Electronic Supplementary Information

C-Glycosylation enabled by *N*-(glycosyloxy)acetamides

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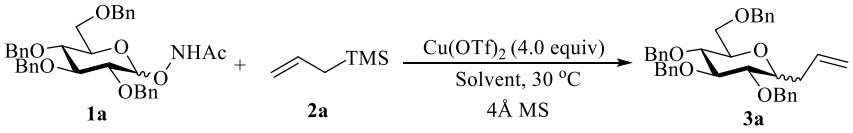
1. Experimental Procedures

1.1 General methods

Unless otherwise noted, all commercial reagents were used without further purification. Solvents were dried and redistilled commonly before using. Reactions were monitored by thin layer chromatography (TLC) on silica gel-coated plates (60 F_{254}). The spots were visualized under UV light (254 nm) and charring with a solution of $(NH_4)_6Mo_7O_{24}$•$4H_2O$ (19.4 mmol, 24.00 g) and $Ce(NH_4)_2(NO_3)_6$ (0.90 mmol, 0.50 g) in H_2SO_4 (5%, 500 mL). Silica gel (200 - 300 mesh) was used for flash column chromatography. ^1H and ^{13}C NMR spectra were recorded with Bruker AM 400 MHz spectrometer at room temperature. ^1H NMR spectra were reported using tetramethylsilane as the internal standard (δ = 0) in $CDCl_3$, ^{13}C NMR spectra were reported relative to the residual solvent peak (δ = 77.16) of $CDCl_3$. Optical rotation values were obtained using Hanon P850 instrument. HRMS were obtained on a Waters Xevo G2 Q-TOF mass spectrometer.

1.2 Optimization of the reaction

Table S1. Solvent screening[a, b]

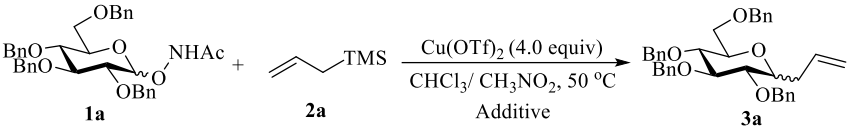


Entry	Solvent	Yield (%)
1	DCM	10%
2	DCE	trace
3	Ether	10%
4	CH_3CN	0
5	CH_3NO_2	40%
6	$CHCl_3$	35%
7[c]	$CHCl_3$	45%
8[d]	$CHCl_3$	25%
9[c]	$CHCl_3$: CH_3NO_2= 2: 1	37%
10[c]	$CHCl_3$: CH_3NO_2= 1: 1	75%
11[c]	$CHCl_3$: CH_3NO_2= 1: 2	50%

[a] Reaction conditions: **1a** (30.0 mg, 0.05 mmol), **2a** (15.9 μL, 0.1 mmol), 4Å MS (100 mg) and solvent (1.0 mL).

[b] Isolated yield. [c] 50 °C. [d] 80 °C, microwave (100 w).

Table S2. Additive screening[a, b]

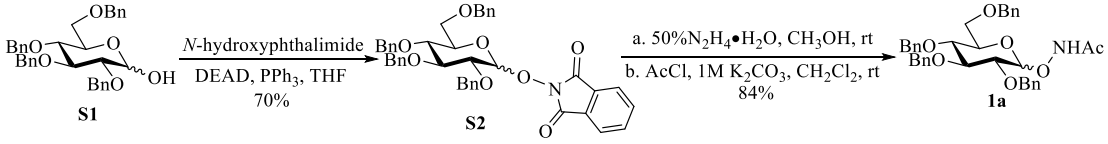


Entry	Additive (equiv.)	Yield (%)
1	K_2CO_3 (1.0)	35%
2	$BF_3 \cdot Et_2O$ (0.2)	32%
3	TBSOTf (0.2)	41%
4	CsF (1.0)	42%
5	TBAF (1.0)	63%

[a] Reaction conditions: **1a** (30.0 mg, 0.05 mmol), **2a** (15.9 μL, 0.1 mmol), 4Å MS (100 mg) and solvent (1.0 mL).

[b] Isolated yield.

1.3 Preparation of *N*-(glycosyloxy)acetamides



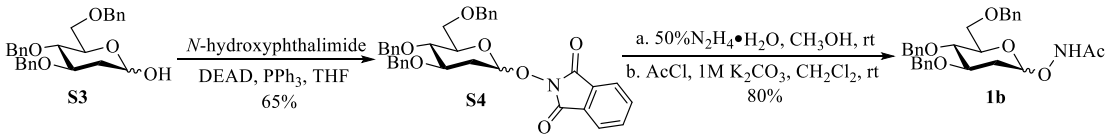
Phthalimidyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside (S2):

To a solution of compound **S1** (1.90 mmol, 1.03 g), *N*-hydroxyphthalimide (2.30 mmol, 0.37 g) and PPh_3 (2.30 mmol, 0.60 g) in dry THF (10 mL) was added diethyl azodicarboxylate (2.30 mmol, 0.5 mL) dropwise at 0 °C under an argon atmosphere. Then the reaction mixture was warmed up to room temperature and stirred overnight. Saturated $NaHCO_3$ solution was added to quench the reaction. The aqueous layer was extracted with ethyl acetate for three times, then the combined organic layer was washed with saturated NaCl solution, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 4: 1) to give **S2** as a white solid (0.91 g, 70%, α/β = 1: 3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 - 7.80 (m, 7.55H), 7.77 - 7.70 (m, 7.57H), 7.53 (d, *J* = 7.0 Hz, 2.27H), 7.49 (d, *J* = 6.8 Hz, 5.76H), 7.40 - 7.23 (m, 59.29H), 7.21 - 7.13 (m, 8.92H), 5.62 (d, *J* = 3.9 Hz, 1H), 5.18 (d, *J* = 10.6 Hz, 2.79H), 5.14 - 5.07 (m, 3.81H), 5.03 (d, *J* = 10.9 Hz, 1.08H), 4.94 (d, *J* = 11.0 Hz, 2.84H), 4.89 - 4.70 (m, 12.70H), 4.62 - 4.51 (m, 10.41H), 4.40 (d, *J* = 12.0 Hz, 1.07H), 4.13 (t, *J* = 9.5 Hz, 1.07H), 3.90 (dd, *J* = 11.0, 2.5 Hz, 1.10H), 3.84 - 3.61 (m, 17.21H), 3.57 - 3.48 (m, 2.86H). The spectroscopic data coincide with the previous report.[1]

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

Compound **S2** (0.24 mmol, 0.17 g) was dissolved in methanol (10 mL) and 50% hydrazine hydrate (1.40 mmol, 84 μL) was added dropwise. After stirring at room temperature for 1 h, the mixture was concentrated in vacuo. Then the residue was dissolved in mixed solvent (CH_2Cl_2/1M K_2CO_3 solution, 1: 1, 16 mL), acetyl chloride (3.70 mmol, 266 μL) was added to the mixture

slowly at 0 °C. After stirring at room temperature for 2 h, the mixture was extracted with CH_2Cl_2 for three times and the combined organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 2: 1) to give **1a** as yellow oil (0.12 g, 84% yield over 2 steps, α/β = 1: 2). ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.95 (s, 0.88H), 8.42 (s, 0.56H), 7.53 - 7.24 (m, 29.05H), 7.19 - 7.09 (m, 3.52H), 5.12 (s, 0.9H), 4.89 (d, *J* = 11.0 Hz, 2.11H), 4.81 (d, *J* = 10.9 Hz, 2.65H), 4.77 - 4.61 (m, 3.27H), 4.59 - 4.44 (m, 4.89H), 3.80 - 3.65 (m, 6.54H), 3.56 (s, 3.4H), 2.11 (s, 1.63H), 1.78 (s, 3H). The spectroscopic data coincide with the previous report.[1]

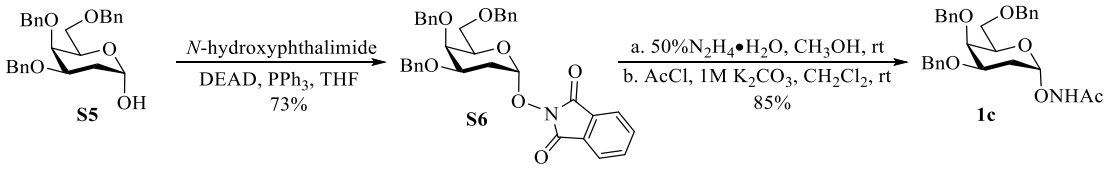


Phthalimidyl 2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranoside (S4):

The similar procedure for synthesizing **S2** was applied to deliver **S4** as yellow oil (0.72 g, 65%, α/β = 1: 2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 - 7.71 (m, 6H), 7.68 - 7.63 (m, 6H), 7.29 - 7.12 (m, 45H), 5.48 (d, *J* = 3.8 Hz, 1H), 5.06 (d, *J* = 8.4 Hz, 2H), 4.85 - 4.80 (m, 3H), 4.68 - 4.61 (m, 4H), 4.57 - 4.45 (m, 11H), 4.35 (d, *J* = 12.1 Hz, 1H), 4.06 - 3.96 (m, 1H), 3.84 (dd, *J* = 10.9, 2.4 Hz, 1H), 3.72 - 3.60 (m, 7H), 3.55 (t, *J* = 8.8 Hz, 3H), 3.43 - 3.37(m, 2H), 2.67 - 2.55 (m, 3H), 1.89 - 1.79 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.53, 163.28, 138.62, 138.59, 138.54, 138.23, 138.17, 138.15, 134.61, 134.54, 129.07, 129.04, 128.60, 128.55, 128.50, 128.42, 128.36, 128.20, 128.06, 127.95, 127.89, 127.83, 127.77, 127.73, 127.69, 127.65, 127.46, 123.76, 123.63, 103.78, 103.50, 78.78, 77.65, 76.71, 76.37, 75.09, 75.05, 73.65, 73.56, 72.95, 72.19, 71.71, 69.27, 68.39, 34.00, 33.49. HRMS (ESI) calcd for $C_{35}H_{37}N_2O_7$ $[M+NH_4]^+$ 597.2595, found 597.2598.

Acetamidyl 2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranoside (1b):

Glycosyl donor **1b** was obtained according to the similar procedure for the synthesis of **1a** as yellow oil (0.09 g, 80% yield over 2 steps, α/β = 1: 2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 0.65H), 8.82 (s, 0.28H), 7.36 - 7.25 (m, 16.14H), 7.22 - 7.16 (m, 2.60H), 5.20 (s, 0.33H), 4.91 - 4.79 (m, 1.91H), 4.67 (t, *J* = 11.3 Hz, 1.41H), 4.62 - 4.45 (m, 5.11H), 3.94 (s, 0.66H), 3.77 (dd, *J* = 10.6, 4.6 Hz, 1.01H), 3.72 - 3.64 (m, 2.42H), 3.58 (t, *J* = 8.5 Hz, 1.11H), 3.52 (s, 1.21H), 2.55 (s, 1H), 2.35 (s, 0.29H), 2.12 (s, 1.07H), 1.85 (s, 1.11H), 1.80 (s, 2.03H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.54, 138.30, 138.23, 138.14, 138.00, 137.83, 137.78, 137.70, 128.47, 128.41, 128.39, 128.35, 127.98, 127.91, 127.83, 127.77, 127.74, 127.70, 127.64, 102.47, 101.97, 78.08, 77.73, 74.88, 74.75, 73.58, 73.44, 72.27, 71.75, 71.41, 69.19, 33.32, 33.16, 19.87. HRMS (ESI) calcd for $C_{29}H_{37}N_2O_6$ $[M+NH_4]^+$ 509.2646, found 509.2652.

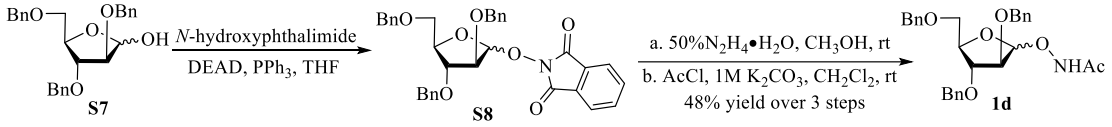


Phthalimidyl 2-deoxy-3,4,6-tri-*O*-benzyl-α-D-galactopyranoside (S6):

The similar procedure for synthesizing **S2** was applied to deliver **S6** as yellow oil (0.80 g, 73%, α only). $[\alpha]_D^{25}$ +116.5 (*c* 1.10, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 - 7.77 (m, 2H), 7.75 - 7.70 (m, 2H), 7.37 - 7.25 (m, 15H), 5.59 (d, *J* = 2.5 Hz, 1H), 4.94 (d, *J* = 11.4 Hz, 1H), 4.79 (t, *J* = 6.7 Hz, 1H), 4.68 - 4.61 (m, 3H), 4.54 (d, *J* = 11.9 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.15 - 4.05 (m, 2H), 3.65 (dd, *J* = 9.2, 7.8 Hz, 1H), 3.54 (dd, *J* = 9.4, 5.8 Hz, 1H), 2.42 - 2.38 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.57, 138.75, 138.32, 138.26, 134.39, 129.02, 128.49, 128.28, 128.26, 128.18, 127.65, 127.57, 127.49, 127.35, 123.53, 103.89, 74.52, 73.67, 73.20, 72.60, 71.69, 70.54, 68.68, 28.82. HRMS (ESI) calcd for $C_{35}H_{37}N_2O_7$ $[M+NH_4]^+$ 597.2595, found 597.2603.

Acetamidyl 2-deoxy-3,4,6-tri-*O*-benzyl-α-D-galactopyranoside (1c):

Glycosyl donor **1c** was obtained according to the similar procedure for the synthesis of **1a** as yellow oil (0.10 g, 85% yield over 2 steps, α only). $[\alpha]_D^{25}$ +139.3 (*c* 0.30, $CHCl_3$). ^1H NMR (400 MHz,$CDCl_3$) δ 8.59 (s, 1H), 7.39 - 7.19 (m, 15H), 5.23 (s, 1H), 4.92 (d, *J* = 11.6 Hz, 1H), 4.62 - 4.55 (m, 3H), 4.50 (d, *J* = 11.8 Hz, 1H), 4.41 (d, *J* = 11.8 Hz, 1H), 4.04 (s, 1H), 3.85 (s, 2H), 3.67 - 3.57 (m, 1H), 3.53 - 3.44 (m, 1H), 2.34 - 2.21 (m, 2H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.60, 138.54, 138.22, 137.82, 128.48, 128.32, 127.91, 127.89, 127.72, 127.69, 127.35, 102.46, 74.31, 73.93, 73.56, 72.73, 71.69, 70.55, 70.04, 28.82, 19.91. HRMS (ESI) calcd for $C_{29}H_{37}N_2O_6$ $[M+NH_4]^+$ 509.2646, found 509.2649.



Acetamidyl 2,3,5-tri-*O*-benzyl-α-D-arabinofuranoside (1d):

To a solution of compound **S7**[2] (1.90 mmol, 0.80 g), *N*-hydroxyphthalimide (2.30 mmol, 0.37 g) and PPh_3 (2.30 mmol, 0.60 g) in dry THF (10 mL) was added diethyl azodicarboxylate (2.30 mmol, 0.5 mL) dropwise at 0 °C under an argon atmosphere. Then the reaction mixture was warmed up to room temperature and stirred overnight. Saturated $NaHCO_3$ solution was added to quench the reaction. The aqueous layer was extracted with ethyl acetate for three times, then the combined organic layer was washed with saturated NaCl solution, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to give **S8**. Compound **S8** (1.23 mmol, 0.70 g) was dissolved in methanol (20 mL) and 50% hydrazine hydrate (7.20 mmol, 504 μL) was added dropwise. After stirring at room temperature for 1 h, the mixture was concentrated in vacuo. Then the residue was dissolved in mixed solvent (CH_2Cl_2/1M K_2CO_3 solution, 1: 1, 30 mL), acetyl chloride (22.20 mmol, 1.60 mL) was added to the mixture slowly at 0 °C. After stirring at room temperature for 2 h, the mixture was extracted with CH_2Cl_2 for three times and the combined organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 1: 1) to give **1d** as yellow oil (0.44 g, 48% yield over 3 steps, α/β = 1: 1.5). ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 0.97H), 8.23 (s, 1.57H), 7.65 - 7.51 (m, 1.07H), 7.48 - 7.30 (m, 36.53H), 7.22 (d, *J* = 7.1 Hz, 2.03H), 5.40 (s, 1.00H), 5.34 (s, 1.53H), 4.96 (d, *J* = 9.8 Hz, 1.38H), 4.75 (d, *J* = 11.7 Hz, 2.82H), 4.66 (d, *J* = 11.1 Hz, 3.33H), 4.62 - 4.41 (m, 12.62H), 4.33 - 4.22 (m, 3.28H), 4.16 (s, 3.25H), 4.11 - 4.03 (m, 2.36H), 3.90 (d, *J* = 7.5 Hz, 1.07H), 3.71 - 3.55 (m, 4.24H), 3.54 - 3.44 (m,

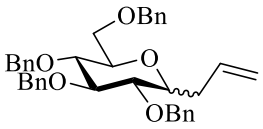
2.07H), 2.18 - 1.84 (m, 5.83H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.55, 167.29, 137.93, 137.81, 137.61, 137.47, 137.15, 130.03, 129.96, 129.91, 129.84, 129.78, 128.60, 128.51, 128.48, 128.43, 128.33, 128.07, 127.96, 127.92, 127.85, 127.78, 110.09, 102.75, 85.62, 83.34, 83.01, 81.46, 80.60, 80.34, 73.54, 73.41, 72.46, 72.34, 72.21, 70.44, 69.80, 19.95, 19.86. HRMS (ESI) calcd for $C_{28}H_{32}NO_6$ $[M+H]^+$ 478.2224, found 478.2230.

1.4 *C*-Glycosylation procedure

To a solution of glycosyl donor (0.05 mmol), *C*-nucleophile (0.1 mmol), activated 4 Å MS (100 mg), dry $CHCl_3$ (0.5 mL) and CH_3NO_2 (0.5 mL) was added $SnBr_4$ (0.075 mmol) at 0 °C under an argon atmosphere. Then the reaction mixture was warmed up to room temperature and stirred for 0.5 h. Then triethylamine (15.0 μL) was added, the reaction mixture was filtered through a pad of celite and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel to deliver the desired product.

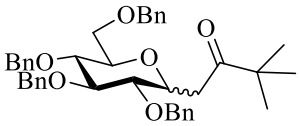
1.5 Characterization of the *C*-glycosides

Compound 3a



C-Glycoside **3a** was obtained (26.0 mg, 95%, α/β = 5: 1) as a colorless oil according to the *C*-glycosylation procedure. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.37 - 7.22 (m, 21.47H), 7.20 - 7.16 (m, 0.40H), 7.15 - 7.09 (m, 2.07H), 6.01 - 5.87 (m, 0.23H), 5.86 - 5.73 (m, 1.00H), 5.16 - 5.02 (m, 2.39H), 4.96 - 4.85 (m, 1.57H), 4.81 (dd, *J* = 10.8, 3.2 Hz, 2.16H), 4.71 - 4.59 (m, 3.46H), 4.58 - 4.54 (m, 0.30H), 4.50 - 4.42 (m, 2.03H), 4.17 - 4.07 (m, 1.00H), 3.84 - 3.56 (m, 6.87H), 3.45 - 3.38 (m, 0.20H), 3.36 - 3.30 (m, 0.31H), 2.64 - 2.55 (m, 0.23H), 2.54 - 2.41 (m, 1.97H), 2.37 - 2.27 (m, 0.21H). The spectroscopic data coincide with the previous report.[3]

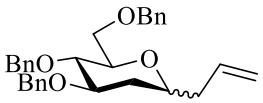
Compound 3b



C-Glycoside **3b** was obtained (25.8 mg, 83%, α/β = 3: 1) as a colorless oil according to the *C*-glycosylation procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.21 (m, 28.94H), 7.21 - 7.16 (m, 0.84H), 7.16 - 7.09 (m, 2.23H), 4.96 - 4.87 (m, 2.74H), 4.85 - 4.74 (m, 2.39H), 4.66 - 4.52 (m, 4.06H), 4.51 - 4.43 (m, 2.36H), 3.83 (d, *J* = 8.6 Hz, 0.24H), 3.77 (dd, *J* = 9.0, 6.0 Hz, 1.20H), 3.73 - 3.64 (m, 2.99H), 3.64 - 3.55 (m, 3.37H), 3.40 (d, *J* = 10.1 Hz, 0.31H), 3.34 (t, *J* = 9.1 Hz, 0.30H), 2.89 (dd, *J* = 16.8, 5.4 Hz, 1H), 2.76 (dd, *J* = 16.8, 7.0 Hz, 1H), 2.63 (dd, *J* = 16.5, 9.1 Hz, 0.30H), 2.50 (d, *J* = 14.8 Hz, 0.30H), 1.08 (s, 8.84H), 1.05 (s, 2.77H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.16, 212.10, 138.65, 138.61, 138.28, 138.23, 138.19, 138.07, 137.87, 128.46, 128.44, 128.40, 128.34, 128.24, 128.15, 128.07, 127.91, 127.89, 127.82, 127.80, 127.76, 127.70, 127.63, 127.55, 87.41, 82.08, 80.81, 79.30, 78.81, 78.47, 77.79, 75.56, 75.39, 75.30, 75.12, 74.93, 74.80, 73.57,

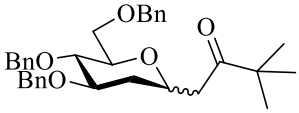
73.42, 73.11, 72.84, 70.34, 69.02, 68.77, 44.39, 44.18, 38.64, 33.48, 26.14, 26.01. HRMS (ESI) calcd for $C_{40}H_{50}NO_6$ $[M+NH_4]^+$ 640.3633, found 640.3639.

