Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Synthesis of branched-chain sugars and higher-carbon sugars enabled by site-selective C─H alkylation relying on 1,5-hydrogen atom transfer of ethylenoxy radicals

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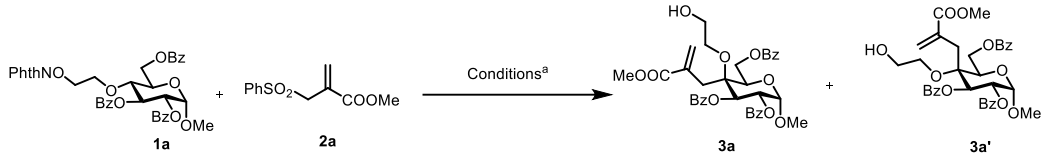
General information

Unless otherwise stated, all commercially obtained reagents were used directly without further purification and all reactions were carried out in glassware or a standard Schlenk technique with magnetic stirring. Anhydrous dichloromethane (DCM), tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF) were obtained from an MBraun solvent purification system (SPS-800). Flash column chromatography was performed on Silica Gel H (300-400 or 200-300 mesh, Qingdao, China) using petroleum ether (PE), ethyl acetate (EA), DCM, methanol (MeOH) and mixtures thereof as the eluent. Analytical thin layer chromatography (TLC) was performed on Silicycle SiliaPlate glass-backed plates coated with silica gel (60 Å pore size, F-254 indicator) and visualized by exposure to ultraviolet light and/or staining with 8% sulfuric acid in methanol. HRMS (High-resolution mass spectra) were determined with a Thermo LTQ Orbitrap XL high-resolution mass spectrometer. Optical rotations were determined with a JASCO P-1010 digital polarimeter. NMR spectra were measured on a Bruker AVENCE NEO 400 MHz spectrometer using chloroform-*d* ($CDCl_3$), methanol-d_4 as the solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (TMS: δ 0.00 for ^1H, Chloroform-*d*: δ 7.26 for ^1H, δ 77.00 for ^{13}C, Methanol-d_4: δ 3.31 for ^1H, δ 49.15 for ^{13}C. Data are reported as follows: chemical shifts (δ), multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet), coupling constants *J* (Hz).

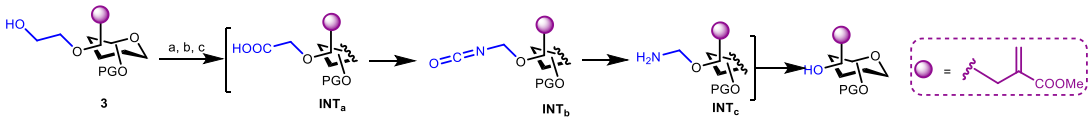
Table S1 Optimization of reaction condition[a]

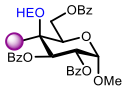
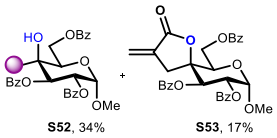
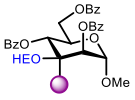
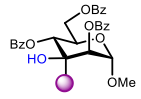
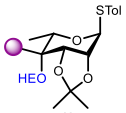
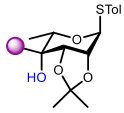
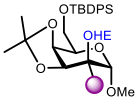
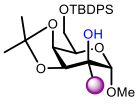


Entry	Solvents	Concentration (mol/L)	Yield of **3a**[b]	Yield of **3a'**[b]
1	1,4-dioxane	0.05	42% (38%)[c]	20% (21%)[c]
2	THF	0.05	trace	
3	CH_3CN	0.05	no reaction	
4	Actone	0.05	34%	12%
5	$PhCF_3$	0.05	40%	20%
6	PhCl	0.05	26%	18%
7	PhMe	0.05	27%	17%
8	DCE	0.05	33%	14%
9	MTBE	0.05	no reaction	
10	MTBE/1,4-dioxane (9:1)	0.05	40%	20%
11	1,4-dioxane	0.1	37%	17%
12	1,4-dioxane	0.2	28%	13%
13[d]	1,4-dioxane	0.1	42%	18%
14[e]	1,4-dioxane	0.05	no reaction	
15[f]	1,4-dioxane	0.05	no reaction	

[a]Conditions: **1a** (0.10 mmol, 1.0 equiv), **2a** (0.30 mmol, 3.0 equiv), *fac*-Ir(ppy)$_3$ (0.001 mmol, 0.01 equiv) and Hantzsch ester (0.15 mmol, 1.5 equiv) in 2.0 mL solvent under argon atmosphere with blue LEDs (450 nm-470 nm) irradiation at 35 °C for 3 h, unless otherwise noted; [b]The Yields were determined by ^{1}H NMR analysis using 3,4,5-trichloropyridine as an internal standard; [c]The yields in the parenthesis were the isolated yields; [d] **2a** (0.60 mmol, 6.0 equiv) was used; [e]no light; [f]no *fac*-Ir(ppy)$_3$.

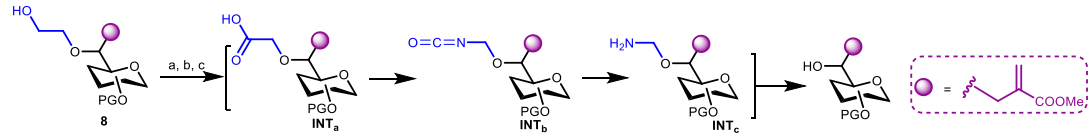
Table S2 Removal of the directing group 2-hydroxyethylene moiety of branched-chain sugars.

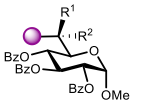
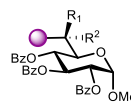
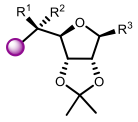
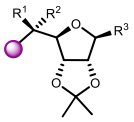
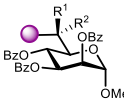
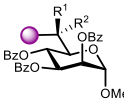
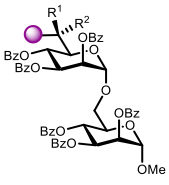
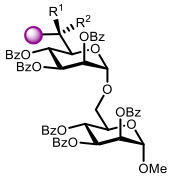
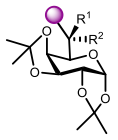
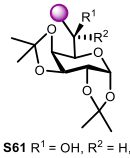


Entry	Substrate	Product	Entry	Substrate	Product
1	 **3a**	 **S52**, 34% **S53**, 17%	3	 **3n**	 **S55**, 57%
2	 **3j**	 **S54**, 60%	4	 **3p**	 **S56**, 58%

Reaction conditions: (a) TEMPO (0.1 equiv), BAIB (2.0 equiv), CH_2Cl_2/H_2O, rt, 3 h; (b) DPPA (1.2 equiv), DIPEA (1.2 equiv), DMF, rt, 3 h; (c) H_2O, 100 °C, 2 h.

Table S3 Removal of the directing group 2-hydroxyethylene moiety of higher-carbon sugars.



Entry	Substrate	Product	Entry	Substrate	Product
1	 **D-8a** R^1 = OHE, R^2 = H **L-8a** R^1 = H, R^2 = OHE	 **S57** R^1 = OH, R^2 = H, 56% **S58** R^1 = H, R^2 = OH, 49%	4	 **D-8d** R^1 = OHE, R^2 = H, R^3 = OMe **L-8d** R^1 = H, R^2 = OHE, R^3 = OMe **D-8e** R^1 = OHE, R^2 = H, R^3 = STol **L-8e** R^1 = H, R^2 = OHE, R^3 = STol	 **S63** R^1 = OH, R^2 = H, R^3 = OMe, 62% **S64** R^1 = H, R^2 = OH, R^3 = OMe, 49% **S65** R^1 = OH, R^2 = H, R^3 = STol, 49% **S66** R^1 = H, R^2 = OH, R^3 = STol, 52%
2	 **D-8b** R^1 = OHE, R^2 = H **L-8b** R^1 = H, R^2 = OHE	 **S59** R^1 = OH, R^2 = H, 54% **S60** R^1 = H, R^2 = OH, 53%	5	 **D-8f** R^1 = OHE, R^2 = H **L-8f** R^1 = H, R^2 = OHE	 **S67** R^1 = OH, R^2 = H, 61% **S68** R^1 = H, R^2 = OH, 53%
3	 **D-8c** R^1 = OHE, R^2 = H **L-8c** R^1 = H, R^2 = OHE	 **S61** R^1 = OH, R^2 = H, 58% **S62** R^1 = H, R^2 = OH, 60%			

Reaction conditions: (a) TEMPO (0.1 equiv), BAIB (2.0 equiv), CH_2Cl_2/H_2O, rt, 3 h; (b) DPPA (1.2 equiv), DIPEA (1.2 equiv), DMF, rt, 3 h; (c) H_2O, 100 °C, 2 h.

Stereochemical confirmation of compound S58 by Mosher ester analysis

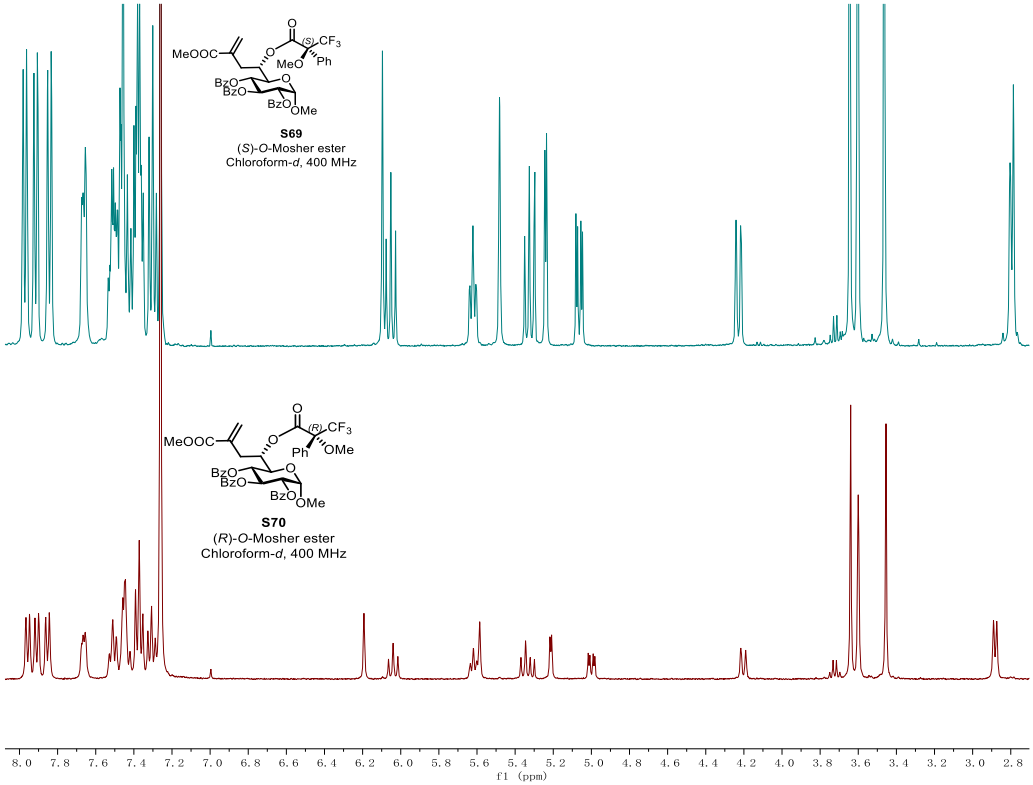
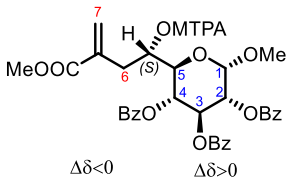
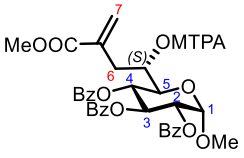


Figure S1 ^{1}H NMR spectra of (*S*)-*O*-mosher ester S69 and (*R*)-*O*-mosher ester S70

Table S4 ^{1}H NMR chemical shifts and Δδ values of (*S*)-*O*-mosher ester S69 and (*R*)-*O*-mosher ester S70



Mosher Model



NO.	δ_S	δ_R	$\Delta\delta=\delta_S-\delta_R$
1	5.24	5.21	0.03
2	5.06	5.00	0.06
3	6.05	6.04	0.01
4	5.35	5.32	0.03
5	4.22	4.21	0.01
6	2.79	2.88	-0.07
7a	6.10	6.19	-0.09
7b	5.48	5.58	-0.1

Stereochemical confirmation of compound S60 by Mosher ester analysis

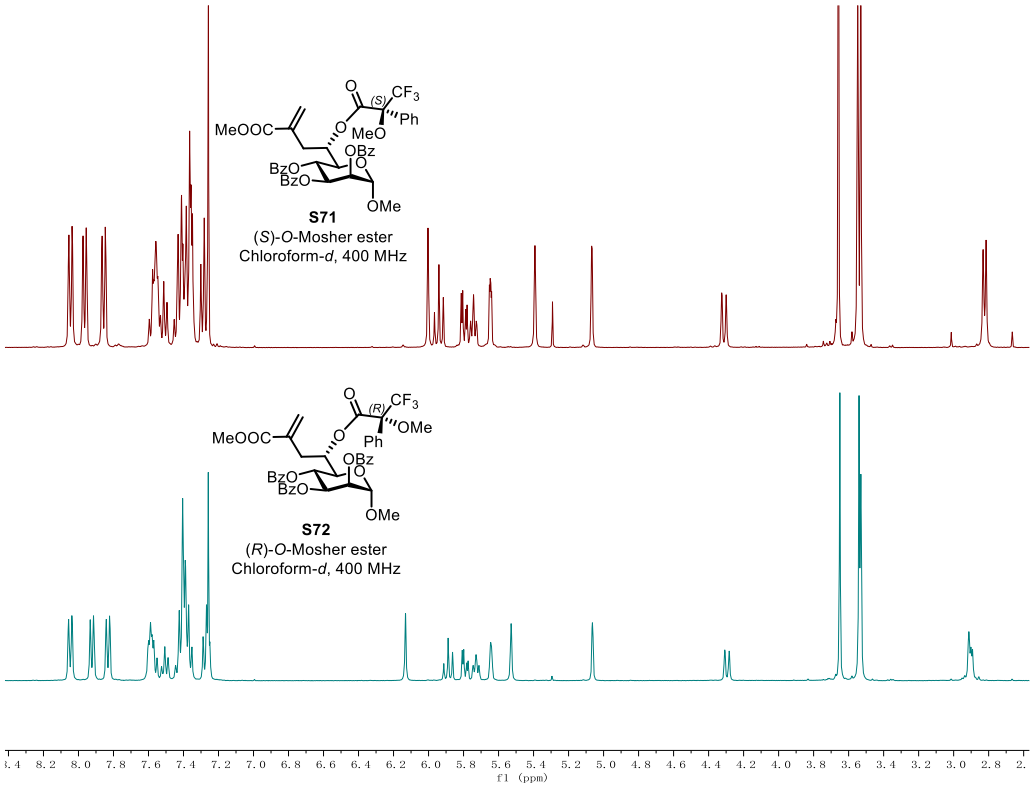
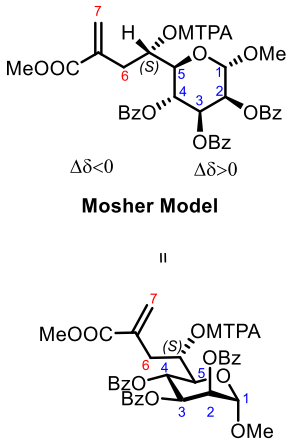


Figure S2 ^{1}H NMR spectra of (*S*)-*O*-mosher ester S71 and (*R*)-*O*-mosher ester S72

Table S5 ^{1}H NMR chemical shifts and Δδ values of (*S*)-*O*-mosher ester S71 and (*R*)-*O*-mosher ester S72



NO.	δ_S	δ_R	$\Delta\delta=\delta_S-\delta_R$
1	5.07	5.06	0.01
2	5.65	5.64	0.01
3	5.80	5.79	0.01
4	5.94	5.89	0.05
5	4.31	4.30	0.01
6	2.82	2.90	-0.08
7a	6.00	6.13	-0.13
7b	5.33	5.53	-0.20

Stereochemical confirmation of compound S61 by Mosher ester analysis

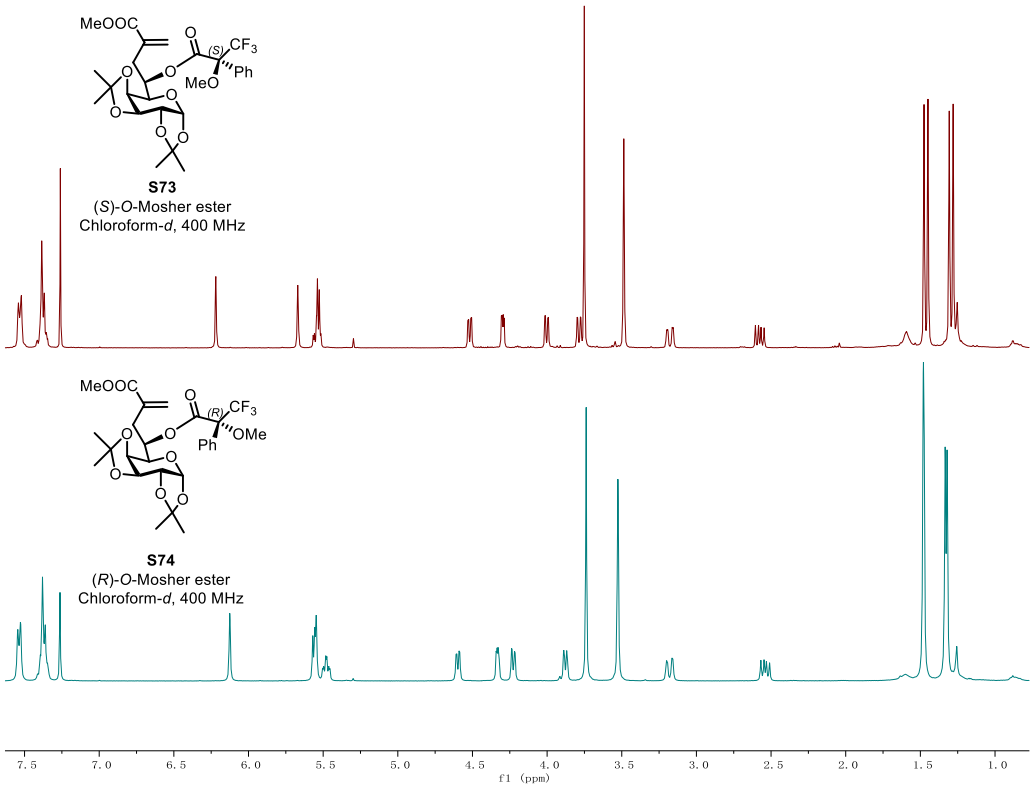
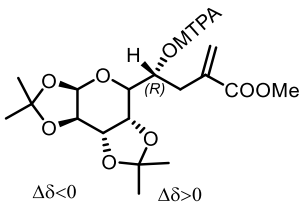
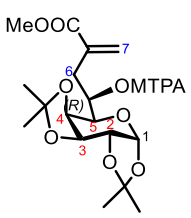


Figure S3 ^{1}H NMR spectra of (*S*)-*O*-mosher ester S73 and (*R*)-*O*-mosher ester S74

Table S6 ^{1}H NMR chemical shifts and Δδ values of (*S*)-*O*-mosher ester S73 and (*R*)-*O*-mosher ester S74



Mosher Model



NO.	δ_S	δ_R	$\Delta\delta=\delta_S-\delta_R$
1	5.53	5.53	0
2	4.30	4.33	-0.03
3	4.52	4.60	-0.08
4	4.00	4.23	-0.23
5	3.79	3.88	-0.09
6a	2.58	2.54	0.04
6b	3.18	3.18	0
7a	5.67	5.55	0.12
7b	6.22	6.13	0.09

Stereochemical confirmation of compound S65 by Mosher ester analysis

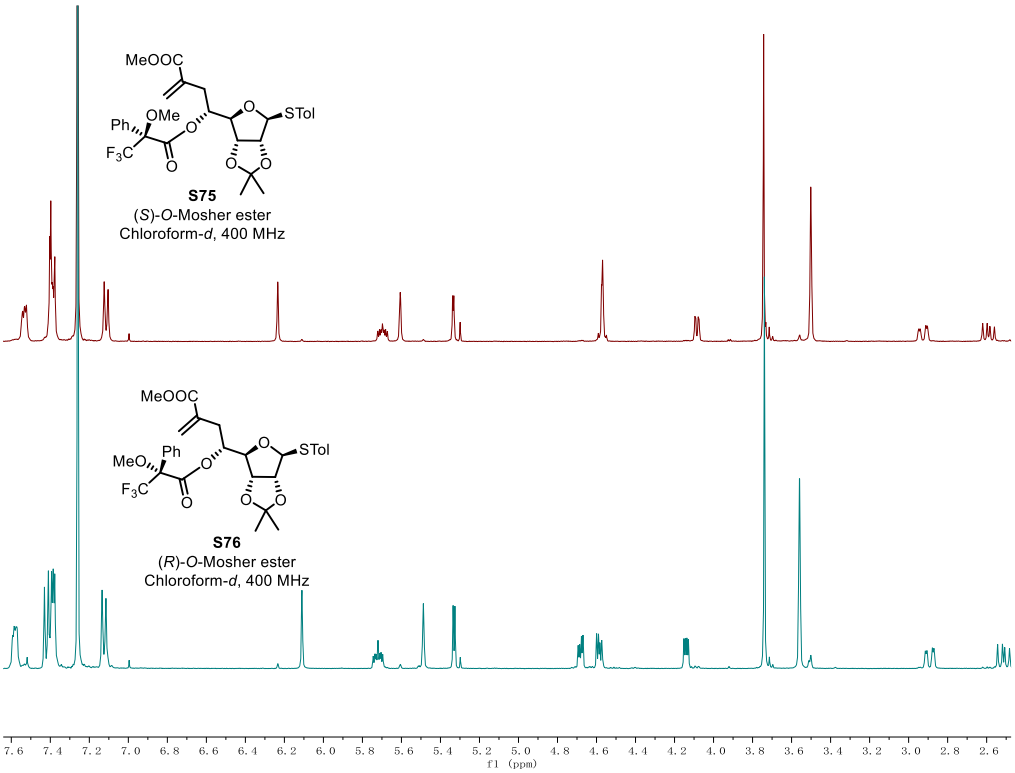
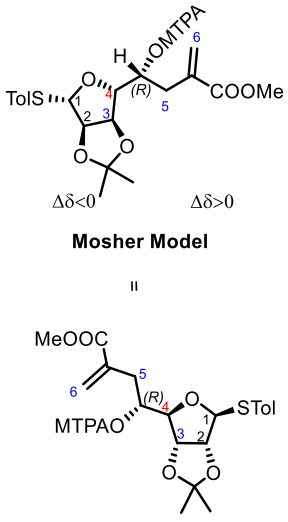


Figure S4 ^{1}H NMR spectra of (*S*)-*O*-mosher ester S75 and (*R*)-*O*-mosher ester S76

Table S7 ^{1}H NMR chemical shifts and Δδ values of (*S*)-*O*-mosher ester S75 and (*R*)-*O*-mosher ester S76



NO.	δ_S	δ_R	$\Delta\delta=\delta_S-\delta_R$
1	5.33	5.33	0
2	4.59	4.59	0
3	4.68	4.59	0.11
4	4.08	4.14	-0.06
5a	2.59	2.51	0.08
5b	2.93	2.89	0.04
6a	6.24	6.11	0.13
6b	5.61	5.49	0.12

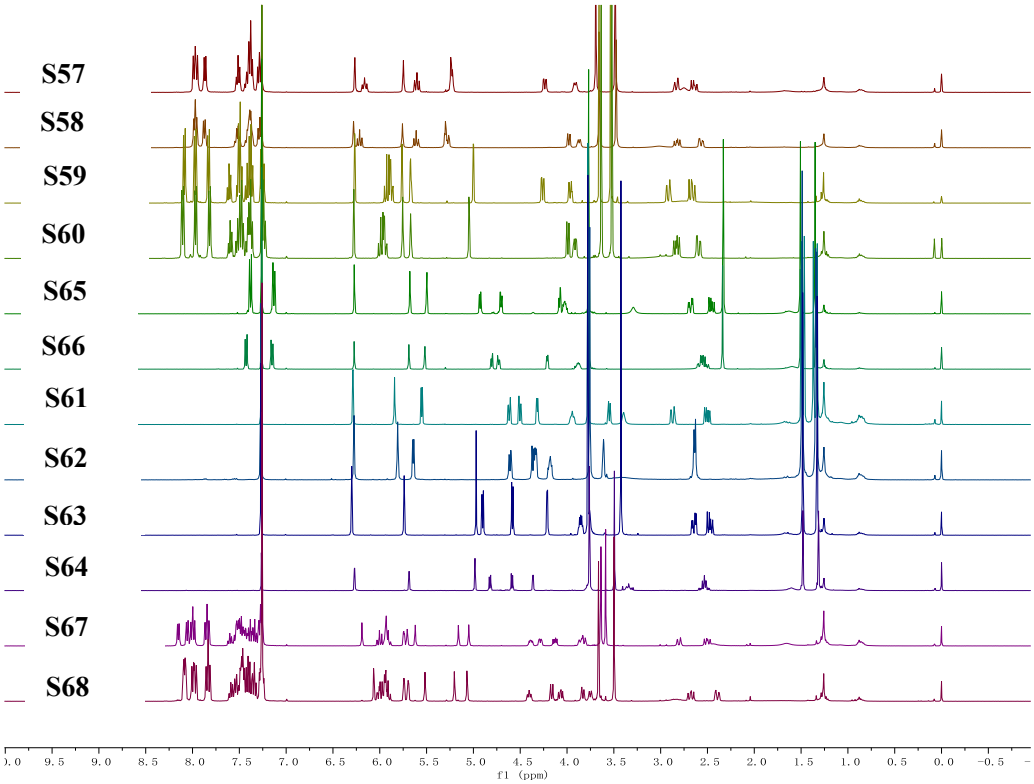


Figure S5 Full ^{1}H NMR spectra of compounds S57, S58, S59, S60, S65, S66, S61, S62, S63, S64, S67, and S68

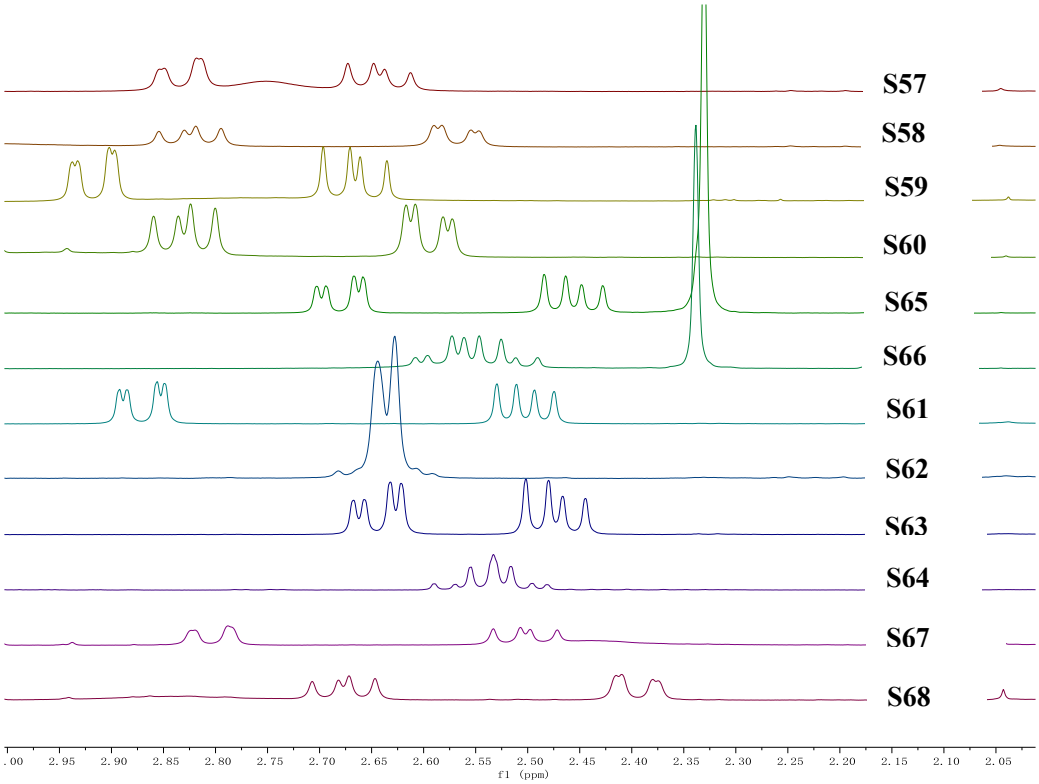


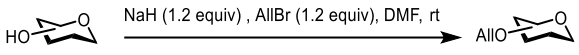
Figure S6 Expanded ^{1}H NMR spectra of compounds S57, S58, S59, S60, S65, S66, S61, S62, S63, S64, S67, and S68 at 2.00–3.00 ppm

Table S8 ^{1}H NMR chemical shifts and coupling constants of the methylene at β position of hydroxy group and of compounds S57, S58, S59, S60, S65, S66, S61, S62, S63, S64, S67, and S68

Compound	δHa (*J*)	δH_b (*J*)
S57	2.83 (dd, *J* = 14.2, 1.8 Hz)	2.64 (dd, *J* = 14.1, 9.9 Hz)
S58[a]	2.82 (dd, *J* = 14.1, 9.7 Hz)	2.57 (dd, *J* = 14.2, 3.0 Hz)
S59	2.92 (dd, *J* = 14.2, 2.0 Hz)	2.67 (dd, *J* = 14.2, 10.3 Hz).
S60[a]	2.83 (dd, *J* = 14.2, 9.5 Hz)	2.59 (dd, *J* = 14.2, 3.5 Hz).
S65[a]	2.68 (dd, *J* = 14.3, 3.5 Hz)	2.46 (dd, *J* = 14.3, 8.2 Hz)
S66	2.52 (dd, *J* = 14.0, 8.4 Hz)	2.58 (dd, *J* = 14.0, 4.6 Hz)
S61[a]	2.87 (dd, *J* = 14.5, 2.8 Hz)	2.50 (dd, *J* = 14.4, 7.6 Hz)
S62	2.67–2.60 (m, -)	2.67–2.60 (m, -)
S63[b]	2.64 (dd, *J* = 14.2, 4.1 Hz)	2.47 (dd, *J* = 14.1, 8.8 Hz)
S64[b]	2.54 (dd, *J* = 14.4, 10.2 Hz)	2.51 (dd, *J* = 14.0, 5.8 Hz)
S67[b]	2.80 (dd, *J* = 14.1, 1.4 Hz)	2.50 (dd, *J* = 14.1, 10.4 Hz)
S68[b]	2.68 (dd, *J* = 14.1, 10.1 Hz)	2.40 (dd, *J* = 14.1, 2.1 Hz)

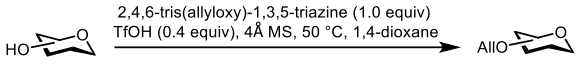
[a]The configuration of C6-OH in pyranoid sugars and C5-OH in in furanoid sugars was determined by use of Mosher ester analysis; [b]The configuration of C6-OH in pyranoid sugars and C5-OH in in furanoid sugars was figured out by analogy.

General Procedure A: Allyl installation using NaH/AllBr.



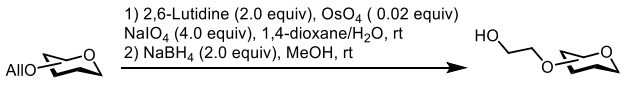
To a solution of alcohol (1.0 equiv) in dry DMF (20.0 mL) were added allyl bromide (AllBr) (1.2 equiv) and 60% dispersion of NaH in mineral oil (1.2 equiv) in ice bath under an argon atmosphere. The resultant solution was stirred at room temperature for 3 h. The reaction was quenched with NH_4Cl solution in ice bath. The resultant mixture was extracted with DCM, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography to give the desired product.

General Procedure B: Allyl installation using 2,4,6-tris(allyloxy)-1,3,5-triazine/TfOH.[1]



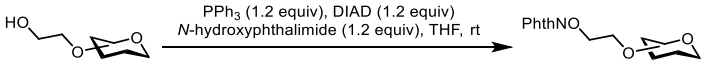
A mixture of alcohol (1.0 equiv) and freshly activated 4Å MS in anhydrous 1,4-dioxane was stirred at room temperature under an argon atmosphere for 1 h. 2,4,6-tris(allyloxy)-1,3,5-triazine (1.0 equiv) and trifluoromethanesulfonic acid (TfOH) (0.4 equiv) were added at room temperature and then warmed to 55 °C. After TLC indicates full conversion, the reaction was filtered through a pad of Celite, the filtrate was diluted with DCM, then washed sequentially with saturated $NaHCO_3$ solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography to give the desired product.

General Procedure C: Oxidative cleavage of double bond to aldehyde and reduction to alcohol.



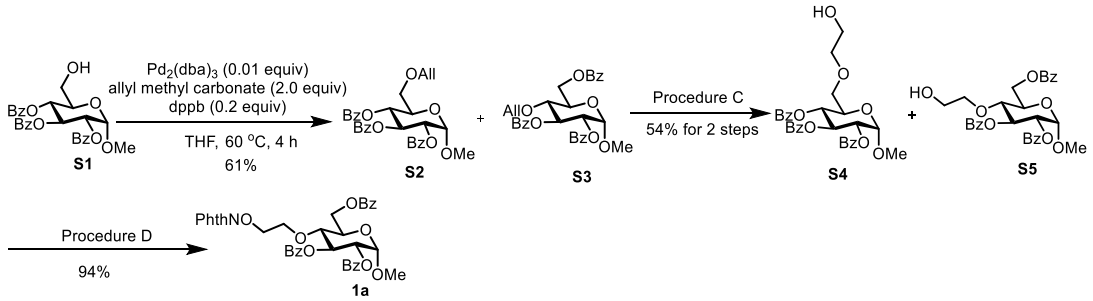
To a solution of olefin (1.0 equiv) in 1,4-dioxane/H_2O (*v*/*v* = 3:1) were added 2,6-lutidine (2.0 equiv), OsO_4 (0.0234 mol/L solution in *t*-BuOH, 0.02 equiv) and $NaIO_4$ (4.0 equiv) at room temperature under an argon atmosphere. The resultant solution was stirred for 12 h and quenched with saturated aqueous Na_2SO_3 solution at 0 °C. The resultant mixture was extracted with EA, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo* to give the crude product without further purification for next step. The crude product obtained as above was dissolved in dry MeOH, $NaBH_4$ (2.0 equiv) was added in ice bath under an argon atmosphere. After stirring for 1 h at room temperature, the reaction was quenched with saturated aqueous NH_4Cl solution in ice bath. The resultant mixture was extracted with DCM, and the organic layer was washed with 1M HCl solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography to give the desired product.

General Procedure D: Synthesis of *N*-alkoxyphthalimide by Mitsunobu reaction.

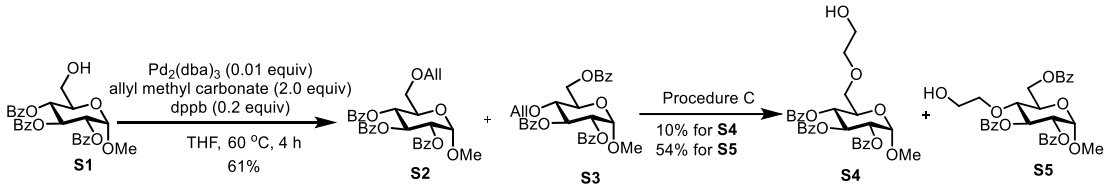


To a solution of alcohol (1.0 equiv), PPh_3 (1.2 equiv) and *N*-hydroxyphthalimide (1.2 equiv) in THF was added diisopropylazodicarboxylate (DIAD) (1.2 equiv) over 3 min at room temperature under an argon atmosphere for 2 h. The mixture was diluted with DCM and washed with saturated $NaHCO_3$ solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography to give the desired product.

Preparation of 1a *via* intermediates S2–S5



Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2-hydroxyethyl)-α-D-glucopyranoside (S4) and Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2-hydroxyethyl)-α-D-glucopyranoside (S5)



To a solution of **S1**[2] (2.02 g, 4.00 mmol, 1.0 equiv) in THF (10.0 mL) was added allyl methyl carbonate (845 μL, 8.00 mmol, 2.0 equiv). A mixture of tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$) (37.0 mg, 40.0 μmol, 0.01 equiv) and 1,4-bis(diphenylphosphino)butane (dppb) (344.0 mg, 800.0 μmol, 0.2 equiv) in degassed THF (3.2 mL) was added at room temperature under an argon atmosphere. The mixture was warmed to 60 °C and stirred for 4 h. The mixture was evaporated to dryness and the residue was purified by flash silica gel column chromatography to give **S2** and **S3** (1.35 g, 2.47 mmol, 61%) as an inseparable mixture.

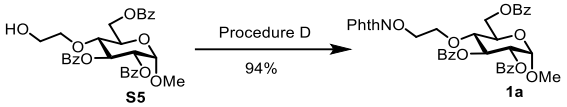
Following the general procedure C, **S2** and **S3** (1.35g, 2.47 mmol, 1.0 equiv) were treated with (575 uL, 4.94 mmol, 2.0 equiv), OsO_4 (0.0234 mol/L solution in *t*-BuOH, 2.1 mL, 49.4 μmol, 0.02 equiv) and $NaIO_4$ (2.12 g, 9.88 mmol, 4.0 equiv) in 1,4-dioxane/H_2O (12.0 mL, *v*/*v* = 3:1) to give the aldehyde. The aldehyde was treated with $NaBH_4$ (280.1 mg, 7.41 mmol, 3.0 equiv) in MeOH (10.0 mL) to give **S4** (136.0 mg, 237.5 μmol, 10%) and **S5** (735.0 mg, 1.34 mmol, 54%) as white foam after purification by silica gel column chromatography (PE:EA = 2:1).

For S4: $[\alpha]_D^{25}$ = +59.17 (*c* 2.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01–7.94 (m, 4H), 7.89–7.84 (m, 2H), 7.55–7.46 (m, 2H), 7.45–7.32 (m, 5H), 7.31–7.26 (m, 2H),

6.17 (t, J = 9.5 Hz, 1H), 5.77 (t, J = 9.9 Hz, 1H), 5.33–5.24 (m, 2H), 4.25–4.15 (m, 1H), 3.83–3.71 (m, 3H), 3.71–3.62 (m, 2H), 3.53–3.45 (m, 4H), 2.71 (brs, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.83, 165.77, 133.6, 133.4, 133.1, 129.95, 129.93, 129.7, 129.2, 129.1, 128.9, 128.5, 128.4, 128.3, 97.2, 73.2, 72.1, 70.5, 69.2, 69.1, 68.7, 61.6, 55.7; HRMS (ESI) *m/z* calcd for $C_{30}H_{34}NO_{10}$ $[M+NH_4]^+$ 568.2177, found 568.2185.

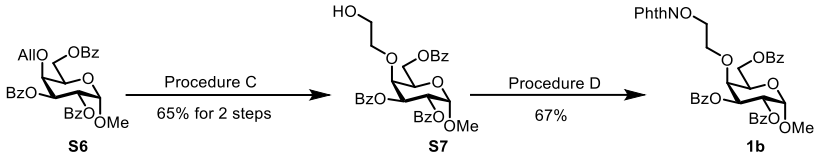
For S5: $[\alpha]_D^{25}$ = +104.89 (*c* 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15–8.07 (m, 2H), 8.04–7.92 (m, 4H), 7.65–7.56 (m, 1H), 7.54–7.46 (m, 4H), 7.42–7.33 (m, 4H), 6.06–5.98 (m, 1H), 5.21 (dd, J = 10.2, 3.6 Hz, 1H), 5.14 (d, J = 3.6 Hz, 1H), 4.76–4.63 (m, 2H), 4.20–4.14 (m, 1H), 3.78 (t, J = 9.6 Hz, 1H), 3.74–3.66 (m, 2H), 3.65–3.52 (m, 2H), 3.44 (s, 3H), 2.18 (t, J = 6.2 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.4, 166.1, 166.0, 133.41, 133.36, 129.9, 129.8, 129.7, 129.1, 128.6, 128.5, 128.4, 97.0, 77.4, 74.2, 72.6, 71.9, 68.9, 63.2, 62.0, 55.5; HRMS (ESI) *m/z* calcd for $C_{30}H_{34}NO_{10}$ $[M+NH_4]^+$ 568.2177, found 568.2169.

Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-α-D-glucopyranoside (1a)

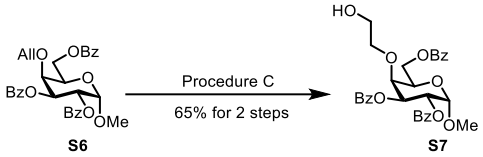


Following the general procedure D, **S5** (550.3 mg, 1.00 mmol, 1.0 equiv) was treated with PPh_3 (520.0 mg, 2.00 mmol, 2.0 equiv), *N*-hydroxyphthalimide (320.0 mg, 2.00 mmol, 2.0 equiv) and diisopropylazodicarboxylate (400 μL, 2.00 mmol, 2.0 equiv) in THF (6.0 mL) to give **1a** (653.0 mg, 936.0 μmol, 94%) as a white foam after purification by silica gel column chromatography (PE:DCM:EA = 5:1:1). $[\alpha]_D^{25}$ = +96.23 (*c* 2.3, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12–8.04 (m, 2H), 8.02–7.94 (m, 4H), 7.79–7.69 (m, 4H), 7.55 (t, J = 7.4 Hz, 1H), 7.52–7.41 (m, 4H), 7.39–7.30 (m, 4H), 6.03 (t, J = 9.6 Hz, 1H), 5.21–5.12 (m, 2H), 4.86–4.75 (m, 2H), 4.29–4.11 (m, 3H), 4.03–3.91 (m, 3H), 3.43 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 166.0, 165.5, 163.3, 134.4, 133.3, 133.2, 133.0, 130.0, 129.7, 129.6, 129.1, 128.9, 128.4, 123.5, 96.9, 77.9, 77.6, 72.8, 72.2, 70.3, 68.7, 63.3, 55.4; HRMS (ESI) *m/z* calcd for $C_{38}H_{37}N_2O_{12}$ $[M+NH_4]^+$ 713.2341, found 713.2340.

Preparation of 1b *via* intermediate S7

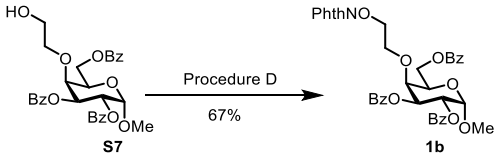


Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2-hydroxyethyl)-α-D-galactopyranoside (S7)



Following the general procedure C, **S6**[3] (1.11 g, 2.00 mmol, 1.0 equiv) was treated with 2,6-lutidine (470 μL, 4.00 mmol, 2.0 equiv), OsO_4 (0.0234 mol/L solution in *t*-BuOH, 1.7 mL, 40.0 μmol, 0.02 equiv) and $NaIO_4$ (1.28 g, 6.00 mmol, 3.0 equiv) in 1,4-dioxane/H_2O (16.0 mL, *v*/*v* = 3:1) to give the aldehyde. The aldehyde was treated with $NaBH_4$ (151.3 mg, 4.00 mmol, 2.0 equiv) in MeOH (10.0 mL) to give **S7** (714.5 mg, 1.30 mmol, 65%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25}$ = +104.30 (*c* 3.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09–7.95 (m, 6H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.54–7.43 (m, 4H), 7.41–7.32 (m, 4H), 5.82 (dd, *J* = 10.8, 3.0 Hz, 1H), 5.72 (dd, *J* = 10.8, 3.6 Hz, 1H), 5.21 (d, *J* = 3.5 Hz, 1H), 4.65–4.59 (m, 2H), 4.38 (t, *J* = 6.5 Hz, 1H), 4.20 (d, *J* = 2.1 Hz, 1H), 3.93–3.85 (m, 1H), 3.78–3.73 (m, 2H), 3.72–3.65 (m, 1H), 3.44 (s, 3H), 2.51 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 166.1, 166.0, 133.5, 133.4, 133.3, 129.9, 129.8, 129.7, 129.6, 129.4, 129.2, 128.6, 128.4, 97.6, 76.7, 75.2, 71.1, 69.3, 68.1, 63.0, 62.2, 55.6; HRMS (ESI) *m/z* calcd for $C_{30}H_{34}NO_{10}$ $[M+NH_4]^+$ 568.2177, found 568.2185.

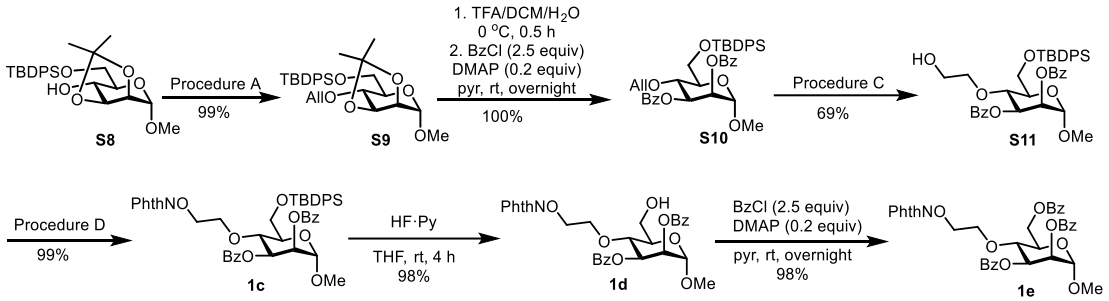
Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-α-D-galactopyranoside (1b)



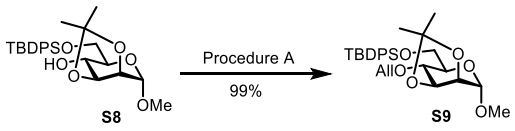
Following the general procedure D, **S7** (624.5 mg, 1.13 mmol, 1.0 equiv) was treated

with PPh_3 (356.7 mg, 1.36 mmol, 1.2 equiv), *N*-hydroxyphthalimide (221.6 mg, 1.36 mmol, 1.2 equiv) and diisopropylazodicarboxylate (271 μL, 1.36 mmol, 1.2 equiv) in THF (10.0 mL) to give **1b** (527.3 mg, 758.0 μmol, 67%) as a white foam after purification by silica gel column chromatography (PE:EA = 2:1). $[\alpha]_D^{25}$ = +87.97 (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08–8.01 (m, 4H), 7.99–7.94 (m, 2H), 7.84–7.79 (m, 2H), 7.75–7.70 (m, 2H), 7.56–7.46 (m, 3H), 7.44–7.32 (m, 6H), 5.83 (dd, *J* = 10.7, 2.9 Hz, 1H), 5.62 (dd, *J* = 10.7, 3.6 Hz, 1H), 5.12 (d, *J* = 3.6 Hz, 1H), 4.76 (dd, *J* = 11.4, 5.7 Hz, 1H), 4.67 (dd, *J* = 11.4, 7.0 Hz, 1H), 4.48–4.41 (m, 1H), 4.39–4.23 (m, 4H), 3.95–3.84 (m, 1H), 3.40 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 166.0, 165.8, 163.5, 134.5, 133.4, 133.2, 133.1, 129.9, 129.8, 129.7, 129.5, 129.3, 128.9, 128.6, 128.5, 128.4, 123.6, 97.4, 71.6, 71.3, 69.5, 68.4, 63.5, 55.4; HRMS (ESI) *m/z* calcd for $C_{38}H_{37}N_2O_{12}$ $[M+NH_4]^+$ 713.2341, found 713.2360.

Preparation of 1c–1e *via* intermediates S9–S11



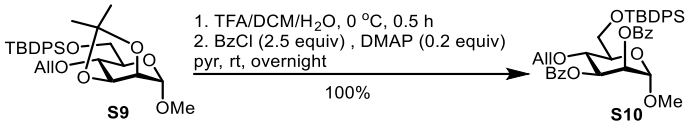
Methyl 4-*O*-allyl-6-*O*-*tert*-butyldiphenylsilyl-2,3-*O*-isopropylidene-α-D-manno-pyranoside (S9)



Following the general procedure A, **S8**[4] (9.42 g, 18.37 mmol, 1.0 equiv) was treated with AllBr (2.4 mL, 27.56 mmol, 1.5 equiv) and 60% dispersion of NaH in mineral oil (1.12 g, 27.56 mmol, 1.5 equiv) in DMF (50.0 mL) to give **S9** (9.31 g, 18.16 mmol, 99%) as a colorless oil after purification by silica gel column chromatography (PE:EA = 25:1). $[\alpha]_D^{25}$ = +10.42 (*c* 4.5, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79–7.69 (m, 4H), 7.46–7.33 (m, 6H), 5.92–5.74 (m, 1H), 5.25–5.16 (m, 1H), 5.14–5.04 (m, 1H),

4.94 (s, 1H), 4.38–4.26 (m, 1H), 4.24 (t, J = 6.0 Hz, 1H), 4.12 (d, J = 5.8 Hz, 1H), 4.06 (dd, J = 12.7, 5.8 Hz, 1H), 3.96–3.84 (m, 2H), 3.66–3.53 (m, 2H), 3.37 (s, 3H), 1.53 (s, 3H), 1.36 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.0, 135.8, 135.1, 133.9, 133.5, 129.7, 127.8, 127.7, 116.9, 109.4, 98.3, 79.0, 76.0, 75.5, 72.1, 69.7, 63.3, 54.8, 28.1, 26.9, 26.5, 19.5; HRMS (ESI) *m/z* calcd for $C_{29}H_{44}NO_6Si$ $[M+NH_4]^+$ 530.2932, found 530.2928.

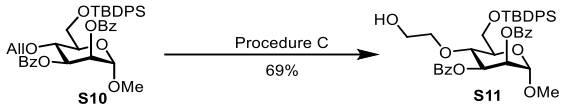
Methyl 4-*O*-allyl-2,3-di-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside (S10)



To a solution of **S9** (9.30 g, 18.10 mmol, 1.0 equiv) in DCM/TFA/H_2O (111.0 mL, *v*/*v*/*v*=100/10/1) in ice bath under an argon atmosphere. The resultant solution was stirred for 30 min in ice bath. The reaction was quenched with saturated $NaHCO_3$ solution in ice bath. The resultant mixture was extracted with DCM, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo* to give the crude product without further purification for next step. The crude product was dissolved in dry pyridine (60.0 mL), BzCl (5.3 mL, 45.25 mmol, 2.5 equiv) and 4-*N*,*N*-dimethylaminopyridine (DMAP) (442.0 mg, 3.62 mmol, 0.2 equiv) were added in ice bath under an argon atmosphere. The resultant solution was stirred for 12 h at room temperature. The reaction mixture was quenched with MeOH and concentrated *in vacuo.* The resulting residue was diluted with DCM and then washed sequentially with 1 M HCl solution, saturated $NaHCO_3$ solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (PE:EA = 1:1) to afford **S10** (12.31 g, 18.08 mmol, 100%) as a colorless oil. $[\alpha]_D^{25}$ = –51.80 (*c* 2.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10–8.05 (m, 2H), 7.96–7.91 (m, 2H), 7.81–7.72 (m, 4H), 7.56 (t, J = 6.9 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.45–7.30 (m, 10H), 5.78–5.66 (m, 2H), 5.65–5.60 (m, 1H), 5.13–5.05

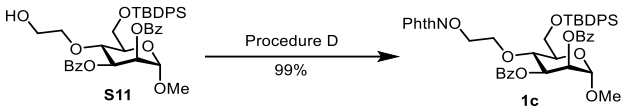
(m, 1H), 5.03–4.97 (m, 1H), 4.90 (d, *J* = 1.4 Hz, 1H), 4.30 (t, *J* = 9.8 Hz, 1H), 4.20–4.14 (m, 2H), 4.07 (dd, *J* = 11.3, 3.3 Hz, 1H), 3.95 (dd, *J* = 11.3, 1.5 Hz, 1H), 3.83 (d, *J* = 9.6 Hz, 1H), 3.41 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 165.5, 136.1, 135.8, 134.8, 133.8, 133.4, 133.2, 133.1, 130.1, 130.0, 129.8, 128.6, 128.5, 127.9, 127.7, 116.9, 98.7, 73.9, 72.9, 72.8, 72.4, 71.1, 62.8, 55.1, 27.0, 19.5; HRMS (ESI) *m/z* calcd for $C_{40}H_{44}O_8SiNa$ $[M+Na]^+$ 703.2698, found 703.2698.

Methyl 2,3-di-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-4-*O*-(2-hydroxyethyl)-α-D-mannopyranoside (S11)



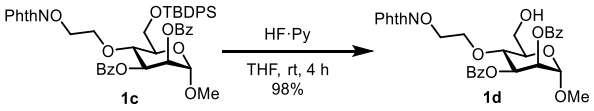
Following the general procedure C, **S10** (10.00 g, 14.70 mmol, 1.0 equiv) was treated with 2,6-lutidine (3.4 mL, 29.40 mmol, 2.0 equiv), OsO_4 (0.0234 mol/L solution in *t*-BuOH, 12.5 mL, 294.0 mmol, 0.02 equiv) and $NaIO_4$ (9.40 g, 44.10 mmol, 3.0 equiv) in 1,4-dioxane/H_2O (130.0 mL, *v*/*v* = 3:1) to give the aldehyde. The aldehyde was treated with $NaBH_4$ (834.0 mg, 22.05 mmol, 1.5 equiv) in MeOH (70.0 mL) to give **S11** (6.93 g, 10.11 mmol, 69%) as a white foam after purification by silica gel column chromatography (PE:EA = 6:1). $[\alpha]_D^{25}$ = −59.20 (*c* 4.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14–8.07 (m, 2H), 7.99–7.90 (m, 2H), 7.83–7.74 (m, 4H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.45–7.33 (m, 10H), 5.73 (dd, *J* = 9.8, 3.4 Hz, 1H), 5.66–5.60 (m, 1H), 4.92–4.89 (m, 1H), 4.29 (t, *J* = 9.8 Hz, 1H), 4.09 (dd, *J* = 11.4, 3.3 Hz, 1H), 3.99 (dd, *J* = 11.4, 1.4 Hz, 1H), 3.84 (d, *J* = 9.6 Hz, 1H), 3.78–3.71 (m, 2H), 3.57–3.48 (m, 2H), 3.42 (s, 3H), 2.07–1.99 (m, 1H), 1.14 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 165.6, 136.1, 135.7, 133.6, 133.5, 133.3, 133.0, 130.0, 129.9, 129.8, 129.7, 128.6, 128.5, 127.9, 127.7, 98.7, 74.2, 73.9, 72.6, 72.3, 71.0, 62.9, 62.2, 55.1, 27.0, 19.5; HRMS (ESI) *m/z* calcd for $C_{39}H_{44}O_9SiNa$ $[M+Na]^+$ 707.2647, found 707.2645.

Methyl 2,3-di-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-4-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-α-D-mannopyranoside (1c)



Following the general procedure D, **S11** (6.84 g, 10.00 mmol, 1.0 equiv) was treated with PPh_3 (3.15 g, 12.00 mmol, 1.2 equiv), *N*-hydroxyphthalimide (1.96 g, 12.00 mmol, 1.2 equiv) and diisopropylazodicarboxylate (2.4 mL, 12.0 mmol, 1.2 equiv) in THF (50.0 mL) to give **1c** (8.20 g, 9.88 mmol, 99%) as a white foam after purification by silica gel column chromatography (PE:EA = 5:1). $[\alpha]_D^{25} = -42.31$ (*c* 2.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11–8.02 (m, 2H), 7.96–7.90 (m, 2H), 7.81–7.68 (m, 8H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46–7.37 (m, 3H), 7.36–7.27 (m, 8H), 5.65–5.60 (m, 2H), 4.89 (s, 1H), 4.31 (t, *J* = 9.4 Hz, 1H), 4.23–4.12 (m, 3H), 4.11–4.04 (m, 1H), 4.03–3.94 (m, 2H), 3.78 (d, *J* = 9.6 Hz, 1H), 3.39 (s, 3H), 1.11 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.6, 165.4, 163.3, 136.1, 135.8, 134.4, 133.7, 133.4, 133.3, 133.0, 129.7, 128.9, 128.6, 128.4, 127.7, 127.6, 123.5, 98.6, 77.2, 74.2, 72.9, 72.1, 70.9, 70.8, 62.8, 55.0, 27.0, 19.5; HRMS (ESI) *m/z* calcd for $C_{47}H_{51}N_2O_{11}Si$ $[M+NH_4]^+$ 847.3257, found 847.3256.

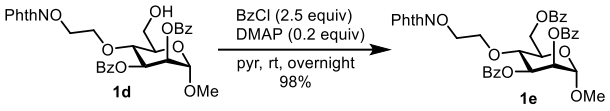
Methyl 2,3-di-*O*-benzoyl-4-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-α-D-mannopyranoside (1d)



To a solution of **1c** (6.88 g, 8.30 mmol, 1.0 equiv) in THF (30.0 mL) was added HF·Py (8.3 mL) in ice bath under an argon atmosphere. The resultant solution was stirred at room temperature for 4 h. The reaction was quenched with saturated $NaHCO_3$ solution. The resultant mixture was extracted with DCM, and the organic layer was washed with 1 M HCl solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (PE:EA = 1:1) to afford **1d** (4.81 g, 8.13 mmol, 98%) as a white foam. $[\alpha]_D^{25} = -21.52$ (*c* 4.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08–8.02 (m, 2H), 7.95–7.89 (m, 2H), 7.83–7.77 (m, 2H), 7.76–7.71 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.50–7.42 (m, 3H), 7.35–7.29 (m, 2H), 5.66 (dd, *J* = 9.6, 3.3 Hz, 1H),

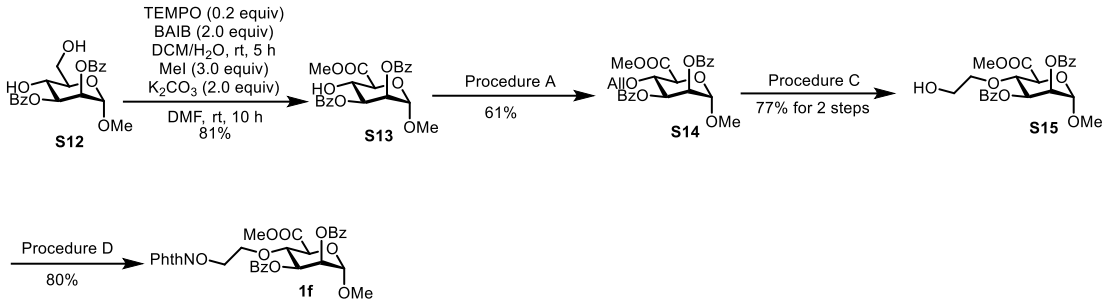
5.61 (dd, J = 3.3, 1.8 Hz, 1H), 4.88 (d, J = 1.5 Hz, 1H), 4.33–4.24 (m, 3H), 4.22–4.12 (m, 1H), 4.08–3.97 (m, 3H), 3.90–3.80 (m, 1H), 3.45 (s, 3H), 2.65 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 165.3, 163.6, 134.7, 133.5, 133.2, 129.9, 129.7, 129.6, 128.8, 128.6, 128.5, 123.7, 98.7, 77.9, 74.2, 73.0, 71.7, 70.7, 70.6, 61.6, 55.3; HRMS (ESI) *m/z* calcd for $C_{31}H_{33}N_2O_{11}$ $[M+NH_4]^+$ 609.2079, found 609.2068.

Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-α-D-mannopyranoside (1e)

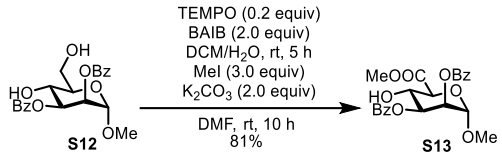


To a solution of **1d** (1.23 g, 2.08 mmol, 1.0 equiv) in dry pyridine (8.0 mL) was added BzCl (320 μL, 2.70 mmol, 1.3 equiv) and DMAP (25.7 mg, 208.0 μmol, 0.1 equiv) in ice bath under an argon atmosphere. The resultant solution was stirred at room temperature for 2 h. The resultant mixture was quenched with MeOH and washed with 1 M HCl solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (PE:EA = 1.5:1) to afford **1e** (1.43 g, 2.05 mmol, 98%) as a white foam. $[\alpha]_D^{25}$ = +97.52 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11–8.07 (m, 2H), 8.02–7.97 (m, 2H), 7.97–7.90 (m, 2H), 7.76–7.69 (m, 4H), 7.60–7.54 (m, 2H), 7.49–7.29 (m, 7H), 5.70 (dd, J = 9.5, 3.3 Hz, 1H), 5.66–5.61 (m, 1H), 4.92–4.85 (m, 2H), 4.82–4.77 (m, 1H), 4.32–4.21 (m, 3H), 4.18–4.11 (m, 1H), 4.10–3.97 (m, 2H), 3.48 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 165.4, 165.3, 163.4, 134.5, 133.4, 133.2, 133.1, 130.0, 129.9, 129.81, 129.78, 128.6, 128.5, 123.6, 98.7, 74.8, 72.9, 70.7, 69.9, 55.4; HRMS (ESI) *m/z* calcd for $C_{38}H_{37}N_2O_{12}$ $[M+NH_4]^+$ 713.2341, found 713.2347.

Preparation of 1f *via* intermediates S13–S15

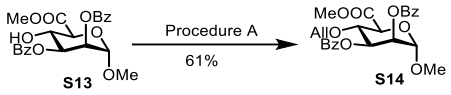


Methyl [methyl 2,3-di-*O*-benzoyl-α-D-mannopyranosyluronate] (S13)



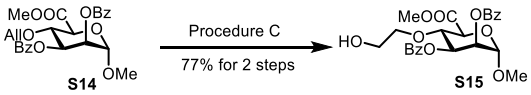
To a solution of **S12**[5] (402.3 mg, 1.00 mmol, 1.0 equiv) in DCM/H_2O (11 mL, *v*/*v* = 10:1) were added 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (31.2 mg, 200.0 μmol, 0.2 equiv) and $PhI(OAc)_2$ (644.2 mg, 2.00 mmol, 2.0 equiv) under an argon atmosphere. After stirring for 5 h at room temperature, the reaction was diluted with DCM and washed with $Na_2S_2O_3$ solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid, and concentrated *in vacuo*. To a solution of the crude product obtained as above in DMF (10.0 mL) while chilled in an ice bath were added K_2CO_3 (262.4 mg, 2.00 mmol, 2.0 equiv) and MeI (185 μL, 3.00 mmol, 3.0 equiv) under an argon atmosphere. After stirring for 10 h at room temperature, the reaction was quenched with water and concentrated to dryness. The resulting residue was purified by silica gel column chromatography (PE:EA = 2:1) to afford **S13** (350.3 mg, 813.9 μmol, 81%) a white foam. $[\alpha]_D^{25} = -55.14$ (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10–8.02 (m, 2H), 7.99–7.89 (m, 2H), 7.65–7.52 (m, 1H), 7.54–7.42 (m, 3H), 7.39–7.30 (m, 2H), 5.64 (dd, *J* = 9.7, 3.4 Hz, 1H), 5.59–5.52 (m, 1H), 5.00 (d, *J* = 1.5 Hz, 1H), 4.57–4.42 (m, 1H), 4.37 (d, *J* = 9.6 Hz, 1H), 3.88 (s, 3H), 3.53 (s, 3H), 3.25 (d, *J* = 3.5 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.4, 165.9, 165.4, 133.5, 133.2, 129.8, 129.7, 129.3, 129.2, 128.5, 128.3, 99.0, 71.2, 69.9, 67.3, 55.7, 52.8; HRMS (ESI) *m/z* calcd for $C_{22}H_{23}O_9$ $[M+H]^+$ 431.1337, found 431.1329.

Methyl [methyl 4-*O*-allyl-2,3-di-*O*-benzoyl-α-D-mannopyranosyluronate] (S14)



Following the general procedure B, **S13** (1.18 g, 2.70 mmol, 1.0 equiv) was treated with 2,4,6-tris(allyloxy)-1,3,5-triazine (3.0 mL, 13.50 mmol, 5.0 equiv) and TfOH (86 μL, 1.08 mmol, 0.4 equiv) in 1,4-dioxane (10.0 mL) to give **S14** (771.3 mg, 1.64 mmol, 61%) as a white foam after purification by silica gel column chromatography (PE:EA = 2:1). $[\alpha]_D^{25} = -59.10$ (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09–7.99 (m, 2H), 7.99–7.89 (m, 2H), 7.60 (t, *J* = 6.9 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.49–7.44 (m, 2H), 7.42–7.34 (m, 2H), 5.83–5.72 (m, 1H), 5.69 (dd, *J* = 9.0, 3.4 Hz, 1H), 5.62–5.56 (m, 1H), 5.20–5.13 (m, 1H), 5.11–5.04 (m, 1H), 5.01 (d, *J* = 2.4 Hz, 1H), 4.40 (d, *J* = 8.9 Hz, 1H), 4.29 (t, *J* = 8.9 Hz, 1H), 4.15 (d, *J* = 5.7 Hz, 2H), 3.81 (s, 3H), 3.52 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 165.5, 165.3, 134.2, 133.5, 133.4, 130.0, 129.8, 129.6, 129.5, 128.6, 128.5, 117.5, 99.0, 74.5, 73.7, 71.6, 71.4, 70.2, 55.9, 52.7; HRMS (ESI) *m/z* calcd for $C_{25}H_{27}O_9$ $[M+H]^+$ 471.1650, found 471.1643.

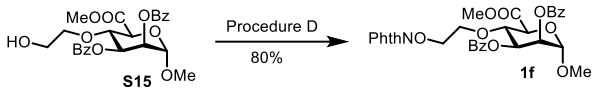
Methyl [methyl 2,3-di-*O*-benzoyl-4-*O*-(2-hydroxyethyl)-α-D-mannopyranosyl-uronate] (S15)



Following the general procedure C, **S14** (921.3 mg, 1.75 mmol, 1.0 equiv) was treated with 2,6-lutidine (410 μL, 3.50 mmol, 2.0 equiv), OsO_4 (0.0234 mol/L solution in *t*-BuOH, 1.5 mL, 35.0 μmol, 0.02 equiv) and $NaIO_4$ (1.49 g, 7.02 mmol, 4.0 equiv) in 1,4-dioxane/H_2O (12.0 mL, *v*/*v* = 3:1) to give the aldehyde. The aldehyde was treated with $NaBH_4$ (198.0 mg, 5.25 mmol, 3.0 equiv) in MeOH (10.0 mL) to give **S15** (638.9 mg, 1.35 mmol, 77%) as a colorless oil after purification by silica gel column chromatography (PE:EA = 1.3:1). $[\alpha]_D^{25} = -64.99$ (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11–7.99 (m, 2H), 7.97–7.87 (m, 2H), 7.65–7.57 (m, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.51–7.45 (m, 2H), 7.42–7.33 (m, 2H), 5.70 (dd, *J* = 9.2, 3.4 Hz, 1H), 5.62–5.54 (m, 1H), 4.99 (d, *J* = 2.2 Hz, 1H), 4.40 (d, *J* = 9.2 Hz, 1H), 4.27 (t, *J* = 9.2

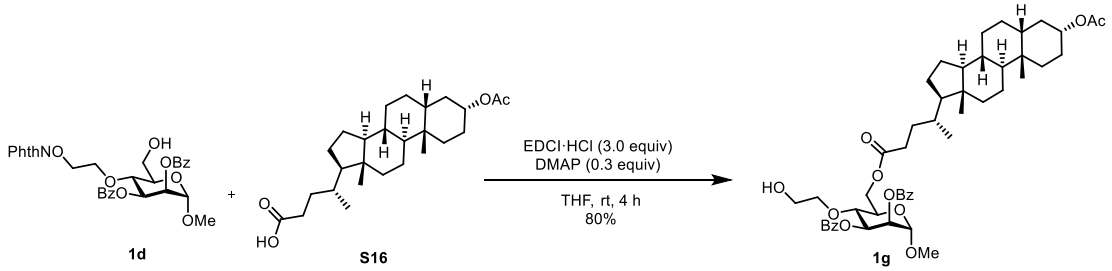
Hz, 1H), 3.85 (s, 3H), 3.81–3.70 (m, 2H), 3.68–3.56 (m, 2H), 3.53 (s, 3H), 2.36 (brs, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 165.5, 165.4, 133.7, 133.5, 130.0, 129.8, 129.4, 128.7, 128.6, 99.1, 75.4, 74.5, 71.8, 71.0, 70.2, 62.1, 56.0, 53.0; HRMS (ESI) *m/z* calcd for $C_{24}H_{30}NO_{10}$ $[M+NH_4]^+$ 492.1864, found 492.1859.

Methyl (methyl 2,3-di-*O*-benzoyl-4-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-α-D-mannopyranosyluronate) (1f)



Following the general procedure D, **S15** (140.0 mg, 295.0 μmol, 1.0 equiv) was treated with PPh_3 (93.0 mg, 354.0 μmol, 1.2 equiv), *N*-hydroxyphthalimide (57.7 mg, 354.0 μmol, 1.2 equiv) and diisopropylazodicarboxylate (70 μL, 354.0 μmol, 1.2 equiv) in THF (5.0 mL) to give **1f** (147.3 mg, 237.7 μmol, 80%) as a white foam after purification by silica gel column chromatography (PE:EA = 2:1). $[\alpha]_D^{25} = -50.21$ (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05–7.99 (m, 2H), 7.98–7.89 (m, 2H), 7.80–7.75 (m, 2H), 7.74–7.70 (m, 2H), 7.64–7.54 (m, 1H), 7.50–7.40 (m, 3H), 7.35–7.28 (m, 2H), 5.64–5.59 (m, 1H), 5.59–5.55 (m, 1H), 4.97 (d, *J* = 2.4 Hz, 1H), 4.38–4.29 (m, 2H), 4.28–4.17 (m, 2H), 4.11–3.97 (m, 2H), 3.83 (s, 3H), 3.49 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.6, 165.5, 165.2, 163.4, 134.5, 133.5, 133.2, 130.0, 129.8, 129.6, 129.5, 129.0, 128.6, 128.5, 123.6, 98.9, 75.8, 71.7, 71.1, 70.7, 70.0, 55.9, 52.8; HRMS (ESI) *m/z* calcd for $C_{32}H_{33}N_2O_{12}$ $[M+NH_4]^+$ 637.2028, found 637.2032.

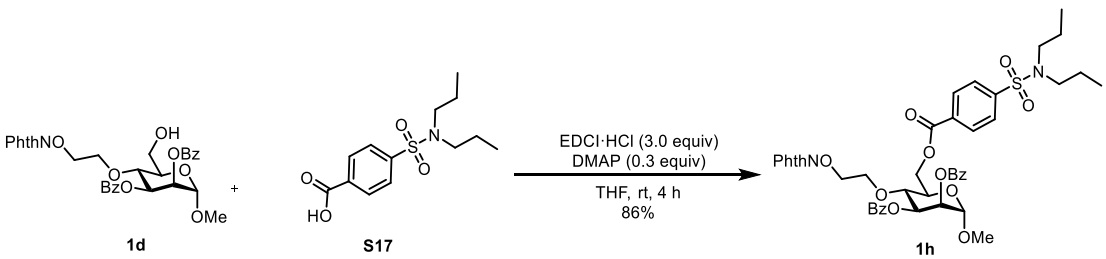
Methyl 2,3-di-*O*-benzoyl-4-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-6-*O*-{3α-acetyloxy-5β-cholan-24-oate}-α-D-mannopyranoside (1g)



To a solution of **1d** (591.6 mg, 1.00 mmol, 1.0 equiv) and lithocholic (**S16**) (591.6 mg,

3.00 mmol, 3.0 equiv) in THF (30.0 mL) were added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI·HCl) (575.1 mg, 3.00 mmol, 3.0 equiv) and DMAP (36.7 mg, 0.3 mmol, 0.3 equiv) in ice bath under an argon atmosphere. The resultant solution was stirred at room temperature for 4 h. The resultant mixture was diluted with DCM and washed with $NaHCO_3$ solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (PE:EA = 2:1) to afford **1g** (793.7 mg, 800.0 μmmol, 80%) as a white foam. $[\alpha]_D^{25}$ = +39.83 (*c* 2.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10–8.02 (m, 1H), 7.95–7.88 (m, 1H), 7.80–7.71 (m, 3H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.51–7.41 (m, 2H), 7.35–7.28 (m, 2H), 5.65 (dd, *J* = 9.4, 3.3 Hz, 1H), 5.61–5.57 (m, 1H), 4.88 (d, *J* = 1.6 Hz, 1H), 4.77–4.67 (m, 1H), 4.63–4.49 (m, 1H), 4.29–4.19 (m, 2H), 4.13 (t, *J* = 9.6 Hz, 1H), 4.09–3.99 (m, 2H), 3.99–3.89 (m, 1H), 3.46 (s, 2H), 2.53–2.41 (m, 1H), 2.39–2.28 (m, 1H), 2.03 (s, 2H), 2.00–1.91 (m, 1H), 1.89–1.75 (m, 5H), 1.73–1.66 (m, 1H), 1.60–1.49 (m, 2H), 1.49–1.31 (m, 6H), 1.30–1.20 (m, 2H), 1.20–0.94 (m, 5H), 0.93 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.0, 170.7, 165.3, 165.2, 163.3, 134.5, 133.4, 133.1, 129.8, 129.7, 129.6, 128.9, 128.5, 128.4, 123.5, 98.5, 77.5, 74.8, 74.4, 72.7, 70.6, 70.5, 69.6, 63.0, 56.5, 56.0, 55.2, 42.7, 41.9, 40.5, 40.2, 35.8, 35.3, 35.1, 34.6, 32.3, 31.1, 30.9, 28.2, 27.0, 26.7, 26.3, 24.2, 23.3, 21.5, 20.9, 18.3, 12.1; HRMS (ESI) *m/z* calcd for $C_{57}H_{69}NO_{14}Na$ $[M+NH_4]^+$ 1014.4610, found 1014.4626.

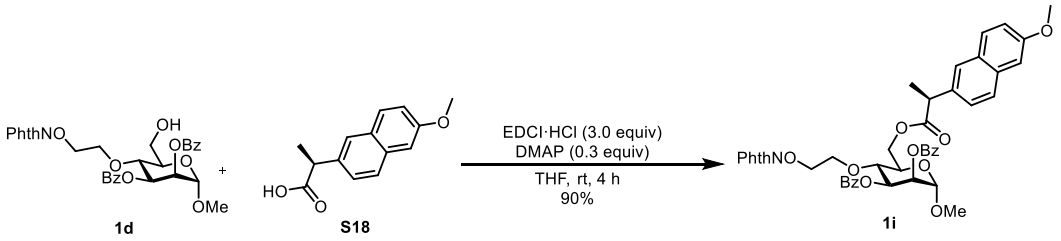
Methyl 2,3-di-*O*-benzoyl-4-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-6-*O*-{4-(*N*,*N*-dipropylsulfamoyl)benzoyl}-α-D-mannopyranoside (1h)



To a solution of **1d** (591.6 mg, 1.00 mmol, 1.0 equiv) and probenecid (**S17**) (855.8 mg, 3.00 mmol, 3.0 equiv) in THF (30.0 mL) were added EDCI·HCl (575.1 mg, 3.00 mmol,

3.0 equiv) and DMAP (36.7 mg, 0.3 mmol, 0.3 equiv) in ice bath under an argon atmosphere. The resultant solution was stirred at room temperature for 4 h. The resultant mixture was diluted with DCM and washed with $NaHCO_3$ solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (PE:EA = 2:1) to afford **1h** (734.6 mg, 855.3 μmol, 86%) as a white foam. $[\alpha]_D^{25}$ = +11.44 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20–8.15 (m, 2H), 8.05–8.00 (m, 2H), 7.97–7.93 (m, 2H), 7.83–7.78 (m, 2H), 7.78–7.69 (m, 4H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.44–7.38 (m, 2H), 7.36–7.30 (m, 2H), 5.72 (dd, *J* = 9.5, 3.3 Hz, 1H), 5.65–5.56 (m, 1H), 4.96–4.89 (m, 2H), 4.86–4.79 (m, 1H), 4.37–4.25 (m, 2H), 4.24–4.14 (m, 2H), 4.08–3.99 (m, 2H), 3.49 (s, 3H), 3.14–3.06 (m, 4H), 1.61–1.50 (m, 4H), 0.92–0.84 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 165.3, 165.0, 163.4, 144.3, 134.6, 133.6, 133.3, 130.3, 129.8, 129.7, 129.6, 128.8, 128.7, 128.5, 127.1, 123.6, 98.6, 77.9, 74.8, 72.8, 70.83, 70.76, 69.7, 64.0, 55.5, 50.1, 22.1, 11.3; HRMS (ESI) *m/z* calcd for $C_{44}H_{50}N_3O_{14}S$ $[M+NH_4]^+$ 876.3008, found 876.3003.

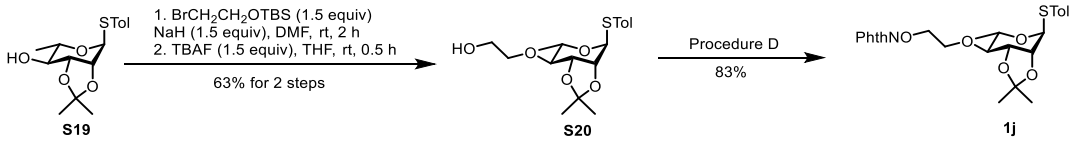
Methyl 2,3-di-*O*-benzoyl-4-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-6-*O*-{(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl}-α-D-mannopyranoside (1i)



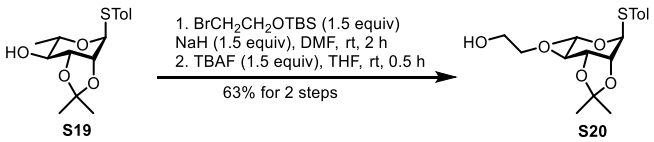
To a solution of **1d** (591.6 mg, 1.00 mmol, 1.0 equiv) and (*S*)-(+)-Naproxen (**S18**) (690.8, 3.00 mmol, 3.0 equiv) in THF (30.0 mL) were added EDCI·HCl (575.1 mg, 3.00 mmol, 3.0 equiv) and DMAP (36.7 mg, 0.3 mmol, 0.3 equiv) in ice bath under an argon atmosphere. The resultant solution was stirred at room temperature for 4 h. The resultant mixture was diluted with DCM and washed with $NaHCO_3$ solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The resulting residue was purified by silica gel column

chromatography (PE:EA = 2:1) to afford **1i** (724.1 mg, 900.8 μmmol, 90%) as a white foam. $[\alpha]_D^{25}$ = −66.83 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17–8.10 (m, 2H), 7.79–7.61 (m, 8H), 7.60–7.52 (m, 3H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.42–7.36 (m, 2H), 7.34–7.28 (m, 2H), 7.05–6.99 (m, 2H), 5.61–5.56 (m, 1H), 5.46 (dd, *J* = 9.6, 3.4 Hz, 1H), 4.82 (d, *J* = 1.5 Hz, 1H), 4.59 (dd, *J* = 12.1, 3.6 Hz, 1H), 4.42 (dd, *J* = 12.1, 1.4 Hz, 1H), 4.01–3.94 (m, 1H), 3.91 (d, *J* = 9.9 Hz, 1H), 3.86 (s, 3H), 3.81 (t, *J* = 9.7 Hz, 1H), 3.75–3.71 (m, 2H), 3.29 (s, 3H), 3.27–3.20 (m, 1H), 2.95–2.70 (m, 1H), 1.61 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.0, 165.3, 165.0, 163.2, 157.7, 135.9, 134.4, 133.7, 133.6, 133.1, 129.9, 129.8, 129.7, 129.5, 129.1, 128.9, 128.8, 128.6, 128.3, 127.2, 126.4, 126.2, 123.4, 119.2, 105.4, 98.7, 77.1, 74.0, 72.6, 70.4, 70.1, 69.3, 63.4, 55.3, 55.1, 45.5, 17.8; HRMS (ESI) *m/z* calcd for $C_{45}H_{41}NO_{13}Na$ $[M+Na]^+$ 826.2470, found 826.2477.

Preparation of 1j *via* intermediate S20



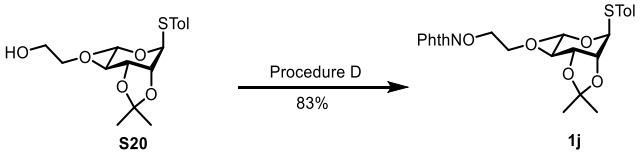
***p*-Tolyl 4-*O*-(2-hydroxyethyl)-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (S20)**



To a solution of **S19**[4] (1.55 g, 5.00 mmol, 1.0 equiv) in DMF (20.0 mL) were added (2-bromoethoxy)-*tert*-butyldimethylsilane (1.6 mL, 7.50 mmol, 1.5 equiv) and 60% dispersion of NaH in mineral oil (300.0 mg, 7.50 mmol, 1.5 equiv) in ice bath under an argon atmosphere. The resultant solution was stirred at room temperature for 3 h. The reaction was quenched with NH_4Cl solution at 0 °C. The resultant mixture was extracted with DCM, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo* to

give the crude product without further purification for next step. To a solution of the crude product obtained as above in THF (10.0 mL) was added TBAF (1 mol/L in THF, 7.5 mL, 7.50 mmol, 1.5 equiv) under an argon atmosphere. After stirring for 0.5 h at room temperature, the reaction mixture was extracted with DCM, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (PE:EA = 4:1) to afford **S20** (1.12 g, 3.16 mmol, 63%) as a colorless oil. $[\alpha]_D^{25} = -96.27$ (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40–7.32 (m, 2H), 7.20–7.08 (m, 2H), 5.66 (s, 1H), 4.34 (d, *J* = 5.6 Hz, 1H), 4.26–4.17 (m, 1H), 4.17–4.02 (m, 1H), 3.84–3.77 (m, 2H), 3.74 (d, *J* = 4.0 Hz, 2H), 3.34–3.15 (m, 1H), 2.75 (brs, 1H), 2.33 (s, 3H), 1.55 (s, 3H), 1.37 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.0, 132.6, 130.0, 129.6, 109.7, 84.1, 83.5, 78.0, 76.7, 73.8, 66.5, 62.4, 28.0, 26.4, 21.2, 17.6; HRMS (ESI) *m/z* calcd for $C_{18}H_{26}O_5NaS$ $[M+Na]^+$ 377.1393, found 377.1389.

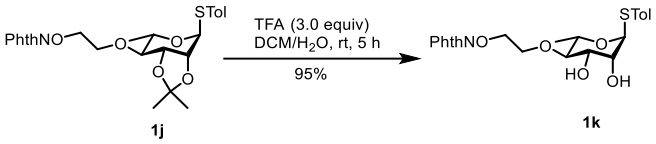
p-Tolyl 4-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (1j)



Following the general procedure D, **S20** (900.0 mg, 2.54 mmol, 1.0 equiv) was treated with PPh_3 (800.0 mg, 3.05 mmol, 1.2 equiv), *N*-hydroxyphthalimide (497.5 mg, 3.05 mmol, 1.2 equiv) and diisopropylazodicarboxylate (600 μL, 3.05 mmol, 1.2 equiv) in THF (10.0 mL) to give **1j** (1.05 g, 2.10 mmol, 83%) as a white foam after purification by silica gel column chromatography (PE:EA = 5:1). $[\alpha]_D^{25} = -158.80$ (*c* 2.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ .90–7.78 (m, 2H), 7.78–7.70 (m, 2H), 7.34–7.30 (m, 2H), 7.15–7.07 (m, 2H), 5.61 (s, 1H), 4.47–4.34 (m, 2H), 4.29 (d, *J* = 5.7 Hz, 1H), 4.26–4.14 (m, 2H), 4.02–3.89 (m, 2H), 3.19 (dd, *J* = 9.7, 7.2 Hz, 1H), 2.32 (s, 3H), 1.51 (s, 3H), 1.32 (s, 3H), 1.18 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6, 137.9, 134.5, 132.6, 129.9, 129.7, 129.1, 123.6, 109.5, 84.2, 82.9, 77.7, 77.2,

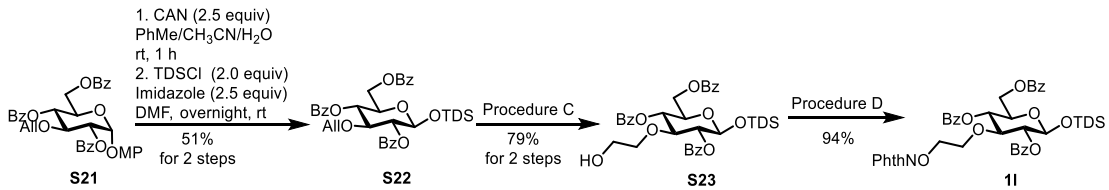
76.6, 69.3, 66.0, 28.1, 26.5, 21.2, 17.5; HRMS (ESI) *m/z* calcd for $C_{26}H_{33}N_2O_7S$ $[M+NH_4]^+$ 517.2003, found 517.1993.

_p_-Tolyl 4-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-1-thio-α-L-rhamno-pyranoside (1k)

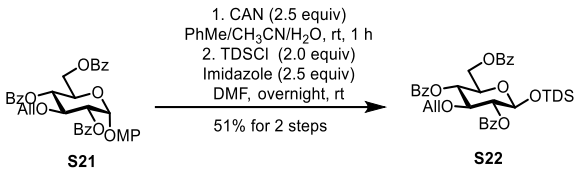


To a solution of **1j** (499.6 mg, 1.00 mmol, 1.0 equiv) in DCM/H_2O (6.0 mL, *v*/*v* = 10:1) was added TFA (220 μL, 3.00 mmol, 3.0 equiv) at room temperature under an argon atmosphere. The resultant solution was stirred at room temperature for 5 h. The reaction was quenched with saturated $NaHCO_3$ solution at 0 °C. The resultant mixture was extracted with EA, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (DCM:EA = 9:1) to afford **1k** (437.2 mg, 951.4 μmol, 95%) as a colorless oil. $[\alpha]_D^{25}$ = −139.54 (*c* 2.9, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88–7.81 (m, 2H), 7.80–7.68 (m, 2H), 7.32–7.28 (m, 2H), 7.14–7.03 (m, 2H), 5.40 (s, 1H), 4.46–4.32 (m, 2H), 4.30–4.22 (m, 1H), 4.19–4.03 (m, 2H), 4.03–3.98 (m, 2H), 3.94 (d, *J* = 9.1 Hz, 1H), 3.39 (t, *J* = 9.3 Hz, 1H), 3.00–2.84 (m, 1H), 2.31 (s, 3H), 1.30 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.0, 137.4, 134.8, 131.9, 130.6, 129.8, 128.7, 123.8, 87.8, 83.2, 78.3, 72.5, 71.4, 70.6, 68.4, 21.1, 17.8; HRMS (ESI) *m/z* calcd for $C_{23}H_{29}N_2O_7S$ $[M+NH_4]^+$ 477.1690, found 477.1693.

Preparation of 1l *via* intermediates S22 and S23

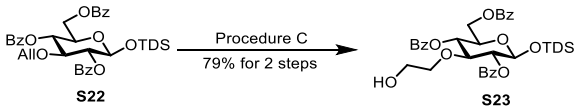


Dimethylthexylsilyl 3-*O*-allyl-2,4,6-tri-*O*-benzoyl-α-D-glucopyranoside (S22)



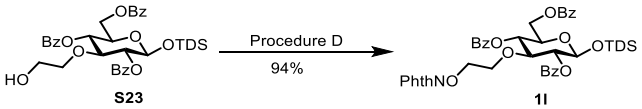
To a solution of **S21**[6] (1.92 g, 3.00 mmol, 1.0 equiv) in PhMe/CH_3CN/H_2O (30 mL, *v*/*v*/*v* = 1:1:1) was added ammonium cerium (IV) nitrate (CAN) (3.51 g, 7.52 mmol, 2.5 equiv) in ice bath under an argon atmosphere. After stirring for 1.5 h at room temperature, the reaction was quenched with saturated $NaHCO_3$ solution. The resultant mixture was extracted with DCM, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo* to give the crude product without further purification for next step. The crude product was dissolved in dry DMF (20.0 mL), imidazole (510.0 mg, 7.50 mmol, 2.5 equiv) and TDSCl (1.07 g, 6.00 mmol, 2.0 equiv) were added under an argon atmosphere. The resultant solution was stirred for 12 h at room temperature. The reaction mixture was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (PE:EA = 10:1) to afford **S22** (1.03 g, 1.53 mmol, 51%) as a colorless oil. $[\alpha]_D^{25} = -3.75$ (*c* 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99–7.86 (m, 6H), 7.51–7.39 (m, 3H), 7.39–7.30 (m, 4H), 7.30–7.23 (m, 2H), 5.54–5.38 (m, 1H), 5.32 (t, *J* = 9.6 Hz, 1H), 5.21 (dd, *J* = 9.5, 7.7 Hz, 1H), 5.00–4.86 (m, 1H), 4.85–4.72 (m, 2H), 4.52–4.36 (m, 1H), 4.36–4.24 (m, 1H), 4.00–3.89 (m, 3H), 3.86 (t, *J* = 9.4 Hz, 1H), 1.41–1.31 (m, 1H), 0.67–0.50 (m, 12H), 0.00 (s, 3H), -0.08 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 165.3, 164.9, 134.4, 133.6, 133.2, 130.2, 129.9, 129.81, 129.78, 129.5, 128.6, 128.5, 128.4, 117.5, 96.3, 79.6, 75.2, 73.1, 72.4, 71.5, 63.9, 33.9, 24.8, 19.9, 18.5, -1.8, -3.4; HRMS (ESI) *m/z* calcd for $C_{38}H_{50}NO_9Si$ $[M+NH_4]^+$ 692.3249, found 692.3251.

Dimethylthexylsilyl 2,4,6-tri-*O*-benzoyl-3-*O*-(2-hydroxyethyl)-α-D-glucopyranoside (S23)



Following the general procedure C, **S22** (675.0 mg, 1.00 mmol, 1.0 equiv) was treated with 2,6-lutidine (230 μL, 2.00 mmol, 2.0 equiv), OsO_4 (0.0234 mol/L solution in *t*-BuOH, 850.0 uL, 20.0 μmol, 0.02 equiv) and $NaIO_4$ (855.5 mg, 4.01 mmol, 4.0 equiv) in 1,4-dioxane/H_2O (8.0 mL, *v*/*v* = 3:1) to give the aldehyde. The aldehyde was treated with $NaBH_4$ (112.9 mg, 3.00 mmol, 3.0 equiv) in MeOH (5.0 mL) to give **S23** (535.2 mg, 788.4 μmol, 79%) as a white foam after purification by silica gel column chromatography (PE:EA = 2.5:1). $[\alpha]_D^{25} = -4.36$ (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98–7.82 (m, 6H), 7.50–7.37 (m, 3H), 7.37–7.22 (m, 6H), 5.33 (t, *J* = 9.6 Hz, 1H), 5.19 (dd, *J* = 9.5, 7.7 Hz, 1H), 4.82 (d, *J* = 7.6 Hz, 1H), 4.50–4.39 (m, 1H), 4.37–4.22 (m, 1H), 3.99–3.88 (m, 1H), 3.83 (t, *J* = 9.3 Hz, 1H), 3.55–3.44 (m, 2H), 3.37–3.27 (m, 2H), 1.78 (brs, 1H), 1.41–1.26 (m, 1H), 0.66–0.49 (m, 12H), 0.00 (s, 3H), -0.08 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 167.4, 167.2, 135.6, 135.2, 135.1, 131.8, 131.7, 131.6, 131.1, 130.6, 130.4, 130.3, 98.0, 83.4, 77.1, 75.7, 74.1, 73.3, 65.6, 63.8, 35.8, 26.7, 21.8, 21.7, 20.3, 0.0, -1.6; HRMS (ESI) *m/z* calcd for $C_{37}H_{50}NO_{10}Si$ $[M+NH_4]^+$ 696.3198, found 696.3196.

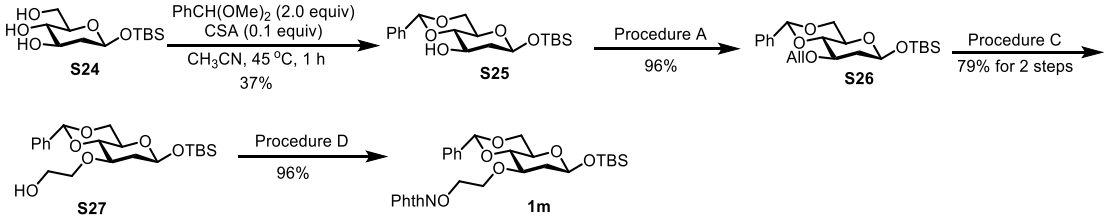
Dimethylthexylsilyl 2,4,6-tri-*O*-benzoyl-3-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]-ethyl}-α-D-glucopyranoside (1l)



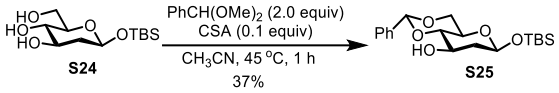
Following the general procedure D, **S23** (380.0 mg, 560.0 μmol, 1.0 equiv) was treated with PPh_3 (221.1 mg, 840.0 μmol, 1.5 equiv), *N*-hydroxyphthalimide (137.0 mg, 840.0 μmol, 1.5 equiv) and diisopropylazodicarboxylate (165 μL, 840.0 μmol, 1.5 equiv) in THF (5.0 mL) to give **1l** (653.0 mg, 792.5 μmol, 94%) as a white foam after purification by silica gel column chromatography (PE:EA = 2:1). $[\alpha]_D^{25} = -1.90$ (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09–7.97 (m, 6H), 7.74–7.68 (m, 4H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.49–7.40 (m, 2H), 7.40–7.30 (m, 6H), 5.42 (t, *J* = 9.6 Hz, 1H), 5.29 (dd, *J* = 9.5, 7.7 Hz, 1H), 4.95 (d, *J* = 7.6 Hz, 1H), 4.60–4.52 (m, 1H), 4.48–4.38 (m, 1H), 4.24 (t, *J* = 9.4 Hz, 1H), 4.12–4.00 (m, 3H), 3.98–3.88 (m, 2H), 1.53–1.42 (m, 1H), 0.74–0.65 (m, 12H), 0.11 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ

166.3, 165.3, 165.1, 163.3, 134.5, 133.3, 133.1, 133.0, 130.0, 130.1, 129.9, 129.5, 128.9, 128.5, 128.38, 128.36, 123.5, 96.2, 81.4, 75.0, 72.4, 71.2, 69.6, 63.8, 33.9, 24.8, 19.9, 18.5, -1.8, -3.4; HRMS (ESI) *m/z* calcd for $C_{45}H_{53}N_2O_{12}Si$ $[M+NH_4]^+$ 841.3362, found 841.3375.

Preparation of 1m *via* intermediates S25–S27

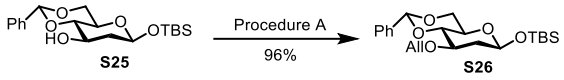


***tert*-Butyldimethylsilyl 4,6-di-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (S25)**



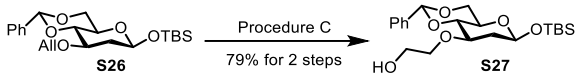
To a solution of **S24**[7] (1.39 g, 5.00 mmol, 1.0 equiv) in CH_3CN (15.0 mL) were added $PhCH(OMe)_2$ (1.4 mL, 10.00 mmol, 2.0 equiv) and camphorsulfonic acid (116.2 mg, 500.0 μmol, 0.1 equiv) in ice bath under an argon atmosphere. The resultant solution was stirred at room temperature for 1.5 h. The reaction was quenched with saturated $NaHCO_3$ solution. The resultant mixture was extracted with DCM, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (PE:EA = 7:1) to afford **S25** (671.4 mg, 1.83 mmol, 37%) as a white foam. $[\alpha]_D^{25} = -28.63$ (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55–7.46 (m, 2H), 7.43–7.33 (m, 3H), 5.53 (s, 1H), 4.90 (dd, *J* = 9.4, 2.1 Hz, 1H), 4.28 (dd, *J* = 10.5, 4.9 Hz, 1H), 3.92–3.83 (m, 1H), 3.80 (t, *J* = 10.3 Hz, 1H), 3.46 (t, *J* = 9.0 Hz, 1H), 3.43–3.26 (m, 1H), 2.60 (s, 1H), 2.31–2.14 (m, 1H), 1.80–1.68 (m, 1H), 0.91 (s, 9H), 0.13 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.4, 129.4, 128.5, 126.4, 102.1, 95.3, 83.2, 69.0, 68.4, 66.6, 41.4, 25.8, 18.2, -4.1, -5.1; HRMS (ESI) *m/z* calcd for $C_{19}H_{30}O_5SiNa$ $[M+Na]^+$ 389.1755, found 389.1759.

***tert*-Butyldimethylsilyl 3-*O*-allyl-4,6-di-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (S26)**



Following the general procedure A, **S25** (540.0 mg, 1.47 mmol, 1.0 equiv) was treated with AllBr (254 μL, 2.94 mmol, 2.0 equiv) and 60% dispersion of NaH in mineral oil (118.0 mg, 2.94 mmol, 2.0 equiv) in DMF (20.0 mL) to give **S26** (576.1 mg, 1.42 mmol, 96%) as a colorless oil after purification by silica gel column chromatography (PE:EA = 30:1). $[\alpha]_D^{25} = -31.44$ (*c* 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55–7.46 (m, 2H), 7.46–7.30 (m, 3H), 6.01–5.81 (m, 1H), 5.57 (s, 1H), 5.35–5.26 (m, 1H), 5.25–5.10 (m, 1H), 4.89 (dd, *J* = 9.5, 2.1 Hz, 1H), 4.38–4.23 (m, 2H), 4.16 (dd, *J* = 13.0, 5.8 Hz, 1H), 3.82 (t, *J* = 10.3 Hz, 1H), 3.75–3.56 (m, 2H), 3.45–3.29 (m, 1H), 2.41–2.20 (m, 1H), 1.77–1.64 (m, 1H), 0.91 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.7, 135.2, 129.0, 128.3, 126.2, 116.9, 101.5, 95.4, 83.1, 74.8, 71.7, 69.1, 66.9, 40.5, 25.8, 18.2, -4.0, -5.1; HRMS (ESI) *m/z* calcd for $C_{22}H_{34}O_5SiNa$ $[M+Na]^+$ 429.2068, found 429.2061.

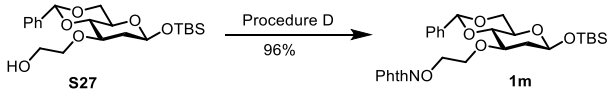
***tert*-Butyldimethylsilyl 4,6-di-*O*-benzylidene-2-deoxy-3-*O*-(2-hydroxyethyl)-β-D-glucopyranoside (S27)**



Following the general procedure C, **S26** (630.0 mg, 1.55 mmol, 1.0 equiv) was treated with 2,6-lutidine (355 μL, 3.10 mmol, 2.0 equiv), OsO_4 (0.0234 mol/L solution in *t*-BuOH, 1.3 mL, 31.0 μmol, 0.02 equiv) and $NaIO_4$ (1.33 g, 6.2 mmol, 4.0 equiv) in 1,4-dioxane/H_2O (16.0 mL, *v*/*v* = 3:1) to give the aldehyde. The aldehyde was treated with $NaBH_4$ (117.3 mg, 3.1 mmol, 2.0 equiv) in MeOH (10.0 mL) to give **S27** (505.0 mg, 1.23 mmol, 79%) as a colorless oil after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25} = -32.88$ (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56–7.40 (m, 2H), 7.42–7.33 (m, 3H), 5.56 (s, 1H), 4.89 (dd, *J* = 9.5, 2.1 Hz, 1H), 4.28 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.91–3.57 (m, 7H), 3.48–3.30 (m, 1H), 2.46 (s, 1H), 2.37–2.18 (m, 1H), 1.82–1.60 (m, 1H), 0.91 (s, 9H), 0.13 (s, 3H), 0.12 (s,

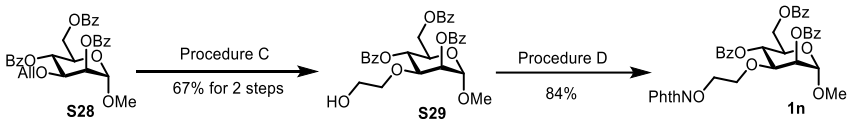
3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.3, 129.2, 128.5, 126.2, 101.7, 95.4, 82.6, 76.2, 72.0, 69.0, 66.8, 62.2, 40.5, 25.8, 18.1, -4.1, -5.1; HRMS (ESI) *m/z* calcd for $C_{21}H_{34}O_6SiNa$ $[M+Na]^+$ 433.2017, found 433.2025.

***tert*-Butyldimethylsilyl 4,6-di-*O*-benzylidene-2-deoxy-3-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-β-D-glucopyranoside (1m)**

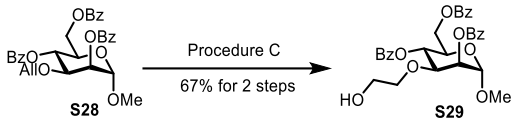


Following the general procedure D, **S27** (460.0 mg, 1.12 mmol, 1.0 equiv) was treated with PPh_3 (351.5 mg, 1.34 mmol, 1.2 equiv), *N*-hydroxyphthalimide (218.6 mg, 1.34 mmol, 1.2 equiv) and diisopropylazodicarboxylate (265 μL, 1.34 mmol, 1.2 equiv) in THF (4.0 mL) to give **1m** (597.3 mg, 1.07 mmol, 96%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25} = -28.74$ (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83–7.75 (m, 2H), 7.74–7.69 (m, 2H), 7.48–7.40 (m, 2H), 7.36–7.28 (m, 3H), 5.52 (s, 1H), 4.86 (dd, *J* = 9.5, 2.1 Hz, 1H), 4.44–4.34 (m, 1H), 4.34–4.27 (m, 1H), 4.25 (dd, *J* = 10.5, 4.9 Hz, 1H), 4.21–4.13 (m, 1H), 4.02–3.94 (m, 1H), 3.78 (t, *J* = 10.3 Hz, 1H), 3.71–3.62 (m, 1H), 3.53 (t, *J* = 9.0 Hz, 1H), 3.37–3.27 (m, 1H), 2.37–2.16 (m, 1H), 1.58–1.40 (m, 1H), 0.89 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6, 137.6, 134.5, 129.0, 128.3, 126.1, 123.5, 101.3, 95.3, 83.4, 77.4, 76.0, 69.6, 69.0, 66.6, 40.3, 25.8, 18.1, -4.1, -5.1; HRMS (ESI) *m/z* calcd for $C_{29}H_{37}NO_8SiNa$ $[M+Na]^+$ 578.2181, found 578.2179.

Preparation of 1n *via* intermediate S29

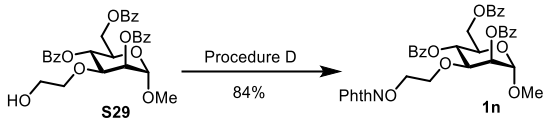


Methyl 2,4,6-tri-*O*-benzoyl-3-*O*-(2-hydroxyethyl)-α-D-mannopyranoside (S29)



Following the general procedure C, **S28**[8] (1.35 g, 2.47 mmol, 1.0 equiv) was treated with 2,6-lutidine (580 μL, 4.94 mmol, 2.0 equiv), OsO_4 (0.0234 mol/L solution in *t*-BuOH, 2.1 mL, 49.4 mmol, 0.02 equiv) and $NaIO_4$ (2.1 g, 9.88 mmol, 4.0 equiv) in 1,4-dioxane/H_2O (24.0 mL, *v*/*v* = 3:1) to give the aldehyde. The aldehyde was treated with $NaBH_4$ (187.0 mg, 4.94 mmol, 2.0 equiv) in MeOH (10.0 mL) to give **S29** (893.5 mg, 1.62 mmol, 67%) as a white foam after purification by silica gel column chromatography (PE:EA = 1.5:1). $[\alpha]_D^{25} = -13.15$ (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14–8.00 (m, 6H), 7.61–7.54 (m, 3H), 7.47–7.34 (m, 6H), 5.78 (t, *J* = 9.9 Hz, 1H), 5.67–5.59 (m, 1H), 4.92 (d, *J* = 1.4 Hz, 1H), 4.70 (dd, *J* = 12.1, 2.6 Hz, 1H), 4.43 (dd, *J* = 12.1, 4.7 Hz, 1H), 4.31–4.22 (m, 1H), 4.13 (dd, *J* = 9.7, 3.3 Hz, 1H), 3.79–3.70 (m, 1H), 3.63–3.56 (m, 1H), 3.55–3.50 (m, 2H), 3.49 (s, 3H), 2.27 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.4, 166.2, 165.7, 133.6, 133.2, 130.1, 130.0, 129.9, 129.5, 129.4, 128.7, 128.6, 99.2, 77.1, 72.9, 69.7, 68.9, 68.8, 63.2, 61.8, 55.6; HRMS (ESI) *m/z* calcd for $C_{30}H_{34}NO_{10}$ $[M+NH_4]^+$ 568.2177, found 568.2183.

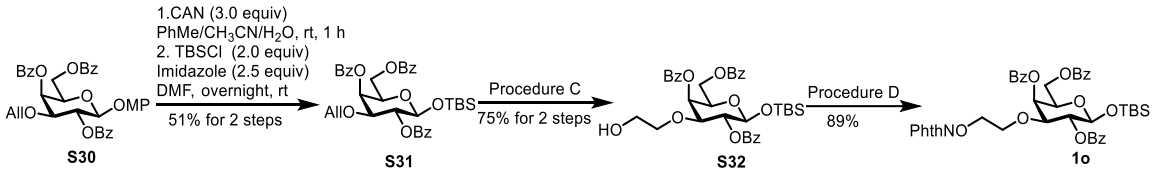
Methyl 2,4,6-tri-*O*-benzoyl-3-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-α-D-mannopyranoside (1n)



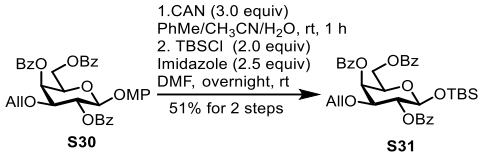
Following the general procedure D, **S29** (722.0 mg, 1.31 mmol, 1.0 equiv) was treated with PPh_3 (412.3 mg, 1.57 μmol, 1.2 equiv), *N*-hydroxyphthalimide (256.4 mg, 1.57 mmol, 1.2 equiv) and diisopropylazodicarboxylate (310 μL, 1.57 mmol, 1.2 equiv) in THF (4.0 mL) to give **1n** (767.8 mg, 1.10 mmol, 84%) as a white foam after purification by silica gel column chromatography (PE:EA = 2:1). $[\alpha]_D^{25} = -2.16$ (*c* 6.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10–8.04 (m, 4H), 8.03–7.99 (m, 2H), 7.72–7.64 (m, 4H), 7.58–7.52 (m, 2H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.42–7.31 (m, 6H), 5.77 (t, *J* =

9.9 Hz, 1H), 5.69–5.64 (m, 1H), 4.93 (d, *J* = 1.5 Hz, 1H), 4.65 (dd, *J* = 12.1, 2.6 Hz, 1H), 4.41 (dd, *J* = 12.1, 4.8 Hz, 1H), 4.33 (dd, *J* = 9.7, 3.3 Hz, 1H), 4.28–4.21 (m, 1H), 4.20–4.15 (m, 2H), 4.05–3.96 (m, 1H), 3.92–3.84 (m, 1H), 3.47 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.4, 165.8, 165.6, 163.4, 134.4, 133.32, 133.27, 133.1, 130.1, 130.0, 129.9, 129.72, 129.69, 128.9, 128.5, 123.6, 99.0, 77.8, 76.8, 69.7, 68.9, 68.8, 68.7, 63.3, 55.5; HRMS (ESI) *m/z* calcd for $C_{38}H_{33}NO_{12}Na$ $[M+Na]^+$ 718.1895, found 718.1899.

Preparation of 1o *via* intermediates S31 and S32



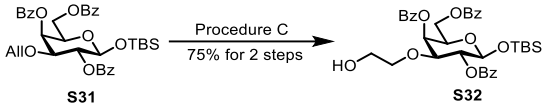
tert-Butyldimethylsilyl 3-*O*-allyl-2,3,6-tri-*O*-benzoyl-β-D-galactopyranoside (S31)



To a solution of **S30**[9] (1.15 g, 1.80 mmol, 1.0 equiv) in PhMe/CH_3CN/H_2O (15.0 mL, *v*/*v*/*v* = 1:1:1) was added CAN (2.53 g, 5.40 mmol, 3.0 equiv) in ice bath under an argon atmosphere. After stirring for 0.5 h in ice bath, the reaction was quenched with saturated $NaHCO_3$ solution. The resultant mixture was extracted with DCM, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo* to give the crude product without further purification for next step. The crude product was dissolved in dry DMF (10.0 mL), imidazole (306.3 mg, 4.50 mmol, 2.5 equiv) and *tert*-butyldimethylsilyl chloride (TBSCl) (542.6 mg, 3.60 mmol, 2.0 equiv) were added under an argon atmosphere. The resultant solution was stirred for 12 h at room temperature. The reaction mixture was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (PE:EA = 10:1) to afford **S31** (586.3 mg, 906.5 μmol, 51%) as a white foam. $[\alpha]_D^{25}$ = +54.17 (*c* 3.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11–8.02

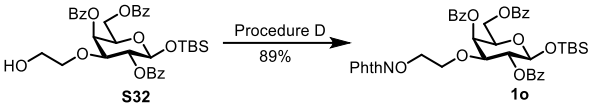
(m, 2H), 8.01–7.89 (m, 4H), 7.52–7.42 (m, 3H), 7.42–7.25 (m, 6H), 5.72 (d, *J* = 2.9 Hz, 1H), 5.63–5.49 (m, 1H), 5.38 (dd, *J* = 10.1, 7.8 Hz, 1H), 5.11–5.02 (m, 1H), 4.98–4.91 (m, 1H), 4.79 (d, *J* = 7.7 Hz, 1H), 4.51–4.28 (m, 2H), 4.11–3.96 (m, 2H), 3.87 (dd, *J* = 13.3, 6.4 Hz, 1H), 3.71 (dd, *J* = 10.1, 3.5 Hz, 1H), 0.67 (s, 9H), -0.00 (s, 3H), -0.08 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 166.1, 165.4, 134.3, 133.5, 133.4, 133.1, 130.3, 129.9, 129.8, 129.7, 129.5, 128.6, 128.5, 117.8, 96.7, 76.6, 73.4, 71.8, 70.8, 67.5, 63.2, 25.6, 18.0, -4.1, -5.1; HRMS (ESI) *m/z* calcd for $C_{36}H_{46}NO_9Si$ $[M+NH_4]^+$ 664.2936, found 664.2950.

tert-Butyldimethylsilyl 2,3,6-tri-*O*-benzoyl-3-*O*-(2-hydroxyethyl)-β-D-galacto-pyranoside (S32)



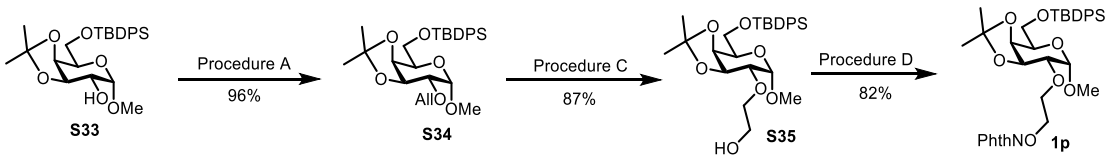
Following the general procedure C, **S31** (400.0 mg, 620.0 μmol, 1.0 equiv) was treated with 2,6-lutidine (145 μL, 1.24 mmol, 2.0 equiv), OsO_4 (0.0234 mol/L solution in *t*-BuOH, 530 μL, 12.4 μmol, 0.02 equiv) and $NaIO_4$ (530.0 mg, 2.48 mmol, 4.0 equiv) in 1,4-dioxane/H_2O (8.0 mL, *v*/*v* = 3:1) to give the aldehyde. The aldehyde was treated with $NaBH_4$ (35.0 mg, 930.0 μmol, 1.5 equiv) in MeOH (3.0 mL) to give **S32** (301.5 mg, 463.3 μmol, 75%) as a colorless oil after purification by silica gel column chromatography (PE:EA = 2:1). $[\alpha]_D^{25}$ = +54.59 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20–8.12 (m, 2H), 8.07–8.00 (m, 4H), 7.64–7.54 (m, 3H), 7.52–7.48 (m, 2H), 7.47–7.41 (m, 4H), 5.84 (d, *J* = 2.8 Hz, 1H), 5.45 (dd, *J* = 10.0, 7.8 Hz, 1H), 4.91 (d, *J* = 7.7 Hz, 1H), 4.59 (dd, *J* = 11.4, 7.4 Hz, 1H), 4.45 (dd, *J* = 11.4, 5.5 Hz, 1H), 4.16 (t, *J* = 6.3 Hz, 1H), 3.82 (dd, *J* = 10.1, 3.5 Hz, 1H), 3.79–3.71 (m, 1H), 3.63–3.57 (m, 1H), 3.54–3.48 (m, 2H), 2.43 (s, 1H), 0.79 (s, 9H), 0.12 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 166.3, 165.5, 133.7, 133.4, 133.3, 130.3, 129.9, 129.7, 129.6, 129.3, 128.7, 128.6, 128.5, 96.6, 79.7, 73.9, 73.5, 71.6, 68.4, 62.9, 61.8, 25.6, 18.0, -4.1, -5.1; HRMS (ESI) *m/z* calcd for $C_{35}H_{46}NO_{10}Si$ $[M+NH_4]^+$ 668.2885, found 668.2899.

***tert*-Butyldimethylsilyl 2,3,6-tri-*O*-benzoyl-3-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]-ethyl}-β-D-galactopyranoside (1o)**

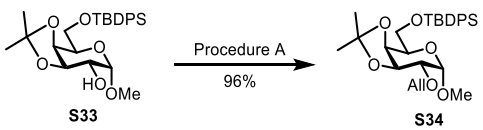


Following the general procedure D, **S32** (260.0 mg, 400.0 μmol, 1.0 equiv) was treated with PPh_3 (125.9 mg, 480.0 μmol, 1.2 equiv), *N*-hydroxyphthalimide (78.3 mg, 480.0 μmol, 1.2 equiv) and diisopropylazodicarboxylate (95 μL, 480.0 μmol, 1.2 equiv) in THF (4.0 mL) to give **1o** (284.1 mg, 356.9 μmol, 89%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25}$ = +31.07 (*c* 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18–8.12 (m, 2H), 8.11–8.05 (m, 4H), 7.75–7.66 (m, 4H), 7.62–7.53 (m, 2H), 7.53–7.45 (m, 3H), 7.45–7.37 (m, 4H), 6.08 (d, *J* = 2.8 Hz, 1H), 5.48 (dd, *J* = 10.1, 7.7 Hz, 1H), 4.97 (d, *J* = 7.7 Hz, 1H), 4.61 (dd, *J* = 11.3, 7.5 Hz, 1H), 4.53–4.41 (m, 2H), 4.32–4.21 (m, 3H), 4.00–3.91 (m, 1H), 3.89–3.82 (m, 1H), 0.79 (s, 9H), 0.12 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 166.1, 165.5, 163.7, 134.6, 133.4, 133.2, 133.0, 129.8, 129.6, 128.9, 128.6, 128.5, 128.4, 123.7, 96.7, 79.7, 78.4, 73.7, 71.7, 68.3, 67.6, 63.1, 25.6, 18.0, -4.1, -5.1; HRMS (ESI) *m/z* calcd for $C_{43}H_{49}N_2O_{12}Si$ $[M+NH_4]^+$ 813.3049, found 813.3061.

Preparation of 1p *via* intermediates S34 and S35.

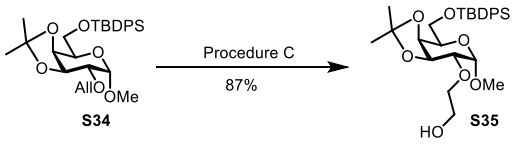


Methyl 2-*O*-allyl-6-*O*-*tert*-butyldiphenylsilyl-3,4-*O*-isopropylidene-α-D-galacto-pyranoside (S34)



Following the general procedure A, **S33**[10] (3.22 g, 6.74 mmol, 1.0 equiv) was treated with AllBr (985 μL, 9.52 mmol, 1.4 equiv) and 60% dispersion of NaH in mineral oil (380.0 mg, 9.52 mmol, 1.4 equiv) in DMF (40.0 mL) to give **S34** (3.31 g, 6.46 mmol, 96%) as a colorless oil after purification by silica gel column chromatography (PE:EA = 8:1). $[\alpha]_D^{25}$ = +54.92 (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76–7.69 (m, 4H), 7.47–7.35 (m, 6H), 6.00–5.88 (m, 1H), 5.32–5.25 (m, 1H), 5.20 (d, *J* = 10.3 Hz, 1H), 4.75 (d, *J* = 3.5 Hz, 1H), 4.32–4.28 (m, 2H), 4.27 (d, *J* = 5.3 Hz, 1H), 4.19 (dd, *J* = 13.0, 6.4 Hz, 1H), 4.05 (t, *J* = 7.2 Hz, 1H), 3.97 (dd, *J* = 9.8, 6.8 Hz, 1H), 3.88 (dd, *J* = 9.8, 6.5 Hz, 1H), 3.53 (dd, *J* = 7.4, 3.5 Hz, 1H), 3.39 (s, 3H), 1.52 (s, 3H), 1.36 (s, 3H), 1.08 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.7, 135.0, 133.6, 133.5, 129.8, 127.8, 127.7, 117.9, 109.1, 98.4, 76.7, 76.2, 73.4, 71.9, 67.7, 63.0, 55.4, 28.4, 26.9, 26.5, 19.3; HRMS (ESI) *m/z* calcd for $C_{29}H_{40}O_6SiNa$ $[M+Na]^+$ 535.2486, found 535.2491.

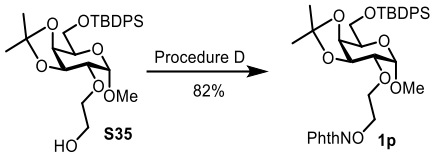
Methyl 6-*O*-*tert*-butyldiphenylsilyl-2-*O*-(2-hydroxyethyl)-3,4-*O*-isopropylidene-α-D-galactopyranoside (S35)



Following the general procedure C, **S34** (3.21 g, 6.24 mmol, 1.0 equiv) was treated with 2,6-lutidine (1.5 mL, 12.48 mmol, 2.0 equiv), OsO_4 (0.0234 mol/L solution in *t*-BuOH, 5.3 mL, 124.8 μmol, 0.02 equiv) and $NaIO_4$ (5.33 g, 24.96 mmol, 4.0 equiv) in 1,4-dioxane/H_2O (40.0 mL, *v*/*v* = 3:1) to give the aldehyde. The aldehyde was treated with $NaBH_4$ (472.3 mg, 12.48 mmol, 2.0 equiv) in MeOH (20.0 mL) to give **S35** (2.81 g, 5.44 mmol, 87%) as a white foam after purification by silica gel column chromatography (PE:EA = 1.5:1). $[\alpha]_D^{25}$ = +52.51 (*c* 2.5, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76–7.67 (m, 4H), 7.47–7.35 (m, 6H), 4.79 (d, *J* = 3.5 Hz, 1H), 4.34–4.25 (m, 2H), 4.05 (dd, *J* = 6.5, 3.2 Hz, 1H), 3.98 (dd, *J* = 9.8, 6.9 Hz, 1H), 3.89 (dd, *J* = 9.9, 6.5 Hz, 1H), 3.81–3.70 (m, 4H), 3.52 (dd, *J* = 7.3, 3.5 Hz, 1H), 3.39 (s, 3H), 3.11 (s, 1H), 1.53 (s, 3H), 1.35 (s, 3H), 1.08 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ

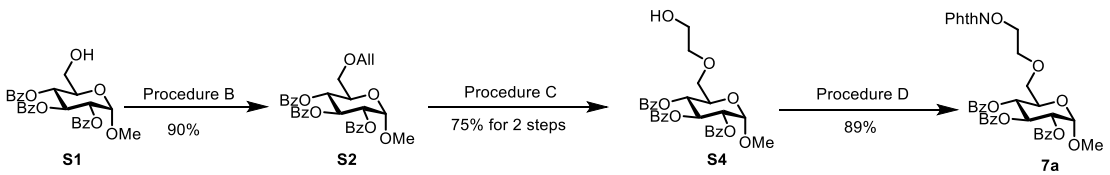
135.6, 133.5, 133.3, 129.7, 127.7, 127.6, 109.2, 97.9, 78.9, 75.7, 73.2, 72.7, 67.8, 62.9, 61.9, 55.3, 28.2, 26.8, 26.4, 19.2; HRMS (ESI) *m/z* calcd for $C_{28}H_{44}NO_7Si$ $[M+NH_4]^+$ 534.2882, found 534.2895.

Methyl 6-*O*-*tert*-butyldiphenylsilyl-2-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-3,4-*O*-isopropylidene-α-D-galactopyranoside (1p)

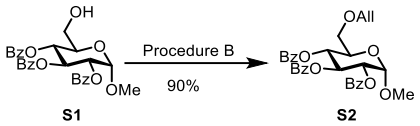


Following the general procedure D, **S35** (1.03 g, 2.00 mmol, 1.0 equiv) was treated with PPh_3 (629.5 mg, 2.40 mmol, 1.2 equiv), *N*-hydroxyphthalimide (391.4 mg, 2.40 mmol, 1.2 equiv) and diisopropylazodicarboxylate (480 μL, 2.4 mmol, 1.2 equiv) in THF (10.0 mL) to give **1p** (1.09 g, 1.65 mmol, 82%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25}$ = +114.49 (*c* 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84–7.79 (m, 2H), 7.75–7.66 (m, 6H), 7.45–7.33 (m, 6H), 4.79 (d, *J* = 3.5 Hz, 1H), 4.48–4.40 (m, 1H), 4.38–4.31 (m, 1H), 4.27–4.21 (m, 2H), 4.18–4.11 (m, 1H), 4.07–4.01 (m, 1H), 4.01–3.92 (m, 2H), 3.85 (dd, *J* = 9.6, 6.2 Hz, 1H), 3.55 (dd, *J* = 7.0, 3.6 Hz, 1H), 3.24 (s, 3H), 1.51 (s, 3H), 1.31 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.4, 135.7, 134.4, 133.4, 129.7, 129.0, 127.7, 123.5, 109.1, 98.3, 78.8, 77.5, 76.2, 73.3, 69.6, 67.6, 63.0, 55.2, 28.4, 26.8, 26.4, 19.2; HRMS (ESI) *m/z* calcd for $C_{36}H_{47}N_2O_9Si$ $[M+NH_4]^+$ 679.3045, found 679.3057.

Preparation of 7a *via* intermediates S2 and S4



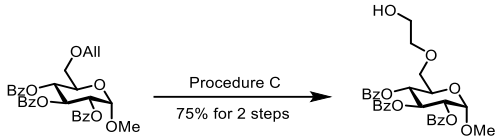
Methyl 6-*O*-allyl-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (S2)



S1 S2

Following the general procedure B, **S1** (1.52 g, 3.00 mmol, 1.0 equiv) was treated with 2,4,6-tris(allyloxy)-1,3,5-triazine (670.0 μL, 3.00 mmol, 1.0 equiv) and TfOH (100 μL, 1.2 mmol, 0.4 equiv) in 1,4-dioxane (3.0 mL) to give **S2** (1.47 g, 2.69 mmol, 90%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25}$ = +47.80 (*c* 3.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06–7.92 (m, 4H), 7.92–7.81 (m, 2H), 7.55–7.47 (m, 2H), 7.46–7.34 (m, 5H), 7.32–7.27 (m, 2H), 6.15 (t, *J* = 9.6 Hz, 1H), 5.92–5.78 (m, 1H), 5.61 (t, *J* = 9.9 Hz, 1H), 5.33–5.18 (m, 3H), 5.13–5.07 (m, 1H), 4.29–4.17 (m, 1H), 4.07–3.94 (m, 2H), 3.72–3.57 (m, 2H), 3.48 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 165.3, 134.3, 133.4, 133.1, 130.0, 129.8, 129.7, 129.3, 129.2, 129.1, 128.4, 128.3, 97.0, 72.7, 72.2, 70.6, 69.6, 68.9, 68.6, 55.6; HRMS (ESI) *m/z* calcd for $C_{31}H_{34}NO_9$ $[M+NH_4]^+$ 564.2228, found 564.2219.

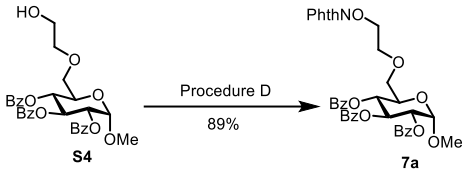
Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2-hydroxyethyl)-α-D-glucopyranoside (S4)



S2 S4

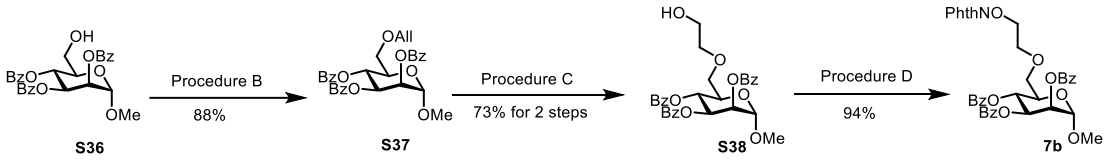
Following the general procedure C, **S2** (1.47 g, 2.69 mmol, 1.0 equiv) was treated with 2,6-lutidine (630 μL, 5.38 mmol, 2.0 equiv), OsO_4 (0.0234 mol/L solution in *t*-BuOH, 2.3 mL, 0.0538 mmol, 0.02 equiv) and $NaIO_4$ (2.31 g, 10.76 mmol, 4.0 equiv) in 1,4-dioxane/H_2O (12.0 mL, *v*/*v* = 3:1) to give the aldehyde. The aldehyde was treated with $NaBH_4$ (203.0 mg, 5.38 mmol, 2.0 equiv) in MeOH (10.0 mL) to give **S4** (1.11 g, 2.02 mmol, 75%) as a white foam after purification by silica gel column chromatography (PE:EA = 1.3:1).

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-α-D-glucopyranoside (7a)

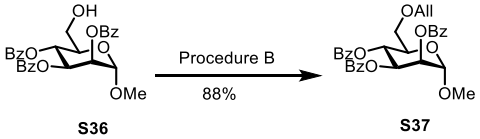


Following the general procedure D, **S4** (330.1 mg, 600.0 μmol, 1.0 equiv) was treated with PPh_3 (315.0 mg, 1.20 mmol, 2.0 equiv), *N*-hydroxyphthalimide (195.9 mg, 1.20 mmol, 2.0 equiv) and diisopropylazodicarboxylate (175 μL, 1.20 mmol, 2.0 equiv) in THF (6.0 mL) to give **7a** (370.0 mg, 531.9 μmol, 89%) as a white foam after purification by silica gel column chromatography (PE:DCM:EA = 5:1:1). $[\alpha]_D^{25}$ = +33.56 (*c* 2.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99–7.91 (m, 4H), 7.89–7.83 (m, 2H), 7.83–7.78 (m, 2H), 7.77–7.70 (m, 2H), 7.54–7.45 (m, 2H), 7.42–7.31 (m, 5H), 7.31–7.26 (m, 2H), 6.09 (t, *J* = 9.9 Hz, 1H), 5.49 (t, *J* = 9.9 Hz, 1H), 5.15 (dd, *J* = 10.2, 3.6 Hz, 1H), 5.03 (d, *J* = 3.6 Hz, 1H), 4.43–4.34 (m, 1H), 4.34–4.25 (m, 1H), 4.18–4.06 (m, 1H), 3.91–3.81 (m, 2H), 3.80–3.62 (m, 2H), 3.34 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 165.5, 163.5, 134.5, 133.44, 133.39, 133.2, 130.0, 129.9, 129.8, 129.4, 129.2, 129.1, 128.50, 128.49, 128.4, 96.8, 72.2, 70.6, 70.3, 70.1, 69.7, 68.9, 55.5; HRMS (ESI) *m/z* calcd for $C_{38}H_{37}N_2O_{12}$ $[M+NH_4]^+$ 713.2341, found 713.2335.

Preparation of 7b *via* intermediates S37 and S38



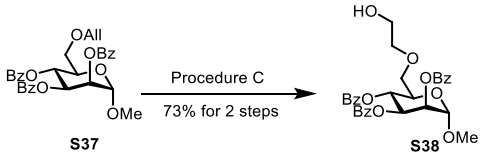
Methyl 6-*O*-allyl-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (S37)



Following the general procedure B, **S36**[11] (2.53 g, 5.00 mmol, 1.0 equiv) was treated with 2,4,6-tris(allyloxy)-1,3,5-triazine (1.2 mL, 5.00 mmol, 1.0 equiv) and TfOH (177 μL, 1.20 mmol, 0.4 equiv) in 1,4-dioxane (17.0 mL) to give **S37** (2.39 g, 4.38 mmol,

88%) as a white foam after purification by silica gel column chromatography (PE:EA = 4:1). $[\alpha]_D^{25} = -157.71$ (*c* 3.2, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 8.14–8.08 (m, 2H), 8.01–7.94 (m, 2H), 7.87–7.77 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.55–7.45 (m, 3H), 7.45–7.34 (m, 3H), 7.29–7.24 (m, 2H), 5.95 (t, *J* = 10.0 Hz, 1H), 5.91–5.82 (m, 2H), 5.71–5.65 (m, 1H), 5.32–5.22 (m, 1H), 5.12 (d, *J* = 11.3 Hz, 1H), 5.03–4.96 (m, 1H), 4.33–4.20 (m, 1H), 4.13–3.92 (m, 2H), 3.79–3.67 (m, 2H), 3.54 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.67, 165.65, 165.6, 134.5, 133.6, 133.4, 133.2, 130.1, 129.9, 129.8, 129.5, 129.4, 129.3, 128.7, 128.5, 128.4, 117.2, 98.7, 72.7, 70.6, 70.3, 70.1, 69.2, 67.5, 55.5; HRMS (ESI) *m/z* calcd for $C_{31}H_{34}NO_9$ $[M+NH_4]^+$ 564.2228, found 564.2219.

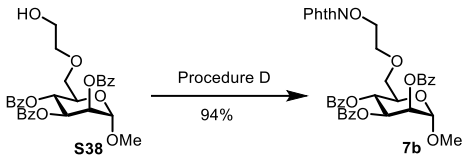
Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2-hydroxyethyl)-α-D-mannopyranoside (S38)



S37 **S38**

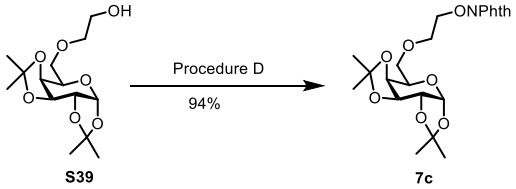
Following the general procedure C, **S37** (1.10 g, 2.00 mmol, 1.0 equiv) was treated with 2,6-lutidine (466 μL, 4.00 mmol, 2.0 equiv), OsO_4 (0.0234 mol/L solution in *t*-BuOH, 1.7 mL, 40.0 μmol, 0.02 equiv) and $NaIO_4$ (1.70 g, 4.00 mmol, 4.0 equiv) in 1,4-dioxane/H_2O (12.0 mL, *v*/*v* = 3:1) to give the aldehyde. The aldehyde was treated with $NaBH_4$ (151.3 mg, 4.00 mmol, 2.0 equiv) in MeOH (10.0 mL) to give **S38** (806.8 mg, 1.47 mmol, 73%) as a white foam after purification by silica gel column chromatography (PE:EA = 1.3:1). $[\alpha]_D^{25} = -122.82$ (*c* 1.3, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 8.15–8.09 (m, 2H), 8.01–7.96 (m, 2H), 7.86–7.79 (m, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.56–7.46 (m, 3H), 7.46–7.35 (m, 3H), 7.30–7.22 (m, 2H), 6.12 (t, *J* = 10.1 Hz, 1H), 5.90 (dd, *J* = 10.2, 3.3 Hz, 1H), 5.67 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.01 (d, *J* = 1.6 Hz, 1H), 4.25–4.17 (m, 1H), 3.83–3.66 (m, 5H), 3.58–3.47 (m, 4H), 2.74 (brs, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.1, 165.7, 165.6, 133.7, 133.3, 130.1, 130.0, 129.8, 129.5, 129.2, 129.1, 128.7, 128.6, 128.4, 98.9, 73.2, 70.5, 70.1, 70.0, 69.6, 67.1, 61.9, 55.7; HRMS (ESI) *m/z* calcd for $C_{30}H_{34}NO_{10}$ $[M+NH_4]^+$ 568.2177, found 568.2174.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-α-D-mannopyranoside (7b)



Following the general procedure D, **S38** (1.45 g, 2.63 mmol, 1.0 equiv) was treated with PPh_3 (828.8 mg, 3.16 mmol, 1.2 equiv), *N*-hydroxyphthalimide (515.5 mg, 3.16 mmol, 1.2 equiv) and diisopropylazodicarboxylate (530 μL, 3.16 mmol, 1.2 equiv) in THF (6.0 mL) to give **7b** (1.72 g, 2.47 mmol, 94%) as a white foam after purification by silica gel column chromatography (PE:EA = 1.5:1). $[\alpha]_D^{25} = -145.23$ (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13–8.04 (m, 2H), 7.98–7.91 (m, 2H), 7.87–7.78 (m, 2H), 7.75–7.66 (m, 4H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.56–7.47 (m, 3H), 7.46–7.32 (m, 3H), 7.26–7.22 (m, 2H), 5.88–5.71 (m, 2H), 5.58 (t, *J* = 1.8 Hz, 1H), 4.70 (d, *J* = 1.5 Hz, 1H), 4.42–4.34 (m, 1H), 4.33–4.26 (m, 1H), 4.20–4.06 (m, 1H), 3.98–3.84 (m, 2H), 3.83–3.67 (m, 2H), 3.39 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 165.74, 165.67, 163.6, 134.5, 133.8, 133.5, 133.3, 130.2, 130.0, 129.9, 129.6, 129.44, 129.40, 129.3, 128.9, 128.6, 128.5, 123.6, 98.5, 77.6, 70.7, 70.6, 70.22, 70.20, 70.1, 67.6, 55.5; HRMS (ESI) *m/z* calcd for $C_{38}H_{37}N_2O_{12}$ $[M+NH_4]^+$ 713.2341, found 713.2339.

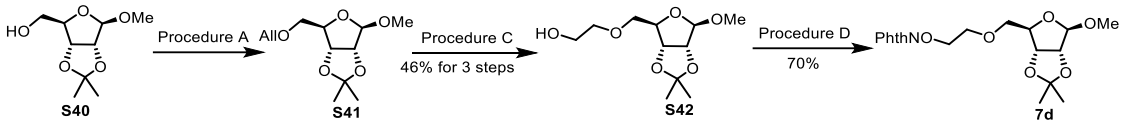
6-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranose (7c)



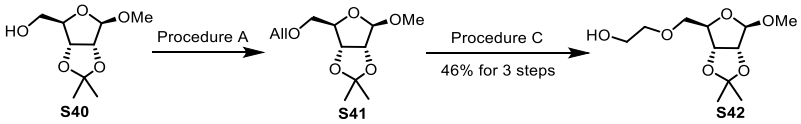
Following the general procedure D, **S39**[15] (430.0 mg, 1.41 mmol, 1.0 equiv) was treated with PPh_3 (443.5 mg, 1.69 mmol, 1.2 equiv), *N*-hydroxyphthalimide (275.1 mg, 1.69 mmol, 1.2 equiv) and diisopropylazodicarboxylate (335 μL, 1.69 mmol, 1.2 equiv) in THF (5.0 mL) to give **7c** (596.3 mg, 1.33 mmol, 94%) as a white foam after purification by silica gel column chromatography (PE:EA = 2:1). $[\alpha]_D^{25} = -38.89$ (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89–7.78 (m, 2H), 7.78–7.71 (m, 2H),

5.48 (d, *J* = 5.0 Hz, 1H), 4.55 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.44–4.32 (m, 2H), 4.27 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.20 (dd, *J* = 7.9, 1.8 Hz, 1H), 4.03–3.82 (m, 3H), 3.74 (dd, *J* = 10.3, 5.5 Hz, 1H), 3.63 (dd, *J* = 10.3, 6.8 Hz, 1H), 1.47 (s, 3H), 1.43 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.5, 134.5, 129.1, 123.6, 109.3, 108.6, 96.4, 77.3, 71.2, 70.7, 70.6, 70.3, 69.5, 66.8, 26.1, 25.0, 24.5; HRMS (ESI) *m/z* calcd for $C_{22}H_{31}N_2O_9$ $[M+NH_4]^+$ 467.2024, found 467.2019.

Preparation of 7d *via* intermediates S40 and S41



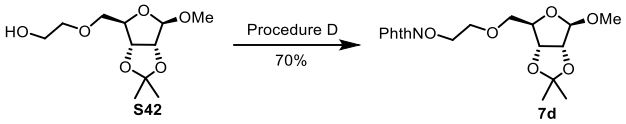
Methyl 5-*O*-(2-hydroxyethyl)-2,3-*O*-isopropylidene-β-D-ribofuranoside (S42)



Following the general procedure A, **S40**[13] (2.04 g, 10.00 mmol, 1.0 equiv) was treated with AllBr (1.1 mL, 12.00 mmol, 1.2 equiv) and 60% dispersion of NaH in mineral oil (480.0 mg, 12.00 mmol, 1.2 equiv) in DMF (20.0 mL) to give the crude product **S41** without further purification for next step. Following the general procedure C, the obtained crude product (1.0 equiv) was treated with 2,6-lutidine (2.3 mL, 20.00 mmol, 2.0 equiv), OsO_4 (0.0234 mol/L solution in *t*-BuOH, 8.5 mL, 20.0 μmol, 0.02 equiv) and $NaIO_4$ (8.50 g, 40.00 mmol, 4.0 equiv) in 1,4-dioxane/H_2O (50.0 mL, *v*/*v* = 3:1) to give the aldehyde. The aldehyde was treated with $NaBH_4$ (756.0 mg, 20.00 mmol, 2.0 equiv) in MeOH (50.0 mL) to give **S42** (1.15 g, 4.63 mmol, 46%) as a colorless oil after purification by silica gel column chromatography (PE:EA = 1:1). $[\alpha]_D^{25}$ = –50.56 (*c* 1.6, $CHCl_3$); 1H NMR (400 MHz, Chloroform-*d*) δ 4.98 (s, 1H), 4.70 (d, *J* = 5.9 Hz, 1H), 4.59 (d, *J* = 5.9 Hz, 1H), 4.37 (d, *J* = 6.1 Hz, 1H), 3.76–3.66 (m, 2H), 3.66–3.46 (m, 4H), 3.35 (s, 3H), 2.71 (brs, 1H), 1.49 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (101 MHz,

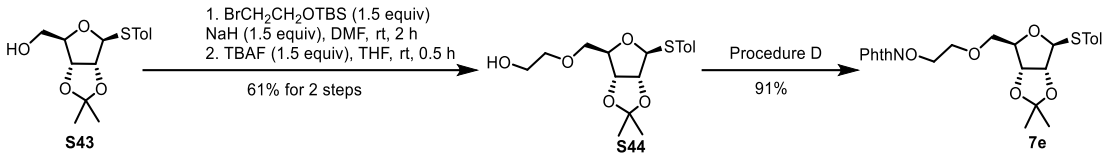
Chloroform-*d*) δ 112.4, 110.0, 85.5, 85.2, 82.0, 72.5, 72.2, 61.7, 55.1, 26.5, 25.0; HRMS (ESI) *m/z* calcd for $C_{11}H_{20}O_6Na$ $[M+Na]^+$ 271.1152, found 271.1156.

Methyl 5-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-2,3-*O*-isopropylidene-β-D-ribofuranoside (7d)

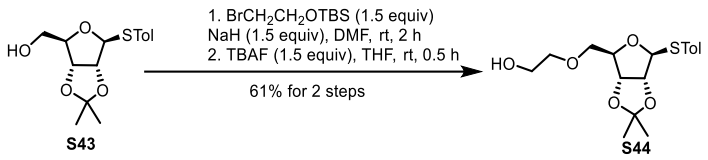


Following the general procedure D, **S42** (1.10 g, 4.40 mmol, 1.0 equiv) was treated with PPh_3 (1.27 g, 4.84 mmol, 1.2 equiv), *N*-hydroxyphthalimide (790.0 mg, 4.84 mmol, 1.2 equiv) and diisopropylazodicarboxylate (960 μL, 4.84 mmol, 1.2 equiv) in THF (5.0 mL) to give **7d** (1.21 g, 3.08 mmol, 70%) as a white foam after purification by silica gel column chromatography (PE:EA = 1.5:1). $[\alpha]_D^{25} = -26.24$ (*c* 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89–7.80 (m, 2H), 7.79–7.67 (m, 2H), 4.92 (s, 1H), 4.64 (d, *J* = 6.0 Hz, 1H), 4.54 (d, *J* = 6.0 Hz, 1H), 4.48–4.31 (m, 2H), 4.31–4.15 (m, 1H), 3.92–3.79 (m, 2H), 3.63–3.44 (m, 2H), 3.30 (s, 3H), 1.44 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6, 134.6, 129.1, 123.7, 112.4, 109.4, 85.2, 84.9, 82.1, 77.3, 72.3, 69.4, 54.9, 26.5, 25.1; HRMS (ESI) *m/z* calcd for $C_{19}H_{27}N_2O_8$ $[M+NH_4]^+$ 411.1762, found 411.1761.

Preparation of 7e *via* intermediate S44

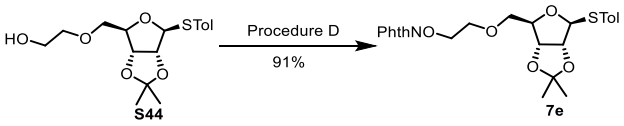


***p*-Tolyl 5-*O*-(2-hydroxyethyl)-2,3-*O*-isopropylidene-1-thio-β-D-ribofuranoside (S44)**



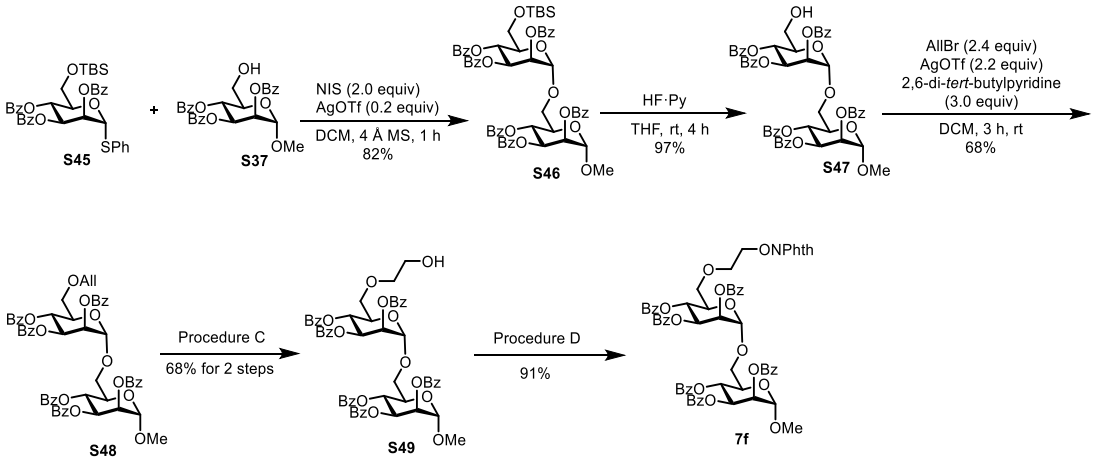
To a solution of **S43**[14] (2.60 g, 8.77 mmol, 1.0 equiv) in DMF (30.0 mL) were added (2-bromoethoxy)-*tert*-butyldimethylsilane (2.8 mL, 13.16 mmol, 1.5 equiv), TBAI (325.0 mg, 880.0 μmol, 0.1 equiv) and 60% dispersion of NaH in mineral oil (526.0 mg, 13.16 mmol, 1.5 equiv) in ice bath under an argon atmosphere. The resultant solution was stirred at room temperature for 3 h. The reaction was quenched with NH_4Cl solution at 0 °C. The resultant mixture was extracted with DCM, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo* to give the crude product without further purification for next step. To a solution of the crude product obtained as above in THF (10.0 mL) was added TBAF (1 mol/L in THF, 13.1 mL, 13.1 mmol, 1.5 equiv) under an argon atmosphere. After stirring for 0.5 h at room temperature, the reaction mixture was extracted with DCM, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (PE:EA = 2.5:1) to afford **S44** (1.81 g, 5.32 mmol, 61%) as a colorless oil. $[\alpha]_D^{25} = -107.48$ (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44–7.35 (m, 2H), 7.17–7.07 (m, 2H), 5.45 (d, *J* = 2.2 Hz, 1H), 4.78–4.69 (m, 2H), 4.39–4.30 (m, 1H), 3.77–3.68 (m, 4H), 3.68–3.57 (m, 2H), 2.52 (brs, 1H), 2.32 (s, 3H), 1.50 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.9, 132.4, 130.1, 129.9, 113.6, 93.4, 86.1, 85.5, 82.6, 72.9, 71.6, 61.8, 27.1, 25.5, 21.2; HRMS (ESI) *m/z* calcd for $C_{17}H_{28}NO_5S$ $[M+NH_4]^+$ 358.1683, found 358.1688.

_p_-Tolyl 5-_O_-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-2,3-_O_-isopropylidene-1-thio-β-D-ribofuranoside (7e)

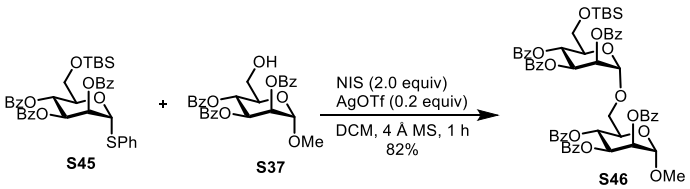


Following the general procedure D, **S43** (435.0 mg, 1.28 mmol, 1.0 equiv) was treated with PPh_3 (403.3 mg, 1.54 mmol, 1.2 equiv), *N*-hydroxyphthalimide (251.0 mg, 1.54 mmol, 1.2 equiv) and diisopropylazodicarboxylate (310 μL, 1.54 mmol, 1.2 equiv) in THF (5.0 mL) to give **7d** (561.1 mg, 1.16 mmol, 91%) as a white foam after purification by silica gel column chromatography (PE:EA = 2:1). $[\alpha]_D^{25} = -151.40$ (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91–7.80 (m, 2H), 7.81–7.72 (m, 2H), 7.43–7.34 (m, 2H), 7.16–7.00 (m, 2H), 5.40 (d, *J* = 1.8 Hz, 1H), 4.88–4.64 (m, 2H), 4.46–4.32 (m, 2H), 4.26 (t, *J* = 6.3 Hz, 1H), 3.98–3.82 (m, 2H), 3.82–3.65 (m, 2H), 2.32 (s, 3H), 1.46 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6, 137.7, 134.6, 132.2, 130.5, 129.9, 129.0, 123.7, 113.4, 93.3, 85.9, 85.3, 82.6, 77.3, 71.7, 69.6, 27.0, 25.5, 21.2; HRMS (ESI) *m/z* calcd for $C_{25}H_{31}N_2O_7S$ $[M+NH_4]^+$ 503.1846, found 503.1840.

Preparation of 7f *via* intermediate S46–S49



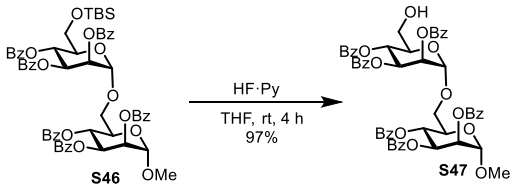
Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (S46)



To a solution of **S45**[12] (1.05 g, 1.50 mmol, 1.0 equiv), **S37** (1.14 g, 2.25 mmol, 1.5

equiv) and freshly activated 4 Å MS in DCM (10.0 mL) were added *N*-iodosuccimide (NIS) (675.0 mg, 3.00 mmol, 2.0 equiv) and silver triflate (AgOTf) (77.0 mg, 0.3 mmol, 0.2 equiv) in ice bath under an argon atmosphere. The resultant solution was stirred in ice bath for 1 h. The reaction was quenched with saturated $NaHCO_3$ solution and $Na_2S_2O_3$ solution in ice bath. The resultant mixture was extracted with DCM, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (PE:EA = 9:1) to afford **S46** (1.35 g, 1.23 mmol, 82%) as a white foam. $[\alpha]_D^{25}$ = −85.77 (*c* 2.5, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28–8.19 (m, 2H), 8.18–8.13 (m, 2H), 8.13–8.02 (m, 4H), 7.99–7.88 (m, 4H), 7.68–7.56 (m, 5H), 7.55–7.40 (m, 8H), 7.37–7.32 (m, 5H), 6.13–6.04 (m, 2H), 6.03–5.96 (m, 2H), 5.83–5.79 (m, 2H), 5.25–5.18 (m, 1H), 5.12 (d, *J* = 1.2 Hz, 1H), 4.51–4.43 (m, 1H), 4.24–4.15 (m, 2H), 3.83 (dd, *J* = 10.8, 1.8 Hz, 1H), 3.81–3.73 (m, 2H), 3.71 (s, 3H), 0.91 (s, 9H), 0.04–-0.04 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 165.7, 165.6, 165.5, 165.40, 165.35, 133.51, 133.47, 133.4, 133.21, 133.17, 133.0, 130.0, 129.88, 129.85, 129.77, 129.75, 129.6, 129.5, 129.43, 129.40, 129.2, 129.1, 128.8, 128.54, 128.53, 128.4, 128.3, 98.7, 97.6, 77.3, 71.5, 70.7, 70.6, 70.3, 69.5, 67.2, 66.7, 66.5, 61.9, 55.6, 25.8, 18.2, -5.5; HRMS (ESI) *m/z* calcd for $C_{61}H_{66}NO_{17}Si$ $[M+NH_4]^+$ 1112.4095, found 1112.4115.

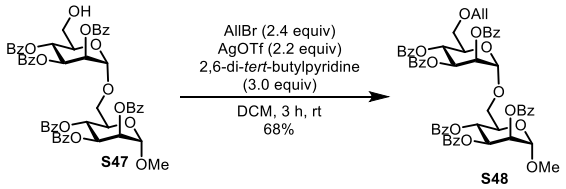
Methyl 2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (S47)



To a solution of **S46** (1.35 g, 1.23 mmol, 1.0 equiv) in THF (10.0 mL) was added HF·Py (1.2 mL) in ice bath under an argon atmosphere. The resultant solution was stirred at room temperature for 4 h. The reaction was quenched with saturated $NaHCO_3$ solution. The resultant mixture was extracted with DCM, and the organic layer was washed with

brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (PE:EA = 1.5:1) to afford **S47** (1.17 g, 1.19 mmol, 97%) as a white foam. $[\alpha]_D^{25} = -102.26$ (*c* 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20–8.14 (m, 2H), 8.11–8.05 (m, 2H), 8.04–7.99 (m, 2H), 7.99–7.93 (m, 2H), 7.90–7.80 (m, 4H), 7.64–7.51 (m, 5H), 7.51–7.37 (m, 7H), 7.34–7.26 (m, 6H), 6.09–6.00 (m, 2H), 5.92 (dd, *J* = 10.1, 3.3 Hz, 1H), 5.82 (t, *J* = 10.1 Hz, 1H), 5.78–5.70 (m, 2H), 5.17 (d, *J* = 1.4 Hz, 1H), 5.03 (d, *J* = 1.4 Hz, 1H), 4.44–4.33 (m, 1H), 4.08 (dd, *J* = 10.9, 5.5 Hz, 1H), 4.06–4.00 (m, 1H), 3.79 (dd, *J* = 10.9, 2.0 Hz, 1H), 3.68–3.58 (m, 4H), 3.58–3.51 (m, 1H), 2.59 (t, *J* = 6.5 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 165.7, 165.6, 165.5, 165.4, 165.3, 133.7, 133.6, 133.54, 133.50, 133.2, 130.04, 129.99, 129.96, 129.8, 129.7, 129.4, 129.3, 129.2, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 98.9, 97.8, 71.1, 70.5, 70.2, 69.6, 69.4, 67.2, 67.1, 66.8, 61.1, 55.6; HRMS (ESI) *m/z* calcd for $C_{55}H_{52}NO_{17}$ $[M+NH_4]^+$ 998.3230, found 998.3249.

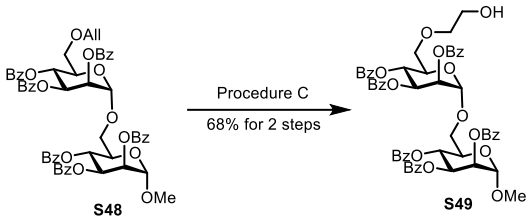
Methyl 6-*O*-allyl-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (S48)



To a solution of **S47** (346.0 mg, 352.7 μmol, 1.0 equiv) in DCM (3.0 mL) were added AllBr (72 μL, 846.5 μmol, 2.4 equiv), AgOTf (198.0 mg, 775.9 μmol, 2.2 equiv) and 2,6-di-*tert*-butylpyridine (235 μL, 1.06 mmol, 3.0 equiv) in ice bath under an argon atmosphere. The resultant solution was stirred for 3 h at room temperature. The resultant mixture was diluted with DCM and washed with 1M HCl solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (PE:EA = 2:1) to afford **S48** (246.0 mg, 240.9 μmol, 68%) as a white foam. $[\alpha]_D^{25} = -91.83$ (*c* 3.3, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22–8.14

(m, 2H), 8.13–8.05 (m, 2H), 8.05–7.97 (m, 4H), 7.91–7.80 (m, 4H), 7.61–7.50 (m, 5H), 7.49–7.36 (m, 7H), 7.35–7.25 (m, 6H), 6.07 (t, *J* = 10.1 Hz, 1H), 5.98–5.90 (m, 3H), 5.79–5.74 (m, 2H), 5.74–5.65 (m, 1H), 5.21–5.10 (m, 2H), 5.10–4.97 (m, 2H), 4.46–4.35 (m, 1H), 4.28–4.20 (m, 1H), 4.14 (dd, *J* = 10.9, 5.6 Hz, 1H), 3.93–3.74 (m, 3H), 3.63 (s, 3H), 3.56 (dd, *J* = 11.0, 5.2 Hz, 1H), 3.48 (dd, *J* = 10.9, 2.5 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 165.6, 165.5, 165.4, 134.4, 133.6, 133.52, 133.48, 133.4, 133.2, 133.1, 130.1, 130.0, 129.92, 129.90, 129.88, 129.8, 129.5, 129.4, 129.2, 129.1, 128.9, 128.6, 128.5, 128.4, 117.0, 98.8, 97.6, 72.4, 70.6, 70.4, 70.34, 70.25, 70.2, 69.5, 68.7, 67.3, 67.1, 66.6, 55.6; HRMS (ESI) *m/z* calcd for $C_{58}H_{56}NO_{17}$ $[M+NH_4]^+$ 1038.3543, found 1038.3563.

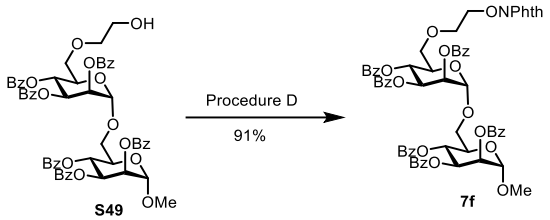
Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2-hydroxyethyl)-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (S49)



Following the general procedure C, **S48** (1.09 g, 1.07 mmol, 1.0 equiv) was treated with 2,6-lutidine (250 μL, 2.14 mmol, 2.0 equiv), OsO_4 (0.0234 mol/L solution in *t*-BuOH, 1.0 mL, 22.0 mmol, 0.02 equiv) and $NaIO_4$ (920.0 mg, 4.31 mmol, 4.0 equiv) in 1,4-dioxane/H_2O (12.0 mL, *v*/*v* = 3:1) to give the aldehyde. The aldehyde was treated with $NaBH_4$ (40.0 mg, 1.07 mmol, 1.0 equiv) in MeOH (10.0 mL) to give **S49** (739.5 mg, 721.5 μmol, 68%) as a white foam after purification by silica gel column chromatography (PE:EA = 1.5:1). $[\alpha]_D^{25}$ = –99.76 (*c* 1.9, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20–8.16 (m, 2H), 8.14–8.07 (m, 2H), 8.07–7.96 (m, 4H), 7.94–7.78 (m, 4H), 7.62–7.51 (m, 5H), 7.51–7.37 (m, 7H), 7.37–7.31 (m, 2H), 7.31–7.26 (m, 4H), 6.10 (t, *J* = 10.0 Hz, 1H), 6.04 (t, *J* = 10.1 Hz, 1H), 5.99 (dd, *J* = 10.2, 3.3 Hz, 1H), 5.93 (dd, *J* = 10.1, 3.3 Hz, 1H), 5.79–5.71 (m, 2H), 5.17 (d, *J* = 1.3 Hz, 1H), 5.04 (s, 1H), 4.39 (dd, *J* = 9.9, 5.3 Hz, 1H), 4.22 (d, *J* = 7.4 Hz, 1H), 4.10 (dd, *J* = 10.9, 5.6 Hz, 1H), 3.79 (dd, *J* = 10.9, 1.7 Hz, 1H), 3.73–3.59 (m, 6H), 3.58–3.51 (m, 2H), 3.47–3.35 (m,

1H), 2.68 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.1, 165.8, 165.7, 165.6, 165.5, 165.4, 133.7, 133.6, 133.3, 133.2, 130.13, 130.05, 130.0, 129.9, 129.8, 129.43, 129.42, 129.3, 129.24, 129.16, 129.1, 128.9, 128.7, 128.6, 128.4, 98.9, 97.8, 73.1, 70.6, 70.4, 70.3, 70.1, 70.0, 69.5, 69.2, 67.1, 67.0, 66.8, 61.8, 55.7; HRMS (ESI) *m/z* calcd for $C_{57}H_{56}NO_{18}$ $[M+NH_4]^+$ 1042.3492, found 1042.3523.

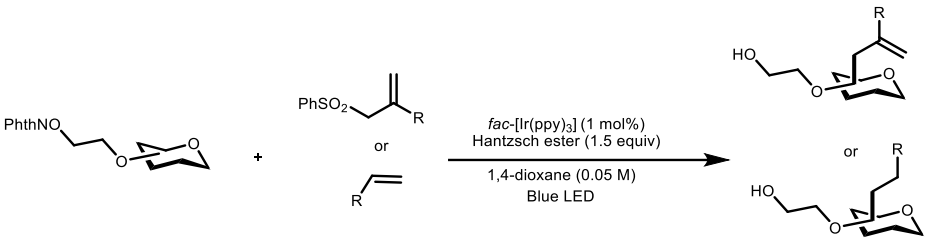
Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]ethyl}-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (7f)



Following the general procedure D, **S49** (653.0 mg, 637.1 μmol, 1.0 equiv) was treated with PPh_3 (201.9 mg, 770.0 μmol, 1.2 equiv), *N*-hydroxyphthalimide (125.6 mg, 770.0 μmol, 1.2 equiv) and diisopropylazodicarboxylate (150 μL, 770.0 μmol, 1.2 equiv) in THF (5.0 mL) to give **7f** (674.1 mg, 576.1 μmol, 91%) as a white foam after purification by silica gel column chromatography (PE:EA = 1.5:1). $[\alpha]_D^{25}$ = –89.28 (*c* 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24–8.14 (m, 2H), 8.12–8.03 (m, 2H), 8.03–7.95 (m, 4H), 7.90–7.76 (m, 4H), 7.74–7.58 (m, 5H), 7.58–7.47 (m, 6H), 7.46–7.40 (m, 3H), 7.39–7.34 (m, 2H), 7.33–7.26 (m, 6H), 6.07 (t, *J* = 10.1 Hz, 1H), 5.97–5.88 (m, 2H), 5.81 (t, *J* = 10.0 Hz, 1H), 5.76 (d, *J* = 1.5 Hz, 1H), 5.69 (d, *J* = 2.9 Hz, 1H), 5.05 (s, 1H), 4.83 (s, 1H), 4.38 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.26–4.10 (m, 3H), 4.05 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.78–3.67 (m, 1H), 3.67–3.46 (m, 7H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 165.9, 165.8, 165.7, 165.6, 165.5, 163.5, 134.5, 133.8, 133.7, 133.64, 133.56, 133.4, 133.3, 130.3, 130.2, 130.1, 130.0, 129.6, 129.5, 129.43, 129.40, 129.3, 129.0, 128.9, 128.71, 128.65, 128.5, 123.6, 99.0, 97.6, 77.7, 70.7, 70.6, 70.5, 70.3, 70.11, 70.08, 69.7, 69.6, 67.4, 67.2, 66.6, 55.8; HRMS (ESI) *m/z* calcd for $C_{65}H_{59}N_2O_{20}$ $[M+NH_4]^+$ 1187.3656, found 1187.3689.

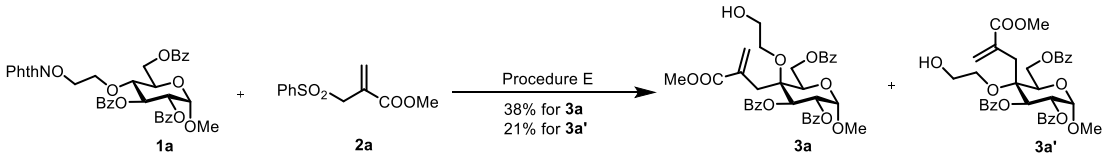
Synthesis of branched-chain sugars and higher-carbon sugars

General Procedure E:



A mixture of sugar-based *N*-alkoxyphthalimide (1.0 equiv), radical acceptor (3.0 equiv), Hantzsch ester (1.5 equiv) and *fac*-Ir(ppy)$_3$ (0.01 equiv) was placed in a 10 mL of clear-colored glass reaction tube. 1,4-Dioxane was added into the tube to result in 0.05 M of a mixture, then the mixture was evacuated and backfilled with argon for three times. After stirring for 3 h at 35 ℃ under the irradiation of blue LEDs (450 nm-470 nm), the mixture was diluted with CH_2Cl_2, and sequentially washed with saturated $NaHCO_3$ solution and brine. The organic layer was collected, dried over anhydrous Na_2SO_4, filtered off the solid, and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography to give the desired product.

Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2-hydroxyethyl)-4-*C*-[2-(methoxycarbonyl)-allyl]-α-D-galactopyranoside (3a) and Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2-hydroxy-ethyl)-4-*C*-[2-(methoxycarbonyl)allyl]-α-D-glucopyranoside (3a′)



Following the general procedure E, **1a** (139.2 mg, 200.0 μmol, 1.0 equiv) and **2a** (152.7 mg, 600.5 μmol, 3.0 equiv) were treated with hantzsch ester (76.1 mg, 300.4 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **3a** (49.0 mg, 75.6 μmol, 38%) and **3a′** (27.6 mg, 42.6 μmol, 21%) as white foam after purification by silica gel column chromatography (PE:EA = 1.5:1).

For **3a**: $[\alpha]_D^{25}$ = +25.91 (*c* 3.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09–8.03 (m, 2H), 8.01–7.94 (m, 2H), 7.94–7.88 (m, 2H), 7.60–7.30 (m, 9H), 6.37 (s, 1H), 5.99 (d, *J* = 10.5 Hz, 1H), 5.94 (s, 1H), 5.55 (dd, *J* = 10.5, 3.6 Hz, 1H), 5.19 (d, *J* = 3.6 Hz, 1H), 4.96 (dd, *J* = 12.0, 1.4 Hz, 1H), 4.61 (dd, *J* = 12.0, 8.4 Hz, 1H), 4.28–4.18 (m, 2H), 4.07–3.98 (m, 1H), 3.94–3.81 (m, 2H), 3.62 (s, 3H), 3.39 (s, 3H), 3.13 (d, *J* = 14.2 Hz, 1H), 2.87 (d, *J* = 14.3 Hz, 1H), 2.47 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.8, 166.6, 166.1, 160.0, 134.6, 133.5, 133.3, 133.2, 130.8, 130.0, 129.9, 129.8, 129.7, 129.5, 129.2, 128.64, 128.55, 128.4, 96.9, 79.9, 71.7, 71.2, 70.9, 67.1, 64.3, 62.6, 55.4, 52.4, 32.3; HRMS (ESI) *m/z* calcd for $C_{35}H_{40}NO_{12}$ $[M+NH_4]^+$ 666.2545, found 666.2542.

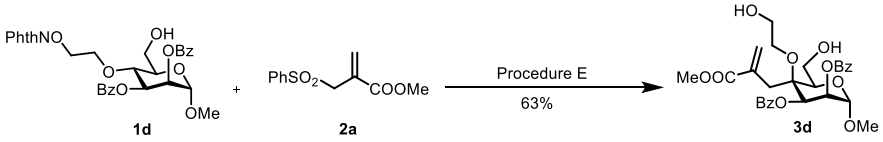
For **3a′**: $[\alpha]_D^{25}$ = +99.25 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09–8.01 (m, 4H), 7.97–7.91 (m, 2H), 7.61–7.55 (m, 1H), 7.54–7.43 (m, 4H), 7.42–7.32 (m, 4H), 6.14 (d, *J* = 10.4 Hz, 1H), 6.06 (d, *J* = 1.3 Hz, 1H), 5.71 (s, 1H), 5.35 (dd, *J* = 10.4, 4.0 Hz, 1H), 5.19 (d, *J* = 4.0 Hz, 1H), 4.78–4.71 (m, 1H), 4.60–4.52 (m, 2H), 3.94–3.88 (m, 1H), 3.83–3.75 (m, 1H), 3.71–3.63 (m, 1H), 3.63–3.55 (m, 1H), 3.55–3.43 (m, 5H), 3.36 (s, 3H), 2.97 (d, *J* = 14.2 Hz, 1H), 2.38 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.2, 166.5, 166.0, 165.8, 138.3, 133.5, 133.4, 130.0, 129.9, 129.8, 129.7, 129.5, 129.1, 128.6, 128.5, 126.7, 96.7, 78.7, 71.5, 69.7, 68.9, 64.0, 62.8, 62.1, 55.3, 51.8, 32.2; HRMS (ESI) *m/z* calcd for $C_{35}H_{40}NO_{12}$ $[M+NH_4]^+$ 666.2545, found 666.2547.

