16 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.48, 170.31, 170.16, 169.51, 161.54, 158.72, 99.42, 95.78, 95.08, 77.36, 71.23, 70.94, 68.68, 67.04, 61.60, 55.49, 20.83, 20.72, 20.65. ESI-HRMS calculated for $C_{22}H_{29}O_{12}$ $[M+H]^+$ 485.1659, found 485.1657.

To a suspension of **S8** (1.50 g, 3.10 mmol) in MeOH (10 mL), 30% NaOMe/MeOH was added dropwise for maintaining the pH at 9-10. When TLC indicated the compound **S8** was disappeared completely, the mixture was neutralized by the addition of Amberlyst (R) 15 and filtered. The filtrate was evaporated in vacuo and the crude product was afforded without further purification.

To a solution of the above crude product in DMF (20 mL), sodium hydride (60% in mineral oil, 0.745 g, 18.6 mmol) was added portionwise at 0 °C under argon. The mixture was stirred for 0.5 h. Benzyl bromide (1.62 mL, 14.8 mmol) was added dropwise. After stirring for 18 h at room temperature, it was quenched by the addition of MeOH (5 mL) and concentrated in vacuo. The residue was diluted with CH_2Cl_2 and washed with water (3 x 100 mL) and saturated aqueous NaCl solution. The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc

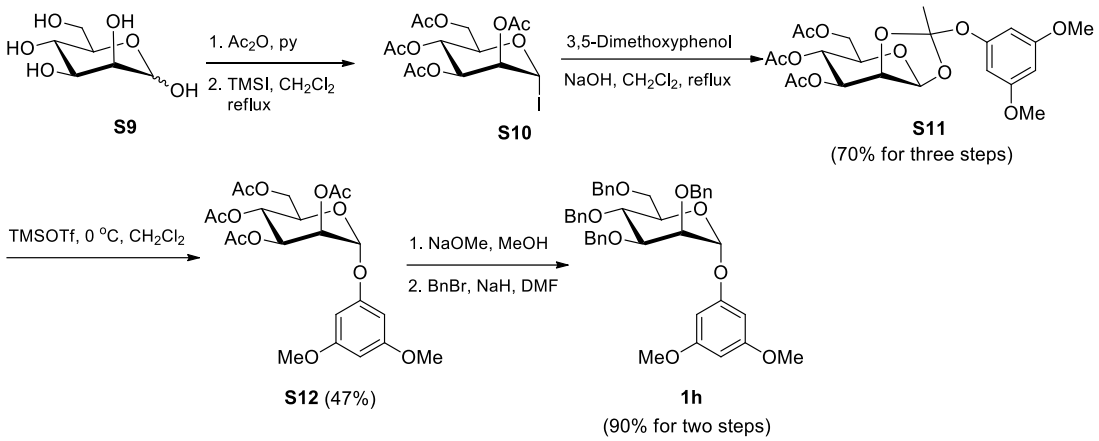
= 15:1) to yield product **1g** (1.87 g, 89%) as a white solid. $[\alpha]^{25}_D$ = -34.0 (c = 0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 20H), 6.26 (d, *J* = 2.2 Hz, 2H), 6.15 (t, *J* = 2.2 Hz, 1H), 5.01 – 4.92 (m, 3H), 4.84 (d, *J* = 10.9 Hz, 1H), 4.77 (d, *J* = 11.8 Hz, 1H), 4.73 (d, *J* = 11.8 Hz, 1H), 4.63 (d, *J* = 11.7 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.38 (d, *J* = 11.6 Hz, 1H), 4.09 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.93 (d, *J* = 2.8 Hz, 1H), 3.68 (s, 6H), 3.67 – 3.57 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.44, 159.44, 138.70, 138.53, 137.99, 128.52, 128.40, 128.33, 128.04, 127.89, 127.76, 127.72, 127.69, 102.10, 95.95, 95.07, 82.27, 79.30, 74.69, 74.00, 73.76, 73.60, 73.22, 69.04, 55.44. ESI-HRMS calculated for $C_{42}H_{45}O_8$ $[M+H]^+$ 677.3114, found 677.3118.

3,5-Dimethoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (1k)



It was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 3:1) to yield product **1k** (2.20 g, 97%, over two steps) as a colorless syrup, following the same procedure for the synthesis of **1f**. $[\alpha]^{25}_D$ = 14.0 (c = 0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (dt, *J* = 8.4, 1.7 Hz, 2H), 8.07 (dt, *J* = 8.4, 1.8 Hz, 2H), 7.99 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.84 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.69 – 7.62 (m, 1H), 7.59 (td, *J* = 7.2, 1.4 Hz, 1H), 7.56 – 7.42 (m, 6H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 3H), 6.26 (d, *J* = 2.2 Hz, 2H), 6.18 (t, *J* = 2.2 Hz, 1H), 6.14 – 6.04 (m, 2H), 5.71 (dd, *J* = 10.4, 3.5 Hz, 1H), 5.42 (d, *J* = 8.0 Hz, 1H), 4.67 (dd, *J* = 11.2, 7.2 Hz, 1H), 4.62 – 4.49 (m, 2H), 3.67 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.11, 165.56, 165.52, 165.28, 161.43, 158.83, 133.68, 133.34, 133.23, 130.08, 129.87, 129.82, 129.77, 129.39, 129.21, 128.91, 128.71, 128.66, 128.46, 128.42, 128.32, 100.05, 95.99, 95.48, 71.94, 71.68, 69.53, 68.08, 62.56, 55.32. ESI-HRMS calculated for $C_{42}H_{37}O_{12}$ $[M+H]^+$ 733.2285, found 733.2288.

3,5-Dimethoxyphenyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (1h)



S9 **S10** **S11** (70% for three steps)

S12 (47%) **1h** (90% for two steps)

To a solution of D-mannose (2.0 g, 11.1 mmol) in pyridine (30 mL), Ac_2O (30 mL) was added. After stirring overnight, the solvent was evaporated in vacuo. The residue was diluted with CH_2Cl_2 and washed with water (3 x 100 mL), saturated aqueous $NaHCO_3$ solution (2 x 100 mL) and saturated aqueous NaCl solution. The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed in vacuo and the crude product was dissolved in dry CH_2Cl_2 (30 mL). Trimethylsilyl iodide (TMSI, 2.37 mL, 16.7 mmol) was added and the reaction mixture was refluxed under argon. When TLC indicated the reaction was complete, the solvent was removed in vacuo. The glycol iodide **S10** was afforded without further purification.

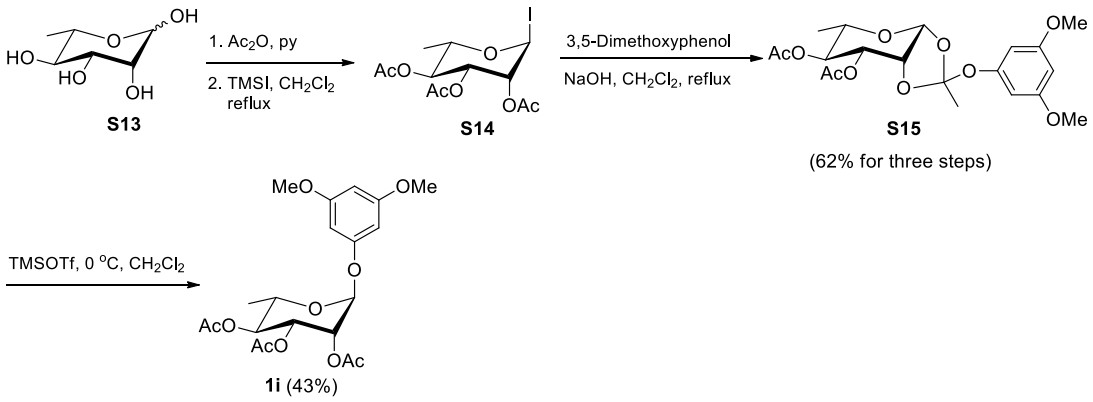
To a solution of **S10** in CH_2Cl_2 (35 mL), NaOH (0.666 g, 16.7 mmol) and 3,5-dimethoxyphenol (2.57 g, 16.7 mmol) were added under argon. The mixture was stirred till TLC indicated the glycol iodide was disappeared completely. The reaction mixture was washed with water (3 x 100 mL) and saturated aqueous NaCl solution. The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 3:1) to yield product **S11** (3.77 g, 70%, over three steps) as a colorless syrup. $[\alpha]^{25}_D$ = -9.12 (c = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (d, *J* = 2.3 Hz, 2H), 6.25 (t, *J* = 2.3 Hz, 1H), 5.43 (d, *J* = 2.6 Hz, 1H), 5.30 (dd, *J* = 10.5, 9.0 Hz, 1H), 5.10 (dd, *J* = 9.9, 4.0 Hz, 1H), 4.34 (dd, *J* = 4.0, 2.7 Hz, 1H), 4.23 (dd, *J* = 12.1, 5.2 Hz, 1H), 4.15 (dd, *J* = 12.2, 2.8 Hz, 1H), 3.75 (s, 6H), 3.67 (ddd, *J* = 9.5, 5.1, 2.8 Hz, 1H), 2.12 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 1.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.74, 170.20, 169.59, 161.11, 154.50, 124.45, 101.22, 97.41, 97.07, 76.00, 71.73, 70.21, 65.71, 62.61, 55.49, 24.27, 20.84, 20.80, 20.75. ESI-HRMS calculated for $C_{22}H_{29}O_{12}$ $[M+H]^+$ 485.1659, found 485.1656.

Compound **S11** (2.00 g, 4.13 mmol) was dissolved in dry CH_2Cl_2 (20 mL) containing freshly

activated 4 Å molecular sieves (2.00 g), and stirred under argon for 0.5 h. TMSOTf (74.7 μL, 0.04 mmol) was added at 0 °C. When TLC indicated the compound **S11** was disappeared completely, the reaction was quenched by Et_3N (1 mL) and filtered through Celite. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 4:1) to yield product **S12** (0.940 g, 47%) as a colorless syrup. $[\alpha]^{25}_D$ = 50.0 (c = 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.28 (d, *J* = 1.7 Hz, 2H), 6.18 (d, *J* = 1.9 Hz, 1H), 5.55 (dd, *J* = 10.0, 3.1 Hz, 1H), 5.50 (s, 1H), 5.46 – 5.41 (m, 1H), 5.36 (t, *J* = 10.2 Hz, 1H), 4.30 (dd, *J* = 12.5, 5.6 Hz, 1H), 4.14 – 4.03 (m, 2H), 3.76 (s, 6H), 2.20 (s, 3H), 2.06 (s, 6H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.56, 169.94, 169.71, 161.49, 157.36, 95.77, 95.40, 95.17, 69.37, 69.14, 68.90, 65.95, 62.12, 55.42, 29.69, 20.86, 20.68, 20.59. ESI-HRMS calculated for $C_{22}H_{29}O_{12}$ $[M+H]^+$ 485.1659, found 485.1659.

It was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 15:1) to yield product **1h** (1.99 g, 90%, over two steps) as a white solid, following the same procedure as the synthesis of **1g**. $[\alpha]^{25}_D$ = 53.5 (c = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.26 (m, 18H), 7.21 (dd, *J* = 7.2, 1.7 Hz, 2H), 6.27 (d, *J* = 2.1 Hz, 2H), 6.17 (t, *J* = 2.1 Hz, 1H), 5.61 (s, 1H), 4.94 (d, *J* = 10.7 Hz, 1H), 4.82 (s, 2H), 4.77 – 4.64 (m, 3H), 4.58 (d, *J* = 10.8 Hz, 1H), 4.49 (d, *J* = 11.9 Hz, 1H), 4.18 (M, 1H), 4.13 (dd, *J* = 9.3, 2.7 Hz, 1H), 4.01 – 3.97 (m, 1H), 3.90 (dd, *J* = 9.2, 4.3 Hz, 1H), 3.84 (dd, *J* = 10.9, 4.4 Hz, 1H), 3.77 – 3.70 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.55, 158.22, 138.60, 138.58, 138.44, 138.28, 128.51, 128.44, 128.36, 128.06, 127.98, 127.95, 127.80, 127.78, 127.74, 127.72, 127.57, 96.48, 95.23, 95.11, 80.14, 75.27, 74.83, 74.61, 73.45, 72.89, 72.64, 72.51, 69.16, 55.49. ESI-HRMS calculated for $C_{42}H_{48}NO_8$ $[M+NH_4]^+$ 694.3380, found 694.3377.

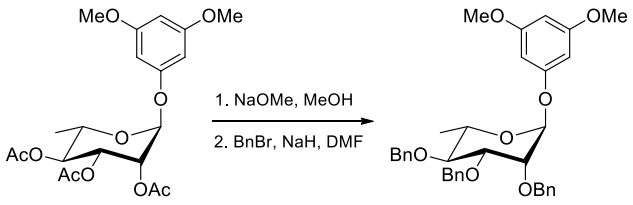
3,5-Dimethoxyphenyl 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranoside (1i)



It was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield product **S15** (3.22 g, 62%, over three steps) as a colorless syrup, following the same procedure as the synthesis of **S11**. $[\alpha]^{25}_{D}$ = 5.00 (c = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (d, *J* = 2.1 Hz, 2H), 6.25 (t, *J* = 2.1 Hz, 1H), 5.36 (d, *J* = 2.2 Hz, 1H), 5.10 – 5.03 (m, 2H), 4.32 (s, 1H), 3.74 (s, 6H), 3.56 – 3.45 (m, 1H), 2.11 (s, 3H), 2.06 (s, 3H), 1.84 (s, 3H), 1.23 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.25, 169.89, 161.03, 154.57, 124.37, 101.13, 97.14, 96.97, 76.26, 70.39, 70.32, 69.35, 55.43, 24.38, 20.86, 20.75, 17.60. ESI-HRMS calculated for $C_{20}H_{27}O_{10}$ $[M+H]^+$ 427.1604, found 427.1606.

It was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield product **1i** (0.866 g, 43%) as a white solid, following the same procedure as the synthesis of **S12**. $[\alpha]^{25}_{D}$ = 50.0 (c = 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 (d, *J* = 2.1 Hz, 2H), 6.17 (t, *J* = 2.1 Hz, 1H), 5.50 (dd, *J* = 10.1, 3.4 Hz, 1H), 5.44 – 5.37 (m, 2H), 5.15 (t, *J* = 10.0 Hz, 1H), 4.06 – 3.93 (m, 1H), 3.76 (s, 6H), 2.19 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.22 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.08, 170.08, 170.02, 161.54, 157.72, 95.70, 95.23, 95.06, 71.02, 69.71, 68.99, 67.22, 55.46, 20.92, 20.82, 20.78, 17.54. ESI-HRMS calculated for $C_{20}H_{27}O_{10}$ $[M+H]^+$ 427.1604, found 427.1601.

3,5-Dimethoxyphenyl 2,3,4-tri-*O*-benzyl-α-L-rhamnopyranoside (1j)

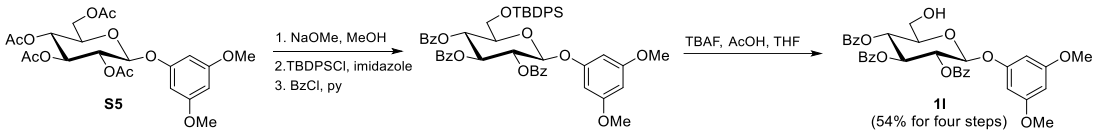


1i **1j** (92% for two steps)

It was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 15:1) to yield product **1j** (1.85 g, 92%, over two steps) as a colorless syrup, following the same procedure as the synthesis of **1g**. $[\alpha]^{25}_{D}$ = 50.0 (c = 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.24 (m, 15H), 6.19 (d, *J* = 2.2 Hz, 2H), 6.13 (t, *J* = 2.1 Hz, 1H), 5.46 (d, *J* = 1.7 Hz, 1H), 4.96 (d, *J* = 10.8 Hz, 1H), 4.82 (d, *J* = 12.4 Hz, 1H), 4.77 (d, *J* = 12.4 Hz, 1H), 4.73 – 4.64 (m, 3H), 4.05 (dd, *J* = 9.2, 3.1 Hz, 1H), 3.97 – 3.93 (m, 1H), 3.84 – 3.76 (m, 1H), 3.76 – 3.65 (m, 7H), 1.31 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.52, 158.22, 138.62, 138.23, 128.55, 128.52, 128.51, 128.13,

128.08, 127.91, 127.80, 127.76, 127.74, 96.33, 95.07, 94.76, 80.55, 80.07, 74.73, 73.09, 72.50, 68.95, 55.48, 18.23. ESI-HRMS calculated for $C_{35}H_{39}O_7$ $[M+H]^+$ 571.2696, found 571.2690.

3,5-Dimethoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (1l)



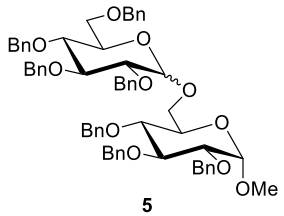
To a suspension of **S5** (1.50 g, 3.10 mmol) in MeOH (10 mL), 30% NaOMe/MeOH was added dropwise to adjust the pH to 9-10. After the disappearance of **S5**, the mixture was neutralized by the addition of Amberlyst (R) 15 and filtered. The filtrate was evaporated in vacuo and the crude product was afforded without further purification. The above crude product was dissolved in (10 mL) DMF. Imidazole (0.42g, 6.20 mmol) and TBDPSCl (0.97 mL, 3.72 mmol) were added. After stirring for 6 h, the reaction was quenched by MeOH (2.0 mL). The solvent was removed in vacuo. The residue was diluted with 20 mL of CH_2Cl_2 and washed with water (20 mL), 1 M HCl (3 x 20 mL), saturated aqueous $NaHCO_3$ solution (2 x 20 mL) and saturated aqueous NaCl solution. The organic layer was dried over Na_2SO_4 and filtered. The crude product was dissolved in pyridine (20 mL) and BzCl (1.61 mL, 14.0 mmol) was added dropwise at 0 ºC. After stirring overnight, the solvent was removed in vacuo. The residue was diluted with CH_2Cl_2 and washed with water (3 x 100 mL), saturated aqueous $NaHCO_3$ solution (2 x 100 mL) and saturated aqueous NaCl solution. The organic layer was dried over Na_2SO_4 and filtered. The filtrate was evaporated in vacuo and the crude product was afforded without further purification.

To a solution of the above crude product in CH_2Cl_2 (20 mL), AcOH (0.71 mL, 12.4 mmol) and TBAF (1 M in THF, 6.2 mL) was added. The mixture was stirred for 7 h at room temperature. Then, the reaction mixture was diluted with CH_2Cl_2 and washed with water (3 x 100 mL), saturated aqueous $NaHCO_3$ solution (2 x 100 mL) and saturated aqueous NaCl solution. The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel (petroleum ether: EtOAc = 5: 1) to yield product **1l** (1.05 g, 54%) as a white solid. $[\alpha]^{25}_D = 21.1$ (c = 0.1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 4H), 7.88 – 7.84 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 6.18 (d, *J*

= 2.1 Hz, 2H), 6.17 – 6.14 (m, 1H), 6.00 (t, *J* = 9.6 Hz, 1H), 5.75 (dd, *J* = 9.7, 7.9 Hz, 1H), 5.58 (t, *J* = 9.7 Hz, 1H), 5.41 (d, *J* = 7.9 Hz, 1H), 3.95 (ddd, *J* = 9.8, 4.8, 2.3 Hz, 1H), 3.92 – 3.87 (m, 1H), 3.82 – 3.76 (m, 1H), 3.70 (s, 6H), 2.56 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.95, 165.81, 165.11, 161.44, 158.70, 133.76, 133.35, 129.97, 129.84, 129.80, 129.11, 128.78, 128.56, 128.53, 128.42, 128.37, 99.42, 95.74, 95.48, 75.06, 72.70, 71.69, 69.31, 61.39, 55.41. ESI-HRMS calculated for $C_{35}H_{33}O_{11}$ $[M+H]^+$ 629.2023, found 629.2025.

5 Characterization data for coupled products

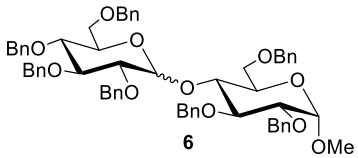
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (5)



5

Compound **5** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.17 (m, 37.53H), 5.01 – 4.87 (m, 3.44H), 4.83 – 4.40 (m, 13.86H), 4.35 (d, *J* = 7.8 Hz, 1.01H), 4.21 – 4.13 (m, 1.07H), 4.02 – 3.96 (m, 1.07H), 3.85 – 3.40 (m, 11.82H), 3.35 (s, 0.22H), 3.32 (s, 3.00H). The ^{1}H NMR data coincide with the previous report.[3]

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (6)

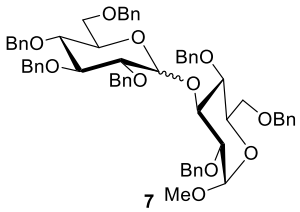


6

Compound **6** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 1.91H), 7.23 – 7.09 (m, 46.82H), 7.05 – 7.00 (m, 0.91H), 5.62 (d, *J* = 3.6 Hz, 0.33H), 5.02 (d, *J* = 11.3 Hz, 1.00H), 4.96 (d, *J* = 11.7 Hz, 0.35H),

4.83 – 4.60 (m, 9.06H), 4.56 – 4.27 (m, 11.01H), 4.20 (d, *J* = 12.1 Hz, 0.35H), 4.05 – 3.93 (m, 0.77H), 3.92 – 3.73 (m, 4.08H), 3.68 – 3.36 (m, 10.20H), 3.34 – 3.26 (m, 5.26H), 3.24 – 3.18 (m, 1.18H). The ^{1}H NMR data coincide with the previous report.[4]

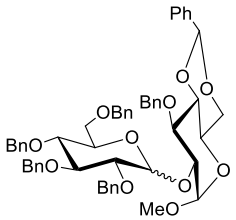
Methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (7)



7

Compound **7** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5:1). **α-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.14 (m, 31H), 7.12 – 7.08 (m, 2H), 7.00 (d, *J* = 6.1 Hz, 2H), 5.59 (d, *J* = 3.4 Hz, 1H), 4.94 (d, *J* = 11.6 Hz, 1H), 4.90 (d, *J* = 10.8 Hz, 1H), 4.85 – 4.78 (m, 2H), 4.70 – 4.56 (m, 5H), 4.52 (d, *J* = 11.5 Hz, 1H), 4.48 – 4.22 (m, 7H), 4.05 (t, *J* = 9.4 Hz, 1H), 3.81 – 3.50 (m, 10H), 3.32 (s, 3H). **β-isomer**:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.29 – 7.02 (m, 54H), 5.03 – 4.95 (m, 3H), 4.93 (d, *J* = 10.8 Hz, 1H), 4.85 – 4.77 (m, 2H), 4.75 (d, *J* = 10.7 Hz, 1H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.53 (dd, *J* = 11.5, 3.5 Hz, 2H), 4.45 – 4.37 (m, 4H), 4.36 – 4.28 (m, 2H), 3.71 – 3.31 (m, 12H), 3.24 (s, 3H). The ^{1}H NMR data coincide with the previous report.[4]

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (8)

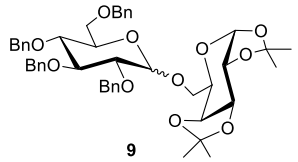


8

Compound **8** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5:1). **α-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 4.1 Hz, 2H), 7.39 – 7.24 (m, 41H), 7.23 – 7.11 (m, 9H), 5.56 (s, 1H), 5.04 (d, *J* = 11.5 Hz, 1H), 4.96 (d, *J* = 3.7 Hz, 1H), 4.92 (d, *J* = 11.0

Hz, 1H), 4.83 – 4.73 (m, 5H), 4.65 (d, *J* = 10.6 Hz, 1H), 4.57 (d, *J* = 12.3 Hz, 1H), 4.53 – 4.47 (m, 2H), 4.32 (dd, *J* = 10.3, 4.9 Hz, 1H), 4.10 (t, *J* = 9.3 Hz, 1H), 3.94 – 3.83 (m, 2H), 3.76 (t, *J* = 10.2 Hz, 1H), 3.68 – 3.51 (m, 6H), 3.46 – 3.38 (m, 4H). **β-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.44 – 7.20 (m, 26H), 7.17 – 7.08 (m, 3H), 7.02 (dd, J = 13.4, 6.2 Hz, 2H), 5.57 (s, 1H), 5.02 (d, *J* = 10.8 Hz, 1H), 4.92 (d, *J* = 3.6 Hz, 1H), 4.90 – 4.78 (m, 5H), 4.75 (d, *J* = 10.3 Hz, 1H), 4.71 (d, *J* = 12.2 Hz, 1H), 4.53 (d, *J* = 12.1 Hz, 1H), 4.45 (d, *J* = 10.9 Hz, 1H), 4.35 – 4.24 (m, 2H), 4.17 – 4.07 (m, 3H), 3.91 – 3.82 (m, 2H), 3.78 – 3.57 (m, 4H), 3.51 – 3.43 (m, 4H), 3.39 (dd, *J* = 10.9, 1.7 Hz, 1H). The ^{1}H NMR data coincide with the previous report.[4]

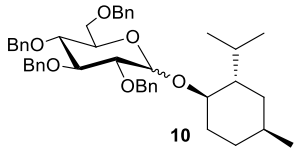
1,2:3,4-Di-*O*-isopropylidene-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-galactopyranose (9)



9

Compound **9** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2.20H), 7.36 – 7.26 (m, 17.51H), 7.16 – 7.11 (m, 2.18H), 5.57 (d, *J* = 5.0 Hz, 1.00H), 5.52 (d, *J* = 4.6 Hz, 0.09H), 5.05 (d, *J* = 11.2 Hz, 1.14H), 5.01 – 4.93 (m, 1.35H), 4.87 – 4.67 (m, 3.98H), 4.65 – 4.42 (m, 6.12H), 4.34 – 4.29 (m, 1.19H), 4.28 – 4.22 (m, 1.14H), 4.20 – 4.13 (m, 1.15H), 4.12 – 4.06 (m, 1.14H), 3.86 – 3.55 (m, 7.20H), 3.51 – 3.38 (m, 2.40H), 1.56 (s, 3.43H), 1.50 (s, 3.33H), 1.45 (s, 3.31H), 1.31 (s, 6.71H). The ^{1}H NMR data coincide with the previous report.[4]

(-)-Menthyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (10)

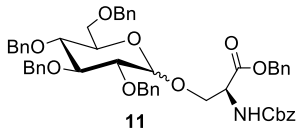


10

Compound **10** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1). **α-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 31H), 7.16 – 7.09 (m, 2H), 5.02 (d, *J* = 3.6 Hz, 1H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.82 (dd, *J* = 10.8, 6.1 Hz, 2H), 4.73 – 4.60 (m, 3H), 4.49 – 4.41 (m, 2H), 4.05 – 3.93 (m, 2H), 3.75 (dd, *J* = 10.5, 3.8 Hz, 1H), 3.68 – 3.58 (m, 2H), 3.54

(dd, *J* = 9.8, 3.6 Hz, 1H), 3.35 (td, *J* = 10.6, 4.3 Hz, 1H), 2.47 – 2.35 (m, 1H), 2.17 – 2.07 (m, 1H), 1.68 – 1.56 (m, 2H), 1.42 – 1.27 (m, 2H), 1.08 – 0.82 (m, 9H), 0.70 (d, *J* = 6.9 Hz, 3H). **β-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 26H), 7.23 – 7.17 (m, 2H), 5.00 – 4.89 (m, 2H), 4.86 – 4.75 (m, 2H), 4.69 (d, *J* = 10.9 Hz, 1H), 4.65 – 4.51 (m, 3H), 4.48 (d, *J* = 7.8 Hz, 1H), 3.73 – 3.68 (m, 2H), 3.68 – 3.57 (m, 2H), 3.51 (td, *J* = 10.6, 4.1 Hz, 1H), 3.46 – 3.38 (m, 2H), 2.41 – 2.30 (m, 1H), 2.20 – 2.10 (m, 1H), 1.67 (d, *J* = 11.8 Hz, 2H), 1.43 – 1.29 (m, 2H), 1.05 – 0.87 (m, 9H), 0.83 (d, *J* = 6.9 Hz, 3H). The ^{1}H NMR data coincide with the previous report.[5]

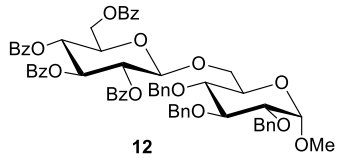
Benzyl *N*-(benzyloxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-L-serinate (11)



11

Compound **11** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.09 (m, 40.00H), 6.06 (d, *J* = 8.9 Hz, 0.33H), 5.75 (d, *J* = 8.1 Hz, 1.00H), 5.25 – 5.04 (m, 5.94H), 4.95 -4.87 (m, 1.54H), 4.85 – 4.74 (m, 4.12H), 4.74 – 4.68 (m, 0.63H), 4.68 – 4.32 (m, 10.15H), 4.21 – 4.15 (m, 0.36H), 3.91 – 3.80 (m, 1.90H), 3.76 – 3.55 (m, 6.29H), 3.54 - 3.49 (dd, *J* = 9.7, 3.6 Hz, 0.41H), 3.43 – 3.33 (m, 2.26H). The ^{1}H NMR data coincide with the previous report.[5]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-glucopyranoside (12)

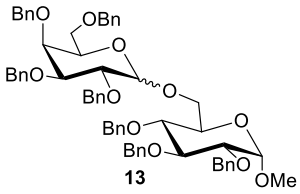


12

Compound **12** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 7.93 – 7.86 (m, 4H), 7.85 – 7.79 (m, 2H), 7.59 – 7.18 (m, 25H), 7.07 – 7.01 (m, 2H), 5.89 (t, *J* = 9.6 Hz, 1H), 5.67 (t, *J* = 9.7 Hz, 1H), 5.59 (dd, *J* = 9.7, 7.8 Hz, 1H), 4.89 (d, *J* = 10.9 Hz, 1H), 4.82 (d, *J* = 7.8 Hz, 1H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.68 (d, *J* = 10.9 Hz, 1H), 4.64 – 4.57 (m, 2H), 4.55 – 4.47 (m, 3H), 4.28 (d, *J* = 11.1 Hz,

1H), 4.15 (d, *J* = 9.1 Hz, 1H), 4.13 – 4.06 (m, 1H), 3.88 (t, *J* = 9.3 Hz, 1H), 3.78 – 3.68 (m, 2H), 3.43 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.37 (t, *J* = 9.3 Hz, 1H), 3.21 (s, 3H). The ^{1}H NMR data coincide with the previous report.[6]

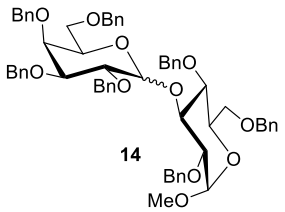
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (13)



13

Compound **13** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5:1). **α-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.14 (m, 35H), 4.98 – 4.89 (m, 3H), 4.80 – 4.68 (m, 6H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.60 – 4.55 (m, 2H), 4.51 (d, *J* = 11.2 Hz, 1H), 4.46 – 4.38 (m, 2H), 4.31 (d, *J* = 7.7 Hz, 1H), 4.14 (dd, *J* = 10.8, 1.7 Hz, 1H), 3.97 (t, *J* = 9.2 Hz, 1H), 3.89 (d, *J* = 2.6 Hz, 1H), 3.88 – 3.79 (m, 2H), 3.65 – 3.43 (m, 7H), 3.30 (s, 3H). **β-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 35H), 4.99 (d, *J* = 3.4 Hz, 1H), 4.98 – 4.90 (m, 2H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.80 (dd, *J* = 11.5, 3.4 Hz, 2H), 4.76 – 4.66 (m, 4H), 4.62 – 4.51 (m, 4H), 4.43 (d, *J* = 11.8 Hz, 1H), 4.36 (d, *J* = 11.8 Hz, 1H), 4.03 (dd, *J* = 9.3, 3.4 Hz, 1H), 4.00 – 3.87 (m, 4H), 3.83 – 3.69 (m, 3H), 3.59 (t, *J* = 9.1 Hz, 1H), 3.55 – 3.45 (m, 2H), 3.41 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.29 (s, 3H). The ^{1}H NMR data coincide with the previous report.[4]

Methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (14)

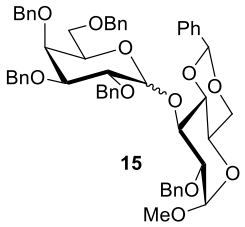


14

Compound **14** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.09 (m, 44.02H), 7.07 – 6.97 (m, 2.53H), 5.59 (d, *J* = 3.5 Hz, 0.33H), 5.06 – 4.87 (m, 5.56H), 4.82 – 4.75 (m, 2.19H), 4.75 – 4.29 (m, 14.99H), 4.28 –

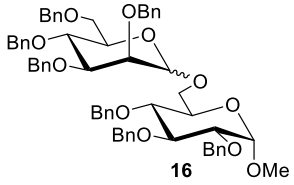
4.21 (m, 0.58H), 4.09 – 3.94 (m, 2.08H), 3.86 (dd, *J* = 9.7, 7.8 Hz, 1.15H), 3.76 (dd, *J* = 10.3, 3.6 Hz, 1.28H), 3.73 – 3.43 (m, 10.91H), 3.28 (s, 3.01H), 3.24 (s, 0.86H). The ^{1}H NMR data coincide with the previous report.[6]

Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (15)



Compound **15** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5:1). **α-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.38 – 7.24 (m, 26H), 7.20 – 7.16 (m, 2H), 5.50 (s, 1H), 5.03 (d, *J* = 11.0 Hz, 1H), 4.93 (d, *J* = 11.6 Hz, 1H), 4.82 – 4.75 (m, 3H), 4.68 (s, 2H), 4.60 (d, *J* = 11.7 Hz, 1H), 4.51 (d, *J* = 12.1 Hz, 1H), 4.44 (d, *J* = 3.8 Hz, 1H), 4.36 – 4.26 (m, 2H), 4.26 – 4.16 (m, 2H), 3.89 – 3.82 (m, 2H), 3.82 – 3.75 (m, 1H), 3.71 – 3.64 (m, 2H), 3.64 – 3.56 (m, 2H), 3.48 (dd, *J* = 9.7, 2.9 Hz, 1H), 3.39 (dd, *J* = 8.7, 5.4 Hz, 1H), 3.36 – 3.31 (m, 4H). **β-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.22 (m, 25H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 2H), 7.02 (d, *J* = 7.3 Hz, 2H), 5.61 (d, *J* = 3.4 Hz, 1H), 5.43 (s, 1H), 4.88 (d, *J* = 11.3 Hz, 1H), 4.85 (d, *J* = 11.9 Hz, 1H), 4.77 – 4.68 (m, 2H), 4.61 – 4.49 (m, 4H), 4.44 (d, *J* = 12.3 Hz, 1H), 4.41 – 4.29 (m, 4H), 4.21 (dd, *J* = 10.1, 4.6 Hz, 1H), 4.02 – 3.90 (m, 3H), 3.83 (td, *J* = 9.9, 4.6 Hz, 1H), 3.74 (t, *J* = 9.3 Hz, 1H), 3.68 (t, *J* = 10.2 Hz, 1H), 3.64 – 3.56 (m, 2H), 3.53 (t, *J* = 8.5 Hz, 1H), 3.33 (s, 3H). The ^{1}H NMR data coincide with the previous report.[4]

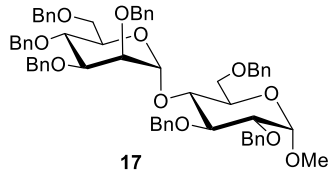
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranosyl)-α-D-glucopyranoside (16)



