Electronic supplementary information (ESI)

Total Synthesis of the *Helicobacter pylori* Serotype O2 O-Antigen α-(1→2)- and α-(1→3)-Linked Oligoglucosides

Guangzong Tian[a,b,†], Chunjun Qin[a,†], Zhonghua Liu[a,†], Dacheng Shen[b], Xiaopeng Zou[a,b], Junjie Fu[a], Jing Hu[a,c], Peter H. Seeberger[b] and Jian Yin*[a]

[a.] *Key Laboratory of Carbohydrate Chemistry and Biotechnology Ministry of Education, School of Biotechnology, Jiangnan University, Wuxi 214122, China. Email: jianyin@jiangnan.edu.cn*

[b.] *Department of Biomolecular Systems, Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1, 14476 Potsdam, Germany.*

[c.] *Wuxi School of Medicine, Jiangnan University, Wuxi 214122, China.*

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

Supporting Information

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1. General information

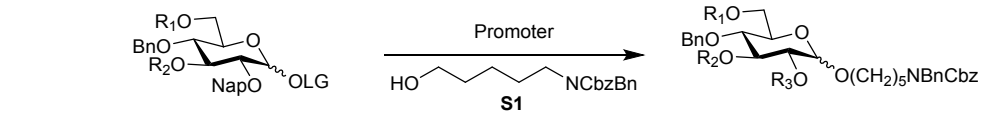
All commercial grade reagents and solvents were used as purchased without further purification, except where noted. Solvents were dried and redistilled prior to use in the usual way. All reactions were conducted in oven-dried glassware with magnetic stirring, under an argon or nitrogen atmosphere. Analytical thin layer chromatography (TLC) was performed on GF_{254} glass plates pre-coated with a thickness of silica gel. The TLC plates were visualized with UV light and by staining with Hanessian solution (ceric sulfate and ammonium molybdate in aqueous sulfuric acid) or 5% sulfuric acid-ethanol solution. Column chromatography was performed on silica gel (200–300 mesh). Optical rotations were measured with an AUTOPOL IVS2 & PLUS & VI at a concentration (c) expressed in g/100 mL. IR spectra were taken with a NICOLET IS5 FT-IR spectrometer. ^{1}H and ^{13}C NMR, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C coupling HSQC spectra were measured with Bruker AVANCE III 400 MHz or Bruker AVANCE III 700 MHz. ^{1}H-NMR and ^{13}C-NMR spectra were obtained at the indicated frequencies. The proton signal of residual, non-deuterated solvent (δ 7.26 ppm for $CHCl_3$, δ 4.87 ppm for H_2O) was used as an internal reference for ^{1}H-NMR spectra. For ^{13}C-NMR NMR spectra, the chemical shifts are reported relative to the δ 77.26 ppm resonance of $CDCl_3$. All NMR chemical shifts (δ) were recorded in ppm and coupling constants (J) were reported in Hertz (Hz). The following abbreviations are used to indicate the multiplicities: s = singlet, br s = broad singlet, d = doublet; t = triplet; dd = doublet of doublets; q = quartet; m = multiplet. High-resolution mass spectra (HRMS) were recorded with an FT-ICR-MS. MALDI-TOF spectra were recorded on a Bruker Daltonics ultrafleXtreme MALDI TOF/TOF, using NaCl/2,5-dihydroxy benzoic acid (DHB).

2. Experimental Procedures.

2.1 Optimization of stereoselective installation of linker.

In order to obtain a building block with remote acyl group participation for the efficient preparation of roxy benzoic acid (DHB)tions are used to indicate the multiplicities: s = singlet*O*3 and *O*6 positions were screened (Table S1). Remote participation of acyl groups at the *O*6 position was initially explored by the coupling of 6-*O*-acylated thioglycosides (**S2** or **S3**) and amine linker **S1**[1], affording the product in low yields and with poor 1,2-*cis*-selectivities (entries 1 and 2, Table S1). The low glycosylation yields were mainly a result of the relatively low reactivity of the two thioglycosides. Glycosylation yields were significantly improved when donors **S4** and **S5** with *N*-phenyl trifluoroacetimidate as leaving group were used (entries 3 and 4, Table S1). Meanwhile, the α-selectivity of the glycosylation was slightly enhanced by using donors **S4** and **S5**, and that remote participation effect of the *O*6 acetyl group was stronger than that of the *O*6 benzoyl group. The α-stereoselectivity in glycosylation is known to be further improved by synergistic remote participation of acyl groups at two or three positions.[2] Gratifyingly, a combination of *O*6 acetyl group and *O*3 benzoyl group in donor **S6** lead to desired product **S9** with a good red producnotion of l10:1) and in high yield (90%) (entry 5, Table S1).

Table S-1. Optimization of remote acyl participation effect-assisted α-stereoselectivity



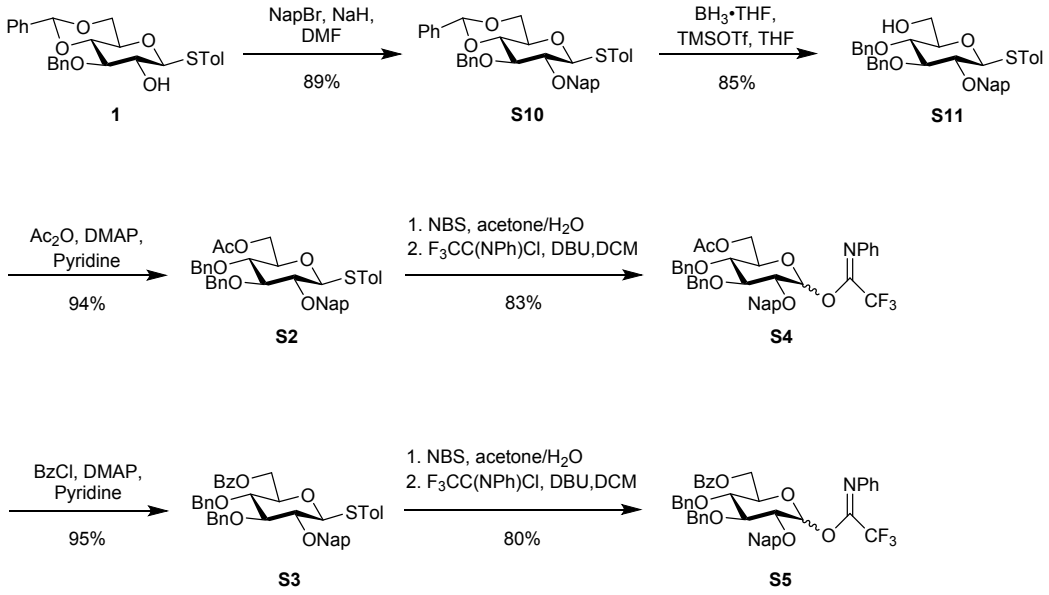
S2 R_1= Ac, R_2= Bn, LG= STol (β)
S3 R_1= Bz, R_2= Bn, LG= STol (β)
S4 R_1= Ac, R_2= Bn, LG= $C(NPh)CF_3$
S5 R_1= Bz, R_2= Bn, LG= $C(NPh)CF_3$
S6 R_1= Ac, R_2= Bz, LG= $C(NPh)CF_3$

S7 R_1= Ac, R_2= Bn, R_3= Nap
S8 R_1= Bz, R_2= Bn, R_3= Nap
S9 R_1= Ac, R_2= Bz, R_3= Nap

entry	donor	acyl group	promoter	product	α:β[a] (yield %)[b]
1	**S2**	6-O-Ac	NIS, TfOH	**S7**	2.5:1 (36)
2	**S3**	6-O-Bz	NIS, TfOH	**S8**	2.0:1 (32)
3	**S4**	6-O-Ac	TMSOTf	**S7**	4:1 (92)
4	**S5**	6-O-Bz	TMSOTf	**S8**	3.1:1 (85)
5	**S6**	3-O-Bz and 6-O-Ac	TMSOTf	**S9**	10:1 (90)

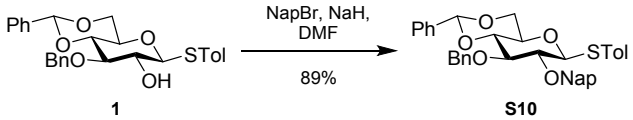
[a] Anomeric α/β ratios were calculated from the ^{1}H NMR spectra.

[b] Isolated yields.



Scheme S-1. Synthesis of building blocks **S2**, **S3**, **S4** and **S5**

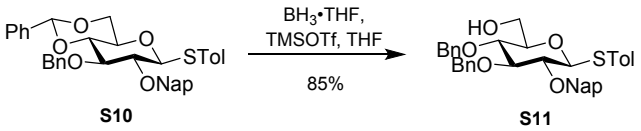
***p*-Methylphenyl 2-*O*-(2-naphthylmethyl)-4,6-*O*-benzylidene-3-*O*-benzyl-1-thio-β-D-glucopyranoside (S10).**



To a solution of compound **1**[3] (6.0 g, 12.93 mmol) in anhydrous DMF (50 mL) were added NaH (1.0 g, 25.85 mmol, 60% dispersion in mineral oil) at 0 °C for 30 min. Then NapBr (4.3 g, 19.40 mmol) was added to the reaction mixture and stirred at room temperature for 2.0 h. Until reaction completion,

the mixture was cooled to 0 °C and H_2O was added dropwise. The residue was extracted with CH_2Cl_2 three times. Combined organic layer was dried over Na_2SO_4 and concentrated in reduced pressure. The crude mixture was purified by recrystallisition (Hexanes/EtOAc: 1/1) to give **S10** (6.95 g, 89%). $[\alpha]^{25}_D$ = - 2.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.01 (m, 21H, Ar-H), 5.60 (s, 1H, Ar*CH*), 5.04 (d, *J* = 10.5 Hz, 1H, Ar*CH*), 4.98 (d, *J* = 10.6 Hz, 1H), 4.97 (d, *J* = 11.1 Hz, 1H, Ar*CH*), 4.80 (d, *J* = 11.1 Hz, 1H, Ar*CH*), 4.74 (d, *J* = 9.8 Hz, 1H, 1-H), 4.40 (dd, *J* = 10.5, 5.0 Hz, 1H, 6'-H), 3.90 – 3.85 (m, 1H, 3-H), 3.82 (d, *J* = 10.3 Hz, 1H, 6-H), 3.72 (t, *J* = 9.4 Hz, 1H, 4-H), 3.55 (dd, *J* = 9.8, 8.4 Hz, 1H, 2-H), 3.48 (td, *J* = 9.7, 5.0 Hz, 1H, 5-H), 2.35 (s, 3H, Ar*CH*$_3$). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.4, 138.4, 137.4, 135.7, 133.4, 133.2, 133.2, 129.9, 129.2, 129.1, 128.5, 128.4, 128.3, 128.3, 128.1, 127.9, 127.8, 127.0, 126.4, 126.2, 126.1, 126.0, 101.2, 88.7, 83.2, 81.6, 80.5, 76.0, 75.5, 70.3, 68.8, 21.3. IR (film): ν = 1090, 810, 752, 698 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{38}H_{36}O_5SNa$ [M+Na]$^+$ 627.2176, found 627.2186.

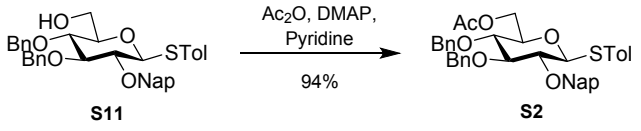
***p*-Methylphenyl 3,4-di-*O*-benzyl-2-*O*-(2-naphthylmethyl)-1-thio-β-D-glucopyranoside (S11).**



S10 **S11**

To a solution of thioglucoside **S10** (0.76 g, 1.25 mmol) in THF (10 mL) were added BH_3·THF (8 mL, 8.10 mmol) and TMSOTf (45 µL, 0.24 mmol) at 0 °C. Reaction mixture was stirred at RT for 4 h. Upon completion of reaction as monitored by TLC, the reaction mixture was quenched by CH_3OH (1 mL). The resulting mixture concentrated for flash chromatography purification over silica gel to furnish the thioglucoside **S11** (0.65 g, 85%) as an amorphous solid. $[\alpha]^{25}_D$ = + 32.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.72 (m, 4H, Ar-H), 7.58 (dd, *J* = 8.4, 1.7 Hz, 1H, Ar-H), 7.53 – 7.43 (m, 4H, Ar-H), 7.39 – 7.29 (m, 10H, Ar-H), 7.15 (d, *J* = 7.9 Hz, 2H, Ar-H), 5.11 (d, *J* = 10.4 Hz, 1H, Ar*CH*), 5.00 – 4.88 (m, 3H, Ar*CH*), 4.89 (d, *J* = 10.9 Hz, 1H, Ar*CH*), 4.71 (d, *J* = 9.9 Hz, 1H, 1-H), 4.69 (d, *J* = 11.2 Hz, 1H, Ar*CH*), 3.91 (dd, *J* = 12.0, 2.7 Hz, 1H, 6'-H), 3.78 (t, *J* = 9.1 Hz, 1H, 3-H), 3.73 (dd, *J* = 12.3, 5.2 Hz, 1H, 6-H), 3.61 (t, *J* = 9.4 Hz, 1H, 4-H), 3.55 (dd, *J* = 9.8, 8.8 Hz, 1H, 2-H), 3.41 (ddd, *J* = 9.8, 4.8, 2.6 Hz, 1H, 5-H), 2.37 (s, 3H, Ar*CH*$_3$). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.3, 138.1, 137.8, 135.4, 133.3, 133.1, 132.7, 129.9, 129.4, 128.6, 128.5, 128.2, 128.1, 128.0, 128.0, 127.8, 127.7, 126.9, 126.2, 126.1, 126.0, 87.9, 86.6, 81.1, 79.3, 77.6, 75.9, 75.6, 75.2, 62.2, 21.2. IR (film): ν = 3477, 3032, 2875, 1495, 1455, 1362, 1212, 1125, 1073, 857, 814, 737, 698. HRMS (ESI) *m/z* calcd for $C_{38}H_{38}O_5SNa$ [M+Na]$^+$ 629.2332, found 629.2348.

***p*-Methylphenyl 6-O-acetyl-3,4-di-*O*-benzyl-2-*O*-(2-naphthylmethyl)-1-thio-β-D-glucopyranoside (S2).**

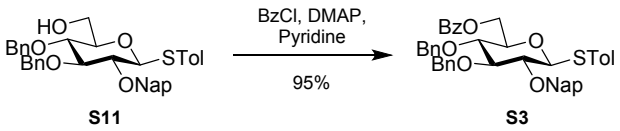


S11 **S2**

To a solution of compound **S11** (120 mg, 0.20 mmol) in pyridine (2 mL) were added Ac_2O (190 µL, 2.0 mmol) and DMAP (cat.) at room temperature. The reaction mixture was stirred for 2h at room temperature. After completion as monitored by TLC, the reaction mixture was evaporated and co-evaporated twice with toluene. The residue was diluted with CH_2Cl_2. The organic layer was washed

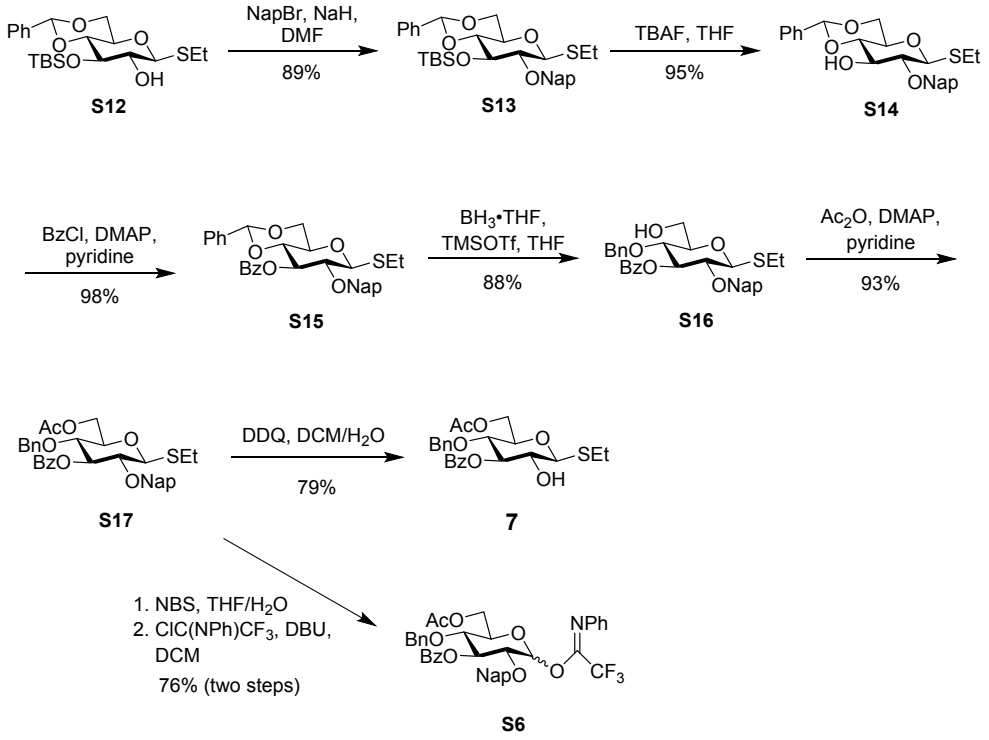
with 1 M HCl (aq), saturated $NaHCO_3$, dried over anhydrous Na_2SO_4, and concentrated to dryness. Chromatographic purification afforded **S2** (122 mg, 94%). $[\alpha]^{25}_D$ = + 33.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.78 (m, 4H, Ar-H), 7.58 (dd, *J* = 8.4, 1.7 Hz, 1H, Ar-H), 7.54 – 7.47 (m, 4H, Ar-H), 7.39 – 7.28 (m, 10H, Ar-H), 7.14 (d, *J* = 7.9 Hz, 2H, Ar-H), 5.12 (d, *J* = 10.4 Hz, 1H, Ar*CH*), 4.98 (d, *J* = 10.9 Hz, 1H, Ar*CH*), 4.92 (d, *J* = 10.3 Hz, 1H, Ar*CH*), 4.90 (d, *J* = 11.0 Hz, 2H, Ar*CH*), 4.66 (d, *J* = 9.8 Hz, 1H, 1-H), 4.62 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.40 (dd, *J* = 11.9, 1.4 Hz, 1H, 6'-H), 4.29 – 4.22 (m, 1H, 6-H), 3.83 – 3.72 (m, 1H, 3-H), 3.64 – 3.51 (m, 3H, 2,4,5-H), 2.37 (s, 3H, Ar*CH*$_3$), 2.10 (s, 3H, CH_3CO). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 138.2, 137.9, 137.6, 135.4, 133.3, 133.1, 132.8, 129.7, 128.6, 128.5, 128.2, 128.1, 128.1, 128.0, 127.8, 127.8, 127.7, 127.0, 126.2, 126.1, 126.0, 87.8, 86.8, 80.8, 77.5, 76.9, 75.9, 75.6, 75.2, 63.3, 21.2, 20.9. IR (film): ν = 3033, 2866, 1743, 1604, 1495, 1455, 1401, 1364, 1236, 1126, 1071, 1039, 897, 857, 812, 752, 737, 699. HRMS (ESI) *m/z* calcd for $C_{40}H_{40}O_6SNa$ $[M+Na]^+$ 671.2438, found 671.2441.

***p*-Methylphenyl 6-O-benzoyl-3,4-di-*O*-benzyl-2-*O*-(2-naphthylmethyl)-1-thio-β-D-glucopyranoside (S3).**



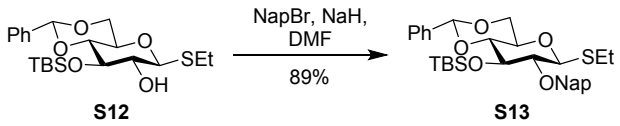
S11 **S3**

To a solution of the compound **S11** (110 mg, 0.18 mmol) and DMAP (2 mg, 0.018, 0.1 eq) in pyridine (1.8 mL), was added BzCl (42 µL, 0.36 mmol). After being stirred at room temperature for 2.5 h, the mixture was evaporated and co-concentrate with toluene. The residue was then diluted with DCM and washed with 1 M HCl, saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to give **S3** (146 mg, 95%). $[\alpha]^{25}_D$ = + 22.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.94 (m, 2H, Ar-H), 7.81 – 7.67 (m, 4H, Ar-H), 7.59 – 7.46 (m, 2H, Ar-H), 7.44 – 7.35 (m, 6H, Ar-H), 7.26 – 7.15 (m, 10H, Ar-H), 6.87 – 6.81 (m, 2H, Ar-H), 5.03 (d, *J* = 10.4 Hz, 1H, Ar*CH*), 4.87 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.85 – 4.77 (m, 3H, Ar*CH*), 4.59 (d, *J* = 9.6 Hz, 1H, 1-H), 4.55 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.63 – 4.59 (m, 1H, 6'-H), 4.39 (dd, *J* = 11.8, 4.3 Hz, 1H, 6-H), 3.75 – 3.68 (m, 1H, 3-H), 3.64 – 3.54 (m, 2H, 4-H, 5-H), 3.48 (dd, *J* = 9.7, 8.8 Hz, 1H, 2-H), 2.20 (s, 3H, Ar*CH*$_3$). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.1, 138.1, 137.9, 137.5, 135.5, 133.3, 133.1, 133.1, 130.0, 129.8, 129.6, 129.1, 128.6, 128.4, 128.2, 128.1, 128.1, 128.0, 127.9, 127.7, 126.9, 126.2, 126.1, 126.0, 87.5, 86.8, 80.6, 77.5, 76.0, 75.5, 75.3, 63.5, 21.2. IR (film): ν = 3034, 2874, 1723, 1603, 1494, 1454, 1401, 1342, 1316, 1274, 1126, 1091, 1069, 1028, 896, 857, 813, 752, 712, 699. HRMS (ESI) *m/z* calcd for $C_{45}H_{42}O_6SNa$ $[M+Na]^+$ 733.2594, found 733.2607.



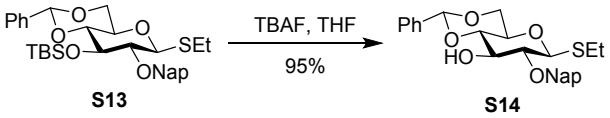
Scheme S-2. Synthesis of building blocks **S6** and **7**.

Ethyl 4,6-*O*-benzylidene-3-*O*-(tert-butyldimethylsilyl)-2-*O*-(2-naphthylmethyl)-1-thio-β-D-glucopyranoside (S13)



To a solution of compound **S12**[4] (7.67 g, 18 mmol) in anhydrous DMF (36 mL) were added NaH (1.5 g, 36 mmol, 60% dispersion in mineral oil) at 0 °C for 10 min. Then NapBr (6.0 mg, 27 mmol) was added to the reaction mixture and stirred at room temperature for 4 h. Upon reaction completion, the mixture was cooled to 0 °C and MeOH was added dropwise. The residue was diluted with CH_2Cl_2 and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo to give a residue that was purified by silica gel column chromatography to give **S13** (9.07 g, 89%). $[\alpha]^{25}_D$ = - 27.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.75 (m, 4H, Ar-H), 7.54 (dd, *J* = 8.4, 1.6 Hz, 1H, Ar-H), 7.46 – 7.39 (m, 4H, Ar-H), 7.31 (dd, *J* = 5.1, 2.0 Hz, 3H, Ar-H), 5.45 (s, 1H, Ar*CH*), 5.02 (d, *J* = 10.4 Hz, 1H, Ar*CH*), 4.91 (d, *J* = 10.4 Hz, 1H, Ar*CH*), 4.56 (d, *J* = 9.8 Hz, 1H, 1-H), 4.30 (dd, *J* = 10.5, 4.8 Hz, 1H, 6'-H), 3.87 (t, *J* = 8.5 Hz, 1H, 3-H), 3.71 (t, *J* = 10.1 Hz, 1H, 6-H), 3.47 (t, *J* = 9.1 Hz, 1H, 4-H), 3.44 – 3.39 (m, 1H, 5-H), 3.36 (dd, *J* = 9.9, 8.2 Hz, 1H, 2-H), 2.74 (qq, *J* = 12.7, 7.4 Hz, 2H, SCH_2), 1.29 (t, *J* = 7.4 Hz, 3H, CH_3), 0.82 (s, 9H, CH_3), 0.00 (s, 3H, CH_3), -0.05 (s, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.3, 135.7, 133.4, 133.1, 129.2, 128.3, 128.1, 128.1, 127.8, 126.8, 126.5, 126.2, 126.1, 125.9, 102.1, 86.0, 82.6, 81.7, 76.2, 75.9, 70.3, 68.9, 26.0, 25.4, 18.4, 15.3, -4.0, -4.3. IR (film): ν = 3058, 2956, 2930, 2858, 1604, 1511, 1459, 1383, 1362, 1340, 1249, 1220, 1173, 1144, 1089, 1030, 1007, 987, 915, 881, 862, 838, 816, 781, 754, 699, 670. HRMS (ESI) *m/z* calcd for $C_{32}H_{42}O_5SSiNa$ $[M+Na]^+$ 589.2414, found 589.2398.

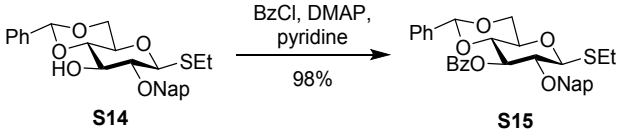
Ethyl 4,6-*O*-benzylidene-2-*O*-(2-naphthylmethyl)-1-thio-β-D-glucopyranoside (S14)



S13 **S14**

To a stirred solution of compound **S13** (4.0 g, 7.06 mmol) in THF (24 mL) was added TBAF in THF (1 M, 10.6 mL, 10.6 mmol) at room temperature and stirring for over night. Until TLC showed complete convertion of starting material, the mixture was diluted with DCM, washed with saturated $NaHCO_3$, brine and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/EtOAc: 8/1→4/1) to afford the corresponding compound **S14** (3.03 g, 95%). $[\alpha]^{25}_D$ = - 23.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.76 (m, 4H, Ar-H), 7.60 (dd, *J* = 8.4, 1.7 Hz, 1H, Ar-H), 7.56 – 7.45 (m, 4H, Ar-H), 7.45 – 7.33 (m, 3H, Ar-H), 5.55 (s, 1H, Ar*CH*), 5.14 (d, *J* = 11.0 Hz, 1H, Ar*CH*), 4.98 (d, *J* = 11.0 Hz, 1H, Ar*CH*), 4.63 (d, *J* = 9.8 Hz, 1H, 1-H), 4.38 (dd, *J* = 10.5, 4.9 Hz, 1H, 6'-H), 3.95 (dd, *J* = 9.3, 8.4 Hz, 1H, 3-H), 3.79 (t, *J* = 10.2 Hz, 1H, 6-H), 3.58 (t, *J* = 9.3 Hz, 1H, 4-H), 3.47 (dd, *J* = 9.8, 8.4 Hz, 1H, 2-H), 2.90 – 2.73 (m, 2H, SCH_2), 1.37 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.1, 135.4, 133.4, 133.3, 129.4, 128.5, 128.5, 128.1, 127.8, 127.3, 126.4, 126.3, 126.2, 101.9, 85.7, 81.6, 80.5, 75.8, 75.4, 70.2, 68.8, 25.4, 15.2. IR (film): ν = 3465, 3058, 2974, 2872, 1603, 1510, 1457, 1380, 1340, 1273, 1216, 1089, 1030, 977, 917, 857, 820, 754, 700, 655. HRMS (ESI) *m/z* calcd for $C_{26}H_{28}O_5SNa$ $[M+Na]^+$ 475.1550, found 475.1557.

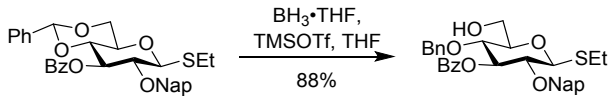
Ethyl 4,6-*O*-benzylidene-3-*O*-benzoyl-2-*O*-(2-naphthylmethyl)-1-thio-β-D-glucopyranoside (S15)



S14 **S15**

A solution of compound **S14** (3.0 g, 6.6 mmol) in pyridine (22 mL) was stirred at 0 °C. Benzoyl chloride (1.5 mL, 13.2 mmol) and a catalyctic amount of *N,N*-dimethylaminopyridine was added. The reaction mixture was stirred at room temperature for 4 h and TLC analysis indicated completion of the reaction. The mixture was evaporated and concentrated to syrup. The desired product **S15** was obtained (3.6 g, 98%) after purified by silica gel flash chromatography. $[\alpha]^{25}_D$ = + 8.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.92 (m, 2H, Ar-H), 7.77 – 7.29 (m, 15H, Ar*CH*), 5.71 (dd, *J* = 9.8, 8.8 Hz, 1H, 3-H), 5.51 (s, 1H, Ar*CH*), 5.04 (d, *J* = 11.0 Hz, 1H, Ar*CH*), 4.80 (d, *J* = 10.7 Hz, 1H, Ar*CH*), 4.78 (d, *J* = 9.5 Hz, 1H, 1-H), 4.43 (dd, *J* = 10.4, 4.9 Hz, 1H, 6'-H), 3.84 (t, *J* = 10.2 Hz, 1H, 6-H), 3.80 (t, *J* = 9.6 Hz, 1H, 4-H), 3.74 (dd, *J* = 9.7, 8.8 Hz, 1H, 2-H), 3.66 (td, *J* = 9.7, 4.9 Hz, 1H, 5-H), 2.96 – 2.77 (m, 2H, SCH_2), 1.40 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 136.9, 134.8, 133.1, 133.0, 129.8, 129.8, 129.1, 128.4, 128.3, 128.2, 128.0, 127.7, 127.3, 126.4, 126.2, 126.0, 125.9, 101.4, 86.2, 79.9, 78.9, 75.6, 74.9, 70.5, 68.8, 25.8, 15.2. IR (film): ν = 2871, 1727, 1603, 1453, 1373, 1315, 1268, 1179, 1087, 1028, 997, 856, 819, 752, 711. HRMS (ESI) *m/z* calcd for $C_{33}H_{32}O_6SNa$ $[M+Na]^+$ 579.1812, found 579.1826.

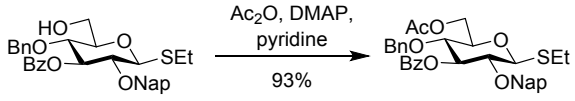
Ethyl 4-*O*-benzyl-3-*O*-benzoyl-2-*O*-(2-naphthylmethyl)-1-thio-β-D-glucopyranoside (S16)



S15 **S16**

A solution of compound **S15** (3.0 g, 5.39 mmol) in anhydrous CH_2Cl_2 (27 mL) was cooled to 0 °C. BH_3·THF (1 M, 35 mL) was added and stirred at 0 °C for 10 minutes. Then TMSOTf (195 µL, 1.1 mmol) was added dropwise and the mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with CH_2Cl_2 and quenched with saturated $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 and combined organic layer was dried over Na_2SO_4 and concentrated in reduced pressure. The crude mixture was purified by silica gel flash chromatography to give **S16** (2.85 g, 88%). $[\alpha]^{25}_D$ = + 38.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.88 (m, 2H, Ar-H), 7.67 (ddt, *J* = 13.1, 9.6, 3.5 Hz, 2H, Ar-H), 7.60 (d, *J* = 1.6 Hz, 1H, Ar-H), 7.58 – 7.50 (m, 2H, Ar-H), 7.45 – 7.33 (m, 4H, Ar-H), 7.31 – 7.25 (m, 1H, Ar-H), 7.22 – 7.11 (m, 5H, Ar-H), 5.63 (t, *J* = 9.2 Hz, 1H, 3-H), 4.99 (d, *J* = 11.1 Hz, 1H, Ar*CH*), 4.73 (d, *J* = 11.1 Hz, 1H, Ar*CH*), 4.69 (d, *J* = 9.7 Hz, 1H, 1-H), 4.56 (s, 2H, Ar*CH*), 3.96 (dd, *J* = 12.2, 2.6 Hz, 1H, 6'-H), 3.83 – 3.75 (m, 2H, 6-H, 4-H) 3.60 (t, *J* = 9.4 Hz, 1H, 2-H), 3.56 – 3.50 (m, 1H, 5-H), 2.84 (qd, *J* = 7.5, 4.2 Hz, 2H, SCH_2), 1.38 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.6, 137.3, 134.8, 133.2, 133.1, 133.0, 129.9, 129.7, 128.5, 128.4, 128.3, 128.2, 128.0, 128.0, 127.7, 127.4, 126.5, 126.0, 125.9, 85.5, 79.4, 79.2, 77.9, 75.7, 75.1, 74.8, 61.9, 25.7, 15.3. IR (film): ν = 3503, 3064, 2930, 2873, 1725, 1603, 1510, 1498, 1453, 1316, 1267, 1177, 1126, 1070, 1028, 1001, 888, 857, 820, 752, 711. HRMS (ESI) *m/z* calcd for $C_{33}H_{34}O_6SNa$ $[M+Na]^+$ 581.1968, found 581.1979.

Ethyl 6-*O*-acetyl-4-*O*-benzyl-3-*O*-benzoyl-2-*O*-(2-naphthylmethyl)-1-thio-β-D-glucopyranoside (S17)

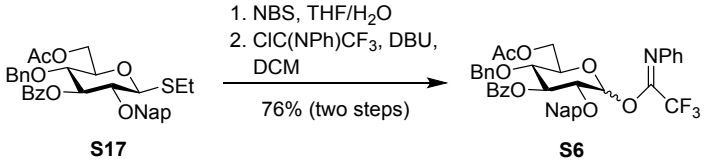


S16 **S17**

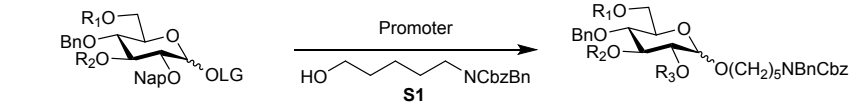
To a solution of compound **S16** (2.5 g, 4.17 mmol) in pyridine (20 mL) was added Ac_2O (3.9 mL, 41.7 mmol) and DMAP (cat.) at room temperature. The reaction mixture was stirred for 2 h at room temperature. After completion as monitored by TLC, the reaction mixture was evaporated and co-evaporated twice with toluene. The residue was extracted with CH_2Cl_2. The organic layer was washed with 1 M HCl (aq), saturated $NaHCO_3$, dried over anhydrous Na_2SO_4, and concentrated to residue. Chromatographic purification afforded **S17** (2.33 g, 93%). $[\alpha]^{25}_D$ = + 46.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.85 (m, 2H, Ar-H), 7.72 – 7.06 (m, 15H, Ar-H), 5.69 – 5.56 (m, 1H, 3-H), 5.00 (d, *J* = 11.2 Hz, 1H, Ar*CH*), 4.74 (d, *J* = 11.2 Hz, 1H, Ar*CH*), 4.66 (d, *J* = 9.7 Hz, 1H, 1-H), 4.53 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.46 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.39 (dd, *J* = 12.0, 1.4 Hz, 1H, 6'-H), 4.29 – 4.22 (m, 1H, 6-H), 3.74 – 3.66 (m, 2H, 4-H, 5-H), 3.62 (t, *J* = 9.4 Hz, 1H, 2-H), 2.83 (qd, *J* = 7.4, 5.8 Hz, 2H, SCH_2), 2.09 (s, 3H, CH_3CO), 1.39 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 165.5, 137.0, 134.8, 133.3, 133.1, 133.0, 129.8, 129.7, 128.5, 128.5, 128.4, 128.2, 128.1, 128.0, 127.7, 127.4, 126.5, 126.0, 125.9, 85.5, 79.2, 77.9, 76.8, 76.0, 75.1, 74.7, 63.3, 25.8, 21.0, 15.3. IR (film): ν = 3063, 2873, 1729, 1603, 1511, 1453, 1367, 1316, 1266, 1240, 1178, 1127, 1091, 1070, 1028, 895, 857, 820, 753, 711. HRMS (ESI) *m/z* calcd for $C_{35}H_{36}O_7SNa$ $[M+Na]^+$ 623.2074, found 623.2086.

***N*-Phenyl trifluoroacetimidate 6-*O*-acetyl-4-*O*-benzyl-3-*O*-benzoyl-2-*O*-(2-naphthylmethyl)-D-**

glucopyranoside (S6)



To a stirred solution of compound **S17** (0.50 g, 0.84 mmol) in THF/H_2O (v/v, 1:1, 8.4 mL) was added NBS (450 mg, 2.52 mmol) at room temperature and stirring about 1.5 h. Until TLC showed complete convertion of starting material, the mixture was diluted with EtOAc, washed with 10% $Na_2S_2O_3$ and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/EtOAc: 5/1→2/1) to afford the corresponding hemiacetal as a colorless syrup. To a solution of the above hemiacetal in CH_2Cl_2 (17 mL) was added 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (0.63 mL, 4.2 mmol) and DBU (375 µL, 2.52 mmol) at 0 °C. The reaction was warmed to room temperature and stirred for 2 h, TLC revealed complete conversion of the starting material. The solution was concentrated in vacuo to a residue, which was purified by silica gel column chromatography (Hexane/EtOAc: 6/1→3/1) to give **S6** (0.42 g, 76%, two steps) as a light yellow syrup. $[\alpha]^{25}_D$ = + 55.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.14 – 7.07 (m, 22H), 6.93 – 6.55 (m, 3H), 5.94 (t, *J* = 9.6 Hz, 0.8H), 5.66 – 5.53 (m, 0.2H), 5.03 – 4.84 (m, 1H), 4.83 – 4.68 (m, 1H), 4.61 – 4.51 (m, 1H), 4.51 – 4.44 (m, 1H), 4.40 (d, *J* = 12.5 Hz, 1H), 4.34 – 4.23 (m, 1H), 4.22 – 4.13 (m, 1H), 3.88 – 3.78 (m, 1H), 3.75 (t, *J* = 9.7 Hz, 1H), 2.08 (s, 3H, CH_3CO). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 170.6, 165.5, 143.6, 137.0, 134.7, 134.6, 133.4, 133.4, 133.2, 133.2, 133.2, 130.0, 129.9, 129.7, 128.9, 128.6, 128.6, 128.5, 128.4, 128.4, 128.2, 128.0, 128.0, 127.8, 127.5, 127.1, 126.3, 126.2, 126.2, 126.1, 126.0, 124.6, 124.4, 119.5, 119.4, 92.6, 75.9, 75.3, 74.8, 74.6, 74.2, 73.8, 73.5, 72.9, 71.4, 62.5. IR (film): ν = 3065, 1731, 1600, 1490, 1453, 1367, 1315, 1268, 1238, 1211, 1164, 1122, 1074, 1027, 923, 858, 822, 754, 711, 697.



S2 R_1= Ac, R_2= Bn, LG= STol (β)
S3 R_1= Bz, R_2= Bn, LG= STol (β)
S4 R_1= Ac, R_2= Bn, LG= C(NPh)CF_3
S5 R_1= Bz, R_2= Bn, LG= C(NPh)CF_3
S6 R_1= Ac, R_2= Bz, LG= C(NPh)CF_3

S7 R_1= Ac, R_2= Bn, R_3= Nap
S8 R_1= Bz, R_2= Bn, R_3= Nap
S9 R_1= Ac, R_2= Bz, R_3= Nap

Procedure 1 (using donor S2)

Donor **S2** (20 mg, 0.031 mmol, 1 eq) and *N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentanol **S1** (20 mg, 0.062 mmol, 2 eq) were coevaporated with toluene and dried under high vacuum overnight. The substances were then dissolved in anhydrous CH_2Cl_2/Dioxane (1:1, v/v, 0.6 mL, 0.05 M) and 4Å MS was added. The mixture was stirred at room temperature for 10 minutes and then cooled to 0 °C, NIS (8.4 mg, 0.037 mmol, 1.2 eq) and TfOH (0.55 µL, 0.0062 mmol, 0,2 eq) was subsequently added and stirred at 0 °C. After 10 h, the reaction was still not completed and most of the starting materials remained. The reaction mixture was quenched with trimethylamine, filtered the 4Å MS and diluted with CH_2Cl_2. The solution was washed with 10% aq $Na_2S_2O_3$, saturated with $NaHCO_3$, dried over Na_2SO_4, filtered and concentrated with reduced pressure to a residue. The residual was purified by

silica gel flash chromatography to give **S7** (10 mg, 36%, α:β = 2.5:1).

Procedure 2 (using donor S3)

Donor **S3** (22 mg, 0.031 mmol, 1 eq) and *N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentanol **S1** (20 mg, 0.062 mmol, 2 eq) were coevaporated with toluene and dried under high vacuum overnight. The substances were then dissolved in anhydrous CH_2Cl_2/Dioxane (1:1, v/v, 0.6 mL, 0.05 M) and 4Å MS was added. The mixture was stirred at room temperature for 10 minutes and then cooled to 0 °C, NIS (8.4 mg, 0.037 mmol, 1.2 eq) and TfOH (0.55 µL, 0.0062 mmol, 0,2 eq) was subsequently added and stirred at 0 °C. After 10 h, the reaction was also still not completed and most of the starting materials remained. The reaction mixture was quenched with trimethylamine, filtered the 4Å MS and diluted with CH_2Cl_2. The solution was washed with 10% aq $Na_2S_2O_3$, saturated with $NaHCO_3$, dried over Na_2SO_4, filtered and concentrated with reduced pressure to a residue. The residual was purified by silica gel flash chromatography to give **S8** (9 mg, 32%, α:β = 2.0:1).

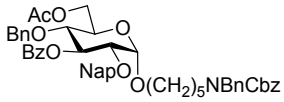
Procedure 3 (using donor S4)

Donor **S4** (78 mg, 0.11 mmol, 1 eq) and *N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentanol **S1** (72 mg, 0.22 mmol, 2 eq) were coevaporated with toluene and dried under high vacuum overnight. The substances were then dissolved in anhydrous CH_2Cl_2/Dioxane (1:1, v/v, 2.2 mL, 0.05 M) and 4Å MS was added. The mixture was stirred at room temperature for 10 minutes and then cooled to 0 °C, TMSOTf (2 µL, 0.011 mmol, 0.1 eq) was subsequently added and stirred at 0 °C until completion as monitored by TLC, the reaction mixture was quenched with trimethylamine, filtered the 4Å MS and diluted with CH_2Cl_2. The solution was washed with saturated $NaHCO_3$, dried over Na_2SO_4, filtered and concentrated with reduced pressure to a residue. The residual was purified by silica gel flash chromatography to give **S7** (86 mg, 92%, α:β = 4:1).

Procedure 4 (using donor S5)

Donor **S5** (61 mg, 0.079 mmol, 1 eq) and *N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentanol **S1** (52 mg, 0.16 mmol, 2 eq) were coevaporated with toluene and dried under high vacuum overnight. The substances were then dissolved in anhydrous CH_2Cl_2/Dioxane (1:1, v/v, 1.6 mL, 0.1 M) and 4Å MS was added. The mixture was stirred at room temperature for 10 minutes and then cooled to 0 °C, TMSOTf (1.4 4MSOTf 08 mmol, 0.1 eq) was subsequently added and stirred at 0 rred at room temperaturndicated the reaction to be complete. The reaction mixture was quenched with trimethylamine, filtered the 4cated the reaction to be$_2Cl_2$. The solution was washed with saturated $NaHCO_3$, dried over Na_2SO_4, filtered and concentrated with reduced pressure to a residue. The residual was purified by silica gel flash chromatography to give **S8** (61 mg, 85%, α:β = 3.1:1).

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl 6-*O*-acetyl-4-*O*-benzyl-3-*O*-benzoyl-2-*O*-(2-naphthylmethyl)-α-D-glucopyranoside (S9)**



S9

Procedure 5 (using donor S6)

Donor **S6** (0.42 g, 0.64 mmol, 1 eq) and *N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentanol **S1** (0.42 g, 1.28 mmol, 2 eq) were coevaporated with toluene and dried under high vacuum overnight. The substances were then dissolved in anhydrous CH_2Cl_2 (12.8 mL,) and 4Å MS was added. The mixture was stirred at room temperature for 10 minutes and then cooled to 0 °C, TMSOTf (12 µL, 0.064 mmol, 0.1 eq) was subsequently added and stirred at 0 °C for 2.5 h. After completion as monitored by TLC, the reaction mixture was quenched with trimethylamine, filtered the 4Å MS and diluted with CH_2Cl_2. The solution was washed with saturated $NaHCO_3$, dried over Na_2SO_4, filtered and concentrated with reduced pressure to a residue. The residual was purified by silica gel flash chromatography to give **S9** (0.50 g, 90%, α/β = 10:1). $[\alpha]^{25}_D$ = + 20.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 – 7.93 (m, 2H, Ar-H), 7.84 – 7.71 (m, 1H, Ar-H), 7.68 – 7.56 (m, 4H, Ar-H), 7.52 – 7.43 (m, 4H, Ar-H), 7.42 – 7.10 (m, 18H, Ar-H), 5.87 (t, *J* = 9.5 Hz, 1H, 3-H), 5.20 (d, *J* = 13.3 Hz, 2H, Ar*CH*), 4.90 – 4.81 (m, 1H, 1-H), 4.80 – 4.63 (m, 2H, Ar*CH*), 4.55 (d, *J* = 10.9 Hz, 1H, Ar*CH*), 4.52 (d, *J* = 7.1 Hz, 2H), 4.45 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.34 – 4.22 (m, 2H, 6-H), 4.02 – 3.91 (m, 1H, 5-H), 3.70 – 3.55 (m, 3H, 2-H, 4-H, CH), 3.46 – 3.33 (m, 1H, CH_2), 3.26 (dt, *J* = 29.3, 7.8 Hz, 2H, CH_2), 2.06 (s, 3H, CH_3CO), 1.61 (tt, *J* = 25.3, 7.4 Hz, 4H, CH_2), 1.44 – 1.25 (m, 2H, CH_2). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.82, 165.62, 156.85, 156.30, 138.03, 137.17, 136.90, 135.28, 133.21, 133.12, 133.10, 130.24, 129.92, 128.66, 128.56, 128.51, 128.43, 128.37, 128.11, 127.97, 127.92, 127.79, 127.36, 126.93, 126.27, 126.13, 126.02, 96.57 (C-1), 75.98, 74.64, 74.59, 74.30, 72.47, 68.47, 67.26, 63.00, 50.66, 50.35, 47.23, 46.32, 29.25, 28.12, 27.66, 23.60, 21.03. IR (film): ν = 3034, 2940, 1731, 1698, 1604, 1498, 1454, 1422, 1367, 1269, 1236, 1126, 1073, 1028, 857, 821, 751, 712, 700. HRMS (ESI) *m/z* calcd for $C_{53}H_{55}NO_{10}Na$ $[M+Na]^+$ 888.3718, found 888.3719.

Ethyl 6-*O*-acetyl-4-*O*-benzyl-3-*O*-benzoyl-1-thio-β-D-glucopyranoside (7)

S17 **7**

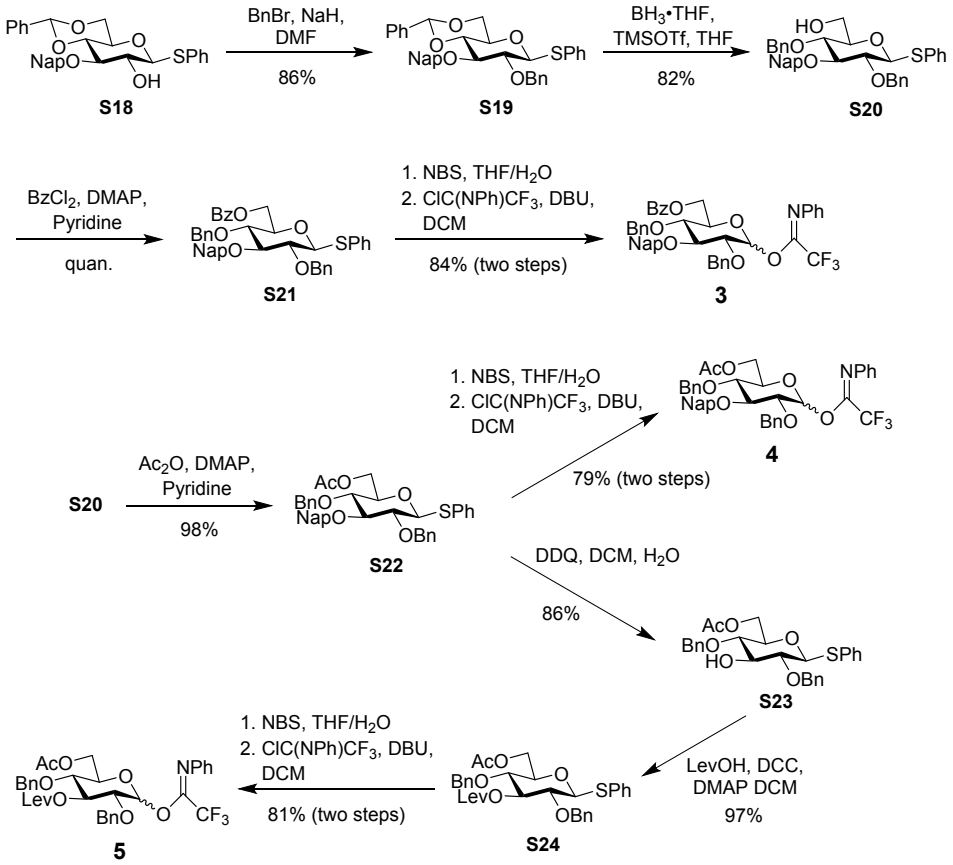
To a solution of compound **S17** (1.0 g, 1.68 mmol) was dissolved in a mixture of CH_2Cl_2/H_2O (9:1, v/v, 33 mL) was added DDQ (572 mg, 2.52 mmol) at 0 °C. Then the reaction mixture was allowed to warm to room temperature and stirred for 12 h, the starting material was completely disappeared. The reaction mixture was diluted with CH_2Cl_2, washed with 10% aq $Na_2S_2O_3$, dried over Na_2SO_4 and concentrated. The residual was purified by silica gel flash chromatography to give **7** (0.61 g, 79%). $[\alpha]^{25}_D$ = - 34.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 – 7.97 (m, 2H, Ar-H), 7.67 – 7.59 (m, 1H, Ar-H), 7.49 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.26 – 7.11 (m, 4H, Ar-H), 5.49 (t, *J* = 9.0 Hz, 1H, 3-H), 4.65 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.54 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.51 (d, *J* = 10.1 Hz, 1H, 1-H), 4.40 (dd, *J* = 12.0, 2.1 Hz, 1H, 6'-H), 4.27 (dd, *J* = 12.0, 5.0 Hz, 1H, 6-H), 3.78 (dd, *J* = 9.8, 8.9 Hz, 1H, 4-H), 3.73 – 3.68 (m, 1H, 5-H), 3.66 (t, *J* = 9.5 Hz, 1H, 2-H), 2.79 (qd, *J* = 7.5, 2.1 Hz, 2H, SCH_2), 2.10 (s, 3H, OAc), 1.36 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 166.5, 137.0, 133.6, 130.0, 129.7, 128.6, 128.6, 128.3, 128.2, 86.7, 79.0, 75.6, 75.0, 71.9, 63.3, 25.2, 21.1, 15.5. IR (film): ν = 3481, 2874, 1726, 1603, 1497, 1453, 1368, 1316, 1268, 1179, 1097, 1071, 1029, 833, 752, 713. HRMS (ESI) *m/z* calcd for $C_{24}H_{28}O_7SNa$ $[M+Na]^+$ 483.1448, found 483.1457.

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl 6-*O*-acetyl-4-*O*-benzyl-3-*O*-benzoyl-α-D-glucopyranoside (8)**

S9 **8**

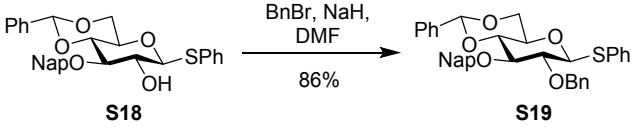
To a solution of compound **S9** (0.45 g, 0.52 mmol) in a mixture of CH_2Cl_2/H_2O (9:1, v/v, 10 mL) was added DDQ (177 mg, 0.78 mmol) at 0 °C, the reaction mixture was allowed to warm to room temperature. After stirred for 3 h, the starting material was completely disappeared. The reaction mixture was diluted with CH_2Cl_2, washed with 10% aq $Na_2S_2O_3$, dried over Na_2SO_4 and concentrated. The residual was purified by silica gel flash chromatography to give **8** (0.31 g, 82%). $[\alpha]^{25}_D$ = + 53.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.69 – 7.10 (m, 18H, Ar-H), 5.61 (td, *J* = 9.5, 4.0 Hz, 1H, 3-H), 5.20 (d, *J* = 17.6 Hz, 2H, Ar*CH*), 5.02 – 4.80 (m, 1H, 1-H), 4.66 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.59 – 4.47 (m, 3H, CH_2), 4.34 (d, *J* = 3.2 Hz, 2H, 6-H), 3.95 (dt, *J* = 12.4, 6.3 Hz, 1H, 5-H), 3.80 – 3.62 (m, 3H, 2-H, 4-H, CH_2), 3.52 – 3.35 (m, 1H, CH_2), 3.35 – 3.17 (m, 2H, CH_2), 2.11 (s, 3H, CH_3CO), 1.72 – 1.47 (m, 4H, CH_2), 1.46 – 1.19 (m, 2H, CH_2). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 166.6, 156.7, 156.2, 137.9, 137.1, 136.9, 136.8, 133.3, 129.8, 128.6, 128.5, 128.5, 128.2, 128.1, 127.9, 127.3, 98.4 (C-1), 76.5, 75.3, 74.8, 71.5, 68.8, 68.5, 67.2, 62.8, 50.6, 50.3, 47.0, 46.1, 29.1, 27.9, 27.5, 23.4, 20.9. IR (film): ν = 3457, 3034, 2939, 1727, 1699, 1604, 1498, 1454, 1423, 1367, 1315, 1271, 1235, 1131, 1097, 1071, 1047, 1029, 770, 735, 699. HRMS (ESI) *m/z* calcd for $C_{42}H_{47}NO_{10}Na$ $[M+Na]^+$ 748.3092, found 748.3102.

2.2 Synthesis of building blocks 3, 4 and 5.



Scheme S-3. Synthesis of building blocks **3**, **4** and **5**

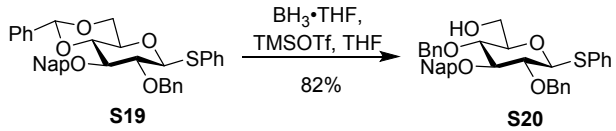
Phenyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2-naphthylmethyl)-1-thio-β-D-glucopyranoside (S19).



To a solution of compound **S18**[5] (4.14 g, 8.27 mmol) in anhydrous DMF (40 mL) were added NaH (660 mg, 16.54 mmol, 60% dispersion in mineral oil) at 0 °C for 10 min. Then benzyl bromide (1.5 mL, 12.45 mmol) was added to the reaction mixture and stirred at room temperature for 3.5 h. Upon reaction completion, the mixture was cooled to 0 °C and water was added dropwise. The residue was extracted with CH_2Cl_2 three times. Combined organic layer was dried over Na_2SO_4 and concentrated in reduced pressure. The crude mixture was purified by silica gel flash chromatography to give **S19** (4.20 g, 86%). $[\alpha]^{25}_D$ = - 12.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.69 (m, 4H, Ar-H), 7.60 – 7.30 (m, 18H, Ar-H), 5.64 (s, 1H, Ar*CH*), 5.11 (d, *J* = 11.4 Hz, 1H, Ar*CH*), 4.97 (d, *J* = 11.4 Hz, 1H, Ar*CH*), 4.91 (d, *J* = 10.2 Hz, 1H, Ar*CH*), 4.86 (d, *J* = 10.2 Hz, 1H, Ar*CH*), 4.80 (d, *J* = 9.8 Hz, 1H, 1-H), 4.42 (dd, *J* = 10.5, 5.0 Hz, 1H, 6'-H), 3.92 (dd, *J* = 9.4, 8.3 Hz, 1H, 3-H), 3.85 (t, *J* = 10.3 Hz, 1H, 6-H), 3.77 (t, *J* = 9.4 Hz, 1H, 4-H), 3.57 (dd, *J* = 9.9, 8.4 Hz, 1H, 2-H), 3.54 – 3.47 (m, 1H, 5-H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.1, 137.3, 135.8, 133.4, 133.2, 133.1, 132.5, 129.2, 128.6, 128.4, 128.3, 128.3, 128.1, 128.0 (d, *J* = 1.3 Hz), 127.8, 127.0, 126.3, 126.2, 126.2, 126.0, 101.3, 88.4, 83.0, 81.6, 80.6, 76.1,

75.5, 70.4, 68.8. IR (film): ν = 3063, 2869, 1586, 1498, 1455, 1441, 1374, 1346, 1272, 1215, 1173, 1091, 1028, 1003, 916, 857, 819, 749, 699, 656. HRMS (ESI) *m/z* calcd for $C_{37}H_{34}O_5SNa$ $[M+Na]^+$ 613.2019, found 613.2026.

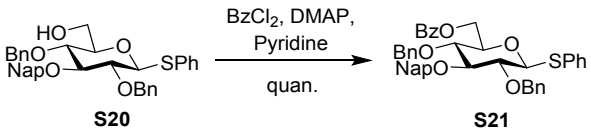
Phenyl 2,4-di-*O*-benzyl-3-*O*-(2-naphthylmethyl)-1-thio-β-D-glucopyranoside (S20).



S19 **S20**

A solution of compound **S19** (4.0 g, 6.78 mmol) in anhydrous CH_2Cl_2 (68 mL) was cooled to 0 °C. BH_3·THF (1 M, 44 mL) was added and stirred at 0 °C for 10 minutes. Then TMSOTf (184 µL, 1.02 mmol) was added dropwise and the mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with CH_2Cl_2 and quenched saturated $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL) and combined organic layer was dried over Na_2SO_4 and concentrated in reduced pressure. The crude mixture was purified by silica gel chromatography to give **S20** (3.29 g, 82%). $[\alpha]^{25}_D$ = + 20.55 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.72 (m, 4H, Ar-H), 7.59 – 7.25 (m, 18H, Ar-H), 5.09 (d, *J* = 11.2 Hz, 1H, Ar*CH*), 5.05 (d, *J* = 11.2 Hz, 1H, Ar*CH*), 4.97 (d, *J* = 10.3 Hz, 1H, Ar*CH*), 4.91 (d, *J* = 11.0 Hz, 1H, Ar*CH*), 4.81 (d, *J* = 10.3 Hz, 1H, Ar*CH*), 4.77 (d, *J* = 9.8 Hz, 1H, 1-H), 4.71 (d, *J* = 10.9 Hz, 1H, Ar*CH*), 3.92 (dd, *J* = 12.0, 2.7 Hz, 1H, 6'-H), 3.82 (t, *J* = 8.9 Hz, 1H, 3-H), 3.74 (dd, *J* = 12.0, 4.9 Hz, 1H, 6-H), 3.64 (t, *J* = 9.4 Hz, 1H, 4-H), 3.55 (dd, *J* = 9.8, 8.8 Hz, 1H, 2-H), 3.44 (ddd, *J* = 9.7, 4.9, 2.7 Hz, 1H, 5-H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.9, 137.8, 135.8, 133.4, 133.3, 133.0, 131.9, 129.1, 128.6, 128.5, 128.2 (d, *J* = 1.3 Hz), 128.0, 128.0, 127.9, 127.7, 127.7, 126.5, 126.1, 125.9, 125.8, 87.6, 86.5, 81.1, 79.3, 77.6, 75.9, 75.6, 75.2, 62.2. IR (film): ν = 3336, 3033, 2905, 1586, 1498, 1480, 1455, 1440, 1401, 1348, 1285, 1217, 1127, 1066, 1029, 988, 891, 857, 817, 746, 697. HRMS (ESI) *m/z* calcd for $C_{37}H_{36}O_5SNa$ $[M+Na]^+$ 615.2176, found 615.2191.

Phenyl 6-*O*-benzoyl-2,4-di-*O*-benzyl-3-*O*-(2-naphthylmethyl)-1-thio-β-D-glucopyranoside (S21).

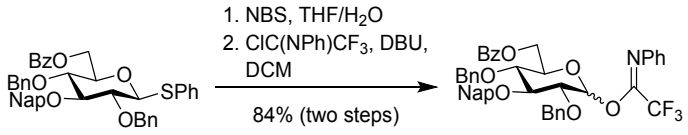


S20 **S21**

A solution of compound **S20** (100 mg, 0.17 mmol) in pyridine (1.7 mL) was stirred at 0 °C. Benzoyl chloride (40 µL, 0.34 mmol) and a catalyctic amount of *N,N*-dimethylaminopyridine was added. The reaction mixture was stirred at room temperature for 2 h and TLC analysis indicated completion of the reaction. The mixture was evaporated to syrup and diluted with DCM. The organic layer was washed with saturated $NaHCO_3$, brine and dried over Na_2SO_4. After evaporating to syrup, the crude mixture was purified by silica gel flash chromatography to give the product **S21** (118 mg, quan.). $[\alpha]^{25}_D$ = + 18.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 8.02 (m, 2H, Ar), 7.91 – 7.72 (m, 4H, Ar), 7.68 – 7.08 (m, 21H, Ar), 5.12 (d, *J* = 11.0 Hz, 1H, Ar*CH*), 5.05 (d, *J* = 11.0 Hz, 1H, Ar*CH*), 4.99 (d, *J* = 10.3 Hz, 1H, Ar*CH*), 4.94 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.80 (d, *J* = 10.3 Hz, 1H, Ar*CH*), 4.75 (d, *J* = 9.8 Hz, 1H, 1-H), 4.73 (dd, *J* = 11.9, 1.8 Hz, 1H, 6'-H), 4.69 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.49 (dd, *J* = 11.9, 4.8 Hz, 1H, 6-H), 3.86 (t, *J* = 8.6 Hz, 1H, 3-H), 3.79 – 3.67 (m, 2H, 4-H, 5-H), 3.60 (dd, *J* = 9.7, 8.8 Hz, 1H, 2-H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.1, 137.9, 137.5, 135.6, 133.3, 133.2, 133.2, 133.0, 132.3,

129.9, 129.8, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 127.7, 127.7, 126.7, 126.2, 126.0, 125.9, 87.3, 86.8, 80.7, 77.6, 76.1, 75.5, 75.3, 63.6. IR (film): ν = 3064, 2904, 1723, 1603, 1585, 1498, 1454, 1343, 1316, 1274, 1091, 1069, 1028, 900, 857, 819, 745, 712, 699. HRMS (ESI) *m/z* calcd for $C_{44}H_{40}O_6SNa$ $[M+Na]^+$ 719.2438, found 719.2453.

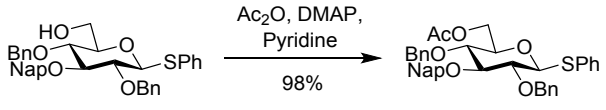
_N_-Phenyl trifluoroacetimidate 6-_O_-benzoyl-2,4-di-_O_-benzyl-3-_O_-(2-naphthylmethyl)-D-Glucopyranoside (3)



S21 **3**

To a solution of compound **S21** (90 mg, 0.13 mmol) in THF/H_2O (2:1, v/v, 3 mL), was added NBS (70 mg, 0.39 mmol) at room temperature and the reaction mixture was stirred for 2 h. The reaction was quenched with 10% $Na_2S_2O_3$ and diluted with ethyl acetate. The mixture was washed with saturated $NaHCO_3$ and organic layer was dried over Na_2SO_4. Concentrated *in vacuo* and the residue was purified by silica gel flash chromatography to afford corresponding hemiacetal as a colorless syrup. To a solution of the above hemiacetal and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (100 µL, 0.65 mmol) in anhydrous CH_2Cl_2 (2.6 mL) was added DBU (58 µL, 0.39 mmol) at 0 °C, and the reaction was stirred at room temperature for 1.5 h. TLC revealed complete conversion of the starting material and the solution was concentrated *in vacuo* and purified by silica gel flash chromatography to give **3** (77 mg, 84%, two steps). $[\alpha]^{25}_D$ = + 71.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 8.00 (m, 5H), 7.94 – 7.73 (m, 12H), 7.68 – 7.07 (m, 37H), 6.87 – 6.67 (m, 5H), 6.55 (bs, 1H, H-1α), 5.80 (bs, 1H, H-1β), 5.27 – 4.80 (m, 13H, Ar*CH*), 4.75 – 4.55 (m, 8H, Ar*CH*, H-6α, H-6β), 4.26 - 4.12 (m, 2H), 3.94 – 3.63 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 166.1, 143.5, 143.4, 137.7, 137.6, 137.5, 137.4, 135.8, 135.6, 133.4, 133.3, 133.2, 133.2, 133.1, 129.8, 129.7, 129.1, 128.8, 128.7, 128.6, 128.6, 128.6, 128.5, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 128.0, 127.8, 127.7, 127.7, 126.9, 126.7, 126.2, 126.2, 126.1, 126.1, 126.0, 126.0, 125.9, 125.3, 124.4, 124.2, 119.4, 119.3, 97.0 (C-1β), 93.0 (C-1α), 84.5, 81.6, 80.8, 79.5, 77.3, 76.1, 75.9, 75.5, 75.5, 75.3, 75.2, 73.9, 73.4, 71.7, 63.2, 63.0, 21.5. HRMS (ESI) *m/z* calcd for $C_{46}H_{40}F_3NO_7Na$ $[M+Na]^+$ 798.2649, found 798.2641.

Phenyl 6-_O_-acetyl-2,4-di-_O_-benzyl-3-_O_-(2-naphthylmethyl)-1-thio-β-D-glucopyranoside (S22).

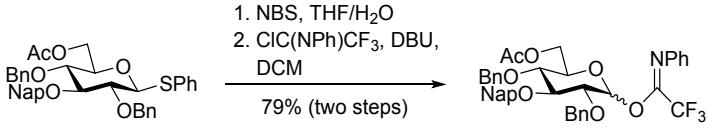


S20 **S22**

To a solution of compound **S20** (1.0 g, 1.69 mmol) in pyridine (17 mL) was added acetic anhydride (1.6 mL, 16.9 mmol) and a catalyctic amount of *N,N*-dimethylaminopyridine at room temperature. The reaction mixture was stirred at room temperature for 4 h and TLC analysis indicated completion of the reaction. The mixture was evaporated to syrup and diluted with DCM. The organic layer was washed with saturated $NaHCO_3$, brine and dried over Na_2SO_4. After evaporating to syrup, the crude mixture was purified by silica gel chromatography to give the product **S22** (1.05 g, 98%). $[\alpha]^{25}_D$ = + 19.7

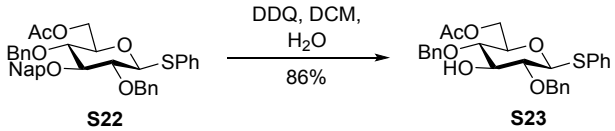
(*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.73 (m, 4H, Ar-H), 7.64 – 7.23 (m, 18H, Ar-H), 5.11 (d, *J* = 11.1 Hz, 1H, Ar*CH*), 5.03 (d, *J* = 11.1 Hz, 1H, Ar*CH*), 4.98 (d, *J* = 10.2 Hz, 1H, Ar*CH*), 4.91 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.79 (d, *J* = 10.2 Hz, 1H, Ar*CH*), 4.71 (d, *J* = 9.8 Hz, 1H, 1-H), 4.41 (dd, *J* = 11.8, 1.4 Hz, 1H, 6'-H), 4.25 (ddd, *J* = 11.7, 3.5, 1.5 Hz, 1H, 6-H), 3.86 – 3.76 (m, 1H, 3-H), 3.63 – 3.53 (m, 3H, 5-H, 4-H, 2-H), 2.08 (s, 3H, CH_3CO). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 137.9, 137.5, 135.7, 133.6, 133.3, 133.0, 132.1, 128.9, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.7, 126.5, 126.2, 126.0, 125.8, 87.5, 86.7, 80.9, 77.5, 76.9, 76.0, 75.6, 75.2, 63.3, 20.9. IR (film): ν = 3062, 3034, 2871, 1742, 1604, 1585, 1510, 1498, 1481, 1455, 1441, 1367, 1348, 1235, 1126, 1067, 1029, 901, 857, 818, 745, 698. HRMS (ESI) *m/z* calcd for $C_{39}H_{38}O_6SNa$ $[M+Na]^+$ 657.2281, found 657.2296.

_N_-Phenyl trifluoroacetimidate 6-_O_-acetyl-2,4-di-_O_-benzyl-3-_O_-(2-naphthylmethyl)-D-Glucopyranoside (4)



To a stirred solution of compound **S22** (42 mg, 0.066 mmol) in THF/H_2O (v/v, 1:1, 1.2 mL) was added NBS (36 mg, 0.2 mmol) at room temperature and stirring about 1.5 h. Until TLC showed complete convertion of starting material, the mixture was diluted with EtOAc, washed with 10% $Na_2S_2O_3$ and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the corresponding hemiacetal as a colorless syrup. To a solution of the above hemiacetal in CH_2Cl_2 (3.3 mL) was added 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (49 μL, 0.33 mmol) and DBU (30 μL, 0.2 mmol) at 0 °C. The reaction was warmed to room temperature and stirred for 2 h, TLC revealed complete conversion of the starting material. The solution was concentrated in vacuo to a residue, which was purified by silica gel column chromatography (Hexane/EtOAc: 10/1→8/1) to give **4** (37 mg, 79%, two steps) as a light yellow syrup. $[\alpha]^{25}_D$ = + 58.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 7.91 – 7.73 (m, 4H, Ar-H), 7.56 – 7.10 (m, 16H, Ar-H), 6.90 – 6.75 (m, 2H), 5.24 – 5.11 (m, 1H), 5.10 – 4.99 (m, 1H), 4.98 – 4.80 (m, 3H), 4.70 – 4.57 (m, 1H), 4.42 – 4.01 (m, 3H), 3.88 – 3.61 (m, 3H), 2.08 (s, 3H, CH_3CO). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 170.7, 170.7, 143.7, 143.5, 137.8, 137.7, 137.7, 137.6, 136.0, 135.8, 133.5, 133.5, 133.2, 128.9, 128.7, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 127.9, 127.8, 124.5, 119.4, 97.1, 84.6, 81.6, 80.9, 79.4, 76.6, 76.0, 75.8, 75.4, 75.2, 75.2, 73.8, 73.5, 71.6, 62.8, 62.7, 20.9. IR (film): ν = 3033, 2878, 1744, 1719, 1599, 1490, 1455, 1367, 1316, 1210, 1163, 1089, 1030, 908, 857, 819, 778, 754, 697.

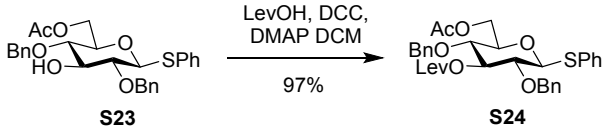
Phenyl 6-_O_-acetyl-2,4-di-_O_-benzyl-1-thio-β-D-glucopyranoside (S23).



To a solution of **S22** (0.98 g, 1.54 mmol) in a mixture of CH_2Cl_2/H_2O (9:1, v/v, 77 mL) was added

DDQ (524 mg, 2.31 mmol) at 0 °C. Then the reaction mixture was stirred at room temperature for overnight. After TLC revealed complete conversion of the starting material, the reaction mixture was diluted with CH_2Cl_2, washed with 10% aq $Na_2S_2O_3$, dried over Na_2SO_4 and concentrated. The residual was purified by silica gel flash chromatography to give **S23** (0.65 g, 86%). $[\alpha]^{25}_D$ = + 7.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.55 (m, 2H, Ar-H), 7.46 – 7.29 (m, 13H, Ar-H), 5.03 (d, *J* = 11.0 Hz, 1H, Ar*CH*), 4.86 (d, *J* = 11.1 Hz, 1H, Ar*CH*), 4.69 (d, *J* = 11.0 Hz, 2H, Ar*CH*), 4.66 (d, *J* = 9.7 Hz, 1H, 1-H), 4.66 (d, *J* = 11.4 Hz, 1H, Ar*CH*), 4.39 (dd, *J* = 11.9, 2.1 Hz, 1H, 6'-H), 4.24 (dd, *J* = 11.9, 5.8 Hz, 1H, 6-H), 3.81 (t, *J* = 8.8 Hz, 1H, 3-H), 3.56 (ddd, *J* = 9.9, 5.8, 2.1 Hz, 1H, 5-H), 3.45 (dd, *J* = 9.8, 8.8 Hz, 1H, 4-H), 3.38 (dd, *J* = 9.8, 8.7 Hz, 1H, 2-H), 2.07 (s, 3H, CH_3CO). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 138.0, 137.9, 133.7, 132.0, 129.1, 128.8, 128.7, 128.4, 128.4, 128.3, 128.2, 127.8, 87.2, 80.8, 78.9, 76.8, 75.4, 74.8, 63.6, 21.0. IR (film): ν = 3460, 2896, 1742, 1498, 1455, 1368, 1240, 1093, 1030, 827, 745, 700. HRMS (ESI) *m/z* calcd for $C_{28}H_{30}O_6SNa$ $[M+Na]^+$ 517.1655, found 517.1669.