Methyl 2,3-di-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-4-*O*-(2-hydroxyethyl)-4-*C*-

[2-(methoxycarbonyl)allyl]-α-D-talopyranoside (3c)

Following the general procedure E, **1c** (166.0 mg, 200.2 μmol, 1.0 equiv) and **2a** (152.7 mg, 603.6 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **3c** (74.6 mg, 95.4 μmol, 48%) as a white foam after purification by silica gel column chromatography (PE:EA = 2:1). $[\alpha]_D^{25}$ = –43.32 (*c* 2.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00–7.94 (m, 2H), 7.90–7.85 (m, 2H), 7.81–7.73 (m, 4H), 7.57–7.50 (m, 2H), 7.48–7.34 (m, 10H), 6.26 (s, 1H), 5.64 (s, 1H), 5.55–5.49 (m, 2H), 4.91 (d, *J* = 2.4 Hz, 1H), 4.23–4.16 (m, 1H), 4.16–4.10 (m, 2H), 3.82–3.74 (m, 2H), 3.59 (s, 3H), 3.57–3.53 (m, 1H), 3.52–3.44 (m, 4H), 3.13 (d, *J* = 14.3 Hz, 1H), 2.60 (d, *J* = 14.3 Hz, 1H), 2.09 (s, 1H), 1.09 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 165.9, 165.5, 135.9, 135.8, 135.5, 133.6, 133.4, 133.3, 130.0, 129.9, 129.8, 129.7, 128.6, 128.5, 127.9, 127.8, 98.6, 77.2, 75.5, 70.4, 69.1, 65.7, 62.8, 62.4, 55.5, 52.4, 32.4, 26.9, 19.3; HRMS (ESI) *m/z* calcd for $C_{44}H_{50}O_{11}SiNa$ $[M+Na]^+$ 805.3015, found 805.3019.

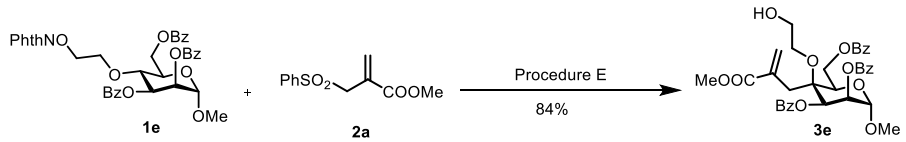
Methyl 2,3-di-*O*-benzoyl-4-*O*-(2-hydroxyethyl)-4-*C*-[2-(methoxycarbonyl)allyl]-α-D-talopyranoside (3d)



Following the general procedure E, **1d** (118.3 mg, 200.0 μmol, 1.0 equiv) and **2a** (152.7 mg, 603.6 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **3d** (68.5 mg, 125.9 μmol, 63%) as a white foam after purification by silica gel column chromatography (PE:EA = 1:2). $[\alpha]_D^{25}$ = –14.8 (*c* 2.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05–7.98 (m, 2H), 7.93–7.87 (m, 2H), 7.58–7.51 (m, 2H), 7.44–7.36 (m, 4H), 6.34 (s, 1H), 5.67 (s, 1H), 5.59 (dd, *J* = 3.7, 1.8 Hz, 1H), 5.48 (d, *J* = 3.8 Hz,

1H), 4.90 (d, *J* = 1.6 Hz, 1H), 4.19 (dd, *J* = 11.9, 5.7 Hz, 1H), 4.10 (dd, *J* = 12.1, 2.9 Hz, 1H), 4.01–3.94 (m, 1H), 3.94–3.86 (m, 2H), 3.79–3.70 (m, 1H), 3.69 (s, 3H), 3.66–3.59 (m, 1H), 3.42 (s, 3H), 3.17 (d, *J* = 14.0 Hz, 1H), 2.97 (s, 1H), 2.75 (d, *J* = 14.0 Hz, 1H), 2.19 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 165.9, 165.5, 135.2, 133.5, 131.0, 130.0, 129.7, 129.6, 128.7, 128.5, 99.1, 78.0, 73.2, 70.1, 68.9, 66.0, 62.3, 61.7, 55.5, 52.6, 32.1; HRMS (ESI) *m/z* calcd for $C_{28}H_{32}O_{11}Na$ $[M+Na]^+$ 567.1837, found 567.1824.

Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2-hydroxyethyl)-4-*C*-[2-(methoxycarbonyl)allyl]-α-D-talopyranoside (3e)



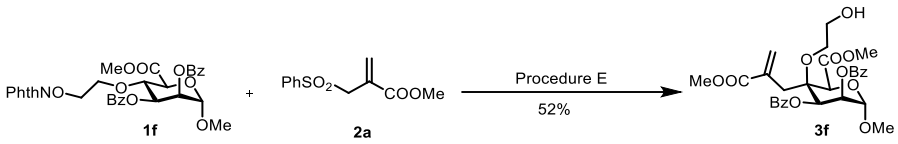
Following the general procedure E, **1e** (139.0 mg, 200.0 μmol, 1.0 equiv) and **2a** (152.6 mg, 600.0 μmol, 3.0 equiv) were treated with hantzsch ester (75.9 mg, 300.0 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **3e** (108.8 mg, 167.8 μmol, 84%) as a white foam after purification by silica gel column chromatography (PE:EA = 1.5:1).

Procedure for Scale Preparation of Compound 3e

Following the general procedure E, **1e** (4.18 g, 6.00 mmol, 1.0 equiv) and **2a** (4.58 g, 18.00 mmol, 3.0 equiv) were treated with hantzsch ester (2.28 g, 9.0 mmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (39.3 mg, 60.0 μmol, 0.01 equiv) in 1,4-dioxane (60.0 mL) to give **3e** (2.27 g, 3.50 mmol, 58%) as a white foam after purification by silica gel column chromatography (PE:EA = 2:1). $[\alpha]_D^{25}$ = +47.08 (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.3 Hz, 2H), 8.02–7.92 (m, 4H), 7.61–7.51 (m, 3H), 7.49–7.36 (m, 6H), 6.40 (s, 1H), 5.81 (s, 1H), 5.64 (d, *J* = 3.6 Hz, 1H), 5.59–5.52 (m, 1H), 4.96 (d, *J* = 2.5 Hz, 1H), 4.95–4.85 (m, 2H), 4.33–4.23 (m, 1H), 4.01–3.82 (m, 2H), 3.76–3.67 (m, 1H), 3.67–3.60 (m, 4H), 3.43 (s, 3H), 3.24 (d, *J* = 14.4 Hz, 1H), 2.84 (d, *J* = 14.4 Hz, 1H), 2.28 (brs, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.4, 166.7, 165.8, 165.5, 135.0, 133.43, 133.42, 133.2, 130.8, 130.0, 129.9, 129.7, 129.6, 129.50,

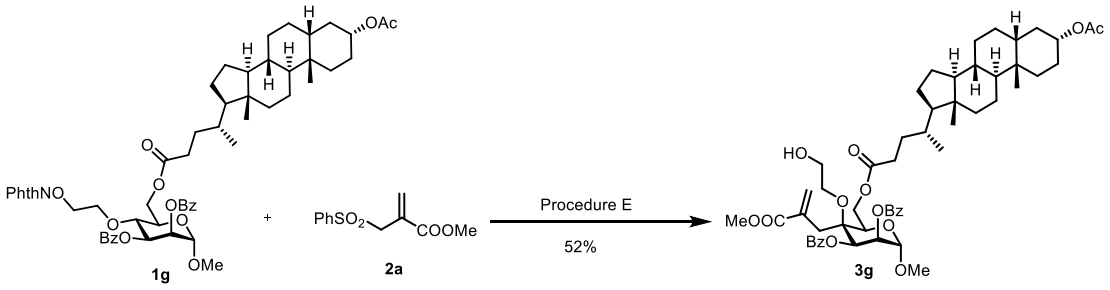
129.46, 128.7, 128.5, 128.4, 98.5, 77.3, 72.3, 70.1, 69.0, 66.0, 63.7, 62.4, 55.5, 52.4, 32.3; HRMS (ESI) *m/z* calcd for $C_{35}H_{40}NO_{12}$ $[M+NH_4]^+$ 666.2545, found 666.2549.

Methyl {methyl 2,3-di-*O*-benzoyl-4-*O*-(2-Hydroxyethyl)-4-*C*-[2-(methoxy-carbonyl)allyl]-α-D-talopyranosyluronate} (3f)



Following the general procedure E, **1f** (62.3 mg, 100.2 μmol, 1.0 equiv) and **2a** (76.0 mg, 300.0 μmol, 3.0 equiv) were treated with hantzsch ester (38.0 mg, 150.0 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (0.7 mg, 1.0 μmol, 0.01 equiv) in 1,4-dioxane (2.0 mL) to give **3f** (32.1 mg, 51.9 μmol, 52%) as a white foam after purification by silica gel column chromatography (PE:EA = 1.5:1). $[\alpha]_D^{25}$ = –2.38 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00–7.95 (m, 2H), 7.94–7.89 (m, 2H), 7.60–7.51 (m, 2H), 7.46–7.35 (m, 4H), 6.40 (s, 1H), 6.00 (s, 1H), 5.60–5.47 (m, 2H), 5.23 (s, 1H), 4.66 (s, 1H), 3.91 (dd, *J* = 6.1, 3.5 Hz, 1H), 3.89–3.80 (m, 4H), 3.73–3.64 (m, 4H), 3.61–3.56 (m, 1H), 3.51 (s, 3H), 3.36 (d, *J* = 14.3 Hz, 1H), 2.98 (d, *J* = 14.2 Hz, 1H), 2.56 (brs, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 167.5, 165.6, 165.5, 136.0, 135.2, 133.4, 133.3, 130.5, 129.9, 129.7, 129.6, 129.4, 128.6, 128.4, 99.0, 72.7, 69.8, 68.5, 65.2, 62.0, 56.3, 52.6, 52.4, 31.7; HRMS (ESI) *m/z* calcd for $C_{29}H_{36}NO_{12}$ $[M+NH_4]^+$ 590.2232, found 590.2233.

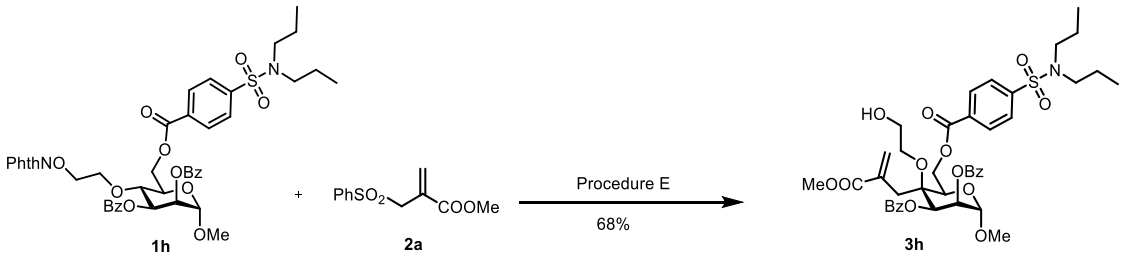
Methyl 2,3-di-*O*-benzoyl-6-*O*-{3α-acetyloxy-5β-cholan-24-oate}-4-*O*-(2-hydroxyethyl)-4-*C*-[2-(methoxycarbonyl)allyl]-α-D-talopyranoside (3g)



Following the general procedure E, **1g** (198.2 mg, 199.9 μmol, 1.0 equiv) and **2a** (152.7

mg, 603.6 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **3g** (99.1 mg, 104.5 μmol, 52%) as a white foam after purification by silica gel column chromatography (PE:EA = 2:1). $[\alpha]_D^{25}$ = +39.83 (*c* 2.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01–7.96 (m, 2H), 7.96–7.92 (m, 2H), 7.60–7.51 (m, 2H), 7.46–7.37 (m, 4H), 6.38 (s, 1H), 5.77 (s, 1H), 5.57 (d, *J* = 3.6 Hz, 1H), 5.56–5.53 (m, 1H), 4.92 (d, *J* = 2.3 Hz, 1H), 4.77–4.58 (m, 3H), 4.12 (d, *J* = 8.6 Hz, 1H), 4.03–3.82 (m, 2H), 3.78–3.67 (m, 4H), 3.66–3.60 (m, 1H), 3.44 (s, 3H), 3.22 (d, *J* = 14.4 Hz, 1H), 2.75 (d, *J* = 14.3 Hz, 1H), 2.46–2.37 (m, 1H), 2.35–2.22 (m, 2H), 2.03 (s, 3H), 2.01–1.94 (m, 1H), 1.90–1.78 (m, 5H), 1.73–1.65 (m, 1H), 1.61–1.49 (m, 2H), 1.49–1.34 (m, 8H), 1.31–1.17 (m, 4H), 1.16–0.97 (m, 6H), 0.95–0.90 (m, 6H), 0.65 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.4, 170.7, 167.4, 165.8, 165.5, 135.0, 133.4, 130.7, 129.9, 129.7, 129.4, 128.6, 128.4, 98.4, 77.1, 74.4, 72.2, 70.0, 68.9, 65.9, 63.0, 62.3, 56.5, 56.0, 55.4, 52.4, 42.8, 41.9, 40.4, 40.2, 35.8, 35.4, 35.0, 34.6, 32.2, 32.2, 31.3, 31.0, 28.2, 27.0, 26.6, 26.3, 24.2, 23.4, 21.5, 20.8, 18.3, 12.1; HRMS (ESI) *m/z* calcd for $C_{54}H_{76}NO_{14}$ $[M+NH_4]^+$ 962.5260, found 962.5281.

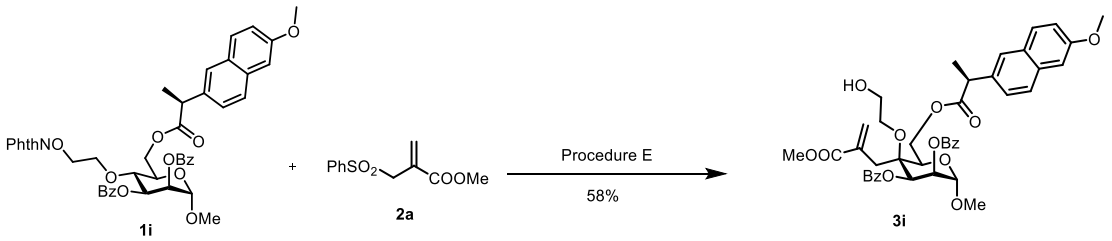
Methyl 2,3-di-*O*-benzoyl-6-*O*-[4-(*N*,*N*-dipropylsulfamoyl)benzoyl]-4-*O*-(2-hydroxyethyl)-4-*C*-[2-(methoxycarbonyl)allyl]-α-D-talopyranoside (3h)



Following the general procedure E, **1h** (171.8 mg, 200.2 μmol, 1.0 equiv) and **2a** (152.7 mg, 603.6 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **3h** (110.2 mg, 135.8 μmol, 68%) as a white foam after purification by silica gel column chromatography (PE:EA = 2:1). $[\alpha]_D^{25}$ = +51.83 (*c* 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21–8.16 (m, 2H), 8.02–7.98 (m, 2H), 7.98–7.94 (m, 2H), 7.92–7.88

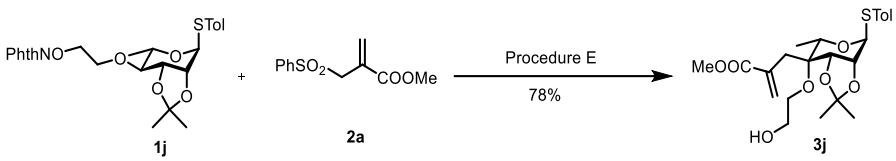
(m, 2H), 7.62–7.52 (m, 2H), 7.47–7.37 (m, 4H), 6.41 (s, 1H), 5.80 (s, 1H), 5.65 (d, *J* = 3.6 Hz, 1H), 5.59–5.55 (m, 1H), 5.00–4.89 (m, 3H), 4.30–4.24 (m, 1H), 4.01–3.88 (m, 2H), 3.78–3.71 (m, 1H), 3.69–3.61 (m, 4H), 3.43 (s, 3H), 3.23 (d, *J* = 14.4 Hz, 1H), 3.15–3.08 (m, 4H), 2.84 (d, *J* = 14.3 Hz, 1H), 2.25 (brs, 1H), 1.62–1.49 (m, 4H), 0.93–0.83 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.4, 165.8, 165.5, 165.3, 144.5, 134.9, 133.5, 133.3, 131.0, 130.2, 129.9, 129.7, 129.4, 129.3, 128.7, 128.5, 127.1, 98.5, 77.3, 72.2, 70.0, 68.9, 66.0, 64.4, 62.4, 52.5, 49.9, 32.3, 22.0, 11.2; HRMS (ESI) *m/z* calcd for $C_{41}H_{49}NO_{14}NaS$ $[M+Na]^+$ 834.2766, found 834.2778.

Methyl 2,3-di-*O*-benzoyl-4-*O*-(2-hydroxyethyl)-4-*C*-[2-(methoxycarbonyl)allyl]-6-*O*-{2-(*S*)-(6-methoxynaphthalen-2-yl)propanoyl}-α-D-talopyranoside (3i)



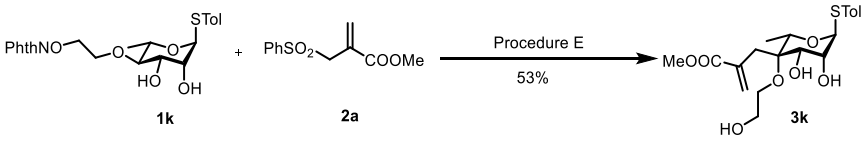
Following the general procedure E, **1i** (160.8 mg, 200.2 μmol, 1.0 equiv) and **2a** (152.7 mg, 603.6 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **3i** (87.8 mg, 116.1 μmol, 58%) as a white foam after purification by silica gel column chromatography (PE:EA = 5:1). $[\alpha]_D^{25}$ = +20.18 (*c* 3.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98–7.94 (m, 2H), 7.93–7.89 (m, 2H), 7.73–7.63 (m, 3H), 7.58–7.49 (m, 2H), 7.44–7.35 (m, 5H), 7.13 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.09 (d, *J* = 2.3 Hz, 1H), 6.32 (s, 1H), 5.70 (s, 1H), 5.51 (d, *J* = 3.5 Hz, 1H), 5.48–5.45 (m, 1H), 4.74 (d, *J* = 2.3 Hz, 1H), 4.70–4.62 (m, 2H), 4.06–3.99 (m, 1H), 3.95–3.82 (m, 6H), 3.74–3.66 (m, 1H), 3.66–3.57 (m, 4H), 3.15 (d, *J* = 14.3 Hz, 1H), 2.96 (s, 3H), 2.70 (d, *J* = 14.3 Hz, 1H), 2.23 (s, 1H), 1.62 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.8, 167.4, 165.8, 165.5, 157.7, 135.5, 134.9, 133.8, 133.5, 130.8, 130.0, 129.7, 129.5, 129.2, 129.0, 128.7, 128.5, 127.2, 126.3, 126.1, 119.1, 105.6, 98.3, 77.1, 72.1, 70.0, 68.9, 65.9, 63.6, 62.4, 55.4, 54.9, 52.4, 45.6, 32.2, 18.6; HRMS (ESI) *m/z* calcd for $C_{42}H_{44}O_{13}Na$ $[M+Na]^+$ 779.2674, found 779.2665.

***p*-Tolyl 4-*O*-(2-hydroxyethyl)-2,3-*O*-isopropylidene-4-*C*-[2-(methoxycarbonyl)-allyl]-1-thio-α-L-talopyranoside (3j)**



Following the general procedure E, **1j** (100.3 mg, 200.0 μmol, 1.0 equiv) and **2a** (152.3 mg, 598.7 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **3j** (70.3 mg, 155.5 μmol, 78%) as a white foam after purification by silica gel column chromatography (PE:EA = 2:1). $[\alpha]_D^{25} = -52.56$ (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55–7.41 (m, 2H), 7.18–7.05 (m, 2H), 6.31 (s, 1H), 5.74 (s, 1H), 4.83 (d, *J* = 9.1 Hz, 1H), 4.30 (d, *J* = 4.9 Hz, 1H), 4.23–4.11 (m, 1H), 3.94 (dd, *J* = 9.1, 5.0 Hz, 1H), 3.79–3.71 (m, 5H), 3.71–3.62 (m, 2H), 2.80 (d, *J* = 14.7 Hz, 1H), 2.59 (brs, 1H), 2.44 (d, *J* = 14.7 Hz, 1H), 2.33 (s, 3H), 1.55 (s, 3H), 1.46 (d, *J* = 6.9 Hz, 3H), 1.37 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 138.2, 135.5, 133.4, 129.6, 129.3, 128.6, 110.4, 79.4, 76.9, 75.0, 74.2, 72.4, 63.5, 62.2, 52.2, 34.3, 28.2, 25.7, 21.2, 13.0; HRMS (ESI) *m/z* calcd for $C_{23}H_{32}O_7SNa$ $[M+Na]^+$ 475.1761, found 475.1756.

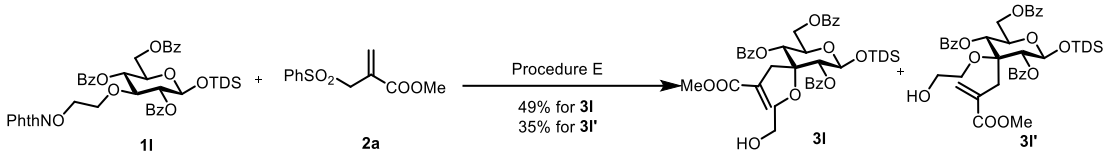
***p*-Tolyl 4-*O*-(2-hydroxyethyl)-4-*C*-[2-(methoxycarbonyl)allyl]-1-thio-α-L-talo-pyranoside (3k)**



Following the general procedure E, **1k** (91.9 mg, 200.0 μmol, 1.0 equiv) and **2a** (152.3 mg, 598.7 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **3k** (43.6 mg, 105.8 μmol, 53%) as a white foam after purification by silica gel column chromatography (PE:EA = 2:1). $[\alpha]_D^{25} = -69.11$ (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.34–7.24 (m, 2H), 7.15–6.99 (m, 2H), 6.44 (d, *J* = 3.0 Hz, 1H), 5.73

(d, J = 2.4 Hz, 1H), 5.37 (s, 1H), 4.54 (d, J = 3.5 Hz, 1H), 4.30–4.17 (m, 1H), 3.98 (d, J = 2.6 Hz, 1H), 3.84–3.67 (m, 1H), 3.67–3.55 (m, 1H), 3.54–3.45 (m, 2H), 3.14 (d, J = 17.6 Hz, 1H), 2.73–2.60 (m, 1H), 2.23 (s, 3H), 1.22 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, Methanol-d_4) δ 165.3, 137.9, 132.3, 132.1, 130.0, 129.8, 129.5, 89.9, 77.1, 75.5, 70.7, 70.1, 67.0, 61.1, 31.8, 19.7, 13.3; HRMS (ESI) *m/z* calcd for $C_{20}H_{28}O_7SNa$ $[M+Na]^+$ 477.1448, found 477.1447.

Dimethylthexylsilyl 2,4,6-tri-*O*-benzoyl-3-*O*-(2-hydroxyethyl)-3-*C*-[2-(methoxycarbonyl)allyl]-β-D-allopyranoside (3l) and Dimethylthexylsilyl 2,4,6-tri-*O*-benzoyl-3-*O*-(2-hydroxyethyl)-3-*C*-[2-(methoxycarbonyl)allyl]-β-D-glucopyranoside (3l′)



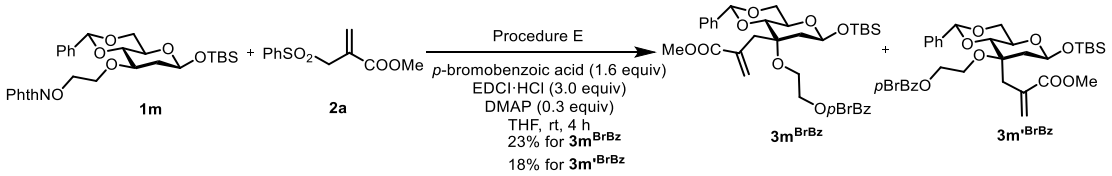
Following the general procedure E, **1l** (82.4 mg, 100.0 μmol, 1.0 equiv) and **2a** (76.3 mg, 300.0 μmol, 3.0 equiv) were treated with hantzsch ester (38.1 mg, 150.1 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (0.7 mg, 1.1 μmol, 0.01 equiv) in 1,4-dioxane (2.0 mL) to give **3l** (38.3 mg, 49.3 μmol, 49%) and **3l′** (27.0 mg, 34.8 μmol, 35%) as white foam after purification by silica gel column chromatography (PE:EA = 1.5:1).

For **3l**: $[\alpha]_D^{25}$ = –2.70 (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01–7.84 (m, 6H), 7.57–7.46 (m, 2H), 7.45–7.33 (m, 5H), 7.33–7.21 (m, 2H), 6.24 (s, 1H), 5.87 (s, 1H), 5.22–5.18 (m, 1H), 5.17–5.10 (m, 2H), 4.43–4.27 (m, 3H), 4.17–4.04 (m, 2H), 3.93–3.80 (m, 2H), 3.39 (s, 3H), 2.93–2.74 (m, 2H), 2.38–2.26 (brs, 1H), 1.39–1.31 (m, 1H), 0.64–0.50 (m, 12H), 0.00 (s, 3H), -0.11 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 166.2, 165.8, 165.1, 134.2, 133.7, 133.3, 133.1, 130.8, 130.2, 129.9, 129.84, 129.82, 129.5, 128.8, 128.6, 128.3, 94.5, 80.2, 74.8, 71.8, 71.1, 66.2, 64.4, 62.8, 52.3, 33.7, 24.7, 19.8, 19.7, 18.5, 18.4, -1.8, -3.3; HRMS (ESI) *m/z* calcd for $C_{42}H_{56}NO_{12}Si$ $[M+NH_4]^+$ 794.3566, found 794.3570.

For **3l′**: $[\alpha]_D^{25}$ = –2.16 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98–7.92 (m, 6H), 7.56–7.46 (m, 3H), 7.42–7.32 (m, 6H), 6.04–6.01 (m, 1H), 5.69 (s, 1H), 5.57

(d, *J* = 9.3 Hz, 1H), 5.43 (d, *J* = 7.4 Hz, 1H), 5.19 (d, *J* = 7.4 Hz, 1H), 4.51 (dd, *J* = 11.4, 2.7 Hz, 1H), 4.44–4.29 (m, 2H), 3.77–3.70 (m, 2H), 3.57–3.47 (m, 5H), 3.26–3.06 (m, 2H), 1.99–1.88 (m, 1H), 1.47–1.35 (m, 1H), 0.66–0.61 (m, 12H), 0.08 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0, 166.2, 165.6, 165.3, 136.3, 133.7, 133.3, 133.2, 130.1, 130.0, 129.9, 129.8, 129.2, 128.6, 128.4, 128.0, 95.0, 79.6, 73.1, 71.3, 69.3, 64.2, 63.4, 62.1, 51.9, 33.9, 24.7, 19.9, 19.8, 18.5, 18.4, -1.8, -3.3; HRMS (ESI) *m/z* calcd for $C_{42}H_{56}NO_{12}Si$ $[M+NH_4]^+$ 794.3566, found 794.3578.

tert-Butyldimethylsilyl 4,6-di-*O*-benzylidene-2-deoxy-3-*O*-[2-*O*-(4-bromobenzoyl)ethyl]-3-*C*-[2-(methoxycarbonyl)allyl]-β-D-allopyranoside (3m^{BrBz}) and _tert_-Butyldimethylsilyl 4,6-di-*O*-benzylidene-2-deoxy-3-*O*-[2-*O*-(4-bromobenzoyl)ethyl]-3-*C*-[2-(methoxycarbonyl)allyl]-β-D-glucopyranoside (3m′^{BrBz})



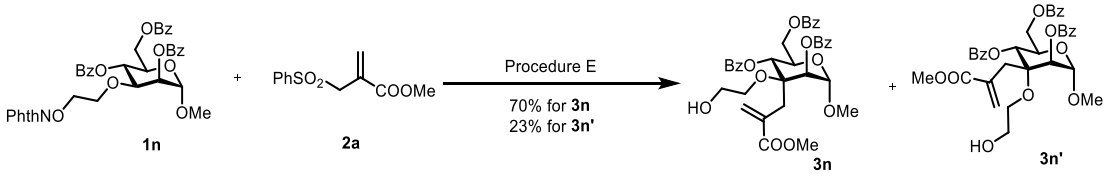
A mixture of **1m** (111.1 mg, 200.0 μmol, 1.0 equiv), **2a** (152.7 mg, 603.6 μmol, 3.0 equiv), hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) were placed in a 10 mL clear-colored glass reaction tube. After 1,4-dioxane (4.0 mL) was added, the reaction was exchanged three times using argon gas and exposed to blue LEDs (450 nm-470 nm) at 35 ℃ with stirring for 3 h. The resultant mixture was diluted with DCM and washed with saturated $NaHCO_3$ solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo* give the crude product without further purification for next step. The crude product was dissolved in THF (10.0 mL), *p*-bromobenzoic acid (63.9 mg, 318.0 μmol, 1.6 equiv), EDCI·HCl (61.0 mg, 318.0 μmol, 1.6 equiv) and DMAP (2.4 mg, 21.0 μmol, 0.1 equiv) were added at temperature under an argon atmosphere. The resultant solution was stirred at room temperature for 8 h. The resultant mixture was diluted with DCM and washed with saturated $NaHCO_3$ solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo.*

The resulting residue was purified by silica gel column chromatography (PE:EA = 10:1) to afford **3m^{BrBz}** (32.1 mg, 46.5 μmol, 23%) and **3m′^{BrBz}** (25.1 mg, 36.4 μmol, 18%) as white foam.

For **3m^{BrBz}**: $[\alpha]_D^{25}$ = –7.35 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91–7.84 (m, 2H), 7.56–7.47 (m, 2H), 7.45–7.38 (m, 2H), 7.36–7.27 (m, 3H), 6.26 (s, 1H), 5.64 (s, 1H), 5.31 (s, 1H), 5.12 (d, *J* = 7.5 Hz, 1H), 4.46–4.35 (m, 2H), 4.30–4.21 (m, 1H), 4.17 (dd, *J* = 10.4, 5.1 Hz, 1H), 3.99–3.90 (m, 1H), 3.90–3.81 (m, 1H), 3.69–3.59 (m, 4H), 3.53 (d, *J* = 9.4 Hz, 1H), 2.88 (d, *J* = 14.0 Hz, 1H), 2.77 (d, *J* = 14.1 Hz, 1H), 1.97–1.88 (m, 1H), 1.41 (dd, *J* = 13.8, 9.1 Hz, 1H), 0.80 (s, 9H), -0.00 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 165.9, 137.7, 135.8, 131.9, 131.3, 129.2, 129.1, 128.5, 128.2, 126.3, 102.4, 93.7, 82.3, 76.4, 69.5, 65.0, 64.1, 62.1, 52.2, 43.6, 33.3, 25.8, 18.2, -4.2, -5.1; HRMS (ESI) *m/z* calcd for $C_{33}H_{47}BrNO_9Si$ $[M+NH_4]^+$ 708.2198, found 708.2217.

For **3m′^{BrBz}**: $[\alpha]_D^{25}$ = –6.00 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89–7.83 (m, 2H), 7.55–7.49 (m, 2H), 7.48–7.41 (m, 2H), 7.38–7.31 (m, 3H), 6.30 (s, 1H), 5.78 (s, 1H), 5.52 (s, 1H), 5.15–5.03 (m, 1H), 4.45–4.37 (m, 2H), 4.32 (dd, *J* = 10.4, 4.7 Hz, 1H), 3.97–3.84 (m, 3H), 3.79 (t, *J* = 10.1 Hz, 1H), 3.70–3.61 (m, 4H), 3.03 (d, *J* = 15.1 Hz, 1H), 2.82 (d, *J* = 15.1 Hz, 1H), 1.97–1.89 (m, 1H), 1.71 (dd, *J* = 13.2, 9.7 Hz, 1H), 0.89 (s, 9H), 0.15–0.09 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.3, 166.0, 137.5, 135.4, 131.8, 131.3, 129.5, 129.2, 128.4, 126.2, 101.6, 94.4, 82.5, 76.4, 69.7, 65.6, 64.8, 60.9, 52.1, 41.5, 30.1, 25.8, -4.2, -5.2; HRMS (ESI) *m/z* calcd for $C_{33}H_{43}BrO_9SiNa$ $[M+Na]^+$ 713.1752, found 713.1757.

Methyl 2,4,6-tri-*O*-benzoyl-3-*O*-(2-hydroxyethyl)-3-*C*-[2-(methoxycarbonyl)allyl]-α-D-mannopyranoside (3n) and Methyl 2,4,6-tri-*O*-benzoyl-3-*O*-(2-hydroxyethyl)-3-*C*-[2-(methoxycarbonyl)allyl]-α-D-altropyranoside (3n′)

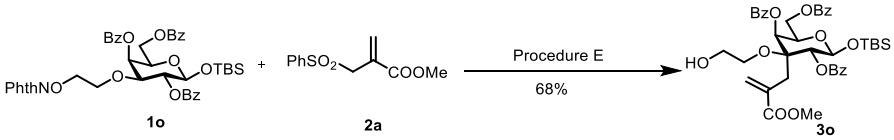


Following the general procedure E, **1n** (487.0 mg, 700.0 μmol, 1.0 equiv) and **2a** (534.2 mg, 2.10 mmol, 3.0 equiv) were treated with hantzsch ester (266.0 mg, 1.05 mmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (4.6 mg, 7.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **3n** (318.7 mg, 491.7 μmol, 70%) and **3n′** (106.6 mg, 164.5 μmol, 23%) as white foam after purification by silica gel column chromatography (PE:EA = 1:1).

For **3n**: $[\alpha]_D^{25} = -11.13$ (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11–8.04 (m, 6H), 7.61–7.53 (m, 3H), 7.49–7.38 (m, 6H), 6.30 (s, 1H), 5.98 (d, *J* = 9.1 Hz, 1H), 5.91 (s, 1H), 5.59 (d, *J* = 2.0 Hz, 1H), 4.88 (d, *J* = 1.9 Hz, 1H), 4.62 (dd, *J* = 12.0, 3.3 Hz, 1H), 4.54 (dd, *J* = 12.0, 5.3 Hz, 1H), 4.40–4.31 (m, 1H), 3.78–3.71 (m, 1H), 3.68 (s, 3H), 3.61–3.55 (m, 1H), 3.55–3.52 (m, 1H), 3.47 (s, 3H), 3.36–3.30 (m, 2H), 3.25 (d, *J* = 14.5 Hz, 1H), 2.26 (brs, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.2, 166.3, 165.6, 165.5, 136.2, 133.8, 133.7, 133.2, 130.0, 129.9, 129.8, 129.4, 129.3, 128.8, 128.5, 99.6, 77.9, 73.4, 69.2, 68.9, 65.8, 63.5, 62.1, 55.9, 52.2, 30.7; HRMS (ESI) *m/z* calcd for $C_{35}H_{36}O_{12}Na$ $[M+Na]^+$ 671.2099, found 671.2095.

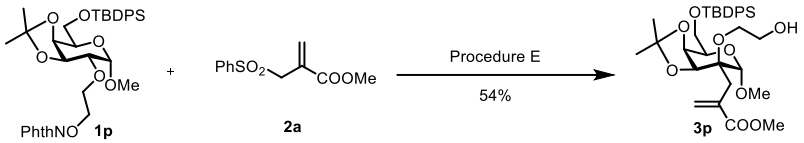
For **3n′**: $[\alpha]_D^{25} = -23.6$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15–7.98 (m, 6H), 7.67–7.59 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.52–7.44 (m, 4H), 7.44–7.38 (m, 2H), 6.09 (s, 1H), 6.02 (d, *J* = 10.3 Hz, 1H), 5.36 (s, 1H), 5.07 (s, 1H), 4.84 (s, 1H), 4.73–4.67 (m, 1H), 4.65–4.59 (m, 1H), 4.47–4.40 (m, 1H), 4.16 (t, *J* = 8.1 Hz, 1H), 4.05 (d, *J* = 8.4 Hz, 1H), 3.74 (d, *J* = 10.5 Hz, 1H), 3.70–3.63 (m, 1H), 3.56 (s, 3H), 3.49 (s, 3H), 3.15 (d, *J* = 14.8 Hz, 1H), 2.60 (d, *J* = 14.8 Hz, 1H), 1.68 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 166.2, 165.6, 164.9, 134.9, 134.0, 133.9, 133.2, 130.0, 129.9, 129.2, 129.0, 128.9, 128.5, 100.1, 78.5, 72.1, 71.8, 66.0, 65.9, 63.3, 62.1, 56.6, 52.1, 31.5; HRMS (ESI) *m/z* calcd for $C_{35}H_{40}NO_{12}$ $[M+NH_4]^+$ 666.2545, found 666.2553.

tert-Butyldimethylsilyl 2,4,6-tri-*O*-benzoyl-3-*O*-(2-hydroxyethyl)-3-*C*-[2-(methoxycarbonyl)allyl]-β-D-galactopyranoside (3o)



Following the general procedure E, **1o** (159.2 mg, 200.2 μmol, 1.0 equiv) and **2a** (152.7 mg, 603.6 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **3o** (102.2 mg, 136.6 μmol, 68%) as a white foam after purification by silica gel column chromatography (PE:EA = 4:1). $[\alpha]_D^{25}$ = +76.37 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09–8.01 (m, 2H), 7.98–7.93 (m, 4H), 7.53–7.43 (m, 3H), 7.42–7.31 (m, 6H), 6.34 (s, 1H), 5.83 (s, 1H), 5.62 (d, *J* = 7.5 Hz, 1H), 5.55 (s, 1H), 4.97 (d, *J* = 7.5 Hz, 1H), 4.49–4.40 (m, 2H), 4.27–4.16 (m, 1H), 3.54 (s, 3H), 3.53–3.49 (m, 1H), 3.38–3.33 (m, 1H), 3.29 (d, *J* = 15.2 Hz, 1H), 3.24–3.13 (m, 2H), 2.88 (d, *J* = 15.2 Hz, 1H), 1.86 (s, 1H), 0.66 (s, 9H), 0.00 (s, 3H), -0.11 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 166.2, 166.1, 164.9, 134.4, 133.6, 133.5, 133.2, 130.5, 130.0, 129.9, 129.8, 129.7, 129.3, 128.8, 128.6, 128.4, 95.8, 78.7, 74.6, 71.5, 70.6, 65.0, 62.7, 62.0, 52.3, 30.5, 25.4, 17.8, -4.1, -5.1; HRMS (ESI) *m/z* calcd for $C_{40}H_{52}NO_{12}Si$ $[M+NH_4]^+$ 766.3253, found 766.3265.

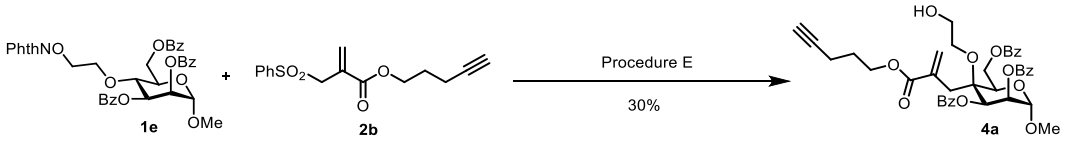
Methyl 6-*O*-*tert*-butyldiphenylsilyl-2-*O*-(2-hydroxyethyl)-3,4-*O*-isopropylidene-2-*C*-[2-(methoxycarbonyl)allyl]-α-D-talopyranoside (3p)



Following the general procedure E, **1p** (132.4 mg, 200.0 μmol, 1.0 equiv) and **2a** (152.7 mg, 603.6 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **3p** (66.7 mg, 108.6 μmol, 54%) as a white foam after purification by silica gel column chromatography (PE:EA = 1:1). $[\alpha]_D^{25}$ = +33.54 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73–7.67 (m, 4H), 7.44–7.33 (m, 6H), 6.17 (d, *J* = 1.1 Hz, 1H), 5.65 (s, 1H), 4.73 (s, 1H), 4.27 (d, *J* = 5.9 Hz, 1H), 4.21 (dd, *J* = 5.9, 3.3 Hz, 1H), 4.01 (dd, *J* = 9.1, 6.2 Hz, 1H), 3.98–3.93 (m, 1H), 3.89 (dd, *J* = 9.1, 5.8 Hz, 1H), 3.76 (s, 3H), 3.71–3.56 (m, 4H), 3.22 (s, 3H), 2.88 (d, *J* = 14.0 Hz, 1H), 2.59 (d, *J* = 14.0 Hz, 1H), 1.49 (s, 3H), 1.30 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1,

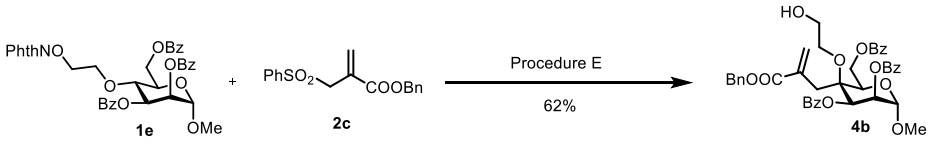
137.1, 135.7, 133.6, 129.7, 127.74, 127.69, 127.2, 109.2, 99.8, 74.5, 73.2, 71.7, 68.3, 63.1, 63.0, 61.7, 55.2, 52.0, 33.5, 26.9, 26.3, 25.6, 19.3; HRMS (ESI) *m/z* calcd for $C_{33}H_{46}O_9SiNa$ $[M+Na]^+$ 637.2803, found 637.2800.

Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2-hydroxyethyl)-4-*C*-{2-[(pent-4-yn-1-yloxy)-carbonyl]allyl}-α-D-talopyranoside (4a)



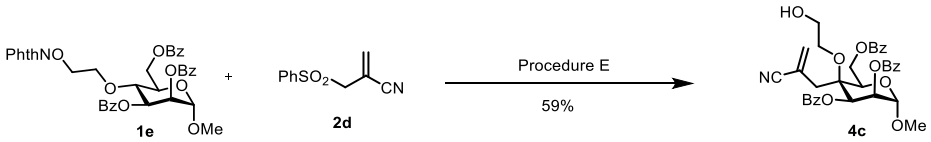
Following the general procedure E, **1e** (139.2 mg, 200.0 μmol, 1.0 equiv) and **2b**[16] (175.4 mg, 600.0 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **4a** (42.1 mg, 60.1 μmol, 30%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25}$ = +17.96 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11–8.05 (m, 2H), 8.01–7.93 (m, 4H), 7.61–7.51 (m, 3H), 7.48–7.36 (m, 6H), 6.37 (s, 1H), 5.80 (s, 1H), 5.64 (d, *J* = 3.4 Hz, 1H), 5.58–5.53 (m, 1H), 4.96 (d, *J* = 2.3 Hz, 1H), 4.93–4.88 (m, 2H), 4.26 (t, *J* = 5.2 Hz, 1H), 4.23–4.08 (m, 2H), 3.99–3.93 (m, 1H), 3.93–3.85 (m, 1H), 3.77–3.69 (m, 1H), 3.68–3.59 (m, 1H), 3.44 (s, 3H), 3.21 (d, *J* = 15.1 Hz, 1H), 2.85 (d, *J* = 14.3 Hz, 1H), 2.27–2.21 (m, 2H), 2.03 (s, 1H), 1.93 (t, *J* = 2.6 Hz, 1H), 1.87–1.78 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0, 166.8, 165.9, 165.6, 135.2, 133.5, 133.3, 130.7, 130.1, 130.0, 129.8, 129.7, 129.5, 128.8, 128.6, 128.5, 98.6, 83.1, 77.4, 72.4, 70.1, 69.2, 69.1, 66.1, 64.1, 63.8, 62.4, 55.6, 32.4, 27.5, 15.3; HRMS (ESI) *m/z* calcd for $C_{39}H_{44}NO_{12}$ $[M+NH_4]^+$ 718.2858, found 718.2876.

Methyl 2,3,6-tri-*O*-benzoyl-4-*C*-[2-(benzyloxycarbonyl)allyl]-4-*O*-(2-hydroxy-ethyl)-α-D-talopyranoside (4b)



Following the general procedure E, **1e** (139.2 mg, 200.0 μmol, 1.0 equiv) and **2c**[16] (189.8 mg, 600.0 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **4b** (90.1 mg, 124.4 μmol, 62%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25}$ = +18.66 (*c* 3.6, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11–8.05 (m, 2H), 8.04–7.94 (m, 4H), 7.61–7.52 (m, 3H), 7.47–7.38 (m, 6H), 7.34–7.28 (m, 5H), 6.43 (s, 1H), 5.83 (s, 1H), 5.68 (d, *J* = 3.8 Hz, 1H), 5.58 (t, *J* = 3.3 Hz, 1H), 5.14 (d, *J* = 12.4 Hz, 1H), 5.08 (d, *J* = 12.4 Hz, 1H), 4.97 (d, *J* = 2.9 Hz, 1H), 4.95–4.90 (m, 2H), 4.28 (t, *J* = 5.3 Hz, 1H), 4.01–3.86 (m, 2H), 3.75–3.60 (m, 2H), 3.40 (s, 3H), 3.24 (d, *J* = 14.4 Hz, 1H), 2.89 (d, *J* = 14.4 Hz, 1H), 2.19 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 166.7, 165.8, 165.6, 135.7, 135.1, 133.5, 133.2, 130.9, 130.1, 130.0, 129.8, 129.7, 129.5, 128.7, 128.6, 128.5, 128.3, 98.5, 77.4, 72.4, 70.2, 69.1, 67.1, 66.1, 63.7, 62.4, 55.5, 32.4; HRMS (ESI) *m/z* calcd for $C_{41}H_{44}NO_{12}$ $[M+NH_4]^+$ 742.2858, found 742.2878.

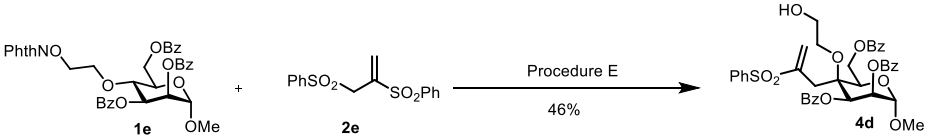
Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2-hydroxyethyl)-4-*C*-[2-(cyano)allyl]-α-D-talo-pyranoside (4c)



Following the general procedure E, **1e** (139.2 mg, 200.0 μmol, 1.0 equiv) and **2d**[16] (124.4 mg, 600.0 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **5c** (72.4 mg, 117.7 μmol, 59%) as a white foam after purification by silica gel column chromatography (PE:EA =1.5:1). $[\alpha]_D^{25}$ = +55.28 (*c* 2.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13–8.07 (m, 2H), 8.00–7.91 (m, 4H), 7.61–7.51 (m, 3H), 7.49–7.42 (m, 4H), 7.41–7.35 (m, 2H), 6.09 (s, 1H), 5.94 (s, 1H), 5.77 (d, *J* = 3.8 Hz, 1H), 5.49 (t, *J* = 3.6 Hz, 1H), 5.17–5.09 (m, 1H), 5.06 (d, *J* = 3.6 Hz, 1H), 4.82 (dd, *J* = 12.3, 2.3 Hz, 1H), 4.48 (dd, *J* = 8.7, 2.2 Hz, 1H), 3.99–3.83 (m, 2H), 3.77–3.61 (m, 2H), 3.45 (s, 3H), 3.08 (d, *J* = 14.6 Hz, 1H), 2.73 (d, *J* = 14.6 Hz, 1H), 2.52 (s, 1H); ^{13}C

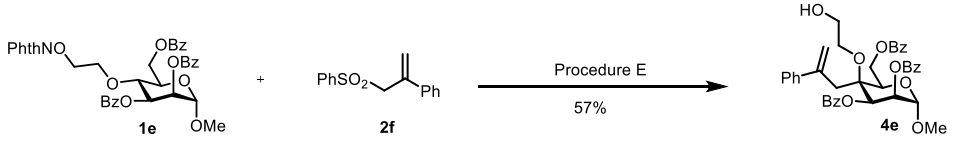
NMR (101 MHz, Chloroform-*d*) δ 166.9, 165.7, 165.5, 137.2, 133.8, 133.6, 133.4, 129.92, 129.89, 129.85, 129.8, 129.3, 129.0, 128.9, 128.6, 128.5, 118.8, 116.7, 98.1, 76.8, 72.6, 69.9, 69.0, 66.3, 62.5, 62.1, 56.0, 36.9; HRMS (ESI) *m/z* calcd for $C_{34}H_{37}N_2O_{10}$ $[M+NH_4]^+$ 633.2443, found 633.2456.

Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2-hydroxyethyl)-4-*C*-[2-(phenylsulfonyl)allyl]-α-D-talopyranoside (4d)



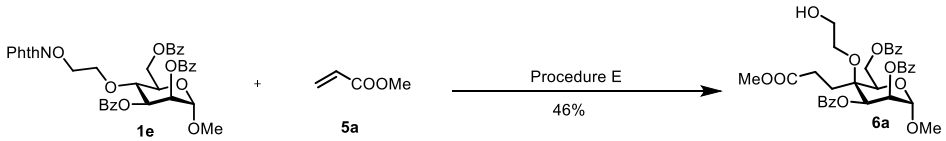
Following the general procedure E, **1e** (139.2 mg, 200.0 μmol, 1.0 equiv) and **2e**[16] (193.4 mg, 600.0 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **4d** (67.5 mg, 92.4 μmol, 46%) as a white foam after purification by silica gel column chromatography (PE:EA =2:1). $[\alpha]_D^{25}$ = +54.88 (*c* 3.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11–8.05 (m, 2H), 7.98–7.93 (m, 2H), 7.93–7.86 (m, 4H), 7.62–7.54 (m, 3H), 7.54–7.43 (m, 7H), 7.39–7.30 (m, 2H), 6.63 (s, 1H), 6.30 (s, 1H), 5.87 (d, *J* = 2.4 Hz, 1H), 5.34 (s, 1H), 5.16 (s, 1H), 5.05 (d, *J* = 4.7 Hz, 1H), 4.72 (dd, *J* = 12.2, 2.4 Hz, 1H), 4.42 (d, *J* = 6.9 Hz, 1H), 3.72–3.53 (m, 4H), 3.41 (s, 3H), 3.07 (d, *J* = 16.9 Hz, 1H), 2.79 (d, *J* = 16.9 Hz, 1H), 2.35 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 165.7, 165.5, 145.0, 138.0, 135.0, 133.9, 133.7, 133.5, 133.3, 130.0, 129.9, 129.78, 129.75, 129.5, 129.3, 129.1, 128.8, 128.6, 128.5, 97.2, 77.3, 73.4, 70.5, 69.2, 65.3, 62.4, 61.9, 56.0, 55.2, 30.0; HRMS (ESI) *m/z* calcd for $C_{39}H_{38}O_{12}NaS$ $[M+Na]^+$ 753.1976, found 753.1982.

Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2-hydroxyethyl)-4-*C*-[2-(phenyl)allyl]-α-D-talopyranoside (4e)



Following the general procedure E, **1e** (139.2 mg, 200.0 μmol, 1.0 equiv) and **2f**[16] (163.4 mg, 600.0 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **4e** (75.5 mg, 113.3 μmol, 57%) as a white foam after purification by silica gel column chromatography (PE:EA = 1:1). $[\alpha]_D^{25}$ = +43.26 (*c* 2.6, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02–7.98 (m, 2H), 7.96–7.92 (m, 2H), 7.92–7.88 (m, 2H), 7.59–7.51 (m, 3H), 7.46–7.37 (m, 6H), 7.35–7.30 (m, 2H), 7.21–7.14 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 5.65 (d, *J* = 3.7 Hz, 1H), 5.61 (d, *J* = 1.5 Hz, 1H), 5.31–5.27 (m, 1H), 5.15 (s, 1H), 4.85 (d, *J* = 1.6 Hz, 1H), 4.63–4.53 (m, 2H), 4.04–3.91 (m, 3H), 3.78–3.69 (m, 1H), 3.66–3.58 (m, 1H), 3.42 (d, *J* = 14.0 Hz, 1H), 3.34 (s, 3H), 2.86 (d, *J* = 13.9 Hz, 1H), 2.29 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.5, 166.0, 165.2, 144.0, 142.1, 133.5, 133.1, 130.1, 130.0, 129.8, 129.7, 129.6, 128.8, 128.7, 128.5, 128.4, 127.9, 126.8, 120.6, 98.6, 78.0, 71.7, 70.2, 69.0, 66.1, 64.0, 62.5, 54.9, 36.8; HRMS (ESI) *m/z* calcd for $C_{39}H_{42}NO_{10}$ $[M+NH_4]^+$ 684.2803, found 684.2814.

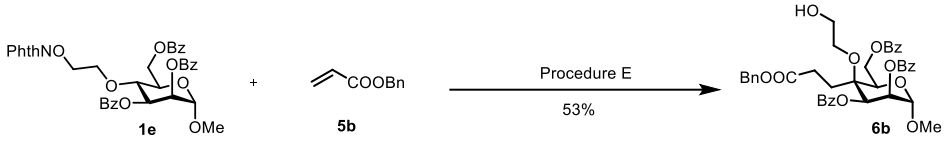
Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2-hydroxyethyl)-4-*C*-[2-(methoxycarbonyl)-ethyl]-α-D-talopyranoside (6a)



Following the general procedure E, **1e** (139.2 mg, 200.0 μmol, 1.0 equiv) and **5a** (54 μL, 600.0 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **6a** (58.6 mg, 92.1 μmol, 46%) as a white foam after purification by silica gel column chromatography (PE:EA =2:1). $[\alpha]_D^{25}$ = +5.24 (*c* 2.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09–8.06 (m, 2H), 8.05–8.00 (m, 2H), 7.97–7.92 (m, 2H), 7.61–7.52 (m, 3H), 7.48–7.38 (m, 6H), 5.77 (d, *J* = 3.6 Hz, 1H), 5.46 (t, *J* = 3.2 Hz, 1H), 5.02 (d, *J* = 2.9 Hz, 1H), 4.90 (s, 1H), 4.78 (dd, *J* = 12.0, 2.6 Hz, 1H), 4.31 (dd, *J* = 8.5, 2.7 Hz, 1H), 3.83–3.65 (m, 4H), 3.63 (s, 3H), 3.41 (s, 3H), 2.69–2.53 (m, 2H), 2.50–2.39 (m, 1H), 2.30 (s, 1H), 2.10–2.01 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.8,

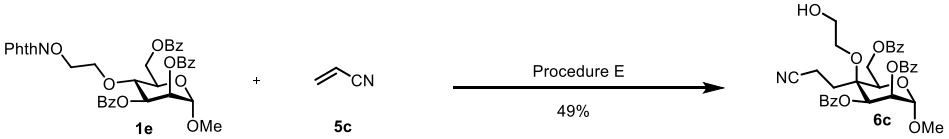
166.8, 165.9, 165.7, 133.7, 133.5, 133.4, 130.0, 129.9, 129.7, 129.5, 129.2, 128.8, 128.6, 128.5, 98.4, 76.3, 72.3, 69.7, 69.4, 65.3, 62.7, 62.4, 55.7, 52.0, 28.4, 26.1; HRMS (ESI) *m/z* calcd for $C_{34}H_{40}NO_{12}$ $[M+NH_4]^+$ 654.2545, found 654.2551.

Methyl 2,3,6-tri-*O*-benzoyl-4-*C*-[2-(benzyloxycarbonyl)ethyl]-4-*O*-(2-hydroxyethyl)-α-D-talopyranoside (6b)



Following the general procedure E, **1e** (139.2 mg, 200.0 μmol, 1.0 equiv) and **5b** (92 μL, 600.0 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **6b** (75.2 mg, 103.8 μmol, 52%) as a white foam after purification by silica gel column chromatography (PE:EA =2:1). $[\alpha]_D^{25}$ = –4.91 (*c* 2.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10–8.05 (m, 2H), 8.05–8.01 (m, 2H), 7.96–7.92 (m, 2H), 7.61–7.53 (m, 3H), 7.48–7.38 (m, 6H), 7.34–7.28 (m, 5H), 5.78 (d, *J* = 3.7 Hz, 1H), 5.46 (t, *J* = 3.4 Hz, 1H), 5.08 (s, 2H), 5.01 (d, *J* = 2.9 Hz, 1H), 4.94–4.84 (m, 1H), 4.77 (dd, *J* = 12.1, 2.7 Hz, 1H), 4.31 (dd, *J* = 8.5, 2.8 Hz, 1H), 3.86–3.60 (m, 4H), 3.40 (s, 3H), 2.74–2.56 (m, 2H), 2.54–2.42 (m, 1H), 2.15–2.00 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.2, 166.7, 165.8, 165.6, 135.6, 133.3, 129.7, 128.3, 98.4, 77.1, 69.6, 69.4, 66.8, 65.2, 62.6, 62.3, 55.7, 28.5, 25.9; HRMS (ESI) *m/z* calcd for $C_{40}H_{44}NO_{12}$ $[M+NH_4]^+$ 730.2858, found 730.2875.

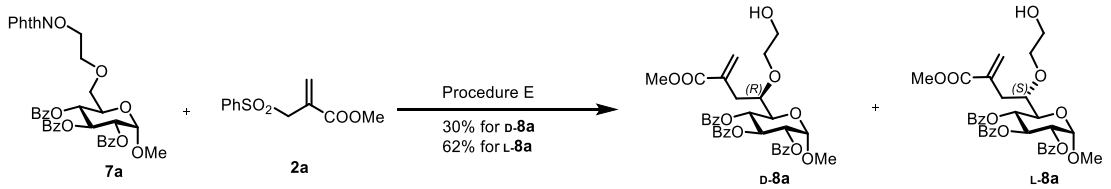
Methyl 2,3,6-tri-*O*-benzoyl-4-*C*-(2-cyanoethyl)-4-*O*-(2-hydroxyethyl)-α-D-talopyranoside (6c)



Following the general procedure E, **1e** (139.2 mg, 200.0 μmol, 1.0 equiv) and **5c** (40 μL, 600.0 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.3 μmol, 1.5

equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **6c** (59.1 mg, 98.0 μmol, 49%) as a white foam after purification by silica gel column chromatography (PE:EA =2:1). $[\alpha]_D^{25}$ = +17.57 (*c* 2.9, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11–8.06 (m, 2H), 8.03–7.99 (m, 2H), 7.99–7.92 (m, 2H), 7.63–7.54 (m, 3H), 7.50–7.39 (m, 6H), 5.76 (d, *J* = 3.6 Hz, 1H), 5.41 (t, *J* = 3.2 Hz, 1H), 5.04 (d, *J* = 3.3 Hz, 1H), 4.93 (d, *J* = 9.1 Hz, 1H), 4.79 (dd, *J* = 12.2, 2.6 Hz, 1H), 4.27 (dd, *J* = 8.4, 2.6 Hz, 1H), 3.82–3.60 (m, 4H), 3.39 (s, 3H), 2.85–2.72 (m, 1H), 2.70–2.59 (m, 1H), 2.50–2.42 (m, 1H), 2.26–2.10 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 165.7, 133.9, 133.6, 133.5, 129.9, 129.7, 129.6, 129.3, 128.8, 128.71, 128.65, 128.5, 118.9, 98.2, 75.9, 72.1, 69.3, 65.5, 62.1, 55.8, 27.4, 12.1; HRMS (ESI) *m/z* calcd for $C_{33}H_{33}NO_{10}Na$ $[M+Na]^+$ 626.1997, found 626.1999.

Methyl [methyl 2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-6-*O*-(2-hydroxyethyl)-8-methylene-D-*glycero*-α-D-nonglucopyranosyluronate] (D-8a) and Methyl [methyl 2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-6-*O*-(2-hydroxyethyl)-8-methylene-L-*glycero*-α-D-nonglucopyranosyluronate] (L-8a)



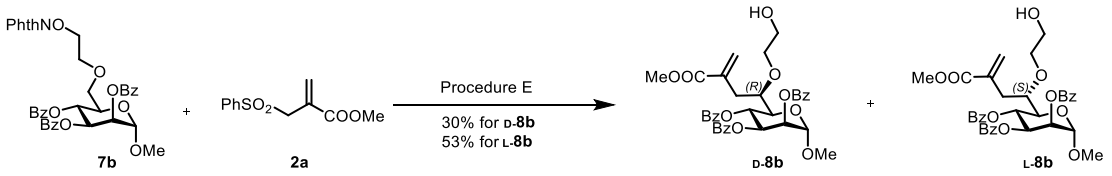
Following the general procedure E, **7a** (118.3 mg, 170.0 μmol, 1.0 equiv) and **2a** (129.9 mg, 510.6 μmol, 3.0 equiv) were treated with hantzsch ester (64.7 mg, 255.5 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.1mg, 1.7 μmol, 0.01 equiv) in 1,4-dioxane (3.4 mL) to give **D-8a** (33.0 mg, 50.9 μmol, 30%) and **L-8a** (68.5 mg, 105.7 μmol, 62%) as white foam after purification by silica gel column chromatography (PE:EA = 1.5:1).

For **D-8a**: $[\alpha]_D^{25}$ = +20.40 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01–7.94 (m, 4H), 7.88–7.84 (m, 2H), 7.61–7.49 (m, 2H), 7.44–7.34 (m, 5H), 7.32–7.27 (m, 2H), 6.20 (d, *J* = 1.5 Hz, 1H), 6.15–6.07 (m, 1H), 5.72 (t, *J* = 9.9 Hz, 1H), 5.59 (d, *J* = 1.5 Hz, 1H), 5.26–5.20 (m, 2H), 4.32 (dd, *J* = 10.2, 1.7 Hz, 1H), 3.83–3.74 (m, 2H), 3.70–3.62 (m, 6H), 3.55–3.48 (m, 1H), 3.46 (s, 3H),

2.67 (d, J = 6.8 Hz, 2H), 2.30 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 165.9, 165.3, 137.3, 134.4, 133.6, 133.5, 133.2, 130.0, 129.9, 129.8, 129.6, 129.3, 129.2, 129.1, 128.6, 128.5, 128.4, 128.3, 127.9, 97.1, 78.4, 72.24, 72.21, 71.0, 69.9, 69.6, 62.1, 55.8, 52.0, 34.1; HRMS (ESI) *m/z* calcd for $C_{35}H_{40}NO_{12}$ $[M+NH_4]^+$ 666.2545, found 666.2541.

For L-**8a**: $[\alpha]_D^{25}$ = +38.06 (*c* 2.6, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00–7.91 (m, 4H), 7.89–7.83 (m, 2H), 7.55–7.47 (m, 2H), 7.43–7.33 (m, 5H), 7.32–7.27 (m, 2H), 6.29 (s, 1H), 6.10 (t, J = 9.9 Hz, 1H), 5.85 (t, J = 9.8 Hz, 1H), 5.74 (s, 1H), 5.34–5.22 (m, 2H), 4.12 (d, J = 10.0 Hz, 1H), 3.82–3.69 (m, 4H), 3.65 (s, 3H), 3.53–3.46 (m, 4H), 2.93 (dd, J = 14.0, 6.2 Hz, 1H), 2.73 (dd, J = 14.0, 7.1 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.1, 165.9, 165.8, 165.7, 136.9, 133.6, 133.4, 133.1, 129.94, 129.87, 129.7, 129.2, 129.1, 129.0, 128.5, 128.4, 128.3, 97.6, 75.0, 72.5, 72.0, 70.7, 69.6, 69.0, 62.1, 56.4, 52.0, 33.3; HRMS (ESI) *m/z* calcd for $C_{35}H_{40}NO_{12}$ $[M+NH_4]^+$ 666.2545, found 666.2545.

Methyl [methyl 2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-6-*O*-(2-hydroxyethyl)-8-methylene-D-*glycero*-α-D-nonmannopyranosyluronate] (D-8b) and Methyl [methyl 2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-6-*O*-(2-hydroxyethyl)-8-methylene-L-*glycero*-α-D-nonmannopyranosyluronate] (L-8b)



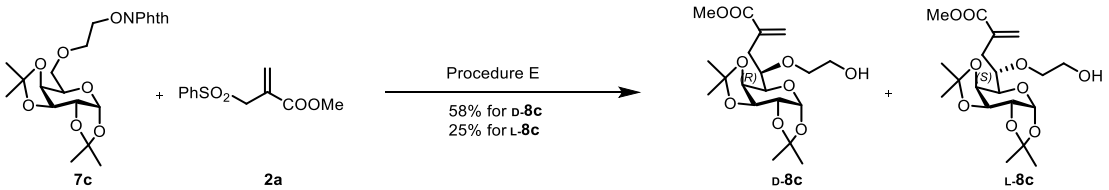
Following the general procedure E, **7b** (695.6 mg, 1.00 mmol, 1.0 equiv) and **2a** (762.9 mg, 3.00 mmol, 3.0 equiv) were treated with hantzsch ester (380.0 mg, 1.5 mmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (6.5 mg, 10.0 μmol, 0.01 equiv) in 1,4-dioxane (20.0 mL) to give D-**8b** (191.7 mg, 295.7 μmol, 30%) and L-**8b** (340.5 mg, 525.3 μmol, 53%) as white foam after purification by silica gel column chromatography (PE:EA = 1.5:1).

For D-**8b**: $[\alpha]_D^{25}$ = –73.40 (*c* 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, J = 7.3 Hz, 2H), 7.98 (d, J = 7.3 Hz, 2H), 7.83 (d, J = 7.3 Hz, 2H), 7.62–7.58 (m, 1H),

7.54–7.46 (m, 3H), 7.45–7.36 (m, 3H), 7.26–7.22 (m, 2H), 6.21–6.19 (m, 1H), 6.14 (t, *J* = 10.1 Hz, 1H), 5.83 (dd, *J* = 10.0, 3.2 Hz, 1H), 5.68–5.63 (m, 1H), 5.57 (s, 1H), 4.99–4.94 (m, 1H), 4.31 (d, *J* = 10.1 Hz, 1H), 3.95–3.87 (m, 1H), 3.86–3.79 (m, 1H), 3.71–3.67 (m, 2H), 3.66 (s, 3H), 3.56–3.53 (m, 1H), 3.51 (s, 3H), 2.85 (brs, 1H), 2.75–2.61 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 165.6, 165.5, 165.4, 133.6, 133.5, 133.1, 130.0, 129.8, 129.5, 129.31, 129.25, 129.1, 128.7, 128.5, 128.3, 128.2, 127.7, 98.6, 78.7, 72.5, 71.4, 70.6, 70.5, 67.1, 62.2, 55.6, 51.9, 34.8; HRMS (ESI) *m/z* calcd for $C_{35}H_{40}NO_{12}$ $[M+NH_4]^+$ 666.2545, found 666.2545.

For **L-8b**: $[\alpha]_D^{25} = -118.66$ (*c* 4.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 7.5 Hz, 2H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 6.2 Hz, 1H), 7.54–7.46 (m, 3H), 7.44–7.34 (m, 3H), 7.26–7.21 (m, 2H), 6.29 (s, 1H), 6.24 (t, *J* = 10.1 Hz, 1H), 5.82 (dd, *J* = 10.1, 3.0 Hz, 1H), 5.75 (s, 1H), 5.66 (s, 1H), 5.06 (s, 1H), 4.10 (d, *J* = 9.9 Hz, 1H), 3.88–3.77 (m, 4H), 3.62 (s, 3H), 3.59–3.51 (m, 4H), 2.95 (dd, *J* = 14.8, 5.4 Hz, 1H), 2.75 (dd, *J* = 13.9, 7.1 Hz, 1H), 2.66 (brs, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 166.1, 165.7, 165.6, 137.0, 133.7, 133.3, 130.1, 129.93, 129.85, 129.5, 129.3, 129.21, 129.17, 128.7, 128.61, 128.57, 128.4, 99.0, 75.1, 72.3, 70.8, 70.4, 67.0, 62.4, 56.2, 52.0, 33.4; HRMS (ESI) *m/z* calcd for $C_{35}H_{40}NO_{12}$ $[M+NH_4]^+$ 666.2545, found 666.2553.

Methyl [7,8-di-deoxy-6-*O*-(2-hydroxyethyl)-1,2,3,4-di-*O*-isopropylidene-8-methylene-D-*glycero*-α-D-nongalactopyranosyluronate] (D-8c) and Methyl [7,8-di-deoxy-6-*O*-(2-hydroxyethyl)-1,2,3,4-di-*O*-isopropylidene-8-methylene-L-*glycero*-α-D-nongalactopyranosyluronate] (L-8c)



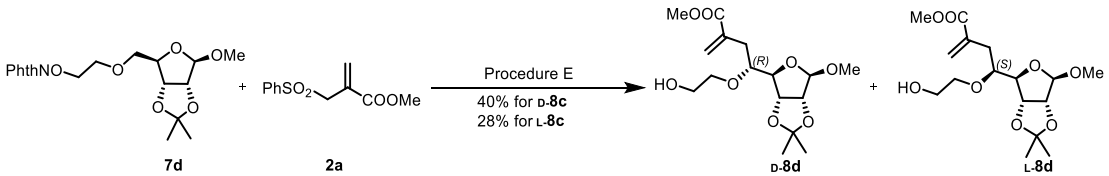
Following the general procedure E, **7c** (89.8 mg, 200.0 μmol, 1.0 equiv) and **2a** (152.3 mg, 598.9 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.2 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give

D-8c (46.6 mg, 115.9 μmol, 58%) and **L-8c** (19.8 mg, 49.2 μmol, 25%) as white foam after purification by silica gel column chromatography (PE:EA = 2:1).

For **D-8c**: $[\alpha]_D^{25} = -65.41$ (*c* 0.8, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 6.22 (d, *J* = 1.5 Hz, 1H), 5.83 (s, 1H), 5.53 (d, *J* = 5.1 Hz, 1H), 4.62 (dd, *J* = 7.9, 2.3 Hz, 1H), 4.44 (dd, *J* = 8.0, 1.9 Hz, 1H), 4.31 (dd, *J* = 5.1, 2.4 Hz, 1H), 3.87–3.69 (m, 5H), 3.69–3.56 (m, 4H), 3.47 (brs, 1H), 2.99 (dd, *J* = 14.1, 4.3 Hz, 1H), 2.50 (dd, *J* = 14.2, 4.1 Hz, 1H), 1.49 (s, 3H), 1.46 (s, 3H), 1.36 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.3, 136.3, 128.8, 109.1, 108.5, 96.5, 76.4, 72.2, 70.8, 70.3, 67.3, 61.9, 51.9, 32.0, 25.9, 25.9, 24.9, 24.5; HRMS (ESI) *m/z* calcd for $C_{19}H_{34}NO_9$ $[M+NH_4]^+$ 420.2228, found 420.2232.

For **L-8c**: $[\alpha]_D^{25} = -28.99$ (*c* 1.8, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 6.23 (s, 1H), 5.74 (s, 1H), 5.61 (d, *J* = 5.1 Hz, 1H), 4.59 (dd, *J* = 7.9, 2.1 Hz, 1H), 4.31 (dd, *J* = 5.1, 2.2 Hz, 1H), 4.27 (dd, *J* = 8.0, 1.4 Hz, 1H), 3.85–3.79 (m, 1H), 3.77 (s, 3H), 3.74–3.71 (m, 1H), 3.65–3.56 (m, 3H), 3.30 (brs, 1H), 2.76 (dd, *J* = 13.9, 4.7 Hz, 1H), 2.57 (dd, *J* = 13.8, 8.1 Hz, 1H), 1.52 (s, 3H), 1.47 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 137.0, 128.0, 109.4, 108.6, 96.6, 78.7, 73.4, 71.6, 71.1, 70.6, 70.3, 61.9, 52.0, 34.2, 26.1, 25.9, 24.8, 24.3; HRMS (ESI) *m/z* calcd for $C_{19}H_{34}NO_9$ $[M+NH_4]^+$ 420.2228, found 420.2228.

Methyl [methyl 6,7-di-deoxy-5-*O*-(2-hydroxyethyl)-2,3-*O*-isopropylidene-7-methylene-D-*glycero*-α-D-octribofuranosyluronate] (D-8d) and Methyl [methyl 6,7-di-deoxy-5-*O*-(2-hydroxyethyl)-2,3-*O*-isopropylidene-7-methylene-L-*glycero*-α-D-octribofuranosyluronate] (L-8d)



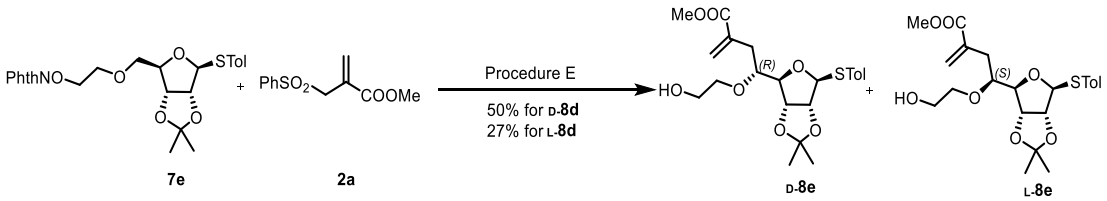
Following the general procedure E, **7d** (78.7 mg, 200.0 μmol, 1.0 equiv) and **2a** (152.3 mg, 598.9 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.2 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give

D-8d (27.5 mg, 79.4 μmol, 40%) and **L-8d** (19.3 mg, 55.8 μmol, 28%) as white foam after purification by silica gel column chromatography (PE:EA = 2:1).

For **D-8d**: $[\alpha]_D^{25} = -75.63$ (*c* 3.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.28 (d, *J* = 1.2 Hz, 1H), 5.74 (s, 1H), 4.97 (s, 1H), 4.81 (d, *J* = 6.0 Hz, 1H), 4.57 (d, *J* = 6.0 Hz, 1H), 4.13 (d, *J* = 5.2 Hz, 1H), 3.79–3.72 (m, 4H), 3.70–3.61 (m, 2H), 3.59–3.53 (m, 1H), 3.52–3.44 (m, 1H), 3.41 (s, 3H), 3.23 (brs, 1H), 2.78–2.54 (m, 2H), 1.48 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 136.3, 128.7, 112.3, 110.9, 87.8, 85.7, 80.8, 79.3, 72.1, 61.8, 55.9, 52.0, 33.9, 26.6, 25.0; HRMS (ESI) *m/z* calcd for $C_{16}H_{30}NO_8$ $[M+NH_4]^+$ 364.1966, found 364.1970.

For **L-8d**: $[\alpha]_D^{25} = -13.44$ (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.26 (d, *J* = 1.2 Hz, 1H), 5.74 (s, 1H), 5.02 (s, 1H), 4.72 (d, *J* = 6.0 Hz, 1H), 4.56 (d, *J* = 6.0 Hz, 1H), 4.18 (dd, *J* = 4.8, 1.7 Hz, 1H), 3.77 (s, 3H), 3.74–3.68 (m, 1H), 3.68–3.58 (m, 3H), 3.58–3.50 (m, 1H), 3.40 (s, 3H), 3.04 (brs, 1H), 2.67–2.54 (m, 2H), 1.49 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.4, 136.6, 128.5, 112.6, 110.0, 88.8, 85.6, 82.0, 78.4, 71.1, 61.9, 55.4, 52.0, 34.1, 26.8, 25.1; HRMS (ESI) *m/z* calcd for $C_{16}H_{30}NO_8$ $[M+NH_4]^+$ 364.1966, found 364.1968.

Methyl [*p*-tolyl 6,7-di-deoxy-5-*O*-(2-hydroxyethyl)-2,3-*O*-isopropylidene-7-methylene-D-*glycero*-1-thio-α-D-octribofuranosyluronate] (D-8e) and Methyl [*p*-tolyl 6,7-di-deoxy-5-*O*-(2-hydroxyethyl)-2,3-*O*-isopropylidene-7-methylene-L-*glycero*-1-thio-α-D-octribofuranosyluronate] (L-8e)

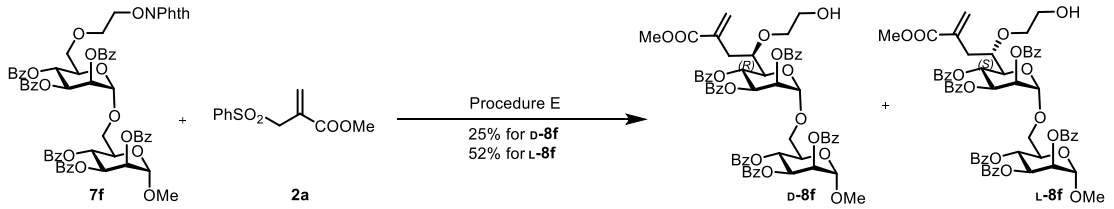


Following the general procedure E, **7e** (97.1 mg, 200.0 μmol, 1.0 equiv) and **2a** (152.3 mg, 598.9 μmol, 3.0 equiv) were treated with hantzsch ester (76.3 mg, 301.2 μmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **D-8e** (43.8 mg, 100.0 μmol, 50%) and **L-8e** (23.9 mg, 54.5 μmol, 27%) as white foam after purification by silica gel column chromatography (PE:EA = 2:1).

For **D-8e**: $[\alpha]_D^{25} = -51.63$ (*c* 0.2, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.42–7.33 (m, 2H), 7.20–7.07 (m, 2H), 6.25 (s, 1H), 5.70 (s, 1H), 5.34 (d, *J* = 3.7 Hz, 1H), 4.81 (dd, *J* = 6.4, 2.8 Hz, 1H), 4.65 (dd, *J* = 6.4, 3.7 Hz, 1H), 4.06 (dd, *J* = 5.0, 2.8 Hz, 1H), 3.87–3.78 (m, 1H), 3.78–3.71 (m, 4H), 3.71–3.60 (m, 3H), 2.75 (s, 1H), 2.68–2.53 (m, 2H), 2.33 (s, 3H), 1.51 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 137.8, 136.4, 132.0, 130.2, 130.0, 128.8, 114.3, 92.3, 87.3, 85.4, 80.8, 78.4, 72.8, 62.1, 52.2, 34.1, 27.3, 25.6, 21.2; HRMS (ESI) *m/z* calcd for $C_{22}H_{34}NO_7S$ $[M+NH_4]^+$ 456.2050, found 456.2048.

For **L-8e**: $[\alpha]_D^{25} = -91.73$ (*c* 0.3, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.44–7.38 (m, 2H), 7.16–7.09 (m, 2H), 6.26 (d, *J* = 1.3 Hz, 1H), 5.75 (s, 1H), 5.38 (d, *J* = 3.0 Hz, 1H), 4.73 (dd, *J* = 6.2, 3.0 Hz, 1H), 4.65 (dd, *J* = 6.2, 2.6 Hz, 1H), 4.15 (dd, *J* = 5.0, 2.7 Hz, 1H), 3.77 (s, 3H), 3.75–3.63 (m, 4H), 3.65–3.55 (m, 1H), 2.71 (dd, *J* = 13.5, 6.1 Hz, 1H), 2.60 (dd, *J* = 13.5, 6.8 Hz, 1H), 2.33 (s, 3H), 1.50 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 137.8, 136.5, 132.3, 129.9, 128.9, 114.0, 93.5, 87.6, 86.3, 82.4, 78.9, 72.1, 62.2, 52.2, 33.8, 27.3, 25.6, 21.2; HRMS (ESI) *m/z* calcd for $C_{22}H_{34}NO_7S$ $[M+NH_4]^+$ 456.2050, found 456.2038.

Methyl {methyl [2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-6-*O*-(2-hydroxyethyl)-8-methylene-D-*glycero*-α-D-nonmannopyranosyluronate]}-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (D-8f) and Methyl {methyl [2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-6-*O*-(2-hydroxyethyl)-8-methylene-L-*glycero*-α-D-nonmanno-pyranosyluronate]}-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (L-8f)



Following the general procedure E, **7f** (234.3 mg, 200.2 μmol, 1.0 equiv) and **2a** (152.5 mg, 599.4 μmol, 3.0 equiv) were treated with hantzsch ester (76.0 mg, 300.0 μmol, 1.5 equiv) and *fac*-$Ir(ppy)_3$ (1.3 mg, 2.0 μmol, 0.01 equiv) in 1,4-dioxane (4.0 mL) to give **D-8f** (56.1 mg, 50.0 μmol, 25%) and **L-8f** (117.7 mg, 104.9 μmol, 52%) as white foam

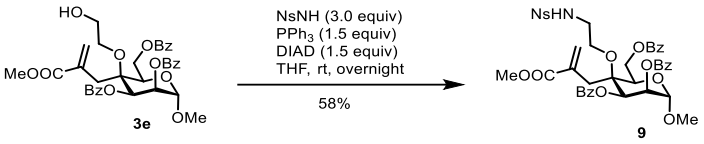
after purification by silica gel column chromatography (PE:EA = 1.5:1).

For **D-8f**: $[\alpha]_D^{25} = -79.74$ (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20–8.15 (m, 2H), 8.14–8.10 (m, 2H), 8.07–7.98 (m, 4H), 7.88–7.82 (m, 4H), 7.61–7.47 (m, 8H), 7.45–7.34 (m, 6H), 7.31–7.26 (m, 4H), 6.10 (s, 1H), 6.08–6.00 (m, 2H), 5.98–5.91 (m, 2H), 5.78–5.72 (m, 2H), 5.46 (s, 1H), 5.14 (s, 1H), 5.06 (s, 1H), 4.47–4.30 (m, 2H), 4.11 (dd, *J* = 10.8, 6.1 Hz, 1H), 3.78 (d, *J* = 10.6 Hz, 1H), 3.69–3.63 (m, 5H), 3.55 (s, 3H), 3.45 (s, 2H), 3.35–3.23 (m, 1H), 2.66 (s, 1H), 2.62–2.54 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 165.7, 165.6, 165.53, 165.45, 165.4, 165.3, 137.4, 134.3, 133.57, 133.55, 133.5, 133.2, 133.1, 130.01, 129.98, 129.9, 129.8, 129.7, 129.6, 129.31, 129.29, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 128.3, 128.2, 127.5, 98.7, 97.4, 78.5, 72.4, 70.6, 70.5, 70.3, 70.2, 69.5, 67.1, 67.0, 66.7, 62.0, 55.6, 51.8, 34.1; HRMS (ESI) *m/z* calcd for $C_{62}H_{62}NO_{20}$ $[M+NH_4]^+$ 1140.3860, found 1140.3888.

For **L-8f**: $[\alpha]_D^{25} = -81.14$ (*c* 4.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19–8.08 (m, 4H), 8.04–7.99 (m, 2H), 7.98–7.89 (m, 2H), 7.89–7.79 (m, 4H), 7.64–7.44 (m, 8H), 7.44–7.33 (m, 6H), 7.28–7.24 (m, 4H), 6.23 (t, *J* = 10.0 Hz, 1H), 6.05 (s, 1H), 5.97 (dd, *J* = 10.0, 3.3 Hz, 1H), 5.94–5.86 (m, 2H), 5.77–5.72 (m, 1H), 5.72–5.67 (m, 1H), 5.64 (s, 1H), 5.23 (s, 1H), 5.09 (s, 1H), 4.41 (t, *J* = 7.6 Hz, 1H), 4.29 (d, *J* = 10.0 Hz, 1H), 4.08 (dd, *J* = 10.7, 7.2 Hz, 1H), 3.90–3.80 (m, 1H), 3.80–3.71 (m, 4H), 3.68 (s, 3H), 3.51 (s, 4H), 2.85 (dd, *J* = 14.0, 7.3 Hz, 1H), 2.64 (dd, *J* = 14.0, 5.5 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 166.0, 165.8, 165.6, 165.49, 165.45, 165.4, 136.7, 133.63, 133.59, 133.5, 133.22, 133.17, 130.0, 129.90, 129.88, 129.8, 129.7, 129.3, 129.2, 129.1, 128.9, 128.73, 128.65, 128.6, 128.5, 128.3, 98.6, 97.3, 75.2, 72.4, 71.4, 70.5, 70.3, 70.2, 69.9, 69.4, 67.5, 67.1, 67.0, 62.3, 55.6, 51.8, 33.8; HRMS (ESI) *m/z* calcd for $C_{62}H_{62}NO_{20}$ $[M+NH_4]^+$ 1140.3860, found 1140.3890.

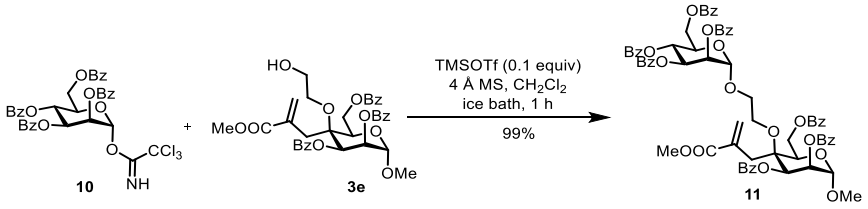
Elaboration of 2-hydroxyethylene moiety

Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2-((2-nitrophenyl)sulfonamido)ethyl)-4-*C*-[2-(methoxycarbonyl)allyl]-α-D-talopyranoside (9)



To a solution of **3e** (64.8 mg, 100.0 μmol, 1.0 equiv), PPh_3 (39.0 mg, 150.0 μmol, 1.5 equiv) and $NsNH_2$ (60.7 mg, 300.0 μmol, 3.0 equiv) in THF (2.0 mL) was added diisopropylazodicarboxylate (30 μL, 150.0 μmol, 1.5 equiv) over 1 min at room temperature under an atmosphere. The resultant solution was stirred overnight at room temperature and quenched with saturated $NaHCO_3$ solution. The resultant mixture was extracted with DCM, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (PhMe:EA = 10:1) to afford **9** (48.5 mg, 58.2 μmol, 58%) as a white foam. $[\alpha]_D^{25}$ = +30.91 (*c* 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10–8.03 (m, 3H), 8.00–7.95 (m, 2H), 7.93–7.86 (m, 3H), 7.76–7.69 (m, 2H), 7.62–7.53 (m, 3H), 7.49–7.38 (m, 6H), 6.37 (s, 1H), 5.84 (t, *J* = 5.8 Hz, 1H), 5.77 (s, 1H), 5.55 (s, 2H), 4.93 (s, 1H), 4.77 (d, *J* = 11.3 Hz, 1H), 4.71–4.63 (m, 1H), 4.21 (d, *J* = 8.4 Hz, 1H), 4.06–3.90 (m, 2H), 3.61 (s, 3H), 3.40 (s, 3H), 3.28–3.18 (m, 2H), 3.13 (d, *J* = 14.2 Hz, 1H), 2.63 (d, *J* = 14.2 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 166.4, 165.8, 165.3, 148.3, 134.7, 133.7, 133.5, 133.4, 133.2, 132.7, 131.0, 130.7, 130.0, 129.9, 129.7, 129.6, 129.4, 129.3, 128.7, 128.6, 128.5, 125.8, 98.5, 77.6, 71.9, 69.9, 63.6, 62.9, 55.4, 53.5, 52.5, 44.5, 32.1; HRMS (ESI) *m/z* calcd for $C_{41}H_{44}N_3O_{15}S$ $[M+HH_4]^+$ 850.2488, found 850.2498.

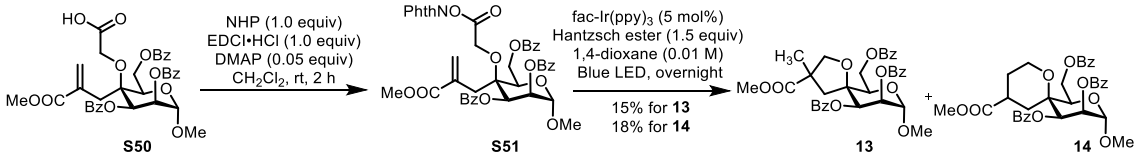
Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2-(2,3,4,6-tetra-*O*-benzoyl-α-D-manno-pyranosyloxy)ethyl)-4-*C*-[2-(methoxycarbonyl)allyl]-α-D-talopyranoside (11)



To a solution of **10** (111.2 mg, 150.0 μmol, 1.5 equiv), **3e** (65.0 mg, 100.0 μmol, 1.0 equiv) and freshly activated 4 Å MS in DCM (2.0 mL) was added TMSOTf (2 μL, 1.0

μmol, 0.1 equiv) in ice bath under an argon atmosphere. The resultant solution was stirred for 1 h in ice bath and quenched with saturated $NaHCO_3$ solution. The resultant mixture was extracted with DCM, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (PE:EA = 2:1) to afford **11** (120.7 mg, 99%) as a white foam. $[\alpha]_D^{25}$ = +10.20 (*c* 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23–8.14 (m, 2H), 8.05–7.97 (m, 8H), 7.93–7.85 (m, 2H), 7.85–7.79 (m, 2H), 7.62–7.47 (m, 6H), 7.46–7.28 (m, 13H), 7.20–7.13 (m, 2H), 6.51 (s, 1H), 6.24 (t, *J* = 10.0 Hz, 1H), 6.00–5.91 (m, 2H), 5.73–5.61 (m, 3H), 5.09–4.96 (m, 4H), 4.89 (d, *J* = 11.7 Hz, 1H), 4.74–4.61 (m, 2H), 4.38–4.24 (m, 2H), 4.16–3.98 (m, 2H), 3.67–3.58 (m, 4H), 3.45 (s, 3H), 3.39 (d, *J* = 14.4 Hz, 1H), 2.99 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.4, 166.3, 166.2, 165.8, 165.7, 165.5, 165.4, 135.1, 133.52, 133.47, 133.1, 133.0, 132.9, 131.1, 130.2, 130.1, 129.91, 129.87, 129.8, 129.7, 129.6, 129.4, 129.2, 128.8, 128.6, 128.5, 128.3, 98.6, 97.5, 77.4, 72.3, 70.5, 70.3, 70.2, 69.4, 69.0, 67.8, 66.7, 64.4, 63.7, 62.8, 55.4, 52.4, 32.2; HRMS (ESI) *m/z* calcd for $C_{69}H_{66}NO_{21}$ $[M+HH_4]^+$ 1244.4122, found 1244.4149.

(5*S*,6*R*,8*S*,9*S*,10*R*)-6-((benzoyloxy)methyl)-8-methoxy-3-(methoxycarbonyl)-3-methyl-1,7-dioxaspiro[4.5]decane-9,10-diyl dibenzoate (13) and (6*S*,7*R*,9*S*,10*S*,11*R*)-7-((benzoyloxy)methyl)-9-methoxy-4-(methoxycarbonyl)-1,8-dioxaspiro[5.5]undecane-10,11-diyl dibenzoate (14)



To a solution of **S50** (132.5 mg, 200.0 μmol, 1.0 equiv) in dry DCM (3.0 mL) were added *N*-hydroxyphthalimide (32.6 mg, 100.0 μmol, 0.1 equiv), EDCI·HCl (38.3 mg, 200.0 μmol, 1.0 equiv) and DMAP (0.3 mg, 2.5 μmol, 0.013 equiv) at room temperature under an argon atmosphere. The resultant solution was stirred for 2 h at room temperature and quenched with saturated $NaHCO_3$ solution. The resultant mixture was

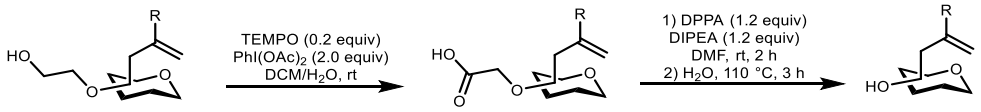
extracted with DCM, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo* to give the crude product **S51** without further purification for next step. The crude product obtained above, *fac*-Ir(ppy)$_3$ (6.5 mg, 10.0 μmol, 0.05 equiv) and hantzsch ester (76.0 mg, 300.0 μmol, 1.5 equiv) were placed in a 100 mL clear-colored glass bottle. After 1,4-dioxane (20.0 mL) was added, the reaction was exchanged three times using argon gas and exposed to blue LEDs (450 nm-470 nm) at 35 ℃ with stirring overnight. The resultant mixture was diluted with DCM and washed with saturated $NaHCO_3$ solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (PE:EA = 8:1) to afford **13** (18.5 mg, 29.9 μmol, 15%) and **14** (21.7 mg, 35.1 μmol, 18%) as white foam.

For **13**: $[\alpha]_D^{25} = -27.22$ (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16–8.10 (m, 2H), 8.10–8.04 (m, 2H), 7.96–7.90 (m, 2H), 7.61–7.51 (m, 3H), 7.50–7.42 (m, 4H), 7.42–7.34 (m, 2H), 5.63 (d, *J* = 3.5 Hz, 1H), 5.42 (t, *J* = 3.1 Hz, 1H), 5.04 (d, *J* = 2.6 Hz, 1H), 4.73–4.65 (m, 2H), 4.55 (d, *J* = 9.0 Hz, 1H), 4.32–4.24 (m, 1H), 3.88 (d, *J* = 9.0 Hz, 1H), 3.78 (s, 3H), 3.44 (s, 3H), 2.98 (d, *J* = 14.4 Hz, 1H), 1.94 (d, *J* = 14.5 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.4, 166.6, 165.9, 165.6, 133.5, 133.3, 133.1, 130.2, 130.1, 129.9, 129.8, 129.6, 129.2, 128.6, 128.5, 128.4, 98.2, 83.6, 78.3, 73.4, 72.7, 69.3, 62.9, 55.4, 52.8, 50.5, 42.9, 22.8; HRMS (ESI) *m/z* calcd for $C_{34}H_{38}NO_{11}$ $[M+HH_4]^+$ 636.2439, found 636.2444.

For **14**: $[\alpha]_D^{25} = +63.47$ (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15–8.05 (m, 4H), 7.91–7.85 (m, 2H), 7.64–7.56 (m, 2H), 7.55–7.44 (m, 5H), 7.37–7.29 (m, 2H), 5.78 (d, *J* = 2.9 Hz, 1H), 5.63–5.47 (m, 1H), 5.36 (dd, *J* = 7.4, 3.3 Hz, 1H), 5.26 (d, *J* = 7.4 Hz, 1H), 4.62–4.52 (m, 2H), 3.93 (d, *J* = 12.5 Hz, 1H), 3.75–3.64 (m, 4H), 3.45 (s, 3H), 2.90–2.72 (m, 1H), 2.66–2.51 (m, 1H), 2.01–1.77 (m, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 166.8, 165.7, 165.2, 133.4, 133.3, 133.2, 130.0, 129.8, 129.7, 129.5, 128.7, 128.5, 128.3, 96.4, 74.6, 74.1, 73.0, 69.0, 61.8, 60.7, 56.7, 52.2, 35.8, 31.6, 26.7; HRMS (ESI) *m/z* calcd for $C_{34}H_{38}NO_{11}$ $[M+HH_4]^+$ 636.2439, found 636.2448.

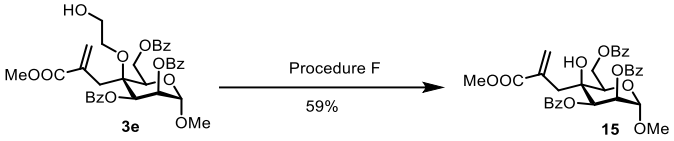
Removal of directing group 2-hydroxyethylene moiety

General Procedure F: Curtius rearrangement reaction



To a solution of **alcohol** (1.0 equiv) in DCM/H_2O (*v*/*v* = 10:1) were added TEMPO (0.2 equiv) and $PhI(OAc)_2$ (2.0 equiv) at room temperature under an argon atmosphere. The resultant solution was stirred for 12 h and quenched with $Na_2S_2O_3$ solution. The resultant mixture was extracted with DCM, and the organic layer was washed and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography for next step without further characterization. The crude product obtained as above was dissolved in DMF, diphenylphosphoryl azide (DPPA) (1.2 equiv) and *N*,*N*-diisopropylethylamine (DIPEA) (1.2 equiv) were added in ice bath under an argon atmosphere. After stirring for 2 h at room temperature, H_2O (0.5 mL) was added to the reaction mixture. The resultant solution was heat to 110 ℃ for 3 h. The resultant mixture was extracted with DCM, and the organic layer was washed sequentially with 1M HCl solution, saturated $NaHCO_3$ solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography to give the desired product.

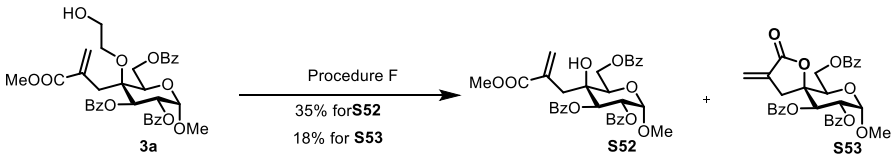
Methyl 2,3,6-tri-*O*-benzoyl-4-*C*-[2-(methoxycarbonyl)allyl]-α-D-talopyranoside (15)



Following the general procedure F, **3e** (648.7 mg, 1.00 mmol, 1.0 equiv) was treated with TEMPO (15.6 mg, 100.0 μmol, 0.1 equiv) and $PhI(OAc)_2$ (644.2 mg, 2.00 mmol, 2.0 equiv) in DCM/H_2O (11.0 mL, *v*/*v* = 10:1) to give the acid (569.3 mg, 859.1 μmol,

86%) as a white foam. The acid (324.7 mg, 490.0 μmol, 1.0 equiv) was treated with DPPA (127 μL, 588.0 μmol, 1.2 equiv) and DIPEA (102 μL, 588.0 μmol, 1.2 equiv) in DMF (5.0 mL) to give **15** (203.4 mg, 336.4 μmol, 69%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25} = -13.05$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11–8.03 (m, 2H), 8.02–7.94 (m, 2H), 7.94–7.87 (m, 2H), 7.63–7.55 (m, 2H), 7.55–7.41 (m, 5H), 7.41–7.31 (m, 2H), 6.16 (s, 1H), 5.74 (s, 1H), 5.55 (dd, *J* = 3.8, 1.8 Hz, 1H), 5.41 (d, *J* = 3.8 Hz, 1H), 5.08–4.86 (m, 2H), 4.81–4.60 (m, 1H), 4.21 (dd, *J* = 8.1, 2.3 Hz, 1H), 4.08 (s, 1H), 3.45 (s, 3H), 3.40 (s, 3H), 2.90 (d, *J* = 14.3 Hz, 1H), 2.74 (d, *J* = 14.3 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 166.7, 165.5, 165.0, 135.5, 133.6, 133.4, 133.3, 130.1, 130.0, 129.9, 129.7, 129.5, 129.4, 128.7, 128.6, 128.4, 98.6, 73.4, 72.9, 69.4, 69.3, 63.8, 55.5, 52.2, 38.3; HRMS (ESI) *m/z* calcd for $C_{33}H_{36}NO_{11}$ $[M+NH_4]^+$ 622.2283, found 622.2296.

Methyl 2,3,6-tri-*O*-benzoyl-4-*C*-[2-(methoxycarbonyl)allyl]-α-D-galatco-pyranoside (S52) and Methyl 2,3,6-tri-*O*-benzoyl-3′-methylenespiro(4-deoxy-α-D-galactopyranose-4,5′-tetrahydrofuran-1-one) (S53)



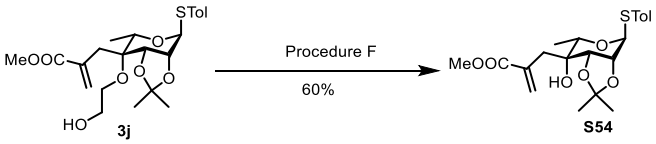
Following the general procedure F, **3a** (64.8 mg, 100.0 μmol, 1.0 equiv) was treated with TEMPO (3.2 mg, 20.0 μmol, 0.2 equiv) and $PhI(OAc)_2$ (64.4 mg, 200.0 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (63.2 mg, 95.5 μmol, 96%) as a colorless oil. The acid (36.5 mg, 55.1 μmol, 1.0 equiv) was treated with DPPA (14 μL, 66.1 μmol, 1.2 equiv) and DIPEA (12 μL, 66.1 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S52** (11.5 mg, 19.0 μmol, 35%) and **S53** (5.7 mg, 10.0 μmol, 18%) as white foam after purification by silica gel column chromatography (PE:EA = 4:1).

For **S52**: $[\alpha]_D^{25} = +47.08$ (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12–8.03 (m, 2H), 7.93–7.86 (m, 4H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.50–7.42 (m, 4H), 7.39–7.30 (m, 4H), 5.99 (s, 1H), 5.76 (s, 1H), 5.71 (d, *J* = 10.0 Hz, 1H), 5.46 (dd, *J* = 10.0, 3.7 Hz,

1H), 5.43 (s, 1H), 5.25 (d, *J* = 3.6 Hz, 1H), 4.94 (dd, *J* = 12.0, 2.7 Hz, 1H), 4.59 (dd, *J* = 11.9, 7.7 Hz, 1H), 4.15 (dd, *J* = 7.6, 2.2 Hz, 1H), 3.38 (s, 3H), 3.29 (s, 3H), 2.92 (d, *J* = 14.5 Hz, 1H), 2.63 (d, *J* = 14.5 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.7, 166.8, 166.1, 165.5, 135.2, 133.3, 133.2, 130.1, 130.0, 129.9, 129.5, 128.6, 128.4, 97.0, 75.1, 73.1, 71.8, 71.4, 63.8, 55.4, 52.3, 41.1; HRMS (ESI) *m/z* calcd for $C_{33}H_{32}O_{11}Na$ $[M+Na]^+$ 627.1837, found 627.1840.

For **S53**: $[\alpha]_D^{25}$ = +48.03 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09–8.02 (m, 2H), 7.94–7.87 (m, 4H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54–7.44 (m, 4H), 7.40–7.31 (m, 4H), 6.18–6.11 (m, 1H), 5.98 (d, *J* = 10.5 Hz, 1H), 5.53 (s, 1H), 5.50 (dd, *J* = 10.4, 3.4 Hz, 1H), 5.31 (d, *J* = 3.5 Hz, 1H), 4.69 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.46 (dd, *J* = 12.0, 6.8 Hz, 1H), 4.32 (dd, *J* = 6.7, 2.7 Hz, 1H), 3.42 (s, 3H), 3.23 (dt, *J* = 18.3, 2.8 Hz, 1H), 2.98 (d, *J* = 18.3 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9, 166.6, 166.1, 165.8, 133.9, 133.7, 133.4, 132.5, 130.0, 130.0, 129.8, 129.5, 129.2, 128.7, 128.5, 123.5, 97.1, 82.9, 71.6, 70.8, 70.4, 62.8, 55.8, 32.2; HRMS (ESI) *m/z* calcd for $C_{32}H_{28}O_{10}Na$ $[M+Na]^+$ 595.1575, found 595.1578.

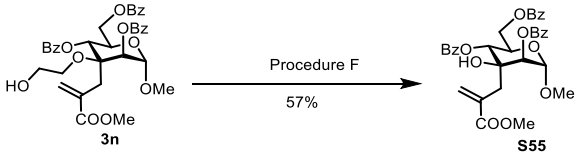
p-Tolyl 2,3-*O*-isopropylidene-4-*C*-[2-(methoxycarbonyl)allyl]-1-thio-α-L-talo-pyranoside (S54)



Following the general procedure F, **3j** (101.2 mg, 223.6 μmol, 1.0 equiv) was treated with TEMPO (7.0 mg, 44.7 μmol, 0.2 equiv) and $PhI(OAc)_2$ (144.1 mg, 447.2 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (101.6 mg, 223.6 μmol, 100%) as a colorless oil. The acid (101.6 mg, 223.6 μmol, 1.0 equiv) was treated with DPPA (58 μL, 268.3 μmol, 1.2 equiv) and DIPEA (46 μL, 268.3 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S54** (54.3 mg, 132.9 μmol, 60%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25}$ = –127.40 (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.26 (s, 1H), 5.68 (s, 1H), 5.59 (d, *J* = 2.2 Hz, 1H), 4.20–4.13 (m, 2H), 4.07–

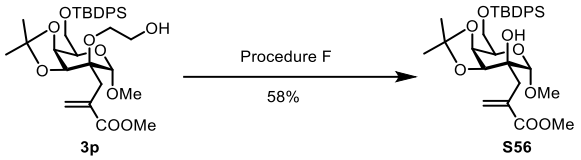
4.00 (m, 1H), 3.77 (s, 3H), 3.23 (s, 1H), 2.53 (d, *J* = 13.7 Hz, 1H), 2.44 (d, *J* = 13.7 Hz, 1H), 2.33 (s, 3H), 1.50 (s, 3H), 1.30 (s, 3H), 1.26 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 137.8, 136.4, 132.5, 129.83, 129.75, 129.1, 109.6, 83.0, 75.8, 74.7, 71.1, 70.7, 52.2, 40.1, 26.3, 25.6, 21.2, 13.9; HRMS (ESI) *m/z* calcd for $C_{21}H_{29}O_6S$ $[M+H]^+$ 409.1679, found 409.1683.

Methyl 2,4,6-tri-*O*-benzoyl-3-*C*-[2-(methoxycarbonyl)allyl]-α-D-mannopyranoside (S55)



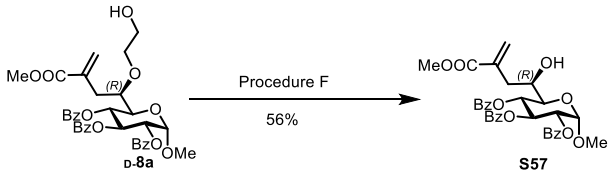
Following the general procedure F, **3n** (25.7 mg, 39.6 μmol, 1.0 equiv) was treated with TEMPO (1.3 mg, 7.9 μmol, 0.2 equiv) and $PhI(OAc)_2$ (25.5 mg, 79.2 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (26.2 mg, 39.6 μmol, 100%) as a colorless oil. The acid (26.2 mg, 39.6 μmol, 1.0 equiv) was treated with DPPA (10 μL, 47.5 μmol, 1.2 equiv) and DIPEA (8 μL, 47.5 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S55** (13.7 mg, 22.7 μmol, 57%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25} = -19.56$ (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12–8.05 (m, 6H), 7.64–7.52 (m, 3H), 7.49–7.38 (m, 6H), 6.38 (s, 1H), 5.91 (s, 1H), 5.63 (d, *J* = 8.3 Hz, 1H), 5.39 (d, *J* = 2.9 Hz, 1H), 4.98 (d, *J* = 2.8 Hz, 1H), 4.68 (dd, *J* = 12.3, 6.4 Hz, 1H), 4.61 (dd, *J* = 12.0, 2.9 Hz, 1H), 4.44–4.36 (m, 1H), 4.34 (s, 1H), 3.70 (s, 3H), 3.48 (s, 3H), 3.24–3.07 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.1, 166.4, 166.0, 165.9, 134.9, 133.7, 133.5, 133.2, 131.4, 130.1, 130.0, 129.9, 129.8, 129.5, 128.7, 128.6, 128.5, 99.3, 73.3, 72.9, 72.6, 63.5, 56.0, 52.7, 29.8; HRMS (ESI) *m/z* calcd for $C_{33}H_{33}O_{11}$ $[M+H]^+$ 605.2017, found 605.2023.

Methyl 6-*O*-*tert*-butyldiphenylsilyl-3,4-*O*-isopropylidene-2-*C*-[2-(methoxycarbonyl)allyl]-α-D-talopyranoside (S56)



Following the general procedure F, **3p** (45.7 mg, 74.3 μmol, 1.0 equiv) was treated with TEMPO (2.3 mg, 14.9 μmol, 0.2 equiv) and $PhI(OAc)_2$ (47.9 mg, 148.6 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (46.7 mg, 74.3 μmol, 100%) as a colorless oil. The acid (46.7 mg, 74.3 μmol, 1.0 equiv) was treated with DPPA (19 μL, 89.2 μmol, 1.2 equiv) and DIPEA (15 μL, 89.2 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S56** (24.8 mg, 43.5 μmol, 58%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25}$ = +33.24 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78–7.63 (m, 4H), 7.47–7.32 (m, 6H), 6.24–6.17 (m, 1H), 5.63 (s, 1H), 4.44 (s, 1H), 4.24 (dd, *J* = 5.7, 2.6 Hz, 1H), 4.12 (d, *J* = 5.7 Hz, 1H), 4.05–3.95 (m, 2H), 3.95–3.84 (m, 1H), 3.75 (s, 3H), 3.28 (s, 3H), 2.84 (d, *J* = 13.6 Hz, 1H), 2.68 (s, 1H), 2.46 (d, *J* = 13.7 Hz, 1H), 1.54 (s, 3H), 1.33 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 136.6, 135.8, 133.7, 133.6, 129.8, 127.9, 127.81, 127.75, 109.3, 102.7, 74.0, 71.7, 70.2, 67.3, 63.1, 55.2, 52.0, 37.1, 26.9, 25.9, 19.3; HRMS (ESI) *m/z* calcd for $C_{31}H_{46}NO_8Si$ $[M+NH_4]^+$ 588.2987, found 588.2995.

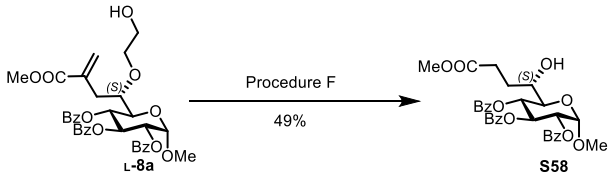
Methyl [methyl 2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-8-methylene-D-*glycero*-α-D-nonglucopyranosyluronate] (S57)



Following the general procedure F, **D-8a** (36.6 mg, 56.4 μmol, 1.0 equiv) was treated with TEMPO (1.8 mg, 11.3 μmol, 0.2 equiv) and $PhI(OAc)_2$ (36.3 mg, 112.8 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (37.3 mg, 56.4 μmol, 100%) as a colorless oil. The acid (37.3 mg, 56.4 μmol, 1.0 equiv) was treated with DPPA (15 μL, 67.7 μmol, 1.2 equiv) and DIPEA (12 μL, 67.7 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S57** (19.1 mg, 31.6 μmol, 56%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25}$ = +38.84 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400

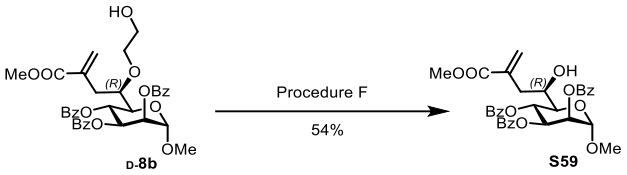
MHz, Chloroform-*d*) δ 8.05–7.91 (m, 4H), 7.87 (d, *J* = 7.3 Hz, 2H), 7.54–7.44 (m, 2H), 7.44–7.34 (m, 5H), 7.33–7.28 (m, 2H), 6.27 (s, 1H), 6.16 (t, *J* = 9.7 Hz, 1H), 5.75 (s, 1H), 5.60 (t, *J* = 9.9 Hz, 1H), 5.31–5.18 (m, 2H), 4.24 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.91 (d, *J* = 9.6 Hz, 1H), 3.69 (s, 3H), 3.49 (s, 3H), 2.87–2.79 (m, 1H), 2.75 (s, 1H), 2.64 (dd, *J* = 14.1, 9.9 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 166.0, 165.9, 165.7, 137.3, 133.6, 133.5, 133.2, 130.1, 130.0, 129.8, 129.4, 129.2, 129.1, 128.6, 128.5, 128.4, 96.9, 72.3, 71.7, 70.8, 70.7, 70.1, 55.7, 52.3, 34.3; HRMS (ESI) *m/z* calcd for $C_{33}H_{33}O_{11}$ $[M+H]^+$ 605.2017, found 605.2032.

Methyl [methyl 2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-8-methylene-L-*glycero*-α-D-nonglucopyranosyluronate] (S58)



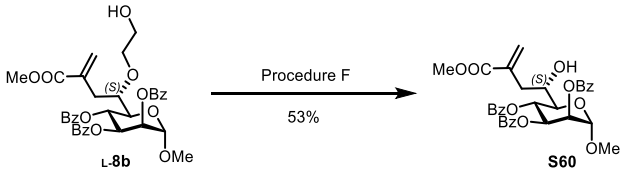
Following the general procedure F, **L-8a** (45.7 mg, 70.5 μmol, 1.0 equiv) was treated with TEMPO (2.2 mg, 14.1 μmol, 0.2 equiv) and $PhI(OAc)_2$ (45.4 mg, 141.0 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (46.7 mg, 70.5 μmol, 100%) as a colorless oil. The acid (46.7 mg, 70.5 μmol, 100%) was treated with DPPA (18 μL, 84.6 μmol, 1.2 equiv) and DIPEA (15 μL, 84.6 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S58** (20.9 mg, 34.6 μmol, 49%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25}$ = +35.11 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03–7.92 (m, 4H), 7.92–7.77 (m, 2H), 7.59–7.47 (m, 2H), 7.46–7.34 (m, 5H), 7.32–7.27 (m, 2H), 6.28 (s, 1H), 6.21 (t, *J* = 9.8 Hz, 1H), 5.76 (s, 1H), 5.61 (t, *J* = 9.9 Hz, 1H), 5.31–5.25 (m, 2H), 3.98 (d, *J* = 10.0 Hz, 1H), 3.91–3.83 (m, 1H), 3.66 (s, 3H), 3.47 (s, 3H), 2.82 (dd, *J* = 14.1, 9.7 Hz, 1H), 2.57 (dd, *J* = 14.2, 3.0 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 166.7, 165.9, 136.9, 133.8, 133.5, 133.3, 130.2, 130.1, 129.8, 129.2, 128.7, 128.6, 128.4, 97.4, 72.1, 71.2, 70.3, 70.2, 67.2, 56.0, 52.1, 35.9; HRMS (ESI) *m/z* calcd for $C_{33}H_{33}O_{11}$ $[M+H]^+$ 605.2017, found 605.2023.

Methyl [methyl 2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-8-methylene-D-*glycero*-α-D-nonmannopyranosyluronate] (S59)



Following the general procedure F, **D-8b** (38.9 mg, 60.0 μmol, 1.0 equiv) was treated with TEMPO (1.9 mg, 12.0 μmol, 0.2 equiv) and $PhI(OAc)_2$ (38.7 mg, 120.1 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (38.9 mg, 58.7 μmol, 98%) as a colorless oil. The acid (38.9 mg, 58.7 μmol, 1.0 equiv) was treated with DPPA (16 μL, 70.4 μmol, 1.2 equiv) and DIPEA (12 μL, 70.4 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S59** (19.7 mg, 32.6 μmol, 55%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25} = -28.88$ (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11–8.06 (m, 2H), 8.00–7.95 (m, 2H), 7.86–7.81 (m, 2H), 7.64–7.58 (m, 1H), 7.54–7.46 (m, 3H), 7.45–7.35 (m, 3H), 7.26–7.23 (m, 2H), 6.27 (d, *J* = 1.2 Hz, 1H), 5.96–5.90 (m, 1H), 5.87 (dd, *J* = 9.8, 3.1 Hz, 1H), 5.76 (s, 1H), 5.67 (dd, *J* = 3.0, 1.8 Hz, 1H), 5.00 (d, *J* = 1.6 Hz, 1H), 4.26 (dd, *J* = 9.6, 2.8 Hz, 1H), 3.97 (dt, *J* = 10.2, 2.6 Hz, 1H), 3.66 (s, 3H), 3.53 (s, 3H), 2.92 (dd, *J* = 14.2, 2.0 Hz, 1H), 2.67 (dd, *J* = 14.2, 10.3 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 165.8, 165.5, 137.3, 133.6, 133.5, 133.2, 129.9, 129.8, 129.7, 129.4, 129.2, 129.1, 128.7, 128.5, 128.4, 128.3, 98.5, 72.7, 70.8, 70.6, 70.3, 67.6, 55.5, 52.1, 34.1; HRMS (ESI) *m/z* calcd for $C_{33}H_{33}O_{11}$ $[M+H]^+$ 605.2017, found 605.2029.

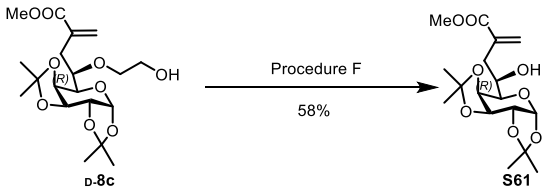
Methyl [methyl 2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-8-methylene-L-*glycero*-α-D-nonmannopyranosyluronate] (S60)



Following the general procedure F, **L-8b** (38.9 mg, 60.0 μmol, 1.0 equiv) was treated

with TEMPO (1.9 mg, 12.0 μmol, 0.2 equiv) and $PhI(OAc)_2$ (38.7 mg, 120.1 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (39.4 mg, 59.4 μmol, 99%) as a colorless oil. The acid (39.4 mg, 59.4 μmol, 1.0 equiv) was treated with DPPA (16 μL, 71.3 μmol, 1.2 equiv) and DIPEA (12 μL, 71.3 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S60** (19.3 mg, 31.9 μmol, 53%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25} = -92.40$ (*c* 2.1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14–8.08 (m, 2H), 8.00–7.94 (m, 2H), 7.85–7.79 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54–7.45 (m, 3H), 7.44–7.34 (m, 3H), 7.25–7.21 (m, 2H), 6.28 (d, *J* = 1.1 Hz, 1H), 6.04–5.96 (m, 1H), 5.96–5.91 (m, 1H), 5.76 (s, 1H), 5.70–5.65 (m, 1H), 5.06–5.03 (m, 1H), 3.99 (d, *J* = 9.2 Hz, 1H), 3.91 (dd, *J* = 9.4, 3.4 Hz, 1H), 3.63 (s, 3H), 3.52 (s, 3H), 2.83 (dd, *J* = 14.2, 9.5 Hz, 1H), 2.59 (dd, *J* = 14.2, 3.5 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 166.5, 165.6, 165.5, 136.9, 133.62, 133.56, 133.2, 130.0, 129.9, 129.7, 129.3, 129.1, 128.8, 128.7, 128.5, 128.3, 128.2, 99.0, 72.2, 70.6, 69.8, 67.7, 67.3, 55.7, 51.9, 36.0; HRMS (ESI) *m/z* calcd for $C_{33}H_{33}O_{11}$ $[M+H]^+$ 605.2017, found 605.2034.

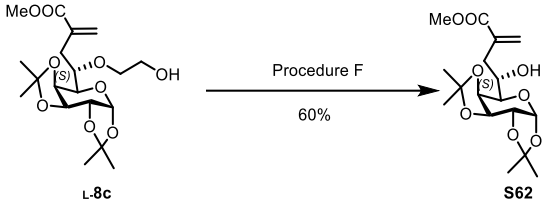
Methyl [7,8-di-deoxy-1,2,3,4-di-*O*-isopropylidene-8-methylene-D-*glycero*-α-D-nongalactopyranosyluronate] (S61)



Following the general procedure F, **D-8c** (30.3 mg, 75.3 μmol, 1.0 equiv) was treated with TEMPO (2.4 mg, 15.1 μmol, 0.2 equiv) and $PhI(OAc)_2$ (48.5 mg, 150.6 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (31.1 mg, 74.7 μmol, 99%) as a colorless oil. The acid (31.1 mg, 74.7 μmol, 1.0 equiv) was treated with DPPA (19 μL, 89.6 μmol, 1.2 equiv) and DIPEA (16 μL, 89.6 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S61** (15.7 mg, 43.8 μmol, 58%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25} = -43.07$ (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.29 (d, *J* = 1.3 Hz, 1H), 5.84 (s, 1H), 5.55 (d, *J* = 5.1 Hz, 1H),

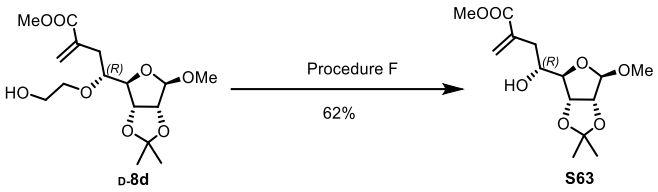
4.62 (dd, *J* = 8.0, 2.3 Hz, 1H), 4.50 (dd, *J* = 8.0, 1.8 Hz, 1H), 4.32 (dd, *J* = 5.1, 2.4 Hz, 1H), 3.98–3.87 (m, 1H), 3.78 (s, 3H), 3.55 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.40 (s, 1H), 2.87 (dd, *J* = 14.5, 2.8 Hz, 1H), 2.50 (dd, *J* = 14.4, 7.6 Hz, 1H), 1.50 (s, 3H), 1.47 (s, 3H), 1.37 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.5, 136.8, 129.3, 109.3, 108.6, 96.6, 70.9, 70.8, 70.7, 69.7, 69.2, 52.5, 36.4, 26.13, 26.09, 25.1, 24.5; HRMS (ESI) *m/z* calcd for $C_{17}H_{27}O_8$ $[M+H]^+$ 359.1700, found 359.1707.

Methyl [7,8-di-deoxy-1,2,3,4-di-*O*-isopropylidene-8-methylene-L-*glycero*-α-D-nongalactopyranosyluronate] (S62)



Following the general procedure F, **L-8c** (30.3 mg, 75.3 μmol, 1.0 equiv) was treated with TEMPO (2.4 mg, 15.1 μmol, 0.2 equiv) and $PhI(OAc)_2$ (48.5 mg, 150.6 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (31.4 mg, 75.3 μmol, 100%) as a colorless oil. The acid (31.4 mg, 75.3 μmol, 1.0 equiv) was treated with DPPA (19 μL, 90.4 μmol, 1.2 equiv) and DIPEA (16 μL, 90.4 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S62** (16.3 mg, 45.5 μmol, 60%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25} = -48.12$ (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.28 (s, 1H), 5.81 (s, 1H), 5.64 (d, *J* = 5.0 Hz, 1H), 4.65–4.52 (m, 1H), 4.40–4.31 (m, 2H), 4.22–4.14 (m, 1H), 3.76 (s, 3H), 3.61 (s, 1H), 2.64 (d, *J* = 6.5 Hz, 2H), 1.49 (s, 6H), 1.34 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 136.4, 128.7, 109.7, 108.7, 96.8, 73.4, 71.2, 70.5, 69.7, 67.9, 52.0, 35.8, 26.2, 25.9, 25.0, 24.2; HRMS (ESI) *m/z* calcd for $C_{17}H_{27}O_8$ $[M+H]^+$ 359.1700, found 359.1707.

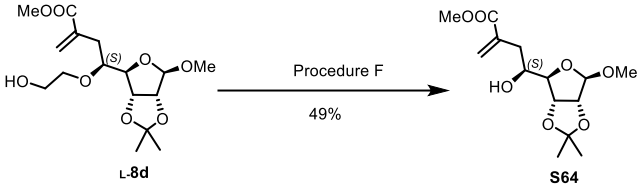
Methyl [methyl 6,7-di-deoxy-2,3-*O*-isopropylidene-7-methylene-D-*glycero*-α-D-octribofuranosyluronate] (S63)



D-8d S63

Following the general procedure F, **D-8d** (34.6 mg, 100.0 μmol, 1.0 equiv) was treated with TEMPO (3.1 mg, 2.0 μmol, 0.2 equiv) and $PhI(OAc)_2$ (64.4 mg, 200.0 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (36.0 mg, 99.8 μmol, 100%) as a colorless oil. The acid (36.0 mg, 99.8 μmol, 1.0 equiv) was treated with DPPA (26 μL, 119.8 μmol, 1.2 equiv) and DIPEA (21 μL, 119.8 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S63** (18.6 mg, 61.6 μmol, 62%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25} = -33.76$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.30 (d, *J* = 1.1 Hz, 1H), 5.74 (s, 1H), 4.97 (s, 1H), 4.90 (d, *J* = 6.0 Hz, 1H), 4.58 (d, *J* = 6.0 Hz, 1H), 4.21 (d, *J* = 3.4 Hz, 1H), 3.91–3.81 (m, 1H), 3.80–3.72 (m, 4H), 3.42 (s, 3H), 2.64 (dd, *J* = 14.2, 4.1 Hz, 1H), 2.47 (dd, *J* = 14.1, 8.8 Hz, 1H), 1.48 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 136.7, 128.3, 112.3, 110.1, 90.9, 85.9, 80.3, 71.0, 55.8, 52.2, 36.0, 26.5, 24.8; HRMS (ESI) *m/z* calcd for $C_{14}H_{22}O_7Na$ $[M+Na]^+$ 325.1258, found 325.1267.

Methyl [methyl 6,7-di-deoxy-2,3-*O*-isopropylidene-7-methylene-L-*glycero*-α-D-octribofuranosyluronate] (S64)

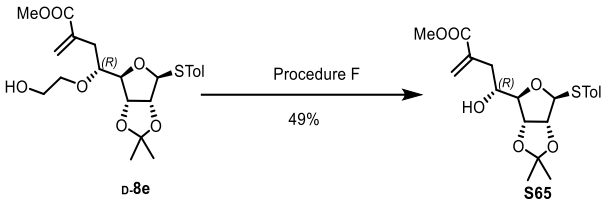


L-8d S64

Following the general procedure F, **L-8c** (17.5 mg, 50.5 μmol, 1.0 equiv) was treated with TEMPO (1.6 mg, 10.1 μmol, 0.2 equiv) and $PhI(OAc)_2$ (32.6 mg, 101.2 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (18.1 mg, 50.2 μmol, 99%) as a colorless oil. The acid (18.1 mg, 50.2 μmol, 1.0 equiv) was treated with DPPA (13 μL, 60.2 μmol, 1.2 equiv) and DIPEA (11 μL, 60.2 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S64** (7.4 mg, 24.5 μmol, 49%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25} = -23.08$ (*c* 0.4, $CHCl_3$); ^{1}H NMR (400

MHz, Chloroform-*d*) δ 6.27 (d, *J* = 1.3 Hz, 1H), 5.73–5.65 (m, 1H), 4.98 (s, 1H), 4.82 (d, *J* = 5.9 Hz, 1H), 4.59 (d, *J* = 6.0 Hz, 1H), 4.36 (d, *J* = 2.6 Hz, 1H), 3.84–3.69 (m, 4H), 3.49 (s, 3H), 3.43–3.30 (m, 1H), 2.64–2.41 (m, 2H), 1.48 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 137.0, 128.0, 112.2, 110.7, 90.0, 85.7, 82.7, 70.8, 56.1, 52.1, 37.1, 26.5, 24.8; HRMS (ESI) *m/z* calcd for $C_{14}H_{22}O_7Na$ $[M+Na]^+$ 325.1258, found 325.1268.

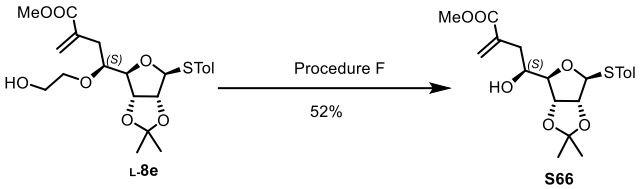
Methyl [*p*-tolyl 6,7-di-deoxy-2,3-*O*-isopropylidene-7-methylene-D-*glycero*-1-thio-α-D-octribofuranosyluronate] (S65)



Following the general procedure F, **D-8e** (68.8 mg, 156.9 μmol, 1.0 equiv) was treated with TEMPO (4.9 mg, 31.4 μmol, 0.2 equiv) and $PhI(OAc)_2$ (101.1 mg, 313.8 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (49.0 mg, 108.3 μmol, 69%) as a colorless oil. The acid (49.0 mg, 108.3 μmol, 1.0 equiv) was treated with DPPA (28 μL, 130.0 μmol, 1.2 equiv) and DIPEA (23 μL, 130.0 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S65** (30.1 mg, 76.4 μmol, 70%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25} = -133.72$ (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.27 (s, 1H), 5.68 (s, 1H), 5.50 (d, *J* = 2.4 Hz, 1H), 4.93 (dd, *J* = 6.3, 1.7 Hz, 1H), 4.70 (dd, *J* = 6.3, 2.4 Hz, 1H), 4.08 (dd, *J* = 5.8, 1.7 Hz, 1H), 4.06–3.98 (m, 1H), 3.77 (s, 3H), 3.29 (s, 1H), 2.68 (dd, *J* = 14.3, 3.5 Hz, 1H), 2.46 (dd, *J* = 14.3, 8.2 Hz, 1H), 2.33 (s, 3H), 1.51 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 137.8, 136.5, 131.8, 129.9, 129.8, 128.8, 113.5, 92.6, 89.9, 85.7, 81.2, 70.4, 52.2, 35.9, 26.9, 25.3, 21.1; HRMS (ESI) *m/z* calcd for $C_{20}H_{30}NO_6S$ $[M+HH_4]^+$ 412.1788, found 412.1791.

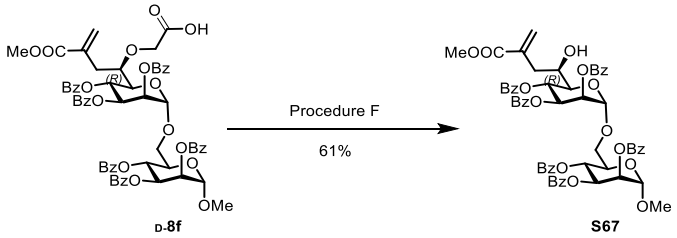
Methyl [*p*-tolyl 6,7-di-deoxy-2,3-*O*-isopropylidene-7-methylene-L-*glycero*-1-thio-

α-D-octribofuranosyluronate] (S66)



Following the general procedure F, **L-8e** (58.7 mg, 133.9 μmol, 1.0 equiv) was treated with TEMPO (4.2 mg, 26.8 μmol, 0.2 equiv) and $PhI(OAc)_2$ (86.3 mg, 267.8 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (37.7 mg, 83.3 μmol, 62%) as a colorless oil. The acid (37.7 mg, 83.3 μmol, 1.0 equiv) was treated with DPPA (22 μL, 99.9 μmol, 1.2 equiv) and DIPEA (17 μL, 99.9 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S66** (27.6 mg, 70.0 μmol, 84%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25} = -71.49$ (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.32–6.24 (m, 1H), 5.69 (s, 1H), 5.52 (d, *J* = 2.6 Hz, 1H), 4.80 (dd, *J* = 6.2, 1.2 Hz, 1H), 4.73 (dd, *J* = 6.1, 2.6 Hz, 1H), 4.25–4.18 (m, 1H), 3.89 (dt, *J* = 8.0, 4.7 Hz, 1H), 3.76 (s, 3H), 2.60–2.49 (m, 2H), 2.34 (s, 3H), 1.51 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 138.1, 136.6, 132.0, 130.0, 129.6, 128.1, 113.4, 93.6, 89.7, 85.7, 82.8, 70.7, 52.0, 36.8, 27.0, 25.3, 21.1; HRMS (ESI) *m/z* calcd for $C_{20}H_{30}NO_6S$ $[M+HH_4]^+$ 412.1788, found 412.1794.

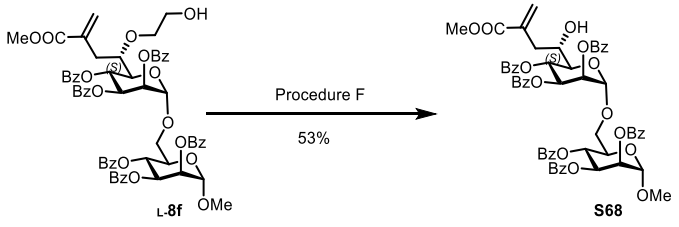
Methyl {methyl [2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-8-methylene-D-*glycero*-α-D-nonmannopyranosyluronate]}-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (S67)



Following the general procedure F, **D-8f** (40.0 mg, 35.6 μmol, 1.0 equiv) was treated with TEMPO (1.1 mg, 7.1 μmol, 0.2 equiv) and $PhI(OAc)_2$ (22.9 mg, 71.2 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (40.4 mg, 35.6 μmol, 100%)

as a colorless oil. The acid (40.4 mg, 35.6 μmol,1.0 equiv) was treated with DPPA (9 μL, 42.7 μmol, 1.2 equiv) and DIPEA (8 μL, 42.7 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S67** (23.3 mg, 21.6 μmol, 61%) as a white foam after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25} = -45.09$ (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18–8.13 (m, 2H), 8.08–8.04 (m, 2H), 8.04–7.95 (m, 4H), 7.90–7.78 (m, 4H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.56–7.36 (m, 11H), 7.36–7.31 (m, 2H), 7.31–7.26 (m, 4H), 6.22–6.17 (m, 1H), 6.00 (t, *J* = 10.0 Hz, 1H), 5.96–5.92 (m, 2H), 5.90 (d, *J* = 10.0 Hz, 1H), 5.74 (dd, *J* = 3.1, 1.7 Hz, 1H), 5.71 (s, 1H), 5.62 (s, 1H), 5.18–5.14 (m, 1H), 5.06–5.02 (m, 1H), 4.42–4.35 (m, 1H), 4.29 (dd, *J* = 9.1, 2.5 Hz, 1H), 4.13 (dd, *J* = 10.9, 5.8 Hz, 1H), 3.90–3.83 (m, 1H), 3.81 (d, *J* = 11.0 Hz, 1H), 3.64 (s, 3H), 3.59 (s, 3H), 2.86–2.70 (m, 1H), 2.50 (dd, *J* = 14.1, 10.4 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 165.8, 165.68, 165.65, 165.5, 165.34, 165.26, 137.2, 133.5, 133.4, 133.1, 130.0, 129.9, 129.83, 129.81, 129.7, 129.4, 129.34, 129.26, 129.2, 129.1, 128.7, 128.50, 128.46, 128.3, 128.2, 98.7, 97.5, 72.9, 70.6, 70.5, 70.4, 70.3, 70.2, 69.5, 67.6, 67.2, 66.9, 55.6, 52.0, 34.2; HRMS (ESI) *m/z* calcd for $C_{60}H_{55}O_{19}$ $[M+H]^+$ 1079.3332, found 1079.3345.

Methyl {methyl [2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-8-methylene-L-*glycero*-α-D-nonmannopyranosyluronate]}-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (S68)



Following the general procedure F, **L-8f** (95.3 mg, 84.9 μmol, 1.0 equiv) was treated with TEMPO (2.6 mg, 17.0 μmol, 0.2 equiv) and $PhI(OAc)_2$ (54.7 mg, 169.8 μmol, 2.0 equiv) in DCM/H_2O (3.3 mL, *v*/*v* = 10:1) to give the acid (90.7 mg, 79.8 μmol, 94%) as a colorless oil. The acid (90.7 mg, 79.8 μmol, 1.0 equiv) was treated with DPPA (21 μL, 95.6 μmol, 1.2 equiv) and DIPEA (17 μL, 95.6 μmol, 1.2 equiv) in DMF (1.0 mL) to give **S68** (48.6 mg, 45.1 μmol, 56%) as a white foam after purification by silica gel

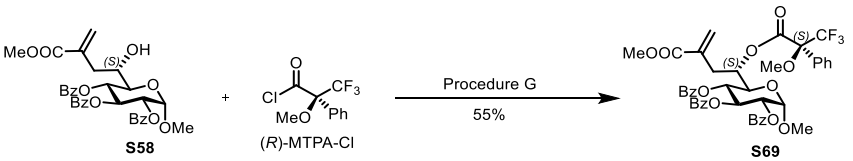
column chromatography (PE:EA = 3:1). $[\alpha]_D^{25} = -47.01$ (*c* 2.0, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 8.11–8.05 (m, 4H), 8.02–7.93 (m, 4H), 7.88–7.80 (m, 4H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.57–7.52 (m, 2H), 7.51–7.43 (m, 6H), 7.43–7.36 (m, 4H), 7.36–7.31 (m, 2H), 7.29–7.26 (m, 3H), 6.06 (d, *J* = 1.1 Hz, 1H), 6.01 (dd, *J* = 10.1, 3.2 Hz, 1H), 5.98–5.93 (m, 2H), 5.93–5.88 (m, 1H), 5.76–5.73 (m, 1H), 5.70 (dd, *J* = 3.0, 1.6 Hz, 1H), 5.52 (s, 1H), 5.20 (s, 1H), 5.10–5.04 (m, 1H), 4.40 (t, *J* = 7.4 Hz, 1H), 4.16 (d, *J* = 9.6 Hz, 1H), 4.07 (dd, *J* = 10.7, 7.0 Hz, 1H), 3.87–3.80 (m, 1H), 3.75 (d, *J* = 8.8 Hz, 1H), 3.66 (s, 3H), 3.50 (s, 3H), 2.85 (s, 1H), 2.68 (dd, *J* = 14.1, 10.1 Hz, 1H), 2.46–2.32 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 166.6, 165.7, 165.54, 165.53, 165.51, 165.4, 136.8, 133.6, 133.5, 133.2, 130.0, 129.92, 129.88, 129.8, 129.7, 129.29, 129.26, 129.2, 128.90, 128.88, 128.7, 128.64, 128.57, 128.5, 128.3, 127.9, 98.6, 97.4, 72.4, 70.5, 70.4, 70.0, 69.8, 69.4, 67.7, 67.5, 67.3, 66.7, 55.6, 51.7, 35.9; HRMS (ESI) *m/z* calcd for $C_{60}H_{55}O_{19}$ $[M+H]^+$ 1079.3332, found 1079.3345.

Mosher's method for the determination of absolute stereochemistry C6-OH on higher-carbon sugars

General Procedure G: Synthesis of *O*-mosher ester

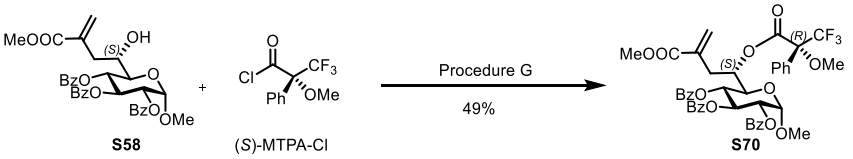
To a solution of alcohol (1.0 equiv) in dry pyridine were added DMAP (2.0 equiv) and (*R*)-(-)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride ((*R*)-MTPA-Cl) (2.0 equiv) at 0 °C. The mixture was warmed to room temperature and stirred for 1 h. After removal of solvent by rotary evaporation, the crude product was purified by flash silica gel column chromatography to give the (*S*)-*O*-Mosher ester. The same procedure was used with (*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride ((*S*)-MTPA-Cl) in preparation of the analogous (*R*)-*O*-Mosher ester.

Methyl {methyl 2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-6-*O*-[(*S*)-(-)-α-methoxy-α-(trifluoromethyl)-phenylacetyl]-8-methylene-L-*glycero*-α-D-nonglucopyranosyl-uronate} (S69)



Following the general procedure G, **S58** (16.1 mg, 26.7 μmol, 1.0 equiv) was treated with DMAP (6.5 mg, 53.4 μmol, 2.0 equiv), (*R*)-MTPA-Cl (10 μL, 53.4 μmol, 2.0 equiv) in pyridine (0.5 mL) to give **S69** ((*S*)-*O*-Mosher ester) (12.1 mg, 14.7 μmol, 55%) as a white foam after purification by silica gel column chromatography (PE:EA = 4:1). $[\alpha]_D^{25}$ = +28.78 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01–7.95 (m, 2H), 7.95–7.89 (m, 2H), 7.87–7.81 (m, 2H), 7.68–7.63 (m, 2H), 7.54–7.48 (m, 2H), 7.49–7.43 (m, 4H), 7.42–7.34 (m, 4H), 7.30 (t, *J* = 7.7 Hz, 2H), 6.10 (s, 1H), 6.05 (t, *J* = 9.9 Hz, 1H), 5.62 (t, *J* = 7.1 Hz, 1H), 5.48 (s, 1H), 5.32 (t, *J* = 9.8 Hz, 1H), 5.24 (d, *J* = 3.5 Hz, 1H), 5.06 (dd, *J* = 10.3, 3.6 Hz, 1H), 4.26–4.19 (m, 1H), 3.64 (s, 3H), 3.60 (s, 3H), 3.46 (s, 3H), 2.79 (d, *J* = 7.0 Hz, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -71.02; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.5, 165.9, 165.8, 165.7, 165.0, 134.7, 133.4, 133.3, 133.1, 131.7, 130.0, 129.8, 129.7, 129.6, 129.3, 129.2, 129.0, 128.5, 128.4, 128.3, 128.1, 124.6, 97.2, 71.8, 70.7, 70.6, 69.6, 68.8, 56.1, 55.4, 52.0, 34.5; HRMS (ESI) *m/z* calcd for $C_{43}H_{43}F_3NO_{13}$ $[M+NH_4]^+$ 838.2681, found 838.2703.

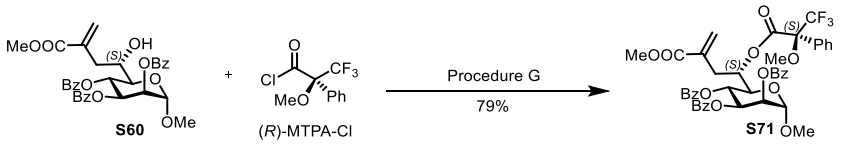
Methyl {methyl 2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-6-*O*-[(*R*)-(-)-α-methoxy-α-(trifluoromethyl)-phenylacetyl]-8-methylene-L-*glycero*-α-D-nonglucopyranosyl-uronate} (S70)



Following the general procedure G, **S58** (16.1 mg, 26.7 μmol, 1.0 equiv) was treated with DMAP (6.5 mg, 53.4 μmol, 2.0 equiv), (*R*)-MTPA-Cl (10 μL, 53.4 μmol, 2.0 equiv) in pyridine (0.5 mL) to give **S70** ((*R*)-*O*-Mosher ester) (10.8 mg, 13.2 μmol, 49%) as a white foam after purification by silica gel column chromatography (PE:EA = 4:1). $[\alpha]_D^{25}$ = +34.46 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.91 (d, *J* = 7.4 Hz, 2H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.70–7.63 (m, 2H), 7.54–7.49

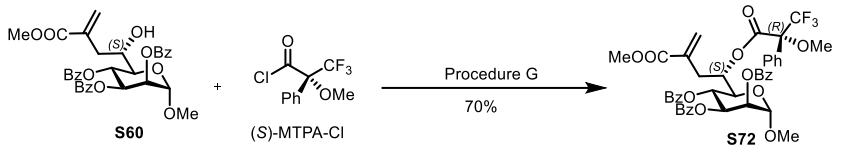
(m, 2H), 7.48–7.43 (m, 4H), 7.40–7.35 (m, 4H), 7.32 (d, *J* = 7.8 Hz, 2H), 6.19 (s, 1H), 6.04 (t, *J* = 9.8 Hz, 1H), 5.62 (t, *J* = 6.9 Hz, 1H), 5.59 (s, 1H), 5.35 (t, *J* = 9.7 Hz, 1H), 5.21 (d, *J* = 3.4 Hz, 1H), 5.00 (dd, *J* = 10.4, 3.5 Hz, 1H), 4.20 (d, *J* = 10.1 Hz, 1H), 3.64 (s, 3H), 3.60 (s, 3H), 3.45 (s, 3H), 2.88 (d, *J* = 6.8 Hz, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -71.21; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.5, 165.9, 165.8, 165.7, 165.0, 134.7, 133.4, 133.3, 133.1, 131.7, 130.0, 129.8, 129.7, 129.6, 129.3, 129.2, 129.0, 128.5, 128.4, 128.3, 128.1, 124.6, 121.8, 97.2, 71.8, 70.7, 70.6, 69.6, 68.8, 56.1, 55.4, 52.0, 34.5; HRMS (ESI) *m/z* calcd for $C_{43}H_{43}F_3NO_{13}$ $[M+NH_4]^+$ 838.2681, found 838.2692.

Methyl {methyl 2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-6-*O*-[(*S*)-(-)-α-methoxy-α-(trifluoromethyl)-phenylacetyl]-8-methylene-D-*glycero*-α-D-Nonmannopyranosyl-uronate} (S71)



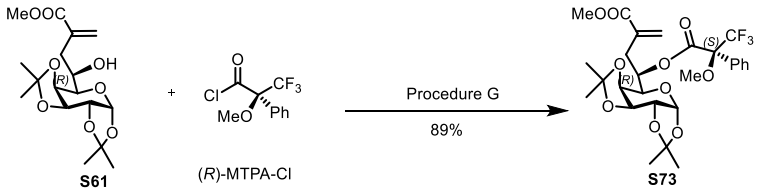
Following the general procedure G, **S60** (16.1 mg, 26.7 μmol, 1.0 equiv) was treated with DMAP (6.5 mg, 53.4 μmol, 2.0 equiv), (*R*)-MTPA-Cl (10 μL, 53.4 μmol, 2.0 equiv) in pyridine (0.5 mL) to give **S71** ((S)-*O*-Mosher ester) (17.3 mg, 21.1 μmol, 79%) as a white foam after purification by silica gel column chromatography (PE:EA = 4:1). $[\alpha]_D^{25}$ = –71.23 (*c* 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.60–7.54 (m, 3H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.46–7.33 (m, 8H), 7.29 (d, *J* = 7.9 Hz, 2H), 6.00 (s, 1H), 5.94 (t, *J* = 10.1 Hz, 1H), 5.80 (dd, *J* = 10.0, 3.3 Hz, 1H), 5.74 (t, *J* = 6.5 Hz, 1H), 5.65 (dd, *J* = 3.2, 1.7 Hz, 1H), 5.39 (s, 1H), 5.07 (s, 1H), 4.31 (d, *J* = 10.2 Hz, 1H), 3.66 (s, 3H), 3.55 (s, 3H), 3.53 (s, 3H), 2.82 (d, *J* = 6.8 Hz, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -72.04; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.5, 166.0, 165.8, 165.5, 165.2, 134.7, 133.6, 133.3, 133.2, 131.6, 129.9, 129.8, 129.7, 129.5, 129.4, 129.2, 129.1, 128.5, 128.4, 128.3, 128.2, 128.0, 121.7, 99.0, 70.7, 70.6, 70.4, 66.4, 56.0, 55.6, 52.0, 34.6; HRMS (ESI) *m/z* calcd for $C_{43}H_{43}F_3NO_{13}$ $[M+NH_4]^+$ 838.2681, found 838.2704.

Methyl {methyl 2,3,4-tri-*O*-benzoyl-7,8-di-deoxy-6-*O*-[(*R*)-(-)-α-methoxy-α-(trifluoromethyl)-phenylacetyl]-8-methylene-D-*glycero*-α-D-nonmannopyranosyl-uronate} (S72)



Following the general procedure G, **S60** (16.1 mg, 26.7 μmol, 1.0 equiv) was treated with DMAP (6.5 mg, 53.4 μmol, 2.0 equiv), (*S*)-MTPA-Cl (10 μL, 53.4 μmol, 2.0 equiv) in pyridine (0.5 mL) to give **S72** ((*R*)-*O*-Mosher ester) (15.4 mg, 18.8 μmol, 70%) as a white foam after purification by silica gel column chromatography (PE:EA = 4:1). $[\alpha]_D^{25} = -56.00$ (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.4 Hz, 2H), 7.92 (d, *J* = 7.4 Hz, 2H), 7.83 (d, *J* = 7.4 Hz, 2H), 7.63–7.55 (m, 3H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.44–7.34 (m, 8H), 7.31–7.26 (m, 2H), 6.13 (s, 1H), 5.89 (t, *J* = 10.0 Hz, 1H), 5.83–5.77 (m, 1H), 5.73 (t, *J* = 6.6 Hz, 1H), 5.66–5.62 (m, 1H), 5.53 (s, 1H), 5.06 (s, 1H), 4.30 (d, *J* = 10.1 Hz, 1H), 3.65 (s, 3H), 3.54 (s, 3H), 3.53 (s, 3H), 2.93–2.88 (m, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -70.99; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 165.9, 165.8, 165.5, 165.1, 135.1, 133.5, 133.3, 133.2, 131.7, 129.9, 129.8, 129.7, 129.6, 129.3, 129.2, 129.1, 129.0, 128.5, 128.4, 128.3, 128.1, 99.0, 71.1, 70.5, 70.5, 66.4, 56.0, 55.3, 34.5; HRMS (ESI) *m/z* calcd for $C_{43}H_{43}F_3NO_{13}$ $[M+NH_4]^+$ 838.2681, found 838.2694.

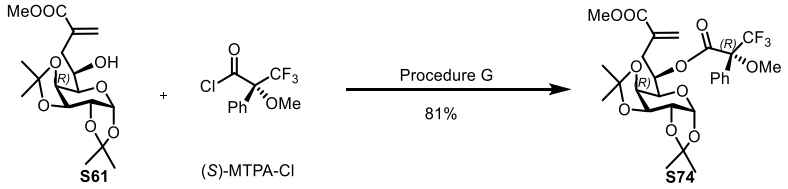
Methyl {7,8-di-deoxy-6-*O*-[(*S*)-(-)-α-methoxy-α-(trifluoromethyl)-phenylacetyl]-1,2,3,4-di-*O*-isopropylidene-8-methylene-D-*glycero*-α-D-nongalactopyranosyl-uronate} (S73)



Following the general procedure G, **S61** (9.6 mg, 26.7 μmol, 1.0 equiv) was treated with DMAP (6.5 mg, 53.4 μmol, 2.0 equiv), (*R*)-MTPA-Cl (10 μL, 53.4 μmol, 2.0 equiv) in pyridine (0.5 mL) to give **S73** ((*S*)-*O*-Mosher ester) (13.7 mg, 23.8 μmol, 89%) as a

white foam after purification by silica gel column chromatography (PE:EA = 5:1). [α]$_D^{25}$ = –53.87 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60–7.50 (m, 2H), 7.45–7.31 (m, 3H), 6.22 (s, 1H), 5.67 (s, 1H), 5.59–5.50 (m, 2H), 4.52 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.30 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.00 (dd, *J* = 7.6, 1.5 Hz, 1H), 3.79 (d, *J* = 10.1 Hz, 1H), 3.75 (s, 3H), 3.49 (s, 3H), 3.18 (dd, *J* = 14.9, 2.5 Hz, 1H), 2.58 (dd, *J* = 14.9, 8.4 Hz, 1H), 1.48 (s, 3H), 1.45 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -71.96; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0, 165.2, 135.9, 131.8, 129.6, 128.5, 128.2, 127.9, 109.5, 108.7, 96.4, 72.7, 70.7, 70.4, 70.1, 68.1, 55.3, 52.0, 33.9, 26.0, 24.8, 24.6; HRMS (ESI) *m/z* calcd for $C_{27}H_{37}F_3NO_{10}$ $[M+NH_4]^+$ 592.2364, found 592.2379.

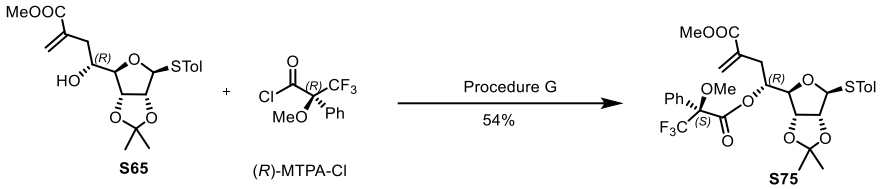
Methyl {7,8-di-deoxy-6-*O*-[(*R*)-(-)-α-methoxy-α-(trifluoromethyl)-phenylacetyl]-1,2,3,4-di-*O*-isopropylidene-8-methylene-L-*glycero*-α-D-Nongalactopyranosyl-uronate} (S74)



Following the general procedure H, **S61** (9.6 mg, 26.7 μmol, 1.0 equiv) was treated with DMAP (6.5 mg, 53.4 μmol, 2.0 equiv), (*S*)-MTPA-Cl (10 μL, 53.4 μmol, 2.0 equiv) in pyridine (0.5 mL) to give **S74** ((*R*)-*O*-Mosher ester) (12.4 mg, 21.6 μmol, 81%) as a white foam after purification by silica gel column chromatography (PE:EA = 5:1). [α]$_D^{25}$ = –39.87 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.0 Hz, 2H), 7.42–7.33 (m, 3H), 6.13 (s, 1H), 5.59–5.53 (m, 2H), 5.48 (td, *J* = 8.3, 3.0 Hz, 1H), 4.60 (dd, *J* = 7.8, 2.1 Hz, 1H), 4.33 (dd, *J* = 4.9, 2.3 Hz, 1H), 4.23 (d, *J* = 9.2 Hz, 1H), 3.88 (d, *J* = 8.0 Hz, 1H), 3.74 (s, 3H), 3.53 (s, 3H), 3.23–3.13 (m, 1H), 2.54 (dd, *J* = 14.8, 8.6 Hz, 1H), 1.48 (s, 6H), 1.33 (s, 3H), 1.32 (s, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -71.84; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0, 165.6, 135.6, 132.2, 129.5, 128.6, 128.2, 127.9, 109.6, 108.7, 96.5, 73.1, 70.8, 70.4, 70.3, 68.0, 55.2, 51.9, 33.7, 26.0, 25.9, 24.9, 24.6; HRMS (ESI) *m/z* calcd for $C_{27}H_{37}F_3NO_{10}$ $[M+NH_4]^+$

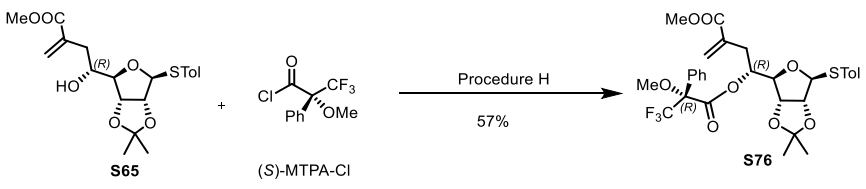
592.2364, found 592.2372.

Methyl {*p*-tolyl 6,7-di-deoxy-5-*O*-[(*S*)-(-)-α-methoxy-α-(trifluoromethyl)-phenyl-acetyl]-2,3-*O*-isopropylidene-7-methylene-D-*glycero*-1-thio-α-D-Octribofuranosyl-uronate} (S75)



Following the general procedure G, **S65** (10.5 mg, 26.7 μmol, 1.0 equiv) was treated with DMAP (6.5 mg, 53.4 μmol, 2.0 equiv), (*R*)-MTPA-Cl (10 μL, 53.4 μmol, 2.0 equiv) in pyridine (0.5 mL) to give **S75** ((*S*)-*O*-Mosher ester) (8.8 mg, 14.4 μmol, 54%) as a white foam after purification by silica gel column chromatography (PE:EA = 5:1). $[\alpha]_D^{25} = -46.54$ (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57–7.49 (m, 2H), 7.42–7.36 (m, 5H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.23 (s, 1H), 5.75–5.65 (m, 1H), 5.61 (s, 1H), 5.33 (d, *J* = 2.5 Hz, 1H), 4.61–4.53 (m, 2H), 4.08 (dd, *J* = 6.7, 1.9 Hz, 1H), 3.74 (s, 3H), 3.50 (s, 3H), 2.93 (dd, *J* = 14.7, 3.2 Hz, 1H), 2.59 (dd, *J* = 14.8, 9.4 Hz, 1H), 2.32 (s, 3H), 1.47 (s, 3H), 1.27 (s, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -71.20; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 166.0, 137.7, 135.1, 131.7, 130.1, 129.9, 129.6, 129.0, 128.4, 127.7, 114.5, 92.1, 86.3, 84.9, 80.9, 73.3, 55.6, 52.1, 34.1, 27.0, 25.2, 22.7, 21.1; HRMS (ESI) *m/z* calcd for $C_{30}H_{37}F_3NO_8S$ $[M+NH_4]^+$ 628.2186, found 628.2189.

Methyl {*p*-tolyl 6,7-di-deoxy-5-*O*-[(*R*)-(-)-α-methoxy-α-(trifluoromethyl)-phenyl-acetyl]-2,3-*O*-isopropylidene-7-methylene-L-*glycero*-1-thio-α-D-octribofuranosyl-uronate} (S76)

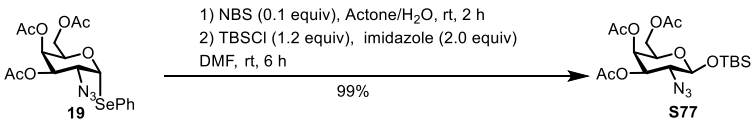


Following the general procedure G, **S65** (16.1 mg, 26.7 μmol, 1.0 equiv) was treated

with DMAP (6.5 mg, 53.4 μmol, 2.0 equiv), (*S*)-MTPA-Cl (10 μL, 53.4 μmol, 2.0 equiv) in pyridine (0.5 mL) to give **S76** ((*R*)-*O*-Mosher ester) (9.3 mg, 15.2 μmol, 57%) as a white foam after purification by silica gel column chromatography (PE:EA = 5:1). $[\alpha]_D^{25}$ = –48.98 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61–7.55 (m, 2H), 7.44–7.37 (m, 5H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.11 (s, 1H), 5.76–5.69 (m, 1H), 5.49 (s, 1H), 5.33 (d, *J* = 3.8 Hz, 1H), 4.68 (dd, *J* = 6.7, 3.1 Hz, 1H), 4.59 (dd, *J* = 6.7, 3.8 Hz, 1H), 4.14 (dd, *J* = 6.2, 3.1 Hz, 1H), 3.74 (s, 3H), 3.56 (s, 3H), 2.89 (dd, *J* = 14.4, 3.2 Hz, 1H), 2.51 (dd, *J* = 14.5, 9.8 Hz, 1H), 2.33 (s, 3H), 1.51 (s, 3H), 1.32 (s, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -70.93; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 166.0, 137.8, 134.7, 132.2, 131.9, 130.1, 129.9, 129.6, 129.3, 128.4, 127.5, 114.8, 91.9, 86.2, 84.8, 80.8, 73.3, 55.6, 52.0, 34.3, 27.1, 25.3, 22.7, 21.1; HRMS (ESI) *m/z* calcd for $C_{30}H_{37}F_3NO_8S$ $[M+NH_4]^+$ 628.2186, found 628.2176.

Synthesis of shewanellose-type building block

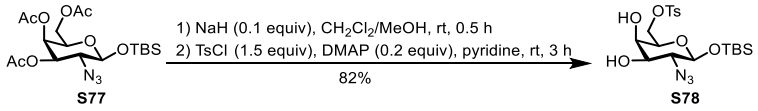
tert-Butyldimethylsilyl 2-azido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranoside (S77)



To a solution of **19** (4.39 g, 9.33 mmol, 1.0 equiv) in actone/H_2O (20.0 mL, *v*/*v* = 9:1) was added *N*-bromosuccinimide (NBS) (2.51 g, 14.00 mmol, 1.5 equiv) in ice bath under an argon atmosphere. After stirring for 2 h at room temperature, the resultant

mixture was diluted with DCM, and washed with $Na_2S_2O_3$ solution, $NaHCO_3$ solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The crude product obtained above was dissolved in dry DMF (20.0 mL), TBSCl (1.69 g, 11.21 mmol, 1.2 equiv) and imidazole (1.27 mg, 18.67 mmol, 2.0 equiv) were added at room temperature under an argon atmosphere. The resultant solution was stirred for 6 h at room temperature and quenched with H_2O. The resultant mixture was extracted with DCM, and the organic layer was washed with 1M HCl solution, saturated $NaHCO_3$ solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (PE:EA = 9:1) to afford **S77**[17] (4.11 g, 9.23 mmol, 99%) as a white foam.

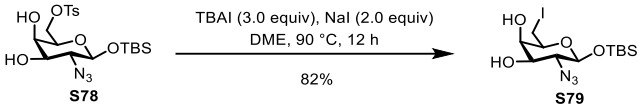
tert-Butyldimethylsilyl 2-azido-2-deoxy-6-_O_-(_p_-toluenesulfonyl)-1-β-D-galacto-pyranoside (S78)



To a solution of **S77** (7.71 g, 17.30 mmol, 1.0 equiv) in dry MeOH (20.0 mL) was added 60% dispersion of NaH in mineral oil (69.2 mg, 1.73 mmol, 0.1 equiv) in ice bath under an argon atmosphere. After stirring for 2 h at room temperature, the reaction was neutralized with seralite acidic resin, which was further removed by filtration. The mixture was evaporated to dryness. The crude product obtained above was dissolved in dry pyridine (40.0 mL), tosyl chloride (TsCl) (3.63 g, 19.03 mmol, 1.1 equiv) and DMAP (211.4 mg, 1.73 mmol, 0.1 equiv) were added at room temperature under an argon atmosphere. The resultant solution was stirred for 1 h at room temperature and quenched with H_2O. The resultant mixture was extracted with DCM, and the organic layer was washed with 1M HCl solution, saturated $NaHCO_3$ solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (PE:EA = 1.5:1) to afford **S78** (6.67 g, 14.11 mmol, 82%) as a colorless oil. $[\alpha]_D^{25}$ = +10.35 (*c* 2.9, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70–7.64 (m, 2H), 7.26–

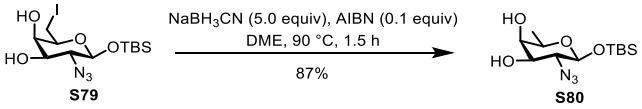
7.21 (m, 2H), 4.36 (d, *J* = 7.2 Hz, 1H), 4.15 (dd, *J* = 10.4, 5.3 Hz, 1H), 4.01 (dd, *J* = 10.4, 7.0 Hz, 1H), 3.78 (s, 1H), 3.58 (t, *J* = 6.2 Hz, 1H), 3.36–3.27 (m, 2H), 3.09 (s, 1H), 2.94–2.87 (m, 1H), 2.33 (s, 3H), 0.79 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.3, 132.3, 130.0, 128.0, 97.3, 72.3, 71.3, 68.2, 67.5, 66.0, 25.6, 21.7, 17.9, -4.3, -5.3; HRMS (ESI) *m/z* calcd for $C_{19}H_{35}N_4O_7SiS$ $[M+HH_4]^+$ 491.1990, found 491.1990.

tert-Butyldimethylsilyl 2-azido-2-deoxy-6-deoxy-6-iodo-1-β-D-galactopyranoside (S79)



To a solution of **S78** (6.67 g, 14.08 mmol, 1.0 equiv) in 1,2-dimethoxyethane (DME) (50.0 mL) were added tetrabutylammonium iodide (TBAI) (15.61 g, 42.24 mmol, 3.0 equiv) and NaI (4.23 g, 28.16 mmol, 2.0 equiv) in ice bath under an argon atmosphere. The resultant solution was stirred for 12 h at 90 ℃. The resultant mixture was diluted with DCM, and washed with $Na_2S_2O_3$ solution and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (PE:EA = 1.5:1) to afford **S79** (4.97 g, 11.58 mmol, 82%) as a yellow oil. $[\alpha]_D^{25}$ = +65.68 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.49 (d, *J* = 7.3 Hz, 1H), 4.05 (s, 1H), 3.60 (t, *J* = 6.9 Hz, 1H), 3.51–3.39 (m, 3H), 3.37–3.30 (m, 2H), 3.22 (s, 1H), 0.94 (s, 9H), 0.21 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 97.5, 75.7, 71.8, 69.0, 66.0, 25.7, 18.0, 2.0, -3.8, -5.2.; HRMS (ESI) *m/z* calcd for $C_{13}H_{25}IN_3O_6Si$ $[M+HCOO]^-$ 474.0563, found 474.0565.

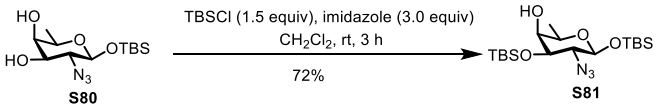
tert-Butyldimethylsilyl 2-azido-2-deoxy-1-β-D-fucopyranoside (S80)



To a solution of **S79** (4.97 g, 11.62 mmol, 1.0 equiv) in DME (40.0.0 mL) were added $NaCNBH_3$ (3.64 g, 57.92 mmol, 5.0 equiv) and 2,2′-azobis(2-methylpropionitrile)

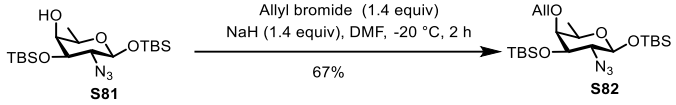
(AIBN) (190.5 mg, 1.16 mmol, 0.1 equiv) in ice bath under an argon atmosphere. The resultant solution was stirred for 1.5 h at 90 ℃. The resultant mixture was diluted with DCM, and washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (PE:EA = 1.5:1) to afford **S80** (3.06 g, 10.09 mmol, 87%) as a colorless oil. $[\alpha]_D^{25}$ = +11.56 (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.46 (d, *J* = 7.5 Hz, 1H), 3.68 (d, *J* = 4.3 Hz, 1H), 3.59–3.51 (m, 1H), 3.42–3.35 (m, 2H), 3.17 (s, 1H), 2.78 (d, *J* = 5.6 Hz, 1H), 1.31 (d, *J* = 6.5 Hz, 3H), 0.92 (s, 9H), 0.14 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 97.3, 72.3, 70.9, 70.5, 66.5, 25.6, 18.0, 16.3, -4.3, -5.2; HRMS (ESI) *m/z* calcd for $C_{13}H_{26}N_3O_6Si$ $[M+HCOO]^-$ 348.1596, found 348.1591.

tert-Butyldimethylsilyl 2-azido-2-deoxy-3-*O*-(_tert_-butyldimethylsilyl)-1-β-D-fucopyranoside (S81)



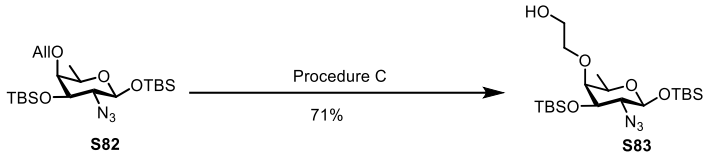
To a solution of **S80** (3.06 g, 10.08 mmol, 1.0 equiv) in DCM (30.0 mL) were added TBSCl (1.83 g, 20.18 mmol, 2.0 equiv) and imidazole (1.38 g, 12.10 mmol, 1.2 equiv) in ice bath under an argon atmosphere. The resultant solution was stirred for 3 h at room temperature and quenched with saturated $NaHCO_3$ solution. The resultant mixture was extracted with DCM, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (PE:EA = 25:1) to afford **S81** (3.03 g, 7.26 mmol, 72%) as a colorless oil. $[\alpha]_D^{25}$ = +18.26 (*c* 2.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.41 (d, *J* = 7.6 Hz, 1H), 3.55–3.45 (m, 2H), 3.41 (dd, *J* = 9.7, 3.3 Hz, 1H), 3.33 (dd, *J* = 9.6, 7.7 Hz, 1H), 2.50 (s, 1H), 1.33 (d, *J* = 6.5 Hz, 3H), 0.92 (s, 9H), 0.91 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H), 0.13 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 97.2, 73.5, 71.5, 70.1, 67.0, 25.8, 18.1, 16.5, -4.1, -4.5, -4.7, -5.2; HRMS (ESI) *m/z* calcd for $C_{19}H_{40}N_3O_6Si_2$ $[M+HCOO]^-$ 462.2461, found 462.2467.

***tert*-Butyldimethylsilyl 4-*O*-allyl-2-azido-2-deoxy-3-*O*-(*tert*-butyldimethylsilyl)-1-β-D-fucopyranoside (S82)**



To a solution of **S81** (2.76 g, 6.00 mmol, 1.0 equiv) in dry DMF (30.0 mL) were added AllBr (2.2 mL, 30.00 mmol, 5.0 equiv) and 60% dispersion of NaH in mineral oil (312.3 mg, 7.80 mmol, 1.3 equiv) at -20 °C under an argon atmosphere. The resultant solution was stirred for 2 h at -20 °C and quenched with NH_4Cl solution. The resultant mixture was extracted with DCM, and the organic layer was washed with brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (PE:EA = 70:1) to afford **S82** (1.83 g, 4.00 mmol, 67%) as a colorless oil. $[\alpha]_D^{25}$ = +2.58 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.04–5.81 (m, 1H), 5.27–5.20 (m, 1H), 5.18–5.12 (m, 1H), 4.50–4.40 (m, 1H), 4.38 (d, *J* = 7.5 Hz, 1H), 4.12 (dd, *J* = 12.7, 6.9 Hz, 1H), 3.55–3.35 (m, 3H), 3.24 (d, *J* = 2.6 Hz, 1H), 1.24 (d, *J* = 6.4 Hz, 3H), 0.94 (s, 9H), 0.92 (s, 9H), 0.16 (s, 3H), 0.13 (s, 3H), 0.13 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.5, 117.0, 97.4, 78.7, 74.44, 74.43, 70.4, 67.2, 25.9, 18.2, 16.9, -4.1, -4.3, -4.7, -5.2; HRMS (ESI) *m/z* calcd for $C_{21}H_{44}N_3O_4Si_2$ $[M+H]^+$ 458.2865, found 458.2871.