Compound **16** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc

= 5:1). **α-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.19 (m, 33H), 7.16 (dd, *J* = 6.8, 2.7 Hz, 2H), 5.03 – 4.96 (m, 2H), 4.93 – 4.85 (m, 2H), 4.84 – 4.78 (m, 2H), 4.77 – 4.68 (m, 3H), 4.66 – 4.60 (m, 3H), 4.59 (d, *J* = 3.5 Hz, 1H), 4.55 – 4.48 (m, 2H), 4.46 (d, *J* = 12.1 Hz, 1H), 4.03 (d, *J* = 9.5 Hz, 1H), 3.98 (d, *J* = 9.2 Hz, 1H), 3.90 – 3.82 (m, 2H), 3.82 – 3.78 (m, 1H), 3.76 – 3.66 (m, 3H), 3.66 – 3.58 (m, 2H), 3.47 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.44 – 3.38 (m, 1H), 3.33 (s, 3H). **β-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) 7.45 – 7.18 (m, 39H), δ 5.03 (d, *J* = 10.9 Hz, 1H), 4.96 (d, *J* = 12.5 Hz, 1H), 4.91 (d, *J* = 10.8 Hz, 1H), 4.88 – 4.77 (m, 4H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.65 – 4.47 (m, 7H), 4.18 (dd, *J* = 10.5, 1.8 Hz, 1H), 4.15 (s, 1H), 4.04 (t, *J* = 9.2 Hz, 1H), 3.89 – 3.70 (m, 5H), 3.53 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.51 – 3.41 (m, 3H), 3.41 – 3.38 (m, 1H), 3.35 (s, 3H). The ^{1}H NMR data coincide with the previous report.[6]

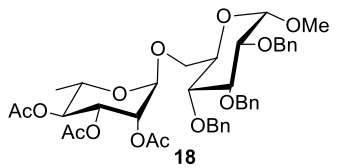
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-*α*-D-mannopyranosyl)-α-D-glucopyranoside (17)



17

Compound **17** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.12 (m, 35H), 5.29 (d, *J* = 1.9 Hz, 1H), 5.08 (d, *J* = 11.7 Hz, 1H), 4.84 (d, *J* = 10.8 Hz, 1H), 4.67 (d, *J* = 12.1 Hz, 1H), 4.62 – 4.50 (m, 7H), 4.48 (d, *J* = 10.9 Hz, 1H), 4.42 (dd, *J* = 12.0, 1.9 Hz, 2H), 4.30 (d, *J* = 12.1 Hz, 1H), 4.20 (d, *J* = 12.1 Hz, 1H), 3.97 (t, *J* = 9.5 Hz, 1H), 3.86 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.84 – 3.68 (m, 7H), 3.66 (dd, *J* = 10.8, 4.7 Hz, 1H), 3.59 – 3.50 (m, 2H), 3.39 (s, 3H). The ^{1}H NMR data coincide with the previous report.[6]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-acetyl-*α*-L-rhamnopyranosyl)-α-D-glucopyranoside (18)

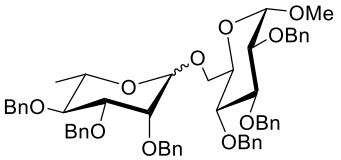


18

Compound **18** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc

= 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.19 (m, 15H), 5.20 (dd, *J* = 10.1, 3.5 Hz, 1H), 5.14 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.97 (t, *J* = 9.9 Hz, 1H), 4.92 (d, *J* = 10.9 Hz, 1H), 4.84 (d, *J* = 11.2 Hz, 1H), 4.78 – 4.70 (m, 2H), 4.64 – 4.57 (m, 2H), 4.53 – 4.45 (m, 2H), 3.92 (t, *J* = 9.2 Hz, 1H), 3.84 – 3.74 (m, 2H), 3.70 (dd, *J* = 10.3, 5.6 Hz, 1H), 3.50 – 3.41 (m, 2H), 3.37 – 3.33 (m, 1H), 3.32 (s, 3H), 2.06 (s, 3H), 1.97 (s, 3H), 1.91 (s, 3H), 1.10 (d, *J* = 6.3 Hz, 3H). The ^{1}H NMR data coincide with the previous report.[7]

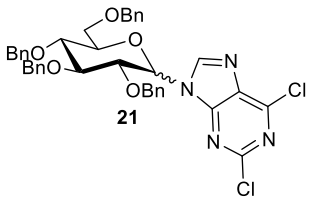
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-α/β-L-rhamnopyranosyl)-α-D-glucopyranoside (19)



19

Compound **19** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1). **α-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.16 (m, 30H), 5.03 – 4.90 (m, 2H), 4.79 (d, *J* = 11.9 Hz, 3H), 4.75 – 4.55 (m, 7H), 4.53 (d, *J* = 3.4 Hz, 1H), 4.37 (d, *J* = 11.0 Hz, 1H), 3.95 (t, *J* = 9.2 Hz, 1H), 3.87 – 3.77 (m, 2H), 3.77 – 3.57 (m, 4H), 3.52 – 3.40 (m, 2H), 3.34 (t, *J* = 9.5 Hz, 1H), 3.26 (s, 3H), 1.30 (d, *J* = 6.1 Hz, 3H). **β-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.41 – 7.20 (m, 28H), 4.98 (d, *J* = 7.6 Hz, 1H), 4.96 – 4.93 (m, 2H), 4.87 (d, *J* = 11.5 Hz, 2H), 4.84 – 4.74 (m, 3H), 4.70 – 4.58 (m, 3H), 4.53 (d, *J* = 11.9 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.43 (s, 1H), 4.28 (dd, *J* = 11.1, 3.1 Hz, 1H), 4.01 – 3.92 (m, 2H), 3.74 (d, *J* = 9.8 Hz, 1H), 3.68 – 3.56 (m, 3H), 3.51 – 3.42 (m, 2H), 3.39 – 3.27 (m, 4H), 1.35 (d, *J* = 6.1 Hz, 3H). The ^{1}H NMR data coincide with the previous report.[8]

2',3',4',6'-Tetra-*O*-benzyl-α/β-D-glucopyranosyl-2,6-dichloropurine (21)

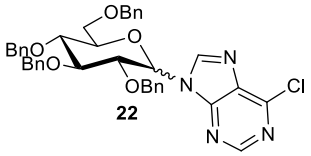


21

Compound **21** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 4:1). **α-isomer**: $[\alpha]^{25}_D$ = 2.59 (c = 0.2, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.46 –

7.06 (m, 20H), 6.88 (d, *J* = 6.8 Hz, 2H), 6.20 (d, *J* = 4.2 Hz, 1H), 4.79 (s, 2H), 4.72 (d, *J* = 11.2 Hz, 1H), 4.63 – 4.52 (m, 3H), 4.48 (d, *J* = 12.1 Hz, 1H), 4.24 (d, *J* = 12.0 Hz, 1H), 4.12 – 4.04 (m, 2H), 3.94 – 3.87 (m, 1H), 3.87 – 3.78 (m, 1H), 3.70 (dd, *J* = 10.8, 4.4 Hz, 1H), 3.63 (dd, *J* = 10.8, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.78, 152.63, 151.38, 145.58, 137.69, 137.63, 137.55, 136.14, 130.43, 128.66, 128.50, 128.41, 128.36, 128.32, 128.19, 128.13, 128.09, 127.99, 127.94, 127.76, 79.87, 79.59, 76.40, 76.09, 74.31, 74.10, 73.92, 73.57, 73.54, 68.46. ESI-HRMS calculated for $C_{39}H_{37}N_4O_5Cl_2$ $[M+H]^+$ 711.2141, found 711.2151. **β-isomer**: $[\alpha]^{25}_D$ = -31.6 (c = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.41 – 7.18 (m, 17H), 7.16 – 7.07 (m, 1H), 7.07 – 6.98 (m, 2H), 6.76 – 6.66 (m, 2H), 5.48 (d, *J* = 9.0 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.94 (d, *J* = 10.9 Hz, 1H), 4.89 (d, *J* = 10.7 Hz, 1H), 4.73 – 4.63 (m, 2H), 4.59 – 4.43 (m, 2H), 4.24 (d, *J* = 12.0 Hz, 1H), 4.13 – 4.02 (m, 1H), 3.96 – 3.81 (m, 2H), 3.81 – 3.63 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.96, 152.52, 151.60, 143.90, 137.87, 137.72, 137.66, 136.35, 130.66, 128.59, 128.55, 128.42, 128.09, 128.08, 128.04, 128.00, 127.99, 127.88, 127.78, 127.72, 85.94, 83.44, 79.41, 78.29, 77.29, 75.97, 75.30, 74.84, 73.56, 68.27. ESI-HRMS calculated for $C_{39}H_{37}N_4O_5Cl_2$ $[M+H]^+$ 711.2141, found 711.2139.

2',3',4',6'-Tetra-*O*-benzyl-α/β-D-glucopyranosyl-6-chloropurine (22)

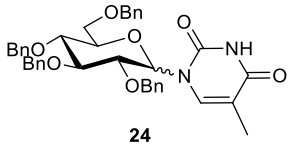


22

Compound **22** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 3:1). **α-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.41 (s, 1H), 7.42 – 7.24 (m, 15H), 7.24 – 7.10 (m, 5H), 6.99 – 6.91 (m, 2H), 6.28 (d, *J* = 4.9 Hz, 1H), 4.87 (d, *J* = 11.4 Hz, 1H), 4.82 (d, *J* = 11.4 Hz, 1H), 4.76 (d, *J* = 11.1 Hz, 1H), 4.65 – 4.54 (m, 3H), 4.47 (d, *J* = 12.0 Hz, 1H), 4.34 (d, *J* = 11.9 Hz, 1H), 4.20 – 4.11 (m, 2H), 3.90 – 3.79 (m, 2H), 3.71 (dd, *J* = 10.8, 3.8 Hz, 1H), 3.62 (dd, *J* = 10.8, 2.1 Hz, 1H). **β-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.03 (s, 1H), 7.40 – 7.24 (m, 15H), 7.24 – 7.18 (m, 2H), 7.16 – 7.08 (m, 1H), 7.05 – 6.95 (m, 2H), 6.66 – 6.60 (m, 2H), 5.59 (d, *J* = 9.0 Hz, 1H), 4.99 (d, *J* = 11.0 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.89 (d, *J* = 10.7 Hz, 1H), 4.66 (d, *J* = 10.7 Hz, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 12.2 Hz, 1H), 4.48 (d, *J* = 12.2 Hz, 1H), 4.17 (d, *J* = 11.7 Hz, 1H), 4.12 – 4.03 (m, 1H), 3.95 – 3.84 (m, 2H), 3.79 – 3.67 (m,

3H). The ^{1}H NMR data coincide with the previous report.[9]

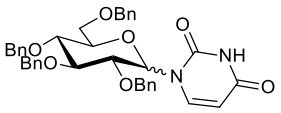
1-(2',3',4',6'-Tetra-*O*-benzyl-α/β-D-glucopyranosyl)-thymine (24)



24

Compound **24** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 3:1). **α-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.45 (d, *J* = 1.4 Hz, 1H), 7.39 – 7.25 (m, 16H), 7.20 (dd, *J* = 7.2, 2.4 Hz, 2H), 7.16 – 7.09 (m, 2H), 6.04 (d, *J* = 3.2 Hz, 1H), 4.61 – 4.38 (m, 7H), 4.38 – 4.26 (m, 2H), 4.04 (t, *J* = 3.2 Hz, 1H), 3.84 (t, *J* = 3.2 Hz, 1H), 3.74 (dd, *J* = 10.5, 3.0 Hz, 1H), 3.70 – 3.59 (m, 2H), 1.81 (d, *J* = 1.2 Hz, 3H). **β-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.38 – 7.27 (m, 13H), 7.26 – 7.22 (m, 3H), 7.19 – 7.11 (m, 4H), 6.66 (d, *J* = 1.4 Hz, 1H), 5.59 (d, *J* = 9.2 Hz, 1H), 4.94 (s, 2H), 4.84 (d, *J* = 10.8 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 10.8 Hz, 1H), 4.57 – 4.44 (m, 3H), 3.86 (t, *J* = 9.0 Hz, 1H), 3.77 – 3.55 (m, 4H), 3.46 (t, *J* = 9.0 Hz, 1H), 1.67 (d, *J* = 1.3 Hz, 3H). The ^{1}H NMR data coincide with the previous report.[10]

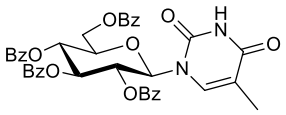
1-(2',3',4',6'-Tetra-*O*-benzyl-α/β-D-glucopyranosyl)-uracil (25)



25

Compound **25** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 3:1). **α-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.38 – 7.27 (m, 17H), 7.19 (dd, *J* = 7.0, 2.6 Hz, 2H), 7.14 (dd, *J* = 7.0, 2.6 Hz, 2H), 6.03 (d, *J* = 3.3 Hz, 1H), 5.61 (dd, *J* = 8.2, 2.4 Hz, 1H), 4.58 – 4.40 (m, 6H), 4.36 – 4.26 (m, 2H), 4.04 (t, *J* = 3.2 Hz, 1H), 3.84 (t, *J* = 3.2 Hz, 1H), 3.78 – 3.59 (m, 4H). **β-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.38 – 7.25 (m, 16H), 7.22 – 7.13 (m, 4H), 6.91 (d, *J* = 8.2 Hz, 1H), 5.59 (d, *J* = 9.2 Hz, 1H), 5.37 (dd, *J* = 8.1, 2.4 Hz, 1H), 4.93 (s, 2H), 4.84 (d, *J* = 10.8 Hz, 1H), 4.79 (d, *J* = 11.8 Hz, 1H), 4.60 (d, *J* = 10.8 Hz, 1H), 4.56 – 4.43 (m, 3H), 3.85 (t, *J* = 9.0 Hz, 1H), 3.76 – 3.56 (m, 4H), 3.47 (t, *J* = 9.0 Hz, 1H). The ^{1}H NMR data coincide with the previous report.[10]

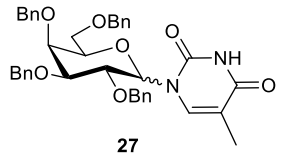
1-(2',3',4',6'-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-thymine (26)



26

Compound **26** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.07 – 8.00 (m, 2H), 7.97 – 7.89 (m, 2H), 7.89 – 7.84 (m, 2H), 7.84 – 7.76 (m, 2H), 7.60 – 7.26 (m, 13H), 6.28 (d, *J* = 9.5 Hz, 1H), 6.09 (t, *J* = 9.6 Hz, 1H), 5.79 (t, *J* = 9.8 Hz, 1H), 5.69 (t, *J* = 9.5 Hz, 1H), 4.67 (dd, *J* = 12.4, 2.7 Hz, 1H), 4.49 (dd, *J* = 12.4, 5.1 Hz, 1H), 4.40 (ddd, *J* = 10.0, 5.0, 2.7 Hz, 1H), 1.93 (d, *J* = 1.2 Hz, 3H). The ^{1}H NMR data coincide with the previous report.[10]

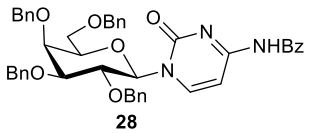
1-(2',3',4',6'-Tetra-*O*-benzyl-α/β-D-galactopyranosyl)-thymine (27)



27

Compound **27** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 3:1). **α-isomer**: $[\alpha]^{25}_D$ = -77.8 (c = 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.42 (d, *J* = 1.3 Hz, 1H), 7.40 – 7.22 (m, 20H), 7.02 (dd, *J* = 6.9, 2.6 Hz, 2H), 6.06 (d, *J* = 1.9 Hz, 1H), 4.67 – 4.47 (m, 7H), 4.35 (d, *J* = 11.5 Hz, 1H), 4.21 – 4.10 (m, 2H), 4.07 (dd, *J* = 6.4, 2.8 Hz, 1H), 3.84 – 3.75 (m, 2H), 3.69 (dd, *J* = 4.0, 2.0 Hz, 1H), 1.84 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.37, 149.50, 138.70, 138.12, 137.78, 137.65, 136.47, 128.50, 128.49, 128.46, 128.42, 128.37, 128.30, 127.91, 127.88, 127.83, 127.79, 127.62, 127.59, 108.67, 74.98, 74.92, 73.66, 73.57, 73.26, 73.15, 72.26, 71.90, 65.49, 29.70, 12.23. ESI-HRMS calculated for $C_{39}H_{44}N_3O_7$ $[M+NH_4]^+$ 666.3179, found 666.3177. **β-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.42 – 7.15 (m, 20H), 6.65 (d, *J* = 1.3 Hz, 1H), 5.56 (d, *J* = 8.9 Hz, 1H), 4.97 (d, *J* = 11.4 Hz, 1H), 4.85 – 4.72 (m, 3H), 4.61 (d, *J* = 11.4 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.42 (d, *J* = 11.9 Hz, 1H), 4.00 (dd, *J* = 2.6, 1.0 Hz, 1H), 3.85 (t, *J* = 9.2 Hz, 1H), 3.80 – 3.66 (m, 2H), 3.63 – 3.45 (m, 2H), 1.64 (d, *J* = 1.2 Hz, 3H). The ^{1}H NMR data coincide with the previous report.[10]

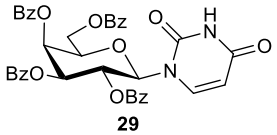
***N*^{4}-benzoyl-1-(2',3',4',6'-tetra-*O*-benzyl-β-D-galactopyranosyl)-cytosine (28)**



28

Compound **28** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.67 – 7.58 (m, 1H), 7.58 – 7.48 (m, 2H), 7.41 – 7.24 (m, 17H), 7.17 (tdd, *J* = 9.7, 4.7, 2.0 Hz, 5H), 5.88 (d, *J* = 9.0 Hz, 1H), 4.98 (d, *J* = 11.3 Hz, 1H), 4.84 – 4.71 (m, 3H), 4.61 (d, *J* = 11.3 Hz, 1H), 4.51 (d, *J* = 11.8 Hz, 1H), 4.47 (d, *J* = 11.9 Hz, 1H), 4.42 (d, *J* = 11.9 Hz, 1H), 4.01 (d, *J* = 2.6 Hz, 1H), 3.92 (t, *J* = 9.2 Hz, 1H), 3.85 – 3.71 (m, 2H), 3.63 – 3.46 (m, 2H). The ^{1}H NMR data coincide with the previous report.[10]

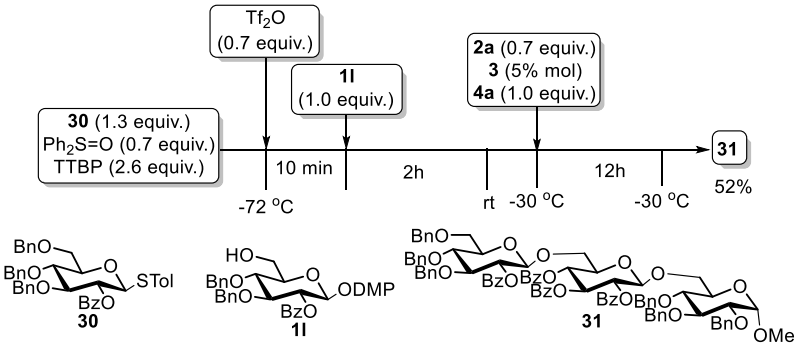
1-(2',3',4',6'-Tetra-*O*-benzoyl-*β*-D-galactopyranosyl)-uracil (29)



29

Compound **29** was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 2.2 Hz, 1H), 8.09 – 8.03 (m, 2H), 8.03 – 7.96 (m, 2H), 7.94 – 7.85 (m, 2H), 7.82 – 7.73 (m, 2H), 7.73 – 7.65 (m, 1H), 7.65 – 7.39 (m, 8H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.23 (m, 2H), 6.23 (d, *J* = 9.2 Hz, 1H), 6.10 (dd, *J* = 3.3, 1.0 Hz, 1H), 5.99 – 5.87 (m, 2H), 5.83 (dd, *J* = 10.1, 3.3 Hz, 1H), 4.70 – 4.55 (m, 2H), 4.45 (dd, *J* = 10.5, 4.9 Hz, 1H). The ^{1}H NMR data coincide with the previous report.[10]

6 One-pot synthesis of trisaccharide 31



30 **1l** **31**

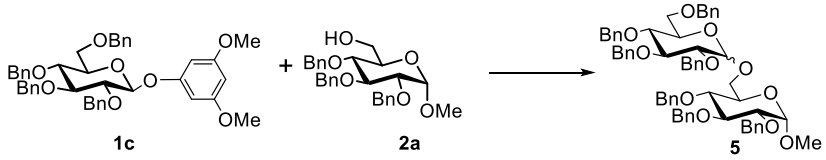
A mixture of donor **30** (42.1 mg, 0.078 mmol), Ph_2SO (8.1 mg, 0.04 mmol), and 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 39.7 mg, 0.16 mmol) was dissolved in dry CH_2Cl_2 (2.0 mL), containing

freshly activated 3 Å molecular sieves (400 mg). After stirring for 0.5 h under argon, the reaction mixture was cooled to –72 °C and Tf_2O (6.7 μL, 0.04 mmol) was added. After the disappearance of **30**, a solution of **1l** (23.2 mg, 0.06 mmol; CH_2Cl_2, 0.5 mL) was added. The temperature was allowed to slowly warm up to room temperature. After the disappearance of **1l**, a solution of **2a** (10.1 mg, 0.04 mmol), $Ru(bpy)_3(PF_6)_2$ (2.1 mg, 0.003 mmol) and Umemoto's reagent (26.3 mg, 0.06 mmol) in dry MeCN (2.0 mL) were added and stirred for 0.5 h. Subsequently, the reaction mixture was cooled to –30 °C and irradiated by blue LEDs for 12 h. the reaction mixture was filtered through Celite. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel (petroleum ether: EtOAc = 5: 1) to yield product **31** (18.3 mg, 52%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.90 – 7.80 (m, 4H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.42 – 7.20 (m, 29H), 7.19 – 7.05 (m, 9H), 7.02 – 6.94 (m, 2H), 5.72 (t, *J* = 9.6 Hz, 1H), 5.42 (dd, *J* = 9.6, 7.9 Hz, 1H), 5.32 – 5.20 (m, 2H), 4.87 (d, *J* = 11.0 Hz, 1H), 4.77 (d, *J* = 10.8 Hz, 1H), 4.74 – 4.60 (m, 5H), 4.60 – 4.42 (m, 6H), 4.38 (d, *J* = 11.3 Hz, 1H), 4.17 (d, *J* = 11.3 Hz, 1H), 3.96 (d, *J* = 10.8 Hz, 1H), 3.88 – 3.71 (m, 6H), 3.69 (d, *J* = 2.8 Hz, 2H), 3.53 – 3.27 (m, 5H), 3.23 (s, 3H). The ^{1}H NMR data coincide with the previous report.[11]

7 Mechanistic studies

Control experiments

Table S5 Mechanistic investigations[a]



Entry	Vis (h)	Additive (equiv.)	Yield[b]
1[c]	12	-	No found
2[d]	12	-	No found
3[e]	12	-	No found

[a]General conditions: donor **1c** (0.03 mmol, 1.5 equiv.), acceptor **2a** (0.02 mmol, 1.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.001 mmol, 5 mol%), Umemoto's reagent (triflate salt) (0.03 mmol, 1.5 equiv.), 3 Å MS (for MeCN) or 4 Å MS (for other solvents) (200 mg), solvent (2.0 mL) at room temperature under the irradiation of blue LEDs for 12 h. [b]Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]No $Ru(bpy)_3(PF_6)_2$. [d]No Umemoto's reagent. [e]No irradiation.

TEMPO-trapping experiments

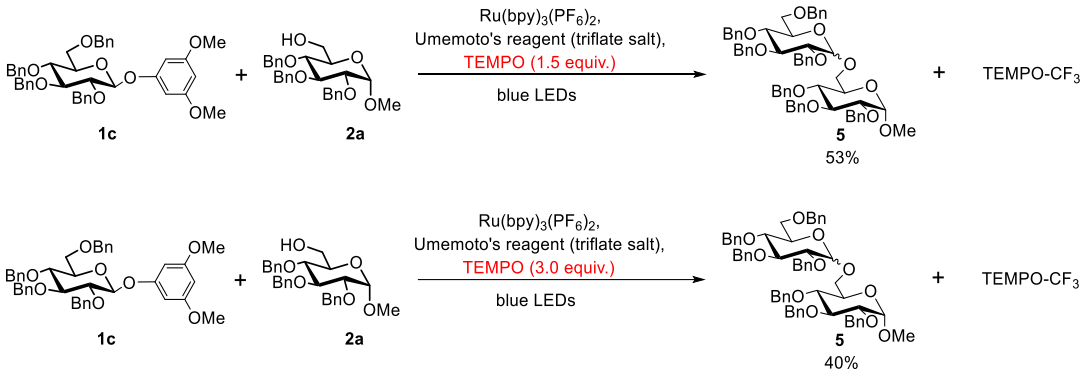


Fig. S1 TEMPO-trapping experiments. TEMPO-CF_3 was detected by ^{19}F NMR analysis.

The identification of by-product

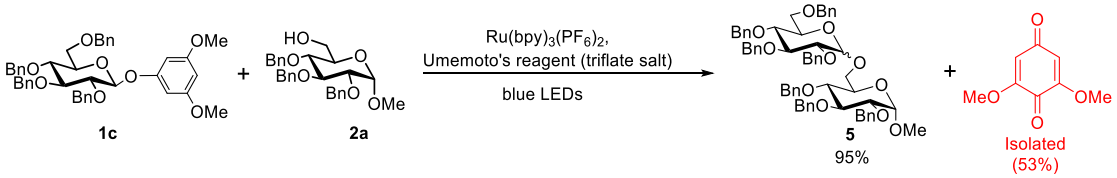


Fig. S2 The identification of by-product

Light-dark interval experiments

A solution of **1c** (0.09 mmol, 9.1 mg), **2a** (0.06 mmol, 16.1 mg), $[Ru(bpy)_3](PF_6)_2$ (0.003 mmol, 0.9 mg), Umemoto's reagent (triflate salt) (0.09 mmol, 7.9 mg) and 3 Å molecular sieves (600 mg) in MeCN (6.0 mL) was stirred at -30 °C. The reaction mixture was determined by ^{1}H NMR analysis at 1 h interval after irradiation with blue LEDs or being kept in the dark. Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

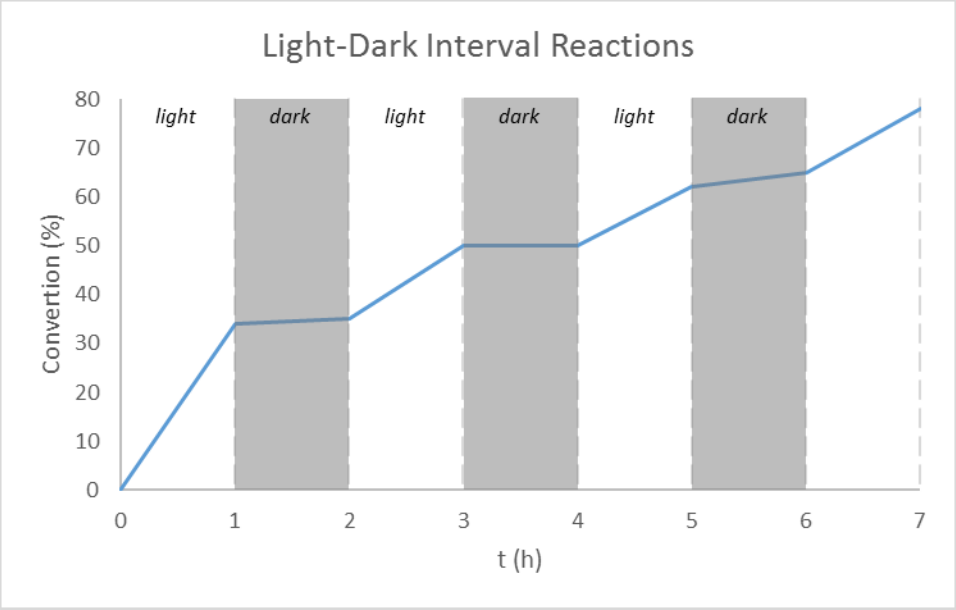


Fig. S3 Light–dark interval experiments

The proposed mechanism

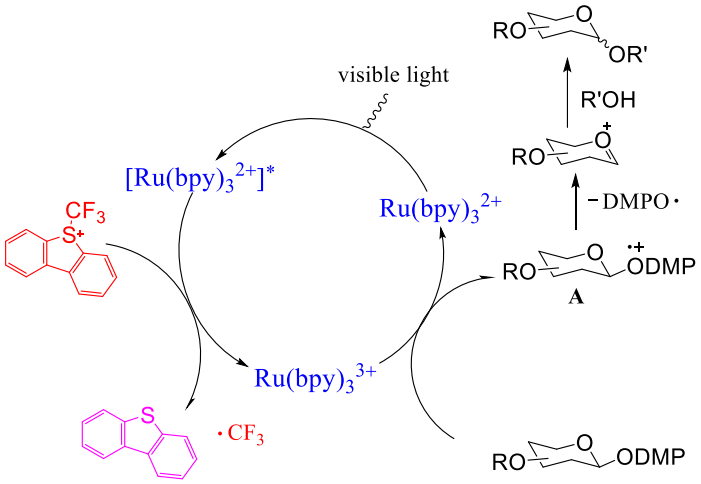


Fig. S4 Proposed mechanism.

8 References

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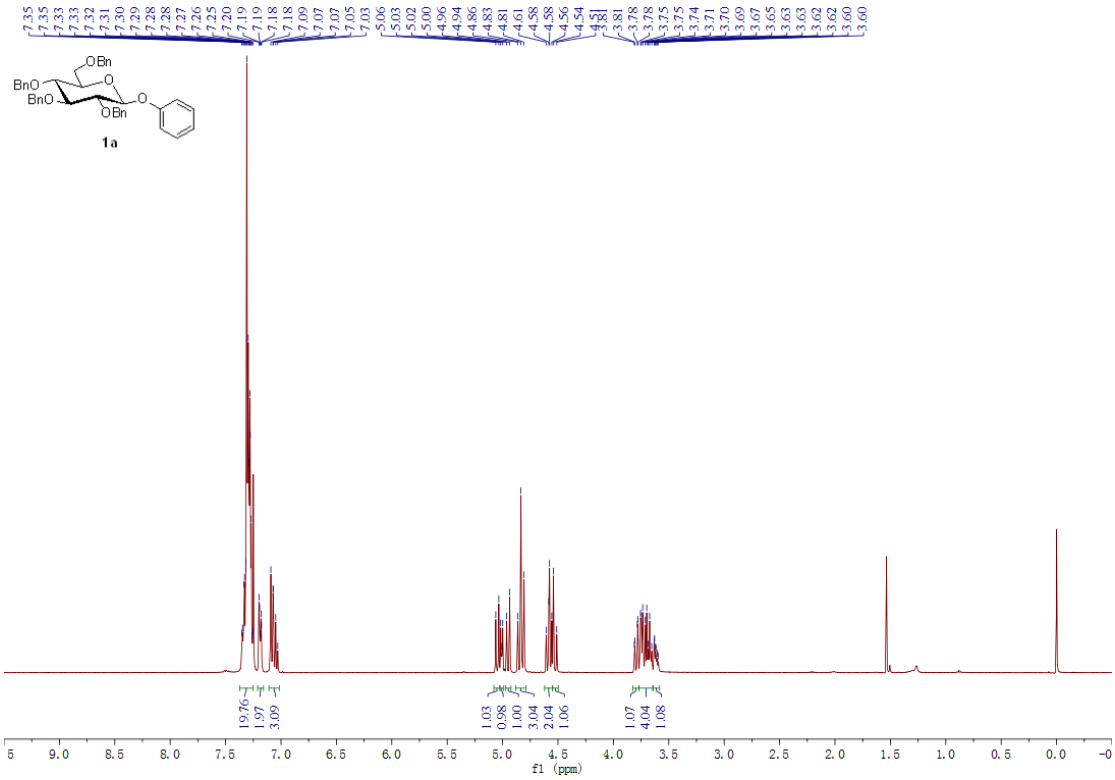
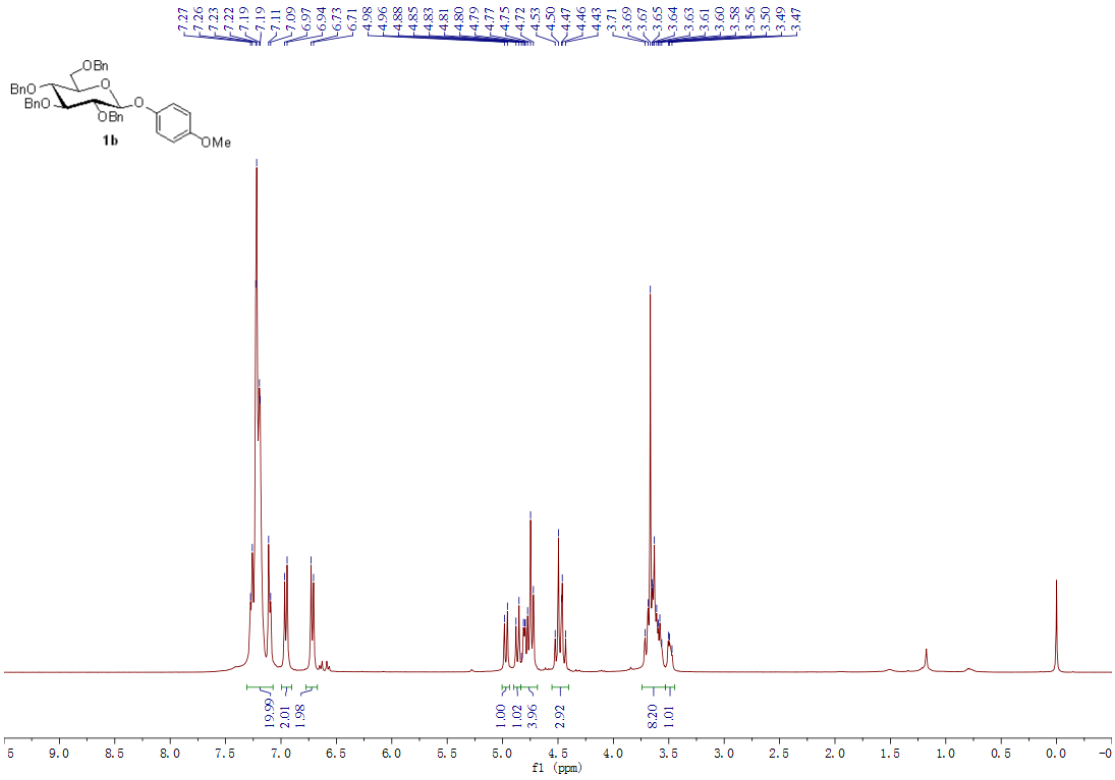
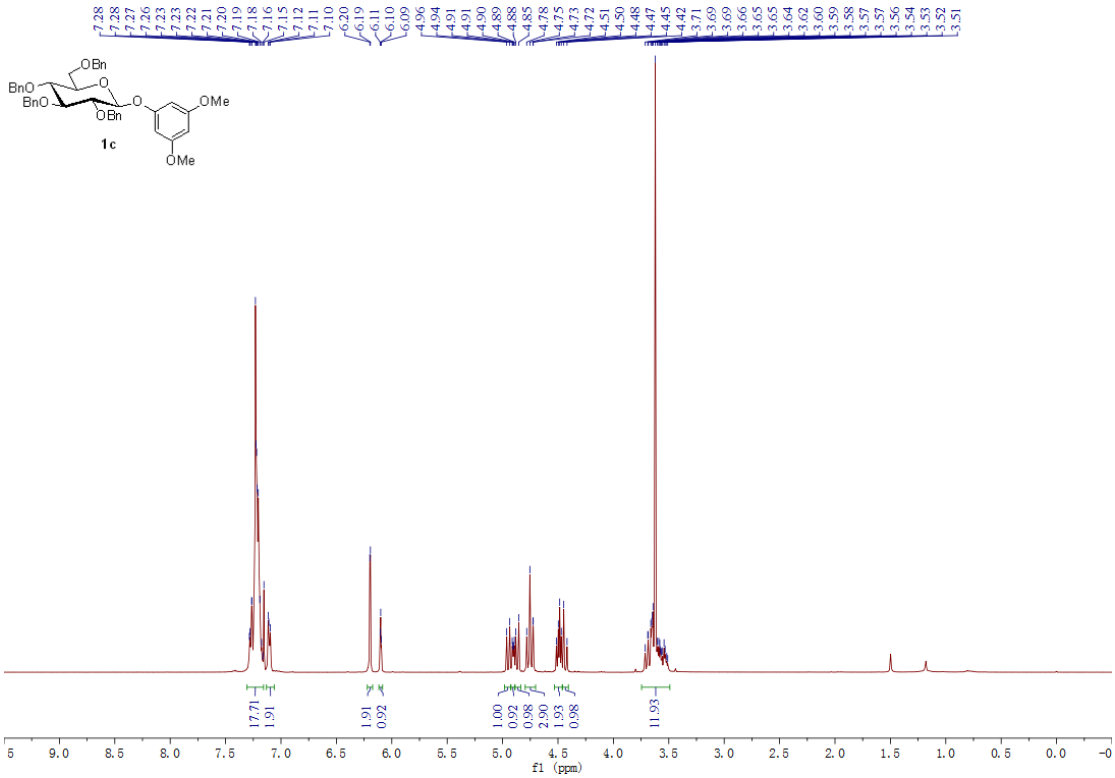
9 Spectra of compounds