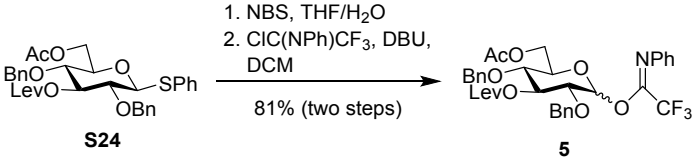
Phenyl 6-*O*-Acetyl-2,4-di-*O*-benzyl-3-O-levulinoyl-1-thio-β-D-glucopyranoside (S24).



S23 **S24**

A soultion of compound **S23** (0.60 g, 1.2 mmol), levulinic acid (210 mg, 1.8 mmol), *N*,*N*-Dicyclohexylcarbodiimide (371 mg, 1.8 mmol), and DMAP (220 mg, 1.8 mmol) in anhydrous CH_2Cl_2 (12 mL) was stirred for 1.5 h at room temperature. Until complete consumption of the starting material, the reaction mixture was diluted with CH_2Cl_2 and filtered. The organic layer was washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo to give a residue that was purified by silica gel column chromatography (petroleum ether/EtOAc: 5/1→3/1) to provide **S24** (0.69 g, 97%). $[\alpha]^{25}_D$ = + 11.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.51 (m, 2H, Ar-H), 7.40 – 7.24 (m, 13H, Ar-H), 5.35 (t, *J* = 8.9 Hz, 1H, 3-H), 4.90 (d, *J* = 11.0 Hz, 1H, Ar*CH*), 4.72 (d, *J* = 9.8 Hz, 1H, 1-H), 4.64 (d, *J* = 11.2 Hz, 1H, Ar*CH*), 4.60 (d, *J* = 11.1 Hz, 1H, Ar*CH*), 4.53 (d, *J* = 11.2 Hz, 1H, Ar*CH*), 4.37 (dd, *J* = 11.9, 2.0 Hz, 1H, 6'-H), 4.21 (dd, *J* = 12.0, 5.3 Hz, 1H, 6-H), 3.66 – 3.53 (m, 2H, 4-H, 5-H), 3.49 (t, *J* = 9.4 Hz, 1H, 2-H), 2.62 (qt, *J* = 18.3, 6.5 Hz, 2H, CH), 2.45 (ddd, *J* = 17.4, 7.4, 6.0 Hz, 1H, CH), 2.34 (dt, *J* = 17.5, 6.5 Hz, 1H, CH), 2.15 (s, 3H, CH_3CO), 2.08 (s, 3H, CH_3CO). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.4, 171.9, 170.7, 137.9, 137.4, 133.3, 132.3, 129.1, 128.6, 128.5, 128.2, 128.2, 128.2, 128.0, 127.9, 87.5, 79.0, 77.7, 76.1, 74.9, 74.6, 63.2, 37.8, 30.0, 28.1, 21.0. IR (film): ν = 3034, 2912, 1743, 1720, 1585, 1498, 1481, 1456, 1441, 1406, 1360, 1234, 1208, 1181, 1160, 1091, 1070, 1030, 913, 831, 747, 700. HRMS (ESI) *m/z* calcd for $C_{33}H_{36}O_8SNa$ $[M+Na]^+$ 615.2023, found 615.2026.

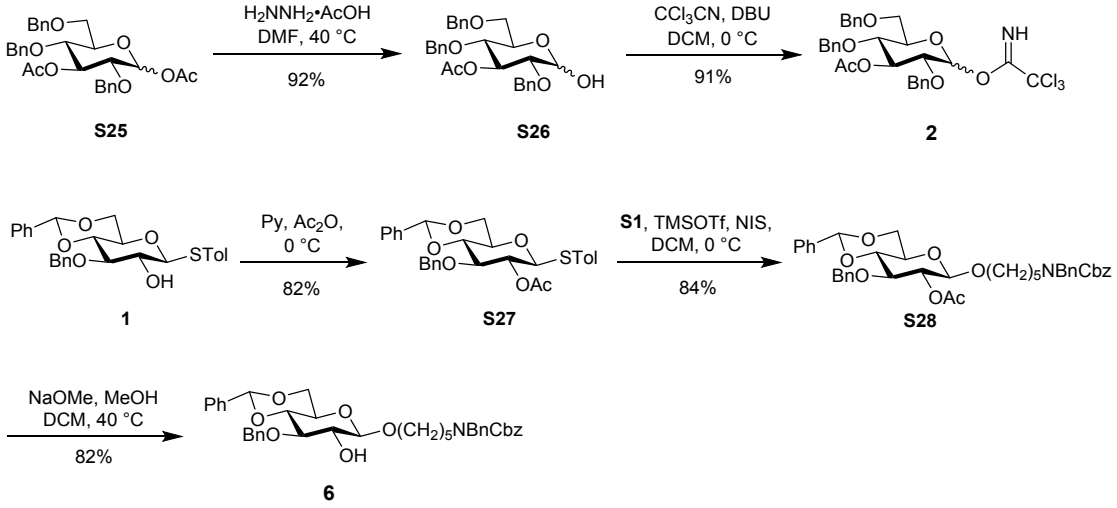
***N*-Phenyl trifluoroacetimidate 6-*O*-acetyl-2,4-di-*O*-benzyl-3-*O*-levulinoyl-D-glucopyranoside (5).**



S24 **5**

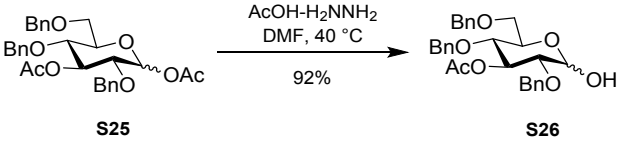
To a solution of compound **S24** (0.65 g, 1.1 mmol) in THF/H_2O (v/v, 1:1, 11 mL) was added NBS (587 mg, 3.3 mmol) at room temperature and stirring about 2.5 h. Until TLC showed complete convertion of starting material, the mixture was diluted with EtOAc, washed with 10% $Na_2S_2O_3$ and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the corresponding hemiacetal as a colorless syrup. To a solution of the above hemiacetal in CH_2Cl_2 (11 mL) was added 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (0.82 mL, 5.5 mmol) and DBU (490 µL, 3.3 mmol) at 0 °C. The reaction was warmed to room temperature and stirred for 2 h, TLC revealed complete conversion of the starting material. The solution was concentrated in vacuo to a residue, which was purified by silica gel column chromatography (Hexane/EtOAc: 5/1→2/1) to give **5** (0.60 g, 81%, two steps) as a light yellow syrup. $[\alpha]^{25}_{D}$ = + 72.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 7.56 – 7.05 (m, 15H, Ar-H), 7.00 – 6.80 (m, 1H), 6.79 – 6.68 (m, 1H), 4.59 – 4.52 (m, 1H), 4.39 – 4.29 (m, 1H), 4.29 – 4.16 (m, 1H), 4.14 – 4.01 (m, 1H), 3.73 – 3.59 (m, 2H), 2.90 – 2.36 (m, 4H), 2.23 – 2.12 (m, 3H, CH_3CO), 2.10 – 1.97 (m, 3H, CH_3CO). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 206.3, 173.4, 171.9 (d, *J* = 6.4 Hz), 170.6, 143.6, 137.6, 137.4, 129.3, 128.9, 128.7, 128.6, 128.3, 128.2, 128.2, 127.9, 127.1, 124.4, 119.4, 118.5, 78.1, 76.5, 75.3, 74.7, 74.4, 73.7, 73.2, 71.3, 62.5, 37.9, 30.0, 28.9, 28.2, 20.9. IR (film): ν = 3036, 1742, 1720, 1598, 1490, 1456, 1363, 1311, 1209, 1158, 1121, 1088, 1029, 924, 744, 698.

2.3 Synthesis of building blocks 2 and 6.



Scheme S-4. Synthesis of building blocks **2** and **6**

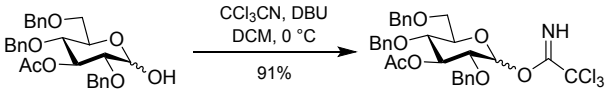
2,4,6-Tri-*O*-benzyl-3-*O*-acetyl-D-glucopyranose (S26)



To a solution of **S25**[6] (1.6 g, 3.0 mmol) in DMF (30 mL) at room temperature, was added hydrazine acetate (305 mg, 3.3 mmol). After being stirred at 40 °C for 2 h, the mixture was diluted with EtOAc, washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography

(Hexane/EtOAc: 2/1) to give compound **S26** (1.36 g, 92%). $[\alpha]^{25}_{D}$ = + 43.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.21 (m, 13H, Ar-H), 7.13 (d, *J* = 7.2 Hz, 2H, Ar-H), 5.50 (t, *J* = 9.6 Hz, 1H, 3-H), 5.27 (d, *J* = 3.6 Hz, 1H, 1-H), 4.67 – 4.37 (m, 6H, Ar*CH*), 4.07 (d, *J* = 10.0 Hz, 1H, 6a-H), 3.78 (s, 1H, 1-OH), 3.73 - 3.58 (m, 3H, 4-H, 5-H, 6b-H), 3.48 (dd, *J* = 9.8, 3.4 Hz, 1H, 2-H), 1.91 (s, 3H, Me). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.1, 138.0, 137.8, 137.6, 128.5, 128.5, 128.4, 128.3, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 90.9, 77.6, 77.5, 77.2, 76.9, 76.1, 74.4, 74.3, 73.9, 73.6, 73.6, 73.5, 72.6, 69.9, 68.4, 21.1. IR (film): ν = 3361, 1736, 1363, 1231, 1145, 1088, 1043, 751, 696. HRMS (ESI) *m/z* calcd for $C_{29}H_{32}O_7Na$ $[M+Na]^+$ 515.2040, found 515.2048.

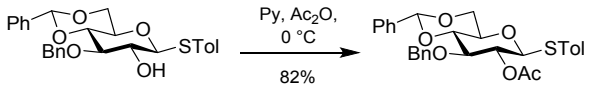
2,4,6-Tri-*O*-benzyl-3-*O*-acetyl-D-glucopyranosyl trichloroacetimidate (2)



S26 **2**

To a solution of the above hemiacetal **S26** (0.65 g, 1.32 mmol) in CH_2Cl_2 (13 mL) was added CCl_3CN (265 µL, 2.64 mmol) and DBU (40 µL, 0.26 mmol) at 0 ºC. After being stirred at 0 ºC for 2.5 h, TLC revealed complete conversion of the starting material. The solution was concentrated in vacuo to a residue, which was purified by silica gel column chromatography (Hexane/EtOAc: 2/1) to give **2** (0.76 g, 91%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (s, 1H, NH), 7.28 (dt, *J* = 19.8, 5.5 Hz, 13H, Ar-H), 7.19 - 7.14 (m, 2H, Ar-H), 6.54 (d, *J* = 3.5 Hz, 1H, H-1), 5.59 (t, *J* = 9.7 Hz, 1H, H-3), 4.65 (d, *J* = 12.4 Hz, 1H, Ar*CH*), 4.60 (d, *J* = 11.9 Hz, 1H, Ar*CH*), 4.55 - 4.48 (m, 3H, Ar*CH*), 4.46 (d, *J* = 11.8 Hz, 1H, Ar*CH*), 4.04 (dt, *J* = 10.1, 2.5 Hz, 1H, H-6a), 3.84 – 3.73 (m, 2H, H-6b, H-4), 3.67 (dd, *J* = 10.0, 3.6 Hz, 2H, H-2, H-5), 1.91 (s, 3H, Me). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 161.3, 137.8, 137.8, 137.7, 94.0, 91.2, 76.5, 75.5, 74.7, 73.7, 73.2, 73.0, 72.5, 67.9, 21.1.

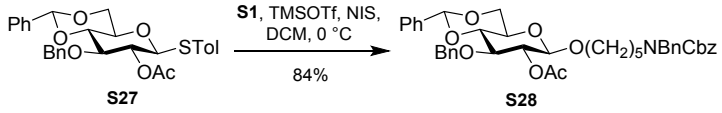
***p*-Methylphenyl 4,6-*O*-benzylidene-3-*O*-benzyl-2-*O*-acetyl-1-thio-β-D-glucopyranoside (S27)**



1 **S27**

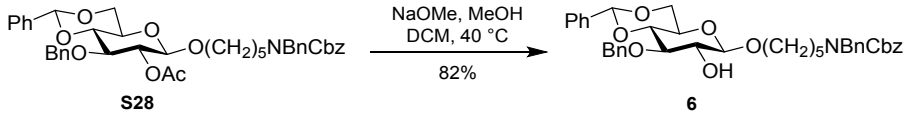
To a solution of compound **1** (2.5 g, 5.39 mmol) in pyridine (20 mL), was added acetic anhydride (5.1 mL, 54 mmol) and a catalyctic amount of *N,N*-dimethylaminopyridine. After being stirred at room temperature for overnight, the mixture was concentrated in vacuo to give a residue, which was purified by silica gel column chromatography (Hexane/EtOAc: 10/1 to 7/1) to give the corresponding ester **S27** (2.24 g, 82%). $[\alpha]^{25}_{D}$ = + 9.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.19 (m, 12H, Ar-H), 7.11 (d, *J* = 7.9 Hz, 2H, Ar-H) 5.56 (s, 1H, PhCH), 4.99 (dd, *J* = 10.0, 8.6 Hz, 1H, 2-H), 4.85 (d, *J* = 12.0 Hz, 1H, Ar*CH*), 4.68 – 4.60 (m, 2H, 1-H, Ar*CH*), 4.37 (dd, *J* = 10.5, 5.0 Hz, 1H, 6a-H), 3.79 (t, *J* = 10.3 Hz, 1H, 6b-H), 3.75 – 3.69 (m, 2H, 3-H, 4-H), 3.47 (dq, *J* = 7.9, 5.0 Hz, 1H, 5-H), 2.33 (s, 3H, Me), 2.03 (s, 3H, Me). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.2, 138.3, 137.1, 133.4, 133.4, 129.7, 129.7, 129.0, 128.3, 128.2, 128.2, 127.9, 127.7, 126.0, 101.2, 87.0, 81.3, 79.8, 74.3, 71.4, 70.5, 68.5, 21.1, 21.0. IR (film): ν = 1740, 1371, 1227, 1062, 1028, 1000, 751, 697. HRMS (ESI) *m/z* calcd for $C_{29}H_{30}O_6SNa$ $[M+Na]^+$ 529.1655, found 529.1656.

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl 4,6-*O*-benzylidene-3-*O*-benzyl-2-*O*-acetyl-β-D-glucopyranoside (S28)**



To a stirred solution of compound **S27** (1.2 g, 2.4 mmol) and linker **S1** (1.6 g, 4.8 mmol) in CH_2Cl_2 (24 mL) was added NIS (0.65 g, 2.9 mmol) at 0 ºC. After stirring at 0 ºC for 15 min, TMSOTf (87 µL, 0.48 mmol) was added dropwise. After being stirred at room temperature for 10 h, the mixture was diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/EtOAc: 3/1) to product **S28** (1.43 g, 84%). $[\alpha]^{25}_D$ = + 19.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 6.8 Hz, 2H, Ar-H), 7.37 (q, *J* = 5.6, 4.7 Hz, 5H, Ar-H), 7.28 (dq, *J* = 15.6, 8.1 Hz, 13H, Ar-H), 5.56 (s, 1H, PhCH), 5.17 (d, *J* = 8.6 Hz, 2H, Ar*CH*), 4.99 (t, *J* = 8.3 Hz, 1H, H-2), 4.87 (d, *J* = 12.0 Hz, 1H, Ar*CH*), 4.67 (d, *J* = 12.0 Hz, 1H, Ar*CH*), 4.48 (s, 2H, Cbz-H), 4.44 – 4.26 (m, 2H, H-1/H-6a), 3.93 – 3.56 (m, 4H, H-3, H-4, H-6b, linker-OCH), 3.53 – 3.32 (m, 2H, H-5, linker-OCH), 3.21 (dt, *J* = 26.9, 7.4 Hz, 2H, linker-CH_2), 1.95 (s, 3H, Me), 1.60 – 1.41 (m, 4H, linker-CH_2), 1.26 (t, *J* = 10.6 Hz, 2H, linker-CH_2). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 138.3, 137.9, 137.2, 129.1, 128.6, 128.5, 128.3, 128.3, 128.0, 127.9, 127.9, 127.7, 127.3, 126.0, 101.6, 101.3, 81.6, 78.5, 77.4, 77.3, 77.1, 76.8, 74.1, 72.9, 68.7, 67.2, 66.3, 29.2, 23.1, 20.8. IR (film): ν = 1749, 1495, 1230, 1069, 1029, 757, 698. HRMS (ESI) *m/z* calcd for $C_{42}H_{47}O_9NNa$ $[M+Na]^+$ 732.3143, found 732.3162.

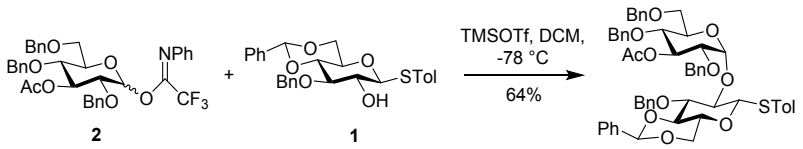
***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl 4,6-*O*-benzylidene-3-*O*-benzyl-β-D-glucopyranoside (6)**



To a stirred solution of compound **S28** (1.4 g, 1.97 mmol) in MeOH/CH_2Cl_2 (4:1, 10 mL) was added NaOMe (210 mg, 3.94 mmol). The mixture was stirred at 40 °C for 20 h, and then neutralized with Amberlite IR120 H^+ resin. Filtration, concentration in vacuo, and purification by silica gel column chromatography (Hexane/EtOAc: 3/1) gave the compound **6** (1.08 g, 82%). $[\alpha]^{25}_D$ = - 23.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 7.3, 2.4 Hz, 2H, Ar-H), 7.47 – 7.22 (m, 18H, Ar-H), 5.60 (s, 1H, PhCH), 5.21 (d, *J* = 8.0 Hz, 2H, Ar*CH*), 5.00 (d, *J* = 11.7 Hz, 1H, Ar*CH*), 4.85 (d, *J* = 11.7 Hz, 1H, Ar*CH*), 4.53 (d, *J* = 6.8 Hz, 2H, Cbz-H), 4.38 (dt, *J* = 10.5, 6.3 Hz, 2H, H-1, 6a-H), 4.06 – 3.77 (m, 2H, 6b-H, linker-OCH), 3.77 – 3.64 (m, 2H, H-3, H-4), 3.66 – 3.37 (m, 4H, H-2, H-5, linker-OCH), 3.28 (dq, *J* = 23.2, 7.7 Hz, 2H, linker-NCH_2), 1.74 – 1.46 (m, 4H, 2linker-CH_2), 1.35 (dd, *J* = 33.2, 10.8 Hz, 2H, linker-CH_2). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.4, 138.5, 137.9, 137.9, 137.3, 136.8, 134.5, 129.8, 129.0, 129.0, 128.6, 128.6, 128.5, 128.4, 128.3, 128.0, 128.0, 127.9, 127.8, 127.3, 126.0, 103.5, 101.3, 81.4, 80.3, 74.6, 74.6, 68.8, 67.3, 67.2, 66.5, 50.3, 47.0, 46.1, 29.7, 29.2, 27.8, 27.3, 23.2. IR (film): ν = 3444, 1688, 1454, 1218, 1071, 1029, 758, 698. HRMS (ESI) *m/z* calcd for $C_{40}H_{45}O_8NNa$ $[M+Na]^+$ 690.3037, found 690.3035.

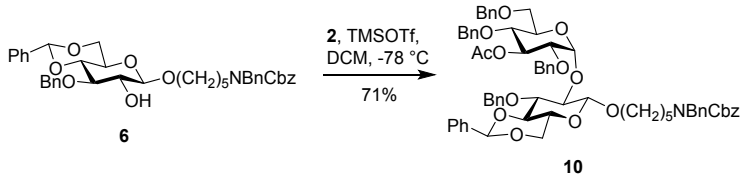
2.4 Synthesis of α-(1→2)- and α-(1→3)-Linked Oligoglucosides

***p*-Methylphenyl 2,4,6-tri-*O*-benzyl-3-*O*-acetyl-α-D-glucopyranosyl-(1→2)-4,6-*O*-benzilidene-3-*O*-benzyl-1-thio-β-D-glucopyranoside (9)**



To a stirred mixture of the donor **2** (0.60 g, 0.94 mmol), acceptor **1** (0.53 g, 1.14 mmol), and freshly activated 4Å MS in dry CH_2Cl_2 (5 mL) at -78 ºC, was added dropwise TMSOTf (34 µL, 0.188 mmol) under nitrogen. After being stirred at 0 °C for 4 h, the mixture was quenched with Et_3N, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/EtOAc: 10/1) to afford **9** (0.57 g, 64%). $[\alpha]^{25}_D$ = + 9.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.45 (m, 2H, Ar-H), 7.41 – 7.23 (m, 21H, Ar-H), 7.14 (td, *J* = 7.5, 1.6 Hz, 3H, Ar-H), 7.07 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.02 (t, *J* = 7.6 Hz, 2H, Ar-H), 5.99 (d, *J* = 3.7 Hz, 1H, 1'-H), 5.60 (s, 1H, Ph*CH*), 5.55 (t, *J* = 9.7 Hz, 1H, 3'-H), 4.99 (d, *J* = 10.1 Hz, 1H, Ar*CH*), 4.90 (d, *J* = 8.9 Hz, 1H, 1-H), 4.85 (d, *J* = 12.2 Hz, 1H, Ar*CH*), 4.64 (d, *J* = 10.2 Hz, 1H, Ar*CH*), 4.61 – 4.51 (m, 2H, 2Ar*CH*), 4.47 (d, *J* = 11.2 Hz, 1H, Ar*CH*), 4.41 – 4.35 (m, 1H, 6a-H), 4.34 (d, *J* = 11.0 Hz, 1H, Ar*CH*), 4.26 (dd, *J* = 11.1, 5.3 Hz, 2H, 5'-H, Ar*CH*), 3.93 – 3.83 (m, 2H, 2-H, 3-H), 3.80 (d, *J* = 10.3 Hz, 1H, 6A-H), 3.74 (dd, *J* = 12.3, 3.3 Hz, 1H, 4-H), 3.71 – 3.66 (m, 1H, 4'-H), 3.56 (dd, *J* = 10.3, 3.6 Hz, 1H, 2'-H), 3.51 (dd, *J* = 9.6, 5.0 Hz, 1H, 5-H), 3.17 – 3.06 (m, 2H, 6'-H), 2.35 (s, 3H, Me), 1.96 (s, 3H, Me). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.4, 170.1, 163.3, 138.4, 138.3, 138.2, 138.2, 137.9, 137.8, 137.8, 137.5, 137.2, 136.4, 134.5, 132.5, 132.3, 129.9, 129.8, 129.8, 129.0, 128.6, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 126.0, 101.3, 95.6, 88.0, 85.2, 82.0, 81.1, 78.9, 76.0, 76.0, 75.6, 74.8, 74.4, 74.4, 74.3, 73.6, 73.5, 72.5, 72.4, 71.3, 70.1, 69.9, 69.8, 68.7, 67.7, 67.4, 62.6, 21.1, 21.1. IR (film): ν = 1748, 1495, 1367, 1217, 1098, 1027, 758, 698. HRMS (ESI) *m/z* calcd for $C_{51}H_{56}O_{11}SNa$ $[M+Na]^+$ 961.3592, found 961.3567.

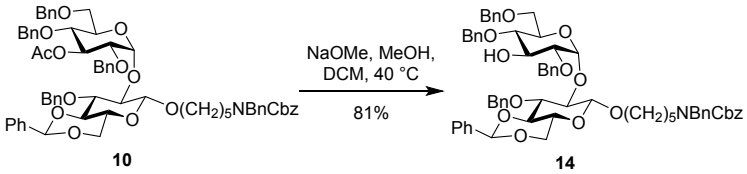
***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl 2,4,6-tri-*O*-benzyl-3-*O*-acetyl-α-D-glucopyranosyl-(1→2)-4,6-*O*-benzilidene-3-*O*-benzyl-β-D-glucopyranoside (10)**



To a stirred mixture of the donor **2** (1.42 g, 2.24 mmol), acceptor **6** (1.11 g, 1.66 mmol), and freshly activated 4Å MS in dry CH_2Cl_2 (11 mL) at -78 °C, was added dropwise TMSOTf (81 µL, 0.45 mmol) under nitrogen. After being stirred at -78 °C for 3 h, the mixture was quenched with Et_3N, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/EtOAc: 4/1) to afford **10** (1.35g, 71%). $[\alpha]^{25}_D$ = + 23.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 6.97 (m, 35H, Ar-H), 5.64 (s, 1H, 1'-H), 5.55 (d, *J* = 7.7 Hz, 2H, Ph*CH*, 3'-H), 5.16 (d, *J* = 10.3 Hz, 2H, 2Ar*CH*), 4.92 (d, *J* = 10.2 Hz, 1H, Ar*CH*), 4.65 (t, *J* = 12.3 Hz, 2H, 2Ar*CH*), 4.55 (t, *J* = 10.5 Hz, 2H, 1-

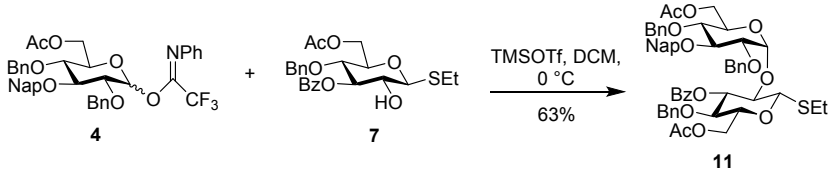
H/Ar*CH*), 4. 50 – 4.40 (m, 4H, 2Cbz-H, 2Ar*CH*), 4.32 (d, *J* = 10.8 Hz, 1H, 6a-H, Ar*CH*), 4.23 (t, *J* = 9.4 Hz, 2H, 5'-H, Ar*CH*), 3.73 (ddt, *J* = 37.9, 19.0, 9.3 Hz, 6H, 2-H, 4-H, 5-H, 6b-H, 4'-H, linker-OCH), 3.50 (d, *J* = 9.7 Hz, 1H, 2'-H), 3.41 (q, *J* = 8.7 Hz, 2H, 3-H, linker-OCH), 3.18 (q, *J* = 11.6, 10.7 Hz, 4H, 6'ab-H, linker-NCH_2), 1.91 (s, 3H, Me), 1.70 – 1.34 (m, 4H, linker-CH_2), 1.22 (d, *J* = 27.7 Hz, 2H, linker-CH_2). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.0, 156.7, 156.2, 138.5, 137.9, 137.6, 137.3, 136.9, 128.6, 128.5, 128.4, 128.3, 128.3, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 127.3, 126.0, 103.9, 101.2, 95.2, 82.4, 79.4, 77.3, 77.2, 76.1, 75.8, 75.6, 74.3, 73.7, 73.5, 71.8, 69.7, 69.5, 68.8, 67.6, 67.2, 65.9, 50.5, 50.3, 47.1, 46.2, 29.7, 27.8, 27.8, 23.4, 21.2. IR (film): ν = 1748, 1697, 1454, 1366, 1231, 1094, 1071, 1028, 755, 697. HRMS (ESI) *m/z* calcd for $C_{69}H_{75}O_{14}NNa$ $[M+Na]^+$ 1164.5080, found 1164.5064.

_N_-Benzyl-_N_-benzyloxycarbonyl-5-aminopentyl 2,4,6-tri-_O_-benzyl-α-D-glucopyranosyl-(1→2)-4,6-_O_-benzilidene-3-_O_-benzyl-β-D-glucopyranoside (14)



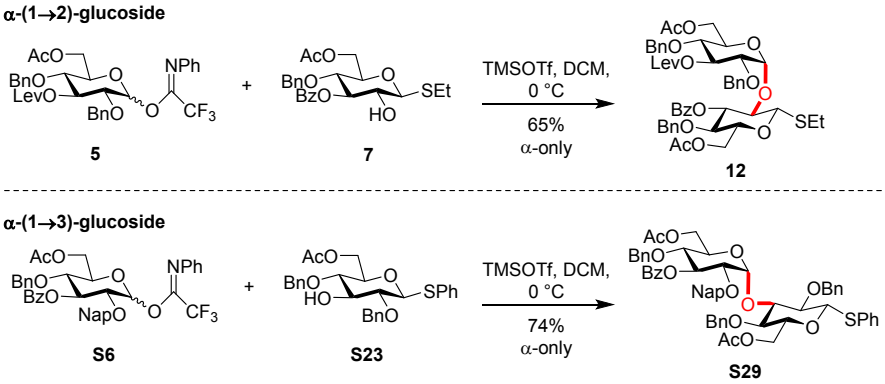
To a stirred solution of compound **10** (1.1 g, 0.96 mmol) in MeOH/CH_2Cl_2 (4:1, 5 mL) was added NaOMe (104 mg, 1.92 mmol). The mixture was stirred at 40 °C for 24 h, and then neutralized with Amberlite IR120 H^+ resin. Filtration, concentration in vacuo, and purification by silica gel column chromatography (Hexane/EtOAc: 3/1) gave the compound **14** (0.86 g, 81%). $[\alpha]^{25}_D$ = + 25.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 6.95 (m, 35H, Ar-H), 5.68 (s, 1H, 1'-H), 5.62 (s, 1H, PhCH), 5.21 (d, *J* = 11.2 Hz, 2H, Ar*CH*), 4.94 (d, *J* = 10.1 Hz, 1H, Ar*CH*), 4.83 (d, *J* = 11.3 Hz, 2H, Ar*CH*), 4.60 (t, *J* = 11.1 Hz, 4H, 1-H, 1Ar*CH*, 2Cbz-H), 4.50 (t, *J* = 10.5 Hz, 3H, 3Ar*CH*), 4.39 (d, *J* = 9.8 Hz, 1H, 6a-H), 4.29 (d, *J* = 12.1 Hz, 1H, Ar*CH*), 4.25 – 4.08 (m, 2H, 3'-H, 5'-H), 3.79 (dq, *J* = 18.3, 9.5 Hz, 5H, 2-H, 3-H, 4-H, 6b-H, linker-OCH), 3.65 (t, *J* = 9.5 Hz, 1H, 4'-H), 3.57 - 3.37 (m, 3H, 5-H, 2'-H, linker-OCH), 3.34 – 3.14 (m, 4H, 6'ab-H, linker-NCH_2), 2.50 (s, 1H, 3'-OH), 1.52 (ddt, *J* = 22.4, 15.3, 7.9 Hz, 4H, linker-CH_2), 1.41 – 1.14 (m, 2H, linker-CH_2). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.7, 156.2, 138.9, 138.0, 137.9, 137.7, 137.3, 129.0, 128.6, 128.5, 128.3, 128.3, 128.3, 128.1, 128.0, 127.9, 127.7, 127.7, 127.6, 127.5, 127.3, 126.0, 104.0, 101.2, 95.1, 82.3, 79.6, 79.0, 77.6, 77.4, 77.3, 77.1, 76.8, 75.7, 75.6, 74.6, 73.5, 73.4, 72.0, 69.6, 69.5, 68.8, 67.9, 67.2, 66.0, 50.5, 50.2, 47.1, 46.2, 29.7, 29.6, 28.0, 27.5, 23.3. IR (film): ν = 3398, 1749, 1696, 1453, 1369, 1230, 1097, 1074, 1029, 757, 698. HRMS (ESI) *m/z* calcd for $C_{67}H_{73}O_{13}NNa$ $[M+Na]^+$ 1122.4974, found 1122.4953.

Ethyl 6-_O_-acetyl-2,4-di-_O_-benzyl-3-O-(2-naphthylmethyl)-α-D-glucopyranosyl-(1→2)- 6-_O_-acetyl-4-_O_-benzyl-3-_O_-benzoyl-1-thio-β-D-glucopyranoside (11)



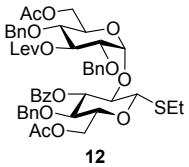
To a stirred mixture of the donor **4** (37 mg, 0.052 mmol), acceptor **7** (20 mg, 0.043 mmol), and freshly activated 4Å MS in DCM (1 mL) at 0 °C, was added dropwise TMSOTf in DCM (10 μL/mL, 94 μL, 0.0052 mmol) under argon atmosphare. The mixture was stirred at 0 °C for 2.5 h. Until TLC showed complete conversion of starting material, the reaction was quenched with Et_3N, then filtered the 4Å MS and concentrated *in vacuo*. The residue was purified silica gel column chromatography (Hexane/EtOAc: 3/1→2/1) provided **11** (27 mg, 63%). $[\alpha]^{25}_D$ = + 68.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 6.70 (m, 27H, Ar-H), 5.86 – 5.59 (m, 2H, 1'-H, 3-H), 5.11 (d, *J* = 11.1 Hz, 1H, Ar*CH*), 4.94 (d, *J* = 11.8 Hz, 1H, Ar*CH*), 4.90 (d, *J* = 11.1 Hz, 1H, Ar*CH*), 4.73 (d, *J* = 11.9 Hz, 1H, Ar*CH*), 4.70 (d, *J* = 9.3 Hz, 1H, 1-H), 4.67 (d, *J* = 11.0 Hz, 1H, Ar*CH*), 4.59 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.50 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.41 (dd, *J* = 12.0, 1.8 Hz, 1H, 6-H), 4.31 (d, *J* = 11.3 Hz, 1H, Ar*CH*), 4.23 (dd, *J* = 12.0, 4.7 Hz, 1H, 6-H), 3.98 (t, *J* = 9.2 Hz, 1H, 2-H), 3.92 (dd, *J* = 9.9, 8.9 Hz, 1H, 3'-H), 3.92 (dd, *J* = 12.2, 2.1 Hz, 1H, 6'-H), 3.76 – 3.67 (m, 3H, 4-H, 5-H, 5'-H), 3.56 (dd, *J* = 12.2, 3.1 Hz, 1H, 6'-H), 3.51 (dd, *J* = 9.9, 3.6 Hz, 1H, 2'-H), 3.36 (dd, *J* = 10.1, 8.9 Hz, 1H, 4'-H), 2.75 (qd, *J* = 7.5, 1.2 Hz, 2H, SCH_2), 2.10 (s, 3H, CH_3CO), 1.97 (s, 3H, CH_3CO), 1.29 (t, *J* = 7.4 Hz, 3H, SCH_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 170.6, 165.5, 138.3, 137.0, 136.3, 133.5, 133.5, 133.1, 129.9, 129.7, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 128.1, 127.9, 127.8, 127.8, 127.7, 127.5, 126.8, 126.3, 126.1, 125.9, 96.0 (C-1), 85.0 (C-1), 81.2, 79.7, 77.0, 76.6, 75.8, 74.9, 74.5, 74.4, 73.1, 69.2, 63.3, 62.5, 25.4, 21.0, 20.9, 14.9. HRMS (ESI) *m/z* calcd for $C_{57}H_{60}O_{13}SNa$ $[M+Na]^+$ 1007.3647, found 1007.3643.

Preliminary study on the glycosylation reactivity of C-2 and C-3 hydroxyl groups in the glucose



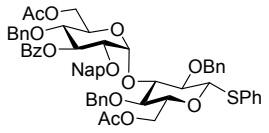
A preliminary experimental exploration of the glycosylation reactivity difference between C-2 and C-3 hydroxyl groups in the glucose has been conducted. The synthesis of α-(1→2)-glucoside **12** and α-(1→3)-glucoside **S29** was carried out under the same conditions, which was activated by TMSOTf in dichloromethane at 0 °C. It seems that the efficiency of preparation of α-(1→3)-glucoside is higher than that of preparation of α-(1→2)-glucoside in this acyl remote participation strategy. The details were shown in the protocol below.

Ethyl 6-*O*-acetyl-2,4-di-*O*-benzyl-3-O-levulinoyl-α-D-glucopyranosyl-(1→2)- 6-*O*-acetyl-4-*O*-benzyl-3-*O*-benzoyl-1-thio-β-D-glucopyranoside (12)



To a stirred mixture of the donor **5** (0.67 g, 1.0 mmol), acceptor **7** (0.55 mg, 1.2 mmol), and freshly activated 4Å MS in DCM (20 mL) at 0 °C, was added dropwise TMSOTf (18 μL, 0.1 mmol) under argon atmosphare. The mixture was stirred at 0 °C for 3 h. Until TLC showed complete conversion of starting material, the reaction was quenched with Et_3N, then filtered the 4Å MS and concentrated *in vacuo*. The residue was purified silica gel column chromatography (petroleum/EtOAc: 2/1→3/2) provided **12** (0.60 g, 65%). $[\alpha]^{25}_D$ = + 56.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 7.81 (m, 2H, Ar-H), 7.58 – 7.42 (m, 1H, Ar-H), 7.41 – 6.96 (m, 17H, Ar-H), 5.67 (t, *J* = 9.3 Hz, 1H, 3-H), 5.66 (d, *J* = 3.7 Hz, 1H, 1'-H), 5.39 (dd, *J* = 10.2, 9.2 Hz, 1H, 3'-H), 4.83 (d, *J* = 12.4 Hz, 1H, Ar*CH*), 4.65 (d, *J* = 9.5 Hz, 1H, 1-H), 4.58 – 4.53 (m, 2H, Ar*CH*), 4.47 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.41 – 4.33 (m, 2H, Ar*CH*, 6-H), 4.24 (d, *J* = 11.3 Hz, 1H, Ar*CH*), 4.21 (dd, *J* = 12.0, 5.0 Hz, 1H, 6-H), 3.93 (t, *J* = 9.1 Hz, 1H, 2-H), 3.85 (dd, *J* = 12.3, 2.1 Hz, 1H, 6-H), 3.78 – 3.66 (m, 3H, 4-H, 5-H, 5'-H), 3.48 (dd, *J* = 12.3, 2.8 Hz, 1H, 6-H), 3.39 (ddd, *J* = 9.7, 6.4, 2.7 Hz, 2H, 2'-H, 4'-H), 2.81 – 2.59 (m, 4H, CH_2), 2.49 – 2.38 (m, 2H, CH_2), 2.15 (s, 3H, CH_3CO), 2.08 (s, 3H, CH_3CO), 1.98 (s, 3H, CH_3CO), 1.26 (t, *J* = 7.4 Hz, 3H, SCH_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.6, 171.6, 170.8, 170.5, 165.2, 138.1, 137.8, 136.9, 133.4, 129.9, 129.7, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 96.0 (C-1'), 84.9 (C-1), 76.6, 76.4, 75.4, 75.1, 74.7, 73.5, 73.2, 72.5, 68.6, 63.2, 62.2, 37.9, 30.1, 28.1, 25.6, 21.0, 21.0, 14.9. IR (film): ν = 1740, 1455, 1366, 1241, 1160, 1093, 1029, 750, 701. HRMS (ESI) *m/z* calcd for $C_{51}H_{58}O_{15}SNa$ $[M+Na]^+$ 965.3389, found 965.3404.

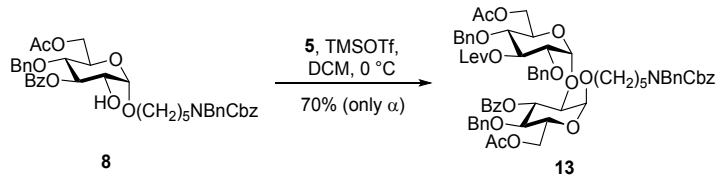
Phenyl 6-*O*-acetyl-4-*O*-benzyl-3-*O*-benzoyl-2-(2-naphthylmethyl)-α-D-glucopyranosyl-(1→3)- 6-*O*-Acetyl-2,4-di-*O*-benzyl-1-thio-β-D-glucopyranoside (S29)



S29

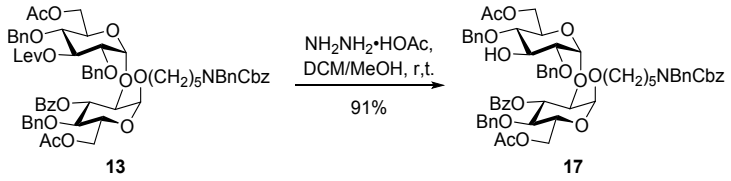
To a stirred mixture of the donor **S6** (24 mg, 0.036 mmol), acceptor **S23** (21 mg, 0.043 mmol), and freshly activated 4Å MS in DCM (3.6 mL) at 0 °C, was added dropwise TMSOTf in DCM (10 μL/mL, 65 μL, 0.0036 mmol) under argon. The mixture was stirred at 0 °C for 3 h. Until TLC showed complete conversion of starting material, the reaction was quenched with Et_3N and then filtered and concentrated *in vacuo*. The residue was purified silica gel column chromatography (petroleum/EtOAc: 4/1→2/1) provided **S29** (27 mg, 74%). R_f = 0.37 (Hexane/EtOAc = 2:1). $[\alpha]^{25}_D$ = + 44.3 (*c* 1.0, CH_3Cl). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.93 (m, 2H, Ar), 7.73 – 7.65 (m, 1H, Ar), 7.63 – 7.55 (m, 3H, Ar), 7.54 – 7.48 (m, 1H, Ar), 7.47 – 6.99 (m, 20H, Ar), 6.08 – 5.96 (m, 1H, 3'-H), 5.76 (d, *J* = 3.5 Hz, 1H, 1'-H), 5.04 (d, *J* = 9.9 Hz, 1H, Ar*CH*), 5.03 (d, *J* = 11.7 Hz, 1H, Ar*CH*), 4.79 (d, *J* = 9.8 Hz, 1H, Ar*CH*), 4.70 (d, *J* = 9.7 Hz, 1H, 1-H), 4.69 (d, *J* = 12.0 Hz, 1H, Ar*CH*), 4.56 (d, *J* = 11.8 Hz, 1H, Ar*CH*), 4.51 (d, *J* = 10.6 Hz, 1H, Ar*CH*), 4.47 (d, *J* = 10.2 Hz, 1H, Ar*CH*), 4.45 – 4.42 (m, 1H, 3'-H), 4.41 – 4.34 (m, 2H, 5-H, Ar*CH*), 4.21 – 4.13 (m, 1H, 6-H), 4.07 (t, *J* = 8.9 Hz, 1H, 4-H), 4.02 (dd, *J* = 12.5, 2.0 Hz, 1H, 6-H), 3.85 – 3.72 (m, 2H, 6-H, 3-H), 3.69 – 3.56 (m, 4H, 2-H, 2'-H, 4'-H, 5'-H), 2.10 (s, 3H, CH_3CO), 2.01 (s, 3H, CH_3CO). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 170.6, 165.7, 137.8, 137.4, 137.4, 134.6, 133.5, 133.3, 133.0, 132.2, 130.1, 129.8, 129.1, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.1, 126.9, 126.1, 126.1, 96.9 (C-1'), 87.9 (C-1), 80.2, 79.0, 78.9, 77.0, 76.0, 75.4, 74.9, 74.4, 73.8, 73.5, 68.7, 63.1, 62.6, 21.1, 21.0. IR (film): ν = 1741, 1454, 1238, 1072, 1028, 749, 700. HRMS (ESI) *m/z* calcd for $C_{61}H_{60}O_{13}SNa$ $[M+Na]^+$ 1055.3647, found 1055.3656.

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl 6-*O*-acetyl-2,4-di-*O*-benzyl-3-O-levulinoyl-α-D-glucopyranosyl-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-benzoyl-α-D-glucopyranoside (13)**



To a stirred solution of the donor **5** (0.44 g, 0.65 mmol), acceptor **8** (0.31 g, 0.43 mmol) and freshly activated 4Å MS in DCM (20 mL) at 0 °C, was added dropwise TMSOTf (12 µL, 0.065 mmol) under argon atmosphare. The mixture was stirred at 0 °C for 3.5 h. Until TLC showed complete conversion of starting material, the reaction was quenched with Et_3N, then filtered the 4Å MS and concentrated *in vacuo*. The residue was purified silica gel column chromatography (Hexane/EtOAc: 4/1→2/1→3/2) provided **13** (0.36 g, 70%). $[\alpha]^{25}_D$ = + 104.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.93 (m, 2H, Ar-H), 7.53 – 7.06 (m, 28H, Ar-H), 5.86 (t, *J* = 9.5 Hz, 1H, 3-H), 5.45 (t, *J* = 9.6 Hz, 1H, 3'-H), 5.19 (d, *J* = 14.2 Hz, 2H, Ar*CH*), 4.96 (q, *J* = 3.3 Hz, 1H, 1-H), 4.88 (d, *J* = 3.3 Hz, 1H, 1'-H), 4.58 (d, *J* = 11.1 Hz, 3H, Ar*CH*), 4.53 – 4.46 (m, 3H, Ar*CH*), 4.40 (d, *J* = 11.3 Hz, 1H, Ar*CH*), 4.35 – 4.28 (m, 3H, 6-H, Ar*CH*), 4.05 – 3.93 (m, 1H, 5-H), 3.88 (dd, *J* = 12.3, 2.8 Hz, 1H, 6'-H), 3.84 – 3.78 (m, 1H, 6'-H, CH_2), 3.79 – 3.73 (m, 1H, 2-H), 3.70 – 3.64 (m, 1H, 4-H), 3.63 – 3.51 (m, 1H, CH_2), 3.49 – 3.32 (m, 3H, 2-H, 4-H, CH_2), 3.22 (dd, *J* = 31.0, 8.4 Hz, 2H, CH_2), 2.66 – 2.59 (m, 2H, CH_2), 2.48 – 2.40 (m, 2H, CH_2), 2.10 (s, 3H, CH_3CO), 2.09 (s, 3H, CH_3CO), 1.94 (s, 3H, CH_3CO), 1.66 – 1.44 (m, 4H, CH_2), 1.39 – 1.19 (m, 2H, CH_2). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.5, 206.5, 171.5, 170.8, 170.5, 165.3, 156.8, 156.2, 138.2, 138.1, 137.7, 137.1, 137.0, 136.9, 133.2, 130.0, 129.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.4, 97.8 (C-1), 96.9 (C-1), 77.9, 77.9, 76.1, 75.2, 74.6, 74.5, 74.0, 73.7, 73.5, 72.6, 69.1, 68.9, 68.4, 67.2, 63.0, 62.2, 60.5, 50.6, 50.3, 47.2, 46.3, 37.9, 29.9, 29.3, 28.1, 27.6, 23.5, 21.0, 20.9, 14.3. IR (film): ν = 2938, 1742, 1699, 1498, 1455, 1422, 1366, 1237, 1159, 1073, 1029, 771, 749, 700. HRMS (ESI) *m/z* calcd for $C_{69}H_{77}NO_{18}Na$ $[M+Na]^+$ 1230.5033, found 1230.5048.

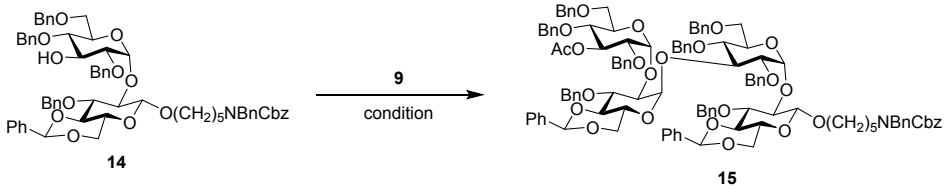
***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl 6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-glucopyranosyl-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-benzoyl-α-D-glucopyranoside (17)**



To a solution of compound **13** (0.36 g, 0.30 mmol) in CH_2Cl_2/MeOH (20/1) (3.0 mL) was added hydrazine acetate (42 mg, 0.45 mmol). The reaction mixture was stirred for 3.5 h at room temperature until TLC showed complete conversion of the starting material. The mixture was diluted with DCM, washed with water, saturated $NaHCO_3$, brine, and concentrated in *vacuo*. The residue was purified with column chromatography (Hexane/EtOAc: 4/1→2/1) to give compound **17** (0.30 g, 91%). $[\alpha]^{25}_D$ = + 97.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.66 – 7.04 (m, 28H, Ar-H), 5.95 – 5.80 (m, 1H, 3-H), 5.17 (d, *J* = 22.9 Hz, 2H, Ar*CH*), 4.98 (d, *J* = 3.4 Hz, 1H, 1-H), 4.95 – 4.86 (m, 1H, 1-H), 4.82 – 4.40 (m, 8H, Ar*CH*), 4.36 – 4.26 (m, 2H, Ar*CH*), 4.11 – 3.55 (m, 9H),

3.33 (dt, *J* = 8.8, 4.0 Hz, 4H), 3.23 – 3.09 (m, 1H, CH_2), 2.10 (s, 3H, CH_3CO), 1.95 (d, *J* = 16.5 Hz, 3H, CH_3CO), 1.61 – 1.41 (m, 4H, CH_2), 1.42 – 1.16 (m, 2H, CH_2). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6, 165.4, 157.0, 156.4, 138.4, 137.9, 137.1, 133.3, 130.0, 129.8, 128.7, 128.6, 128.5, 128.5, 128.3, 128.1, 128.0, 127.9, 127.9, 127.6, 127.4, 127.3, 98.2 (C-1), 96.5 (C-1), 96.1 (C-1), 79.1, 78.8, 77.9, 76.6, 76.4, 76.1, 75.8, 74.7, 74.6, 74.2, 73.9, 73.5, 73.1, 72.4, 69.1, 68.8, 68.6, 68.4, 68.0, 67.4, 63.0, 62.5, 50.5, 50.1, 47.2, 46.1, 29.2, 28.0, 27.6, 23.5, 21.1, 20.9. IR (film): ν = 3475, 2935, 1737, 1698, 1498, 1455, 1423, 1366, 1238, 1095, 1072, 1029, 772, 739, 699. HRMS (ESI) *m/z* calcd for $C_{64}H_{71}NO_{16}Na$ $[M+Na]^+$ 1132.4665, found 1132.4650.

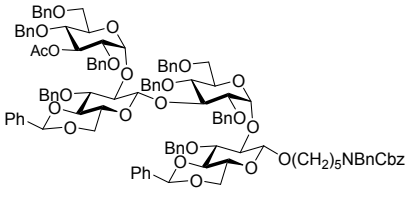
_N_-Benzyl-_N_-benzyloxycarbonyl-5-aminopentyl 2,4,6-tri-_O_-benzyl-3-_O_-acetyl-α-D-glucopyranosyl-(1→2)-4,6-_O_-benzilidene-3-_O_-benzyl-α-D- glucopyranosyl-(1→3)-2,4,6-tri-_O_-benzyl-α-D-glucopyranosyl-(1→2)-4,6-_O_-benzilidene-3-_O_-benzyl-β-D-glucopyranoside (15)



Procedure 1 (AgOTf, NIS, TMSOTf, 10 eq thiophene, DCM/Et_2O (1:1, v/v), 0 °C)

To a stirred solution of donor **9** (0.29 g, 0.31 mmol, 1.5 eq), acceptor **14** (0.23 g, 0.21 mmol, 1 eq) and freshly activated 4Å MS in CH_2Cl_2/Et_2O (1:1, v/v, 4 mL) was added thiophene (0.17 mL, 10 eq). After stirring at 0 ºC for 15 min, NIS (139 mg, 0.62 mmol, 3eq), AgOTf (26 mg, 0.1 mmol, 0.45 eq) and TMSOTf (11 µL, 0.062 mmol, 0.3eq) was added. The mixture was stirred at 0 °C for 12 h until TLC revealed complete conversion of the starting material, then filtration and diluted with CH_2Cl_2, washed with 10% $Na_2S_2O_3$, saturated $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/EtOAc: 4/1) to product **15** (0.24 g, 59%, α/β = 10:1). $[\alpha]^{25}_D$ = + 49.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 6.83 (m, 60H, Ar-H), 5.81 (s, 1H, b1-H), 5.73 (t, *J* = 9.7 Hz, 1H, d3-H), 5.63 (s, 1H, c1-H), 5.55 (d, *J* = 5.6 Hz, 2H, 2PhCH), 5.25 – 5.13 (m, 3H, d1-H, 2Ar*CH*), 4.90 (d, *J* = 10.9 Hz, 1H, Ar*CH*), 4.86 – 4.73 (m, 3H, 3Ar*CH*), 4.72 – 4.37 (m, 13H, a1-H, a3-H, 2Cbz-H, 9Ar*CH*), 4.38 – 4.14 (m, 8H, a3-H, b5-H, d5-H, d6-H, 3Ar*CH*), 4.03 (t, *J* = 9.3 Hz, 1H, b3-H), 3.89 – 3.61 (m, 9H, a6-H, a2-H, b4-H, a2-H, a5-H, d4-H, a5-H), 3.61 – 3.35 (m, 6H, a6-H, a4-H, b2-H, a2-H, a4-H), 3.32 – 3.11 (m, 5H, b6-H, linker-NH_2), 1.89 (s, 3H, Me), 1.57 – 1.34 (m, 4H, CH_2-linker), 1.23 – 1.05 (m, 2H, CH_2-linker). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.6, 138.6, 138.3, 138.2, 138.0, 138.0, 137.7, 137.6, 137.3, 136.9, 130.9, 129.0, 128.8, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 127.3, 126.2, 126.0, 103.9, 101.2, 95.0, 94.7, 94.5, 82.6, 82.2, 79.4, 78.5, 78.3, 77.4, 77.0, 76.7, 76.3, 75.7, 75.5, 75.4, 75.2, 74.2, 73.4, 73.4, 73.2, 72.1, 71.4, 69.9, 69.4, 69.2, 68.9, 68.8, 68.2, 67.9, 67.2, 65.8, 65.6, 62.4, 50.5, 47.1, 46.2, 29.7, 29.6, 27.9, 27.5, 23.2, 21.1, 19.2, 13.7. IR (film): ν = 1748, 1496, 1454, 1422, 1366, 1231, 1094, 1071, 1028, 755, 697.HRMS (ESI) *m/z* calcd for $C_{116}H_{123}O_{24}NNa$ $[M+Na]^+$ 1936.8327, found 1936.8304.

_N_-Benzyl-_N_-benzyloxycarbonyl-5-aminopentyl 2,4,6-tri-_O_-benzyl-3-_O_-acetyl-α-D-glucopyranosyl-(1→2)-4,6-_O_-benzilidene-3-_O_-benzyl-β-D- glucopyranosyl-(1→3)-2,4,6-tri-_O_-benzyl-α-D-glucopyranosyl-(1→2)-4,6-_O_-benzilidene-3-_O_-benzyl-β-D-glucopyranoside (15β)



15β

$[\alpha]^{25}_{D}$ = + 63.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 6.97 (m, 58H, Ar-H), 6.90 (t, *J* = 7.6 Hz, 2H, Ar-H), 5.79 – 5.71 (m, 2H, d3-H, b1-H), 5.54 (s, 1H, PhCH), 5.50 (s, 1H, PhCH), 5.38 (d, *J* = 3.7 Hz, 1H, d1-H), 5.25 (d, *J* = 7.8 Hz, 1H, c1-H), 5.21 – 5.11 (m, 2H, Ar*CH*), 4.94 (d, *J* = 10.6 Hz, 1H, Ar*CH*), 4.87 (d, *J* = 10.2 Hz, 1H, Ar*CH*), 4.80 (d, *J* = 10.0 Hz, 1H, Ar*CH*), 4.78 (d, *J* = 12.2 Hz, 1H, Ar*CH*), 4.69 (d, *J* = 10.2 Hz, 1H, Ar*CH*), 4.64 – 4.52 (m, 5H, Ar*CH*, a1-H), 4.49 – 4.40 (m, 4H, Ar*CH*, CH_2-linker, b3-H), 4.39 – 4.23 (m, 7H, Ar*CH*, 6-H, c3-H), 4.23 – 4.16 (m, 3H, 6-H, a3-H), 3.77 – 3.49 (m, 17H, 2-H, 4-H, 5-H, 6-H), 3.38 – 3.11 (m, 10H, 5-H, 6-H, CH_2-linker), 1.88 (s, 3H, Me), 1.52 – 1.32 (m, 4H, CH_2-linker), 1.19 (s, 2H, CH_2-linker). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.0, 139.1, 138.5, 138.3, 137.9, 137.8, 137.8, 137.7, 137.4, 137.3, 137.3, 134.5, 129.7, 129.2, 129.1, 129.0, 128.9, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 127.3, 126.0, 103.9, 101.9, 101.2, 96.9, 94.7, 82.9, 82.3, 81.2, 79.4, 79.2, 78.3, 76.5, 76.0, 75.5, 75.4, 75.3, 74.8, 74.4, 73.9, 73.8, 73.4, 73.3, 72.0, 69.8, 69.1, 68.8, 68.0, 67.7, 67.2, 65.8, 29.5, 23.2, 21.2. IR (film): ν = 1734, 1699, 1454, 1367, 1230, 1093, 1072, 1028, 754, 697. HRMS (ESI) *m/z* calcd for $C_{116}H_{123}O_{24}NNa$ $[M+Na]^+$ 1936.8327, found 1936.8287.

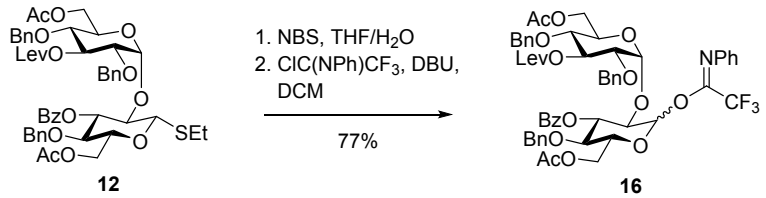
Procedure 2 (TMSOTf, NIS, DCM, 0 °C)

To a stirred solution of donor **9** (60 mg, 0.064 mmol, 1.5 eq), acceptor **14** (47 mg, 0.043 mmol, 1 eq) and freshly activated 4Å MS in CH_2Cl_2 (0.9 mL, 0.05 M). After stirring at 0 °C for 15 min, NIS (29 mg, 0.13 mmol, 3 eq) and TMSOTf (2.3 µL, 0.013 mmol, 0.3 eq) was added. The mixture was stirred at 0 °C until TLC revealed complete conversion of the starting material, then filtration and diluted with CH_2Cl_2, washed with washed with 10% $Na_2S_2O_3$, saturated $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/EtOAc: 4/1) to product **15α** and **15β** (54 mg, 66%, α/β = 5:1).

Procedure 3 (AgOTf, NIS, 10 eq thiophene, DCM/Et_2O (1:1, v/v), 0 °C)

To a stirred solution of donor **9** (60 mg, 0.064 mmol, 1.5 eq), acceptor **14** (47 mg, 0.043 mmol, 1 eq) and freshly activated 4Å MS in CH_2Cl_2 (0.9 mL, 0.05 M) was added thiophene (34 µL, 10 eq). After stirring at 0 °C for 15 min, NIS (29 mg, 0.13 mmol, 3 eq) and AgOTf (5 mg, 0.019 mmol, 0.45 eq) was added. The mixture was stirred at 0 °C until TLC revealed complete conversion of the starting material, then filtration and diluted with CH_2Cl_2, washed with washed with 10% $Na_2S_2O_3$, saturated $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/EtOAc: 4/1) to product **15α** and **15β** (39 mg, 48%,α/β = 10:1).

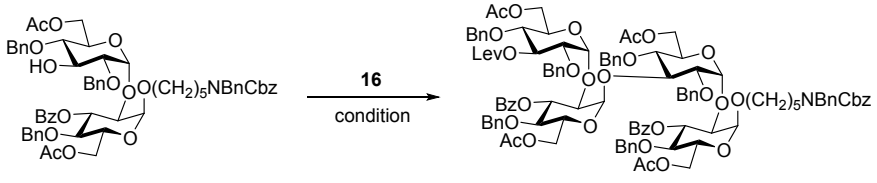
***N*-Phenyl trifluoroacetimidate 6-*O*-acetyl-2,4-di-*O*-benzyl-3-O-levulinoyl-α-D-glucopyranosyl-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-benzoyl-D-glucopyranoside (16)**



12 **16**

To a stirred solution of compound **12** (0.60 g, 0.65 mmol) in THF/H_2O (v/v, 1:1, 6.5 mL) was added NBS (345 mg, 1.94 mmol) at room temperature and stirring for 3 h. Until TLC showed complete convertion of starting material, the mixture was diluted with EtOAc, washed with 10% $Na_2S_2O_3$ and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/EtOAc: 2/1→1/1) to afford the corresponding hemiacetal as a colorless syrup. To a solution of the above hemiacetal in CH_2Cl_2 (13 mL) was added 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (485 µL, 3.25 mmol) and DBU (290 µL, 1.95 mmol) at 0 °C. The reaction was warmed to room temperature and stirred for 2 h, TLC revealed complete conversion of the starting material. The solution was concentrated in vacuo to a residue, which was purified by silica gel column chromatography (Hexane/EtOAc: 3/1→3/2) to give **16** (0.54 g, 77%, two steps) as a light yellow syrup. $[\alpha]^{25}_{D}$ = + 98.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 7.94 (m, 2H, Ar-H), 7.58 – 7.48 (m, 1H, Ar-H), 7.47 – 7.38 (m, 2H, Ar-H), 7.34 – 7.01 (m, 20H, Ar-H), 6.83 (d, *J* = 7.8 Hz, 2H), 6.53 (s, 1H), 5.91 (t, *J* = 9.5 Hz, 1H), 5.43 (t, *J* = 9.6 Hz, 1H), 4.85 (d, *J* = 3.4 Hz, 1H), 4.61 – 4.51 (m, 3H), 4.49 (d, *J* = 10.9 Hz, 1H), 4.42 (d, *J* = 11.4 Hz, 1H), 4.39 – 4.27 (m, 3H), 4.12 (dd, *J* = 9.9, 3.2 Hz, 1H), 3.95 – 3.73 (m, 4H), 3.67 (dd, *J* = 12.2, 2.1 Hz, 1H), 3.46 – 3.40 (m, 1H), 3.39 (dd, *J* = 9.2, 2.8 Hz, 1H), 2.63 (t, *J* = 6.6 Hz, 2H), 2.50 – 2.31 (m, 2H), 2.12 (s, 3H, CH_3CO), 2.09 (s, 3H, CH_3CO), 1.89 (s, 3H, CH_3CO). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.6, 171.4, 170.7, 170.4, 165.3, 143.6, 137.9, 137.8, 136.8, 133.5, 129.8, 129.7, 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.0, 128.0, 127.8, 124.4, 119.8, 99.2 (C-1), 77.7, 75.2, 75.0, 74.8, 73.6, 73.6, 73.5, 72.9, 70.9, 69.3, 62.6, 62.1, 37.9, 30.0, 28.1, 21.0, 20.9. IR (film): ν =1742, 1455, 1366, 1312, 1239, 1210, 1161, 1074, 1028, 743, 699.

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl 6-*O*-acetyl-2,4-di-*O*-benzyl-3-O-levulinoyl-α-D-glucopyranosyl-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-benzoyl-α-D-glucopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-glucopyranosyl-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-benzoyl-α-D-glucopyranoside (18)**



17 **18**

Procedure 1 (TMSOTf, DCM, 0 °C)

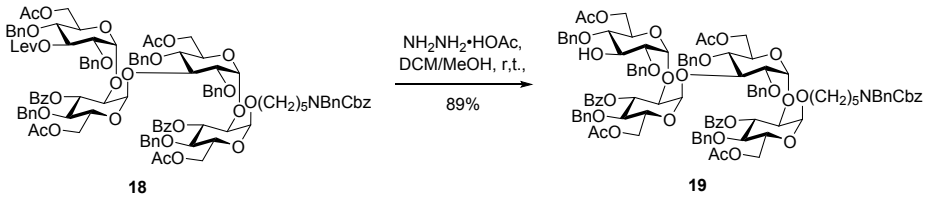
To a stirred mixture of the donor **16** (182 mg, 0.17 mmol, 1.2 eq), acceptor **17** (155 mg, 0.14 mmol, 1 eq), and freshly activated 4Å MS in DCM (2.8 mL) at 0 °C, was added dropwise TMSOTf (7.3 µL, 0.034 mmol, 0.24 eq) under argon. The mixture was stirred at 0 °C for 3.5 h. Until TLC showed complete conversion of starting material, the reaction was quenched with Et_3N, then filtered and concentrated *in vacuo*. The residue was purified with silica gel column chromatography (Hexane/EtOAc: 2/1→3/2)

provided **18** (186 mg, 67%). $[\alpha]^{25}_{D}$ = + 107.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.99 (m, 2H, Ar-H), 7.97 – 7.90 (m, 2H, Ar-H), 7.53 – 7.42 (m, 2H, Ar-H), 7.41 – 7.10 (m, 38H, Ar-H), 7.07 – 6.98 (m, 6H, Ar-H), 5.88 (t, *J* = 9.6 Hz, 1H, 3-H), 5.84 (t, *J* = 9.5 Hz, 1H, 3-H), 5.57 (d, *J* = 3.5 Hz, 1H, 1-H), 5.41 (t, *J* = 9.6 Hz, 1H, 3-H), 5.26 – 5.13 (m, 2H, Ar*CH*), 4.99 (d, *J* = 3.3 Hz, 1H, 1-H), 4.97 (dd, *J* = 11.3 Hz, 1H, Ar*CH*), 4.96 (d, *J* = 3.4 Hz, 1H, 1-H), 4.69 – 4.60 (m, 2H, Ar*CH*), 4.64 (d, *J* = 3.6 Hz, 1H, 1-H), 4.58 (d, *J* = 10.8 Hz, 1H, Ar*CH*), 4.58 – 4.52 (m, 1H), 4.52 – 4.40 (m, 4H, Ar*CH*, CH_2), 4.37 – 4.22 (m, 8H, Ar*CH*), 4.22 – 4.05 (m, 6H, Ar*CH*, CH_2), 4.05 – 3.88 (m, 4H), 3.84 (dd, *J* = 10.1, 3.4 Hz, 1H, 2-H), 3.78 (dd, *J* = 12.3, 3.2 Hz, 1H, 6-H), 3.74 – 3.65 (m, 2H), 3.61 (dd, *J* = 10.1, 8.6 Hz, 1H), 3.55 – 3.51 (m, 1H, 4-H), 3.56 – 3.42 (m, 4H), 3.48 – 3.43 (m, 1H, 2-H), 3.37 (t, *J* = 9.6 Hz, 1H, 4-H), 3.32 – 3.18 (m, 2H, CH_2), 3.24 (dd, *J* = 10.1, 3.5 Hz, 1H, 2-H), 3.13 (t, *J* = 7.6 Hz, 1H, CH_2), 2.71 – 2.51 (m, 2H, CH_2), 2.49 – 2.29 (m, 2H, CH_2), 2.17 (s, 3H, CH_3CO), 2.15 (s, 3H, CH_3CO), 2.09 (s, 3H, CH_3CO), 2.01 (s, 3H, CH_3CO), 1.82 (s, 3H, CH_3CO), 1.60 – 1.38 (m, 4H, CH_2), 1.32 – 1.08 (m, 2H, CH_2). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.4, 171.4, 171.1, 170.9, 170.8, 170.5, 165.5, 165.3, 156.8, 156.2, 138.9, 138.3, 138.1, 137.5, 137.4, 137.4, 137.1, 137.0, 133.2, 132.8, 130.5, 129.9, 129.7, 129.6, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.0, 128.0, 127.9, 127.8, 127.3, 127.1, 126.9, 98.5 (C-1), 96.1 (C-1), 95.7 (C-1), 95.2 (C-1), 79.3, 78.6, 76.2, 76.1, 75.3, 75.2, 74.6, 74.3, 74.2, 73.9, 73.6, 73.5, 73.5, 72.7, 72.6, 69.0, 68.8, 68.5, 67.8, 67.2, 63.0, 62.8, 62.3, 62.2, 50.6, 50.2, 47.1, 46.2, 37.8, 30.0, 29.3, 28.0, 23.5, 21.2, 21.0, 20.9, 20.8. IR (film): ν = 2932, 1740, 1498, 1455, 1366, 1238, 1159, 1073, 750, 700. HRMS (ESI) *m/z* calcd for $C_{113}H_{123}NO_{31}Na$ $[M+Na]^+$ 2012.7971, found 2012.8004.

Procedure 2 (TMSOTf, DCM/Dioxane (1:1), 0 °C)

To a stirred mixture of the donor **16** (58 mg, 0.054 mmol, 1.2 eq), acceptor **17** (50 mg, 0.045 mmol, 1 eq), and freshly activated 4Å MS in DCM/Dioxane (0.9 mL, 0.05M) at 0 °C, was added dropwise TMSOTf (2 µL, 0.011 mmol, 0.24 eq) under argon. The mixture was stirred at 0 °C until TLC showed complete conversion of starting materials. The reaction was quenched with Et_3N, then filtered and concentrated *in vacuo*. The residue was purified with silica gel column chromatography (Hexane/EtOAc: 2/1→3/2) provided compound **18α** and **18β** (62 mg, 69%, α/β = 2.7:1).

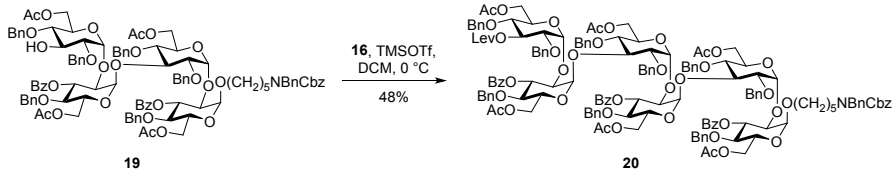
***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl 6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-glucopyranosyl-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-benzoyl-α-D-glucopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-glucopyranosyl-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-benzoyl-α-D-glucopyranoside (19)**



To a solution of **18** (100 mg, 0.05 mmol) in CH_2Cl_2/MeOH (20/1) (1.0 mL) was added hydrazine acetate (20 mg, 0.075 mmol). The reaction mixture was stirred for 2.5 h at room temperature until TLC showed complete conversion of the starting material. The mixture was diluted with DCM and washed with water, saturated $NaHCO_3$, brine, concentrated *in vacuo*. The residue was purified with column chromatography (Hexane/EtOAc: 2/1→3/2) to give compound **19** (84 mg, 89%). $[\alpha]^{25}_{D}$ = + 130.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 8.05 (m, 2H, Ar-H), 8.04 – 7.99 (m, 2H, Ar-H), 7.61 – 7.52 (m, 1H, Ar-H), 7.52 – 7.07 (m, 45H, Ar-H), 5.97 – 5.86 (m, 3H, 3-H, 1-H), 5.19 (d, *J* =

5.8 Hz, 2H, Ar*CH*), 5.15 (d, *J* = 12.0 Hz, 1H, Ar*CH*), 5.11 – 5.05 (m, 1H, Ar*CH*), 4.97 (d, *J* = 11.4 Hz, 2H, Ar*CH*), 4.96 (d, *J* = 3.5 Hz, 1H, 1-H), 4.88 (d, *J* = 10.0 Hz, 1H, Ar*CH*), 4.78 (d, *J* = 3.1 Hz, 1H, 1-H), 4.76 – 4.68 (m, 1H), 4.65 (d, *J* = 10.6 Hz, 1H, Ar*CH*), 4.61 – 4.52 (m, 3H, Ar*CH*), 4.52 – 4.45 (m, 3H, Ar*CH*), 4.45 – 4.35 (m, 4H), 4.34 – 4.20 (m, 5H), 4.28 (d, *J* = 3.5 Hz, 1H, 1-H), 3.90 (dd, *J* = 12.3, 2.2 Hz, 1H), 3.87 – 3.83 (m, 1H), 3.81 (dd, *J* = 10.2, 3.2 Hz, 1H), 3.76 (t, *J* = 9.4 Hz, 1H), 3.68 (t, *J* = 9.5 Hz, 1H), 3.65 – 3.60 (m, 1H), 3.60 – 3.55 (m, 1H), 3.51 (dt, *J* = 10.0, 2.3 Hz, 1H), 3.47 – 3.40 (m, 2H), 3.36 (dd, *J* = 10.1, 8.9 Hz, 1H), 3.26 – 3.10 (m, 1H), 3.05 (dd, *J* = 12.2, 2.5 Hz, 1H), 3.02 – 2.95 (m, 1H, CH_2), 2.93 – 2.74 (m, 3H), 2.09 (s, 3H, CH_3CO), 1.97 (s, 3H, CH_3CO), 1.93 (s, 3H, CH_3CO), 1.84 (s, 3H, CH_3CO), 1.02 – 0.79 (m, 4H, CH_2), 0.77 – 0.58 (m, 2H, CH_2). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 170.7, 170.4, 170.3, 166.8, 165.4, 156.6, 156.0, 138.9, 138.8, 138.7, 137.9, 137.0, 136.8, 133.7, 133.4, 129.8, 129.8, 129.7, 129.4, 129.1, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.4, 127.1, 103.0 (C-1), 97.6 (C-1), 96.4 (C-1), 96.0 (C-1), 83.1, 81.0, 79.1, 77.9, 76.4, 76.3, 76.1, 75.5, 75.1, 74.5, 74.3, 74.2, 73.9, 73.7, 73.4, 67.1, 63.7, 62.6, 62.2, 61.9, 50.2, 49.9, 46.8, 29.0, 27.5, 27.1, 22.8, 20.9, 20.9, 20.9, 20.7. IR (film): ν = 3485, 2941, 2325, 2196, 2174, 2036, 1995, 1741, 1604, 1498, 1455, 1366, 1269, 1240, 1134, 1073, 1030, 809, 747, 699. HRMS (ESI) *m/z* calcd for $C_{108}H_{117}NO_{29}Na$ $[M+Na]^+$ 1914.7603, found 1914.7622.