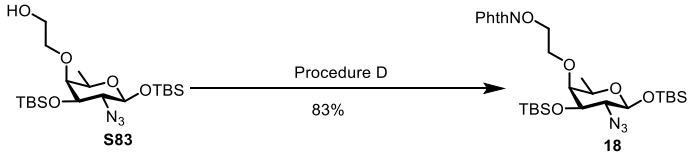
***tert*-Butyldimethylsilyl 2-azido-2-deoxy-4-*O*-(2-hydroxyethyl)-3-*O*-(*tert*-butyl-dimethylsilyl)-1-β-D-fucopyranoside (S83)**



Following the general procedure C, **S82** (1.83 g, 3.99 mmol, 1.0 equiv) was treated with 2,6-lutidine (930 μL, 8.04 mmol, 2.0 equiv), OsO_4 (0.0234 mol/L solution in *t*-BuOH, 3.4 mL, 80.0 μmol, 0.02 equiv) and $NaIO_4$ (3.41 g, 15.96 mmol, 4.0 equiv) in 1,4-dioxane/H_2O (40.0 mL, *v*/*v* = 3:1) to give the aldehyde. The aldehyde was treated with $NaBH_4$ (307.6 mg, 8.00 mmol, 2.0 equiv) in MeOH (10.0 mL) to give **S83** (1.31 g, 2.84

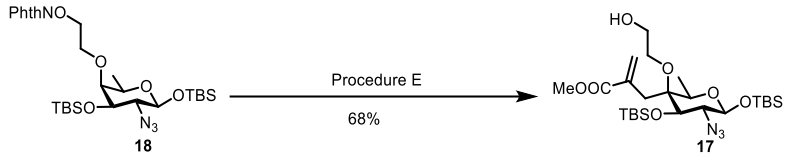
mmol, 71%) as a colorless oil after purification by silica gel column chromatography (PE:EA = 7:1). $[\alpha]_D^{25}$ = +5.89 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.24 (d, *J* = 7.2 Hz, 1H), 3.78–3.68 (m, 1H), 3.66–3.61 (m, 1H), 3.61–3.53 (m, 2H), 3.37–3.23 (m, 3H), 3.11 (d, *J* = 2.4 Hz, 1H), 2.71 (s, 1H), 1.14 (d, *J* = 6.4 Hz, 3H), 0.79 (s, 9H), 0.78 (s, 9H), 0.02 (s, 3H), -0.00 (s, 3H), -0.01 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 97.4, 81.0, 75.7, 74.3, 70.6, 67.1, 62.3, 26.0, 25.8, 18.3, 18.1, 16.9, -4.1, -4.2, -4.6, -5.1; HRMS (ESI) *m/z* calcd for $C_{20}H_{43}ClN_3O_5Si_2$ $[M+Cl]^-$ 496.2435, found 496.2440.

tert-Butyldimethylsilyl 2-azido-2-deoxy-4-*O*-{2-[(1,3-dioxoisoindolin-2-yl)oxy]-ethyl}-3-*O*-(_tert_-butyldimethylsilyl)-1-β-D-fucopyranoside (18)



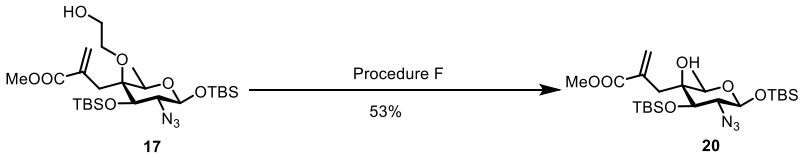
Following the general procedure D, **S83** (1.31 g, 2.84 mmol, 1.0 equiv) was treated with PPh_3 (894.4 mg, 3.41 mmol, 1.2 equiv), *N*-hydroxyphthalimide (556.3 mg, 3.41 mmol, 1.2 equiv) and diisopropylazodicarboxylate (680 μL, 3.41 mmol, 1.2 equiv) in THF (10.0 mL) to give **18** (1.43 g, 2.36 mmol, 83%) as a colorless oil after purification by silica gel column chromatography (PE:EA = 8:1). $[\alpha]_D^{25}$ = +6.72 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73–7.66 (m, 2H), 7.65–7.59 (m, 2H), 4.37–4.28 (m, 1H), 4.23 (d, *J* = 7.1 Hz, 1H), 4.22–4.11 (m, 2H), 3.93–3.80 (m, 1H), 3.39–3.32 (m, 1H), 3.31–3.28 (m, 1H), 3.28–3.17 (m, 2H), 1.21 (d, *J* = 6.4 Hz, 3H), 0.79 (s, 9H), 0.78 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H), -0.01 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6, 134.6, 129.0, 123.6, 97.4, 81.1, 78.2, 74.7, 71.4, 70.5, 67.0, 25.9, 25.8, 18.2, 18.1, 16.7, -4.1, -4.3, -4.7, -5.1; HRMS (ESI) *m/z* calcd for $C_{28}H_{46}ClN_4O_7Si_2$ $[M+Cl]^-$ 641.2599, found 641.2607.

tert-Butyldimethylsilyl 2-azido-2-deoxy-4-*O*-(2-hydroxyethyl)-4-*C*-[2-(methoxy-carbonyl)allyl]-3-*O*-(_tert_-butyldimethylsilyl)-1-β-D-fucopyranoside (17)



Following the general procedure E, **18** (1.48 g, 2.44 mmol, 1.0 equiv) and **2a** (1.86 g, 7.32 mmol, 3.0 equiv) were treated with hantzsch ester (927.0 mg, 3.66 mmol, 1.5 equiv) and *fac*-Ir(ppy)$_3$ (16.0 mg, 24.4 μmol, 0.01 equiv) in 1,4-dioxane (48.8 mL) to give **17** (932.9 mg, 1.67 mmol, 68%) as a colorless oil after purification by silica gel column chromatography (PE:EA = 6:1). $[\alpha]_D^{25}$ = +18.46xx (*c* 2.9, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.23 (s, 1H), 5.66 (s, 1H), 4.38 (d, *J* = 6.9 Hz, 1H), 4.08–3.99 (m, 1H), 3.88–3.78 (m, 1H), 3.76 (s, 3H), 3.73–3.64 (m, 2H), 3.55–3.44 (m, 2H), 3.31–3.22 (m, 1H), 2.88–2.71 (m, 2H), 2.57 (s, 1H), 1.21 (d, *J* = 6.2 Hz, 3H), 0.92 (s, 9H), 0.91 (s, 9H), 0.20 (s, 3H), 0.17 (s, 3H), 0.12 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 136.7, 128.7, 97.4, 78.5, 75.5, 73.7, 68.0, 66.7, 62.8, 52.4, 32.5, 26.3, 25.8, 18.9, 18.1, 15.4, -3.5, -4.1, -4.2, -5.0; HRMS (ESI) *m/z* calcd for $C_{25}H_{49}ClN_3O_7Si_2$ $[M+Cl]^-$ 594.2803, found 594.2811.

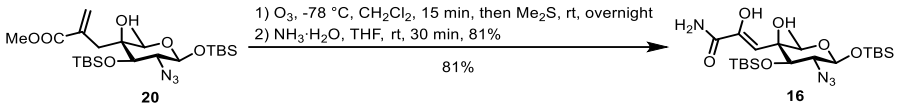
tert-Butyldimethylsilyl 2-azido-2-deoxy-4-*C*-[2-(methoxycarbonyl)allyl]-3-*O*-(_tert_-butyldimethylsilyl)-1-β-D-fucopyranoside (20)



Following the general procedure F, **17** (559.9 mg, 1.00 mmol, 1.0 equiv) was treated with TEMPO (15.6 mg, 100.0 μmol, 0.2 equiv) and PhI(OAc)$_2$ (644.2 mg, 2.00 mmol, 2.0 equiv) in DCM/H_2O (11 mL, *v*/*v* = 10:1) to give the acid (547.5 mg, 954.1 μmol, 95%) as a colorless oil. The acid (274.6 mg, 478.5 μmol, 1.0 equiv) was treated with DPPA (113 μL, 526.4 μmol, 1.1 equiv) and DIPEA (92 μL, 526.4 μmol, 1.1 equiv) in DMF (5.0 mL) to give **20** (137.3 mg, 266.2 μmol, 56%) as a colorless oil after purification by silica gel column chromatography (PE:EA = 3:1). $[\alpha]_D^{25}$ = +13.85 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.11 (s, 1H), 5.51 (s, 1H), 4.27 (d, *J* = 7.6 Hz, 1H), 3.63 (s, 3H), 3.26 (d, *J* = 9.5 Hz, 1H), 3.20 (d, *J* = 7.6 Hz, 1H), 3.19–3.14

(m, 1H), 2.66 (d, *J* = 1.2 Hz, 1H), 2.61 (d, *J* = 14.2 Hz, 1H), 2.35 (d, *J* = 14.3 Hz, 1H), 1.14 (d, *J* = 6.2 Hz, 3H), 0.82 (s, 9H), 0.78 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H), 0.00 (s, 3H), -0.01 (s, 3H).; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 136.7, 129.2, 96.9, 74.7, 74.5, 73.0, 67.8, 52.3, 36.9, 26.2, 25.8, 18.8, 18.1, 15.1, -3.5, -4.1, -4.2, -5.1.; HRMS (ESI) *m/z* calcd for $C_{23}H_{46}N_3O_6Si_2$ $[M+H]^+$ 516.2920, found 516.2925.

3-((2*R*,3*S*,4*R*,5*R*,6*S*)-5-azido-4,6-bis((*tert*-butyldimethylsilyl)oxy)-3-hydroxy-2-methyl-tetrahydro-2*H*-pyran-3-yl)-2-hydroxyacrylamide (16)



To a solution of **20** (30.2 mg, 58.3 μmol, 1.0 equiv) in CH_2Cl_2 (2.0 mL) was cooled to -78 °C. The O_3 (generated from O_2 and carried by the flow of O_2) was bubbled though this solution for 15 min. The colour of the solution turn blue, which indicated the saturation of O_3 in DCM. The excess amount of O_3 was blown off by the flow of O_2 and the purple colour disappeared. To this solution, Me_2S (0.20 mL, excess) was added to reduce the peroxide intermediate. The resultant solution was stirred for overnight at room temperature. The mixture was evaporated to dryness. The crude product obtained above was dissolved in dry THF (2.0 mL), $NH_3{\cdot}H_2O$ (50 μL) was added at room temperature under an argon atmosphere. The resultant solution was stirred for 30 min at room temperature. The resultant mixture was extracted with DCM and washed with H_2O and brine. The organic layer was collected, dried over Na_2SO_4, filtered off the solid and concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (PE:EA = 3.5:1) to afford **16** (23.8 mg, 47.3 μmol, 81%) as a white foam. $[\alpha]_D^{25}$ = +22.03 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.57 (brs, 1H), 5.54 (s, 1H), 4.43 (dd, *J* = 5.5, 2.0 Hz, 1H), 3.74–3.52 (m, 1H), 3.40–3.24 (m, 2H), 1.87 (brs, 1H), 0.96 (d, *J* = 6.4 Hz, 3H), 0.78 (s, 9H), 0.68 (s, 9H), -0.01 (s, 9H), -0.16 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.8, 143.8, 115.5, 97.1, 86.5, 72.4, 71.0, 68.0, 25.6, 18.0, 18.0, 14.0, -4.2, -4.4, -4.7, -5.1; HRMS (ESI) *m/z* calcd for $C_{21}H_{43}N_4O_6Si_2$ $[M+H]^+$ 503.2716, found 503.2724.

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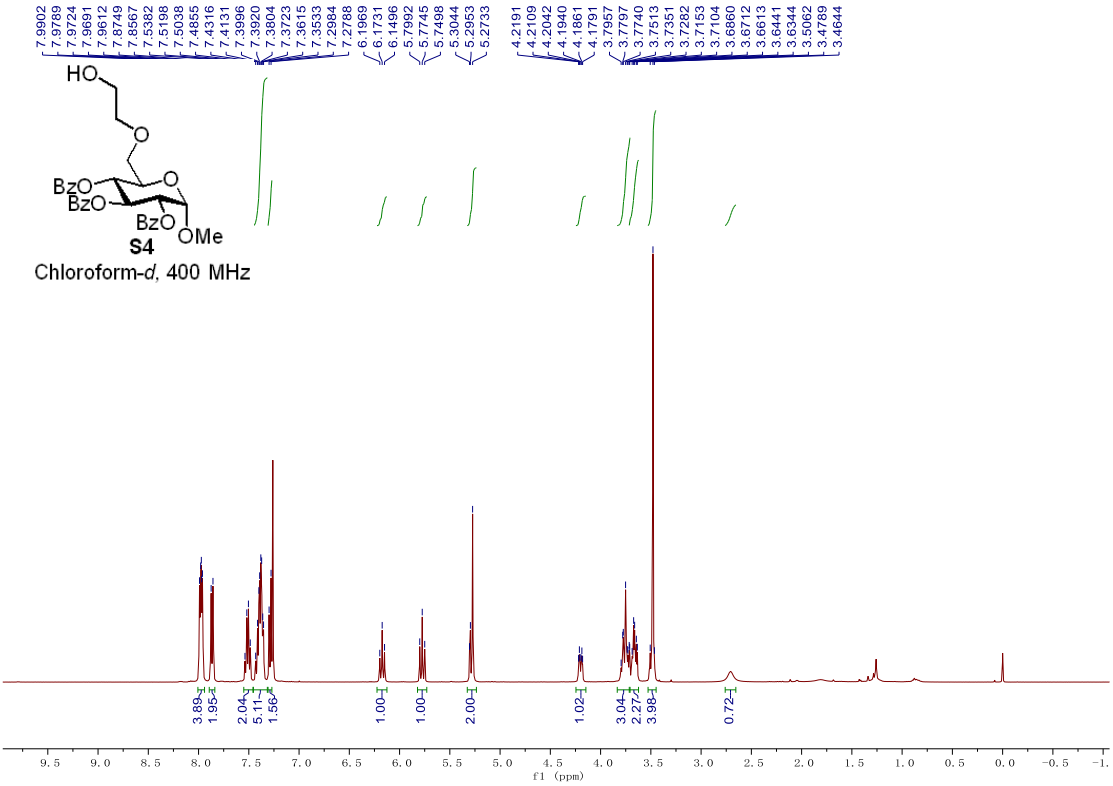
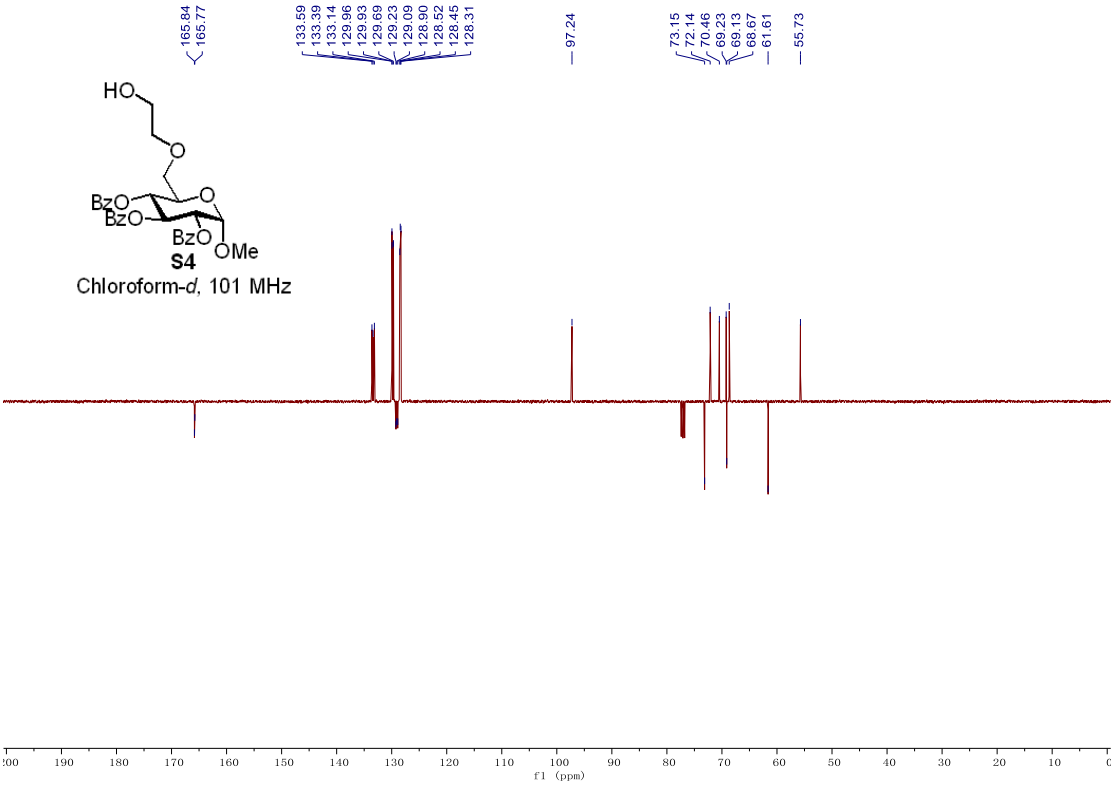
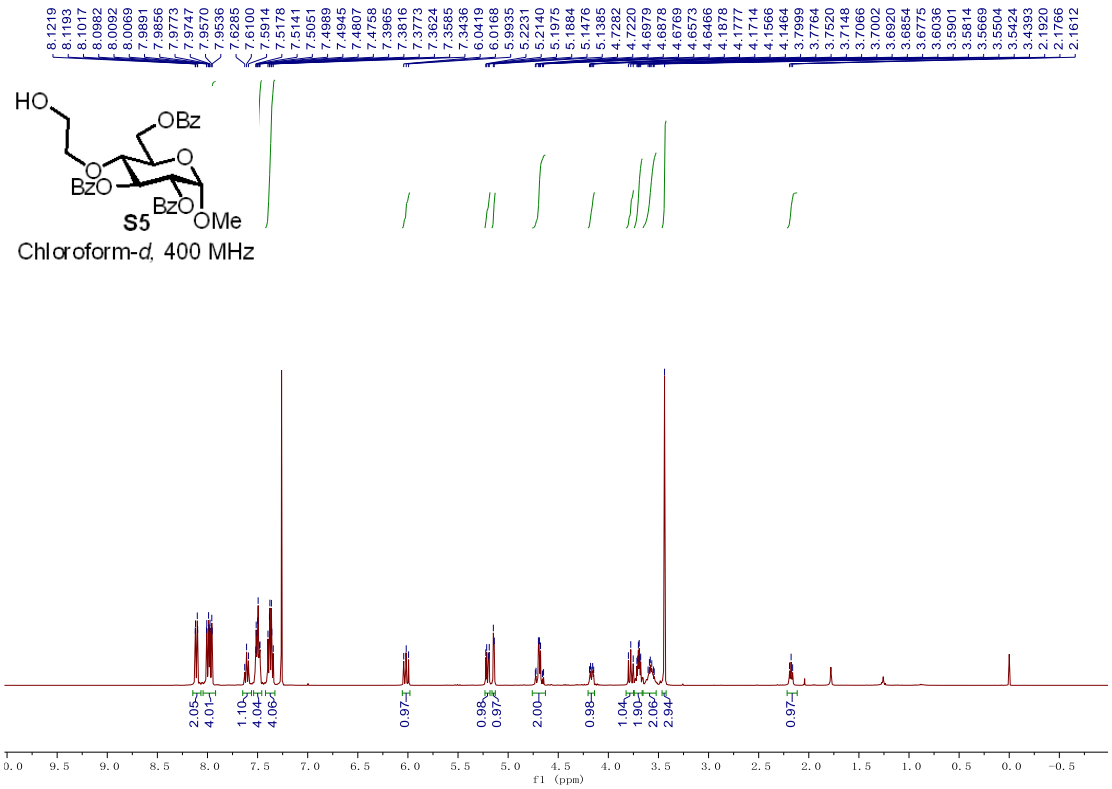
NMR Spectra of new compounds



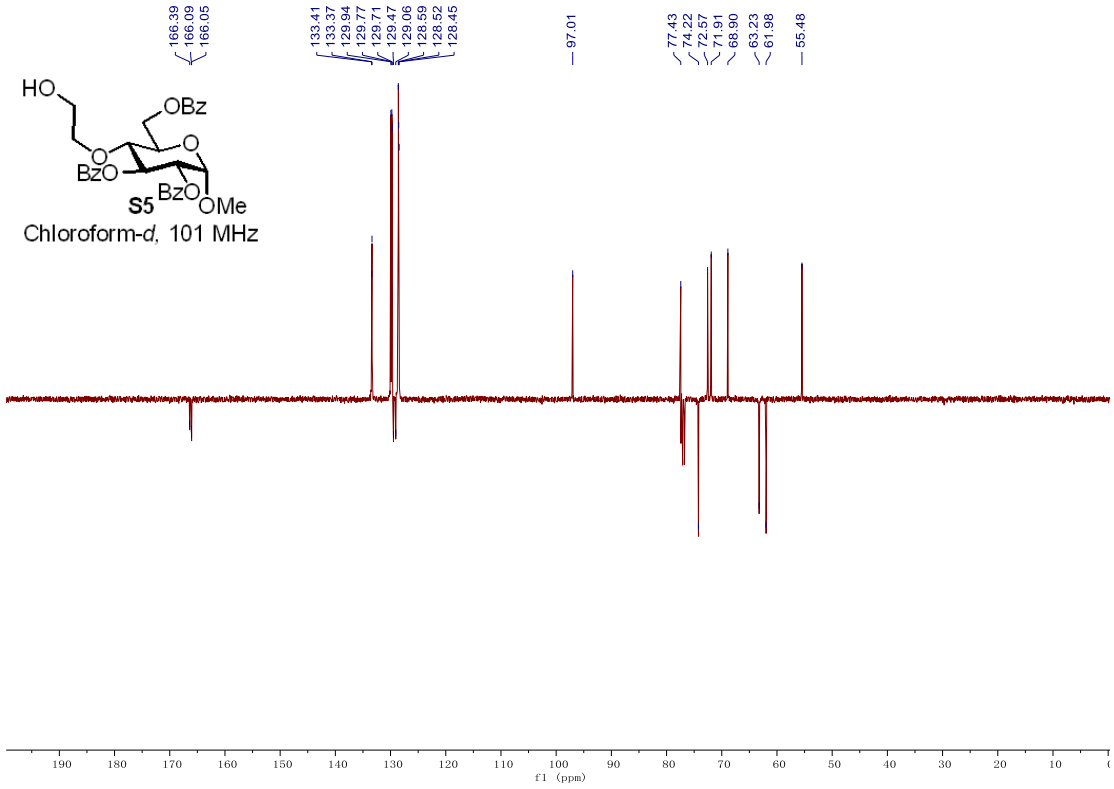
^{1}H NMR Spectra of compound S4



^{13}C NMR Spectra of compound S4



^{1}H NMR Spectra of compound S5



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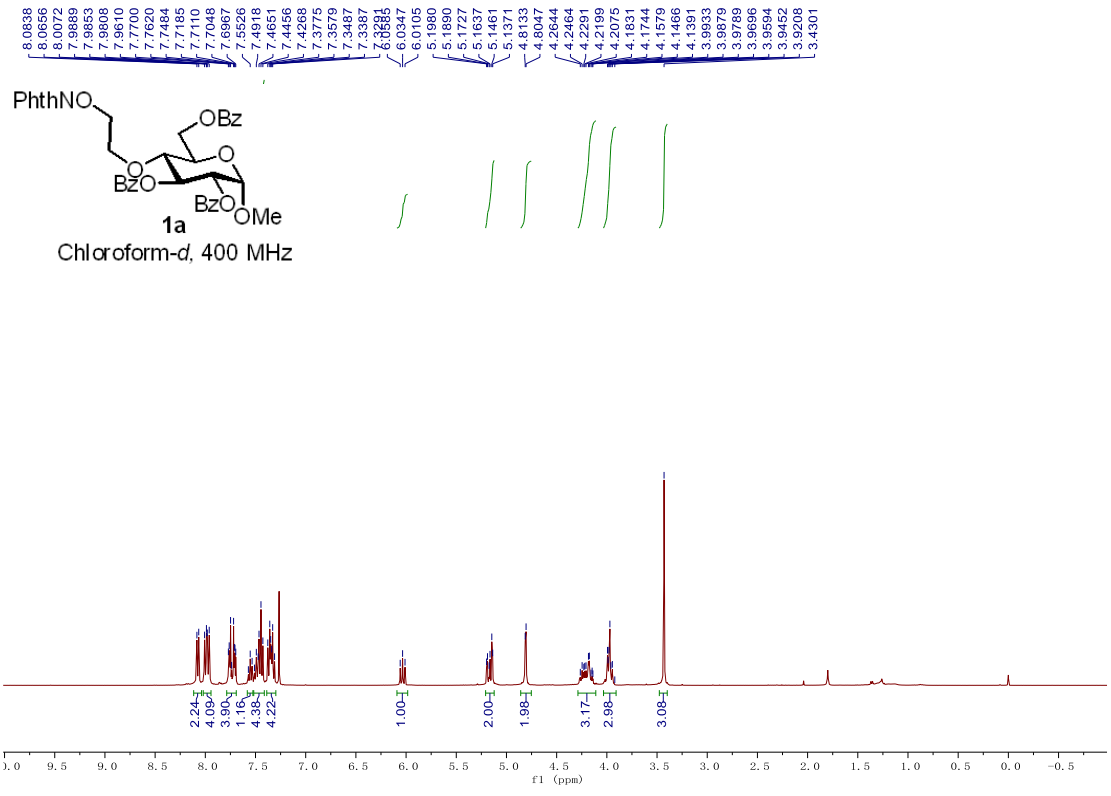
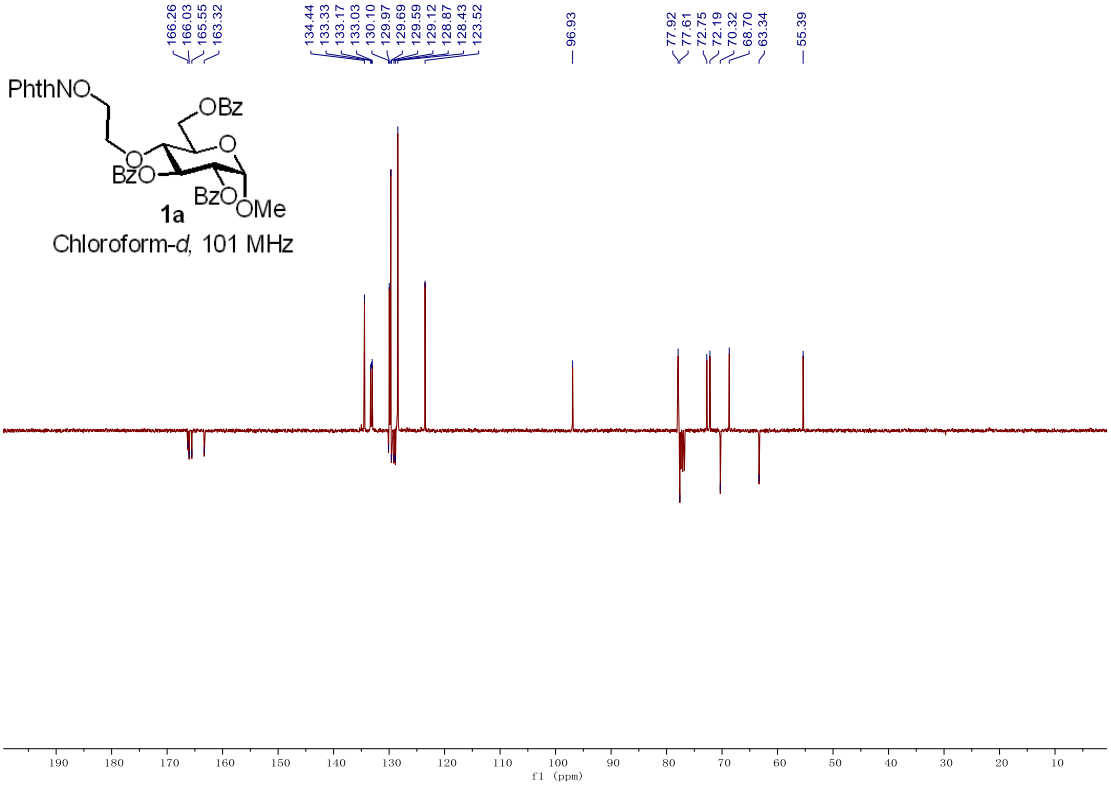


^{1}H NMR Spectra of compound 1a



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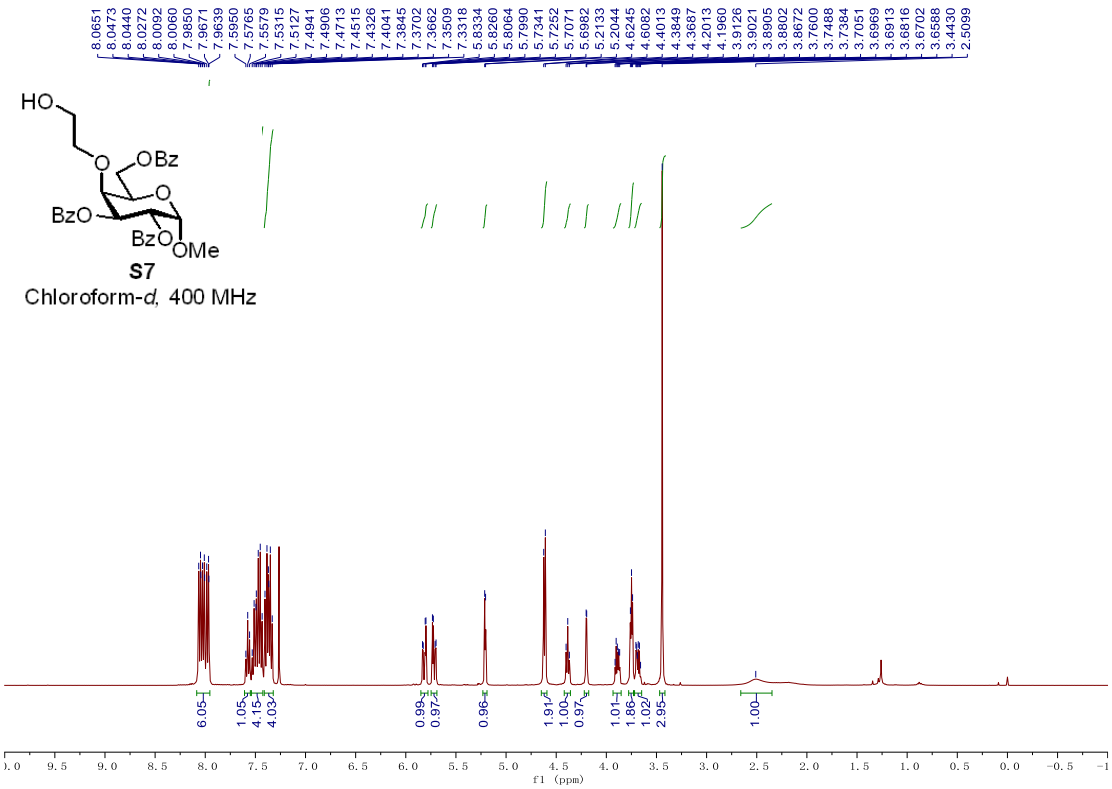

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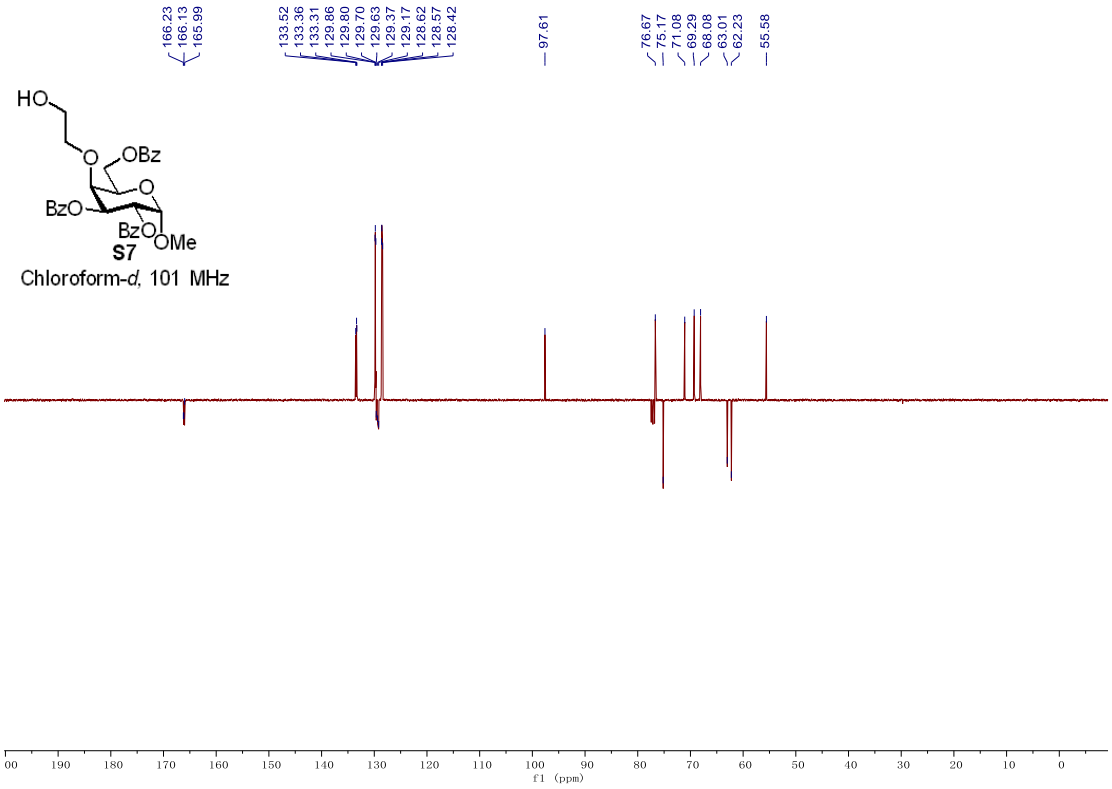

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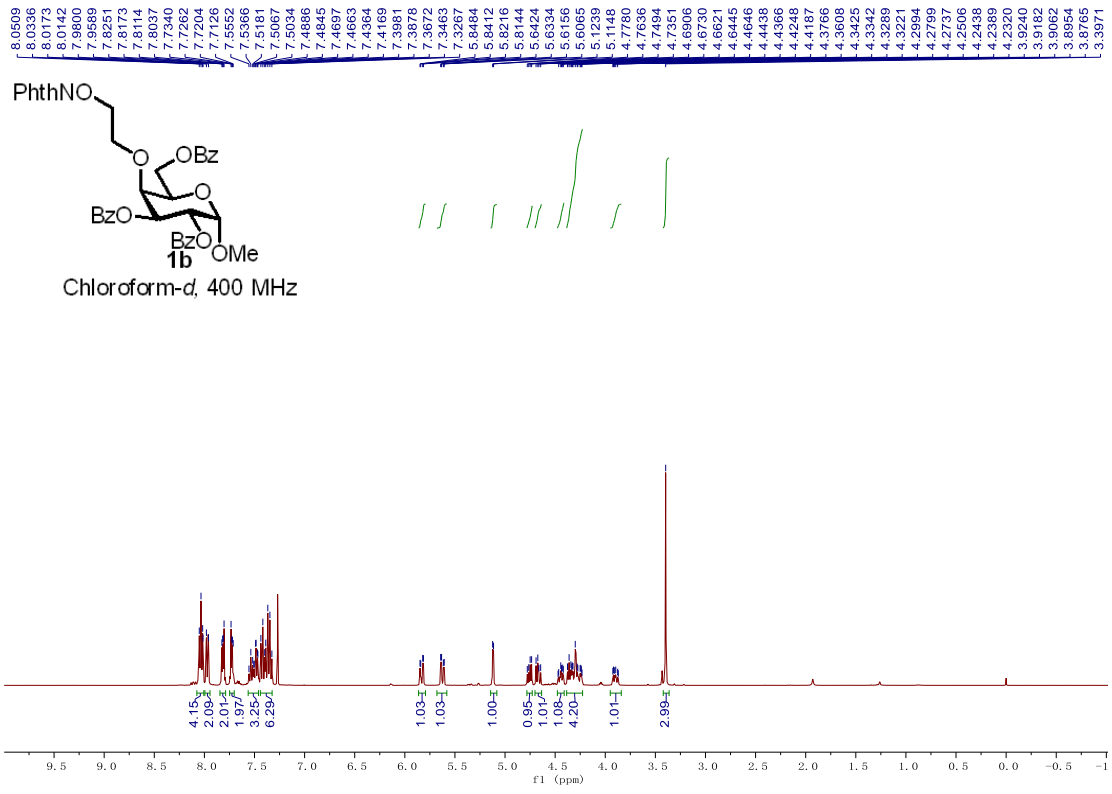

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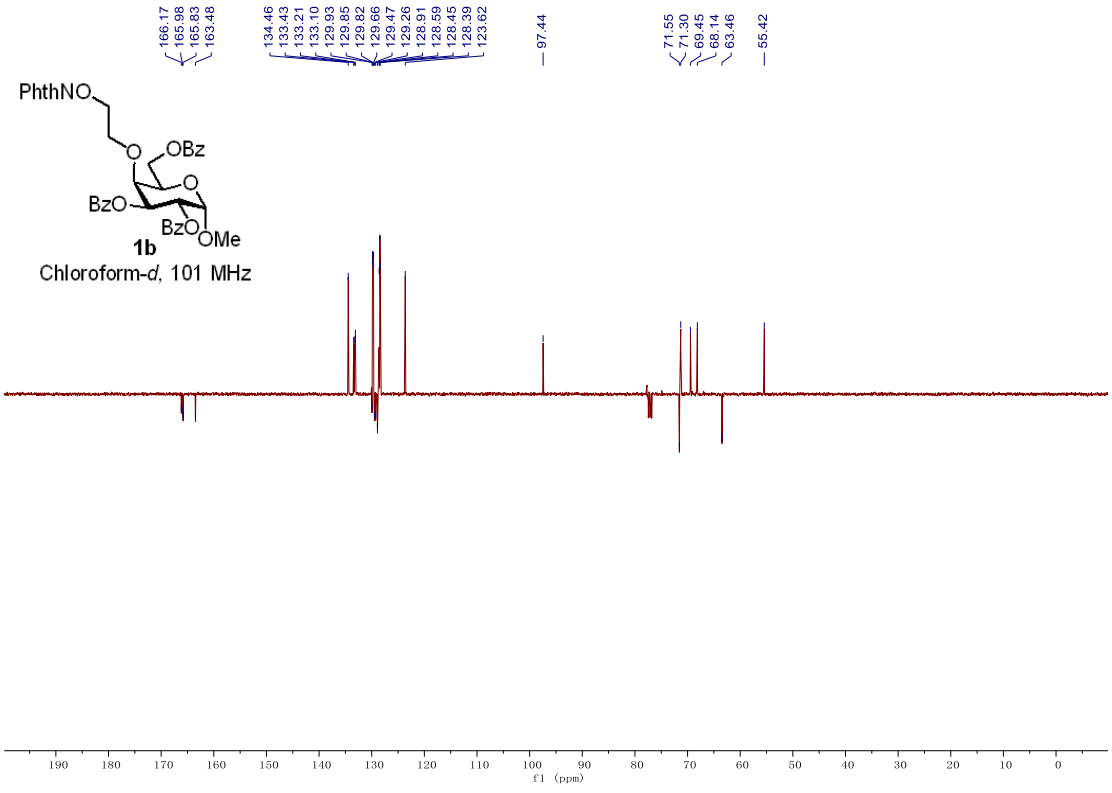

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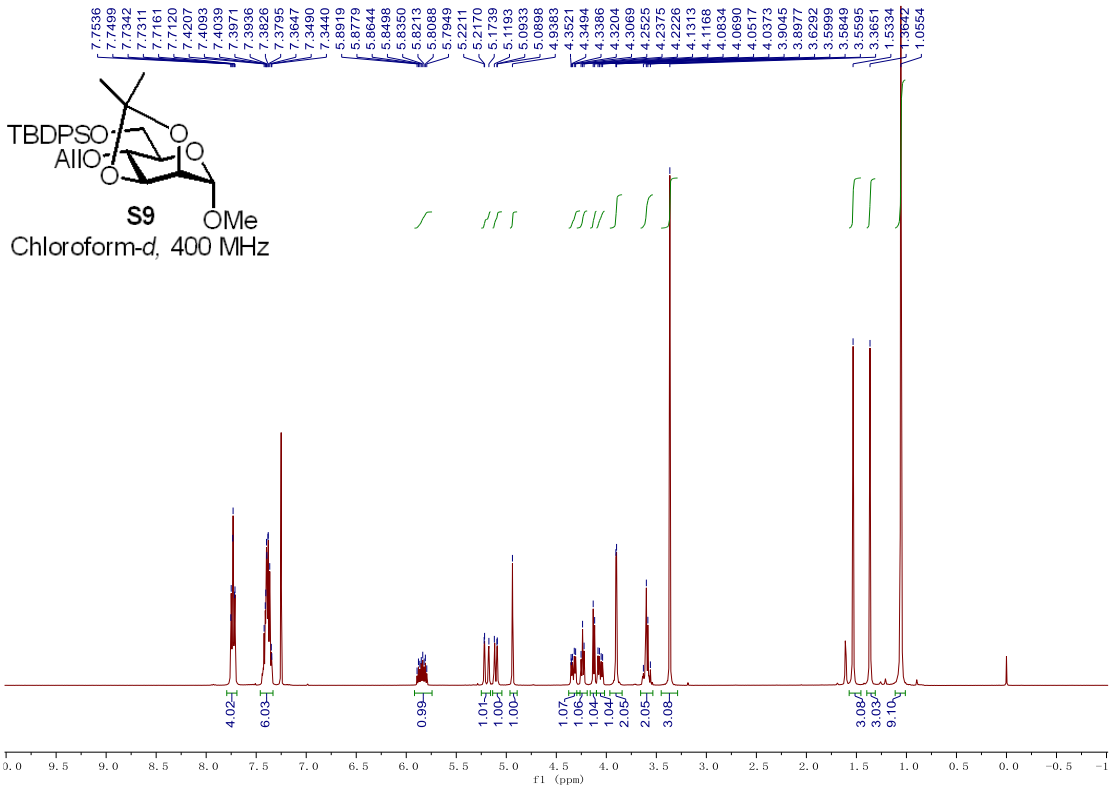

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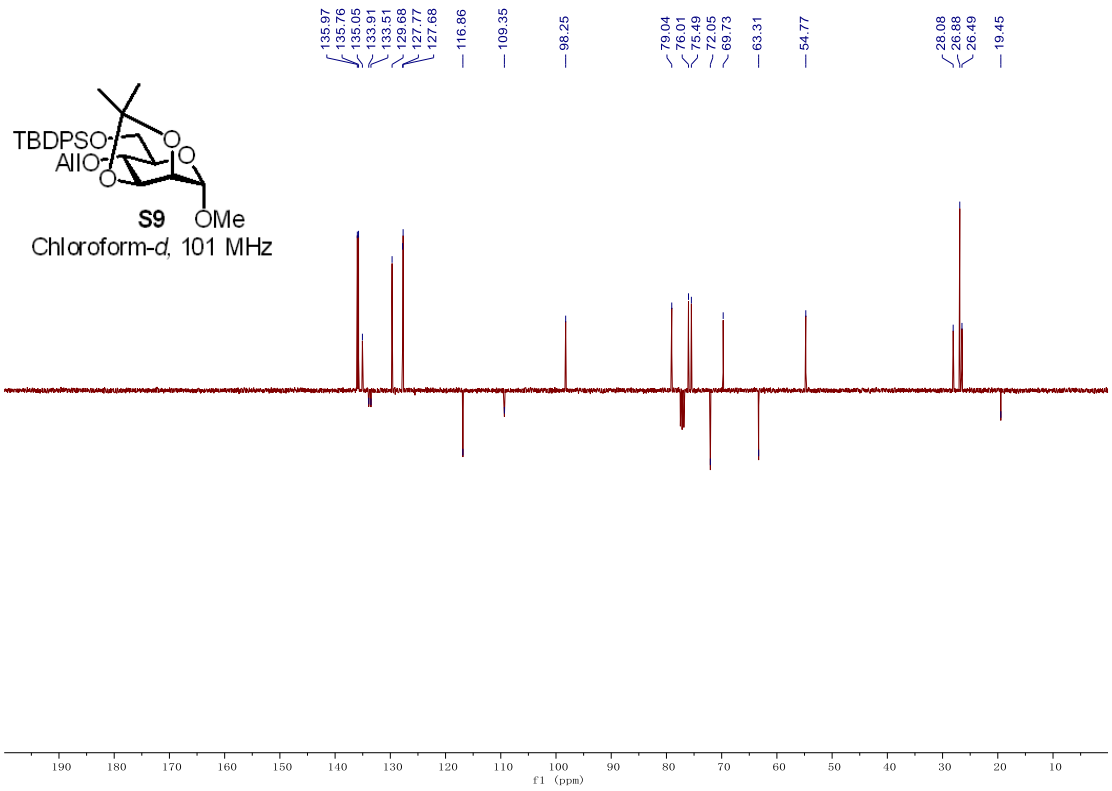
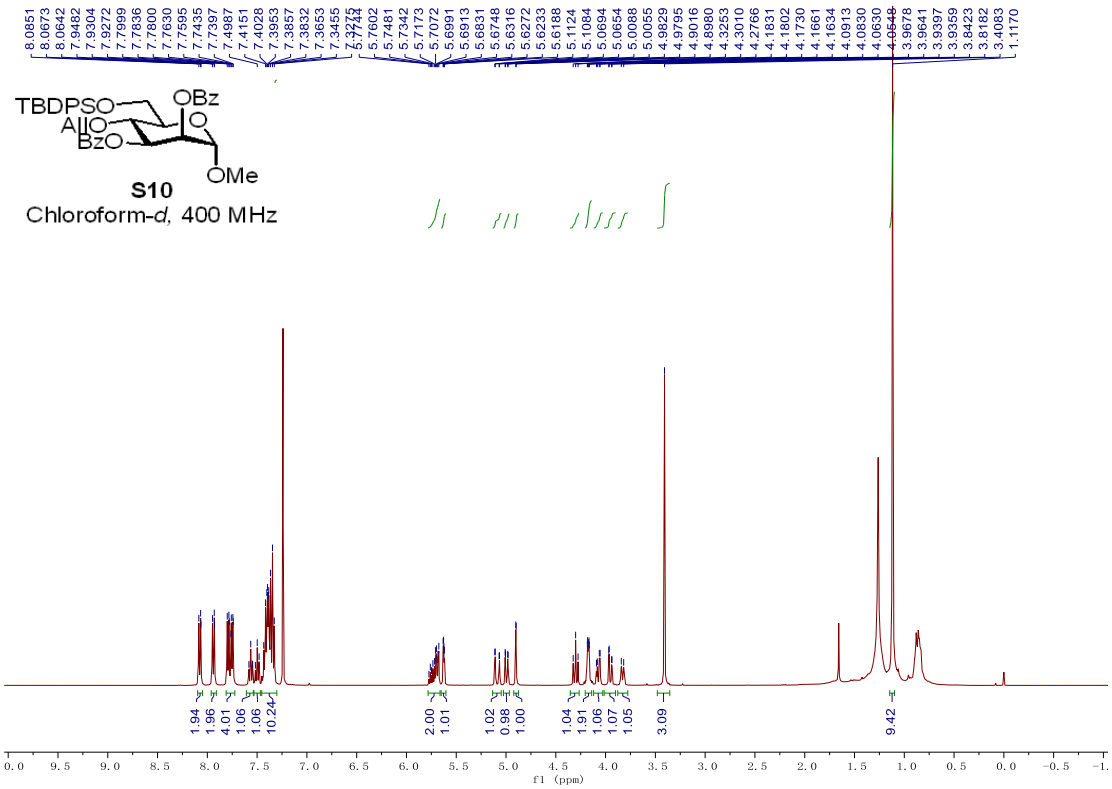


^{13}C NMR Spectra of compound S9



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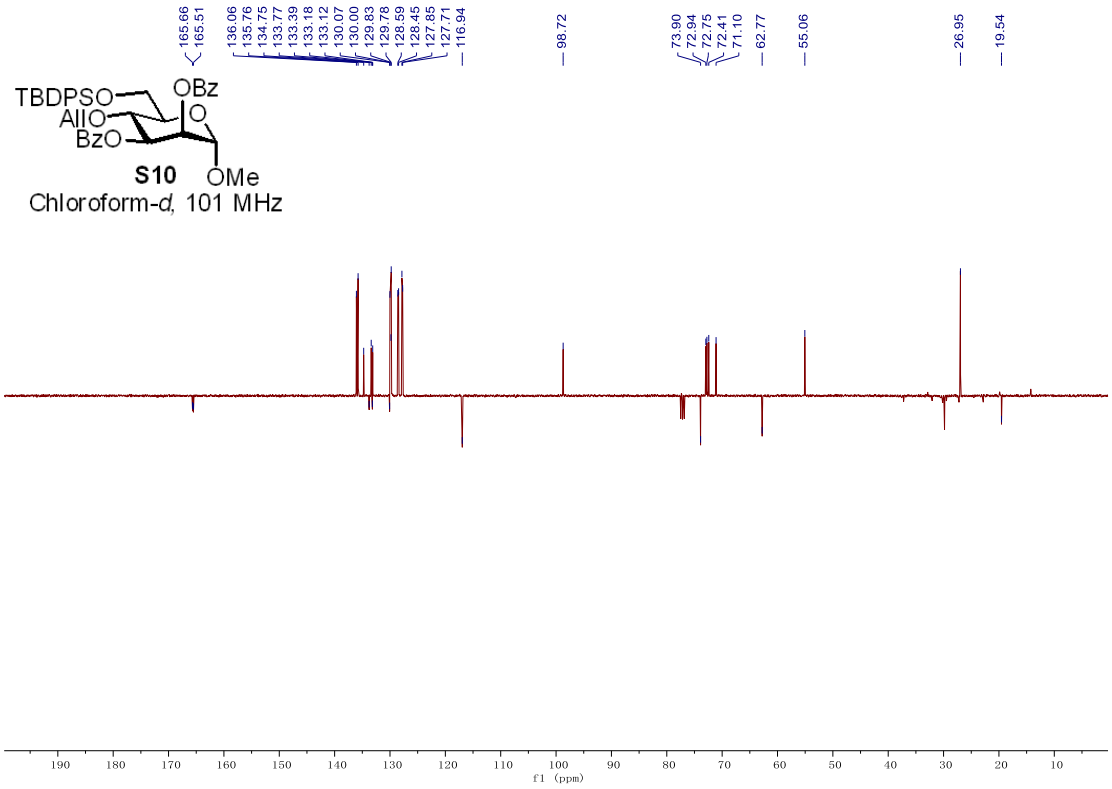

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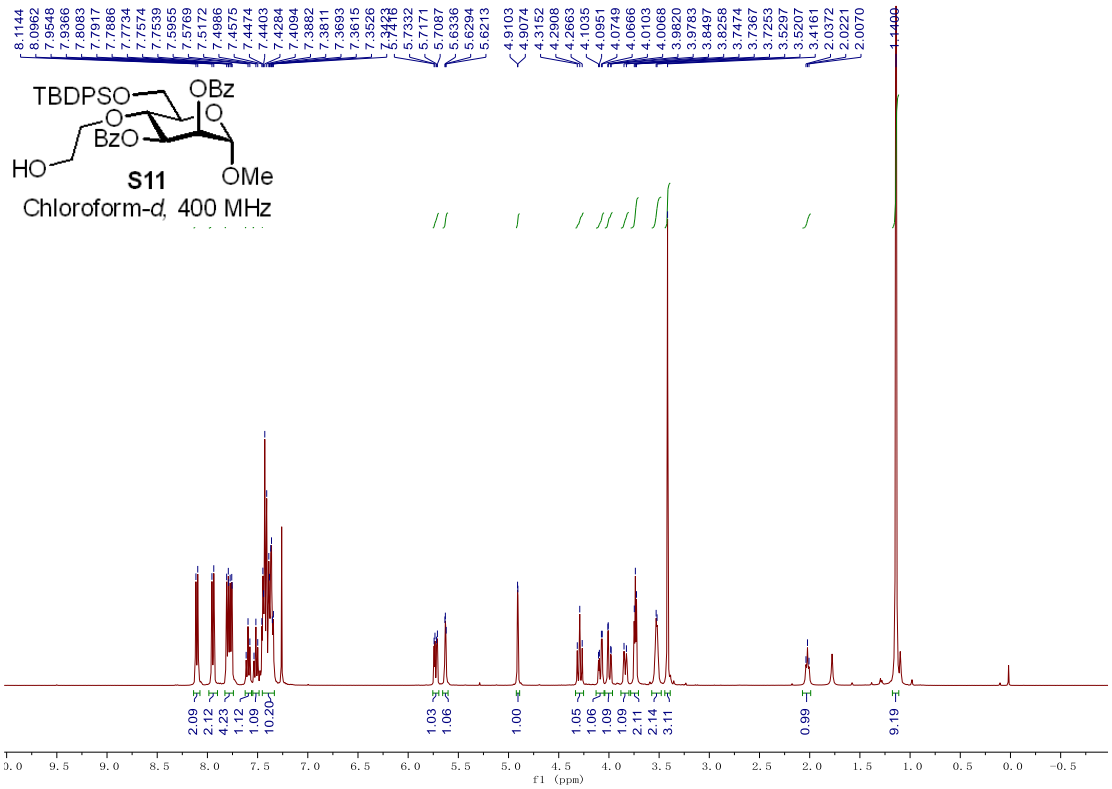
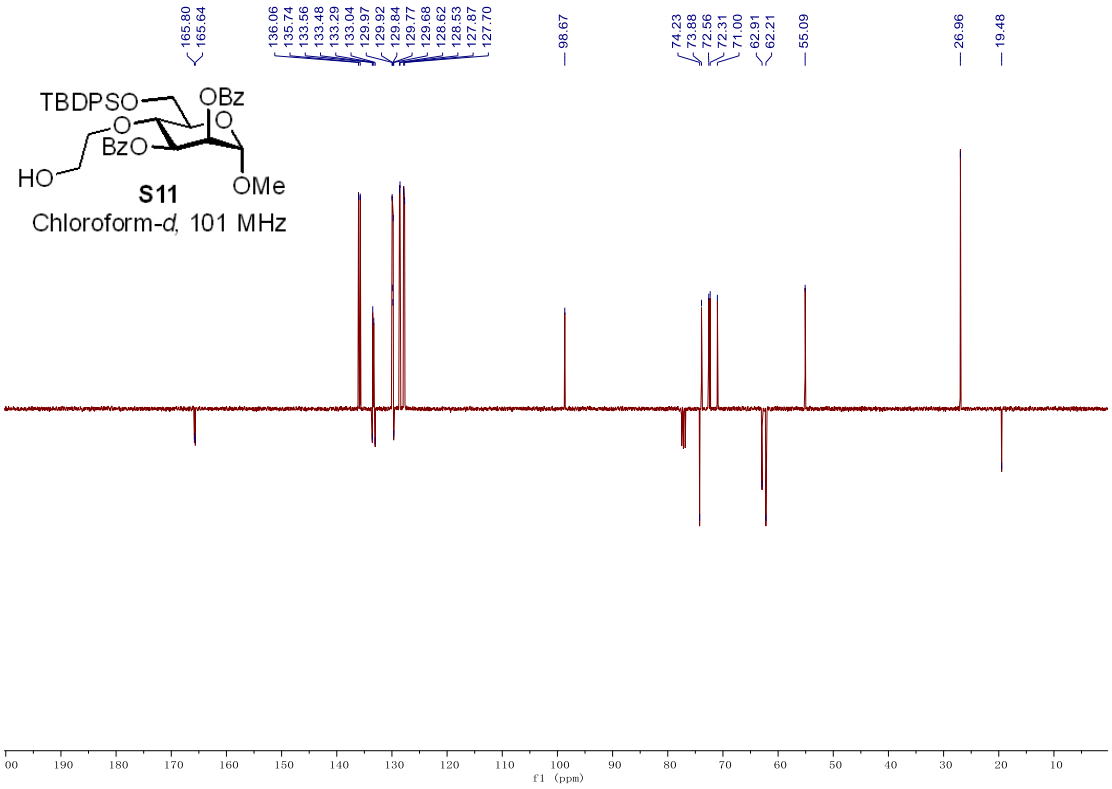


^{1}H NMR Spectra of compound S11



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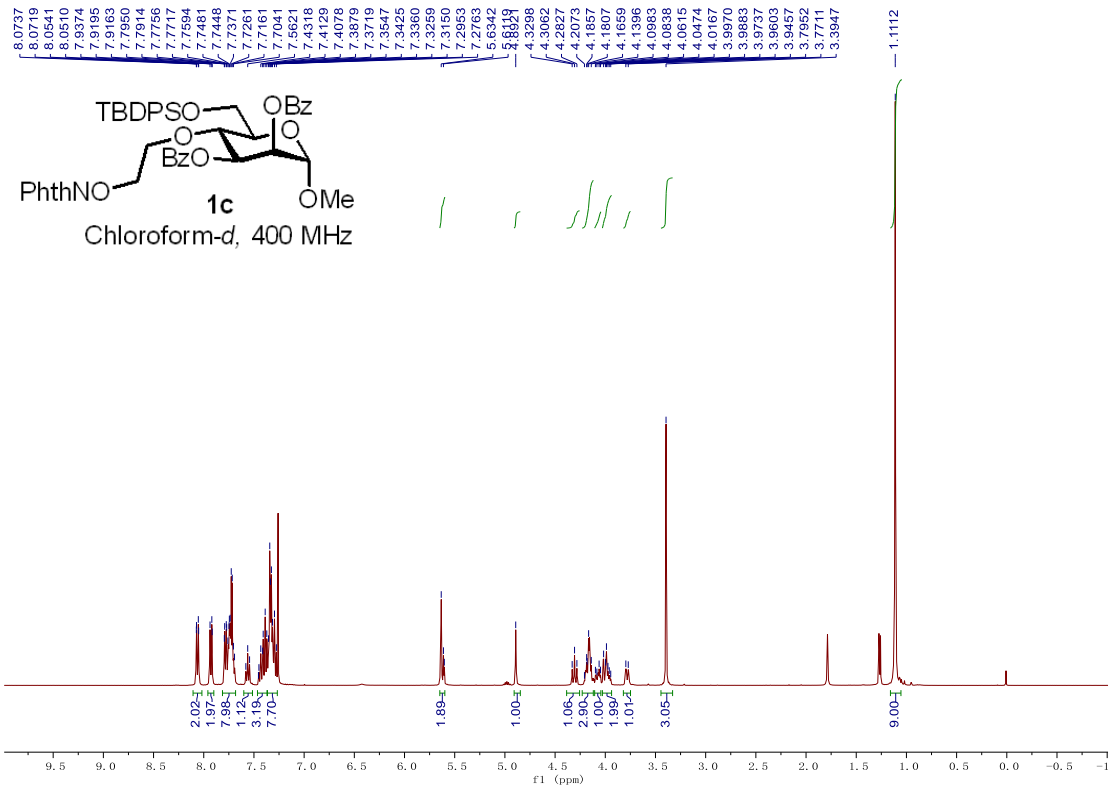

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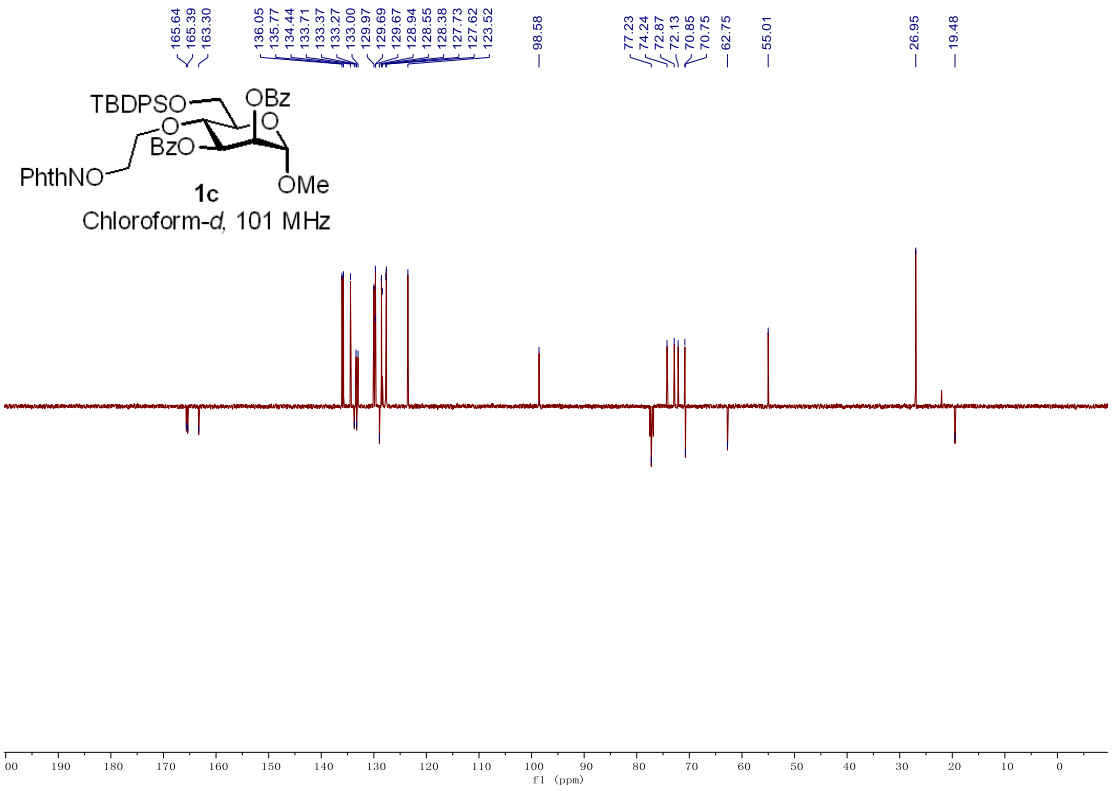

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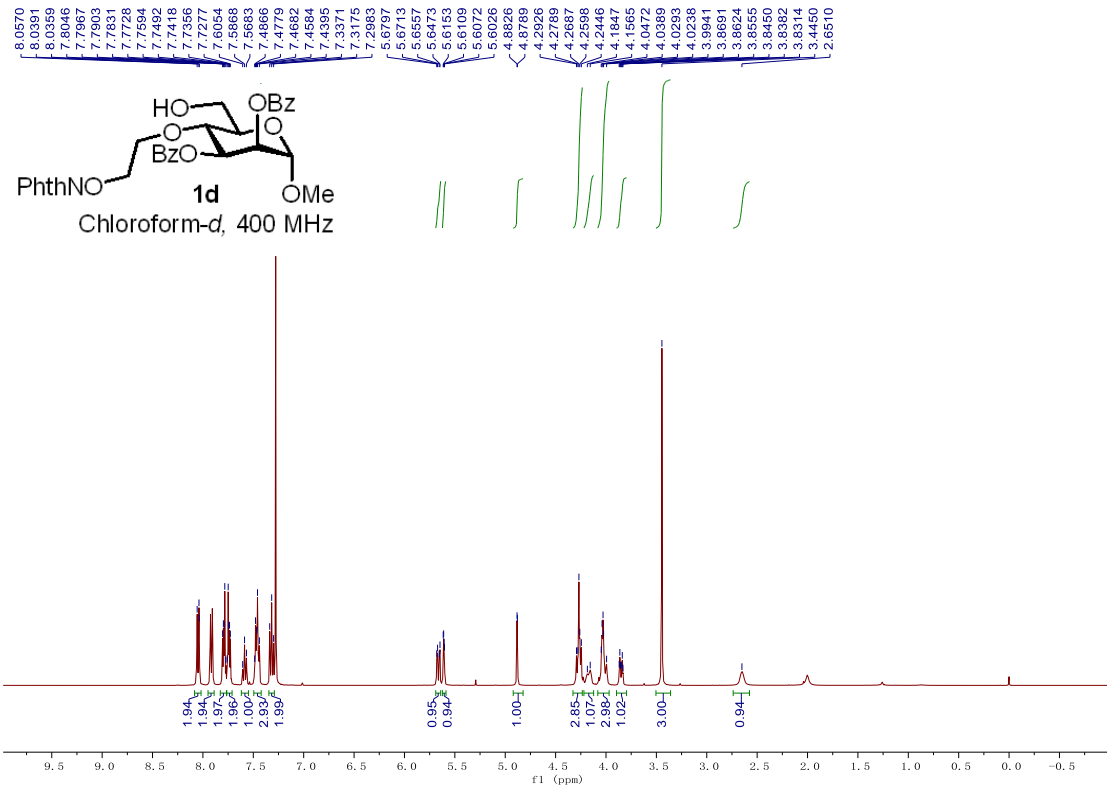

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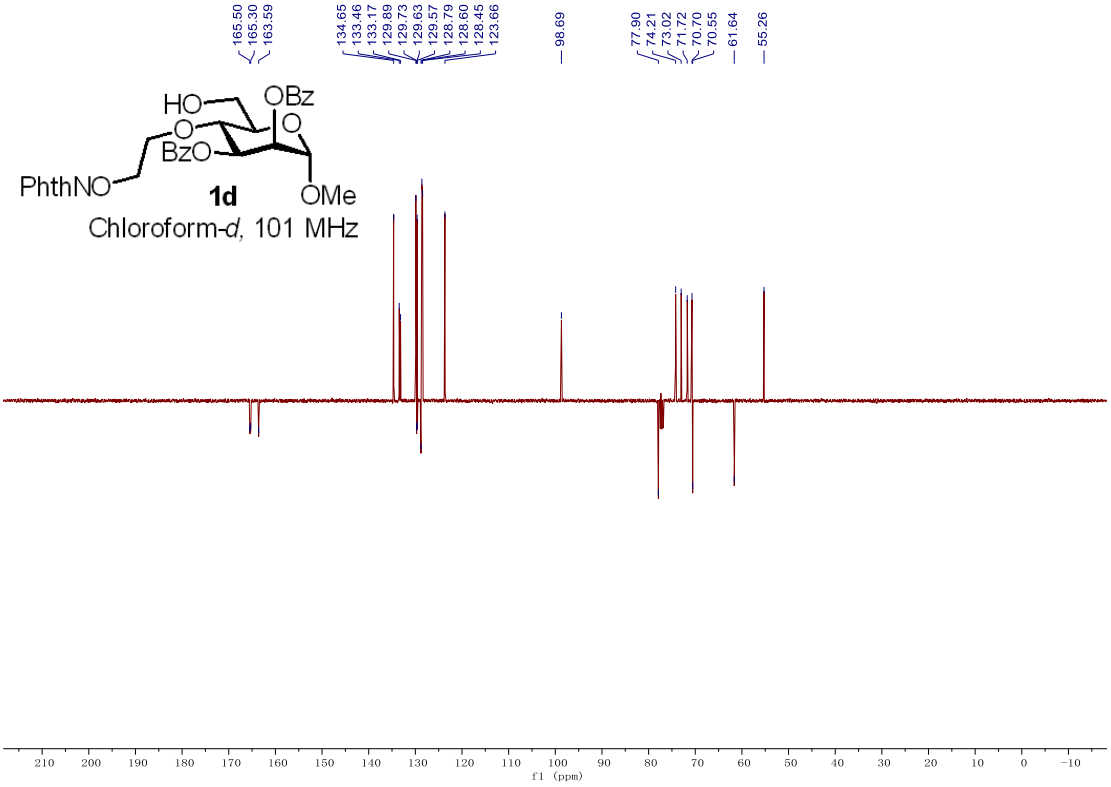

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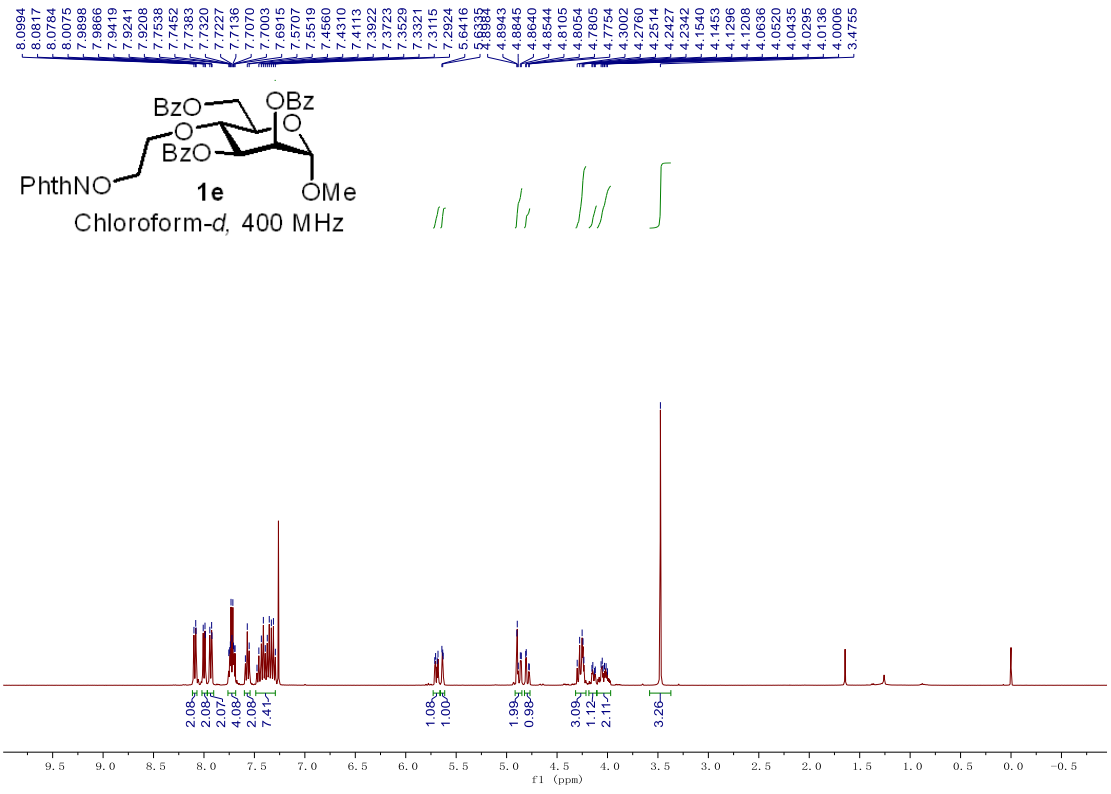

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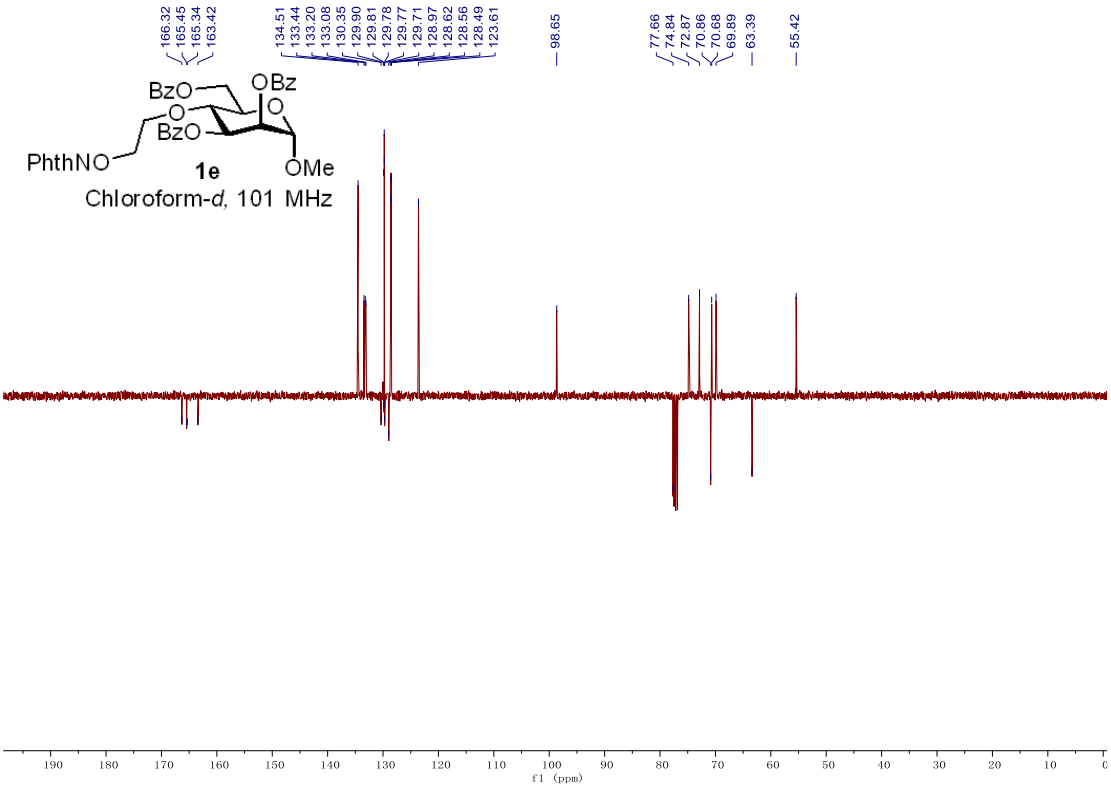

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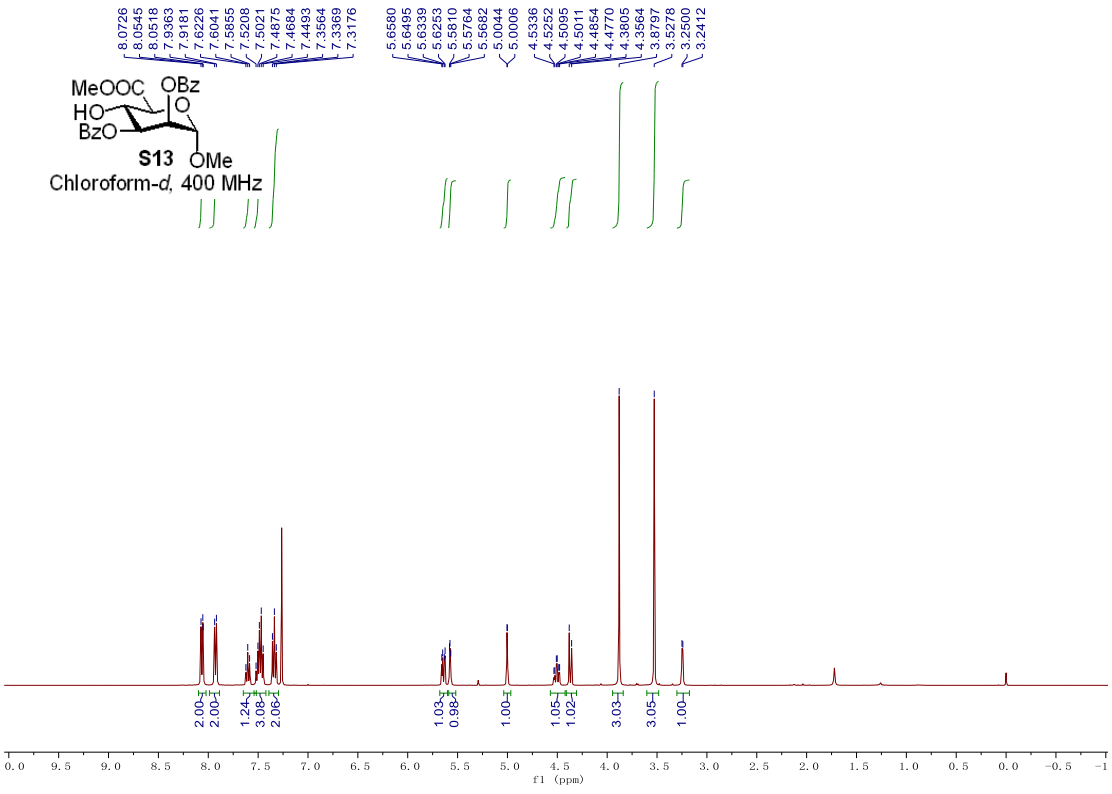

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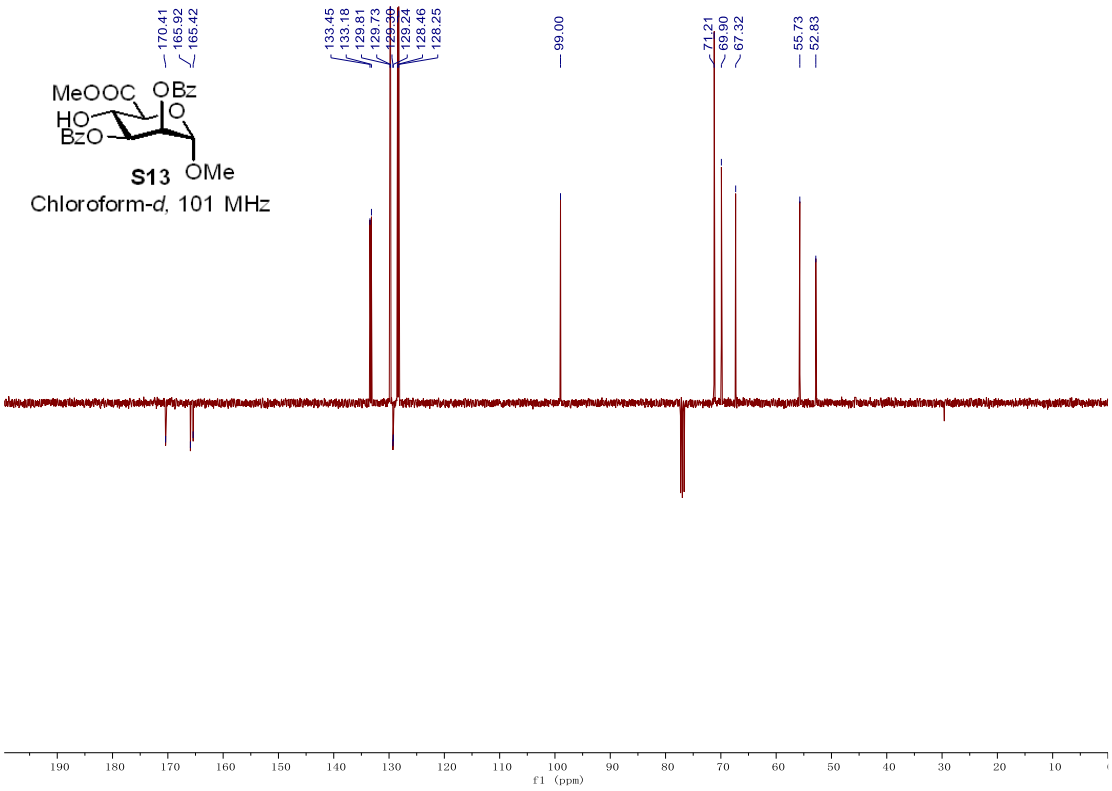

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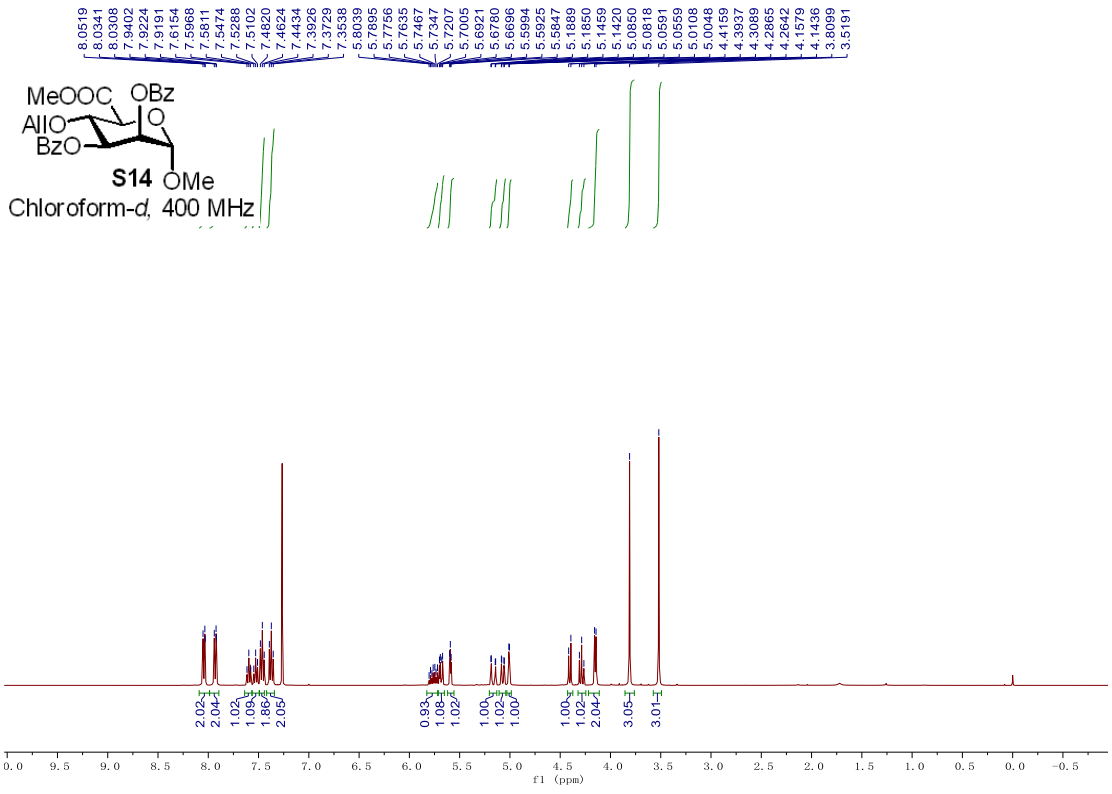
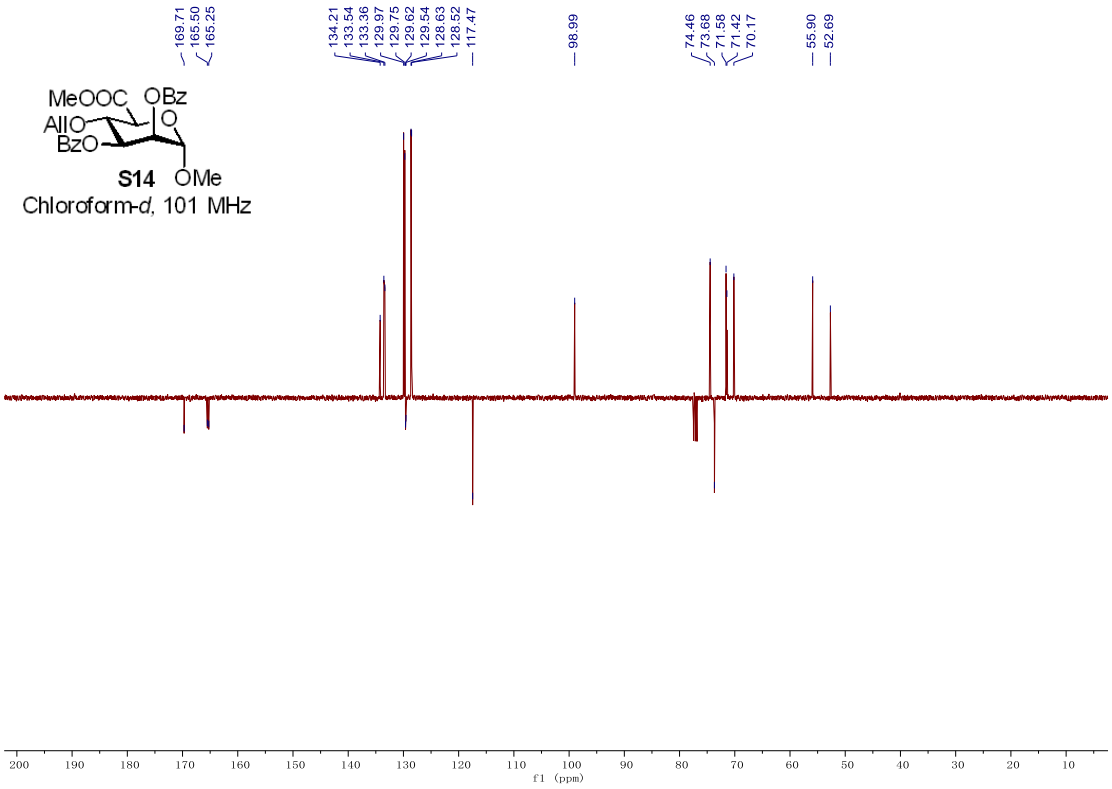
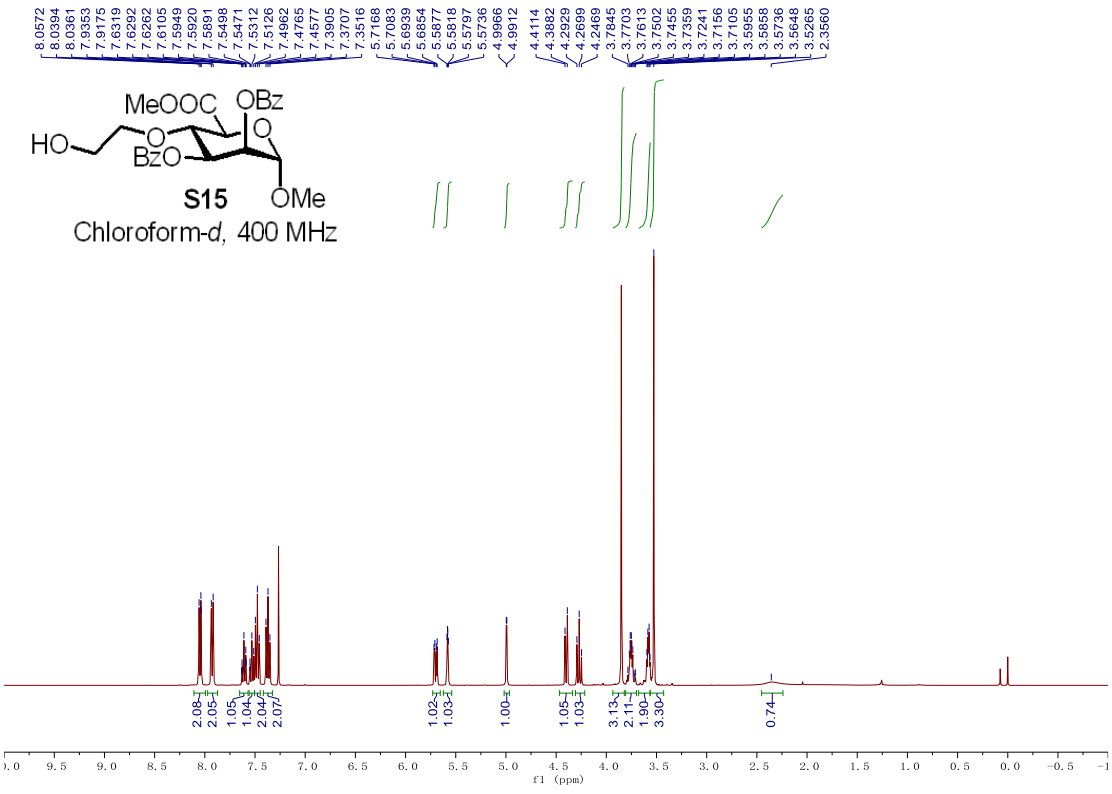


