

Supplemental information

**Programmable selective acylation of saccharides
mediated by carbene and boronic acid**

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Supplemental Experimental Procedures

1. General information

Monosaccharides and boronic acids were purchased from Sigma-Aldrich, Alfa-Aesar, Titan. 3,3,5,5-Tetra-tert-butylidiphenoxquinone (DQ) was used after purification in a pure state. Anhydrous CH₃CN, DCM, THF and DMSO were purchased from Acros and stored under argon. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

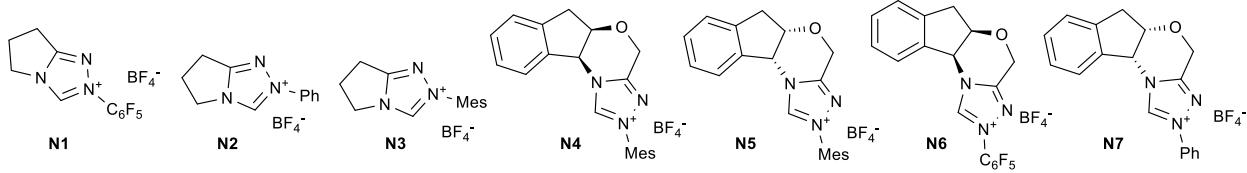
Proton (¹H), Carbon (¹³C) NMR were recorded at 400 MHz, 101 MHz NMR spectrometer, respectively. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV₂₅₄ plates. Visualization was accomplished with short wave UV light, or KMnO₄ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

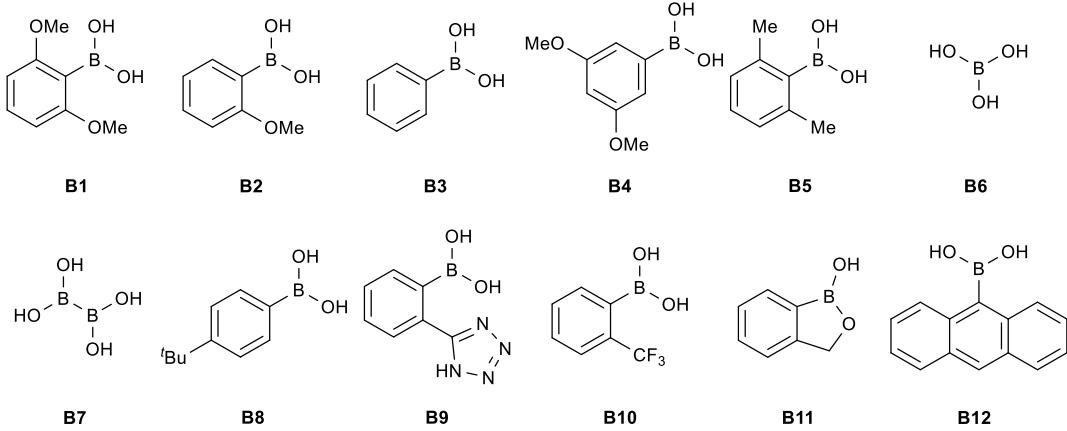
2. Experimental procedures

2.1. Structure of NHC catalysts and boronic acids

NHC pre-catalysts **N1-N7** were prepared according to the reference.^{1,2}



Boronic acids are commercially available.



2.2. Determine the regio-isomers of acylated monosaccharides via 2D NMR

^1H NMR spectrum

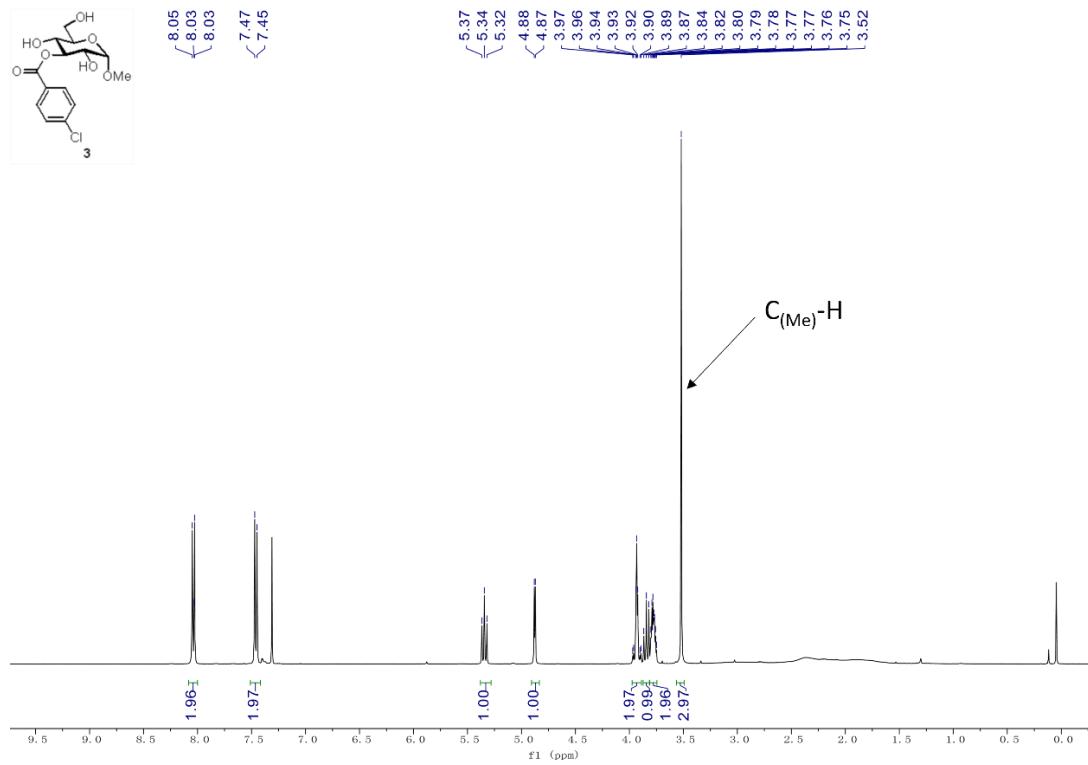


Figure S1. ^1H NMR Spectra of 3

^{13}C NMR spectrum

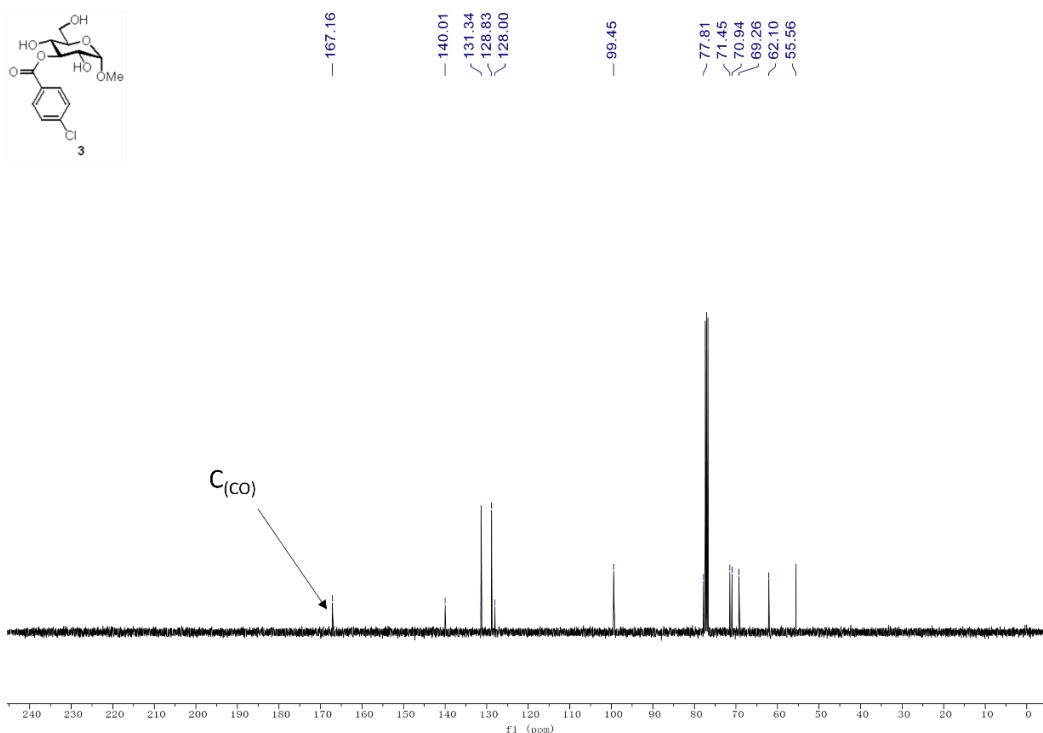


Figure S2. ^{13}C NMR Spectra of 3

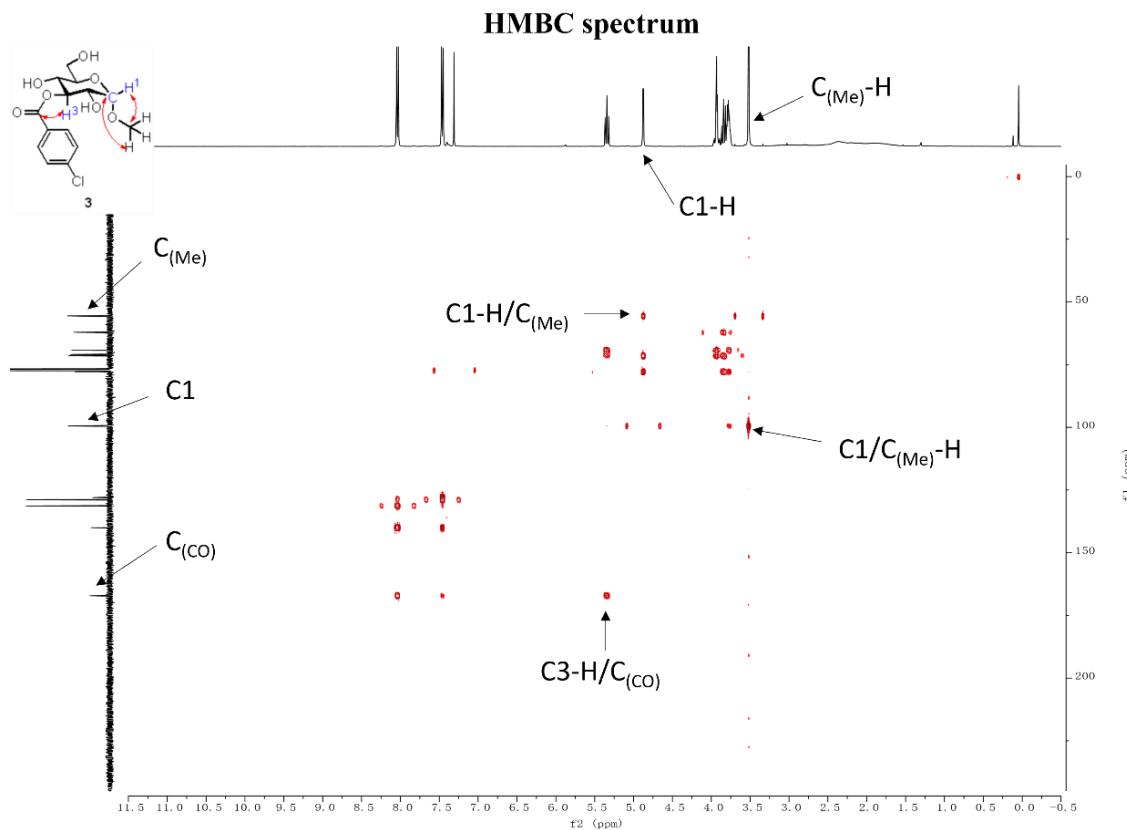


Figure S3. HMBC NMR Spectra of **3**

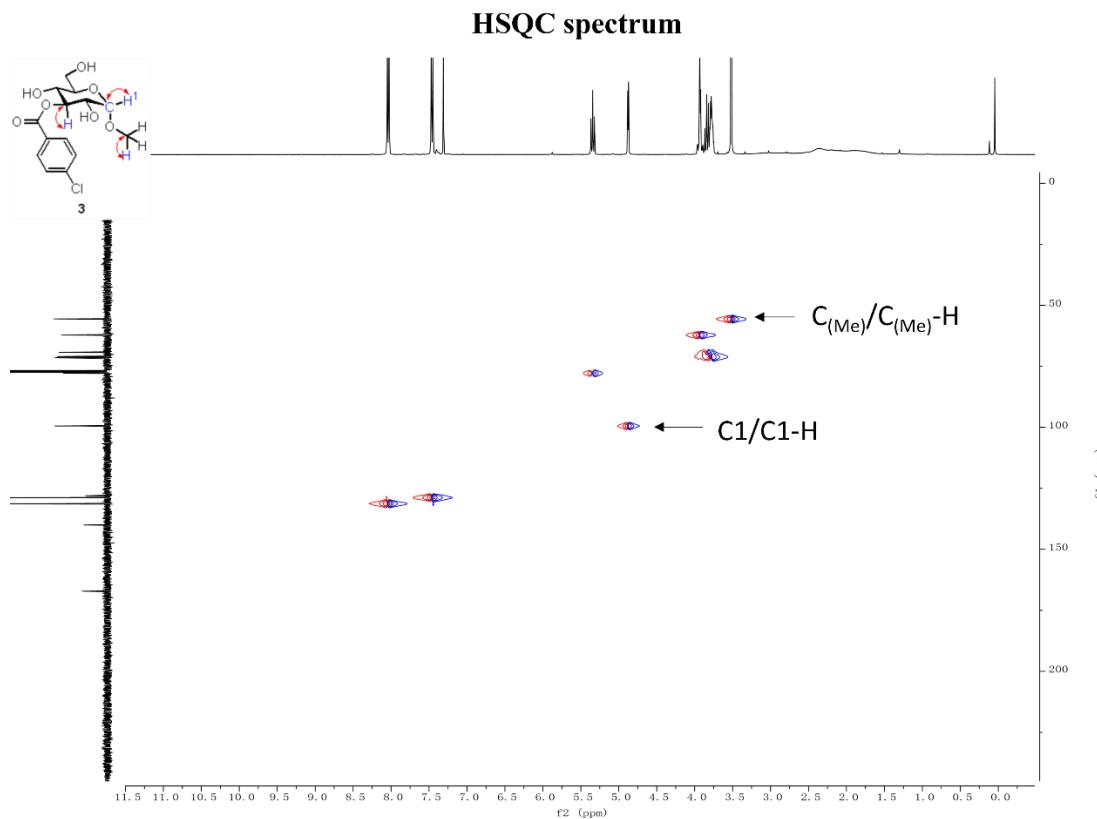


Figure S4. HSQC NMR Spectra of **3**

COSY spectrum

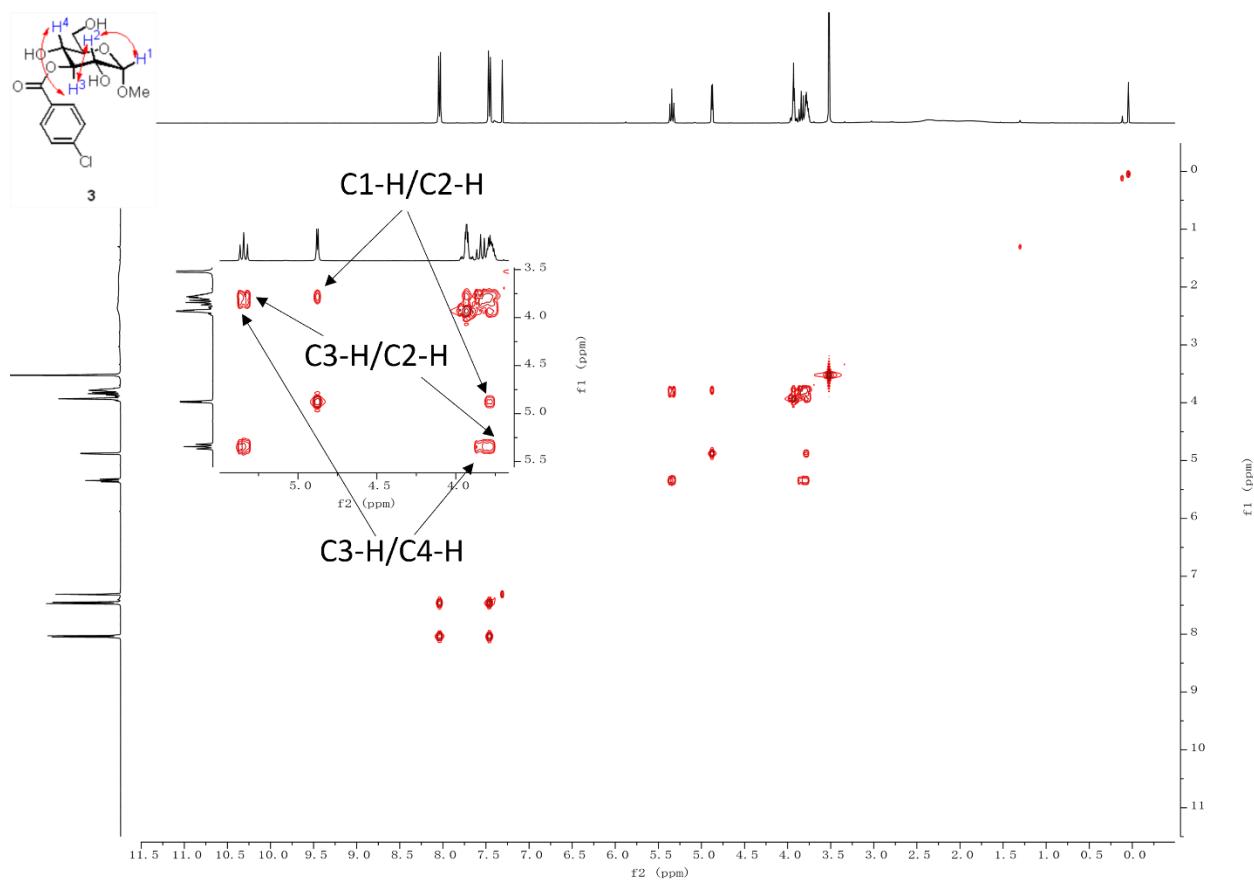


Figure S5. COSY NMR Spectra of **3**

^1H NMR spectrum

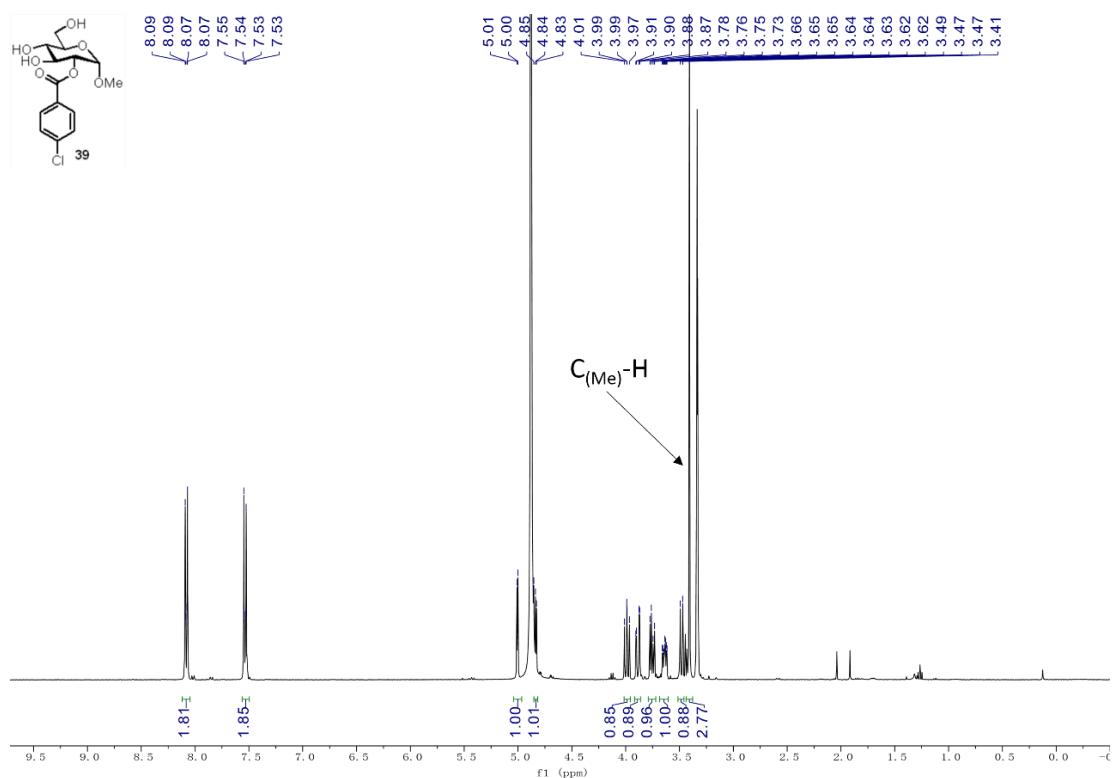


Figure S6. ^1H NMR Spectra of 39

^{13}C NMR spectrum

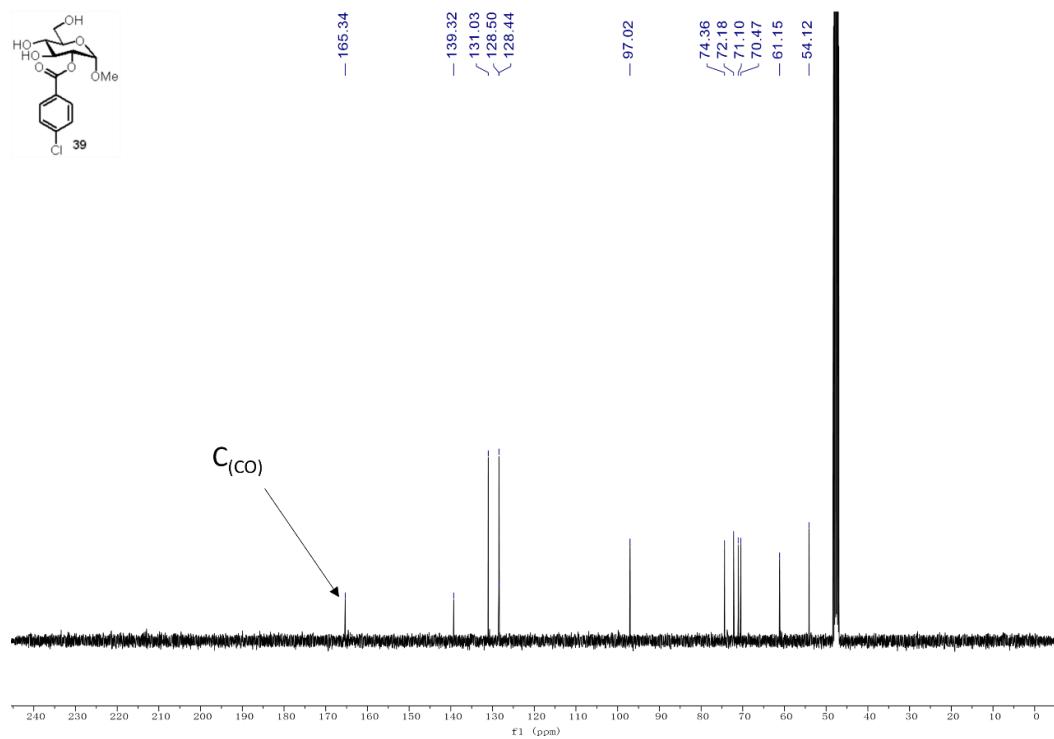


Figure S7. ^{13}C NMR Spectra of 39

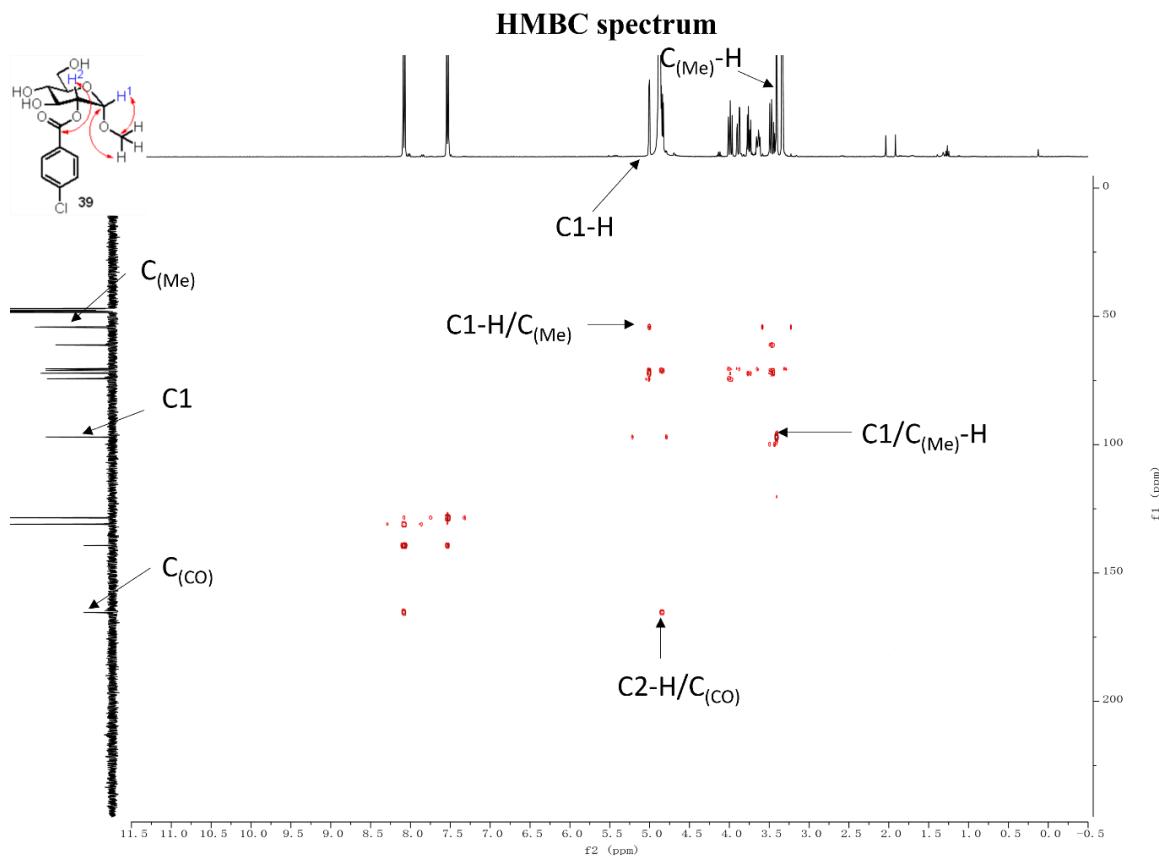


Figure S8. HMBC NMR Spectra of 39

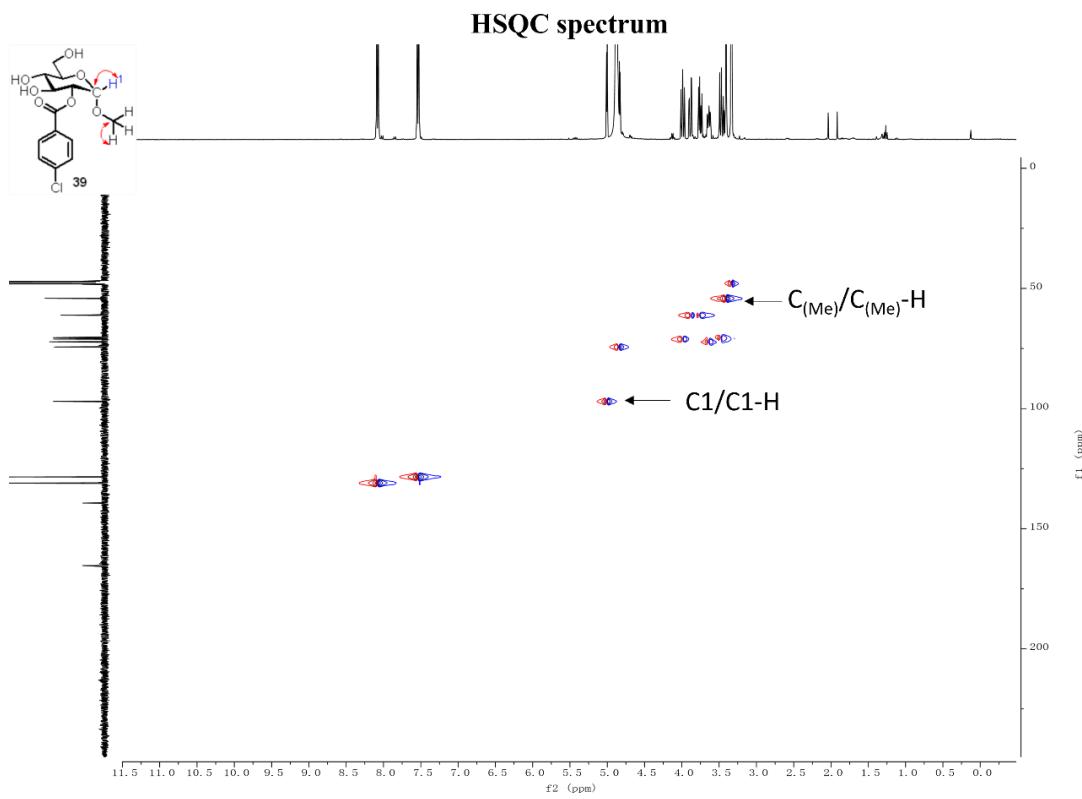


Figure S9. HSQC NMR Spectra of 39

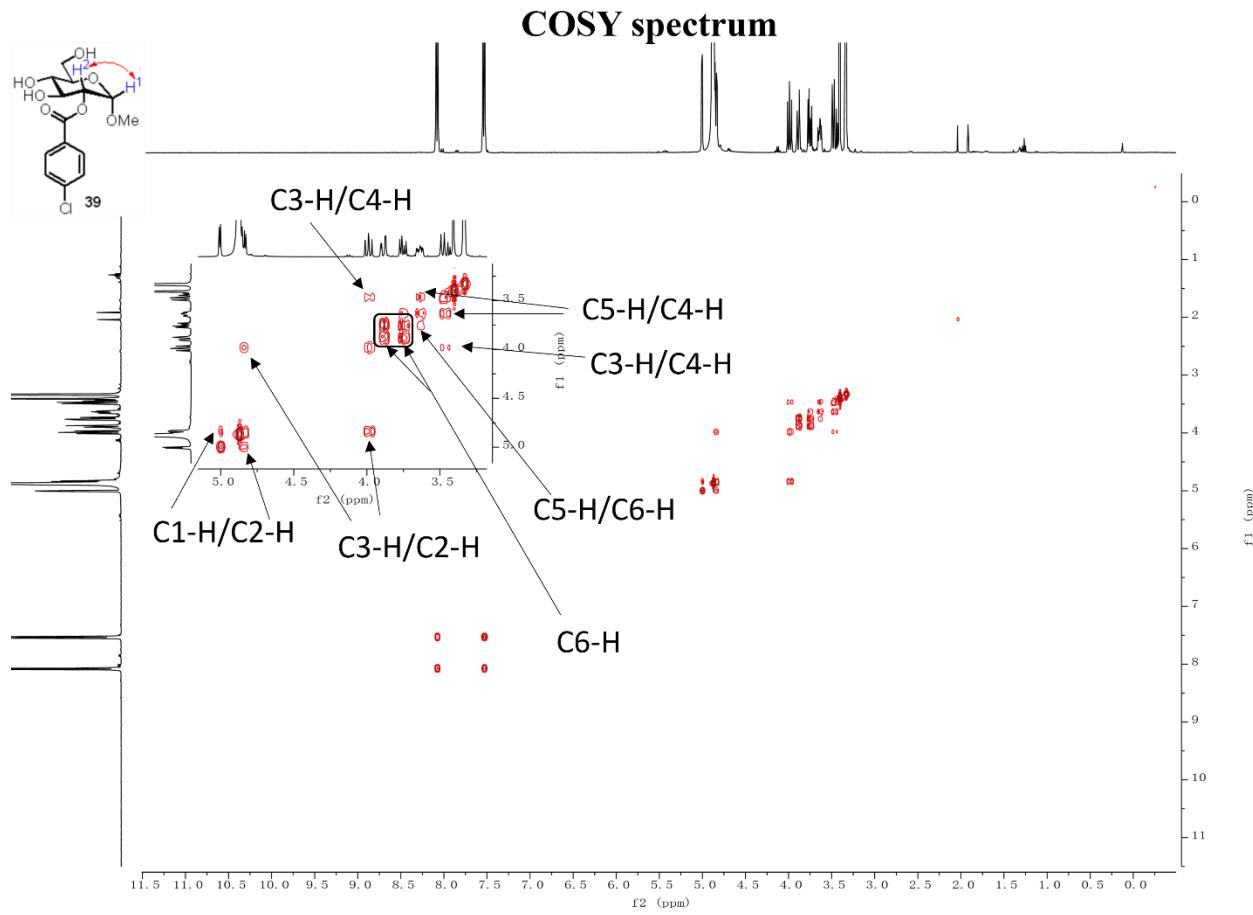


Figure S10. COSY NMR Spectra of 39

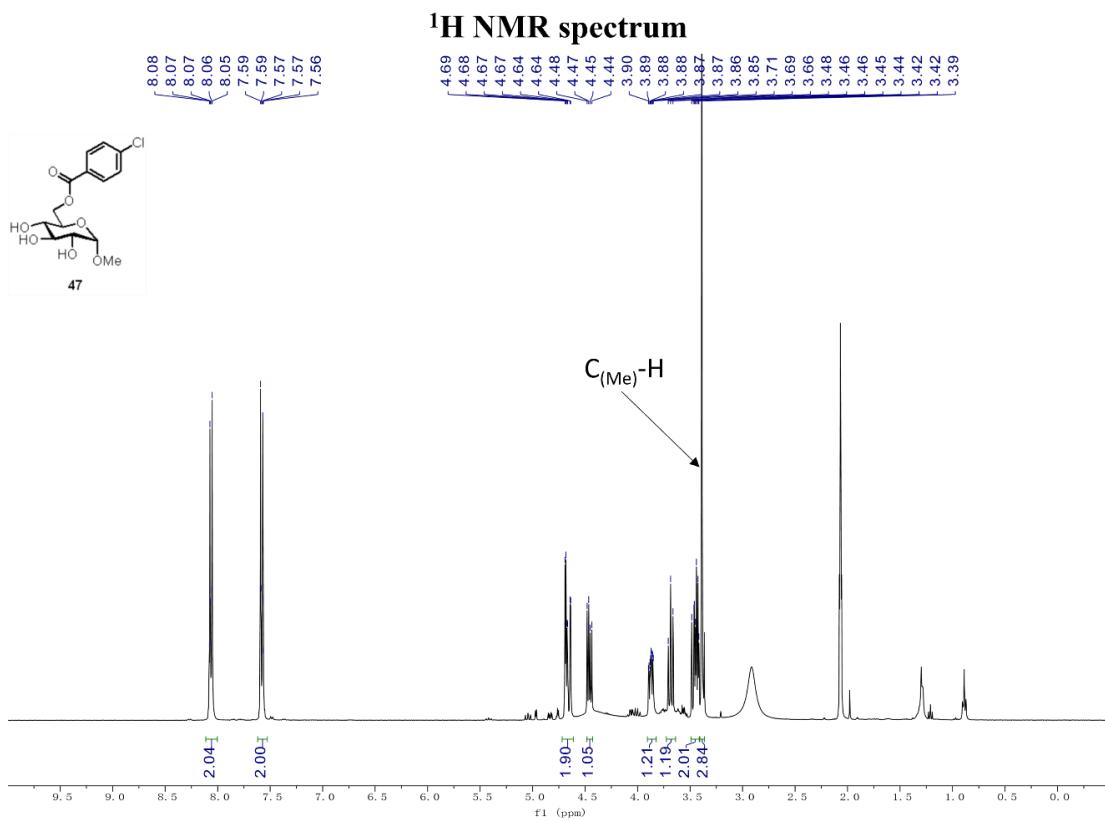


Figure S11. ¹H NMR Spectra of **47**

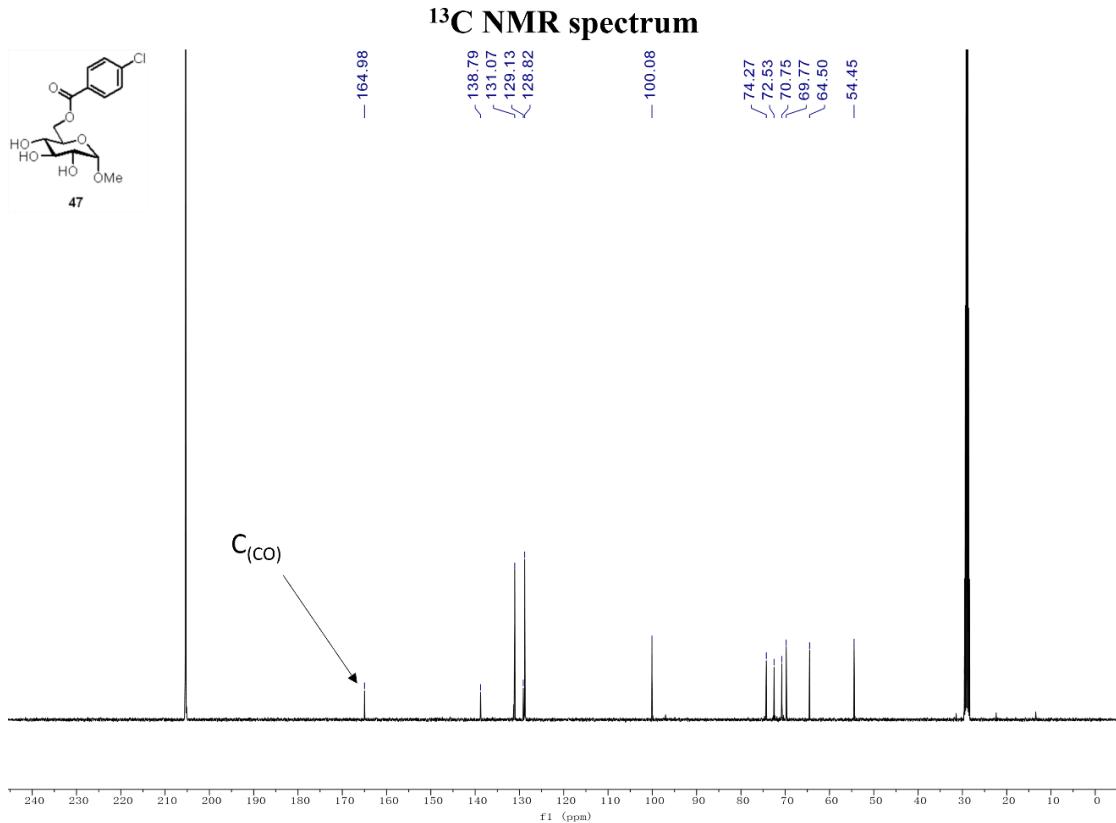


Figure S12. ¹³C NMR Spectra of **47**

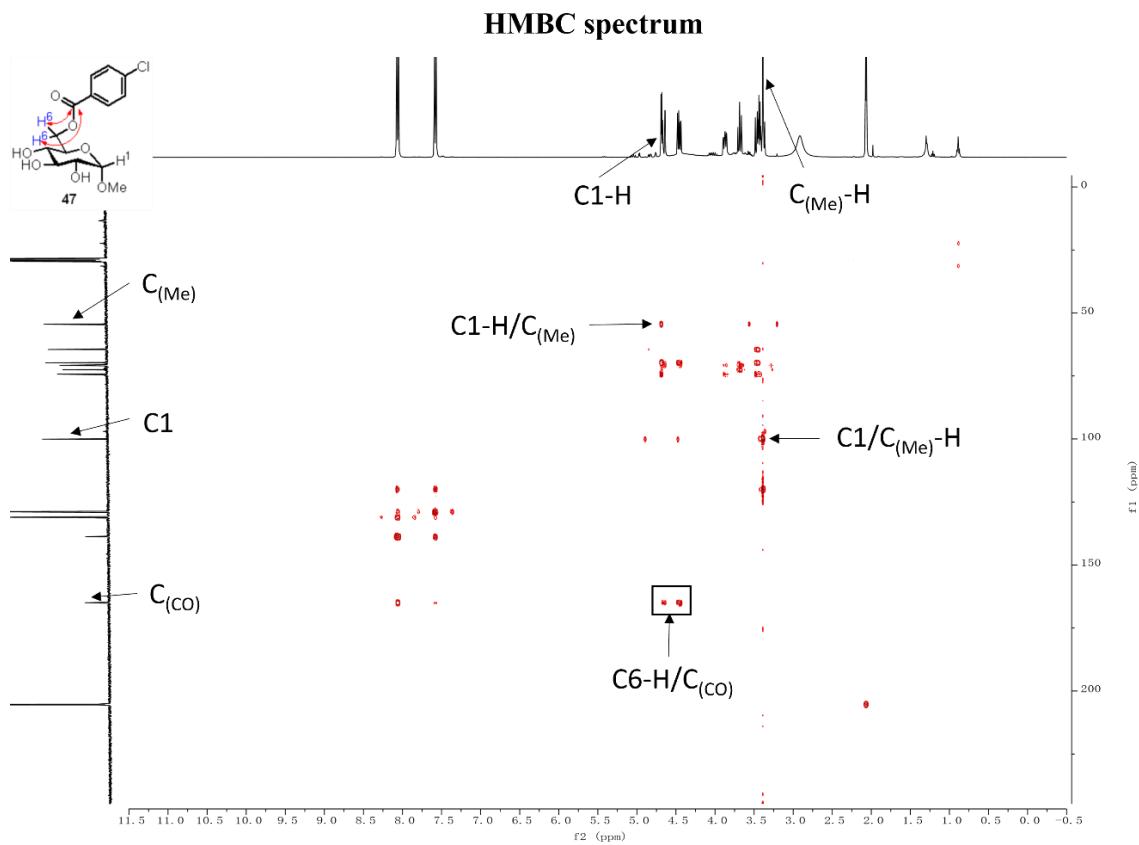


Figure S13. HMBC NMR Spectra of 47

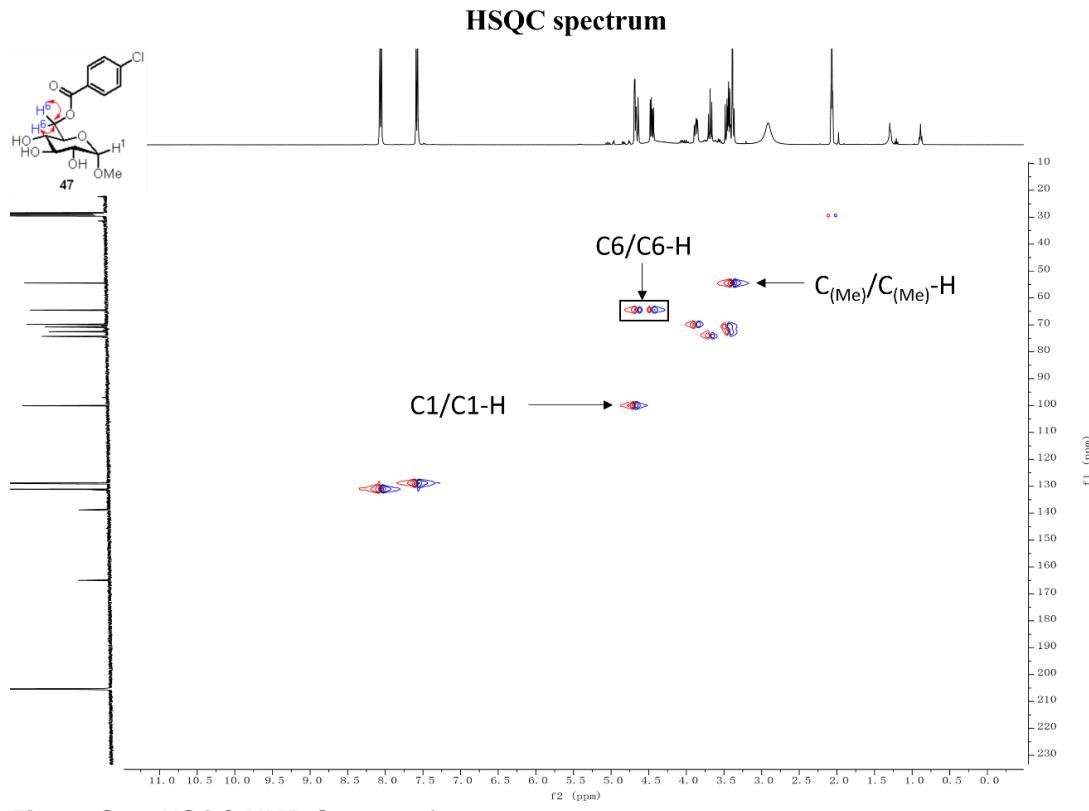


Figure S14. HSQC NMR Spectra of 47

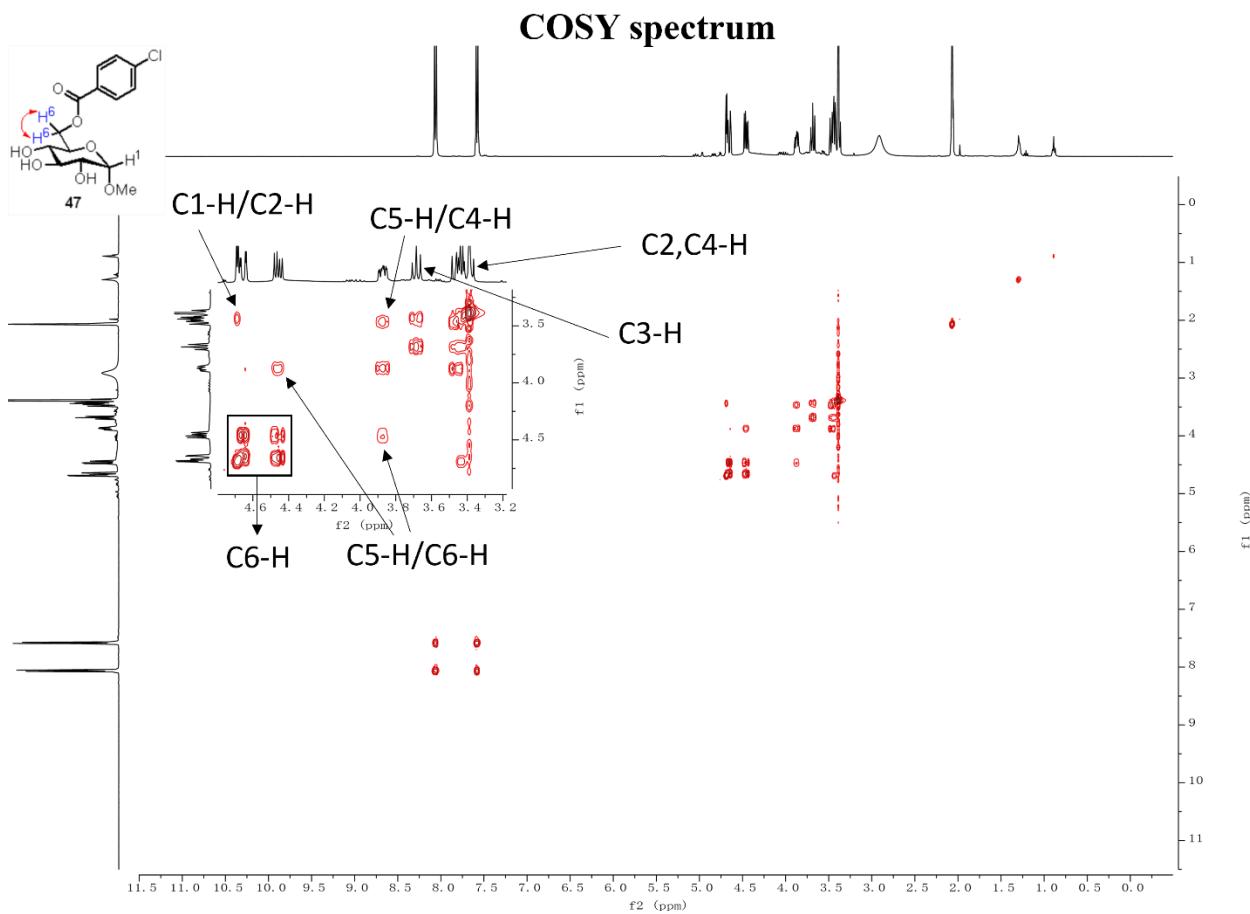
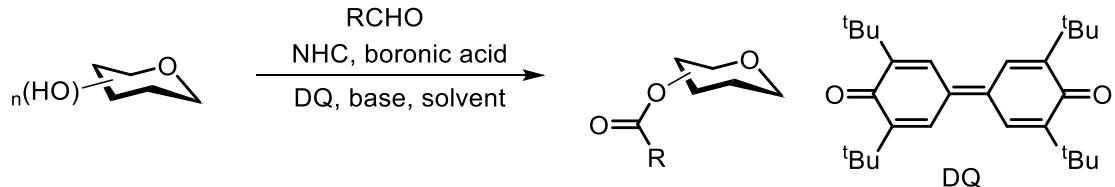


Figure S15. COSY NMR Spectra of 47

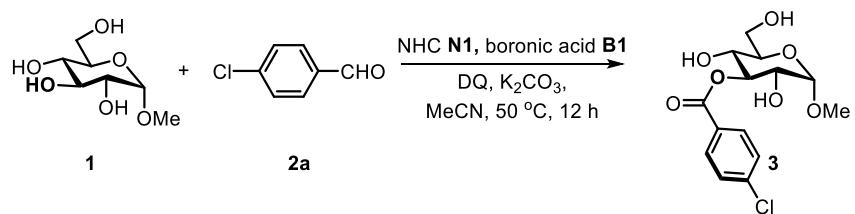
2.3. Acylation using aldehydes

General procedure A: selective acylation with aldehydes as acylation reagents



To a 4 mL screwtop test tube was added monosaccharide (0.1 mmol, 1.0 equiv), aldehyde (0.2 mmol, 2.0 equiv), NHC catalyst (10 mol %), boronic acid (1.0-1.5 equiv), DQ (1.0-1.5 equiv), and base (0.02 mmol, 0.2 equiv). Then, solvent (2 mL) was added to the mixture. The reaction was allowed to stir vigorously at 50 °C for 1-12 h under an N₂ atmosphere. After cooling to the room temperature, the reaction mixture was directly purified by flash column chromatography on silica with an appropriate solvent (EtOAc/hexane 1:5 to 5:1 v/v) to afford the pure product. Extraction with EtOAc/saturated NaHCO₃ aq and NaCl aq is necessary when boronic acid **B5** was used.

Table S1. Selected results of reaction conditions optimization for the synthesis of C3-O-acylate using aldehydes as acylation reagents.



entry	variation from standard conditions	ratio (C2:C3:C4:C6)	yield ^c (%)
1	none ^a	1:5.8:0.5:0.5	78
2	B1 (0 equiv) instead of 1.0 equiv	1:2.3:0.6:2.3	38
3	B1 (0.1 equiv) instead of 1.0 equiv	1:3:0.8:1.6	45
4	B1 (0.3 equiv) instead of 1.0 equiv	1:2.7:0.5:1.5	57
5	B1 (0.5 equiv) instead of 1.0 equiv	1:3.4:0.6:1.1	56
6	B1 (1.5 equiv) instead of 1.0 equiv	1:7:0:0	72
7	B1 (2 equiv) instead of 1.0 equiv	1:7:0:0	75
8	B1 (3 equiv) instead of 1.0 equiv	1:8:0:0	79
9	TFA (1 equiv) instead of B1	-	0
10	HOAc (1 equiv) instead of B1	1:7:0:0	20
11	rt	1:10:0:0	47
12	70 °C	1:8:0:0	63
13	NEt ₃ (0.2 equiv) instead of K ₂ CO ₃	1:11:0:0	61
14	DBU (0.2 equiv) instead of K ₂ CO ₃	1:6:0:0	60
15	NaOAc (0.2 equiv) instead of K ₂ CO ₃	1:10:0:0	68
16	K ₂ CO ₃ (1 equiv) instead of 0.2 equiv	1:5:0:0	32
17	MnO ₂ (1 equiv) instead of DQ	1:4:0:0	21
18	PIDA (1 equiv) instead of DQ	1:3:0:0	9
19	IBX (1 equiv) instead of DQ	1:9:0:0	21
20	THF	1:5:0:0	31
21	DCM	1:14:0:0	15
22	toluene	1:20:0:0	10
23	DMF	1:4.6:0:0	50
24	DMSO	1:4:0:0	33
25	EtOAc	1:10:0:0	74
26	acetone	1:10:0:0	58
27	MeOH	-	0
28	1, 4-dioxane	1:4:0:0	34
29	B1 (1.5 equiv), DQ (1.5 equiv) instead of 1.0 equiv	1:14:0:0	62
30 ^b	B1 (1.5 equiv), DQ(1.5 equiv) instead of 1.0 equiv and EtOAc instead of MeCN	1:16:0:0	70

[a] Reaction conditions: **1** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv), **N1** (10 mol %), **B1** (1.0 equiv), DQ (1.0 equiv), K₂CO₃ (0.2 equiv), MeCN (2 mL), 50 °C, 12 h.

[b] Reaction conditions: **1** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv), **N1** (10 mol %), **B1** (1.5 equiv), DQ (1.5 equiv), K₂CO₃ (0.2 equiv), EtOAc (2 mL), 50 °C, 12 h.

[c] NMR yield of total acylates.

The method for determining ratio and yield of the reaction

entry 2

table S1

without boronic acid

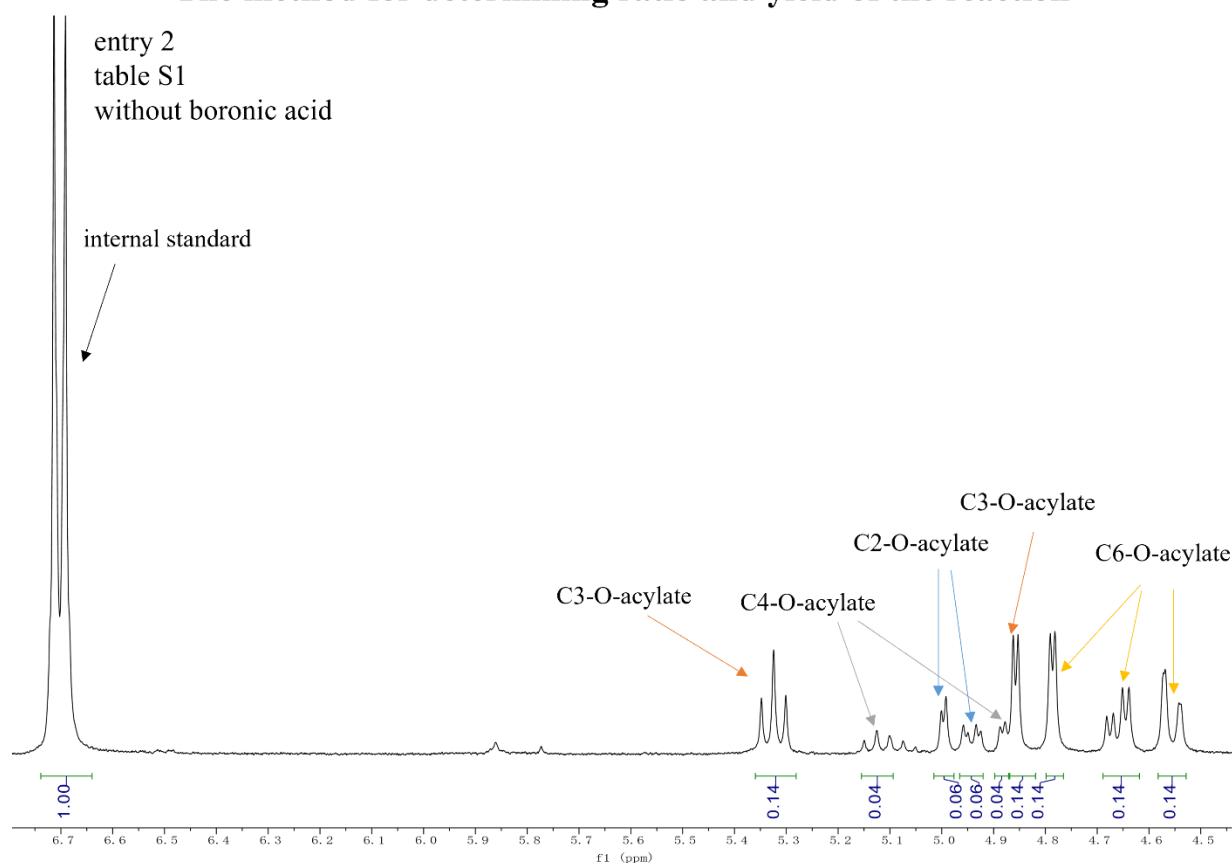
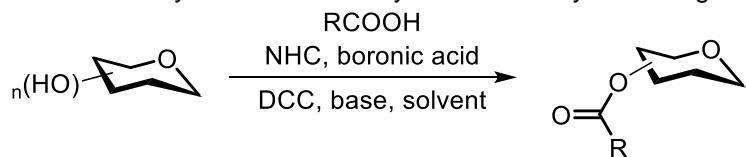


Figure S16. The method for determining ratio and yield of the reaction: The reaction mixture was purified by flash column chromatography on silica with an appropriate solvent (ethyl acetate/hexane 1:1 to 1:0 v/v) to afford the mixture acylates. Paraiodoanisole (0.05 mmol) was used as internal standard to measure the NMR yield (with the reaction of entry 2 in table S1 as example). ¹H NMR of C4-O-acylate was referred to ³.

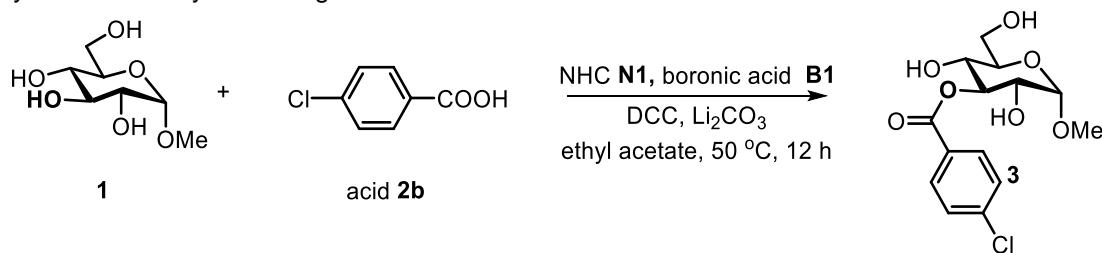
2.4. Acylation using carboxylic acids

General procedure B: selective acylation with carboxylic acids as acylation reagents



To a 4 mL screwtop test tube was added monosaccharide (0.1 mmol, 1.0 equiv), carboxylic acid (0.2 mmol, 2.0 equiv), NHC catalyst (20 mol %), boronic acid (0.1 mmol, 1.0 equiv), DCC (0.2 mmol, 2.0 equiv), and base (0.2 mmol, 2.0 equiv). Then, solvent (2 mL) was added to the mixture. The reaction was allowed to stir vigorously at 50 °C for 12 h under an N_2 atmosphere. After cooling to the room temperature, the reaction mixture was filtered, and then directly purified by silica gel flash column chromatography with an appropriate solvent (EtOAc/hexane 1:5 to 5:1 v/v) to afford the pure product.