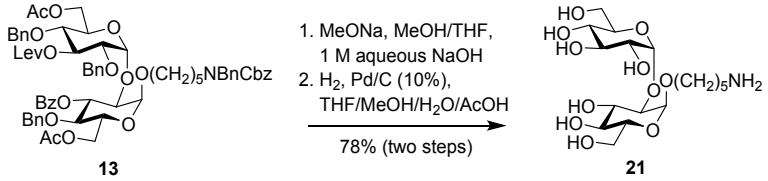
_N_-Benzyl-_N_-benzyloxycarbonyl-5-aminopentyl 6-_O_-acetyl-2,4-di-_O_-benzyl-3-O-levulinoyl-α-D-glucopyranosyl-(1→2)-6-_O_-acetyl-4-_O_-benzyl-3-_O_-benzoyl-α-D-glucopyranosyl-(1→3)-6-_O_-acetyl-2,4-di-_O_-benzyl-3-O-levulinoyl-α-D-glucopyranosyl-(1→2)-6-_O_-acetyl-4-_O_-benzyl-3-_O_-benzoyl-α-D-glucopyranosyl-(1→3)-6-_O_-acetyl-2,4-di-_O_-benzyl-α-D-glucopyranosyl-(1→2)-6-_O_-acetyl-4-_O_-benzyl-3-_O_-benzoyl-α-D-glucopyranoside (20)



To a stirred mixture of the donor **16** (26 mg, 0.024 mmol), acceptor **19** (30 mg, 0.016 mmol), and freshly activated 4Å MS in DCM (1 mL) at 0 °C, was added dropwise TMSOTf in DCM (10 µL/mL, 43 µL, 0.0024 mmol) under argon. The mixture was stirred at 0 °C for 4 h. Until TLC showed complete conversion of starting material, the reaction was quenched with Et_3N and then filtered and concentrated *in vacuo*. The residue was purified silica gel column chromatography (Hexane/EtOAc: 2/1→3/2→1/1) provided **20** (21 mg, 48%). $[\alpha]^{25}_D$ = + 104.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.03 – 7.97 (m, 4H, Ar-H), 7.94 – 7.84 (m, 2H, Ar-H), 7.53 – 7.45 (m, 1H, Ar-H), 7.45 – 7.41 (m, 1H, Ar-H), 7.40 – 7.34 (m, 6H, Ar-H), 7.34 – 7.23 (m, 25H, Ar-H), 7.22 – 7.11 (m, 21H, Ar-H), 7.11 – 7.02 (m, 4H, Ar-H), 7.02 – 6.92 (m, 6H, Ar-H), 5.98 (t, *J* = 9.6 Hz, 1H, 3-H), 5.87 (t, *J* = 9.5 Hz, 1H, 3-H), 5.77 (t, *J* = 9.4 Hz, 1H, 3-H), 5.59 (d, *J* = 3.4 Hz, 1H, 1-H), 5.43 (d, *J* = 3.6 Hz, 1H, 1-H), 5.36 (t, *J* = 9.7 Hz, 1H, 3-H), 5.22 – 5.14 (m, 2H, Ar*CH*), 5.00 (d, *J* = 3.8 Hz, 1H, 1-H), 4.96 – 4.90 (m, 2H, 1-H), 4.89 (d, *J* = 12.4 Hz, 1H, Ar*CH*), 4.71 (d, *J* = 11.4 Hz, 1H, Ar*CH*), 4.70 – 4.65 (m, 1H, 6-H), 4.65 – 4.60 (m, 1H, 6-H), 4.59 (d, *J* = 3.6 Hz, 1H, 1-H), 4.56 (d, *J* = 10.9 Hz, 1H, Ar*CH*), 4.53 – 4.44 (m, 7H), 4.41 (d, *J* = 11.1 Hz, 2H, Ar*CH*), 4.33 (d, *J* = 11.2 Hz, 1H, Ar*CH*), 4.31 – 4.26 (m, 5H), 4.25 (d, *J* = 10.9 Hz, 1H, Ar*CH*), 4.21 (d, *J* = 12.4 Hz, 1H, Ar*CH*), 4.19 – 4.05 (m, 9H), 3.96 (t, *J* = 9.1 Hz, 2H), 3.92 – 3.83 (m, 4H), 3.80 (dt, *J* = 10.0, 4.1 Hz, 2H), 3.71 – 3.66 (m, 2H), 3.64 (t, *J* = 9.6 Hz, 1H), 3.62 – 3.55 (m, 2H), 3.52 – 3.42 (m, 2H),

3.41 – 3.36 (m, 3H), 3.34 (t, *J* = 9.7 Hz, 1H), 3.29 – 3.16 (m, 2H), 3.16 – 3.09 (m, 1H), 2.63 – 2.53 (m, 2H, Lev-CH_2), 2.43 – 2.34 (m, 2H, Lev-CH_2), 2.15 (s, 2H,, CH_3CO), 2.14 (s, 6H, CH_3CO), 2.08 (s, 3H, CH_3CO), 1.99 (s, 3H, CH_3CO), 1.81 (s, 3H, CH_3CO), 1.73 (s, 3H, CH_3CO), 1.51 – 1.38 (m, 6H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 206.1, 171.2, 170.9, 170.7, 170.5, 170.5, 170.3, 165.3, 165.1, 165.1, 138.8, 138.3, 137.5, 137.5, 137.4, 137.4, 137.3, 137.0, 133.3, 132.8, 132.6, 130.5, 129.9, 129.6, 129.6, 129.5, 129.5, 128.6, 128.5, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 127.8, 127.8, 127.7, 127.7, 127.6, 127.2, 126.9, 126.8, 98.2 (C-1), 96.0 (C-1), 95.5 (C-1), 95.3 (C-1), 93.6 (C-1), 92.7 (C-1), 79.0, 78.8, 77.5, 76.2, 76.0, 75.9, 75.8, 75.3, 74.1, 74.1, 73.5, 73.4, 73.1, 72.9, 72.6, 72.3, 68.8, 68.5, 68.4, 68.2, 67.5, 62.7, 62.5, 62.1, 37.7, 29.9, 29.7, 29.2, 27.9, 23.4, 22.7, 21.1, 21.0, 20.9, 20.7, 20.7, 20.4. IR (film): ν = 1741, 1239, 1071, 710. HRMS (ESI) *m/z* calcd for $C_{157}H_{169}NO_{44}Na$ $[M+Na]^+$ 2795.0910, found 2795.0869.

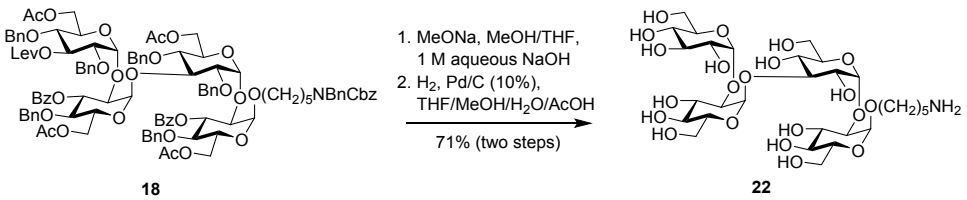
5-Aminopentyl α-D-glucopyranosyl-(1→2)-α-D-glucopyranoside (21)



13 **21**

To a solution of compound **13** (20 mg, 0.018 mmol) in MeOH/THF (1:1, v/v, 2.0 mL) was added MeONa (15 mg). The reaction mixture was stirred at room temperature for 0.5 h, then 1M aqueous NaOH (100 μL) was added. After stirred at 40 °C for 10 h, the mixture was diluted with MeOH and neutralized with Amberlite IR120 H^+ resin. After filteration, the filtrate was concentrated in reduce pressure and purified by silica gel column chromatography (DCM/MeOH: 20/1) to afford half-deprotected product. To a solution of the above product in THF/MeOH/H_2O/AcOH (2 mL, v/v/v/v, 10:5:4:1) was added Pd/C (30 mg, 10%). The mixture was stirred under H_2 atmosphere for 12 h. Filtration, concentration *in vacuo* and elution through Sephadex LH-20 column (H_2O) provided **21** (5.5 mg, 78% for two steps) as a white solid. ^{1}H NMR (700 MHz, Deuterium Oxide) δ 5.19 (d, *J* = 3.5 Hz, 1H, b1-H), 5.11 (d, *J* = 3.8 Hz, 1H, a1-H), 3.95 (ddd, *J* = 9.7, 4.6, 2.3 Hz, 1H), 3.92 – 3.85 (m, 3H), 3.84 – 3.77 (m, 6H), 3.71 (dd, *J* = 10.1, 4.0 Hz, 2H), 3.60 (ddd, *J* = 14.1, 10.4, 5.1 Hz, 2H), 3.49 (td, *J* = 9.6, 5.0 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 2H), 1.72 (dhept, *J* = 14.2, 8.0, 7.1 Hz, 5H), 1.50 (dp, *J* = 19.0, 6.8, 6.4 Hz, 2H). ^{13}C NMR (176 MHz, Deuterium Oxide) δ 95.9, 95.2, 75.0, 72.8, 71.9, 71.7, 71.5, 71.3, 69.6, 69.5, 67.8, 60.6, 60.4, 39.4, 28.0, 26.5, 22.5. HRMS (ESI) *m/z* calcd for $C_{17}H_{34}NO_{11}$ $[M+H]^+$ 428.2126, found 428.2134.

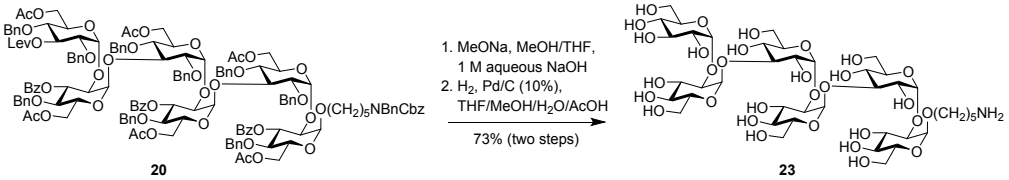
5-Aminopentyl α-D-glucopyranosyl-(1→2)-α-D-glucopyranosyl-(1→3)-α-D-glucopyranosyl-(1→2)-α-D-glucopyranoside (22)



18 **22**

To a solution of compound **18** (20 mg, 0.011 mmol) in MeOH/THF (1:1, v/v, 2.0 mL) was added MeONa (20 mg). The reaction mixture was stirred at 40 °C for 0.5 h, 1M aqueous NaOH (100 μL) was added. After stirred at room temperature for 12 h, the mixture was diluted with methanol/THF (1:1) and neutralized with Amberlite IR120 H^+ resin. After filteration, the filtrate was concentrated in reduce pressure and purified by silica gel column chromatography (DCM/MeOH: 20/1) to afford half-deprotected product. To a solution of the half-deprotected tetrasaccharide in THF/MeOH/H_2O/AcOH (2 mL, v/v/v/v, 10:5:4:1) was added Pd/C (30 mg, 10%). The mixture was stirred under H_2 atmosphere for 48 h. Filtration, concentration *in vacuo* and elution through Sephadex LH-20 column (H_2O) provided **22** (5.3 mg, 71% for two steps) as a white solid. ^{1}H NMR (700 MHz, Deuterium Oxide) δ 5.54 (d, *J* = 3.7 Hz, 1H, c1-H), 5.22 (d, *J* = 3.8 Hz, 2H, d1-H, b1-H), 5.14 (d, *J* = 3.8 Hz, 1H, a1-H), 4.11 (dd, *J* = 10.2, 3.6 Hz, 1H), 4.01 (ddd, *J* = 10.0, 4.5, 2.2 Hz, 1H), 3.97 (q, *J* = 9.7, 8.2 Hz, 2H), 3.91 – 3.77 (m, 12H), 3.76 – 3.69 (m, 2H), 3.69 – 3.64 (m, 2H), 3.62 (dt, *J* = 9.5, 6.3 Hz, 1H), 3.56 (t, *J* = 9.7 Hz, 1H), 3.50 (td, *J* = 9.4, 2.1 Hz, 2H), 3.04 (t, *J* = 7.6 Hz, 2H), 1.73 (tp, *J* = 14.3, 8.3, 7.4 Hz, 5H), 1.56 – 1.45 (m, *J* = 6.6 Hz, 2H). ^{13}C NMR (176 MHz, Deuterium Oxide) δ 96.7 (C-1), 95.9 (C-1), 95.8 (C-1), 95.0 (C-1), 80.0, 75.3, 74.5, 72.9, 71.8, 71.7, 71.5, 71.3, 71.3, 69.9, 69.6, 69.5, 69.3, 69.2, 67.7, 61.5, 60.6, 60.3, 60.2, 60.1, 39.4, 28.0, 26.5, 22.4. HRMS (ESI) *m/z* calcd for $C_{29}H_{54}NO_{21}$ $[M+H]^+$ 752.3183, found 752.3187.

5-Aminopentyl α-D-glucopyranosyl-(1→2)-α-D-glucopyranosyl-(1→3)-α-D-glucopyranosyl-(1→2)-α-D-glucopyranosyl-(1→3)-α-D-glucopyranosyl-(1→2)-α-D-glucopyranoside (23)



To a solution of compound **20** (10 mg, 0.0037 mmol) in MeOH/THF (1:1, v/v, 1.0 mL) was added MeONa (15 mg). The reaction mixture was stirred at 40 °C for 0.5 h, 1M aqueous NaOH (100 μL) was added. After stirred at room temperature for 12 h, the mixture was diluted with methanol/THF (1:1) and neutralized with Amberlite IR120 H^+ resin. After filteration, the filtrate was concentrated in reduce pressure and purified by silica gel column chromatography (DCM/MeOH: 20/1) to afford half-deprotected product. To a solution of the half-deprotected hexasaccharide in THF/MeOH/H_2O/AcOH (10:5:4:1, 2 mL) was added Pd/C (20 mg, 10%). The mixture was stirred under H_2 atmosphere for 48 h. Filtration, concentration *in vacuo* and elution through Sephadex LH-20 column (H_2O) provided **23** (2.9 mg, 73% for two steps) as a white solid. ^{1}H NMR (700 MHz, Deuterium Oxide) δ 5.59 (t, *J* = 4.5 Hz, 2H, e1-H, c1-H), 5.24 (d, *J* = 3.8 Hz, 1H, f1-H), 5.22 (d, *J* = 3.5 Hz, 2H, d1-H, b1-H), 5.16 – 5.11 (m, 1H, a1-H), 4.12 (d, *J* = 9.9 Hz, 1H), 4.08 (dt, *J* = 10.1, 2.4 Hz, 1H), 4.00 (dt, *J* = 21.5, 12.3 Hz, 4H), 3.93 – 3.77 (m, 14H), 3.77 – 3.59 (m, 8H), 3.55 (dt, *J* = 14.8, 9.7 Hz, 2H), 3.50 (t, *J* = 9.7 Hz, 2H), 3.05 (q, *J* = 7.3 Hz, 2H), 1.73 (qt, *J* = 13.9, 8.4 Hz, 5H), 1.57 – 1.42 (m, *J* = 6.6 Hz, 2H). ^{13}C NMR (176 MHz, Deuterium Oxide) δ 96.6 (C-1), 96.6 (C-1), 96.0 (C-1), 96.0 (C-1), 95.7 (C-1), 95.0 (C-1), 79.8, 79.6, 75.4, 75.0, 74.5, 72.9, 71.8, 71.7, 71.6, 71.5, 71.5, 71.5, 71.3, 71.2, 71.2, 70.0, 69.8, 69.7, 69.5, 69.5, 69.3, 69.3, 69.2, 67.7, 61.5, 60.6, 60.4, 60.3, 60.2, 60.0, 39.4, 29.9, 28.0, 27.9, 26.5, 22.4. HRMS (ESI) *m/z* calcd for $C_{41}H_{74}NO_{31}$ $[M+H]^+$ 1076.4239, found 1076.4236.

3. References

[1] (a) T. K. K. Mong, M. K. Lee, S. G.Duron, C. H. Wong, *Proc. Natl. Acad. Sci*. *USA* 2003, **100**, 797. (b) A. Adibekian, P. Bindschädler, M. S. M. Timmer, C. Noti, N. Schützenmeister, P. H. Seeberger, *Chem. Eur. J*., 2007, **13**, 4510.

[2] (a) B. S. Komarova, Y. E. Tsvetkov, G. B. Pier and N. E. Nifantiev, *Carbohydr. Res.*, 2012, **360**, 56. (b) B. S. Komarova, Y. E. Tsvetkov, G. B. Pier and N. E. Nifantiev, *J. Org. Chem.*, 2008, **73**, 8411.

[3] M. W. Weishaupt, S. Matthies, M. Hurevich, C. L. Pereira, H. S. Hahm and P. H. Seeberger, *Beilstein J. Org. Chem*., 2016, **12**, 1440.

[4] K. F. Mo, H. Q. Li, J. T. Mague, H. E. Ensley, *Carbohydr. Res.*, 2009, **344**, 439.

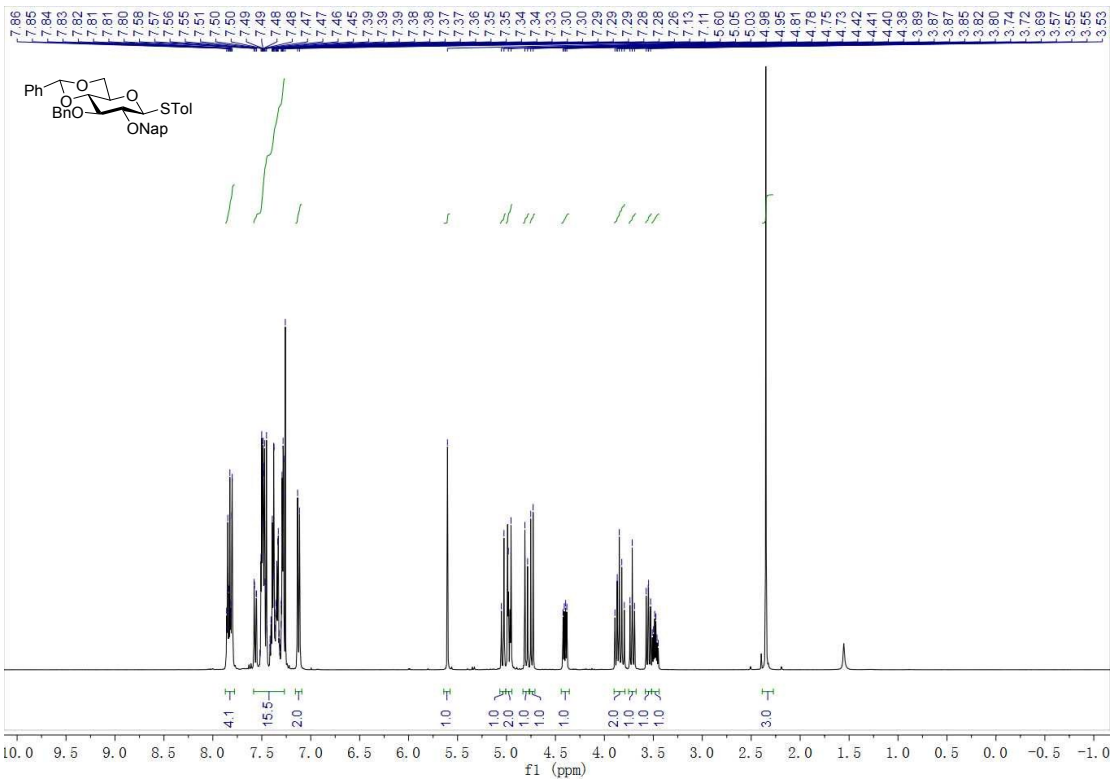
[5] T. A. d'Ortoli, G. Widmalm, *Tetrahedron*, 2016, **72**, 912.

[6] F. Good and C. Schuerch, *Carbohydr. Res.*, 1984, **125**, 165.

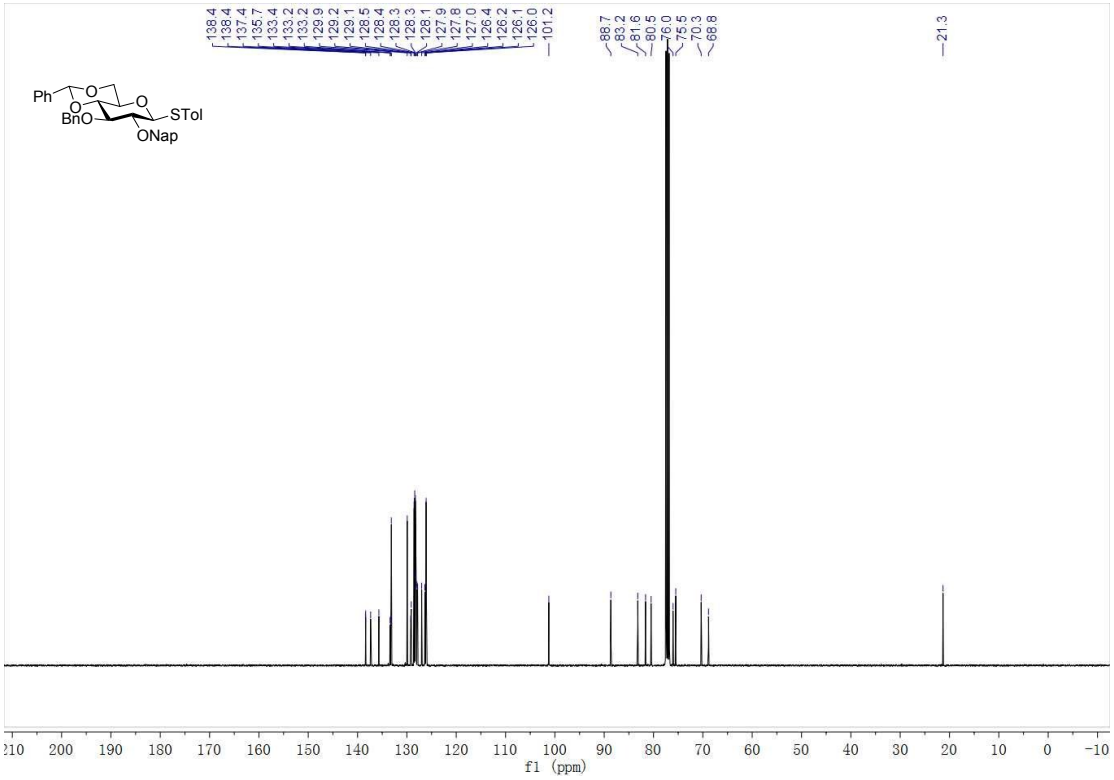
[7] S. Britton, E. Papp-Szabo, J. Simala-Grant, L. Morrison, D. E. Taylor and M. A. Monteiro, *Carbohydr. Res.*, 2005, **340**, 1605.