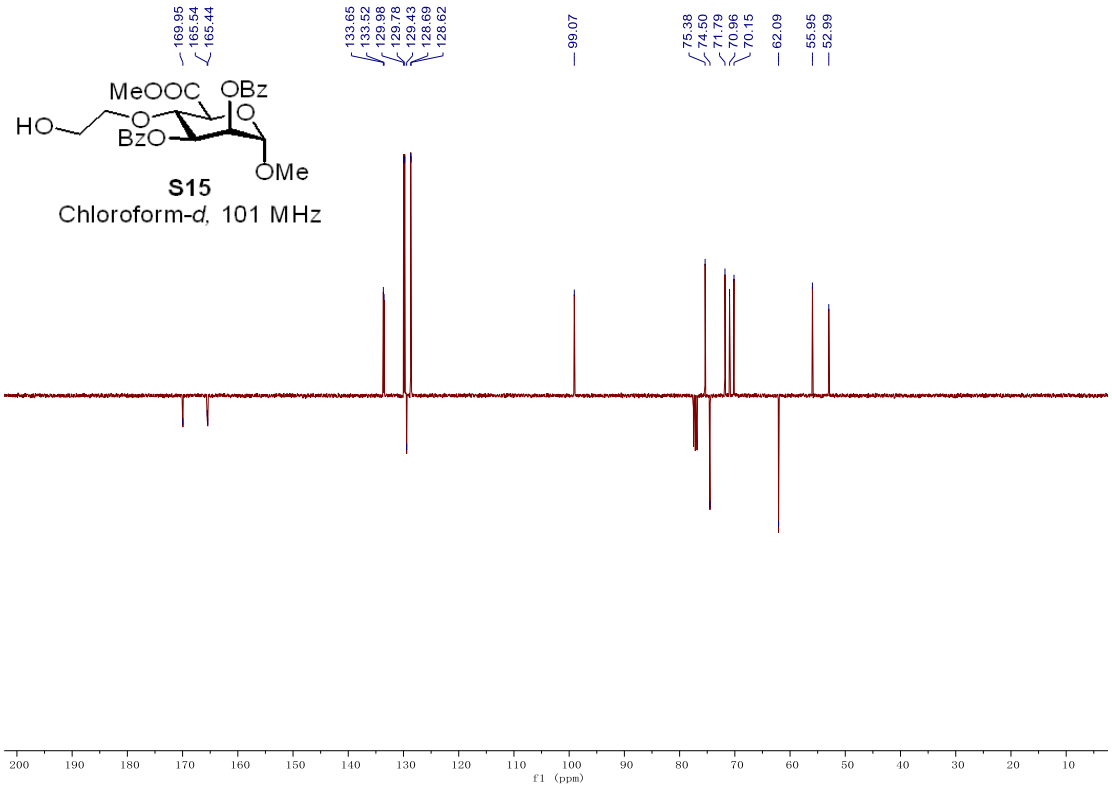
^{1}H NMR Spectra of compound S14



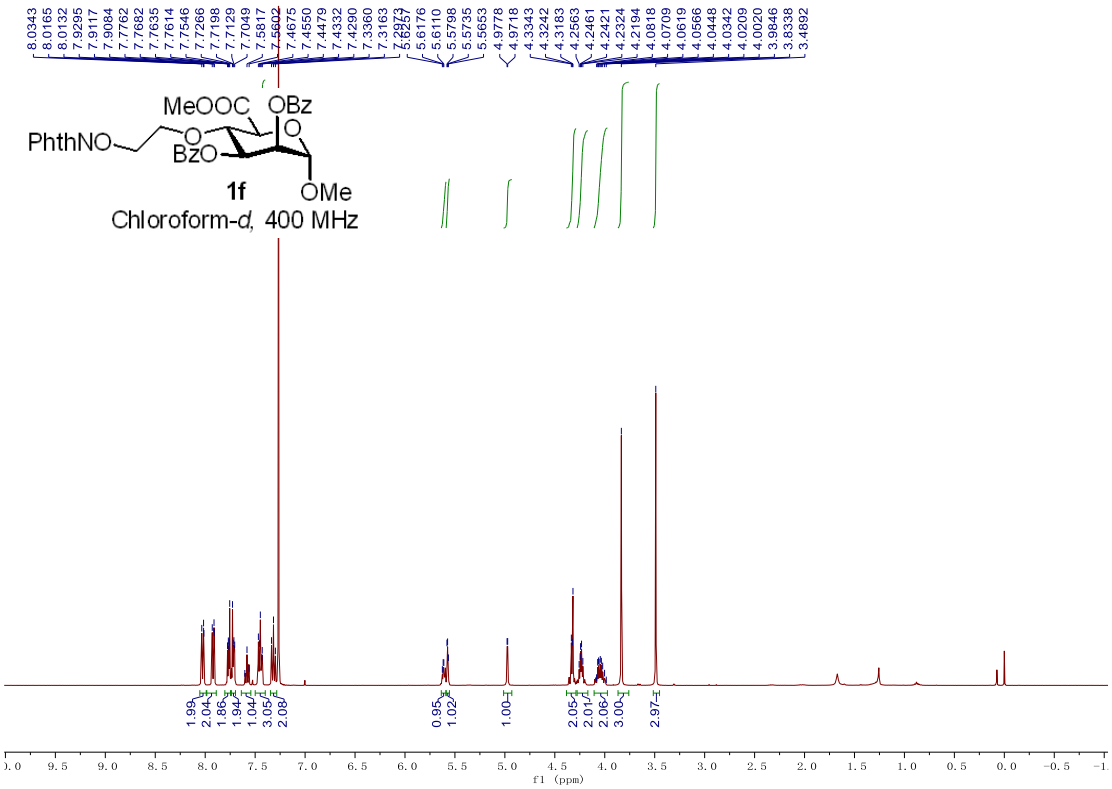
^{13}C NMR Spectra of compound S14



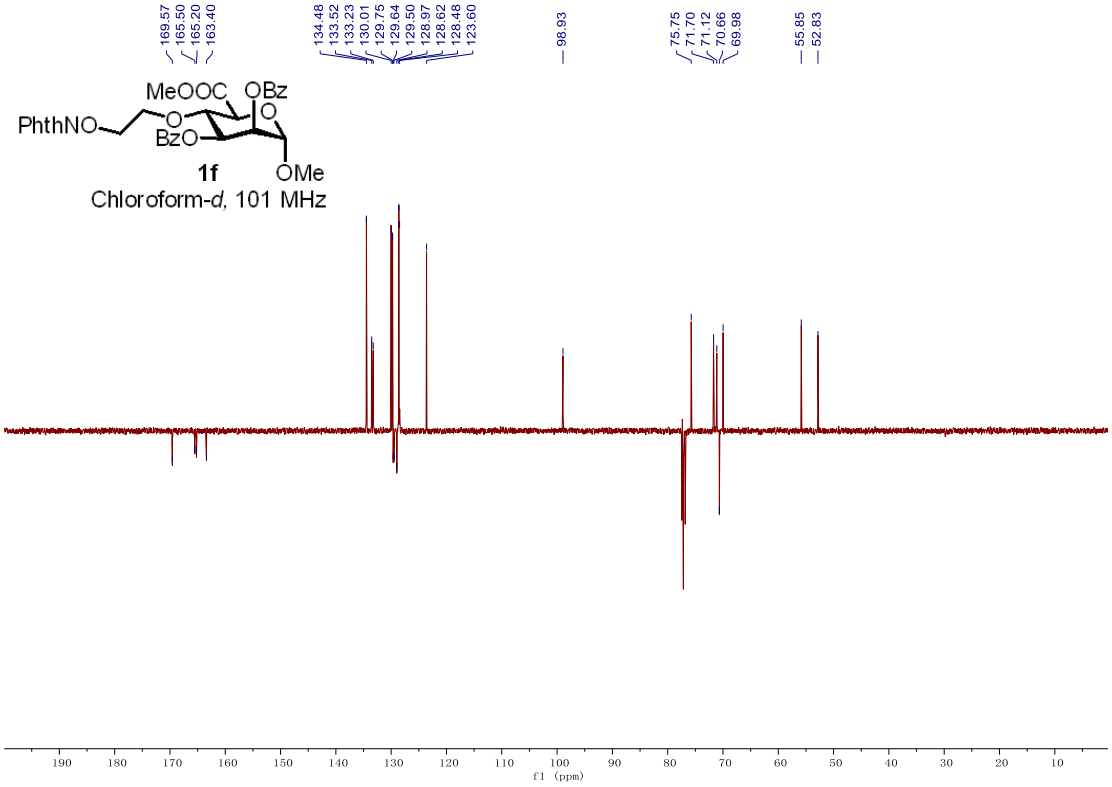
^{1}H NMR Spectra of compound S15



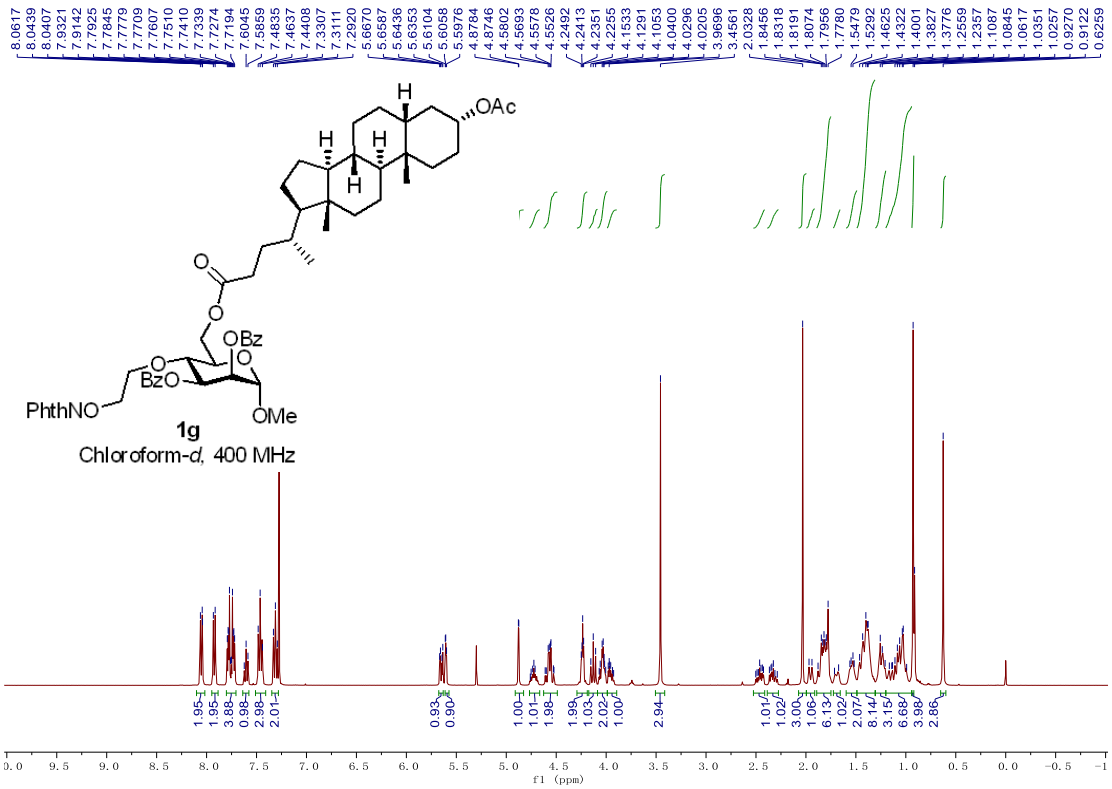
^{13}C NMR Spectra of compound S15



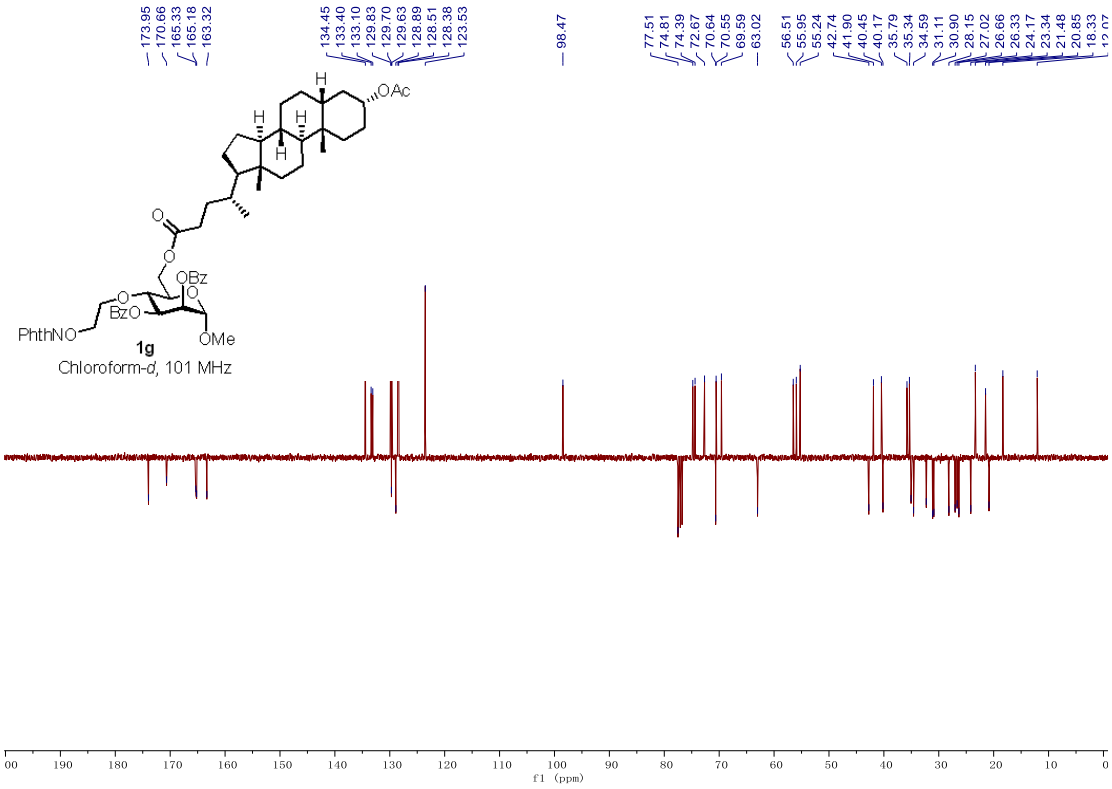
^{1}H NMR Spectra of compound 1f



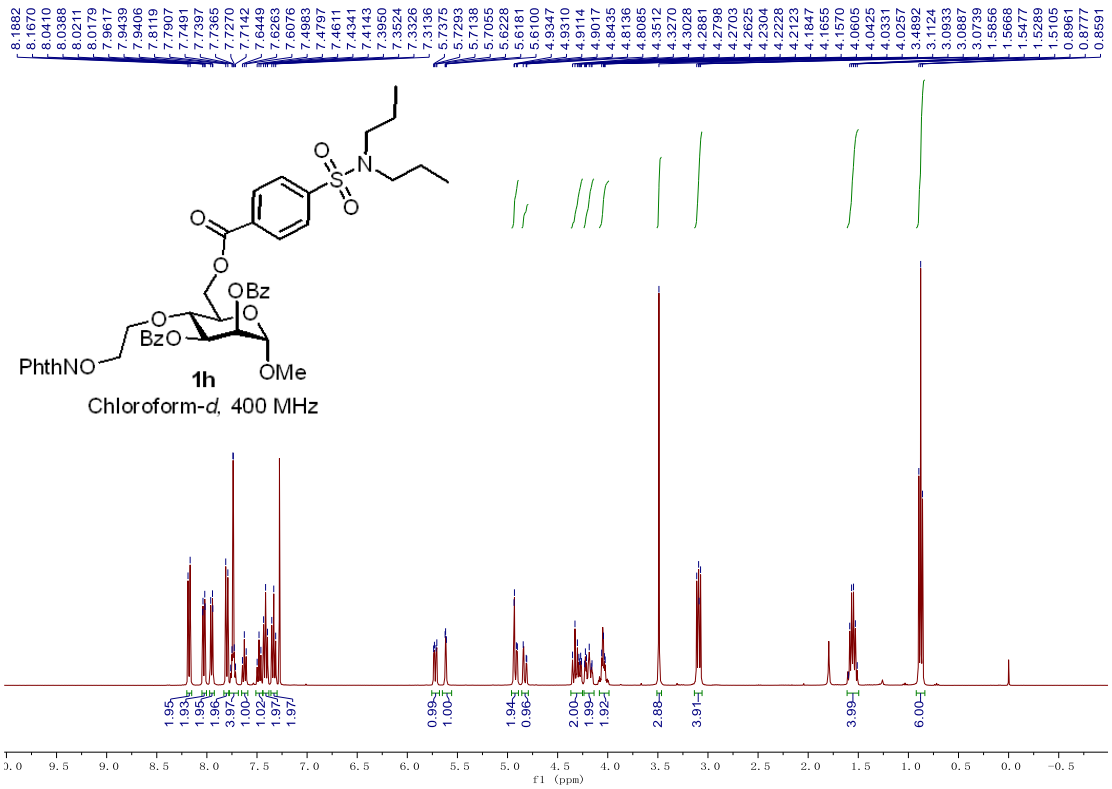
^{13}C NMR Spectra of compound 1f



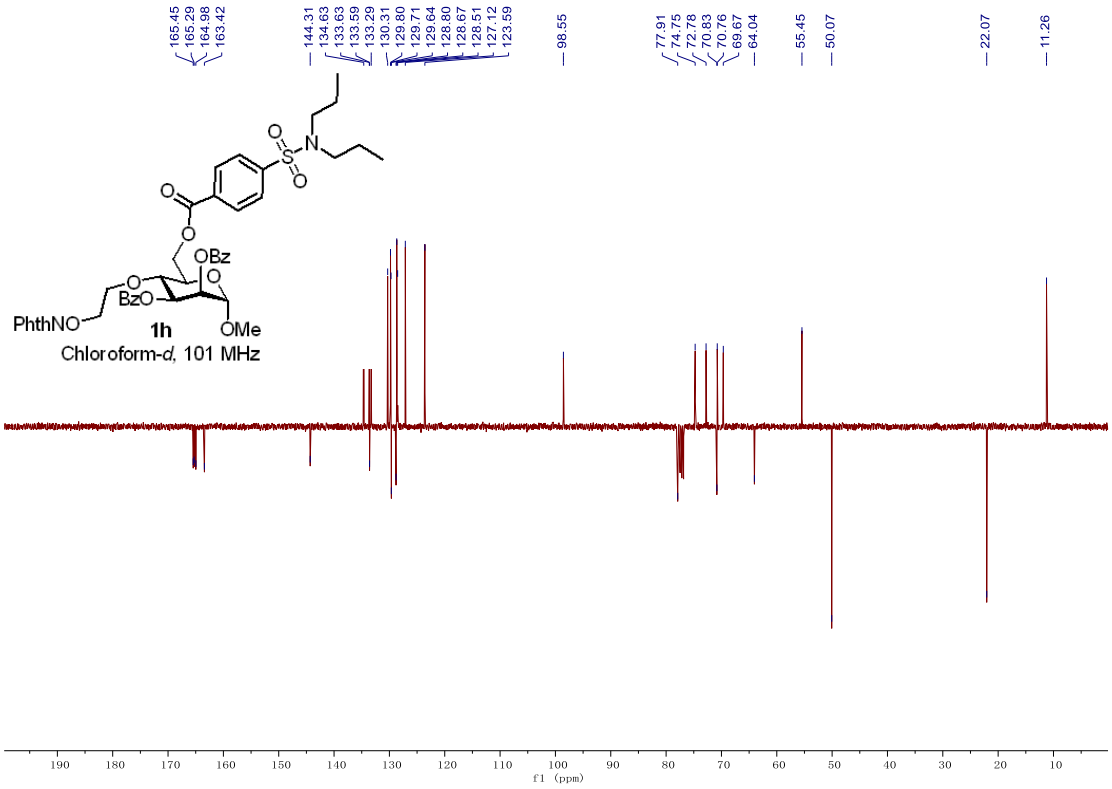
^{1}H NMR Spectra of compound 1g



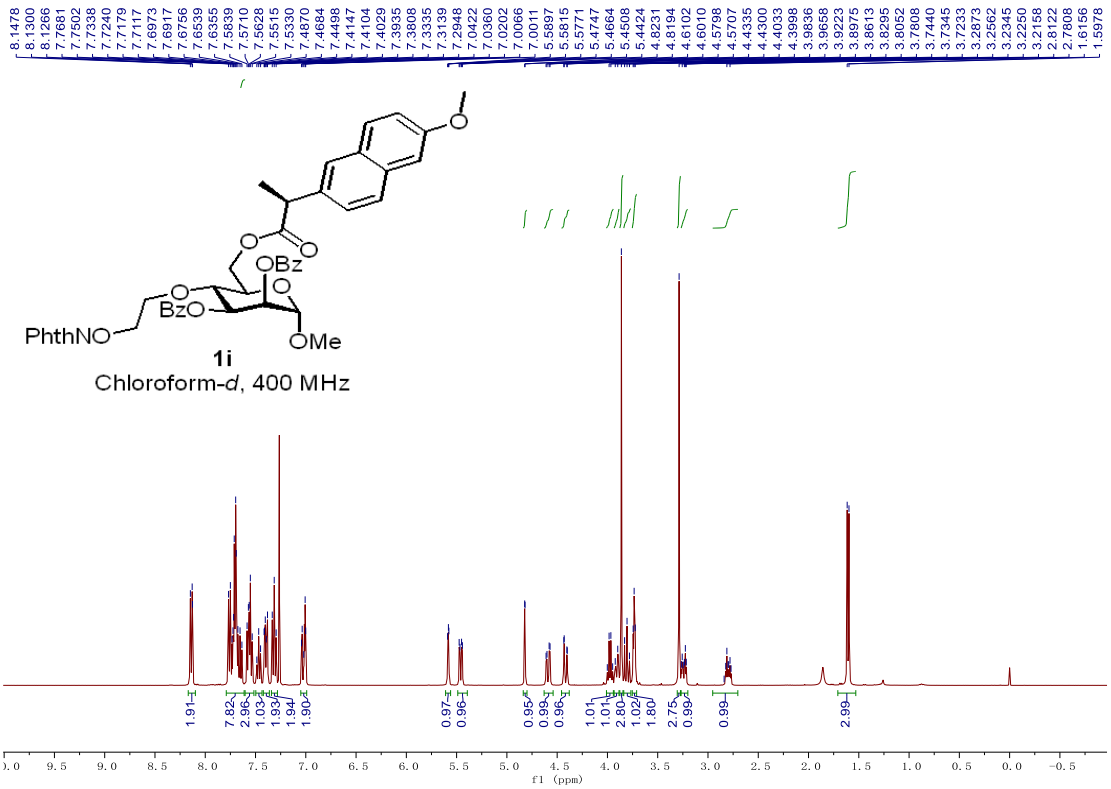
^{13}C NMR Spectra of compound 1g



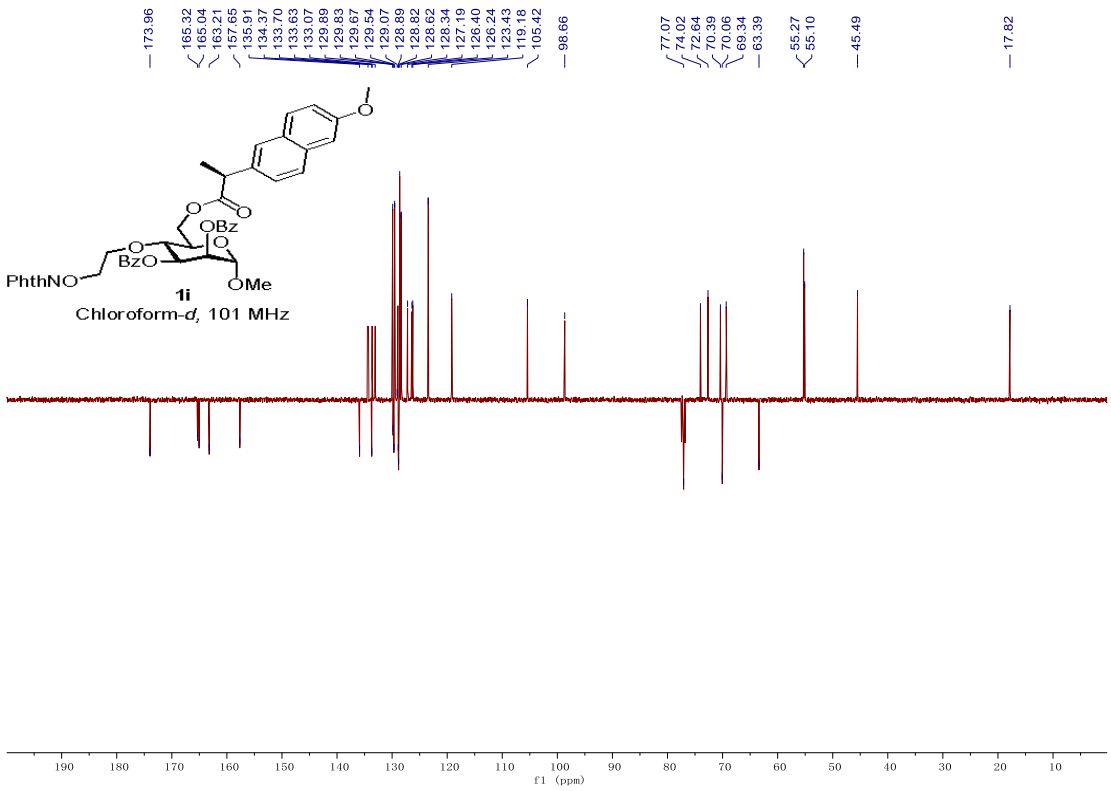
^{1}H NMR Spectra of compound 1h



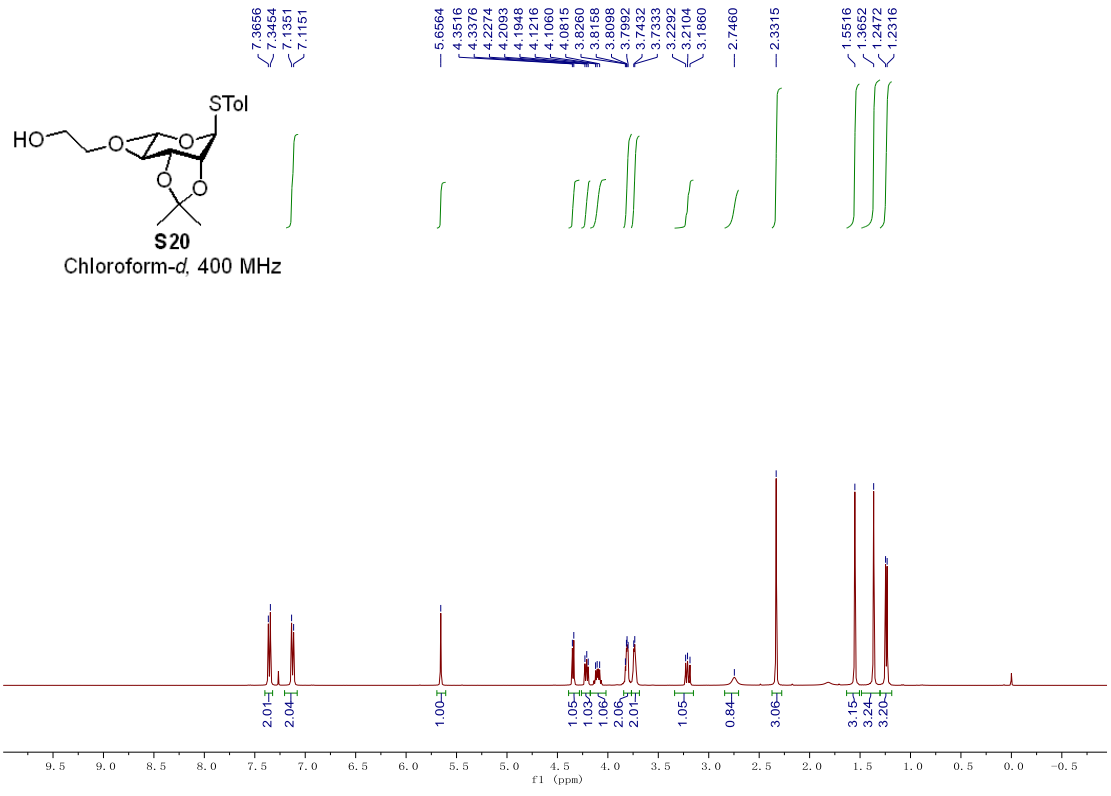
^{13}C NMR Spectra of compound 1h



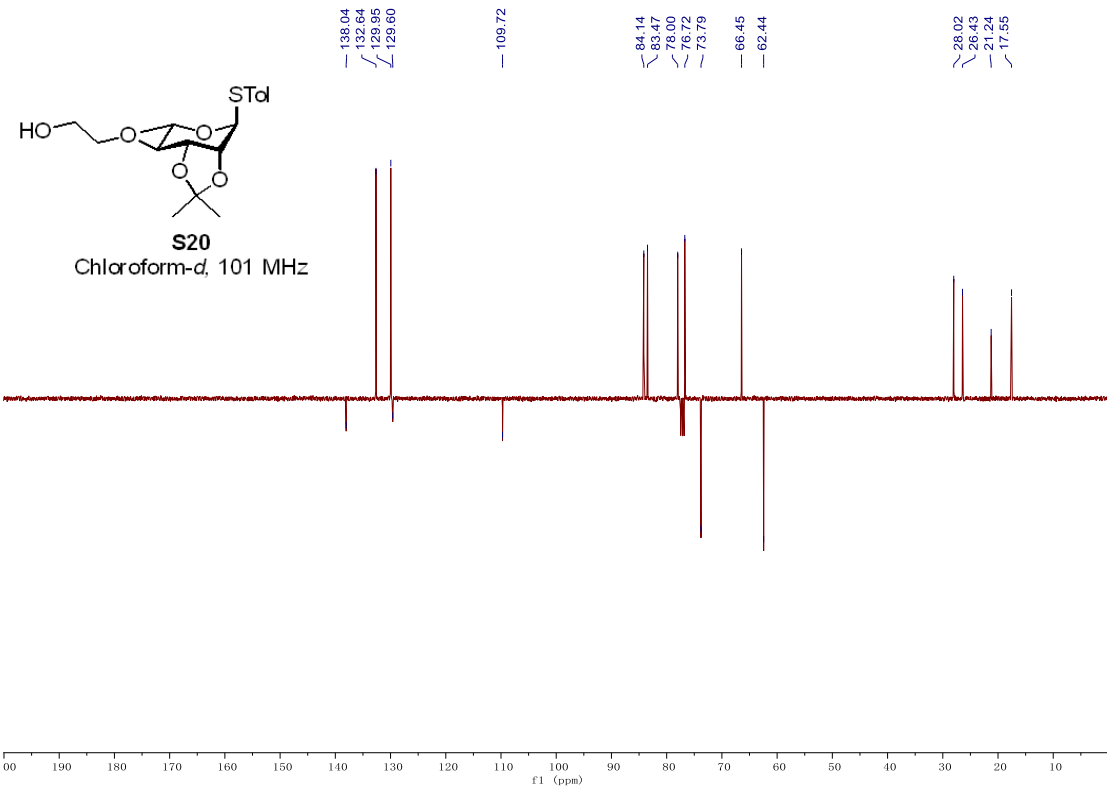
^{1}H NMR Spectra of compound 1i



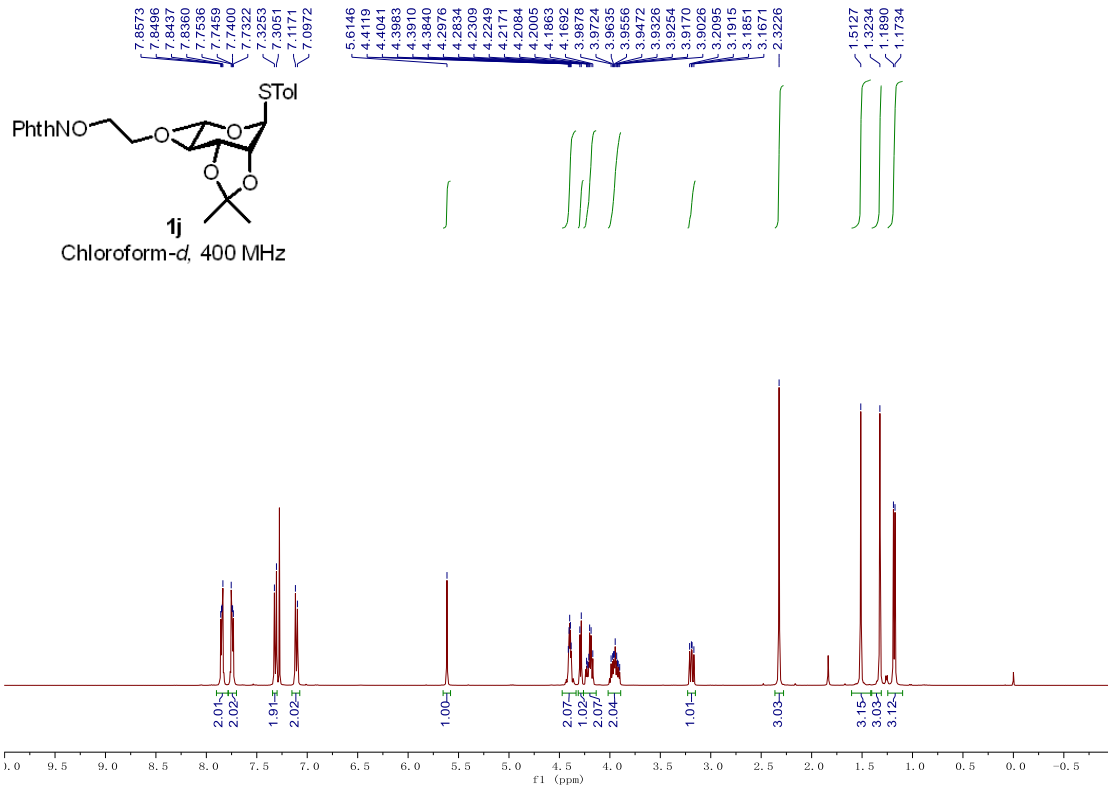
^{13}C NMR Spectra of compound 1i



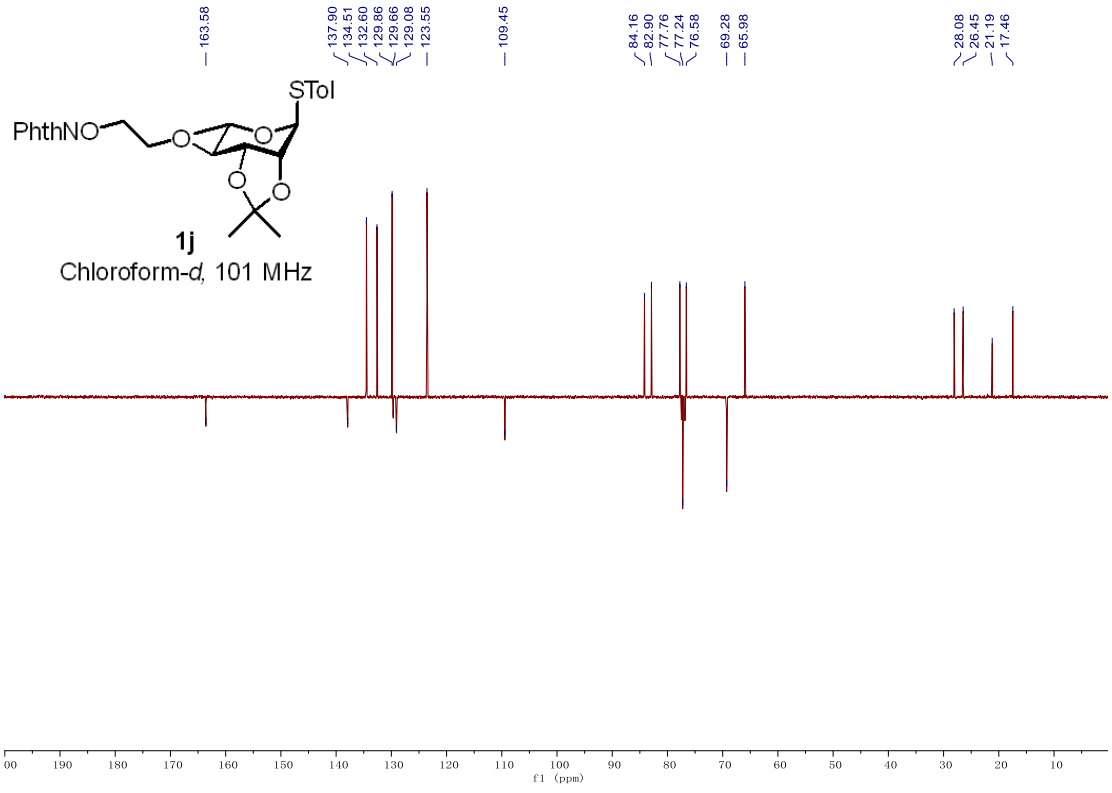
^{1}H NMR Spectra of compound S20



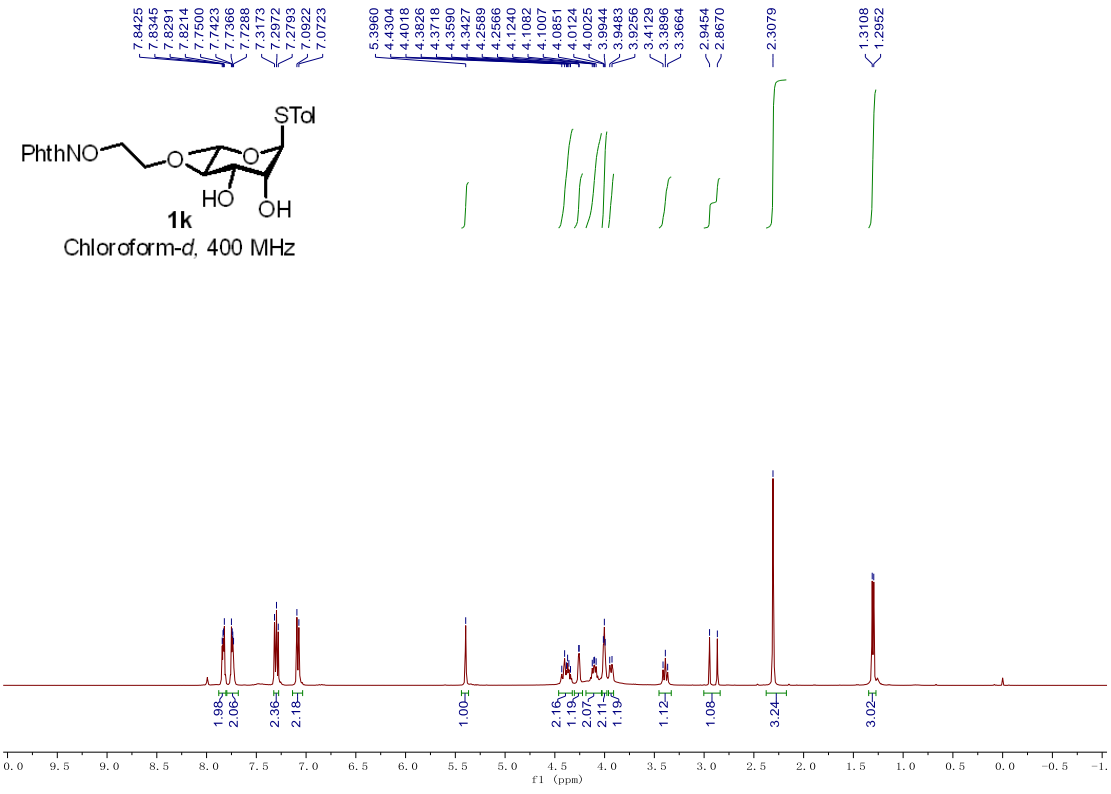
^{13}C NMR Spectra of compound S20



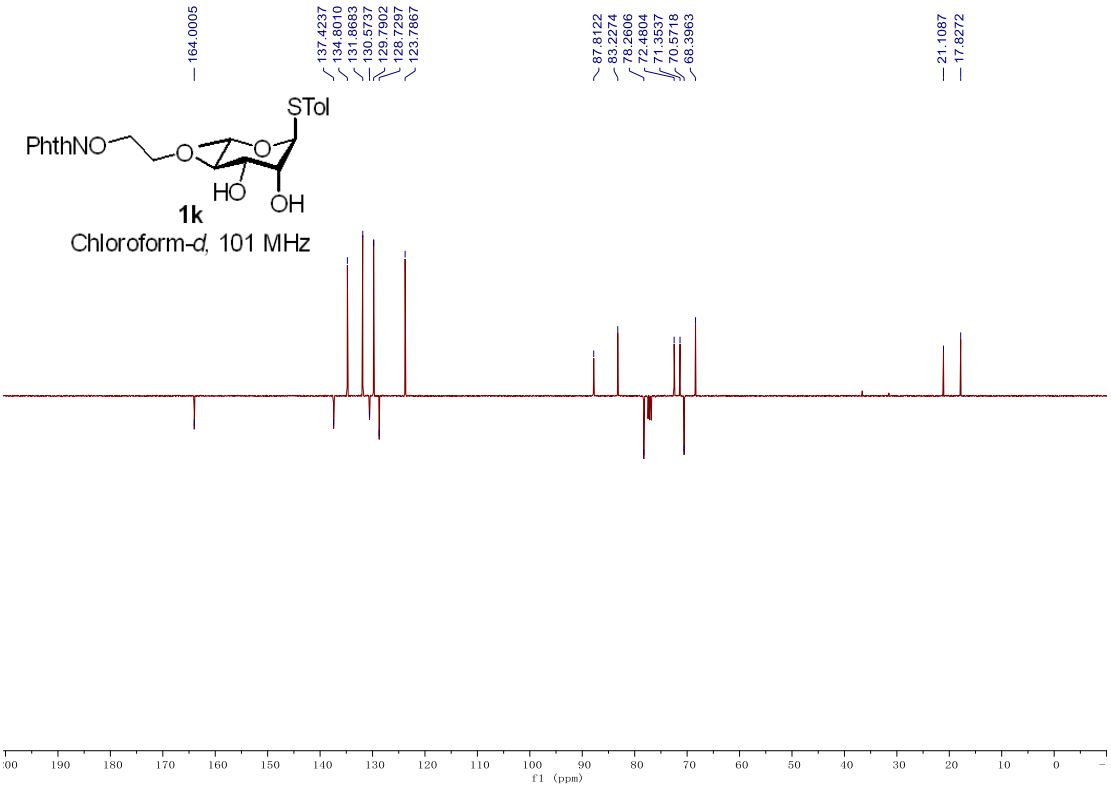
^{1}H NMR Spectra of compound 1j



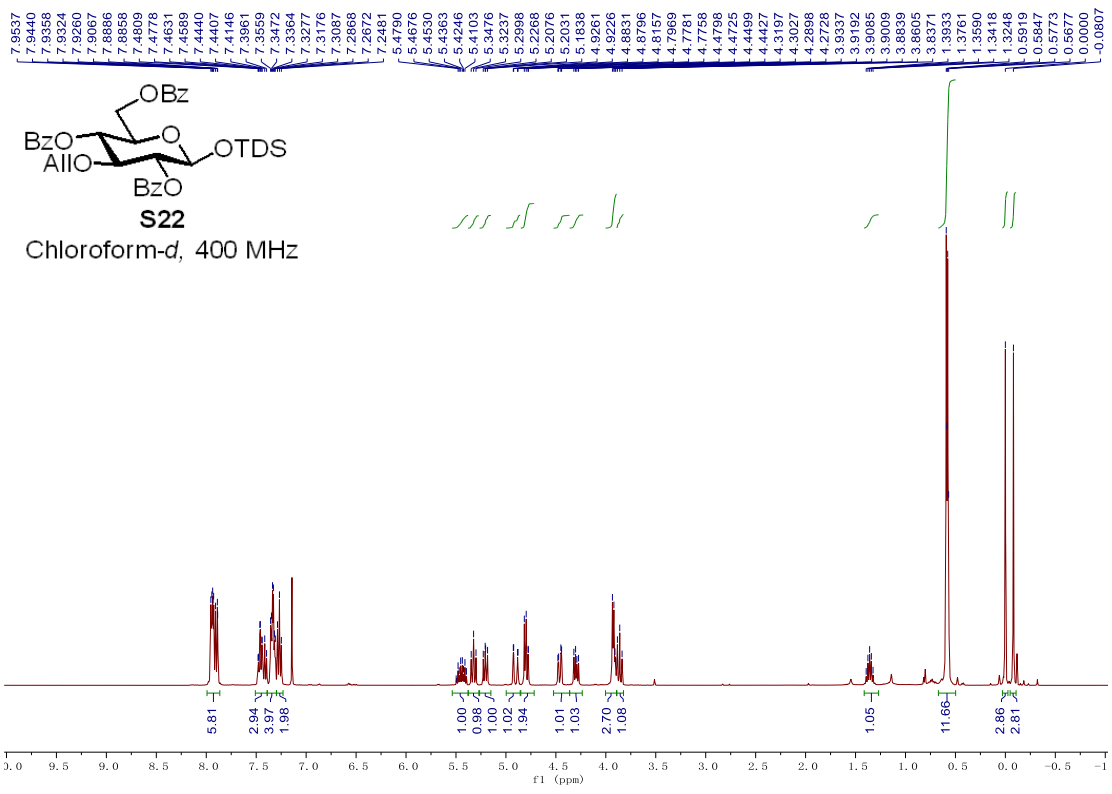
^{13}C NMR Spectra of compound 1j



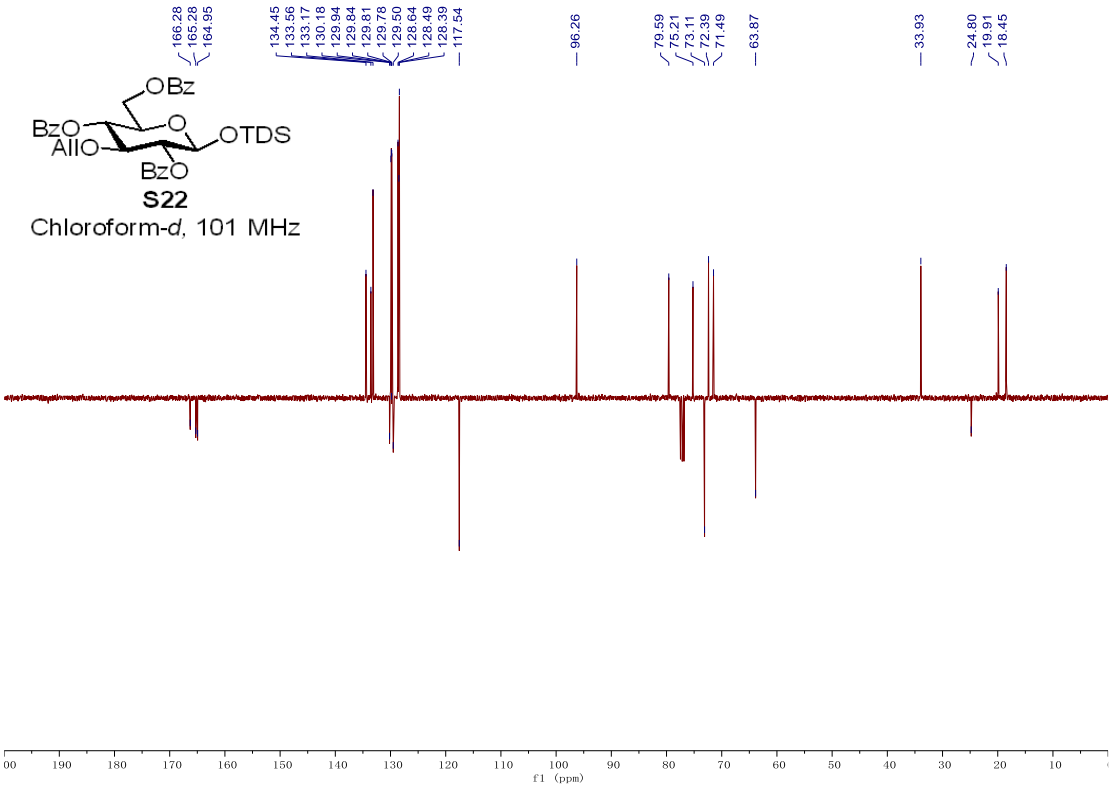
^{1}H NMR Spectra of compound 1k



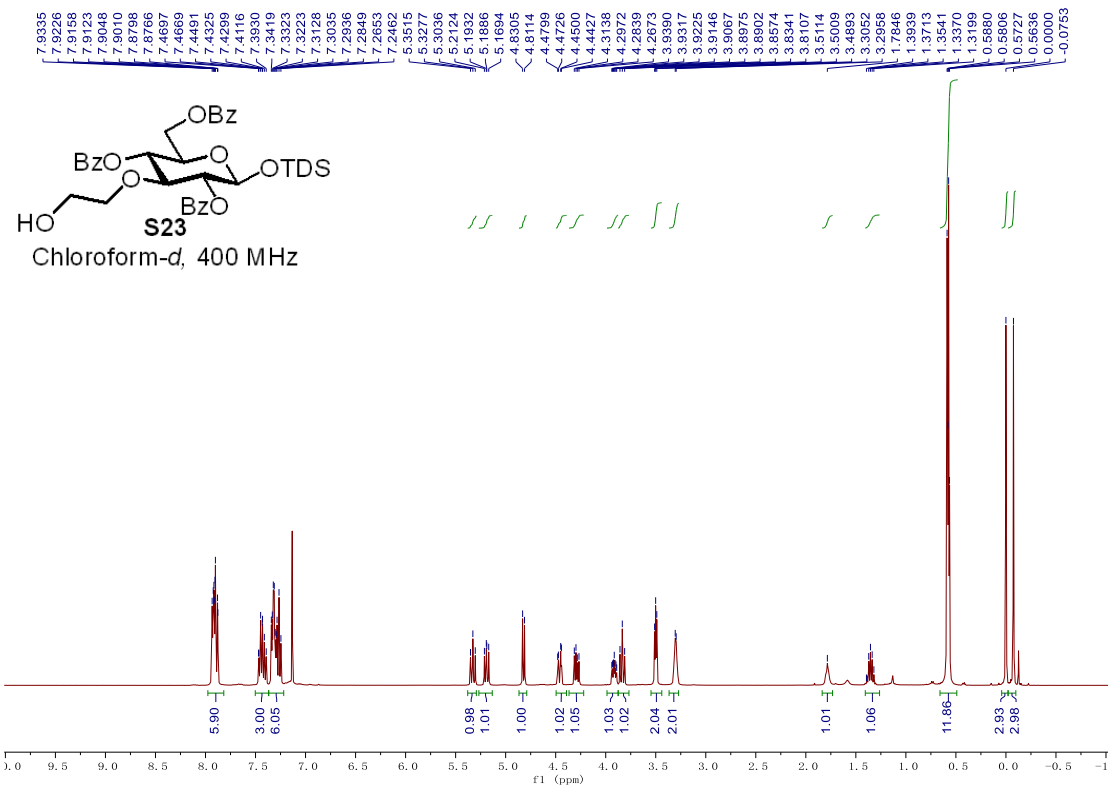
^{13}C NMR Spectra of compound 1k



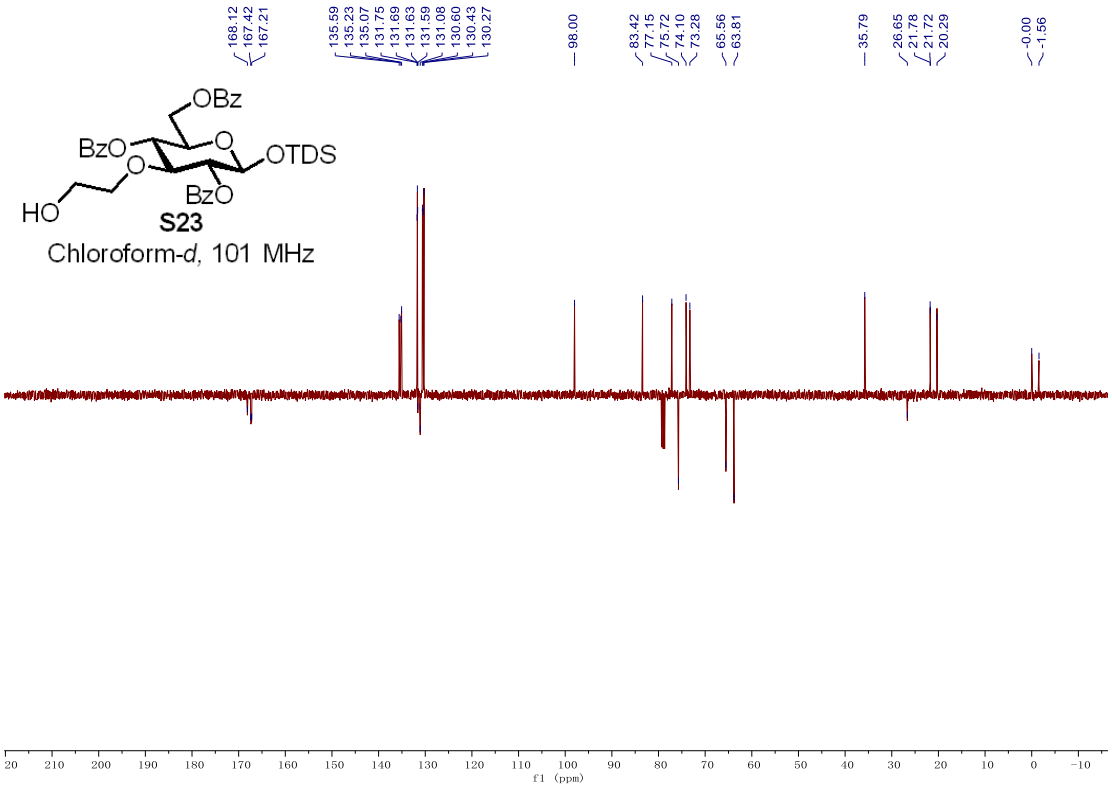
^{1}H NMR Spectra of compound S22



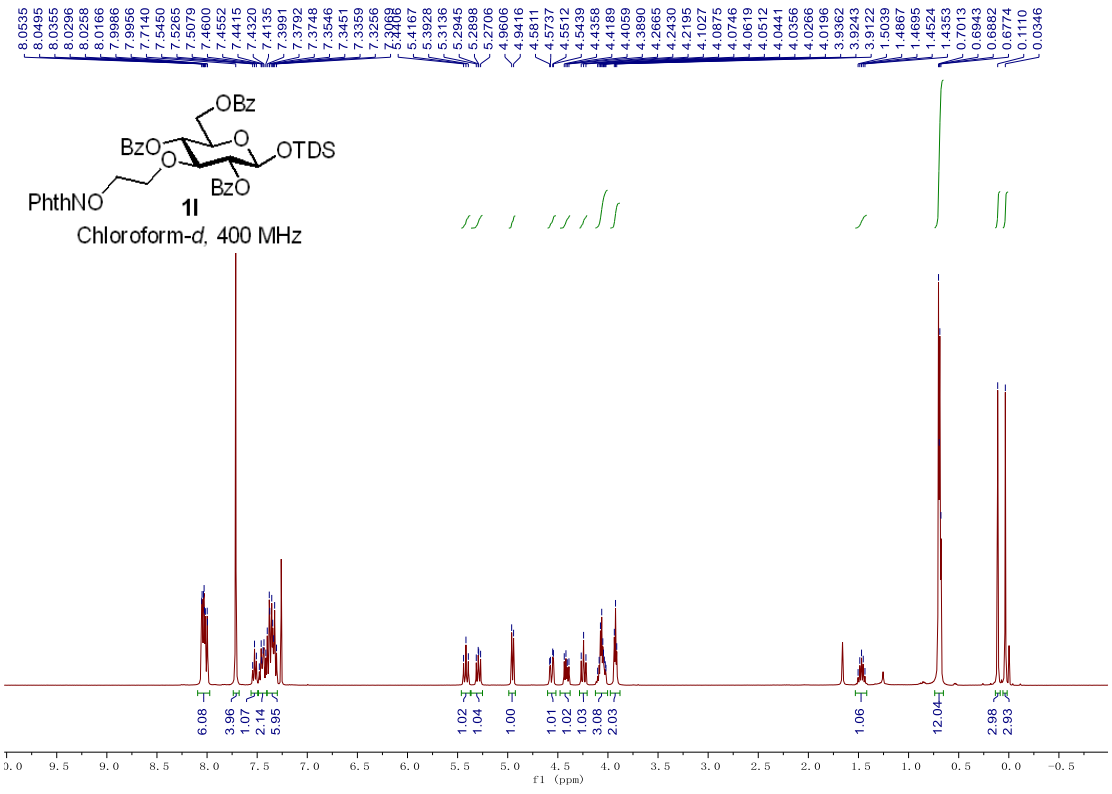
^{13}C NMR Spectra of compound S22



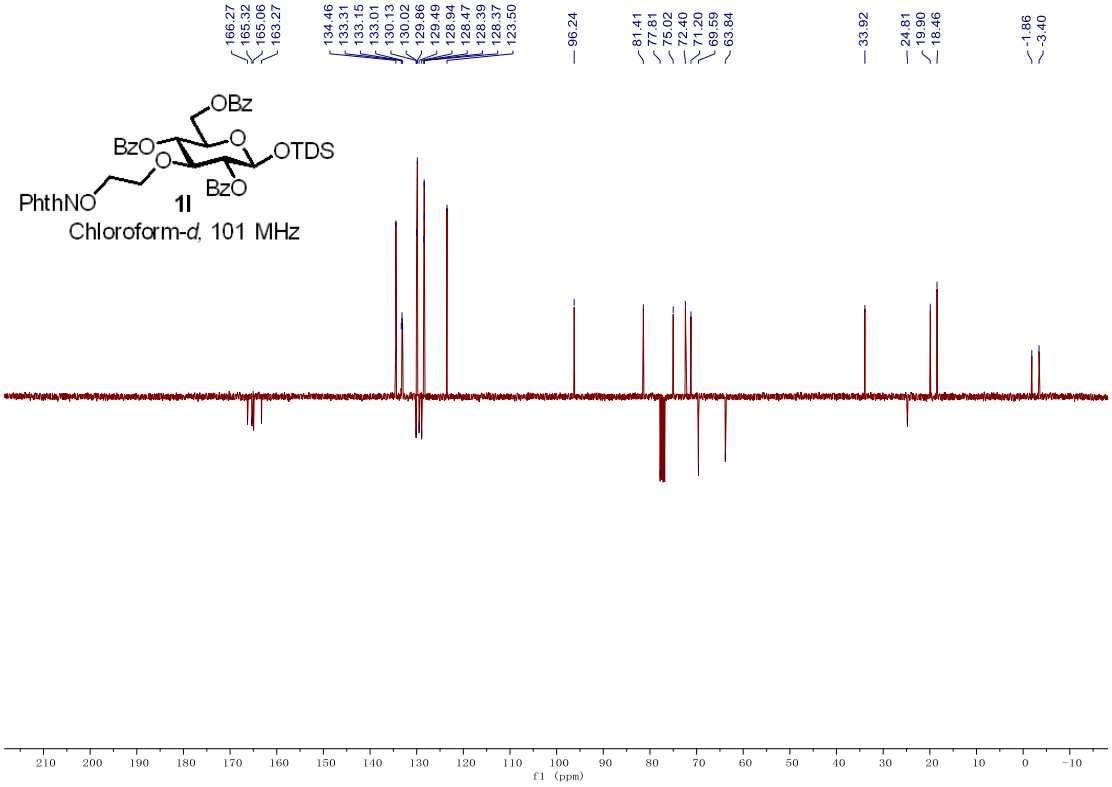
^{1}H NMR Spectra of compound S23



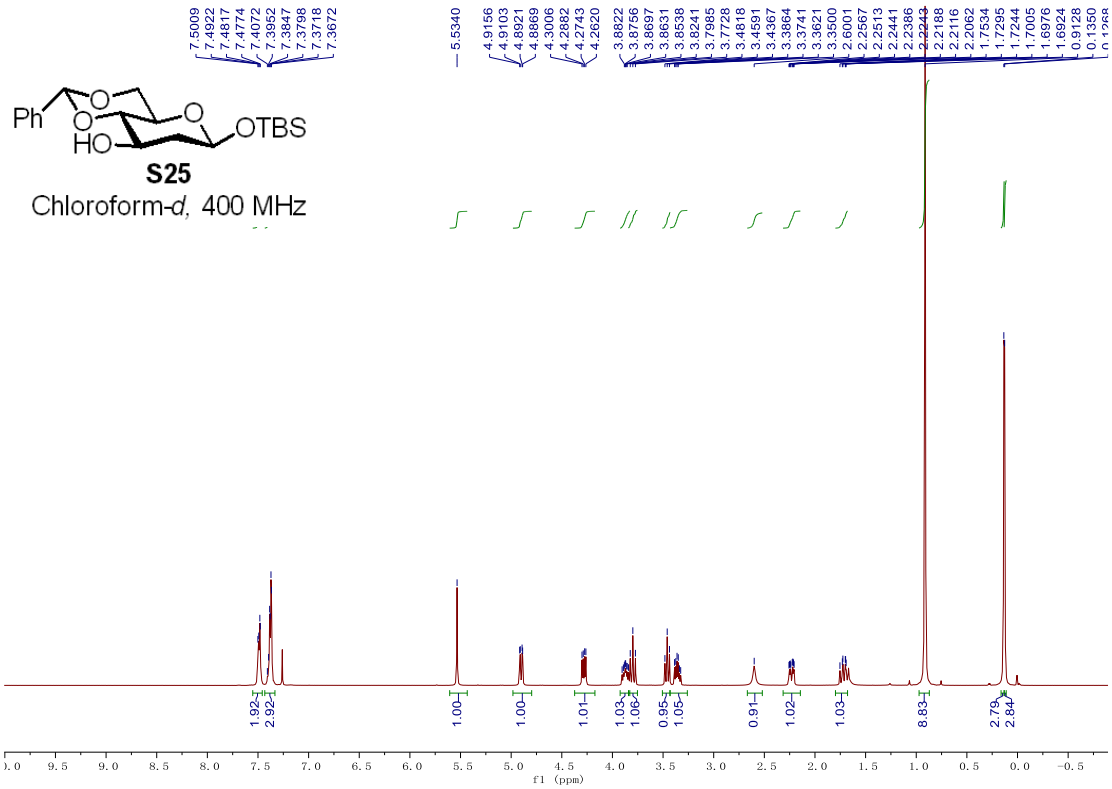
^{13}C NMR Spectra of compound S23



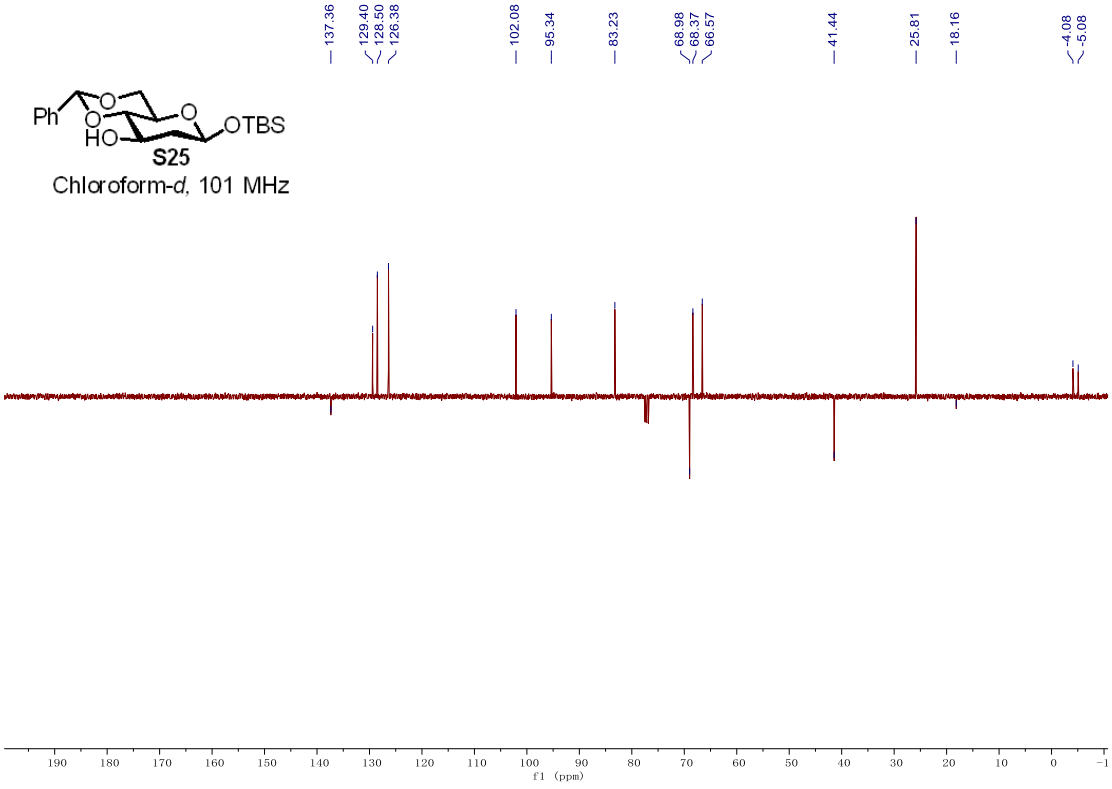
^{1}H NMR Spectra of compound 1l



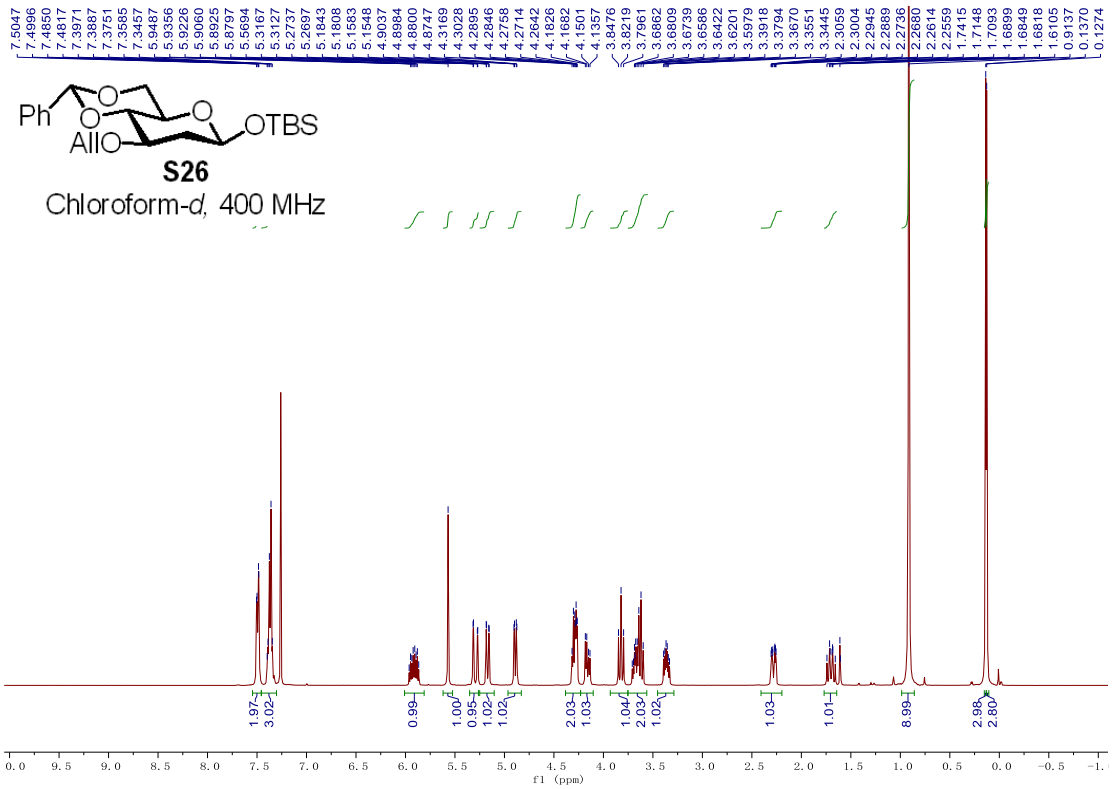
^{13}C NMR Spectra of compound 1l



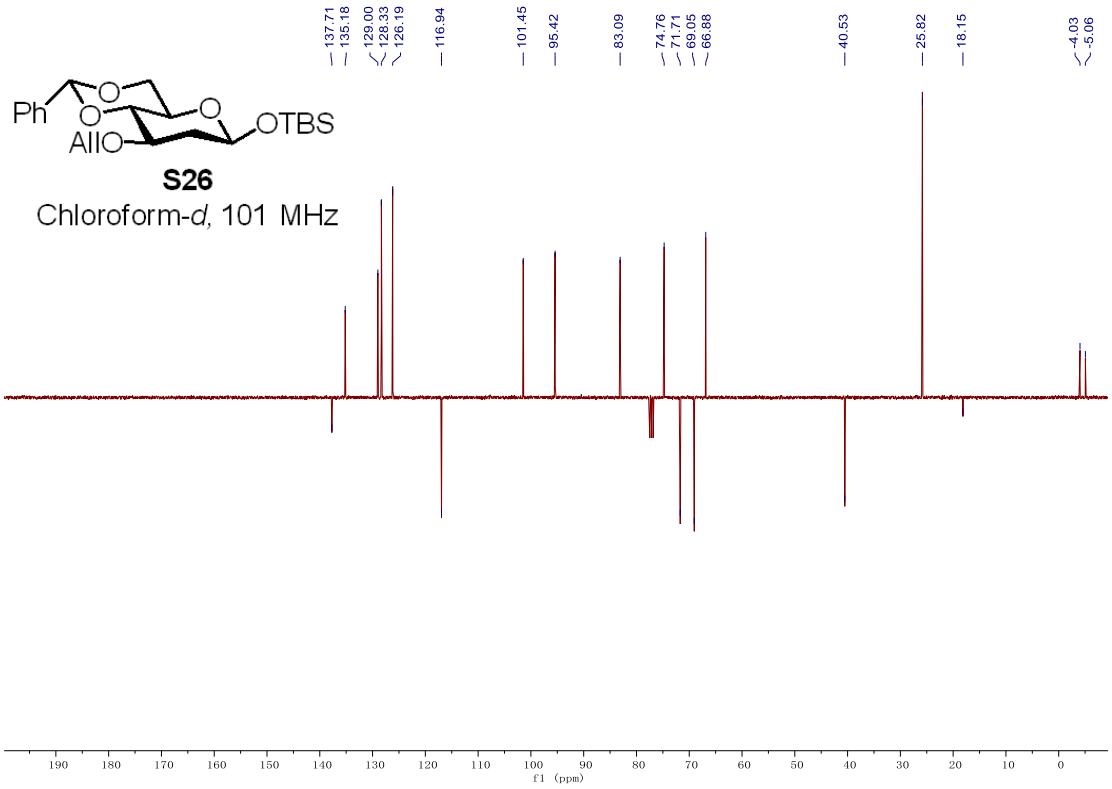
^{1}H NMR Spectra of compound S25



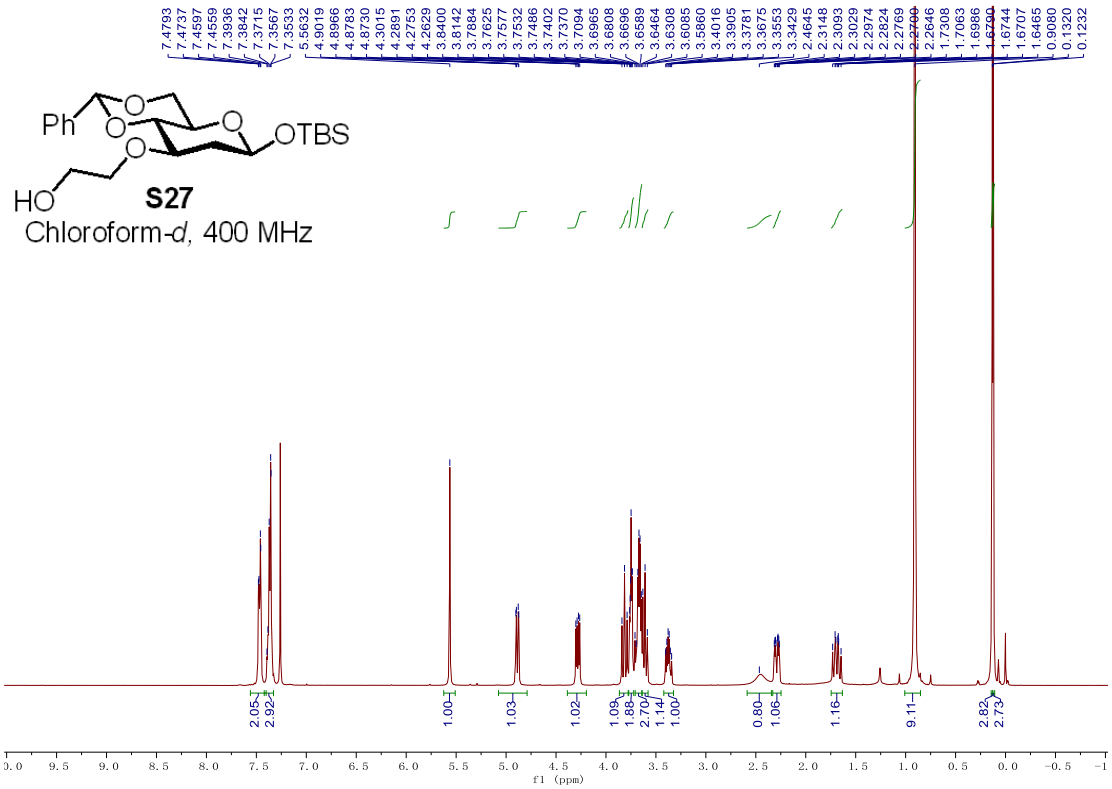
^{13}C NMR Spectra of compound S25



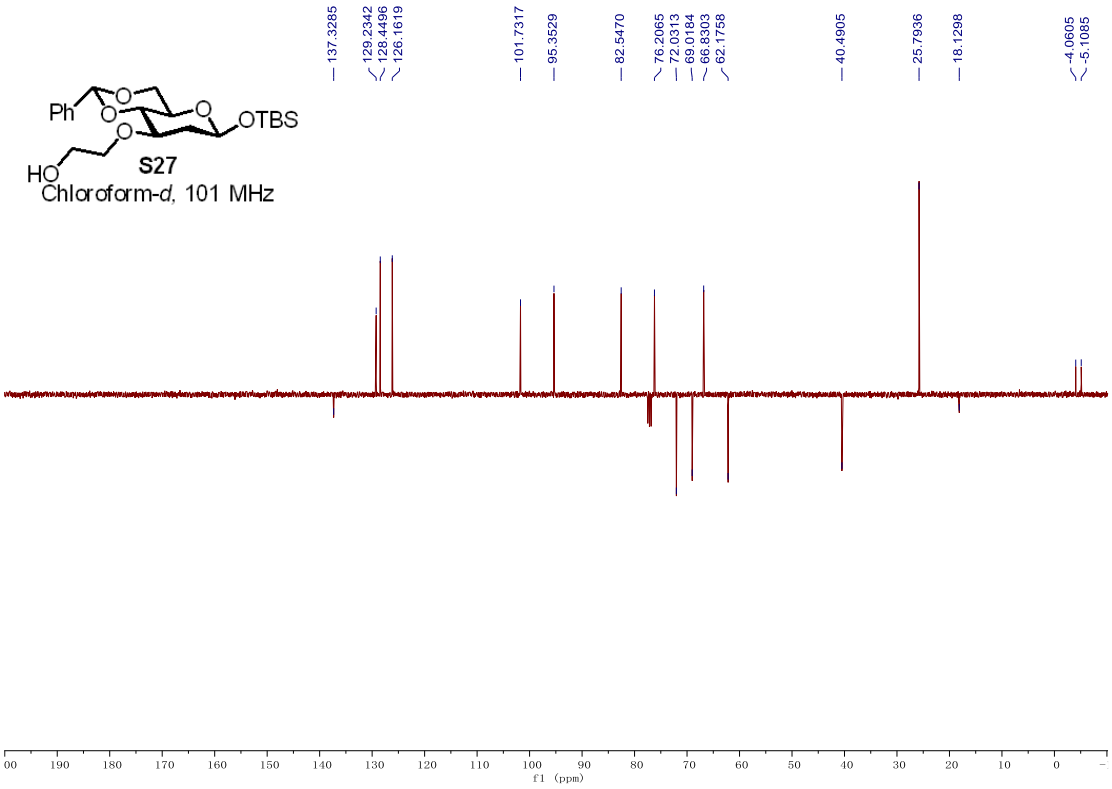
^{1}H NMR Spectra of compound S26



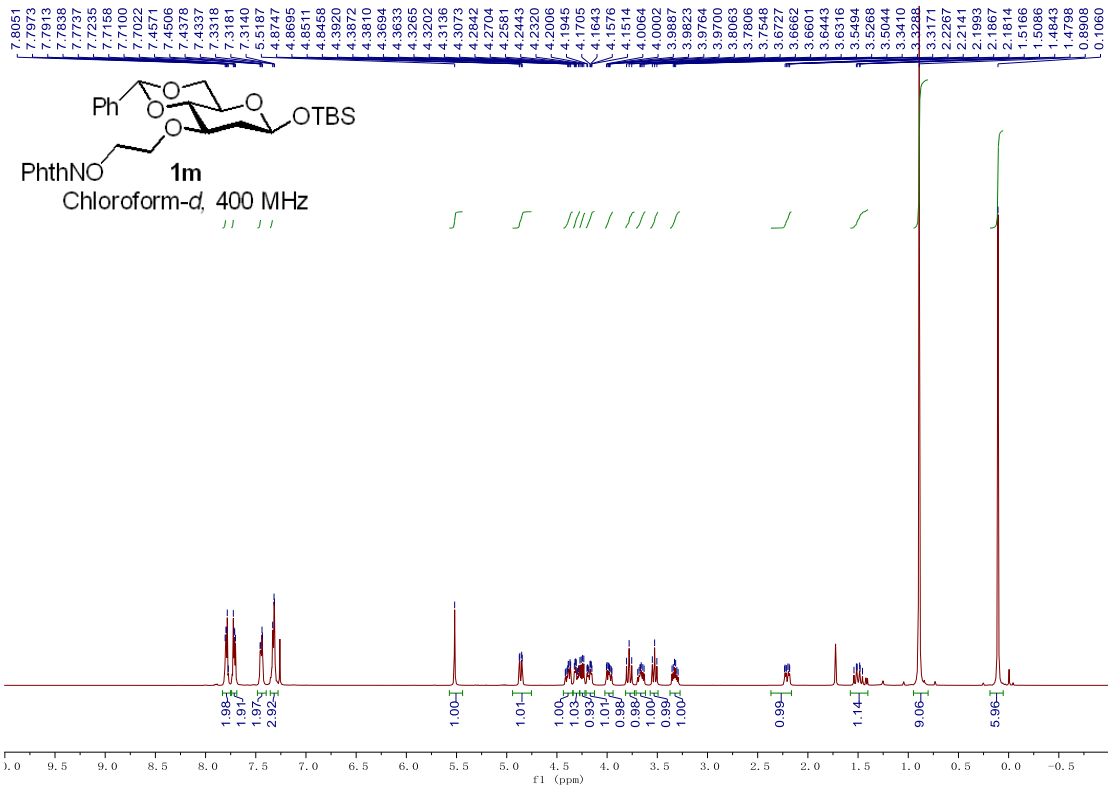
^{13}C NMR Spectra of compound S26



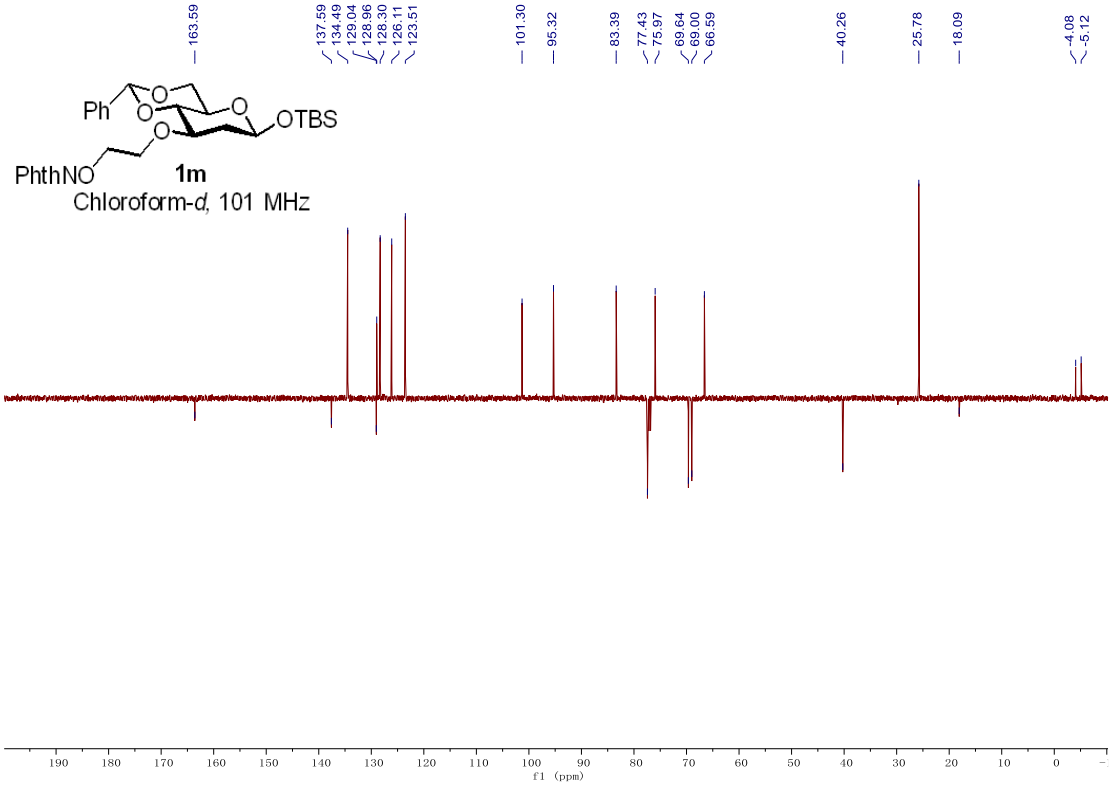
^{1}H NMR Spectra of compound S27



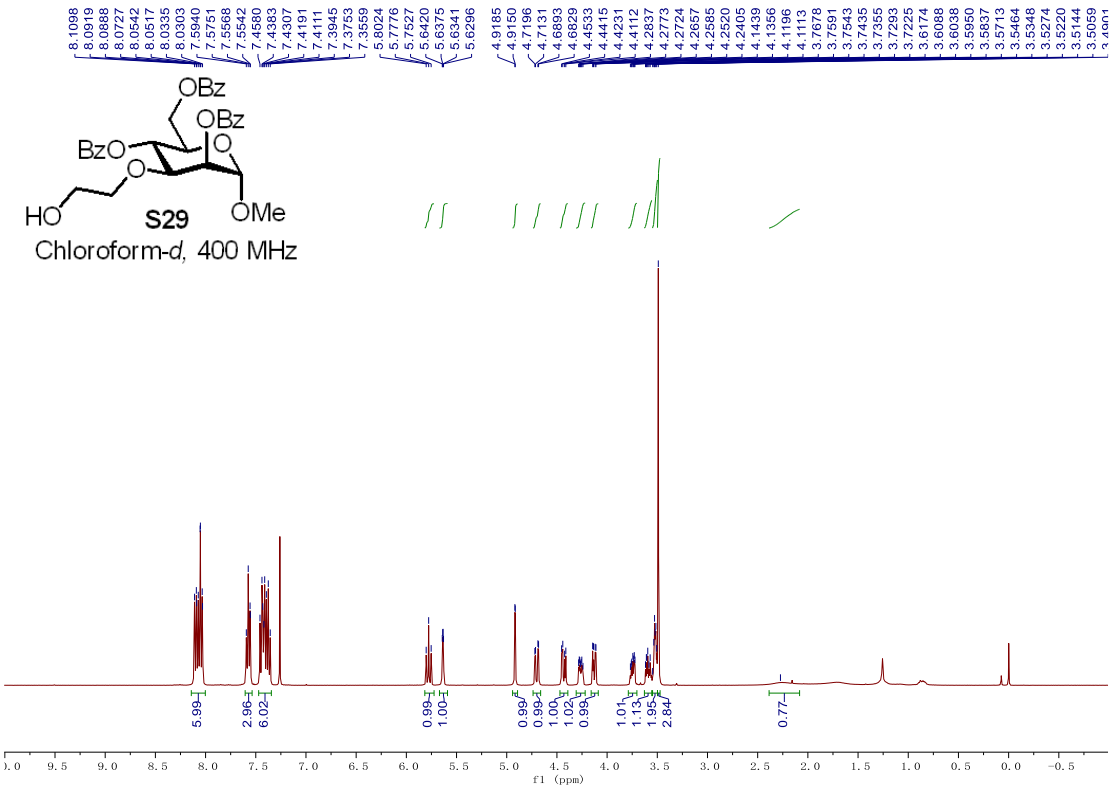
^{13}C NMR Spectra of compound S27



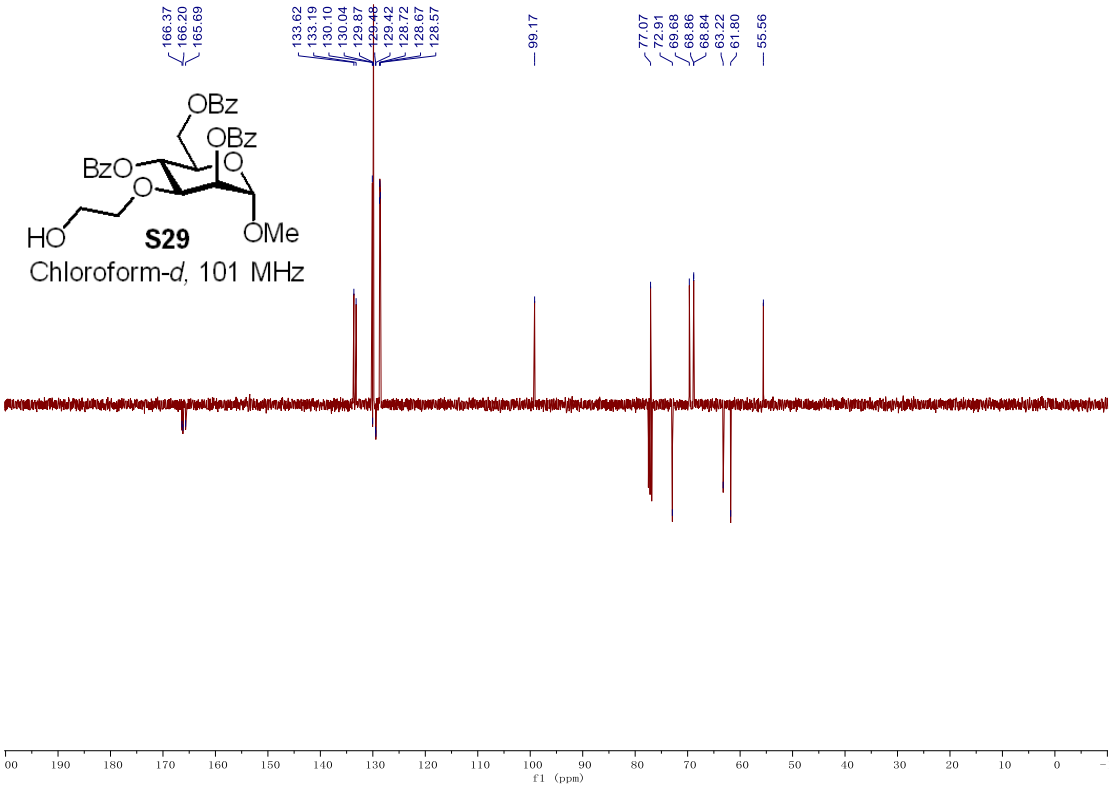
^{1}H NMR Spectra of compound 1m



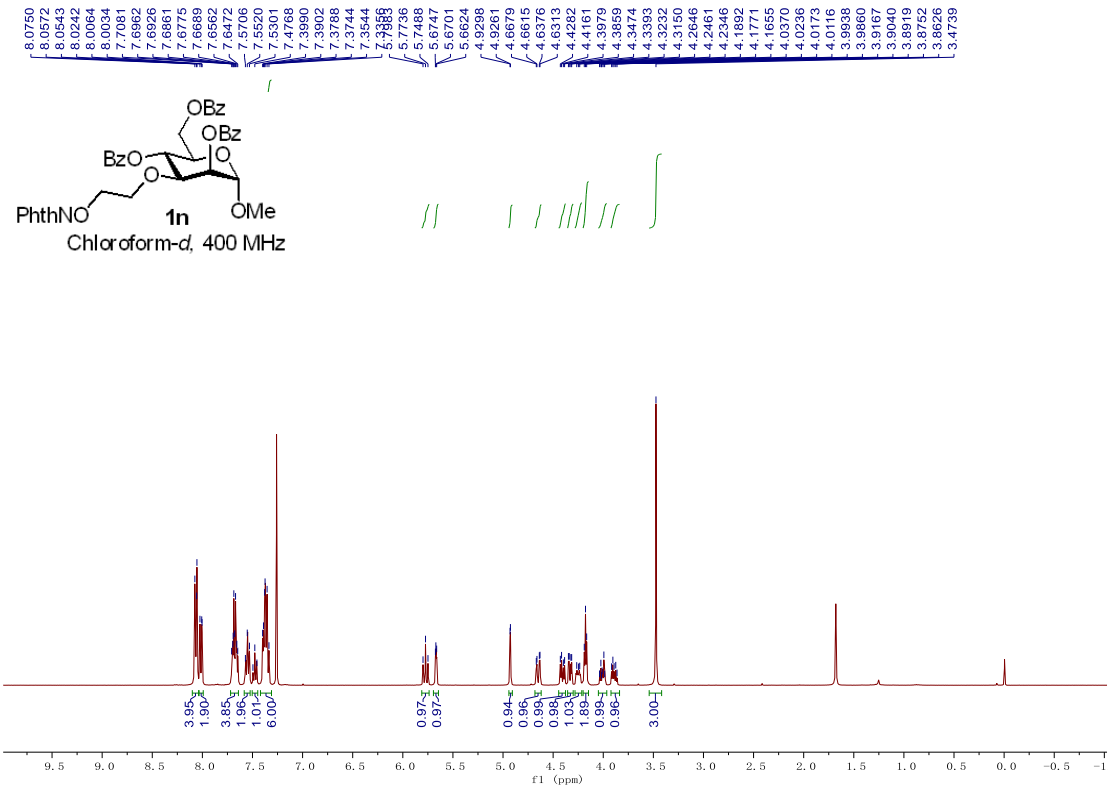
^{13}C NMR Spectra of compound 1m



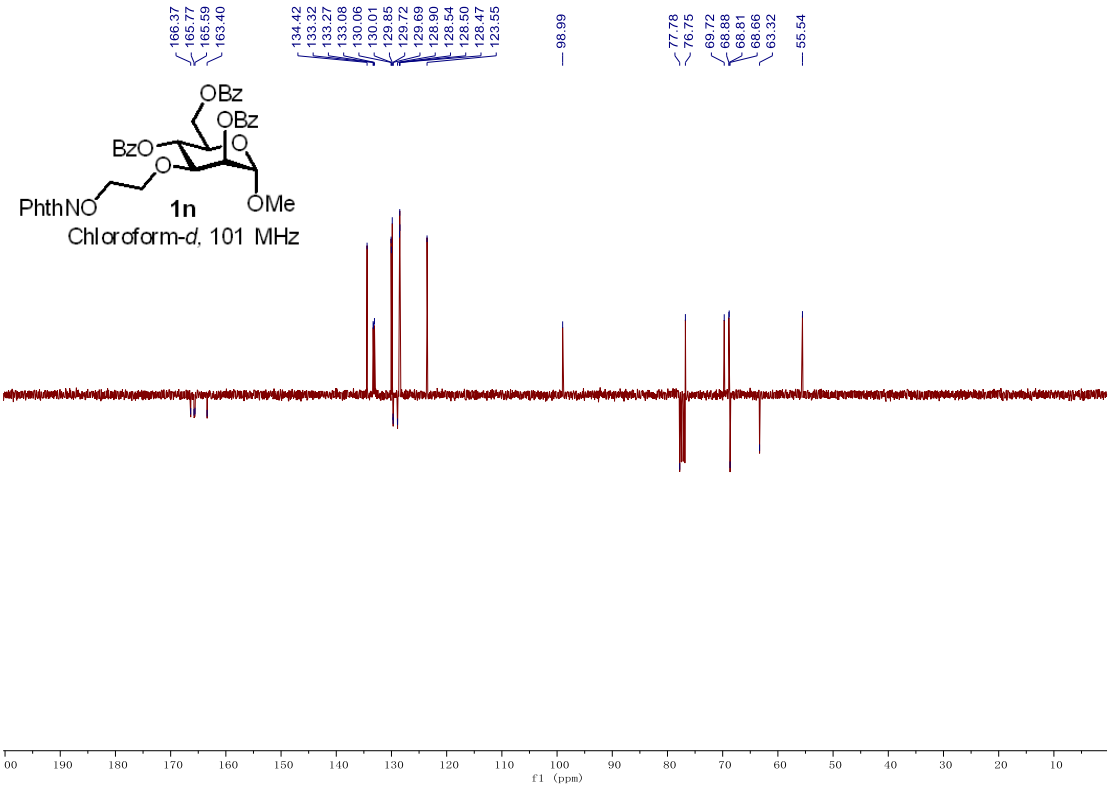
^{1}H NMR Spectra of compound S29



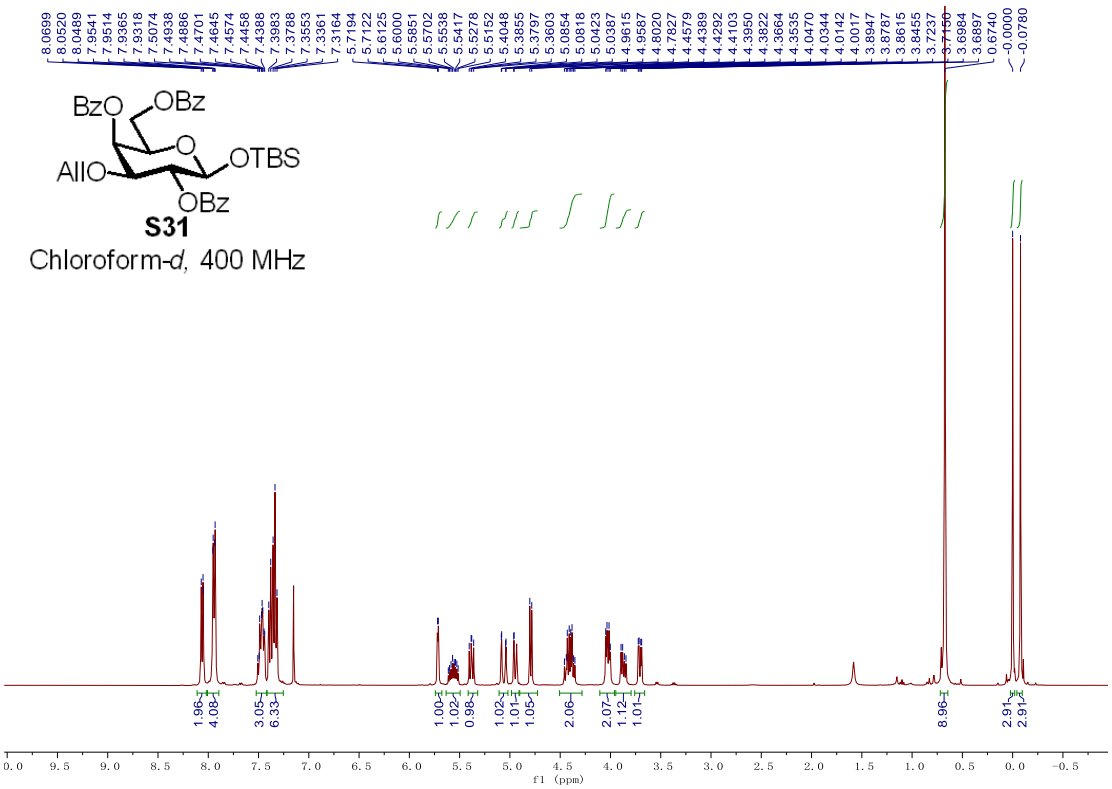
^{13}C NMR Spectra of compound S29



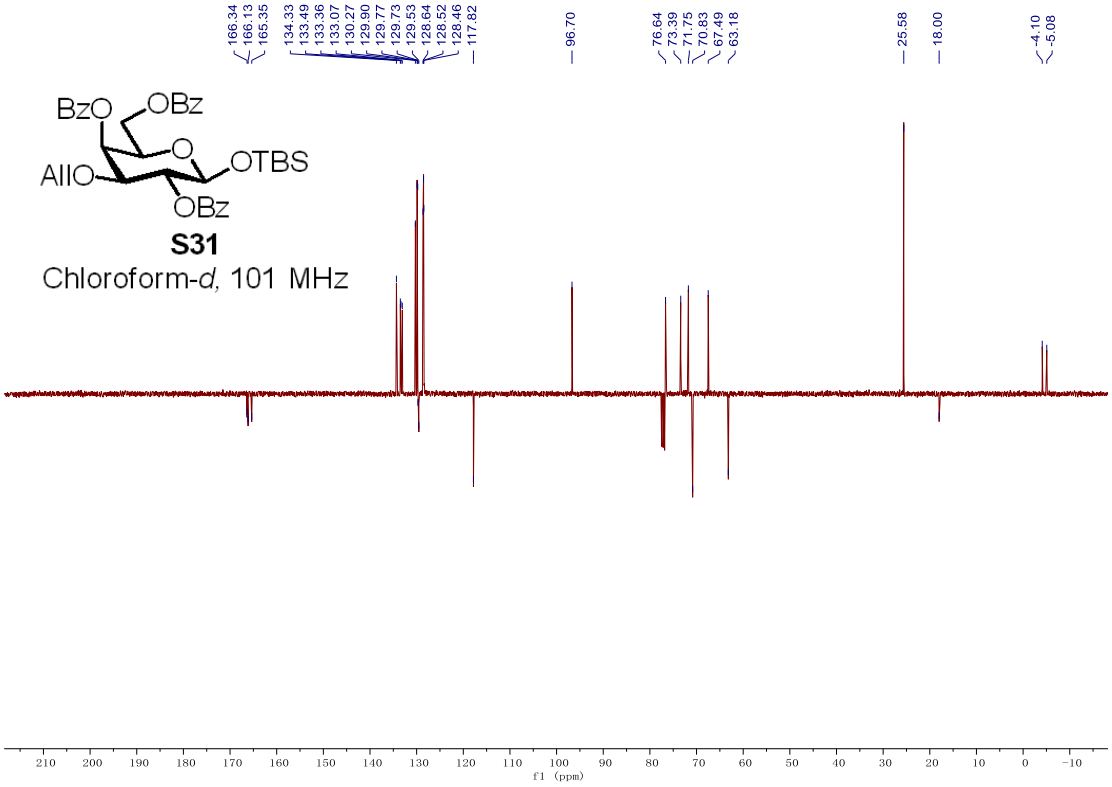
^{1}H NMR Spectra of compound 1n



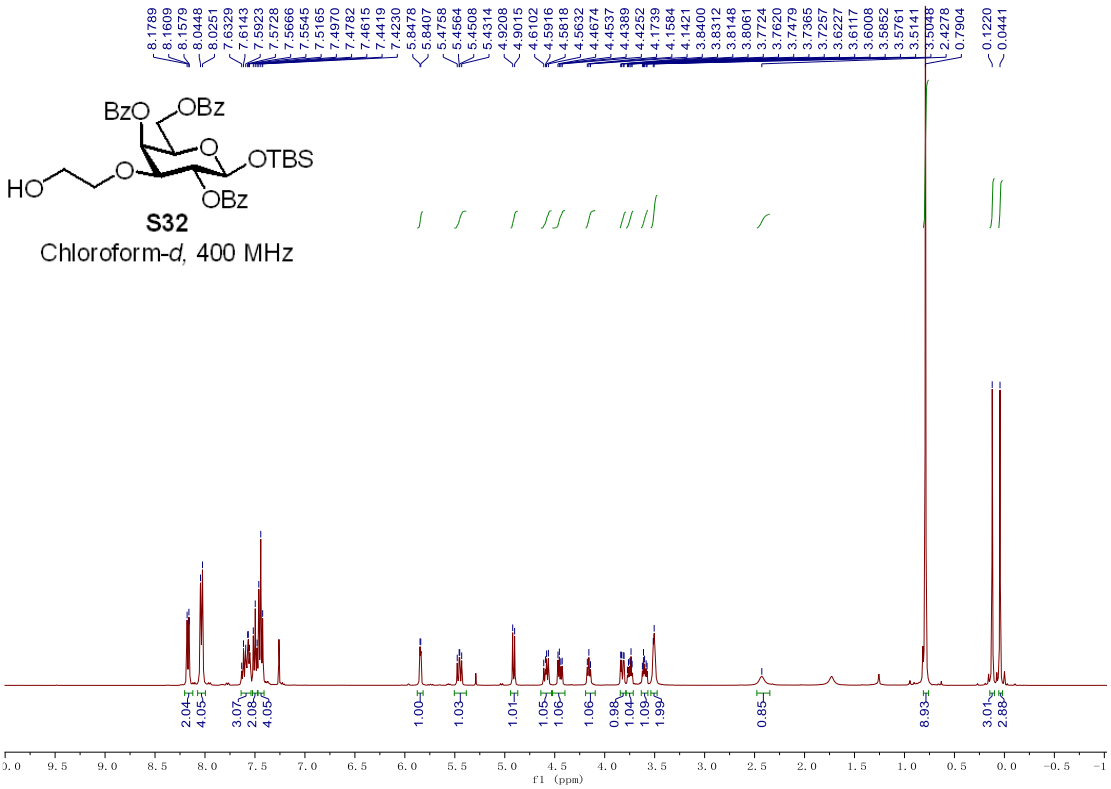
^{13}C NMR Spectra of compound 1n



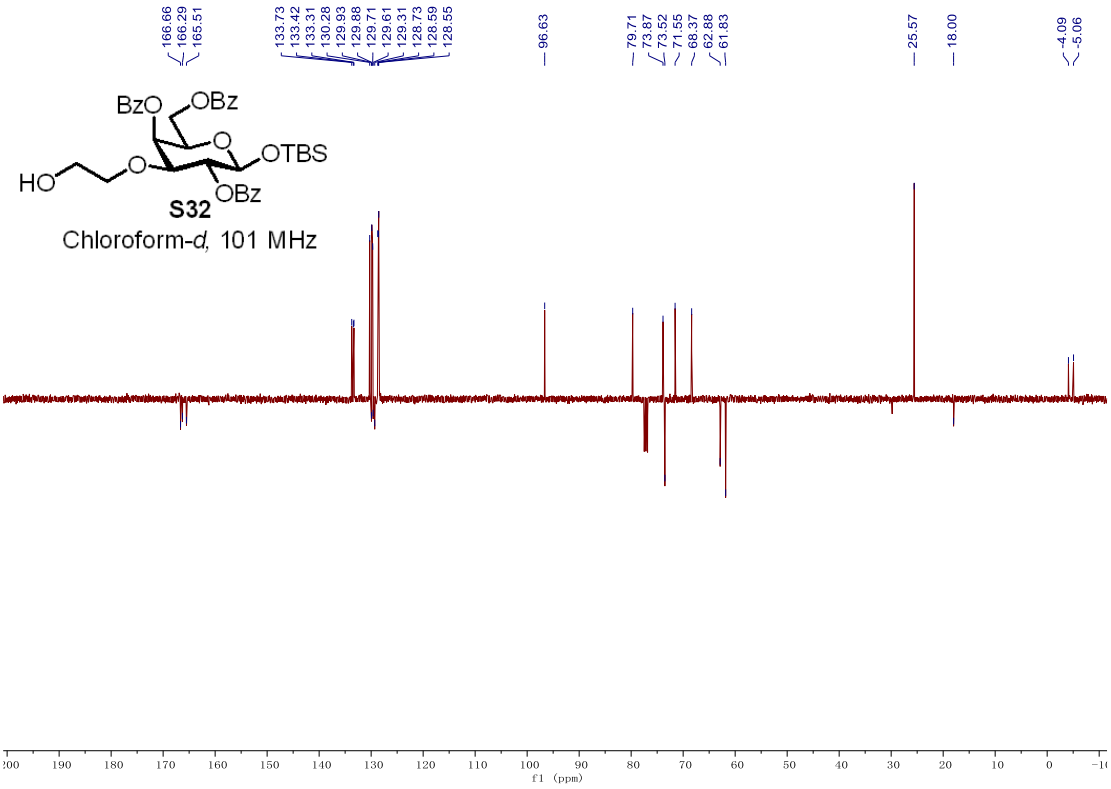
^{1}H NMR Spectra of compound S31



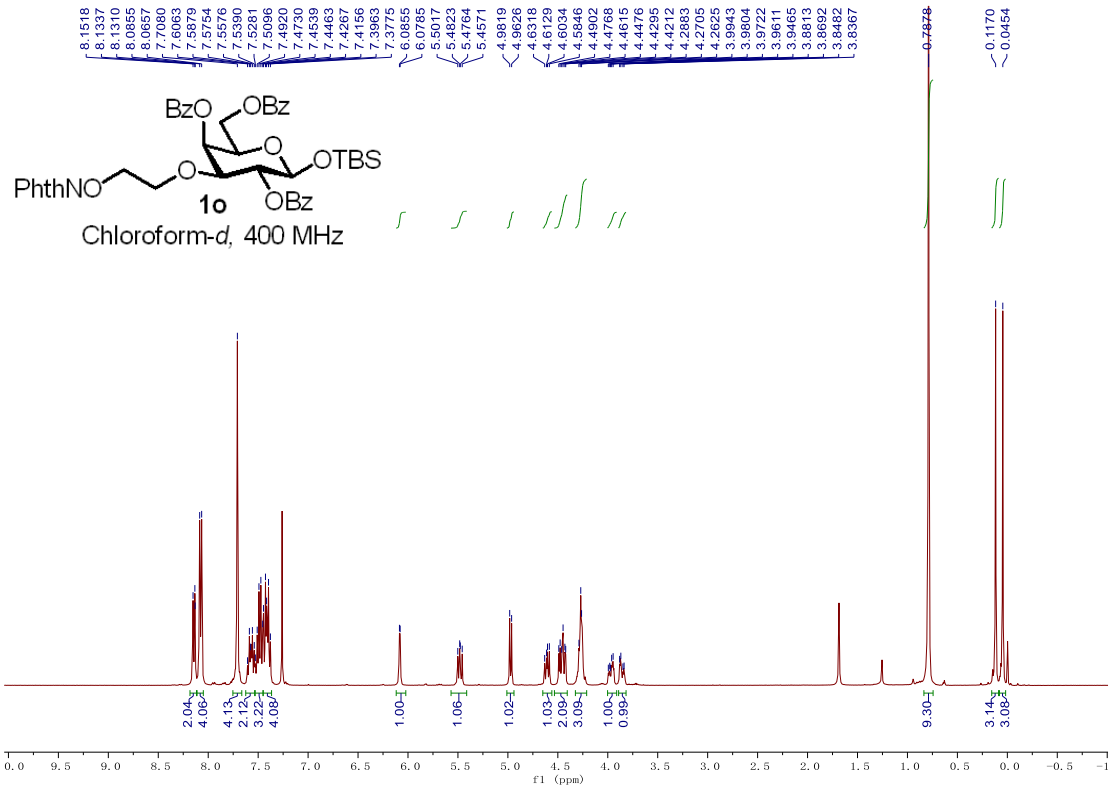
^{13}C NMR Spectra of compound S31



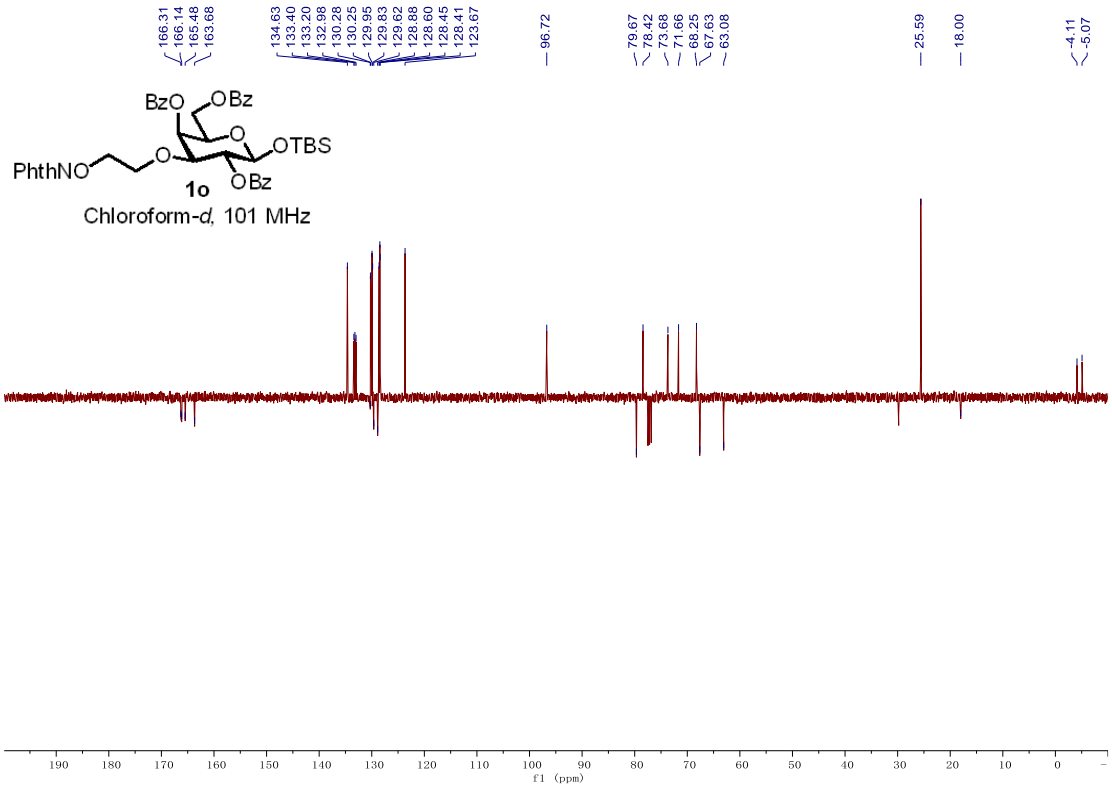
^{1}H NMR Spectra of compound S32



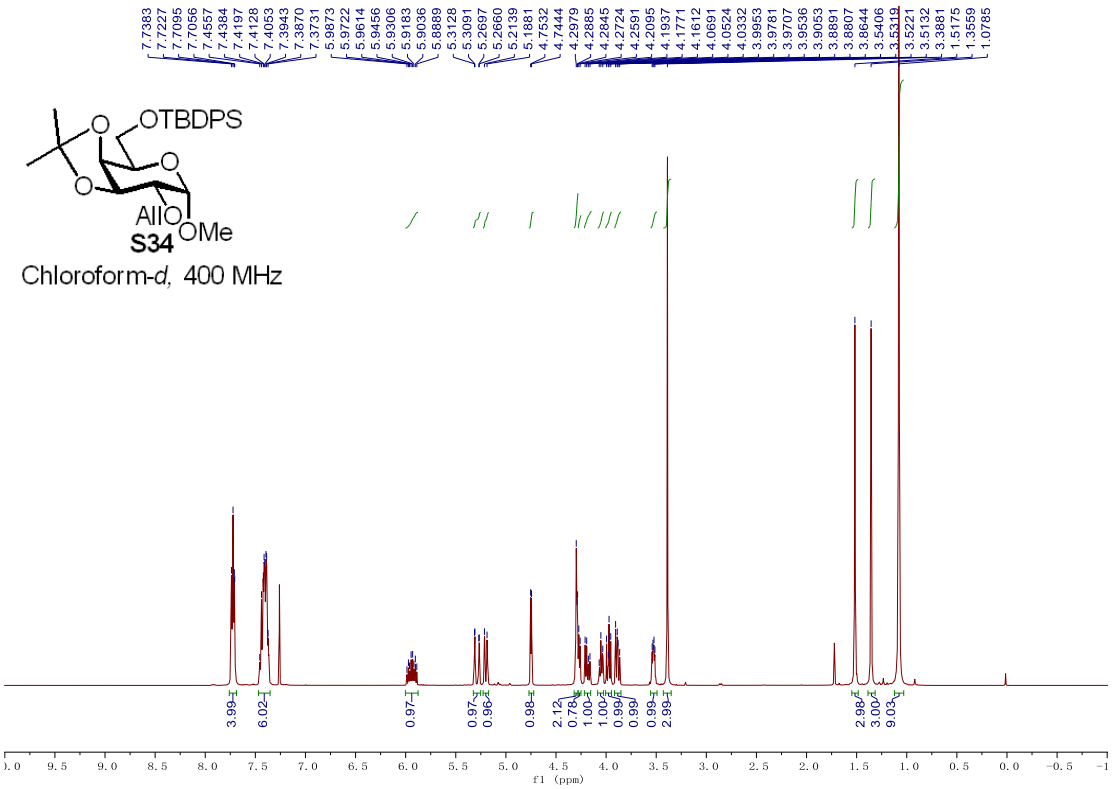
^{13}C NMR Spectra of compound S32



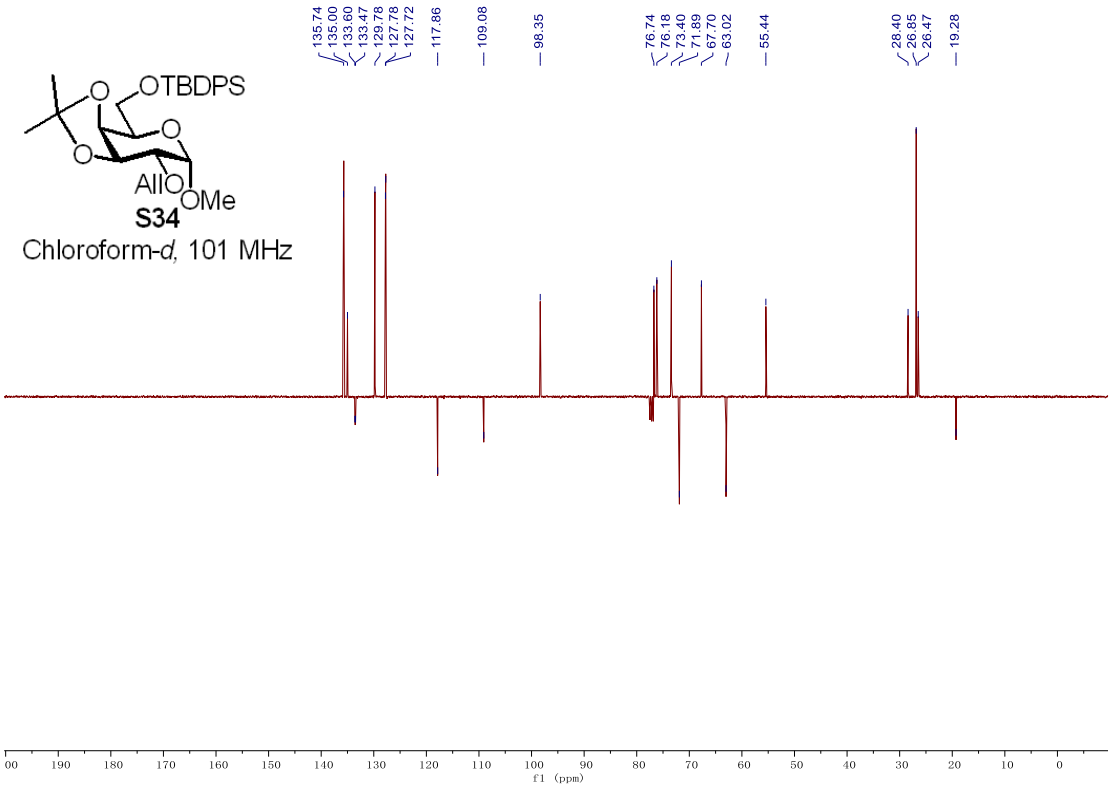
^{1}H NMR Spectra of compound 1o



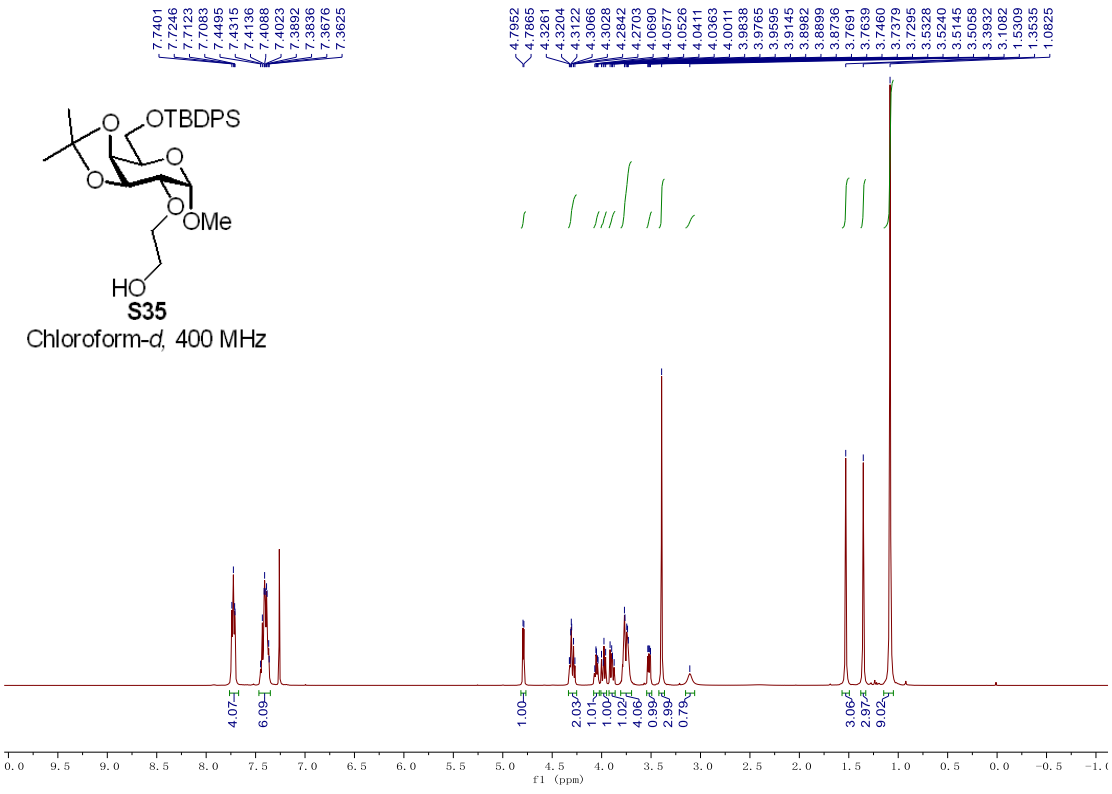
^{13}C NMR Spectra of compound 1o



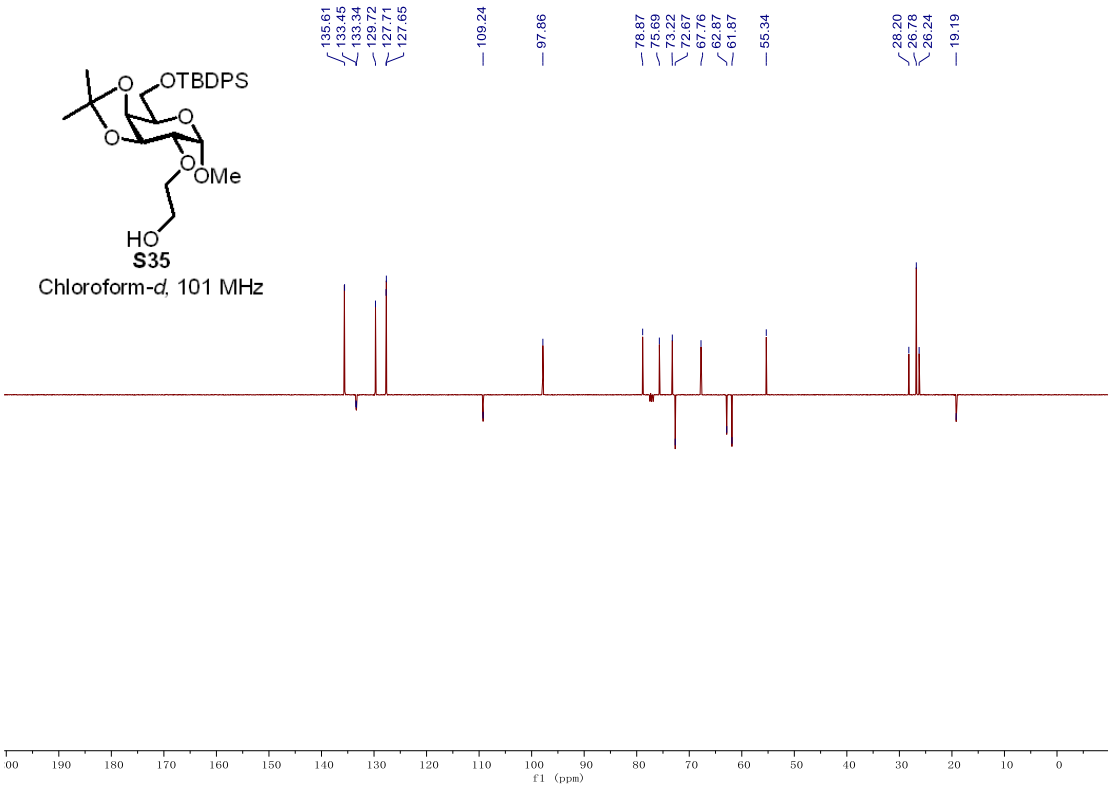
^{1}H NMR Spectra of compound S34



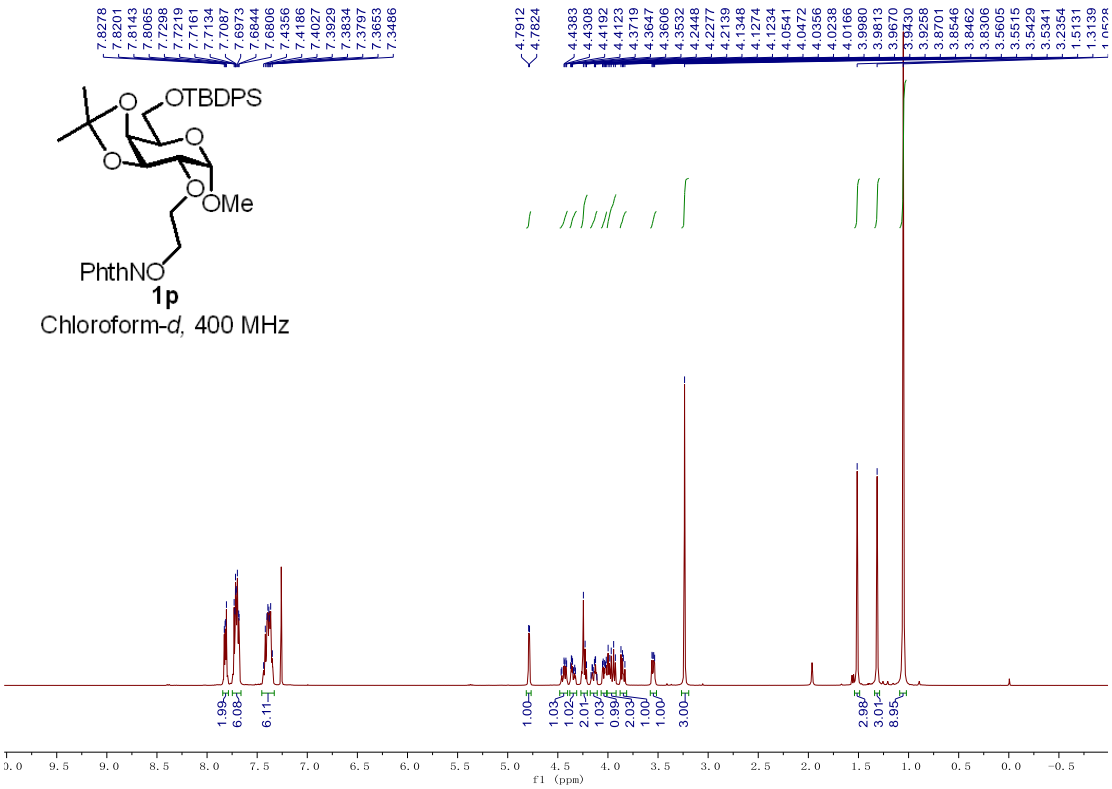
^{13}C NMR Spectra of compound S34



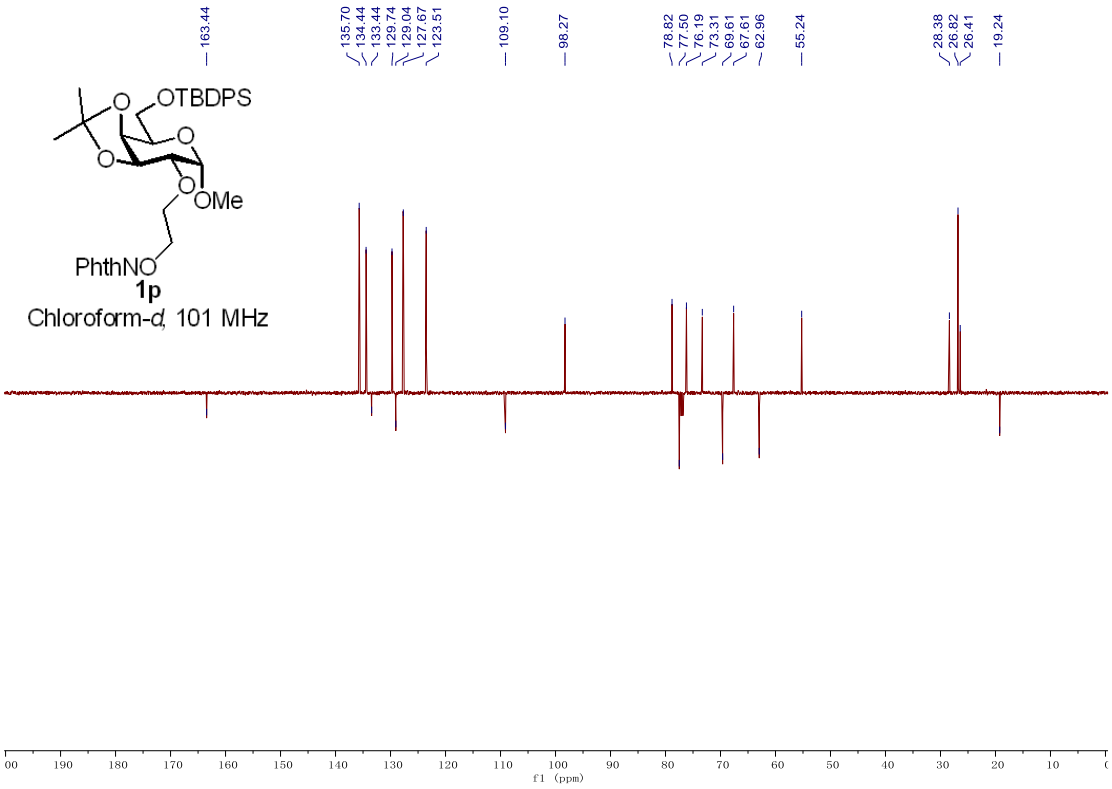
^{1}H NMR Spectra of compound S35



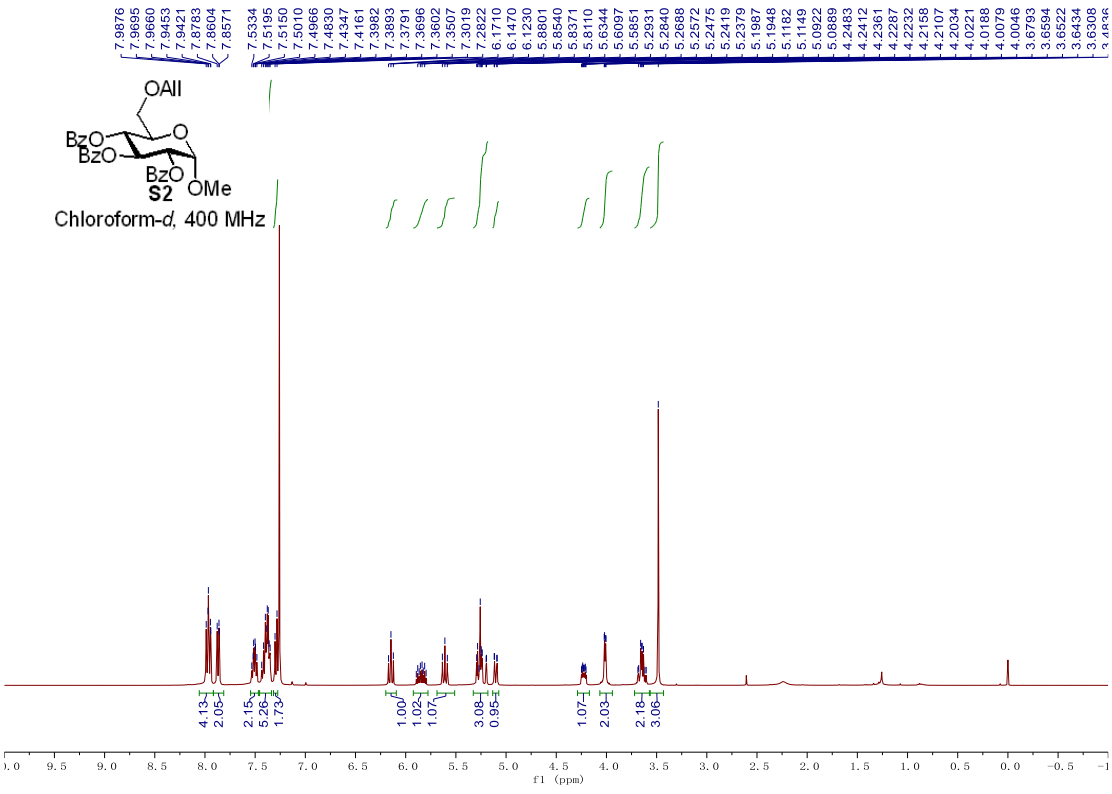
^{13}C NMR Spectra of compound S35



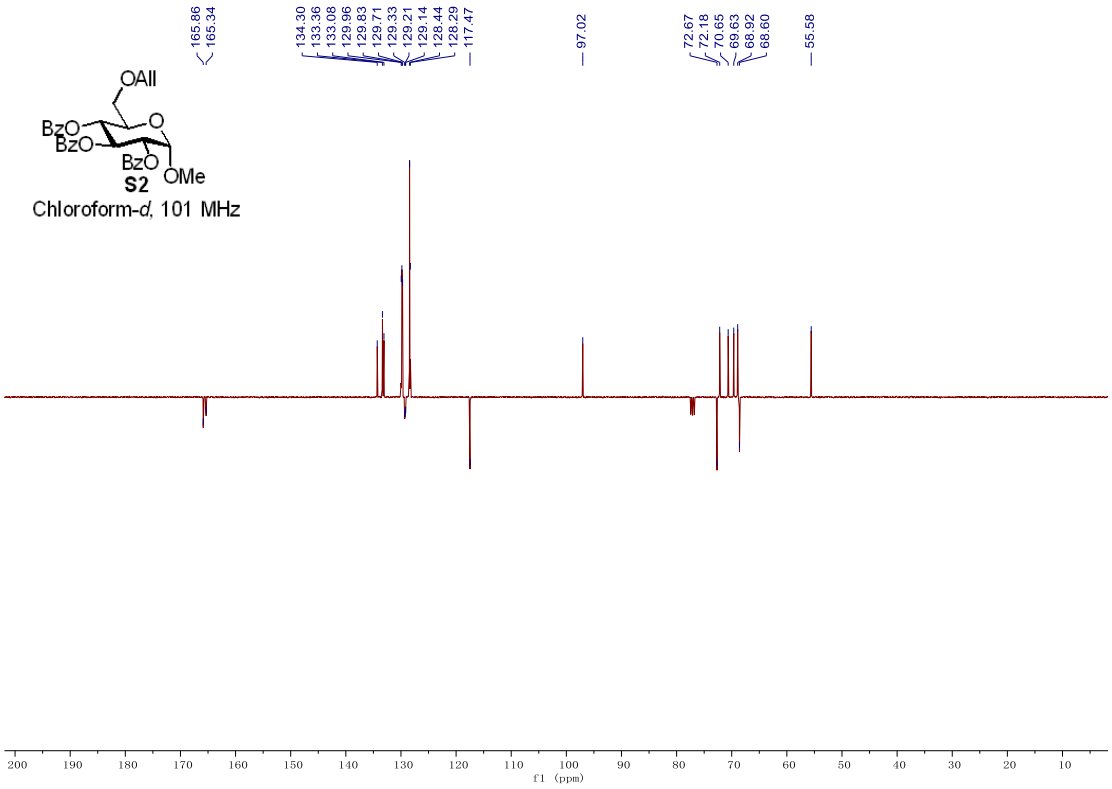
^{1}H NMR Spectra of compound 1p



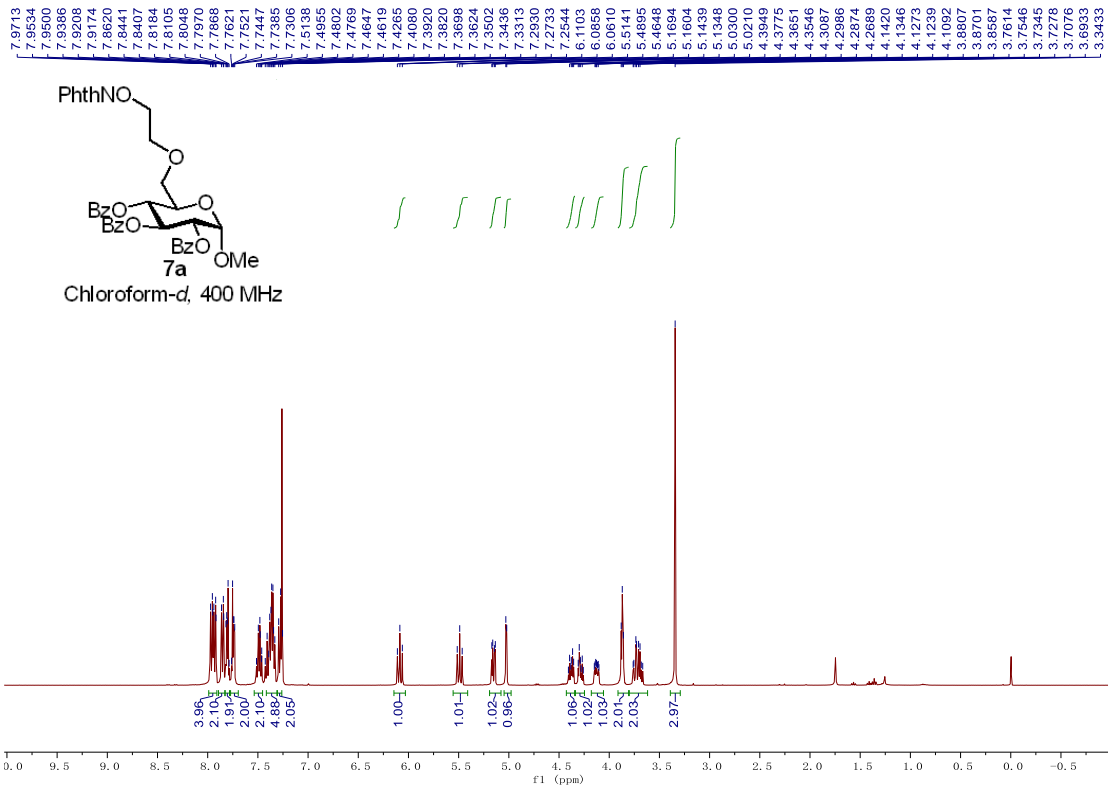
^{13}C NMR Spectra of compound 1p



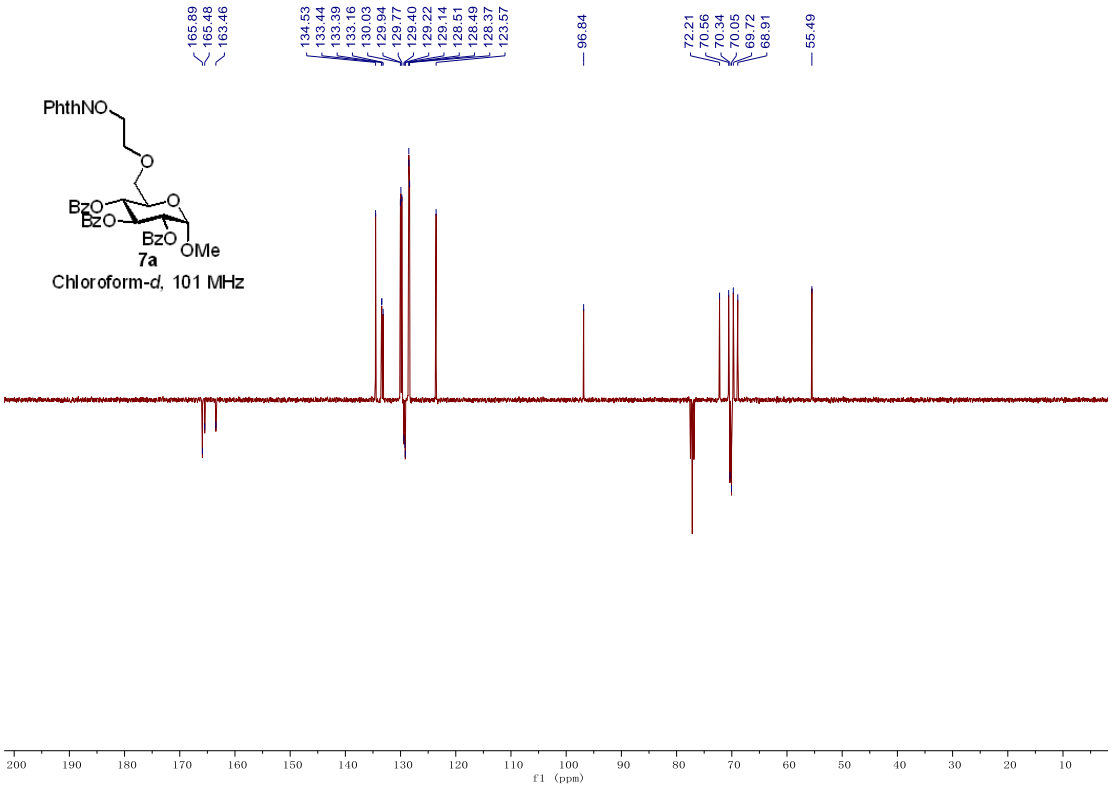
^{1}H NMR Spectra of compound S2



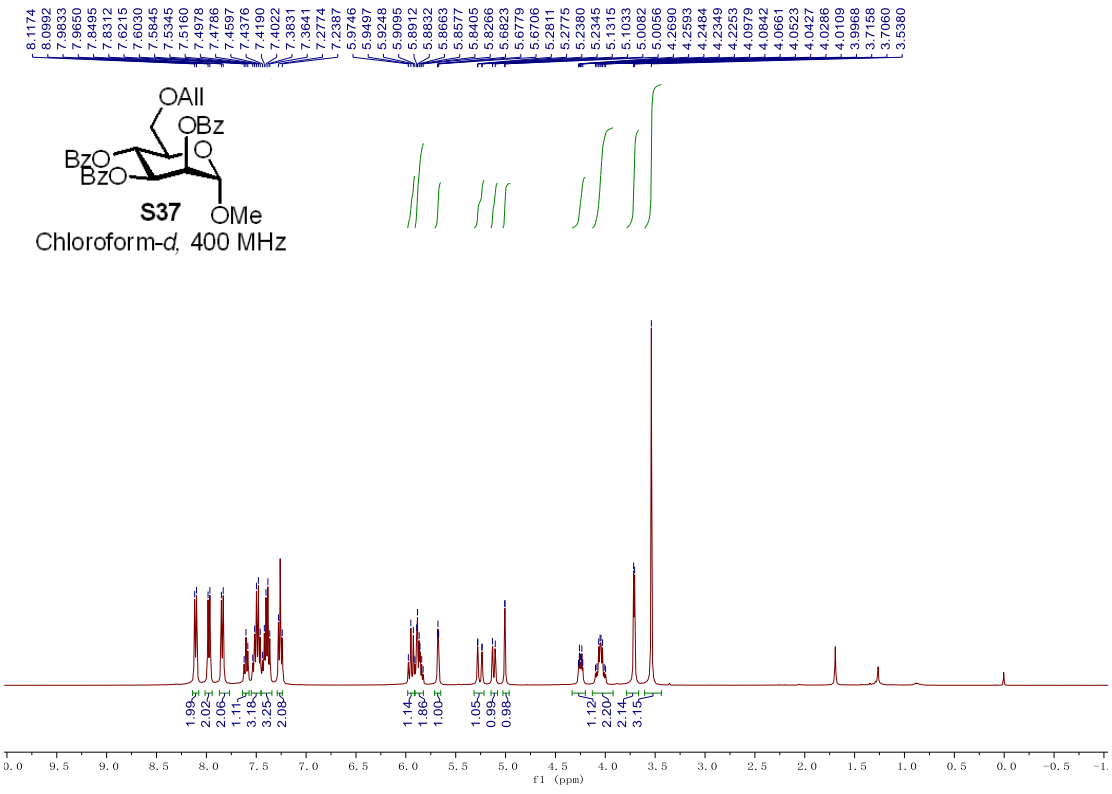
^{13}C NMR Spectra of compound S2



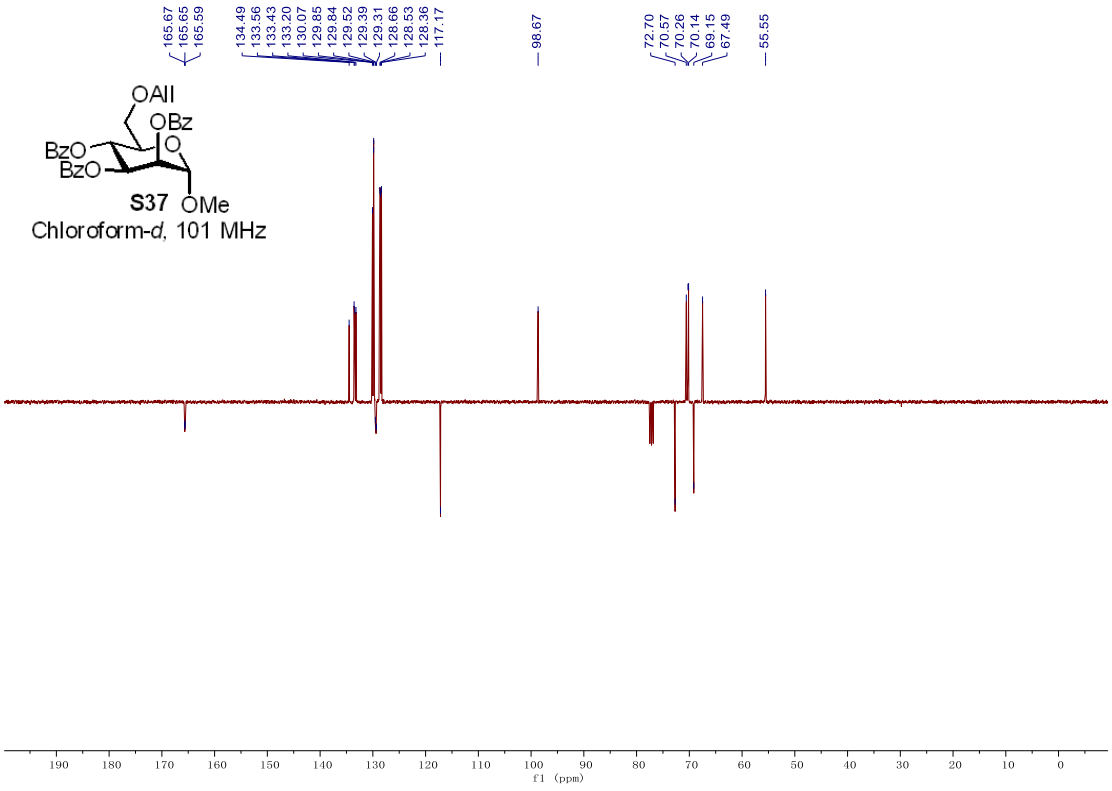
^{1}H NMR Spectra of compound 7a



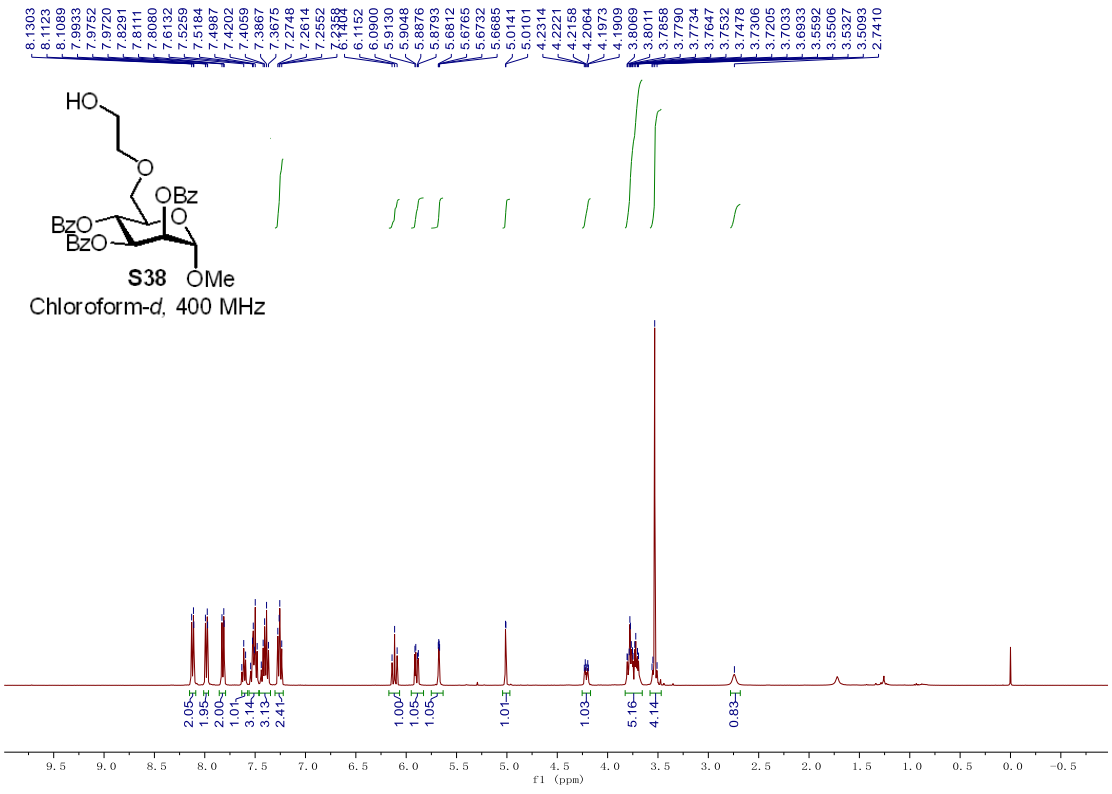
^{13}C NMR Spectra of compound 7a



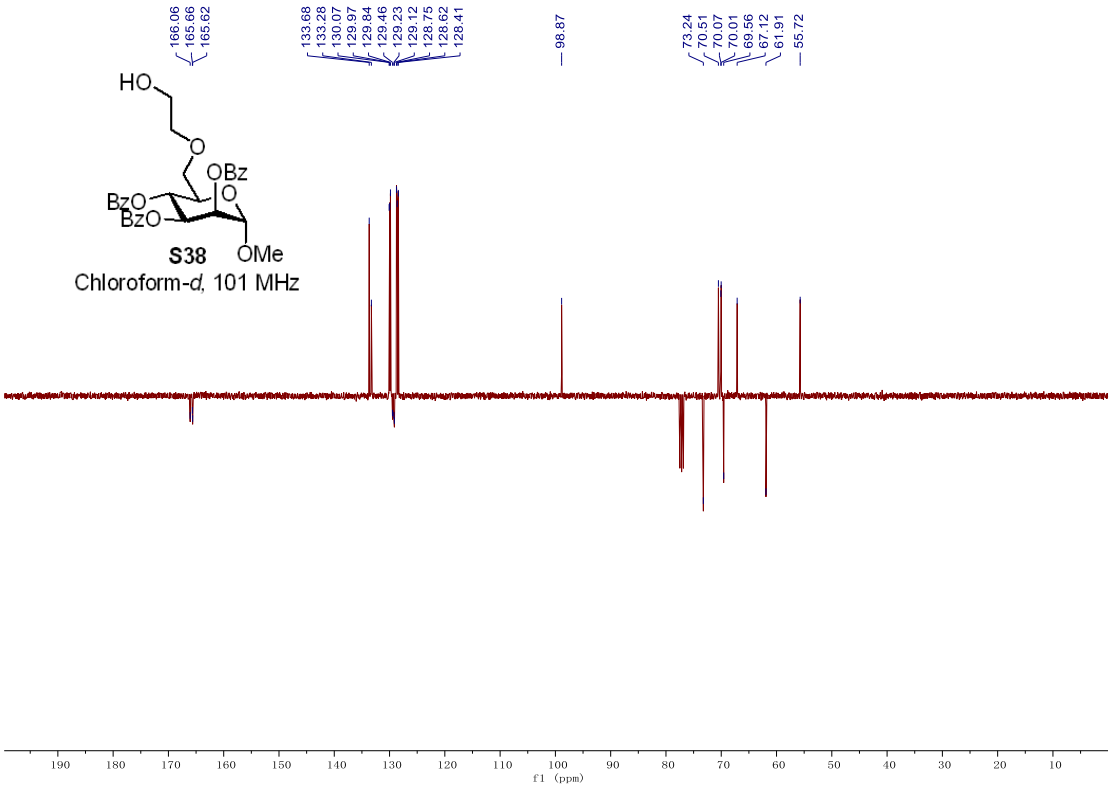
^{1}H NMR Spectra of compound S37



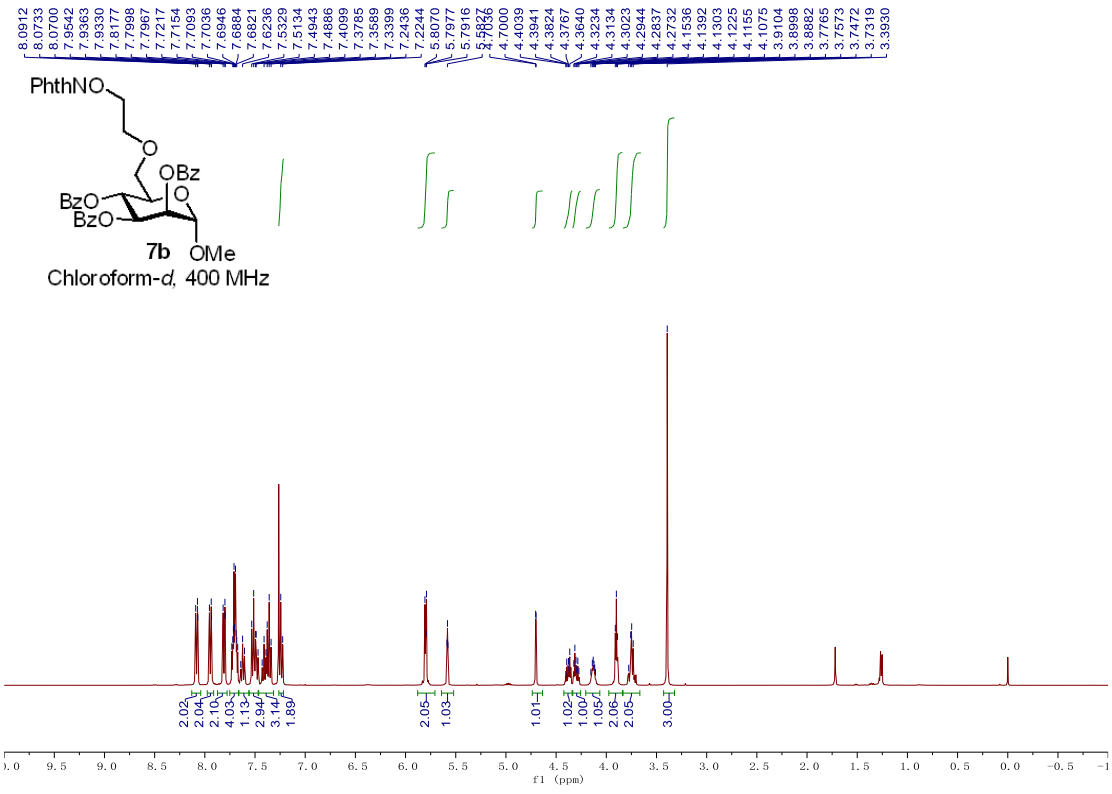
^{13}C NMR Spectra of compound S37



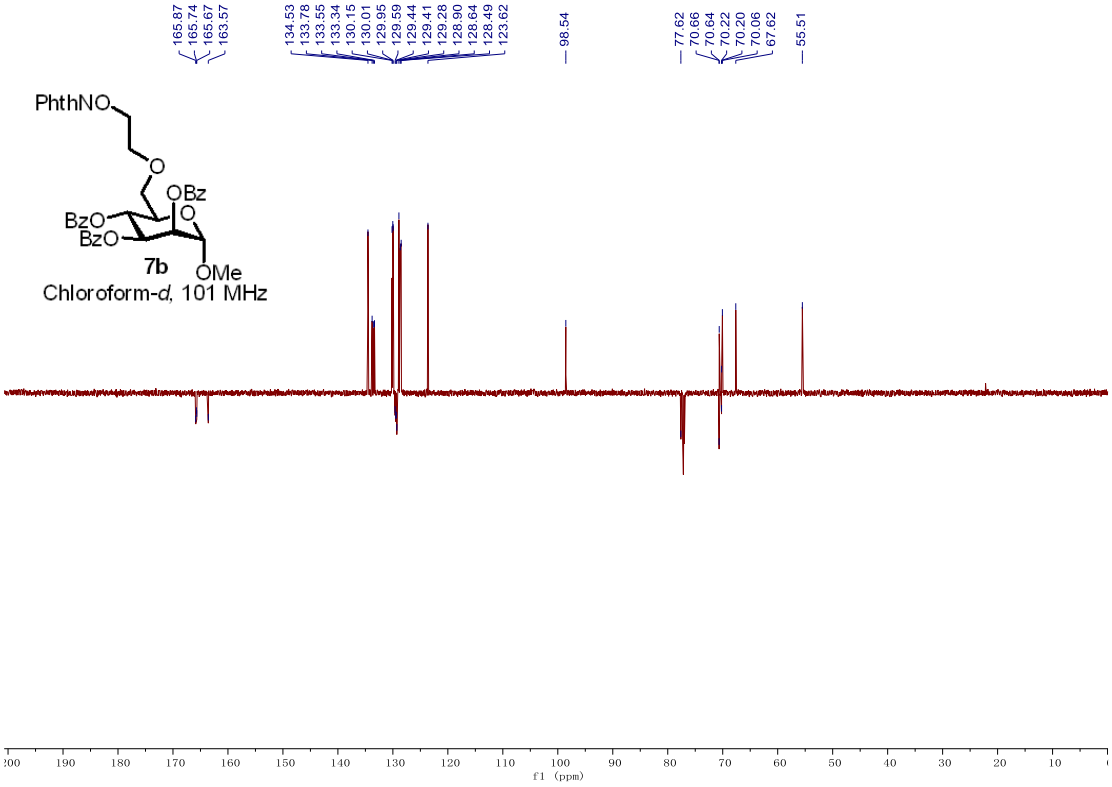
^{1}H NMR Spectra of compound S38



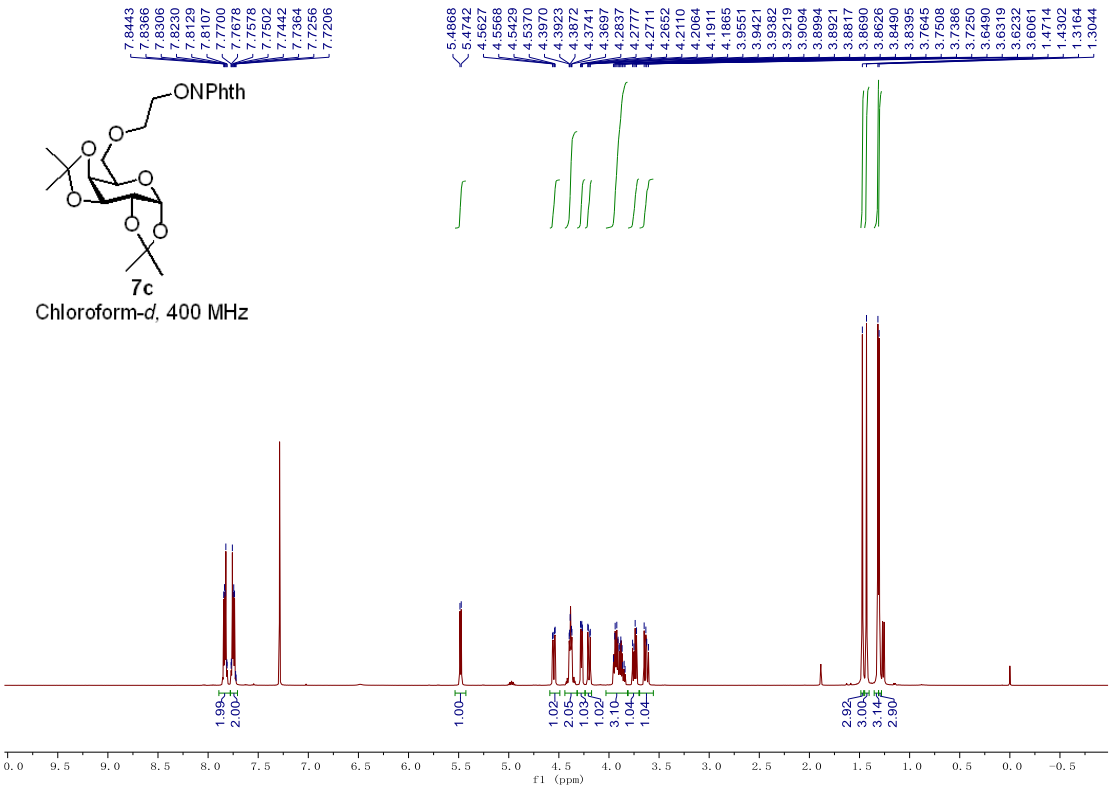
^{13}C NMR Spectra of compound S38



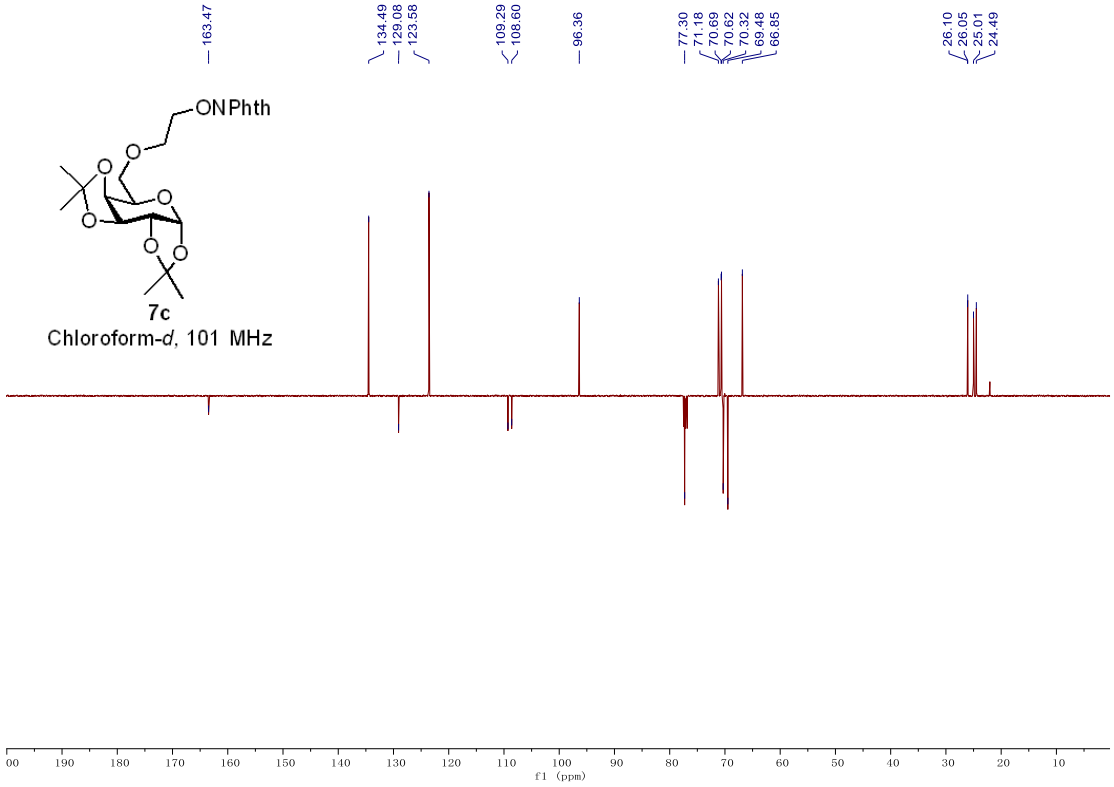
^{1}H NMR Spectra of compound 7b



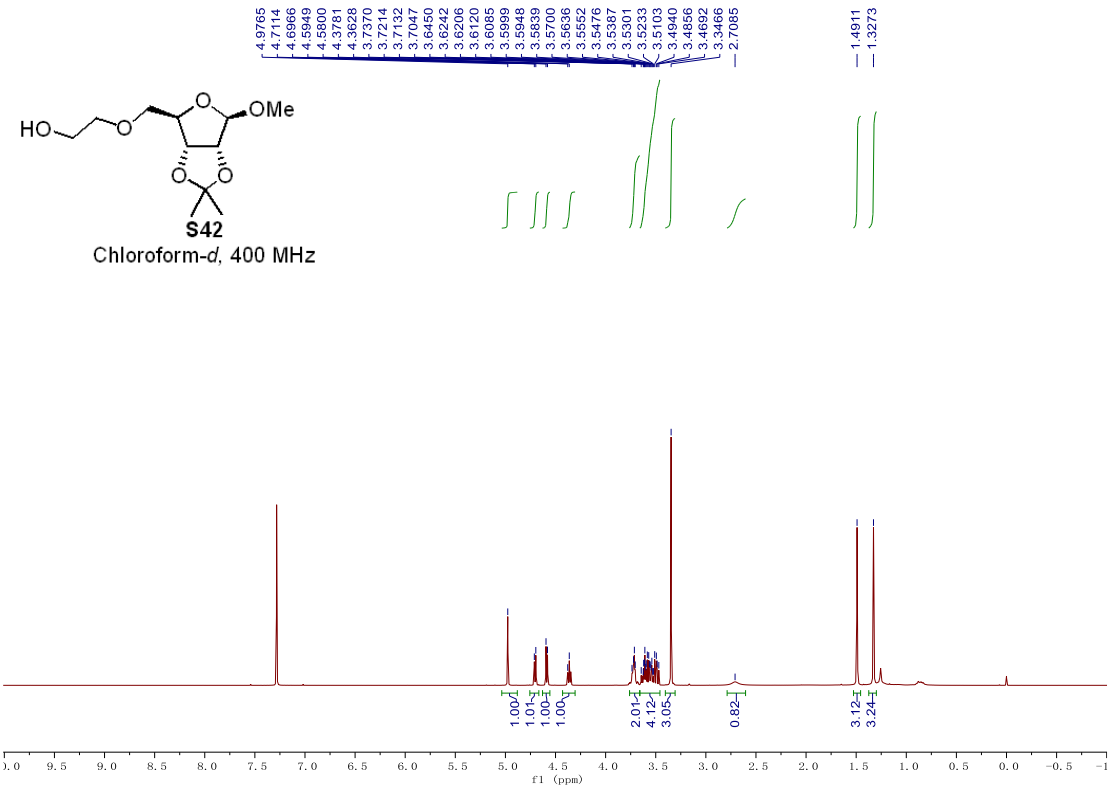
^{13}C NMR Spectra of compound 7b



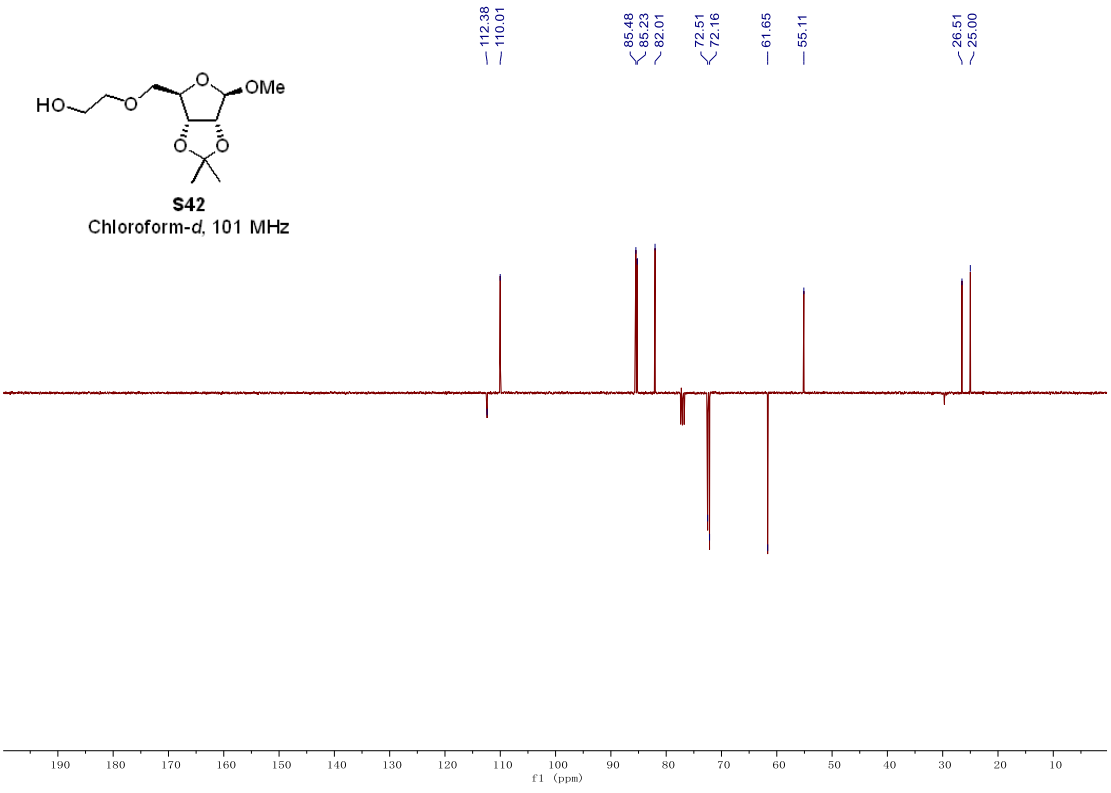
^{1}H NMR Spectra of compound 7c



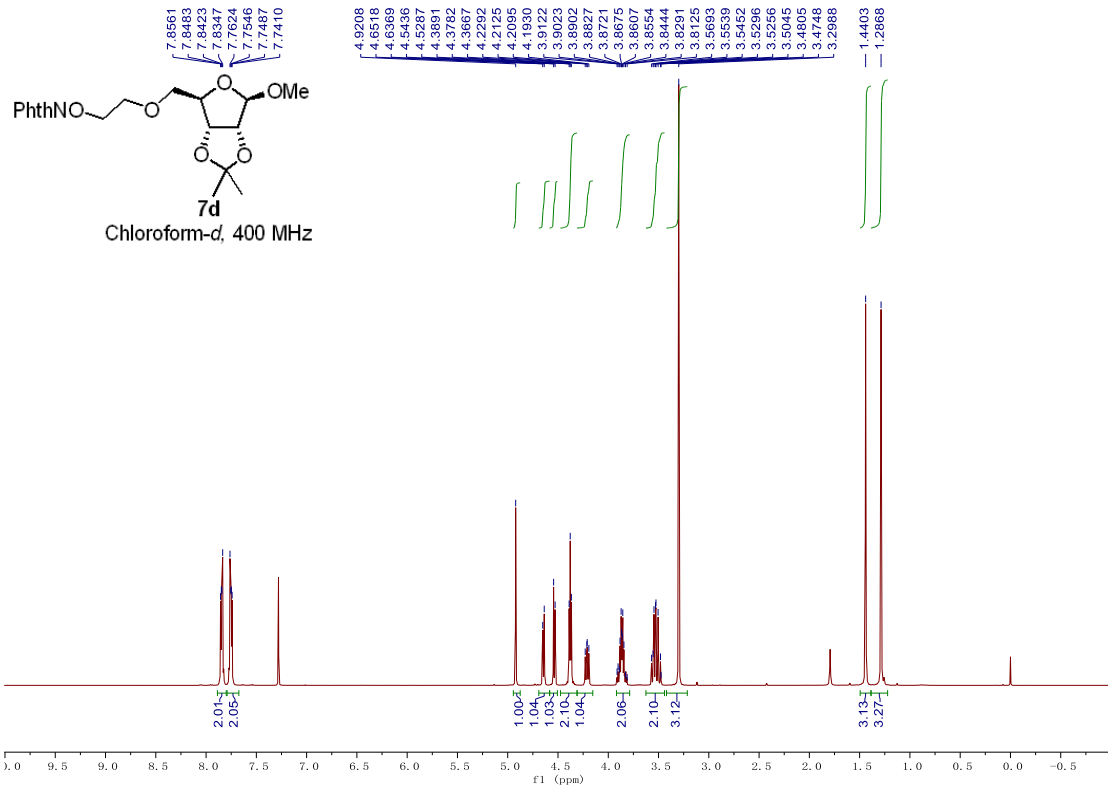
^{13}C NMR Spectra of compound 7c



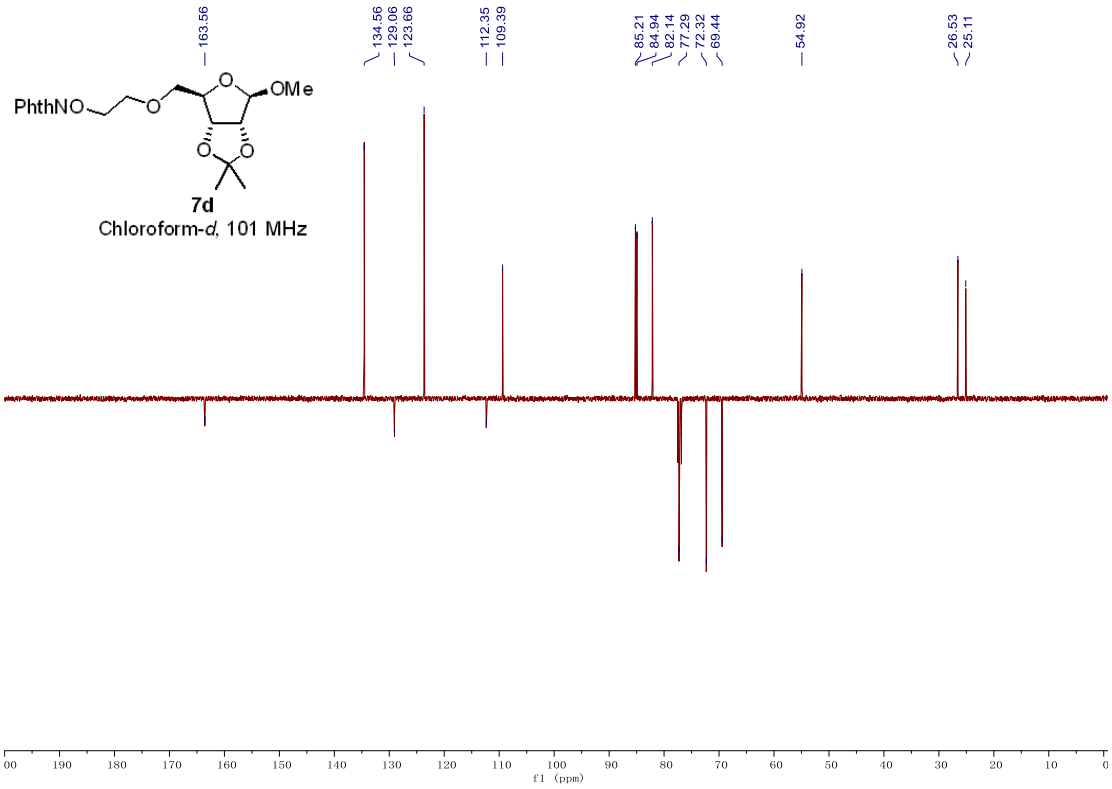
^{1}H NMR Spectra of compound S42



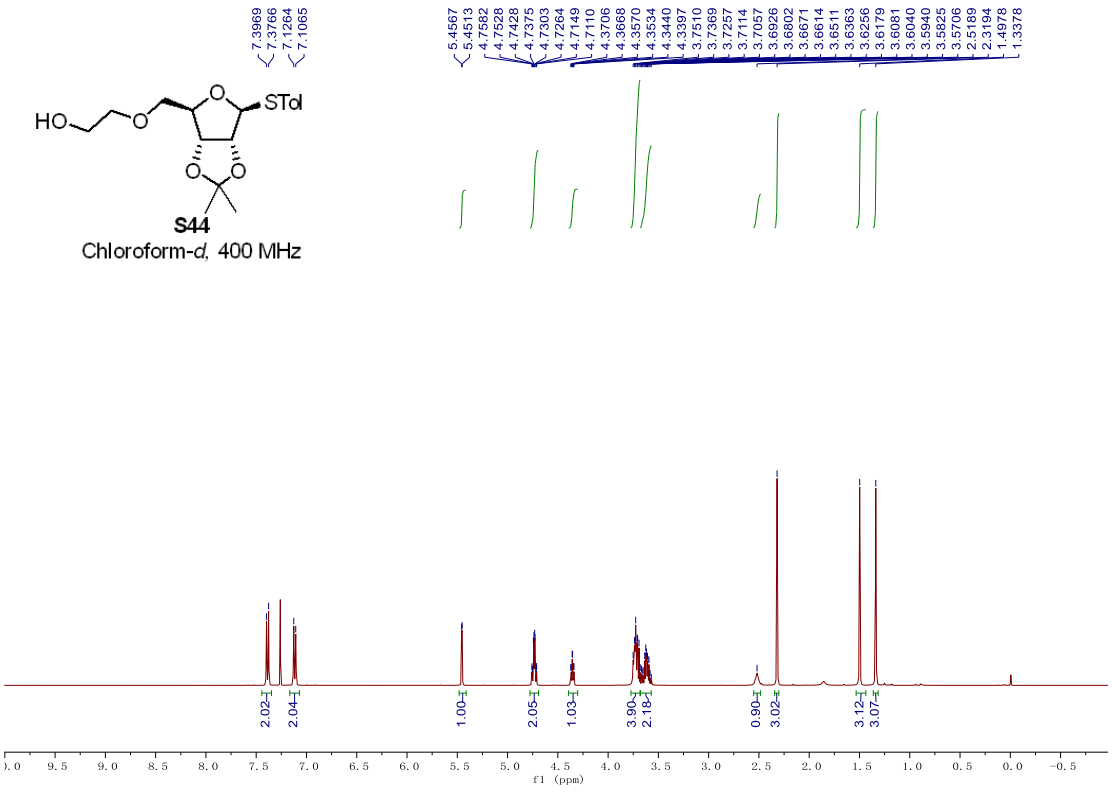
^{13}C NMR Spectra of compound S42



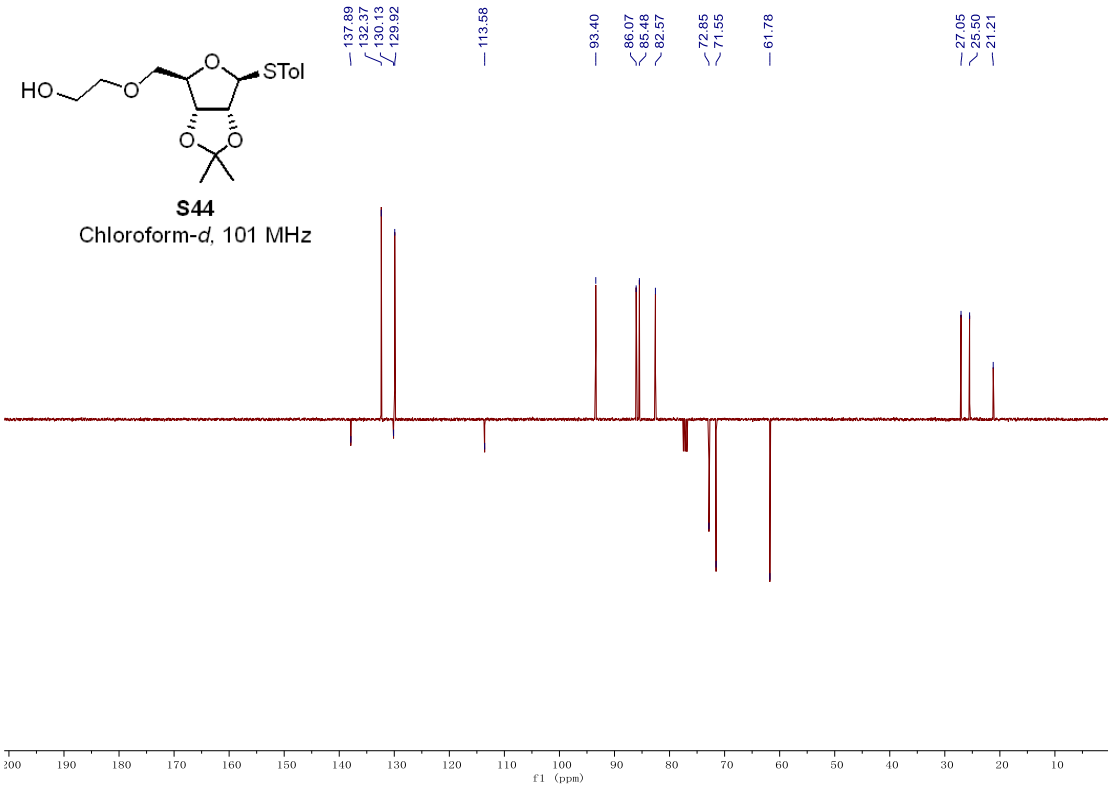
^{1}H NMR Spectra of compound 7d



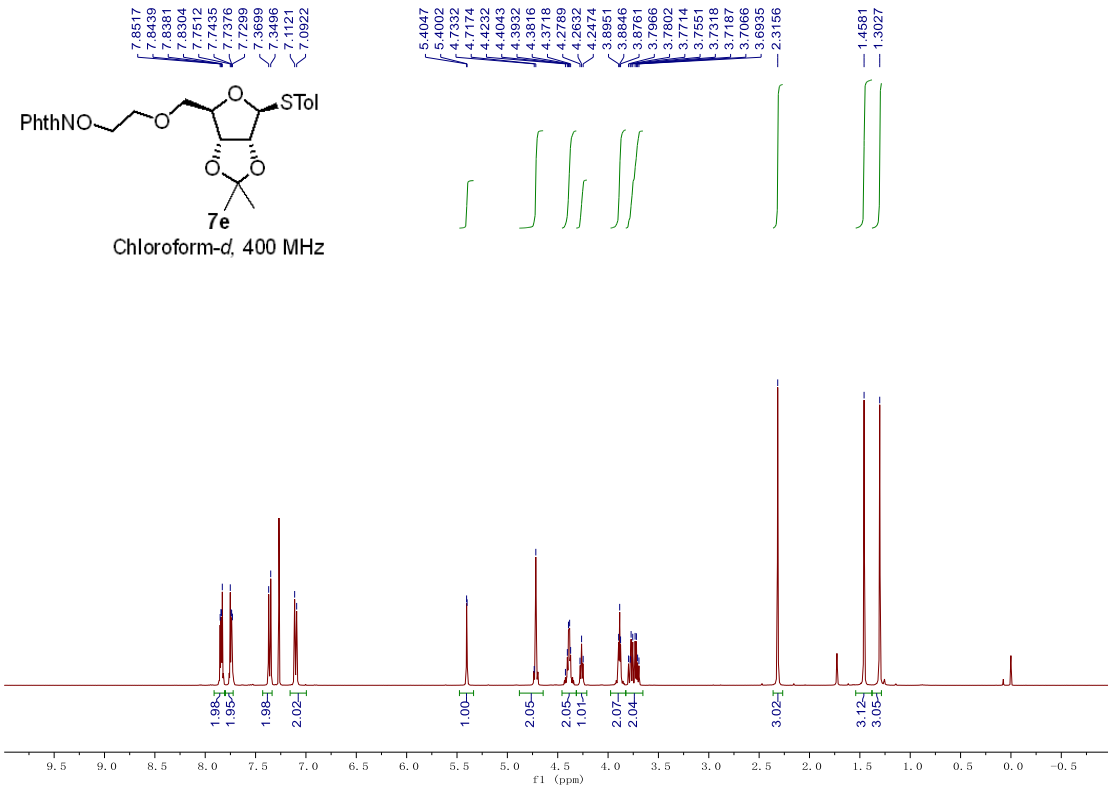
^{13}C NMR Spectra of compound 7d



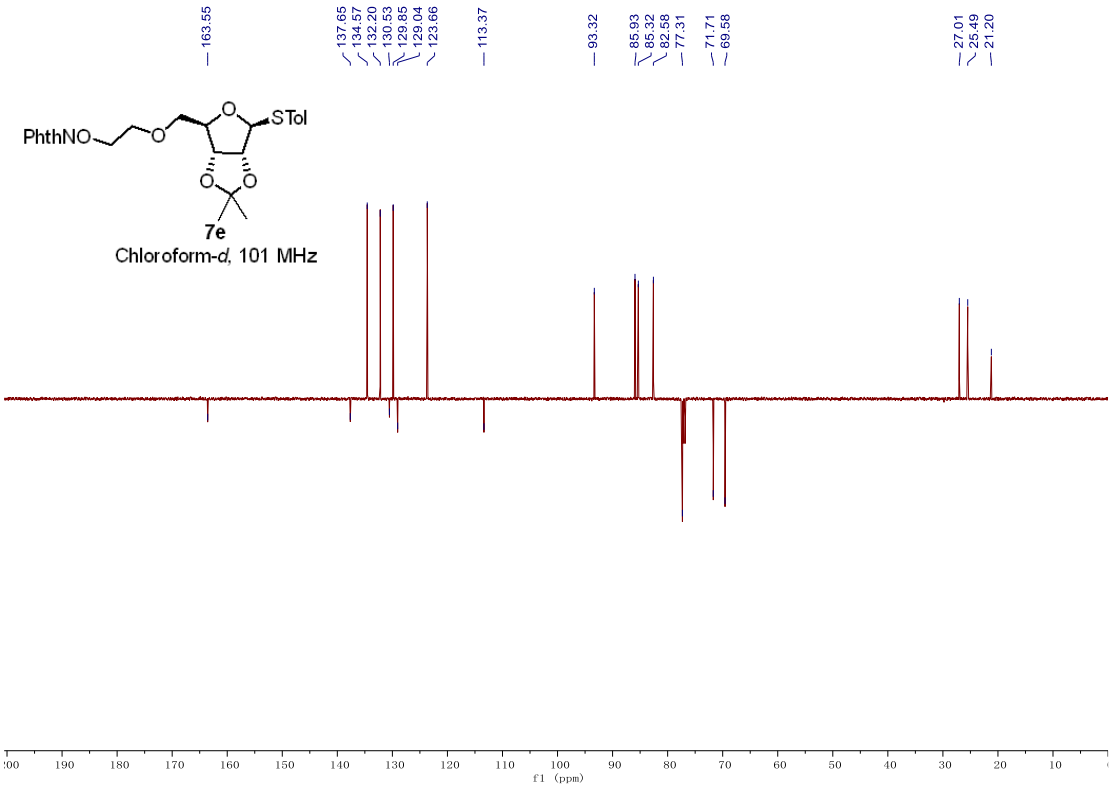
^{1}H NMR Spectra of compound S44



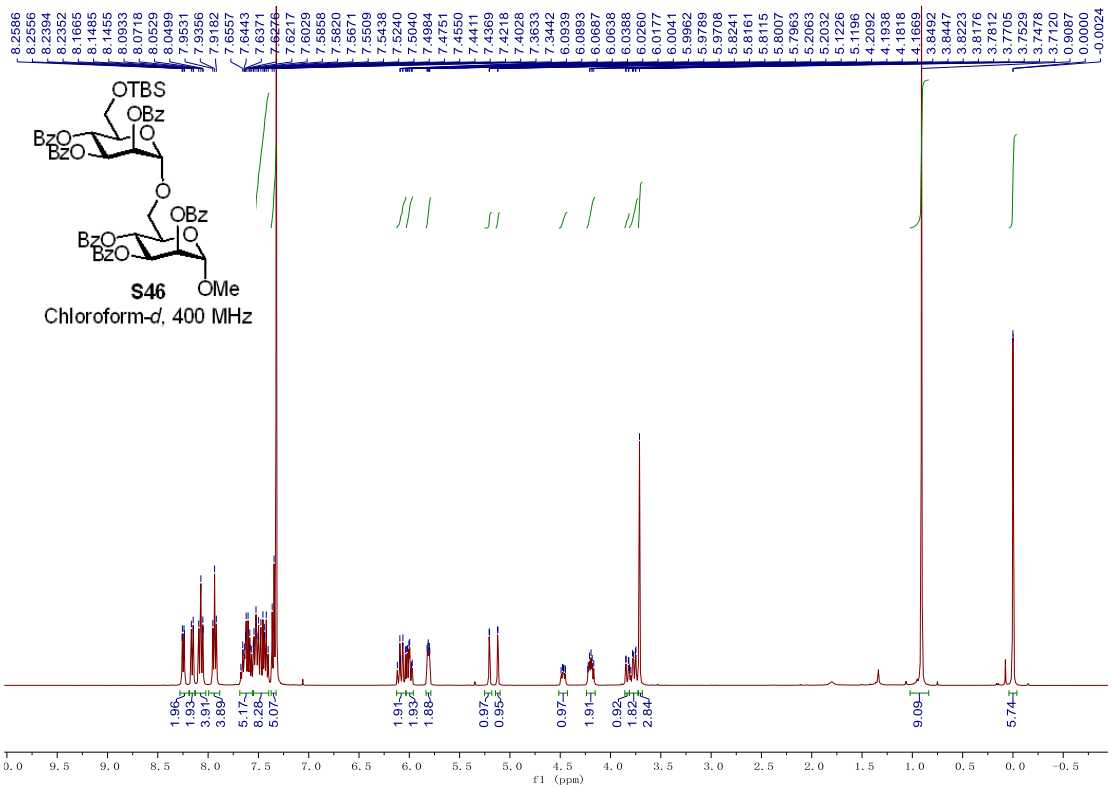
^{13}C NMR Spectra of compound S44



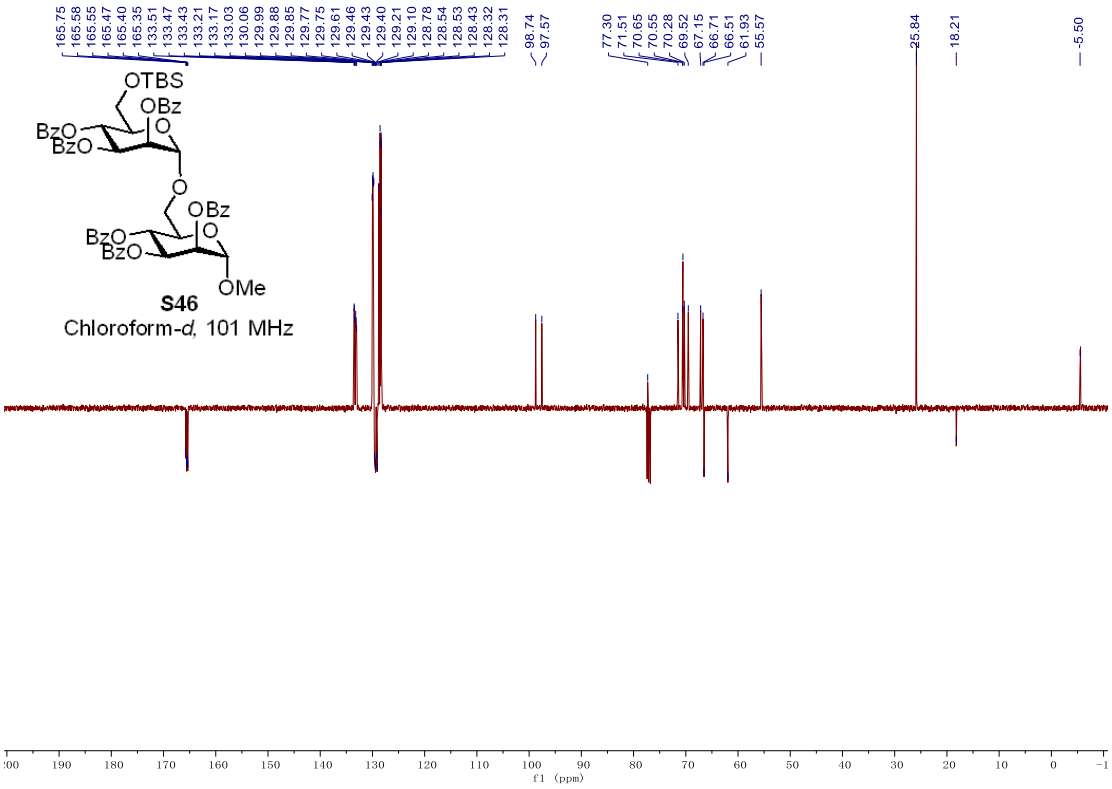
^{1}H NMR Spectra of compound 7e



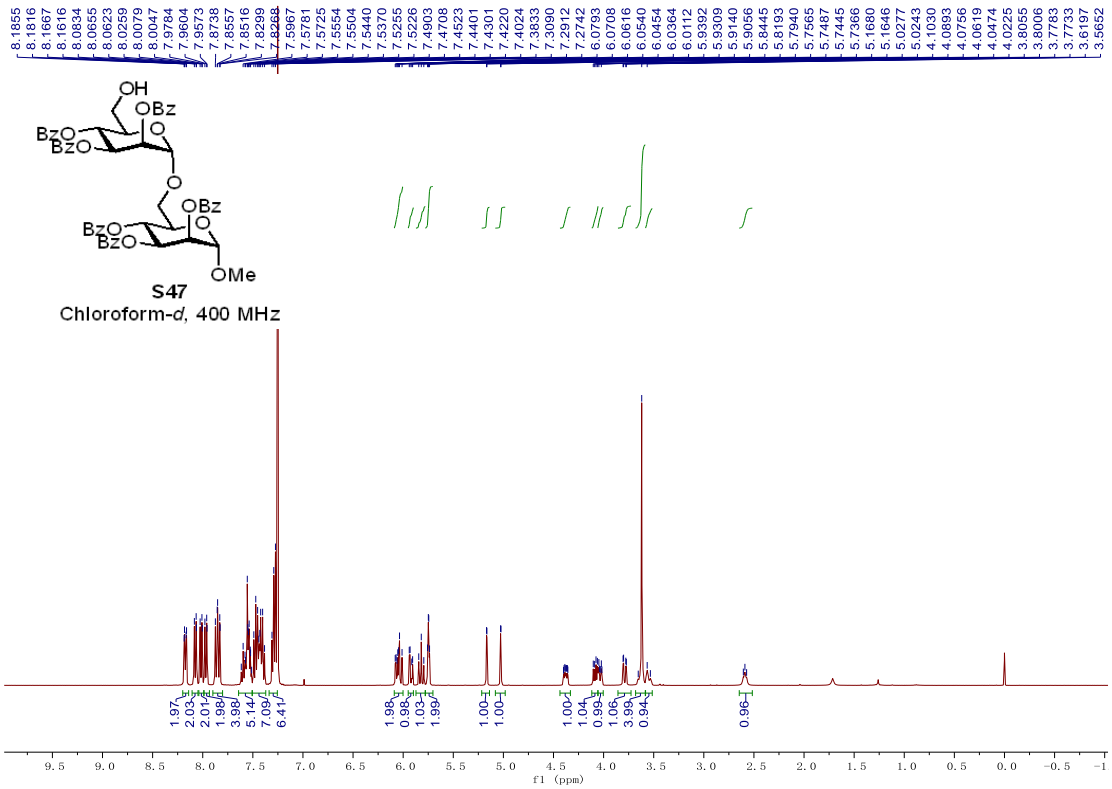
^{13}C NMR Spectra of compound 7e



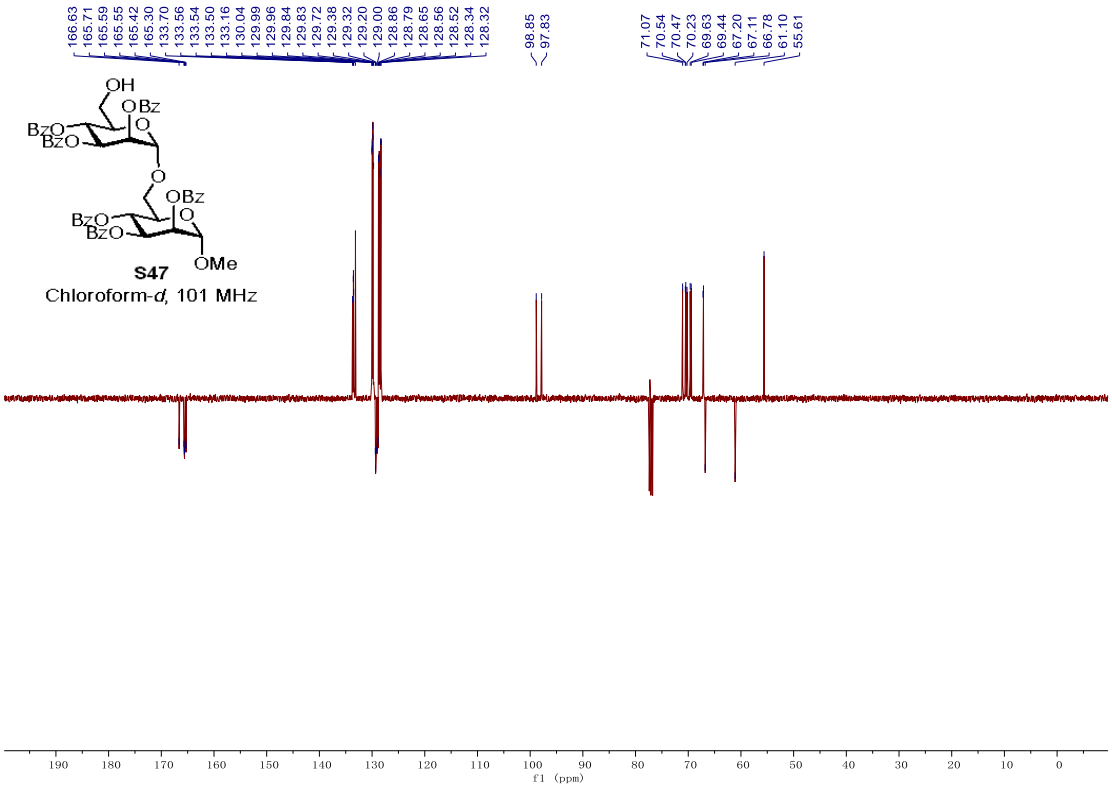
^{1}H NMR Spectra of compound S46



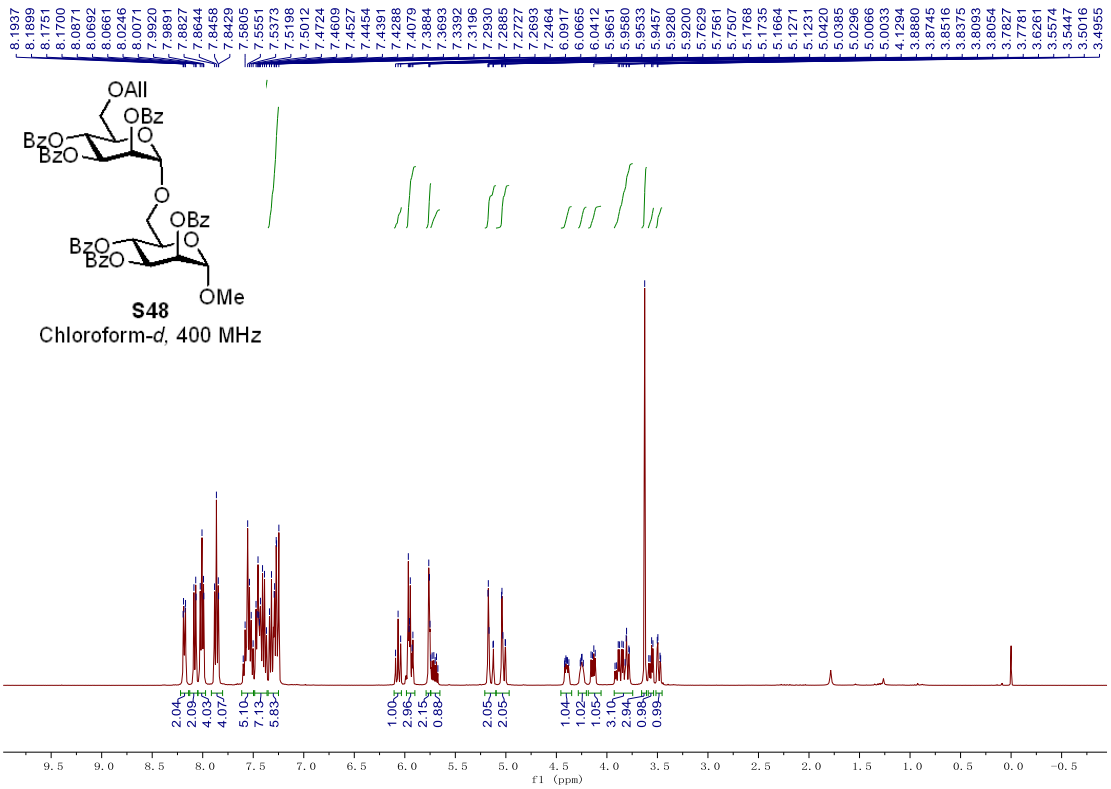
^{13}C NMR Spectra of compound S46



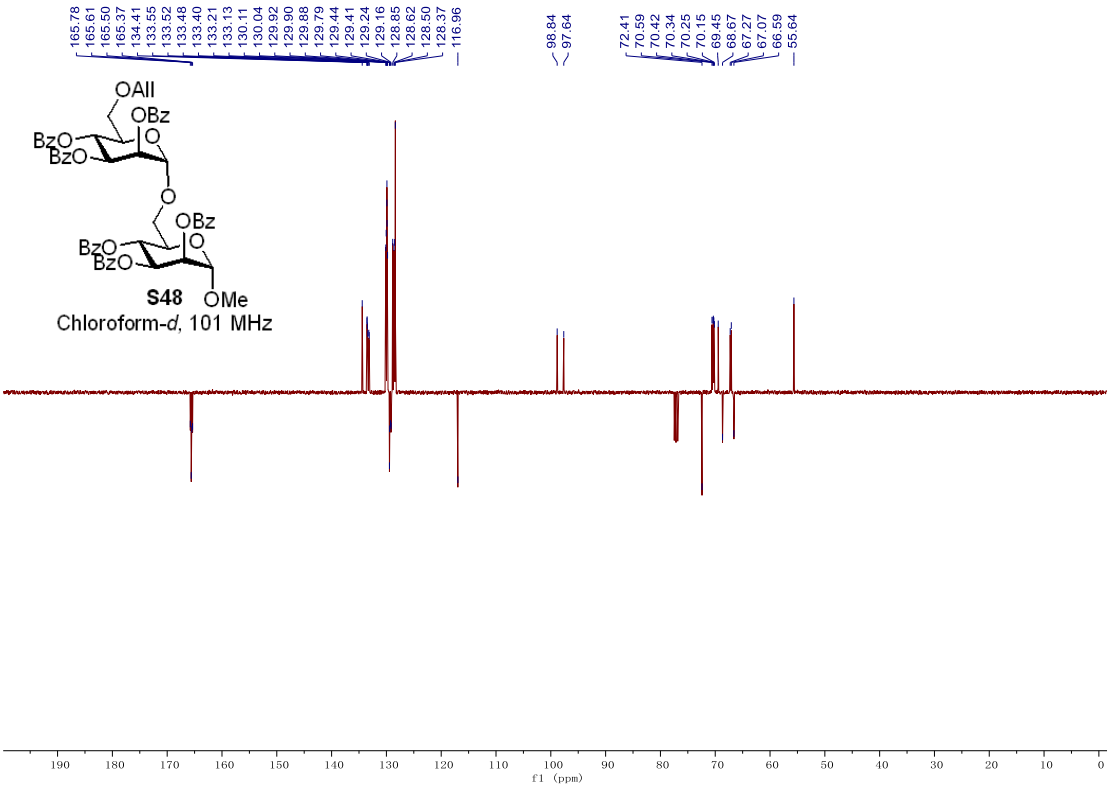
^{1}H NMR Spectra of compound S47



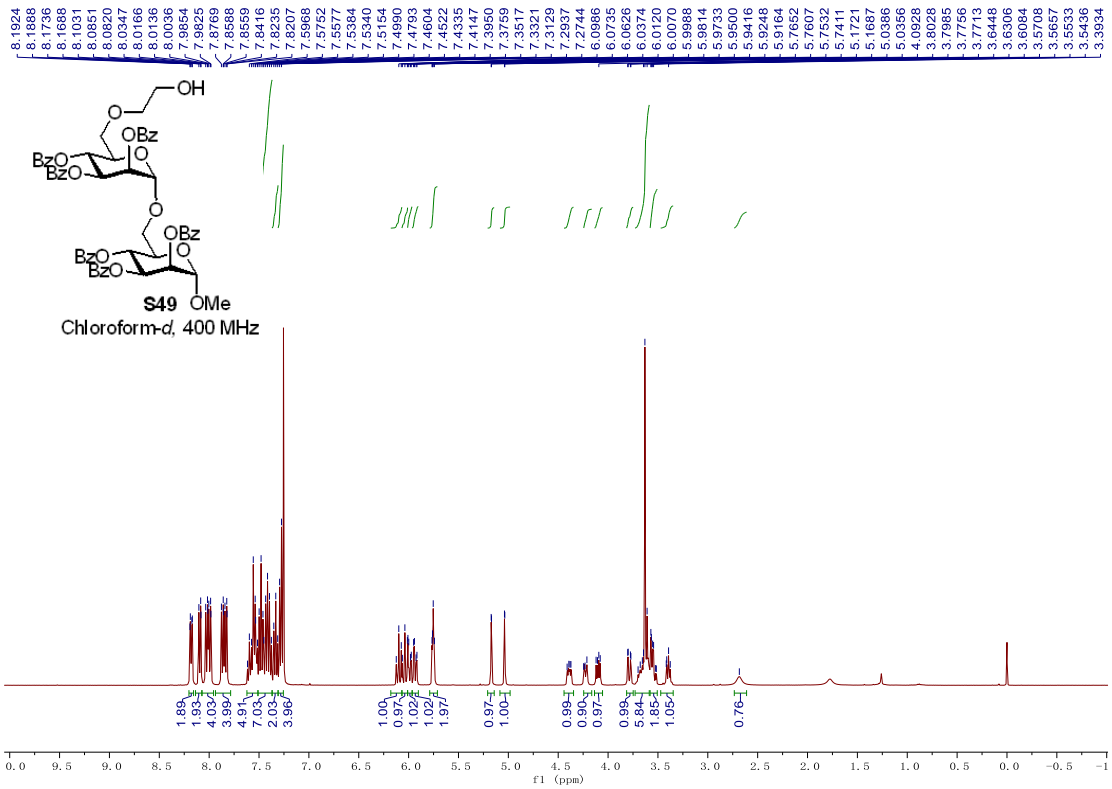
^{13}C NMR Spectra of compound S47