Table S2. Selected results of reaction conditions optimization for the synthesis of C3-O-acylate using carboxylic acids as acylation reagents.



entry	variation from standard conditions	ratio (C2:C3:C4:C6)	yield ^c (%)
1	none ^a	1:14:0:0	60
2	without N1	1:0.4:0:0	14
3	without B1	1:12:1:1	15
4	without N1 and B1	1:1:0.3:0.3	8
5	B3 instead of B1	1:1.5:0:0	55
6	B6 instead of B1	0:100:0:0	4
7	B7 instead of B1	1:3.7:0:0	14
8	B8 instead of B1	1:1.5:0:0	53
9	B10 instead of B1	1:3.3:0:0	57
10	B11 instead of B1	1:5.5:1.5:0.5	17
11	N4 instead of N1	1:4.4:0:0	27
12	N5 instead of N1	1:2:0:0	40
13	N6 instead of N1	1:1.5:0:0	25
14	THF instead of EtOAc	1:9:0:0	39
15	acetone instead of EtOAc	1:10:0.8:1	52
16	DCM instead of EtOAc	1:7.7:0.3:0.3	28
17	MeCN instead of EtOAc	1:8:0.5:0.3	63
18 ^b	NaOAc instead of Li ₂ CO ₃	1:7:1:1	63
19 ^b	K ₂ CO ₃ instead of Li ₂ CO ₃	-	trace
20 ^b	Cs ₂ CO ₃ instead of Li ₂ CO ₃	-	trace
21 ^b	DPEA instead of Li ₂ CO ₃	-	trace
22 ^b	DBU instead of Li ₂ CO ₃	-	trace
23 ^b	K ₃ PO ₄ instead of Li ₂ CO ₃	-	trace
24 ^b	DABCO instead of Li ₂ CO ₃	1:3.5:0.4:0.5	60

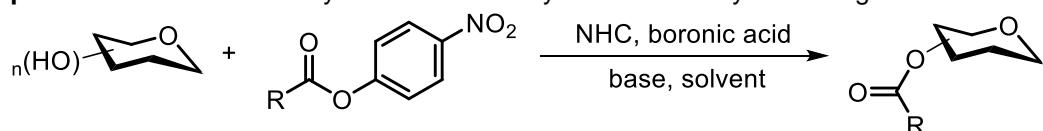
[a] Reaction conditions: **1** (0.1 mmol), carboxylic acid **2b** (0.2 mmol, 2.0 equiv), NHC **N1** (20 mol %), boronic acid **B1** (1.0 equiv), DCC (2.0 equiv), Li₂CO₃ (2.0 equiv), EtOAc (2 mL), 50 °C, 12 h.

[b] MeCN as solvent

[c] NMR yield of total acylates.

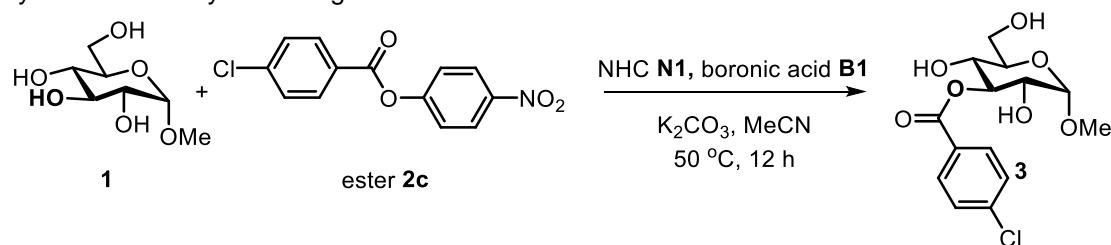
2.5. Acylation using carboxylic esters

General procedure C: selective acylation with carboxylic esters as acylation reagents



To a 4 mL screwtop test tube was added monosaccharide (0.1 mmol, 1.0 equiv), ester (0.2 mmol, 2.0 equiv), NHC catalyst (10 mol %), boronic acid (1.0-1.5 equiv), and base (0.02 mmol, 0.2 equiv). Then, solvent (2 mL) was added to the mixture. The reaction was allowed to stir vigorously at 50 °C for 1-12 h under an N₂ atmosphere. Then the reaction mixture was directly purified by flash column chromatography on silica with an appropriate solvent (EtOAc/hexane 1:5 to 5:1 v/v) to afford the pure product.

Table S3. Selected results of reaction conditions optimization for the synthesis of C3-O-acylate using carboxylic esters as acylation reagents.



entry	variation from standard conditions	ratio (C2:C3:C4:C6)	yield ^d (%)
1	none ^a	1:4:0:0	70
2	NHC N4 instead of NHC N1	1:1:0.3:0.4	45
3	NHC N5 instead of NHC N1	1:1:0.1:0.1	43
4	NHC N6 instead of NHC N1	1:0.9:0.1:0.2	36
5	B5 instead of B1	1:3.5:0:0	18
6	B6 instead of B1	-	0
7	B7 instead of B1	-	0
8	B8 instead of B1	1:0.7:0:0	49
9	B10 instead of B1	1:1.2:0:0	55
10	B11 instead of B1	1:2.1:0.7:1.1	49
11	THF instead of MeCN	-	0
12	DCM instead of MeCN	1:5.5:0:0	26
13	acetone instead of MeCN	1:3.8:0:0	48
14	EtOAc instead of MeCN	1:5:0:0	60
15 ^b	K ₃ PO ₄ instead of K ₂ CO ₃	1:5.7:0:0	67
16 ^b	NaOAc instead of K ₂ CO ₃	1:5.8:0:0	61
17 ^b	Li ₂ CO ₃ instead of K ₂ CO ₃	0:23:0:0	23
18 ^b	DBU instead of K ₂ CO ₃	1:5.4:0:0	64
19 ^b	DIPEA instead of K ₂ CO ₃	1:6.2:0:0	72
20 ^c	without NHC N1	-	0
21 ^c	without B1	1:4:1:1	14
22 ^c	without NHC N1 and B1	-	0

[a] Reaction conditions: **1** (0.1 mmol), ester **2c** (0.2 mmol, 2.0 equiv), NHC **N1** (10 mol %), boronic acid **B1** (1.5 equiv), K₂CO₃ (0.2 equiv), MeCN (2 mL), 50 °C, 12 h.

[b] EtOAc as solvent.

[c] DIPEA as base, EtOAc as solvent.

[d] NMR yield of total acylates.

2.6. Observation/preparation of intermediate I, its reactivity, and mechanistic implications

2.6.1 Identification of the intermediates in C2-OH selective acylation

To gain insight into the reaction mechanism, preliminary mechanistic studies were conducted. The reaction employing glucoside **1** and aldehyde **2a** as substrates was conducted in *d*-acetone for 15 minutes by using **N6** and **B8** (combination #11, Figure 4). Intermediate **I** and adduct **III** were efficiently afforded respectively in 25% and 50% NMR yield, clearly demonstrating that boronic esters were generated in the reaction (Figure S17, eq a). Intermediate **I⁴** previously prepared by heating boronic acid **B8** with glucoside **1** in toluene with removal of water proposed in the C(2)-OH selective acylation with NHC **N6** as pre-catalyst to gain adduct **III** (Figure S17, eq b), which is unstable and could be instantaneously converted into the final product **39** in the presence of water (Figure S17, eq c). **39** as the substrate could also give adduct **III** under otherwise identical condition (Figure S17, eq c), suggesting that this process is reversible in the reaction.

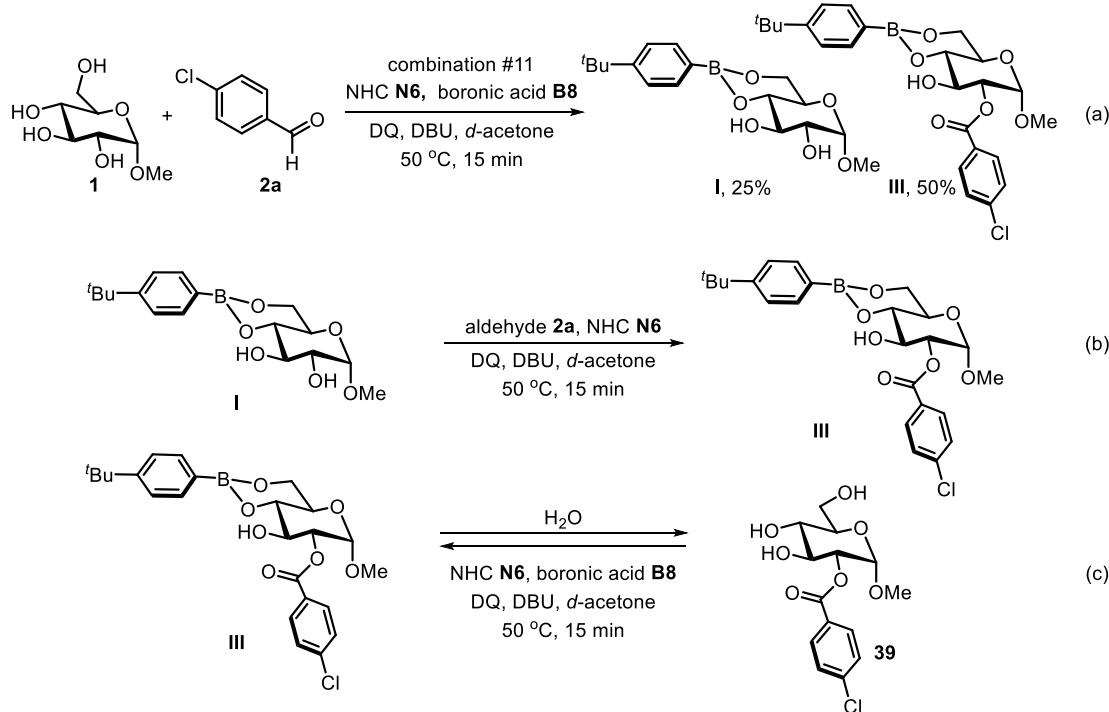


Figure S17. Intermediate **I** and its reactivity

Based on the literature precedent and these experiments, a plausible catalytic cycle is proposed in Figure S18. Boronic ester **I**, generating via reversible reactions between C4 and C6 hydroxyl groups of glucoside with boronic acid, could react with intermediate **II** generated from NHC catalyst and aldehyde **2a** under the oxidation of DQ to give the adduct **III** and regenerate NHC catalyst. The proper match of monosaccharide, NHC and boronic acid provides providential stereo electronic effects and covalent/non-covalent interactions to site-specifically amplify C2-OH and attenuate other OHs selective acylation. Eventually the adduct **III** undergoes hydrolysis in the same reaction mixture or in the presence of water to eventually form the site-selective acylated saccharide product and regenerate boronic acid.

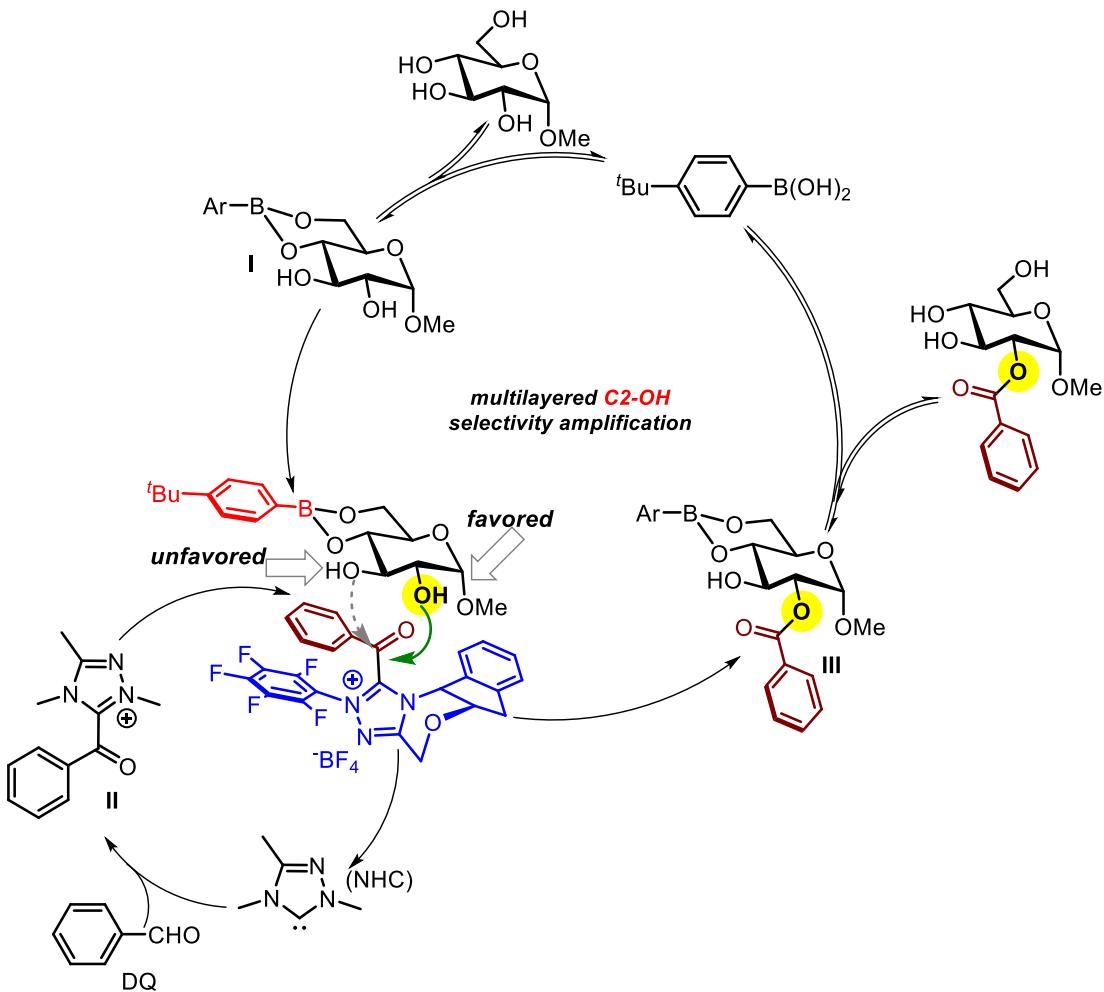


Figure S18. A plausible catalytic cycle

Experimental procedures:

Preparation of the intermediate **I** and adduct **III**:⁴

A suspension of glucoside **1** (1 mmol) in toluene (10 mL) was heated at reflux for 1 h using a Dean–Stark apparatus. Then arylboronic acid **B8** (1.2 equiv) was added, and the reaction mixture was heated at reflux for 1 h using a Dean–Stark apparatus. Then the solution was cooled to room temperature and the solvent was evaporated under vacuum. The crude material was dissolved in CH₂Cl₂, and the solution was filtered and concentrated under vacuum. The solid residue was dissolved in a minimum amount of boiling toluene. The resulting solution was cooled to room temperature to give methyl 4,6-boronato- α -D-glucopyranoside **I**.

A suspension of **39** (1 mmol) in toluene (10 mL) was added arylboronic acid **B8** (1.2 equiv). The reaction mixture was heated at reflux for 3 h using a Dean–Stark apparatus. Then the solution was cooled to room temperature and evaporated under vacuum to give **III** as a crude material.

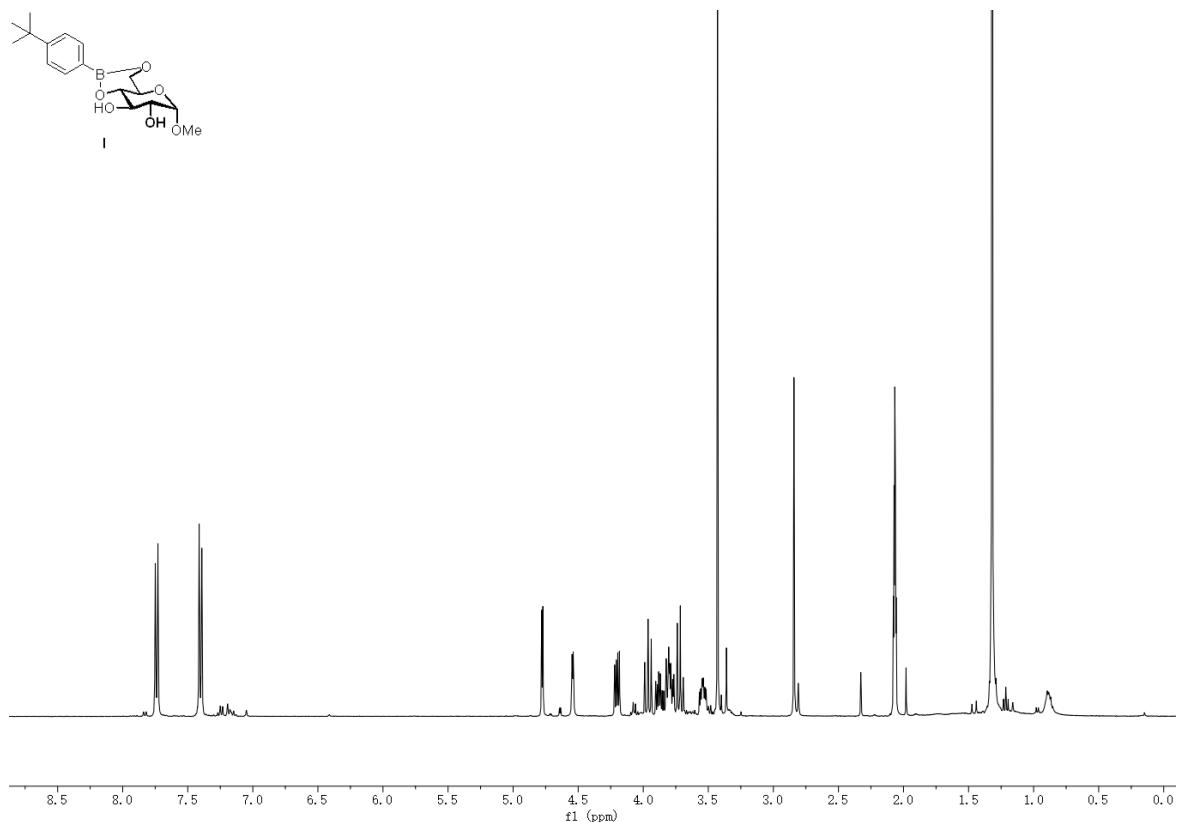


Figure S19. ¹H NMR Spectra of intermediate I

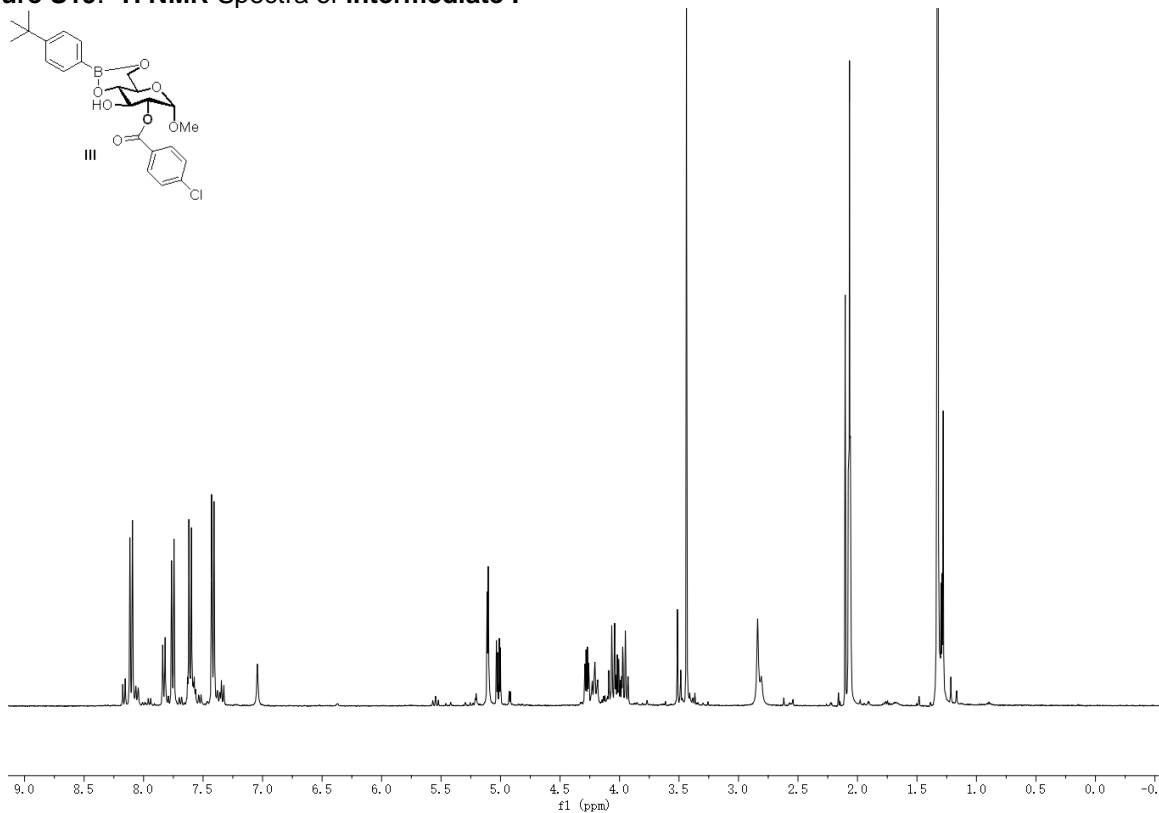


Figure S20. ¹H NMR Spectra of intermediate III

Identification of the intermediates **I** and adduct **III** (Figure S17, eq a):

To a 4 mL screwtop test tube was added glucoside **1** (0.1 mmol, 1.0 equiv), aldehyde **2a** (0.2 mmol, 2.0 equiv), NHC catalyst **N6** (10 mol %), boronic acid **B8** (1.5 equiv), DQ (1.5 equiv), and DBU (0.02 mmol, 0.2 equiv). Then, *d*-acetone (2 mL) was added to the mixture. The reaction was allowed to stir vigorously at 50 °C for 15 minutes under an N₂ atmosphere. After the reaction mixture cooling to room temperature, paraiodoanisole (0.05 mmol) as internal standard was added to measure the NMR yield of the intermediate.

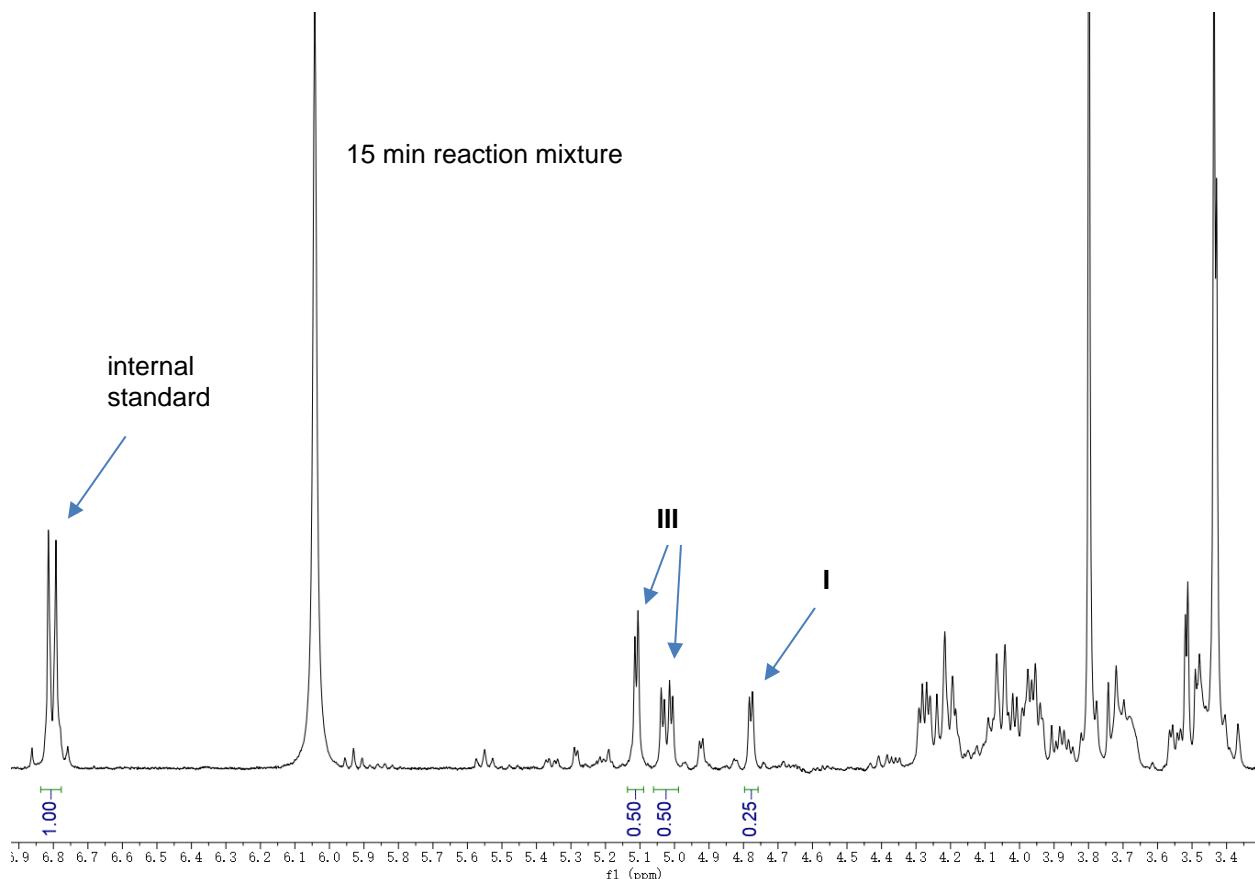


Figure S21. ¹H NMR Spectra of reaction mixture

Possible transformation in the reaction (Figure S17, eq b and c):

To a 4 mL screwtop test tube was added intermediate **I** (0.1 mmol, 1.0 equiv), aldehyde **2a** (0.2 mmol, 2.0 equiv), NHC catalyst **N6** (10 mol %), DQ (1.5 equiv), and DBU (0.02 mmol, 0.2 equiv). Then, *d*-acetone (2 mL) was added to the mixture. The reaction was allowed to stir vigorously at 50 °C for 15 minutes under an N₂ atmosphere. Then the reaction mixture was cooling to room temperature to measure the ¹H NMR spectrum (Figure S17, eq b).

To a 4 mL screwtop test tube was added **39** (0.1 mmol, 1.0 equiv), NHC catalyst **N6** (10 mol %), boronic acid **B8** (1.5 equiv), DQ (1.5 equiv), and DBU (0.02 mmol, 0.2 equiv). Then, *d*-acetone (2 mL) was added to the mixture. The reaction was allowed to stir vigorously at 50 °C for 15 minutes under an N₂ atmosphere. Then the reaction mixture was cooling to room temperature to measure the ¹H NMR spectrum (Figure S17, eq c).

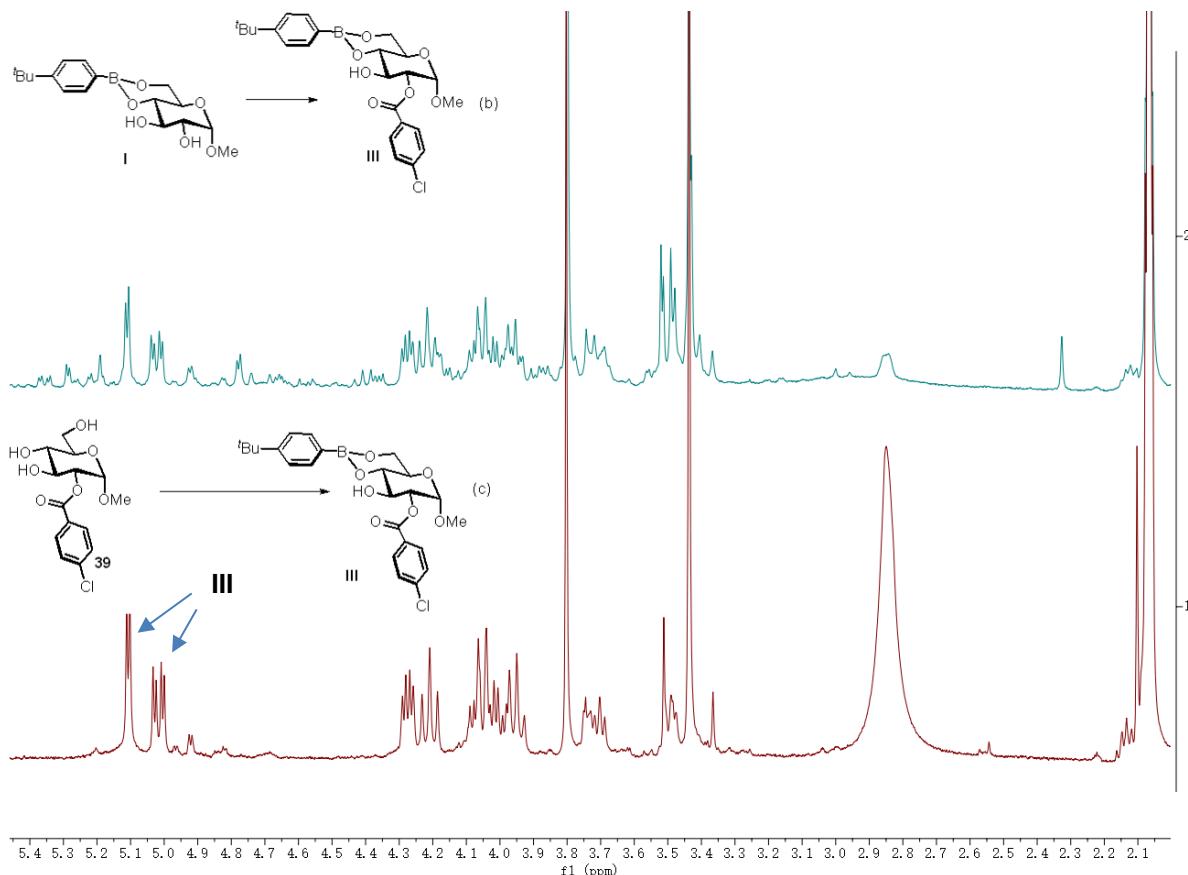


Figure S22. ^1H NMR Spectra of reaction mixture

2.6.2 Identification of the intermediates in C3-OH selective acylation

The reaction employing glucoside **1** and aldehyde **2a** as substrates was conducted in *d*-acetone for 3 minutes by using **N1** and **B1** (combination #2, Figure 4). Adduct **III** and product **3** were efficiently afforded respectively in 14% and 12% NMR yield, clearly demonstrating that boronic ester was generated in the reaction (Figure S23, eq a). Intermediate **I** (Figure 2) previously prepared by heating boronic acid **B1** with glucoside **1** in toluene with removal of water proposed in the C(3)-OH selective acylation with NHC **N1** as pre-catalyst to gain adduct **III** (Figure S23, eq b), which is unstable and could be instantaneously converted into the final product **3** in the same reaction mixture or in the presence of water (Figure S23, eq b, c). **3** as the substrate could also give adduct **III** under otherwise identical condition (Figure S23, eq c), suggesting that this process is reversible in the reaction.

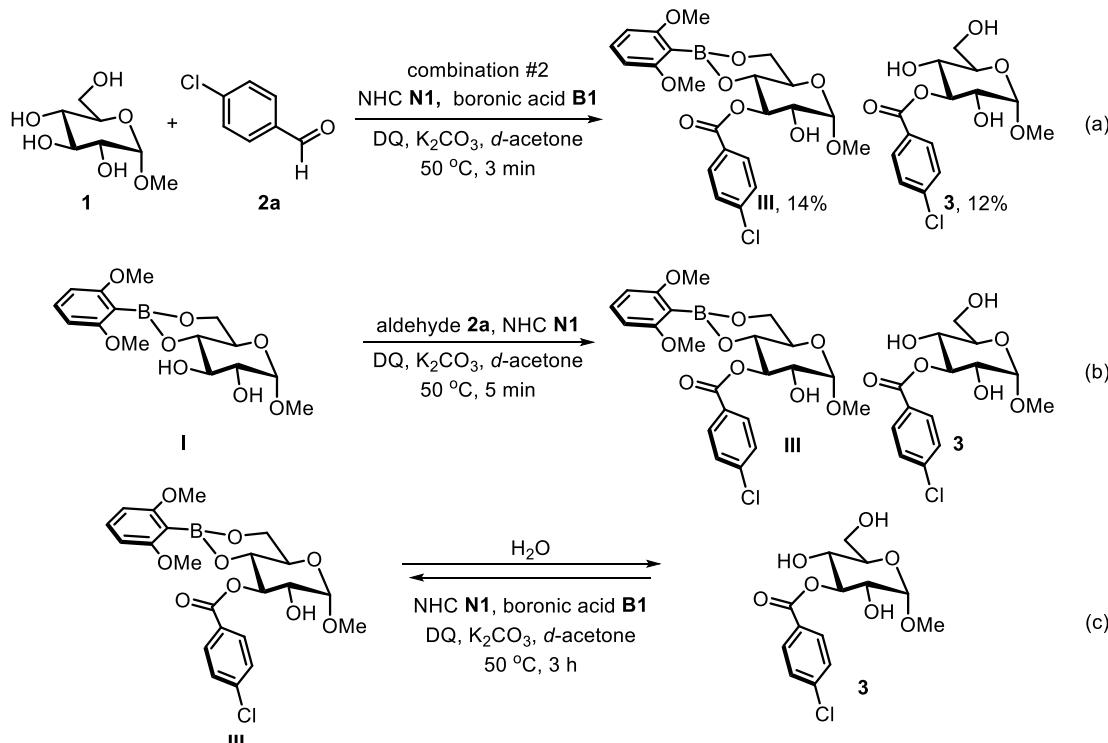


Figure S23. Intermediate **I** and its reactivity

Based on these experiments, a plausible catalytic cycle is proposed in Figure S24. Boronic ester **I**, generating via reversible reactions between C4 and C6 hydroxyl groups of glucoside with boronic acid, could react with intermediate **II** generated from NHC catalyst and aldehyde **2a** under the oxidation of DQ to give the adduct **III** and regenerate NHC catalyst. The proper match of monosaccharide, NHC and boronic acid provides providential stereo electronic effects and covalent/non-covalent interactions to site-specifically amplify C3-OH and attenuate other OHs selective acylation. Eventually the adduct **III** undergoes hydrolysis in the same reaction mixture or in the presence of water to eventually form the site-selective acylated saccharide product and regenerate boronic acid.

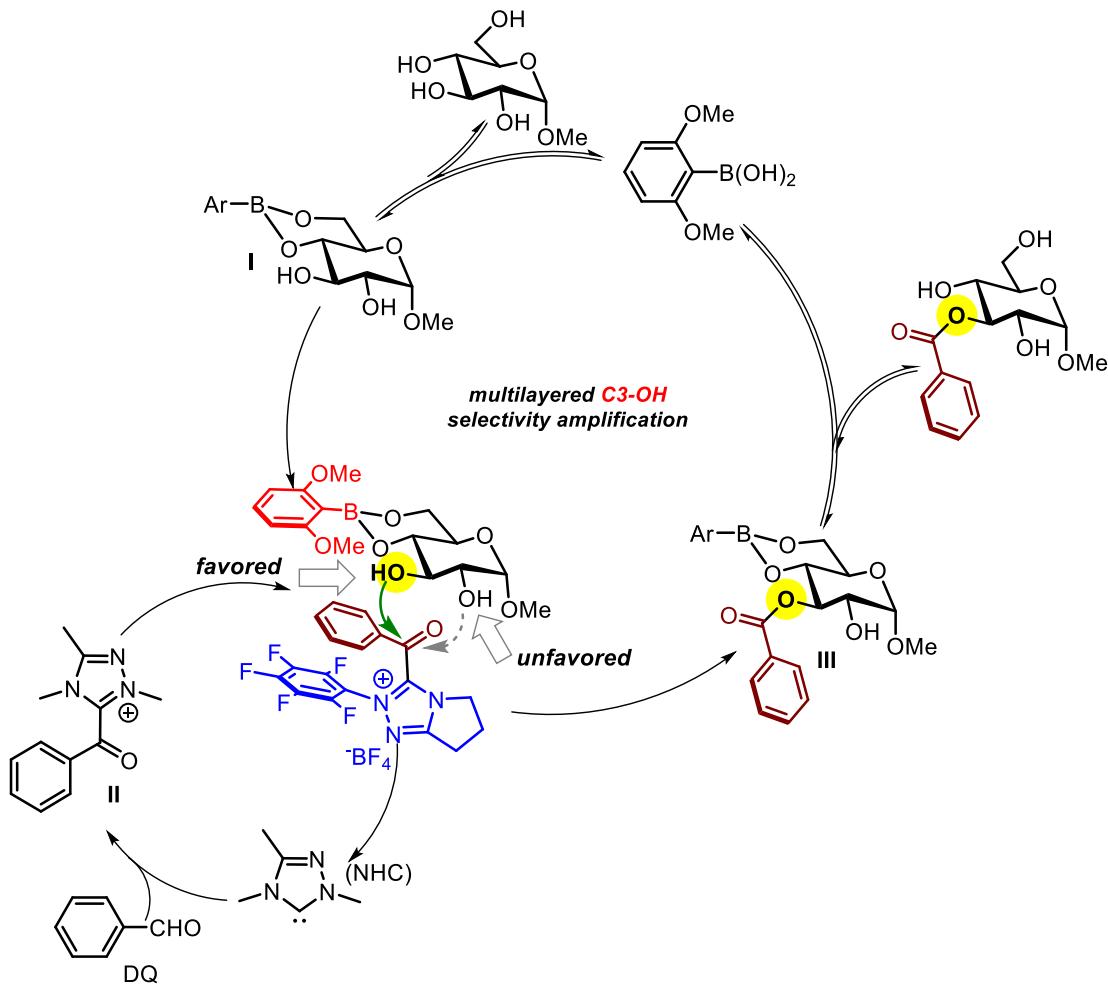


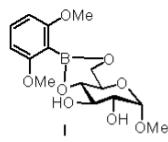
Figure S24. A plausible catalytic cycle

Experimental procedures:

Preparation of the intermediate **I** and adduct **III**:⁴

A suspension of glucoside **1** (1 mmol) in toluene (10 mL) was heated at reflux for 1 h using a Dean–Stark apparatus. Then arylboronic acid **B1** (1.2 equiv) was added, and the reaction mixture was heated at reflux for 1 h using a Dean–Stark apparatus. Then the solution was cooled to room temperature and the solvent was evaporated under vacuum to give **I** as a crude material, which is very unstable and undergoes hydrolysis quickly in the NMR test tube.

A suspension of **3** (1 mmol) in toluene (10 mL) was added arylboronic acid **B1** (1.2 equiv). The reaction mixture was heated at reflux for 3 h using a Dean–Stark apparatus. The solution was cooled to room temperature and evaporated under vacuum to give **III** as a crude material, which is very unstable and undergoes hydrolysis quickly in the NMR test tube.



Acetone-d6

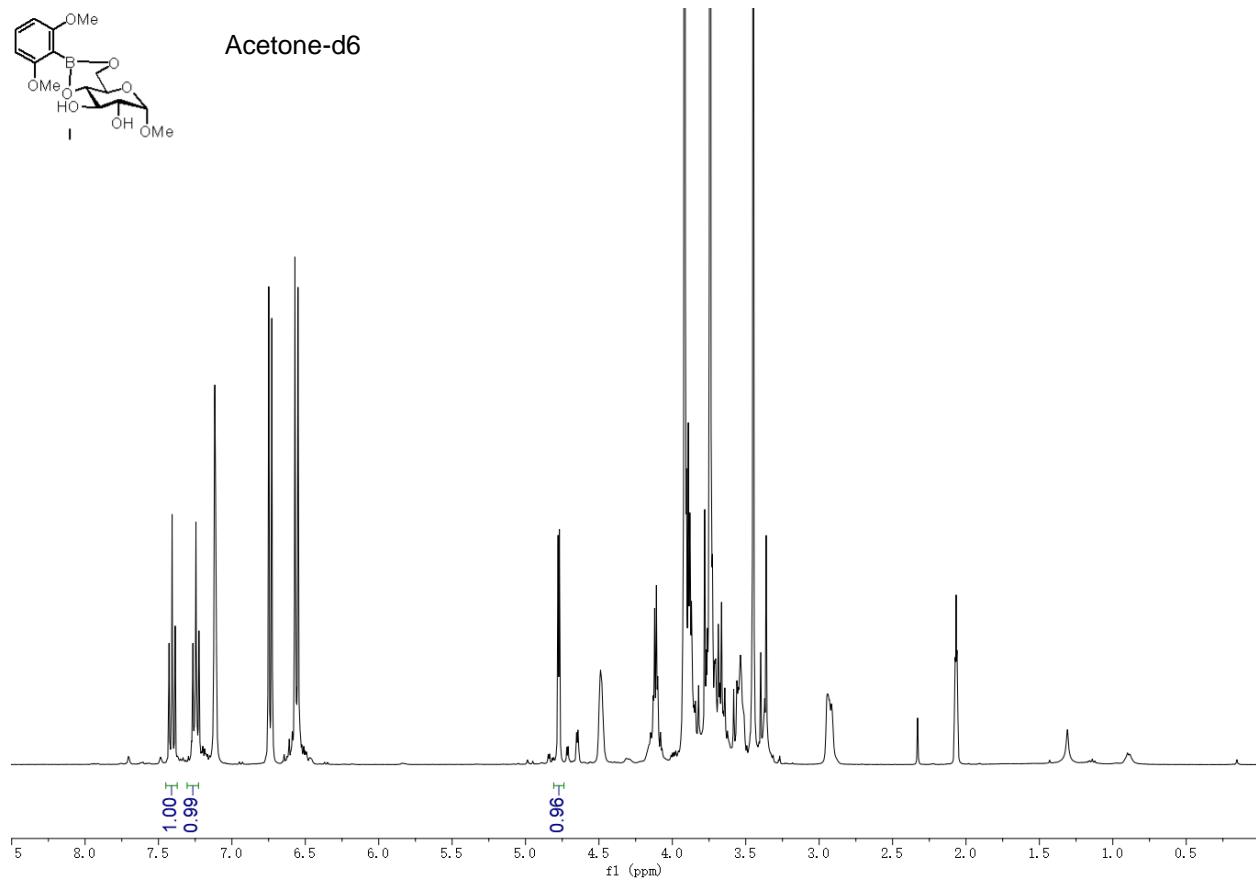


Figure S25. ^1H NMR Spectra of intermediate I

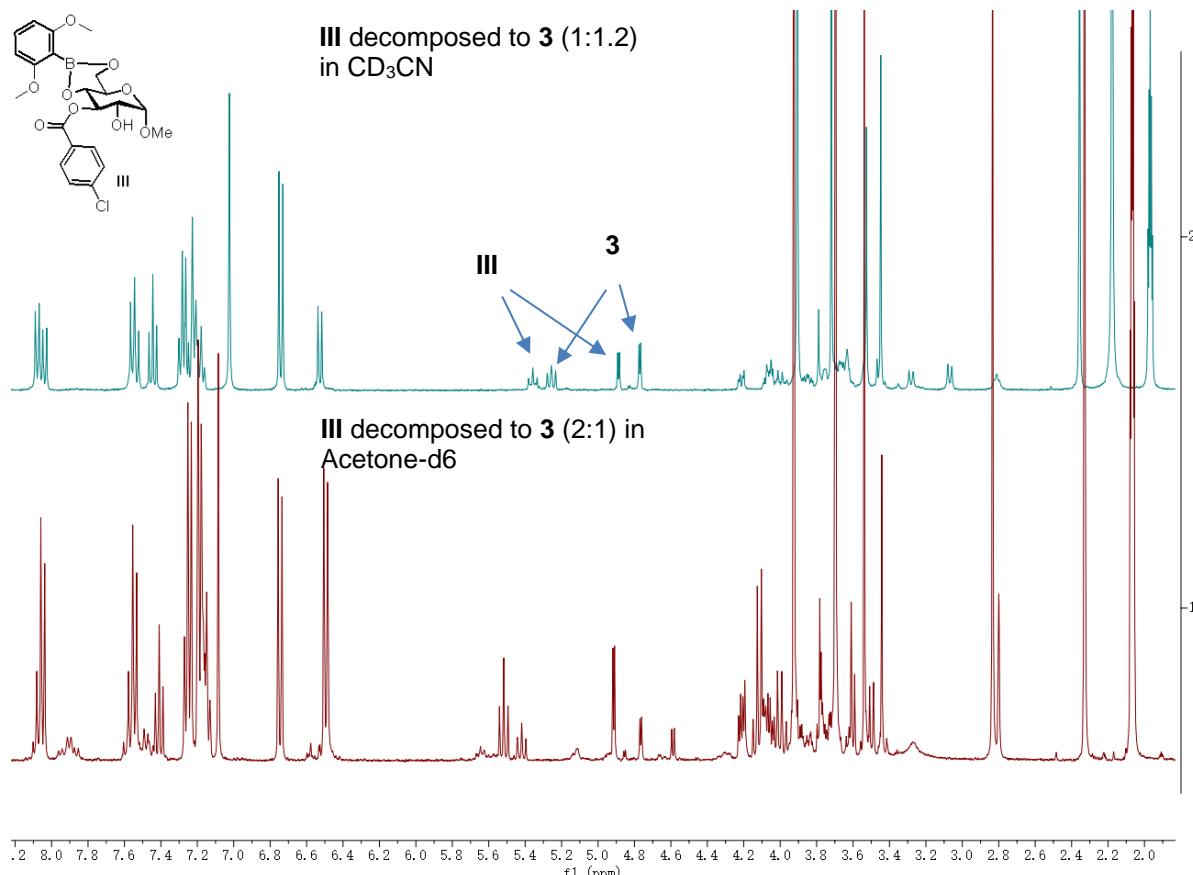


Figure S26. ^1H NMR Spectra of intermediate **III**

Identification of the intermediate (Figure S23, eq a):

To a 4 mL screwtop test tube was added glucoside **1** (0.1 mmol, 1.0 equiv), aldehyde **2a** (0.2 mmol, 2.0 equiv), NHC catalyst **N1** (10 mol %), boronic acid **B1** (1 equiv), DQ (1 equiv), and K_2CO_3 (0.02 mmol, 0.2 equiv). Then, *d*-acetone (2 mL) was added to the mixture. The reaction was allowed to stir vigorously at 50 °C for 3 minutes under an N_2 atmosphere. After the reaction mixture cooling to room temperature, paraiodoanisole (0.05 mmol) as internal standard was added to measure the NMR yield of the intermediate.

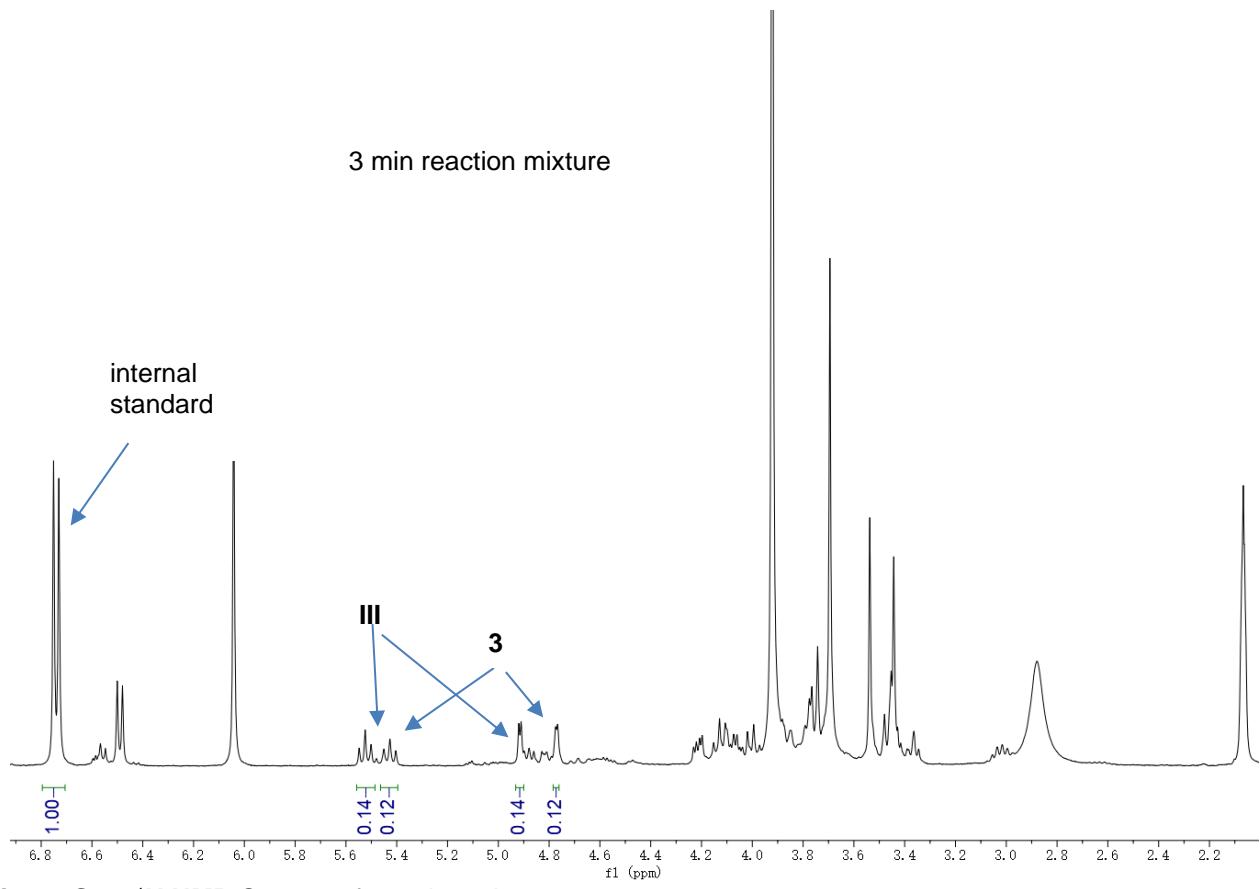


Figure S27. ^1H NMR Spectra of reaction mixture

Possible transformation in the reaction (Figure S23, eq b and c):

To a 4 mL screwtop test tube was added intermediate **I** (0.1 mmol, 1.0 equiv), aldehyde **2a** (0.2 mmol, 2.0 equiv), NHC catalyst **N1** (10 mol %), DQ (1 equiv), and K_2CO_3 (0.02 mmol, 0.2 equiv). Then, *d*-acetone (2 mL) was added to the mixture. The reaction was allowed to stir vigorously at 50 °C for 5 minutes under an N_2 atmosphere. Then the reaction mixture was cooling to room temperature to measure the ^1H NMR spectrum (Figure S23, eq b).

To a 4 mL screwtop test tube was added **3** (0.1 mmol, 1.0 equiv), NHC catalyst **N1** (10 mol %), boronic acid **B1** (1 equiv), DQ (1 equiv), and K_2CO_3 (0.02 mmol, 0.2 equiv). Then, *d*-acetone (2 mL) was added to the mixture. The reaction was allowed to stir vigorously at 50 °C for 3 h under an N_2 atmosphere. Then the reaction mixture was cooling to room temperature to measure the ^1H NMR spectrum (Figure S23, eq c).

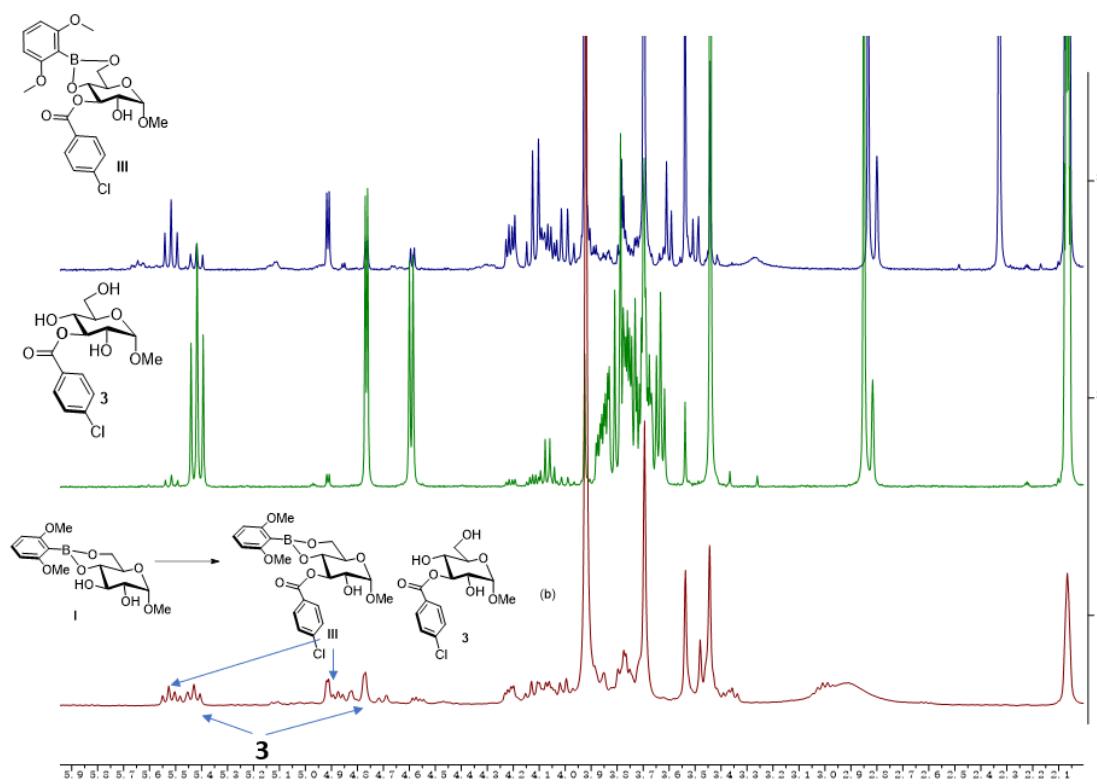


Figure S28. ^1H NMR Spectra of reaction mixture

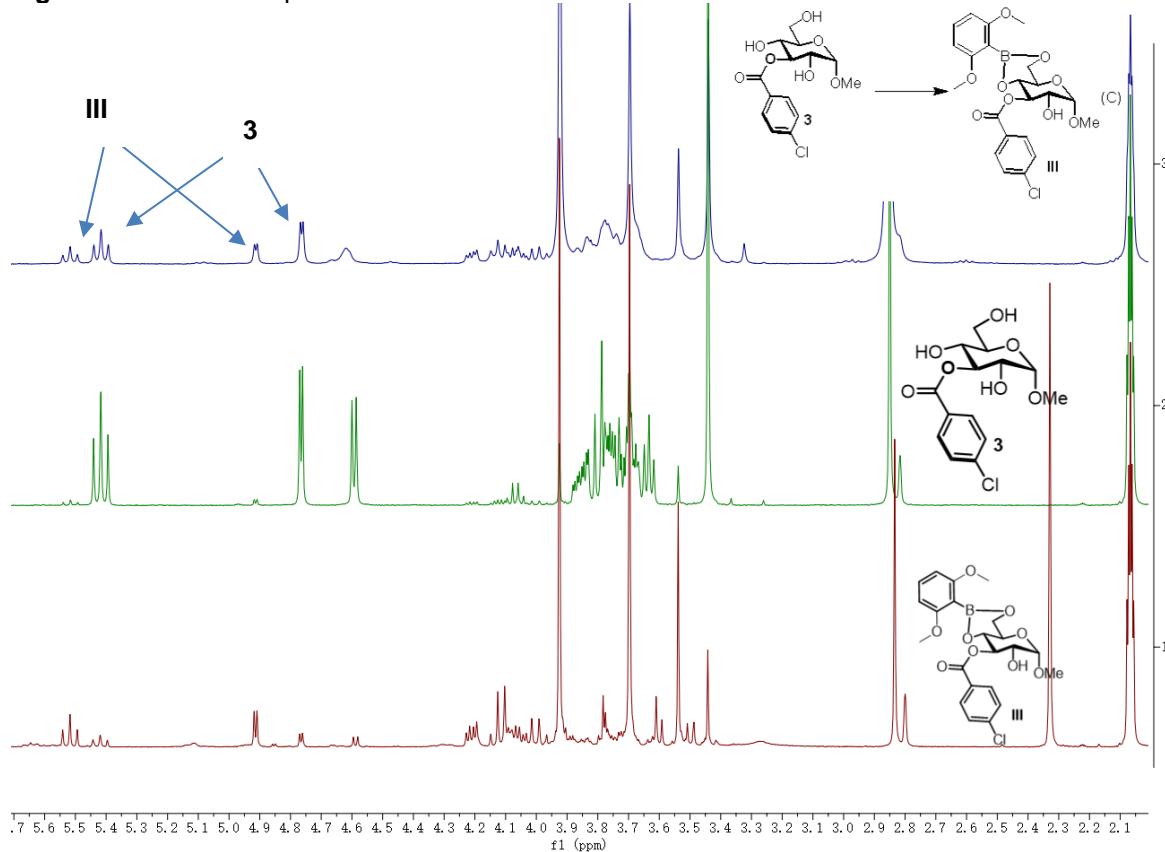
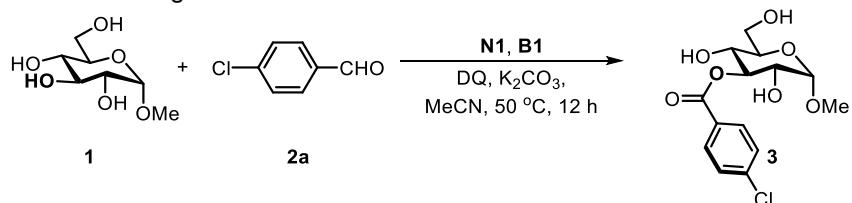


Figure S29. ^1H NMR Spectra of reaction mixture

2.7. Experimental procedures for Figure 3A, Figure 3B, and Figure 3C.

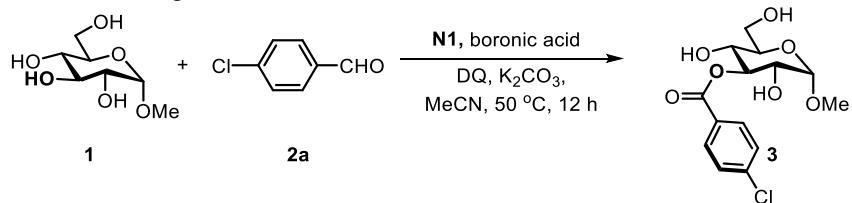
Experimental procedures for Figure 3A



	0	0.1	0.3	0.5	1.0	1.5	2	3
	38%	45%	57%	56%	78%	72%	75%	79%
dosage (equiv)	6:14:4:14	7:21:6:11	10:27:5:15	9:31:6:10	10:58:5:5	9:63:0:0	9:65:0:0	9:70:0:0

To a 4 mL screwtop test tube was added monosaccharide **1** (0.1 mmol, 1.0 equiv), aldehyde **2a** (0.2 mmol, 2.0 equiv), NHC **N1** (10 mol %), boronic acid **B1** (0-3.0 equiv), DQ (1.0 equiv), and K_2CO_3 (0.02 mmol, 0.2 equiv). Then, MeCN (2 mL) was added to the mixture. The reaction was allowed to stir vigorously at 50°C for 12 h under an N_2 atmosphere. After cooling to the room temperature, the reaction mixture was directly purified by flash column chromatography on silica with an appropriate solvent (EtOAc/hexane 1:5 to 1:0 v/v) to afford the mixture product. Paraiodoanisole (0.05 mmol) was used as internal standard to measure the NMR yield (C2:C3:C4:C6).

