Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


# Supporting Information

## 1,4-Dithiothreitol Mediated Cleavage of Acetal and Ketal Type of Diol Protecting Groups

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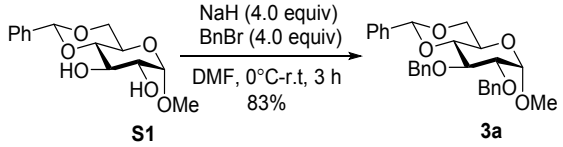
**CONTENTS**

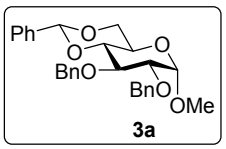
# 1. General Comments

All reactions were monitored by thin-layer chromatography over silica-gel-coated TLC plates (Yantai Chemical Industry Research Institute). The spots on TLC were visualized by warming 10% $H_2SO_4$ (10% $H_2SO_4$ in ethanol) sprayed plates on a hot plate. Column chromatography was performed using silica gel (Qingdao Marine Chemical Inc., China), and Sephadex LH-20 (GE Healthcare Bio-Sciences AB, Sweden). 1,4-Dithiothreitol (DTT), (+)-camphor-10-sulfonic acid (CSA), $Tf_2O$, TMSOTf, 4-dimethylaminopyridine (DMAP), 4-allyl-1,2-dimethoxbenzene (ADMB), 2,6-di-tert-butyl-4-methylpyridine (DTBMP) and all other commercially available chemicals were purchased from Adamas and used without further purification. Molecular sieves (4Å, powder < 50 μm) for reactions were flame dried immediately before use. NMR spectra were recorded on a Bruker AM-400 (400 MHz, $^1H$; 100 MHz, $^{13}C$) spectrometer, and the $^1H$ and $^{13}C$ NMR chemical shifts were referenced to the solvent or solvent impurity peaks for $CDCl_3$ at $\delta$H 7.24 and $\delta$C 77.23. Optical rotations were measured on a Rudolph Autopol IV automatic polarimeter using a quartz cell with 2 mL capacity and a 1 dm path length. Concentrations (*c*) are given in g/100 mL. High resolution mass spectra were recorded on a Bruker micrOTOF II spectrometer using electrospray ionization (ESI).

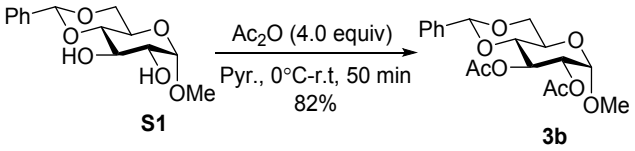
## 2. Preparation of Starting Materials



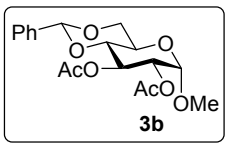

**Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-benzylidene-*α*-D-glucopyranoside (3a)**



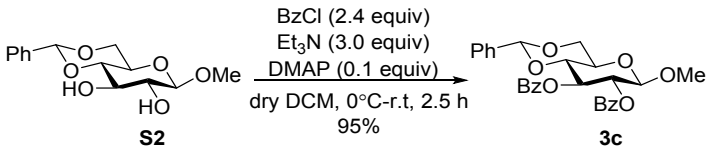

Compound **S1**[1] (6.2 g, 21.30 mmol) was dissolved in DMF (42.4 mL), and the solution was cooled to 0 °C. NaH (3.4 g, 85.02 mmol) was added slowly, followed by benzyl bromide (10.0 mL, 85.02 mmol). The mixture was then warmed to room temperature and stirred for 3 h. MeOH (10.0 mL) was added to quench the reaction, and the mixture was stirred for a further 1 h. The mixture was then concentrated under diminished pressure and purified by chromatography to give **3a** (8.0 g, 83%) as white solid. $R_f$ = 0.33 (petroleum ether-EtOAc 8:1). $[\alpha]_D^{20}$ -31.2 (*c*, 5.0 in $CHCl_3$). m.p. 93.0-94.5 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.49-7.26 (15H, m, Ar-H), 5.54 (1H, s, $PhCHO_2$), 4.90 (1H, d, *J* = 11.2 Hz, $PhCH_2O$), 4.85 (1H, d, *J* = 8.0 Hz, $PhCH_2O$), 4.82 (1H, d, *J* = 8.0 Hz, $PhCH_2O$), 4.69 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.58 (1H, d, *J* = 3.6 Hz, H-1), 4.25 (1H, dd, *J* = 10.0, 4.8 Hz, H-6a), 4.03 (1H, t, *J* = 9.6 Hz, H-3), 3.81 (1H, m, H-5), 3.69 (1H, t, *J* = 10.0 Hz, H-6b), 3.61-3.53 (2H, m, H-2, H-4), 3.39 (3H, s, OMe). Analytical data for **3a** were essentially the same as reported in the literature.[2]



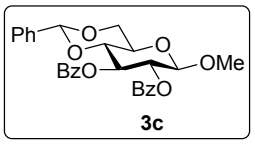

**Methyl 2,3-di-*O*-acetyl-4,6-di-*O*-benzylidene-*α*-D-glucopyranoside (3b)**



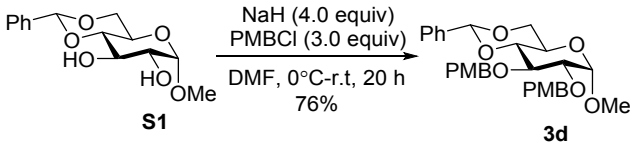

Compound **S1** (100.0 mg, 0.35 mmol), pyridine (1.2 mL), and acetic anhydride (0.2 mL, 1.42 mmol) were combined in a round-bottom flask and stirred at room temperature for 50 minutes until starting material was completely consumed. The reaction mixture was diluted with ice-water and extracted with EtOAc. The organic layers were combined and washed with 1 M HCl, water, saturated aqueous $NaHCO_3$ and brine sequentially, dried over anhydrous $Na_2SO_4$, concentrated in vacuo. The residue was purified by silica gel chromatography to give **3b** (103.0 mg, 82%) as white solid. $R_f$ = 0.35 (petroleum ether-EtOAc 6:1). $[\alpha]_D^{20}$ +75.5 (*c*, 2.0 in $CHCl_3$). m.p. 108.0-109.0 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.44-7.32 (5H, m, Ar-H), 5.56 (1H, t, *J* = 9.6 Hz, H-3), 5.49 (1H, s, $PhCHO_2$), 4.92 (1H, d, *J* = 4.0 Hz, H-1), 4.89 (1H, dd, *J* = 9.6, 3.6 Hz, H-2), 4.29 (1H, dd, *J* = 10.4, 4.0 Hz, H-6a), 3.91 (1H, m, H-5), 3.75 (1H, t, *J* = 10.4 Hz, H-6b), 3.63 (1H, t, *J* = 9.6 Hz, H-4), 3.39 (3H, s, OMe), 2.08 (3H, s, OAc), 2.03 (3H, s, OAc). Analytical data for **3b** were essentially the same as reported in the literature.[3]



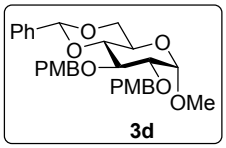

**Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranoside (3c)**




Compound **S2**[4] (83.0 mg, 0.29 mmol) and 4-dimethylamino-pyridine (DMAP, 3.6 mg, 0.029 mmol) was dissolved in dry DCM (1.5 mL), and the solution was cooled to 0 °C. BzCl (82.0 μL, 0.71 mmol) was added slowly followed by $Et_3N$ (0.2 mL, 0.88 mmol). The mixture was then warmed to room temperature and stirred for 2.5 h until starting material was completely consumed. The reaction mixture was diluted with water and extracted with EtOAc. The organic layers were combined and washed with water, saturated aqueous $NaHCO_3$ and brine sequentially, dried over anhydrous $Na_2SO_4$, concentrated in vacuo. And the residue was purified by silica gel chromatography to give **3c** (137.0 mg, 95%) as white solid. $R_f$ = 0.42 (petroleum ether-EtOAc 6:1). $[\alpha]_D^{25}$ -10.8 (*c*, 1.2 in $CHCl_3$). m.p. 187.4-188.5 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.96-7.29 (15H, m, Ar-H), 5.78 (1H, t, *J* = 9.6 Hz, H-3), 5.54 (1H, s, $PhCHO_2$), 5.45 (1H, dd, *J* = 9.2, 8.0 Hz, H-2), 4.70 (1H, d, *J* = 7.6 Hz, H-1), 4.44 (1H, dd, *J* = 10.4, 4.8 Hz, H-6a), 3.90 (2H, m, H-6b, H-4), 3.69 (1H, m, H-5), 3.52 (3H, s, OMe). Analytical data for **3c** were essentially the same as reported in the literature.[5]

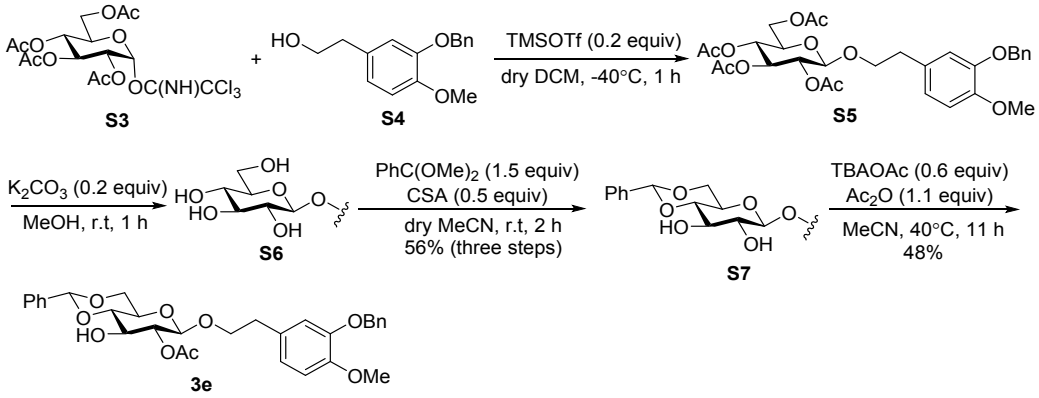



**Methyl 2,3-di-*O*-*p*-methoxybenzyl-4,6-di-*O*-benzylidene-*α*-D-glucopyranoside (3d)**

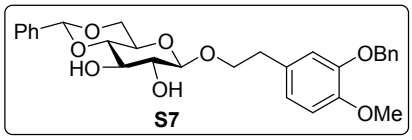



Compound **S1** (200.0 mg, 0.71 mmol) was dissolved in DMF (2.8 mL), and the solution was cooled to 0 °C. NaH (113.4 mg, 2.83 mmol) was added slowly, followed by *p*-methoxybenzyl chloride (0.29 ml, 2.13 mmol). The mixture was then warmed to room temperature and stirred for 20 h. MeOH (1.0 mL) was added to quench the reaction, and the mixture was stirred for a further 10 min. The reaction mixture was diluted with water and extracted with EtOAc. The organic layers were combined and washed with water and brine sequentially, dried over anhydrous $Na_2SO_4$, concentrated in vacuo. And the residue was purified by silica gel chromatography to give **3d** (282.6 mg, 76%) as white solid. $R_f$= 0.53 (petroleum ether-EtOAc 5:1). $[\alpha]_D^{20}$ -39.4 (*c*, 1.0 in $CHCl_3$). m.p. 97.1-98.3 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.48-7.46 (2H, m, Ar-H), 7.39-7.34 (3H, m, Ar-H), 7.29-7.25 (4H, m, Ar-H), 6.83 (4H, dd, *J* = 11.2, 8.8 Hz, Ar-H), 5.52 (1H, s, $PhCHO_2$), 4.80 (1H, d, *J* = 11.2 Hz, $PhCH_2O$), 4.75 (2H, t, *J* = 12.4 Hz, $PhCH_2O$), 4.61 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.51 (1H, d, *J* = 3.6 Hz, H-1), 4.23 (1H, dd, *J* = 10.0, 4.8 Hz, H-6a), 4.98 (1H, t, *J* = 9.2 Hz), 3.79 (3H, s, OMe), 3.77 (3H, s, OMe), 3.68 (1H, t, *J* = 10.0 Hz), 3.55 (1H, t, *J* = 9.2 Hz), 3.49 (1H, dd, *J* = 9.6, 4.0

Hz, H-6b), 3.37 (3H, s, OMe). Analytical data for **3d** were essentially the same as reported in the literature.[6]




**2-(3-(Benzyloxy)-4-methoxyphenyl)ethyl-4,6-*O*-benzylidene-*β*-D-glucopyranoside (S7)**



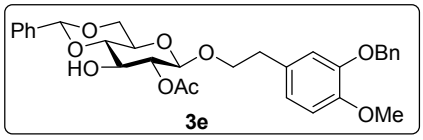

A solution of the glycosyl donor **S3**[7] (2.0 g, 4.06 mmol), glycosyl acceptor 2-(3-(benzyloxy)-4-methoxyphenyl)ethan-1-ol **S4** [8] (2.1 g, 8.12 mmol) in dry $CH_2Cl_2$ (13.5 mL) in the presence of 4 Å MS (100 wt%) was stirred for 10 min at -40 °C. After addition of TMSOTf (0.2 mL, 0.97 mmol), the solution was stirred at -40 °C for 1 h. The reaction mixture was quenched with $Et_3N$, then filtered through Celite and extracted with EtOAc. The organic phase was washed with water, saturated aqueous $NaHCO_3$ and brine sequentially, dried over anhydrous $Na_2SO_4$, concentrated to give **S5** as yellow oil. $R_f$ = 0.33 (petroleum ether-EtOAc 2:1).

To a solution of the above product in MeOH (5.0 mL) was added $K_2CO_3$ (102.0 mg, 0.8 mmol) and the mixture was stirred at room temperature for 1 h, then filtered off and evaporated to dryness to give the deacetylated compound **S6** as white foam. $R_f$ = 0.35 ($CH_2Cl_2$-MeOH 10:1).

To a solution of the above deprotect product (1.2 g, 2.85 mmol) in dry MeCN (19.0 mL) was added benzaldehyde dimethylacetal (0.7 mL, 4.28 mmol) followed by CSA (134.0 mg, 0.57 mmol). The mixture was stirred at room temperature for 2 h until TLC revealed complete consumption of the starting material. The reaction mixture was quenched with $Et_3N$ and then evaporated to remove the solvents. The residue was diluted with water and extracted with EtOAc. The organic layers were combined and washed with water, saturated aqueous $NaHCO_3$ and brine sequentially, dried over anhydrous $Na_2SO_4$, concentrated in vacuo. And the residue was purified by silica gel chromatography to give benzylidene-protected compound **S7** (1.0 g, 56%, three steps) as white solid. $R_f$ = 0.32 (petroleum ether-EtOAc 1:1). $[\alpha]_D^{20}$ -26.1 (*c*, 1.05 in $CHCl_3$). m.p. 152.2-153.4 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.52-7.48 (4H, m, Ar-H), 7.41-7.30 (6H, m, Ar-H), 7.04 (1H, d, $J$ = 2.0 Hz, Ar-H), 6.89 (1H, d, $J$ = 8.4 Hz, Ar-H), 6.82 (1H, dd, $J$ = 8.0, 2.0 Hz, Ar-H), 5.58 (1H, s, $PhCHO_2$), 5.11 (2H, s, $PhCH_2O$), 4.54(1H, d, $J$ = 3.6 Hz), 4.48 (1H, d, $J$ = 8.0 Hz, H-1), 4.39 (1H, d, $J$ = 3.6 Hz), 4.24

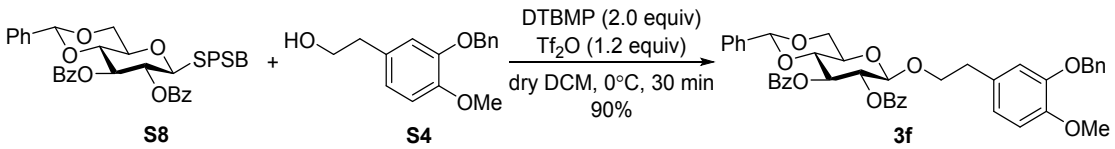
(1H, dd, $J$ = 10.4, 4.8 Hz, H-6a), 4.02-3.96 (1H, m), 3.79 (3H, s, OMe ), 3.77-3.71 (2H, m), 3.69-3.64 (1H, m), 3.49-3.40 (2H,m), 3.36-3.31 (1H, m), 2.83 (2H, d, $J$ = 7.2 Hz). $^{13}$C NMR (100 MHz, $CD_3COCD_3$) $\delta$ 149.3, 149.2, 139.2, 138.7, 132.4, 129.5, 129.2, 129.2, 128.7, 128.7, 128.6, 128.6, 128.5, 127.3, 127.3, 122.3, 116.1, 113.2 (Ar-C),, 104.7 ($PhCHO_2$), 102.1 (C-1), 82.0, 75.8, 74.4, 71.4, 71,3, 69.3, 67.2, 56.2 (OMe), 36.3 (Ar<u>C</u>$H_2CH_2O$). HRMS calc. for $C_{31}H_{34}NaO_9$ $[M+Na]^+$: 531.1995, found: 531.1982.

**2-(3-(Benzyloxy)-4-methoxyphenyl)ethyl-2-*O*-acetyl-4,6-*O*-benzylidene-*β*-D-glucopyranoside (3e)**



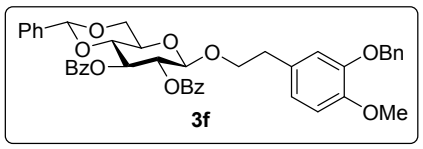
**3e**

A solution of compound **S7** (193.0 mg, 0.38 mmol), TBAOAc (69.0 mg, 0.23 mmol) and $Ac_2O$ (39.0 μL, 0.42 mmol) was dissolved in MeCN (1.9 mL) and the mixture was stirred for 11 h at 40 °C. The reaction mixture was diluted with water and extracted with EtOAc. The organic layers were combined and washed with water, saturated $NaHCO_3$ solution and brine sequentially, dried with anhydrous $Na_2SO_4$, concentrated in vacuo. And the residue was purified by silica gel column chromatography to give **3e** (100.3 mg, 48%) as white solid. $R_f$ = 0.35 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ -39.4 ($c$, 1.0 in $CHCl_3$). m.p. 128.6-131.1 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.53-7.31 (10H, m, Ar-H), 6.96 (1H, d, $J$ = 2.0 Hz, Ar-H), 6.89 (1H, d, $J$ = 8.0 Hz, Ar-H), 6.78 (1H, dd, $J$ = 8.4, 2.0 Hz, Ar-H), 5.61 (1H, s, $PhCHO_2$), 5.14 (1H, d, $J$ = 12.0 Hz, $PhCH_2O$), 5.09 (1H, d, $J$ = 12.0 Hz, $PhCH_2O$), 4.87 (1H, t, $J$ = 8.4 Hz, H-2), 4.78 (1H, d, $J$ = 4.4 Hz), 4.61 (1H, d, $J$ = 8.0 Hz, H-1), 4.26 (1H, dd, $J$ = 10.4, 4.8 Hz, H-6a), 4.03-3.97 (1H, m), 3.86-3.76 (5H, m), 3.69-3.63 (1H, m), 3.57 (1H, t, $J$ = 9.6 Hz), 3.49 (1H, m, H-5), 2.77 (2H, t, $J$ = 6.8 Hz), 1.94 (3H, s, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 170.4 (C=O), 148.5, 148.2, 137.4, 137.0, 131.2, 129.6, 128.7, 128.7, 128.6, 128.6, 128.0, 127.7, 127.7, 126.5, 126.5, 121.7, 115.4, 112.1 (Ar-C), 102.1 ($PhCHO_2$), 101.5 (C-1), 81.1, 74.1, 72.4, 71.2, 71.1, 68.8, 66.3, 56.3 (OMe), 35.7 (Ar<u>C</u>$H_2CH_2O$), 21.0 (<u>C</u>$H_3CO$). HRMS calc. for $C_{31}H_{34}NaO_9$ $[M+Na]^+$: 573.2091, found: 573.2095.



**S8** **S4** **3f**

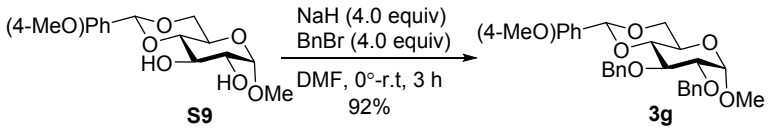
**2-(3-(Benzyloxy)-4-methoxyphenyl)ethyl-2,3-di-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranoside (3f)**



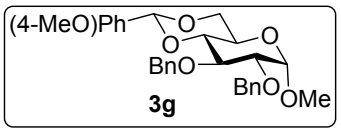
**3f**

A solution of the glycosyl donor **S8**[9] (20.0 mg, 0.03 mmol), glycosyl acceptor 2-(3-(benzyloxy)-4-methoxyphenyl)ethan-1-ol **S4**[8] (6.4 mg, 0.03 mmol) and DTBMP (10.4 mg, 0.06 mmol) in dry $CH_2Cl_2$ (0.5 mL) in the presence of 4 Å MS (100 wt%) was stirred for 10 min at 0 °C. After addition of $Tf_2O$ (5.0 μL, 0.30 mmol), the solution was stirred at 0 °C for 30 min. The reaction mixture was quenched with $Et_3N$, then filtered through Celite and extracted

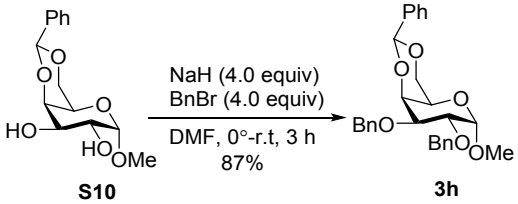
with EtOAc. The organic phase was washed with water, saturated aqueous $NaHCO_3$ and brine sequentially, dried over anhydrous $Na_2SO_4$, concentrated, and purified by silica gel column chromatography to give **3f** (15.9 mg, 90%) as white solid. $R_f$ = 0.30 (petroleum ether-EtOAc 4:1). $[\alpha]_D^{25}$ +7.32 (*c*, 0.71 in $CHCl_3$). m.p. 145.3-147.5 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.94 (2H, d, *J* = 7.2 Hz, Ar-H), 7.89 (2H, d, *J* = 7.6 Hz, Ar-H), 7.51-7.45 (2H, m, Ar-H), 7.42-7.39 (4H, m, Ar-H), 7.37-7.29 (10H, m, Ar-H), 6.66 (1H, d, *J* = 1.6 Hz, Ar-H), 6.62 (1H, dd, *J* = 8.0, 1.6 Hz, Ar-H), 6.49 (1H, d, *J* = 8.4 Hz, Ar-H), 5.74 (1H, t, *J* = 9.6 Hz), 5.51 (1H, s, $PhCHO_2$), 5.46 (1H, t, *J* = 8.0 Hz), 5.07 (2H, t, *J* = 13.2 Hz), 4.74 (1H, d, *J* = 7.6 Hz, H-1), 4.40 (1H, dd, *J* = 10.4, 4.8 Hz, H-6a), 4.07-4.01 (1H, m), 3.90 (1H, t, *J* = 9.2 Hz), 3.84 (1H, t, *J* = 10.4 Hz), 3.72 (3H, s, OMe), 3.69-3.60 (2H, m), 2.73-2.69 (2H, m). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$165.8 (C=O), 165.3 (C=O), 148.2, 148.0, 137.4, 136.9, 133.2, 133.2, 130.8, 129.9, 129.9, 129.9, 129.9, 129.5, 129.4, 129.2, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 127.9, 127.5, 127.5, 126.2, 126.2, 121.6, 115.0, 111.7 (Ar-C), 101.7 ($PhCHO_2$), 101.6 (C-1), 78.9, 72.5, 72.2, 71.2, 71.0, 68.8, 66.7, 56.0 (OMe), 35.6 ($ArCH_2CH_2O$). HRMS calc. for $C_{43}H_{40}NaO_{10}$ $[M+Na]^+$: 739.2514, found: 739.2503.



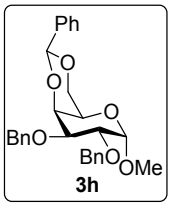

**Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-(*p*-methoxybenzylidene)-*α*-D-glucopyranoside (3g)**



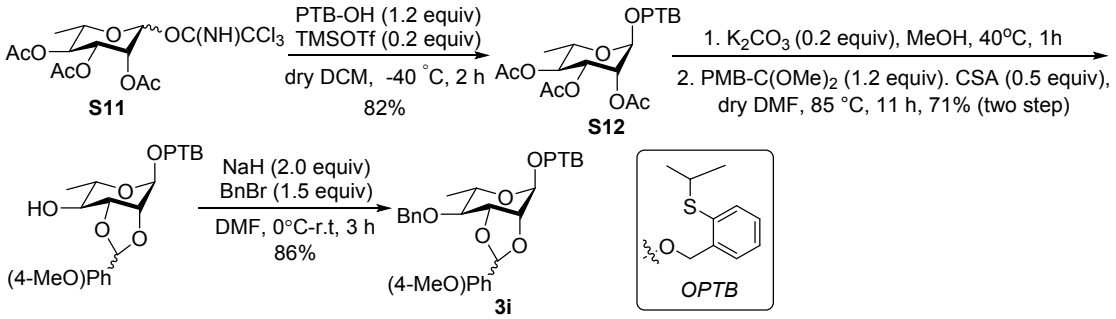

Compound **S9** [10] (70.0 mg, 0.23 mmol) was dissolved in DMF (2.2 mL), and the solution was cooled to 0 °C. NaH (35.9 mg, 0.90 mmol) was added slowly followed by benzyl bromide (0.1 mL, 0.90 mmol). The mixture was then warmed to room temperature and stirred for 3 h for complete conversion of the starting material. MeOH (1.0 mL) was added to quench the reaction, and the mixture was stirred for a further 10 minutes. The mixture was then concentrated under diminished pressure and purified by silica gel column chromatography to give **3g** as white solid (101.0 mg, 92%). $R_f$ = 0.36 (petroleum ether-EtOAc 5:1). $[\alpha]_D^{20}$ +104.8 (*c*, 1.0 in $CHCl_3$). m.p. 193.0-195.0 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.40-7.25 (12H, m, Ar-H), 6.88 (2H, d, *J* = 8.3 Hz, Ar-H from PMB), 5.49 (1H, s, $ArCHO_2$), 4.89 (1H, d, *J* = 11.2 Hz, $PhCH_2O$), 4.83 (2H, t, *J* = 10.8 Hz, $PhCH_2O$), 4.68 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.57 (1H, d, *J* = 3.6 Hz, H-1), 4.23 (1H, dd, *J* = 10.4, 4.8 Hz, H-6a), 4.02 (1H, t, *J* = 9.2 Hz, H-3), 3.83-3.77 (4H, m, $OCH_3$, H-5), 3.67 ( 1H, t, *J* = 10.4 Hz, H-6b), 3.54 (2H, m, H-2, H-4), 3.38 (3H, s, OMe). Analytical data for **3g** were essentially the same as reported in the literature. [11]



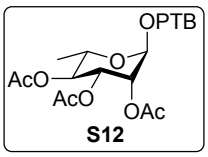
**Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-benzylidene-*α*-D-galactopyranoside (3h)**




Compound **S10**[12] (0.6 g, 2.13 mmol) was dissolved in DMF (4.2 mL), and the solution was cooled to 0 °C. NaH (0.3 g, 8.50 mmol) was added slowly, followed by benzyl bromide (1.0 mL, 8.50 mmol). The mixture was then warmed to room temperature and stirred for 3 h. MeOH (1.0 mL) was added to quench the reaction, and the mixture was stirred for a further 0.5 h. The mixture was then concentrated under diminished pressure and purified by silica gel column chromatography to give **3h** (8.4 g, 87%) as white solid. $R_f$ = 0.40 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{20}$ +144.0 (*c*, 0.57 in $CHCl_3$). m.p. 171.3-172.5 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.43-7.41 (2H, m, Ar-H), 7.32-7.15 (13H, m, Ar-H), 5.38 (1H, s, $PhCHO_2$), 4.78 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.73 (1H, d, *J* = 12.4 Hz, $PhCH_2O$), 4.66 (1H, d, *J* = 4.0 Hz, H-1), 4.64 (1H, d, *J* = 12.4 Hz, $PhCH_2O$), 4.58 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.12-4.06 （2H, m），3.96 (1H, dd, *J* = 10.0, 3.2 Hz, H-6a), 3.91-3.86 （2H, m），3.48 （1H, s），3.28 （3H, s, OMe). Analytical data for **3h** were essentially the same as reported in the literature.[13]



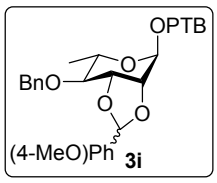

**2-[(Propan-2-yl)sulfanyl]benzyl 2,3,4-tri-*O*-acetyl-*α*-L-rhamnose (S12)**




A solution of the glycosyl donor **S11**[14] (7.9 g, 18.18 mmol) and acceptor PTB-OH [9] (5.0 g, 27.26 mmol) in dry $CH_2Cl_2$ (90.0 mL) in the presence of 4 Å MS (100 wt%) was stirred for 10 min at room temperature under argon. Then the mixture was stirred for 10 min at -40 °C. After addition of TMSOTf (0.7 mL, 3.60 mmol), the solution was stirred at -40 °C for 2 h. The reaction mixture was quenched with $Et_3N$, then filtered through Celite and extracted with EtOAc. The organic phase was washed with water and brine, dried with anhydrous $Na_2SO_4$, concentrated, and purified by silica gel column chromatography give **S12** (6.8 g, 82%) as white syrup. $R_f$ = 0.50 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ -55.5 (*c*, 1.0 in $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.44-7.39 (2H, m, Ar-H), 7.26-7.22 (2H, m, Ar-H), 5.32 (1H, dd, *J* = 10.0, 3.6 Hz, H-3), 5.28 (1H, dd, *J* = 3.6, 1.6 Hz, H-2), 5.05 (1H, t, *J* = 10.0 Hz, H-4), 4.87 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.84 (1H, d, *J* = 1.6 Hz, H-1), 4.65 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 3.98-3.91 (1H, m, H-5), 3.36-3.26 [1H, m, $(CH_3)_2C\underline{H}$], 2.12 (3H, s, $COCH_3$), 2.01 (3H, s, $COCH_3$), 1.95 (3H, s, $COCH_3$), 1.25 [6H, dd, *J* = 2.4 Hz, $(C\underline{H}_3)_2CH$], 1.19 (3H, d, *J* = 6.4 Hz, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 170.3, 170.2, 170.1 (C=O), 138.5, 134.8, 133.0, 129.0, 128.5, 127.3 (Ar-C), 97.3 (C-1), 71.3, 70.1, 69.4, 68.0, 66.7, 39.0 [$S\underline{C}(CH_3)_2$], 23.3 (isopropylidene $CH_3$), 23.3 (isopropylidene $CH_3$), 21.1 ($\underline{C}H_3CO$),

21.0 ($\underline{C}H_3CO$), 20.9 ($\underline{C}H_3CO$), 17.5 (C-6). HRMS calc. for $C_{22}H_{30}NaO_8S$ $[M+Na]^+$: 477.1559 found: 477.1585.

**2-[(Propan-2-yl)sulfanyl]benzyl 4-benzyl-2,3-di-*O*-(*p*-methoxybenzylidene)-*α*-L-rhamnose (3i)**

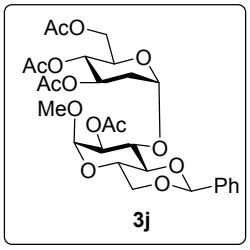



Compound **S12** (7.7 g, 17.09 mmol) was dissolved in MeOH (34.0 mL). After addition of $K_2CO_3$ (164.0 mg, 5.13 mmol) the mixture was stirred for 1 h at 40 °C, then filtered off and evaporated to dryness to give the deacetylated compound as white syrup.

To a solution of the above deprotect product (150.0 mg, 0.77 mmol) in dry DMF (7.7 ml) was added benzaldehyde dimethylacetal (0.2 ml, 0.93 mmol) followed by CSA (19.6 mg, 0.08 mmol). The mixture was stirred at 85 °C under reduced pressure for 11 h until TLC revealed complete consumption of the starting material. The reaction mixture was quenched with $Et_3N$ and then evaporated to remove the solvents. The residue was diluted with water and extracted with EtOAc. The organic layers were combined and washed with water, saturated aqueous $NaHCO_3$ and brine sequentially, dried over anhydrous $Na_2SO_4$, concentrated in vacuo. And the residue was purified by silica gel chromatography to give *p*-methoxybenzylidene protected compound (171.0 mg, 71%) as white solid. $R_f$ = 0.40 (petroleum ether-EtOAc 1:1).

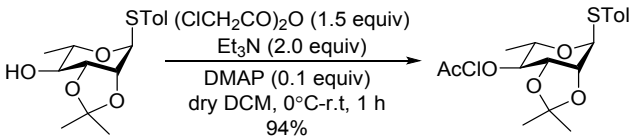
The above protected compound (100.0 mg, 0.23 mmol) was dissolved in DMF (0.2 mL), and the solution was cooled to 0 °C. NaH (18.0 mg, 0.45 mmol) was added slowly followed by benzyl bromide (43.0 μL, 0.33 mmol). The mixture was then warmed to room temperature and stirred for 3 h for complete conversion of the starting material. MeOH was added to quench the reaction, and the mixture was stirred for a further 10 minutes. The mixture was then concentrated under diminished pressure and purified by chromatography to give **3i** (103.0 mg, 86%) as white syrup. $R_f$ = 0.42 (petroleum ether-EtOAc 16:1). $[\alpha]_D^{20}$ -50.8 (*c*, 0.16 in $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.45-6.88 (23.7H, m, Ar-H), 5.99 (1H, s, $ArCHO_2$), 5.85 (0.85H, s, $ArCHO_2$), 5.20 (0.85H, s, H-1), 5.10 (1H, s, H-1), 4.93 (1H, d, $J$ = 11.6 Hz, $PhCH_2O$), 4.86 (0.85 H, d, $J$ = 5.6 Hz), 4.84 (0.85 H, d, $J$ = 3.2 Hz), 4.81 (1H, d, $J$ = 9.2 Hz), 4.70 (1H, d, $J$ = 11.6 Hz, $PhCH_2O$), 4.66 (1H, d, $J$ = 13.2 Hz, $PhCH_2O$), 4.62-4.61 (1.85H, m), 4.54 (0.85H, d, $J$ = 11.6 Hz, $PhCH_2O$), 4.40 (0.85H, t, $J$ = 6.4 Hz, H-3), 4.25 (0.85H, d, $J$ = 6.4 Hz), 4.18 (1H, d, $J$ = 5.6 Hz), 3.90-3.84 (1.85H, m, H-5), 3.81 (2.55H, s, OMe), 3.80 (3H, s, OMe), 3.39-3.26 [3.77H, m, $SC(CH_3)_2$], 1.33 (3H, d, $J$ = 6.4 Hz, H-6), 1.29-1.25 [13.65H, m, $SC(CH_3)_2$, H-6]. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 160.7, 160.6, 138.7, 138.4, 138.3, 135.5, 135.3, 132.6, 131.0, 129.6, 129.5, 129.4, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.0, 127.9, 127.9, 127.8, 127.1, 114.1, 114.1, 114.0, 114.0 (Ar-C), 104.2, 103.0, 96.8, 96.6, 81.6, 80.0, 78.6, 78.4, 75.8, 75.8, 73.1, 72.8, 67.8, 67.8, 64.9, 64.9, 55.6 (OMe), 55.5 (OMe), 38.9 [$S\underline{C}(CH_3)_2$], 38.9 [$S\underline{C}(CH_3)_2$], 23.3 (isopropylidene $CH_3$), 23.3 (isopropylidene $CH_3$), 23.3 (isopropylidene $CH_3$), 23.3 (isopropylidene $CH_3$), 18.1 (C-6), 18.0 (C-6). HRMS calc. for $C_{31}H_{36}NaO_6S$ $[M+Na]^+$: 559.2130 found: 559.2146.