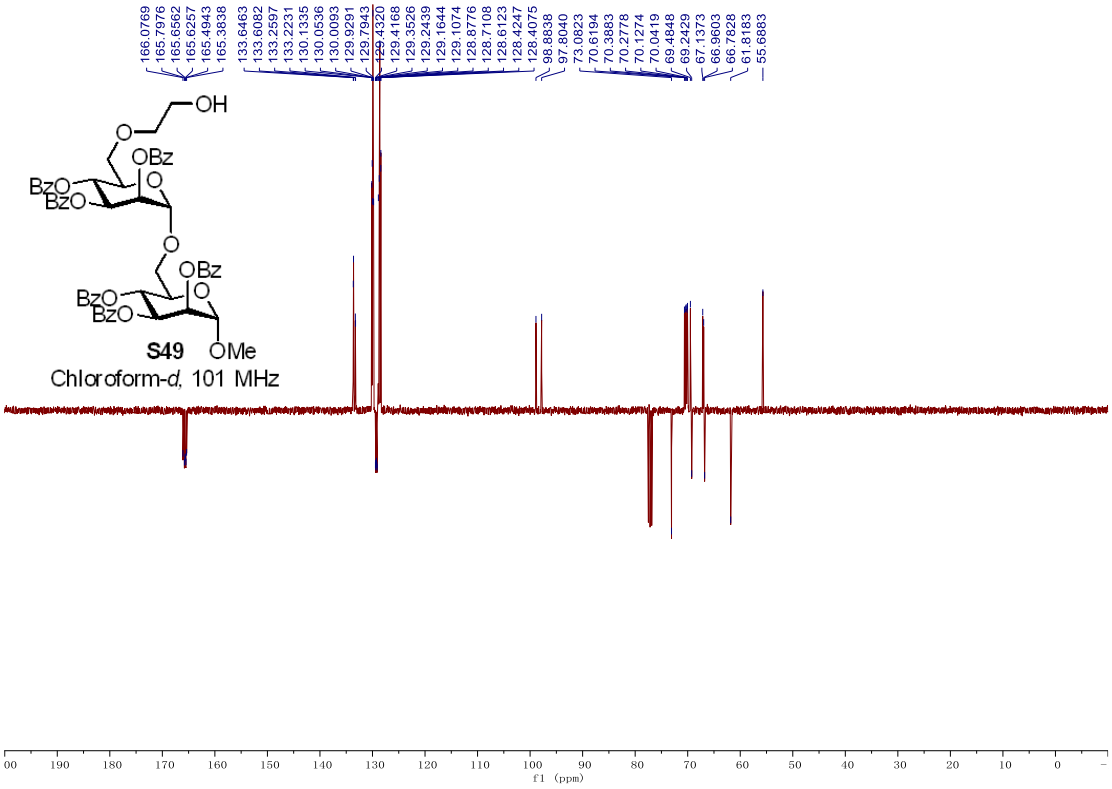
^{1}H NMR Spectra of compound S48



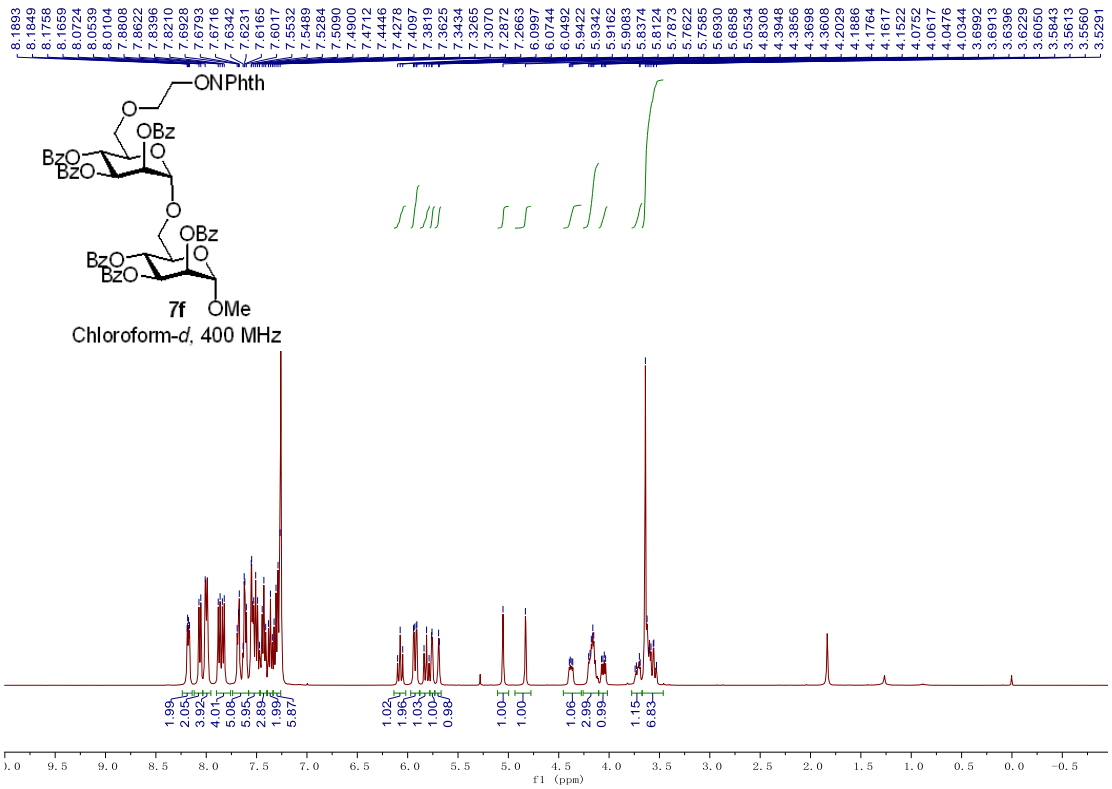
^{13}C NMR Spectra of compound S48



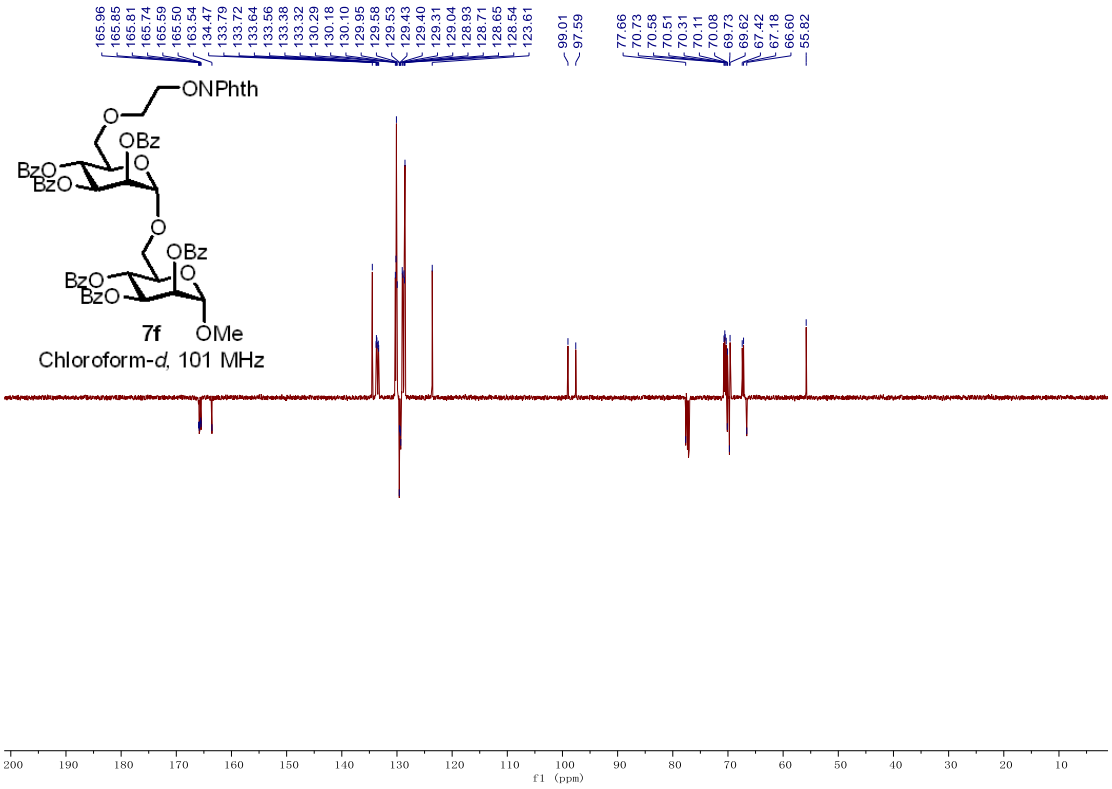
^{1}H NMR Spectra of compound S49



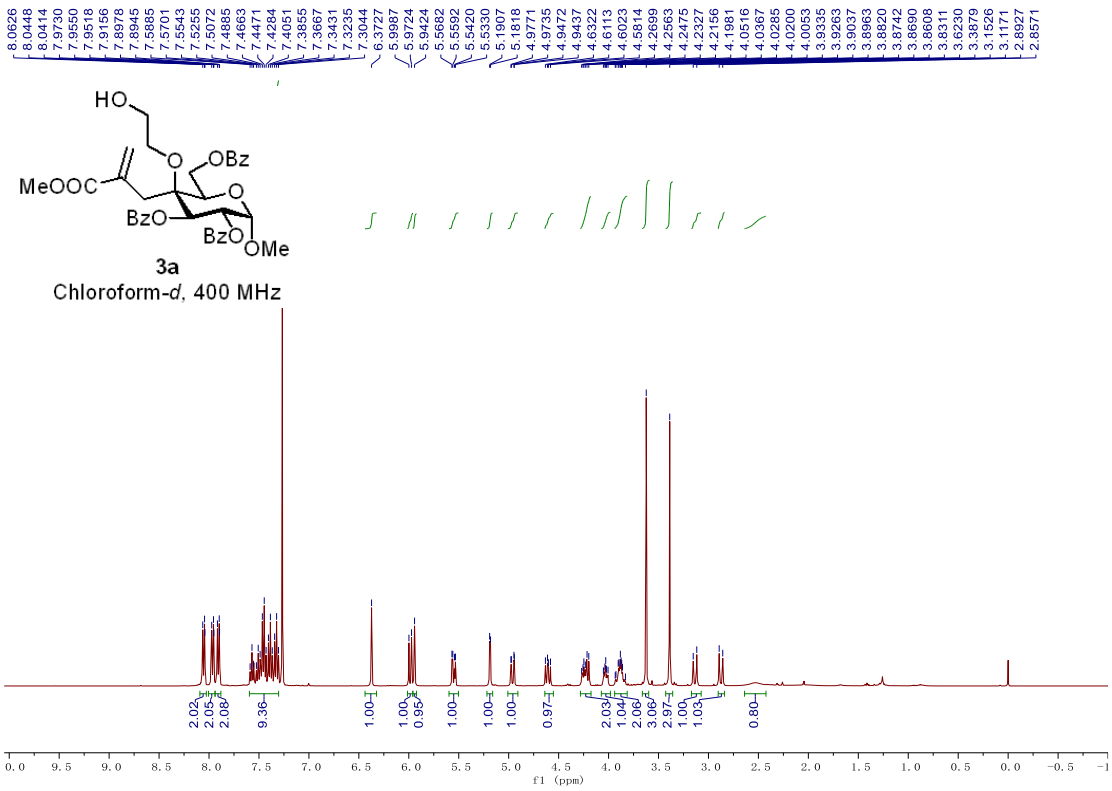
^{13}C NMR Spectra of compound S49



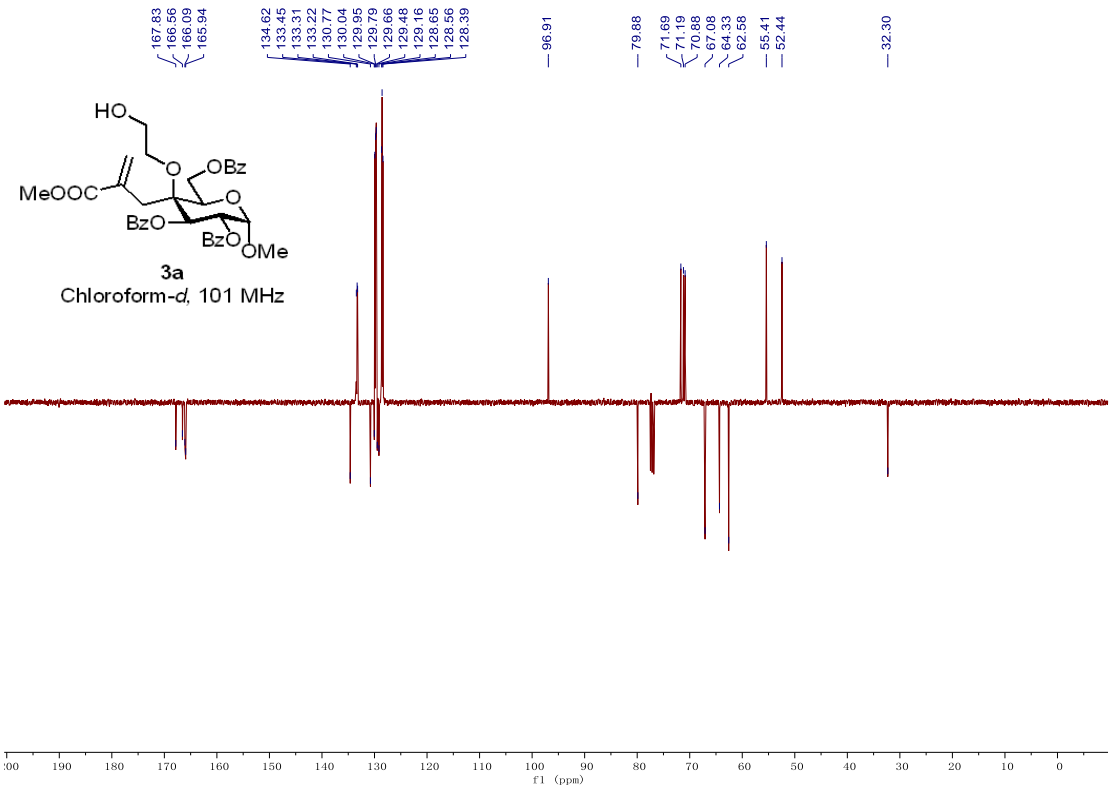
^{1}H NMR Spectra of compound 7f



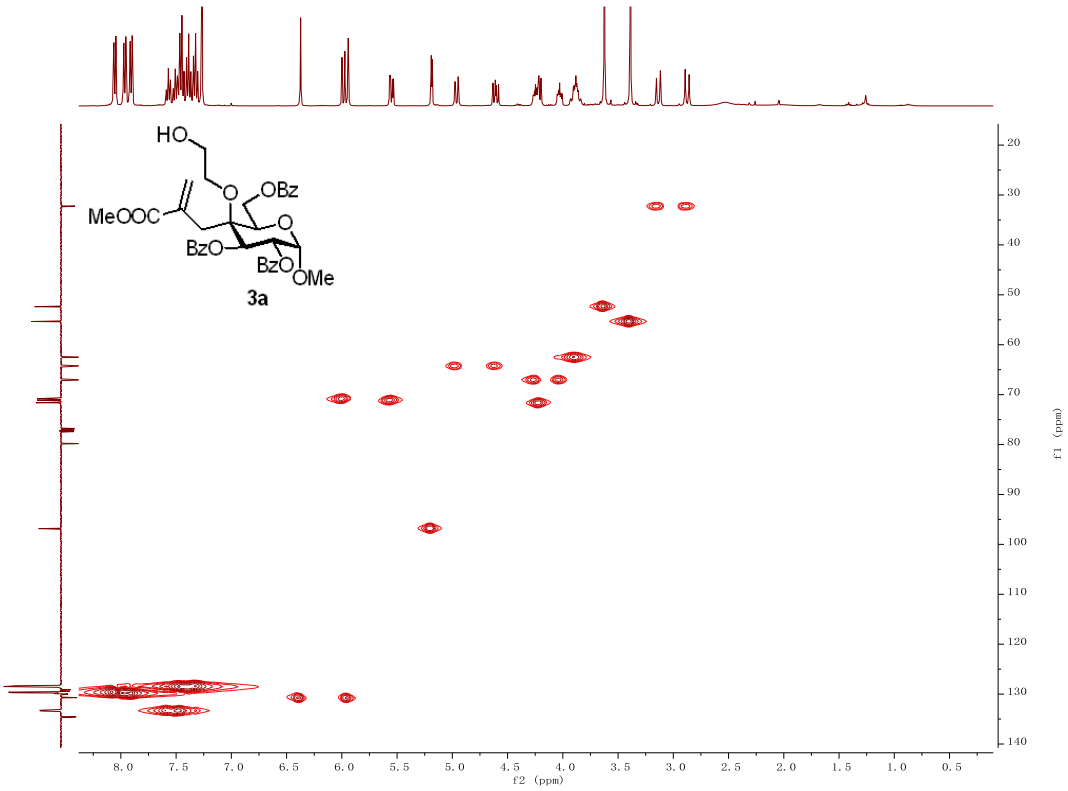
^{13}C NMR Spectra of compound 7f



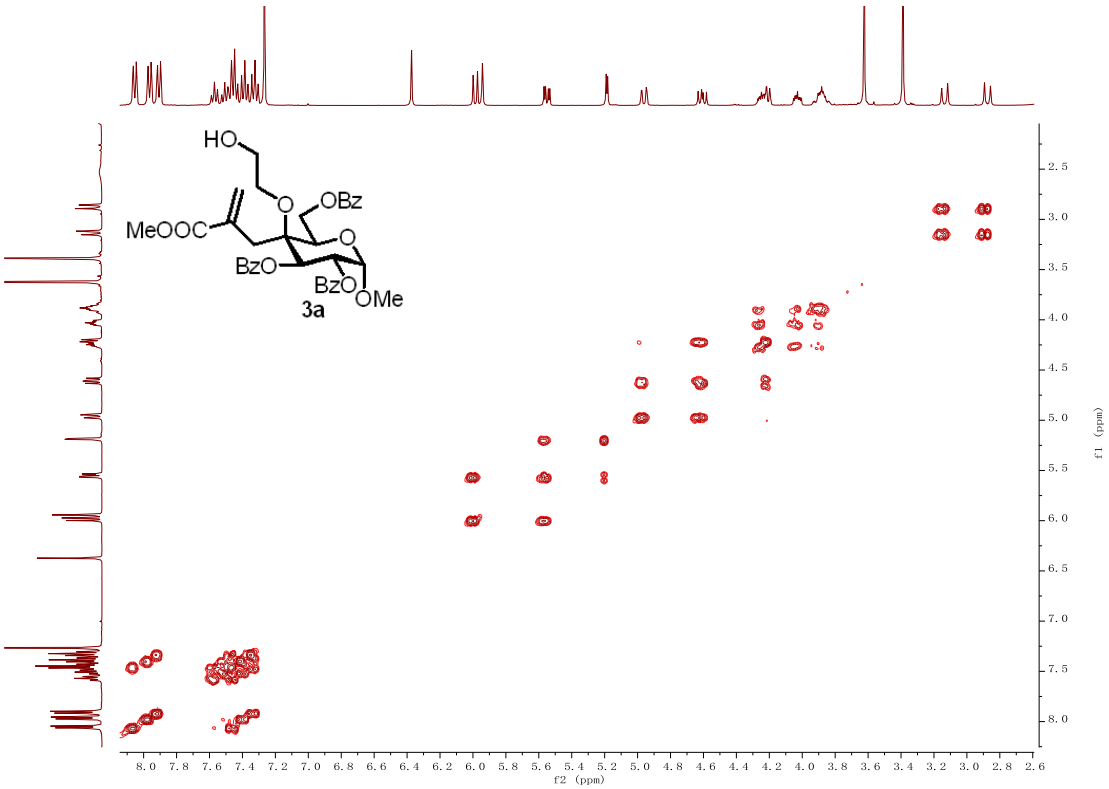
^{1}H NMR Spectra of compound 3a



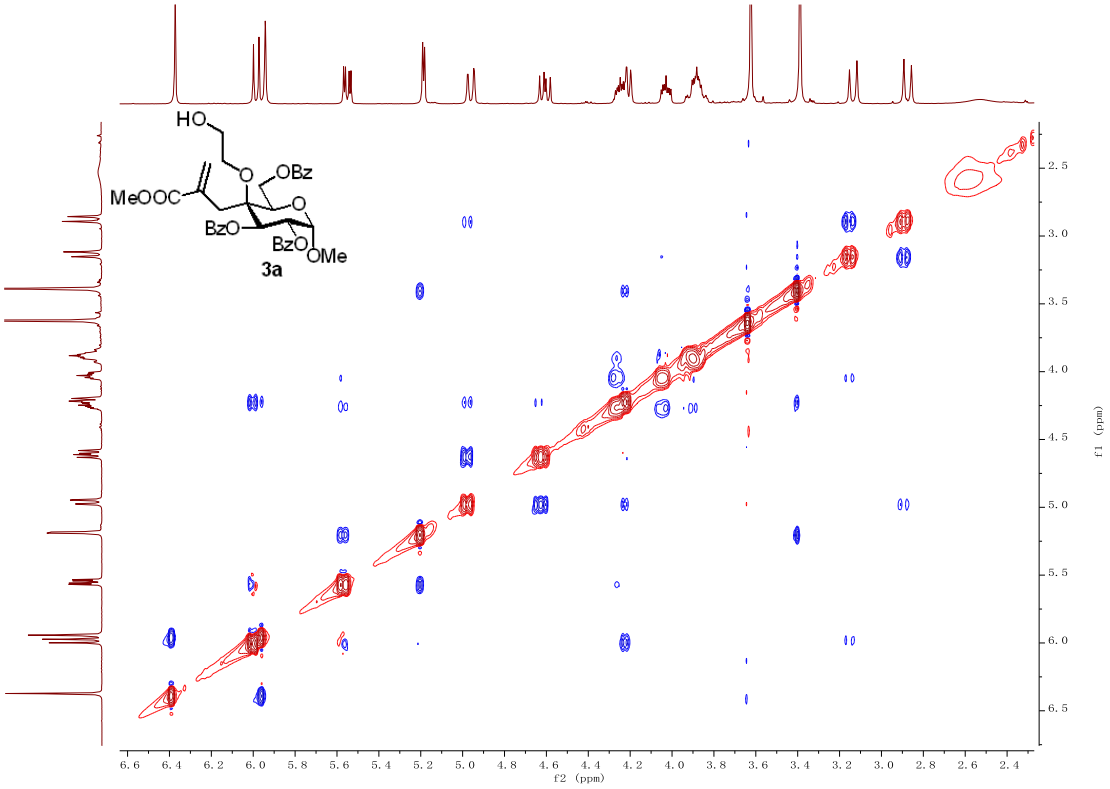
^{13}C NMR Spectra of compound 3a



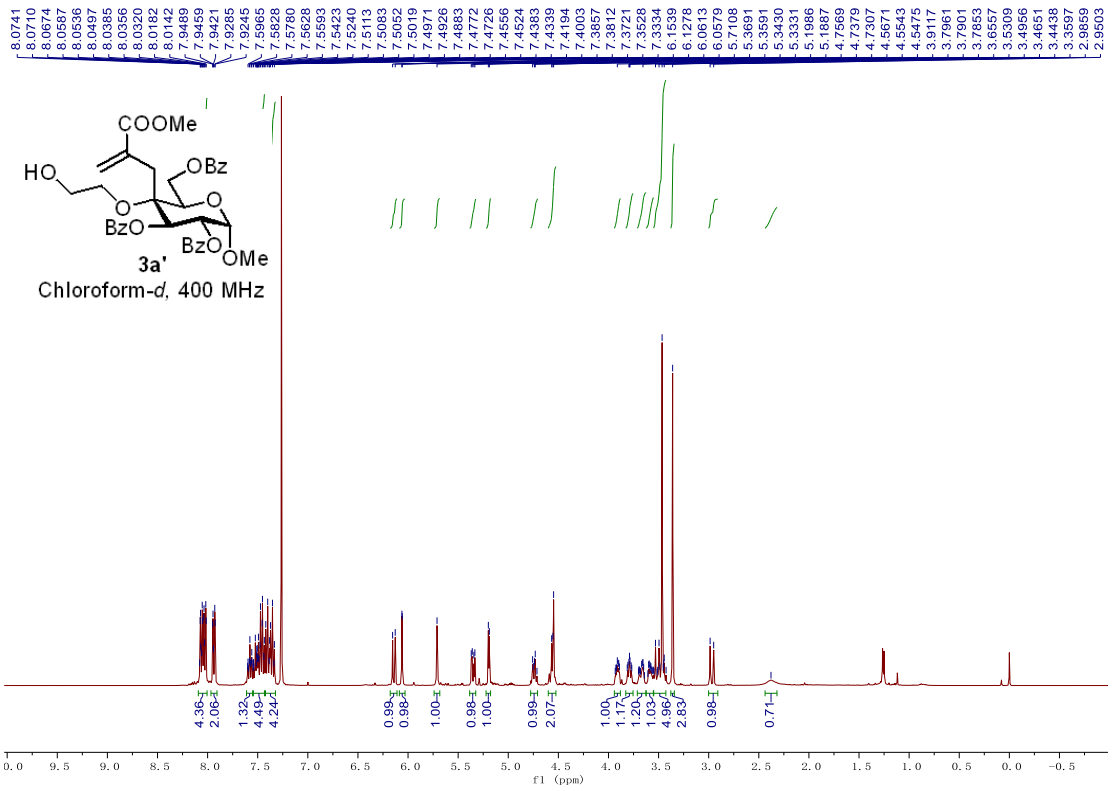
HSQC NMR Spectra of compound 3a



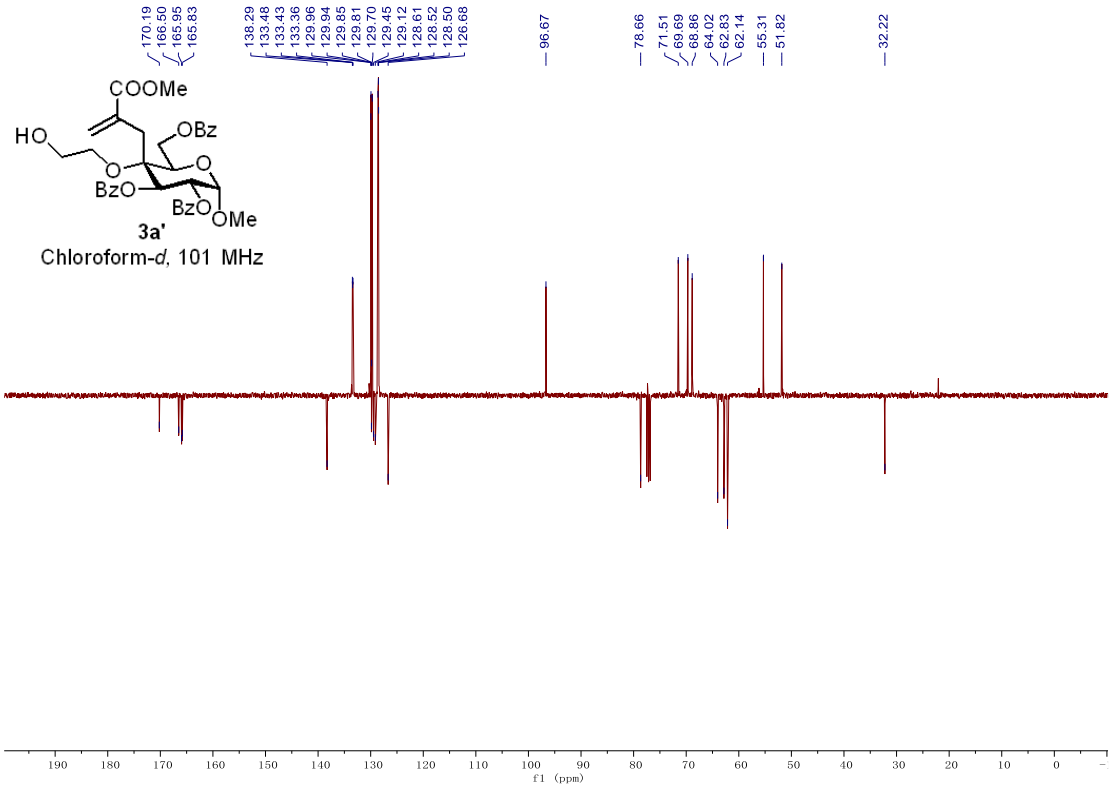
COSY NMR Spectra of compound 3a



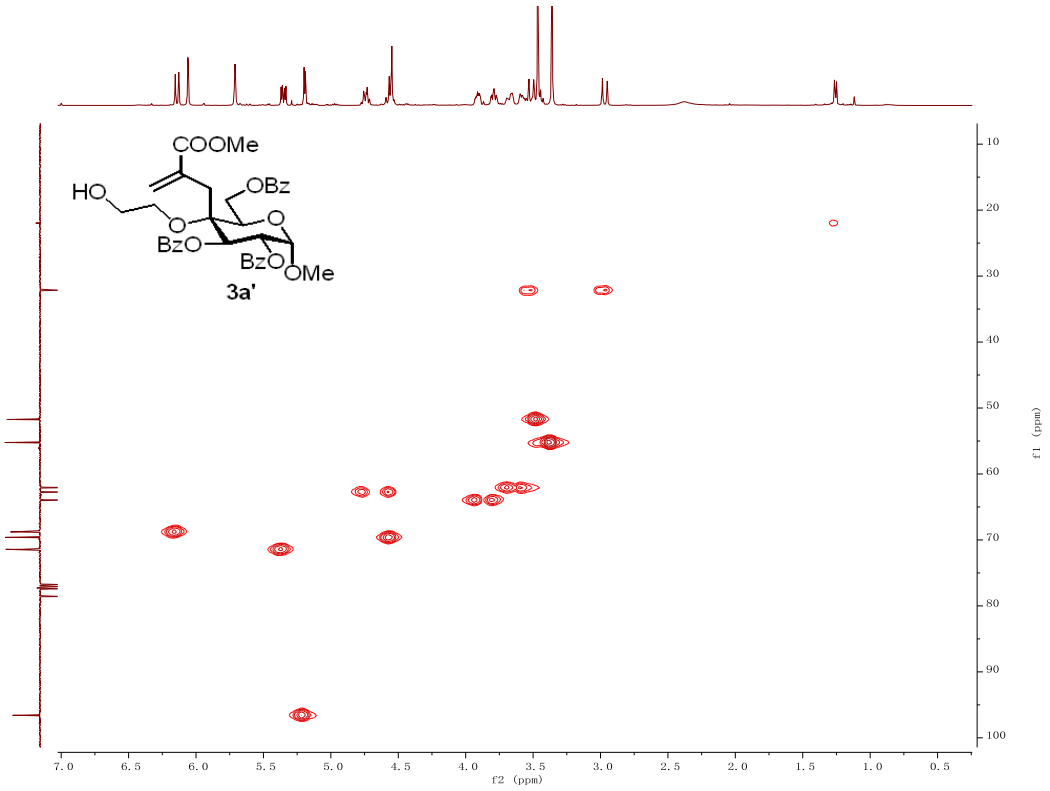
NOESY NMR Spectra of compound 3a



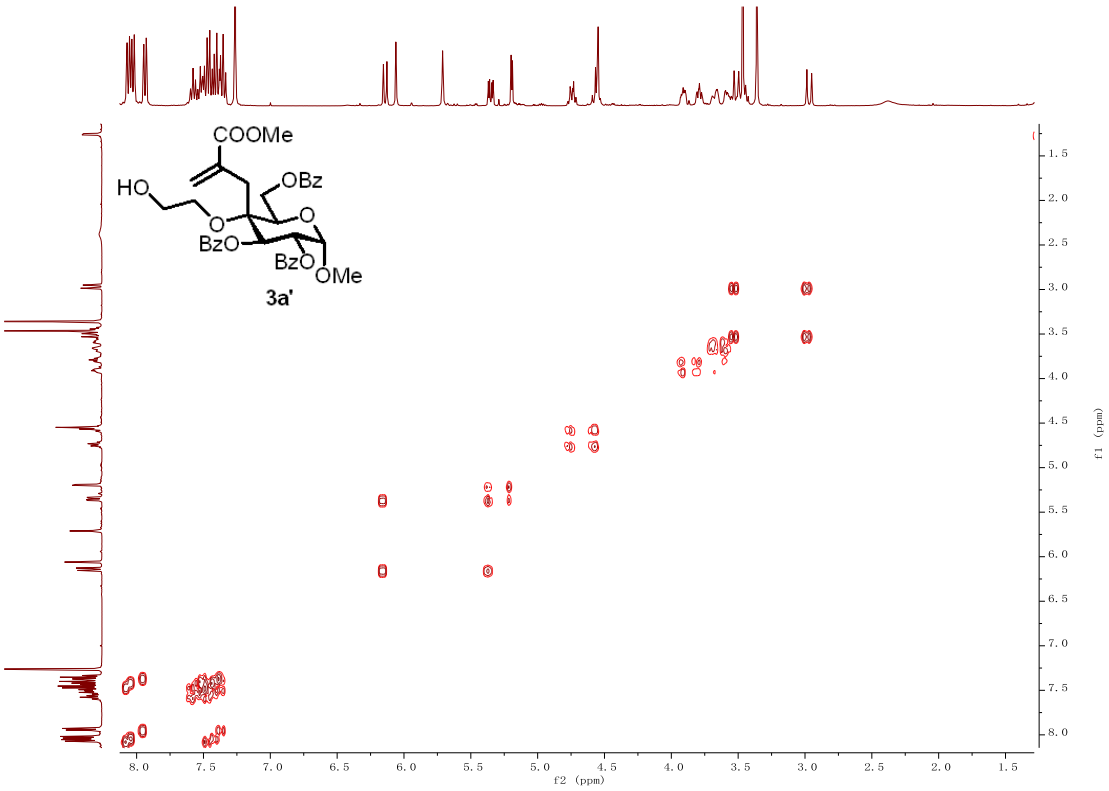
^{1}H NMR Spectra of compound 3a′



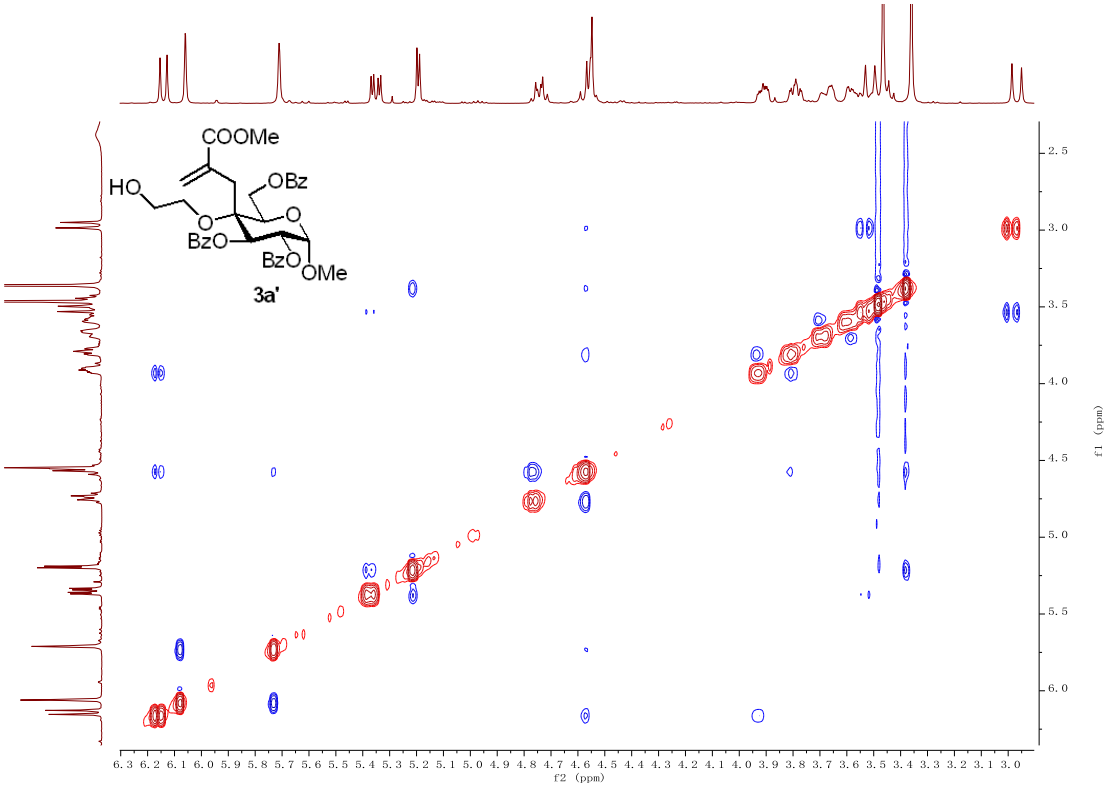
^{13}C NMR Spectra of compound 3a′



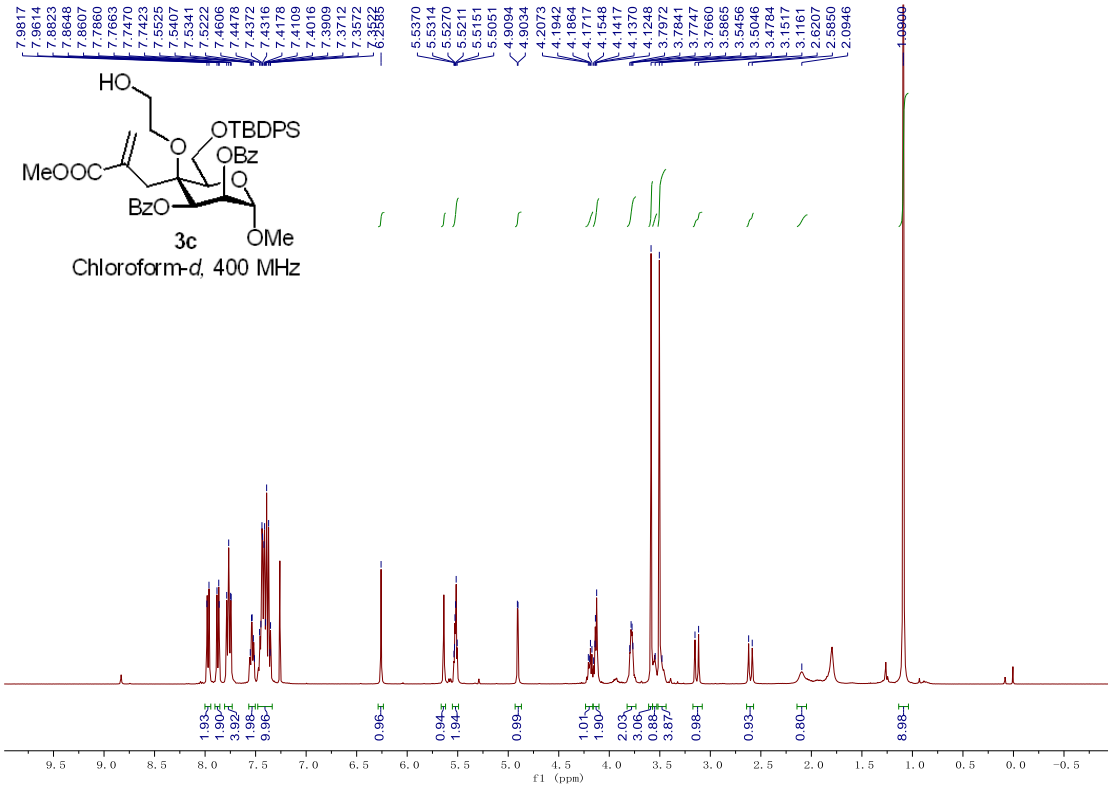
HSQC NMR Spectra of compound 3a′



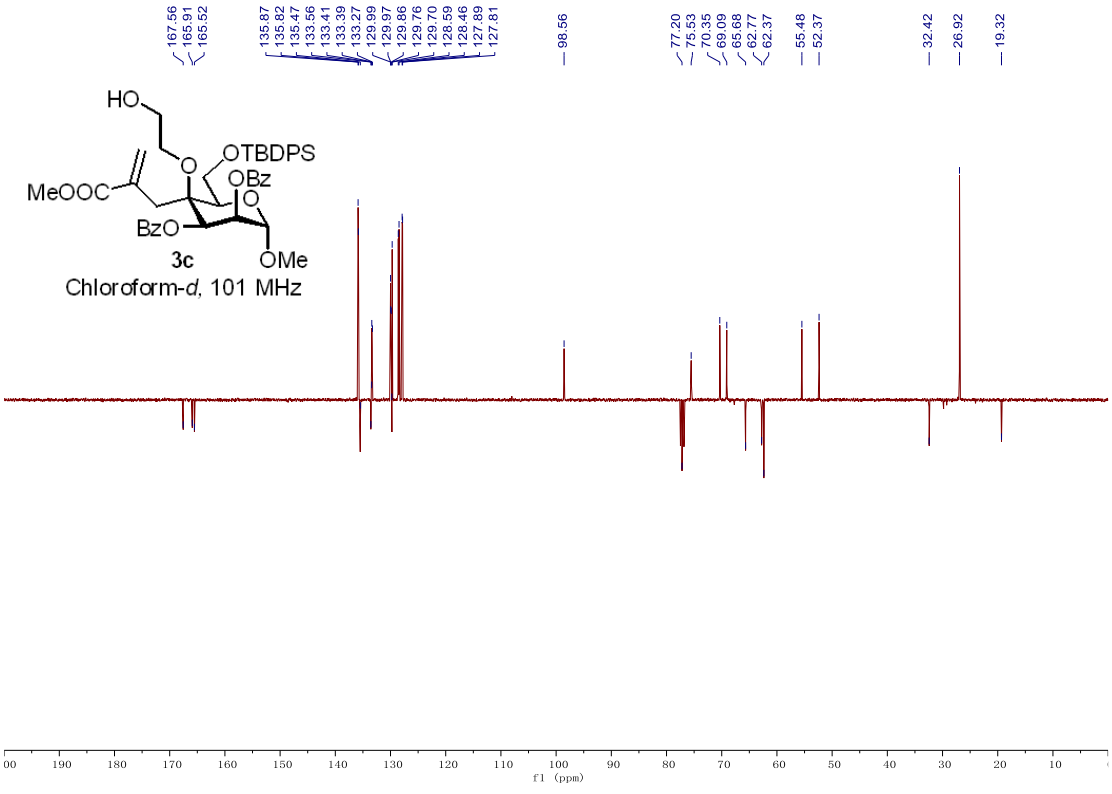
COSY NMR Spectra of compound 3a′



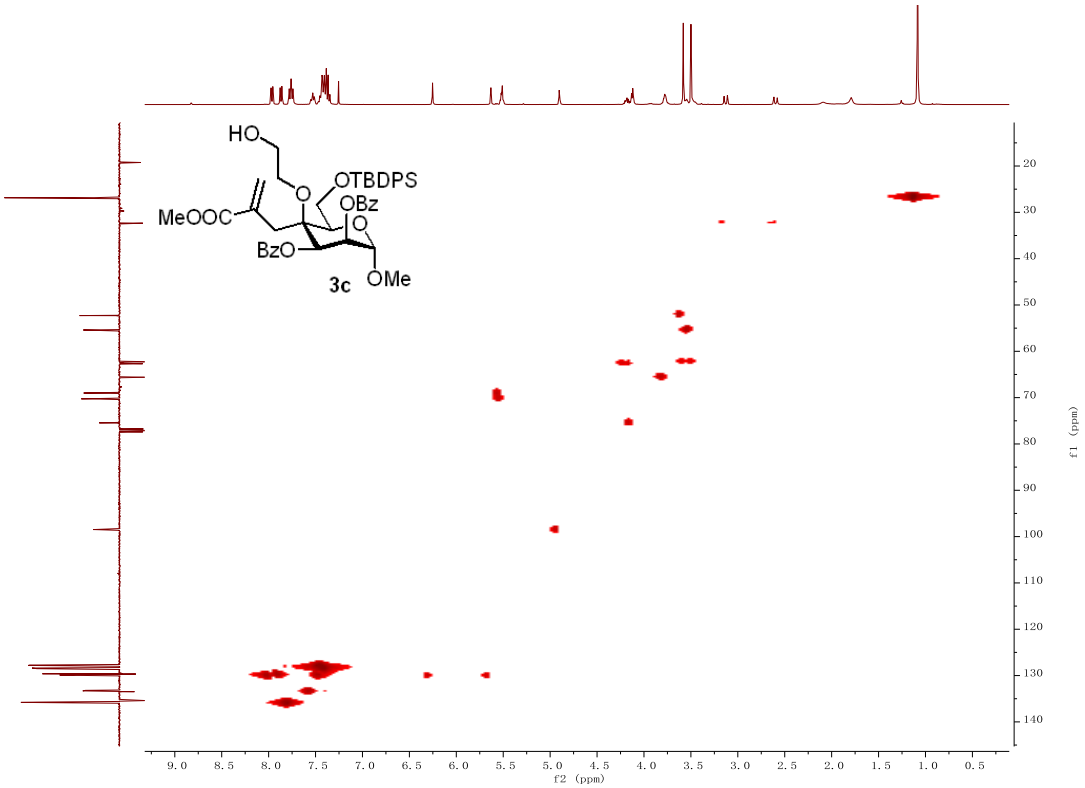
NOESY NMR Spectra of compound 3a′



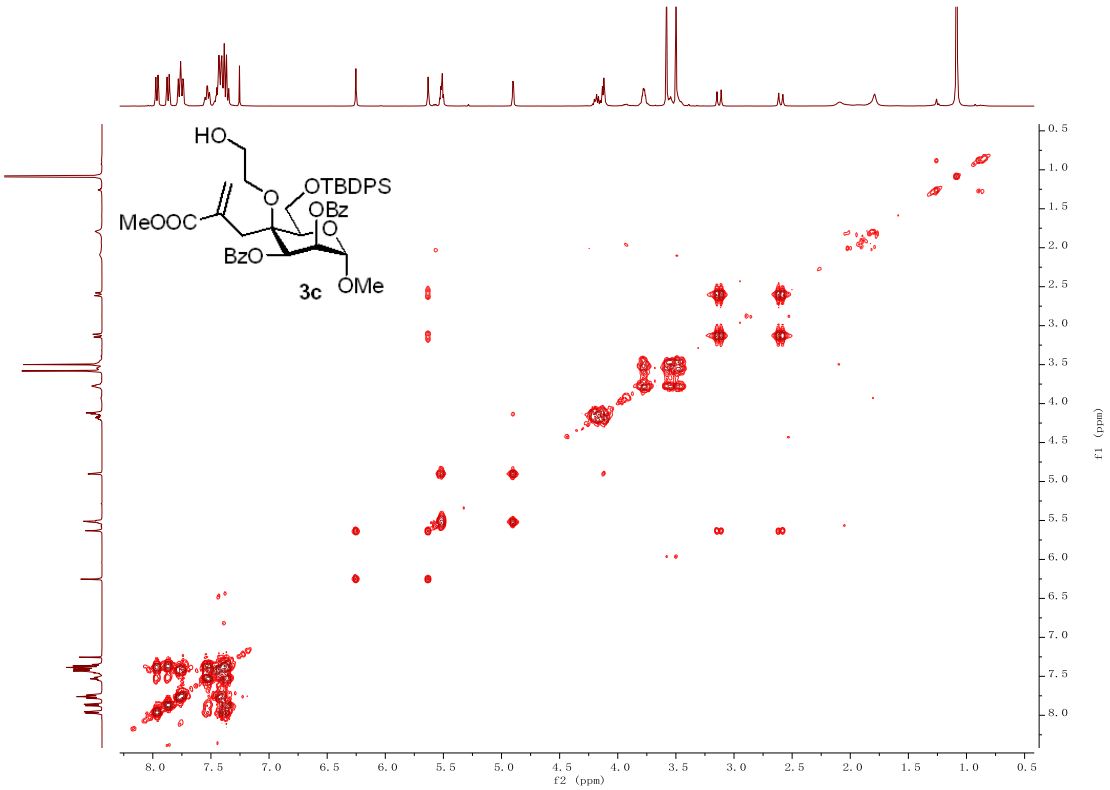
^{1}H NMR Spectra of compound 3c



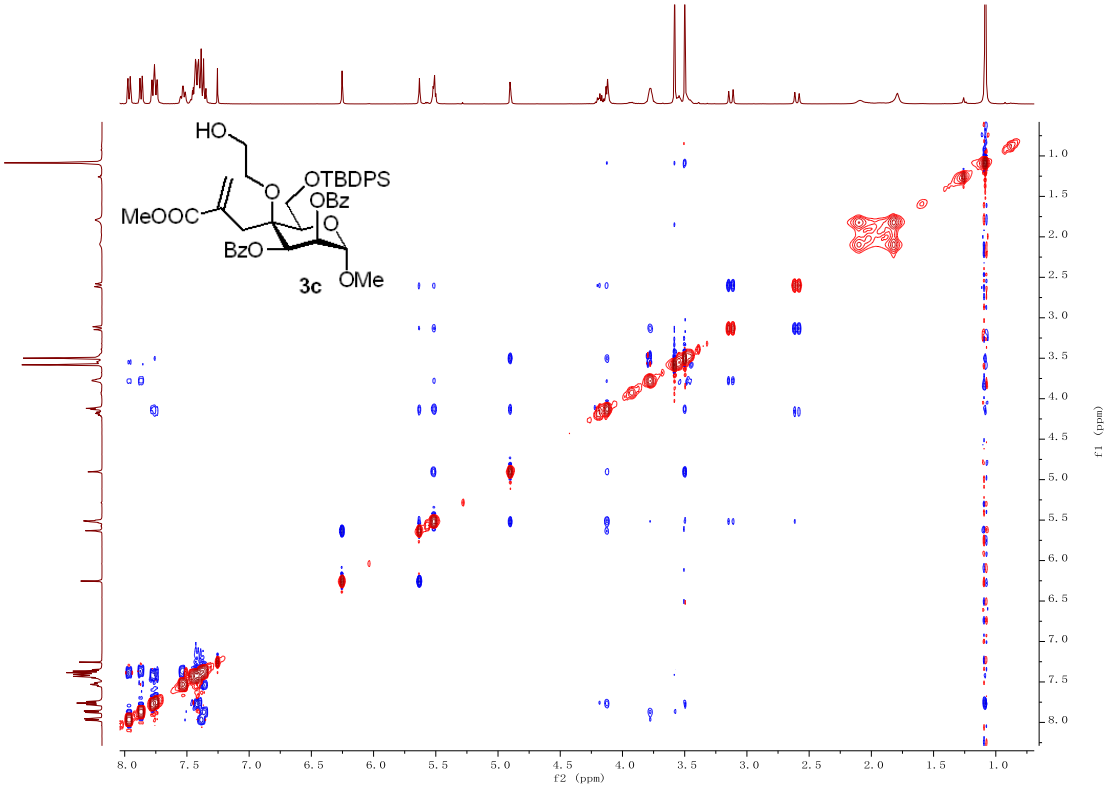
^{13}C NMR Spectra of compound 3c



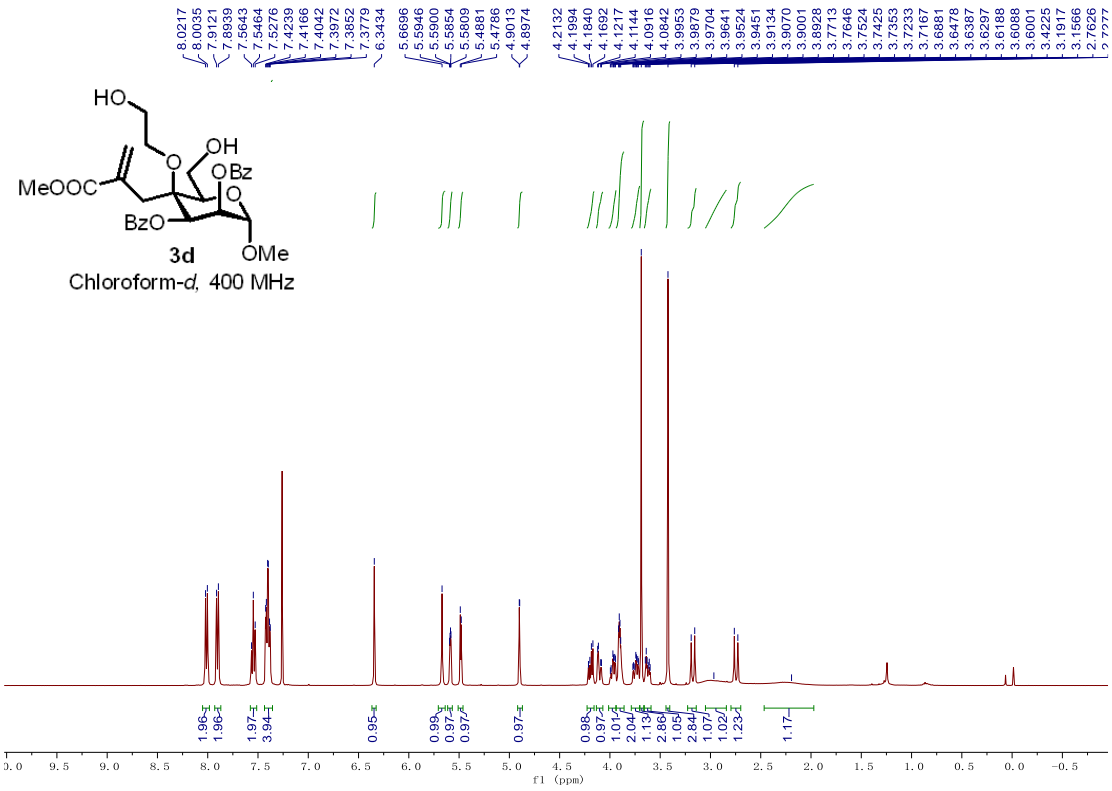
HSQC Spectra of compound 3c



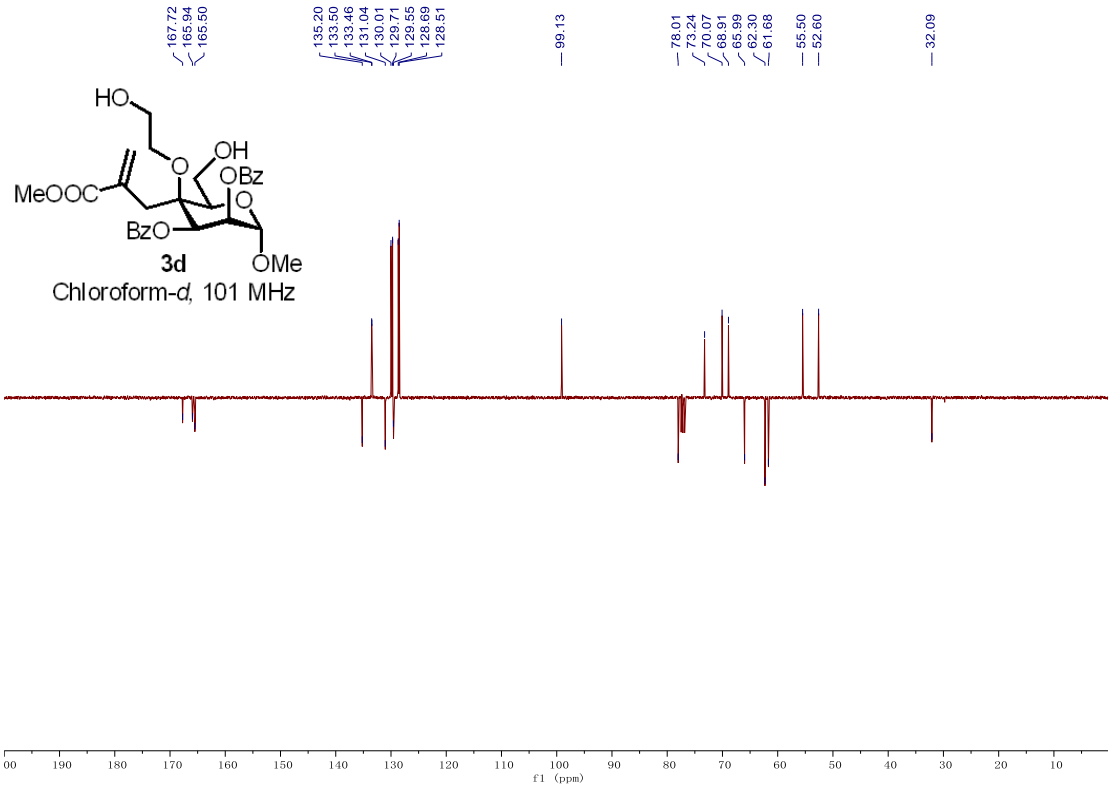
COSY Spectra of compound 3c



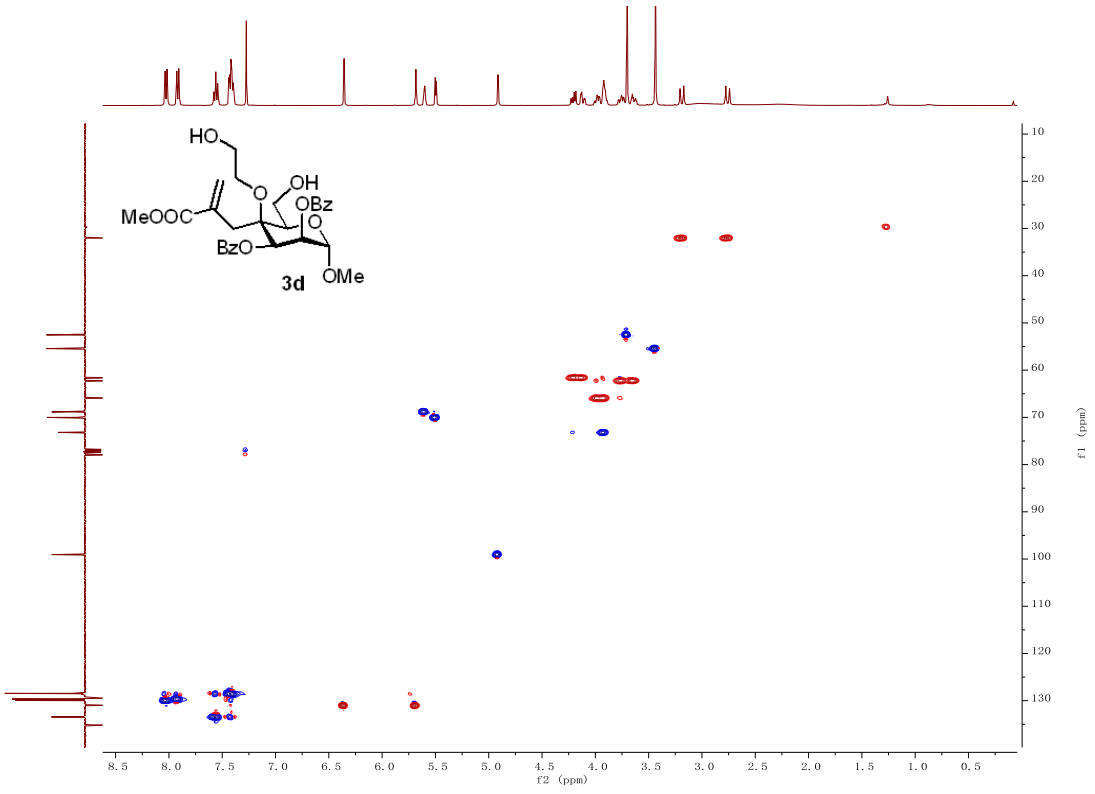
NOESY Spectra of compound 3c



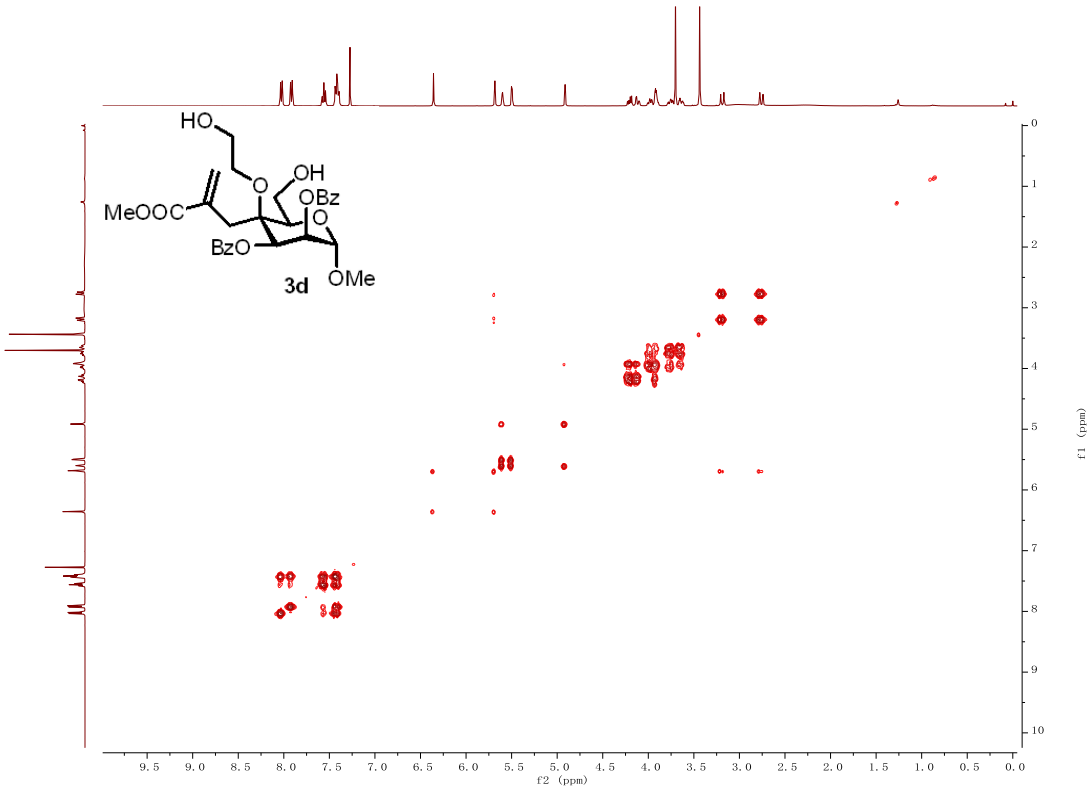
^{1}H NMR Spectra of compound 3d



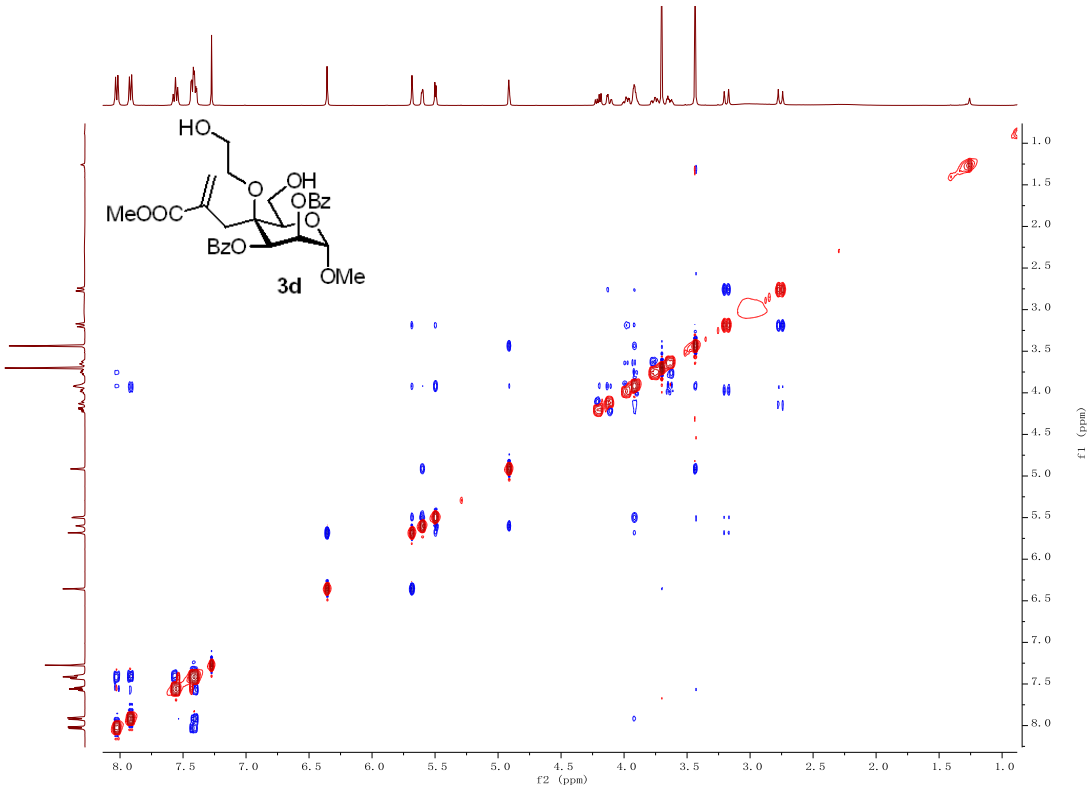
^{13}C NMR Spectra of compound 3d



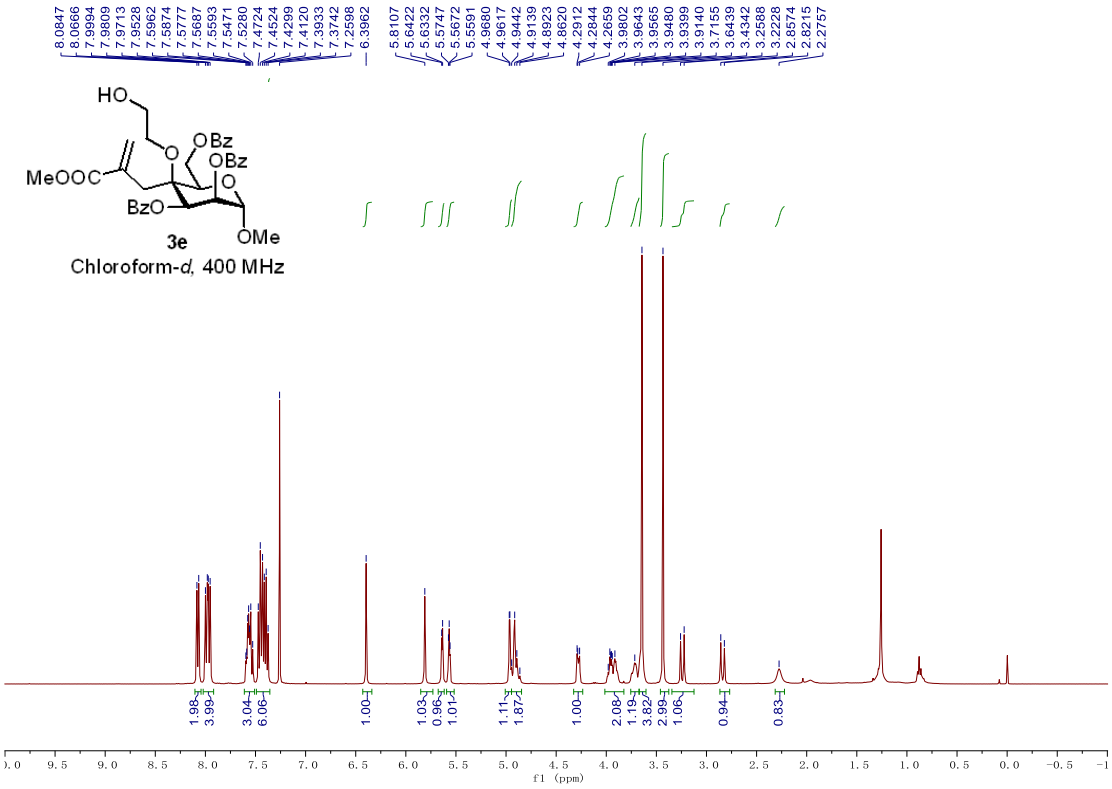
HSQC Spectra of compound 3d



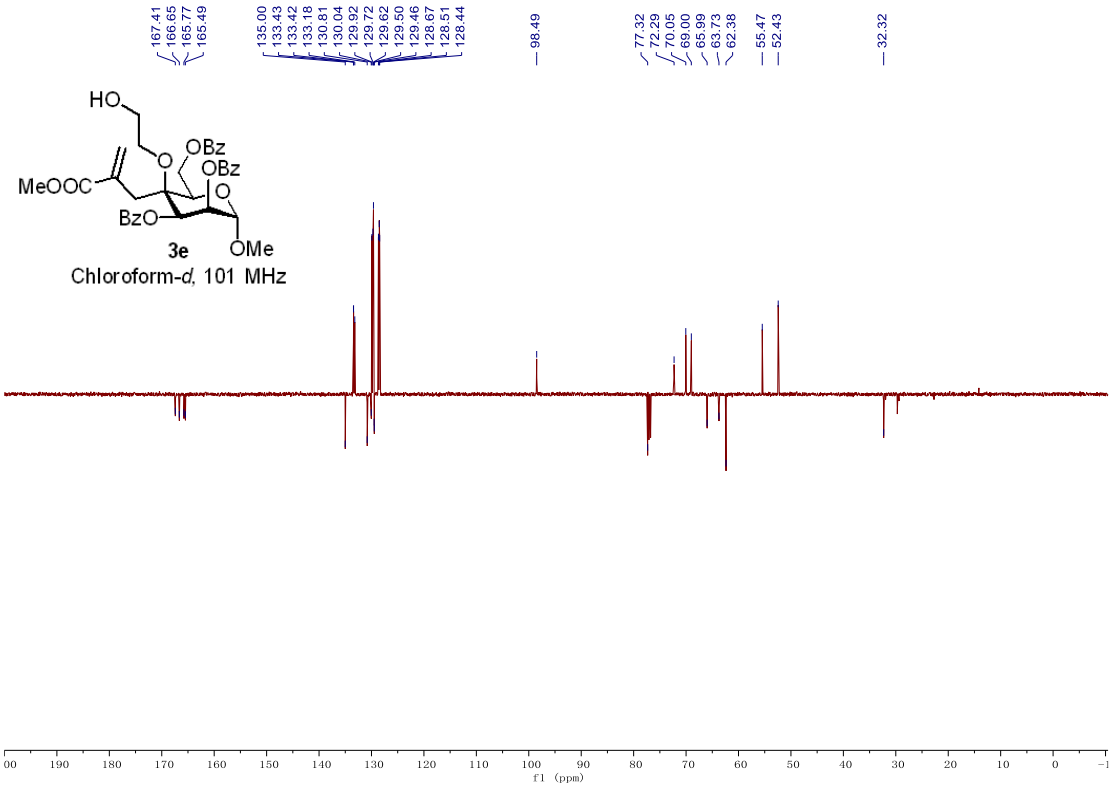
COSY Spectra of compound 3d



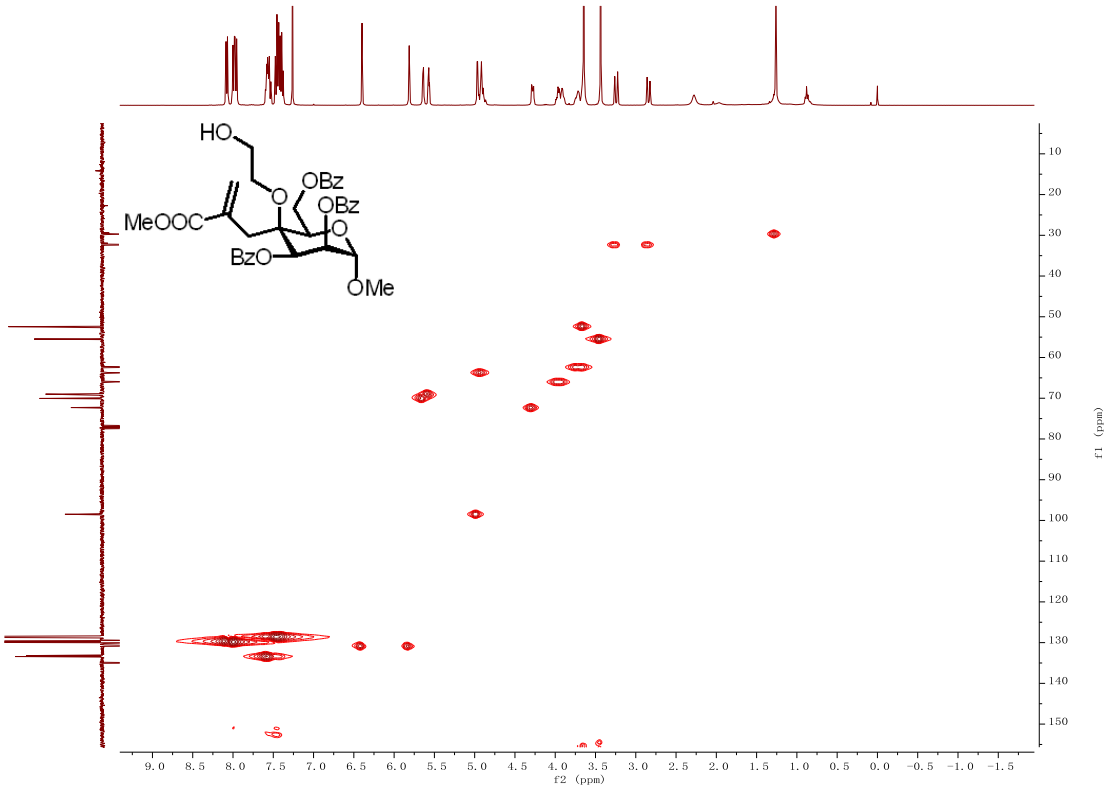
NOESY Spectra of compound 3d



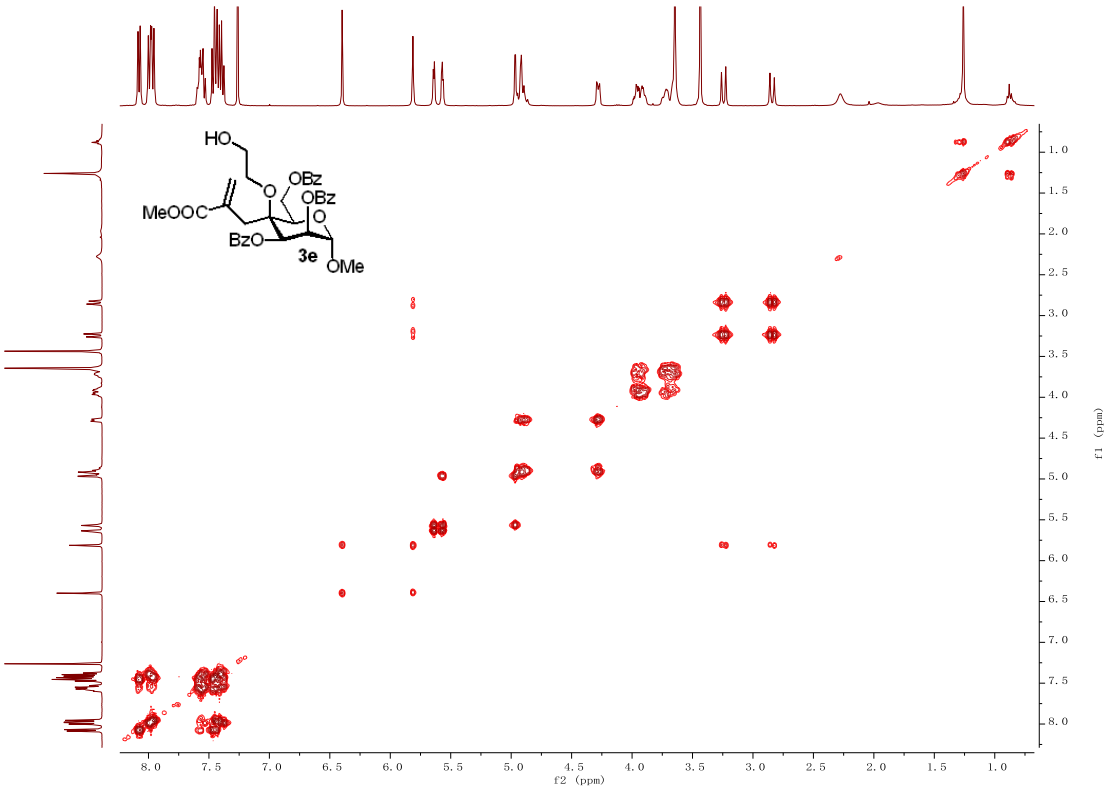
^{1}H NMR Spectra of compound 3e



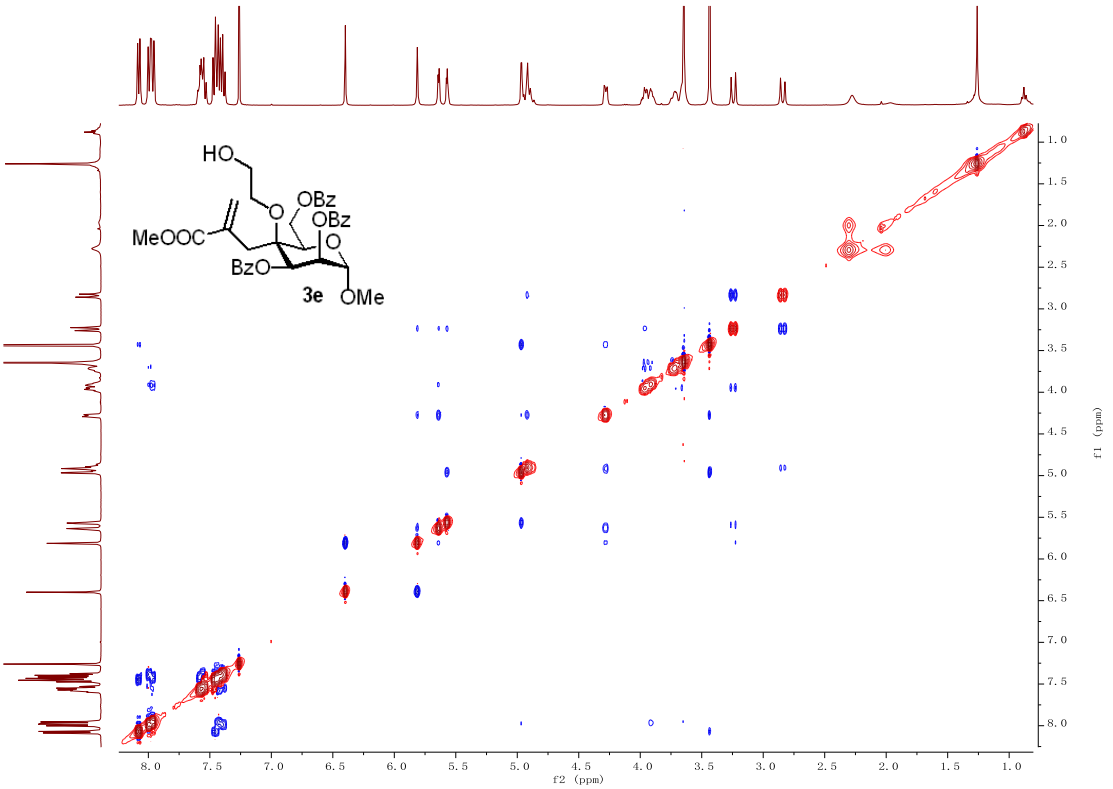
^{13}C NMR Spectra of compound 3e



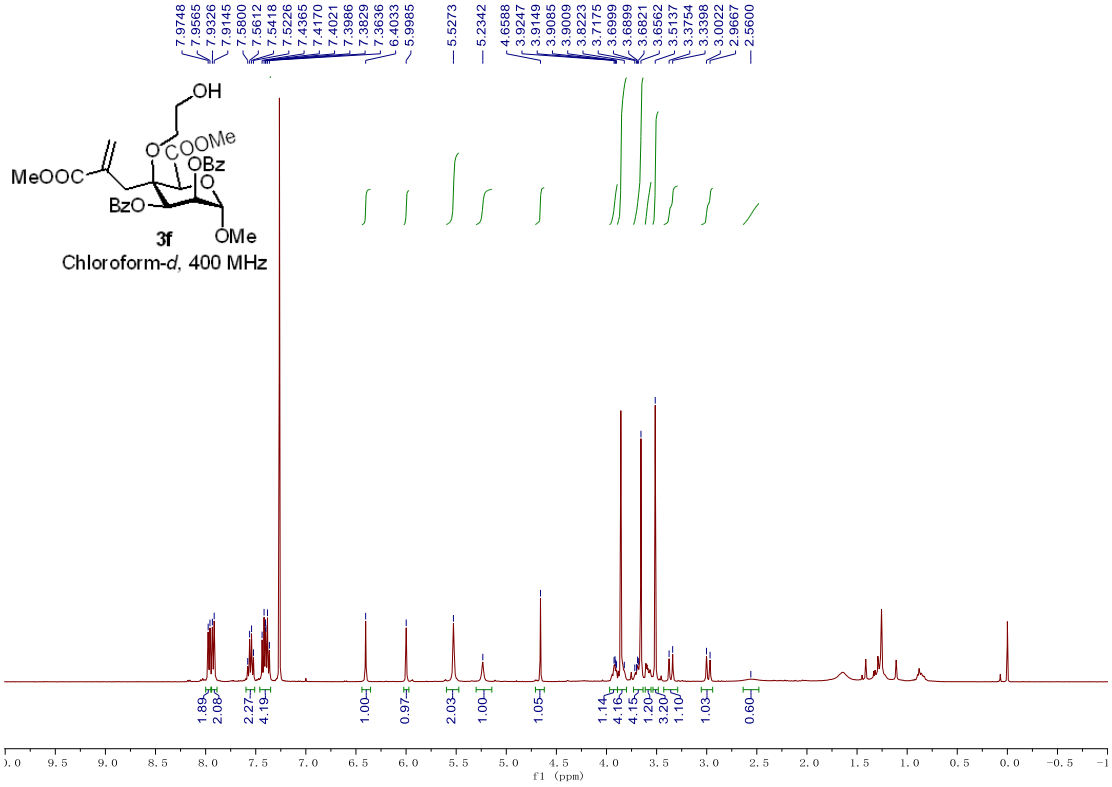
HSQC NMR Spectra of compound 3e



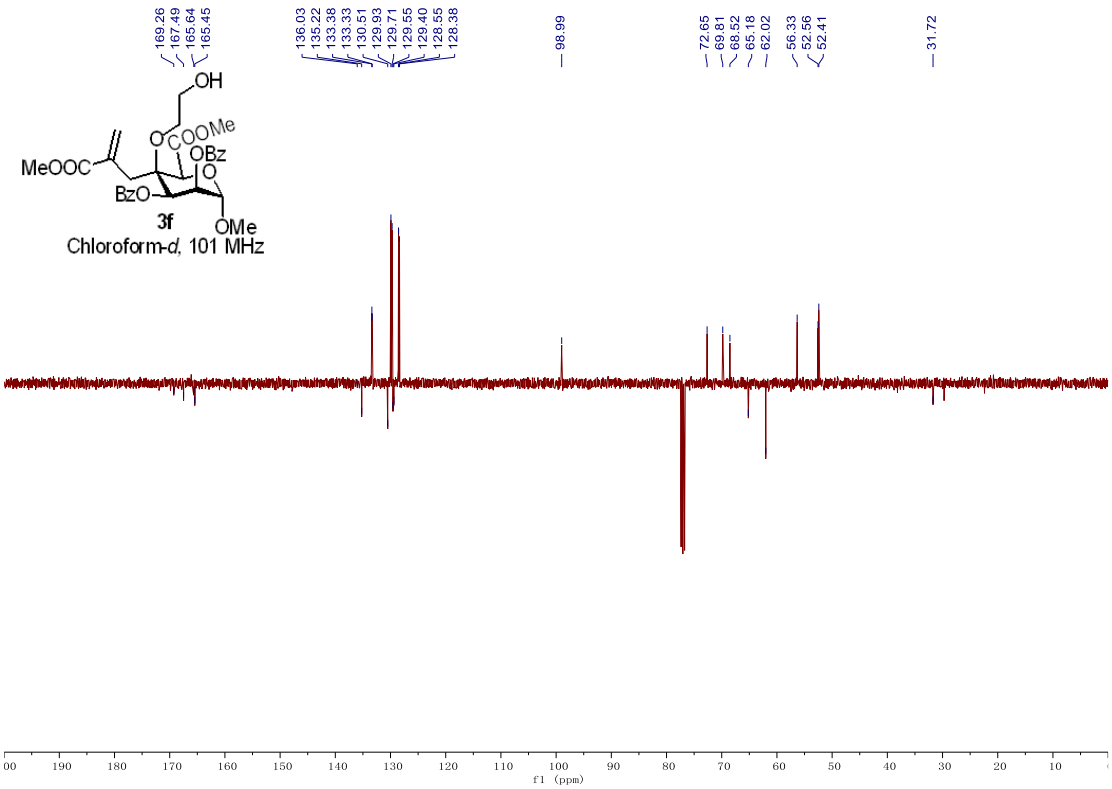
COSY NMR Spectra of compound 3e



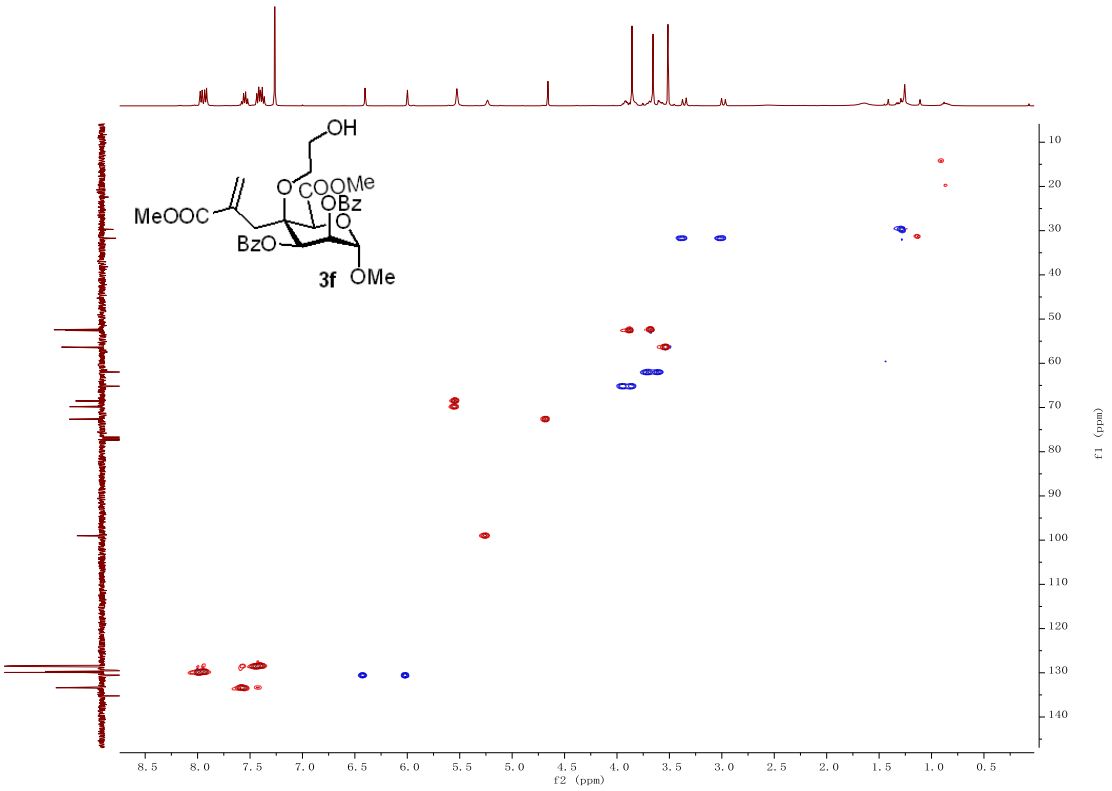
NOESY NMR Spectra of compound 3e



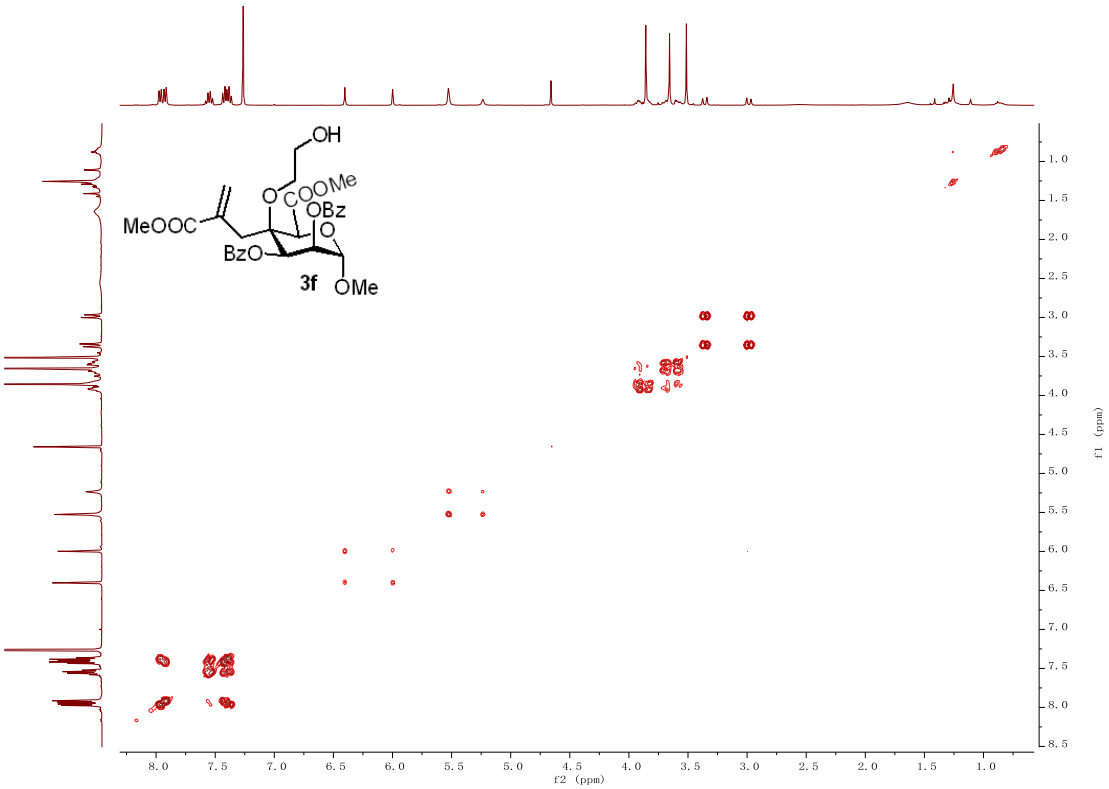
^{1}H NMR Spectra of compound 3f



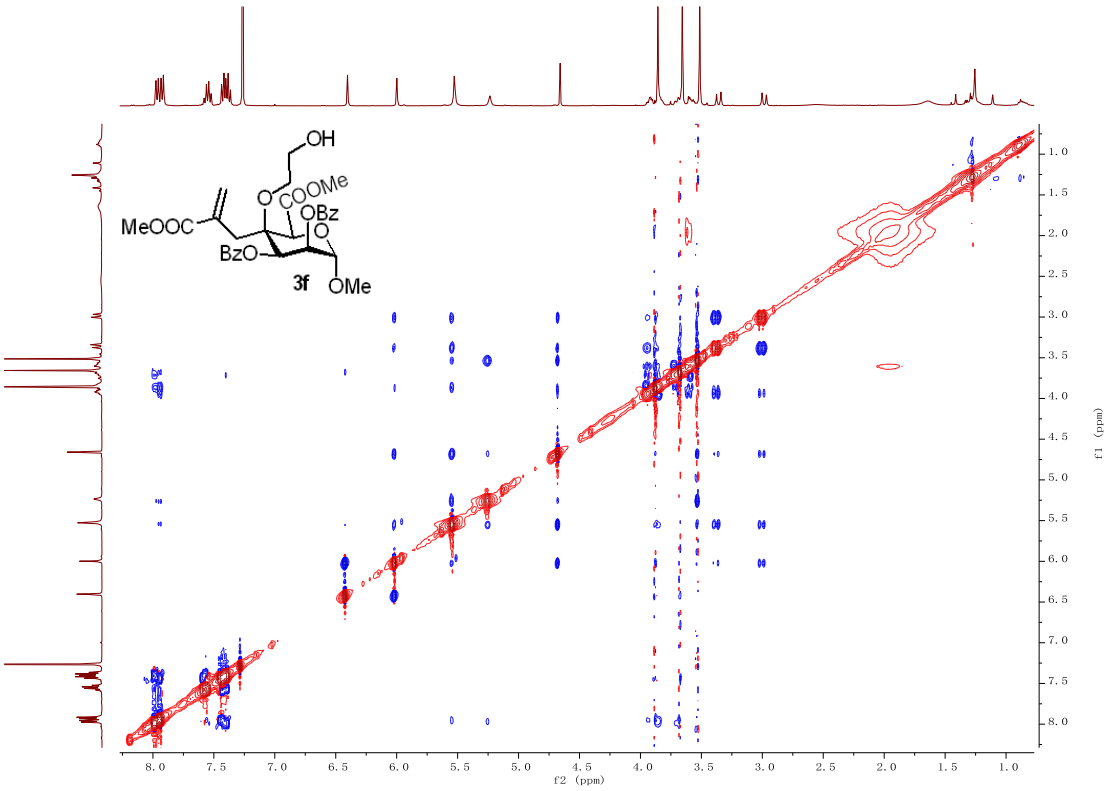
^{13}C NMR Spectra of compound 3f



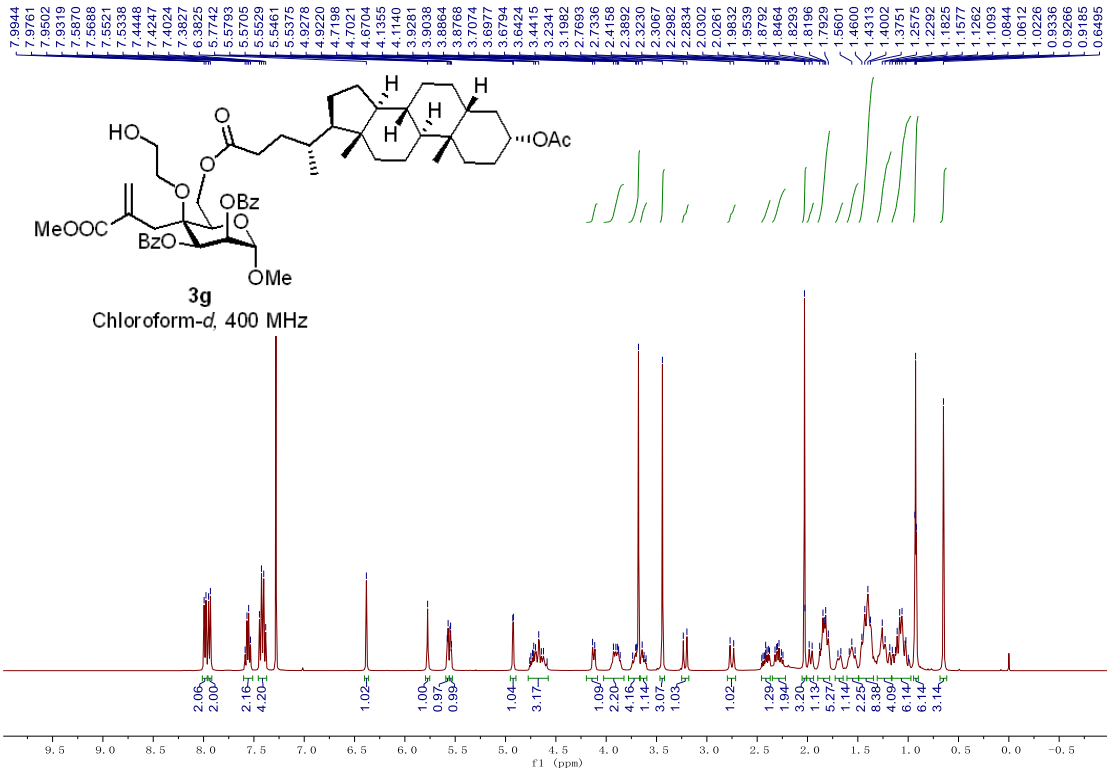
HSQC NMR Spectra of compound 3f



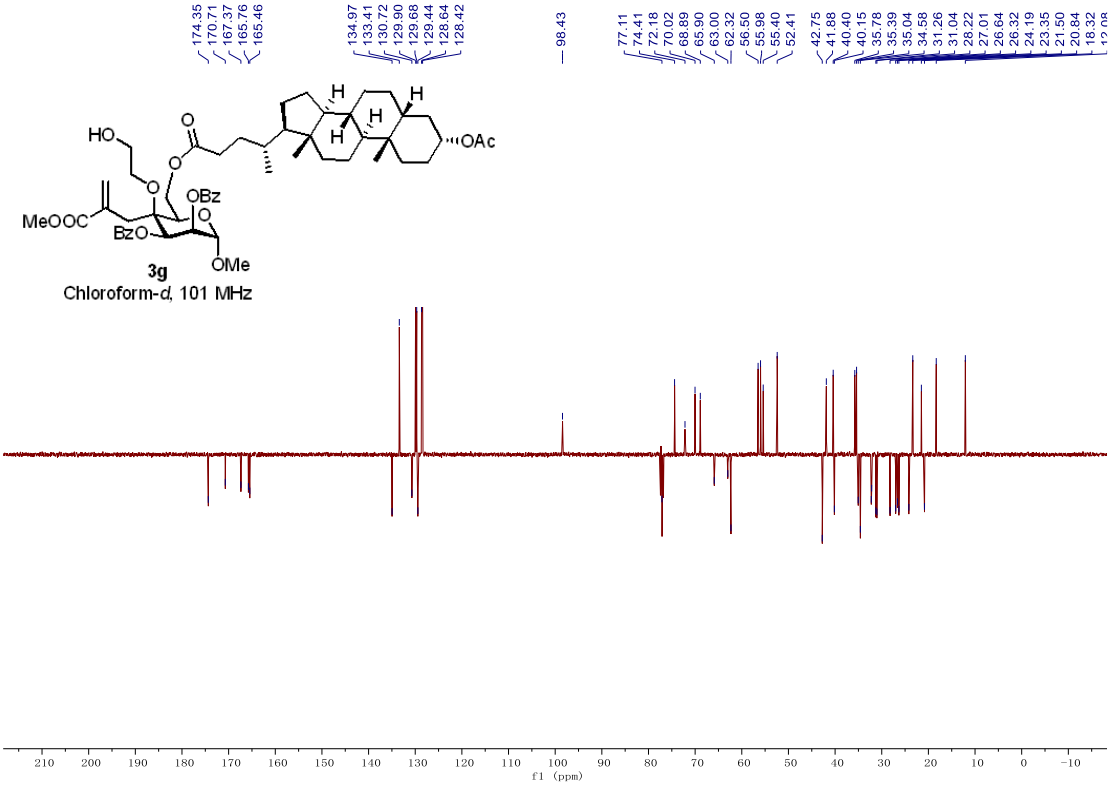
COSY NMR Spectra of compound 3f



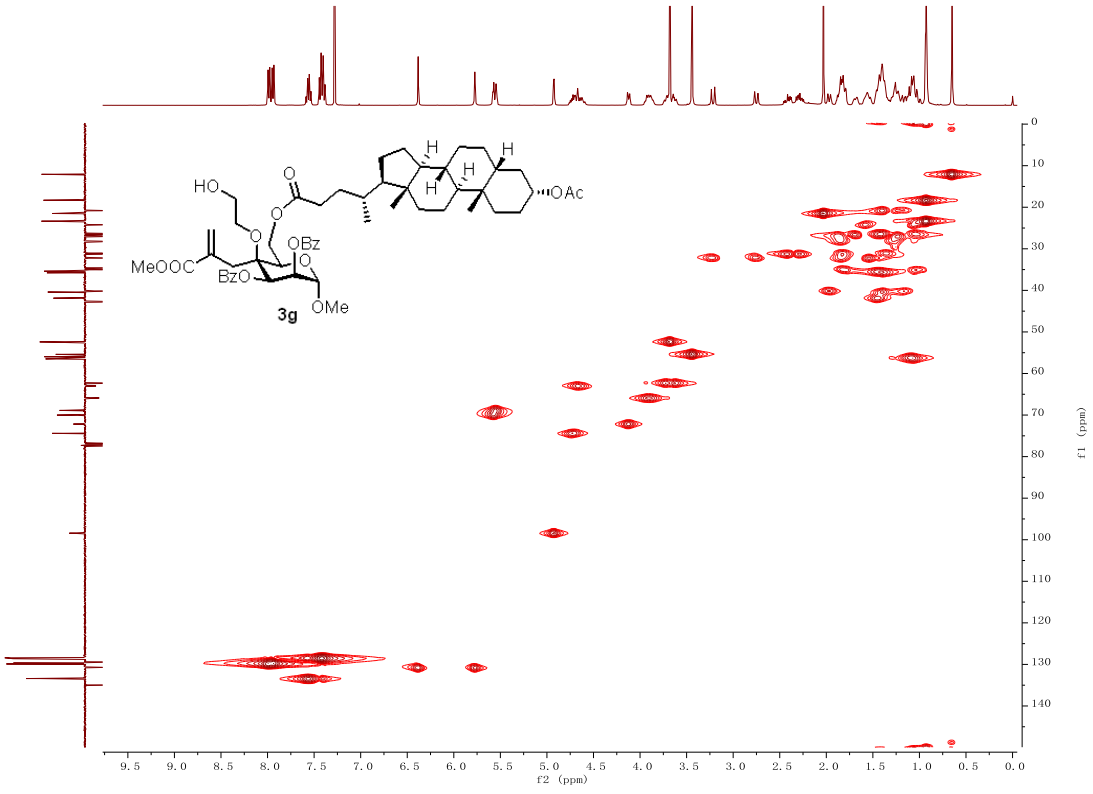
NOESY NMR Spectra of compound 3f



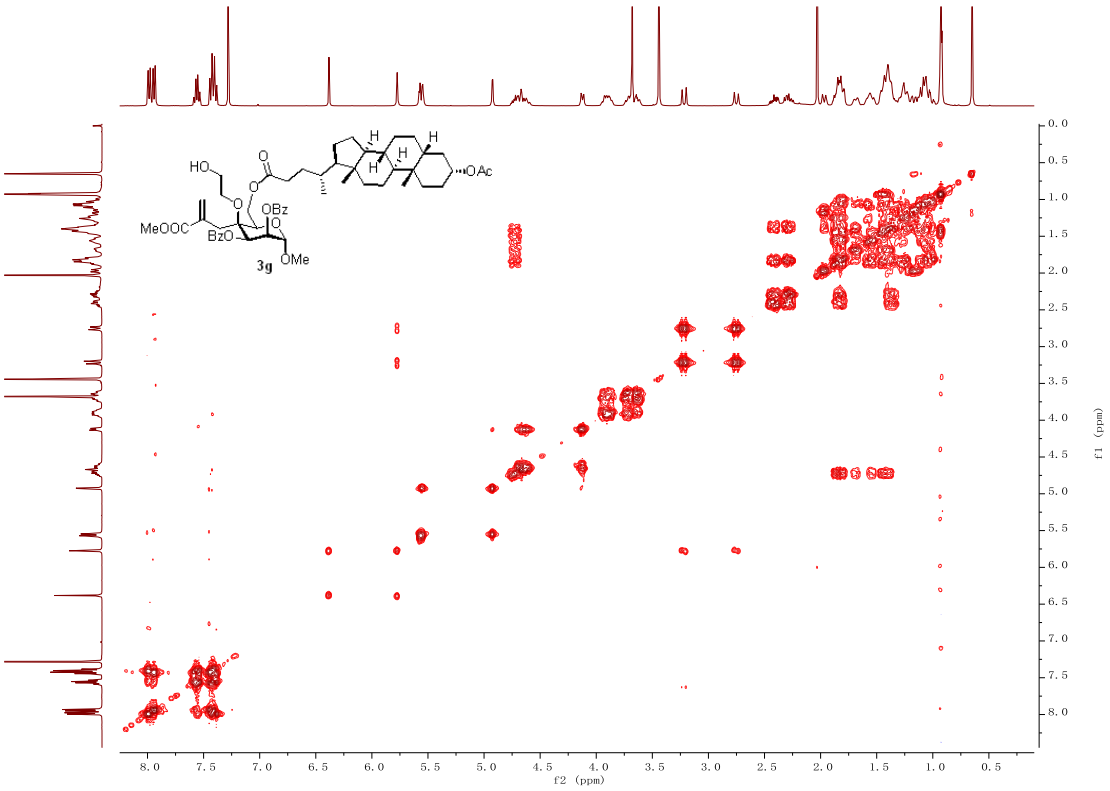
^{1}H NMR Spectra of compound 3g



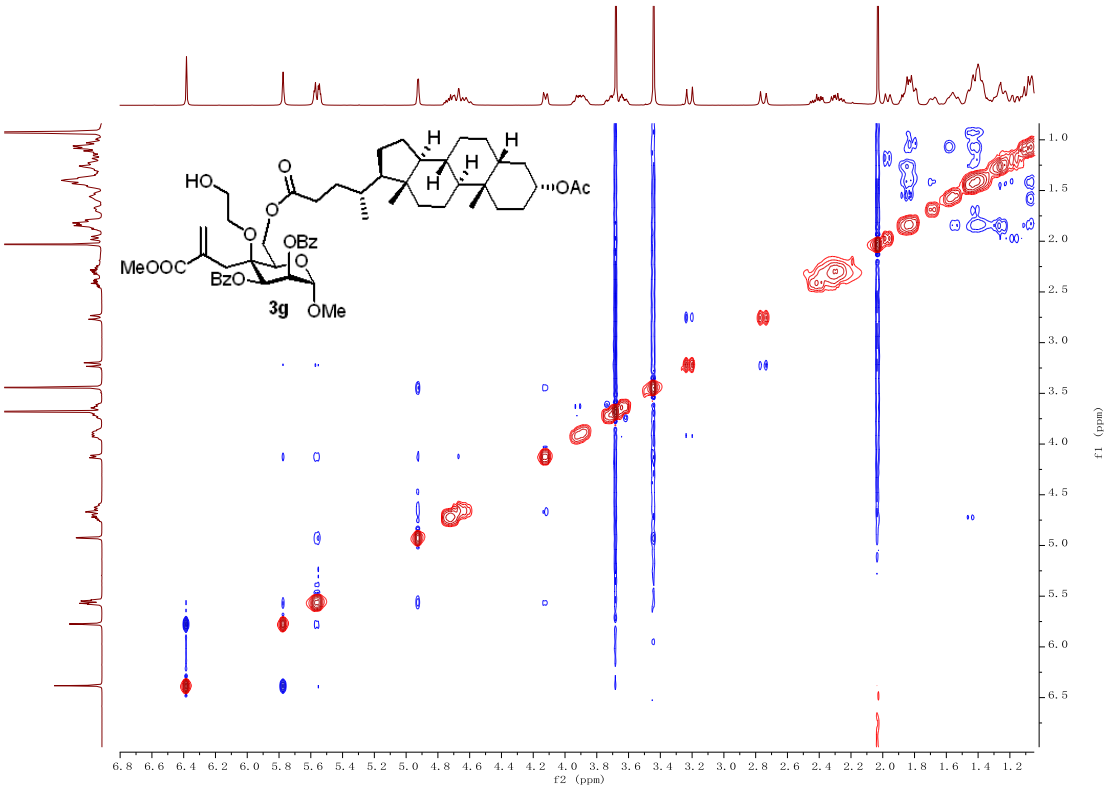
^{13}C NMR Spectra of compound 3g



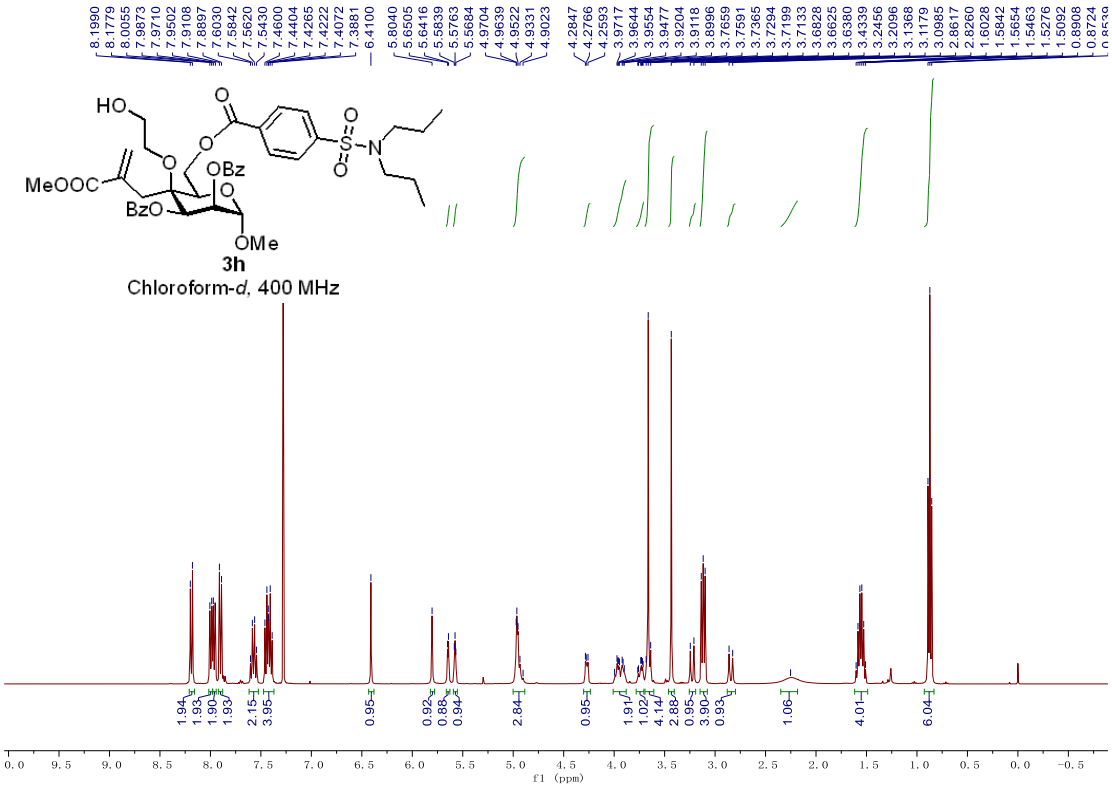
HSQC Spectra of compound 3g



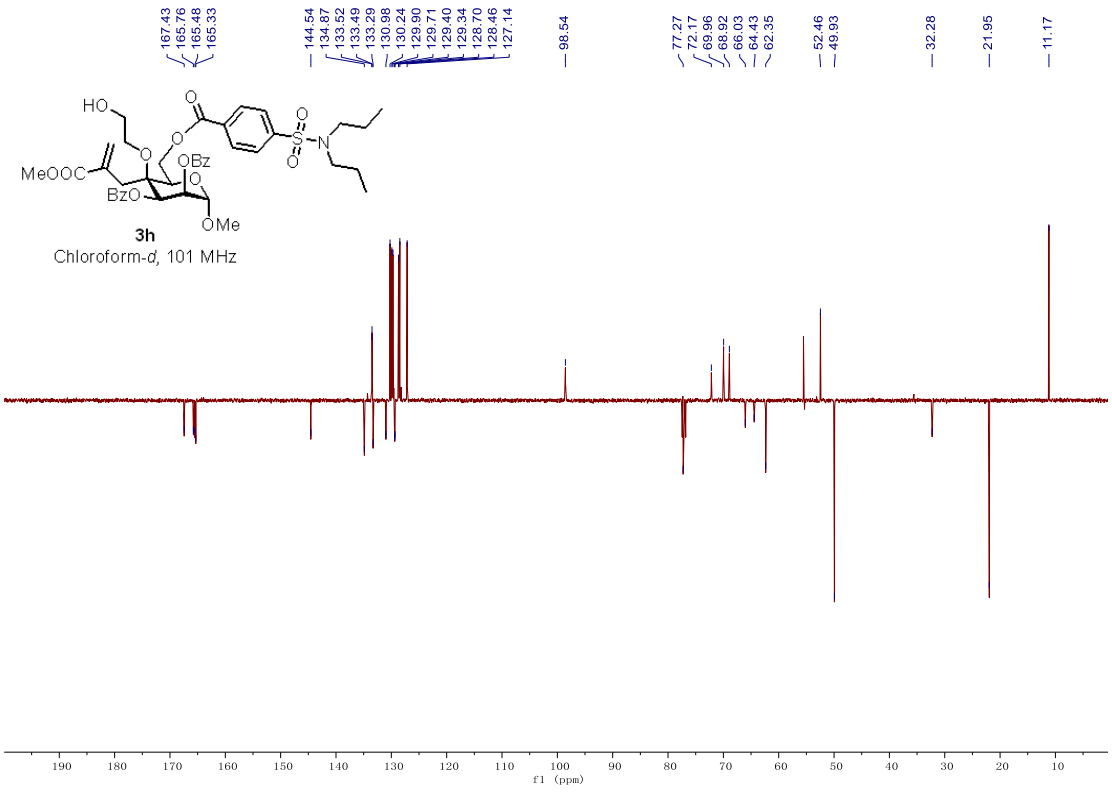
COSY Spectra of compound 3g



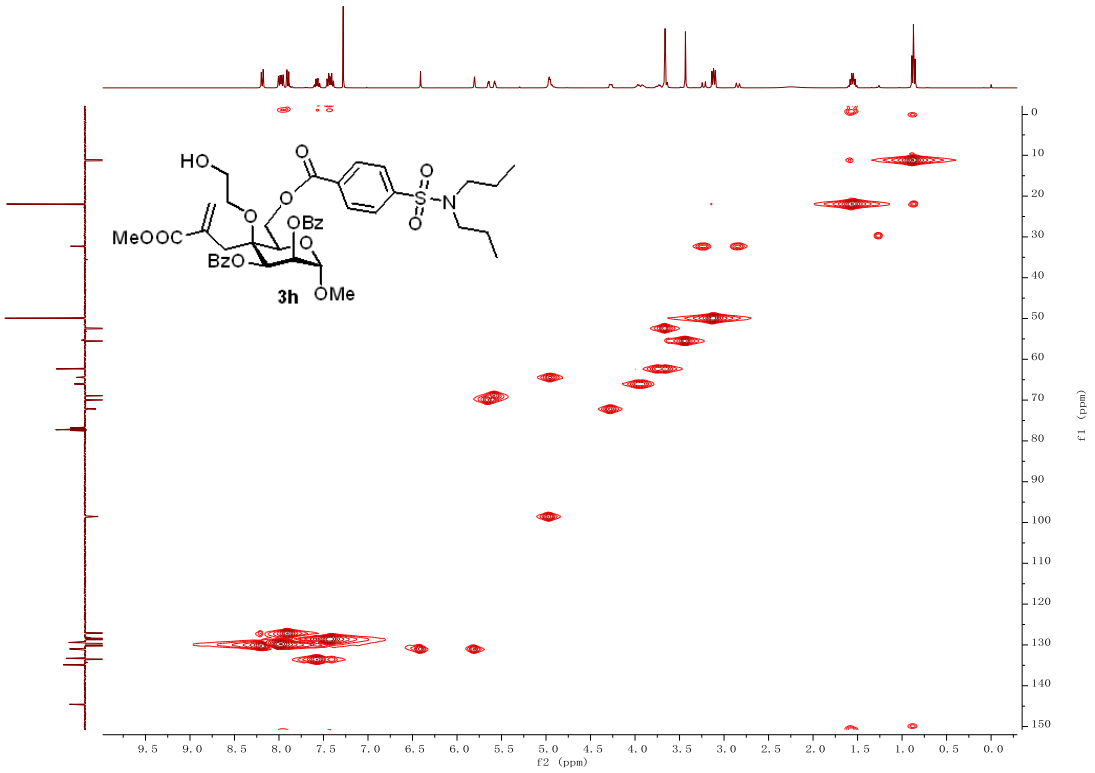
NOESY Spectra of compound 3g



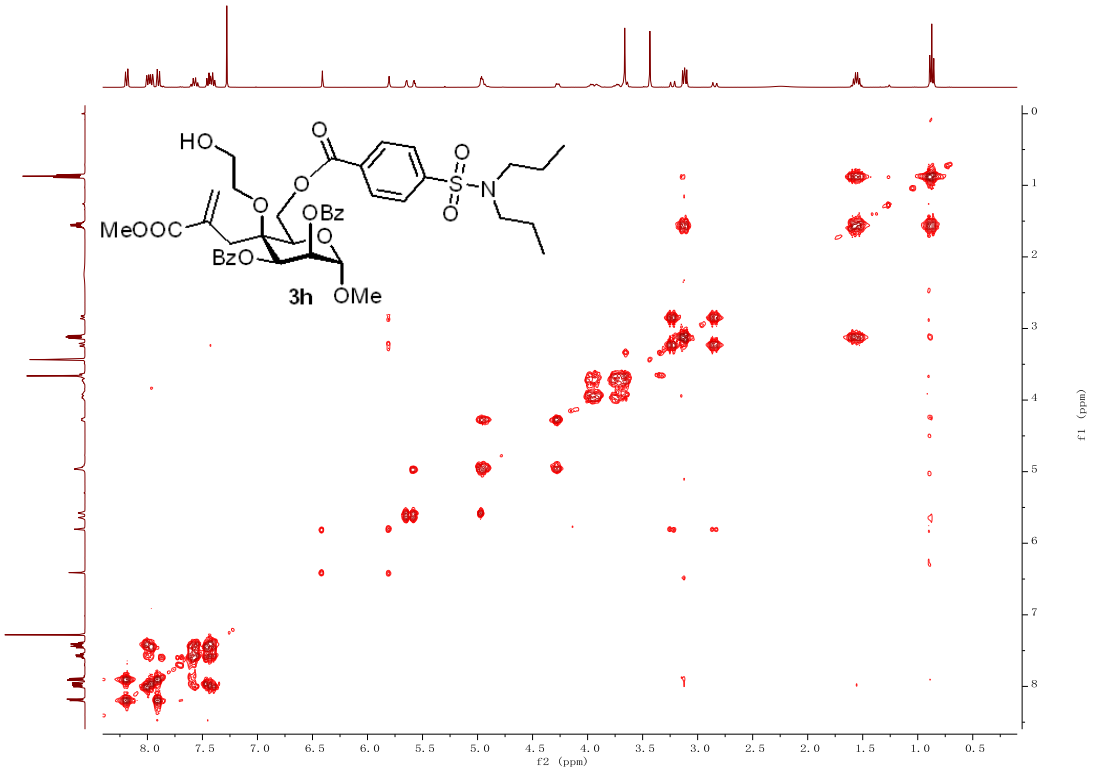
^{1}H NMR Spectra of compound 3h



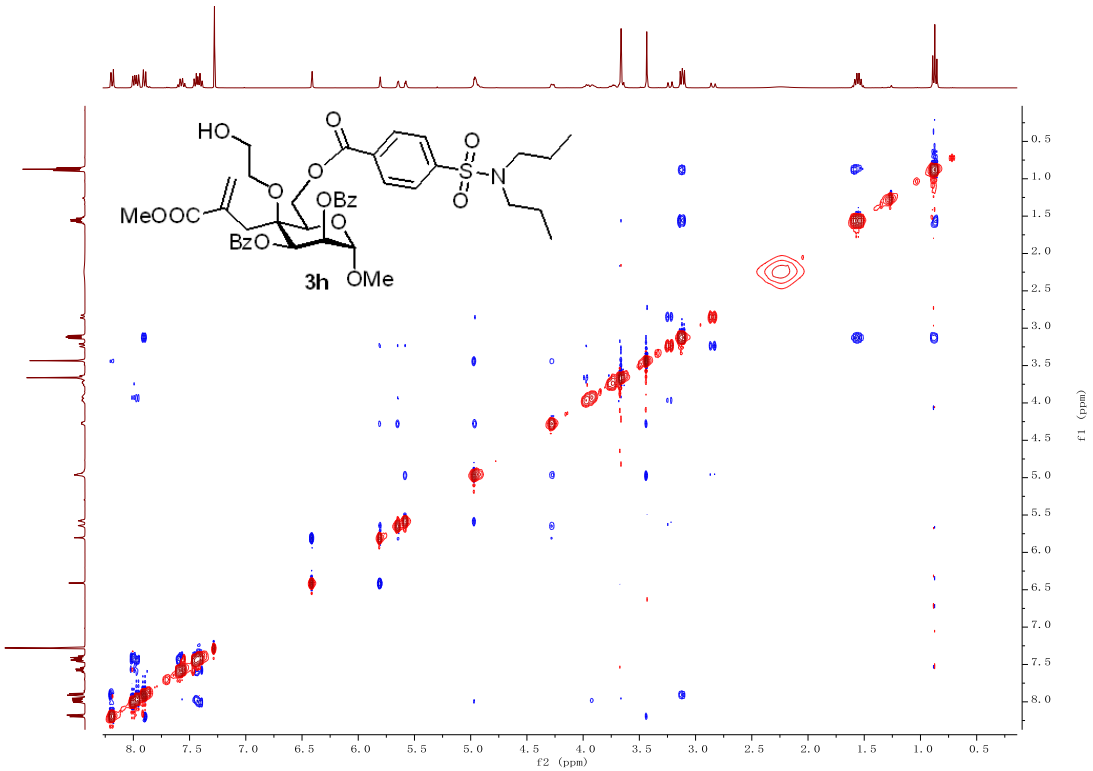
^{13}C NMR Spectra of compound 3h



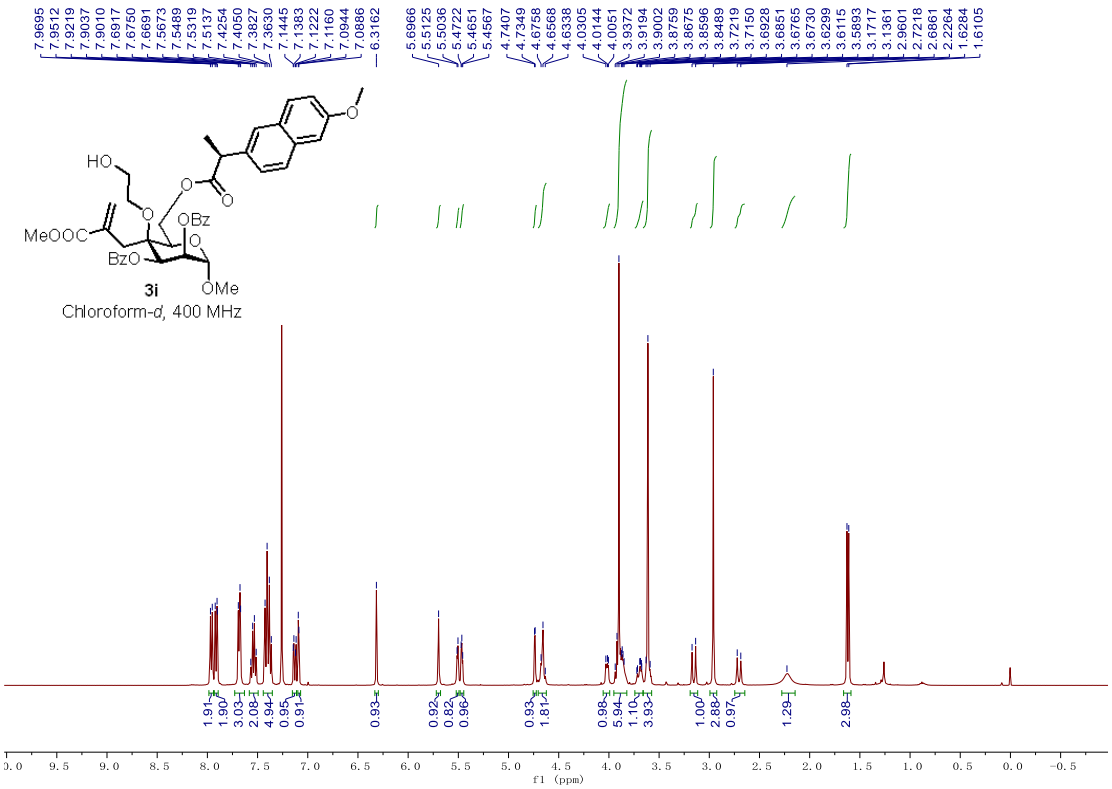
HSQC Spectra of compound 3h



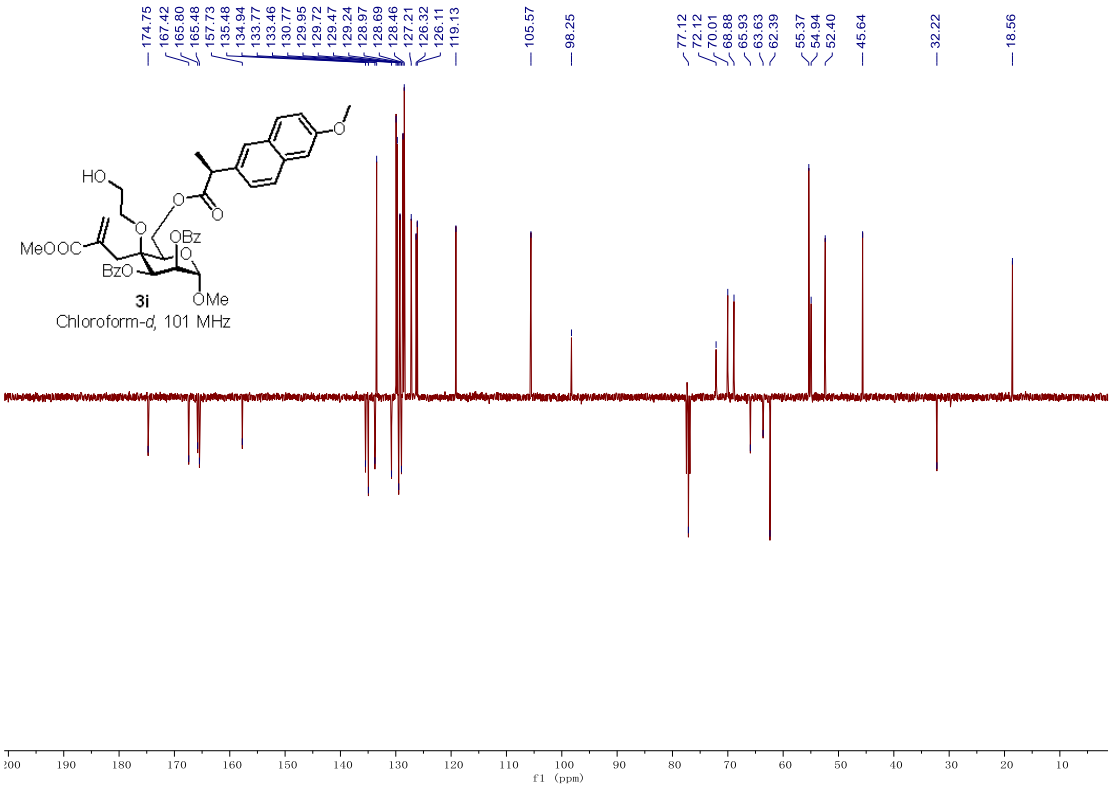
COSY Spectra of compound 3h



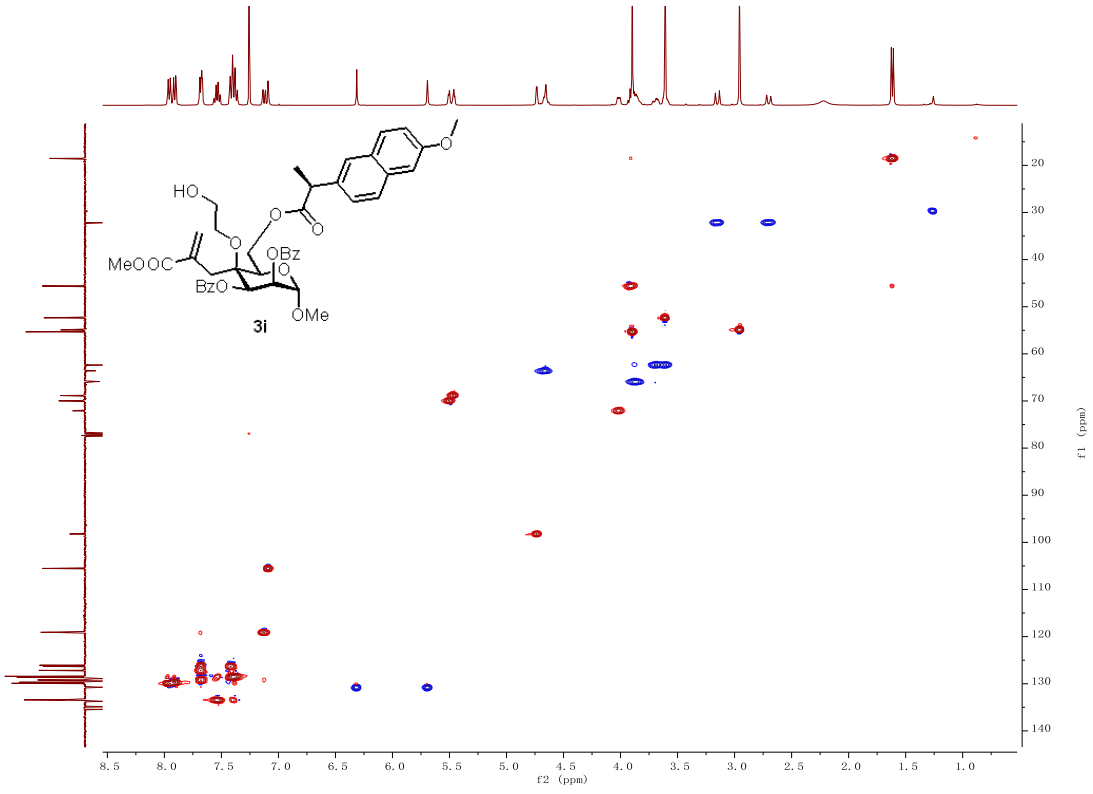
NOESY Spectra of compound 3h



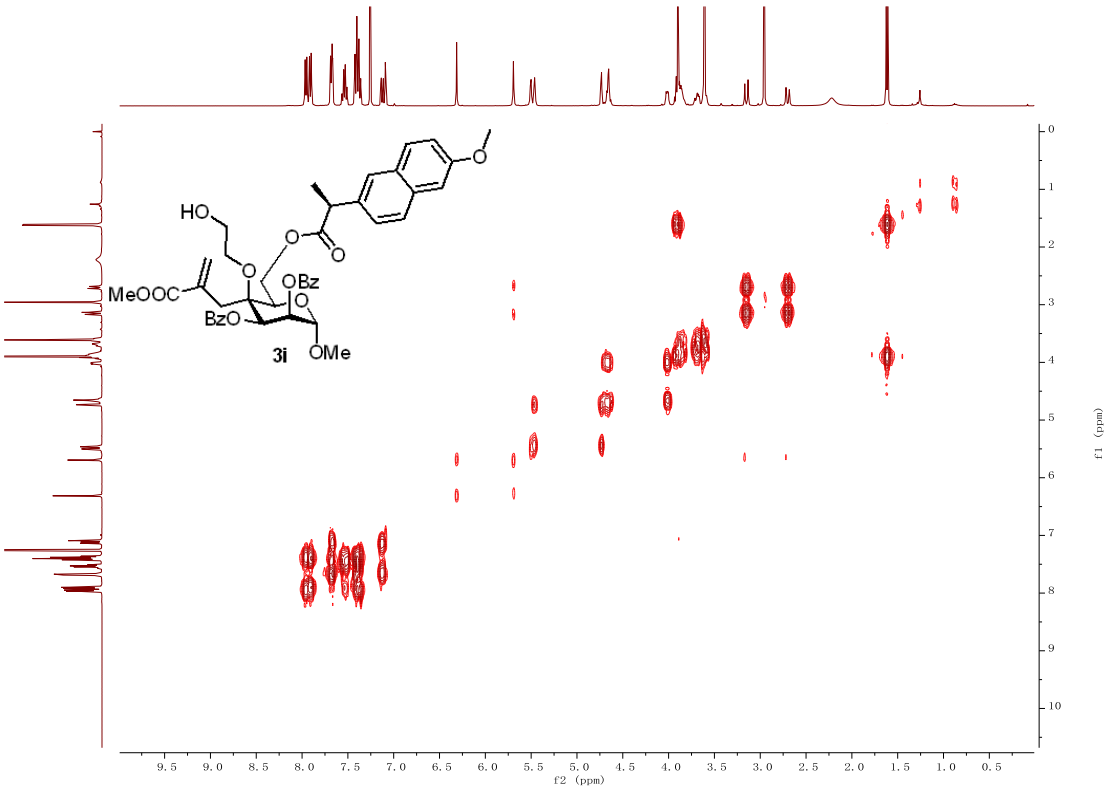
^{1}H NMR Spectra of compound 3i



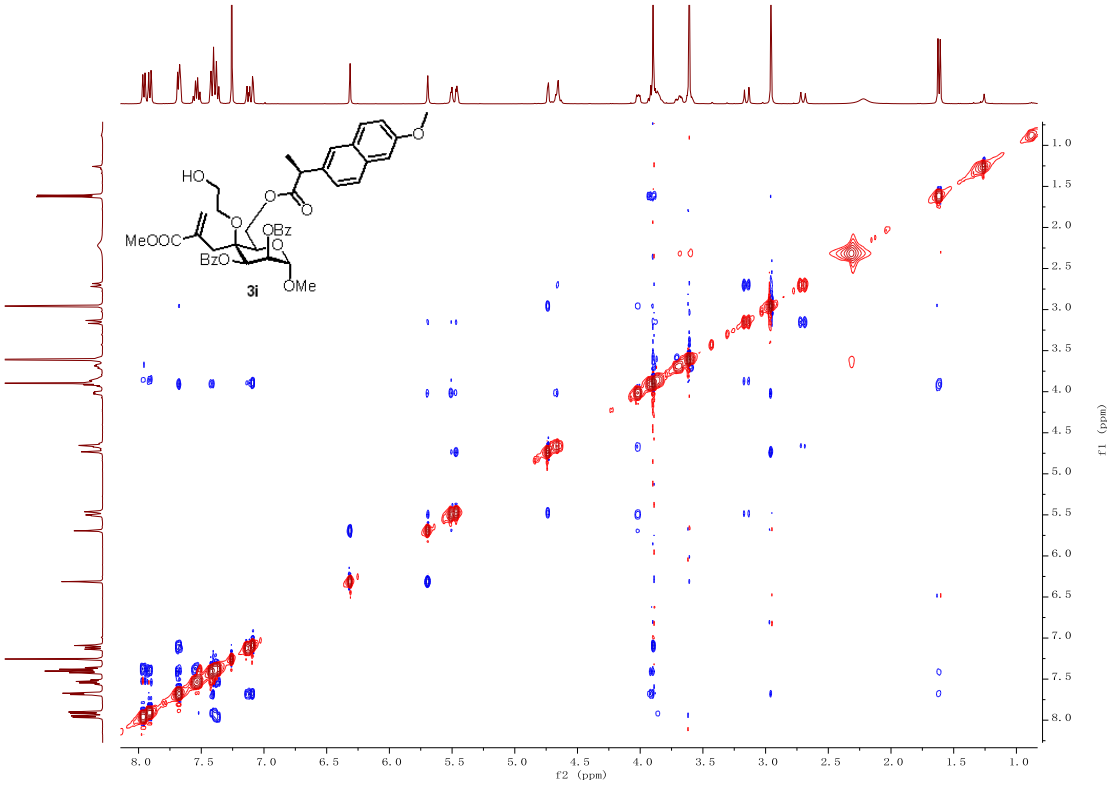
^{13}C NMR Spectra of compound 3i



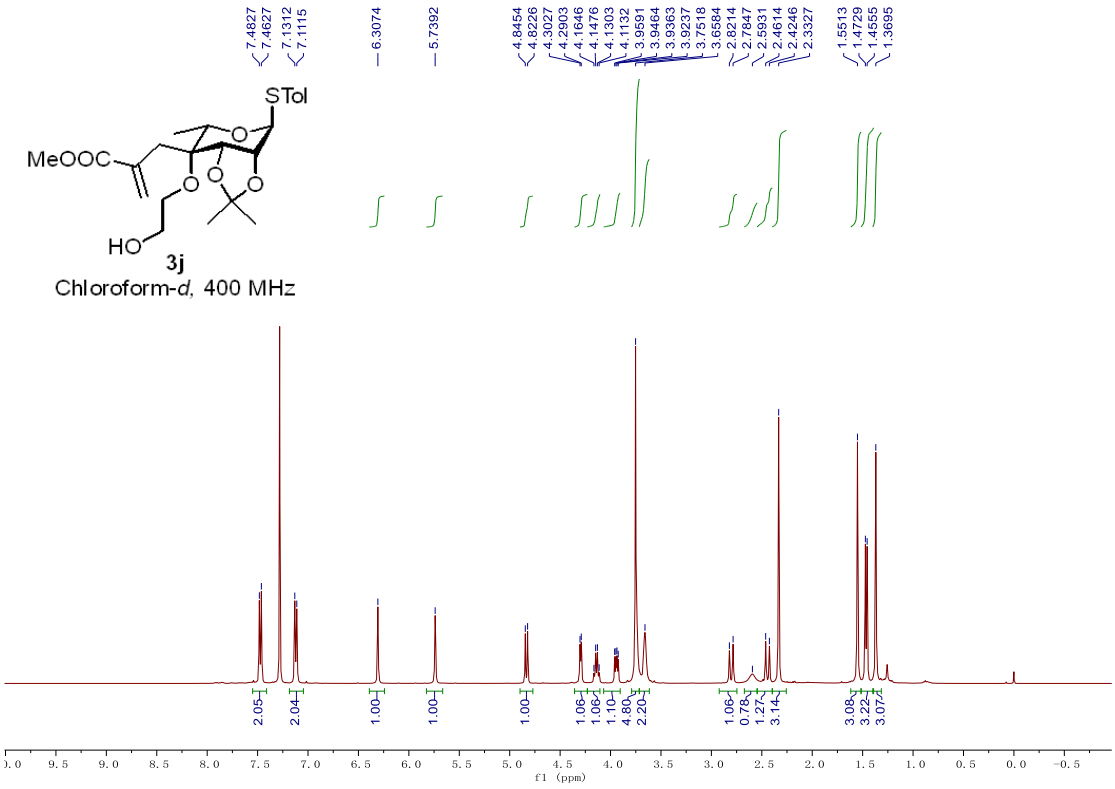
HSQC Spectra of compound 3i



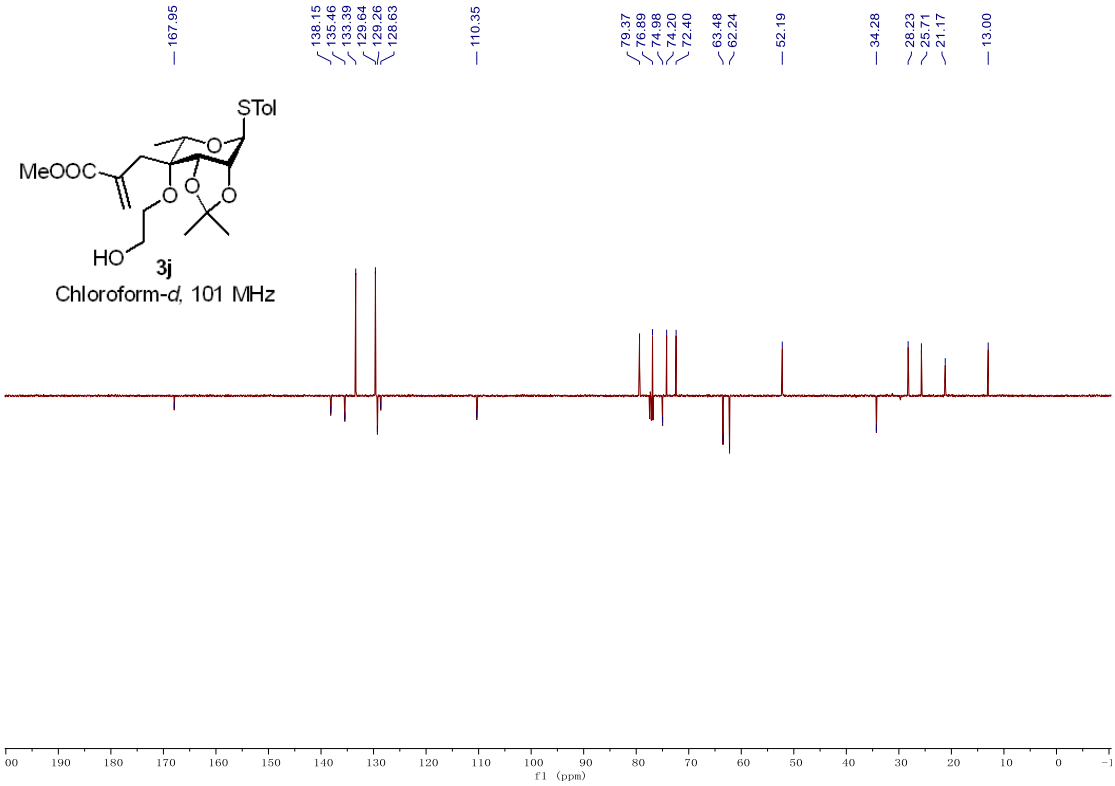
COSY Spectra of compound 3i



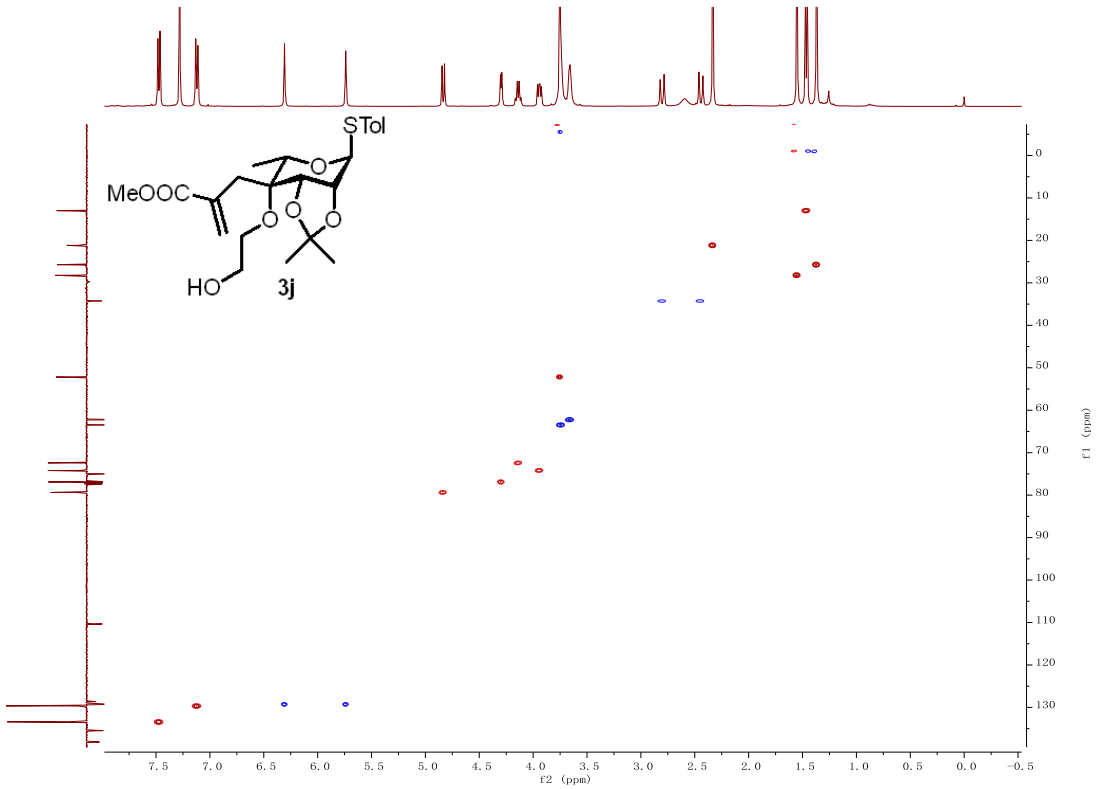
NOESY Spectra of compound 3i



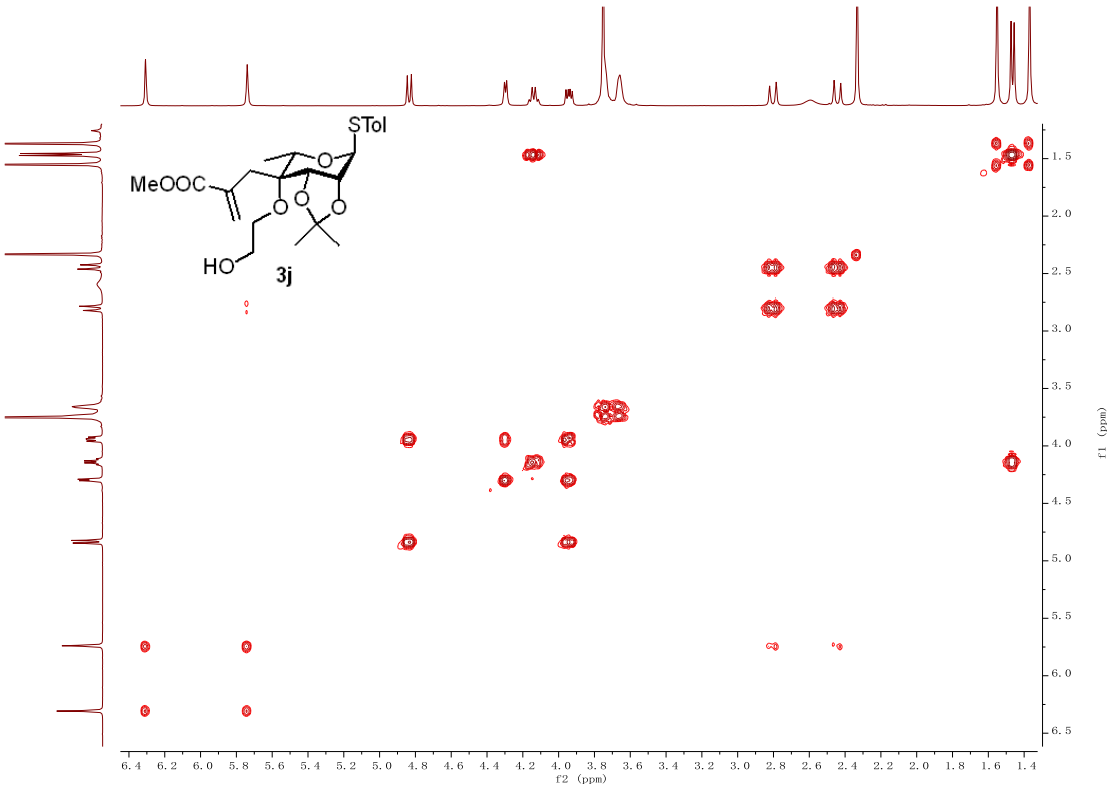
^{1}H NMR Spectra of compound 3j



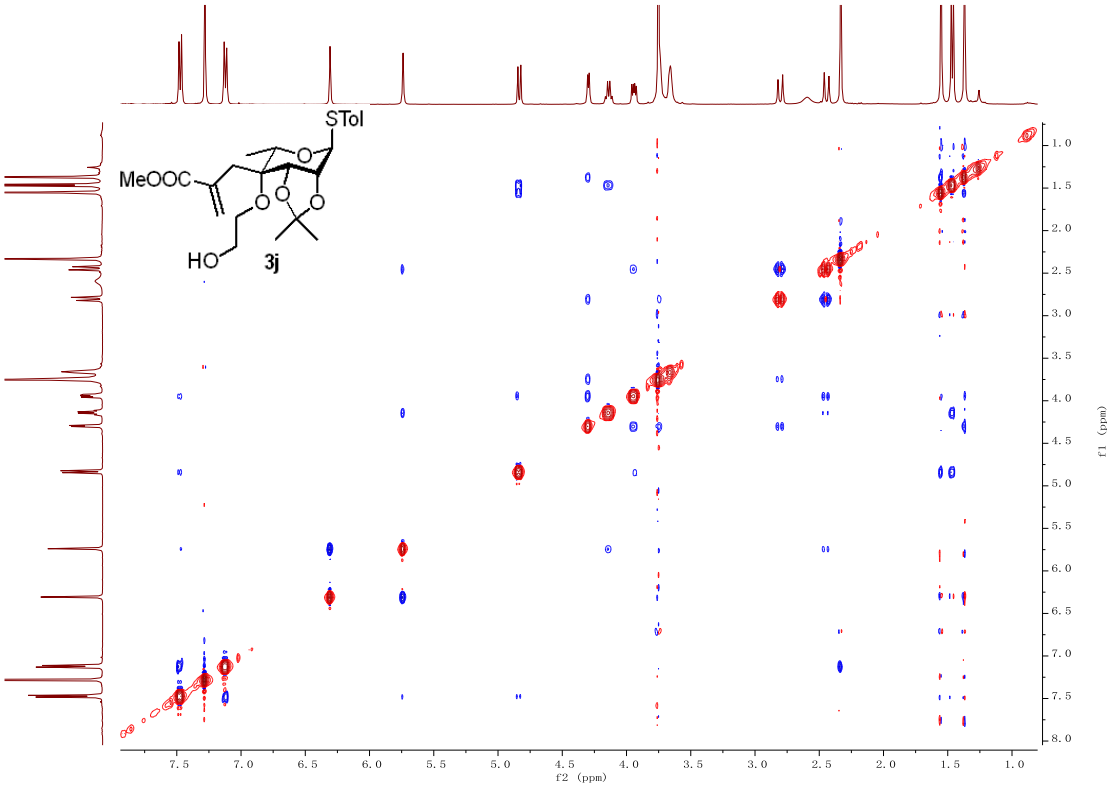
^{13}C NMR Spectra of compound 3j



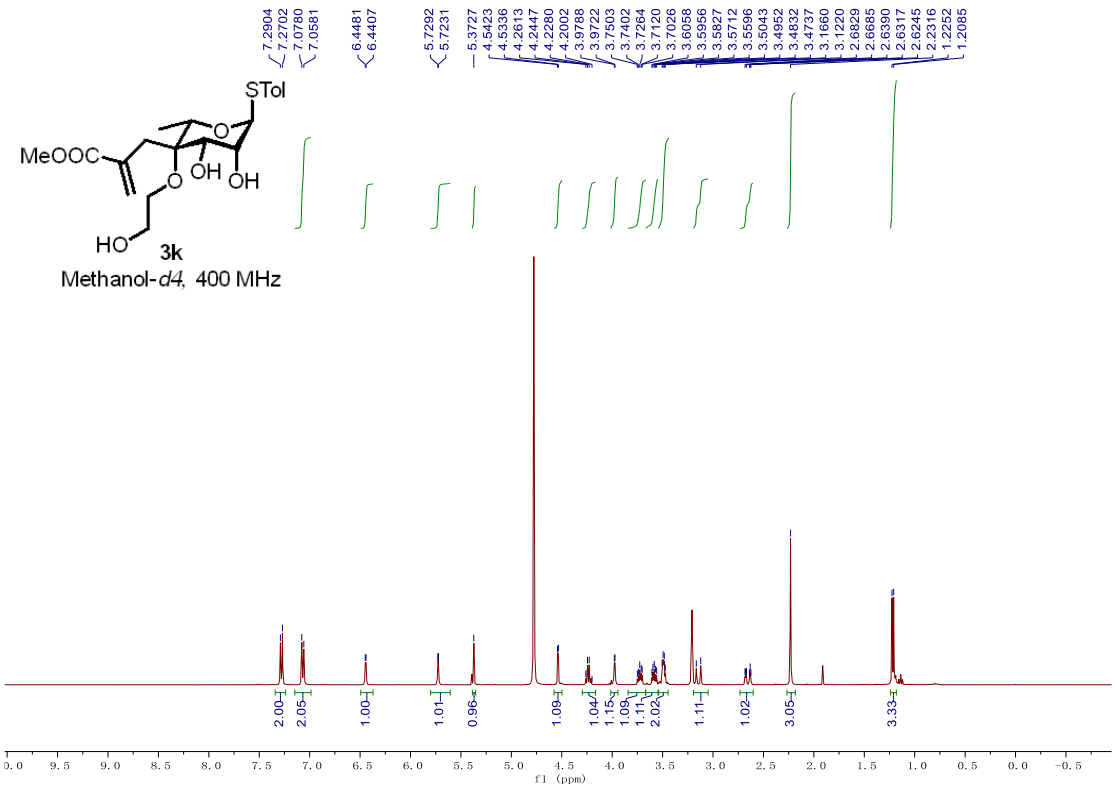
HSQC Spectra of compound 3j



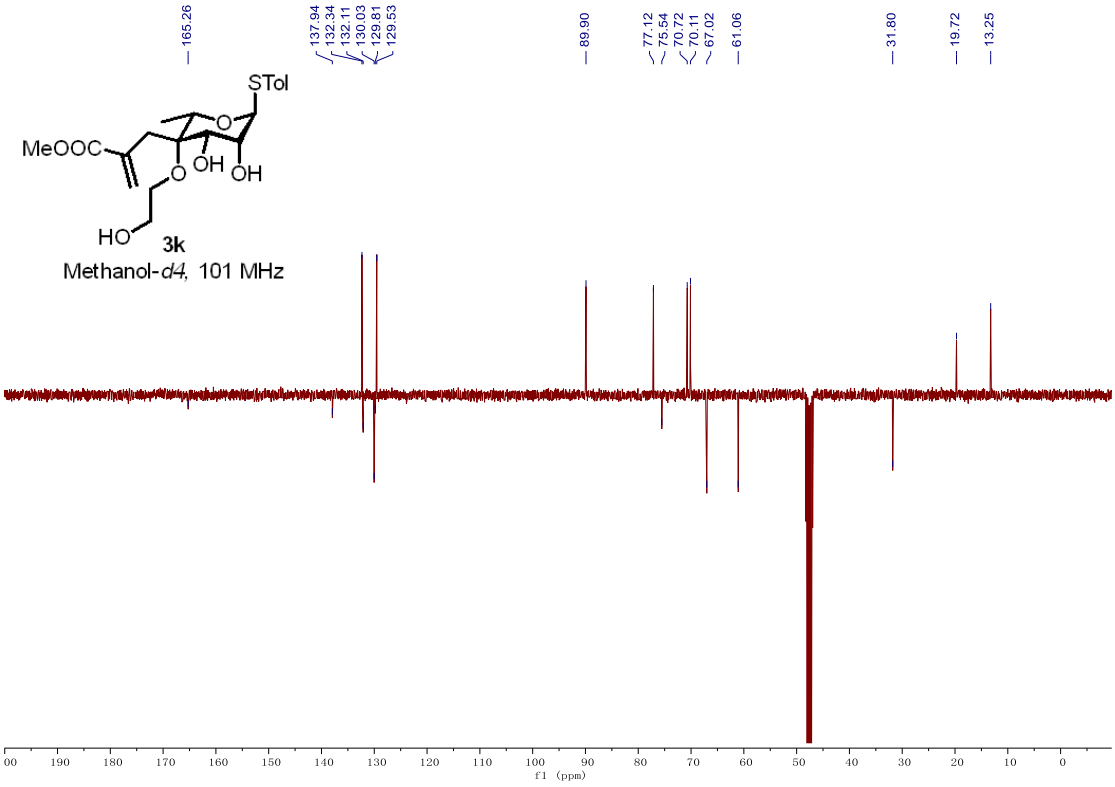
COSY Spectra of compound 3j



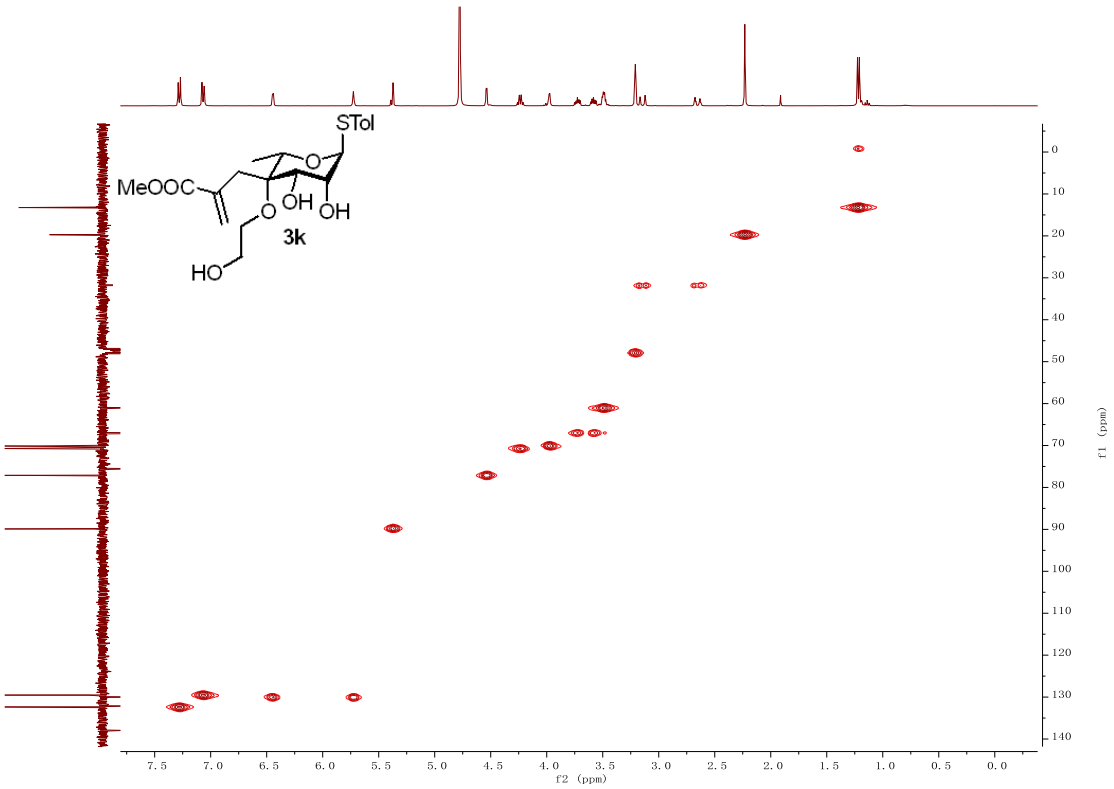
NOESY Spectra of compound 3j



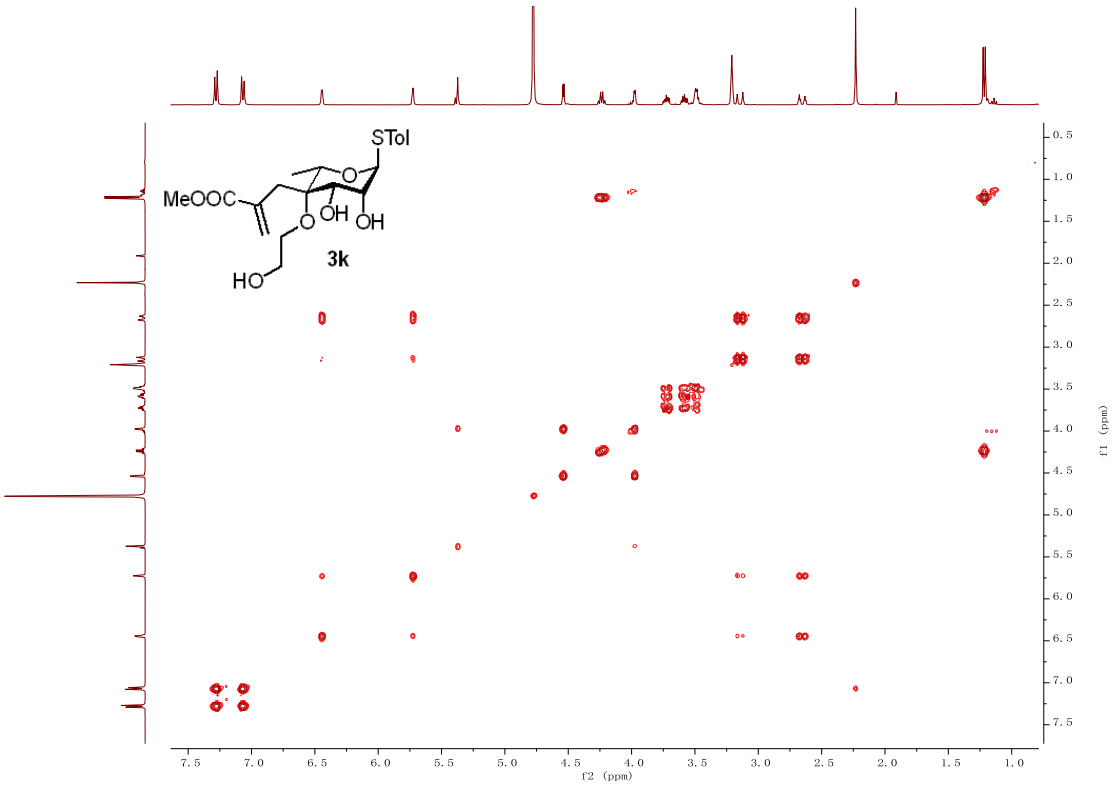
^{1}H NMR Spectra of compound 3k



^{13}C NMR Spectra of compound 3k



HSQC Spectra of compound 3k



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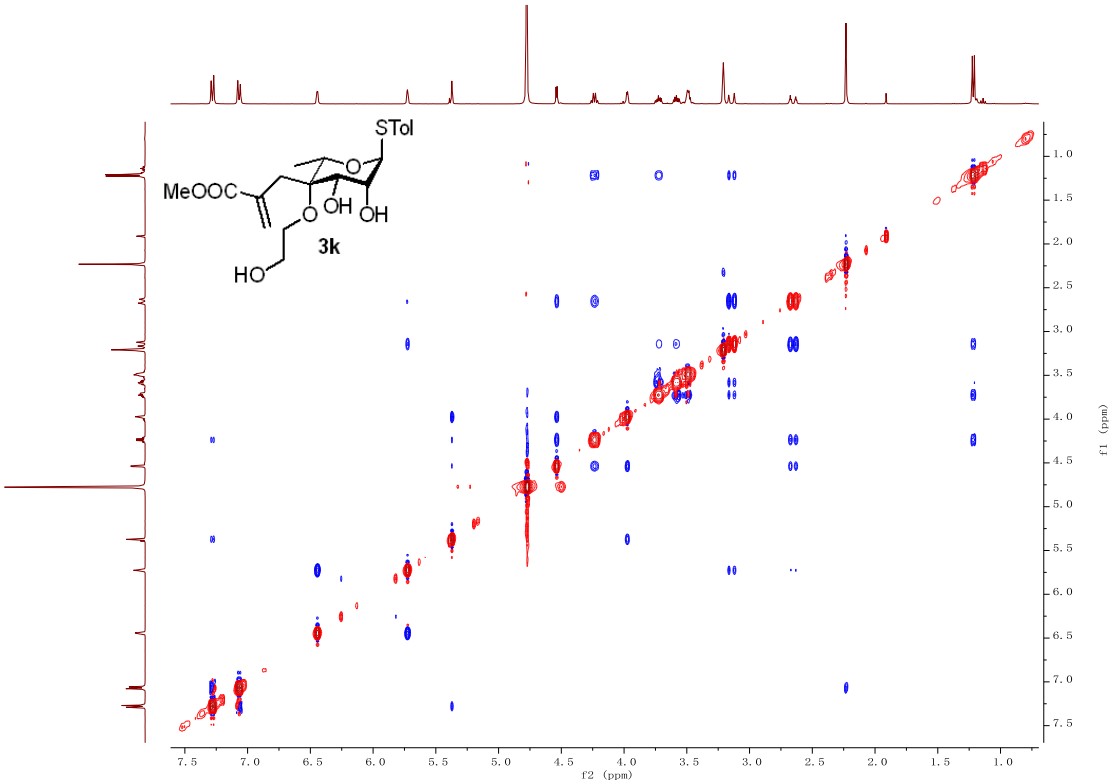

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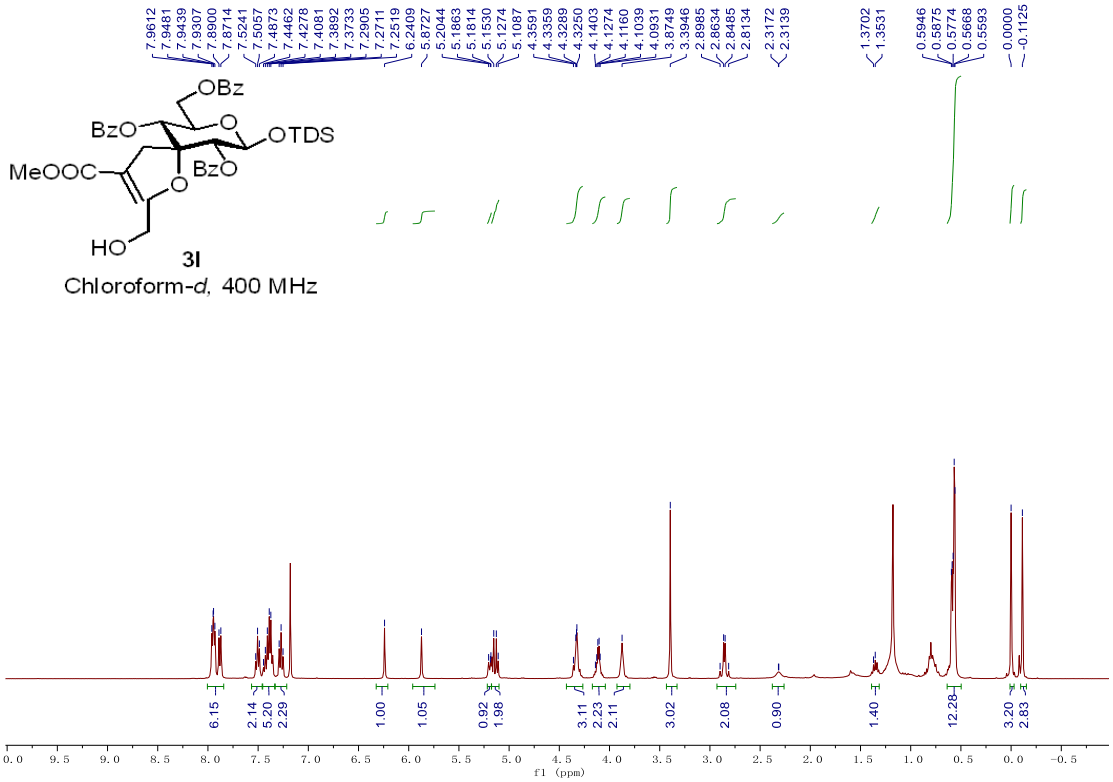
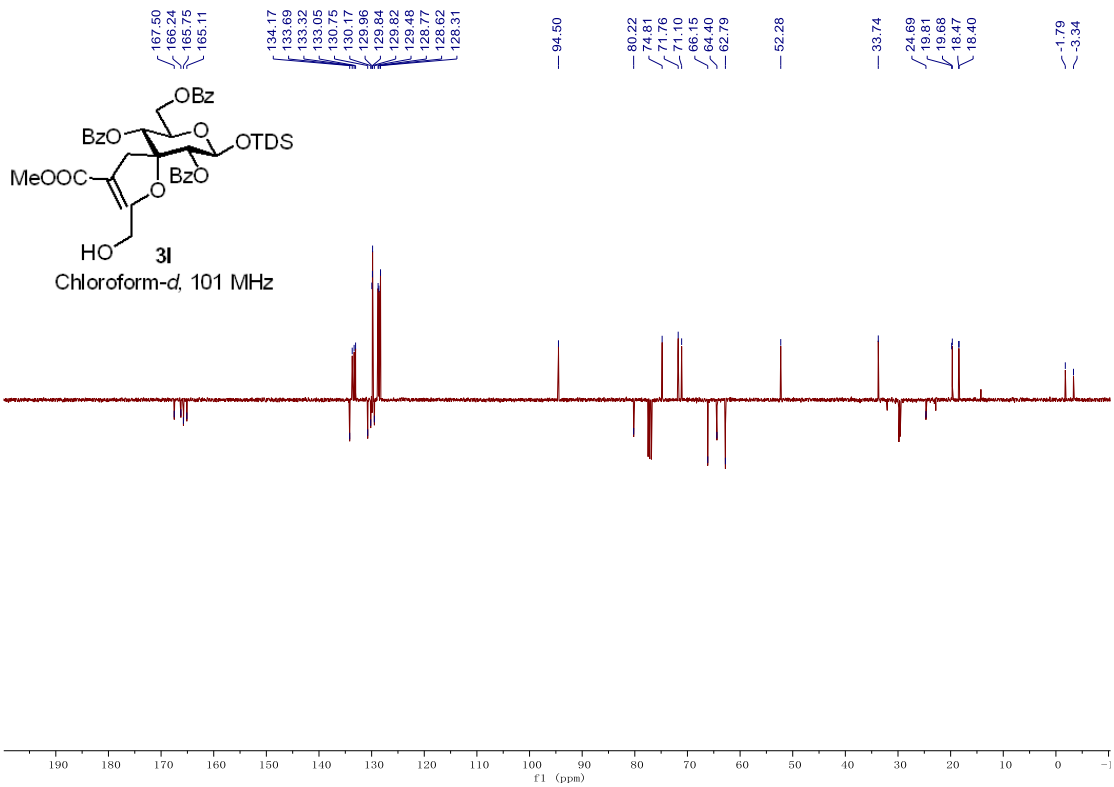
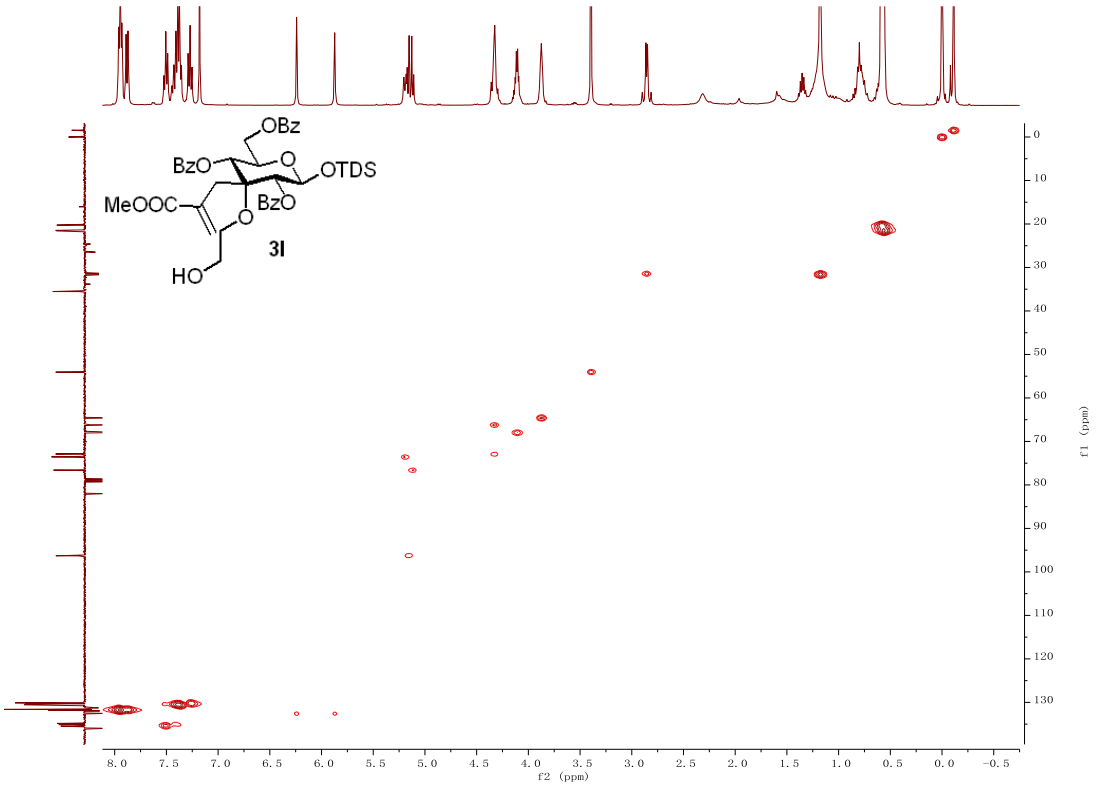


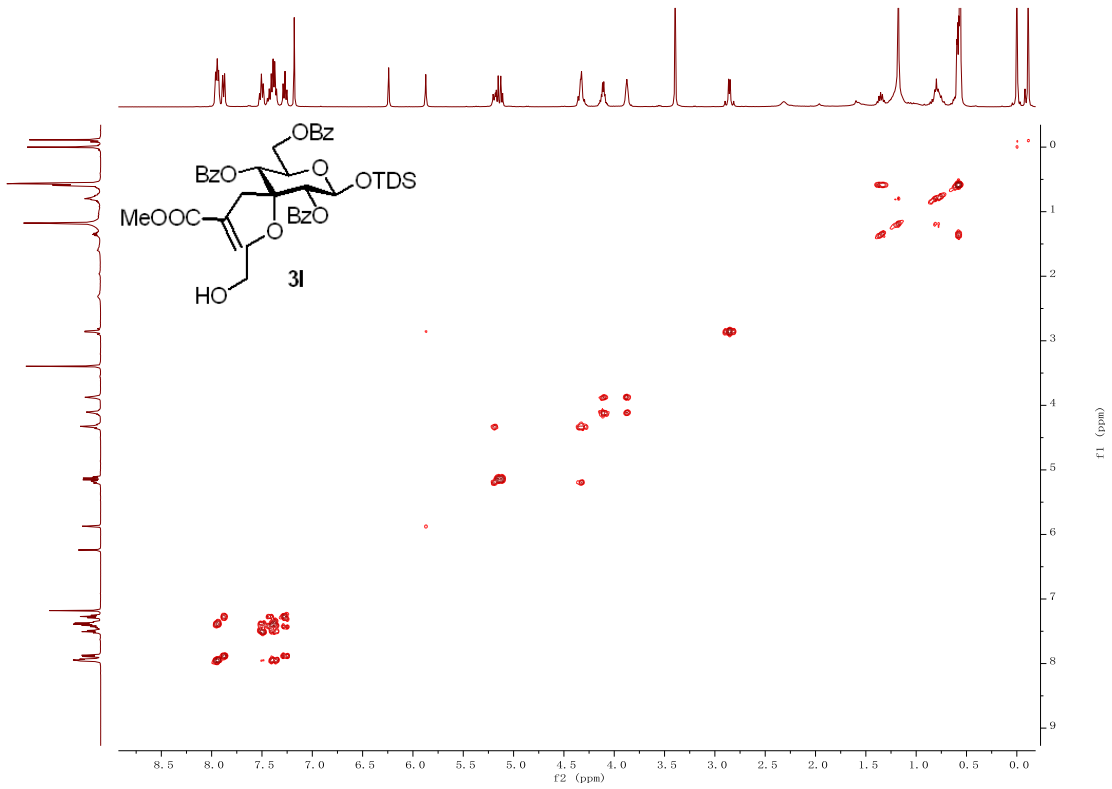
^{1}H NMR Spectra of compound 3l



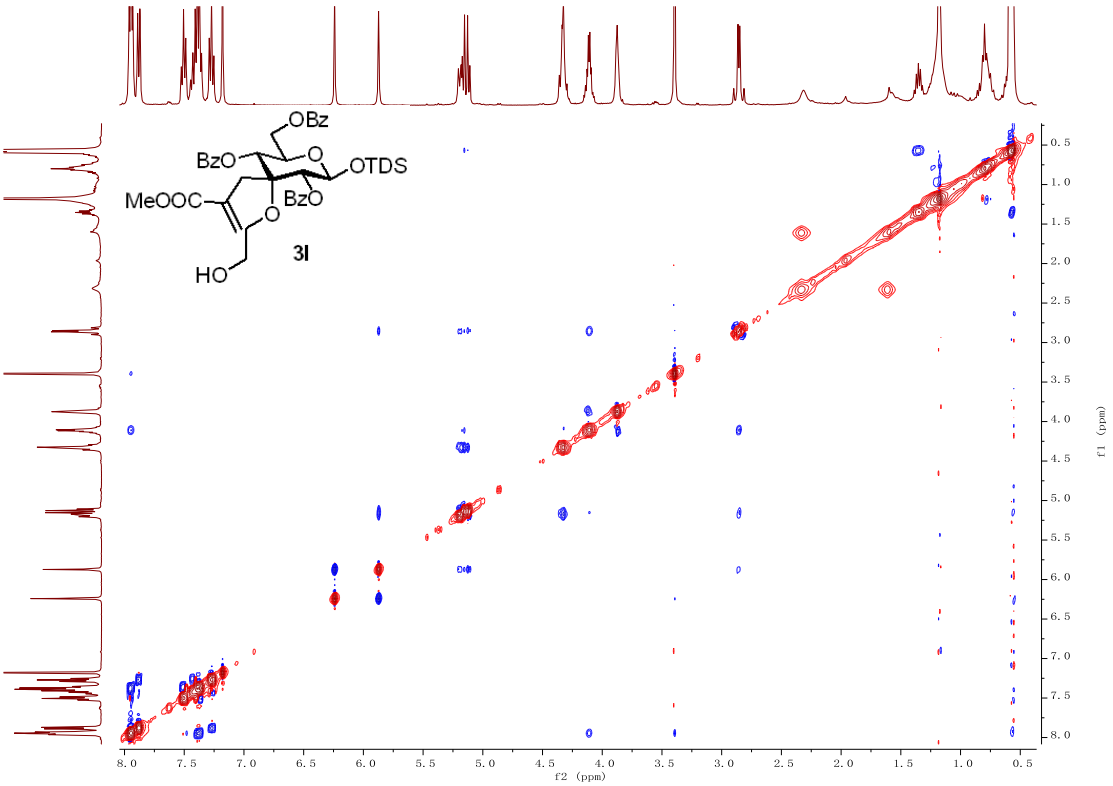
^{13}C NMR Spectra of compound 3l



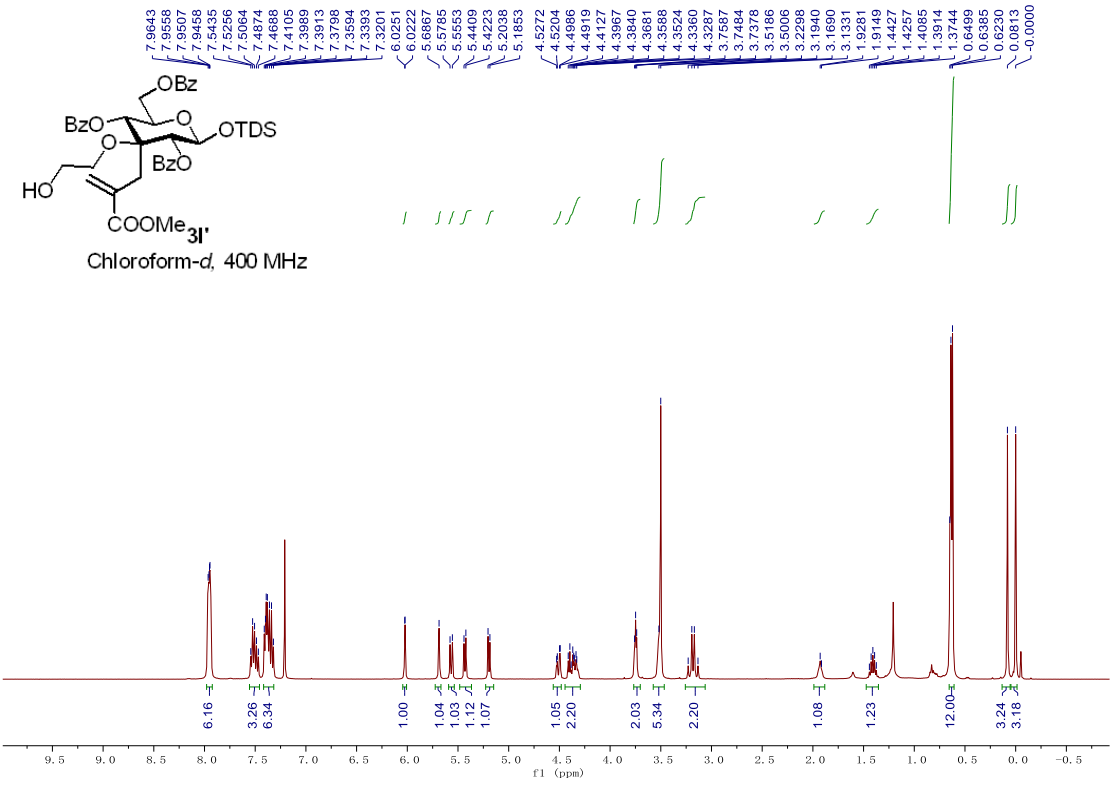
HSQC NMR Spectra of compound 3l



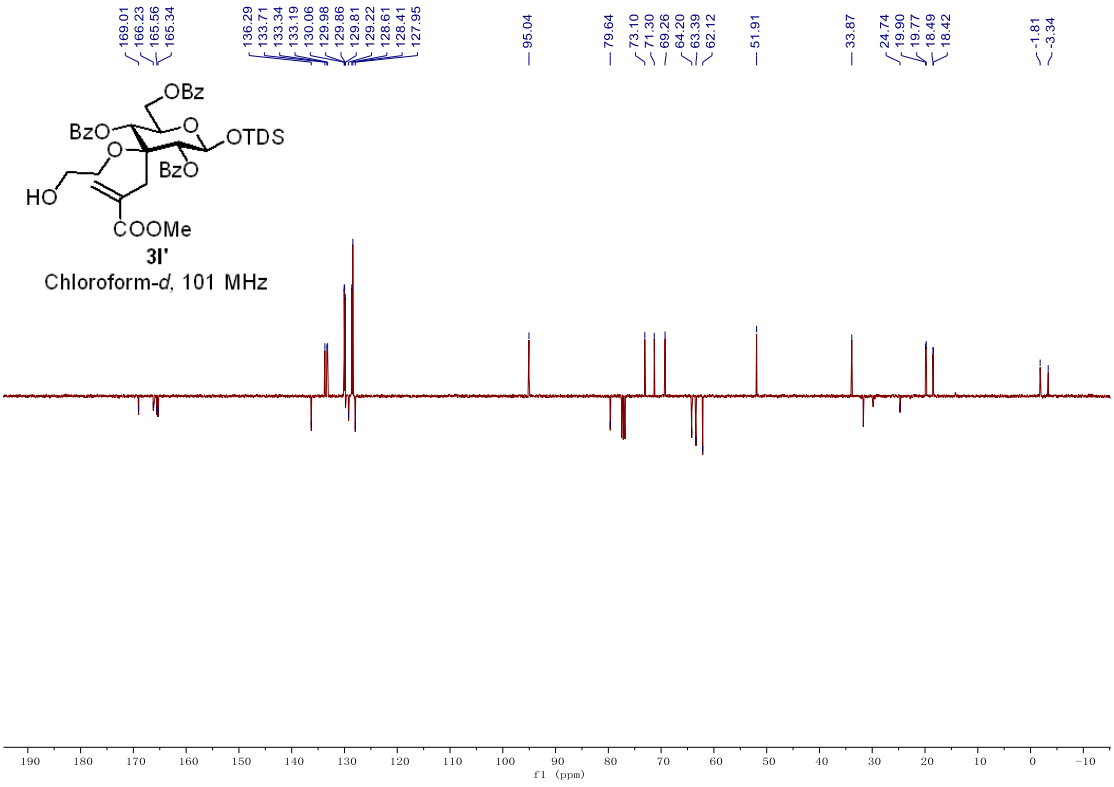
COSY NMR Spectra of compound 3l



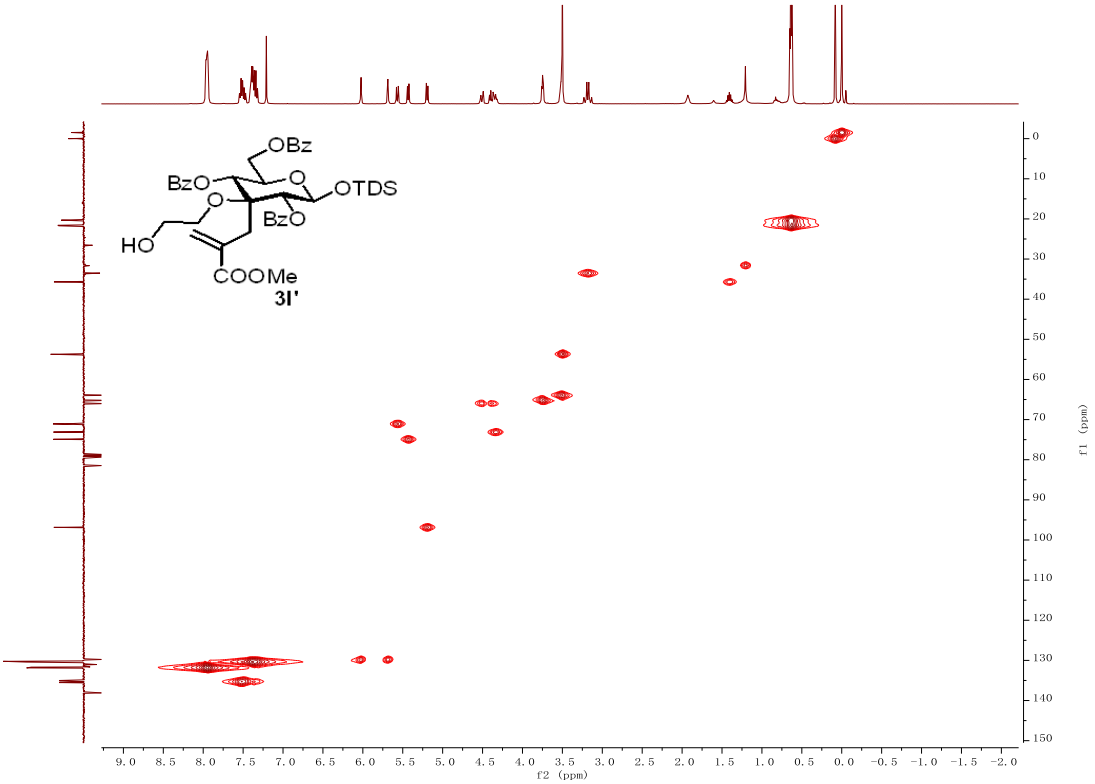
NOESY NMR Spectra of compound 3l



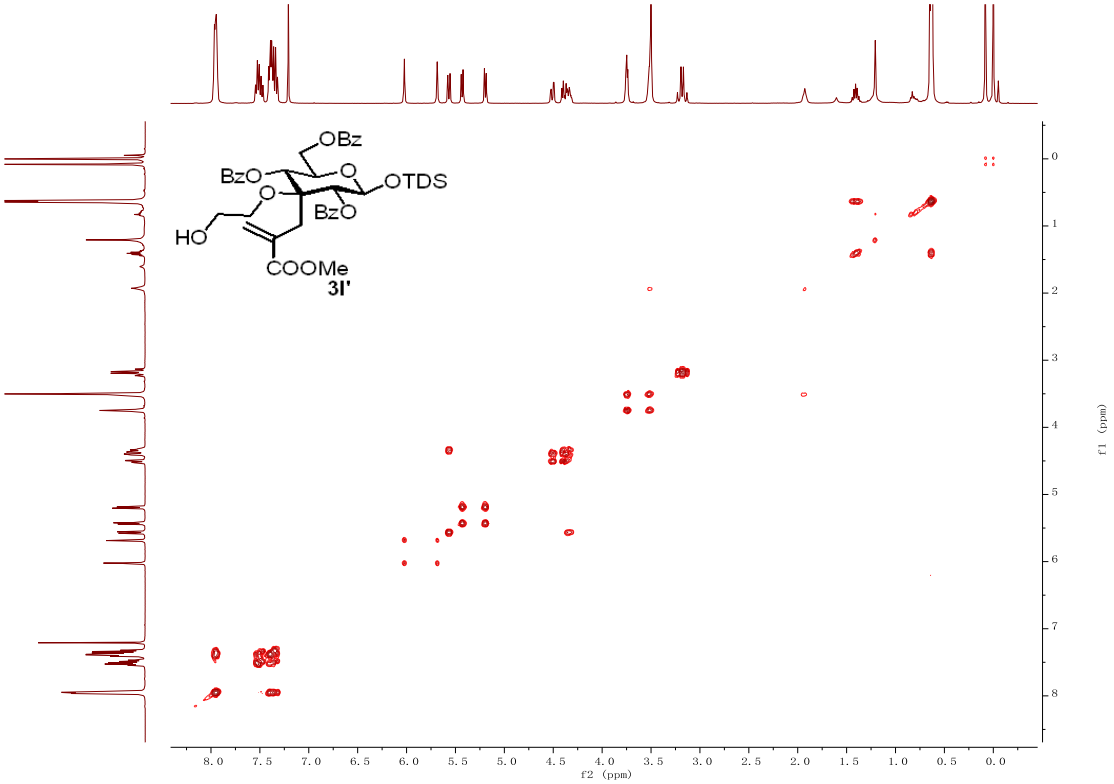
^{1}H NMR Spectra of compound 3l′



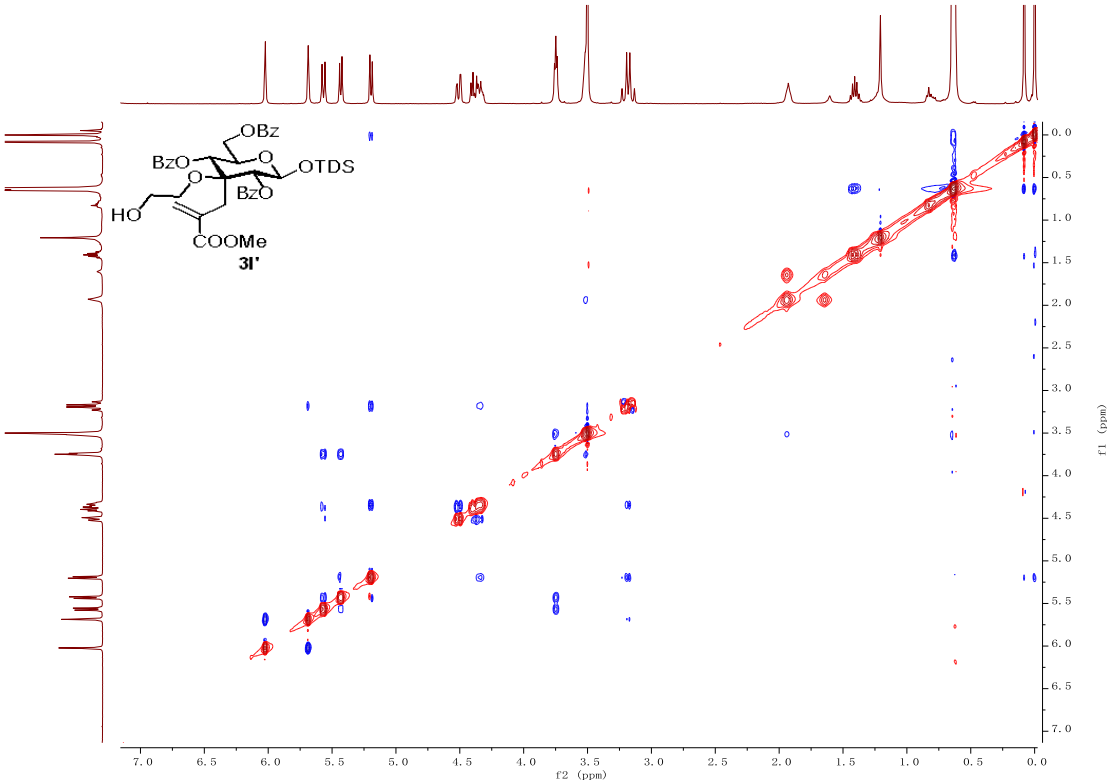
^{13}C NMR Spectra of compound 3l′



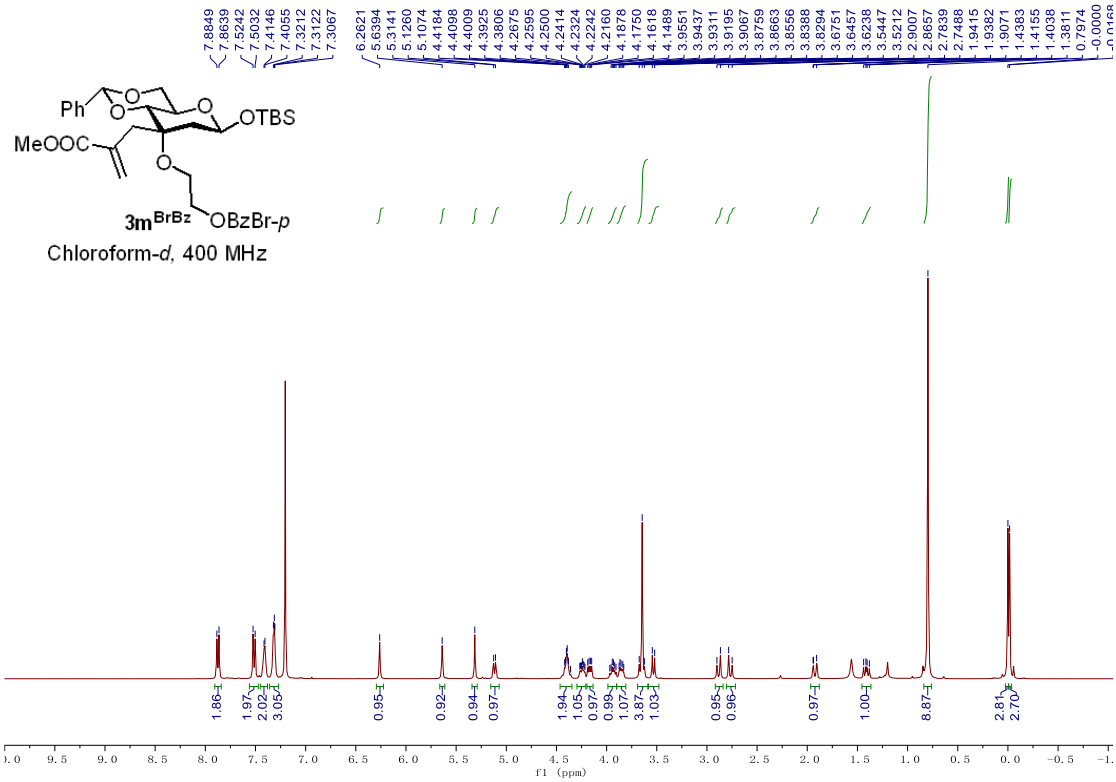
HSQC NMR Spectra of compound 3l′



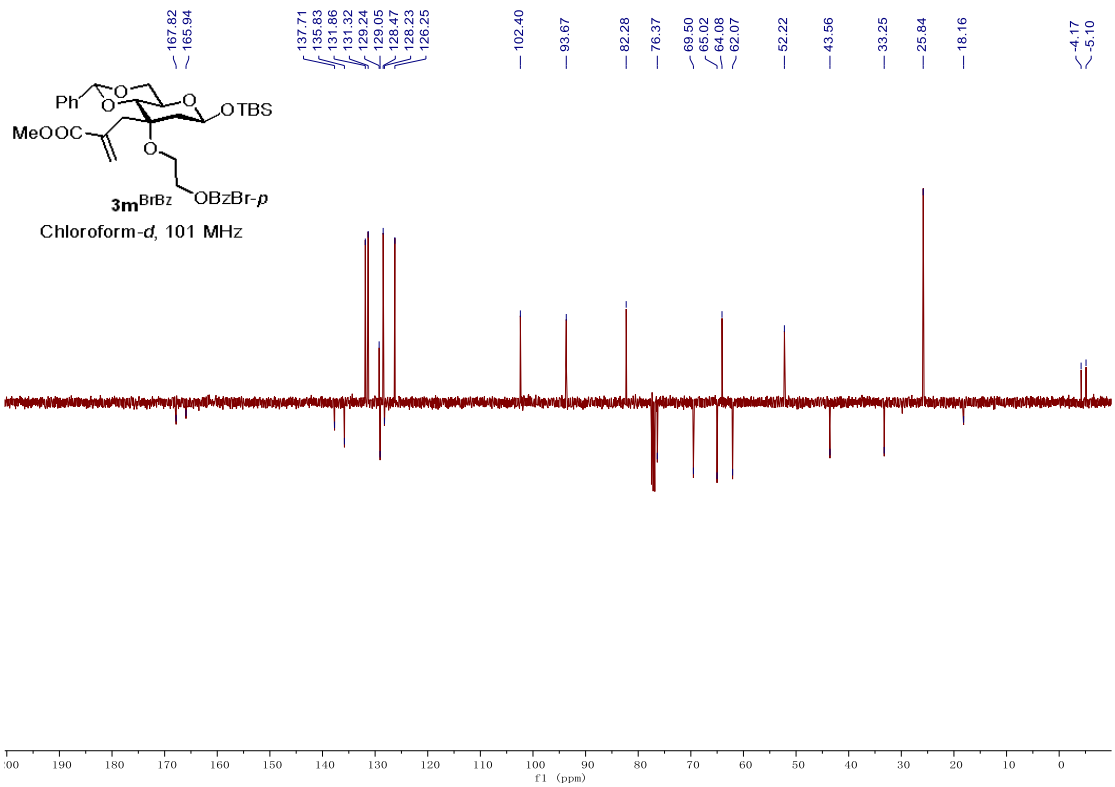
COSY NMR Spectra of compound 3l′



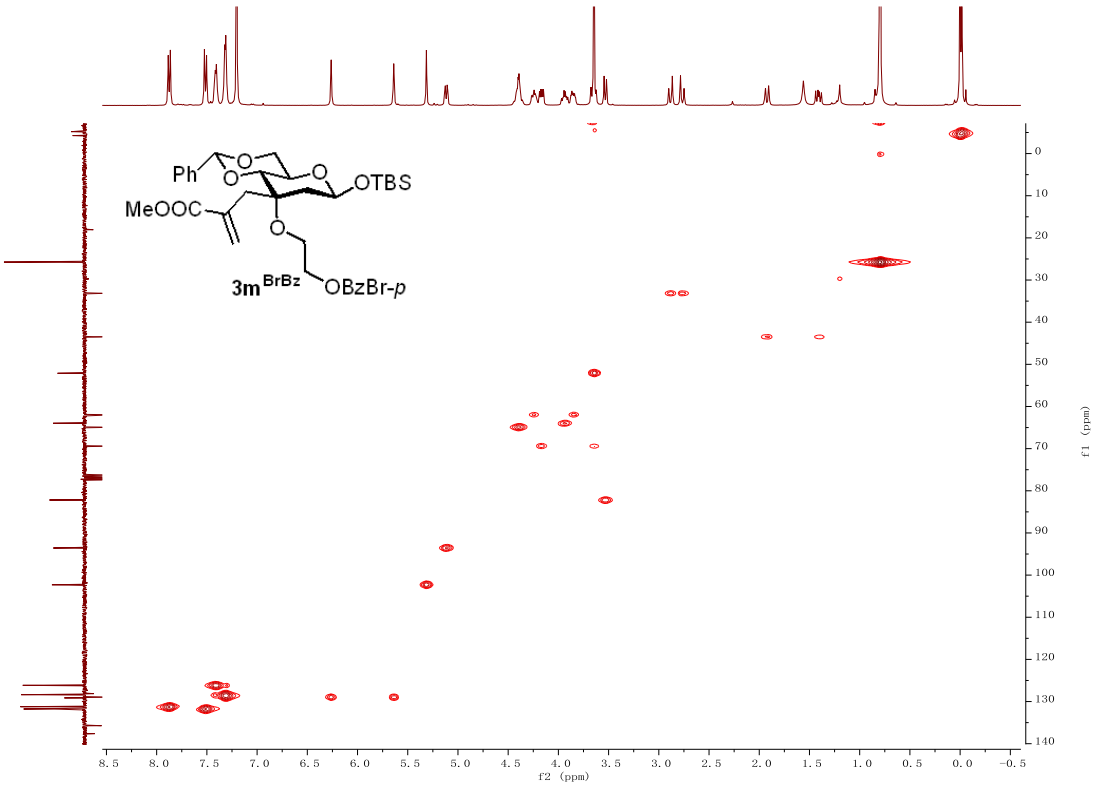
NOESY NMR Spectra of compound 3l′



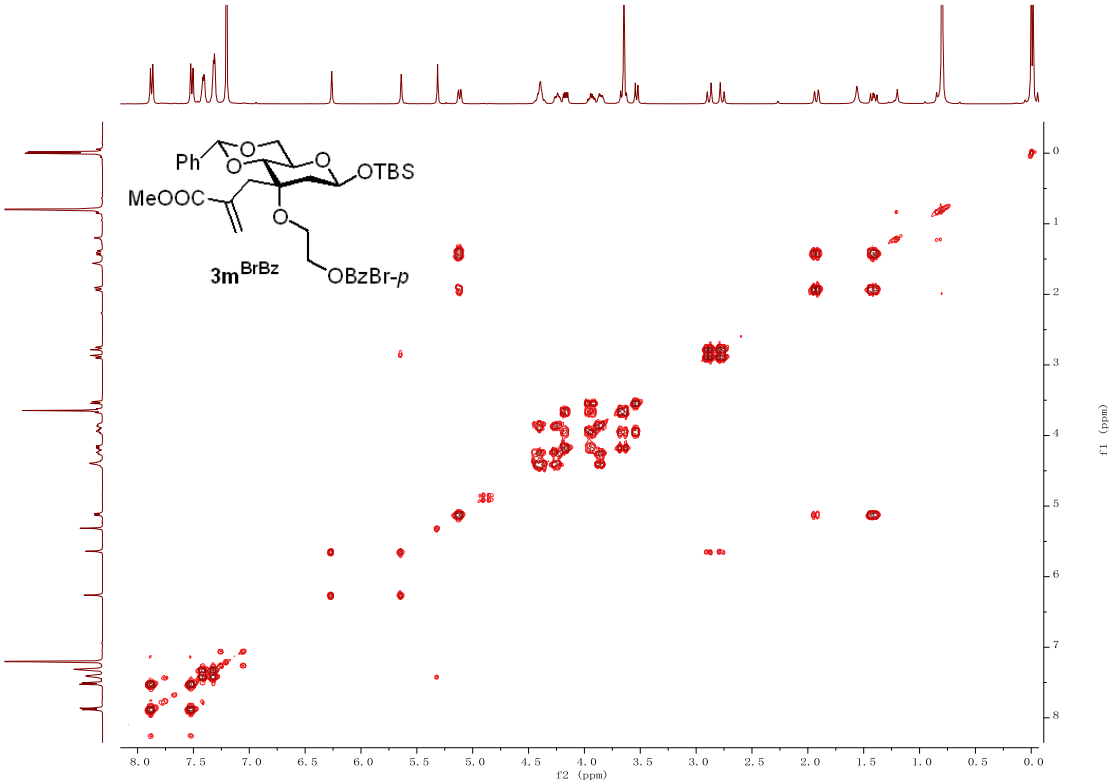
^{1}H NMR Spectra of compound 3m^{BrBz}



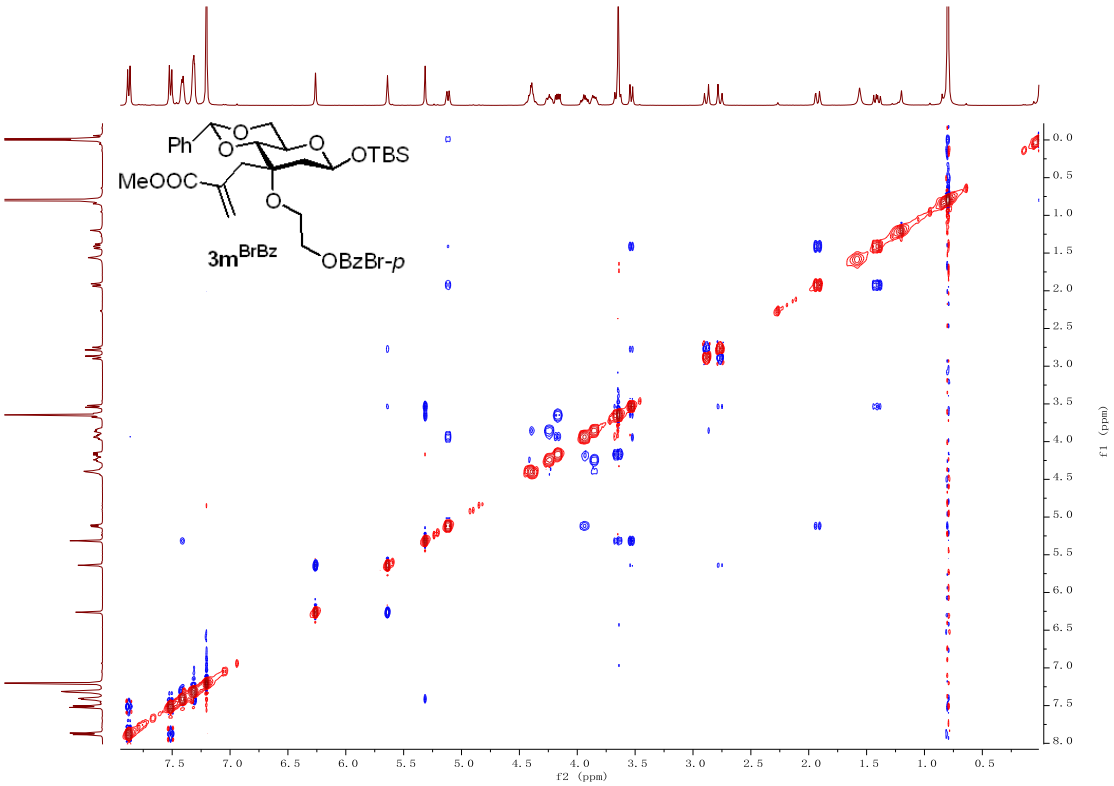
^{13}C NMR Spectra of compound 3m^{BrBz}