4. NMR Spectra of Compounds

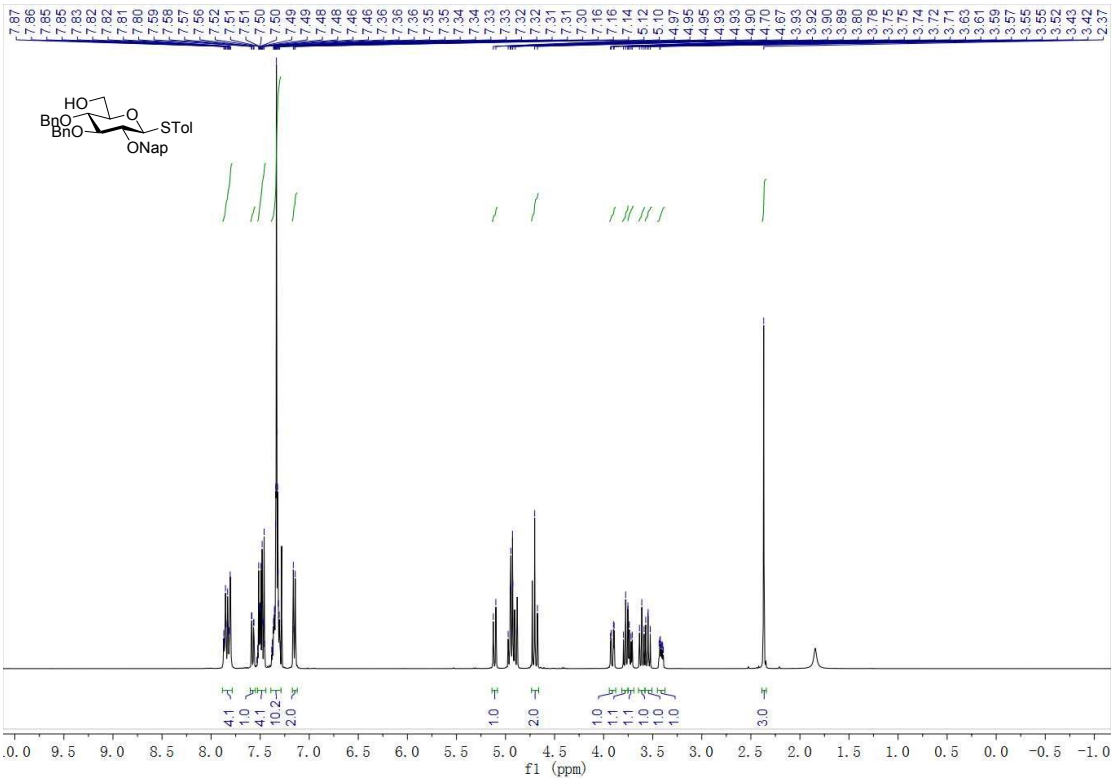
^{1}H NMR spectra of compound **S10**



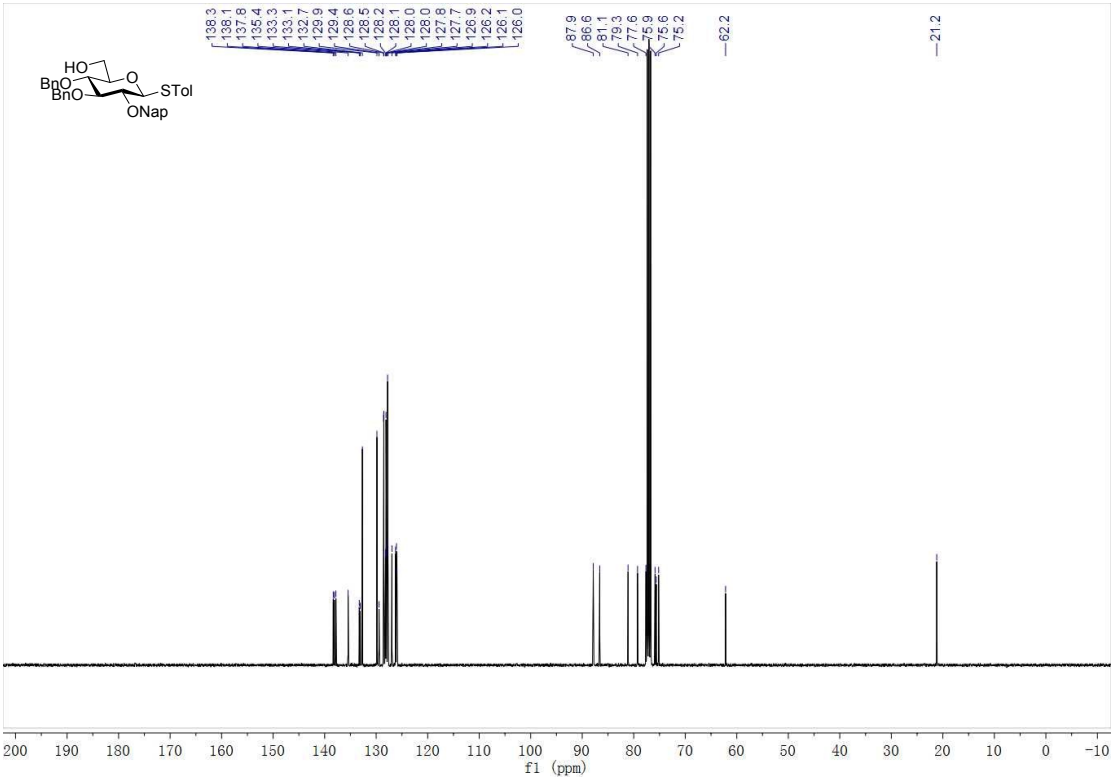
^{13}C NMR spectra of compound **S10**



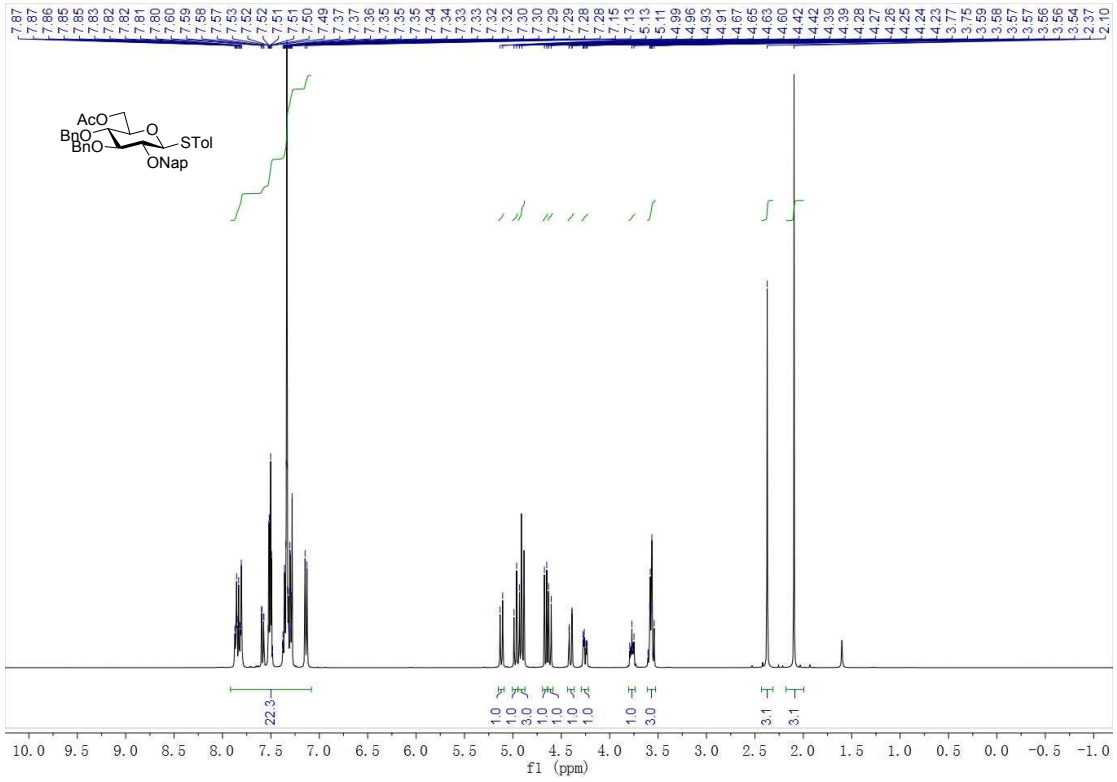
^{1}H NMR spectra of compound **S11**



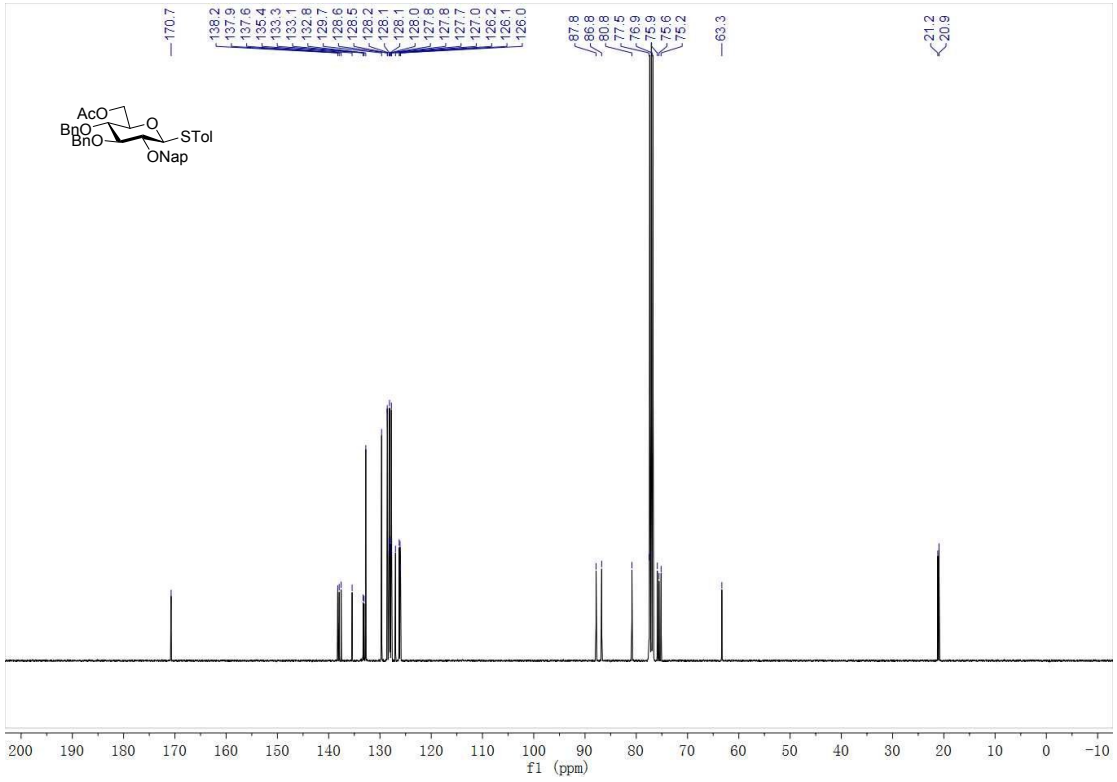
^{13}C NMR spectra of compound **S11**



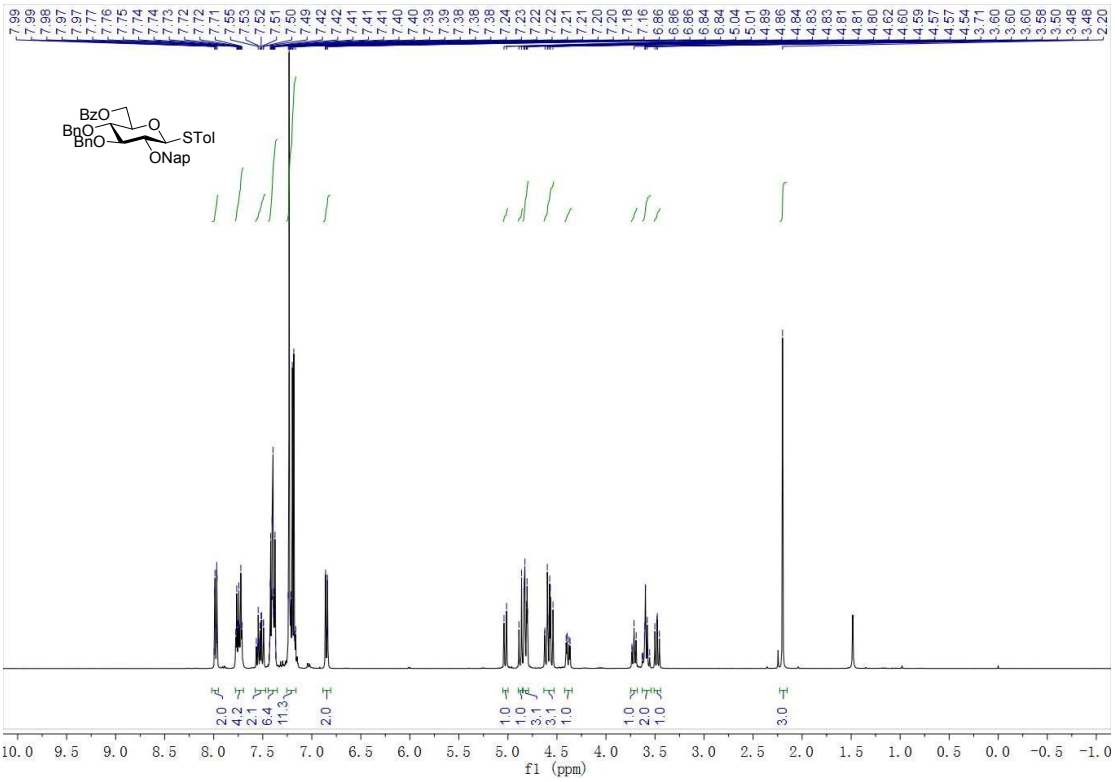
^{1}H NMR spectra of compound **S2**



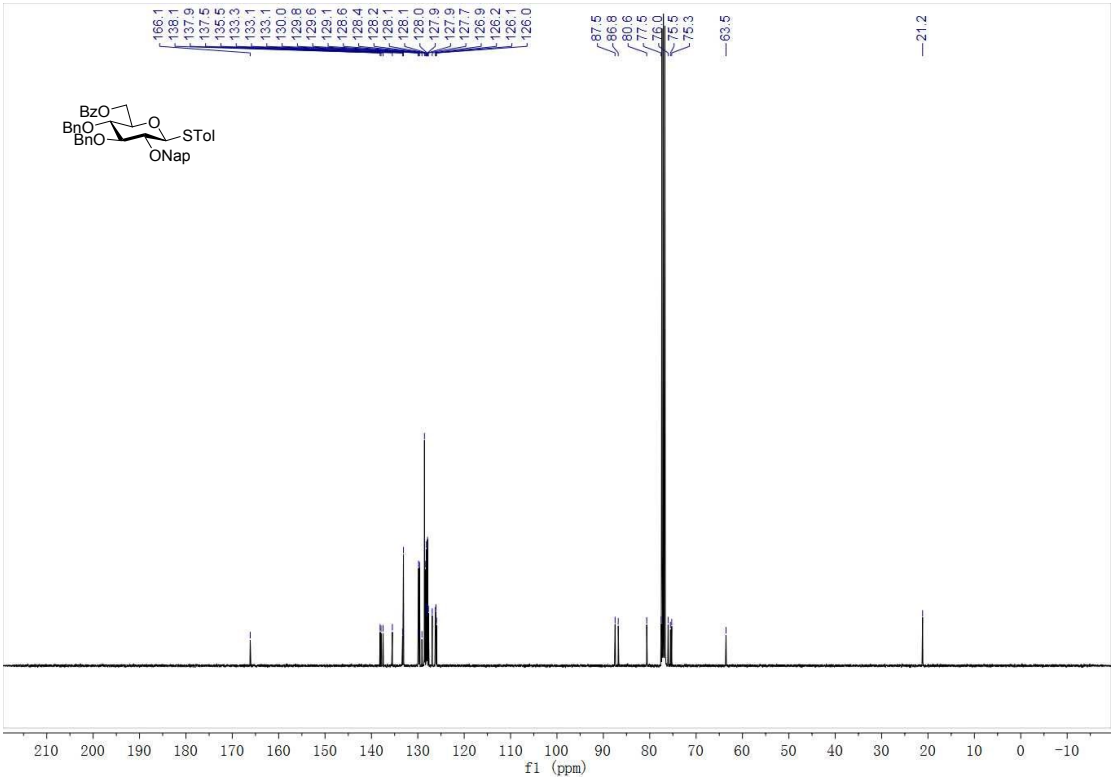
^{13}C NMR spectra of compound **S2**



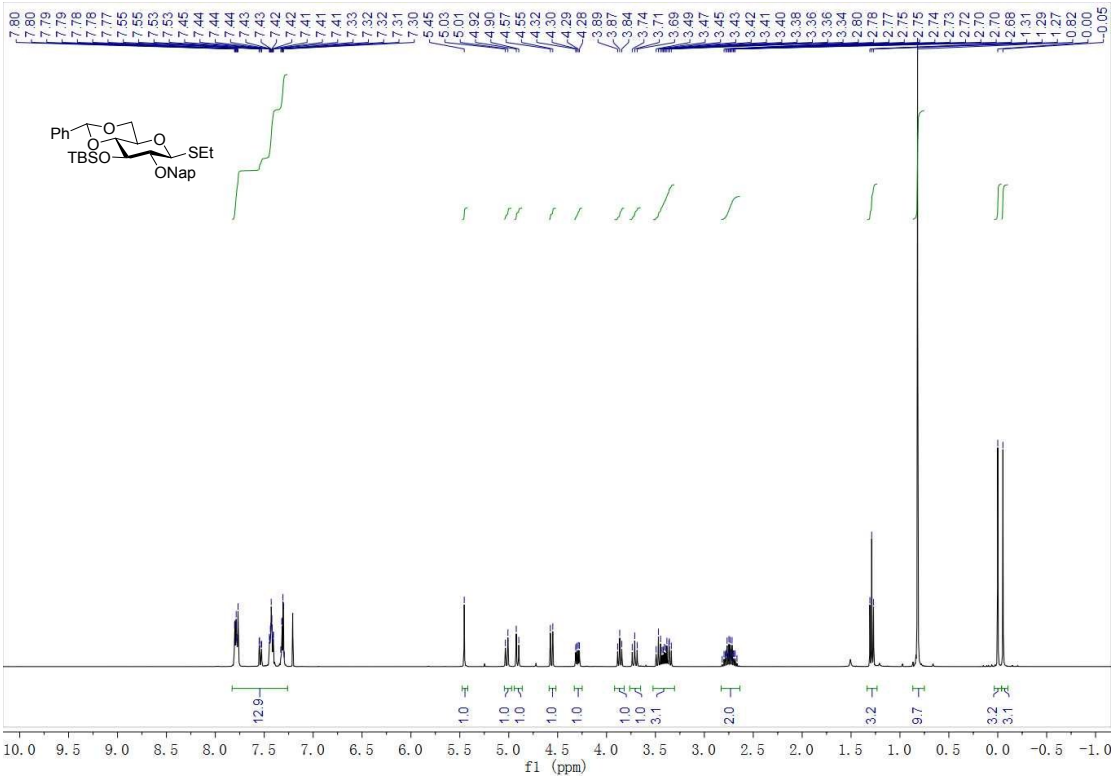
^{1}H NMR spectra of compound **S3**



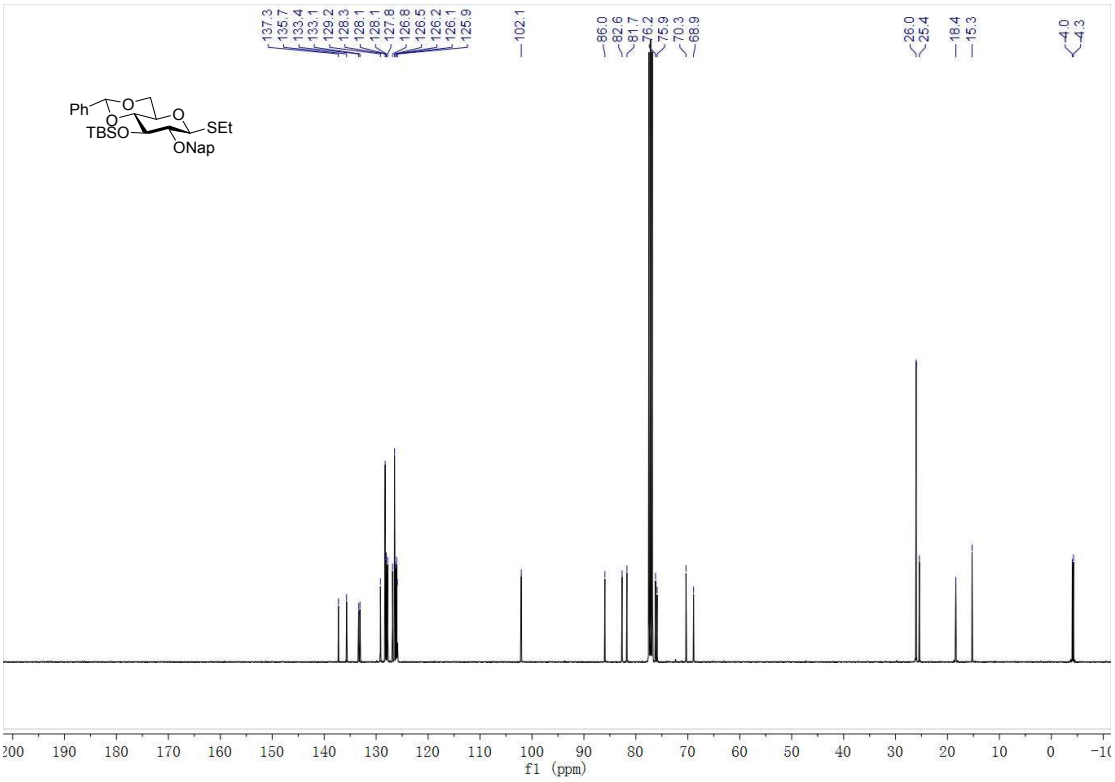
^{13}C NMR spectra of compound **S3**



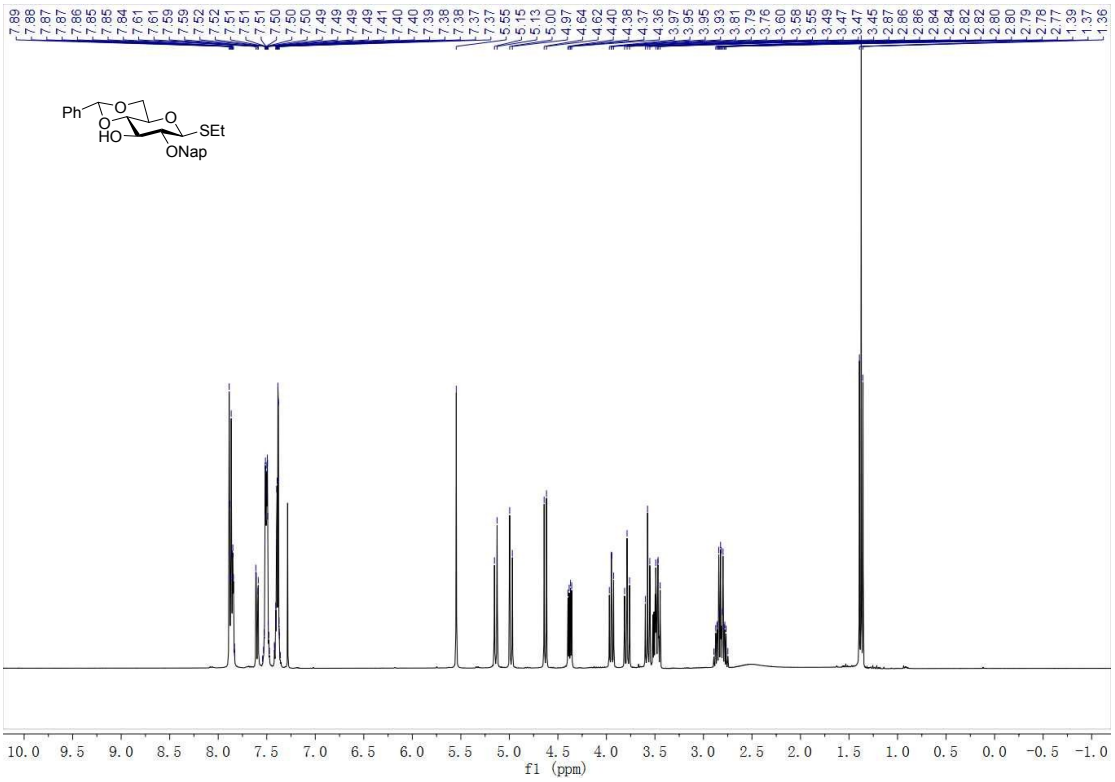
^{1}H NMR spectra of compound **S13**



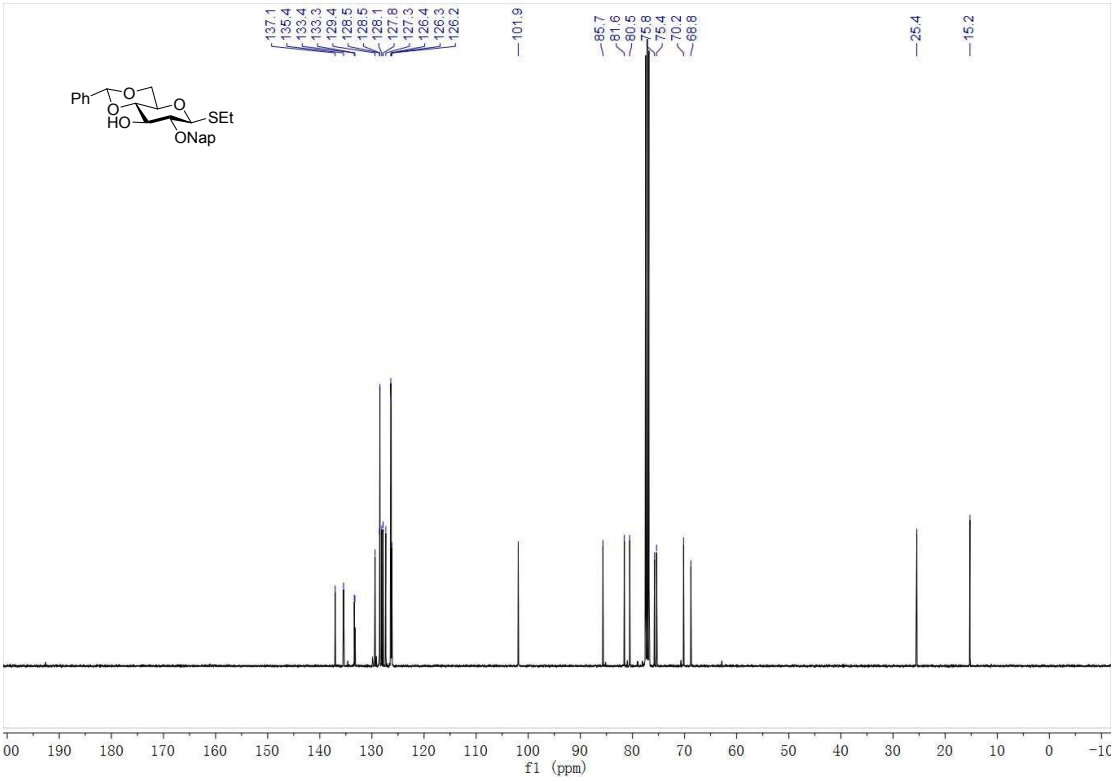
^{13}C NMR spectra of compound **S13**



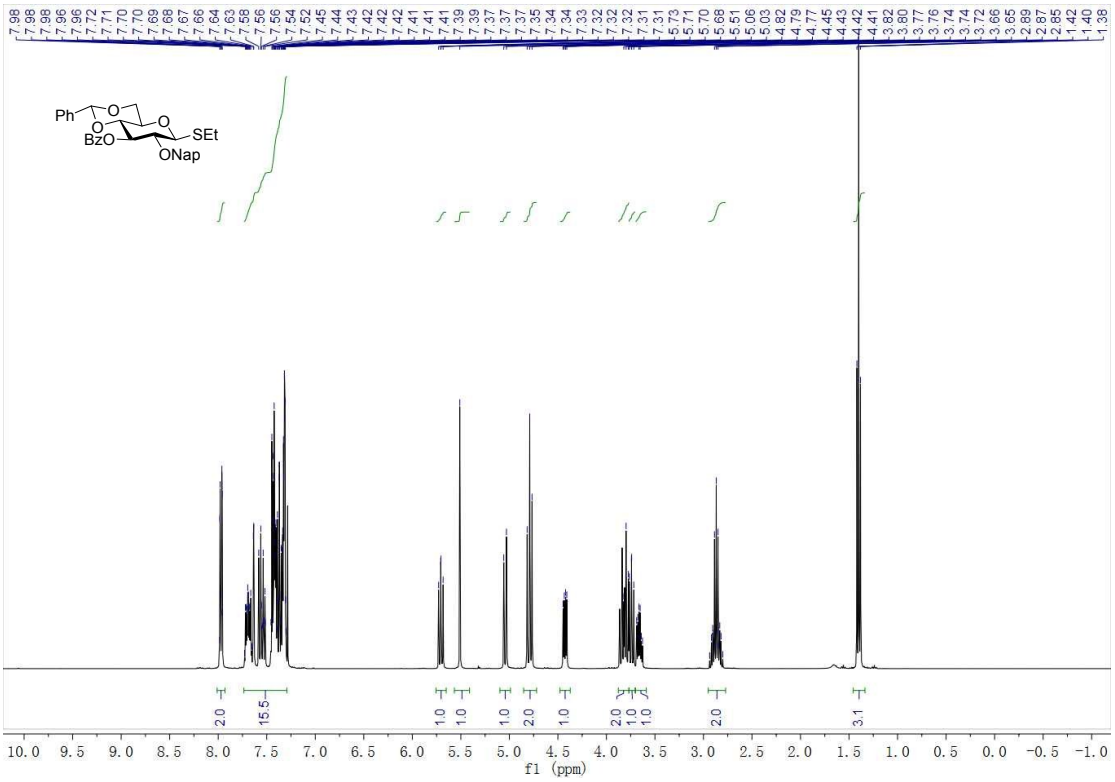
^{1}H NMR spectra of compound **S14**



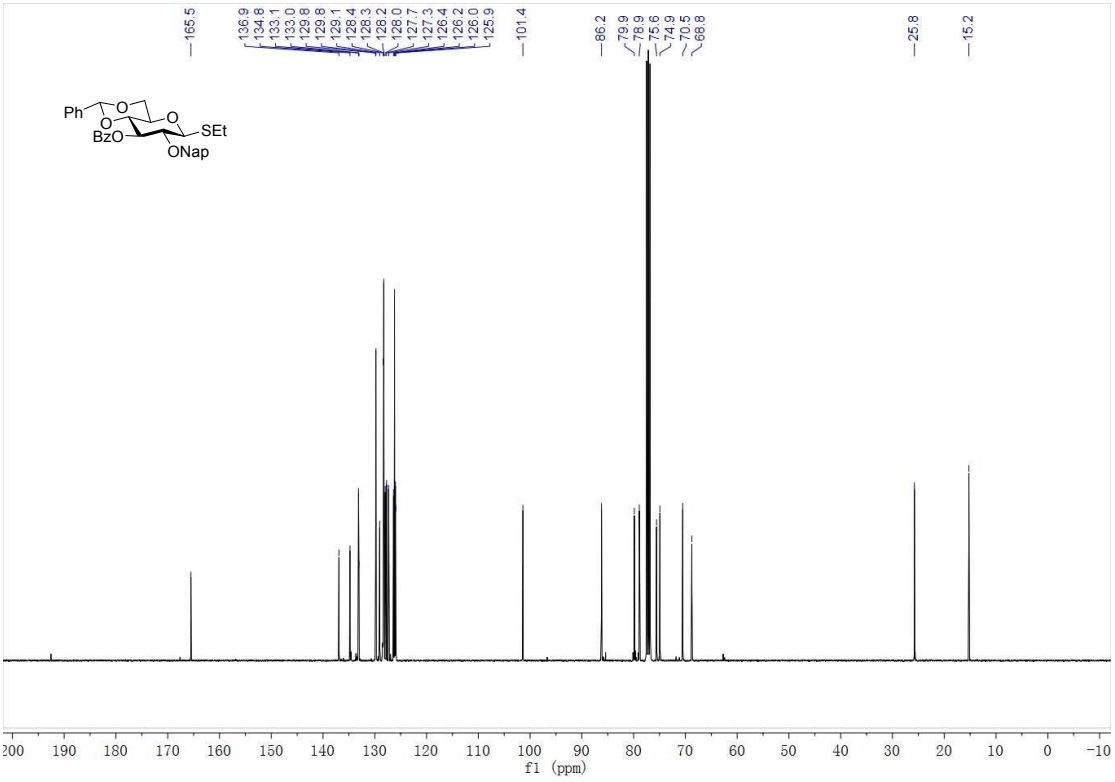
^{13}C NMR spectra of compound **S14**



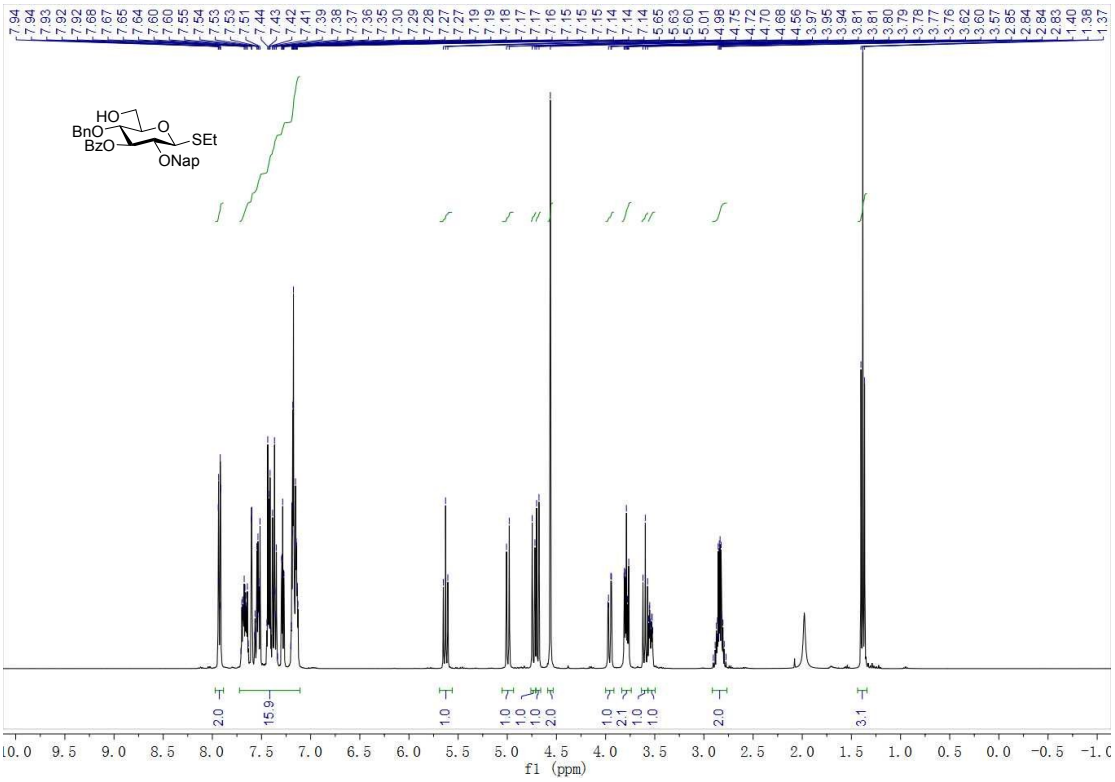
^{1}H NMR spectra of compound **S15**



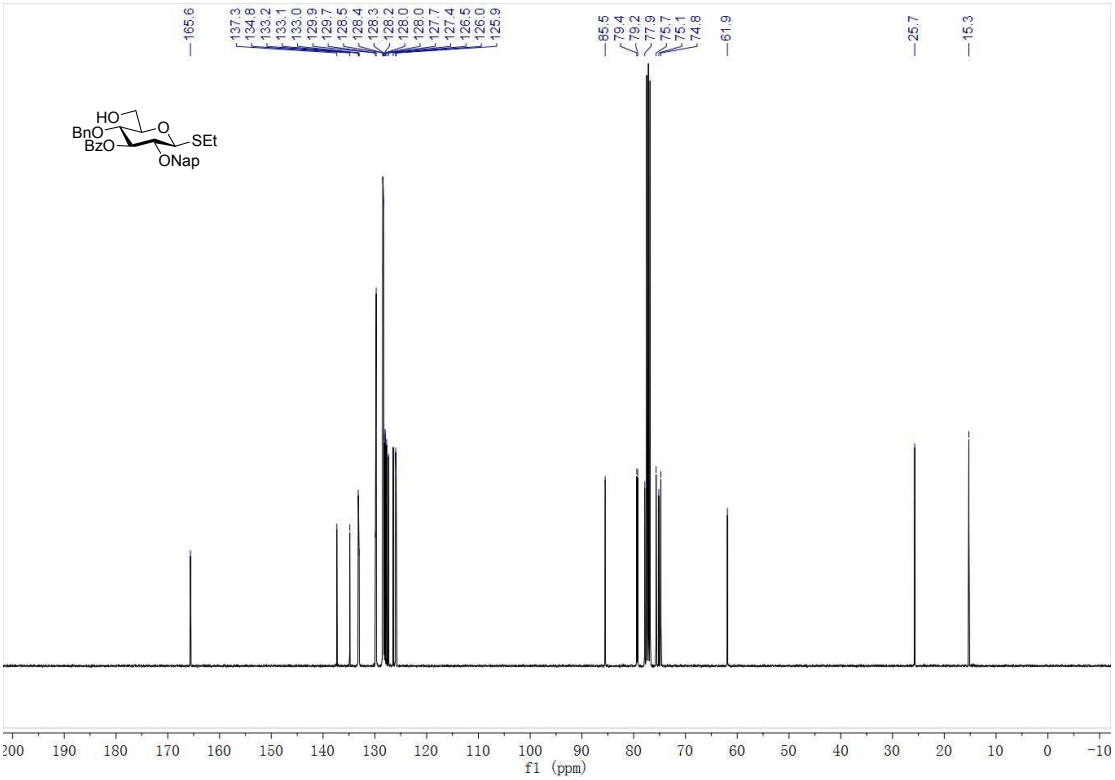
^{13}C NMR spectra of compound **S15**



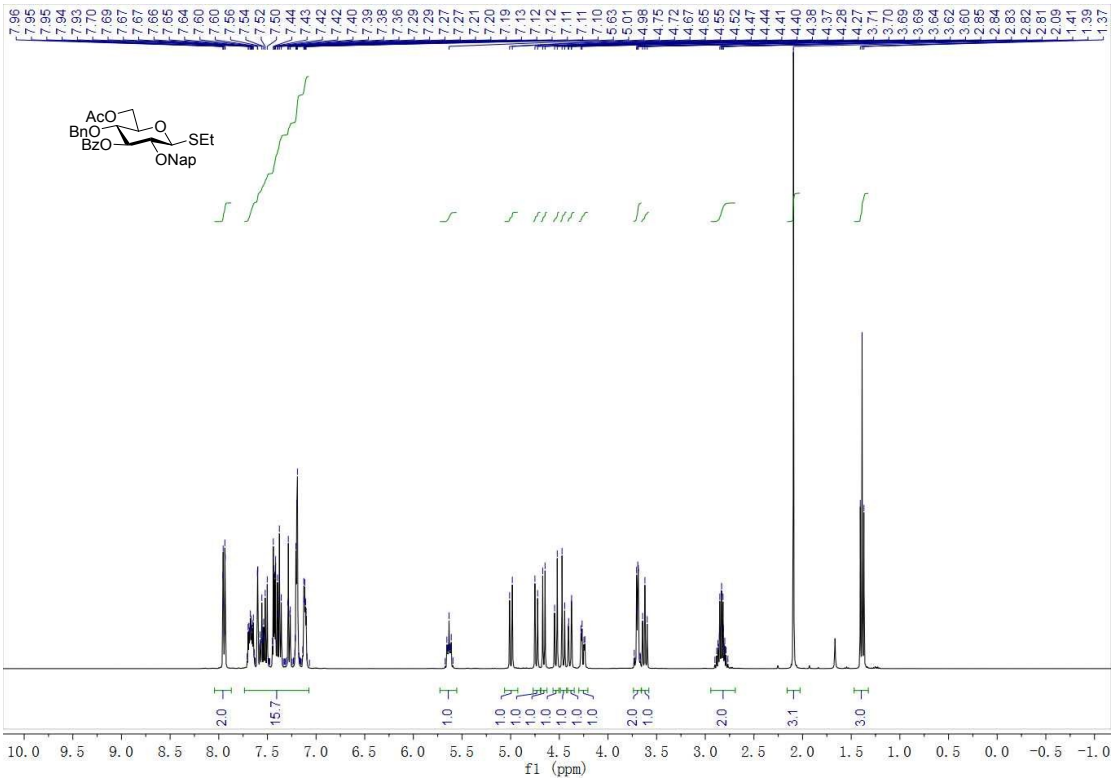
^{1}H NMR spectra of compound **S16**



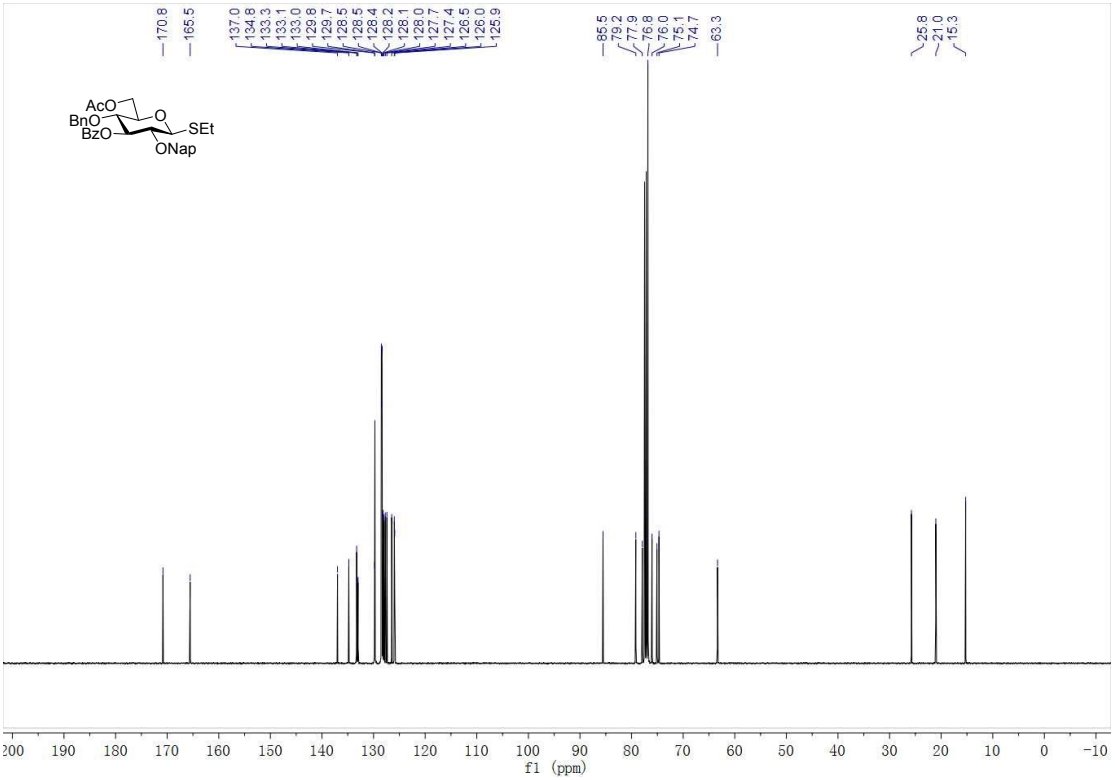
^{13}C NMR spectra of compound **S16**



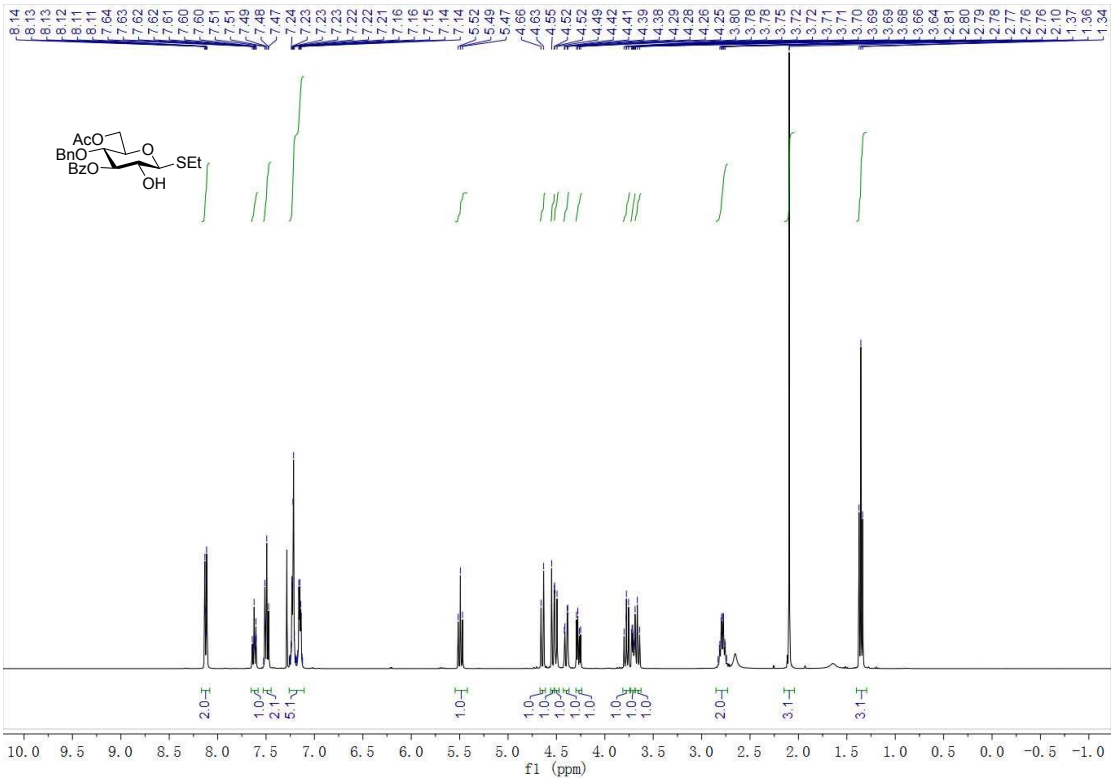
^{1}H NMR spectra of compound **S17**



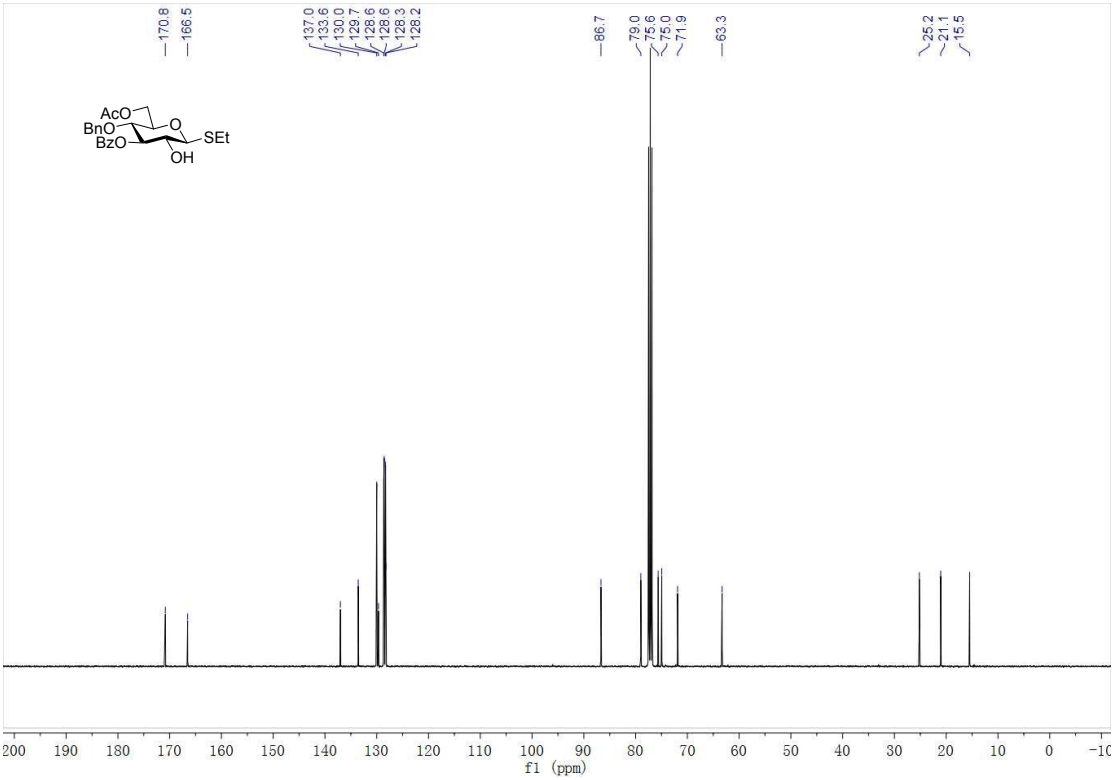
^{13}C NMR spectra of compound **S17**



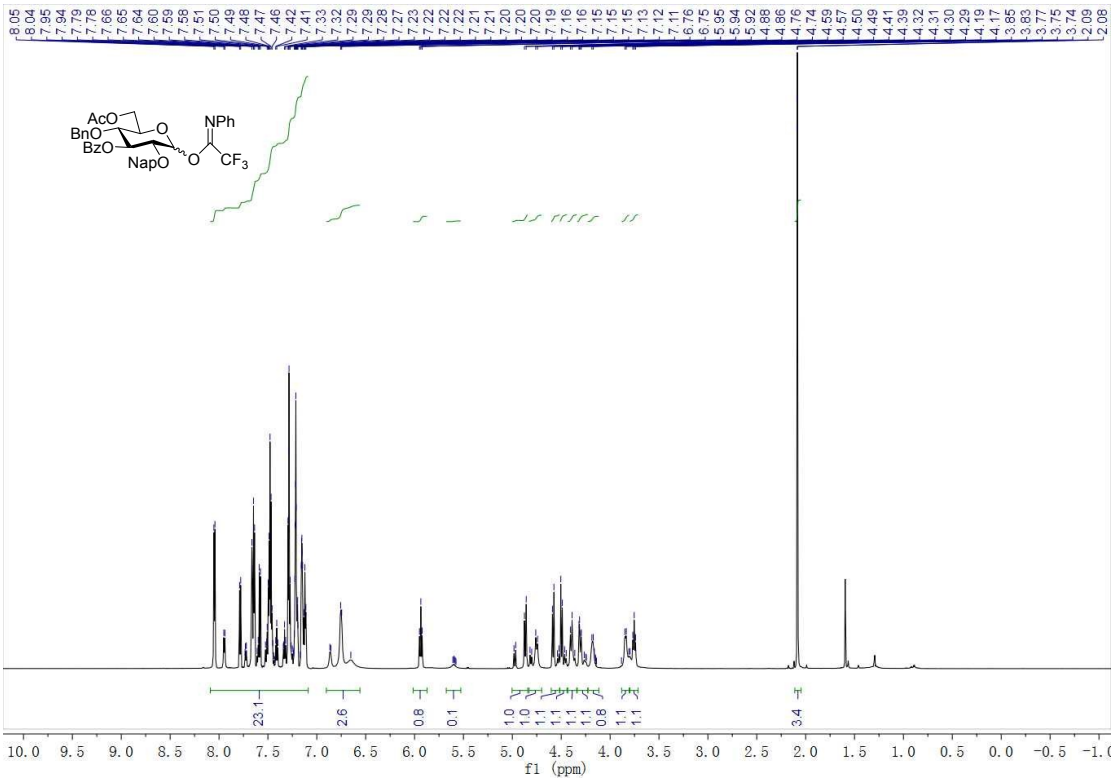
^{1}H NMR spectra of compound **7**



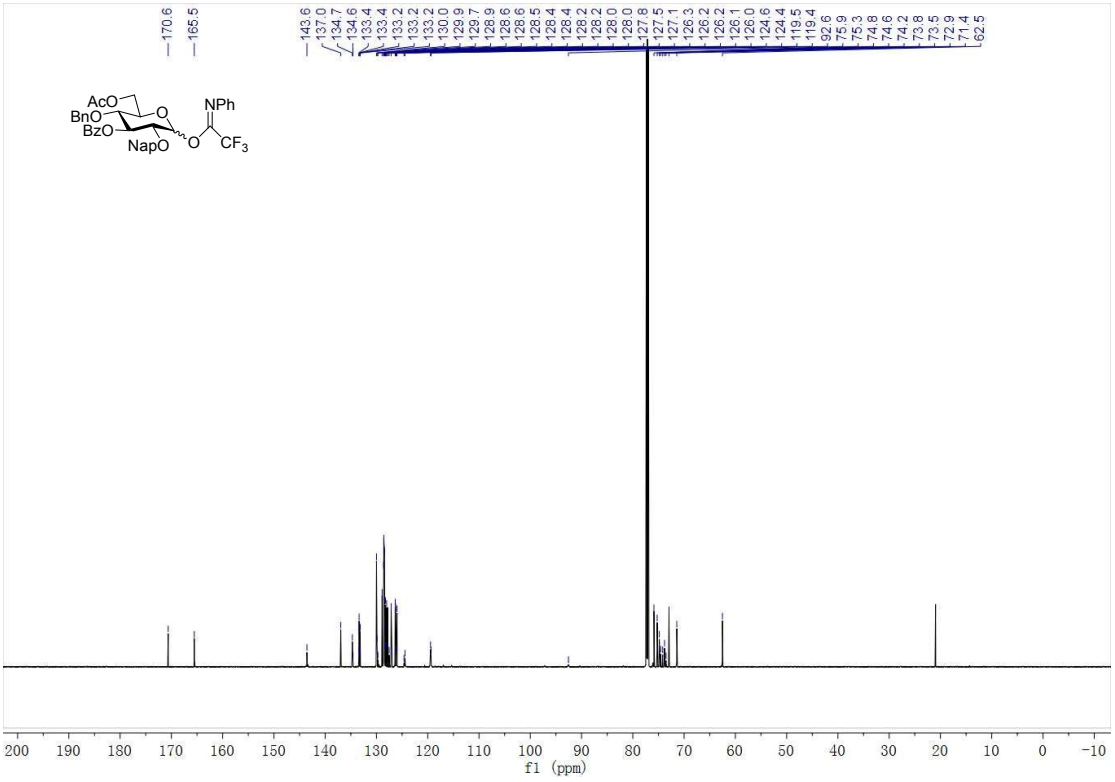
^{13}C NMR spectra of compound **7**



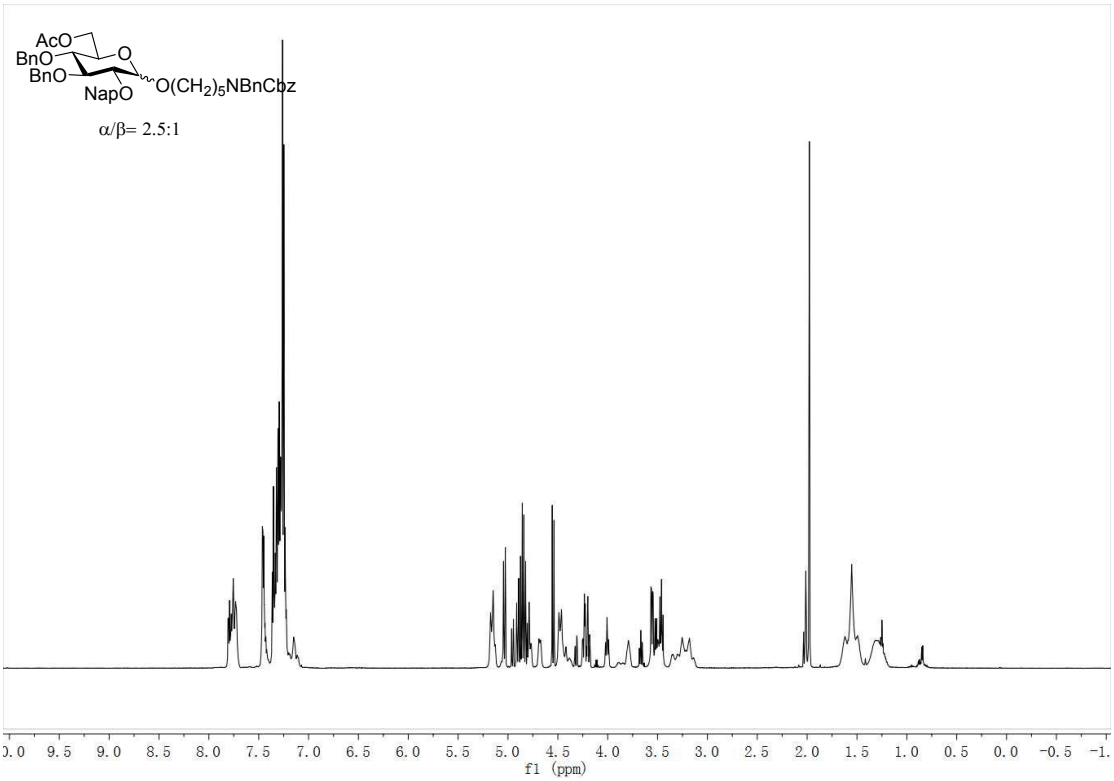
^{1}H NMR spectra of compound **S6**



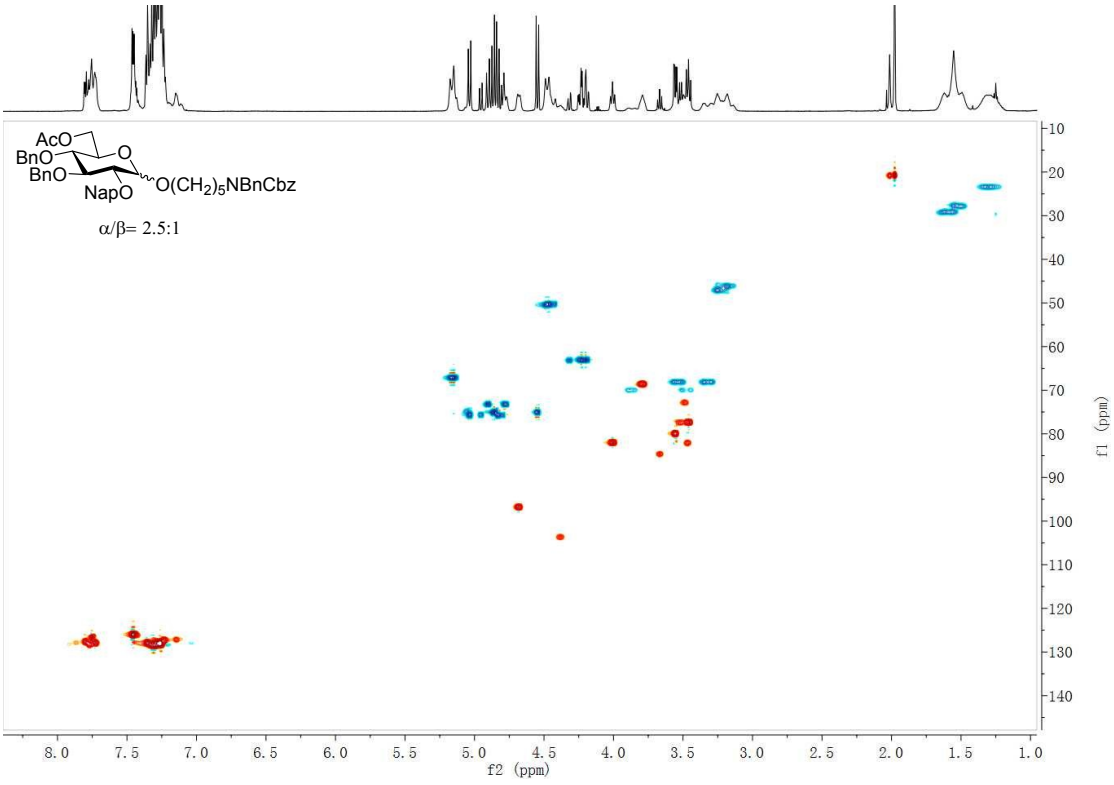
^{13}C NMR spectra of compound **S6**



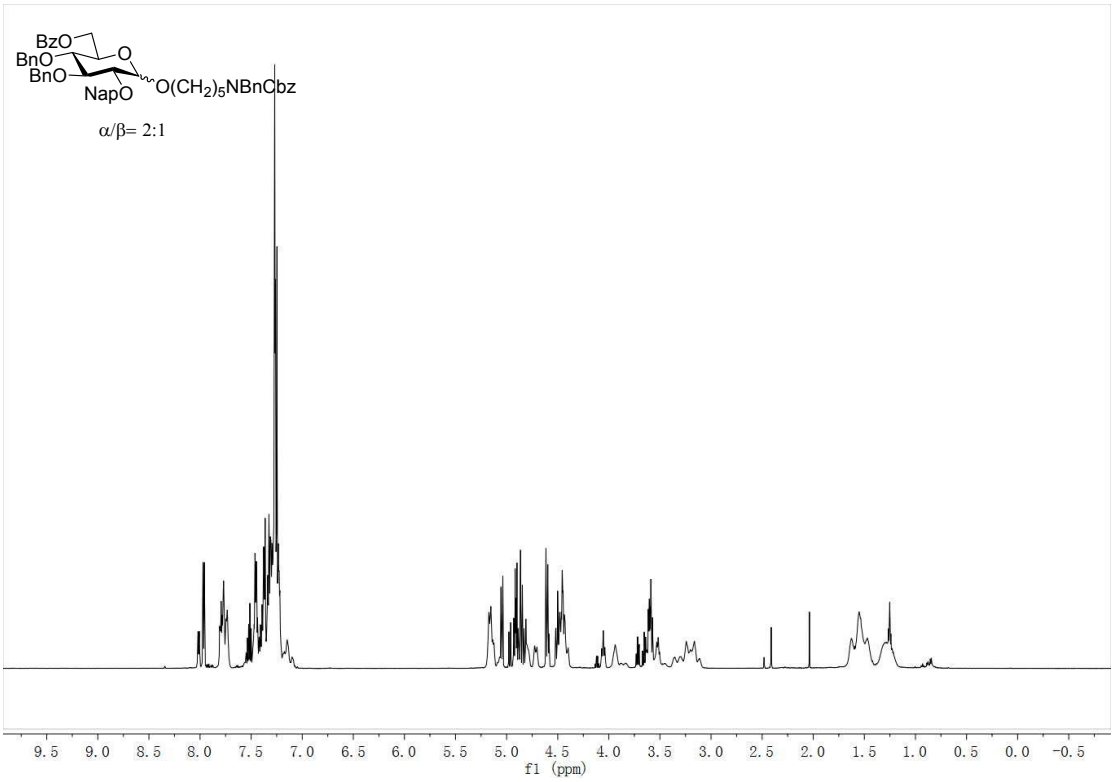
^{1}H NMR spectra of compound **S7** (α/β= 2.5:1)



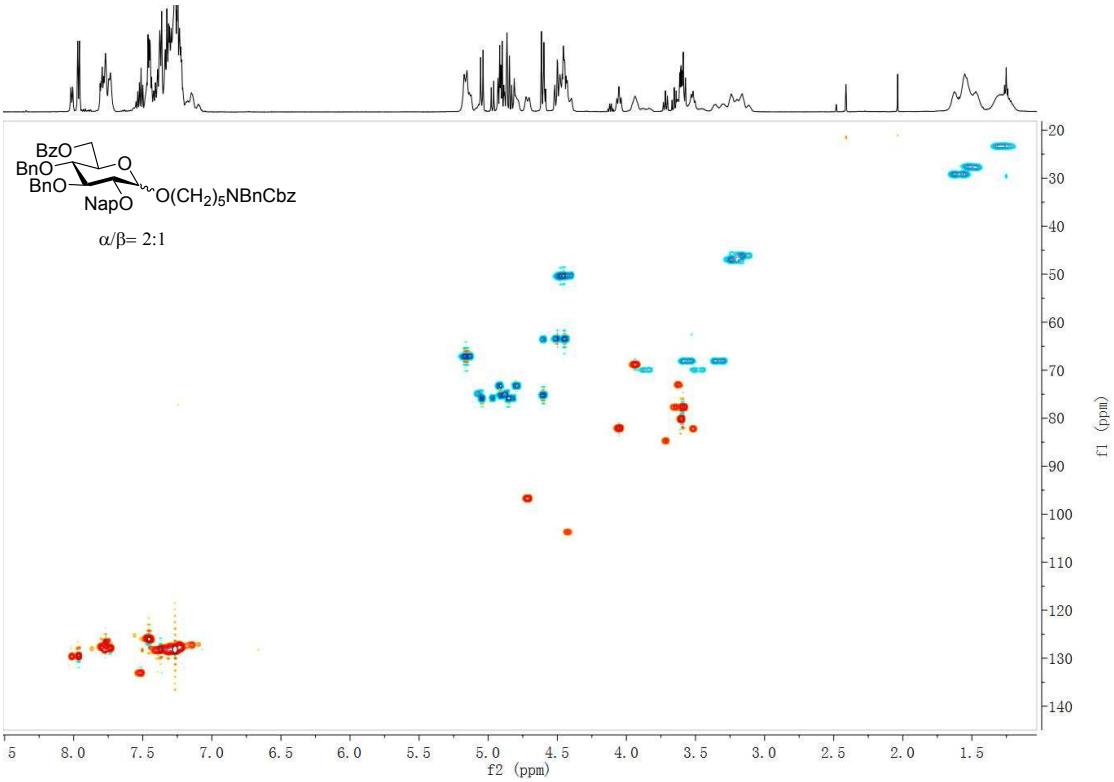
^{1}H-^{13}C HSQC NMR spectra of compound **S7** (α/β= 2.5:1)



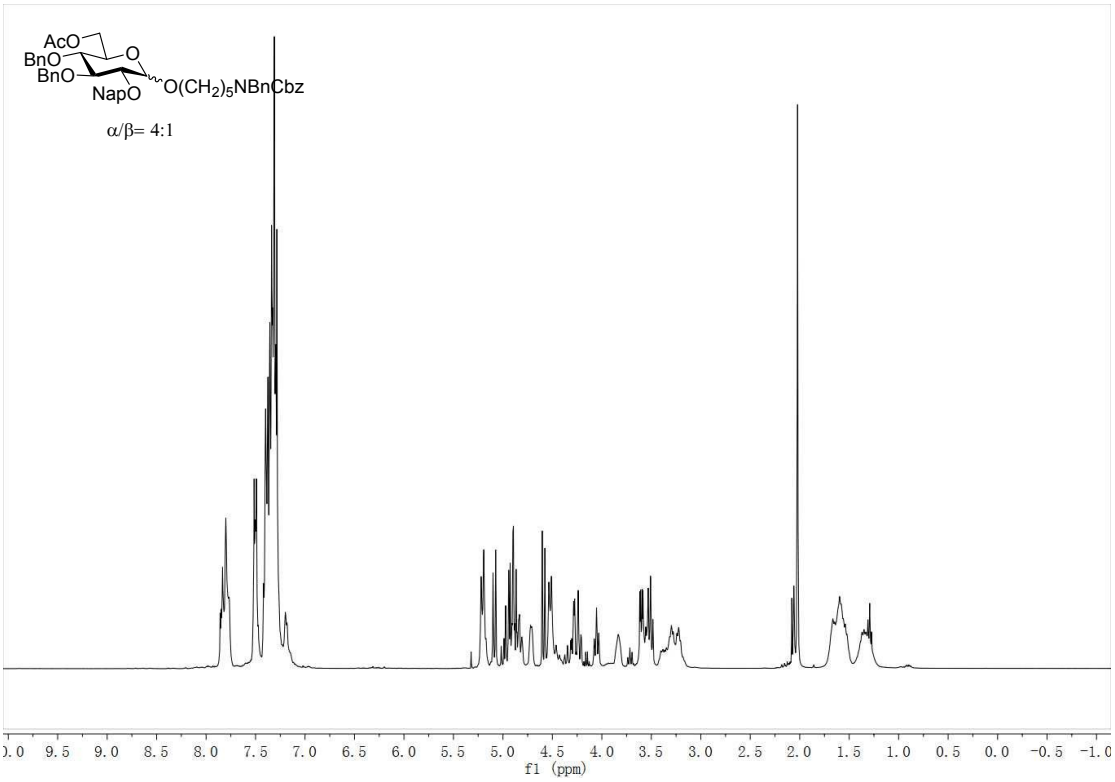
^{1}H NMR spectra of compound **S8** (α/β= 2:1)



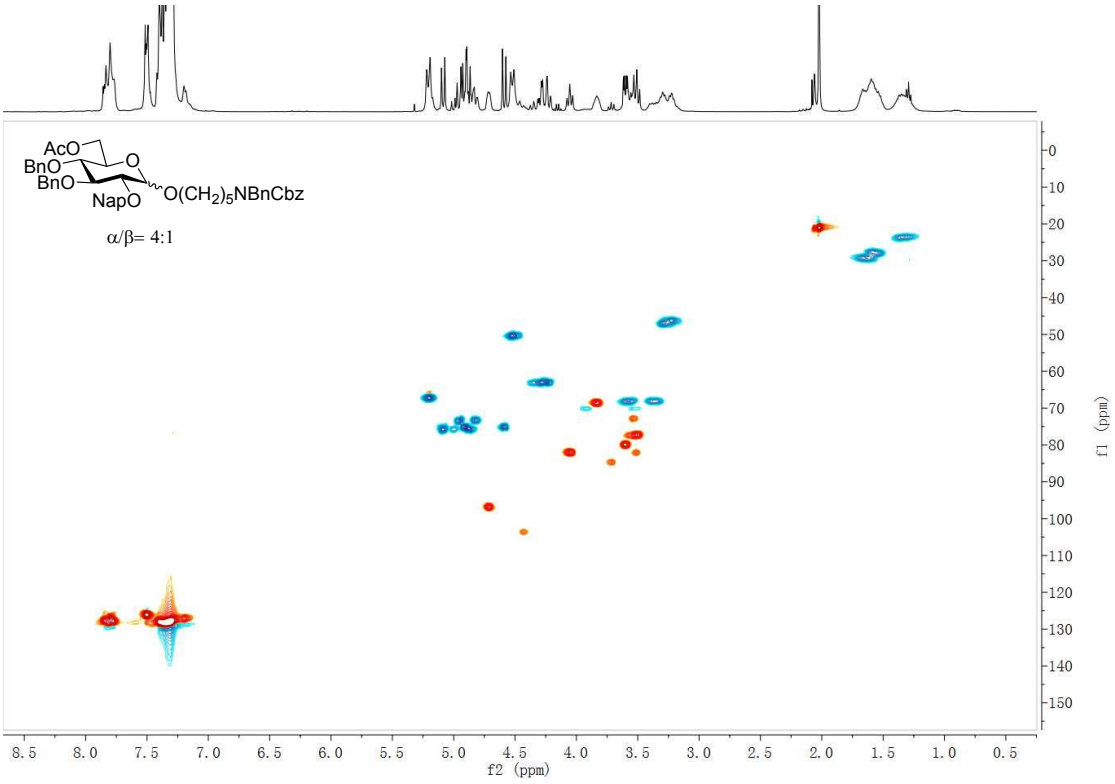
^{1}H-^{13}C HSQC NMR spectra of compound **S8** (α/β= 2:1)



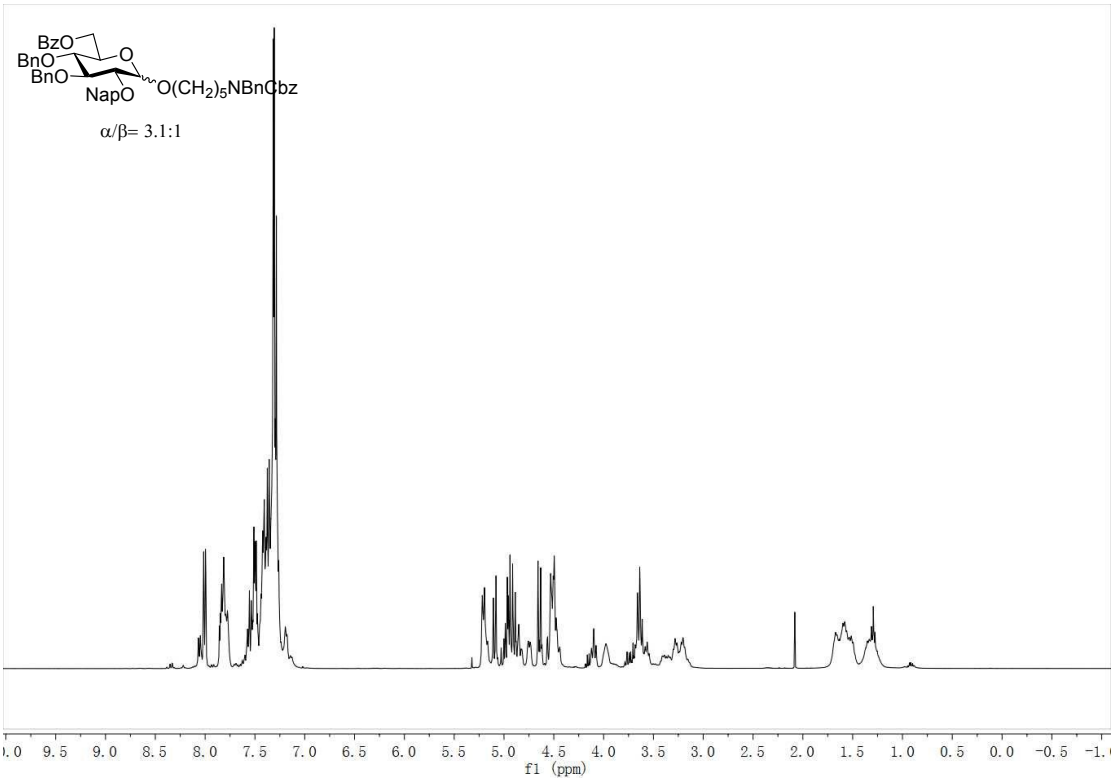
^{1}H NMR spectra of compound **S7** (α/β= 4:1)



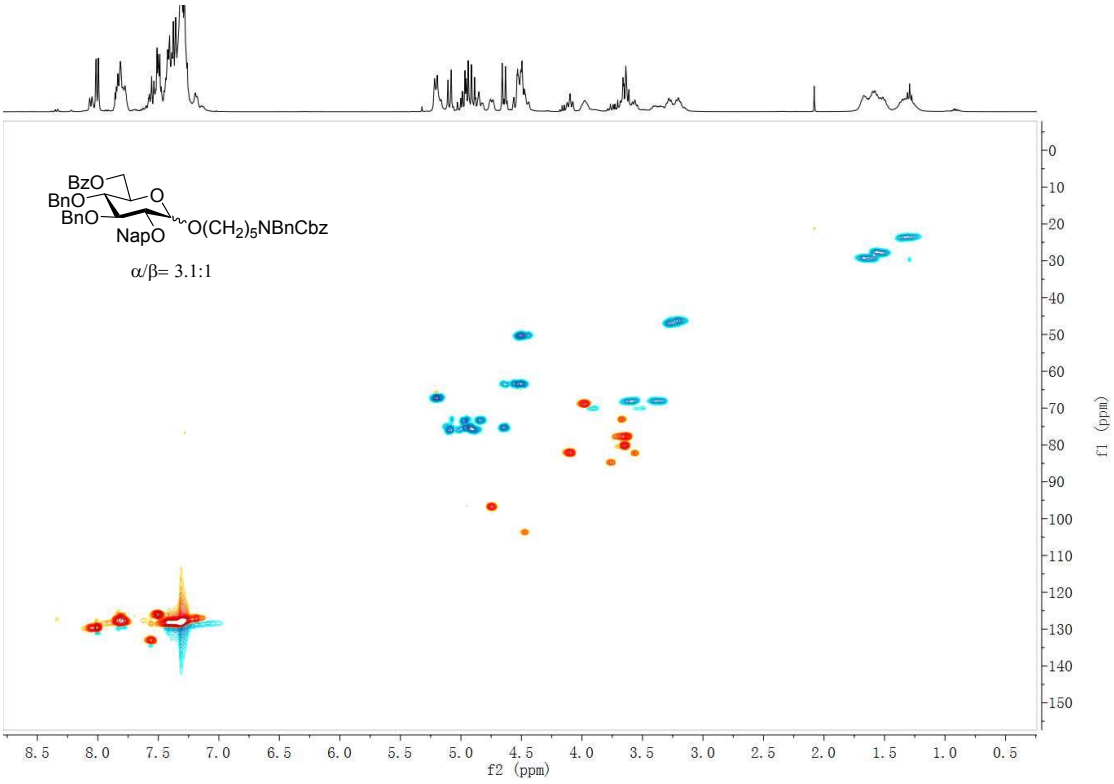
^{1}H-^{13}C HSQC NMR spectra of compound **S7** (α/β= 4:1)



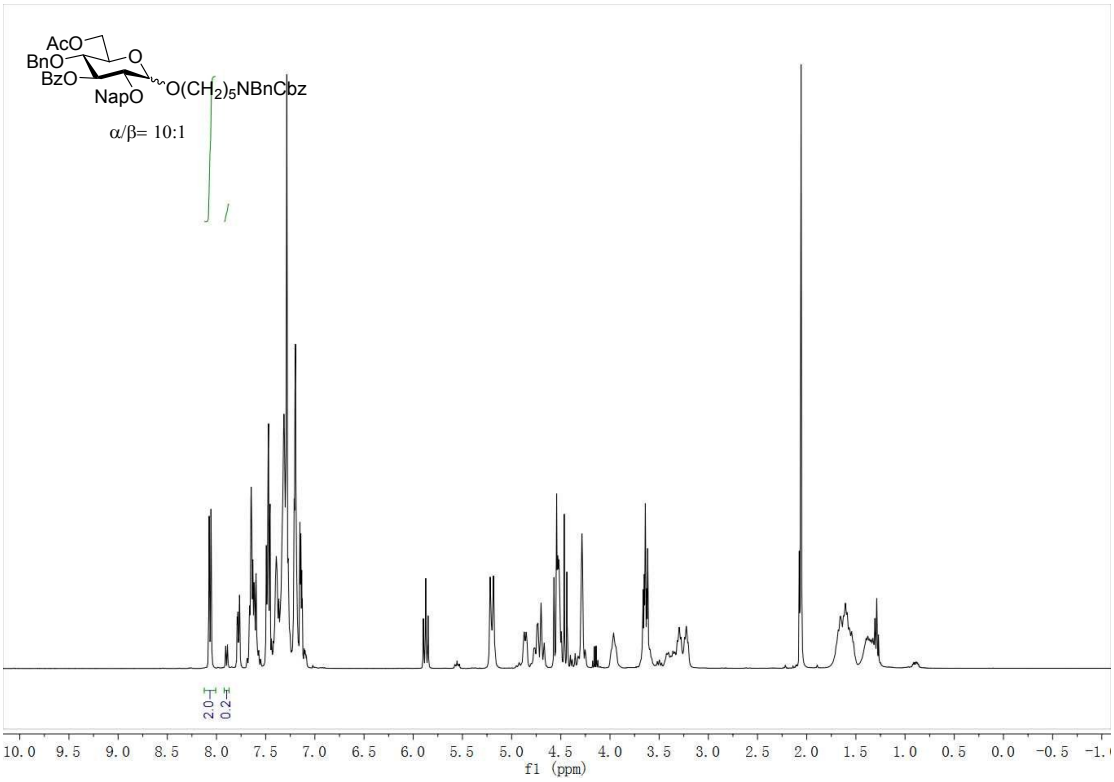
^{1}H NMR spectra of compound **S8** (α/β= 3.1:1)



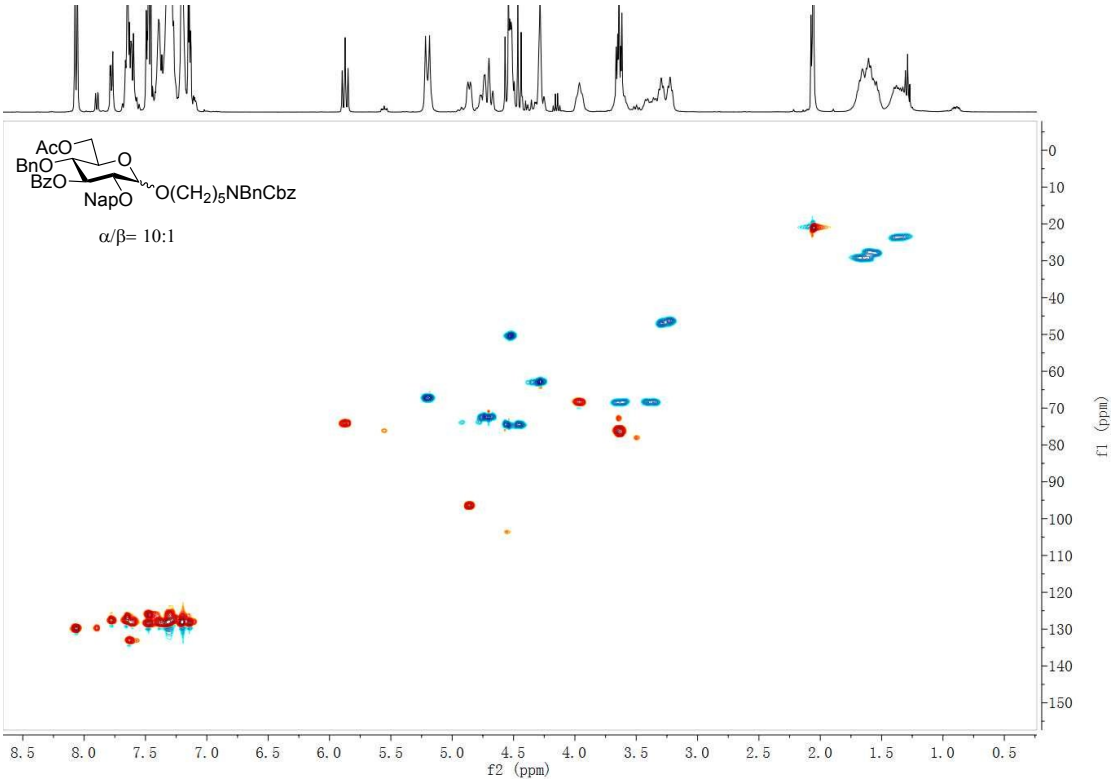
^{1}H-^{13}C HSQC NMR spectra of compound **S8** (α/β= 3.1:1)



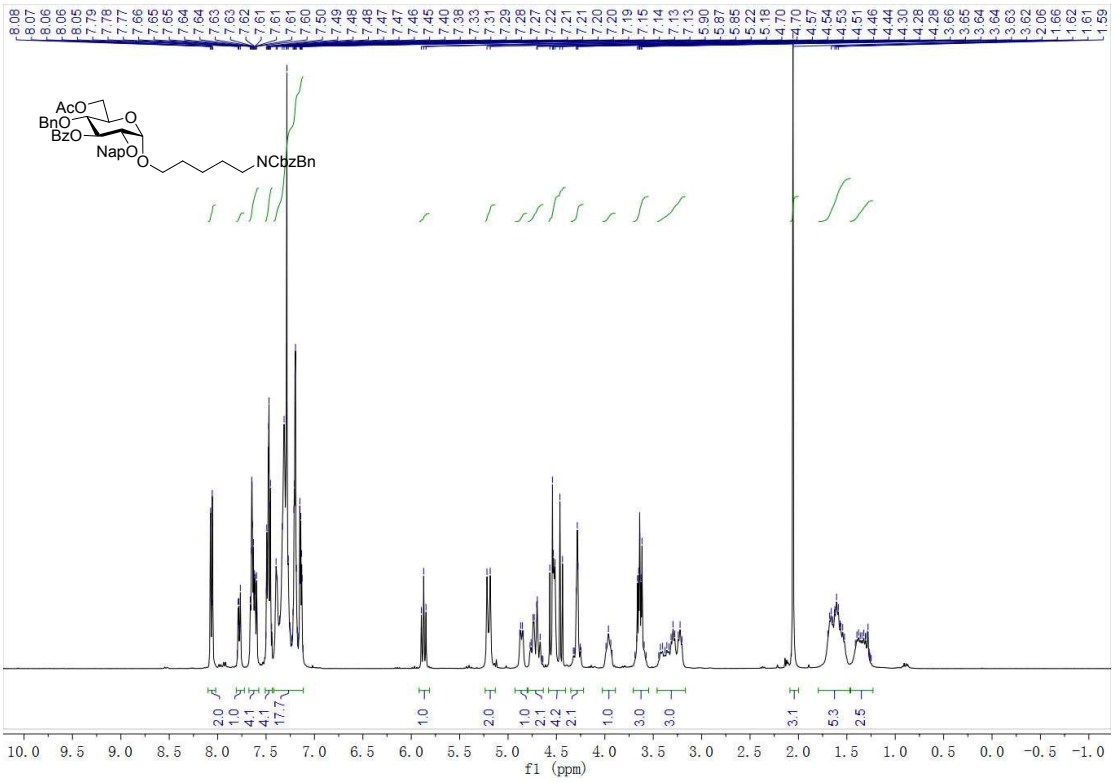
^{1}H NMR spectra of compound **S9** (α/β=10:1)



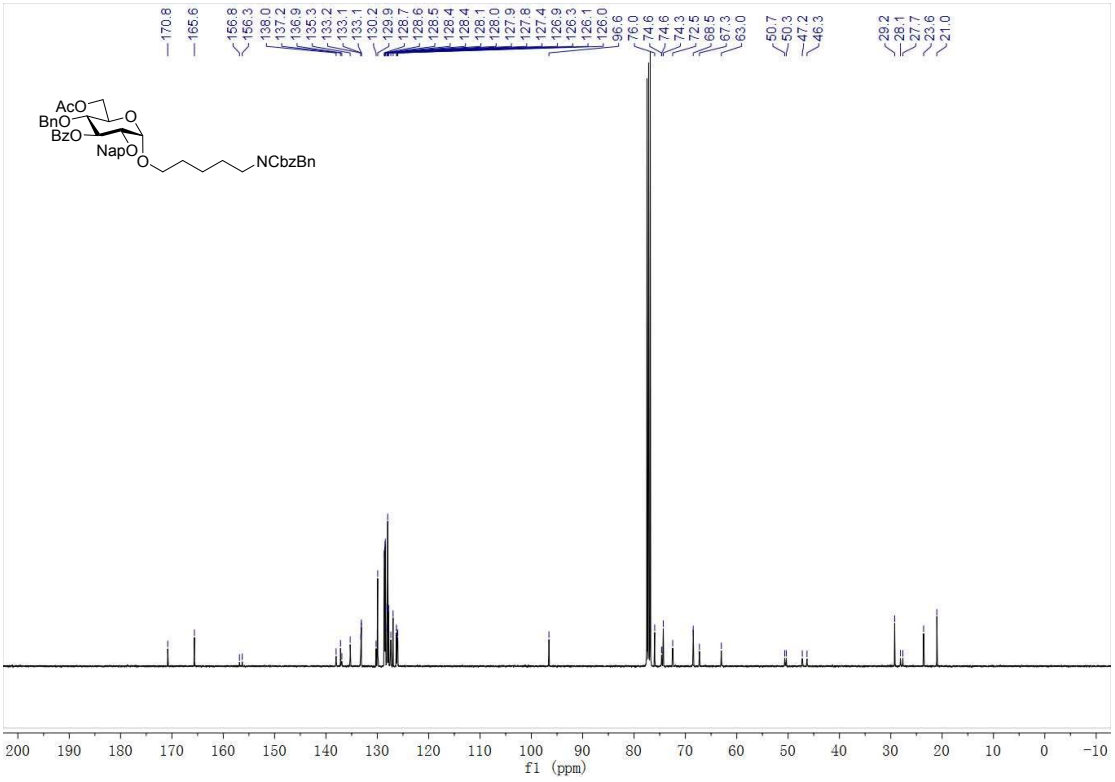
^{1}H-^{13}C HSQC NMR spectra of compound **S9** (α/β=10:1)



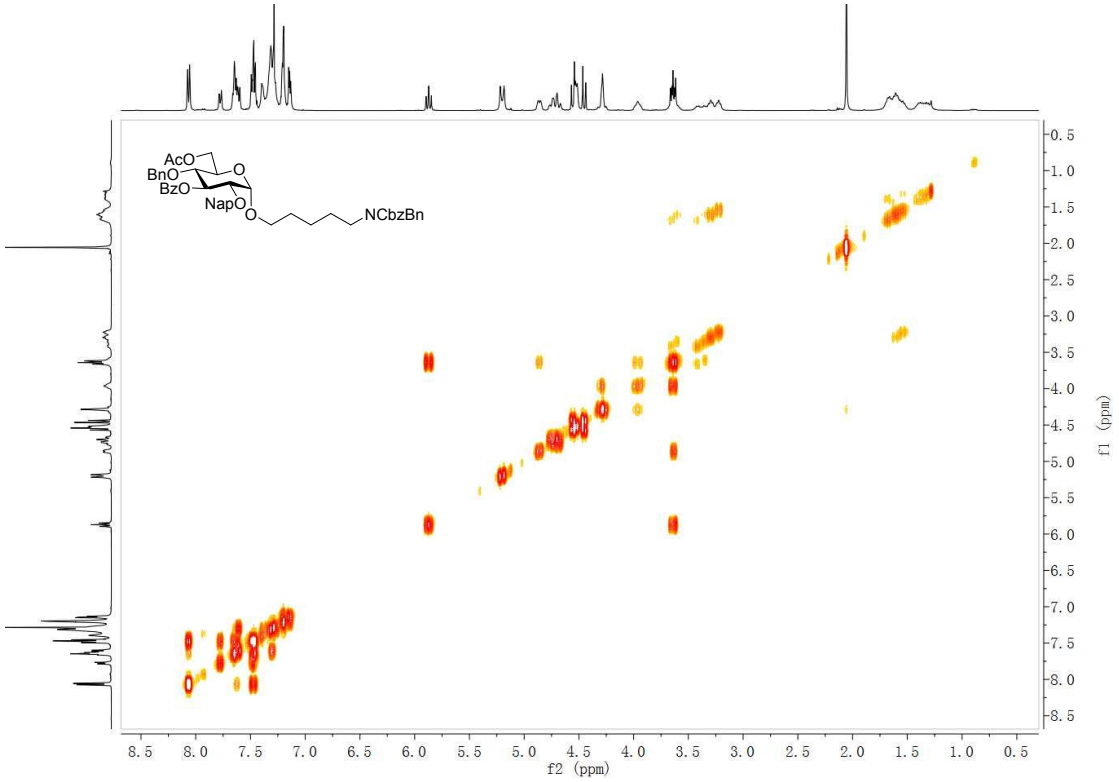
^{1}H NMR spectra of compound **S9-α**



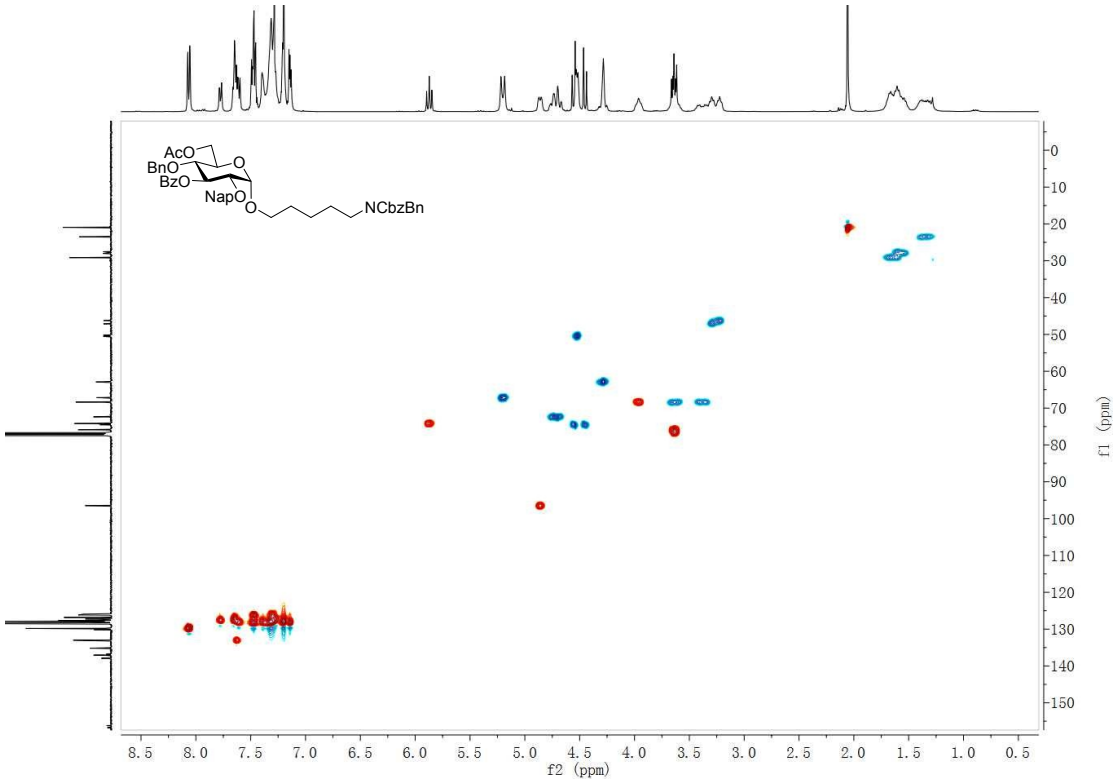
^{13}C NMR spectra of compound **S9-α**



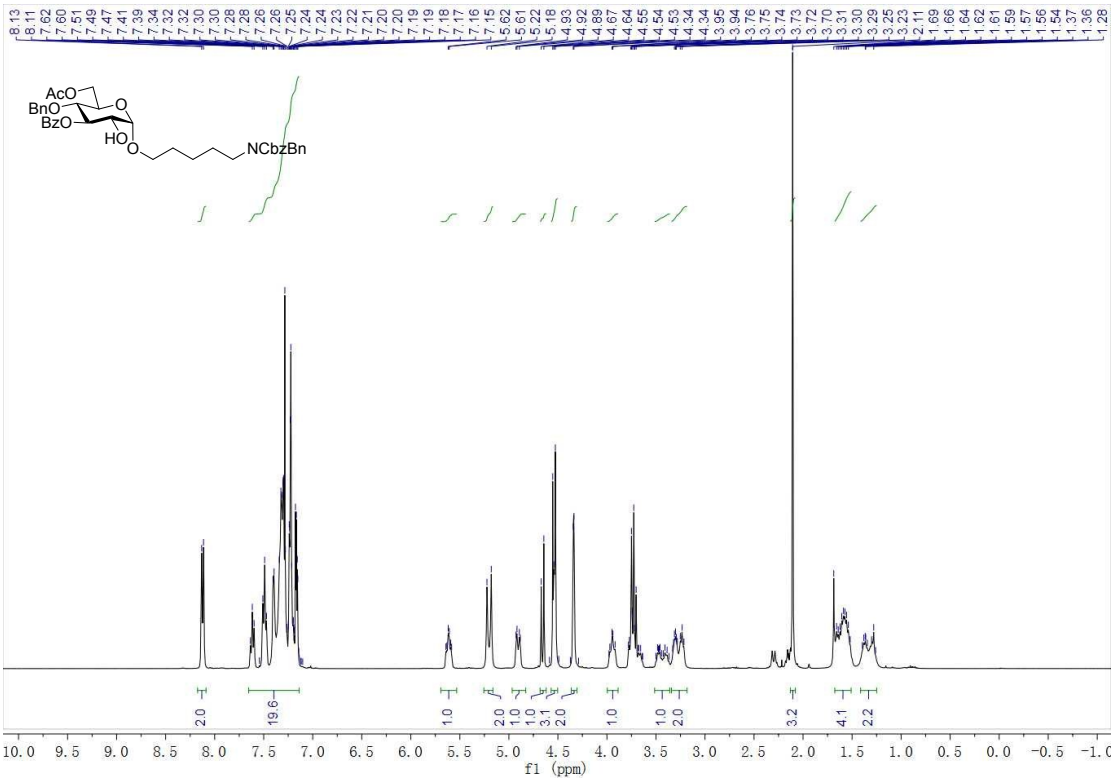
^{1}H-^{1}H COSY NMR spectra of compound **S9-α**



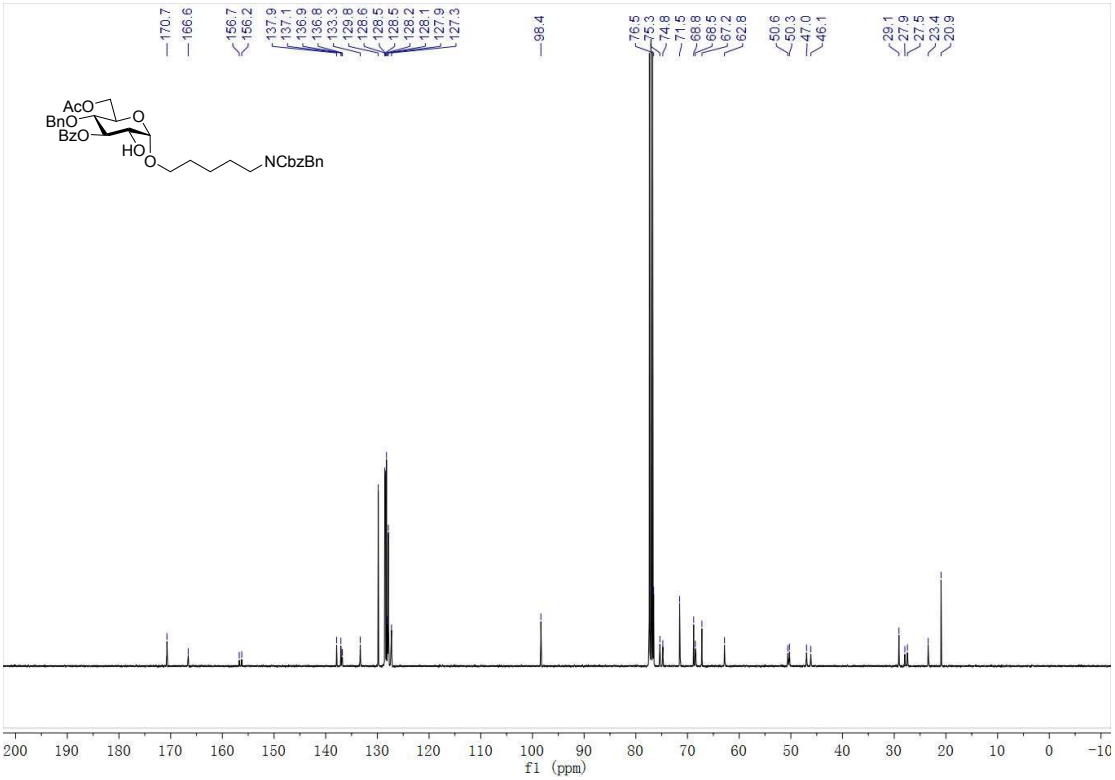
^{1}H-^{13}C HSQC NMR spectra of compound **S9-α**



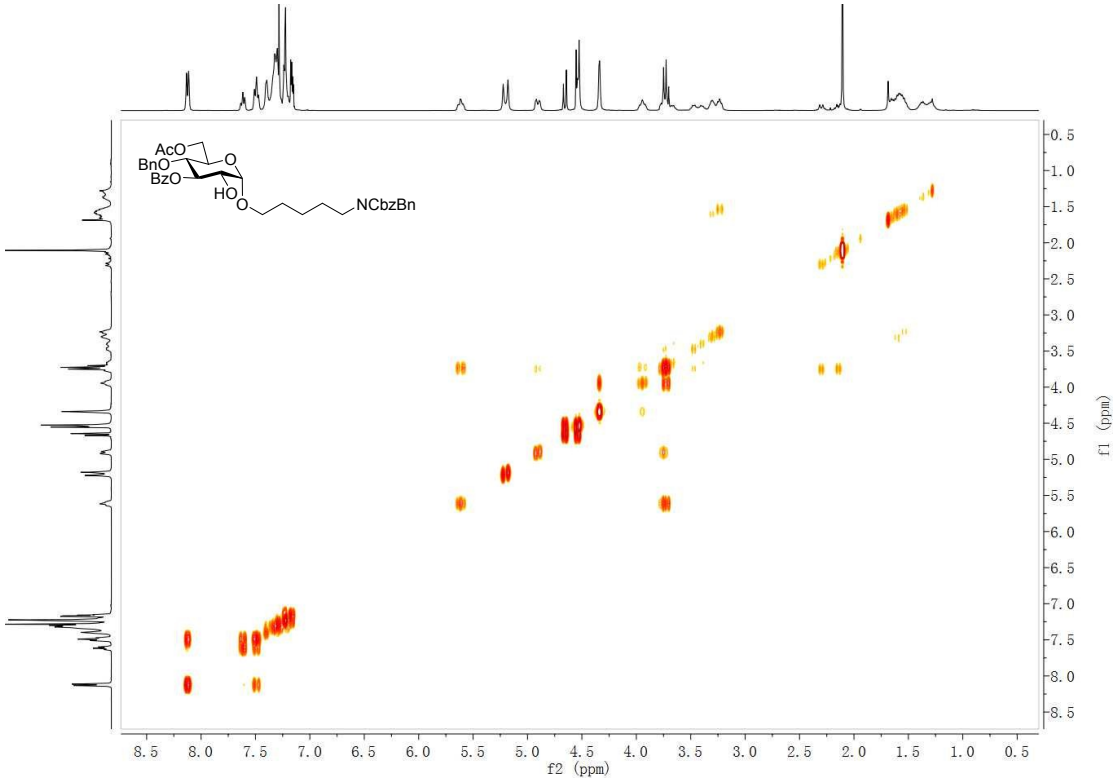
^{1}H NMR spectra of compound **8**



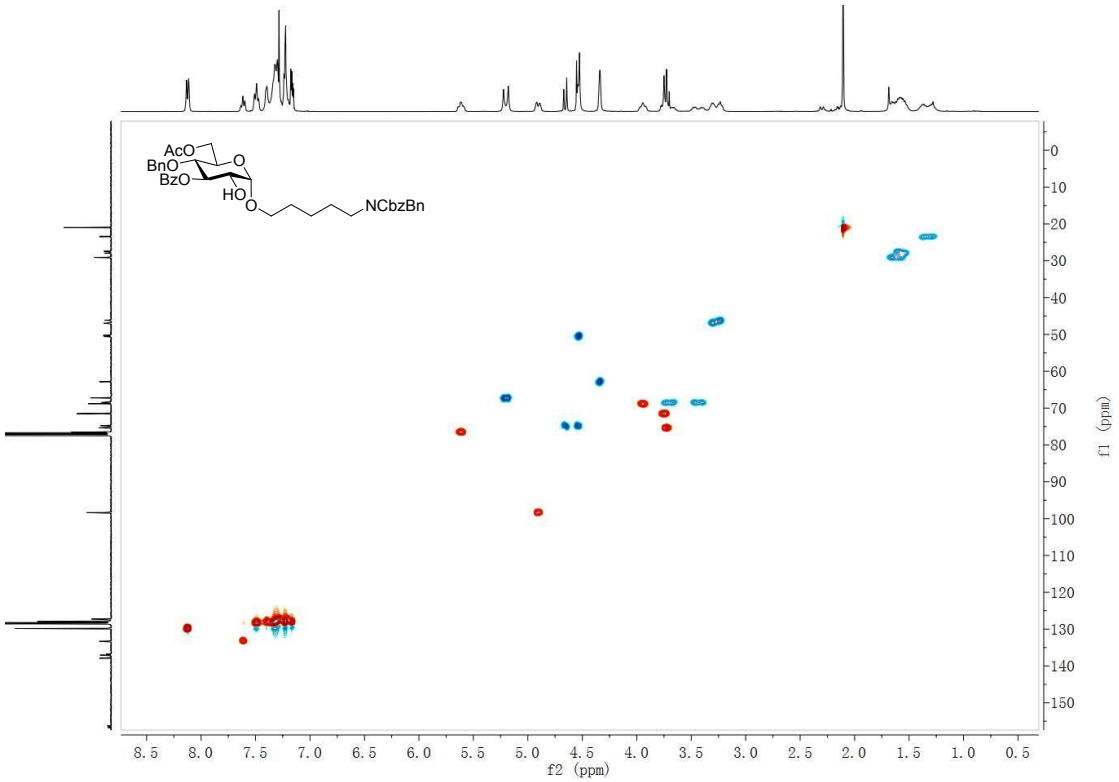
^{13}C NMR spectra of compound **8**



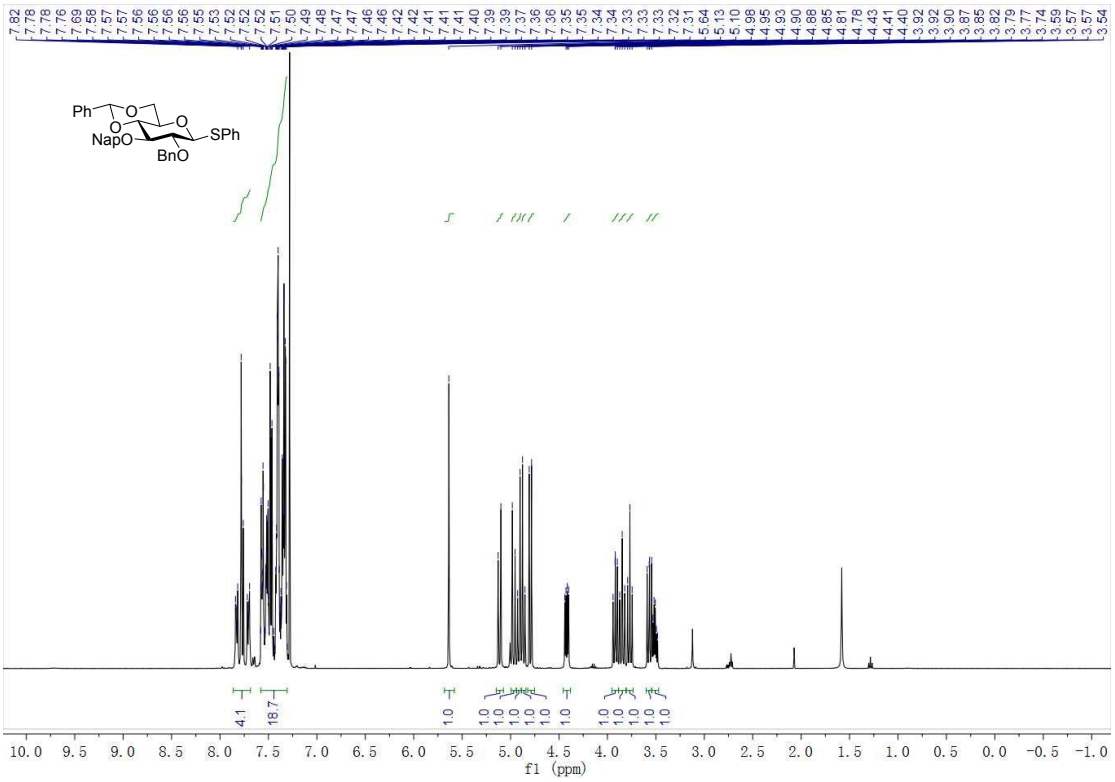
^{1}H-^{1}H COSY NMR spectra of compound **8**



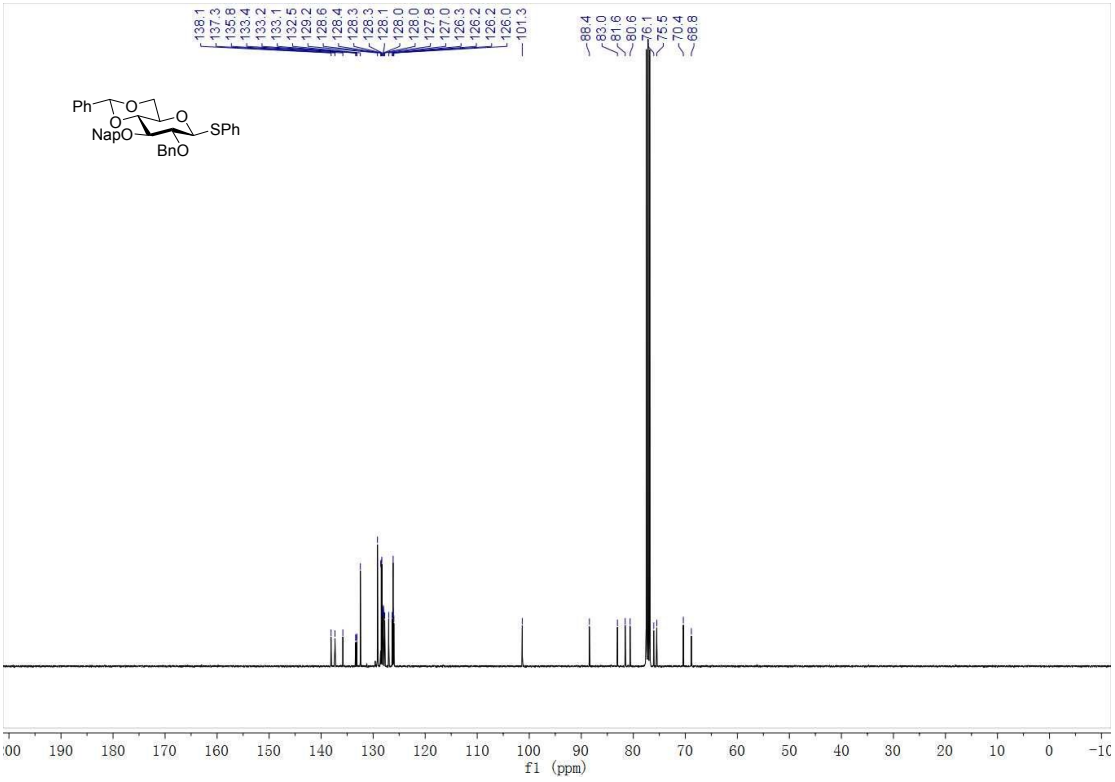
^{1}H-^{13}C HSQC NMR spectra of compound **8**