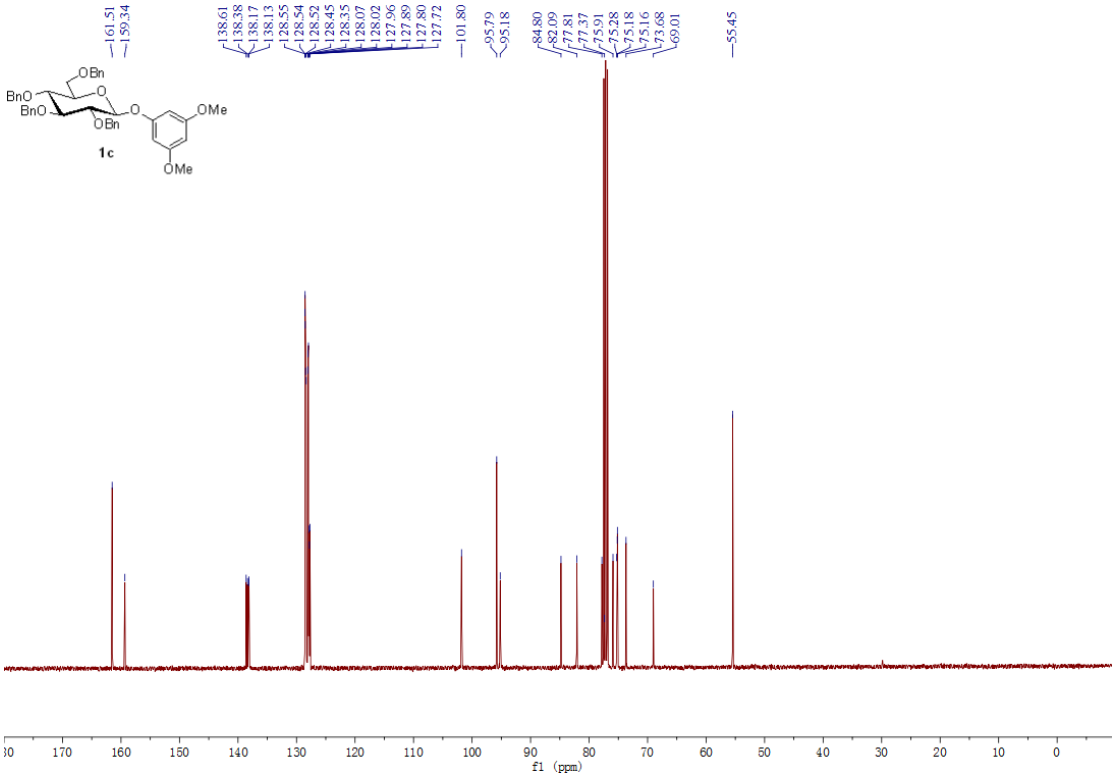
^{1}H NMR spectrum of compound 1a



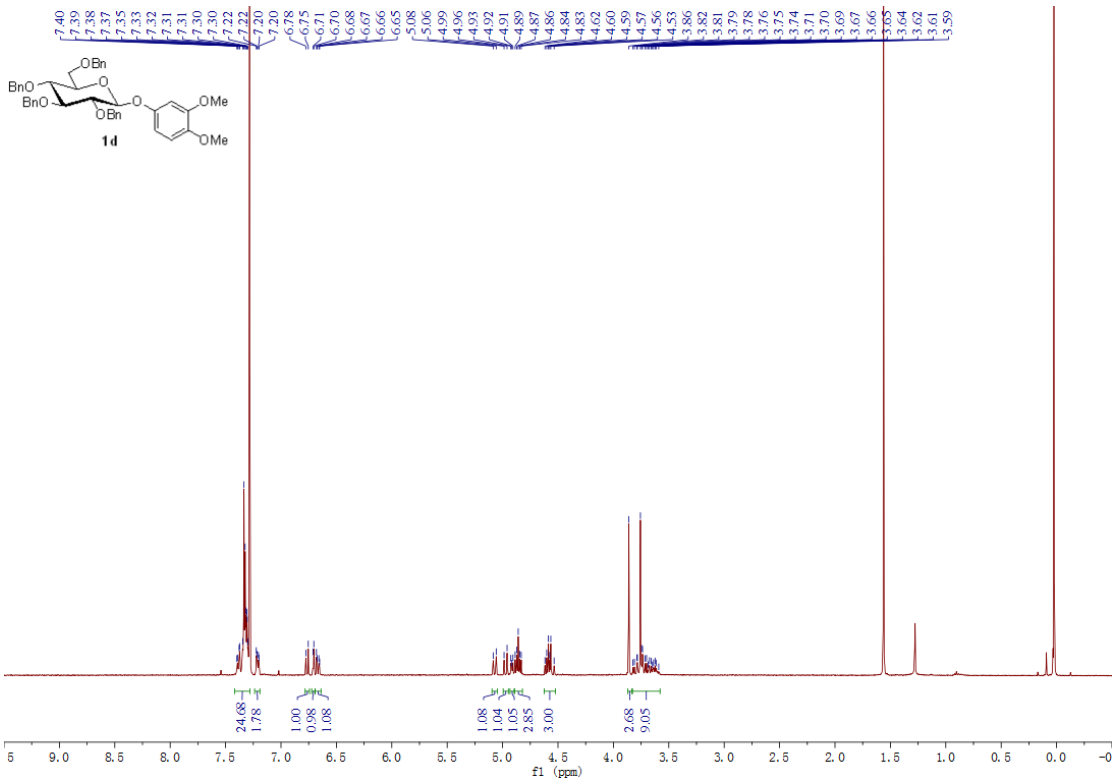
^{1}H NMR spectrum of compound 1b



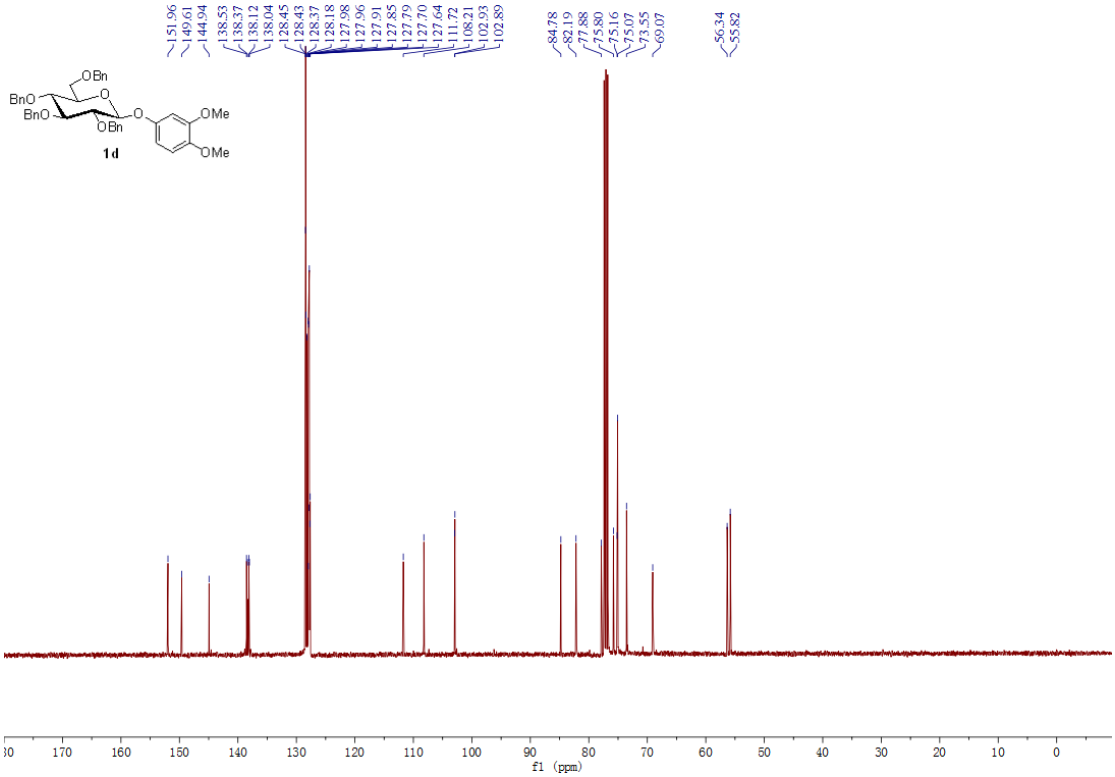
^{1}H NMR spectrum of compound 1c



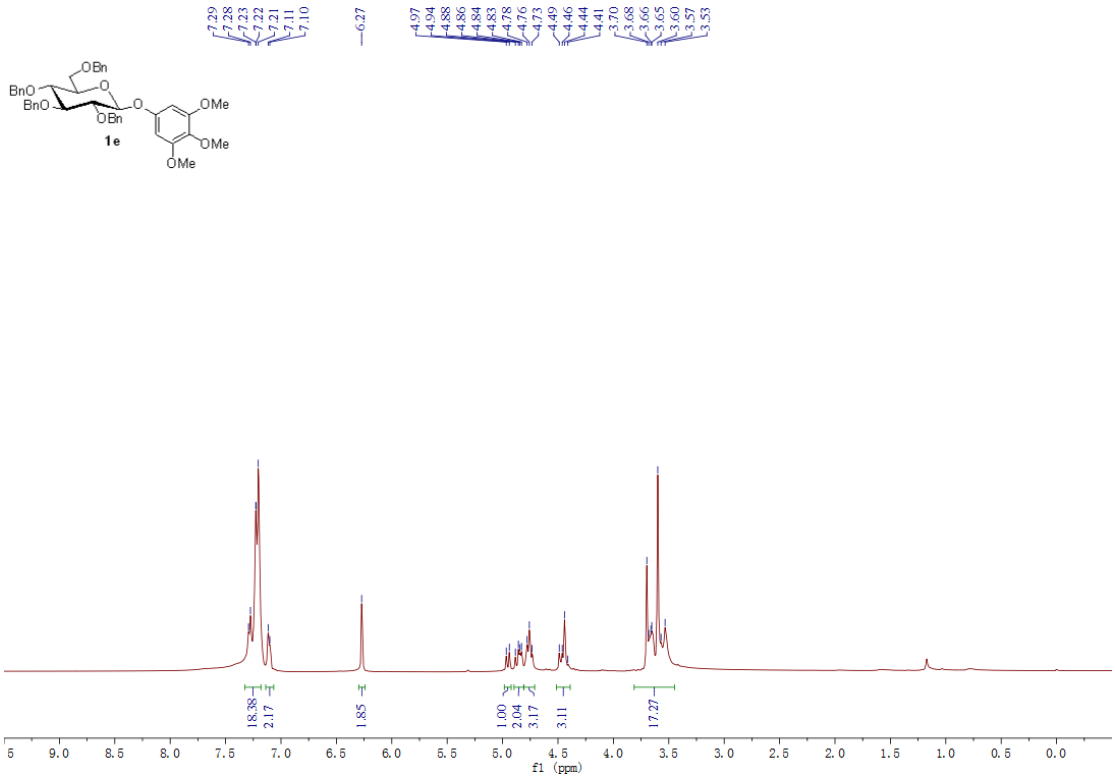
^{13}C NMR spectrum of compound 1c



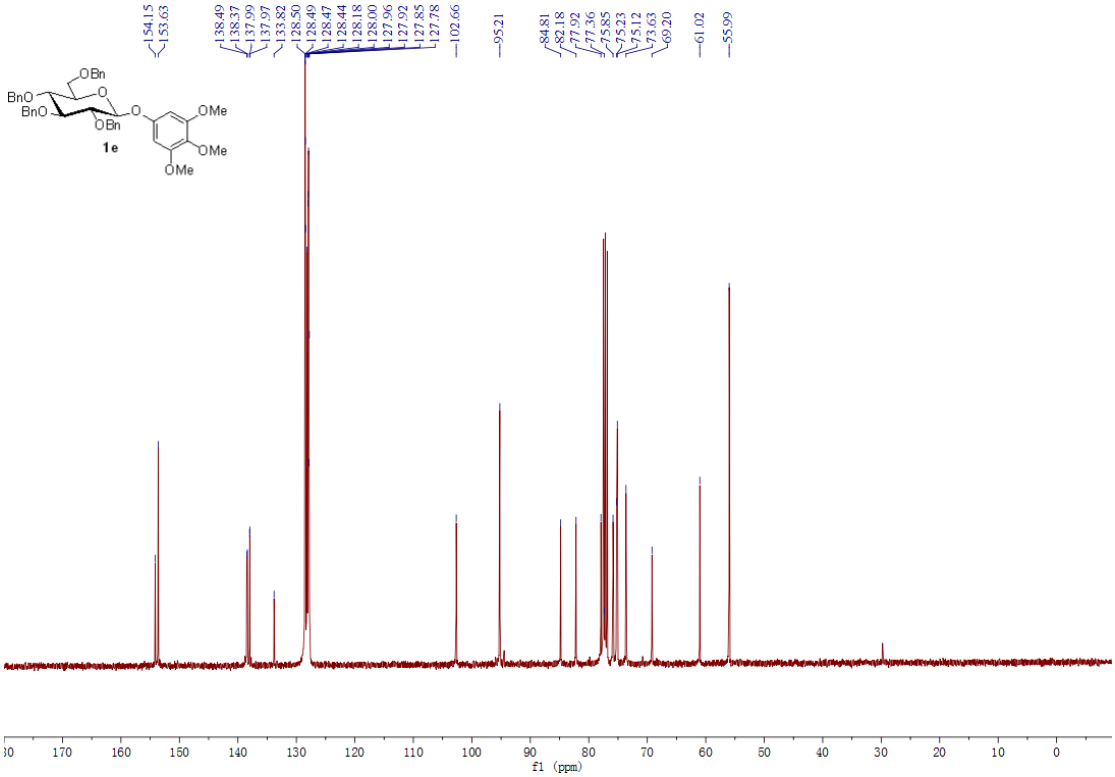
^{1}H NMR spectrum of compound 1d



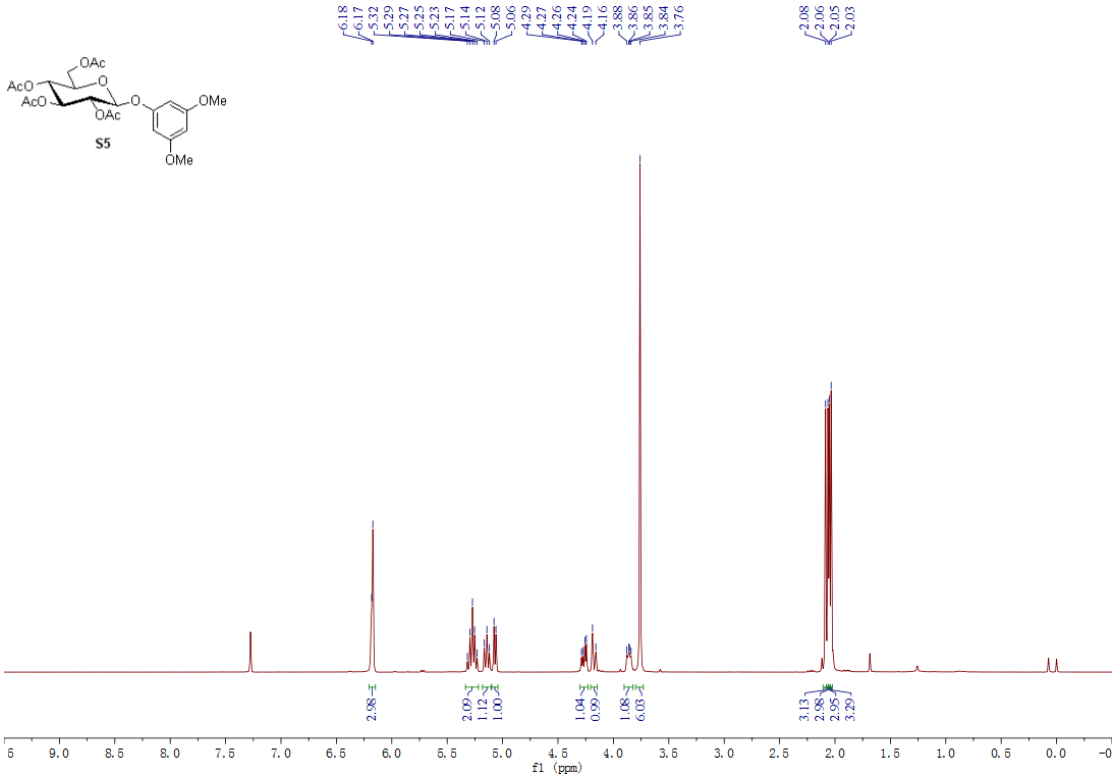
^{13}C NMR spectrum of compound 1d



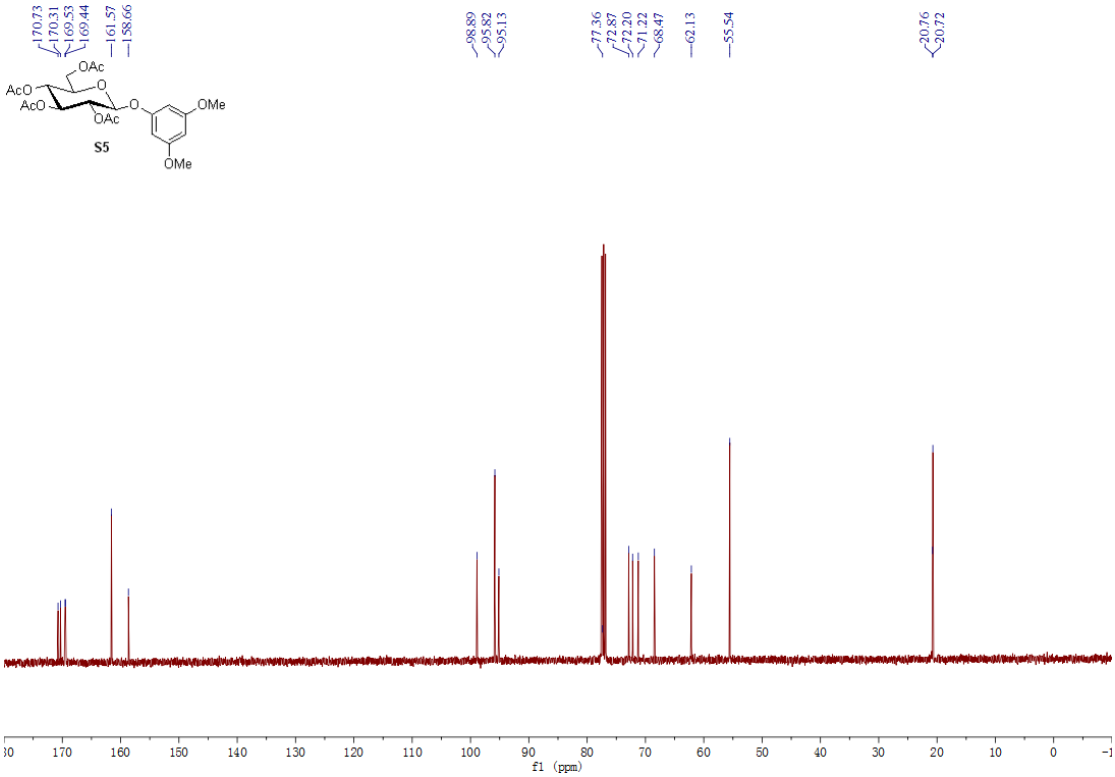
^{1}H NMR spectrum of compound 1e



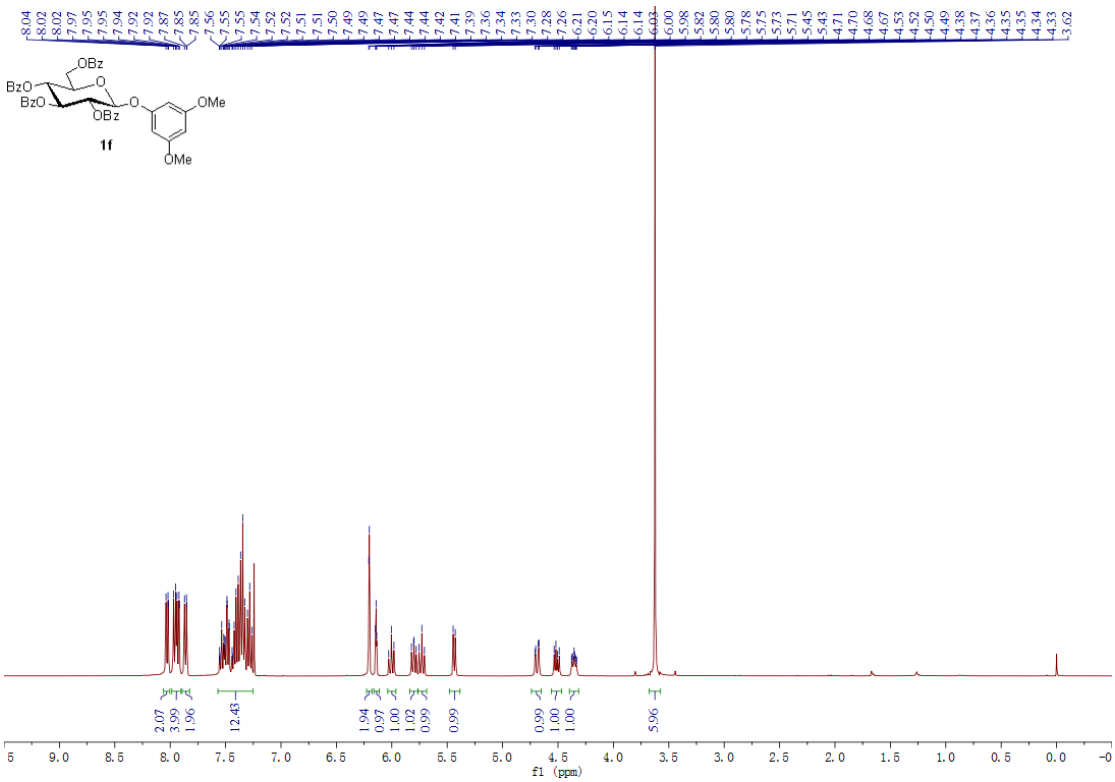
^{13}C NMR spectrum of compound 1e



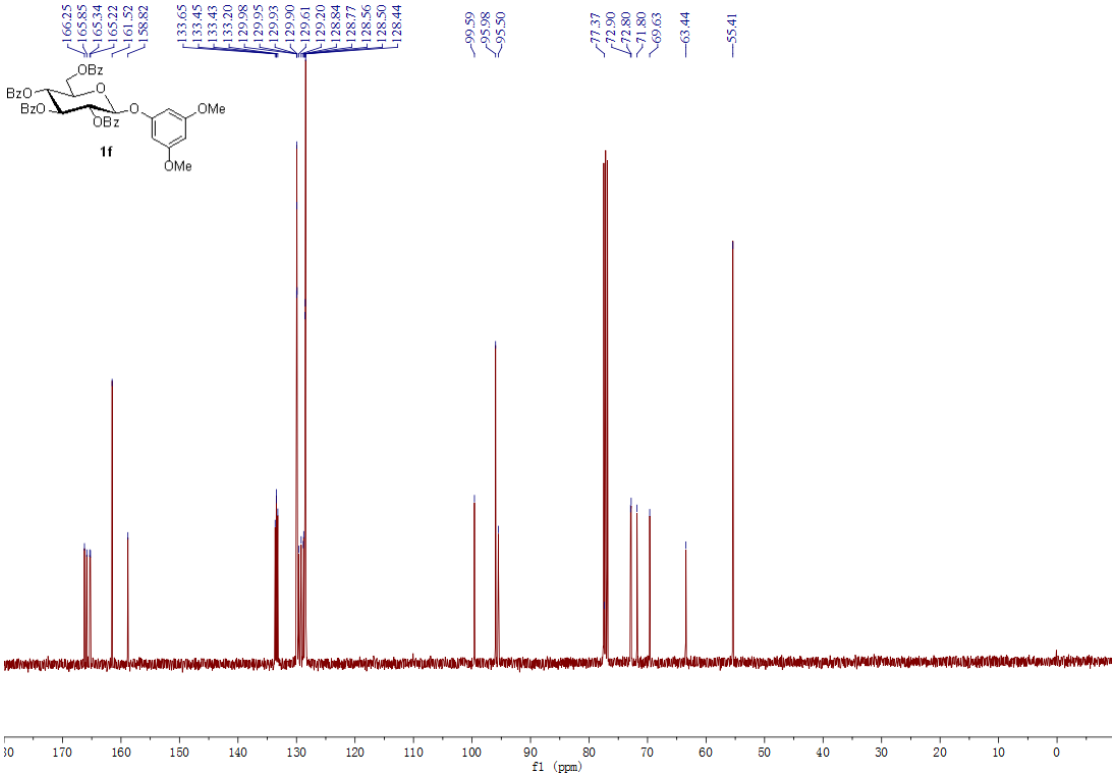
^{1}H NMR spectrum of compound S5



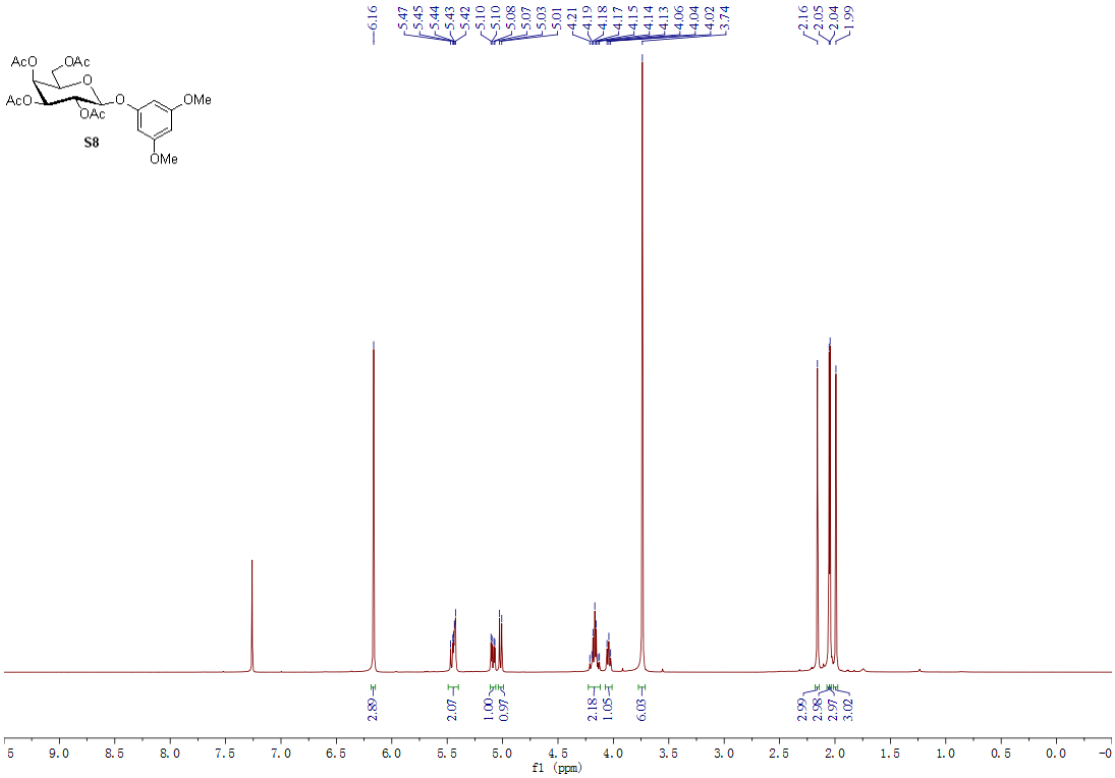
^{13}C NMR spectrum of compound S5



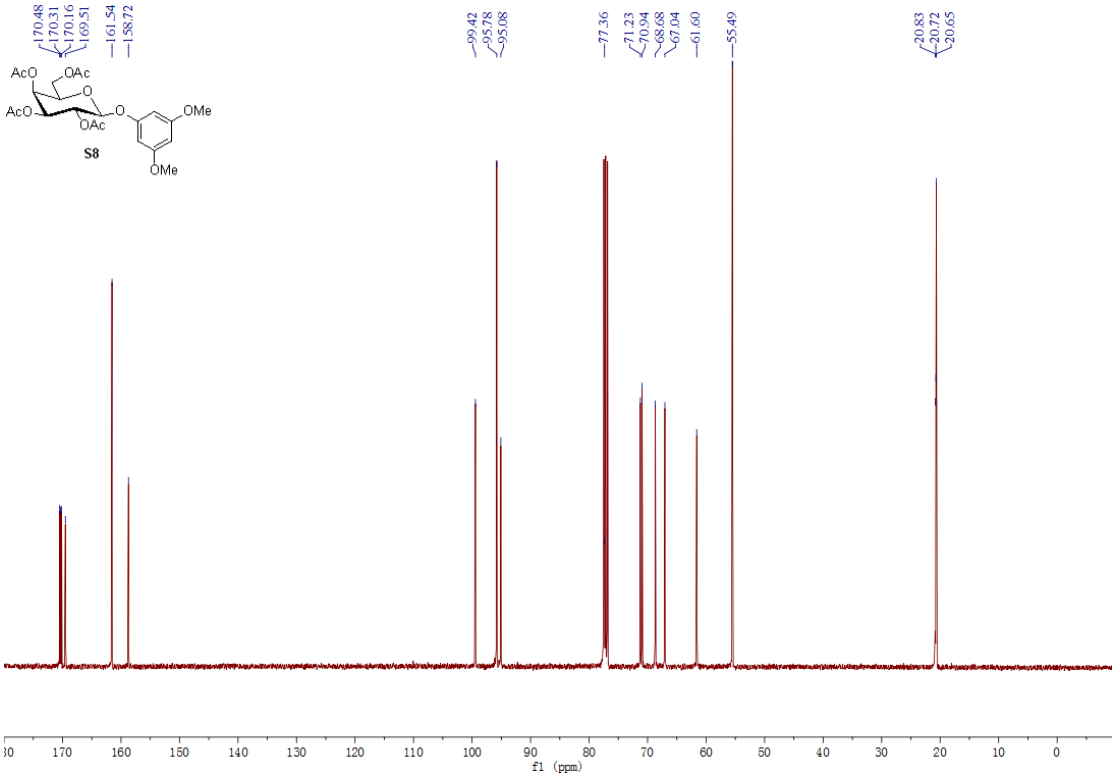
^{1}H NMR spectrum of compound 1f



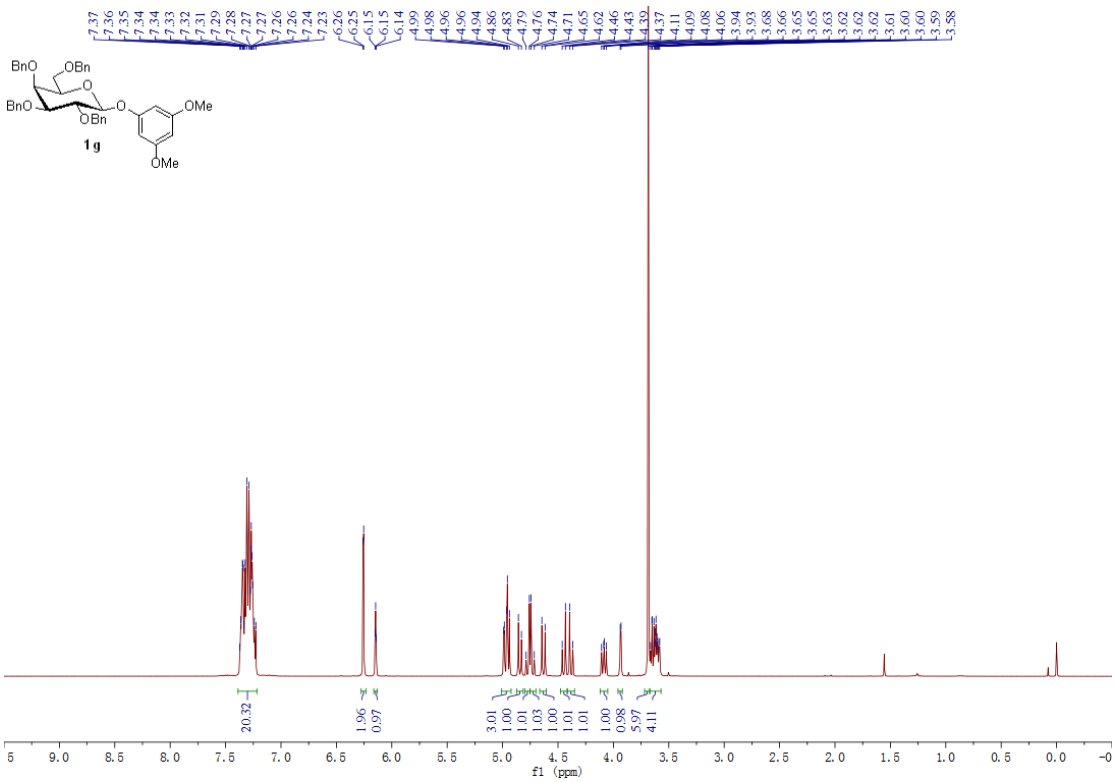
^{13}C NMR spectrum of compound 1f



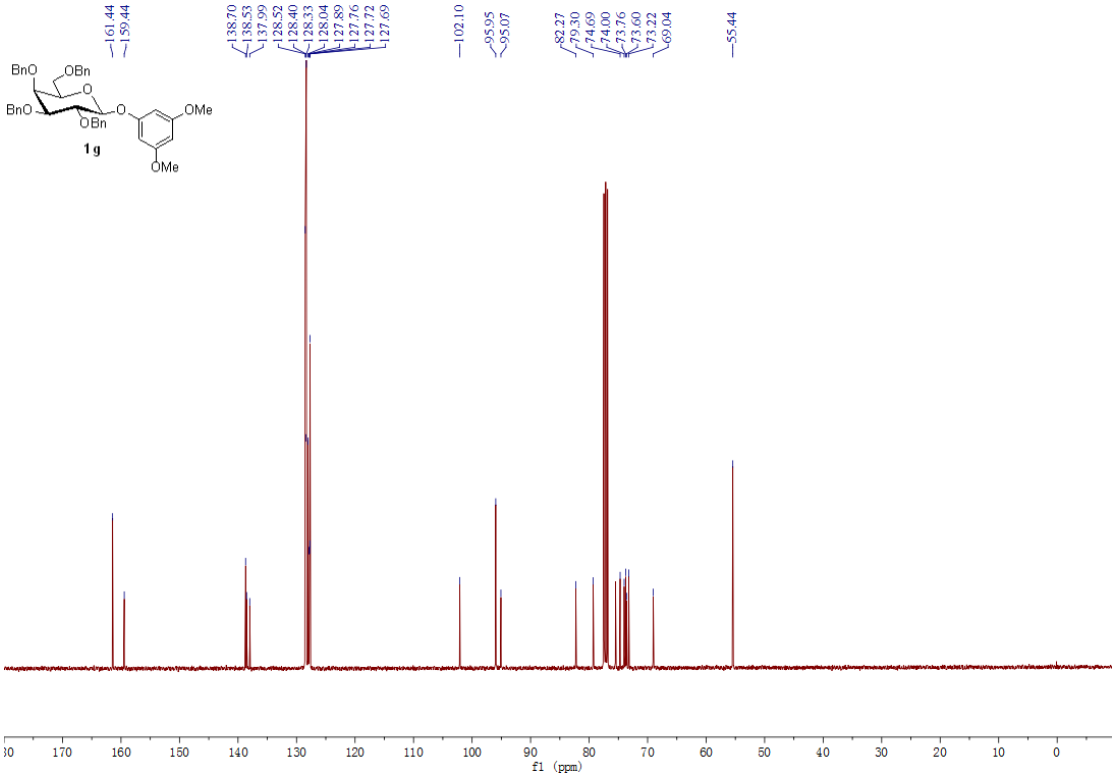
^{1}H NMR spectrum of compound S8



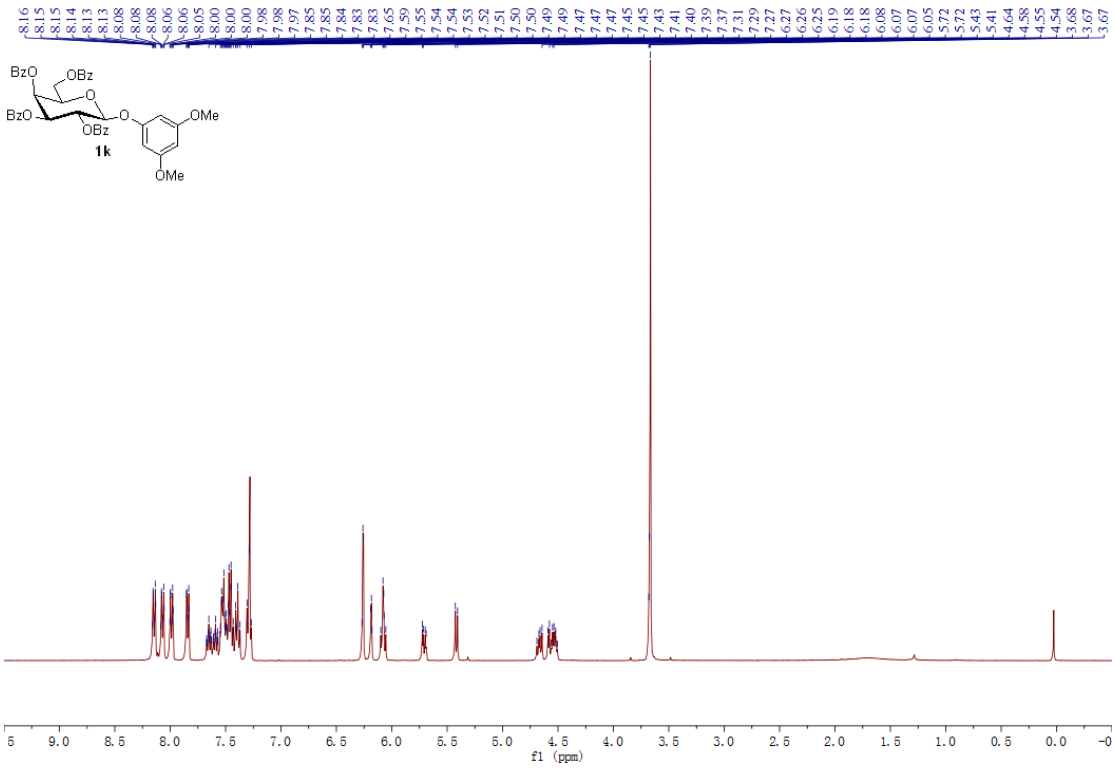
^{13}C NMR spectrum of compound S8



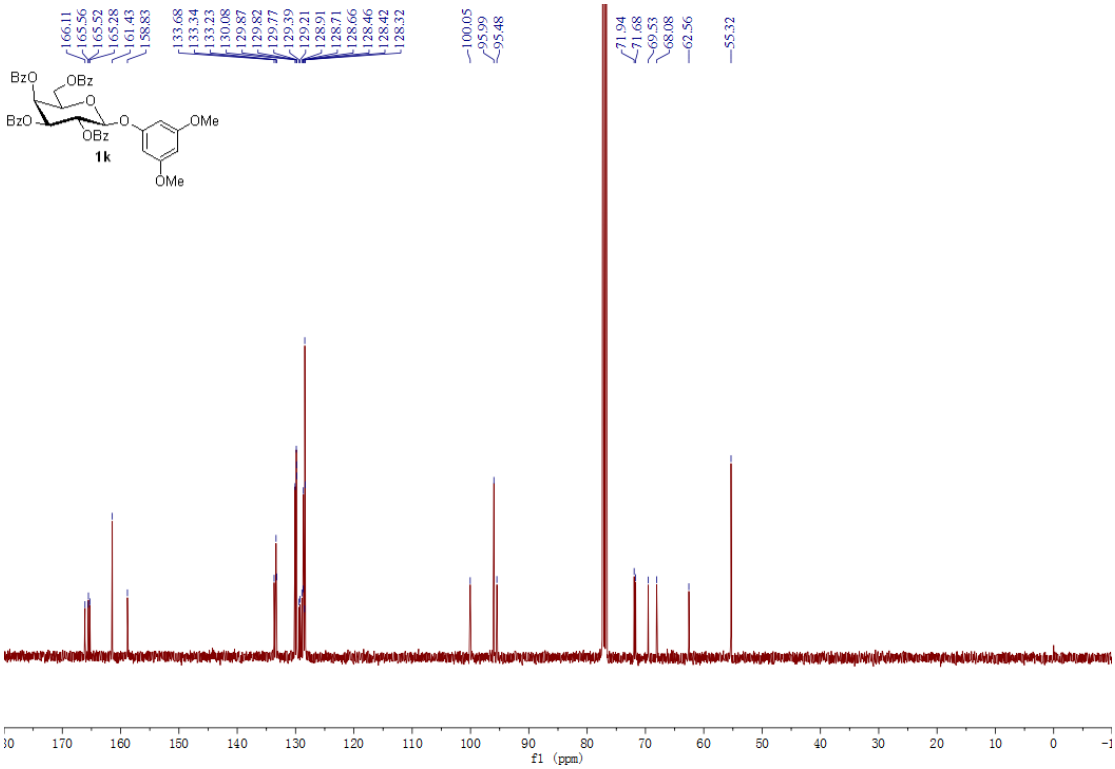
^{1}H NMR spectrum of compound 1g



^{13}C NMR spectrum of compound 1g



^{1}H NMR spectrum of compound 1k



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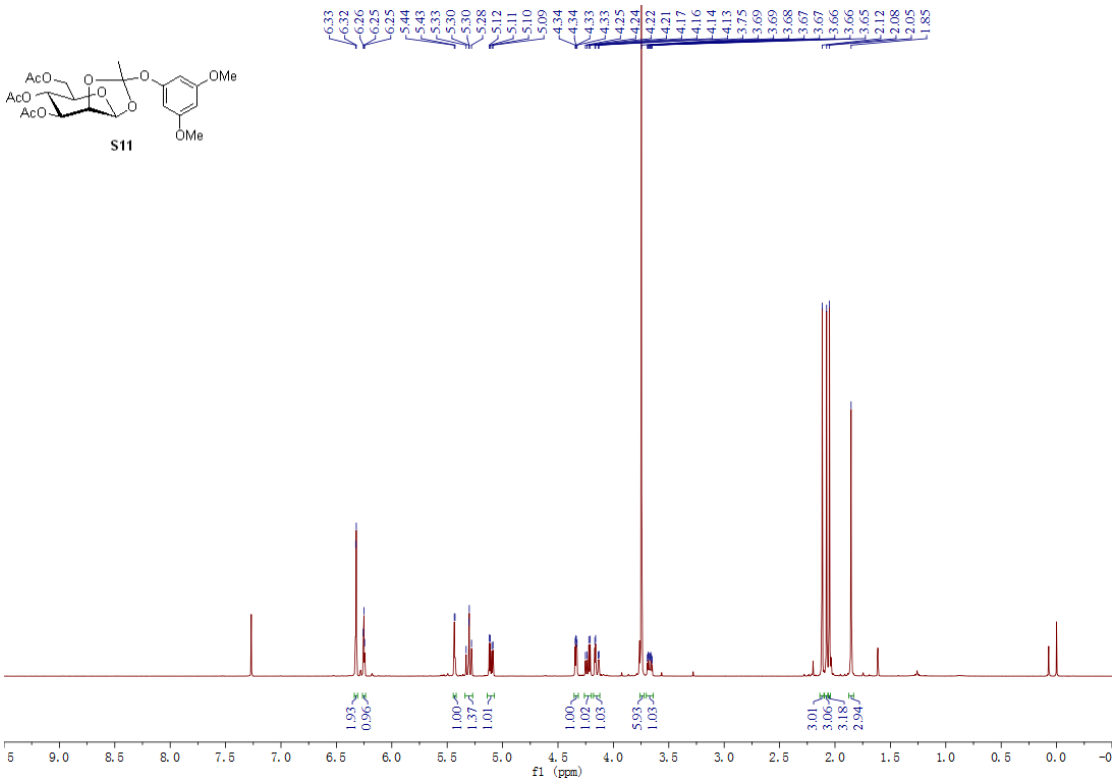
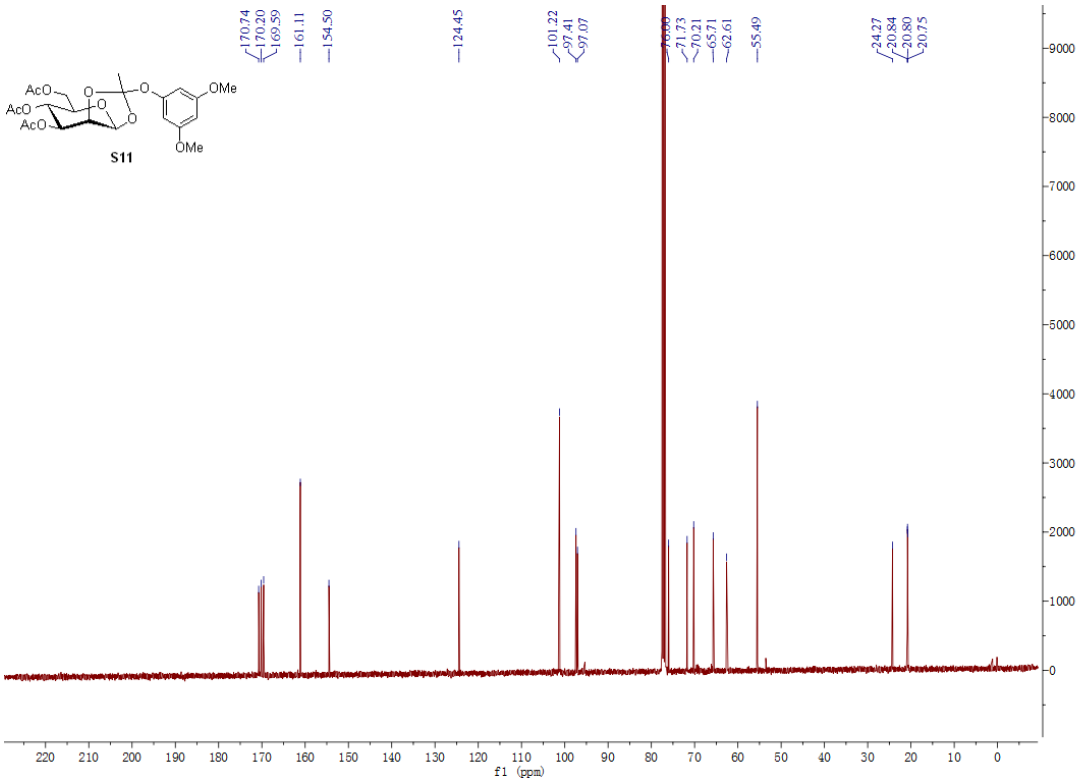
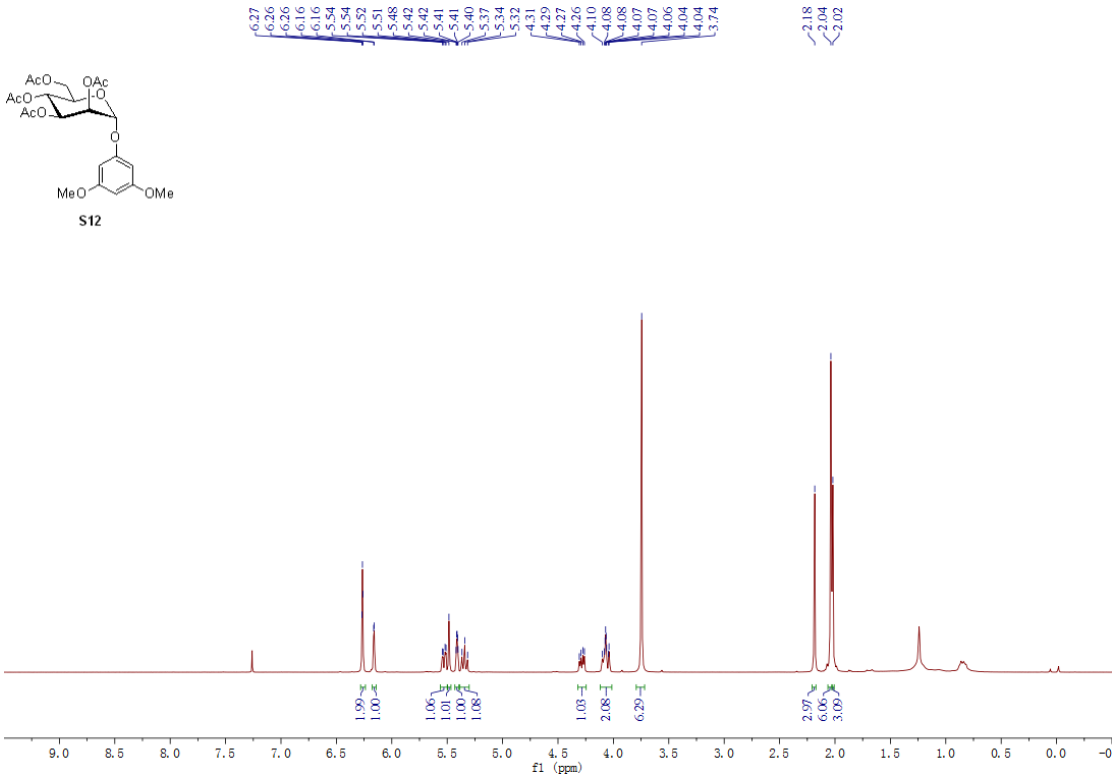