**Methyl 3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-*α*-D-arabino-hexopyranosyl)-4,6-O-benzylidene-2-*O*-acetyl-*α*-D-arabinopyranose (3j)**



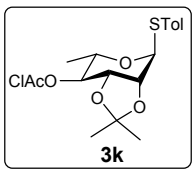
**3j**

Compound **3j** was prepared according to the literature[15] as colorless oil. $R_f$ = 0.56 (petroleum ether-EtOAc 1:1). $[\alpha]_D^{20}$ +91.2 (*c*, 0.3 in $CHCl_3$). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 7.40-7.32 (5H, m, Ar-H), 5.50 (1H, s, PhCH), 5.40 (1H, d, *J*=2.8Hz, H-1'), 5.21-5.15 (1H, m, H-3'), 4.97-4.92 (m, 2H, H-1, H-4'), 4.76 (1H, dd, *J*=3.2 Hz, 10.0 Hz, H-2), 4.30-4.20 (3H, m), 4.07 (1H, dd, *J*= 12.0, 2.4 Hz Hz, H-6a), 3.90 (1H, ddd, *J*=10.0, 5.6, 2.0 Hz, H-3), 4.17-4.13 (2H, m), 3.85-3.78 (1H, m), 3.73 (1H, t, *J*= 10.0 Hz), 3.66 (1H, t, *J*=9.2 Hz), 3.35 (3H, s, OMe), 2.26-2.22 (1H, m, H-2'eq), 2.10 (3H, s, $COCH_3$), 2.08 (3H, s, $COCH_3$), 1.99 (3H, s, $COCH_3$), 1.96 (3H, s, $COCH_3$), 1.75-1.68 (m, 1H, H-2'ax).



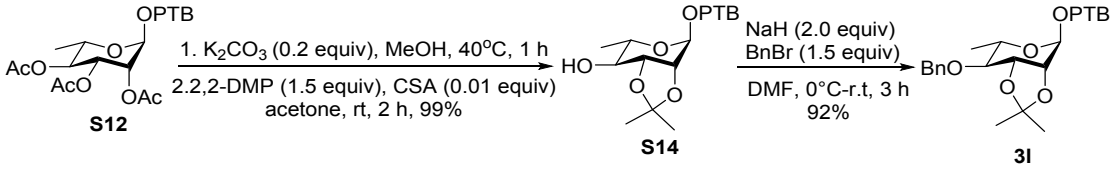
**S13** **3k**

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

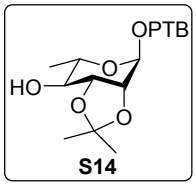


**3k**

Compound **S13** [16] (100.0 mg, 0.32 mmol), chloroacetic anhydride (82.5 mg, 0.48 mmol) and DMAP (4.0 mg, 0.03 mmol) were dissolved in dry $CH_2Cl_2$ (1.6 mL), and the solution was cooled to 0 °C. To the solution was added $Et_3N$ (90.0 μL, 0.64 mmol) under argon. The reaction mixture was warmed to room temperature and stirred for 1 h until the starting material was consumed. The mixture was diluted with water, extracted with EtOAc. The organic layer was washed with water, saturated $NaHCO_3$ and NaCl, dried over anhydrous $Na_2SO_4$, filtered, and the residue was concentrated in vacuo. And purified by silica gel column chromatography to afford the compound **3k** (140.0 mg, 94%) as white solid. $R_f$ = 0.45 (petroleum ether-EtOAc 6:1). $[\alpha]_D^{25}$ -146.1 (*c*, 2.0 in $CHCl_3$). m.p. 74.0-78.3 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.34 (2H, d, *J* = 8.0 Hz, Ar-H), 7.11 (2H, d, *J* = 8.0 Hz, Ar-H), 5.68 (1H, s, H-1), 4.95 (1H, dd, *J* = 10.0, 8.0 Hz, H-4), 4.35 (1H, d, *J* = 5.2 Hz, H-2), 4.25-4.20 (2H, m, H-3, H-5), 4.10 (2H, s, $COCH_2Cl$), 2.32 (3H, s, $SC_6H_4C\underline{H}_3$), 1.55 (3H, s, isopropylidene $CH_3$), 1.34 (3H, s, isopropylidene $CH_3$), 1.12 (3H, d, *J* = 6.4 Hz, H-6). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 166.8 ($ClCH_2\underline{C}O$), 138.4, 132.8, 132.8, 130.1, 130.1, 129.3 (Ar-C), 110.4 [$\underline{C}(CH_3)_2$], 84.2 (C-1), 76.9 (C-3), 76.7 (C-2), 75.4 (C-4), 65.2 (C-5), 41.0 ($CO\underline{C}H_2Cl$), 27.9 (isopropylidene $CH_3$), 26.7 (isopropylidene $CH_3$), 21.4 ($S–C_6H_4–\underline{C}H_3$), 17.0 (C-6). HRMS calc. for $C_{18}H_{23}ClNaO_6S$ $[M+Na]^+$: 425.0796 found: 425.0775.

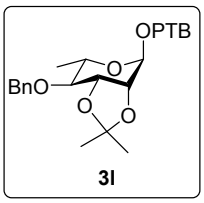



**2-[(Propan-2-yl)sulfanyl]benzyl-2,3-*O*-isopropylidene-*α*-L-rhamnopyranoside (S14)**



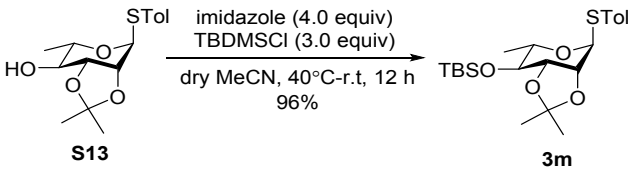

Compound **S12** (7.7 g, 17.09 mmol) was dissolved in MeOH (34.0 mL). After addition of $K_2CO_3$ (164.0 mg, 5.13 mmol) the mixture was stirred for 1 h at 40 °C, then filtered off and evaporated to dryness to give the deacetylated compound as white syrup. The above coarse products (53.0 mg, 0.16 mmol) was dissolved in 2,2-dimethoxyl propane (2,2-DMP, 0.6 mL). To the solution was added CSA (3.8 mg, 0.02 mmol) and stirred for 0.5 h at room temperature for complete conversion of the starting material. The reaction mixture was quenched with $Et_3N$, then concentrated and purified by silica gel column chromatography to give **S14** (58.8 mg, 99%) as yellow syrup. $[\alpha]_D^{20}$ -26.0 (*c*, 0.1 in $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.44 (1H, dd, *J* = 8.0, 1.6 Hz, Ar-H), 7.39 (1H, dd, *J* = 7.2, 1.6 Hz, Ar-H), 7.25 (1H, m, Ar-H), 7.21 (1H, m, Ar-H), 5.07 (1H, s, H-1), 4.87 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.63 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.17 (1H, d, *J* = 5.6 Hz H-2), 4.09 (1H, dd, *J* = 6.8, 6.0 Hz, H-4), 3.77 (1H, m, H-3 ),3.40 (1H, m, H-5), 3.35 [1H, m, C<u>H</u>$(CH_3)_2$], 2.33(1H, 4-OH), 1.51 (3H, s, isopropylidene $CH_3$), 1.33 (3H, s, isopropylidene $CH_3$)，1.29 (3H, d, *J* = 5.6 Hz, H-6), 1.28 (3H, d, *J* = 2.4 Hz, $CH_3$), 1.26 (3H, d, *J* = 2.4 Hz, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 138.6, 135.5, 132.6, 129.5, 128.6, 127.1 (Ar-H), 109.7, 96.9, 78.6, 76.1, 74.8, 67.9, 66.3, 38.9 [S<u>C</u>$(CH_3)_2$], 28.2 (isopropylidene $CH_3$), 26.4 (isopropylidene $CH_3$), 23.4 [SC(<u>C</u>$H_3)_2$], 23.3 [SC(<u>C</u>$H_3)_2$], 17.6 (C-6). HRMS calc. for $C_{19}H_{28}NaO_5S$ $[M+Na]^+$: 391.1555 found: 391.1557.

**2-[(Propan-2-yl)sulfanyl]benzyl-4-*O*-benzyl-2,3-*O*-isopropylidene-*α*-L-rhamnopyranoside (3l)**

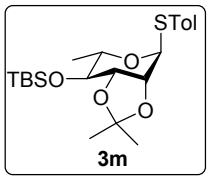



The isopropylidene protected compound **S14** (58.8 mg, 0.16 mmol) was dissolved in DMF (0.80 mL), and the solution was cooled to 0 °C. NaH (19.2 mg, 0.48 mmol) was added slowly followed by benzyl bromide (38.0 μL, 0.32 mmol). The mixture was then warmed to room temperature and stirred for 1 h for complete conversion of the starting material. MeOH was added to quench the reaction, and the mixture was stirred for a further 10 minutes. The mixture was then concentrated under diminished pressure and purified by chromatography to give **3l** (67.0 mg, 92%) as colorless syrup. $R_f$ = 0.42 (petroleum ether-EtOAc 20:1). $[\alpha]_D^{20}$ -47.4 (*c*, 1.3 in $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.44-7.19 (9H, m, Ar-H), 5.07 (1H, s, H-1), 4.88 (1H, d, *J* = 11.6 Hz, $PhCH_2O$), 4.84 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.64 (1H, d, *J* = 8.4 Hz, $PhCH_2O$), 4.61 (1H, d, *J* = 8.4 Hz, $PhCH_2O$), 4.28 (1H, t, *J* = 6.8 Hz, H-3), 4.18 (1H, d, *J* = 6.0 Hz, H-2), 3.79 (1H, m, H-5), 3.34 [1H, m, C<u>H</u>$(CH_3)_2$], 3.22 (1H, dd, *J* = 10.0, 7.2 Hz, H-4), 1.49 (3H, s, isopropylidene $CH_3$), 1.35 (3H, s,

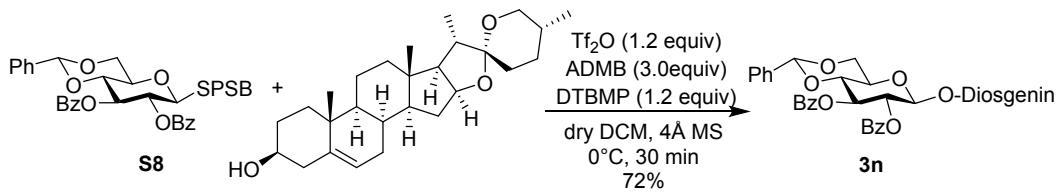
isopropylidene $CH_3$), 1.27 (9H, m, $S(CH_3)_2$, H-6). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.8, 138.6, 135.3, 132.7, 129.5, 128.5, 128.5, 128.5, 128.2, 128.2, 127.8, 127.1 (Ar-C), 109.4, 96.7, 81.4, 78.9, 76.4, 73.2, 67.7, 65.0, 38.9 [S<u>C</u>$(CH_3)_2$], 28.2 (isopropylidene $CH_3$), 26.6 (isopropylidene $CH_3$), 23.4 [SC(<u>C</u>$H_3)_2$], 23.3 [SC(<u>C</u>$H_3)_2$], 18.0 (C-6). HRMS calc. for $C_{26}H_{34}NaO_5S$ $[M+Na]^+$: 481.2025 found: 481.2037.



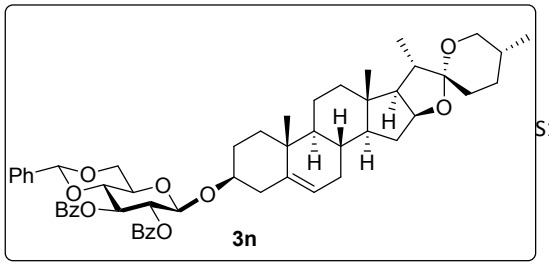

**_p_-Tolyl 4-_O_-tert-butyl-dimethylsilyl-2,3-_O_-isopropylidene-1-thio-_α_-L-rhamnopyranoside (3m)**




Compound **S13** [16] (100.0 mg, 0.32 mmol) and imidazole (87.7 mg, 1.29 mmol) were dissolved in dry MeCN (3.2 mL), and the solution was cooled to 0 °C. To the solution was added TBDMSCl (146.0 mg, 0.97 mmol) under argon. The reaction mixture was warmed to 40 °C and stirred for 12 h until the starting material was consumed. The mixture was diluted with water, extracted with EtOAc. The organic layer was washed with water and saturated NaCl, dried over anhydrous $Na_2SO_4$, filtered, and the residue was concentrated in vacuo. And purified by silica gel column chromatography to afford the compound **3m** (132.0 mg, 96%) as white solid. $R_f$ = 0.80 (petroleum ether-EtOAc 10:1). $[\alpha]_D^{25}$ -175.0 (*c*, 1.0 in $CHCl_3$). m.p. 69.4-71.2 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$7.34 (2H, d, $J$ = 8.4 Hz, Ar-H), 7.10 (2H, d, $J$ = 8.0 Hz, Ar-H), 5.63 (1H, s, H-1), 4.29 (1H, d, $J$ = 5.6 Hz, H-2), 4.01 (2H, m, H-3, H-5), 3.28 (1H, dd, $J$ = 9.6, 7.2 Hz, H-4), 2.31 (3H, s, S-$C_6H_4$-$CH_3$), 1.50 (3H, s, isopropylidene $CH_3$), 1.33 (3H, s, isopropylidene $CH_3$), 1.16 (3H, d, $J$ = 6.4 Hz, H-6), 0.89 (9H, s, $C(CH_3)_3$), 0.13 (3H, s, $CSiCH_3$), 0.067 (3H, s, $CSiCH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.0, 132.7, 132.7, 130.0, 130.0, 129.3 (Ar-H), 109,4 [$(CH_3)_2$ <u>C</u>$O_2$], 84.5 (C-1), 79.1 (C-3), 77.4 (C-2), 76.4 (C-4), 67.7 (C-5), 28.4 (isopropylidene $CH_3$), 26.8 (isopropylidene $CH_3$), 26.1 [SiC(<u>C</u>$H_3)_3$], 26.1 [SiC(<u>C</u>$H_3)_3$], 26.1 [SiC(<u>C</u>$H_3)_3$], 21.4 (S-$C_6H_4$–<u>C</u>$H_3$), 18.3 [Si<u>C</u>$(CH_3)_3$], 17.8 (C-<u>6</u>), -3.7 ($SiCH_3$), -4.7 ($SiCH_3$). HRMS calc. for $C_{22}H_{36}NaO_4SSi$ $[M+Na]^+$: 447.1996 found: 447.2019.

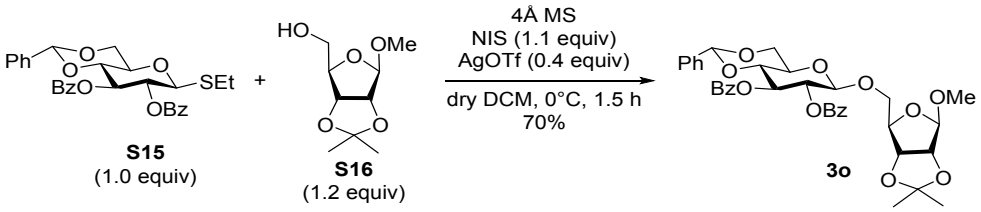



**Diosgenyl 2,3-di-_O_-benzoyl-4,6-_O_-benzylidene-_β_-D-glucopyranoside (3n)**

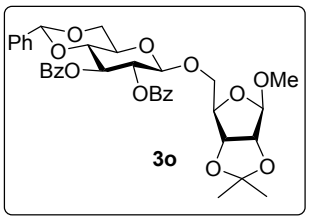



A solution of the glycosyl donor **S8** [9] (89.6 mg, 0.13 mmol), 4-allyl-1,2-dimethoxbenzene (ADMB, 57.2 μL, 0.33

mmol) and 2,6-di-tert-butyl-4-methylpyri-dine (DTBMP, 27.4 mg, 0.13 mmol) in dry $CH_2Cl_2$ (2.0 mL) in the presence of 4 Å MS (100 wt%) was stirred for 15 min at 0 °C. After addition of $Tf_2O$ (22.5 μL, 0.13 mmol), the solution was stirred at 0 °C for 5 min, and then the glycosyl acceptor diosgenin (46.0 mg, 0.11 mmol) in dry $CH_2Cl_2$ (0.7 mL) was added. The solution was stirred at 0 °C for 30 min. The reaction mixture was quenched with $Et_3N$, then filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried over anhydrous $Na_2SO_4$, concentrated, and purified by silica gel column chromatography to give **3n** (83.5 mg, 72%) as white solid. $R_f$ = 0.43 (petroleum ether-EtOAc 5:1). $[\alpha]_D^{22}$ +8.5 (*c*, 1.2 in $CHCl_3$). m.p. 75.8-80.5 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.94 (4H, d, *J* = 8.0 Hz, Ar-H), 7.52-7.28 (11H, m, Ar-H), 5.74 (1H, t, *J* = 9.6 Hz, H-3), 5.52 (1H, s, $PhCHO_2$), 5.42 (1H, dd, *J* = 9.2, 8.0 Hz, H-2), 5.21 (1H, d, *J* = 4.8 Hz, H-6), 4.88 (1H, d, *J* = 8.0 Hz, H-1), 4.38 (2H, m), 3.90 (1H, t, *J* = 9.2 Hz, H-4), 3.87 (1H, t, *J* = 10.4 Hz), 3.66 (1H, dt, *J* = 10.0, 5.2 Hz), 3.55-3.43 (2H, m), 3.35 (1H, t, *J* = 10.8 Hz), 0.94 (3H, d, *J* = 6.8 Hz), 0.89 (3H, s), 0.76 (3H, d, *J* = 6.0 Hz), 0.73 (3H, s), 2.20-0.83 (24H, m). Analytical data for **3n** were essentially the same as reported in the literature.[8]

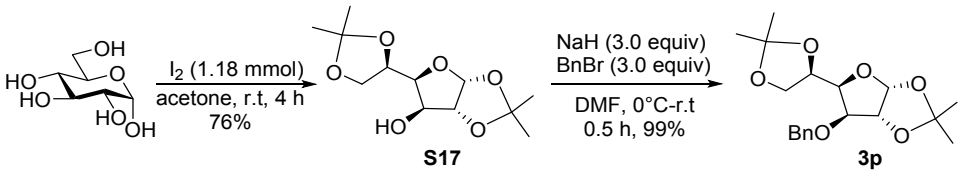



**Methyl 2,3-*O*-methylethylidene-5-*O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranosyl)-*β*-D-ribofuranoside (3o)**

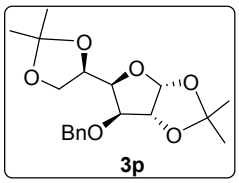



Glycosyl donor **S15**[17] (18.7 mg, 0.036 mmol, 1.0 equiv) and acceptor **S16**[18] (8.8 mg, 0.043 mmol, 1.2 equiv) were azeotroped with toluene and dissolved in anhydrous $CH_2Cl_2$ (0.72 mL, C = 0.05 mol/L). Freshly activated 4 Å molecμLar sieves (40.0 mg), NIS (9.7 mg, 0.043 mmol, 1.2 equiv) and AgOTf (3.5 mg, 0.0015 mmol, 0.4 equiv) were added successively. The mixture was stirred at 0°C for 1.5 h under argon, then was treated with $NaHCO_3$/$Na_2S_2O_3$ (sat. aq.), diluted with EtOAc and filtered through a pad of celite. The organic layer was washed with brine, dried over $Na_2SO_4$, filtered, concentrated in vacuo, and purified by s silica gel column chromatograph (petroleum-acetone 8:1) to give **3o** (16.6 mg, 70%) as white solid. $R_f$ = 0.41 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{25}$ -19.5 (*c*, 0.87 in $CHCl_3$). m.p. 176.1-177.2 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.95-7.93 (4H, m, Ar-H), 7.50-7.28 (11H, m, Ar-H), 5.76 (1H, t, *J* = 9.6 Hz, H-3'), 5.53 (1H, s, $PhCHO_2$), 5.47 (1H, dd, *J* = 9.2, 8.0 Hz, H-2'), 4.85 (2H, d, *J* = 8.8 Hz, H-1, H-1'), 4.56 (1H, d, *J* = 5.6 Hz, H-2), 4.48 (1H, d, *J* = 6.0 Hz, H-3), 4.43 (1H, dd, *J* = 10.8, 5.2 Hz, H-6a'), 4.23 (1H, t, *J* = 7.2 Hz), 3.86 (3H, m), 3.66 (2H, m), 3.20 (3H, s, $OCH_3$), 1.35 (3H, s, $CH_3$), 1.15 (3H, s, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.8 (C=O), 165.3 (C=O), 136.9, 133.4, 133.3, 130.1, 130.1, 130.0, 130.0, 129.6, 129.5, 129.3, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 126.3, 126.3 (Ar-C), 112.5,

109.5, 101.7, 101.5, 85.1, 84.8, 82.0, 78.9, 72.4, 72.2, 70.3, 68.3, 66.9, 50.0 (OMe), 26.5 [($\underline{C}H_3$)$_2$CO$_2$], 24.9 [($\underline{C}H_3$)$_2$CO$_2$]. HRMS calc. for $C_{36}H_{38}NaO_{12}$ $[M+Na]^+$: 685.2255, found: 685.2252.

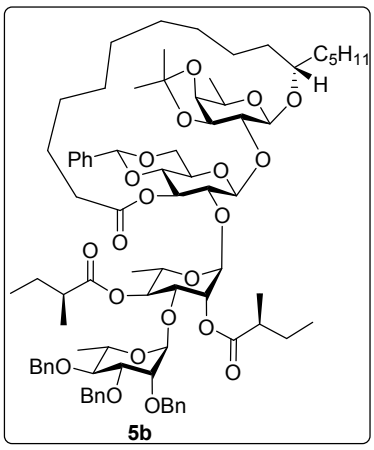



**1,2:5,6-Di-*O*-isopropylidene-3-*O*-benzyl-*α*-D-glucofuranose (3p)**




Add D-glucose (1.0 g, 5.55 mmol) to a solution of iodine (0.3 g, 1.18 mmol) in acetone (50.0 mL) and stir the suspension at room temperature for 4 h. After this time the sugar will have dissolved completely and the reaction will have gone to completion by TLC analysis. Quench the reaction by the addition of dilute sodium thiosulfate solution to render the reaction mixture colourless, then remove the acetone *in vacuo*. Transfer the aqueous solution to a separatory funnel and extract with EtOAc, then wash the combined organic layers with distilled water, dry $Na_2SO_4$ and remove solvents *in vacuo* to afford the crude product. Recrystallization from petroleum ether gave **S17** (1.1 g, 76%) of white crystals. The crystals are not processed directly for the next step. The di-isopropylidene protected compound **S17** (250.0 mg, 0.96 mmol) was dissolved in DMF (4.8 mL), and the solution was cooled to 0 °C. NaH (115.0 mg, 2.88 mmol) was added slowly followed by benzyl bromide (0.3 mL, 2.88 mmol). The mixture was then warmed to room temperature and stirred for 3 h for complete conversion of the starting material. MeOH was added to quench the reaction, and the mixture was stirred for a further 10 minutes. The mixture was then concentrated under diminished pressure and purified by chromatography to give **3p** (101.0 mg, 99%) as colorless syrup. $R_f$= 0.35 (petroleum ether-EtOAc 1:1). $[\alpha]_D^{20}$ -21.5 (*c*, 1.34 in $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.33-7.27 (5H, m, Ar-H), 5.88 (1H, d, $J$ = 3.6 Hz, H-1), 4.67 (1H, d, $J$ = 11.6 Hz, $PhCH_2O$), 4.62 (1H, d, $J$ = 12.0 Hz, $PhCH_2O$), 4.57 (1H, d, $J$ = 4.0 Hz, H-2), 4.35 (1H, m, H-5),4.11 (2H, m, H-3, H-4), 3.99 (2H, m), 1.47 (3H, s, $CH_3$), 1.41 (3H, s, $CH_3$), 1.36 (3H, s, $CH_3$), 1.29 (3H, s, $CH_3$). Analytical data for **3p** were essentially the same as reported in the literature.[19]

**1,3(B)-Lactone of (S)-1-(Hydroxycarbonyl)pentadec-10-yl *O*-(2,3,4-Tri-*O*-benzyl-*α*-L-rhamnopyranosyl)-(1→3)-2,4-di-*O*-(2S-methylbutyryl)-*α*-L-rhamnopyranosyl)-(1→2)-4,6-benzylidene-*β*-D-glucopyranosyl-(1→2)-3,4-*O*-isopropylidene-*β*-D-fucopyranoside (5b)**

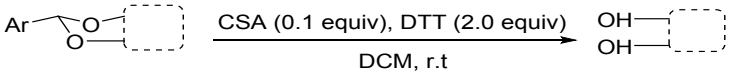



Compound **5b** was prepared according to the literature[20] as white solid. $R_f$ = 0.55 (petroleum ether-EtOAc 5:1). m.p. 55-60 °C. $[\alpha]_D^{19}$ -13.0 (*c*, 1.1 in $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.44-7.22 (20H,

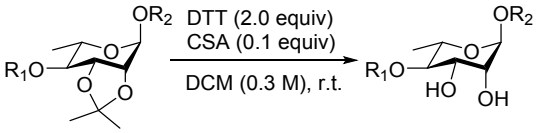
m, Ar-H), 5.51 (1H, s), 5,31 (1H, dd, $J$ = 7.2 $H_Z$, $J$ = 9.2 Hz), 5.18 (1H, d, $J$ = 6.4 Hz), 5.11 (1H, t, $J$ = 2.8 Hz), 5.07 (1H, d, $J$ = 2.0 Hz), 5.03 (1H, t, $J$ = 10.0 Hz), 4.96 (1H, d, $J$ = 1.2 Hz), 4.86 (1H, d, $J$ = 11.6 Hz), 4.72 (1H, d, $J$ = 12.8 Hz), 4.68 (1H, d, $J$ = 12.8 Hz), 4.58 (1H, d, $J$ = 11.6 Hz), 4.52 (1H, d, $J$ = 11.6 Hz), 4.48 (1H, d, $J$ = 11.6 Hz), 4.39-4.24 (2H, m), 4.12-4.08 (2H, m), 3.99 (1H, m), 3.90-3.44 (12H, m), 2.44 (3H, m), 2.18 (1H, m), 1.47 (3H, s), 1.36 (3H, d, $J$ = 6.4 Hz), 1.29 (3H, s), 1.23 (6H, m), 1.13 (3H, m), 1.04 (3H, d, $J$ = 6.8 Hz), 0.87 (6H, m), 0.81 (3H, m).

# 3. DTT Mediated Cleavage of Acetal and Ketal Protecting Groups

## 3.1 General Procedures



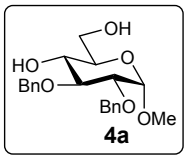

**General Procedure A:** To a stirred solution of the acetal protected subtrates **3** or **5** (1.0 equiv) and DL-1,4-dithiothreitol (DTT, 2.0 equiv) in $CH_2Cl_2$ (c = 0.1 M) was added (+)-camphor-10-sulfonic acid (CSA, 0.1 equiv) at room temperature. After completion of the reaction (monitored by TLC), the solution was extracted with EtOAc, washed with aqueous NaCl, dried with anhydrous $Na_2SO_4$ and the solvent removed under vacuo. The residue was purified by column chromatography to afford the pure product **4** or **6**. If the acid-sensitive functional groups exist, it is necessary to quench the reaction with $Et_3N$ after completion of the reaction.




**General Procedure B:** To a stirred solution of the ketal protected subtrates **3** (1.0 equiv) and DL-1,4-dithiothreitol (DTT, 2.0 equiv) in $CH_2Cl_2$ (c = 0.3 M) was added (+)-camphor-10-sulfonic acid (CSA, 0.1 equiv) at room temperature. After completion of the reaction (monitored by TLC), the solution was extracted with EtOAc, washed with aqueous NaCl, dried with anhydrous $Na_2SO_4$ and the solvent removed under vacuo. The residue was purified by column chromatography to afford the pure product **4**. If the acid-sensitive functional groups exist, it is necessary to quench the reaction with $Et_3N$ after completion of the reaction.

## 3.2 Product Characterization Data

**Methyl 2,3-di-*O*-benzyl-*α*-D-glucopyranoside (4a)**



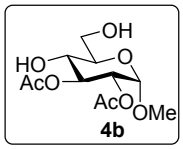
**4a**

Deprotected from **3a** (26.0 mg, 0.056 mmol) according to the General Procedure **A** to give product **4a** (19.7 mg, 94%) as white solid. $R_f$ =

0.26 (petroleum ether-EtOAc 1:1). $[\alpha]_D^{25}$ +17.4 (*c*, 1.0 in $CHCl_3$). m.p. 75.1-76.2 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.27-7.15 (10H, m, Ar-H), 4.91 (1H, d, *J* = 11.6 Hz, $PhCH_2O$), 4.66 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.59 (1H, d, *J* = 11.6 Hz, $PhCH_2O$), 4.54 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.48 (1H, d, *J* = 3.6 Hz, H-1), 3.71-3.59 (3H, m, H-3, H-6a, H-6b), 3.52-3.48 (1H, m, H-5), 3.42-3.36 (2H, m, H-2, H-4), 3.26 (3H, s, OMe), 2.28 (1H, br s, OH), 1.88 (1H, br s, OH). Analytical data for **4a** were essentially the same as reported in the literature.[21]

Gram scale: To a stirred solution of the acetal protected subtrates **3a** (1.5 g, 3.24 mmol) and DL-1,4-dithiothreitol (DTT, 1.0 g, 6.48 mmol) in $CH_2Cl_2$ (16.2 ml) was added (+)-camphor-10-sulfonic acid (CSA, 75.3 mg, 0.32 mmol) at room temperature. After completion of the reaction (monitored by TLC), the solution was extracted with EtOAc, washed with aqueous NaCl, dried with anhydrous $Na_2SO_4$ and the solvent removed under vacuo. The residue was purified by column chromatography to afford the pure product **4a** (1.1 g, 92%).

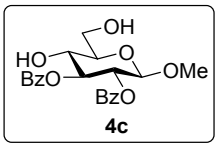
**Methyl 2,3-di-*O*-acetyl-*α*-D-glucopyranoside (4b)**



**4b**

Deprotected from **3b** (20.5 mg, 0.057 mmol) according to the General Procedure **A** to give product **4b** (15.6 mg, 98%) as white solid. $R_f$ = 0.31 (petroleum ether-EtOAc 1:1). $[\alpha]_D^{20}$ +137.8 (*c*, 1.0 in $CHCl_3$). m.p. 116.0-117.0 °C.$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.27 (1H, m, H-3), 4.88 (1H, d, *J* = 3.6 Hz, H-1), 4.80 (1H, dd, *J* = 10.0, 3.6 Hz, H-2), 3.85 (2H, m, H-5, H-6a), 3.68 (2H, m, H-4, H-6b), 3.38 (3H, s, OMe), 2.08 (3H, s, OAc), 2.06 (3H, s, OAc). Analytical data for **4b** were essentially the same as reported in the literature.[22]

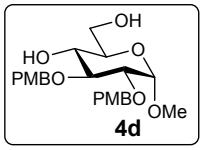
**Methyl 2,3-di-*O*-benzoyl-*β*-D-glucopyranoside (4c)**



**4c**

Deprotected from **3c** (21.0 mg, 0.043 mmol) according to the General Procedure **A** to give product **4c** (15.9 mg, 93%) as white syrup. $R_f$ = 0.21 (petroleum ether-EtOAc 1:1). $[\alpha]_D^{20}$ +92.8 (*c*, 1.0 in $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.95-7.92 (4H, m, Ar-H), 7. 50-7.46 (2H, m, Ar-H), 7.37-7.32 (4H, m, Ar-H), 5.42 (1H, dd, *J* = 9.6, 8.8 Hz, H-3), 5.37 (1H, dd, *J* = 9.2, 7.2 Hz, H-2), 4.63 (1H, d, *J* = 7.6 Hz, H-1), 4.01-3.89 (3H, m, H-4, H-6a, H-6b), 3.57 (1H, ddd, *J* = 9.6, 7.6 4.0 Hz, H-5), 3.50 (3H, s, OMe), 3.45 (1H, br s, OH), 2.36 (1H, br s, OH). Analytical data for **4c** were essentially the same as reported in the literature.[23]

**Methyl 2,3-di-*O*-*p*-methoxybenzyl-*α*-D-glucopyranoside (4d)**

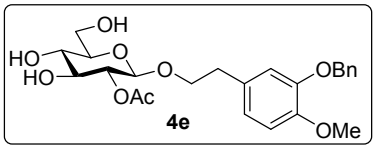


**4d**

Deprotected from **3d** (14.8 mg, 0.028 mmol) according to the General Procedure **A** to give product **4d** (10.2 mg, 83%) as colorless oil. $R_f$ =0.47 (petroleum ether-EdetOAc 1:2). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.29-7.27 (4H, m, Ar-H), 6.88-6.85 (4H, m, Ar-H), 4.92 (1H, d, *J* = 11.2 Hz, $PhCH_2O$), 4.70 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.59 (1H, d, *J* = 11.2 Hz, $PhCH_2O$), 4.58 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.52 (1H, d, *J* = 3.6 Hz, H-1), 3.79 (3H, s, OMe), 3.78 (3H, s, OMe), 3.75 (1H, m), 3.72-3.68 (2H, m), 3.60-3.55 (1H, m, H-5), 3.47-3.42 (2H, m, H-2, H-4), 3.35 (3H, s, OMe). Analytical data for **4d**

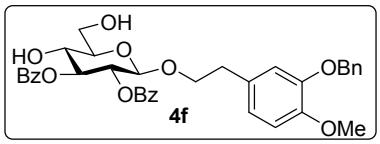
were essentially the same as reported in the literature.[24]

**2-(3-(Benzyloxy)-4-methoxyphenyl)ethyl-2-*O*-acetyl-*β*-D-glucopyranoside (4e)**



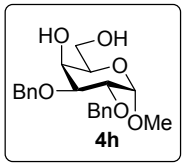

Deprotected from **3e** (33.1 mg, 0.060 mmol) according to the General Procedure **A** to give product **4e** (23.9 mg, 86%) as white solid. $R_f$=0.20 (petroleum ether-EtOAc 1:1). $[\alpha]_D^{25}$ -21.7 (*c*, 1.20 in $CHCl_3$). m.p. 117.8-119.0 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.43-7.26 (5H, m, Ar-H), 6.78-6.68 (3H, m, Ar-H), 5.11 (1H, d, *J* = 12.4 Hz, $PhCH_2O$), 5.07 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.73 (1H, dd, *J* = 8.8, 8.0 Hz), 4.49 (1H, d, *J* = 3.6 Hz), 4.33 (1H, d, *J* = 8.0 Hz, H-1), 4.18 (1H, d, *J* = 5.2 Hz), 4.00 (1H, m), 3.83 (2H, br s), 3.80 (3H, s, OMe), 3.64 (1H, td, *J* = 9.6, 4.0 Hz), 3.55-3.49 (2H, m), 3.34-3.30 (1H, m), 3.24 (1H, dt, *J* = 9.2, 2.8 Hz), 2.71 (2H, m), 1.93 (3H, s, OAc). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 171.1 (C=O), 149.4, 149.1, 137.4, 131.2, 128.7, 128.7, 128.0, 127.6, 127.6, 121.7, 115.3, 112.0 (Ar-C), 101.1 (C-1), 75.6, 75.3, 73.8, 71.2, 71.1, 70.2, 61.7, 56.2 (OMe), 35.6 ($ArCH_2CH_2O$), 21.1 ($CH_3CO$). HRMS calc. for $C_{24}H_{30}NaO_9$ $[M+Na]^+$: 485.1782, found: 485.1783.