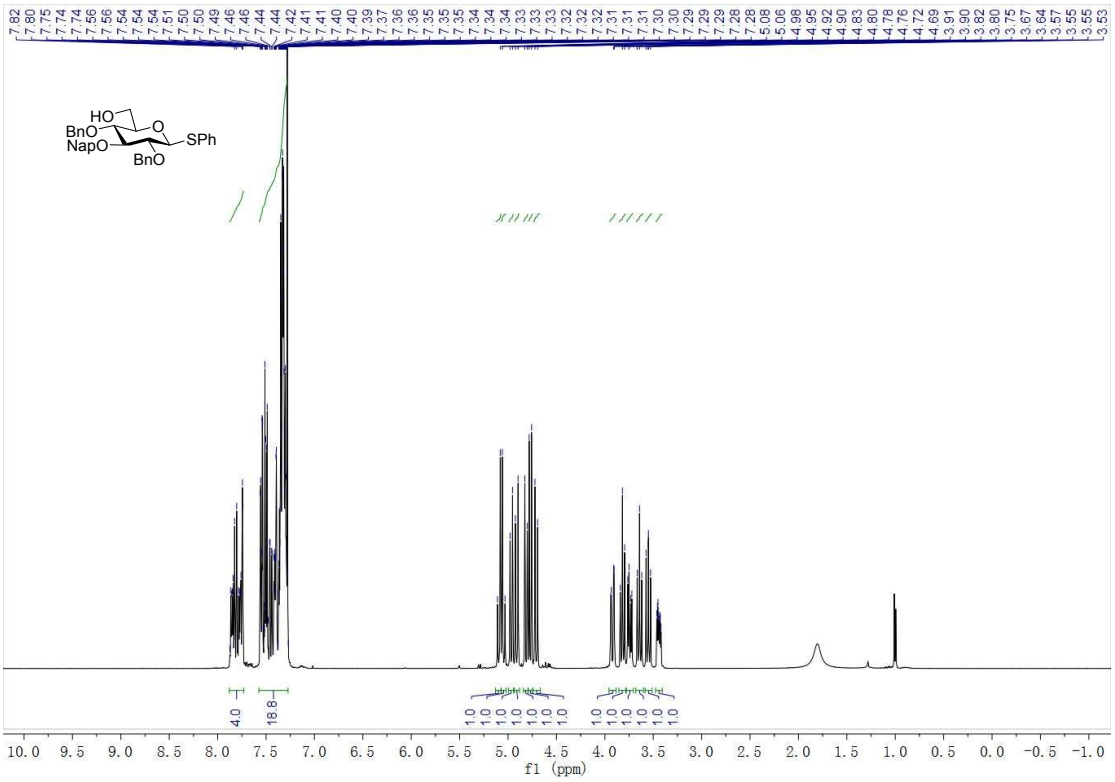
^{1}H NMR spectra of compound **S19**



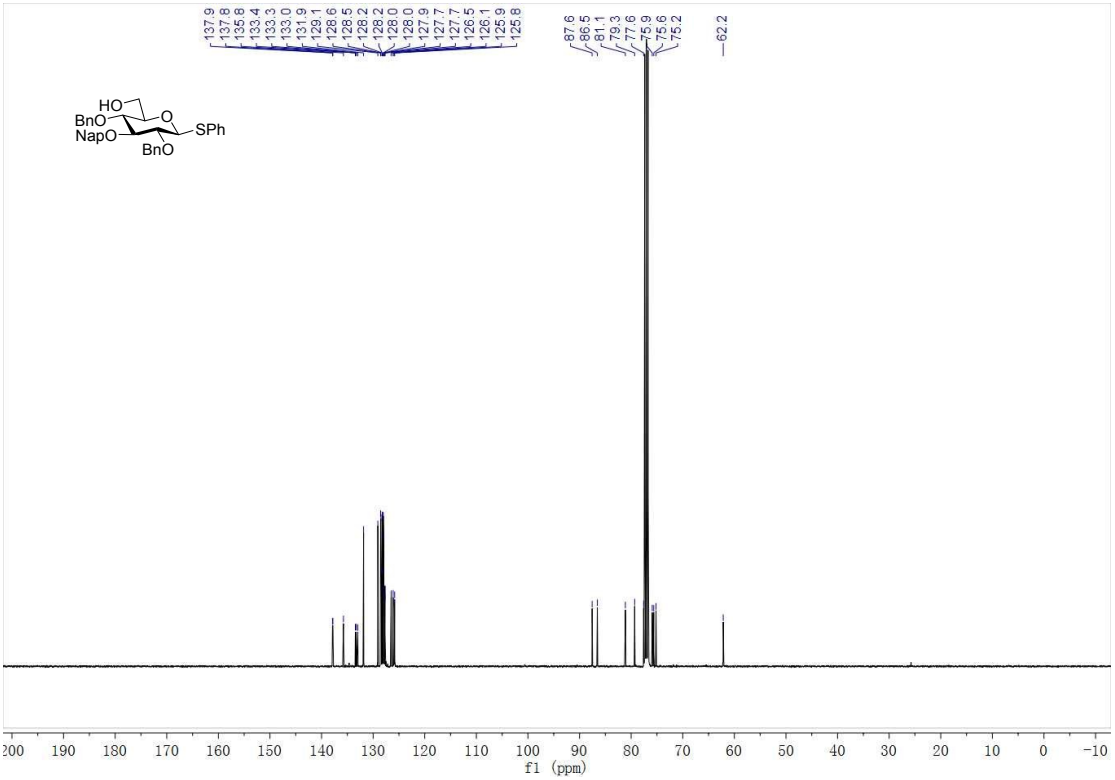
^{13}C NMR spectra of compound **S19**



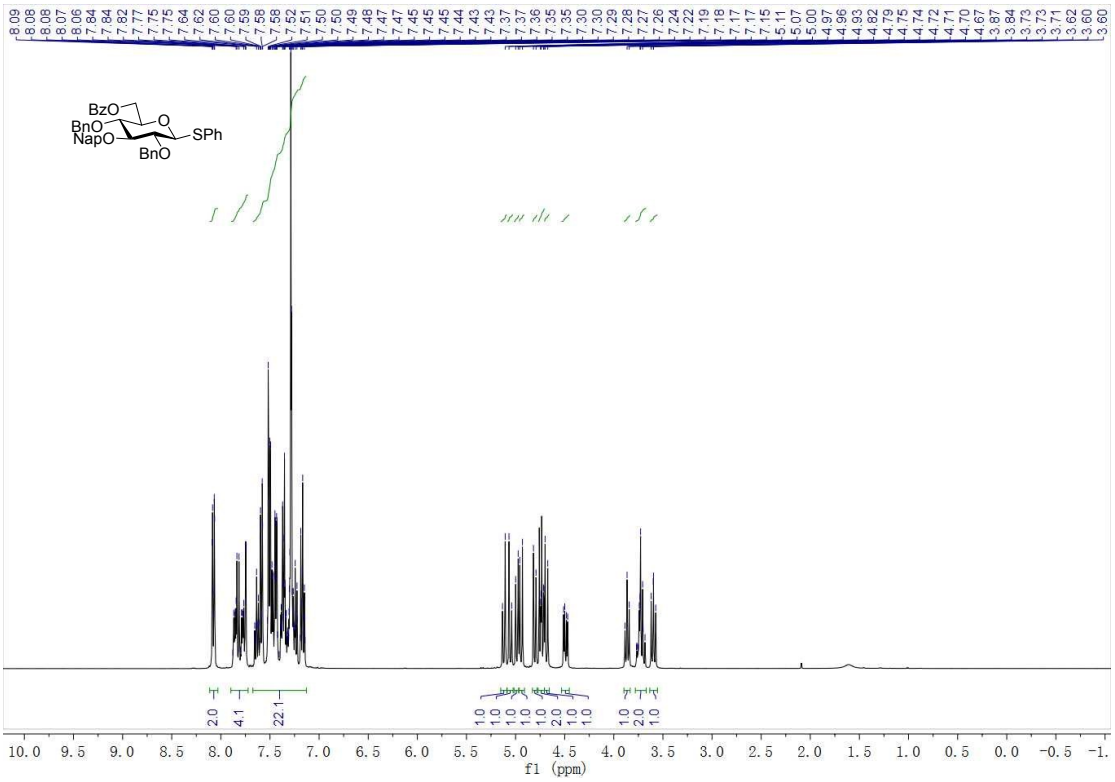
^{1}H NMR spectra of compound **S20**



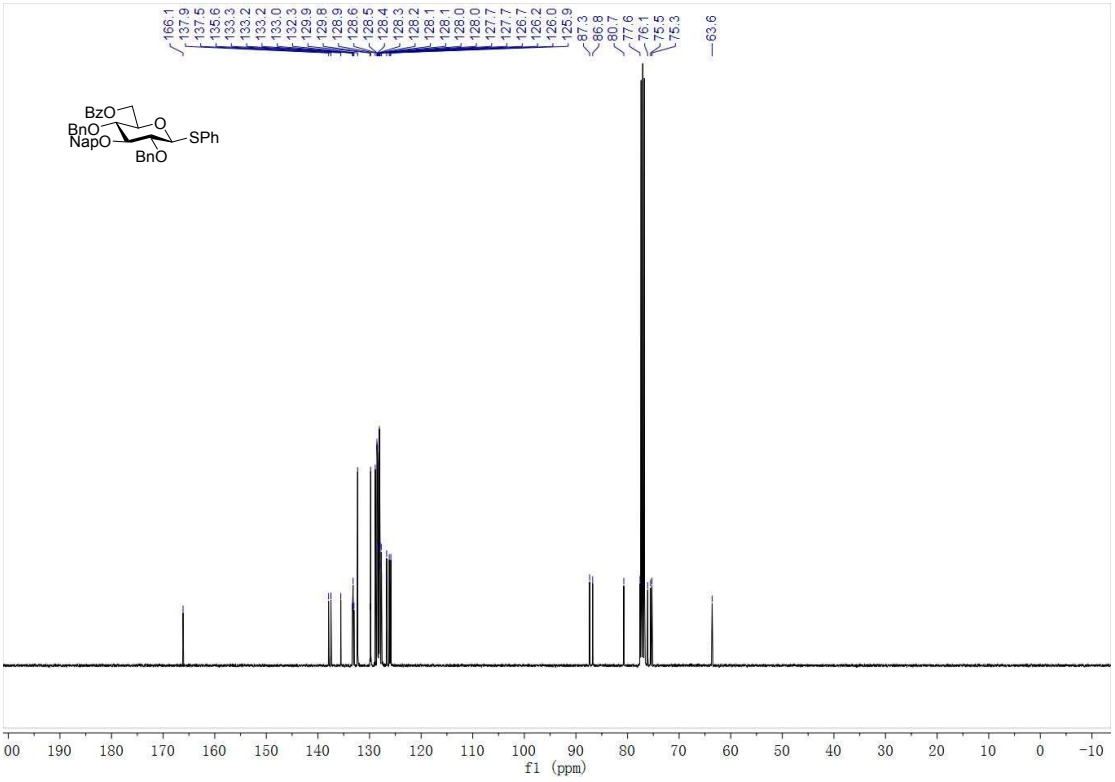
^{13}C NMR spectra of compound **S20**



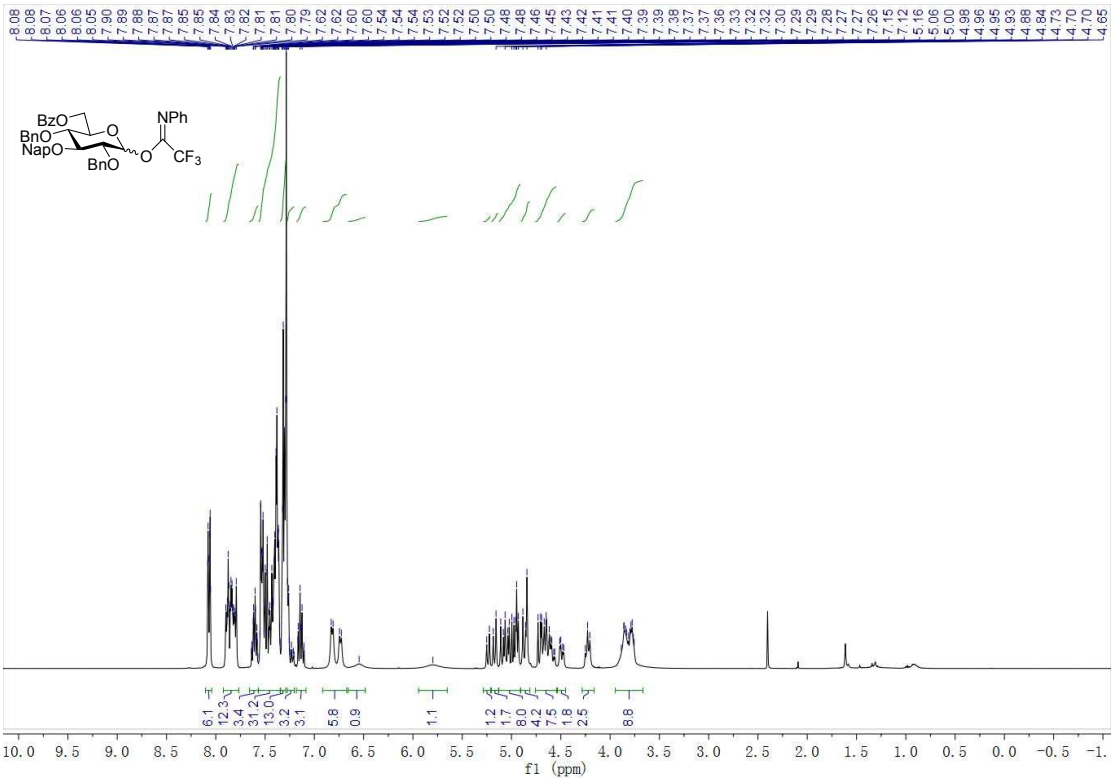
^{1}H NMR spectra of compound **S21**



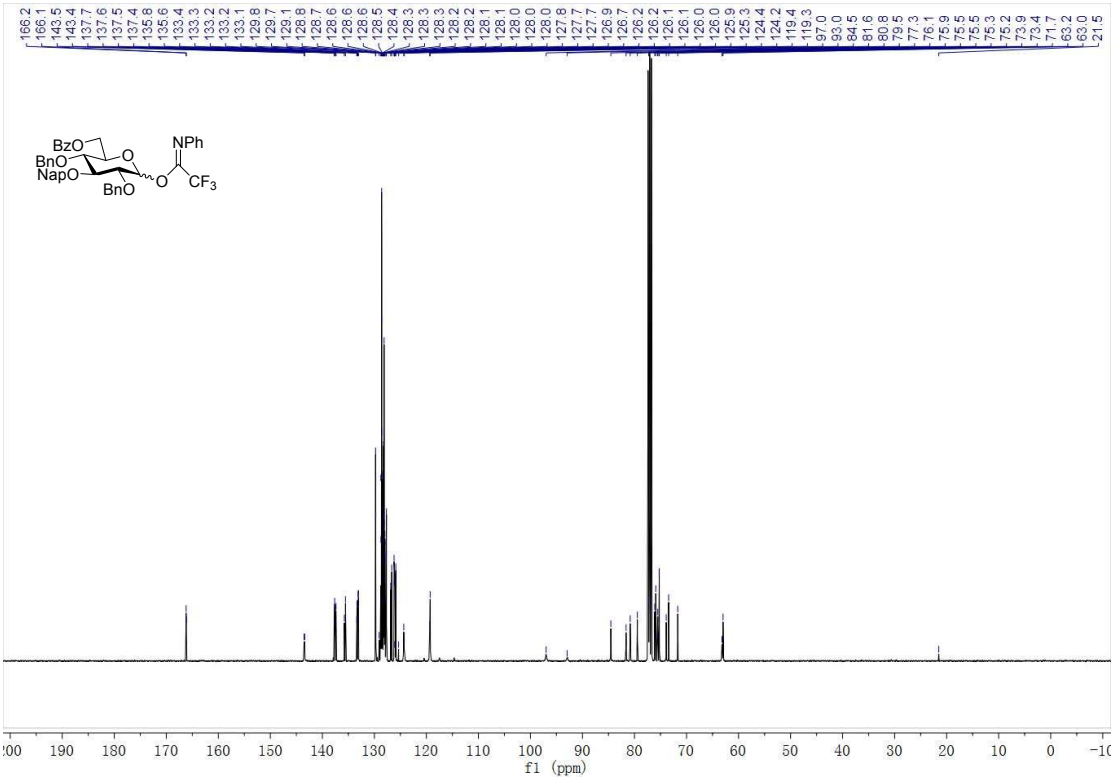
^{13}C NMR spectra of compound **S21**



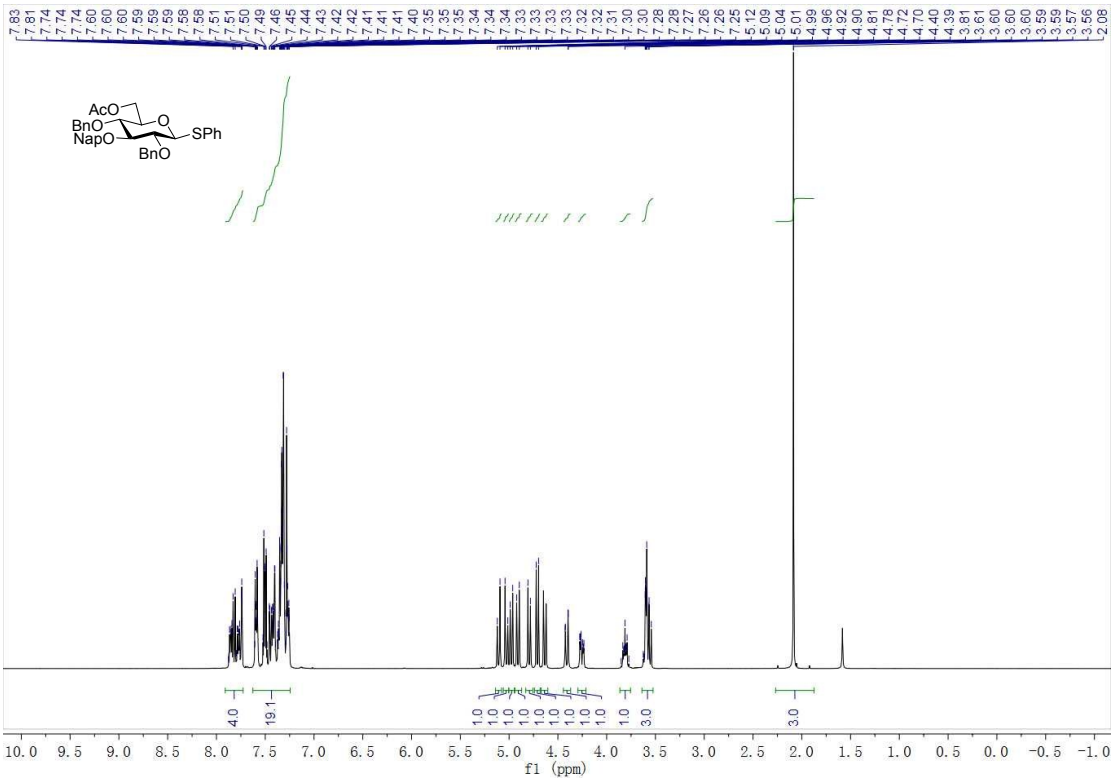
^{1}H NMR spectra of compound **3**



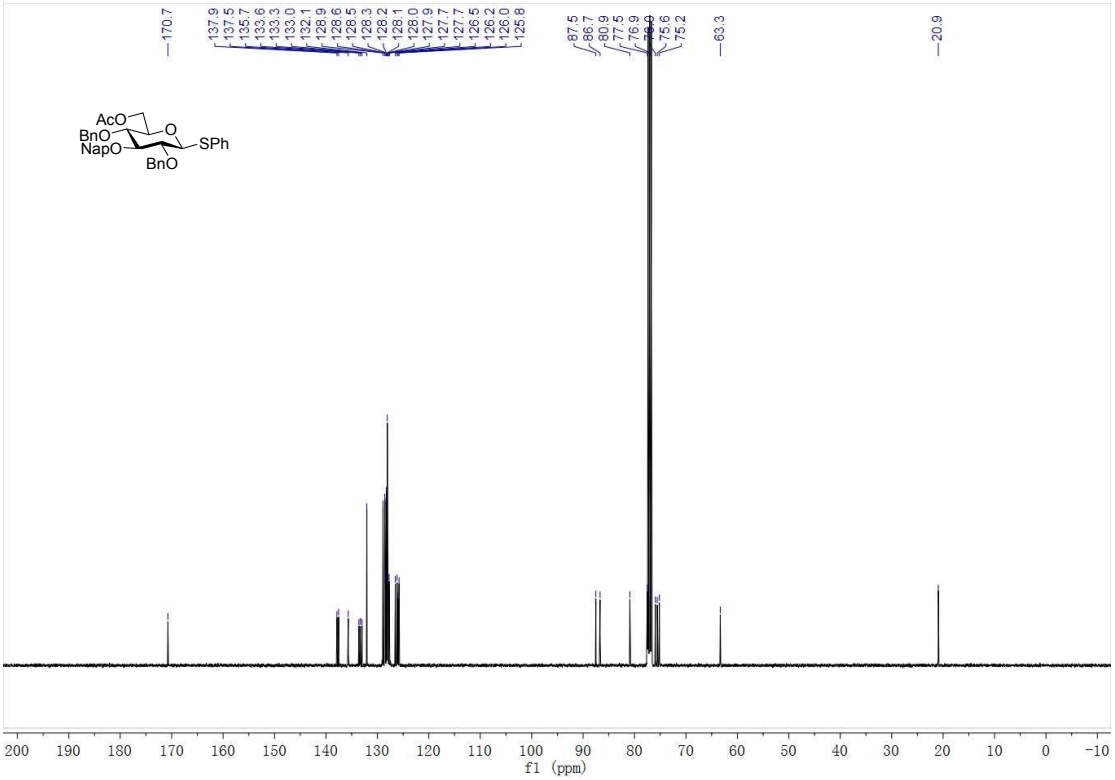
^{13}C NMR spectra of compound **3**



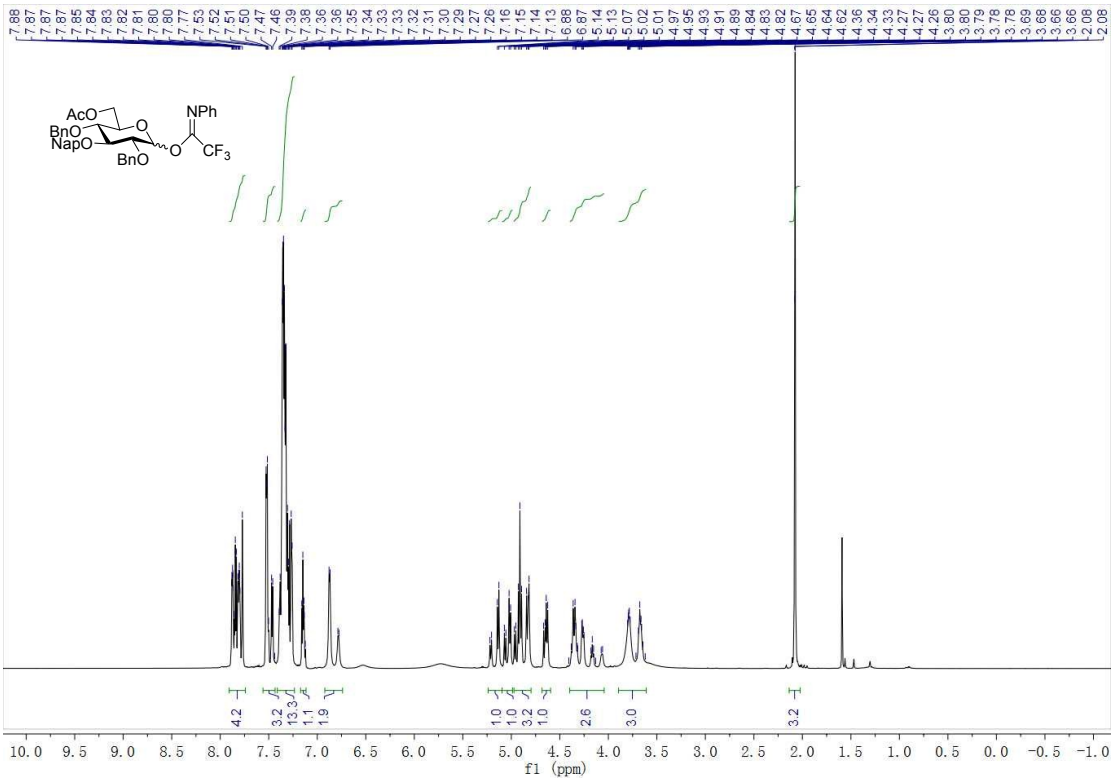
^{1}H NMR spectra of compound **S22**



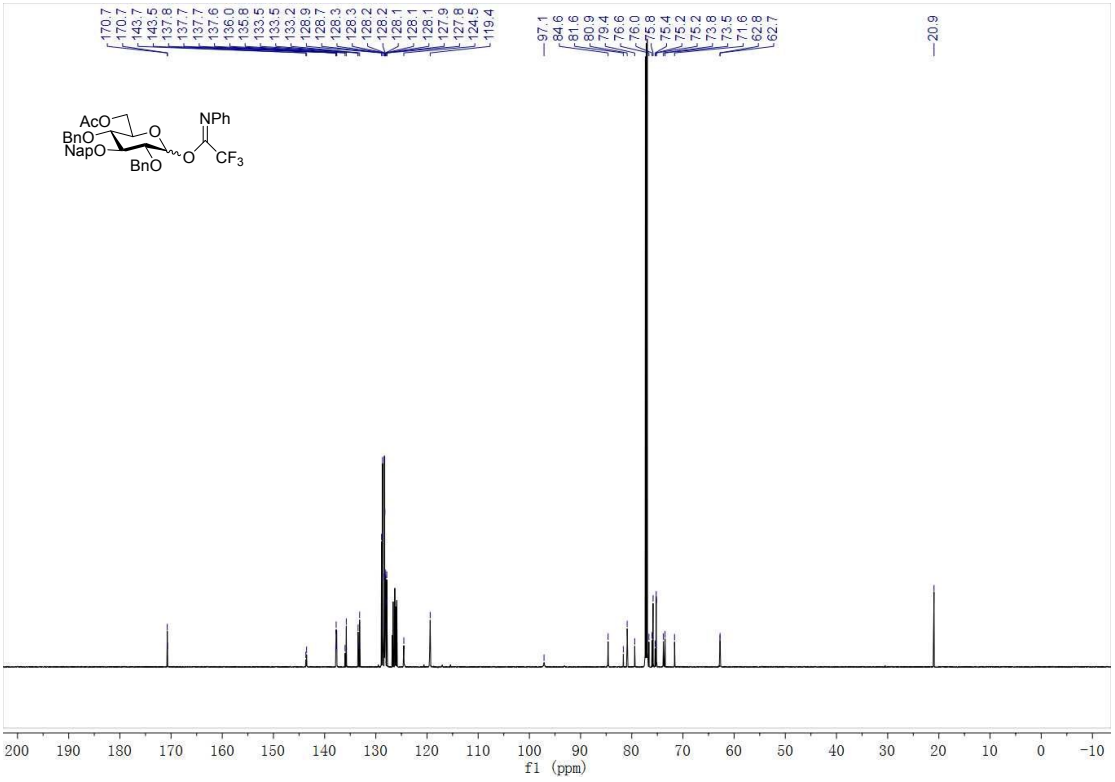
^{13}C NMR spectra of compound **S22**



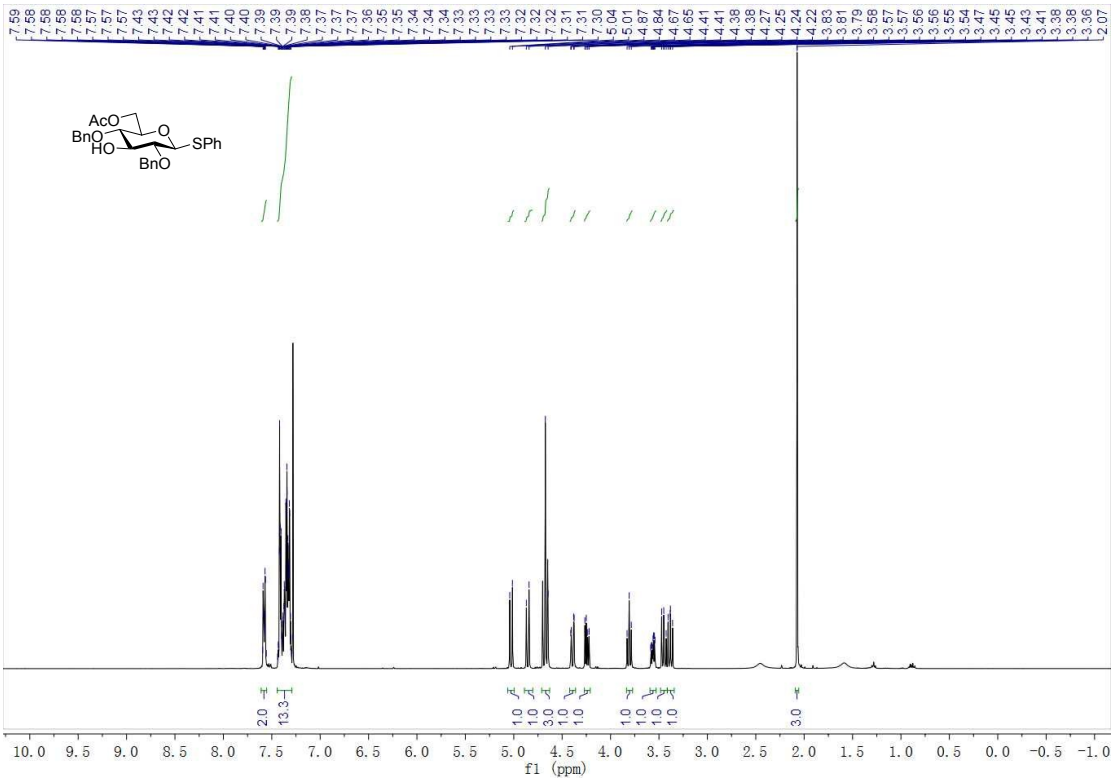
^{1}H NMR spectra of compound **4**



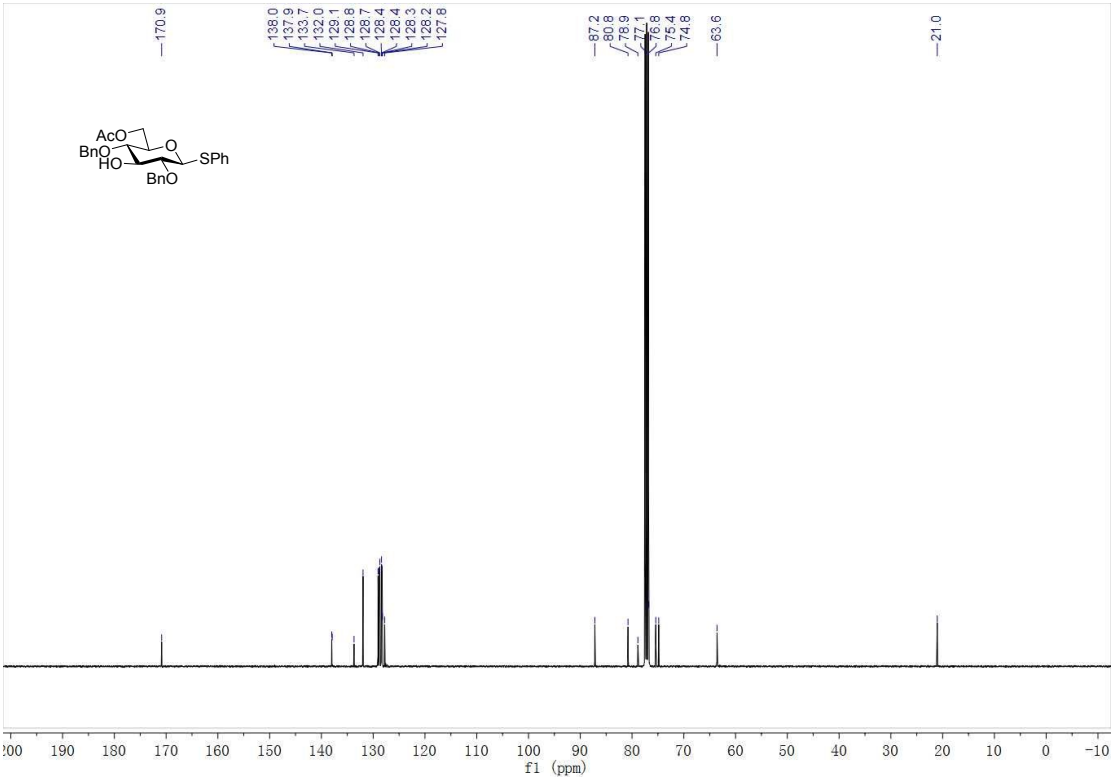
^{13}C NMR spectra of compound **4**



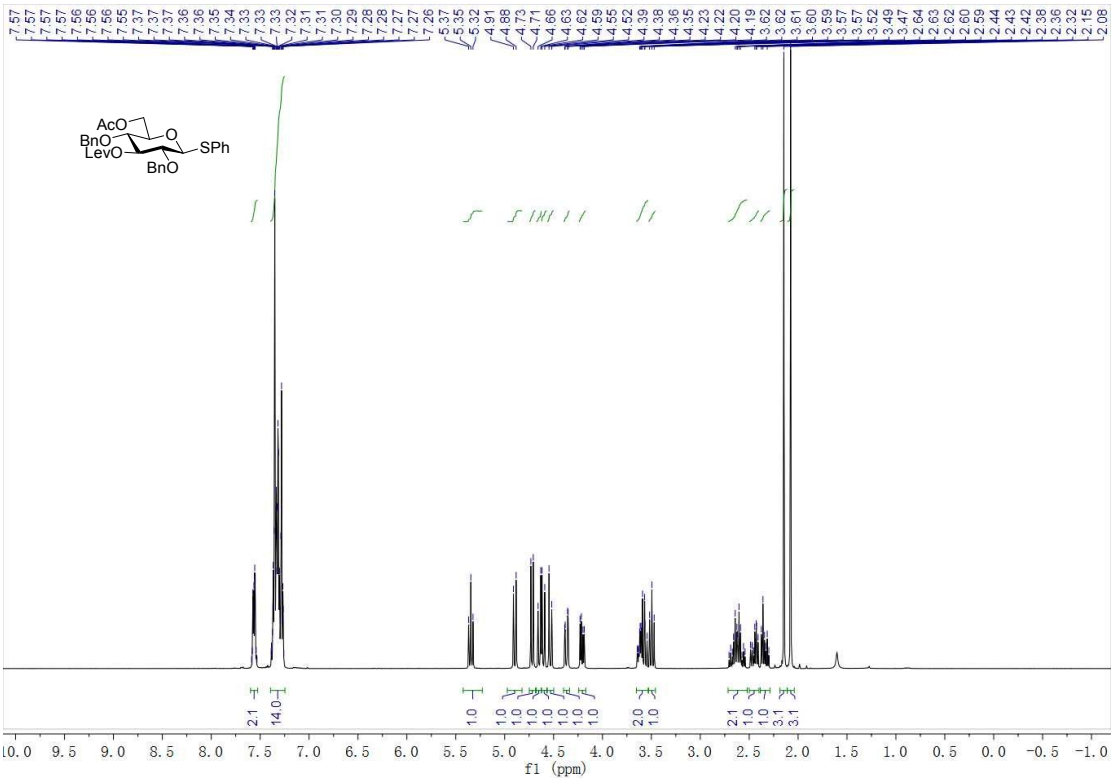
^{1}H NMR spectra of compound **S23**



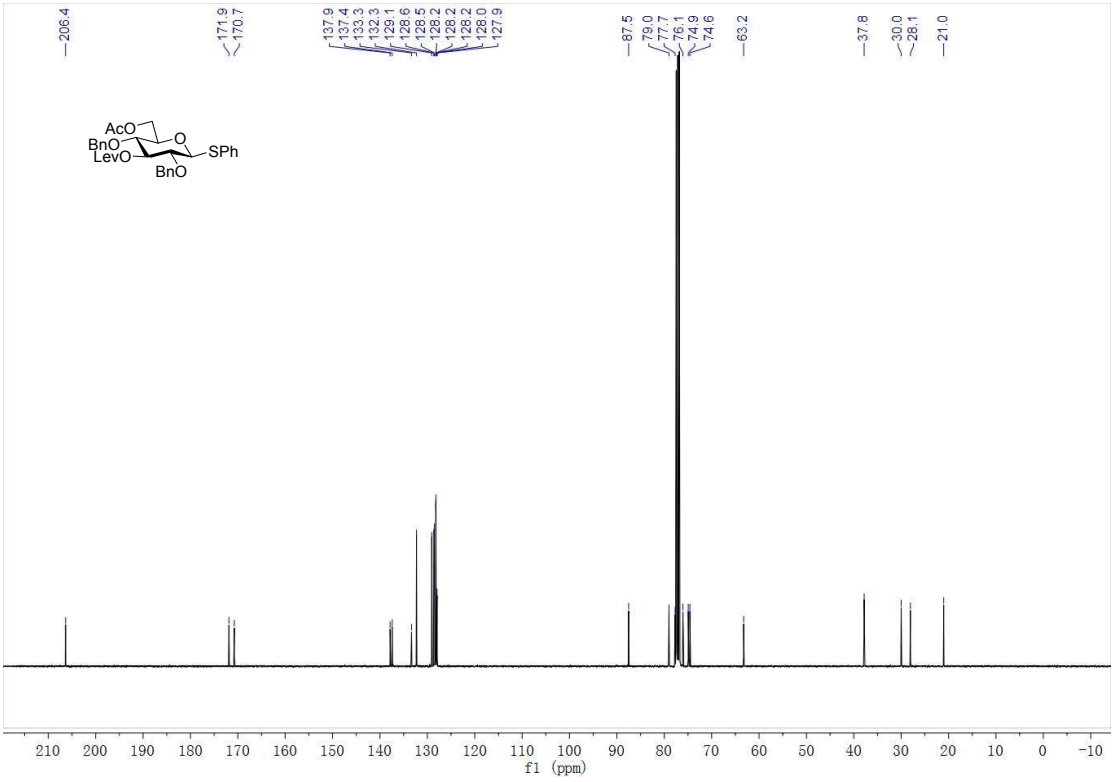
^{13}C NMR spectra of compound **S23**



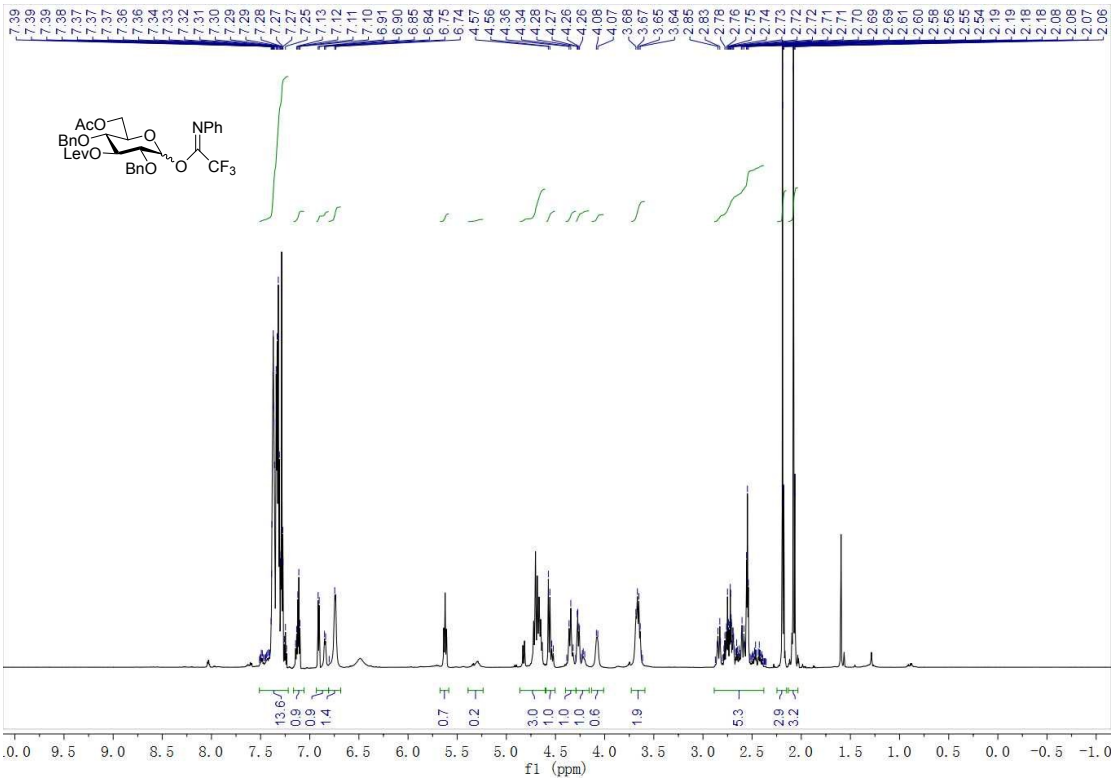
^{1}H NMR spectra of compound **S24**



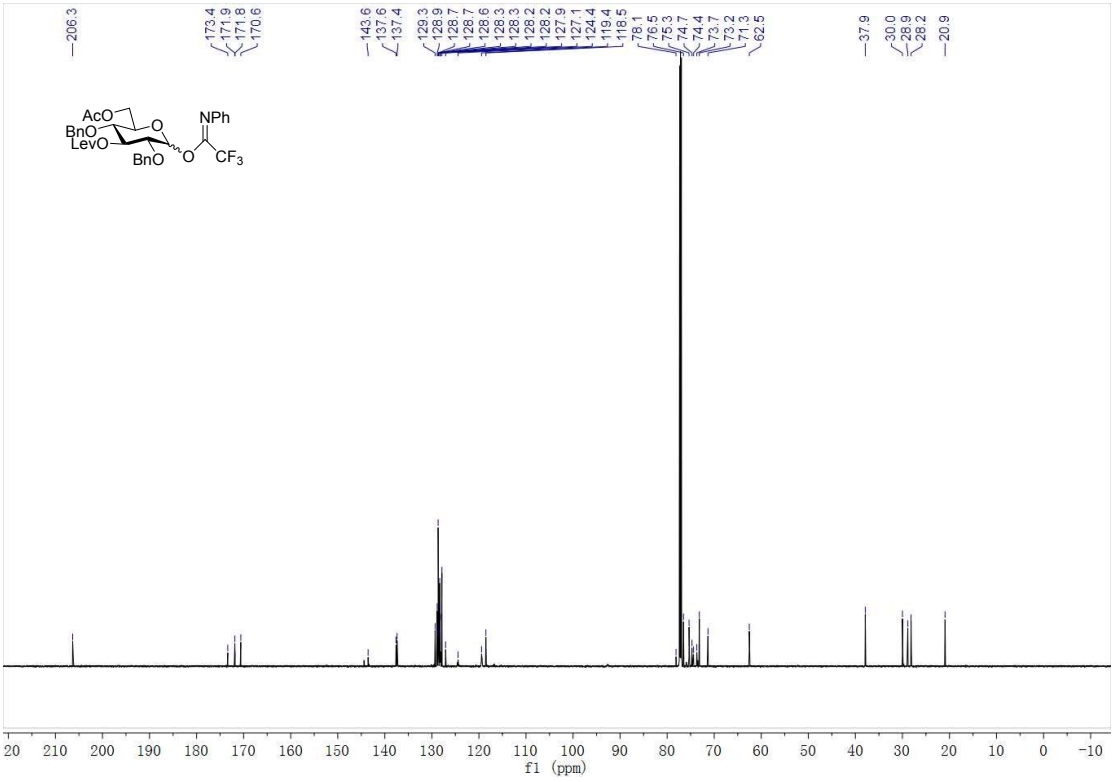
^{13}C NMR spectra of compound **S24**



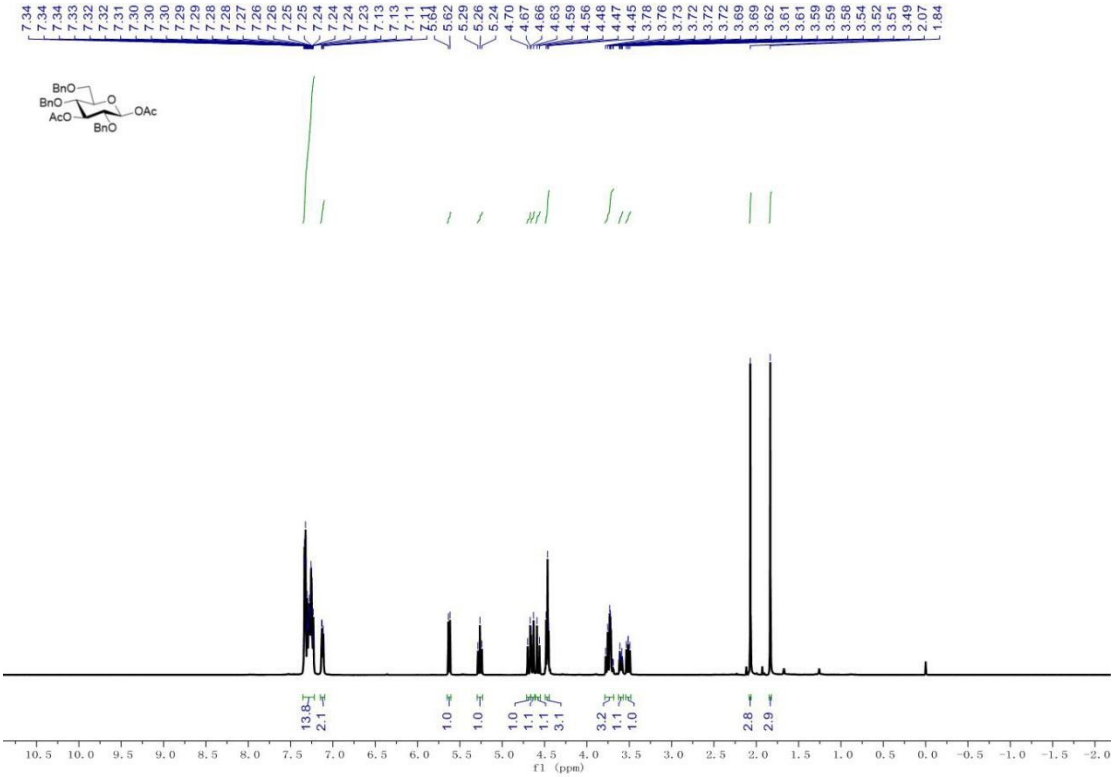
^{1}H NMR spectra of compound **5**



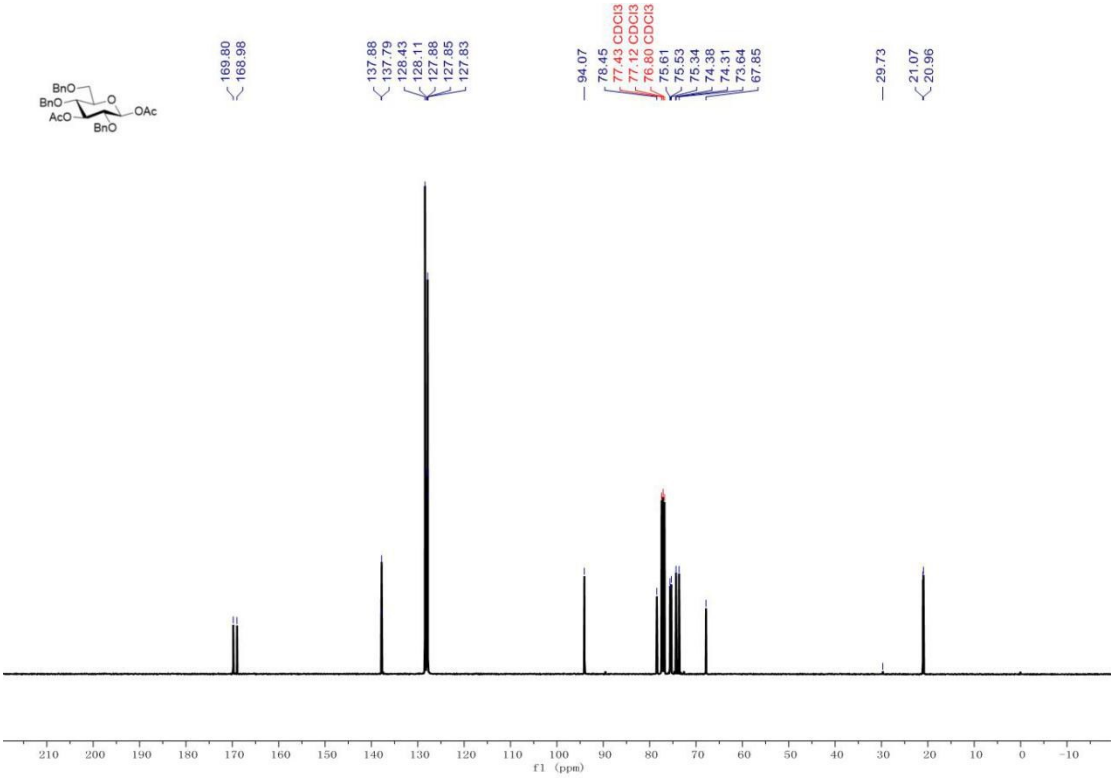
^{13}C NMR spectra of compound **5**



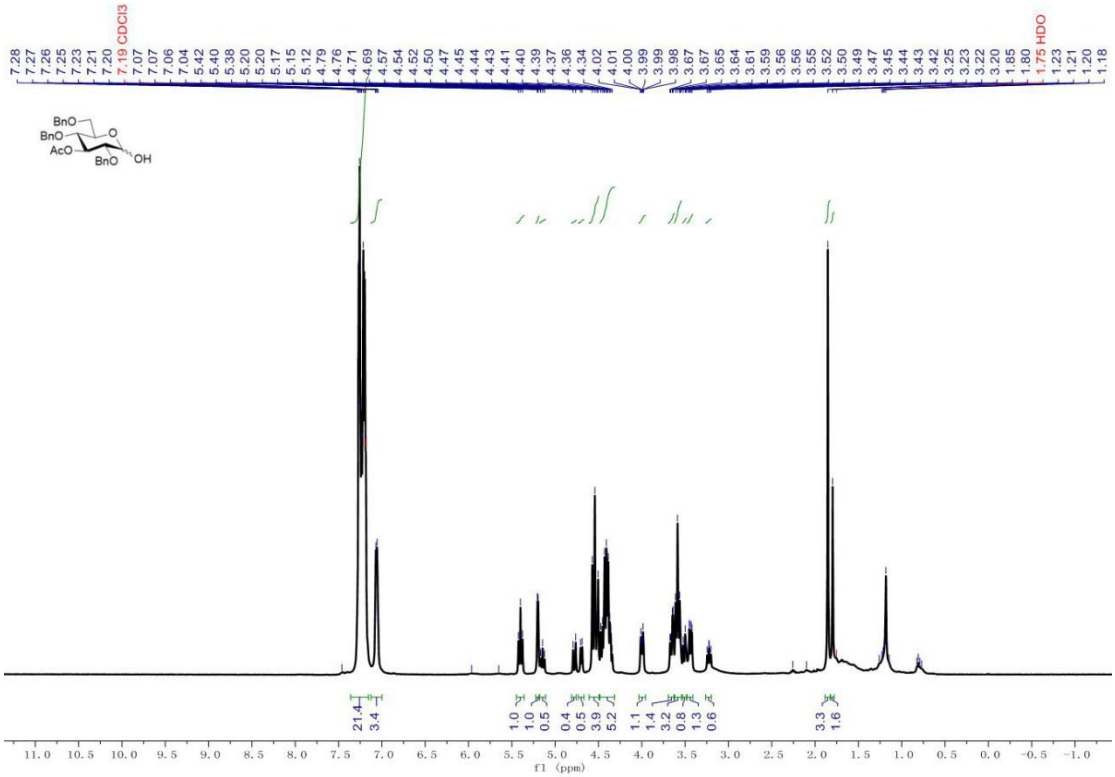
^{1}H NMR spectra of compound **S25**



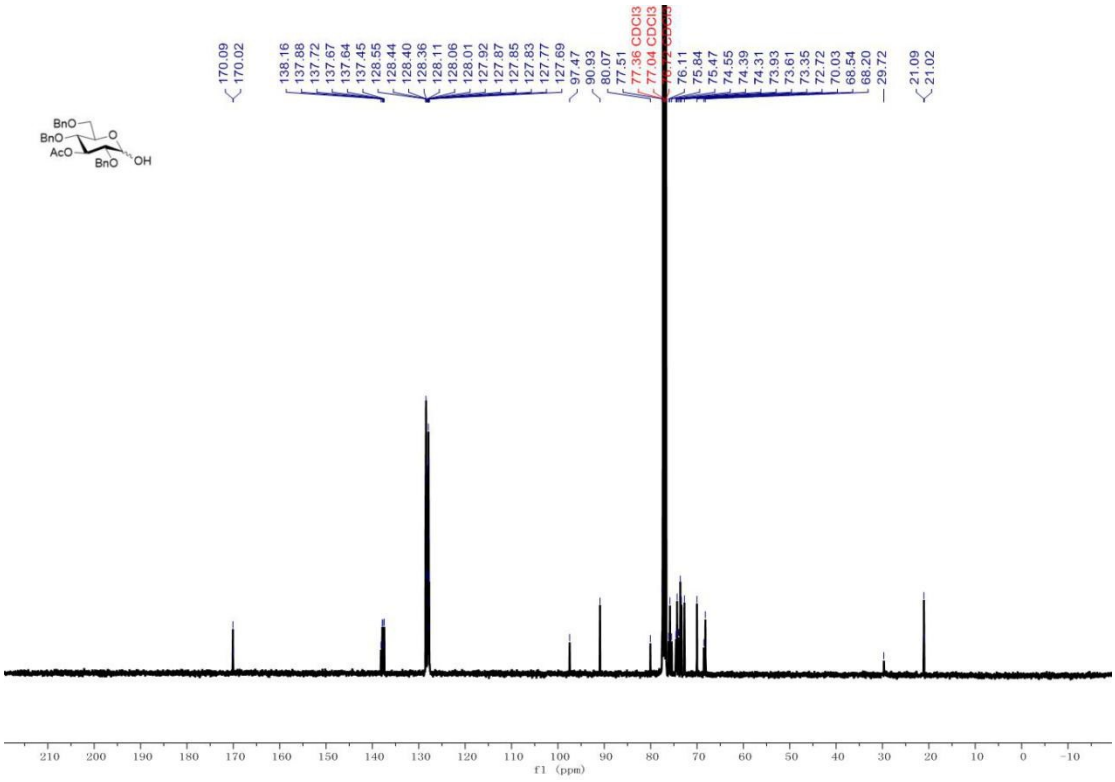
^{13}C NMR spectra of compound **S25**



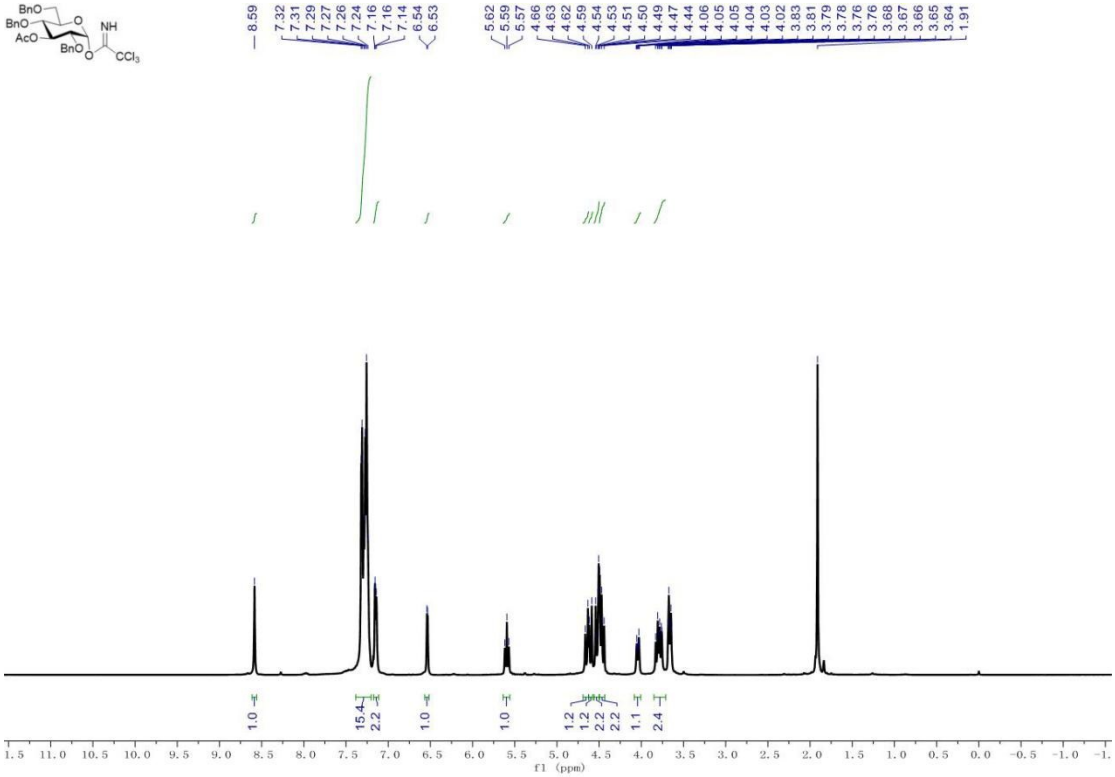
^{1}H NMR spectra of compound **S26**



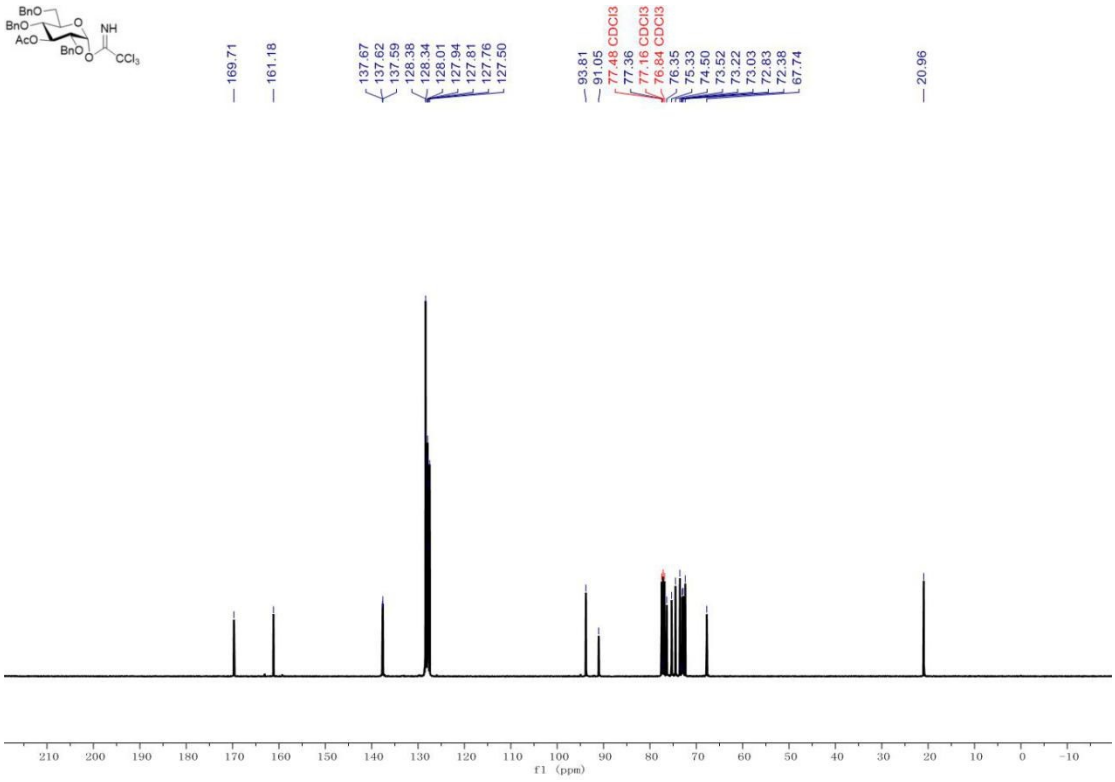
^{13}C NMR spectra of compound **S26**



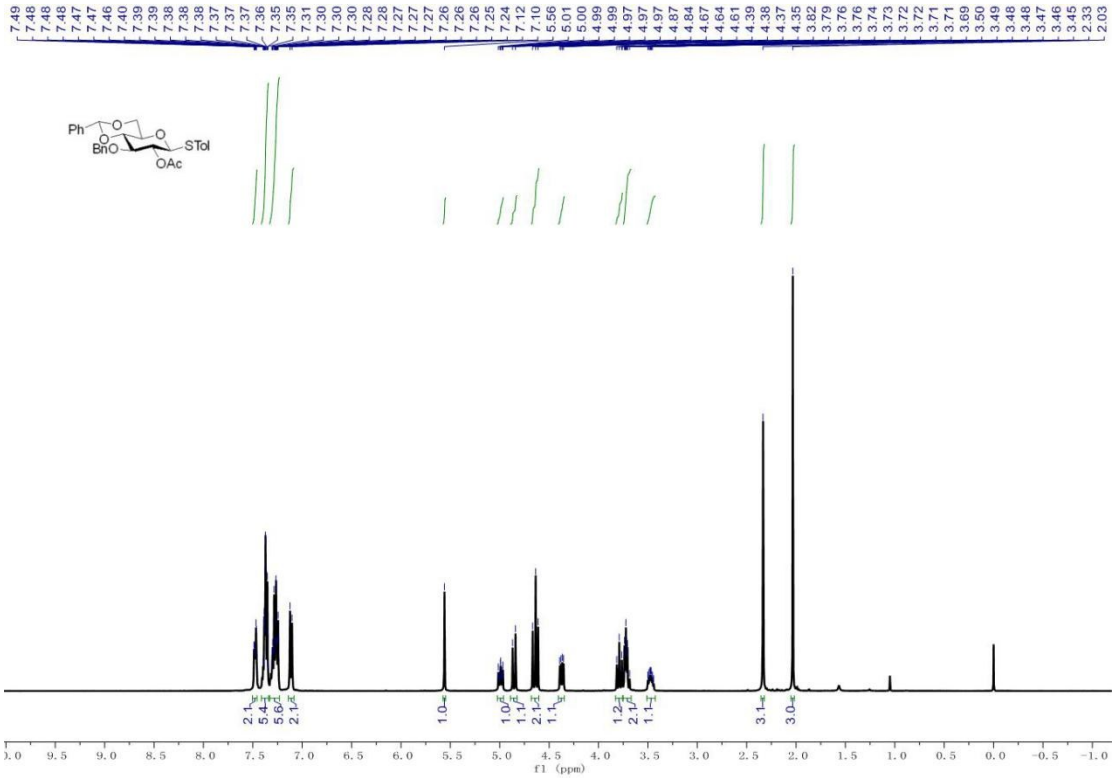
^{1}H NMR spectra of compound **2**



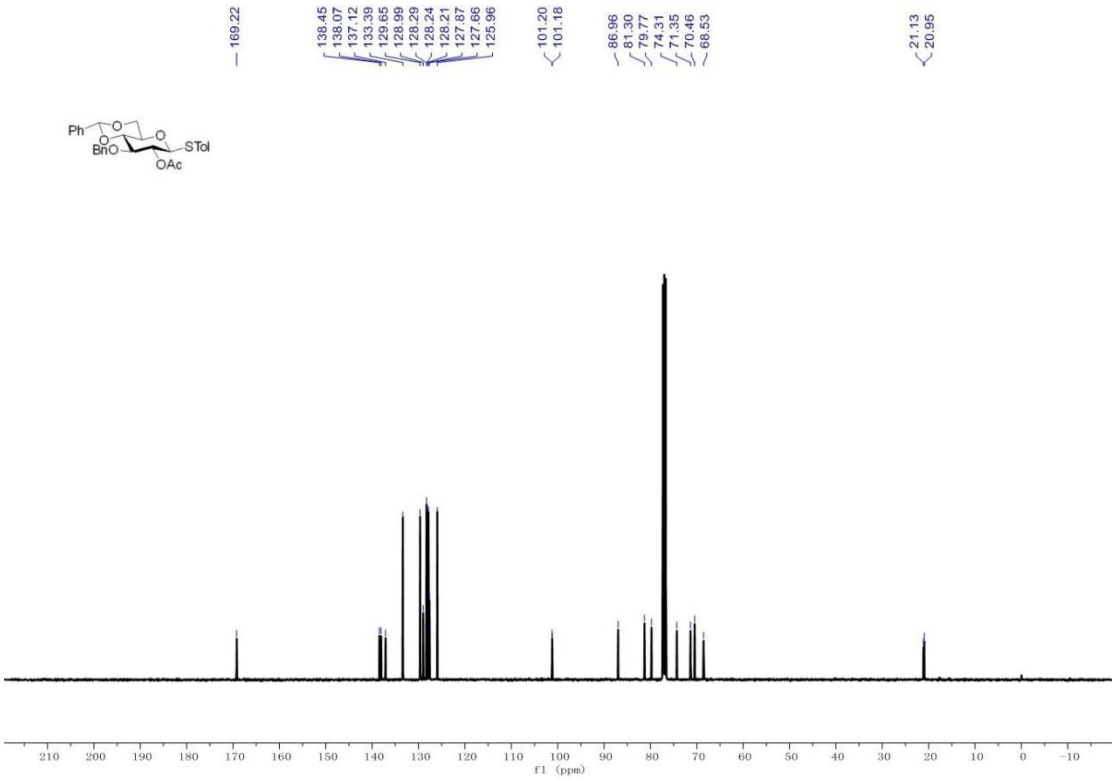
^{13}C NMR spectra of compound **2**



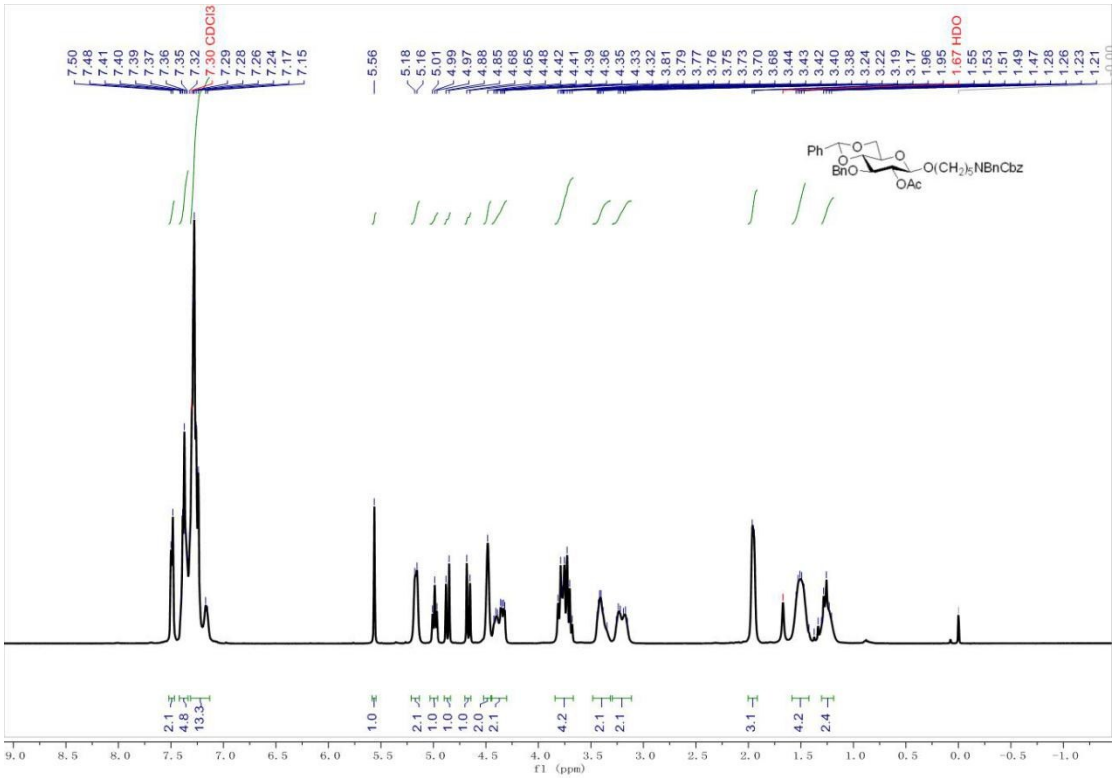
^{1}H NMR spectra of compound **S27**



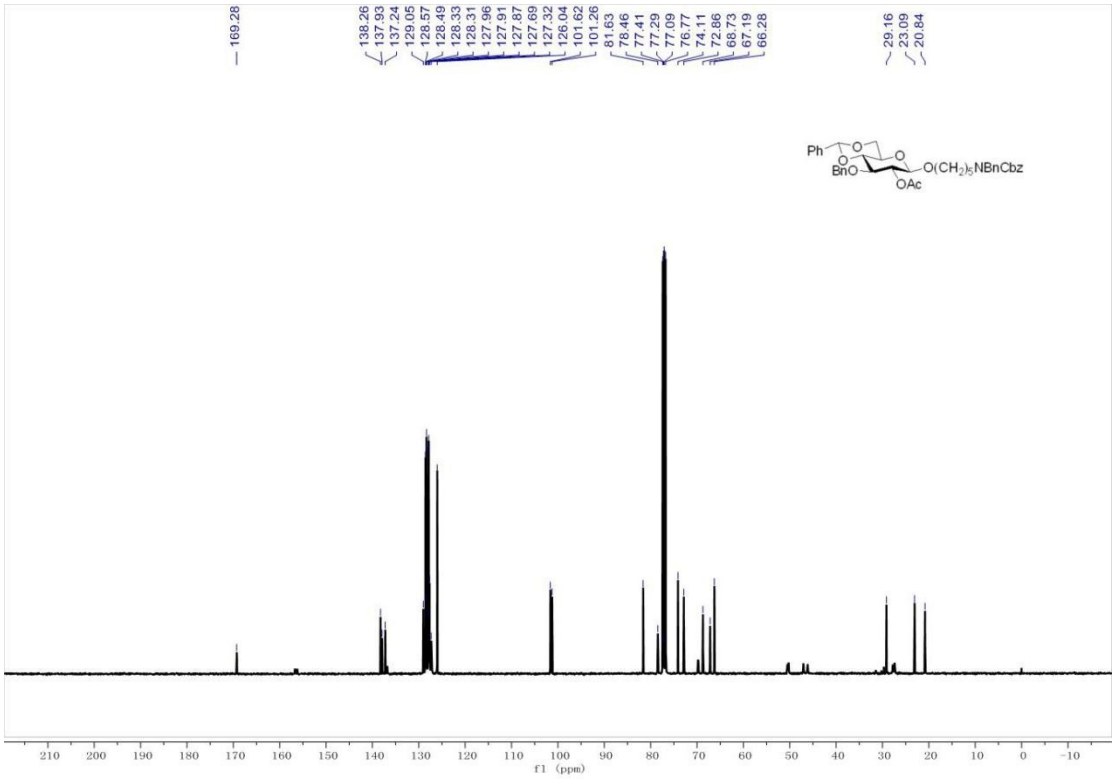
^{13}C NMR spectra of compound **S27**



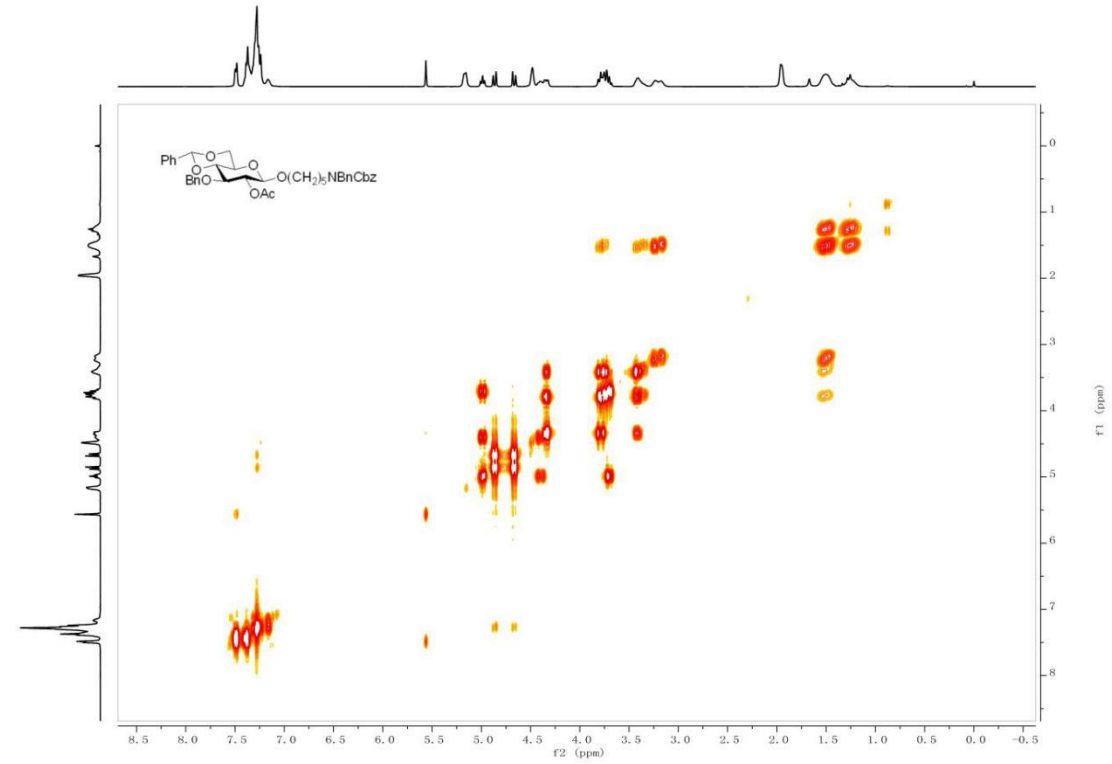
^{1}H NMR spectra of compound **S28**



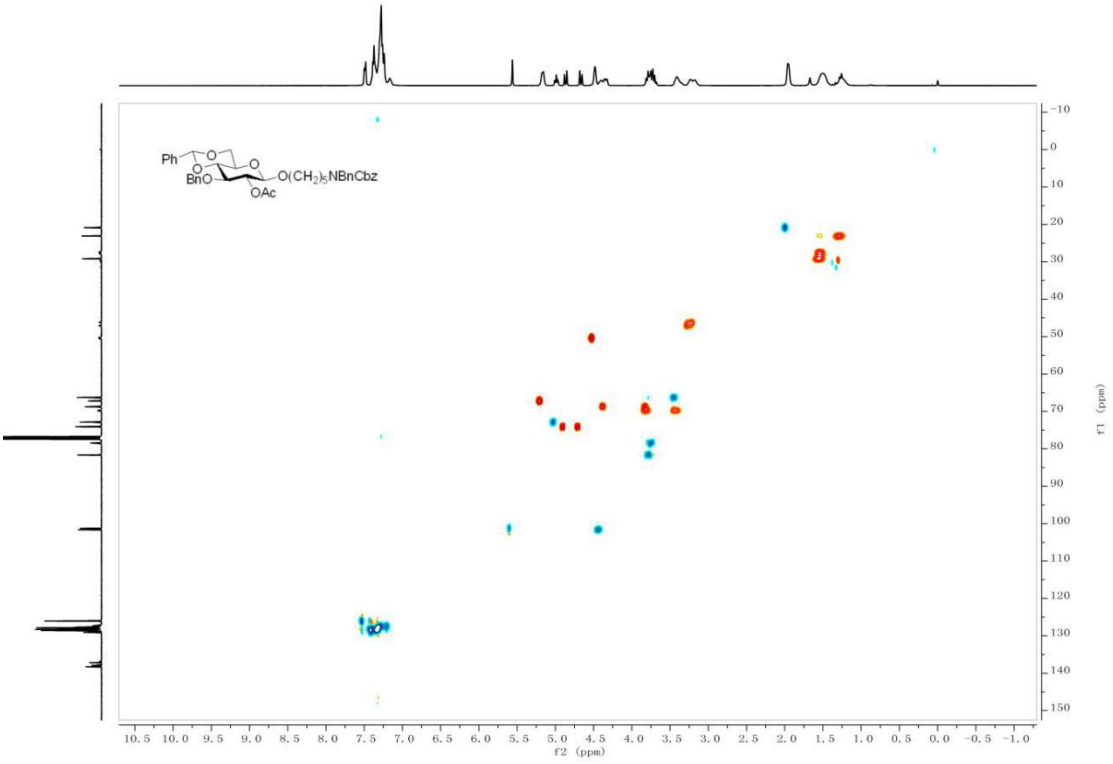
^{13}C NMR spectra of compound **S28**



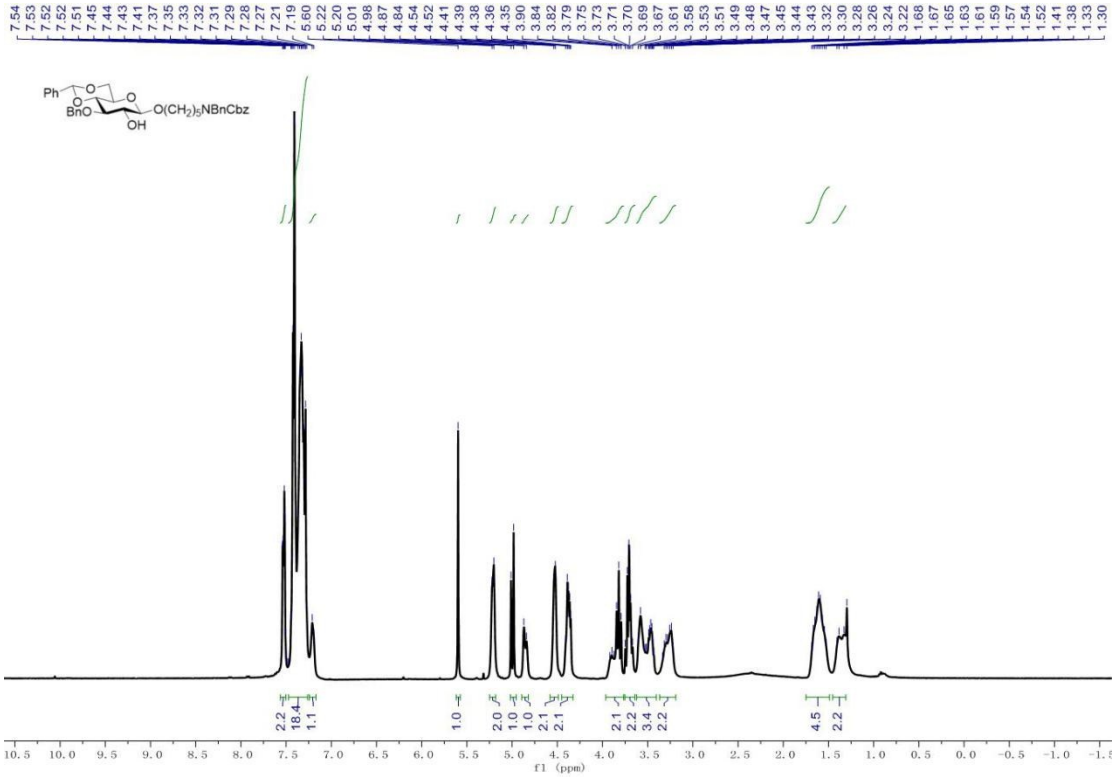
^{1}H-^{1}H COSY NMR spectra of compound **S28**



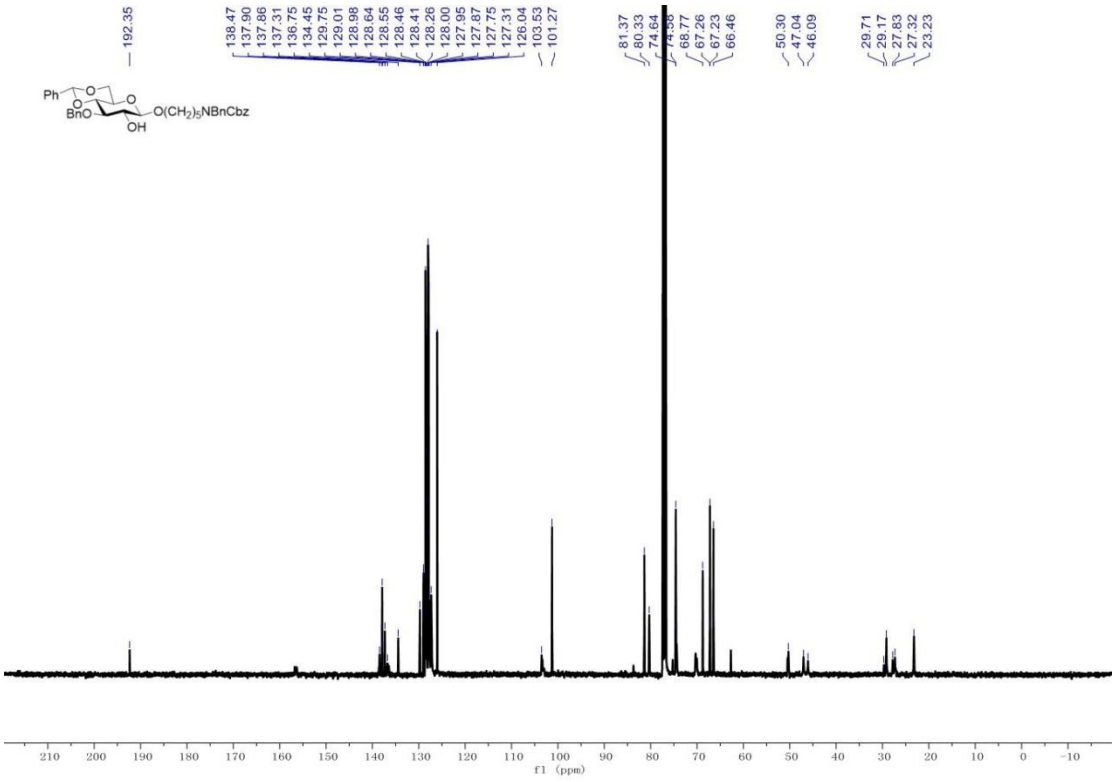
^{1}H-^{13}C HSQC NMR spectra of compound **S28**