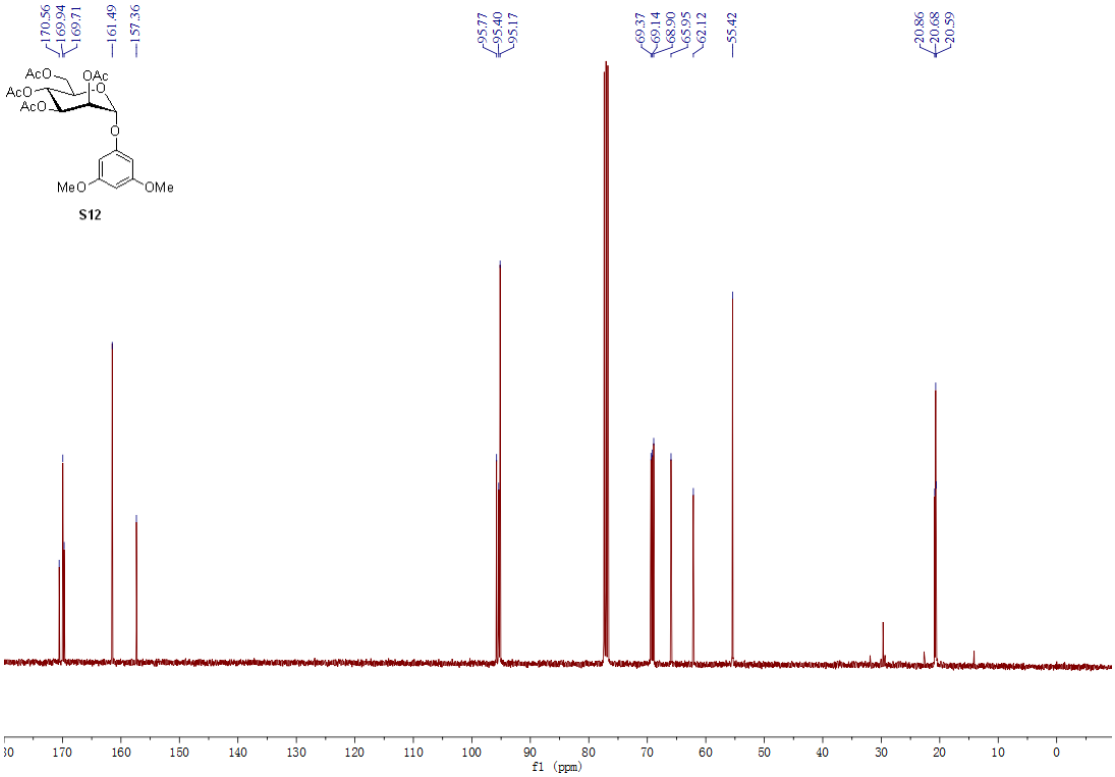
^{1}H NMR spectrum of compound S11



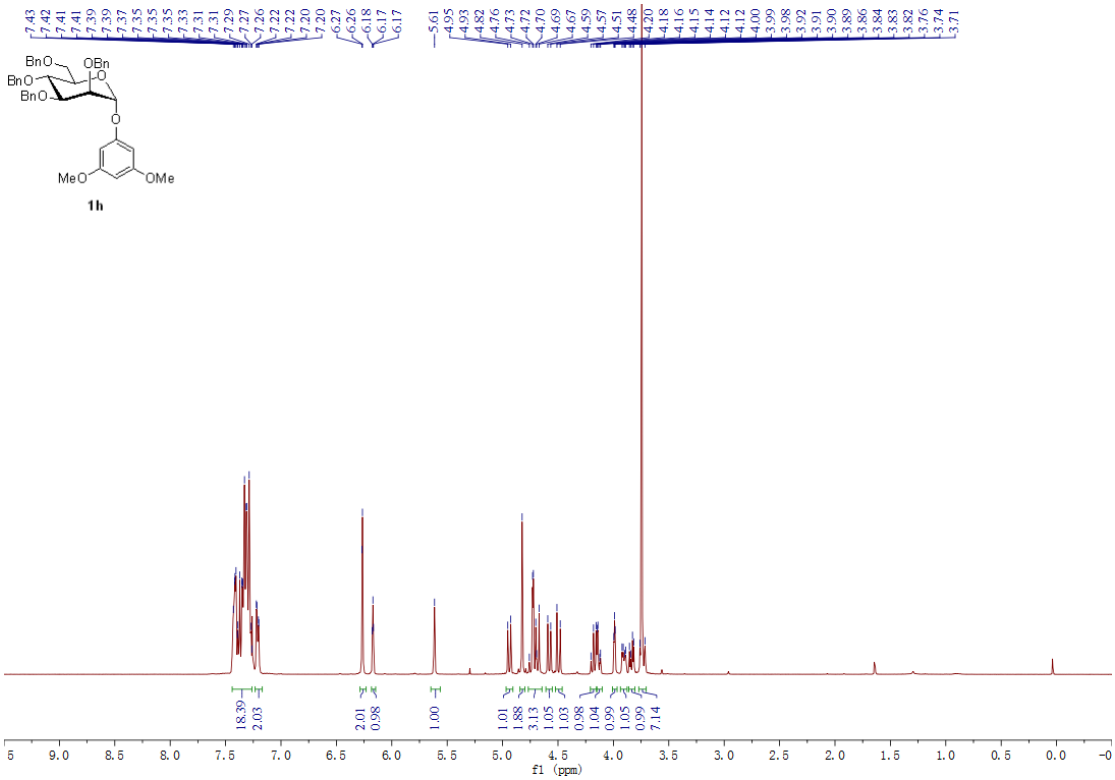
^{13}C NMR spectrum of compound S11



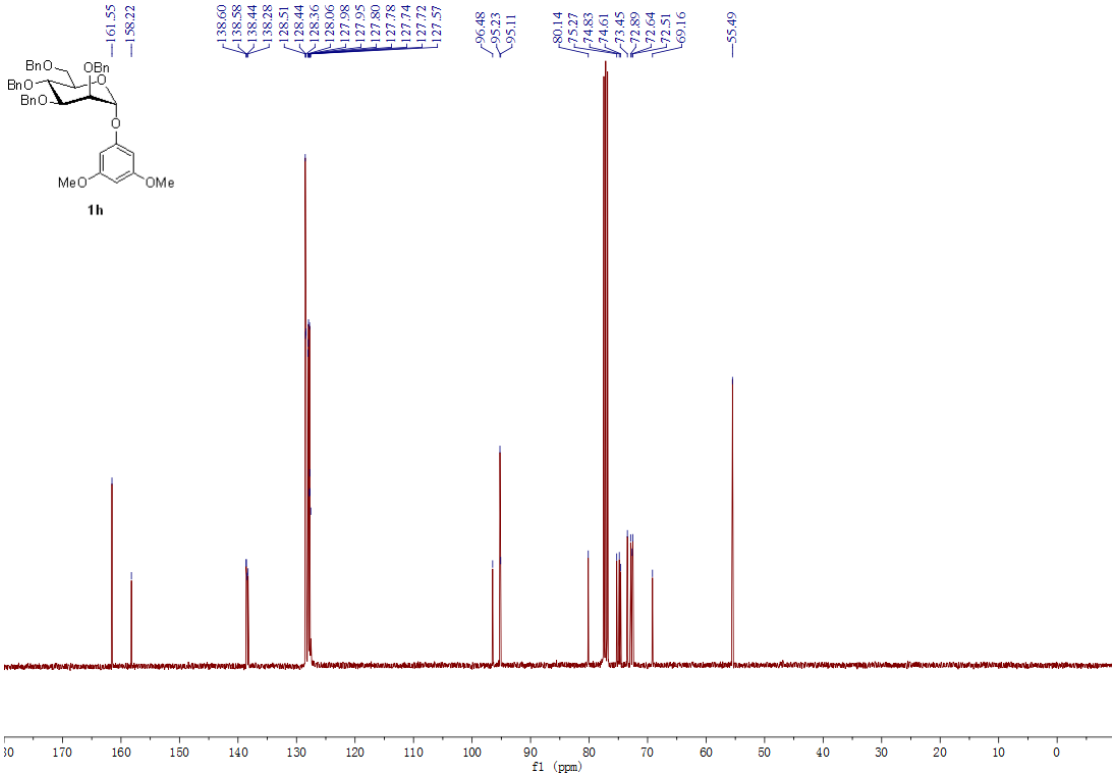
^{1}H NMR spectrum of compound S12



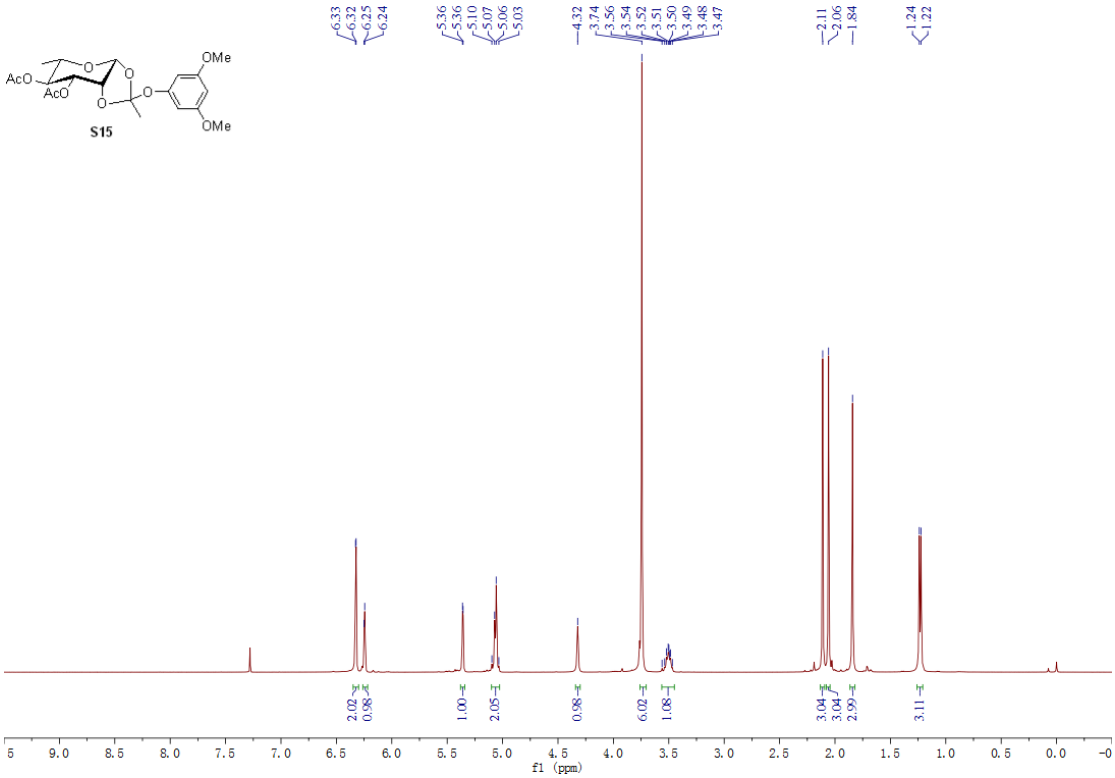
^{13}C NMR spectrum of compound S12



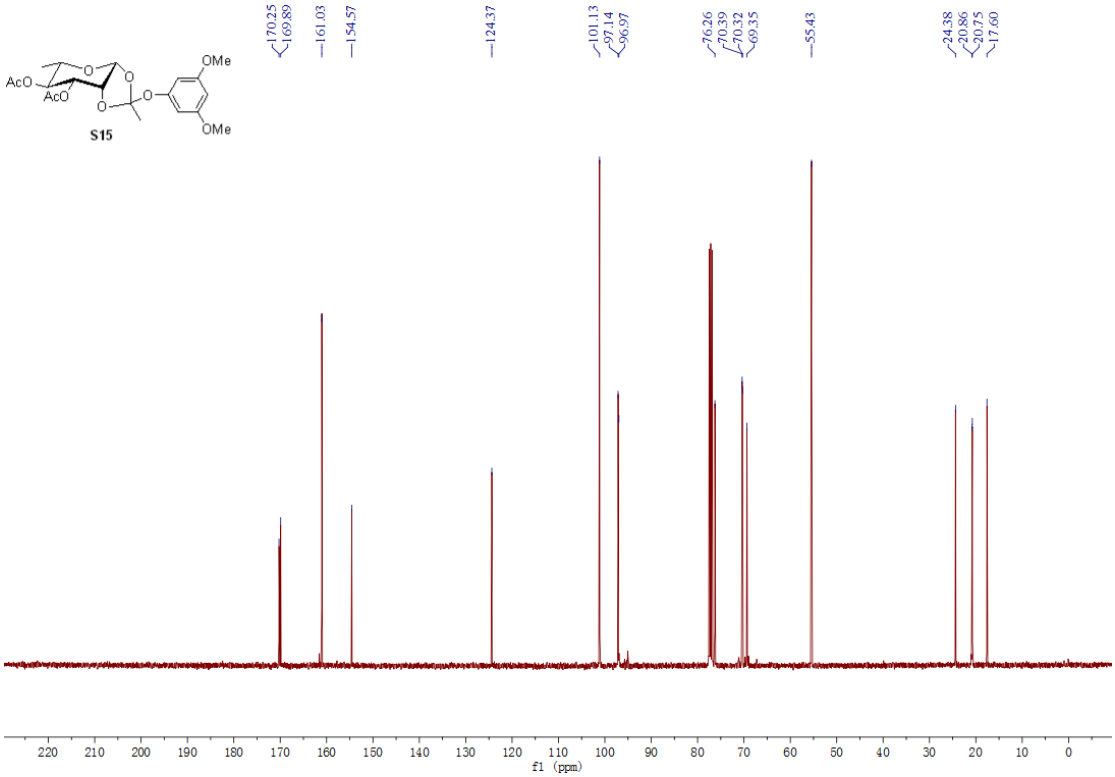
^{1}H NMR spectrum of compound 1h



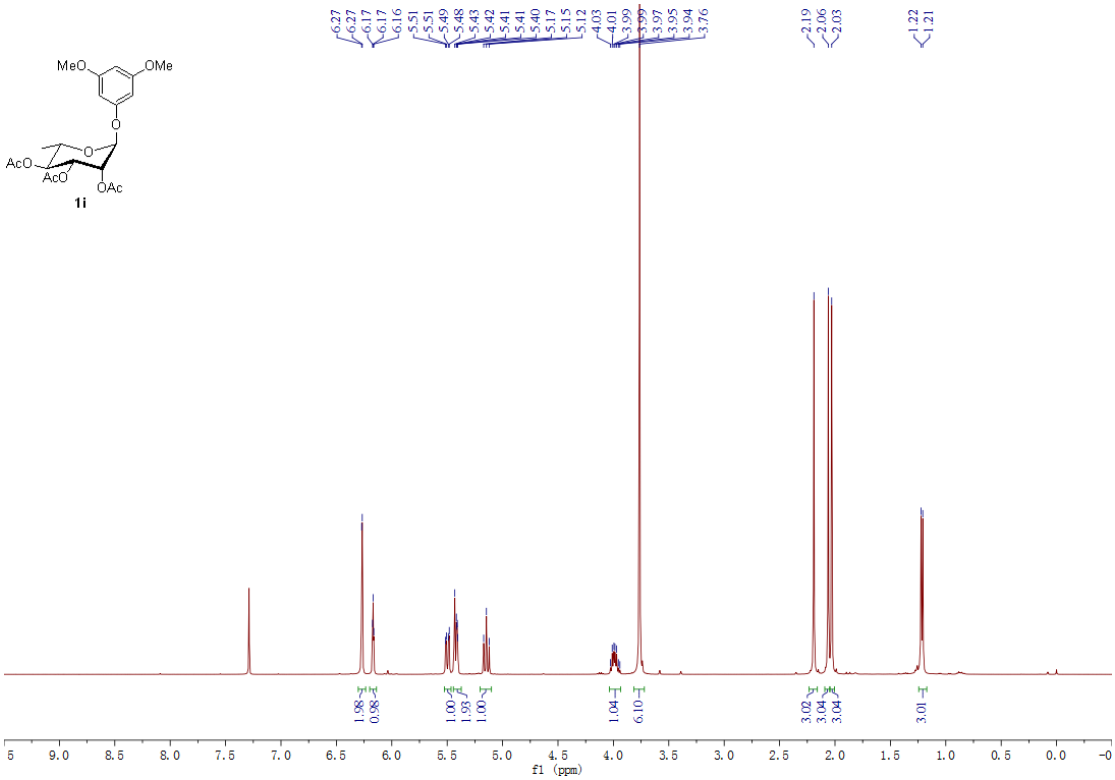
^{13}C NMR spectrum of compound 1h



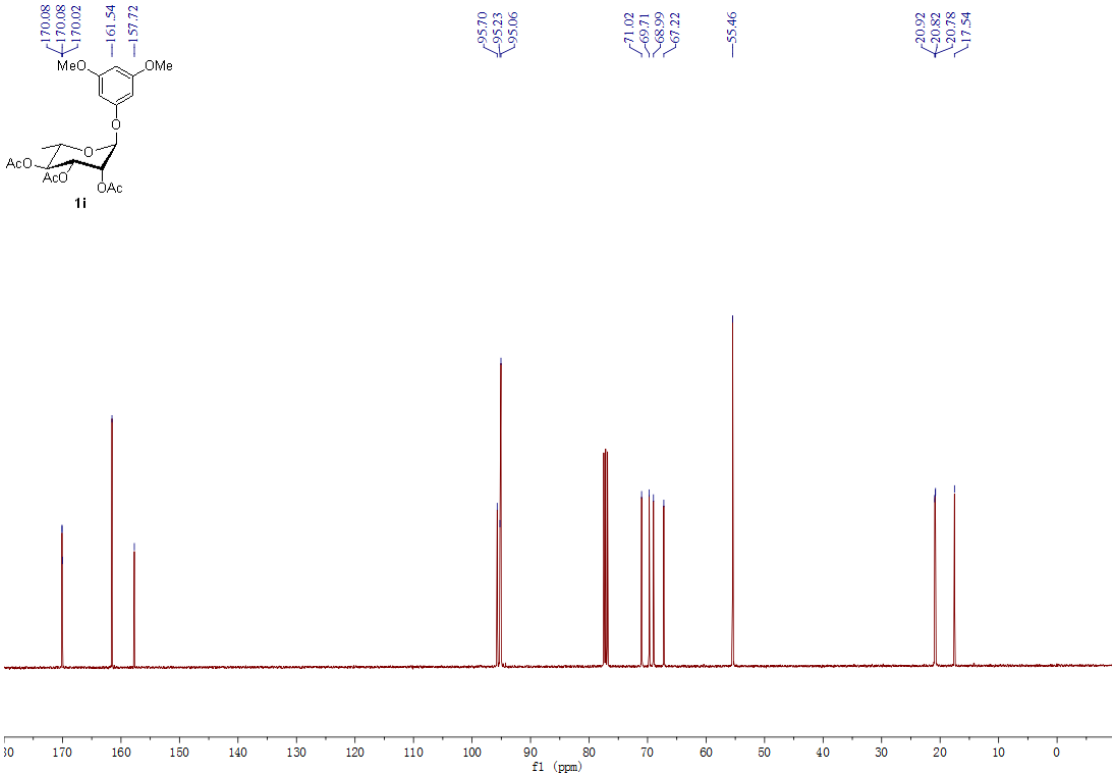
^{1}H NMR spectrum of compound S15



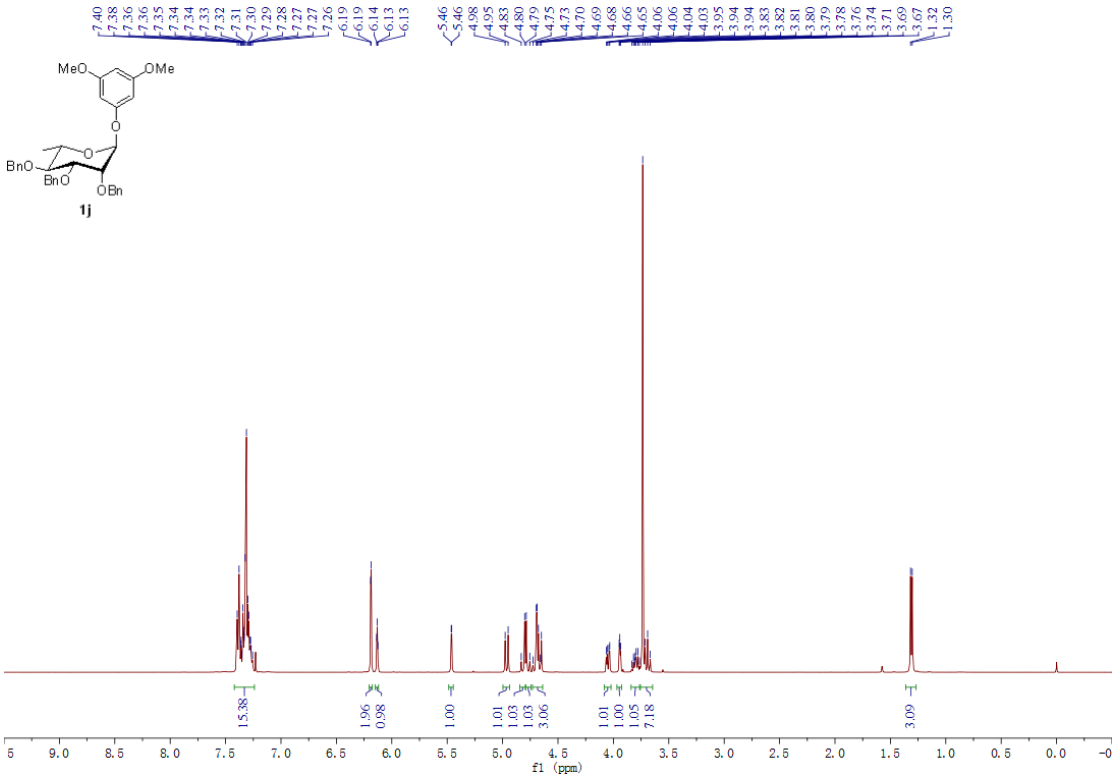
^{13}C NMR spectrum of compound S15



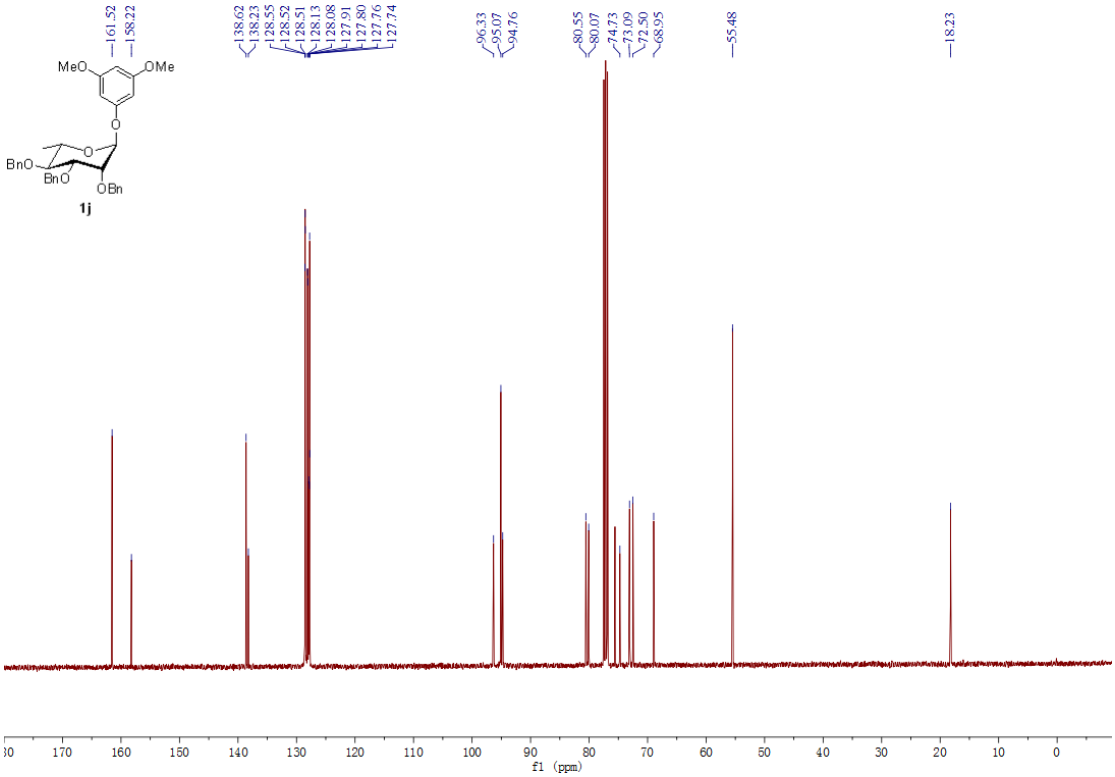
^{1}H NMR spectrum of compound 1i



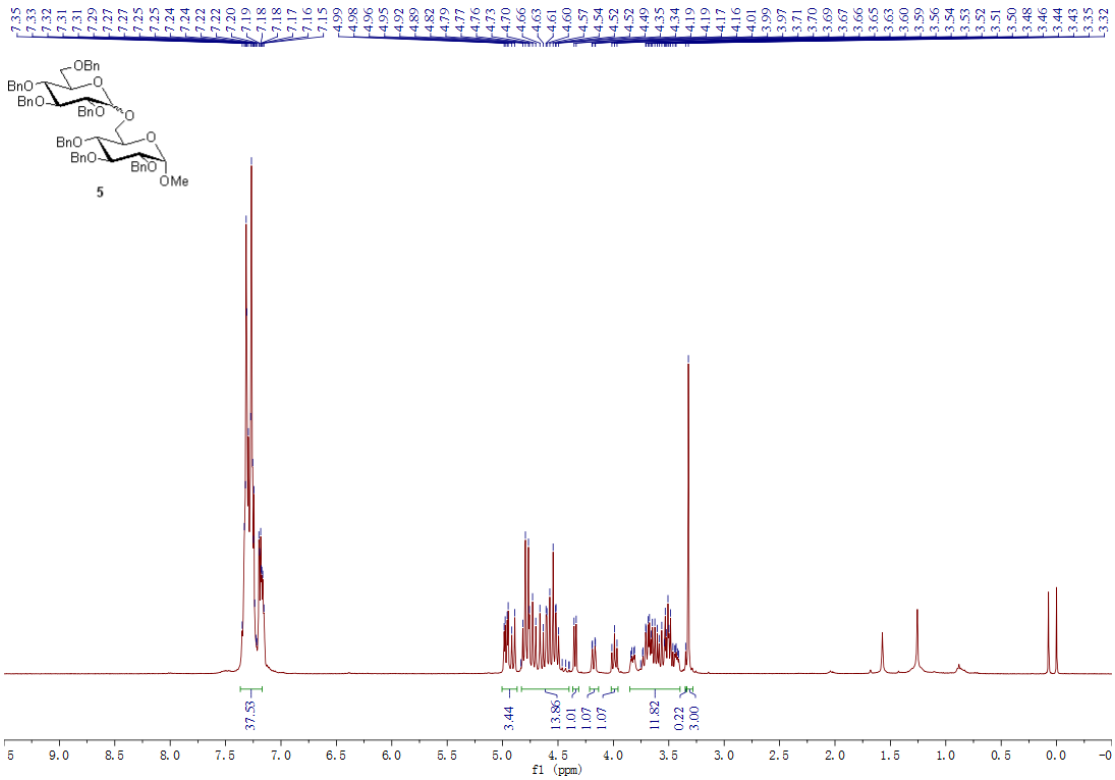
^{13}C NMR spectrum of compound 1i



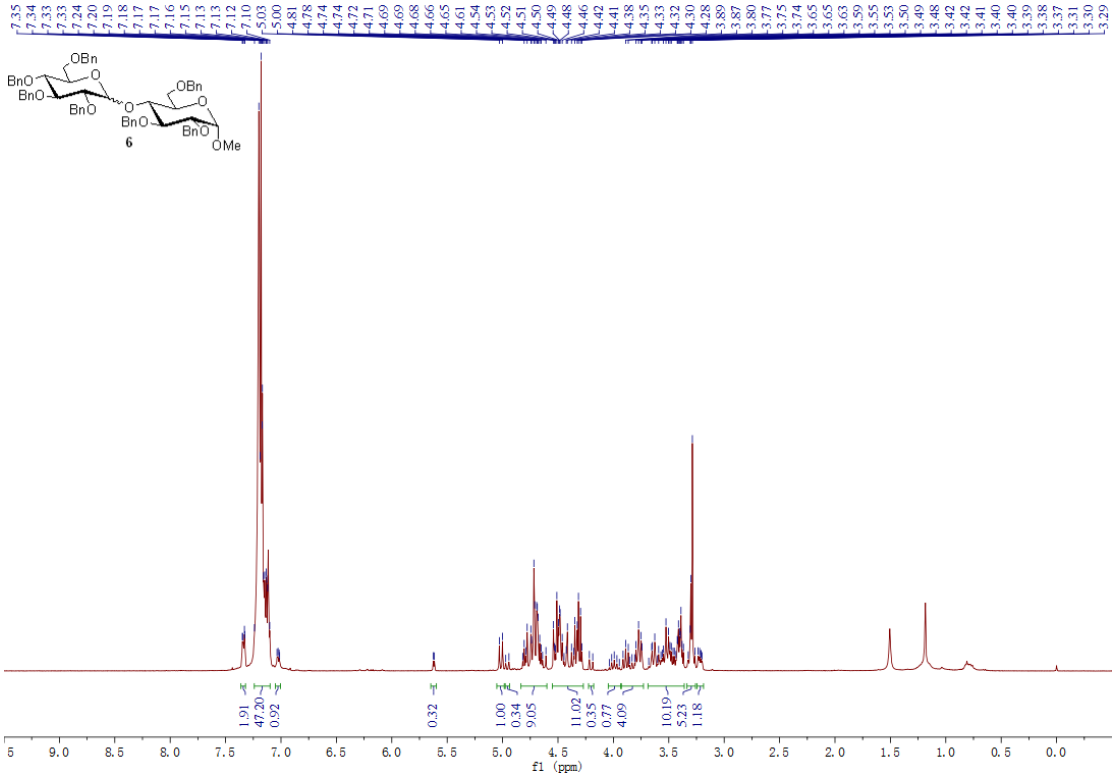
^{1}H NMR spectrum of compound 1j



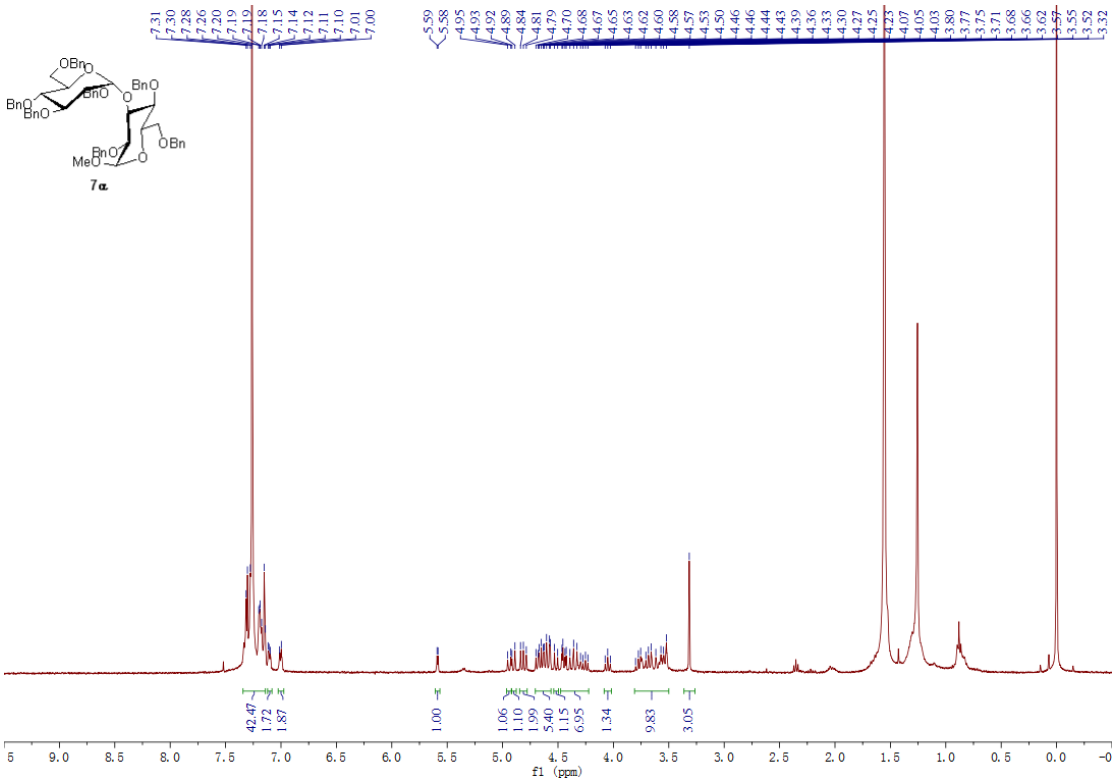
^{13}C NMR spectrum of compound 1j