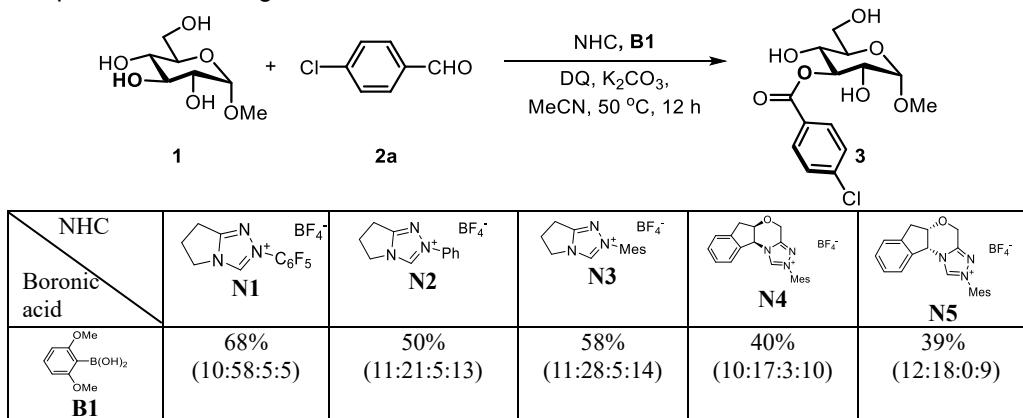
Experimental procedures for Figure 3B



								NA
	68% (10:58:5:5)	54% (10:44:0:0)	60% (23:37:0:0)	43% (15:28:0:0)	37% (4:29:0:4)	66% (8:53:3:2)	26% (5:18:2:1)	38% (6:14:4:14)

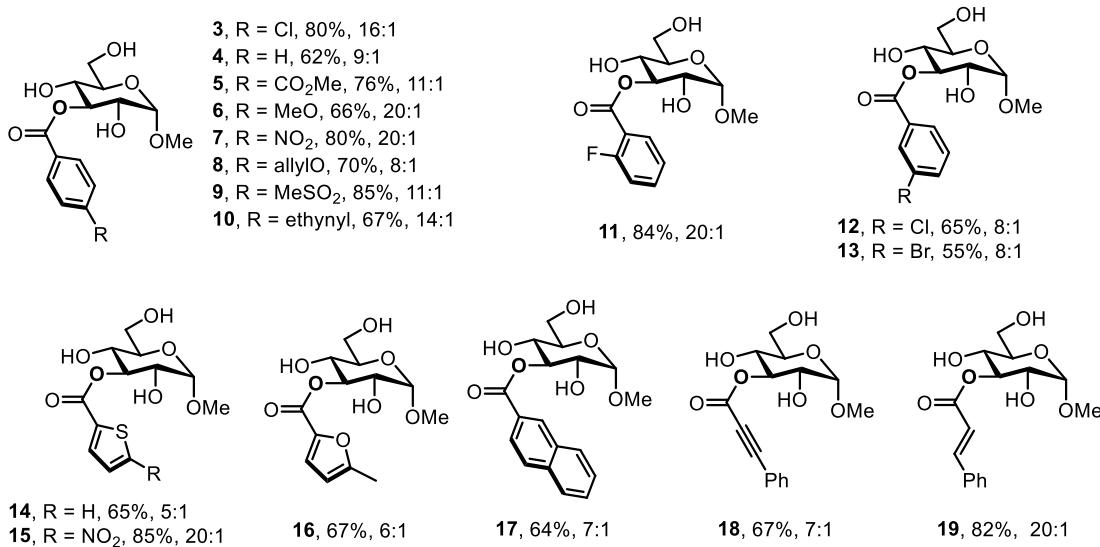
To a 4 mL screwtop test tube was added monosaccharide **1** (0.1 mmol, 1.0 equiv), aldehyde **2a** (0.2 mmol, 2.0 equiv), NHC **N1** (10 mol %), boronic acid (1.0 equiv), DQ (1.0 equiv), and K_2CO_3 (0.02 mmol, 0.2 equiv). Then, MeCN (2 mL) was added to the mixture. The reaction was allowed to stir vigorously at 50°C for 12 h under an N_2 atmosphere. After cooling to the room temperature, the reaction mixture was directly purified by flash column chromatography on silica with an appropriate solvent (EtOAc/hexane 1:5 to 1:0 v/v) to afford the mixture product. Paraiodoanisole (0.05 mmol) was used as internal standard to measure the NMR yield (C2:C3:C4:C6).

Experimental procedures for Figure 3C



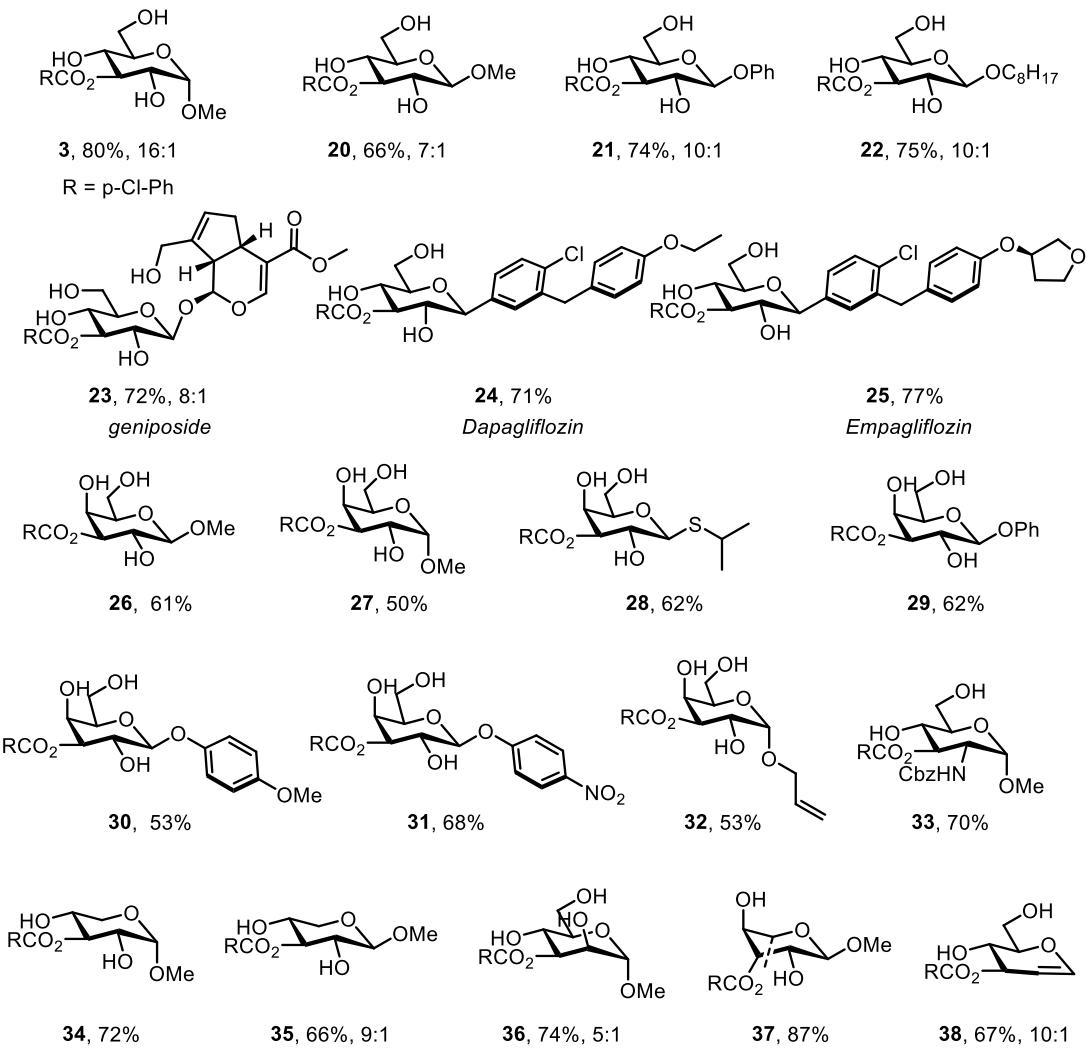
To a 4 mL screwtop test tube was added monosaccharide **1** (0.1 mmol, 1.0 equiv), aldehyde **2a** (0.2 mmol, 2.0 equiv), NHC catalyst (10 mol %), boronic acid **B1** (1.0 equiv), DQ (1.0 equiv), and K_2CO_3 (0.02 mmol, 0.2 equiv). Then, MeCN (2 mL) was added to the mixture. The reaction was allowed to stir vigorously at 50 °C for 12 h under an N_2 atmosphere. After cooling to the room temperature, the reaction mixture was directly purified by flash column chromatography on silica with an appropriate solvent (EtOAc/hexane 1:5 to 1:0 v/v) to afford the mixture product. Paraiodoanisole (0.05 mmol) was used as internal standard to measure the NMR yield (C2:C3:C4:C6).

2.8. Detailed experimental data for Figure 5 and Figure 7



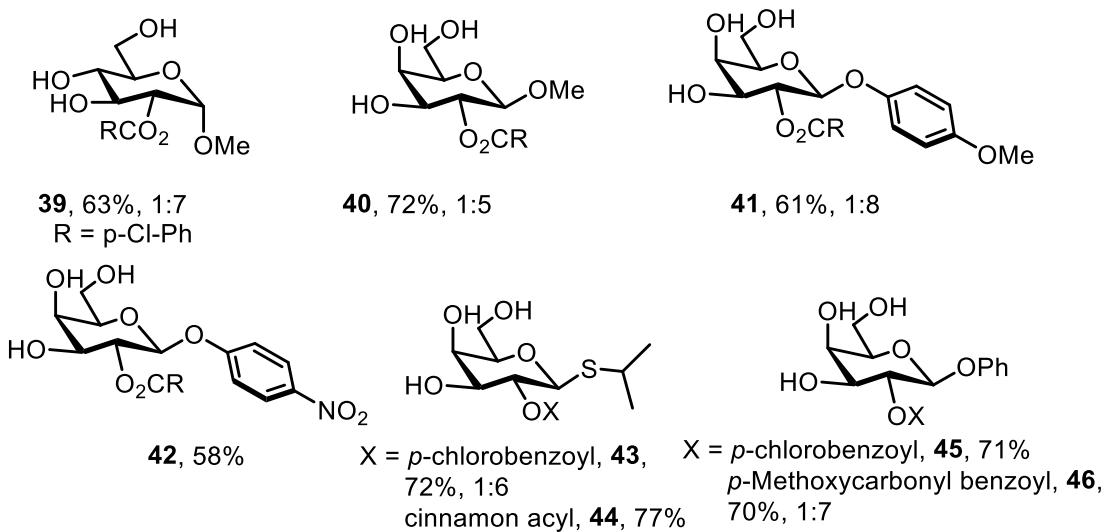
Yields are isolated yields of C3-O-acylate, regioselectivity refers to C3/C2-O-acylate for **3-19**

Figure S30. Scope of aldehydes amenable to site-selective monoacetylation, related to figure 5.



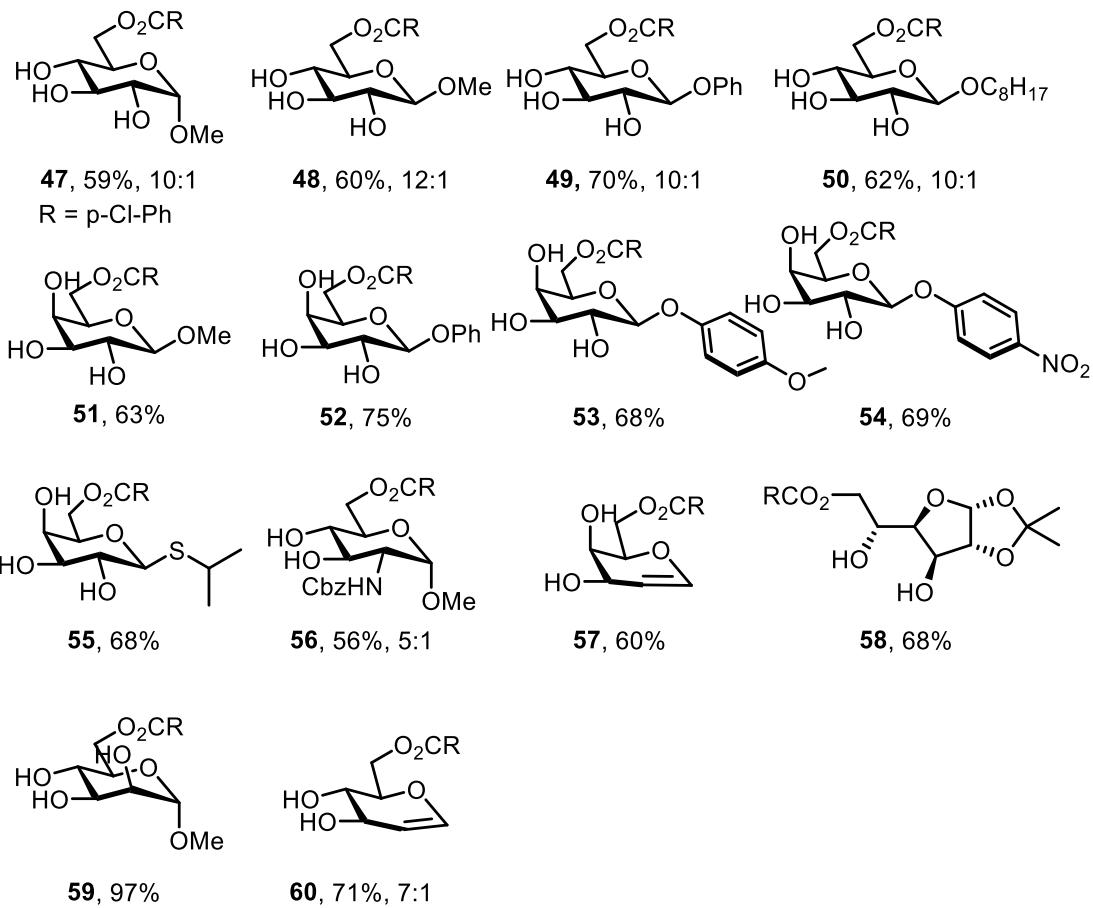
Yields are isolated yields of C3-O-acylate, regioselectivity refers to C3/C2-O-acylate for **3-37**, and C3/C6-O-acylate for **38**. Yield of **36** is isolated yield of C3-O-acylate and C2-O-acylate.

Figure S31. Scope of saccharides amenable to C3-OH selective monoacetylation, related to figure 5.

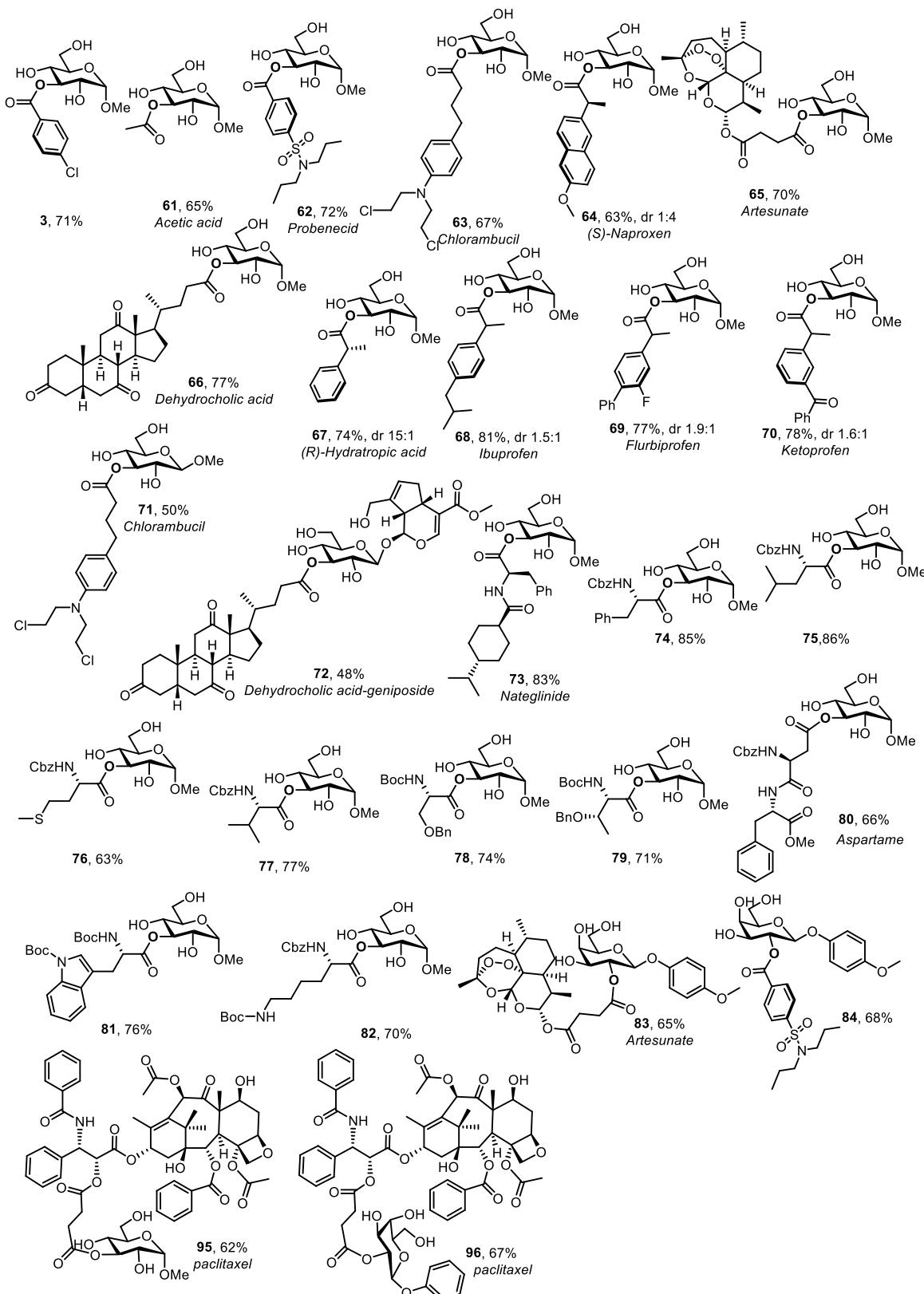


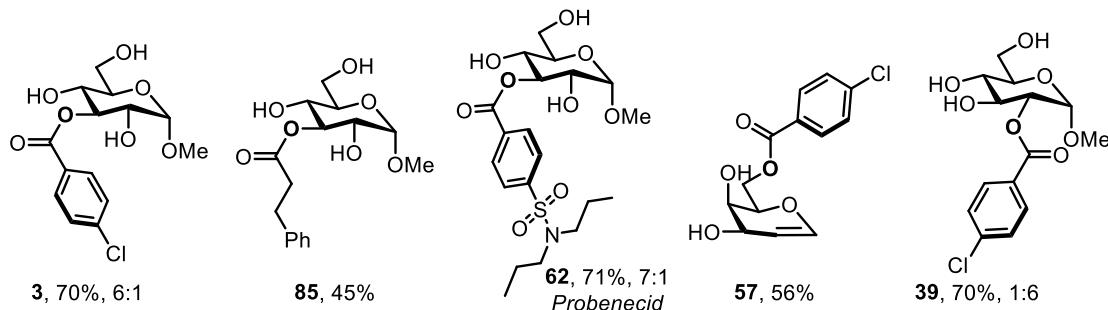
Yields are isolated yields of C2-O-acylate, regioselectivity refers to C3/C2-O-acylate for **39-46**. Yield of **40** is isolated yield of C3-O-acylate and C2-O-acylate.

Figure S32. Scope of saccharides amenable to C2-OH selective monoacetylation, related to figure 5.



Yields are isolated yields of C6-O-acylate, regioselectivity refers to C6/C3-O-acylate for **47-60**.
Figure S33. Scope of saccharides amenable to C6-OH selective monoacetylation, related to figure 5.





Yields are isolated yields of monoacylate, regioselectivity refers to C3/C2-O-acylate for **3,62,39**.

Yield of **62** and **39** are isolated yield of C3-O-acylate and C2-O-acylate.

Figure S35. Scope of esters amenable to site-selective monoacylation, related to figure 7.

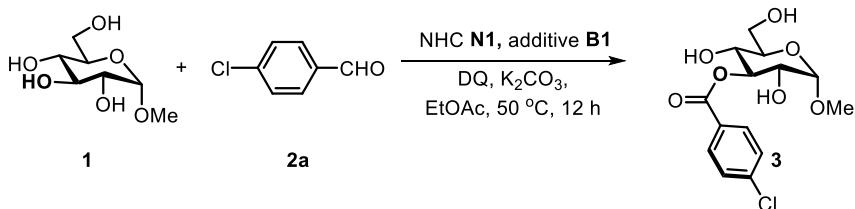
2.9. Conditions in using the different NHC/boronic acid combinations (Figure 4) for the various acylation reactions to prepare products 3 to 84, 95, 96. (Table S4)

entry	NHC/boronic acid combination (Fig. 4)	conditions	Products made under this condition
1	#1 (N1)	aldehyde (0.2 mmol, 2.0 equiv), NHC N1 (10 mol %), DQ (1.0 equiv), K ₂ CO ₃ (0.2 equiv), MeCN (2 mL), rt, 24 h.	37
		ester 2c (0.2 mmol, 2.0 equiv), NHC N1 (10 mol %), DBU (0.2 equiv), MeCN (2 mL), rt, 24 h.	57
		aldehyde (0.2 mmol, 2.0 equiv), NHC N1 (10 mol %), DQ (1.0 equiv), K ₂ CO ₃ (0.2 equiv), MeCN (2 mL).	56,57,58
2	#2 (N1, B1)	aldehyde (0.2 mmol, 2.0 equiv), NHC N1 (10 mol %), boronic acid B1 (1.5 equiv), DQ (1.5 equiv), K ₂ CO ₃ (0.2 equiv), EtOAc (2 mL).	3-22, 24, 25
		aldehyde (0.3 mmol, 3.0 equiv), NHC N1 (10 mol %), boronic acid B1 (1.0 equiv), DQ (1.0 equiv), DBU (0.2 equiv), MeCN (2 mL).	23
		carboxylic ester (0.2 mmol, 2.0 equiv), NHC N1 (10 mol %), boronic acid B1 (1.5 equiv), DIPEA (0.2 equiv), EtOAc (2 mL).	3,62,85
		carboxylic acid (0.2 mmol, 2.0 equiv), NHC N1 (20 mol %), boronic acid B1 (1.0 equiv), DCC (2.0 equiv).	3,61,62
			63-71, 73-82, 95
			72
3	#3 (N1, B3)	aldehyde (0.2 mmol, 2.0 equiv), NHC N1 (10 mol %), boronic acid B3 (1.0 equiv), DQ (1.0 equiv), K ₂ CO ₃ (0.2 equiv), MeCN (2 mL).	33
4	#4 (N1, B7)	aldehyde (0.2 mmol, 2.0 equiv), NHC N1 (10 mol %), boronic acid B7 (1.0 equiv), DQ (1.0 equiv), K ₂ CO ₃ (0.2 equiv), MeCN (2 mL).	34,35
5	#5 (N1, B9)	aldehyde (0.2 mmol, 2.0 equiv), NHC N1 (10 mol %), boronic acid B9 (1.0 equiv), DQ (1.0 equiv), DBU (0.2 equiv), THF (2 mL).	26-32
6	#6 (N1, B10)	aldehyde (0.2 mmol, 2.0 equiv), NHC N1 (10 mol %), boronic acid B10 (1.0 equiv), DQ (1.0 equiv), K ₂ CO ₃ (0.2 equiv), MeCN (2 mL).	41-46
		aldehyde (0.2 mmol, 2.0 equiv), NHC N1 (10 mol %), boronic acid B5 or B10 (1.0 equiv), DQ (1.0 equiv), K ₂ CO ₃ (0.2 equiv), acetone (2 mL).	40
		carboxylic acid (0.2 mmol, 2.0 equiv), NHC N1 (20 mol %), boronic acid B10 (1.0 equiv), DCC (2.0 equiv), NaOAc (2.0 equiv), MeCN (2 mL).	83, 84, 96
7	#7 (N4)	aldehyde (0.2 mmol, 2.0 equiv), NHC N4 (10 mol %), DQ (1.0 equiv), K ₂ CO ₃ (0.2 equiv), MeCN (2 mL).	47-50

entry	NHC/boronic acid combination (Fig. 4)	conditions	Products made under this condition
8	#8 (N4, B2)	aldehyde (0.2 mmol, 2.0 equiv), NHC N4 (10 mol %), boronic acid B2 (1.0 equiv), DQ (1.0 equiv), DBU (0.2 equiv), THF (2 mL).	38
9	#9 (N4, B11)	aldehyde (0.2 mmol, 2.0 equiv), NHC N4 (10 mol %), boronic acid B11 (1.0 equiv), DQ (1.0 equiv), DBU (0.2 equiv), MeCN (2 mL).	36
		aldehyde (0.3 mmol, 3.0 equiv), NHC N4 (20 mol %), boronic acid B11 (1.0 equiv), DQ (1.5 equiv), DBU (0.2 equiv), THF (2 mL).	51-55
10	#10 (N5)	aldehyde (0.3 mmol, 3.0 equiv), NHC N5 (20 mol %), DQ (1.5 equiv), DBU (0.2 equiv), THF (2 mL).	59
11	#11 (N6, B8)	aldehyde (0.2 mmol, 2.0 equiv), NHC N6 (10 mol %), boronic acid B8 (1.5 equiv), DQ (1.5 equiv), DBU (0.2 equiv), THF (2 mL).	39
		ester 2c (0.2 mmol, 2.0 equiv), NHC N6 (10 mol %), boronic acid B8 (1.5 equiv), DBU (0.2 equiv), THF (2 mL), rt, 24 h.	
12	#12 (N7, B11)	aldehyde (0.2 mmol, 2.0 equiv), NHC N7 (10 mol %), boronic acid B11 (1.0 equiv), DQ (1.0 equiv), DBU (0.2 equiv), THF (2 mL).	60

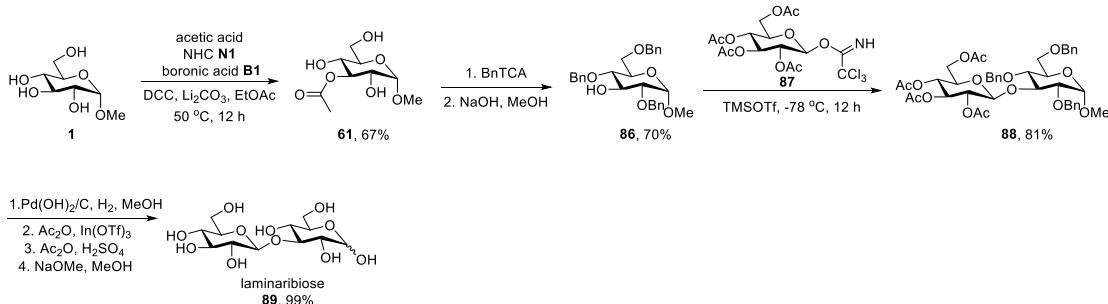
Common conditions (saccharide (0.1 mmol), 50 °C, 12 h) are not given.

2.10. Procedure for a gram scale reaction



To a 250 mL flask was added monosaccharide **1** (5.0 mmol, 1.0 equiv), aldehyde **2a** (10 mmol, 2.0 equiv), NHC **N1** (10 mol %), boronic acid **B1** (7.5 mmol, 1.5 equiv), DQ (7.5 mmol, 1.5 equiv), and K₂CO₃ (1.0 mmol, 0.2 equiv). Then, EtOAc (100 mL) was added to the mixture. The reaction was allowed to stir vigorously at 50 °C for 12 h under an N₂ atmosphere. After cooling to the room temperature, the reaction mixture was concentrated to 15 mL, and then directly purified by flash column chromatography on silica with an appropriate solvent (EtOAc/hexane 1:5 to 5:1 v/v) to afford **3** (1.16 g, 70%).

2.11. Synthesis of disaccharide laminaribiose, related to figure 8A.



To a 100 mL flask was added monosaccharide **1** (2.0 mmol, 1.0 equiv), NHC **N1** catalyst (20 mol %), boronic acid **B1** (2.0 mmol, 1.0 equiv), DCC (4.0 mmol, 2.0 equiv), and Li₂CO₃ (4.0 mmol, 2.0 equiv). Then, EtOAc (40 mL) and carboxylic acid (4.0 mmol, 2.0 equiv) was added to the mixture. The reaction was allowed to stir vigorously at 50 °C for 12 h under an N₂ atmosphere. After cooling to the room temperature, the reaction mixture was filtered and concentrated to 15 mL, then directly purified by silica gel flash column chromatography with an appropriate solvent (EtOAc/hexane 1:5 to 1:0 v/v) to afford the pure product **61** (316 mg, 67%).

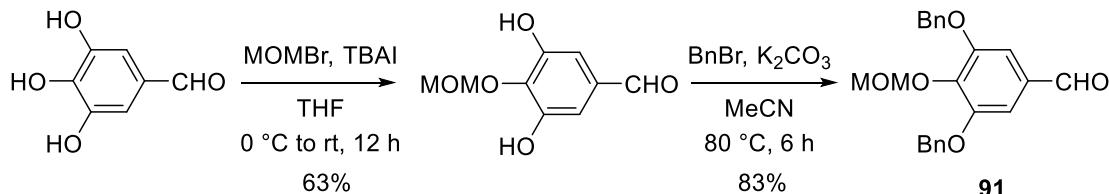
To a mixture of **61** (236 mg, 1.0 mmol), BnTCA (1.25 g, 5.0 mmol), powdered 4 Å molecular sieves (1 g), and anhydrous dioxane (30 mL) was added trimethylsilyl trifluoromethanesulfonate (0.3 mmol) at 0 °C. The mixture was stirring at room temperature for 7 h under an N₂ atmosphere. Then more BnTCA (2 mmol) and trimethylsilyl trifluoromethanesulfonate (0.05 mmol) was added and the reaction mixture was stirred for another 12 h. Then the mixture was concentrated and purified by silica gel flash column chromatography with an appropriate solvent (EtOAc/hexane 1:10 to 1:4 v/v) to afford the crude product. To the crude product was added MeOH (10 mL) and NaOH (3.0 mmol), the mixture was stirring at room temperature for 20 h. Then the mixture was concentrated and purified by silica gel flash column chromatography with an appropriate solvent (EtOAc/hexane 1:10 to 1:4 v/v) to afford the pure product **86** (325 mg, 70%).

A solution of **86** (0.3 g, 0.646 mmol), **87** (476 mg, 0.97 mmol), and powdered 4 Å molecular sieves (0.6 g) in CH₂Cl₂ (12 mL) was cooled to -78 °C. Then trimethylsilyl trifluoromethanesulfonate (0.13 mmol) was added and the reaction mixture was stirred for 12 h at -78 °C under an N₂ atmosphere. When complete conversion of the starting material was observed, the reaction mixture was allowed to attain room temperature, concentrated, and purified by silica gel flash column chromatography with an appropriate solvent (EtOAc/hexane 1:10 to 1:3 v/v) to afford the pure product **88** (416 mg, 81%).

88 (794 mg, 1 mmol) in MeOH (15 mL) was stirred with Pd(OH)₂/C (700 mg) and H₂ (1 atm) for 24 h at 25 °C. Then the mixture was filtered and concentrated. The crude product was treated with Ac₂O (3 mL), then In(OTf)₃ (0.1 mmol) was added to the mixture at 0 °C. The reaction mixture was stirred for 3 h at 25 °C under an N₂ atmosphere. Then another portion of Ac₂O (12 mL) and H₂SO₄ (250 µL) was added to the mixture successively at 0 °C. The reaction was stirred at 0 °C for another 6 h, then poured onto ice. The mixture was extracted with EtOAc, the extracts were washed with water, saturated NaHCO₃, saturated NaCl

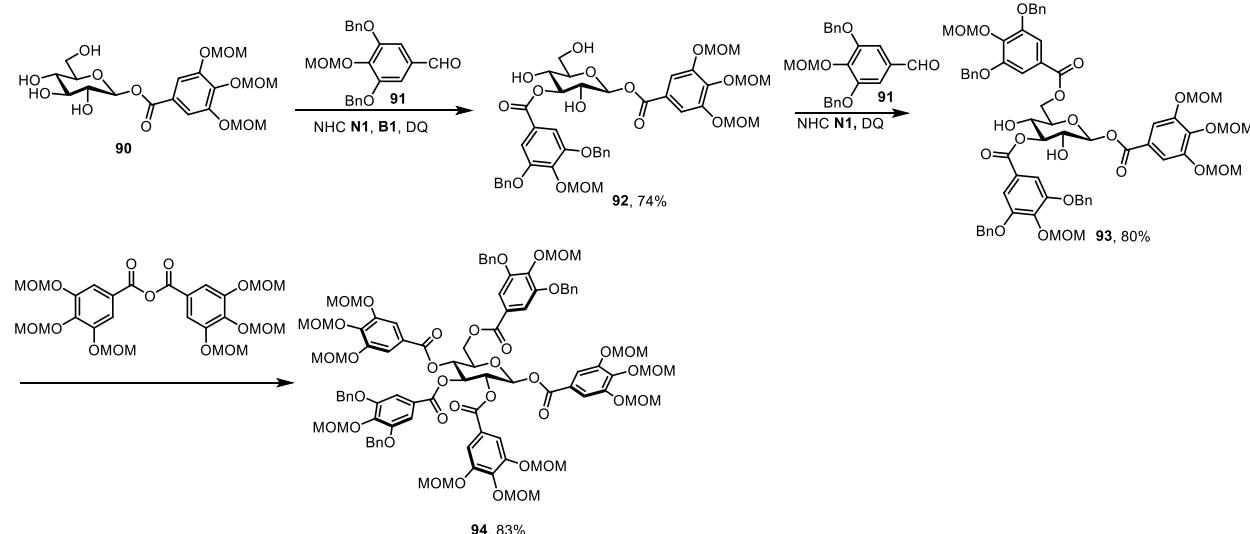
and dried with Na_2SO_4 . Concentration of the organic extract gave acetyl-2,4,6-tri-O-acetyl-3-O-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosyl)-D-glucopyranoside as a colourless oil and as a mixture of anomers (680 mg, 99%, $\alpha:\beta$, 7:1). NaOMe (0.1 mmol) in MeOH (1 mL) was added to acetyl-2,4,6-tri-O-acetyl-3-O-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosyl)-D-glucopyranoside (0.3 mmol) in MeOH (4 mL) at 0 °C and the solution was stirred at 25 °C for 4 h. Then the solution was directly purified by silica gel flash column chromatography with an appropriate solvent (EtOAc/MeOH 1:0 to 1:1 v/v) to afford laminaribiose **89** (103 mg, 99%) as a white solid.

2.12. Formal total synthesis of punicafolin and macaranganin, related to figure 8B.



MOMBr (7.15 mmol, 1.2 equiv) was added dropwise to a solution of 3,4,5-trihydroxybenzaldehyde (918 mg, 5.96 mmol, 1 equiv), TBAI (1.79 mmol, 0.3 equiv) and DIPEA (7.15 mmol, 1.2 equiv) in 60 mL dry THF at 0 °C. Then the reaction mixture was warmed to room temperature and stirred at room temperature for 12 h. The reaction was quenched by saturated NaHCO₃ aqueous solution, and extracted by EtOAc (60 mL × 3). The organic layers were combined, dried over Na₂SO₄ and concentrated. The crude mixture was purified by flash column chromatography on silica with an appropriate solvent to afford 3,5-dihydroxy-4-(methoxymethoxy)benzaldehyde (741 mg, 63%) as yellow solid.

To a solution of 3,5-dihydroxy-4-(methoxymethoxy)benzaldehyde (112 mg, 0.57 mmol, 1 equiv) in 6 mL dry MeCN was added K₂CO₃ (1.70 mmol, 3 equiv) and benzyl bromide (1.25 mmol, 2.2 equiv). Then the reaction mixture was stirred at 80 °C for 6 h. After cooling to the room temperature, the solution was filtered and concentrated. The crude mixture was purified by flash column chromatography on silica with an appropriate solvent to afford **91** (178 mg, 83%) as white solid.



90 and acid anhydride were prepared according to the reference⁵.

To a 4 mL screwtop test tube was added **90** (0.1 mmol, 1.0 equiv), aldehyde **91** (0.2 mmol, 2.0 equiv), NHC **N1** (10 mol %), boronic acid **B1** (0.1 mmol, 1.0 equiv), DQ (0.2 mmol, 2.0 equiv), and K_2CO_3 (0.02 mmol, 0.2 equiv). Then, acetonitrile (2 mL) was added to the mixture. The reaction was allowed to stir vigorously at room temperature for 24 h under an N_2 atmosphere. Then the reaction mixture was directly purified by flash column chromatography on silica with an appropriate solvent to afford **92** (62 mg, 74%; 84% brsm) as colorless gum.

To a 4 mL screwtop test tube was added **92** (45 mg, 0.054 mmol, 1.0 equiv), aldehyde **91** (0.108 mmol, 2.0 equiv), NHC **N1** (10 mol %), DQ (0.108 mmol, 2.0 equiv), and DBU (0.011 mmol, 0.2 equiv). Then, acetonitrile (1 mL) was added to the mixture. The reaction was allowed to stir vigorously at room

temperature for 24 h under an N₂ atmosphere. Then the reaction mixture was directly purified by flash column chromatography on silica with an appropriate solvent to afford **93** (52 mg, 80%) as colorless gum.

To a 4 mL screwtop test tube was added monosaccharide **93** (40 mg, 0.033 mmol, 1.0 equiv), acid anhydride (0.132 mmol, 2.0 equiv), DMAP (0.033 mmol, 1 equiv) and acetonitrile (0.8 mL). The reaction was allowed to stir vigorously at 50 °C for 24 h under an N₂ atmosphere. After cooling to the room temperature, the reaction mixture was directly purified by flash column chromatography on silica with an appropriate solvent to afford **94** (49 mg, 83%) as a colorless gum.

3. Density functional theory (DFT) calculations

3.1. Computational Methods

For conformational sampling of structures, Grimme's *crest* program,^{6,7} which used metadynamics (MTD) with genetic z-matrix crossing (GC) performed at the GFN2-xTB^{8–10} extended semiempirical tight-binding level of theory, was used. The resulting lowest energy structures were further optimized using global hybrid DFT functional M06-2X⁶ with Karlsruhe-family double- ζ valence def2-SVP^{12,13} basis set for all atoms as implemented in *Gaussian 16 rev. B.01*.¹⁴ Single point (SP) corrections were performed using M06-2X functional and def2-TZVP¹² basis set for all atoms. Minima and transition structures on the potential energy surface (PES) were confirmed as such by harmonic frequency analysis, showing respectively zero and one imaginary frequency. The implicit SMD continuum solvation model¹⁵ for acetonitrile solvent was used to account for the effect of solvent on the potential energy surface. Gibbs energies were evaluated at 50°C, which was used in the experiments, using a quasi-RRHO treatment of vibrational entropies.¹⁶ Vibrational entropies of frequencies below 100 cm⁻¹ were obtained according to a free rotor description, using a smooth damping function to interpolate between the two limiting descriptions.¹⁷ The free energies were further corrected using standard concentration of 1 mol/L for gas-phase-to-solvent correction. All molecular structures are visualized using *PyMOL* software.¹⁸

3.2. Model systems

To understand how the interactions between the NHC and the boronic acids employed effect the regioselective O-acylation, we chose the model reactions in figure S36 for our computational studies. (1) Comparing Reactions 1 and 2, we aim to see how a difference in the substituent group in the boronic acid affects the regioselective outcome. (2) Comparing Reactions 3 and 4, which employ the same reaction conditions, except the sugar used, we aim to understand how sugar stereochemistry affects regioselective outcome. (3) Finally, comparing Reactions 4 and 5, where enantiomeric NHCs are used on the same sugar, we aim to understand how NHC chirality affects regioselective outcome.

We considered the key step of the hydroxyl group attacking the carbonyl group of the acyl azonium as this step is regio-determining. The mechanistic study of the full catalytic cycle for the present reaction is underway in our laboratories.

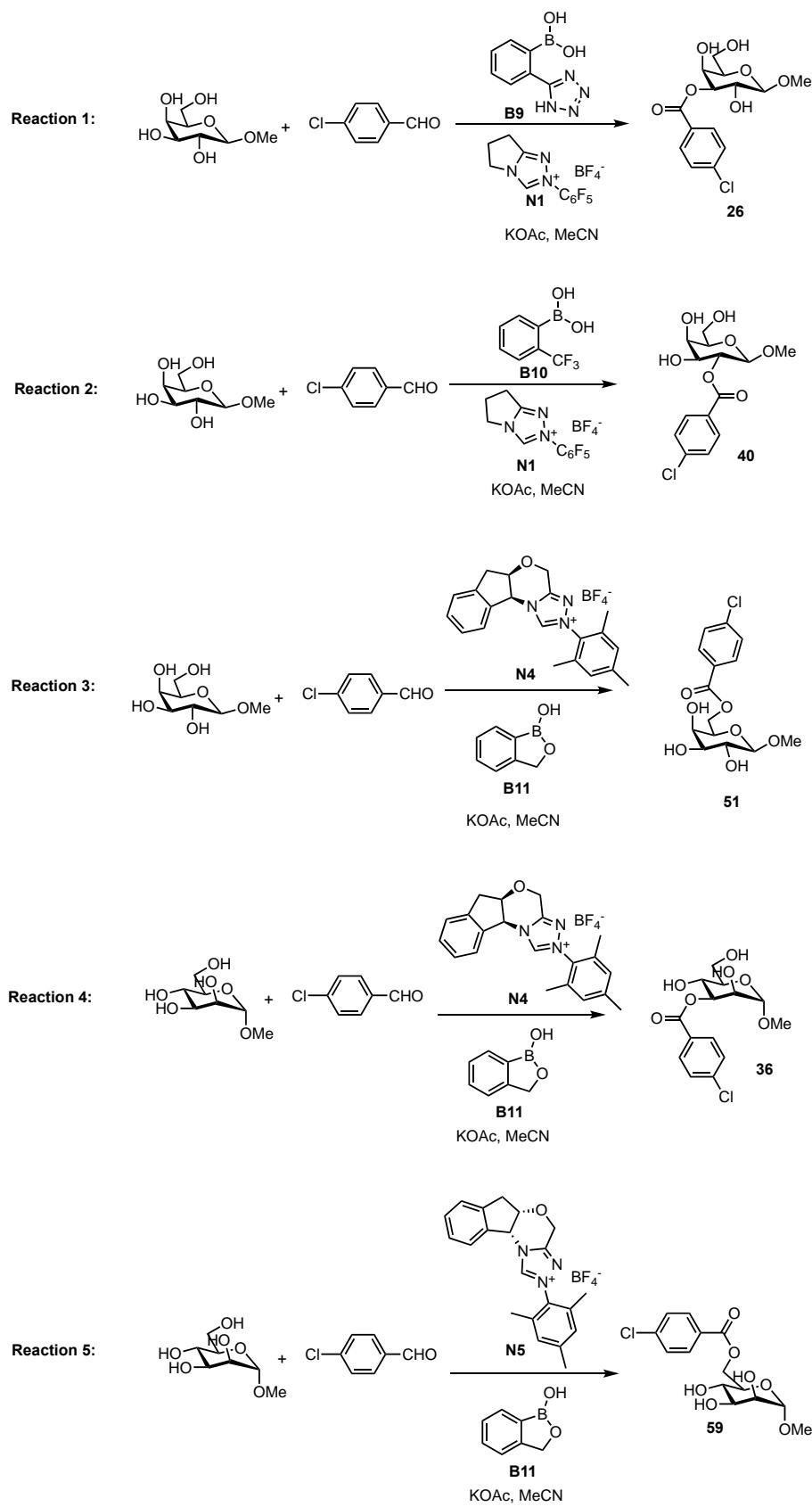


Figure S36. Model reactions for computational mechanistic studies.

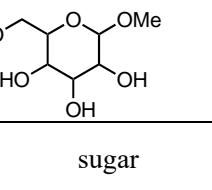
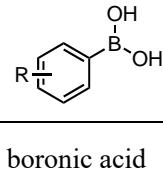
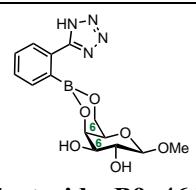
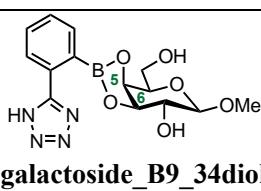
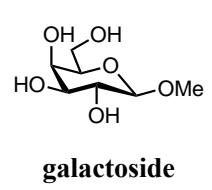
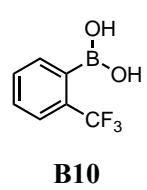
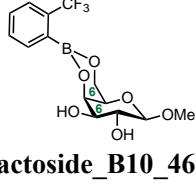
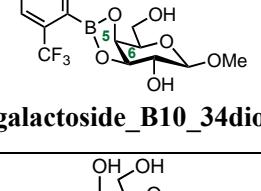
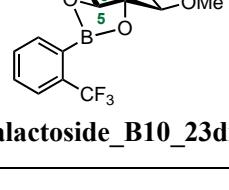
3.3. Thermodynamics for the formation of boronic ester from the condensation reaction between boronic acid and sugar

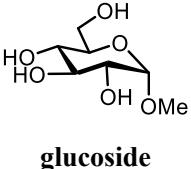
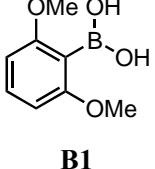
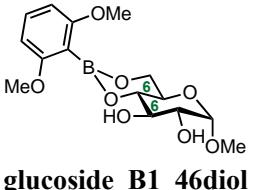
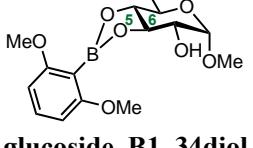
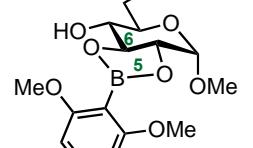
We computed the Gibbs energy of reaction for the condensation between boronic acid and monosaccharide. The results are shown in Table S5. A general feature of our type of reaction, from the three reactions considered (where different monosaccharides, glucoside and galactoside, were used), is that the formation of boronic ester between the boronic acid and 4,6-diol of the sugar is exergonic (thermodynamically downhill), while that with 3,4-diol or 2,3-diol of the sugar are endergonic (thermodynamically uphill). This suggests that the formation with 4,6-diol of the sugar is favorable whereas the formations with 3,4-diol or 2,3-diol of the sugar are unfavorable. This means that under our reaction conditions where boronic acids can form boronic esters with monosaccharides, the hydroxyl groups at C4 and C6 will be involved in boronic ester formation, leaving hydroxyl groups at C2 and C3 exposed for subsequent acylation. We note that the hydroxyl groups on C4 and C6 can be of either *cis*- (as in galactoside) or *trans*-relationship (as in glucoside), without affecting this observation, as the C6 methylene group is flexible enough to ensure the formation of [6,6]-bicyclic rings in both cases. In addition, this observation is valid for all 3 boronic acids tested (**B1**, **B9**, **B10**, Table S5) and is likely to be valid for other boronic acids as well.

The formation of [6,6]-bicyclic boronic ester is more stable than that of [5,6]-bicyclic boronic ester. From Table S5, we can see that for the reaction involving galactoside and boronic acid **B9**, the formation of boronic ester **galactoside_B9_46diol** is 2.9 kcal mol⁻¹ and 8.8 kcal mol⁻¹ more stable than boronic esters **galactoside_B9_34diol** and **galactoside_B9_23diol**, respectively. Similarly, for the reaction between galactoside and boronic acid **B10**, the formation of boronic ester **galactoside_B10_46diol** is 6.0 kcal mol⁻¹ and 13.1 kcal mol⁻¹ more stable than boronic esters **galactoside_B10_34diol** and **galactoside_B10_23diol**, respectively. For the reaction between glucoside and boronic ester **B1**, the formation of boronic ester **glucoside_B1_46diol** is 9.6 kcal mol⁻¹ and 9.7 kcal mol⁻¹ more stable than boronic esters **glucoside_B1_34diol** and **glucoside_B1_23diol**, respectively. The boronic ester formed with 4,6-diol of the sugar is expected to be the dominant species present and subsequently takes part in the reaction. This is consistent with the experimental verification of the involvement of boronic ester formed with 4,6-diol of the sugar (intermediates **I** and **III**) in the reaction between glucoside **1** with NHC **N1** and boronic acid **B1** (section 2.6.2 and Figure S23).

We conclude that for our reaction protocols, where boronic acids employed can form boronic ester with the monosaccharide, the most stable adduct that reacts further in the reaction will be the boronic acid–4,6-diol adduct, leaving only exposed OH groups at C2 and C3 for selective acylation.

Table S5. Computed Gibbs energy of reaction for the condensation between monosaccharides and the boronic acids.

sugar	boronic acid	boronic ester, X	ΔG_r / kcal mol ⁻¹
 galactoside	 B9	 galactoside_B9_46diol	-1.0
		 galactoside_B9_34diol	1.9
		 galactoside_B9_23diol	7.8
 galactoside	 B10	 galactoside_B10_46diol	-5.0
		 galactoside_B10_34diol	1.0
		 galactoside_B10_23diol	8.1

sugar	boronic acid	boronic ester, X	$\Delta G_r / \text{kcal mol}^{-1}$
 glucoside	 B1	 glucoside_B1_46diol	-5.1
		 glucoside_B1_34diol	4.5
		 glucoside_B1_23diol	4.6

3.4. Conformational analyses

To study the key regio-determining step of C–O bond formation between sugar hydroxyl group and the carbonyl C of acyl azolium intermediate, we need to consider the conformations of these transition states (TS). As such TS structures could not be located at the *xtb* level, we consider the conformations of the key intermediates as a proxy to the conformations in the regio-determining TSs as we expect the side group interactions to be similar in the intermediate and the TSs. In other words, favorable interactions such as π – π interactions and hydrogen bonding interactions in the intermediates are expected to be also present in the TSs.

Figure S37 shows the examples of the intermediates arising from the attack of the acyl azolium carbonyl group by the hydroxyl groups from the boronic ester (sugar). Two possibilities can occur, namely that a particular OH group can attack the carbonyl group from either the (*Si*)-face or the (*Re*)-face, giving rise to different stereoisomers with differing interactions among the side groups. Note that, although the interactions in these intermediates, and their corresponding TSs, are different, the subsequent loss of NHC as the oxyanion reforms the carbonyl group generates the same acylated sugar product in each case.

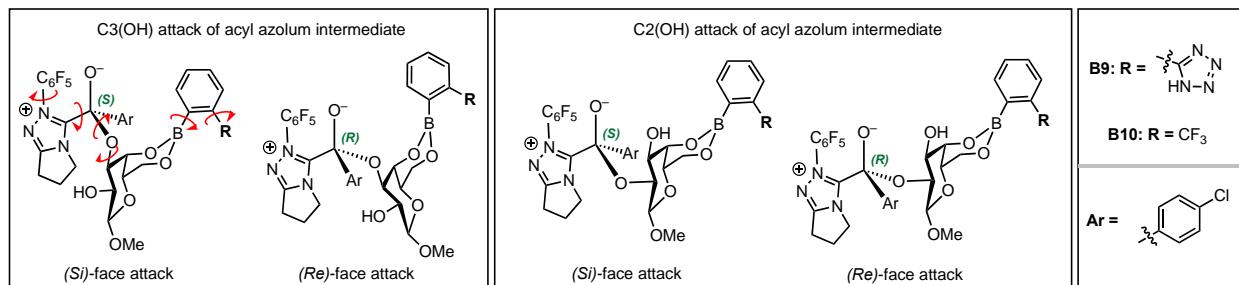


Figure S37. Example intermediate structures for conformational sampling. Example rotational degrees of freedom about single bonds are shown in red arrows.

Conformational sampling of the acyl azolium-sugar intermediate was performed using the *crest* program, as outlined in the methods section. An implicit solvation of acetonitrile using the generalized Born (GB) model with surface area (SA) contribution (GBSA) was included in the conformational sampling. The lowest energy conformer from this procedure was further optimized at DFT SMD(acetonitrile)-M06-2X/def2-TZVP//M06-2X/def2-SVP level of theory.

Figure S38 shows the DFT optimized structures. In **Reaction 1**, the NH group of the tetrazole ring of the boronic acid can form hydrogen bonding interaction with the oxyanion oxygen atom in formation of O(C3)–C(carbonyl) from either the (*Re*)- (**INT_gal_N1_B9_O3_Re**) or the (*Si*)-face attack (**INT_gal_N1_B9_O3_Si**). We can imagine that the formation of this hydrogen bonding strategically places the C(3)-OH group close to the carbonyl C=O group for productive C–O bond formation in the transition state, as illustrated in figure S39. For the formation of O(C2)–C(carbonyl) bond however, no such hydrogen bonding is possible due to the geometric restraints. In **INT_gal_N1_B9_O2_Si**, instead, a hydrogen bonding between the NH group of the tetrazole ring of the boronic acid and the anomeric oxygen atom is formed. This is in addition to the hydrogen bonding between C(3)-OH and the oxyanion oxygen atom. In **INT_gal_N1_B9_O2_Re**, however, no such interactions are possible, and only weak CH...O interaction is possible, thus explaining its much higher energy. In addition, the intermediates at C(3)-OH functionalization have π – π interactions that are absent in the C(2)-OH functionalization. These could be the origins for favoring C(3)-OH functionalized galactoside using the combination of NHC **N1** and boronic acid **B9**.

In **Reaction 2**, the most stable intermediate, **INT_gal_N1_B10_O2_Si**, benefits from various favorable interactions such as H bonding, CH...F and CF... π interactions. The H bond in this intermediate is stronger than the H bond in **INT_gal_N1_B10_O3_Re** ($\Delta\Delta G = 2.4 \text{ kcal mol}^{-1}$) as the former has a shortest distance of 1.50 Å than the latter of 1.68 Å (Figure S38). On the other hand, only weak interactions are present in **INT_gal_N1_B10_O2_Re** and **INT_gal_N1_B10_O3_Si** (CH...O and CF... π interactions), and there is no H bonding present, thus giving much higher relative energies (by 8.0 and 12.2 kcal mol⁻¹) than the most stable intermediate, **INT_gal_N1_B10_O2_Si**. Thus C(2)-OH functionalization of galactoside using the combination of NHC **N1** and boronic acid **B10** will be favored.

Comparing **Reactions 1** and **2**, we see that in **Reaction 2**, by changing the tetrazole ring of the boronic acid in **Reaction 1** to trifluoromethyl group in **Reaction 2**, no H-bonding from the boronic acid moiety via the NH group of the tetrazole ring is possible in **Reaction 2**, thus, no directed “delivery” of C(3)-OH bond to the carbonyl group for addition is possible.

In **Reactions 3**, **4** and **5**, the monosaccharides are not protected by forming 4,6-boronato-monosaccharides as the boronic acids do not have two OH groups. Therefore, we consider the possibility of functionalization at all OH groups on the sugar substrate. For each intermediate, our independent *crest* conformer search converges to the lowest energy structures with same backbone orientations demonstrating similar interactions. For example, the interactions between the NHC moiety and the aryl ring of the acyl group in **INT_gal_N4_B11_Ox_Si** ($x=2, 3, 4, 6$) are all the same; similar observation can be made in **INT_gal_N4_B11_Ox_Re** ($x=2, 3, 4, 6$). This demonstrates that within each reaction, the acyl azonium intermediate forms specific interactions, priming the carbonyl group for the regioselective addition of a particular OH group of the monosaccharide over other OH groups depending on the monosaccharide chirality and the specific interactions that the monosaccharide can form with the acyl azonium intermediate.

Looking at all the lowest energy intermediates from either the (*Re*)- or (*Si*)-face attack of the carbonyl group of the acyl azonium intermediate by various OH groups, we can see that all these structures form favorable $\pi\cdots\pi$ interactions between the aryl ring of the acyl group and the mesityl group on the NHC. For **Reaction 3**, the (*Re*)-face attacks give more stable intermediates than the corresponding (*Si*)-face attack at each C(OH) functionalization whereas for **Reactions 4** and **5**, due to the different stereochemical orientation of the sugar and the chiral NHC, the (*Si*)-face attacks give more stable intermediates than the corresponding (*Re*)-face attack.

In **Reaction 3**, comparing the intermediates of different O-site functionalization (**INT_gal_N1_B10_Ox_Re** where $x=2, 3, 4, 6$), we see that **INT_gal_N4_B11_O6_Re** is the most stable, as this structure benefits from additional CH...O(anomeric) and CH... π interactions that are not present in the other 3 intermediates (**INT_gal_N1_B10_Ox_Re** where $x=2, 3, 4$). In addition, although H-bonding between one of the OH groups on the monosaccharide and the oxyanion oxygen atom is formed in all cases, the H-bonding is the strongest in **INT_gal_N4_B11_O6_Re** as evidenced by its much shorter H-bond length of (1.49 \AA) as compared to others (1.52 \AA in **INT_gal_N4_B11_O2_Re**, 1.57 \AA in **INT_gal_N4_B11_O4_Re**, and 1.65 \AA in **INT_gal_N4_B11_O3_Re**). This suggests that the TS for the regio-determining C-O(C(6)-OH) bond formation will likely benefit from similar interactions and give the lowest energy barriers, thus suggesting that C(6)-OH acylation is the most likely.

In **Reaction 4**, as compared to **Reaction 3**, now the mannose used has different stereochemistry than the galactoside at C(2)-OH and C(4)-OH. Now, the most stable intermediates, and by extension the corresponding TSs leading to their formation, result from the (*Si*)-face attacks rather than the (*Re*)-face attacks in **Reaction 3**. The intermediate formed at C(3)-OH, **INT_man_N4_B11_O3_Si**, is the most stable, as it has two H-bonds and additional CH...O interaction and it has the strongest H-bond between the OH of mannoside and oxyanion oxygen atom (bond distance of 1.52 \AA , Figure S38).

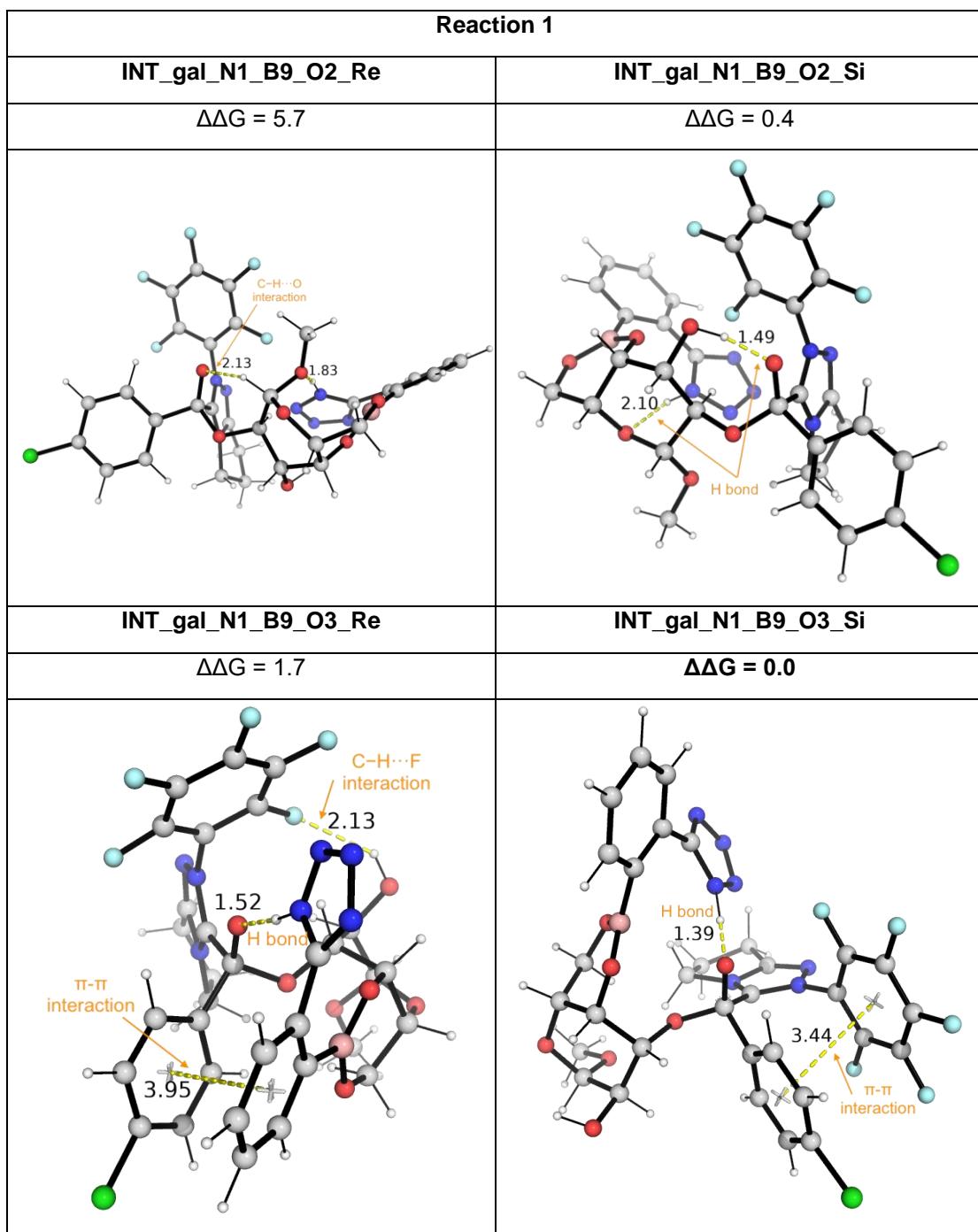
In **Reaction 5**, both the mannoside and the NHC have different stereochemistry from the galactoside and NHC used in **Reaction 3**. The most stable intermediates result from the (*Re*)-face attacks in **Reaction 3**, but from the (*Si*)-face attacks in **Reaction 5**. The double inversion of the stereochemistry in both the sugar and the NHC could explain why both **Reactions 3** and **5** favor the same OH-functionalization (both at C(6)-OH). For example, comparing **INT_gal_N4_B11_O6_Re** and **INT_man_N5_B11_O6_Si**, the most stable intermediate in **Reactions 3** and **Reactions 5**, respectively (Figure S38), the dihydroindene group of the NHC in both cases have similar orientation (point “downwards”) as the sugar hydroxyl groups form various interactions. These two structures are almost mirror images, except where the stereochemistry of the sugar substrate differs. Both structures have the most favorable interactions than intermediates from other O-site functionalization within each of **Reactions 3** and **5**. The intermediate formed at C(3)-OH, **INT_man_N4_B11_O3_Si**, is the most stable, as it has two H-bonds and additional CH...O interaction and it has the strongest H-bond between the OH of mannoside and oxyanion oxygen atom (bond distance of 1.52 \AA , Figure S38).