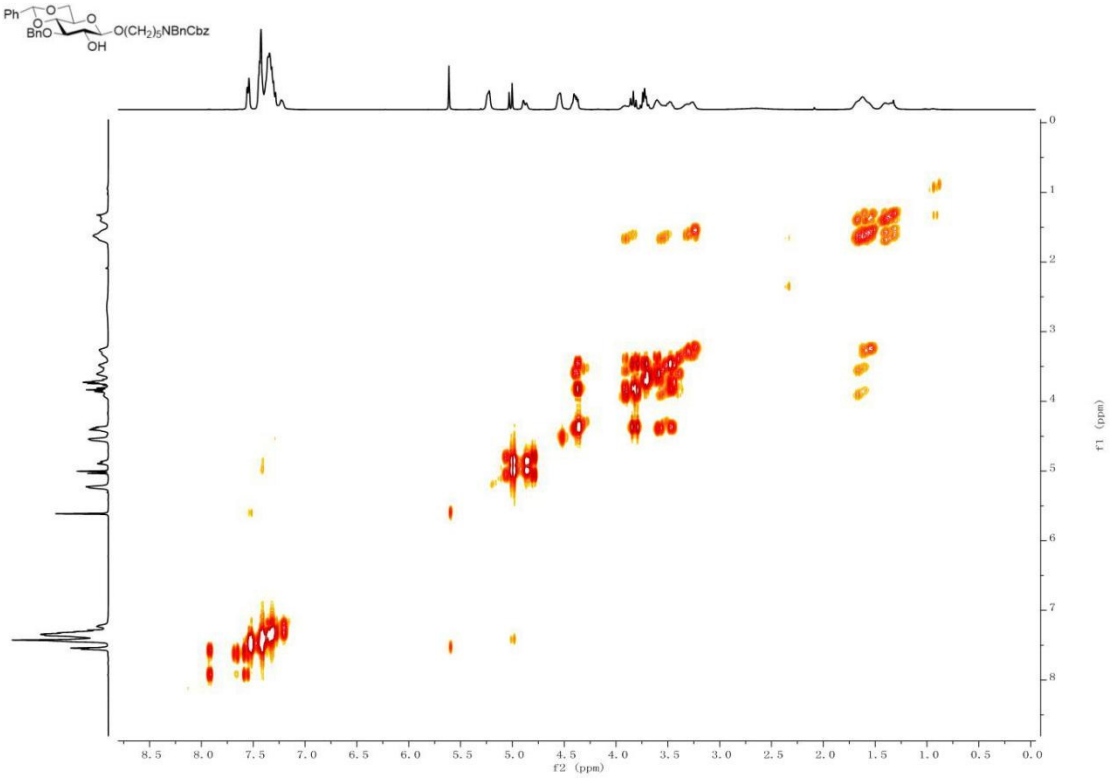
^{1}H NMR spectra of compound **6**



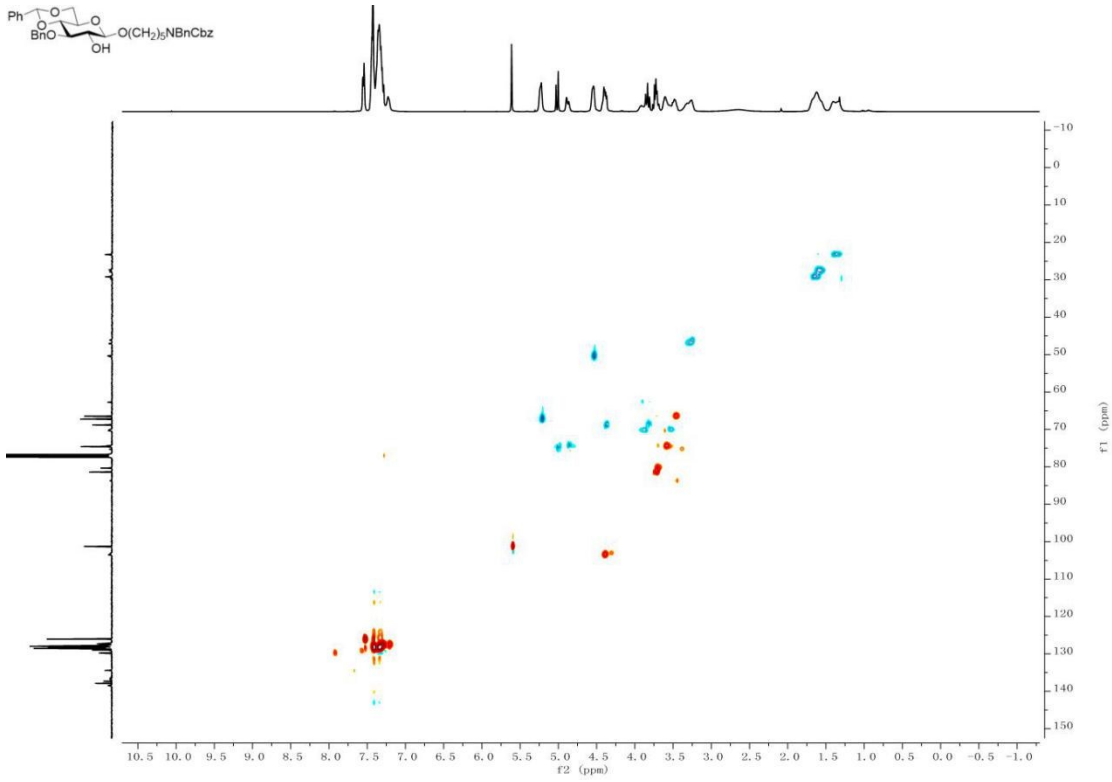
^{13}C NMR spectra of compound **6**



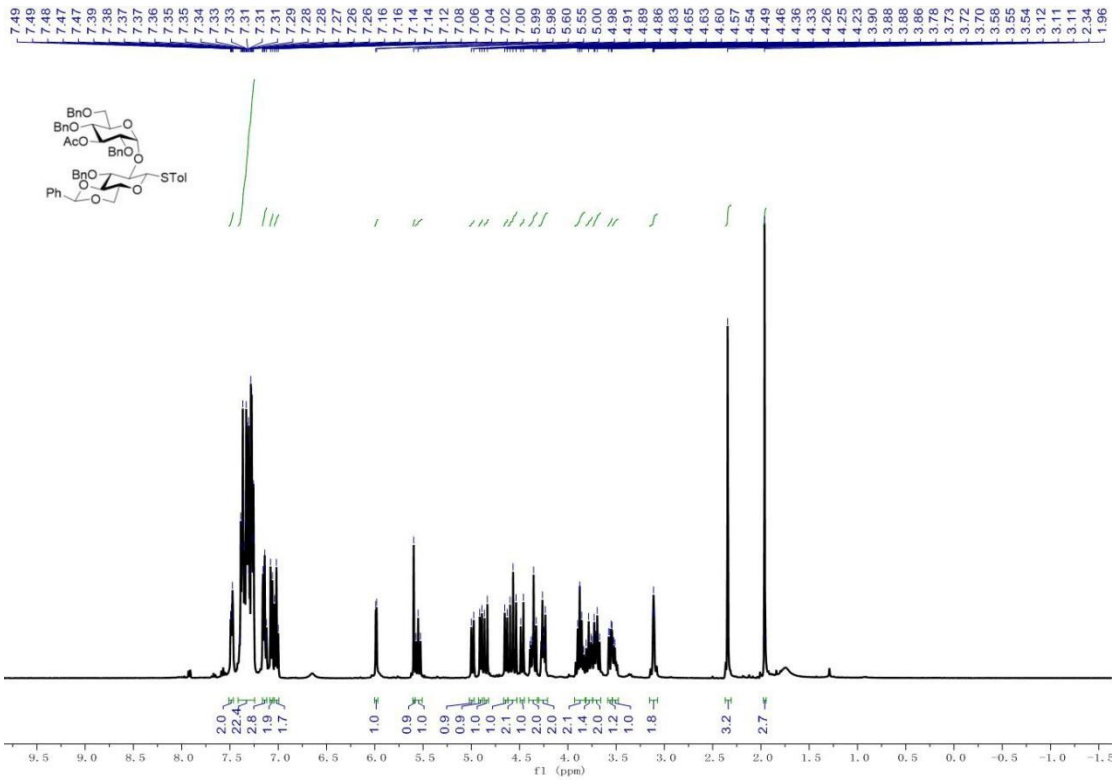
^{1}H-^{1}H COSY NMR spectra of compound **6**



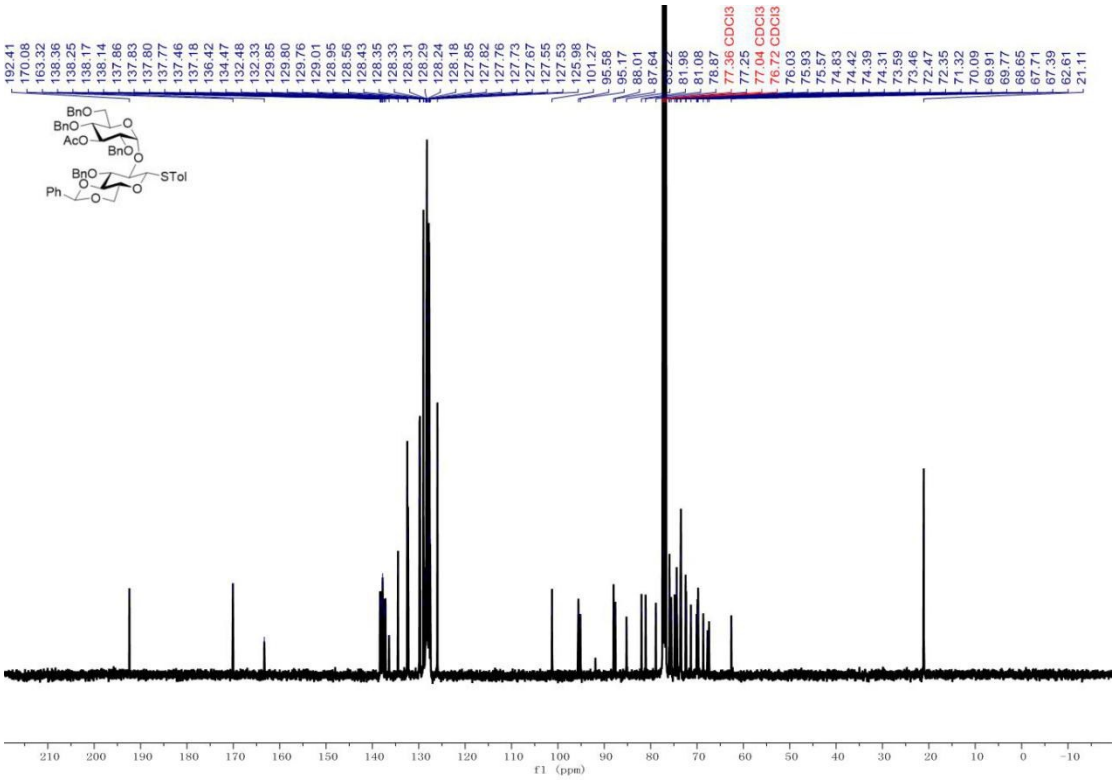
^{1}H-^{13}C HSQC NMR spectra of compound **6**



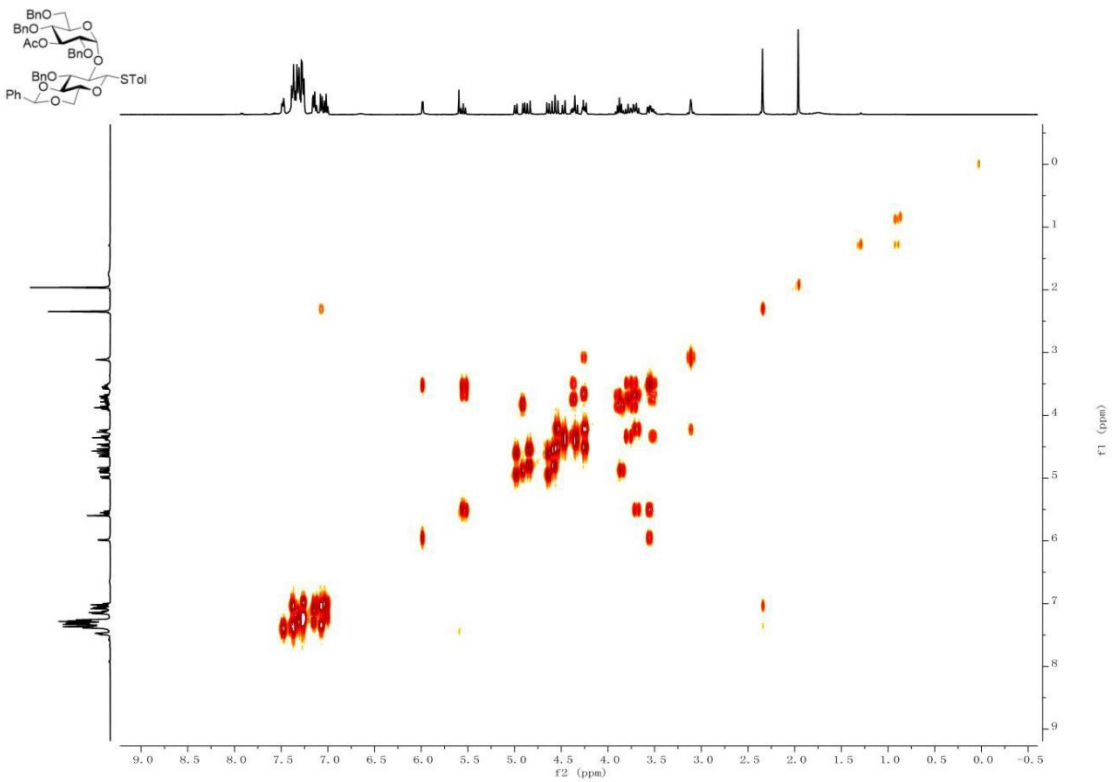
^{1}H NMR spectra of compound **9**



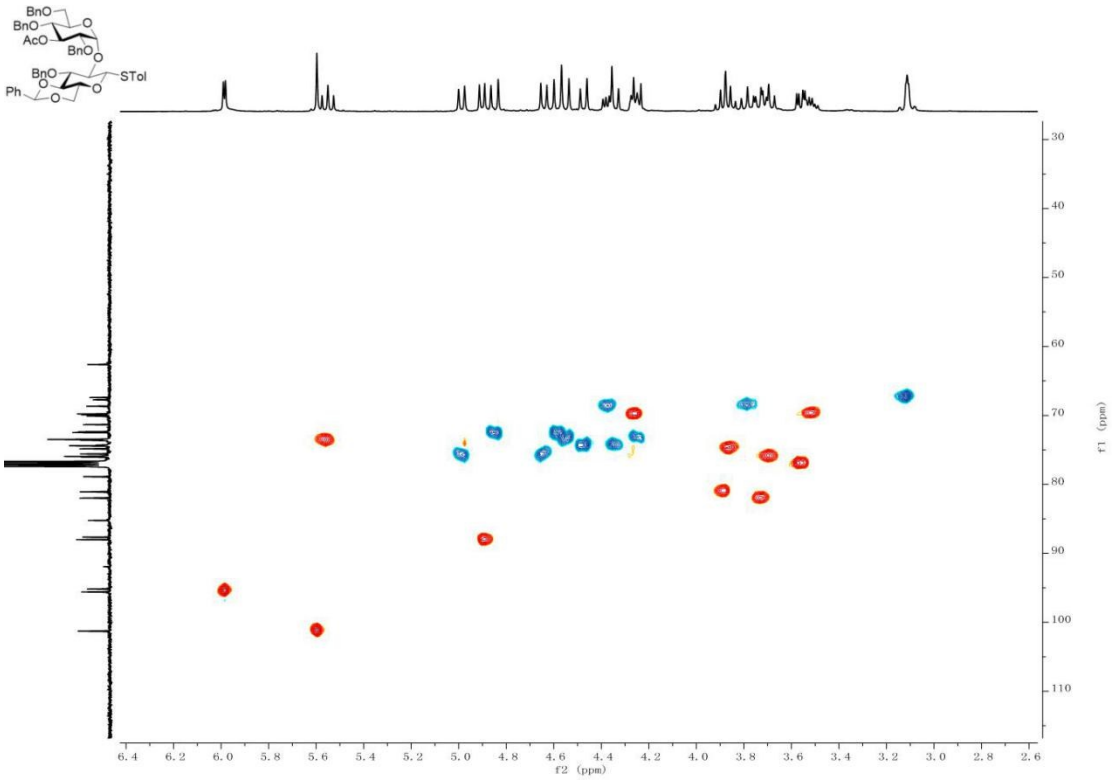
^{13}C NMR spectra of compound **9**



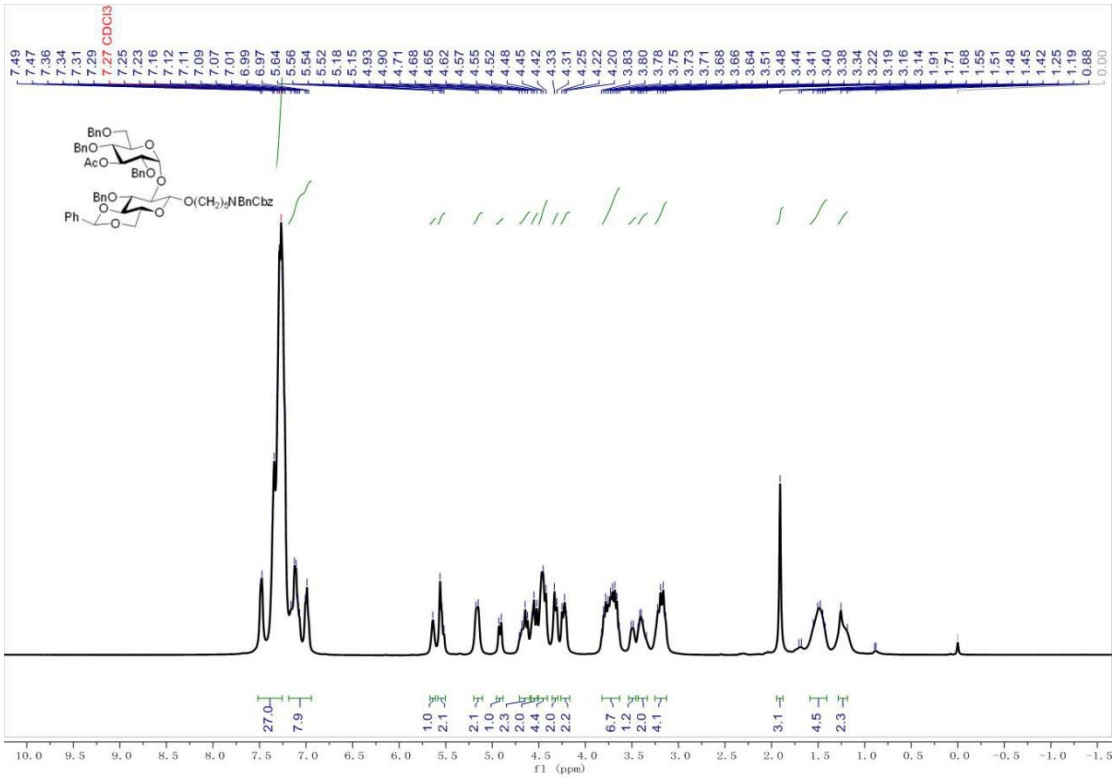
^{1}H-^{1}H COSY NMR spectra of compound **9**



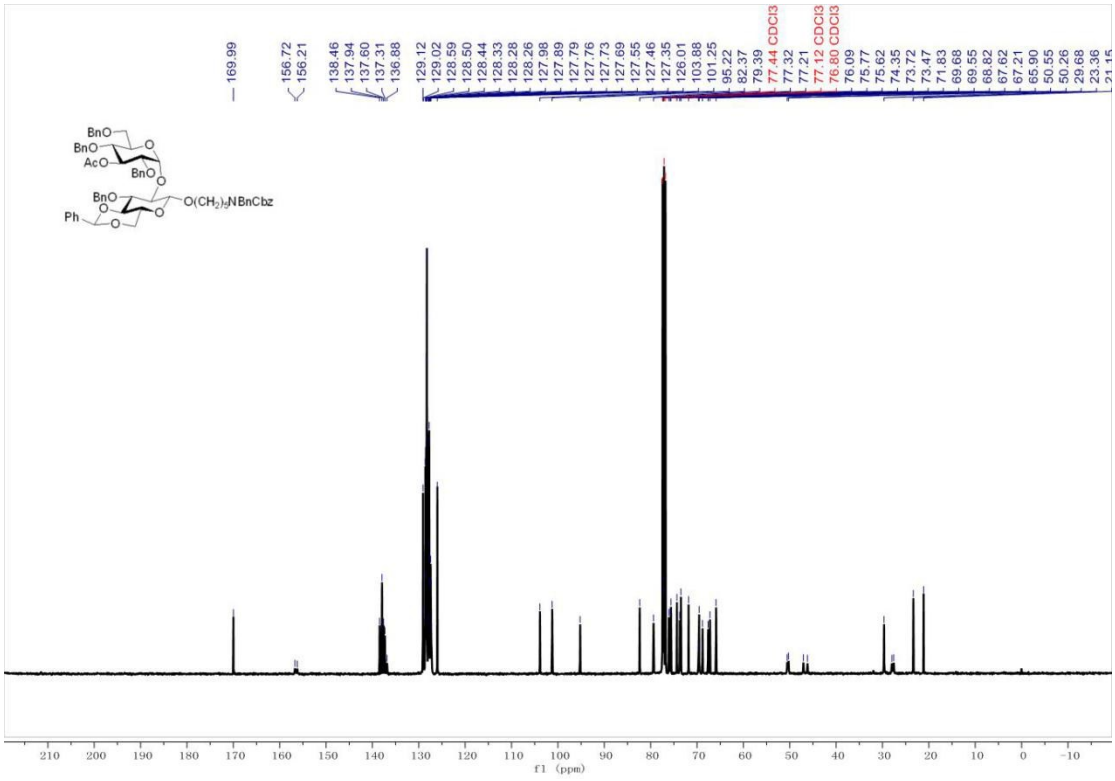
^{1}H-^{13}C HSQC NMR spectra of compound **9**



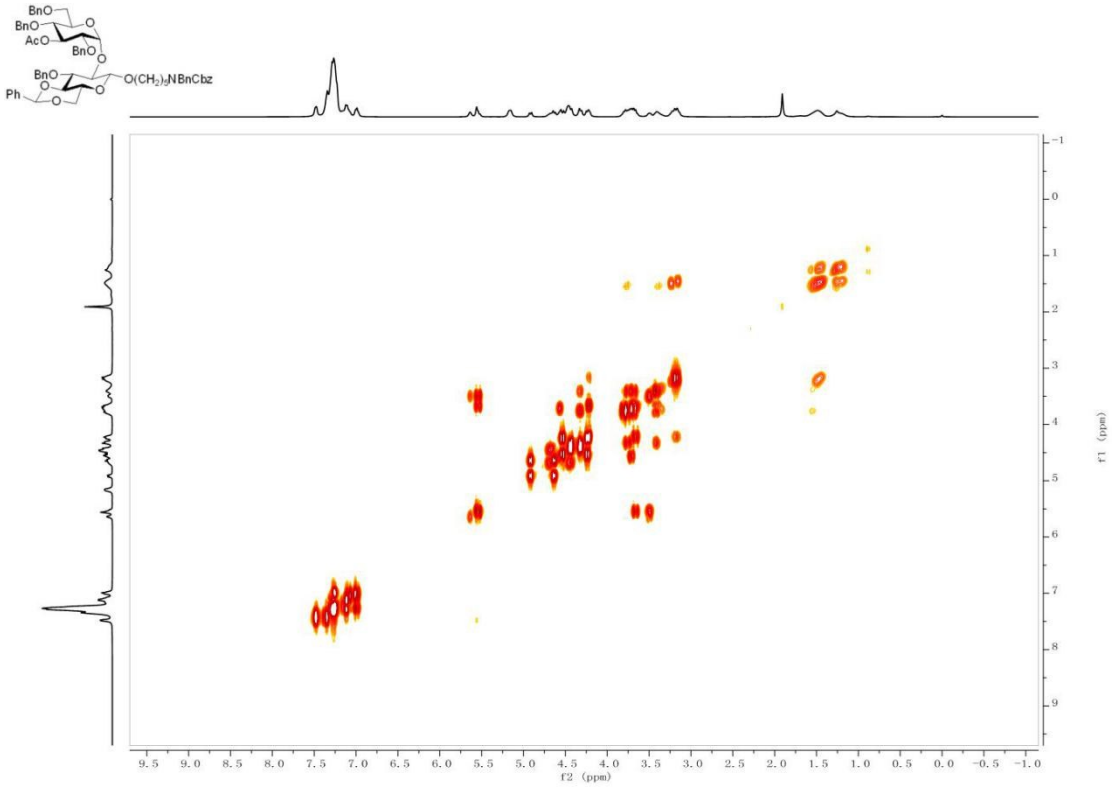
^{1}H NMR spectra of compound **10**



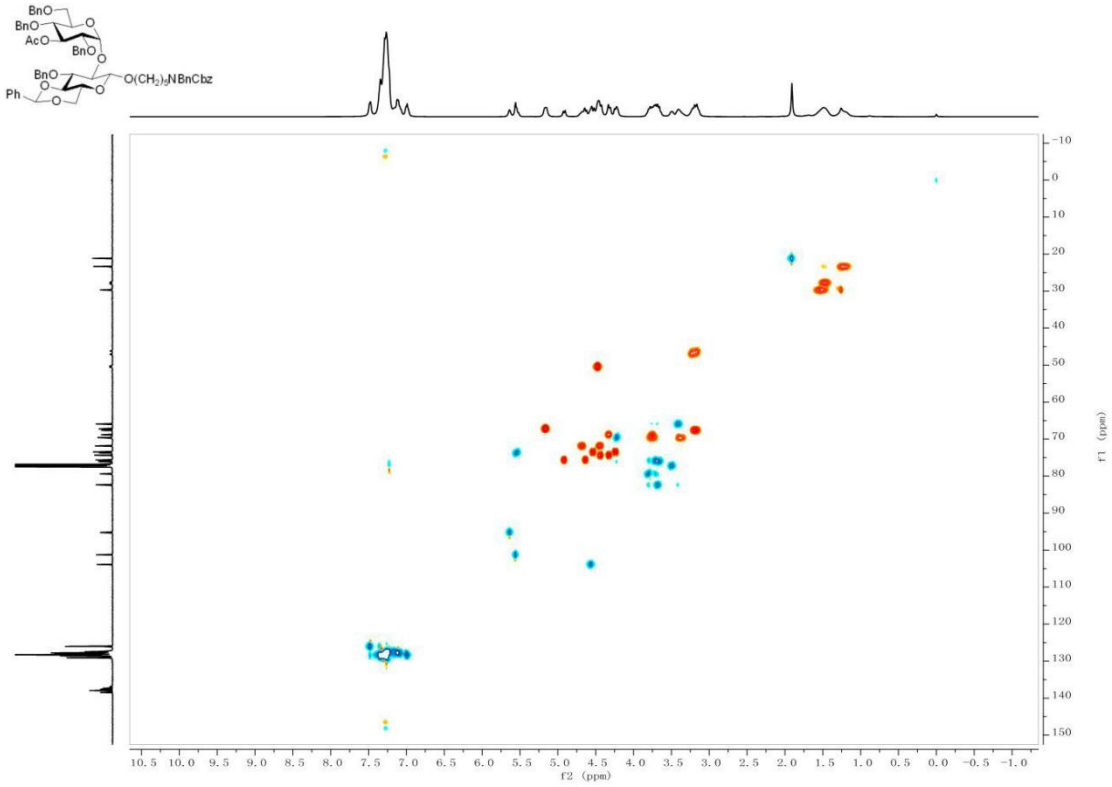
^{13}C NMR spectra of compound **10**



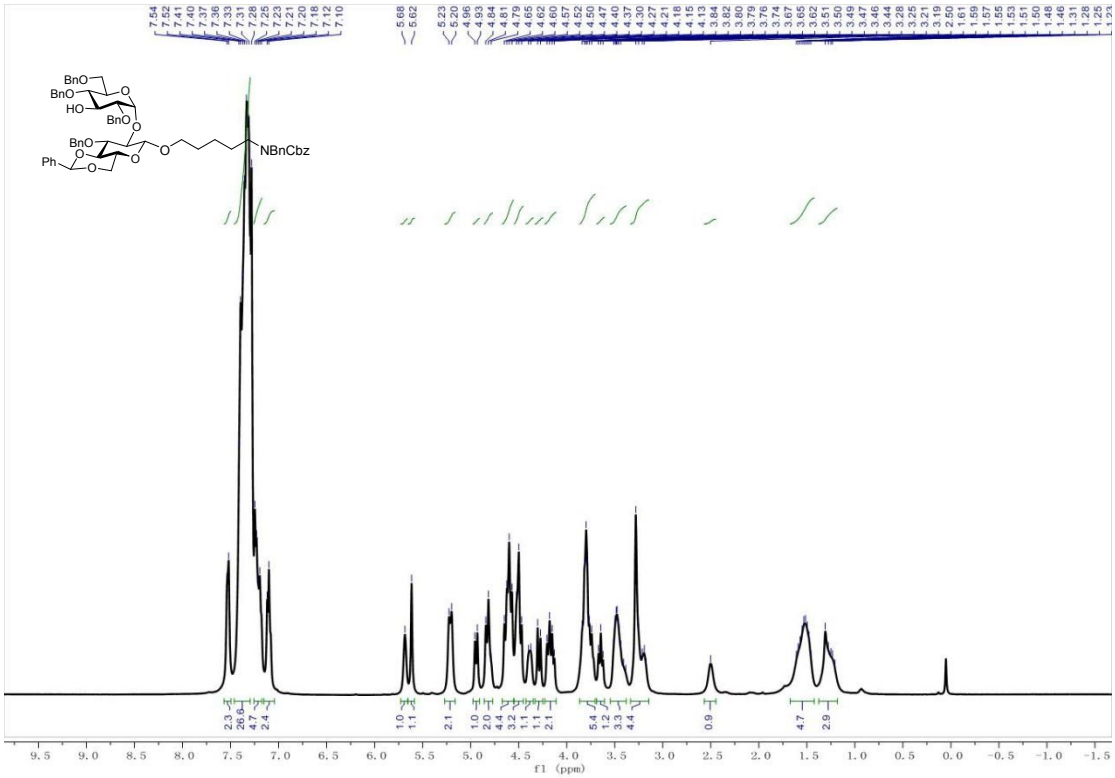
^{1}H-^{1}H COSY NMR spectra of compound **10**



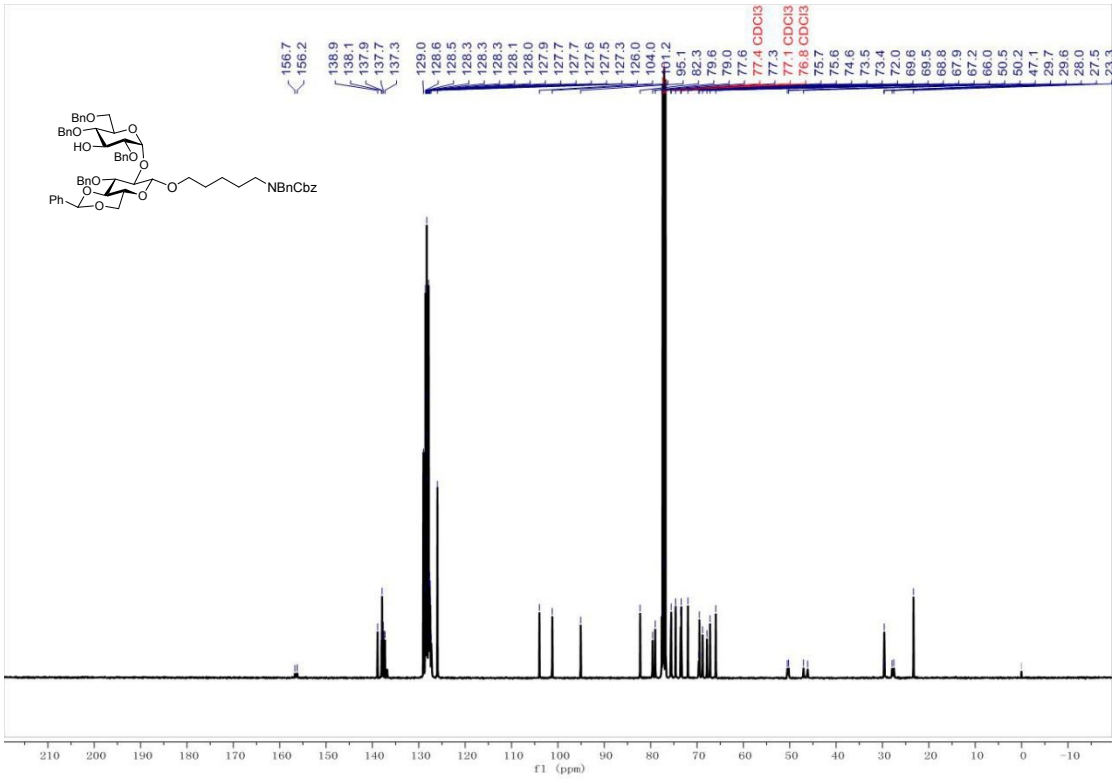
^{1}H-^{13}C HSQC NMR spectra of compound **10**



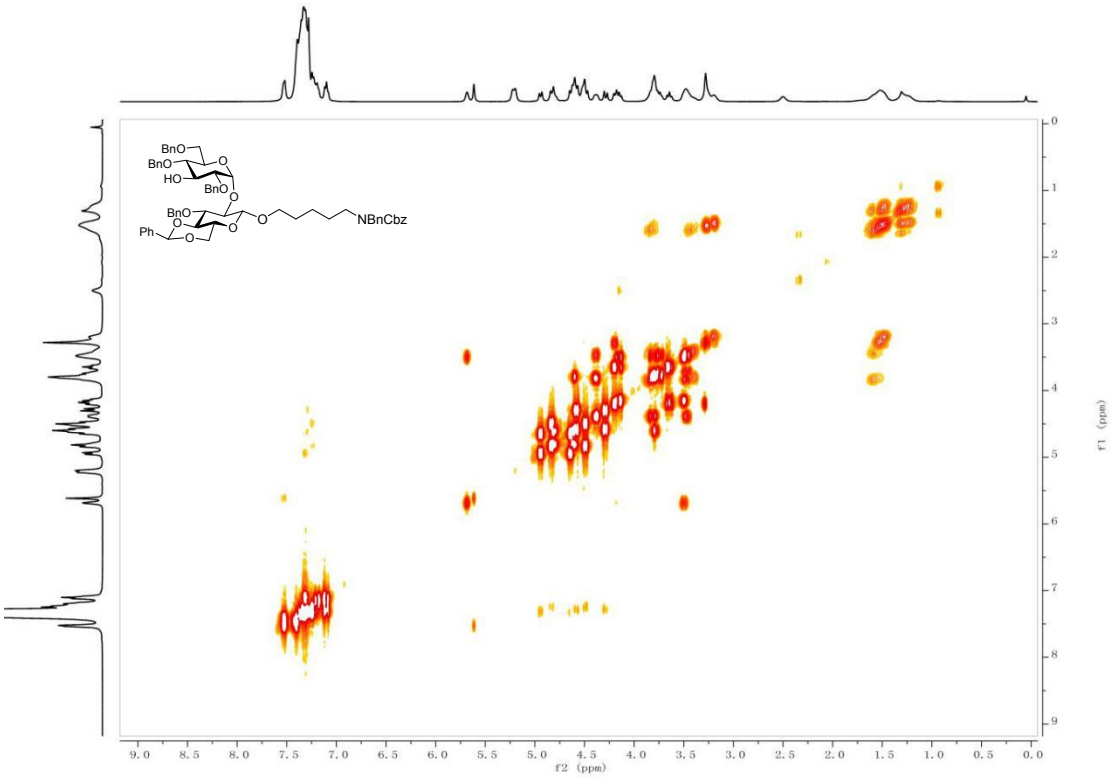
^{1}H NMR spectra of compound **14**



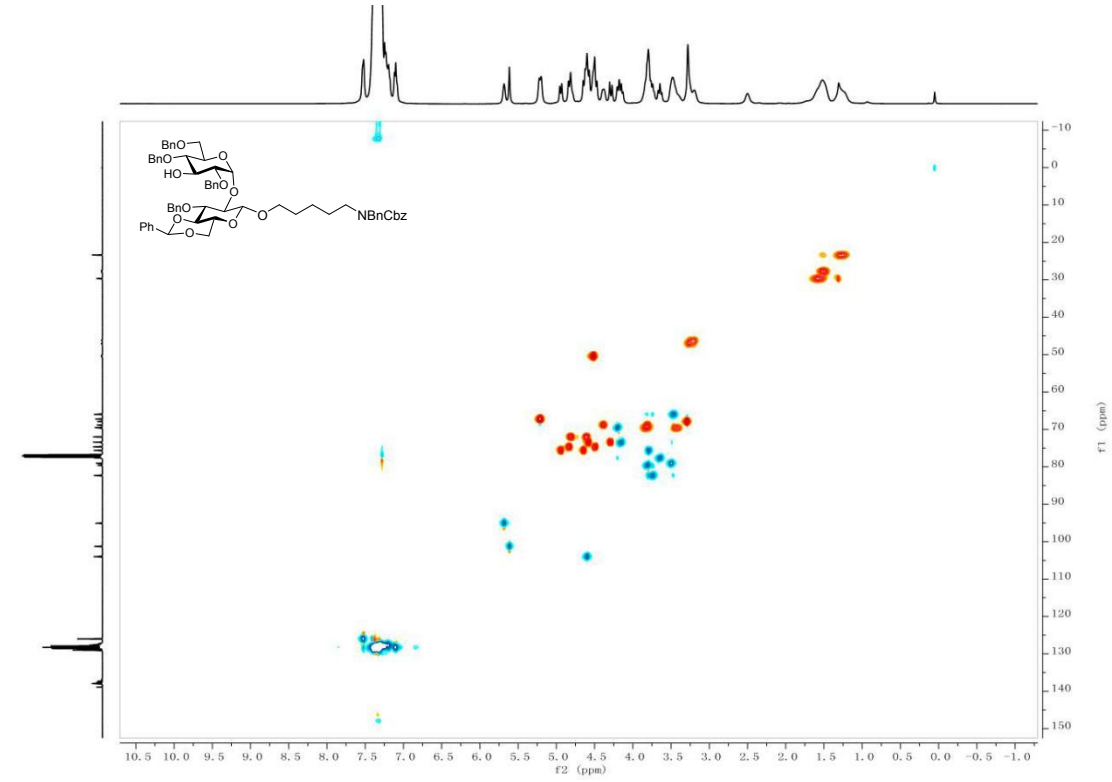
^{13}C NMR spectra of compound **14**



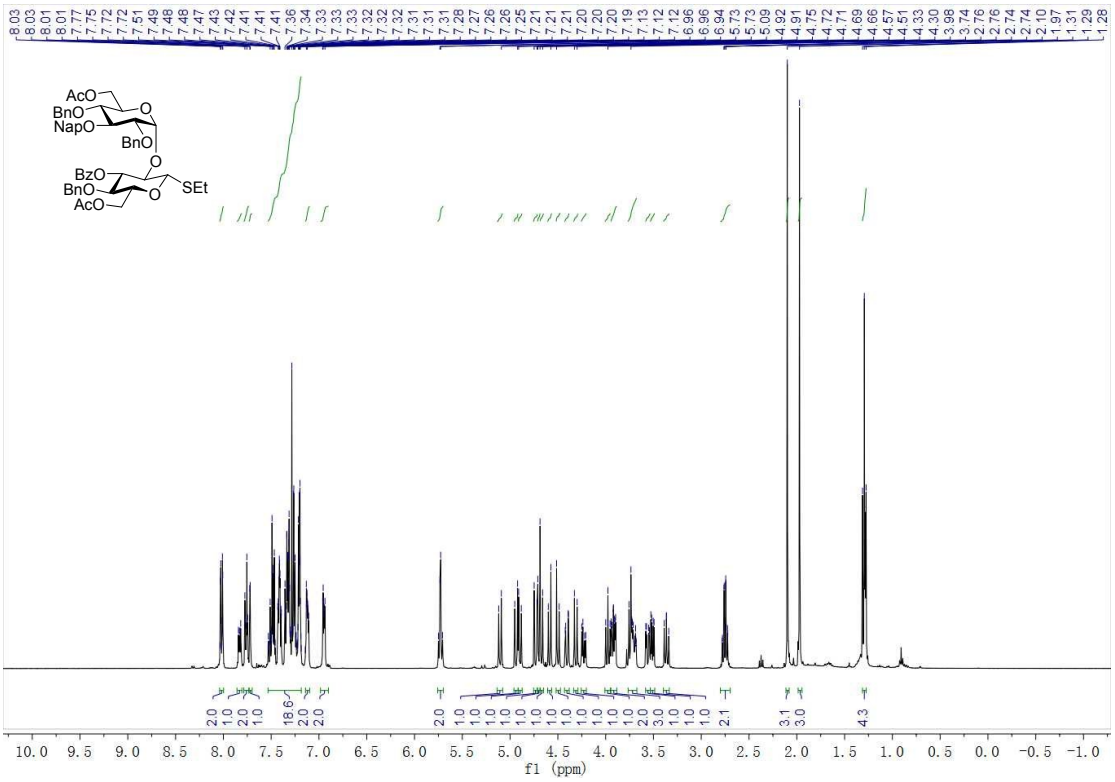
^{1}H-^{1}H COSY NMR spectra of compound **14**



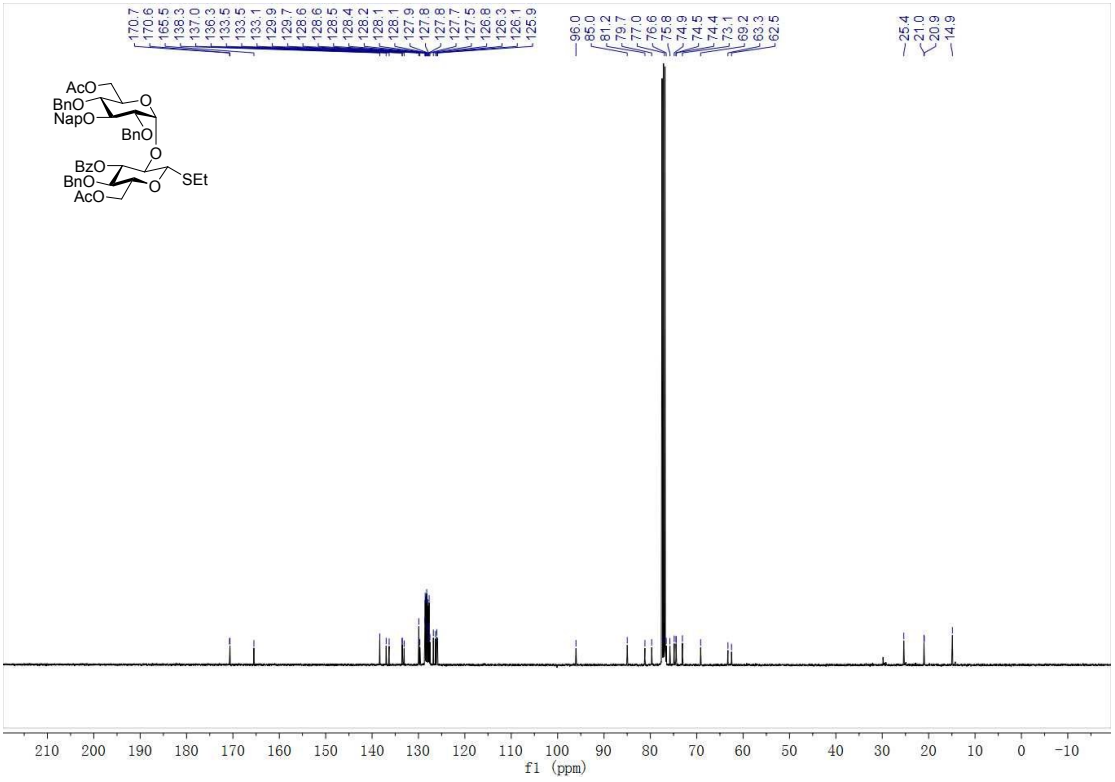
^{1}H-^{13}C HSQC NMR spectra of compound **14**



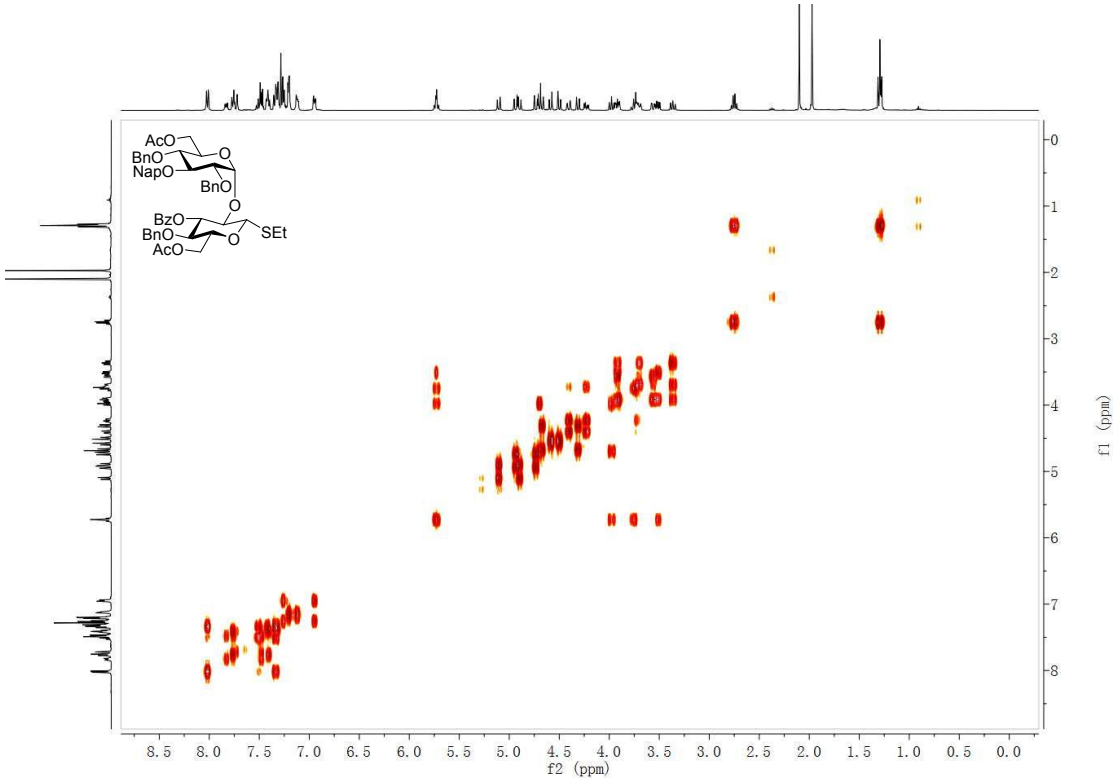
^{1}H NMR spectra of compound **11**



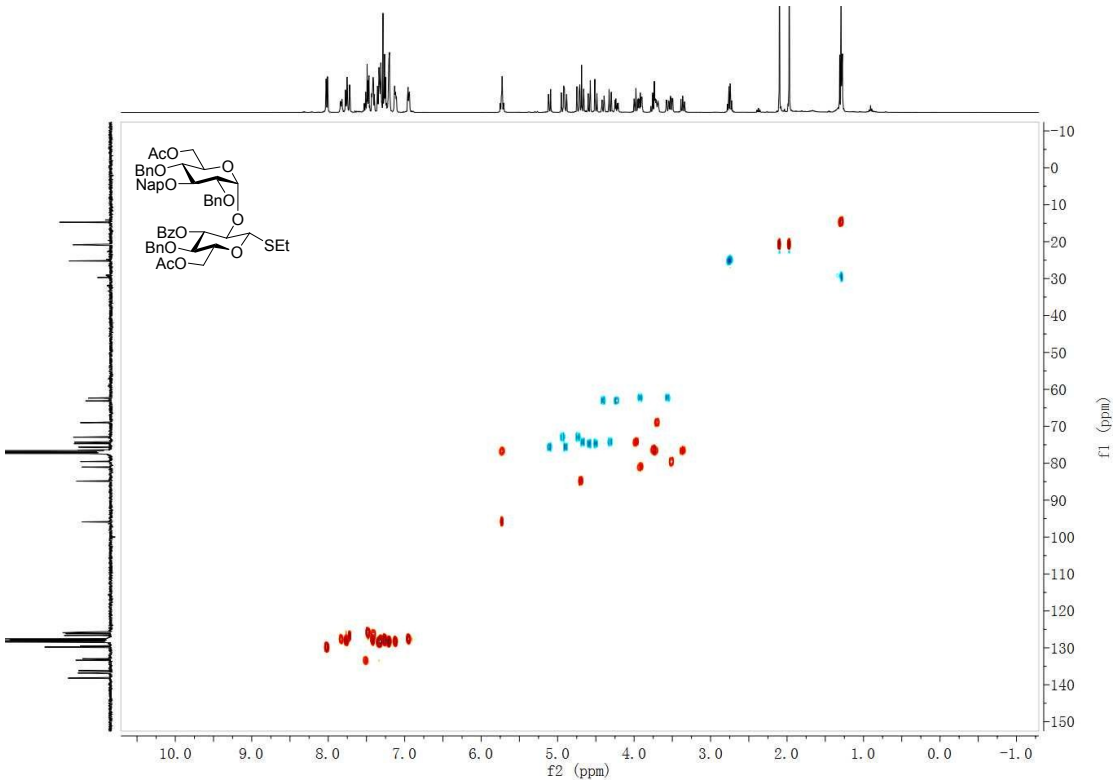
^{13}C NMR spectra of compound **11**



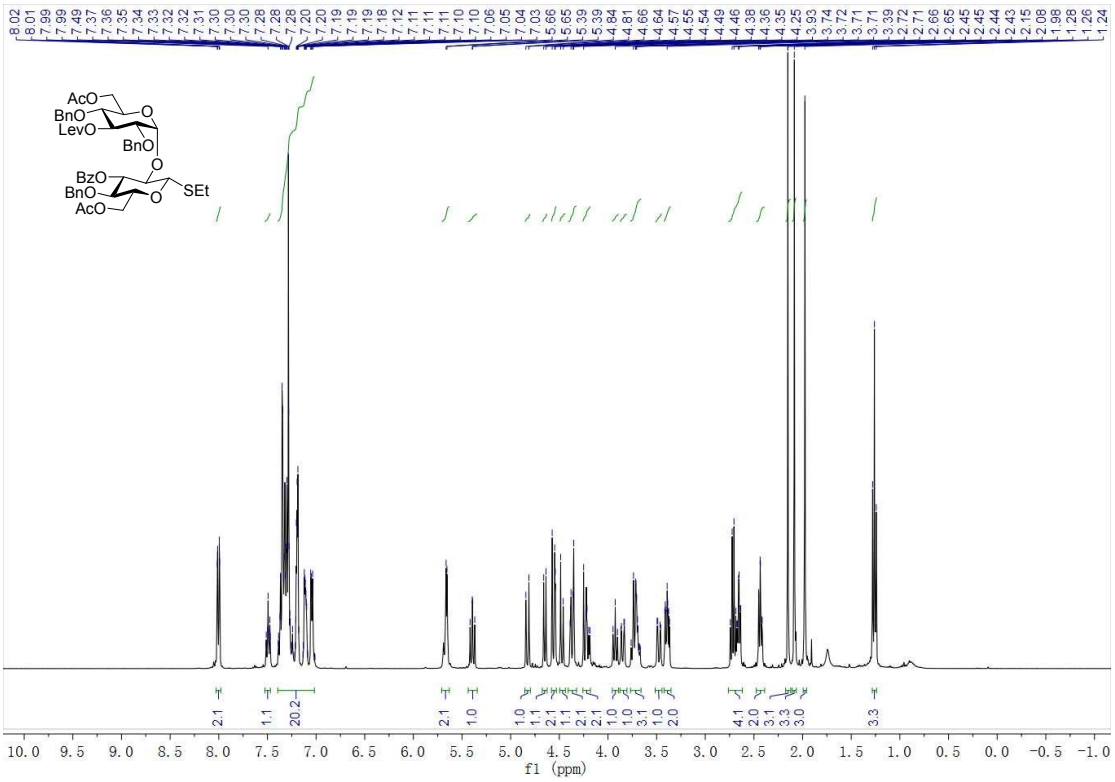
^{1}H-^{1}H COSY NMR spectra of compound **11**



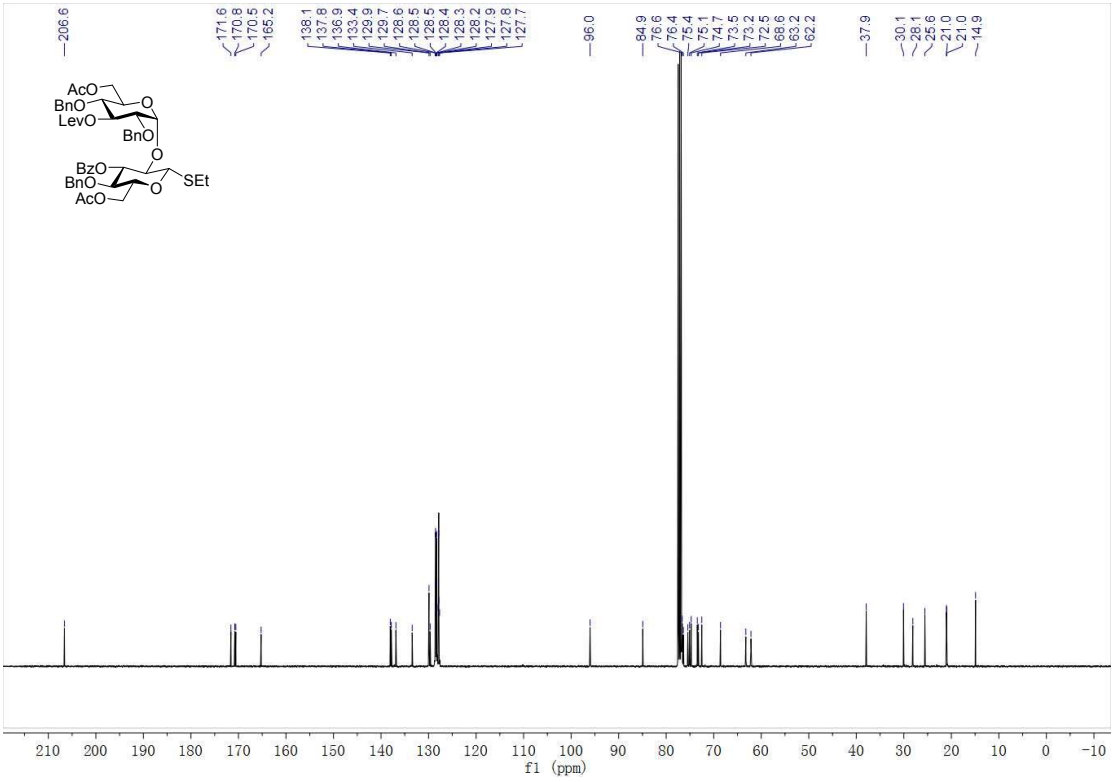
^{1}H-^{13}C HSQC NMR spectra of compound **11**



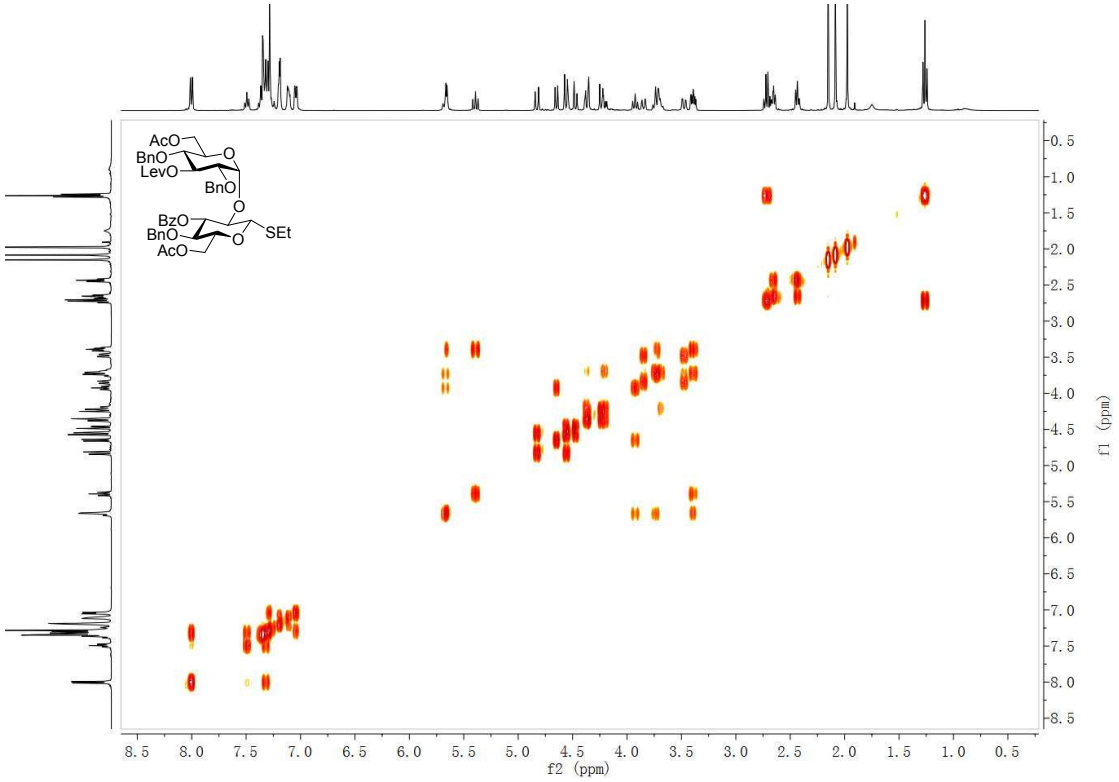
^{1}H NMR spectra of compound **12**



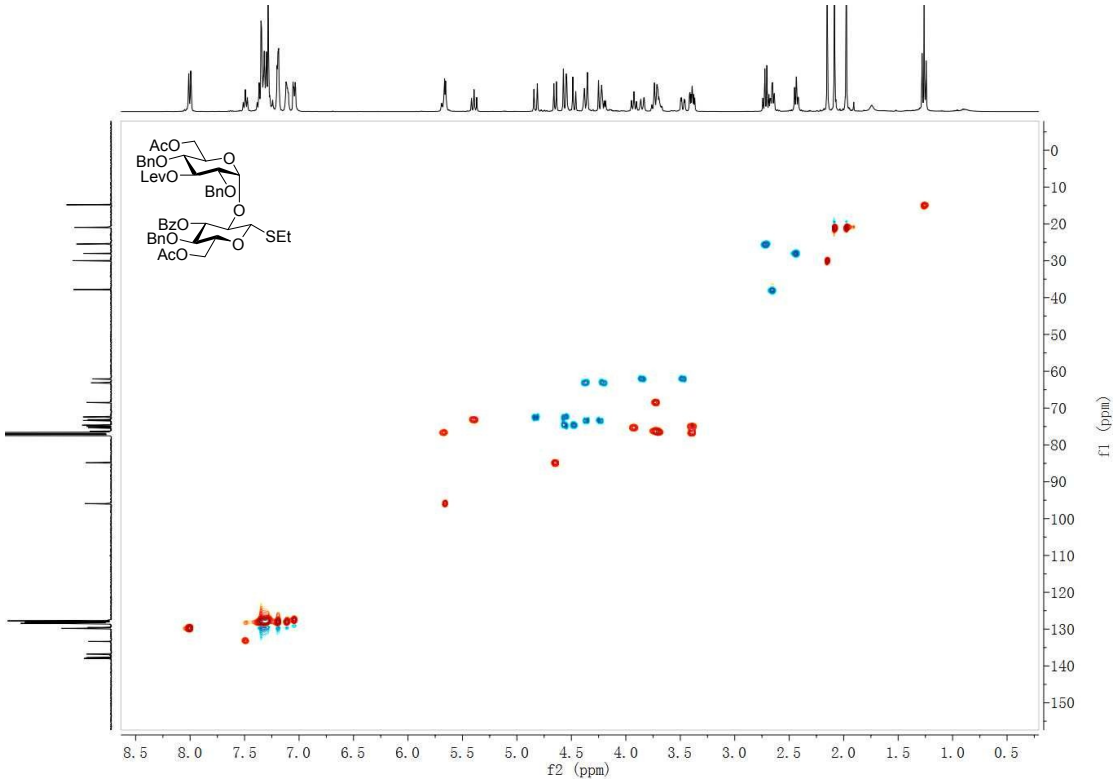
^{13}C NMR spectra of compound **12**



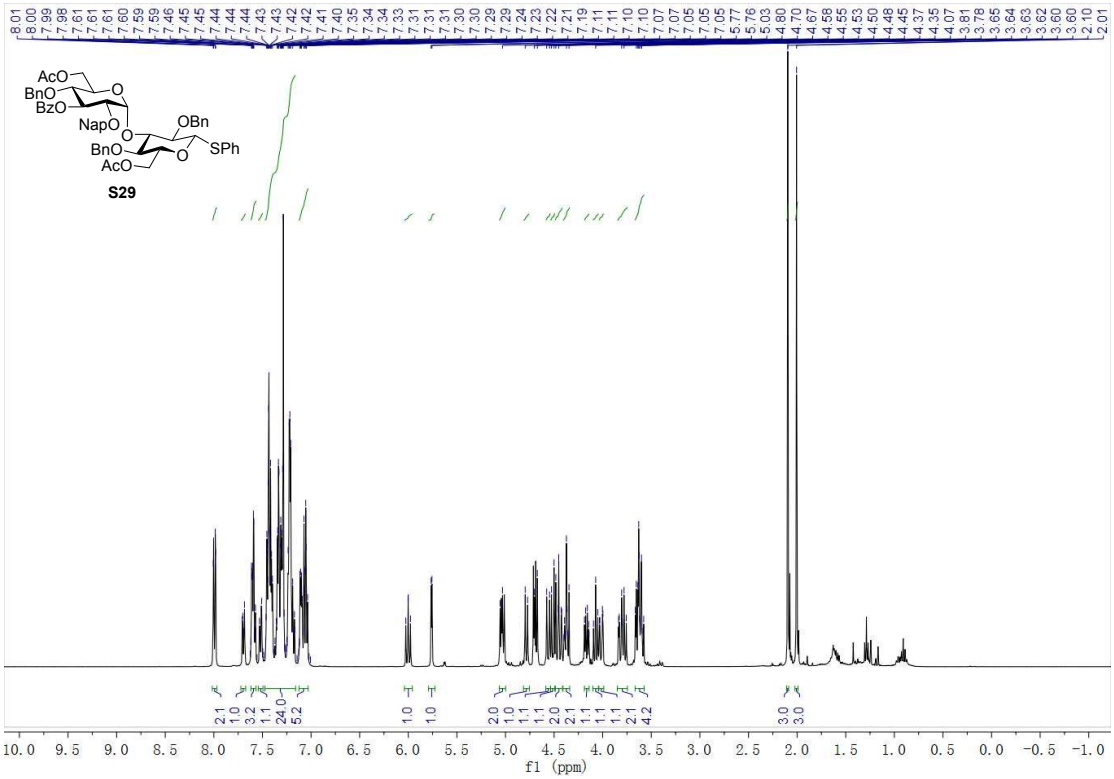
^{1}H-^{1}H COSY NMR spectra of compound **12**



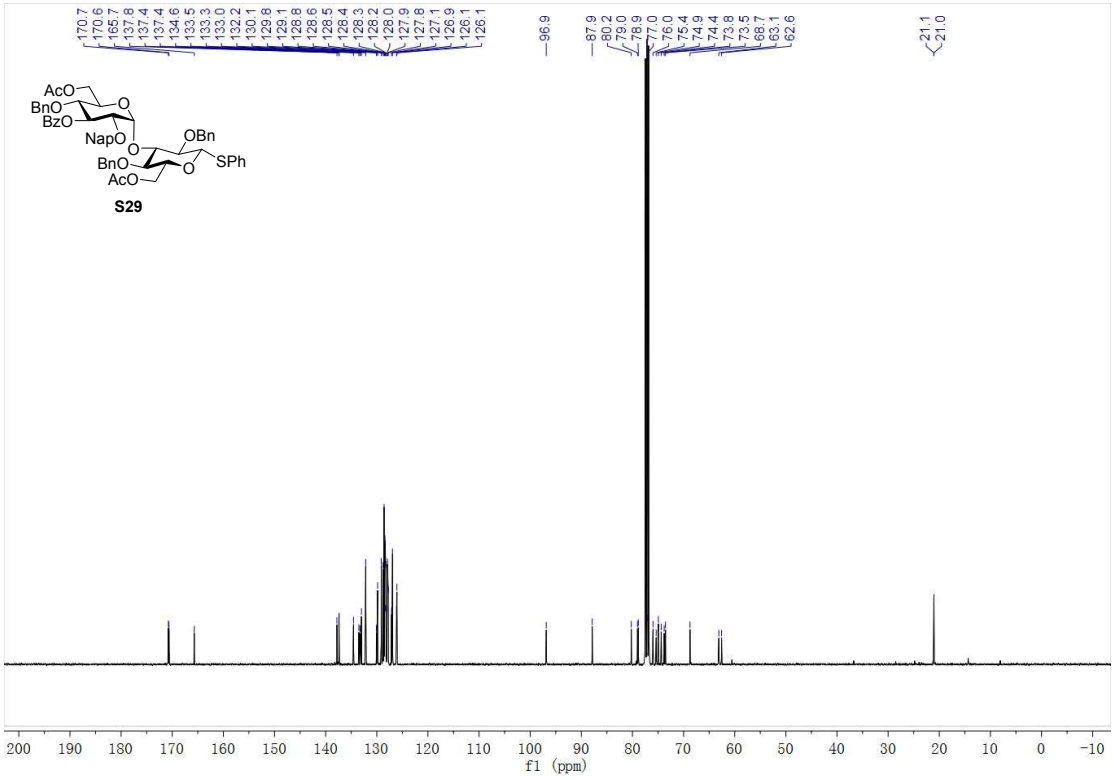
^{1}H-^{13}C HSQC NMR spectra of compound **12**



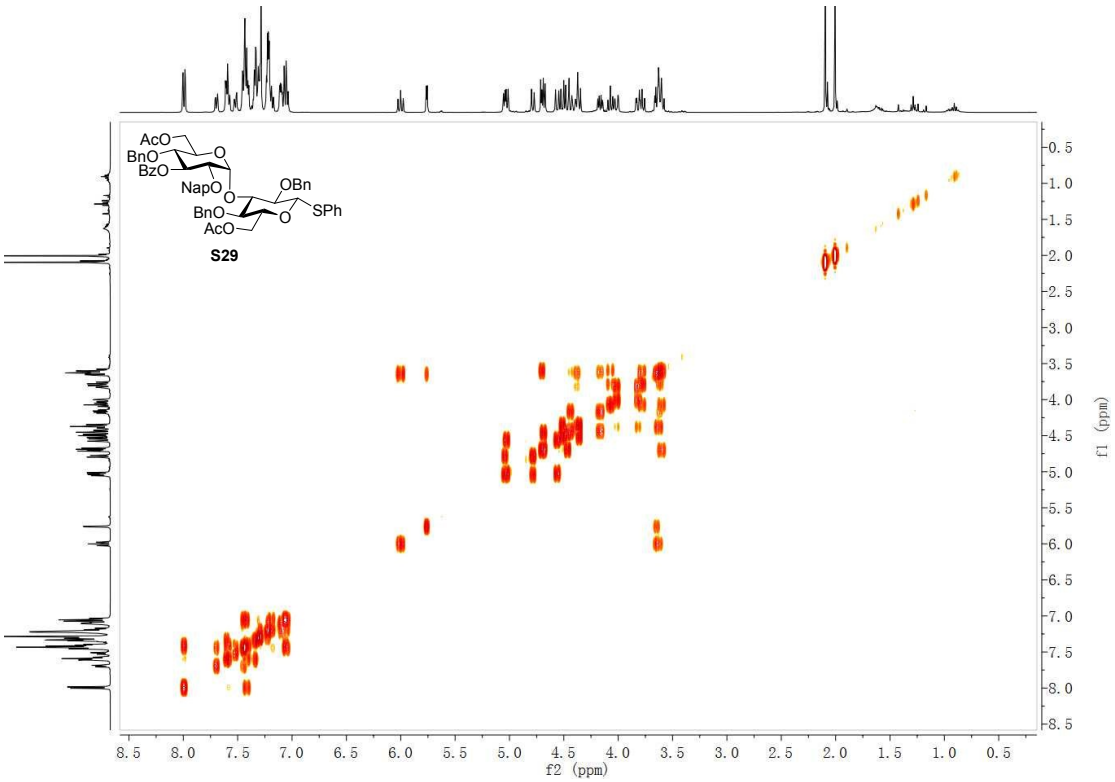
^{1}H NMR spectra of compound **S29**



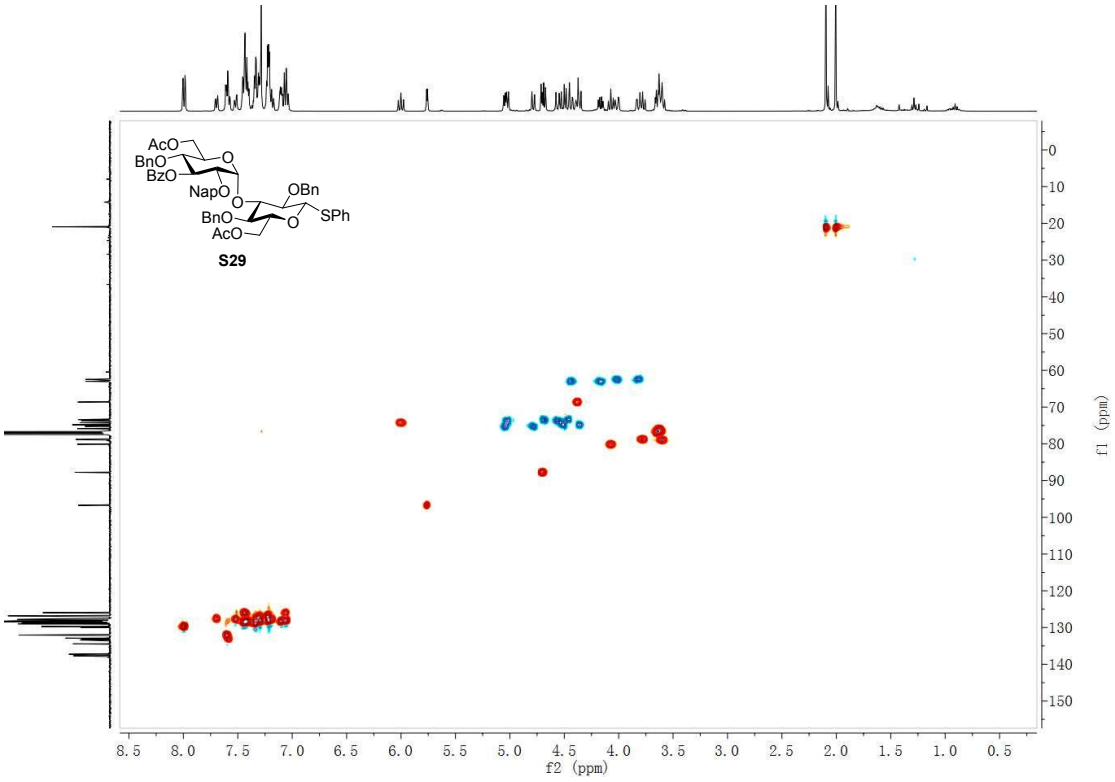
^{13}C NMR spectra of compound **S29**



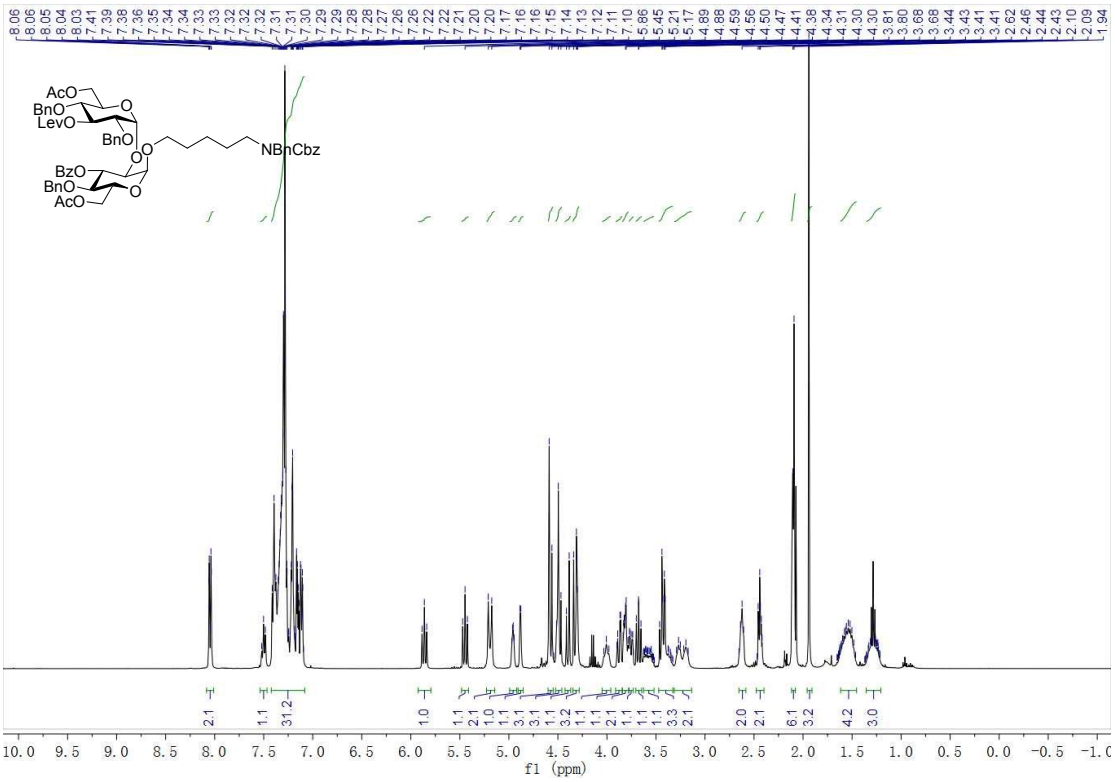
^{1}H-^{1}H COSY NMR spectra of compound **S29**