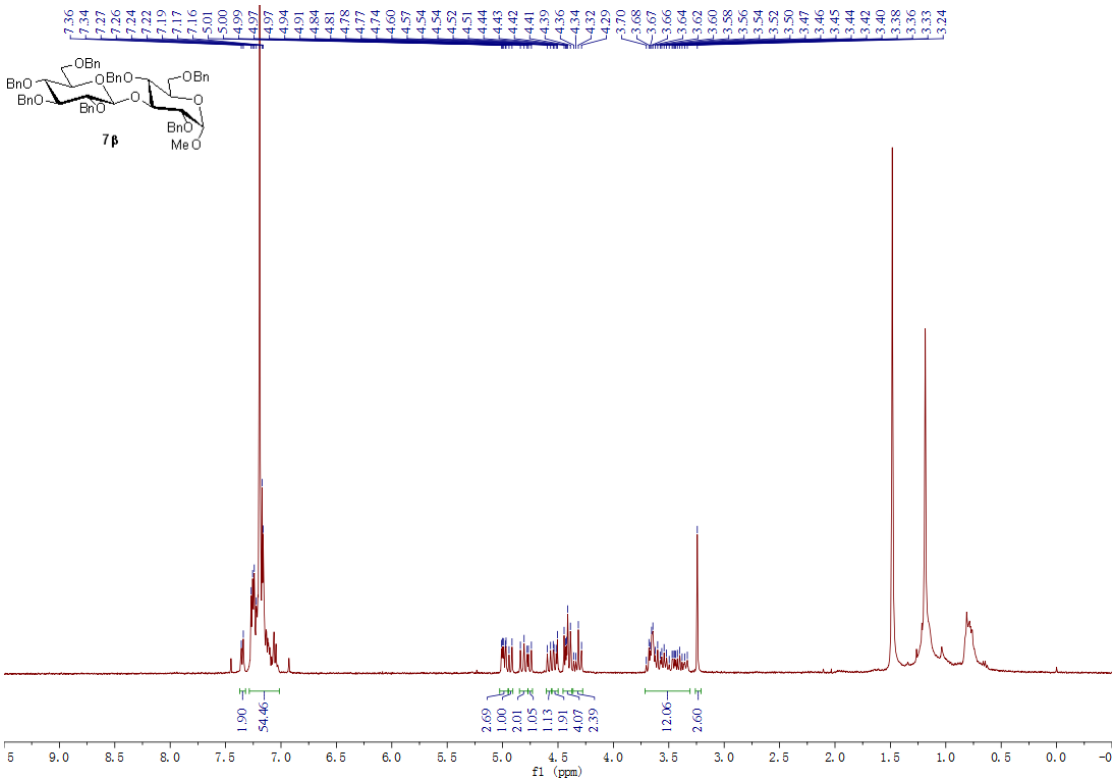
^{1}H NMR spectrum of compound 5



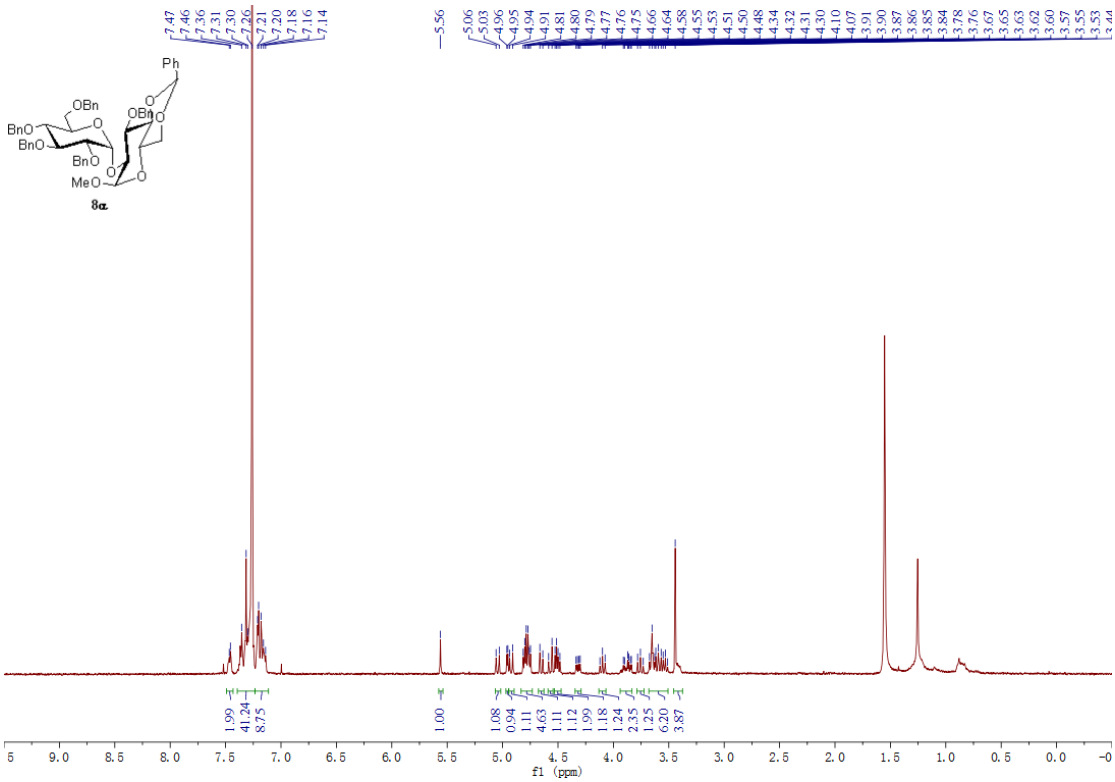
^{1}H NMR spectrum of compound 6



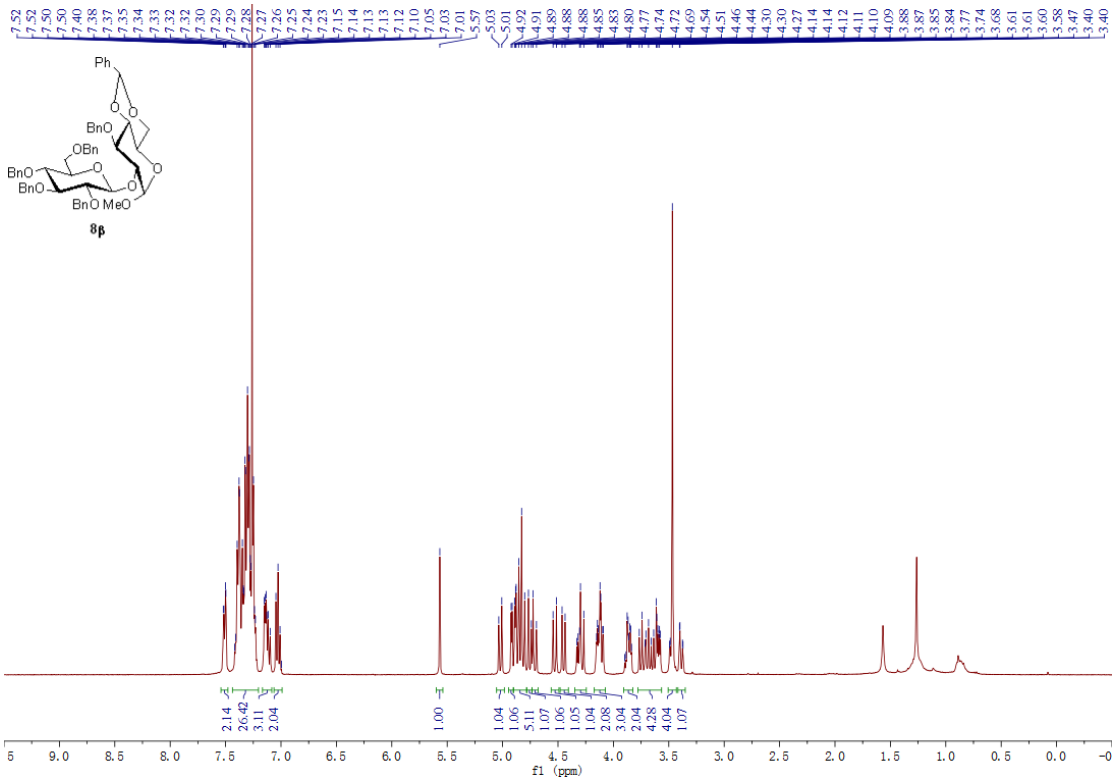
^{1}H NMR spectrum of compound 7α



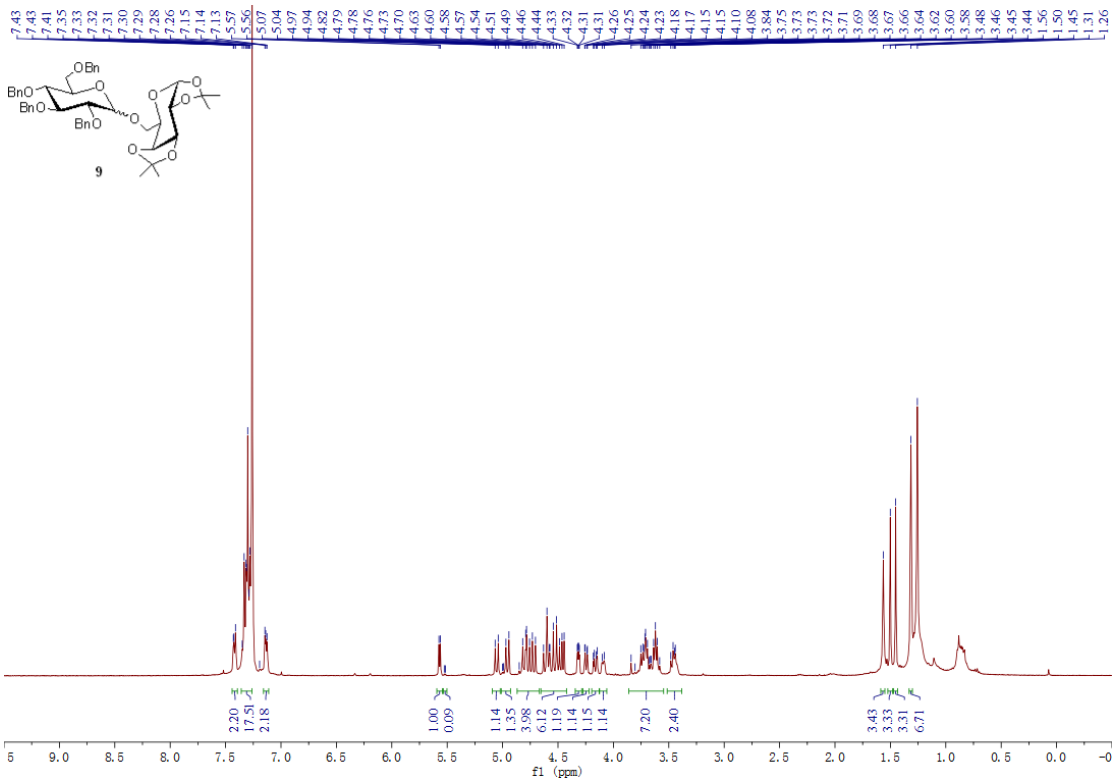
^{1}H NMR spectrum of compound 7β



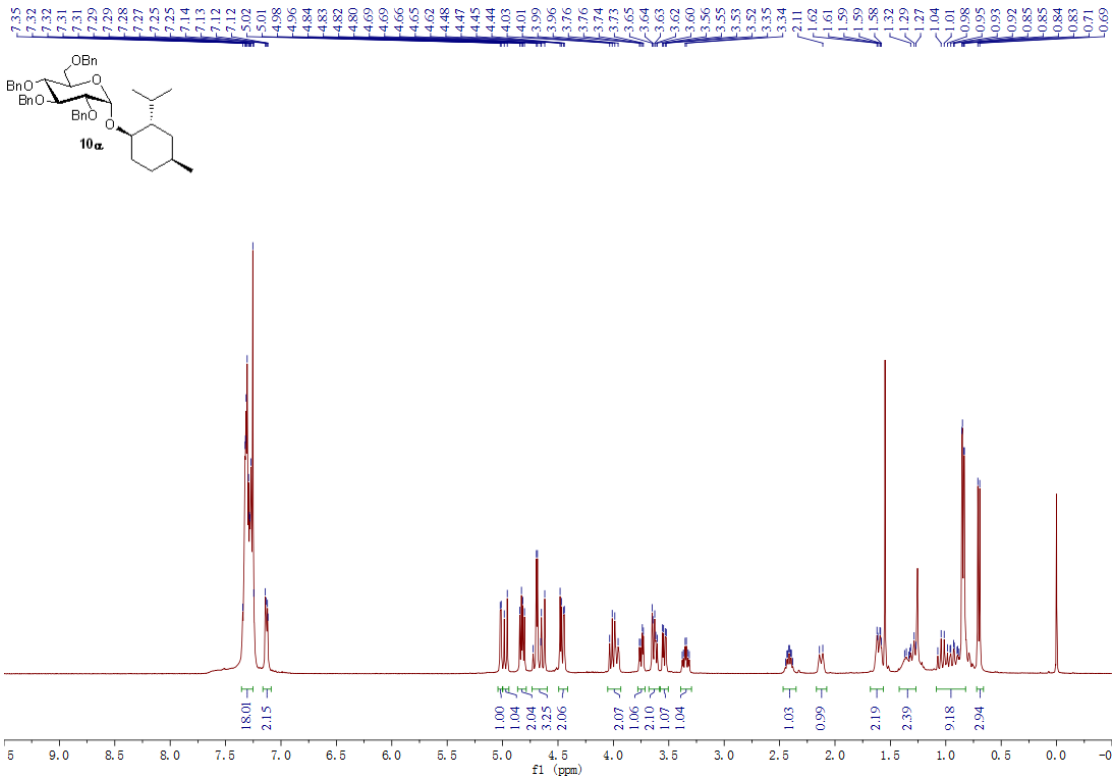
^{1}H NMR spectrum of compound 8α



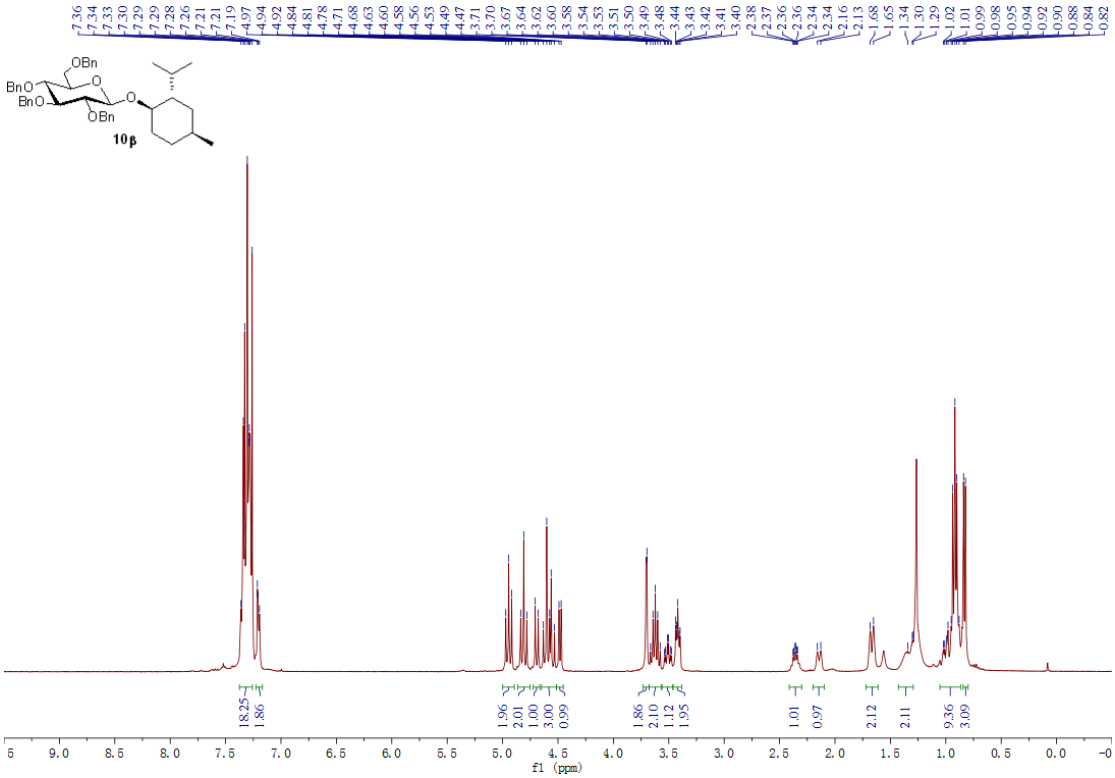
^{1}H NMR spectrum of compound 8β



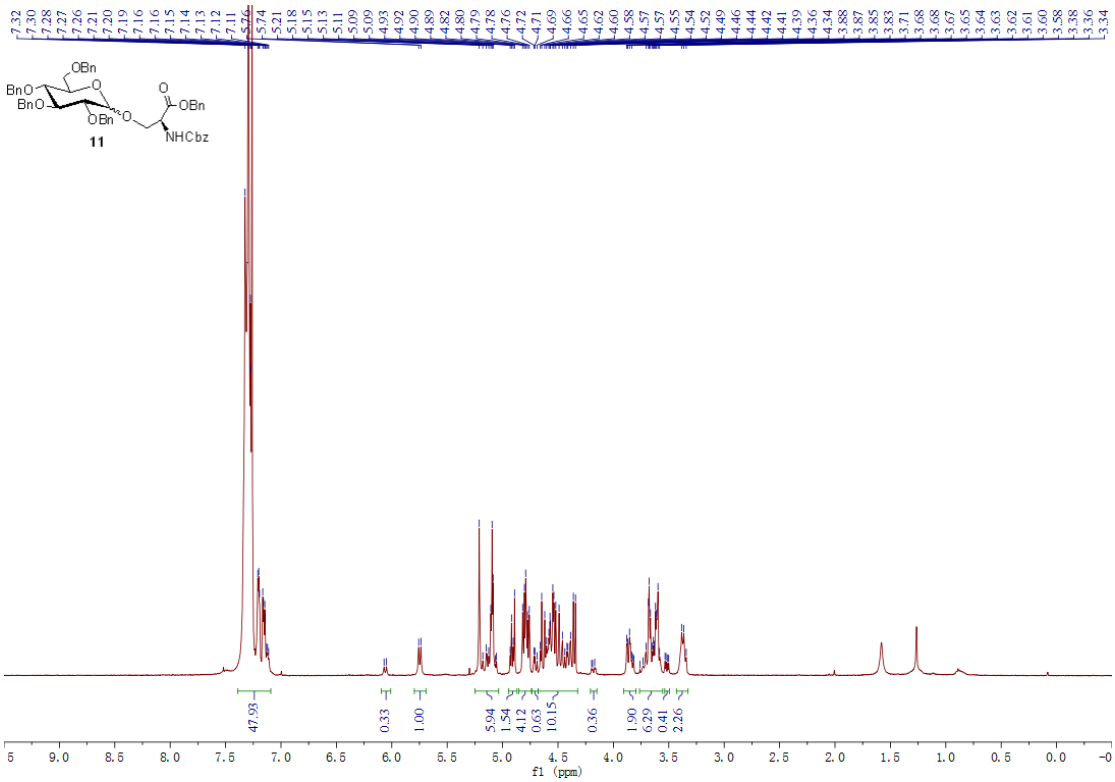
^{1}H NMR spectrum of compound 9



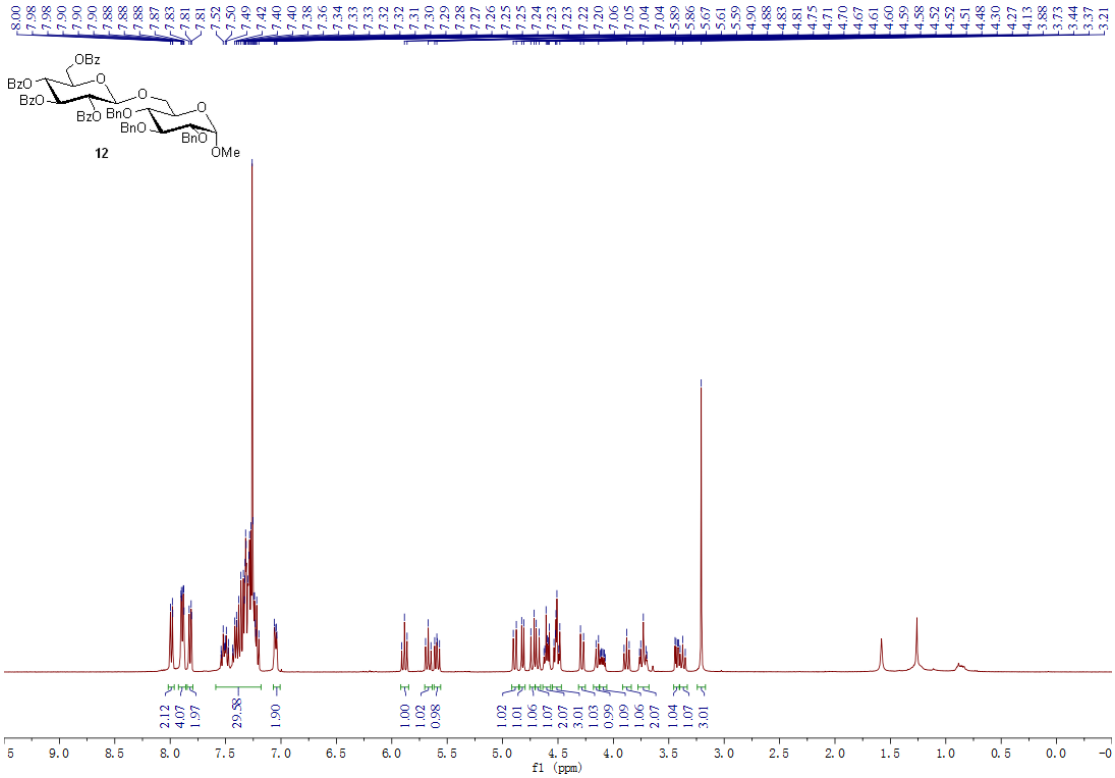
^{1}H NMR spectrum of compound 10α



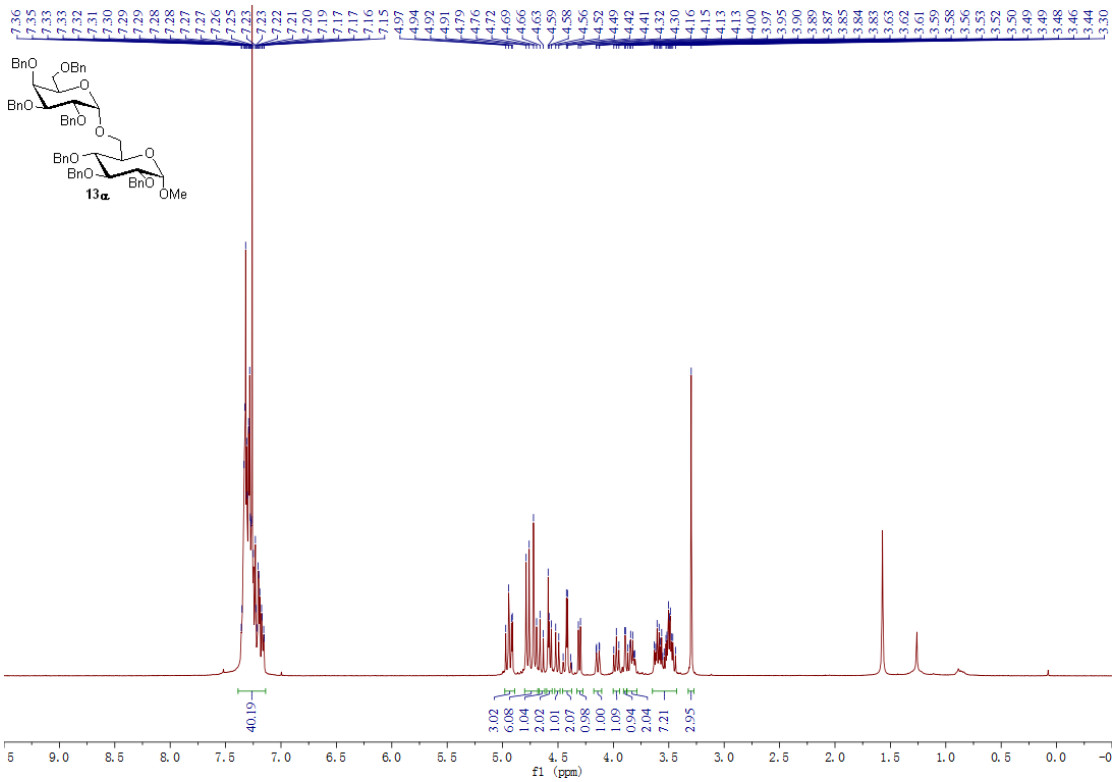
^{1}H NMR spectrum of compound 10β



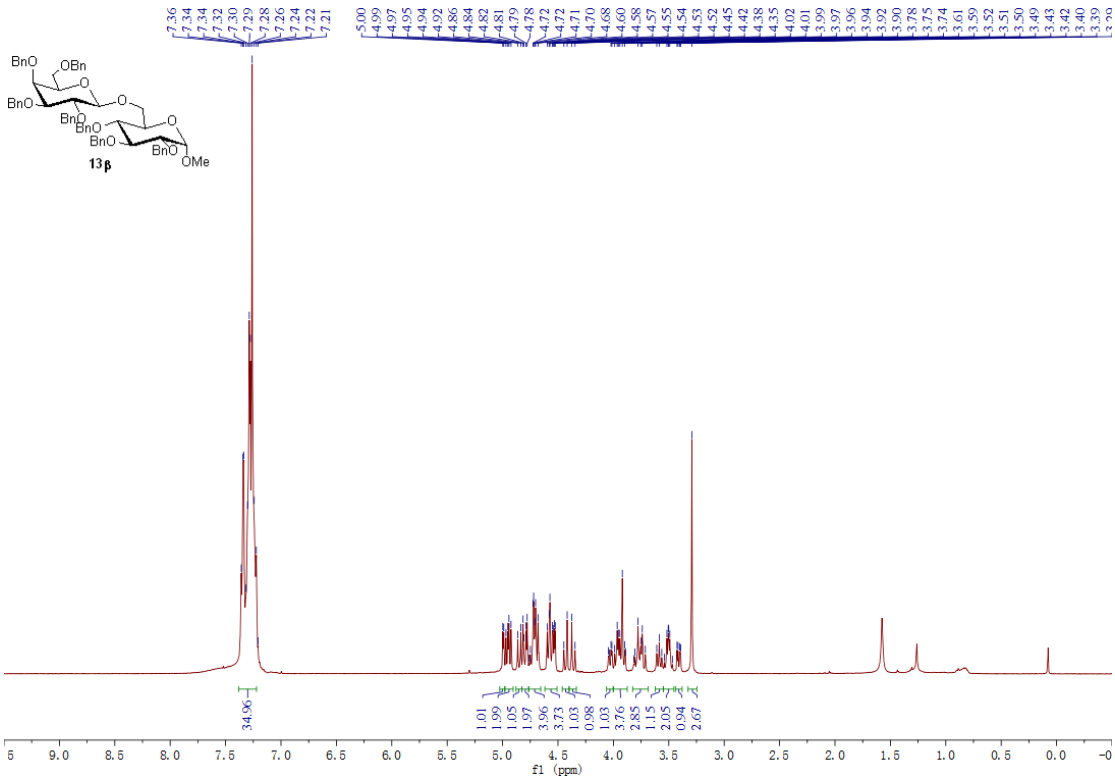
^{1}H NMR spectrum of compound 11



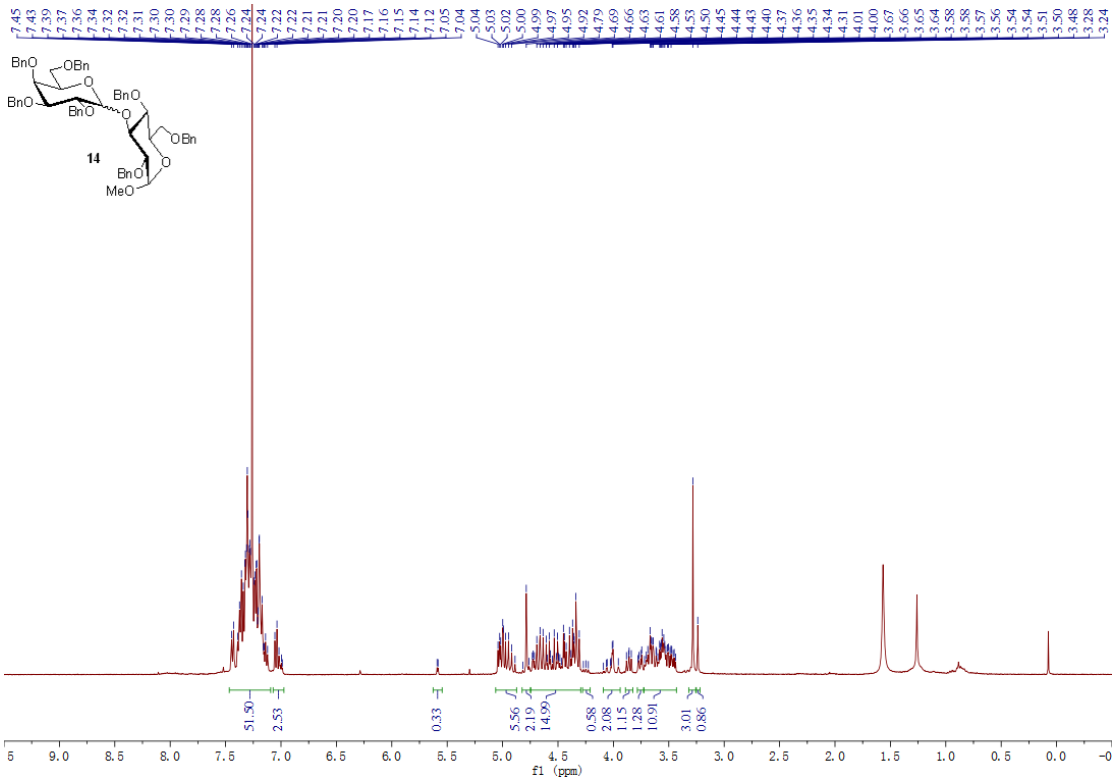
^{1}H NMR spectrum of compound 12



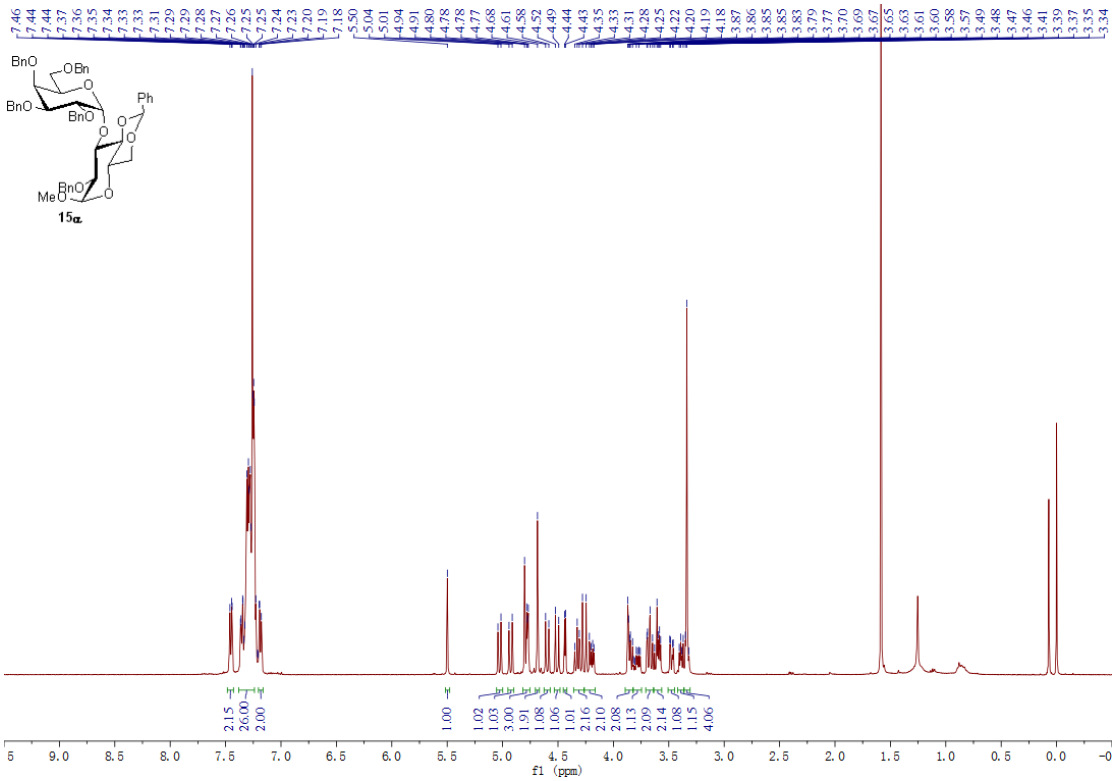
^{1}H NMR spectrum of compound 13α