**2-(3-(Benzyloxy)-4-methoxyphenyl)ethyl-2,3-di-*O*-benzyl-*β*-D-glucopyranoside (4f)**




Deprotected from **3f** (23.5 mg, 0.033 mmol) according to the General Procedure **A** to give product **4f** (19.0 mg, 93%) as white solid. $R_f$ = 0.34 (petroleum ether-EtOAc 1:1). $[\alpha]_D^{24}$ +48.4 (*c*, 1.1 in $CHCl_3$). m.p. 46.8-49.1 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.94 (2H, d, *J* = 7.2 Hz, Ar-H), 7.88 (2H, d, *J* = 7.2 Hz, Ar-H), 7.51-7.28 (11H, m, Ar-H), 6.65 (1H, d, *J* = 1.6 Hz, Ar-H), 6.61 (1H, dd, *J* = 8.0, 1.6 Hz, Ar-H), 6.48 (1H, d, *J* = 8.0 Hz, Ar-H), 5.37 (2H, m, ), 5.06 (2H, s), 4.67 (1H, d, *J* = 7.2 Hz, H-1), 4.06-3.83 (4H, m), 3.71 (3H, s, OMe), 3.65-3.59 (1H, m), 3.56-3.52 (1H, m), 2.74-2.67 (2H, m). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 167.7 (C=O), 165.4 (C=O), 148.2, 148.0, 137.4, 133.7, 133.3, 130.9, 130.1, 130.1, 129.8, 129.8, 129.5, 128.9, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 127.9, 127.5, 127.5, 121.6, 115.1, 111.8 (Ar-C), 101.1 (C-1), 77.4, 75.9, 71.5, 71.1, 71.0, 70.2, 62.4 (C-6), 56.0 (OMe), 35.6 ($ArCH_2CH_2O$). HRMS calc. for $C_{36}H_{36}NaO_{10}$ $[M+Na]^+$: 651.2200, found: 651.2212.

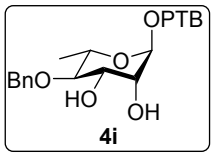
**Methyl 2,3-di-*O*-benzyl-*α*-D-galactopyranoside (4h)**




Deprotected from **3h** (26.7 mg, 0.058 mmol) according to the General Procedure **A** to give product **4h** (20.8 mg, 96%) as colourless oil. $R_f$= 0.38 (petroleum ether-EtOAc 1:1). $[\alpha]_D^{25}$ +43.0 (*c*, 0.74 in $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.27-7.17 (10H, m, Ar-H), 4.91 (1H, d, *J* = 11.6 Hz, $PhCH_2O$), 4.66 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.59 (1H, d, *J* = 11.6 Hz, $PhCH_2O$), 4.55 (1H, d, *J* = 12.0 Hz, $PhCH_2O$), 4.48 (1H, d, *J* = 3.6 Hz, H-1), 3.69-3.59 (3H, m, H-3, H-6a, H-6b), 3.52-3.48 (1H, m, H-5), 3.42-3.36 (2H, m, H-2, H-4), 3.26 (3H, s, OMe), 2.22 (1H, br s, OH), 1.82 (1H, br s, OH). Analytical data for **4h**

were essentially the same as reported in the literature.[25]

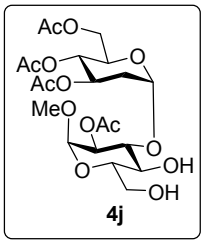
**2-[(Propan-2-yl)sulfanyl]benzyl 4-*O*-benzyl-*α*-L-rhamnose (4i)**



**4i**

Deprotected from **3i** (22.0 mg, 0.043 mmol) according to the General Procedure **A** to give product **4i** (17.3 mg, 96%) as white solid. $R_f$ = 0.54 (petroleum ether-EtOAc 1:1). $[\alpha]_D^{25}$ -50.2 (*c*, 1.29 in $CHCl_3$). m.p. 50.5-52.9 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.34-7.09 (9H, m, Ar-H), 4.80 (1H, s, H-1), 4.73 (1H, d, $J$ = 12.0 Hz, $PhCH_2O$), 4.63 (2H, t, $J$ = 12.0 Hz, $PhCH_2O$), 4.54 (1H, d, $J$ = 12.0 Hz, $PhCH_2O$), 3.87-3.83 (2H, m, H-2, H-3), 3.76-3.69 (1H, m, H-5), 3.28-3.21 [2H, m, H-4, $C\underline{H}(CH_3)_2$], 2.34 (1H, d, $J$ = 3.6 Hz, OH), 2.26 (1H, d, $J$ = 4.8 Hz, OH), 1.25 (3H, d, $J$ = 6.0 Hz, H-6), 1.16 (6H, d, $J$ = 6.8 Hz, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 138.8, 138.4, 135.0, 132.6, 129.0, 128.8, 128.8, 128.4, 128.2, 128.2, 128.2, 127.1 (Ar-C), 99.1 (C-1), 81.9 (C-4), 75.2 (C-2), 71.7 (C-3), 71.4 (C-5)，67.8 ($Ph\underline{C}H_2O$), 67.7 ($Ph\underline{C}H_2O$), 38.8[$S\underline{C}H(CH_3)_2$], 23.3 [$SCH(\underline{C}H_3)_2$], 23.3 [$SCH(\underline{C}H_3)_2$], 18.2 (C-6). HRMS calc. for $C_{23}H_{30}NaO_5S$ $[M+Na]^+$: 441.1706, found: 441.1717.

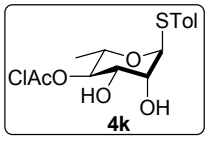
**Methyl3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-*α*-D-arabino-hexopyranosyl)-2-*O*-acetyl-*α*-D-arabinopyranose (4j)**



**4j**

Deprotected from **3j** (11.8 mg, 0.020 mmol) according to the General Procedure **A** to give product **4j** (9.5 mg, 95%) as colorless oil. $R_f$ = 0.18 (petroleum ether-EtOAc 1:2). $[\alpha]_D^{20}$ +127.3 (*c*, 0.88 in $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.39 (1H, d, $J$ = 1.6 Hz, H-1'), 5.23-5.17 (1H, m, H-3'), 4.98 (1H, t, $J$ = 9.6 Hz,H-4'), 4.85 (1H, d, $J$ = 3.6 Hz, H-1), 4.72 (1H, dd, $J$ = 10.4, 3.6 Hz, H-2), 4.20 (1H, dd, $J$ = 12.0, 4.4 Hz, H-6a' ), 4.14-4.08 (2H, m), 4.00 (1H, t, $J$ = 9.6 Hz), 3.83 (2H, d, $J$ = 3.6 Hz), 3.77 (1H, t, $J$ = 9.6 Hz), 3.62-3.58 (1H, m, H-5), 3.40 (1H, brs, OH), 3.34 (3H, s, OMe), 2.28 (1H, m), 2.10, 2.08, 2.01, 1.99 (12H, 4s, 4 $COCH_3$), 1.75 (2H, td, $J$ = 12.4, 3.2 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 171.0, 170.8, 170.7, 170.1 ($\underline{C}$=O), 97.6, 97.3, 72.0, 71.1, 70.9, 69.4, 69.2, 68.9, 62.5, 62.2, 55.4 ($OCH_3$), 35.3 (C-2'), 21.2 ($CH_3$), 21.1 ($CH_3$), 20.9 ($CH_3$), 20.9 ($CH_3$). HRMS calc. for $C_{21}H_{32}NaO_{14}$ $[M+Na]^+$: 531.1690, found: 531.1693.

***S*-*p*-Tolyl 4-chloroacetyl-1-thio-*α*-L-rhamnose (4k)**

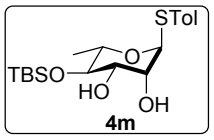


**4k**

Deprotected from **3k** (24.2 mg, 0.062 mmol) according to the General Procedure **B** to give product **4k** (20.2 mg, 93%) as white solid. $R_f$ = 0.22 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ -211.8 (*c*, 0.51 in $CHCl_3$). m.p. 145.5-146.9 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.34-7.32 (2H, d, Ar-H), 7.12-7.10 (2H, d, Ar-H), 5.41 (1H, s, H-1), 4.94 (1H, t, $J$ = 9.6 Hz, H-4), 4.34 (1H, m, H-5), 4.21 (1H, s, H-2 ), 4.13 (2H, s, $CH_2$),3.91 (1H, m, H-3), 2.75 (1H, d, $J$ = 7.6 Hz, OH), 2.66 (1H, d, $J$ = 4.0 Hz, OH), 2.32 (3H, s, $CH_3$), 1.22 (3H, d, $J$ = 6.4 Hz, H-6). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.1 ($\underline{C}$=O), 138.3, 132.4, 132.4, 130.2, 130.2, 129.8 (Ar-C), 88.1 (C-1), 77.4 (C-3), 72.7 (C-2), 70.5 (C-4), 67.0 (C-5), 41.0 ($Cl\underline{C}H_2CO$), 21.3 ($S\text{-}C_6H_4\text{-}\underline{C}H_3$), 17.5 (C-6). HRMS calc. for

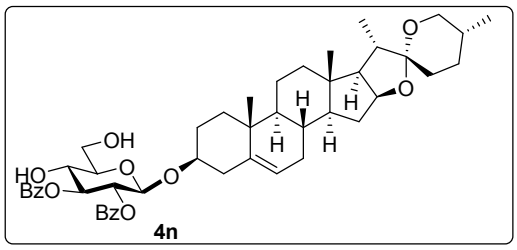
$C_{15}H_{20}ClNaO_6S$ [M+Na]$^+$: 369.0539, found: 369.0526.

**_S-p_-Tolyl 4-tert-butyldimethylsilyl-1-thio-_α_-L-rhamnose (4m)**



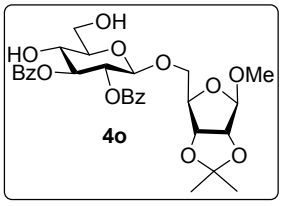

Deprotected from **3m** (24.0 mg, 0.057 mmol) according to the General Procedure **B** to give product **4m** (16.0 mg, 75%) as white syrup. $R_f$ = 0.20 (petroleum ether-EtOAc 5:1). $[\alpha]_D^{25}$ -182.5 (*c*, 1.25 in $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.35-7.09 (4H, m, Ar-H), 5.37 (1H, d, *J* = 0.8 Hz, H-1), 4.15 (1H, s, H-2), 4.10 (1H, m, H-3), 3.75 (1H, m, H-5), 3.51 (1H, t, *J* = 8.8 Hz, H-4), 2.56 (1H, brs, OH), 2.31 (3H, s, $CH_3$), 2.28 (1H, brs, OH), 1.25 (3H, d, *J* = 6.4 Hz, H-6), 0.90 [9H, s, $C(CH)_3$], 0.13 [3H, s, $Si(CH_3)_2$], 0.10 [3H, s, $Si(CH_3)_2$]. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 137.9, 132.4, 132.4, 130.4, 130.1, 130.1 (Ar-C), 88.1 (C-1), 75.2 (C-3), 72.9 (C-2), 72.8 (C-4), 69.9 (C-5), 26.1 [$SiC(\underline{C}H_3)_3$], 26.1 [$SiC(\underline{C}H_3)_3$], 26.1 [$SiC(\underline{C}H_3)_3$], 21.3 ($Ar\underline{C}H_3$), 18.4 [$Si\underline{C}(CH_3)_3$], 18.1 (C-6), -3.6 [$Si(CH_3)_2$], -4.2 [$Si(CH_3)_2$], HRMS calc. for $C_{19}H_{32}NaO_5SSi$ [M+Na]$^+$: 407.1688, found: 407.1690.

**Diosgenyl 2,3-Di-*O*-benzoyl-*β*-D-glucopyranoside (4n)**




Deprotected from **3n** (26.0 mg, 0.030 mmol) according to the General Procedure **A** to give product **4n** (19.6 mg, 85%) as white syrup. $R_f$ = 0.47 (petroleum ether-EtOAc 1:1). $[\alpha]_D^{20}$ +92.8 (*c*, 1.0 in $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.96-7.93 (4H, m, Ar-H), 7.49 (2H, td, *J* = 7.2, 1.2 Hz, Ar-H), 7.36 (4H, t, *J* = 7.2 Hz, Ar-H), 5.40-5.33 (2H, m, H-2, H-3), 5.21 (2H, d, *J* = 5.2 Hz), 4.81 (1H, d, *J* = 7.6 Hz, H-1), 4.37 (1H, q, *J* = 7.6 Hz), 3.95 (2H, m), 3.87 (1H, dd, *J* = 12.0, 4.8 Hz), 3.58-3.43 (3H, m), 3.34 (1H, t, *J* = 10.8 Hz), 2.18-1.00 (26H, m), 0.94 (3H, d, *J* = 6.8 Hz, Me), 0.89 (3H, s, Me), 0.76 (3H, d, *J* = 6.4 Hz, Me), 0.73 (3H, s, Me). Analytical data for **4n** were essentially the same as reported in the literature.[26]

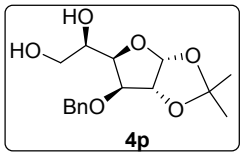
**Methyl 2,3-*O*-methylethylidene-5-*O*-(2,3-di-*O*-benzyl-*β*-D-glucopyranosyl)-*β*-D-ribofuranoside (4o)**




Deprotected from **3o** (13.2 mg, 0.020 mmol) according to the General Procedure **A** to give product **4o** (10.2 mg, 90%) as white solid. $R_f$ = 0.22 (petroleum ether-EtOAc 1:1). $[\alpha]_D^{24}$ +26.3 (*c*, 0.3 in $CHCl_3$). m.p. 175.0-180.5 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.95-7.93 (4H, m, Ar-H), 7.52-7.46 (2H, m, Ar-H), 7.38-7.33 (4H, m, Ar-H),5.40 (2H, m), 4.86 (1H, s, H-1), 4.77 (1H, d, *J* = 7.6 Hz, H-1′), 4.62 (1H, d, *J* = 6.0 Hz, H-2), 4.49 (1H, d, *J* = 5.6 Hz, H-3), 4.26 (1H, t, *J* = 6.8 Hz), 4.00 (1H, dd, *J* = 12.0, 2.8 Hz), 3.89 (2H, m), 3.72 (2H, m), 3.59 (1H, m), 3.24(3H, s, $OCH_3$), 1.37 (3H, s, $CH_3$), 1.18 (3H, s, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$)

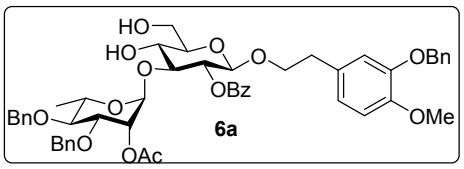
$\delta$ 167.9 (C=O), 165.3 (C=O), 133.8, 133.4, 130.2, 130.2, 130.0, 130.0, 129.5, 128.9, 128.6, 128.6, 128.5, 128.5 (Ar-C), 112.6, 109.2, 101.3, 85.4, 85.1, 82.3, 77.4, 76.5, 71.3, 71.3, 70.2, 62.4, 55.0 (OMe), 26.5 [CH($CH_3$)], 24.9 [CH($CH_3$)]. HRMS calc. for $C_{29}H_{34}NaO_{12}$ $[M+Na]^+$: 597.1942, found: 597.1955.

**3-*O*-Benzyl-1,2-*O*-isopropylidene-*α*-D-glucofuranose (4p)**



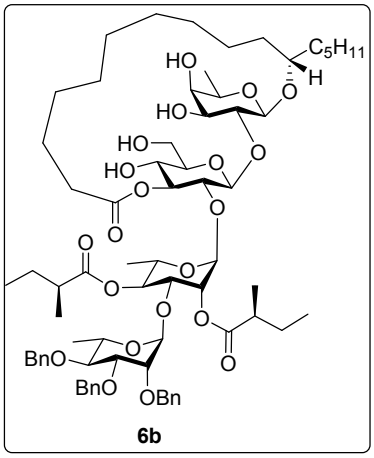

Deprotected from **3p** (22.5 mg, 0.064 mmol) according to the General Procedure **A** to give product **4p** (18.5 mg, 93%) as colourless oil. $R_f$ = 0.20 (petroleum - EtOAc 1:1). $[\alpha]_D^{20}$ -49.5 (*c*, 1.05 in $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.29-7.15 (5H, m, Ar-H), 5.83 (1H, d, *J* = 4.0 Hz, H-1), 4.63 (1H, d, *J* = 12.0 Hz, PhC$H_2$O), 4.52 (1H, d, *J* = 3.6 Hz, H-2), 4.44 (1H, d, *J* = 12.0 Hz, PhC$H_2$O), 4.01 (2H, m, H-3, H-4), 3.92 (1H, m, H-5), 3.70 (1H, dd, *J* = 11.6, 3.6 Hz, H-6a), 3.58 (1H, dd, *J* = 11.6, 5.6 Hz, H-6b), 2.91 (2H, brs, OH), 1.38 (3H, s, $CH_3$), 1.21 (3H, s, $CH_3$). Analytical data for **4p** were essentially the same as reported in the literature.[27]

**2-(4-(Benzyloxy)-3-methoxyphenyl)ethyl 2-*O*-benzoyl-3-*O*-(2-*O*-acetyl-3,4-di-*O*-benzyl-*α*-L-rhamnopyranosyl)-*β*-D-glucopyranoside (6a)**




Deprotected from **5a** (20.0 mg, 0.020 mmol) according to the General Procedure **A** to give **6a** (16.4 mg, 90%). Altertively, increase the amount of CSA to 1.0 equiv shortened the reaction to 10 h and gave **6a** (17.9 mg, 98%) as white solid, $R_f$ = 0.24 (petroleum - EtOAc 1:1). $[\alpha]_D^{20}$ +19.8 (*c*, 0.41 in $CHCl_3$). m.p. 110.9-112.8 °C $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.03-8.01 (2H, d, *J* = 8.0 Hz, Ar-H), 7.58-7.11 (18H, m, Ar-H), 6.66 (1H, brs, H-2), 6.63 (1H, d, *J* = 8.0 Hz, H-6), 6.50 (1H, d, *J* = 8.0 Hz, H-5), 5.14 (1H, t, *J* = 8.8 Hz, H-$2_{Glu}$), 5.06 (2H, s, PhC$H_2$O), 4.95 (1H, appar. s, H-$2_{Rham}$), 4.84-4.82 (2H, m), 4.54 (1H, d, *J* = 8.0 Hz, H-$1_{Glu}$), 4.52 (1H, d, *J* = 11.2 Hz, PhC$H_2$), 4.21 (2H, s, PhC$H_2$), 4.04-4.00 (2H, m), 3.98-3.90 (2H, m), 3.84-3.77 (2H, m), 3.71 (3H, s, OMe), 3.68-3.56 (3H, m), 3.41-3.34 (2H, m), 2.70 (2H, m, ArC$H_2$C$H_2$O), 2.12 (1H, brs. OH), 1.97 (3H, s, OAc), 1.30 (3H, d, *J* = 6.0 Hz, H-$6_{Rham}$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 170.0 (C=O), 165.3 (C=O), 148.2, 148.0, 138.3, 137.7, 137.4, 133.4, 130.9, 129.9, 129.9, 129.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.3, 128.3, 128.0, 128.0, 127.9, 127.9, 127.8, 127.5, 127.5, 121.6, 115.1, 111.8 (Ar-C), 101.0 (C-1'), 99.8 (C-1''), 86.6, 79.4, 77.0, 75.4, 75.3, 72.1, 71.5, 71.0, 70.9, 70.4, 69.6, 68.8, 62.6, 56.0 (OMe), 35.6 (ArCH$_2$CH$_2$O), 21.0 (CH$_3$CO), 18.2 (C-$6_{Rham}$). HRMS calc. for $C_{51}H_{56}NaO_{14}$ $[M+Na]^+$: 915.3562, found: 915.3549.

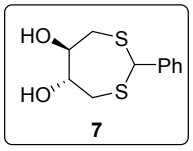
**1,3(B)-Lactone of (S)-1-(Hydroxycarbonyl)pentadec-10-yl *O*-(2,3,4-Tri-*O*-benzyl-*α*-L-rhamnopyranosyl)-(1→3)-2,4-di-*O*-(2S-methylbutyryl)-*α*-L-rhamnopyranosyl)-(1→2)-*β*-D-glucopyranosyl-(1→2)-*β*-D-fucopyranoside (6b)**



**6b**

Deprotected from **5b** (22.0 mg, 0.015 mmol) to give **6b** (18.3 mg, 90%) as white solid with 4.0 equiv DTT and 1.0 equiv CSA. $R_f$ = 0.51 (DCM-MeOH 10:1). $[\alpha]_D^{20}$ +0.39 (*c*, 1.8 in $CHCl_3$). m.p. 56.0-64.0 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.33-7.21 (15H, m, Ar-H), 5.10 (1H, d, *J* = 7.2 Hz), 5.04-4.98 (4H, m), 4.92 (1H, s), 4.86 (1H, d, *J* = 11.6 Hz), 4.71 (1H, d, *J* = 12.8 Hz), 4.66 (1H, d, *J* = 12.8 Hz), 4.58-4.49 (3H, m), 4.17-4.12 (2H, m), 4.07 (1H, dd, *J* = 10.0, 2.4 Hz), 3.97 (1H, d, *J* = 11.6 Hz), 3.89 (2H, m), 3.71-3.47 (14H, m), 2.73 (1H, m), 2.45-2.35 (2H, m), 2.19 (1H, m), 1.71-1.53 (6H, m), 1.45-1.19 (29H, m), 1.13 (3H, d, *J* = 6.4 $H_Z$), 1.11 (3H, d, *J* = 7.2 $H_Z$), 1.03 (3H, d, *J* = 6.8 $H_Z$), 0.88-0.84 (6H, m), 0.79 (3H, t, *J* = 7.2 $H_Z$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 176.1, 175.5, 175.3, 139.1, 138.6, 138.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.3, 128.3, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 102.2, 101.1, 98.9, 97.2, 81.9, 80.7, 80.2, 80.2, 79.0, 75.8, 75.5, 75.3, 75.0, 74.6, 72.8, 72.8, 72.5, 72.2, 72.0, 71.2, 70.7, 69.1, 67.2, 62.2, 41.4, 34.6, 34.3, 32.0, 31.5, 29.5, 27.9, 27.7, 26.8, 26.6, 26.4, 25.5, 24.3, 23.5, 22.8, 18.0, 17.0, 17.0, 16.7, 14.3, 12.0, 11.9. HRMS calc. for $C_{71}H_{104}NaO_{21}$ $[M+Na]^+$: 1315.6962, found: 1315.7015.

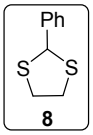
**1,3-Dithiepane (7)**



**7**

Separated from the deprotection of **3a** to **4a** according to the General Procedure **A**. 67%. White solid. $R_f$ = 0.44 (petroleum-EtOAc 1:1). m.p. 102.3-104.4 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.43 (2H, d, *J* = 7.2 Hz, Ar-H), 7.34-7.26 (3H, m, Ar-H), 5.21 (1H, s, $PhCHS_2$), 3.95 (1H, t, *J* = 6.4 Hz, CHOH), 3.88 (1H, t, *J* = 6.0 Hz, CHOH), 3.29 (1H, dd, *J* = 15.2, 2.0 Hz, $CH_2SR$), 3.16 (1H, dd, *J* = 15.2, 6.8 Hz, $CH_2SR$), 3.01 (1H, dd, *J* = 15.2, 1.6 Hz, $CH_2SR$), 2.92 (1H, dd, *J* = 15.6, 8.8 Hz, $CH_2SR$), 2.74 (2H, brs, OH). $^{13}$C NMR (100 MHz, $CD_3COCD_3$) $\delta$ 141.3, 128.5, 128.5, 128.0, 127.5, 127.5 (Ar-C), 77.6 (CHOH), 77.5 (CHOH), 54.9 ($PhCHS_2$), 35.1 ($CH_2$), 34.2 ($CH_2$). HRMS calc. for $C_{11}H_{14}NaO_2S_2$ $[M+Na]^+$: 265.0333, found: 265.0302.

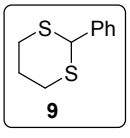
**2-Phenyl-1,3-dithiolane (8)**



**8**

Separated from the deprotection of **3a** to **4a** according to the General Procedure **A** with 1,2-ethanedithiol instead of DTT. 80%. White solid. $R_f$ = 0.50 (petroleum-EtOAc 100:1). m.p. 68.3-70.5 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.50 (2H, d, *J* = 7.2 Hz, Ar-H), 7.31-7.26 (3H, m, Ar-H), 5.62 (1H, s, $PhCHS_2$), 3.52-3.46 (2H, m, $CH_2$), 3.38-3.32 (2H, m, $CH_2$). Analytical data for **8** were essentially the same as reported in the literature.[28]

**2-Phenyl-1,3-dithiane (9)**

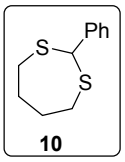


**9**

Separated from the deprotection of **3a** to **4a** according to the General Procedure **A** with 1,3-propanedithiol instead of DTT. 87%. White solid.

$R_f$ = 0.30 (petroleum-EtOAc 100:1). m.p. 74.3-75.4 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.45 (2H, d, $J$ = 7.2 Hz, Ar-H), 7.34-7.28 (3H, m, Ar-H), 5.15 (1H, s, $PhCHS_2$), 3.09-3.02 (2H, m, $CH_2$), 2.90 (2H, dt, $J$ = 14.0, 4.0 Hz, $CH_2$), 2.19-2.13 (1H, m, $CH_2$), 1.96-1.88 (1H, m, $CH_2$). Analytical data for **9** were essentially the same as reported in the literature.[28]

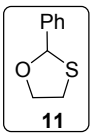
**2-Phenyl-1,3-dithiepane (10)**



**10**

Separated from the deprotection of **3a** to **4a** according to the General Procedure **A** with 1,4-butanedithiol instead of DTT. 91%. White solid. $R_f$ = 0.40 (petroleum-EtOAc 100:1). m.p. 58.0-59.7 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.45 (2H, d, $J$ = 7.6 Hz, Ar-H), 7.32-7.26 (3H, m, Ar-H), 5.28 (1H, s, $PhCHS_2$), 3.13-3.08 (2H, m, $SCH_2$), 2.85-2.79 (2H, m, $SCH_2$), 2.13-2.02 (4H, m, 2×$CH_2$). Analytical data for **10** were essentially the same as reported in the literature.[29]

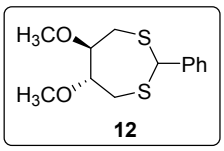
**2-Phenyl-1,3-oxathiolane (11)**



**11**

Separated from the deprotection of **3a** to **4a** according to the General Procedure **A** with 2-mercaptoethanol instead of DTT. 84%. Colourless oil. $R_f$ = 0.52 (petroleum-EtOAc 100:1). $[\alpha]_D^{20}$ -2.1 ($c$, 0.24 in $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.45 (2H, d, $J$ = 8.0 Hz, Ar-H), 7.36-7.28 (3H, m, Ar-H), 6.04 (1H, s, PhCHOS), 4.54-4.50 (1H, m, $CH_2$), 3.98-3.92 (1H, m, $CH_2$), 3.30-3.23 (1H, m, $CH_2$), 3.21-3.16 (1H, m, $CH_2$). Analytical data for **11** were essentially the same as reported in the literature.[30]

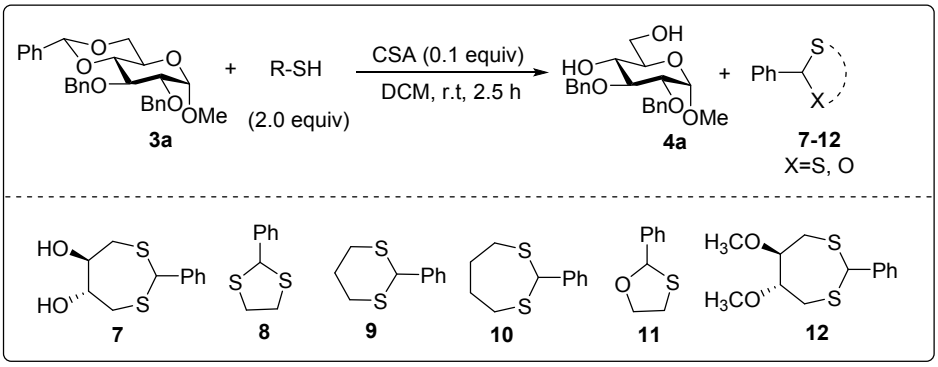
**5,6-Dimethoxy-2-phenyl-1,3-dithiepane (12)**



**12**

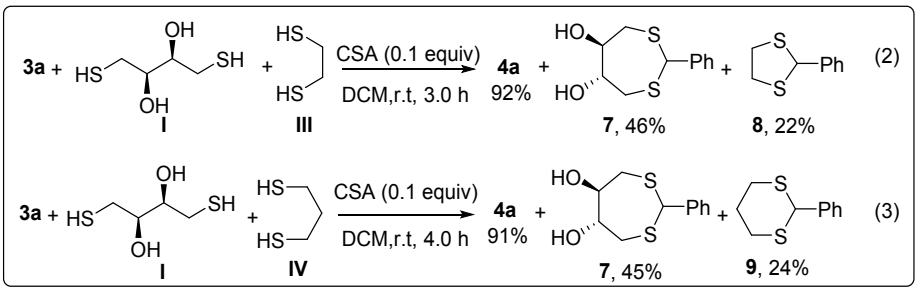
Separated from the deprotection of **3a** to **4a** according to the General Procedure **A** with 2,3-dimethoxybutane-1,4-dithiol instead of DTT. White solid. $R_f$ = 0.55 (petroleum-EtOAc 3:1). m.p. 84.7-87.0 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.43 (2H, d, $J$ = 7.2 Hz, Ar-H), 7.32-7.25 (3H, m, Ar-H), 5.22 (1H, s, $PhCHS_2$), 3.72 (1H, t, $J$ = 7.2 Hz, C<u>H</u>$OCH_3$), 3.50 (1H, td, $J$ = 5.6, 2.0 Hz, C<u>H</u>$OCH_3$), 3.46 (3H, s, $OCH_3$), 3.44 (3H, s, $OCH_3$), 3.20 (1H, dd, $J$ = 15.6, 6.0 Hz, $CH_2SR$), 3.10 (1H, d, $J$ = 15.2 Hz, $CH_2SR$), 2.94-2.92 (1H, m, $CH_2SR$), 2.90-2.88 (1H, m, $CH_2SR$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 140.4, 128.9, 128.9, 128.5, 127.6, 127.6 (Ar-C), 85.4 (<u>C</u>$HOCH_3$), 84.8 (<u>C</u>$HOCH_3$), 58.1 ($OCH_3$), 57.9 ($OCH_3$), 56.1 (Ph<u>C</u>$HS_2$), 32.1 ($CH_2$), 31.1 ($CH_2$). HRMS calc. for $C_{13}H_{18}NaO_2S_2$ $[M+Na]^+$: 293.0640, found: 293.0621.

## 3.3 Thiols mediated cleavage of the benzylidene acetal.




| Entry | R-SH | Yield of **4a** | Recovery of **3a** | Yield of **7-12** |
|---|---|---|---|---|
| 1 | / | 23% | 72% | / |
| 2 | DTT | 94% | / | **7**: 67% |
| 3 | 1,2-Ethanedithiol | 82% | 16% | **8**: 80% |
| 4 | 1,3-Propanedithiol | 67% | 25% | **9**: 87% |
| 5 | 1,4-Butanedithiol | 72% | 26% | **10**: 91% |
| 6 | 2-Mercaptoethanol | 80% | 16% | **11**: 84% |
| 7 | 2,3-dimethoxybutane-1,4-dithiol | 58% | 36% | **12**: 78% |

## 3.4 The competitive reactions of different thiols.

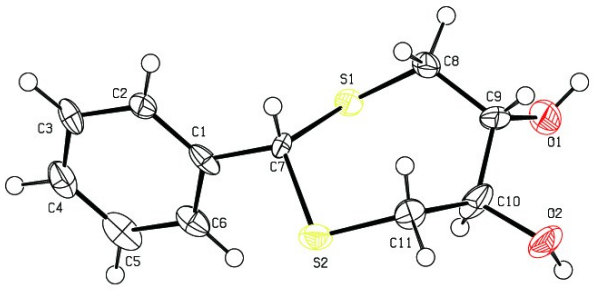



Procedure of the equations (2): To a stirred solution of the acetal protected subtrates **3a** (1.0 equiv), DL-1,4-dithiothreitol (DTT, I, 2.0 equiv) and 1,2-ethanedithiol (III, 2.0 equiv) in $CH_2Cl_2$ (c = 0.1 M) was added (+)-camphor-10-sulfonic acid (CSA, 0.1 equiv) at room temperature. After completion of the reaction (monitored by TLC), the solvent was removed under vacuo and the residue was purified by column chromatography to afford the pure product **4** (92%) . At the same time, we isolated the closed loop compound **7** (46%) as white solid and **8** as white solid (22%).