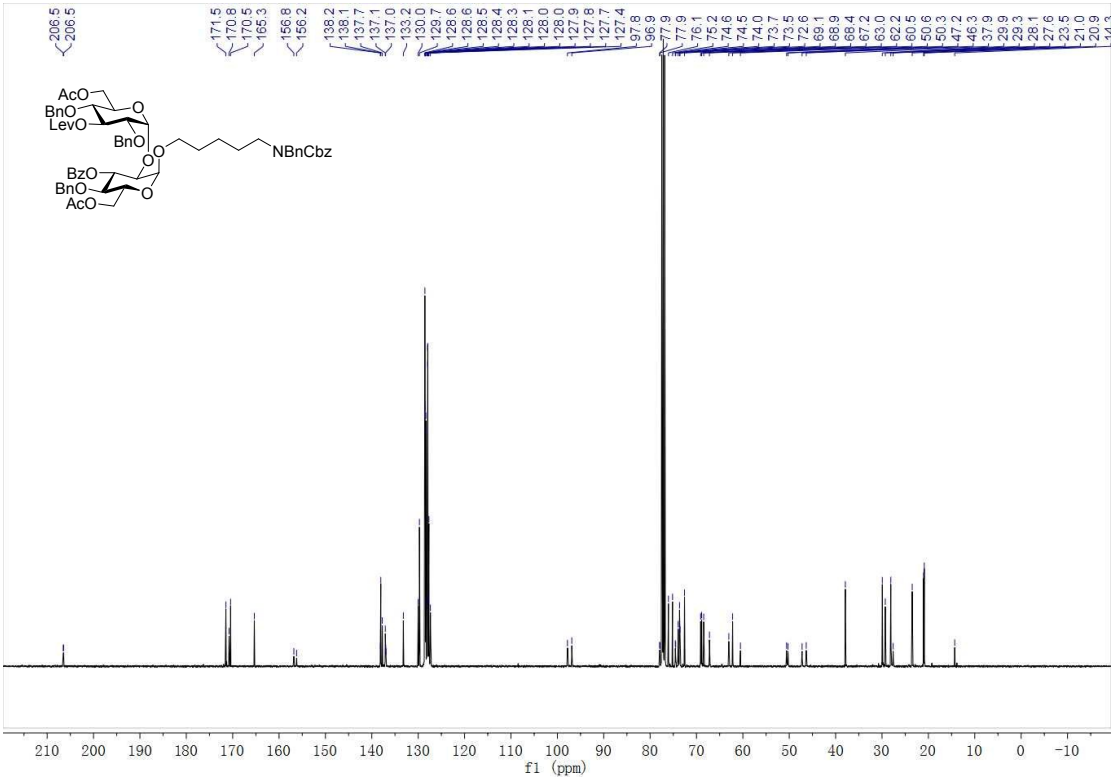
^{1}H-^{13}C HSQC NMR spectra of compound **S29**



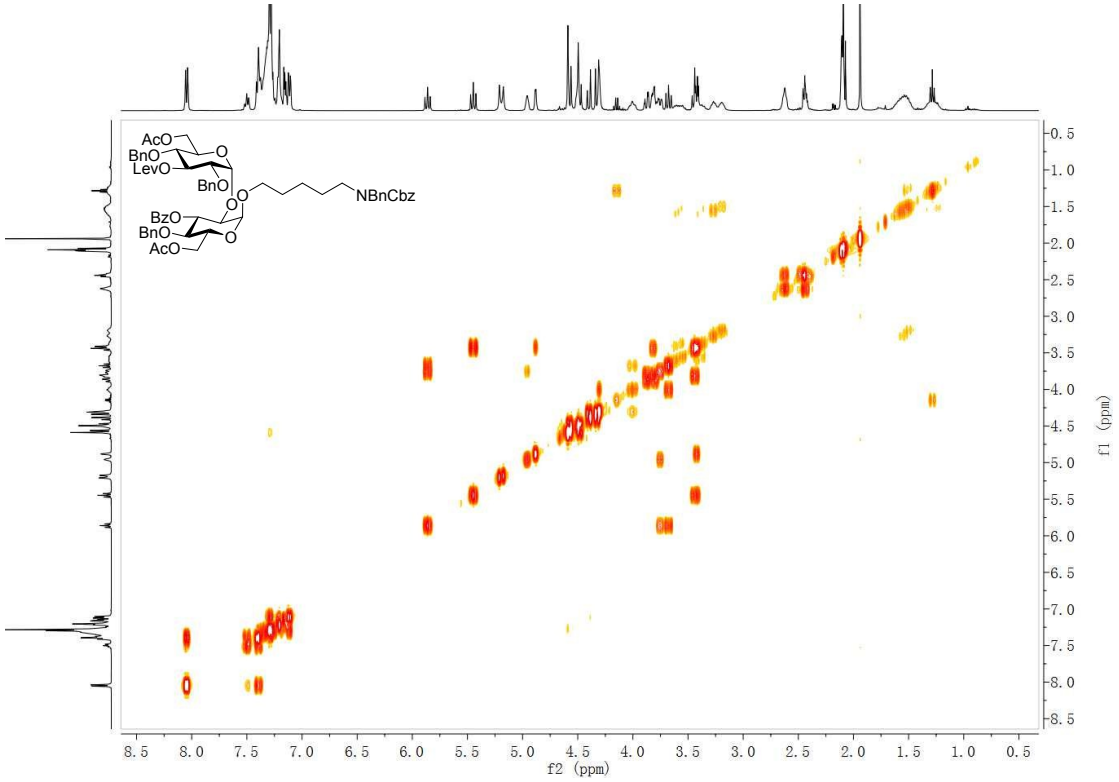
^{1}H NMR spectra of compound **13**



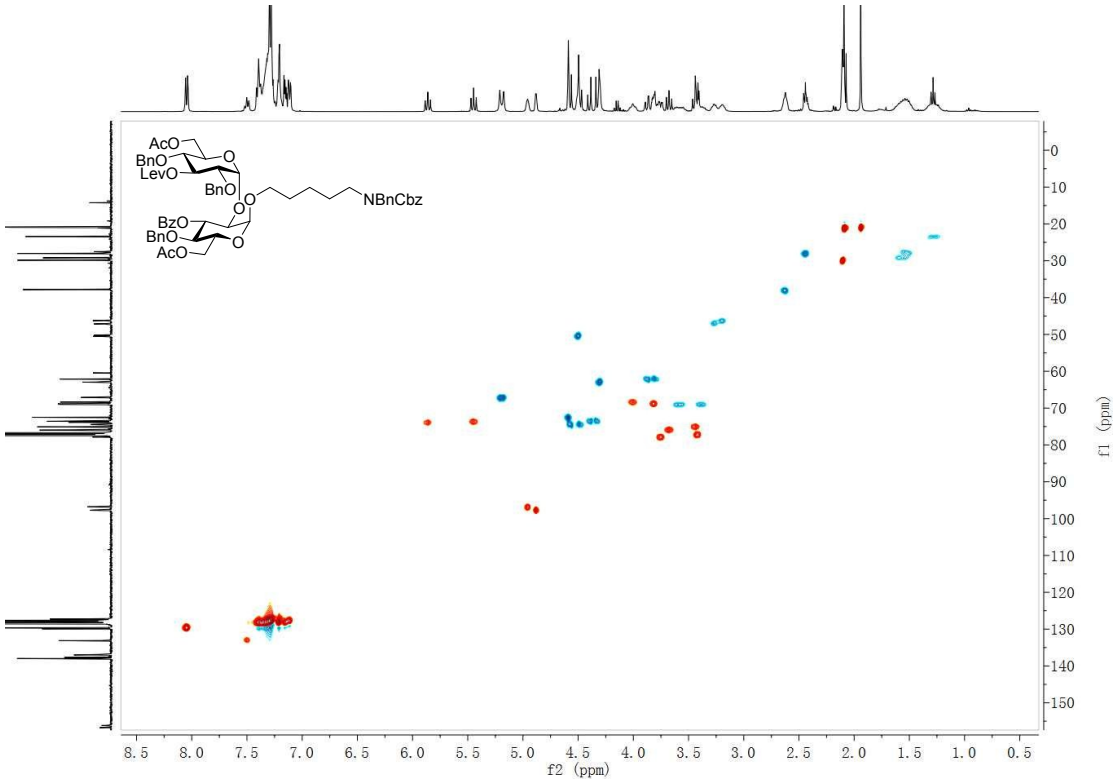
^{13}C NMR spectra of compound **13**



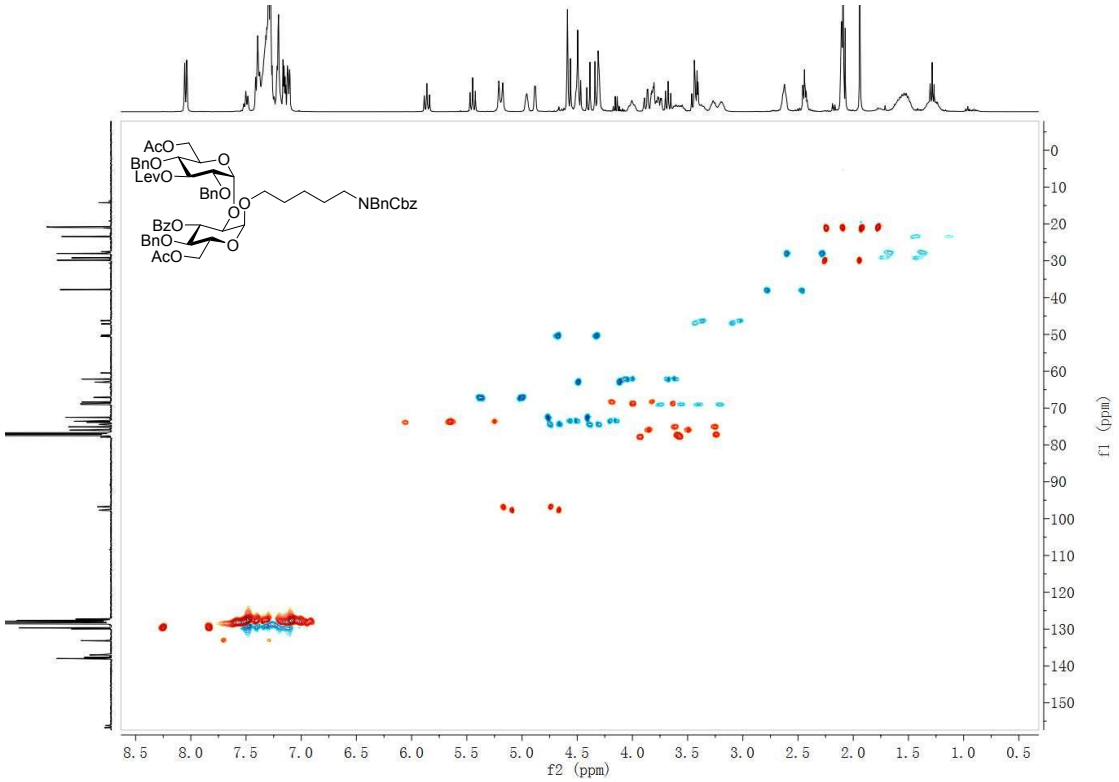
^{1}H-^{1}H COSY NMR spectra of compound **13**

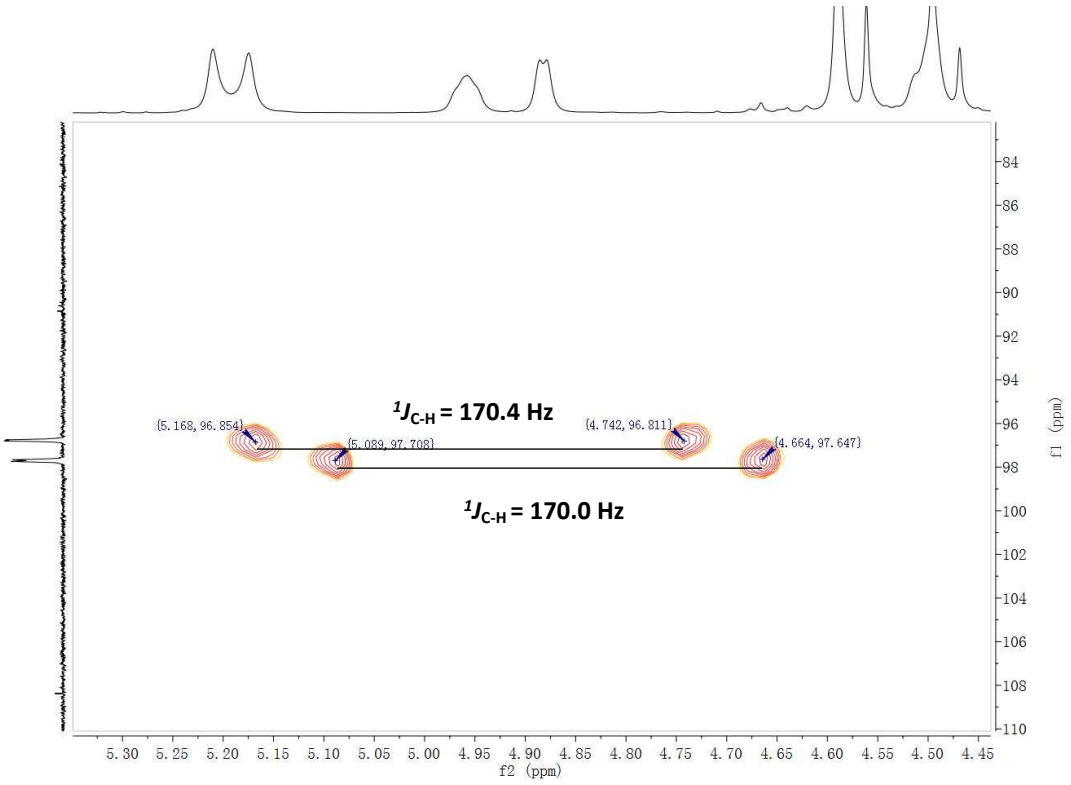


^{1}H-^{13}C HSQC NMR spectra of compound **13**

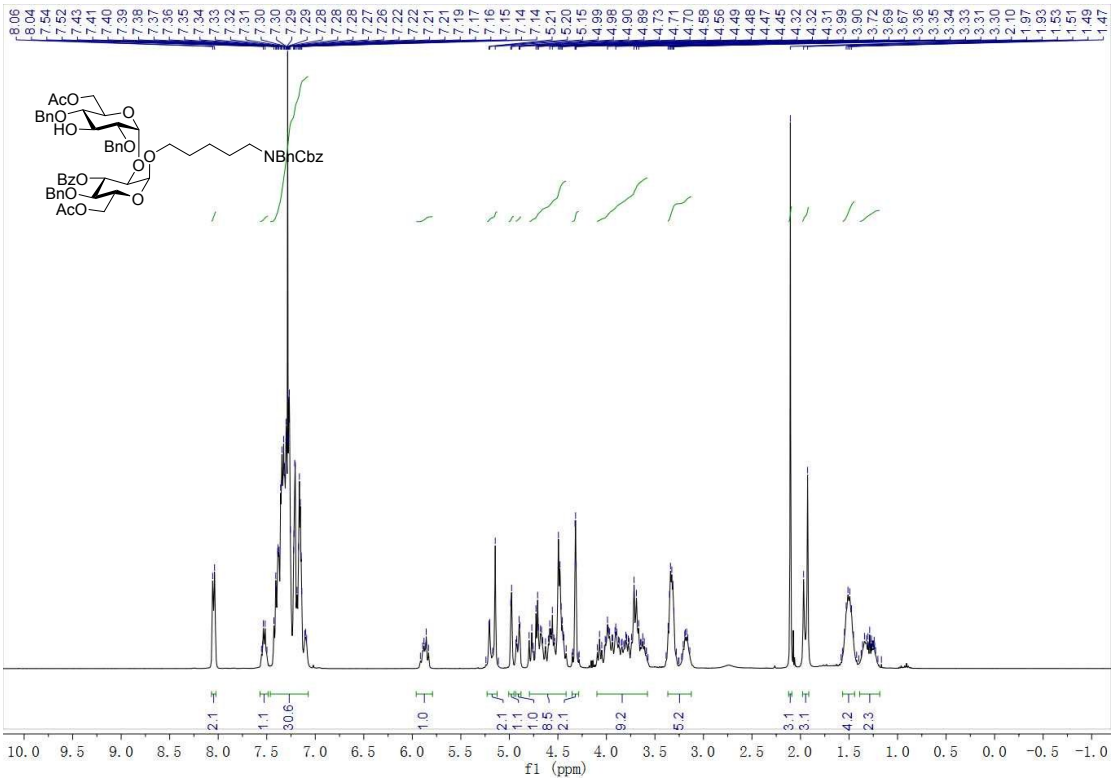


^{1}H-^{13}C coupling HSQC NMR spectrum of compound **13**

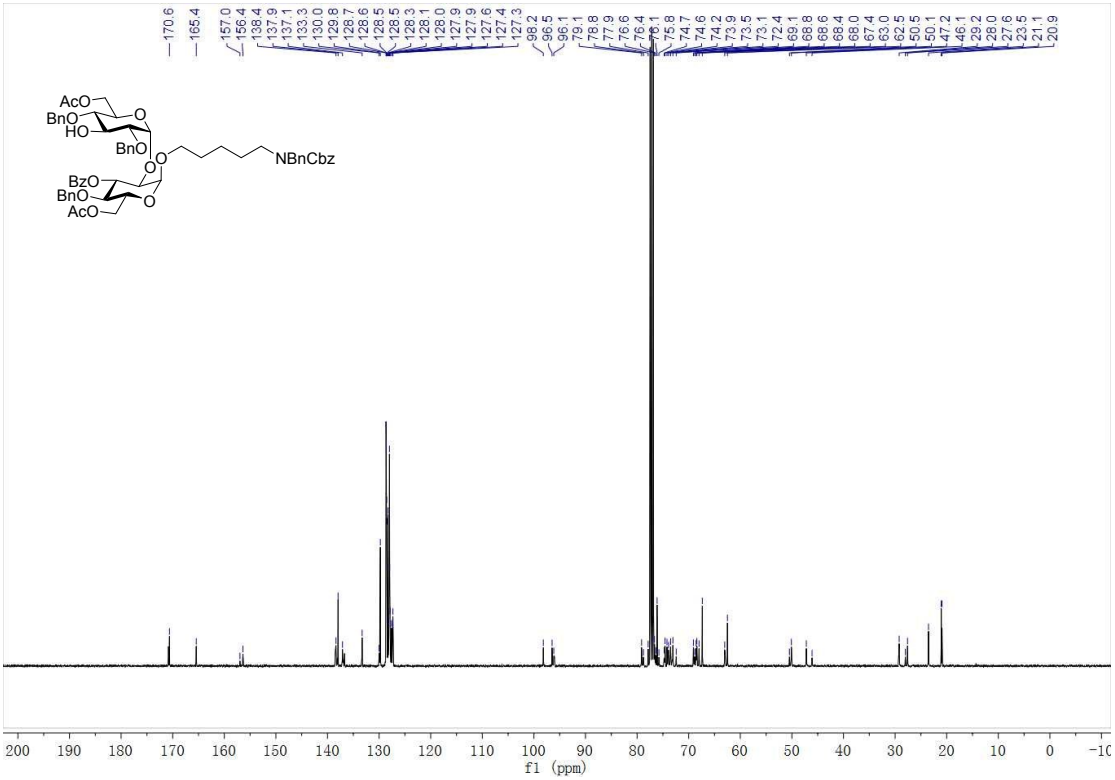




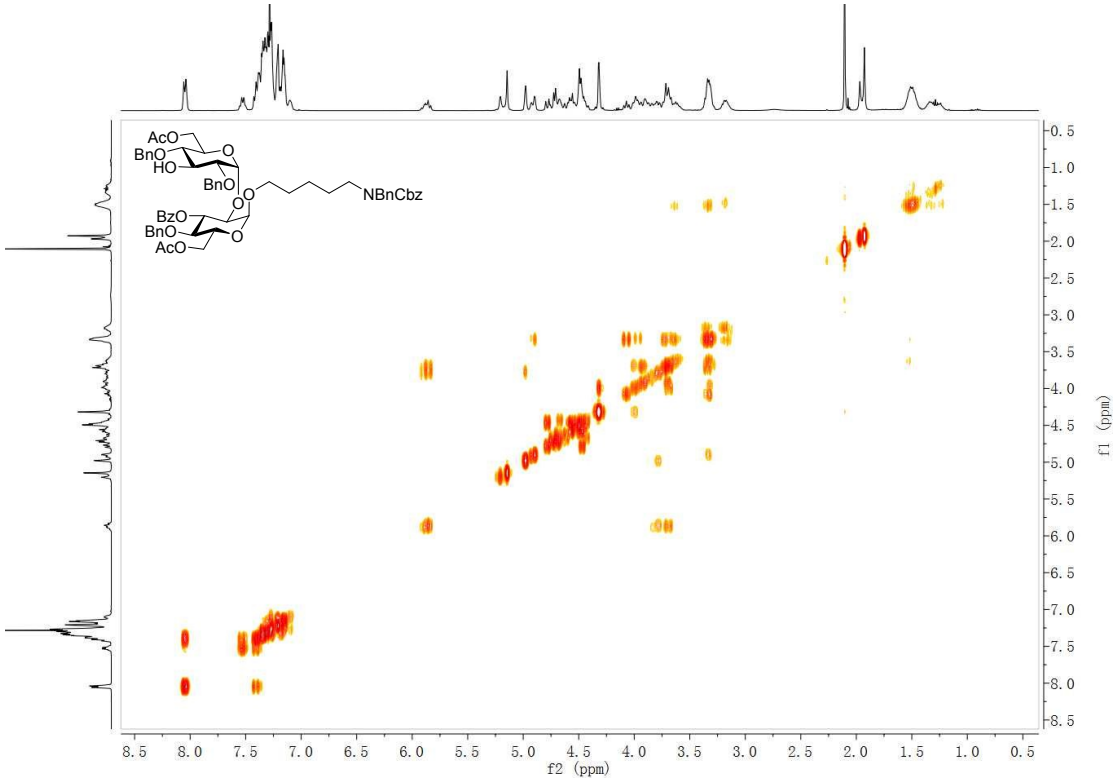
^{1}H NMR spectra of compound **17**



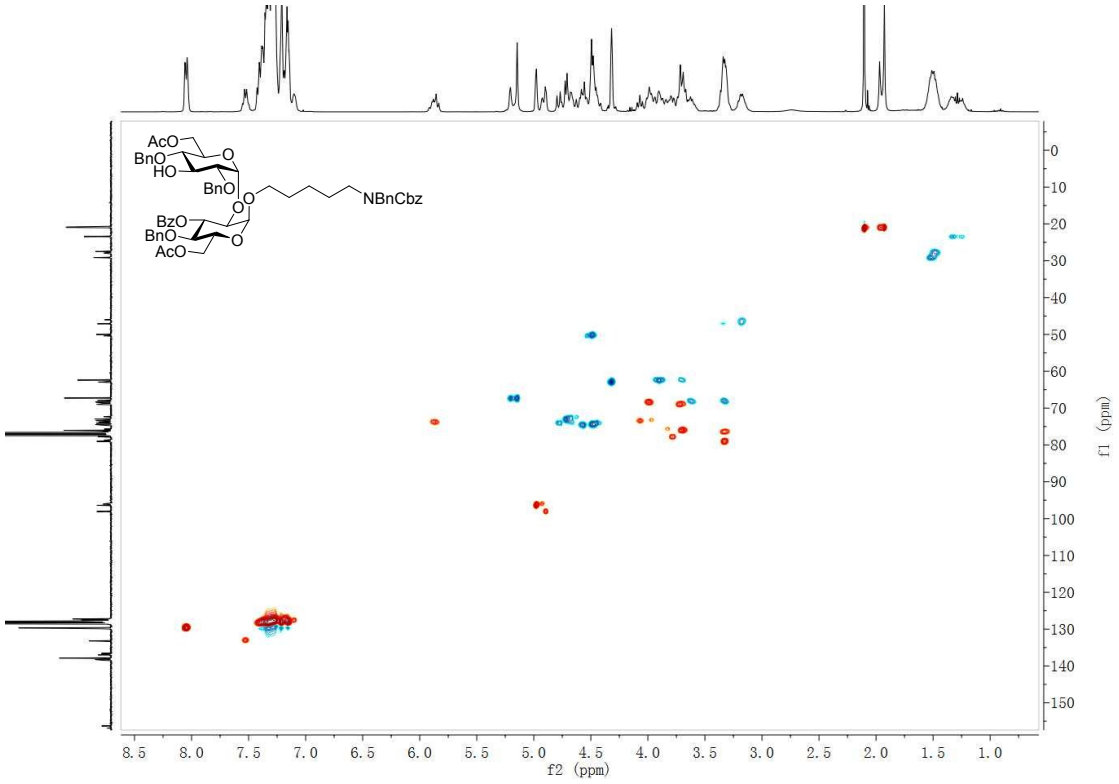
^{13}C NMR spectra of compound **17**



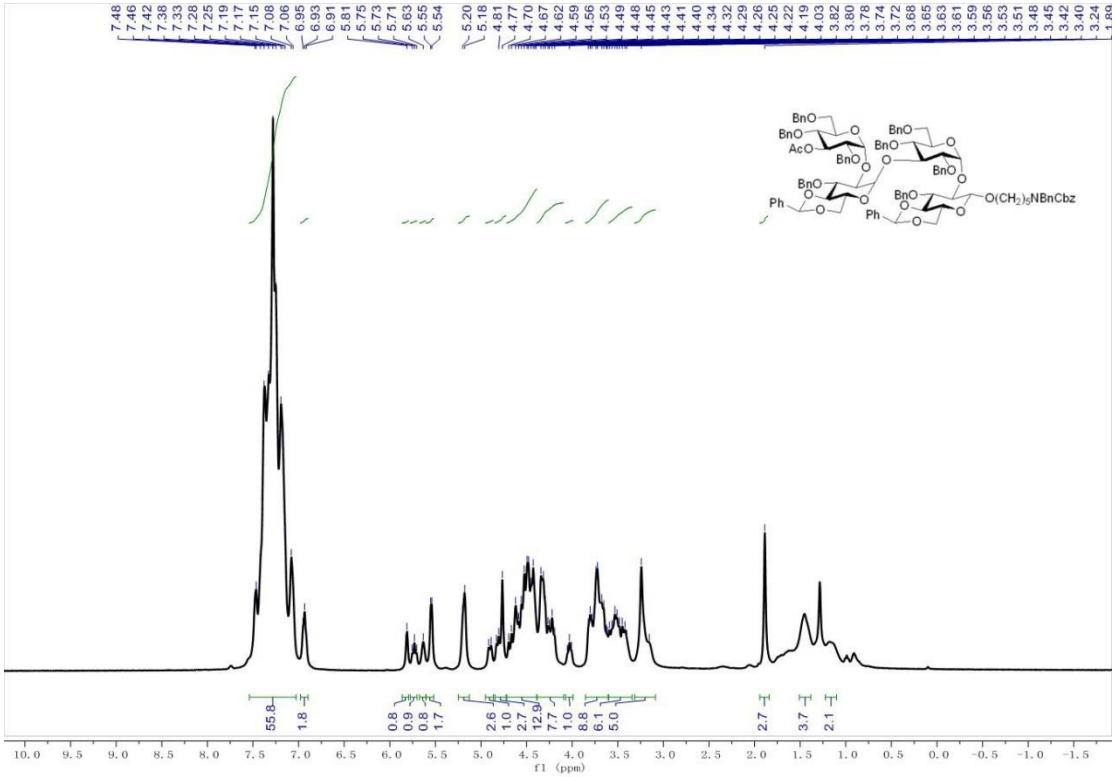
^{1}H-^{1}H COSY NMR spectra of compound **17**



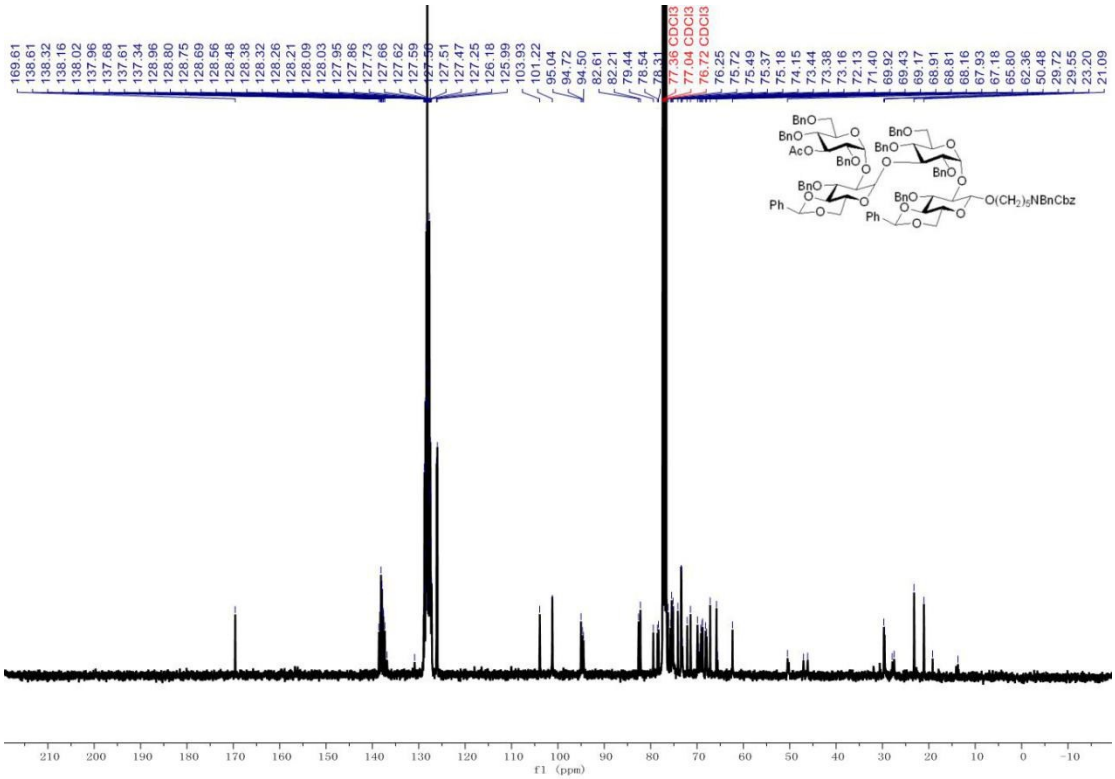
^{1}H-^{13}C HSQC NMR spectra of compound **17**



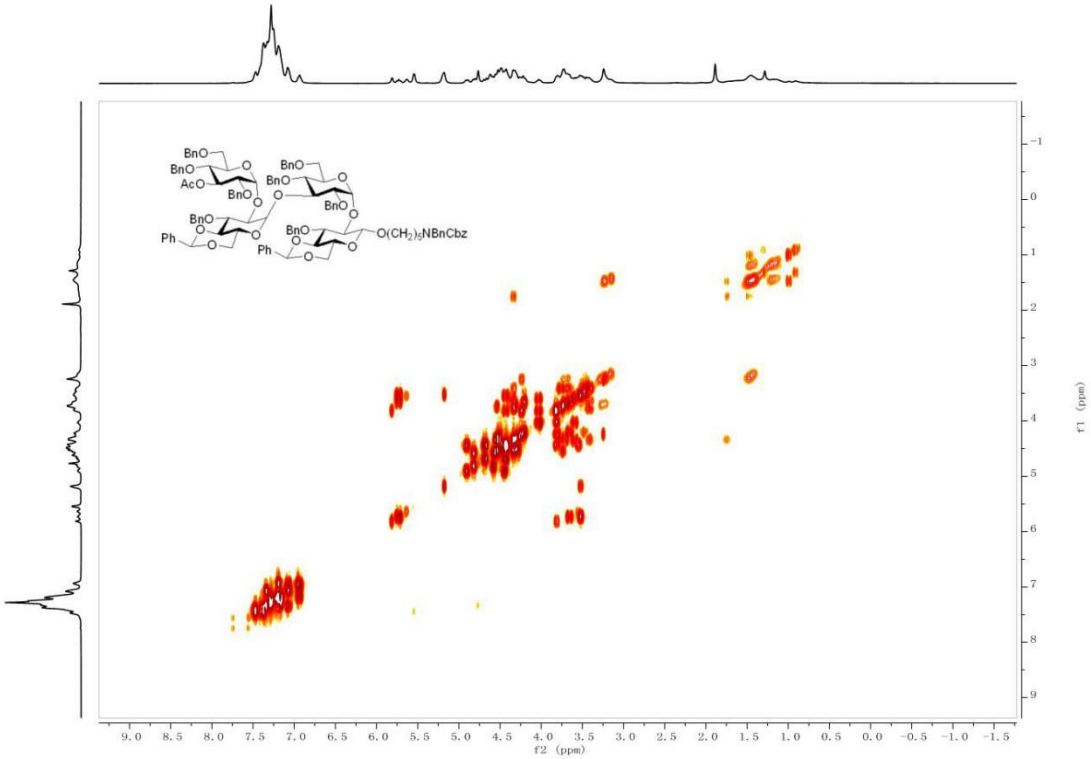
^{1}H NMR spectra of compound **15**



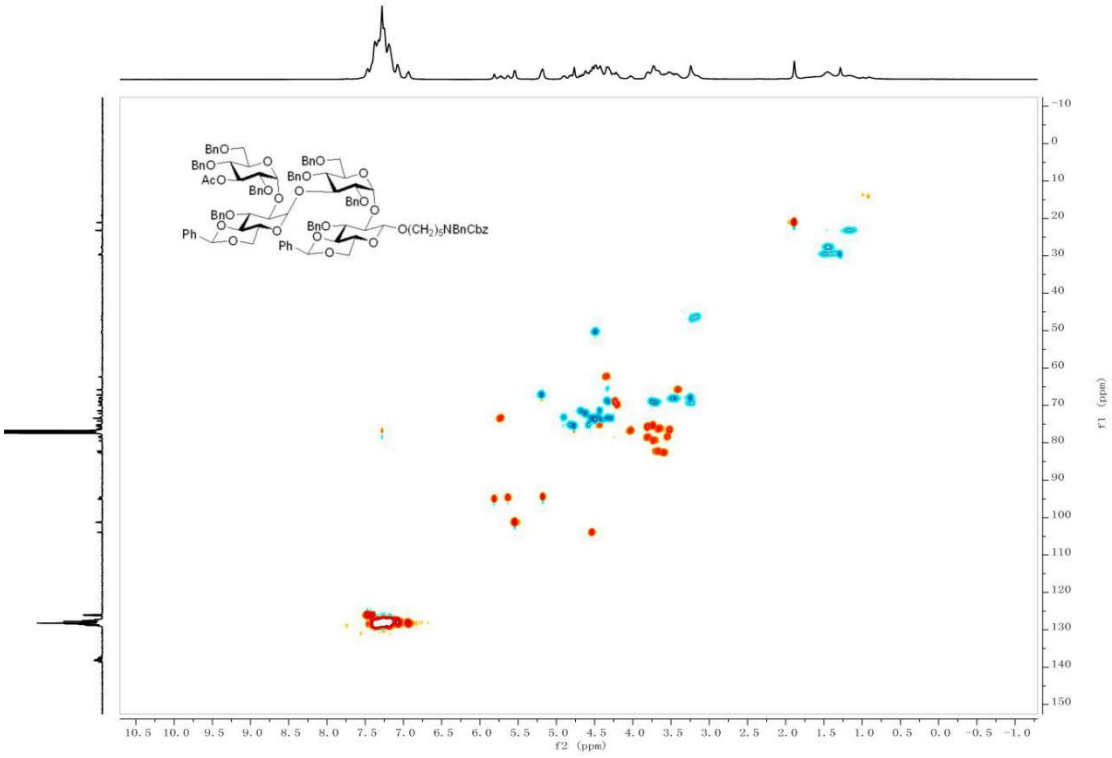
^{13}C NMR spectra of compound **15**



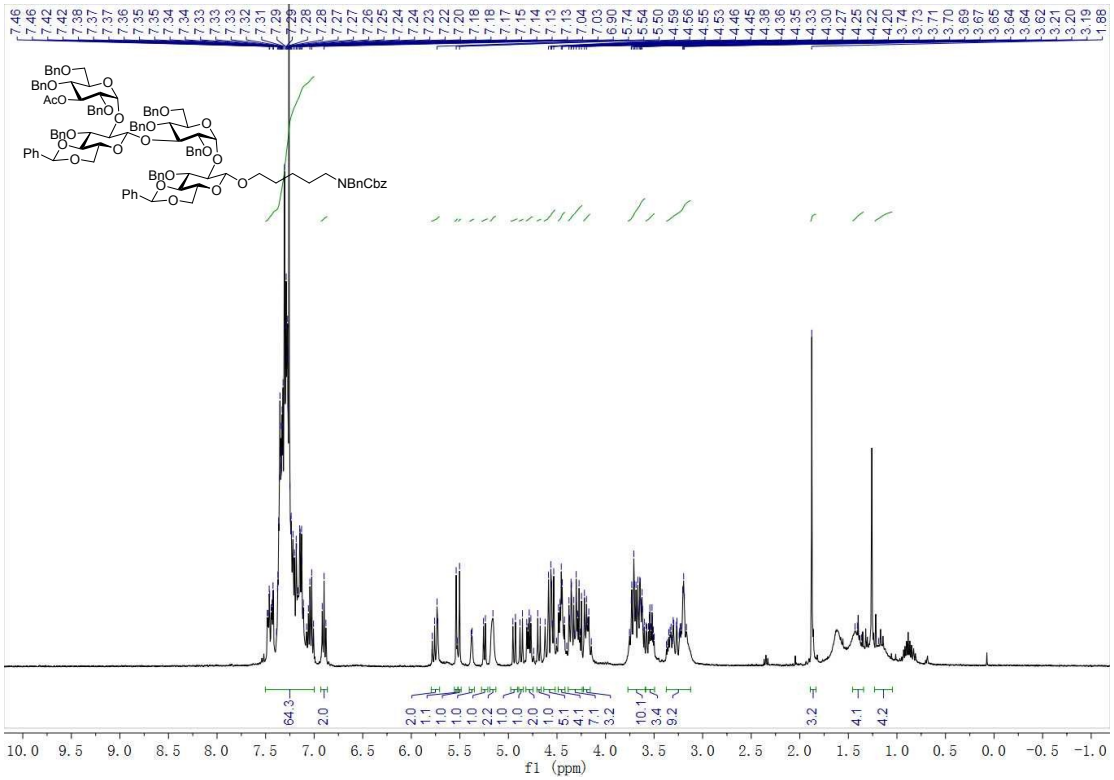
^{1}H-^{1}H COSY NMR spectra of compound **15**



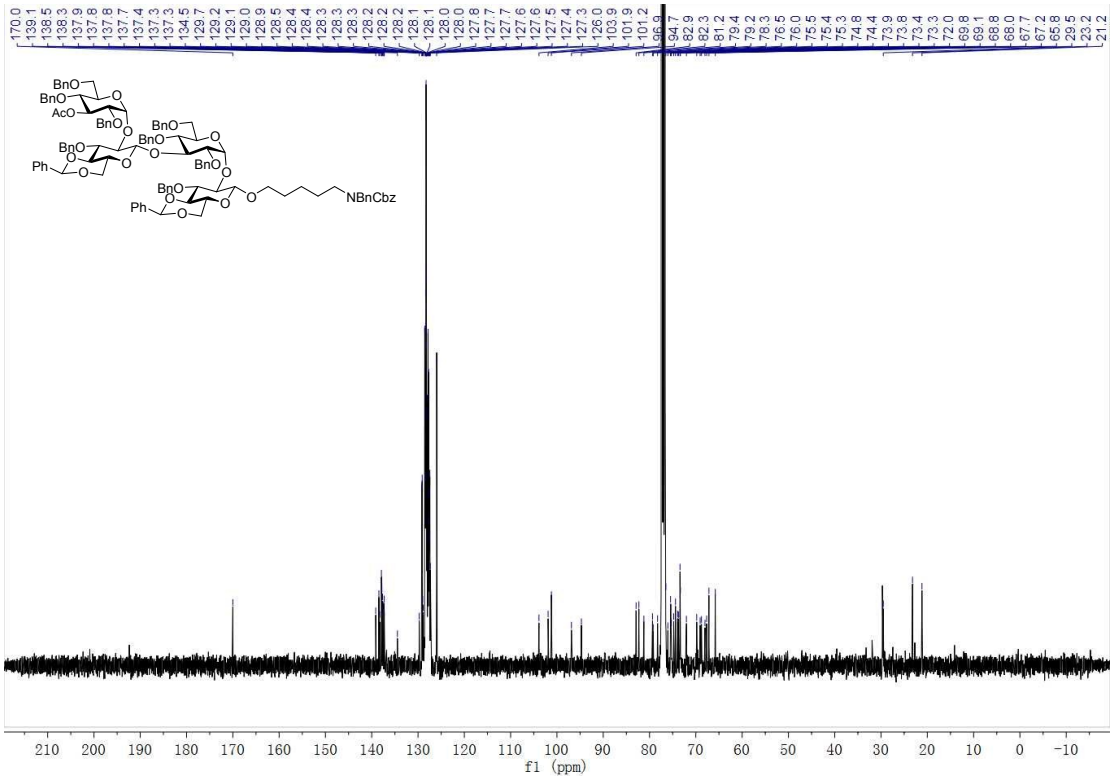
^{1}H-^{13}C HSQC NMR spectra of compound **15**



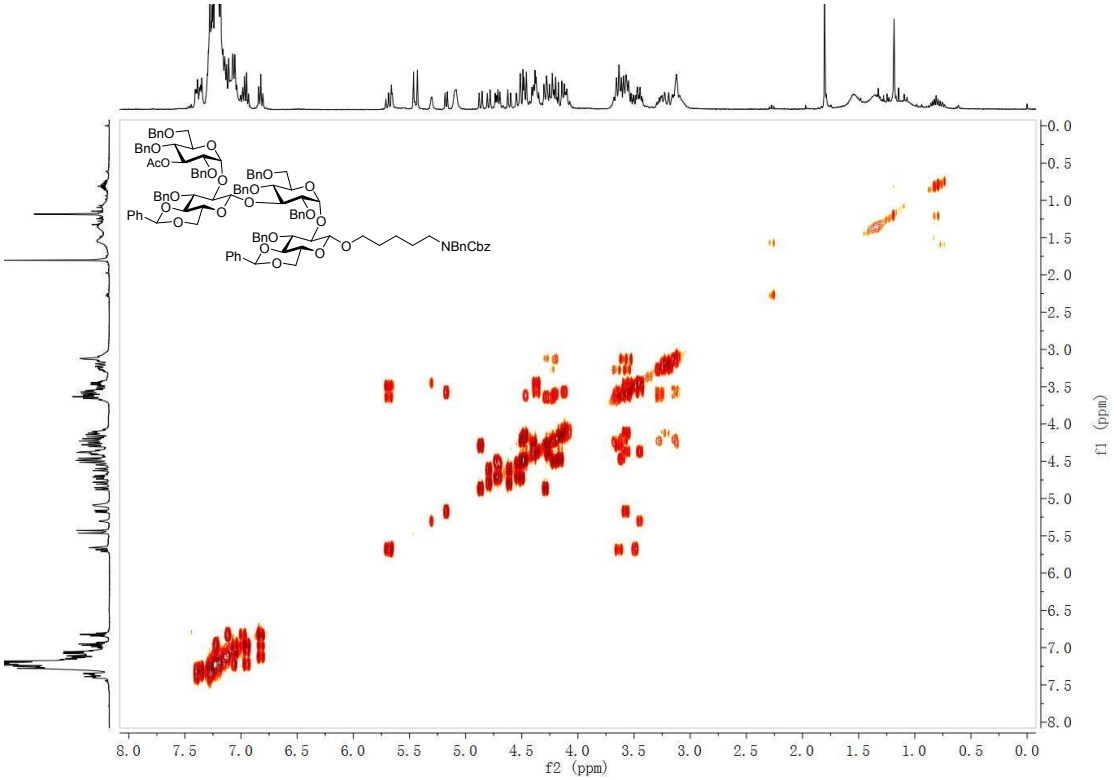
^{1}H NMR spectra of compound **15β**



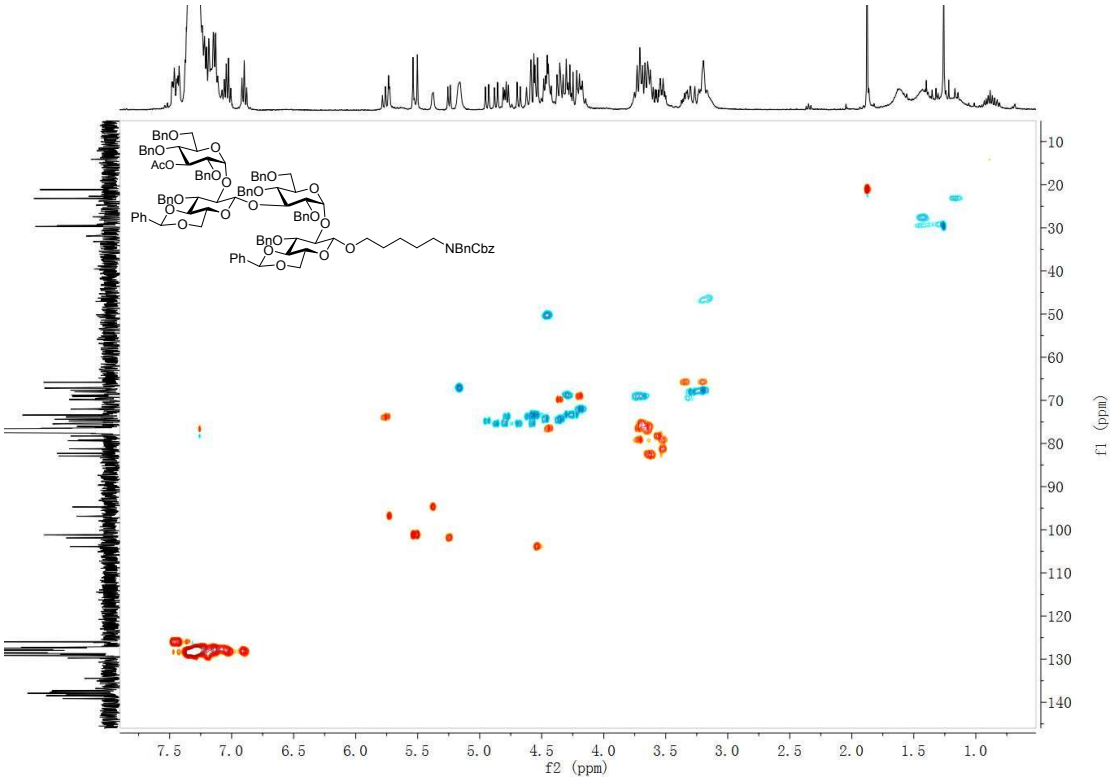
^{13}C NMR spectra of compound **15β**



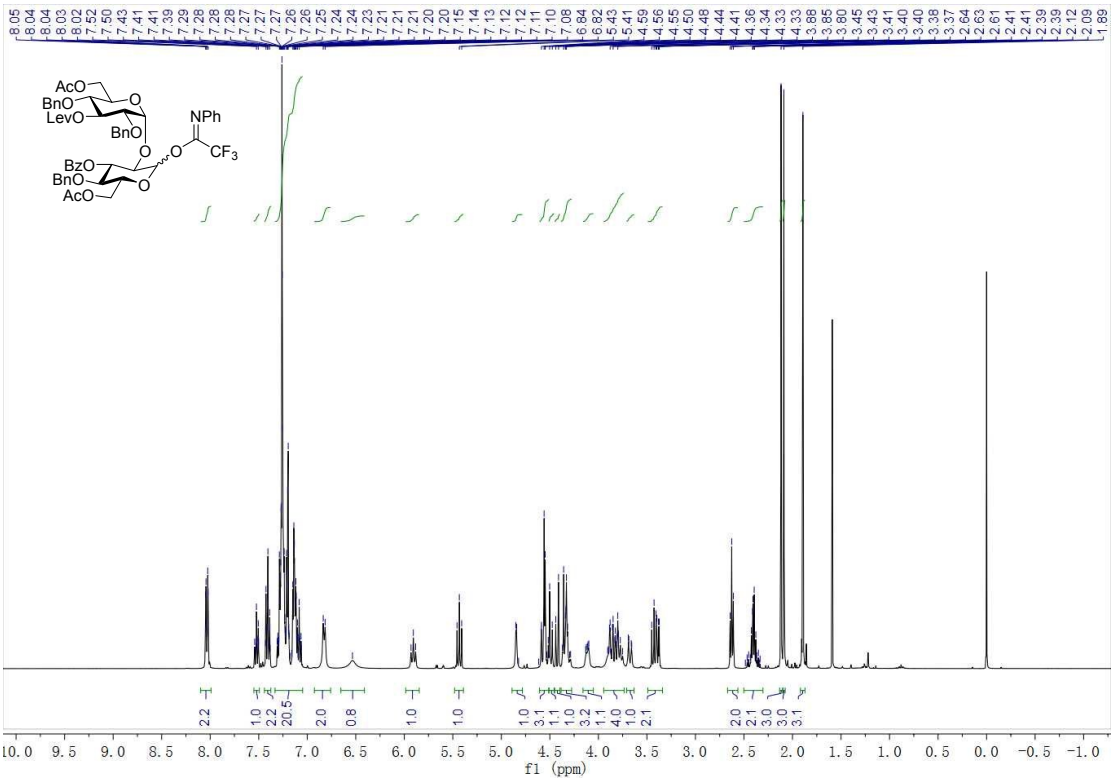
^{1}H-^{1}H COSY NMR spectra of compound **15β**



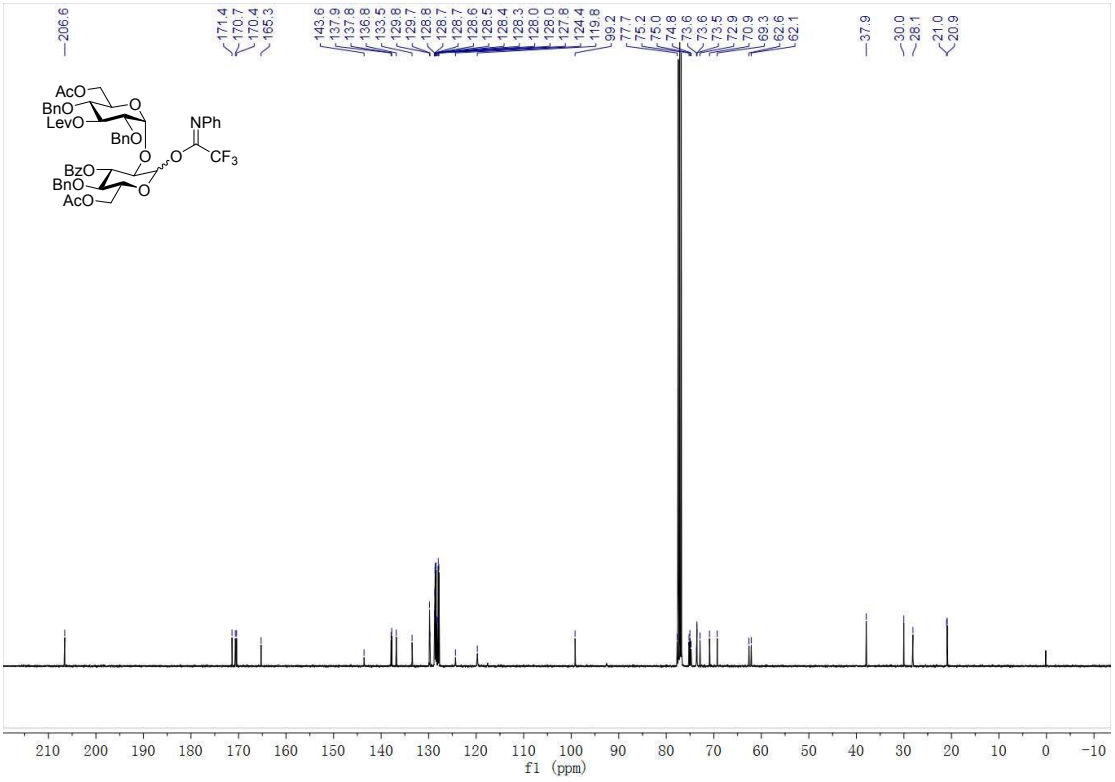
^{1}H-^{13}C HSQC NMR spectra of compound **15β**



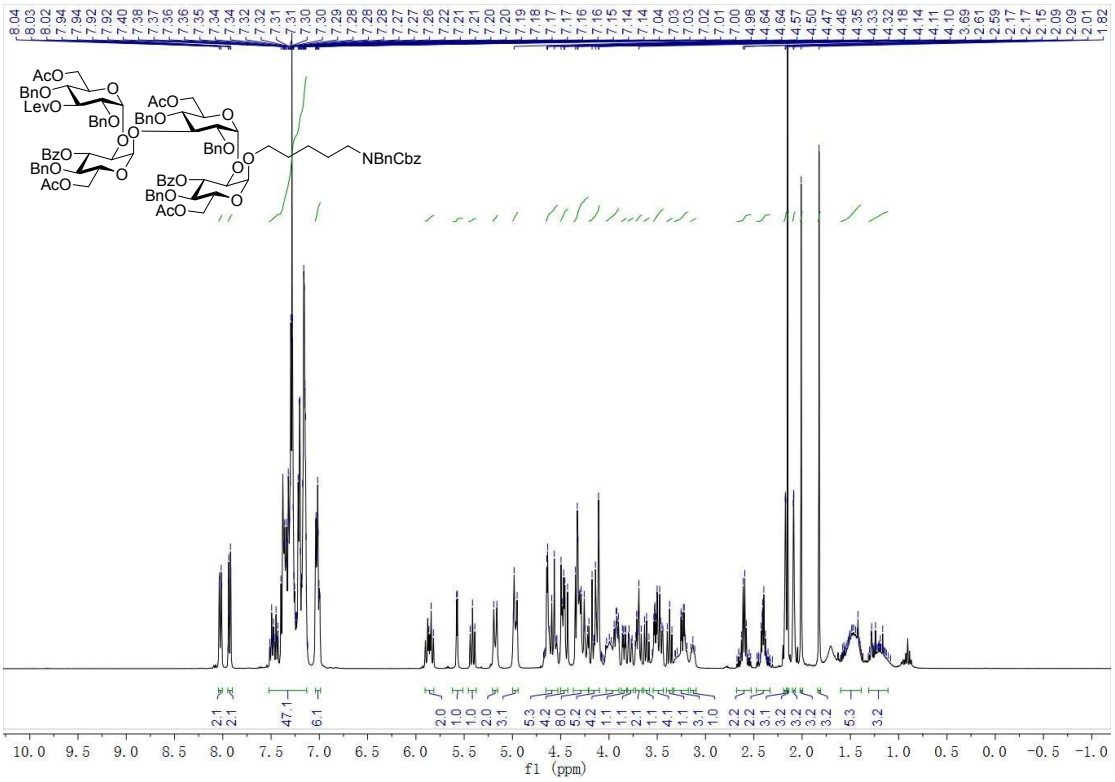
^{1}H NMR spectra of compound **16**



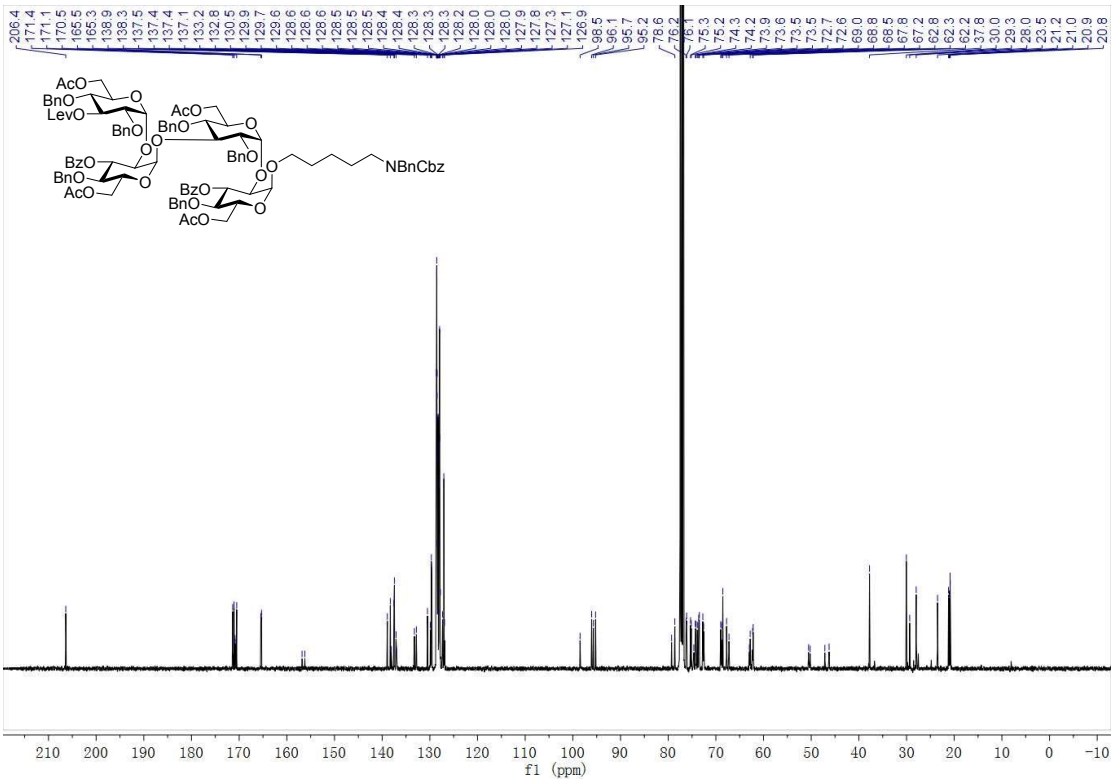
^{13}C NMR spectra of compound **16**



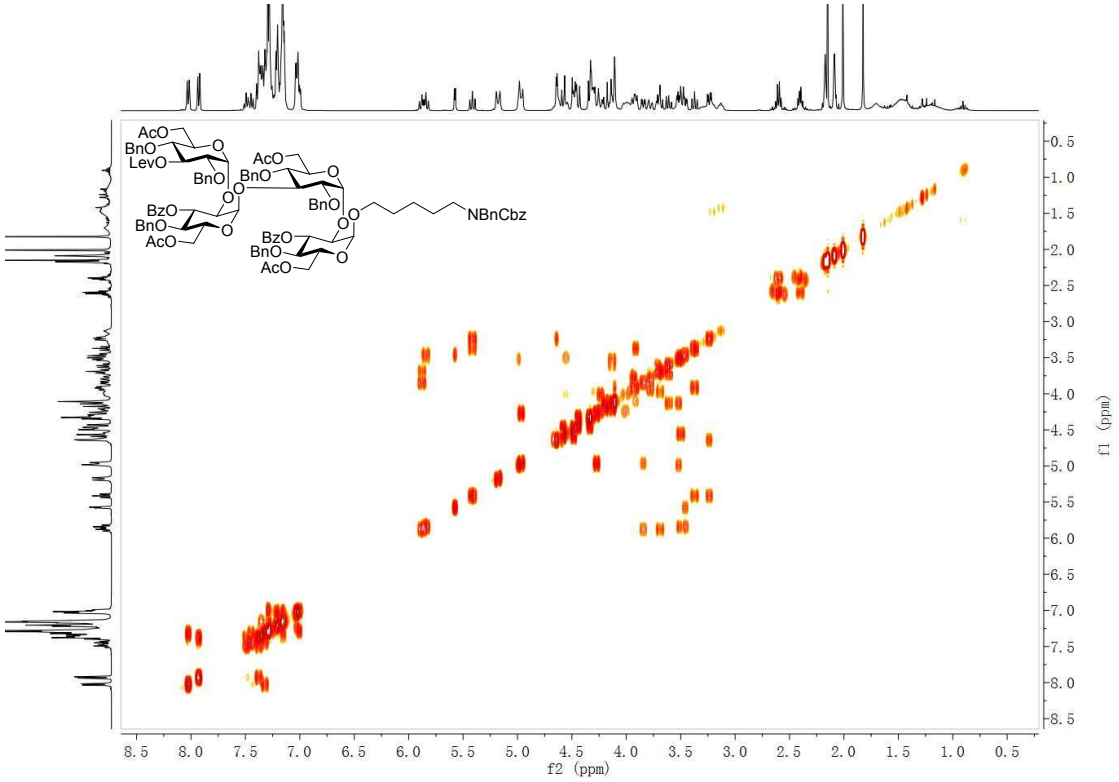
^{1}H NMR spectra of compound **18**



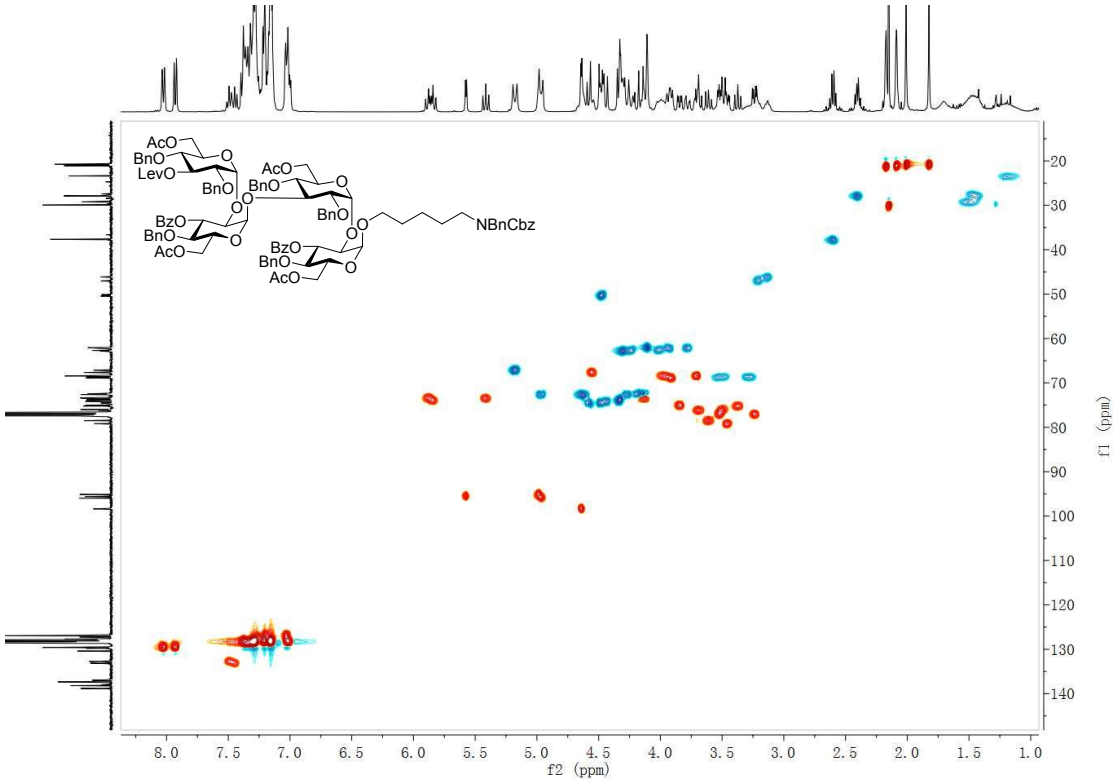
^{13}C NMR spectra of compound **18**



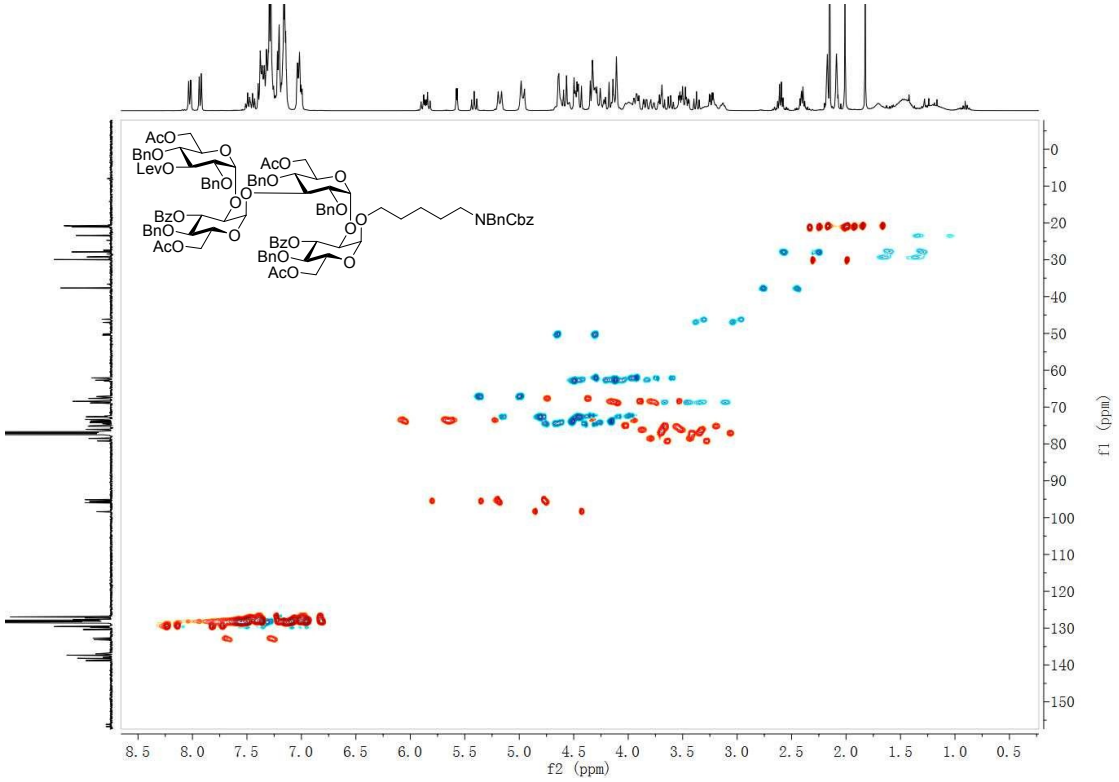
^{1}H-^{1}H COSY NMR spectra of compound **18**

