Supplementary Information

for

Glycosylation Enabled by Successive Rhodium (II) and Brønsted Acid Catalysis

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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) with a hot gun. Column chromatography was performed using silica gel (Qingdao Marine Chemical Inc.; China), and Sephadex LH-20 (GE Healthcare Bio-Sciences AB, Sweden). NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz) and Bruker Ascend TM-600 spectrometer (600 MHz), and the ^1H and ^{13}C NMR chemical shifts were referenced to the solvent or solvent impurity peaks for $CDCl_3$ at δ H 7.24 and δ C 77.23, and for CD_2Cl_2 at δ H 5.32 and δ C 53.80. Optical rotations were measured at 25 °C with 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. Materials

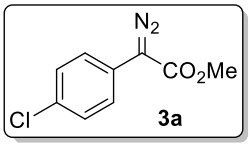
2.1. General materials

Thio-glycosides, glyco-acceptors and diazo compounds were synthesized according to literature procedures, and they were dried by repeated azeotropic removal of water using toluene and a rotary evaporator at 30 °C before glycosylation reactions. Reaction solvents were dried on an Innovative Technologies Pure Solv400 solvent purifier. Molecular sieves (4Å, powder < 50 μm) for reactions were flame dried immediately before use. $Rh_2(oct)_4$ was purchased from Adamas and dissolved in DCM. 4-Acetamidobenzenesulfonyl azide, methyl (4-Chlorophenyl)acetate and all other commercial available chemicals were purchased from Adamas and used without further purification.

2.2. Preparation of diazoesters

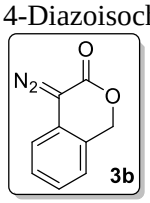
To a mixture of corresponding ester (1.0 equiv) and acetamidobenzenesulfonyl azide (1.5 equiv) in anhydrous MeCN (c = 0.1 M), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.5 equiv) was added at 0 ºC. The reaction mixture was stirred at room temperature for 1 h. Upon consumption of the starting materials, the reaction mixture was quenched with saturated aqueous NH_4Cl solution, extracted with DCM, washed with brine, dried over Na_2SO_4, concentrated and purified by flash chromatography to afford the desire diazoester.

Methyl 4-chlorophenyldiazoacetate (**3a**)



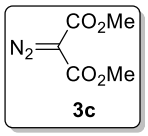
Yield: 87%, yellow Solid, R_f = 0.62 (petroleum ether-EtOAc 20:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (2H, d, J = 8.8 Hz, Ar-H), 7.32 (2H, d, J = 8.8 Hz, Ar-H), 3.84 (s, 3H, OCH_3). Analytical data for **3a** were essentially the same as reported in the literature[1].

4-Diazoisochroman-3-one (**3b**)



Yield: 60%, yellow Solid, R_f = 0.65 (petroleum ether-EtOAc 4:1). ^1H NMR (600 MHz, $CDCl_3$): δ 7.38–7.32 (1H, m, Ar-H), 7.17-7.13 (2H, m, Ar-H), 6.93 (1H, d, J = 7.8 Hz, Ar-H), 5.31 (2H, s, OCH_2). Analytical data for **3b** were essentially the same as reported in the literature[2].

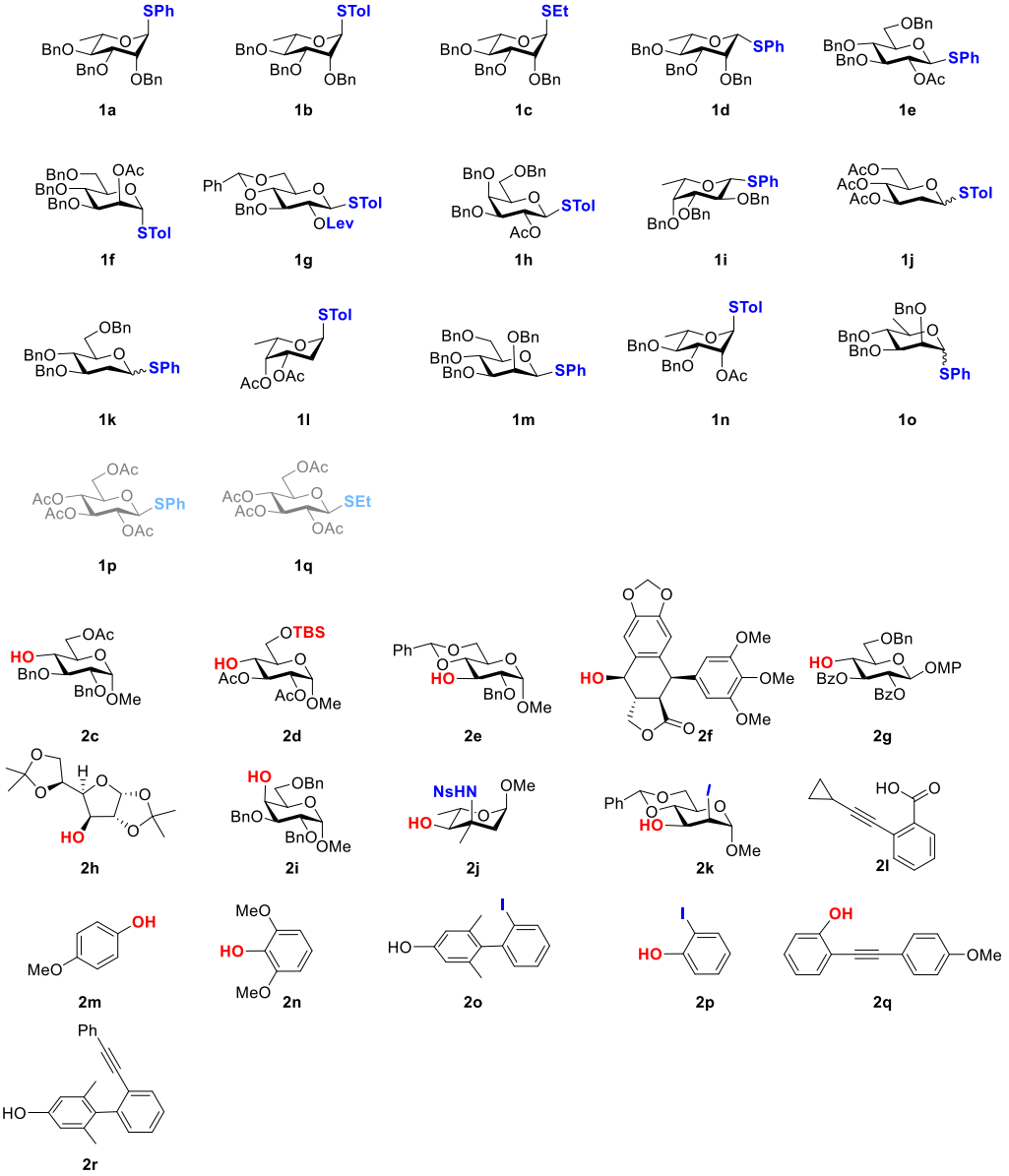
Dimethyl diazomalonate (**3c**)



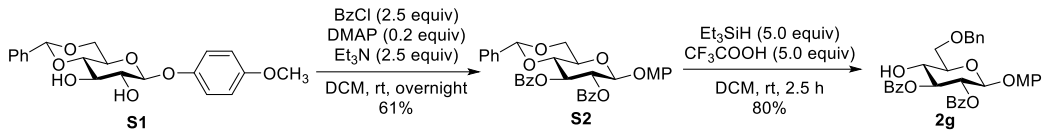
Yield: 99%, yellow Oil, R_f = 0.35 (petroleum ether-EtOAc 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 6H, CO_2Me). Analytical data for **3c** were essentially the same as reported in the literature[3].

2.3. Preparation of glycosyl donors and acceptors

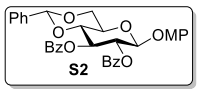
2.3.1 Table S1. Glycosyl donors and acceptors, related to Table 2



The known glycosyl donors **1a**[4], **1b**[5], **1c**[6], **1d**[7], **1e**[8], **1f**[9], **1g**[10], **1h**[11], **1i**[12], **1j**[13], **1k**[14], **1l**[15], **1m**[16], **1n**[17], **1o**[18], **1p**[19] and the known glycosyl acceptors **2c**[20], **2d**[21], **2e**[22], **2h**[23], **2i**[24], **2j**[25], **2k**[26], **2l**[27], **2o**[28], **2q**[29], were synthesized following literature procedures. **2f**, **2m**, **2n**, **2p** are commercial available. Glycosyl acceptors **2g** and **2r** were synthesized as follows.

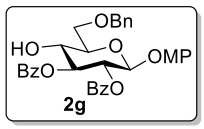


_p_-methoxybenzyl 2,3-di-_O_-benzoyl-4,6-_O_-benzylidene-β-D-glucopyranoside (S2)

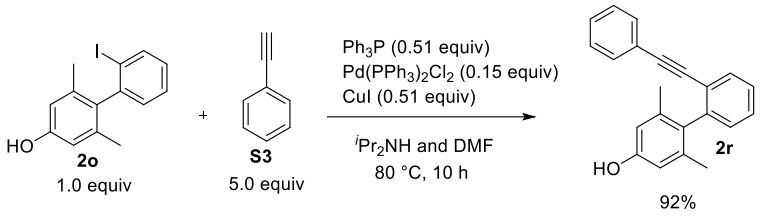


A solution of **S1**[30] (227 mg, 0.61 mmol) and DMAP (15 mg, 0.12 mmol) in dry DCM (3.0 mL) was stirred at room temperature under argon. Then, BzCl (176 µL, 1.52 mmol) and Et_3N (221 µL, 1.52 mmol) were added at 0 °C. The reaction mixture was stirred overnight at room temperature, then diluted with EtOAc, washed with water, dried over Na_2SO_4, concentrated, and purified by flash column chromatography (petroleum-EtOAc 4:1) to give **S2** (226 mg, 61%) as a white solid. R_f = 0.62 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ +32.29 (c, 0.08 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.95 (4H, m, Ar-CH), 7.52-7.47 (2H, m, Ar-CH), 7.42-7.37 (6H, m, Ar-CH), 7.29-7.31 (3H, m, Ar-CH), 6.91 (2H, d, J = 8.8 Hz, Ar-CH), 6.76 (2H, d, J = 8.8 Hz, Ar-CH), 5.82 (1H, t, J = 9.6 Hz, H-3), 5.69 (1H, dd, J = 8.0, 9.6 Hz, H-2), 5.56(1H, s, $PhCHO_2$), 5.24 (1H, d, J = 7.6 Hz, H-1), 4.45 (1H, dd, J = 5.2, 10.8 Hz, H-6a), 4.02 (1H, t, J = 9.6 Hz, H-4), 3.92 (1H, t, J = 10.4 Hz, H-6b), 3.83-3.74 (1H, m, H-5), 3.73 (3H, s, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.4, 156.1, 151.2, 136.9, 133.5, 133.4, 130.1, 130.0, 129.6, 129.4, 129.3, 128.6, 128.5, 128.4, 126.3, 119.2, 114.8, 101.8, 101.7, 78.8, 72.6, 72.2, 68.9 67.0, 55.8. HRMS (ESI^+): calc. for $C_{34}H_{30}NaO_9$ $[M+Na]^+$ 605.1782, found: 605.1780.

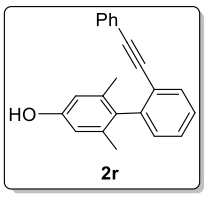
_p_-methoxybenzyl 2,3-di-_O_-benzoyl-6-_O_-benzyl-β-D-glucopyranoside (2g)



A suspension of **S2** (226 mg, 0.39 mmol) and activated 4 Å molecular sieves (100 wt%) in dry DCM (6.0 mL) was stirred at room temperature for 5 min under argon. After the mixture was cooled to 0 °C, Et_3SiH (310 µL, 1.94 mmol) was added. The reaction mixture was stirred for 15 min, then CF_3COOH (144 µL, 1.94 mmol) was added slowly. The reaction mixture was stirred at room temperature for 2.5 h, then diluted with EtOAc, filtered through Celite, concentrated, and purified by flash column chromatography (petroleum-EtOAc 3:1) to give **2g** (198 mg, 80%) as a white foam. R_f = 0.35 (petroleum ether- EtOAc 2:1). $[\alpha]_D^{25}$ +56.42 (c, 1.27 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.94 (4H, m, Ar-CH), 7.53-7.47 (2H, m, Ar-CH), 7.39-7.27 (9H, m, Ar-CH), 6.95-6.91 (2H, m, Ar-CH), 6.75-6.71 (2H, m, Ar-CH), 5.65 (1H, dd, J = 8.0, 10.0 Hz, H-2), 5.48 (1H, t, J = 9.6 Hz, H-3), 5.12 (1H, d, J = 8.0 Hz, H-1), 4.64 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.60 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.02 (1H, td, J = 9.2, 0.8 Hz, H-4), 3.91 (1H, dd, J = 4.0, 10.4 Hz, H-6a), 3.85 (1H, dd, J = 5.2, 10.4 Hz, H-6b), 3.81-3.76 (1H, m, H-5), 3.72 (3H, s, OCH_3), 3.29 (1H, d, J = 3.2 Hz, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 165.5, 155.8, 151.4, 137.9, 133.7, 133.5, 130.2, 130.0, 129.5, 129.1, 128.69, 128.65, 128.6, 128.1, 127.9, 119.1, 114.7, 101.0, 75.2, 74.0, 71.6, 71.1, 70.1, 55.8. HRMS (ESI^+): calc. for $C_{34}H_{32}NaO_9$ $[M+Na]^+$ 607.1939, found: 607.1947.

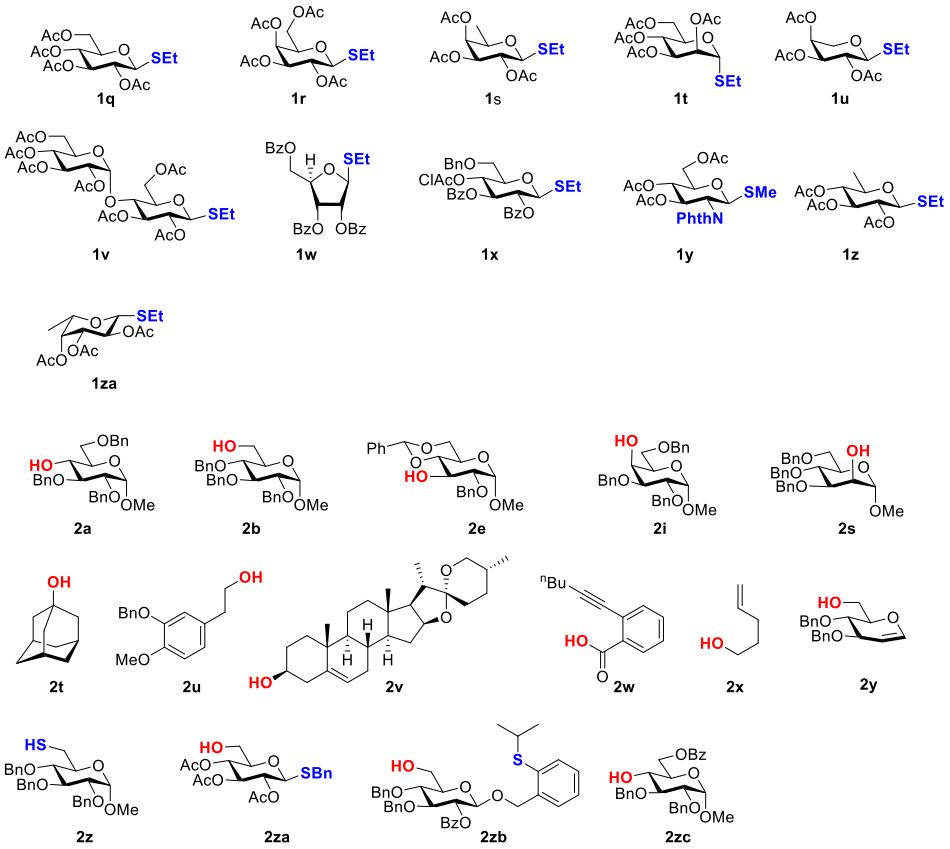


3,5-Dimethyl-4-(2'-phenylethynylphenyl)phenol(2r)

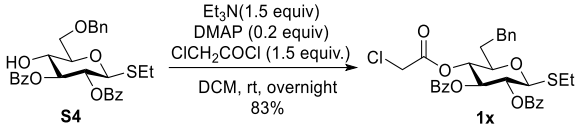


To a mixture of **2o** (50 mg, 0.15 mmol), **S3** (76.6 mg, 0.75 mmol), $PdCl_2(PPh_3)_2$ (15.8 mg, 0.0225 mmol), PPh_3 (20 mg, 0.076 mmol) and CuI (14.5 mg, 0.076 mmol) in DMF (1.3 mL), diisopropylamine (2.9 mL) was added under argon atmosphere. The reaction mixture was heated at 80 °C for 10 h until the starting material was consumed and then quenched with water. The mixture was extracted with ethyl acetate, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography over silica gel to give **2r** (41.1 mg, 92%). Yellow Syrup. R_f = 0.16 (petroleum ether- EtOAc 10:1). $[\alpha]_D^{25}$ +1.11 (c, 0.45 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (1H, dd, J = 1.6, 7.6 Hz, Ar-CH), 7.36 (1H, td, J = 7.6, 1.6 Hz, Ar-CH), 7.31 (1H, td, J = 7.6, 1.6 Hz, Ar-CH), 7.22-7.20 (3H, m, Ar-CH), 7.16 (1H, dd, J = 1.2, 8.4 Hz, Ar-CH), 7.12-7.09 (2H, m, Ar-CH), 6.61 (2H, s, Ar-CH), 4.65 (1H, s, OH), 1.98 (6H, s, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 144.0, 138.3, 133.6, 132.0, 131.7, 130.1, 128.6, 128.4, 128.2, 127.1, 123.8, 123.6, 113.9, 92.1, 88.7, 20.7. HRMS (ESI$^+$): calc. for $C_{22}H_{18}NaO$ $[M+Na]^+$ 321.1250, found: 321.1254.

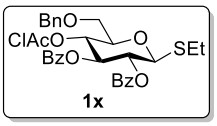
2.3.2 Table S2. Glycosyl donors and acceptors, related to Table 3



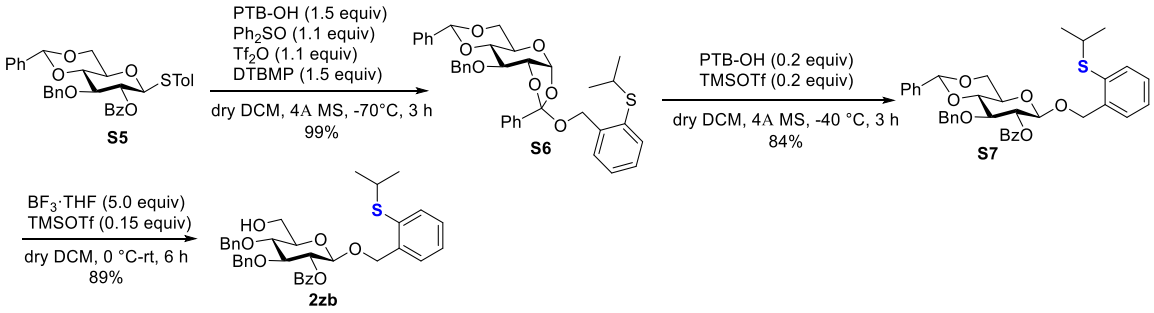
The known glycosyl donors **1q**[31], **1r**[31], **1s**[31], **1t**[31], **1u**[32], **1v**[33], **1w**[34], **1y**[35], **1z**[36], **1za**[31] and the known glycosyl acceptors **2a**[37], **2b**[38], **2e**[22], **2i**[24], **2s**[39], **2u**[40], **2w**[41], **2y**[42], **2z**[43], **2za**[20], **2zc**[44] were synthesized following literature procedures. **2t**, **2v**, **2x** are commercial available. Glycosyl donors **1x** and acceptor **2zb** were synthesized as follows.



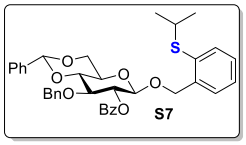
Ethyl 2,3-di-*O*-benzoyl-4-*O*-chloroacetyl-6-*O*-benzyl-1-thio-β-D-glucopyranoside (1x)



A solution of **S4**[45] (150 mg, 0.29 mmol) and DMAP (7 mg, 0.06 mmol) in dry DCM (2.6 mL) was stirred at room temperature under argon. After the reaction was cooled to 0 °C, chloroacetyl chloride (53 ul, 0.72 mmol) and Et_3N (92 ul, 0.72 mmol) were added. The reaction mixture was stirred overnight at room temperature. Then the reaction mixture was diluted with EtOAc, washed with water, dried over Na_2SO_4, concentrated, and purified by flash column chromatography (petroleum-EtOAc 4:1) to give **1x** (145 mg, 84%) as a colorless syrup. R_f = 0.69 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ +57.37 (c, 1.95 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (2H, d, *J* = 7.2 Hz, Ar-H), 7.86 (2H, t, *J* = 7.2 Hz, Ar-H), 7.51-7.46 (2H, m, Ar-H), 7.37-7.26 (9H, m, Ar-H), 5.67 (1H, t, *J* = 9.6 Hz), 5.46 (1H, t, *J* = 9.6 Hz), 5.40 (1H, t, *J* = 9.6 Hz), 4.71 (1H, d, *J* = 9.6 Hz, H-1), 4.57 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.49 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 3.88-3.83 (1H, m, H-5), 3.78 (1H, d, *J* = 14.4 Hz, $ClCH_2CO$), 3.73 (1H, d, *J* = 14.4 Hz, $ClCH_2CO$), 3.69-3.62 (2H, m, H-6a, H-6b), 2.82-2.68 (2H, m, SCH_2), 1.25 (3H, t, *J* = 7.6 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.1, 165. 3, 137.71, 133.65, 133.5, 130.1, 130.0, 129.3, 128.9, 128.7, 128.6, 128.2, 128.1, 83.9, 74.4, 73.9, 71.3, 70.6, 69.1, 40.6, 24.4, 15.0. HRMS (ESI^+): calc. for $C_{31}H_{31}ClNaO_8S$ $[M+Na]^+$ 621.1320, found: 621.1332.



2-Isopropylmercaptobenzyl 2-*O*-benzoyl-3-benzyl-4,6-*O*-benzylidene-1-thio-β-D-gluco-pyranoside (S7)

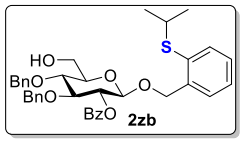


A suspension of **S5**[46] (650 mg, 1.14 mmol), DTBMP (352 mg, 1.71 mmol), Ph_2SO (254 mg, 1.26 mmol) and activated 4 Å molecular sieves (100 wt%) in dry DCM (15.0 mL) was stirred at room temperature for 10 min under argon. Then the reaction mixture was colled to -70 °C and Tf_2O (212 µL, 1.26 mmol) was added. After 10 min, PTB-OH[39] (312 mg, 1.71 mmol) in DCM (8.0 mL) was added. The reaction mixture was stirred for 3 h and quenched with Et_3N. The

suspension was diluted with EtOAc, filtered through Celite, washed with water, dried over Na_2SO_4, concentrated, and purified by flash column chromatography (petroleum-EtOAc 10:1) to give **S6** (710 mg, 99%).

A suspension of **S6** (710 mg, 1.11 mmol), PTB-OH (40 mg, 0.11 mmol) and activated 4 Å molecular sieves (100 wt%) in dry DCM (11.0 mL) was stirred at room temperature for 10 min under argon. After cooling to -40 °C, TMSOTf (41 µL, 0.23 mmol) was added. The reaction mixture was stirred for 3 h and quenched with Et_3N. The suspension was diluted with EtOAc, filtered through Celite, washed with water, dried over Na_2SO_4, concentrated and purified by flash column chromatography to give **S7** (710 mg, 99%) as a colorless syrup. R_f = 0.65 (petroleum ether-EtOAc 7:1). $[\alpha]_D^{25}$ +6.69 (c, 2.33 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (2H, d, *J* = 7.2 Hz, Ar-H), 7.57 (1H, t, *J* = 7.2 Hz, Ar-H), 7.52-7.50 (2H, m, Ar-H), 7.45-7.35 (5H, m, Ar-H), 7.31 (1H, d, *J* = 8.0 Hz, Ar-H), 7.28 (1H, d, *J* = 7.6 Hz, Ar-H), 7.16-7.11 (4H, m, Ar-H), 7.08-7.04 (2H, m, Ar-H), 6.97 (1H, t, *J* = 7.2 Hz, Ar-H), 5.61 (1H, s, $PhCHO_2$), 5.38 (1H, dd, *J* = 8.0, 8.4 Hz, H-2), 4.93 (1H, d, *J* = 13.2 Hz, $PhCH_2$), 4.87 (1H, d, *J* = 13.2 Hz, $PhCH_2$), 4.81 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.68 (1H, d, *J* = 11.2 Hz, $PhCH_2$), 4.66 (1H, d, *J* = 7.6 Hz, H-1), 4.42 (1H, dd, *J* = 4.8, 10.4 Hz, H-6a), 3.91-3.82 (3H, m, H-3, H-4, H-6b), 3.53-3.47 (1H, m, H-5), 3.20 (1H, m, $CH(CH_3)_2$), 1.15 (3H, d, *J* = 6.8 Hz, CH_3), 1.14 (3H, d, *J* = 6.4 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 138.6, 138.1, 137.5, 134.4, 133.2, 132.5, 130.2, 129.2, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.7, 127.1, 126.2, 101.5, 100.7, 81.9, 78.2, 74.2, 73.6, 68.98, 68.95, 66.5, 38.7, 23.22, 23.17. HRMS (ESI^+): calc. for $C_{37}H_{38}NaO_7S$ $[M+Na]^+$ 649.2230, found: 649.2343.

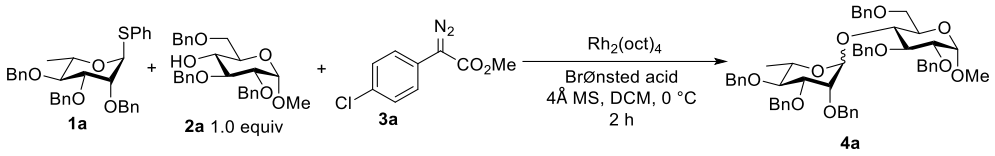
2-Isopropylmercaptobenzyl 2-*O*-benzoyl-3,4-benzyl-1-thio-β-D-glucopyranoside (2zb)



A suspension of **S7** (304 mg, 0.48 mmol) and activated 4 Å molecular sieves (100 wt%) in dry DCM (4.8 mL) was stirred at room temperature for 10 min under argon. After cooling to 0 °C, BF_3•THF (425 µL, 0.42 mmol) and TMSOTf (13.2 µL, 0.073 mmol) was added. The reaction mixture was stirred for 6 h and quenched with CH_3OH. The suspension was diluted with EtOAc, filtered through Celite, washed with brine, dried over Na_2SO_4, concentrated and purified by flash column chromatography to give **2zb** (270 mg, 89%) as a white solid. R_f = 0.32 (petroleum ether-EtOAc 4:1). $[\alpha]_D^{25}$ +35.88 (c, 1.08 in $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (2H, d, *J* = 7.2 Hz, Ar-H), 7.55 (1H, t, *J* = 7.2 Hz, Ar-H), 7.41 (2H, d, *J* = 8.0 Hz, Ar-H), 7.34-7.26 (7H, m, Ar-H), 7.16-7.11 (6H, m, Ar-H), 6.98 (1H, t, *J* = 7.6 Hz, Ar-H), 5.32 (1H, dd, *J* = 8.4, 8.8 Hz, H-2), 4.93-4.84 (3H, m, $PhCH_2$), 4.72 (1H, d, *J* = 10.8 Hz, $PhCH_2$), 4.68-4.63 (2H, m, $PhCH_2$), 4.61 (1H, d, *J* = 8.0 Hz, H-1), 3.91 (1H, ddd, *J* = 2.8, 6.0, 12.0 Hz, H-6a), 3.81 (1H, d, *J* = 9.2 Hz, H-4), 3.79-3.71 (2H, m, H-3, H-6b), 3.46-3.42 (1H, m, H-5), 3.21 (1H, m, $CH(CH_3)_2$), 1.97 (1H, t, *J* = 2.8 Hz, OH), 1.16 (3H, d, *J* = 6.8 Hz, CH_3), 1.15 (3H, d, *J* = 6.4 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 138.7, 138.05, 137.96, 134.4, 133.2, 132.3, 130.2, 130.1, 128.7, 128.50, 128.46, 128.3, 128.20, 128.18, 128.1, 127.9, 127.1, 100.2, 82.8, 77.9, 75.6, 75.30, 75.26, 74.0, 68.8, 62.1, 38.7, 23.22, 23.17. HRMS (ESI^+): calc. for $C_{37}H_{40}NaO_7S$ $[M+Na]^+$ 651.2387, found: 651.2397.

3. Reaction Developments

3.1. Table S3. Optimization of glycosylation reaction conditions[a]

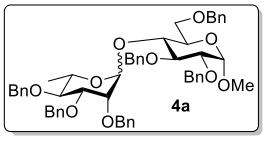


Entry	**1a**	**3a**	$Rh_2(oct)_4$	Brønsted acid	**4a**[b]
1	2.0	4.0	2 mol%	TFA•DTBMP (0.20 eq.)	trace
2	2.0	4.0	2 mol%	CSA•DTBMP (0.20 eq.)	trace
3	2.0	4.0	2 mol%	CSA (0.10 eq.)	44%
4	2.0	4.0	2 mol%	Pivalic acid (0.10 eq.)	41%
5	2.0	4.0	2 mol%	TfOH•DTBMP (0.20 eq.)	98%
6	2.0	3.0	0.5 mol%	TfOH•DTBMP (0.20 eq.)	98%
7	2.0	2.0	0.5 mol%	TfOH•DTBMP (0.20 eq.)	78%
8	1.2	3.0	0.5 mol%	TfOH•DTBMP (0.20 eq.)	93%
9	1.2	3.0	0.5 mol%	TfOH•DTBMP (0.10 eq.)	96%
10	1.2	3.0	0.5 mol%	TfOH•DTBMP (0.05 eq.)	95%
11	1.2	3.0	0.5 mol%	TfOH•DTBMP (0.03 eq.)	70%
12	1.2	2.5	0.5 mol%	TfOH•DTBMP (0.05 eq.)	82%

[a] Procedure : to the mixture of **1a**, **2a** and **3a** in CH_2Cl_2 at 0 °C, $Rh_2(oct)_4$ in CH_2Cl_2 and Brønsted acid in CH_2Cl_2 were added, the resulting mixture was stirred at 0 °C until the reaction was completed.
[b] Isolated yields based on **2a**.

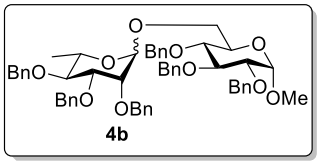
3.2. Reaction developments and data analysis, related to table 1.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-L-rhamnosyl)-α-D-glucopyranoside (4a)



Analysis by ^{1}H NMR indicated an anomeric mixture (α/β=11:1), colorless syrup. R_f = 0.36 (petroleum ether-EtOAc 4:1). $[\alpha]_D^{25}$ -8.78 (c, 3.43 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.18 (30H, m, Ar-CH), 5.00 (1H, s, H-1), 4.90 (1H, d, J = 10.4 Hz, $PhCH_2$), 4.86 (1H, d, J = 11.2 Hz, $PhCH_2$), 4.69 (2H, d, J = 11.6 Hz, $PhCH_2$), 4.56-4.51 (7H, m, 6x$PhCH_2$, H-1'), 4.44 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.37 (1H, d, J = 12.0 Hz, $PhCH_2$), 3.91-3.84 (1H, m, H-5), 3.77-3.70 (3H, m), 3.66-3.39 (6H, m), 3.30 (3H, s, OCH_3), 1.01 (3H, d, J = 6.0 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.7, 138.5, 138.1, 138.0, 129.8, 129.1, 128.5, 128.44, 128.40, 128.31, 128.25, 128.0, 127.91, 127.86, 127.7, 127.64, 127.58, 127.5, 127.4, 98.2, 98.0, 80.8, 80.6, 80.1, 79.8, 75.6, 75.2, 73.6, 73.4, 72.5, 72.2, 70.1, 69.0, 68.8, 55.3, 17.9. Analytical data for **4a** were essentially the same as reported in the literature[47].

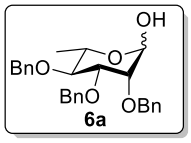
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-L-rhamnosyl)-α-D-glucopyranoside (4b)



4b

For α-isomer: colorless syrup. R_f = 0.60 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{25}$ -5.34 (c, 1.71 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.18 (30H, m, Ar-CH), 4.96 (1H, d, *J* = 10.8 Hz, $PhCH_2$), 4.93 (1H, d, *J* = 11.2 Hz, $PhCH_2$), 4.77 (2H, d, *J* = 10.8 Hz, $PhCH_2$), 4.75 (1H, s, H-1), 4.72-4.56 (7H, m, $PhCH_2$), 4.52 (1H, d, *J* = 3.2 Hz, H-1'), 4.36 (1H, d, *J* = 11.2 Hz, $PhCH_2$), 4.94 (1H, t, *J* = 9.2 Hz, H-3'), 3.82-3.79 (2H, m, H-3, H-6a'), 3.72-3.66 (3H, m, H-5, H-5', H-2), 3.59 (1H, t, *J* = 9.6 Hz, H-4), 3.46 (1H, dd, *J* = 3.2, 10.8 Hz, H-2'), 3.42 (1H, dd, *J* = 5.2, 10.8 Hz, H-6b'), 3.33 (1H, t, *J* = 9.6 Hz, H-4'), 3.25 (3H, s, OCH_3), 1.28 (3H, d, *J* = 6.0 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 138.8, 138.7, 138.5, 138.4, 138.3, 128.7, 128.63, 128.61, 128.58, 128.5, 128.33, 128.29, 128.2, 128.1, 128.0, 127.95, 127.92, 127.88, 127.85, 127.83, 127.79, 98.4, 90.0, 82.2, 80.8, 80.2, 78.0, 78.1, 76.0, 75.7, 75.25, 75.20, 73.5, 73.0, 72.5, 70.1, 68.3, 66.3, 55.2, 18.2. For β-isomer: colorless syrup. R_f = 0.44 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{25}$ +41.26 (c, 1.29 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.19 (30H, m, Ar-CH), 4.97-4.92 (3H, m, 3x$PhCH_2$), 4.85 (2H, d, *J* = 11.6 Hz, $PhCH_2$), 4.79 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.77-4.72 (2H, m, $PhCH_2$), 4.65 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.61 (1H, d, *J* = 10.8 Hz, $PhCH_2$), 4.59 (1H, d, *J* = 3.2 Hz, H-1'), 4.52 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.45 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.41 (1H, s, H-1), 4.26 (1H, dd, *J* = 3.2, 10.4 Hz, H-5'), 3.96 (1H, t, *J* = 9.2 Hz, H-3'), 3.94 (1H, s, H-2), 3.74-3.71 (1H, m, H-6a'), 3.65-3.60 (2H, m, H-6b', H-4), 3.58 (1H, t, *J* = 9.2 Hz, H-4'), 3.47 (1H, dd, *J* = 3.6, 9.6 Hz, H-2'), 3.43 (1H, dd, *J* = 2.8, 9.4 Hz, H-3), 3.34 (3H, s, OCH_3), 3.32-3.26 (1H, m, H-5), 1.33 (3H, d, *J* = 6.0 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 139.0, 138.8, 138.6, 138.45, 138.43, 128.7, 128.6, 128.5, 128.43, 128.38, 128.32, 128.31, 128.27, 128.1, 127.9, 127.80, 127.79, 127.7, 127.6, 101.6, 98.5, 82.2, 82.1, 80.4, 80.1, 78.0, 75.9, 75.6, 75.4, 74.5, 74.3, 73.7, 72.2, 71.6, 70.3, 67.5, 55.4, 18.2. Analytical data for **4b** were essentially the same as reported in the literature[48].

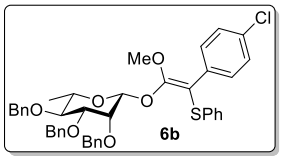
2,3,4-tri-*O*-benzyl-L-rhamnoside (6a)



6a

Colorless syrup. R_f = 0.22 (petroleum ether-EtOAc 5:1). Analysis by ^1H NMR indicated an anomeric mixture (α/β, 5:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.41-7.28 (15H, m, Ar-CH), 5.20 (1H, s, H-1), 4.93 (1H, d, *J* = 10.8 Hz, $PhCH_2$), 4.75 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.68-4.63 (4H, m, $PhCH_2$), 3.91-3.84 (3H, m), 3.56 (1H, t, *J* = 9.2 Hz, H-4), 2.83 (1H, s, OH) , 1.30 (3H, d, *J* = 6.8 Hz, H-6). Analytical data for **6a** were essentially the same as reported in the literature[49].

(Z)-1-*p*-chlorphenylthio-2-methoxy-2-*O*-(2,3,4-tri-*O*-benzyl-L-rhamnosyl)-1-*p*-chlorphenylethylen (6b)

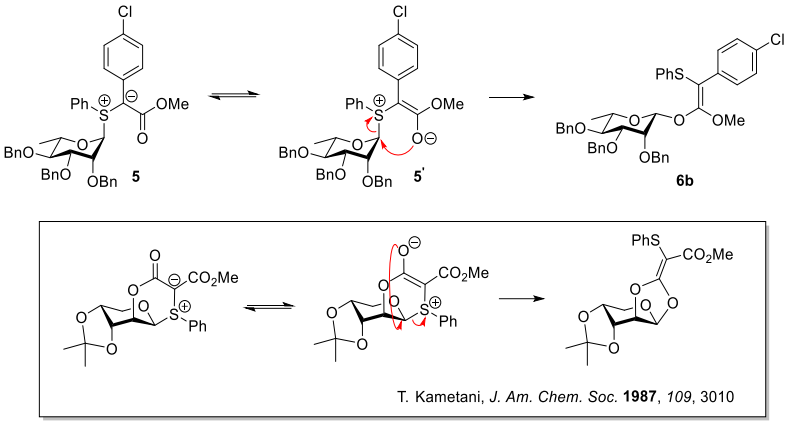


6b

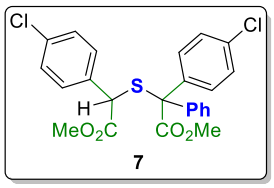
Colorless syrup. R_f = 0.24 (petroleum ether-EtOAc 15:1). $[\alpha]_D^{25}$ -18.71 (c, 1.80 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (2H, d, *J* = 8.8 Hz, Ar-CH), 7.30-6.97 (22H, m, Ar-CH), 5.42 (1H, s, H-1), 4.87 (1H, d, *J* = 10.8 Hz, $PhCH_2$), 4.66 (1H, d, *J* = 13.2 Hz, $PhCH_2$), 4.58 (1H, d, *J* = 10.8 Hz, $PhCH_2$), 4.53 (1H, d, *J* = 12.4 Hz, $PhCH_2$), 4.49 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.43 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.01-3.94 (1H, m, H-5), 3.93-3.88 (2H, m, H-2, H-3), 3.60

(1H, d, *J* = 9.2 Hz, H-4), 3.47 (3H, s, OMe), 1.21 (3H, d, *J* = 6.0 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 138.7, 138.6, 138.3, 137.3, 135.8, 132.1, 130.7, 129.0, 128.6, 128.6, 128.5, 128.21, 128.18, 128.0, 127.9, 127.84, 127.77, 126.6, 125.3, 98.6, 94.6, 79.9, 79.6, 75.4, 74.7, 73.2, 72.5, 70.8, 58.6, 18.2. HRMS (ESI$^+$): calc. for $C_{42}H_{41}ClNaO_6S$ $[M+Na]^+$ 731.2205, found: 731.2228.

Proposal for the generation of compound 6b:

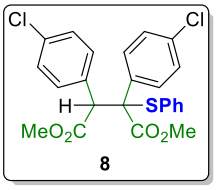


Dimethyl 1-phenyl-1,1'-dichlorophenylthiodiacetate (7)



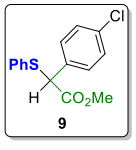
Colorless syrup. R_f = 0.18 (petroleum ether-Acetone 20:1). $(\alpha)_D^{25}$ -27.57 (c, 1.38 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.32 (3H, n, Ar-CH), 7.27-7.22 (4H, m, Ar-CH), 7.14 (4H, t, *J* = 8.8 Hz, Ar-CH), 6.74 (2H, d, *J* = 8.4 Hz, Ar-CH), 4.66 (1H, s), 3.57 (3H, s, COOMe), 3.55 (3H, s, COOMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 170.9, 136.0, 134.6, 134.1, 133.5, 132.9, 132.6, 131.9, 130.7, 130.1, 129.1, 128.1, 126.9, 66.5, 57.5, 52.6, 52.5. HRMS (ESI$^+$): calc. for $C_{24}H_{20}Cl_2NaO_4S$ $(M+Na)^+$ 497.0352, found: 497.0343.

Dimethyl 1-phenylthio-1,1'-dichlorophenyldiacetate (8)



White Solid. mp 168-171 °C. R_f = 0.33 (petroleum ether-Acetone 20:1). $(\alpha)_D^{25}$ +11.71 (c, 1.14 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (2H, d, *J* = 8.0 Hz, Ar-CH), 7.40 (1H, t, *J* = 7.2 Hz, Ar-CH), 7.33 (2H, d, *J* = 7.6 Hz, Ar-CH), 7.18 (2H, d, *J* = 8.0 Hz, Ar-CH), 7.07 (2H, d, *J* = 8.4 Hz, Ar-CH), 6.97 (2H, d, *J* = 8.0 Hz, Ar-CH), 6.87 (2H, d, *J* = 8.4 Hz, Ar-CH), 4.86 (1H, s), 3.71 (3H, s, COOMe), 3.42 (3H, s, COOMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.3, 137.0, 134.4, 134.2, 133.8, 132.9, 132.4, 132.2, 130.4, 130.3, 129.2, 127.9, 126.9, 66.2, 56.9, 52.6, 52.3. HRMS (ESI$^+$): calc. for $C_{24}H_{20}Cl_2NaO_4S$ $(M+Na)^+$ 497.0352, found: 497.0344.

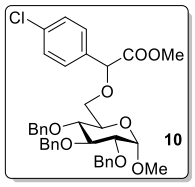
Methyl 2-(4-chlorophenyl)-2-(phenythio)acetate (9)



Colorless syrup. R_f = 0.18 (petroleum ether-EtOAc 15:1). $[\alpha]_D^{25}$ +28.99 (c, 0.77 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.32 (4H, m, Ar-CH), 7.28-7.24 (5H, m, Ar-CH), 4.84 (1H, s), 3.66 (3H, s, COOMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ

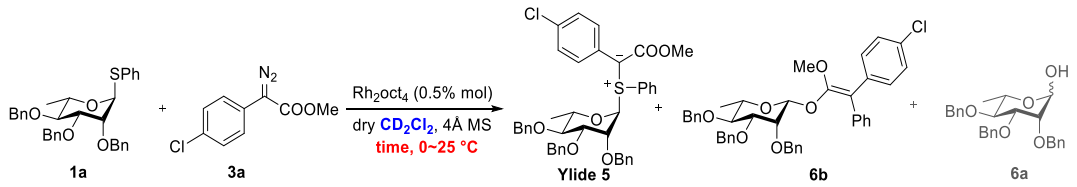
170.7, 134.5, 134.4, 133.3, 130.1, 129.3, 129.0, 128.6, 55.9, 53.1. HRMS (ESI$^+$): calc. for $C_{15}H_{13}ClNaO_2S$ $[M+Na]^+$ 315.0217, found: 315.0126. Analytical data for **9** were essentially the same as reported in the literature[50]

Methyl 2,3,4-tri-O-benzyl-6-O-(2-(4-chlorophenyl)carboxymethyl)-α-D-glucopyranoside (10)



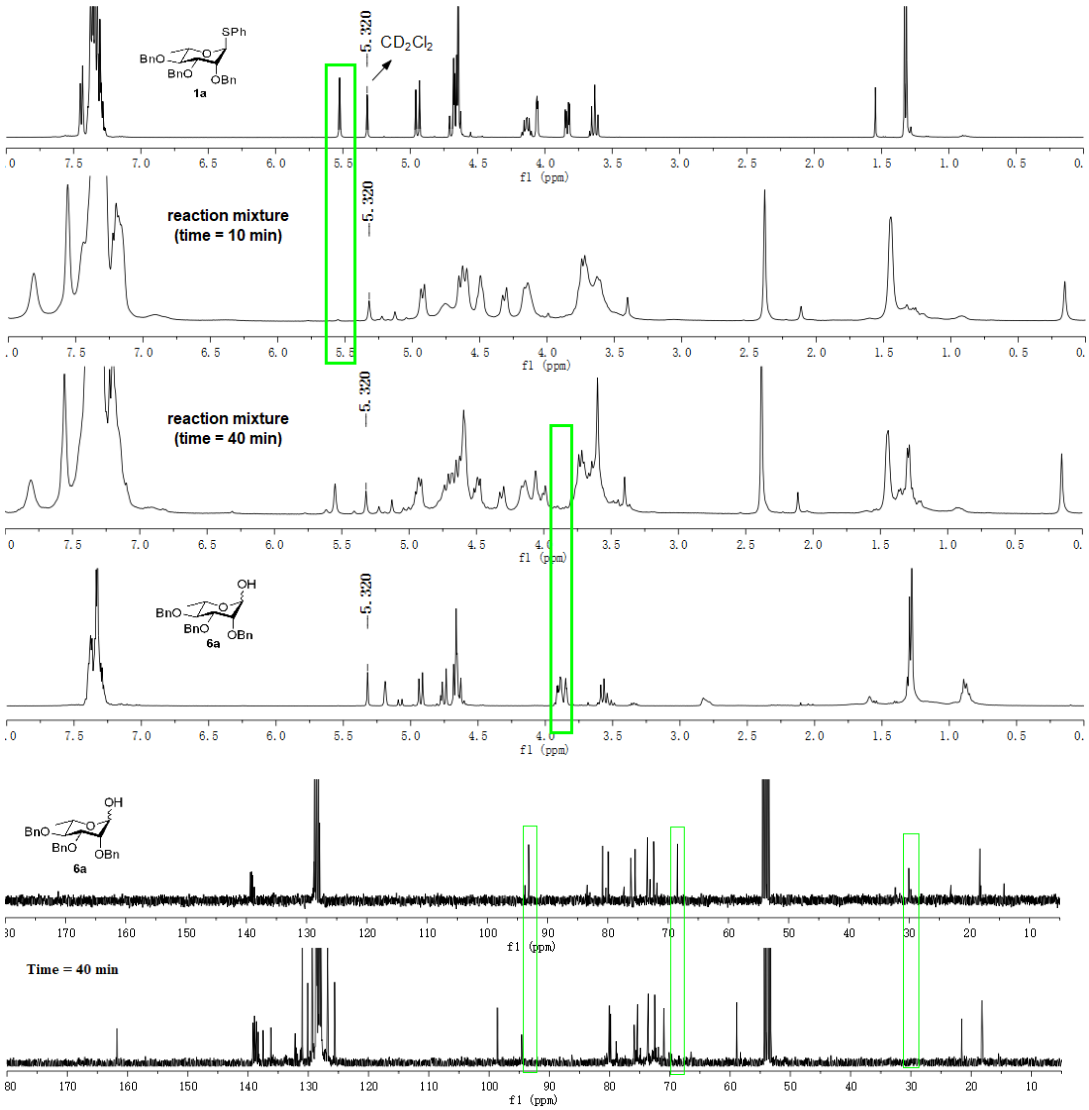
Colorless syrup. R_f = 0.47 (petroleum ether-EtOAc 3:1). A mixture (R and S 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.24 (36H, m, Ar-CH), 7.15 (2H, dd, J = 2.4, 7.6 Hz, Ar-CH), 4.962 (1H, d, J = 10.8 Hz, $PhCH_2$), 4.958 (1H, d, J = 10.8 Hz, $PhCH_2$), 4.90 (1H, s), 4.88 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.85 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.82 (1H, s), 4.82-4.76 (4H, m, $PhCH_2$), 4.74 (1H, d, J = 10.8 Hz, $PhCH_2$), 4.65 (1H, d, J = 12.4 Hz, $PhCH_2$), 4.64 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.60 (1H, d, J = 3.6 Hz, H-1), 4.58 (1H, d, J = 3.6 Hz, H-1), 4.48 (1H, d, J = 11.2 Hz, $PhCH_2$), 3.97 (2H, t, J = 9.2 Hz), 3.86 (1H, dd, J = 4.0, 10.8 Hz), 3.78-3.73 (3H, m), 3.66-3.55 (4H, m), 3.64 (3H, s, OCH_3), 3.63 (3H, s, OCH_3), 3.53 (1H, dd, J = 3.6, 9.6 Hz, H-2), 3.48 (1H, dd, J = 3.2, 9.6 Hz, H-2), 3.34 (6H, s, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.; 138.9, 138.6, 138.5, 138.4, 135.1, 135.0, 134.8, 134.7, 129.0, 128.70, 128.69, 128.68, 128.64, 128.63, 128.61, 128.60, 128.34, 128.29, 128.26, 128.2, 128.14, 128.13, 128.08, 127.90, 127.87, 127.86, 127.8, 98.3, 82.35, 82.29, 81.1, 80.9, 80.1, 80.0, 77.8, 77.7, 76.1, 76.0, 75.2, 73.63, 73.60, 70.42, 70.39, 69.1, 68.7, 55.40, 55.39, 52.53, 52.50. HRMS (ESI$^+$): calc. for $C_{37}H_{39}ClNaO_8$ $[M+Na]^+$ 669.2226, found: 669.2221.

4. Characterization of ylide 5 by NMR spectracscopy

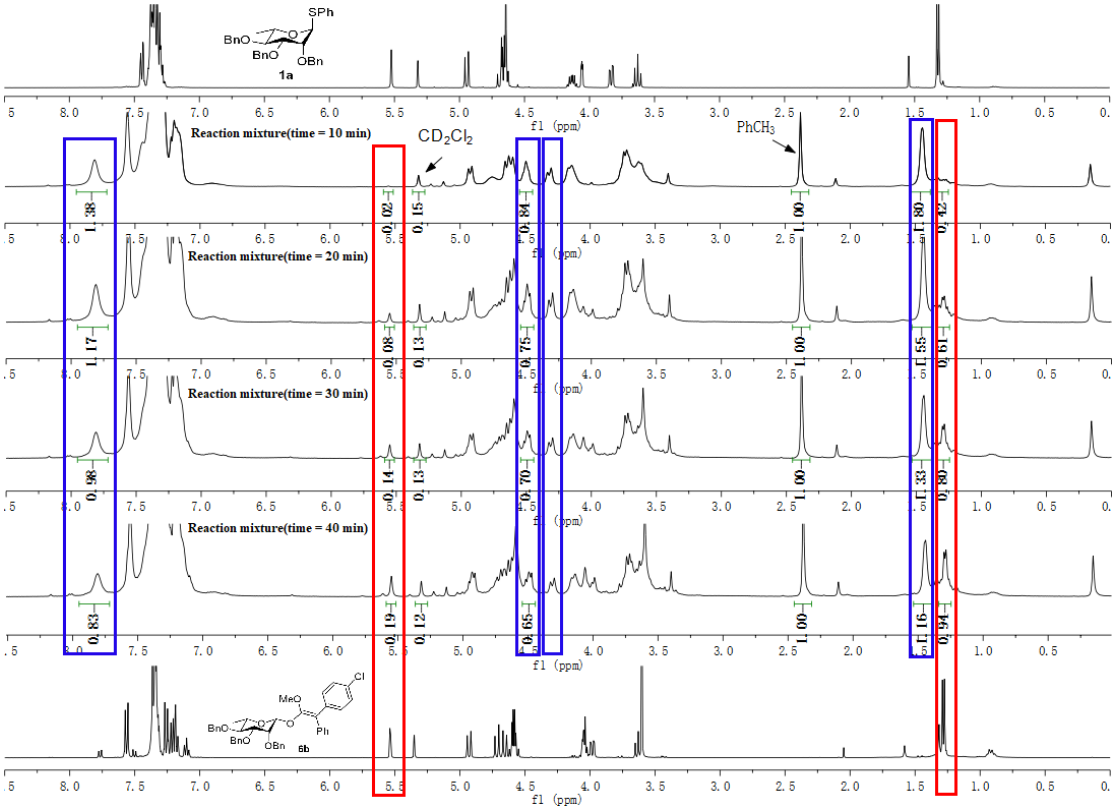


A solution of compound **1a** (50 mg, 0.095 mmol), diazo compounds **3a** (20 mg, 0.095 mmol) in CD_2Cl_2 (0.6 mL) in the presence of 4 Å MS (100 wt%) was stirred for 10 min at 0 °C. After transferring the reaction mixture to the nuclear magnetic tube(containing 4 Å MS), a solution of $Rh_2(oct)_4$ in CD_2Cl_2 (90 μL, c = 4 mg/mL) was added at 0 °C. The reaction mixture was monitored by NMR at room temperature.

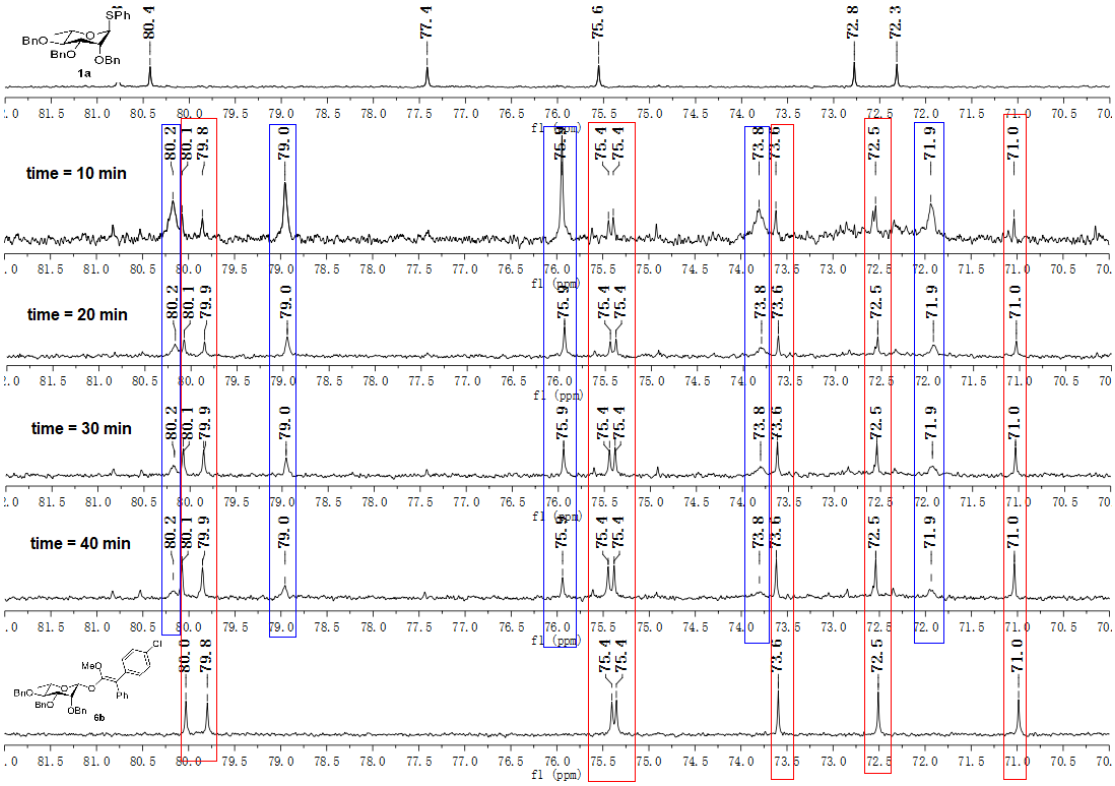
4.1 Comparison of ^{1}H NMR and ^{13}C NMR spectra of compound 1a and 6a with the reaction mixture



4.2 Comparison of ^{1}H NMR spectra of reaction mixture with different reaction times



4.3 Comparison of ^{13}C NMR spectra of reaction mixture with different reaction times



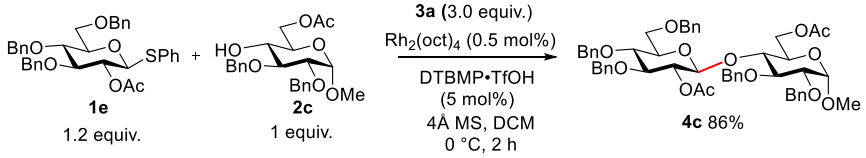
5. Glycosylation procedures, reactions and characteration data

5.1 General procedures

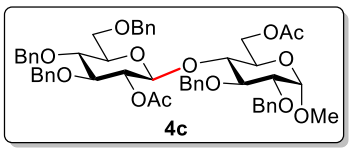
Procedure A: To A mixture of **1** (1.2 equiv), **2** (1.0 equiv) and **3a** (3.0 equiv) in CH_2Cl_2 (c = 0.1 M) at 0 °C in the presence of 4 Å MS (100 wt%) were added a solutions of $Rh_2(oct)_4$ (0.5 mol%) in CH_2Cl_2 and TfOH·DTBMP (5.0 mol%) in CH_2Cl_2. The resulting mixture was stirred at 0 °C until the reaction was completed. Then it was quenched with saturated aqueous $NaHCO_3$, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried with Na_2SO_4, concentrated, and purified by silica gel flash column chromatography.

Procedure B (stepwise activation): A mixture of **1** (1.2 equiv), **3a** (1.5 equiv) and $Rh_2(oct)_4$ (0.5 mol%) in CH_2Cl_2 (c = 0.1 M) in the presence of 4 Å MS (100 wt%) was stirred at 0 °C until the yellow color was disappeared, then **2** (1.0 equiv) and TfOH·DTBMP (5.0 mol%) were added. The resulting mixture was stirred at 0 °C until the reaction was completed. Then it was quenched with saturated aqueous $NaHCO_3$, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried with Na_2SO_4, concentrated, and purified by silica gel flash column chromatography.

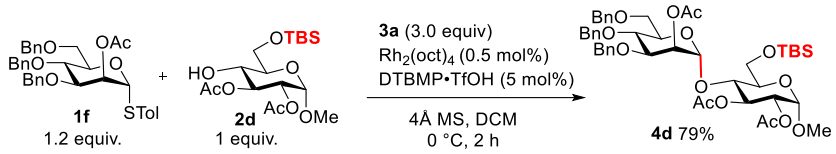
5.2 Glycosylation reactions with superarmed and armed donors, related to Table 2



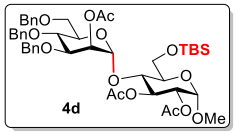
Methyl 2,3-*O*-benzyl-4-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-6-*O*-acetyl-α-D-glucopyranoside (4c)



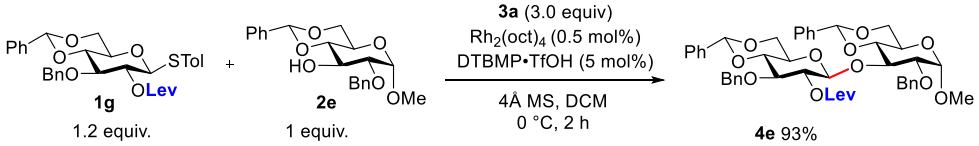
Prepared according to **Procedure A**. Colorless syrup. R_f = 0.45 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ +33.44 (c, 0.90 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.24 (23H, m, Ar-CH), 7.17-7.16 (2H, m, Ar-CH), 5.06 (1H, d, *J* = 11.4 Hz, $PhCH_2$), 5.02 (1H, dd, *J* = 8.4, 9.6 Hz, H-2), 4.88 (1H, d, *J* = 11.4 Hz, $PhCH_2$), 4.81 (1H, d, *J* = 11.4 Hz, $PhCH_2$), 4.76 (1H, d, *J* = 10.8 Hz, $PhCH_2$), 4.74 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.66 (1H, d, *J* = 11.4 Hz, $PhCH_2$), 4.59 (1H, d, *J* = 12.6 Hz, $PhCH_2$), 4.56 (1H, d, *J* = 7.8 Hz, H-1), 4.56 (1H, d, *J* = 3.0 Hz, H-1´), 4.54 (1H, d, *J* = 10.2 Hz, $PhCH_2$), 4.42 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.38 (1H, d, *J* = 12.6 Hz, $PhCH_2$), 4.36 (1H, dd, *J* = 3.6, 12.0 Hz, H-6a´), 4.20 (1H, dd, *J* = 5.4, 11.4 Hz, H-6b´), 3.96 (1H, d, *J* = 9.6 Hz, H-4´), 3.81 (1H, ddd, *J* = 1.8, 5.4, 9.6 Hz, H-5´), 3.72 (1H, t, *J* = 9.0 Hz, H-4), 3.70 (1H, dd, *J* = 9.0, 9.6 Hz, H-3), 3.62 (1H, dd, *J* = 9.6 Hz, H-3´), 3.60 (1H, dd, *J* = 1.8, 9.6 Hz, H-6a), 3.50 (1H, dd, *J* = 4.8, 10.8 Hz, H-6b), 3.46 (1H, dd, *J* = 3.6, 9.6 Hz, H-2´), 3.38 (3H, s, OCH_3), 3.38-3.35 (1H, m, H-5), 2.08 (3H, s, $COCH_3$), 1.99 (3H, s, $COCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 169.7, 139.6, 138.4, 138.3, 138.0, 128.7, 128.64, 128.60, 128.5, 128.32, 128.30, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.4, 127.3, 101.1, 98.2, 83.3, 80.1, 79.5, 78.2, 78.0, 75.6, 75.4, 75.21, 75.17, 73.8, 73.7, 73.5, 68.7, 68.4, 62.9, 55.5, 21.09, 21.08. HRMS (ESI$^+$): calc. for $C_{52}H_{58}NaO_{13}$ $[M+Na]^+$ 913.3770, found: 913.3761.