Compound 3c



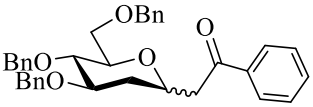
C-Glycoside **3c** was obtained (21.0 mg, 92%, α/β = 13: 1) as a colorless oil according to the *C*-glycosylation procedure. The α isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.25 (m, 13H), 7.23 - 7.17 (m, 2H), 5.82 - 5.70 (m, 1H), 5.06 - 5.01 (m, 2H), 4.78 (d, *J* = 11.1 Hz, 1H), 4.63 - 4.48 (m, 5H), 4.08 - 4.00 (m, 1H), 3.82 - 3.72 (m, 3H), 3.69 - 3.63 (m, 1H), 3.54 (t, *J* = 7.1 Hz, 1H), 2.49 - 2.40 (m, 1H), 2.26 - 2.18 (m, 1H), 2.03 - 1.96 (m, 1H), 1.81 - 1.71 (m, 1H). The spectroscopic data coincide with the previous report.[4]

Compound 3d



C-Glycoside **3d** was obtained (22.4 mg, 87%, α/β = 1.5: 1) as a colorless oil according to the *C*-glycosylation procedure. The α isomer: $[\alpha]_D^{25}$ -1.0 (*c* 0.60, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.27 (m, 13H), 7.24 - 7.19 (m, 2H), 4.74 (d, *J* = 11.3 Hz, 1H), 4.62 - 4.49 (m, 6H), 3.79 - 3.69 (m, 4H), 3.51 (t, *J* = 6.4 Hz, 1H), 2.85 (dd, *J* = 17.0, 5.5 Hz, 1H), 2.66 (dd, *J* = 17.0, 7.9 Hz, 1H), 1.97 - 1.91 (m, 1H), 1.88 - 1.81 (m, 1H), 1.10 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.74, 138.74, 138.67, 138.40, 128.53, 128.46, 128.10, 127.98, 127.79, 127.71, 81.09, 78.98, 78.41, 75.10, 73.58, 72.13, 71.61, 69.52, 44.37, 42.74, 36.74, 26.26; HRMS (ESI) calcd for $C_{33}H_{44}NO_5$ $[M+NH_4]^+$ 534.3214, found 534.3222. The β isomer: $[\alpha]_D^{25}$ +7.5 (*c* 0.80, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.25 (m, 13H), 7.20 - 7.14 (m, 2H), 4.89 (d, *J* = 10.8 Hz, 1H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.63 - 4.48 (m, 4H), 3.92 - 3.82 (m, 1H), 3.74 - 3.62 (m, 3H), 3.50 (t, *J* = 9.1 Hz, 1H), 3.44 - 3.36 (m, 1H), 2.98 (dd, *J* = 17.2, 5.5 Hz, 1H), 2.59 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.33 - 2.20 (m, 1H), 1.40 - 1.25 (m, 1H), 1.13 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.32, 138.46, 138.39, 128.53, 128.45, 128.13, 127.94, 127.85, 127.74, 127.68, 76.12, 75.75, 74.20, 73.86, 73.55, 71.15, 69.21, 66.68, 44.49, 39.90, 32.41, 26.27; HRMS (ESI) calcd for $C_{33}H_{44}NO_5$ $[M+NH_4]^+$ 534.3214, found 534.3216.

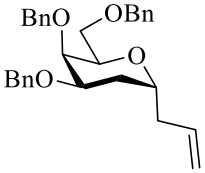
Compound 3e



C-Glycoside **3e** was obtained (20.1 mg, 75%, α/β = 2: 1) as a colorless oil according to the *C*-glycosylation procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 - 7.88 (m, 5.39H), 7.61 - 7.51 (m, 3.02H), 7.51 - 7.40 (m, 6.19H), 7.38 - 7.12 (m, 40.86H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.78 - 4.46 (m, 16.54H), 4.10 - 3.99 (m, 1.09H), 3.89 - 3.87 (m, 1.70H), 3.84 - 3.65 (m, 7.87H), 3.60 - 3.50 (m, 2.67H), 3.51 - 3.42 (m, 2.12H), 3.39 (d, *J* = 5.9 Hz, 0.86H), 3.35 (d, *J* = 5.8 Hz, 1.04H), 3.16 - 3.01 (m, 2.73H), 2.40 (dd, *J* = 12.4, 3.8 Hz, 0.97H), 2.13 - 1.99 (m, 2.19H), 1.98 - 1.84 (m, 2.04H),

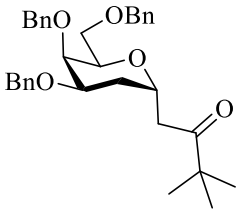
1.75 - 1.53 (m, 1.81H), 1.50 - 1.40 (m, 1.47H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.00, 197.94, 138.66, 138.41, 137.17, 137.10, 133.37, 128.79, 128.75, 128.52, 128.44, 128.34, 128.30, 128.09, 128.08, 127.93, 127.82, 127.81, 127.75, 127.73, 127.67, 81.04, 79.13, 78.37, 76.00, 75.85, 75.12, 74.14, 73.81, 73.57, 73.51, 72.19, 71.58, 71.26, 69.46, 69.08, 67.08, 42.04, 36.98, 32.61. HRMS (ESI) calcd for $C_{35}H_{40}NO_5$ $[M+NH_4]^+$ 554.2901, found 554.2909.

Compound 3f



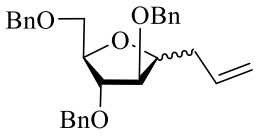
C-Glycoside **3f** was obtained (22.2 mg, 97%, α only) as a colorless oil according to the *C*-glycosylation procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.25 (m, 15H), 5.82 - 5.72 (m, 1H), 5.07 - 5.05 (m, 1H), 5.02 (s, 1H), 4.72 (d, *J* = 11.9 Hz, 1H), 4.64 - 4.49 (m, 5H), 4.07 - 4.02 (m, 1H), 4.01 - 3.96 (m, 1H), 3.93 - 3.88 (m, 1H), 3.83 - 3.79 (m, 1H), 3.77 - 3.76 (m, 1H), 3.71 - 3.68 (m, 1H), 2.40 - 2.33 (m, 1H), 2.21 - 2.14 (m, 1H), 2.09 - 2.03 (m, 1H), 1.58 - 1.52 (m, 1H). The spectroscopic data coincide with the previous report.[5]

Compound 3g



C-Glycoside **3g** was obtained (24.5 mg, 95%, α only) as a colorless oil according to the *C*-glycosylation procedure. $[\alpha]_D^{25}$ +6.0 (*c* 0.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 - 7.25 (m, 15H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.66 - 4.54 (m, 4H), 4.53 - 4.45 (m, 2H), 4.05 - 4.01 (m, 1H), 3.96 - 3.91 (m, 1H), 3.79 - 3.77 (m, 1H), 3.75 - 3.71 (m, 2H), 2.84 (dd, *J* = 16.9, 5.4 Hz, 1H), 2.55 (dd, *J* = 16.9, 7.7 Hz, 1H), 2.23 - 2.17 (m, 1H), 1.49 - 1.43 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.19, 138.60, 138.57, 138.49, 128.32, 128.30, 127.84, 127.74, 127.56, 127.49, 127.42, 127.37, 74.92, 74.39, 73.35, 72.95, 72.17, 70.90, 67.87, 64.77, 44.30, 40.57, 32.43, 26.17. HRMS (ESI) calcd for $C_{33}H_{44}NO_5$ $[M+NH_4]^+$ 534.3214, found 534.3221.

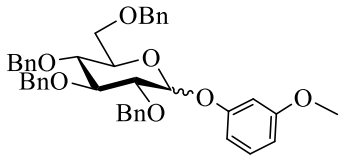
Compound 3h



C-Glycoside **3h** was obtained (20.4 mg, 92%, α/β = 1: 1) as a colorless oil according to the *C*-glycosylation procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.18 (m, 15.00H), 5.82 - 5.65 (m, 1.07H), 5.07 - 4.93 (m, 2.09H), 4.53 - 4.40 (m, 5.54H), 4.29 (d, *J* = 11.9 Hz, 0.58H), 4.19 - 4.11 (m, 0.53H), 4.03 - 3.93 (m, 2.05H), 3.85 (d, *J* = 2.6 Hz, 0.57H), 3.80 (dd, *J* = 4.3, 2.8 Hz, 0.52H),

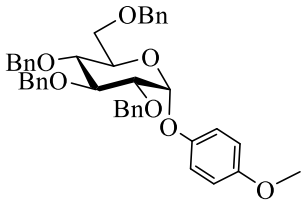
3.74 (d, *J* = 3.5 Hz, 0.54H), 3.58 - 3.41 (m, 2.04H), 2.45 - 2.39 (m, 1.00H), 2.37 - 2.29 (m, 1.02H). The spectroscopic data coincide with the previous report.[6]

Compound 5a



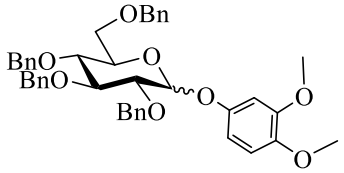
Glycoside **5a** was obtained (29.4 mg, 91%, α/β = 2: 1) as a colorless oil according to the *C*-glycosylation procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.24 (m, 30.12H), 7.21 - 7.12 (m, 4.75H), 6.71 - 6.64 (m, 3.06H), 6.62 - 6.56 (m, 1.55H), 5.47 (d, *J* = 3.5 Hz, 1.00H), 5.04 (dd, *J* = 10.9, 7.1 Hz, 1.60H), 4.99 (dd, *J* = 5.4, 1.9 Hz, 0.59H), 4.94 (d, *J* = 11.0 Hz, 0.62H), 4.91 - 4.75 (m, 4.88H), 4.68 (d, *J* = 12.0 Hz, 1.03H), 4.61 - 4.47 (m, 3.86H), 4.41 (d, *J* = 12.0 Hz, 1.03H), 4.19 (t, *J* = 9.2 Hz, 1.00H), 3.91 - 3.85 (m, 1.04H), 3.81 - 3.55 (m, 12.72H). The spectroscopic data coincide with the previous report.[7]

Compound 5b



Glycoside **5b** was obtained (29.7 mg, 92%, α only) as a colorless oil according to the *C*-glycosylation procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.26 (m, 18H), 7.18 - 7.12 (m, 2H), 7.05 - 6.98 (m, 2H), 6.83 - 6.77 (m, 2H), 5.36 (d, *J* = 3.5 Hz, 1H), 5.04 (d, *J* = 10.8 Hz, 1H), 4.87 (dd, *J* = 10.8, 6.7 Hz, 2H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 10.8 Hz, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.18 (t, *J* = 9.3 Hz, 1H), 3.97 - 3.89 (m, 1H), 3.79 - 3.68 (m, 6H), 3.59 (dd, *J* = 10.7, 1.8 Hz, 1H). The spectroscopic data coincide with the previous report.[8]

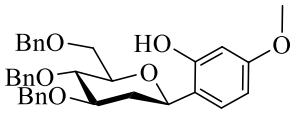
Compound 5c



Glycoside **5c** was obtained (29.7 mg, 88%, α/β = 2: 1) as a colorless oil according to the *C*-glycosylation procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.25 (m, 27.06H), 7.20 - 7.17 (m, 0.85H), 7.16 - 7.12 (m, 1.96H), 6.74 (d, *J* = 8.7 Hz, 1.46H), 6.68 (d, *J* = 2.3 Hz, 1.43H), 6.66 - 6.61 (m, 1.38H), 5.38 (d, *J* = 3.5 Hz, 1.00H), 5.39 - 5.36 (m, 1.45H), 4.95 (d, *J* = 10.9 Hz, 0.49H), 4.91 - 4.78 (m, 4.79H), 4.68 (d, *J* = 12.0 Hz, 1.08H), 4.60 - 4.49 (m, 3.18H), 4.42 (d, *J* = 12.0 Hz, 1.02H), 4.18 (t, *J* = 9.3 Hz, 1.02H), 3.94 - 3.90 (m, 1.05H), 3.83 (s, 4.43H), 3.80 (s, 3.36H), 3.77 - 3.56 (m, 8.04H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.94, 151.16, 149.59, 144.92, 144.54, 138.81,

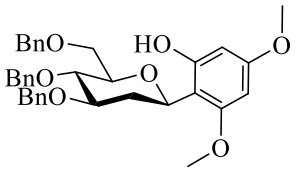
138.51, 138.35, 138.19, 138.11, 138.02, 137.81, 128.50, 128.44, 128.41, 128.40, 128.36, 128.17, 128.07, 127.95, 127.89, 127.83, 127.78, 127.74, 127.69, 127.65, 127.63, 111.68, 111.60, 108.18, 107.29, 102.90, 102.87, 102.54, 96.18, 84.76, 82.17, 82.06, 79.83, 77.85, 77.54, 75.83, 75.79, 75.16, 75.06, 73.54, 73.45, 73.36, 70.74, 69.05, 68.41, 56.30, 55.89, 55.80. HRMS (ESI) calcd for $C_{42}H_{48}NO_8$ $[M+NH_4]^+$ 694.3374, found 694.3373.

Compound 5d



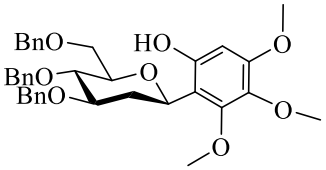
C-Glycoside **5d** was obtained (19.2 mg, 71%, β only) as a colorless oil according to the *C*-glycosylation procedure. $[\alpha]_D^{25}$ +0.8 (*c* 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.38 - 7.24 (m, 13H), 7.22 - 7.20 (m, 2H), 6.86 (d, *J* = 8.5 Hz, 1H), 6.49 (d, *J* = 2.5 Hz, 1H), 6.39 (dd, *J* = 8.4, 2.6 Hz, 1H), 4.92 (d, *J* = 10.9 Hz, 1H), 4.72 (d, *J* = 11.6 Hz, 1H), 4.65 - 4.47 (m, 5H), 3.80 - 3.75 (m, 4H), 3.72 - 3.64 (m, 3H), 3.61 - 3.55 (m, 1H), 2.41 - 2.36 (m, 1H), 1.93 (dd, *J* = 13.0, 11.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.65, 156.98, 138.34, 138.28, 137.93, 128.43, 128.40, 128.07, 127.79, 127.76, 127.69, 127.63, 126.99, 117.39, 105.84, 102.91, 80.48, 78.58, 77.96, 77.66, 75.21, 73.42, 71.45, 68.59, 55.29, 36.93. HRMS (ESI) calcd for $C_{34}H_{36}NaO_6$ $[M+Na]^+$ 563.2404, found 563.2408.

Compound 5e



C-Glycoside **5e** was obtained (22.8 mg, 80%, β only) as a colorless oil according to the *C*-glycosylation procedure. $[\alpha]_D^{25}$ +34.7 (*c* 0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.40 - 7.24 (m, 13H), 7.23 - 7.19 (m, 2H), 6.11 (d, *J* = 2.2 Hz, 1H), 6.00 (d, *J* = 2.2 Hz, 1H), 5.02 (dd, *J* = 11.7, 2.0 Hz, 1H), 4.93 (d, *J* = 10.9 Hz, 1H), 4.70 (d, *J* = 11.6 Hz, 1H), 4.64 - 4.53 (m, 3H), 4.46 (d, *J* = 12.1 Hz, 1H), 3.79 - 3.73 (m, 9H), 3.67 (dd, *J* = 10.2, 1.9 Hz, 1H), 3.56 - 3.49 (m, 1H), 2.38 - 2.27 (m, 1H), 1.90 - 1.75 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.78, 157.64, 156.86, 138.61, 138.55, 138.07, 128.42, 128.39, 128.36, 128.05, 127.79, 127.66, 127.59, 127.55, 106.17, 94.83, 90.74, 80.55, 78.77, 75.19, 73.43, 73.36, 71.24, 68.35, 55.54, 55.30, 36.19. HRMS (ESI) calcd for $C_{35}H_{38}NaO_7$ $[M+Na]^+$ 593.2510, found 593.2520.

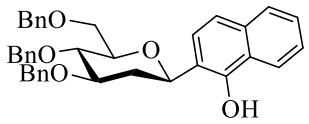
Compound 5f



C-Glycoside **5f** was obtained (24.6 mg, 82%, β only) as a colorless oil according to the *C*-glycosylation procedure. ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.31 (s, 1H), 7.36 - 7.25 (m, 13H), 7.24

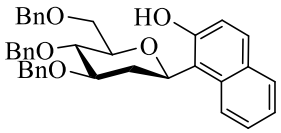
- 7.19 (m, 2H), 6.27 (s, 1H), 4.96 - 4.91 (m, 2H), 4.70 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 4.61 - 4.52 (m, 2H), 4.46 (d, *J* = 12.1 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.80 - 3.74 (m, 6H), 3.67 (dd, *J* = 10.2, 2.2 Hz, 1H), 3.57 - 3.51 (m, 1H), 2.33 - 2.23 (m, 1H), 1.94 - 1.82 (m, 1H). The spectroscopic data coincide with the previous report.[9]

Compound 5g



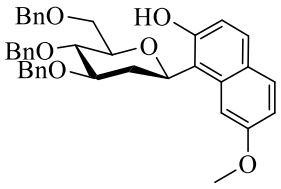
C-Glycoside **5g** was obtained (20.1 mg, 72%, β only) as a colorless oil according to the *C*-glycosylation procedure. $[\alpha]_D^{25}$ -5.0 (*c* 0.40, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.35 - 8.28 (m, 1H), 7.78 - 7.71 (m, 1H), 7.49 -7.45 (m, 2H), 7.41 - 7.27 (m, 14H), 7.25 - 7.19 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.80 (dd, *J* = 11.9, 2.2 Hz, 1H), 4.73 (d, *J* = 11.6 Hz, 1H), 4.67 - 4.52 (m, 4H), 3.87 - 3.74 (m, 4H), 3.68 - 3.62 (m, 1H), 2.49 - 2.44 (m, 1H), 2.08 - 1.96 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.32, 138.40, 138.30, 137.97, 134.01, 128.45, 128.41, 128.11, 127.90, 127.78, 127.73, 127.68, 127.62, 127.17, 126.34, 125.77, 125.15, 124.15, 122.44, 119.11, 117.44, 80.51, 79.09, 78.76, 77.56, 75.26, 73.45, 71.41, 68.51, 37.22. HRMS (ESI) calcd for $C_{37}H_{40}NO_5$ $[M+NH_4]^+$ 578.2901, found 578.2906.

Compound 5h



C-Glycoside **5h** was obtained (25.2 mg, 90%, β only) as a colorless oil according to the *C*-glycosylation procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.47 - 7.42 (m, 1H), 7.39 - 7.25 (m, 14H), 7.24 - 7.19 (m, 2H), 7.15 (d, *J* = 8.9 Hz, 1H), 5.47 (dd, *J* = 11.9, 2.1 Hz, 1H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.70 (d, *J* = 11.6 Hz, 1H), 4.66 - 4.55 (m, 3H), 4.49 (d, *J* = 12.1 Hz, 1H), 3.92 - 3.86 (m, 2H), 3.83 (dd, *J* = 10.2, 2.6 Hz, 1H), 3.73 (dd, *J* = 10.2, 2.2 Hz, 1H), 3.67 - 3.62 (m, 1H), 2.53 - 2.45 (m, 1H), 2.05 - 1.95 (m, 1H). The spectroscopic data coincide with the previous report.[10]

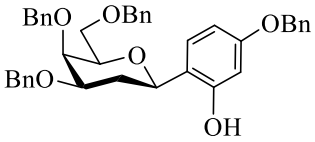
Compound 5i



C-Glycoside **5i** was obtained (26.8 mg, 91%, β only) as a colorless oil according to the *C*-glycosylation procedure. $[\alpha]_D^{25}$ +103.8 (*c* 0.13, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.40 - 7.26 (m, 13H), 7.25 - 7.21 (m, 2H), 6.99 (dd, *J* = 8.9, 2.6 Hz, 2H), 6.88 (d, *J* = 2.1 Hz, 1H), 5.35 (dd, *J* = 11.9, 1.9 Hz, 1H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.72 - 4.56 (m, 4H), 4.49 (d, *J* = 12.1 Hz, 1H), 3.93 - 3.85 (m, 5H), 3.83 (dd, *J* =

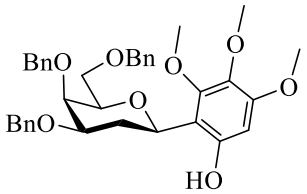
10.2, 2.6 Hz, 1H), 3.73 (dd, *J* = 10.2, 2.2 Hz, 1H), 3.69 - 3.61 (m, 1H), 2.52 - 2.43 (m, 1H), 2.05 - 1.95 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.39, 154.66, 138.42, 138.26, 137.94, 131.91, 130.50, 129.48, 128.46, 128.44, 128.40, 128.05, 127.86, 127.74, 127.70, 124.07, 117.79, 114.18, 113.87, 101.07, 80.13, 79.05, 75.69, 75.25, 73.45, 71.28, 68.07, 55.34, 35.69. HRMS (ESI) calcd for $C_{38}H_{42}NO_6$ $[M+NH_4]^+$ 608.3007, found 608.3013.

Compound 5j



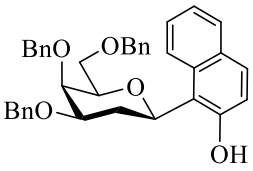
C-Glycoside **5j** was obtained (24.0 mg, 78%, β only) as a colorless oil according to the *C*-glycosylation procedure. $[\alpha]_D^{25}$ -18.0 (*c* 0.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.43 - 7.26 (m, 20H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.54 (d, *J* = 2.5 Hz, 1H), 6.43 (dd, *J* = 8.4, 2.5 Hz, 1H), 5.05 - 4.97 (m, 3H), 4.69 - 4.57 (m, 3H), 4.54 (dd, *J* = 11.8, 2.7 Hz, 1H), 4.47 (d, *J* = 11.9 Hz, 1H), 4.40 (d, *J* = 11.8 Hz, 1H), 3.94 (s, 1H), 3.73 - 3.67 (m, 1H), 3.66 - 3.51 (m, 3H), 2.53 - 2.41 (m, 1H), 2.11 - 2.02 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.92, 157.02, 138.72, 138.27, 137.79, 137.04, 128.54, 128.48, 128.43, 128.27, 127.92, 127.88, 127.80, 127.66, 127.48, 127.45, 127.40, 127.29, 118.44, 106.36, 103.74, 78.55, 77.90, 77.72, 74.06, 73.57, 72.18, 70.12, 69.96, 69.24, 32.28. HRMS (ESI) calcd for $C_{40}H_{44}NO_6$ $[M+NH_4]^+$ 634.3163, found 634.3176.