When comparing **Reaction 5** to **Reaction 4**, both the intermediates resulting from the (*Si*)-face attack of the acyl azonium have lower energy than the corresponding intermediates from the (*Re*)-face attack. Comparing the intermediates from the (*Si*)-face attack in **Reactions 4** and **5** (Figure S38), we see that only the orientation of the dihydroindene group of the NHCs differs across these two reactions (e.g., **INT_man_N4_B11_Ox_Si** vs **INT_man_N5_B11_Ox_Si**, where $x=2, 3, 4$). This is consistent with our expectation, as the NHCs used are enantiomers (**N4** vs **N5**). This difference in the NHC side group

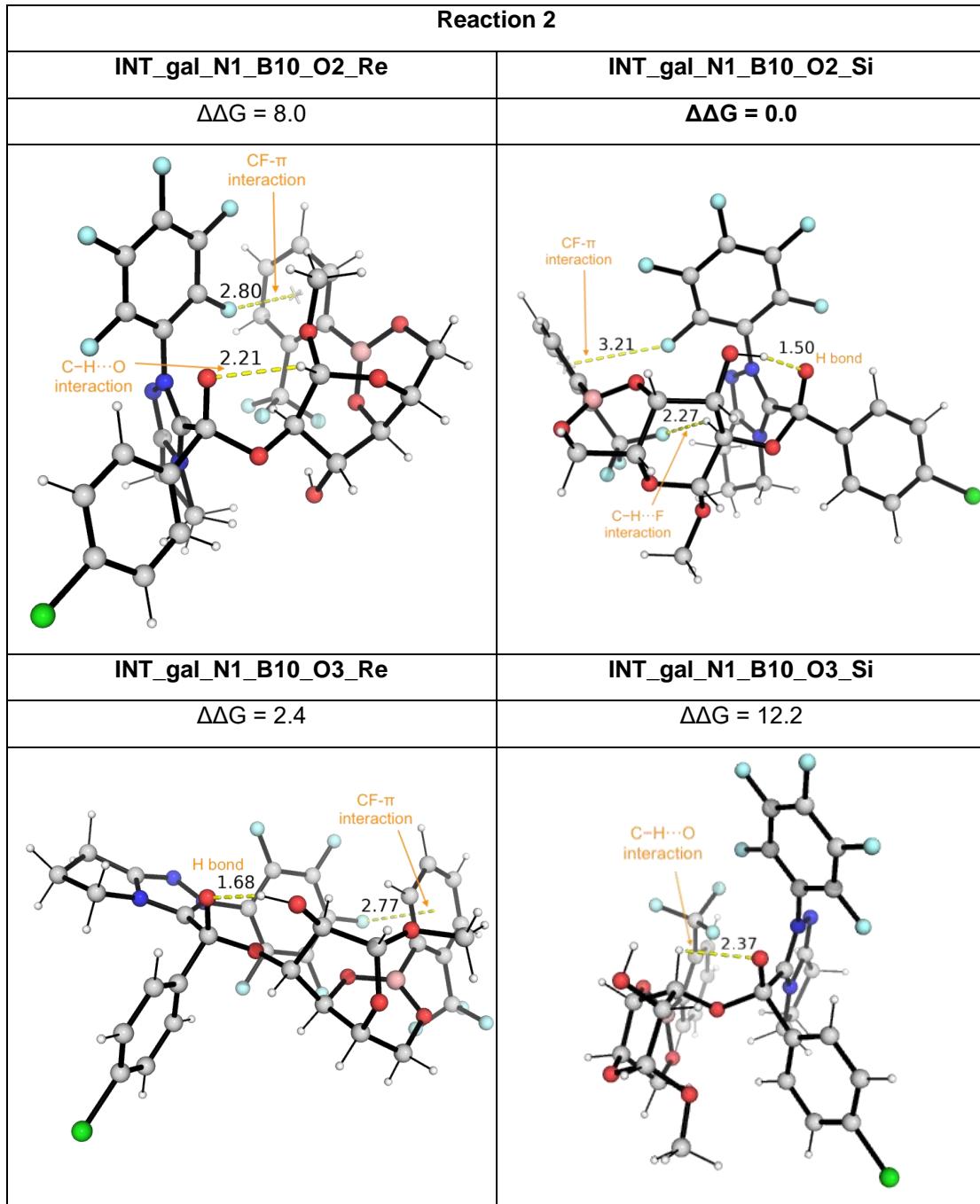
orientation favors different O-functionalization (C(6)-OH in **Reaction 5** vs C(3)-OH in **Reaction 4** due to the resultant differing electronic and steric interactions present.

Within **Reaction 5**, the most stable intermediate is **INT_man_N5_B11_O6_Si**, at C(6)-OH functionalization. This intermediate forms three H-bonds whereas the other intermediates only have two H-bonds.

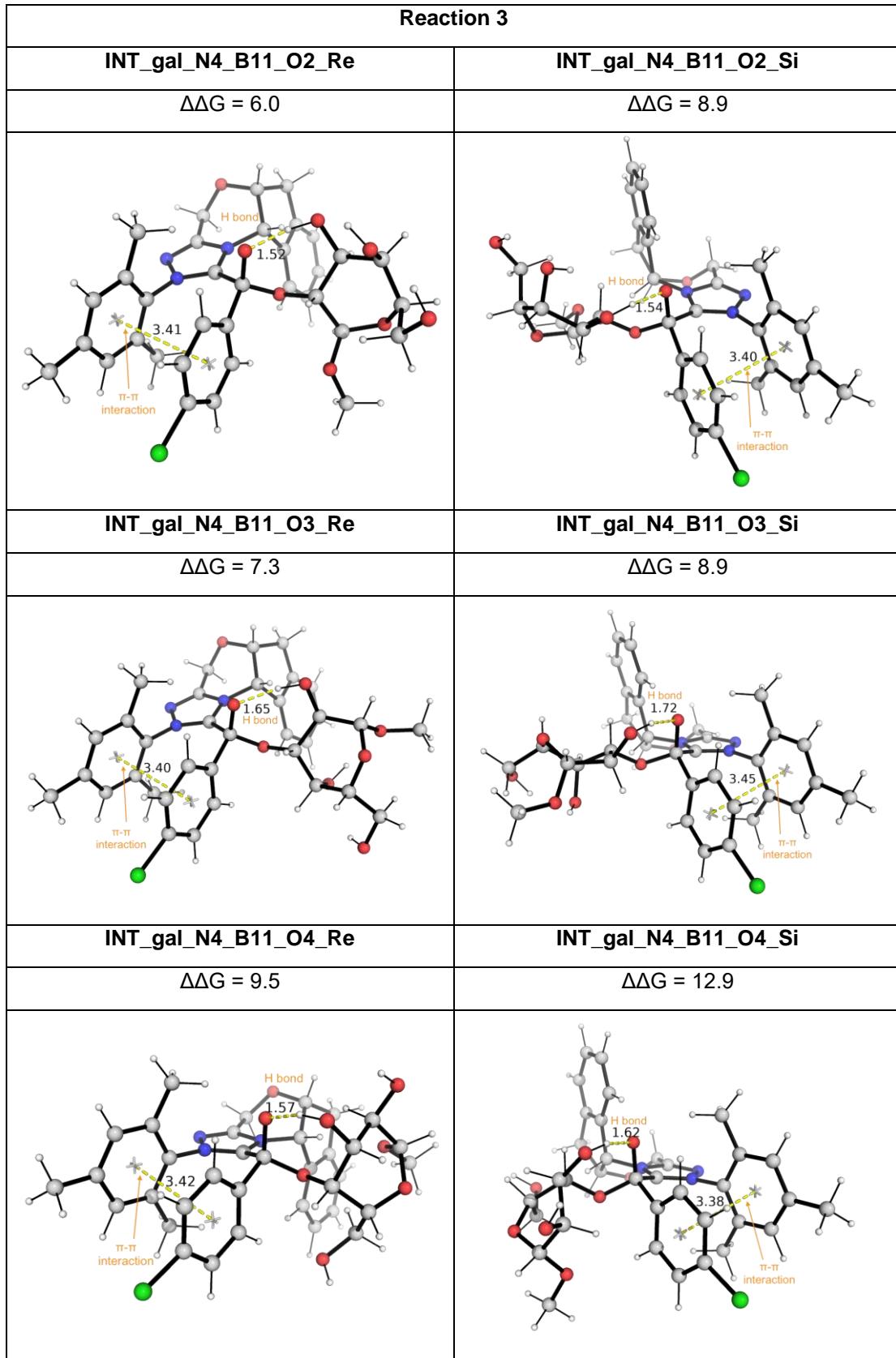
In summary, the regioselective outcome of sugar O-functionalization results from a combination of sterics (due to side groups of the NHCs/boronic acids used) and electronic interactions between the sugar OH/CH groups and the NHC side chains. The acyl azolium intermediate is stereogenic as the carbonyl carbon can be attacked by sugar hydroxyl group from either the (*Re*)- or (*Si*)-face. This provides opportunities for unique interactions as different OH groups attack into the carbonyl carbon of acyl azolium, thus giving unique regioselective outcomes.

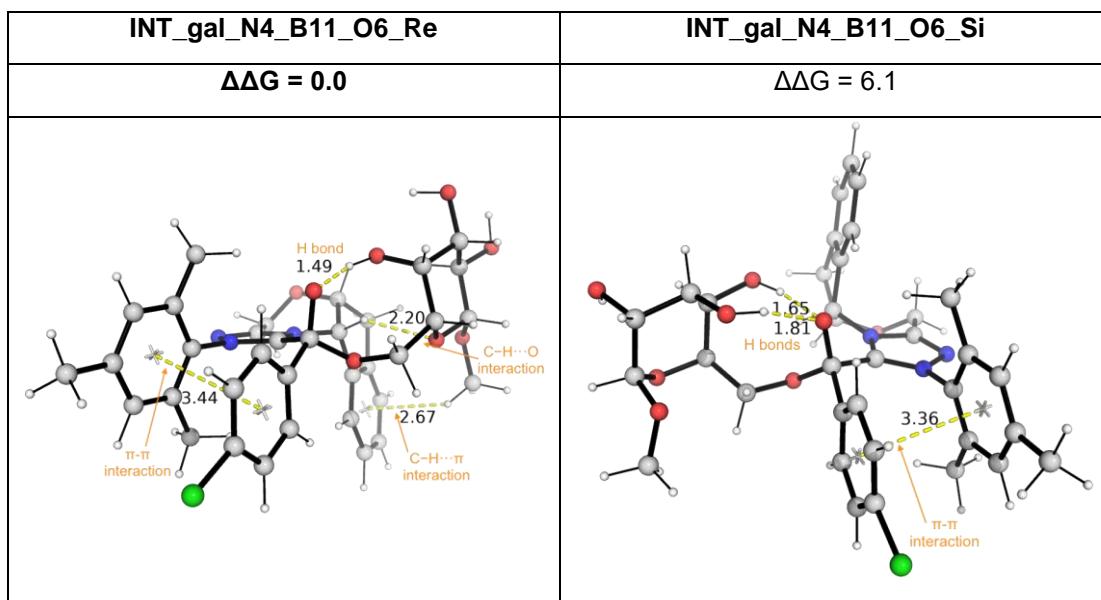


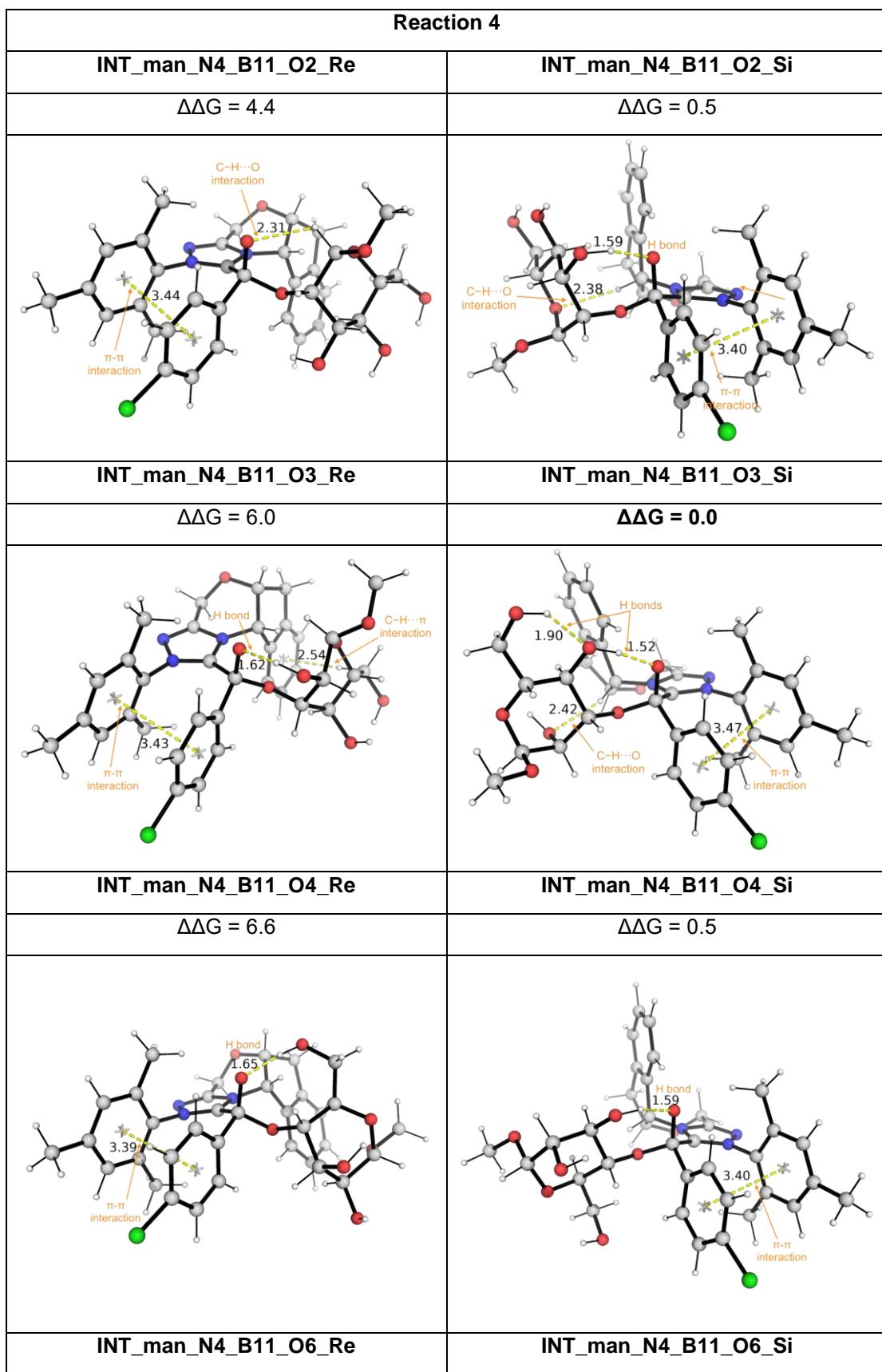
Reaction 2

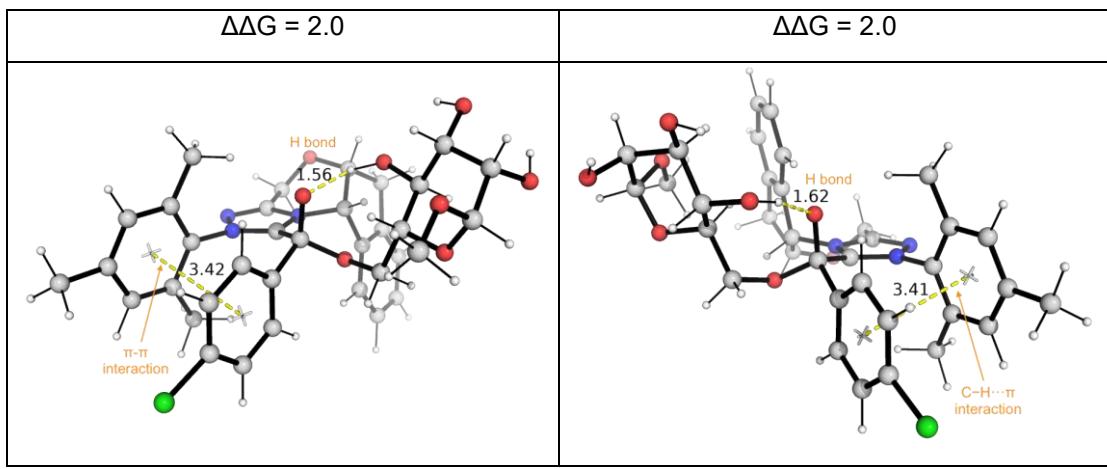


Reaction 3









Reaction 5

INT_man_N5_B11_O2_Re	INT_man_N5_B11_O2_Si
$\Delta\Delta G = 5.5$	$\Delta\Delta G = 1.3$
INT_man_N5_B11_O3_Re	INT_man_N5_B11_O3_Si
$\Delta\Delta G = 7.5$	$\Delta\Delta G = 1.2$
INT_man_N5_B11_O4_Re	INT_man_N5_B11_O4_Si
$\Delta\Delta G = 6.7$	$\Delta\Delta G = 1.8$

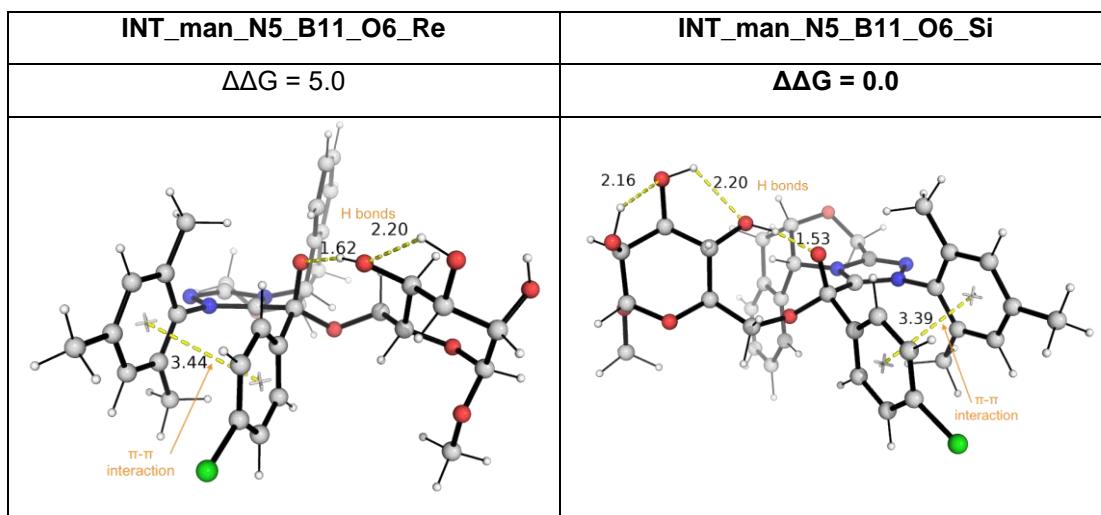


Figure S38. DFT optimized structures of the lowest energy conformers resulting from each of the reactions in figure S36. Relative Gibbs energy is taken with respect to the lowest energy conformer within each reaction.

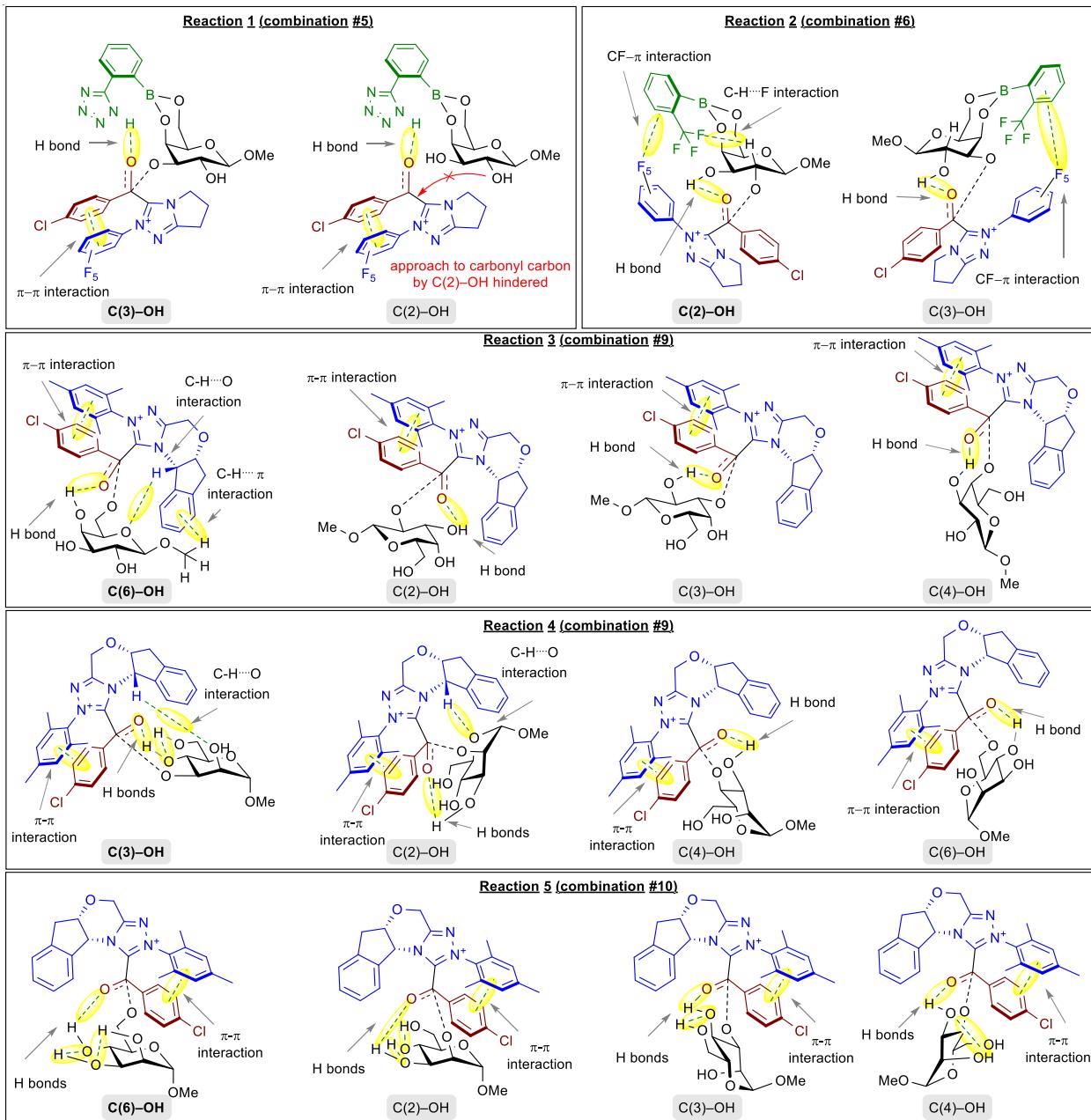
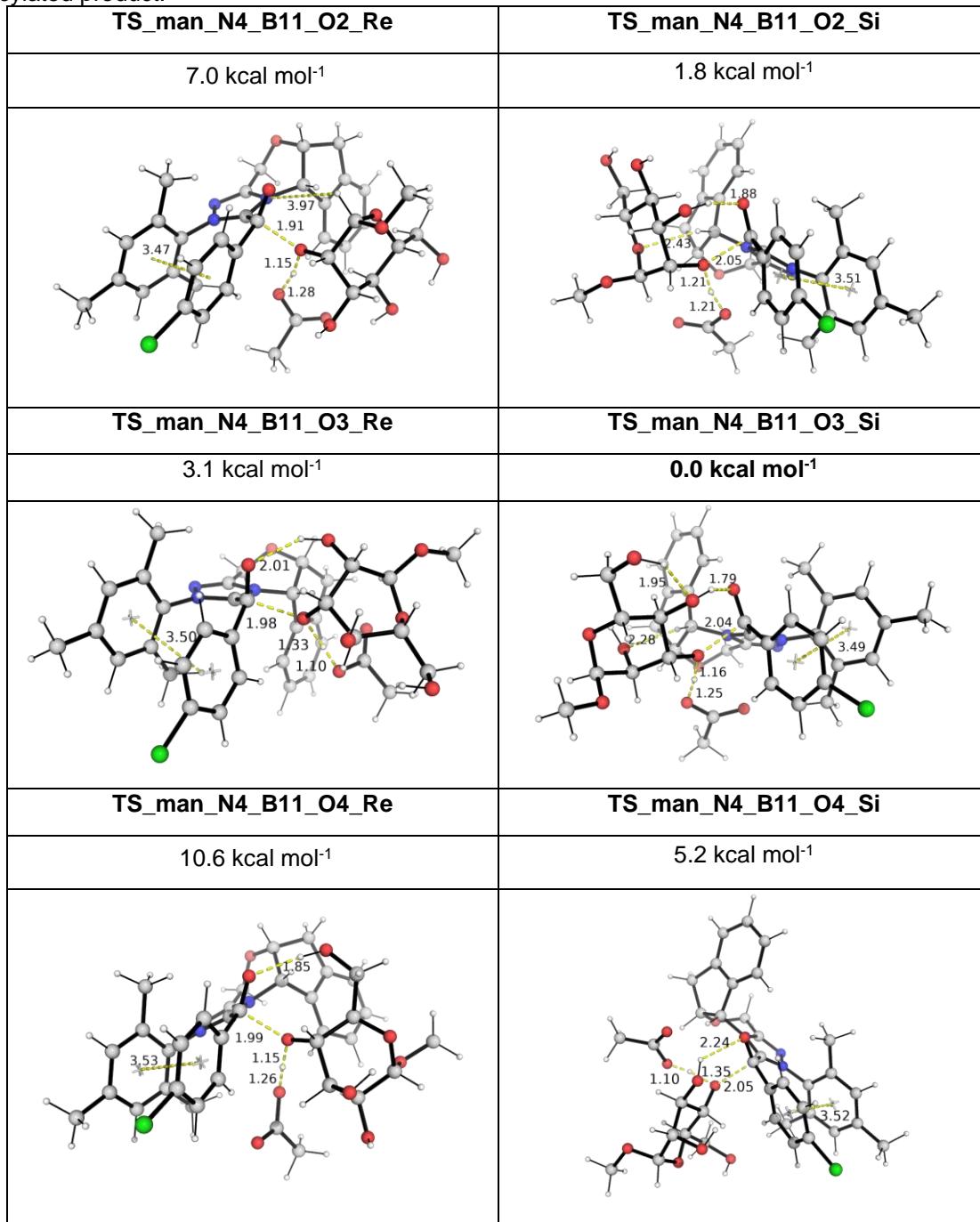


Figure S39. Schematic representations of the possible interactions that will occur in the regioselective intermediates and similarly transition states. The major C–OH acylation is in bold for each reaction.

3.5. Regio-determining TSs – case study using Reaction 4

To verify that our usage of intermediates as a proxy to the interactions in the corresponding TSs is appropriate, we analyzed the TSs for the regio-determining step in **Reaction 4** (figure S36). The optimized DFT TS structures are given in figure S40. Comparing the TSs with their corresponding intermediates in figure S38, we can see that the same interactions present in the intermediates are also present in the TSs, thus suggesting that the stabilizing interactions giving stable intermediates also possibly stabilize the transition states.

The following TS barriers for **Reaction 4** indicates that C(3)-OH acylation has the lowest activation barrier and is predicted to be kinetically most favorable, consistent with the experimentally observed C(3)-OH acylated product.



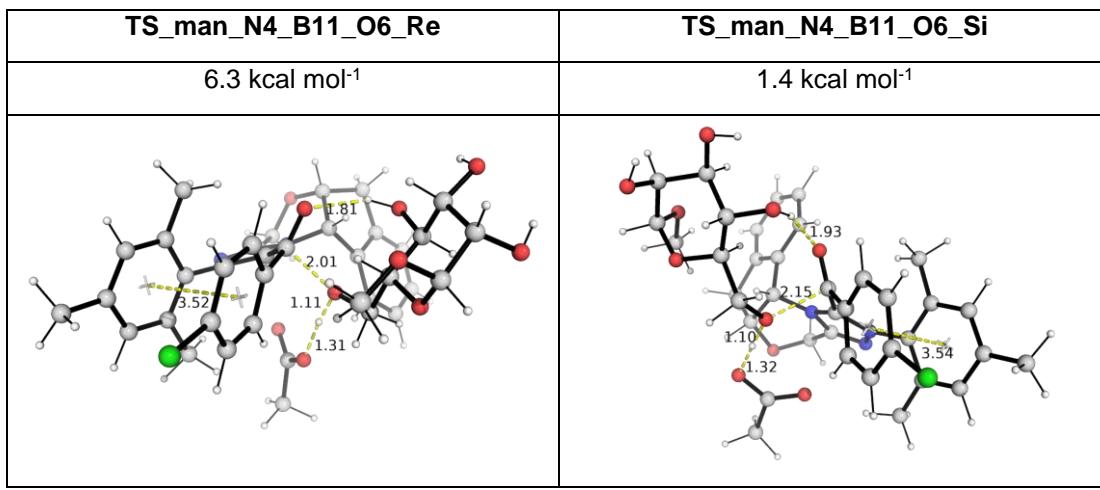


Figure S40. Optimized TS structures for the regio-determining transition states for the formation of C–O bond in the intermediate in **Reaction 4**. Key bond distances are given in Å. Relative activation barriers are given in kcal mol⁻¹ and taken relative to the lowest activation barrier.

3.6. Table S6. Optimized structures and absolute energies, zero-point energies

Geometries of all optimized structures (in .xyz format with their associated energy in Hartrees) are included in a separate folder named *final_xyz_structures*. All these data have been uploaded to zenodo.org (DOI: 10.5281/zenodo.6327868).

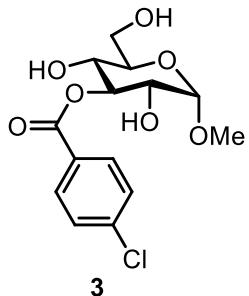
Absolute values (in Hartrees) for SCF energy, zero-point vibrational energy (ZPE), enthalpy and quasi-harmonic Gibbs free energy (at 323.15K) for M06-2X/def2-SVP optimized structures are given below. Single point corrections in SMD(acetonitrile) using M06-2X/def2-TZVP functional are also included.

Structure	E/au	ZPE/au	H/au	T.S/au	qh-G/au	SP M06-2X/def2TZVP
aldehyde_2a	-804.614711	0.101454	-804.5037	0.042369	-804.545817	-805.1709337
boronic_acid_B1	-636.582931	0.192172	-636.37469	0.057562	-636.430201	-637.3348694
H2O	-76.323214	0.021594	-76.297521	0.020204	-76.317725	-76.43444235
NHC_N1	-1084.927573	0.165762	-1084.7433	0.063464	-1084.804623	-1086.209713
AA_N1_c3	-1888.769838	0.260864	-1888.4813	0.085925	-1888.561962	-1890.656312
AA_N1_c2	-1888.775772	0.260836	-1888.4873	0.084881	-1888.567396	-1890.656851
AA_N1	-1888.775793	0.260793	-1888.4874	0.084921	-1888.567482	-1890.65731
glucoside_1	-725.643582	0.228916	-725.39783	0.057656	-725.454409	-726.5196905
glucoside_B1_23diol	-1209.552171	0.371438	-1209.1532	0.084759	-1209.232985	-1210.966597
glucoside_B1_34diol	-1209.54895	0.370831	-1209.1503	0.085577	-1209.230795	-1210.965661
glucoside_B1_46diol	-1209.568717	0.371562	-1209.1697	0.084526	-1209.249196	-1210.982336
galactoside	-725.652674	0.229552	-725.40666	0.056875	-725.462639	-726.5227902
B9	-664.583683	0.154897	-664.41454	0.053859	-664.466841	-665.3702877
galactoside_B9_23diol	-1237.543626	0.333305	-1237.1843	0.081445	-1237.261347	-1238.998131
galactoside_B9_34diol	-1237.548714	0.332787	-1237.1896	0.082703	-1237.267408	-1239.006574
galactoside_B9_46diol	-1237.569034	0.33439	-1237.2093	0.078775	-1237.284232	-1239.014657
B10	-744.489932	0.13184	-744.34411	0.052736	-744.395522	-745.3714579
galactoside_B10_23diol	-1317.449561	0.310053	-1317.1136	0.080815	-1317.19033	-1318.998229
galactoside_B10_34diol	-1317.463306	0.310522	-1317.127	0.081408	-1317.20371	-1319.009917
galactoside_B10_46diol	-1317.475216	0.310907	-1317.139	0.079975	-1317.214353	-1319.020695
mannoside	-725.64122	0.228852	-725.39554	0.057456	-725.452092	-726.517678

INT_gal_N1_B10_O2_Re	-3205.89074	0.56323	-3205.2762	0.133772	-3205.400908	-3209.21994
INT_gal_N1_B10_O2_Si	-3205.893766	0.561634	-3205.2807	0.13518	-3205.4059	-3209.230654
INT_gal_N1_B10_O3_Re	-3205.890674	0.562229	-3205.2767	0.137606	-3205.403266	-3209.22644
INT_gal_N1_B10_O3_Si	-3205.879828	0.563202	-3205.2649	0.135125	-3205.390642	-3209.212477
INT_gal_N1_B9_O2_Re	-3125.996992	0.586357	-3125.3589	0.136407	-3125.485177	-3129.224536
INT_gal_N1_B9_O2_Si	-3126.004327	0.585693	-3125.3673	0.135464	-3125.49276	-3129.232675
INT_gal_N1_B9_O3_Re	-3125.992594	0.585915	-3125.3551	0.13613	-3125.480944	-3129.230787
INT_gal_N1_B9_O3_Si	-3126.001052	0.584743	-3125.3649	0.134511	-3125.490114	-3129.232745
INT_gal_N4_B11_O2_Re	-2580.250711	0.698388	-2579.5032	0.130524	-2579.623753	-2582.824691
INT_gal_N4_B11_O2_Si	-2580.24786	0.698512	-2579.5002	0.131113	-2579.621057	-2582.820042
INT_gal_N4_B11_O3_Re	-2580.249975	0.699057	-2579.5019	0.129462	-2579.622199	-2582.823436
INT_gal_N4_B11_O3_Si	-2580.244493	0.699531	-2579.4959	0.130745	-2579.616763	-2582.820846
INT_gal_N4_B11_O4_Re	-2580.246036	0.698219	-2579.4986	0.128967	-2579.618901	-2582.819359
INT_gal_N4_B11_O4_Si	-2580.239243	0.697611	-2579.492	0.130624	-2579.613261	-2582.812778
INT_gal_N4_B11_O6_Re	-2580.266552	0.698464	-2579.5196	0.126204	-2579.638061	-2582.835848
INT_gal_N4_B11_O6_Si	-2580.251766	0.699229	-2579.5037	0.128197	-2579.623172	-2582.826279
INT_man_N4_B11_O2_Re	-2580.245541	0.697508	-2579.498	0.132607	-2579.620421	-2582.823866
INT_man_N4_B11_O3_Re	-2580.24213	0.697429	-2579.495	0.130691	-2579.616371	-2582.822096
INT_man_N4_B11_O4_Re	-2580.248702	0.698415	-2579.501	0.130245	-2579.621721	-2582.822366
INT_man_N4_B11_O6_Re	-2580.256535	0.698533	-2579.5089	0.130708	-2579.629701	-2582.829512
INT_man_N4_B11_O2_Si	-2580.259454	0.698493	-2579.5118	0.129824	-2579.632256	-2582.832234

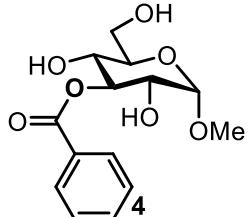
INT_man_N4						
_B11_O3_Si	-2580.258888	0.698013	-2579.5116	0.130913	-2579.632655	-2582.832067
INT_man_N4						
_B11_O4_Si	-2580.255714	0.698096	-2579.5082	0.132583	-2579.630093	-2582.83073
INT_man_N4						
_B11_O6_Si	-2580.255623	0.698992	-2579.5079	0.127901	-2579.62715	-2582.831125
INT_man_N5						
_B11_O2_Re	-2580.24795	0.698137	-2579.5004	0.130962	-2579.621589	-2582.825599
INT_man_N5						
_B11_O3_Re	-2580.244282	0.697631	-2579.4971	0.130823	-2579.61835	-2582.822082
INT_man_N5						
_B11_O4_Re	-2580.253342	0.698956	-2579.5055	0.128142	-2579.625152	-2582.825638
INT_man_N5						
_B11_O6_Re	-2580.249624	0.698248	-2579.5021	0.131858	-2579.623538	-2582.826188
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_B11_O2_Si	-2580.25843	0.698057	-2579.511	0.130152	-2579.631821	-2582.83253
INT_man_N5						
_B11_O3_Si	-2580.25833	0.69756	-2579.5114	0.130902	-2579.632522	-2582.831964
INT_man_N5						
_B11_O4_Si	-2580.256943	0.698314	-2579.5095	0.129624	-2579.629921	-2582.832262
INT_man_N5						
_B11_O6_Si	-2580.260399	0.698206	-2579.513	0.130915	-2579.63397	-2582.834486
TS_man_N4						
_B11_O2_Re	-2809.076249	0.758052	-2808.2625	0.14227	-2808.395197	-2811.915257
TS_man_N4						
_B11_O3_Re	-2809.080915	0.757859	-2808.2673	0.143717	-2808.400763	-2811.920635
TS_man_N4						
_B11_O4_Re	-2809.07105	0.75845	-2808.2571	0.142367	-2808.38959	-2811.909957
TS_man_N4						
_B11_O6_Re	-2809.076314	0.759873	-2808.261	0.144518	-2808.394092	-2811.917624
TS_man_N4						
_B11_O2_Si	-2809.083887	0.758013	-2808.2701	0.143355	-2808.403344	-2811.923044
TS_man_N4						
_B11_O3_Si	-2809.085262	0.758016	-2808.2714	0.145222	-2808.405577	-2811.925105
TS_man_N4						
_B11_O4_Si	-2809.07664	0.759658	-2808.2612	0.145359	-2808.395015	-2811.918819
TS_man_N4						
_B11_O6_Si	-2809.082656	0.759436	-2808.2678	0.143292	-2808.400629	-2811.925177

4. Characterizations of compounds (3 to 96)



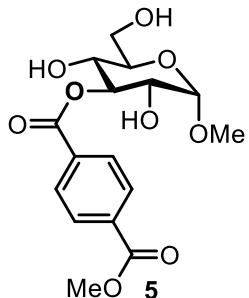
Methyl-3-O-(4-chlorobenzoyl)- α -D-glucopyranoside (3)

Following the general procedure A, the product **3** (26.5 mg, 80%) was obtained as white solid. Following the general procedure B, the product **3** (23.6 mg, 71%) was obtained. Following the general procedure C, the product **3** (23.2 mg, 70%) was obtained. **$^1\text{H NMR}$ (400 MHz, Chloroform-*d*)** δ 8.04 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 5.34 (t, J = 9.4 Hz, 1H), 4.88 (d, J = 3.8 Hz, 1H), 3.99 – 3.88 (m, 2H), 3.84 (t, J = 9.4 Hz, 1H), 3.78 (dq, J = 10.1, 3.7 Hz, 2H), 3.52 (s, 3H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*)** δ 167.16, 140.01, 131.34, 128.83, 128.00, 99.45, 77.81, 71.45, 70.94, 69.26, 62.10, 55.56. **ESI-MS:** calcd for $\text{C}_{14}\text{H}_{17}\text{O}_7\text{ClNa}$ [M + Na] $^+$: 355.0561, found: 355.0556.



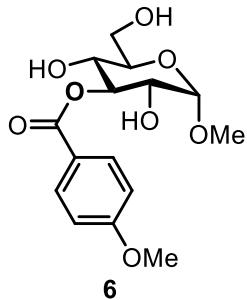
Methyl-3-O-benzoyl- α -D-glucopyranoside (4)

The product **4** (18.5 mg, 62%) was obtained as white solid. **$^1\text{H NMR}$ (500 MHz, Chloroform-*d*)** δ 8.09 (dd, J = 8.3, 1.4 Hz, 2H), 7.68 – 7.55 (m, 1H), 7.46 (t, J = 7.7 Hz, 2H), 5.34 (t, J = 9.4 Hz, 1H), 4.85 (d, J = 3.8 Hz, 1H), 3.95 – 3.85 (m, 2H), 3.85 – 3.72 (m, 3H), 3.49 (s, 3H), 3.16 (s, 1H), 2.42 (d, J = 10.5 Hz, 1H), 2.25 (s, 1H). **$^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*)** δ 168.10, 133.48, 129.96, 129.51, 128.45, 99.46, 77.59, 71.45, 70.95, 69.31, 62.10, 55.50. **ESI-MS:** calcd for $\text{C}_{14}\text{H}_{18}\text{O}_7\text{Na}$ [M + Na] $^+$: 321.0950, found: 321.0955.



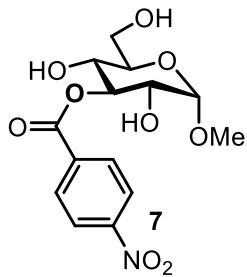
Methyl-3-O-(4-methoxycarbonyl benzoyl)- α -D-glucopyranoside (5)

The product **5** (27.0 mg, 76%) was obtained as white solid. **$^1\text{H NMR}$ (500 MHz, Chloroform-*d*)** δ 8.13 (q, J = 8.5 Hz, 4H), 5.36 (t, J = 9.5 Hz, 1H), 4.87 (d, J = 3.8 Hz, 1H), 3.98 (s, 3H), 3.95 – 3.71 (m, 5H), 3.51 (s, 3H), 2.89 (d, J = 4.8 Hz, 1H), 2.30 (d, J = 11.0 Hz, 1H), 2.08 (s, 1H). **$^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*)** δ 167.08, 166.22, 134.31, 133.33, 129.90, 129.59, 99.42, 77.95, 71.41, 70.93, 69.25, 62.11, 55.56, 52.52. **ESI-MS:** calcd for $\text{C}_{16}\text{H}_{21}\text{O}_9$ [M + H] $^+$: 357.1186, found: 357.1190.



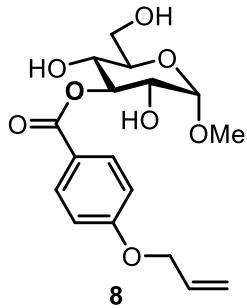
Methyl-3-O-(4-methoxybenzoyl)-α-D-glucopyranoside (6)

The product **6** (21.6 mg, 66%) was obtained as white solid. **¹H NMR (400 MHz, Chloroform-d)** δ 8.15 – 7.92 (m, 2H), 7.09 – 6.74 (m, 2H), 5.30 (t, *J* = 9.1 Hz, 1H), 4.89 (d, *J* = 3.8 Hz, 1H), 3.92 (s, 5H), 3.88 – 3.74 (m, 3H), 3.53 (s, 3H), 3.03 (s, 1H), 2.31 (d, *J* = 10.7 Hz, 1H), 2.07 (s, 1H). **¹³C NMR (101 MHz, Chloroform-d)** δ 168.10, 163.91, 132.13, 121.73, 113.77, 99.44, 77.62, 77.24, 71.50, 70.93, 69.66, 62.29, 55.52. **ESI-MS:** calcd for C₁₅H₂₁O₈ [M + H]⁺: 329.1237, found: 329.1239.



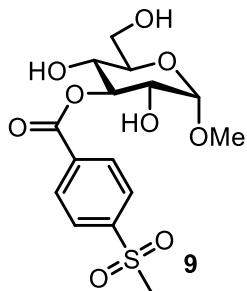
Methyl-3-O-(4-nitrobenzoyl)-α-D-glucopyranoside (7)

The product **7** (27.4 mg, 80%) was obtained as white solid. **¹H NMR (400 MHz, Acetonitrile-d₃)** δ 8.46 – 8.08 (m, 4H), 5.30 (dd, *J* = 9.9, 8.8 Hz, 1H), 4.78 (d, *J* = 3.7 Hz, 1H), 3.88 – 3.54 (m, 6H), 3.45 (s, 3H), 3.13 (d, *J* = 8.5 Hz, 1H), 2.83 (s, 1H). **¹³C NMR (101 MHz, Acetonitrile-d₃)** δ 164.70, 150.77, 135.85, 130.76, 123.67, 99.63, 77.81, 71.91, 70.33, 68.23, 61.23, 54.66. **ESI-MS:** calcd for C₁₄H₁₇O₉NNa [M + Na]⁺: 366.0801, found: 366.0782.



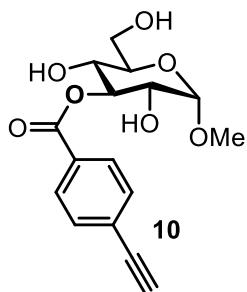
Methyl-3-O-(4-(allyloxy)benzoyl)-α-D-glucopyranoside (8)

The product **8** (24.8 mg, 70%) was obtained as white solid. **¹H NMR (400 MHz, Chloroform-d)** δ 8.15 – 7.80 (m, 2H), 7.10 – 6.76 (m, 2H), 6.06 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1H), 5.44 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.38 – 5.21 (m, 2H), 4.85 (d, *J* = 3.8 Hz, 1H), 4.61 (dt, *J* = 5.3, 1.6 Hz, 2H), 3.93 (d, *J* = 12.4 Hz, 2H), 3.84 – 3.68 (m, 3H), 3.49 (s, 3H), 3.16 (s, 1H), 2.38 (d, *J* = 10.5 Hz, 1H), 2.17 (s, 1H). **¹³C NMR (101 MHz, Chloroform-d)** δ 167.99, 162.84, 132.44, 132.08, 121.84, 118.22, 114.43, 99.44, 77.50, 71.47, 70.93, 69.51, 68.90, 62.20, 55.48. **ESI-MS:** calcd for C₁₇H₂₂O₈Na [M + Na]⁺: 377.1212, found: 377.1194.



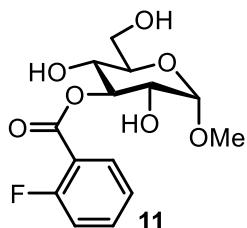
Methyl-3-O-(4-(methylsulfonyl)benzoyl)- α -D-glucopyranoside (9)

The product **9** (32.0 mg, 85%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.32 – 8.27 (m, 2H), 8.13 – 8.07 (m, 2H), 5.46 (t, J = 9.4 Hz, 1H), 4.78 (d, J = 3.6 Hz, 1H), 3.98 – 3.61 (m, 5H), 3.45 (s, 3H), 3.20 (s, 3H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 164.74, 145.01, 135.25, 130.38, 127.41, 99.98, 77.90, 72.42, 70.71, 68.57, 61.42, 54.52, 43.22. **ESI-MS:** calcd for $\text{C}_{15}\text{H}_{20}\text{O}_9\text{SNa}$ [M + Na] $^+$: 399.0726, found: 399.0712



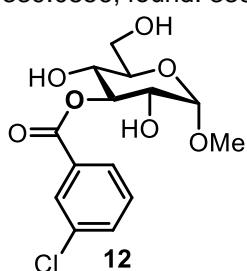
Methyl-3-O-(4-ethynylbenzoyl)- α -D-glucopyranoside (10)

The product **10** (21.6 mg, 67%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.07 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 5.43 (t, J = 9.4 Hz, 1H), 4.77 (d, J = 3.6 Hz, 1H), 3.91 (s, 1H), 3.85 (dd, J = 11.6, 2.6 Hz, 1H), 3.76 (dd, J = 10.2, 7.4 Hz, 2H), 3.69 (ddd, J = 7.2, 4.7, 2.4 Hz, 2H), 3.44 (s, 3H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 165.30, 131.83, 130.97, 129.62, 126.64, 100.02, 82.52, 81.15, 77.36, 72.47, 70.82, 68.67, 61.50, 54.48. **ESI-MS:** calcd for $\text{C}_{16}\text{H}_{18}\text{O}_7\text{Na}$ [M + Na] $^+$: 345.0950, found: 345.0941.



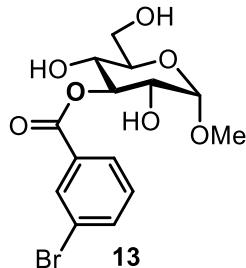
Methyl-3-O-(2-fluorobenzoyl)- α -D-glucopyranoside (11)

The product **11** (26.5 mg, 84%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Chloroform- d)** δ 8.03 (td, J = 7.5, 1.9 Hz, 1H), 7.67 – 7.51 (m, 1H), 7.27 (td, J = 7.6, 1.1 Hz, 1H), 7.20 (ddd, J = 10.9, 8.3, 1.1 Hz, 1H), 5.38 (t, J = 9.4 Hz, 1H), 4.89 (d, J = 3.8 Hz, 1H), 4.04 – 3.70 (m, 5H), 3.53 (s, 3H), 2.85 (s, 1H), 2.37 (d, J = 10.6 Hz, 1H), 2.06 (s, 1H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform- d)** δ 165.89 (d, J = 3.8 Hz), 162.10 (d, J = 260.2 Hz), 135.04 (d, J = 9.2 Hz), 132.45, 124.13 (d, J = 3.8 Hz), 118.25 (d, J = 9.6 Hz), 117.08 (d, J = 22.4 Hz), 99.48, 78.14, 71.41, 70.99, 69.28, 62.19, 55.55. **ESI-MS:** calcd for $\text{C}_{14}\text{H}_{17}\text{O}_7\text{FNa}$ [M + Na] $^+$: 339.0856, found: 339.0843



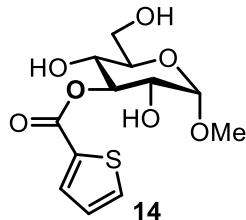
Methyl-3-O-(3-chlorobenzoyl)- α -D-glucopyranoside (12)

The product **12** (21.6 mg, 65%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Chloroform- d)** δ 8.09 (t, J = 1.9 Hz, 1H), 8.00 (dt, J = 7.7, 1.4 Hz, 1H), 7.60 (ddd, J = 7.9, 2.2, 1.1 Hz, 1H), 7.44 (t, J = 7.9 Hz, 1H), 5.36 (t, J = 9.4 Hz, 1H), 4.88 (d, J = 3.8 Hz, 1H), 4.00 – 3.72 (m, 5H), 3.52 (s, 3H), 2.99 (s, 1H), 2.36 (d, J = 11.0 Hz, 1H), 2.18 (s, 1H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform- d)** δ 166.71, 134.63, 133.47, 131.34, 129.97, 129.80, 128.11, 99.45, 77.90, 71.44, 70.94, 69.23, 62.10, 55.57. **ESI-MS:** calcd for $\text{C}_{14}\text{H}_{17}\text{O}_7\text{ClNa} [\text{M} + \text{Na}]^+$: 355.0561, found: 355.0554.



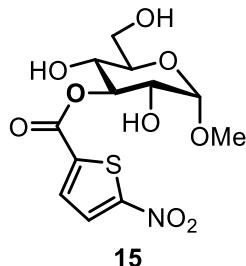
Methyl-3-O-(3-bromobenzoyl)- α -D-glucopyranoside (13)

The product **13** (20.7 mg, 55%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Chloroform- d)** δ 8.21 (s, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.82 – 7.64 (m, 1H), 7.34 (t, J = 7.9 Hz, 1H), 5.33 (t, J = 9.4 Hz, 1H), 4.85 (d, J = 3.8 Hz, 1H), 3.95 – 3.68 (m, 5H), 3.49 (s, 3H), 3.09 (s, 1H), 2.40 (d, J = 11.0 Hz, 1H), 2.24 (s, 1H). **$^{13}\text{C NMR}$ (126 MHz, Chloroform- d)** δ 166.53, 136.35, 132.83, 131.52, 130.03, 128.54, 122.50, 99.44, 77.82, 71.41, 70.91, 69.11, 62.03, 55.54. **ESI-MS:** calcd for $\text{C}_{14}\text{H}_{17}\text{O}_7\text{BrNa} [\text{M} + \text{Na}]^+$: 399.0055, found: 399.0033.



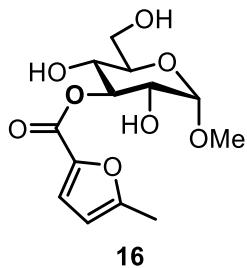
Methyl-3-O-(thiophene-2-carbonyl)- α -D-glucopyranoside (14)

The product **14** (19.8 mg, 65%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Chloroform- d)** δ 7.91 (dd, J = 3.8, 1.3 Hz, 1H), 7.65 (dd, J = 5.0, 1.3 Hz, 1H), 7.16 (dd, J = 5.0, 3.8 Hz, 1H), 5.30 (t, J = 9.3 Hz, 1H), 4.87 (d, J = 3.8 Hz, 1H), 3.98 – 3.89 (m, 2H), 3.84 (t, J = 9.4 Hz, 1H), 3.77 (dt, J = 9.6, 3.8 Hz, 2H), 3.52 (s, 3H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform- d)** δ 163.50, 134.39, 133.30, 132.93, 127.96, 99.47, 77.86, 71.41, 70.90, 69.18, 62.13, 55.53. **ESI-MS:** calcd for $\text{C}_{12}\text{H}_{16}\text{O}_7\text{SNa} [\text{M} + \text{Na}]^+$: 327.0514, found: 327.0511.



Methyl-3-O-(5-nitrothiophene-2-formyl)- α -D-glucopyranoside (15)

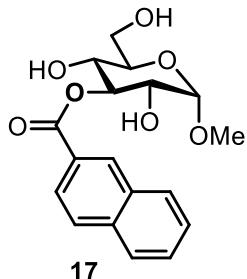
The product **15** (30.0 mg, 85%) was obtained as yellow solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.08 (d, J = 4.3 Hz, 1H), 7.85 (d, J = 4.3 Hz, 1H), 5.38 (t, J = 9.5 Hz, 1H), 4.78 (d, J = 3.7 Hz, 1H), 4.74 (d, J = 5.6 Hz, 1H), 4.02 (d, J = 8.8 Hz, 1H), 3.85 (ddd, J = 11.6, 5.9, 2.6 Hz, 1H), 3.81 – 3.61 (m, 5H), 3.44 (s, 3H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 160.27, 155.00, 139.15, 132.07, 128.79, 99.91, 78.91, 72.37, 70.51, 68.37, 61.36, 54.51. **ESI-MS:** calcd for $\text{C}_{12}\text{H}_{15}\text{O}_9\text{NSNa} [\text{M} + \text{Na}]^+$: 372.0365, found: 372.0368.



16

Methyl-3-O-(5-methylfuran-2-carbonyl)- α -D-glucopyranoside (16)

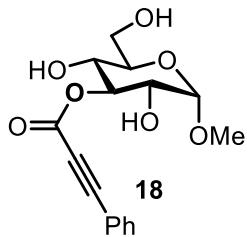
The product **16** (20.2 mg, 67%) was obtained as white solid. **$^1\text{H NMR}$ (500 MHz, Chloroform-*d*)** δ 7.20 (d, *J* = 3.5 Hz, 1H), 6.17 (dd, *J* = 3.4, 1.0 Hz, 1H), 5.26 (t, *J* = 9.4 Hz, 1H), 4.85 (d, *J* = 3.8 Hz, 1H), 3.91 (qd, *J* = 11.8, 3.8 Hz, 2H), 3.83 – 3.71 (m, 3H), 3.50 (s, 3H), 2.93 (s, 1H), 2.41 (s, 3H), 2.38 – 2.29 (m, 1H), 2.11 (s, 1H). **$^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*)** δ 159.97, 158.07, 142.29, 120.83, 108.77, 99.42, 77.36, 71.40, 70.85, 69.25, 62.17, 55.49, 14.05. **ESI-MS:** calcd for $\text{C}_{13}\text{H}_{18}\text{O}_8\text{Na}$ [M + Na] $^+$: 325.0899, found: 325.0882.



17

Methyl-3-O-(2-naphthoyl)- α -D-glucopyranoside (17)

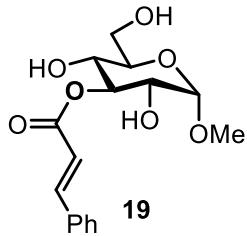
The product **17** (22.3 mg, 64%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Chloroform-*d*)** δ 8.80 – 8.64 (m, 1H), 8.11 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.03 – 7.95 (m, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.62 (dd, *J* = 22.7, 8.1, 6.8, 1.3 Hz, 2H), 5.42 (t, *J* = 9.5 Hz, 1H), 4.91 (d, *J* = 3.8 Hz, 1H), 4.09 – 3.73 (m, 5H), 3.53 (s, 3H), 3.09 (s, 1H), 2.41 (s, 1H), 2.15 (s, 1H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*)** δ 168.34, 135.79, 132.44, 131.68, 129.47, 128.56, 128.29, 127.81, 126.79, 126.69, 125.32, 99.50, 77.86, 71.50, 71.01, 69.51, 62.22, 55.55. **ESI-MS:** calcd for $\text{C}_{18}\text{H}_{21}\text{O}_7$ [M + H] $^+$: 349.1287, found: 349.1281.



18

Methyl-3-O-(3-phenylpropioyl)- α -D-glucopyranoside (18)

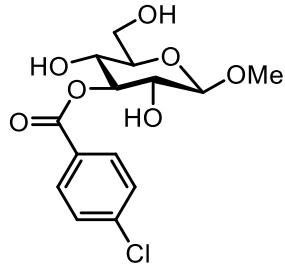
The product **18** (21.6 mg, 67%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Chloroform-*d*)** δ 7.71 – 7.56 (m, 2H), 7.50 – 7.43 (m, 1H), 7.38 (dd, *J* = 8.2, 6.7 Hz, 2H), 5.24 (t, *J* = 9.4 Hz, 1H), 4.82 (d, *J* = 3.8 Hz, 1H), 3.89 (t, *J* = 3.4 Hz, 2H), 3.78 (t, *J* = 9.4 Hz, 1H), 3.73 – 3.65 (m, 2H), 3.47 (s, 3H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*)** δ 153.74, 131.98, 129.79, 127.53, 118.29, 98.31, 87.23, 79.11, 77.19, 70.21, 69.72, 67.80, 60.98, 54.46. **ESI-MS:** calcd for $\text{C}_{16}\text{H}_{18}\text{O}_7\text{Na}$ [M + Na] $^+$: 345.0950, found: 345.0945



19

Methyl-3-O-cinnamoyl- α -D-glucopyranoside (19)

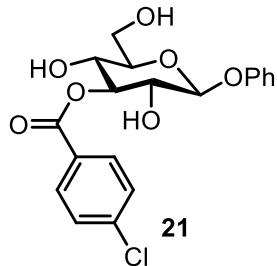
The product **19** (26.6 mg, 82%) was obtained as white solid. **¹H NMR (400 MHz, Chloroform-d)** δ 7.80 (d, *J* = 16.0 Hz, 1H), 7.67 – 7.53 (m, 2H), 7.43 (dd, *J* = 5.1, 1.9 Hz, 3H), 6.56 (d, *J* = 16.0 Hz, 1H), 5.24 (t, *J* = 9.4 Hz, 1H), 4.87 (d, *J* = 3.9 Hz, 1H), 3.91 (d, *J* = 19.1 Hz, 2H), 3.76 (dq, *J* = 9.8, 6.2, 4.8 Hz, 3H), 3.52 (s, 3H), 3.13 (s, 1H), 2.41 (d, *J* = 10.7 Hz, 1H), 2.21 (s, 1H). **¹³C NMR (101 MHz, Chloroform-d)** δ 168.63, 146.42, 134.16, 130.66, 128.96, 128.30, 117.28, 99.44, 77.24, 71.48, 70.92, 69.49, 62.22, 55.51. **ESI-MS:** calcd for C₁₆H₂₀O₇Na [M + Na]⁺: 347.1107, found: 347.1101.