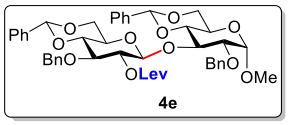
Methyl 2,3-*O*-acetyl-4-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-6-*O*-[(1,1-di-methylethyl)dimethylsilyl]-α-D-glucopyranoside (4d)



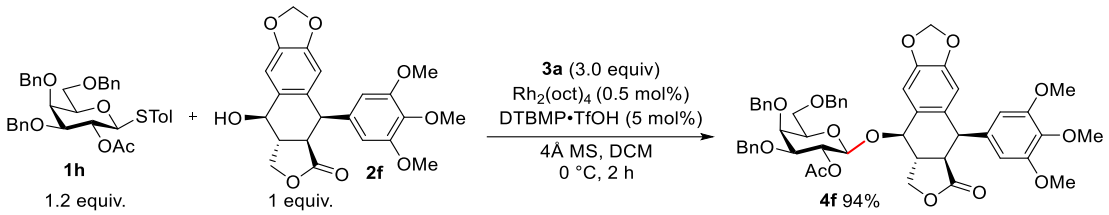
Prepared according to **Procedure A**. Colorless syrup. R_f = 0.58 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{25}$ +54.01 (c, 1.52 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.23 (13H, m, Ar-CH), 7.12-7.10 (2H, m, Ar-CH), 5.48 (1H, dd, *J* = 8.8, 10.0 Hz, H-3´), 5.13 (1H, t, *J* = 2.4 Hz, H-2), 4.98 (1H, d, *J* = 2.0 Hz, H-1), 4.82-4.80 (2H, m, $PhCH_2$), 4.72 (1H, dd, *J* = 3.6, 10.4 Hz, H-2´), 4.67 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.61 (1H, d, *J* = 11.2 Hz, $PhCH_2$), 4.47 (1H, d, *J* = 11.2 Hz, $PhCH_2$), 4.60-4.42 (2H, m, H-1´, $PhCH_2$), 3.94-3.87 (2H, m), 3.83-3.75 (4H, m), 3.72 (1H, t, *J* = 9.2 Hz), 3.64-3.59 (2H, m), 3.35 (3H, s, OCH_3), 2.11 (3H, s, $COCH_3$), 2.09 (3H, s, $COCH_3$), 2.05 (3H, s, $COCH_3$), 0.86 (9H, s, CH_3), 0.02 (6H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.48, 170.46, 138.6, 138.4, 138.1, 128.6, 128.52, 128.47, 128.3, 128.0, 128.95, 129.92, 127.8, 127.7, 100.2, 96.6, 77.8, 75.2, 74.1, 73.7, 72.8, 72.3, 71.9, 71.6, 71.1, 69.2, 68.8, 62.4, 55.2, 26.1, 21.3, 21.2, 21.0, 18.6. HRMS (ESI^+): calc. for $C_{46}H_{62}NaO_{14}Si$ $[M+Na]^+$ 889.3801, found: 889.3795.



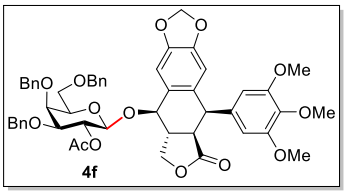
Methyl 2-*O*-benzyl-3-*O*-(2-*O*-levulinic-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside)-4,6-*O*-benzylidene-β-D-glucopyranoside (4e)



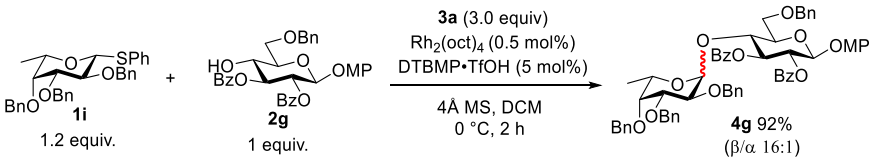
Prepared according to **Procedure A**. White Solid. R_f = 0.13 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{25}$ -9.12 (c, 1.70 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.48-7.46 (2H, m, Ar-CH), 7.41-7.24 (18H, m, Ar-CH), 5.49 (1H, s, $PhCHO_2$), 5.32 (1H, s, $PhCHO_2$), 5.08 (1H, t, *J* = 7.6 Hz, H-2), 4.93 (1H, d, *J* = 7.2 Hz, H-1), 4.82 (1H, d, *J* = 12.4 Hz, $PhCH_2$), 4.79 (1H, d, *J* = 12.8 Hz, $PhCH_2$), 4.67 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.52 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.47 (1H, d, *J* = 4.0 Hz, H-1´), 4.21 (1H, dd, *J* = 4.4, 10.0 Hz), 4.17 (1H, t, *J* = 9.2 Hz), 4.10 (1H, dd, *J* = 5.2, 10.4 Hz), 3.84 (1H, t, *J* = 9.2 Hz), 3.77 (1H, td, *J* = 9.6, 4.4 Hz), 3.70-3.62 (3H, m), 3.55 (1H, dd, *J* = 4.0, 9.2 Hz, H-2´), 3.54 (1H, t, *J* = 9.6 Hz), 3.34-3.28 (1H, m), 3.32 (3H, s, OCH_3), 2.61-2.50 (3H, m), 2.44-2.37 (1H, m), 2.11 (3H, s, $COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 171.6, 138.5, 138.4, 137.51, 137.46, 129.4, 129.1, 128.7, 128.443, 128.435, 128.36, 128.3, 128.2, 128.1, 127.8, 126.3, 126.2, 101.7, 101.1, 99.0, 81.2, 80.5, 79.7, 78.9, 74.1, 74.0, 73.9, 69.2, 68.9, 66.2, 62.5, 55.5, 37.9, 30.0, 28.1. HRMS (ESI^+): calc. for $C_{46}H_{50}NaO_{13}$ $[M+Na]^+$ 833.3144, found: 833.3142.



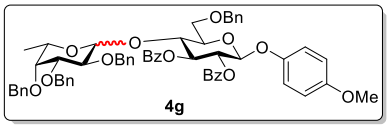
Podophyllotoxinyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranose (4f)



Prepared according to **Procedure A**. Colorless syrup. R_f = 0.21 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ -42.69 (c, 2.25 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34-7.25 (13H, m, Ar-CH), 7.20-7.19 (2H, m, Ar-CH), 7.14 (1H, s, Ar-CH), 6.45 (1H, s, Ar-CH), 6.33 (2H, s, Ar-CH), 5.95 (1H, d, *J* = 1.8 Hz), 5.93 (1H, d, *J* = 1.2 Hz), 5.41 (1H, dd, *J* = 7.8, 10.2 Hz, H-2), 4.91 (1H, d, *J* = 11.4 Hz, $PhCH_2$), 4.88 (1H, d, *J* = 9.6 Hz), 4.65 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.57 (1H, d, *J* = 11.4 Hz, $PhCH_2$), 4.54-4.52 (2H, m), 4.48 (1H, d, *J* = 12.6 Hz, $PhCH_2$), 4.40 (1H, d, *J* = 9.6 Hz, H-1), 4.40 (1H, d, *J* = 11.4 Hz, $PhCH_2$), 4.38 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.03 (1H, dd, *J* = 9.0, 10.2 Hz), 3.91 (1H, d, *J* = 2.4 Hz, H-4), 3.76 (3H, s, OCH_3), 3.71 (6H, s, OCH_3), 3.59 (1H, dd, *J* = 6.0, 9.0 Hz, H-6a), 3.55 (1H, dd, *J* = 6.0, 9.0 Hz, H-6b), 3.50 (1H, t, *J* = 6.0 Hz, H-5), 3.47 (1H, dd, *J* = 3.0, 10.2 Hz, H-3), 2.88-2.81 (1H, m), 2.74 (1H, dd, *J* = 4.8, 14.4 Hz), 1.98 (3H, s, $COCH_3$).^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 169.4, 152.8, 148.0, 147.6, 138.4, 137.9, 137.8, 137.3, 135.5, 132.1, 130.3, 128.70, 128.67, 128.5, 128.09, 128.06, 128.03, 127.97, 127.6, 109.5, 108.7, 108.3, 101.6, 99.8, 80.6, 79.0, 74.7, 74.3, 73.8, 72.6, 72.3, 71.7, 71.4, 69.0, 60.9, 56.4, 45.8, 44.1, 39.0, 21.2. HRMS (ESI$^+$): calc. for $C_{51}H_{52}NaO_{14}$ $[M+Na]^+$ 911.3249, found: 911.3294.

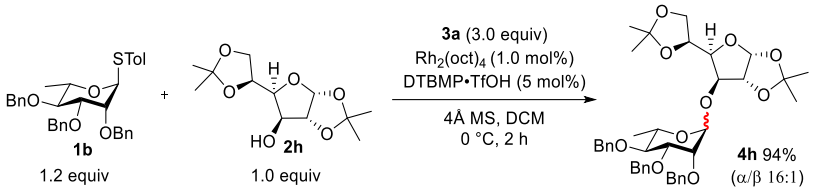


***p*-methoxybenzyl 2,3-di-*O*-benzoyl-6-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-L-fucopyranoside)-β-D-glucopyranoside (4g)**

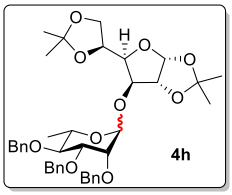


Prepared according to **Procedure A**. Colorless syrup. R_f = 0.55 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{25}$ -11.93 (c, 2.75 in $CHCl_3$). Analysis by ^{1}H NMR indicated an anomeric mixture (α/β, 1:16), for β-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (4H, d, *J* = 8.0 Hz, Ar-CH), 7.42-7.38 (2H, m, Ar-CH), 7.31-7.15 (24H, m, Ar-CH), 6.87 (2H, d, *J* = 8.8 Hz, Ar-CH), 6.66 (2H, d, *J* = 8.8 Hz, Ar-CH), 5.66 (1H, t, *J* = 9.6 Hz, H-3´), 5.48 (1H, dd, *J* = 8.0, 9.6 Hz, H-2´), 5.02 (1H, d, *J* = 8.0 Hz, H-1´), 4.95 (1H, d, *J* = 3.6 Hz, H-1), 4.79 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.76 (1H, d, *J* = 11.2 Hz, $PhCH_2$), 4.69 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.63 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.53 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.44 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.36 (1H, d, *J* = 12.4 Hz, $PhCH_2$), 4.33 (1H, d, *J* = 12.4 Hz, $PhCH_2$), 4.04 (1H, t, *J* = 9.2 Hz, H-4´), 3.92-3.88 (2H, m, H-2, H-6a´), 3.80-3.72 (3H, m, H-3, H-6b´, H-5´), 3.66 (3H, s, OCH_3), 3.66-3.62 (1H, m, H-5), 3.39 (1H, s, H-4), 0.57 (3H, d, *J* = 6.4 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.4, 155.7, 151.5, 138.8, 138.7, 138.62, 138.58, 133.26, 133.25, 130.0, 129.9, 129.8, 129.6, 128.6, 128.5, 128.44, 128.40, 128.3, 127.9,

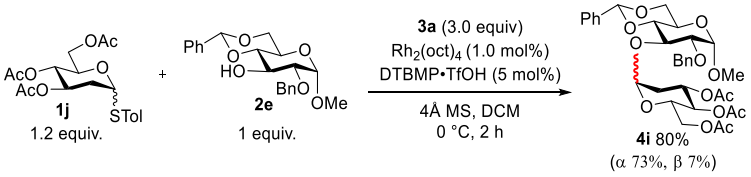
127.74, 127.71, 127.67, 127.6, 119.1, 114.6, 100.7, 100.0, 79.5, 77.8, 76.5, 76.0, 75.1, 74.7, 74.6, 73.5, 72.9, 72.6, 68.7, 67.7, 55.8, 16.2. HRMS (ESI$^+$): calc. for $C_{61}H_{60}NaO_{13}$ $[M+Na]^+$ 1023.3926, found: 1023.3932.



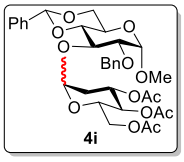
1,2,5,6-Di-*O*-isopropylidene-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-rhamnosyl)-α-D-glucofuranose (4h)



Prepared according to **Procedure A**. Colorless syrup. R_f = 0.47 (petroleum ether-EtOAc 5:1). $[\alpha]_D^{25}$ -45.55 (c, 1.19 in $CHCl_3$). Analysis by ^{1}H NMR indicated an anomeric mixture (α/β, 16:1), for α-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.24 (15H, m, Ar-CH), 5.74 (1H, d, J = 3.6 Hz, H-1´), 4.90 (1H, d, J = 11.2 Hz, $PhCH_2$), 4.82 (1H, d, J = 12.4 Hz, $PhCH_2$), 4.72 (1H, s, H-1), 4.66-4.60 (4H, m, $PhCH_2$), 4.24 (1H, d, J = 2.8 Hz), 4.17-4.11 (2H, m), 4.06-4.02 (2H, m), 3.97-3.90 (1H, m, H-5), 3.87 (1H, dd, J = 6.0, 8.4 Hz), 3.72 (1H, dd, J = 3.2, 9.2 Hz, H-3), 3.66 (1H, br s, H-2), 3.57 (1H, t, J = 9.2 Hz, H-4), 1.46 (3H, s, CH_3), 1.35 (3H, s, CH_3), 1.28 (3H, s, CH_3), 1.25 (3H, s, CH_3), 1.25 (3H, d, J = 6.0 Hz, H-6). HRMS (ESI$^+$): calc. for $C_{39}H_{48}NaO_{10}$ $[M+Na]^+$ 699.3140, found: 699.3088. Analytical data for **4h** were essentially the same as reported in the literature[51].

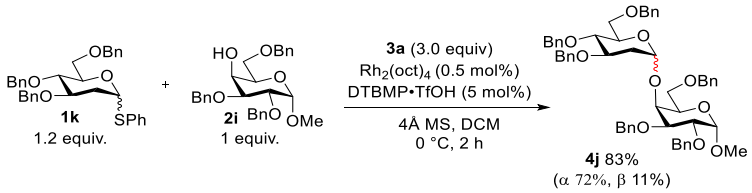


Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosyl)-α-D-glucopyranoside (4i)

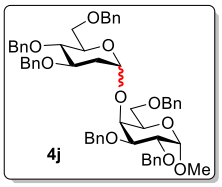


To a mixture of **1j** (20.3 mg, 0.051 mmol), diazo compounds **3a** (27 mg, 0.13 mmol) and acceptor **2e** (15.9 mg, 0.043 mmol) in CH_2Cl_2 (0.4 ml) in the presence of 4 Å MS (100 wt%) was added a solutions of DTBMP•TfOH (50 µL, c = 0.043 M) in CH_2Cl_2 and $Rh_2(oct)_4$ (165 µL, c = 2 mg/ml) in CH_2Cl_2, the reaction mixture was stirred at 0 °C for 2 h and quenched with saturated aqueous $NaHCO_3$, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried with Na_2SO_4, concentrated, and purified by silica gel flash column chromatography to give compound **4i** (α: 20.6 mg, 73%, β: 1.9 mg, 7%). α-Isomer: colorless syrup. R_f = 0.24 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{25}$ +64.80 (c, 1.55 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (10H, m, Ar-CH), 5.46 (1H, s, $PhCHO_2$), 5.39 (1H, d, J = 2.8 H, H-1'), 5.33-5.26 (1H, m, H-3'), 4.94 (1H, t, J = 9.6 Hz, H-4'), 4.67-4.63 (2H, m, $PhCH_2$, H-1), 4.62 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.33-4.30 (1H, m, H-5'), 4.24-4.18 (2H, m, H-3, H-6a), 3.97 (1H, dd, J = 3.6, 12.4 Hz, H-6a'), 3.91 (1H, d, J = 11.6 Hz, H-6b'), 3.78 (1H, td, J = 10.0, 4.8 Hz, H-5), 3.67 (1H, t, J = 10.0 Hz, H-4), 3.56 (1H, t, J = 9.2 Hz, H-6b), 3.49 (1H, dd, J = 3.6, 9.6 Hz,

H-2), 3.37 (3H, s, OCH_3), 2.25 (1H, dd, *J* = 5.6, 13.3 Hz, H-2a'), 2.05 (3H, s, $COCH_3$), 1.98 (3H, s, $COCH_3$), 1.96 (3H, s, $COCH_3$), 1.72 (td, 1H, *J* = 12.4, 3.2 Hz, H-2b'). β-Isomer: colorless syrup. R_f = 0.13 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{25}$ +18.47 (c, 0.18 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.46 (2H, m, Ar-CH), 7.38-7.29 (8H, m, Ar-CH), 5.52 (1H, s, $PhCHO_2$), 4.98-4.90 (2H, m), 4.87 (1H, dd, *J* = 1.2, 9.2 H, H-1'), 4.73 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.60 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.56 (1H, d, *J* = 3.6 Hz, H-1), 4.22 (1H, d, *J* = 4.0 Hz), 4.19 (1H, t, *J* = 4.0 Hz), 4.13 (1H, d, *J* = 9.6 Hz), 3.96 (1H, dd, *J* = 3.6, 12.0 Hz), 3.76 (1H, dd, *J* = 4.4, 8.0 Hz), 3.69 (1H, t, *J* = 10.0 Hz), 3.55-3.46 (3H, m), 3.36 (3H, s, OCH_3), 2.34-2.30 (1H, m, H-2a'), 2.00 (3H, s, $COCH_3$), 1.99 (3H, s, $COCH_3$), 1.96 (3H, s, $COCH_3$), 1.81-1.73 (1H, m, H-2b'). Analytical data for **4i** were essentially the same as reported in the literature[52].

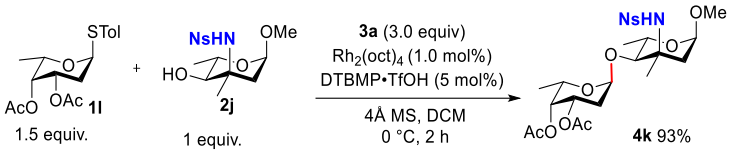


Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-α-D-galactopyranose (4j)

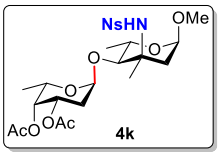


Prepared according to **Procedure A**. For α-isomer: colorless syrup. R_f = 0.39 (petroleum ether-EtOAc 4:1). $[\alpha]_D^{25}$ +45.45 (c, 0.56 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.11 (30H, m, Ar-CH), 4.95 (1H, d, *J* = 2.8 H, H-1'), 4.81 (2H, d, *J* = 11.2 Hz, $PhCH_2$), 4.75 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.67 (2H, d, *J* = 12.4 Hz, $PhCH_2$), 4.61-4.58 (3H, m, 2x$PhCH_2$, H-1), 4.51 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.49 (1H, d, *J* = 12.4 Hz, $PhCH_2$), 4.42 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.41 (1H, d, *J* = 10.8 Hz, $PhCH_2$), 4.16 (1H, d, *J* = 12.4 Hz, $PhCH_2$), 4.13-4.10 (2H, m, H-5', H-4), 3.90-3.78 (4H, m, H-3', H-3, H-2, H-6a), 3.65 (1H, t, *J* = 9.6 Hz, H-4'), 3.45-3.41 (2H, m, H-6b, H-5), 3.39 (1H, dd, *J* = 7.6, 9.6 Hz, H-6a'), 3.33 (3H, s, OCH_3), 3.04 (1H, dd, *J* = 1.6, 10.4 Hz, H-6b'), 2.09 (1H, dd, *J* = 5.6, 12.4 Hz, H-2a'), 1.59 (1H, dd, *J* = 3.2, 12.0 Hz, H-2b'). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.14, 139.11, 139.10, 138.5, 138.4, 137.5, 128.8, 128.60, 128.56, 128.54, 128.50, 128.42, 128.40, 128.36, 128.2, 128.1, 127.9, 127.8 127.71, 127.67, 127.62, 127.58, 127.5, 99.5, 99.1, 78.4, 77.9, 75.4, 75.3, 75.0, 74.0, 73.7, 73.5, 72.8, 72.2, 71.2, 69.1, 68.3, 68.2, 55.6, 36.0, 32.1, 29.9, 29.6, 22.9, 14.3. HRMS (ESI^+): calc. for $C_{55}H_{60}NaO_{10}$ $[M+Na]^+$ 903.4079, found: 903.4088. For β-isomer: Colorless syrup. R_f = 0.41 (petroleum ether-EtOAc 4:1). $[\alpha]_D^{25}$ +9.75 (c, 0.20 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.17 (30H, m, Ar-CH), 4.85 (1H, d, *J* = 10.8 H, $PhCH_2$), 4.80 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.78 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.73-4.69 (2H, m, H-1', $PhCH_2$), 4.65 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.61 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.59 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.54-4.46 (4H, m, $PhCH_2$), 4.40 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.17 (1H, d, *J* = 2.0 Hz, H-1), 3.92-3.84 (3H, m, H-2, H-3, H-5), 3.76 (1H, dd, *J* = 4.8, 10.0 Hz, H-6a), 3.66-3.59 (3H, m, H-6b, H-6a', H-4), 3.54-3.44 (3H, m, H-3', H-4', H-6b'), 3.37 (3H, s, OCH_3), 3.30-3.27 (1H, m, H-5'), 2.43-2.38 (1H, m, H-2a'), 1.59-1.56 (1H, m, H-2b'). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.62, 138.60, 138.51, 138.46, 138.42, 138.39, 128.5, 128.42, 128.37, 128.35, 128.29, 128.09, 128.07, 127.74, 127.69, 127.66, 127.60, 127.57, 127.52, 127.46, 127.4, 100.5, 100.0, 98.5, 93.3, 79.8, 78.4, 78.0, 76.4, 75.2, 75.0, 74.3, 73.4, 73.3, 71.4, 70.1, 69.6, 69.5, 55.3, 36.6. HRMS (ESI^+): calc.

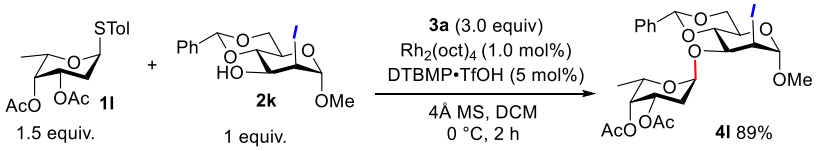
for $C_{55}H_{60}NaO_{10}$ $[M+Na]^+$ 903.4079 found: 903.4077.



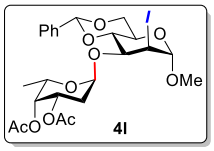
Methyl 3-(*p*-methylpenylsulfonyl)amido-4-*O*-(3,4-di-*O*-acetyl-α-L-*lyxo*-hexopyranosyl) -2,3,6-tri-deoxy-α-L-*ribo*-hexopyranoside (4k)



To a mixture of **1l** (7.3 mg, 0.022 mmol), diazo compounds **3a** (9.1 mg, 0.042 mmol) and acceptor **2j** (5 mg, 0.014 mmol) in CH_2Cl_2 (0.2 mL) in the presence of 4 Å MS (100 wt%) was added a solutions of DTBMP•TfOH (50 μL, c = 0.014 M) in CH_2Cl_2 and $Rh_2(oct)_4$ (55 μL, c = 2 mg/ml) in CH_2Cl_2, The reaction mixture was stirred at 0 °C for 2 h and quenched with saturated aqueous $NaHCO_3$, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried with Na_2SO_4, concentrated, and purified by silica gel flash column chromatography to give the compound **4k** (7.4 mg, 93%). Colorless syrup. R_f = 0.17 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ -88.49 (c, 0.53 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (2H, d, *J* = 8.8 Hz, Ar-CH), 8.05 (2H, d, *J* = 8.8 Hz, Ar-CH), 6.32 (1H, s, NH), 5.24-5.18 (2H, m, H-3, H-4), 5.08 (1H, d, *J* = 2.8 Hz, H-1), 4.65 (1H, d, *J* = 3.6 Hz, H-1´), 4.13-4.08 (1H, m, H-5), 3.83-3.76 (1H, m, H-5´), 3.34 (3H, s, OCH_3), 3.09 (1H, d, *J* = 9.2 Hz, H-4´), 2.13 (3H, s, $COCH_3$), 2.07-1.93 (3H, m, H-2a´, H-2a, H-2b), 2.01 (3H, s, $COCH_3$), 1.65 (1H, dd, *J* = 4.0, 14.4 Hz, H-2b´), 1.35 (3H, s, CH_3), 1.24 (3H, d, *J* = 6.8 Hz, H-6´), 1.09 (3H, d, *J* = 6.8 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.5, 149.8, 128.3, 124.3, 100.5, 97.8, 85.3, 69.7, 66.6, 66.2, 63.7, 59.3, 55.5, 41.9, 29.5, 24.6, 21.1, 20.9, 18.4, 16.6. HRMS (ESI$^+$): calc. for $C_{24}H_{34}N_2NaO_{12}S$ $[M+Na]^+$ 597.1725, found: 597.1800.



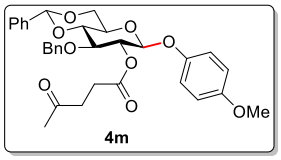
Methyl 2-deoxyl-2-iodo-4,6-*O*-benzylidene-3-*O*-(3,4-di-*O*-acetyl-α-L-*lyxo*-hexopyranosyl)-α-D-mannopyranoside (4l)



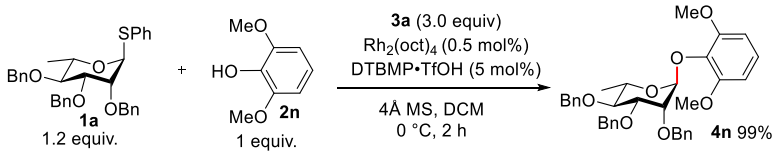
Prepared according to the synthesis of compound **4k**. Colorless syrup. R_f = 0.49 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ -90.69 (c, 0.89 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (2H, m, Ar-CH), 7.36-7.31 (3H, m, Ar-CH), 5.59 (1H, s, PhC<u>H</u>O_2), 5.34-5.29 (1H, m, H-3), 5.11 (1H, s, H-1´), 5.03 (1H, d, *J* = 1.2 Hz, H-4), 4.96 (1H, d, *J* = 2.8 Hz, H-1), 4.46 (1H, d, *J* = 4.4 Hz, H-2´), 4.27-4.22 (2H, m, H-5, H-5´), 3.98 (1H, t, *J* = 9.2 Hz, H-4´), 3.91 (1H, td, *J* = 10.0, 4.0 Hz, H-6a´), 3.86 (1H, t, *J* = 10.0 Hz, H-6b´), 3.42 (1H, dd, *J* = 4.4, 9.2 Hz, H-3´), 3.36 (3H, s, OCH_3), 2.10 (3H, s, $COCH_3$), 2.03 (1H, td, *J* = 12.4, 3.6 Hz, H-2a), 1.95 (3H, s, $COCH_3$), 1.87 (1H, dd, *J* = 4.8, 12.0 Hz, H-2b), 0.82 (1H, d, *J* = 6.4 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.3, 137.5, 129.3, 128.5, 126.3, 103.9, 102.1, 94.5, 78.9, 70.1, 69.1, 68.9, 66.8, 65.2, 64.8, 55.3, 33.1, 30.2, 21.2, 21.0, 16.3. HRMS (ESI$^+$): calc. for $C_{24}H_{31}INaO_{10}$ $[M+Na]^+$ 629.0854,

found: 629.0870.

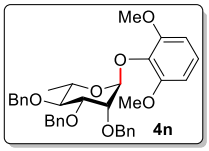
_p_-Methoxybenzyl 2-_O_-levulinic-3-_O_-benzyl-4,6-_O_-benzylidene-β-D-glucopyranoside (4m)



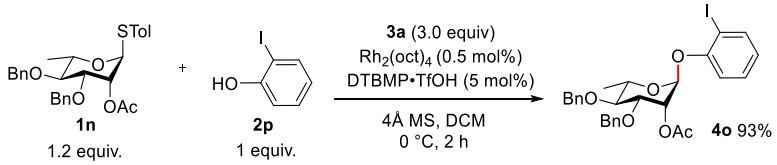
Prepared according to **Procedure A**. Colorless syrup. R_f = 0.33 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{25}$ +3.66 (c, 1.85 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.41 (2H, m, Ar-CH), 7.35-7.30 (2H, m, Ar-CH), 7.25-7.18 (6H, m, Ar-CH), 6.90-6.87 (2H, m, Ar-CH), 6.76-6.73 (2H, m, Ar-CH), 5.53 (1H, s, $PhCHO_2$), 5.18 (1H, t, J = 8.4 Hz, H-2), 4.85 (1H, d, J = 8.0 Hz, H-1), 4.82 (1H, d, J = 12.4 Hz, $PhCH_2$), 4.65 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.31 (1H, dd, J = 5.2, 10.8 Hz, H-6a), 3.81-3.75 (2H, m, H-6b, H-3), 3.73 (1H, t, J = 9.2 Hz, H-4), 3.69 (3H, s, OCH_3), 3.49-3.43 (1H, m, H-5), 2.67-2.63 (2H, m), 2.54-2.30 (2H, m), 2.09 (3H, s, $COCH_3$). Analytical data for **4m** were essentially the same as reported in the literature[53].



2,6-dimethoxy-phenyl 2,3,4-_O_-benzyl-α-L-rhamnose (4n)

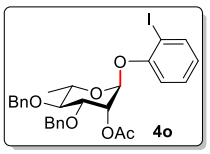


Prepared according to **Procedure A**. Colorless syrup. R_f = 0.43 (petroleum ether-EtOAc 5:1). $[\alpha]_D^{25}$ -28.99 (c, 0.89 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.24 (15H, m, Ar-CH), 6.97 (1H, t, J = 8.4 Hz, Ar-CH), 6.52 (2H, d, J = 8.4 Hz, Ar-CH), 5.29 (1H, d, J = 1.2 Hz, H-1), 4.97 (1H, d, J = 11.2 Hz, $PhCH_2$), 4.78 (1H, d, J = 11.6 Hz, $PhCH_2$), 4.75 (1H, d, J = 11.6 Hz, $PhCH_2$), 4.66 (1H, d, J = 11.2 Hz, $PhCH_2$), 4.65 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.62 (1H, d, J = 11.6 Hz, $PhCH_2$), 4.46-4.39 (1H, m, H-5), 4.17 (1H, dd, J = 2.0, 2.8 Hz, H-2), 4.12 (1H, dd, J = 3.2, 9.6 Hz, H-3), 3.72 (6H, s, OCH_3), 3.67 (1H, t, J = 9.6 Hz, H-4), 1.30 (3H, d, J = 6.0 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 139.1, 139.0, 138.7, 135.1, 128.54, 128.52, 128.3, 128.2, 127.78, 127.76, 127.6, 124.5, 105.3, 100.6, 80.6, 80.5, 75.5, 74.8, 72.7, 72.4, 69.5, 56.1, 18.1. HRMS (ESI^+): calc. for $C_{35}H_{38}NaO_7$ $[M+Na]^+$ 593.2510, found: 593.2487.

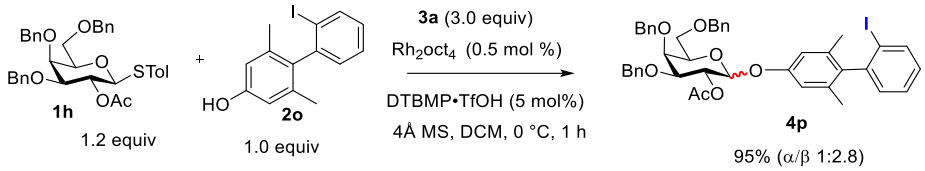


2-Iodo-phenyl 2-_O_-acetyl-3,4-_O_-benzyl-α-L-rhamnose (4o)

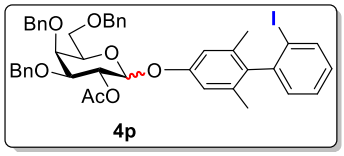
Prepared according to **Procedure A**. Yellow Syrup. R_f = 0.19 (petroleum ether-EtOAc 15:1).



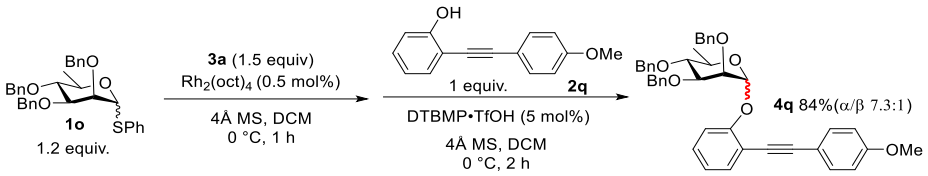
$[\alpha]_D^{25}$ -13.86 (c, 1.27 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (1H, dd, *J* = 1.6, 8.0 Hz, Ar-CH), 7.38-7.24 (11H, m, Ar-CH), 7.04 (1H, dd, *J* = 0.4, 8.4 Hz, Ar-CH), 6.75 (1H, td, *J* = 7.6, 0.8 Hz, Ar-CH), 6.54 (1H, dd, *J* = 2.0, 2.8 Hz, H-2), 5.45 (1H, d, *J* = 1.2 Hz, H-1), 4.94 (1H, d, *J* = 10.8 Hz, $PhCH_2$), 4.77 (1H, d, *J* = 11.2 Hz, $PhCH_2$), 4.64 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.63 (1H, d, *J* = 10.8 Hz, $PhCH_2$), 4.26 (1H, dd, *J* = 3.2, 9.2 Hz, H-3), 3.85-3.79 (1H, m, H-5), 3.52 (1H, t, *J* = 9.2 Hz, H-4), 2.18 (3H, s, $COCH_3$), 1.27 (3H, d, *J* = 6.4 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 155.0, 139.6, 138.6, 138.0, 129.7, 128.7, 128.6, 128.6, 128.2, 128.1, 128.0, 124.3, 114.8, 96.6, 79.9, 75.6, 72.2, 69.4, 69.1, 21.3, 18.2. HRMS (ESI^+): calc. for $C_{28}H_{29}INaO_6$ $[M+Na]^+$ 611.0901, found: 611.0914.



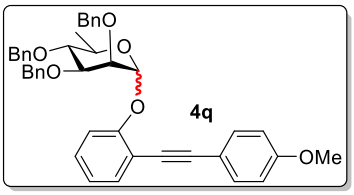
3,5-Dimethyl-4-(2'-iodophenyl)phenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranose (4p)



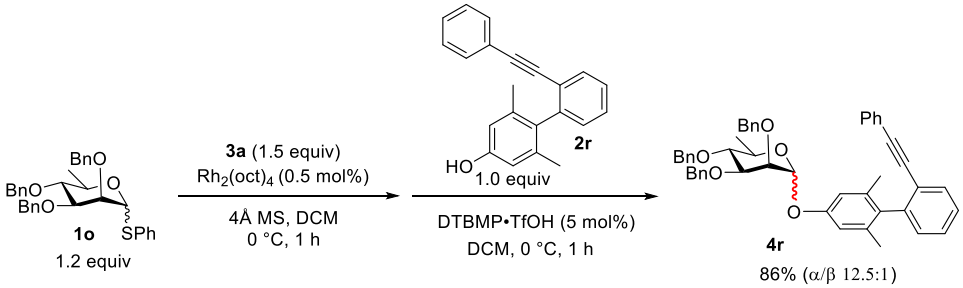
Prepared according to **Procedure A**. For β isomer: White solid. mp 110-118 °C. R_f = 0.52 (petroleum ether-EtOAc 5:1). $[\alpha]_D^{25}$ +7.50 (c, 0.12 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (1H, dd, *J* = 0.8, 7.6 Hz, Ar-CH), 7.39-7.23 (16H, m, Ar-CH), 7.06 (1H, dd, *J* = 1.6, 7.6 Hz, Ar-CH), 7.00 (1H, td, *J* = 7.6, 1.6 Hz, Ar-CH), 6.72 (2H, s, Ar-CH), 5.62 (1H, dd, *J* = 8.0, 10.0 Hz, H-2), 4.98 (1H, d, *J* = 8.0 Hz, H-1), 4.97 (1H, d, *J* = 12.4 Hz, $PhCH_2$), 4.70 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.60 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.54 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.47 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.40 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 3.99 (1H, d, *J* = 4.2 Hz, H-4), 3.75-3.63 (3H, m, H-5, H-6a, H-6b), 3.60 (1H, dd, *J* = 2.8, 10.0 Hz, H-3), 2.04 (3H, s, $COCH_3$), 1.85 (6H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 156.7, 145.9, 139.3, 138.7, 138.6, 138.1, 137.3, 137.2, 130.2, 128.70, 128.67, 128.66, 128.5, 128.4, 128.1, 128.04, 128.02, 127.8, 127.7, 115.8, 115.4, 101.4, 99.7, 80.4, 74.7, 74.4, 73.9, 72.8, 72.3, 71.4, 69.1, 21.3, 20.79, 20.75. HRMS (ESI^+): calc. for $C_{43}H_{43}INaO_7$ $[M+Na]^+$ 821.1946, found: 821.1937. For α isomer: Colorless syrup. R_f = 0.78 (petroleum ether-EtOAc 5:1). $[\alpha]_D^{25}$ +50.63 (c, 0.24 in $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.91 (1H, dd, *J* = 0.6, 7.8 Hz, Ar-CH), 7.39-7.21 (16H, m, Ar-CH), 7.05 (1H, dd, *J* = 1.8, 7.8 Hz, Ar-CH), 7.00 (1H, td, *J* = 7.8, 1.2 Hz, Ar-CH), 6.80-6.78 (2H, m, Ar-CH), 5.76 (1H, d, *J* = 3.6 Hz, H-1), 5.46 (1H, dd, *J* = 3.6, 10.8 Hz, H-2), 4.96 (1H, d, *J* = 11.4 Hz, $PhCH_2$), 4.75 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.73 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.58 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.42 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.36 (1H, d, *J* = 11.4 Hz, $PhCH_2$), 4.17-4.14 (2H, m, H-3, H-5), 3.07 (1H, d, *J* = 2.4 Hz, H-4), 3.64 (1H, dd, *J* = 7.2, 9.6 Hz, H-6a), 3.57 (1H, dd, *J* = 6.0, 9.6 Hz, H-6b), 2.08 (3H, s, $COCH_3$), 1.873 (3H, s, CH_3), 1.867 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 156.3, 145.8, 139.3, 138.8, 138.7, 138.6, 138.2, 137.4, 137.4, 130.1, 128.72, 128.67, 128.6, 128.5, 128.3, 128.0, 127.92, 127.91, 127.8, 127.6, 116.1, 115.7, 101.4, 95.6, 75.1, 74.8, 73.6, 73.1, 71.1, 70.4, 68.9, 21.3, 20.78. HRMS (ESI^+): calc. for $C_{43}H_{43}INaO_7$ $[M+Na]^+$ 821.1946, found: 821.1935.



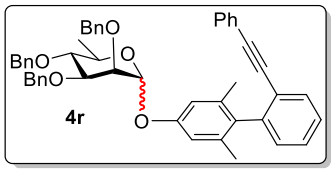
2-[2-(4-Methoxyphenyl)ethynyl]-phenyl 2,3,4-tri-*O*-benzyl-6-deoxy-D-mannopyranoside (4q)



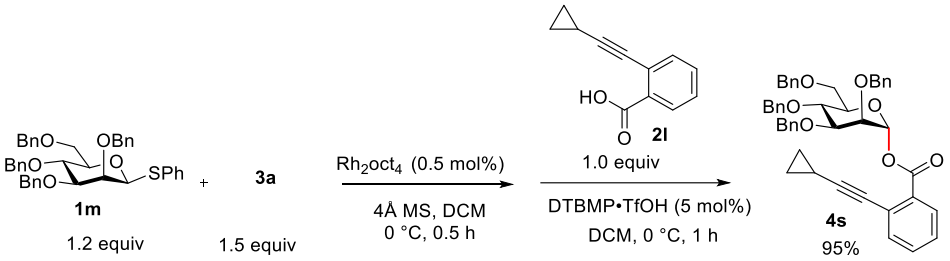
Prepared according to **Procedure B**. Analysis by ^{1}H NMR indicated an anomeric mixture (α/β, 7.3:1). Yellow Syrup. R_f = 0.20 (petroleum ether-Acetone 20:1). $[\alpha]_D^{25}$ +3.66 (c, 1.94 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-6.90 (21H, m, Ar-CH), 6.59 (2H, d, J = 8.8 Hz, Ar-CH), 5.54 (1H, d, J = 2.0 Hz, H-1), 4.89 (1H, d, J = 10.8 Hz, $PhCH_2$), 4.75 (1H, d, J = 12.4 Hz, $PhCH_2$), 4.67 (1H, d, J = 12.4 Hz, $PhCH_2$), 4.60 (1H, d, J = 10.8 Hz, $PhCH_2$), 4.54 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.51 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.18 (1H, dd, J = 3.2, 9.6 Hz, H-3), 4.01 (1H, dd, J = 2.0, 2.8 Hz, H-2), 3.98-3.91 (1H, m, H-5), 3.66 (3H, s, OCH_3), 3.65 (1H, t, J = 9.6 Hz, H-4), 1.25 (3H, d, J = 6.4 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 156.6, 138.9, 138.8, 138.4, 133.2, 129.5, 128.6, 128.54, 128.51, 128.2, 128.1, 127.9, 127.8, 127.7, 122.5, 115.7, 114.8, 114.1, 96.9, 93.8, 84.2, 80.7, 80.6, 75.5, 75.3, 73.3, 72.8, 69.5, 55.5, 18.3. HRMS (ESI^+): calc. for $C_{42}H_{40}NaO_6$ $[M+Na]^+$ 663.2717, found: 663.2753.



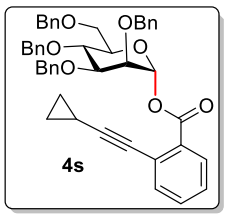
3,5-Dimethyl-4-(2'-phenylethynylphenyl)phenyl 2,3,4-tri-*O*-benzyl-6-deoxy-D-mannopyranoside (4r)



Prepared according to **Procedure B**. Analysis by ^{1}H NMR indicated an anomeric mixture (α/β, 12.5:1). Colorless Syrup. R_f = 0.39 (petroleum ether-Acetone 15:1). $[\alpha]_D^{25}$ +28.98 (c, 1.08 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (1H, dd, J = 0.8, 7.6 Hz, Ar-CH), 7.32-6.97 (23H, m, Ar-CH), 6.70 (1H, s, Ar-CH), 6.66 (1H, s, Ar-CH), 5.44 (1H, d, J = 1.6 Hz, H-1), 4.90 (1H, d, J = 10.8 Hz, $PhCH_2$), 4.74 (1H, d, J = 12.4 Hz, $PhCH_2$), 4.70 (1H, d, J = 12.8 Hz, $PhCH_2$), 4.64 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.61 (1H, d, J = 11.6 Hz, $PhCH_2$), 4.51 (1H, d, J = 10.8 Hz, $PhCH_2$), 4.02 (1H, dd, J = 3.2, 9.6 Hz, H-3), 3.90 (1H, t, J = 2.0 Hz, H-2), 3.83-3.78 (1H, m, H-5), 3.62 (1H, t, J = 9.6 Hz, H-4), 1.91 (3H, s, CH_3), 1.90 (3H, s, CH_3), 1.23 (3H, d, J = 6.4 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 143.9, 138.84, 138.78, 138.4, 138.05, 138.04, 134.9, 131.9, 131.596, 129. 9, 128.65, 128.62, 128.59, 128.4, 128.174, 128.168, 128.0, 127.89, 127.86, 127.8, 127.1, 123.6, 115.3, 114.8, 96.4, 92.2, 88.6, 80.8, 80.2, 75.6, 75.0, 73.1, 72.6, 69.0, 20.9, 20.8, 18.4. HRMS (ESI^+): calc. for $C_{49}H_{46}NaO_5$ $[M+Na]^+$ 737.3237, found: 737.3228.



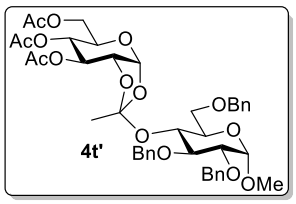
2,3,4,6-Tetra-O-benzyl-α-D-mannopyranosyl *ortho*-cyclopropylethynylbenzoate (4s)



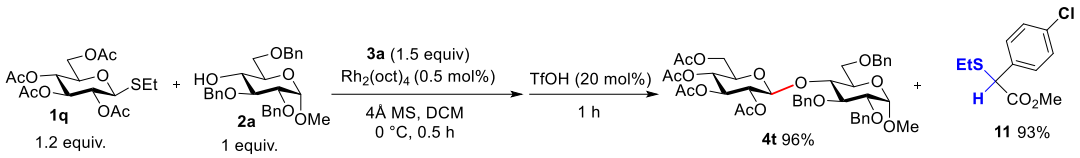
Prepared according to **Procedure B**. Colorless syrup. R_f = 0.43 (petroleum ether-Acetone 5:1). $[\alpha]_D^{25}$ +22.1 (c, 1.47 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (1H, d, J = 7.6 Hz, Ar-CH), 7.44-7.23 (21H, m, Ar-CH), 7.13-7.11 (2H, m, Ar-CH), 6.51 (1H, d, J = 1.6 Hz, H-1), 4.89 (1H, d, J = 10.8 Hz, $PhCH_2$), 4.84 (1H, d, J = 12.4 Hz, $PhCH_2$), 4.77 (1H, d, J = 12.4 Hz, $PhCH_2$), 4.69 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.60-4.52 (4H, m, $PhCH_2$), 4.17 (1H, t, J = 9.6 Hz, H-4), 4.06 (1H, dd, J = 3.2, 9.6 Hz, H-3), 4.05-4.02 (1H, m, H-5), 3.88 (1H, t, J = 2.4 Hz, H-2), 3.83 (1H, dd, J = 4.0, 10.8 Hz, H-6a), 3.73 (1H, dd, J = 1.6, 11.2 Hz, H-6b), 1.54-1.49 (1H, m), 0.79-0.67 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 138.6, 138.5, 138.4, 138.1, 134.8, 132.3, 131.0, 130.8, 128.58, 128.57, 128.51, 128.47, 128.23, 128.21, 128.1, 128.0, 127.92, 127.87, 127.8, 127.7, 127.2, 125.1, 100.2, 93.0, 79.5, 75.5, 75.1, 75.0, 74.4, 73.8, 73.7, 72.7, 72.4, 69.0, 9.2. HRMS (ESI^+): calc. for $C_{46}H_{44}NaO_7$ $[M+Na]^+$ 731.2979, found: 731.2951.

5.3 Glycosylation reactions with disarmed donors, related to Table 3.

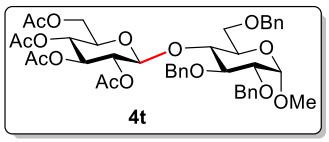
Methyl 2,3,6-*O*-tri-benzyl-4-*O*-(2,3,4-*O*-tri-acetyl-1,2-orthoester-α-D-glucopyranosyl)-β-D-glucopyranoside (4t')



Prepared according to **Procedure A**. Colorless syrup. R_f = 0.28 (petroleum ether-EtOAc 4:1). $[\alpha]_D^{25}$ +29.09 (c, 5.50 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (15H, m, Ar-H), 5.75 (1H, d, J = 5.2 Hz, H-1), 4.91 (1H, t, J = 3.2 Hz, H-3), 4.84-4.81 (3H, m, $PhCH_2$, $PhCH_2$, H-4), 4.75 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.60 (2H, d, J = 11.6 Hz, $PhCH_2$), 4.56 (1H, d, J = 3.6 Hz, H-1'), 4.50 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.39 (1H, dd, J = 3.6, 5.2 Hz, H-2), 4.16 (2H, d, J = 3.6 Hz, H-6a, H-6b), 3.90-3.85 (1H, m, H-5), 3.79 (1H, t, J = 8.8 Hz, H-3'), 3.72 (1H, t, J = 8.8 Hz, H-4'), 3.66-3.59 (3H, m, H-6a', H-6b', H-5'), 3.46 (1H, dd, J = 3.6, 9.6 Hz, H-2'), 3.34 (3H, s, OCH_3), 2.06 (3H, s, $COCH_3$), 2.03 (3H, s, $COCH_3$), 2.01 (3H, s, $COCH_3$), 1.74 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 169.7, 169.2, 138.9, 138.4, 138.3, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 122.7, 98.1, 97.5, 80.8, 79.7, 76.1, 73.6, 73.5, 72.6, 70.6, 70.1, 68.8, 68.0, 67.7, 63.3, 55.4, 24.0, 20.9. HRMS (ESI^+): calc. for $C_{42}H_{50}NaO_{15}$ $[M+Na]^+$ 817.3042, found: 817.3049.

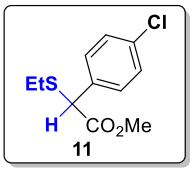


Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranoside (4t)

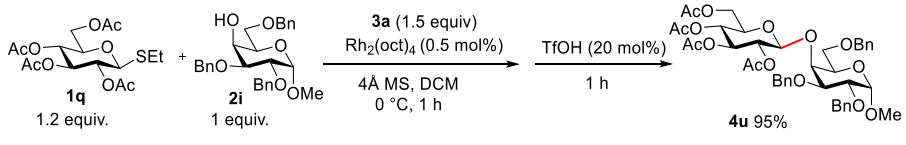


A mixture of donor **1q** (20.1 mg, 0.051 mmol), acceptor **2a** (19.8 mg, 0.043 mmol), diazo compound **3a** (13.5 mg, 0.064 mmol) and $Rh_2(oct)_4$ (85 μL, c = 2 mg/ml) in CH_2Cl_2 (0.4 mL) in the presence of 4 Å MS (100 wt%) was stirred at 0 °C for 30 min while the yellow color of **3a** was disappeared, then TfOH (0.76 μL, 0.0086 mmol) was added. The resulting mixture was stirred at 0 °C until the reaction was completed, It was then quenched with saturated aqueous $NaHCO_3$, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried with Na_2SO_4, concentrated, and purified by silica gel flash column chromatography to give compound **4t** (32.5 mg, 96%) as a colorless syrup. R_f = 0.26 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ -6.99 (c, 2.94 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.20 (15H, m, Ar-H), 5.00 (1H, t, J = 9.2 Hz), 4.97-4.91 (2H, m), 4.87 (1H, t, J = 9.2 Hz), 4.75-4.70 (3H, m, $PhCH_2$), 4.57 (1H, d, J = 11.6 Hz, $PhCH_2$), 4.55 (1H, d, J = 3.2 Hz, H-1), 4.47 (1H, d, J = 8.0 Hz, H-1′), 4.40 (1H, d, J = 12.0 Hz, $PhCH_2$) 4.12 (1H, dd, J = 12.0, 4.0 Hz, H-6a), 3.88-3.79 (3H, m), 3.74 (1H, dd, J = 10.8, 2.8 Hz), 3.60-3.56 (2H, m), 3.45 (1H, dd, J = 8.4, 4.4 Hz) 3.34 (3H, s, -OCH_3), 3.30-3.26 (1H, m), 1.98 (3H, s, -$COCH_3$), 1.96 (3H, s, -$COCH_3$), 1.93 (3H, s, -$COCH_3$), 1.92 (3H, s, -$COCH_3$). Analytical data for **4t** were essentially the same as reported in the literature[30].

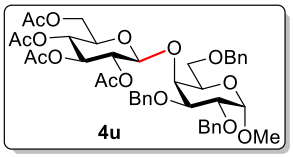
methyl 2-(4-chlorophenyl)-2-(ethylthio)acetate (11)



Colorless syrup. R_f = 0.34 (petroleum ether-EtOAc 15:1). $[\alpha]_D^{25}$ +11.45 (c, 1.52 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (4H, m, Ar-H), 4.55 (1H, s), 3.71 (3H, s, COOMe), 2.58-2.43 (2H, m, SCH_2), 1.20 (3H, t, J = 7.6 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 134.9, 134.2, 130.0, 129.0, 53.0, 51.3, 26.2, 14.2. HRMS (ESI^+): calc. for $C_{11}H_{13}ClNaO_2S$ $[M+Na]^+$ 267.0217, found: 267.0193.

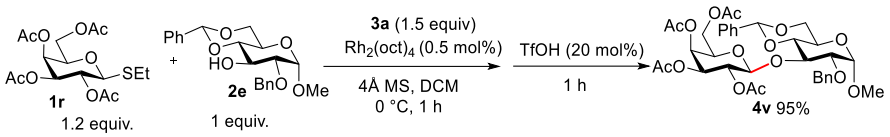


Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-galactopyranoside (4u)

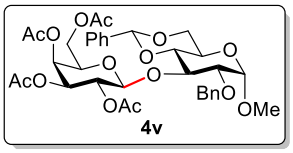


Prepared according to the synthetic preocedure of compound **4t**. Colorless syrup. R_f = 0.22 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ +14.90 (c, 1.55 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.21 (15H, m, Ar-CH), 5.17 (1H, t, J = 9.6 Hz), 5.02 (1H, t, J = 9.6 Hz),

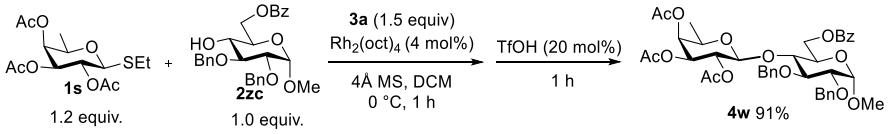
4.97 (1H, dd, J = 8.0, 9.2 Hz, H-2), 4.83 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.78 (1H, d, J = 8.0 Hz, H-1), 4.73 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.65 (1H, d, J = 11.6 Hz, $PhCH_2$), 4.62 (1H, d, J = 3.6 Hz, H-1´), 4.57 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.53 (1H, d, J = 12.4 Hz, $PhCH_2$), 4.48 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.13 (1H, dd, J = 4.4, 12.4 Hz), 4.03-3.99 (2H, m), 3.88-3.84 (2H, m), 3.75 (1H, dd, J = 3.6, 10.0 Hz), 3.65 (1H, dd, J = 5.2, 10.0 Hz), 3.57-3.49 (2H, m), 3.34 (3H, s, OCH_3), 2.00 (3H, s, $COCH_3$), 1.99 (3H, s, $COCH_3$), 1.98 (3H, s, $COCH_3$), 1.79 (3H, s, $COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.5, 169.70, 169.67, 138.8, 138.6, 138.5, 128.7, 128.6, 128.5, 128.1, 128.01, 127.96, 127.8, 127.6, 101.6, 98.6, 78.3, 76.4, 73.9, 73.8, 73.5, 72.9, 71.8, 71.7, 69.9, 69.2, 68.6, 62.0, 55.5, 20.9, 20.85, 20.84, 20.81. HRMS (ESI^+): calc. for $C_{42}H_{50}NaO_{15}$ $[M+Na]^+$ 817.3042, found: 817.3043.



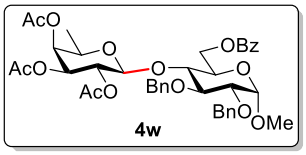
Methyl 2-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-4,6-*O*-benzylidene -α-D-glucopyranoside (4v)



Prepared according to the synthetic procedure of compound **4t.** White Solid. R_f = 0.36 (petroleum ether-EtOAc 1.5:1). $[\alpha]_D^{25}$ -16.26 (c, 2.11 in $CHCl_3$). ^1H NMR (400MHz, $CDCl_3$): 7.47-7.44 (2H, m, Ar-CH), 7.35-7.26 (8H, m, Ar-CH), 5.50 (1H, s, $PhCHO_2$), 5.29 (1H, d, J = 2.4 Hz, H-4), 5.26 (1H, dd, J = 8.4, 10.0 Hz, H-2), 4.94 (1H, dd, J = 3.6, 10.4 Hz, H-3), 4.80 (1H, d, J = 8.0 Hz, H-1), 4.77 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.47 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.42 (1H, d, J = 4.0 Hz, H-1´), 4.21-4.17 (1H, m, H-6a), 4.17 (1H, t, J = 9.2 Hz, H-4´), 4.05 (1H, dd, J = 8.0, 10.8 Hz, H-6a´), 3.81-3.74 (2H, m, H-6b, H-6b´), 3.68 (1H, t, J = 10.4 Hz, H-3), 3.61-3.58 (2H, m, H-5, H-5´), 3.50 (1H, dd, J = 4.0, 9.2 Hz, H-2´), 3.32 (3H, s, OCH_3), 2.11 (3H, s, $COCH_3$), 1.98 (3H, s, $COCH_3$), 1.95 (3H, s, $COCH_3$), 1.89 (3H, s, $COCH_3$). Analytical data for **4v** were essentially the same as reported in the literature[54].

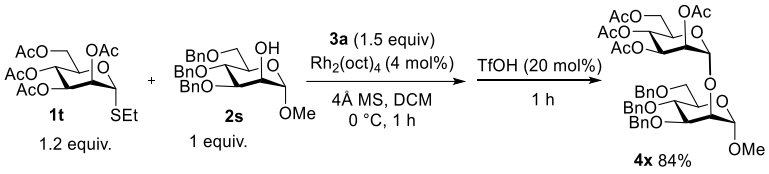


Methyl 2,3-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-acetyl-6-deoxyl-β-D-galactopyranosyl)-6-*O*-benzo-yl-α-D-glucopyranoside (4w)

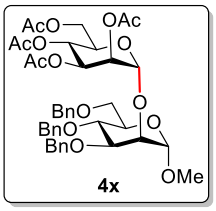


A mixture of donor **1s** (17.1 mg, 0.051 mmol), acceptor **2zc** (20.4 mg, 0.043 mmol), diazo compound **3a** (13.5 mg, 0.064 mmol) and $Rh_2(oct)_4$ (1.3 mg, 0.0017 mmol) in CH_2Cl_2 (0.4 mL) in the presence of 4 Å MS (100 wt%) was stirred at 0 °C for 1 h while the yellow color of **3a** was disappeared, then TfOH (0.76 μL, 0.0086 mmol) was added. The resulting mixture was stirred at 0 °C until the reaction was completed. It was then quenched with saturated aqueous $NaHCO_3$, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried with Na_2SO_4, concentrated, and purified by silica gel flash column chromatography to give compound **4w** (29.2 mg, 91%) as a colorless syrup. R_f = 0.53

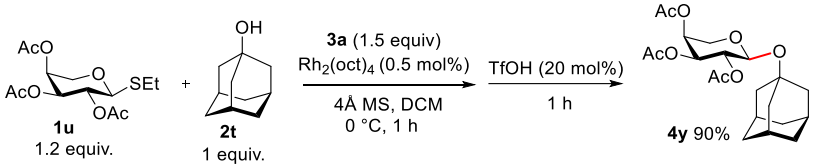
(petroleum ether-EtOAc 3:1). $[\alpha]_D^{25}$ +38.24 (c, 0.85 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (2H, d, *J* = 7.6 Hz, Ar-CH), 7.56 (1H, d, *J* = 7.6 Hz, Ar-CH), 7.45-7.38 (4H, m, Ar-CH), 7.33-7.24 (8H, m, Ar-CH), 5.16 (1H, dd, *J* = 8.0, 10.4 Hz, H-2), 5.08 (1H, d, *J* = 3.2 Hz, H-4), 4.98 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.95 (1H, d, *J* = 11.2 Hz, $PhCH_2$), 4.88 (1H, dd, *J* = 3.6, 10.4 Hz, H-3), 4.73 (1H, d, *J* = 8.0 Hz, H-1), 4.73 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.61 (1H, dd, *J* = 1.2, 11.6 Hz, H-6a´), 4.59 (1H, d, *J* = 12.4 Hz, $PhCH_2$), 4.56 (1H, d, *J* = 3.6 Hz, H-1´), 4.34 (1H, dd, *J* = 5.2, 11.6 Hz, H-6b´), 3.98 (1H, t, *J* = 9.2 Hz, H-4´), 3.94-3.91 (1H, m, H-5´), 3.82 (1H, dd, *J* = 8.8, 9.6 Hz, H-3´), 3.51 (1H, dd, *J* = 3.6, 9.6 Hz, H-2´), 3.49-3.44 (1H, m, H-5), 3.36 (3H, s, OCH_3), 2.12 (3H, s, $COCH_3$), 2.02 (3H, s, $COCH_3$), 1.93 (3H, s, $COCH_3$), 0.97 (3H, d, *J* = 6.4 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.4, 169.8, 139.4, 138.2, 133.5, 130.0, 129.8, 128.72, 128.65, 128.4, 128.3, 128.1, 127.5, 127.2, 101.1, 98.1, 80.2, 79.9, 78.1, 75.2, 73.7, 71.8, 70.4, 70.1, 69.5, 68.4, 63.3, 55.6, 21.0, 20.9, 20.8, 16.1. HRMS (ESI^+): calc. for $C_{40}H_{46}NaO_{14}$ $[M+Na]^+$ 773.2780, found: 773.2800.