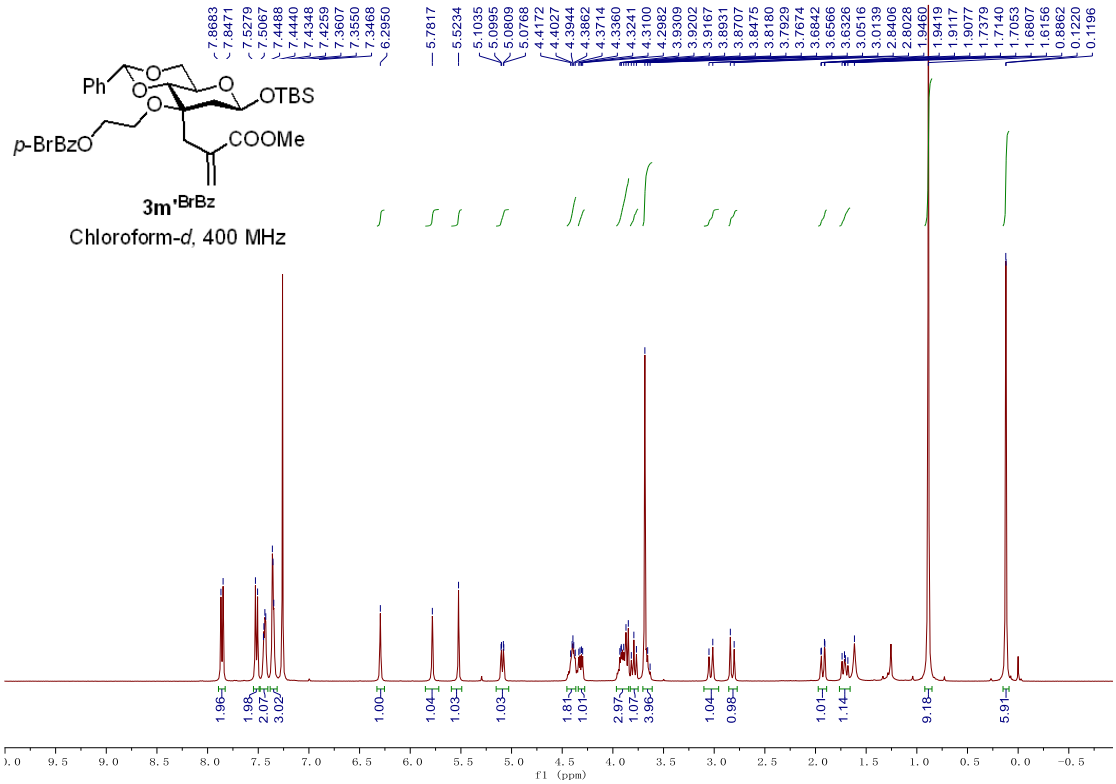
HSQC Spectra of compound 3m^{BrBz}



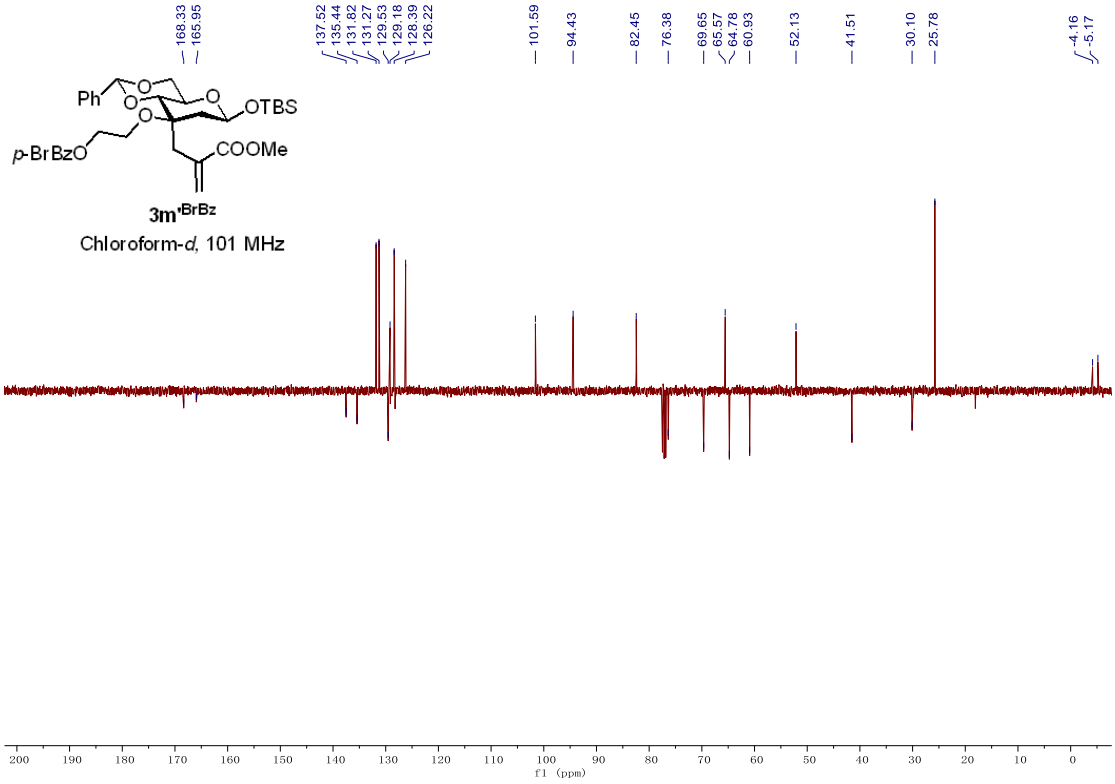
COSY Spectra of compound 3m^{BrBz}



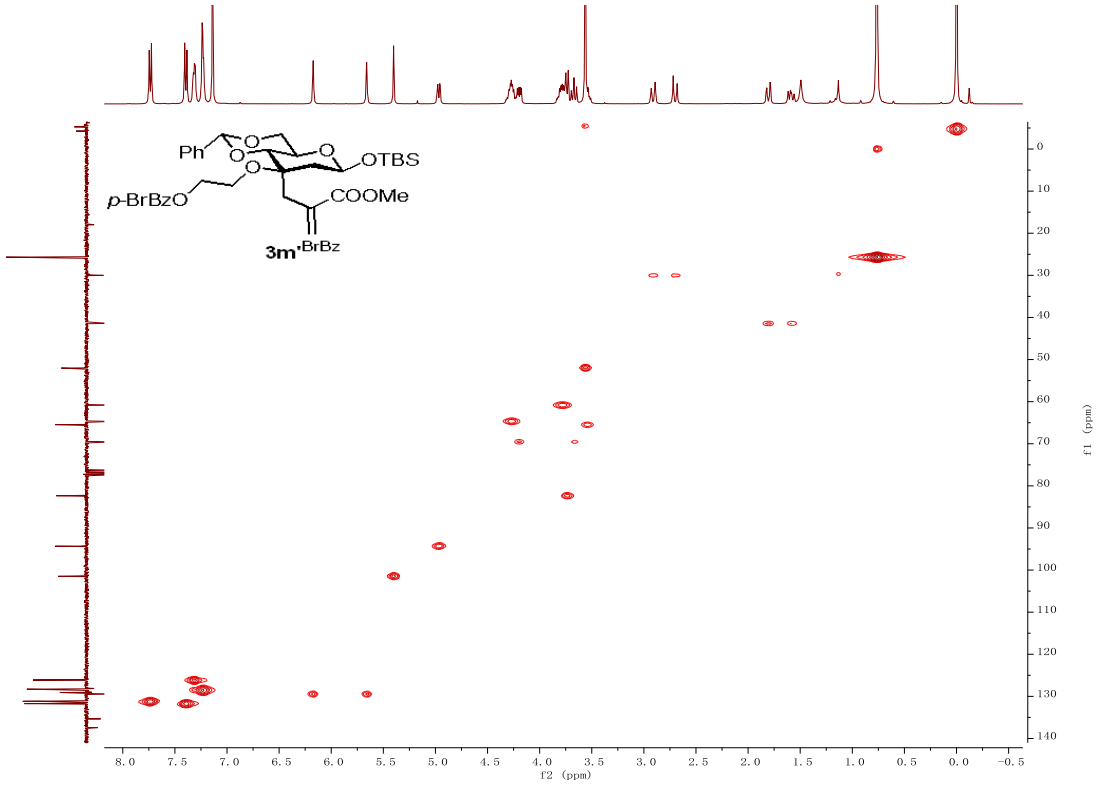
NOESY Spectra of compound 3m^{BrBz}



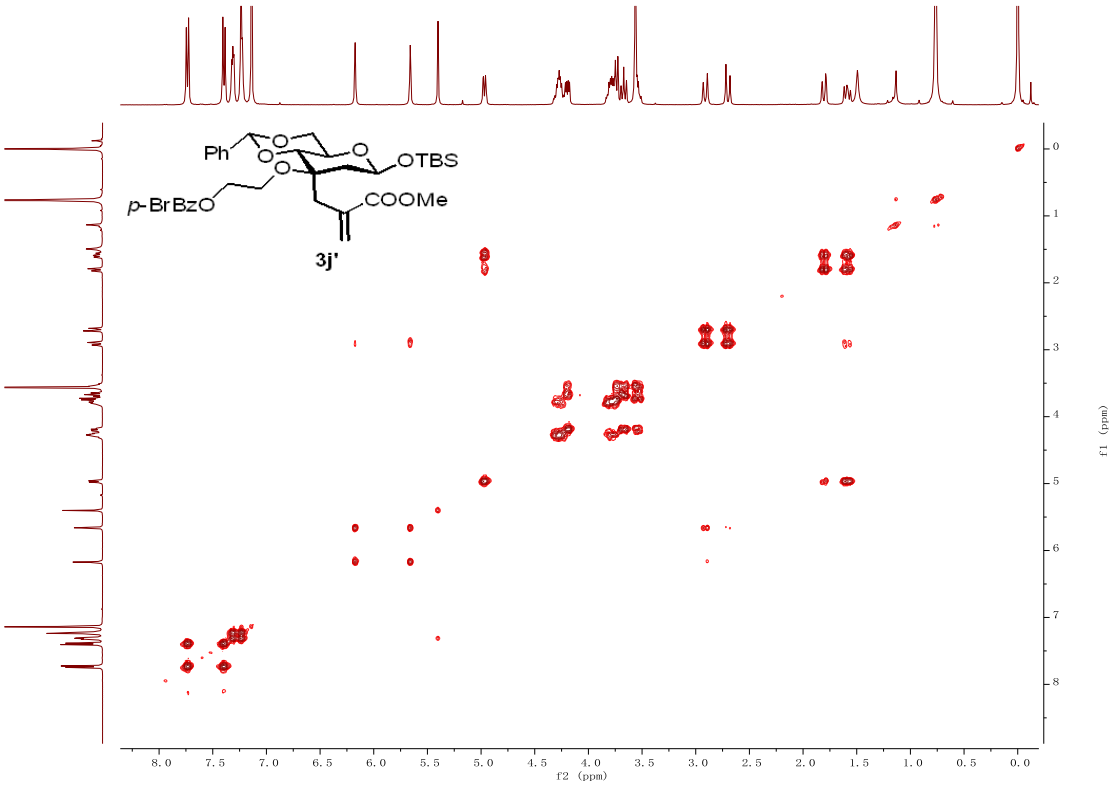
^{1}H NMR Spectra of compound 3m′^{BrBz}



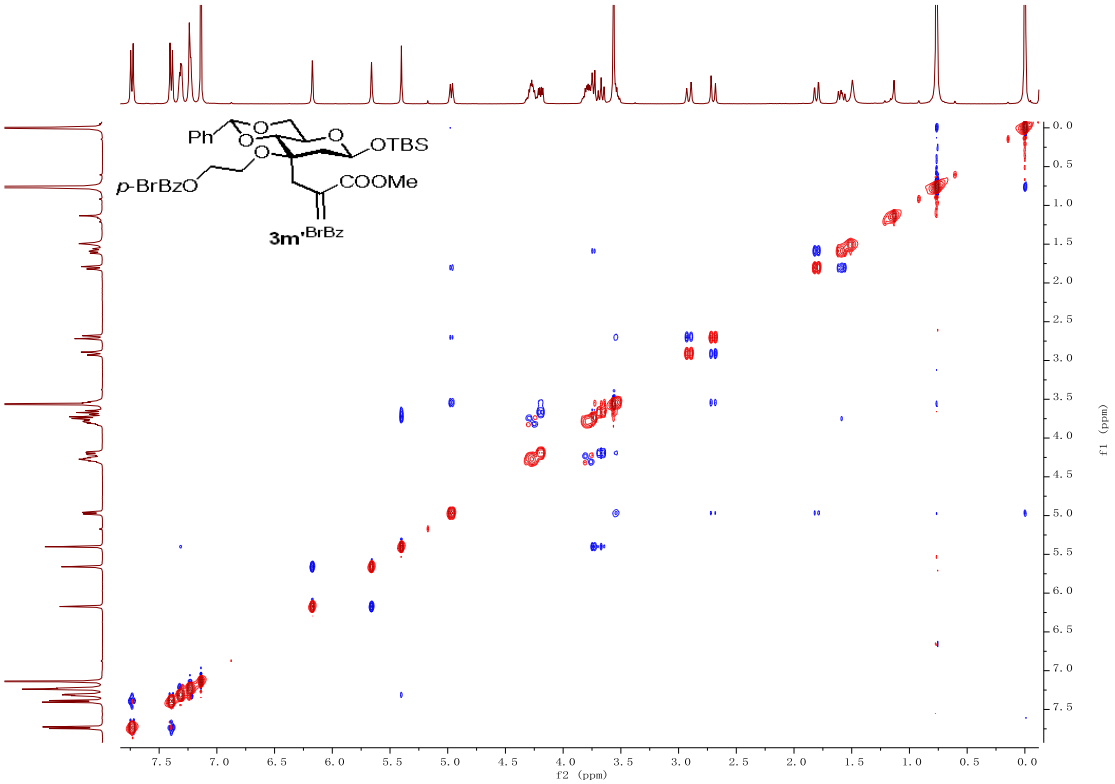
^{13}C NMR Spectra of compound 3m′^{BrBz}



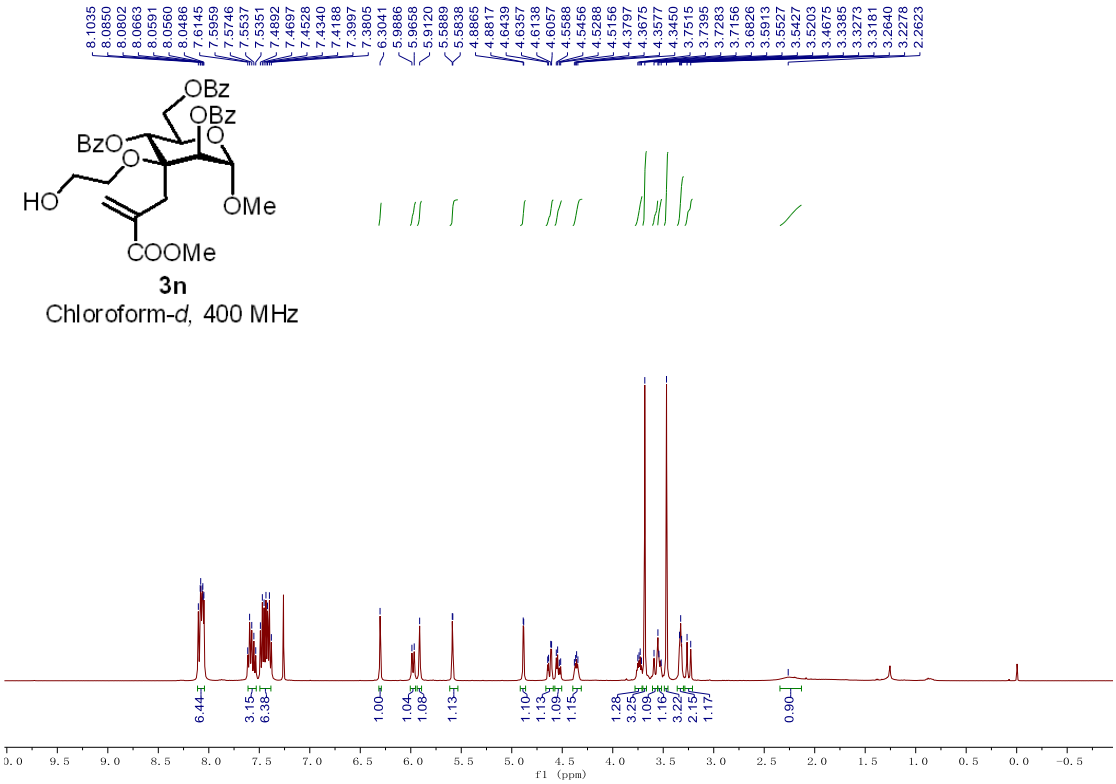
HSQC Spectra of compound 3m′^{BrBz}



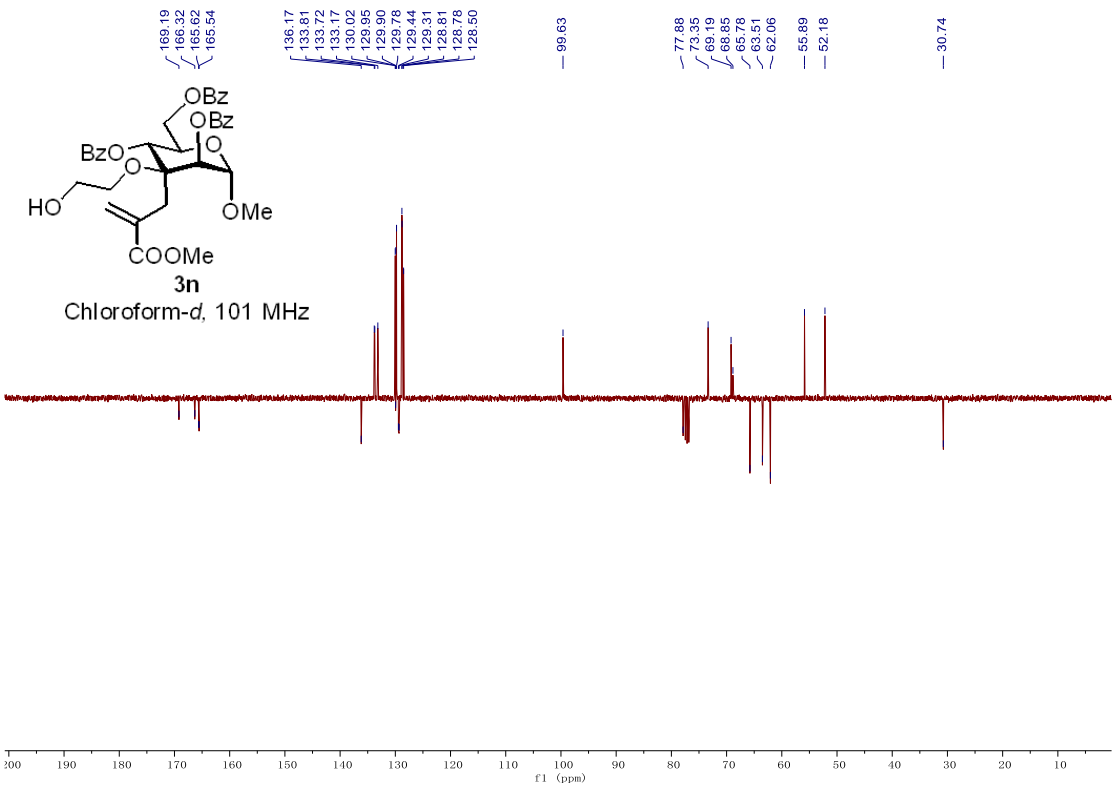
COSY Spectra of compound 3m′ ^{BrBz}



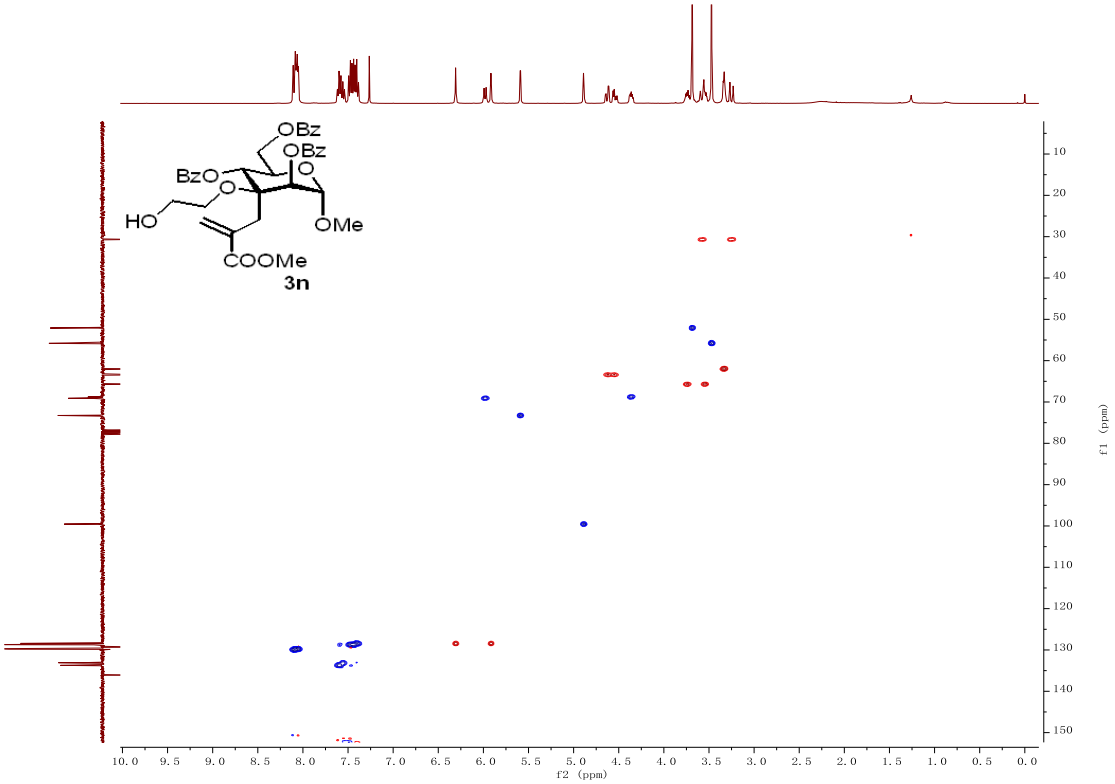
NOESY Spectra of compound 3m′ ^{BrBz}



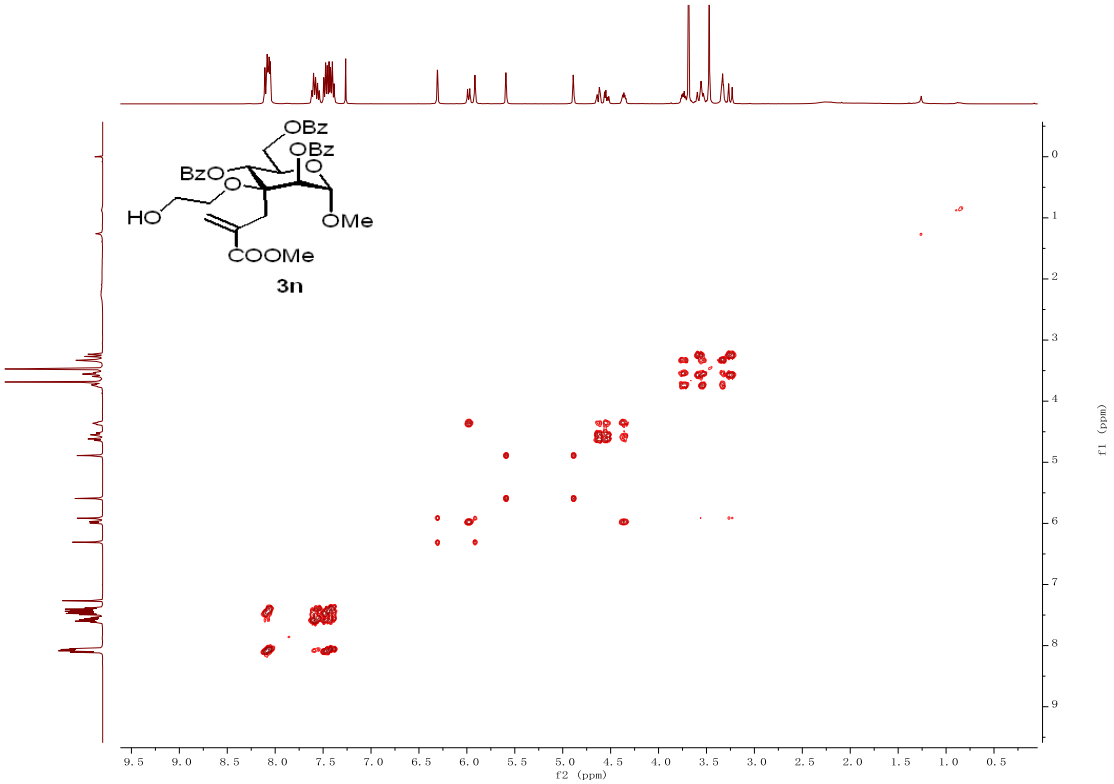
^{1}H NMR Spectra of compound 3n



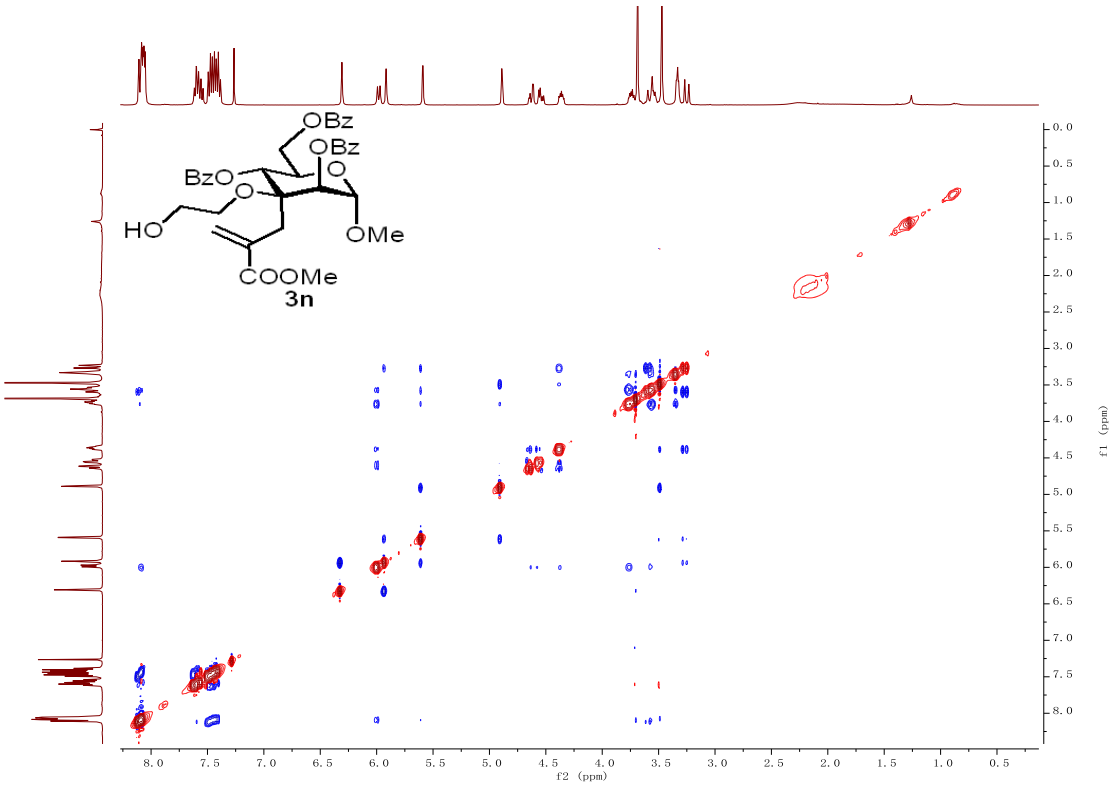
^{13}C NMR Spectra of compound 3n



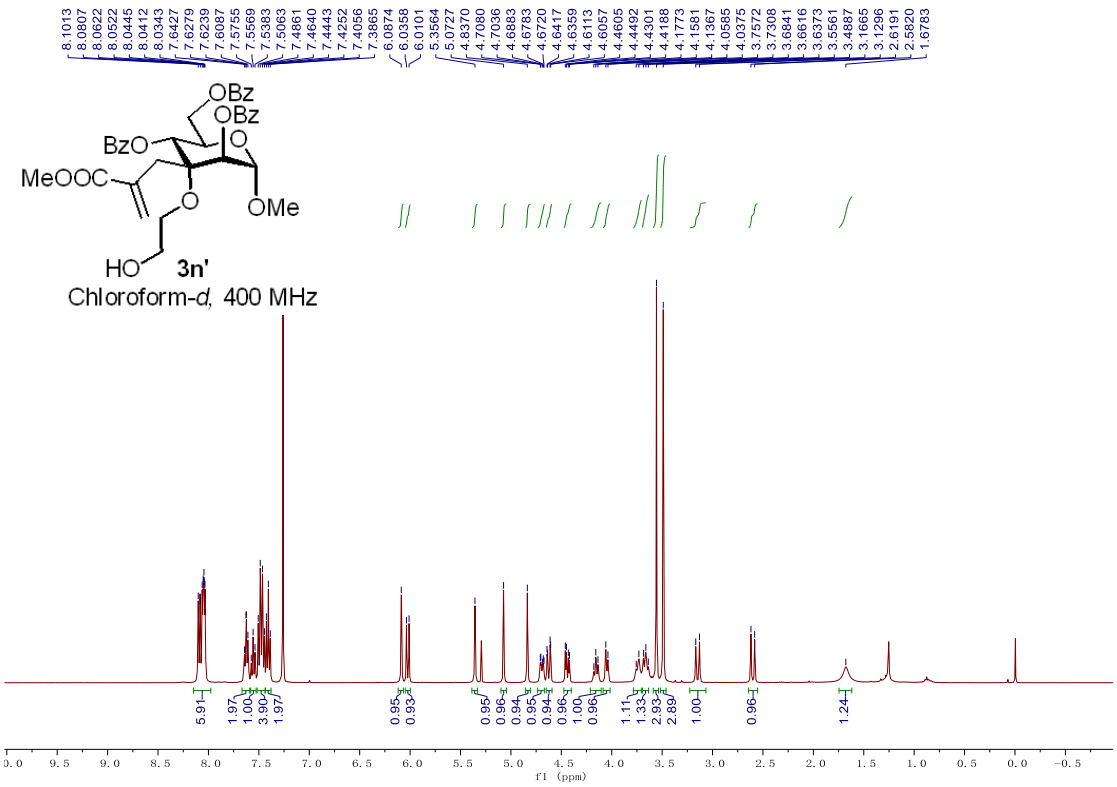
HSQC Spectra of compound 3n



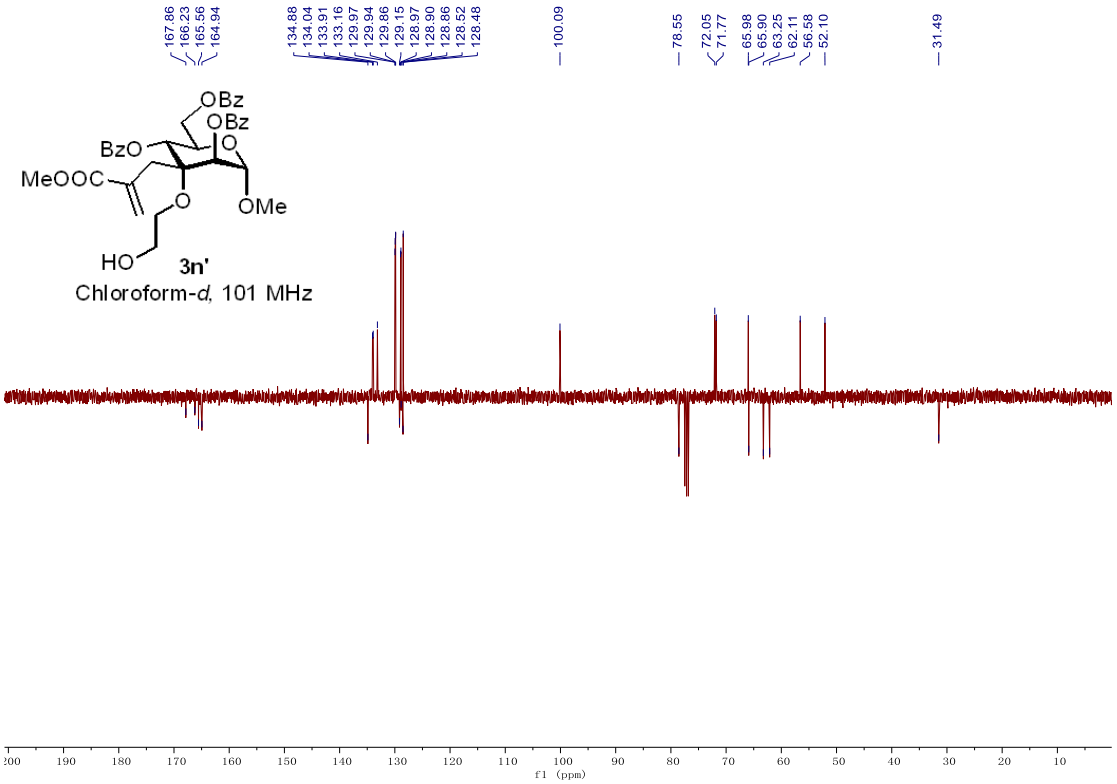
COSY Spectra of compound 3n



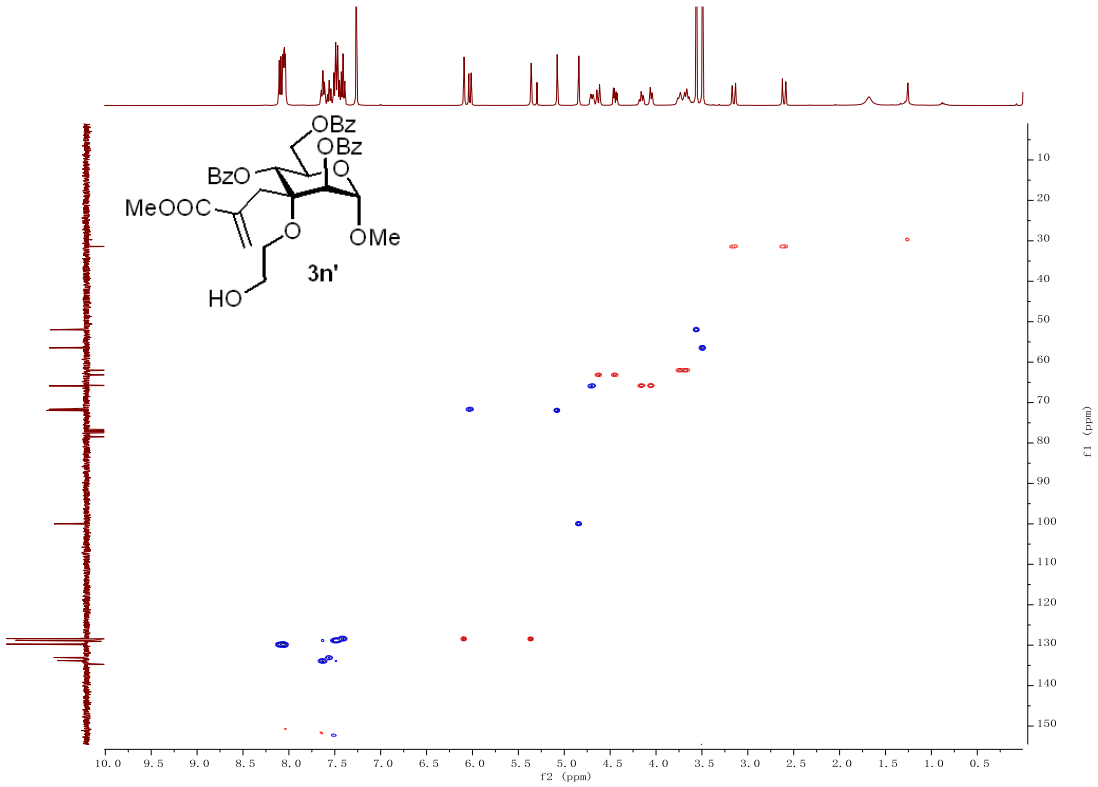
NOESY Spectra of compound 3n



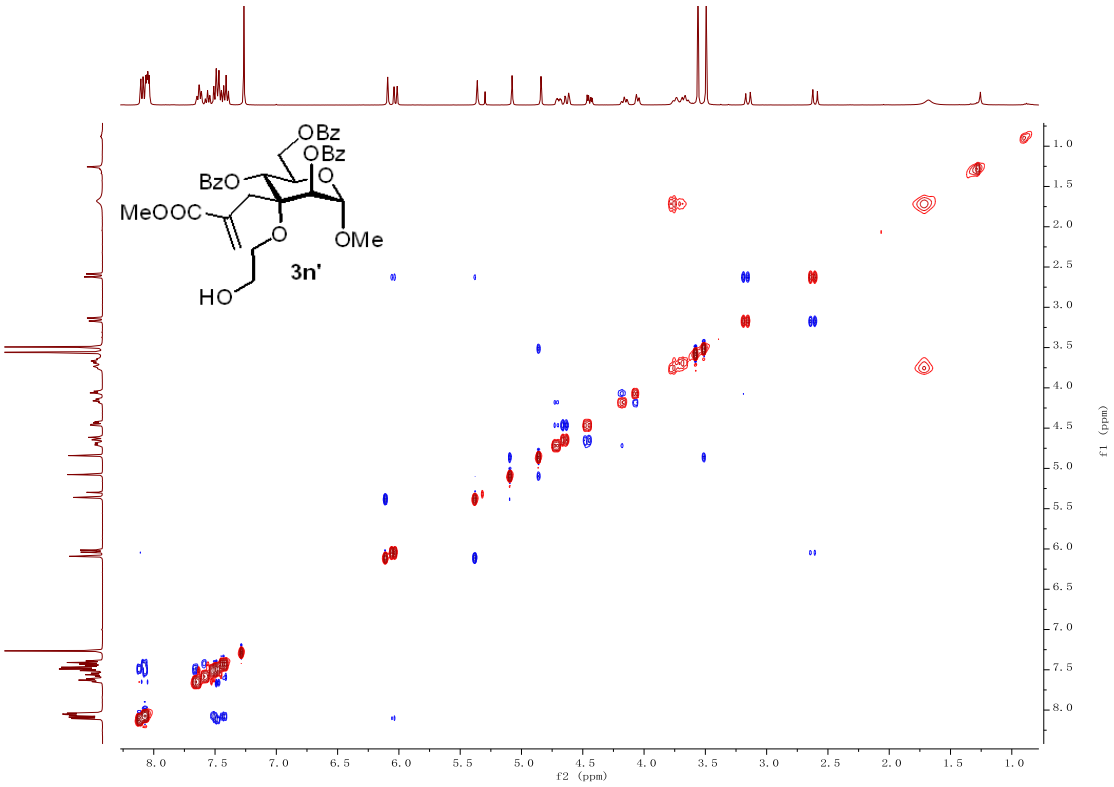
^{1}H NMR Spectra of compound 3n′



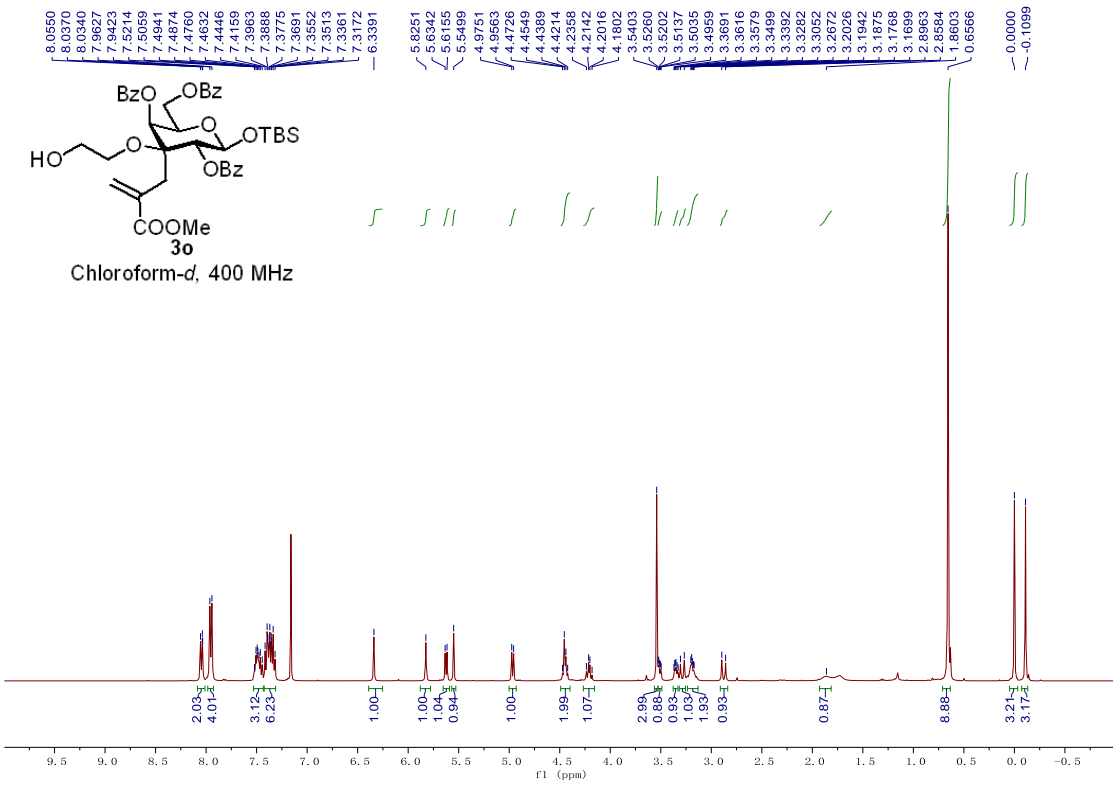
^{13}C NMR Spectra of compound 3n′



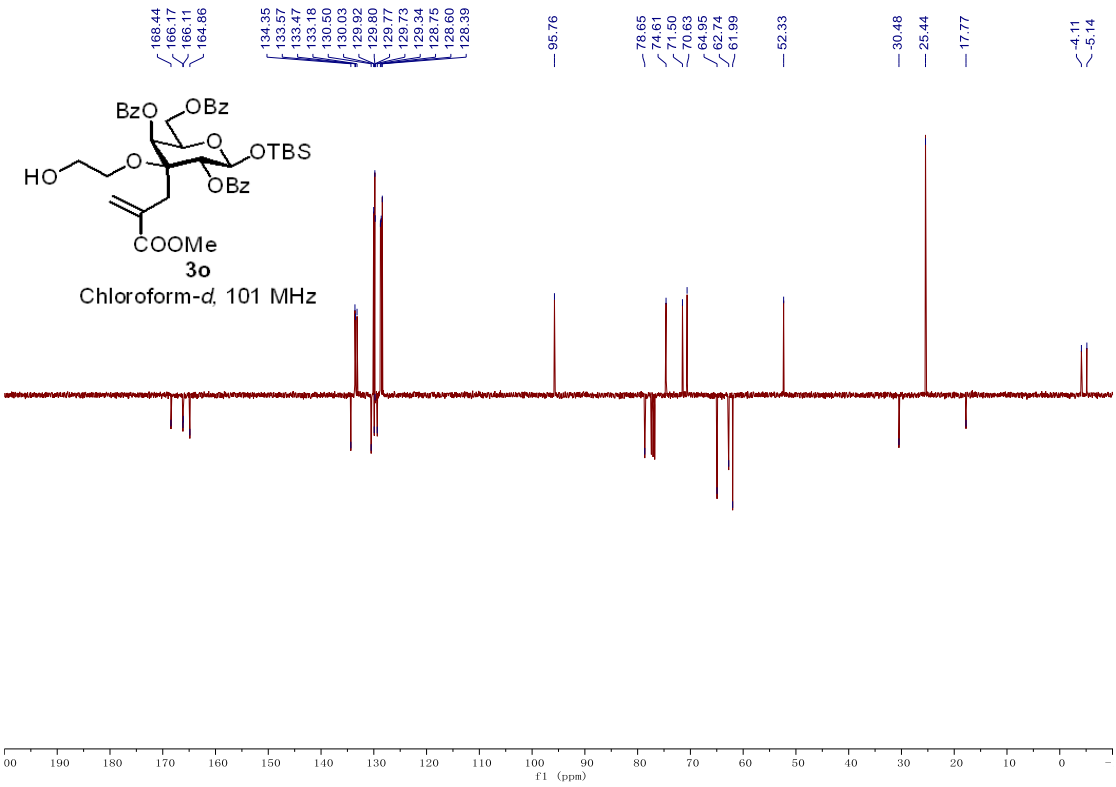
HSQC Spectra of compound 3n′



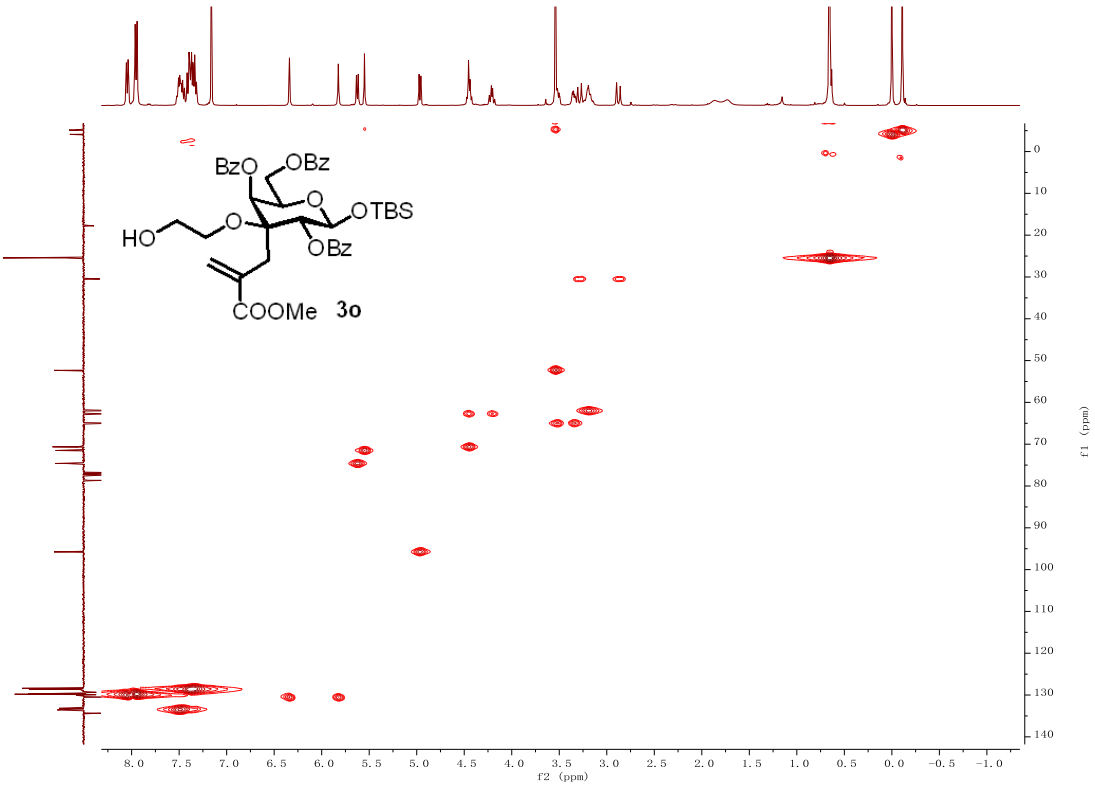
NOESY Spectra of compound 3n′



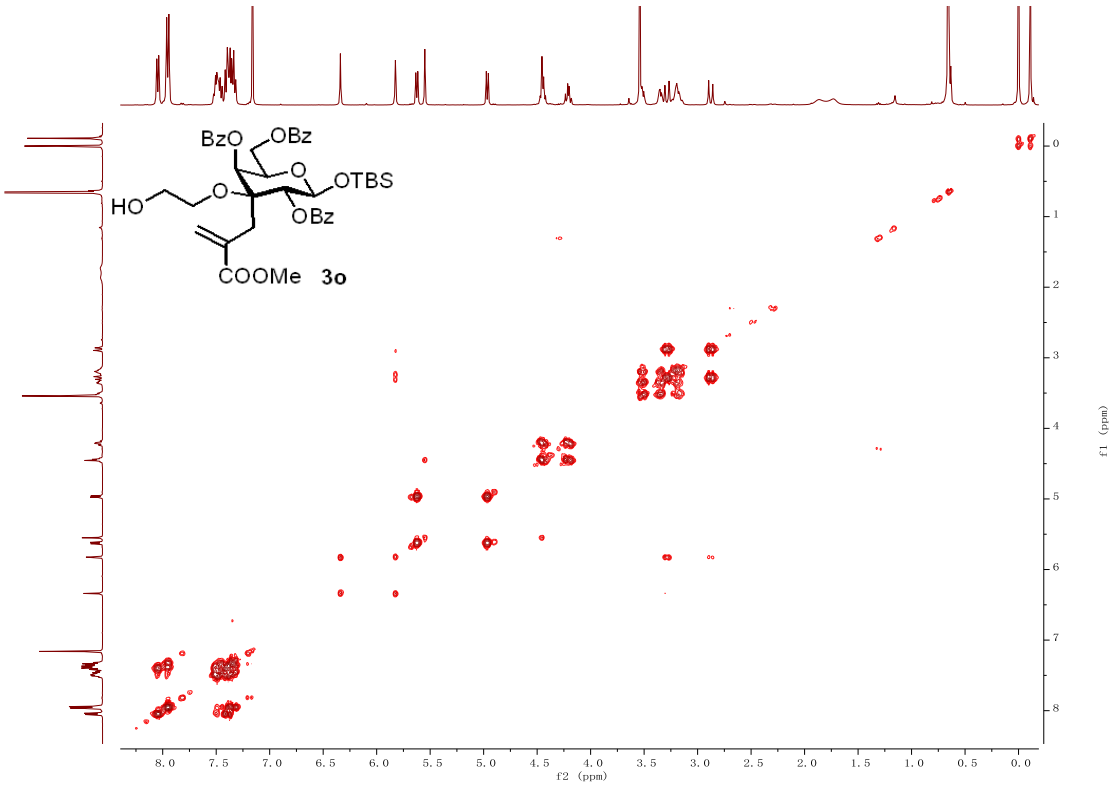
^{1}H NMR Spectra of compound 3o



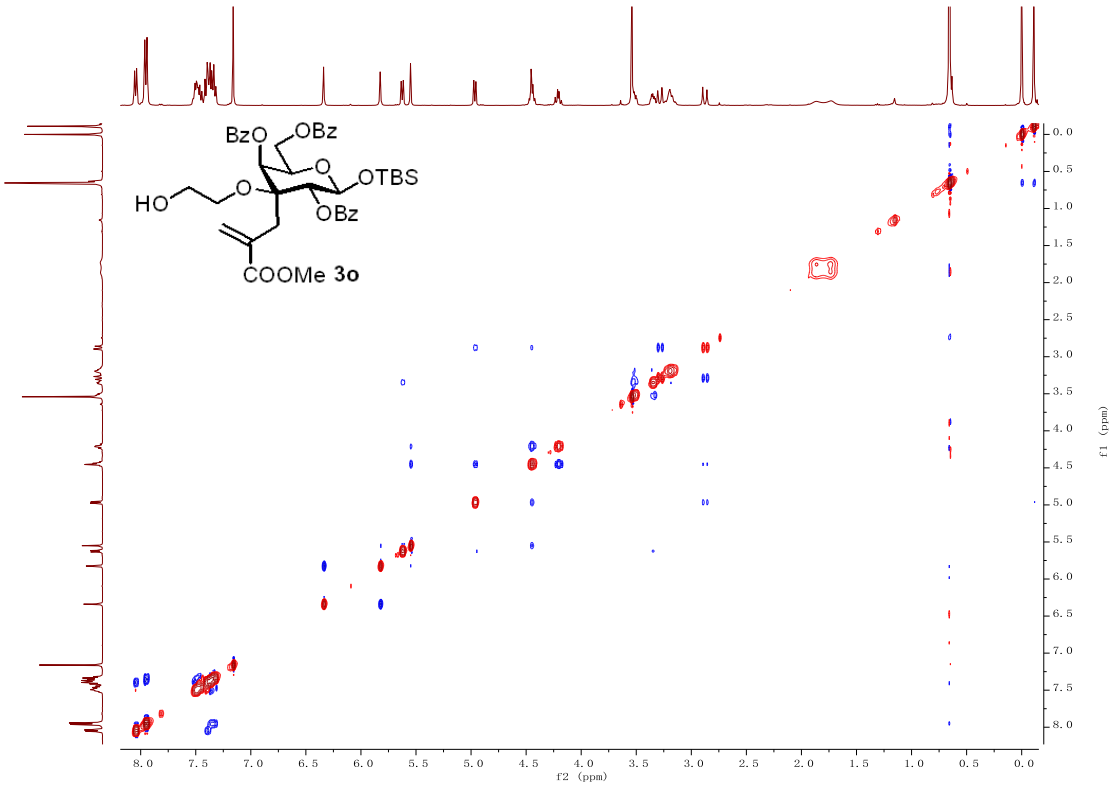
^{13}C NMR Spectra of compound 3o



HSQC Spectra of compound 3o



COSY Spectra of compound 3o



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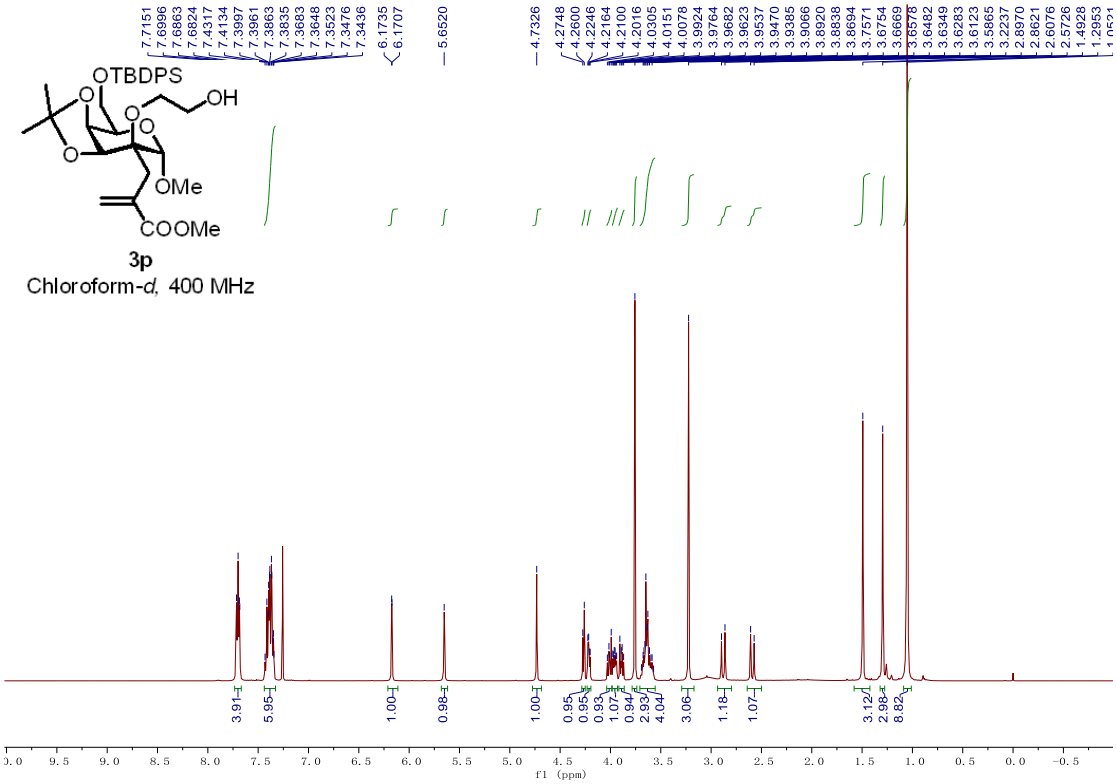
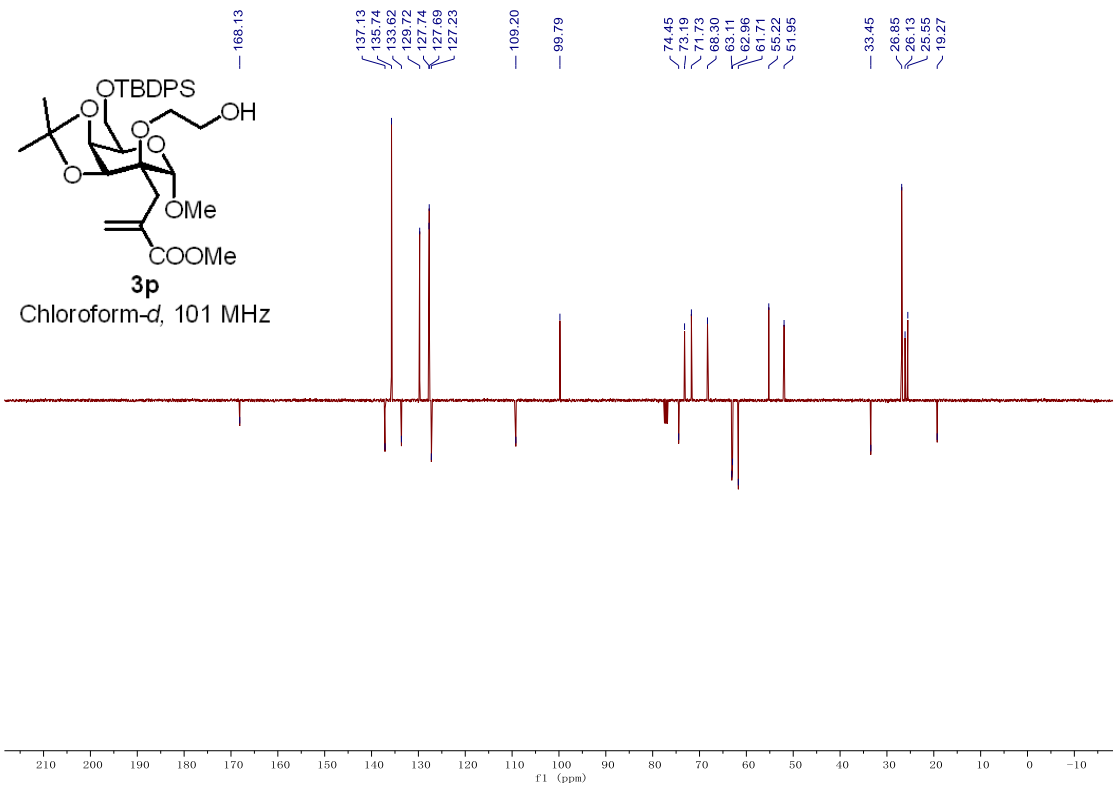
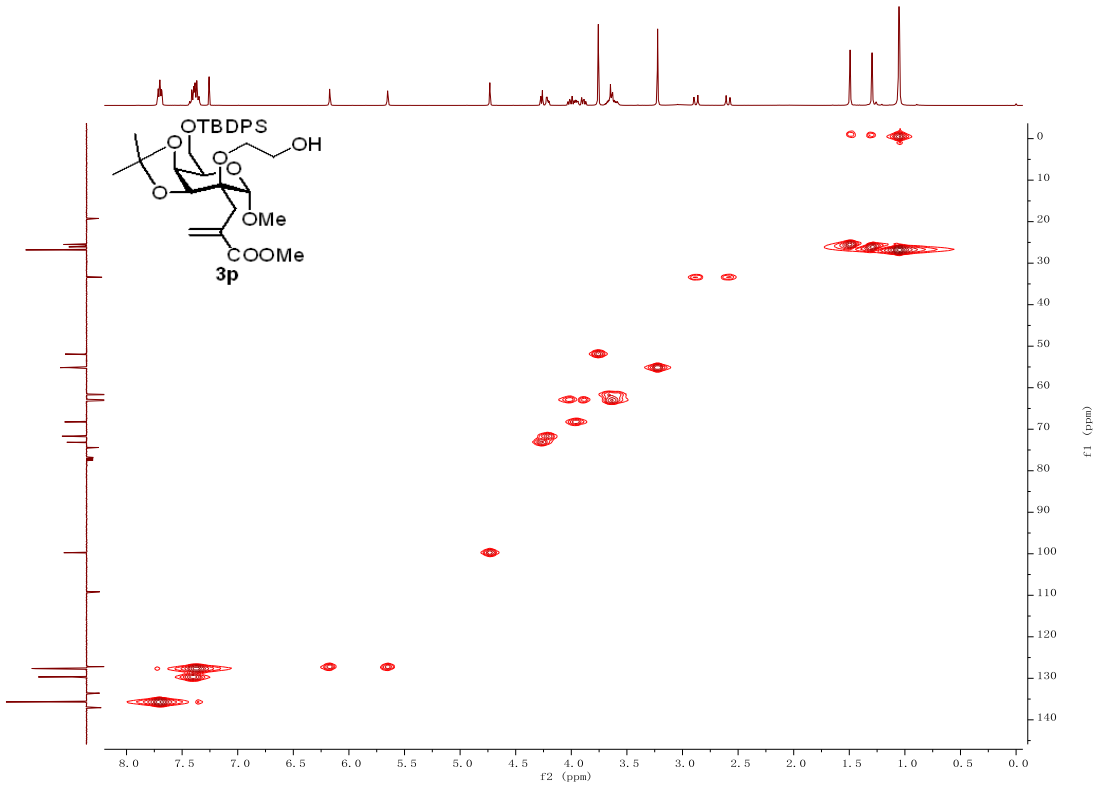


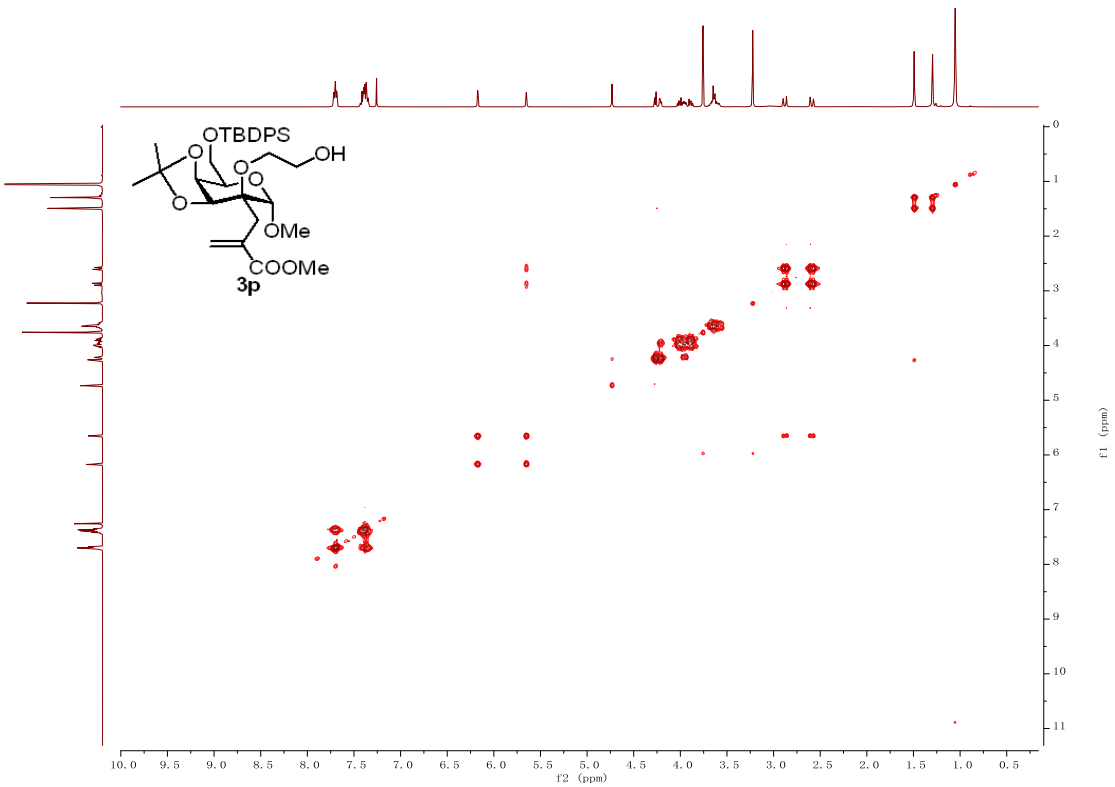
^{1}H NMR Spectra of compound 3p



^{13}C NMR Spectra of compound 3p



HSQC Spectra of compound 3p



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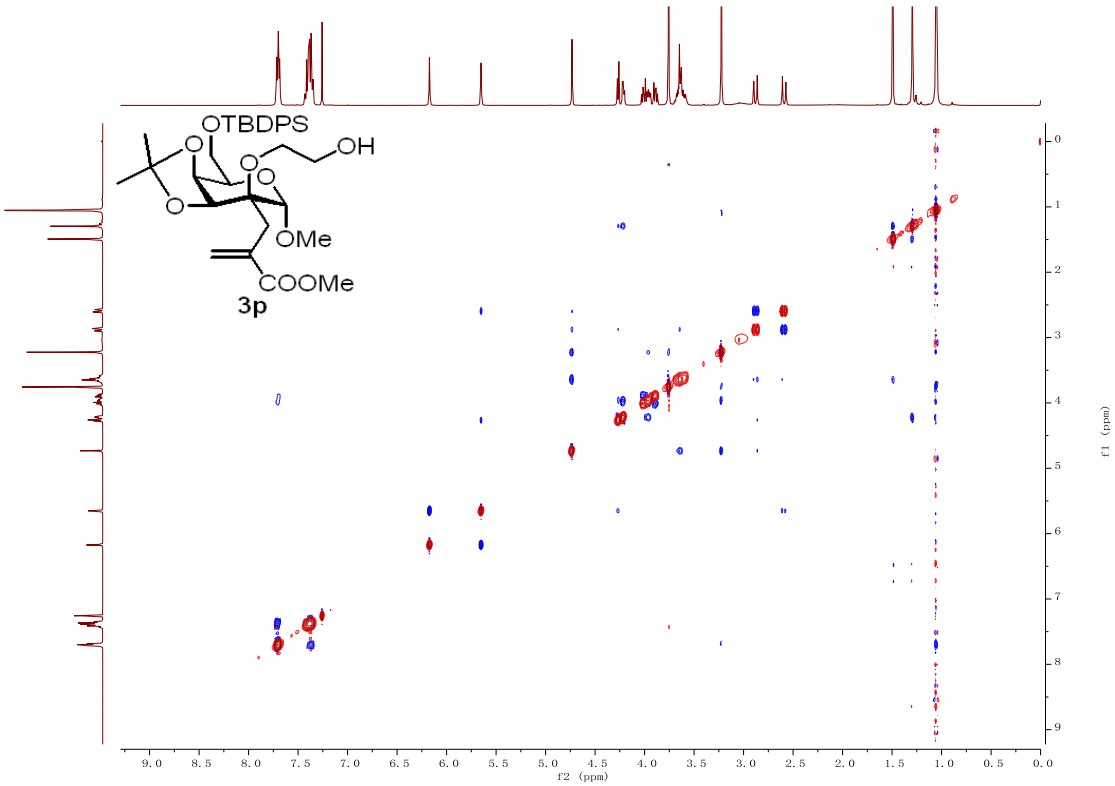

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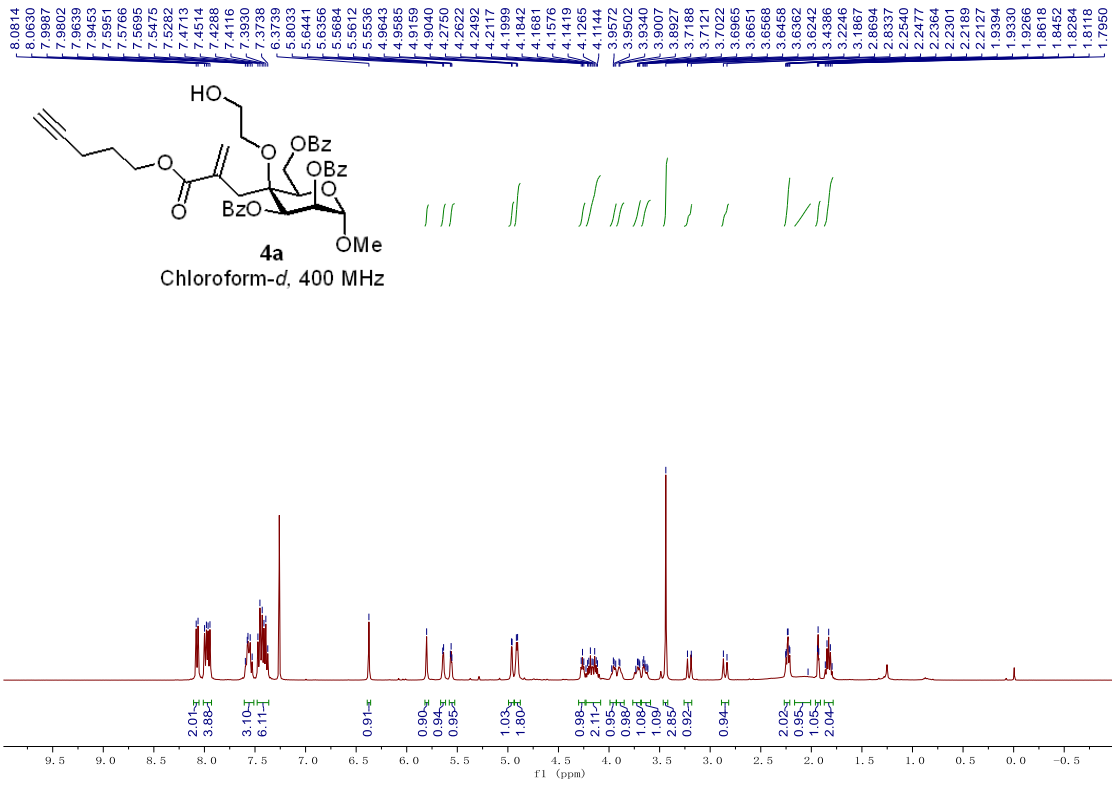
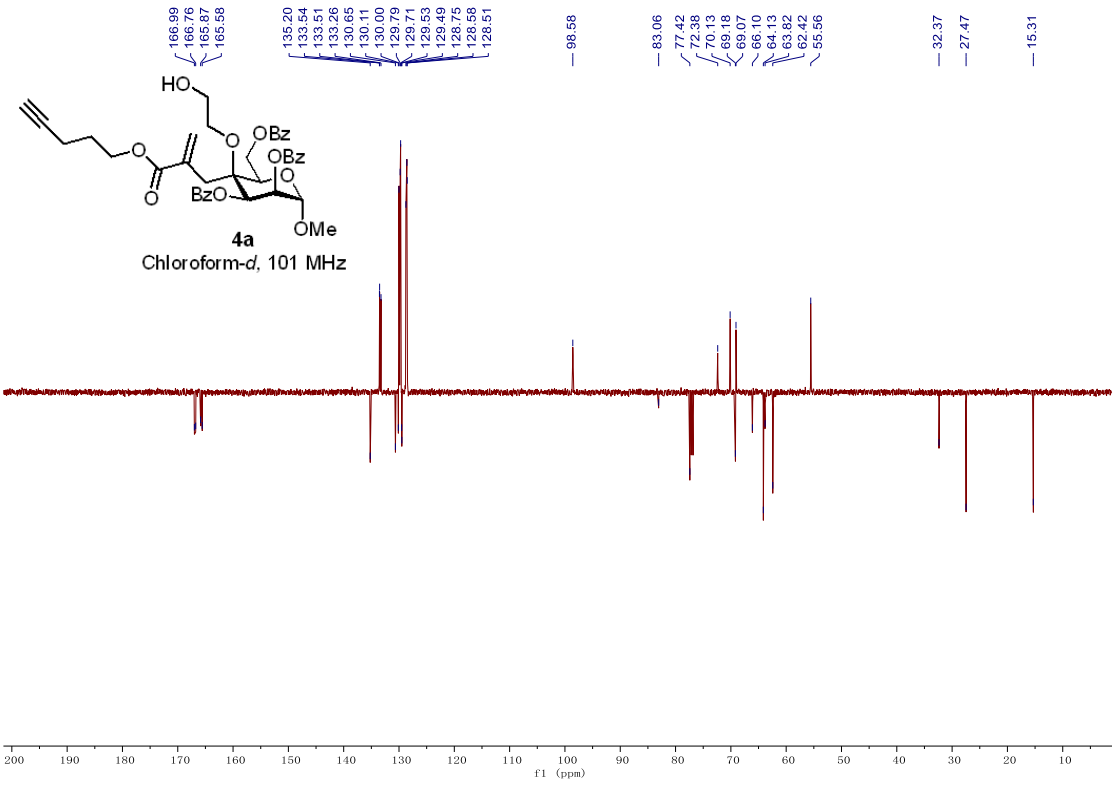


^{1}H NMR Spectra of compound 4a



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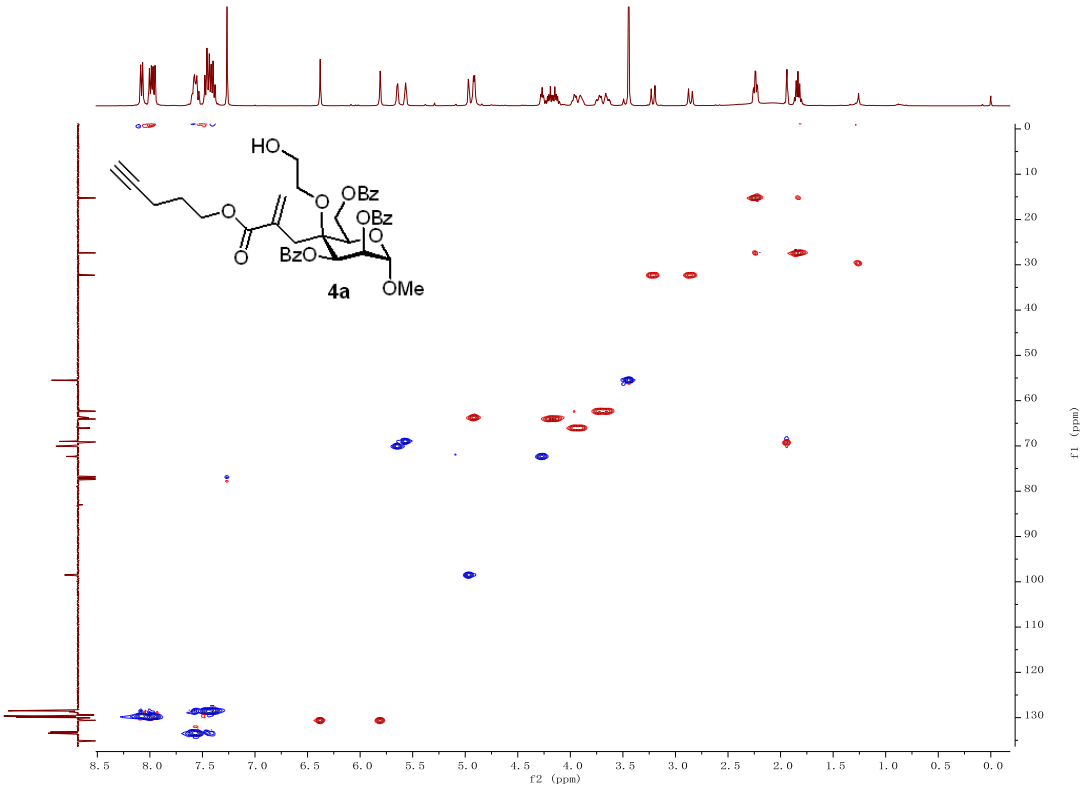
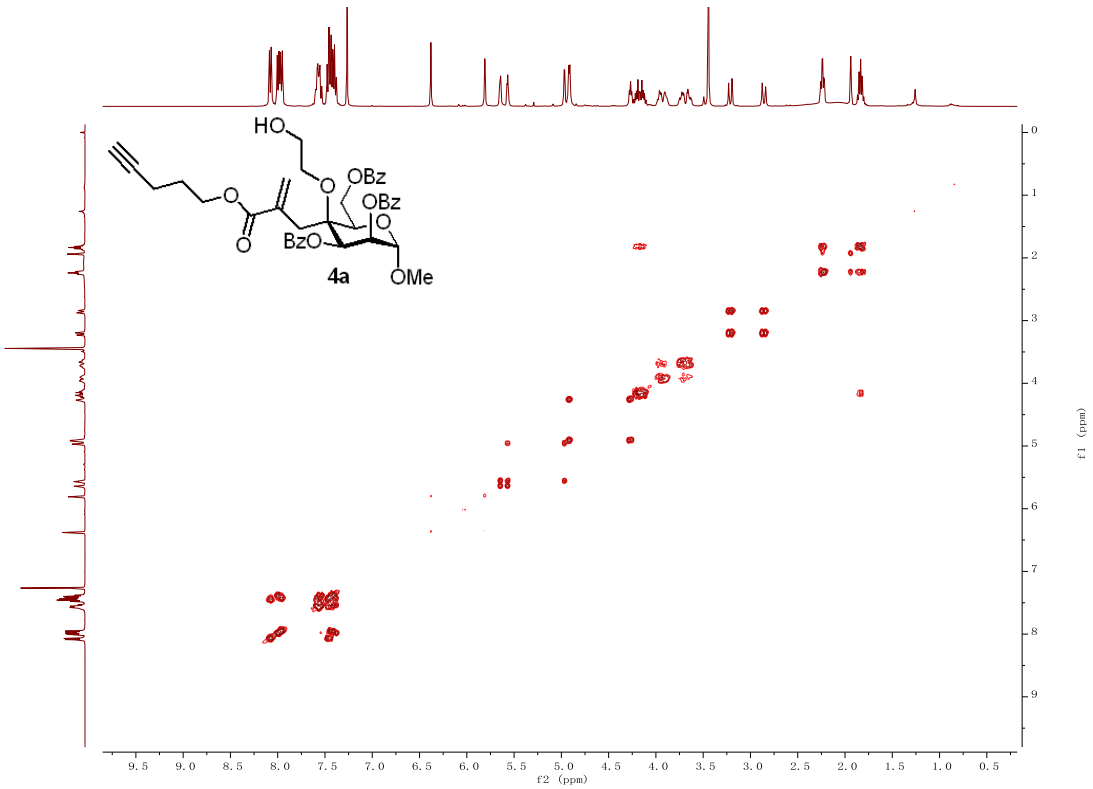


HSQC Spectra of compound 4a



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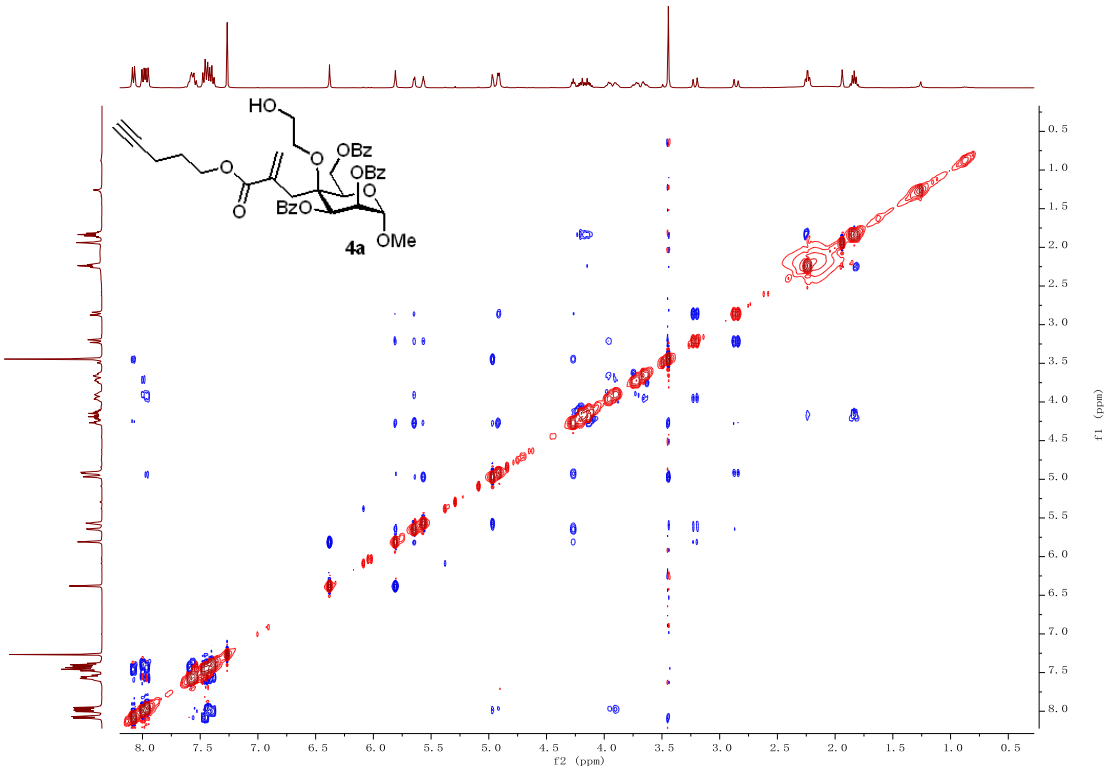

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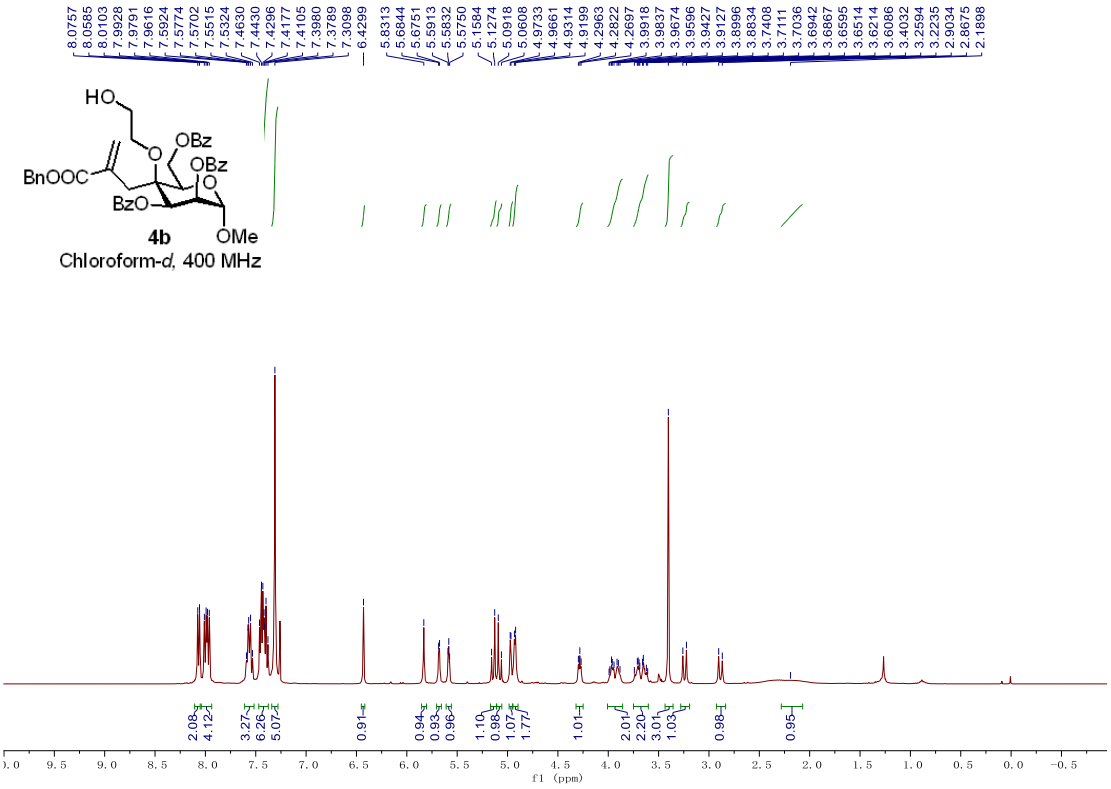
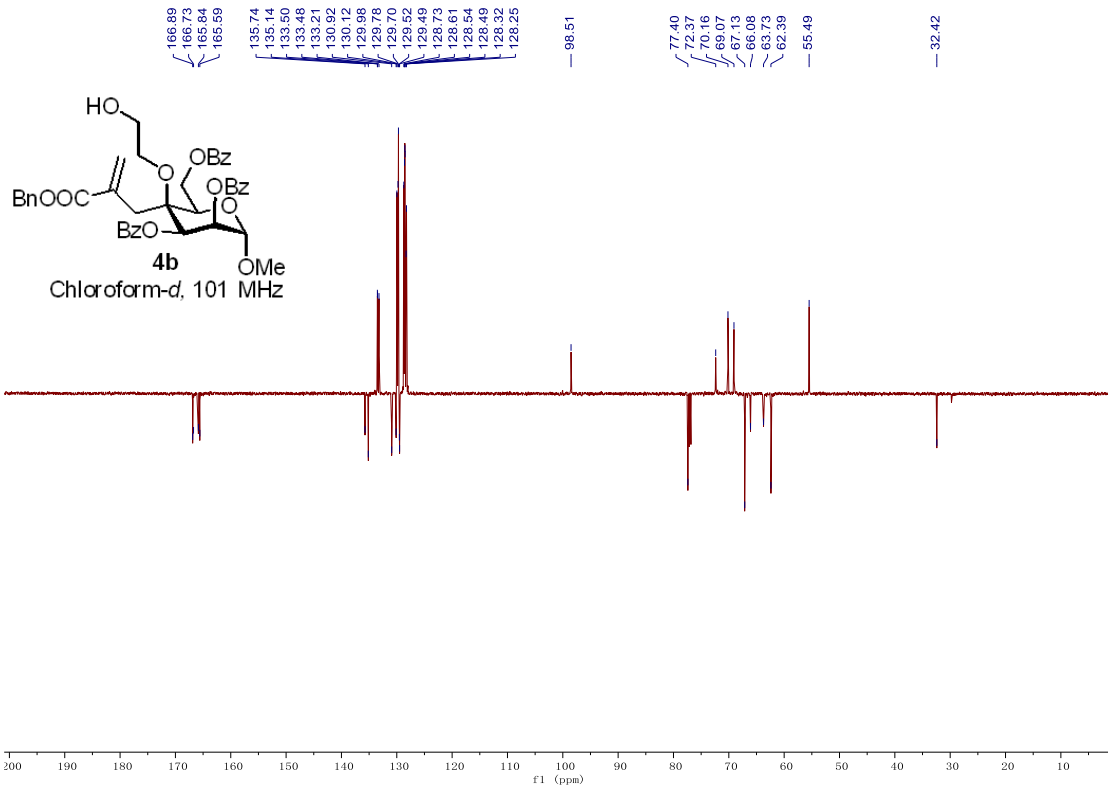
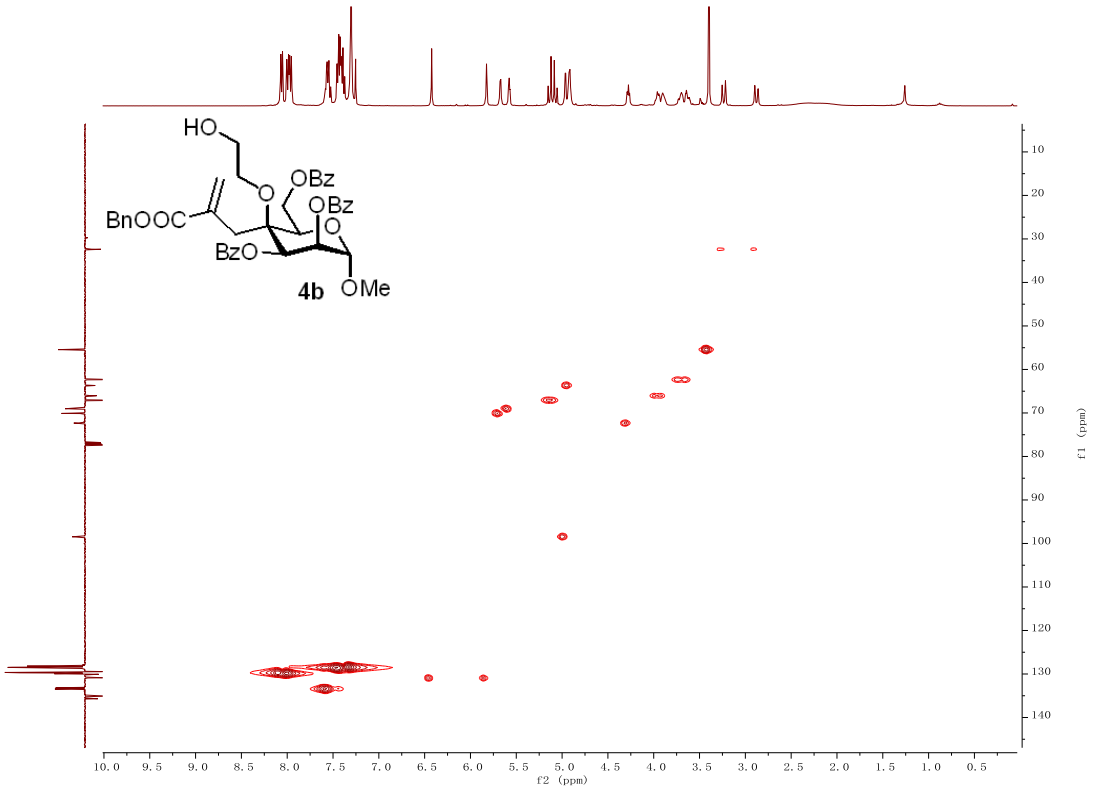


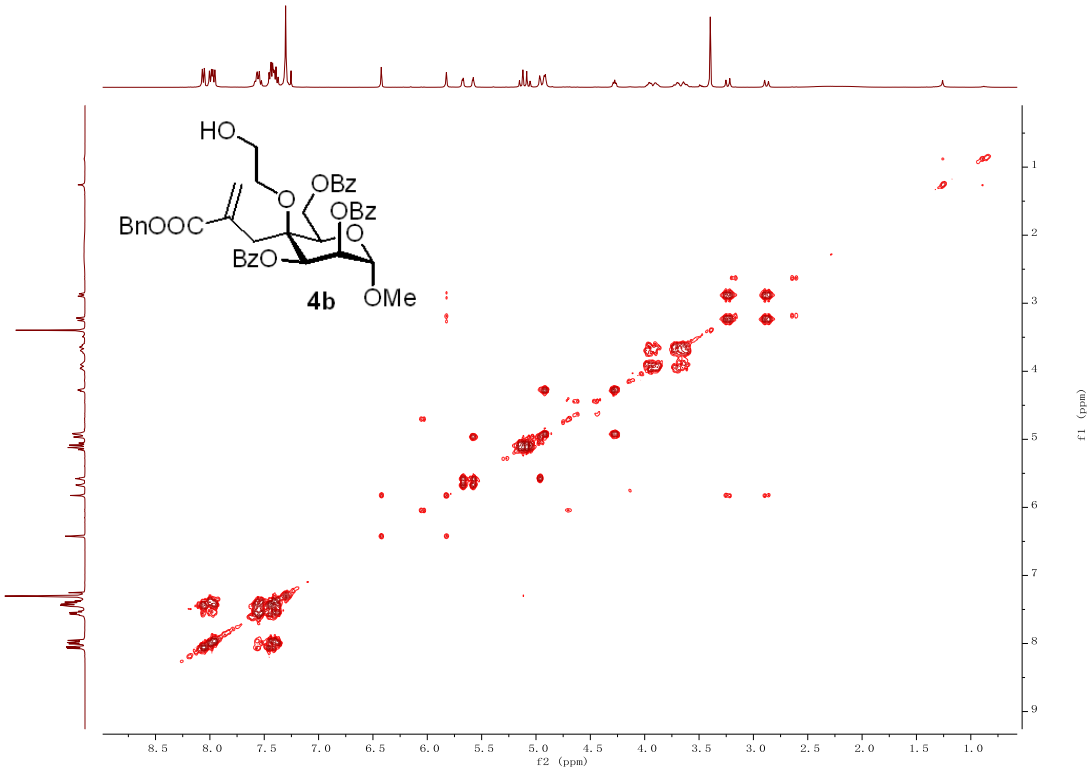
^{1}H NMR Spectra of compound 4b



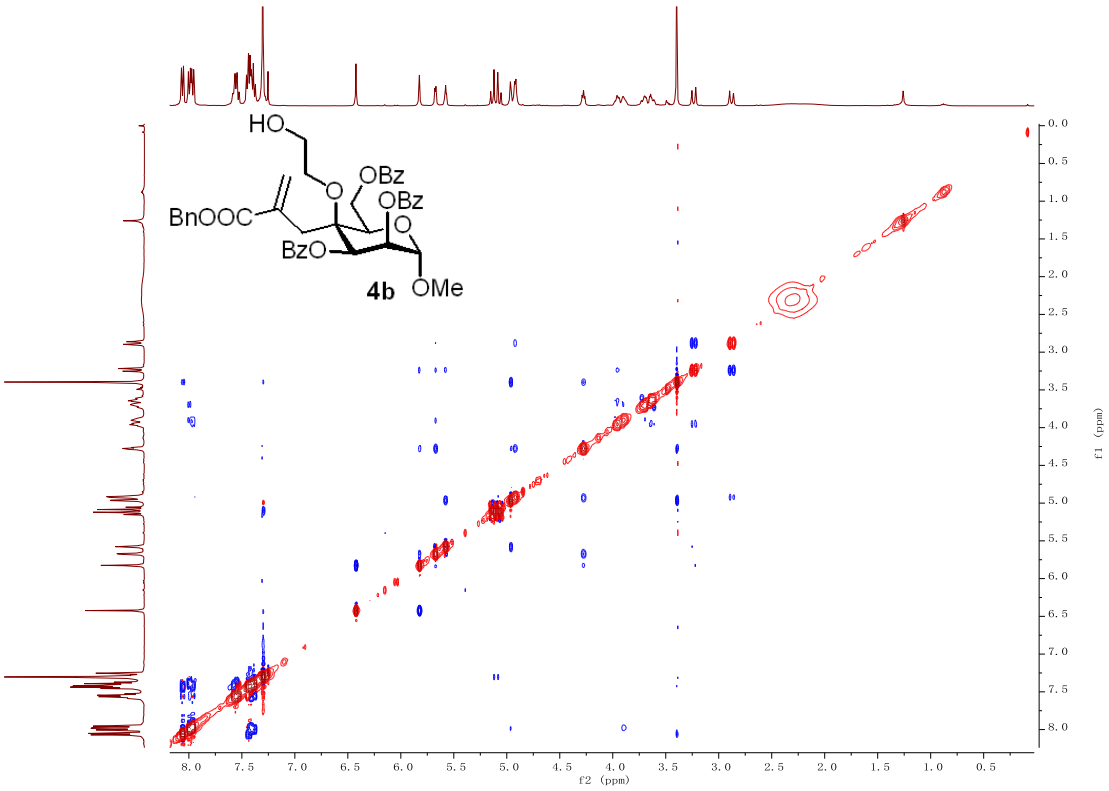
^{13}C NMR Spectra of compound 4b



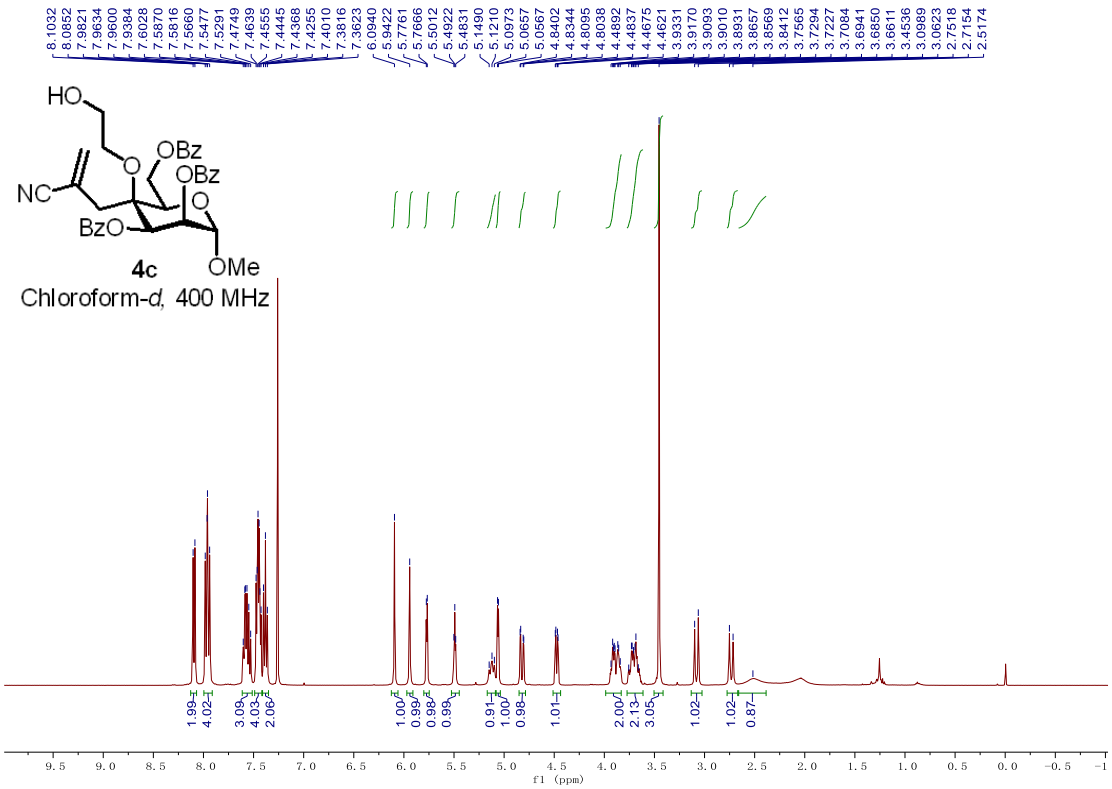
HSQC Spectra of compound 4b



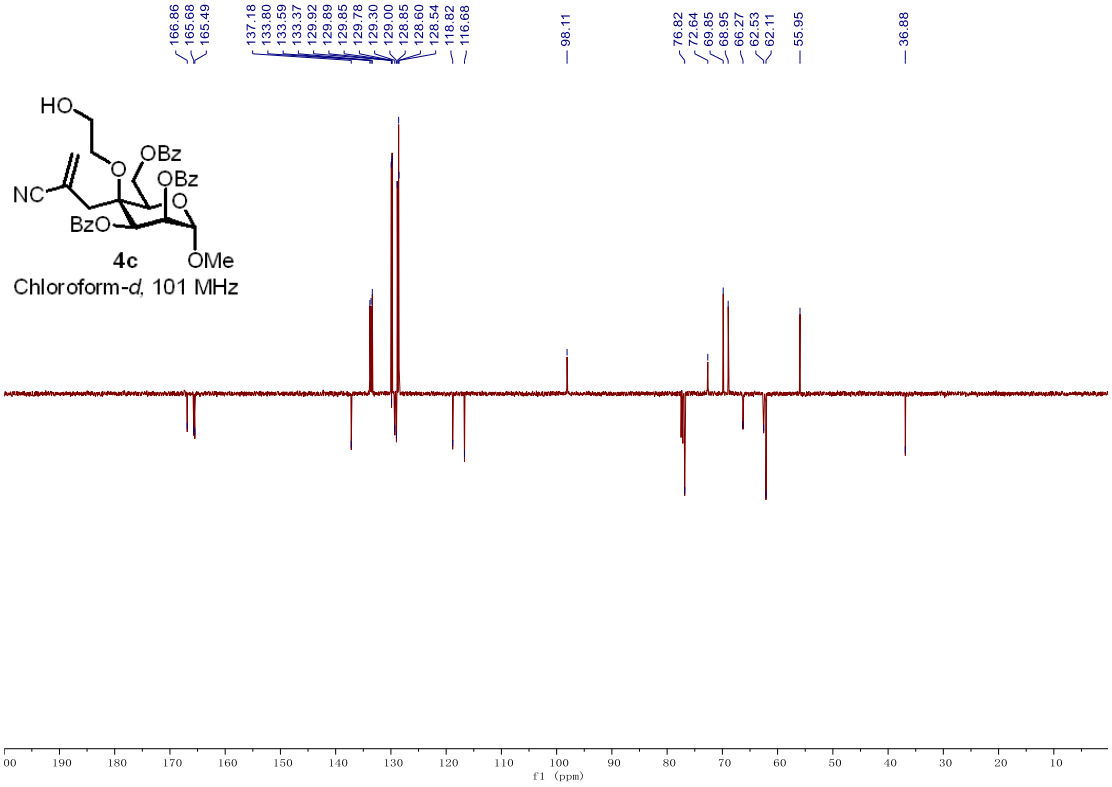
COSY Spectra of compound 4b



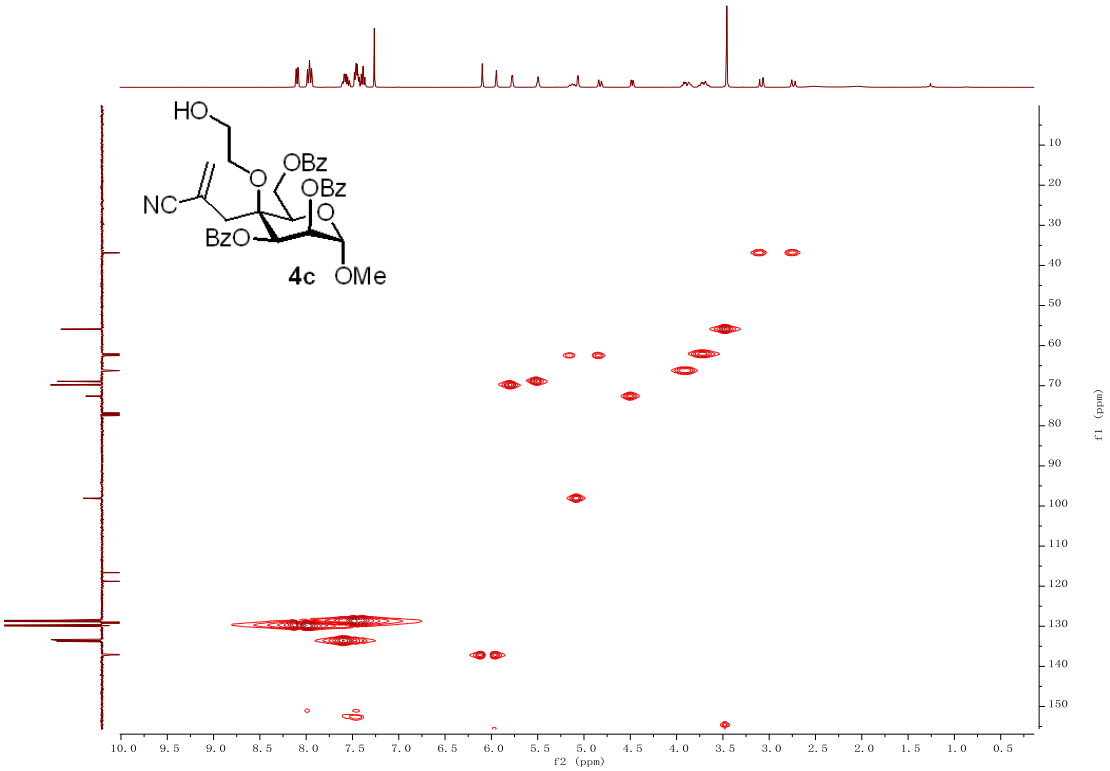
NOESY Spectra of compound 4b



^{1}H NMR Spectra of compound 4c



^{13}C NMR Spectra of compound 4c



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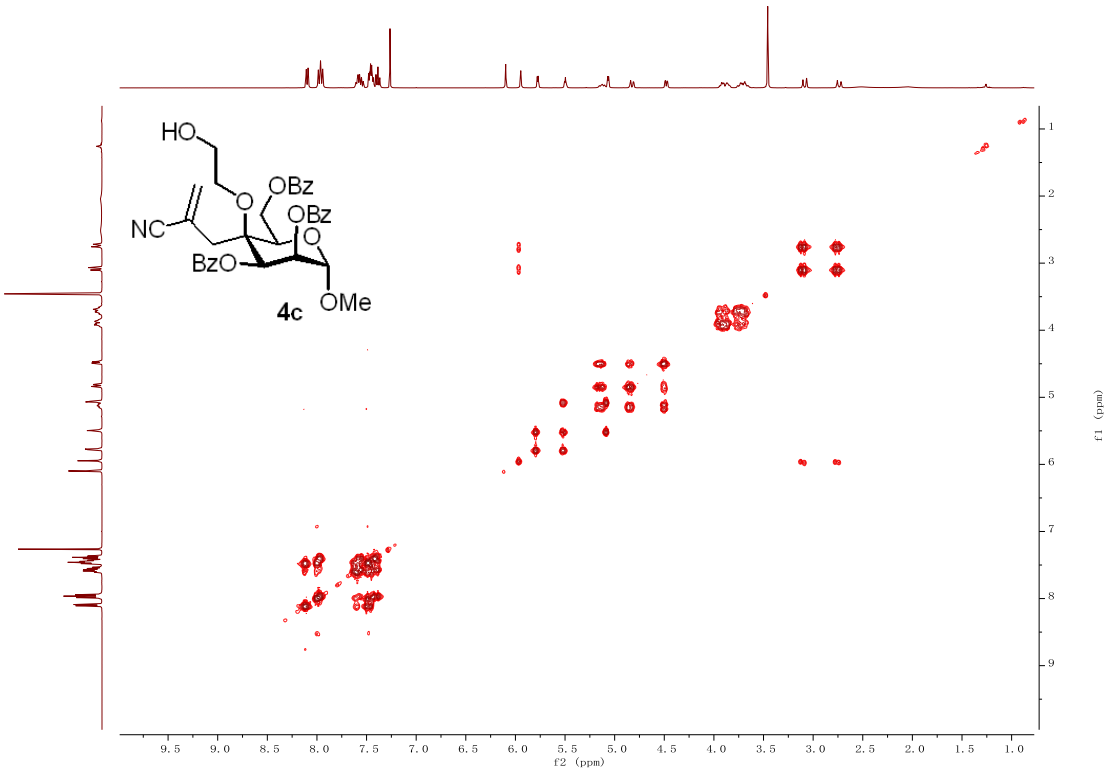

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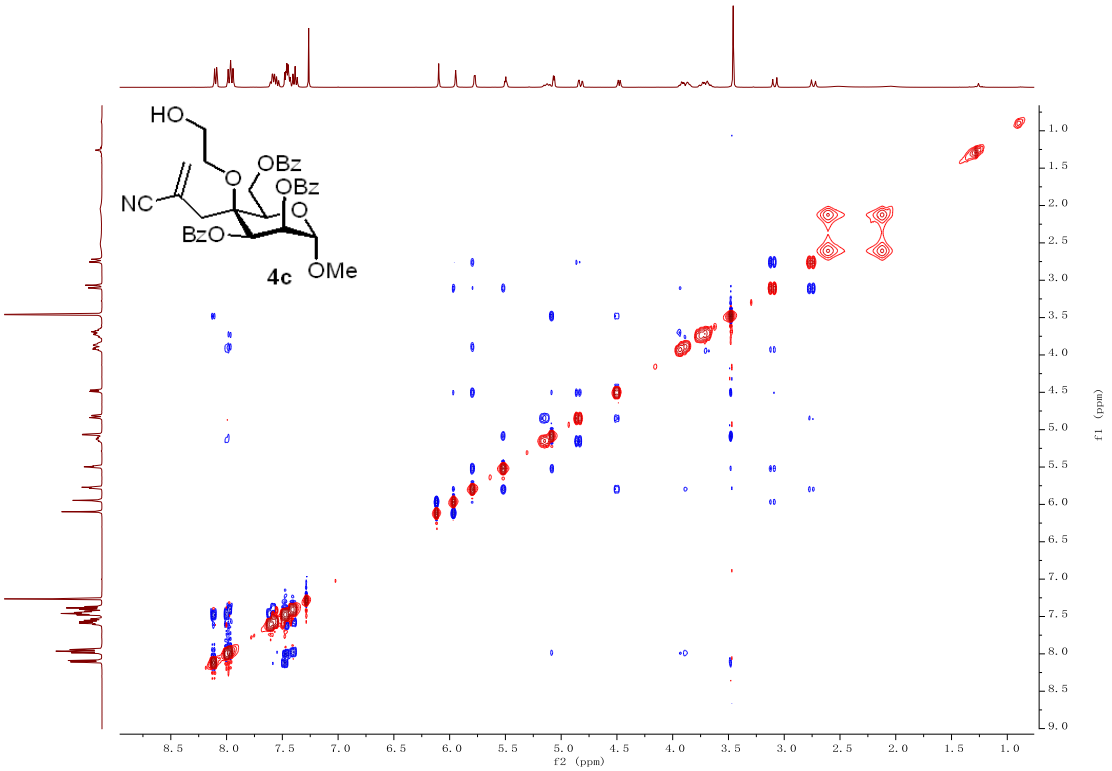

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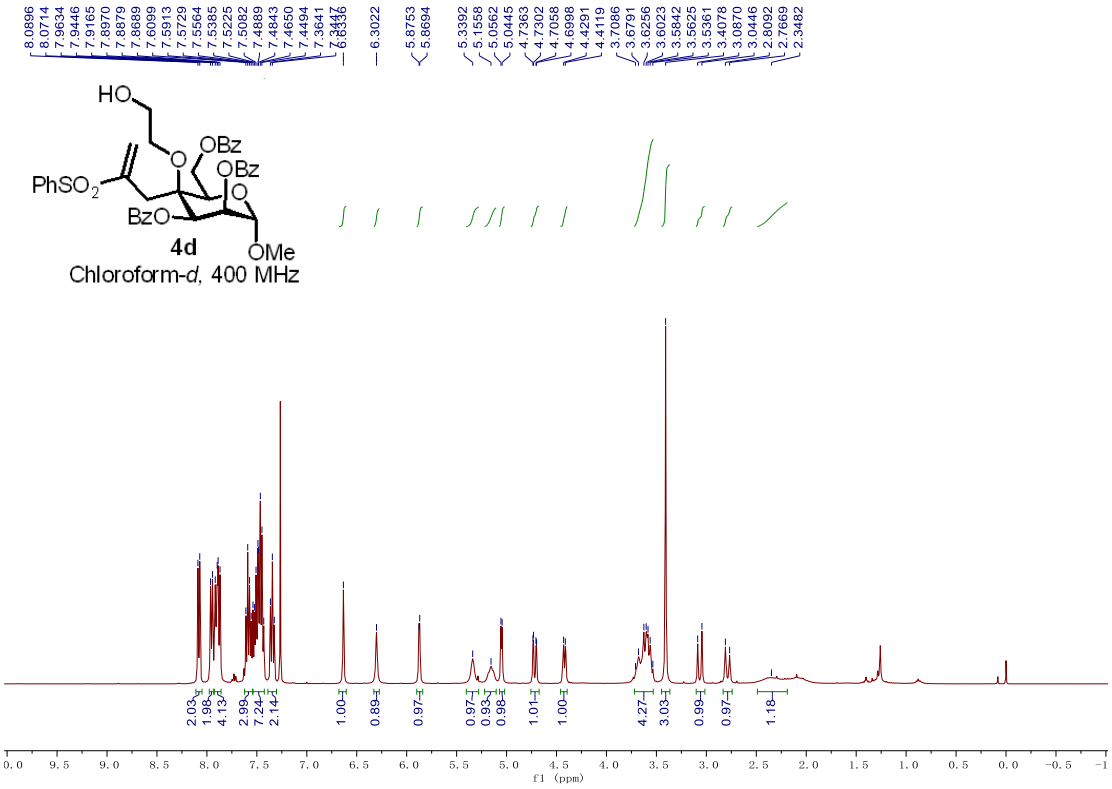
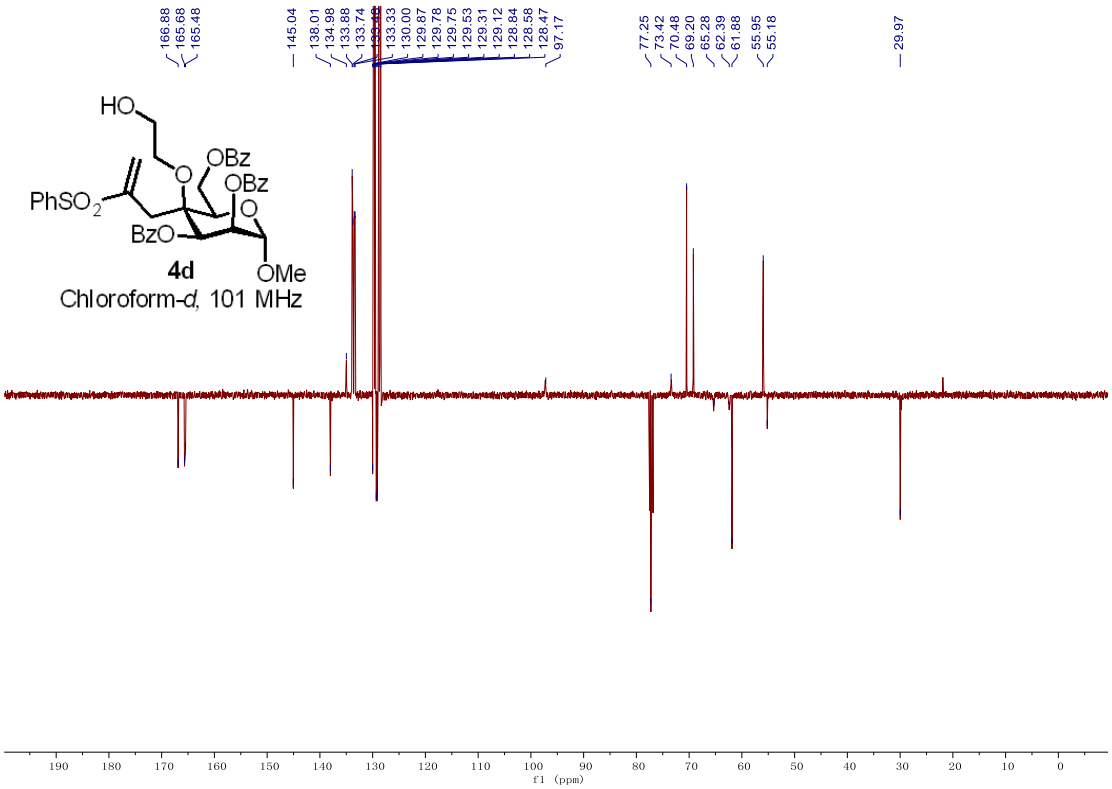
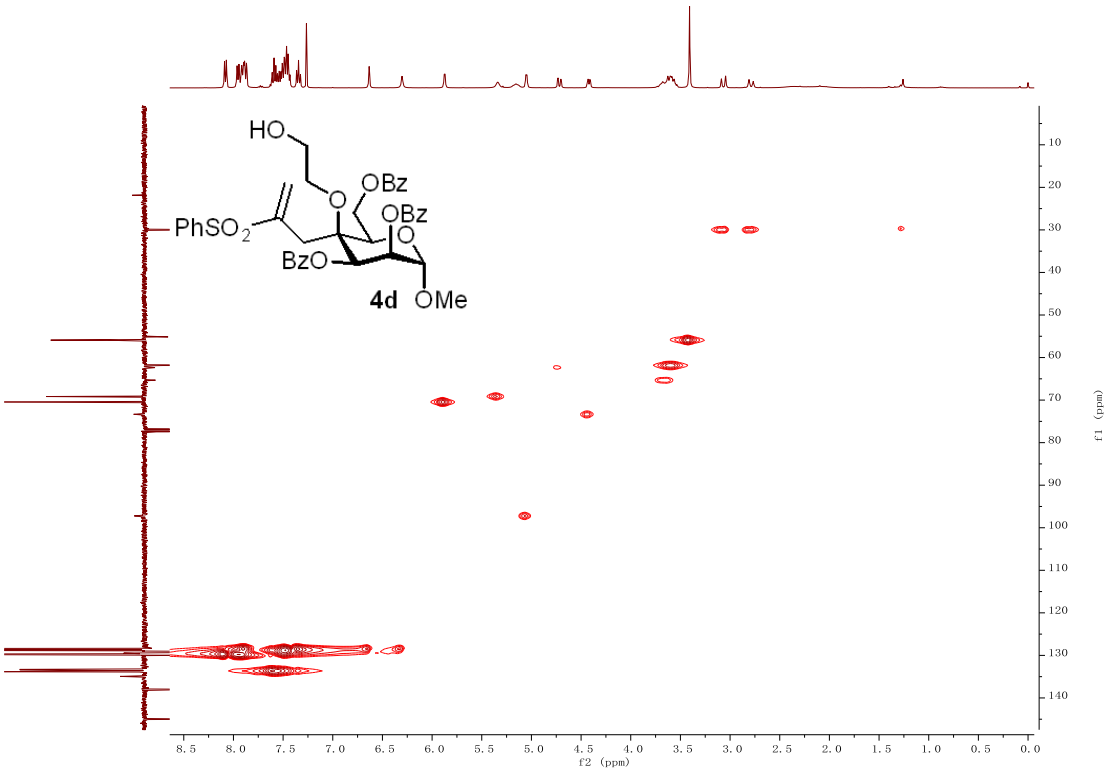


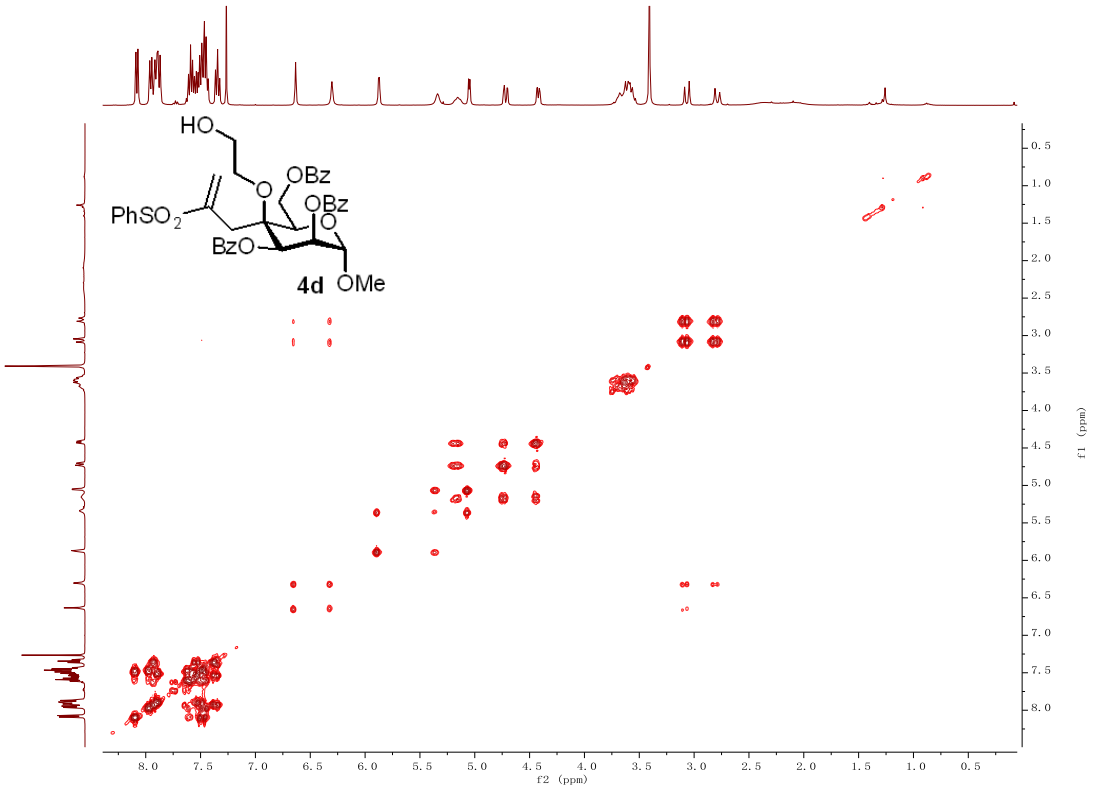
^{1}H NMR Spectra of compound 4d



^{13}C NMR Spectra of compound 4d



HSQC Spectra of compound 4d



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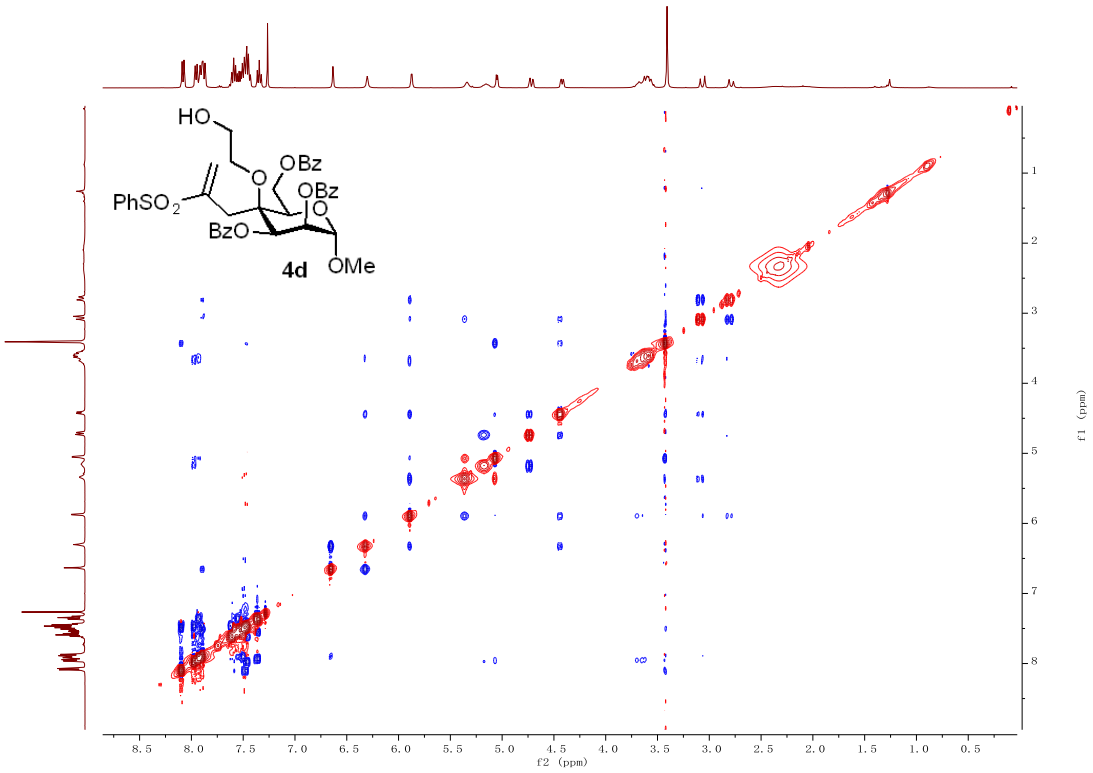
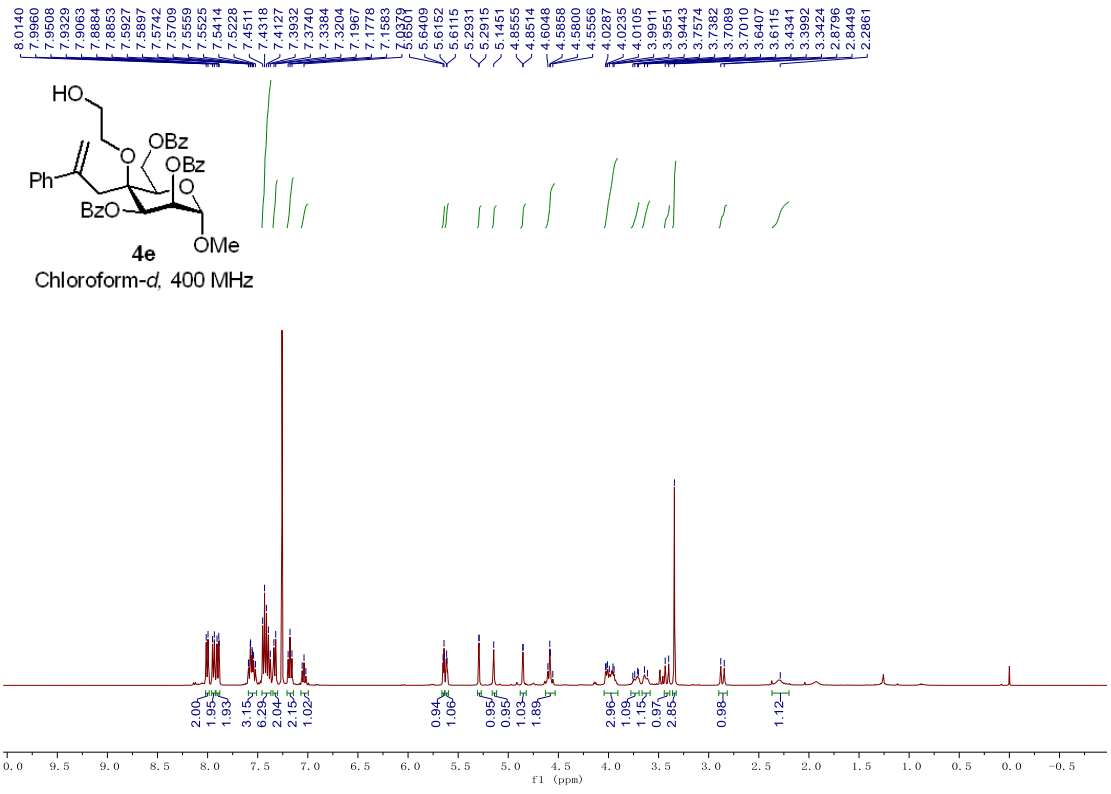
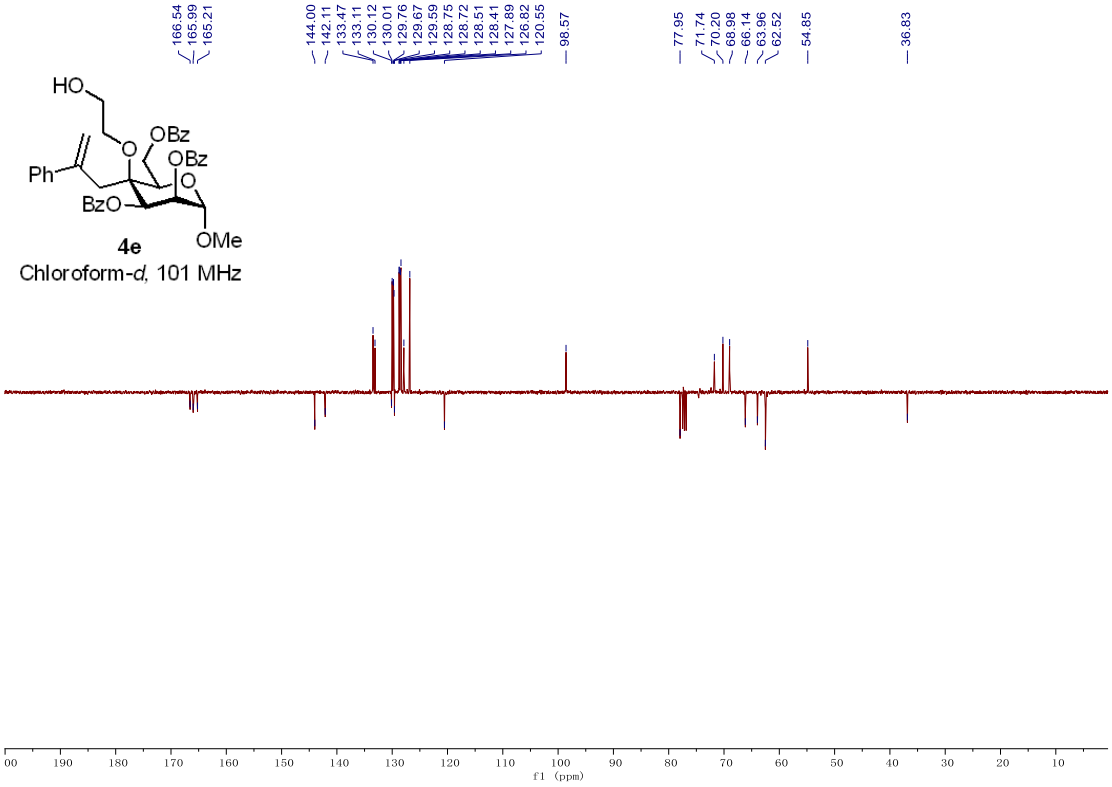


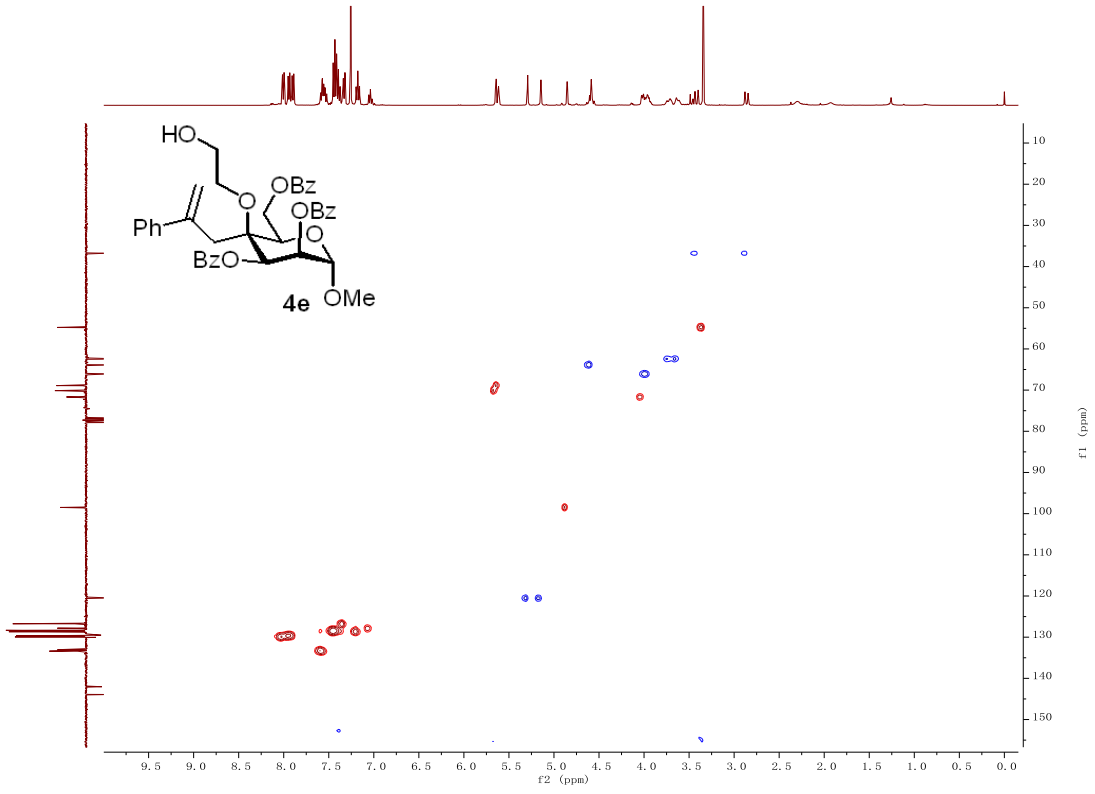
NOESY Spectra of compound 4d



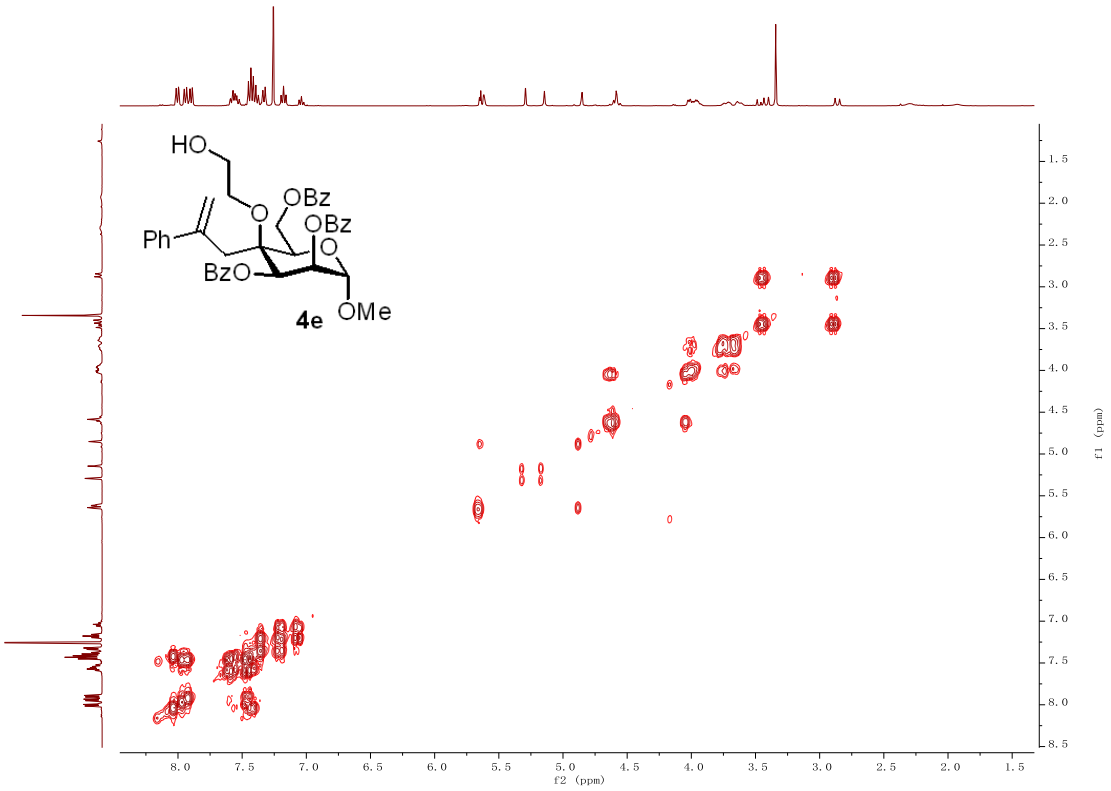
^{1}H NMR Spectra of compound 4e



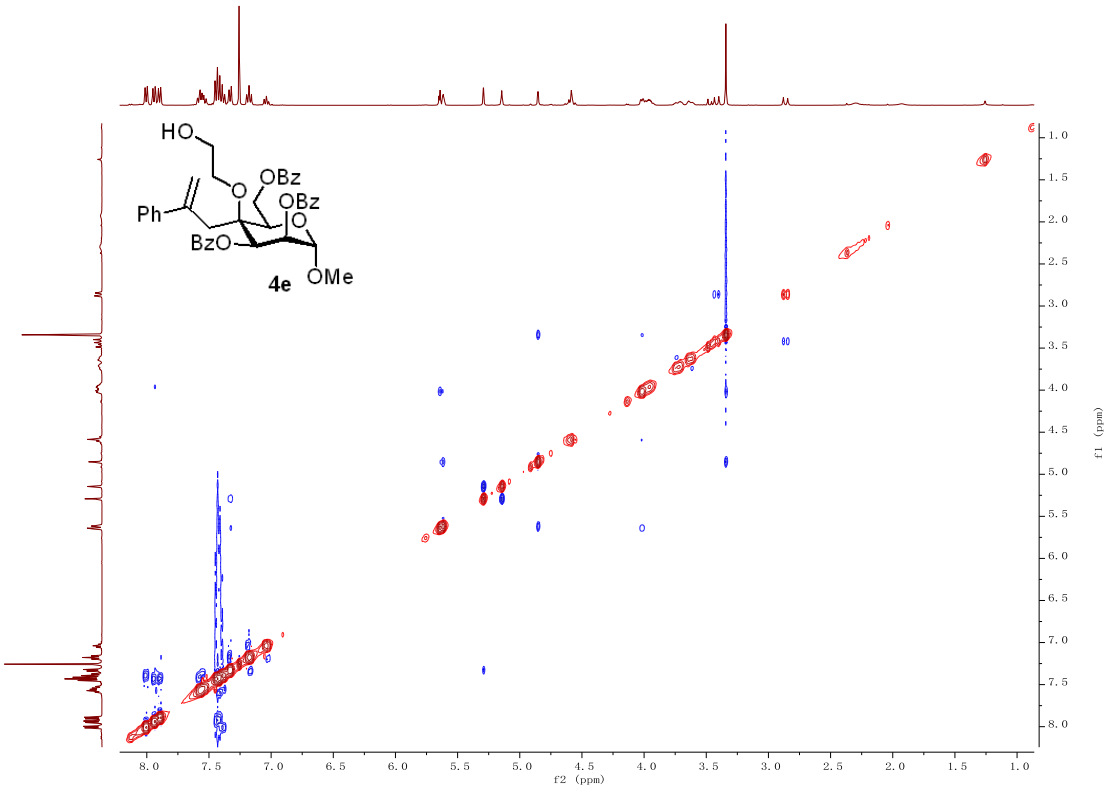
^{13}C NMR Spectra of compound 4e



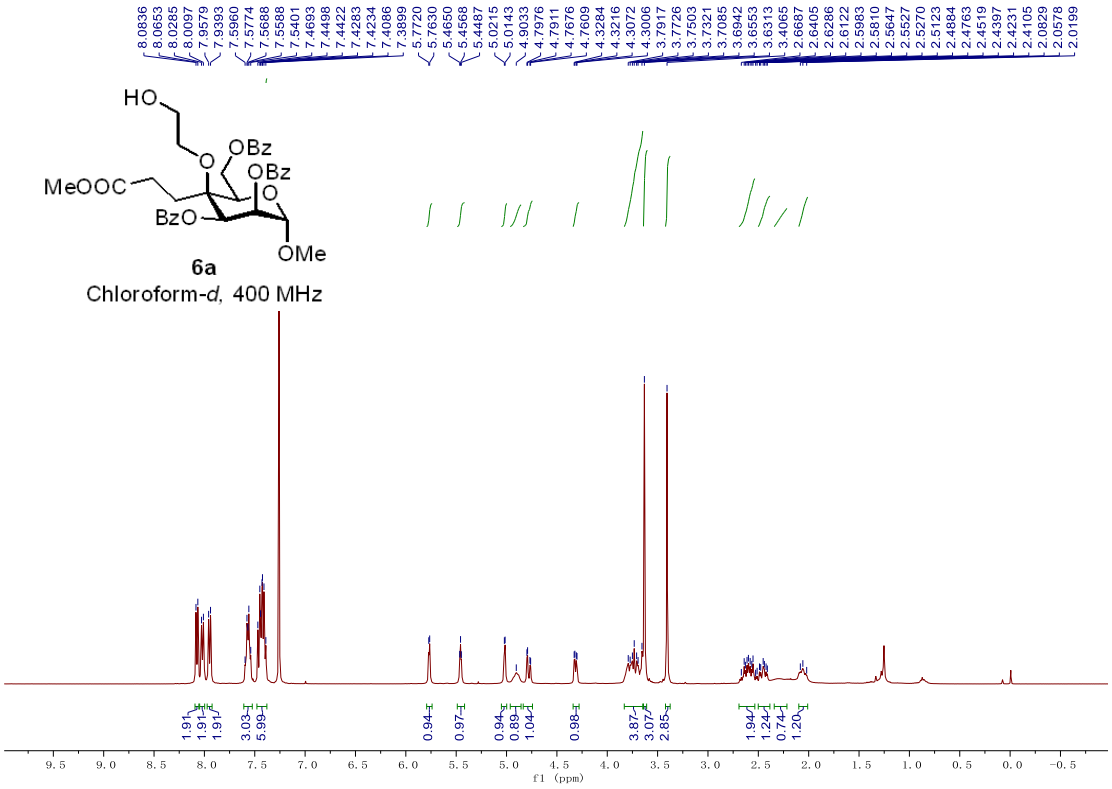
HSQC Spectra of compound 4e



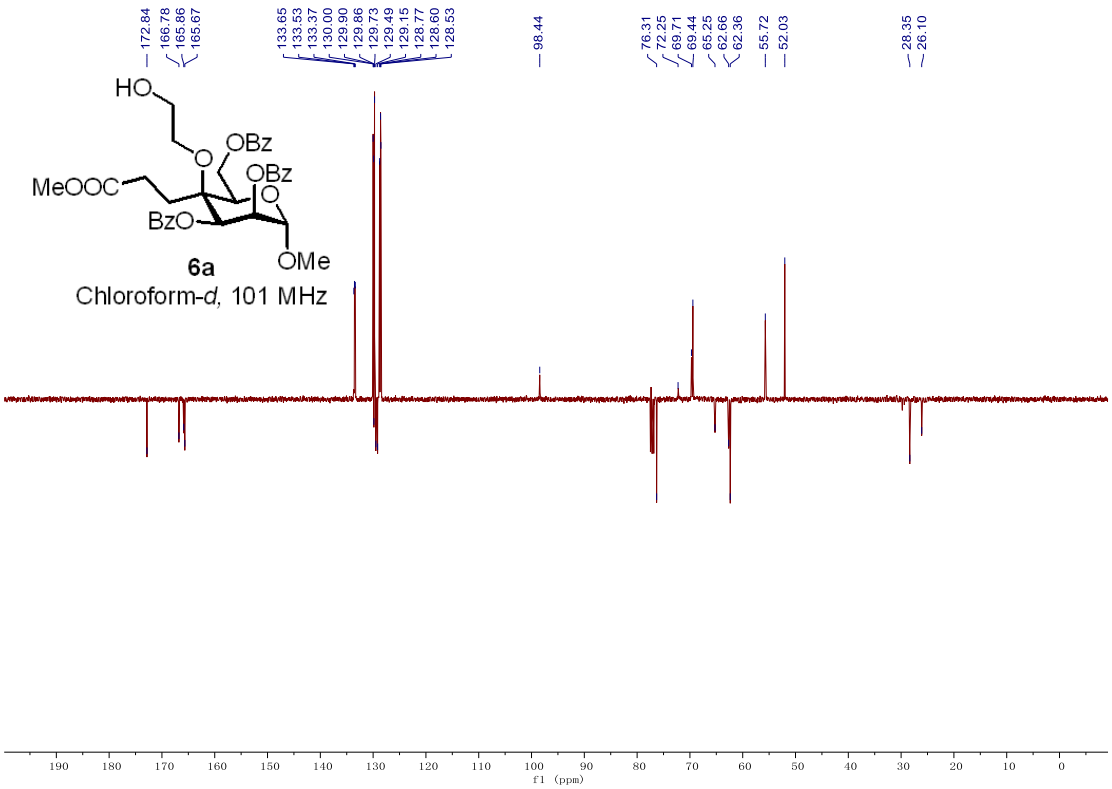
COSY Spectra of compound 4e



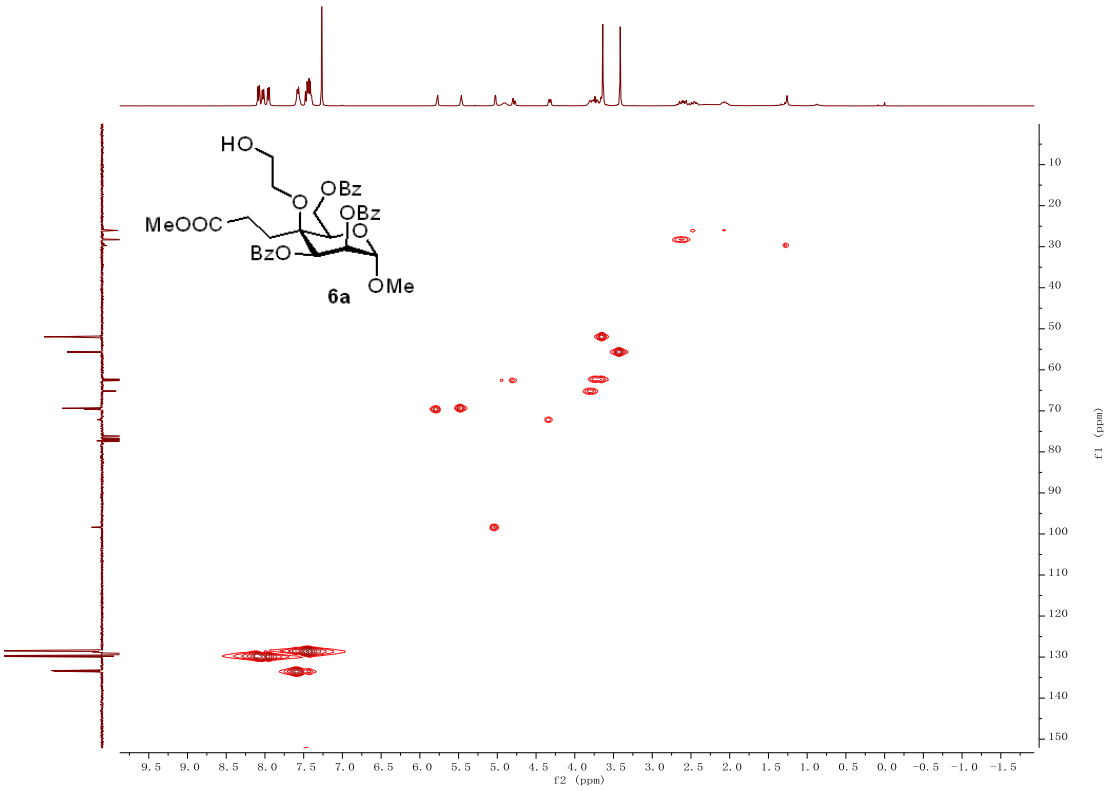
NOESY Spectra of compound 4e



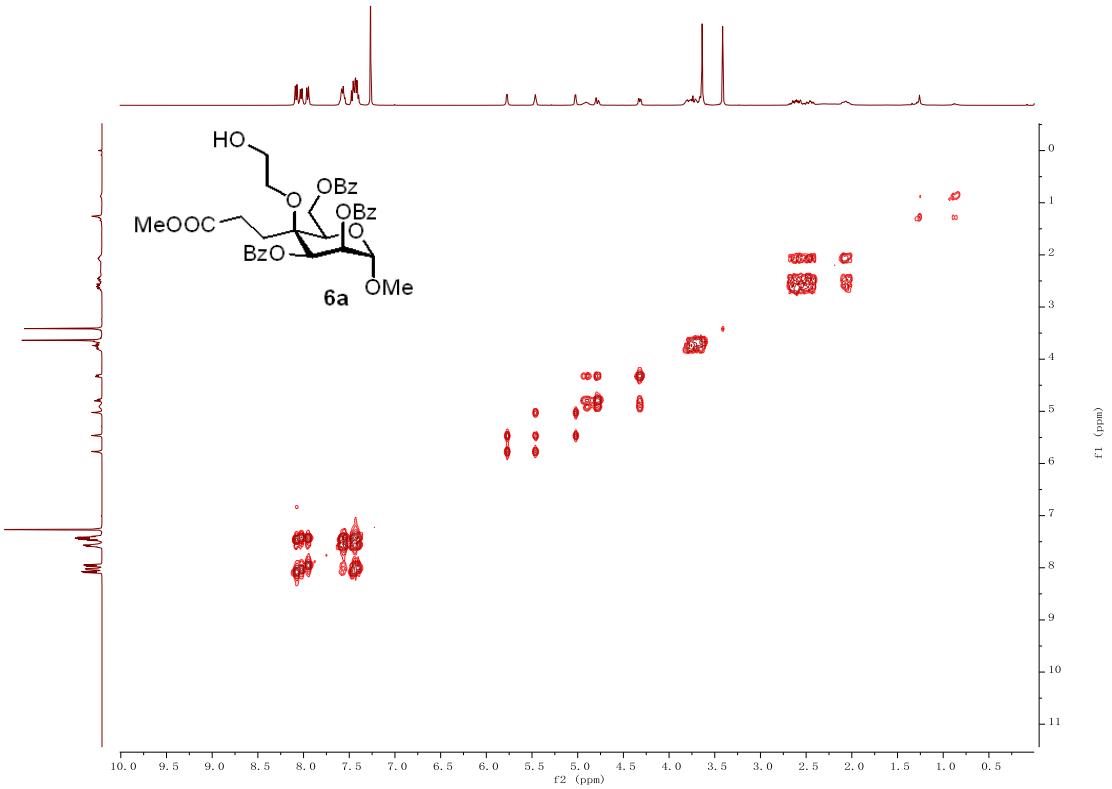
^{1}H NMR Spectra of compound 6a



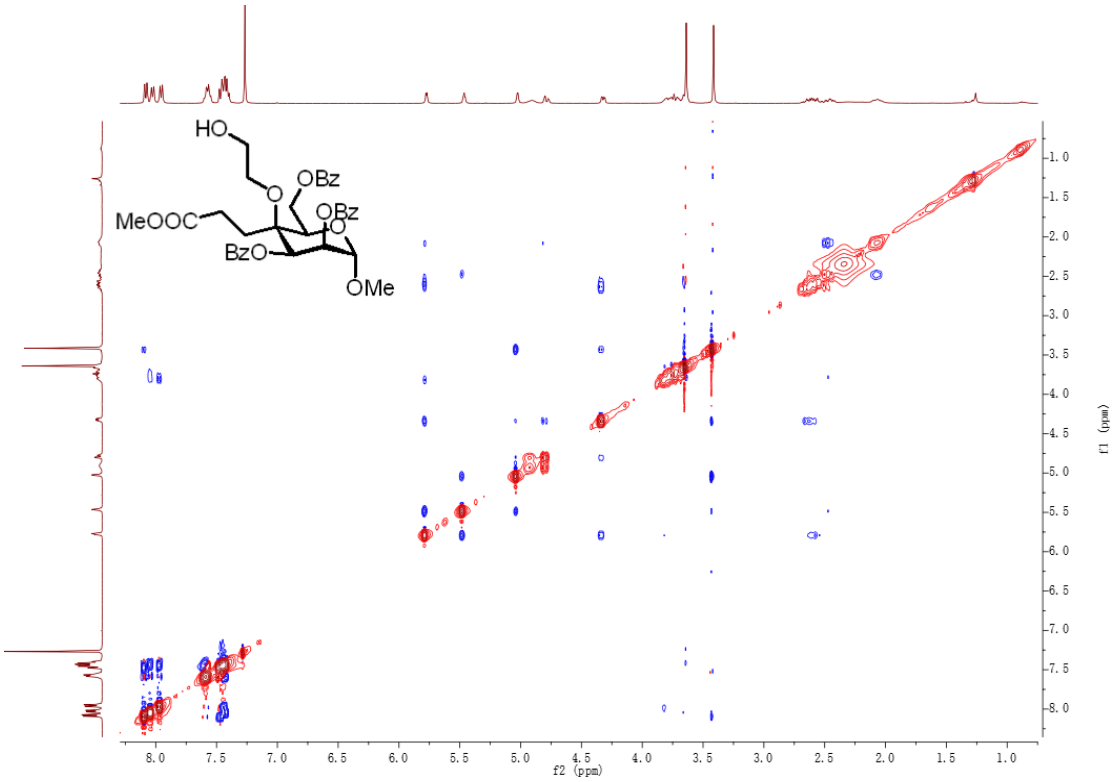
^{13}C NMR Spectra of compound 6a



HSQC Spectra of compound 6a



COSY Spectra of compound 6a



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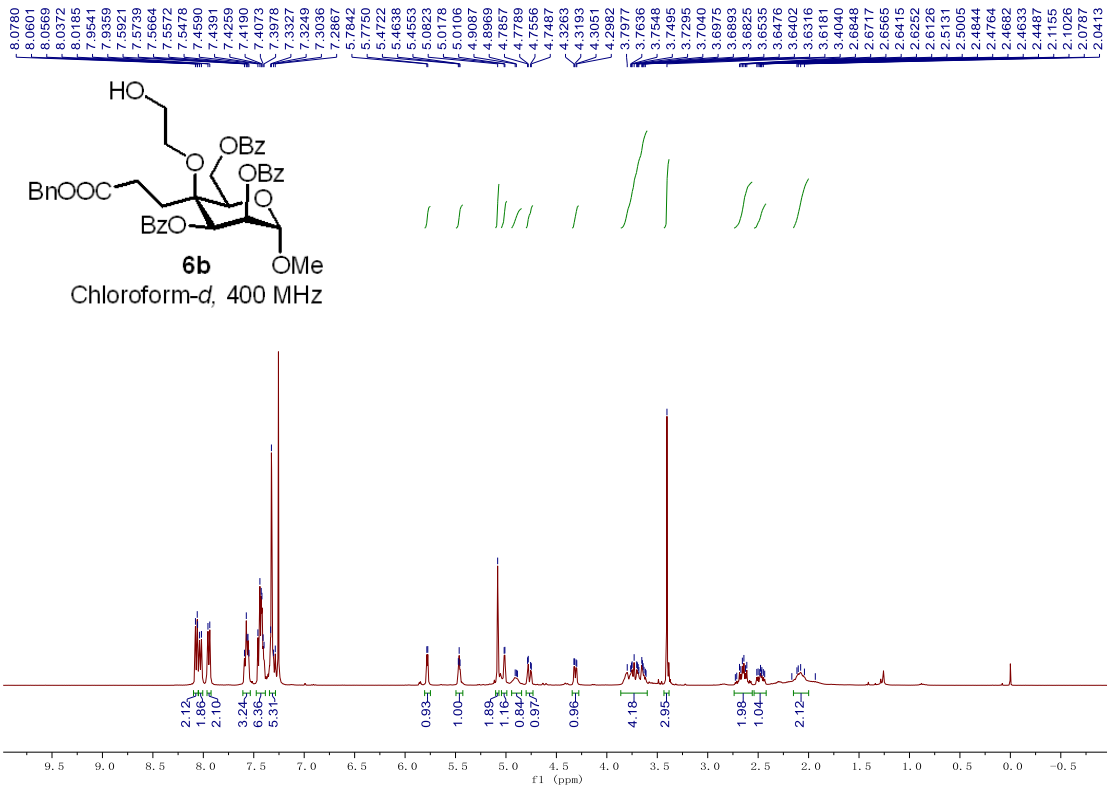
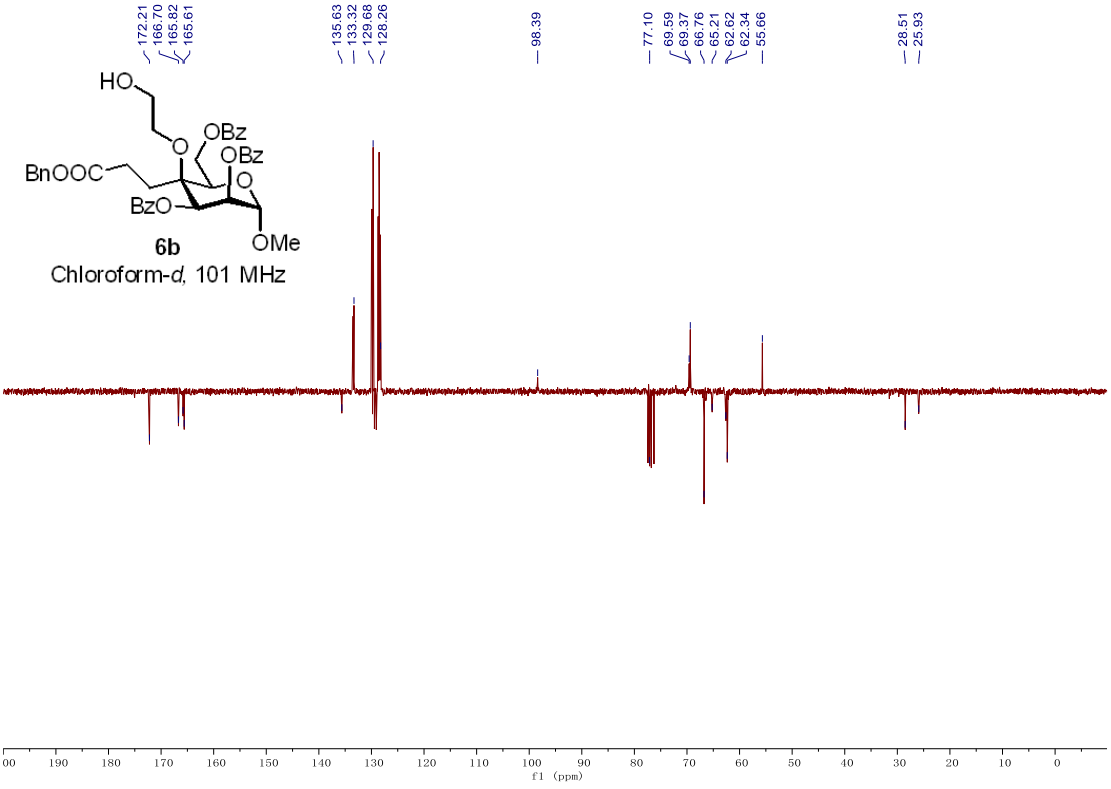
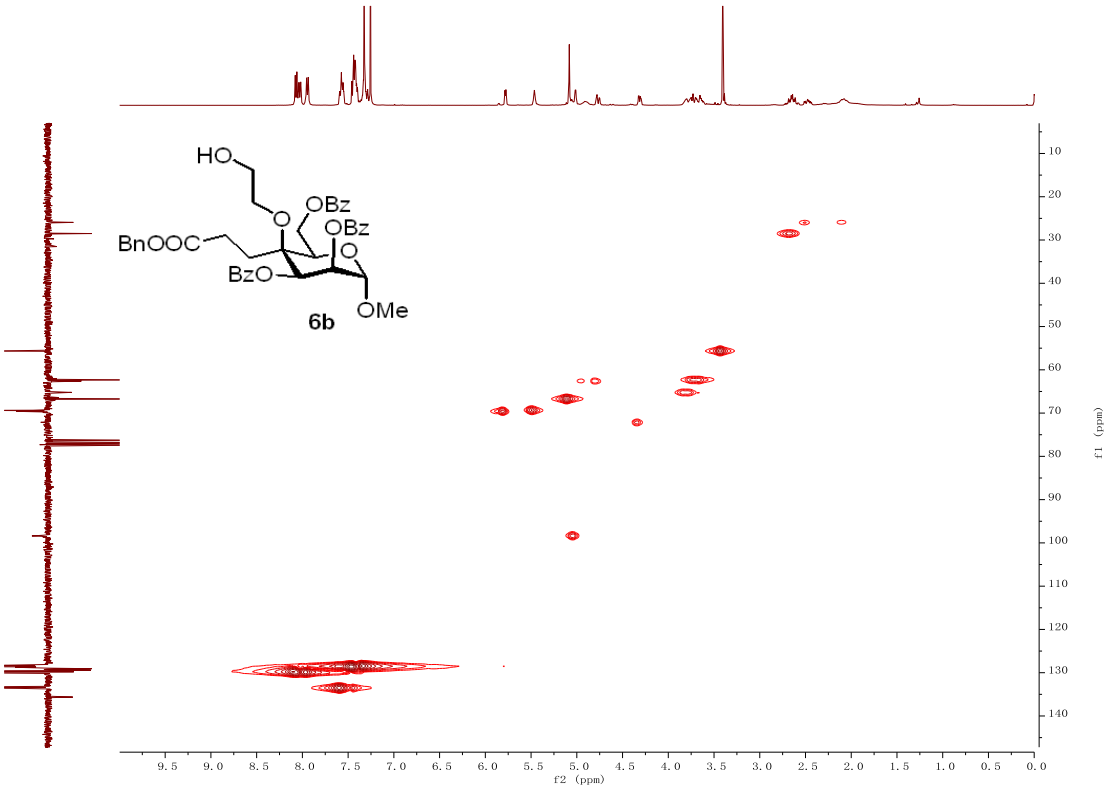


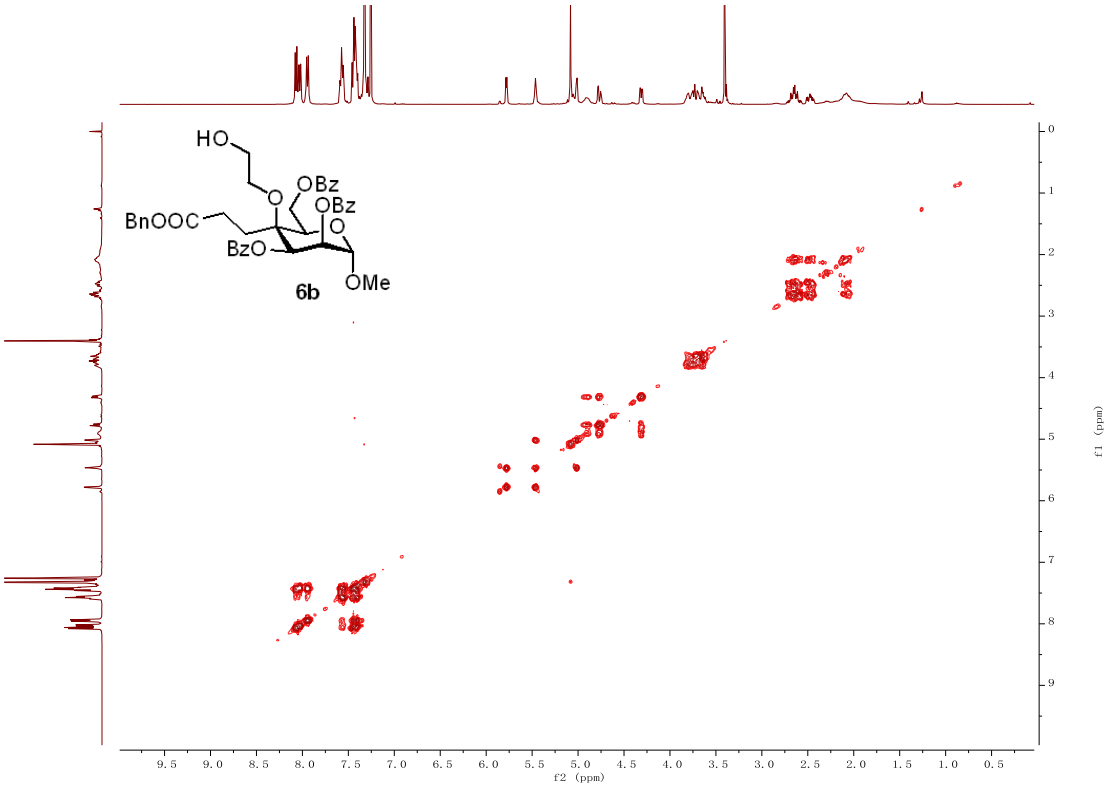
^{1}H NMR Spectra of compound 6b



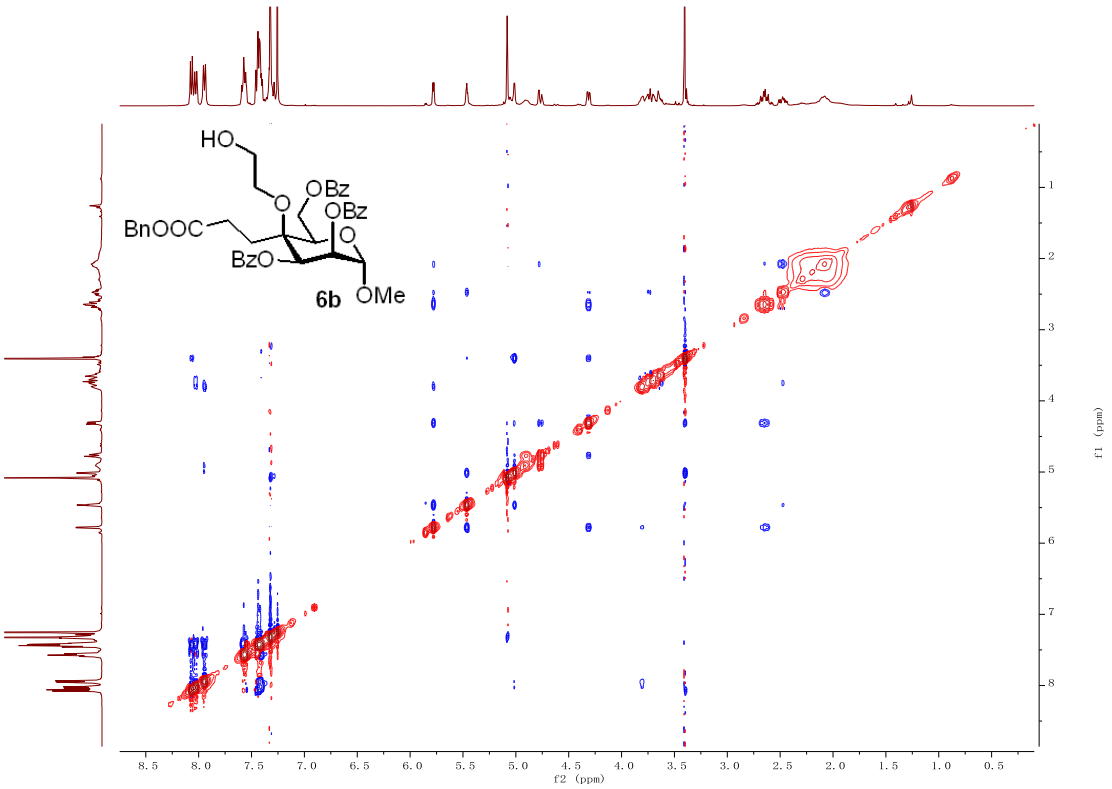
^{13}C NMR Spectra of compound 6b



HSQC Spectra of compound 6b



COSY Spectra of compound 6b



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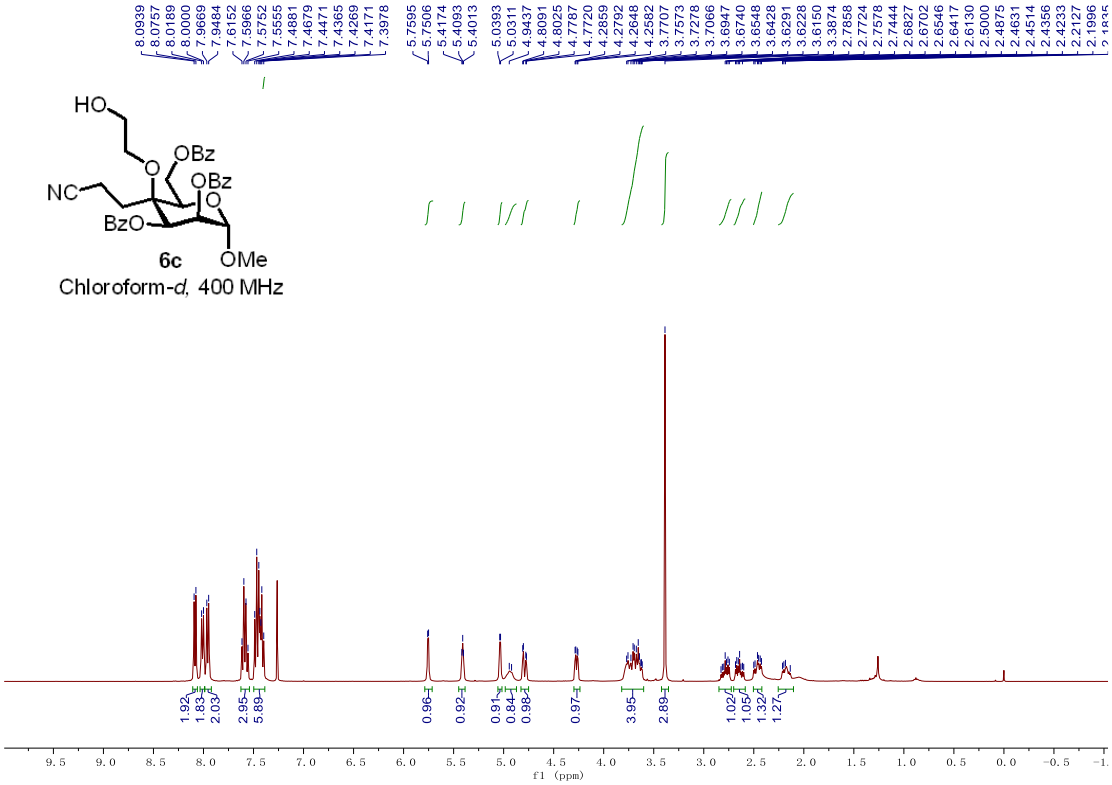
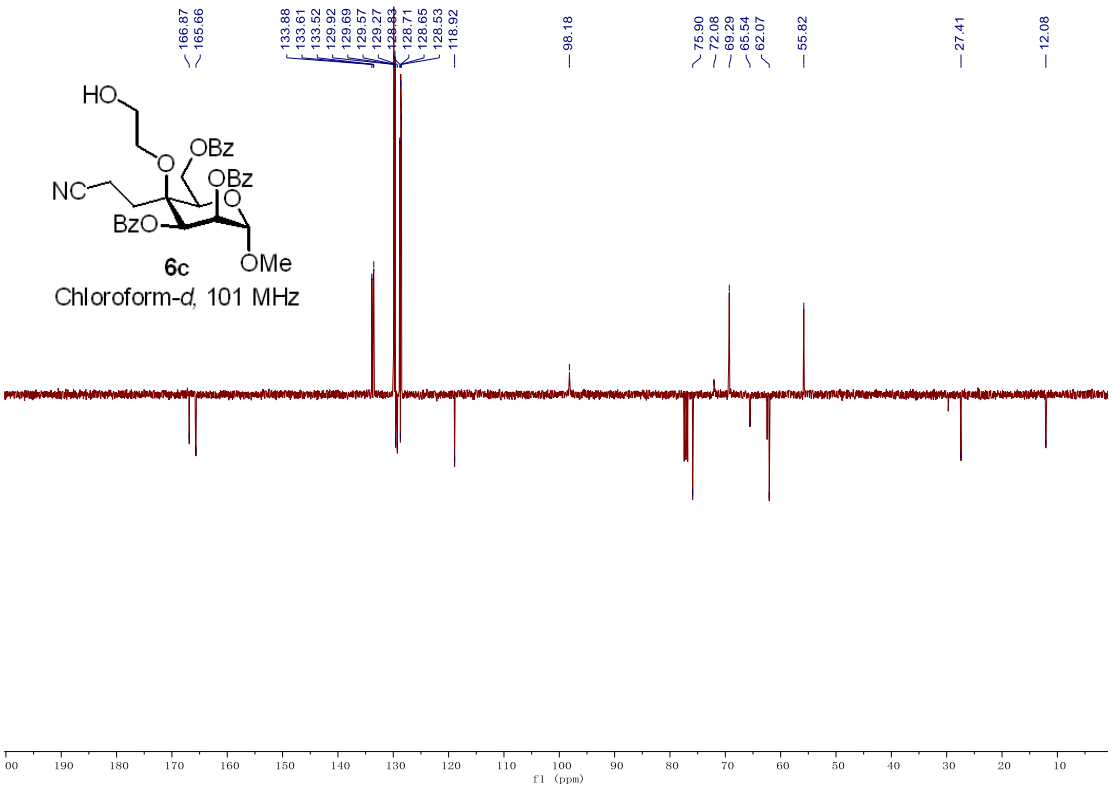