20

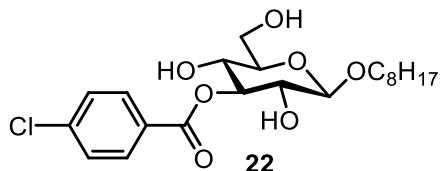
Methyl-3-O-(4-chlorobenzoyl)-β-D-glucopyranoside (**20**)

The product **20** (21.9 mg, 66%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-d₆)** δ 8.14 – 7.97 (m, 2H), 7.69 – 7.49 (m, 2H), 5.24 (t, *J* = 9.4 Hz, 1H), 4.64 (d, *J* = 5.7 Hz, 1H), 4.52 (d, *J* = 4.6 Hz, 1H), 4.38 (d, *J* = 7.8 Hz, 1H), 3.98 – 3.82 (m, 1H), 3.79 – 3.67 (m, 3H), 3.52-3.47 (m, 5H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 164.79, 138.51, 131.26, 129.64, 128.57, 104.10, 79.09, 76.45, 72.17, 68.87, 61.67, 56.01. **ESI-MS:** calcd for C₁₄H₁₇O₇ClNa [M + Na]⁺: 355.0561, found: 355.0543.



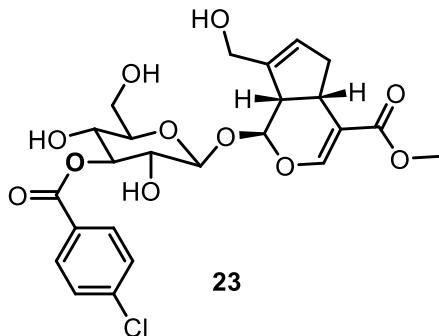
Phenyl-3-O-(4-chlorobenzoyl)-β-D-glucopyranoside (**21**)

The product **21** (29.1 mg, 74%) was obtained as white solid. *R*_F (hexane: ethyl acetate = 1:1): 0.30. **¹H NMR (400 MHz, Acetone-d₆)** δ 8.18 – 7.97 (m, 2H), 7.69 – 7.51 (m, 2H), 7.42 – 7.26 (m, 2H), 7.19 – 7.08 (m, 2H), 7.04 (tt, *J* = 7.3, 1.1 Hz, 1H), 5.39 (t, *J* = 9.4 Hz, 1H), 5.20 (d, *J* = 7.7 Hz, 1H), 4.02 – 3.67 (m, 5H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 164.79, 157.84, 138.59, 131.31, 129.61, 129.34, 128.61, 122.09, 116.52, 100.83, 78.92, 76.70, 72.05, 68.48, 61.33. **ESI-MS:** calcd for C₁₉H₁₉O₇ClNa [M + Na]⁺: 417.0717, found: 417.0695.



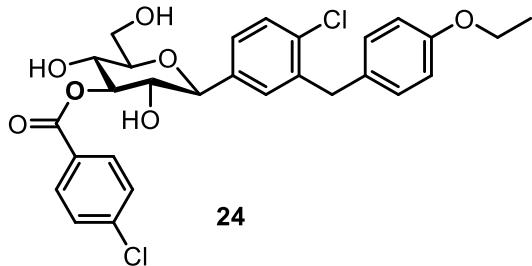
Octyl-3-O-(4-chlorobenzoyl)-β-D-glucopyranoside (**22**)

The product **22** (32.2 mg, 75%) was obtained as white solid. **¹H NMR (400 MHz, Chloroform-d)** δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 5.19 (t, *J* = 9.4 Hz, 1H), 4.46 (d, *J* = 7.8 Hz, 1H), 4.15 – 3.77 (m, 4H), 3.73 – 3.55 (m, 2H), 3.51 (dt, *J* = 9.6, 4.0 Hz, 1H), 1.65 (q, *J* = 6.9 Hz, 2H), 1.41 – 1.15 (m, 10H), 0.90 (t, *J* = 6.6 Hz, 3H). **¹³C NMR (101 MHz, Chloroform-d)** δ 166.98, 140.11, 131.37, 128.87, 127.83, 102.79, 78.93, 75.67, 72.26, 70.61, 69.74, 62.32, 31.79, 29.60, 29.35, 29.22, 25.93, 22.64, 14.09. **ESI-MS:** calcd for C₂₁H₃₁O₇ClNa [M + Na]⁺: 453.1656, found: 453.1650.



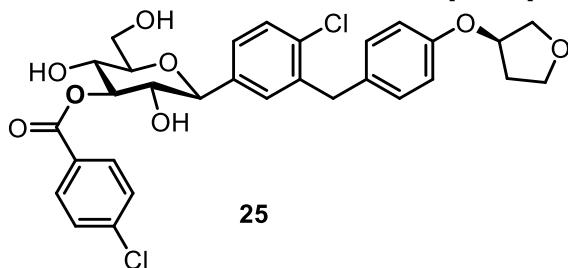
3-O-(4-chlorobenzoyl)-geniposide (23)

The product **23** (37.9 mg, 72%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-d₆)** δ 8.22 – 7.96 (m, 2H), 7.65 – 7.50 (m, 2H), 5.80 (s, 1H), 5.30 (t, J = 9.4 Hz, 1H), 5.22 (d, J = 7.3 Hz, 1H), 4.94 (d, J = 7.8 Hz, 1H), 4.71 (dd, J = 10.4, 5.3 Hz, 2H), 4.37 (d, J = 14.7 Hz, 1H), 4.18 (d, J = 14.3 Hz, 1H), 3.99 – 3.72 (m, 5H), 3.68 (s, 3H), 3.62 (ddd, J = 9.5, 7.9, 4.8 Hz, 1H), 3.55 (ddd, J = 9.8, 4.9, 2.5 Hz, 1H), 3.17 (qd, J = 7.9, 1.3 Hz, 1H), 2.79 (dd, J = 16.4, 8.4 Hz, 2H), 2.70 (t, J = 7.6 Hz, 1H), 2.12 (dt, J = 7.7, 2.4 Hz, 1H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 166.93, 164.75, 151.38, 144.51, 138.57, 131.29, 129.58, 128.59, 126.09, 111.50, 99.51, 97.21, 78.77, 76.75, 72.03, 68.49, 61.27, 60.21, 50.39, 46.07, 38.42, 35.21. **ESI-MS:** calcd for C₂₄H₂₇O₁₁ClNa [M + Na]⁺: 549.1140, found: 549.1141.



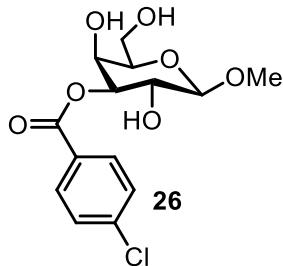
3-O-(4-chlorobenzoyl)-dapagliflozin (24)

The product **24** (38.8 mg, 71%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-d₆)** δ 8.16 – 7.92 (m, 2H), 7.62 – 7.51 (m, 2H), 7.46 (s, 1H), 7.38 (s, 2H), 7.15 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 5.36 (t, J = 9.2 Hz, 1H), 4.37 (d, J = 9.4 Hz, 1H), 4.12 – 3.96 (m, 4H), 3.94 – 3.85 (m, 2H), 3.78 (dd, J = 11.9, 5.0 Hz, 1H), 3.72 – 3.64 (m, 1H), 3.61 (ddd, J = 9.5, 4.9, 2.6 Hz, 1H), 1.34 (t, J = 7.0 Hz, 3H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 165.03, 157.57, 139.01, 138.49, 138.36, 132.85, 131.40, 131.28, 130.91, 129.71, 129.68, 128.89, 128.53, 127.08, 114.27, 81.21, 80.89, 80.80, 73.52, 68.91, 62.98, 61.81, 38.01, 14.25. **ESI-MS:** calcd for C₂₈H₂₉O₇Cl₂ [M + H]⁺: 547.1290, found: 547.1295.



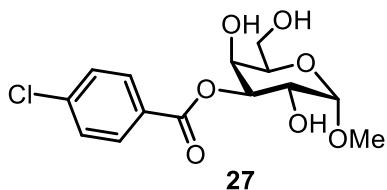
3-O-(4-chlorobenzoyl)-empagliflozin (25)

The product **25** (45.3 mg, 77%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-d₆)** δ 8.15 – 7.86 (m, 2H), 7.62 – 7.52 (m, 2H), 7.47 (s, 1H), 7.38 (s, 2H), 7.29 – 7.02 (m, 2H), 6.94 – 6.70 (m, 2H), 5.36 (t, J = 9.2 Hz, 1H), 4.99 (td, J = 4.5, 2.3 Hz, 1H), 4.67 (d, J = 5.7 Hz, 1H), 4.48 (d, J = 6.1 Hz, 1H), 4.38 (d, J = 9.4 Hz, 1H), 4.13 – 4.00 (m, 2H), 3.97 – 3.85 (m, 4H), 3.80 (tdd, J = 11.1, 5.1, 2.8 Hz, 3H), 3.73 – 3.58 (m, 3H), 2.23 (td, J = 14.3, 8.2, 6.2 Hz, 1H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 165.02, 156.12, 139.04, 138.50, 138.27, 132.85, 131.81, 131.28, 130.92, 129.80, 129.71, 128.90, 128.54, 127.13, 115.22, 81.21, 80.91, 80.80, 77.35, 73.55, 72.60, 68.95, 66.58, 61.86, 37.99, 32.82. **ESI-MS:** calcd for C₃₀H₃₁O₈Cl₂ [M + H]⁺: 589.1396, found: 589.1387.



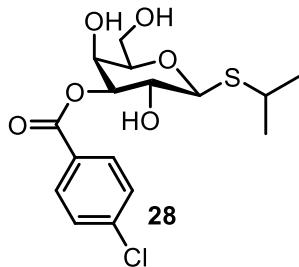
Methyl-3-O-(4-chlorobenzoyl)- β -D-galactopyranoside (26)

The product **26** (20.2 mg, 61%) was obtained as white solid. **¹H NMR (500 MHz, Acetone-*d*₆)** δ 8.09 (d, *J* = 8.6 Hz, 2H), 7.67 – 7.46 (m, 2H), 5.00 (dd, *J* = 10.0, 3.3 Hz, 1H), 4.34 (d, *J* = 7.7 Hz, 1H), 4.24 (d, *J* = 3.3 Hz, 1H), 3.96 (dd, *J* = 10.0, 7.7 Hz, 1H), 3.81 (dd, *J* = 6.0, 1.8 Hz, 2H), 3.72 – 3.64 (m, 1H), 3.51 (s, 3H). **¹³C NMR (101 MHz, Acetone-*d*₆)** δ 164.82, 138.68, 131.32, 129.42, 128.59, 104.77, 77.55, 74.88, 68.63, 66.75, 61.08, 55.85. **ESI-MS:** calcd for C₁₄H₁₇O₇ClNa [M + Na]⁺: 355.0561, found: 355.0545.



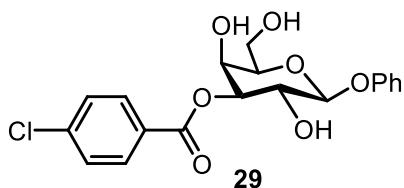
Methyl-3-O-(4-chlorobenzoyl)- α -D-galactopyranoside (27)

The product **27** (16.6 mg, 50%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-*d*₆)** δ 8.14 – 7.93 (m, 2H), 7.65 – 7.42 (m, 2H), 5.22 (dd, *J* = 10.4, 3.1 Hz, 1H), 4.80 (d, *J* = 3.8 Hz, 1H), 4.30 (dd, *J* = 3.2, 1.3 Hz, 1H), 4.22 (dd, *J* = 10.4, 3.8 Hz, 1H), 3.93 – 3.84 (m, 1H), 3.84 – 3.71 (m, 2H), 3.43 (s, 3H). **¹³C NMR (101 MHz, Acetone-*d*₆)** δ 165.04, 138.66, 131.33, 129.48, 128.58, 100.43, 75.10, 70.77, 67.54, 66.68, 61.32, 54.53. **ESI-MS:** calcd for C₁₄H₁₇O₇ClNa [M + Na]⁺: 355.0561, found: 355.0543.



Isopropylthio-3-O-(4-chlorobenzoyl)- β -D-galactopyranoside (28)

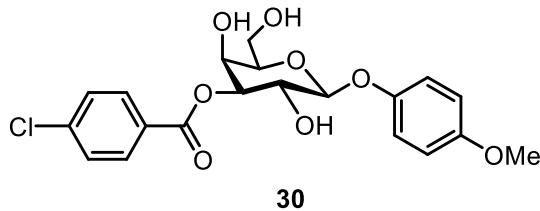
The product **28** (23.3 mg, 62%) was obtained as white solid. **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.11 – 7.87 (m, 2H), 7.53 – 7.38 (m, 2H), 5.12 (dd, *J* = 9.6, 3.2 Hz, 1H), 4.57 (d, *J* = 9.7 Hz, 1H), 4.34 (d, *J* = 3.1 Hz, 1H), 4.14 – 3.85 (m, 3H), 3.71 (t, *J* = 5.0 Hz, 1H), 3.28 (p, *J* = 6.8 Hz, 1H), 1.39 (dd, *J* = 6.7, 2.8 Hz, 6H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 165.30, 139.94, 131.31, 128.84, 128.05, 86.83, 77.86, 76.93, 68.80, 67.88, 63.02, 36.11, 24.22, 24.08. **ESI-MS:** calcd for C₁₆H₂₁O₆ClSNa [M + Na]⁺: 399.0645, found: 399.0625.



Phenyl-3-O-(4-chlorobenzoyl)- β -D-galactopyranoside (29)

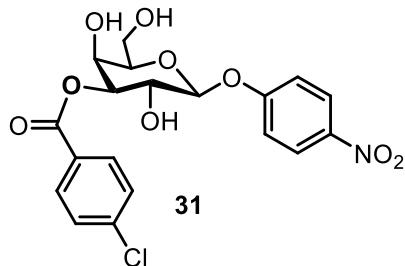
The product **29** (24.4 mg, 62%) was obtained as white solid. **¹H NMR (400 MHz, Methanol-*d*₄)** δ 8.20 – 8.06 (m, 2H), 7.59 – 7.49 (m, 2H), 7.36 – 7.27 (m, 2H), 7.20 – 7.12 (m, 2H), 7.04 (td, *J* = 7.3, 1.1 Hz, 1H), 5.10 (dd, *J* = 10.1, 3.3 Hz, 1H), 5.06 (d, *J* = 7.7 Hz, 1H), 4.27 – 4.24 (m, 1H), 4.20 (dd, *J* = 10.1, 7.7 Hz, 1H), 3.89 – 3.74 (m, 3H). **¹³C NMR (101 MHz, Methanol-*d*₄)** δ 165.32, 157.77, 139.18, 131.07, 129.02,

128.83, 128.38, 122.07, 116.48, 101.54, 76.70, 75.27, 68.50, 66.42, 60.71. **ESI-MS:** calcd for $C_{19}H_{19}O_7ClNa$ $[M + Na]^+$: 417.0717, found: 417.0698.



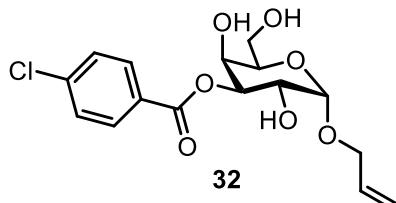
(4-methoxyphenyl)-3-O-(4-chlorobenzoyl)- β -D-galactopyranoside (30)

The product **30** (22.5 mg, 53%) was obtained as white solid. **1H NMR (400 MHz, Methanol- d_4)** δ 8.23 – 8.01 (m, 2H), 7.69 – 7.43 (m, 2H), 7.19 – 7.05 (m, 2H), 6.97 – 6.76 (m, 2H), 5.08 (dd, J = 10.1, 3.3 Hz, 1H), 4.93 (d, J = 7.8 Hz, 1H), 4.24 (d, J = 3.3 Hz, 1H), 4.16 (dd, J = 10.2, 7.8 Hz, 1H), 3.86 – 3.73 (m, 3H), 3.78 (s, 3H). **^{13}C NMR (101 MHz, Methanol- d_4)** δ 165.32, 155.34, 151.82, 139.17, 131.07, 128.83, 128.37, 117.97, 114.06, 102.70, 76.71, 75.22, 68.54, 66.42, 60.71, 54.65. **ESI-MS:** calcd for $C_{20}H_{21}O_8ClNa$ $[M + Na]^+$: 447.0823, found: 447.0816.



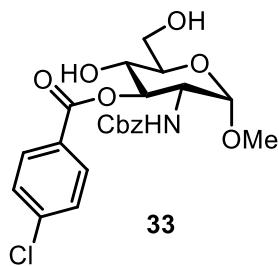
4-Nitrophenyl-3-O-(4-chlorobenzoyl)- β -D-galactopyranoside (31)

The product **31** (29.9 mg, 68%) was obtained as white solid. **1H NMR (400 MHz, Acetone- d_6)** δ 8.33 – 8.21 (m, 2H), 8.19 – 8.06 (m, 2H), 7.69 – 7.51 (m, 2H), 7.41 – 7.24 (m, 2H), 5.39 (d, J = 7.6 Hz, 1H), 5.18 (dd, J = 10.0, 3.2 Hz, 1H), 5.07 (d, J = 4.8 Hz, 1H), 4.60 (d, J = 5.1 Hz, 1H), 4.36 (ddd, J = 9.9, 7.6, 4.5 Hz, 2H), 4.05 (dt, J = 18.7, 5.9 Hz, 2H), 3.86 (t, J = 5.7 Hz, 2H). **^{13}C NMR (101 MHz, Acetone- d_6)** δ 164.79, 162.64, 142.47, 138.82, 131.37, 129.25, 128.65, 125.53, 116.65, 100.96, 77.14, 75.57, 68.29, 66.54, 60.98. **ESI-MS:** calcd for $C_{19}H_{18}O_9ClNa$ $[M + Na]^+$: 462.0568, found: 462.0559.



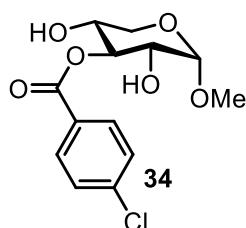
Allyl-3-O-(4-chlorobenzoyl)- α -D-galactopyranoside (32)

The product **32** (19.0 mg, 53%) was obtained as white solid. **1H NMR (400 MHz, Acetone- d_6)** δ 8.22 – 7.94 (m, 2H), 7.69 – 7.43 (m, 2H), 6.13 – 5.86 (m, 1H), 5.39 (dq, J = 17.3, 1.8 Hz, 1H), 5.27 (dd, J = 10.5, 3.1 Hz, 1H), 5.18 (dq, J = 10.4, 1.5 Hz, 1H), 4.97 (d, J = 3.8 Hz, 1H), 4.45 (s, 1H), 4.36 – 4.18 (m, 3H), 4.09 (ddt, J = 13.2, 5.8, 1.5 Hz, 1H), 3.96 (td, J = 5.9, 1.4 Hz, 1H), 3.87 – 3.68 (m, 4H). **^{13}C NMR (101 MHz, Acetone- d_6)** δ 165.05, 138.66, 134.67, 131.33, 129.46, 128.58, 116.08, 98.62, 75.13, 71.01, 68.02, 67.55, 66.66, 61.30. **ESI-MS:** calcd for $C_{16}H_{19}O_7ClNa$ $[M + Na]^+$: 381.0717, found: 381.0704.



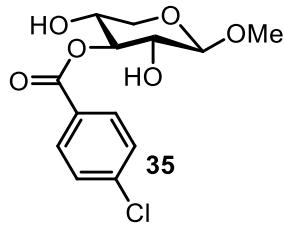
Methyl 2-(benzyloxy)carbonyl)amino-2-deoxy-3-O-(4-chlorobenzoyl)- α -D-glucopyranoside (33)

The product **33** (32.5 mg, 70%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Chloroform- d)** δ 7.96 (d, $J = 8.6$ Hz, 2H), 7.38 (d, $J = 8.6$ Hz, 2H), 7.26 – 7.12 (m, 5H), 5.27 (t, $J = 9.9$ Hz, 1H), 5.18 (d, $J = 10.1$ Hz, 1H), 5.06 – 4.89 (m, 2H), 4.79 (d, $J = 3.6$ Hz, 1H), 4.16 (td, $J = 10.4, 3.8$ Hz, 1H), 3.94 – 3.84 (m, 3H), 3.75 (dt, $J = 9.8, 3.8$ Hz, 1H), 3.43 (s, 3H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform- d)** δ 167.13, 155.96, 140.00, 136.03, 131.44, 128.81, 128.39, 128.10, 127.76, 127.65, 98.73, 76.02, 71.65, 69.70, 66.88, 62.11, 55.35, 53.44. **ESI-MS:** calcd for $\text{C}_{22}\text{H}_{24}\text{O}_8\text{ClNa} [\text{M} + \text{Na}]^+$: 488.1088, found: 488.1070.



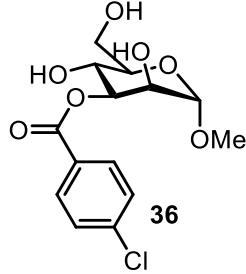
Methyl-3-O-(4-chlorobenzoyl)- α -D-xylopyranoside (34)

The product **34** (21.7 mg, 72%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.15 – 7.95 (m, 2H), 7.73 – 7.40 (m, 2H), 5.34 (t, $J = 9.4$ Hz, 1H), 4.72 (d, $J = 3.5$ Hz, 1H), 4.53 (d, $J = 5.6$ Hz, 1H), 3.92 – 3.82 (m, 1H), 3.79 (d, $J = 9.0$ Hz, 1H), 3.67 (dd, $J = 11.0, 5.7$ Hz, 2H), 3.58 (t, $J = 10.8$ Hz, 1H), 3.43 (s, 3H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 165.06, 138.53, 131.22, 129.63, 128.57, 100.24, 77.40, 70.71, 68.32, 61.76, 54.61. **ESI-MS:** calcd for $\text{C}_{13}\text{H}_{15}\text{O}_6\text{ClNa} [\text{M} + \text{Na}]^+$: 325.0455, found: 325.0440.



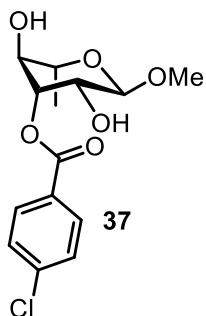
Methyl-3-O-(4-chlorobenzoyl)- β -D-xylopyranoside (35)

The product **35** (19.9 mg, 66%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Chloroform- d)** δ 8.21 – 7.95 (m, 2H), 7.61 – 7.43 (m, 2H), 5.13 (t, $J = 8.1$ Hz, 1H), 4.40 (d, $J = 6.4$ Hz, 1H), 4.17 (dd, $J = 11.9, 4.9$ Hz, 1H), 3.96 (td, $J = 8.4, 4.8$ Hz, 1H), 3.71 (dd, $J = 8.3, 6.5$ Hz, 1H), 3.60 (s, 3H), 3.48 (dd, $J = 11.9, 8.7$ Hz, 1H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform- d)** δ 166.75, 140.15, 131.40, 128.90, 127.85, 103.79, 77.59, 71.09, 68.74, 64.87, 57.04. **ESI-MS:** calcd for $\text{C}_{13}\text{H}_{15}\text{O}_6\text{ClNa} [\text{M} + \text{Na}]^+$: 325.0455, found: 325.0438.



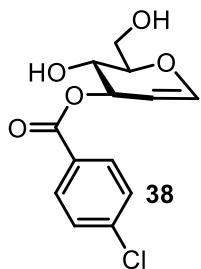
Methyl-3-O-(4-chlorobenzoyl)- α -D-mannopyranoside (36)

The product **36** (20.5 mg) was obtained as white solid (total acylates 24.6 mg, 74%). **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.09 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 8.1$ Hz, 2H), 5.23 (dd, $J = 9.8, 3.2$ Hz, 1H), 4.72 (s, 1H), 4.54 (d, $J = 5.5$ Hz, 2H), 4.22 – 4.08 (m, 2H), 3.93 – 3.84 (m, 1H), 3.79 (p, $J = 5.8, 5.1$ Hz, 1H), 3.71 – 3.59 (m, 2H), 3.41 (s, 3H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 164.86, 138.63, 131.36, 129.47, 128.53, 101.41, 76.21, 73.45, 68.54, 64.90, 61.88, 53.98. **ESI-MS:** calcd for $\text{C}_{14}\text{H}_{17}\text{O}_7\text{ClNa} [\text{M} + \text{Na}]^+$: 355.0561, found: 355.0543.



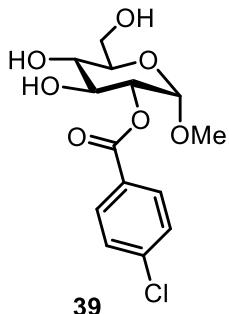
Methyl-3-O-(4-chlorobenzoyl)- α -L-Rhamnopyranoside (37)

The product **37** (27.5 mg, 87%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Chloroform- d)** δ 8.18 – 7.86 (m, 2H), 7.58 – 7.41 (m, 2H), 5.33 – 5.24 (m, 1H), 4.76 (d, J = 1.9 Hz, 1H), 4.19 (dd, J = 3.2, 1.8 Hz, 1H), 3.96 – 3.68 (m, 2H), 3.47 (s, 3H), 1.44 (d, J = 5.9 Hz, 3H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform- d)** δ 166.10, 140.07, 131.28, 128.90, 128.04, 100.64, 75.74, 71.50, 69.74, 68.49, 55.07, 17.63. **ESI-MS:** calcd for $\text{C}_{14}\text{H}_{17}\text{O}_6\text{ClNa}$ [M + Na] $^+$: 339.0611, found: 339.0598.



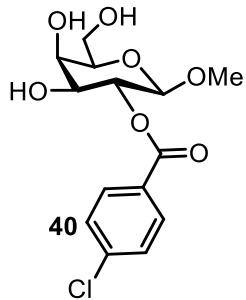
3-O-(4-chlorobenzoyl)-D-glucal (38)

The product **38** (19.0 mg, 67%) was obtained as white solid. **$^1\text{H NMR}$ (500 MHz, Acetone- d_6)** δ 8.06 (d, J = 8.3 Hz, 2H), 7.70 – 7.37 (m, 2H), 6.52 (d, J = 5.9 Hz, 1H), 5.53 (d, J = 6.9 Hz, 1H), 4.82 (dd, J = 6.1, 2.5 Hz, 1H), 4.17 (dd, J = 9.3, 6.9 Hz, 1H), 4.05 – 3.82 (m, 3H). **$^{13}\text{C NMR}$ (126 MHz, Acetone- d_6)** δ 165.16, 146.04, 138.80, 131.17, 129.29, 128.73, 98.91, 79.34, 73.45, 66.18, 60.61. **ESI-MS:** calcd for $\text{C}_{13}\text{H}_{13}\text{O}_5\text{ClNa}$ [M + Na] $^+$: 307.0349, found: 307.0339.



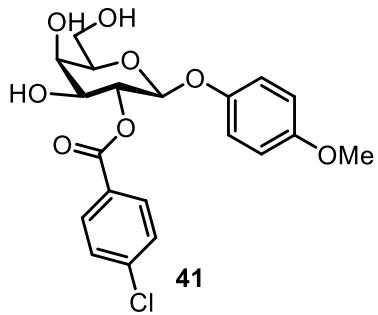
Methyl-2-O-(4-chlorobenzoyl)- α -D-glucopyranoside (39)

Following the general procedure A, the product **39** (20.9 mg, 63%) was obtained as white solid. Following the general procedure C, the product **39** (20.0 mg) was obtained (total acylates 23.2 mg, 70%). **$^1\text{H NMR}$ (400 MHz, Methanol- d_4)** δ 8.13 – 7.98 (m, 2H), 7.58 – 7.39 (m, 2H), 5.01 (d, J = 3.7 Hz, 1H), 4.86 – 4.82 (m, 1H), 3.99 (dd, J = 10.0, 8.8 Hz, 1H), 3.89 (dd, J = 11.9, 2.3 Hz, 1H), 3.75 (dd, J = 11.9, 5.6 Hz, 1H), 3.64 (ddd, J = 10.0, 5.6, 2.4 Hz, 1H), 3.51 – 3.45 (m, 1H), 3.41 (s, 3H). **$^{13}\text{C NMR}$ (101 MHz, Methanol- d_4)** δ 165.34, 139.32, 131.03, 128.50, 128.44, 97.02, 74.36, 72.18, 71.10, 70.47, 61.15, 54.12. **ESI-MS:** calcd for $\text{C}_{14}\text{H}_{17}\text{O}_7\text{ClNa}$ [M + Na] $^+$: 355.0561, found: 355.0547.



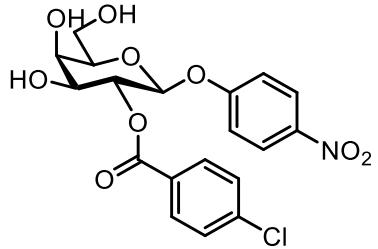
Methyl-2-O-(4-chlorobenzoyl)- β -D-galactopyranoside (40)

The product **40** (20.0 mg) was obtained as white solid (total acylates 23.9 mg, 72%). **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.19 – 7.90 (m, 2H), 7.67 – 7.47 (m, 2H), 5.29 (dd, J = 9.8, 8.0 Hz, 1H), 4.53 (d, J = 8.0 Hz, 1H), 4.04 (dd, J = 3.4, 1.2 Hz, 1H), 3.90 (dd, J = 9.8, 3.4 Hz, 1H), 3.83 (d, J = 5.9 Hz, 2H), 3.67 (td, J = 6.0, 1.2 Hz, 1H), 3.42 (s, 3H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 164.47, 138.64, 131.16, 129.48, 128.68, 101.97, 75.41, 73.59, 71.97, 69.31, 61.22, 55.44. **ESI-MS:** calcd for $\text{C}_{14}\text{H}_{17}\text{O}_7\text{ClNa}$ [M + Na] $^+$: 355.0561, found: 355.0545.



(4-methoxyphenyl)-2-O-(4-chlorobenzoyl)- β -D-galactopyranoside (41)

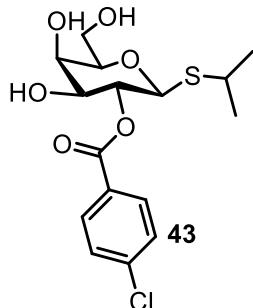
The product **41** (25.9 mg, 61%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.07 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 7.00 – 6.86 (m, 2H), 6.84 – 6.70 (m, 2H), 5.54 (dd, J = 9.8, 8.0 Hz, 1H), 5.13 (d, J = 8.0 Hz, 1H), 4.34 (d, J = 7.2 Hz, 1H), 4.22 (s, 1H), 4.10 (d, J = 3.5 Hz, 1H), 4.01 (td, J = 12.1, 11.0, 4.5 Hz, 2H), 3.86 (dt, J = 4.1, 2.3 Hz, 3H), 3.73 (s, 3H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 164.52, 155.35, 151.73, 138.74, 131.17, 129.32, 128.73, 118.16, 114.35, 100.74, 75.77, 73.58, 71.88, 69.29, 61.28, 54.90. **ESI-MS:** calcd for $\text{C}_{20}\text{H}_{21}\text{O}_8\text{ClNa}$ [M + Na] $^+$: 447.0823, found: 447.0821.



42

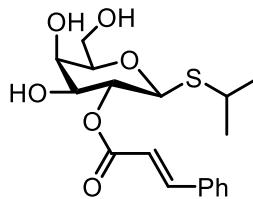
4-Nitrophenyl-2-O-(4-chlorobenzoyl)- β -D-galactopyranoside (42)

The product **42** (25.5 mg, 58%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, DMSO- d_6)** δ 8.17 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.9 Hz, 2H), 5.51 (d, J = 8.0 Hz, 1H), 5.40 (t, J = 8.7 Hz, 1H), 5.33 (s, 1H), 5.04 (d, J = 4.3 Hz, 1H), 4.81 (s, 1H), 3.92 – 3.77 (m, 3H), 3.67 – 3.52 (m, 2H). **$^{13}\text{C NMR}$ (101 MHz, DMSO- d_6)** δ 164.74, 162.17, 142.47, 138.80, 131.60, 129.38, 129.00, 126.25, 117.06, 98.44, 76.58, 73.27, 71.31, 68.63, 60.55. **ESI-MS:** calcd for $\text{C}_{19}\text{H}_{18}\text{O}_9\text{NClNa}$ [M + Na] $^+$: 462.0568, found: 462.0573.



Isopropylthio-2-O-(4-chlorobenzoyl)- β -D-galactopyranoside (43)

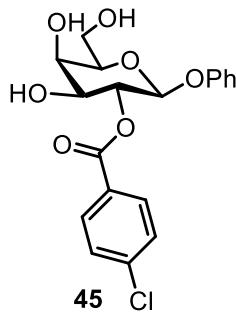
The product **43** (27.0 mg, 72%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.11 – 7.92 (m, 2H), 7.62 – 7.49 (m, 2H), 5.32 (t, J = 9.7 Hz, 1H), 4.79 (d, J = 10.0 Hz, 1H), 4.10 (dd, J = 3.4, 1.2 Hz, 1H), 3.95 (dd, J = 9.3, 3.4 Hz, 1H), 3.81 (d, J = 6.3 Hz, 2H), 3.72 (ddd, J = 6.4, 5.3, 1.2 Hz, 1H), 3.22 (p, J = 6.8 Hz, 1H), 1.24 (dd, J = 13.1, 6.8 Hz, 6H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 164.50, 138.68, 131.20, 129.49, 128.68, 83.01, 79.27, 73.01, 72.39, 69.44, 61.41, 34.39, 23.73, 23.26. **ESI-MS:** calcd for $\text{C}_{16}\text{H}_{21}\text{O}_6\text{SNa} [\text{M} + \text{Na}]^+$: 399.0645, found: 399.0632.



44

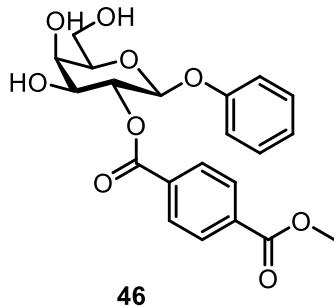
Isopropylthio-2-O-cinnamon acyl- β -D-galactopyranoside (44)

The product **44** (28.3 mg, 77%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 7.80 – 7.57 (m, 3H), 7.46 (dd, J = 5.0, 2.0 Hz, 3H), 6.57 (d, J = 16.1 Hz, 1H), 5.21 (t, J = 9.7 Hz, 1H), 4.68 (d, J = 10.0 Hz, 1H), 4.24 (s, 1H), 4.07 (t, J = 6.7 Hz, 2H), 3.81 (dd, J = 20.9, 7.5 Hz, 4H), 3.72 – 3.60 (m, 1H), 3.22 (p, J = 6.8 Hz, 1H), 1.26 (dd, J = 15.6, 6.7 Hz, 6H). **$^{13}\text{C NMR}$ (126 MHz, Acetone- d_6)** δ 165.60, 144.53, 134.56, 130.30, 128.96, 128.15, 118.41, 83.15, 79.18, 73.12, 71.46, 69.44, 61.45, 34.32, 23.72, 23.32. **ESI-MS:** calcd for $\text{C}_{18}\text{H}_{24}\text{O}_6\text{SNa} [\text{M} + \text{Na}]^+$: 391.1191, found: 391.1191.



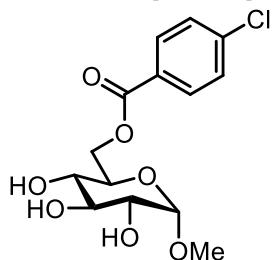
Phenyl-2-O-(4-chlorobenzoyl)- β -D-galactopyranoside (45)

The product **45** (28.0 mg, 71%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.15 – 7.88 (m, 2H), 7.66 – 7.40 (m, 2H), 7.35 – 7.20 (m, 2H), 7.09 – 6.91 (m, 3H), 5.59 (dd, J = 9.8, 8.0 Hz, 1H), 5.29 (d, J = 8.0 Hz, 1H), 4.14 (d, J = 3.4 Hz, 1H), 4.07 (dd, J = 9.8, 3.4 Hz, 1H), 3.95 – 3.77 (m, 3H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 164.52, 157.73, 138.75, 131.17, 129.36, 129.27, 128.72, 122.33, 116.67, 99.58, 75.85, 73.48, 71.85, 69.26, 61.23. **ESI-MS:** calcd for $\text{C}_{19}\text{H}_{19}\text{O}_7\text{ClNa} [\text{M} + \text{Na}]^+$: 417.0717, found: 417.0708.



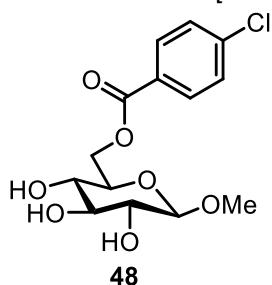
Phenyl-2-O-(4-methoxycarbonyl benzoyl)- β -D-galactopyranoside (46)

The product **46** (29.3 mg, 70%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.27 – 8.04 (m, 4H), 7.24 (dd, J = 8.8, 7.2 Hz, 2H), 7.09 – 6.84 (m, 3H), 5.62 (dd, J = 9.8, 8.0 Hz, 1H), 5.31 (d, J = 8.0 Hz, 1H), 4.44 (s, 1H), 4.28 (s, 1H), 4.14 (d, J = 3.4 Hz, 1H), 4.09 (dd, J = 9.7, 3.4 Hz, 2H), 3.96–3.92 (m, 4H), 3.88 (d, J = 5.5 Hz, 2H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 165.62, 164.64, 157.70, 134.30, 134.06, 129.59, 129.37, 122.34, 116.65, 99.54, 75.86, 73.66, 71.83, 69.28, 61.24, 51.83. **ESI-MS:** calcd for $\text{C}_{21}\text{H}_{22}\text{O}_9\text{Na}$ [M + Na] $^+$: 441.1162, found: 441.1163.



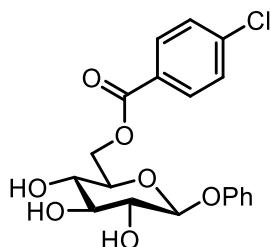
Methyl-6-O-(4-chlorobenzoyl)- α -D-glucopyranoside (47)

The product **47** (19.6 mg, 59%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.13 – 7.93 (m, 2H), 7.69 – 7.44 (m, 2H), 4.72 – 4.56 (m, 2H), 4.46 (dd, J = 11.7, 6.1 Hz, 1H), 3.87 (ddd, J = 10.1, 6.2, 2.2 Hz, 1H), 3.69 (t, J = 9.1 Hz, 1H), 3.50 – 3.41 (m, 2H), 3.39 (s, 3H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 164.98, 138.79, 131.07, 129.13, 128.82, 100.08, 74.27, 72.53, 70.75, 69.77, 64.50, 54.45. **ESI-MS:** calcd for $\text{C}_{14}\text{H}_{17}\text{O}_7\text{ClNa}$ [M + Na] $^+$: 355.0561, found: 355.0547.



Methyl-6-O-(4-chlorobenzoyl)- β -D-glucopyranoside (48)

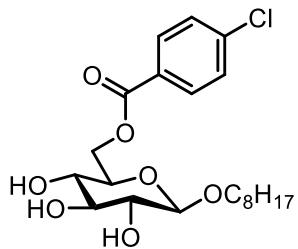
The product **48** (19.9 mg, 60%) was obtained as white solid. **$^1\text{H NMR}$ (500 MHz, DMSO- d_6)** δ 8.07 – 7.78 (m, 2H), 7.75 – 7.49 (m, 2H), 5.27 (d, J = 4.6 Hz, 1H), 5.15 (d, J = 4.9 Hz, 1H), 5.09 (s, 1H), 4.56 (dd, J = 11.7, 2.1 Hz, 1H), 4.35 (dd, J = 11.8, 6.1 Hz, 1H), 4.13 (d, J = 7.8 Hz, 1H), 3.57 – 3.44 (m, 1H), 3.36 (s, 3H), 3.22 (d, J = 5.1 Hz, 2H), 3.01 (q, J = 7.9, 7.3 Hz, 1H). **$^{13}\text{C NMR}$ (101 MHz, DMSO- d_6)** δ 165.28, 138.76, 131.46, 129.48, 129.07, 104.39, 76.79, 74.00, 73.77, 70.49, 64.92, 56.35. **ESI-MS:** calcd for $\text{C}_{14}\text{H}_{17}\text{O}_7\text{ClNa}$ [M + Na] $^+$: 355.0561, found: 355.0559.



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Phenyl-6-O-(4-chlorobenzoyl)- β -D-glucopyranoside (49)

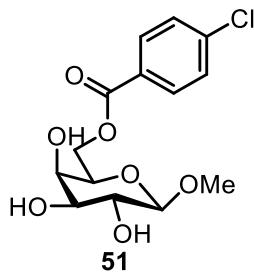
The product **49** (27.6 mg, 70%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.10 – 7.99 (m, 2H), 7.69 – 7.54 (m, 2H), 7.27 – 7.20 (m, 2H), 7.09 (d, J = 7.9 Hz, 2H), 6.99 (t, J = 7.3 Hz, 1H), 5.05 (d, J = 7.4 Hz, 1H), 4.76 (dd, J = 11.8, 2.2 Hz, 2H), 4.65 (s, 1H), 4.58 (s, 1H), 4.44 (dd, J = 11.8, 7.3 Hz, 1H), 3.95 (ddd, J = 9.5, 7.3, 2.2 Hz, 1H), 3.67 – 3.47 (m, 3H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 164.85, 157.78, 138.84, 131.12, 129.22, 129.07, 128.79, 122.00, 116.42, 100.80, 76.98, 74.02, 73.77, 70.60, 64.50. **ESI-MS:** calcd for $\text{C}_{19}\text{H}_{19}\text{O}_7\text{ClNa}$ [M + Na] $^+$: 417.0717, found: 417.0711.



50

Octyl-6-O-(4-chlorobenzoyl)- β -D-glucopyranoside (50)

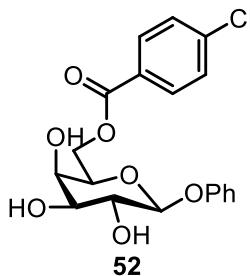
The product **50** (26.7 mg, 62%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.11 – 7.86 (m, 2H), 7.72 – 7.19 (m, 2H), 4.67 (dd, J = 11.7, 2.2 Hz, 1H), 4.47 (dd, J = 11.7, 6.2 Hz, 2H), 4.33 (d, J = 7.7 Hz, 2H), 4.27 (s, 1H), 3.78 (dt, J = 9.8, 6.7 Hz, 1H), 3.65 (dq, J = 6.2, 3.3, 2.2 Hz, 1H), 3.55 – 3.49 (m, 1H), 3.49 – 3.41 (m, 2H), 3.23 (dd, J = 9.5, 6.3 Hz, 1H), 1.55 (p, J = 6.9 Hz, 2H), 1.37 – 1.16 (m, 10H), 0.86 (dt, J = 13.3, 6.9 Hz, 3H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 166.16, 139.76, 131.21, 128.77, 128.16, 102.69, 76.12, 73.91, 73.59, 70.45, 70.27, 64.23, 31.82, 29.62, 29.37, 29.27, 25.90, 22.65, 14.09. **ESI-MS:** calcd for $\text{C}_{21}\text{H}_{31}\text{O}_7\text{ClNa}$ [M + Na] $^+$: 453.1656, found: 453.1654.



51

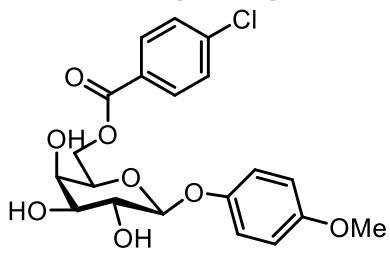
Methyl-6-O-(4-chlorobenzoyl)- β -D-galactopyranoside (51)

The product **51** (20.9 mg, 63%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.18 – 7.92 (m, 2H), 7.63 – 7.45 (m, 2H), 4.54 (qd, J = 11.1, 6.3 Hz, 2H), 4.19 (d, J = 7.3 Hz, 1H), 4.00 – 3.91 (m, 2H), 3.62 – 3.49 (m, 2H), 3.44 (s, 3H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 164.90, 138.82, 131.09, 129.08, 128.80, 104.57, 73.54, 72.35, 71.23, 68.78, 64.13, 55.68. **ESI-MS:** calcd for $\text{C}_{14}\text{H}_{17}\text{O}_7\text{ClNa}$ [M + Na] $^+$: 355.0561, found: 355.0552.



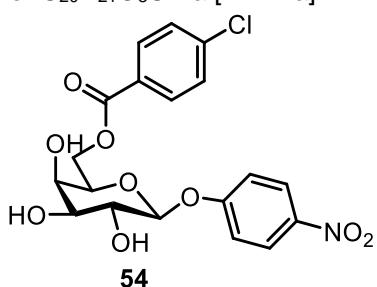
Phenyl-6-O-(4-chlorobenzoyl)- β -D-galactopyranoside (52)

The product **52** (29.6 mg, 75%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.11 – 7.98 (m, 2H), 7.68 – 7.51 (m, 2H), 7.23 (t, J = 7.9 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 6.98 (t, J = 7.3 Hz, 1H), 4.99 (d, J = 7.7 Hz, 1H), 4.59 (qd, J = 11.4, 6.2 Hz, 3H), 4.31–4.20 (m, 2H), 4.08–4.04 (m, 2H), 3.91 – 3.85 (m, 1H), 3.76 (dd, J = 9.5, 3.3 Hz, 1H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 164.85, 157.89, 138.88, 131.11, 129.19, 129.04, 128.80, 121.91, 116.45, 101.18, 73.57, 72.78, 71.05, 68.87, 64.46. **ESI-MS:** calcd for $\text{C}_{19}\text{H}_{19}\text{O}_7\text{ClNa} [\text{M} + \text{Na}]^+$: 417.0717, found: 417.0696.



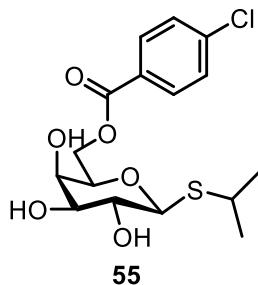
(4-methoxyphenyl)-6-O-(4-chlorobenzoyl)- β -D-galactopyranoside (53)

The product **53** (28.8 mg, 68%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, DMSO- d_6)** δ 8.06 – 7.83 (m, 2H), 7.65 (d, J = 8.5 Hz, 2H), 6.98 – 6.83 (m, 2H), 6.78 – 6.51 (m, 2H), 5.23 (d, J = 5.0 Hz, 1H), 4.98 (d, J = 5.6 Hz, 1H), 4.86 (d, J = 4.9 Hz, 1H), 4.73 (d, J = 7.6 Hz, 1H), 4.51 (dd, J = 11.3, 8.7 Hz, 1H), 4.34 (dd, J = 11.3, 3.7 Hz, 1H), 4.00 (dd, J = 9.0, 3.7 Hz, 1H), 3.77 (t, J = 4.2 Hz, 1H), 3.66 (s, 3H), 3.57 (td, J = 8.6, 7.8, 4.8 Hz, 1H), 3.50 – 3.42 (m, 1H). **$^{13}\text{C NMR}$ (101 MHz, DMSO- d_6)** δ 165.11, 154.58, 151.69, 138.82, 131.53, 129.43, 128.99, 117.85, 114.62, 101.99, 73.49, 72.83, 70.60, 68.82, 64.97, 55.66. **ESI-MS:** calcd for $\text{C}_{20}\text{H}_{21}\text{O}_8\text{ClNa} [\text{M} + \text{Na}]^+$: 447.0823, found: 447.0817.



4-Nitrophenyl-6-O-(4-chlorobenzoyl)- β -D-galactopyranoside (54)

The product **54** (30.3 mg, 69%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.09 (dd, J = 13.7, 8.9 Hz, 4H), 7.71 – 7.39 (m, 2H), 7.31 – 7.08 (m, 2H), 5.22 (d, J = 7.7 Hz, 1H), 4.80 (s, 1H), 4.66 (dd, J = 11.5, 8.4 Hz, 1H), 4.56 (dd, J = 11.5, 4.0 Hz, 1H), 4.41 (s, 1H), 4.32 (ddd, J = 8.4, 4.1, 1.2 Hz, 1H), 4.20 – 4.14 (m, 1H), 4.10 (d, J = 3.5 Hz, 1H), 3.94 (dd, J = 9.5, 7.7 Hz, 1H), 3.79 (dd, J = 9.5, 3.4 Hz, 1H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 164.78, 162.49, 142.31, 139.02, 131.13, 128.95, 128.84, 125.36, 116.51, 100.49, 73.42, 73.13, 70.76, 68.72, 64.23. **ESI-MS:** calcd for $\text{C}_{19}\text{H}_{18}\text{O}_9\text{ClNa} [\text{M} + \text{Na}]^+$: 462.0568, found: 462.0554.

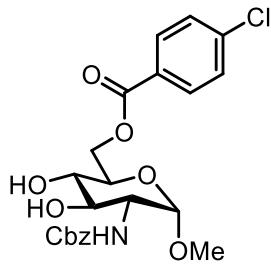


Isopropylthio-6-O-(4-chlorobenzoyl)- β -D-galactopyranoside (55)

The product **55** (25.6 mg, 68%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.14 – 7.90 (m, 2H), 7.66 – 7.44 (m, 2H), 4.67 – 4.41 (m, 3H), 4.17 – 3.82 (m, 5H), 3.69 – 3.52 (m, 2H), 3.18 (p, J = 6.8 Hz, 1H), 1.26 (d, J = 6.7 Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6) δ 164.86, 138.82, 131.07, 129.07, 128.75, 85.46, 76.03, 74.88, 70.52, 69.15, 64.60, 34.41, 23.60, 23.29.

ESI-MS: calcd for $\text{C}_{16}\text{H}_{21}\text{O}_6\text{CISNa}$ $[\text{M} + \text{Na}]^+$: 399.0645, found: 399.0641.



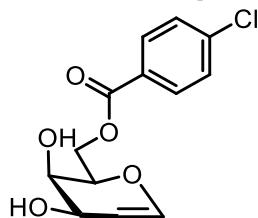
56

Methyl 2-(benzyloxy)carbonylamino-2-deoxy-6-O-(4-chlorobenzoyl)- α -D-glucopyranoside (56)

The product **56** (26.0 mg, 56%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Chloroform- d)** δ 8.00 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.37 (m, 5H), 5.30 (d, J = 9.3 Hz, 1H), 5.12 (q, J = 12.0 Hz, 2H), 4.73 (d, J = 3.7 Hz, 1H), 4.69 – 4.49 (m, 2H), 3.86 (m, 2H), 3.72 (t, J = 9.5 Hz, 1H), 3.55 (t, J = 9.3 Hz, 1H), 3.37 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) δ 166.08, 157.15, 139.75, 135.94, 131.15, 128.83, 128.60, 128.36, 128.31, 128.18, 98.66, 73.71, 71.01, 69.78, 67.42, 63.94, 55.26, 55.14.

ESI-MS: calcd for $\text{C}_{22}\text{H}_{24}\text{NO}_8\text{CINa}$ $[\text{M} + \text{Na}]^+$: 488.1088, found: 488.1071



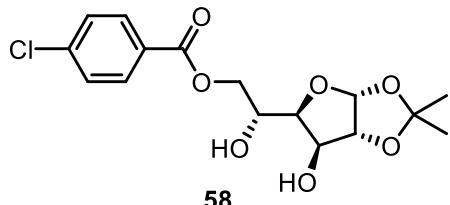
57

6-O-(4-chlorobenzoyl)-D-galactal (57)

Following the general procedure A, the product **57** (17.0 mg, 60%) was obtained as white solid. Following the general procedure C, the product **57** (15.9 mg, 56%) was obtained. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.11 – 7.94 (m, 2H), 7.65 – 7.45 (m, 2H), 6.35 (dd, J = 6.3, 1.7 Hz, 1H), 4.73 – 4.62 (m, 2H), 4.56 (dd, J = 11.6, 4.5 Hz, 1H), 4.42 (dt, J = 4.4, 2.1 Hz, 1H), 4.33 (ddd, J = 8.1, 4.5, 1.6 Hz, 1H), 4.03 (dt, J = 4.7, 1.7 Hz, 1H).

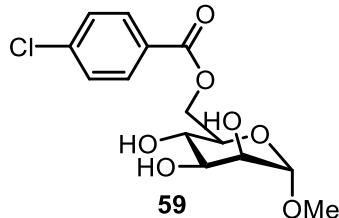
$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6) δ 164.93, 143.28, 138.88, 131.13, 128.97, 128.80, 103.23, 74.51, 65.31, 64.16, 63.10.

ESI-MS: calcd for $\text{C}_{13}\text{H}_{13}\text{O}_5\text{CINa}$ $[\text{M} + \text{Na}]^+$: 307.0349, found: 307.0340.



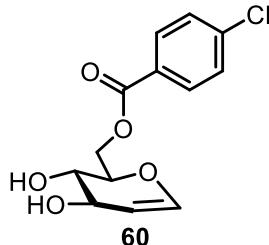
1,2-O-Isopropylidene-6-O-(4-chlorobenzoyl)-D-glucofuranose (58)

The product **58** (24.3 mg, 68%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-d₆)** δ 8.15 – 7.92 (m, 2H), 7.70 – 7.37 (m, 2H), 5.90 (d, *J* = 3.7 Hz, 1H), 4.61 (dd, *J* = 11.2, 2.4 Hz, 1H), 4.52 (dd, *J* = 13.1, 4.1 Hz, 3H), 4.37 (dd, *J* = 11.2, 6.2 Hz, 1H), 4.31 (tq, *J* = 6.0, 3.3 Hz, 2H), 4.18 (dd, *J* = 8.3, 2.8 Hz, 1H), 1.43 (s, 3H), 1.28 (s, 3H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 165.09, 138.71, 131.15, 129.26, 128.69, 111.04, 105.13, 85.32, 80.26, 74.21, 67.64, 66.73, 26.29, 25.62. **ESI-MS:** calcd for C₁₆H₁₉O₇ClNa [M + Na]⁺: 381.0717, found: 381.0708.



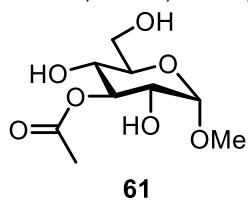
Methyl-6-O-(4-chlorobenzoyl)-α-D-mannopyranoside (59)

The product **59** (32.2 mg, 97%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-d₆)** δ 8.16 – 7.87 (m, 2H), 7.61 – 7.41 (m, 2H), 4.67 (td, *J* = 5.9, 5.0, 1.8 Hz, 2H), 4.47 (dd, *J* = 11.7, 5.9 Hz, 1H), 4.30 (d, *J* = 4.1 Hz, 1H), 4.01 (dd, *J* = 11.1, 5.1 Hz, 2H), 3.89 – 3.73 (m, 3H), 3.72 – 3.64 (m, 1H), 3.37 (s, 3H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 165.04, 138.75, 131.08, 129.20, 128.78, 101.34, 71.69, 70.71, 70.62, 67.68, 64.70, 53.97. **ESI-MS:** calcd for C₁₄H₁₇O₇ClNa [M + Na]⁺: 355.0561, found: 355.0565.



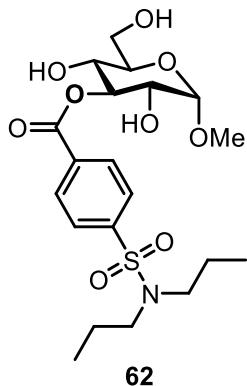
6-O-(4-chlorobenzoyl)-D-glucal (60)

The product **60** (20.2 mg, 71%) was obtained. **¹H NMR (400 MHz, Acetone-d₆)** δ 8.13 – 7.93 (m, 2H), 7.73 – 7.47 (m, 2H), 6.33 (dd, *J* = 6.0, 1.7 Hz, 1H), 4.74 (dd, *J* = 6.1, 2.2 Hz, 1H), 4.70 (dd, *J* = 12.1, 2.3 Hz, 1H), 4.61 (dd, *J* = 12.1, 5.3 Hz, 1H), 4.22 (dt, *J* = 7.0, 2.0 Hz, 1H), 4.09 (ddd, *J* = 9.8, 5.3, 2.3 Hz, 1H), 3.76 (dd, *J* = 9.7, 7.0 Hz, 1H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 164.95, 142.96, 138.85, 131.12, 129.04, 128.81, 104.49, 76.40, 69.75, 69.11, 63.77. **ESI-MS:** calcd for C₁₃H₁₃O₅ClNa [M + Na]⁺: 307.0349, found: 307.0334.



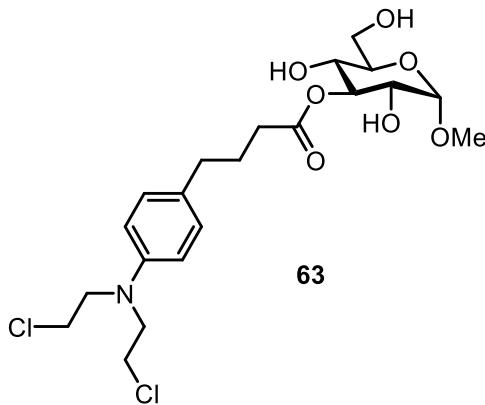
Methyl-3-O-acetyl-α-D-glucopyranoside (61)

The product **61** (15.4 mg, 65%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-d₆)** δ 5.13 (dd, *J* = 9.9, 8.8 Hz, 1H), 4.71 (d, *J* = 3.6 Hz, 1H), 4.43 (s, 1H), 3.81 (dd, *J* = 11.4, 2.6 Hz, 1H), 3.71 (dd, *J* = 12.0, 4.6 Hz, 3H), 3.63 – 3.45 (m, 3H), 3.40 (s, 3H), 2.03 (s, 3H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 170.48, 99.88, 76.09, 72.37, 70.72, 68.67, 61.48, 54.45, 20.28. **ESI-MS:** calcd for C₉H₁₇O₇ [M + H]⁺: 237.0974, found: 237.0983.