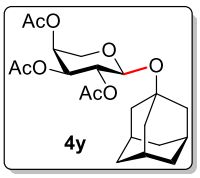
Methyl 3,4,6-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-benzoyl -α-D-galactopyranose (4x)



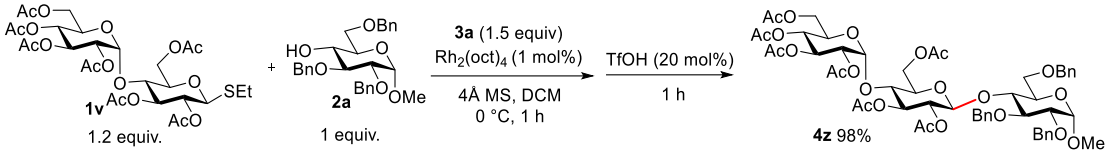
Prepared according to the synthetic procedure of compound **4w**. Yellow syrup. R_f = 0.14 (petroleum ether-Acetone 4:1). $[\alpha]_D^{25}$ +30.74 (c, 0.95 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.23 (13H, d, *J* = 7.6 Hz, Ar-CH), 7.15-7.13 (2H, m, Ar-CH), 5.43 (1H, dd, *J* = 1.2, 4.0 Hz, H-2), 5.39 (1H, dd, *J* = 3.6, 10.0 Hz, H-3), 5.23 (1H, t, *J* = 9.6 Hz, H-4), 4.95 (1H, s, H-1), 4.81 (1H, d, *J* = 10.8 Hz, $PhCH_2$), 4.77 (1H, d, *J* = 1.2 Hz, H-1´), 4.69 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.63-4.54 (3H, m, $PhCH_2$), 4.48 (1H, d, *J* = 10.8 Hz, $PhCH_2$), 4.22 (1H, dd, *J* = 5.2, 11.6 Hz, H-6a), 4.20-4.15 (1H, m, H-5), 4.09 (1H, dd, *J* = 1.2, 11.6 Hz, H-6b), 3.92 (1H, br s, H-2´), 3.90-3.82 (2H, m, H-6a´, H-4´), 3.75-3.70 (3H, m, H-3´, H-5´, H-6b´), 3.33 (3H, s, OCH_3), 2.09 (3H, s, $COCH_3$), 2.07 (3H, s, $COCH_3$), 1.98 (3H, s, $COCH_3$), 1.97 (3H, s, $COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.1, 170.0, 169.9, 138.6, 138.5, 128.6, 128.54, 128.53, 128.2, 127.9, 127.80, 127.77, 127.7, 127.6, 99.7, 99.6, 79.8, 76.3, 75.4, 75.0, 73.4, 72.6, 71.8, 69.6, 69.32, 69.28, 69.0, 66.4, 62.8, 55.0, 21.1, 20.95, 20.93, 20.89. HRMS (ESI^+): calc. for $C_{42}H_{50}NaO_{15}$ $[M+Na]^+$ 817.3042, found: 817,3038.



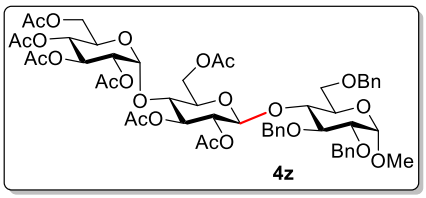
1-Adamantanyl 2,3,4-tri-*O*-acetyl-α-L-arabinopyranoside (4y)



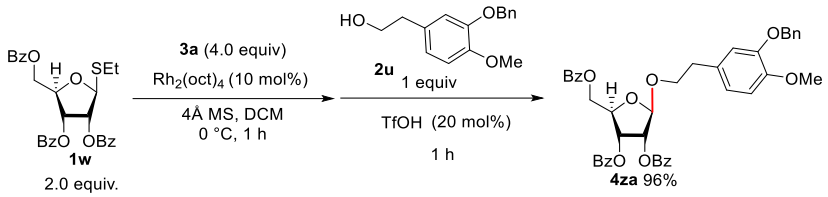
Prepared according to the synthetic procedure of compound **4t.** Colorless syrup. R_f = 0.48 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ +16.64 (c, 2.74 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (1H, br s, H-4), 5.13 (1H, dd, *J* = 7.2, 9.6 Hz, H-2), 5.01 (1H, dd, *J* = 3.2, 9.6 Hz, H-3), 4.66 (1H, d, *J* = 7.2 Hz, H-1), 3.96 (1H, dd, *J* = 2.8, 13.4 Hz, H-5a), 3.58 (1H, dd, *J* = 1.2, 13.4 Hz, H-5b), 2.12-2.10 (3H, m), 2.10 (3H, s, $COCH_3$), 2.03 (3H, s, $COCH_3$), 1.98 (3H, s, $COCH_3$), 1.81-1.78 (3H, m), 1.67-1.50 (9H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.5, 169.6, 94.4, 75.5, 70.9, 69.8, 68.3, 63.6, 42.6, 36.3, 30.8, 21.2, 21.1, 20.9. HRMS (ESI$^+$): calc. for $C_{21}H_{30}NaO_8$ $[M+Na]^+$ 433.1833, found: 433.1869.



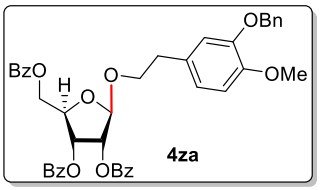
Methyl 2,3,4,6-tetra-*O*-aceyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-aceyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranose (4z)



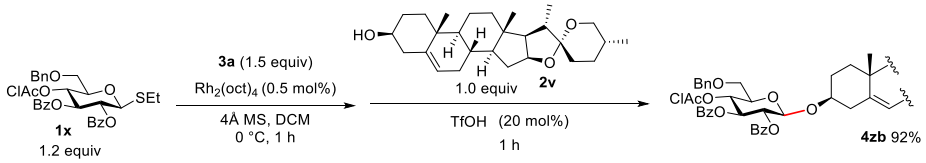
A mixture of donor **1v** (34.9 mg, 0.051 mmol,), acceptor **2a** (19.8 mg, 0.043 mmol), diazo compound **3a** (13.5 mg, 0.064 mmol) and $Rh_2(oct)_4$ (165 μL, c = 2 mg/ml) in CH_2Cl_2 (0.4 mL) in the presence of 4 Å MS (100 wt%) was stirred at 0 °C for 1 h while the yellow color of **3a** was disappeared, then TfOH (0.76 μL, 0.0086 mmol) was added. The resulting mixture was stirred at 0 °C until the reaction was completed, then it was quenched with saturated aqueous $NaHCO_3$, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried with Na_2SO_4, concentrated, and purified by silica gel flash column chromatography to give compound **4z** (45.3 mg, 98%) as a colorless syrup. R_f = 0.24 (petroleum ether-EtOAc 1:1). $[\alpha]_D^{25}$ +42.61 (c, 2.30 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) 7.44-7.21 (15H, m, Ar-CH), 5.36 (1H, dd, *J* = 9.6, 10.4 Hz, H-3''), 5.31 (1H, d, *J* = 4.0 Hz, H-l''), 5.04 (1H, t, *J* = 10.0 Hz, H-4''), 5.00 (1H, t, *J* = 9.2 Hz, H-3'), 4.93 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.84 (1H, dd, *J* = 4.0, 10.4 Hz, H-2''), 4.76 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.72-4.67 (3H, m, $PhCH_2$), 4.54 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.54 (1H, d, *J* = 3.6 Hz, H-1), 4.43 (1H, d, *J* = 8.4 Hz, H-l'), 4.39 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.19 (1H, dd, *J* = 3.2, 12.4 Hz, H-6a''), 4.11 (1H, dd, *J* = 2.8, 12.0 Hz, H-6a'), 4.04 (1H, dd, *J* = 4.0, 12.0 Hz, H-6b'), 3.96 (1H, dd, *J* = 2.0, 12.4 Hz, H-6b''), 3.88-3.83 (1H, m, H-5''), 3.85 (1H, t, *J* = 9.2 Hz, H-4'), 3.83 (1H, t, *J* = 9.2 Hz, H-4), 3.77 (1H, t, *J* = 9.2 Hz, H-3), 3.76 (1H, dd, *J* = 2.0, 11.2 Hz, H-6a), 3.60 (1H, dd, *J* = 1.2, 11.2 Hz, H-6b), 3.58-3.56 (1H, m, H-5), 3.44 (1H, dd, *J* = 3.6, 9.2 Hz, H-2), 3.34 (3H, s, OCH_3), 3.15-3.10 (1H, m, H-5'), 2.08 (3H, s, $COCH_3$), 2.05 (3H, s, $COCH_3$), 2.01 (3H, s, $COCH_3$), 1.99 (3H, s, $COCH_3$), 1.95 (3H, s, $COCH_3$), 1.922 (3H, s, $COCH_3$), 1.920 (3H, s, $COCH_3$). Analytical data for **4z** were essentially the same as reported in the literature[55].



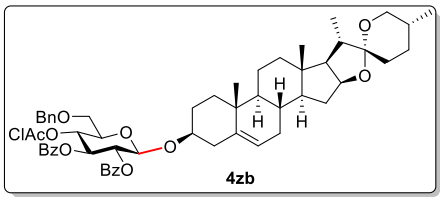
3-Methoxyl-4-benzoxylphenylethyl 2,3,5-tri-*O*-benzyl-β-D-ribofuranoside (4za)



A mixture of donor **1w** (43.3 mg, 0.085 mmol), diazo compound **3a** (36 mg, 0.17 mmol) and $Rh_2(oct)_4$ (3.3 mg, 0.0043 mmol) in CH_2Cl_2 (0.4 mL) in the presence of 4 Å MS (100 wt%) was stirred at 0 °C for 1 h while the yellow color disappeared, then acceptor **2u** (11.0 mg, 0.043 mmol) and TfOH (0.76 μL, 0.0086 mmol) was added. The resulting mixture was stirred at 0 °C until the reaction was completed. It was then quenched with saturated aqueous $NaHCO_3$, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried with Na_2SO_4, concentrated, and purified by silica gel flash column chromatography to give the compound **4za** (28.7 mg, 96%). Colorless syrup. R_f = 0.65 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ +21.14 (c, 1.76 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (2H, dd, *J* = 1.2, 8.4 Hz, Ar-CH), 7.99 (2H, dd, *J* = 0.8, 8.0 Hz, Ar-CH), 7.86 (2H, dd, *J* = 1.2, 8.4 Hz, Ar-CH), 7.57-7.26 (14H, m, Ar-CH), 6.78 (1H, d, *J* = 8.0 Hz, Ar-CH), 7.11-6.69 (2H, m, Ar-CH), 5.81 (1H, dd, *J* = 5.2, 7.2 Hz, H-3), 5.64 (1H, d, *J* = 4.8 Hz, H-2), 5.20 (1H, s, H-1), 5.09 (2H, s, $PhCH_2O$), 4.70-4.66 (1H, m, H-4), 5.57 (1H, dd, *J* = 4.4, 12.0 Hz, H-5a), 4.40 (1H, dd, *J* = 5.2, 12.0 Hz, H-5b), 3.92-3.86 (1H, m, OCH_2), 3.82 (3H, s, OCH_3), 3.60-3.54 (1H, m, OCH_2), 2.72 (2H, t, *J* = 7.2 Hz, $PhCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.6, 165.5, 148.5, 148.3, 137.5, 133.7, 133.6, 133.3, 131.1, 130.01, 129.98, 129.9, 129.5, 129.2, 128.70, 128.68, 128.59, 128.57, 128.0, 127.6, 121.7, 115.2, 112.2, 105.5, 79.0, 75.8, 72.8, 71.2, 69.4, 65.1, 56.3, 35.7. HRMS (ESI^+): calc. for $C_{42}H_{38}NaO_{10}$ $[M+Na]^+$ 725.2357, found: 725.2358.

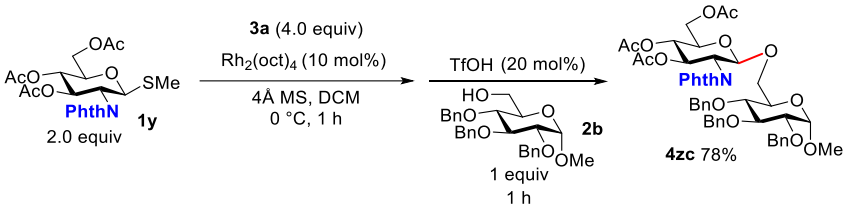


Diosgenyl 2,3-di-*O*-benzoyl-4-*O*-chloroacetyl-6-*O*-benzyl-β-D-glucopyranose (4zb)

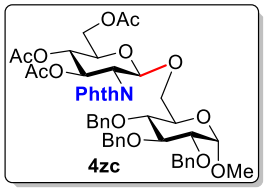


A mixture of donor **1x** (30.3 mg, 0.051 mmol), diazo compound **3a** (13.5 mg, 0.064 mmol) and $Rh_2(oct)_4$ (85 μL, c = 2 mg/ml) in CH_2Cl_2 (0.4 mL) in the presence of 4 Å MS (100 wt%) was stirred at 0 °C for 1 h while the yellow color disappeared, then acceptor **2v** (17.7 mg, 0.043 mmol) and TfOH (0.76 μL, 0.0086 mmol) was added. The resulting mixture was stirred at 0 °C until the reaction was completed. It was then quenched with saturated aqueous $NaHCO_3$, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried with Na_2SO_4, concentrated, and purified by silica gel flash column chromatography to give compound **4zb** (37.4 mg, 92%). Colorless syrup. R_f = 0.67 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{25}$ +11.92 (c, 1.25 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (2H, dd, *J* = 1.2, 8.4 Hz, Ar-H), 7.88 (2H, dd, *J* = 1.2, 8.4 Hz, Ar-H), 7.51-7.46 (2H, m, Ar-H), 7.37-7.26 (9H, m, Ar-H),

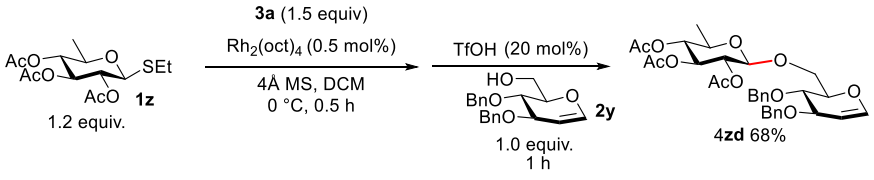
5.63 (1H, t, *J* = 9.6 Hz, H-3), 5.38 (1H, dd, J = 8.0, 9.6 Hz, H-2), 5.34 (1H, t, *J* = 9.6 Hz, H-4), 5.22 (1H, d, *J* = 4.8 Hz), 4.81 (1H, d, *J* = 8.0 Hz, H-1), 4.57 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.48 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.41-4.35 (1H, m), 3.84 (1H, dt, *J* = 10.0, 4.0 Hz), 3.76 (2H, d, *J* = 4.4 Hz), 3.64 (2H, d, *J* = 3.6 Hz), 3.60-3.48 (1H, m), 3.45 (1H, dd, *J* = 3.6, 10.8 Hz), 3.35 (1H, t, *J* = 10.8 Hz), 2.20-0.83 (24H, m), 0.94 (3H, d, *J* = 6.8 Hz, CH_3), 0.90 (3H, s, CH_3), 0.77 (3H, d, *J* = 7.2 Hz, CH_3), 0.74 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.1, 165.3, 140.6, 137.8, 133.6, 133.4, 130.1, 129.9, 129.6, 128.7, 128.6, 128.2, 128.1, 121.9, 109.5, 100.0, 81.0, 80.1, 73.9, 73.3, 73.0, 72.1, 71.7, 69.3, 67.1, 62.3, 56.7, 50.3, 41.8, 40.6, 40.5, 40.0, 39.0, 37.4, 37.0, 32.3, 32.0, 31.6, 30.5, 29.7, 27.0, 21.0, 19.5, 17.4, 16.5, 14.7. HRMS (ESI$^+$): calc. for $C_{56}H_{67}ClNaO_{11}$ $[M+Na]^+$ 973.4264, found: 973.4333.



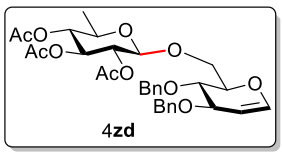
Methyl 6-*O*-(2-N-phthalimido-2-deoxy-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (4zc)



Prepared according to the synthetic procedure of compound **4za**. White Solid. R_f = 0.18 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ +31.00 (c, 0.98 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (4 H, br s, Ar-H), 7.30-7.19 (13H, m, Ar-H), 7.01-6.98 (2H, m, Ar-H), 5.77 (1H, dd, *J* = 8.8, 10.4 Hz, H-2), 5.42 (1H, d, *J* = 8.4 Hz, H-1), 5.16 (1H, t, *J* = 9.2, 10.0 Hz, H-3), 4.83 (1H, d, *J* = 10.8 Hz, $PhCH_2$), 4.70 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.63 (1H, d, *J* = 10.8 Hz, $PhCH_2$), 4.55 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.40-4.34 (3H, m), 4.30 (1H, dd, *J* = 4.4, 12.4 Hz), 4.15 (1H, dd, *J* = 2.4, 12.0 Hz), 4.09-4.05 (2H, m), 3.87-3.83 (1H, m), 3.82 (1H, dd, *J* = 9.2 Hz), 3.64 (2H, dd, *J* = 4.0, 12.8 Hz), 3.36 (1H, dd, *J* = 4.4, 10.0 Hz), 3.21 (1H, t, *J* = 9.2 Hz), 3.15 (3H, s, OCH_3), 2.07 (3H, s, $COCH_3$), 2.01 (3H, s, $COCH_3$), 1.83 (3H, s, $COCH_3$). Analytical data for **4zc** were essentially the same as reported in the literature[49]

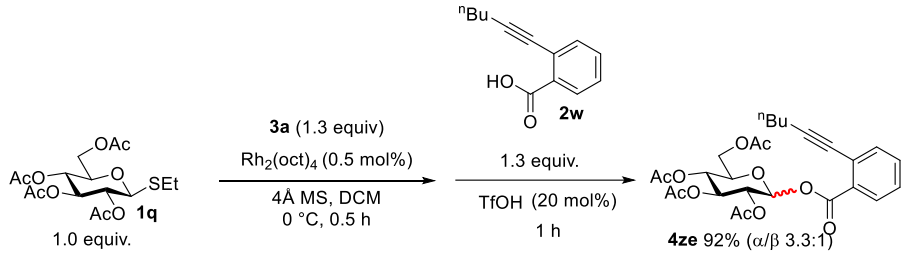


3,4-di-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-acetyl-6-deoxy-β-D-glucopyranosyl)-2-deoxy-D-*arabino*-hex-1-enitol (4zd)

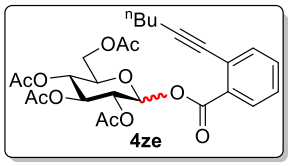


Prepared according to the synthetic precedure of compound **4zb**. Colorless syrup. R_f = 0.38 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{25}$ +26.79 (c, 0.78 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.24 (10H, m, Ar-H), 6.05 (1H, d, *J* = 10.4 Hz, H-1'), 5.79-5.76 (1H, m, H-2'), 5.14 (1H, t, *J* = 9.2 Hz, H-4), 5.07 (1H, d, *J* = 2.4 Hz, H-3'), 5.04 (1H, dd, *J* = 8.0, 9.6 Hz, H-2), 4.82 (1H, t, *J* = 9.6 Hz, H-3), 4.78 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.63 (1H, d, *J* = 11.2 Hz, $PhCH_2$),

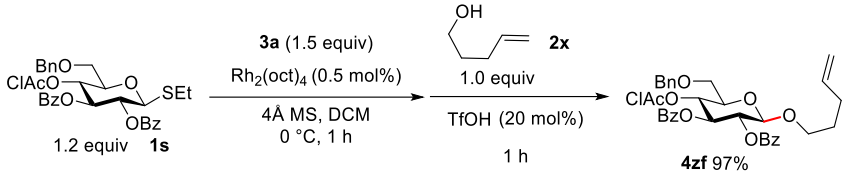
4.54 (1H, d, *J* = 12.0 Hz, $PhCH_2$), 4.53 (1H, d, *J* = 8.0 Hz, H-1), 4.47 (1H, d, *J* = 11.6 Hz, $PhCH_2$), 4.06-3.98 (3H, m, H-4', H-5', H-6a'), 3.72 (1H, dd, *J* = 4.8, 11.2 Hz, H-6b'), 3.58-3.51 (1H, m, H-5), 2.02 (3H, s, $COCH_3$), 1.98 (3H, s, $COCH_3$), 1.91 (3H, s, $COCH_3$), 1.23 (3H, d, *J* = 6.4 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.9, 169.4, 138.23, 138.20, 130.6, 128.7, 128.6, 128.2, 128.1, 127.8, 127.0, 100.9, 93.9, 73.6, 73.2, 71.9, 71.0, 70.7, 70.3, 70.2, 69.2, 68.8, 20.93, 20.89, 17.6. HRMS (ESI^+): calc. for $C_{32}H_{38}NaO_{11}$ $[M+Na]^+$ 621.2306, found: 621.2379.



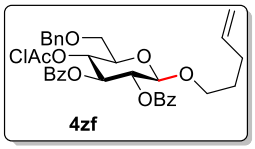
2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl ortho-hexynylbenzoate (4ze)



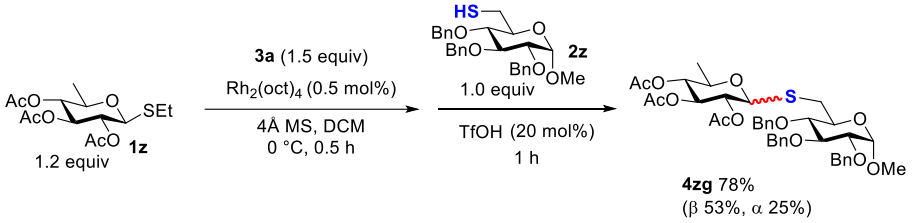
Reaction mixture of donor **1q** (16.8 mg, 0.043 mmol), diazo compound **3a** (11.7 mg, 0.056 mmol) and $Rh_2(oct)_4$ (85 µL, c = 2 mg/ml) in CH_2Cl_2 (0.4 mL) in the presence of 4 Å MS (100 wt%) was stirred at 0 °C for 30 min while the yellow color disappeared, then acceptor **2w** (11.2 mg, 0.056 mmol) and TfOH (0.76µL, 0.0086 mmol) was added. The resulting mixture was stirred at 0 °C until the reaction was completed. It was then quenched with saturated aqueous $NaHCO_3$, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried with Na_2SO_4, concentrated, and purified by silica gel flash column chromatography to give the compound **4ze** (α: 16.0 mg, 71%; β: 4.8 mg, 21%). For α-isomer: colorless syrup. R_f = 0.47 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ +122.39 (c, 0.94 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (1H, dd, *J* = 0.8, 7.6 Hz, Ar-H), 7.56 (1H, dd, *J* = 3.2, 8.0 Hz, Ar-H), 7.48 (1H, td, *J* = 7.6, 1.2 Hz, Ar-H), 7.36 (1H, td, *J* = 7.6, 1.2 Hz, Ar-H), 6.60 (1H, d, *J* = 3.6 Hz, H-1), 5.58 (1H, t, *J* =10.0 Hz, H-4), 5.21-5.16 (2H, m, H-2, H-3), 4.32-4.27 (2H, m, H-5, H-6a), 4.11-4.06 (1H, m, H-6b), 2.58-2.44 (2H, m), 2.07 (3H, s, $COCH_3$), 2.02 (3H, s, $COCH_3$), 2.01 (3H, s, $COCH_3$), 2.98 (3H, s, $COCH_3$), 1.65-1.58 (2H, m), 1.52-1.43 (2H, m), 0.93 (3H, t, *J* = 7.2 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.4, 170.0, 169.6, 164.2, 135.4, 132.7, 131.0, 130.0, 127.6, 125.5, 97.4, 90.1, 79.9, 70.4, 70.3, 69.6, 68.2, 61.6, 31.0, 22.3, 20.92, 20.90, 20.8, 20.7, 19.8, 13.9. For β-isomer: colorless syrup. R_f = 0.43 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ -17.36 (c, 0.35 in $CHCl_3$).^1H NMR (600 MHz, $CDCl_3$) δ 7.92 (1H, dd, *J* = 1.2, 7.8 Hz, Ar-H), 7.51 (1H, dd, *J* = 1.2, 7.2 Hz, Ar-H), 7.45 (1H, td, *J* = 7.2, 1.2 Hz, Ar-H), 7.30 (1H, td, *J* = 7.8, 1.2 Hz, Ar-H), 5.97-5.93 (1H, m, H-1), 5.33-5.28 (2H, m, H-2, H-4), 5.18-5.16 (1H, m, H-3), 4.31 (1H, dd, *J* = 4.2, 12.6 Hz, H-6a), 4.11 (1H, dd, *J* = 2.4, 12.6 Hz, H-6b), 3.92-3.90 (1H, m, H-5), 2.48 (2H, t, *J* = 7.2 Hz), 2.06 (3H, s, $COCH_3$), 2.03 (3H, s, $COCH_3$), 2.02 (3H, s, $COCH_3$), 1.97 (3H, s, $COCH_3$), 1.64-1.59 (2H, m), 1.52-1.46 (2H, m), 0.94 (3H, t, *J* = 7.2 Hz, CH_3). Analytical data for **4ze** were essentially the same as reported in the literature.[56]



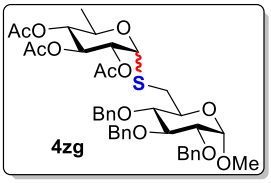
4-Pentenyl 2,3-di-*O*-benzyl-4-chloroacetyl-6-*O*-benzyl-β-D-glucopyranose (4zf)



Prepared according to the synthesis of compound **4zb**. Colorless syrup. R_f = 0.59 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{25}$ +51.78 (c, 0.73 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (2H, dd, J = 1.8, 8.4 Hz, Ar-H), 7.88 (2H, dd, J = 1.2, 8.4 Hz, Ar-H), 7.50-7.46 (2H, m, Ar-H), 7.37-7.27 (9H, m, Ar-H), 5.67-5.60 (1H, m, =CH), 5.64 (1H, t, J = 9.6 Hz, H-4), 5.41 (1H, dd, J = 8.4, 9.6 Hz, H-2), 5.37 (1H, t, J = 9.6 Hz, H-3), 4.83-4.79 (2H, m, =CH_2), 4.67 (1H, d, J = 7.8 Hz, H-1), 4.58 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.50 (1H, d, J = 12.0 Hz, $PhCH_2$), 3.92-3.88 (1H, m, OCH_2), 3.85-3.82 (1H, m, OCH_2), 3.77 (1H, d, J = 14.4 Hz, ClAcO-), 3.74 (1H, d, J = 14.4 Hz, ClAcO-), 3.67 (1H, dd, J = 4.2, 10.8 Hz, H-6a), 3.64 (1H, dd, J = 4.2, 10.2 Hz, H-6b), 3.52-3.48 (1H, m, H-5), 2.01-1.91 (2H, m), 1.66-1.55 (2H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 166.1, 165.2, 138.0, 137.7, 133.6, 133.4, 130.1, 130.0, 129.5, 129.0, 128.67, 128.66, 128.6, 128.2, 128.1, 115.1, 101.3, 73.9, 73.3, 73.1, 72.0, 71.6, 69.6, 69.0, 40.6, 30.0, 28.8. HRMS (ESI$^+$): calc. for $C_{34}H_{35}ClNaO_9$ $[M+Na]^+$ 645.1862, found: 645.1851.

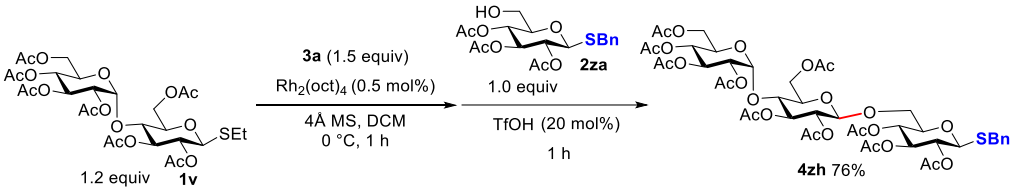


Methyl 2,3,4-tri-*O*-benzyl-6-*S*-(2,3,4-tri-*O*-aceyl-6-deoxy-D-glucopyranosyl)-α-D-gluco-Pyranose (4zg)

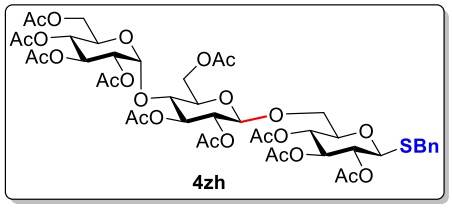


Prepared according to the synthesis of compound **4zb**. For β-isomer: Colorless syrup. R_f = 0.39 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ +2.44 (c, 0.82 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (15H, m, Ar-H), 5.11 (1H, t, J = 9.6 Hz), 4.96 (1H, d, J = 10.8 Hz, $PhCH_2$), 4.91 (1H, t, J = 9.6 Hz), 4.89 (1H, d, J = 11.2 Hz, $PhCH_2$), 4.78 (1H, d, J = 9.6 Hz, H-1), 4.77 (1H, t, J = 9.6 Hz), 4.76 (1H, d, J = 12.4 Hz, $PhCH_2$), 4.64 (1H, d, J = 11.6 Hz, $PhCH_2$), 4.61 (1H, d, J = 10.4 Hz, $PhCH_2$), 4.53-4.49 (2H, m, H-1´, $PhCH_2$), 3.94 (1H, t, J = 9.2 Hz), 3.80 (1H, td, J = 9.2, 2.4 Hz), 3.49-3.42 (2H, m), 3.37 (3H, s, OCH_3), 3.31 (1H, t, J = 9.2 Hz), 2.99 (1H, dd, J = 2.4, 13.2 Hz, H-6a´), 2.66 (1H, dd, J = 4.0, 13.2 Hz, H-6b´), 2.01 (3H, s, $COCH_3$), 1.98 (6H, s, $COCH_3$), 1.14 (3H, d, J = 6.4 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.9, 169.5, 138.9, 138.34, 138.27, 128.7, 128.6, 128.3, 128.21, 128.19, 128.1, 127.9, 98.0, 83.4, 82.1, 80.8, 80.1, 76.0, 75.3, 74.4, 74.1, 73.54, 73.48, 71.0, 70.7, 55.4, 31.4, 20.9, 17.7. HRMS (ESI$^+$): calc. for $C_{40}H_{48}NaO_{12}S$ $[M+Na]^+$ 775.2759, found: 775.2791. For α-isomer: colorless syrup. R_f = 0.42 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ +92.39 (c, 0.46 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.24 (15H, m, Ar-H), 5.64 (1H, d, J = 6.0 Hz, H-1), 5.29 (1H, t, J = 9.6 Hz), 4.99-4.93 (2H, m), 4.88 (1H, d, J = 11.2 Hz, $PhCH_2$), 4.79-4.72 (3H, m),

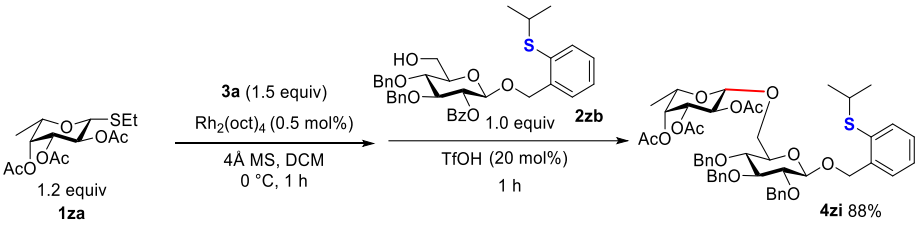
4.65 (1H, d, *J* = 12.4 Hz, $PhCH_2$), 4.57 (1H, d, *J* = 10.8 Hz, $PhCH_2$), 4.54 (1H, d, *J* = 3.6 Hz, H-1´), 4.24-4.17 (1H, m), 3.95 (1H, t, *J* = 9.2 Hz), 3.80-3.76 (1H, m), 3.46 (1H, dd, *J* = 3.2, 9.6 Hz), 3.89 (1H, t, *J* = 9.6 Hz), 3.35 (3H, s, OCH_3), 2.91 (1H, dd, *J* = 2.4, 14.0 Hz, H-6a´), 2.58 (1H, dd, *J* = 3.2, 14.0 Hz, H-6b´), 2.01 (3H, s, $COCH_3$), 1.98 (3H, s, $COCH_3$), 1.97 (3H, s, $COCH_3$), 1.11 (3H, d, *J* = 6.4 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 170.1, 170.0, 138.9, 138.24, 138.21, 128.70, 128.69, 128.6, 128.3, 128.2, 128.1, 127.9, 98.0, 82.1, 82.0, 80.4, 80.2, 75.9, 75.4, 74.0, 73.5, 71.3, 70.6, 69.8, 65.8, 55.4, 31.2, 21.0, 20.9, 17.4. HRMS (ESI^+): calc. for $C_{40}H_{48}NaO_{12}S$ $[M+Na]^+$ 775.2759, found: 775.2827.



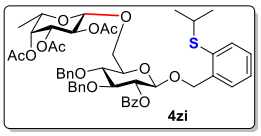
benzyl 2,3,4,6-tetra-*O*-aceyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-aceyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-aceyl-1-thoi-β-D-glucopyranose(4zh)



Prepared according to the synthesis of compound **4zb**. Colorless syrup. R_f = 0.24 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ -4.41 (c, 1.45 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) 7.31-7.24 (5H, m, Ar-CH), 5.38 (1H, d, *J* = 4.0 Hz, H-1''), 5.31 (1H, dd, *J* = 9.6, 10.4 Hz), 5.23 (1H, t, *J* = 9.2 Hz), 5.09 (1H, t, *J* = 9.2 Hz), 5.03 (1H, t, *J* = 10.0 Hz), 5.00 (1H, t, *J* = 9.6 Hz), 4.88 (1H, t, *J* = 9.6 Hz), 4.84 (1H, dd, *J* = 8.0, 9.6 Hz), 4.83 (1H, dd, *J* = 4.4, 10.8 Hz), 4.55 (1H, d, *J* = 8.0 Hz, H-1'), 4.47 (1H, dd, *J* = 2.4, 12.0 Hz), 4.25-4.19 (3H, m), 4.03 (1H, dd, *J* = 2.0, 12.4 Hz), 3.98 (1H, t, *J* = 9.2 Hz), 3.96-3.91 (1H, m), 3.89 (1H, d, *J* = 13.2 Hz, $PhCH_2$), 3.84 (1H, d, *J* = 9.2 Hz, H-1), 3.77 (1H, d, *J* = 13.2 Hz, $PhCH_2$), 3.66-3.62(1H, m), 3.59-3.52 (2H, m), 2.12 (3H, s, $COCH_3$), 2.08 (3H, s, $COCH_3$), 2.02 (3H, s, $COCH_3$), 2.01 (3H, s, $COCH_3$), 2.00 (3H, s, $COCH_3$), 1.98 (3H, s, $COCH_3$), 1.972 (3H, s, $COCH_3$), 1.966 (3H, s, $COCH_3$), 1.96 (3H, s, $COCH_3$), 1.95 (3H, s, $COCH_3$). ^{13}C NMR (100 MHz, CDCl3) δ 170.8, 170.6, 170.38, 170.35, 170.2, 167.0, 169.8, 169.7, 169.6, 137.0, 129.3, 128.8, 127.6, 100.5, 95.8, 81.8, 75.6, 74.0, 72.9, 72.5, 72.2, 70.2, 70.0, 69.5, 69.2, 68.7, 68.2, 62.8, 61.7, 33.7, 21.10, 21.06, 20.91, 20.87, 20.8. HRMS (ESI^+): calc. for $C_{45}H_{58}NaO_{25}S$ $[M+Na]^+$ 1053.2880, found: 1053.2989.

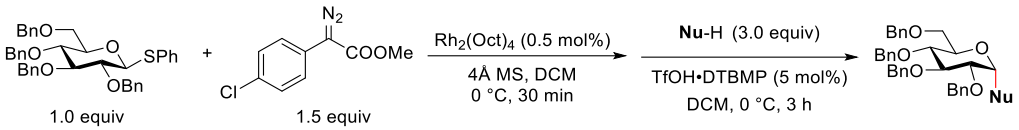


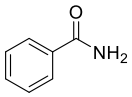
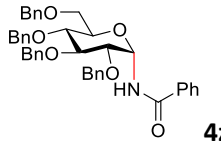
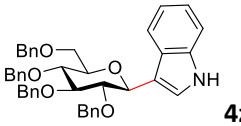
2-Isopropylmercaptobenzyl 2-*O*-benzyl-3,4-di-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-β-L-fucopyranosyl)-β-D-glucopyranose(4zi)

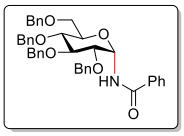


Prepared according to the synthesis of compound **4zb**. Colorless syrup. R_f = 0.17 (petroleum ether-EtOAc 4:1). $[\alpha]_D^{25}$ +15.09 (c, 2.14 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (2H, d, J = 7.2 Hz, Ar-H), 7.69 (1H, t, J = 3.6 Hz, Ar-H), 7.55 (2H, t, J = 8.0 Hz, Ar-H), 7.47-7.39 (9H, m, Ar-H), 7.29 (1H, td, J = 7.6, 0.8 Hz, Ar-H), 7.26 (3H, m, Ar-H), 7.17 (1H, t, J = 7.6 Hz, Ar-H), 5.43-5.35 (3H, m), 5.16 (1H, dd, J = 3.2, 10.4 Hz), 5.06 (1H, d, J = 13.2 Hz, $PhCH_2$), 4.97 (1H, d, J = 13.2 Hz, $PhCH_2$), 4.93 (1H, d, J = 10.8 Hz, $PhCH_2$), 4.87 (1H, d, J = 11.2 Hz, $PhCH_2$), 4.84 (1H, d, J = 9.6 Hz, $PhCH_2$), 4.81 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.78 (1H, d, J = 8.4 Hz, H-1), 4.68 (1H, d, J = 8.4 Hz, H-1´), 4.32 (1H, dd, J = 2.4, 12.4 Hz), 4.04 (1H, d, J = 11.2 Hz), 3.95-3.85 (3H, m), 3.57-3.55 (1H, m), 3.37 (1H, m, C<u>H</u>$(CH_3)_2$), 2.32 (3H, s, $COCH_3$), 2.29 (3H, s, $COCH_3$), 2.13 (3H, s, $COCH_3$), 1.35 (3H, d, J = 6.4 Hz), 1.31 (3H, d, J = 6.8 Hz), 1.30 (3H, d, J = 6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.4, 170.1, 165.4, 139.1, 138.3, 138.1, 134.1, 133.2, 132.2, 130.2, 130.0, 128.6, 128.53, 128.48, 128.39, 128.38, 128.04, 128.00, 127.98, 127.7, 127.1, 101.7, 100.4, 82.4, 75.4, 75.3, 75.0, 73.8, 71.6, 70.5, 69.3, 69.2, 68.7, 66.9, 38.6, 23.23, 23.20, 21.3, 20.93, 20.86, 16.3. HRMS (ESI$^+$): calc. for $C_{49}H_{56}NaO_{14}S$ $[M+Na]^+$ 923.3283, found: 923.3341.

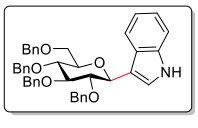
5.3 Preliminary results on glycosylation reactions with benzamide and indols



entry	**Nu**-H	Glycosylation product	Yield
1	 benzamide	 **4zl**	41% (α)
2	 indole	 **4zm**	31% (β)



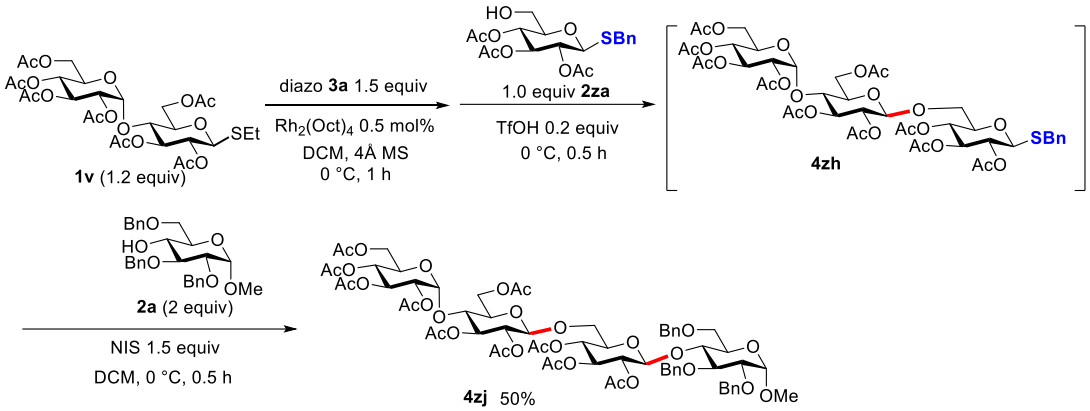
Prepared according to **Procedure B**. Colorless syrup. R_f = 0.56 (petroleum ether-EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (2H, d, J = 7.6 Hz, Ar-H), 7.51 (1H, t, J = 7.2 Hz, Ar-H), 7.42 (2H, t, J = 7.2 Hz, Ar-H), 7.33-7.22 (18H, m, Ar-H), 7.13-7.11 (2H, m, Ar-H), 6.76 (1H, d, J = 6.4 Hz, NH), 5.94 (1H, t, J = 5.2 Hz, H-1), 4.93 (1H, d, J = 10.8 Hz, $PhCH_2$), 4.79 (2H, t, J = 10.2 Hz, CH_2), 4.64-4.59 (3H, m, $PhCH_2$), 4.52 (1H, d, J = 10.8 Hz, $PhCH_2$), 4.46 (1H, d, J = 12.0 Hz, $PhCH_2$), 3.90 (1H, dd, J = 5.4 Hz, J = 9.0 Hz, H-2), 3.81-3.66 (5H, m, H-5, H-3, H-4, H-6). Analytical data for **4zl** were essentially the same as reported in the literature[57].

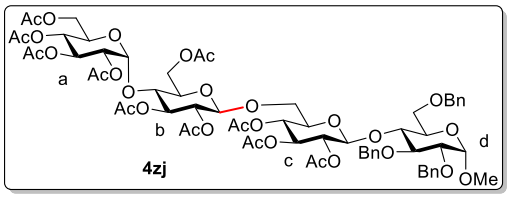


Prepared according to **Procedure B**. Colorless syrup. R_f = 0.20 (petroleum ether-EtOAc 7:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (1H, s), 7.90 (1H, d, J = 7.6 Hz), 7.64 (1H, s), 7.36-7.19 (20H, m), 7.10-7.04 (3H, m), 5.72 (1H,

d, *J* = 5.6 Hz), 5.05 (1H, d, *J* = 10.8 Hz), 4.84 (1H, d, *J* = 10.8 Hz), 4.79 (1H, d, *J* = 10.8 Hz), 4.71 (1H, d, *J* = 11.6 Hz), 4.68 (1H, d, *J* = 12.8 Hz), 4.65 (1H, d, *J* = 12.0 Hz), 4.44 (1H, d, *J* = 10.8 Hz), 4.41 (1H, d, *J* = 12.4 Hz), 4.20 (1H, t, *J* = 9.2 Hz), 4.10 (1H, dd, *J* = 5.6, 9.6 Hz), 3.79 (1H, t, *J* = 9.6 Hz), 3.64 (1H, dd, *J* = 2.8, 10.8 Hz), 3.56 (1H, dd, *J* = 1.6, 10.4 Hz), 3.37-3.34 (1H, m). Analytical data for **4zm** were essentially the same as reported in the literature[58].

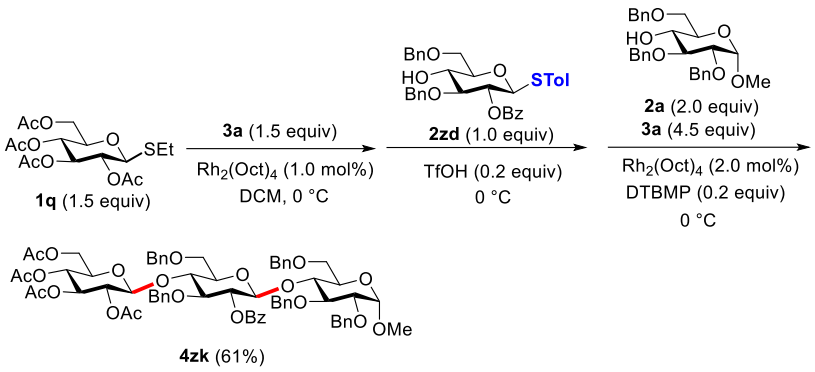
6. Results on one-pot sequentional glycosyaltions

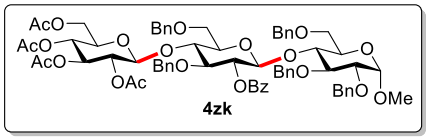




A mixture of donor **1v** (34.9 mg, 0.051 mmol), diazo compound **3a** (13.5 mg, 0.064 mmol) and $Rh_2(oct)_4$ (33 μL, c = 5 mg/ml) in CH_2Cl_2 (0.4 mL) in the presence of 4 Å MS (100 wt%) was stirred at 0 °C for 1 h, then acceptor **2za** (17.6 mg, 0.043 mmol) and TfOH (0.76 μL, 0.0085 mmol) was added. The resulting mixture was stirred at 0 °C until **2za** was disappeared. Then **2a** (39.7 mg, 0.085 mmol), NIS (14.4 mg, 0.064 mmol) were added to the reaction mixture. After the reaction was completed, it was quenched with saturated aqueous $NaHCO_3$, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried with Na_2SO_4, concentrated, and purified by silica gel flash column chromatography to give the compound **4zj** (50%). Colorless syrup. R_f = 0.53 (petroleum ether-EtOAc 1:1). $[\alpha]_D^{25}$ +24.38 (c, 0.80 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.22 (15H, m, Ar-CH), 5.38 (1H, t, *J* = 10.0 Hz, H-3a), 5.28 (1H, d, *J* = 4.0 Hz, H-1a), 5.09 (1H, t, *J* = 9.2 Hz, H-3b), 5.03 (1H, t, *J* = 9.2 Hz, H-4a), 4.94 (1H, t, *J* = 9.2 Hz, H-3c), 4.93 (2H, d, *J* = 11.2 Hz, PhC$\underline{H}_2$, PhC$\underline{H}_2$), 4.87 (1H, t, *J* = 8.8 Hz, H-2c), 4.82-4.77 (2H, m, H-2a, H-4c), 4.74-4.66 (4H, m, PhC$\underline{H}_2$, PhC$\underline{H}_2$, PhC$\underline{H}_2$, H-2b), 4.55 (1H, d, *J* = 4.4 Hz, H-1d), 4.54 (1H, d, *J* = 7.2 Hz, H-1b), 4.45 (1H, d, *J* = 7.6 Hz, H-1c), 4.39 (1H, d, *J* = 11.6 Hz, PhC$\underline{H}_2$), 4.20 (1H, dd, *J* = 2.8, 12.4 Hz, H-6a$_1$), 4.11 (1H, dd, *J* = 2.4, 12.8 Hz, H-6d$_1$), 4.00 (1H, dd, *J* = 1.6, 12.4 Hz, H-6a$_2$), 3.93 (1H, d, *J* = 13.2 Hz, H-6b$_1$), 3.83-3.72 (5H, m, H-5a, H-6d$_2$, H-4d, H-3d, H-4b), 3.69 (1H, dd, *J* = 3.6, 9.6 Hz, H-2d), 3.61-3.56 (3H, m, H-5b, H-6b$_2$, H-6c$_1$), 3.43 (1H, dd, *J* = 8.4, 11.6 Hz, H-6c$_2$), 3.38-3.34 (1H, m, H-5c), 3.27 (3H, s, OMe), 2.38 (1H, d, *J* = 10.0 Hz, H-5d), 2.08 (3H, s, $COCH_3$), 2.06 (3H, s, $COCH_3$), 2.01 (3H, s, $COCH_3$), 2.00 (3H, s, $COCH_3$), 1.98 (9H, s, $COCH_3$), 1.95 (3H, s, $COCH_3$), 1.93 (3H, s, $COCH_3$), 1.78 (3H, s, $COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.7, 170.65, 170.4, 170.2, 170.1, 169.8, 169.7, 169.3, 140.0, 139.0, 137.3, 129.1, 128.7, 128.65, 128.6, 128.5, 128.1, 128.0, 127.7, 100.0, 99.6, 98.6, 95.9, 81.3, 80.2, 76.3, 76.2, 75.6, 73.9, 73.8, 73.6, 73.5, 72.6, 72.3, 70.9, 70.2, 69.56, 69.54, 69.4,

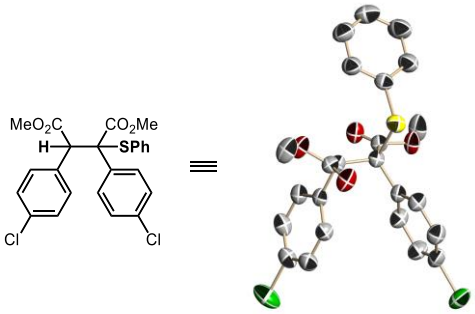
68.7, 68.3, 67.7, 67.3, 62.6, 61.6, 55.5, 21.2, 21.1, 21.0, 20.9, 20.83, 20.80, 20.5. HRMS (ESI$^+$): calc. for $C_{66}H_{82}NaO_{31}$ $[M+Na]^+$ 1393.4732, found: 1393.4731.





A mixture of donor **1q** (20.6 mg, 0.053 mmol), diazo compound **3a** (11.1 mg, 0.053 mmol) and $Rh_2(oct)_4$ (55 μL, c = 5 mg/ml) in CH_2Cl_2 (0.4 mL) in the presence of 4 Å MS (100 wt%) was stirred at 0 °C for 30 min, then acceptor **2zd** (11.2 mg, 0.035 mmol) and TfOH (0.62 μL, 0.007 mmol) was added. The resulting mixture was stirred at 0 °C until **2zd**[59] was disappeared. Then DTBMP (1.4 mg, 0.007 mmol), **2a** (32.5 mg, 0.07 mmol), **3a** (33.2 mg, 0.16 mmol) and $Rh_2(oct)_4$ (109 μL, c = 5 mg/ml) in CH_2Cl_2 (0.4 mL) were added. After the reaction was completed, it was quenched with saturated aqueous $NaHCO_3$, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried with Na_2SO_4, concentrated, and purified by silica gel flash column chromatography to give the compound **4zk** (61%). White foam. R_f = 0.36 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{25}$ +5.93 (c, 2.14 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.83 (2H, d, J = 8.0 Hz, Ar-H), 7.55 (1H, t, J = 7.2 Hz, Ar-H), 7.41-7.15 (22H, m, Ar-H), 7.07-6.99 (5H, m, Ar-H), 5.14 (1H, t, J = 8.8 Hz), 5.07 (1H, d, J = 11.6 Hz, $PhCH_2$), 5.04-4.93 (3H, m), 4.81 (2H, t, J = 12.8 Hz, $PhCH_2$), 4.71 (1H, d, J = 12.4 Hz, $PhCH_2$), 4.58 (1H, d, J = 12.4 Hz, $PhCH_2$), 4.57 (1H, d, J = 11.6 Hz, $PhCH_2$), 4.54 (1H, d, J = 7.6 Hz, H-1″), 4.53 (1H, d, J = 12.4 Hz, $PhCH_2$), 4.52 (1H, d, J = 3.6 Hz, H-1), 4.50 (1H, d, J = 7.2 Hz, H-1′), 4.48 (1H, d, J = 11.2 Hz, $PhCH_2$), 4.27 (1H, d, J = 12.0 Hz, $PhCH_2$), 4.20 (1H, d, J = 12.4 Hz, $PhCH_2$), 4.12 (1H, dd, J = 4.0, 12.4 Hz), 4.05 (1H, t, J = 9.2 Hz), 3.91-3.75 (3H, m), 3.60-3.55 (2H, m), 3.52 (1H, dd, J = 3.2, 11.2 Hz), 3.48-3.39 (3H, m), 3.35 (1H, d, J = 10.0 Hz), 3.32-3.27 (1H, m), 3.25 (3H, s, OMe), 3.13-3.08 (1H, m), 1.99 (6H, s, $COCH_3$), 1.97 (3H, s, $COCH_3$), 1.93 (3H, s, $COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.4, 169.6, 169.3, 165.0, 139.9, 138.6, 138.5, 138.2, 138.1, 133.2, 130.0, 129.9, 128.8, 128.5, 128.4, 128.3, 128.26, 128.13, 128.10, 127.9, 127.86, 127.4, 127.1, 100.8, 100.1, 98.4, 80.5, 80.4, 79.2, 75.2, 74.6, 73.7, 73.68, 73.62, 73.57, 73.2, 71.9, 71.7, 69.7, 68.4, 68.1, 67.6, 61.8, 55.4, 20.9, 20.8, 20.79, 20.76. HRMS (ESI$^+$): calc. for $C_{69}H_{76}NaO_{21}$ $[M+Na]^+$ 1263.4771, found: 1263.4760.