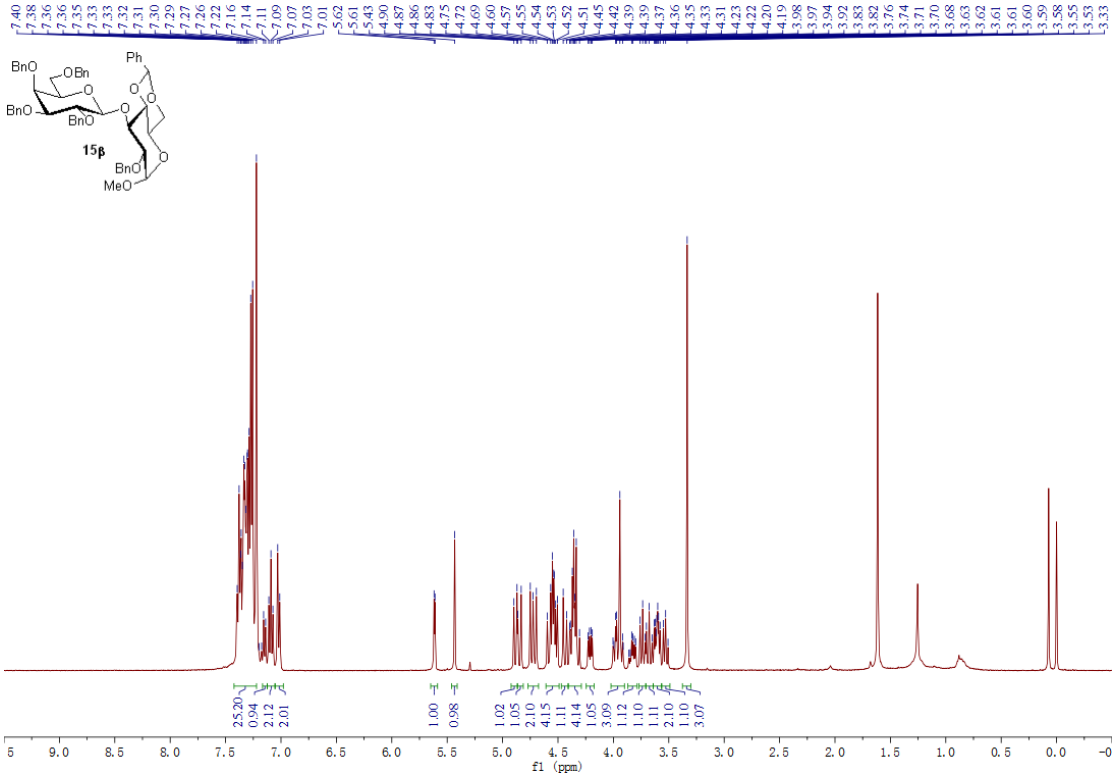
^{1}H NMR spectrum of compound 13β



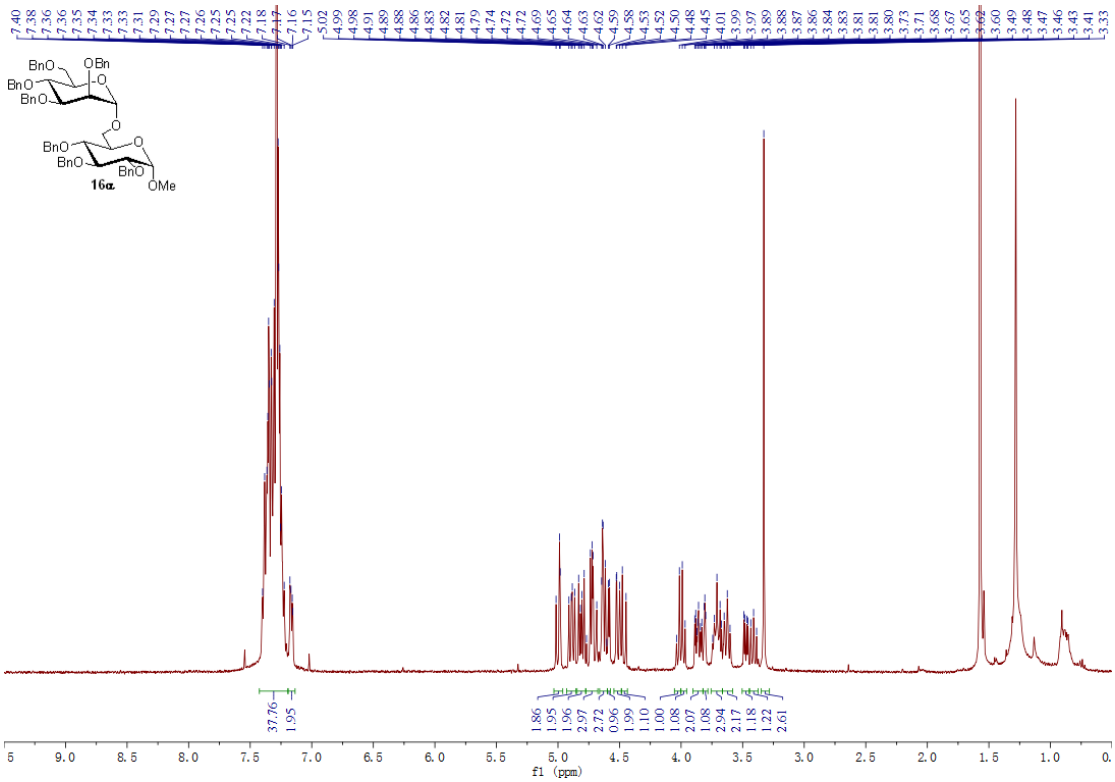
^{1}H NMR spectrum of compound 14



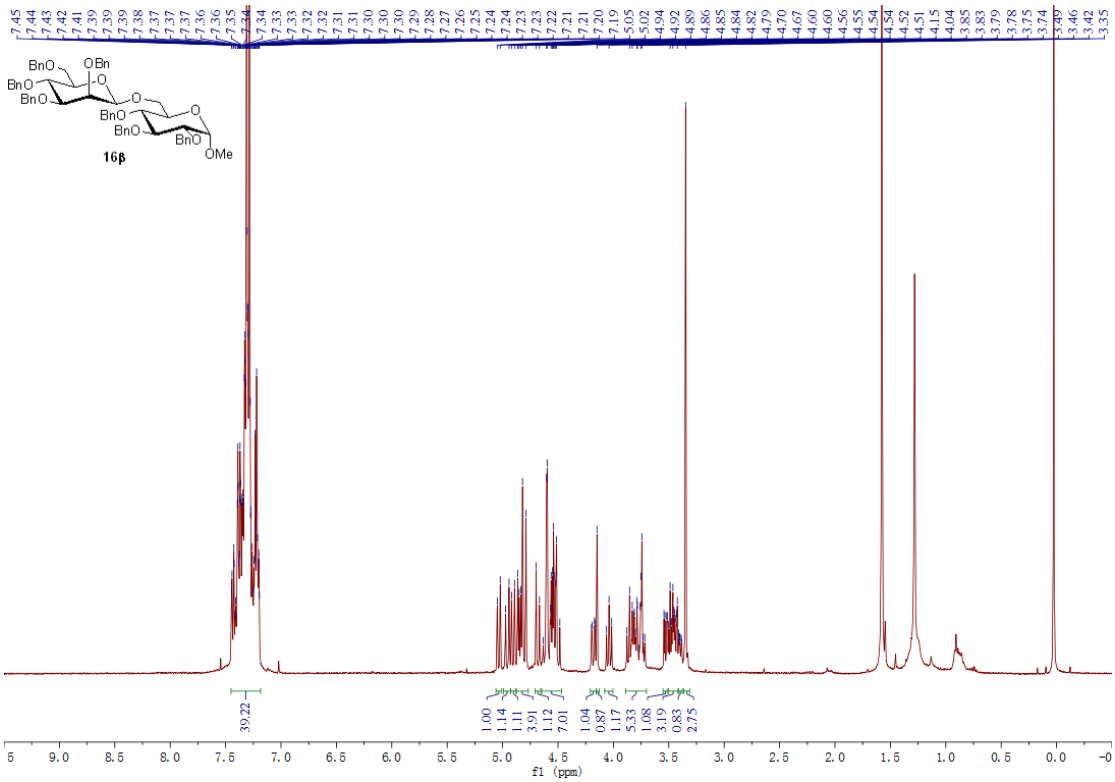
^{1}H NMR spectrum of compound 15α



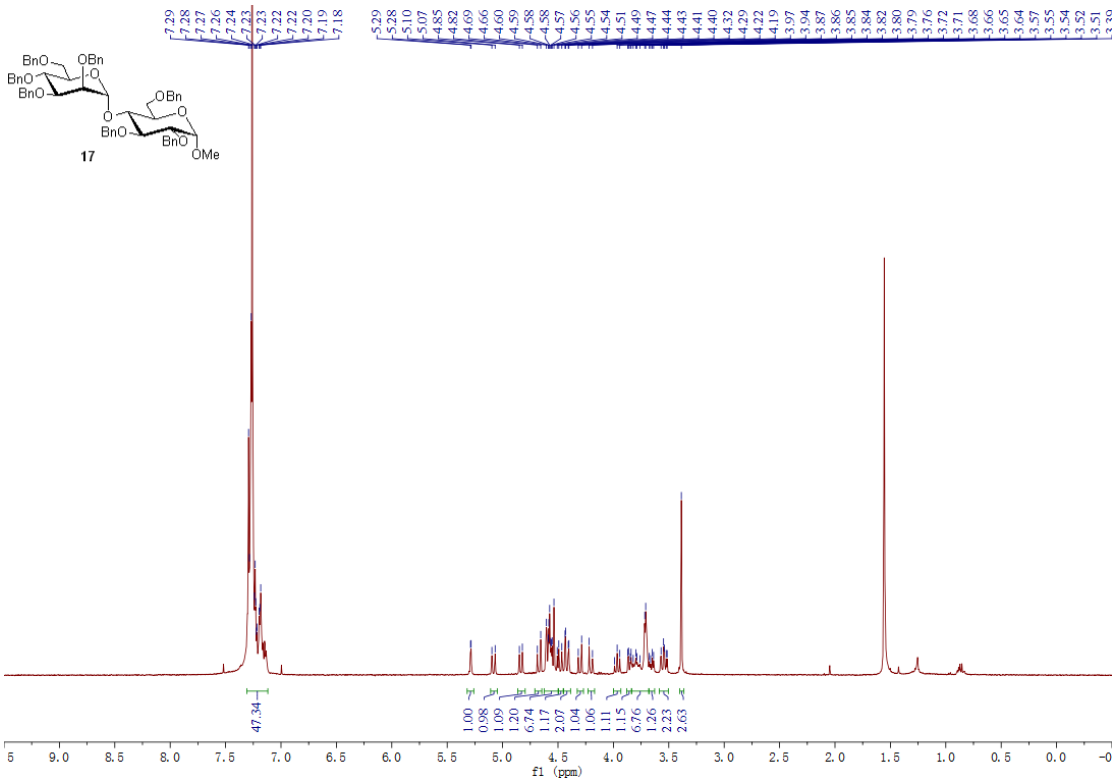
^{1}H NMR spectrum of compound 15β



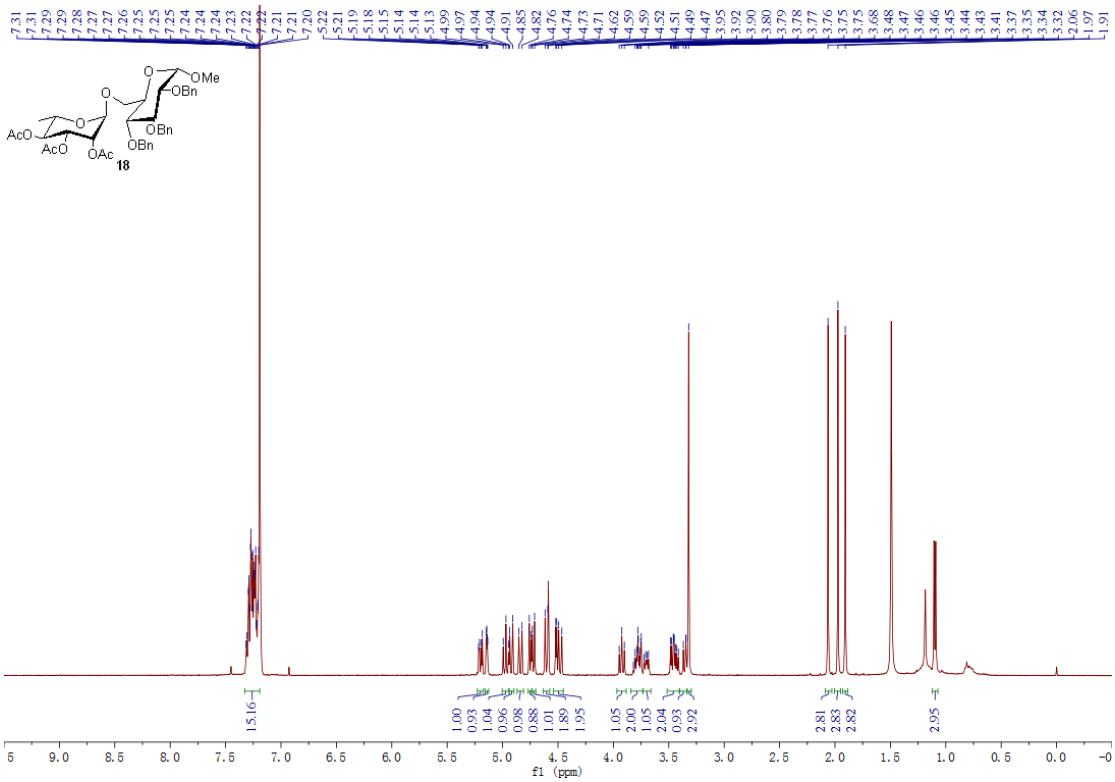
^{1}H NMR spectrum of compound 16α



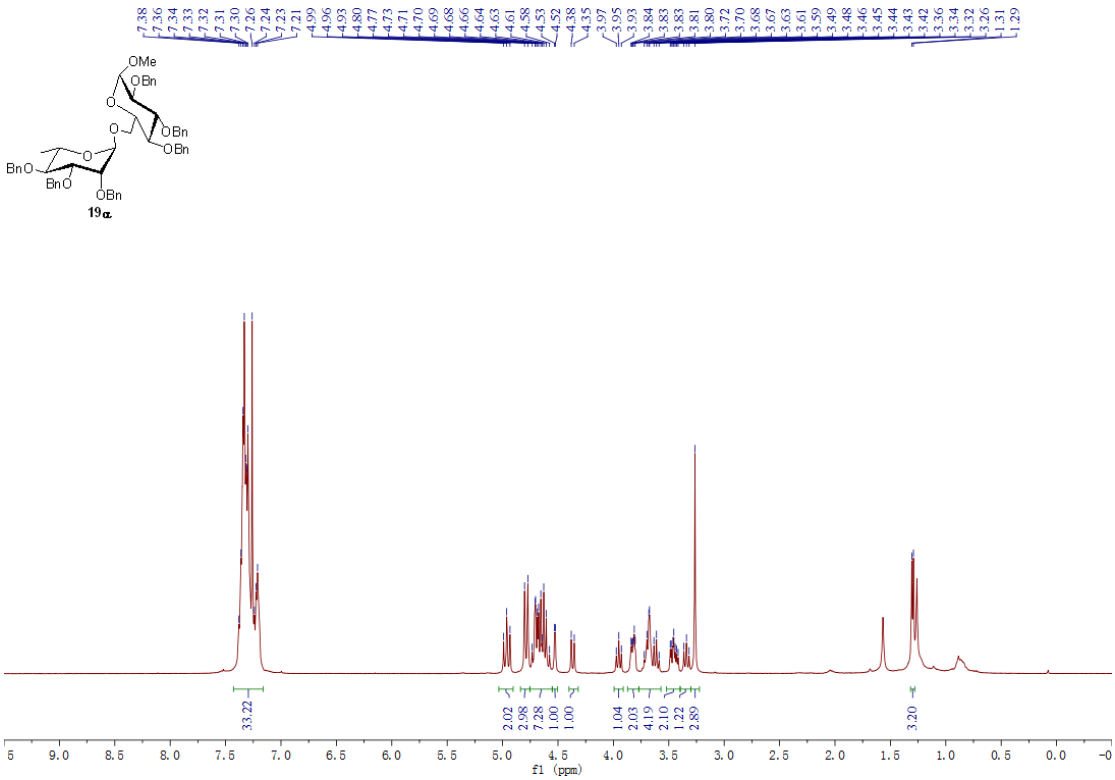
^{1}H NMR spectrum of compound 16β



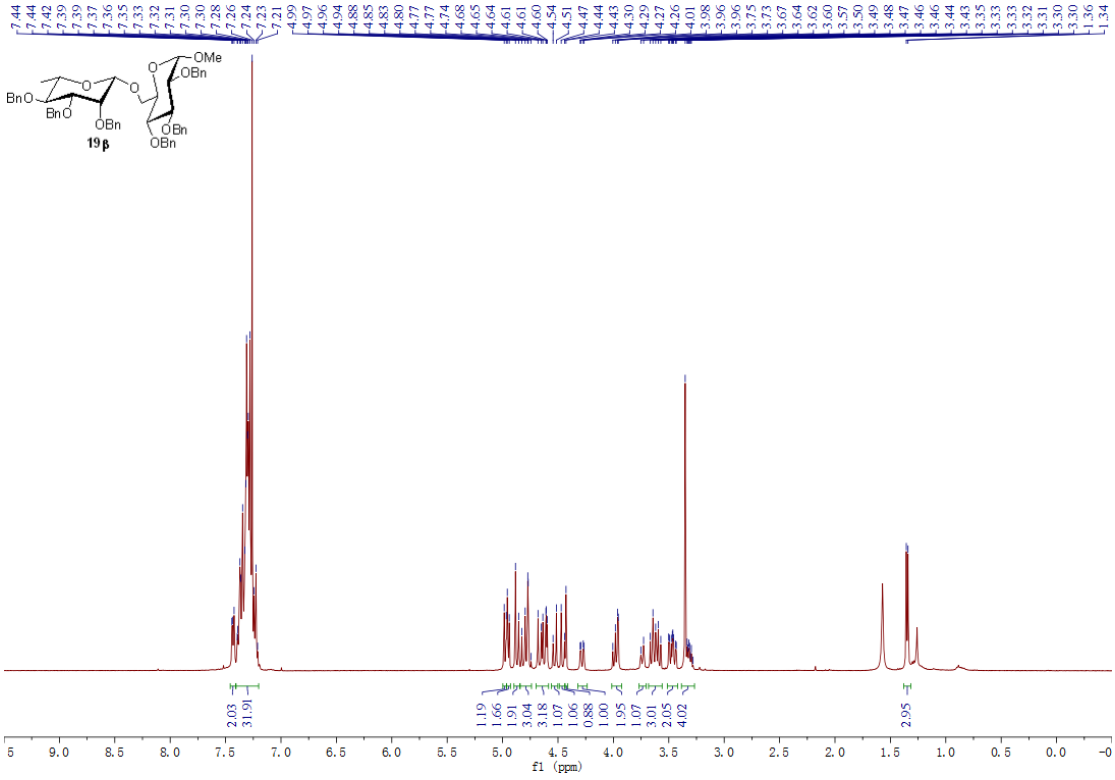
^{1}H NMR spectrum of compound 17



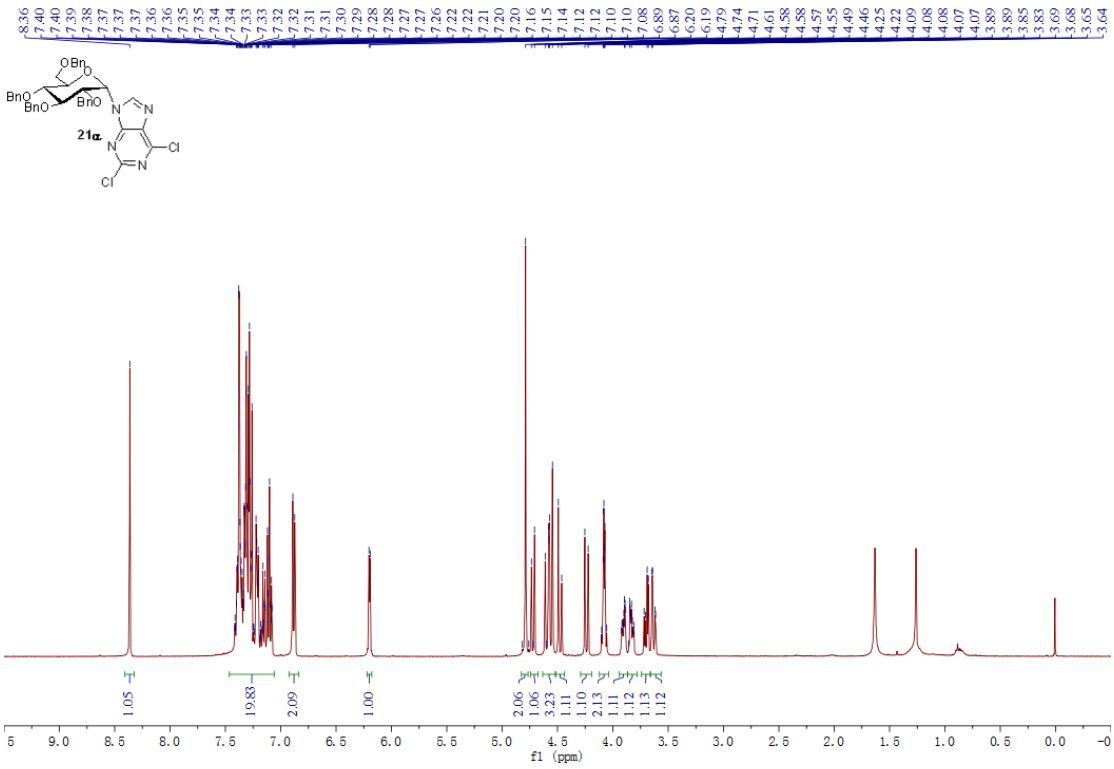
^{1}H NMR spectrum of compound 18



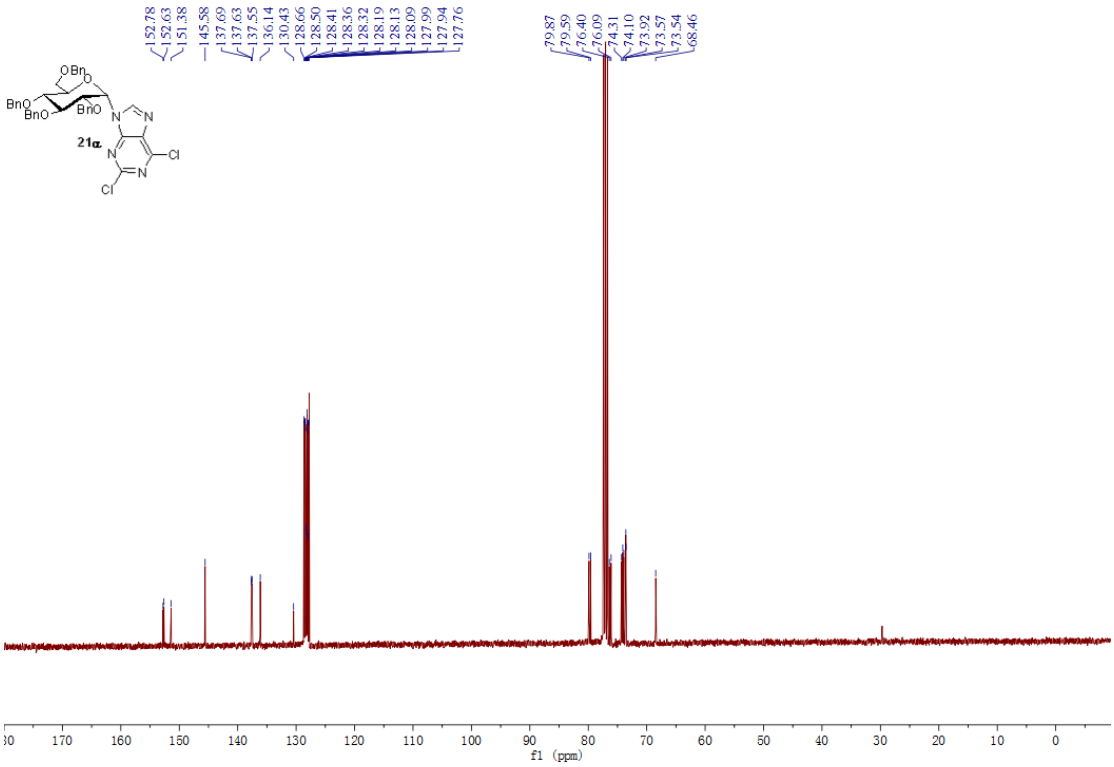
^{1}H NMR spectrum of compound 19α



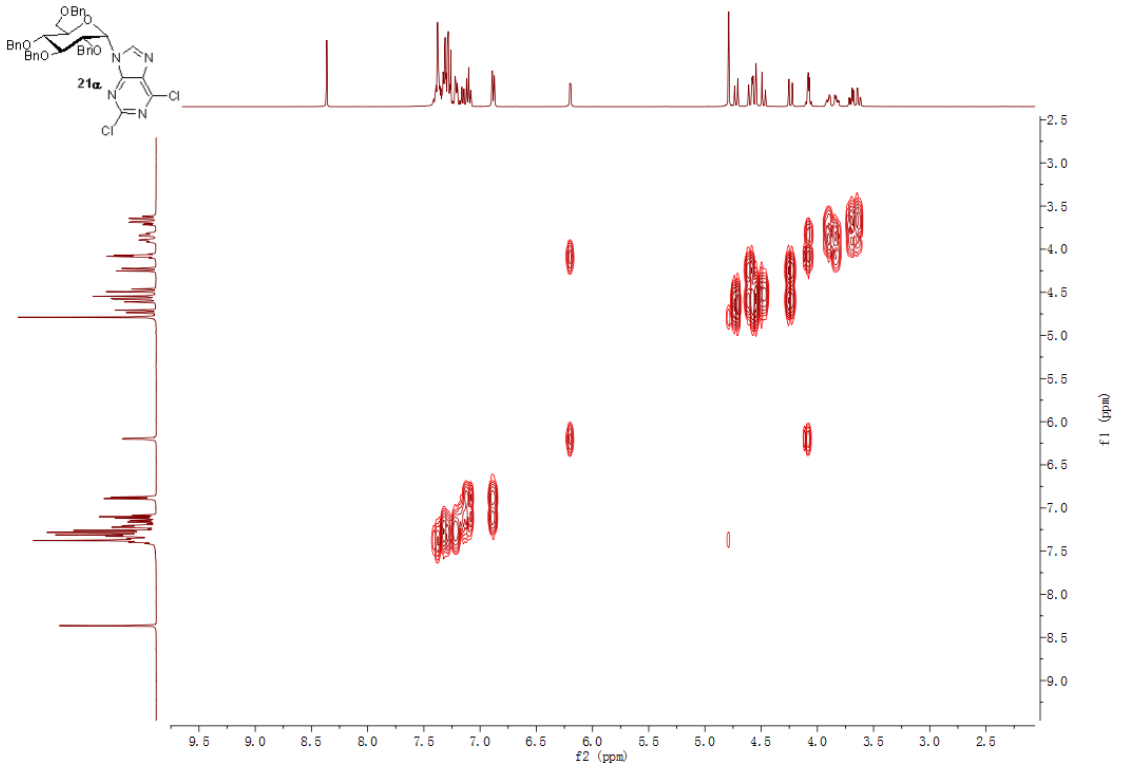
^{1}H NMR spectrum of compound 19β



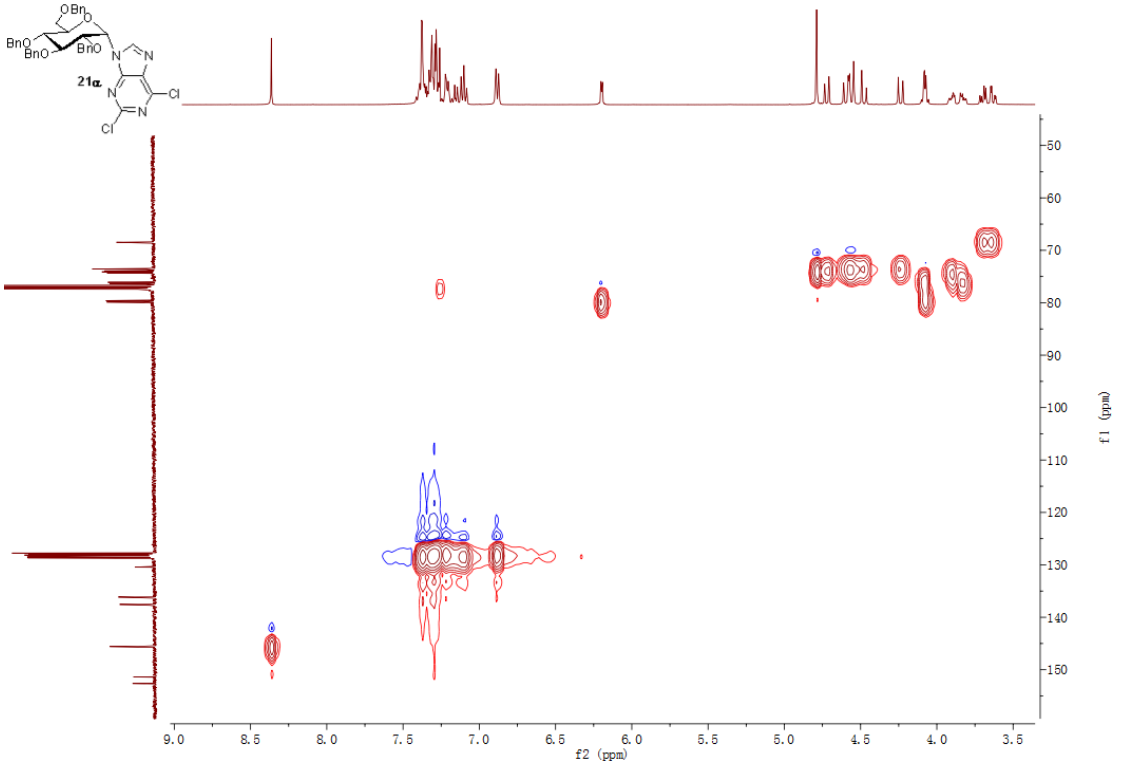
^{1}H NMR spectrum of compound 21α



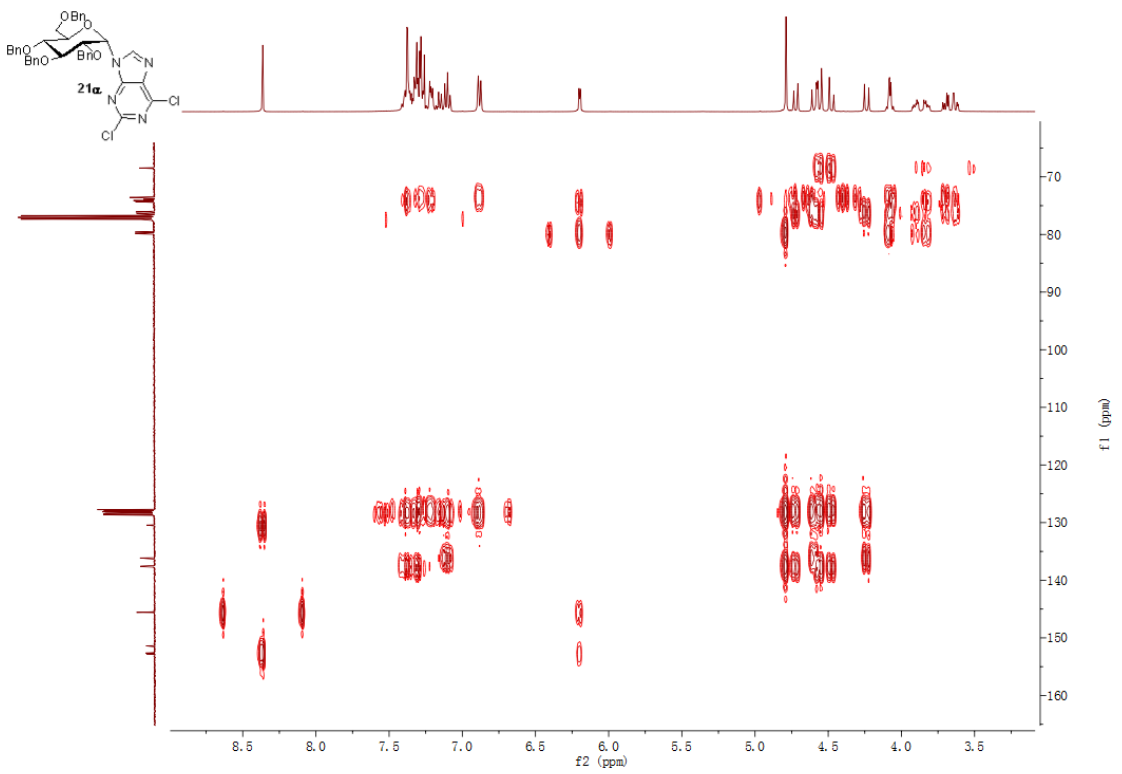
^{13}C NMR spectrum of compound 21α