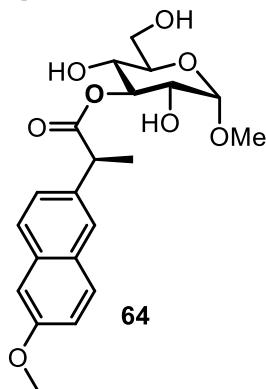
Methyl-3-O-(4-(N,N-dipropylsulfamoyl)benzoyl)- α -D-glucopyranoside (62)

Following the general procedure B, the product **62** (33.2 mg, 72%) was obtained as white solid. Following the general procedure C, the product **62** (28.6 mg) was obtained (total acylates 32.7 mg, 71%). **$^1\text{H NMR}$ (500 MHz, Chloroform- d)** δ 8.20 (d, $J = 8.6$ Hz, 2H), 7.87 (d, $J = 8.5$ Hz, 2H), 5.37 (t, $J = 9.5$ Hz, 1H), 4.86 (d, $J = 3.8$ Hz, 1H), 3.98 – 3.80 (m, 3H), 3.76 (tt, $J = 9.8, 3.8$ Hz, 2H), 3.50 (s, 3H), 3.21 – 2.98 (m, 4H), 3.05 (s, 1H), 2.36 (d, $J = 11.2$ Hz, 1H), 2.21 (s, 1H), 1.63 – 1.48 (m, 4H), 0.89 (t, $J = 7.4$ Hz, 6H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform- d)** δ 166.39, 144.57, 132.95, 130.57, 127.00, 99.40, 78.00, 71.37, 70.93, 69.14, 62.07, 55.56, 49.92, 21.91, 11.15. **ESI-MS:** calcd for $\text{C}_{20}\text{H}_{32}\text{O}_9\text{NS} [\text{M} + \text{H}]^+$: 462.1798, found: 462.1799.



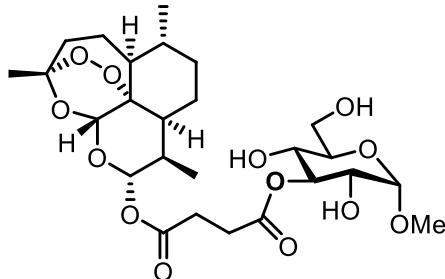
Methyl-3-O-(bis(2-chloroethyl)amino)phenylbutanoyl- α -D-glucopyranoside (63)

The product **63** (32.2 mg, 67%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 7.18 – 6.99 (m, 2H), 6.85 – 6.54 (m, 2H), 5.18 (t, $J = 9.4$ Hz, 1H), 4.71 (d, $J = 3.6$ Hz, 1H), 4.40 (d, $J = 5.6$ Hz, 1H), 3.85 – 3.67 (m, 10H), 3.65 – 3.46 (m, 5H), 3.41 (s, 3H), 2.58 (t, $J = 7.6$ Hz, 2H), 2.35 (t, $J = 7.4$ Hz, 2H), 1.88 (p, $J = 7.5$ Hz, 2H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 173.00, 144.72, 130.52, 129.57, 112.22, 99.95, 75.89, 72.47, 70.84, 68.76, 61.54, 54.45, 53.03, 40.76, 33.62, 33.38, 27.05. **ESI-MS:** calcd for $\text{C}_{21}\text{H}_{32}\text{O}_7\text{NCl}_2 [\text{M} + \text{H}]^+$: 480.1556, found: 480.1567.



Methyl-3-O-(2-(6-methoxynaphthyl) propionyl)- α -D-glucopyranoside (64)

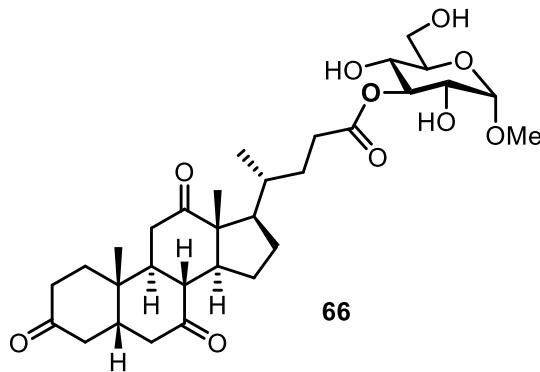
The product **64** (25.6 mg, 63%, dr 1:4) was obtained as white solid. **¹H NMR (400 MHz, Chloroform-d)** δ 7.72 (dd, *J* = 8.9, 2.1 Hz, 3H), 7.43 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.19 – 7.01 (m, 2H), 5.07 (t, *J* = 9.2 Hz, 1H), 4.73 (d, *J* = 3.8 Hz, 1H), 3.99 (q, *J* = 7.2 Hz, 1H), 3.93 (s, 3H), 3.88 – 3.79 (m, 2H), 3.67 – 3.58 (m, 2H), 3.55 – 3.49 (m, 1H), 3.42 (s, 3H), 1.63 (d, *J* = 7.3 Hz, 3H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 174.14, 157.69, 136.50, 133.74, 129.20, 129.00, 126.77, 126.65, 125.92, 118.60, 105.55, 99.96, 76.38, 72.44, 70.83, 68.68, 61.51, 54.71, 54.45, 45.37, 18.76. **ESI-MS:** calcd for C₂₁H₂₆O₈Na [M + Na]⁺: 429.1525, found: 429.1524.



65

Methyl-3-O-artesunate-α-D-glucopyranoside (**65**)

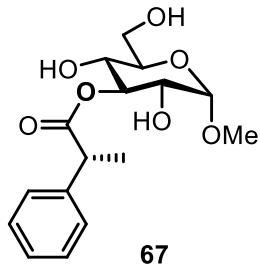
The product **65** (39.2 mg, 70%) was obtained as white solid. **¹H NMR (400 MHz, Chloroform-d)** δ 5.79 (d, *J* = 9.9 Hz, 1H), 5.45 (s, 1H), 5.23 – 5.06 (m, 1H), 4.79 (d, *J* = 3.8 Hz, 1H), 3.88 (d, *J* = 3.3 Hz, 2H), 3.77 – 3.66 (m, 2H), 3.65 – 3.55 (m, 1H), 3.46 (s, 3H), 2.98 – 2.64 (m, 4H), 2.58 (ddd, *J* = 9.9, 7.2, 4.5 Hz, 1H), 2.46 – 2.33 (m, 1H), 2.05 (ddd, *J* = 14.8, 4.8, 3.0 Hz, 1H), 1.92 (ddd, *J* = 13.8, 6.5, 3.4 Hz, 1H), 1.76 (ddt, *J* = 16.4, 13.1, 3.7 Hz, 2H), 1.64 (dt, *J* = 14.0, 4.4 Hz, 1H), 1.55 – 1.29 (m, 7H), 1.09 – 1.00 (m, 1H), 0.98 (d, *J* = 5.9 Hz, 3H), 0.87 (d, *J* = 7.1 Hz, 3H). **¹³C NMR (101 MHz, Chloroform-d)** δ 172.68, 172.43, 104.65, 99.46, 92.49, 91.57, 80.13, 77.25, 71.15, 70.63, 69.07, 62.27, 55.39, 51.53, 45.18, 37.22, 36.17, 34.03, 31.60, 29.58, 29.42, 25.88, 24.56, 21.96, 20.18, 12.04. **ESI-MS:** calcd for C₂₆H₄₀O₁₃Na [M + Na]⁺: 583.2367, found: 583.2365.



66

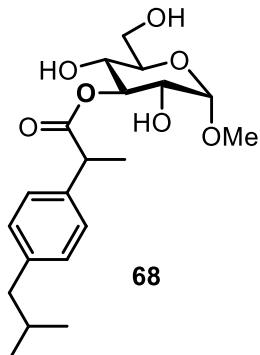
Methyl-3-O-dehydrocholyl-α-D-glucopyranoside (**66**)

The product **66** (44.5 mg, 77%) was obtained as white solid. **¹H NMR (400 MHz, Chloroform-d)** δ 5.08 (t, *J* = 9.1 Hz, 1H), 4.81 (d, *J* = 3.8 Hz, 1H), 3.98 – 3.81 (m, 2H), 3.75 – 3.57 (m, 3H), 3.47 (s, 3H), 3.04 – 2.78 (m, 3H), 2.53 (ddd, *J* = 14.9, 9.1, 5.3 Hz, 1H), 2.46 – 2.12 (m, 10H), 2.09 – 1.98 (m, 4H), 1.97 – 1.80 (m, 2H), 1.64 (td, *J* = 14.2, 13.4, 4.9 Hz, 3H), 1.48 (ddt, *J* = 13.2, 8.4, 4.4 Hz, 1H), 1.42 (s, 3H), 1.38 – 1.24 (m, 3H), 1.09 (s, 3H), 0.88 (d, *J* = 6.6 Hz, 3H). **¹³C NMR (101 MHz, Chloroform-d)** δ 212.14, 209.11, 208.71, 175.92, 99.36, 77.22, 76.78, 71.41, 70.78, 69.39, 62.19, 56.93, 55.47, 51.78, 49.00, 46.85, 45.55, 44.98, 42.80, 38.63, 36.49, 36.02, 35.36, 35.29, 31.55, 30.40, 27.60, 25.14, 21.91, 18.64, 11.85. **ESI-MS:** calcd for C₃₁H₄₆O₁₀Na [M + Na]⁺: 601.2989, found: 601.2977.



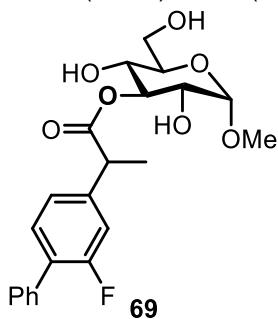
Methyl-3-O-(2-phenyl propionyl)-α-D-glucopyranoside (67)

The product **67** (24.1 mg, 74%, dr 15:1) was obtained as white solid. **¹H NMR (400 MHz, Chloroform-d)** δ 7.39 – 7.27 (m, 5H), 5.02 (t, *J* = 9.5 Hz, 1H), 4.76 (d, *J* = 3.8 Hz, 1H), 3.89 – 3.66 (m, 3H), 3.63 – 3.46 (m, 3H), 3.42 (s, 3H), 2.25 (s, 1H), 2.17 (s, 1H), 1.98 (s, 1H), 1.51 (d, *J* = 7.1 Hz, 3H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 174.04, 141.36, 128.29, 127.65, 126.63, 99.92, 76.33, 72.51, 70.81, 68.73, 61.45, 54.45, 45.47, 18.88. **ESI-MS:** calcd for C₁₆H₂₂O₇Na [M + Na]⁺: 349.1263, found: 349.1251.



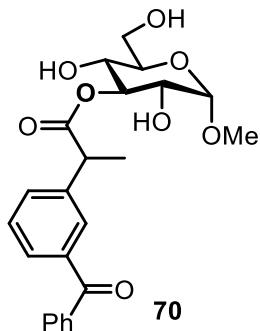
Methyl-3-O-(2-(4-isobutylphenyl) propionyl)-α-D-glucopyranoside (68)

The product **68** (30.9 mg, 81%, dr 1.5:1) was obtained as white solid. **¹H NMR (400 MHz, Chloroform-d)** δ 7.22 (dd, *J* = 8.2, 2.9 Hz, 2H), 7.11 (dd, *J* = 8.2, 2.3 Hz, 2H), 5.03 (t, *J* = 9.5 Hz, 1H), 4.77 (d, *J* = 3.8 Hz, 1H), 3.86-3.73 (m, 3H), 3.67 – 3.48 (m, 3H), 3.43 (s, 3H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.85 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.52 (d, *J* = 7.1 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H). **¹³C NMR (101 MHz, Chloroform-d)** δ (176.40)176.12, 140.83(140.71), 137.93(137.47), 129.53(129.40), (127.15)127.07, 99.46(99.32), 77.18(71.38), 71.15, 70.80(70.72), (69.09)68.95, (62.00)61.90, 55.41(55.38), (45.32)45.27, (45.01)44.99, 30.15, (22.37)22.35, (18.32)18.27. **ESI-MS:** calcd for C₂₀H₃₀O₇Na [M + Na]⁺: 405.1889, found: 405.1896.



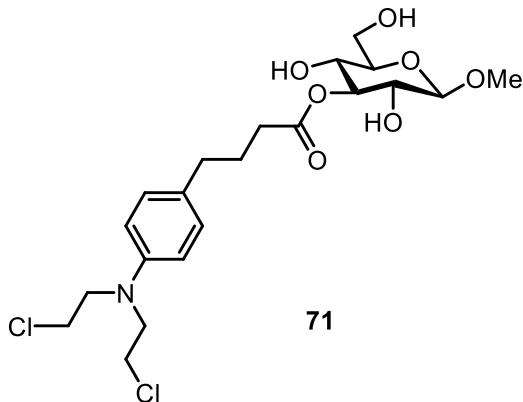
Methyl-3-O-(2-(2-fluoro-[1,1'-biphenyl]-4-yl) propionyl)-α-D-glucopyranoside (69)

The product **69** (32.3 mg, 77%, dr 1.9:1) was obtained as white solid. **¹H NMR (400 MHz, Chloroform-d)** δ 7.55 (dt, *J* = 8.1, 1.5 Hz, 2H), 7.50 – 7.34 (m, 4H), 7.22 – 6.94 (m, 2H), 5.11 (t, *J* = 9.3 Hz, 1H), 4.79 (d, *J* = 3.8 Hz, 1H), 4.05 – 3.74 (m, 3H), 3.72 – 3.55 (m, 3H), 3.46 (s, 3H), 2.84 (s, 1H), 2.49 (s, 1H), 2.28 (d, *J* = 11.1 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 173.51, 159.45 (d, *J* = 245.9 Hz), (143.16 (d, *J* = 8.0 Hz)143.14 (d, *J* = 8.0 Hz), 135.57, 130.55 (d, *J* = 3.7 Hz), 128.82 (d, *J* = 3.0 Hz), 128.48, 127.13 (d, *J* = 13.5 Hz)(127.11 (d, *J* = 13.5 Hz), 127.06, 124.16 (d, *J* = 3.2 Hz), 115.31 (d, *J* = 23.8 Hz), (99.96)99.93, (96.63)76.54, 72.52(72.43), 70.80(70.69), 68.68(68.63), (61.48)61.43, (54.48)54.47, 44.96(44.91), 18.70(18.64). **ESI-MS:** calcd for C₂₂H₂₅O₇FNa [M + Na]⁺: 443.1482, found: 443.1476.



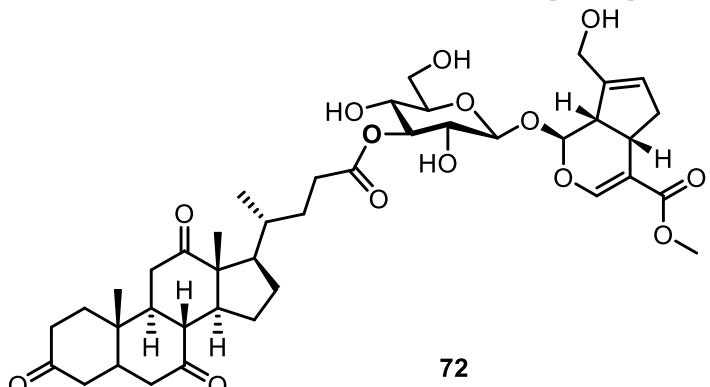
Methyl-3-O-(2-(3-benzoylphenyl) propionyl)- α -D-glucopyranoside (70)

The product **70** (33.5 mg, 78%, dr 1.6:1) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Chloroform- d)** δ 7.90 – 7.77 (m, 3H), 7.68 – 7.54 (m, 3H), 7.47 (dtd, J = 25.8, 7.9, 1.6 Hz, 3H), 5.12 (t, J = 9.26 Hz, 1H), 4.78 (d, J = 3.8 Hz, 1H), 3.93 (p, J = 7.0 Hz, 1H), 3.84 (d, J = 4.6 Hz, 2H), 3.70 – 3.52 (m, 3H), 3.45 (s, 3H), 3.26 (d, J = 4.0 Hz, 1H), 3.14 (d, J = 5.2 Hz, 1H), 2.40 (d, J = 11.0 Hz, 1H), 1.58 (d, J = 7.2 Hz, 3H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform- d)** δ 197.13(197.03), (175.31)175.20, 141.17(140.79), 137.99(137.86), (137.26)137.13, 132.81(132.71), (131.70)131.53, 130.26(130.22), (129.20)129.16, (129.12)129.04, 128.49(128.45), 128.38(128.36), 99.43, (77.19)77.08, 71.44, 70.82(70.76), (68.90)68.69, (61.98)61.87, 55.44, (45.68)45.46, (18.46)18.37. **ESI-MS:** calcd for $\text{C}_{23}\text{H}_{26}\text{O}_8\text{Na} [\text{M} + \text{Na}]^+$: 453.1525, found: 453.1520.



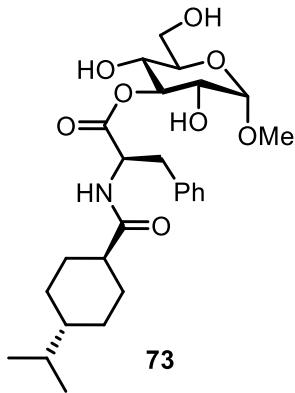
Methyl-3-O-(bis(2-chloroethyl)amino)phenylbutanoyl- β -D-glucopyranoside (71)

The product **71** (24.0 mg, 50%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 7.26 – 6.98 (m, 2H), 6.85 – 6.58 (m, 2H), 5.00 (t, J = 9.4 Hz, 1H), 4.30 (d, J = 7.7 Hz, 1H), 3.86 (dd, J = 11.7, 2.8 Hz, 1H), 3.82 – 3.68 (m, 10H), 3.53 (t, J = 9.5 Hz, 1H), 3.48 (s, 3H), 3.31 (dd, J = 9.6, 7.8 Hz, 1H), 2.58 (t, J = 7.6 Hz, 2H), 2.35 (t, J = 7.5 Hz, 2H), 1.95 – 1.79 (m, 2H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 172.62, 144.73, 130.50, 129.57, 112.23, 104.13, 77.62, 76.48, 72.14, 68.96, 61.68, 55.98, 53.03, 40.76, 33.62, 33.35, 27.03. **ESI-MS:** calcd for $\text{C}_{21}\text{H}_{32}\text{O}_7\text{NCl}_2 [\text{M} + \text{H}]^+$: 480.1556, found: 480.1548.



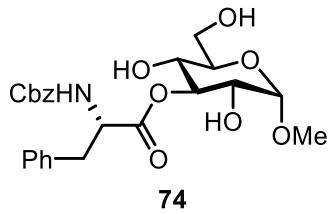
3-O-Dehydrocholyl-geniposide (72)

The product **72** (37.0 mg, 48%) was obtained as white solid. **¹H NMR (400 MHz, Chloroform-d)** δ 7.48 (d, *J* = 1.3 Hz, 1H), 5.90 (s, 1H), 5.03 – 4.93 (m, 2H), 4.92 – 4.75 (m, 1H), 4.37 – 4.14 (m, 2H), 3.91 – 3.77 (m, 2H), 3.74 (s, 3H), 3.72–3.70 (m, 1H), 3.58 – 3.48 (m, 1H), 3.46 – 3.38 (m, 1H), 3.23 (q, *J* = 8.2 Hz, 1H), 2.99 – 2.81 (m, 4H), 2.67 (t, *J* = 8.0 Hz, 1H), 2.56–2.50 (m, 1H), 2.45 – 2.28 (m, 5H), 2.25 (s, 1H), 2.23 – 2.18 (m, 2H), 2.18 – 2.11 (m, 2H), 2.10 – 1.94 (m, 4H), 1.98–1.92 (m, 3H), 1.91 – 1.81 (m, 3H), 1.63 (td, *J* = 14.5, 4.4 Hz, 1H), 1.54 – 1.43 (m, 1H), 1.41 (s, 3H), 1.38 – 1.23 (m, 3H), 1.08 (s, 3H), 0.87 (d, *J* = 6.6 Hz, 3H). **¹³C NMR (101 MHz, Chloroform-d)** δ 212.52, 209.34, 208.90, 175.46, 167.51, 151.44, 142.59, 130.00, 111.61, 100.20, 98.77, 77.51, 76.44, 71.96, 68.31, 61.16, 60.83, 56.95, 51.82, 51.40, 48.98, 46.84, 46.41, 45.53, 45.45, 44.98, 42.76, 38.94, 38.64, 36.46, 36.02, 35.64, 35.33, 35.26, 31.36, 30.34, 27.61, 25.12, 21.88, 18.65, 11.84. **ESI-MS:** calcd for C₄₁H₅₆O₁₄Na [M + Na]⁺: 795.3568, found: 795.3568.



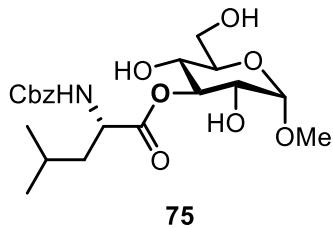
Methyl-3-O-(4-isopropylcyclohexane-1-carbonyl-D-phenylalanyl)-α-D-glucopyranoside (73)

The product **73** (40.9 mg, 83%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-d₆)** δ 7.53 – 7.13 (m, 5H), 5.21 (dd, *J* = 10.0, 8.8 Hz, 1H), 4.72 (d, *J* = 3.7 Hz, 1H), 4.62 – 4.39 (m, 1H), 3.81 (d, *J* = 11.5 Hz, 1H), 3.76 – 3.66 (m, 1H), 3.65 – 3.49 (m, 3H), 3.41 (s, 3H), 3.27 (dd, *J* = 13.9, 5.1 Hz, 1H), 3.05 (dd, *J* = 13.9, 9.0 Hz, 1H), 2.13 (tt, *J* = 12.3, 3.5 Hz, 1H), 1.84–1.75 (m, 4H), 1.48 – 1.28 (m, 3H), 1.07 – 0.93 (m, 3H), 0.86 (d, *J* = 6.8 Hz, 6H). **¹³C NMR (101 MHz, DMSO-d₆)** δ 175.85, 171.65, 138.17, 129.71, 128.50, 126.74, 99.92, 77.04, 72.92, 70.24, 68.13, 60.89, 54.89, 53.44, 44.26, 43.27, 37.28, 32.78, 29.58, 29.50, 28.97, 28.91, 20.10. **ESI-MS:** calcd for C₂₆H₄₀O₈N [M + H]⁺: 494.2754, found: 494.2755.



Methyl-3-O-((benzyloxy)carbonyl)-D-phenylalanyl-α-D-glucopyranoside (74)

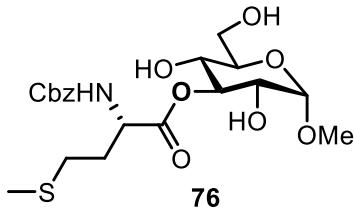
The product **74** (40.4 mg, 85%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-d₆)** δ 7.46 – 7.02 (m, 10H), 6.65 (d, *J* = 8.3 Hz, 1H), 5.22 (t, *J* = 9.2 Hz, 1H), 5.05 (s, 2H), 4.73 (d, *J* = 3.6 Hz, 1H), 4.53 (td, *J* = 8.6, 4.8 Hz, 2H), 3.87 – 3.79 (m, 1H), 3.72 (dd, *J* = 11.8, 4.6 Hz, 2H), 3.67 – 3.49 (m, 4H), 3.42 (s, 3H), 3.31 (dd, *J* = 14.0, 4.8 Hz, 1H), 3.03 (dd, *J* = 14.1, 9.0 Hz, 1H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 171.53, 156.23, 137.45, 137.16, 129.44, 128.33, 128.24, 127.78, 127.68, 126.51, 99.90, 77.65, 72.27, 70.57, 68.54, 65.92, 61.46, 55.68, 54.45, 37.29. **ESI-MS:** calcd for C₂₄H₂₉O₉NNa [M + Na]⁺: 498.1740, found: 498.1727.



Methyl-3-O-(N-Cbz-L-leucine acyl)-α-D-glucopyranoside (75)

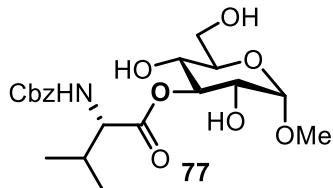
The product **75** (38.0 mg, 86%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-d₆)** δ 7.52 – 7.06 (m, 5H), 6.73 (d, *J* = 8.1 Hz, 1H), 5.15 (t, *J* = 9.1 Hz, 1H), 5.08 (s, 2H), 4.68 (d, *J* = 3.6 Hz, 1H), 4.41 (s,

1H), 4.28 (td, J = 9.1, 8.6, 5.3 Hz, 1H), 3.80 (d, J = 11.9 Hz, 1H), 3.69 (dd, J = 12.8, 3.9 Hz, 1H), 3.62 – 3.50 (m, 4H), 3.46 (d, J = 7.9 Hz, 1H), 3.39 (s, 3H), 1.81 (dq, J = 12.7, 6.5 Hz, 1H), 1.67 (qdd, J = 14.1, 9.0, 5.6 Hz, 2H), 0.93 (dd, J = 6.6, 3.5 Hz, 6H). **^{13}C NMR (101 MHz, Acetone- d_6)** δ 173.57, 157.45, 138.09, 129.24, 128.72, 128.64, 100.79, 78.18, 73.18, 71.51, 69.47, 66.90, 62.40, 55.33, 53.81, 41.53, 25.38, 23.27, 21.89. **ESI-MS:** calcd for $\text{C}_{21}\text{H}_{32}\text{NO}_9$ [M + H] $^+$: 442.2077, found: 442.2073.



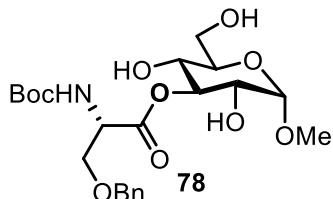
Methyl-3-O-(N-Cbz-L-methionine acyl)- α -D-glucopyranoside (76)

The product **76** (29.0 mg, 63%) was obtained as white solid. **^1H NMR (400 MHz, Chloroform- d)** δ 7.43 – 7.28 (m, 5H), 5.72 (d, J = 7.1 Hz, 1H), 5.25 – 4.96 (m, 3H), 4.77 (d, J = 3.8 Hz, 1H), 4.44 (q, J = 7.1 Hz, 1H), 3.84 (d, J = 3.0 Hz, 2H), 3.64 (d, J = 8.4 Hz, 2H), 3.54 (d, J = 9.3 Hz, 1H), 3.43 (s, 3H), 2.65 – 2.46 (m, 2H), 2.18 (tt, J = 12.4, 5.8 Hz, 1H), 2.08–1.99 (m, 4H). **^{13}C NMR (101 MHz, Chloroform- d)** δ 172.72, 156.55, 135.92, 128.60, 128.35, 128.17, 99.40, 77.93, 71.15, 70.59, 68.59, 67.39, 61.99, 55.45, 53.66, 31.01, 29.81, 15.37. **ESI-MS:** calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_9\text{SNa}$ [M + Na] $^+$: 482.1461, found: 482.1454.



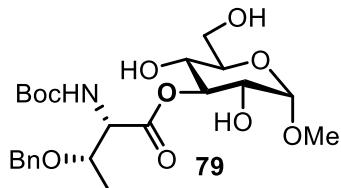
Methyl-3-O-(N-Cbz-L-valine acyl)- α -D-glucopyranoside (77)

The product **77** (33.0 mg, 77%) was obtained as white solid. **^1H NMR (400 MHz, Acetone- d_6)** δ 7.53 – 7.17 (m, 5H), 6.58 (d, J = 8.4 Hz, 1H), 5.18 (t, J = 8.9 Hz, 1H), 5.08 (s, 2H), 4.69 (d, J = 3.6 Hz, 1H), 4.48 (s, 1H), 4.19 (dd, J = 8.5, 5.0 Hz, 1H), 3.80 (d, J = 11.5 Hz, 1H), 3.70 (d, J = 11.0 Hz, 1H), 3.60 (q, J = 8.5, 6.9 Hz, 4H), 3.49 (td, J = 9.2, 3.3 Hz, 1H), 3.39 (s, 3H), 2.23 (dq, J = 13.3, 6.6 Hz, 1H), 0.99 (t, J = 7.5 Hz, 6H). **^{13}C NMR (101 MHz, Acetone- d_6)** δ 171.67, 156.66, 137.19, 128.35, 127.82, 127.80, 99.93, 77.17, 72.31, 70.64, 68.55, 66.04, 61.47, 59.82, 54.46, 30.65, 18.53, 17.12. **ESI-MS:** calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_9\text{Na}$ [M + Na] $^+$: 450.1740, found: 450.1738.



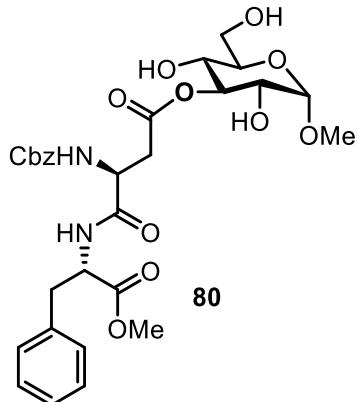
Methyl-3-O-(N-Boc-O-benzyl-L-serine acyl)- α -D-glucopyranoside (78)

The product **78** (35.0 mg, 74%) was obtained as white solid. **^1H NMR (400 MHz, Chloroform- d)** δ 7.41 – 6.97 (m, 5H), 5.49 (d, J = 7.6 Hz, 1H), 5.17 (t, J = 8.7 Hz, 1H), 4.79 (d, J = 3.7 Hz, 1H), 4.54 (s, 2H), 4.40 (s, 1H), 3.94 – 3.78 (m, 3H), 3.77 – 3.56 (m, 4H), 3.44 (s, 3H), 1.44 (s, 9H). **^{13}C NMR (101 MHz, Chloroform- d)** δ 171.17, 156.10, 137.14, 128.55, 128.05, 127.93, 99.34, 80.73, 78.38, 73.59, 71.13, 70.45, 69.55, 68.78, 62.04, 55.38, 54.42, 28.29. **ESI-MS:** calcd for $\text{C}_{22}\text{H}_{33}\text{NO}_{10}\text{Na}$ [M + Na] $^+$: 494.2002, found: 494.1996.



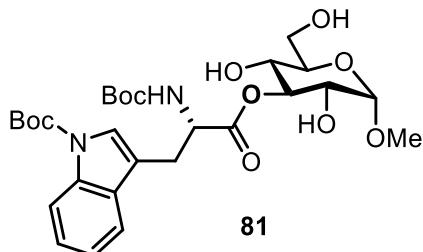
Methyl-3-O-(N-Boc-O-benzyl-L-threonine acyl)- α -D-glucopyranoside (79)

The product **79** (34.4 mg, 71%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-d₆)** δ 7.43 – 7.03 (m, 5H), 5.94 (d, *J* = 8.9 Hz, 1H), 5.37 – 5.11 (m, 1H), 4.71 (d, *J* = 3.3 Hz, 1H), 4.57 (d, *J* = 2.8 Hz, 2H), 4.28 (dd, *J* = 8.9, 3.1 Hz, 1H), 4.19 (qd, *J* = 6.2, 2.8 Hz, 1H), 3.81 (d, *J* = 11.6 Hz, 1H), 3.71 (d, *J* = 12.3 Hz, 1H), 3.67 – 3.52 (m, 3H), 3.39 (s, 3H), 1.42 (s, 9H), 1.25 (d, *J* = 6.3 Hz, 3H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 170.88, 156.03, 138.90, 128.01, 127.81, 127.22, 99.88, 78.83, 77.66, 74.90, 72.33, 70.95, 70.75, 70.64, 68.57, 61.47, 58.39, 54.46, 27.63, 16.39. **ESI-MS:** calcd for C₂₃H₃₆NO₁₀ [M + H]⁺: 486.2339, found: 486.2335.



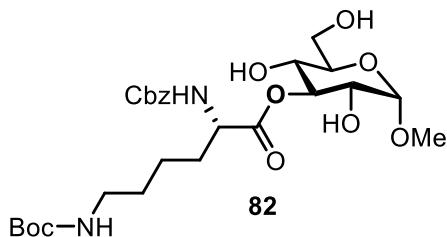
Methyl-3-O-(Methyl L-α-aspartyl-L-phenylalaninate)-α-D-glucopyranoside (80)

The product **80** (40.0 mg, 66%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-d₆)** δ 7.68 (d, *J* = 7.8 Hz, 1H), 7.46 – 7.12 (m, 10H), 6.75 (d, *J* = 8.6 Hz, 1H), 5.16 (t, *J* = 9.3 Hz, 1H), 5.08 (s, 2H), 4.74 – 4.56 (m, 3H), 4.38 (s, 1H), 3.83 – 3.72 (m, 2H), 3.67 (s, 4H), 3.62 – 3.48 (m, 4H), 3.38 (s, 3H), 3.18 – 2.99 (m, 2H), 2.75 (dd, *J* = 15.8, 6.6 Hz, 2H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 171.35, 170.96, 170.04, 169.66, 136.95, 136.68, 129.28, 128.37, 127.86, 127.81, 126.73, 99.84, 77.11, 72.17, 70.49, 68.65, 66.32, 61.53, 54.39, 53.82, 51.58, 37.12, 36.73. **ESI-MS:** calcd for C₂₉H₃₇N₂O₁₂ [M + H]⁺: 605.2346, found: 605.2347.



Methyl-3-O-(N_α-Boc-N-in-Boc-L-trypophan acyl)-α-D-glucopyranoside (81)

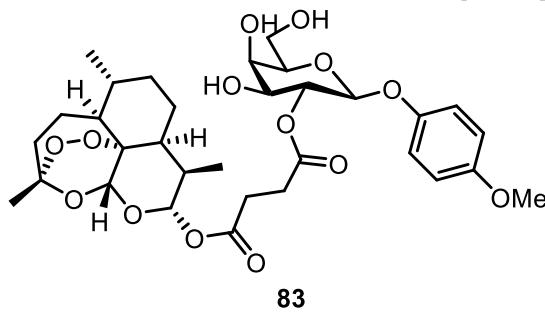
The product **81** (44 mg, 76%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-d₆)** δ 8.13 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.29 (m, 1H), 7.28 – 7.21 (m, 1H), 6.40 (d, *J* = 7.9 Hz, 1H), 5.25 (dd, *J* = 9.8, 8.0 Hz, 1H), 4.73 (d, *J* = 3.5 Hz, 1H), 4.51 (td, *J* = 8.2, 4.9 Hz, 1H), 3.81 (d, *J* = 11.5 Hz, 1H), 3.75 – 3.67 (m, 1H), 3.66 – 3.55 (m, 3H), 3.41 (s, 4H), 3.15 (dd, *J* = 14.9, 8.5 Hz, 1H), 1.66 (s, 9H), 1.37 (s, 9H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 171.64, 155.76, 149.41, 135.44, 130.85, 124.47, 124.14, 122.39, 119.03, 116.27, 114.96, 99.93, 83.22, 78.89, 77.69, 72.23, 70.55, 68.59, 61.47, 54.48, 54.15, 27.65, 27.38, 26.95. **ESI-MS:** calcd for C₂₈H₄₁N₂O₁₁ [M + H]⁺: 581.2710, found: 581.2706.



Methyl-3-O-(N_α-Cbz-N_ε-Boc-L-Lysine acyl)-α-D-glucopyranoside (82)

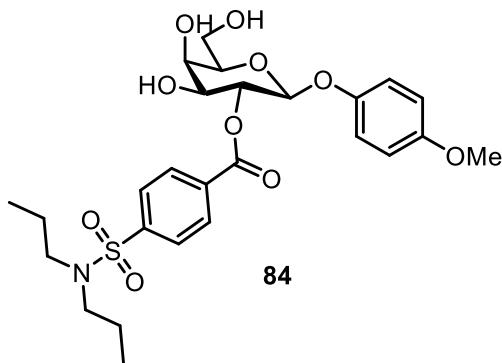
The product **82** (39.0 mg, 70%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-d₆)** δ 7.65 – 7.14 (m, 5H), 6.74 (d, *J* = 7.6 Hz, 1H), 5.98 (s, 1H), 5.18 (t, *J* = 9.1 Hz, 1H), 5.10 (s, 2H), 4.70 (d, *J* = 3.6 Hz, 1H), 4.25 (q, *J* = 7.2, 6.8 Hz, 1H), 3.82 (dd, *J* = 11.7, 2.2 Hz, 1H), 3.71 (dd, *J* = 11.7, 4.4 Hz, 1H), 3.65 –

3.46 (m, 3H), 3.41 (s, 3H), 3.07 (d, J = 6.0 Hz, 2H), 1.91 (q, J = 6.8, 5.1 Hz, 1H), 1.79 (t, J = 7.1 Hz, 1H), 1.50 (t, J = 4.9 Hz, 4H), 1.41 (s, 9H). **^{13}C NMR (101 MHz, Acetone- d_6)** δ 172.20, 156.46, 155.96, 137.16, 128.35, 127.83, 127.81, 99.91, 77.59, 77.25, 72.32, 70.54, 68.57, 66.03, 61.48, 54.44, 39.79, 31.30, 27.79, 22.42. **ESI-MS:** calcd for $\text{C}_{26}\text{H}_{41}\text{N}_2\text{O}_{11}$ [M + H] $^+$: 557.2710, found: 557.2708.



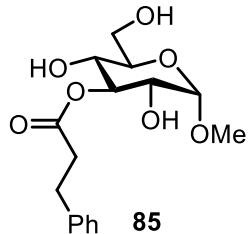
(4-methoxyphenyl)-2-O-artesunate- β -D-galactopyranoside (83)

The product **83** (42.4 mg, 65%) was obtained as white solid. **^1H NMR (400 MHz, Chloroform- d)** δ 7.04 – 6.89 (m, 2H), 6.88 – 6.66 (m, 2H), 5.75 (d, J = 9.8 Hz, 1H), 5.39 (s, 1H), 5.28 (dd, J = 9.8, 8.0 Hz, 1H), 4.87 (d, J = 8.0 Hz, 1H), 4.10 (d, J = 3.4 Hz, 1H), 3.91 (qd, J = 11.8, 5.6 Hz, 2H), 3.76 (s, 4H), 3.65 (t, J = 5.7 Hz, 1H), 2.86 – 2.68 (m, 4H), 2.55 (ddd, J = 9.8, 7.2, 4.5 Hz, 1H), 2.37 (td, J = 14.0, 3.9 Hz, 1H), 2.03 (ddd, J = 14.4, 4.9, 2.1 Hz, 1H), 1.89 (ddt, J = 13.5, 6.5, 3.5 Hz, 1H), 1.73 (ddt, J = 13.6, 10.1, 3.6 Hz, 2H), 1.61 (dt, J = 13.9, 4.4 Hz, 1H), 1.43 (s, 4H), 1.38 – 1.22 (m, 3H), 1.08 – 0.93 (m, 4H), 0.83 (d, J = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform- d)** δ 172.01, 171.34, 155.45, 151.29, 118.58, 114.57, 104.58, 100.53, 92.34, 91.55, 80.13, 74.58, 72.98, 72.11, 69.36, 61.93, 55.63, 51.53, 45.18, 37.19, 36.20, 34.06, 31.73, 29.33, 29.12, 25.88, 24.56, 21.93, 20.19, 12.03. **ESI-MS:** calcd for $\text{C}_{32}\text{H}_{44}\text{O}_{14}\text{Na}$ [M + Na] $^+$: 675.2629, found: 675.2628.



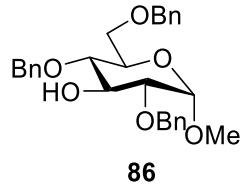
(4-methoxyphenyl)-2-O-(4-(N,N-dipropylsulfamoyl)benzoyl)- β -D-galactopyranoside (84)

The product **84** (37.8 mg, 68%) was obtained as white solid. **^1H NMR (400 MHz, Chloroform- d)** δ 8.17 (d, J = 8.3 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.03 – 6.86 (m, 2H), 6.85 – 6.67 (m, 2H), 5.52 (dd, J = 9.7, 8.0 Hz, 1H), 5.07 (d, J = 8.0 Hz, 1H), 4.21 (d, J = 3.4 Hz, 1H), 4.09 – 3.98 (m, 2H), 3.92 (dd, J = 9.9, 3.3 Hz, 1H), 3.77 (m, 4H), 3.26 – 2.91 (m, 4H), 1.57 (h, J = 7.4 Hz, 4H), 0.89 (t, J = 7.4 Hz, 6H). **^{13}C NMR (101 MHz, Chloroform- d)** δ 165.49, 155.62, 151.03, 144.67, 132.83, 130.56, 127.07, 118.42, 114.63, 100.71, 74.47, 73.96, 72.34, 69.58, 61.95, 55.60, 50.02, 22.00, 11.15. **ESI-MS:** calcd for $\text{C}_{26}\text{H}_{35}\text{O}_{10}\text{NSNa}$ [M + Na] $^+$: 576.1879, found: 576.1880.



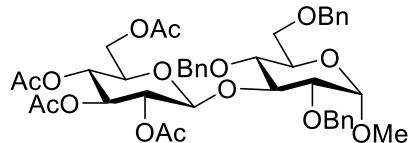
Methyl-3-O-(3-phenylpropanoyl)- α -D-glucopyranoside (85)

The product **85** (14.7 mg, 45%) was obtained as white solid. **¹H NMR (400 MHz, Acetone-d₆)** δ 7.28 (d, *J* = 4.4 Hz, 4H), 7.19 (dt, *J* = 8.8, 4.1 Hz, 1H), 5.18 (t, *J* = 9.3 Hz, 1H), 4.71 (d, *J* = 3.6 Hz, 1H), 4.36 (d, *J* = 5.4 Hz, 1H), 3.85 – 3.77 (m, 1H), 3.72 (dt, *J* = 11.6, 5.4 Hz, 1H), 3.66 – 3.48 (m, 5H), 3.41 (s, 3H), 2.94 (t, *J* = 7.9 Hz, 2H), 2.74 – 2.58 (t, *J* = 7.9 Hz, 2H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 172.41, 141.06, 128.34, 128.26, 125.98, 99.94, 76.24, 72.42, 70.79, 68.73, 61.51, 54.43, 35.66, 30.62. **ESI-MS:** calcd for C₁₆H₂₂O₇Na [M + Na]⁺: 349.1263, found: 349.1273.



Methyl-2,4,6-O-benzyl- α -D-glucopyranoside (**86**)

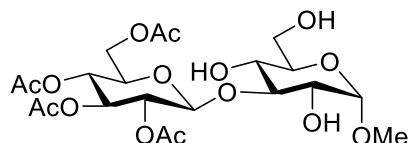
The product **86** (325 mg, 70%) was obtained as colorless liquid. **¹H NMR (400 MHz, Acetone-d₆)** δ 7.44 (d, *J* = 7.1 Hz, 2H), 7.39–7.25 (m, 13H), 4.99 (d, *J* = 11.3 Hz, 1H), 4.78 (d, *J* = 3.5 Hz, 1H), 4.75 – 4.50 (m, 5H), 4.46 (s, 1H), 4.02 (t, *J* = 9.2 Hz, 1H), 3.77 – 3.66 (m, 3H), 3.52 – 3.42 (m, 1H), 3.41 – 3.29 (m, 4H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 139.36, 139.23, 138.91, 128.16, 128.10, 128.03, 127.65, 127.65, 127.52, 127.31, 127.27, 127.17, 97.67, 80.11, 78.37, 74.20, 73.57, 72.86, 72.02, 70.11, 69.44, 54.25. **ESI-MS:** calcd for C₂₈H₃₂O₆Na [M + Na]⁺: 487.2097, found: 487.2087.



88

Methyl 2,4,6-tri-O-benzyl-3-O-(2,3,4,6-tetra-O-acetyl-beta-D-glucopyranosyl)-alpha-D-glucopyranoside (**88**)

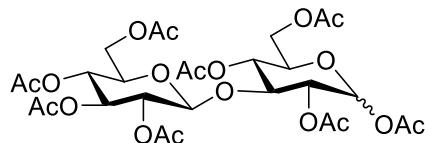
The product **88** (416 mg, 81%) was obtained as colorless liquid. **¹H NMR (400 MHz, Acetone-d₆)** δ 7.54 (d, *J* = 7.3 Hz, 2H), 7.48 – 7.20 (m, 13H), 5.38 – 5.23 (m, 2H), 5.15 – 4.99 (m, 3H), 4.83 – 4.74 (m, 2H), 4.69 (d, *J* = 11.4 Hz, 1H), 4.60 – 4.47 (m, 3H), 4.35 – 4.16 (m, 2H), 4.08 (dd, *J* = 12.3, 2.6 Hz, 1H), 3.89 (ddd, *J* = 10.1, 4.6, 2.5 Hz, 1H), 3.72 – 3.61 (m, 3H), 3.58 – 3.45 (m, 2H), 3.34 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.93 (s, 3H). **¹³C NMR (101 MHz, Acetone-d₆)** δ 169.83, 169.43, 169.13, 168.92, 139.26, 138.79, 138.76, 128.31, 128.20, 128.14, 127.94, 127.94, 127.65, 127.60, 127.35, 127.20, 100.45, 97.06, 81.00, 79.09, 75.98, 74.21, 72.91, 72.79, 72.24, 71.86, 71.53, 69.95, 69.16, 68.60, 62.03, 54.26, 19.93, 19.74, 19.71, 19.65. **ESI-MS:** calcd for C₄₂H₅₀O₁₅Na [M + Na]⁺: 817.3047, found: 817.3050.



89-1

Methyl-3-O-(2,3,4,6-tetra-O-acetyl-beta-D-glucopyranosyl)-alpha-D-glucopyranoside (**89-1**)

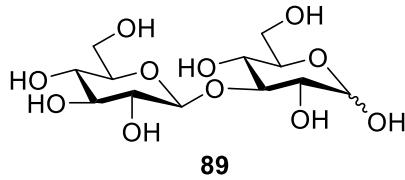
¹H NMR (400 MHz, Chloroform-d) δ 5.24 (t, *J* = 9.6 Hz, 1H), 5.09 – 4.94 (m, 2H), 4.75 (d, *J* = 3.2 Hz, 1H), 4.65 (d, *J* = 8.0 Hz, 1H), 4.22 (d, *J* = 12.0 Hz, 1H), 4.11 (dd, *J* = 12.2, 6.6 Hz, 1H), 3.93 – 3.73 (m, 4H), 3.64 – 3.48 (m, 4H), 3.43 (s, 3H), 2.40 (s, 2H), 2.08 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H). **¹³C NMR (101 MHz, Chloroform-d)** δ 170.62, 170.11, 169.97, 169.46, 102.43, 99.19, 87.68, 72.29, 71.88, 71.32, 71.08, 70.67, 69.24, 69.22, 68.53, 62.38, 62.33, 62.03, 55.28, 20.64, 20.53. **ESI-MS:** calcd for C₂₁H₃₂O₁₅Na [M + Na]⁺: 547.1639, found: 547.1638.



89-2

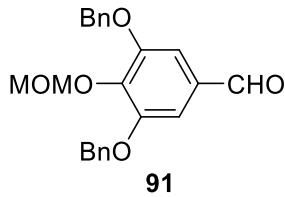
Acetyl-2,4,6-tri-O-acetyl-3-O-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosyl)-D-glucopyranoside (89-2)

The product (680 mg, 99%) was obtained as colorless liquid. **$^1\text{H NMR}$ (400 MHz, Chloroform- d)** δ 6.25 (d, J = 3.8 Hz, 1H), 5.25 – 5.00 (m, 4H), 4.91 (t, J = 8.7 Hz, 1H), 4.66 (d, J = 8.1 Hz, 1H), 4.49 – 4.33 (m, 1H), 4.26 – 4.01 (m, 5H), 3.75 (ddd, J = 9.7, 3.9, 2.5 Hz, 1H), 2.32 – 1.88 (m, 24H). R_F (hexane: ethyl acetate = 1:2): 0.37. **(H NMR (400 MHz, Chloroform-d))** δ 5.63 (d, J = 8.4 Hz, 1H), 5.25 – 5.00 (m, 4H), 4.91 (dd, J = 9.3, 8.1 Hz, 1H), 4.61 (d, J = 8.1 Hz, 1H), 4.49 – 4.33 (m, 1H), 4.26 – 4.01 (m, 4H), 3.95 (t, J = 9.4 Hz, 1H), 3.75 (ddd, J = 9.7, 3.9, 2.5 Hz, 1H), 2.32 – 1.88 (m, 24H). **$^{13}\text{C NMR}$ (101 MHz, Acetone- d_6)** δ 169.82, 169.79, 169.68, 169.43, 169.00, 168.98, 168.77, 168.63, 100.47, 88.77, 76.29, 72.77, 71.41, 71.29, 71.19, 69.86, 68.24, 67.45, 61.69, 61.63, 19.88, 19.87, 19.79, 19.74, 19.69, 19.67, 19.60, 19.52. **ESI-MS:** calcd for $\text{C}_{26}\text{H}_{35}\text{O}_{17}$ [M - OAc] $^+$: 619.1874, found: 619.1899.



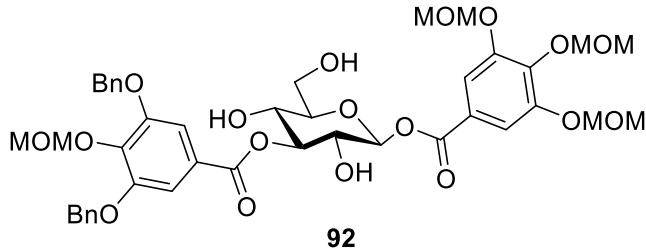
Laminaribiose (89)¹⁹

The product **89** (103 mg, 99%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, D_2O)** δ 5.15 (d, J = 3.8 Hz, 1H), 4.66 – 4.56 (m, 2H), 3.92 – 3.04 (m, 19H). **$^{13}\text{C NMR}$ (101 MHz, D_2O)** δ (102.93, 102.84), 95.70, 92.03, 84.72, 82.46, (76.04, 76.01), 75.59, (73.80, 73.51, 73.48), (71.24, 71.02), 69.60, (68.19, 68.15), (60.71, 60.58). **ESI-MS:** calcd for $\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{Na}$ [M + Na] $^+$: 365.1060, found: 365.1064.



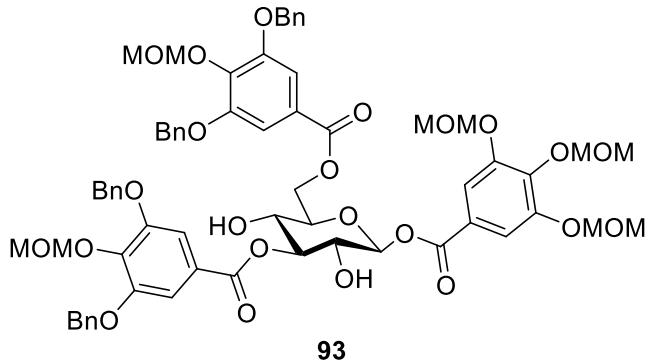
3,5-bis(benzyloxy)-4-(methoxymethoxy) benzaldehyde (91)

The product **91** (178 mg, 83%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Chloroform- d)** δ 9.80 (s, 1H), 7.52 – 7.28 (m, 10H), 7.19 (s, 2H), 5.24 (s, 2H), 5.16 (s, 4H), 3.49 (s, 3H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform- d)** δ 190.93, 153.12, 141.36, 136.26, 132.08, 128.67, 128.22, 127.53, 108.50, 98.38, 71.21, 57.36. **ESI-MS:** calcd for $\text{C}_{23}\text{H}_{23}\text{O}_5$ [M + H] $^+$: 379.1545, found: 379.1546.



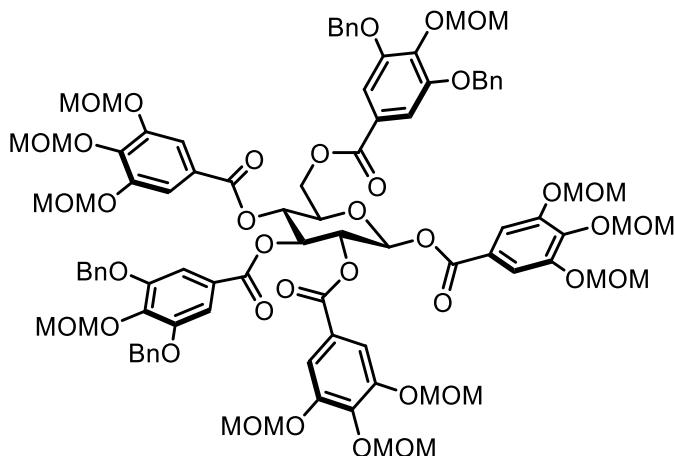
3,4,5-tris(methoxymethoxy)benzoyl-3-O-(3,5-bis(benzyloxy)-4-(methoxymethoxy)benzoyl)- β -D-glucopyranoside (92)

The product **92** (62.0 mg, 74%) was obtained as colorless gum. **$^1\text{H NMR}$ (400 MHz, Chloroform- d)** δ 7.59 (s, 2H), 7.49 – 7.43 (m, 6H), 7.42 – 7.37 (m, 4H), 7.36 – 7.31 (m, 2H), 5.87 (d, J = 8.1 Hz, 1H), 5.29 – 5.13 (m, 13H), 4.03 – 3.79 (m, 4H), 3.61 (s, 4H), 3.50 (d, J = 6.8 Hz, 9H), 3.20 (d, J = 25.0 Hz, 2H), 2.33 (s, 1H). **$^{13}\text{C NMR}$ (126 MHz, Chloroform- d)** δ 167.34, 164.39, 152.46, 150.78, 141.40, 140.58, 136.51, 128.61, 128.14, 127.64, 124.55, 124.43, 111.92, 109.21, 98.51, 98.31, 95.16, 94.82, 79.48, 76.39, 71.42, 71.27, 68.94, 61.82, 57.31, 57.26, 56.45. **ESI-MS:** calcd for $\text{C}_{42}\text{H}_{48}\text{O}_{18}\text{Na}$ [M + Na] $^+$: 863.2738, found: 863.2744.



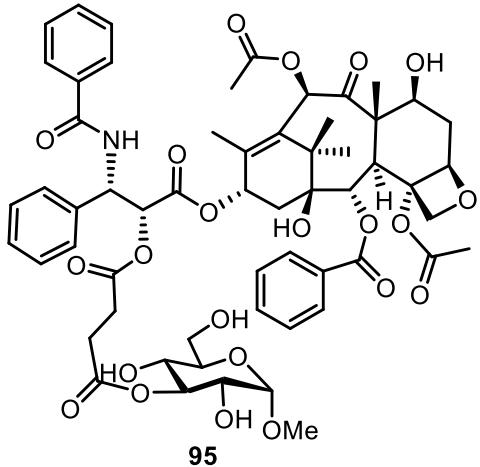
3,4,5-tris(methoxymethoxy)benzoyl-3,6-bis-O-(3,5-bis(benzyloxy)-4-(methoxymethoxy) benzoyl)- β -D-glucopyranoside (93)

The product **93** (52.0 mg, 80%) was obtained as colorless gum. **$^1\text{H NMR}$ (500 MHz, Chloroform- d)** δ 7.55 (s, 2H), 7.42 (dt, J = 7.3, 3.2 Hz, 11H), 7.38 – 7.26 (m, 13H), 5.89 (d, J = 8.1 Hz, 1H), 5.26 (t, J = 9.3 Hz, 1H), 5.23 – 5.05 (m, 18H), 4.67 (dd, J = 12.4, 5.0 Hz, 1H), 4.57 (dd, J = 12.3, 2.3 Hz, 1H), 3.98 (t, J = 8.8 Hz, 1H), 3.89 (ddd, J = 9.9, 5.0, 2.4 Hz, 1H), 3.71 (t, J = 9.5 Hz, 1H), 3.58 (s, 3H), 3.55 (s, 1H), 3.49 – 3.37 (m, 12H), 3.06 (s, 1H). **$^{13}\text{C NMR}$ (126 MHz, Chloroform- d)** δ 167.16, 166.76, 164.30, 152.44, 152.38, 150.76, 141.39, 140.63, 140.31, 136.51, 136.48, 128.60, 128.56, 128.15, 128.07, 127.65, 124.75, 124.61, 124.45, 111.89, 109.29, 109.03, 98.51, 98.35, 98.33, 95.14, 94.93, 78.80, 75.32, 71.41, 71.29, 71.13, 68.93, 63.69, 57.31, 57.27, 57.25, 56.42. **ESI-MS:** calcd for $\text{C}_{65}\text{H}_{68}\text{O}_{23}\text{Na} [\text{M} + \text{Na}]^+$: 1239.4049, found: 1239.4053.



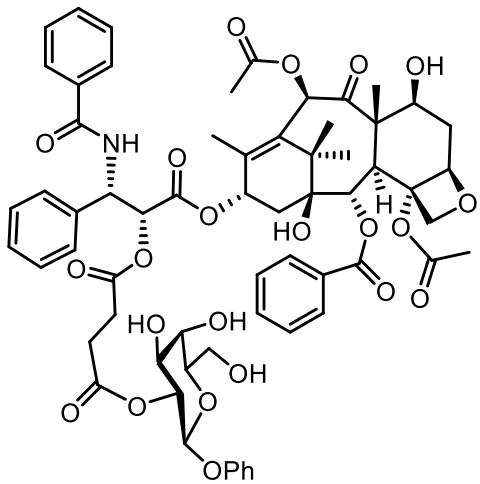
1,2,4-Tris-O-[3,4,5-tris(methoxymethoxy)benzoyl]-3,6-bis-O-[3,5-dibenzylxy-4-(methoxymethoxy)benzoyl]- β -D-glucopyranoside (94)

The product **94** (49.0 mg, 83%) was obtained as colorless gum. **$^1\text{H NMR}$ (500 MHz, Acetone- d_6)** δ 7.62 – 7.21 (m, 30H), 6.48 (d, J = 8.3 Hz, 1H), 6.21 (t, J = 9.7 Hz, 1H), 5.96 (t, J = 9.7 Hz, 1H), 5.84 (dd, J = 9.9, 8.3 Hz, 1H), 5.31 – 5.16 (m, 22H), 5.13 (s, 2H), 5.07 (s, 6H), 4.89 (dd, J = 12.5, 2.2 Hz, 1H), 4.79 (ddd, J = 10.0, 4.8, 2.4 Hz, 1H), 4.44 (dd, J = 12.5, 4.6 Hz, 1H), 3.55 (d, J = 1.4 Hz, 6H), 3.51 (s, 3H), 3.49 – 3.40 (m, 21H), 3.35 (s, 3H). **$^{13}\text{C NMR}$ (126 MHz, Acetone- d_6)** δ 165.84, 165.80, 165.68, 165.49, 164.54, 153.36, 153.26, 151.94, 151.93, 151.88, 142.87, 142.76, 142.71, 141.22, 141.02, 138.00, 137.63, 129.43, 129.31, 128.90, 128.87, 128.59, 125.93, 125.32, 125.23, 125.19, 124.66, 112.73, 112.70, 112.64, 109.41, 109.37, 99.12, 99.10, 99.08, 98.94, 98.81, 96.15, 96.12, 96.01, 93.77, 74.08, 73.70, 72.59, 71.69, 71.45, 70.41, 63.34, 57.26, 57.24, 57.22, 57.19, 57.17, 56.60, 56.53, 56.50. **ESI-MS:** calcd for $\text{C}_{91}\text{H}_{100}\text{O}_{37}\text{Na} [\text{M} + \text{Na}]^+$: 1807.5841, found: 1807.5846.



Methyl- α -D-glucopyranoside conjugated succinyl paclitaxel (95)

The product (70 mg, 62%) was obtained as white solid. **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.46 (d, J = 9.1 Hz, 1H), 8.24 – 8.12 (m, 2H), 7.98 – 7.83 (m, 2H), 7.75 – 7.67 (m, 1H), 7.66 – 7.59 (m, 4H), 7.57 – 7.41 (m, 5H), 7.33 (t, J = 7.4 Hz, 1H), 6.43 (s, 1H), 6.17 (t, J = 9.2 Hz, 1H), 6.04 – 5.94 (m, 1H), 5.70 (d, J = 7.2 Hz, 1H), 5.59 (d, J = 5.9 Hz, 1H), 5.16 (t, J = 9.1 Hz, 1H), 4.99 (d, J = 7.8 Hz, 1H), 4.69 (d, J = 3.6 Hz, 1H), 4.44 (dt, J = 11.2, 6.0 Hz, 1H), 4.35 (d, J = 4.8 Hz, 1H), 4.25 – 4.13 (m, 2H), 3.89 (s, 1H), 3.86 (d, J = 7.2 Hz, 1H), 3.83 – 3.76 (m, 1H), 3.74 – 3.66 (m, 1H), 3.63 – 3.46 (m, 6H), 3.40 (s, 3H), 2.78 – 2.72 (m, 2H), 2.71 – 2.65 (m, 2H), 2.53–2.45 (m, 4H), 2.36 (dd, J = 15.4, 9.4 Hz, 1H), 2.18 (s, 3H), 1.96 (d, J = 1.5 Hz, 3H), 1.80 (ddd, J = 13.9, 11.0, 2.3 Hz, 1H), 1.68 (s, 3H), 1.24 – 1.10 (m, 7H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform- d)** δ 203.77, 172.81, 171.46, 171.23, 169.97, 168.49, 167.33, 167.01, 142.46, 136.90, 133.70, 133.66, 132.90, 131.83, 130.28, 129.25, 129.09, 128.73, 128.54, 127.41, 126.69, 99.28, 84.44, 81.13, 79.12, 75.57, 75.07, 74.85, 72.44, 72.07, 71.15, 70.69, 68.64, 61.93, 58.50, 55.38, 52.91, 45.64, 43.21, 35.60, 35.52, 29.67, 29.43, 26.77, 22.69, 22.14, 20.82, 14.80, 9.62. **ESI-MS:** calcd for $\text{C}_{58}\text{H}_{67}\text{NO}_{22}\text{Na}$ [M + Na] $^+$: 1152.4052, found: 1152.4066.