6. Crystal data and structure refinement for compound 8



Chemical formula	$C_{24}H_{20}Cl_2O_4S$	
Formula weight	475.36 g/mol	
Temperature	206(2) K	
Wavelength	1.54178 Å	
Crystal size	0.100 x 0.120 x 0.150 mm	
Crystal habit	clear light colourless block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.3310(14) Å	α = 95.499(5)°
	b = 11.3580(19) Å	β = 103.944(5)°
	c = 12.437(2) Å	γ = 90.227(5)°
Volume	1136.5(3) $Å^3$	
Z	2	
Density (calculated)	1.389 g/cm^3	
Absorption coefficient	3.667 mm^{-1}	
F(000)	492	
Diffractometer	d8 venture	
Theta range for data collection	3.91 to 74.57°	
Index ranges	-10<=h<=10, -13<=k<=14, -15<=l<=15	
Reflections collected	24304	
Independent reflections	4448 [R(int) = 0.0470]	
Coverage of independent reflections	95.4%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7110 and 0.6090	

Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	4448 / 0 / 282	
Goodness-of-fit on F2	1.264	
Δ/σmax	0.001	
Final R indices	3530 data; I>2σ(I)	R1 = 0.0436, wR2 = 0.1251
	all data	R1 = 0.1173, wR2 = 0.1637
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0735P)^2+0.3830P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.769 and -0.708 eÅ^{-3}	
R.M.S. deviation from mean	0.097 eÅ^{-3}	