Procedure of the equations (3): To a stirred solution of the acetal protected subtrates **3a** (1.0 equiv), DL-1,4-dithiothreitol (DTT, I, 2.0 equiv) and 1,3-propanedithiol (IV, 2.0 equiv) in $CH_2Cl_2$ (c = 0.1 M) was added (+)-camphor-10-sulfonic acid (CSA, 0.1 equiv) at room temperature. After completion of the reaction (monitored by TLC), the

solvent was removed under vacuo and the residue was purified by column chromatography to afford the pure product **4** (91%). At the same time, we isolated the closed loop compound **7** (45%) as white solid and **9** as white solid (24%).

## 4. ORTEP Representation of compound 7




| | | |
|---|---|---|
| Empirical formula | $C_{11}H_{14}O_2S2$ | |
| Formula weight | 242.34 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | *P*1 | |
| Unit cell dimensions | *a* = 27.169(18) Å | *a* = 90°. |
| | *b* = 5.157(4) Å | *b* = 121.19(3)°. |
| | *c* = 18.764(9) Å | *g* = 90°. |
| Volume | 2249(3) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.431 $Mg/m^3$ | |
| Absorption coefficient | 0.450 $mm^{-1}$ | |
| F(000) | 1024 | |
| Crystal size | 0.050 x 0.030 x 0.020 $mm^3$ | |
| Crystal color and habit | colourless block | |
| Diffractometer | Bruker Apex II | |
| Theta range for data collection | 1.54 to 26.50°. | |
| Index ranges | -33<=h<=34, -6<=k<=6, -23<=l<=23 | |
| Reflections collected | 11352 | |
| Independent reflections | 4598 [*R*(int) = 0.2046] | |
| Observed reflections (I > 2sigma(I)) | 1957 | |
| Completeness to theta = 26.50° | 99.7 % | |
| Absorption correction | None | |
| Max. and min. transmission | 0.9911 and 0.9779 | |

| | |
|---|---|
| Solution method | SHEL XS -97 (Sheldrick, 1990) |
| Refinement method | SHELXL-97 (Sheldrick, 1997) |
| Data / restraints / parameters | 4598 / 1 / 275 |
| Goodness-of-fit on $F^2$ | 0.927 |
| Final R indices [I>2sigma(I)] | $R1$ = 0.0758, $wR_2$ = 0.0911 |
| R indices (all data) | R1 = 0.2056, wR2 = 0.1239 |
| Absolute structure parameter | -0.11(16) |
| Largest diff. peak and hole | 0.476 and -0.538 e.Å$^{-3}$ |

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# 6. $^{1}$H NMR and $^{13}$C NMR Spectra