Phenyl- β -D-galactoside conjugated succinyl paclitaxel (96)

The product (79.8 mg, 67%) was obtained as white solid (axial chirality exist in this compound). **$^1\text{H NMR}$ (400 MHz, Acetone- d_6)** δ 8.49 (d, J = 9.1 Hz, 1H), 8.20 – 8.11 (m, 2H), 7.93 – 7.84 (m, 2H), 7.74 – 7.65 (m, 1H), 7.61 (td, J = 7.0, 6.5, 1.6 Hz, 4H), 7.56 – 7.40 (m, 5H), 7.35 – 7.20 (m, 3H), 7.10 – 6.92 (m, 3H), 6.42 (s, 1H), 6.18 (t, J = 9.1 Hz, 1H), 5.99 (dd, J = 9.1, 5.8 Hz, 1H), 5.70 (d, J = 7.2 Hz, 1H), 5.55 (d, J = 5.7 Hz, 1H), 5.33 (dd, J = 9.9, 8.0 Hz, 1H), 5.03 (d, J = 8.0 Hz, 1H), 5.01 – 4.96 (m, 1H), 4.43 (dt, J = 11.4, 6.1 Hz, 1H), 4.28 – 4.12 (m, 4H), 4.09 – 3.98 (m, 2H), 3.92 – 3.88 (m, 1H), 3.87 – 3.76 (m, 5H), 3.56 – 3.45 (m, 1H), 2.79 – 2.61 (m, 4H), 2.53–2.45 (m, 4H), 2.36 (dd, J = 15.4, 9.6 Hz, 1H), 2.17 (s, 3H), 1.97 (d, J =

1.5 Hz, 3H), 1.79 (ddd, J = 12.9, 11.0, 2.2 Hz, 1H), 1.68 (s, 3H), 1.20 (s, 3H), 1.19 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 203.72, 171.99, 171.72, 171.26, 169.96, 168.20, 167.33, 166.96, 157.08, 142.49, 136.78, 133.71, 133.69, 132.80, 132.01, 130.25, 129.63, 129.25, 129.11, 129.04, 128.71, 127.21, 126.82, 123.13, 116.87, 99.21, 84.41, 81.10, 79.08, 75.62, 75.00, 74.61, 74.44, 73.23, 72.16, 72.04, 72.00, 69.59, 62.31, 58.45, 53.05, 45.74, 43.16, 35.64, 35.45, 29.00, 28.87, 26.70, 22.66, 22.00, 20.82, 14.84, 9.63. **ESI-MS:** calcd for $\text{C}_{63}\text{H}_{69}\text{NO}_{22}\text{Na} [\text{M} + \text{Na}]^+$: 1214.4209, found: 1214.4202.

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Full reference for Gaussian software:

Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

6. NMR spectra

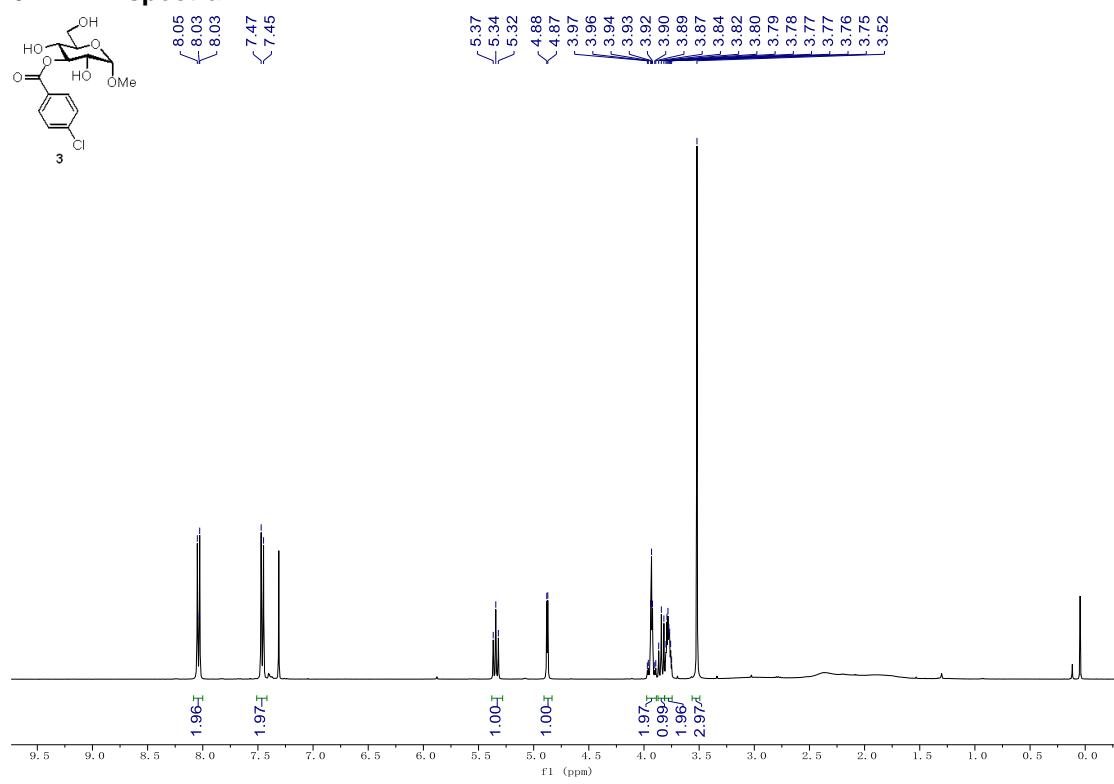


Figure S41. ^1H NMR Spectra of 3

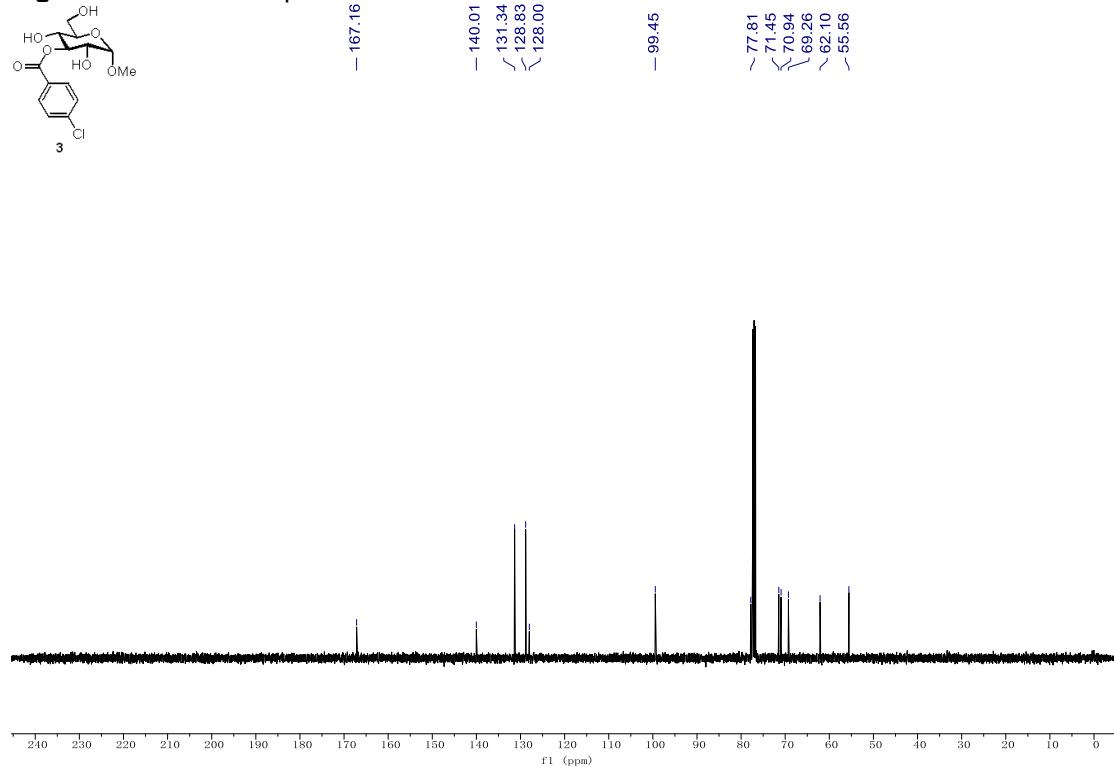


Figure S42. ^{13}C NMR Spectra of 3

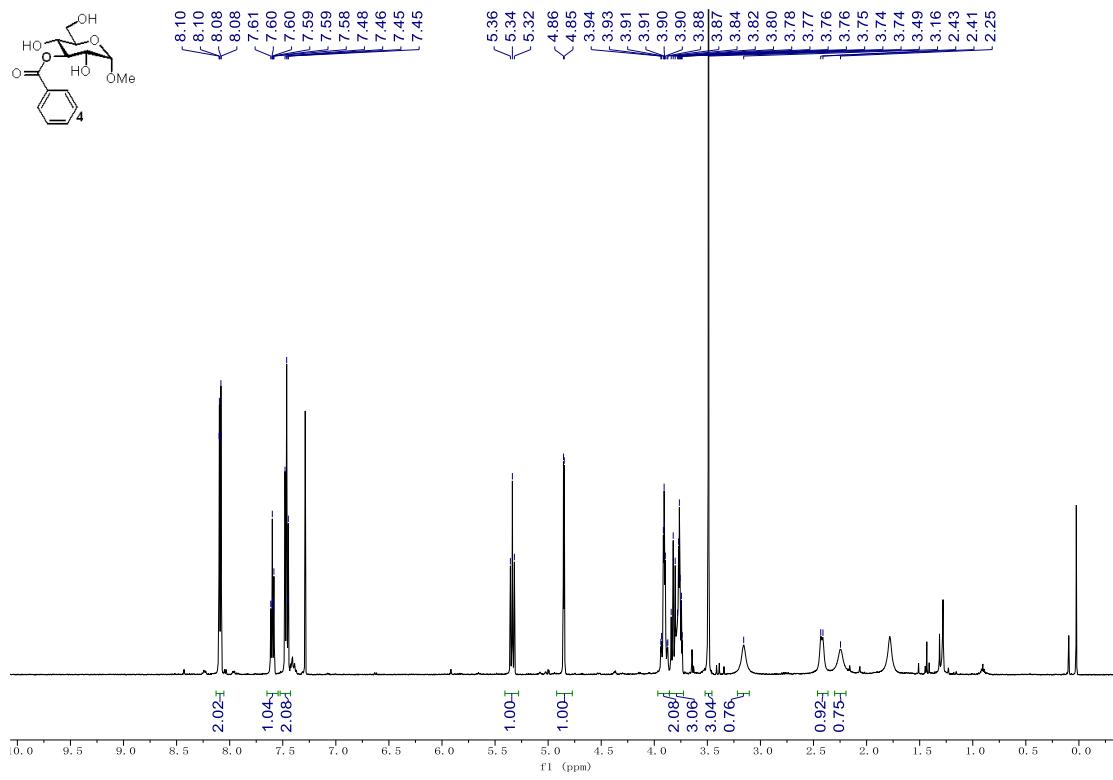


Figure S43. ^1H NMR Spectra of 4

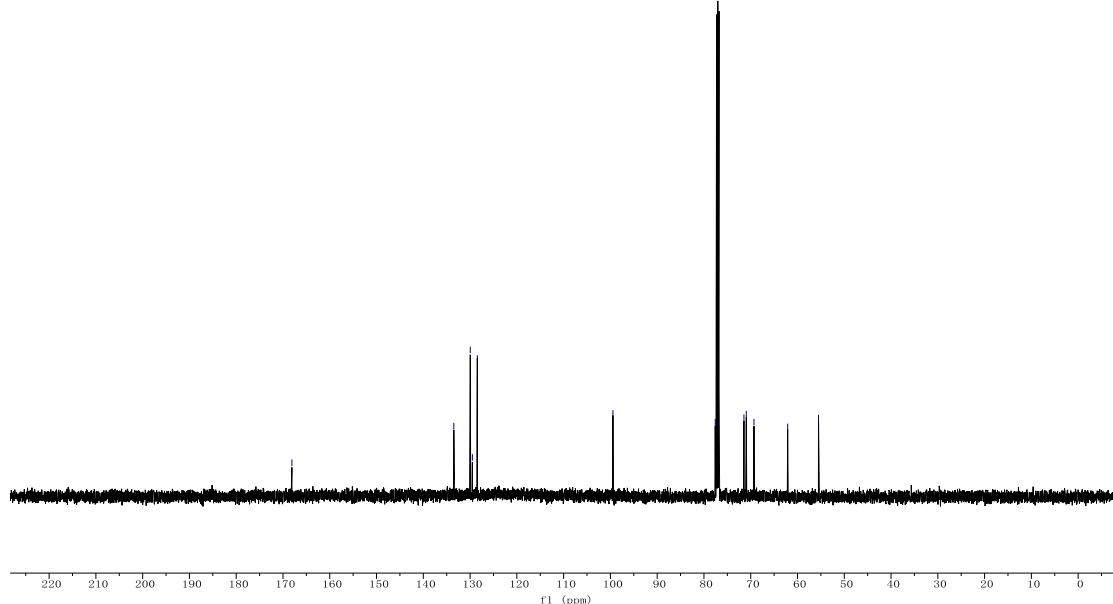


Figure S44. ^{13}C NMR Spectra of 4

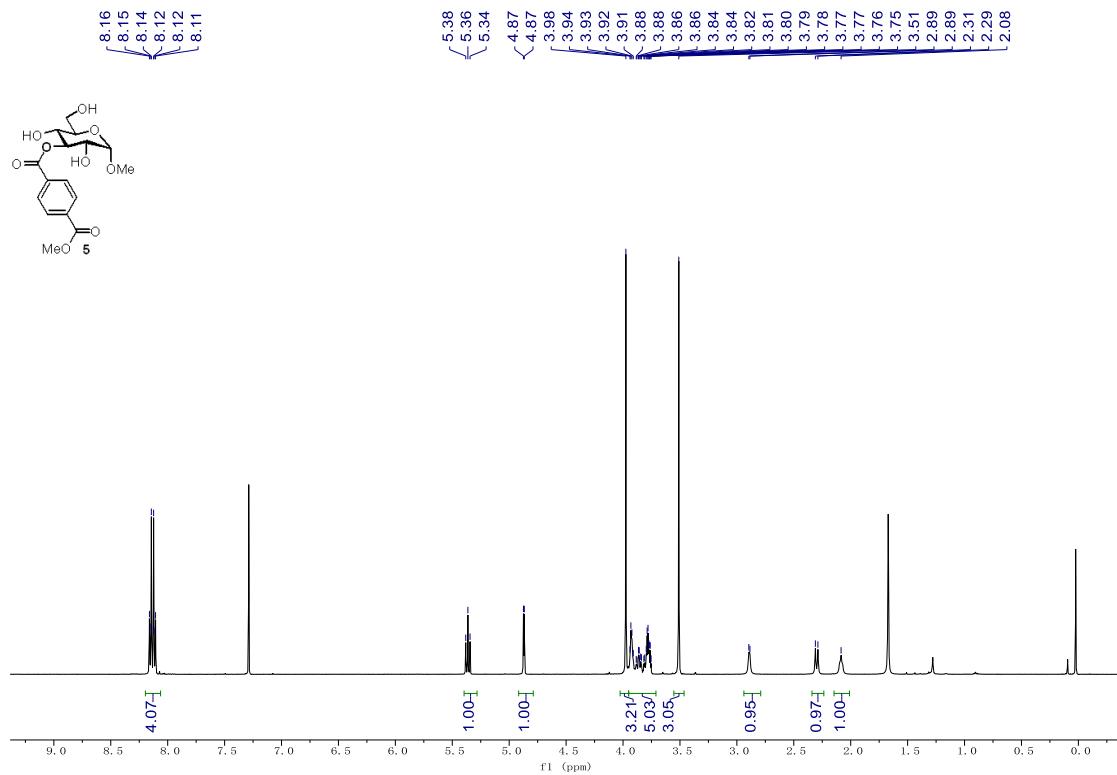


Figure S45. ^1H NMR Spectra of 5

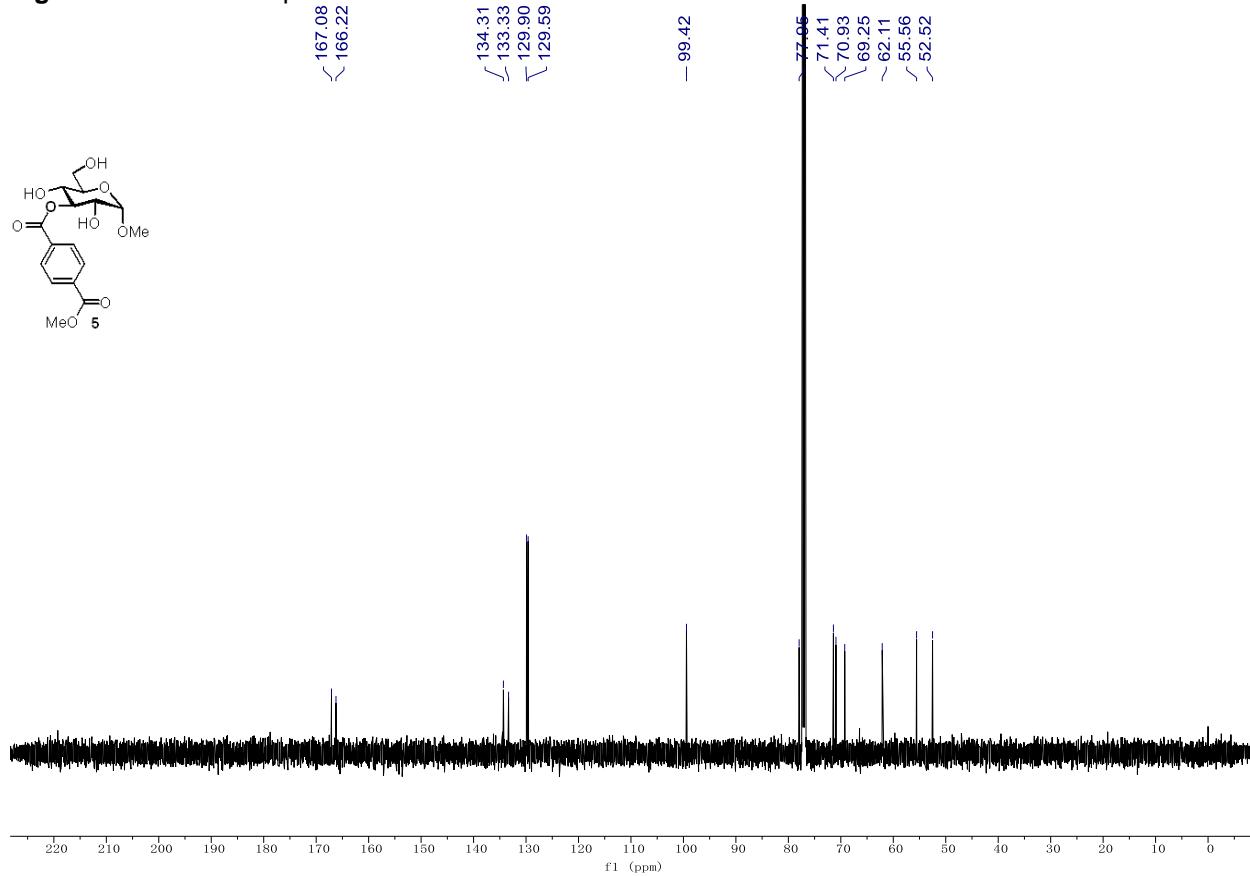


Figure S46. ^{13}C NMR Spectra of 5

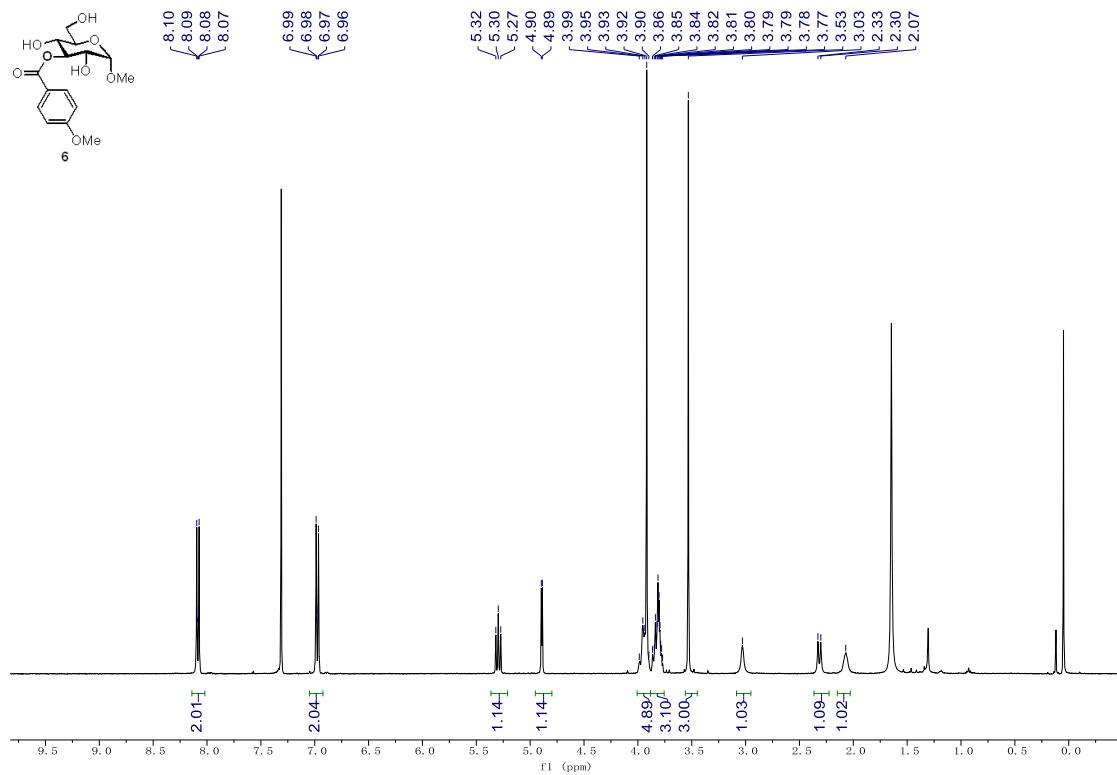


Figure S47. ^1H NMR Spectra of 6

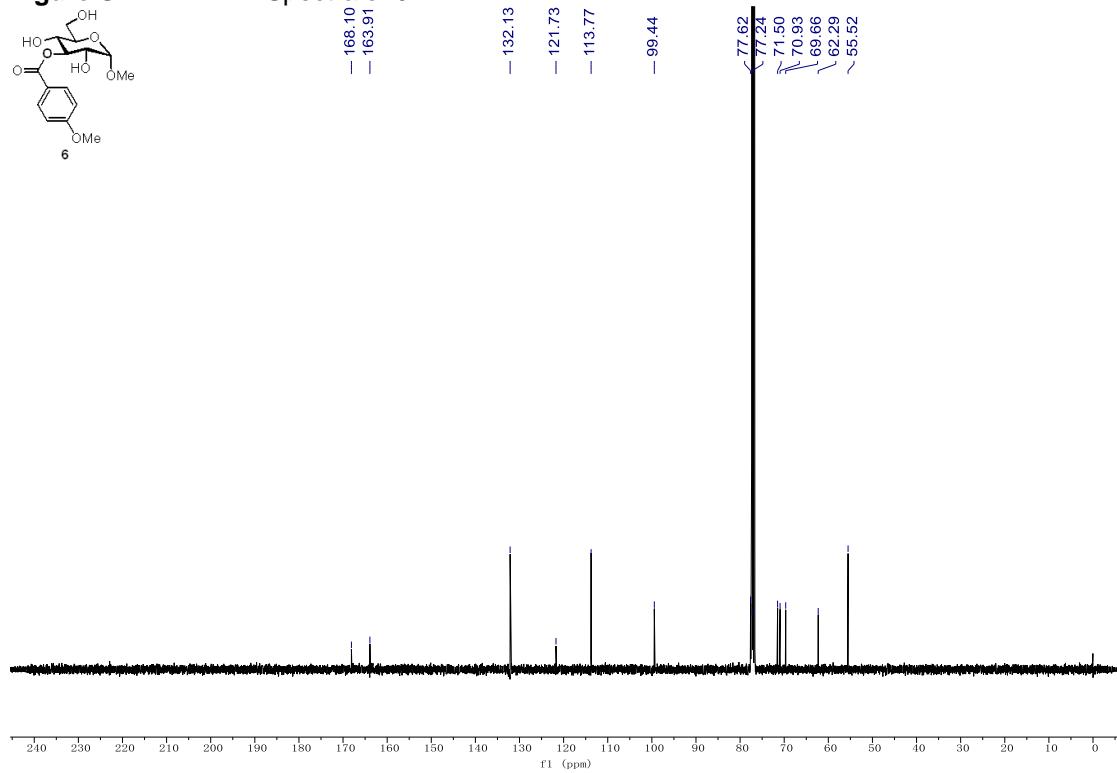


Figure S48. ^{13}C NMR Spectra of 6

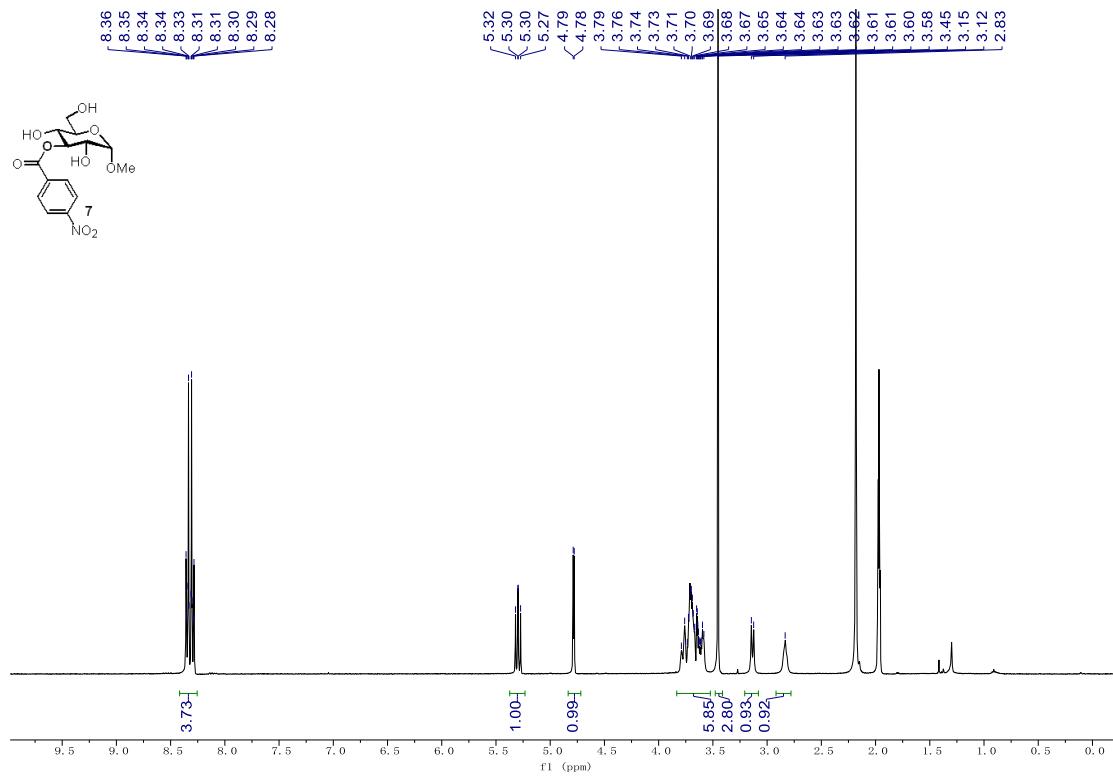


Figure S49. ^1H NMR Spectra of 7

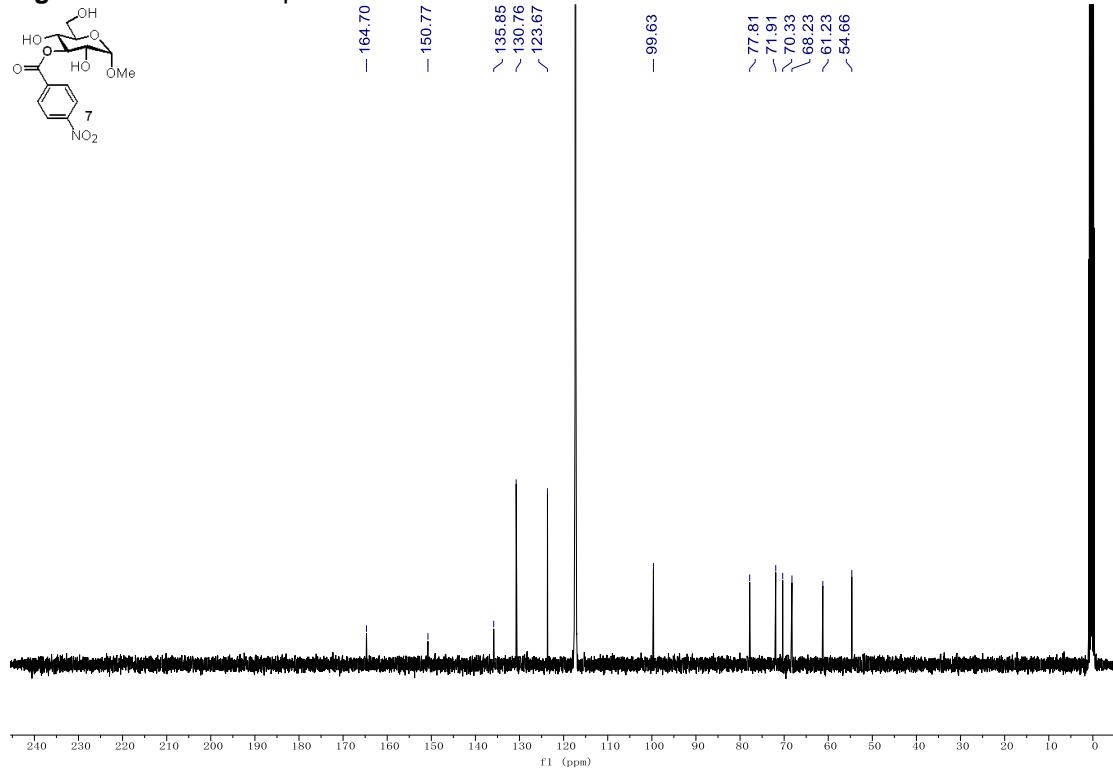


Figure S50. ^{13}C NMR Spectra of 7

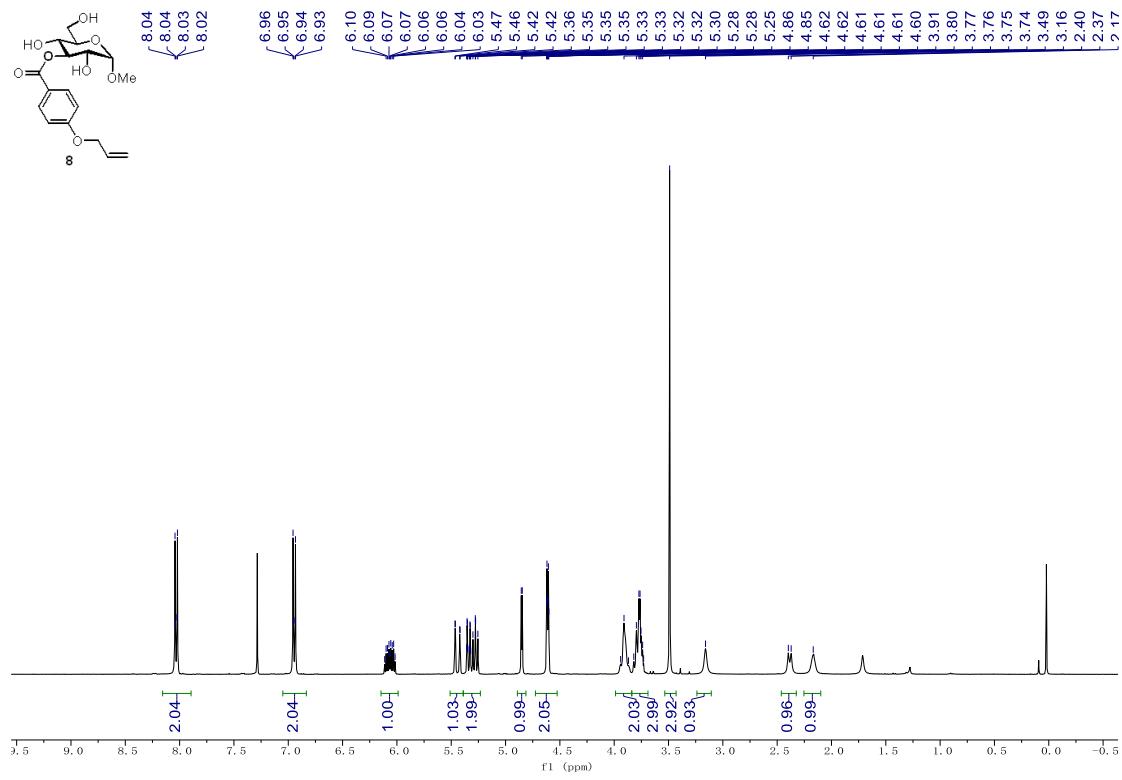


Figure S51. ^1H NMR Spectra of **8**

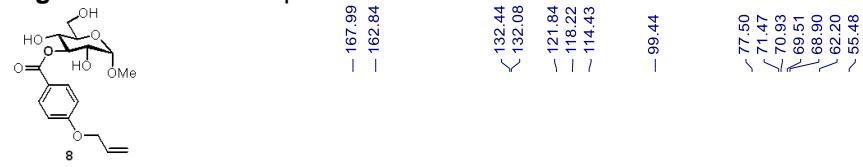


Figure S52. ^{13}C NMR Spectra of **8**

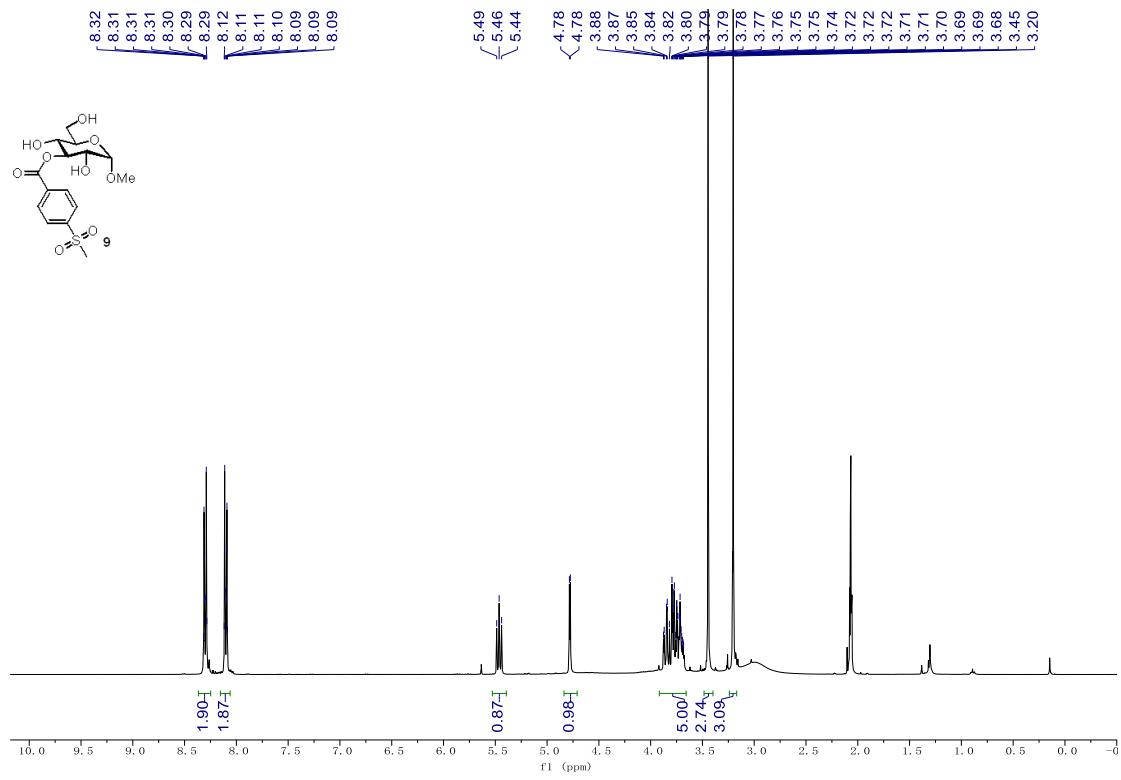


Figure S53. ^1H NMR Spectra of **9**

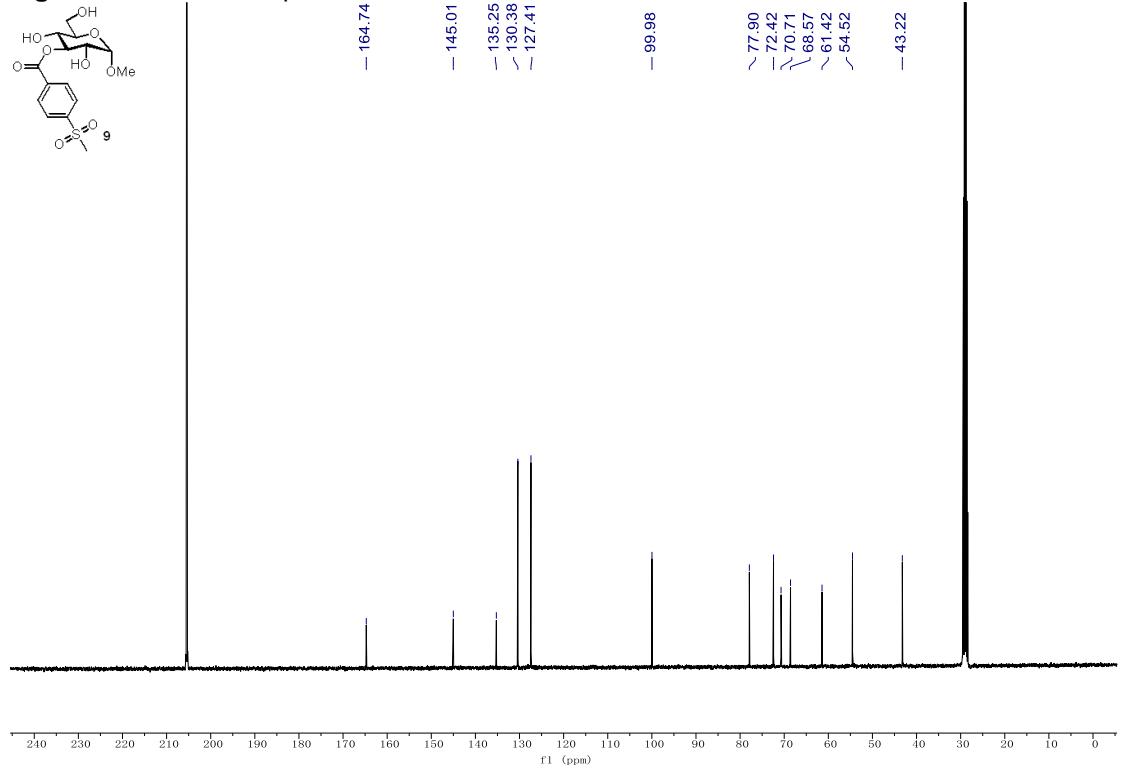


Figure S54. ^{13}C NMR Spectra of **9**

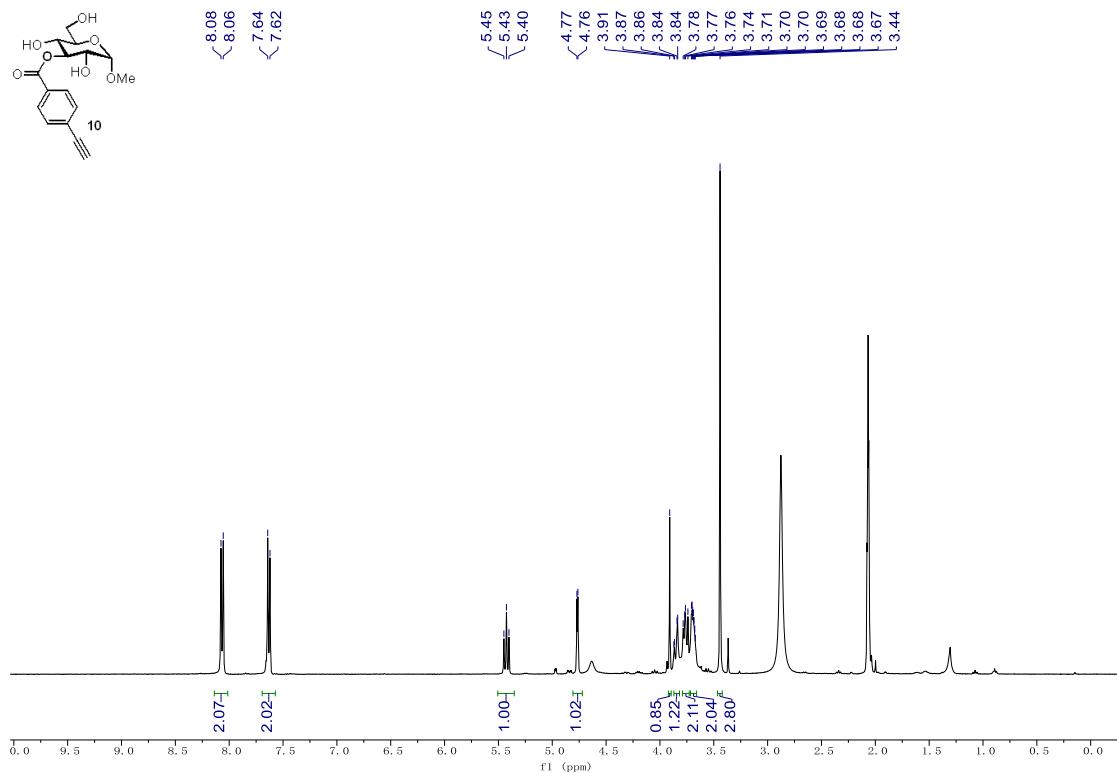


Figure S55. ^1H NMR Spectra of 10

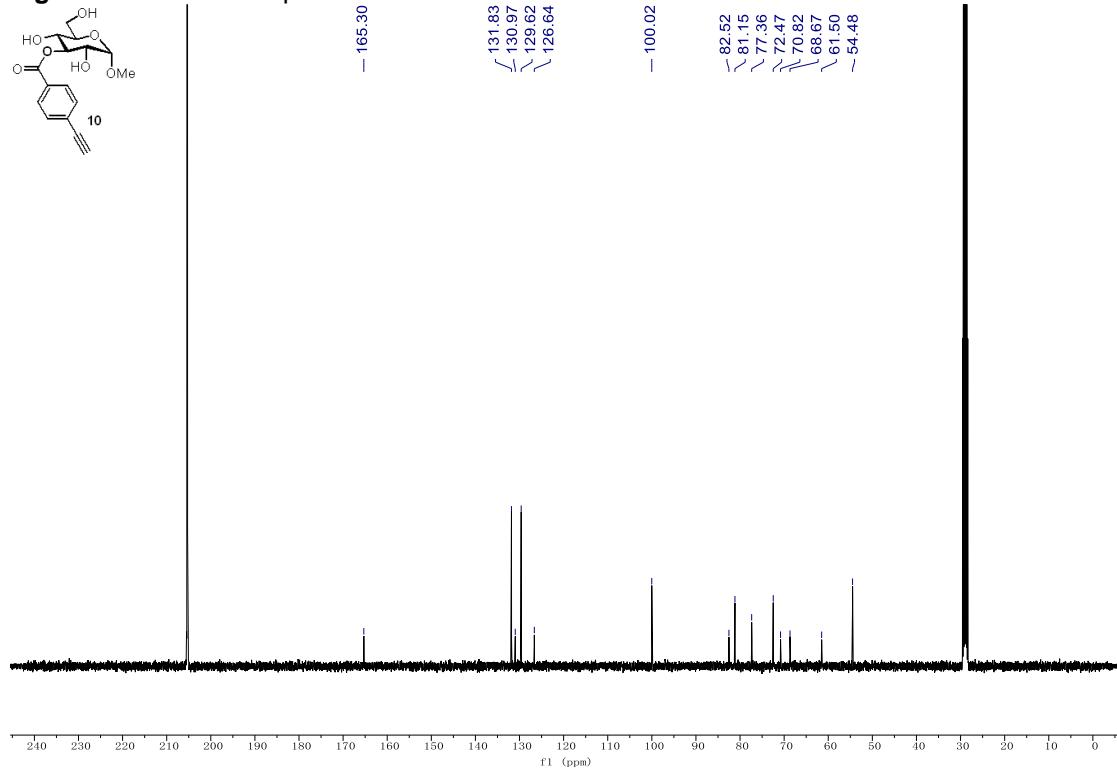


Figure S56. ^{13}C NMR Spectra of 10

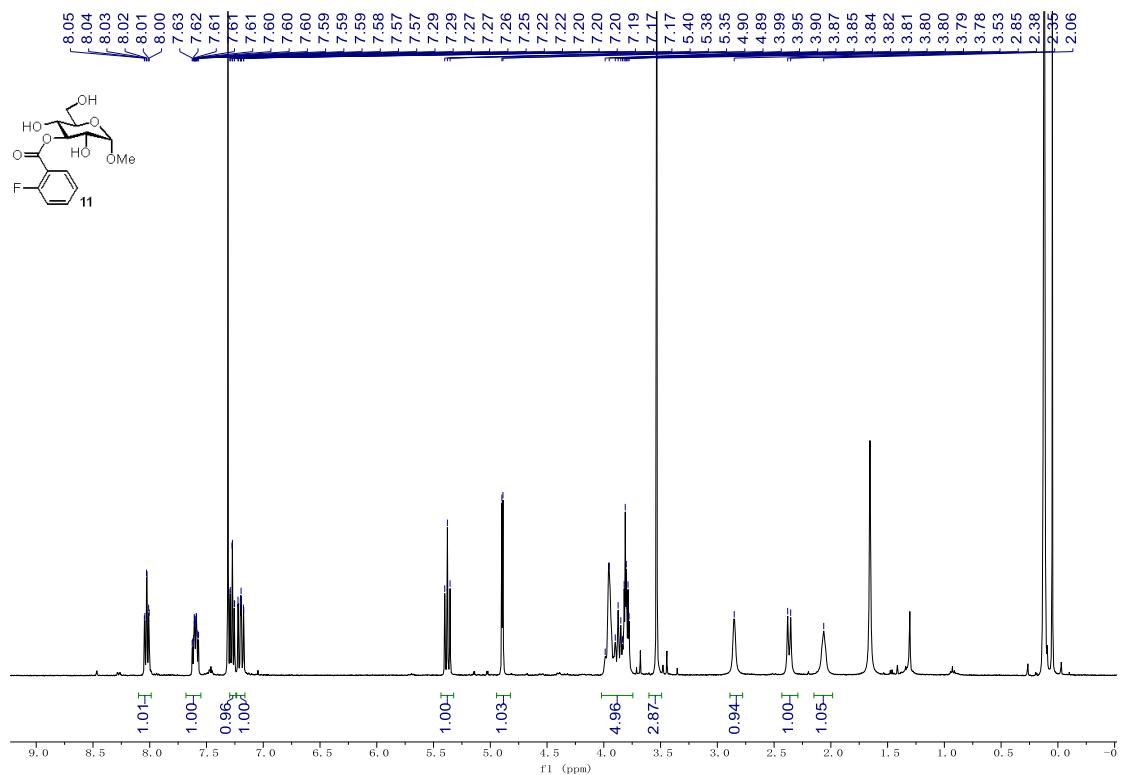


Figure S57. ^1H NMR Spectra of 11

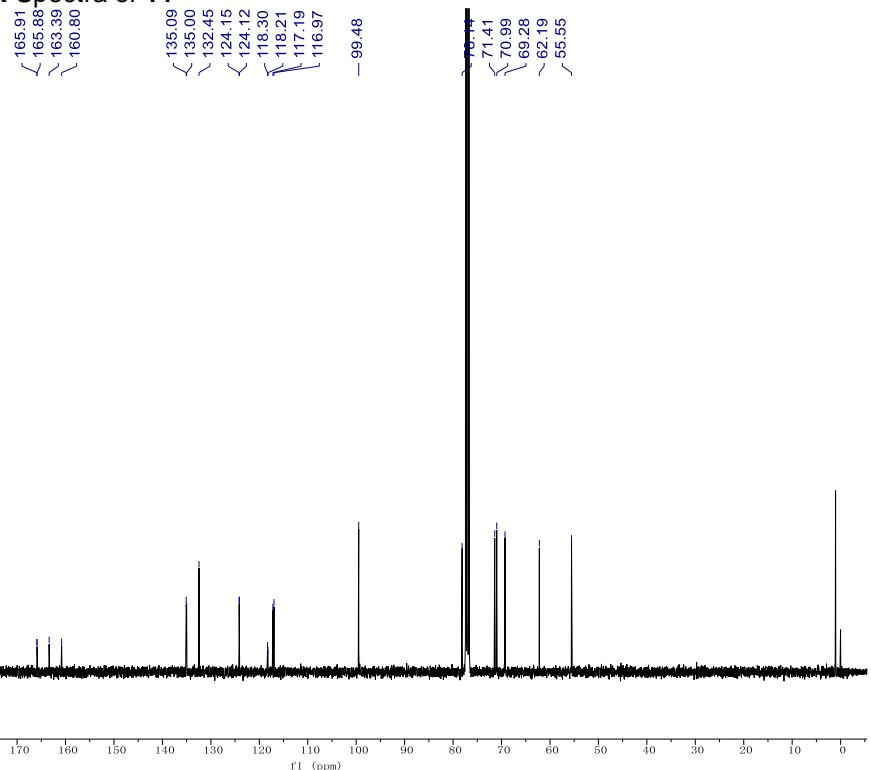
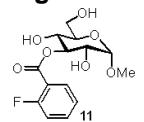
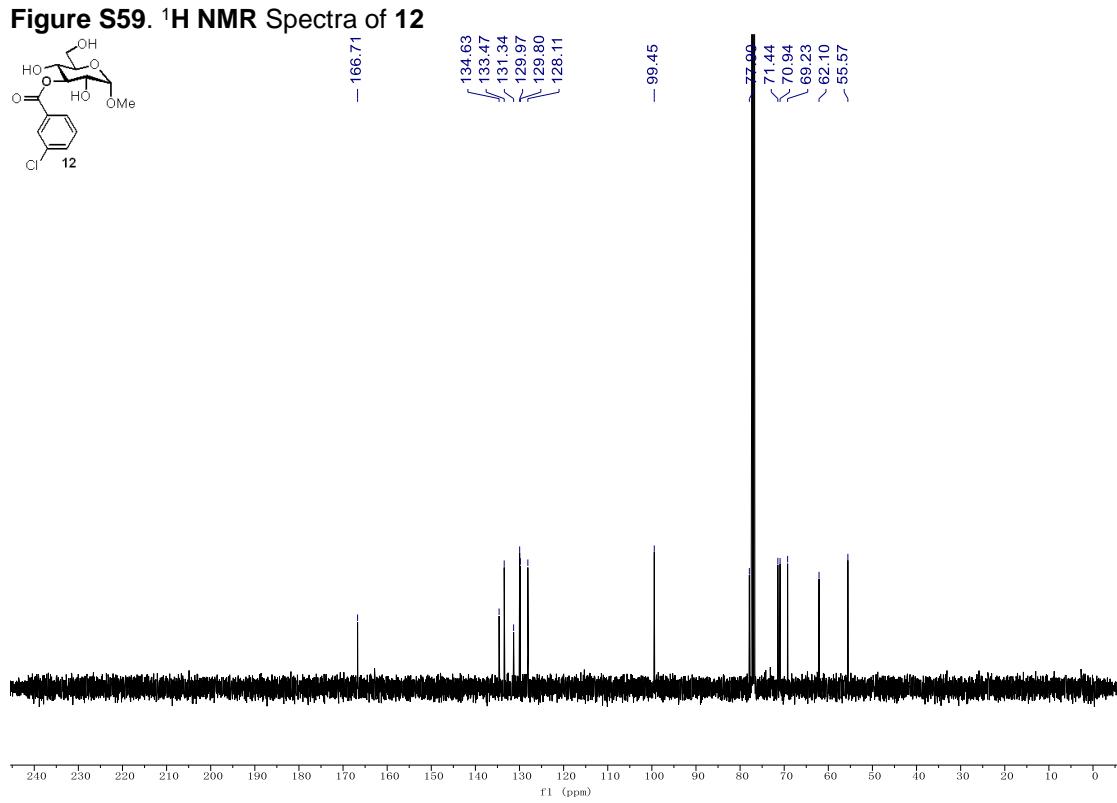
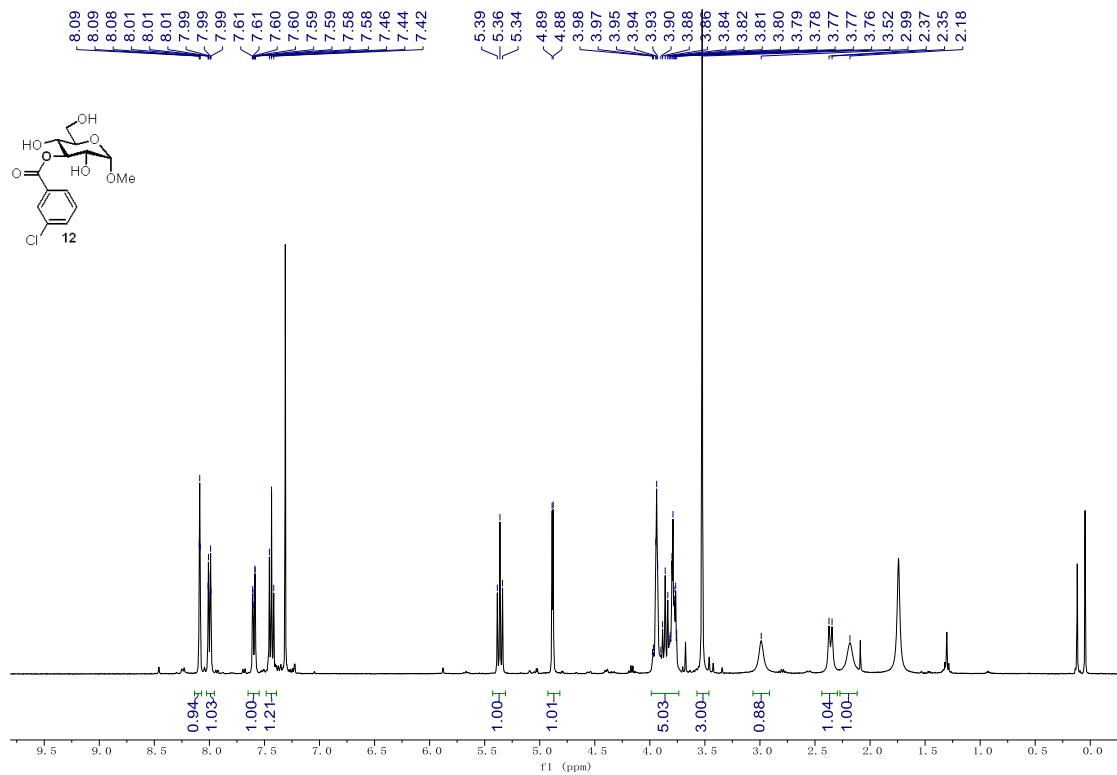