7. Copies of NMR Spectra

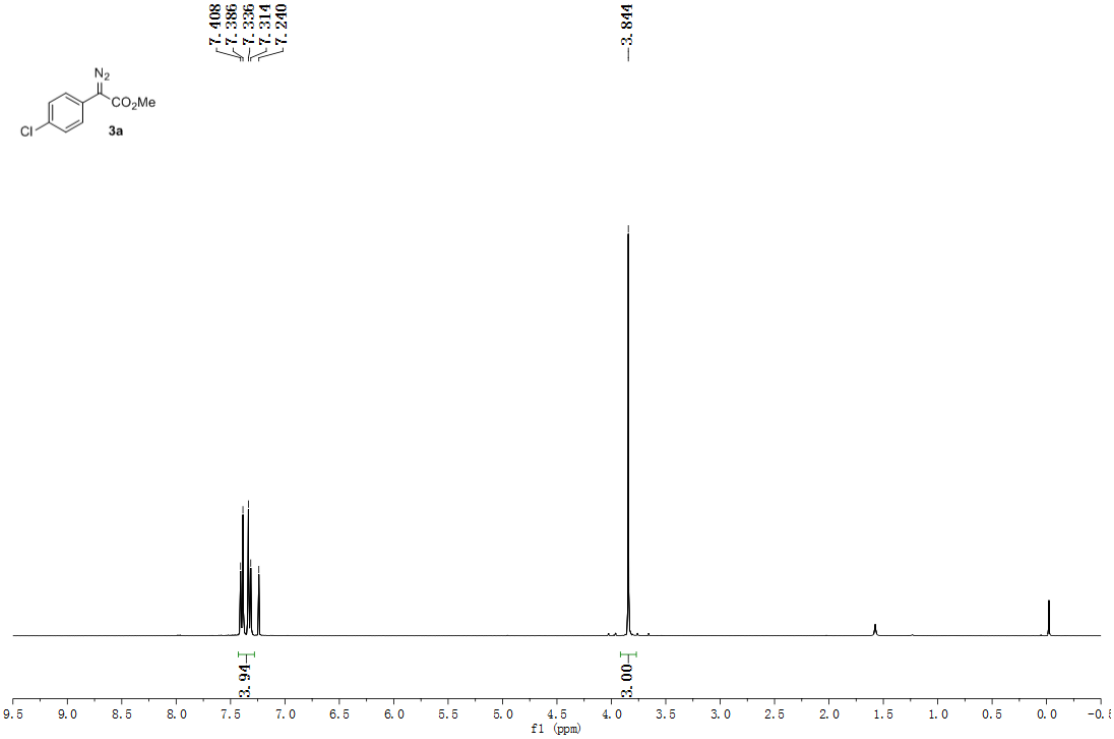


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**

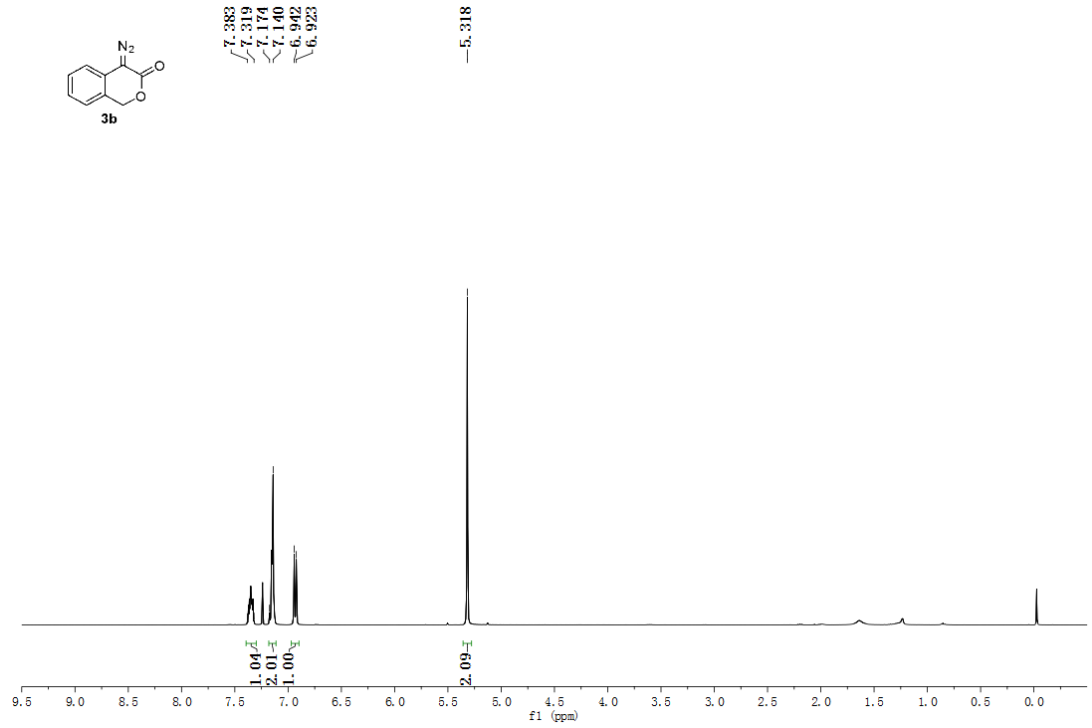


Figure S2. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3b**

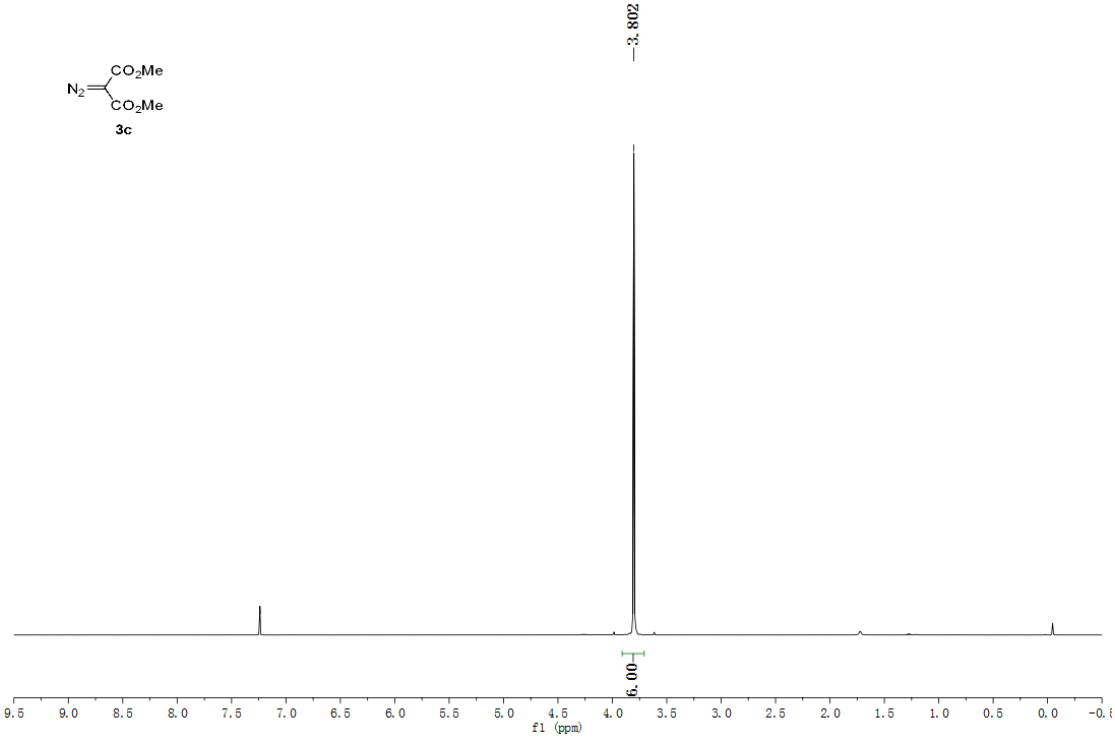


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**

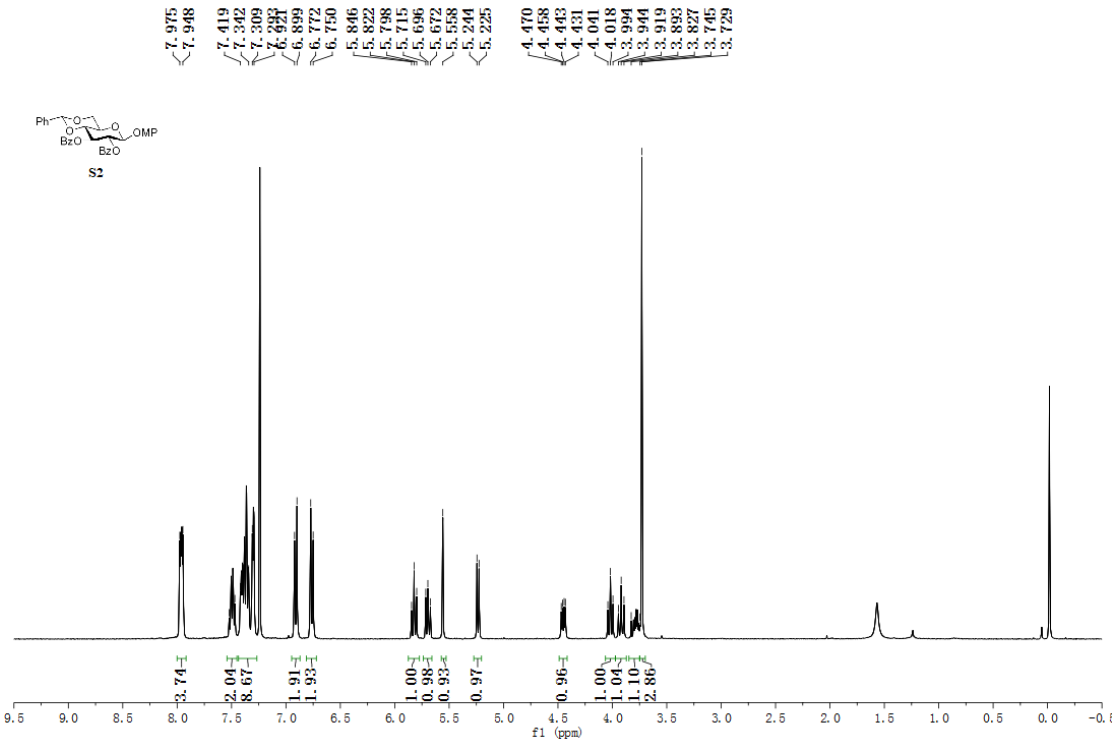


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S2**

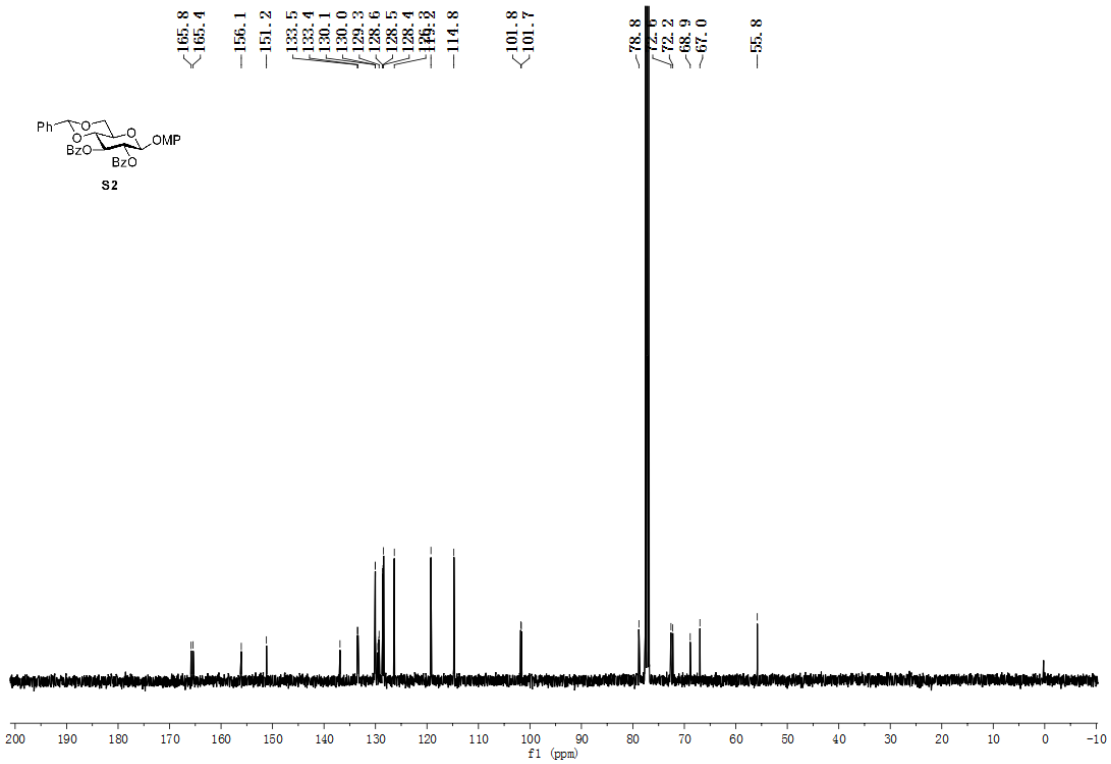


Figure S5. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **S2**

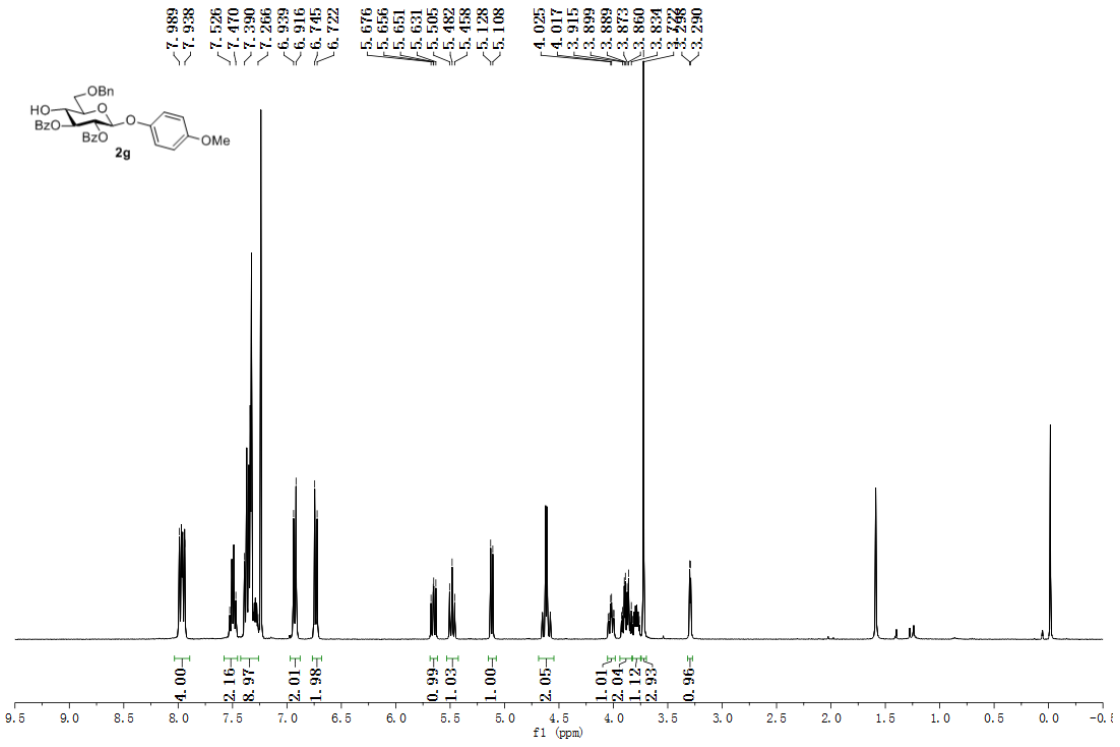


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2g**

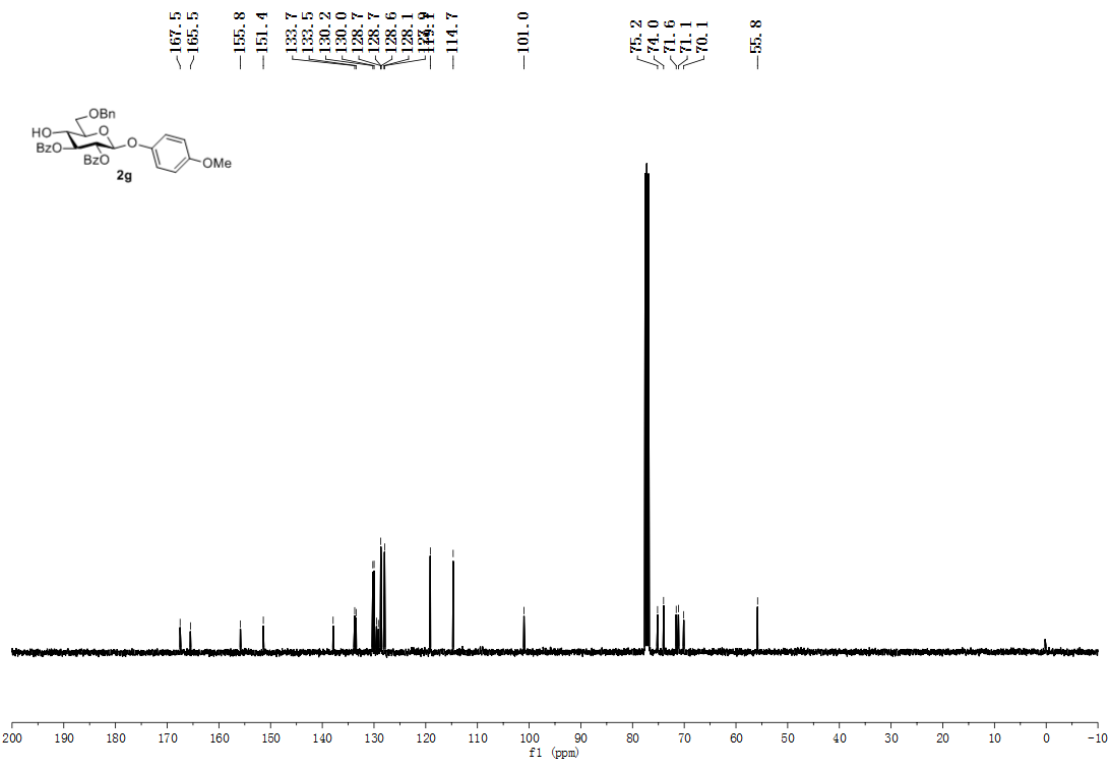


Figure S7. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2g**

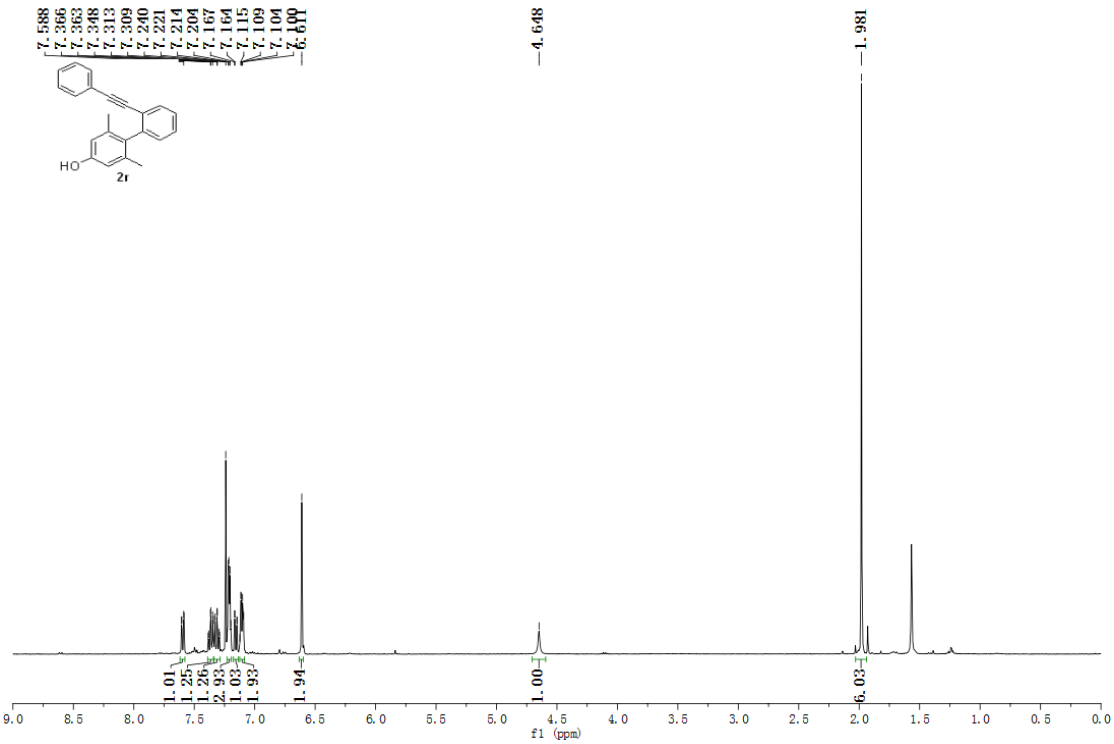


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2r**

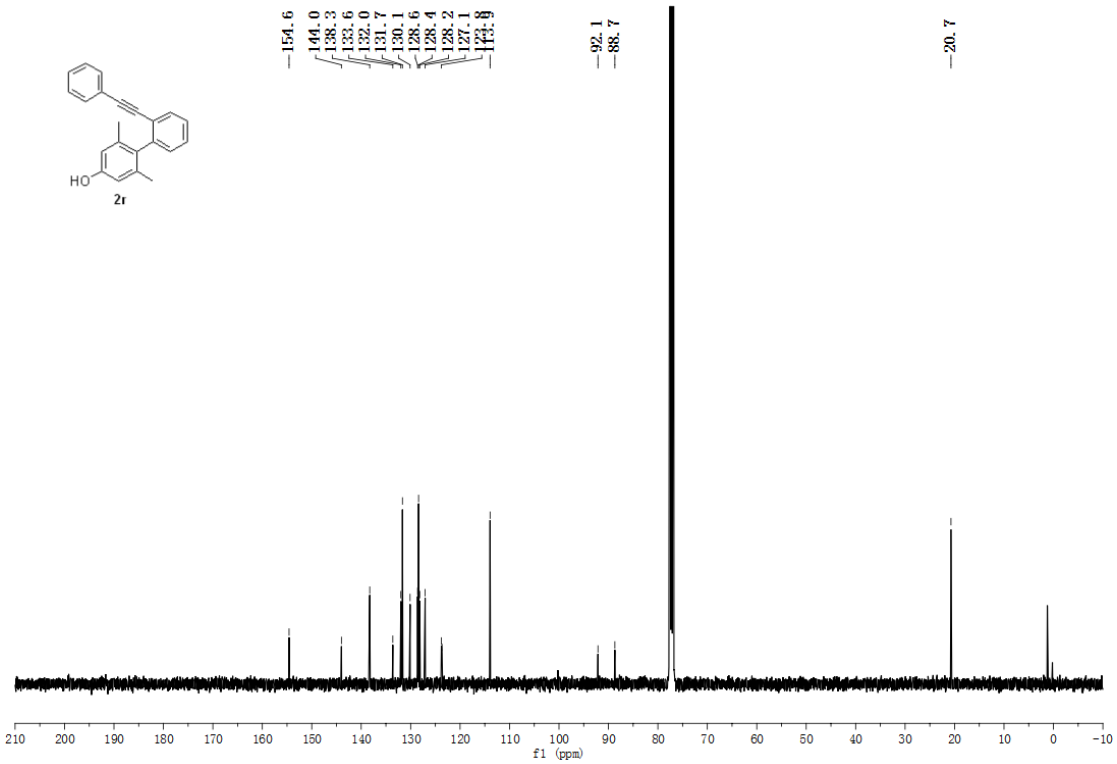


Figure S9. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2r**

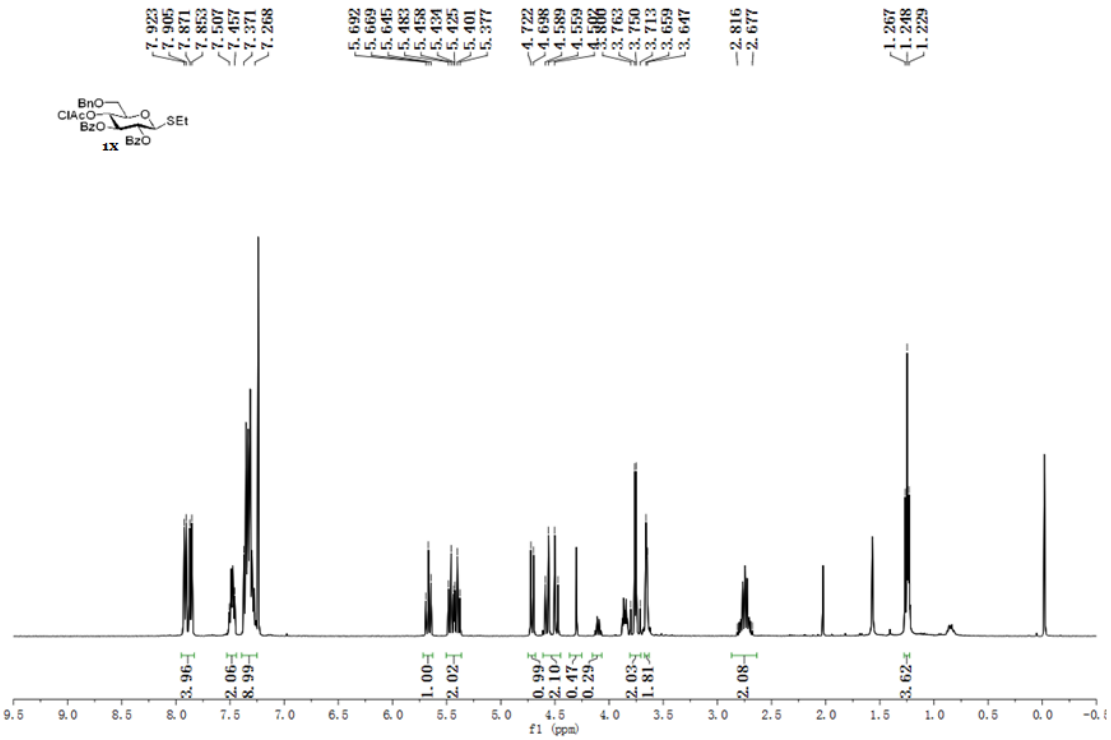


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1x**

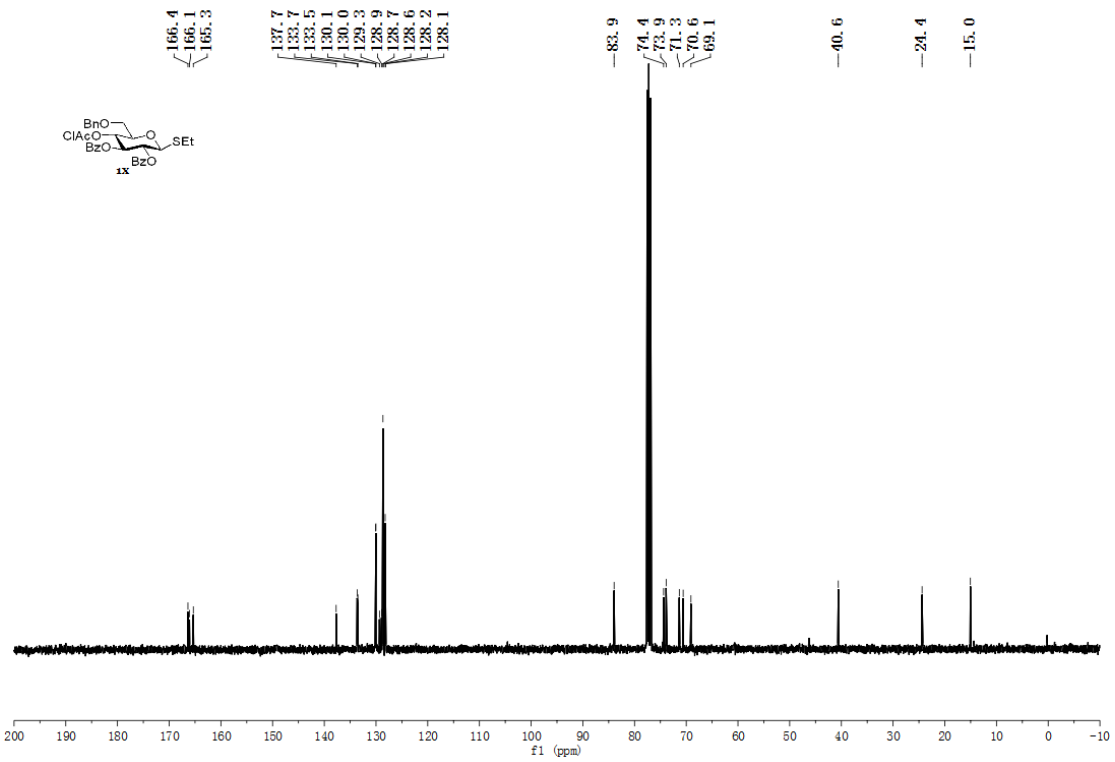


Figure S11. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1x**

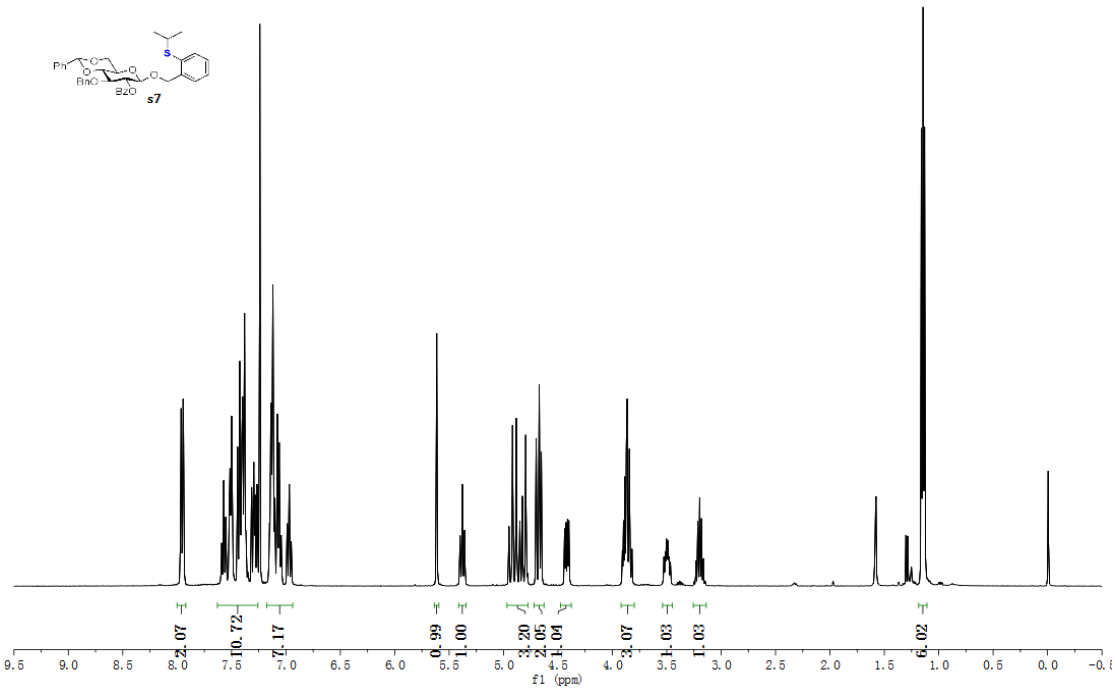


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S7**

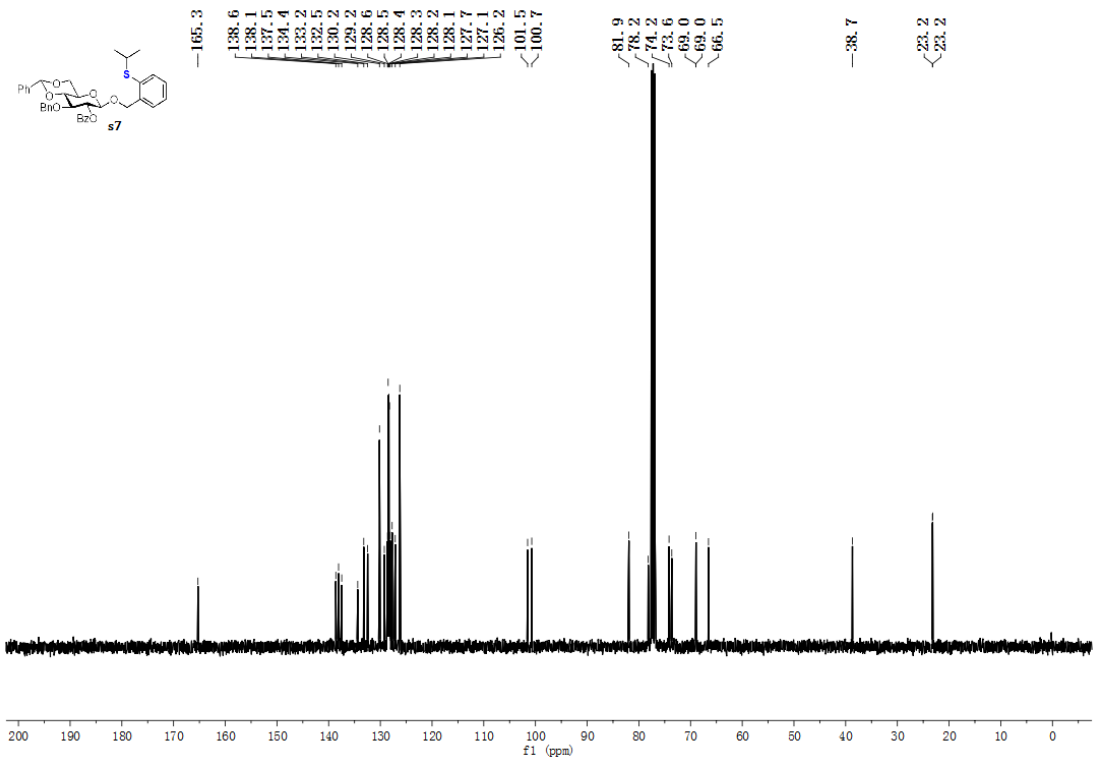


Figure S13. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **S7**

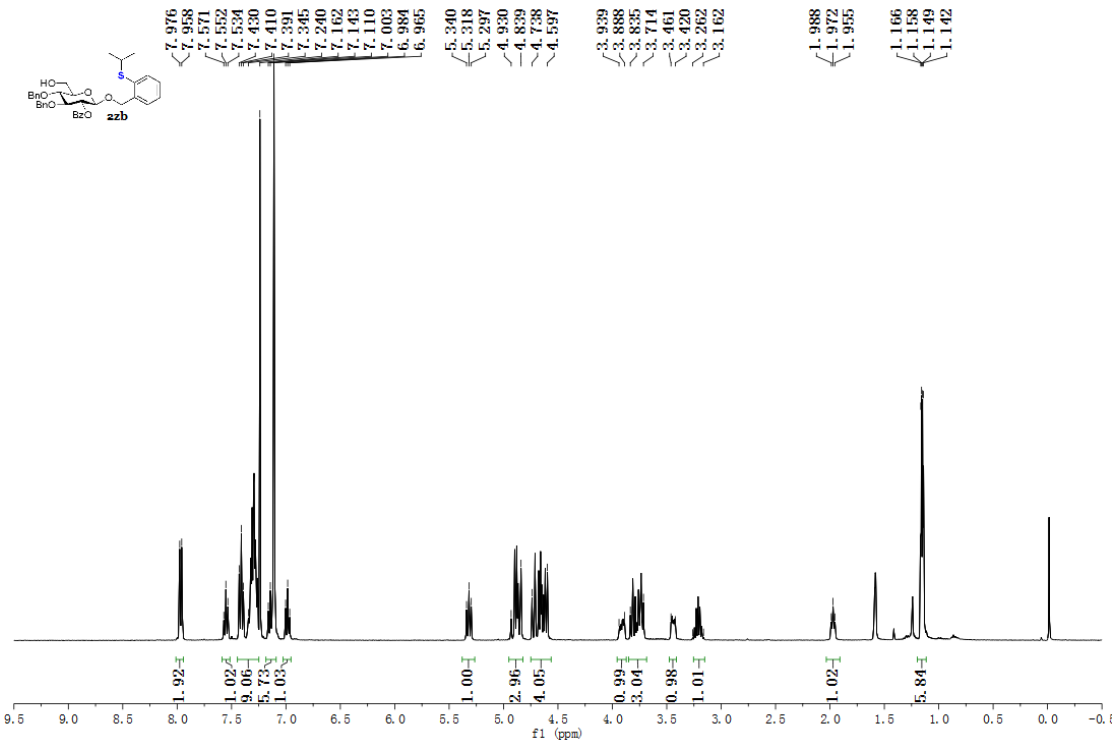


Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2zb**

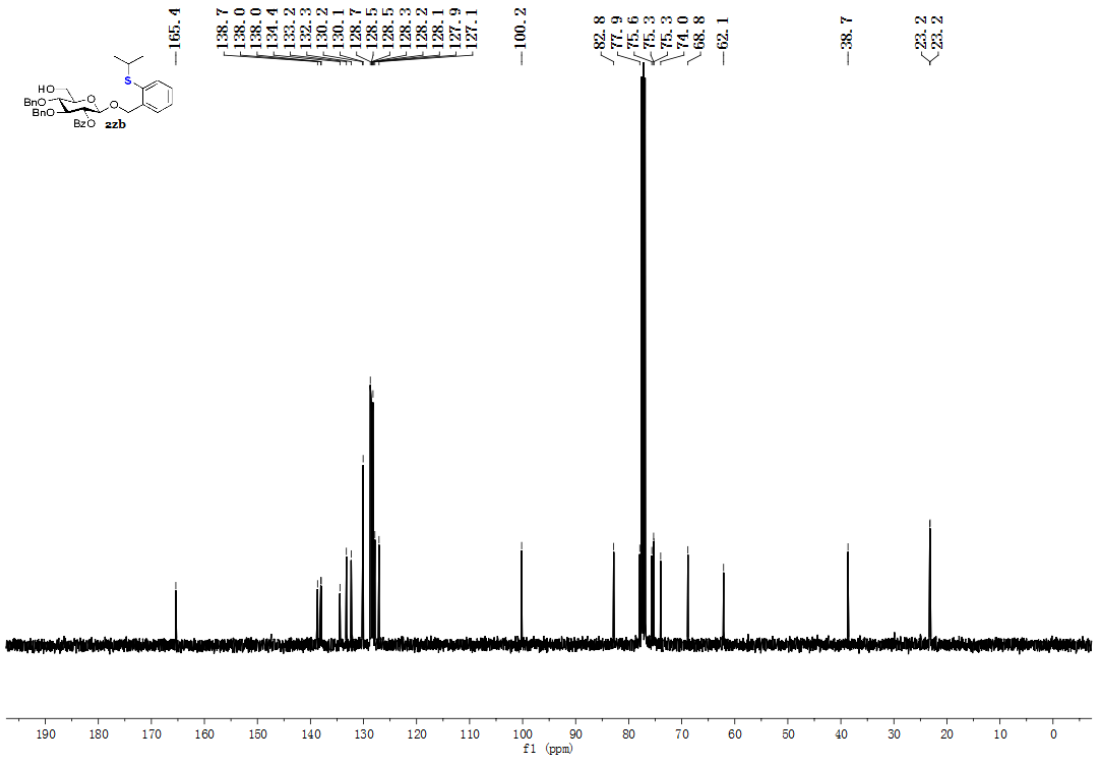


Figure S15. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2zb**

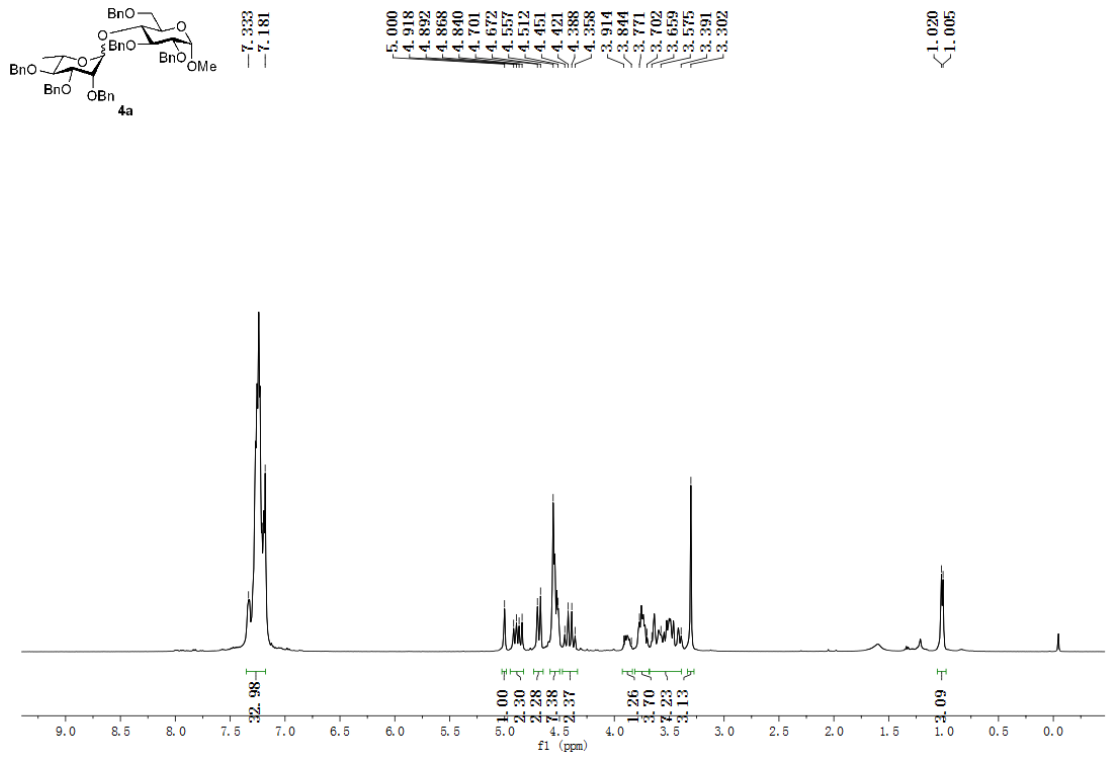


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a**

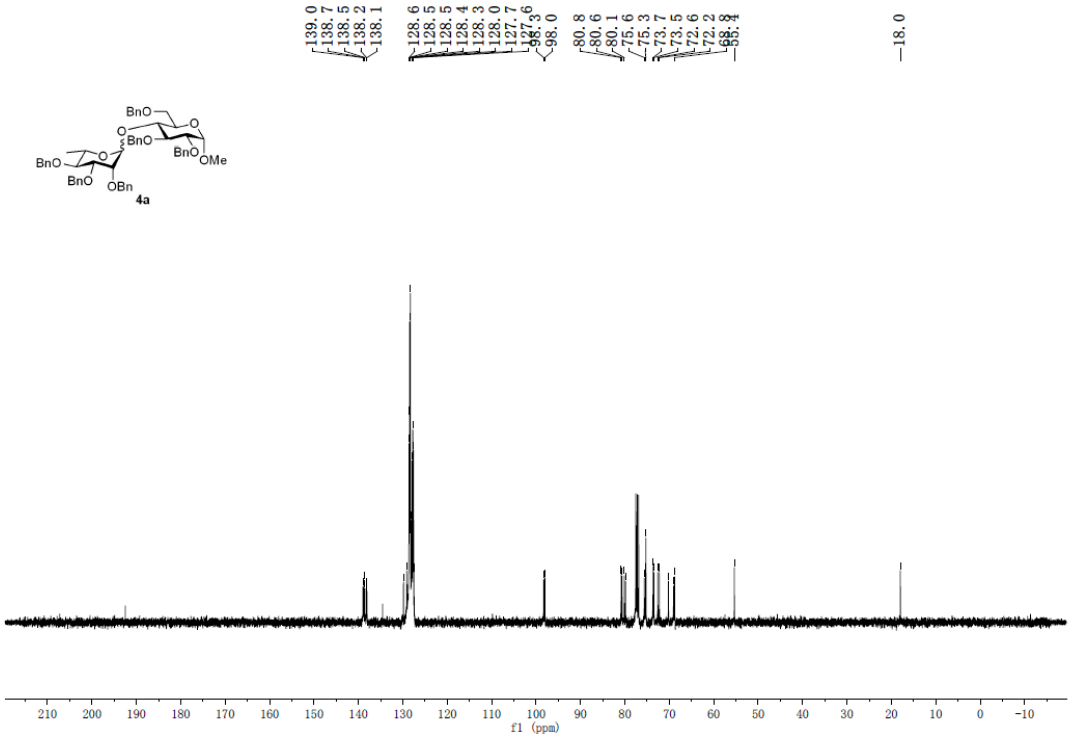


Figure S17. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4a**

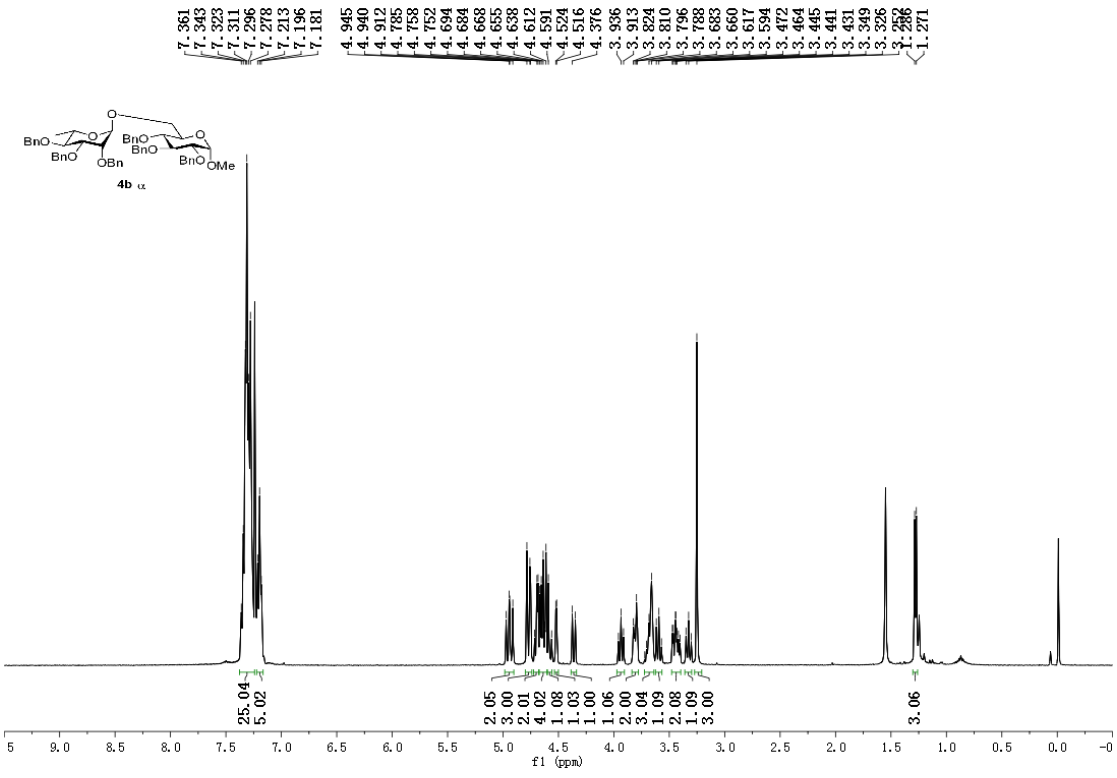


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4b**

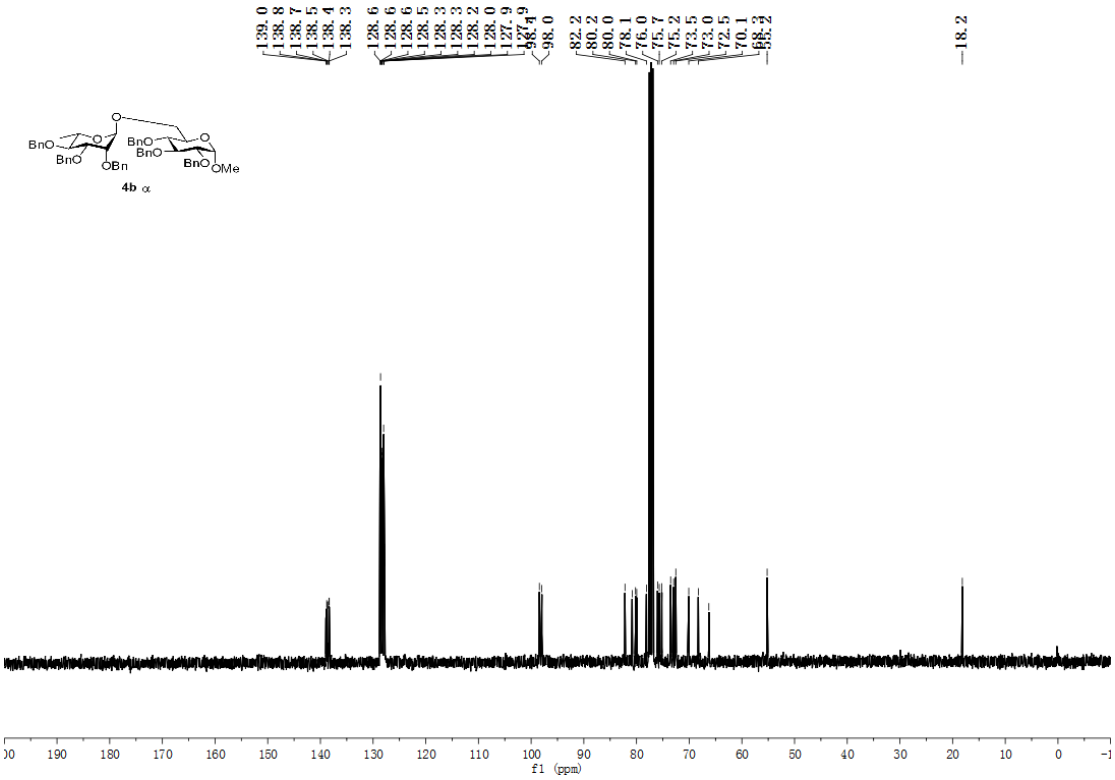


Figure S19. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4b**

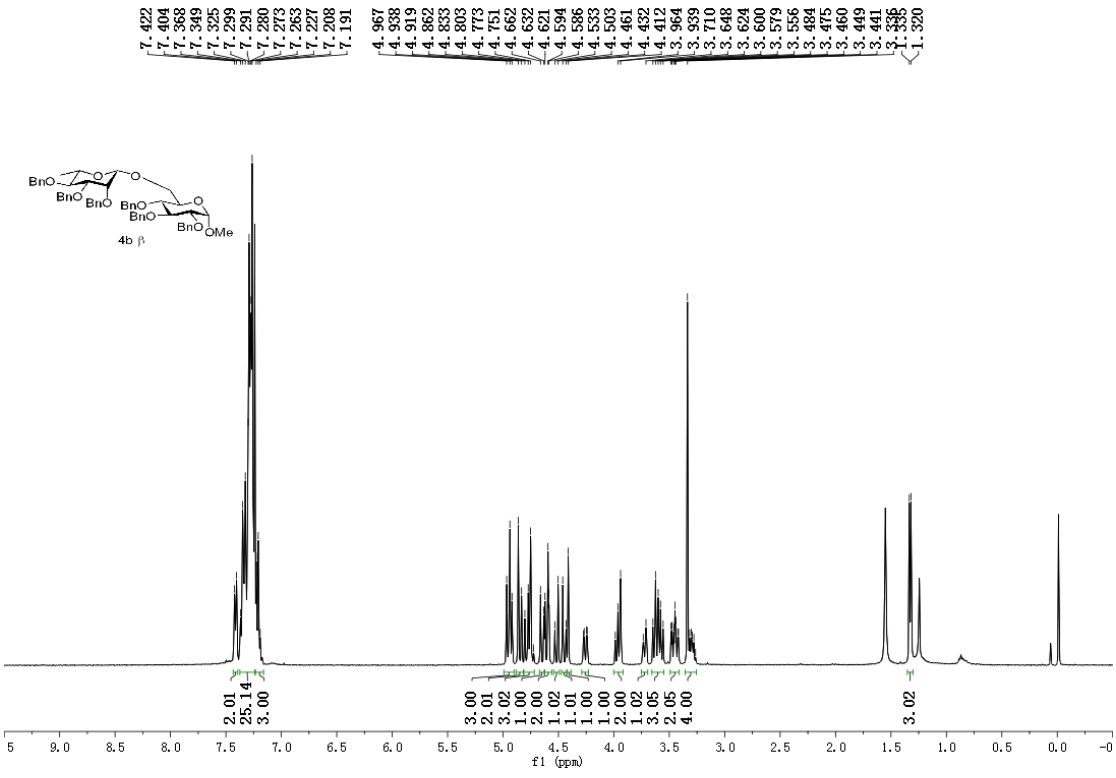


Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4b**

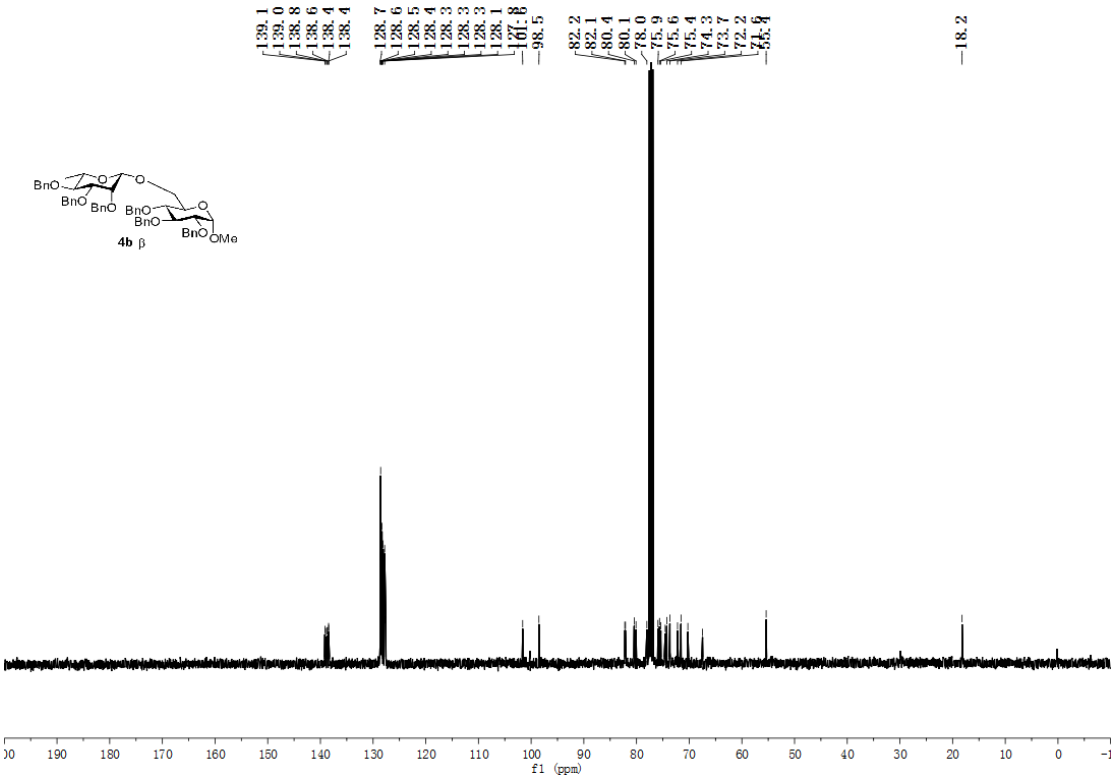


Figure S21. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4b**

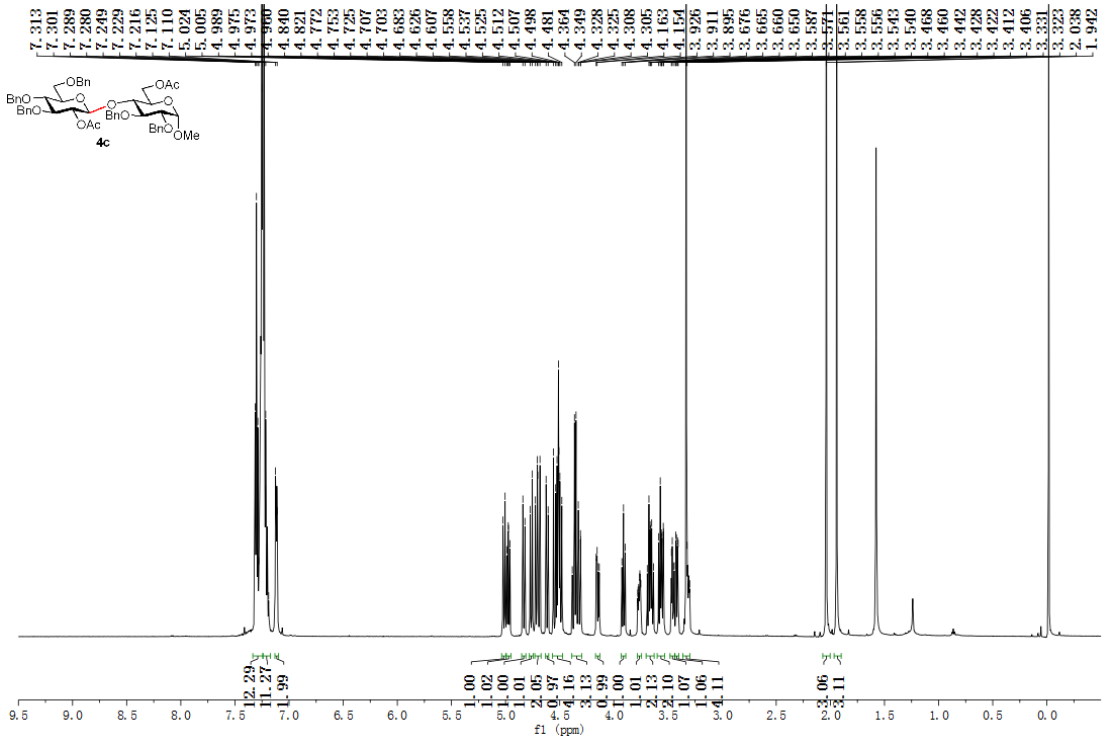


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4c**

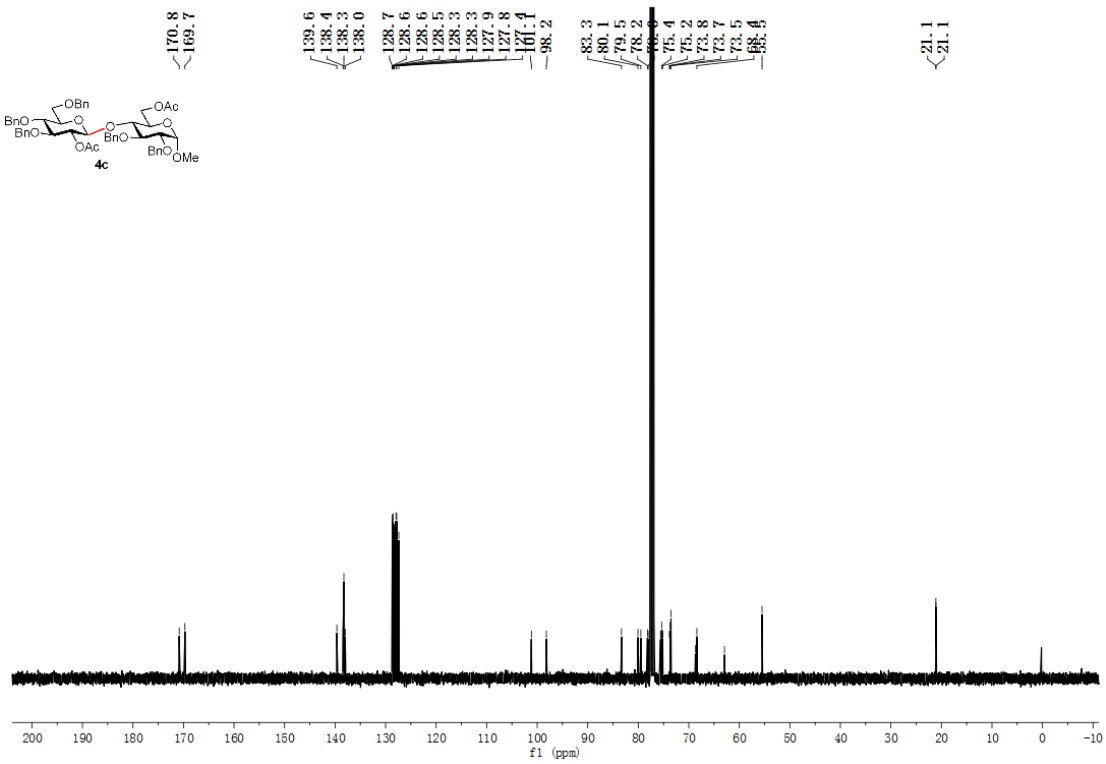


Figure S23. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4c**

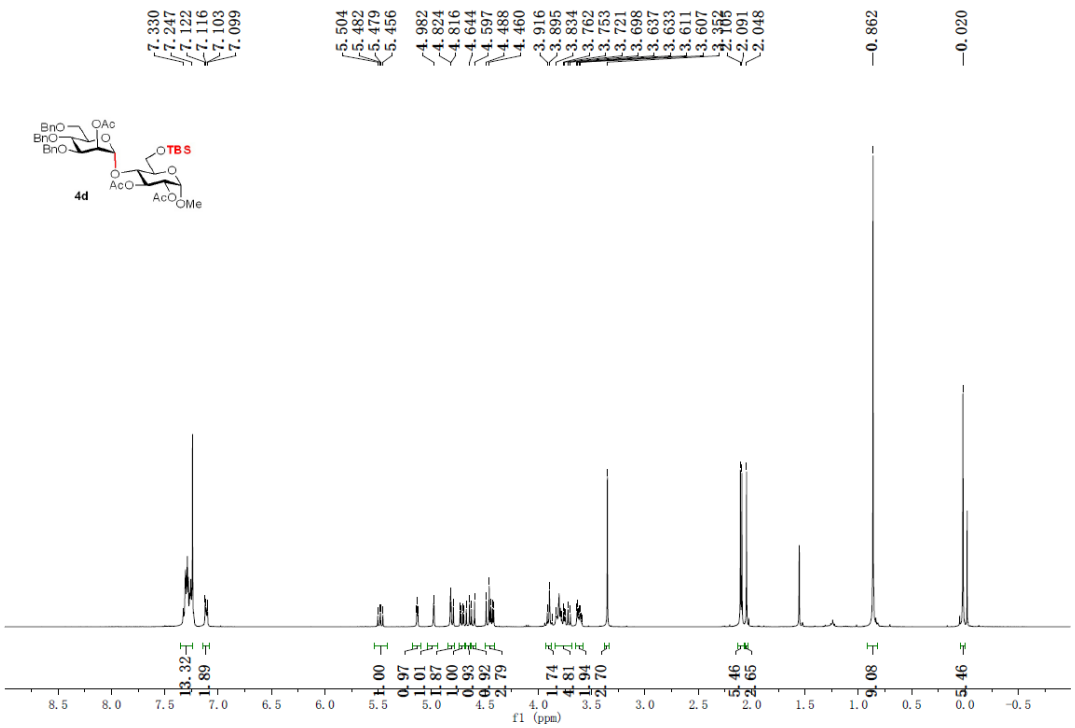


Figure S24. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4d**

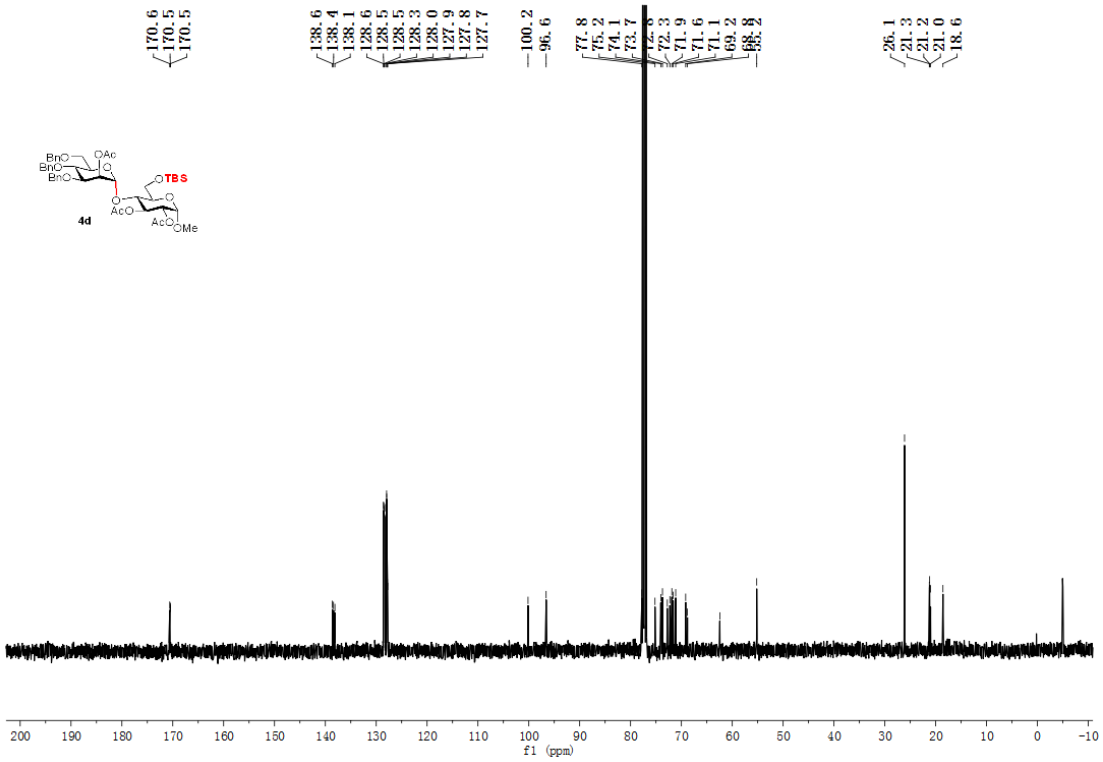


Figure S25. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4d**

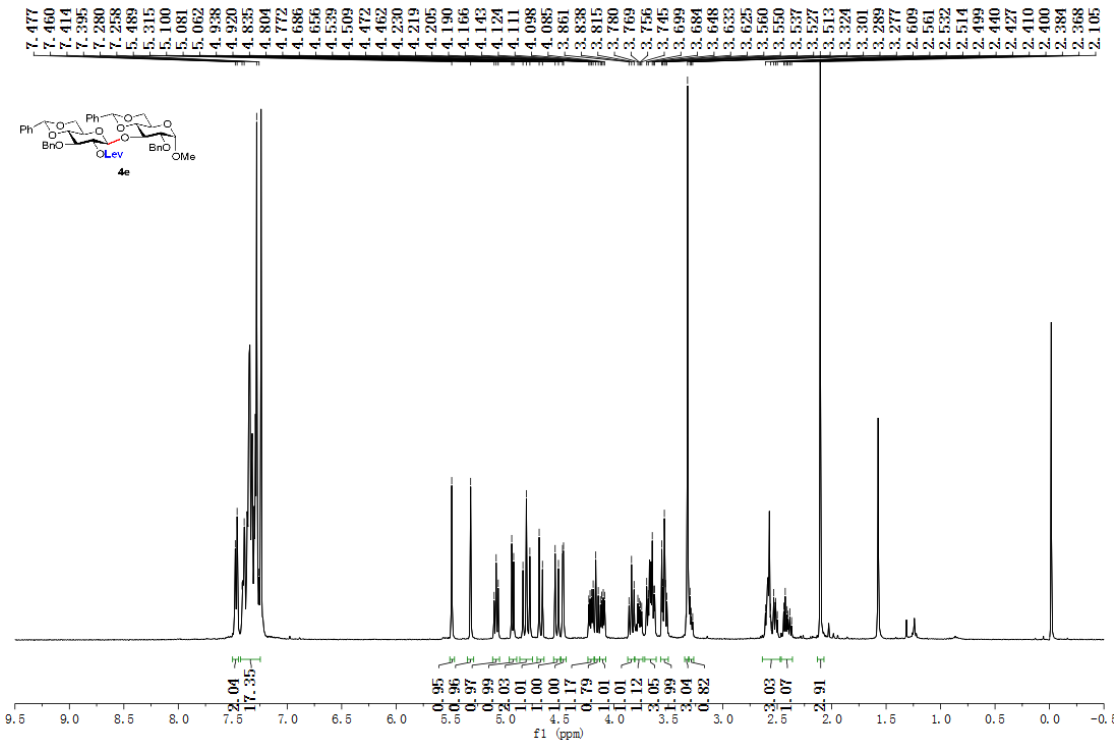


Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4e**

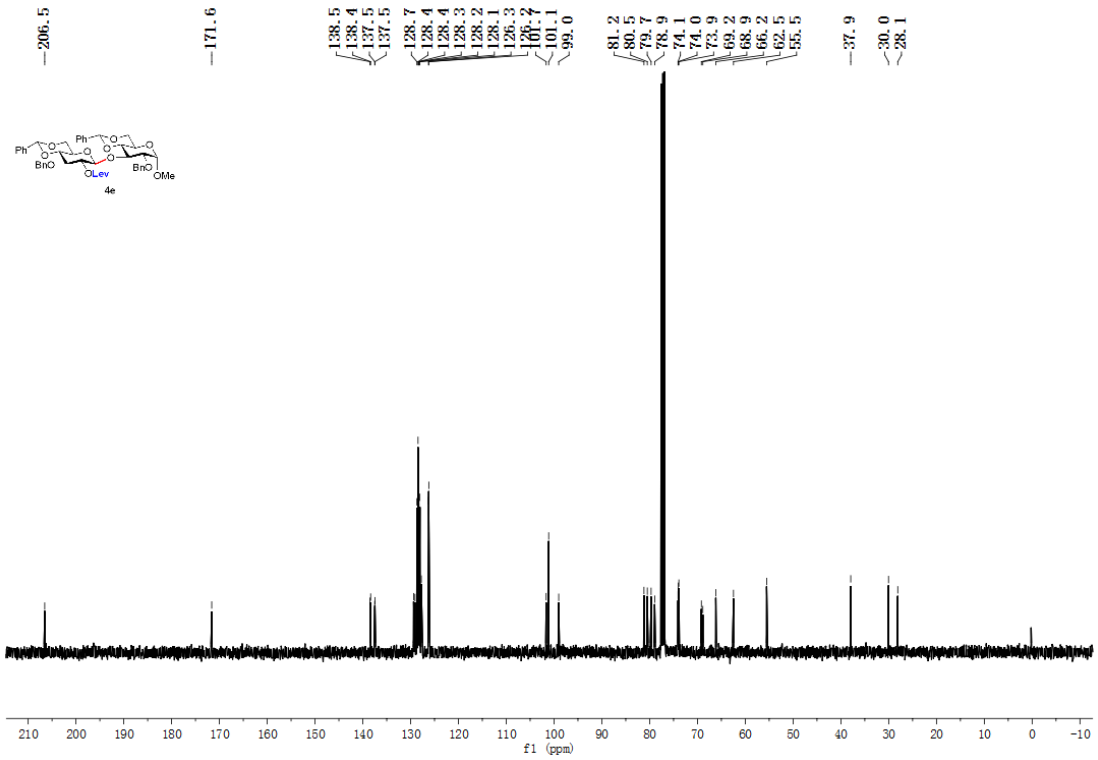


Figure S27. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4e**

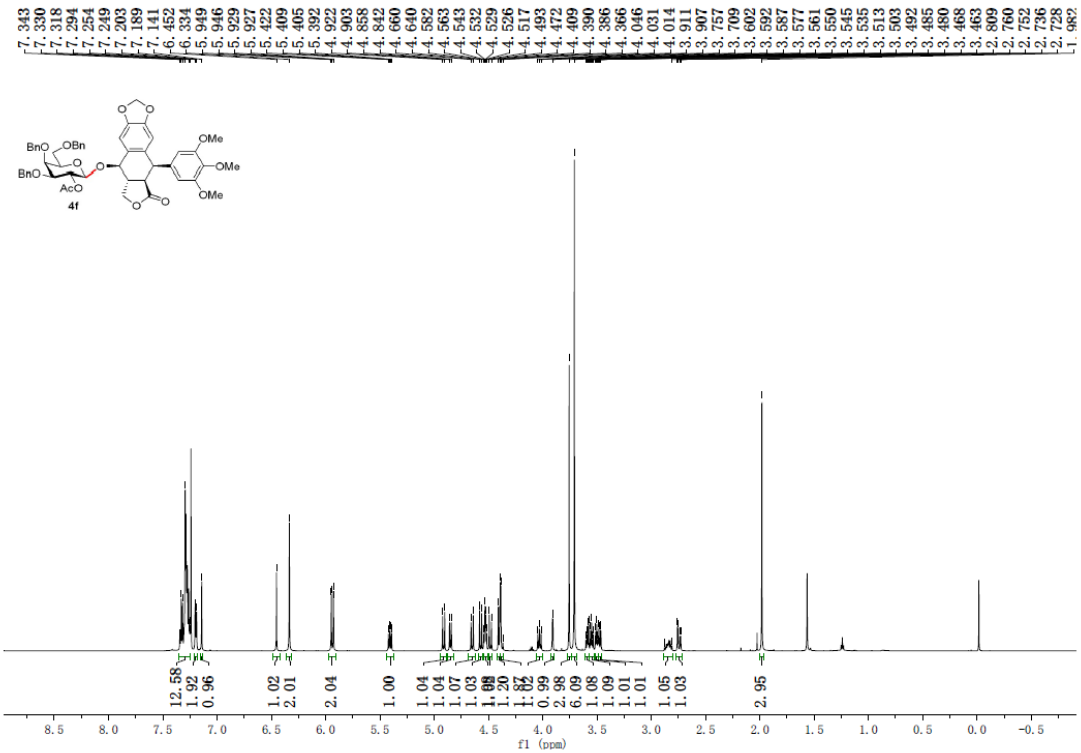


Figure S28. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4f**

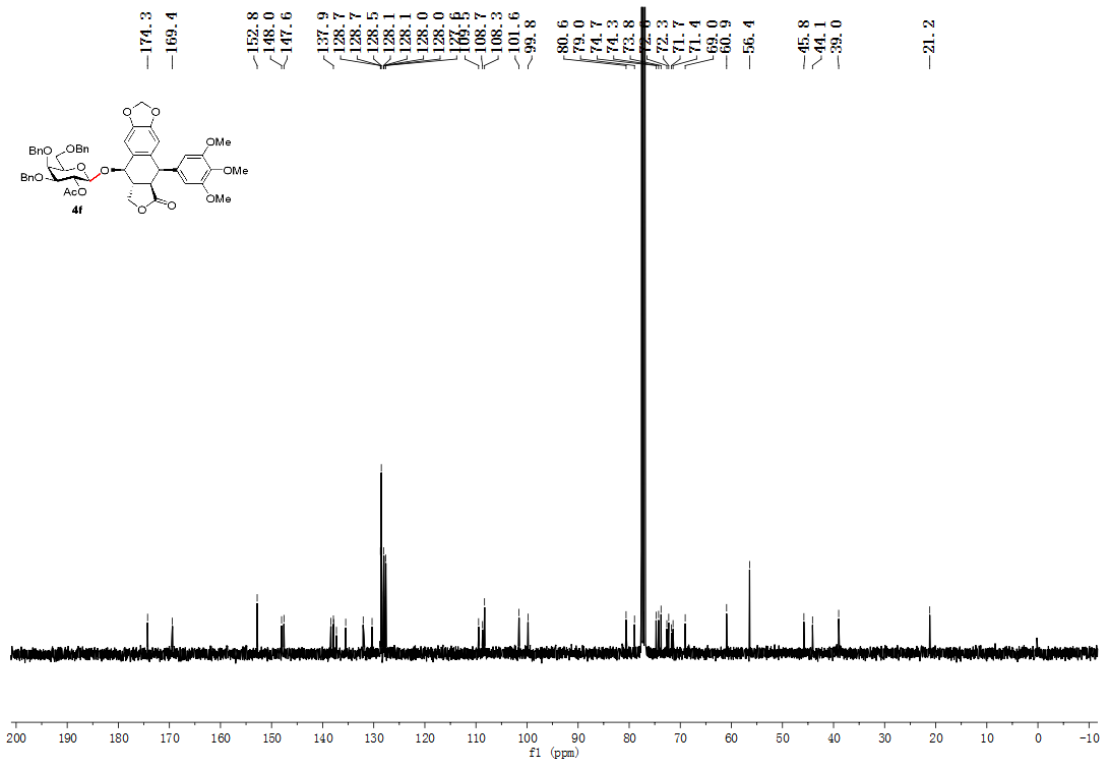


Figure S29. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4f**