Compound 5k



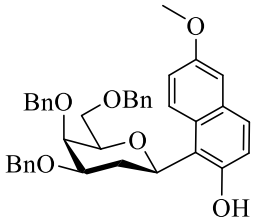
C-Glycoside **5k** was obtained (24.3 mg, 81%, β only) as a colorless oil according to the *C*-glycosylation procedure. $[\alpha]_D^{25}$ +20.4 (*c* 0.46, $CHCl_3$). ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.85 (s, 1H), 7.34 - 7.25 (m, 15H), 6.25 (s, 1H), 5.04 (d, *J* = 11.8 Hz, 1H), 4.95 (dd, *J* = 11.9, 3.1 Hz, 1H), 4.66 - 4.60 (m, 3H), 4.43 (dd, *J* = 11.9 Hz, 2H), 3.97 (s, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 3.77 (s, 3H), 3.75 - 3.69 (m, 1H), 3.68 - 3.63 (m, 1H), 3.62 - 3.57 (m, 2H), 2.49 - 2.40 (m, 1H), 2.01 - 1.96 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.56, 152.34, 149.89, 138.88, 138.37, 137.81, 134.85, 128.42, 128.25, 127.89, 127.79, 127.57, 127.36, 127.25, 111.23, 97.13, 77.92, 77.73, 74.02, 73.53, 73.08, 72.32, 70.12, 68.98, 61.37, 60.94, 55.82, 32.17. HRMS (ESI) calcd for $C_{36}H_{44}NO_8$ $[M+NH_4]^+$ 618.3061, found 618.3068.

Compound 5l



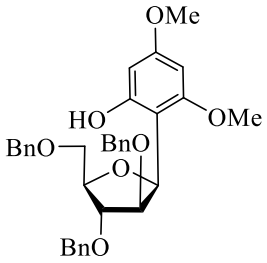
C-Glycoside **5l** was obtained (23.8 mg, 85%, β only) as a colorless oil according to the *C*-glycosylation procedure. $[\alpha]_D^{25}$ +56.9 (*c* 0.16, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.71 - 7.67 (m, 2H), 7.46 - 7.41 (m, 1H), 7.38 - 7.25 (m, 16H), 7.14 (d, *J* = 8.9 Hz, 1H), 5.45 (dd, *J* = 12.0, 2.9 Hz, 1H), 5.07 (d, *J* = 11.9 Hz, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.47 (d, *J* = 11.9 Hz, 1H), 4.41 (d, *J* = 11.9 Hz, 1H), 4.04 (s, 1H), 3.84 - 3.79 (m, 1H), 3.77 (d, *J* = 6.4 Hz, 1H), 3.68 - 3.61 (m, 2H), 2.62 - 2.50 (m, 1H), 2.19 - 2.14 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.23, 138.82, 138.25, 137.78, 130.80, 129.72, 128.90, 128.58, 128.48, 128.45, 128.32, 127.93, 127.84, 127.69, 127.66, 127.46, 127.29, 126.58, 122.73, 120.62, 119.90, 116.12, 78.27, 77.90, 75.02, 74.13, 73.61, 72.36, 70.13, 69.08, 31.36. HRMS (ESI) calcd for $C_{37}H_{40}NO_5$ $[M+NH_4]^+$ 578.2901, found 578.2909.

Compound 5m



C-Glycoside **5m** was obtained (25.9 mg, 88%, β only) as a colorless oil according to the *C*-glycosylation procedure. $[\alpha]_D^{25}$ +46.4 (*c* 0.11, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.60 (dd, *J* = 12.7, 9.1 Hz, 2H), 7.39 - 7.25 (m, 15H), 7.14 - 7.08 (m, 3H), 5.40 (dd, *J* = 12.0, 2.7 Hz, 1H), 5.07 (d, *J* = 11.9 Hz, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.66 - 4.55 (m, 2H), 4.50 - 4.37 (m, 2H), 4.04 (s, 1H), 3.89 (s, 3H), 3.83 - 3.78 (m, 1H), 3.76 (d, *J* = 6.3 Hz, 1H), 3.64 (d, *J* = 6.3 Hz, 2H), 2.63 - 2.50 (m, 1H), 2.17 - 2.09 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.31, 152.50, 138.82, 138.24, 137.77, 129.51, 128.47, 128.45, 128.40, 128.30, 127.93, 127.83, 127.68, 127.65, 127.44, 127.28, 125.99, 122.20, 120.31, 118.95, 116.49, 107.22, 78.23, 77.91, 75.11, 74.11, 73.60, 72.33, 70.13, 69.07, 55.31, 31.42. HRMS (ESI) calcd for $C_{38}H_{42}NO_6$ $[M+NH_4]^+$ 608.3007, found 608.3018.

Compound 5n



C-Glycoside **5n** was obtained (19.4 mg, 70%, β only) as a yellow solid according to the *C*-glycosylation procedure. ^1H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.39 - 7.29 (m, 10H), 7.28 - 7.25 (m, 3H), 7.05 (dd, *J* = 6.6, 2.9 Hz, 2H), 6.13 (d, *J* = 2.3 Hz, 1H), 6.01 (d, *J* = 2.4 Hz, 1H), 5.51 (d, *J* = 3.5 Hz, 1H), 4.61 (d, *J* = 5.6 Hz, 2H), 4.49 (s, 2H), 4.22 (d, *J* = 1.6 Hz, 2H), 4.20 – 4.15 (m, 1H), 4.09 (d, *J* = 3.5 Hz, 1H), 4.00 (d, *J* = 3.4 Hz, 1H), 3.80 (s, 3H), 3.74 - 3.64 (m, 5H). The spectroscopic data coincide with the previous report.[11]

3. References

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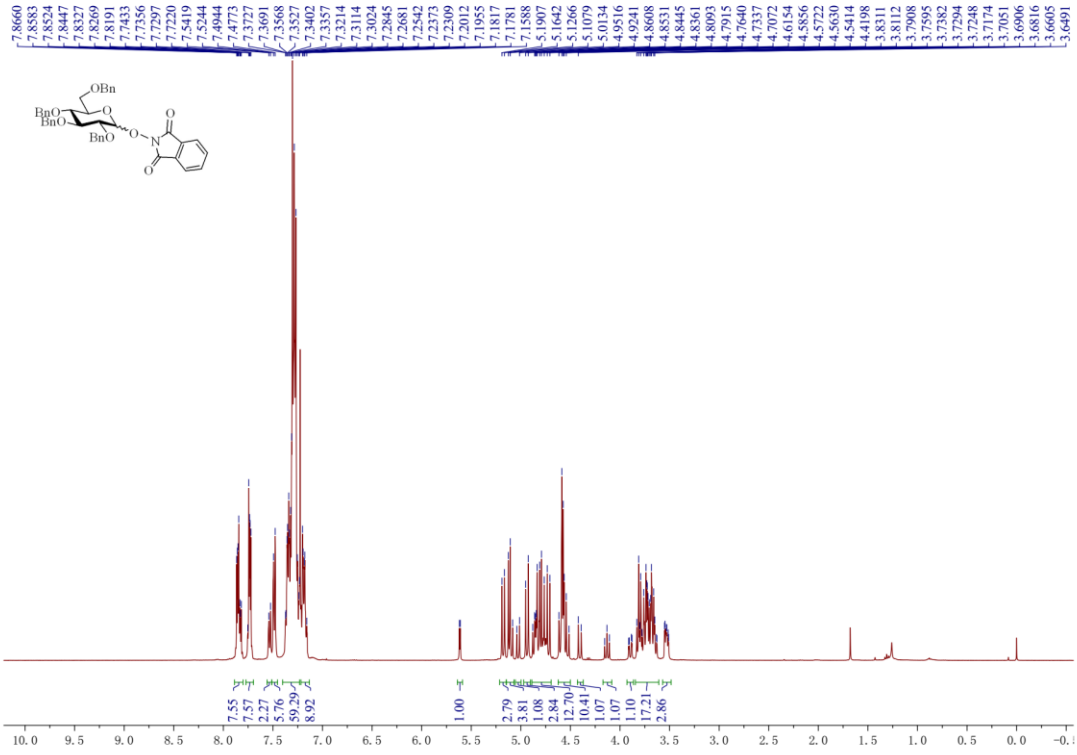
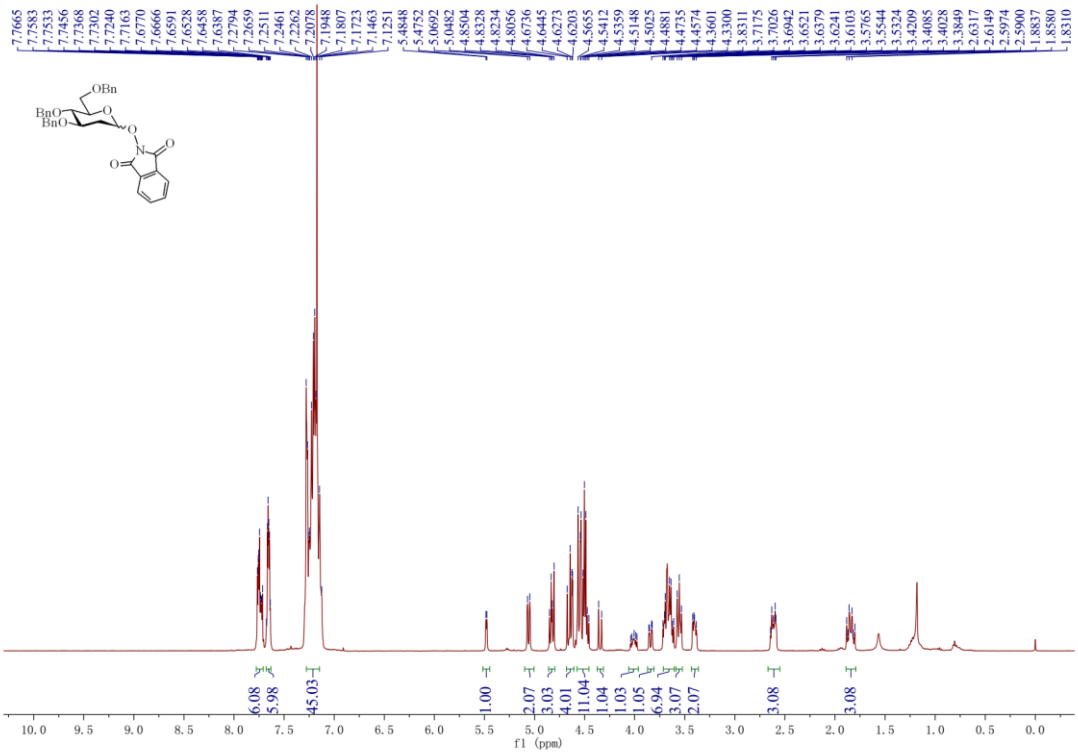
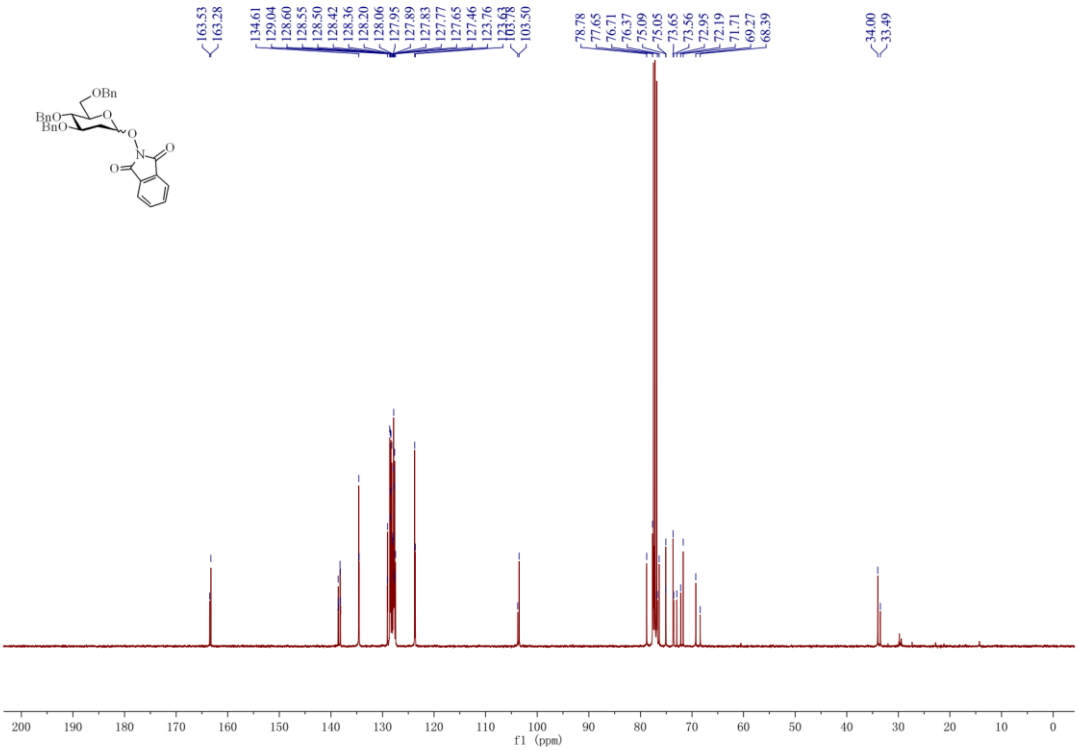
4. Copies of NMR Spectra



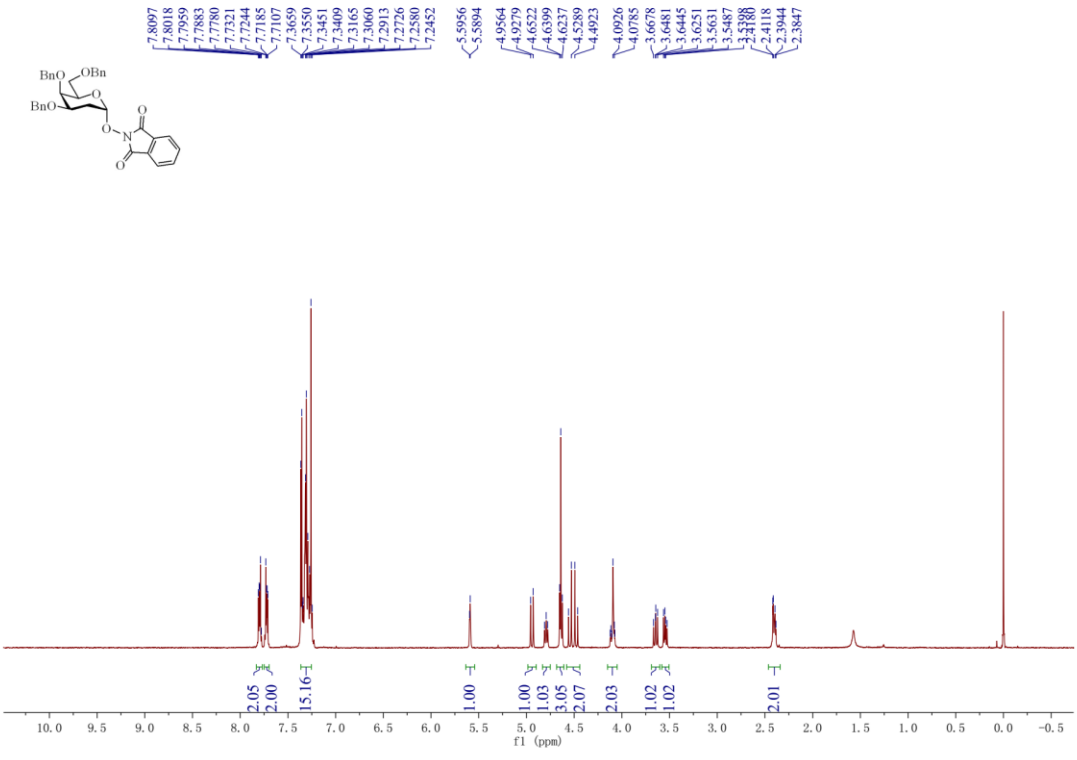
^{1}H NMR of compound **S2**



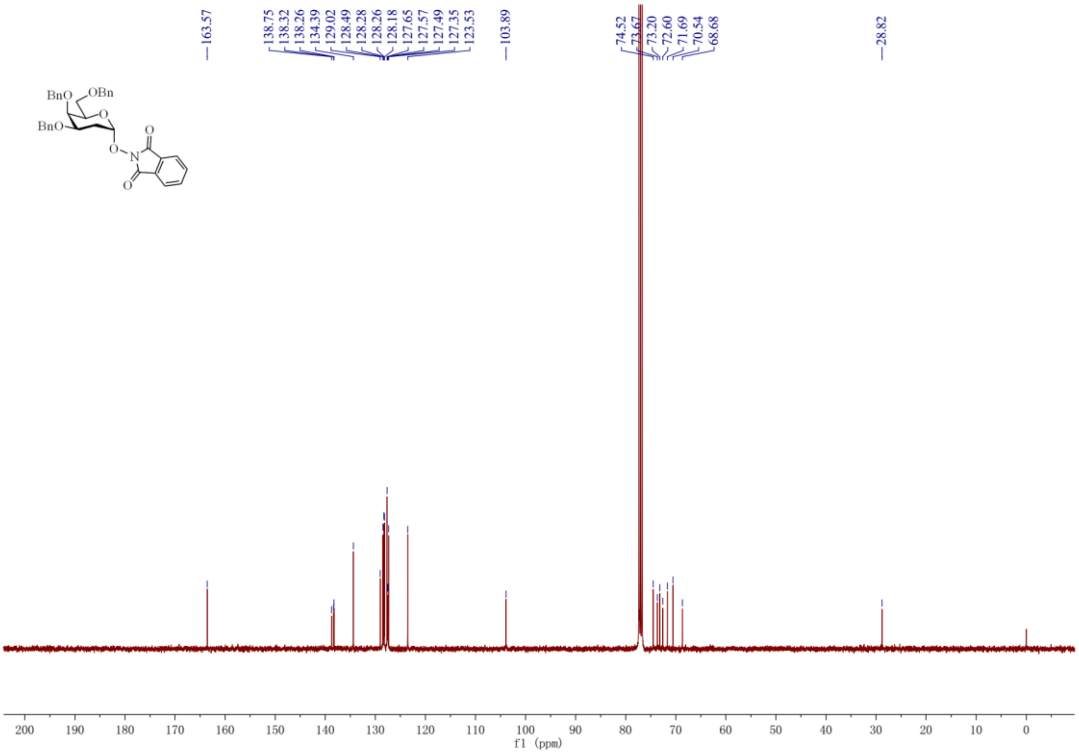
^{1}H NMR of compound **S4**



^{13}C NMR of compound **S4**



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



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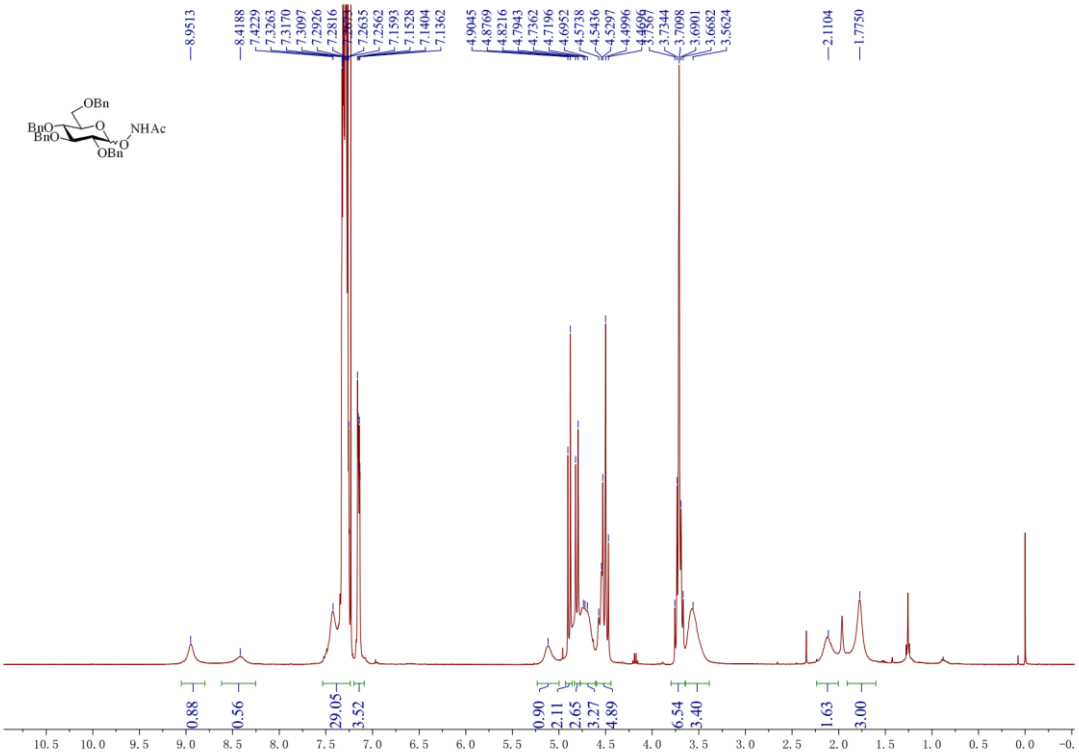
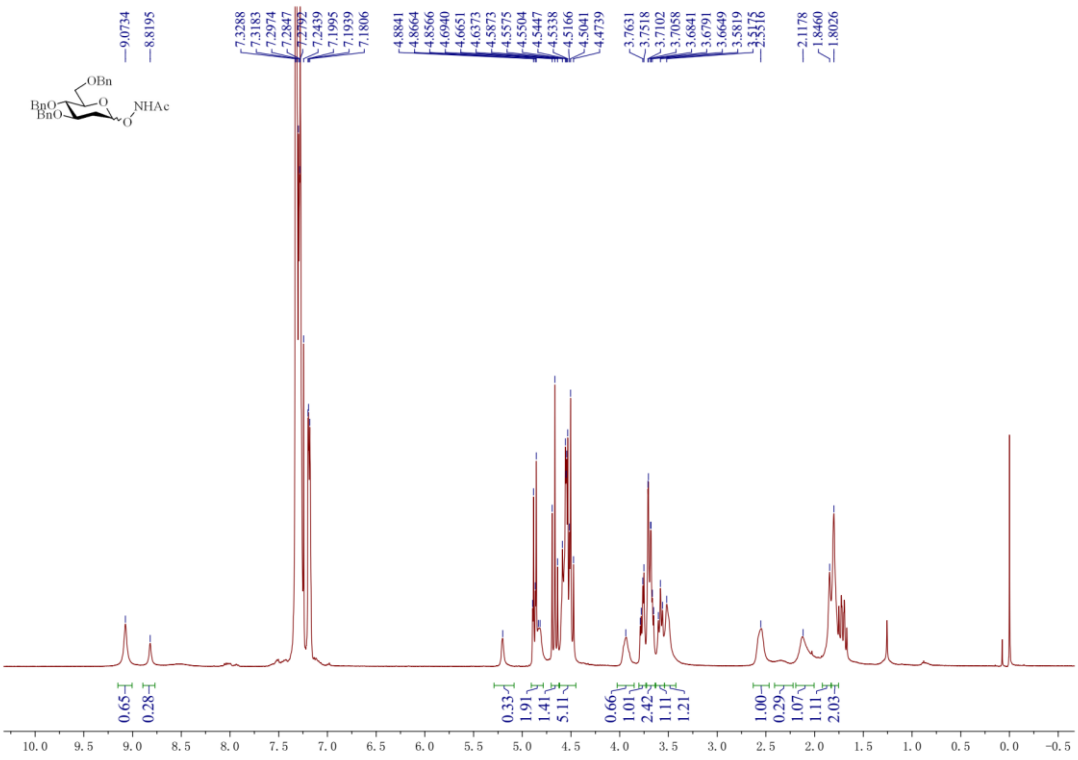
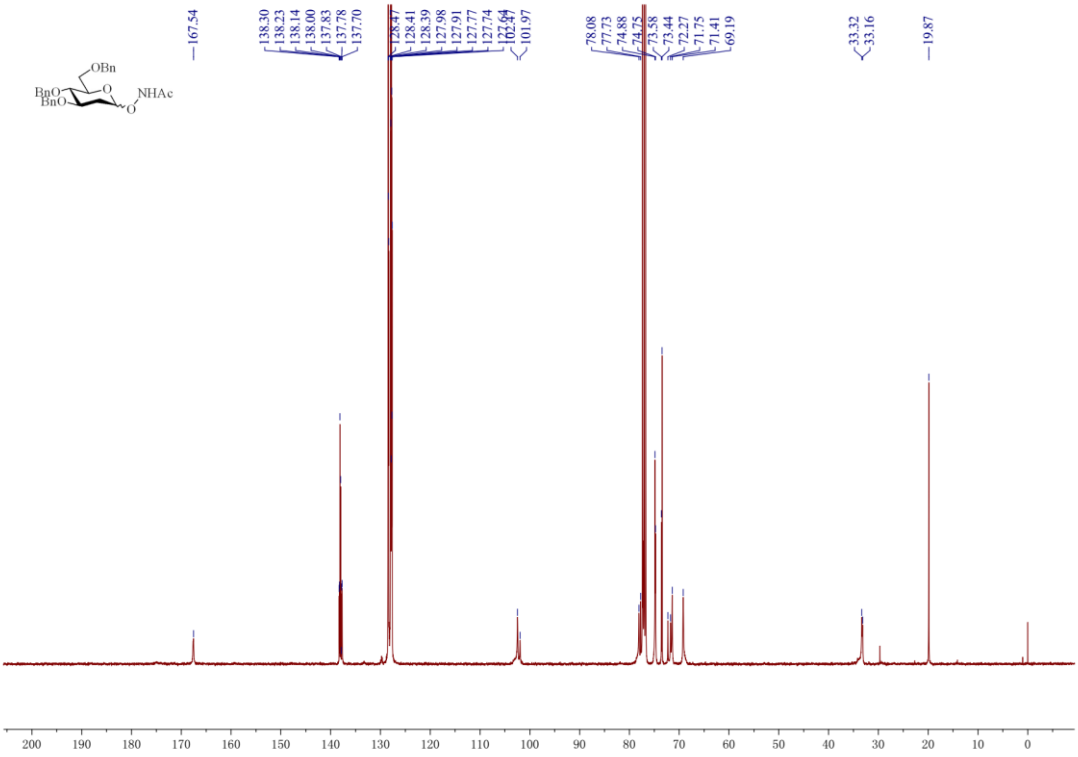