^{1}H NMR Spectra of compound 6c



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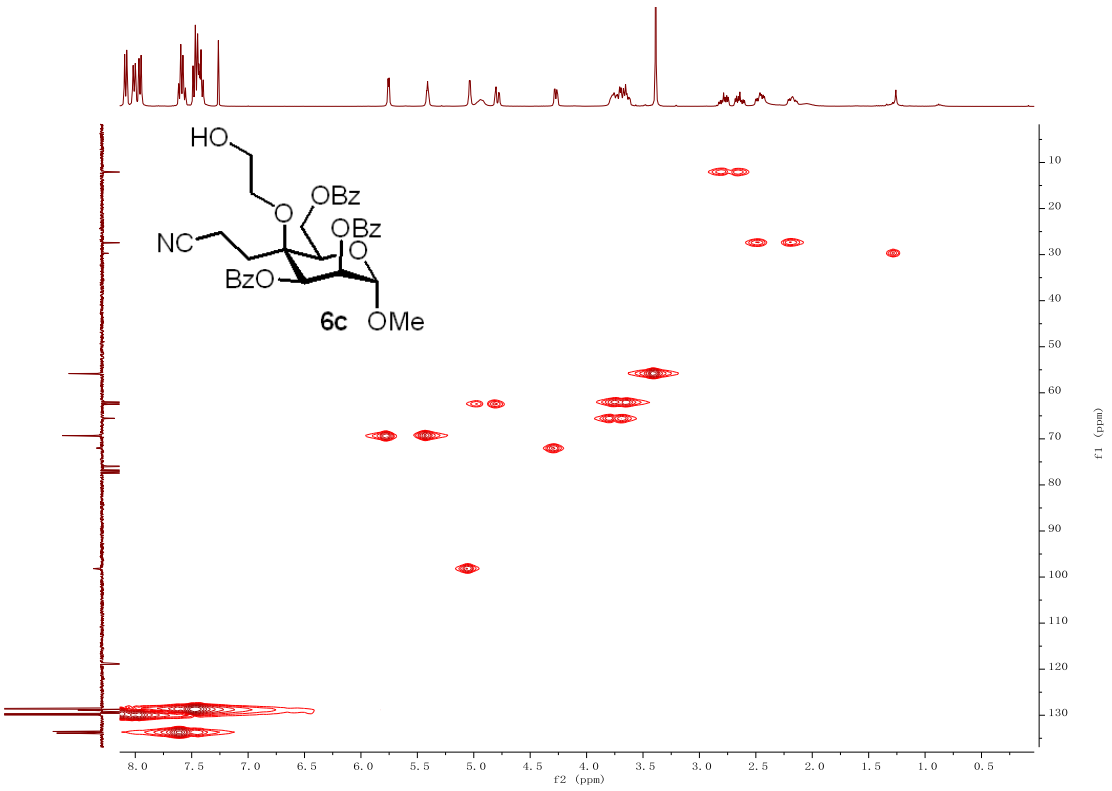
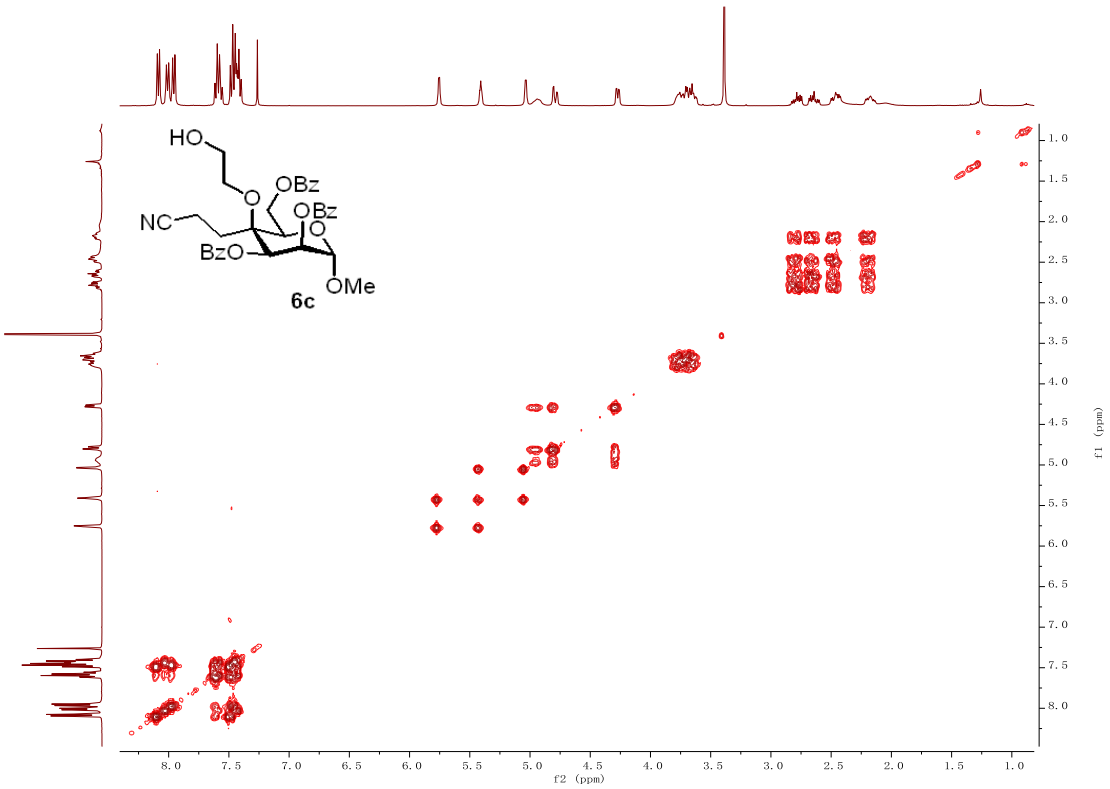


HSQC Spectra of compound 6c



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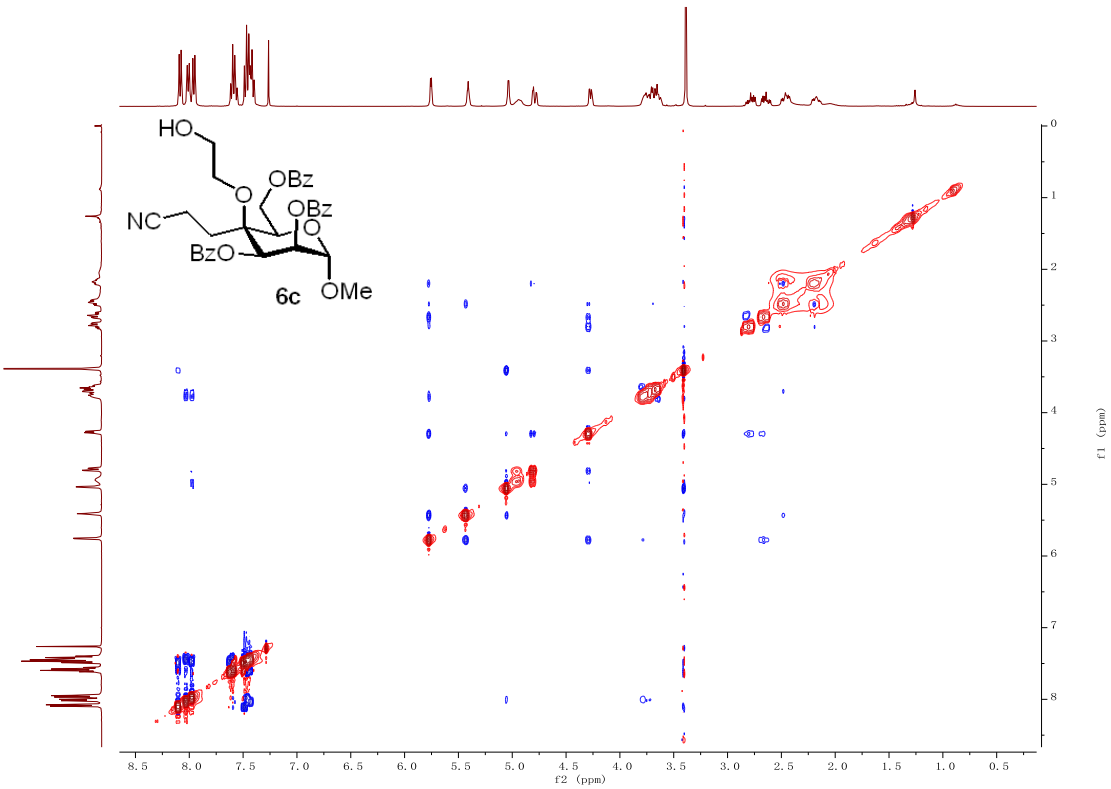
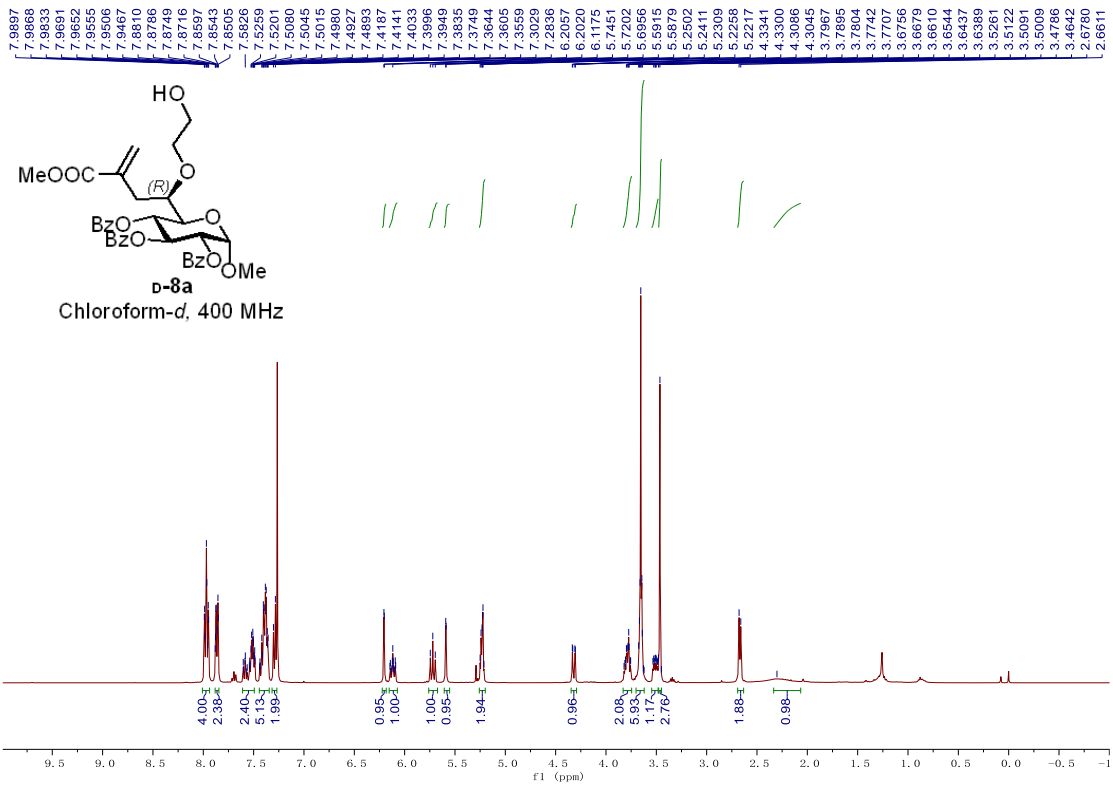
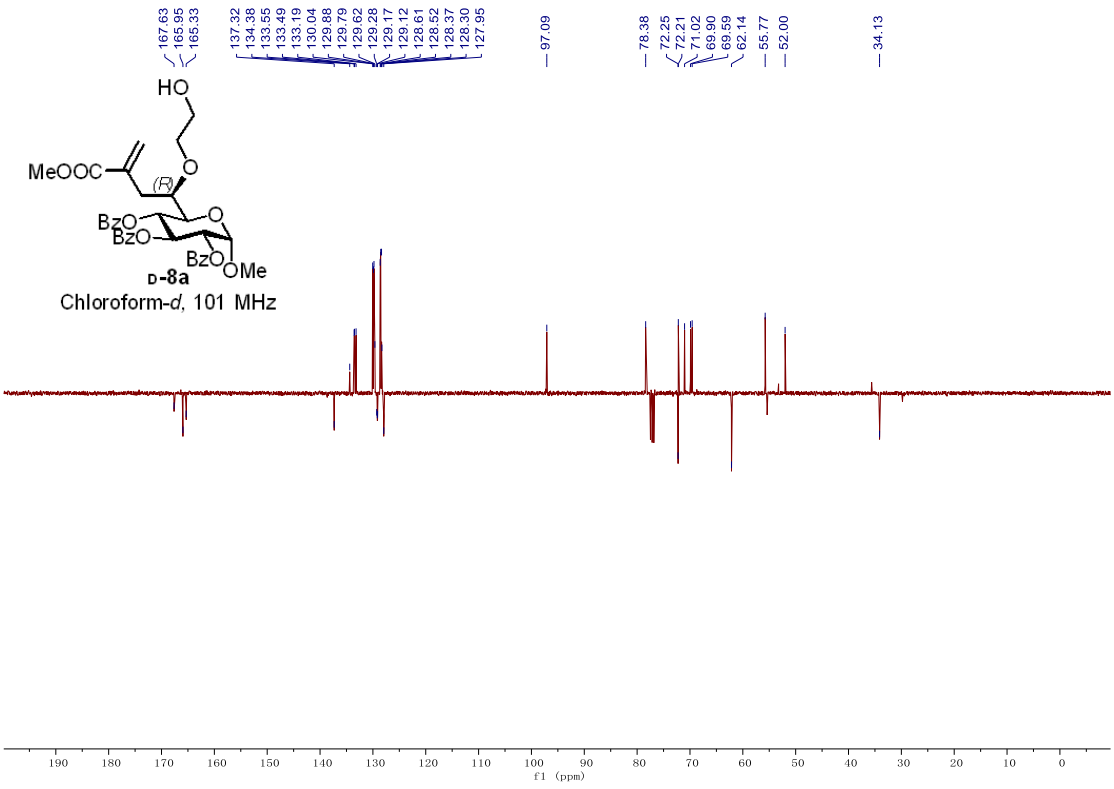


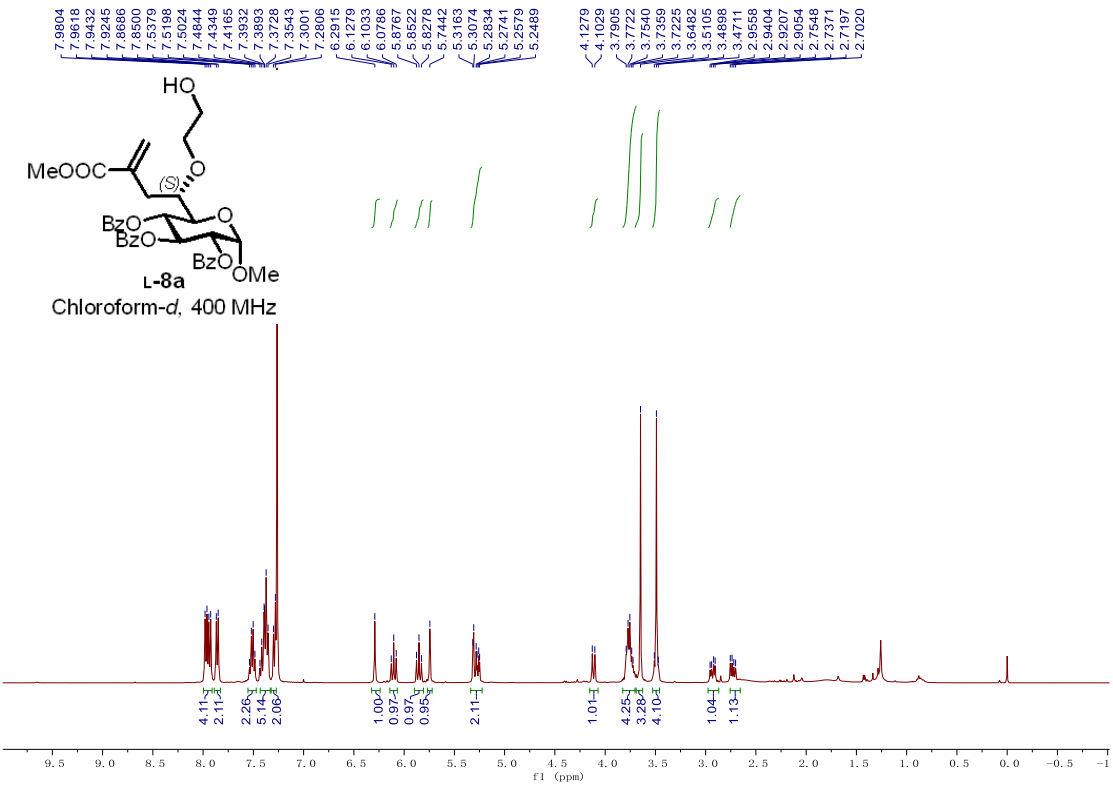
NOESY Spectra of compound 6c



^{1}H NMR Spectra of compound D-8a



^{13}C NMR Spectra of compound D-8a



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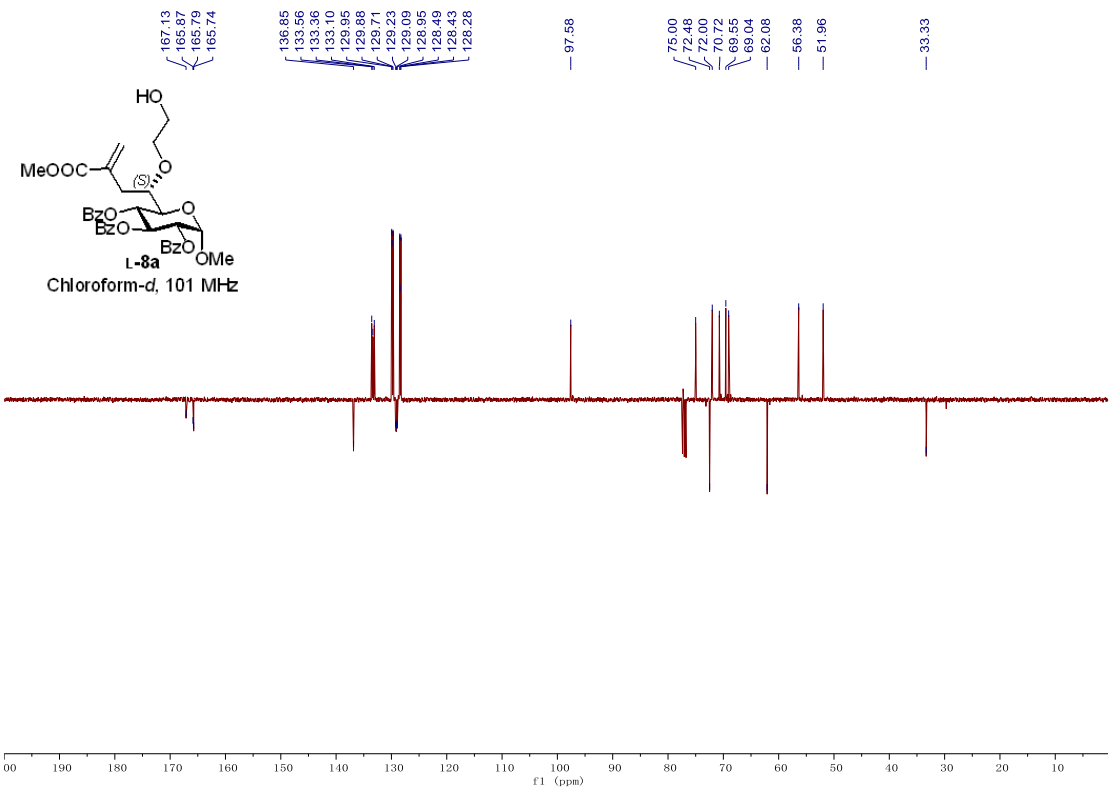
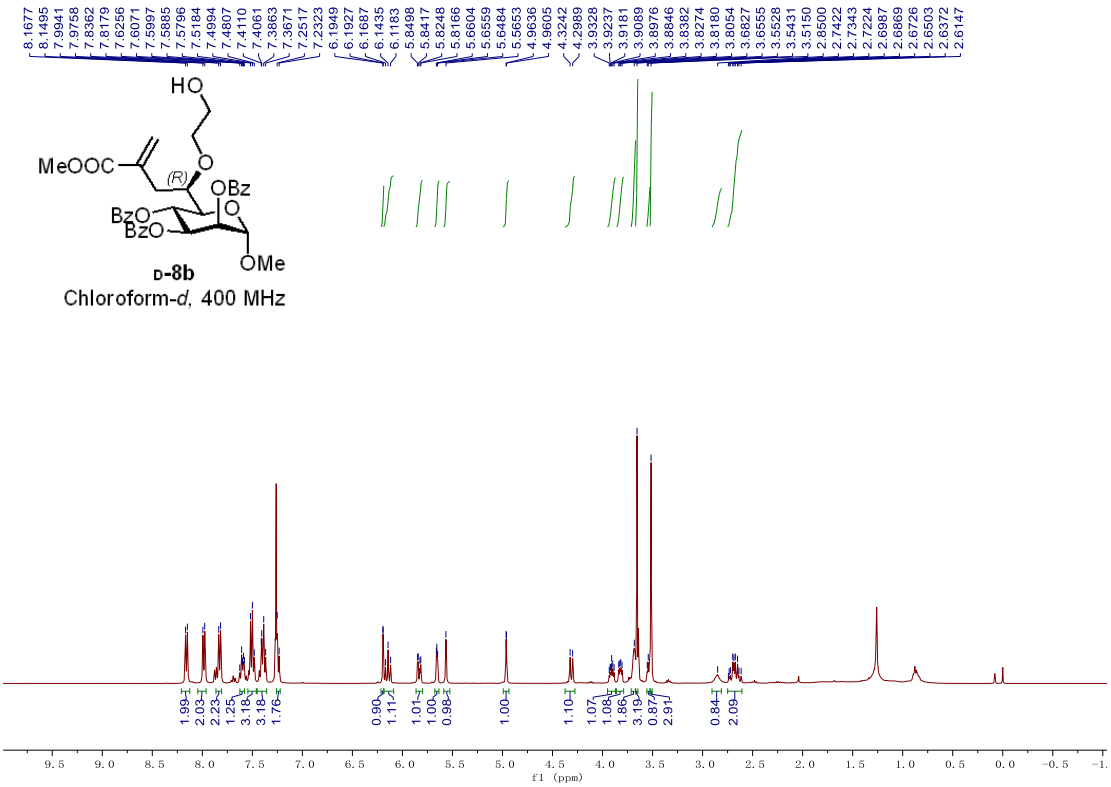


^{13}C NMR Spectra of compound L-8a



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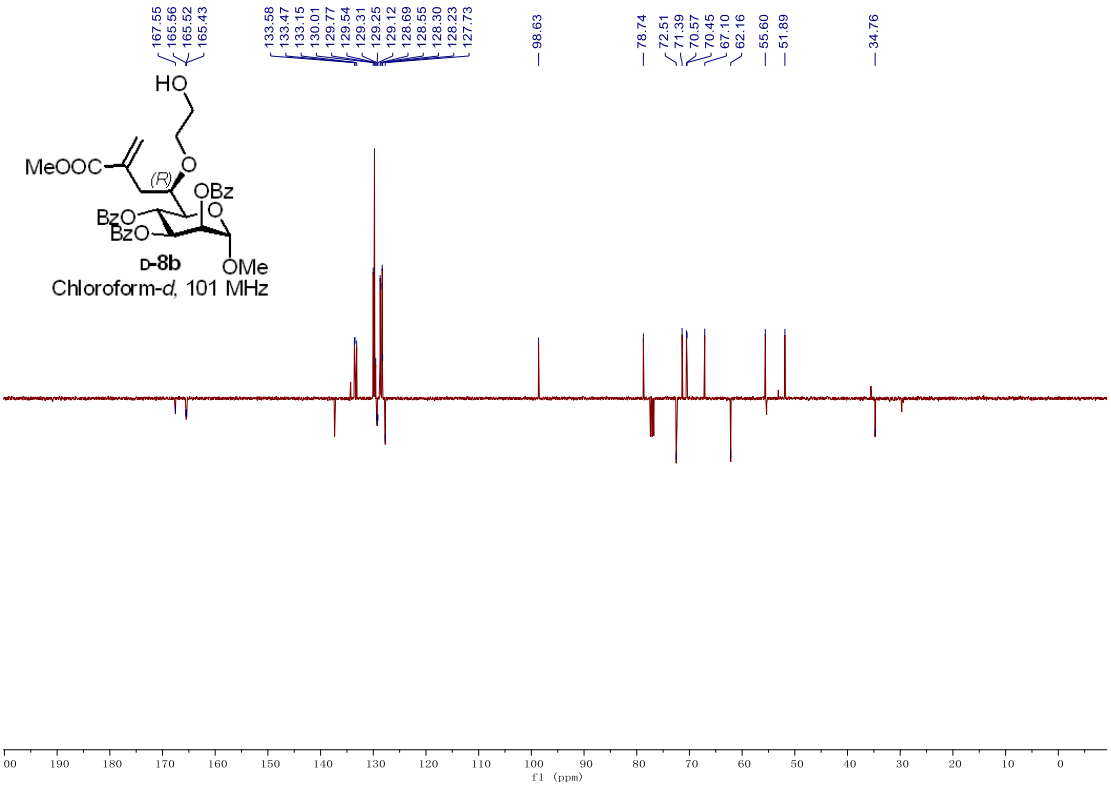
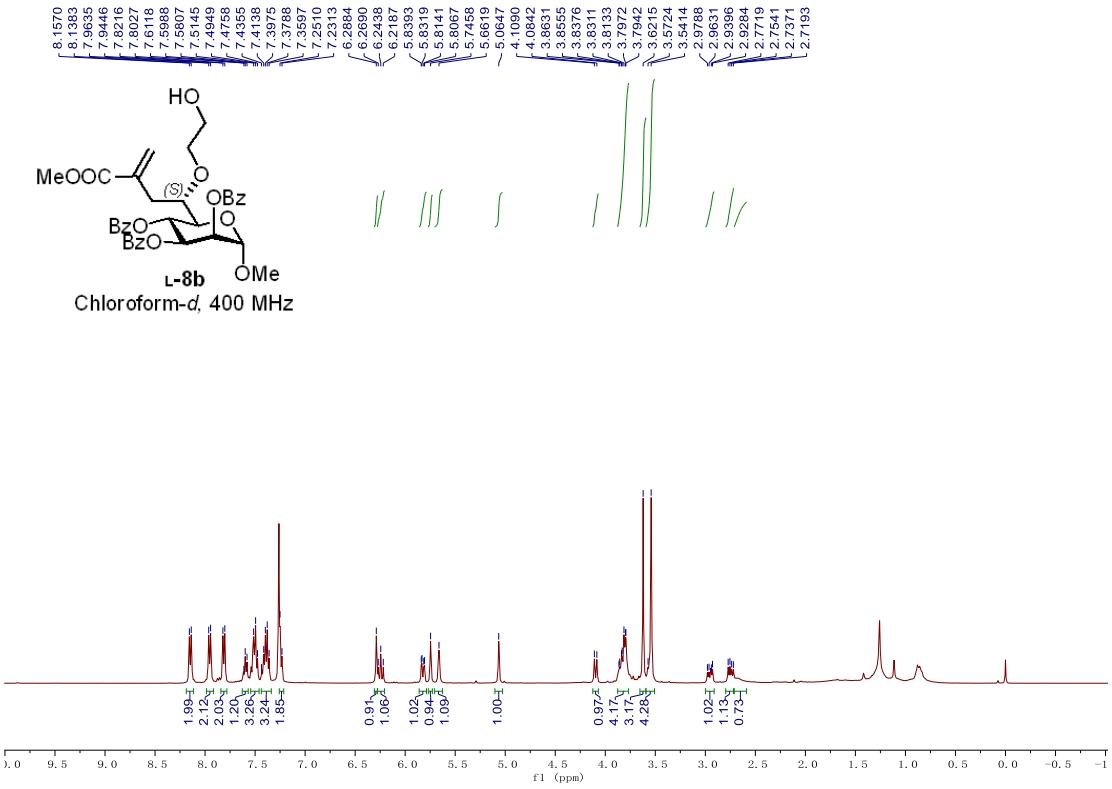
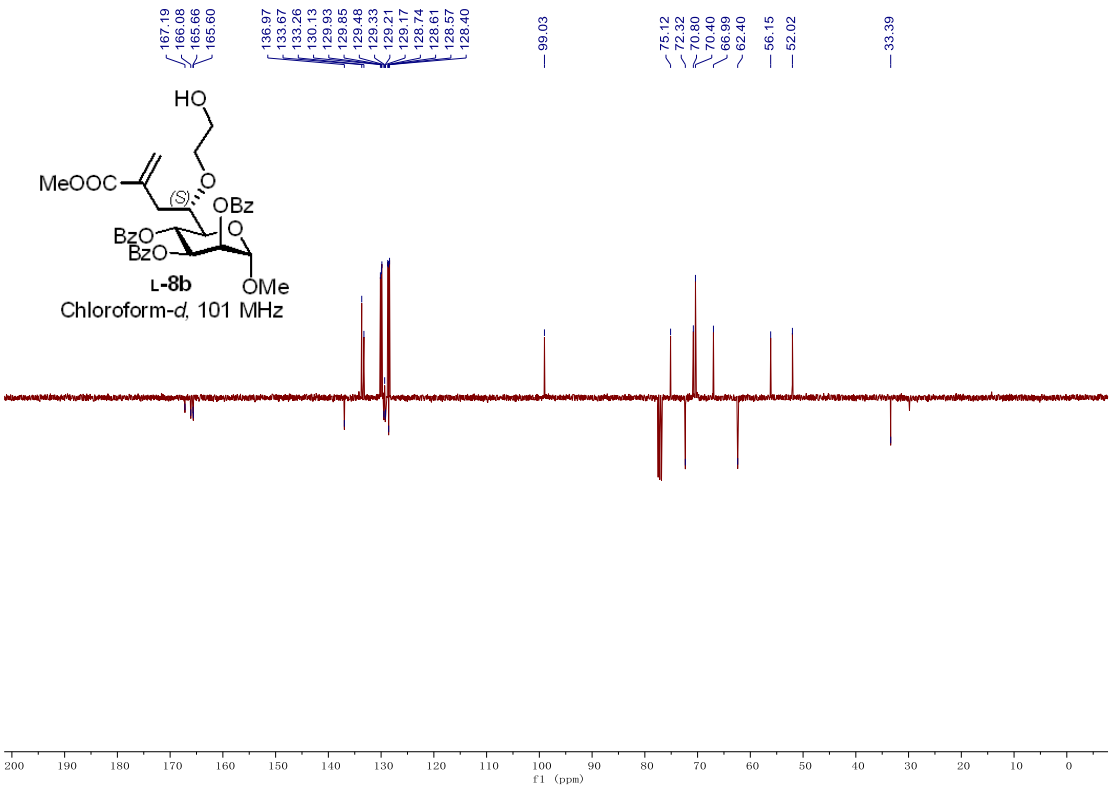


^{13}C NMR Spectra of compound D-8b



^{1}H NMR Spectra of compound L-8b



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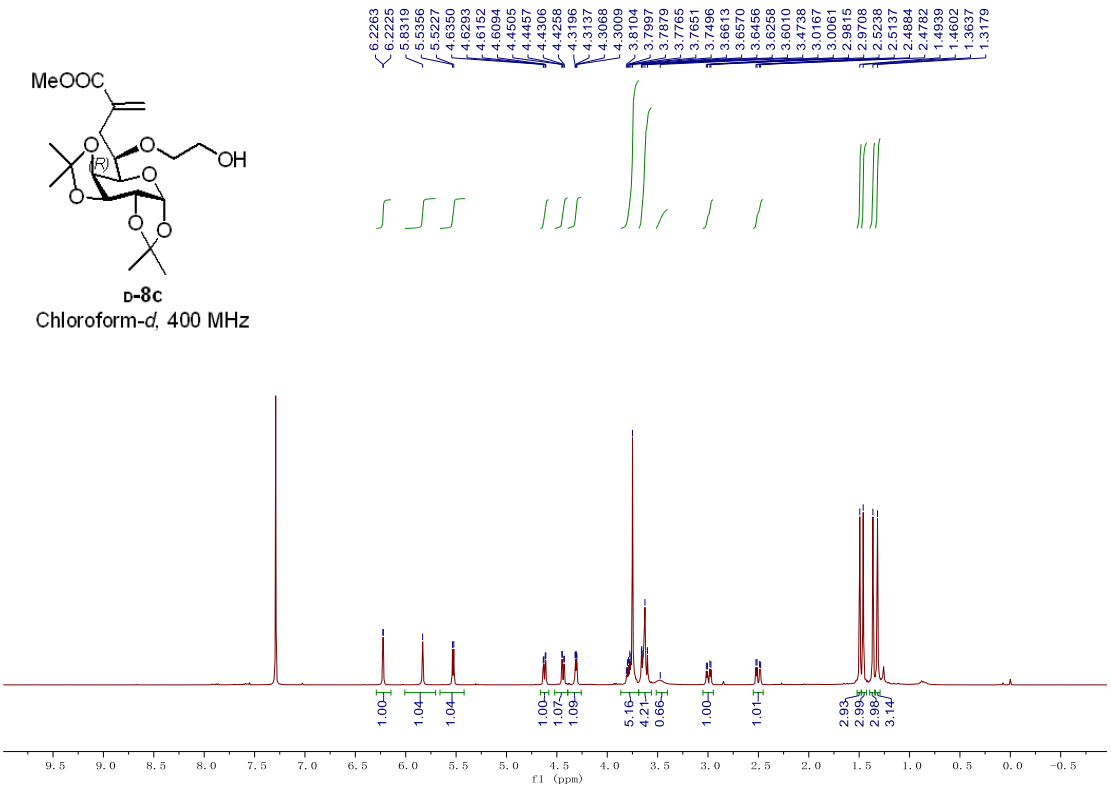
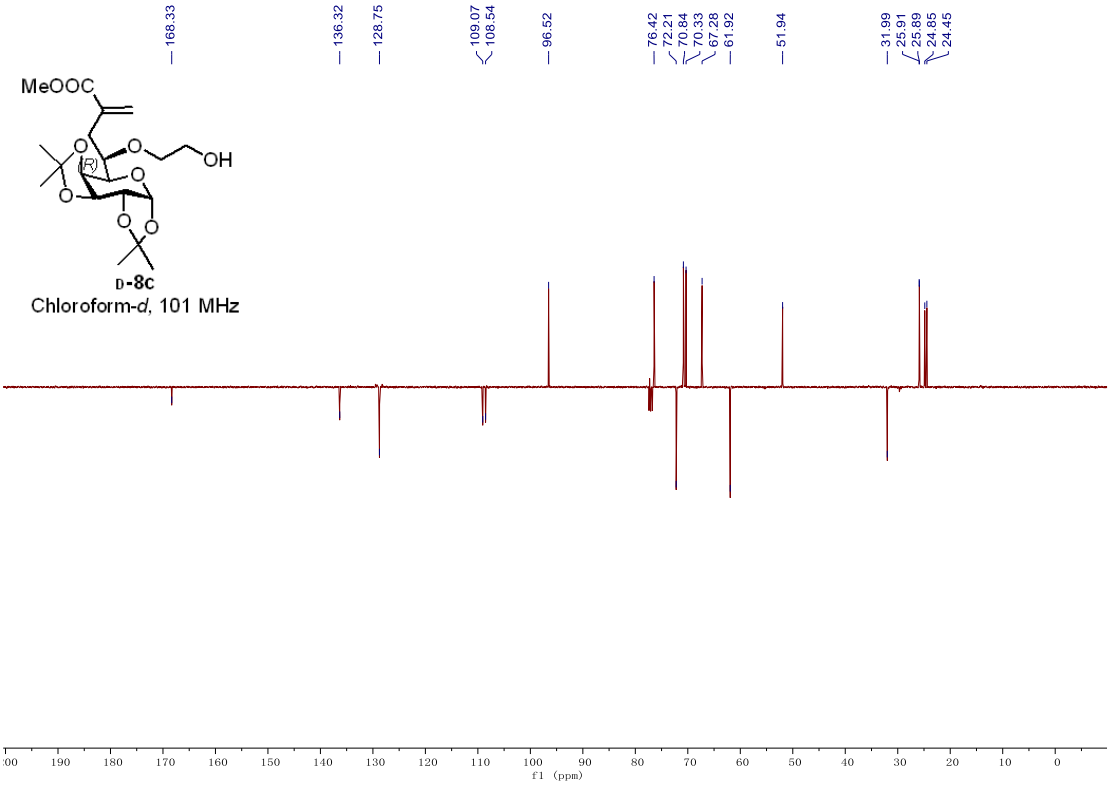
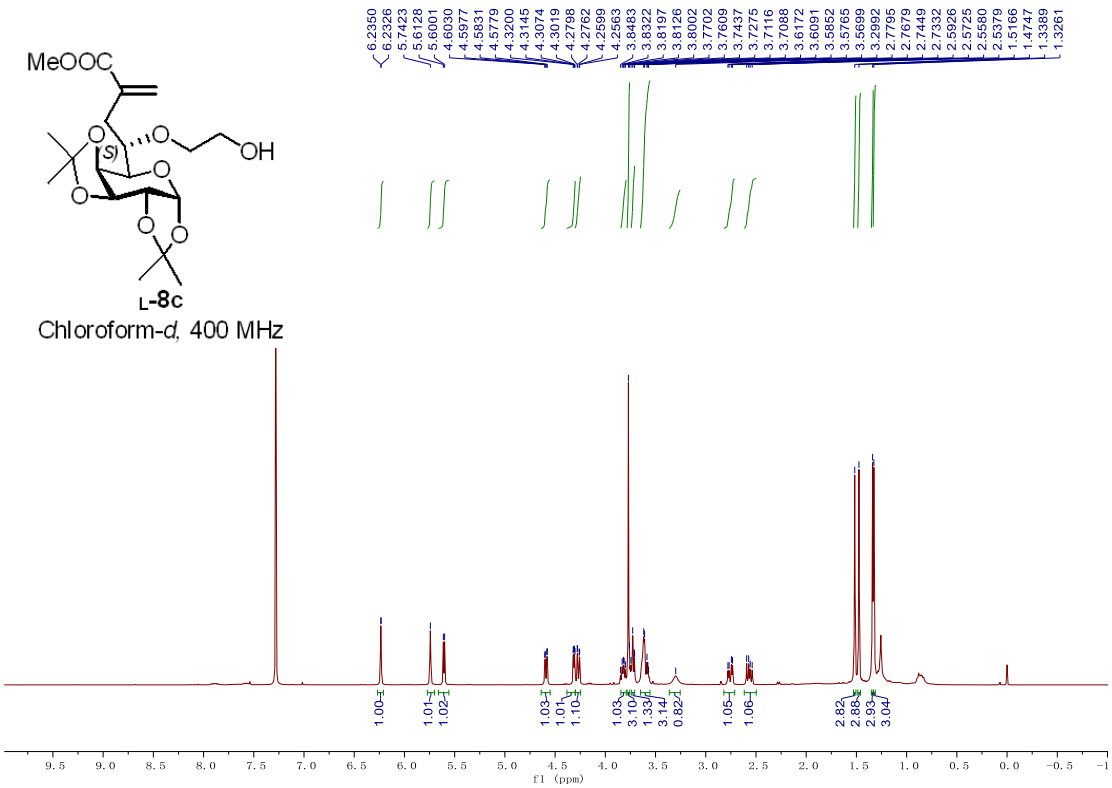