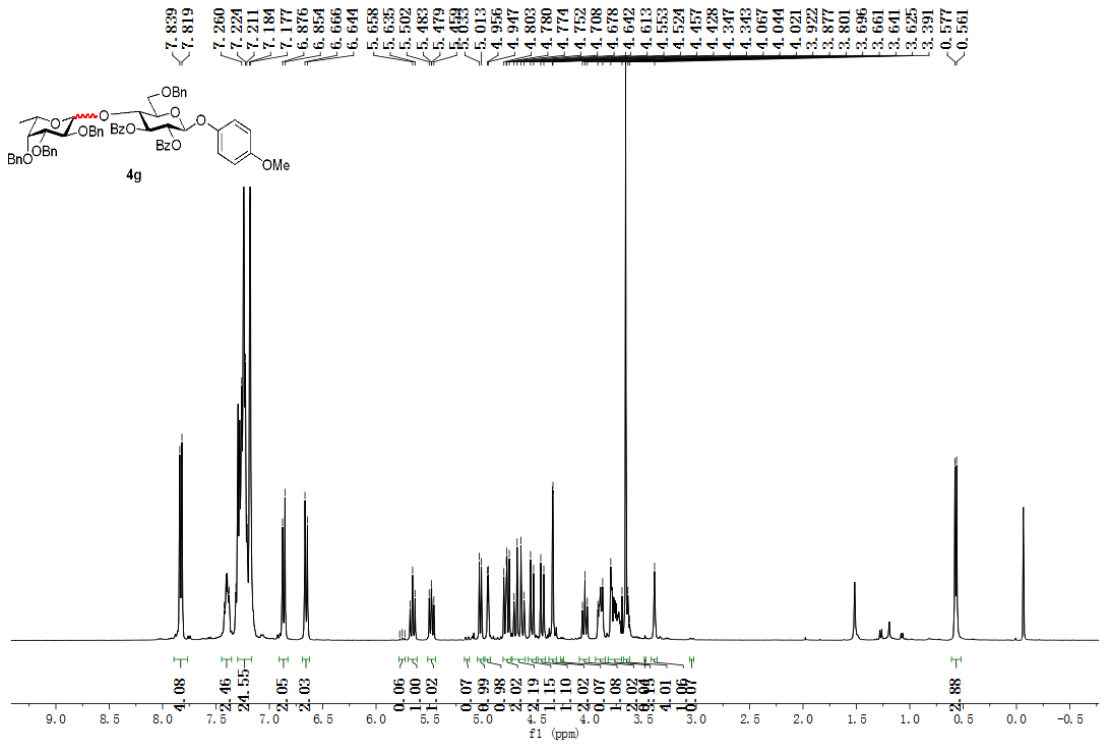


Figure S30. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4g**

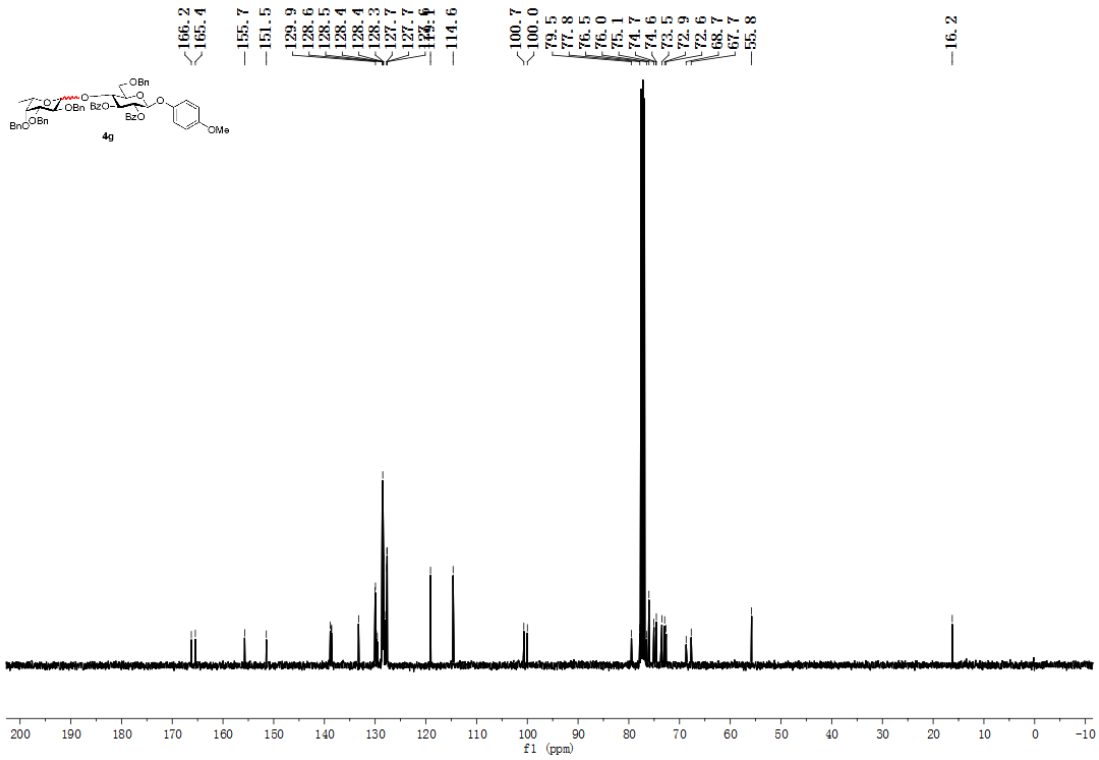


Figure S31. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4g**

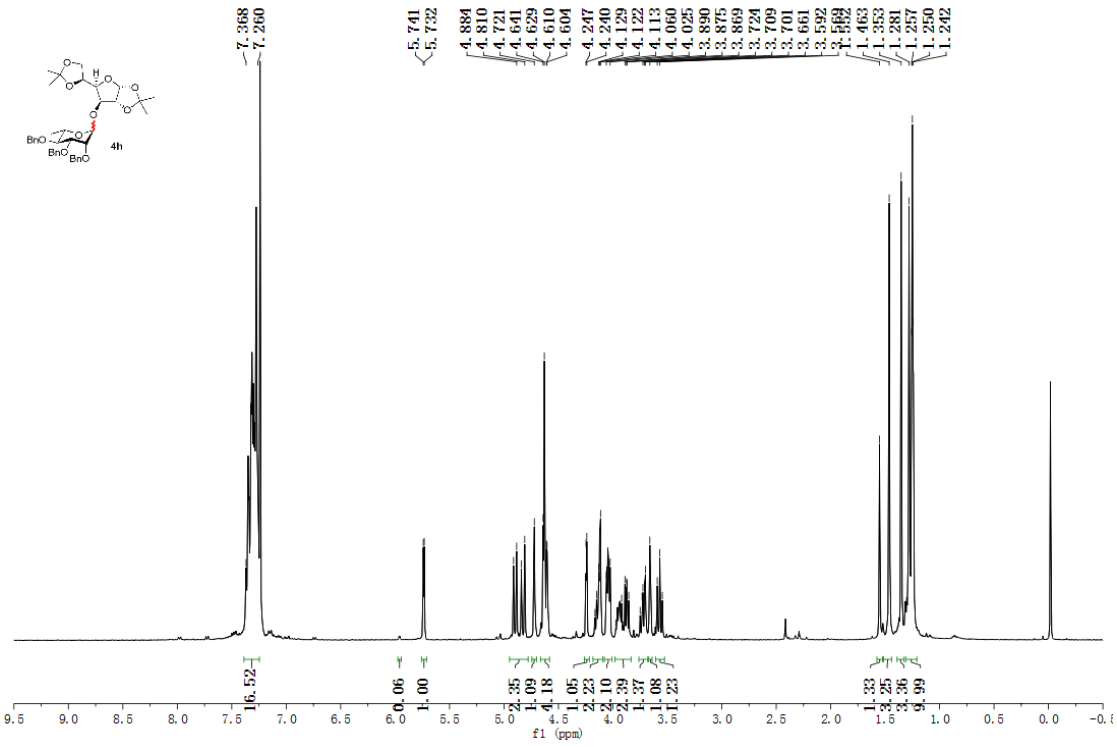


Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4h**

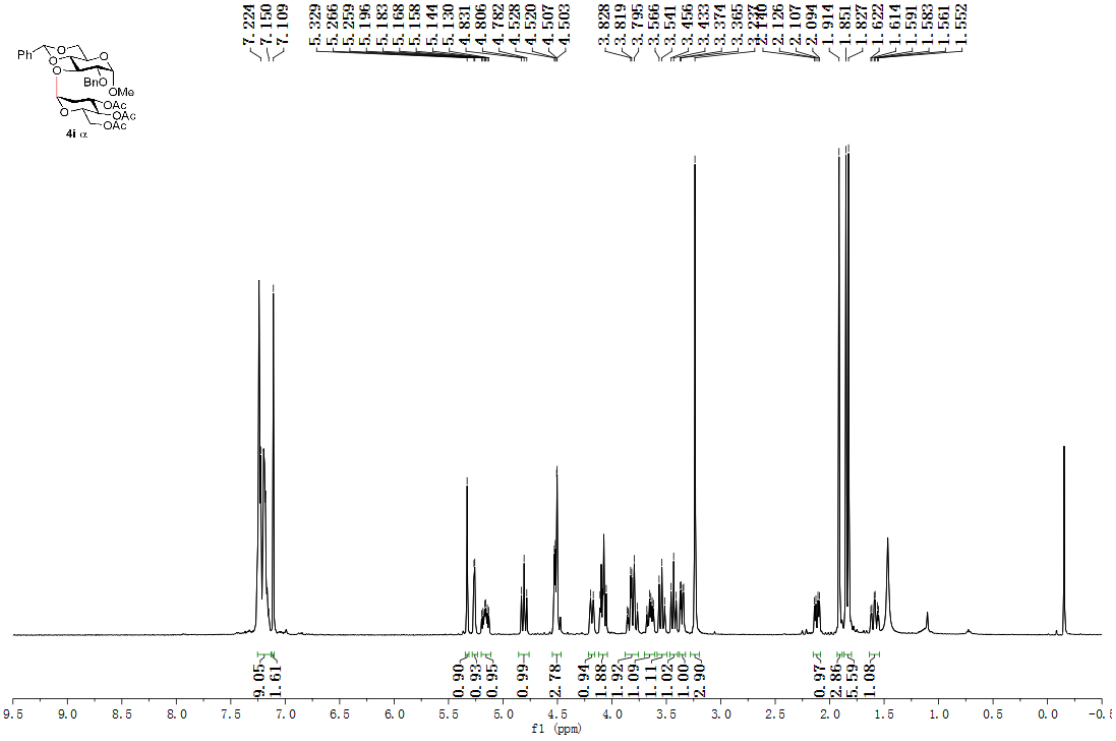


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4i(α)**

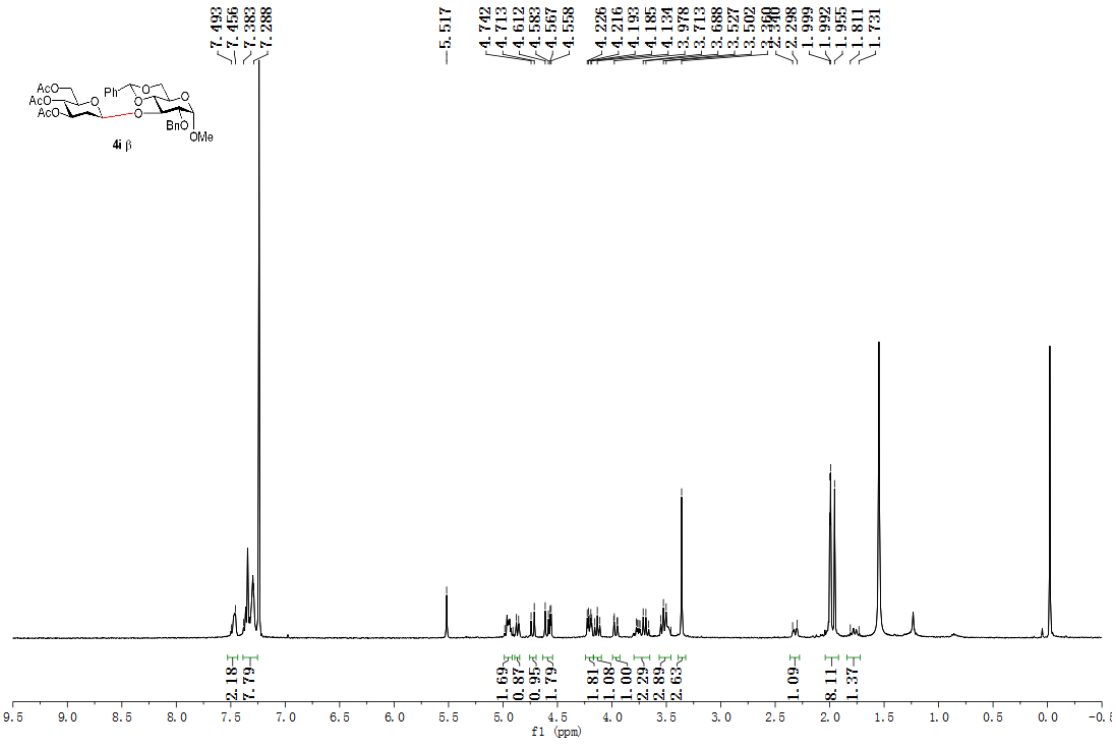


Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4i(β)**

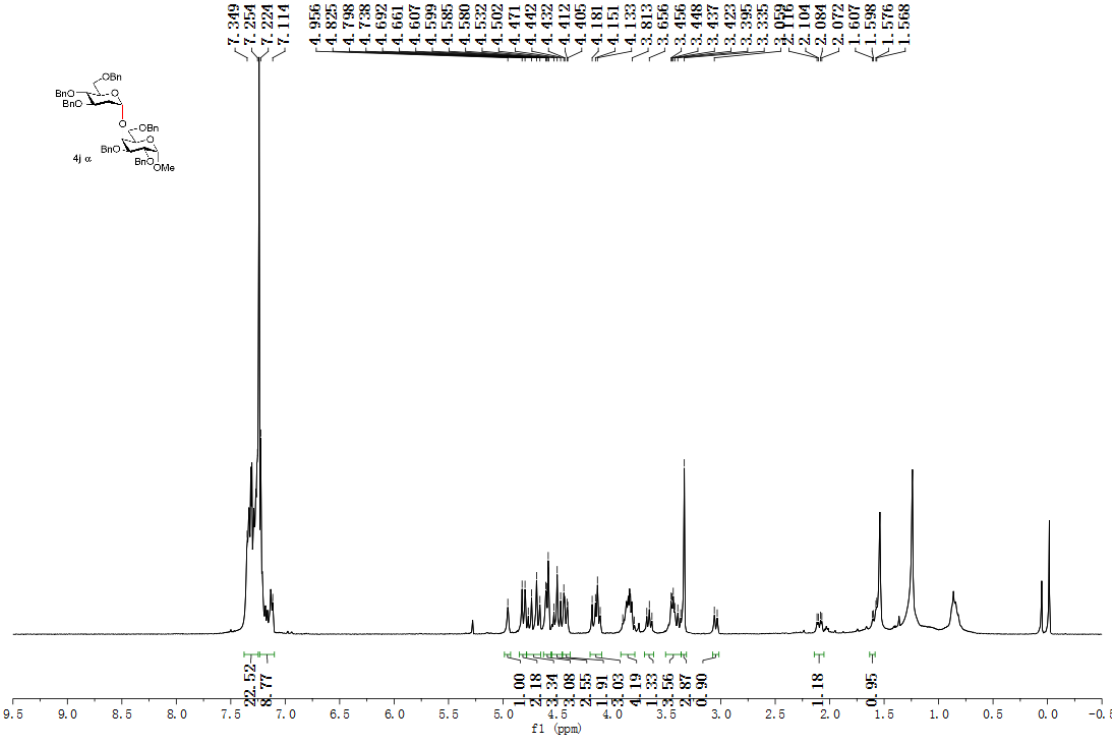


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4j(α)**

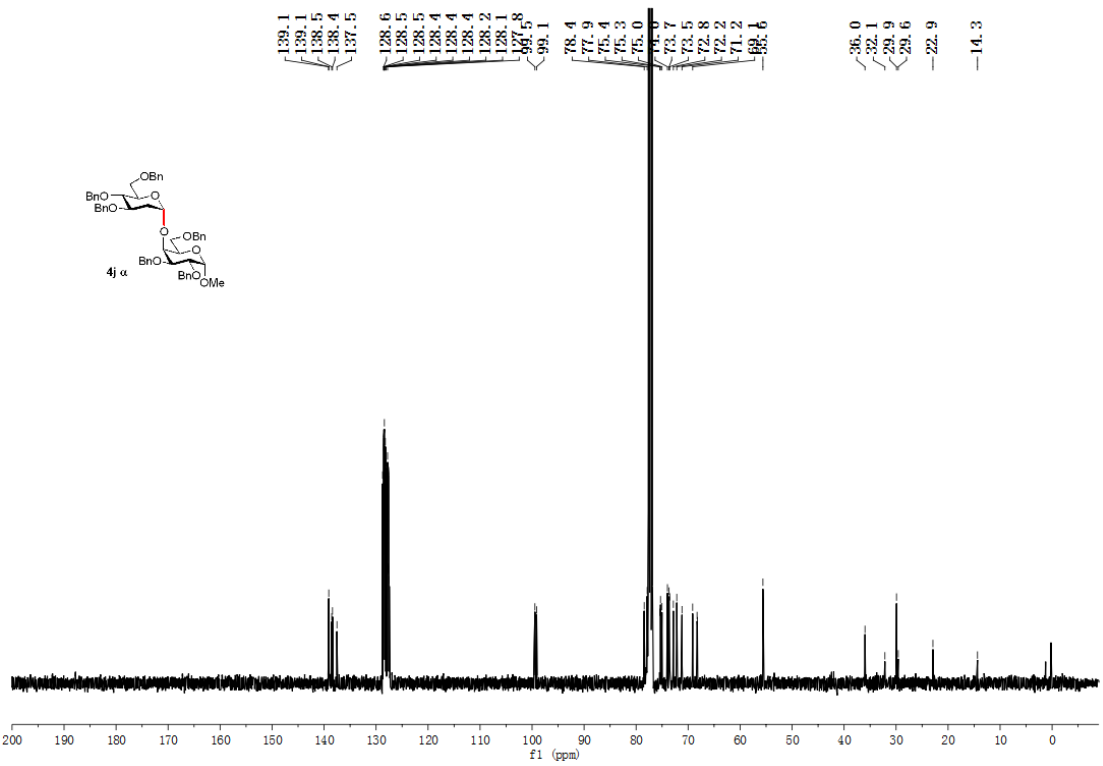


Figure S36. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4j(α)**

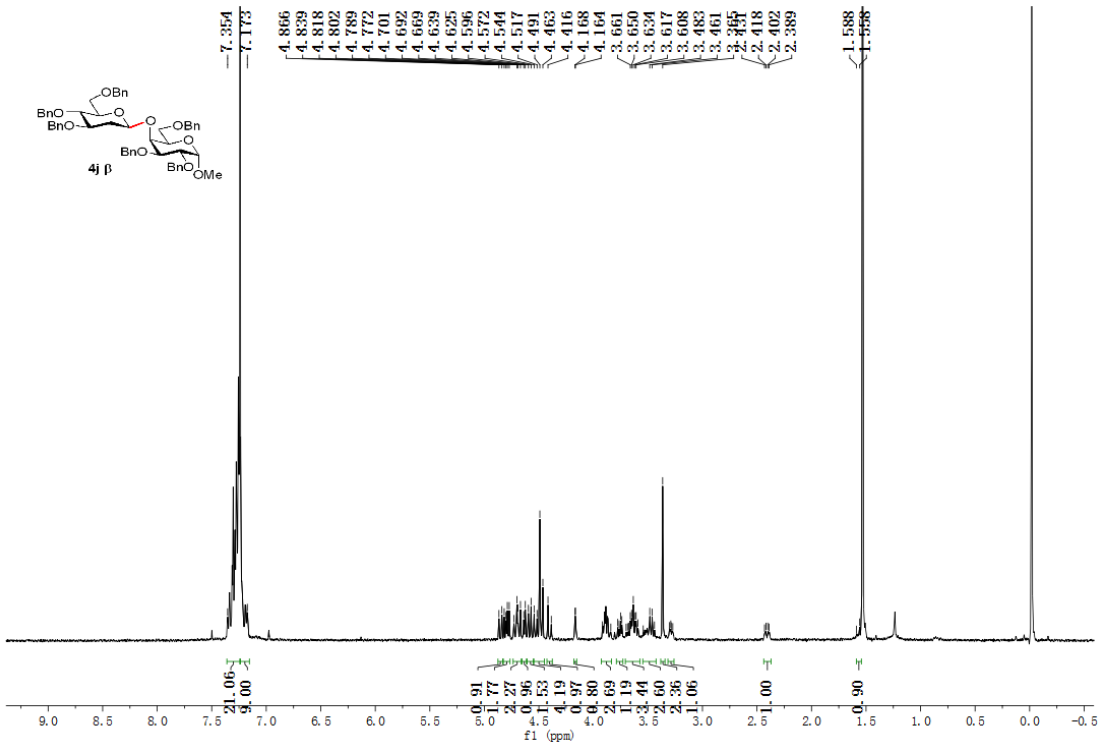


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4j(β)**

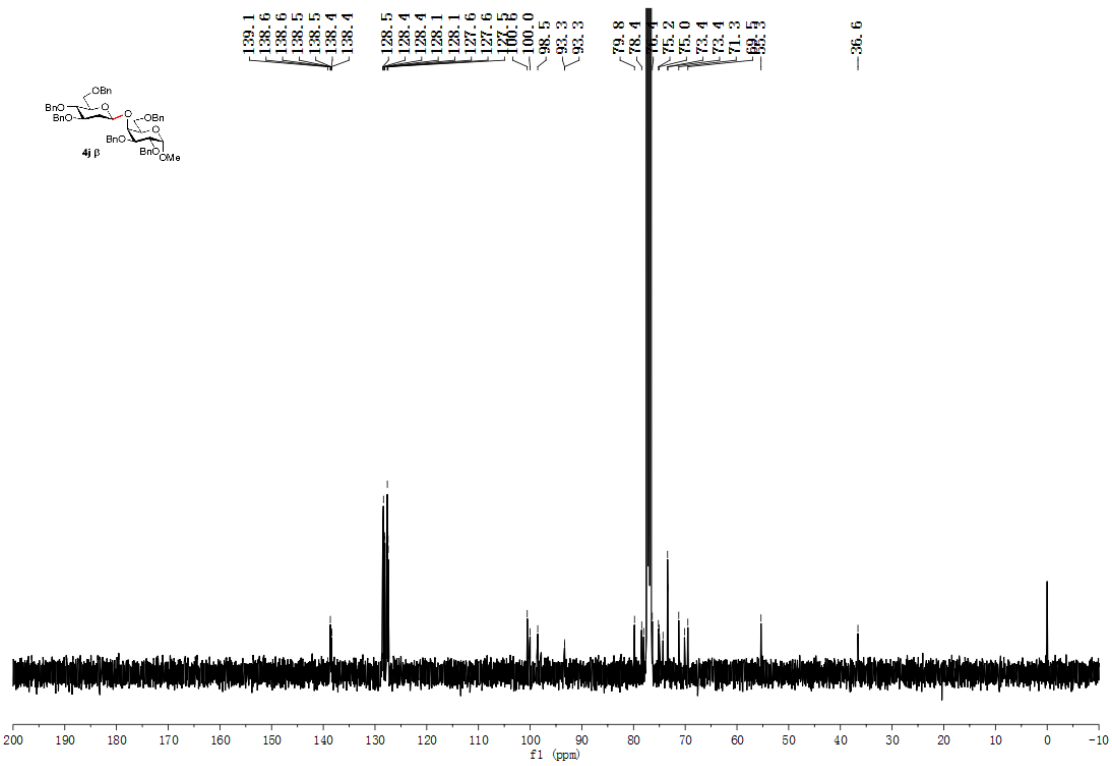


Figure S38. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4j(β)**

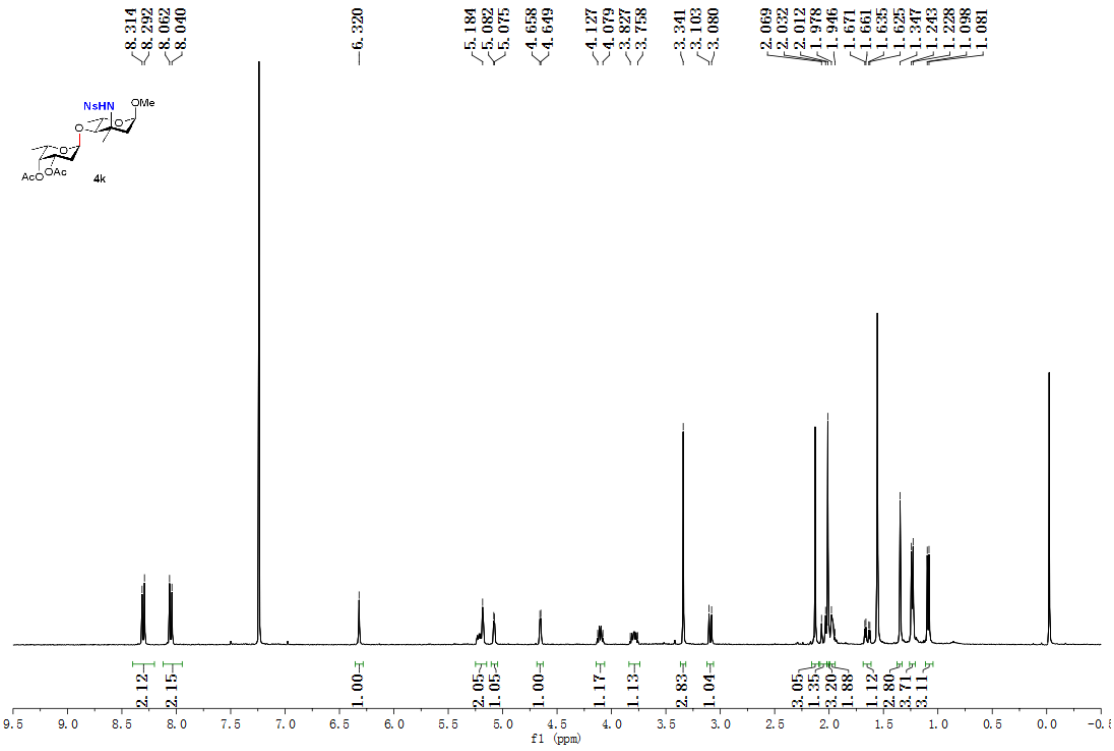


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4k**

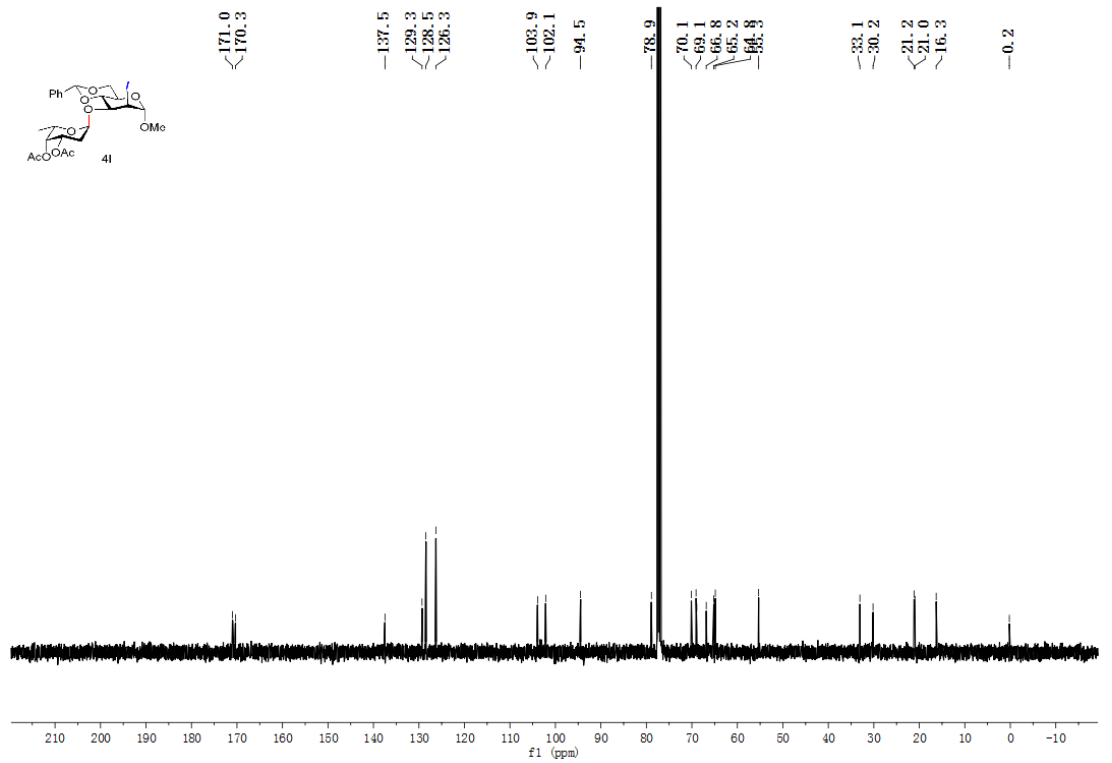


Figure S40. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4k**

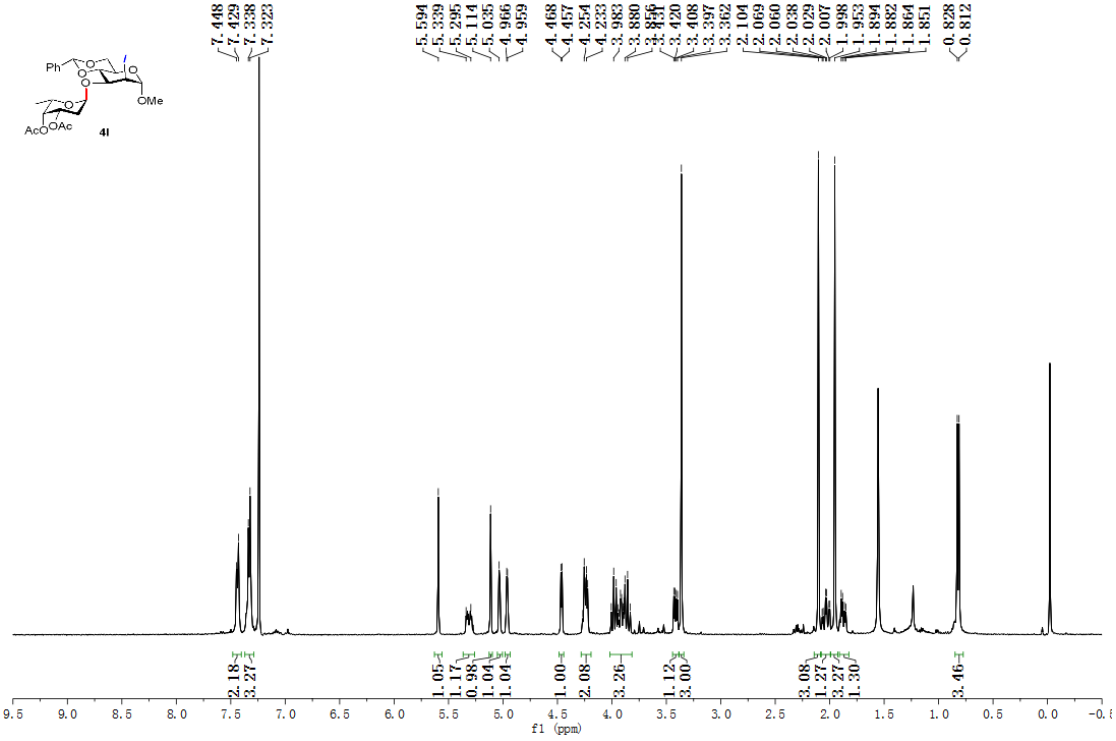


Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4l**

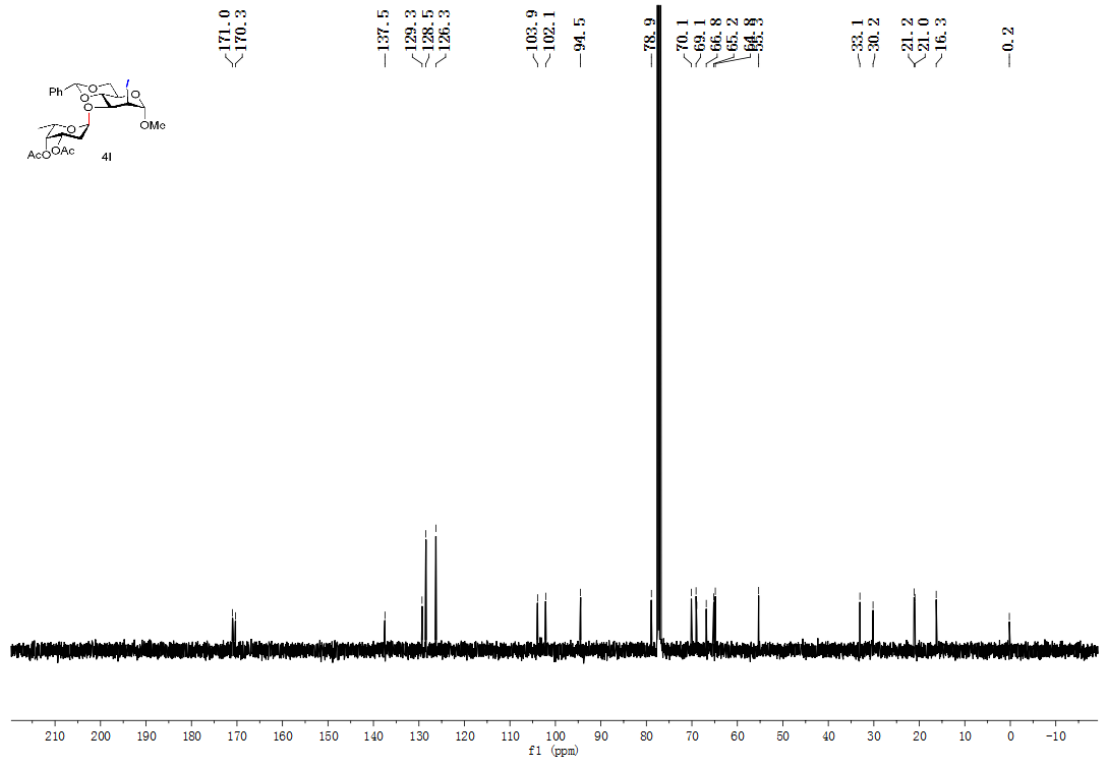


Figure S42. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4l**

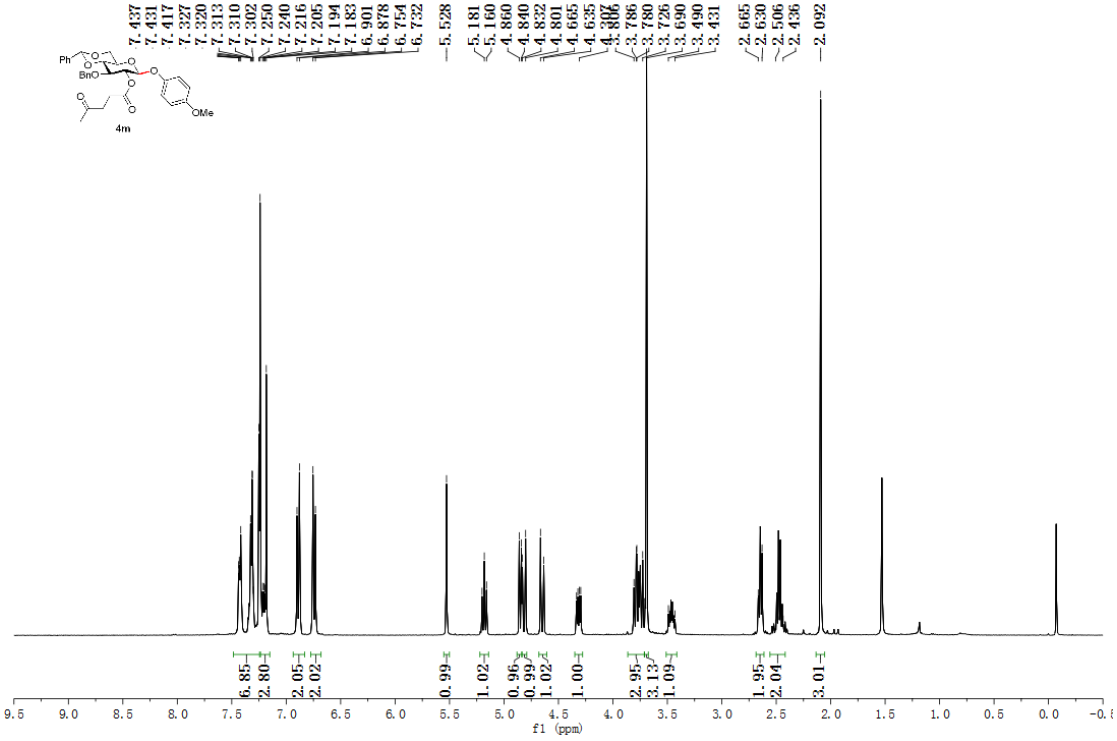


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4m**

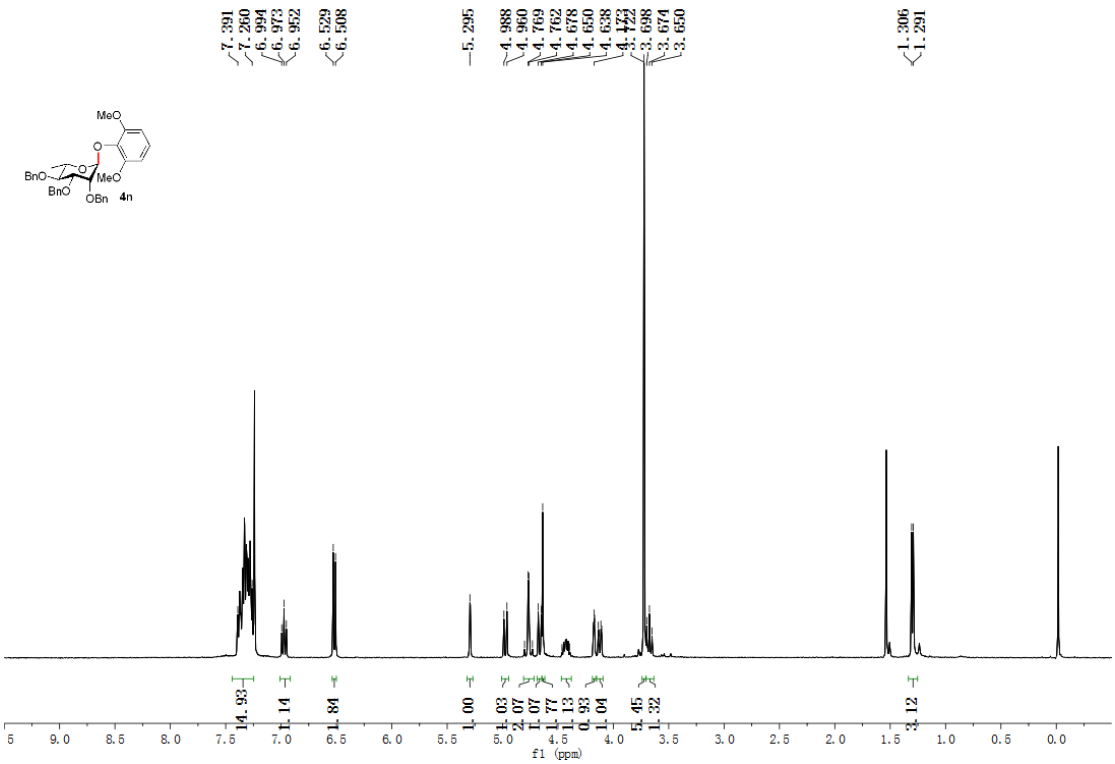


Figure S44. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4n**

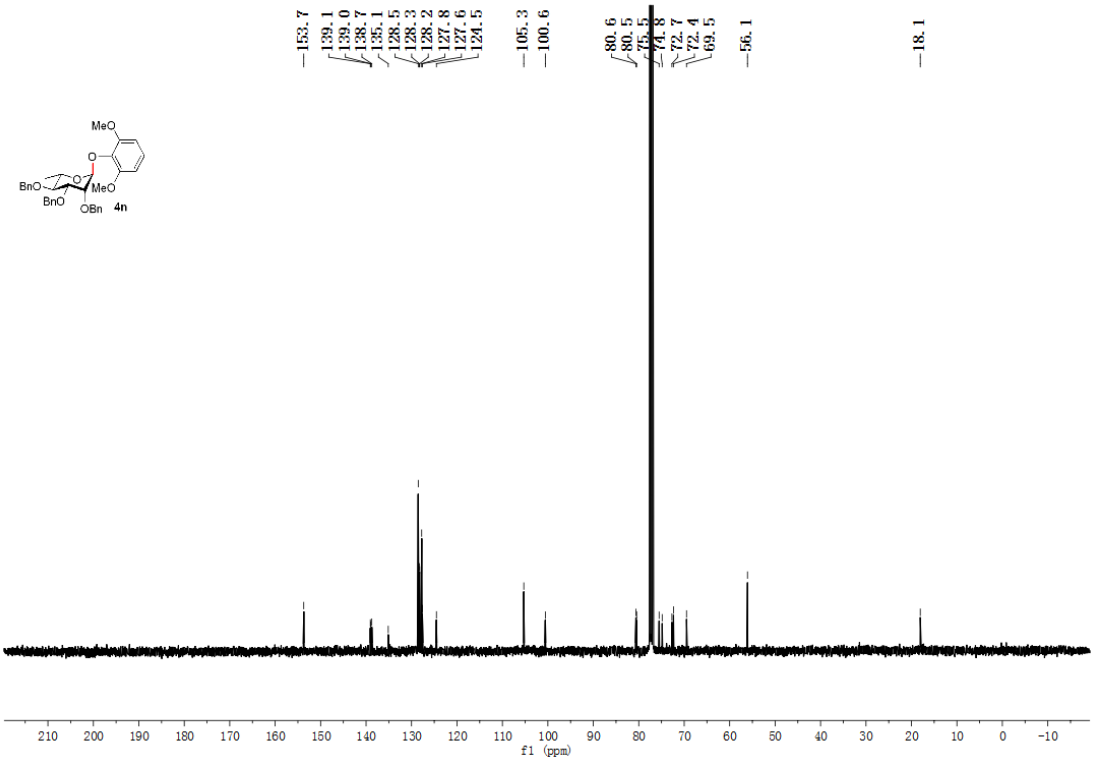


Figure S45. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4n**

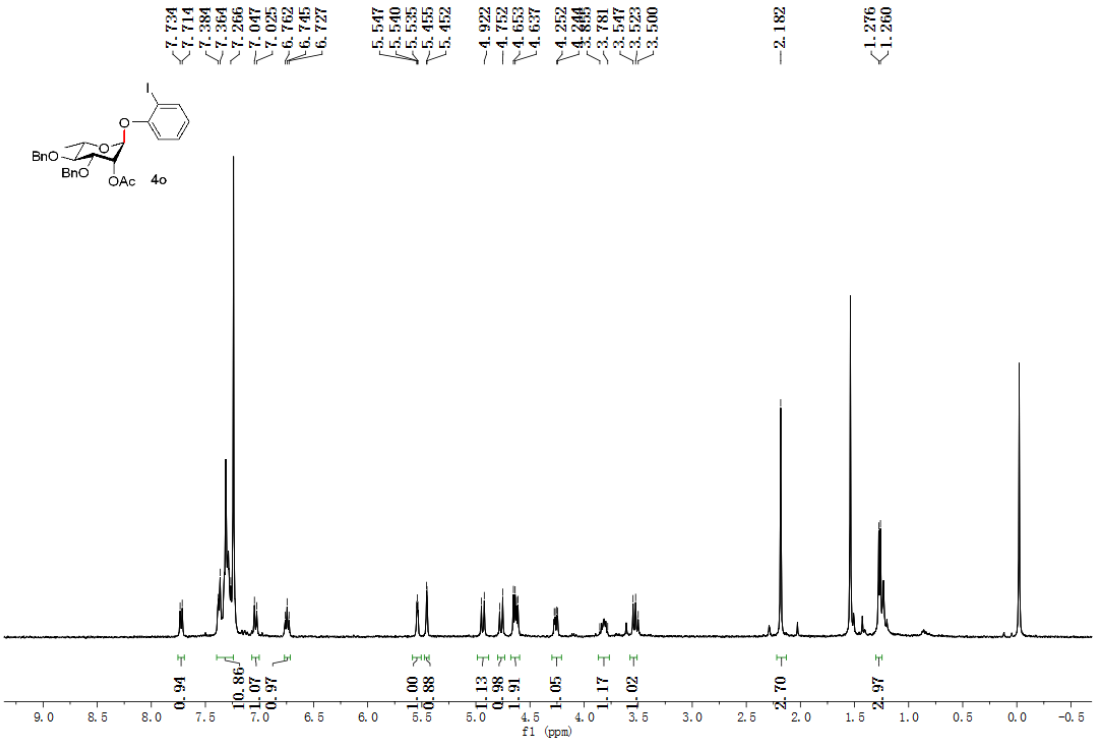


Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4o**

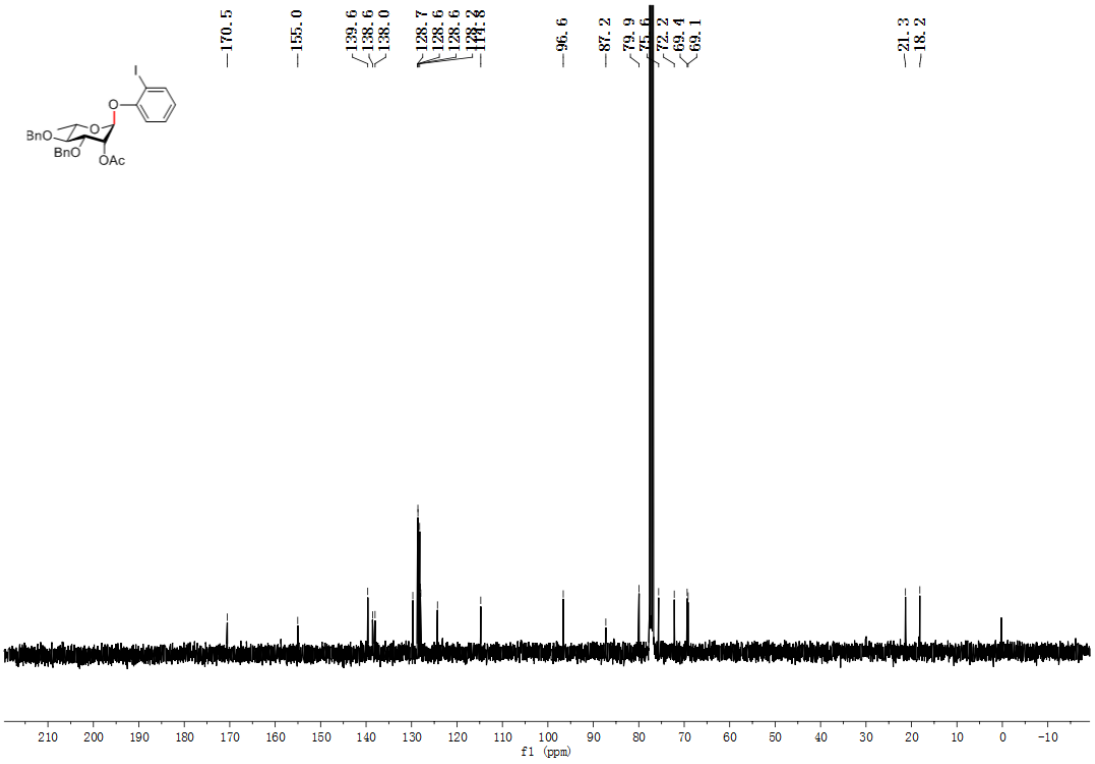


Figure S47. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4o**

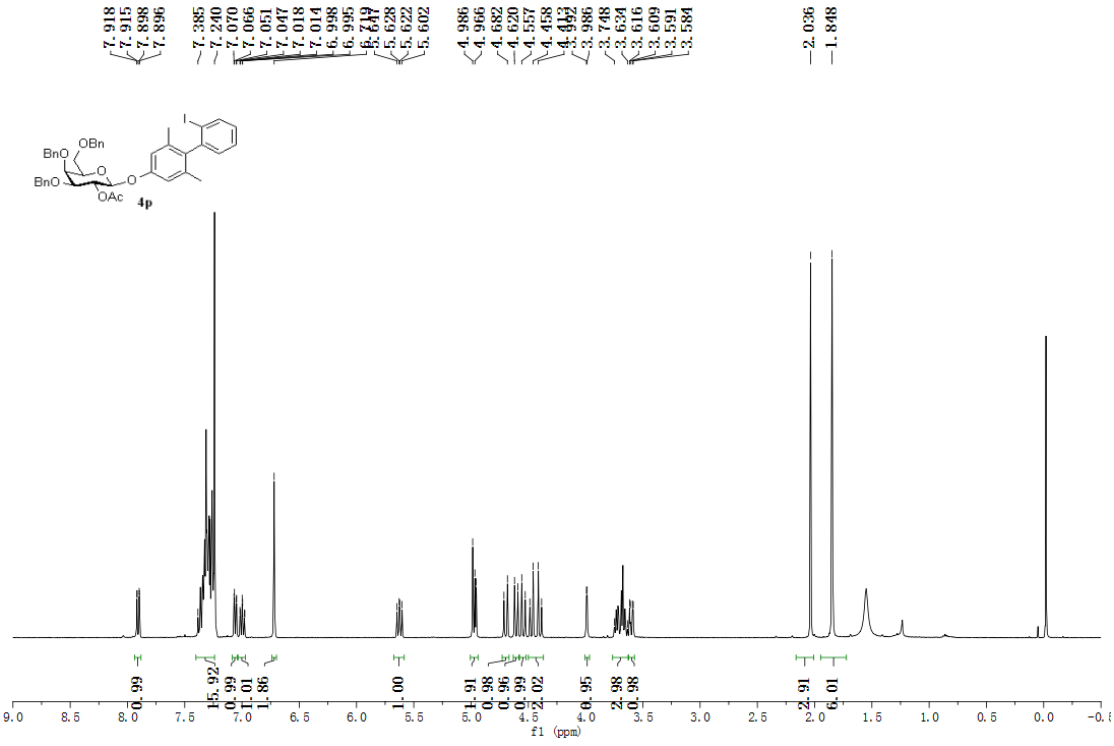


Figure S48. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4p(β)**

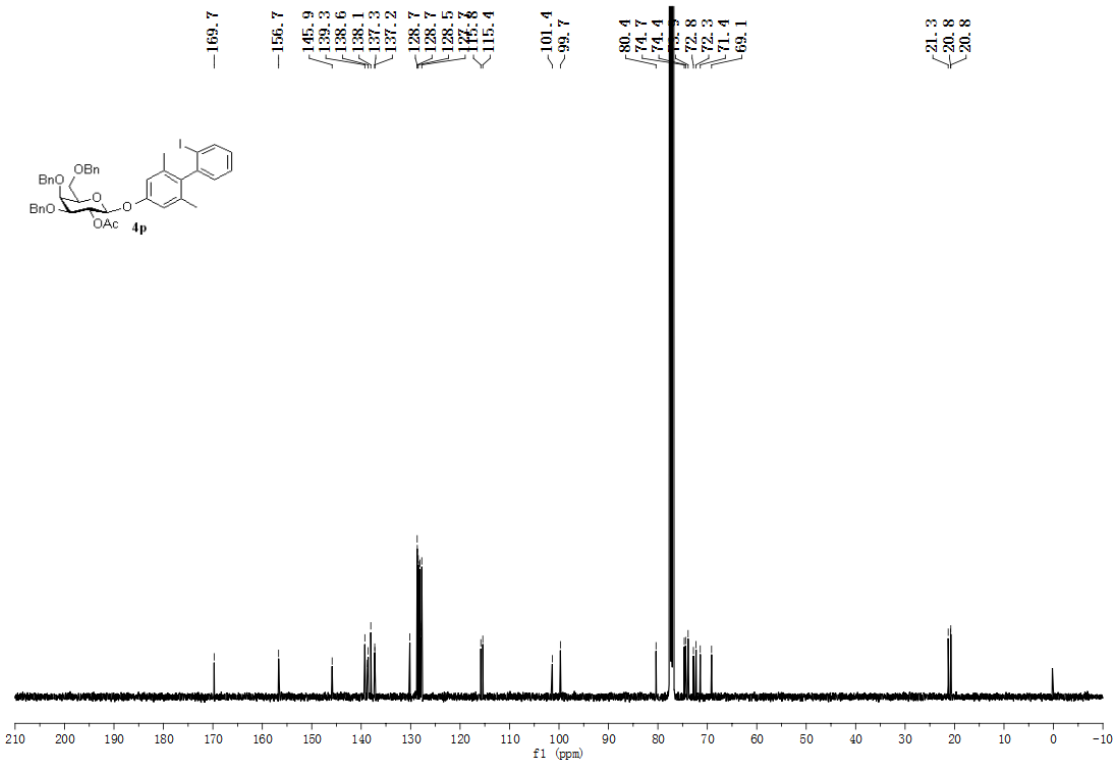


Figure S49. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4p(β)**

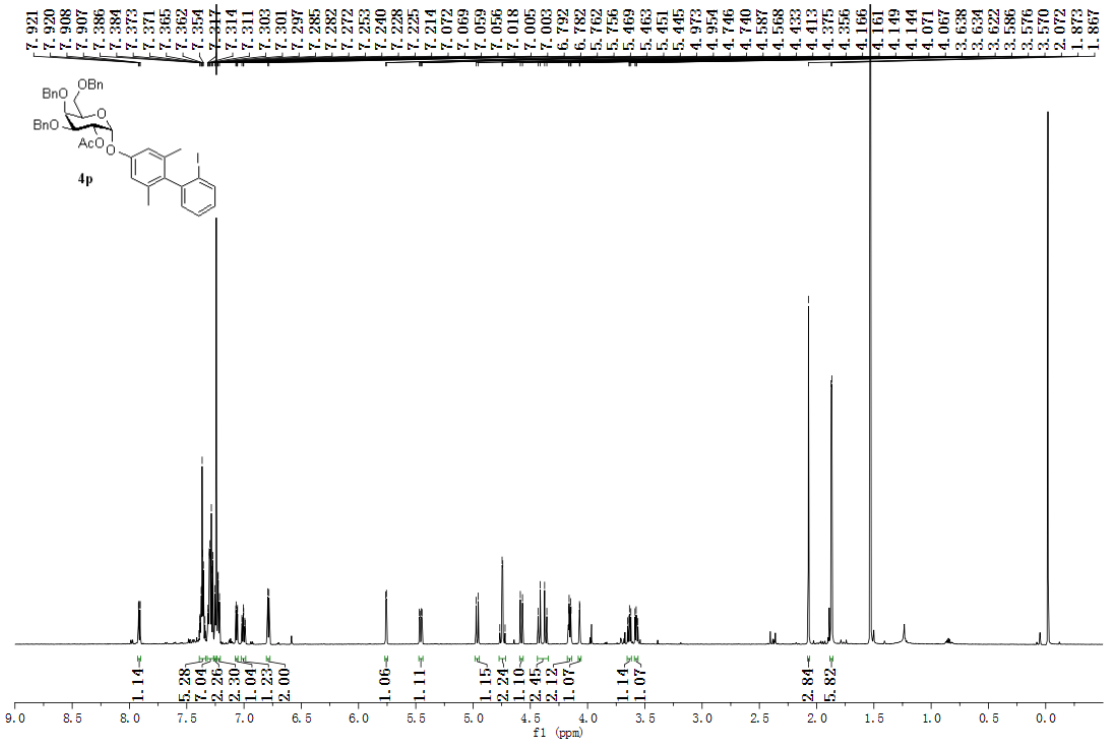


Figure S50. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4p(α)**

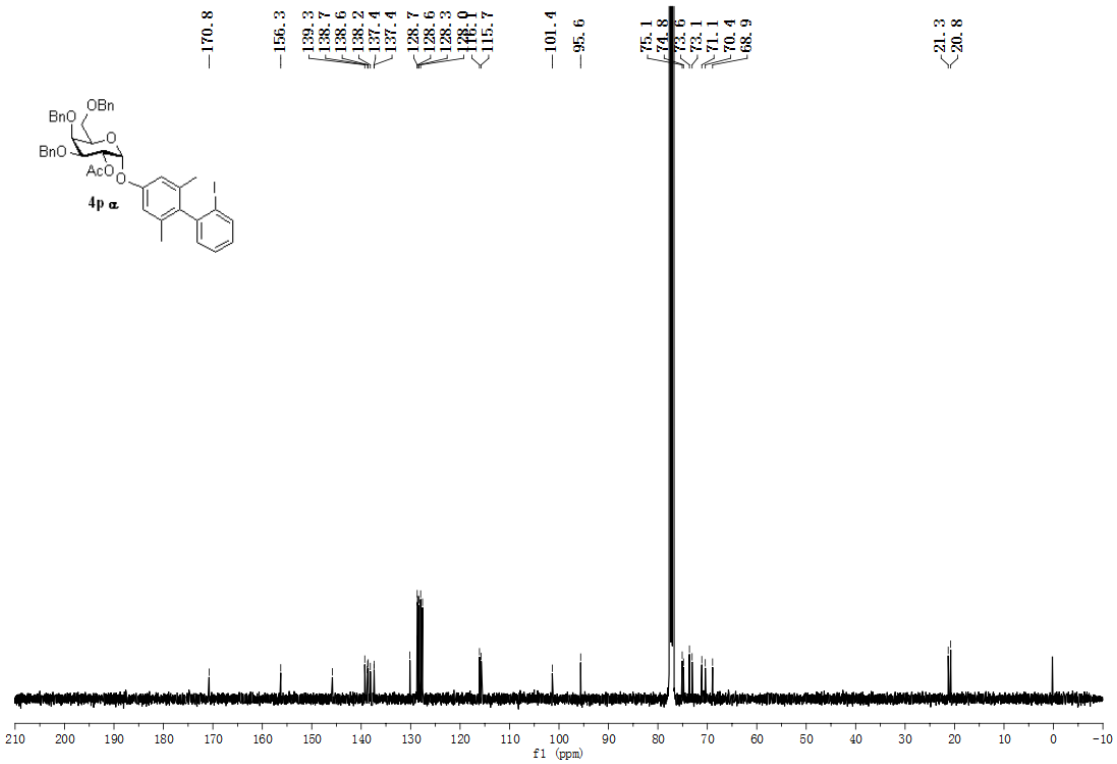


Figure S51. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4p(α)**

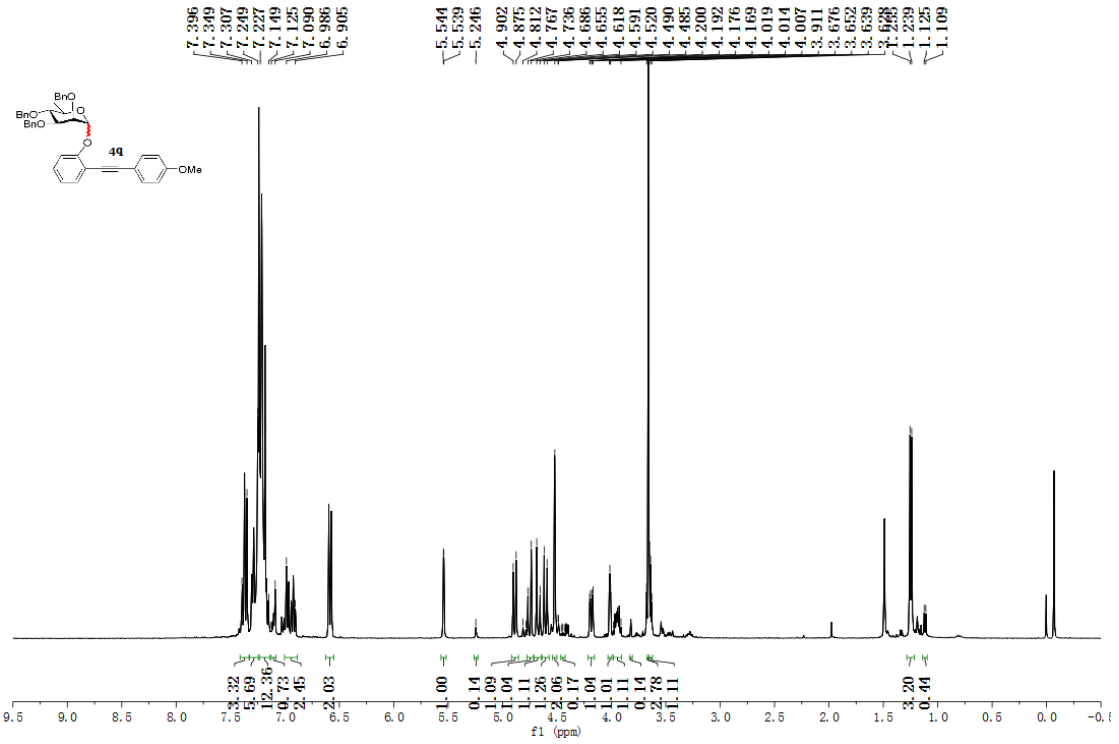


Figure S52. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4q**

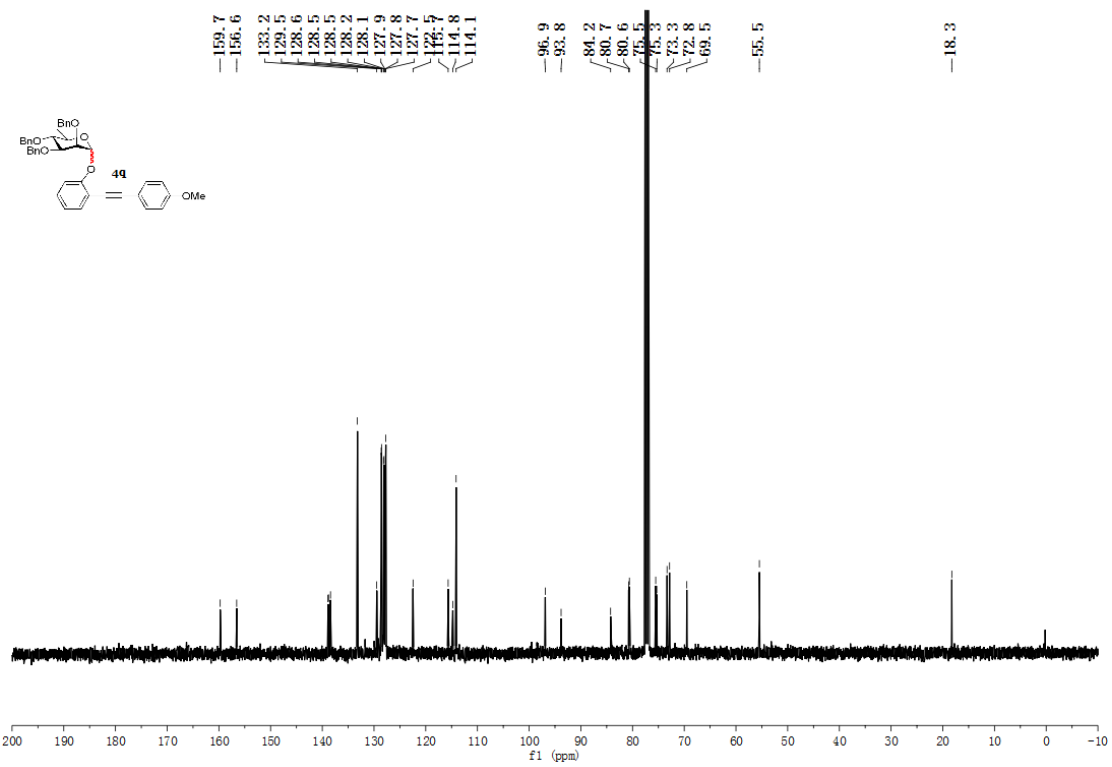


Figure S53. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4q**

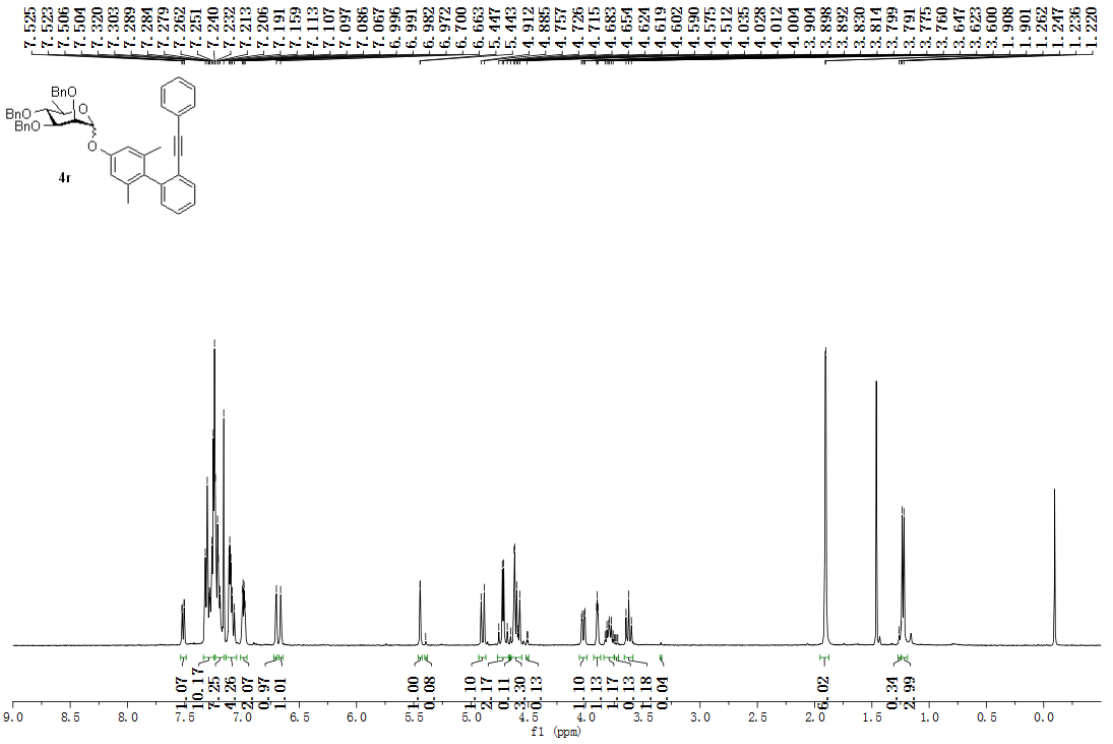


Figure S54. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4r**

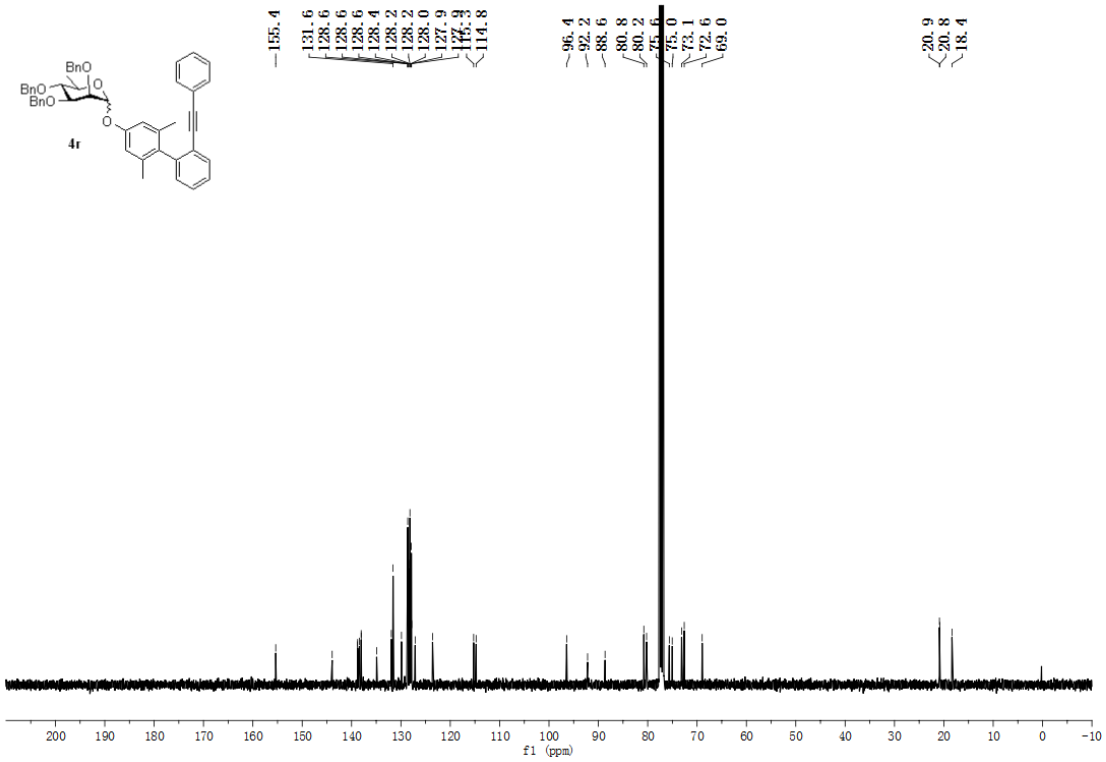


Figure S55. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4r**

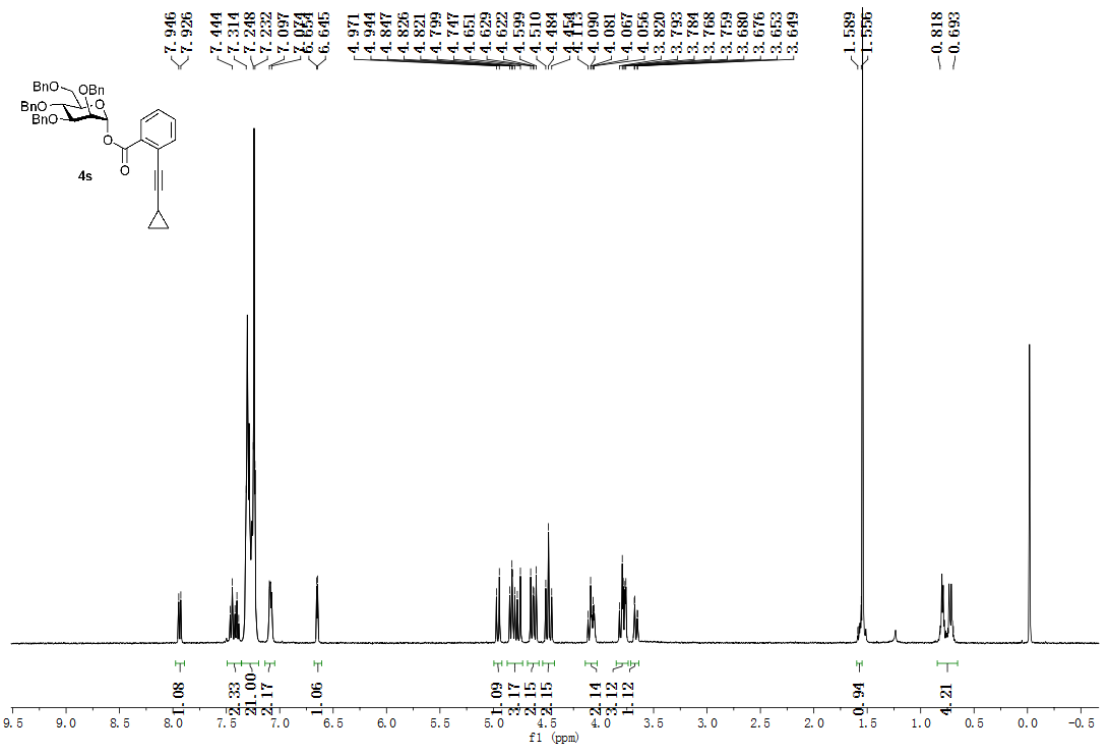


Figure S56. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4s**

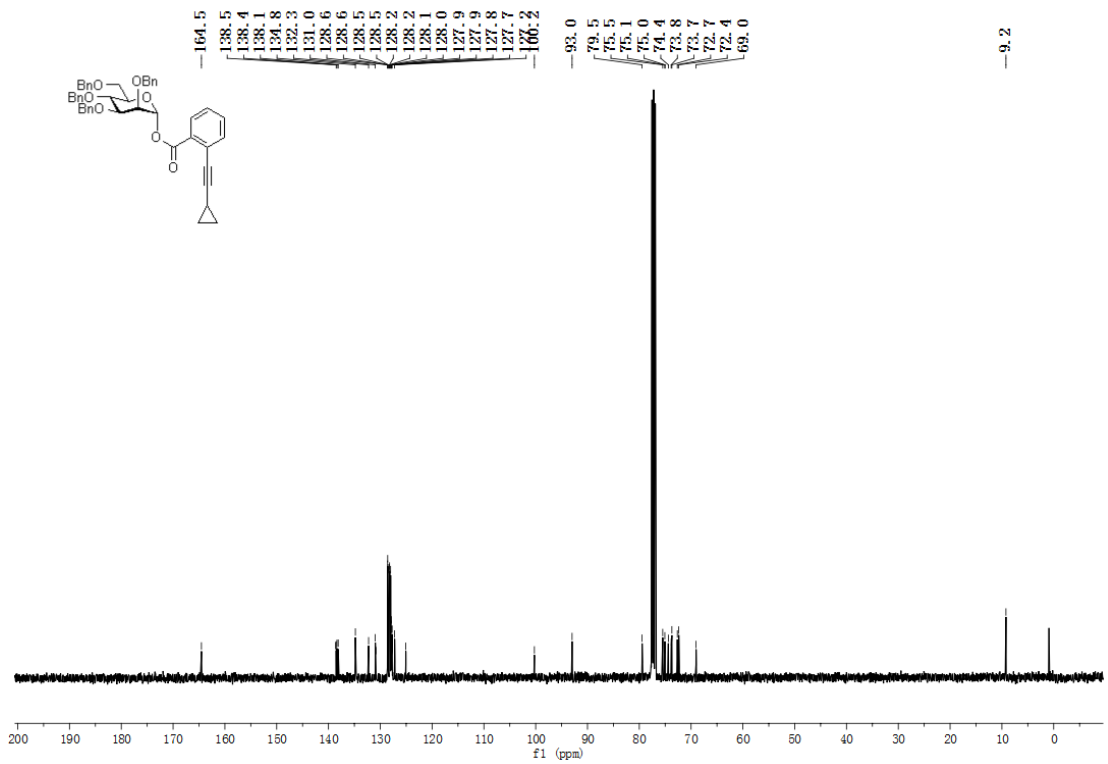


Figure S57. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4s**

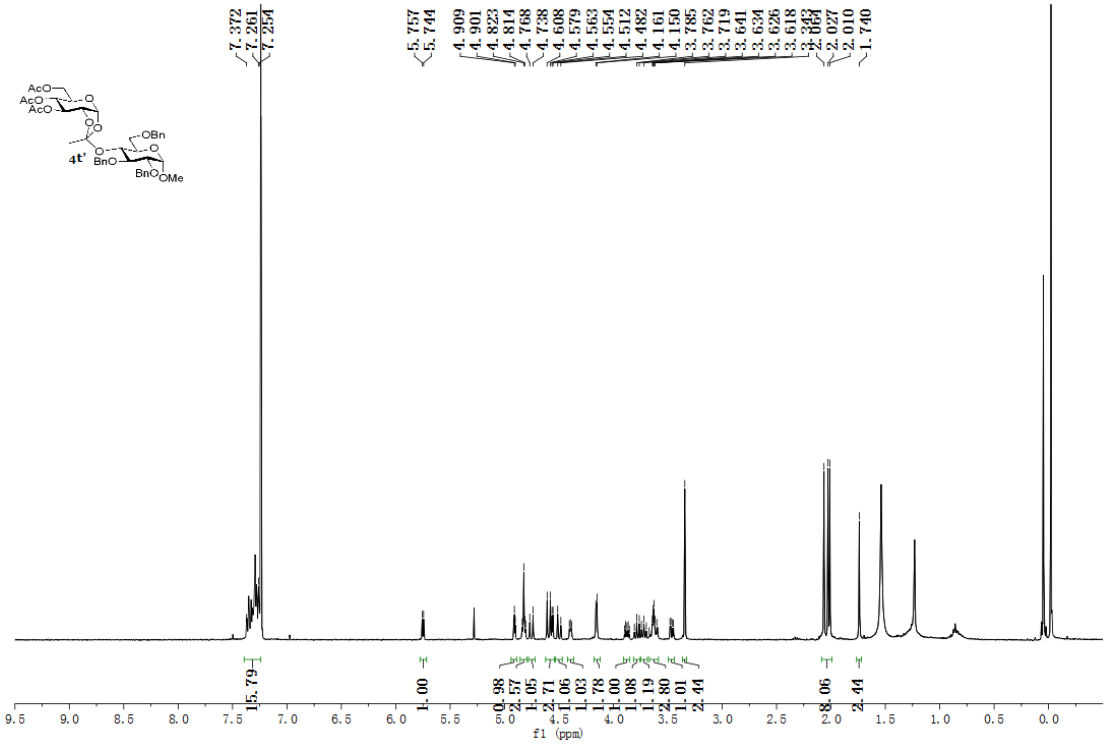


Figure S58. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4t´**