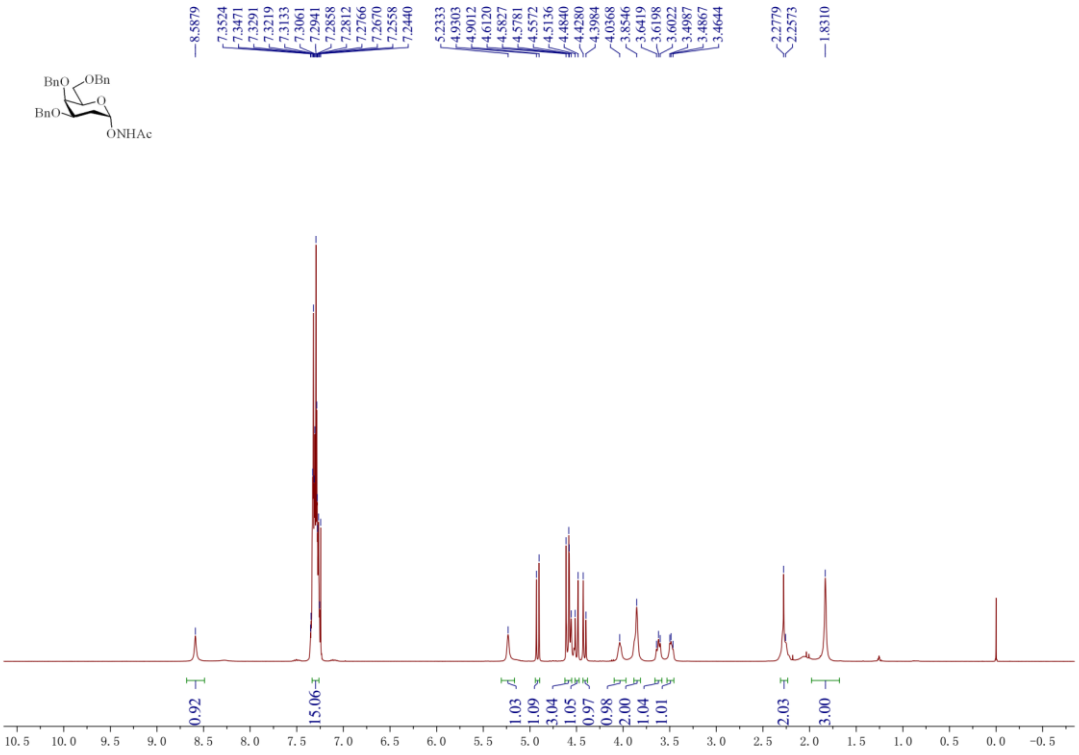
^{1}H NMR of compound **1a**



^{1}H NMR of compound **1b**



^{13}C NMR of compound **1b**



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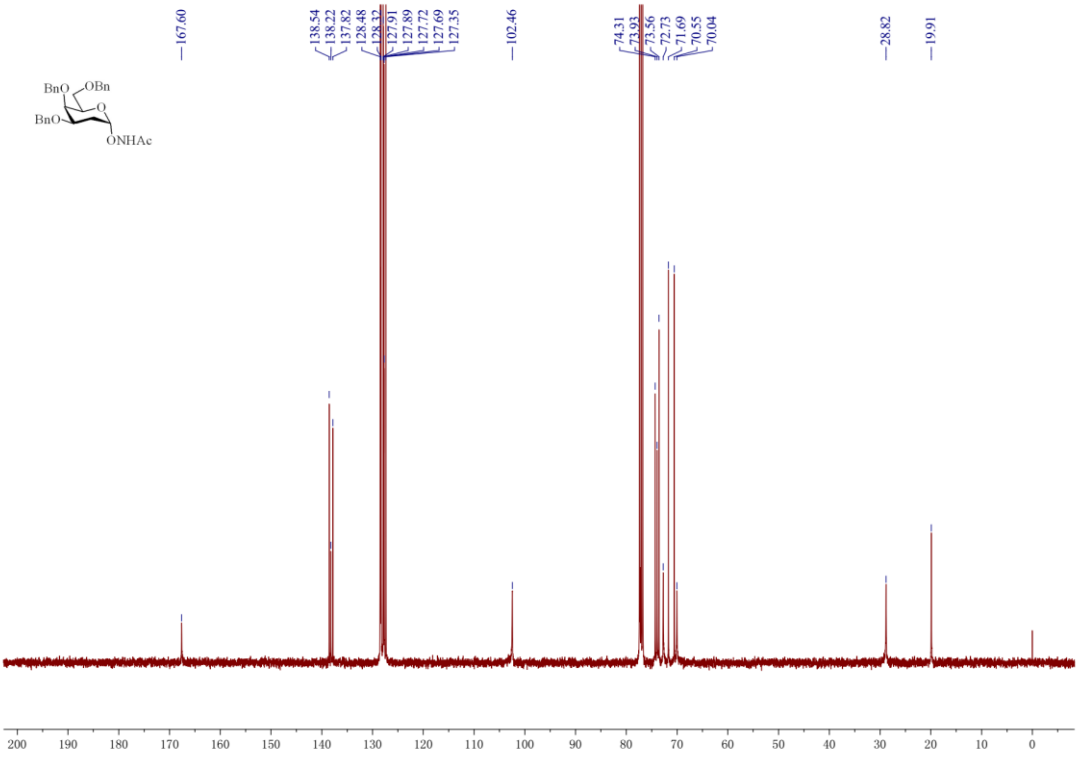

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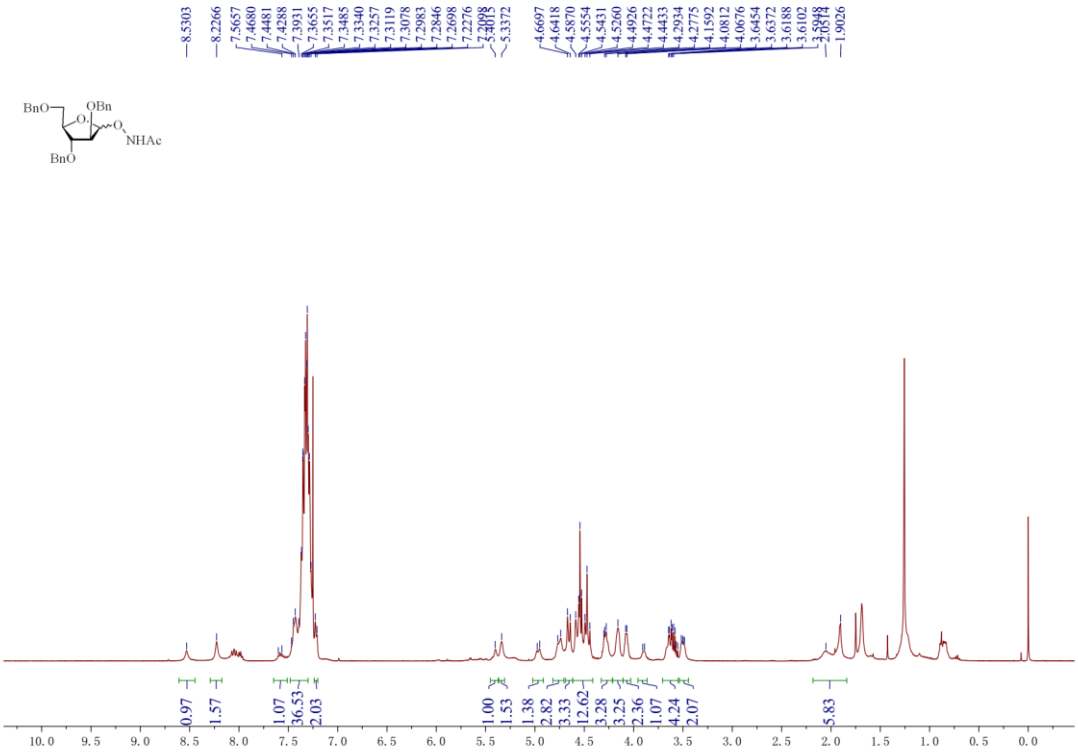
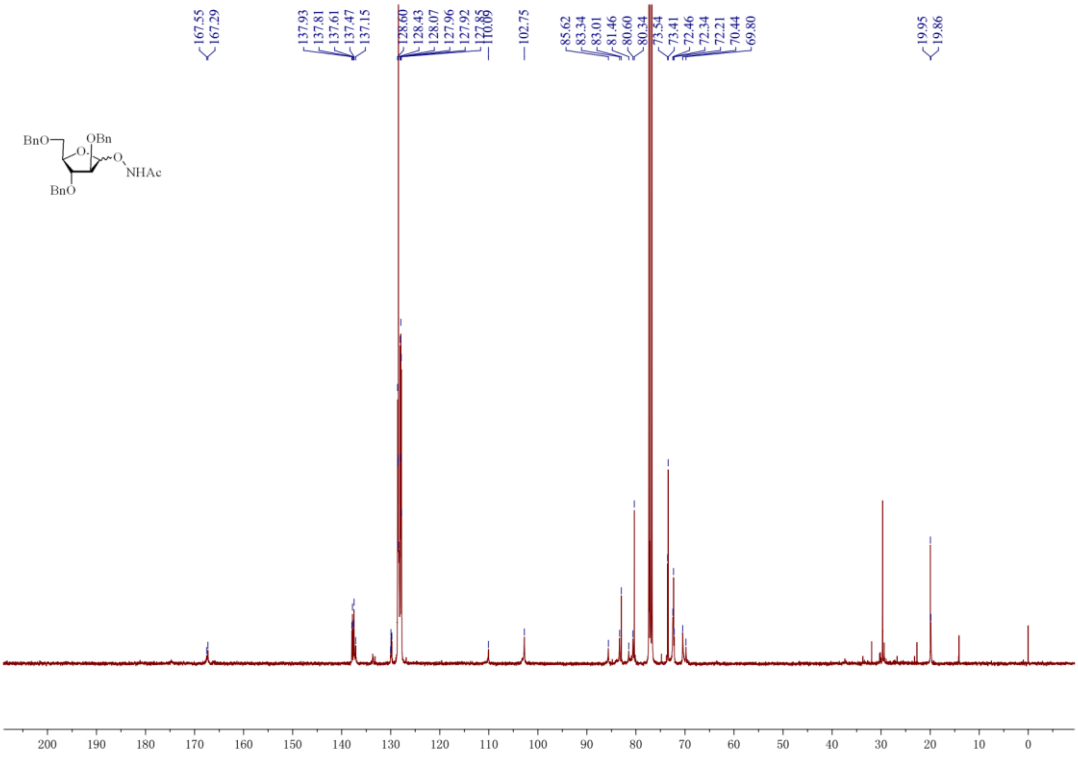
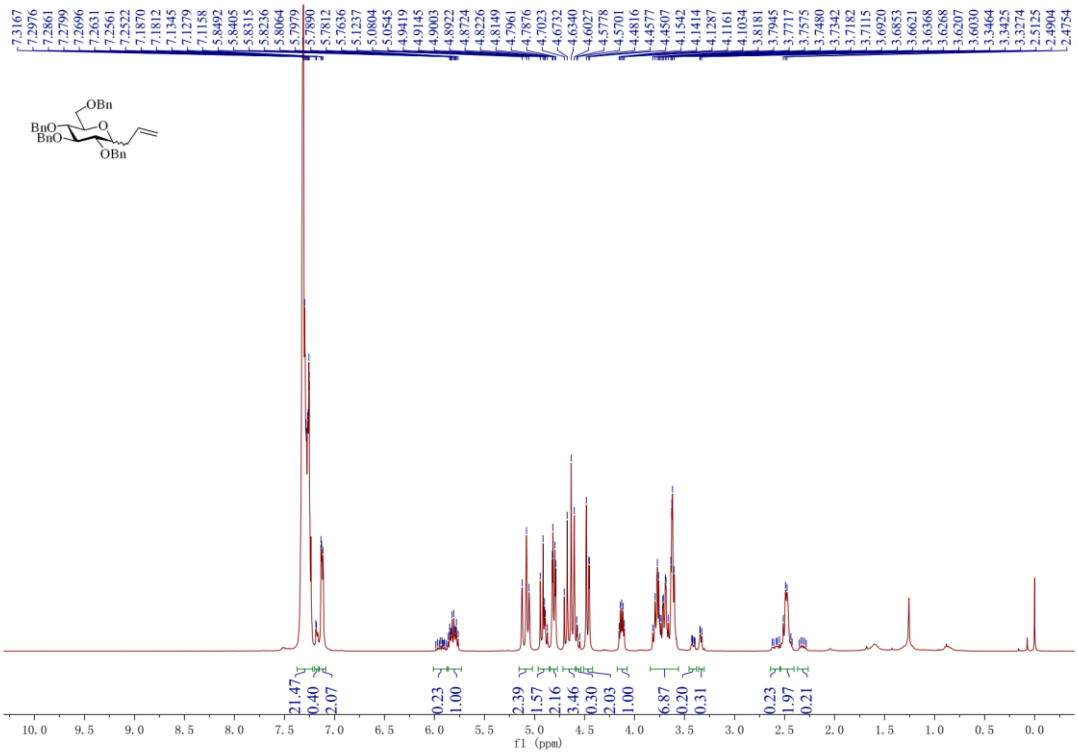