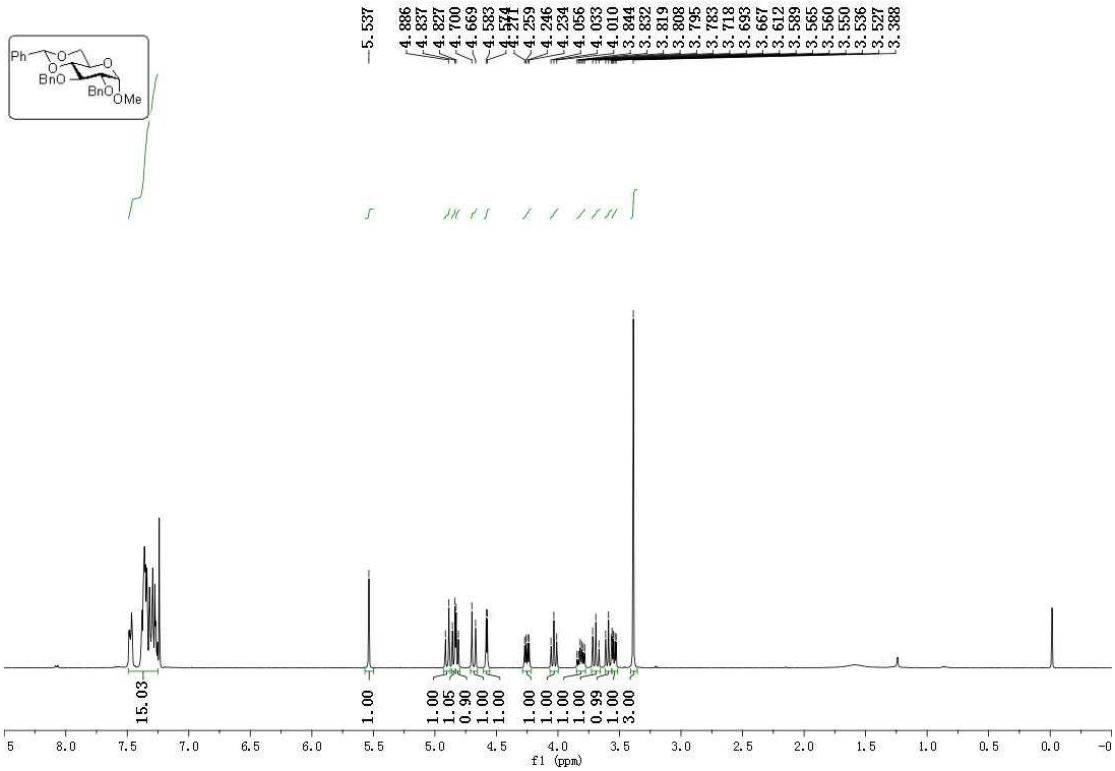


**Figure S1.** $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3a**

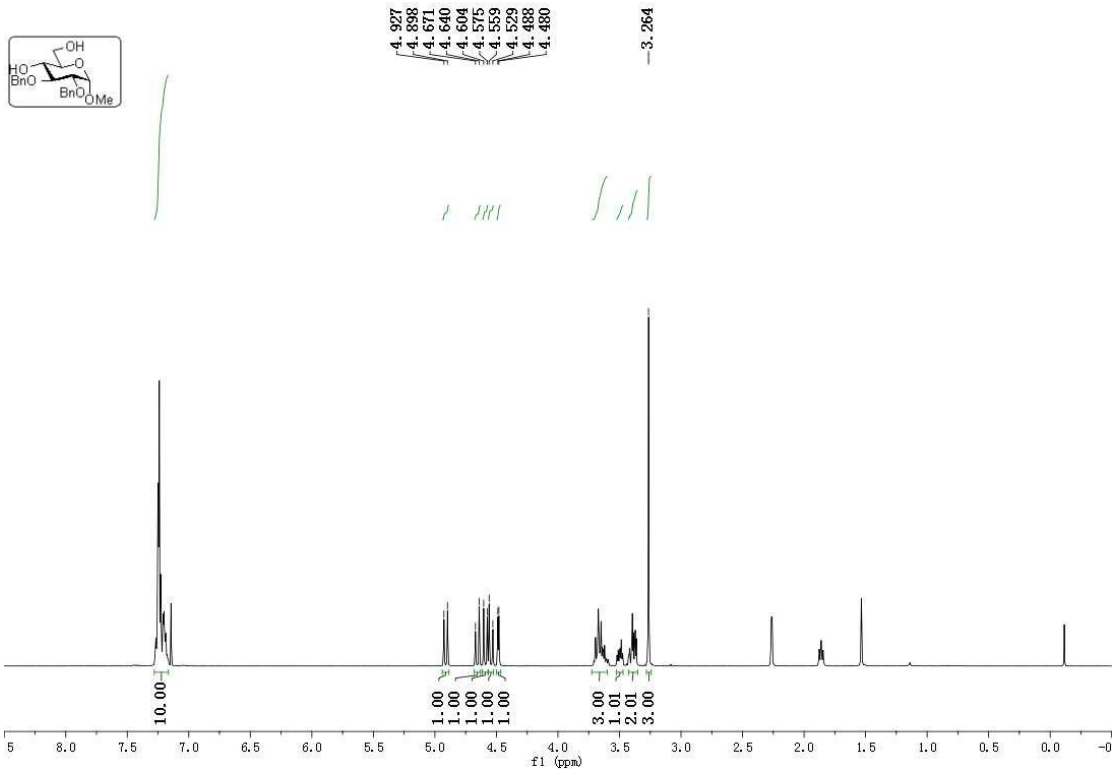


**Figure S2.** $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **4a**

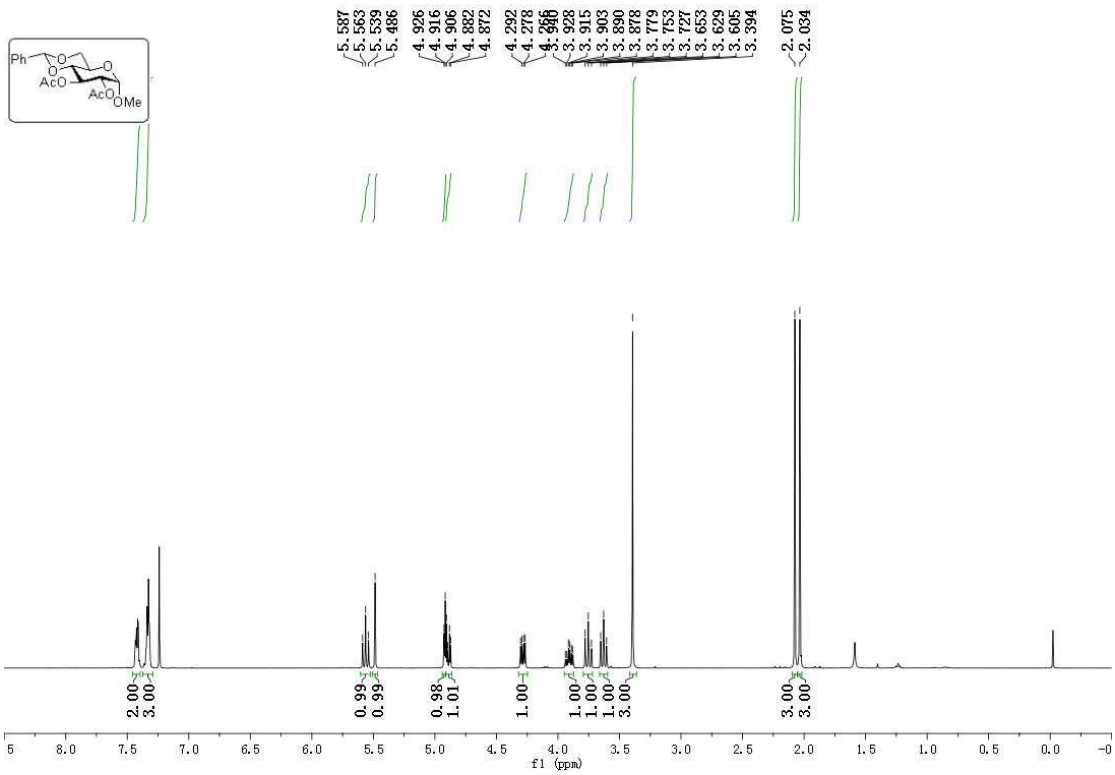


**Figure S3.** $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3b**

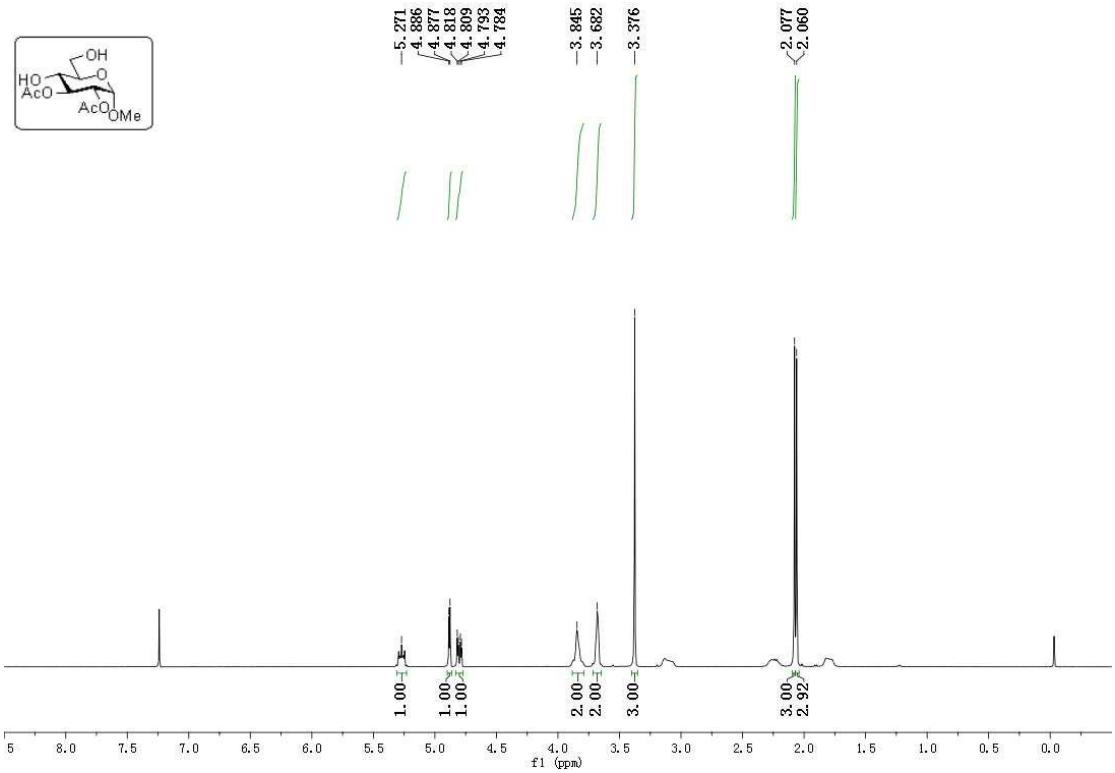


**Figure S4.** $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **4b**

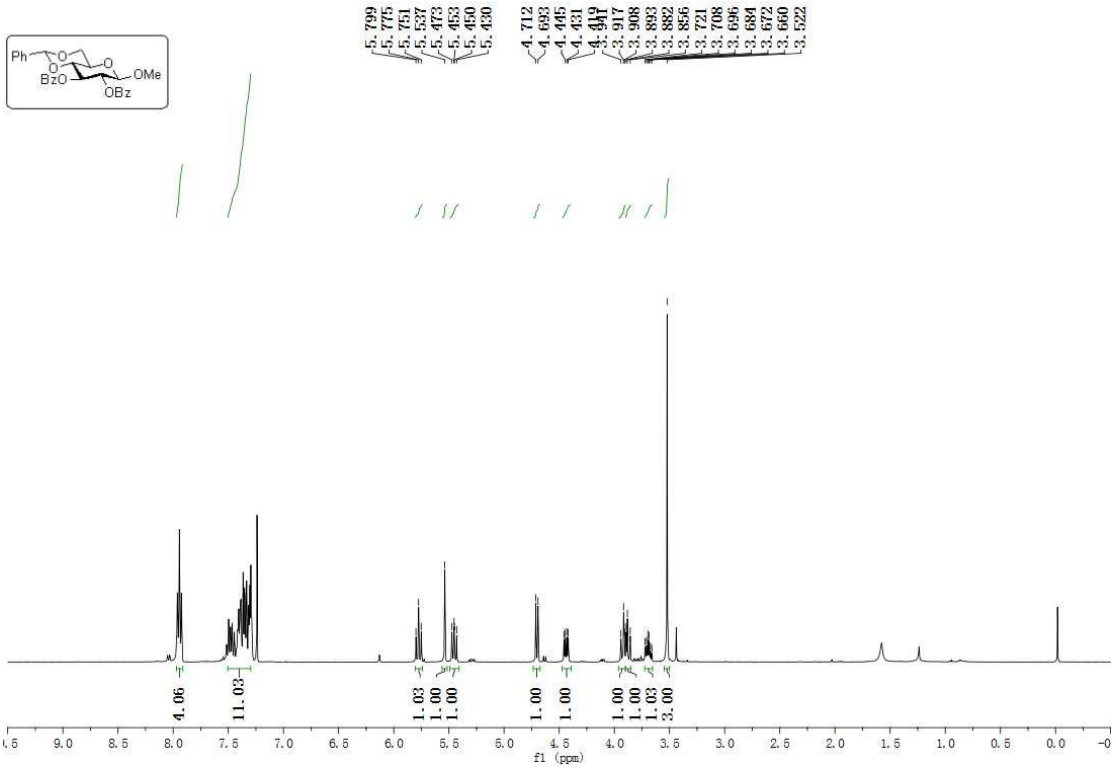

**Figure S5.** $^1$H NMR (400 MHz, $CDCl_3$) spectrum of **3c**

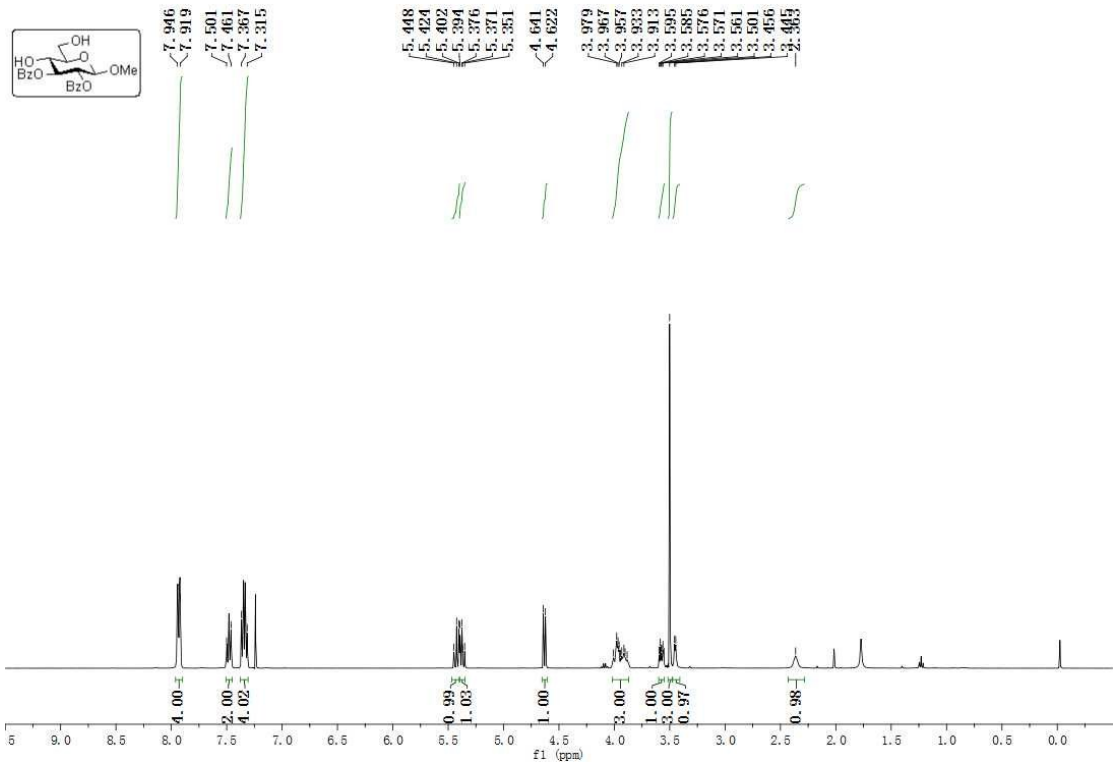

**Figure S6.** $^1$H NMR (400 MHz, $CDCl_3$) spectrum of **4c**

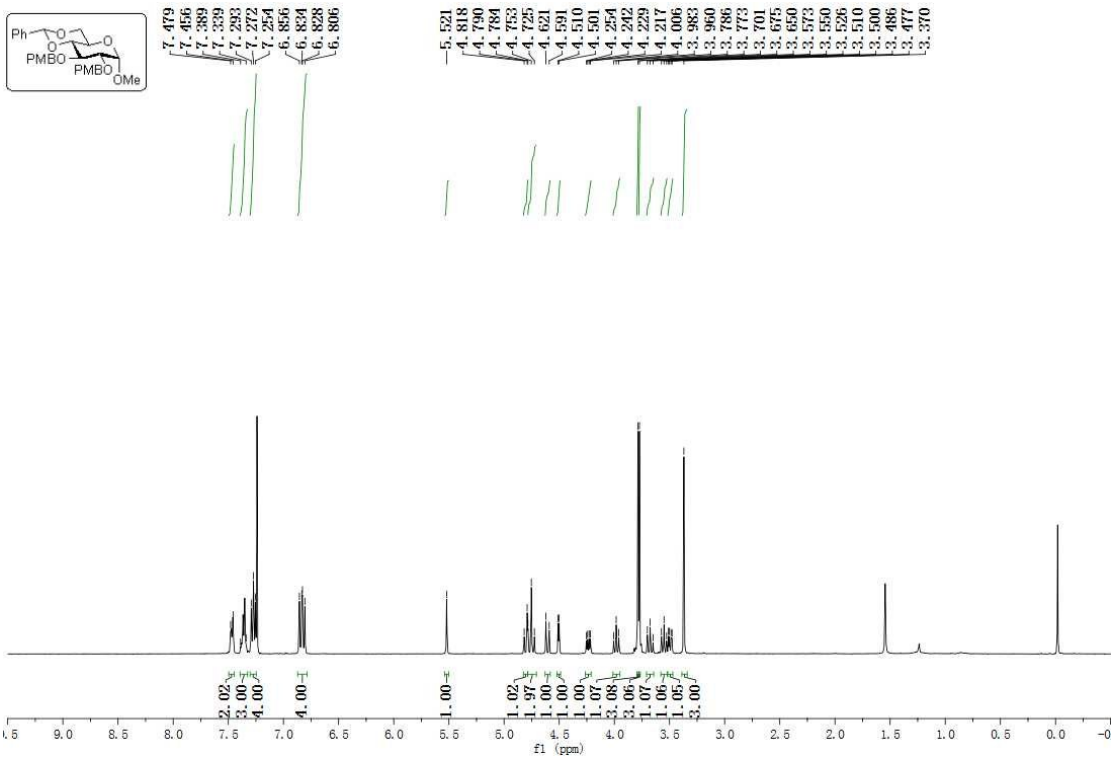

**Figure S7.** $^1$H NMR (400 MHz, $CDCl_3$) spectrum of **3d**

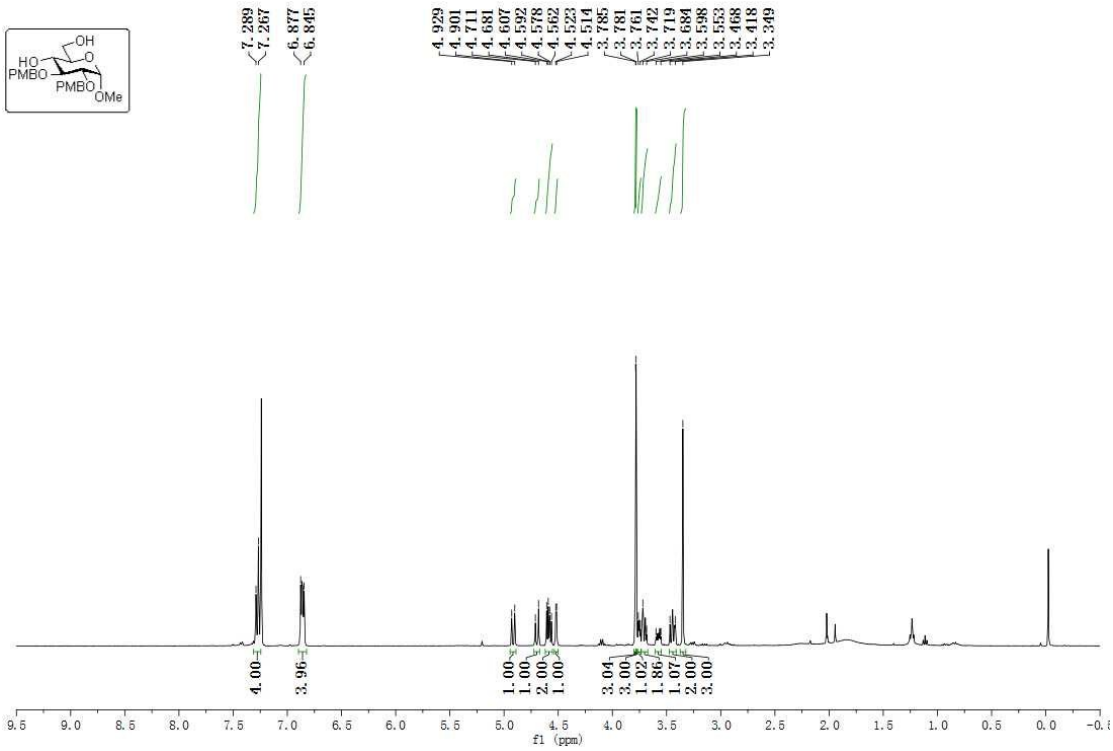

**Figure S8.** $^1$H NMR (400 MHz, $CDCl_3$) spectrum of **4d**

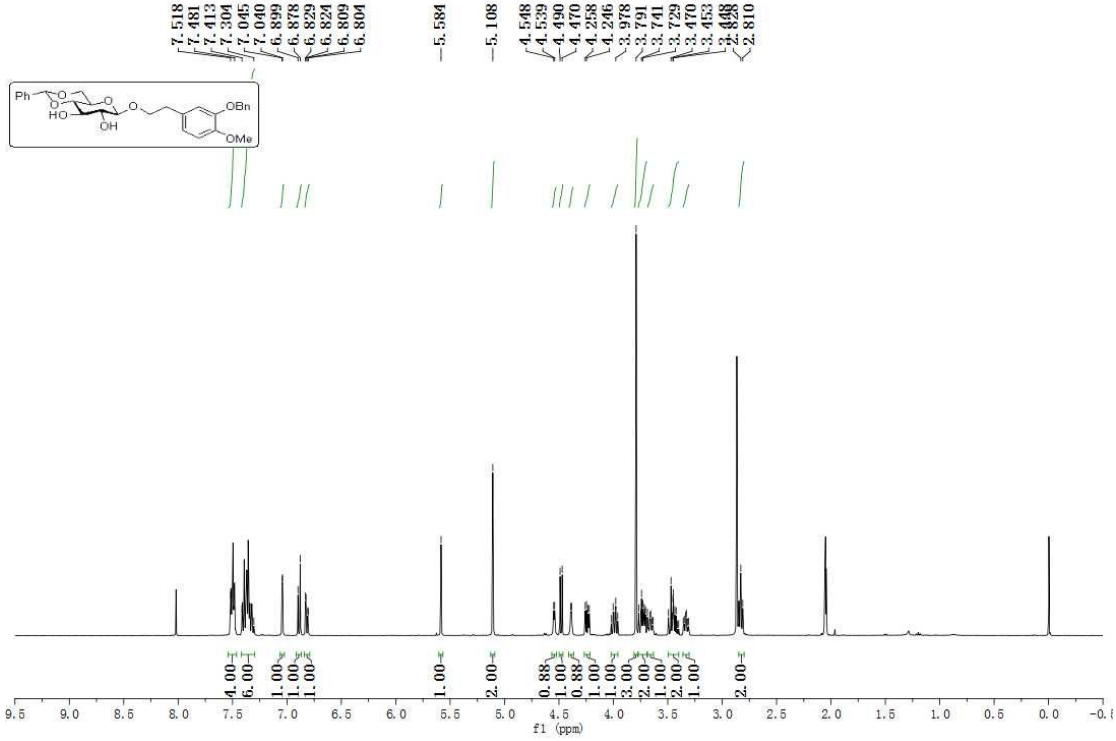

**Figure S9. $^{1}$H NMR (400 MHz, $CD_3COCD_3$) spectrum of S7**

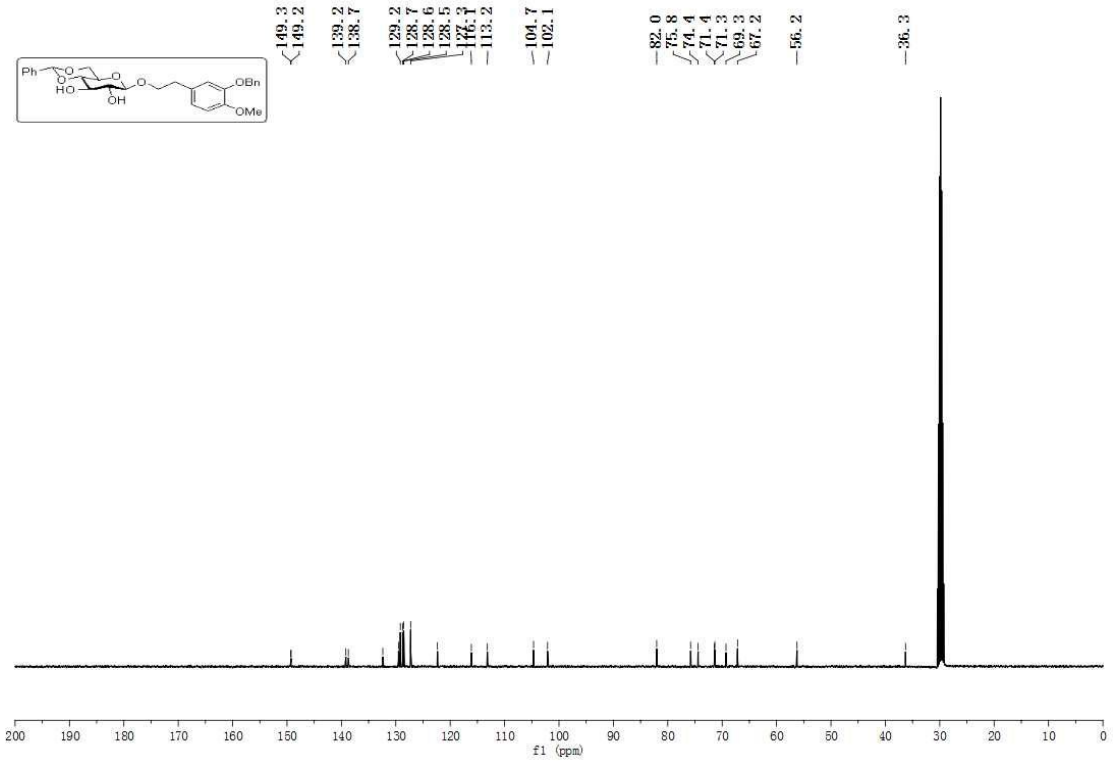

**Figure S10. $^{13}$C NMR (100 MHz, $CD_3COCD_3$) spectrum of S7**

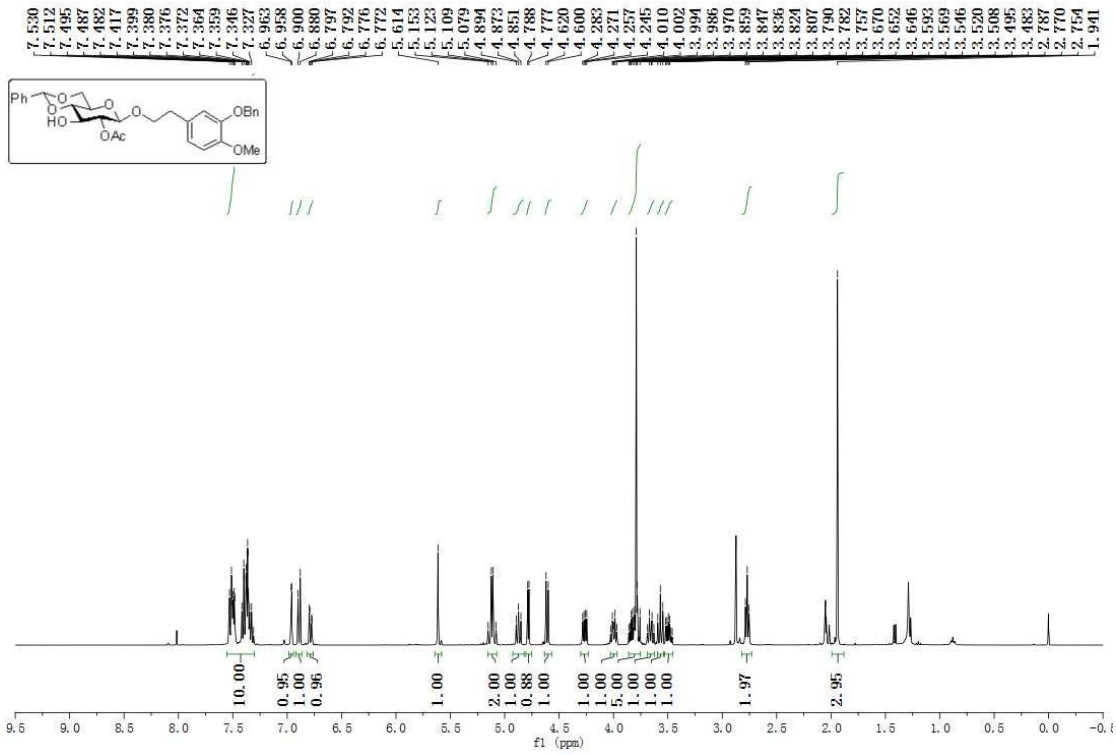


**Figure S11.** $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3e**

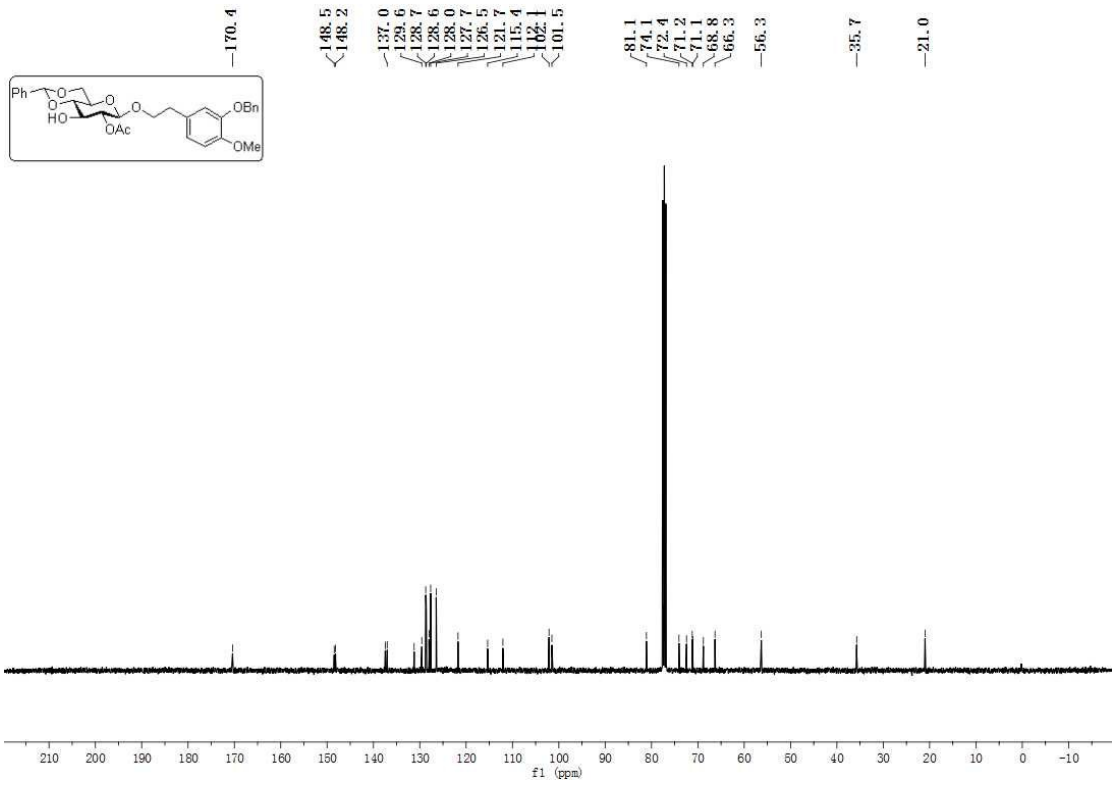


**Figure S12. $^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of 3e**

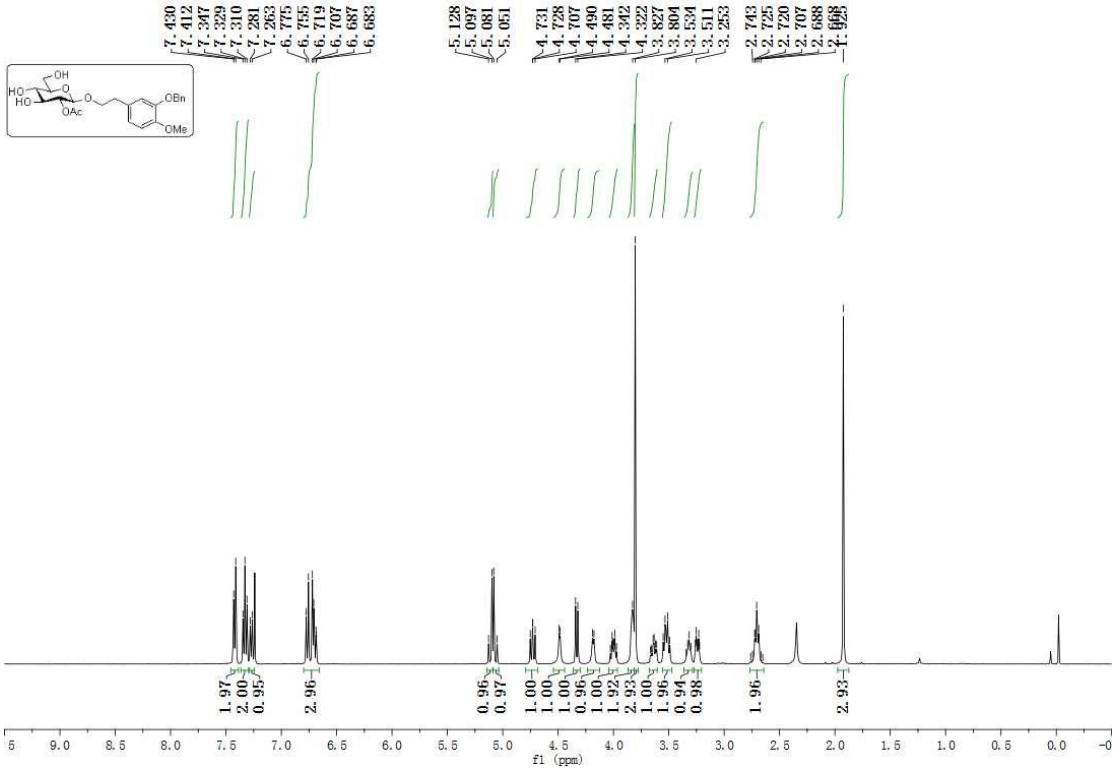

**Figure S13.** $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **4e**

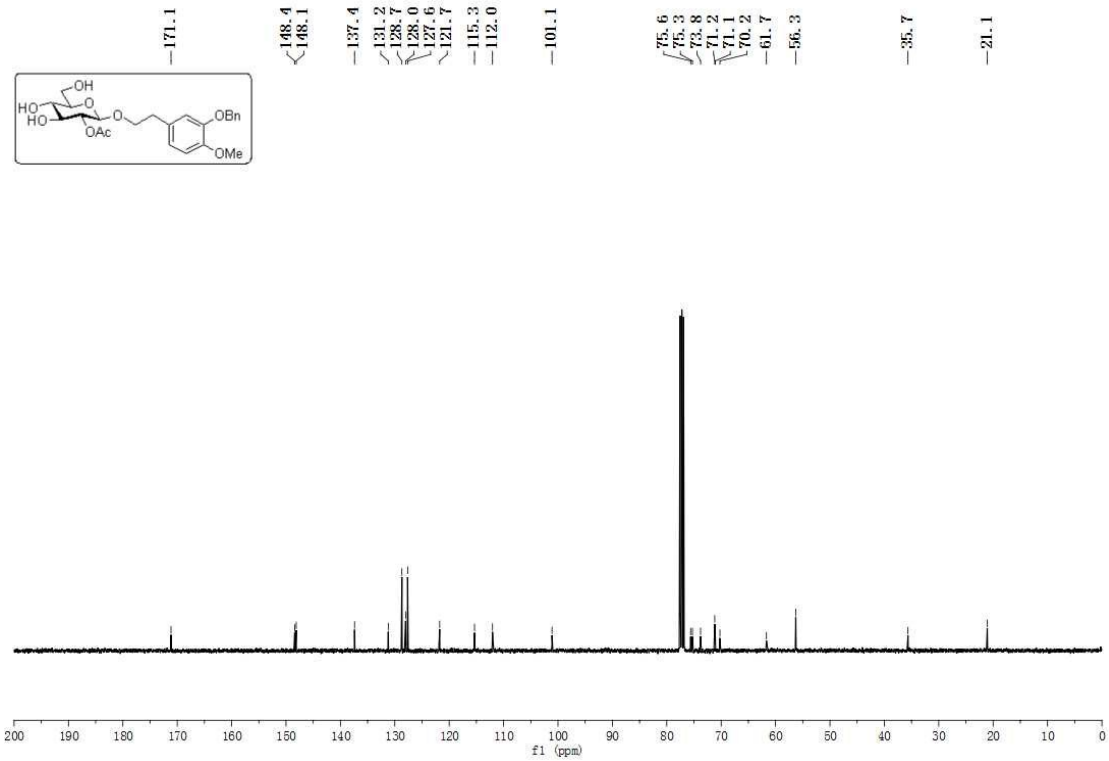

**Figure S14.** $^{13}$**C NMR (100 MHz, $CDCl_3$) spectrum of 4e**

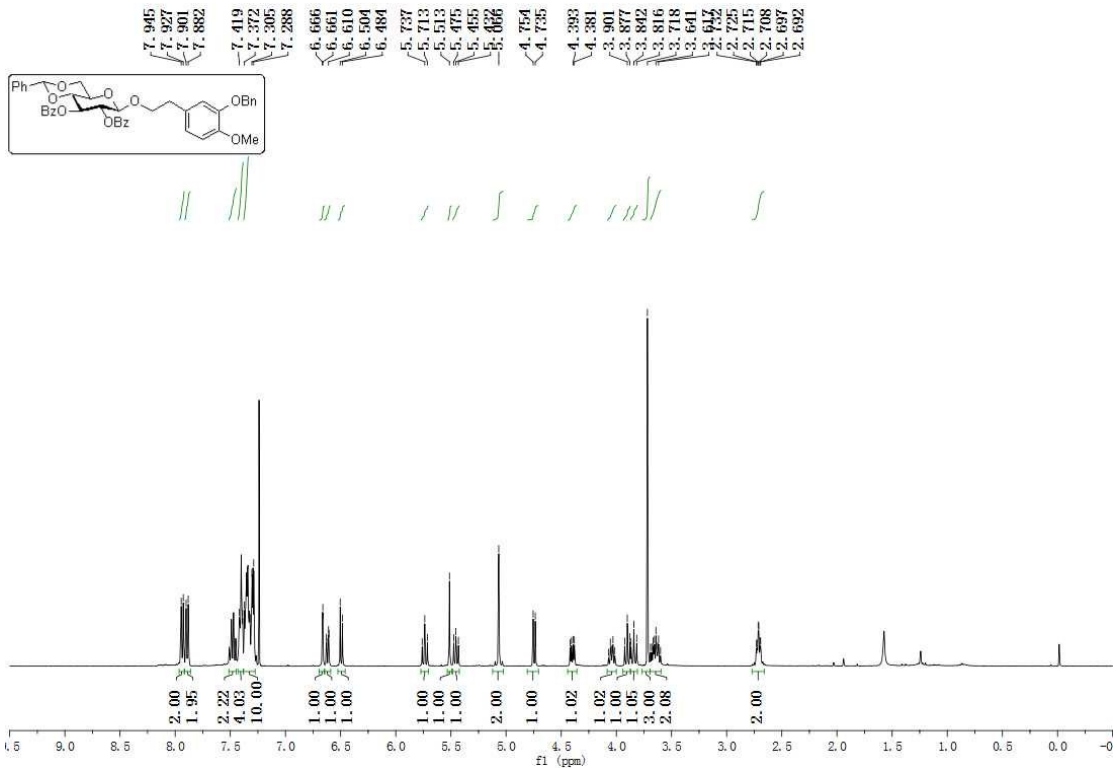


**Figure S15. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of 3f**

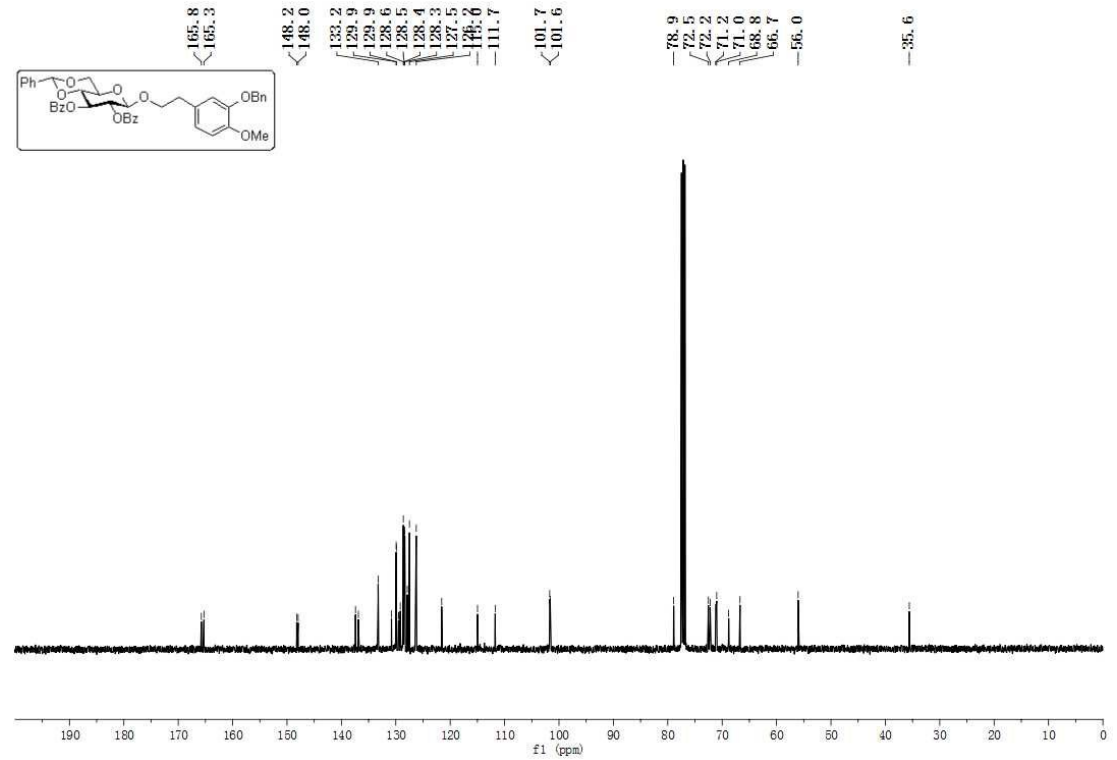


**Figure S16. $^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of 3f**

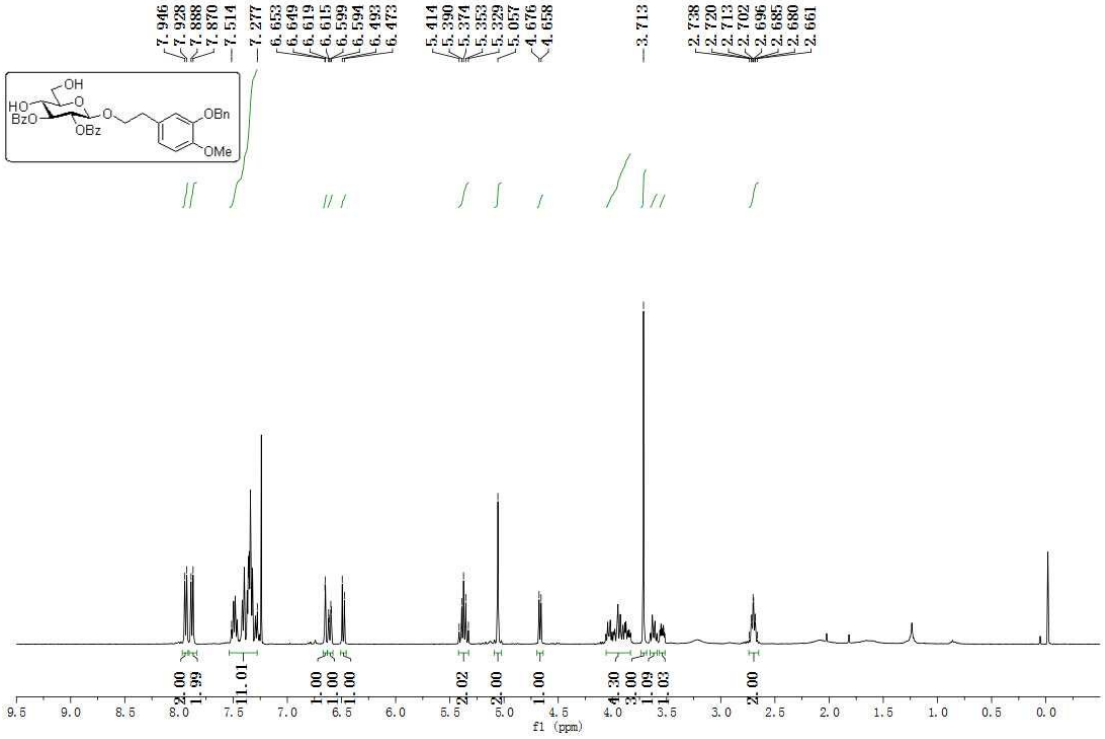