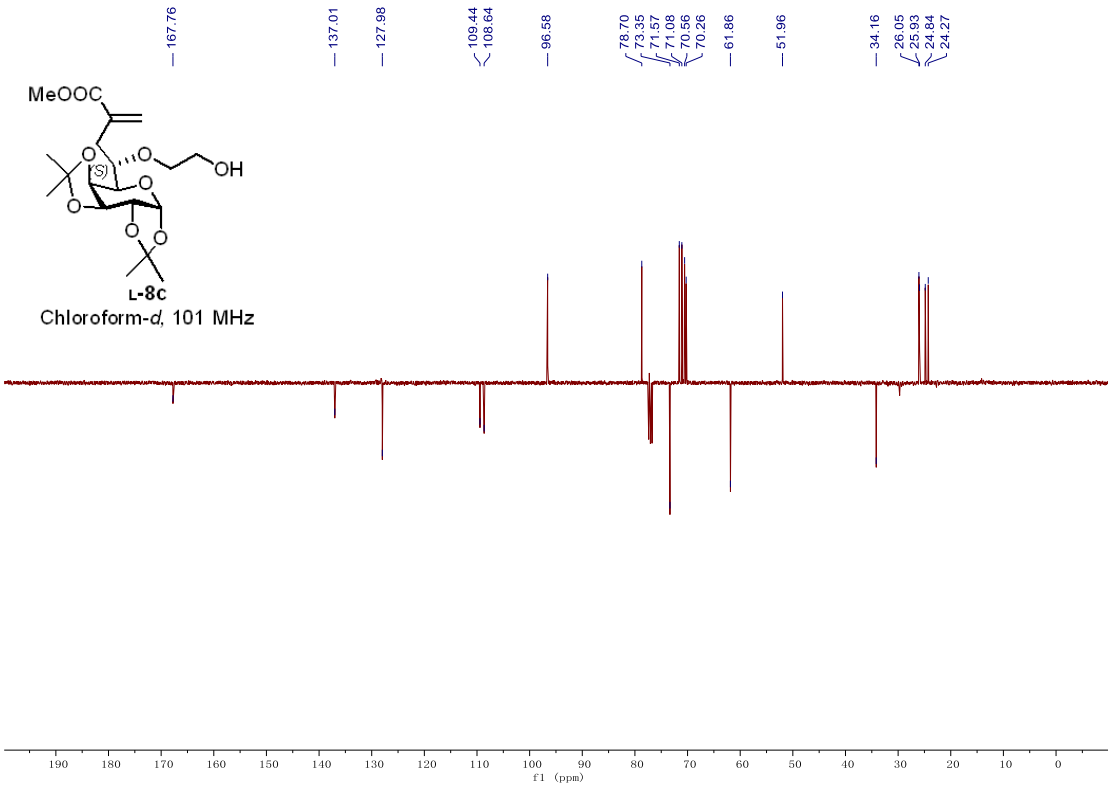
^{1}H NMR Spectra of compound D-8c



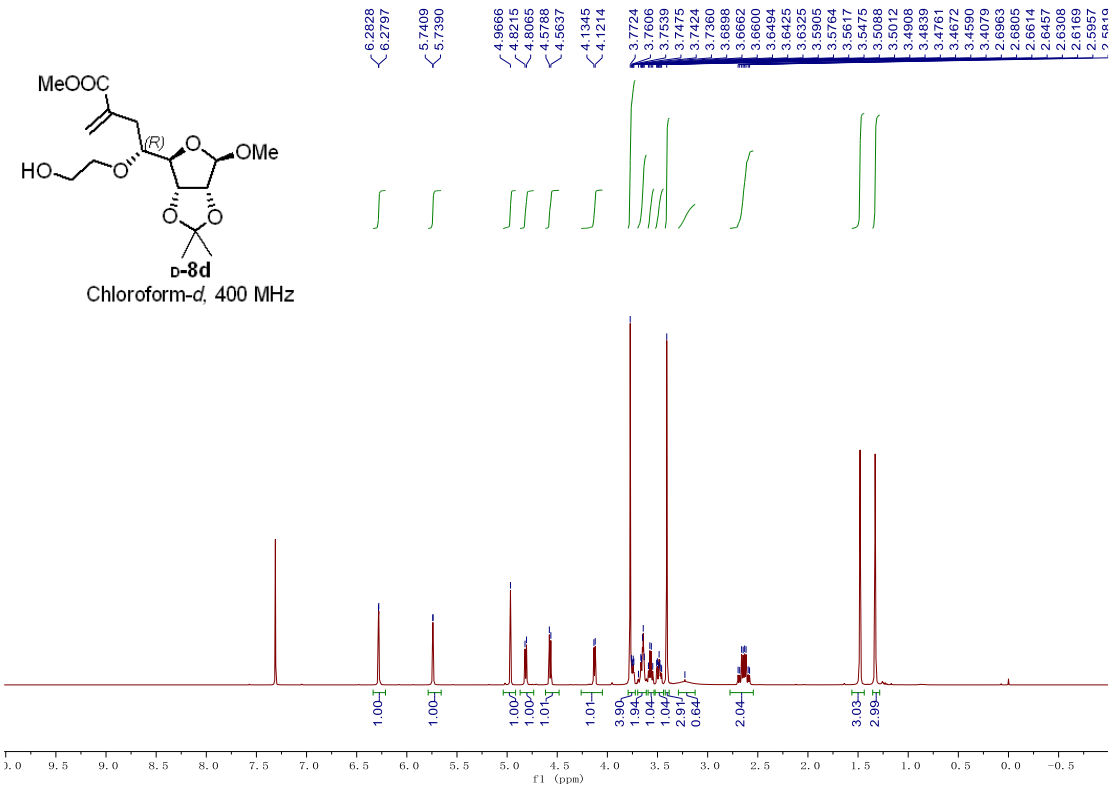
^{13}C NMR Spectra of compound D-8c



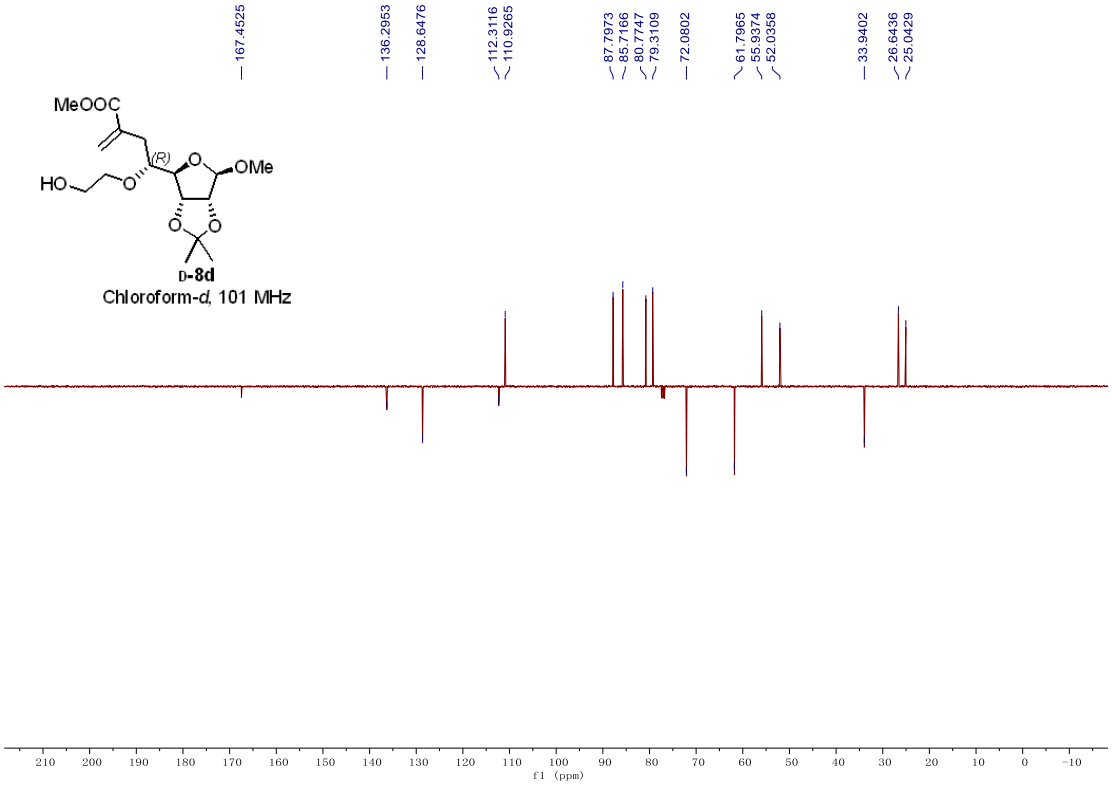
^{1}H NMR Spectra of compound L-8c



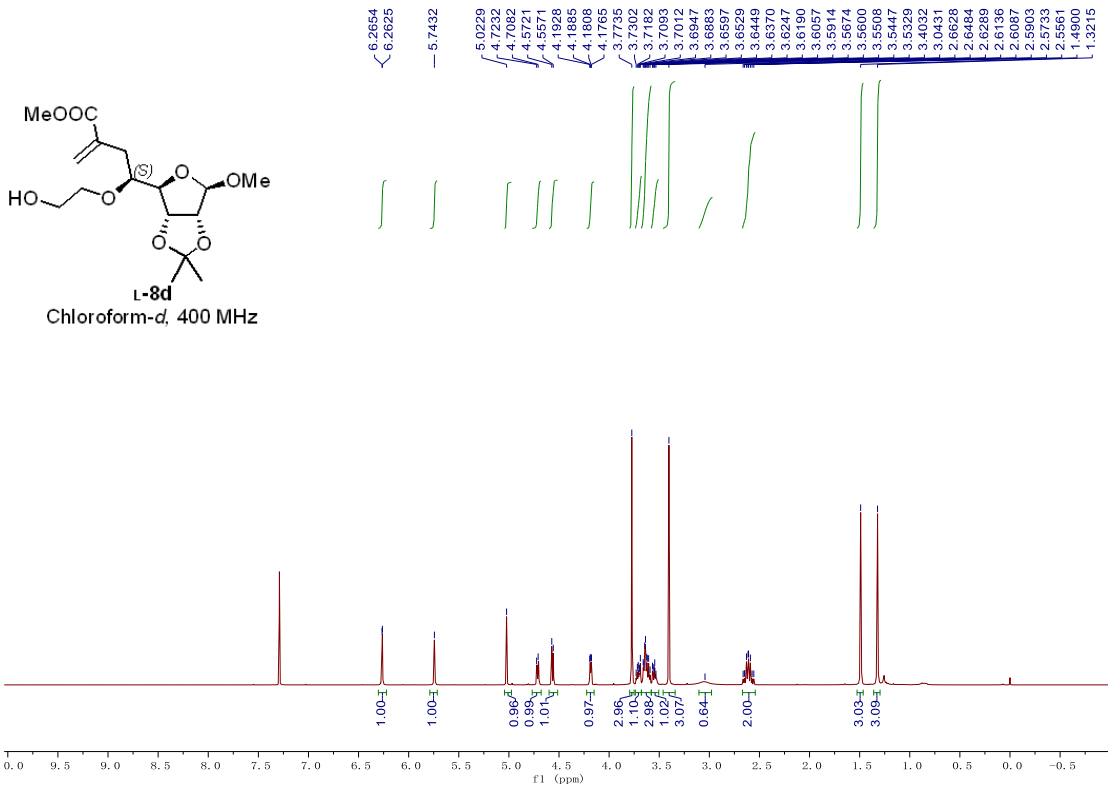
^{13}C NMR Spectra of compound L-8c



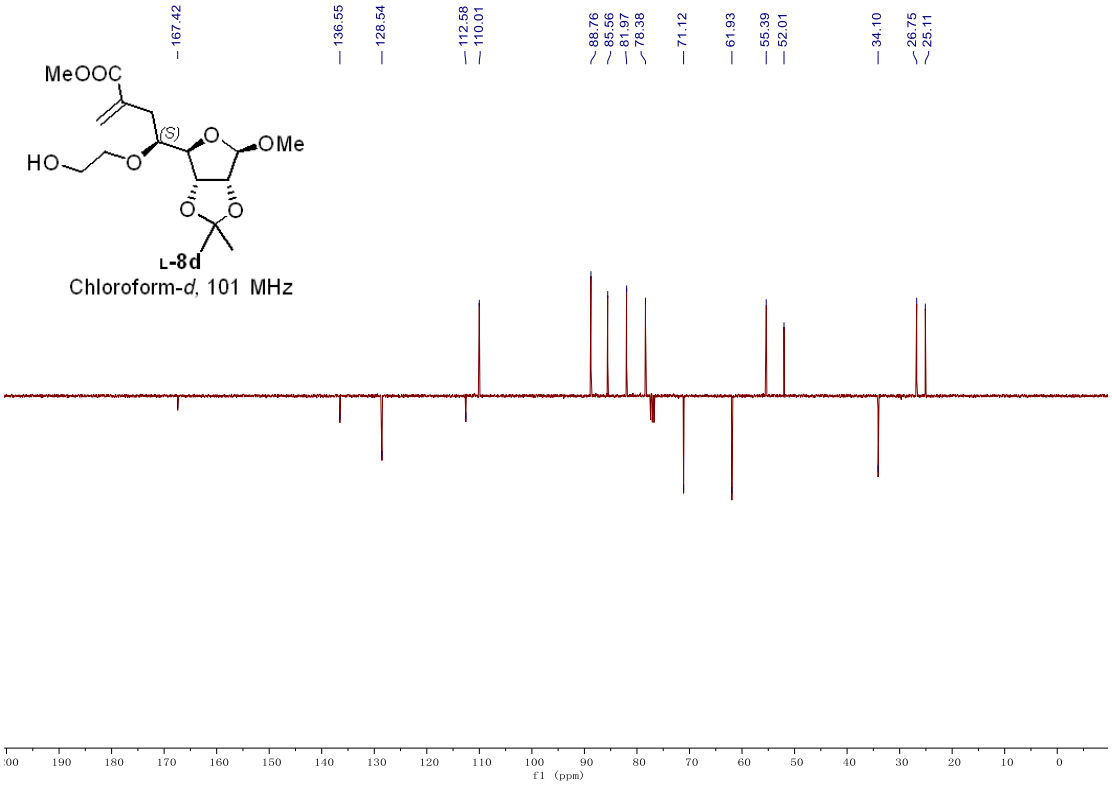
^{1}H NMR Spectra of compound D-8d



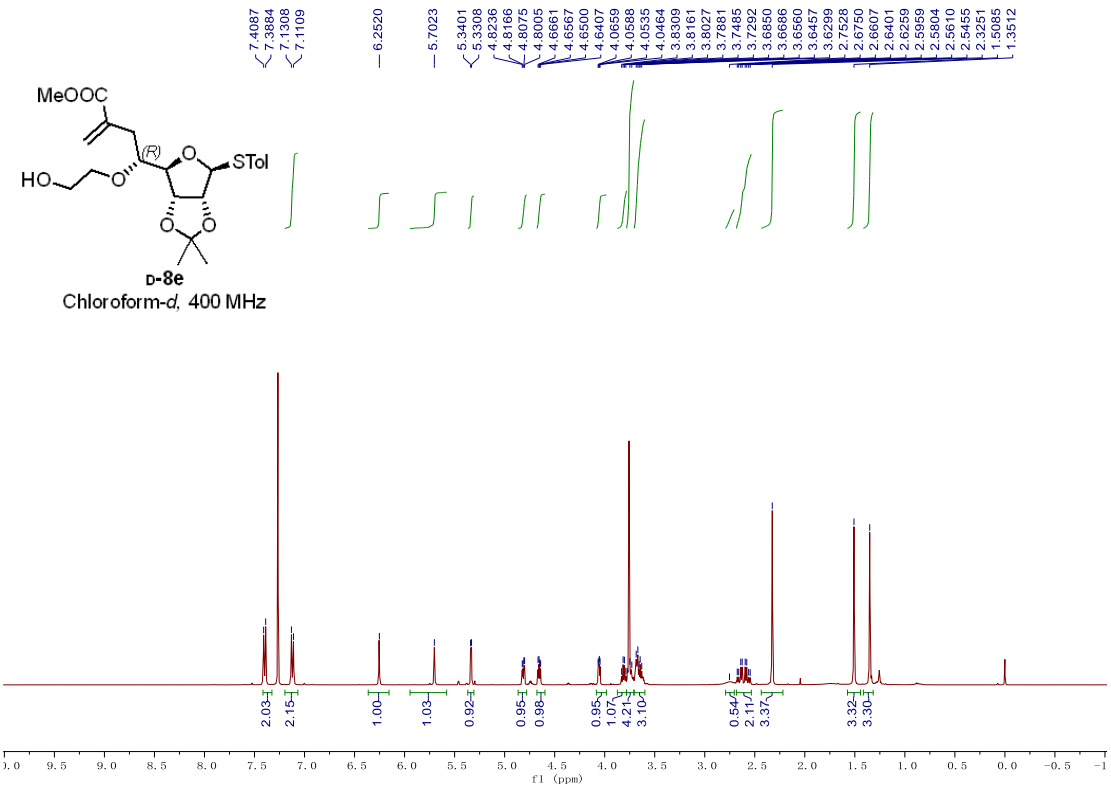
^{13}C NMR Spectra of compound D-8d



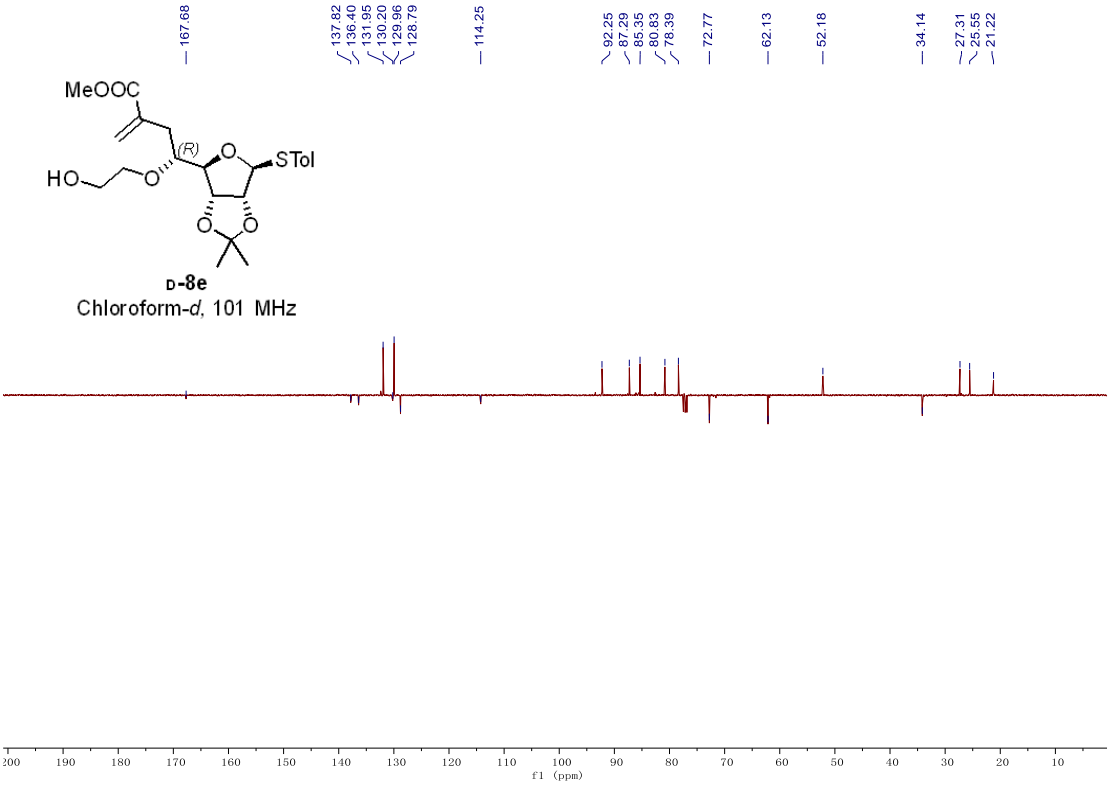
^{1}H NMR Spectra of compound L-8d



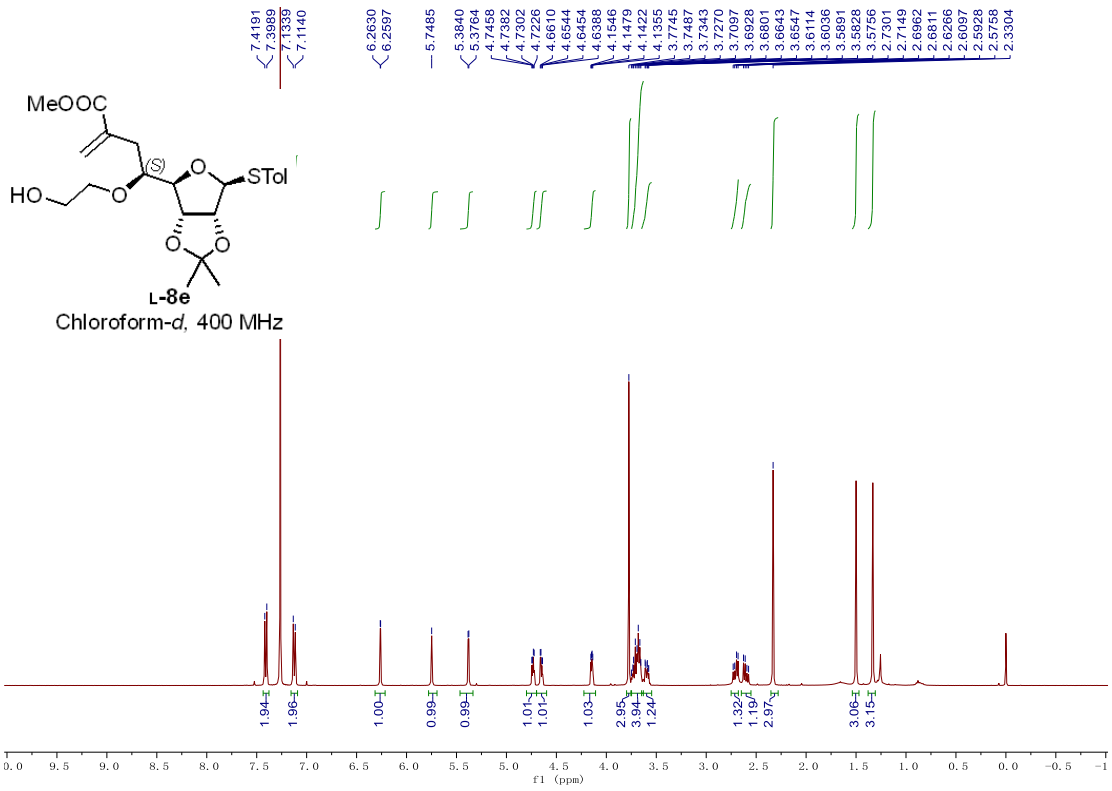
^{13}C NMR Spectra of compound L-8d



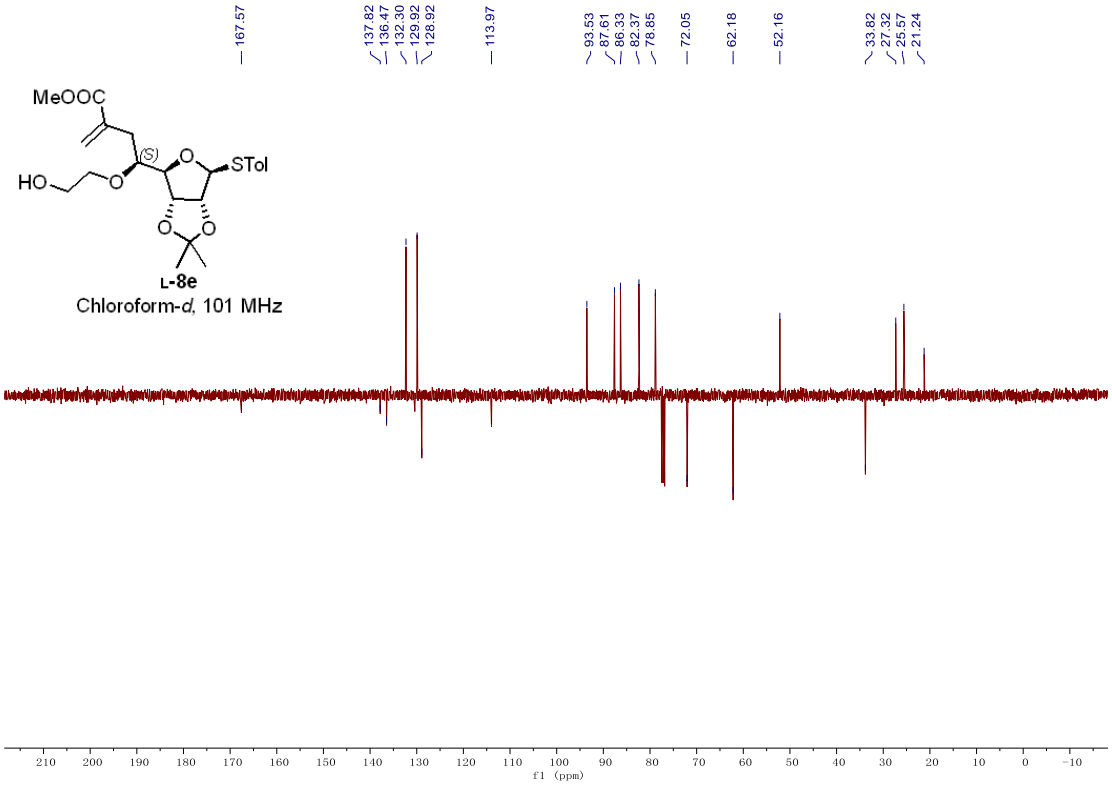
^{1}H NMR Spectra of compound D-8e



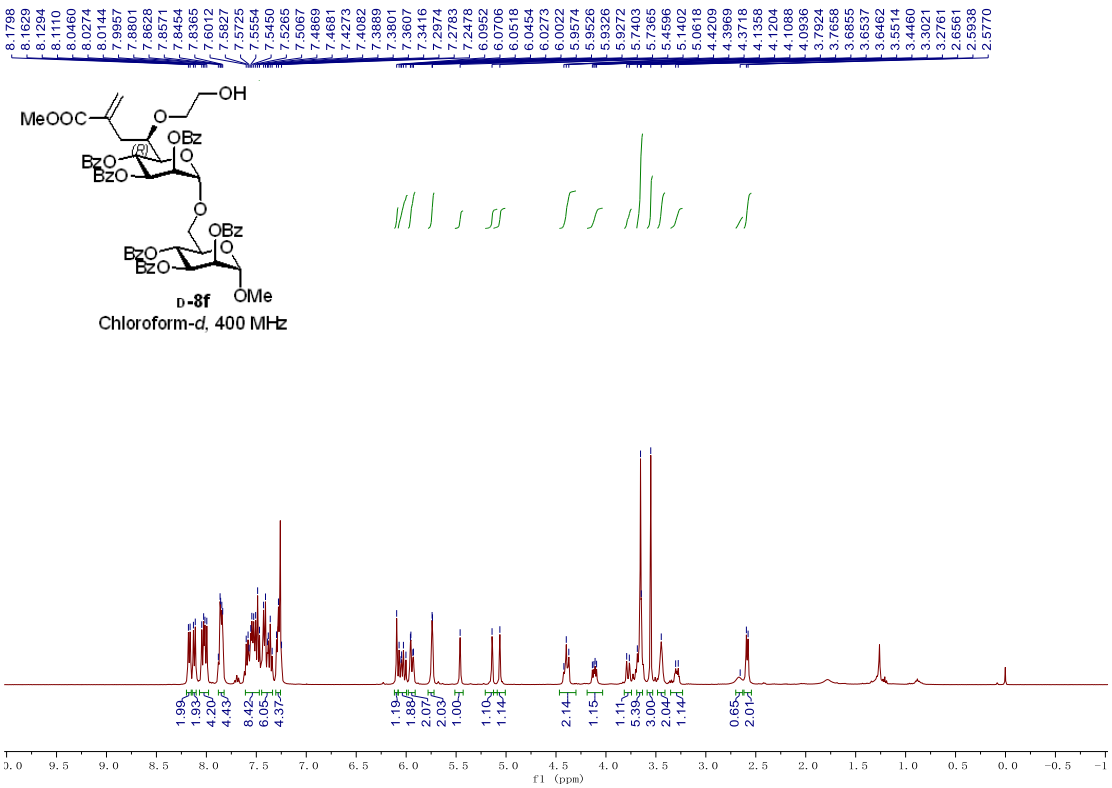
^{13}C NMR Spectra of compound D-8e



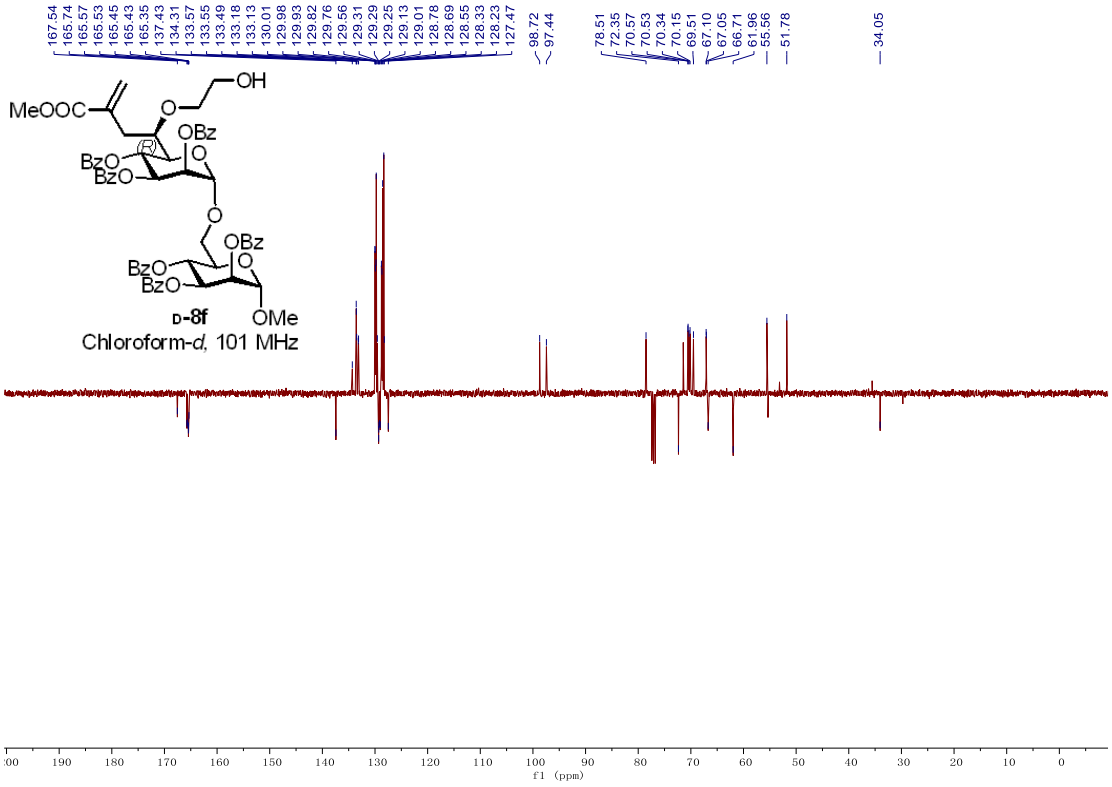
^{1}H NMR Spectra of compound L-8e



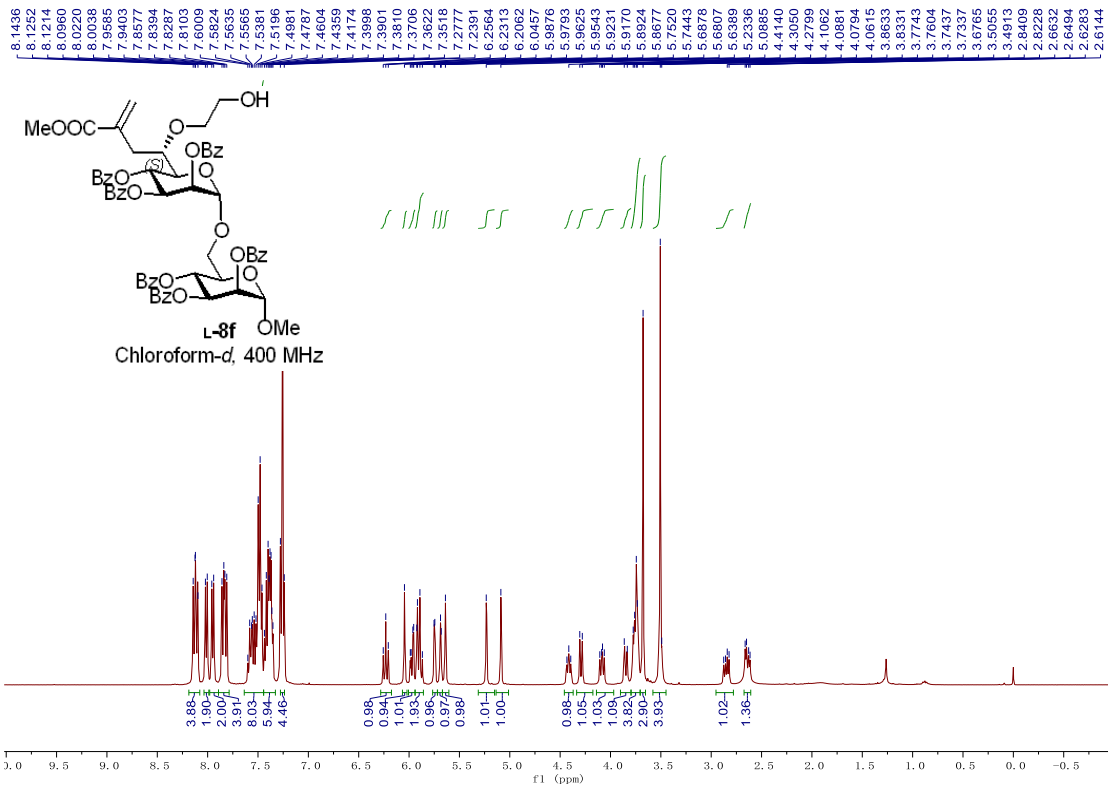
^{13}C NMR Spectra of compound L-8e



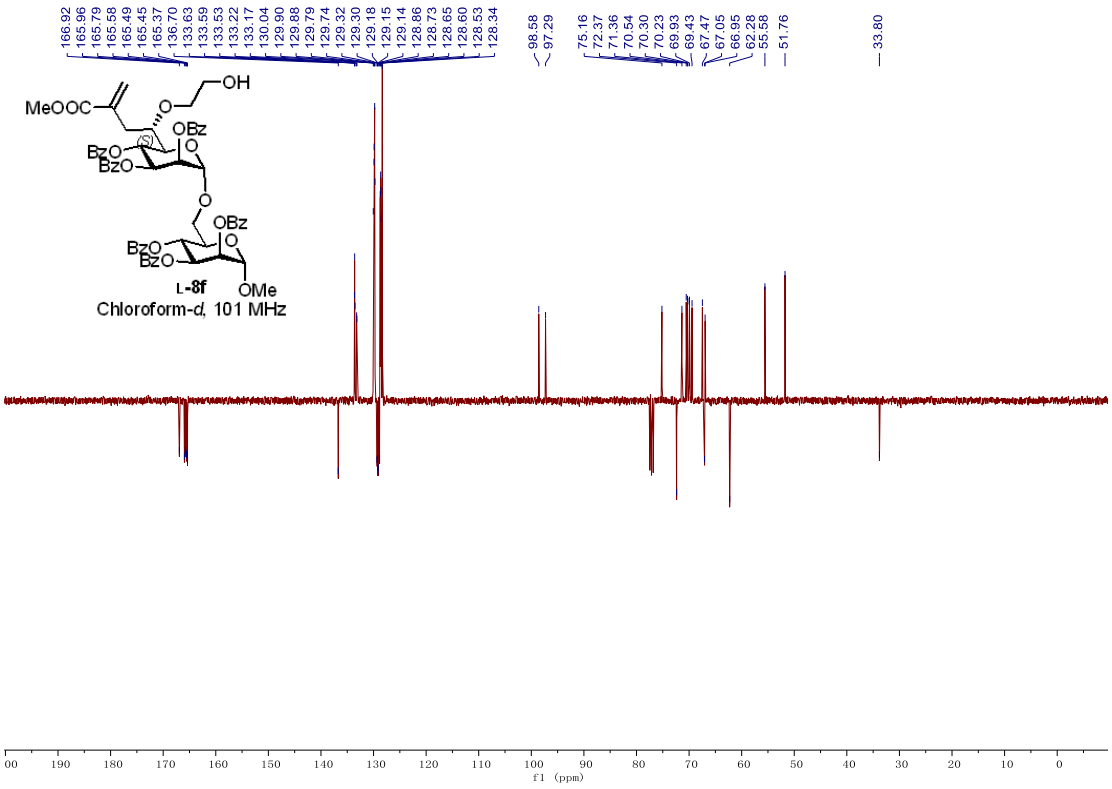
^{1}H NMR Spectra of compound D-8f



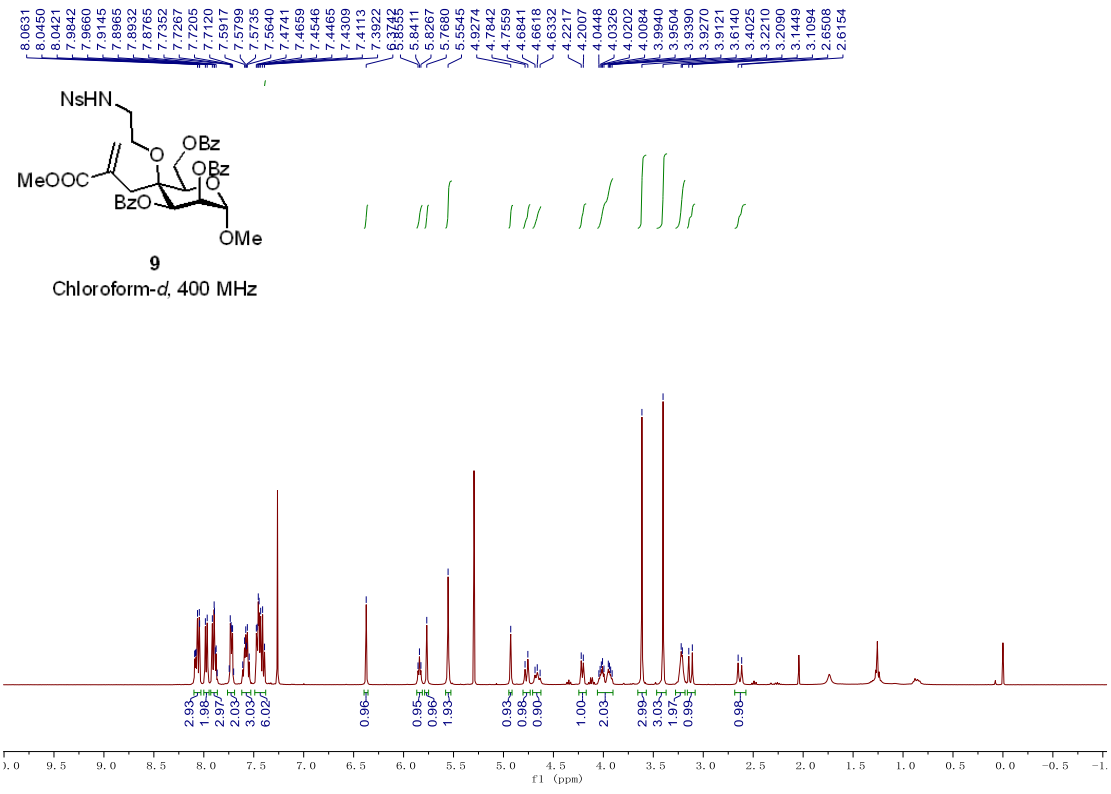
^{13}C NMR Spectra of compound D-8f



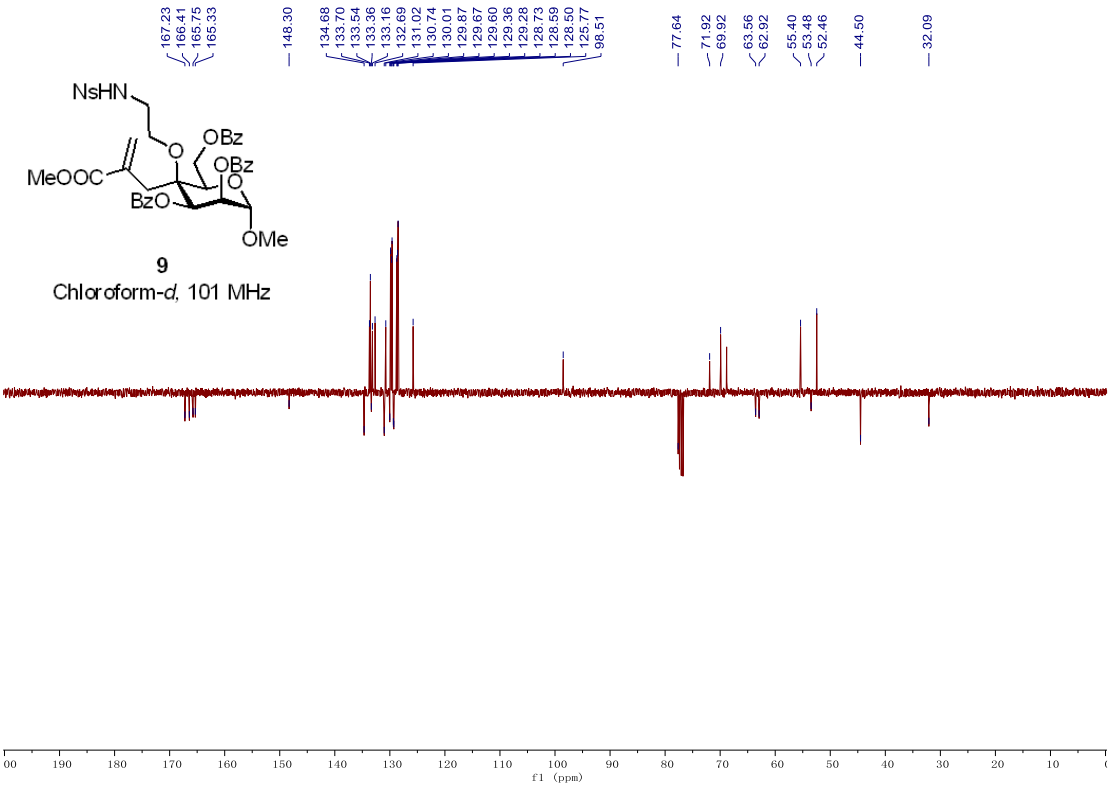
^{1}H NMR Spectra of compound L-8f



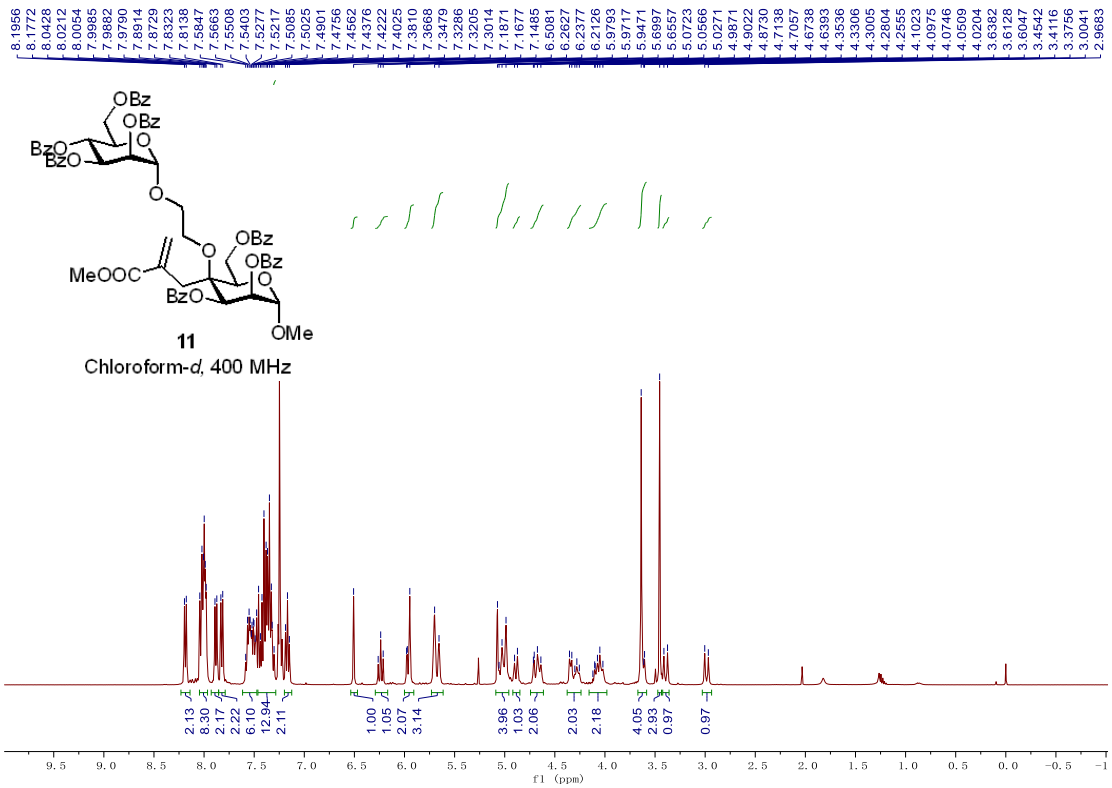
^{13}C NMR Spectra of compound L-8f



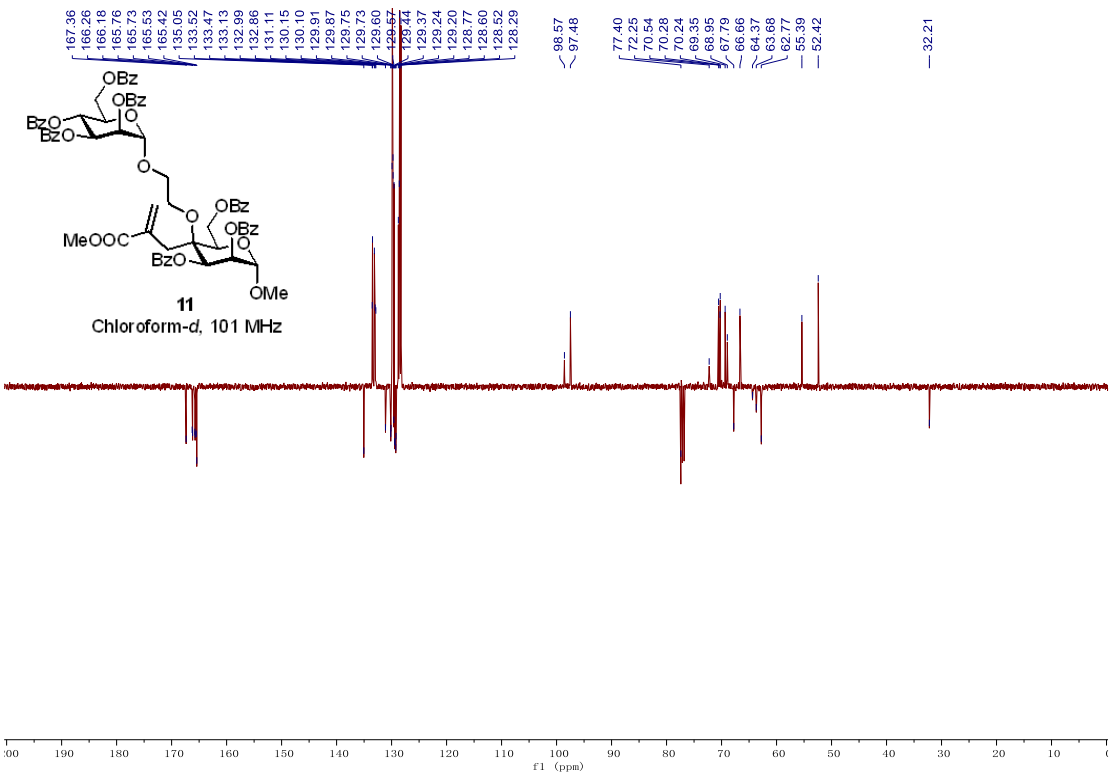
^{1}H NMR Spectra of compound 9



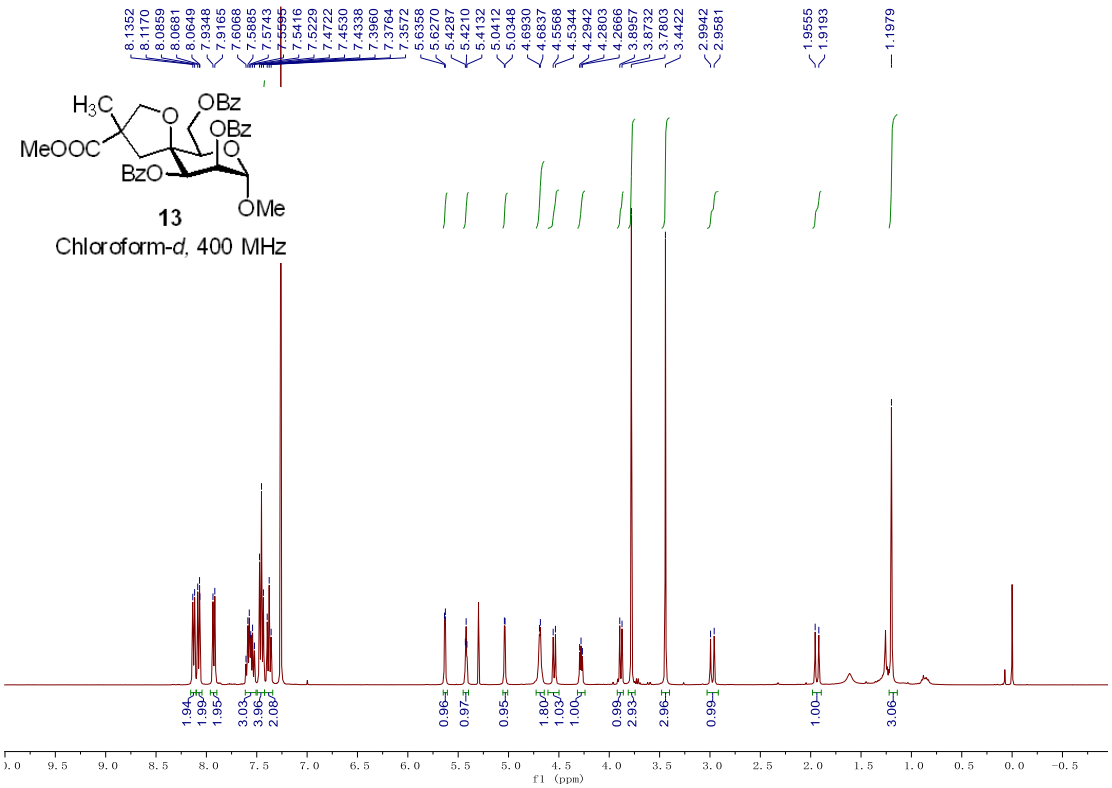
^{13}C NMR Spectra of compound 9



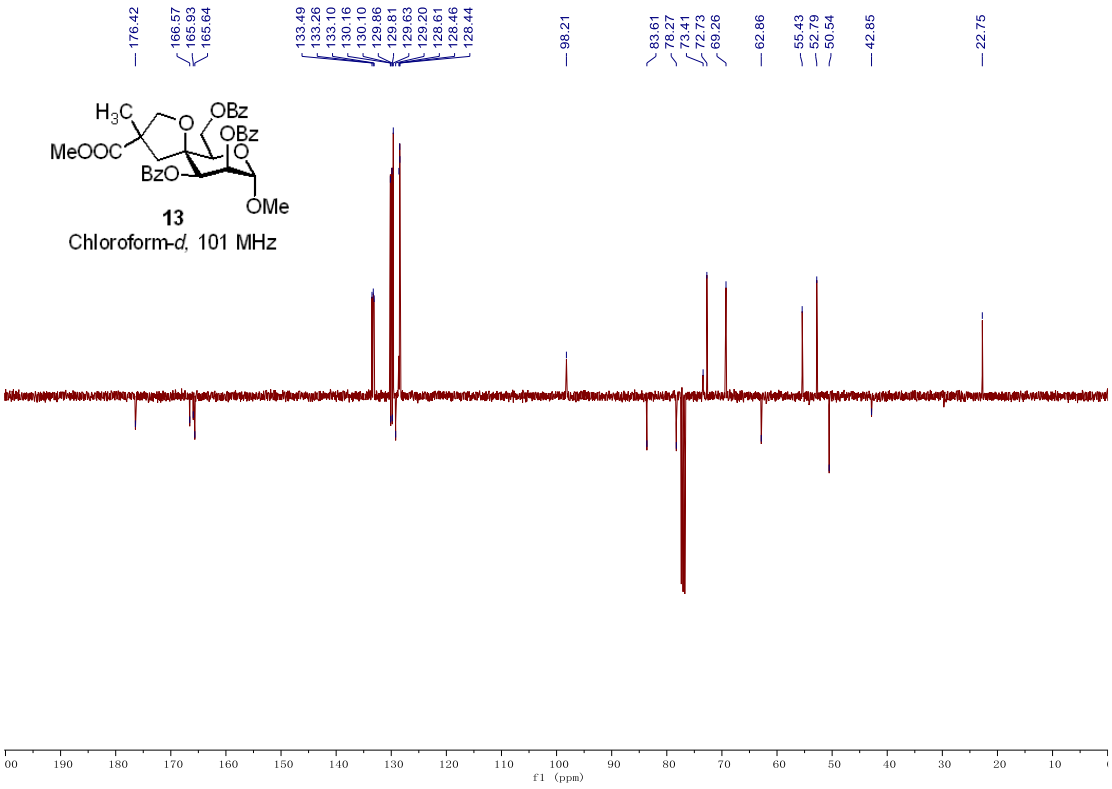
^{1}H NMR Spectra of compound 11



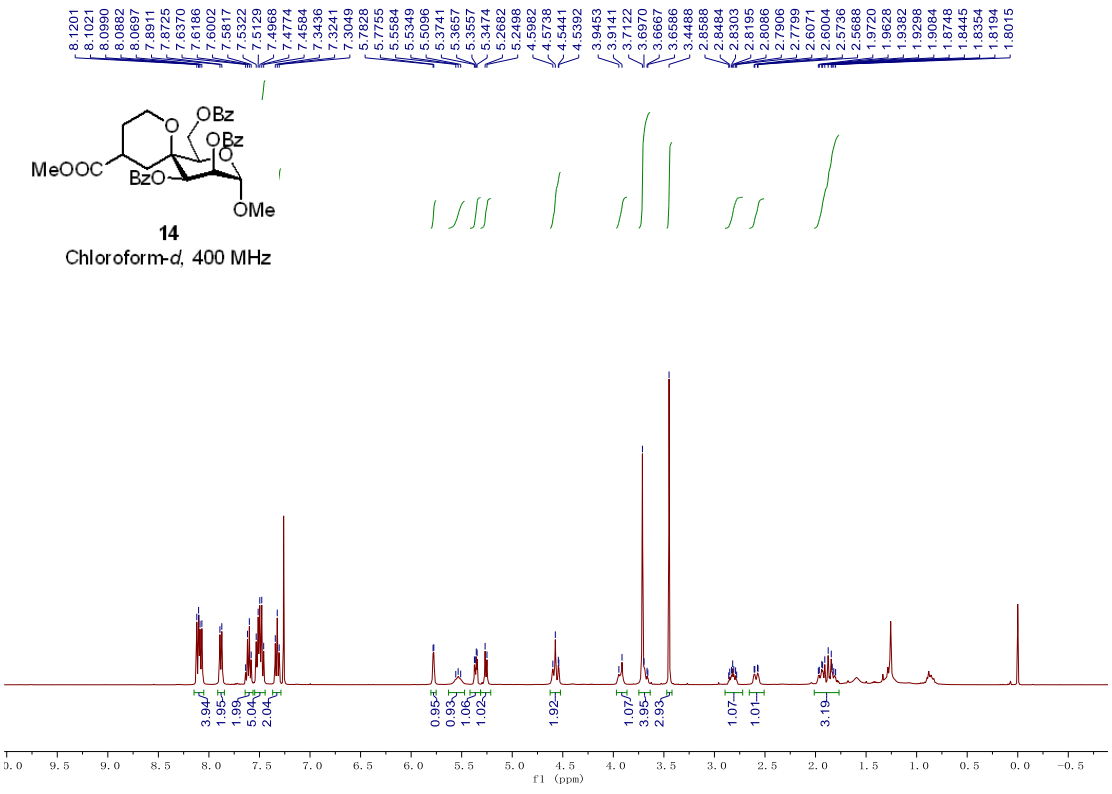
^{13}C NMR Spectra of compound 11



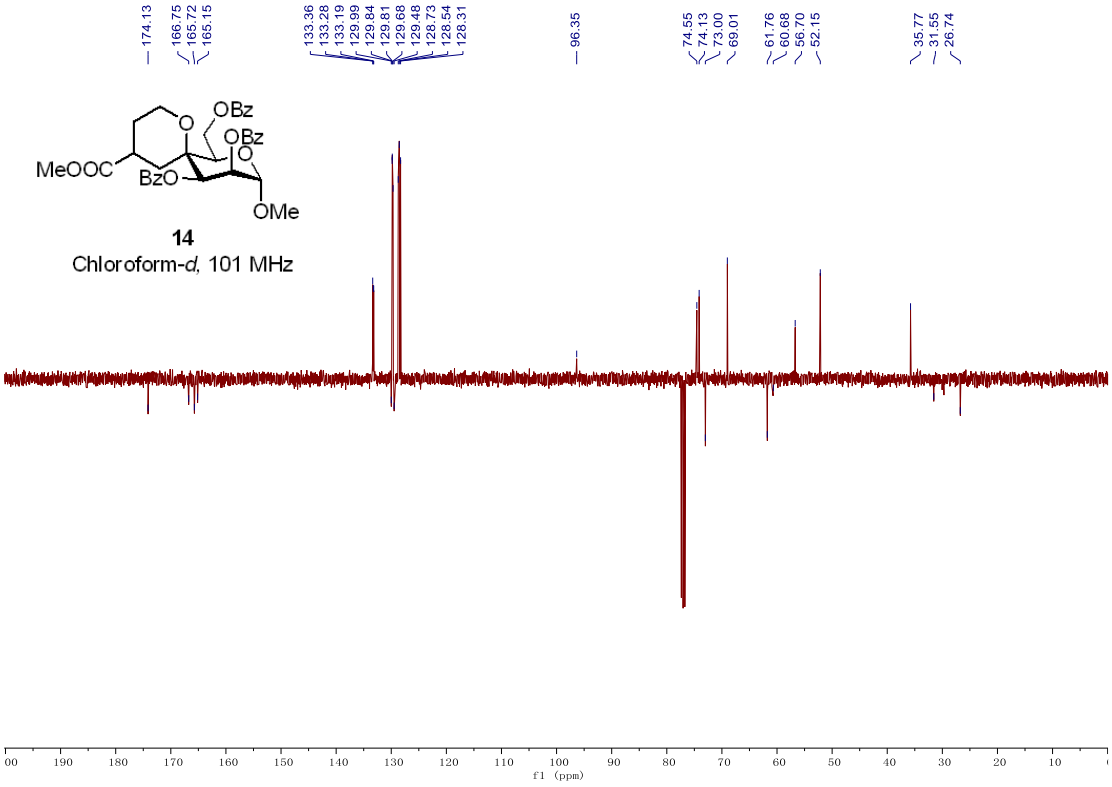
^{1}H NMR Spectra of compound 13



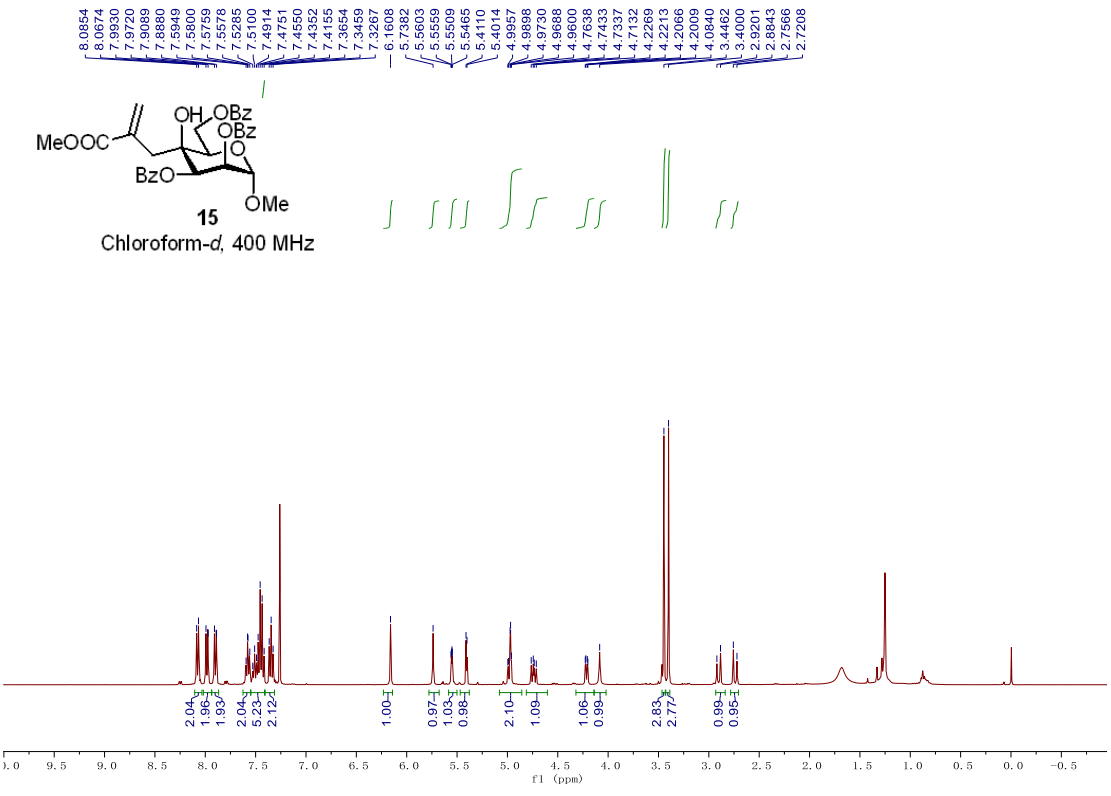
^{13}C NMR Spectra of compound 13



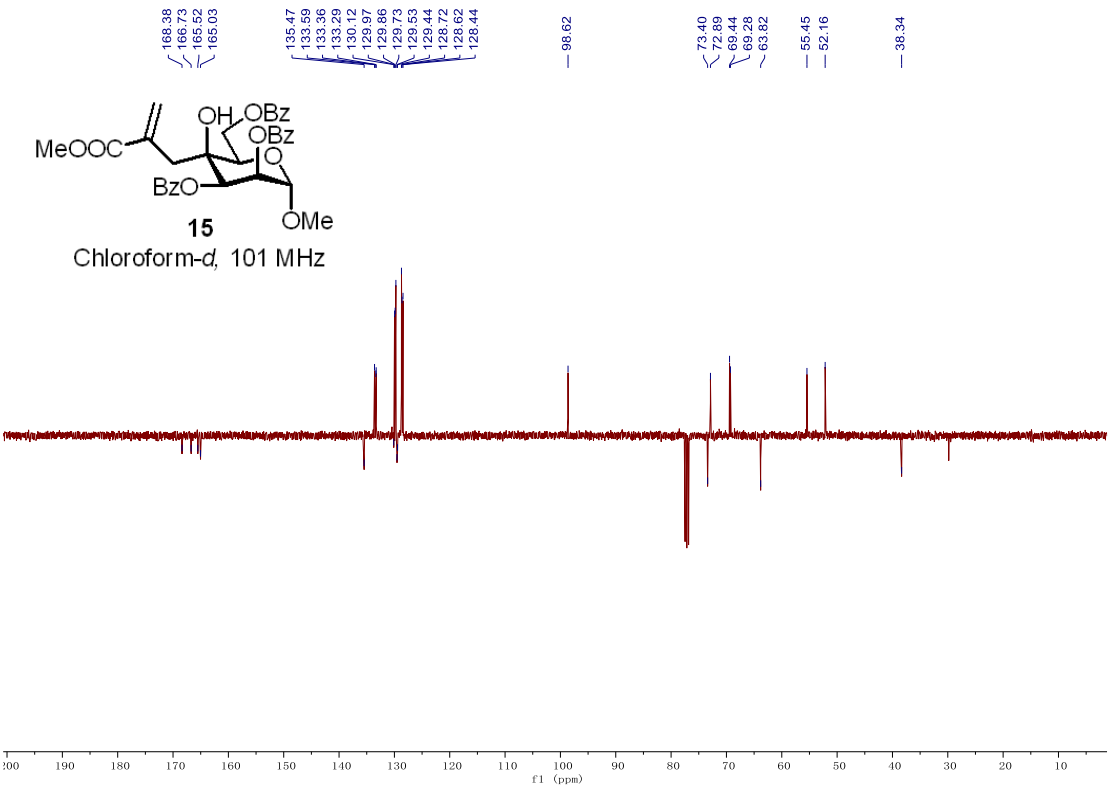
^{1}H NMR Spectra of compound 14



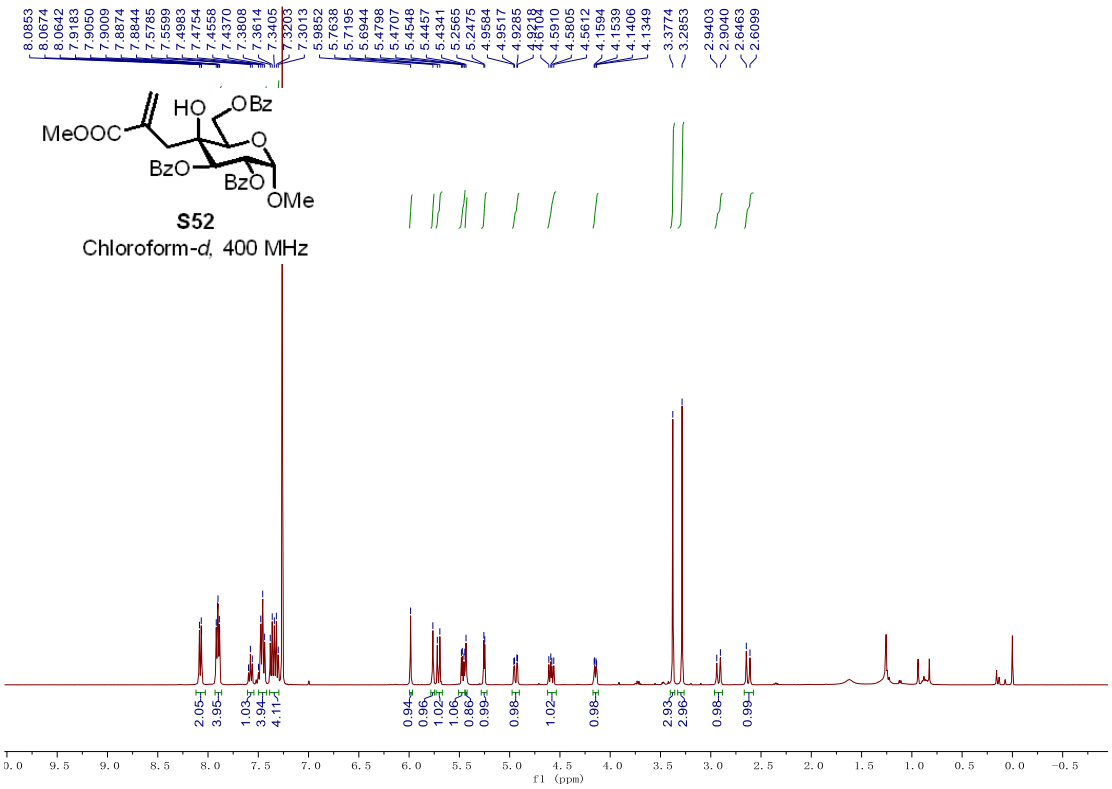
^{13}C NMR Spectra of compound 14



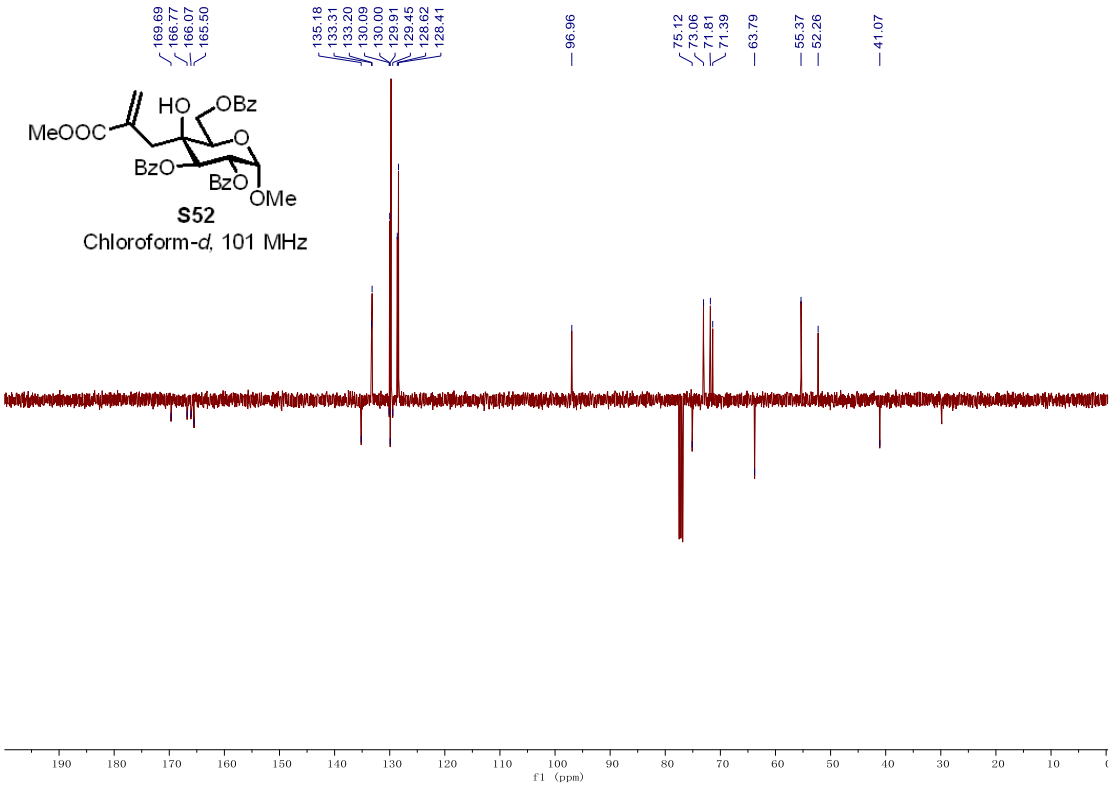
^{1}H NMR Spectra of compound 15



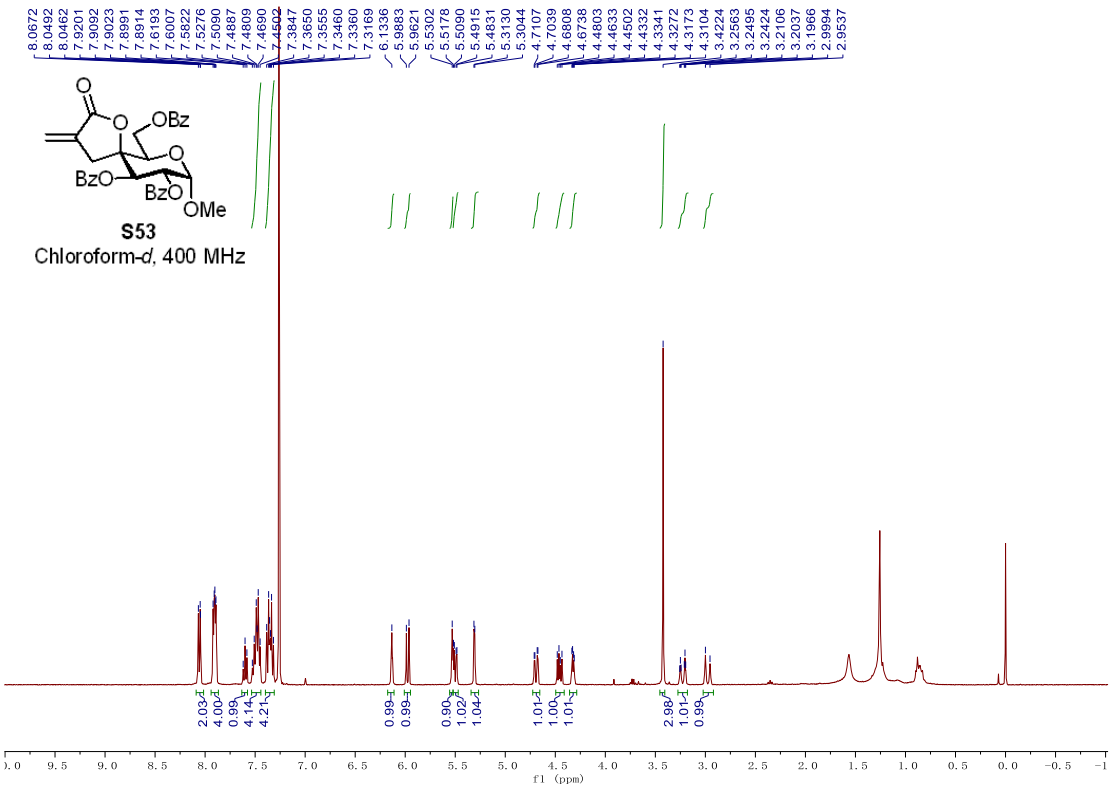
^{13}C NMR Spectra of compound 15



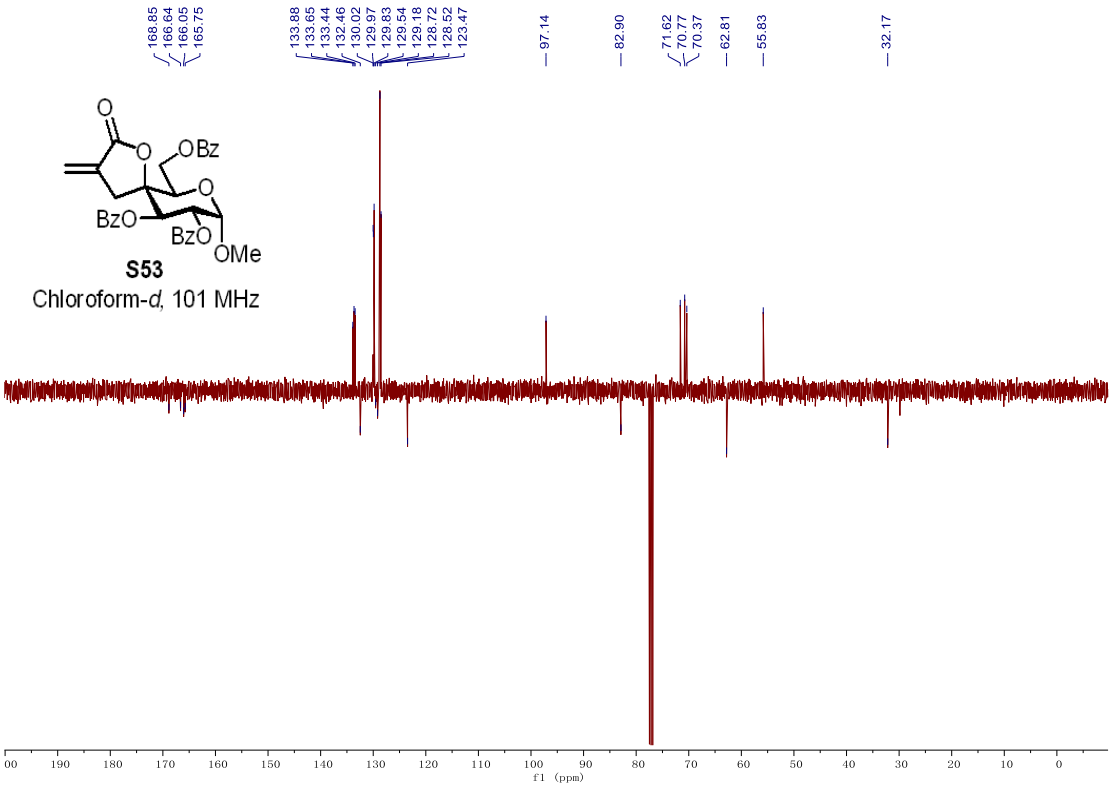
^{1}H NMR Spectra of compound S52



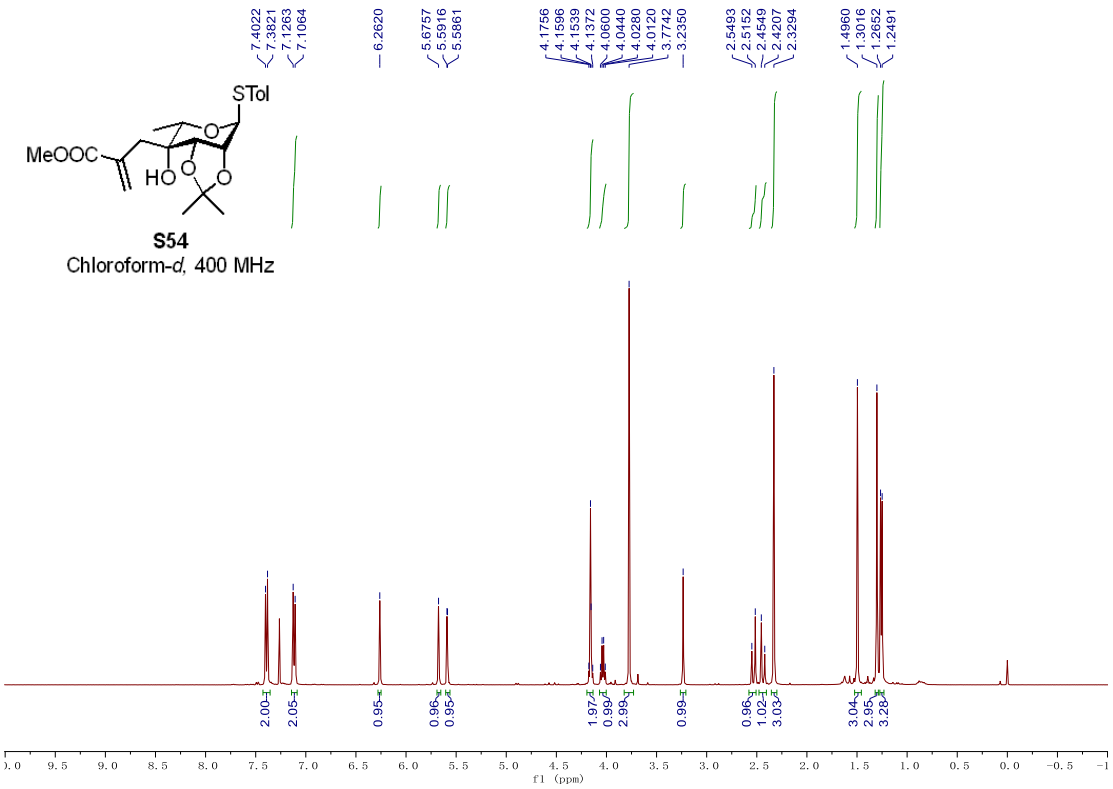
^{13}C NMR Spectra of compound S52



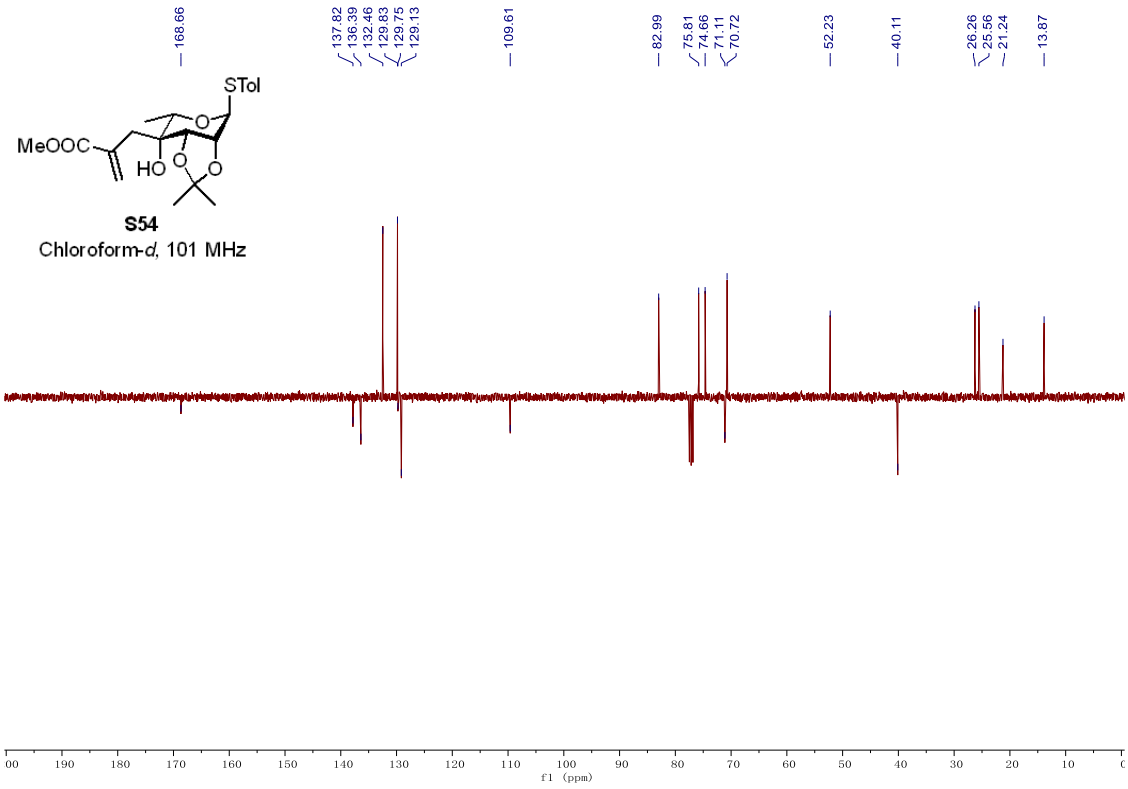
^{1}H NMR Spectra of compound S53



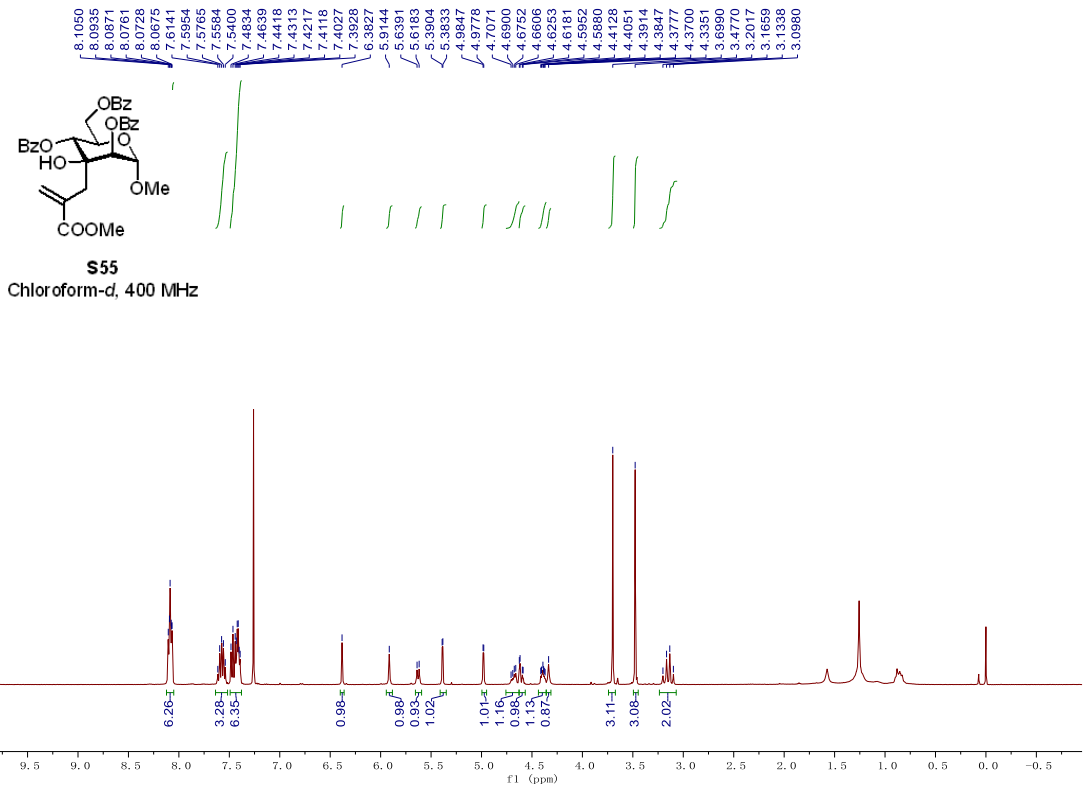
^{13}C NMR Spectra of compound S53



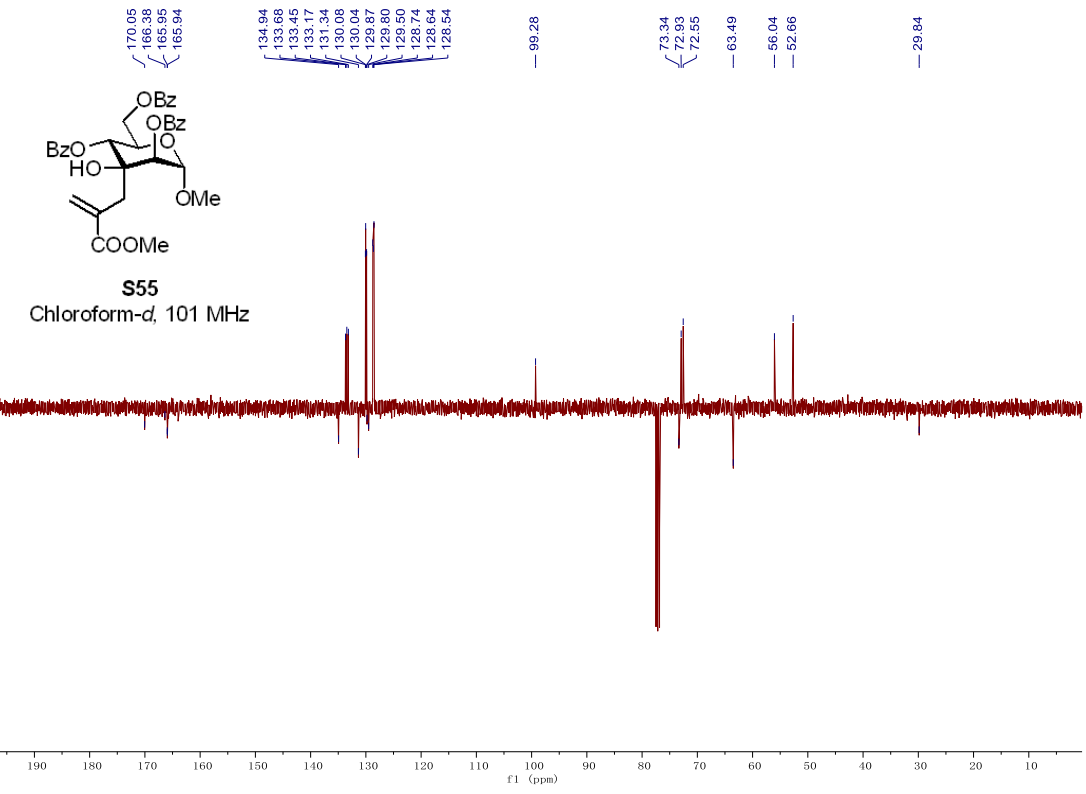
^{1}H NMR Spectra of compound S54



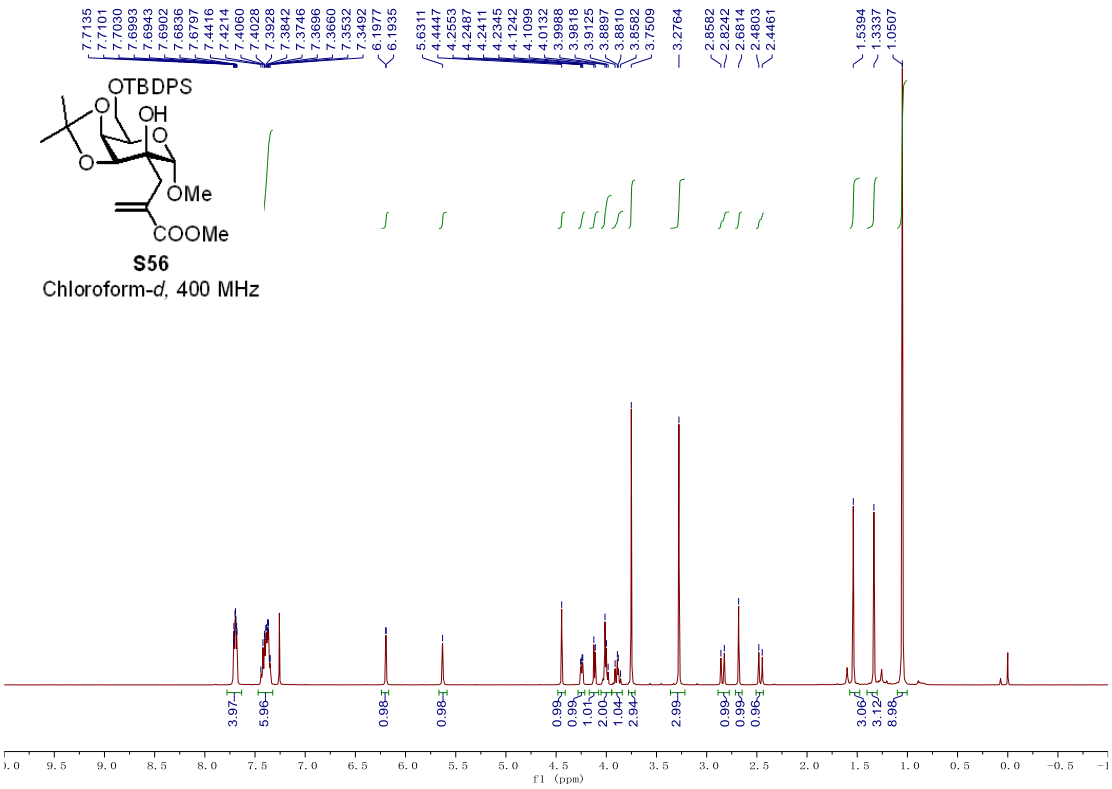
^{13}C NMR Spectra of compound S54



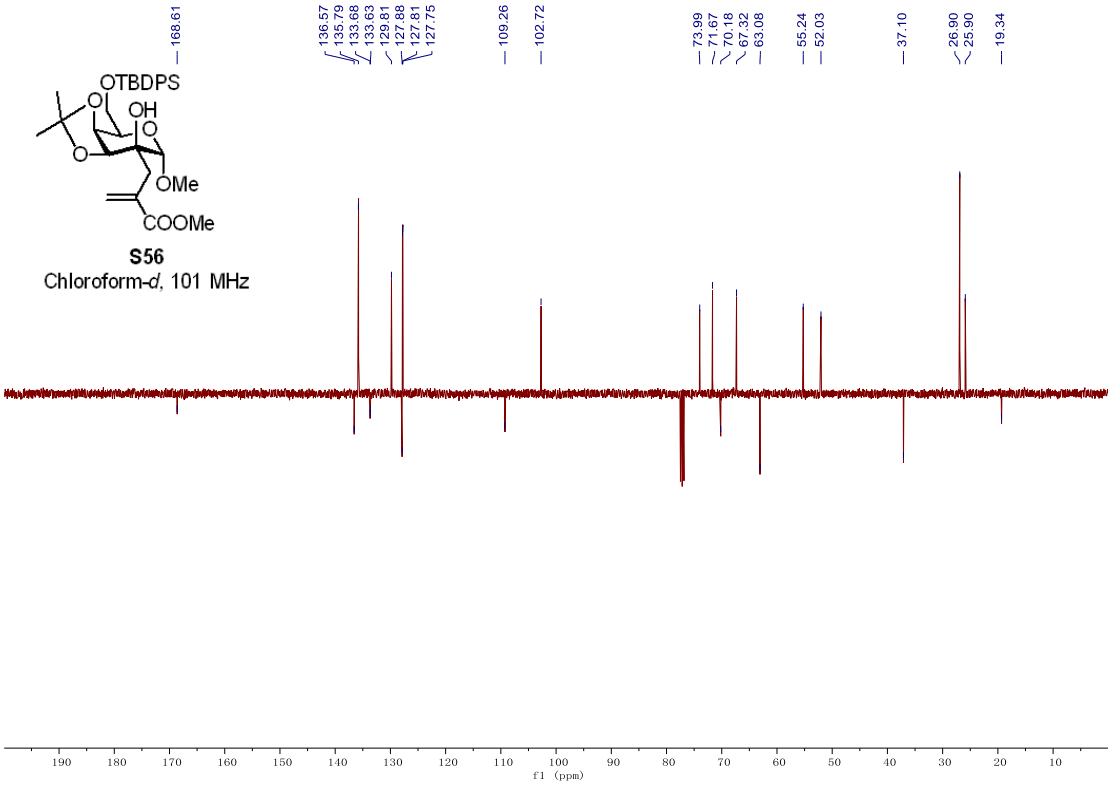
^{1}H NMR Spectra of compound S55



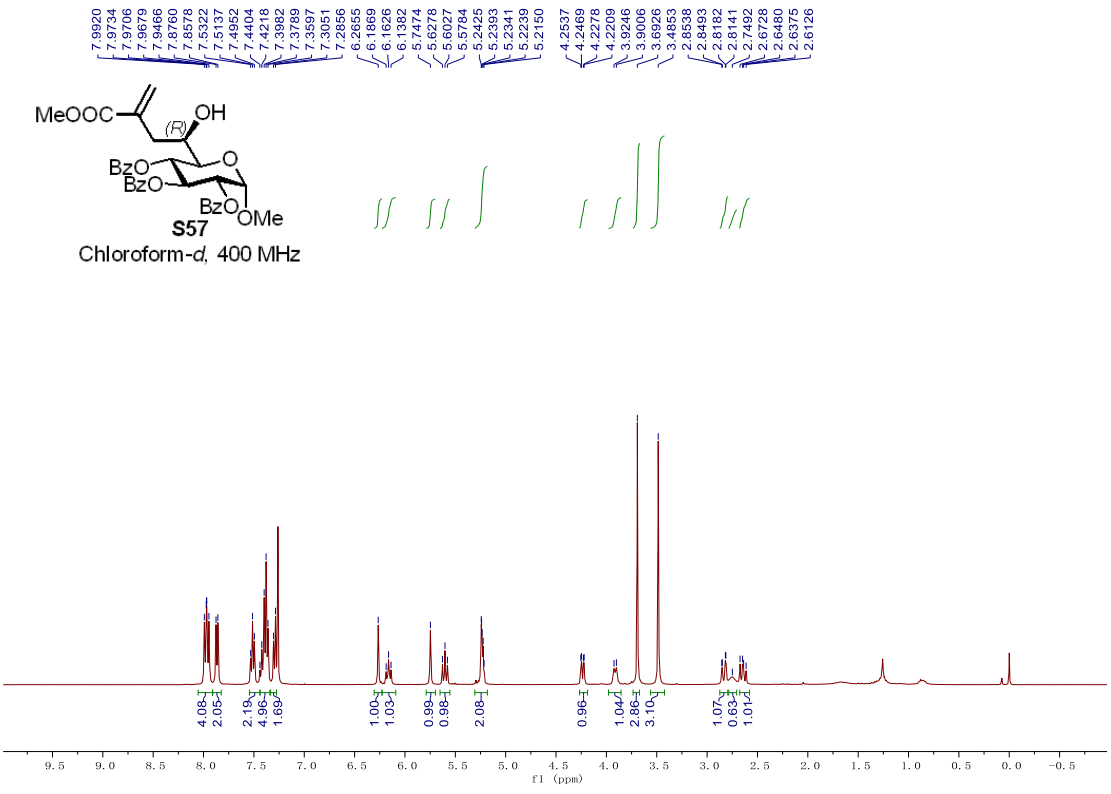
^{13}C NMR Spectra of compound S55



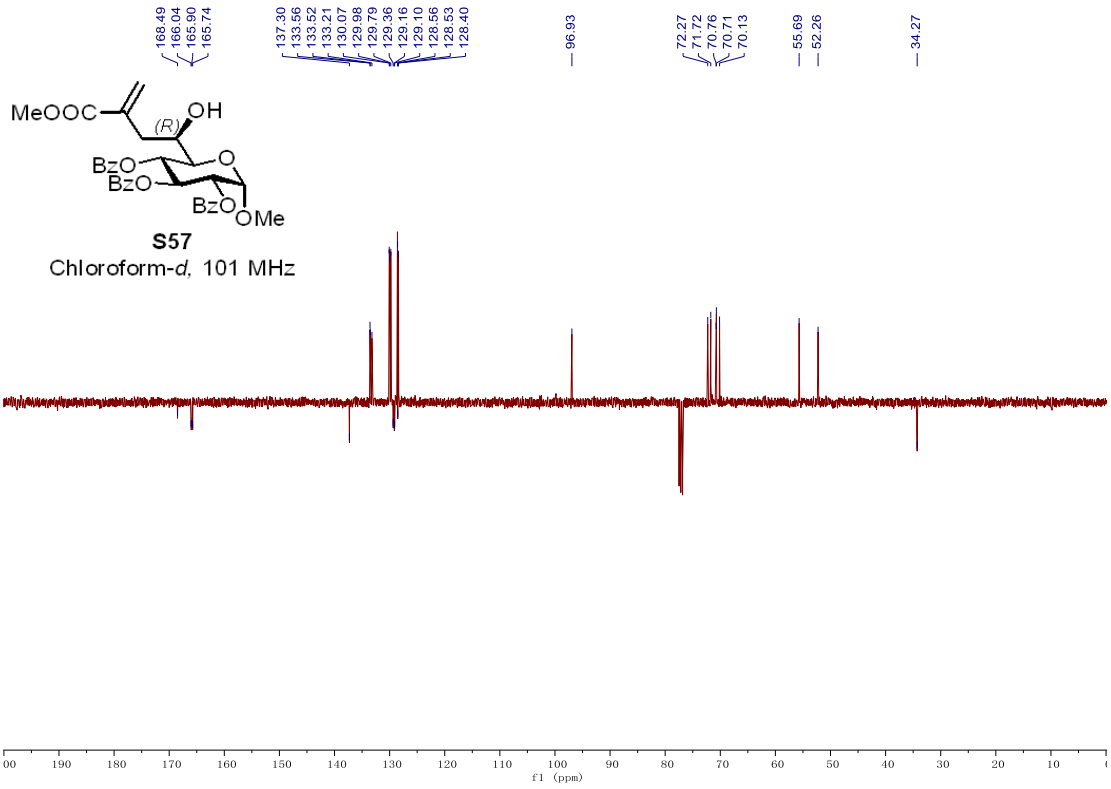
^{1}H NMR Spectra of compound S56



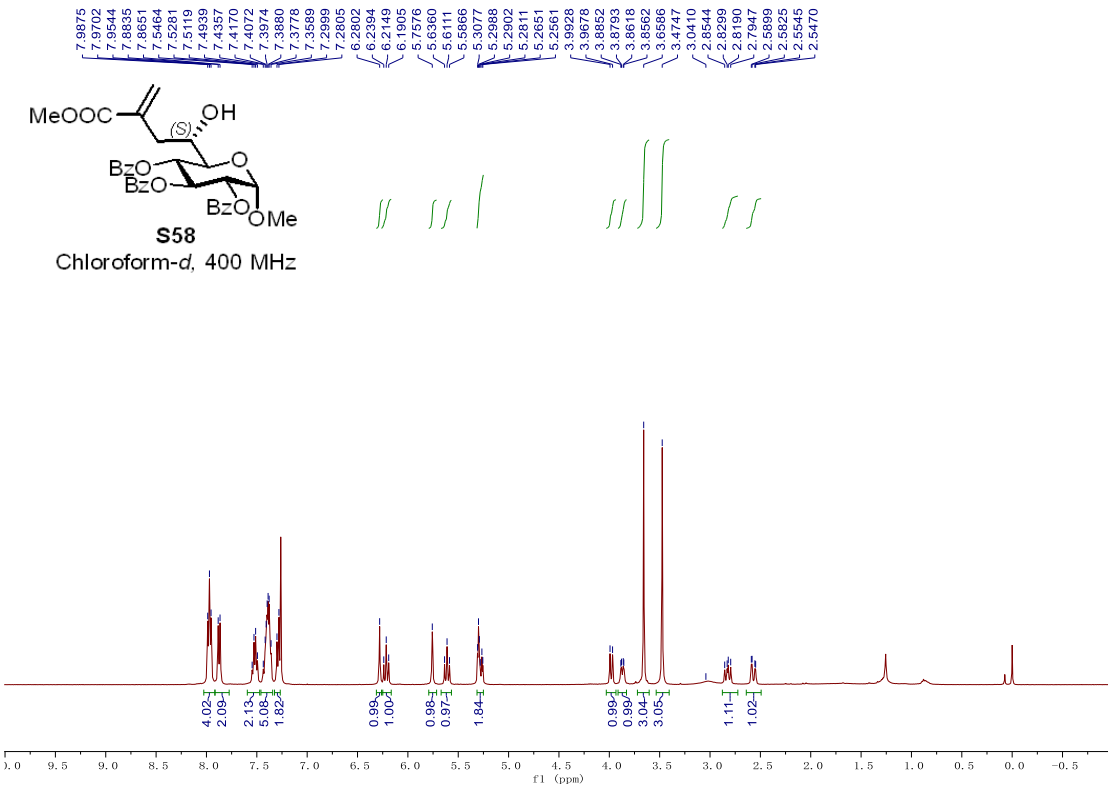
^{13}C NMR Spectra of compound S56



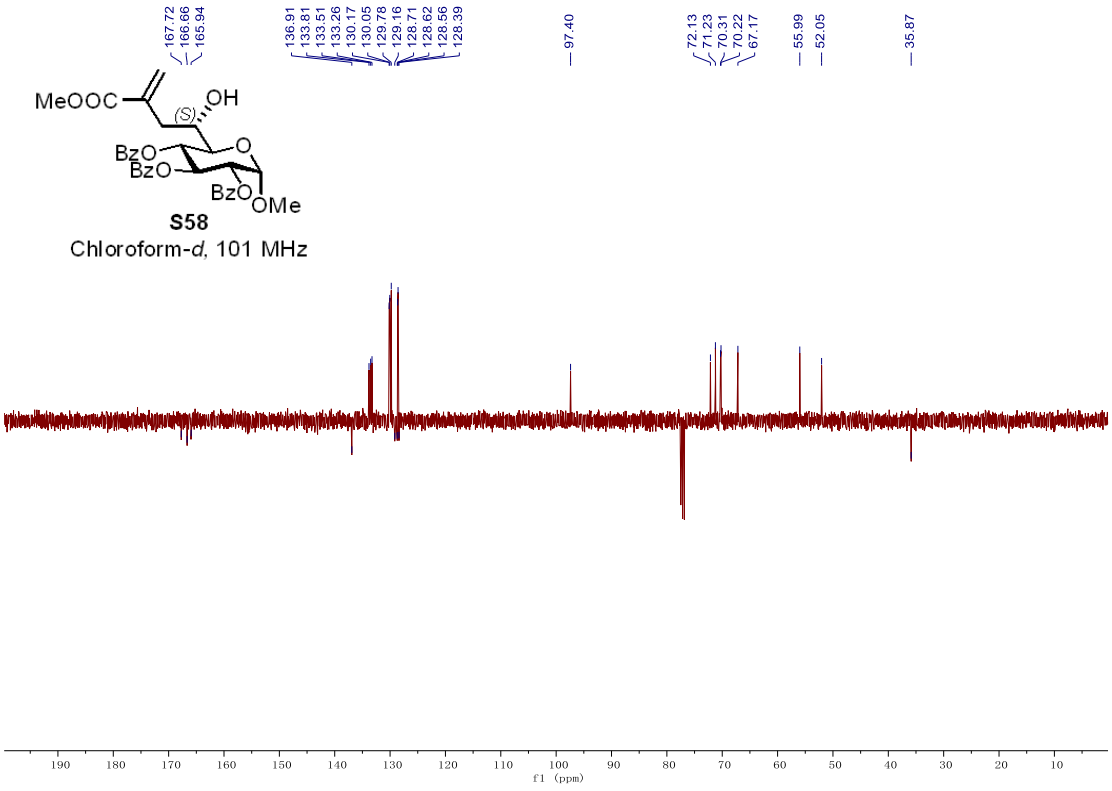
^{1}H NMR Spectra of compound S57



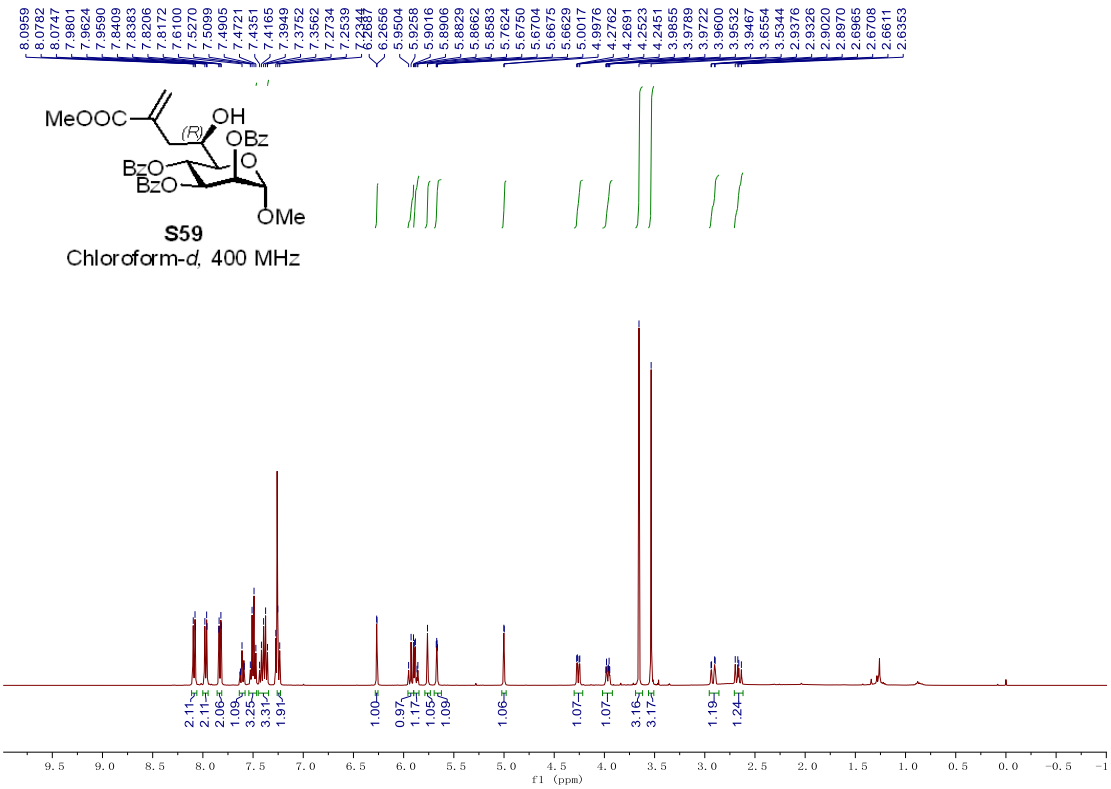
^{13}C NMR Spectra of compound S57



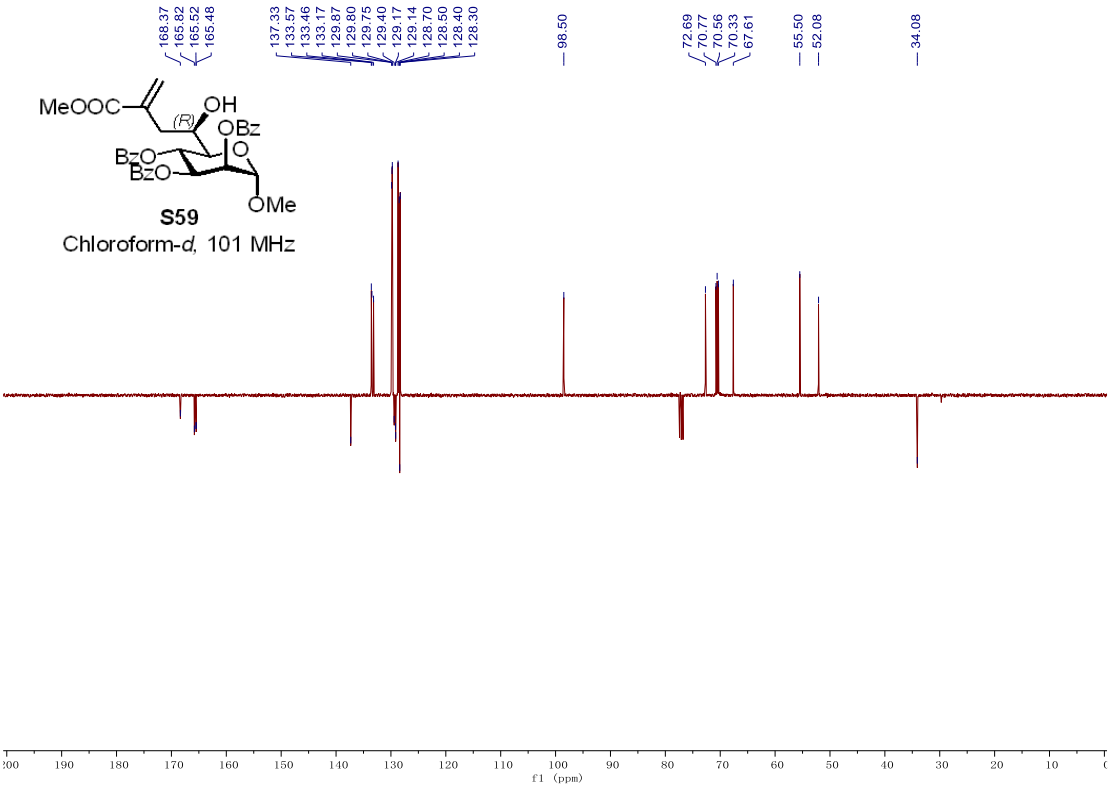
^{1}H NMR Spectra of compound S58



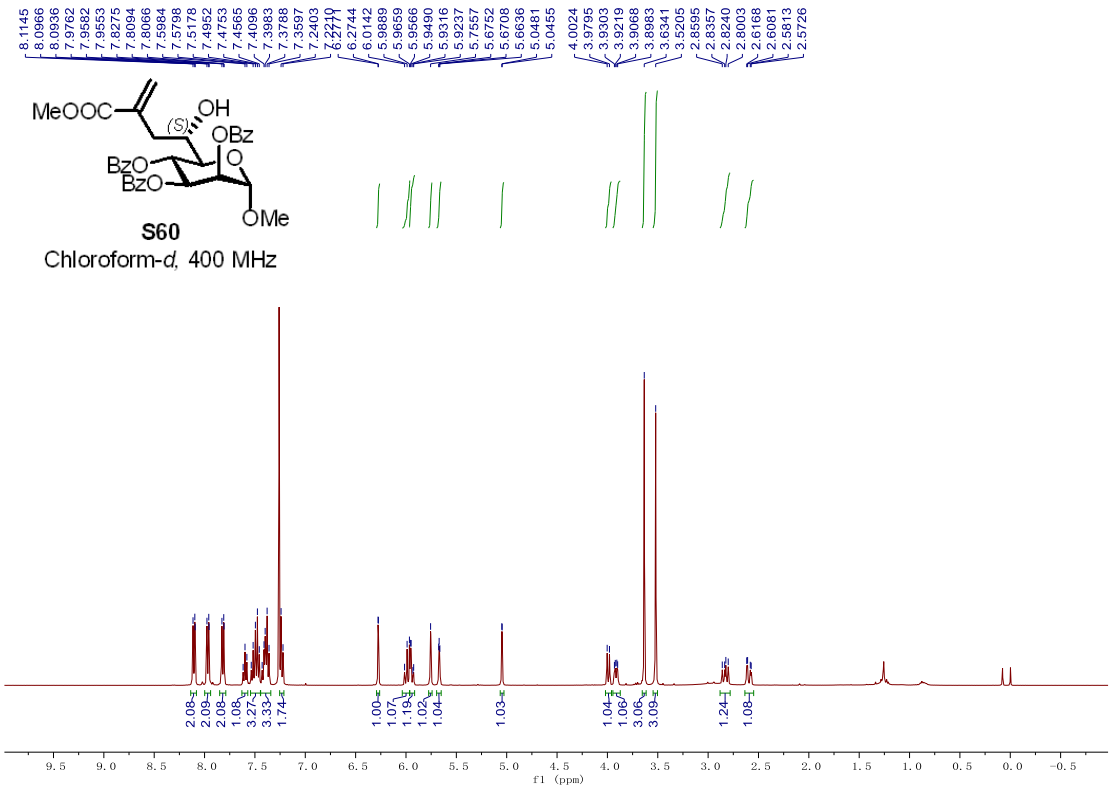
^{13}C NMR Spectra of compound S58



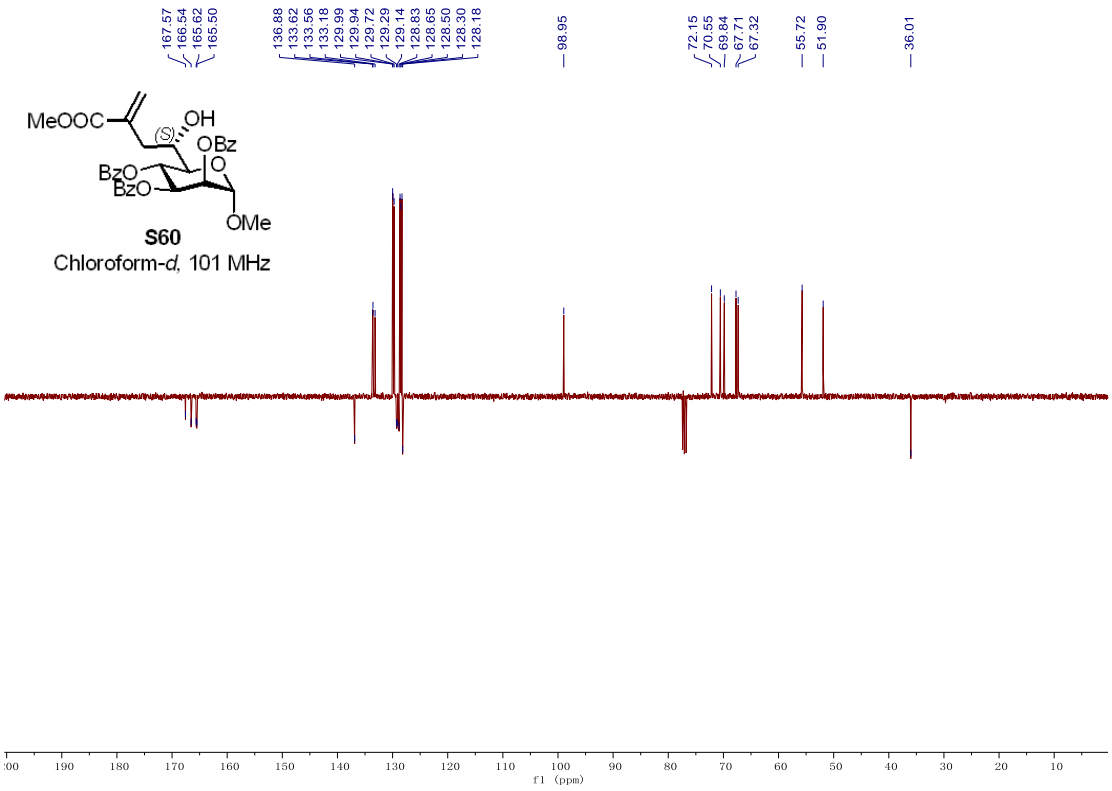
^{1}H NMR Spectra of compound S59



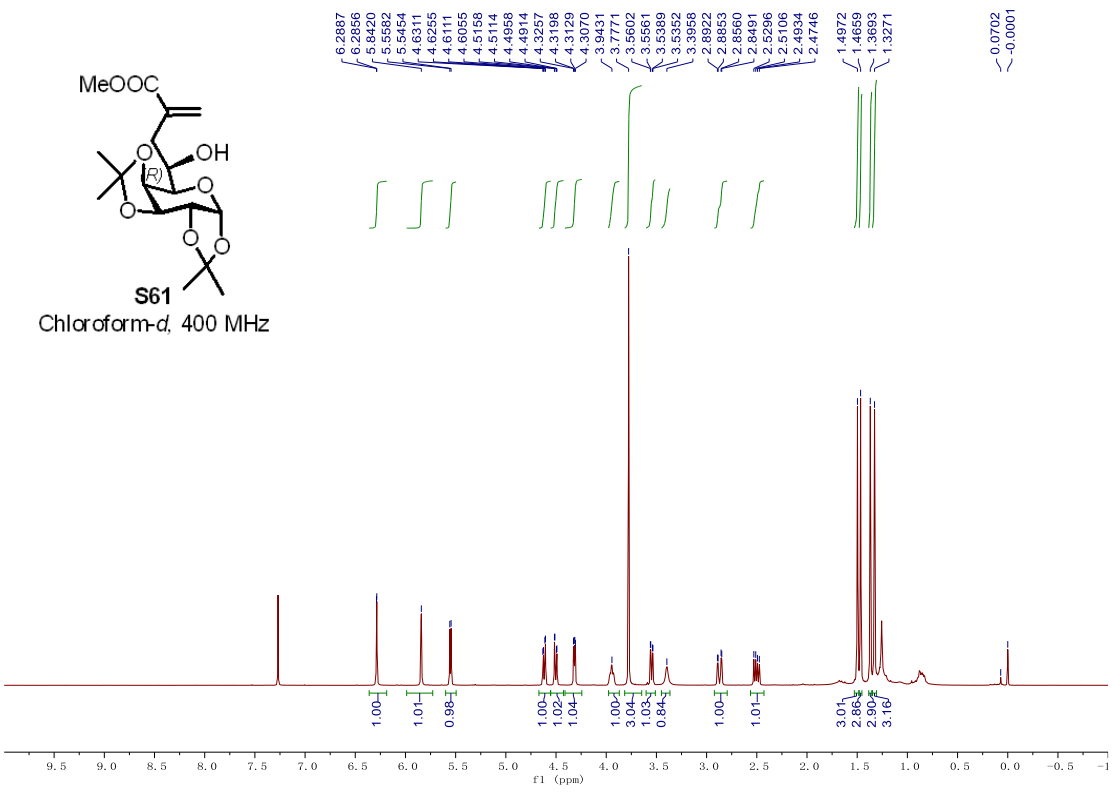
^{13}C NMR Spectra of compound S59



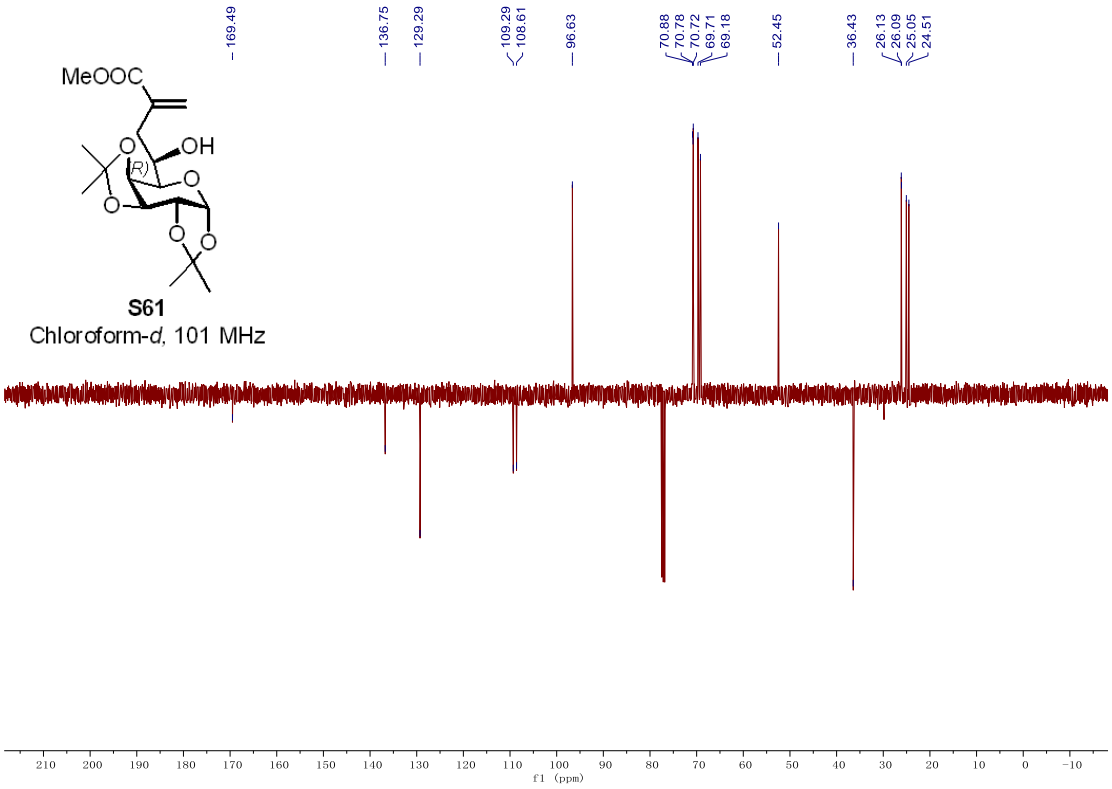
^{1}H NMR Spectra of compound S60



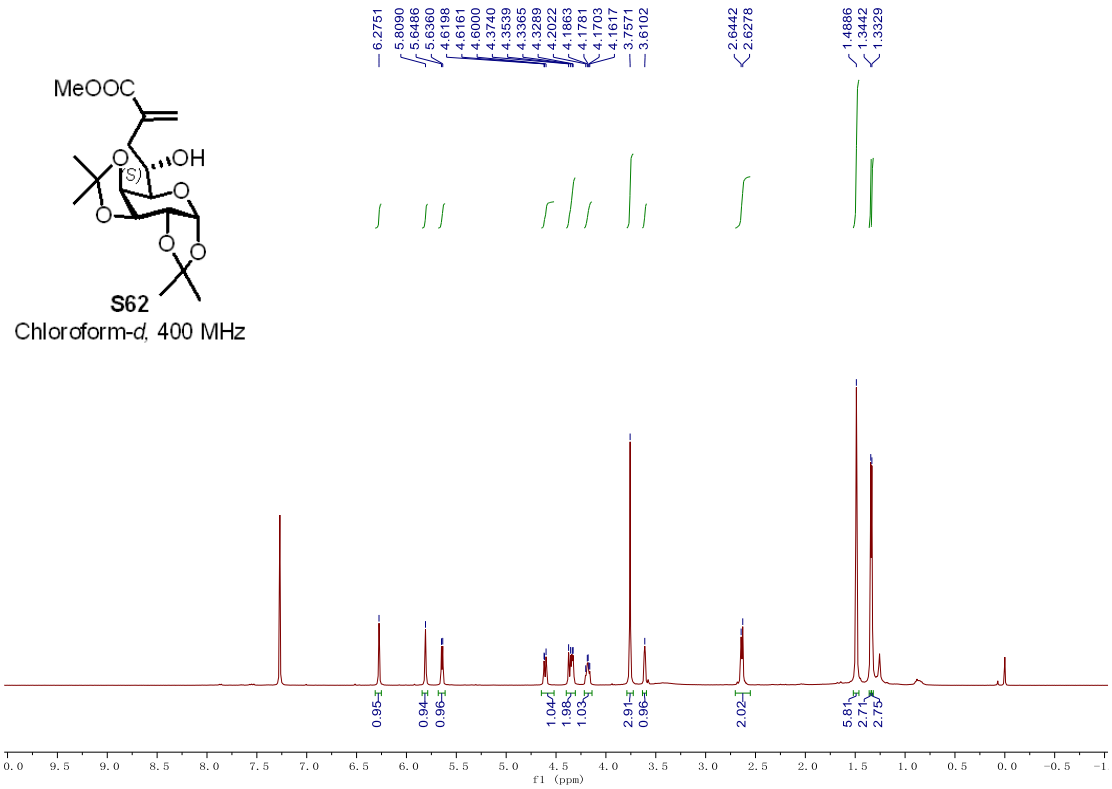
^{13}C NMR Spectra of compound S60



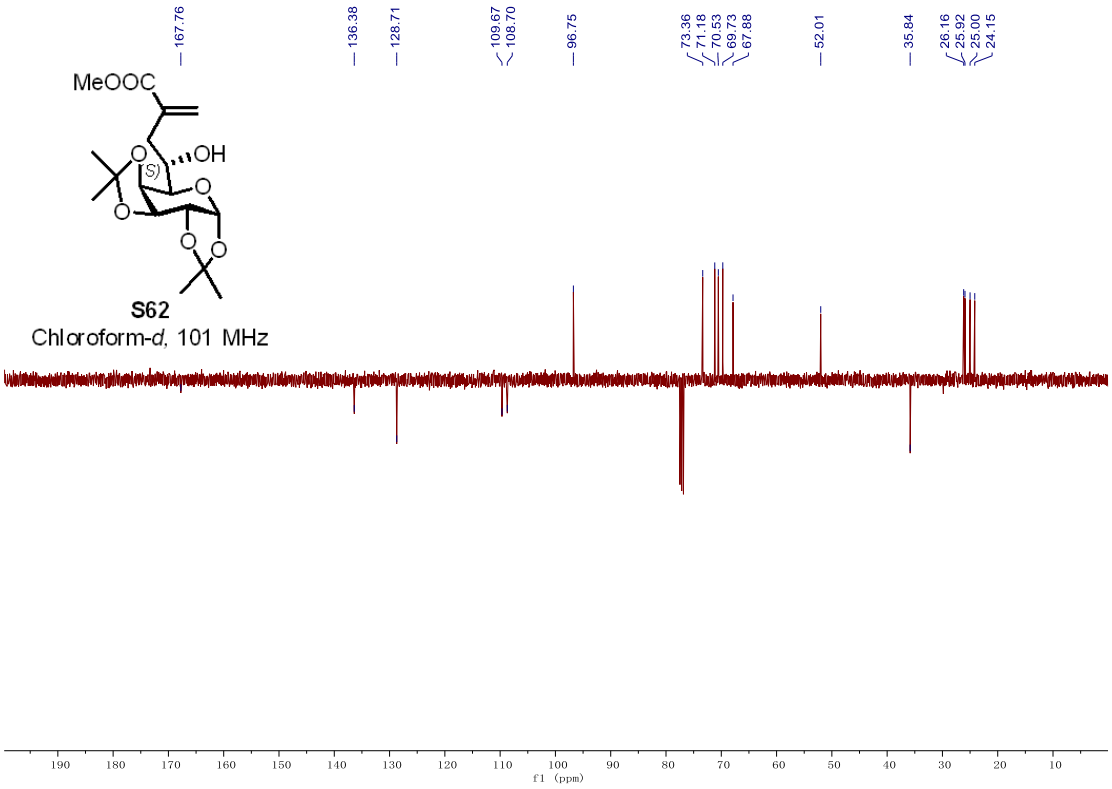
^{1}H NMR Spectra of compound S61



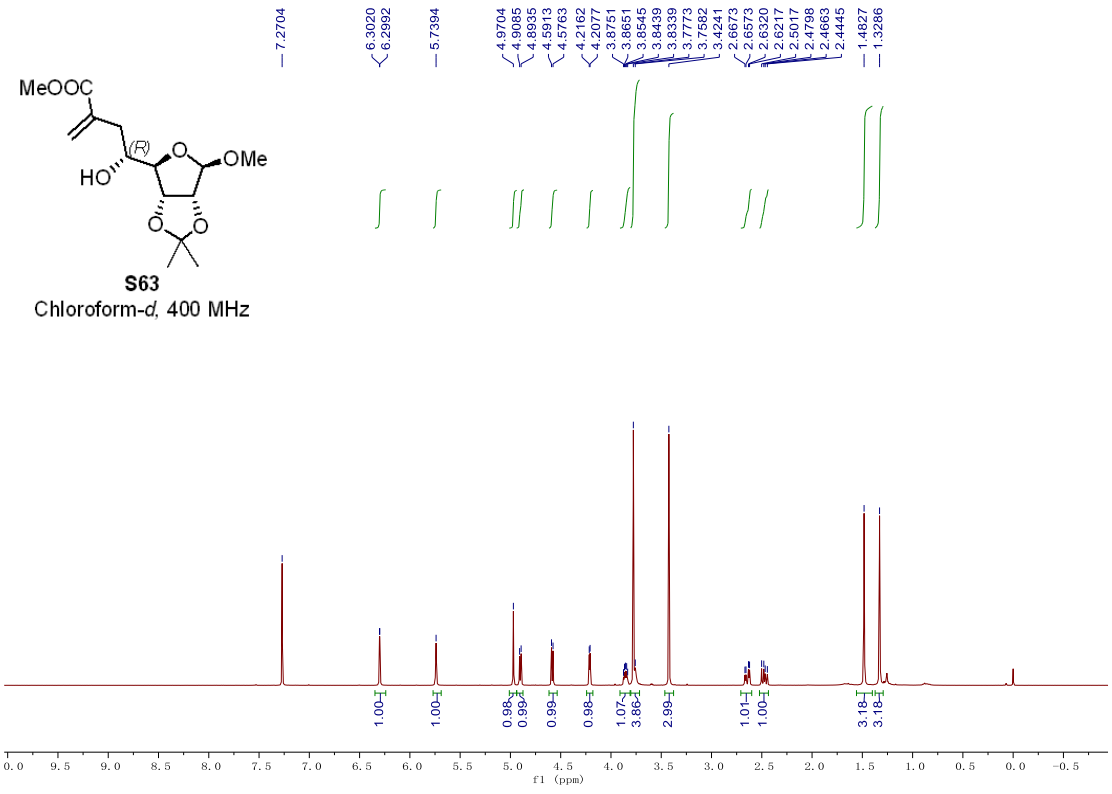
^{13}C NMR Spectra of compound S61



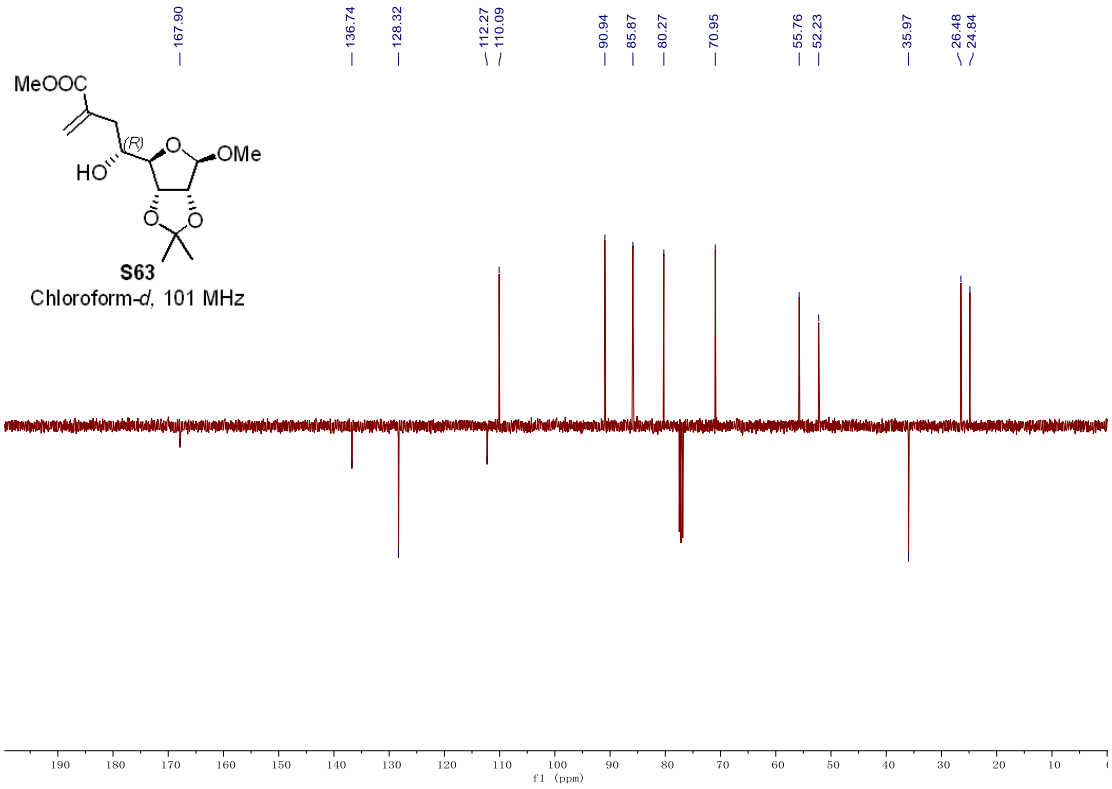
^{1}H NMR Spectra of compound S62



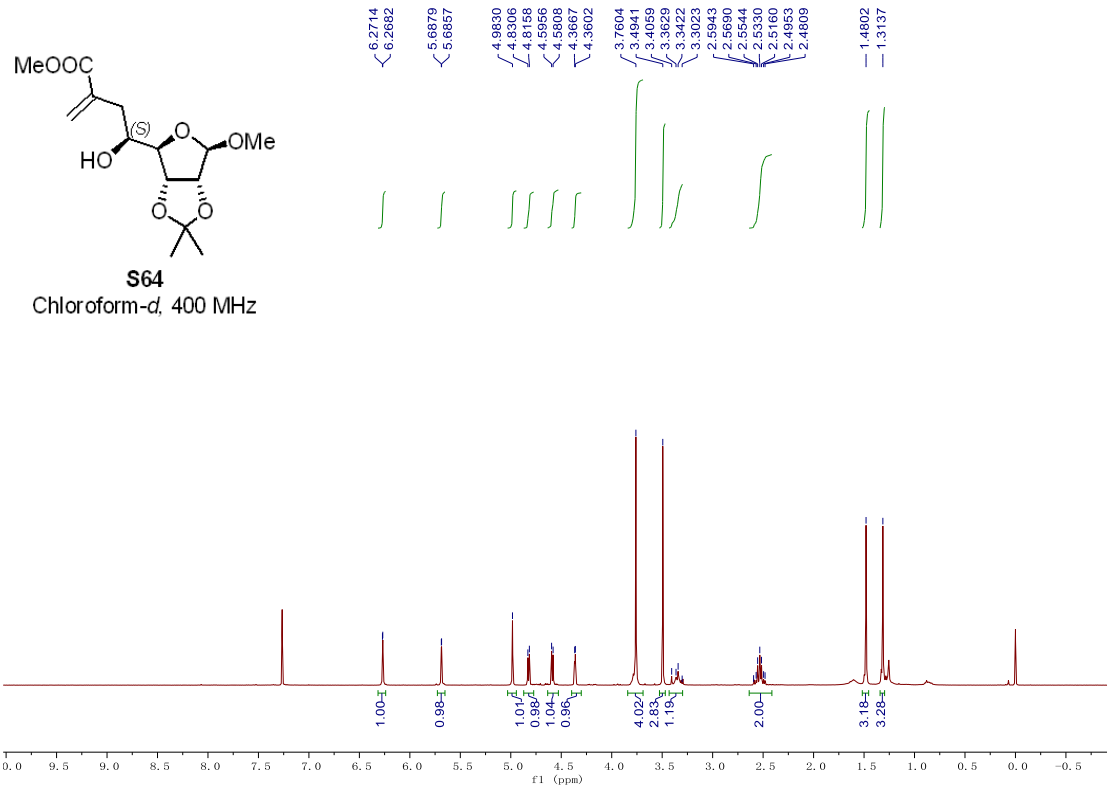
^{13}C NMR Spectra of compound S62



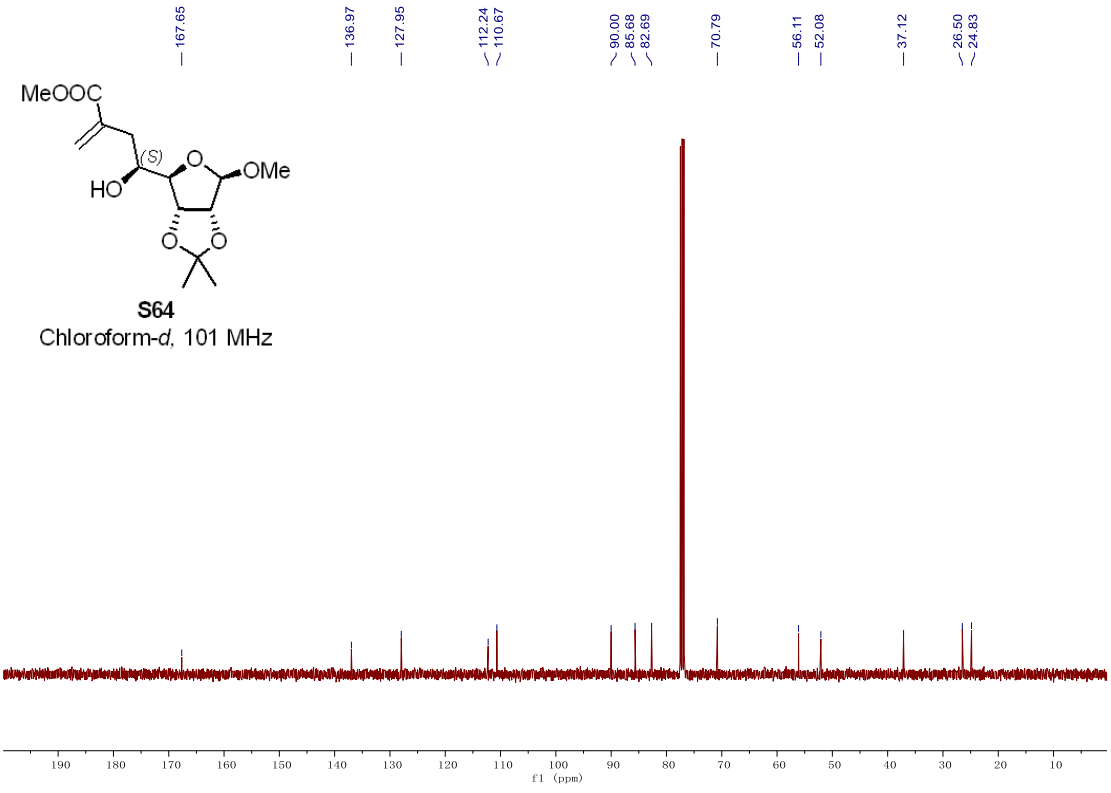
^{1}H NMR Spectra of compound S63



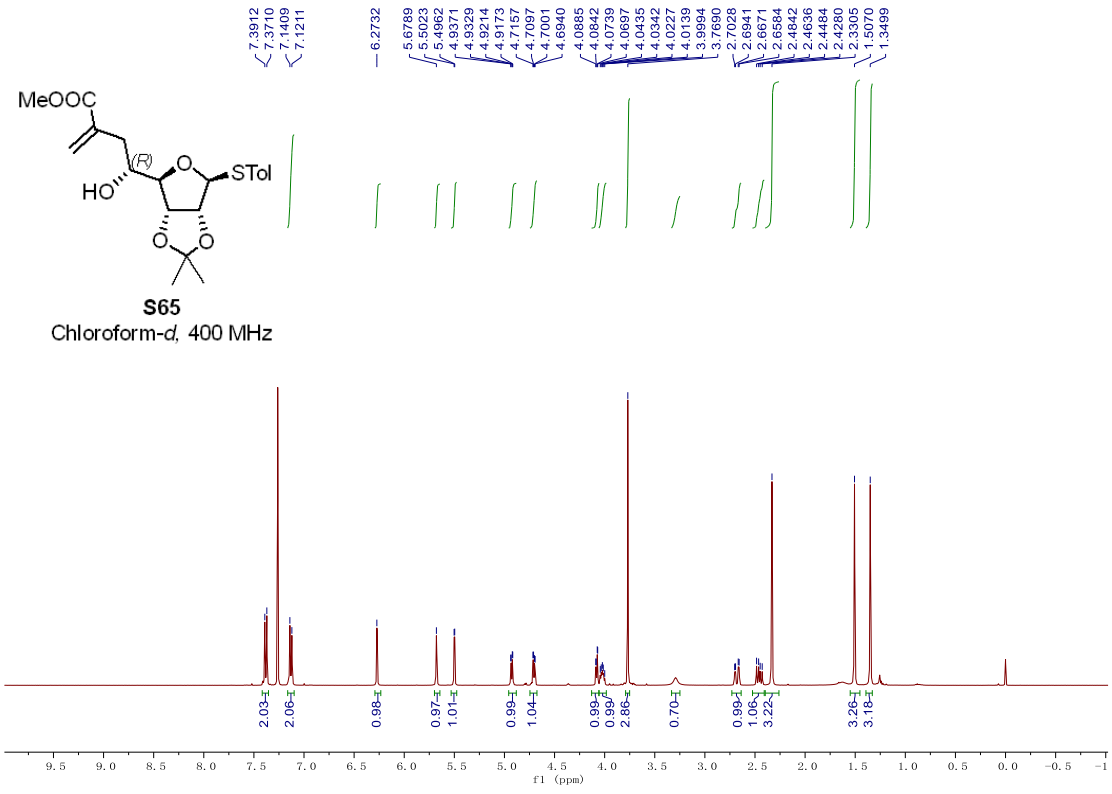
^{13}C NMR Spectra of compound S63



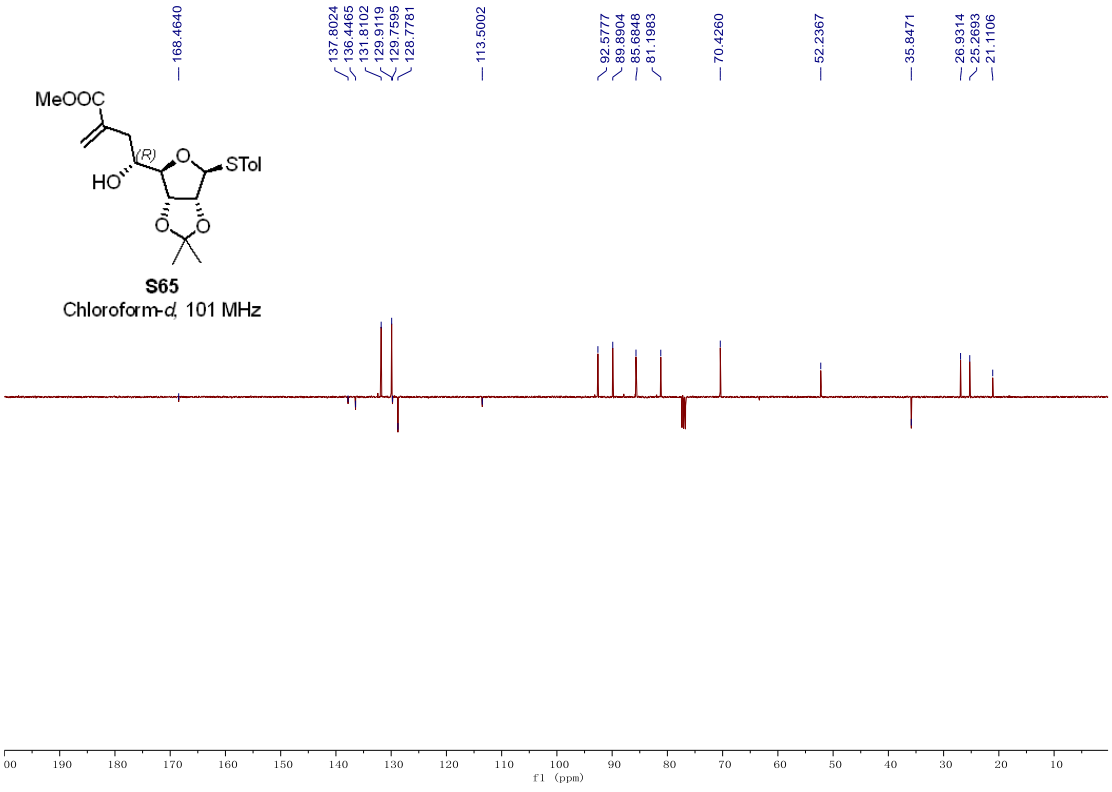
^{1}H NMR Spectra of compound S64



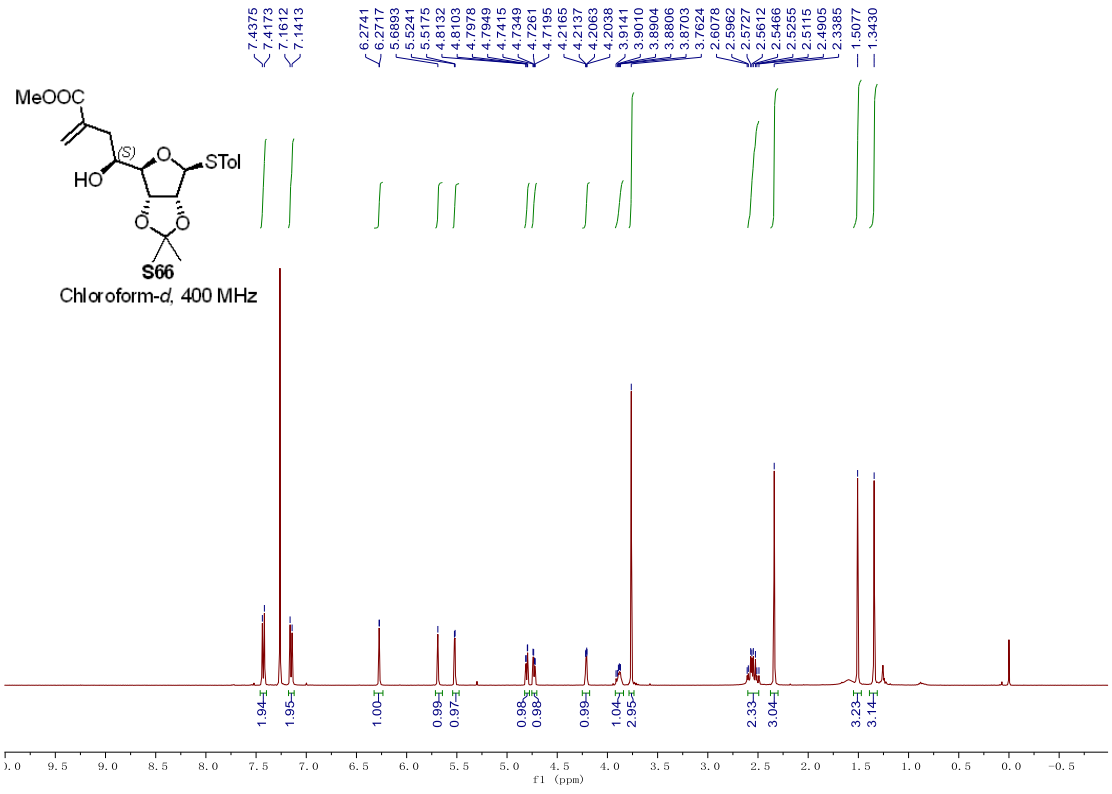
^{13}C NMR Spectra of compound S64



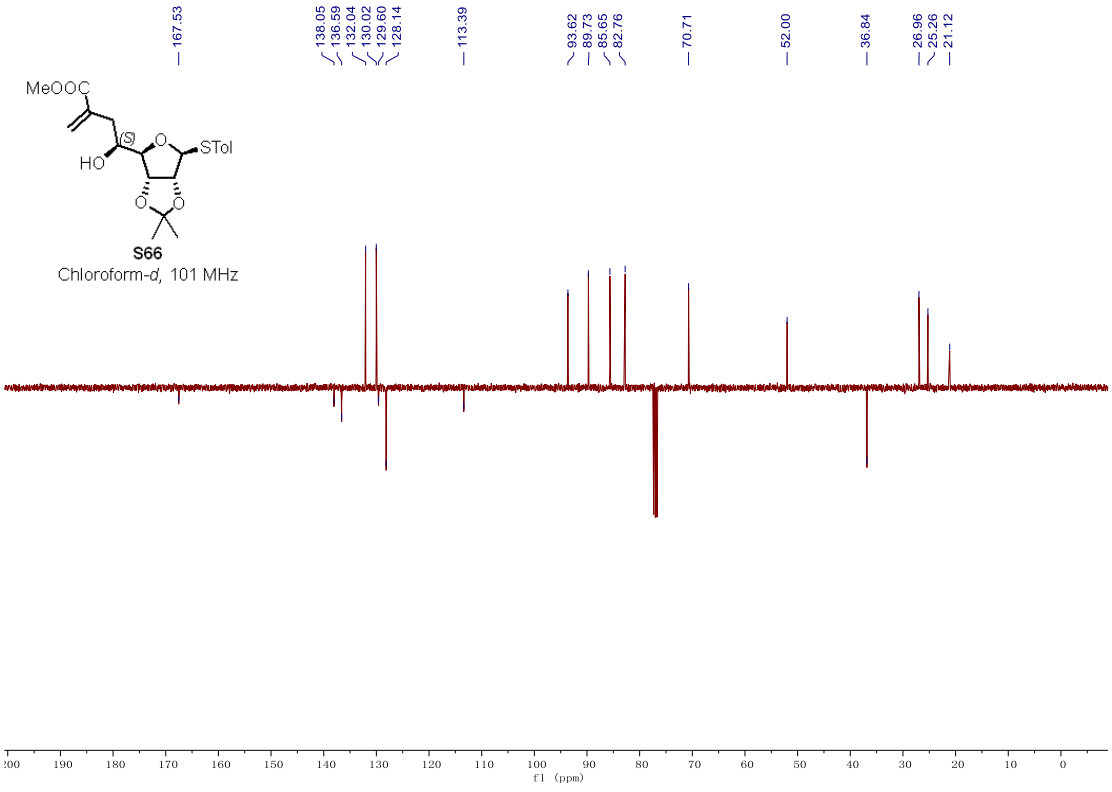
^{1}H NMR Spectra of compound S65



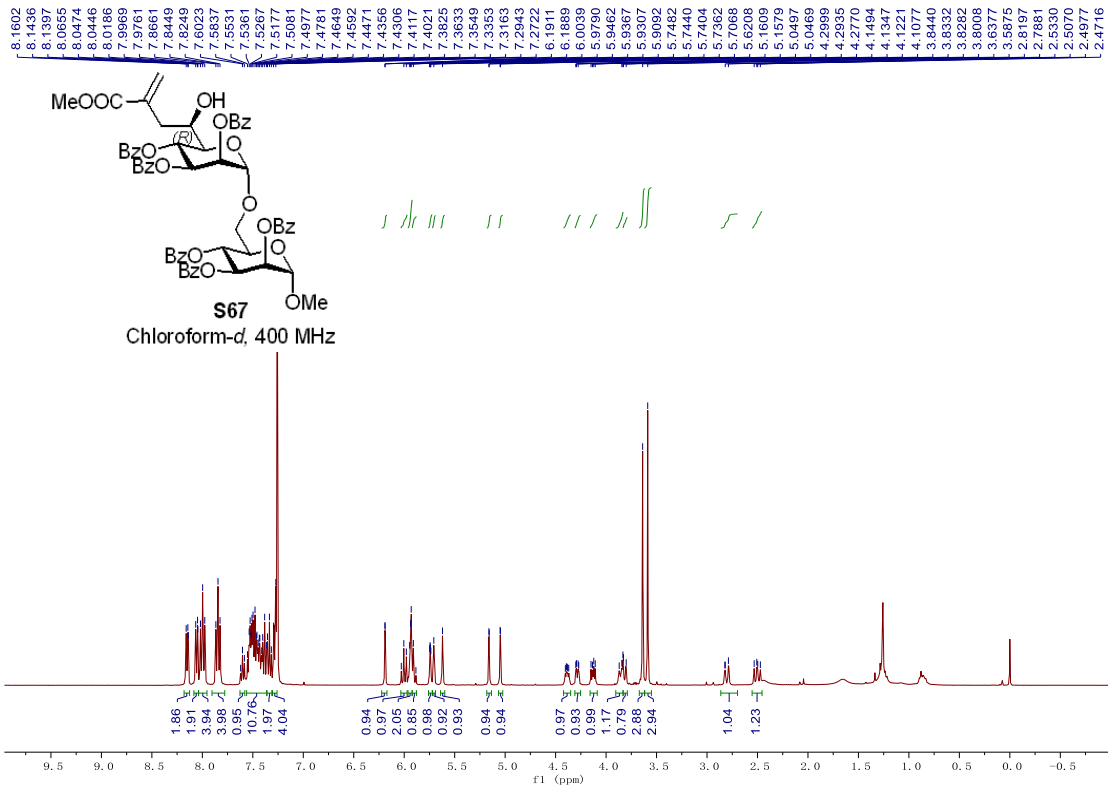
^{13}C NMR Spectra of compound S65



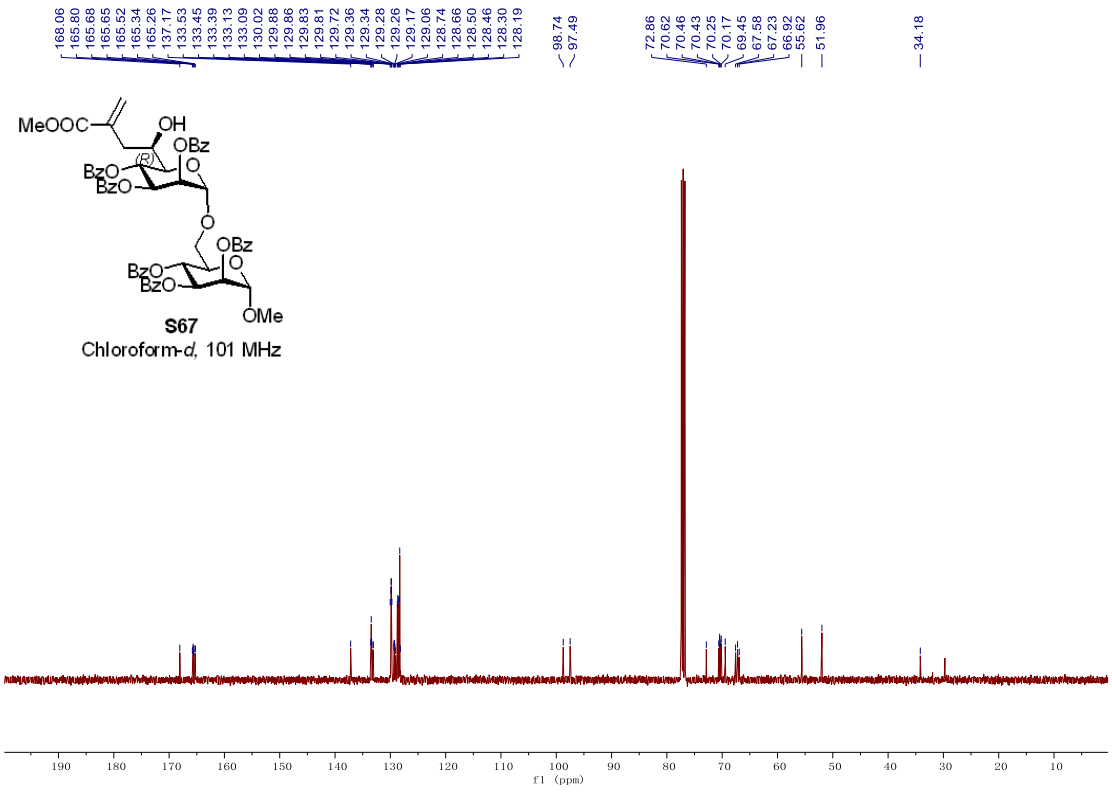
^{1}H NMR Spectra of compound S66



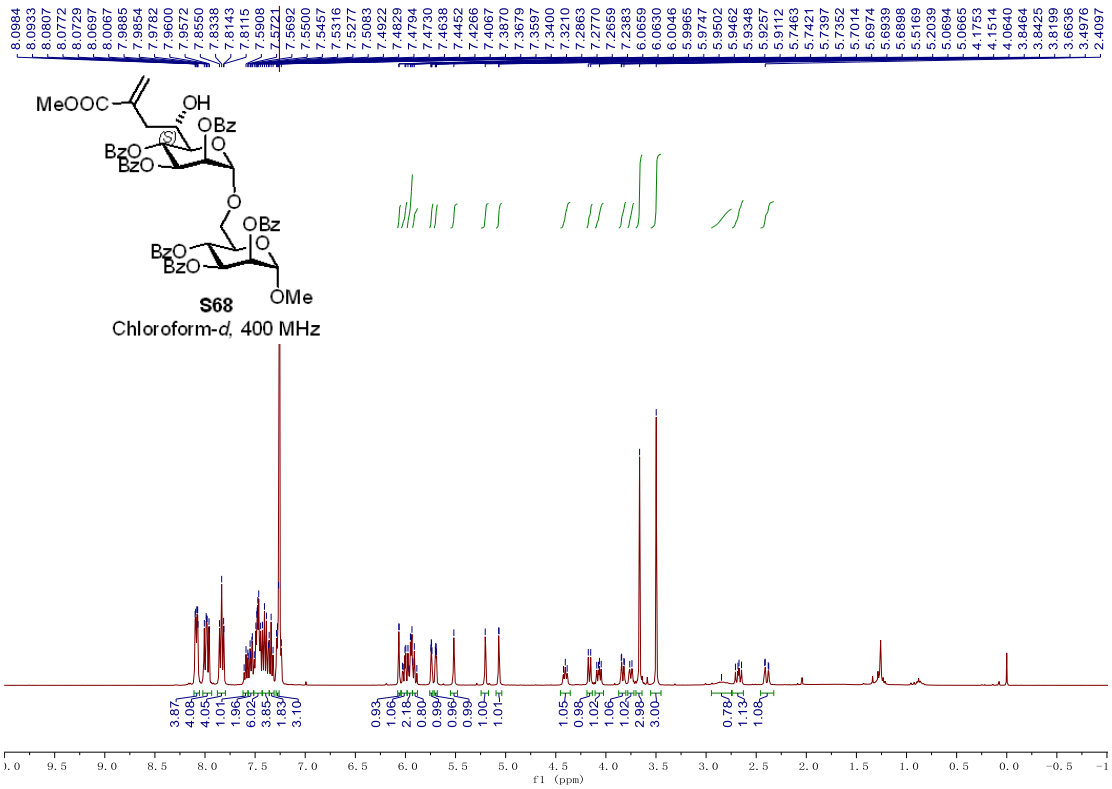
^{13}C NMR Spectra of compound S66



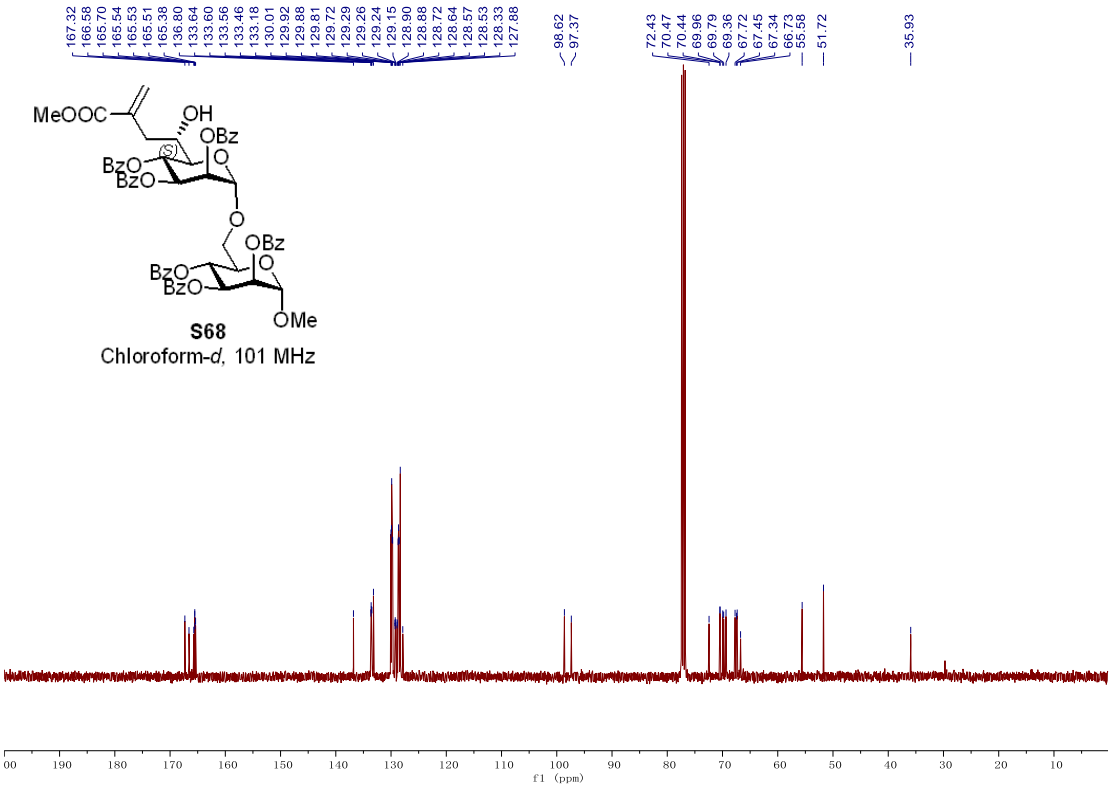
^{1}H NMR Spectra of compound S67



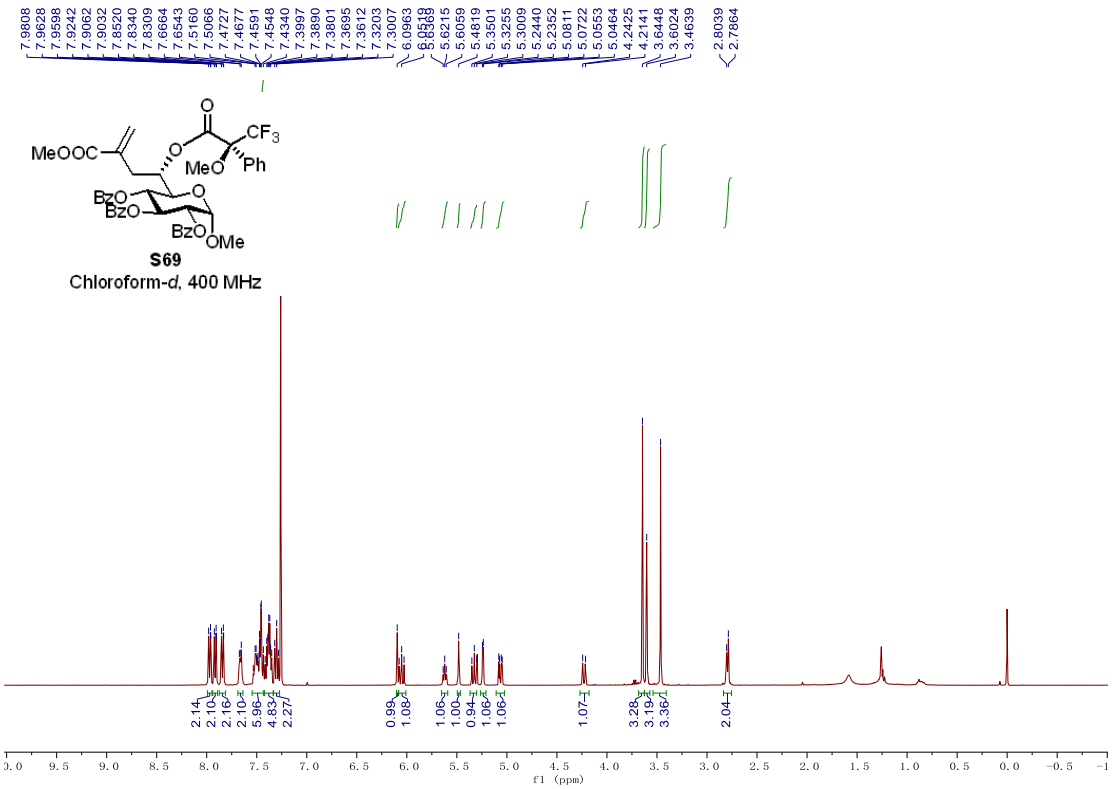
^{13}C NMR Spectra of compound S67



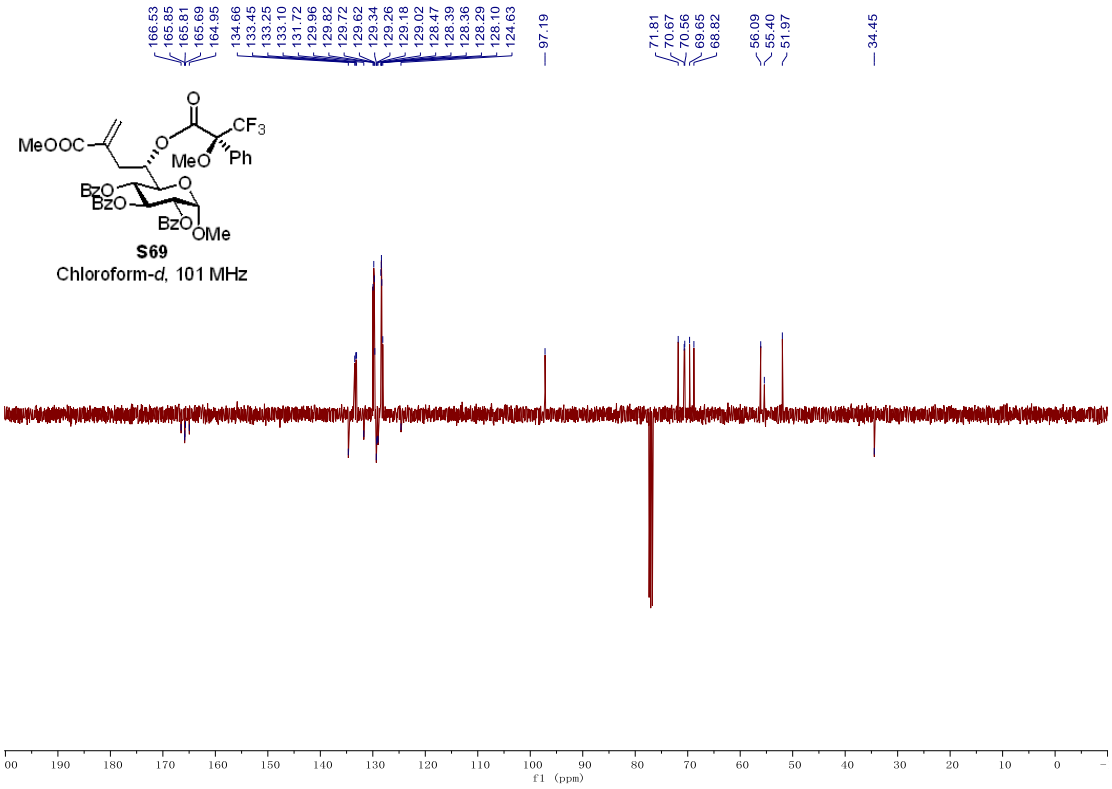
^{1}H NMR Spectra of compound S68



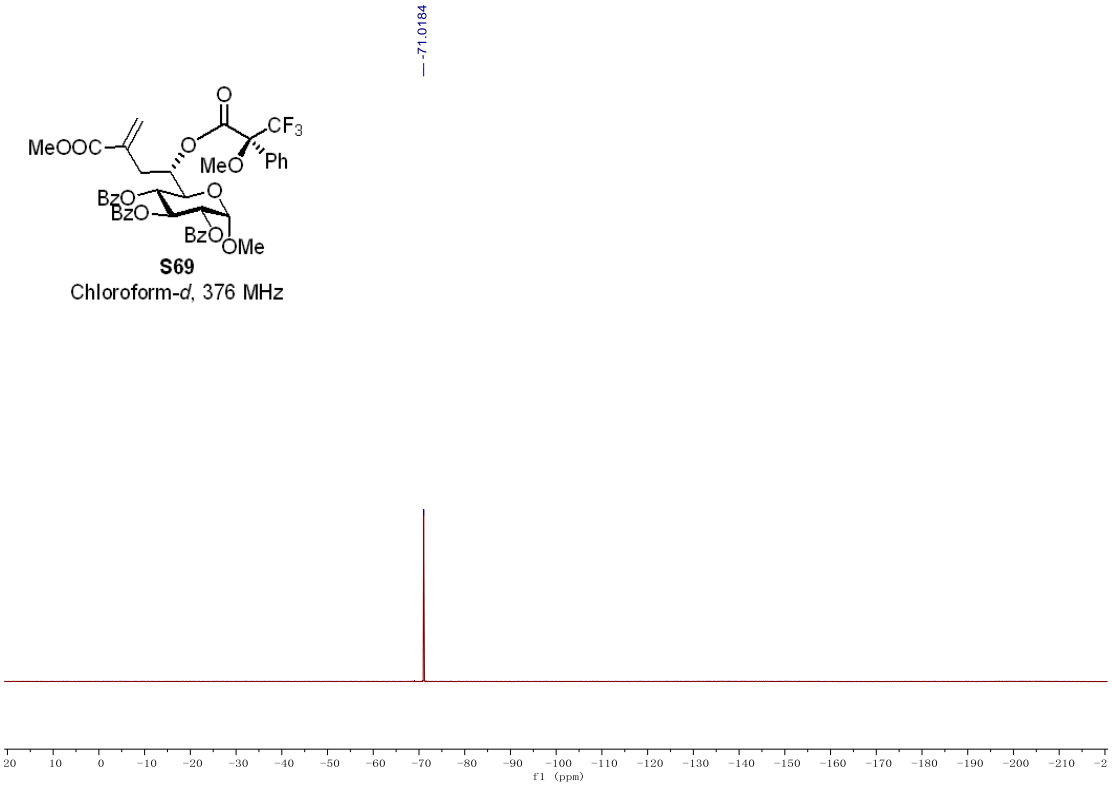
^{13}C NMR Spectra of compound S68



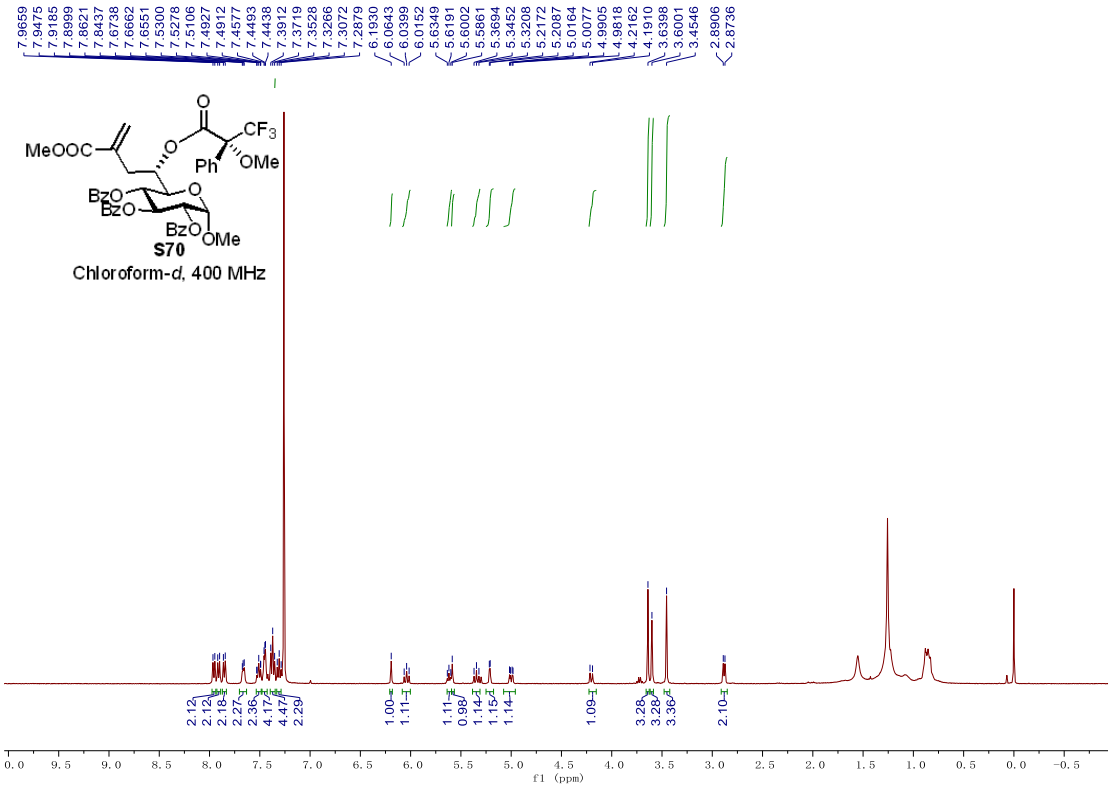
^{1}H NMR Spectra of compound S69



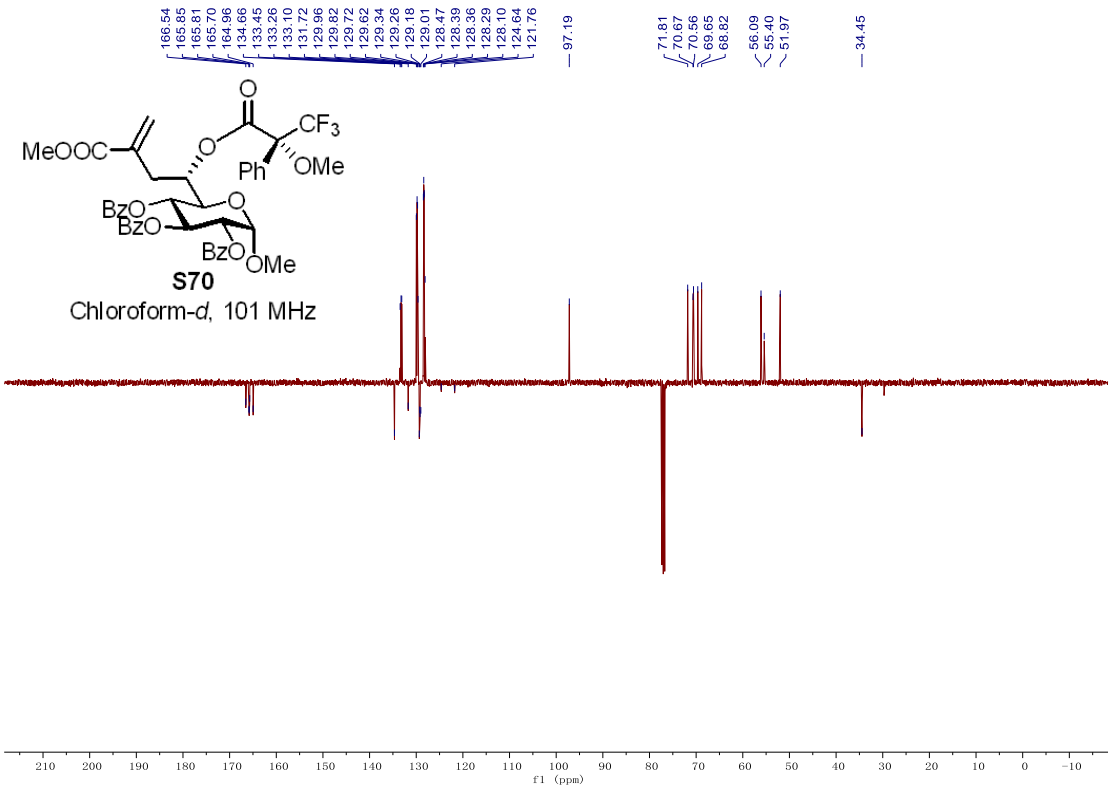
^{13}C NMR Spectra of compound S69



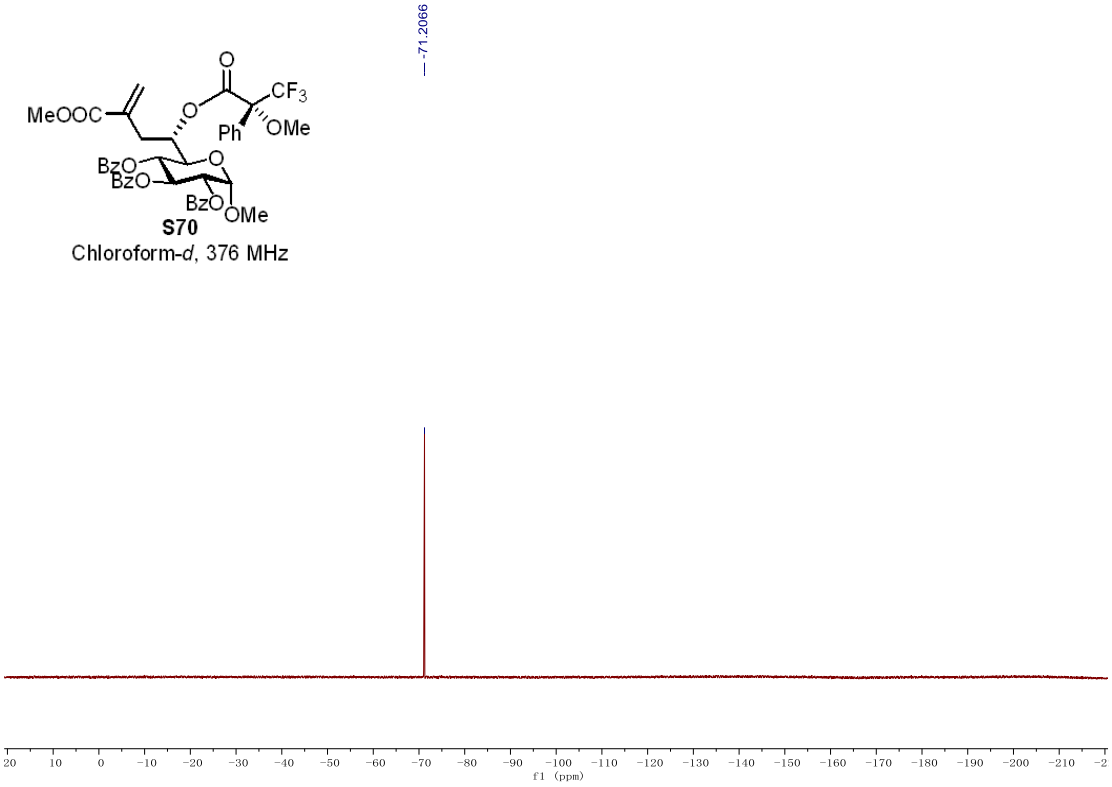
^{19}F NMR Spectra of compound S69



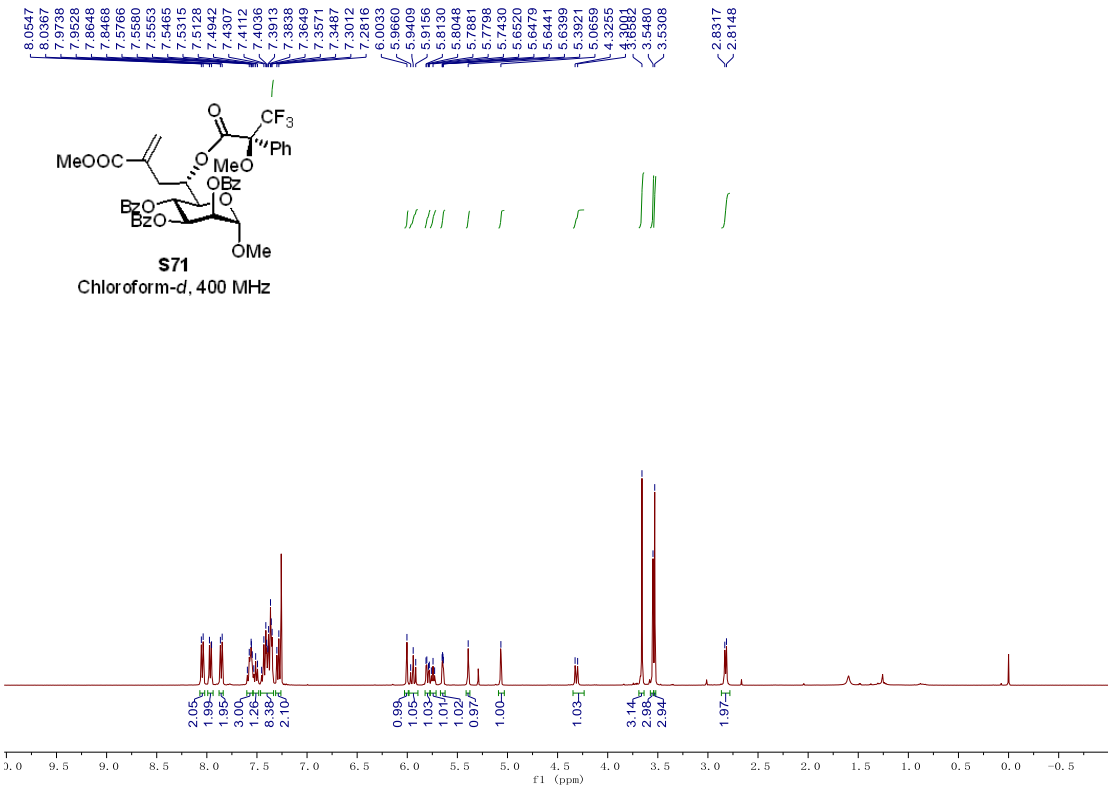
^{1}H NMR Spectra of compound S70



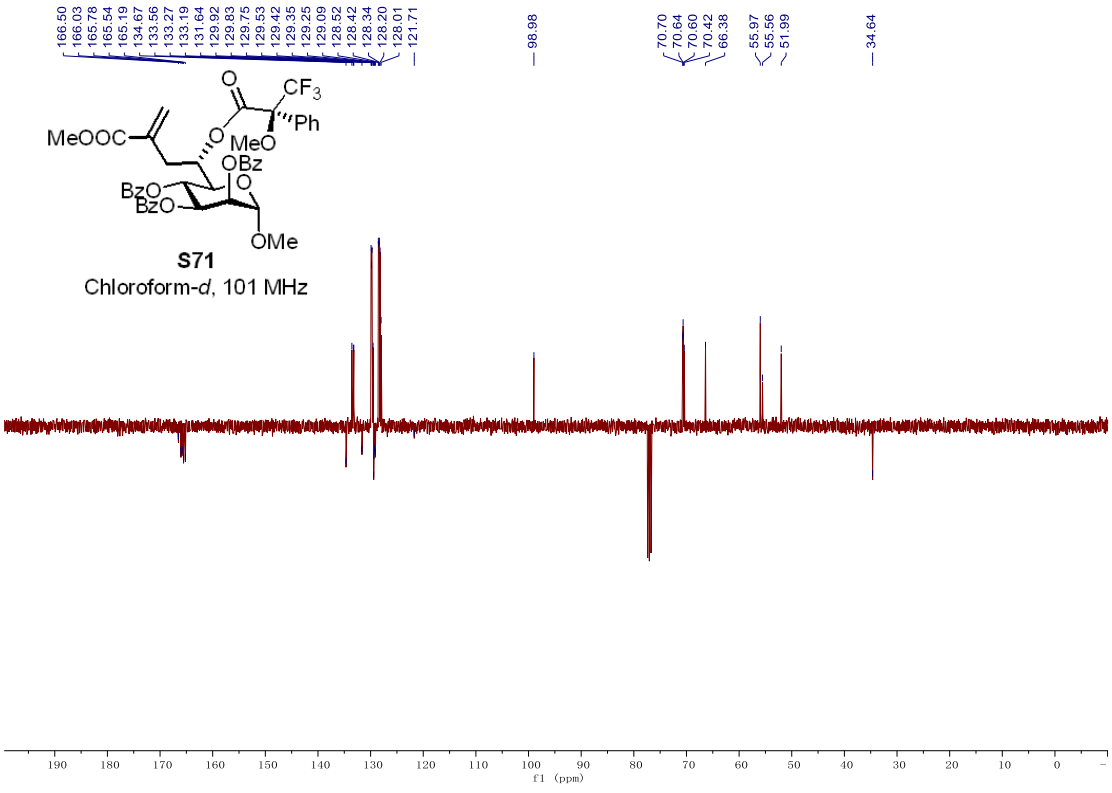
^{13}C NMR Spectra of compound S70



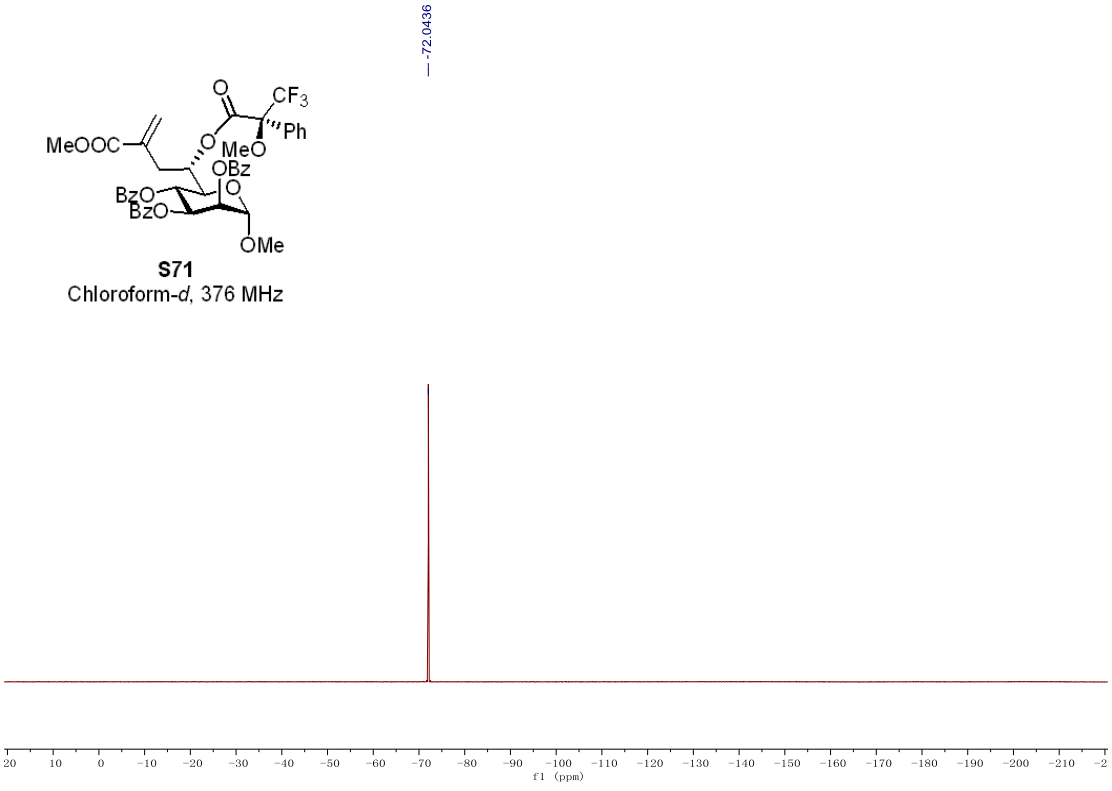
^{19}F NMR Spectra of compound S70



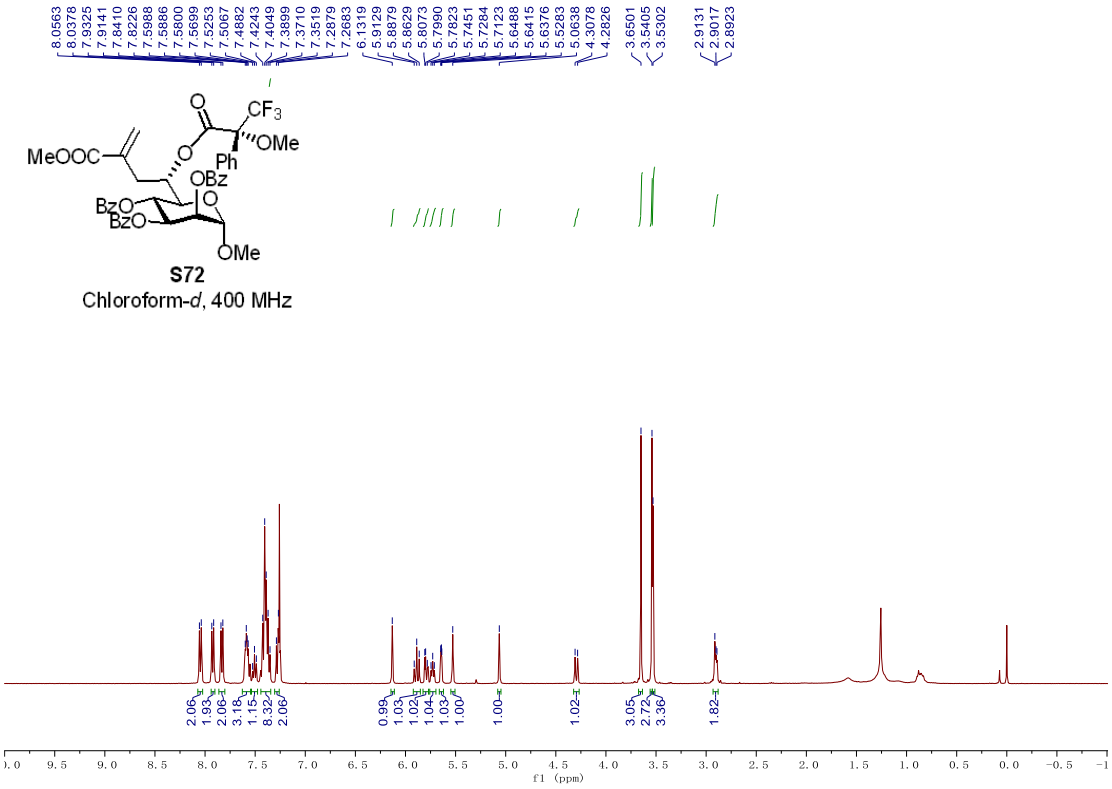
^{1}H NMR Spectra of compound S71



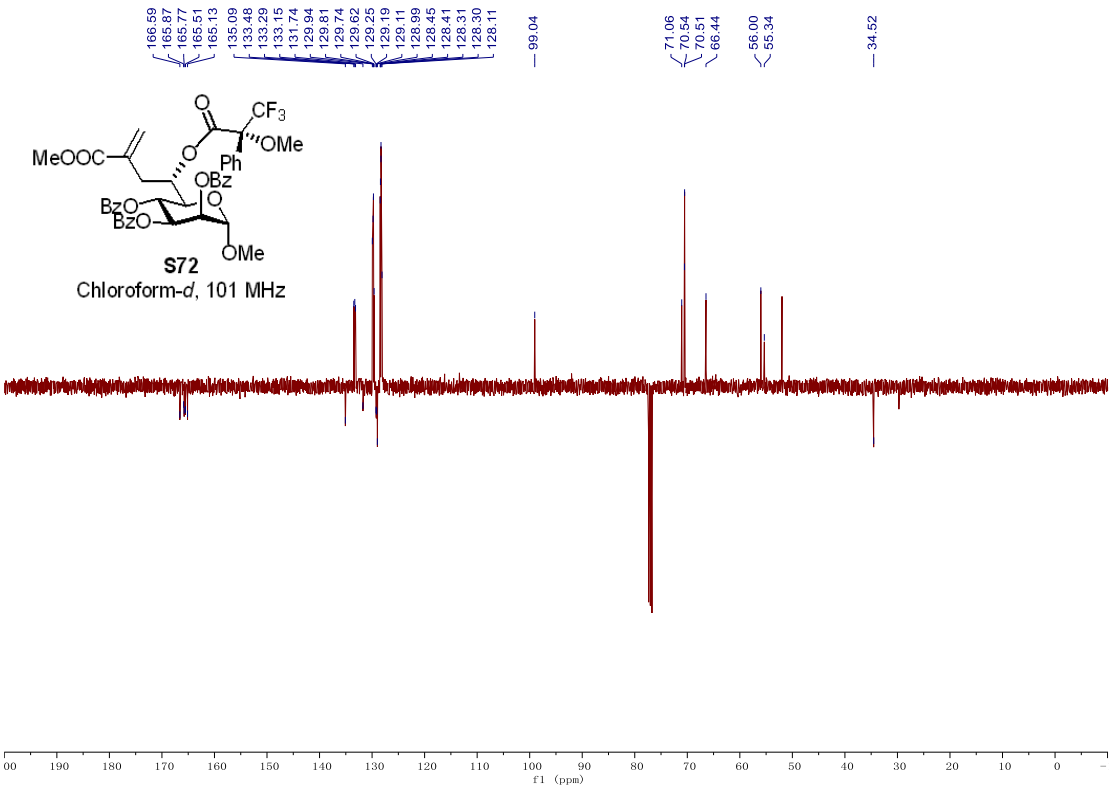
^{13}C NMR Spectra of compound S71



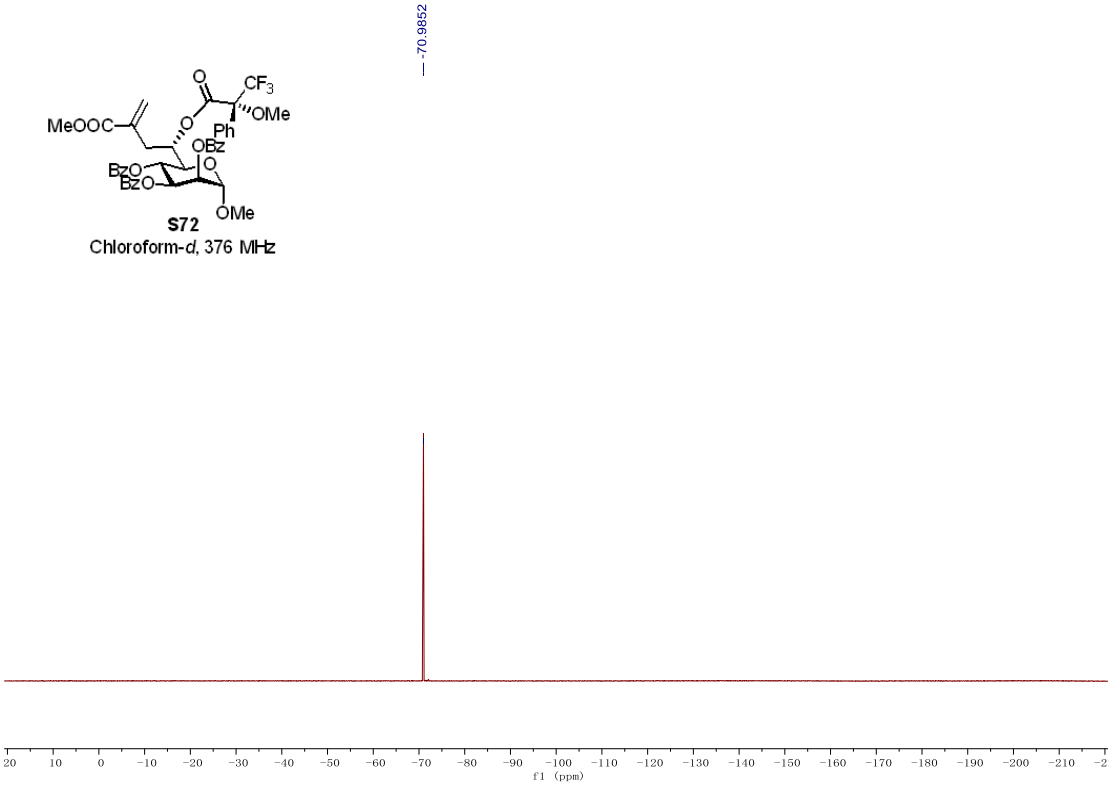
^{19}F NMR Spectra of compound S71



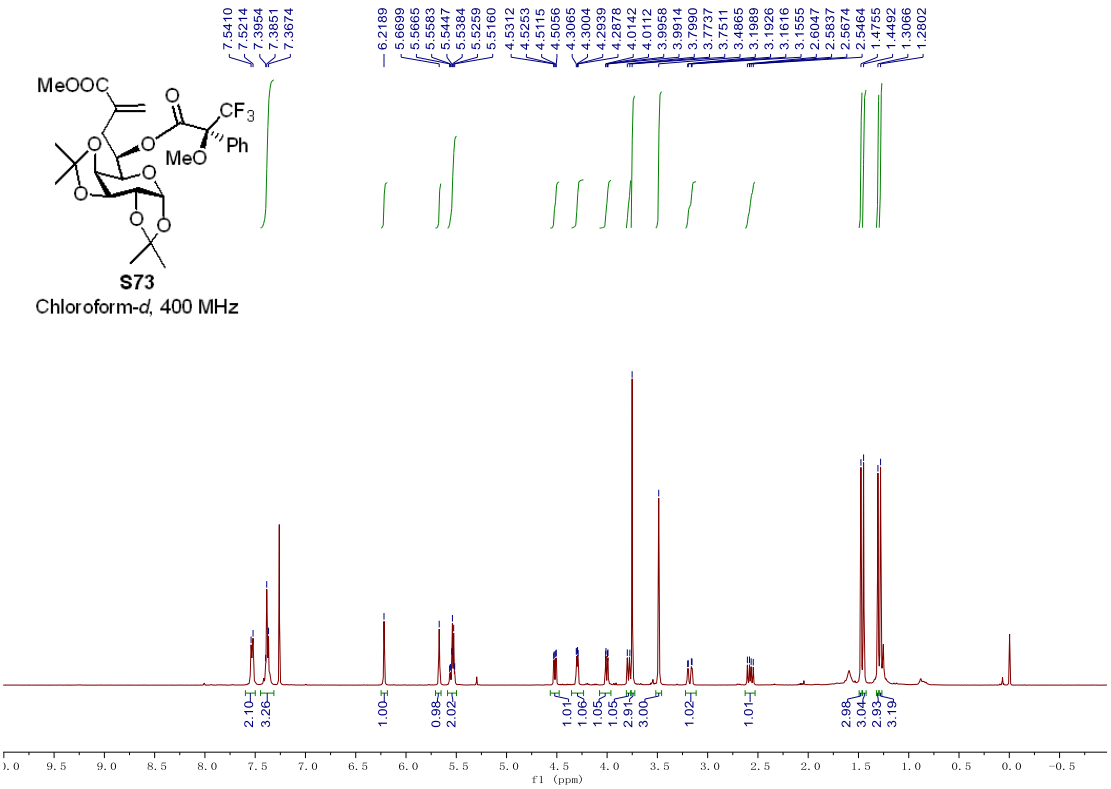
^{1}H NMR Spectra of compound S72



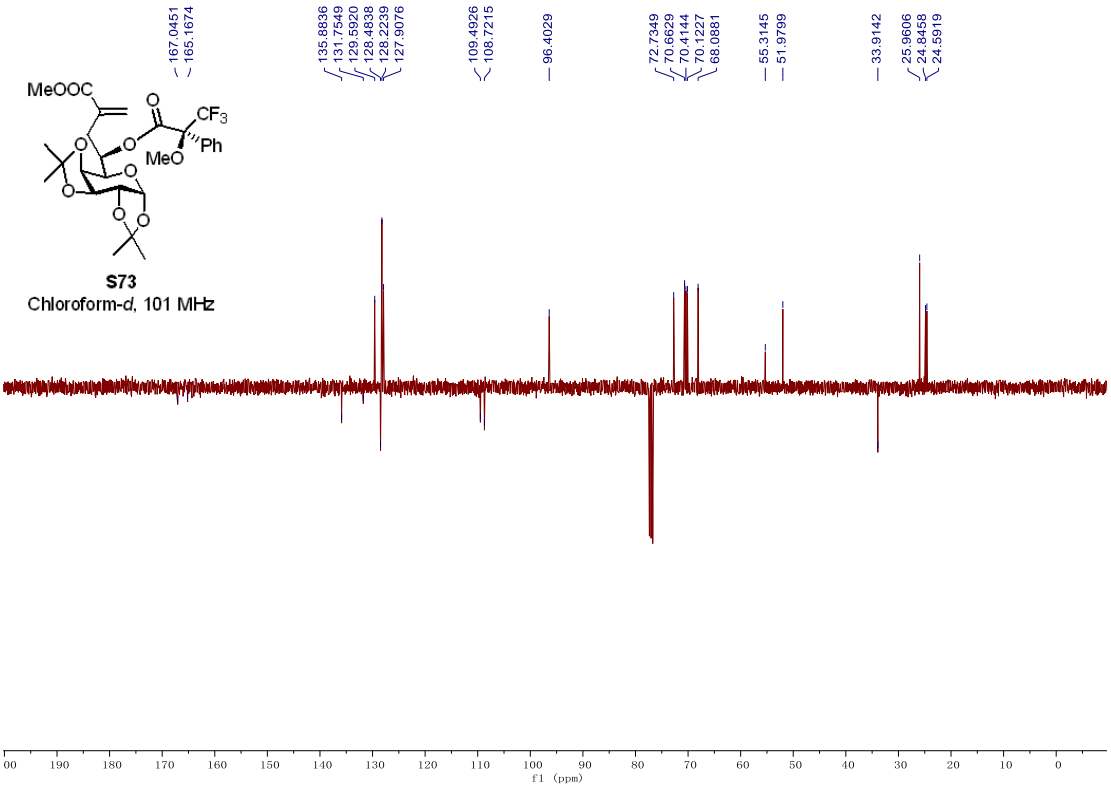
^{13}C NMR Spectra of compound S72



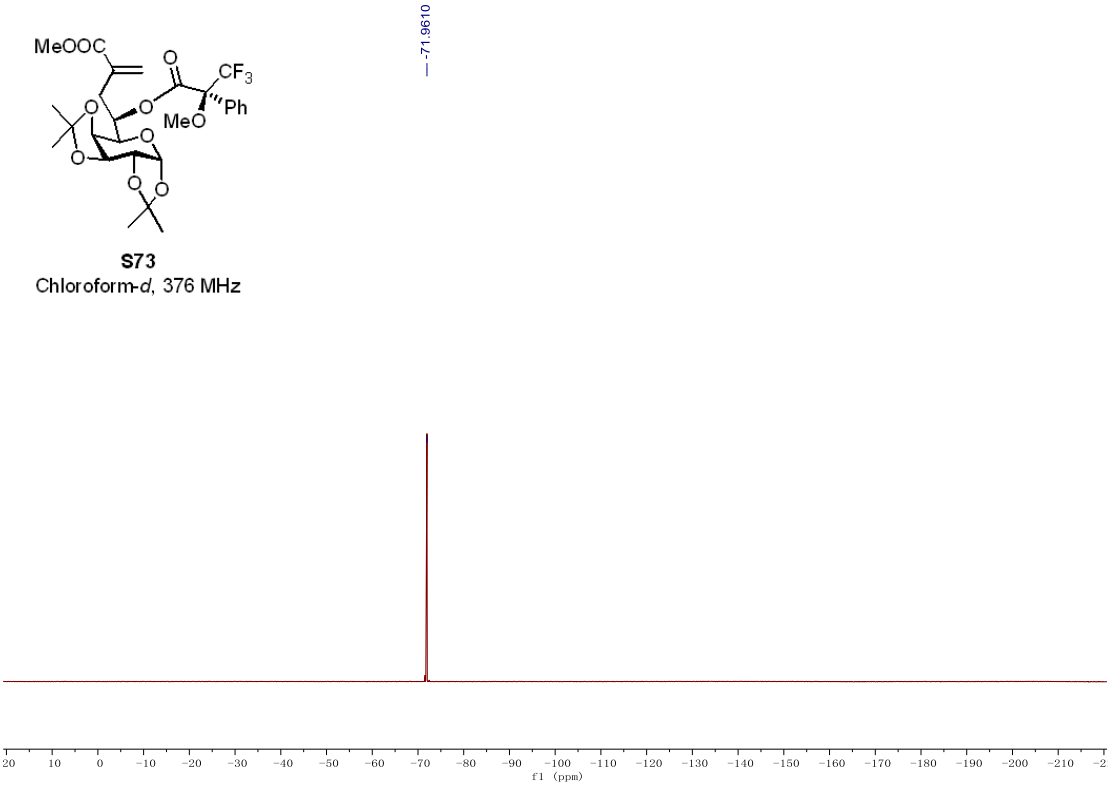
^{19}F NMR Spectra of compound S72



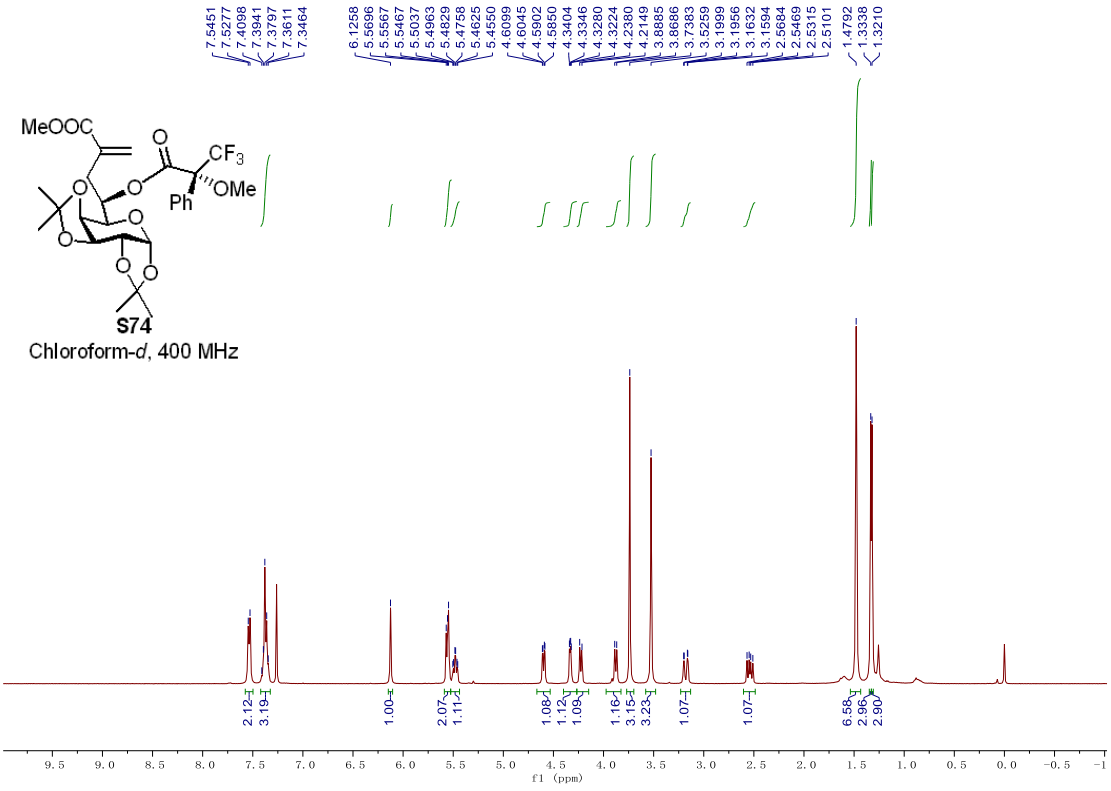
^{1}H NMR Spectra of compound S73



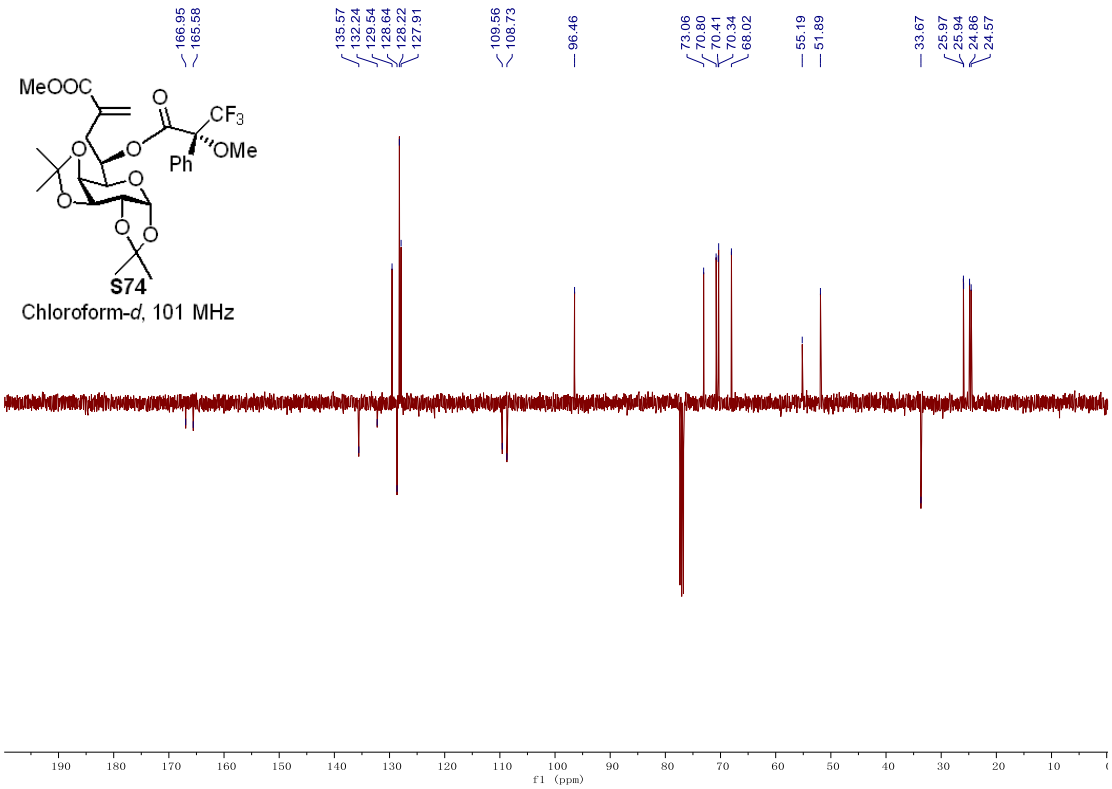
^{13}C NMR Spectra of compound S73



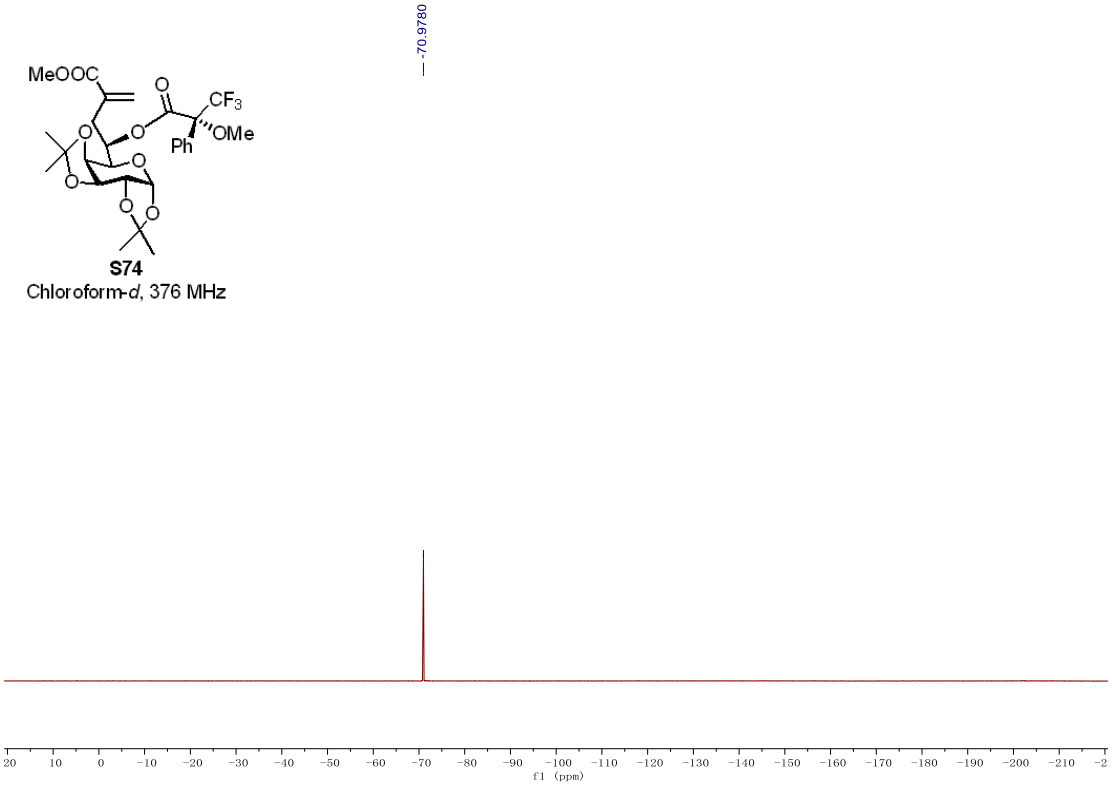
^{19}F NMR Spectra of compound S73



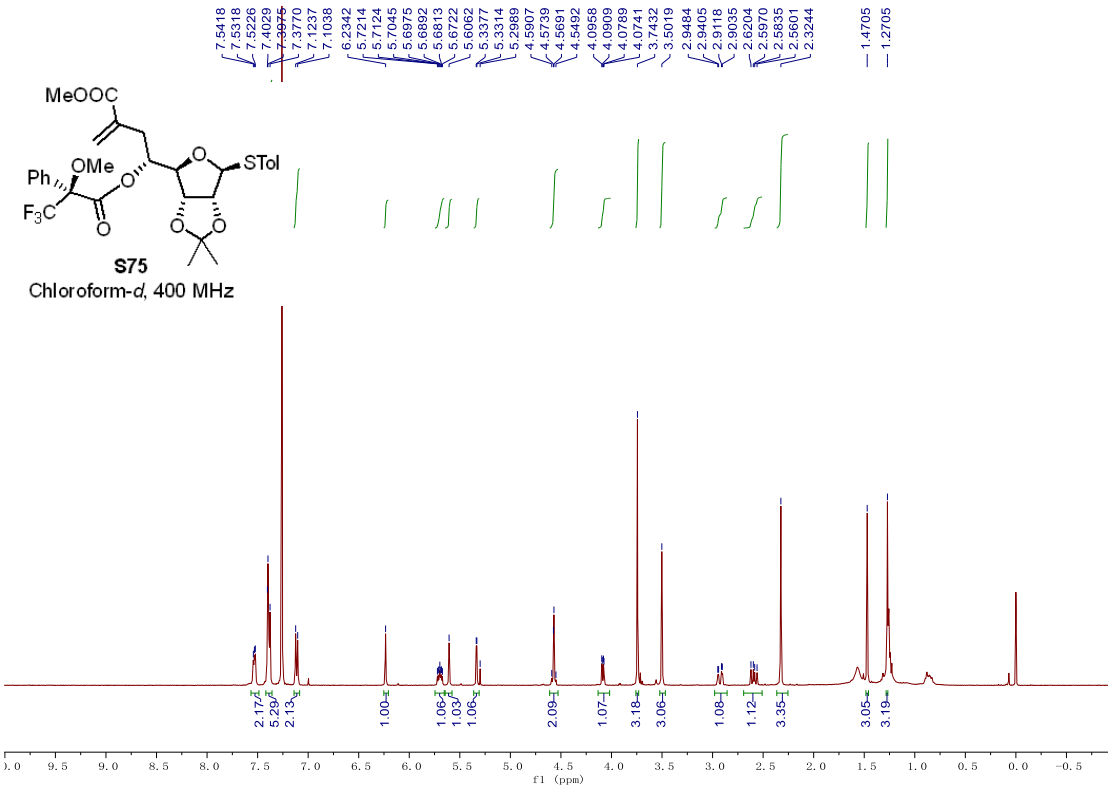
^{1}H NMR Spectra of compound S74



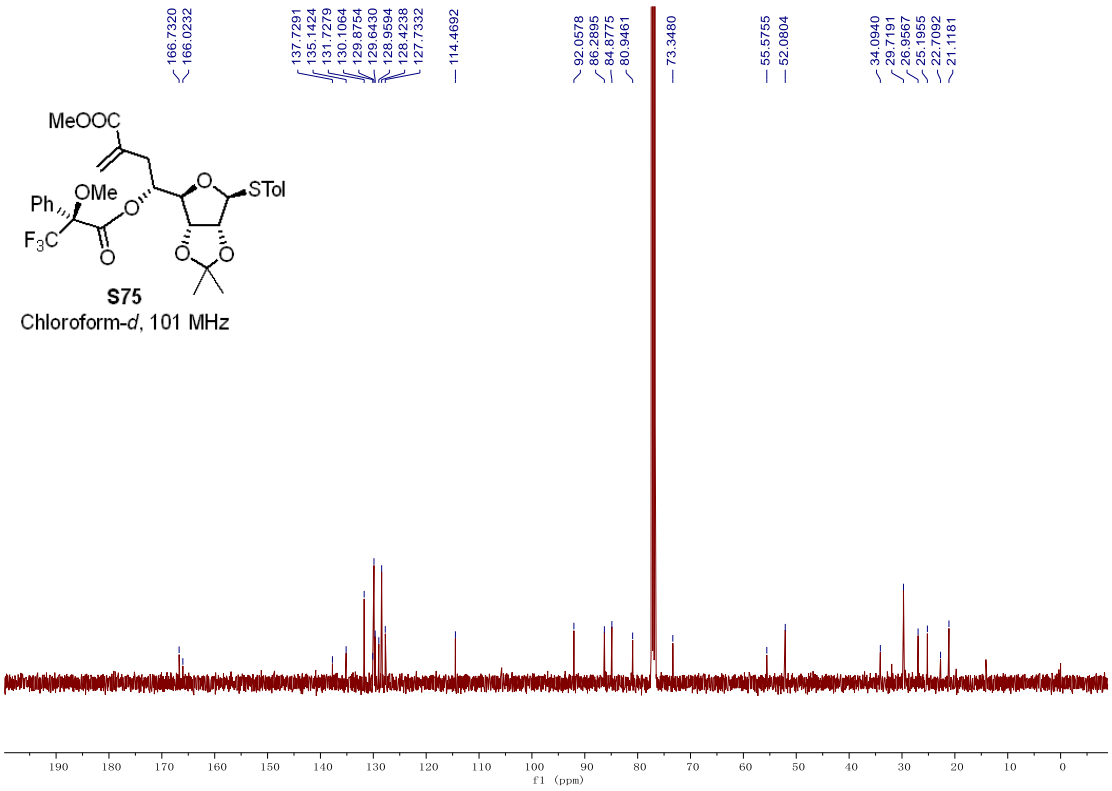
^{13}C NMR Spectra of compound S74



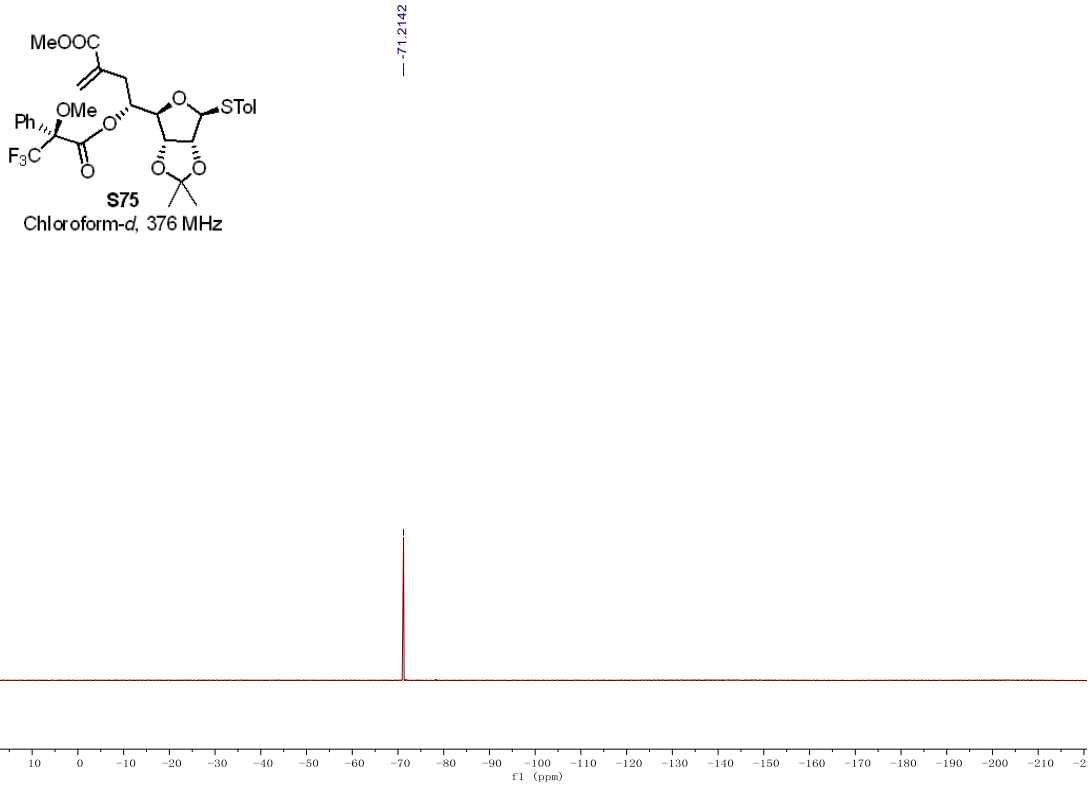
^{19}F NMR Spectra of compound S74



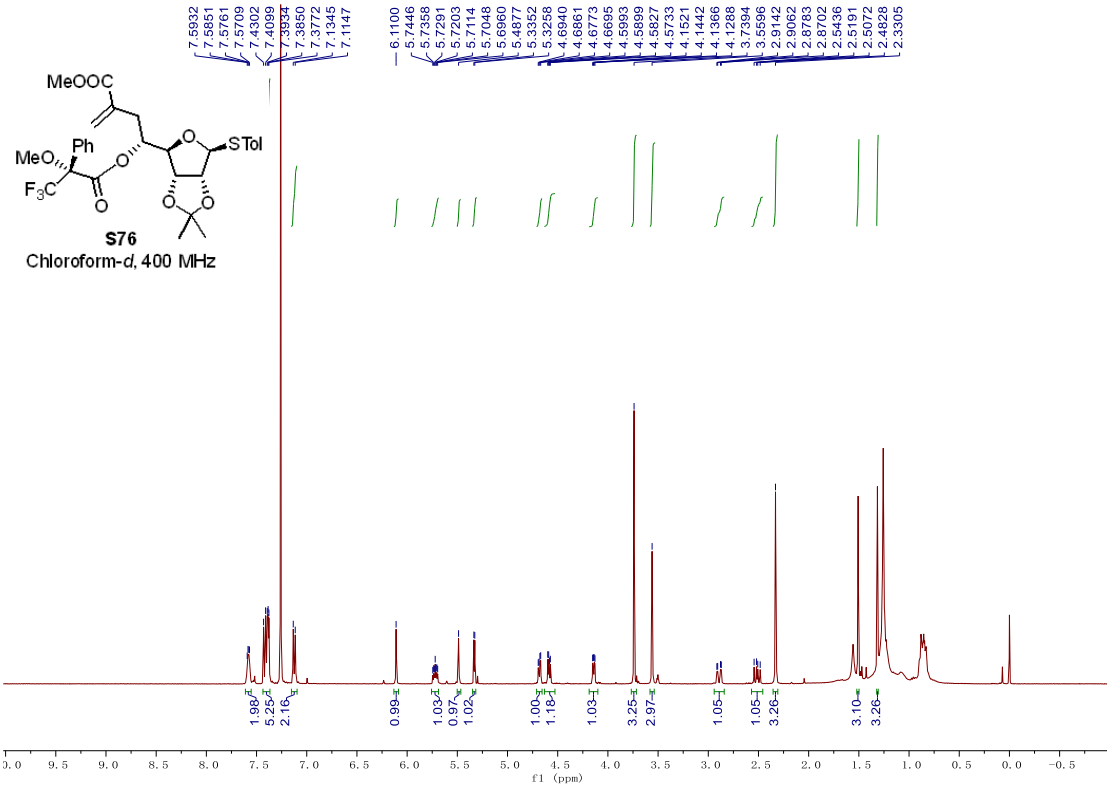
^{1}H NMR Spectra of compound S75



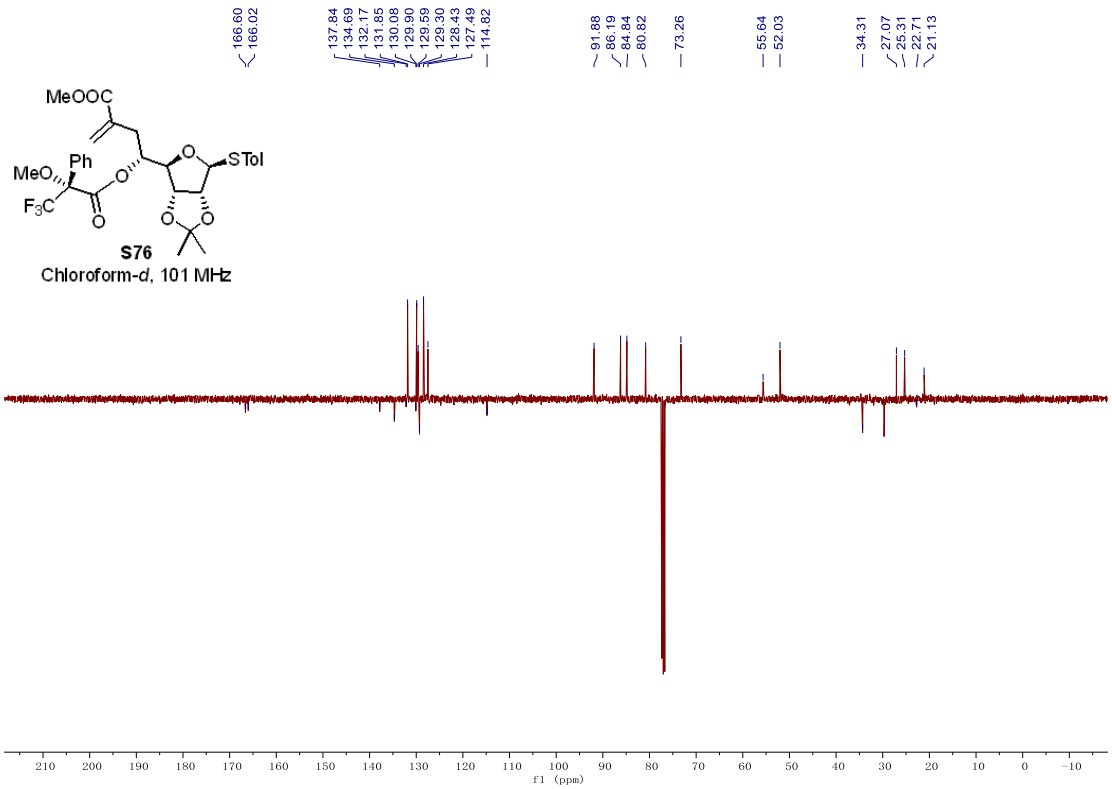
^{13}C NMR Spectra of compound S75



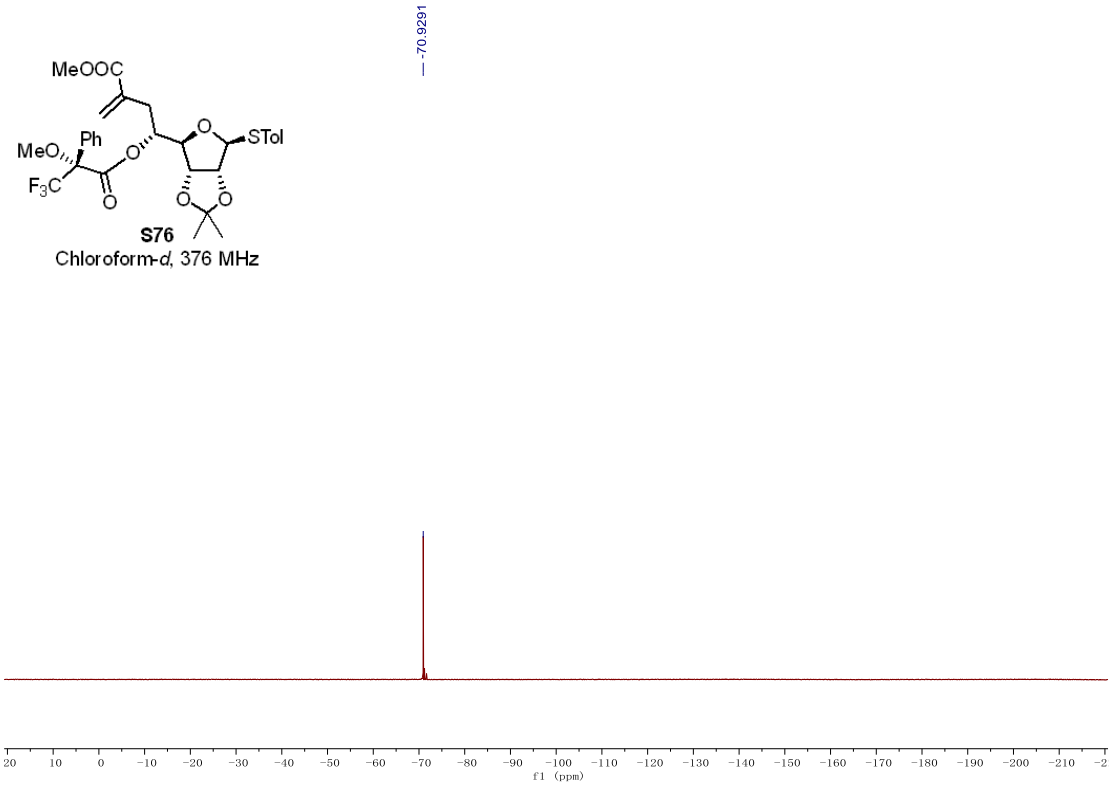
^{19}F NMR Spectra of compound S75



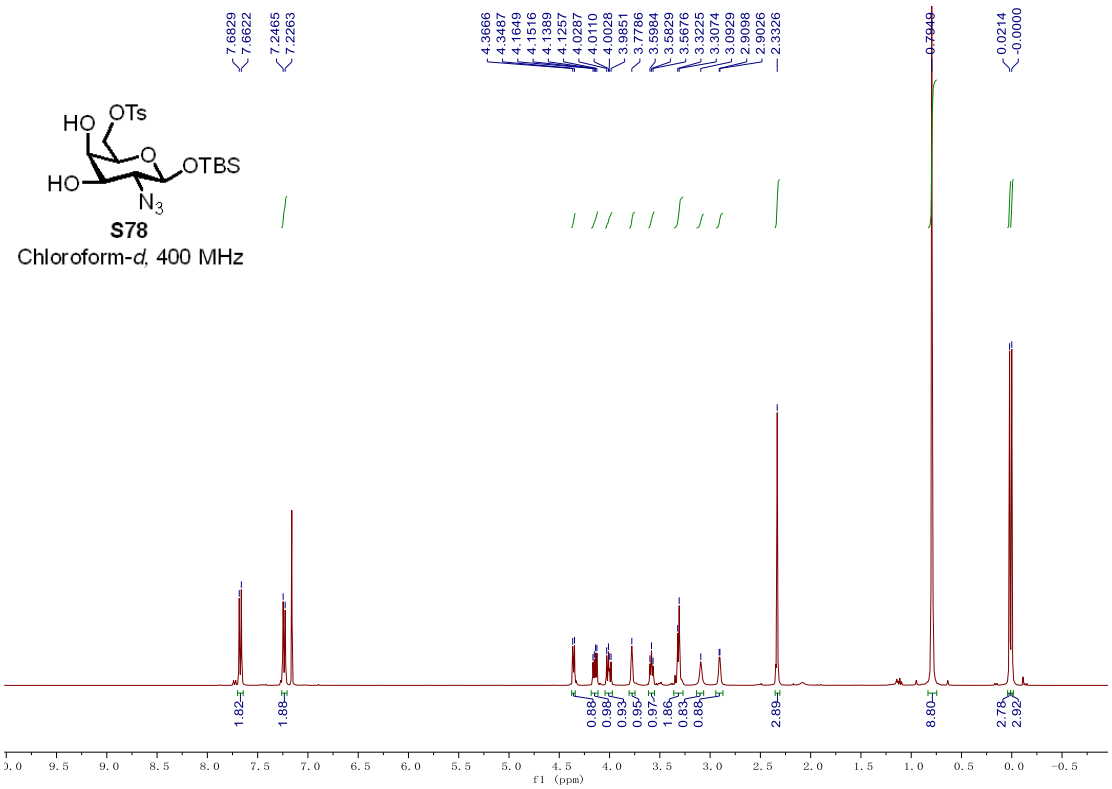
^{1}H NMR Spectra of compound S76



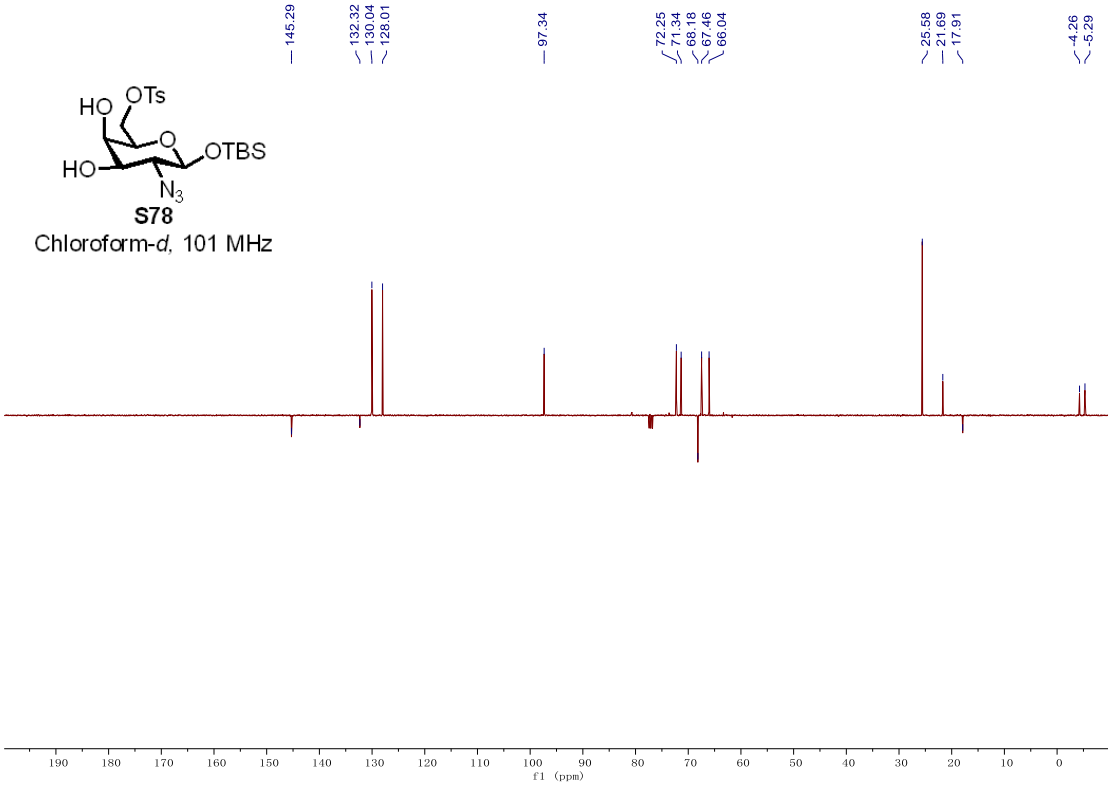
^{13}C NMR Spectra of compound S76



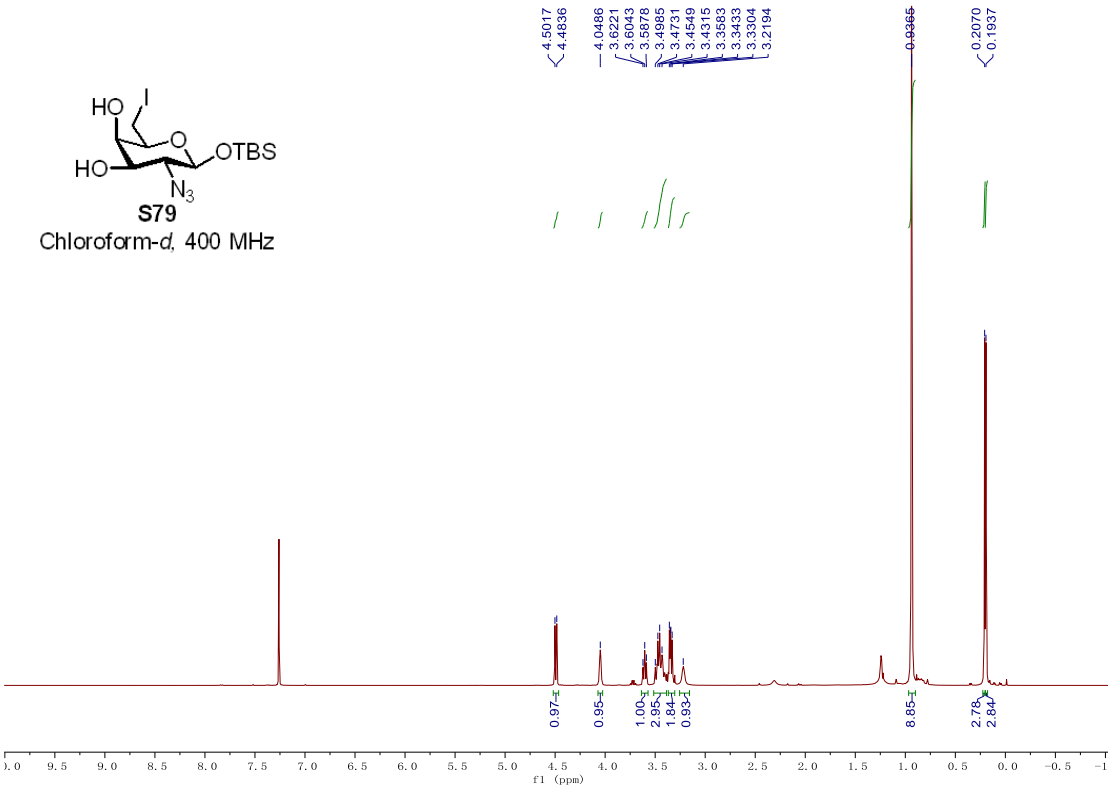
^{19}F NMR Spectra of compound S76



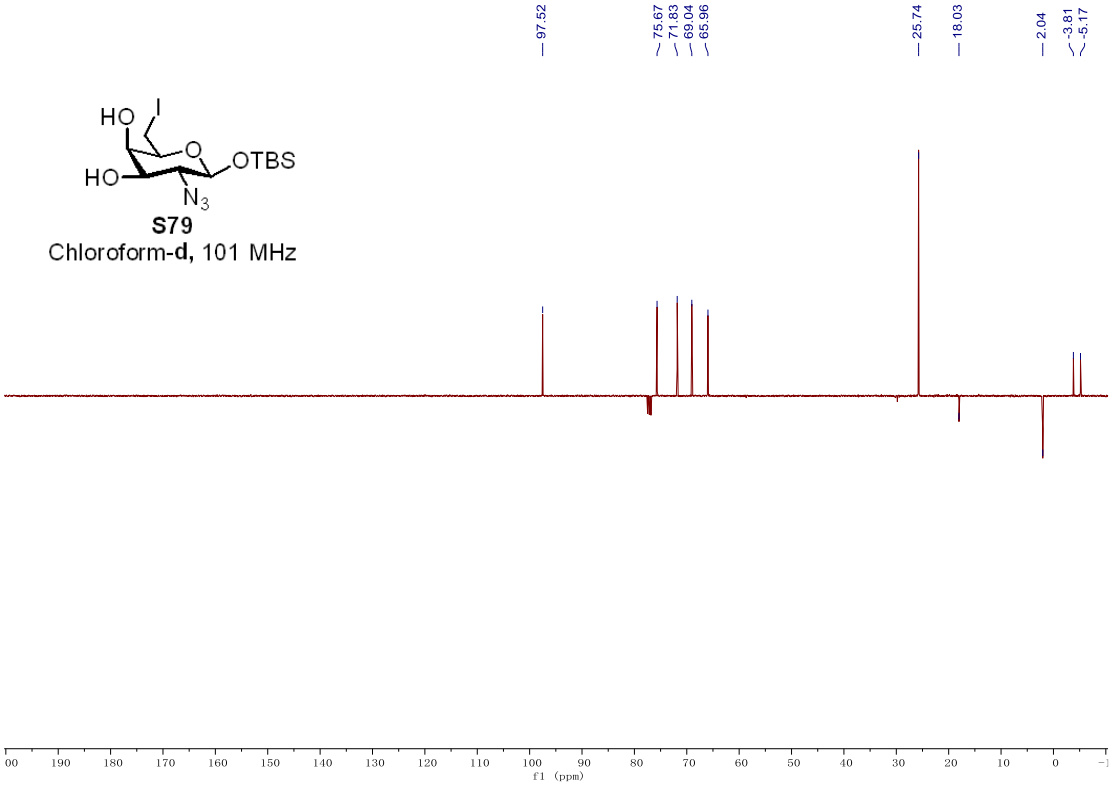
^{1}H NMR Spectra of compound S78



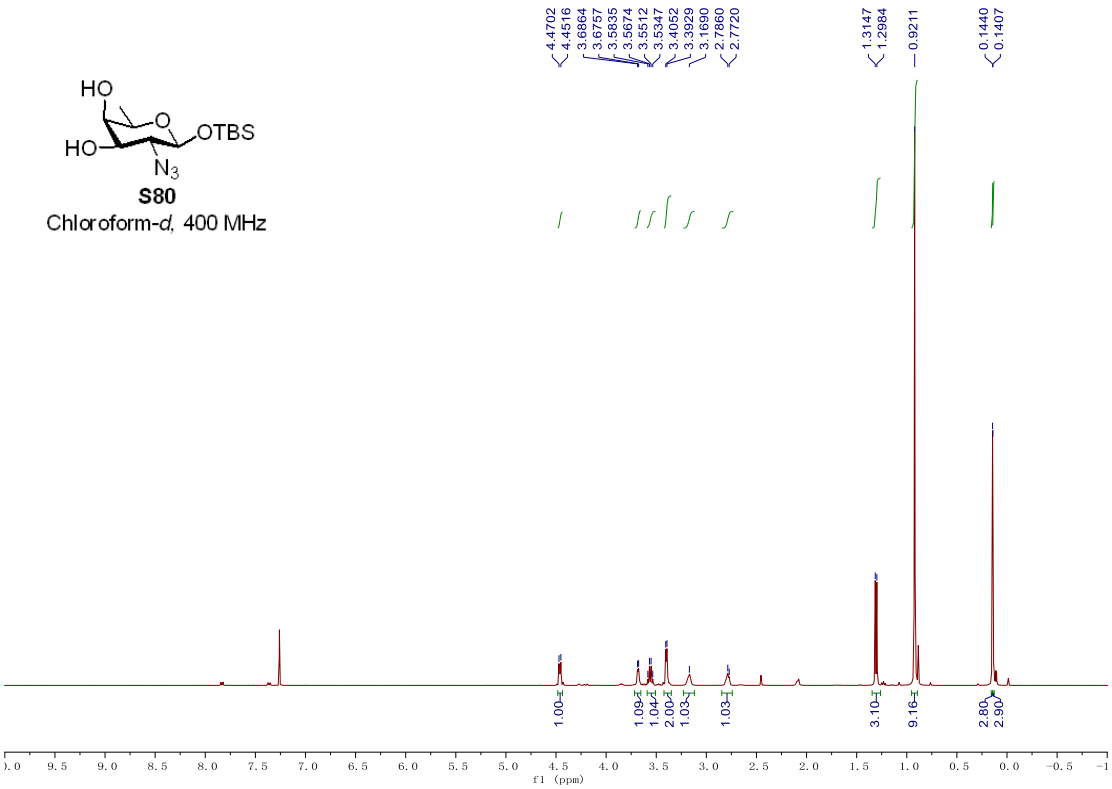
^{13}C NMR Spectra of compound S78



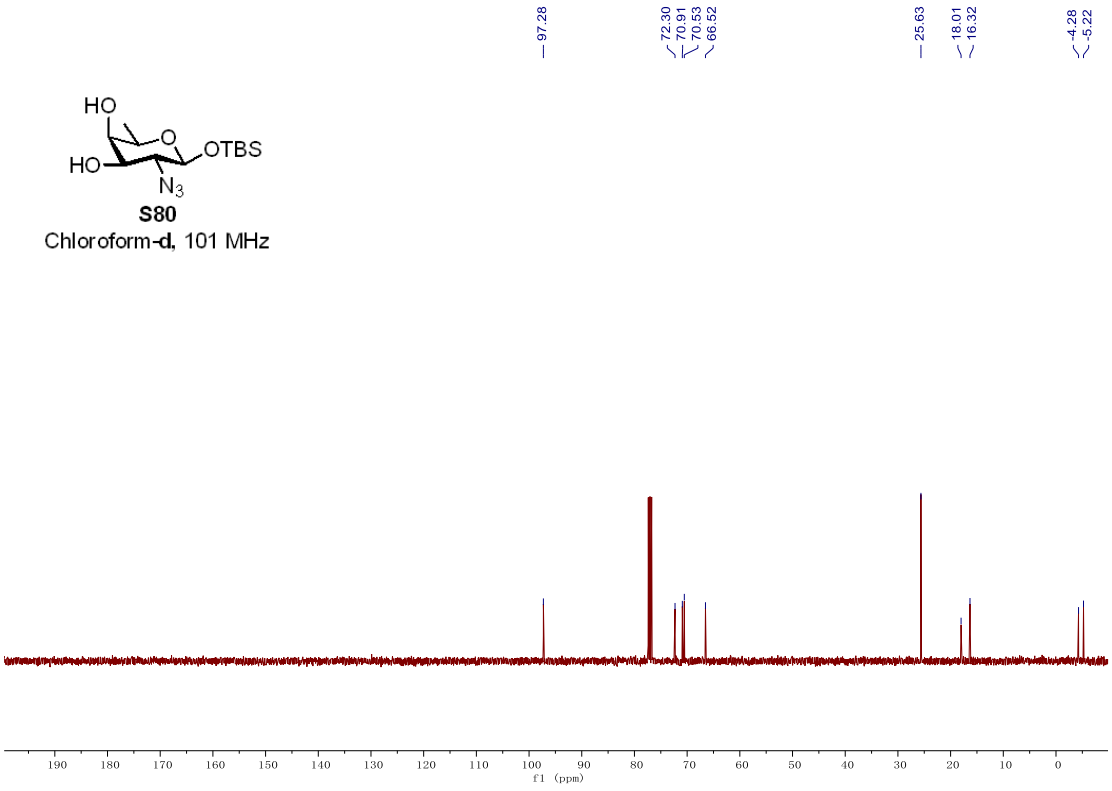
^{1}H NMR Spectra of compound S79



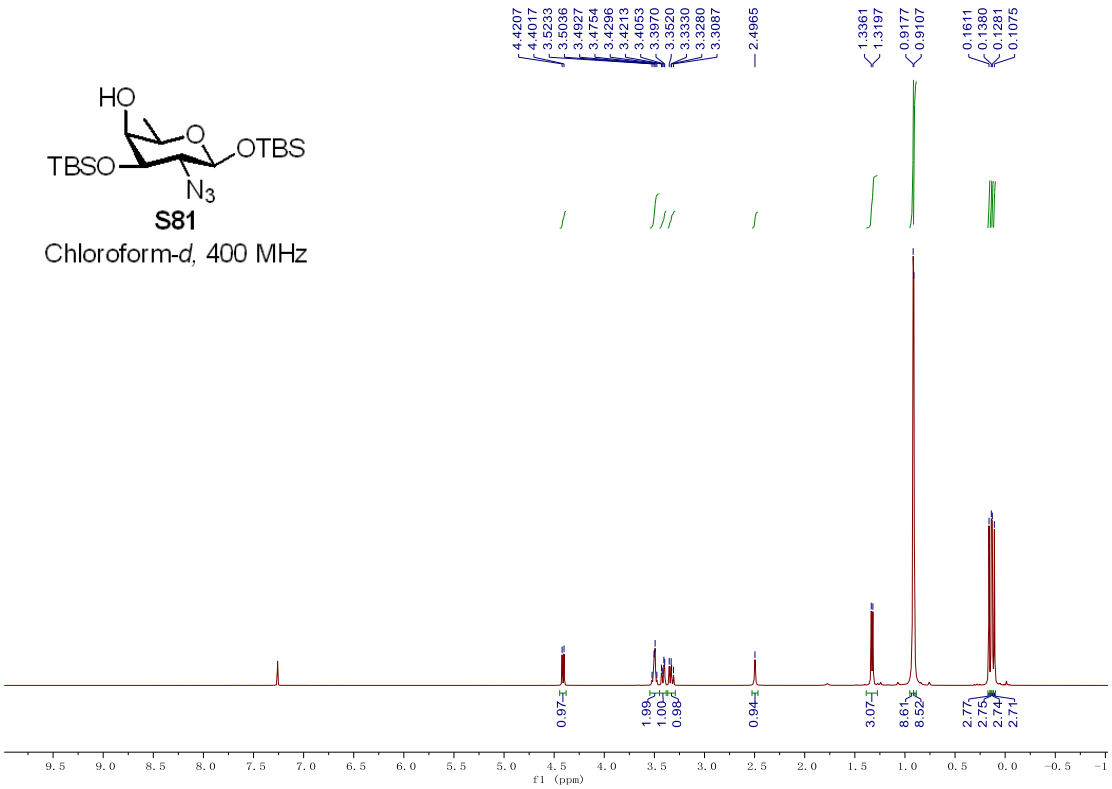
^{13}C NMR Spectra of compound S79



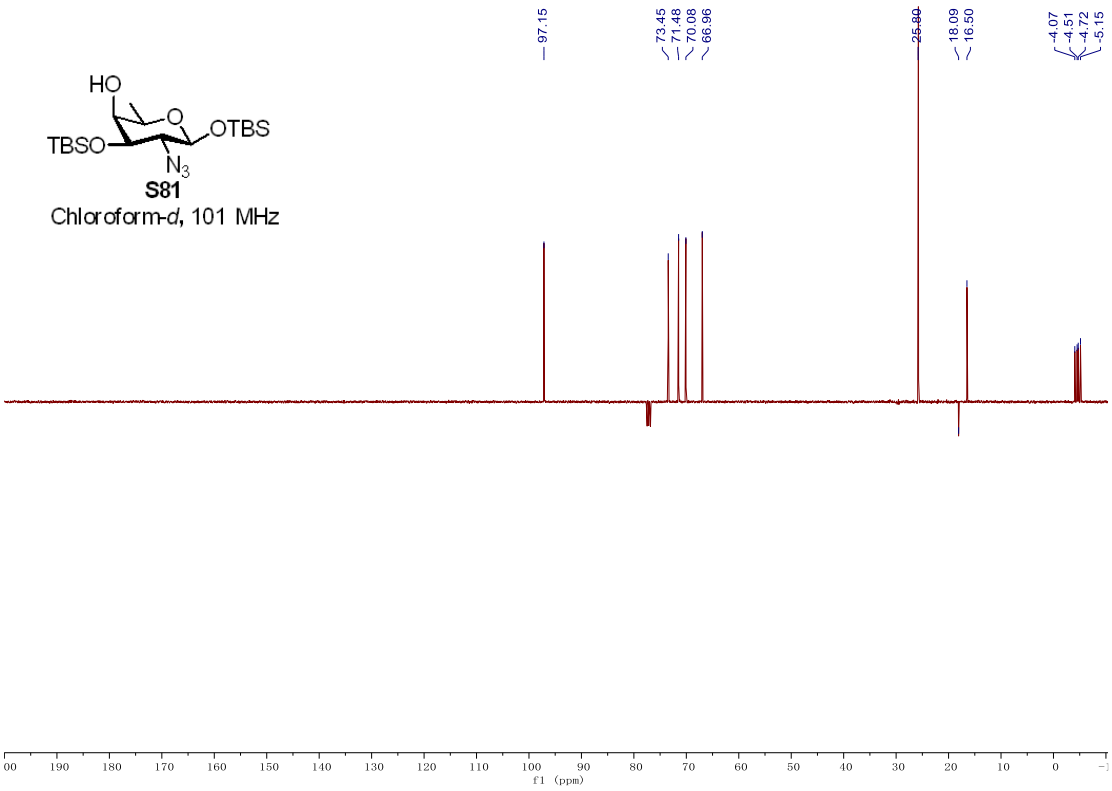
^{1}H NMR Spectra of compound S80



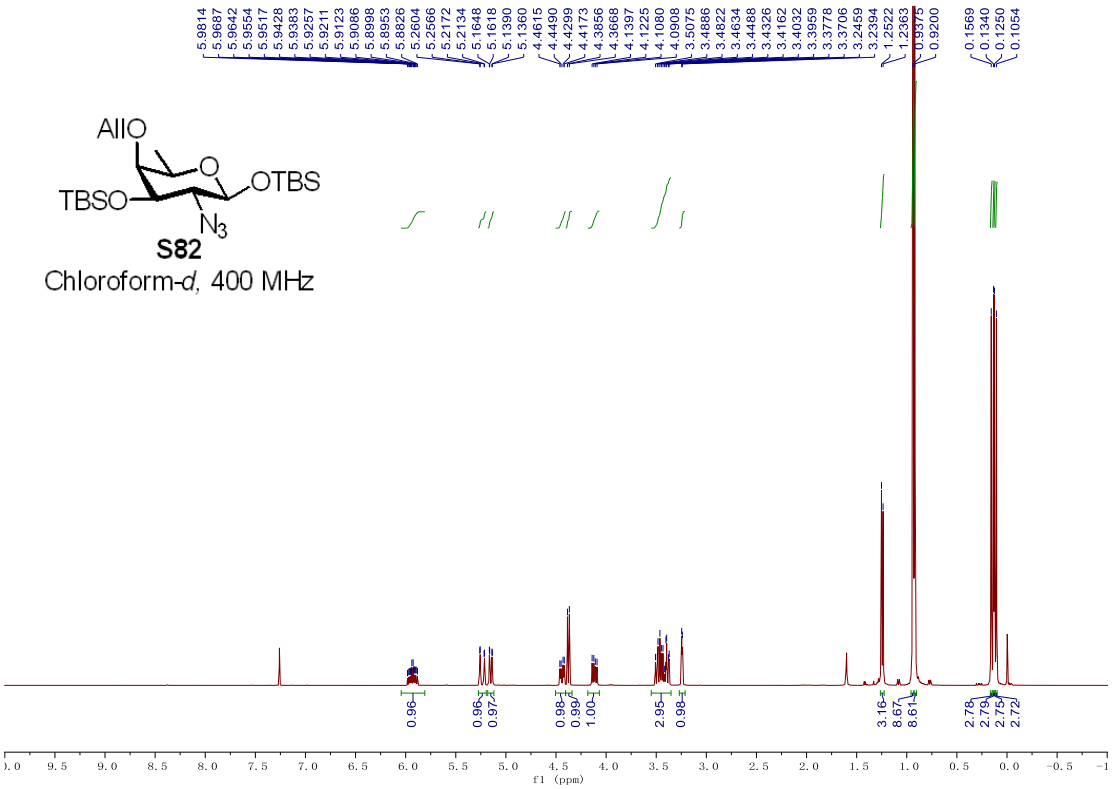
^{13}C NMR Spectra of compound S80



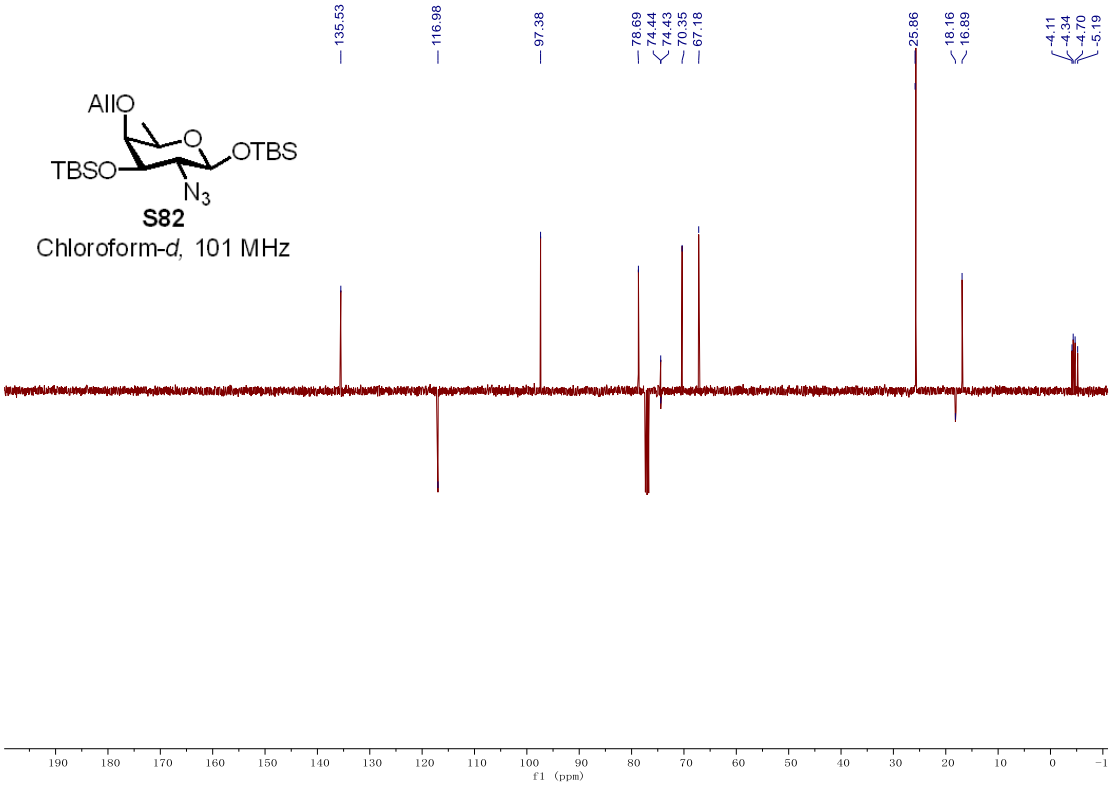
^{1}H NMR Spectra of compound S81



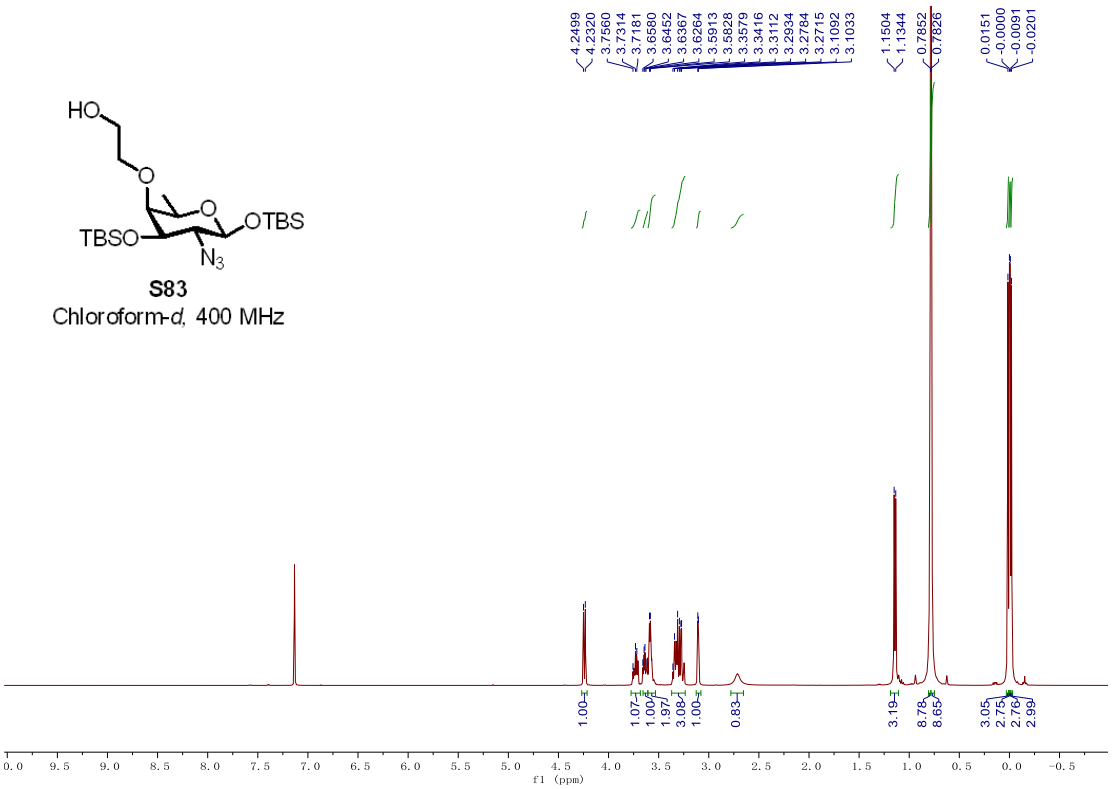
^{13}C NMR Spectra of compound S81



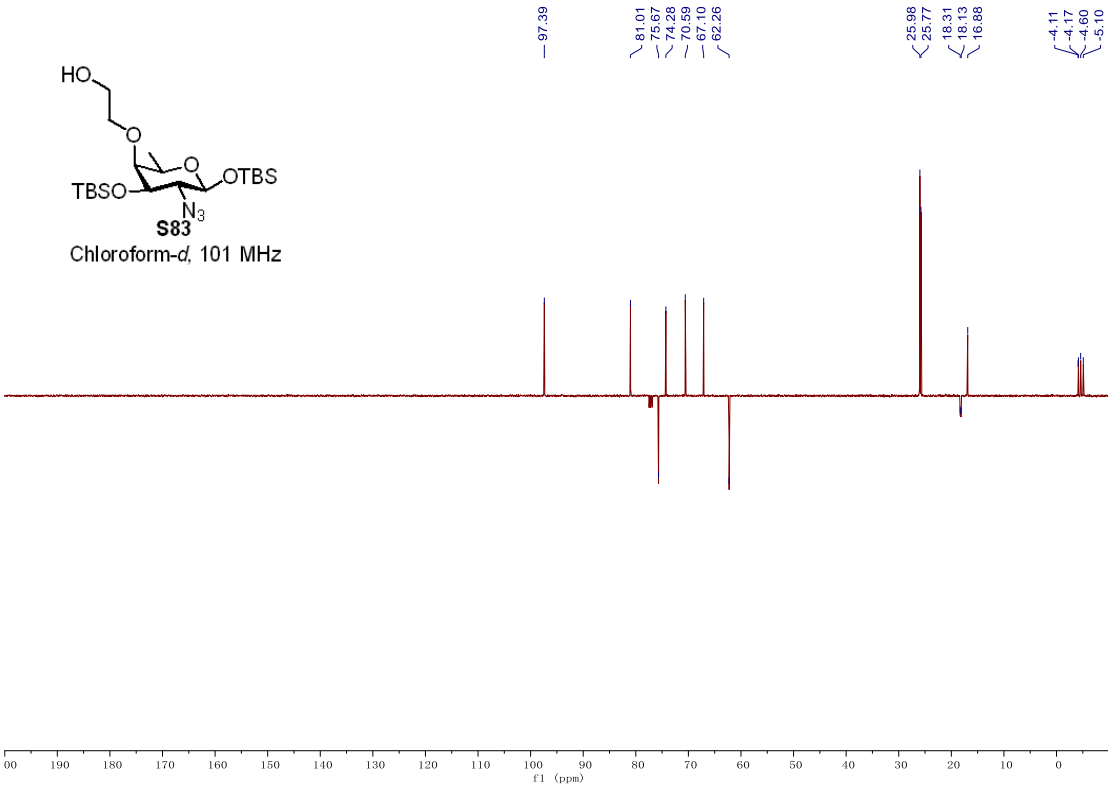
^{1}H NMR Spectra of compound S82



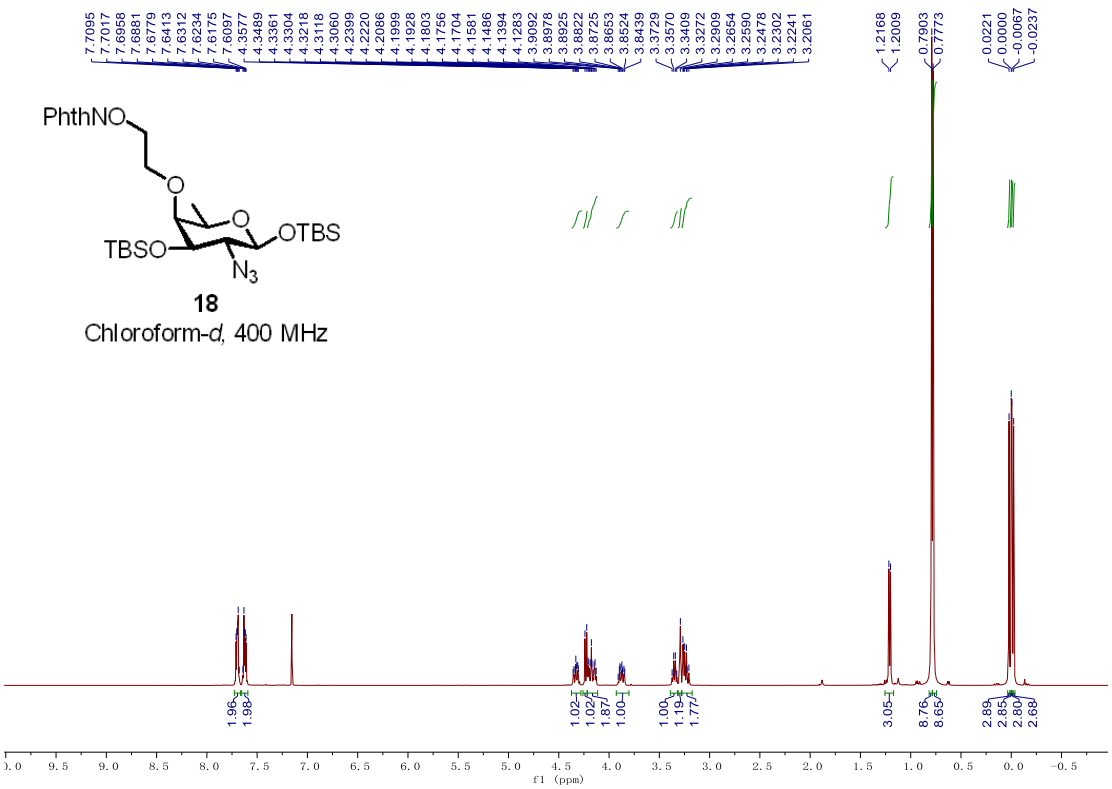
^{13}C NMR Spectra of compound S82



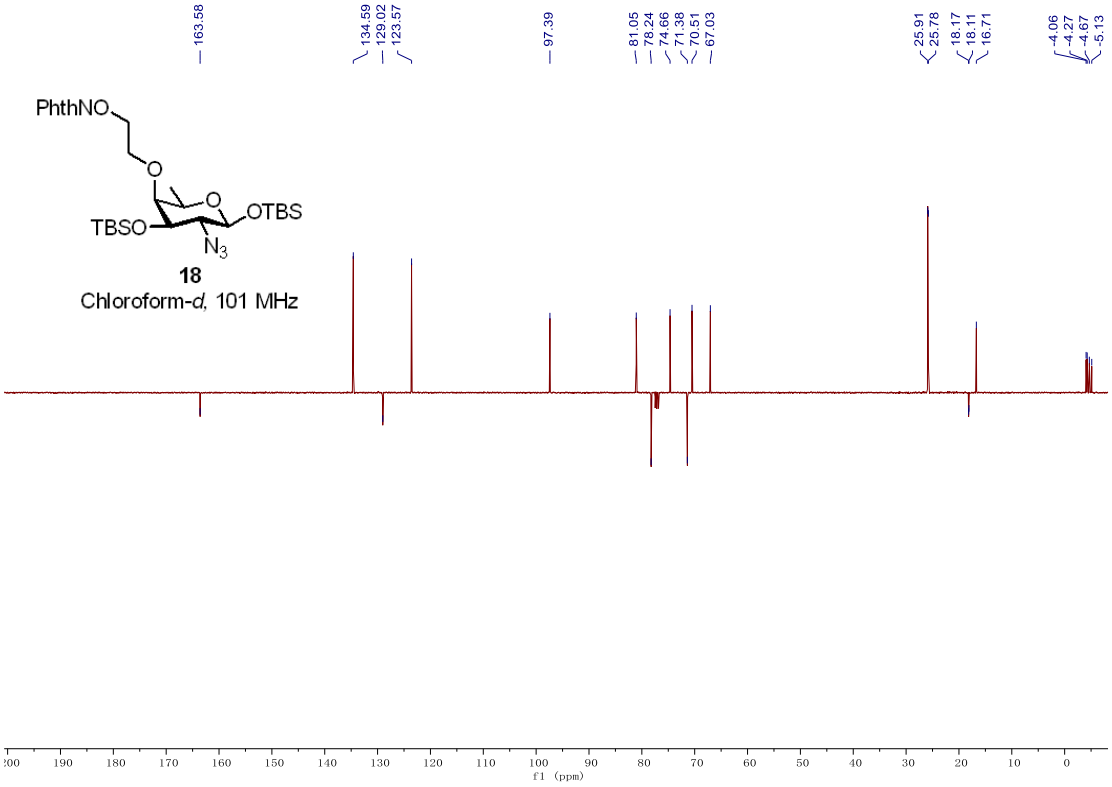
^{1}H NMR Spectra of compound S83



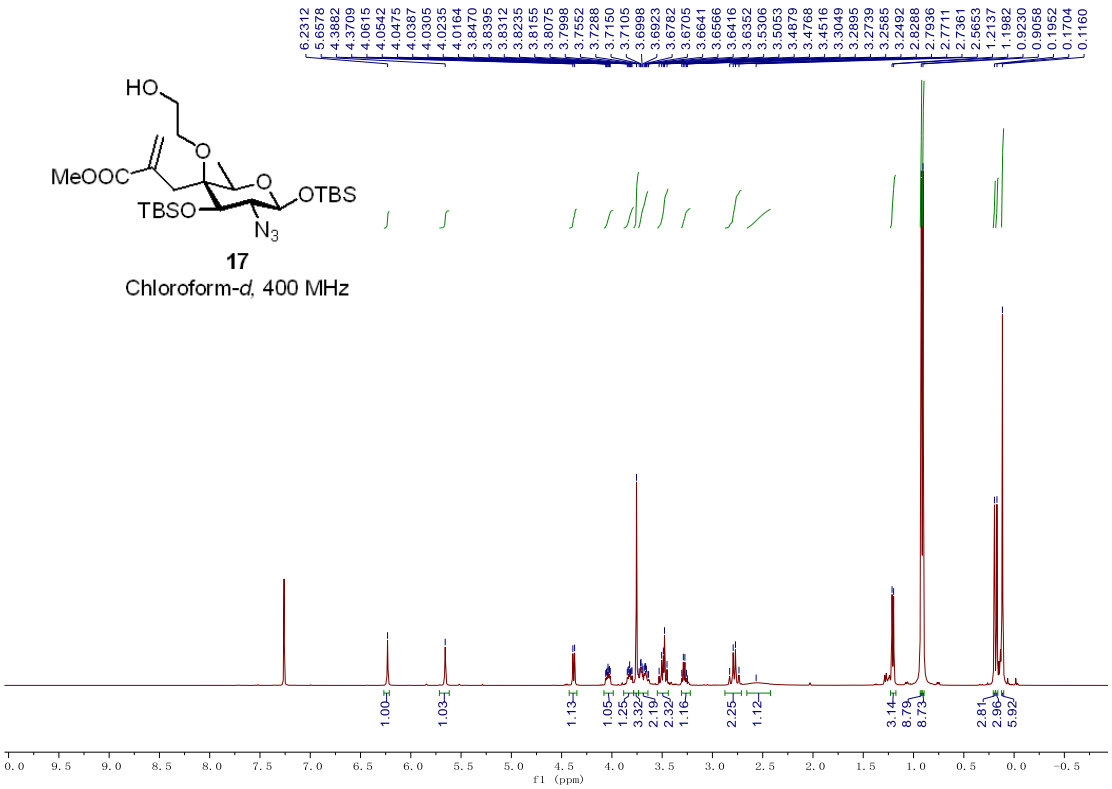
^{13}C NMR Spectra of compound S83



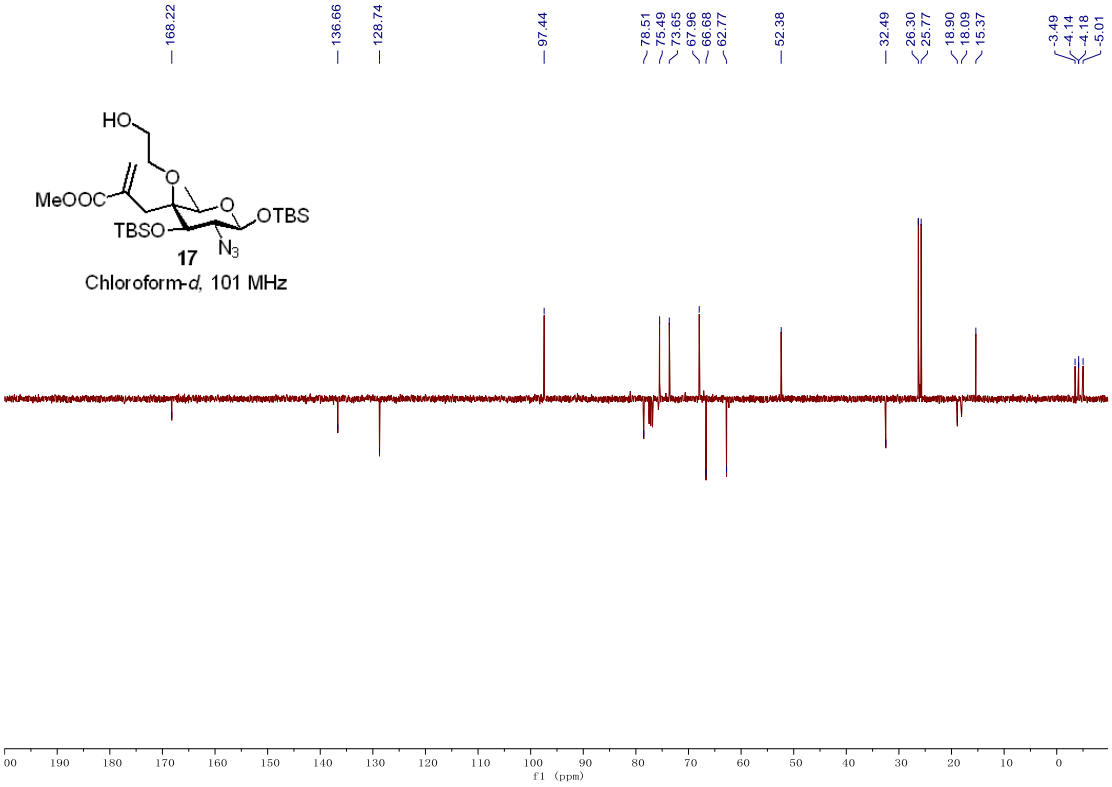
^{1}H NMR Spectra of compound 18



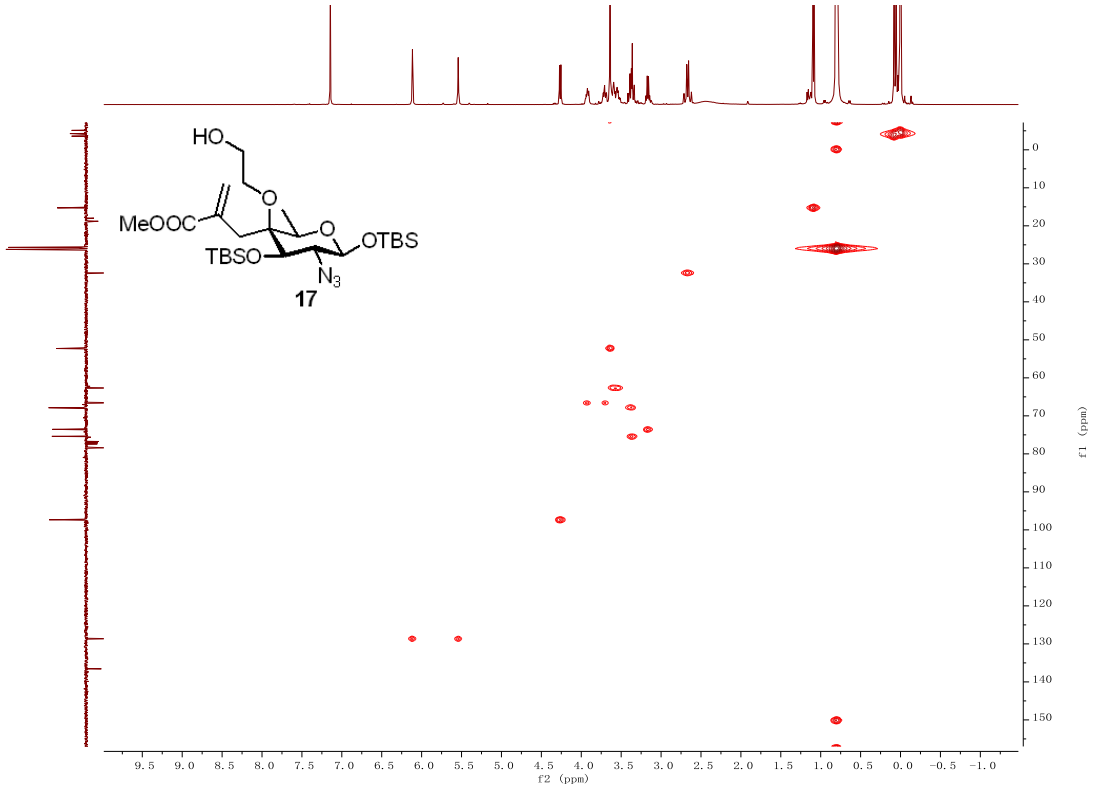
^{13}C NMR Spectra of compound 18



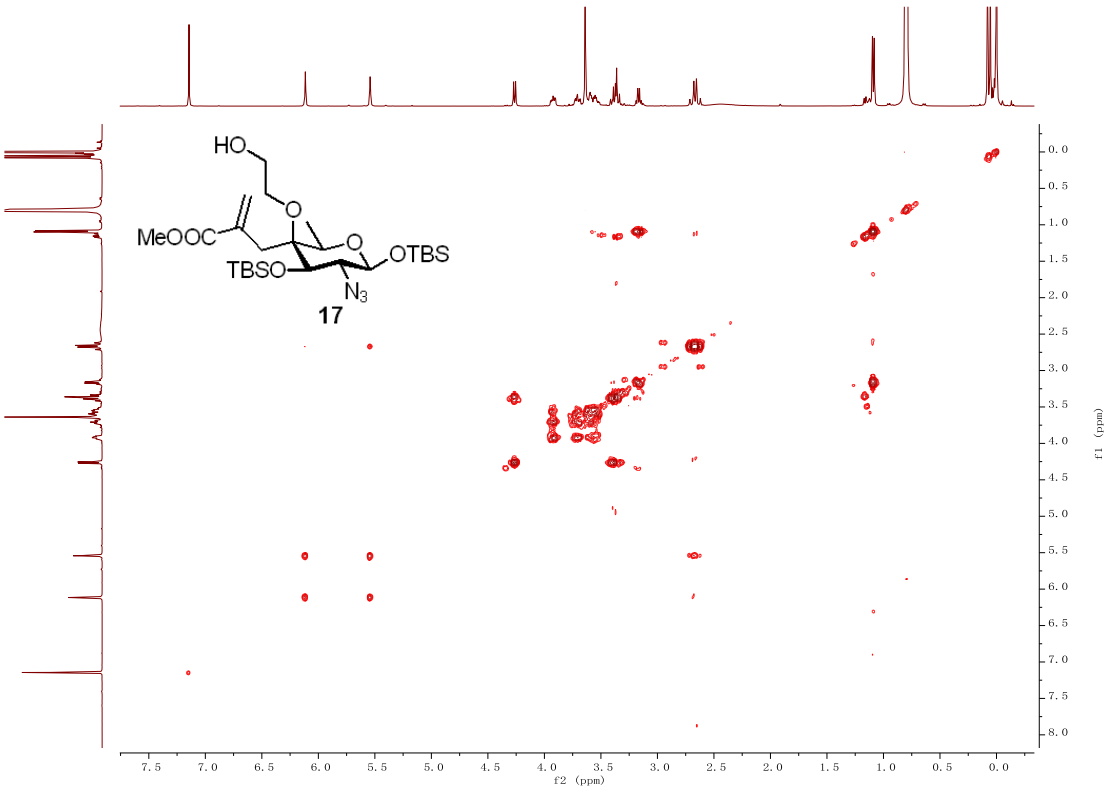
^{1}H NMR Spectra of compound 17



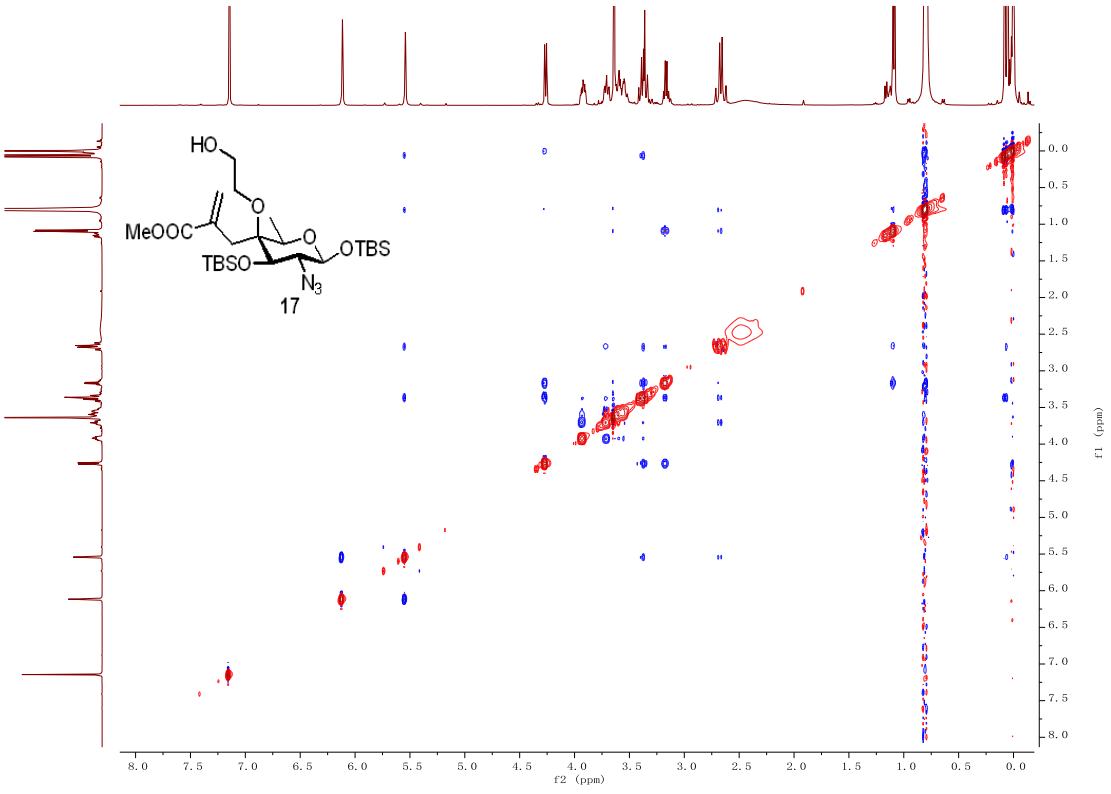
^{13}C NMR Spectra of compound 17



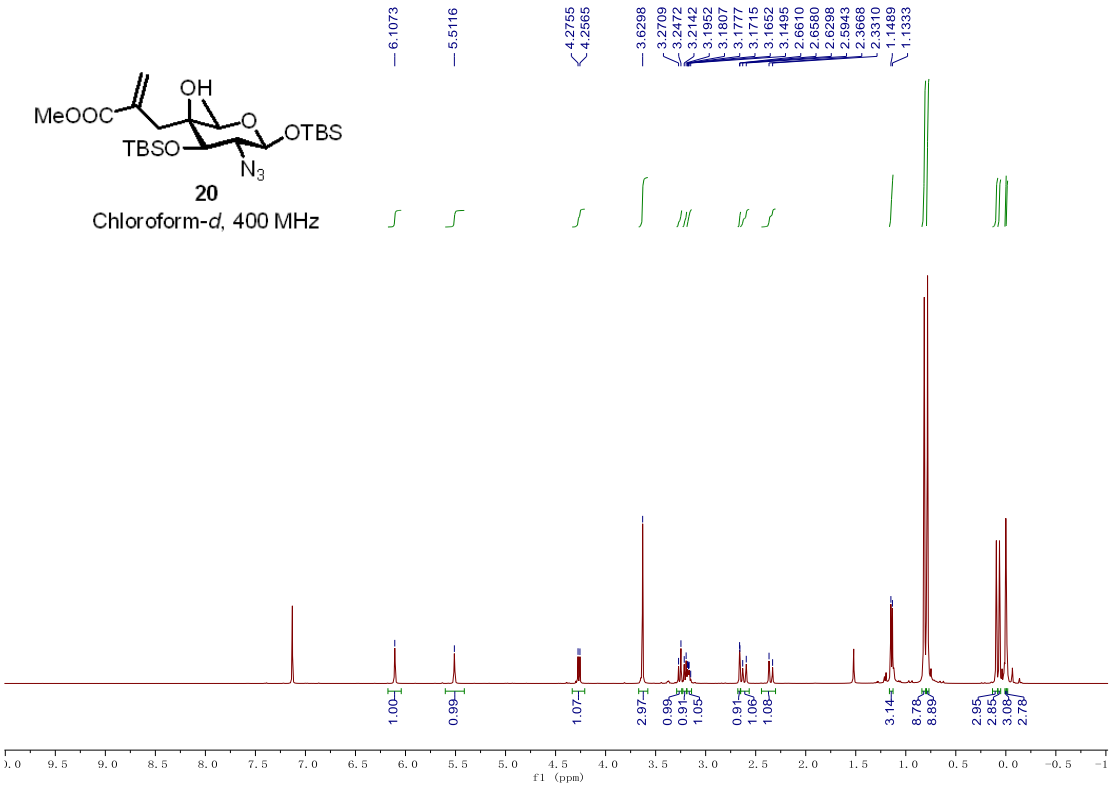
HSQC NMR Spectra of compound 17



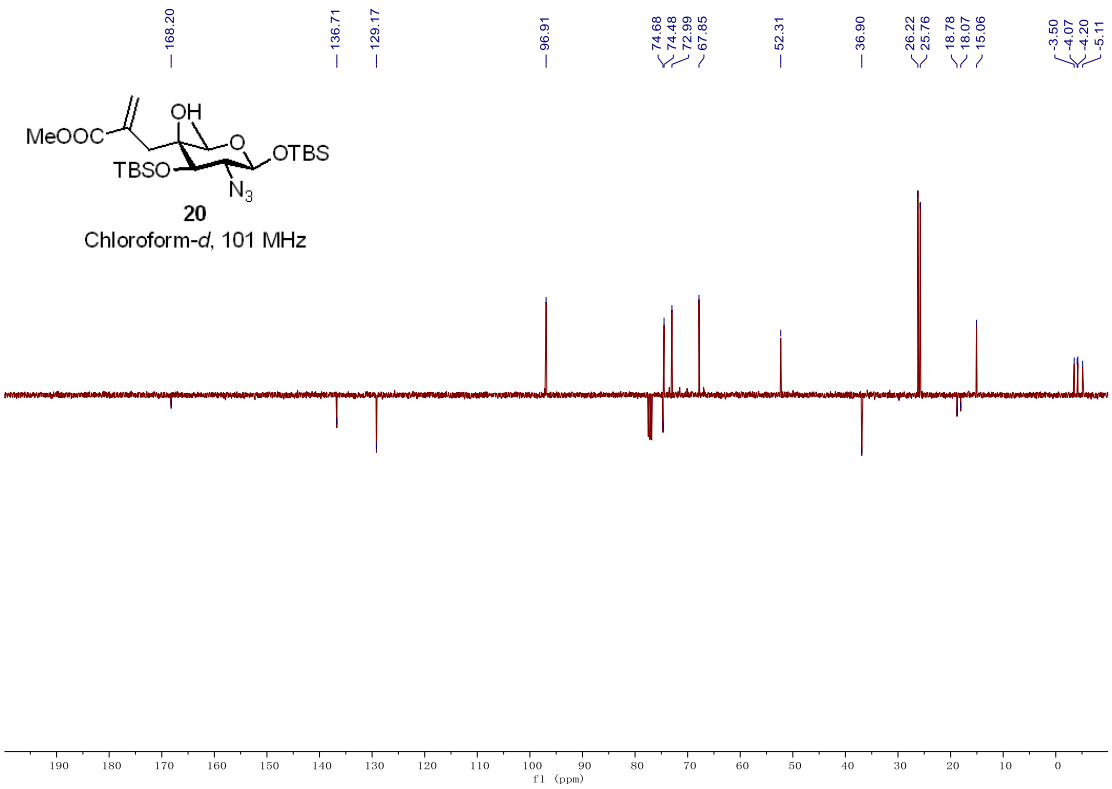
COSY NMR Spectra of compound 17



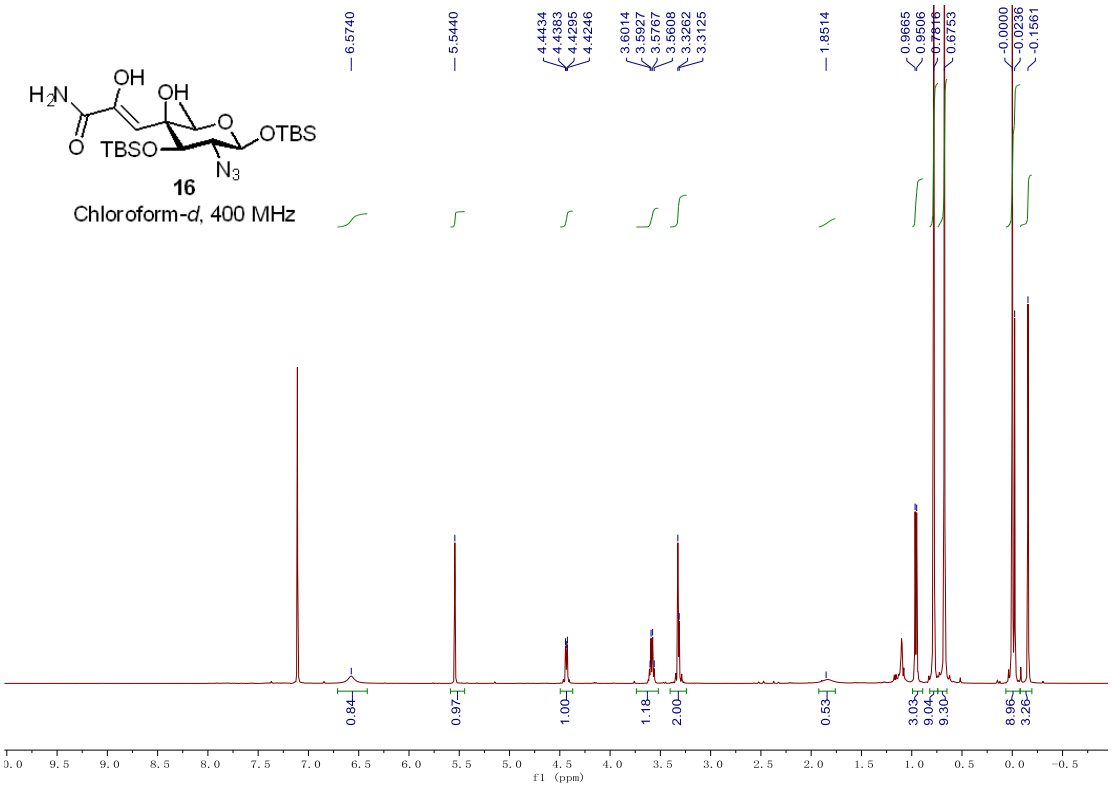
NOESY NMR Spectra of compound 17



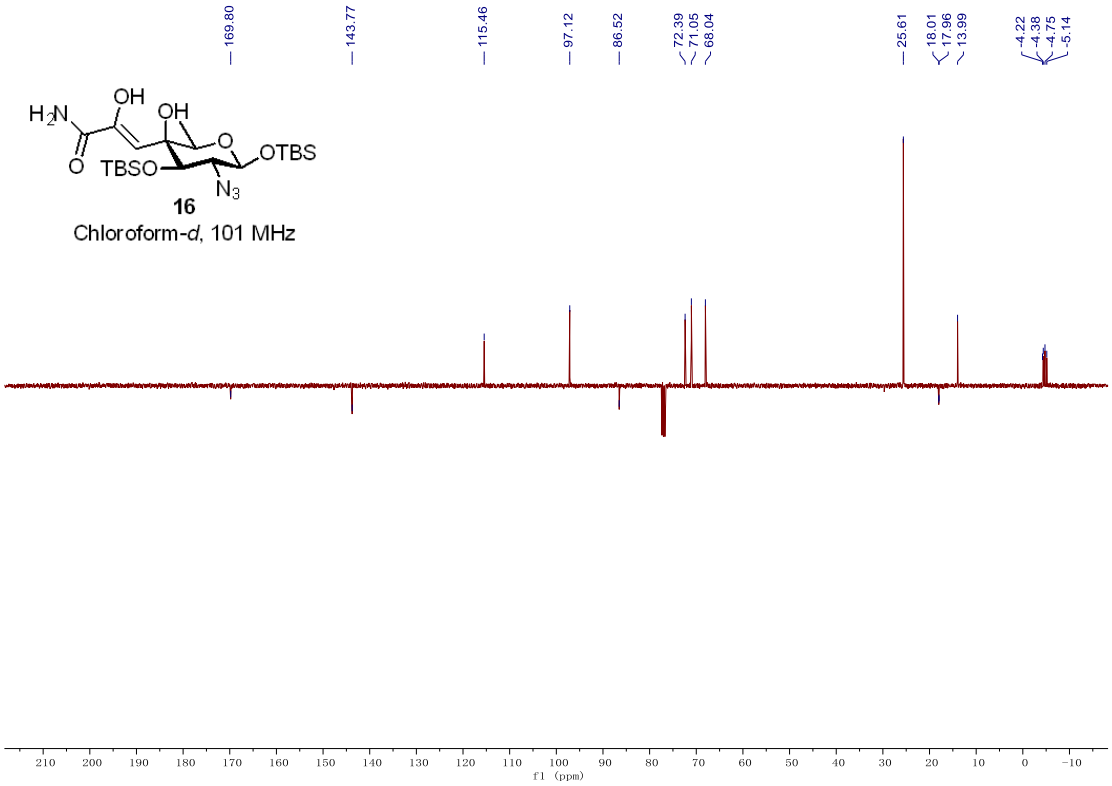
^{1}H NMR Spectra of compound 20



^{13}C NMR Spectra of compound 20



^{1}H NMR Spectra of compound 16



^{13}C NMR Spectra of compound 16