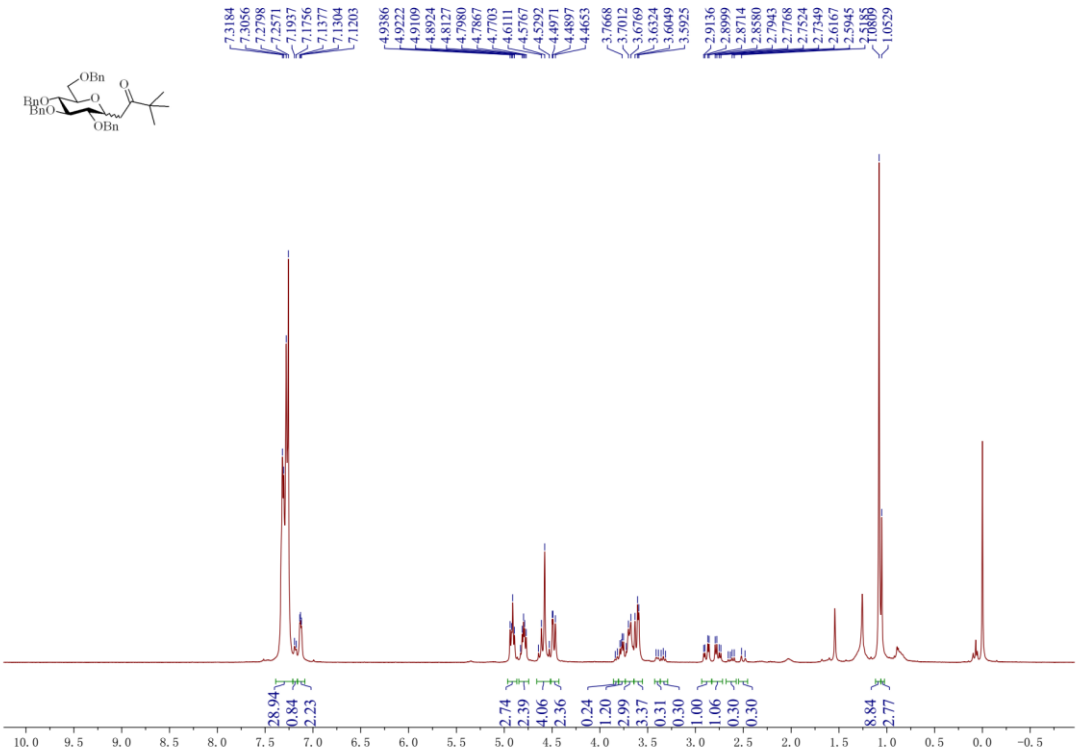
^{1}H NMR of compound **1d**



^{13}C NMR of compound **1d**



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



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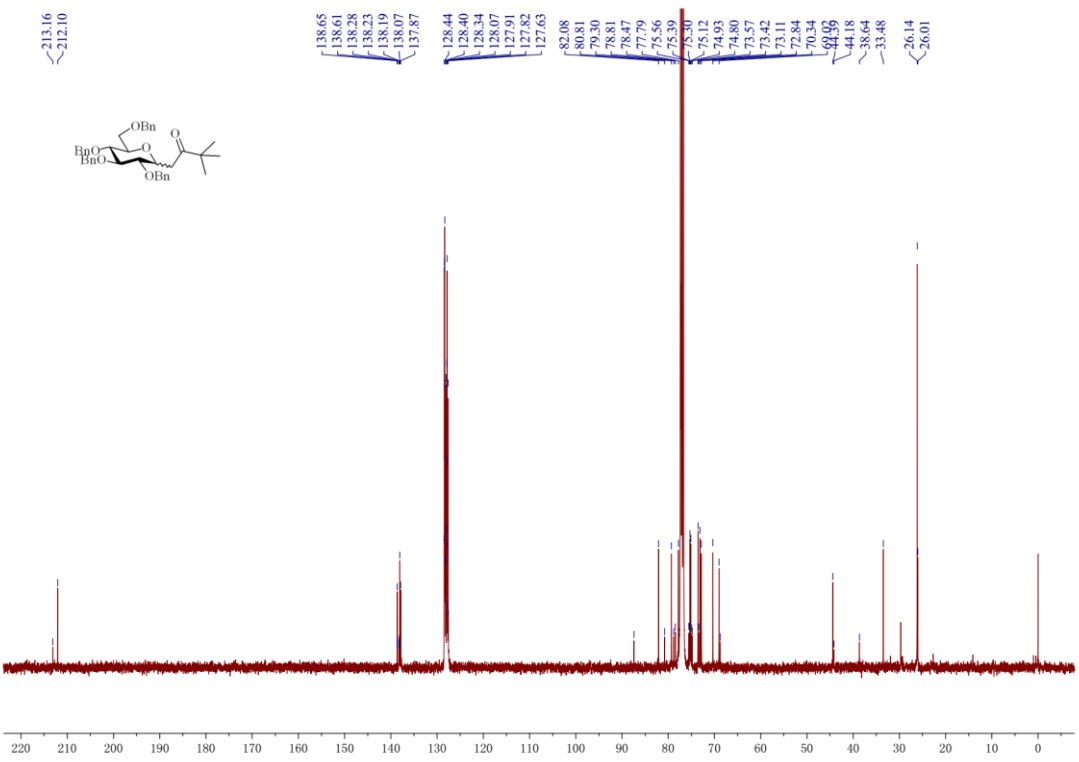
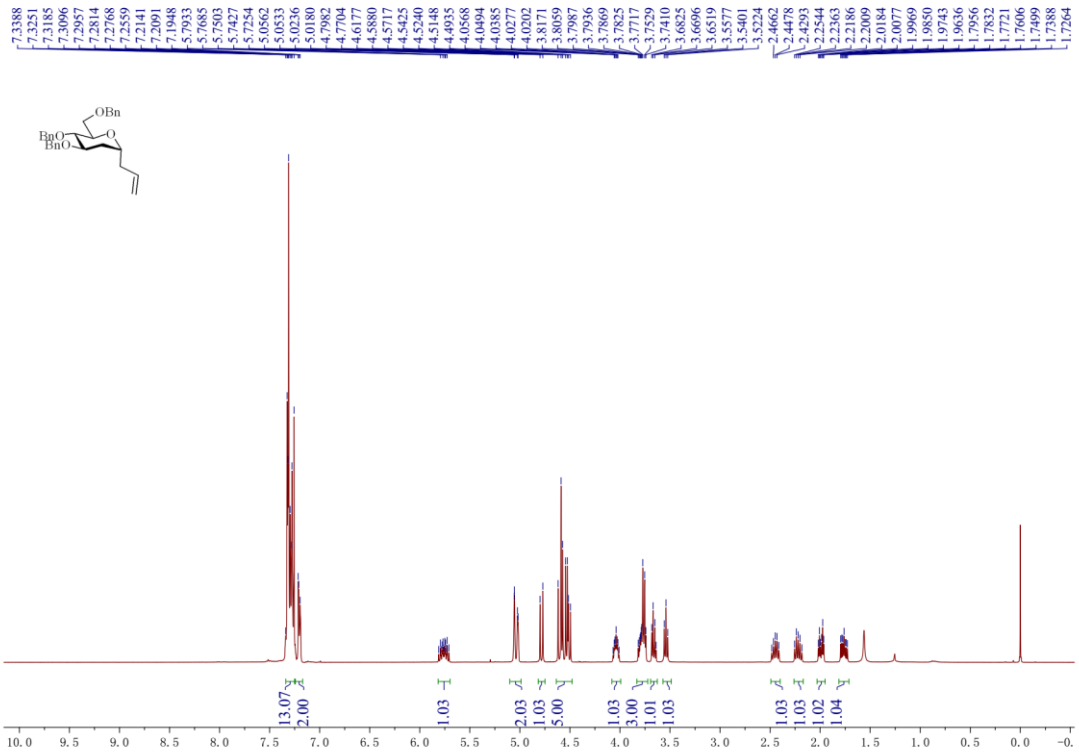
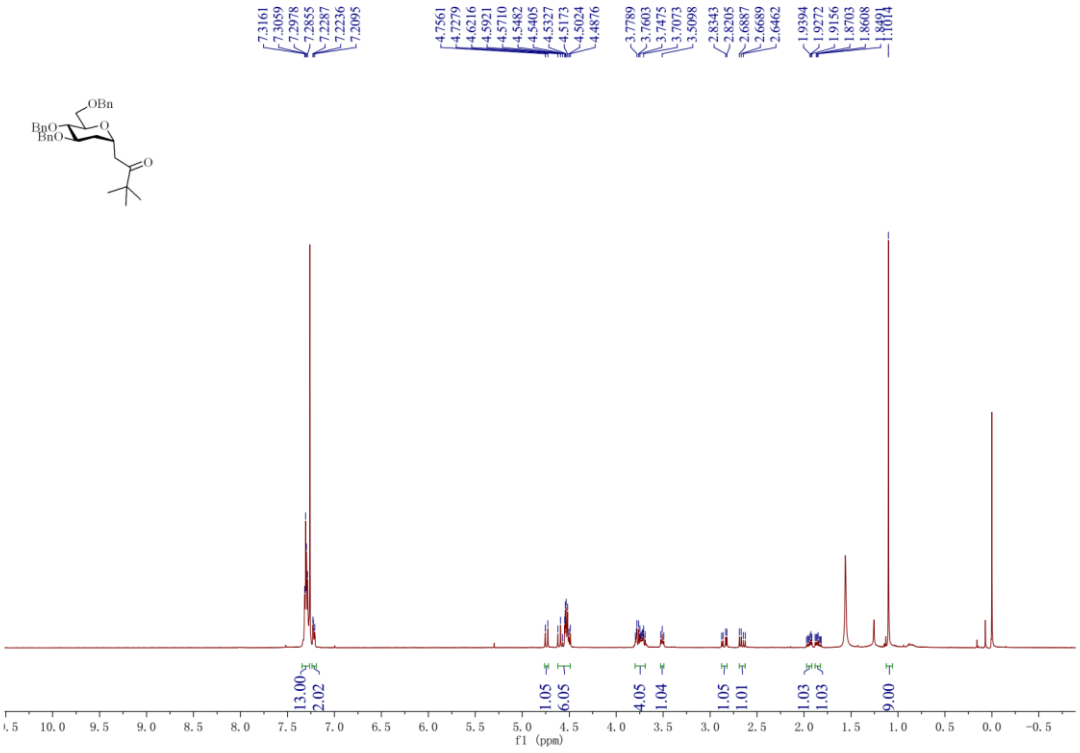


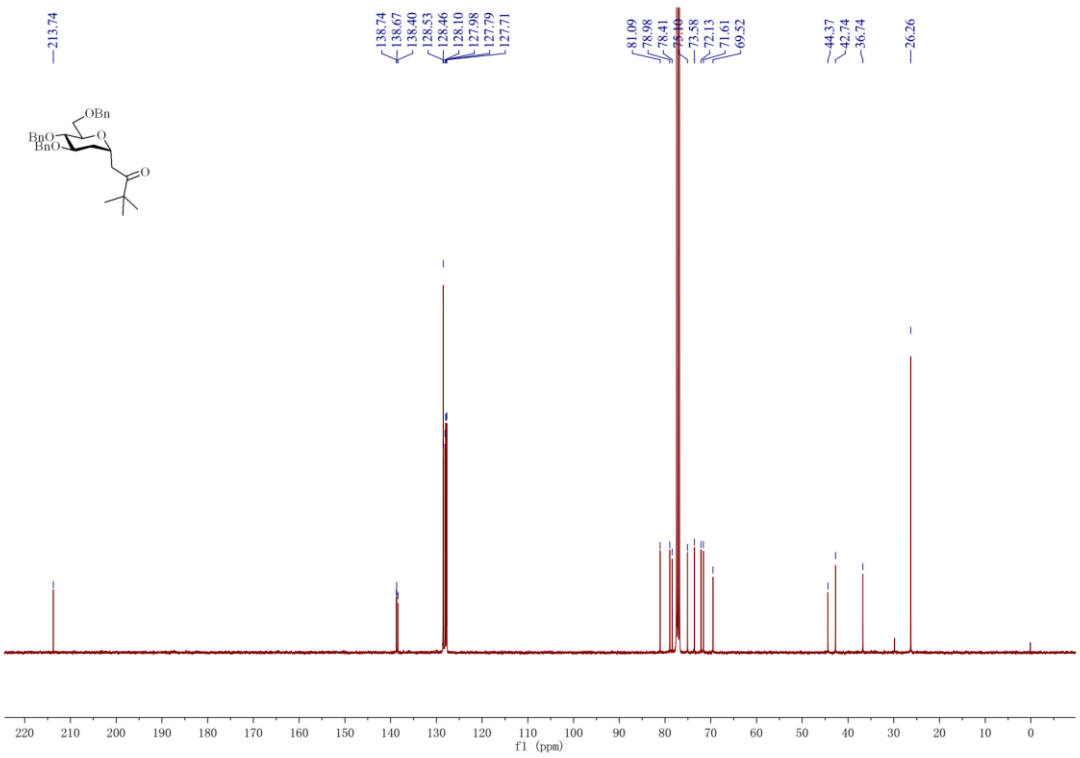
^{13}C NMR of compound **3b**



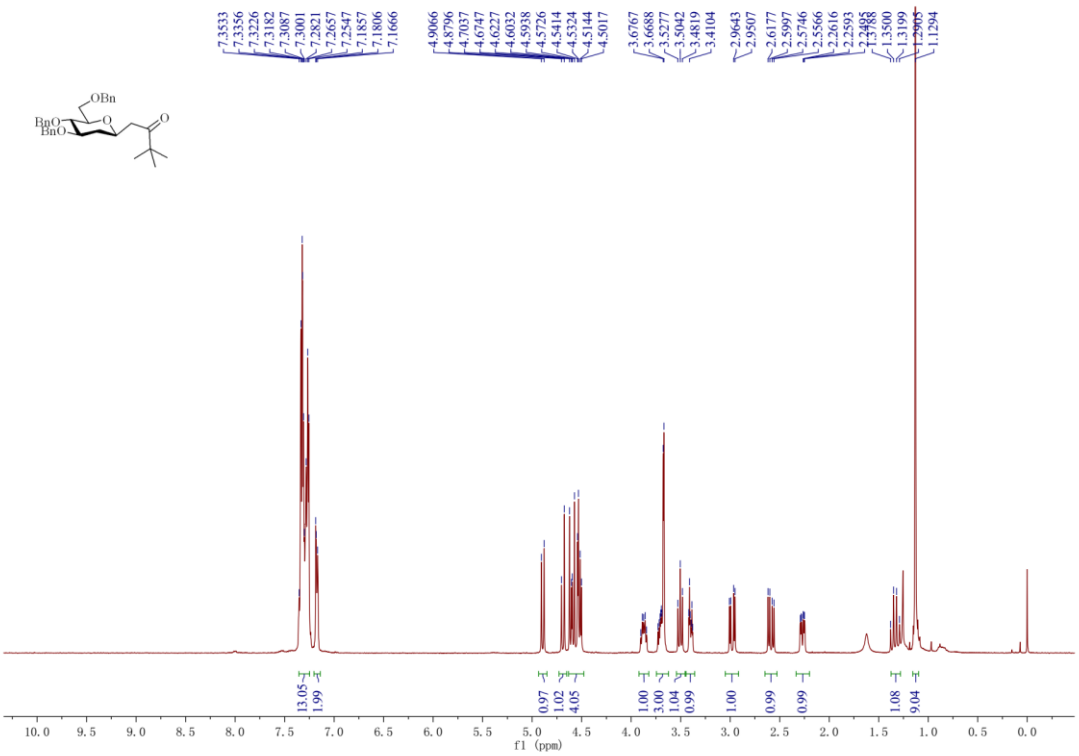
^{1}H NMR of compound **3cα**



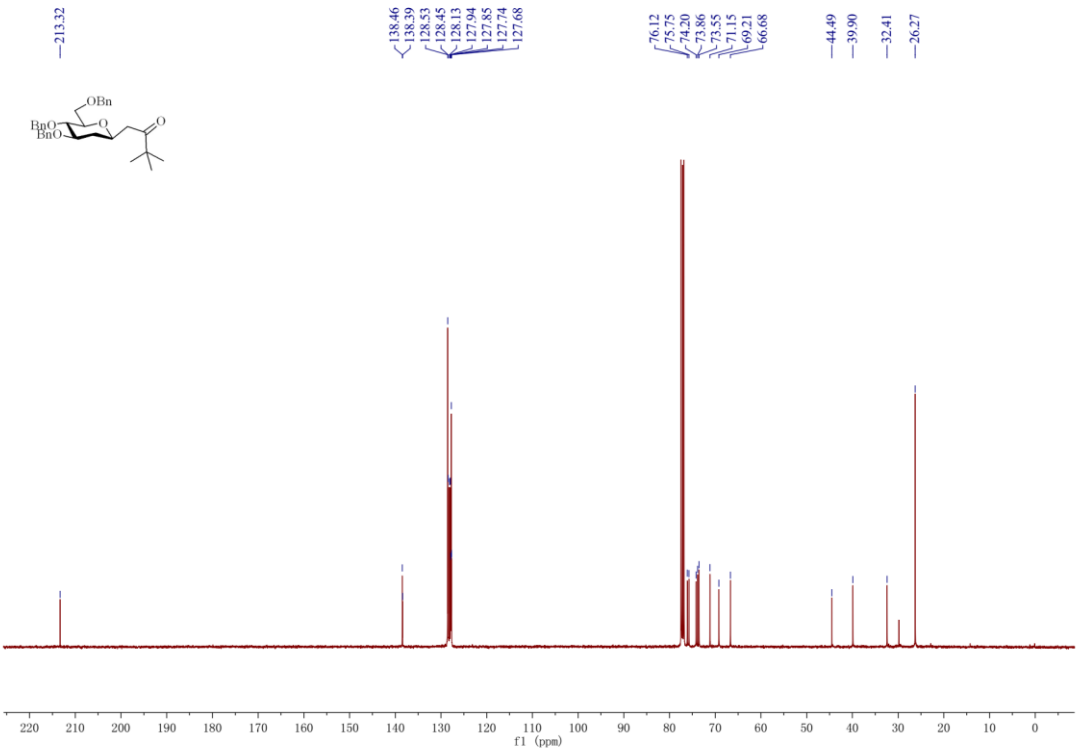
^{1}H NMR of compound **3dα**



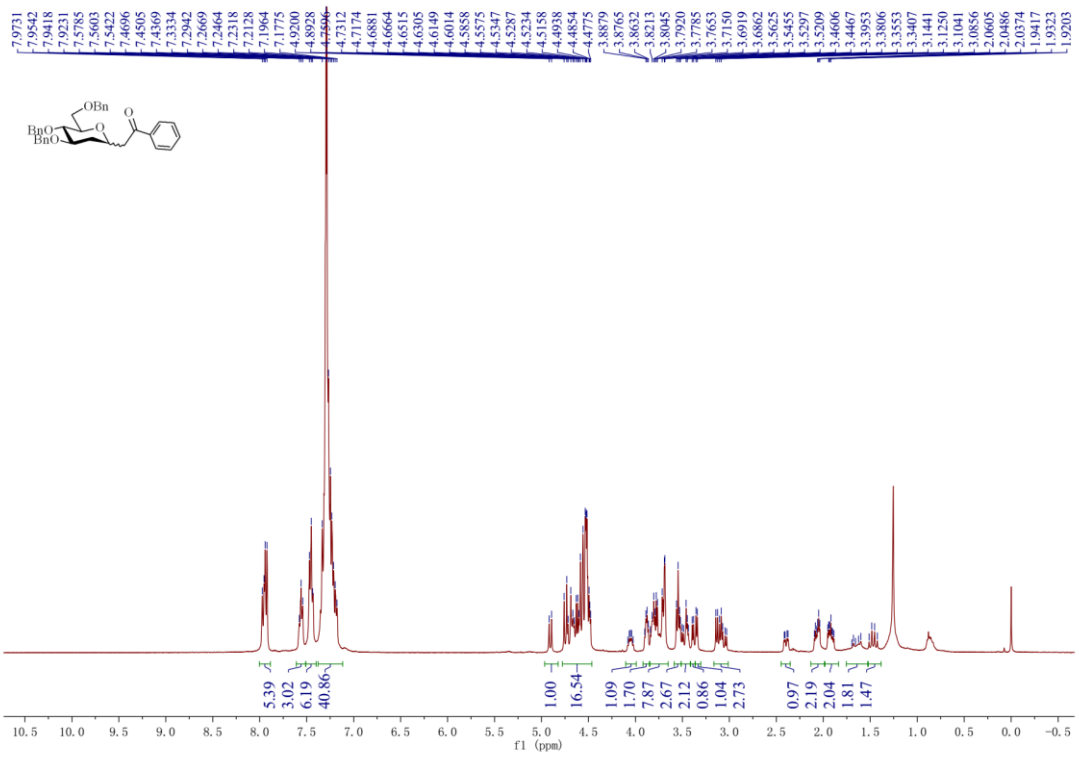
^{13}C NMR of compound **3dα**



^{1}H NMR of compound **3dβ**



^{13}C NMR of compound **3dβ**



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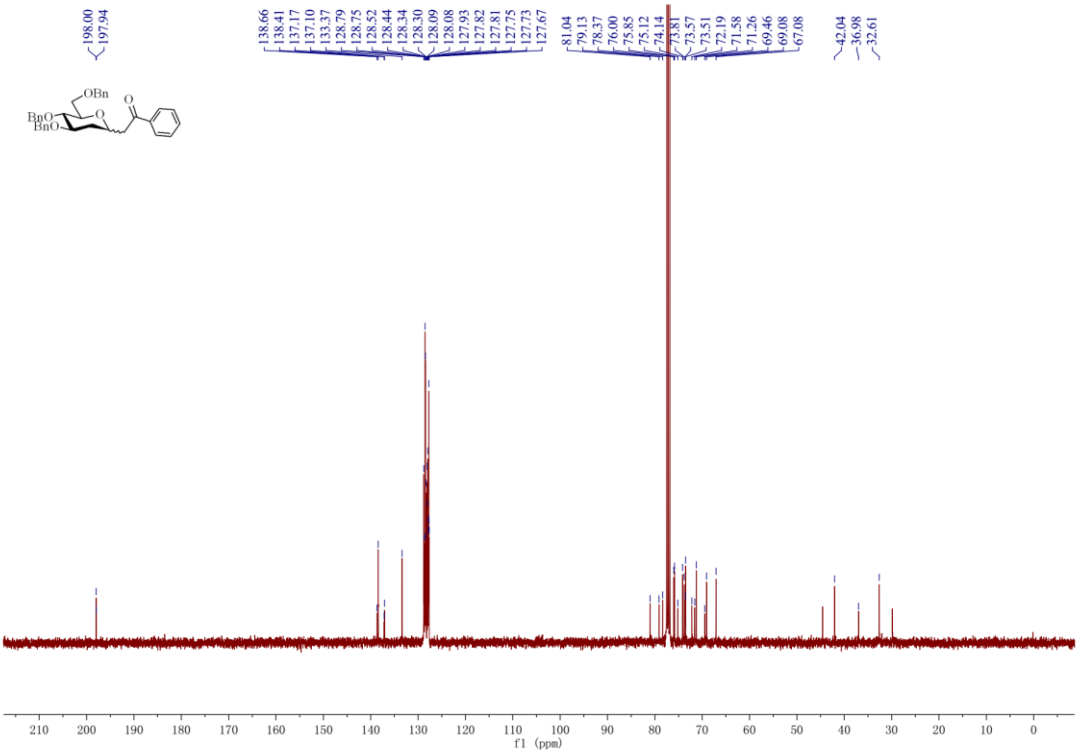

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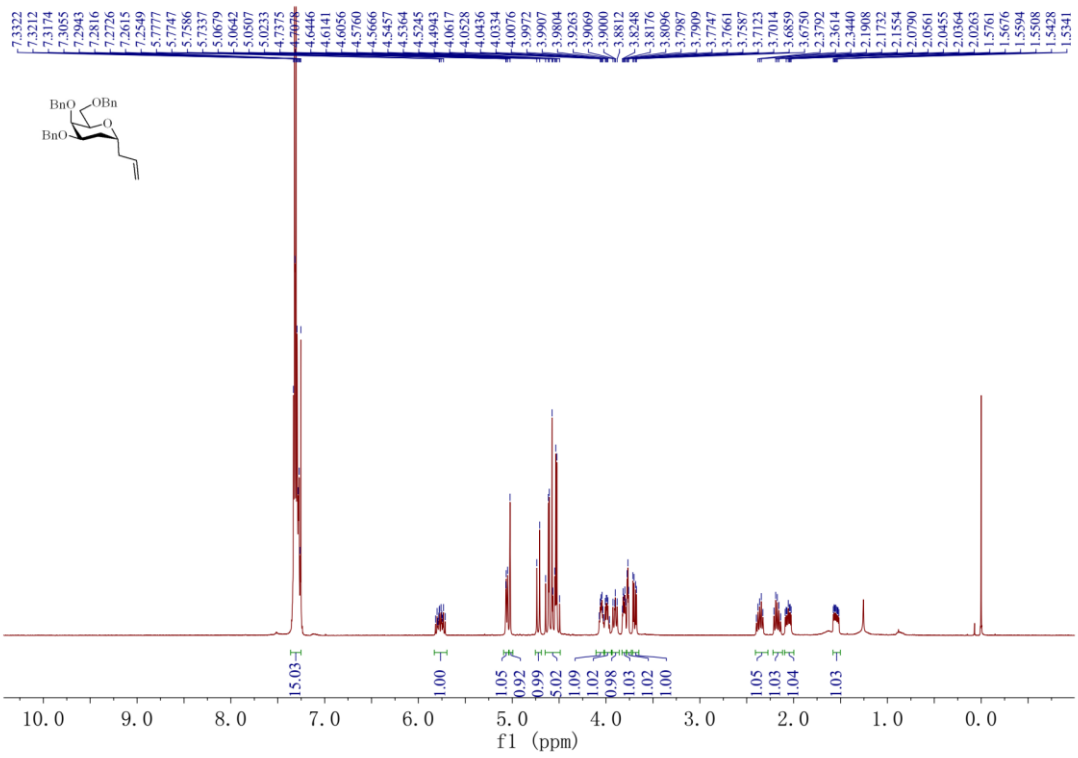