**Figure S17. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of 4f**

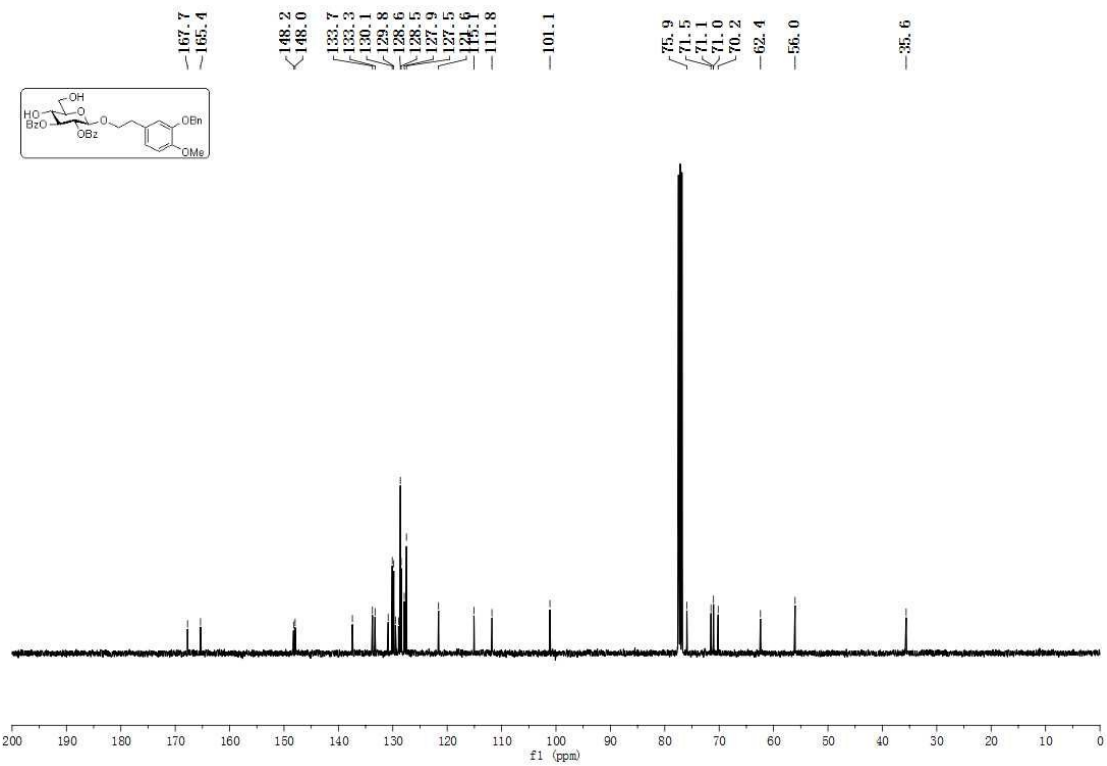


**Figure S18. $^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of 4f**

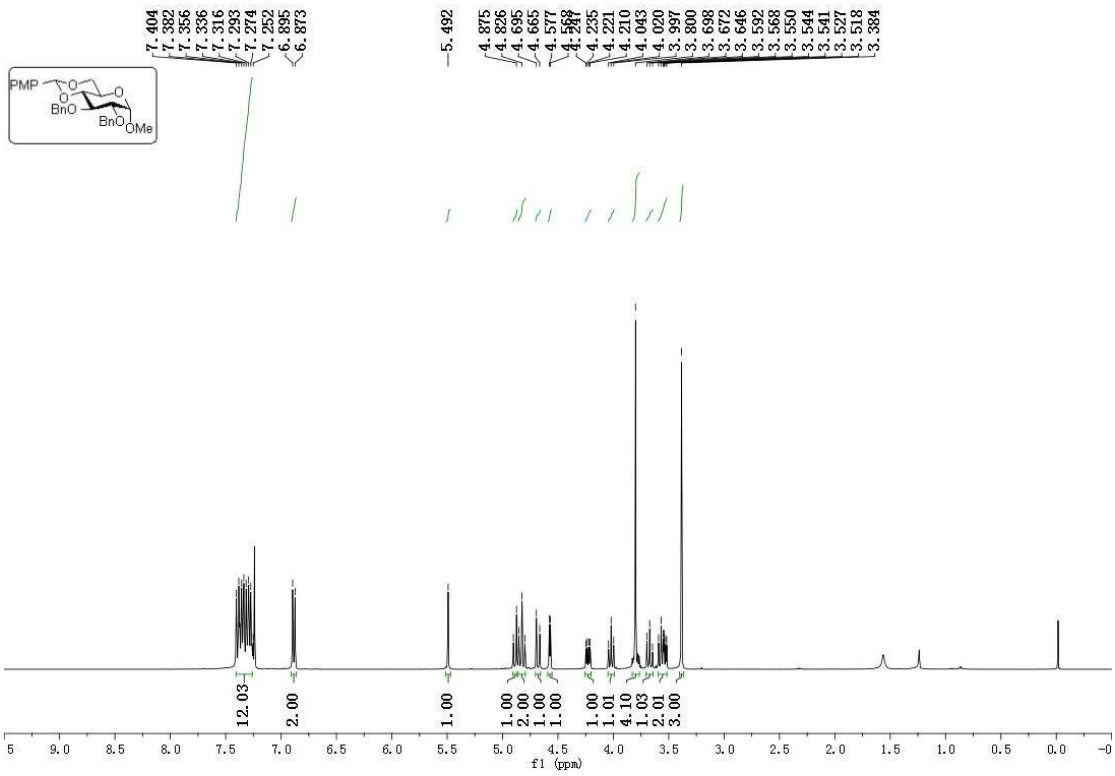


**Figure S19.** $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3g**

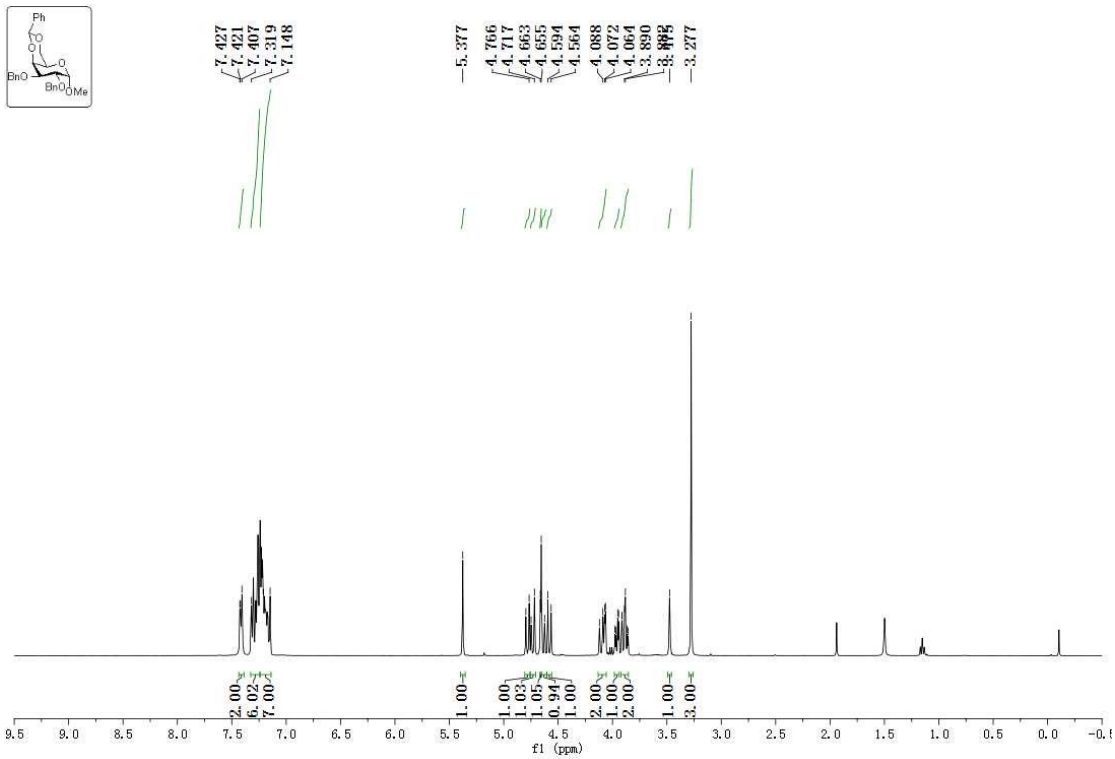


**Figure S20. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of 3h**

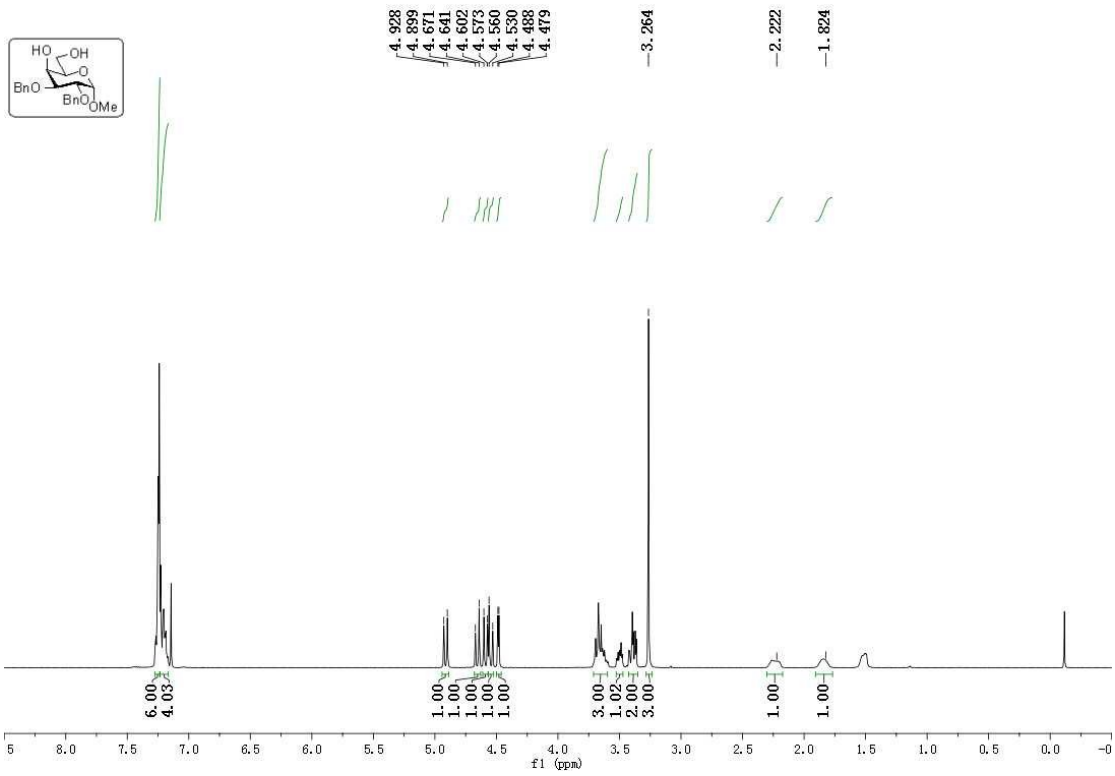


**Figure S21.** $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **4h**

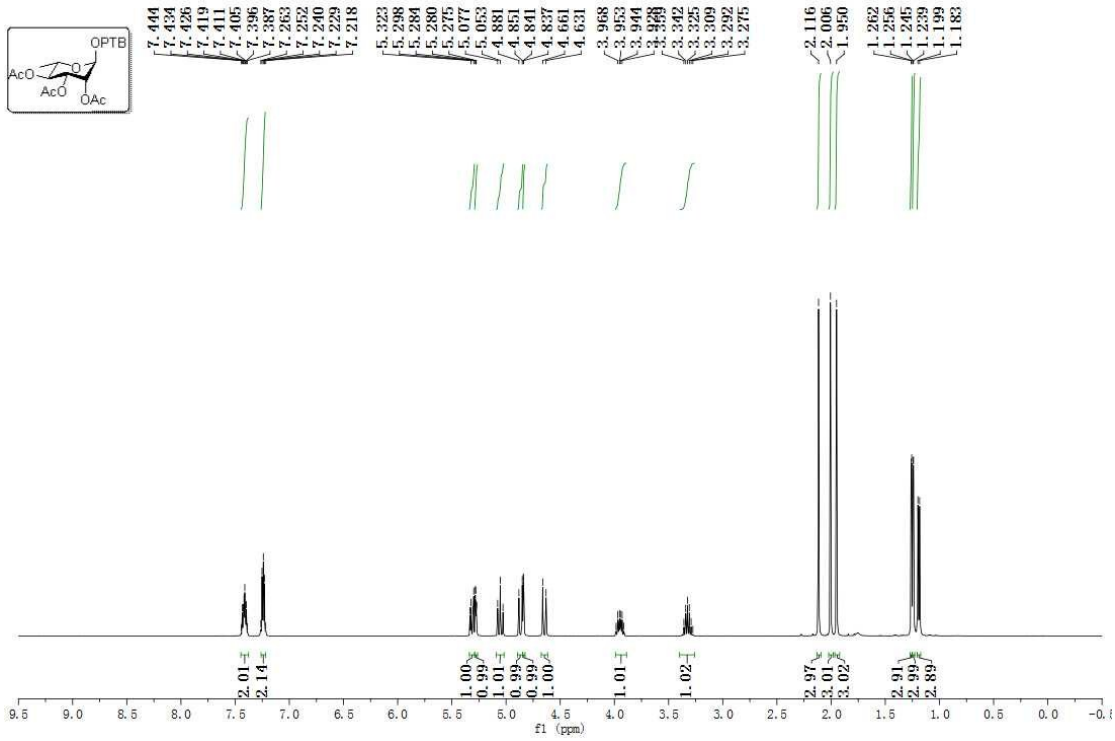


**Figure S22.** $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **S12**

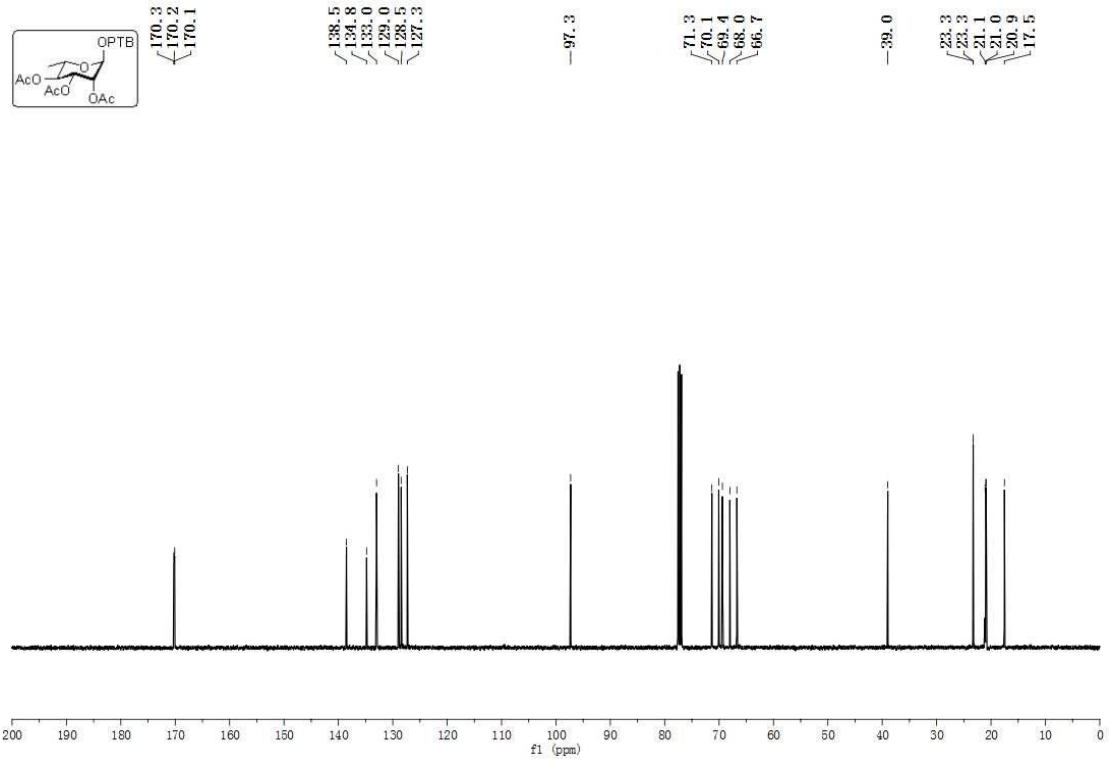


**Figure S23. $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of S12**

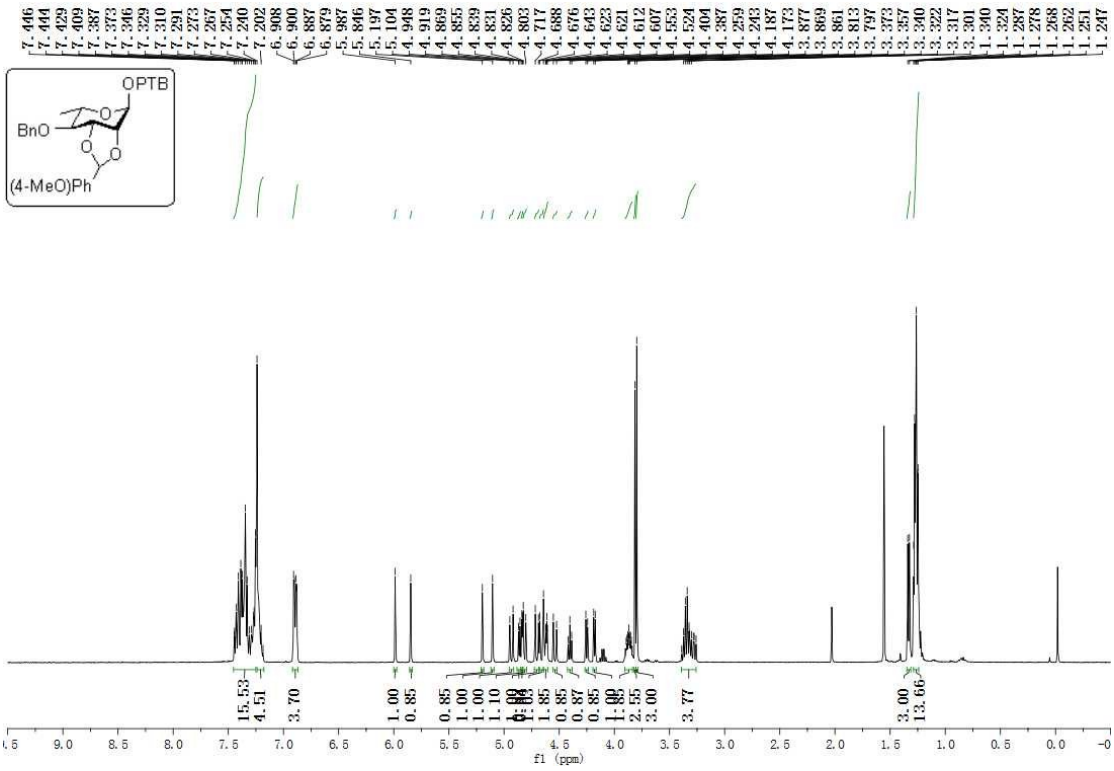


**Figure S24.** $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of **3i**

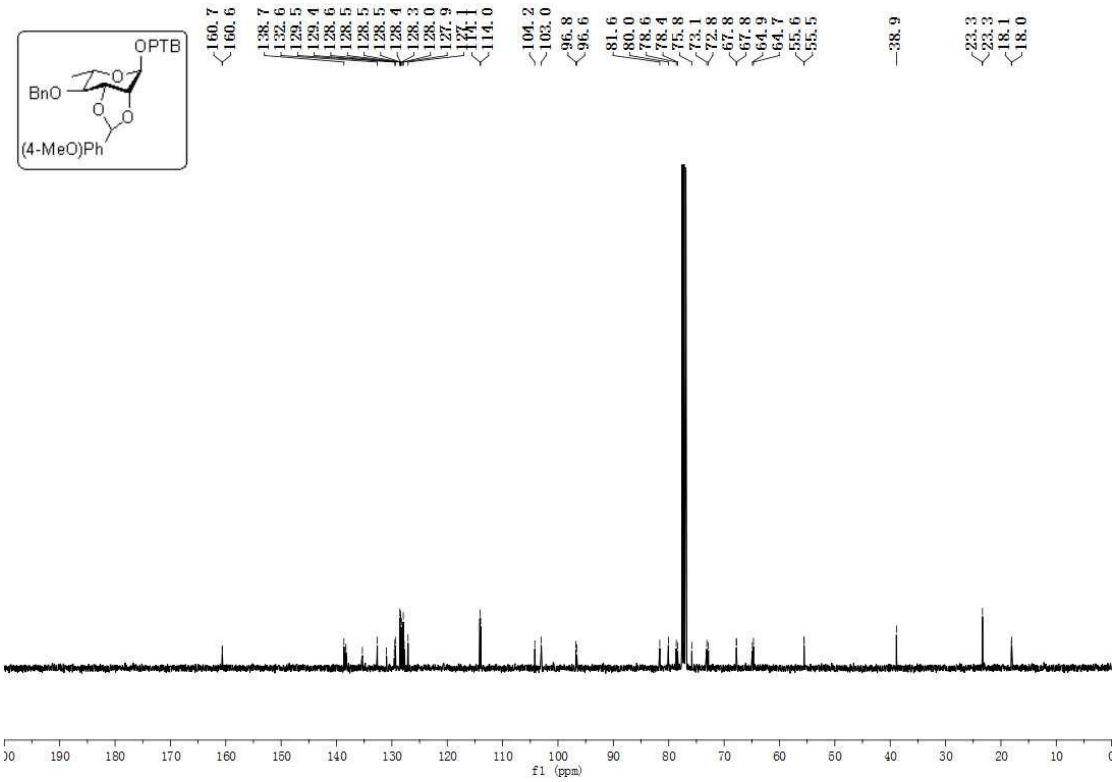


**Figure S25. $^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of 3i**

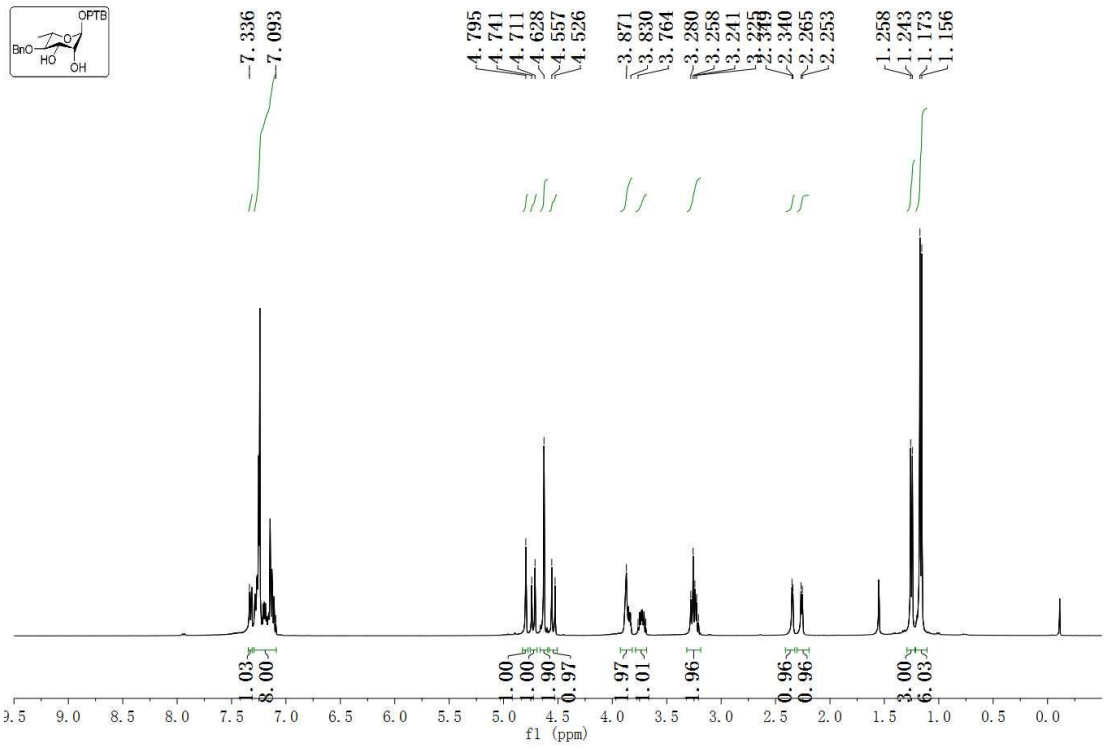


**Figure S26.** $^1$H NMR (400 MHz, $CDCl_3$) spectrum of **4i**

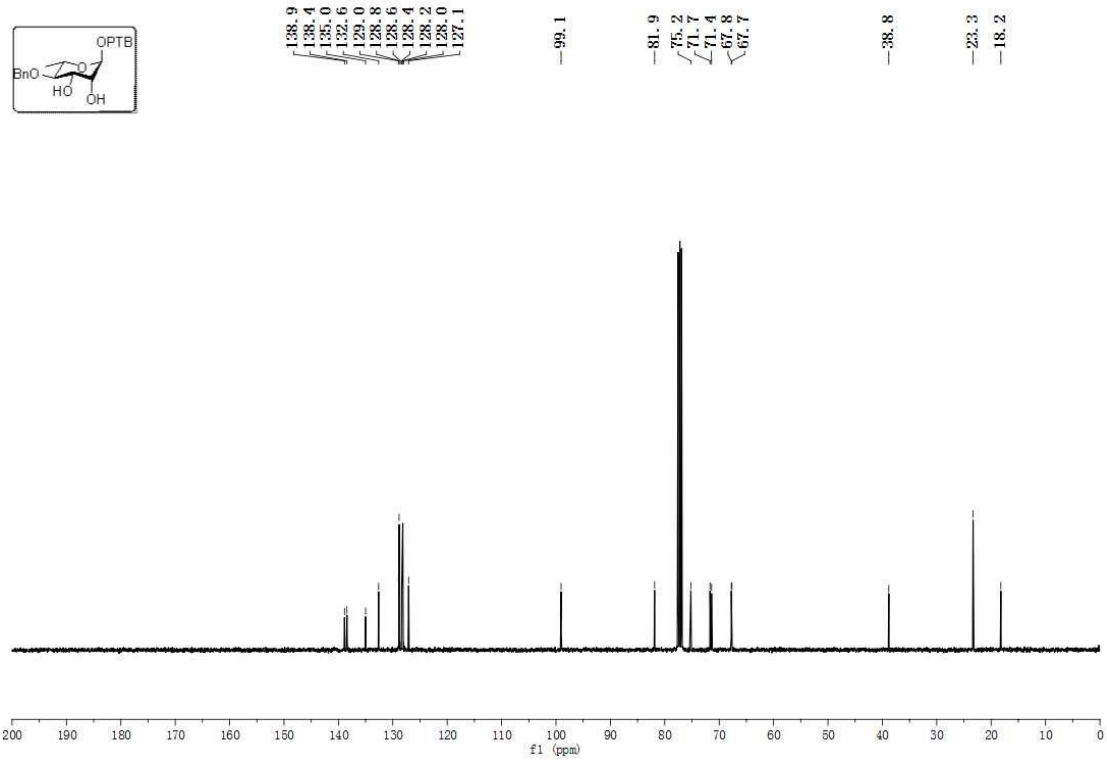


**Figure S27. $^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of 4i**

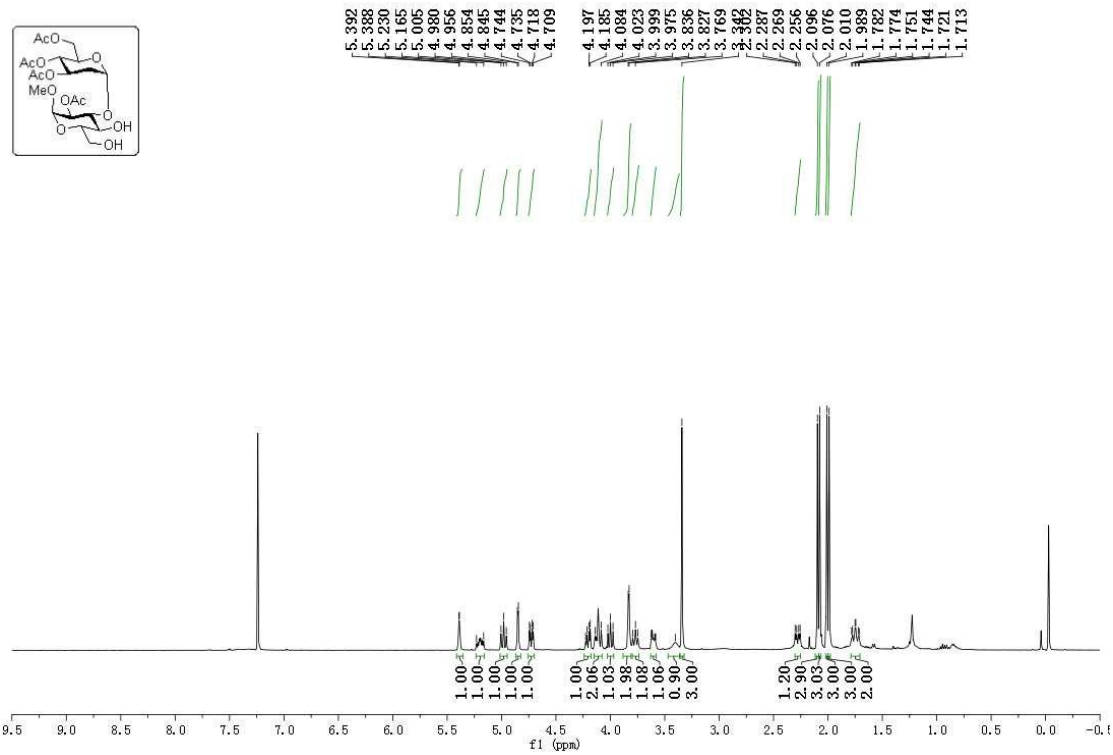


**Figure S28.** $^1$H NMR (400 MHz, $CDCl_3$) spectrum of **4j**

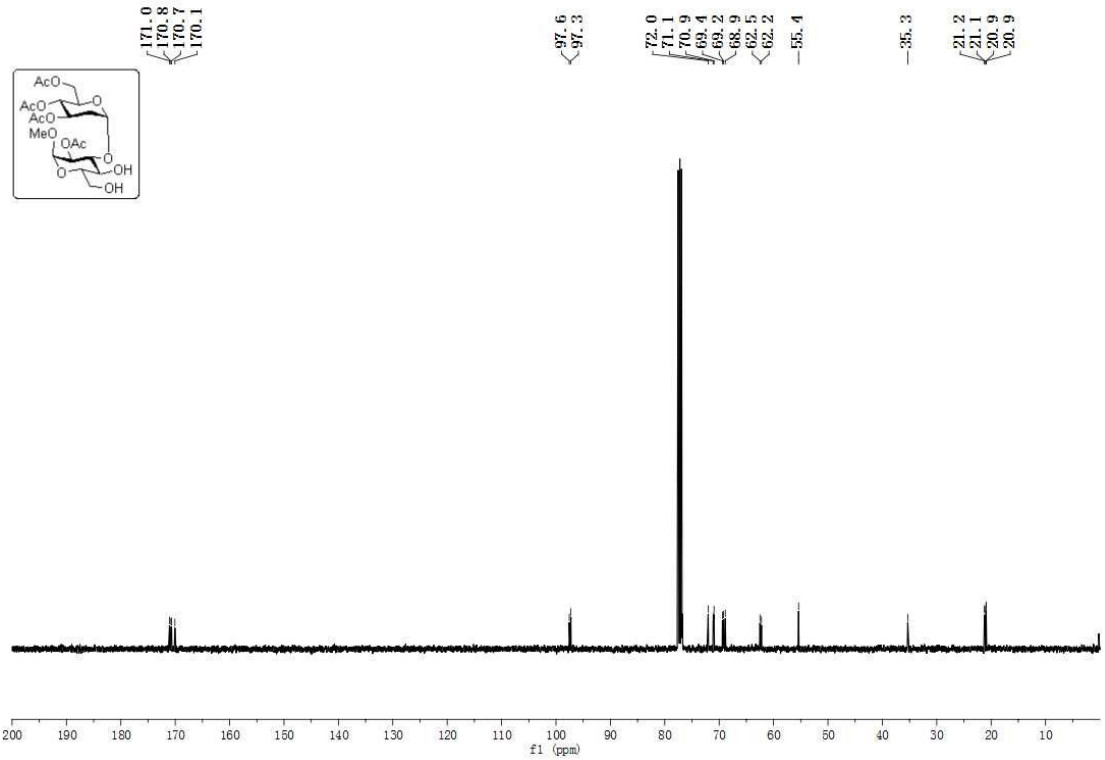


**Figure S29. $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of 4j**

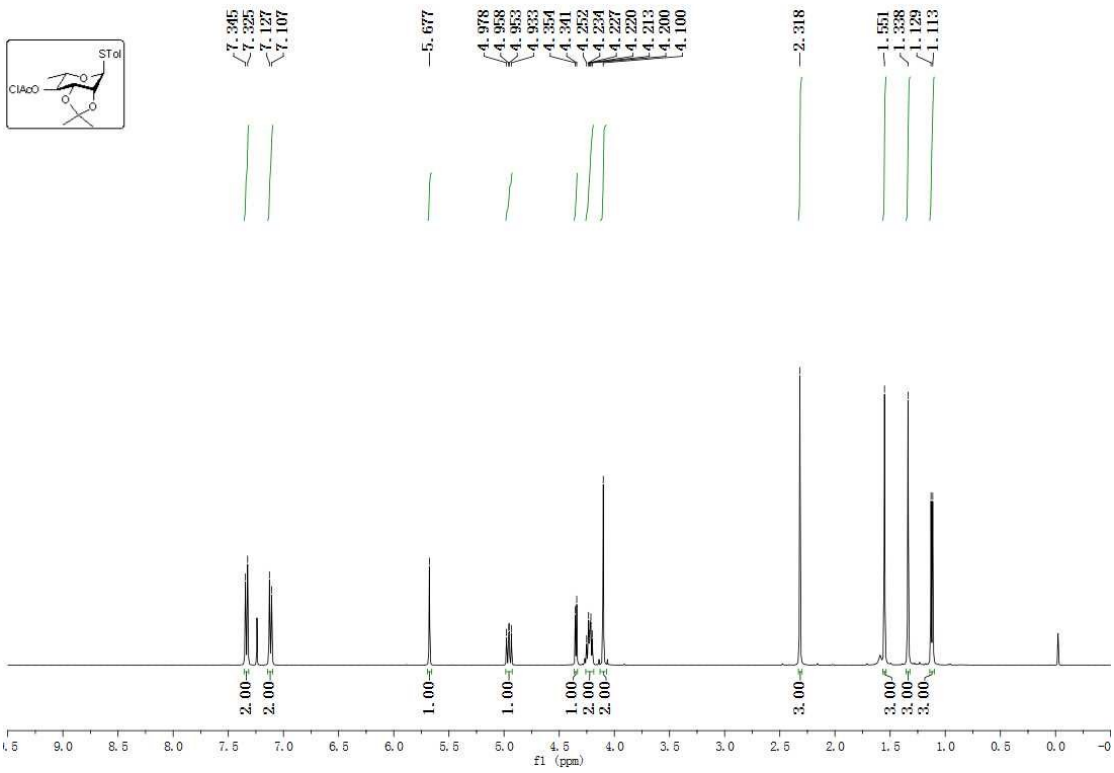


**Figure S30. $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of 3k**

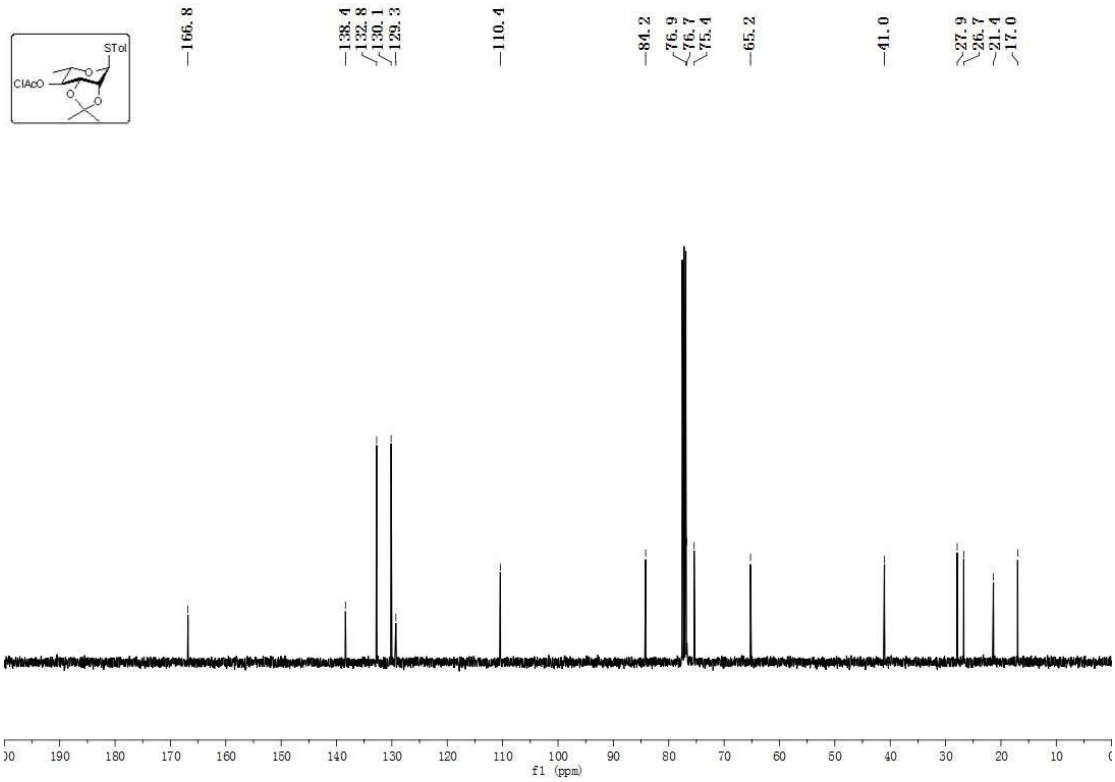


**Figure S31. $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of 3k**

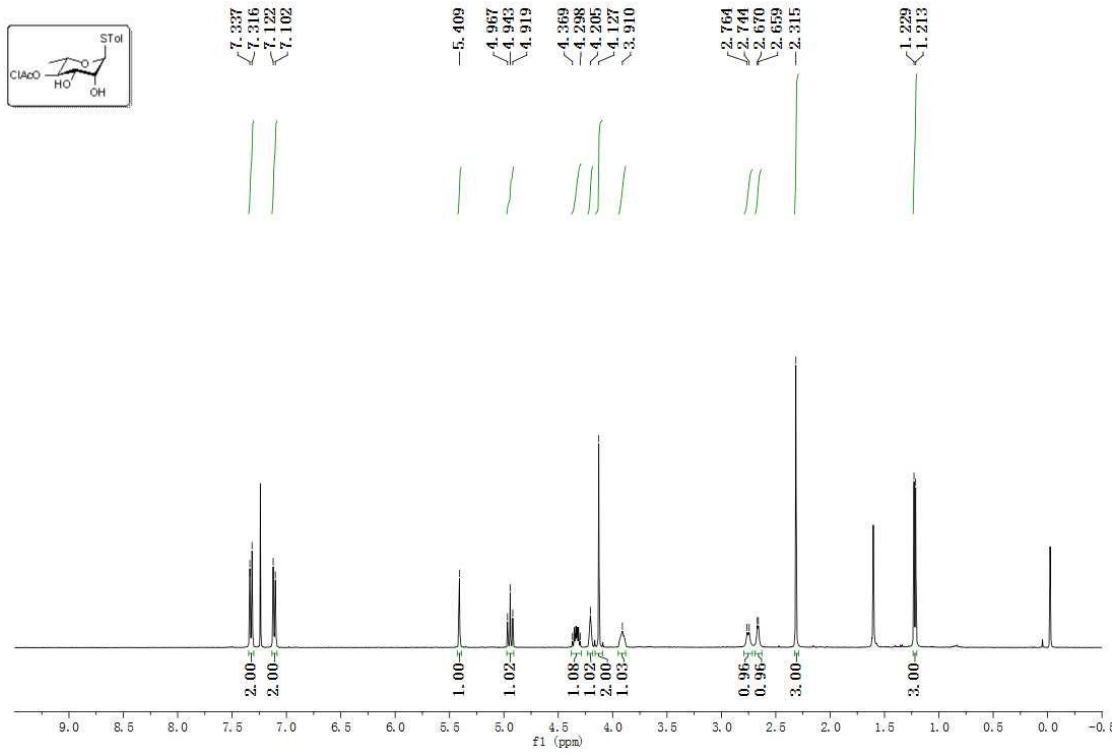