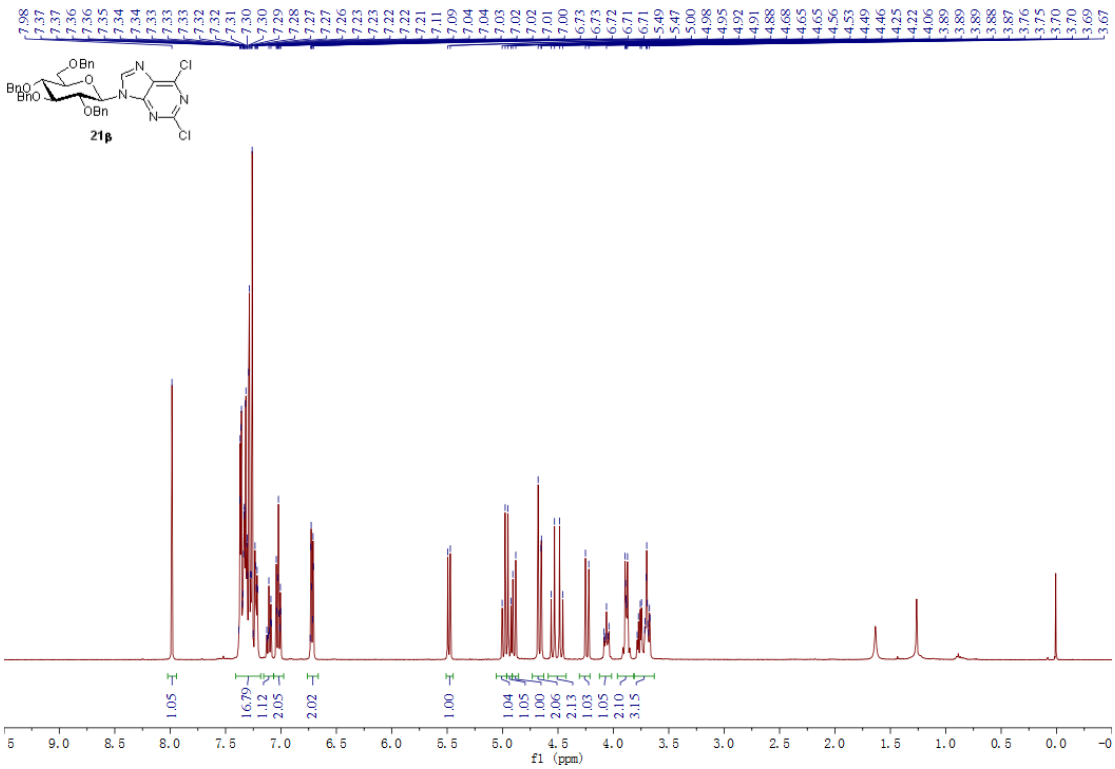
HH-COSY spectrum of compound 21α



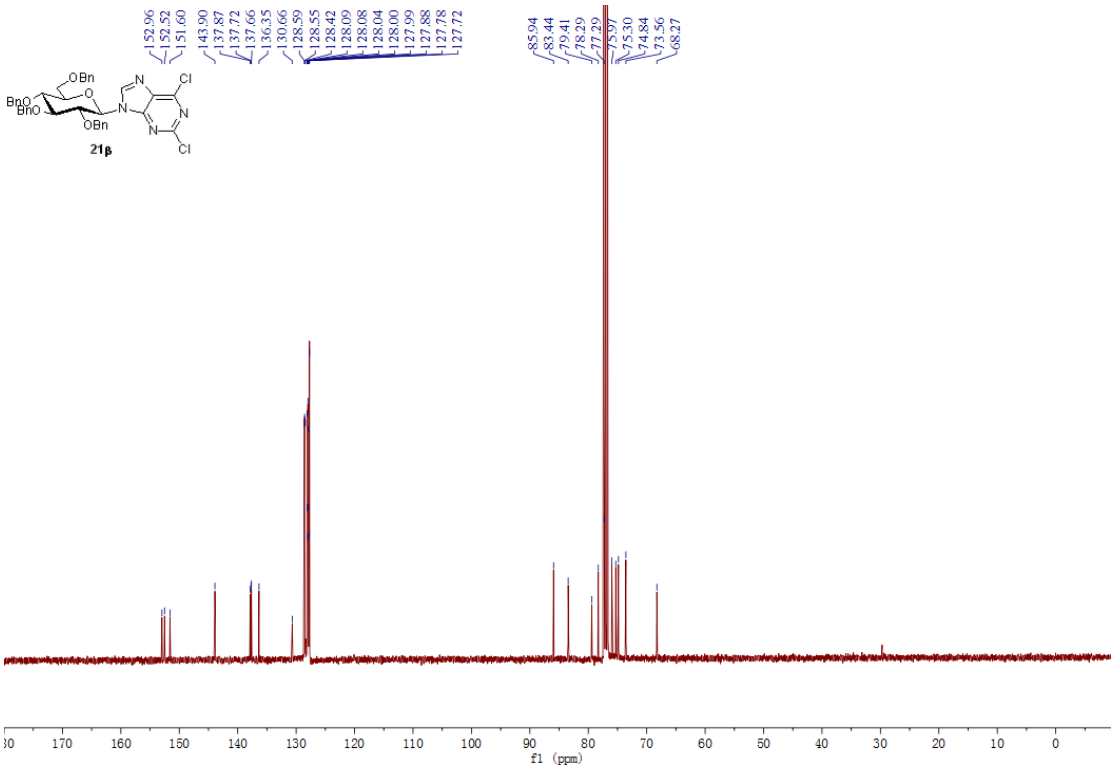
HSQC NMR spectrum of compound 21α



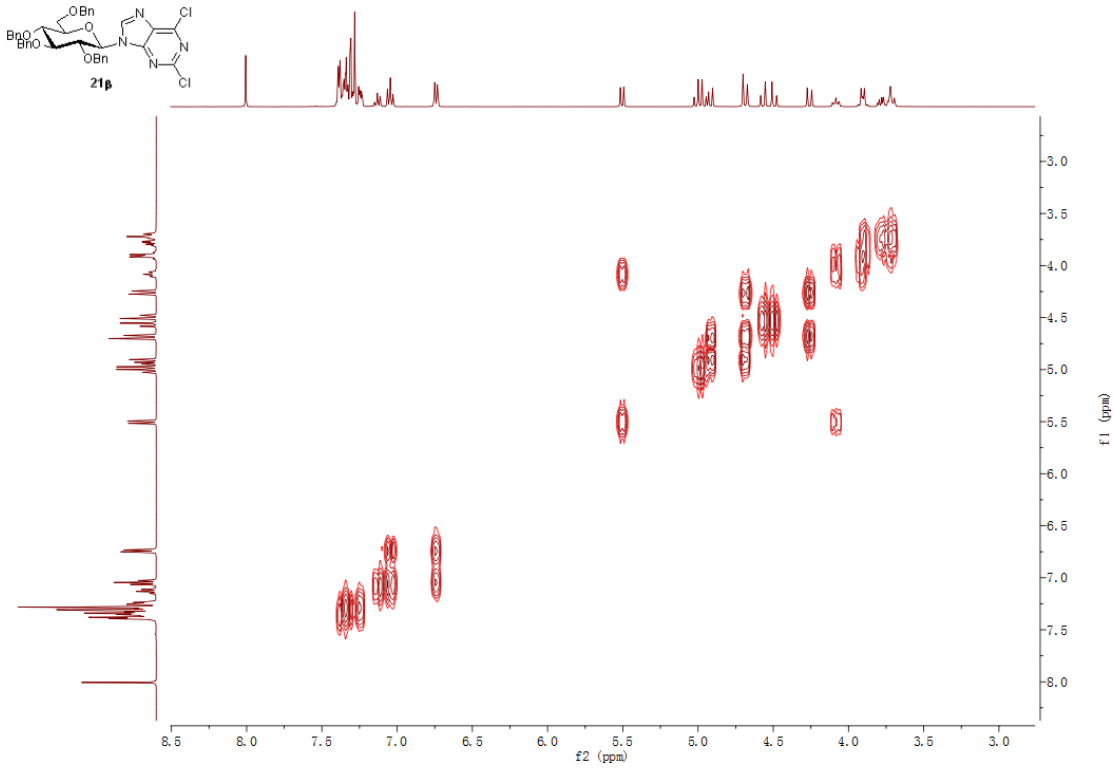
HMBC NMR spectrum of compound 21α



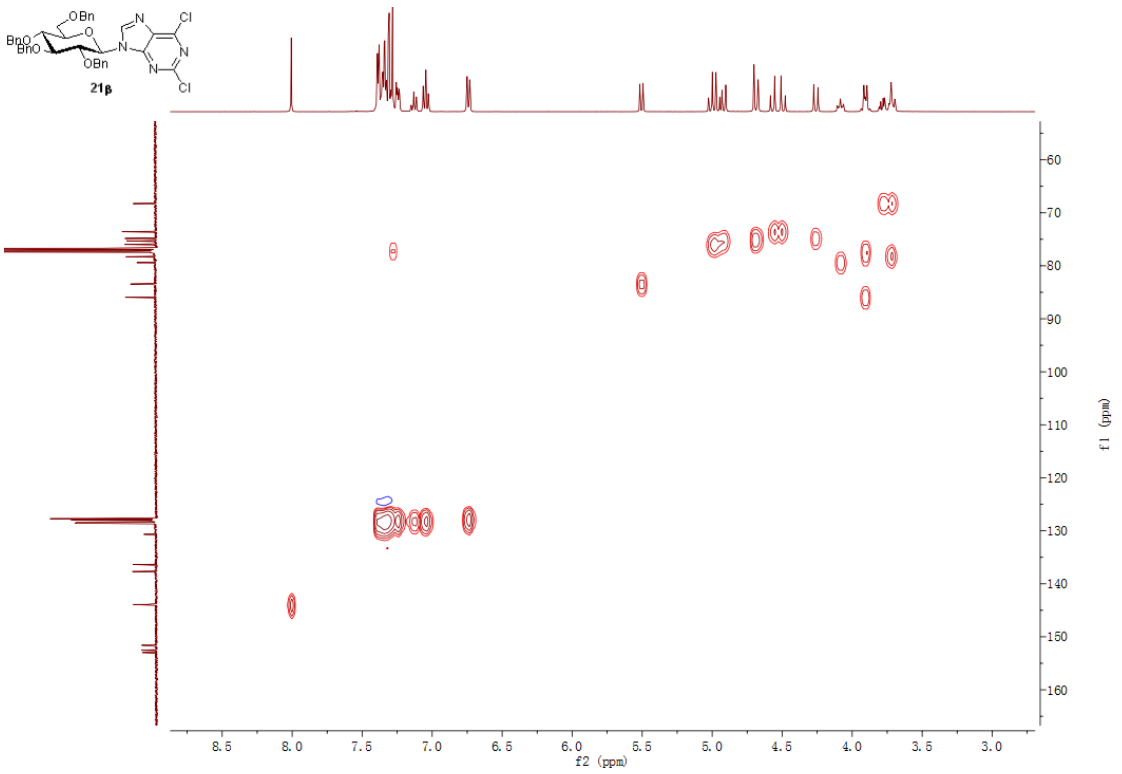
^{1}H NMR spectrum of compound 21β



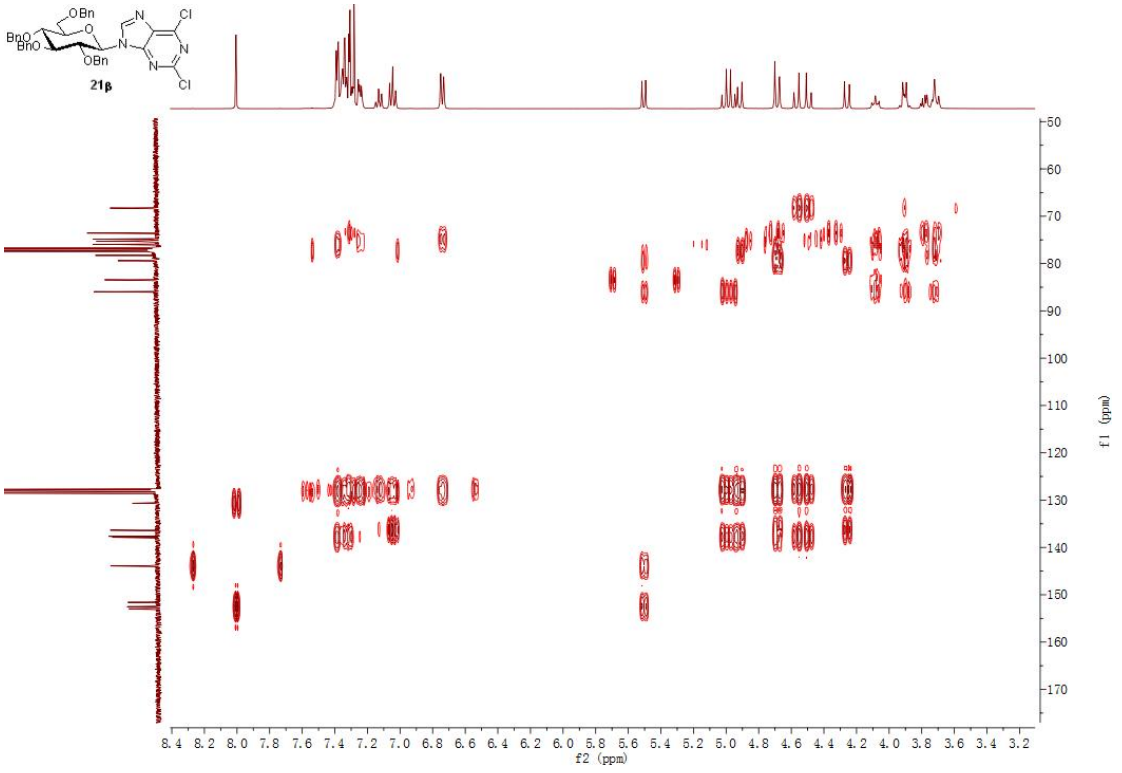
^{13}C NMR spectrum of compound 21β



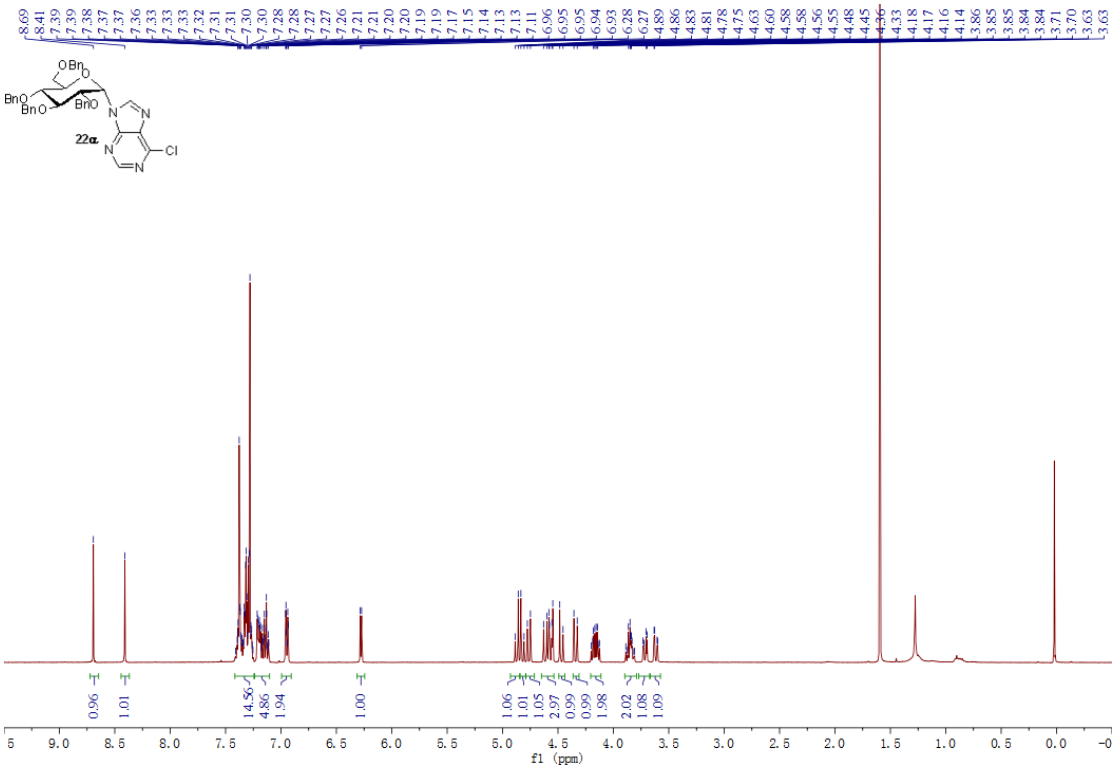
HH-COSY spectrum of compound 21β



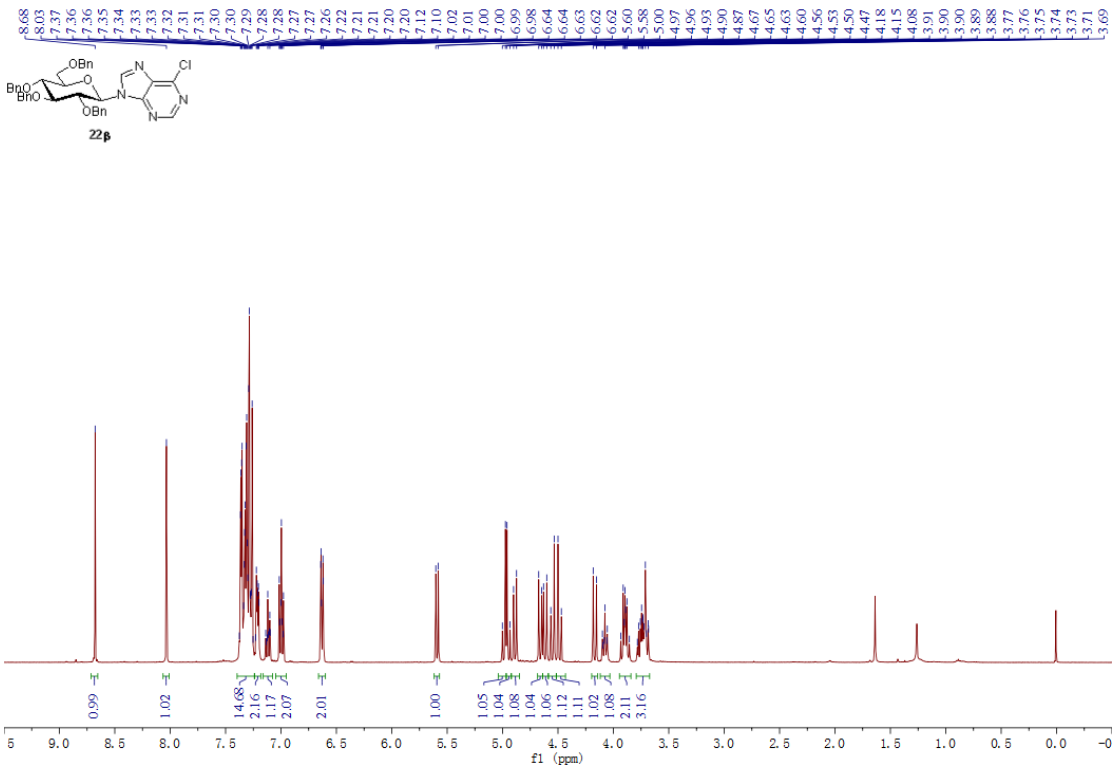
HSQC NMR spectrum of compound 21β



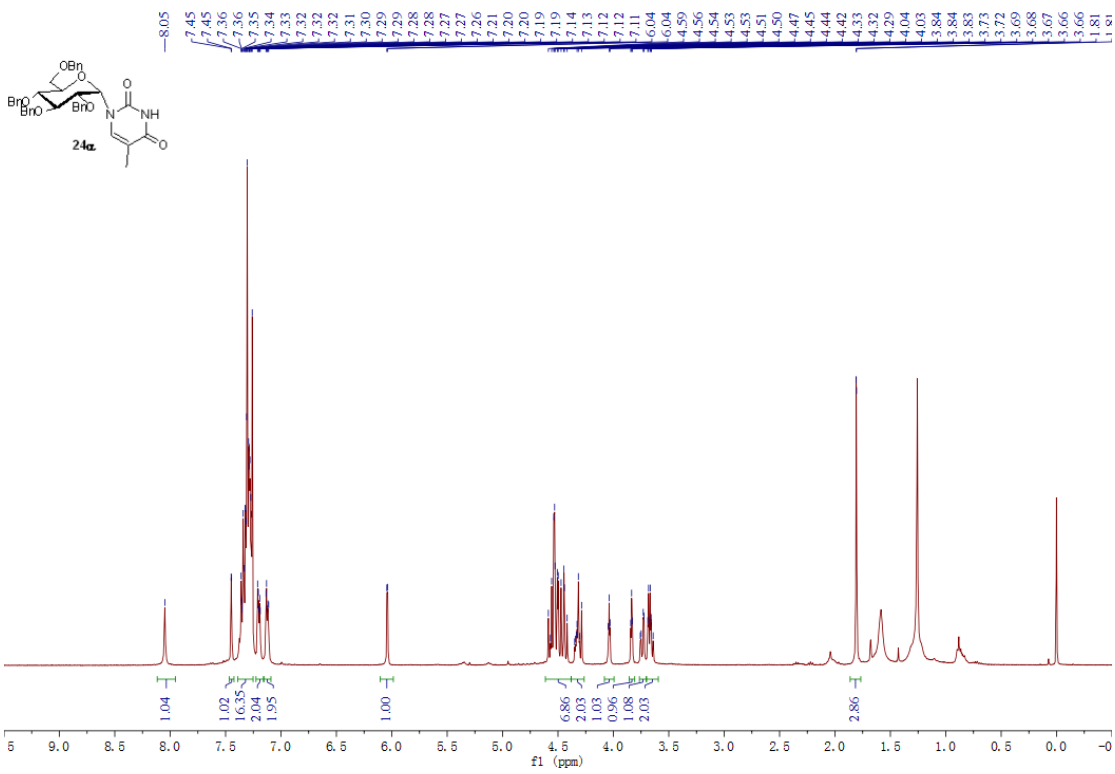
HMBC NMR spectrum of compound 21β



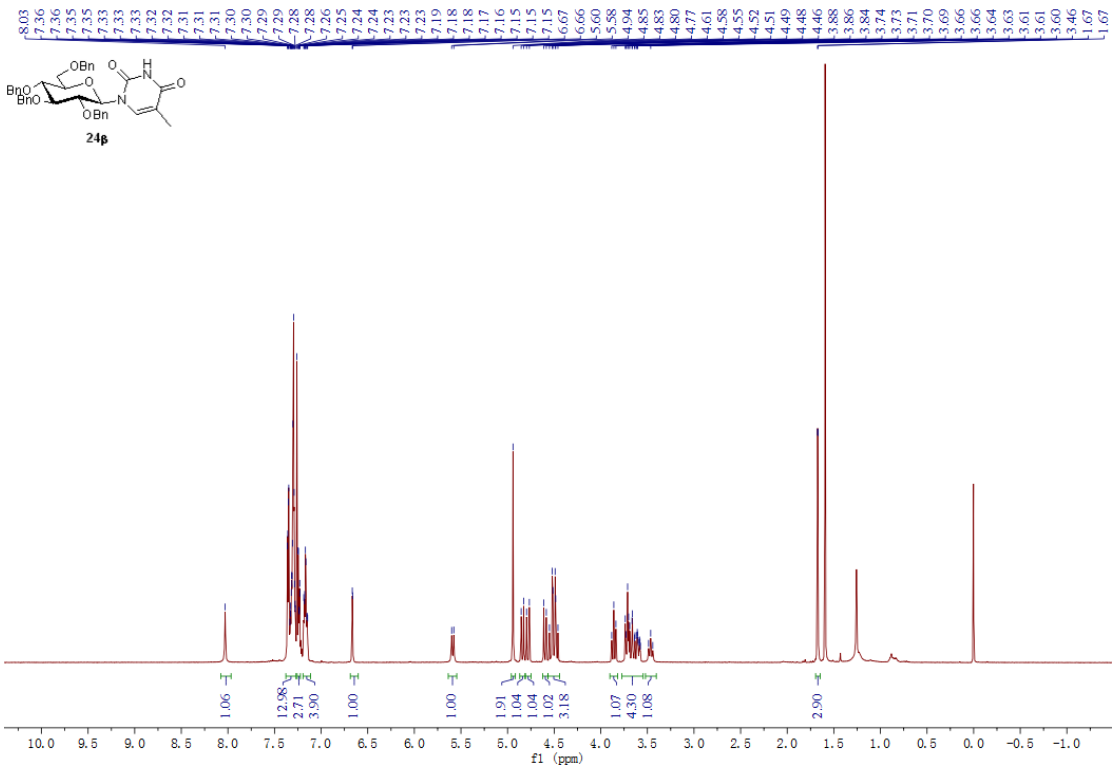
^{1}H NMR spectrum of compound 22α



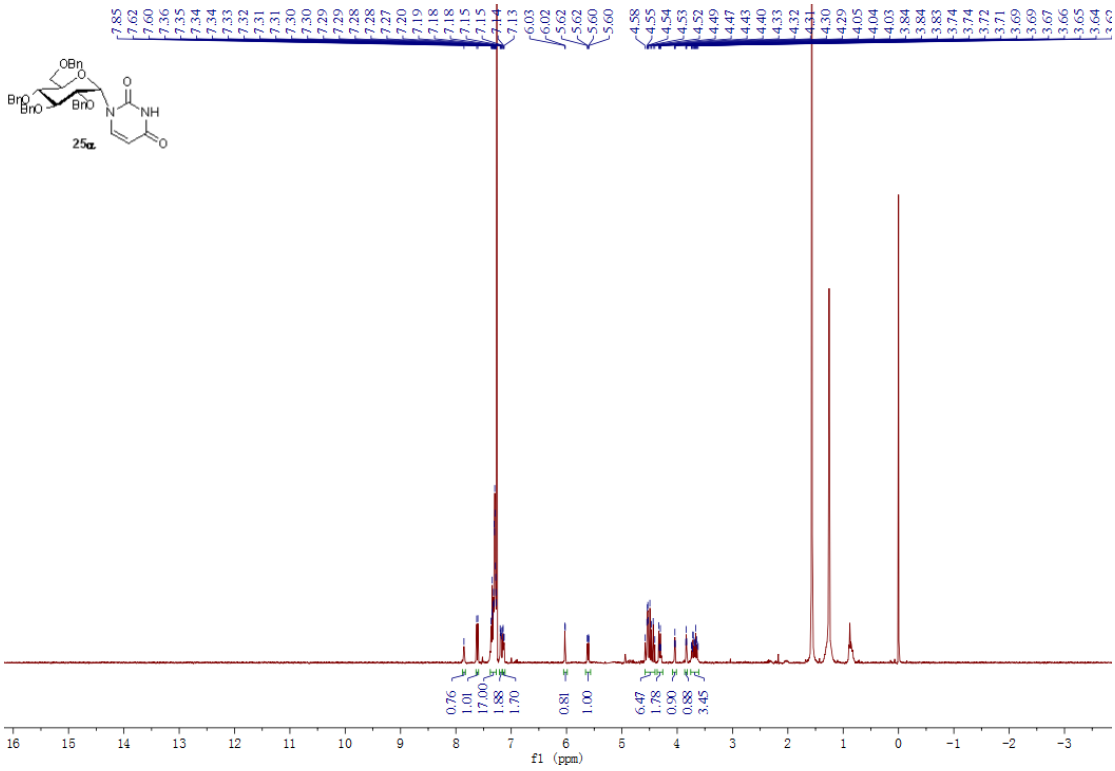
^{1}H NMR spectrum of compound 22β



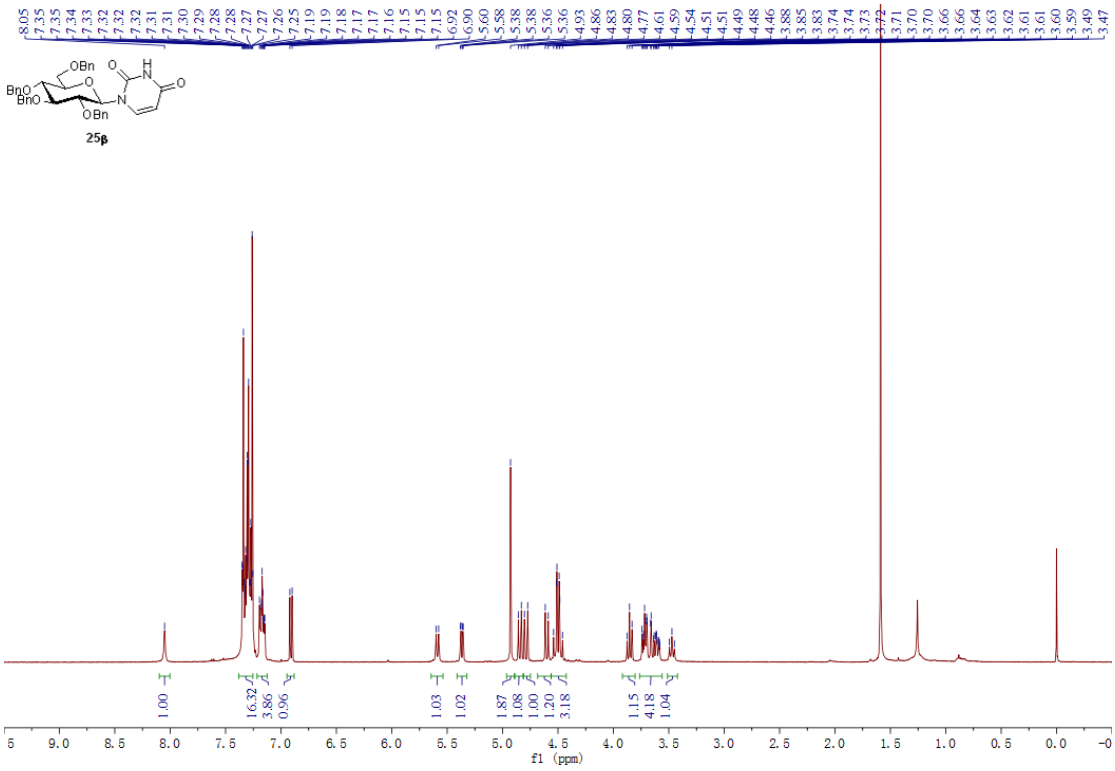
^{1}H NMR spectrum of compound 24α



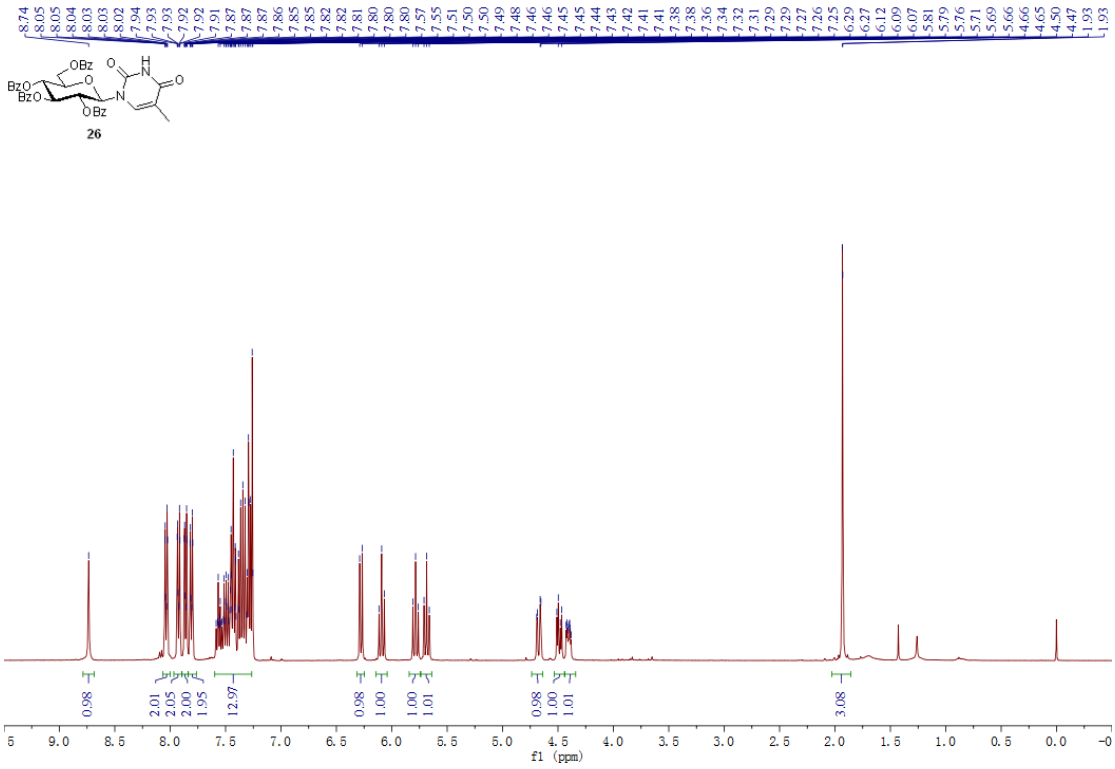
^{1}H NMR spectrum of compound 24β



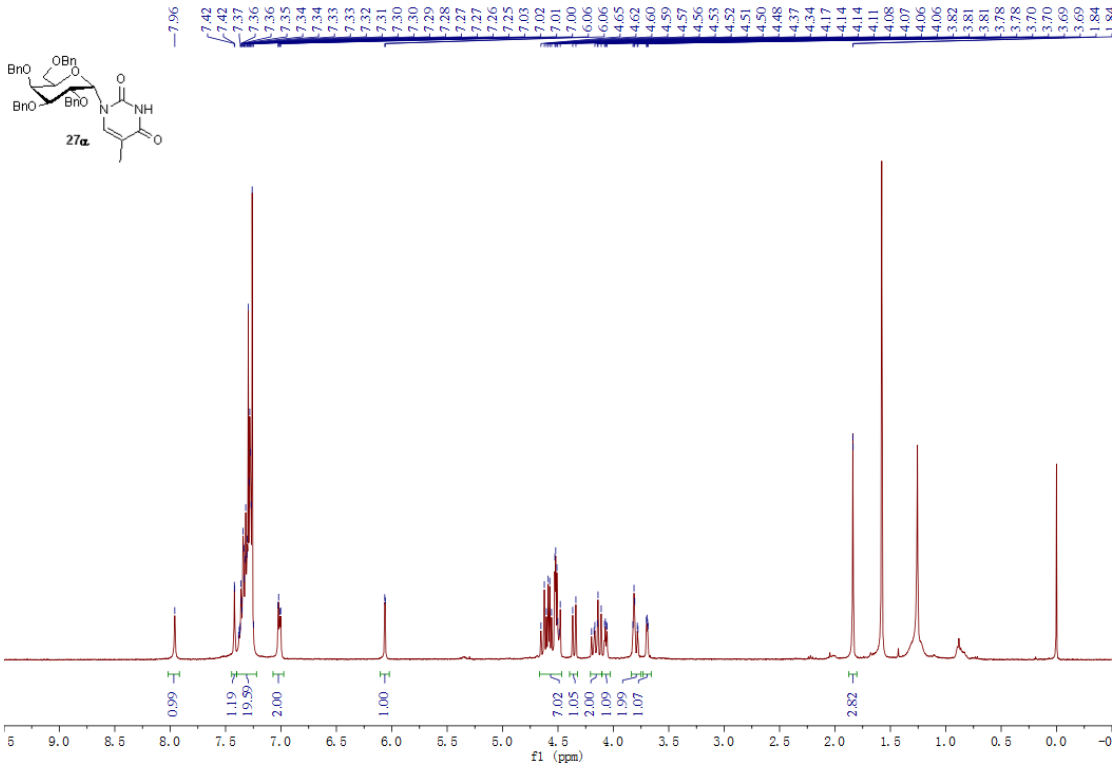