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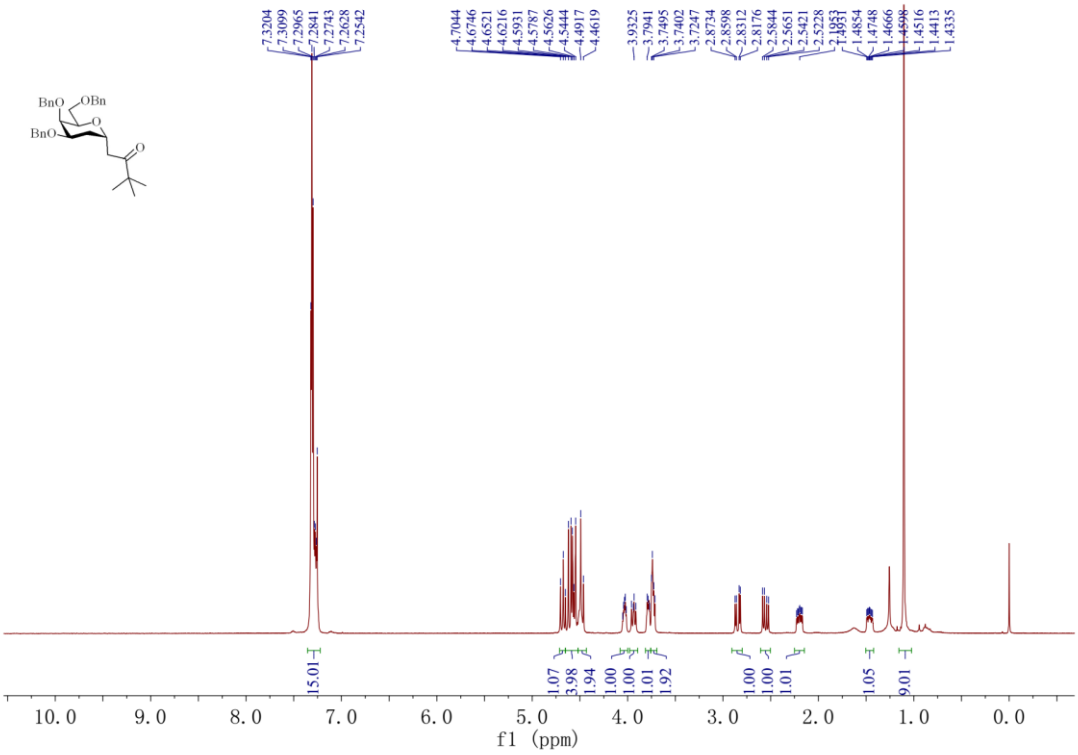
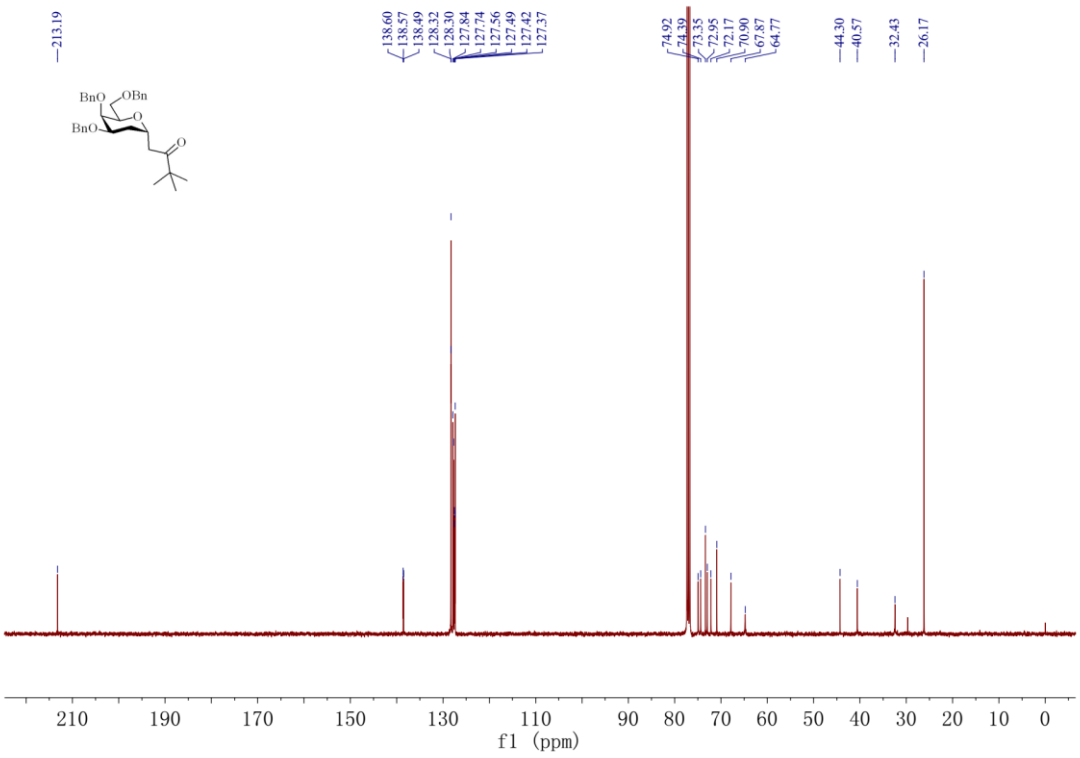
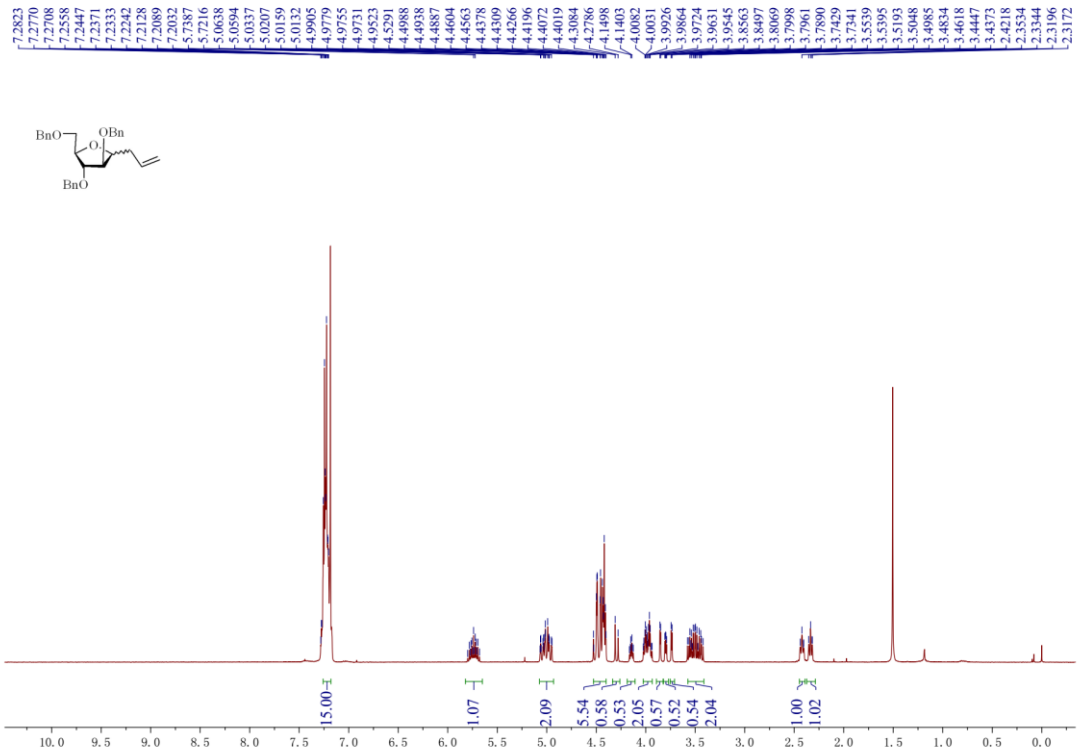