**Figure S32. $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of 4k**

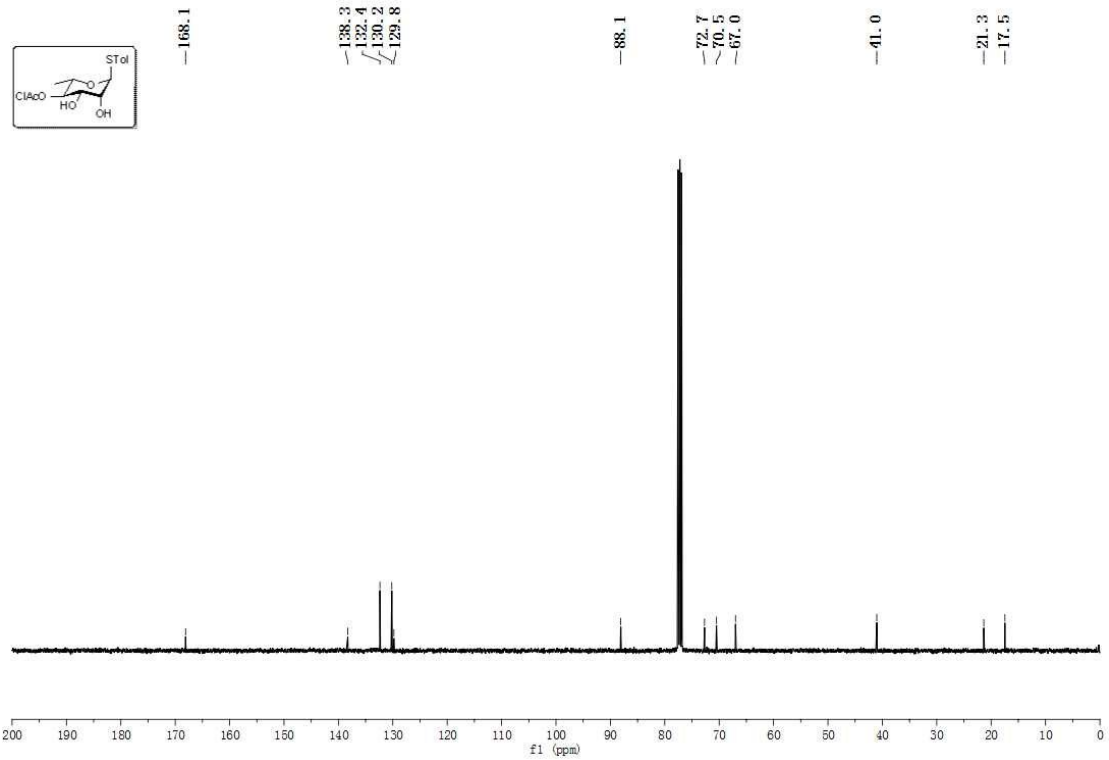


**Figure S33. $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of 4k**

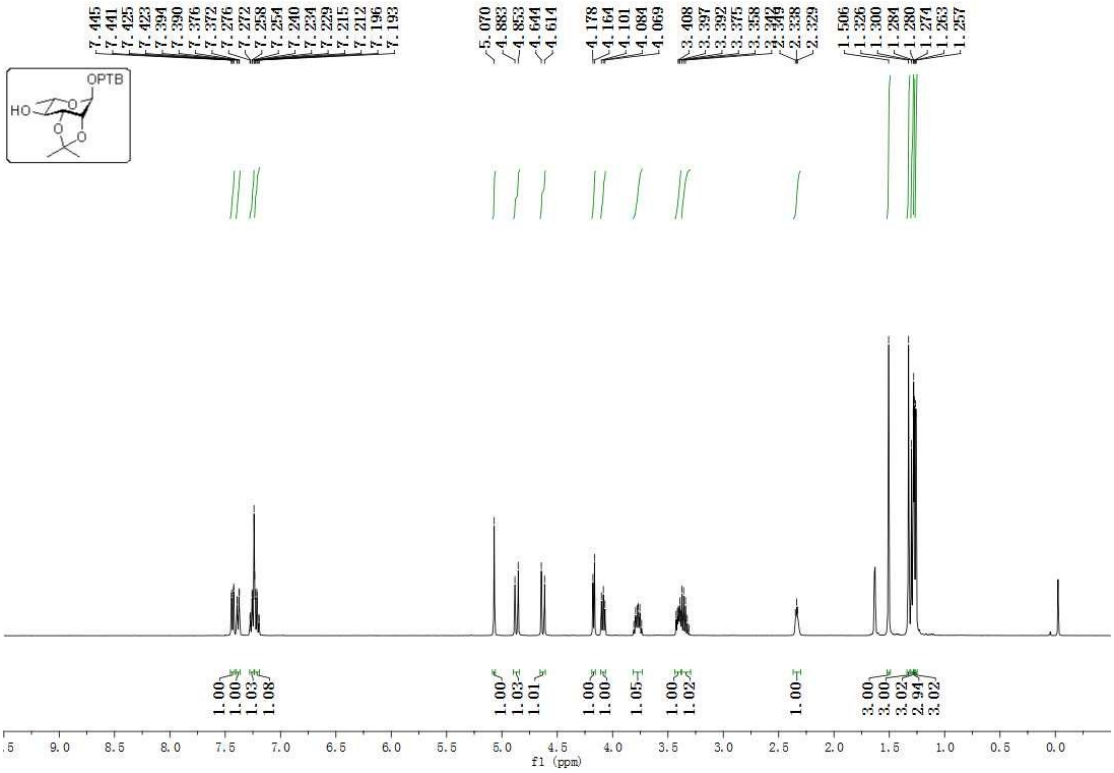


**Figure S34. $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of S14**

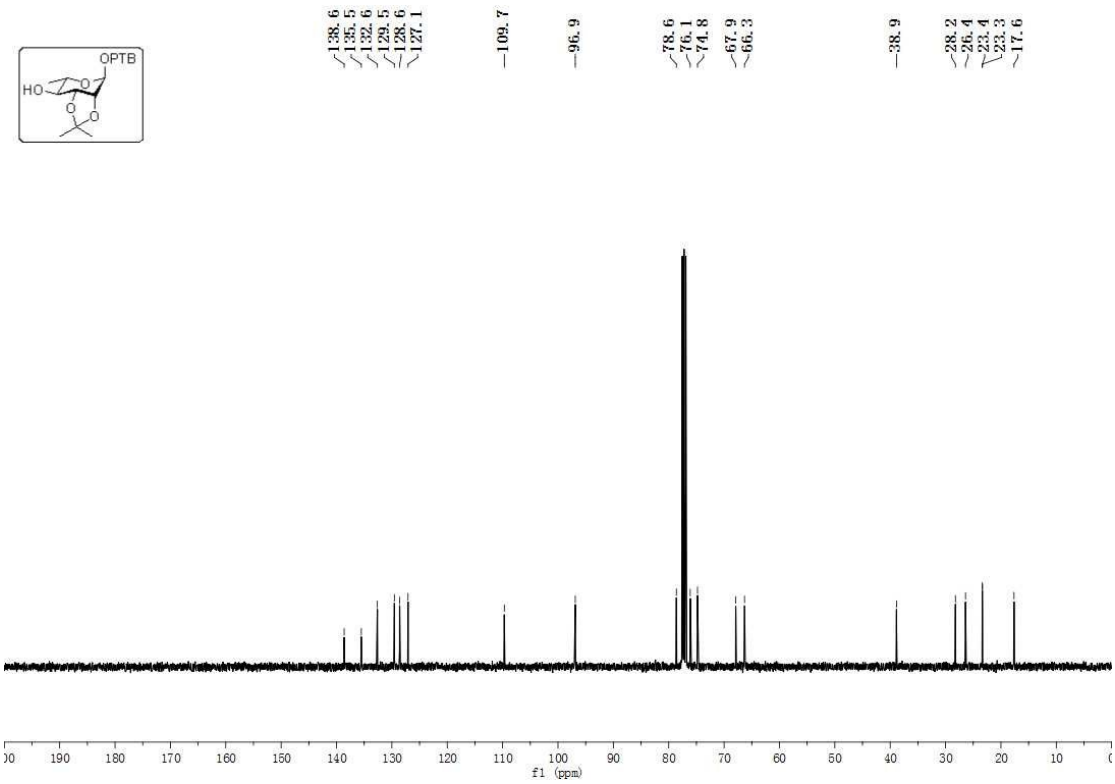


**Figure S35. $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of S14**

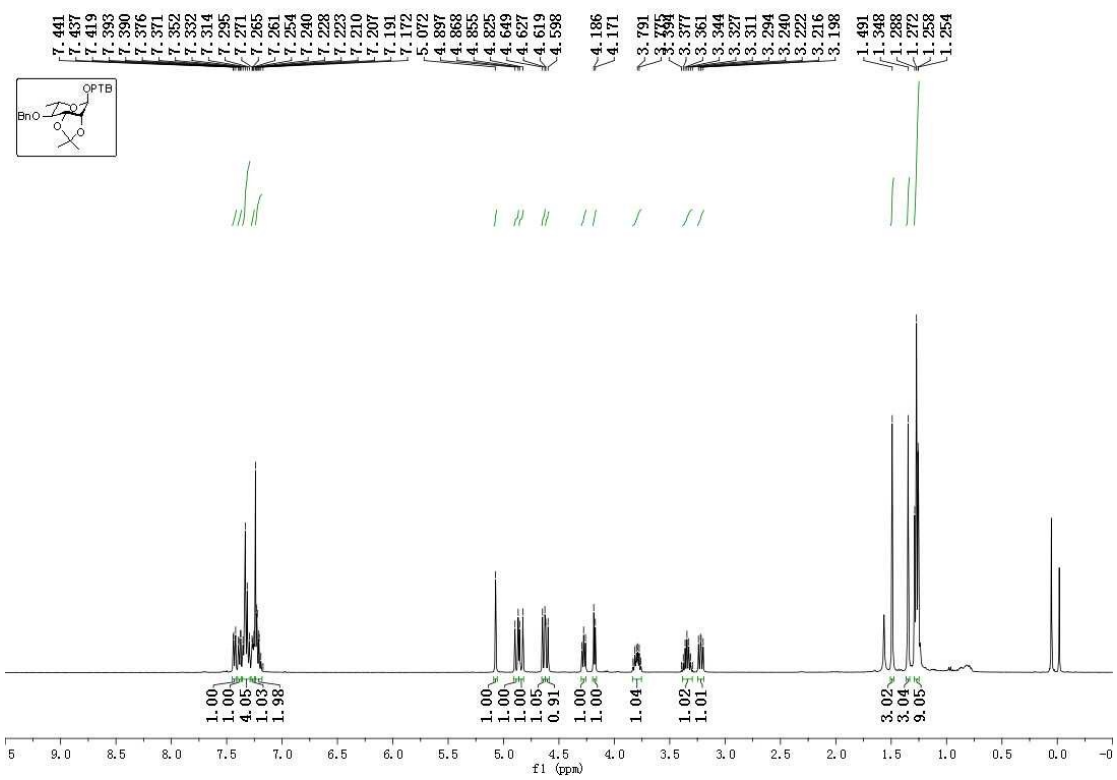


**Figure S36. $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of 3l**

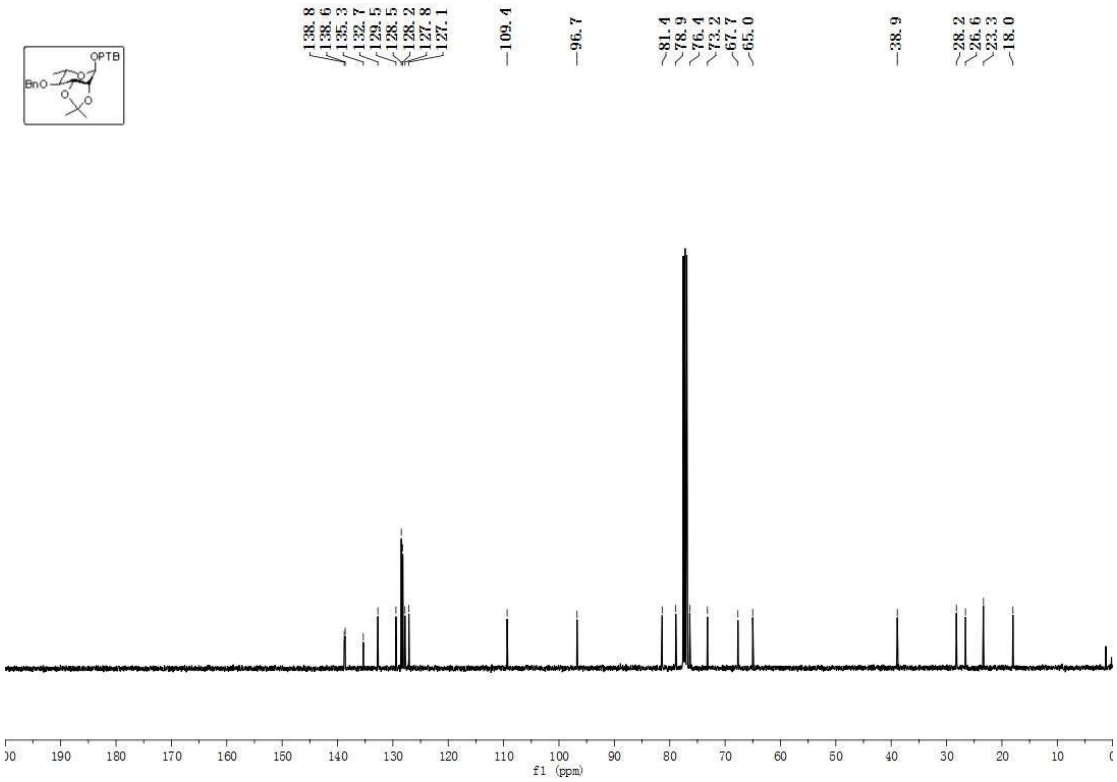


**Figure S37. $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of 3l**

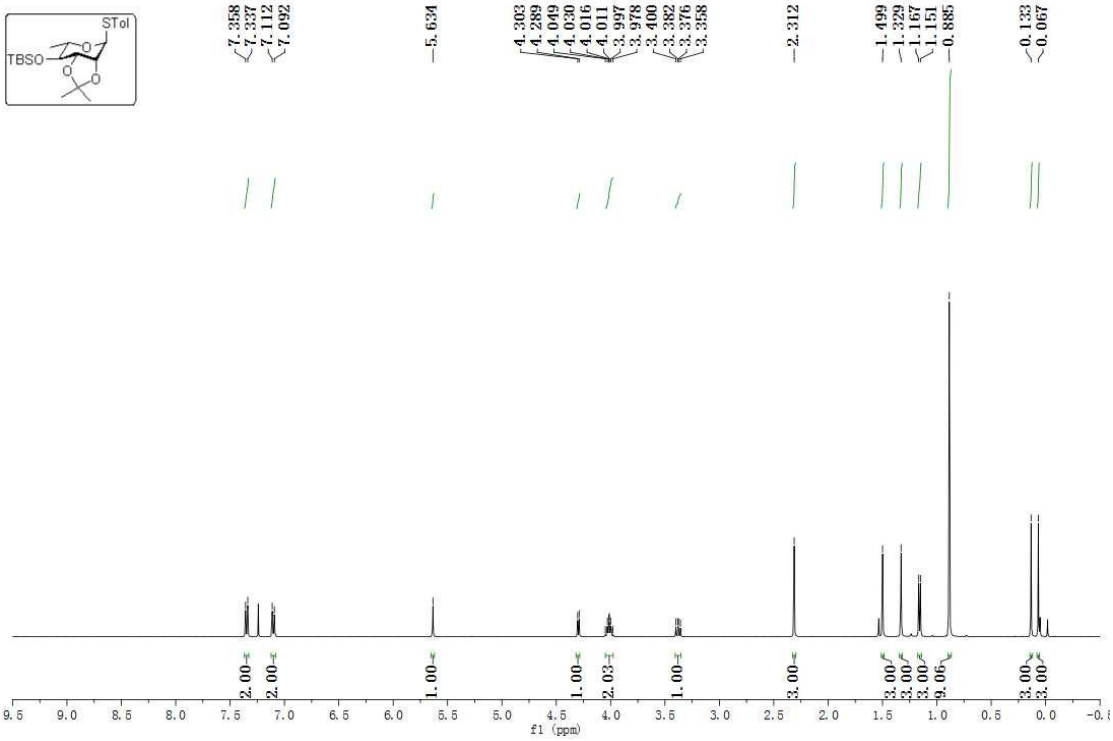


**Figure S38. $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of 3m**

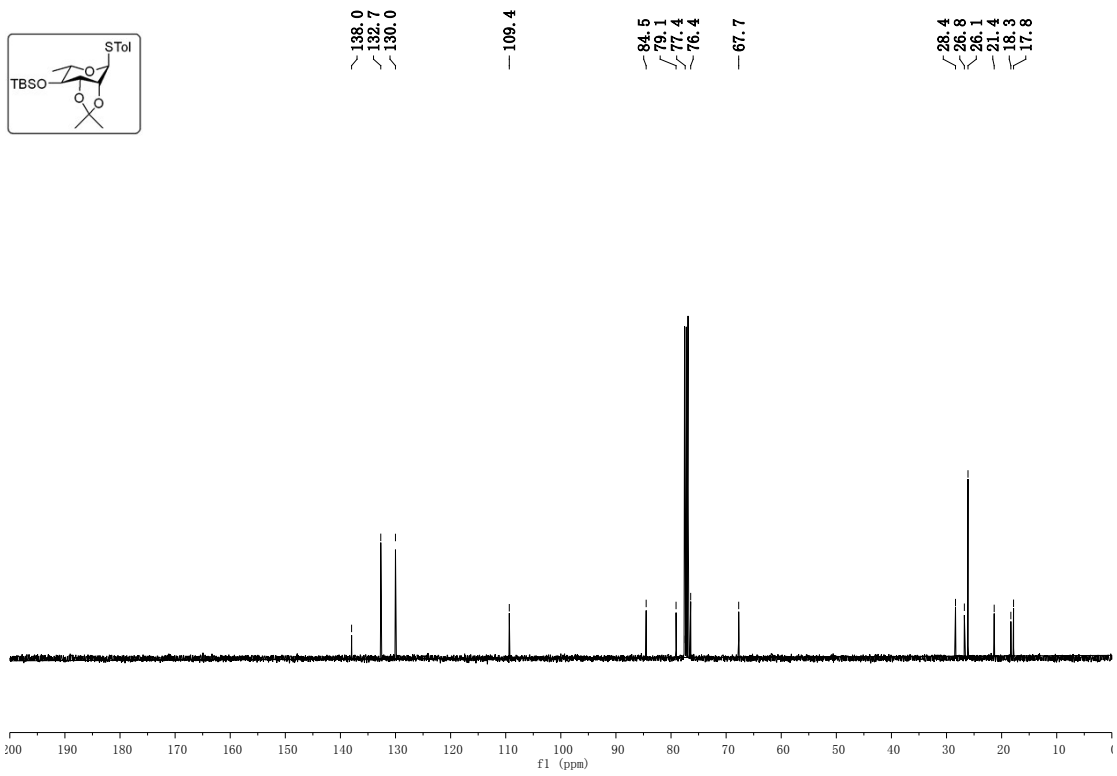


**Figure S39. $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of 3m**

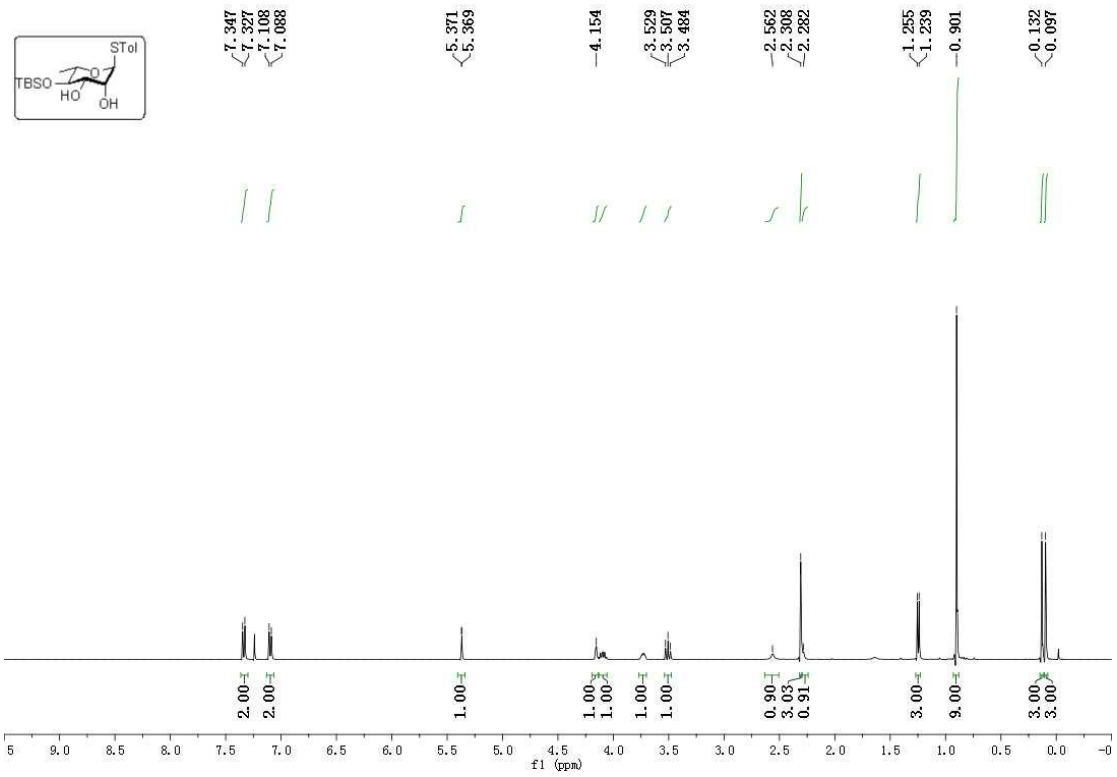


**Figure S40. $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of 4m**

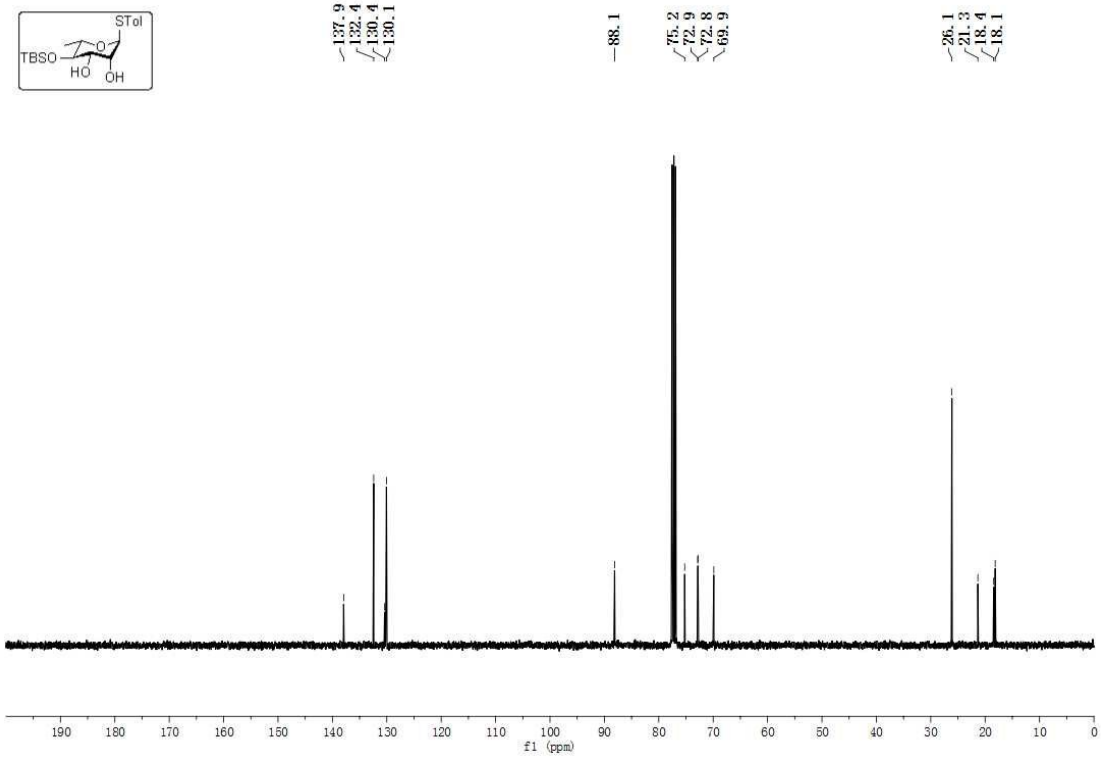


**Figure S41. $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of 4m**

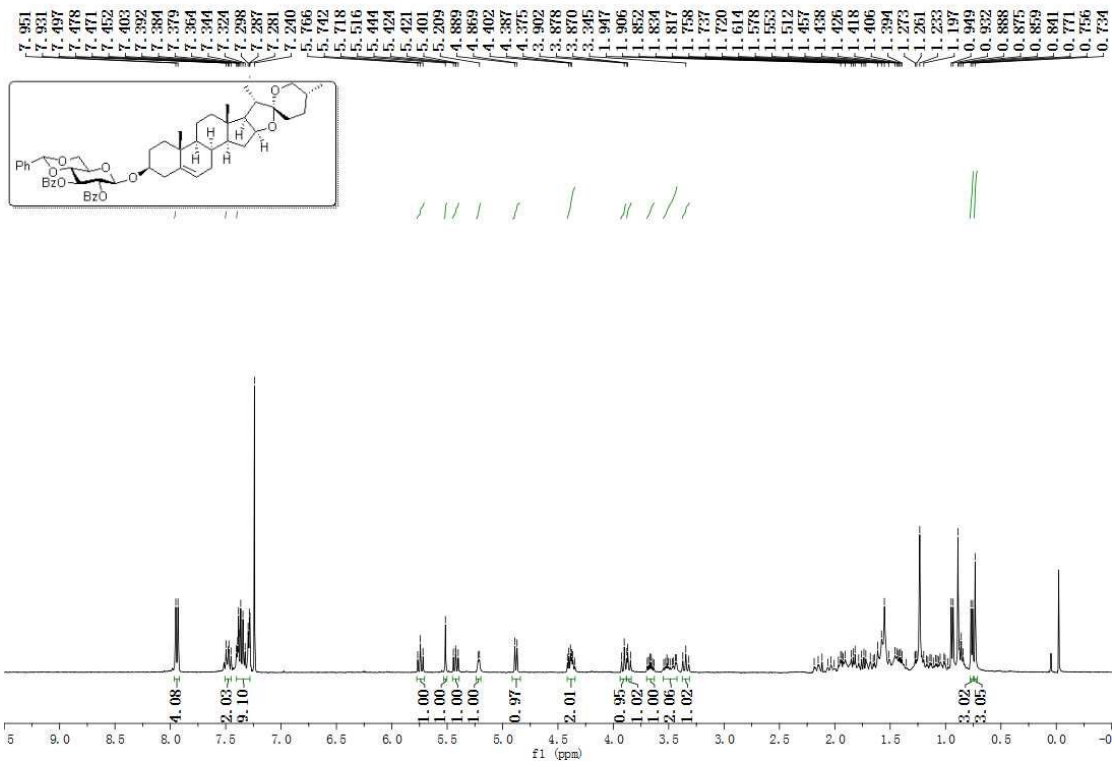


**Figure S42. $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of 3n**

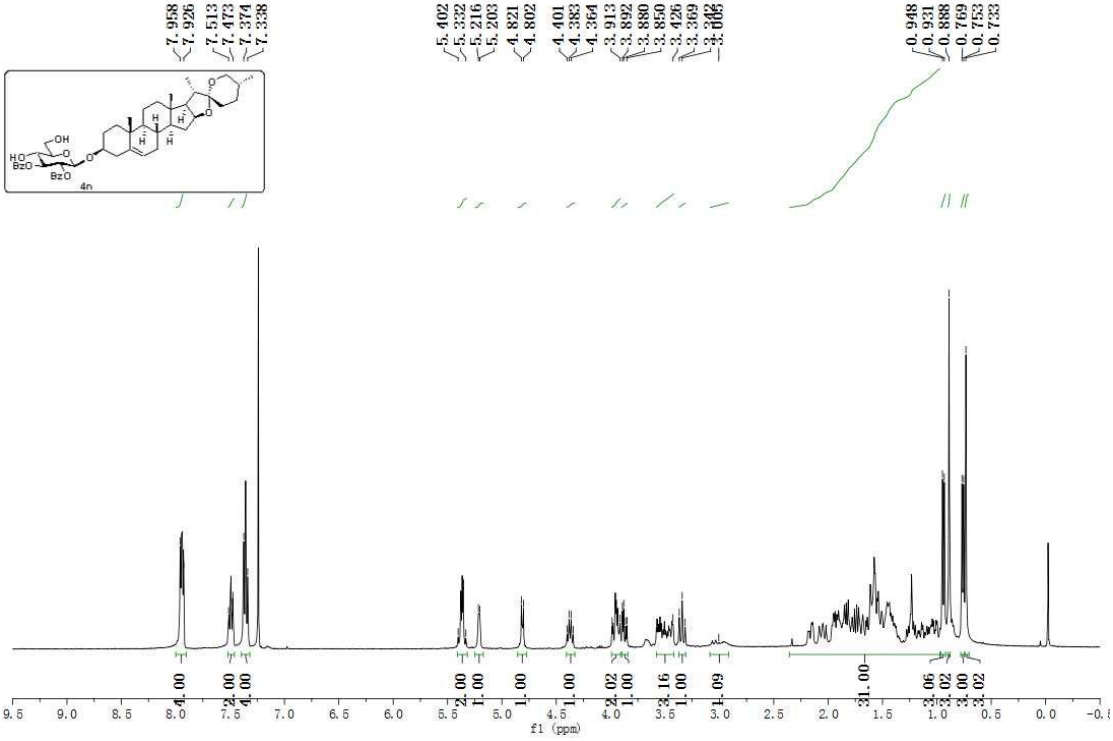

**Figure S43. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of 4n**

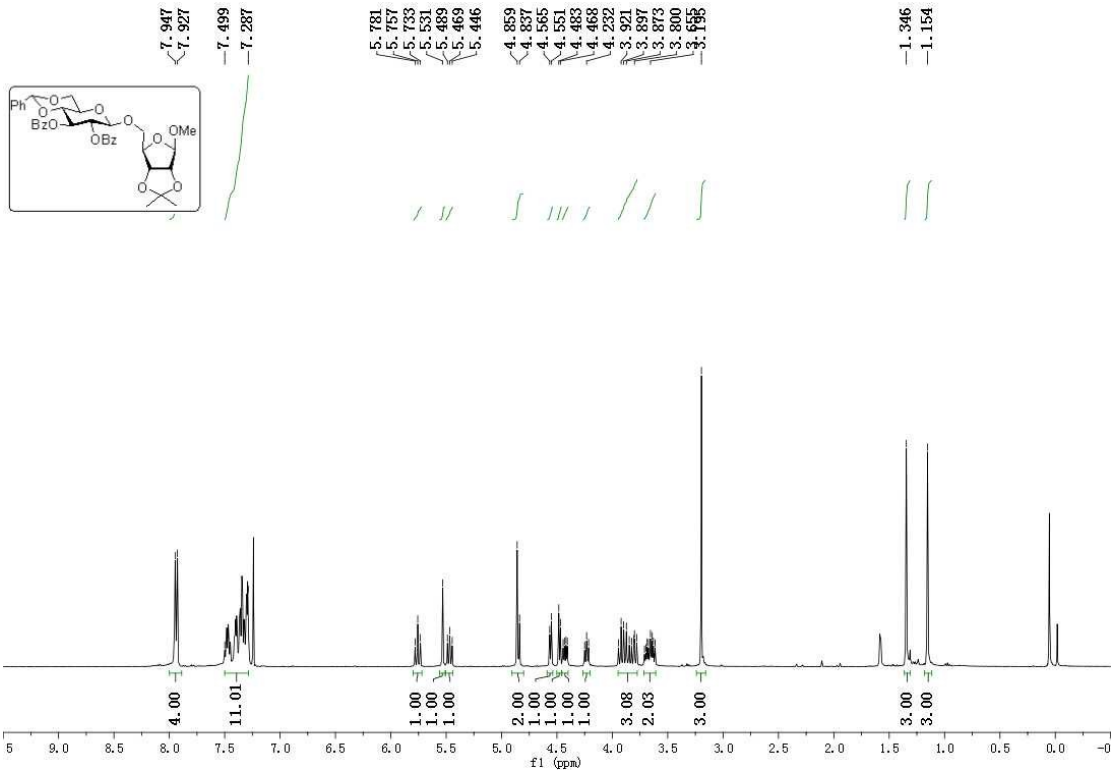

**Figure S44. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of 3o**

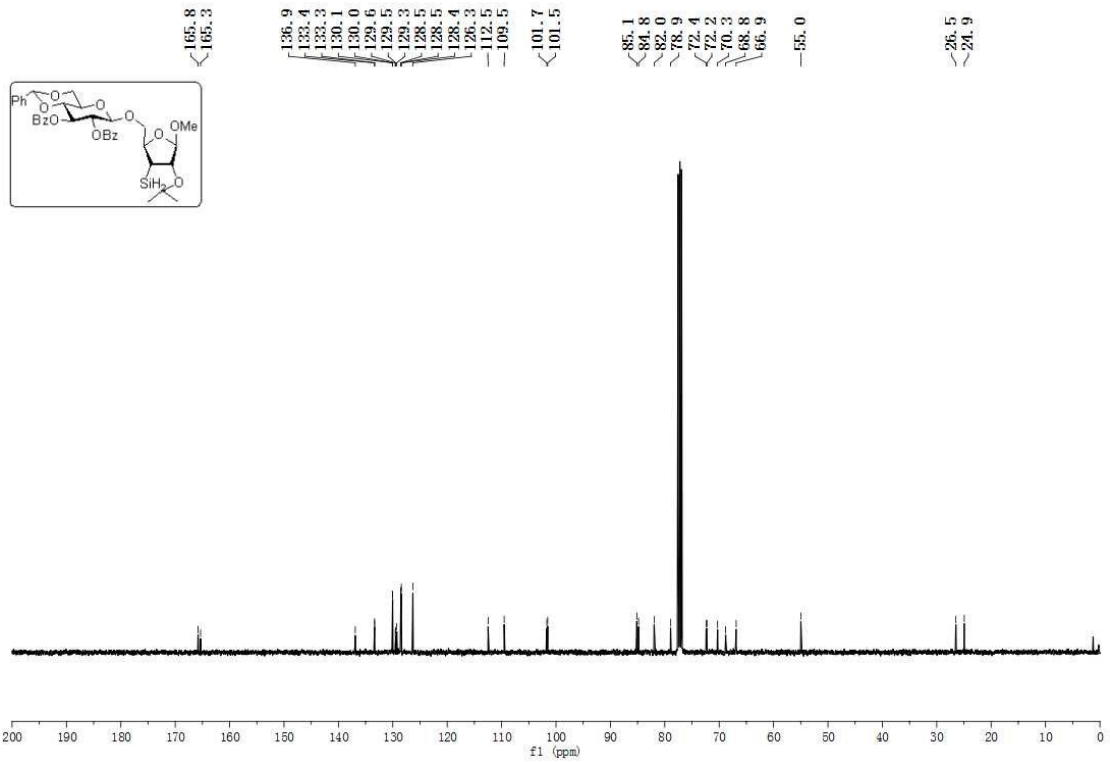


**Figure S45. $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of 3o**

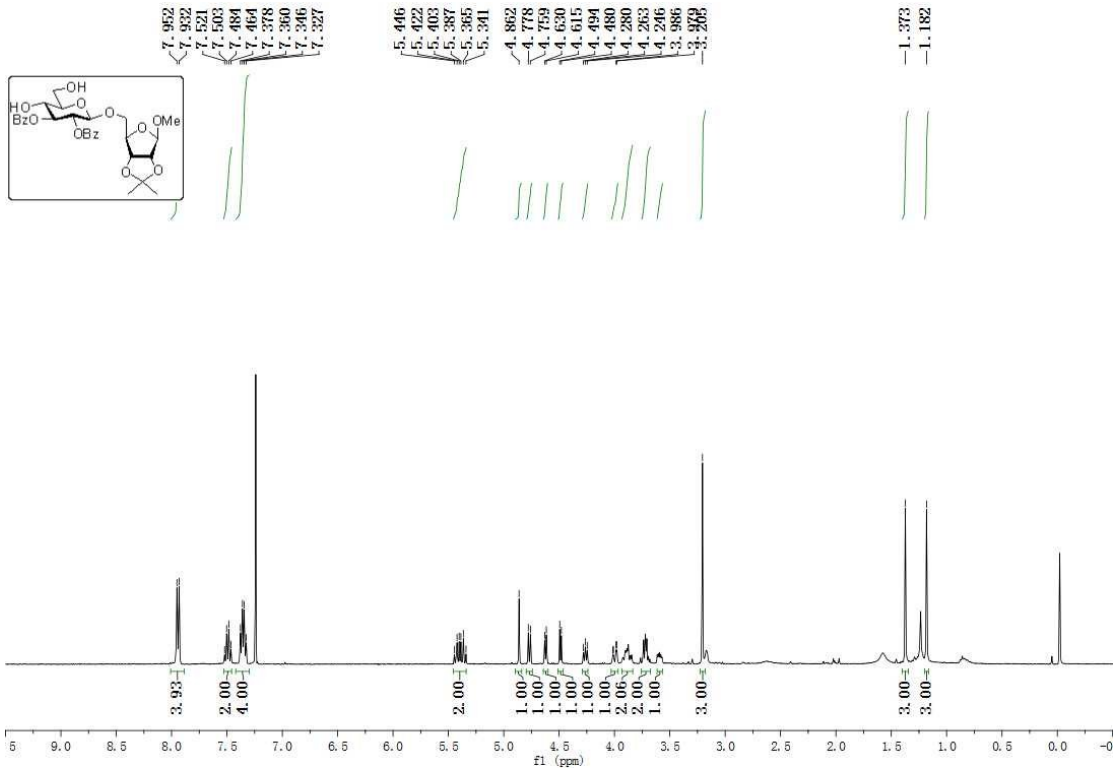


**Figure S46. $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of 4o**

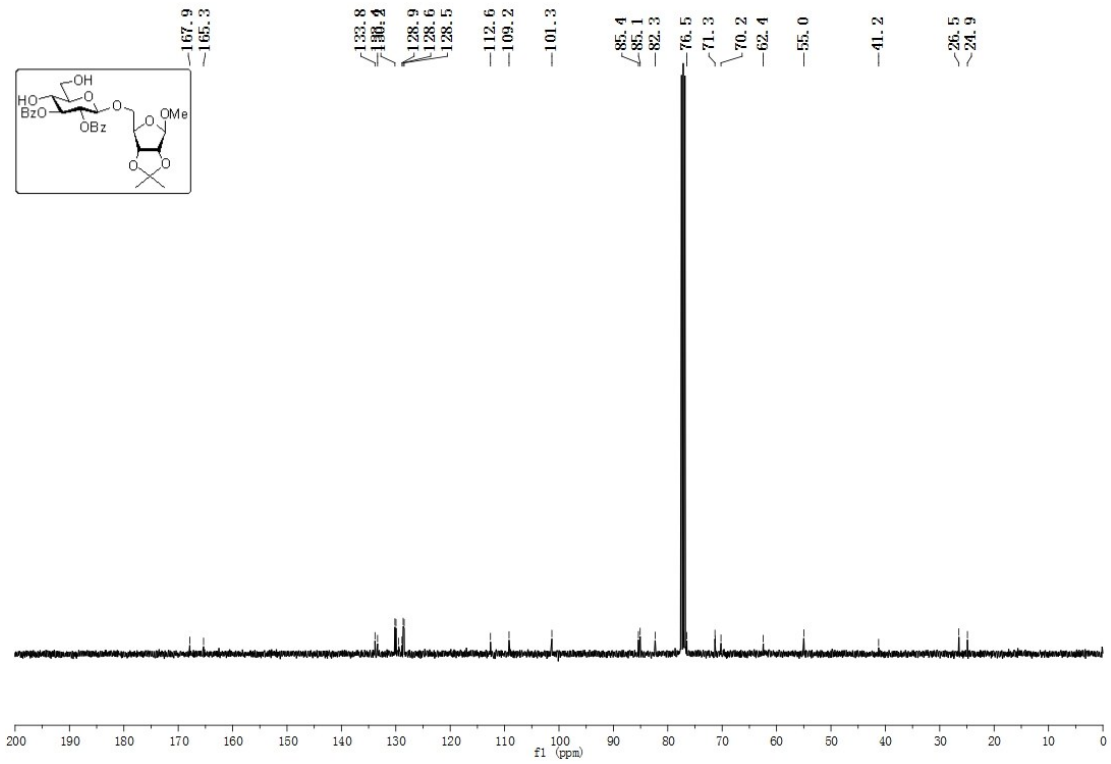