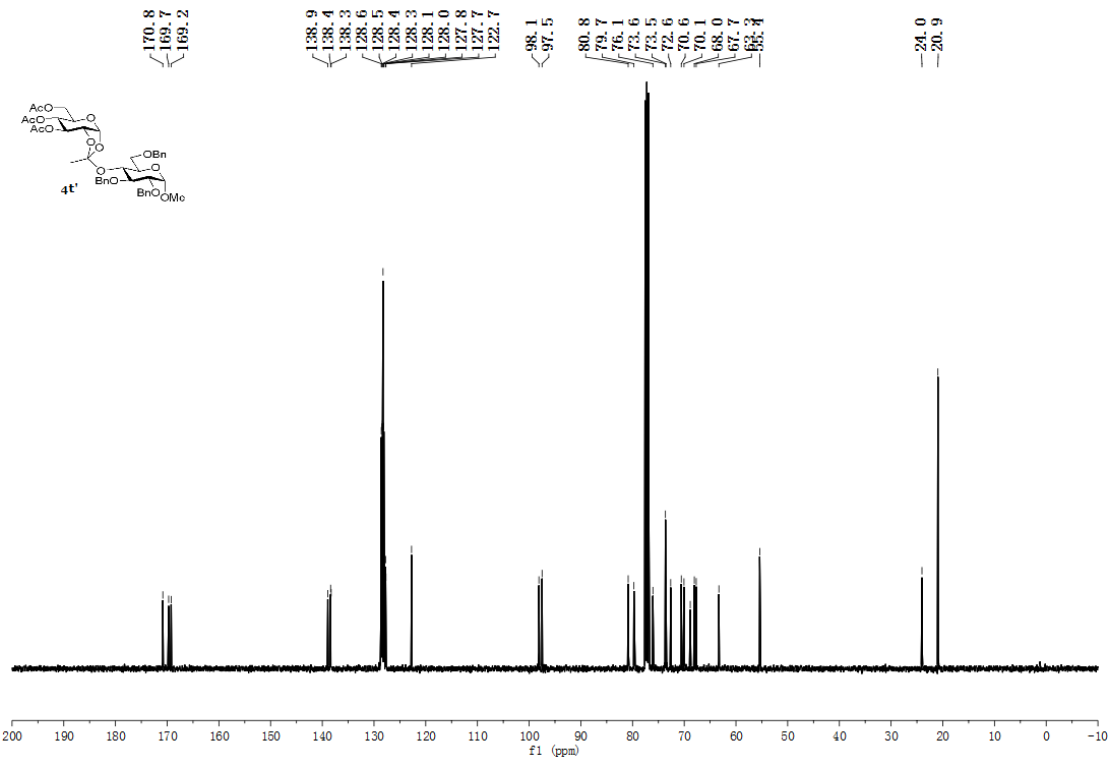


Figure S59. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4t´**

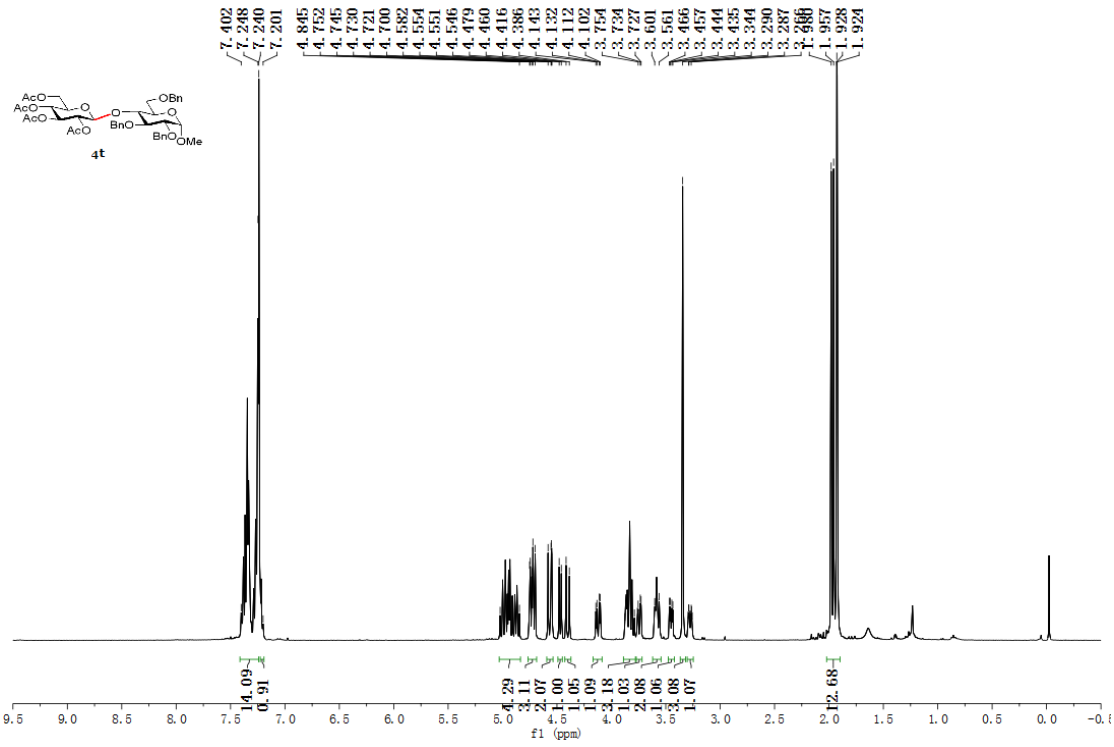


Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4t**

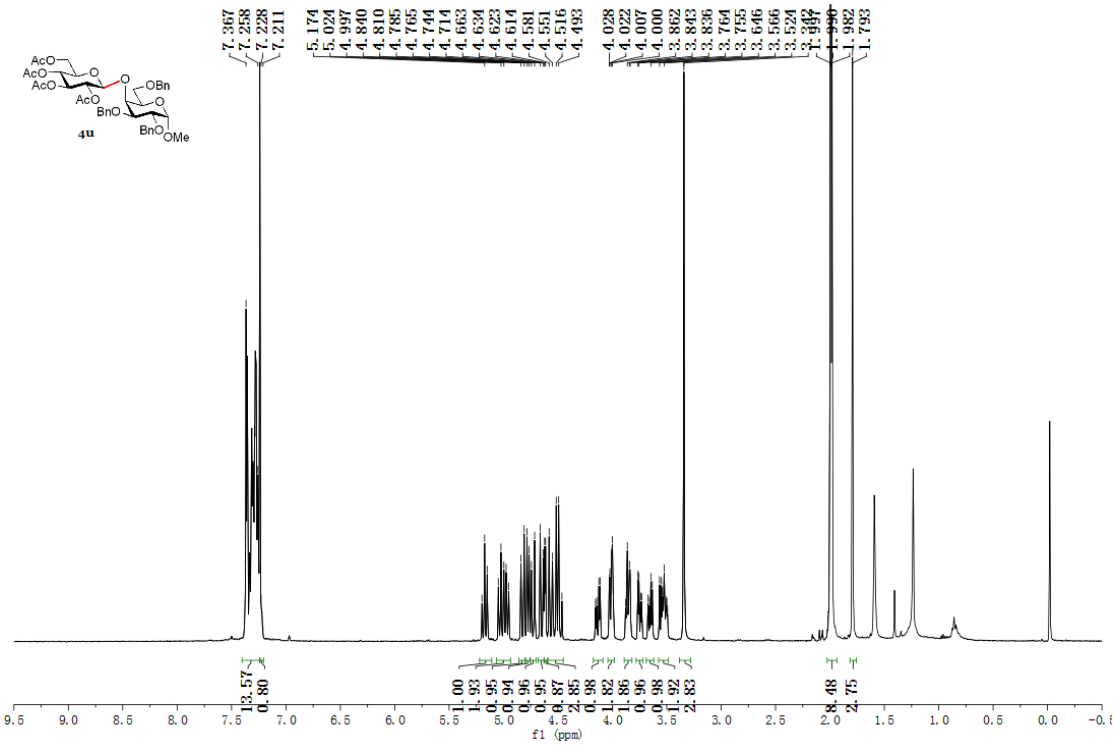


Figure S61. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4u**

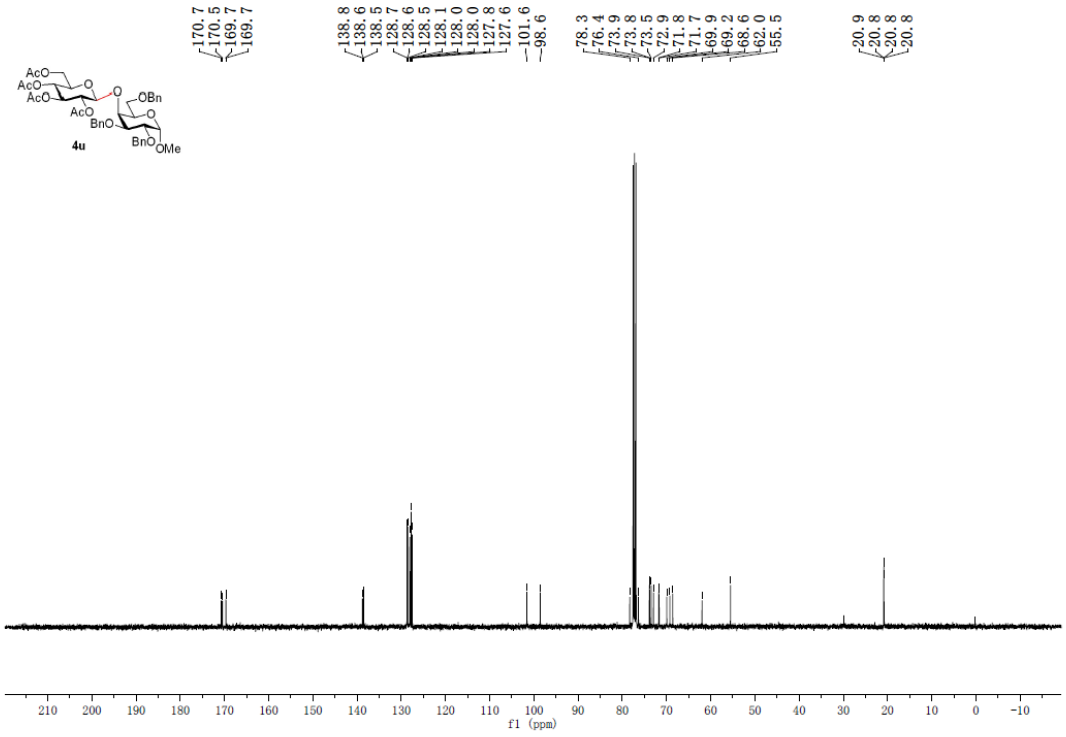


Figure S62. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4u**

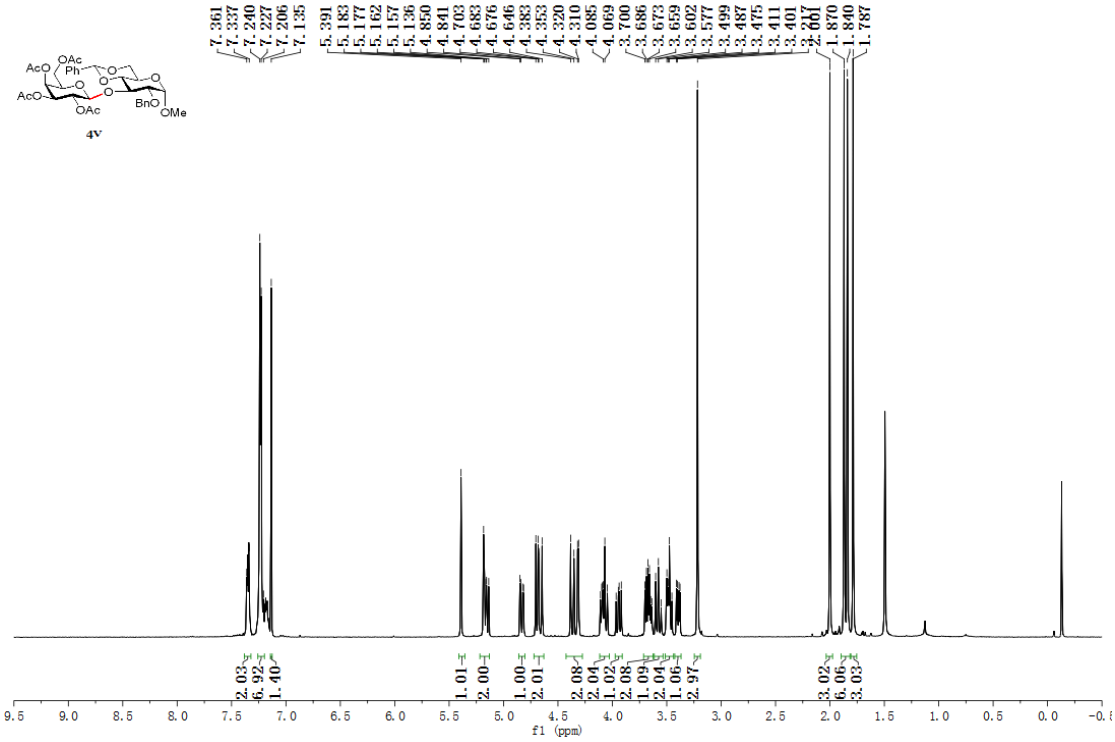


Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4v**

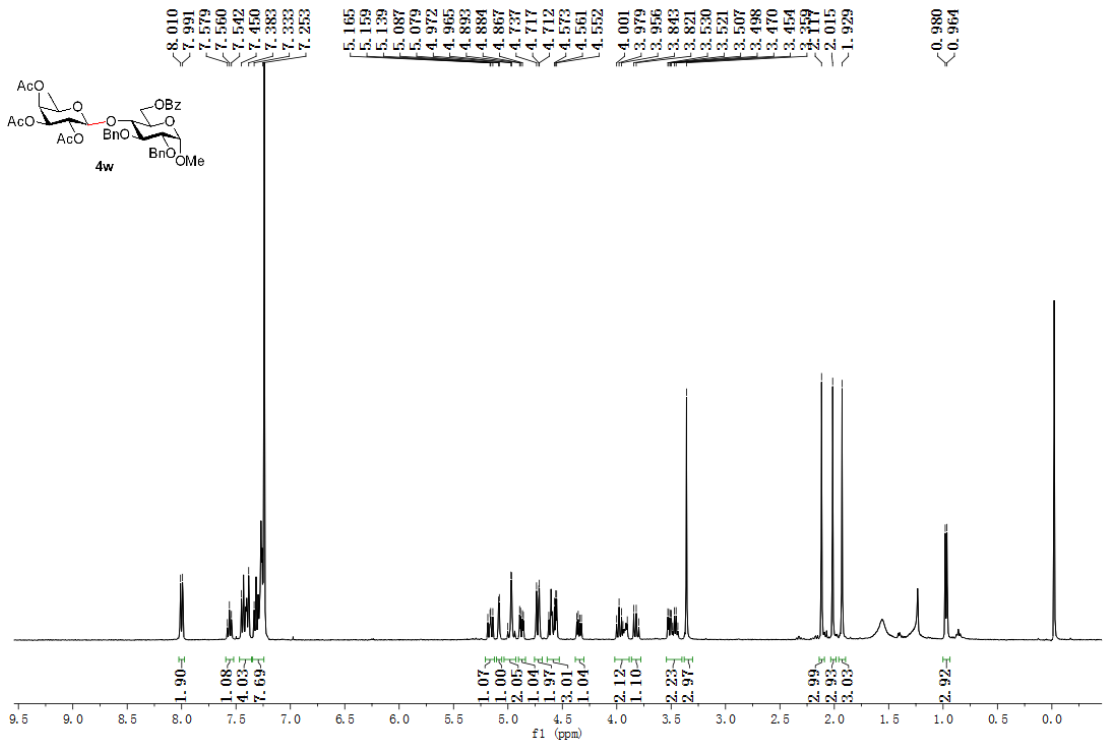


Figure S64. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4w**

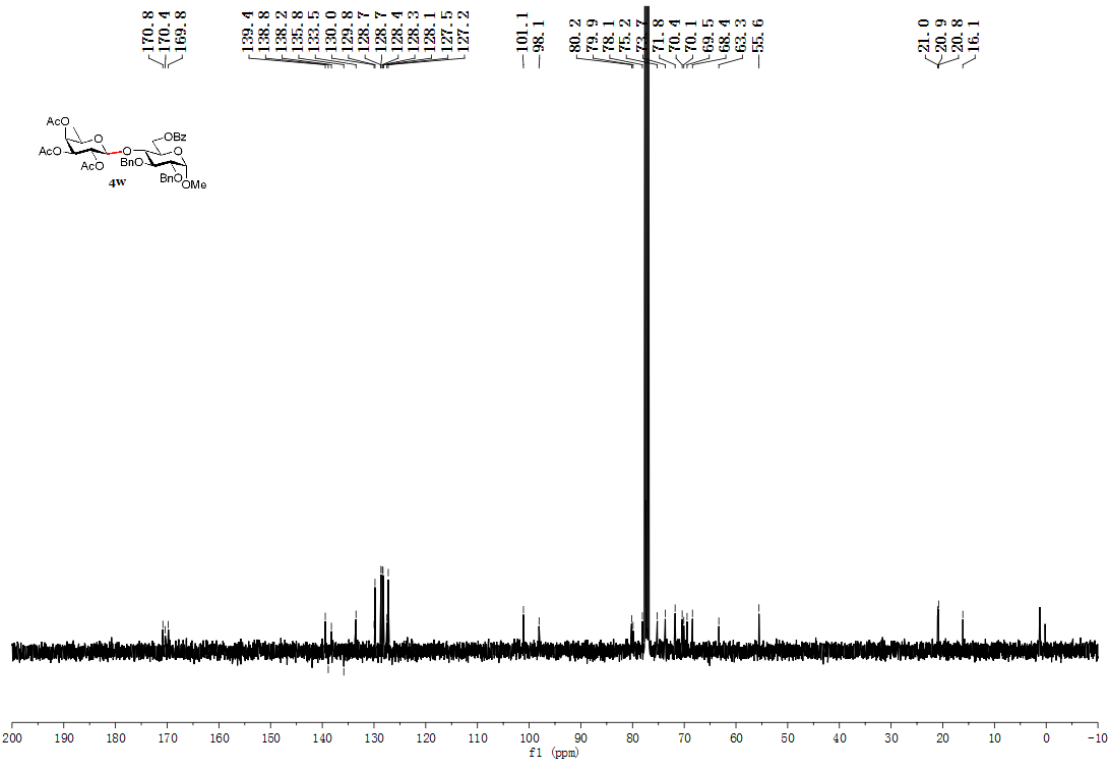


Figure S65. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4w**

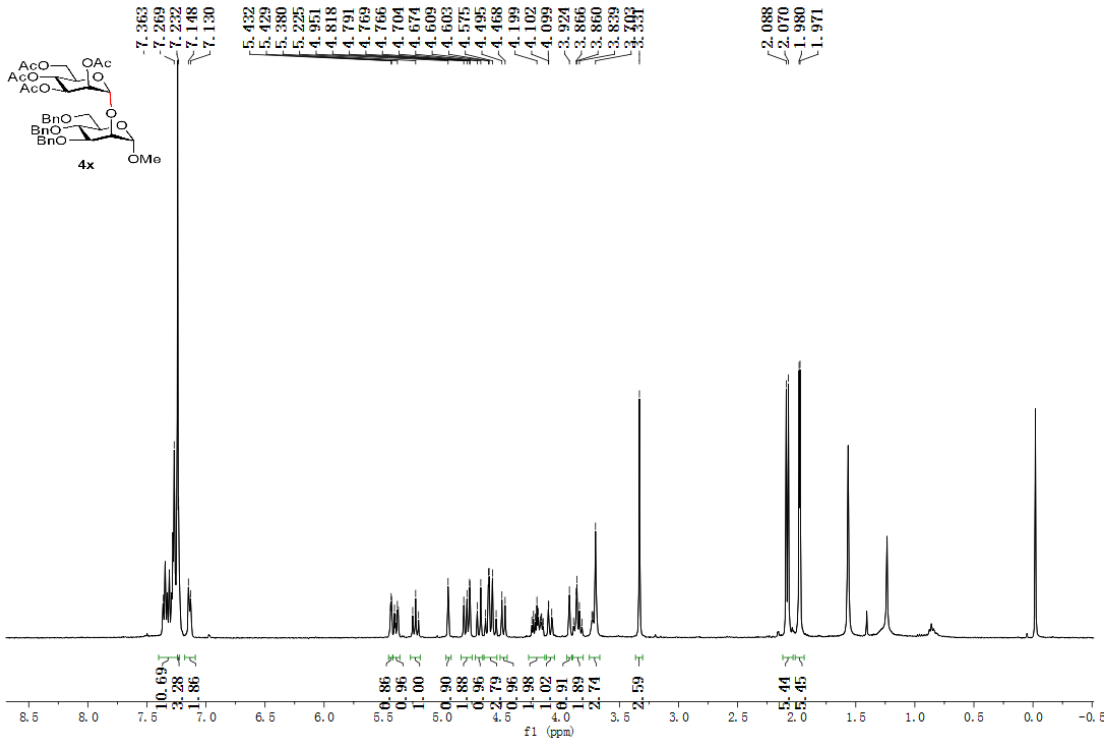


Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4x**

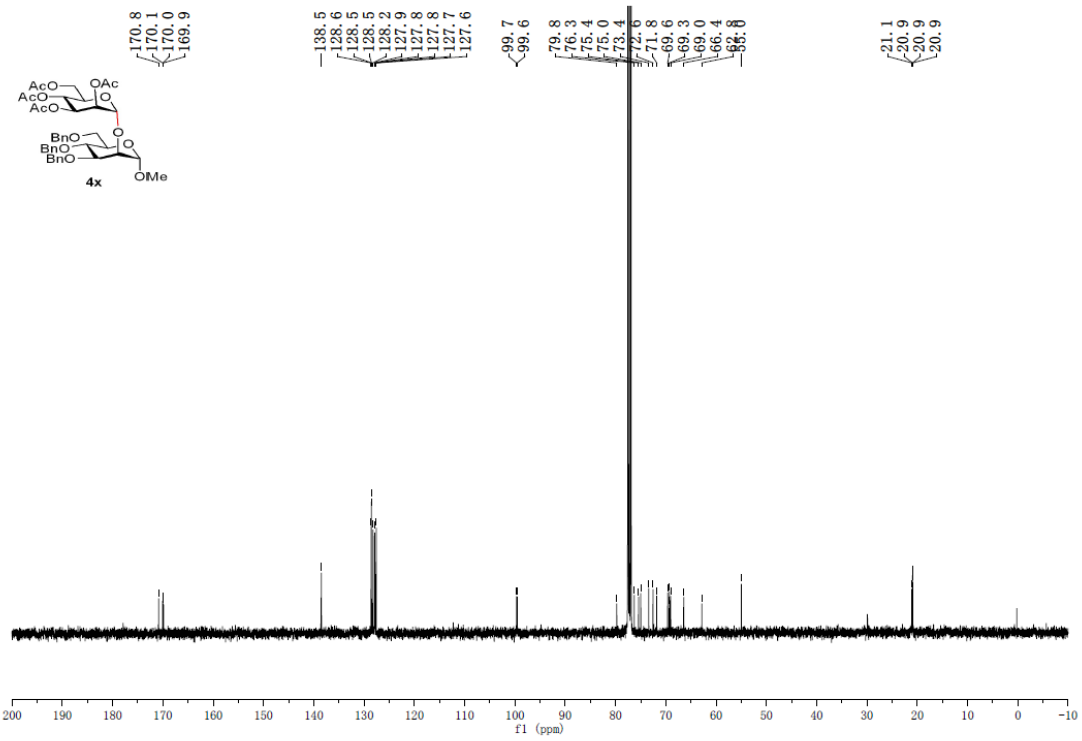


Figure S67. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4x**

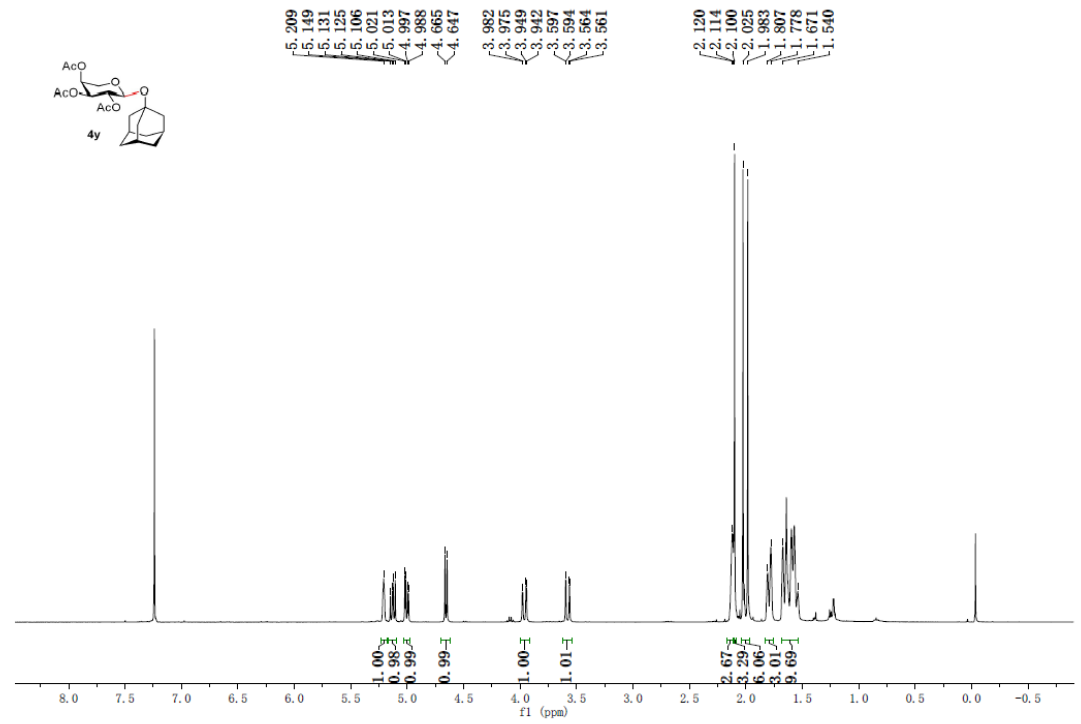


Figure S68. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4y**

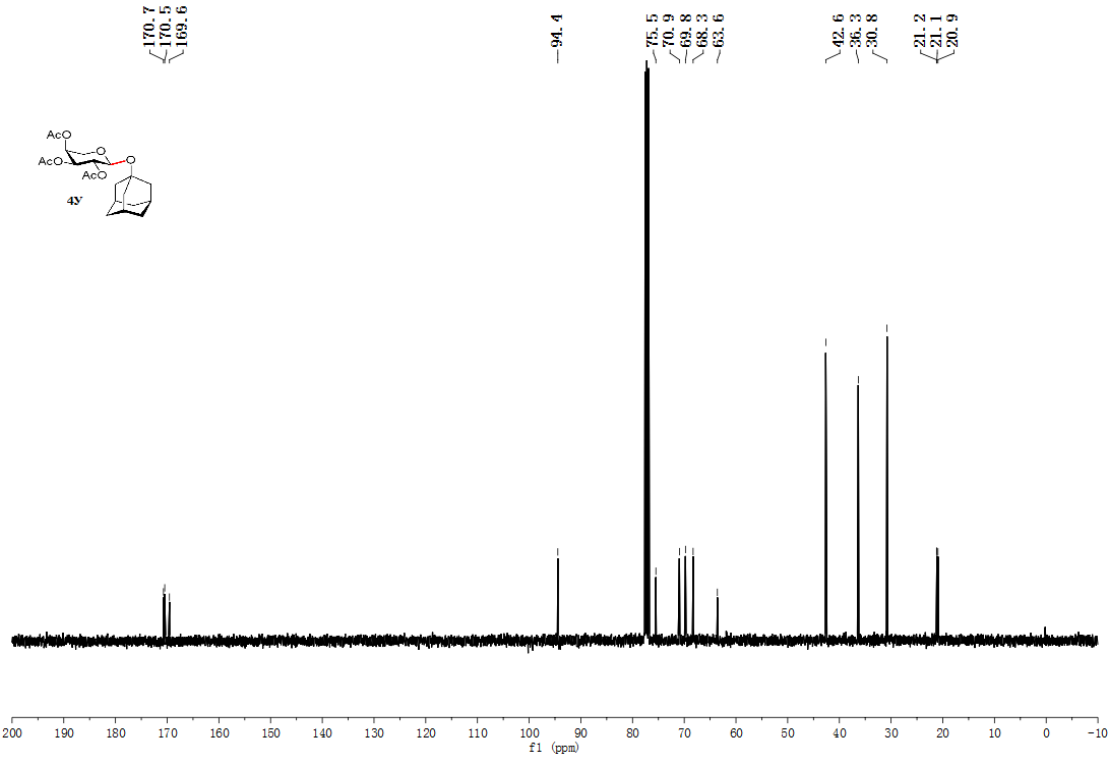


Figure S69. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4y**

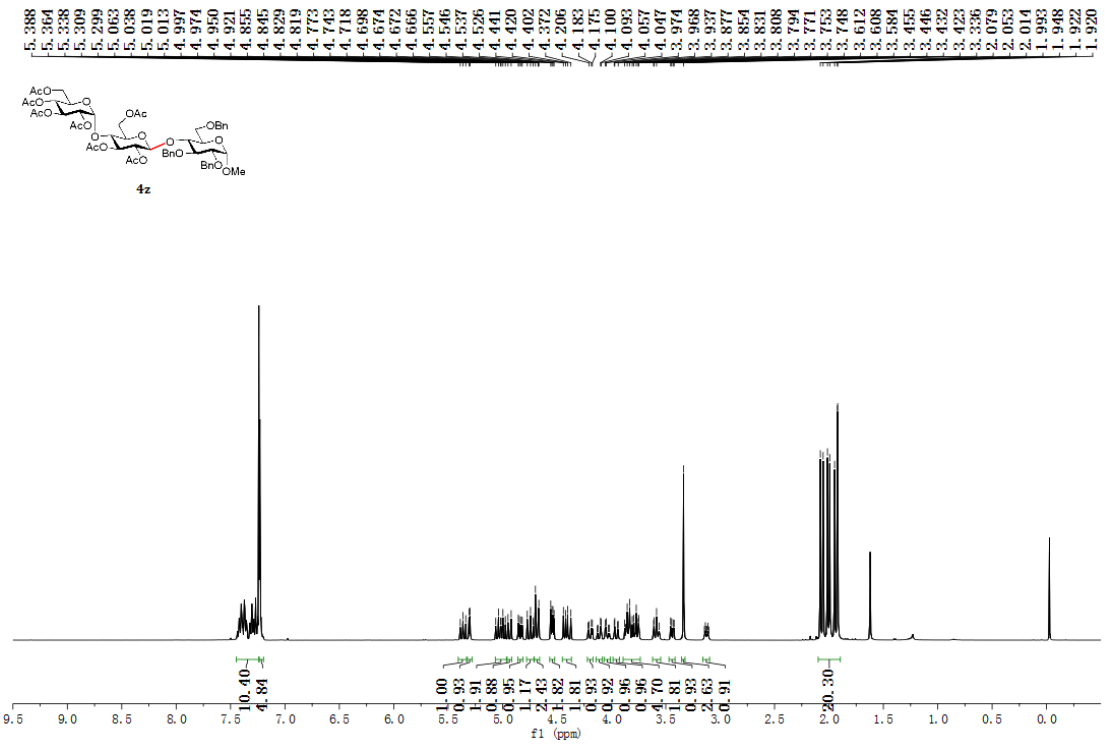


Figure S70. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4z**

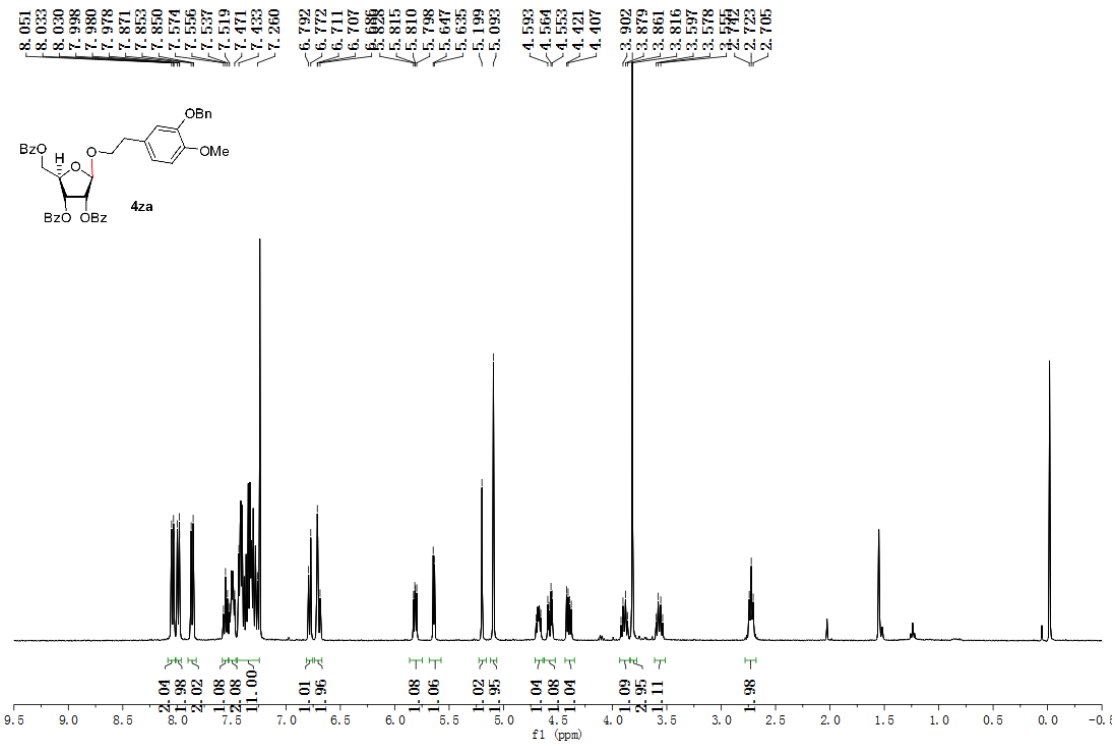


Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4za**

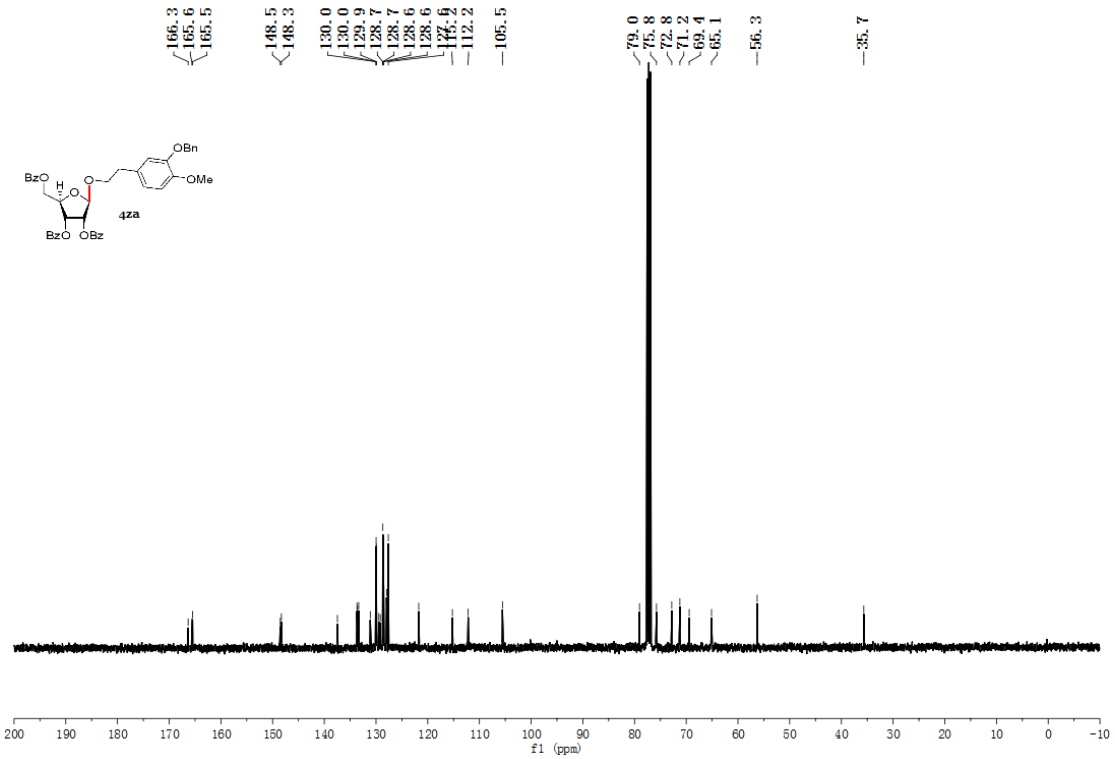


Figure S72. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4za**

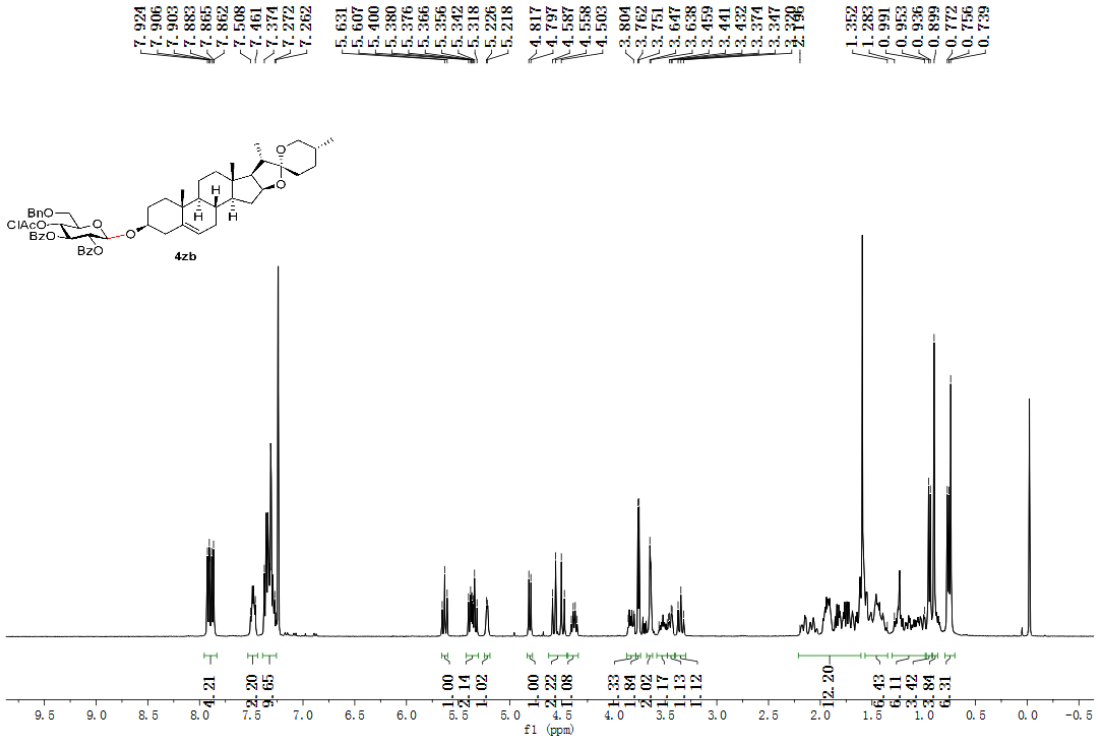


Figure S73. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4zb**

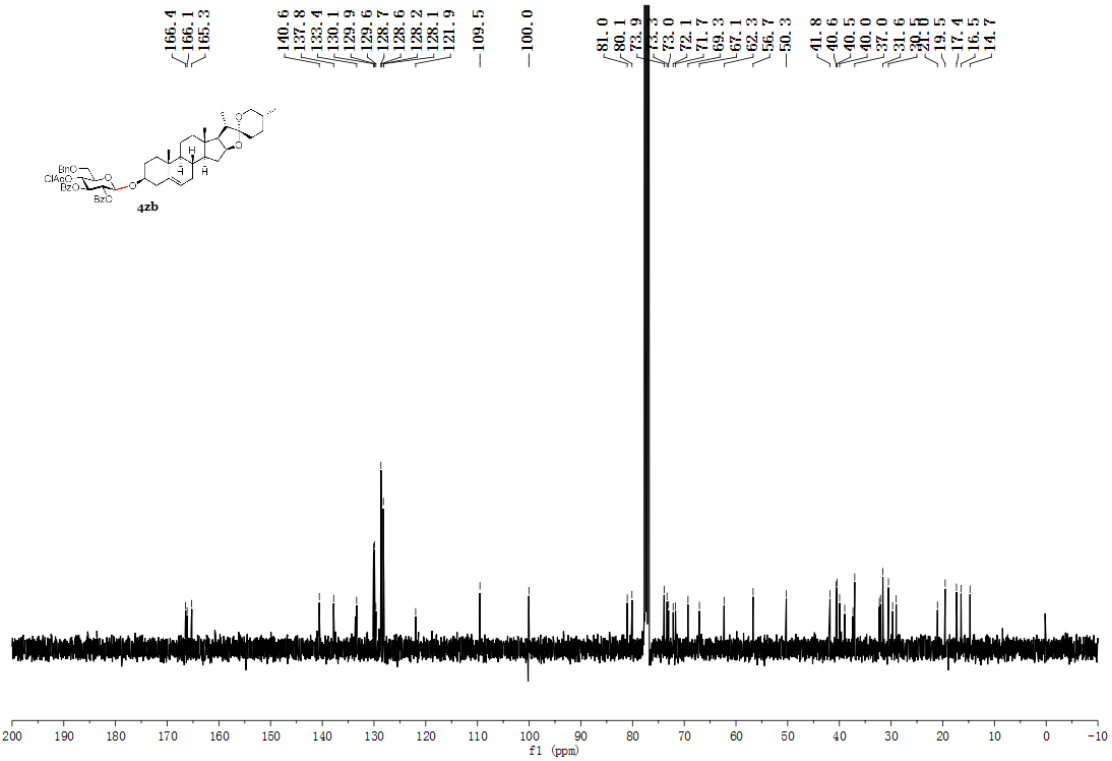


Figure S74. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4zb**

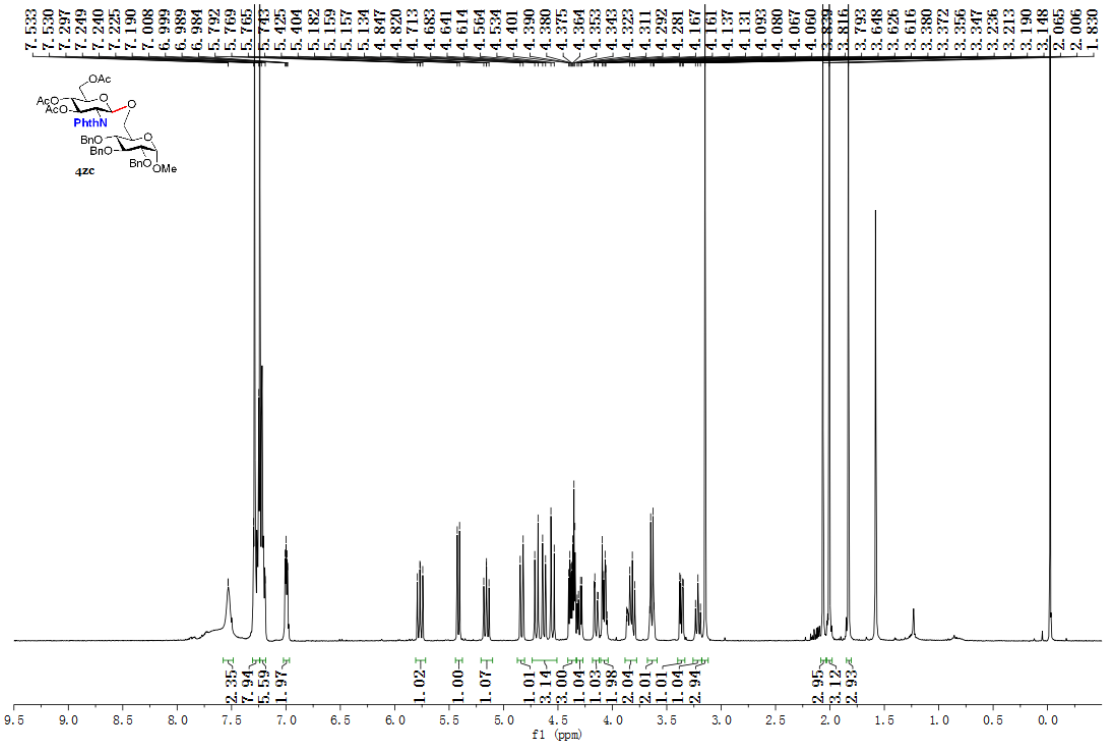


Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4zc**

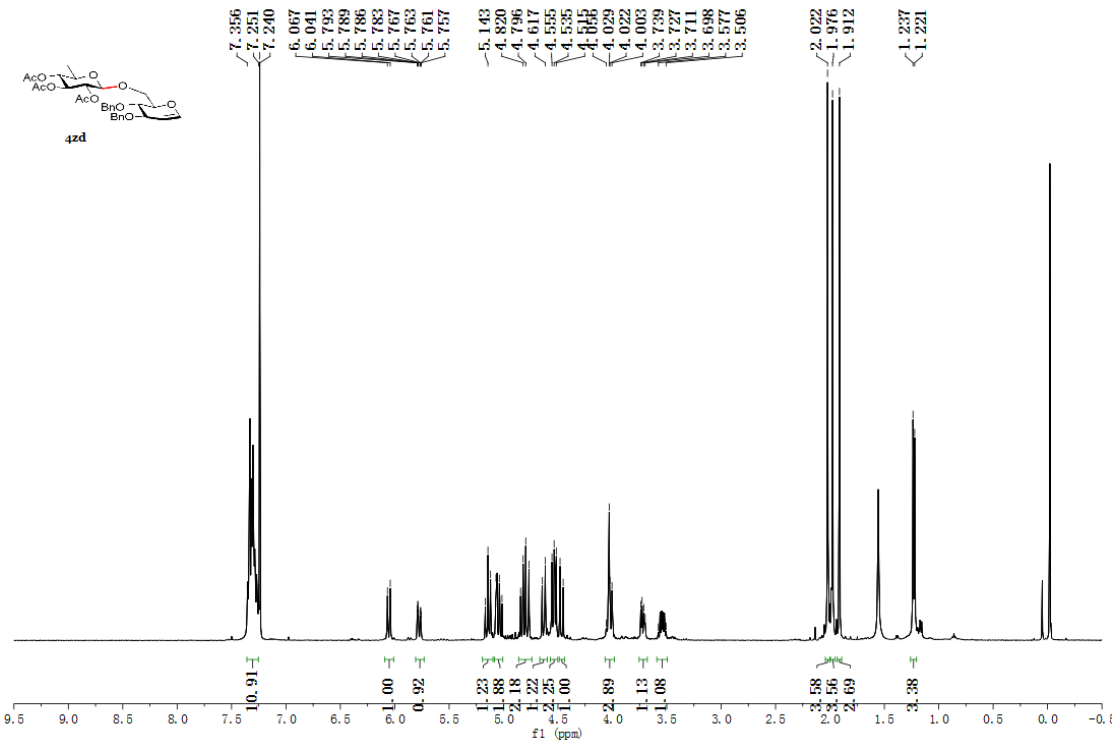


Figure S76. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4zd**

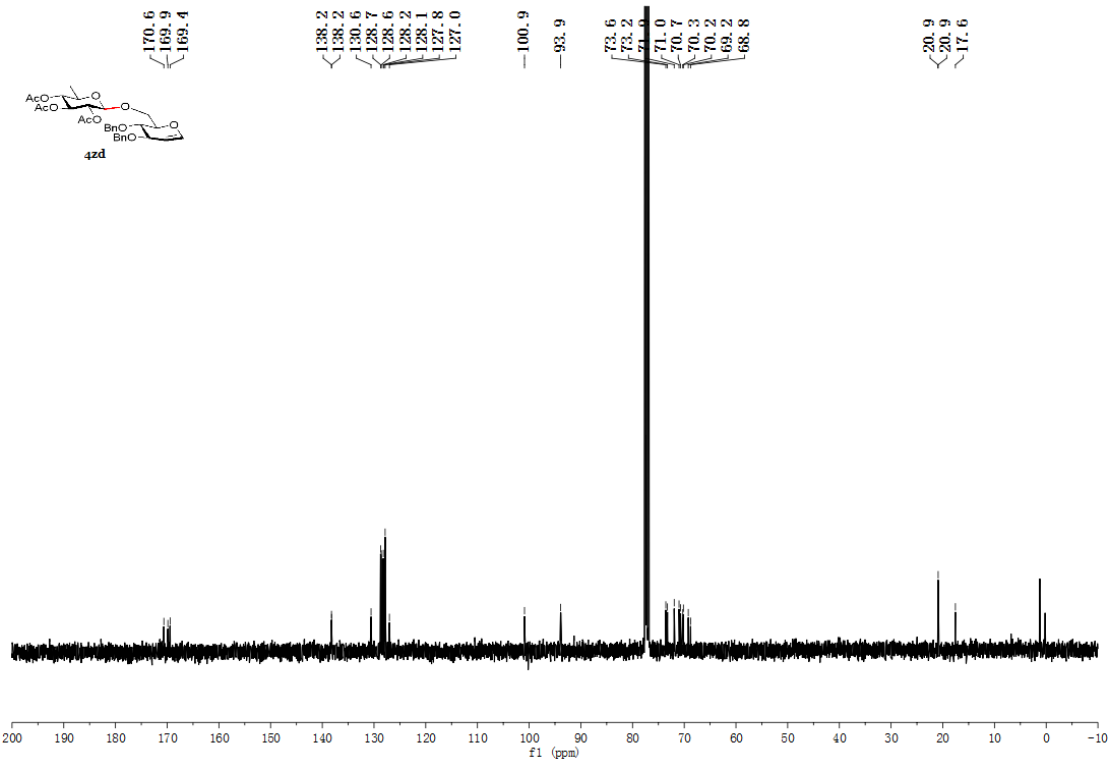


Figure S77. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4zd**

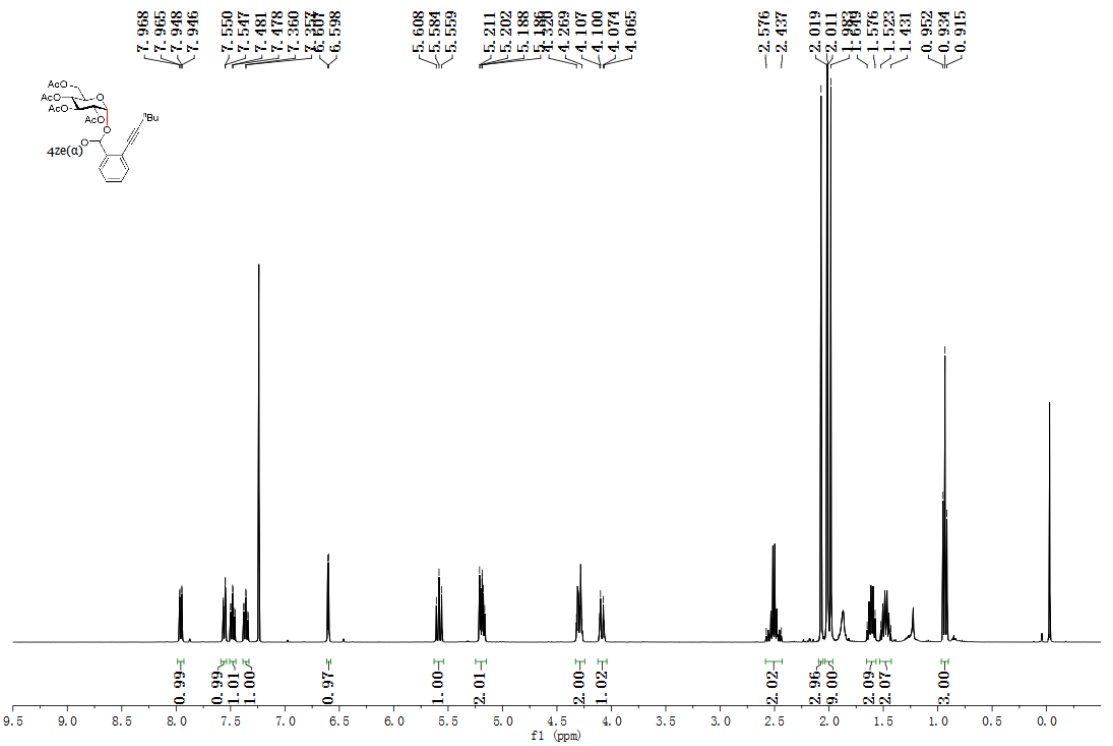


Figure S78. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ze(α)**

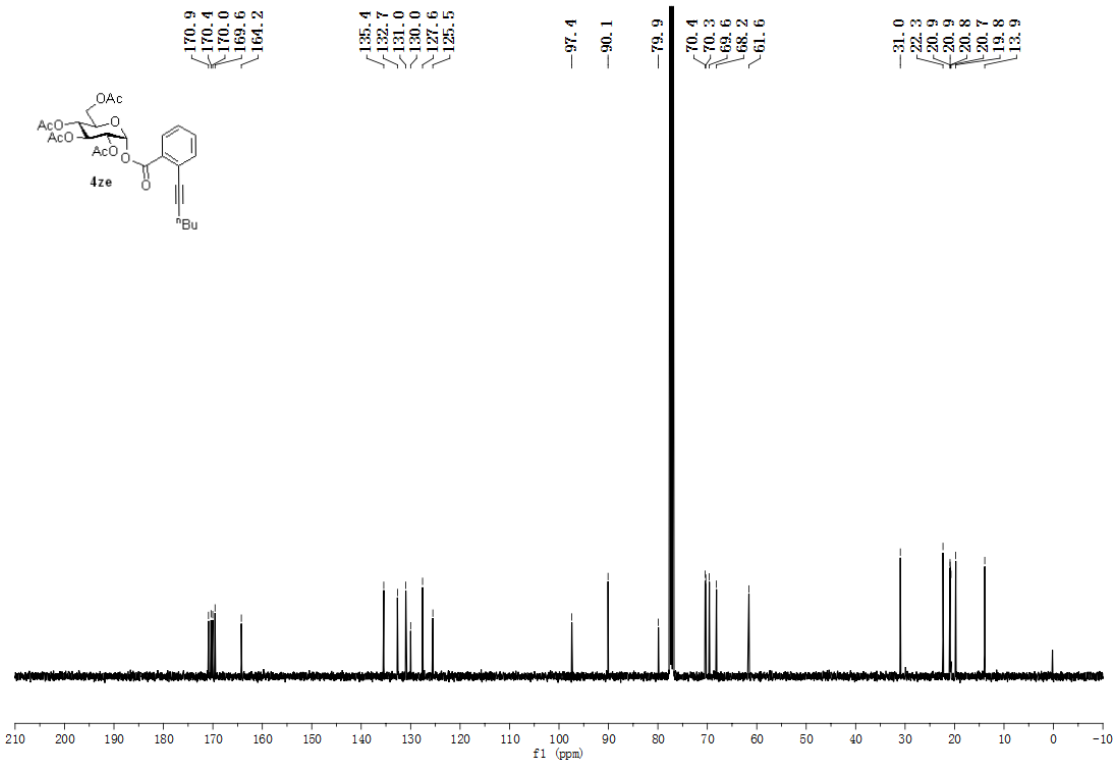


Figure S79. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4ze(α)**

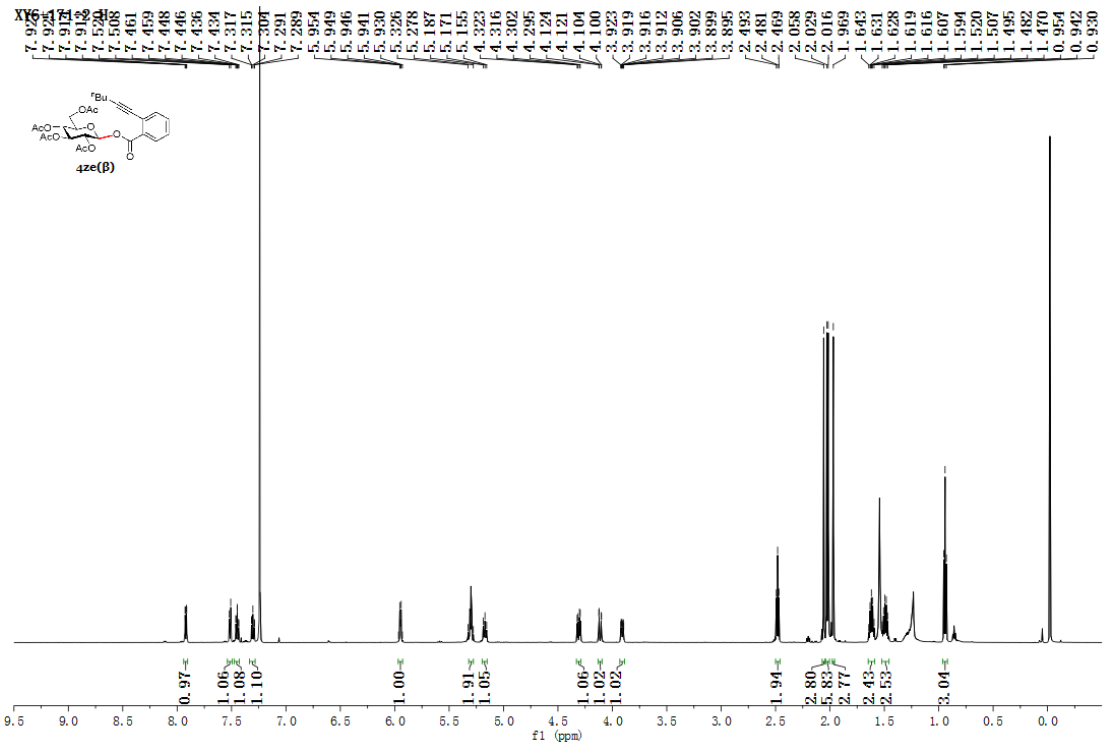


Figure S80. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ze(β)**

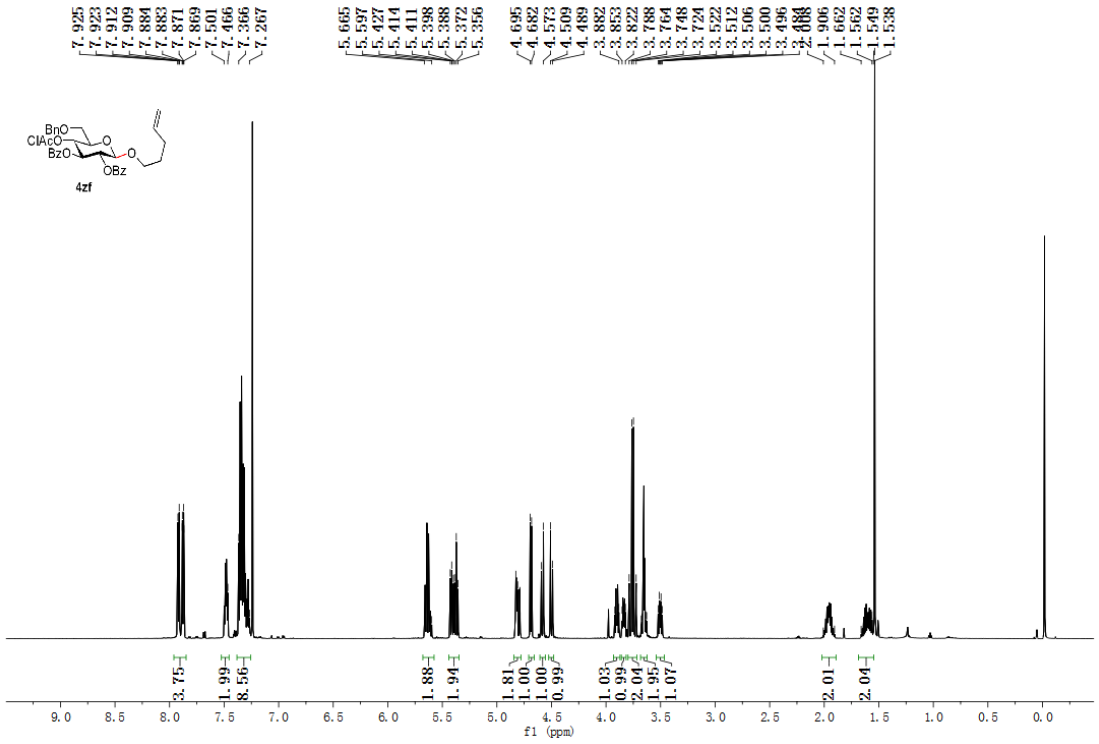


Figure S81. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4zf**

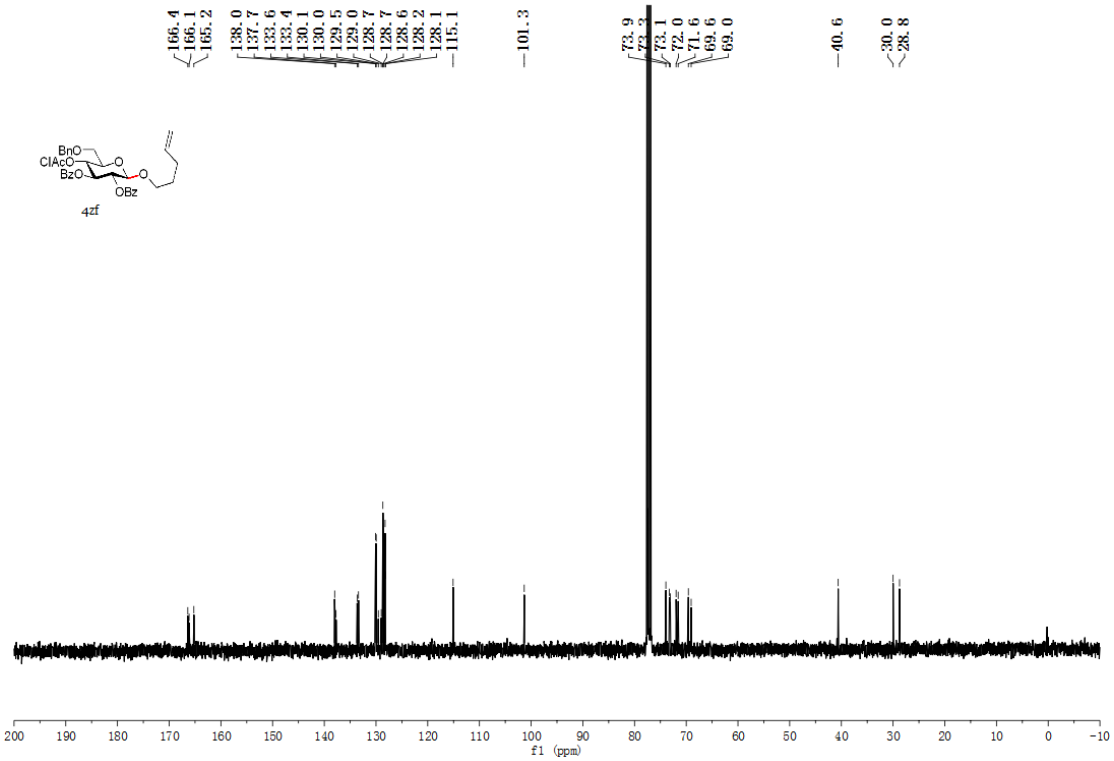


Figure S82. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4zf**

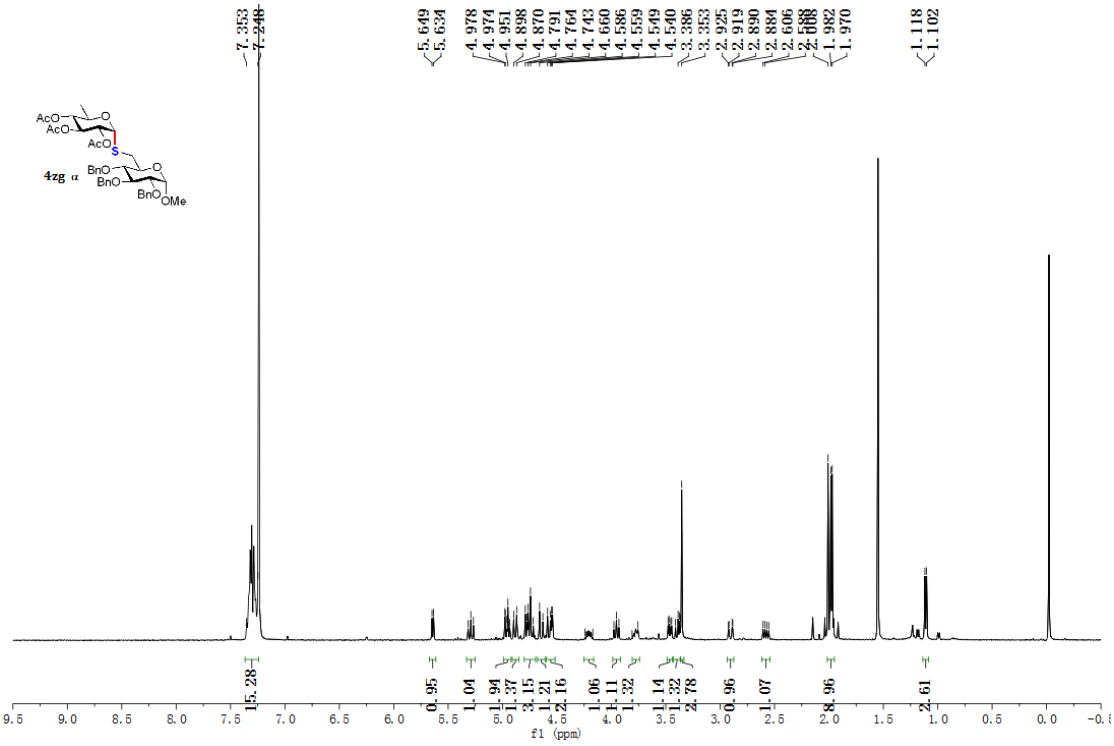


Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4zg(α)**

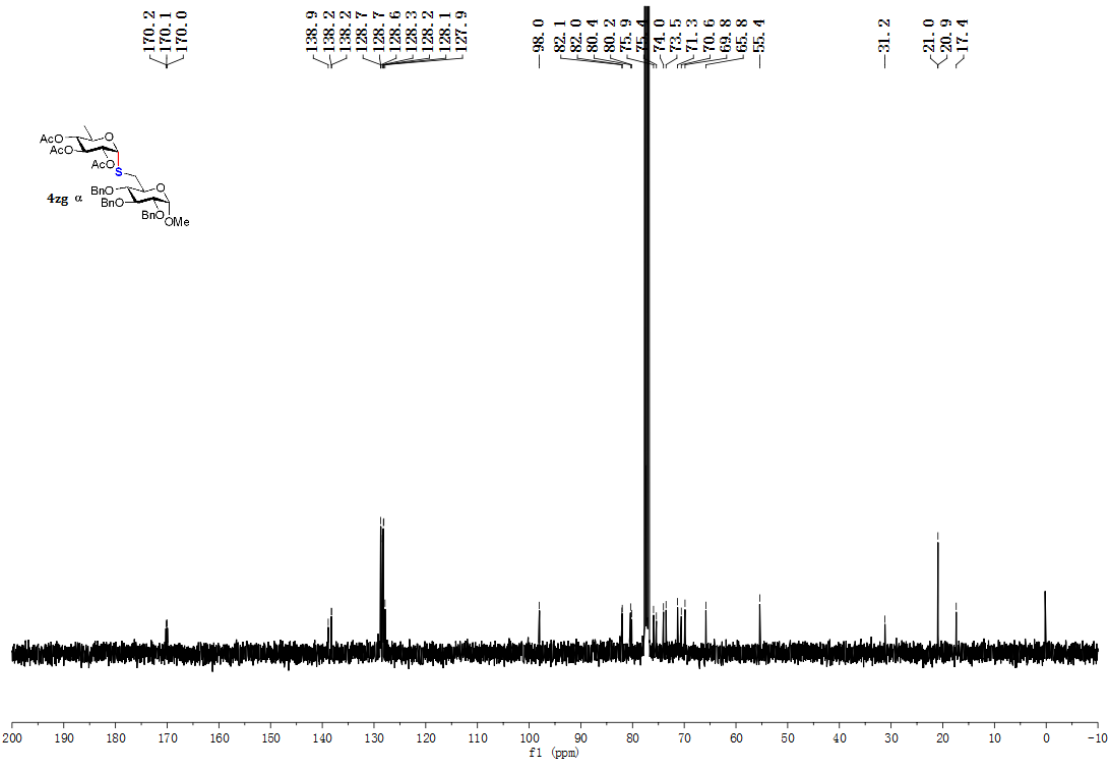


Figure S84. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4zg(α)**

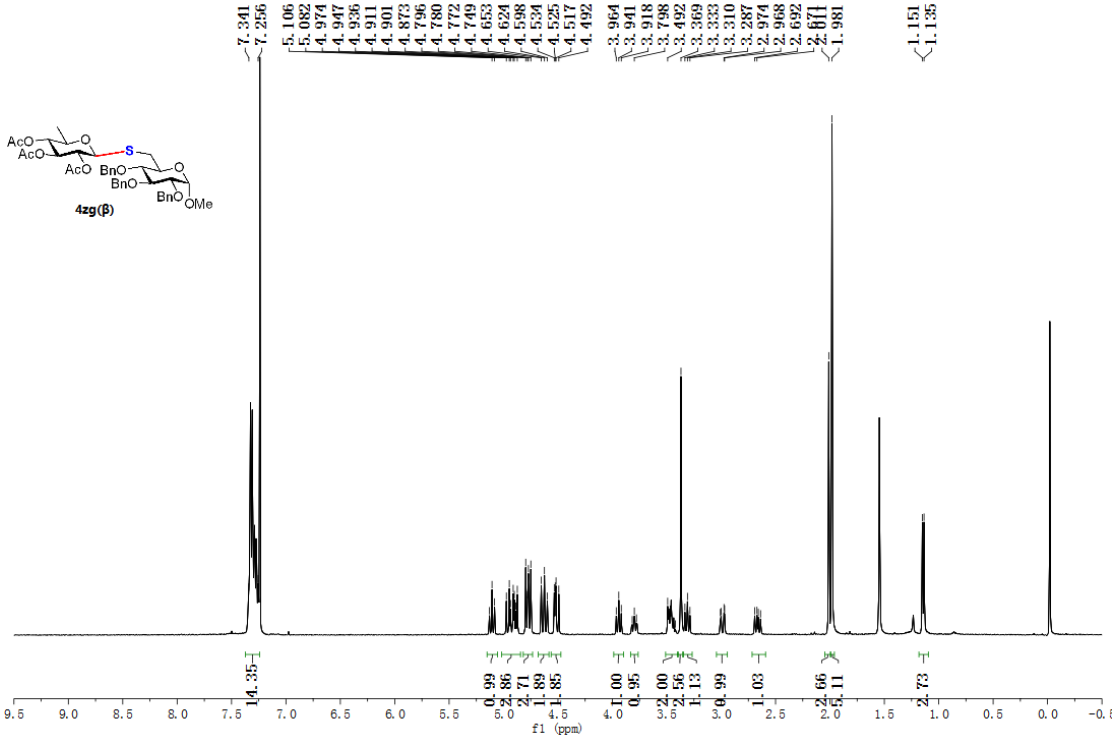


Figure S85. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4zg(β)**

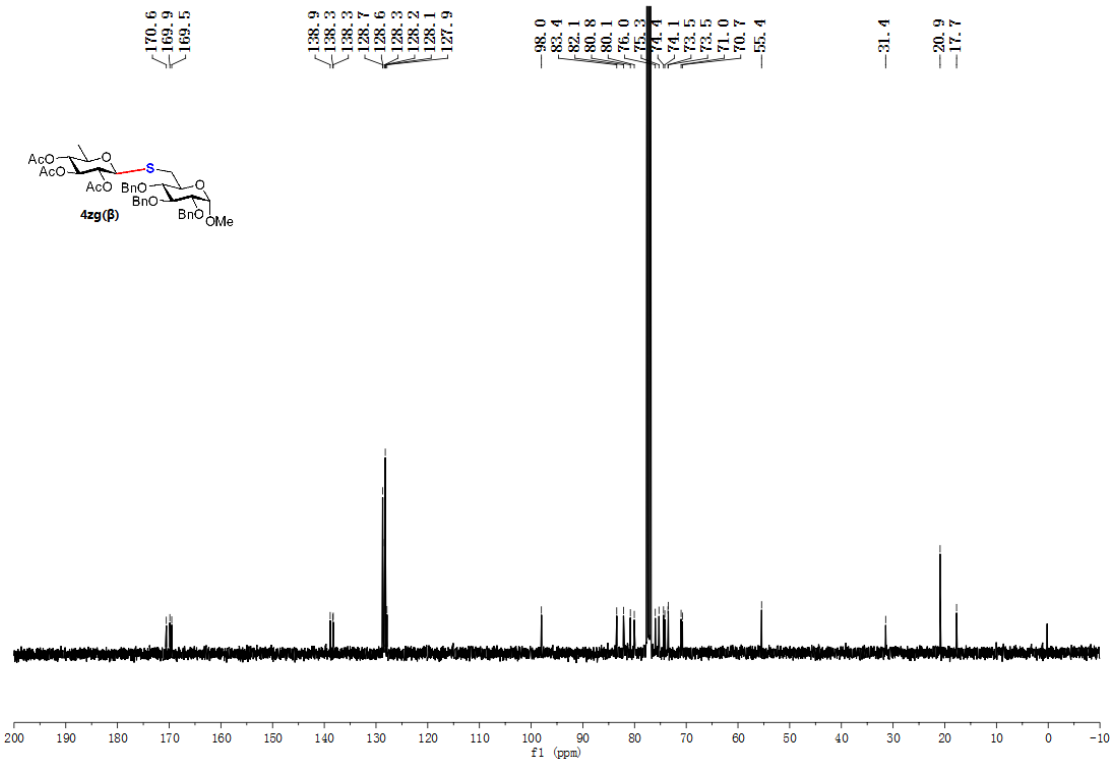


Figure S86. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4zg(β)**

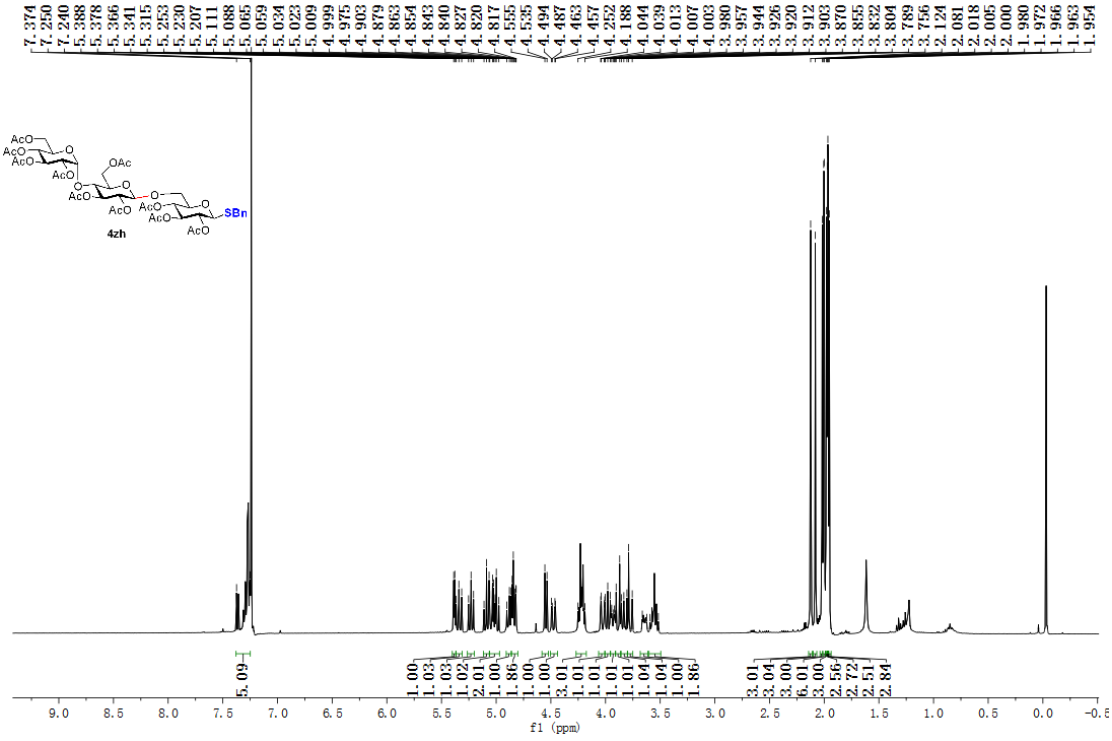


Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4zh**

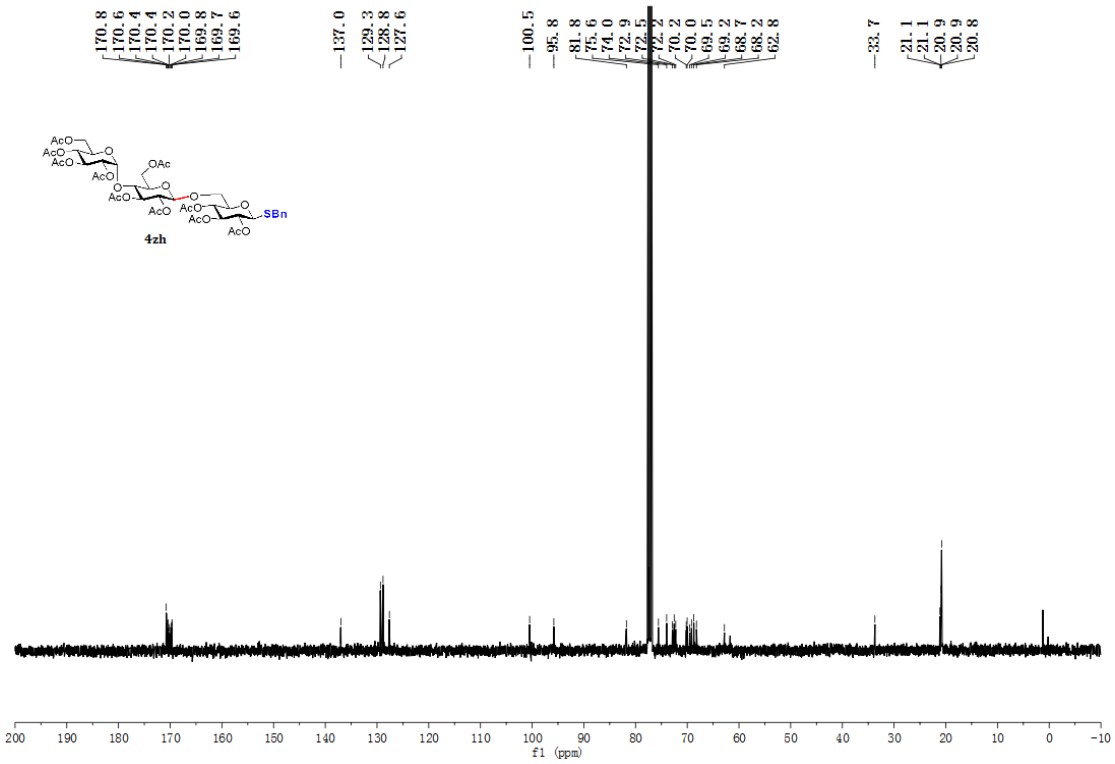


Figure S88. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4zh**

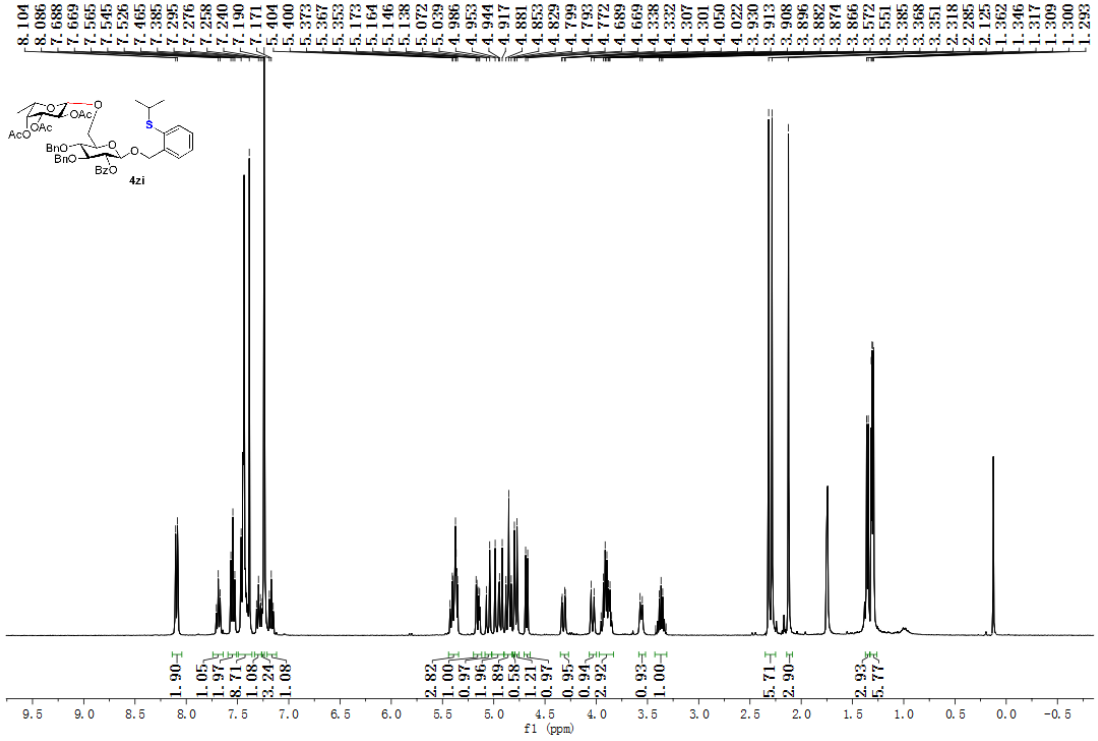


Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4zi**

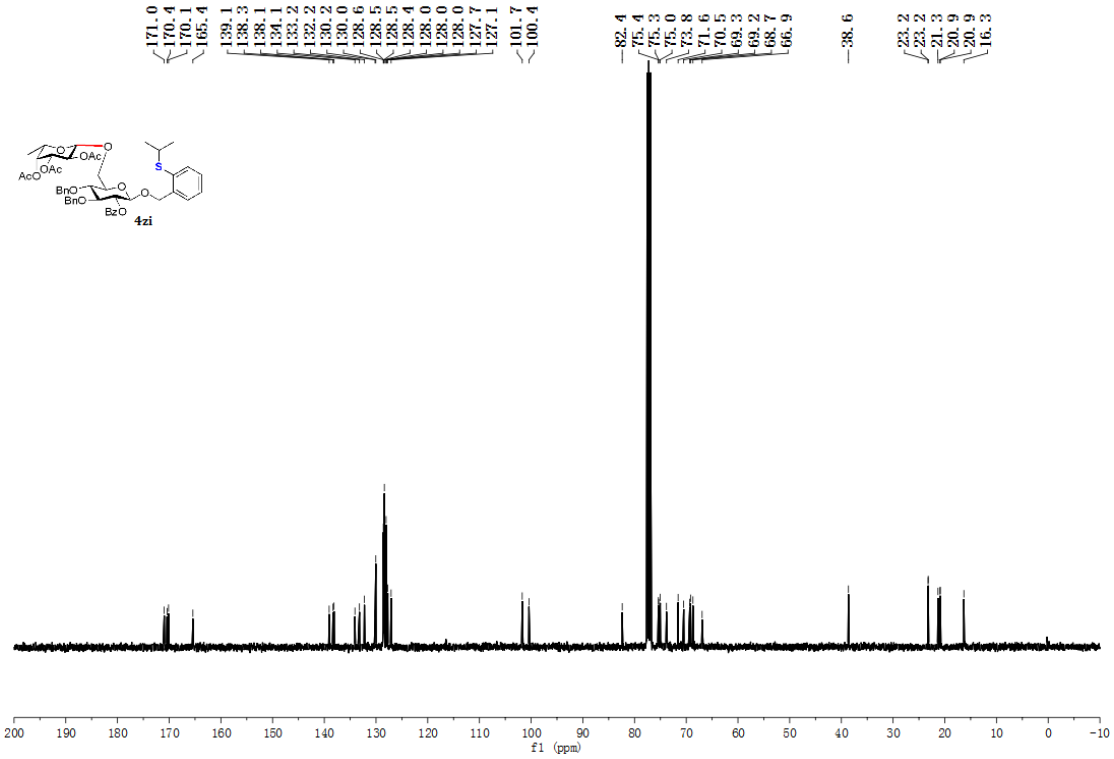


Figure S90. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4zi**

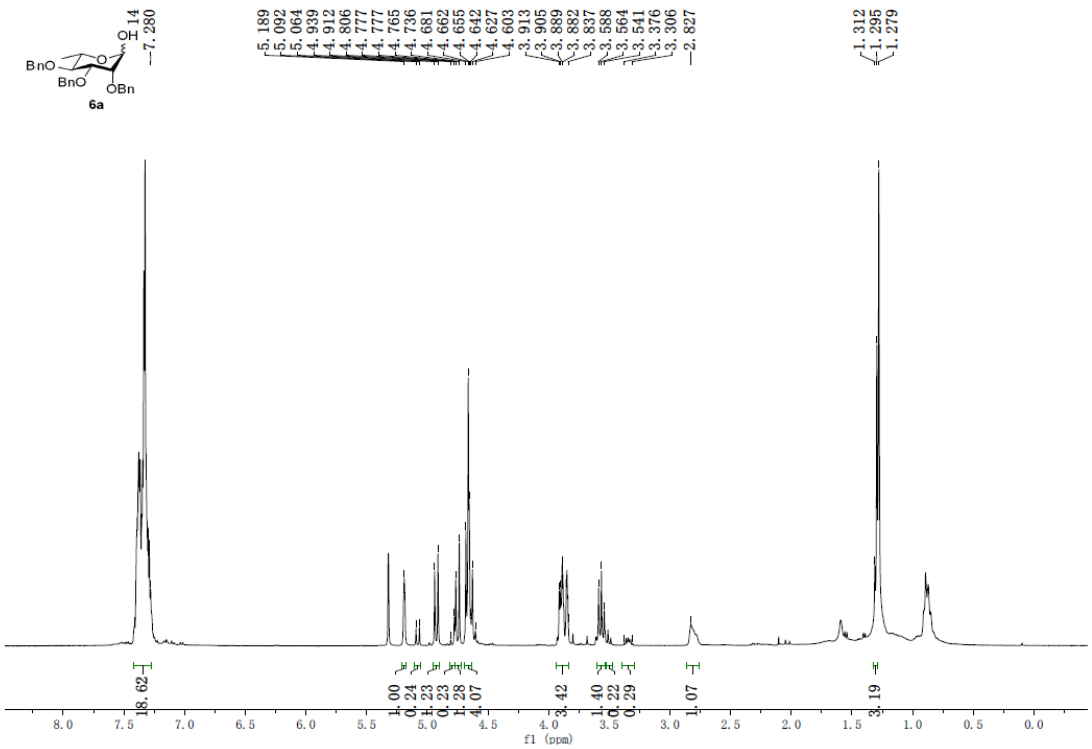


Figure S91. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **6a**

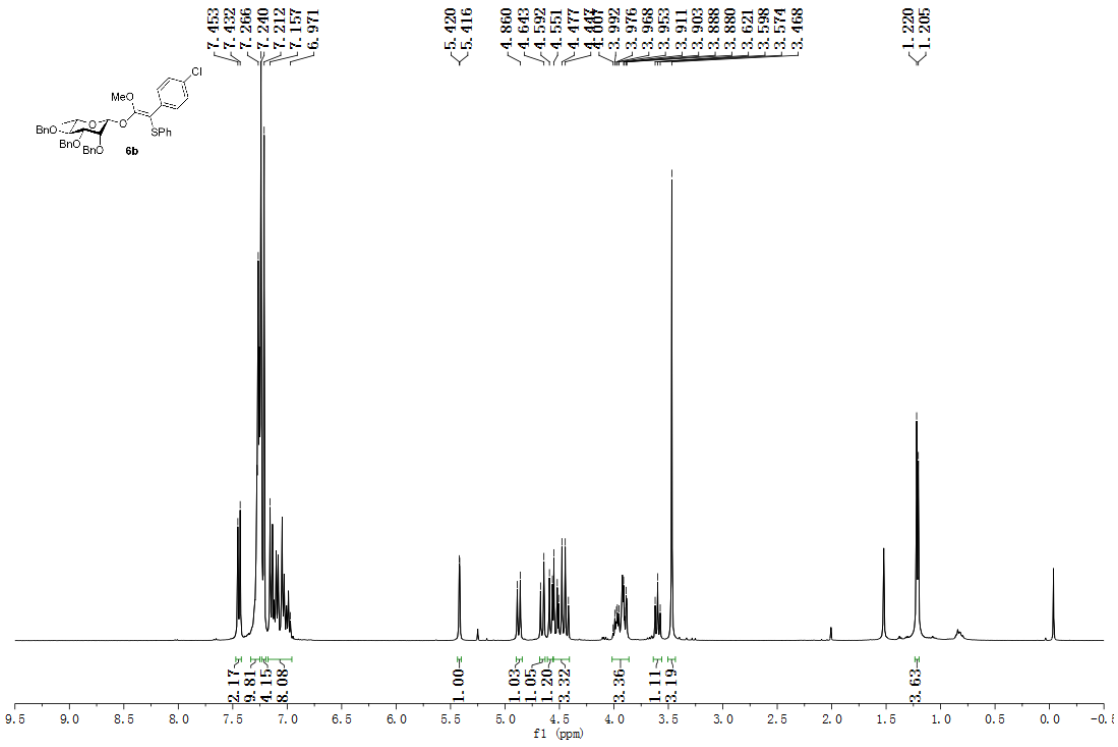


Figure S92. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6b**

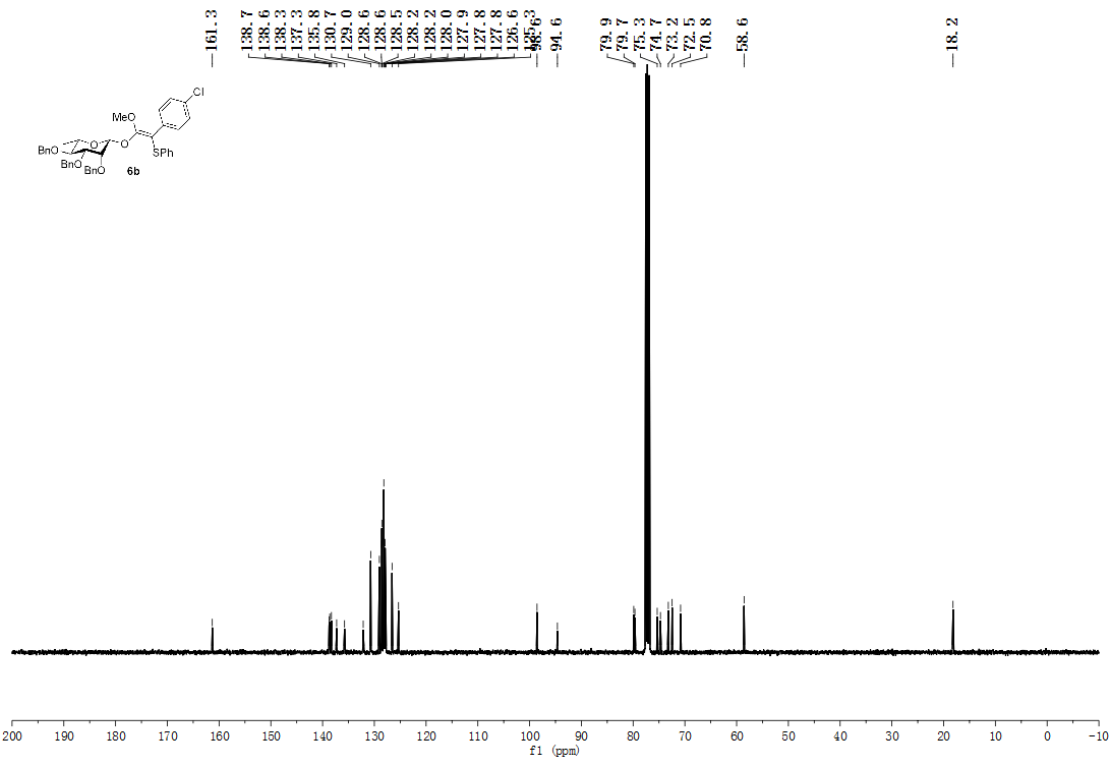


Figure S93. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6b**

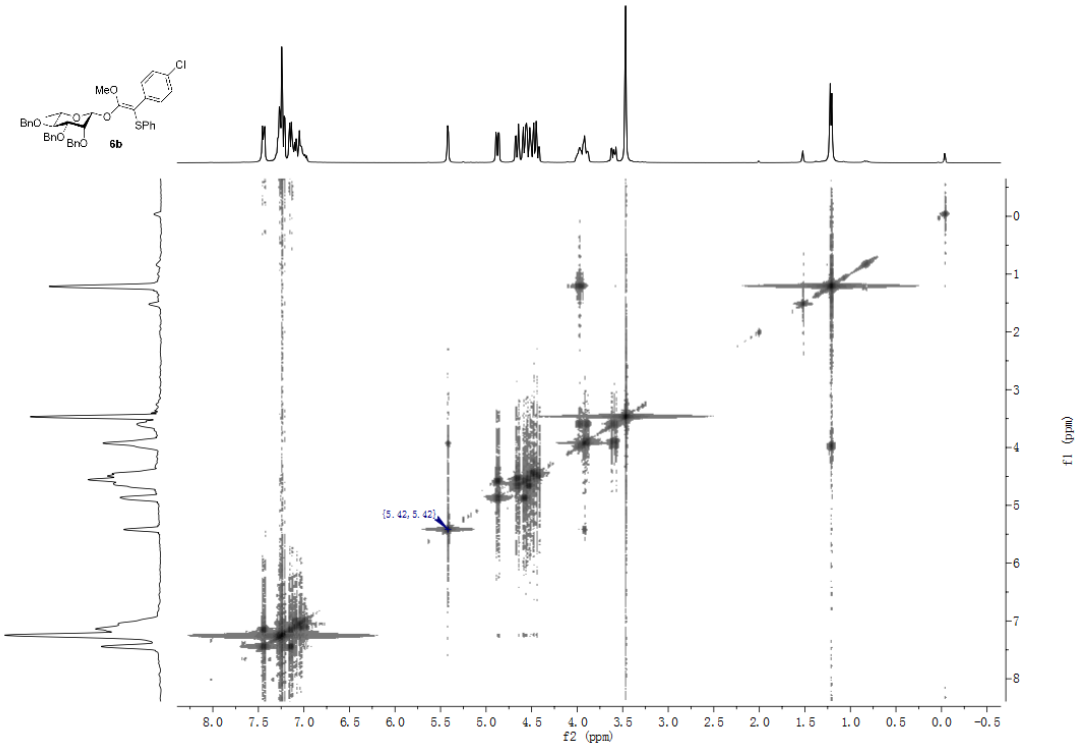


Figure S94. ^{1}H-^{1}H COSY spectrum of **6b**

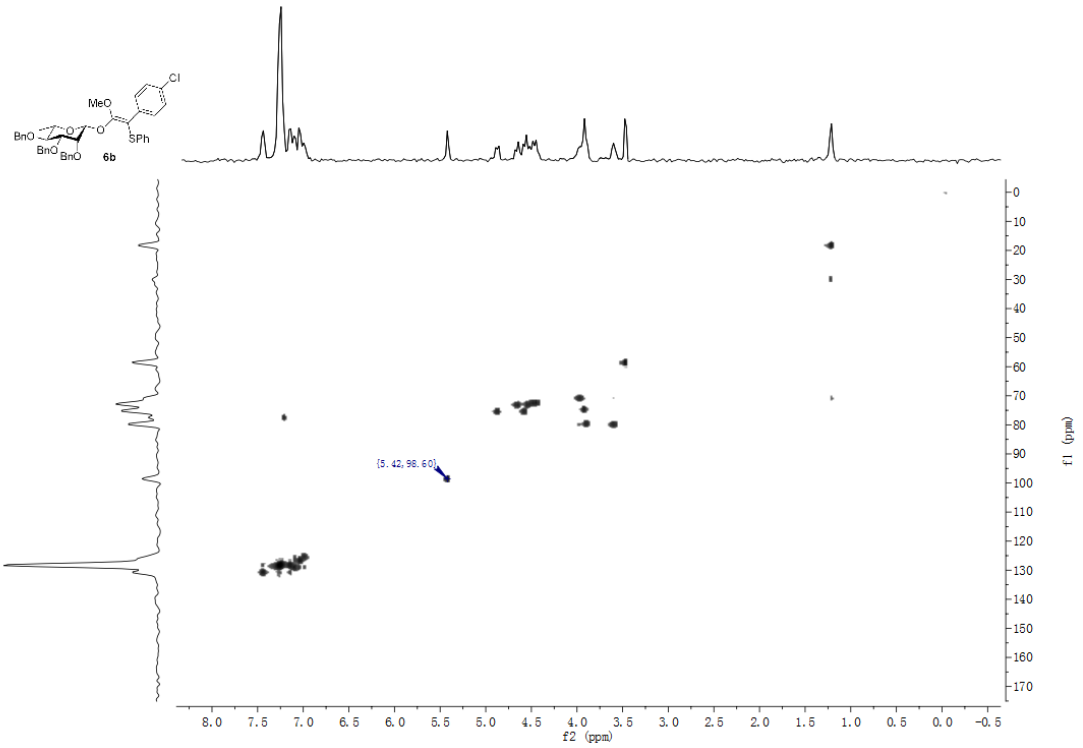


Figure S95. HSQC spectrum of **6b**

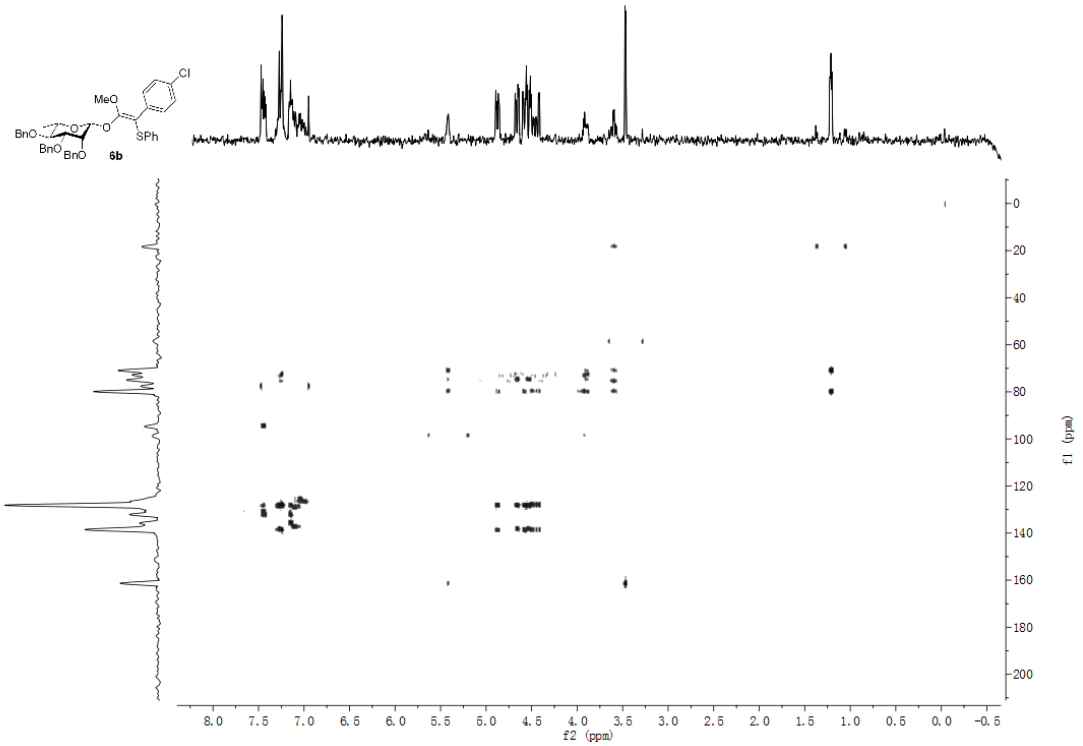


Figure S96. HMBC spectrum of **6b**

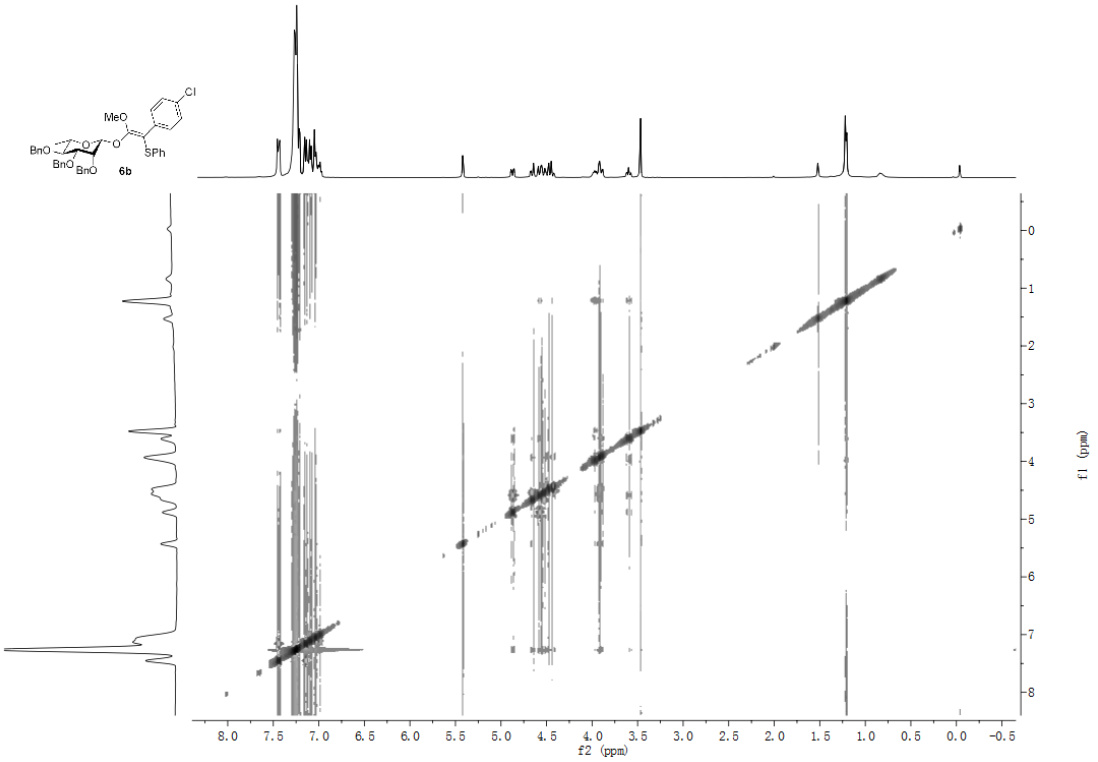


Figure S97. NOESY spectrum of **6b**

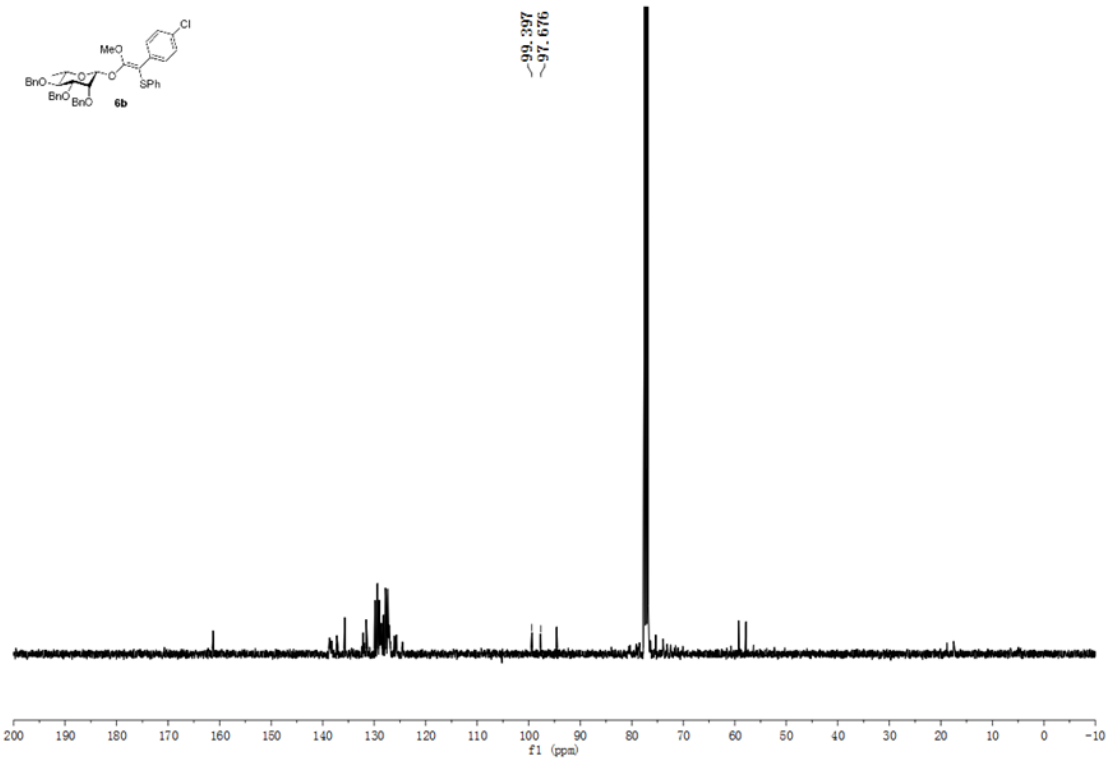


Figure S98. Proton undecoupled ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6b**

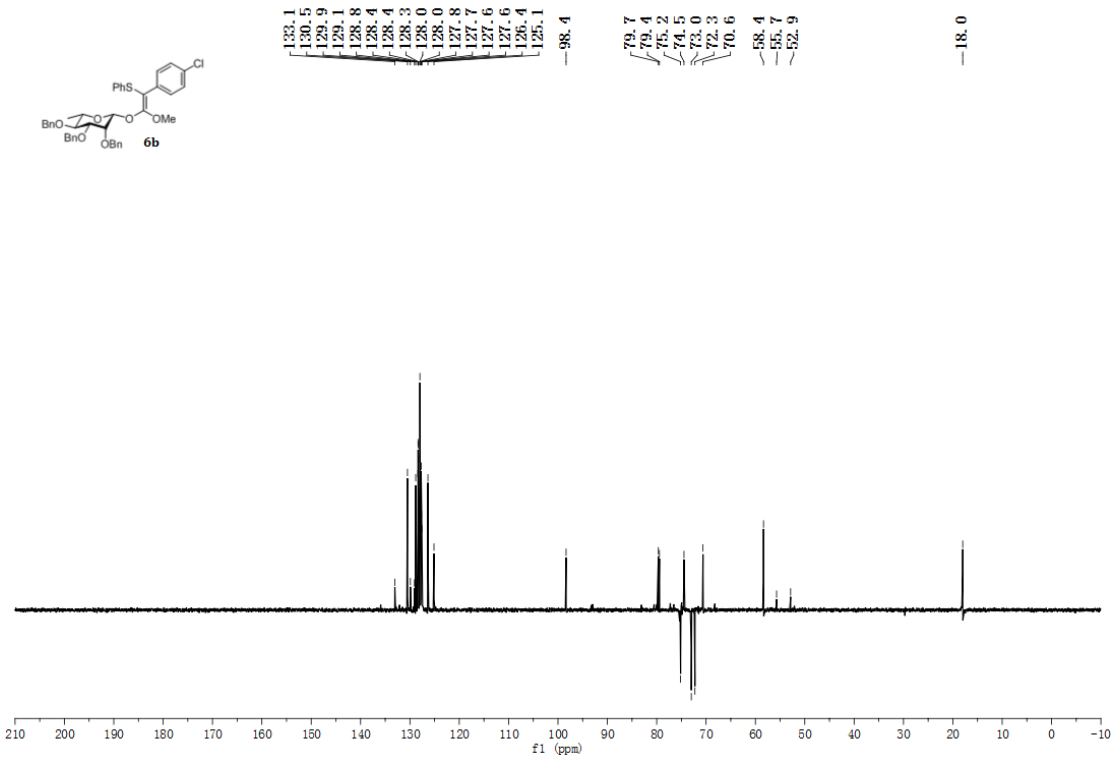


Figure S99. DEPT-135 spectrum of **6b**

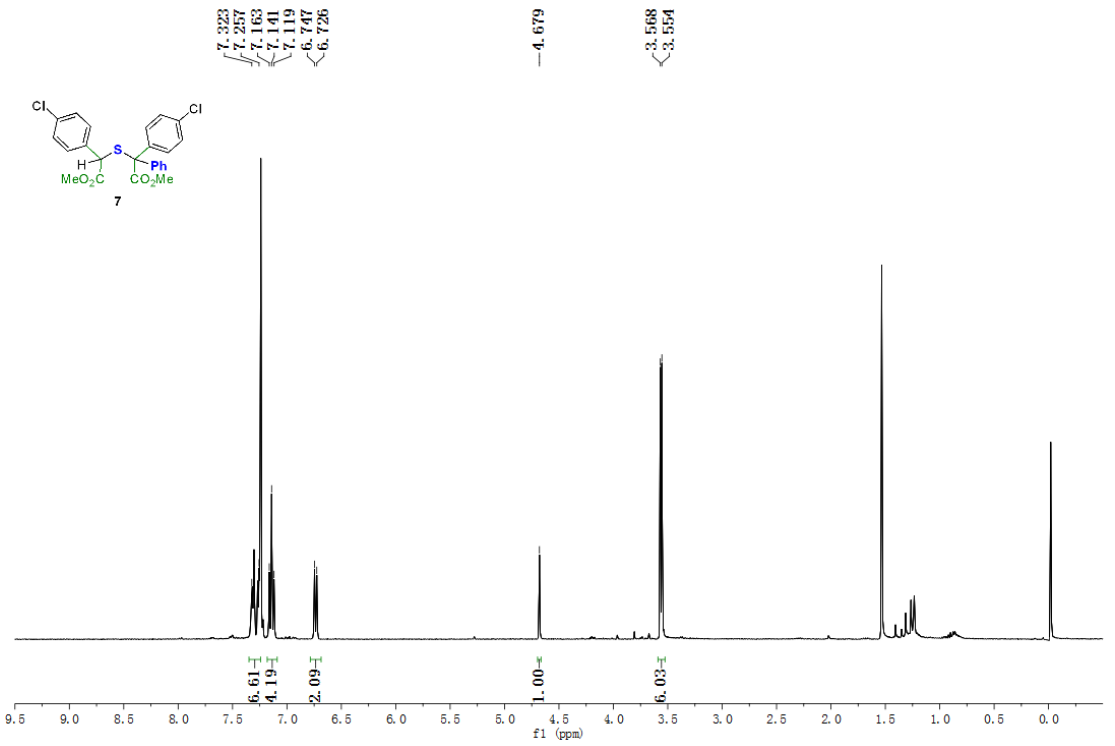


Figure S100. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7**

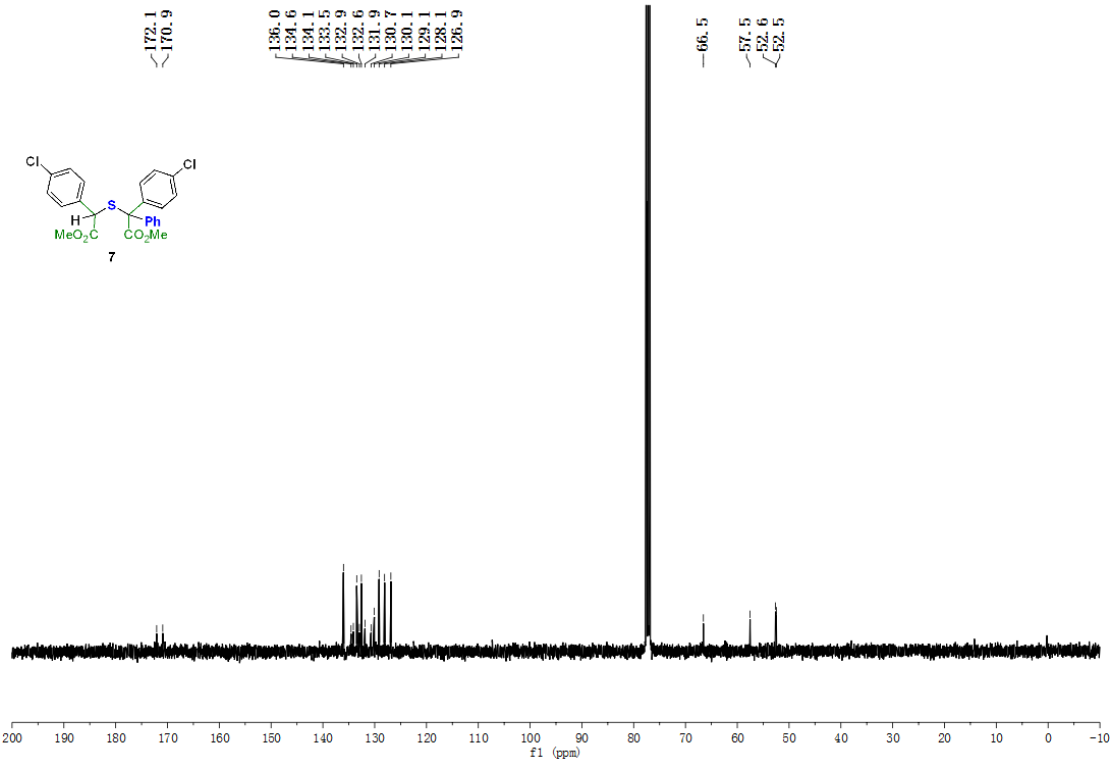


Figure S101. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **7**

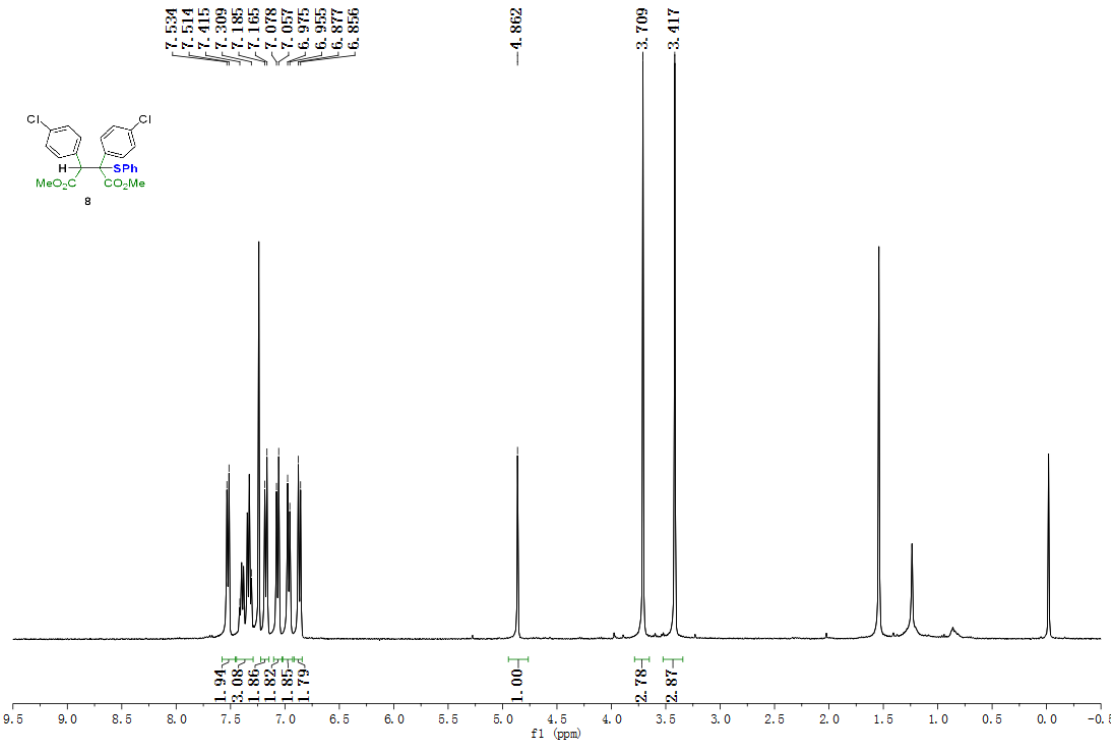


Figure S102. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8**

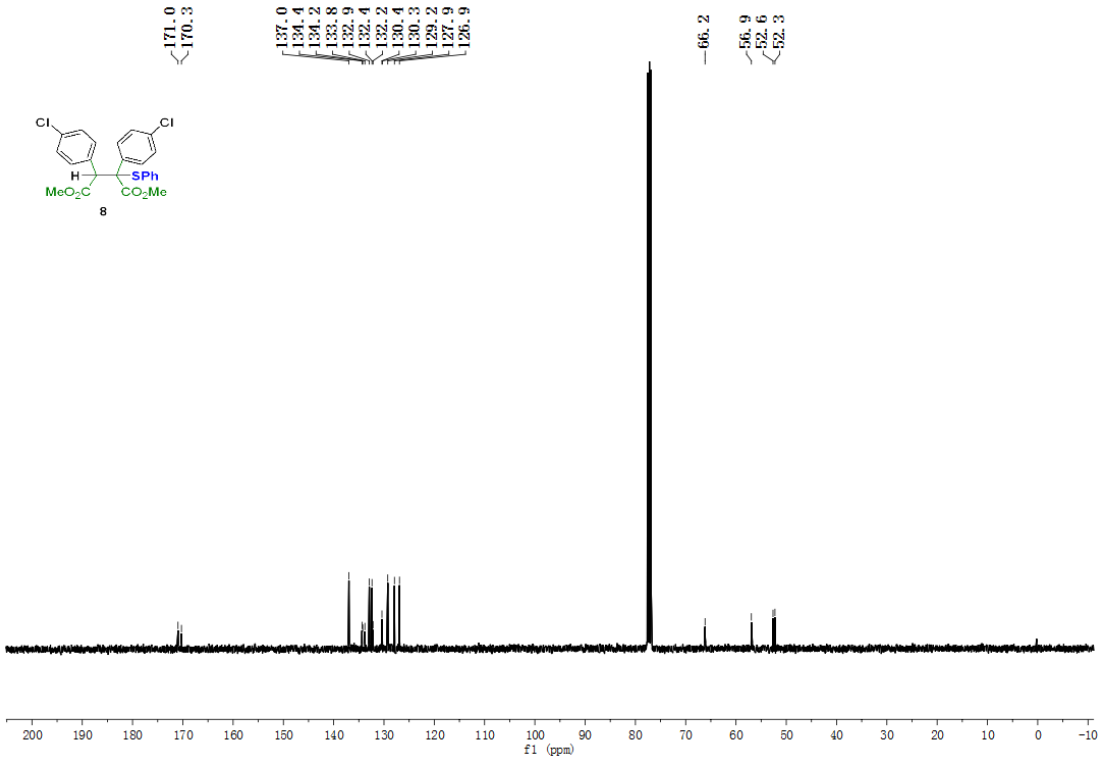


Figure S103. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **8**

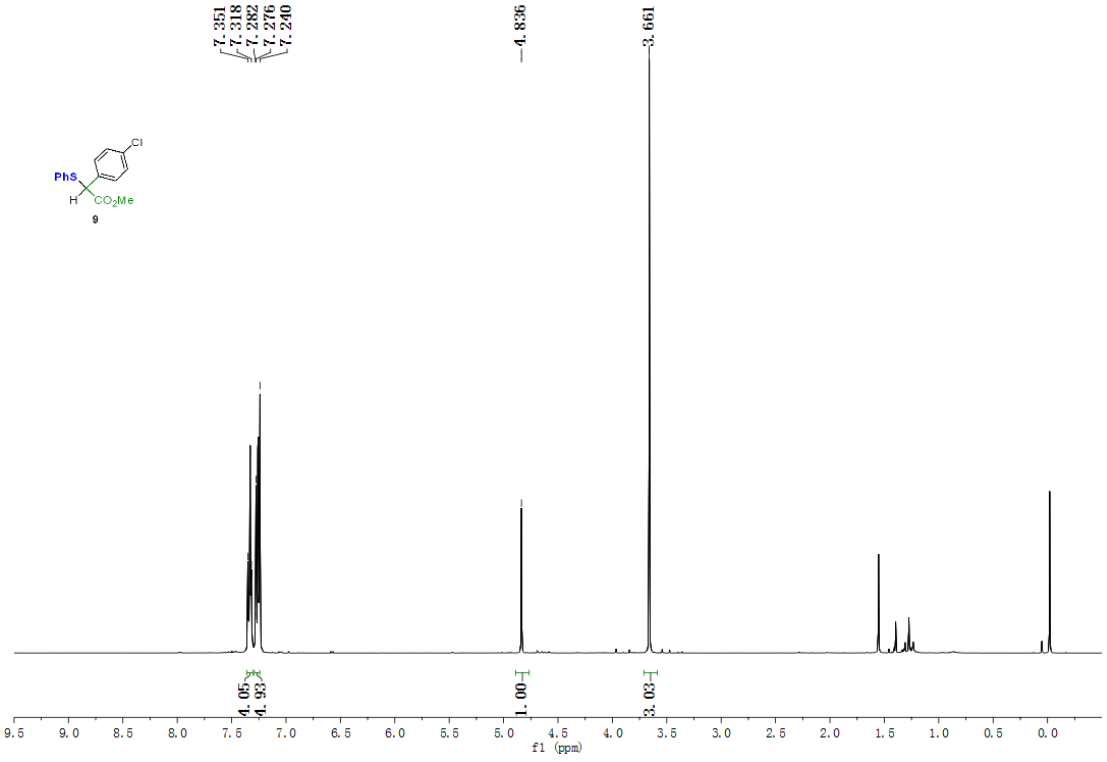


Figure S104. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9**

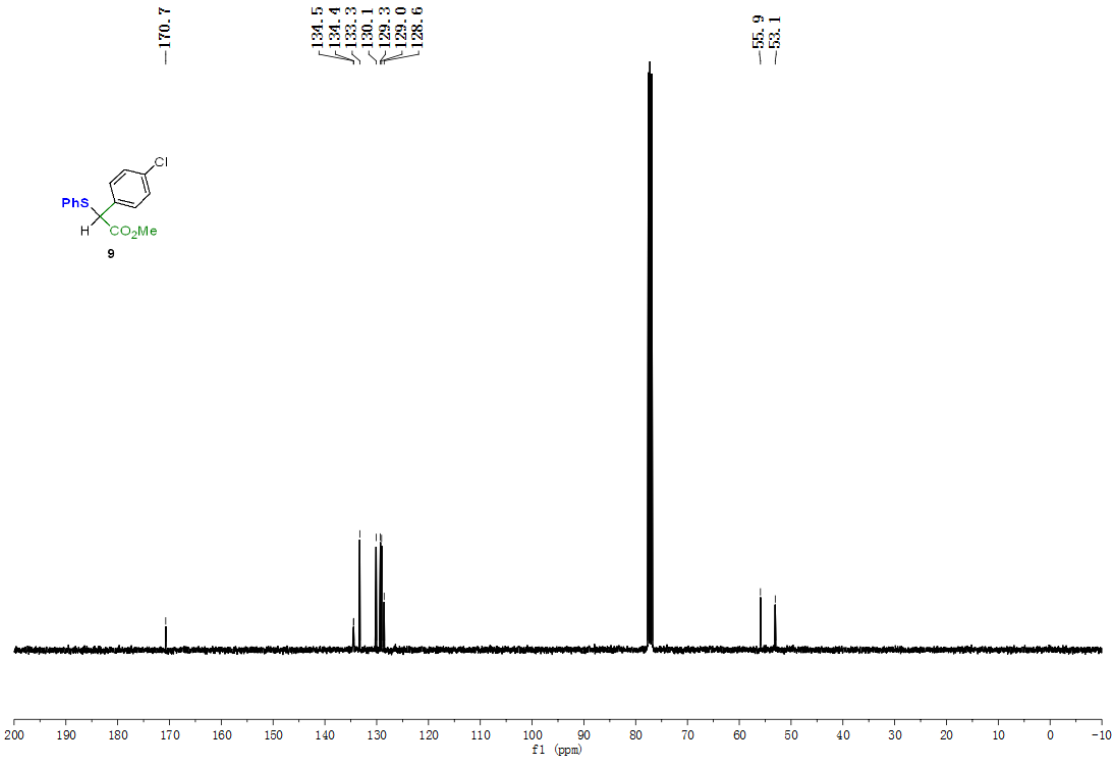


Figure S105. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9**

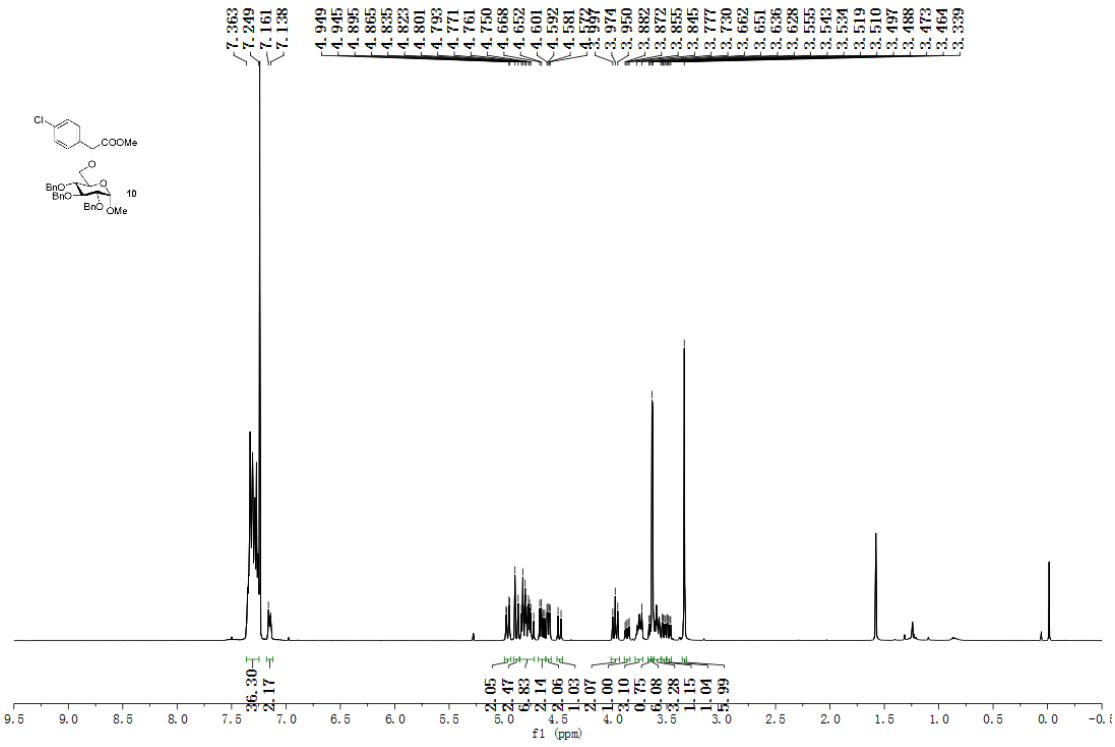


Figure S106. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10**

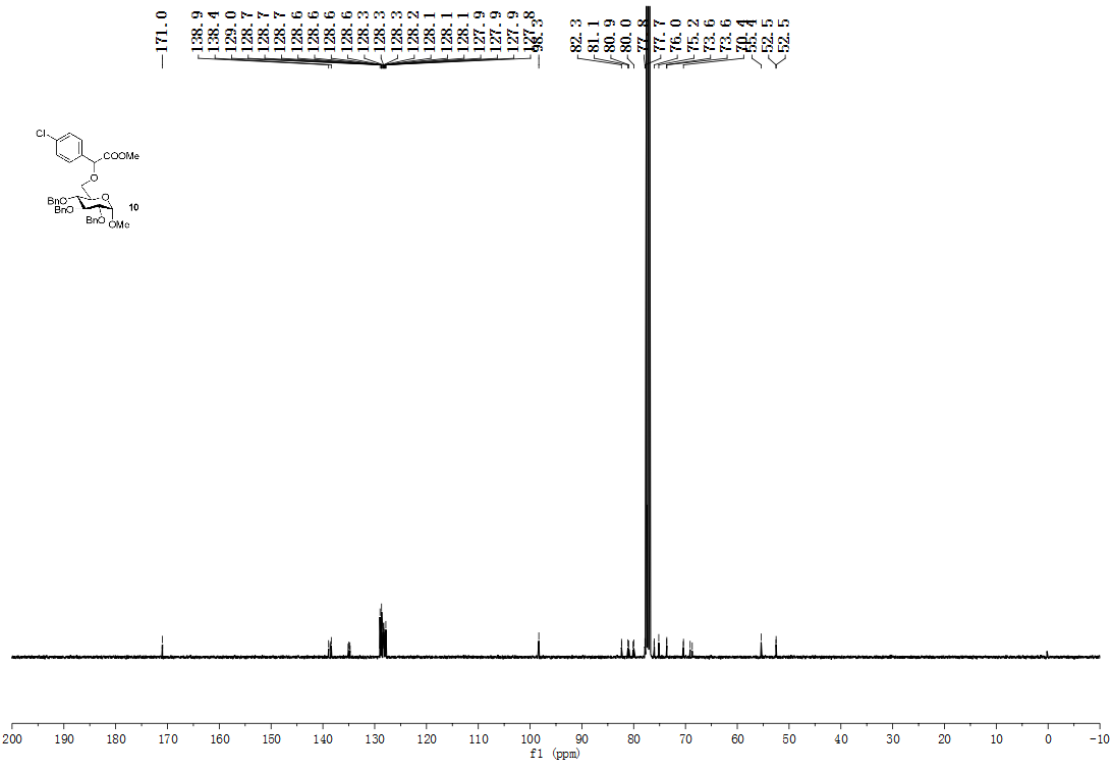


Figure S107. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10**

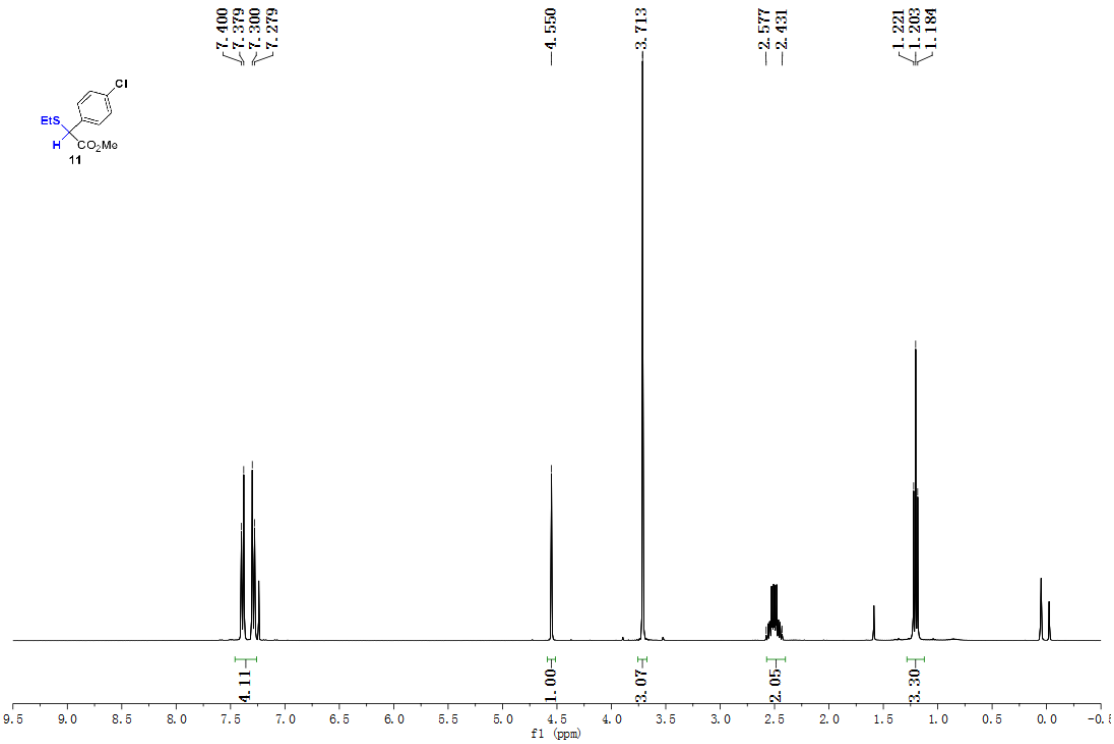


Figure S108. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11**

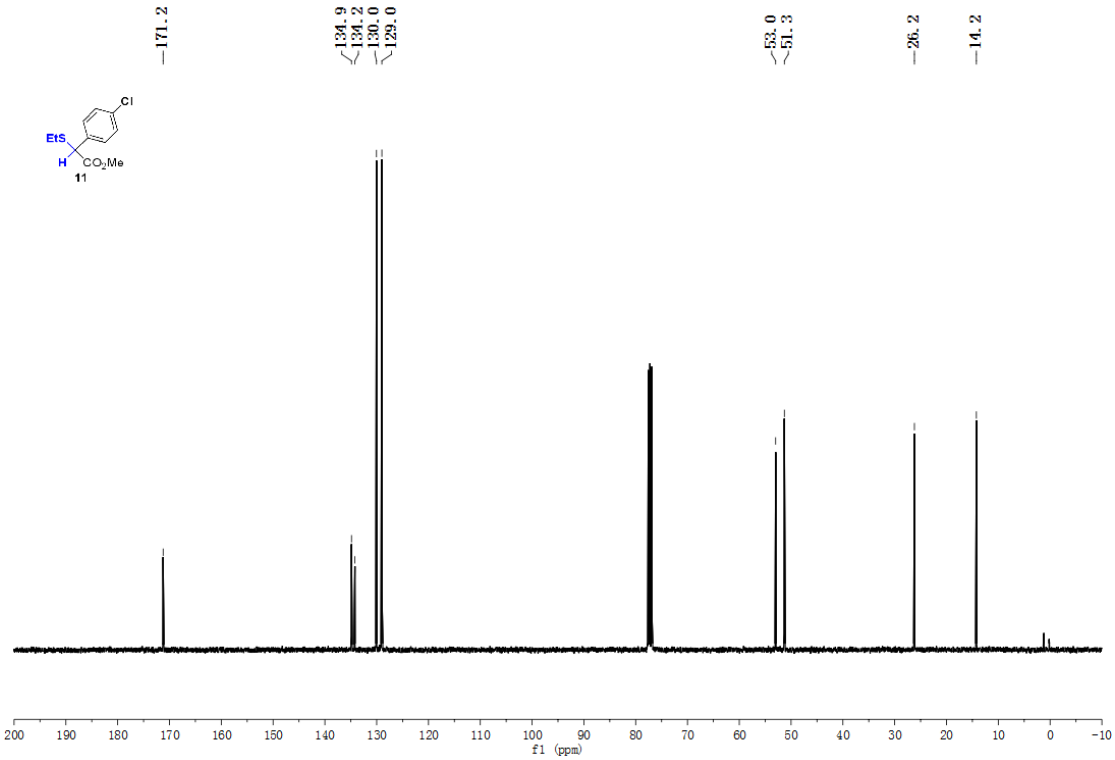


Figure S109. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11**

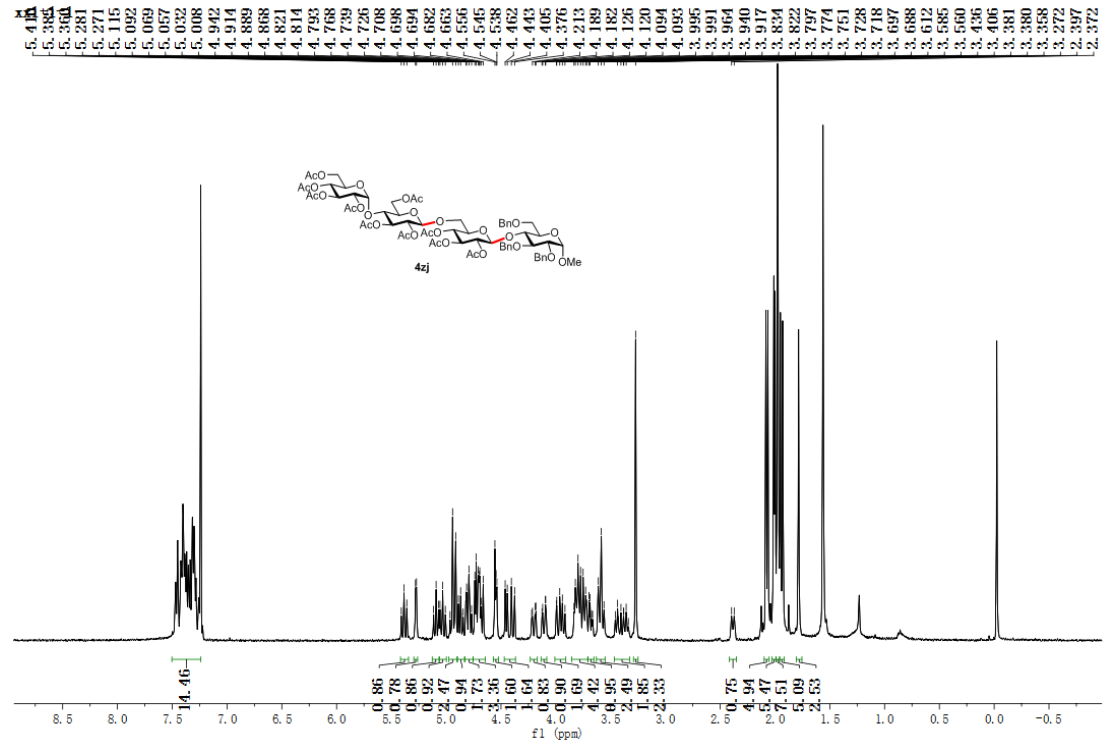


Figure S110. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4zj**

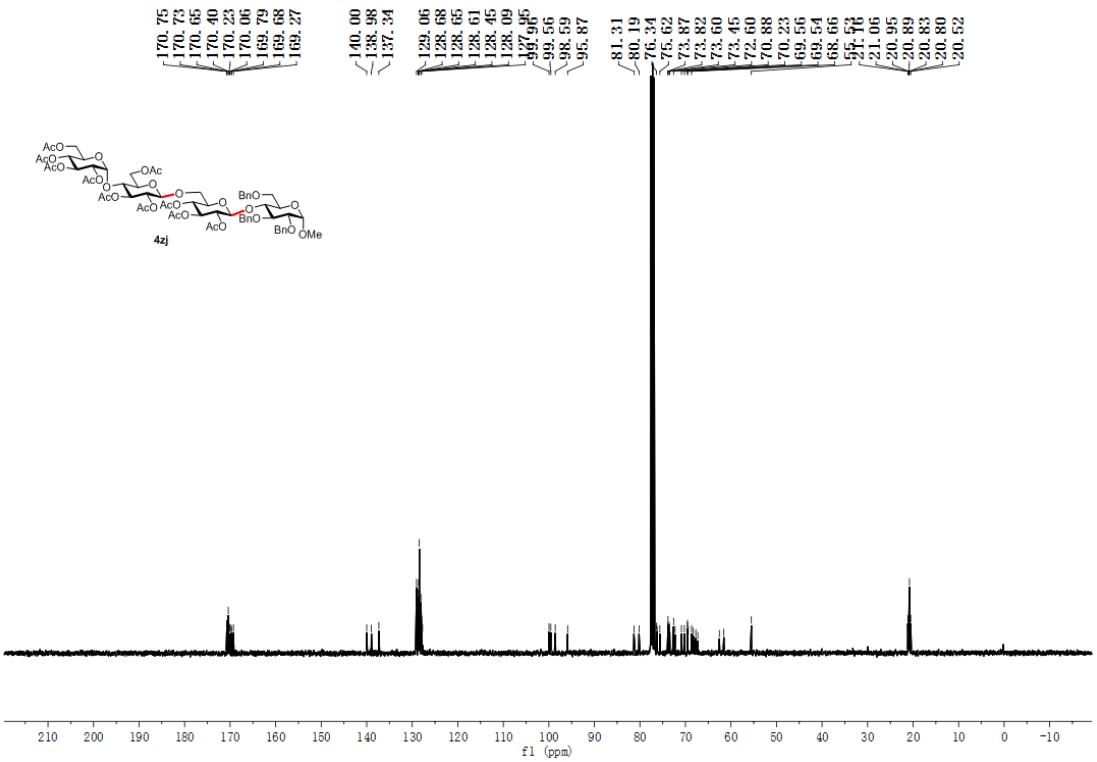


Figure S111. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4zj**

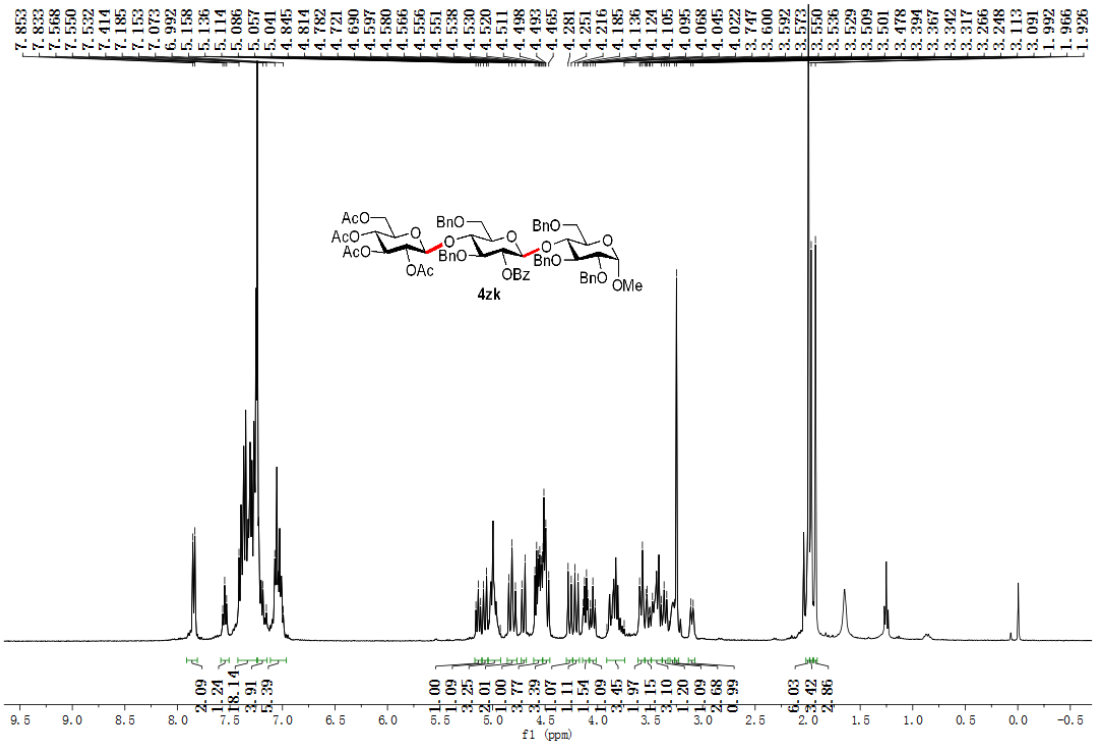


Figure S112. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4zk**

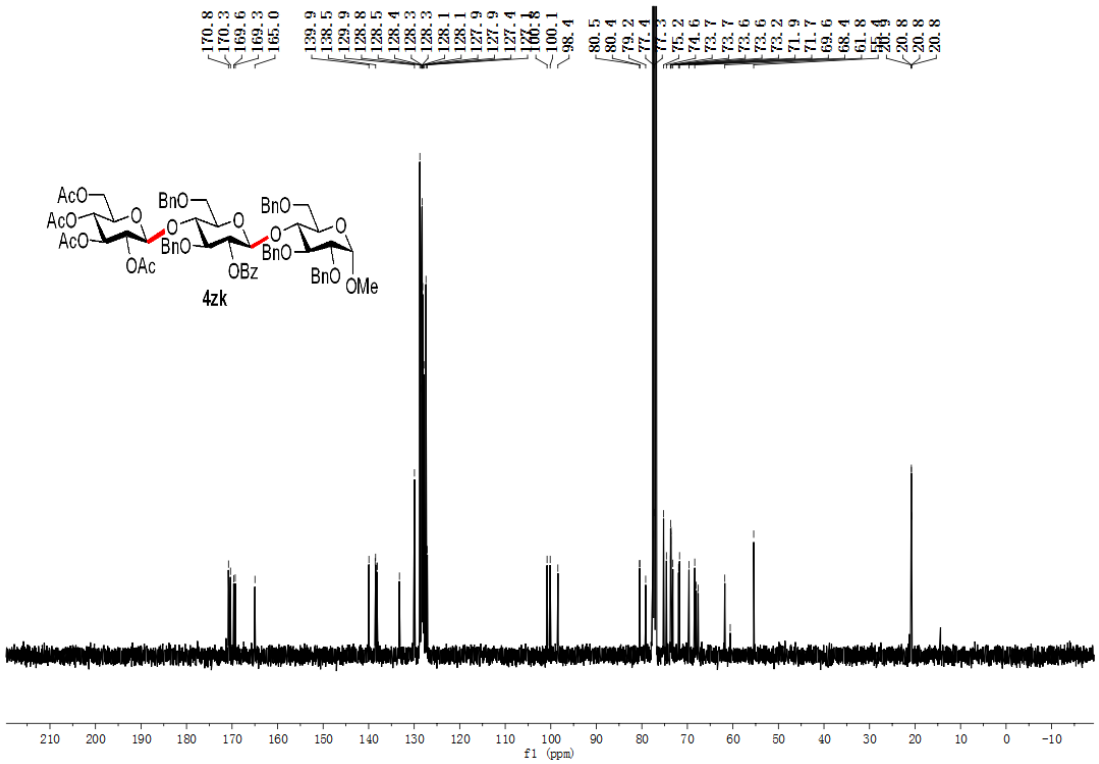


Figure S113. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4zk**

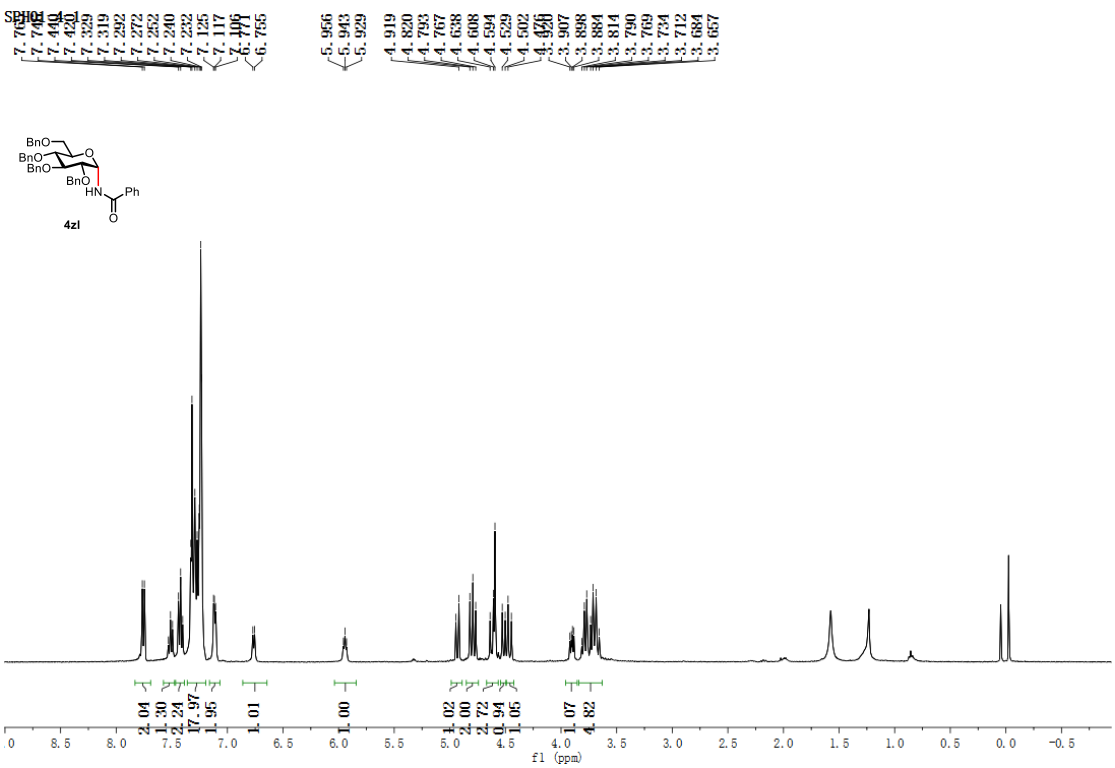


Figure S114. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4zl**

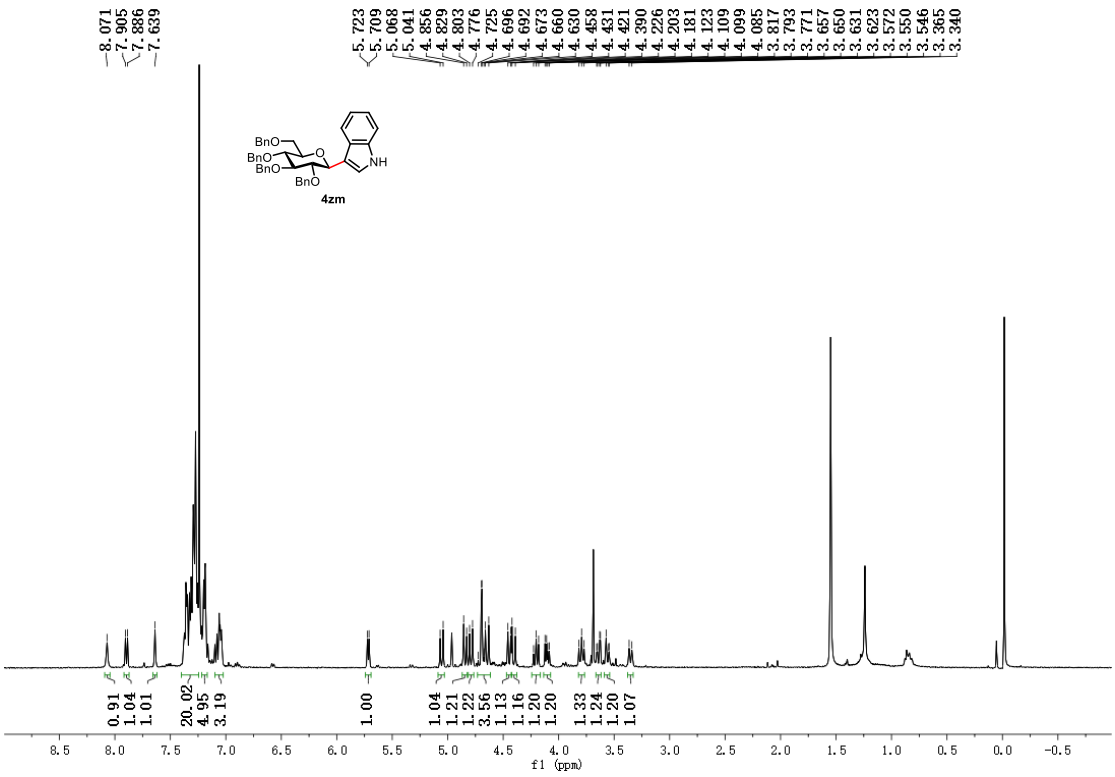


Figure S115. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4zm**

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