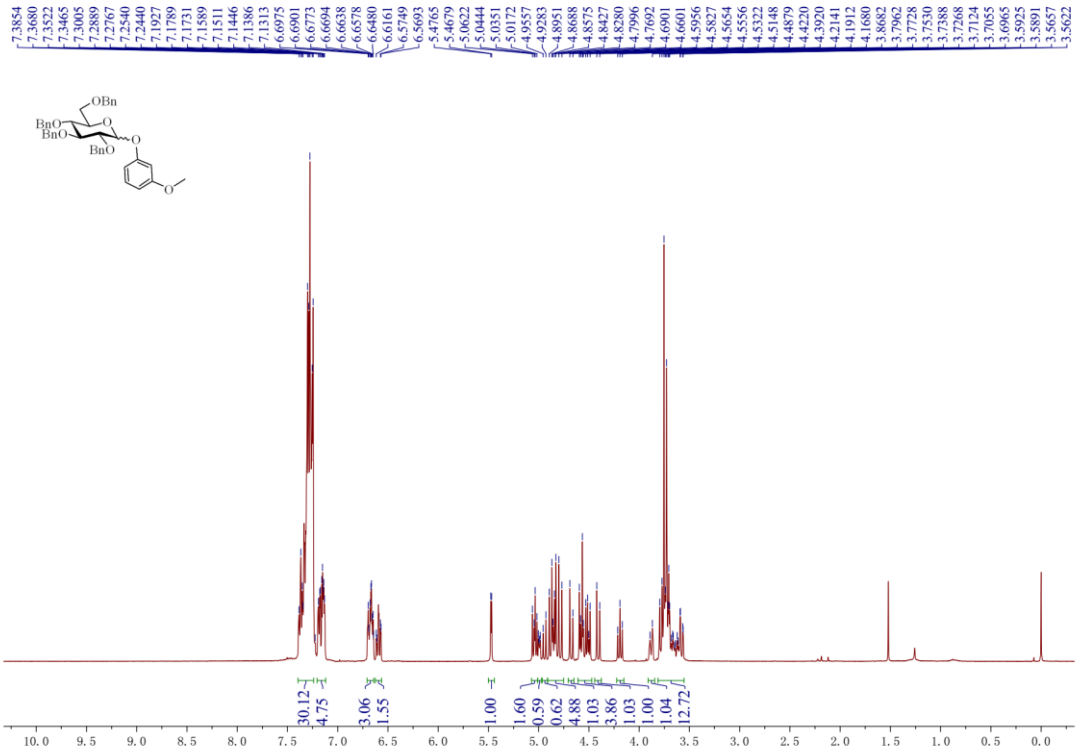
^{1}H NMR of compound **3g**



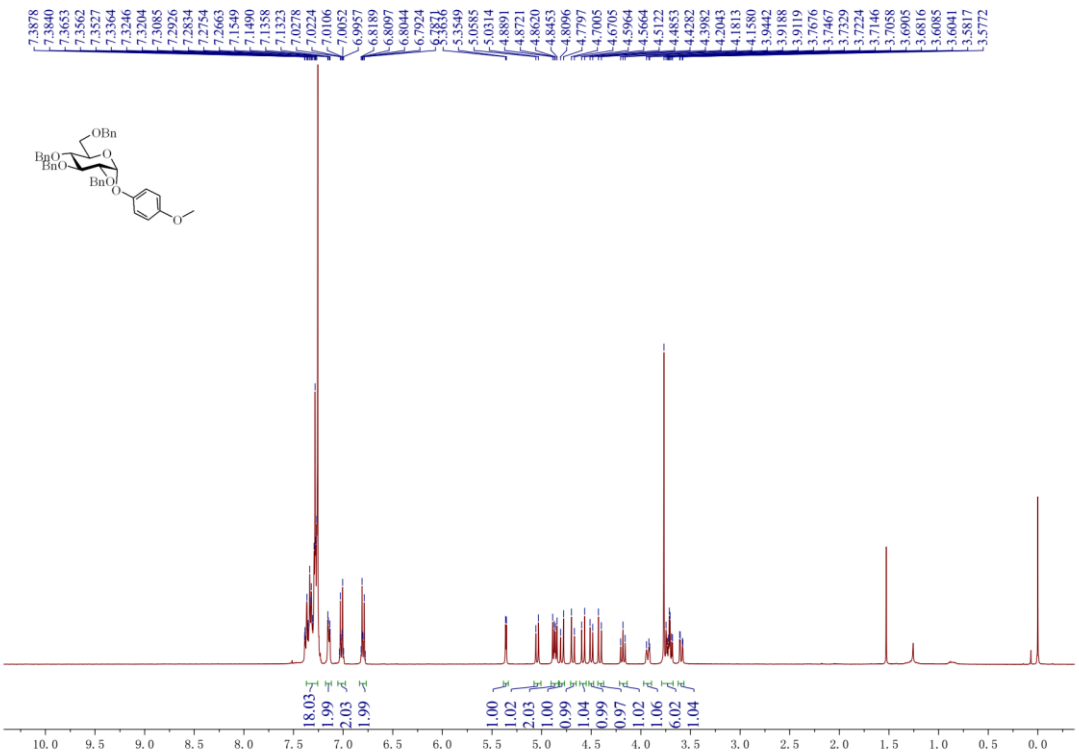
^{13}C NMR of compound **3g**



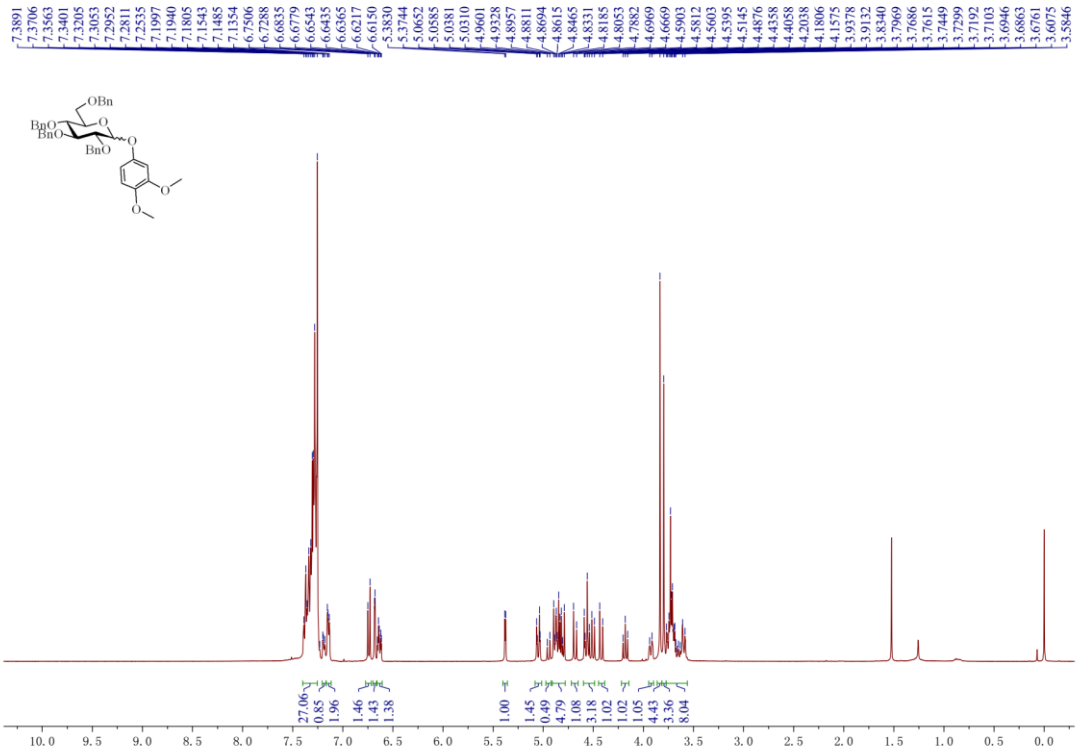
^{1}H NMR of compound **3h**



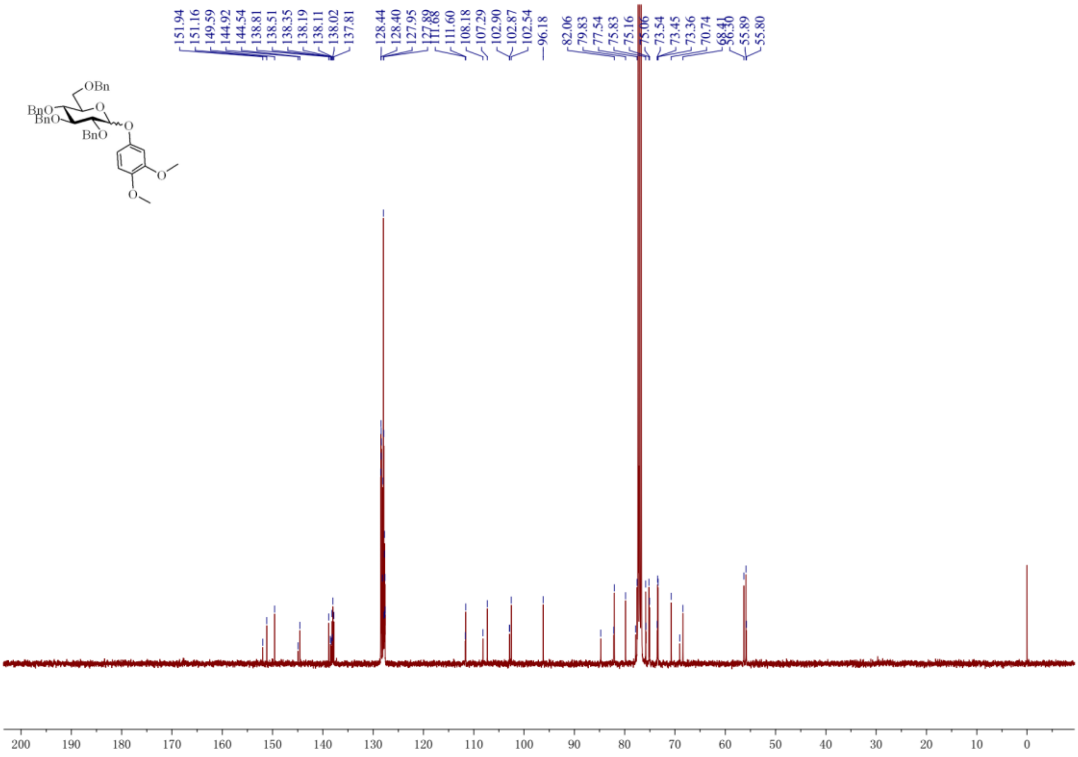
^{1}H NMR of compound **5a**



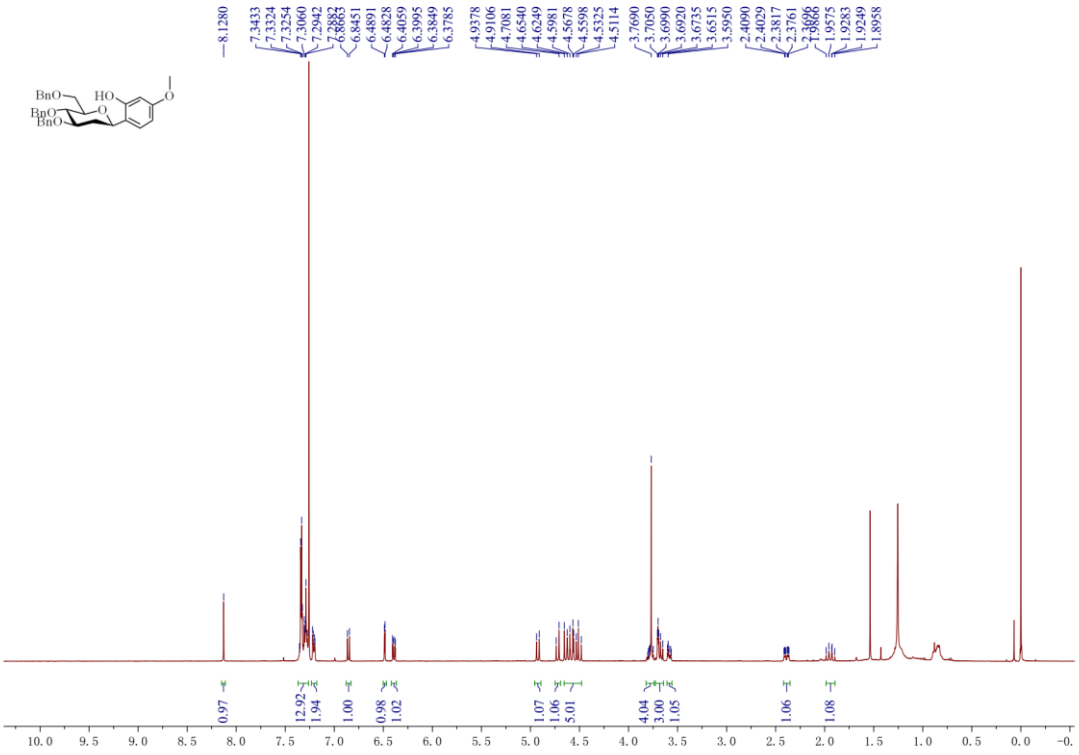
^{1}H NMR of compound **5b**



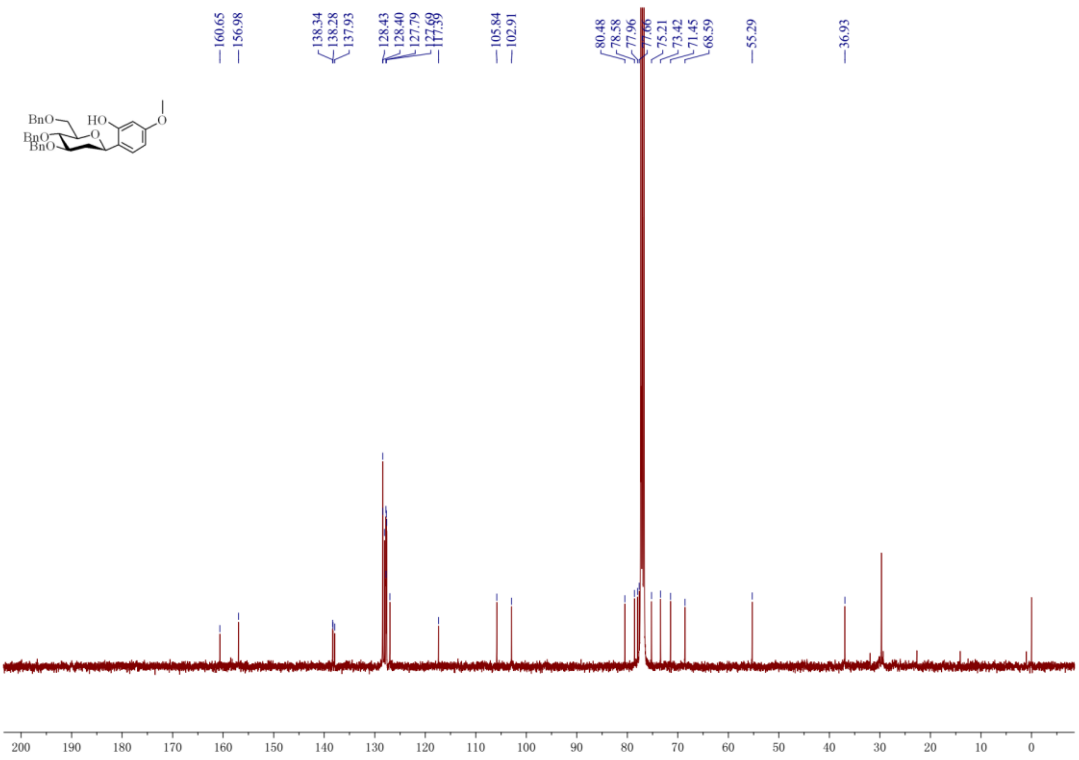
^{1}H NMR of compound **5c**



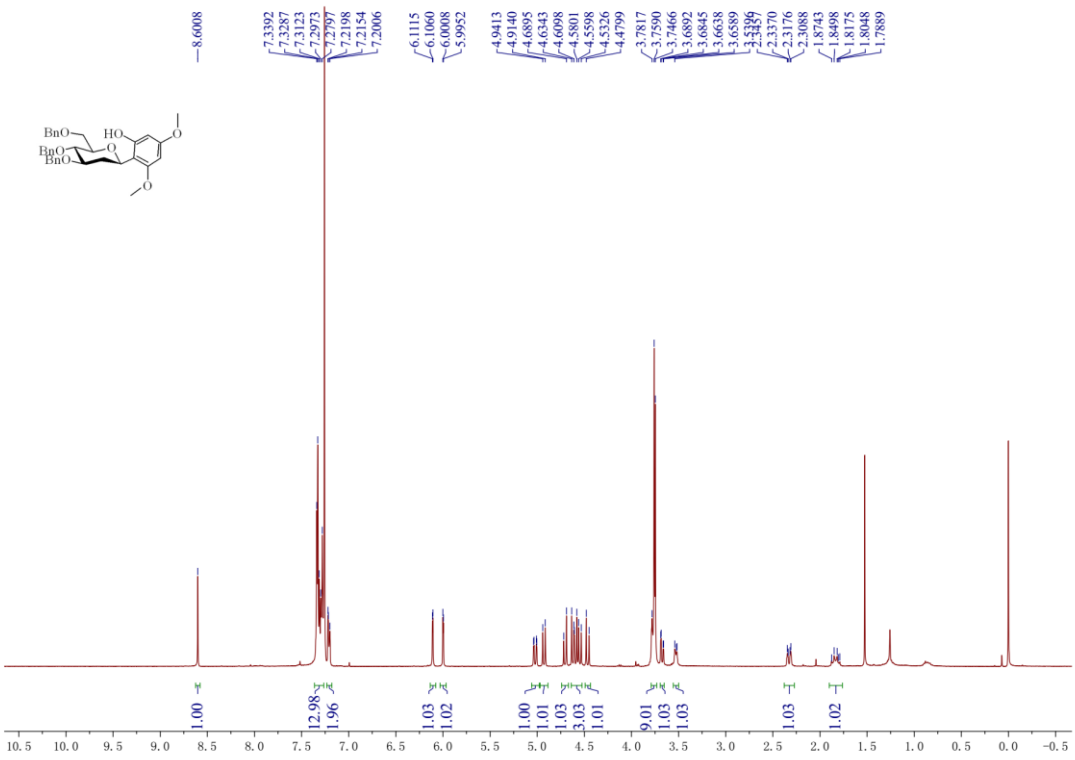
^{13}C NMR of compound **5c**



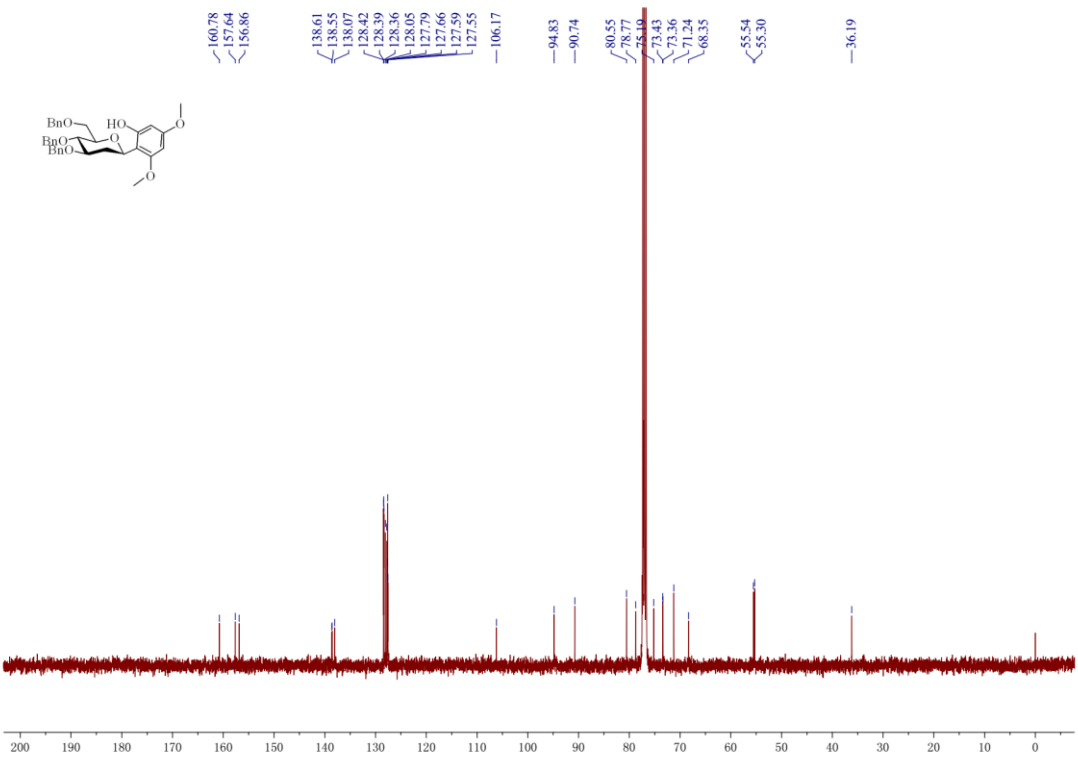
^{1}H NMR of compound **5d**



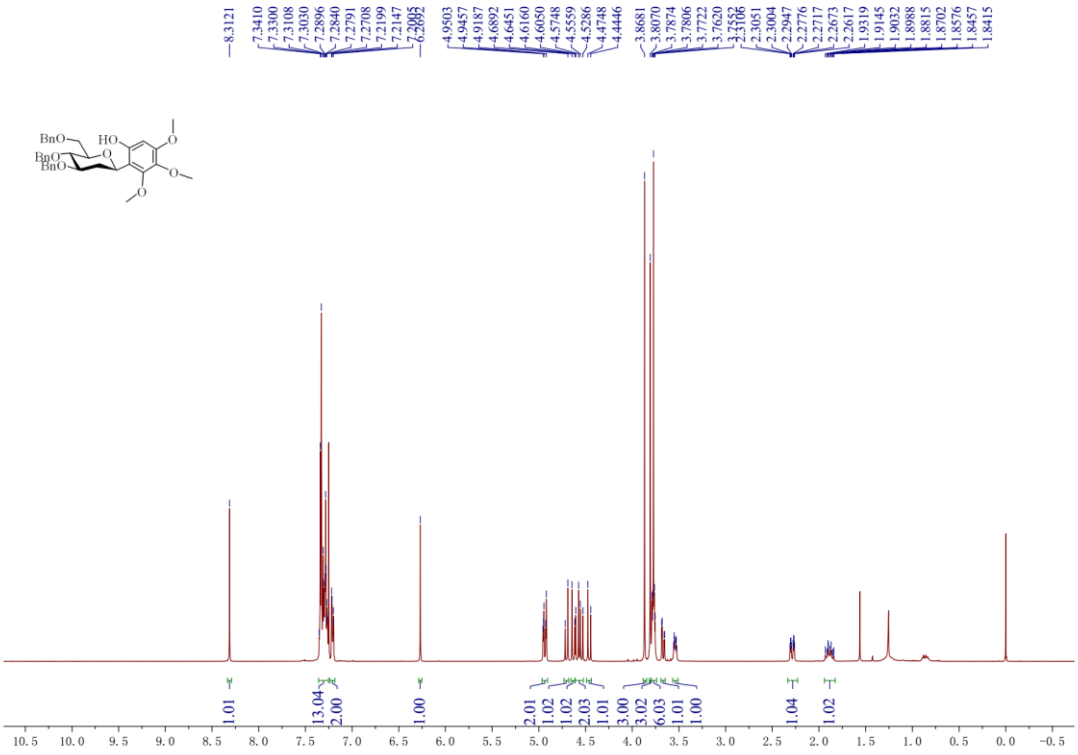
^{13}C NMR of compound **5d**



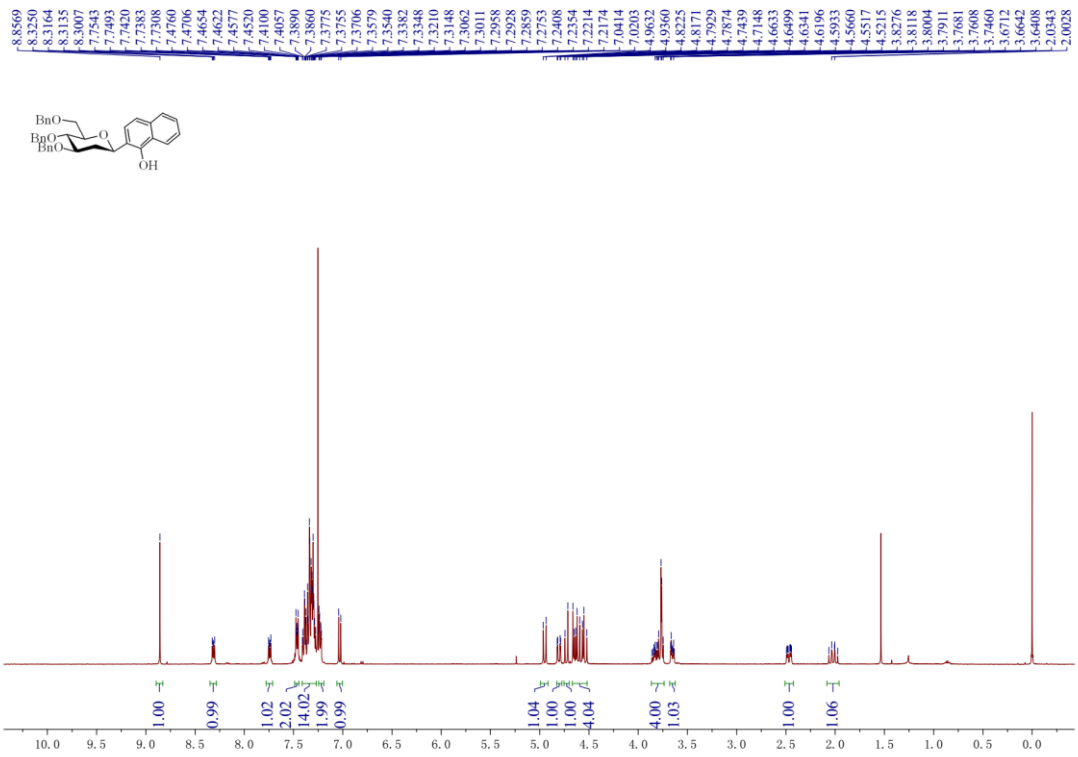
^{1}H NMR of compound **5e**



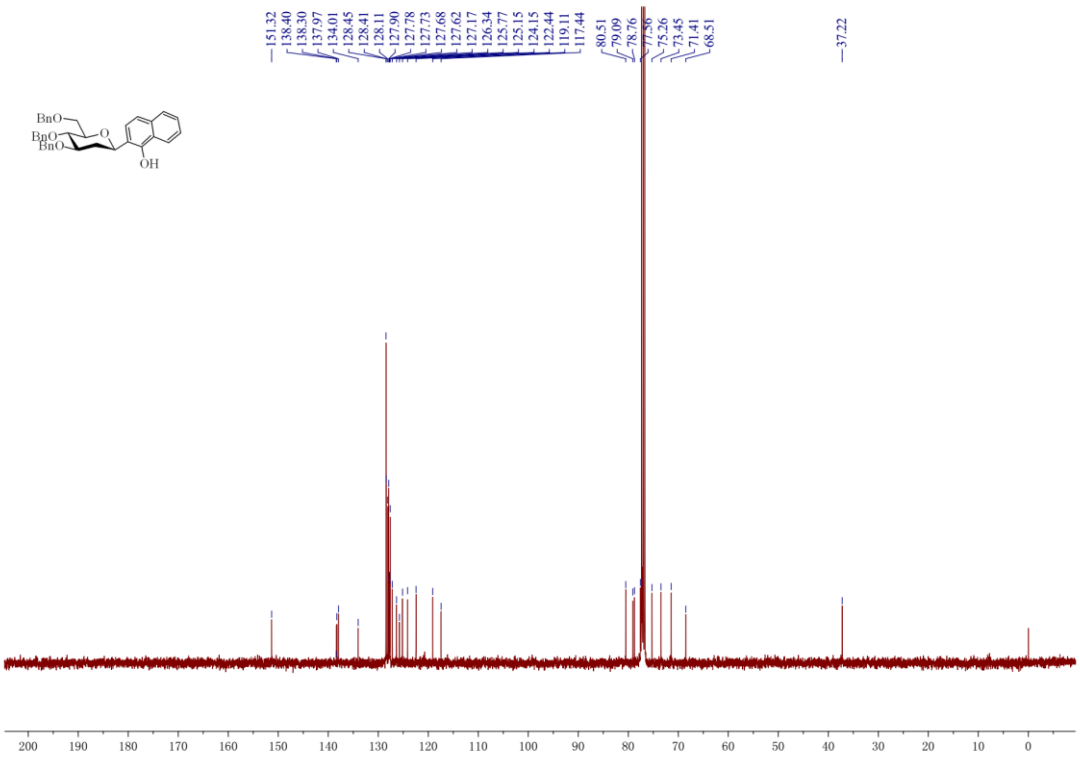
^{13}C NMR of compound **5e**



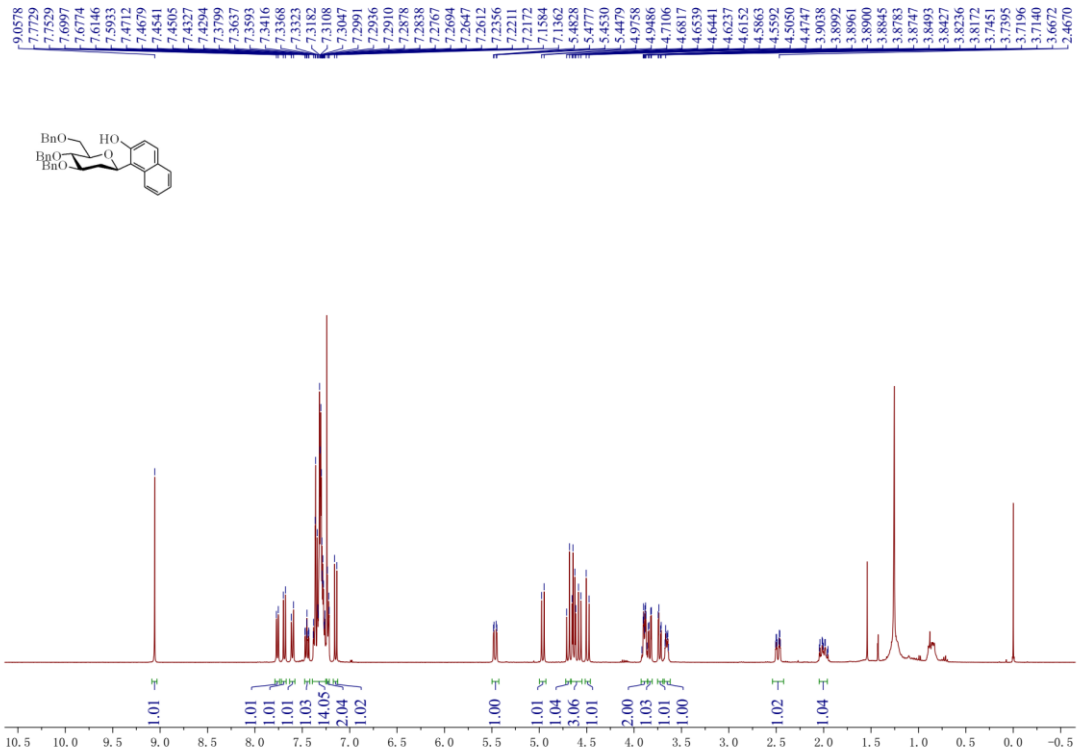
^{1}H NMR of compound **5f**



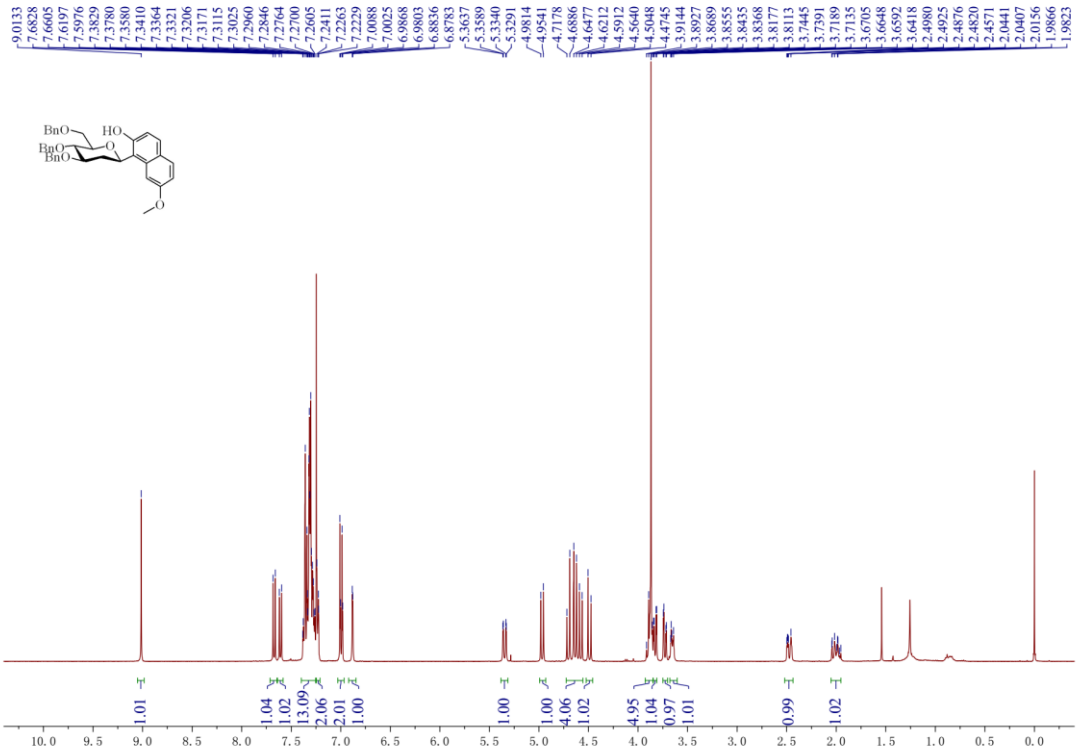