^{1}H NMR spectrum of compound 25α



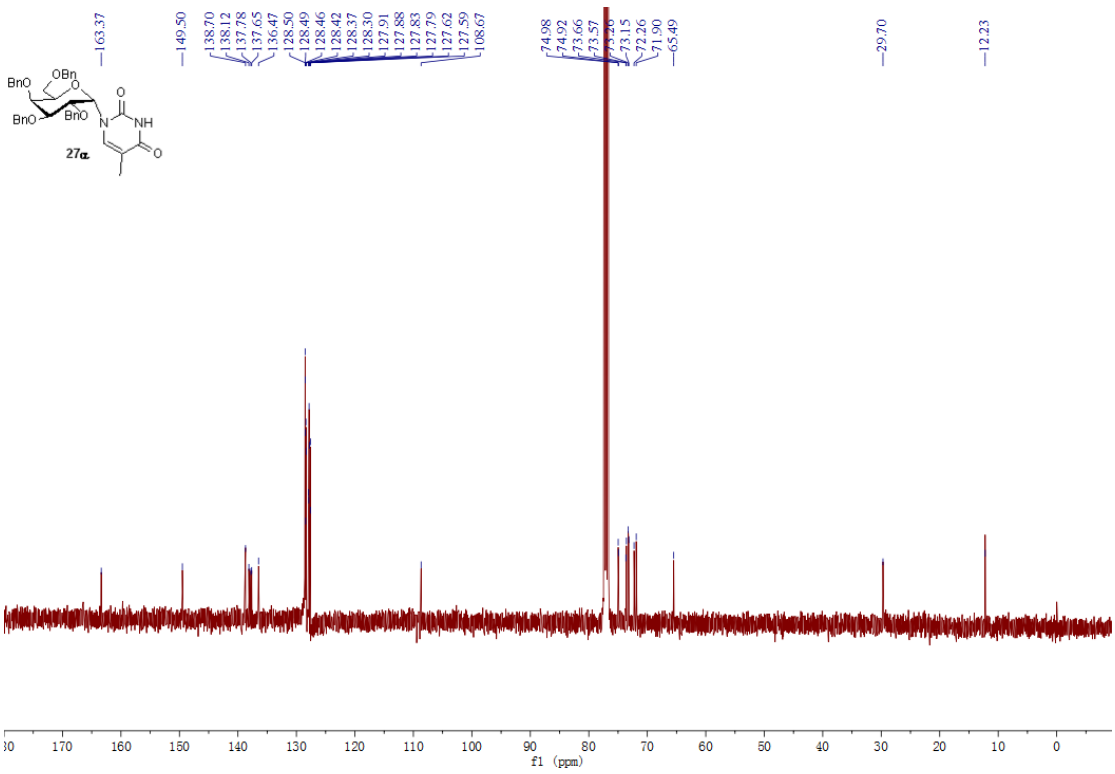
^{1}H NMR spectrum of compound 25β



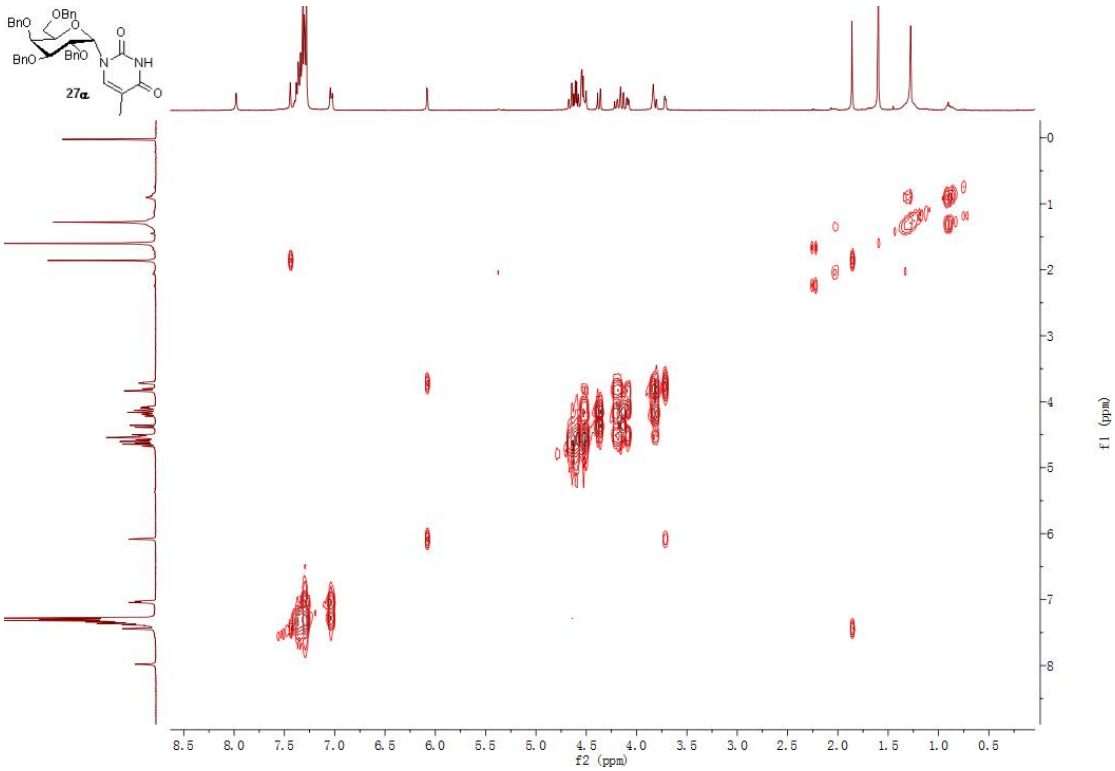
^{1}H NMR spectrum of compound 26



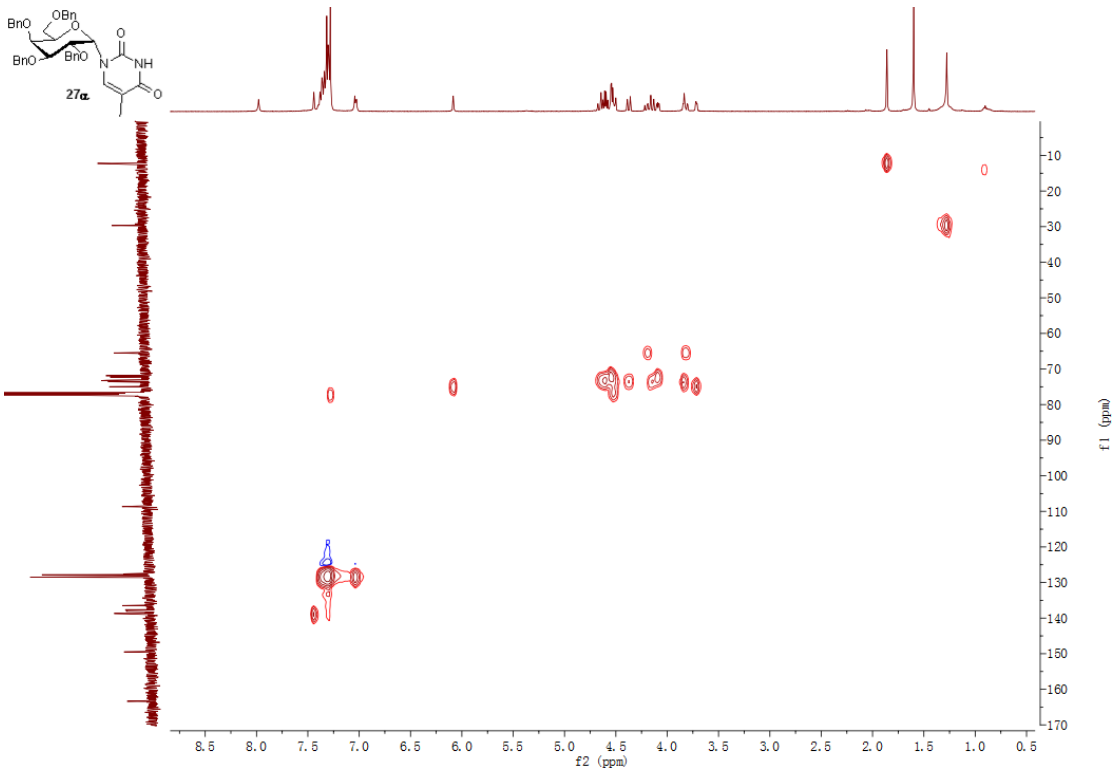
^{1}H NMR spectrum of compound 27α



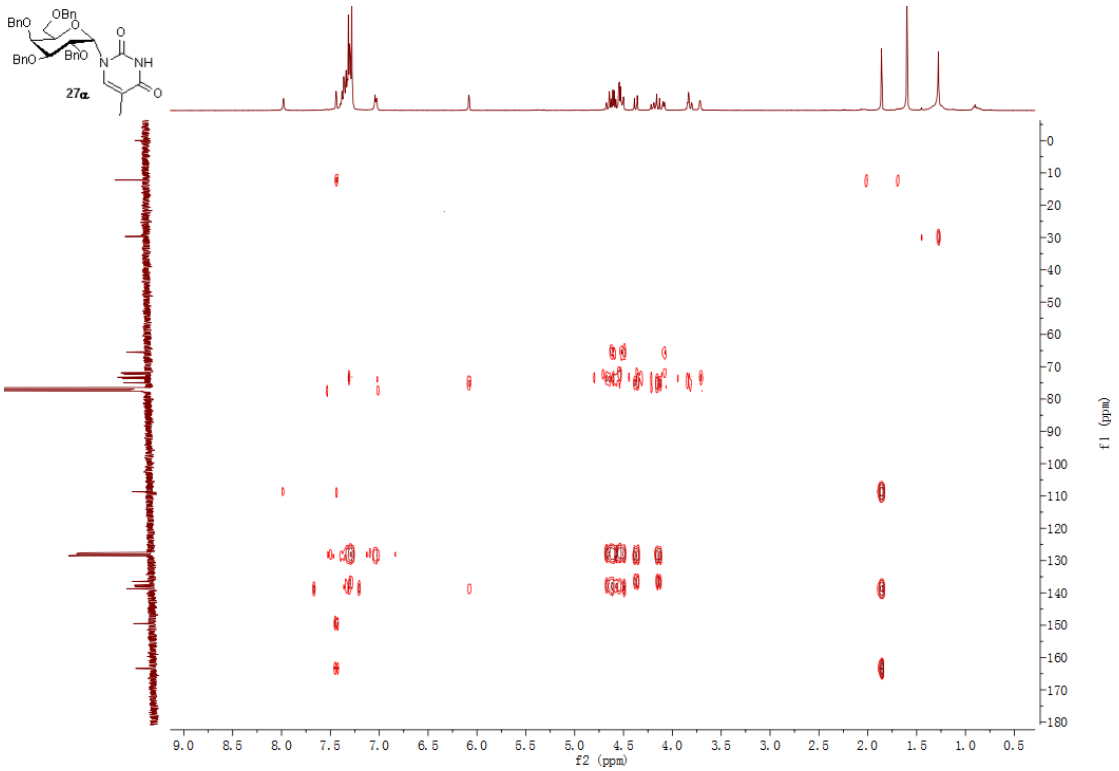
^{13}C NMR spectrum of compound 27α



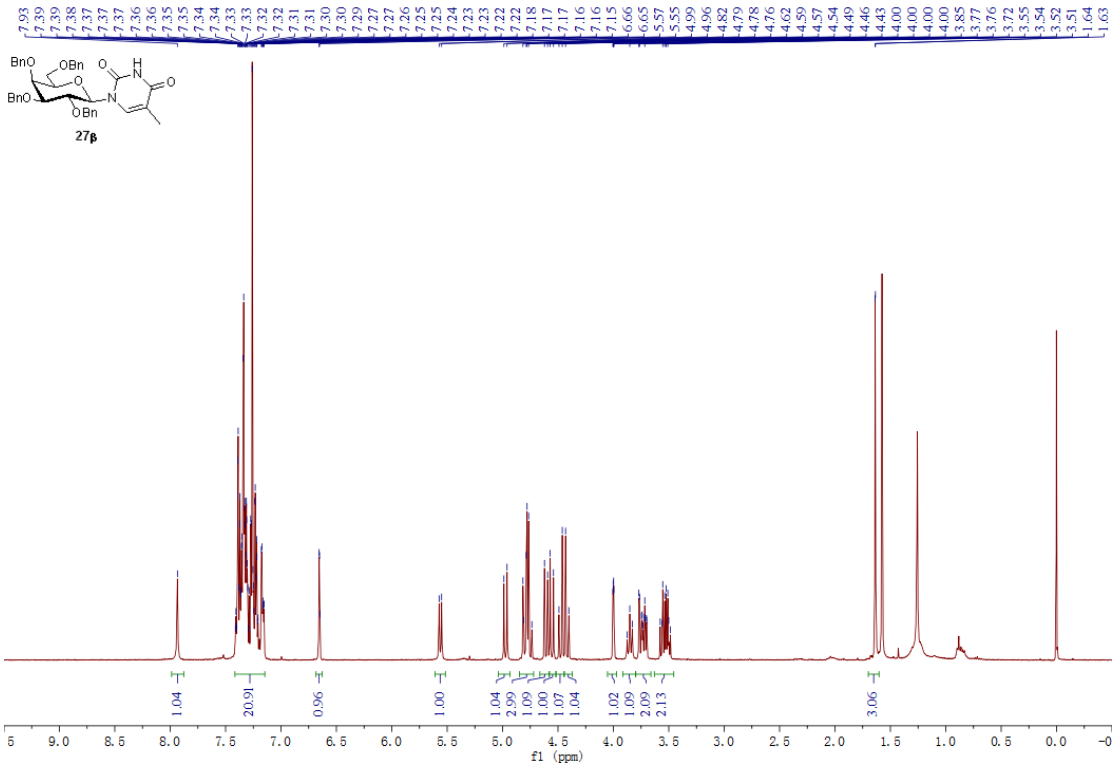
HH-COSY spectrum of compound 27α



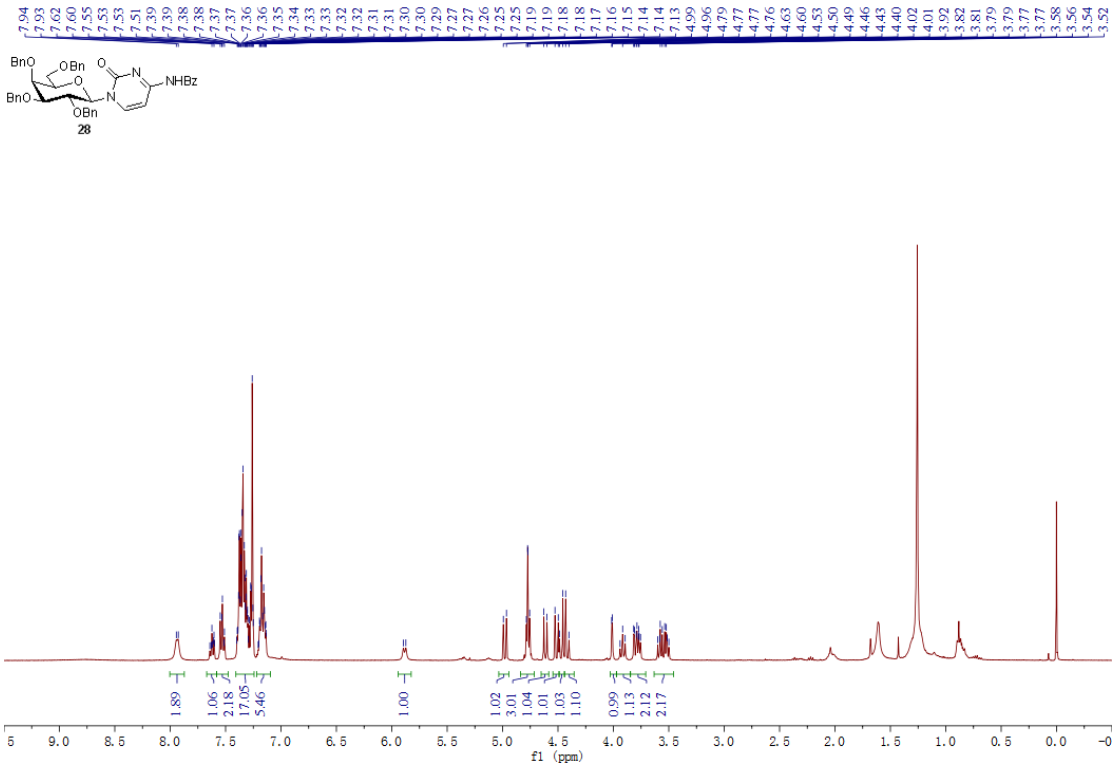
HSQC NMR spectrum of compound 27α



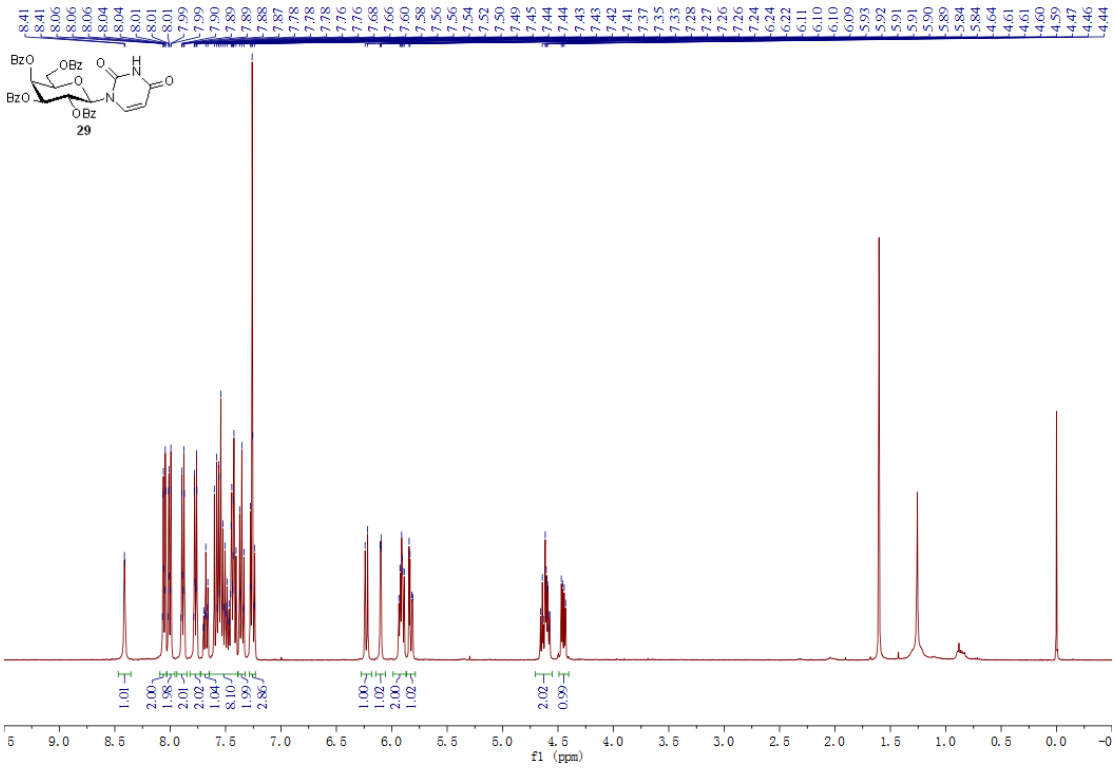
HMBC NMR spectrum of compound 27α



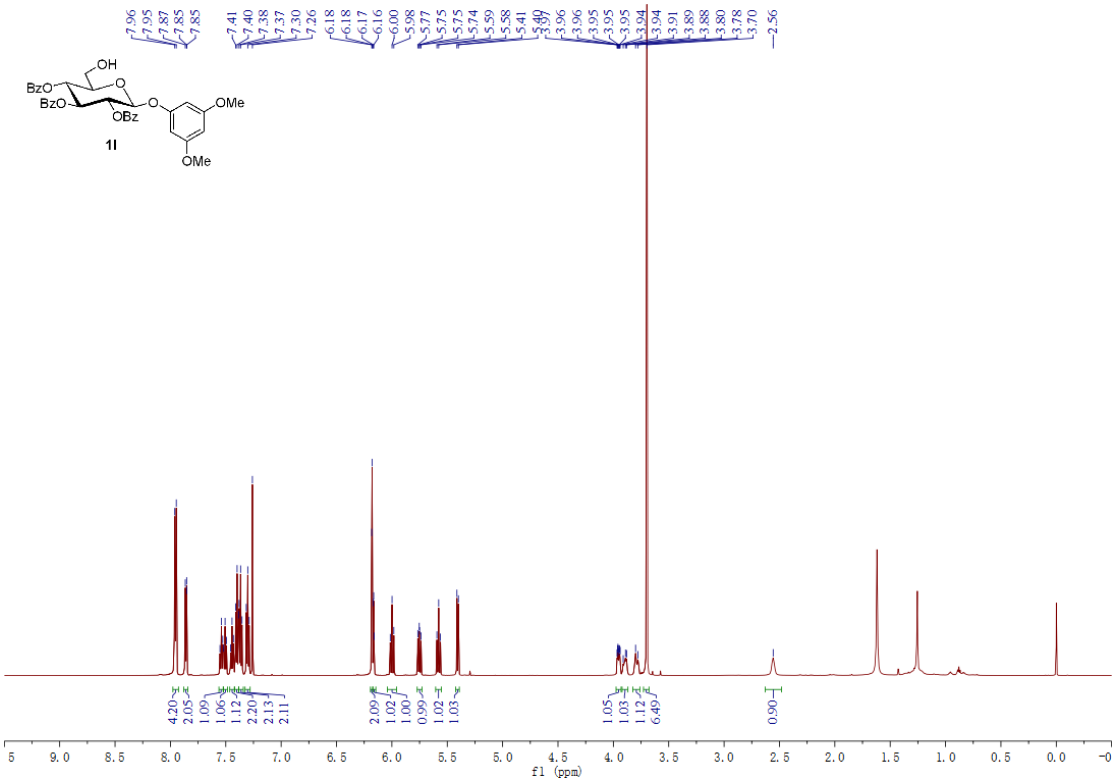
^{1}H NMR spectrum of compound 27β



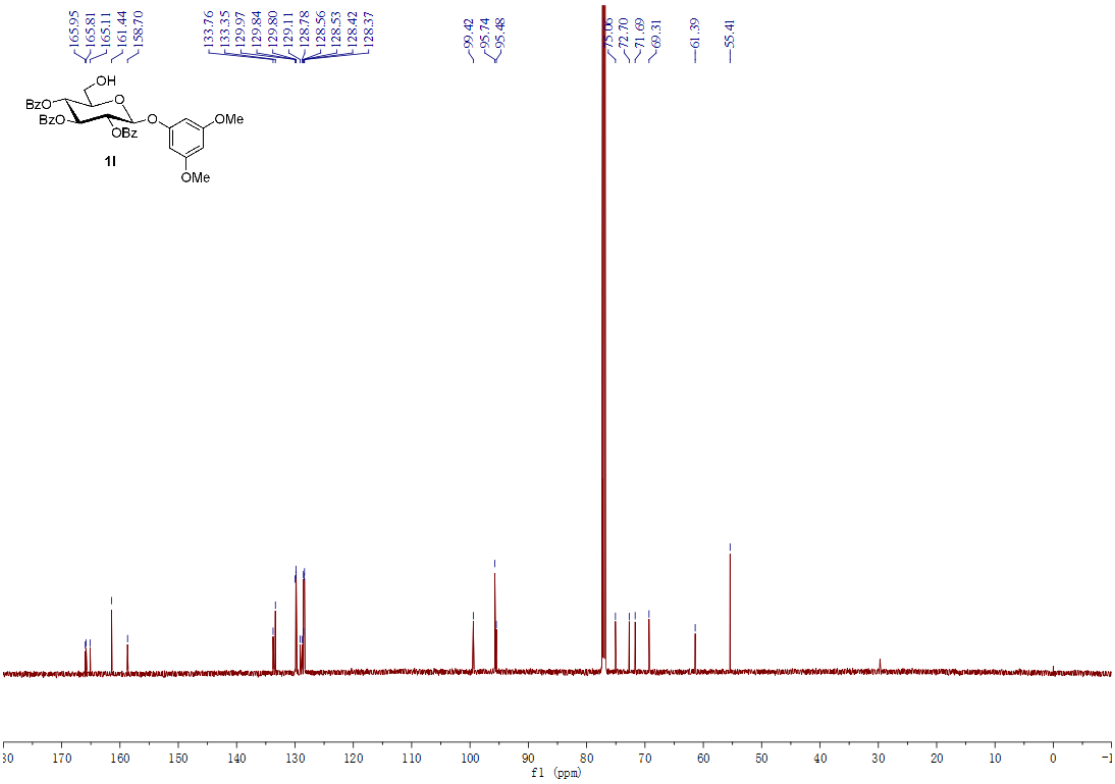
^{1}H NMR spectrum of compound 28β



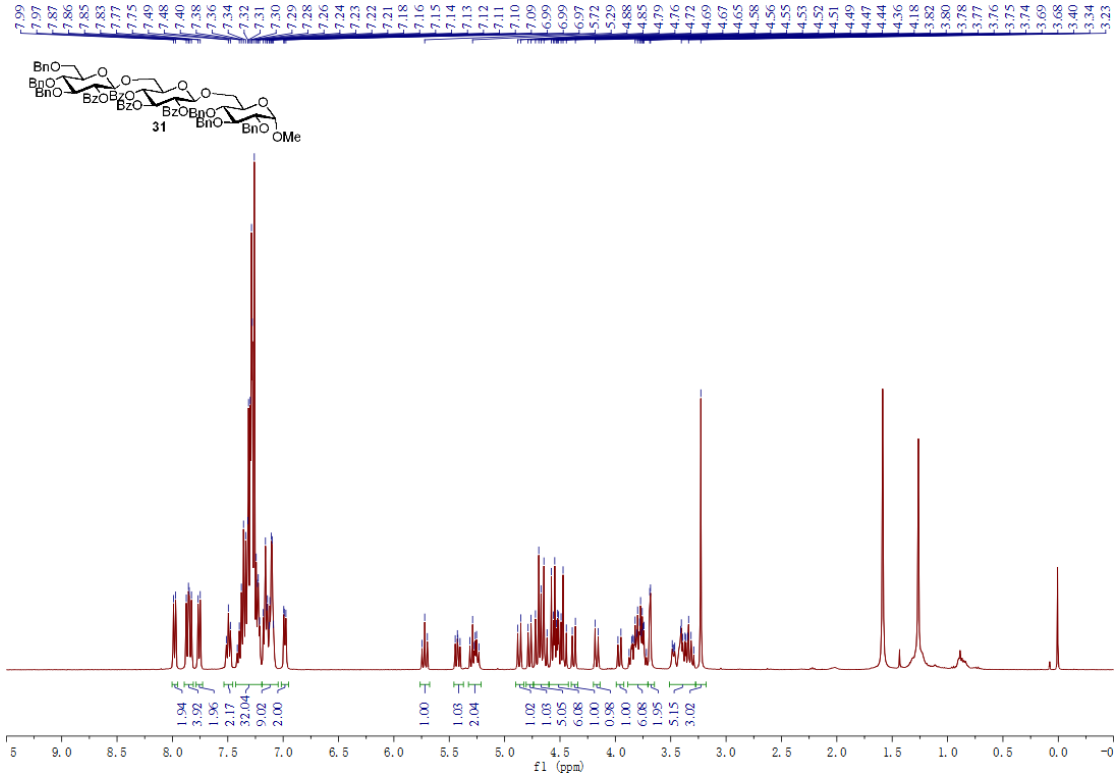
^{1}H NMR spectrum of compound 29



^{1}H NMR spectrum of compound 1l



^{13}C NMR spectrum of compound 1l



^{1}H NMR spectrum of compound 31