**Figure S47. $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of 4o**

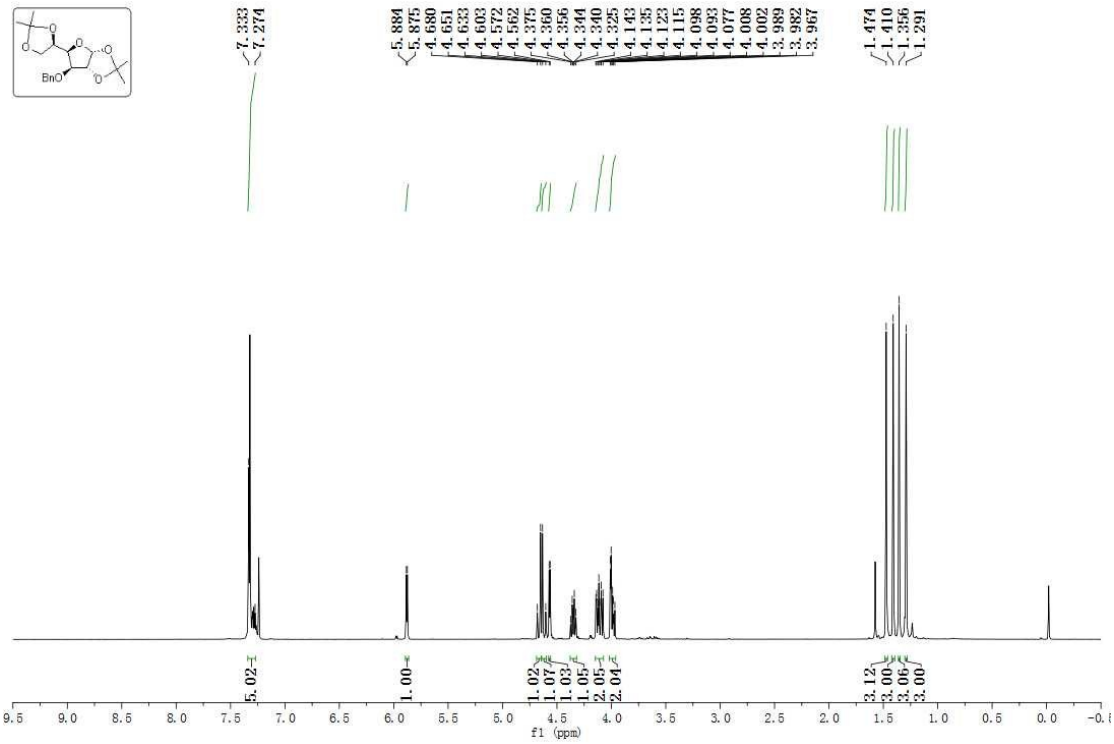


**Figure S48. $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of 3p**

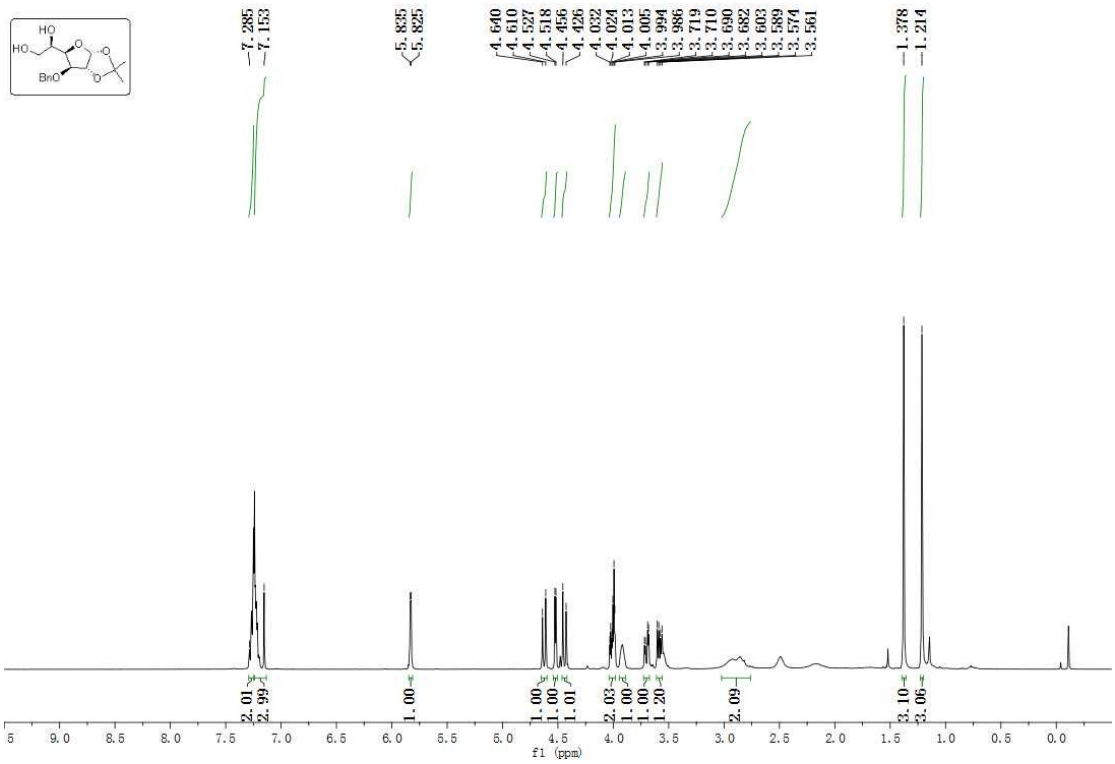

**Figure S49. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of 4p**

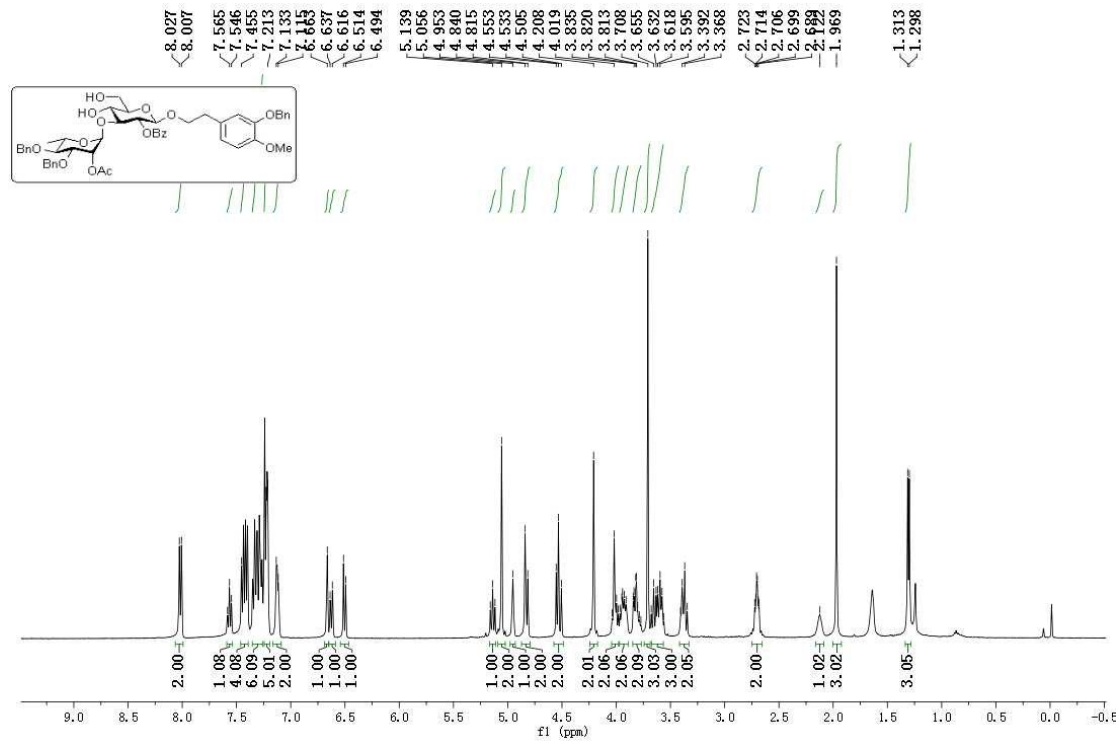

**Figure S50. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of 6a**

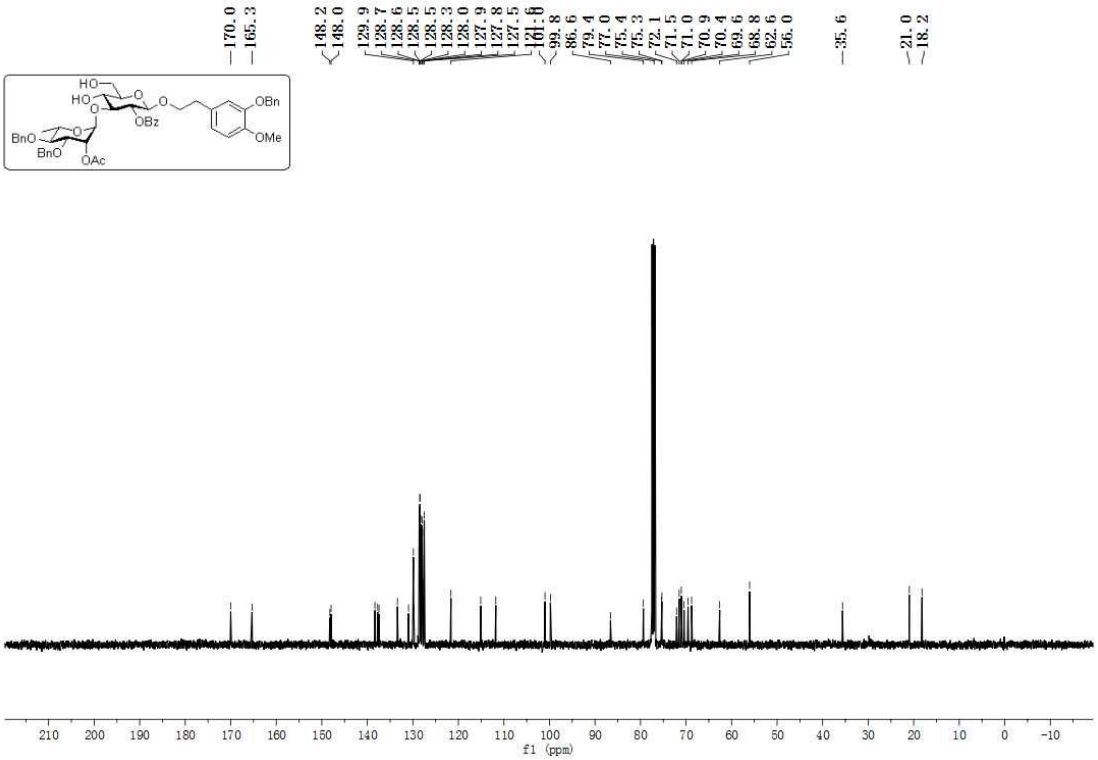

**Figure S51. $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of 6a**

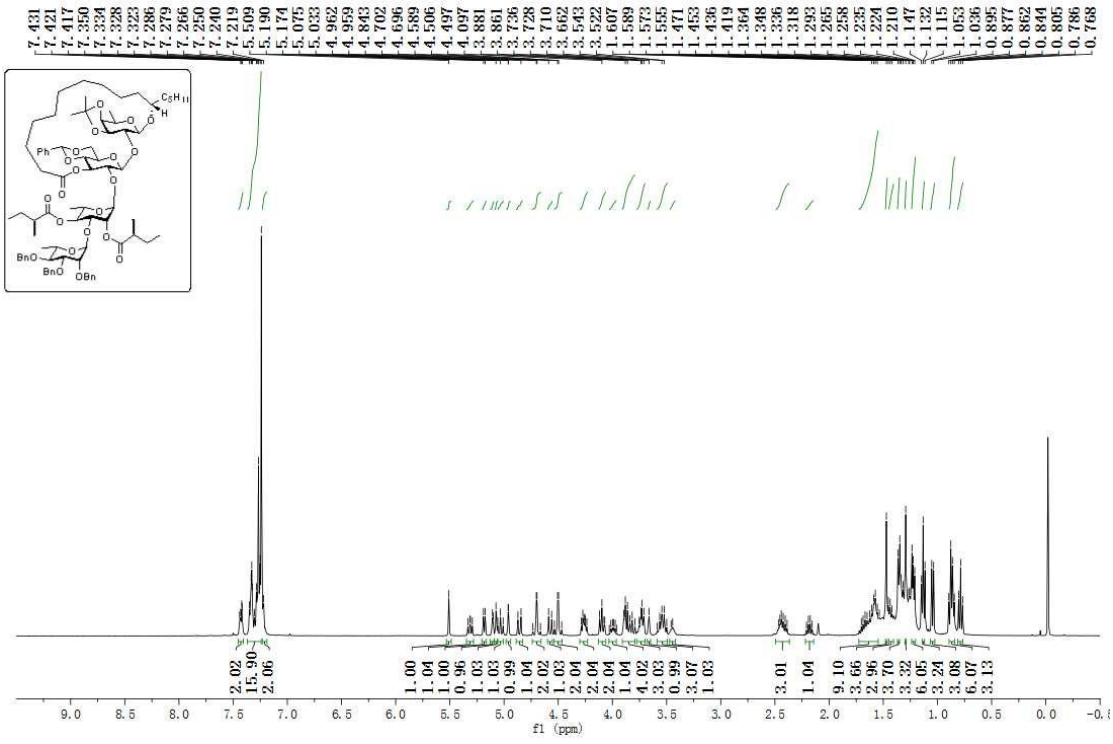

**Figure S52. $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of 5b**

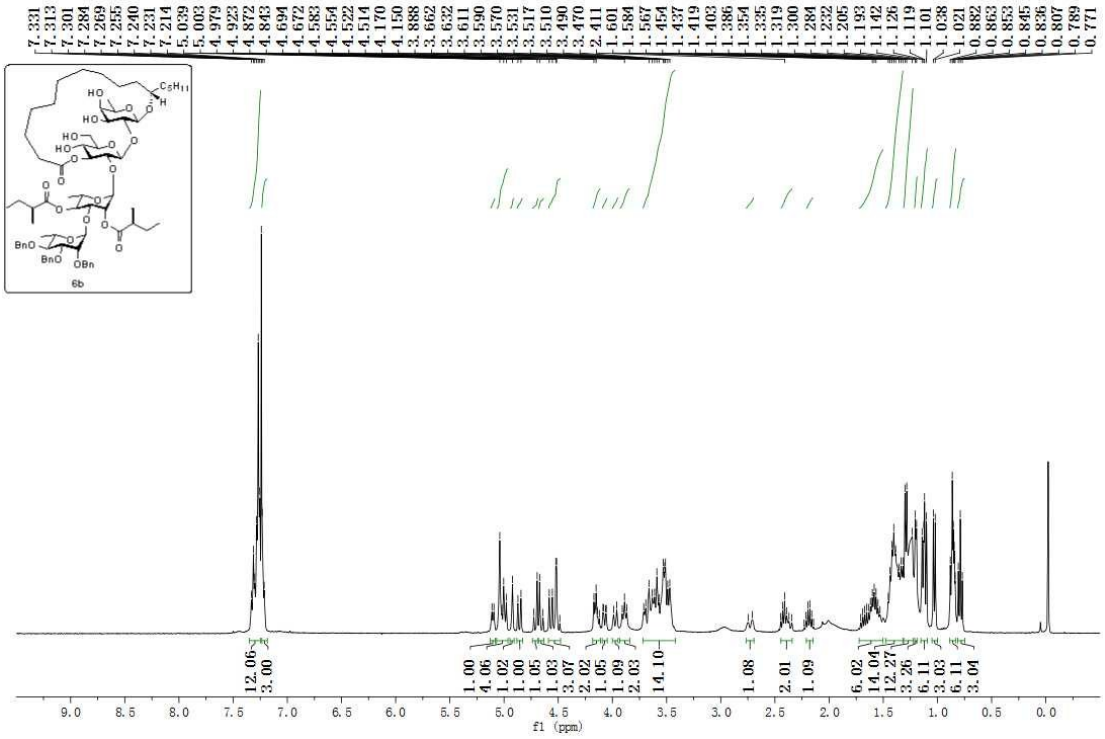

**Figure S53. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of 6b**

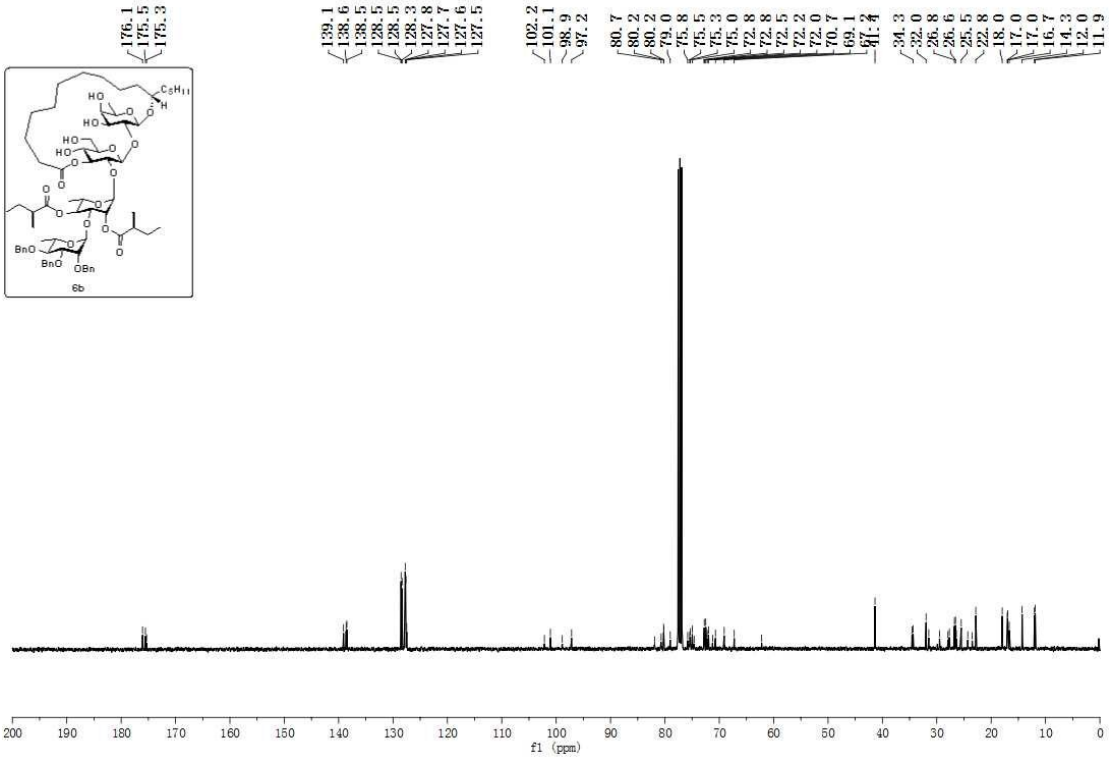

**Figure S54. $^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of 6b**

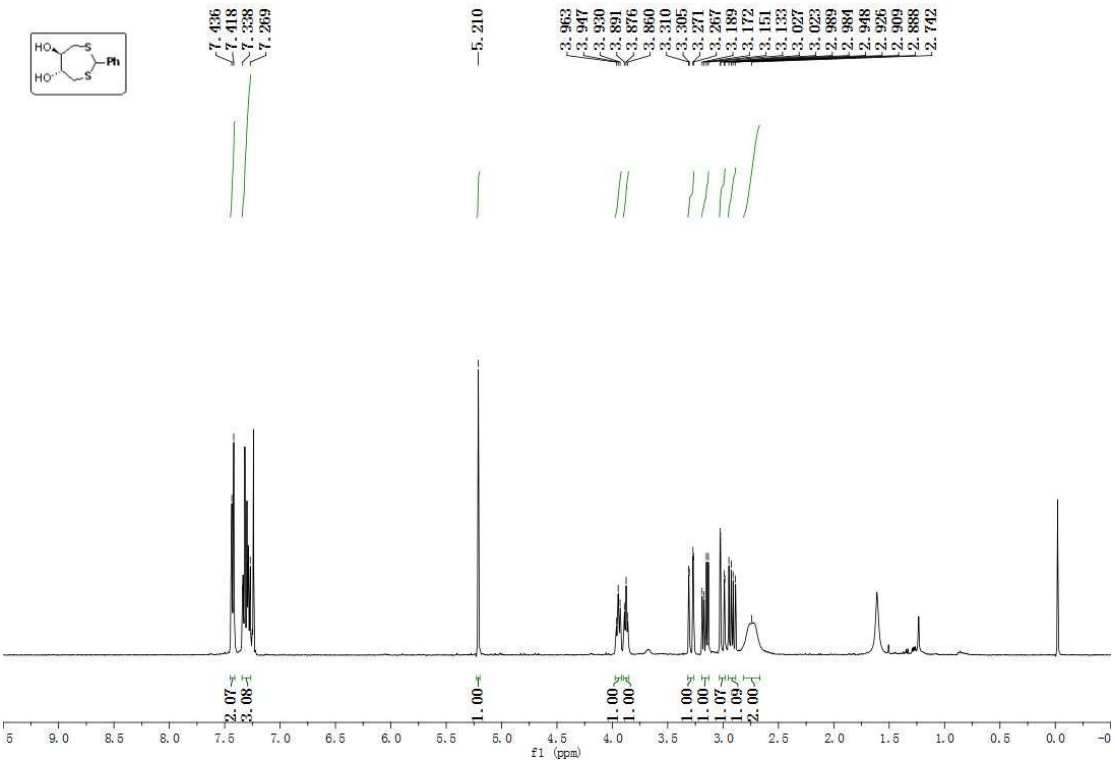


**Figure S55. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of 7**

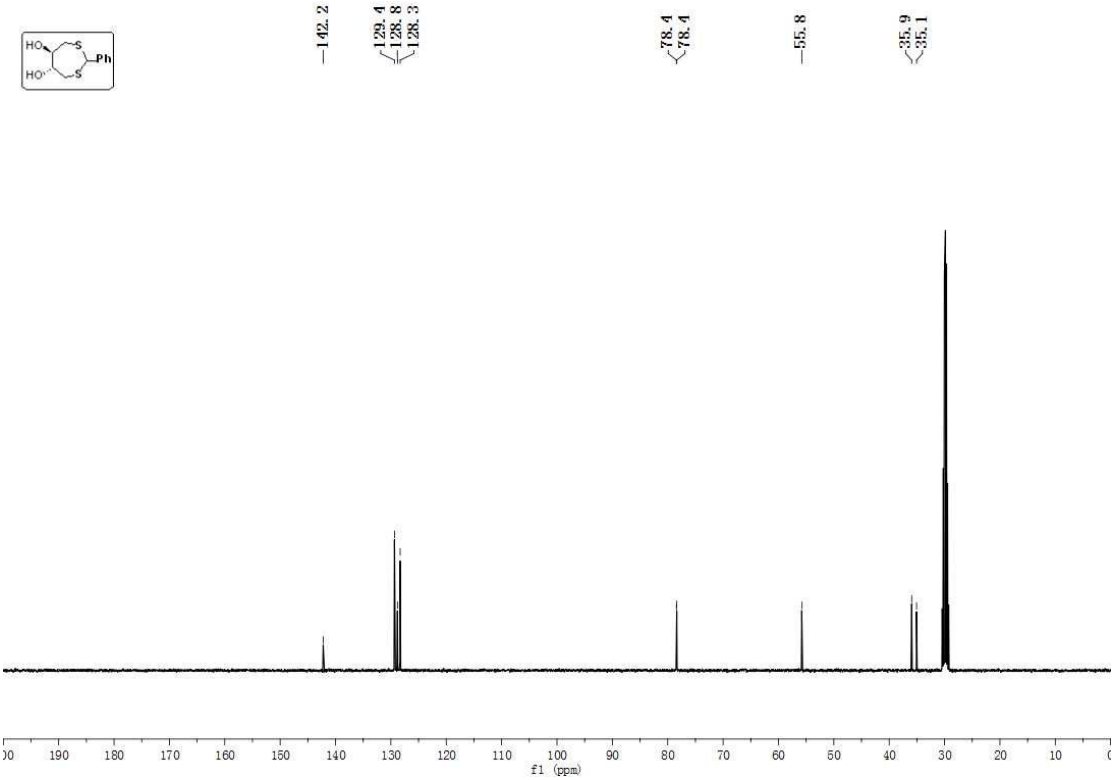


**Figure S56. $^{13}$C NMR (100 MHz, $CD_3COCD_3$) spectrum of 7**

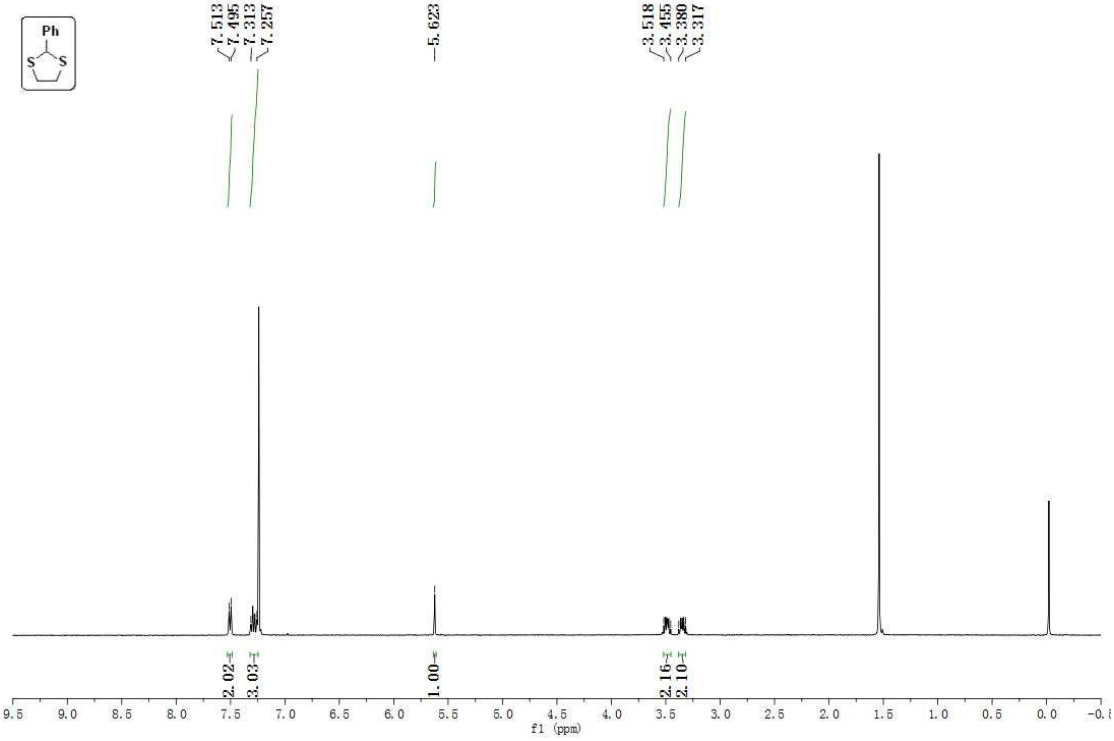


**Figure S57. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of 8**

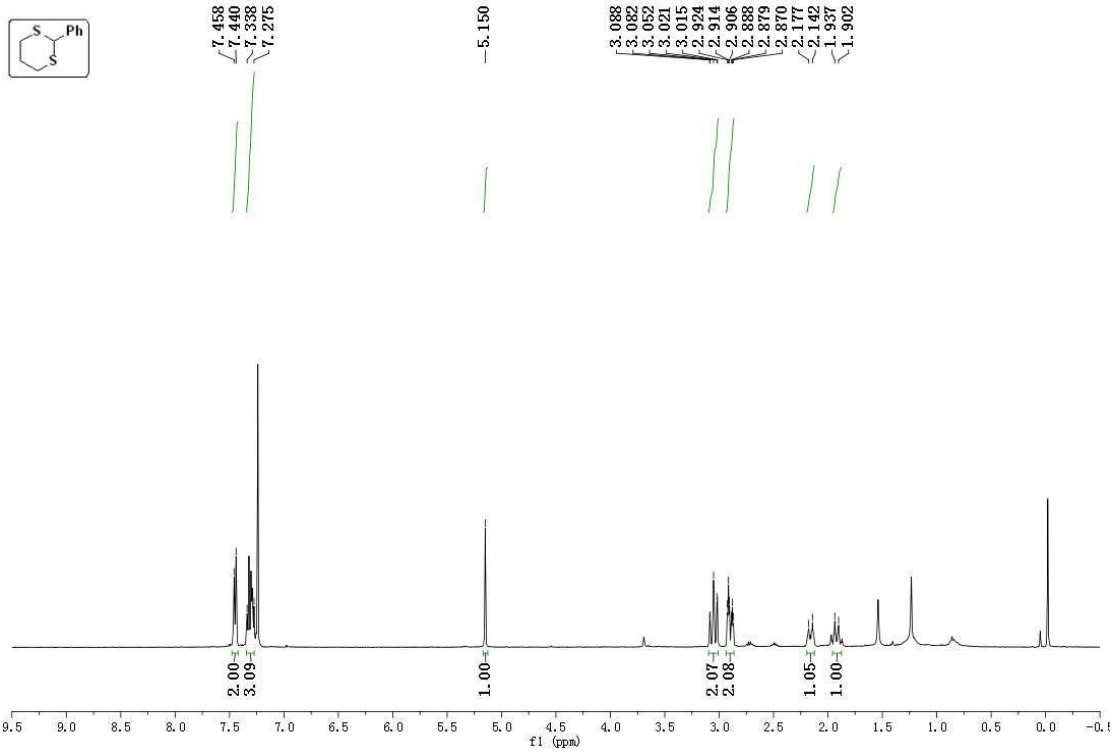


**Figure S58. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of 9**

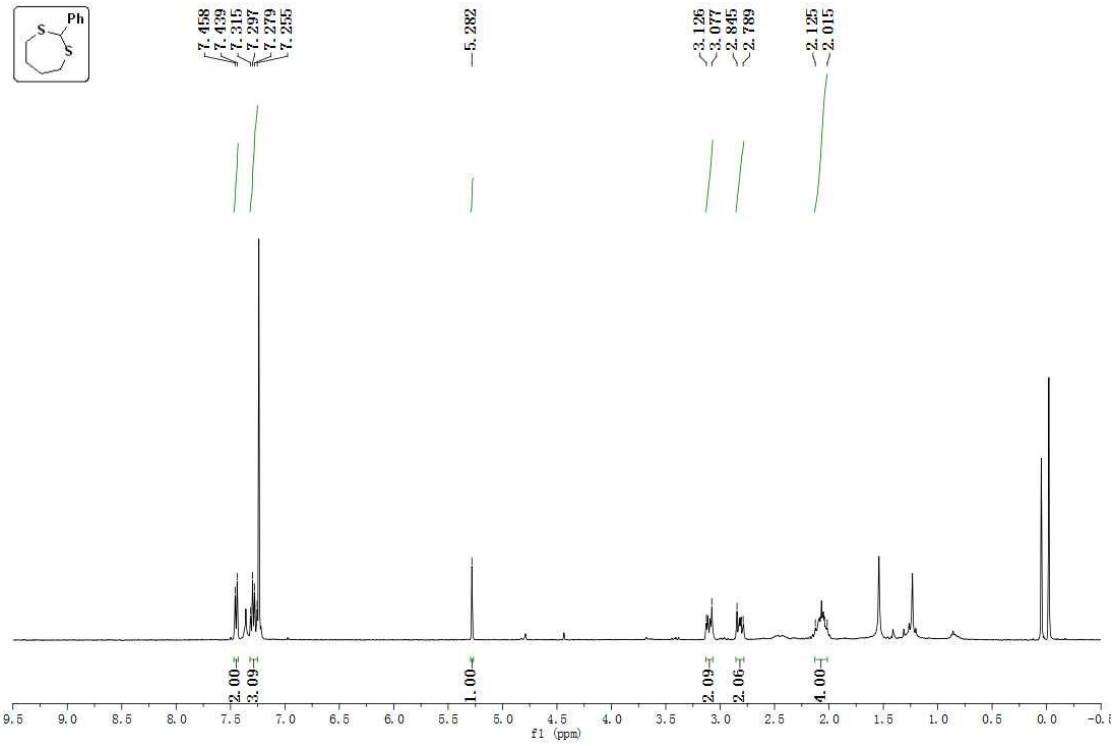


**Figure S59. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of 10**

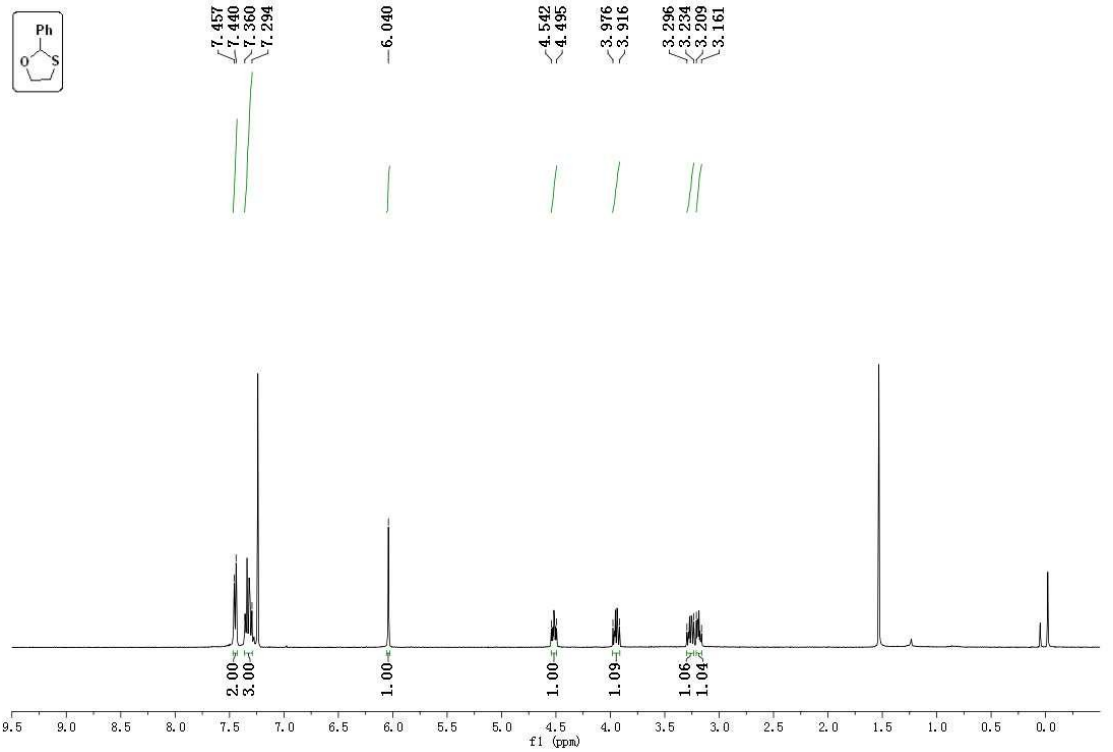


**Figure S60. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of 11**

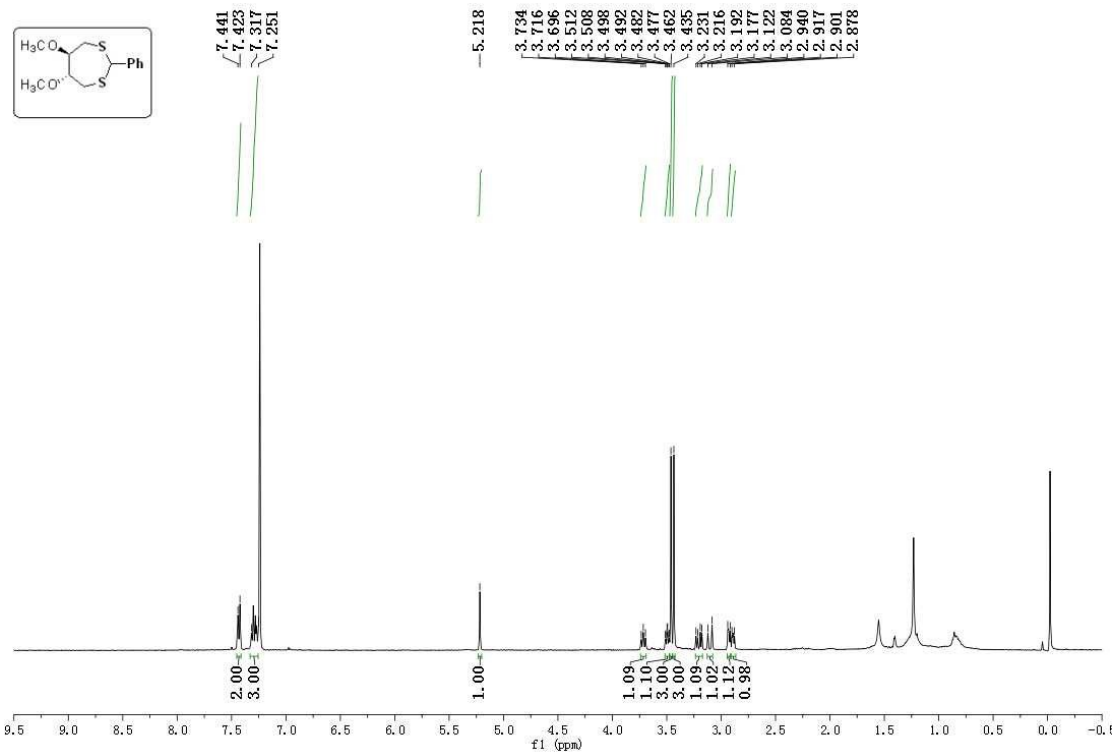


**Figure S61. $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of 12**

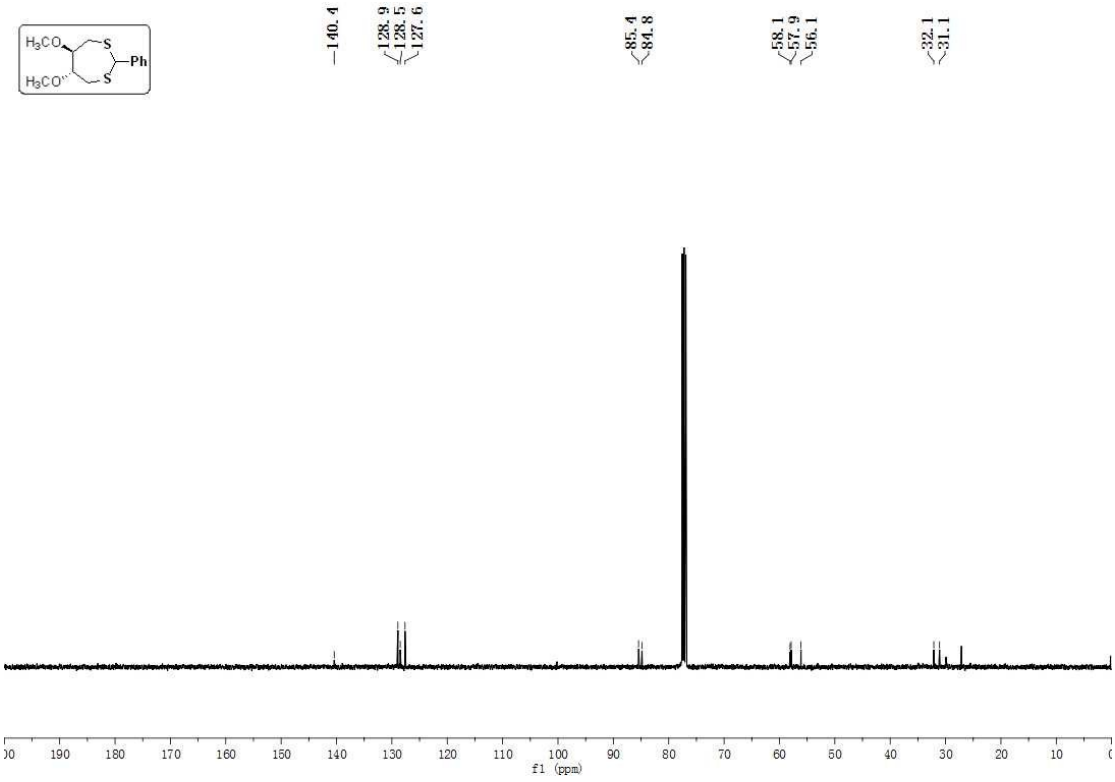


**Figure S62. $^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of 12**