^{1}H NMR of compound **5g**



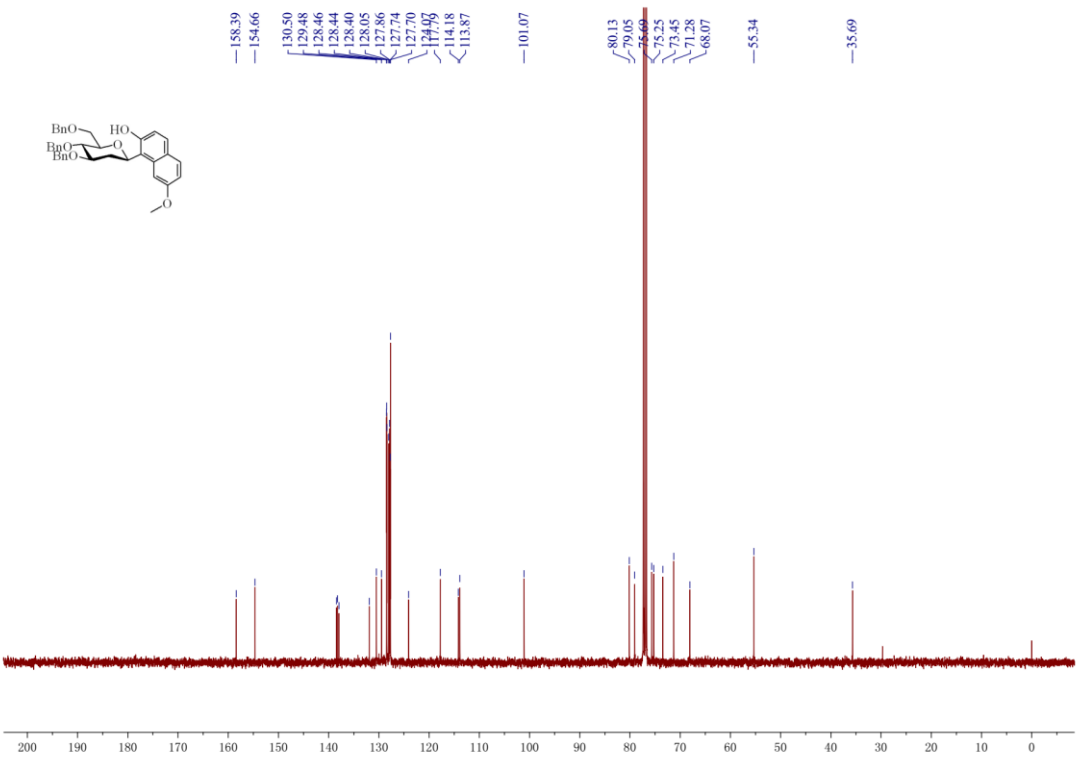
^{13}C NMR of compound **5g**



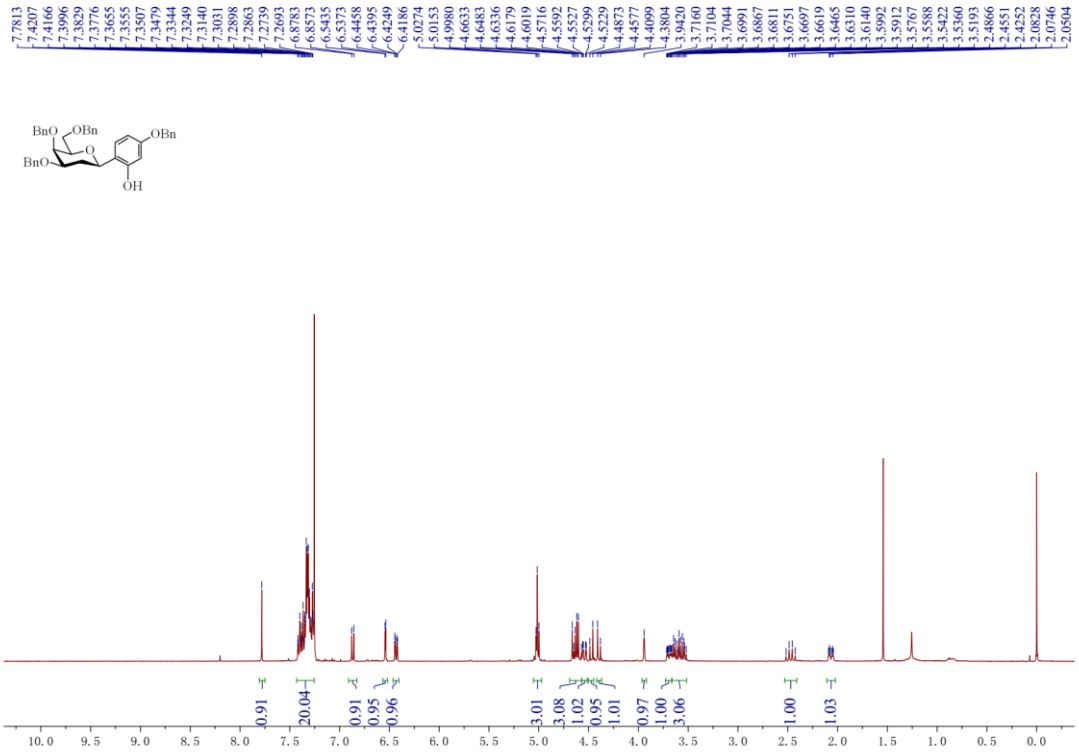
^{1}H NMR of compound **5h**



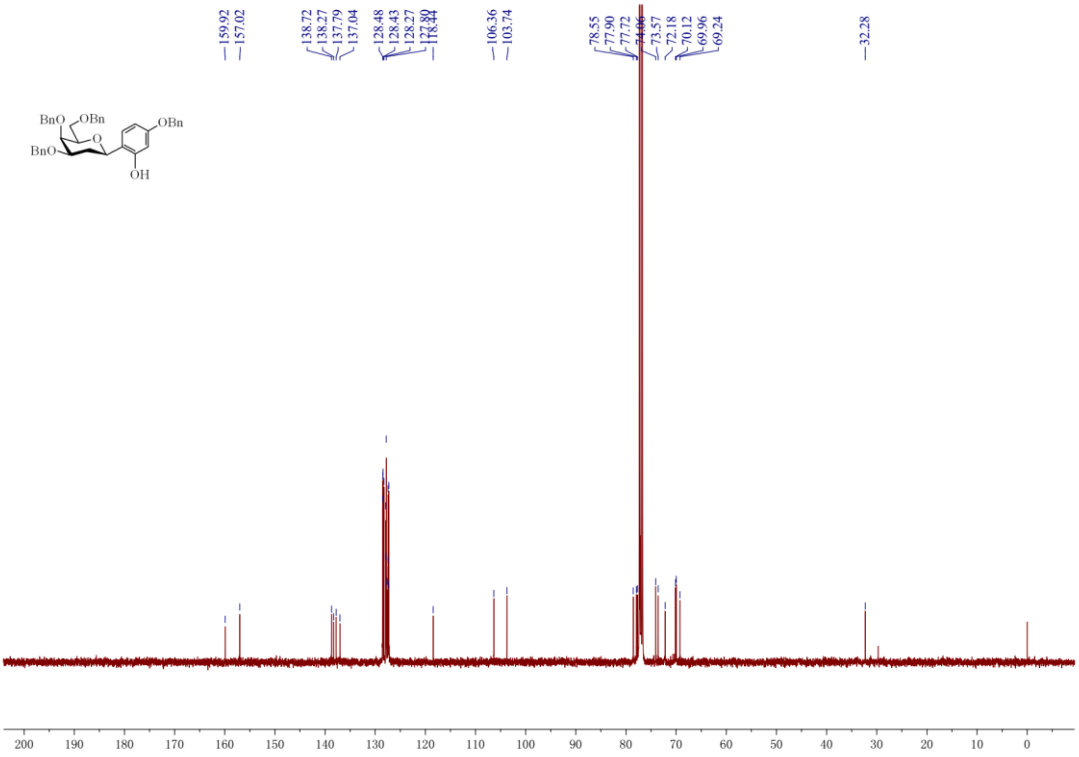
^{1}H NMR of compound **5i**



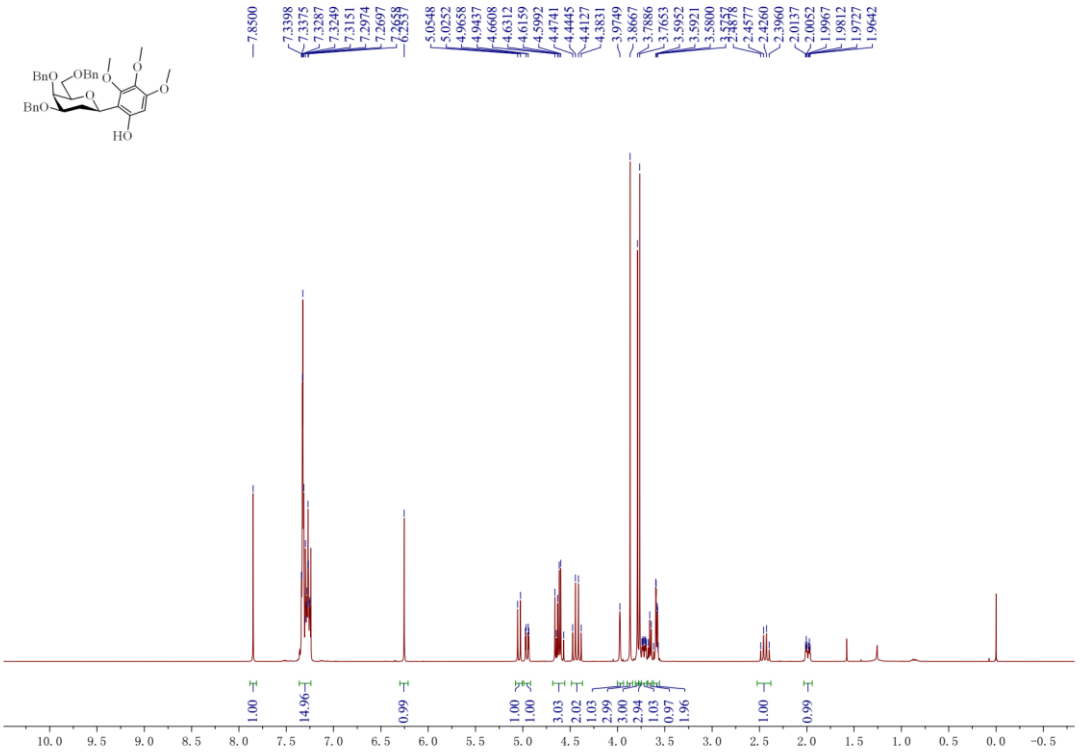
^{13}C NMR of compound **5i**



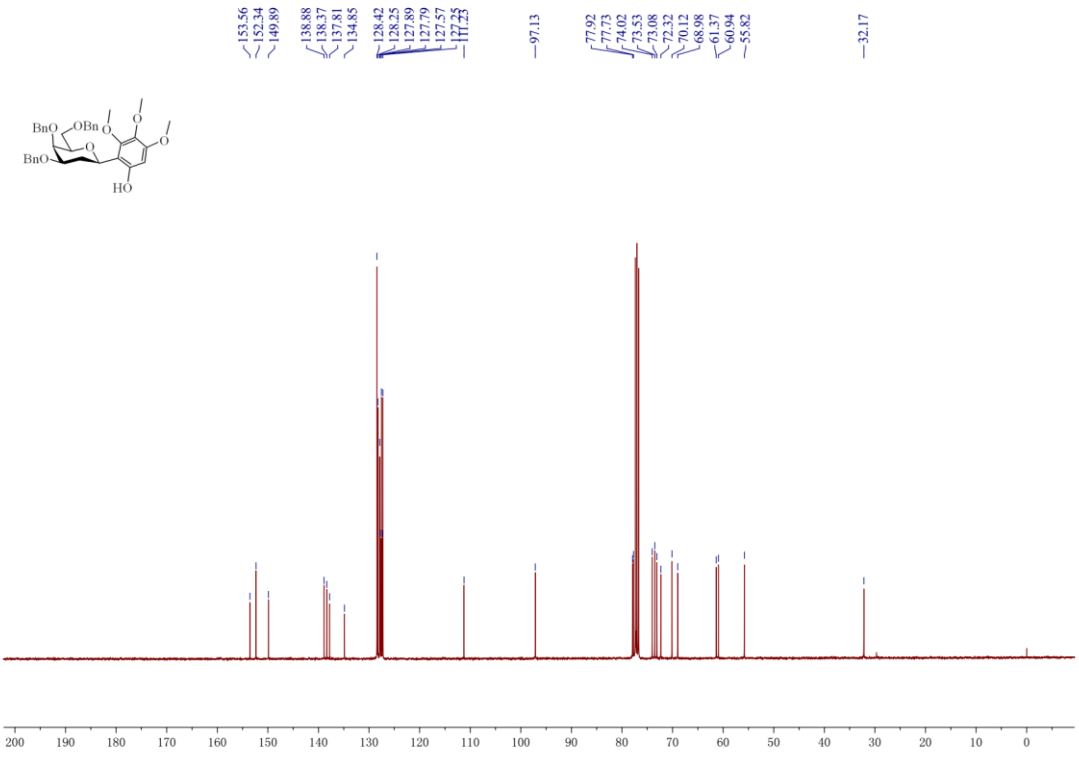
^{1}H NMR of compound **5j**



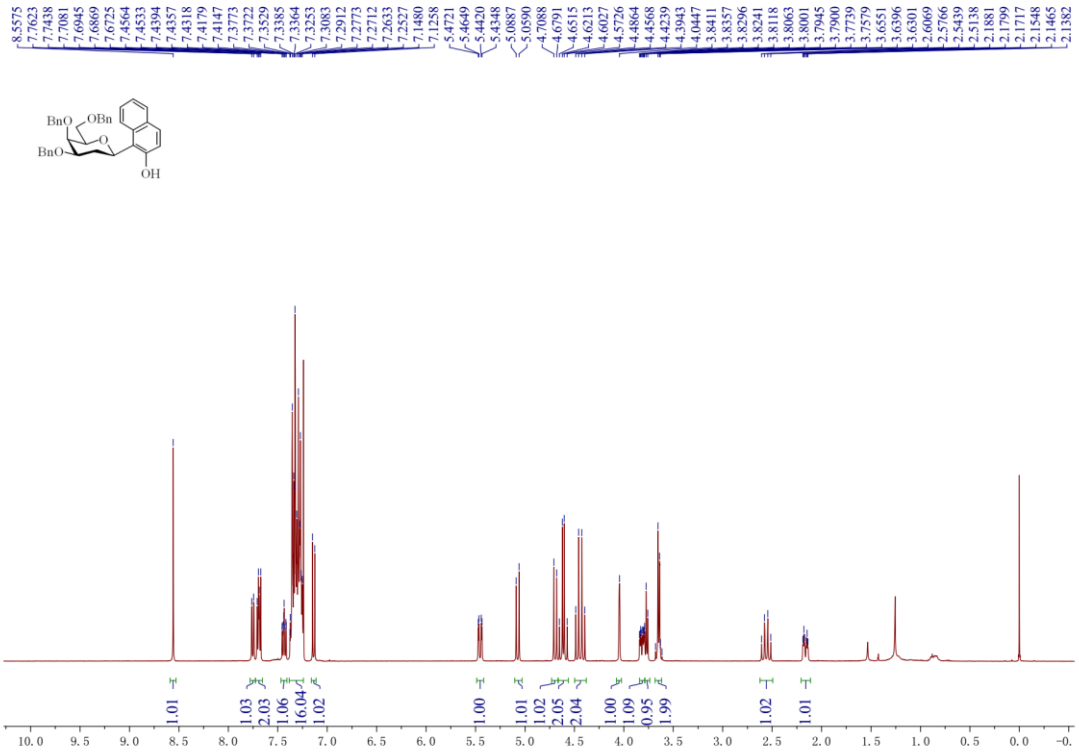
^{13}C NMR of compound **5j**



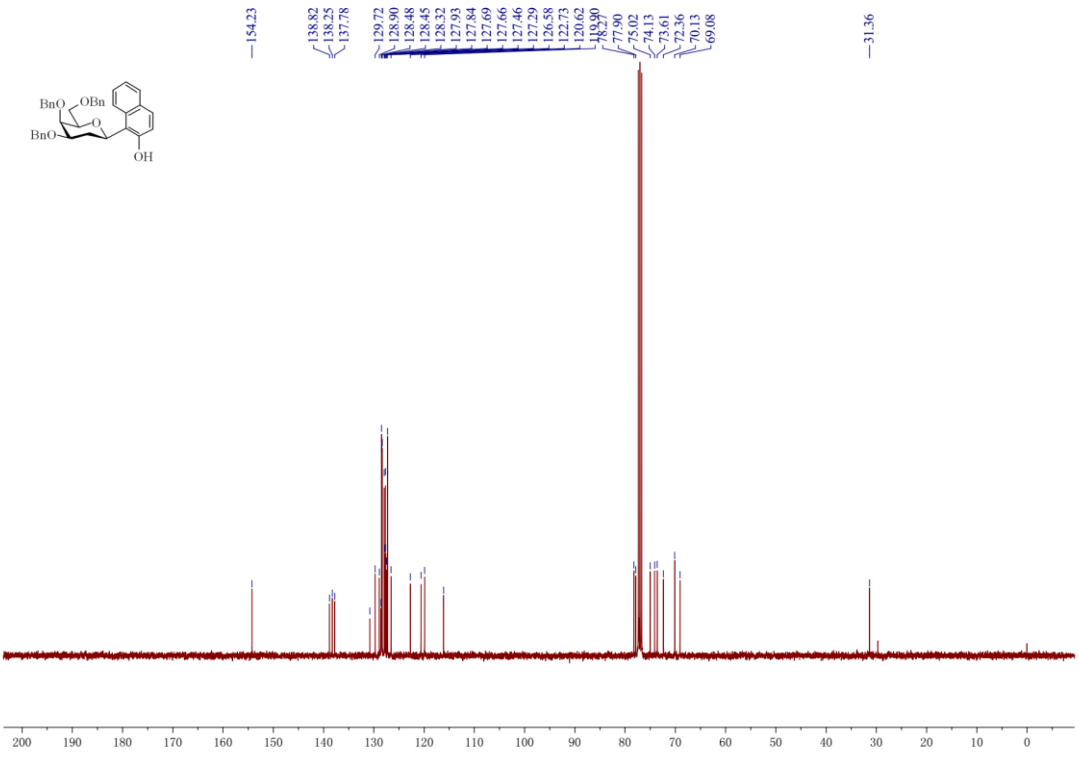
^{1}H NMR of compound **5k**



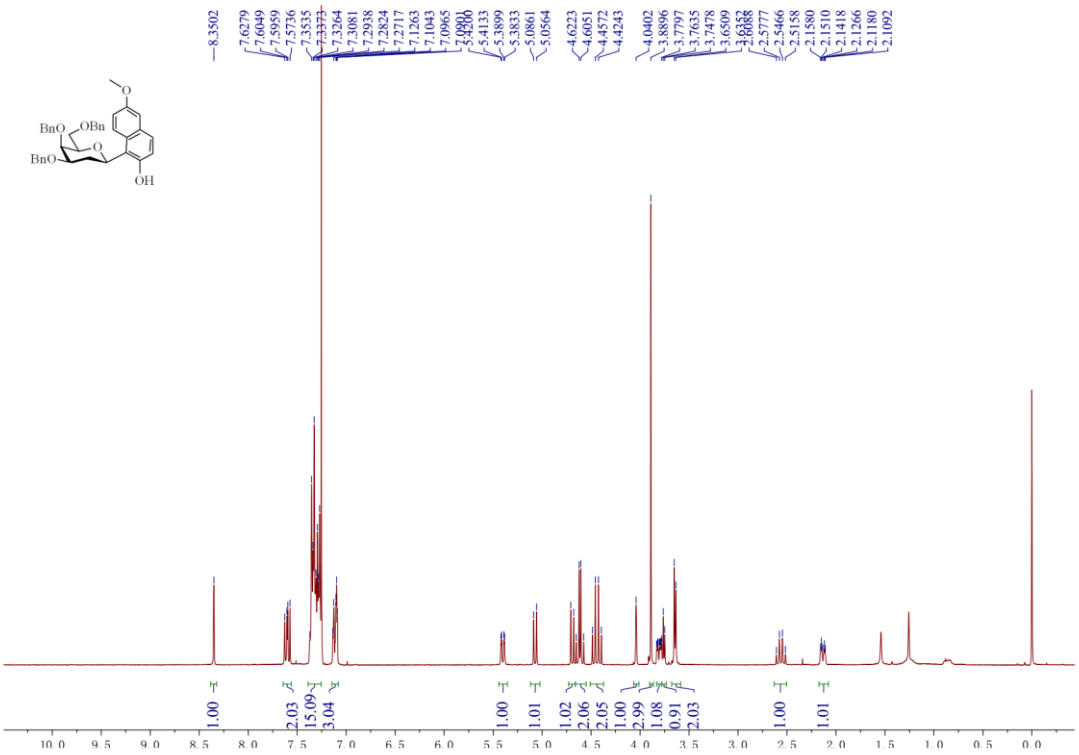
^{13}C NMR of compound **5k**



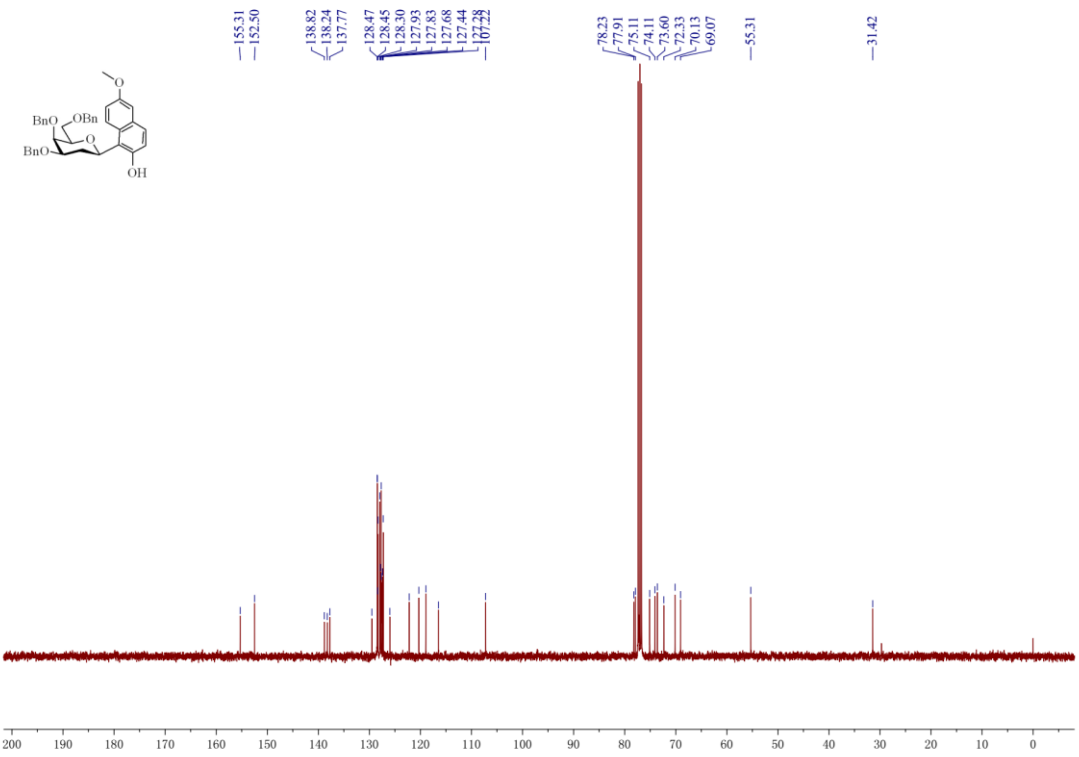
^{1}H NMR of compound **5l**



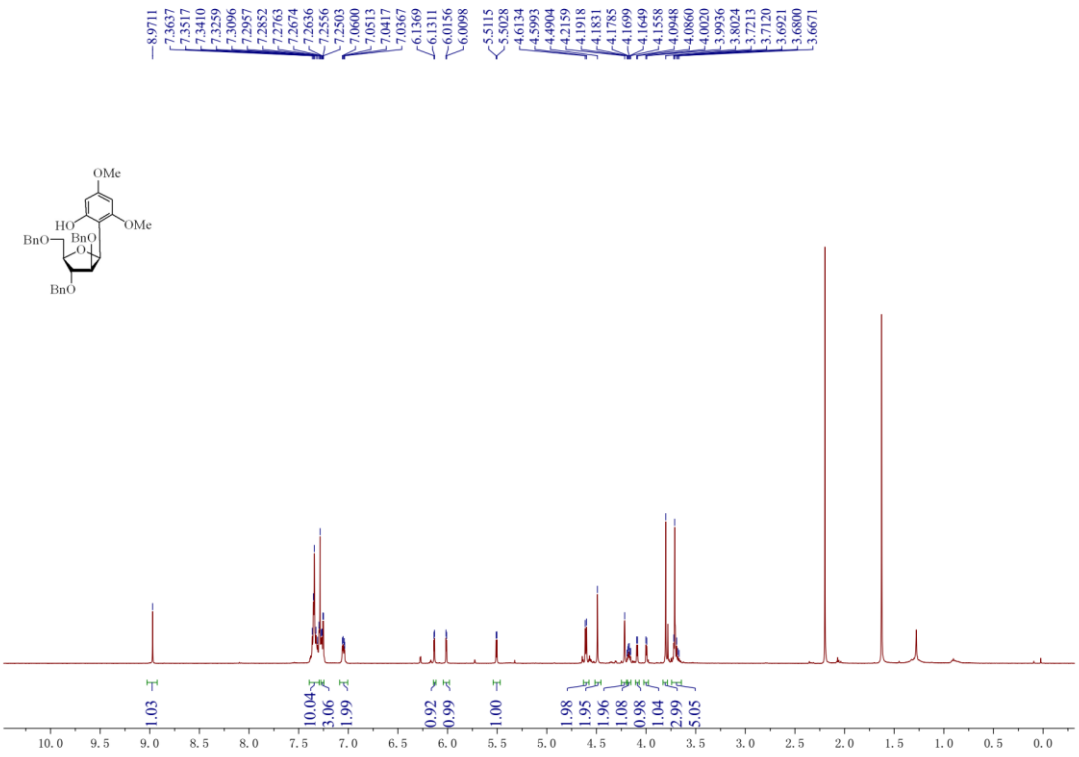
^{13}C NMR of compound **5l**



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



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



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