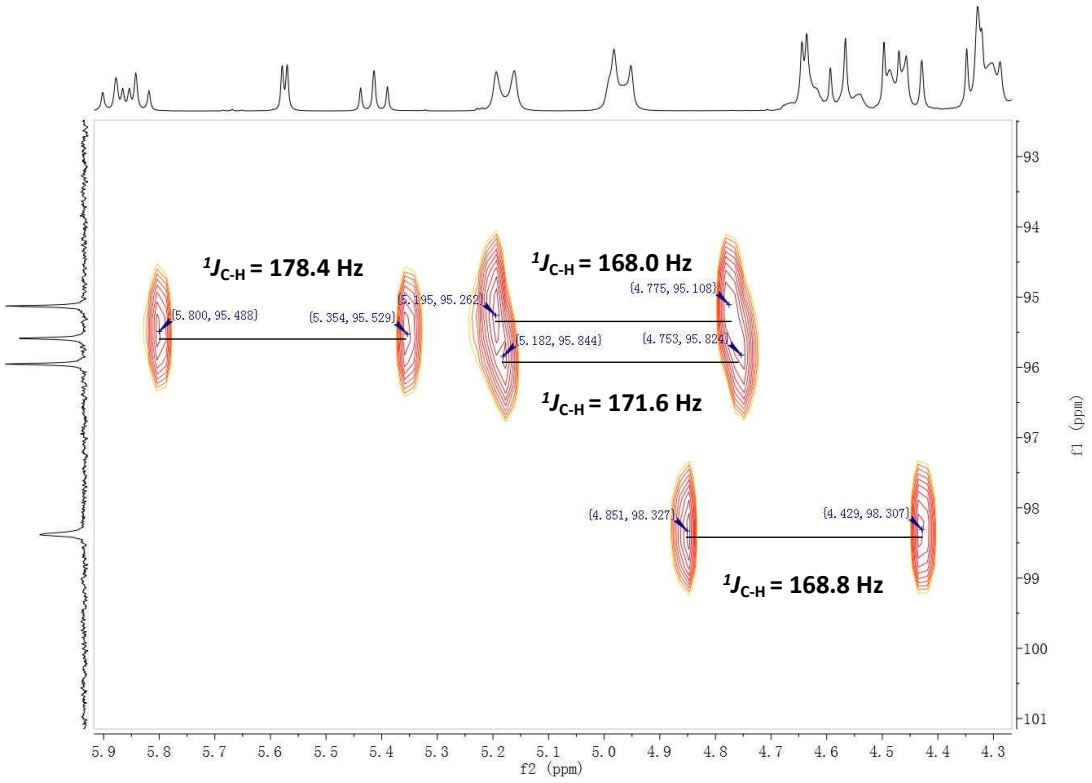


^{1}H-^{13}C HSQC NMR spectra of compound **18**

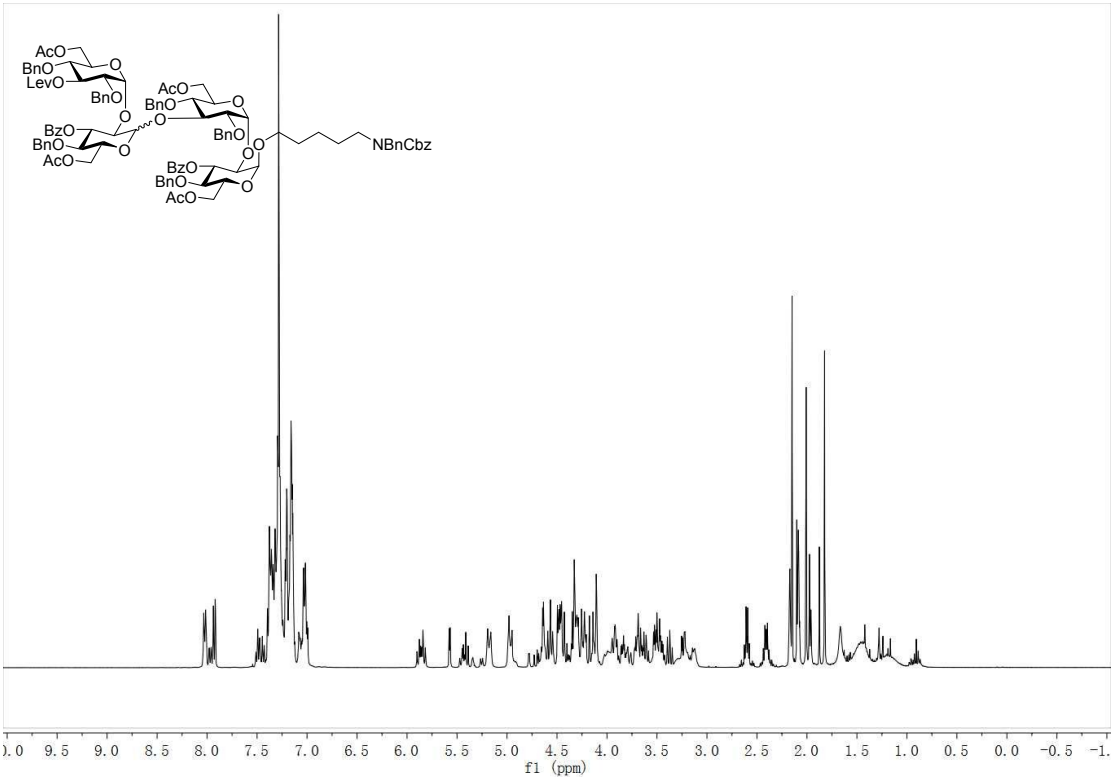


^{1}H-^{13}C coupling HSQC NMR spectrum of compound **18**

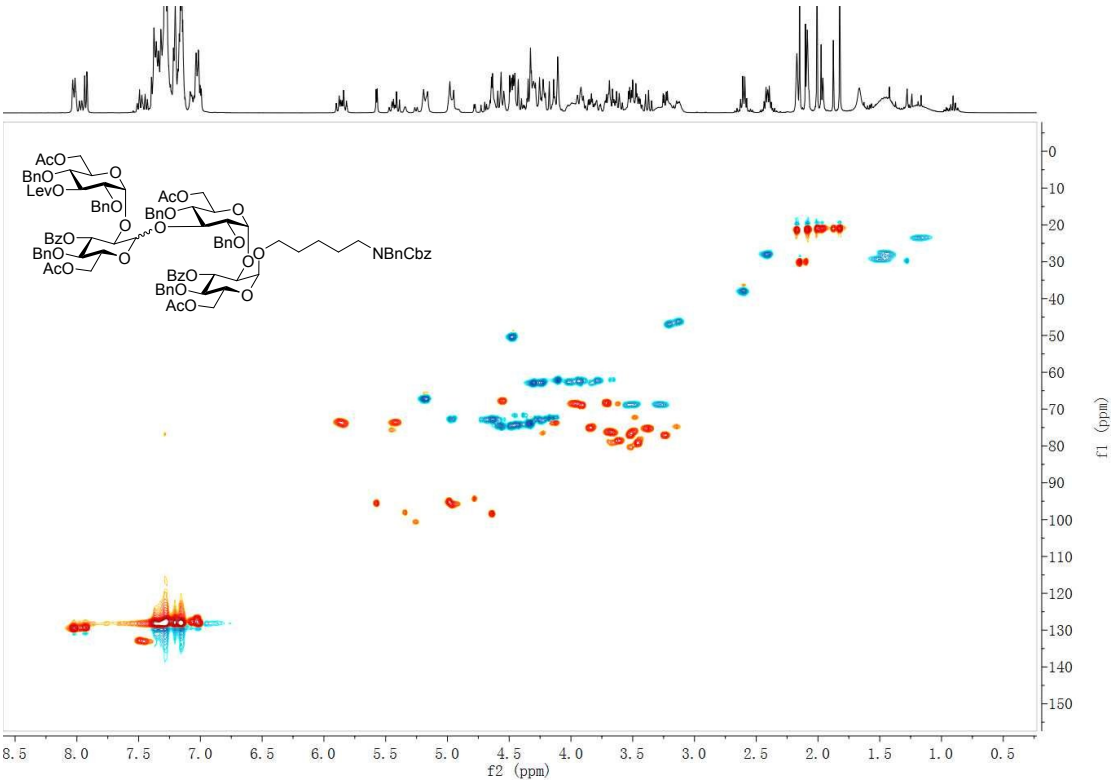




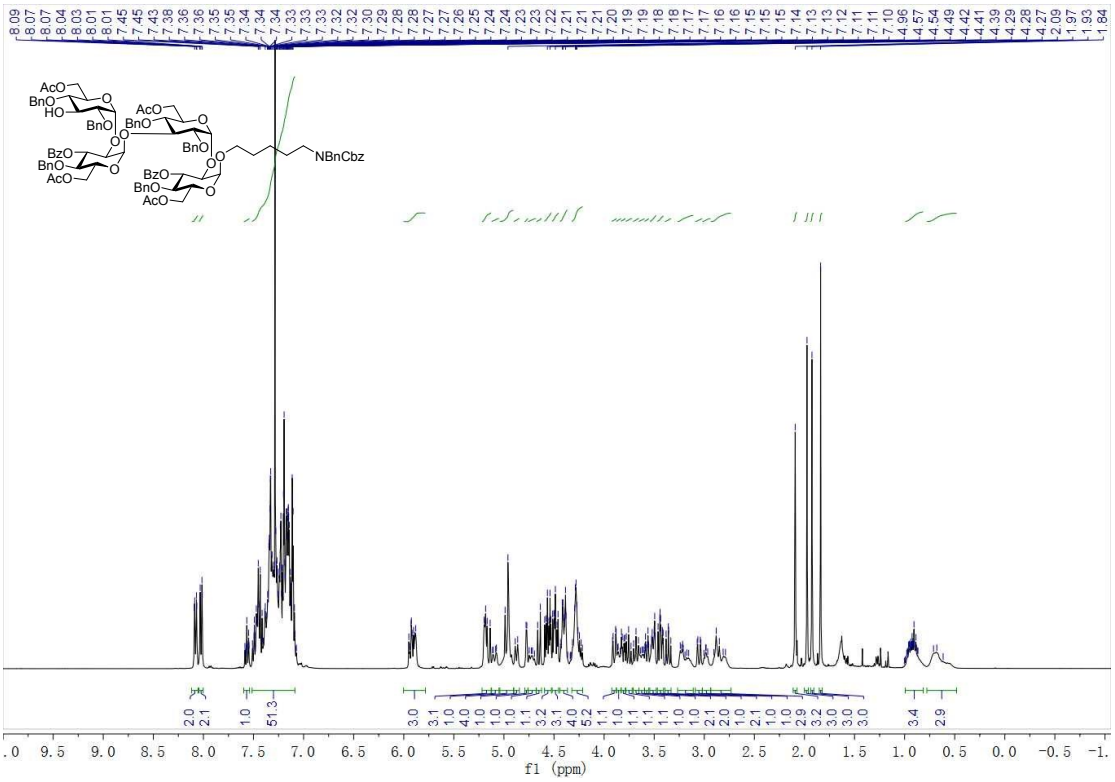
^{1}H NMR spectra of compound **18α** and **18β** (α/β= 2.7:1)



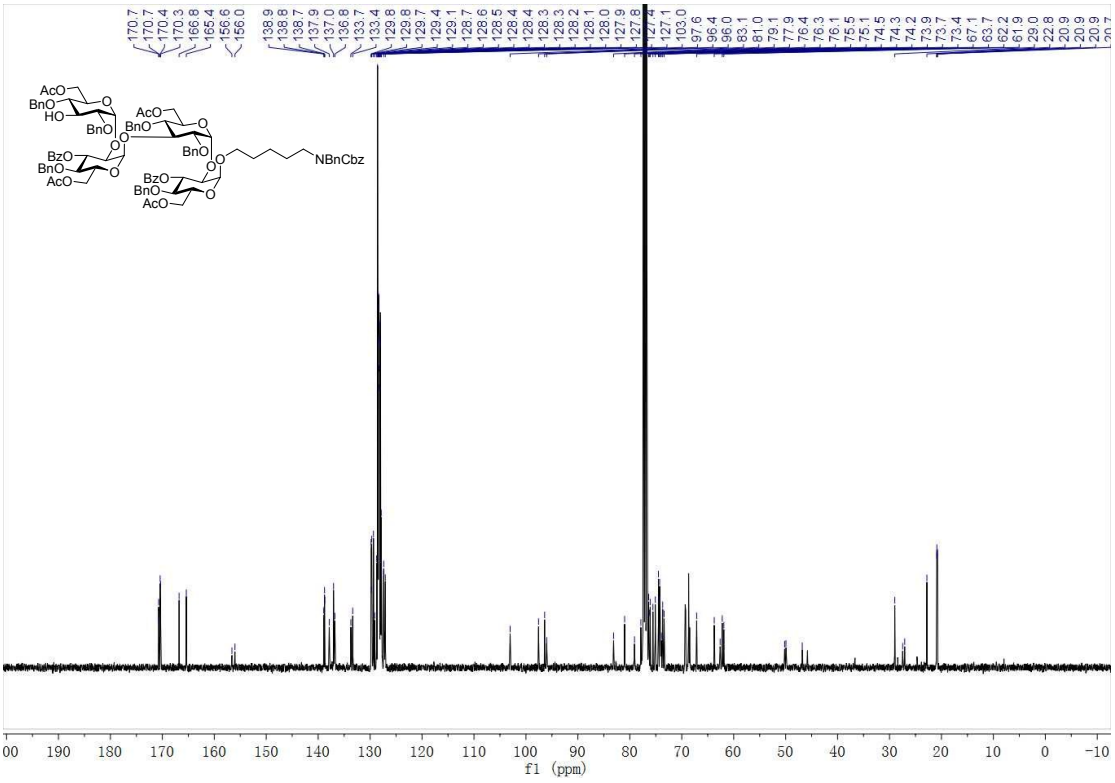
^{1}H-^{13}C HSQC NMR spectra of compound **18**



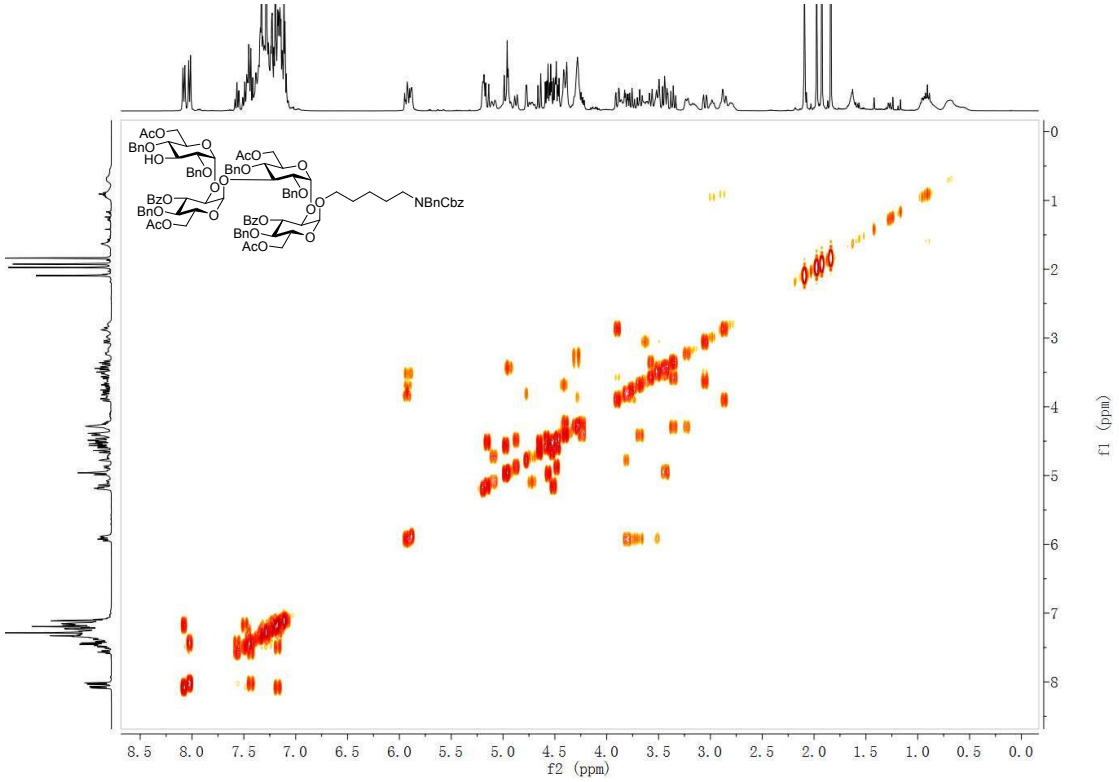
^{1}H NMR spectra of compound **19**



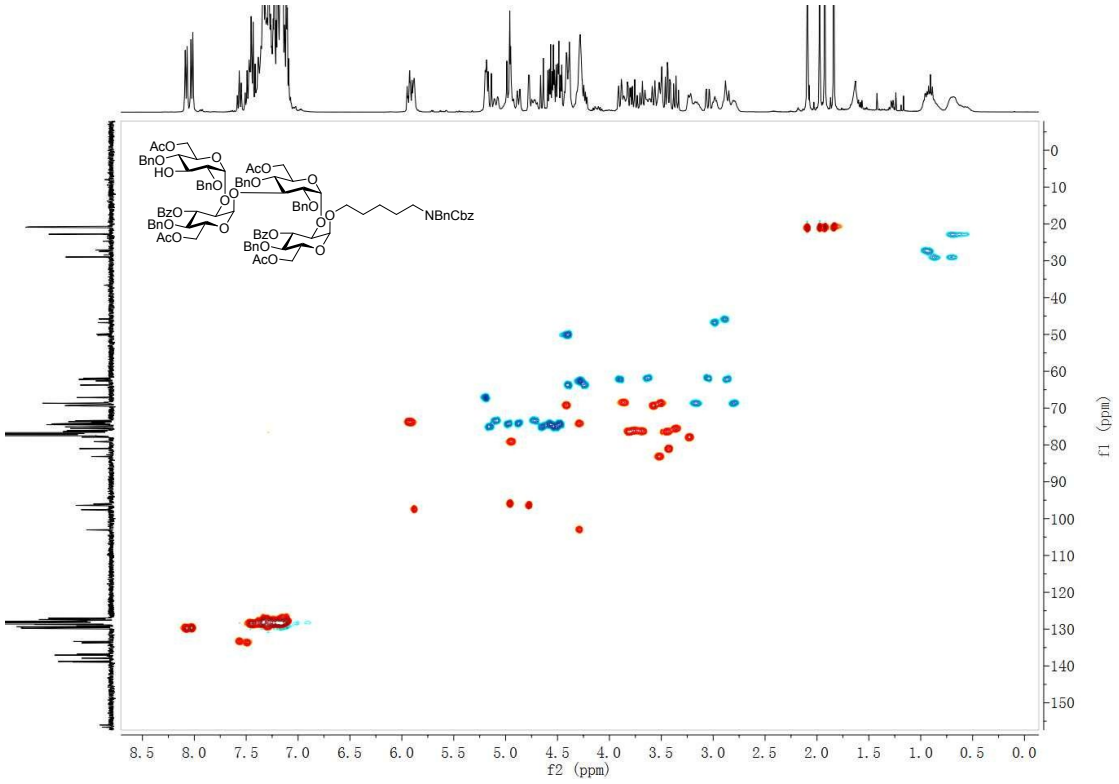
^{13}C NMR spectra of compound **19**



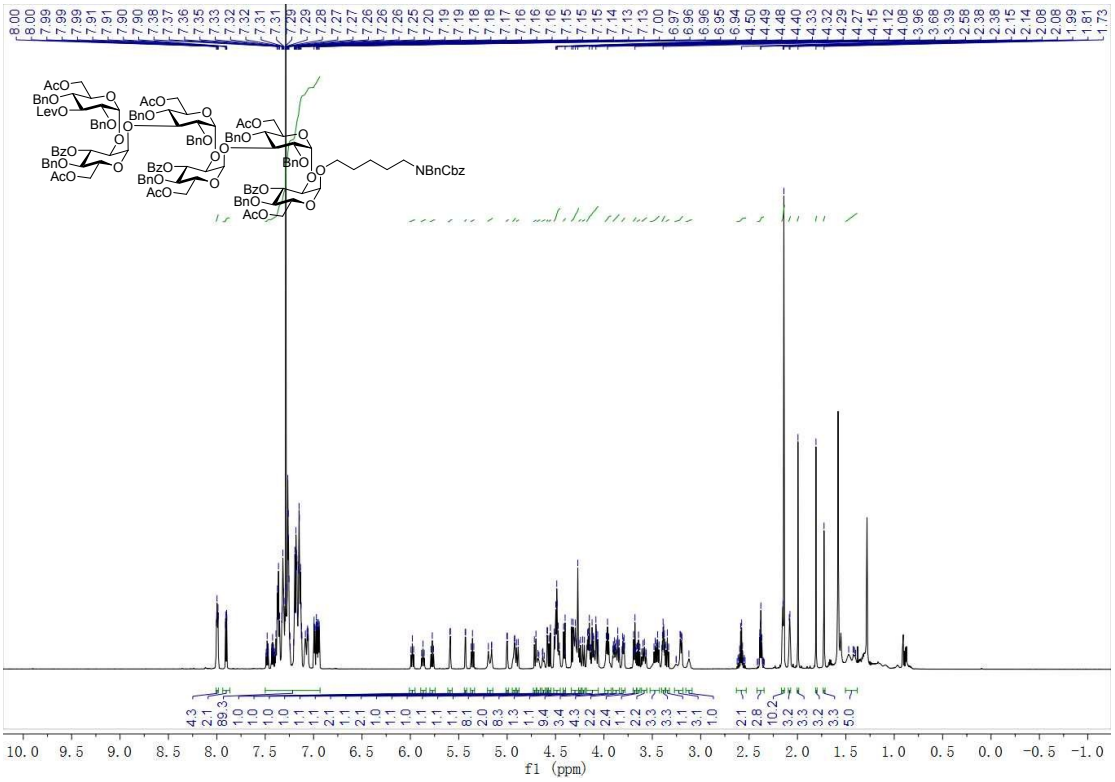
^{1}H-^{1}H COSY NMR spectra of compound **19**



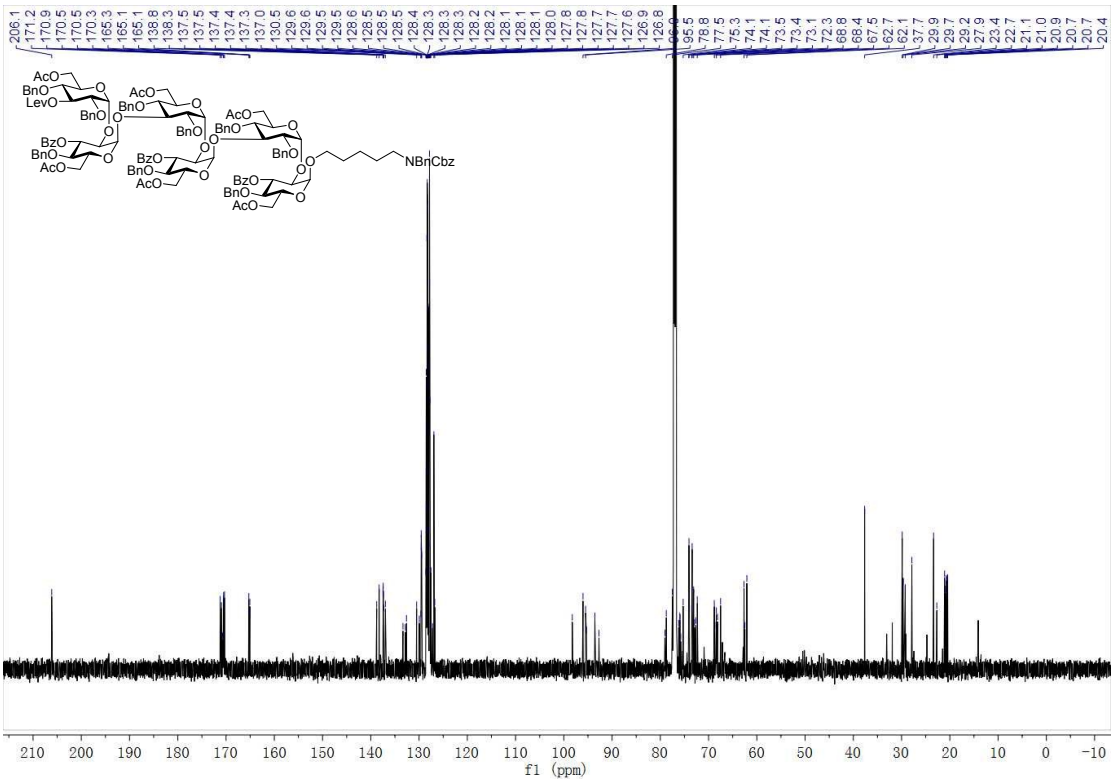
^{1}H-^{13}C HSQC NMR spectra of compound **19**



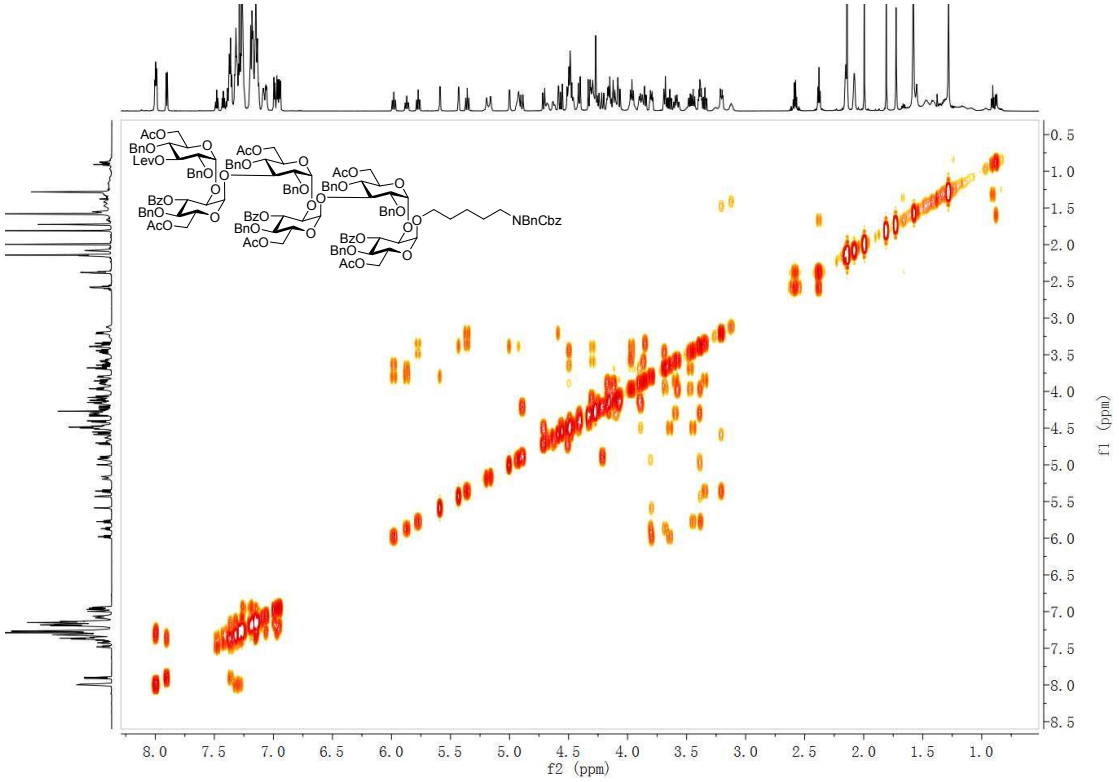
^{1}H NMR spectra of compound **20**



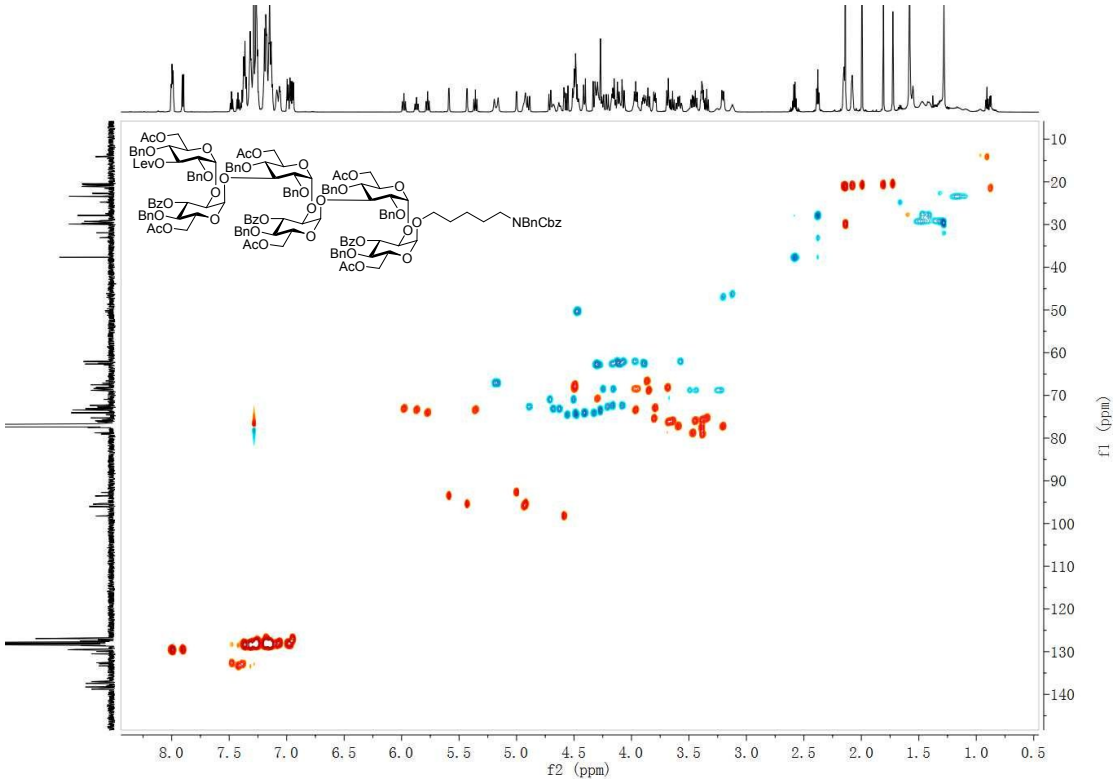
^{13}C NMR spectra of compound **20**



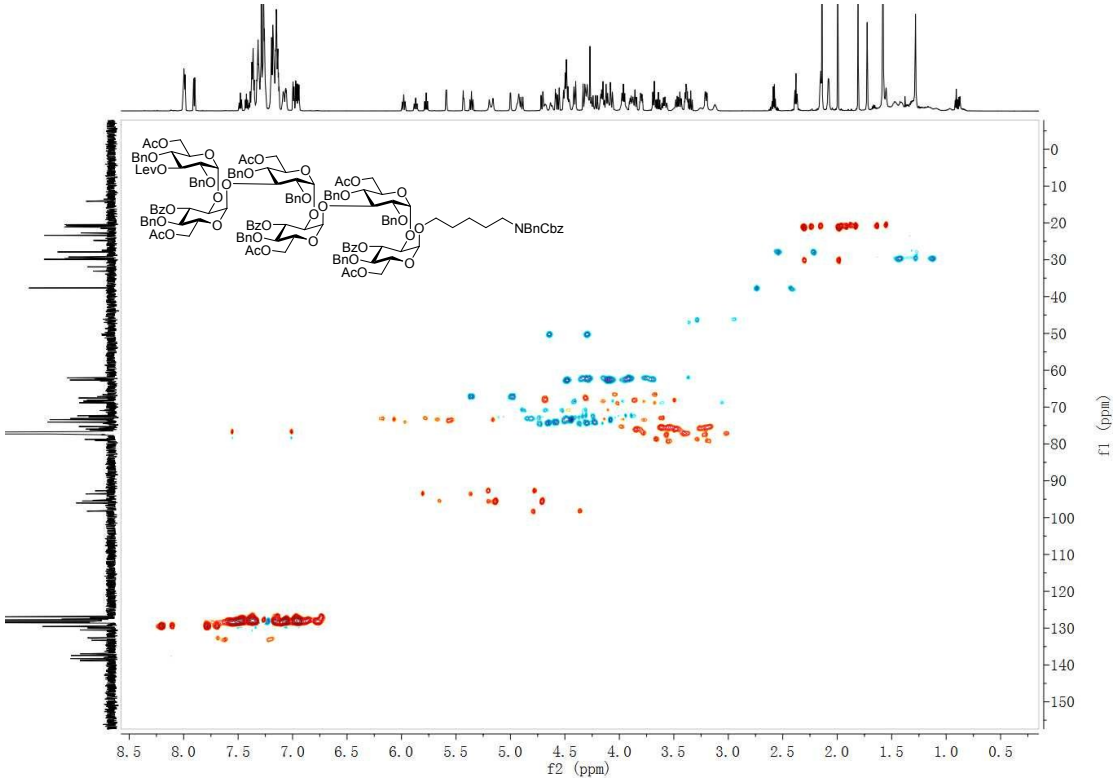
^{1}H-^{1}H COSY NMR spectra of compound **20**

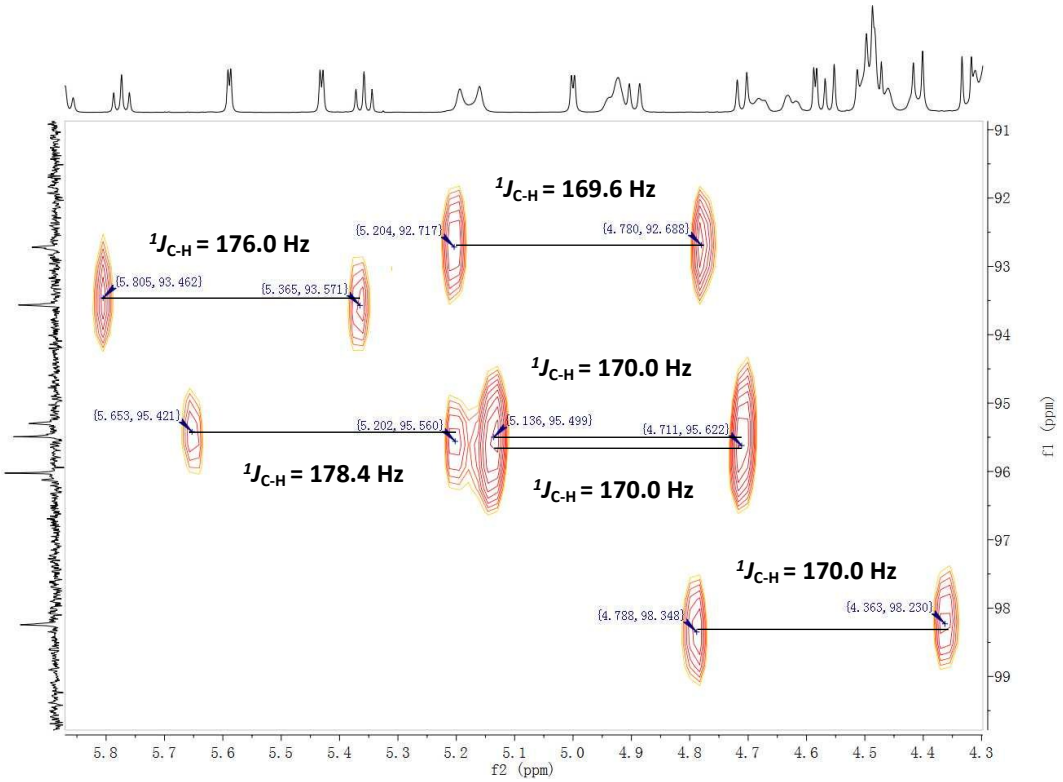


^{1}H-^{13}C HSQC NMR spectra of compound **20**

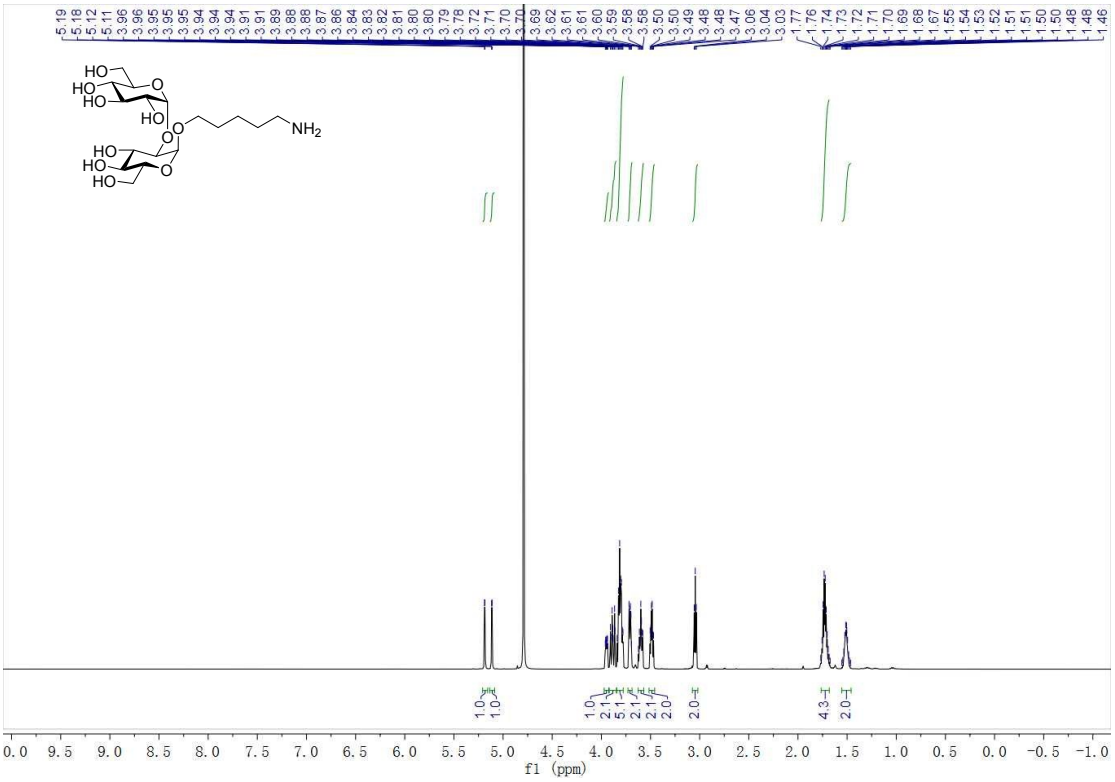


^{1}H-^{13}C coupling HSQC NMR spectrum of compound **20**

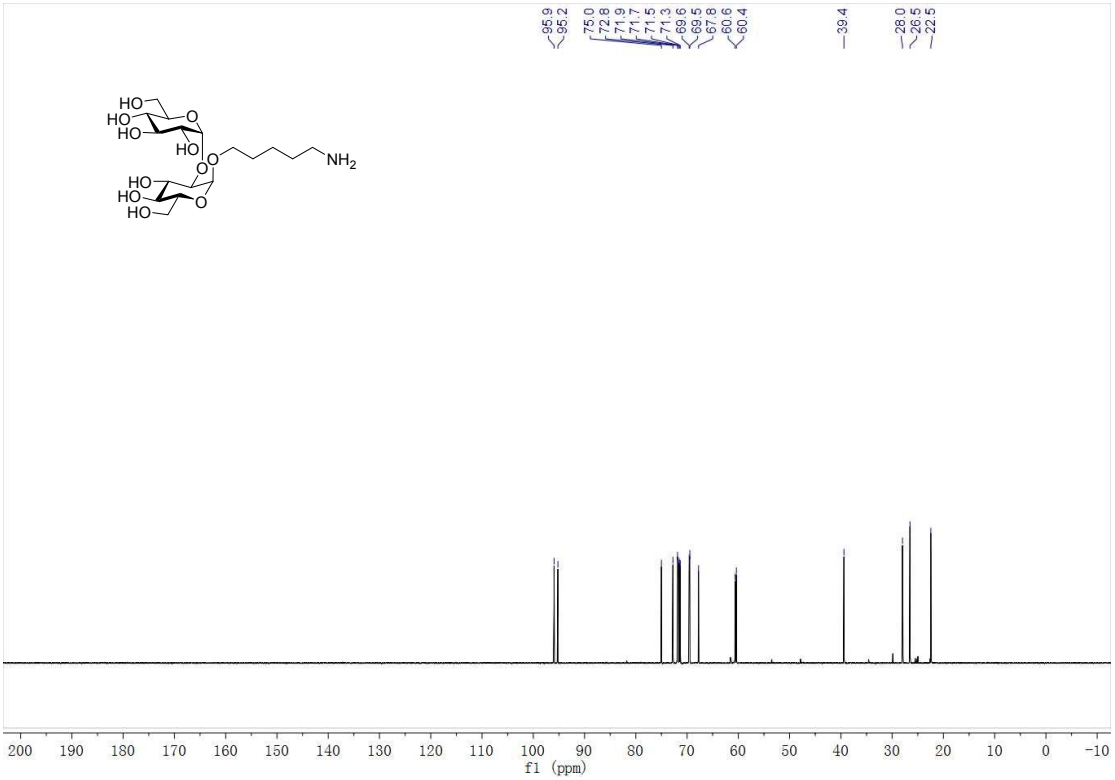




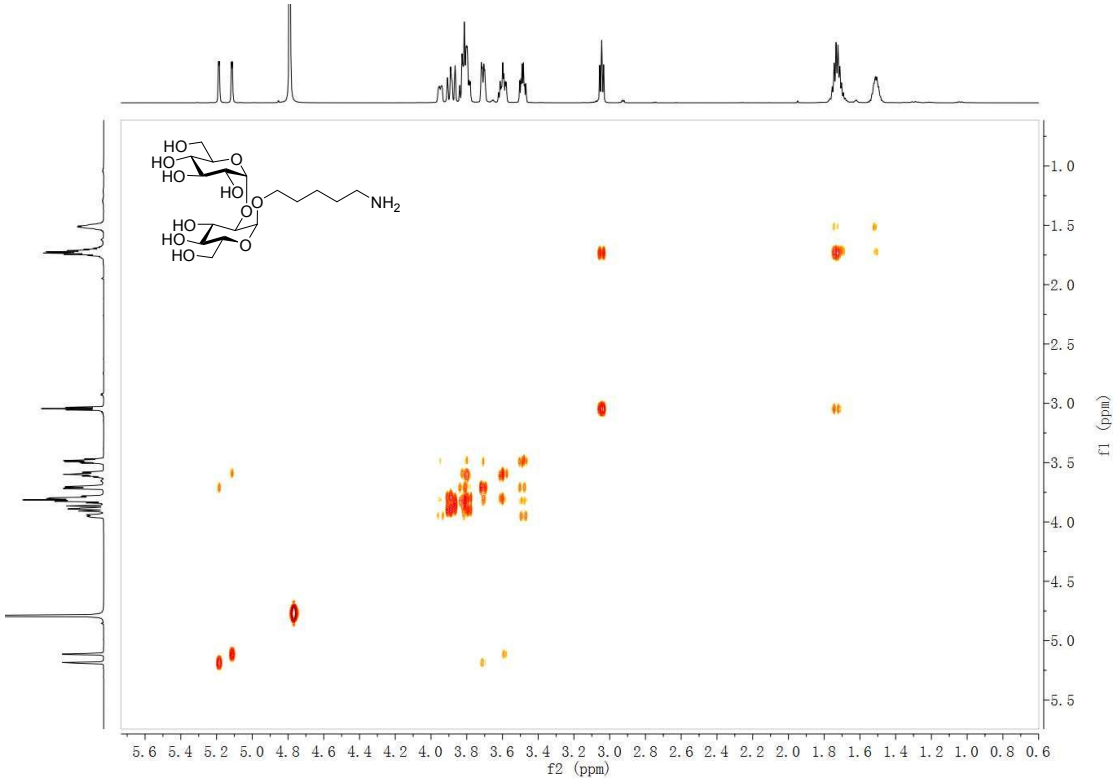
^{1}H NMR spectra of compound **21**



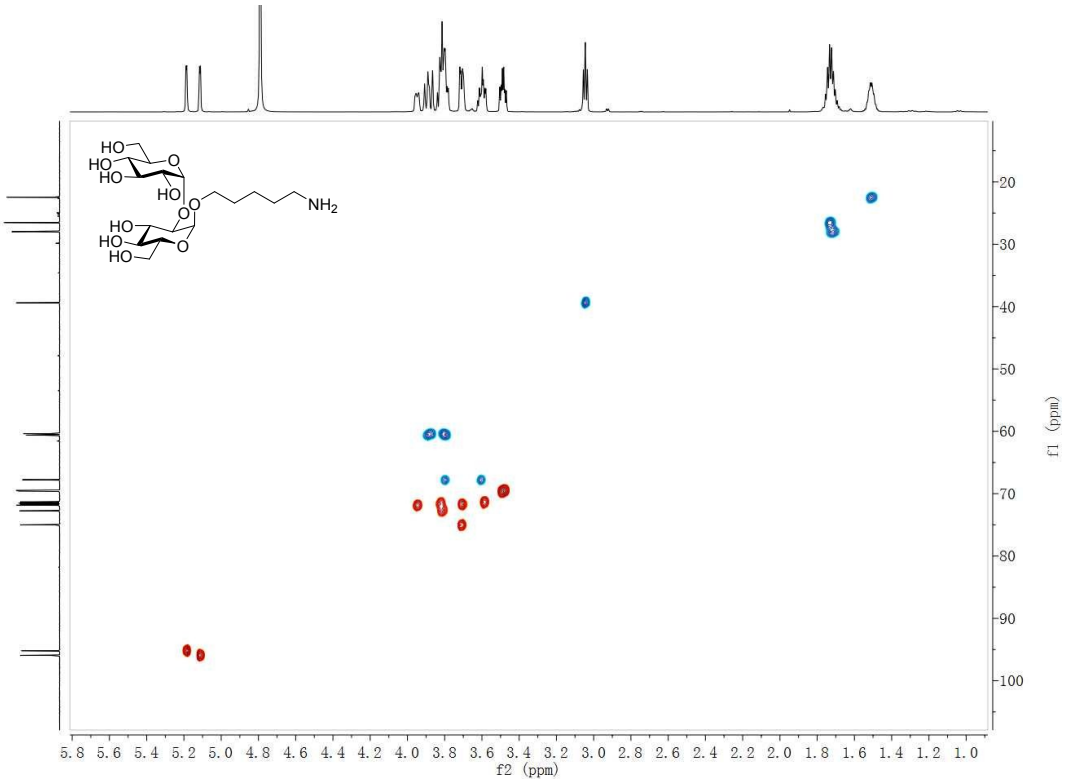
^{13}C NMR spectra of compound **21**



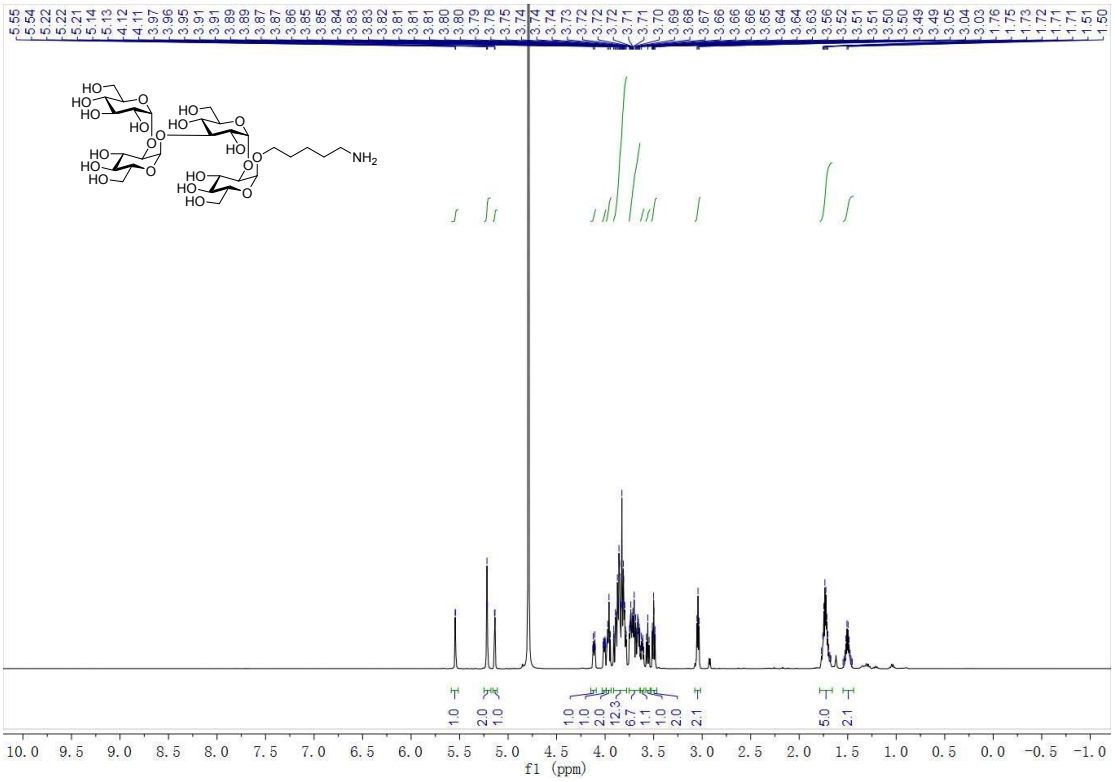
^{1}H-^{1}H COSY NMR spectra of compound **21**



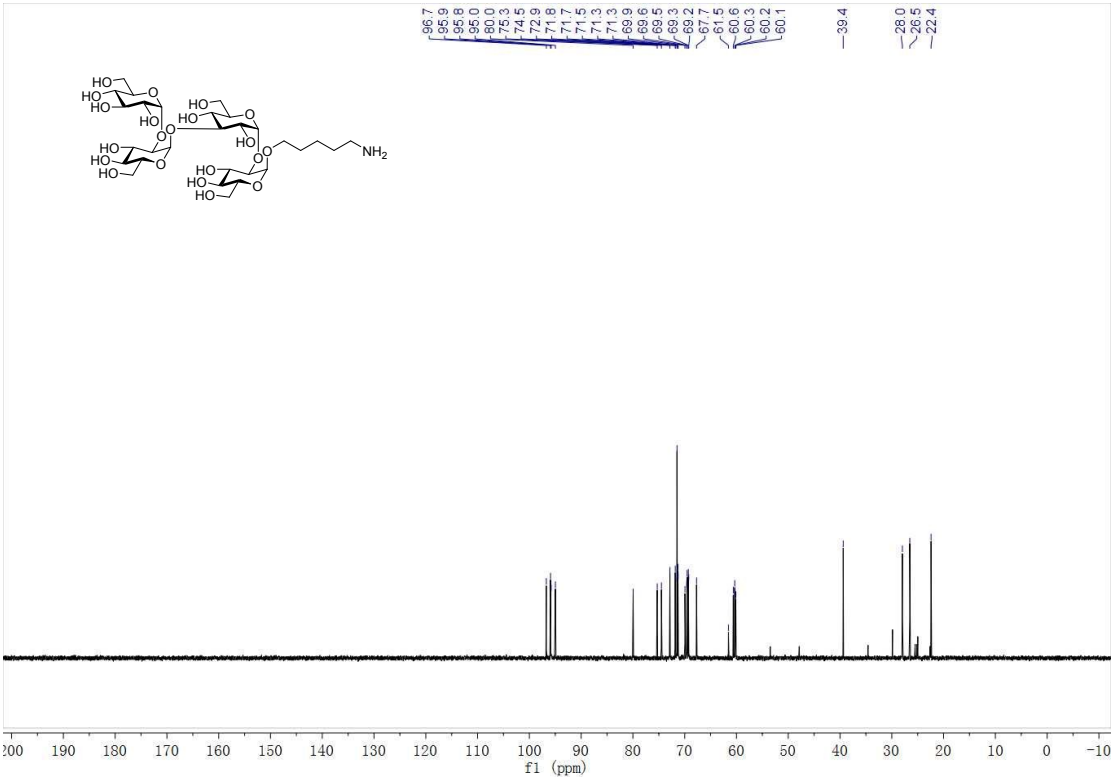
^{1}H-^{13}C HSQC NMR spectra of compound **21**



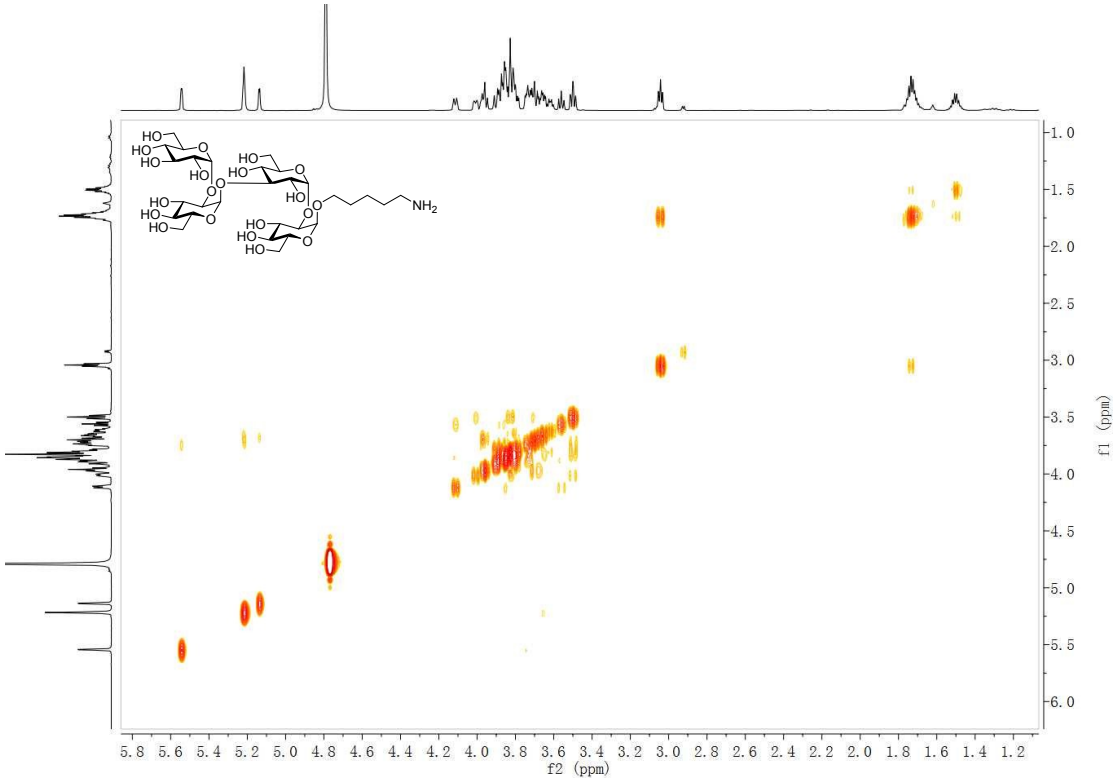
^{1}H NMR spectra of compound **22**



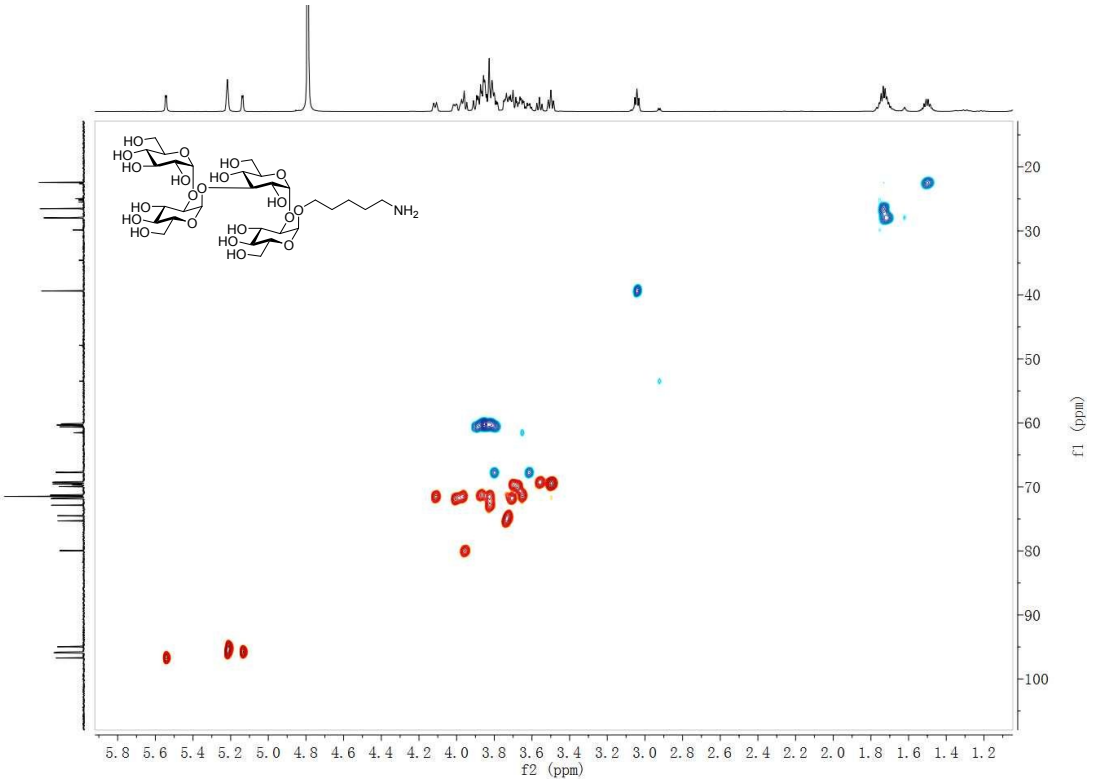
^{13}C NMR spectra of compound **22**



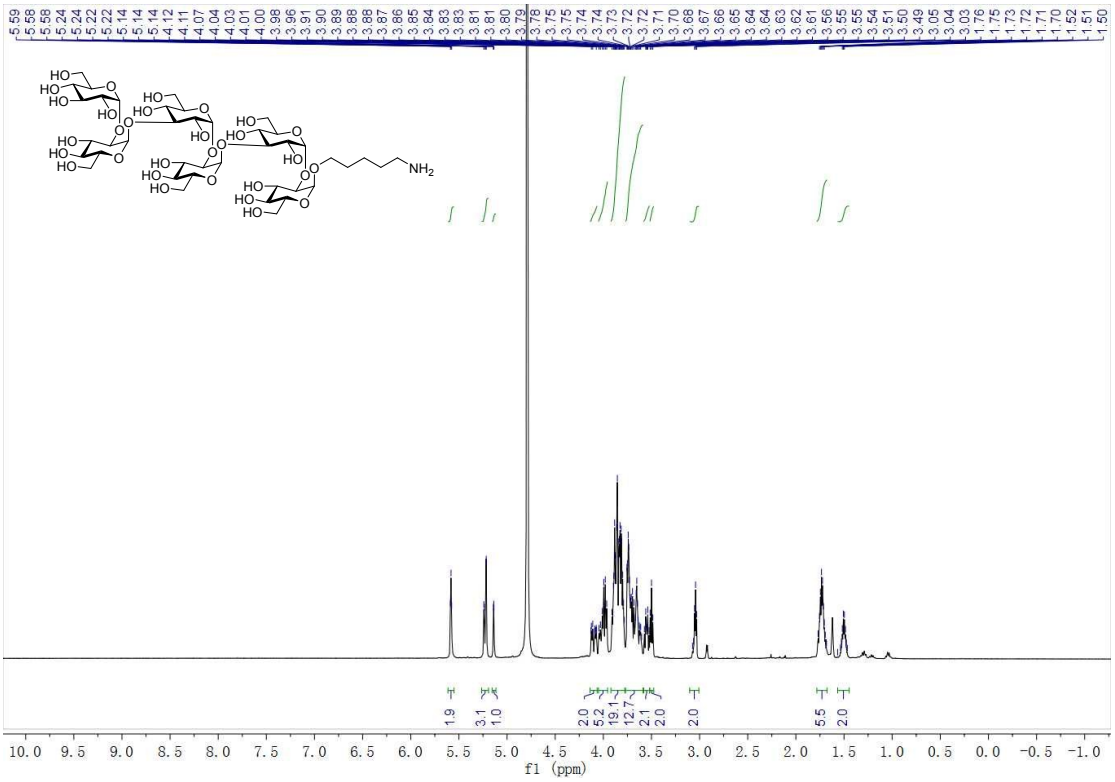
^{1}H-^{1}H COSY NMR spectra of compound **22**



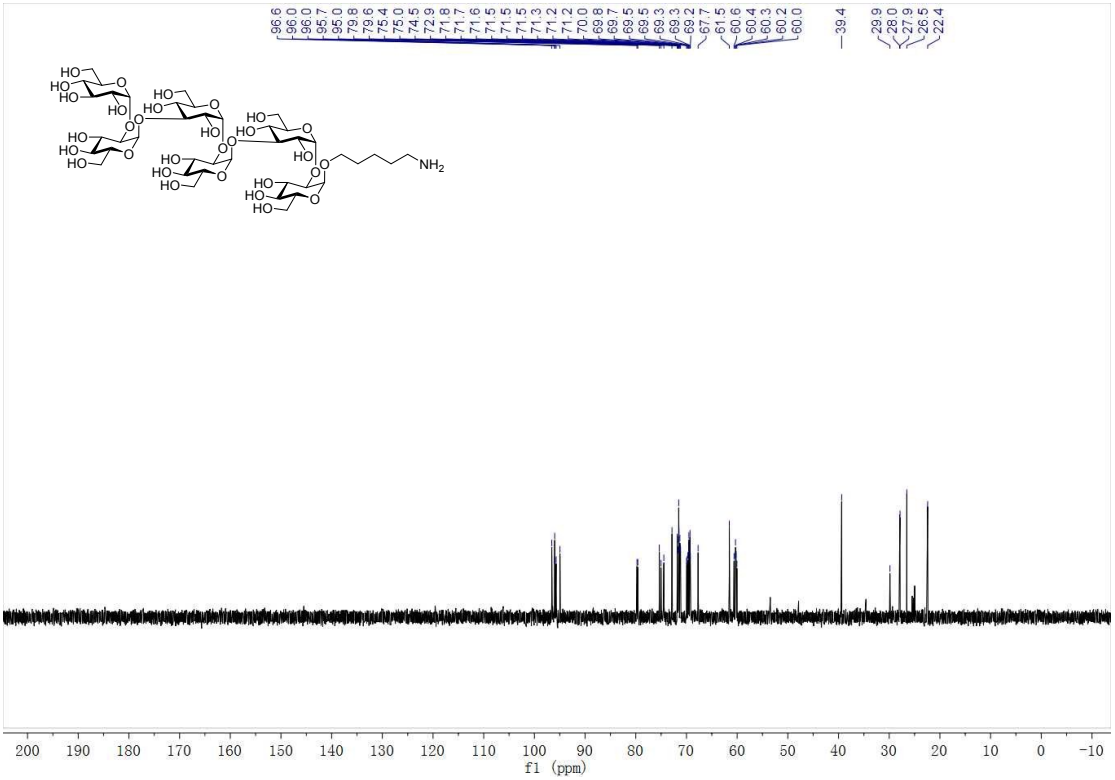
^{1}H-^{13}C HSQC NMR spectra of compound **22**



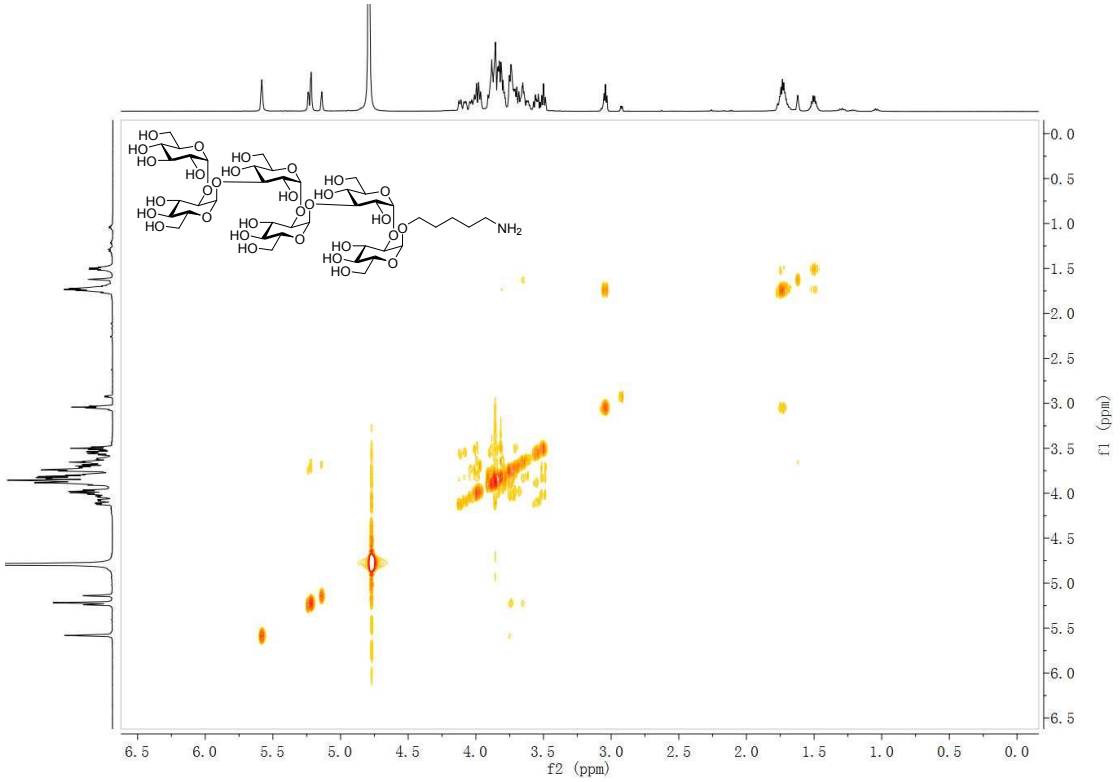
^{1}H NMR spectra of compound **23**



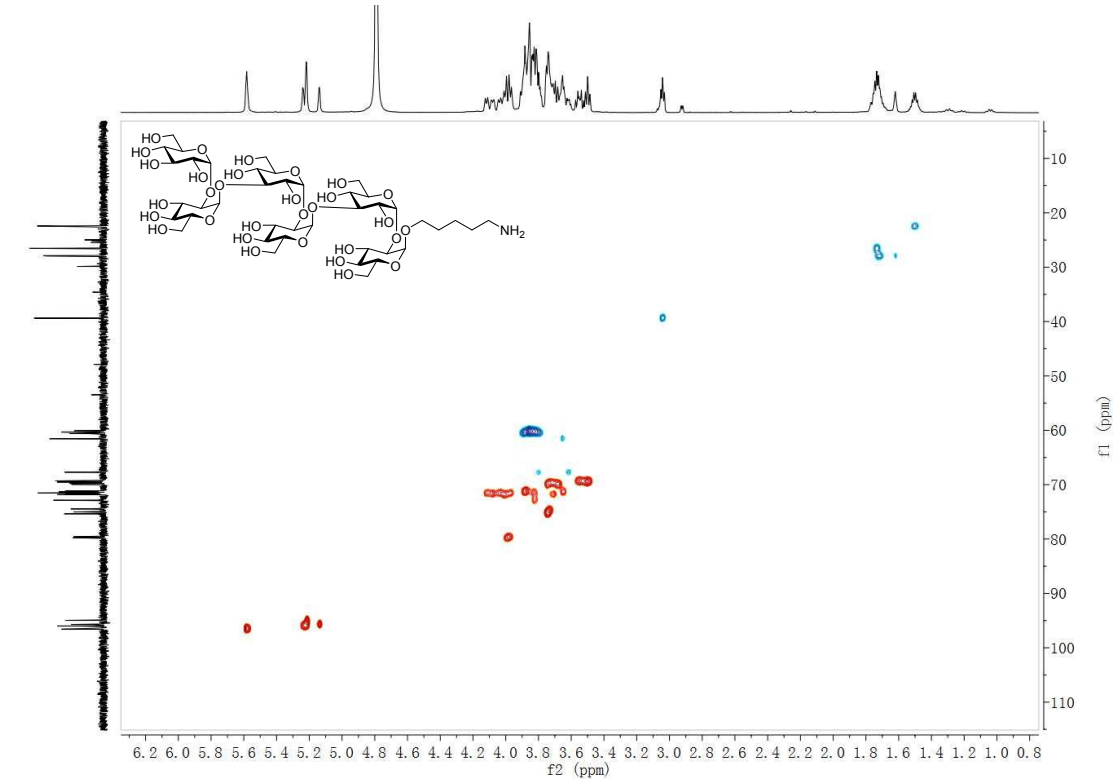
^{13}C NMR spectra of compound **23**



^{1}H-^{1}H COSY NMR spectra of compound **23**



^{1}H-^{13}C HSQC NMR spectra of compound **23**



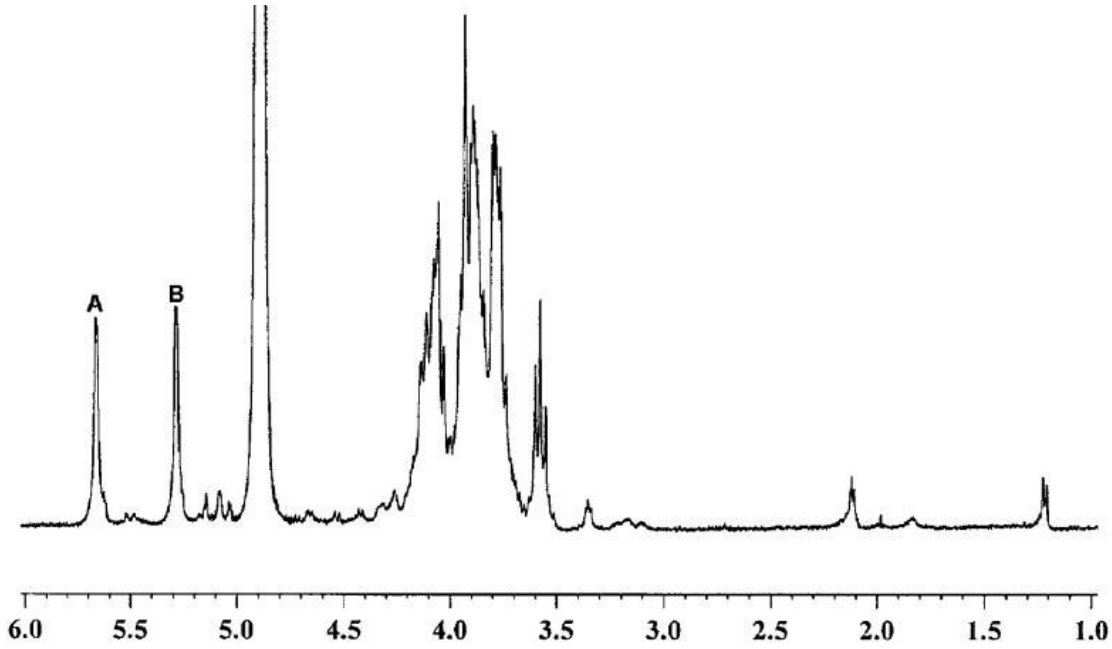


Figure S-1. [1]H NMR spectrum of isolated *H. pylori* O2 O-antigen PS[7].

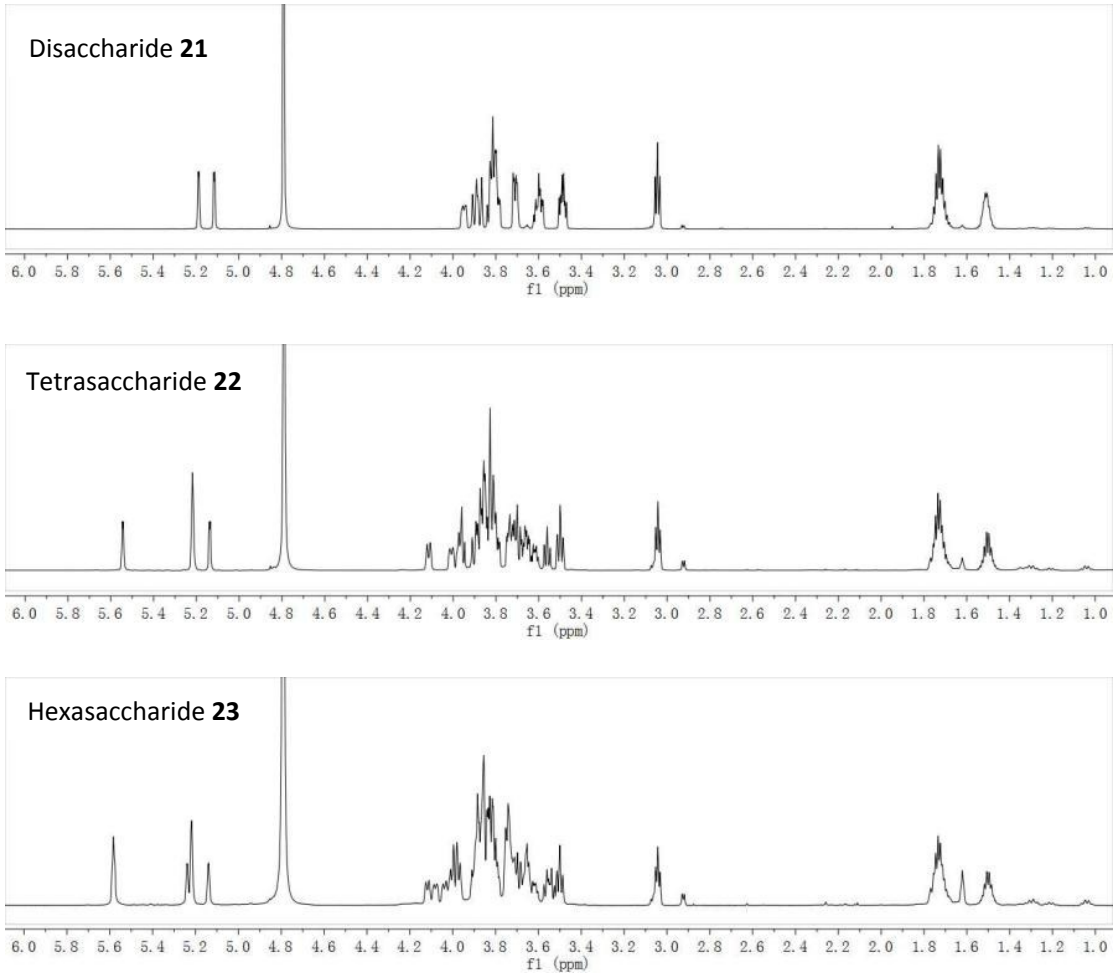


Figure S-2. [1]H NMR spectrum of synthetic *H. pylori* O2 oligosaccharide (di, tetra and hexasaccharides)