Figure S58. ^{13}C NMR Spectra of 11



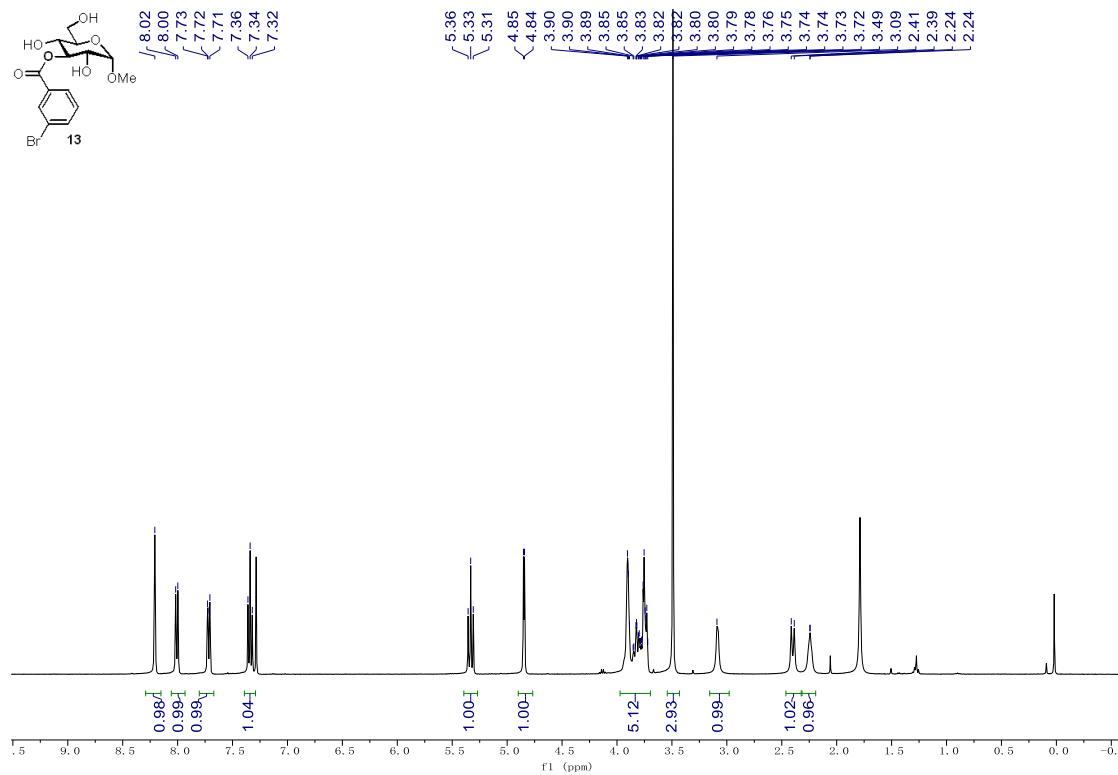


Figure S61. ^1H NMR Spectra of 13

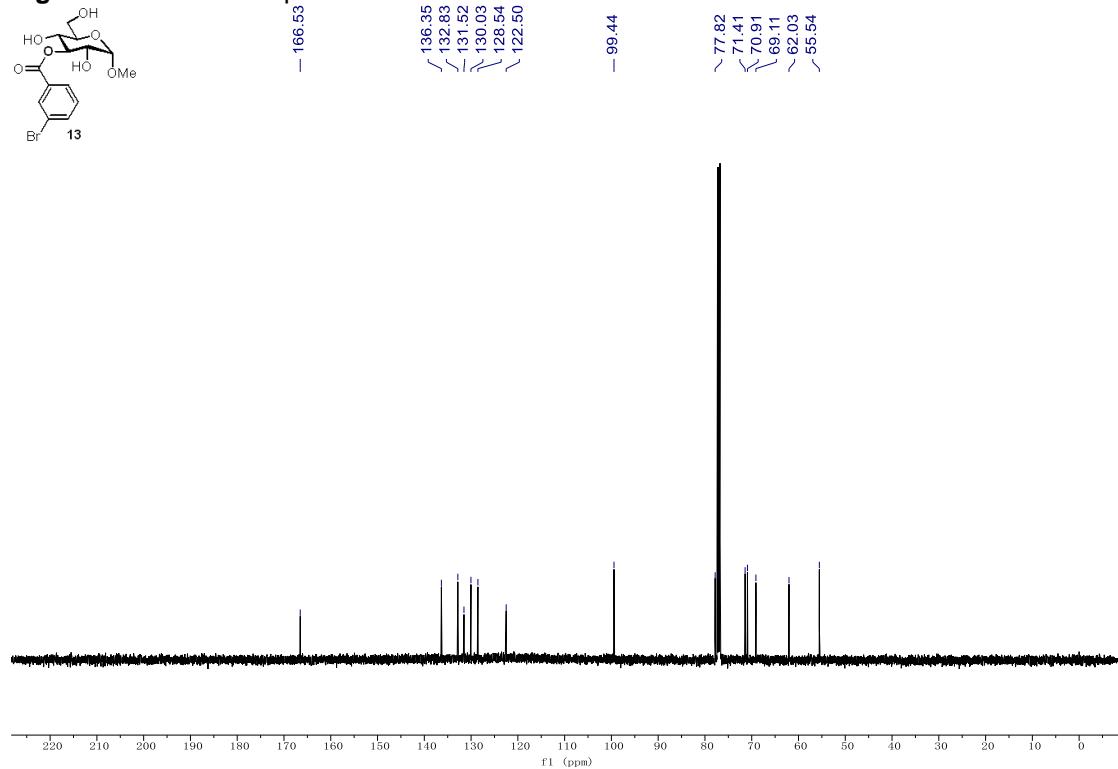


Figure S62. ^{13}C NMR Spectra of 13

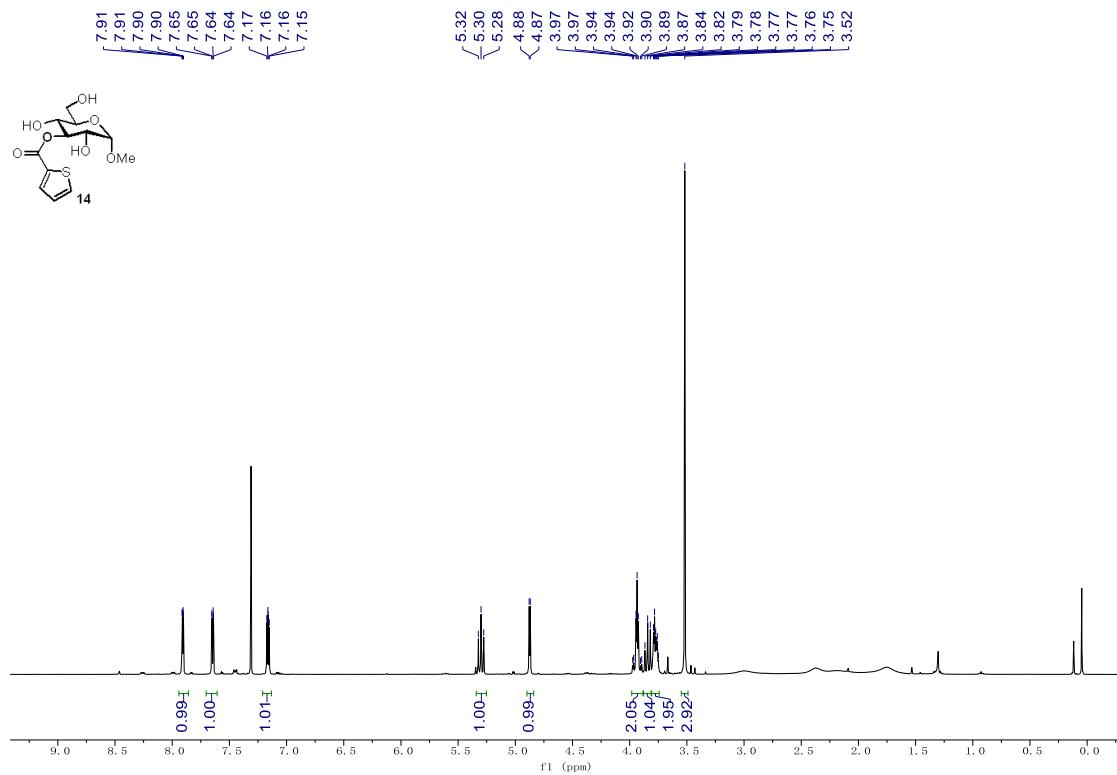


Figure S63. ^1H NMR Spectra of **14**

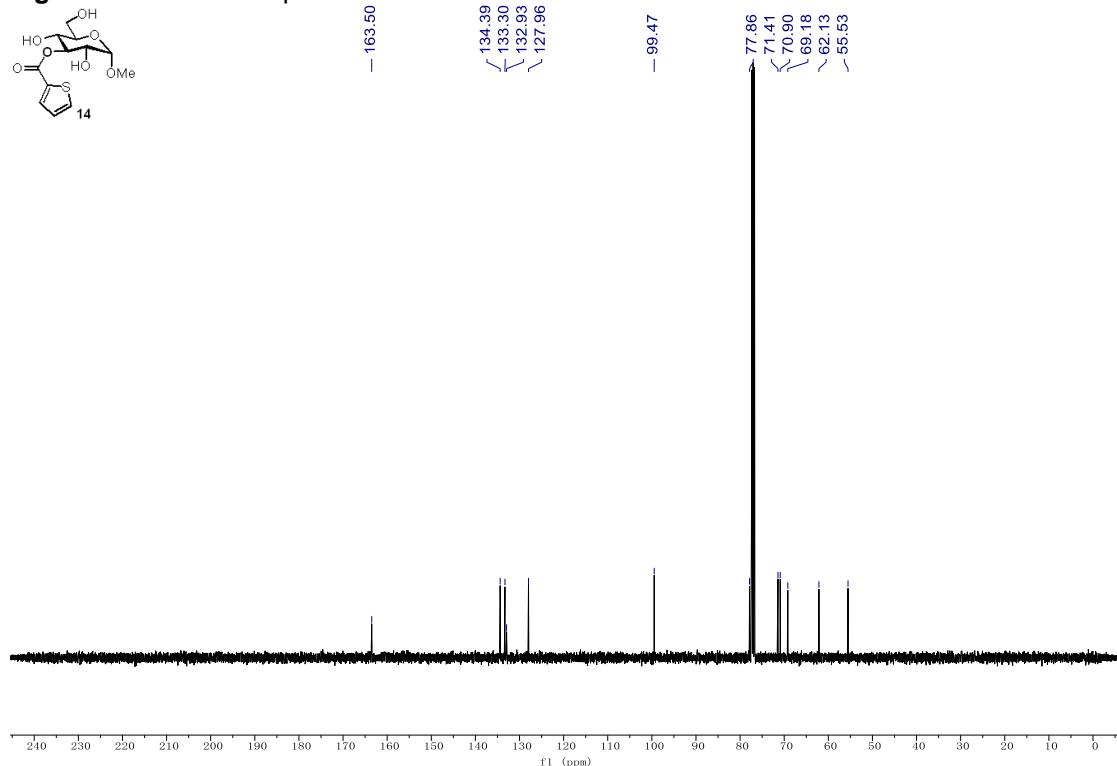


Figure S64. ^{13}C NMR Spectra of **14**

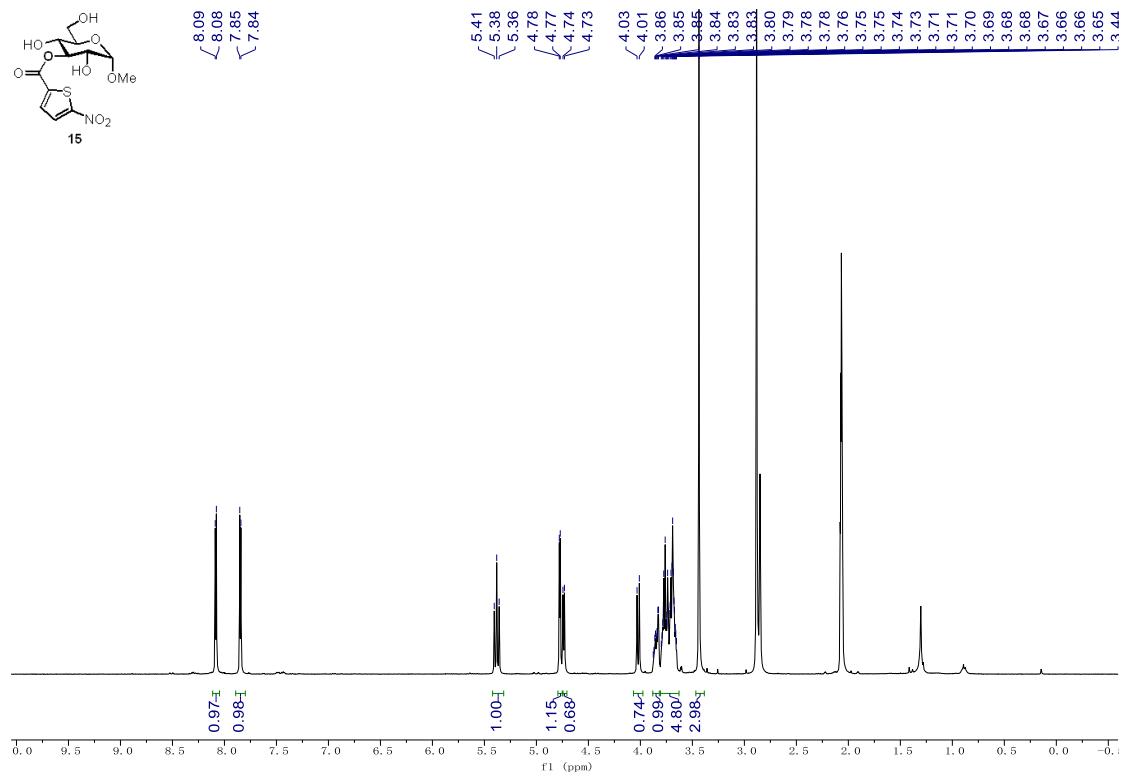


Figure S65. ^1H NMR Spectra of 15

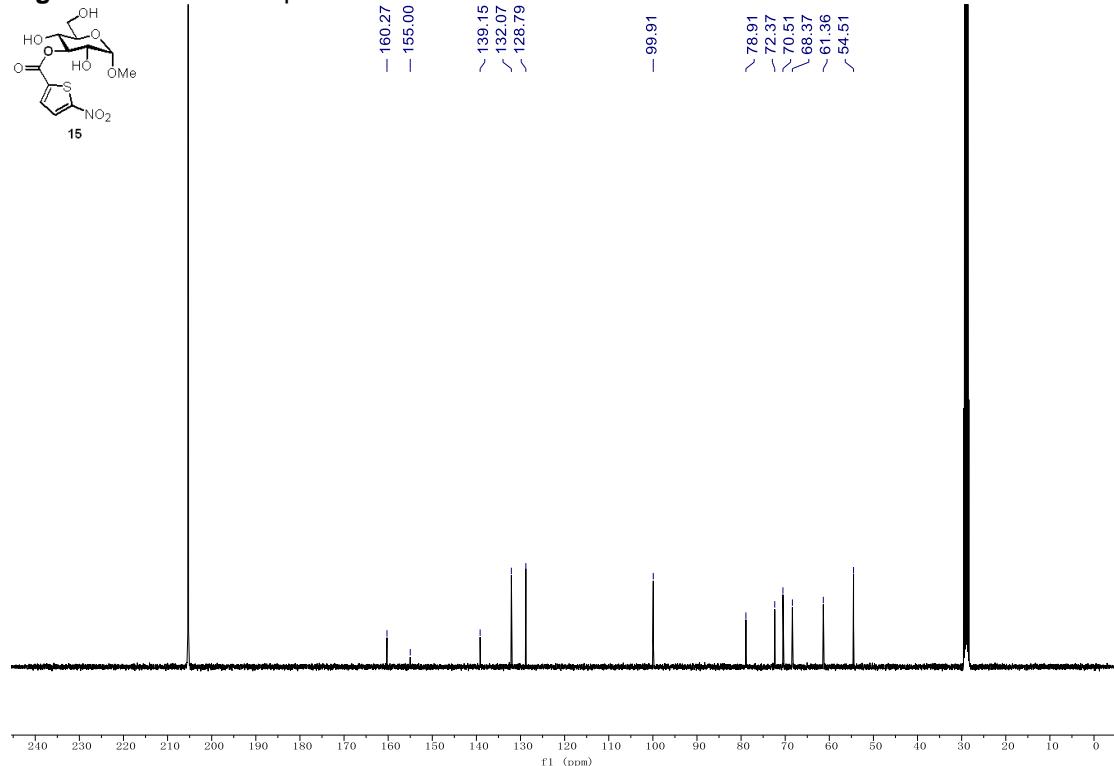


Figure S66. ^{13}C NMR Spectra of 15

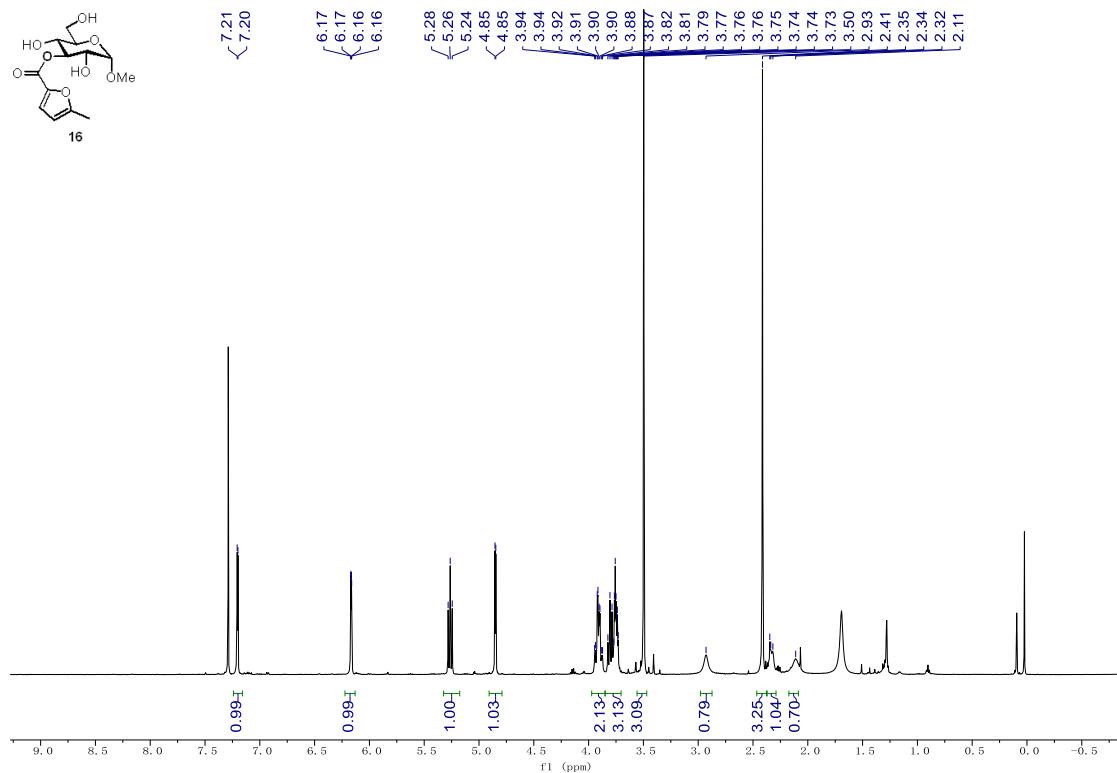


Figure S67. ^1H NMR Spectra of 16

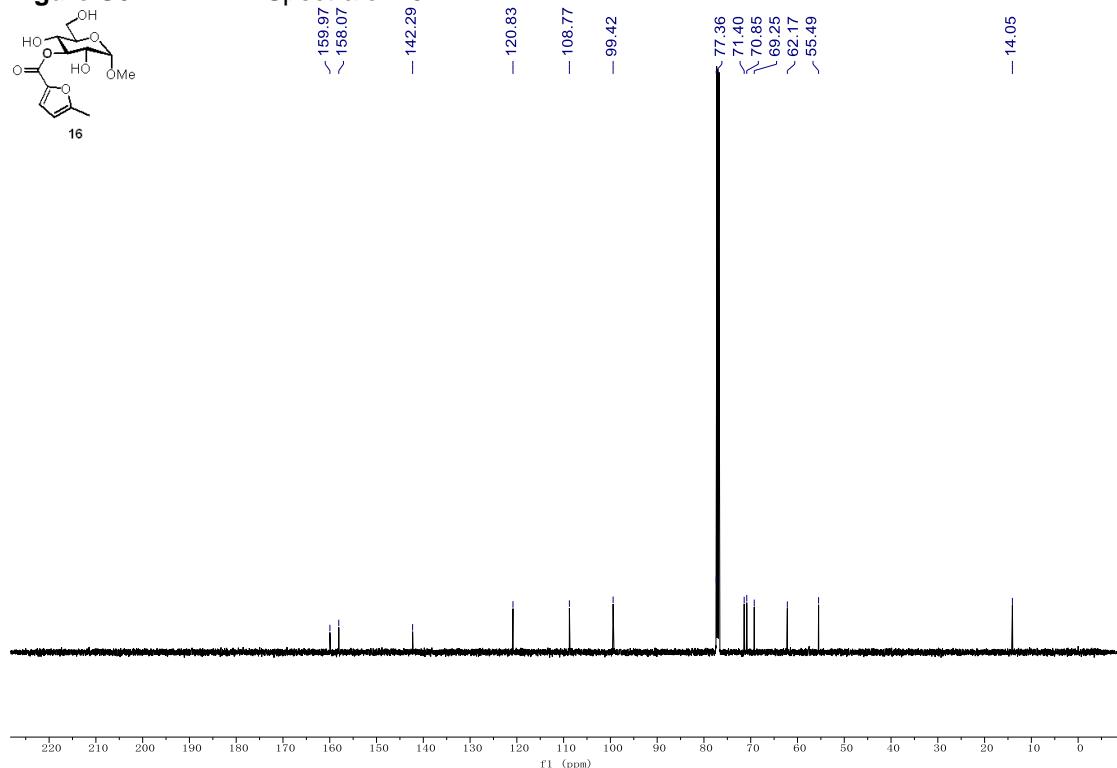


Figure S68. ^{13}C NMR Spectra of 16

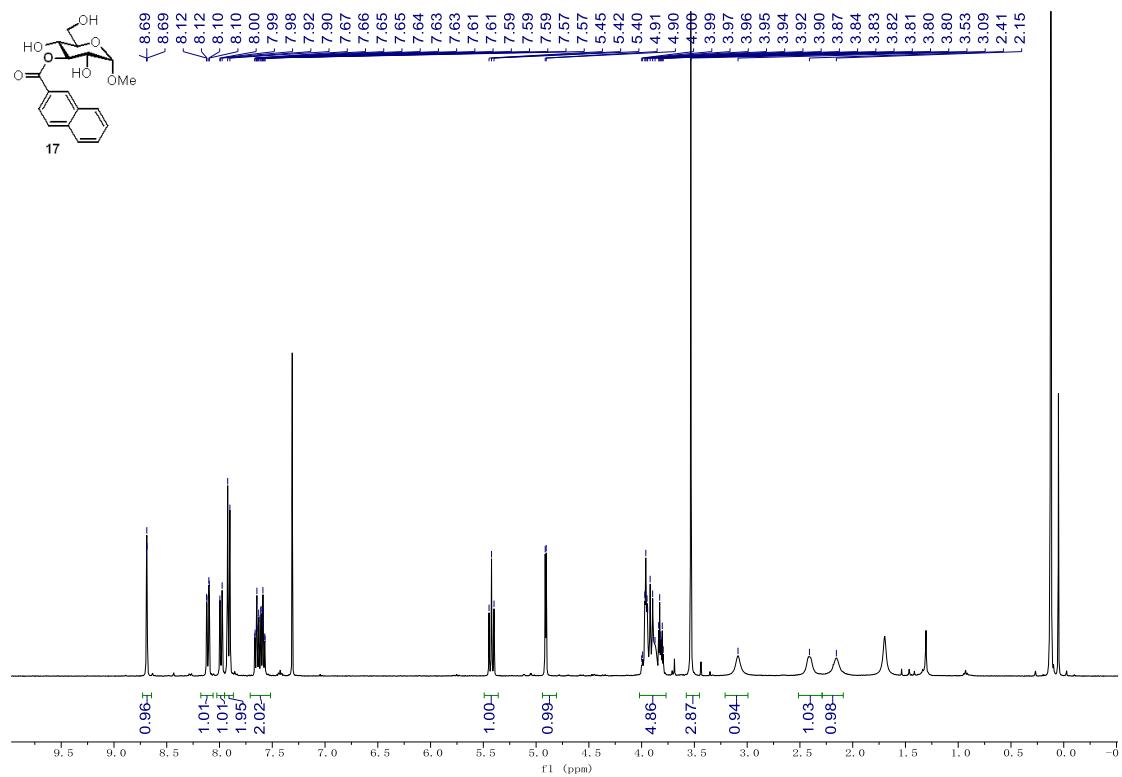


Figure S69. ^1H NMR Spectra of **17**

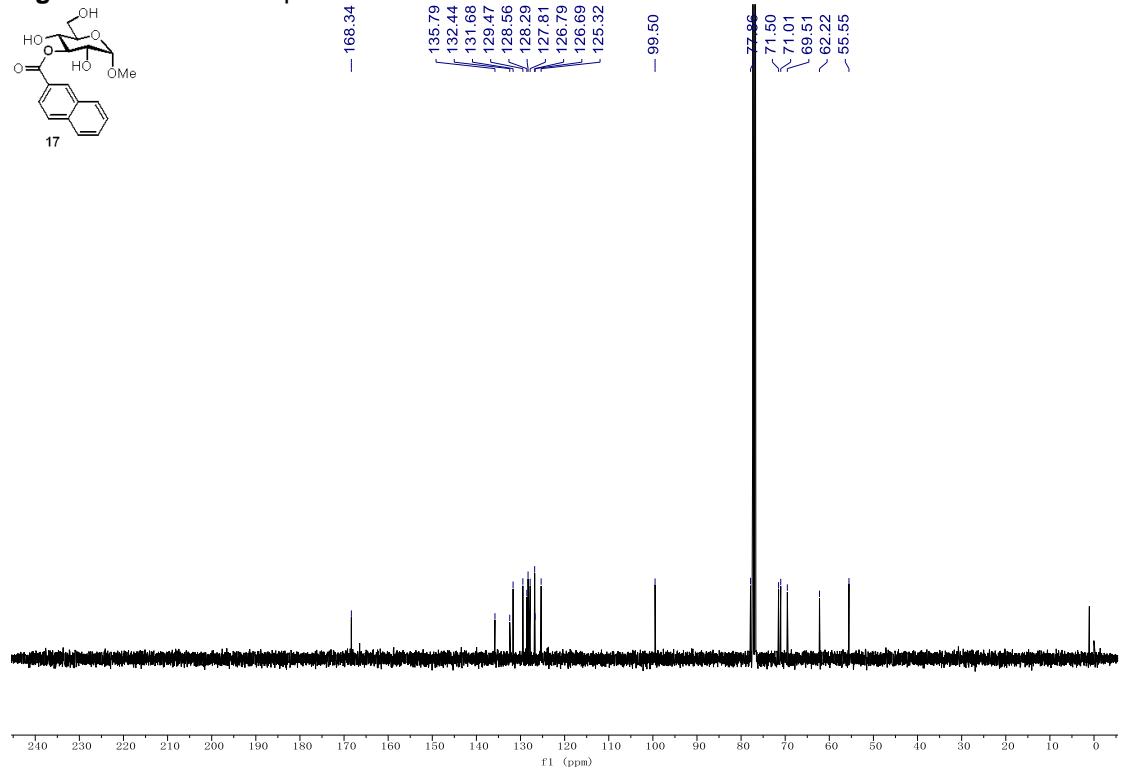


Figure S70. ^{13}C NMR Spectra of **17**

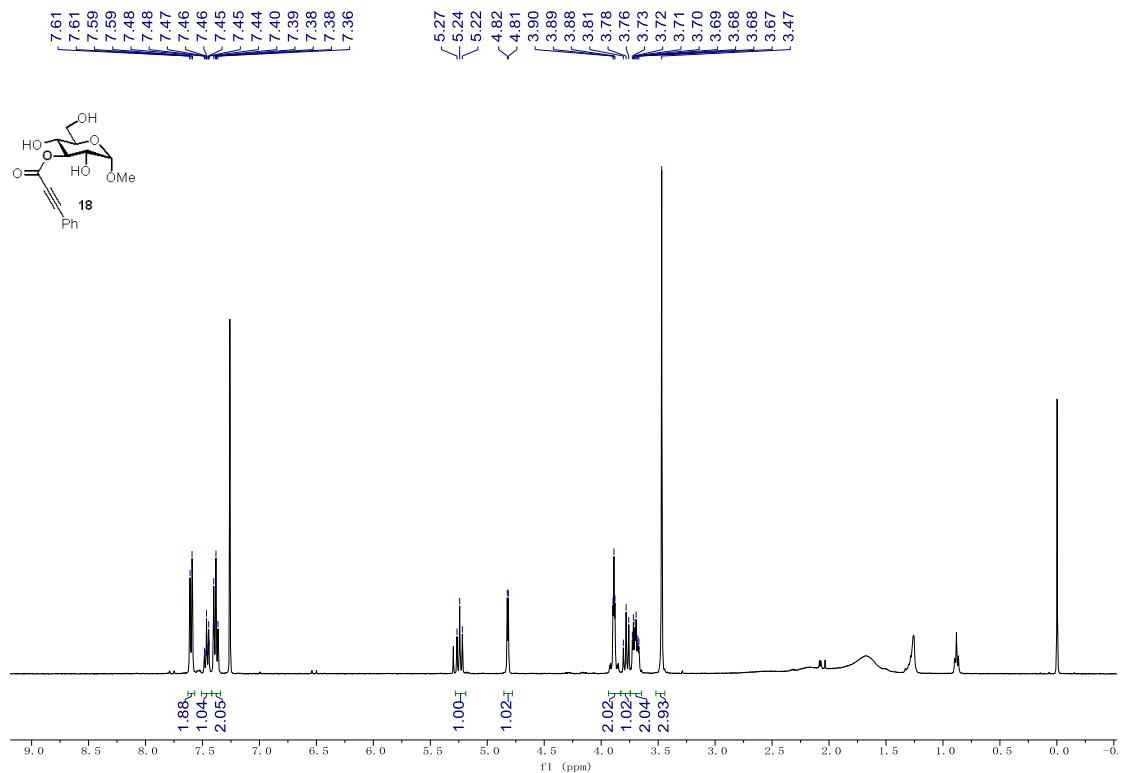


Figure S71. ^1H NMR Spectra of 18

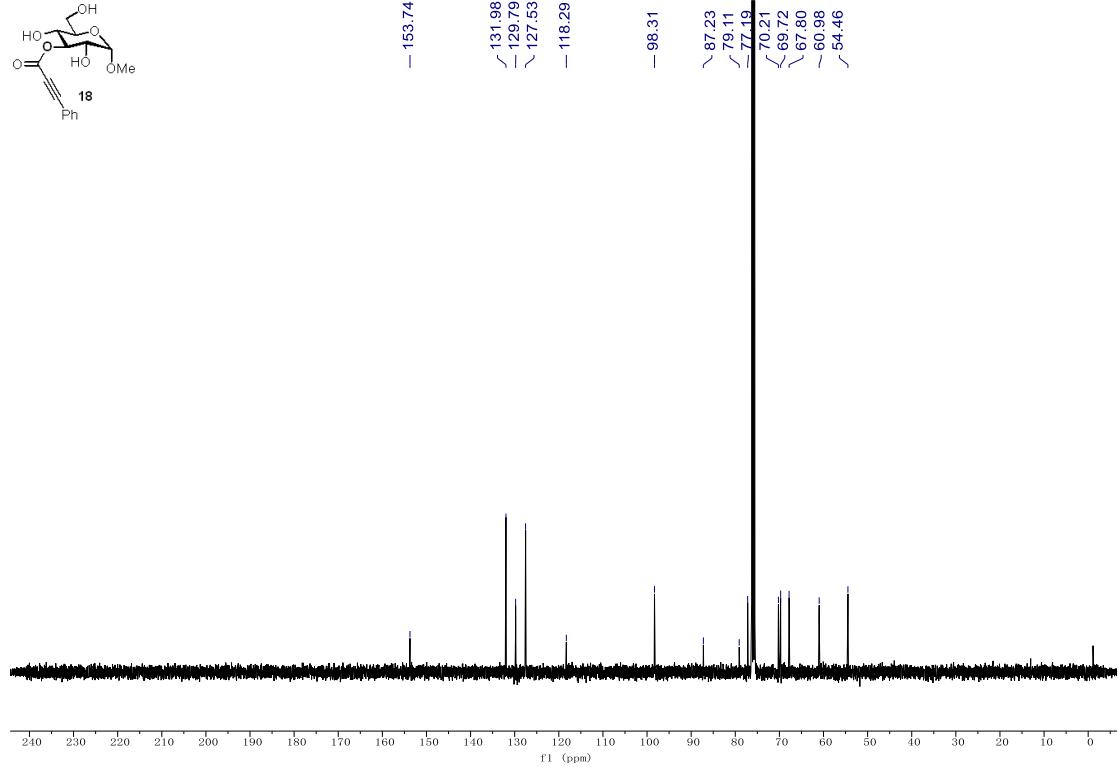
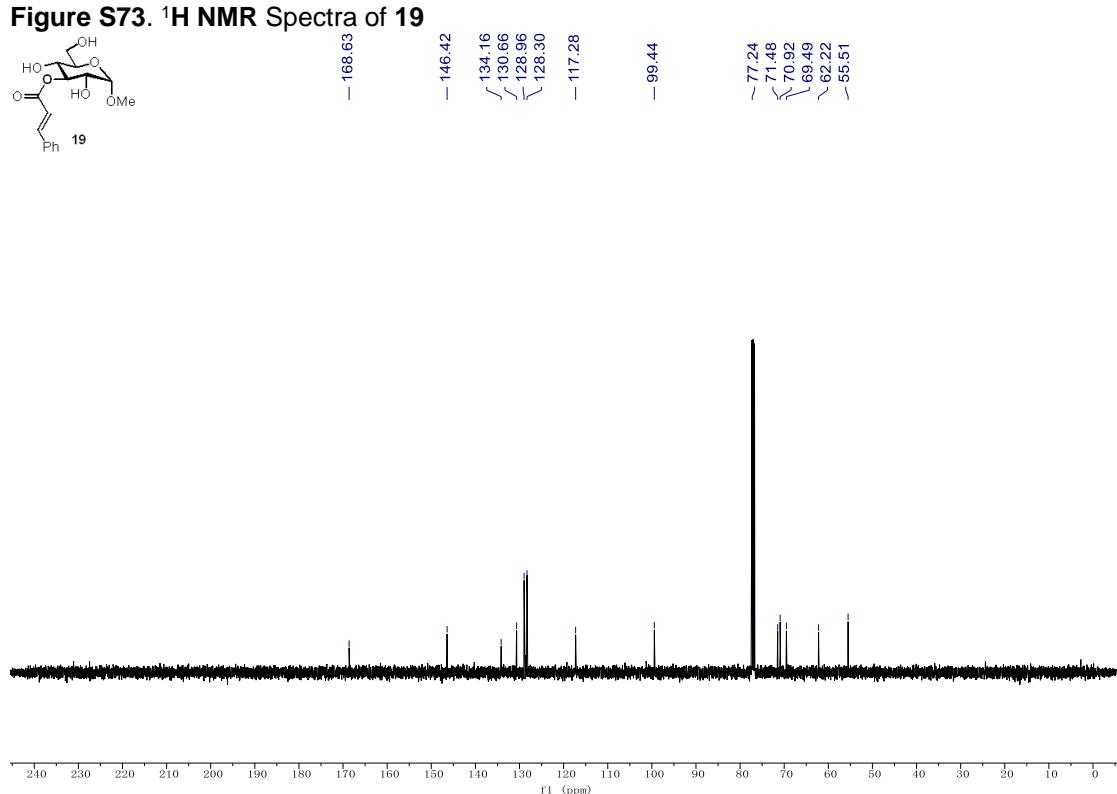
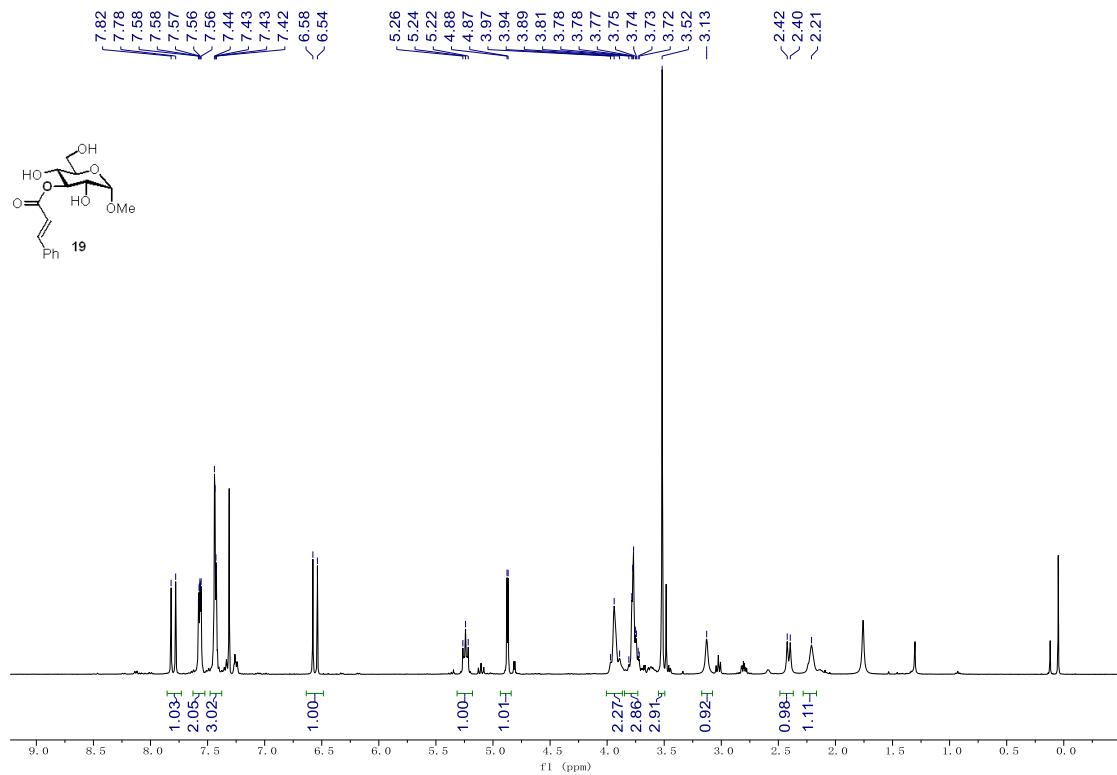


Figure S72. ^{13}C NMR Spectra of 18



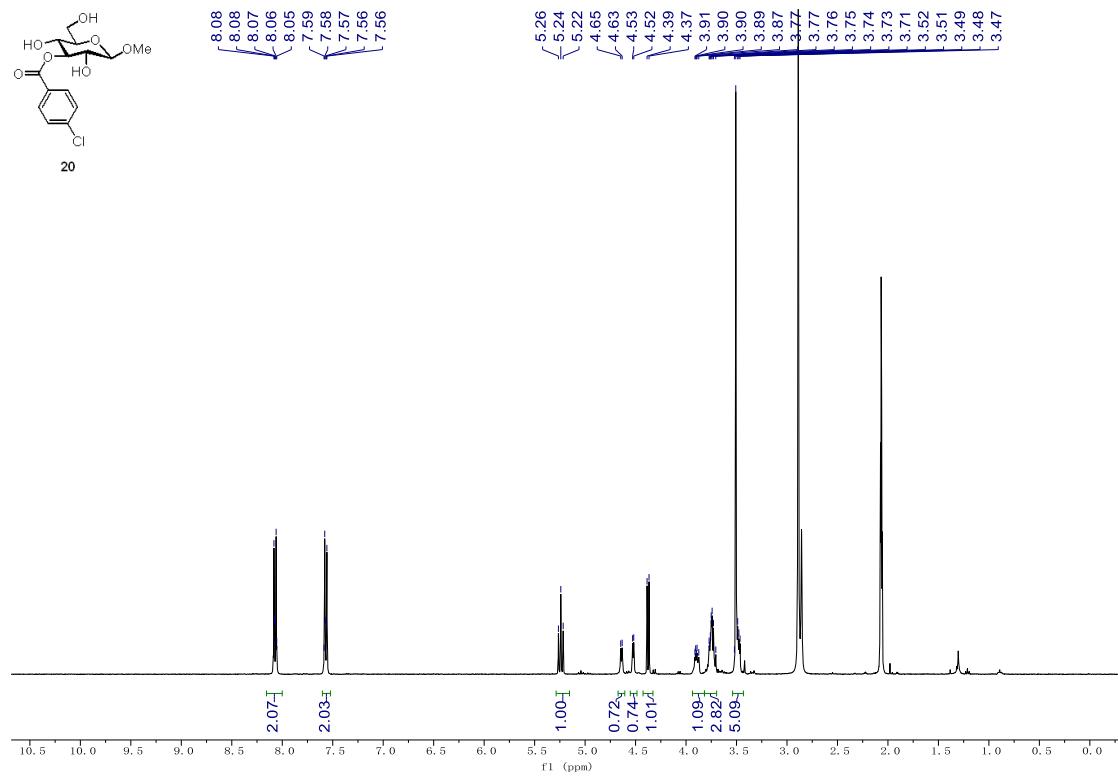


Figure S75. ^1H NMR Spectra of **20**

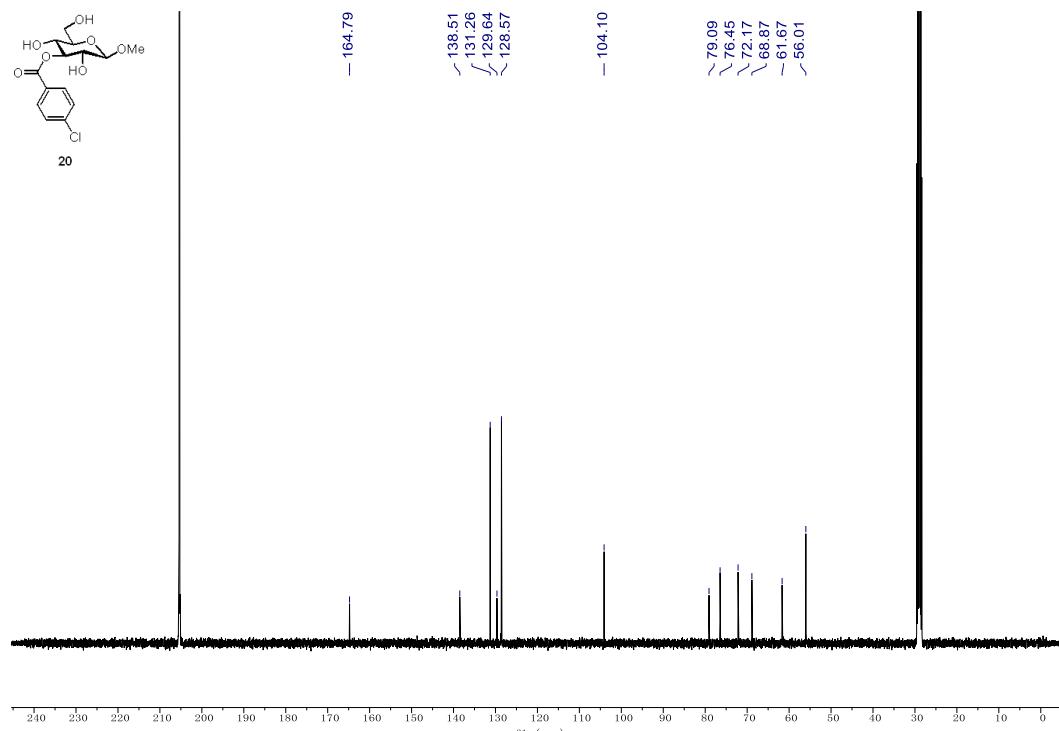


Figure S76. ¹³C NMR Spectra of **21**

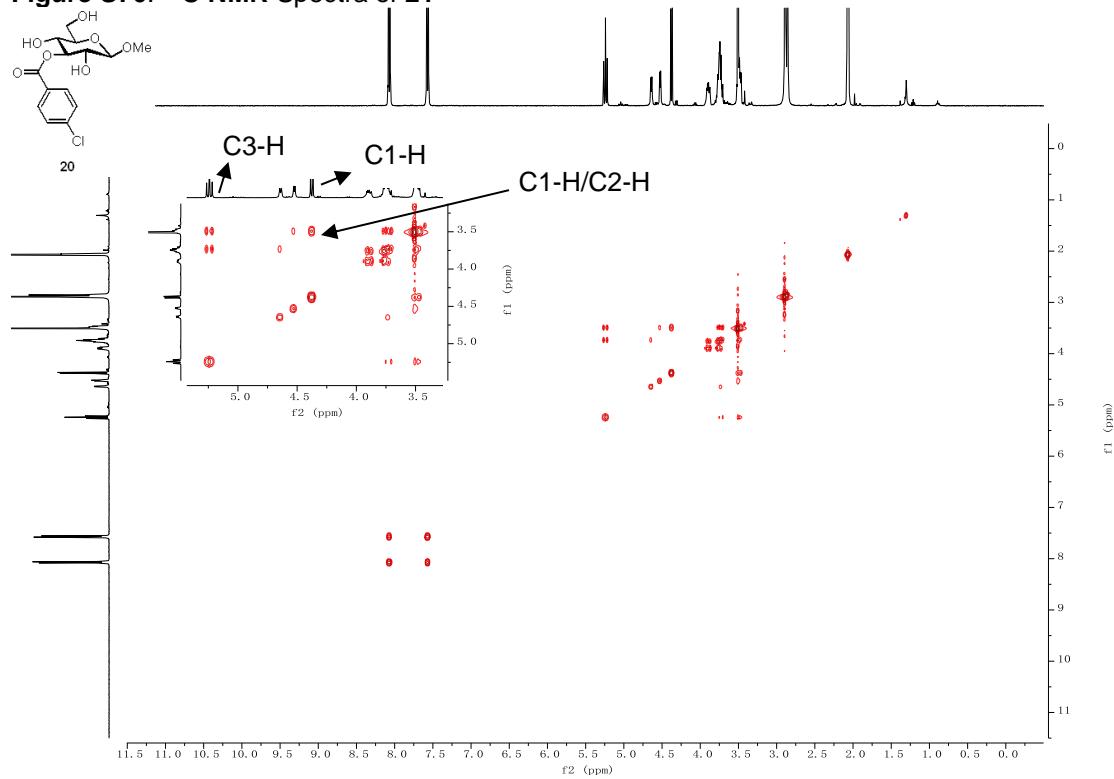


Figure S77. COSY NMR Spectra of **20**

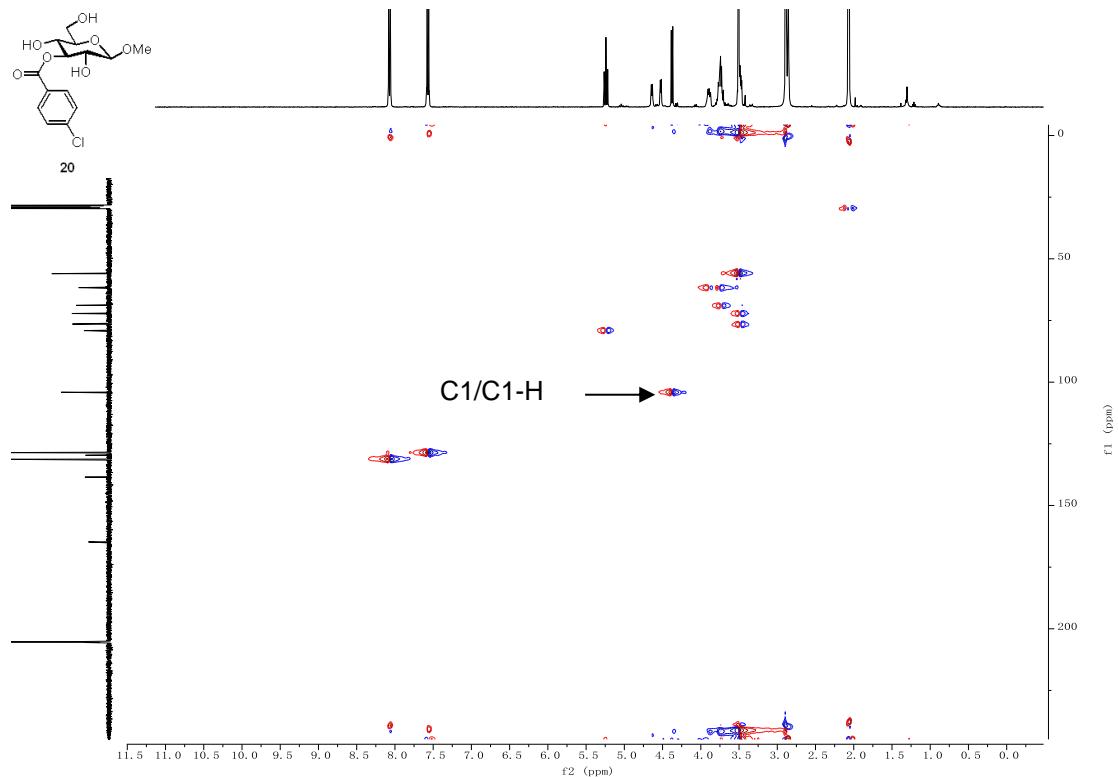


Figure S78. HSQC NMR Spectra of 20

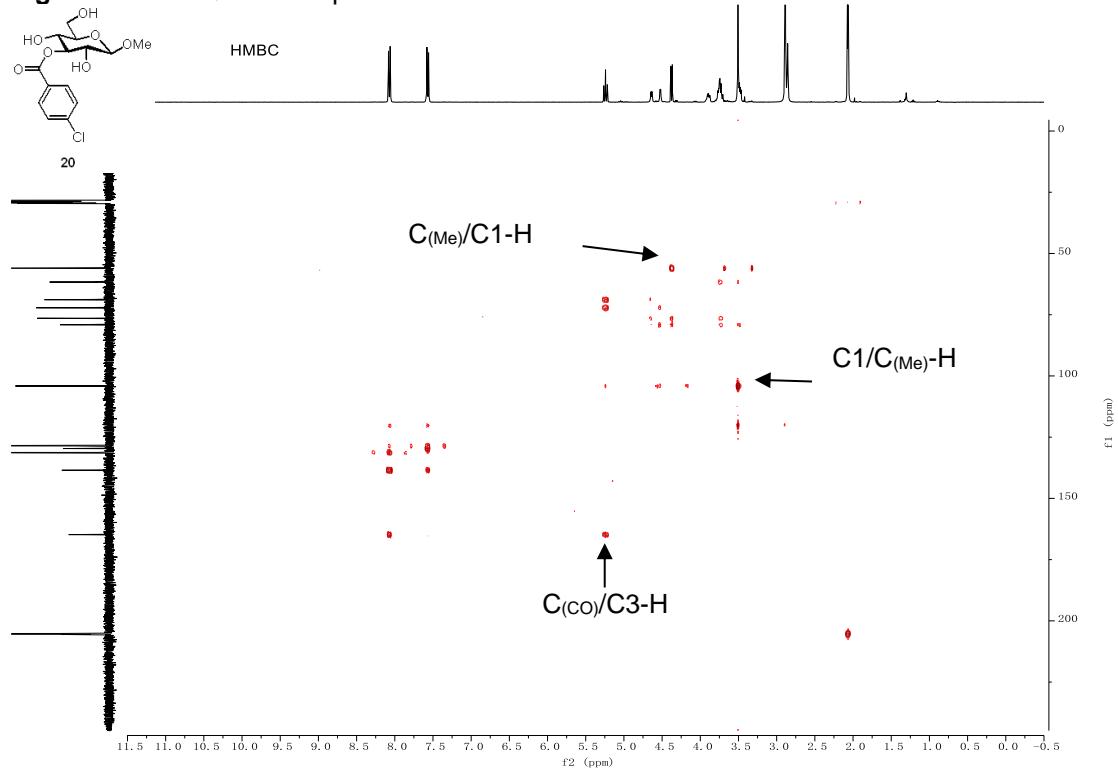
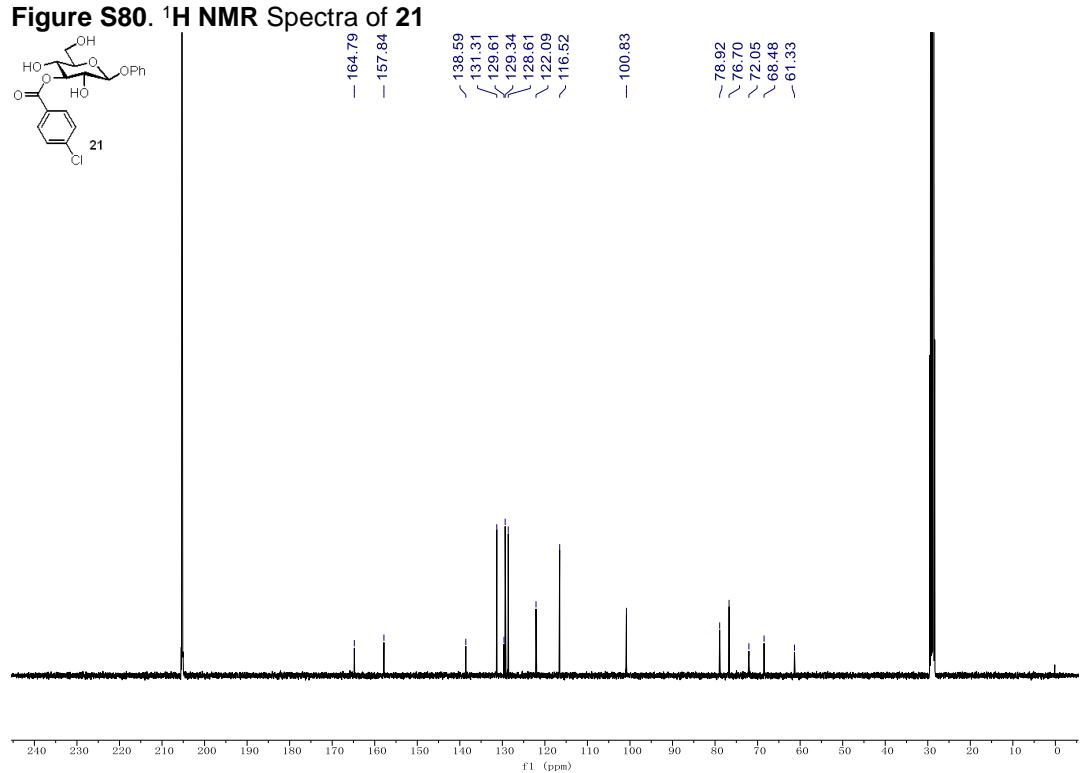
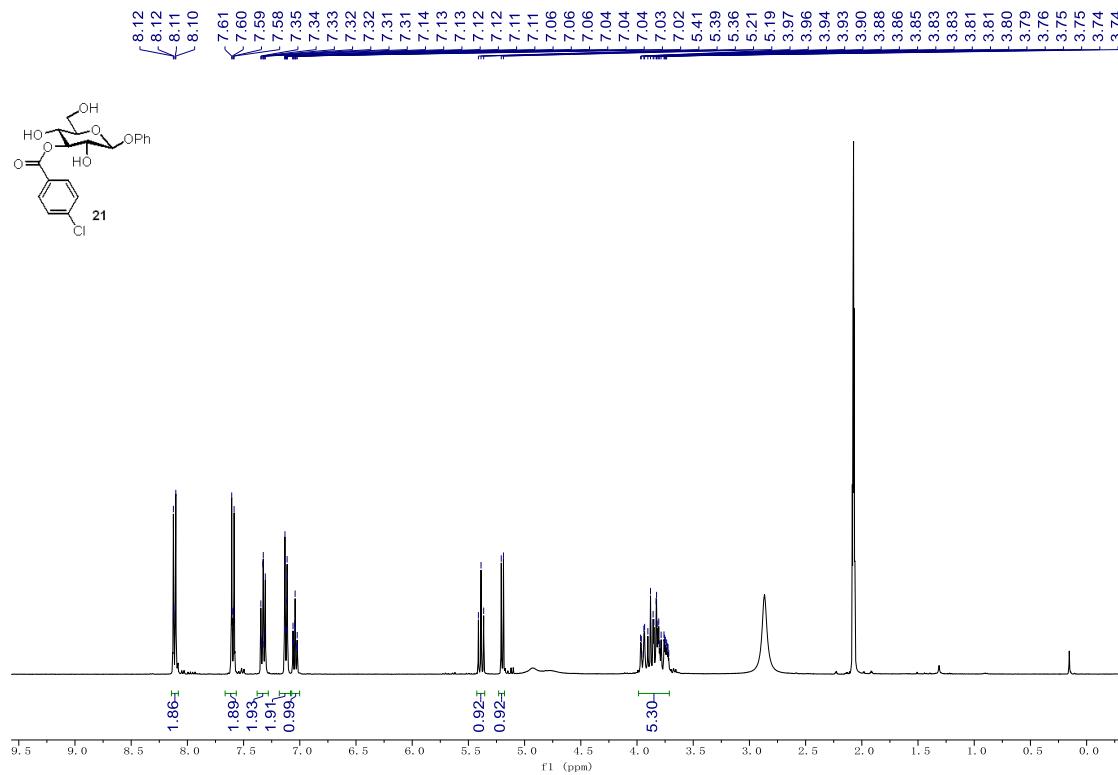


Figure S79. HMBC NMR Spectra of 20



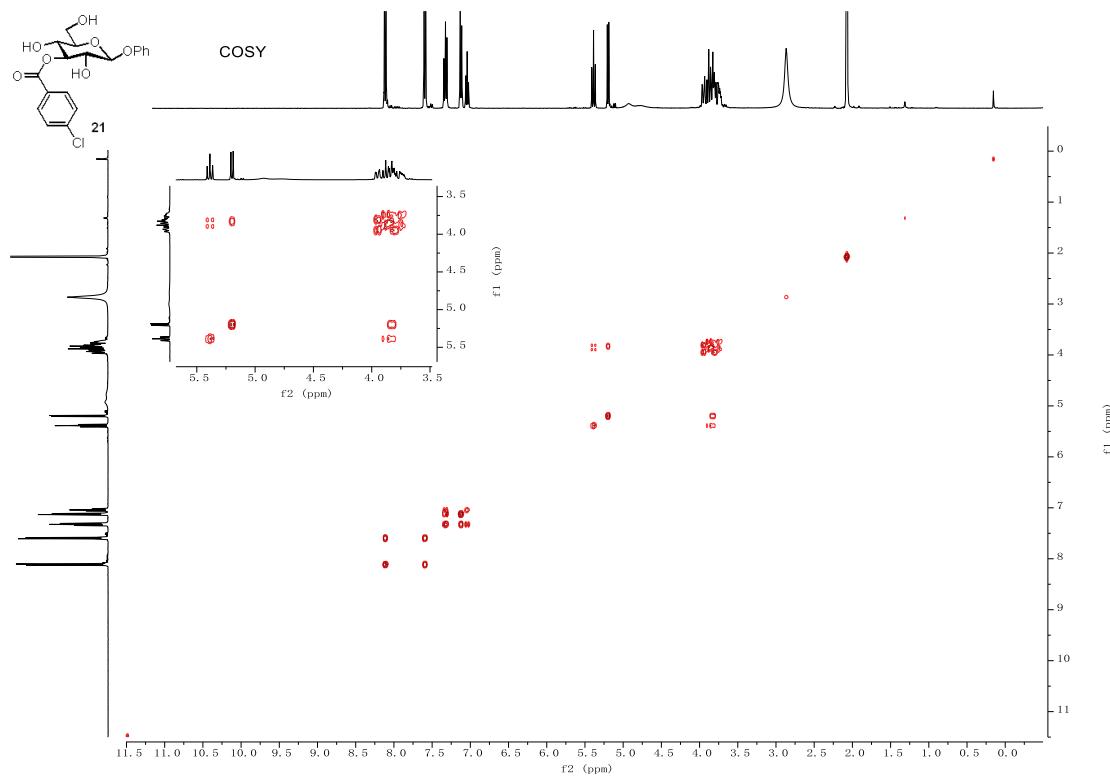


Figure S82. COSY NMR Spectra of 21

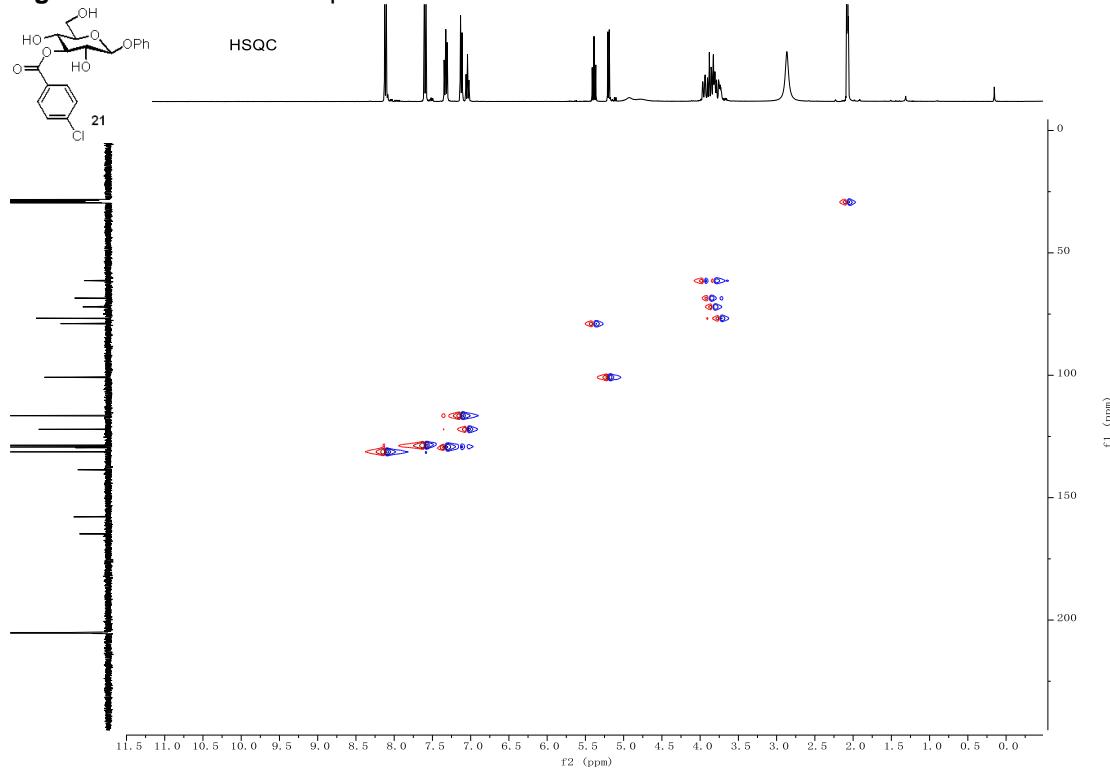


Figure S83. HSQC NMR Spectra of 21

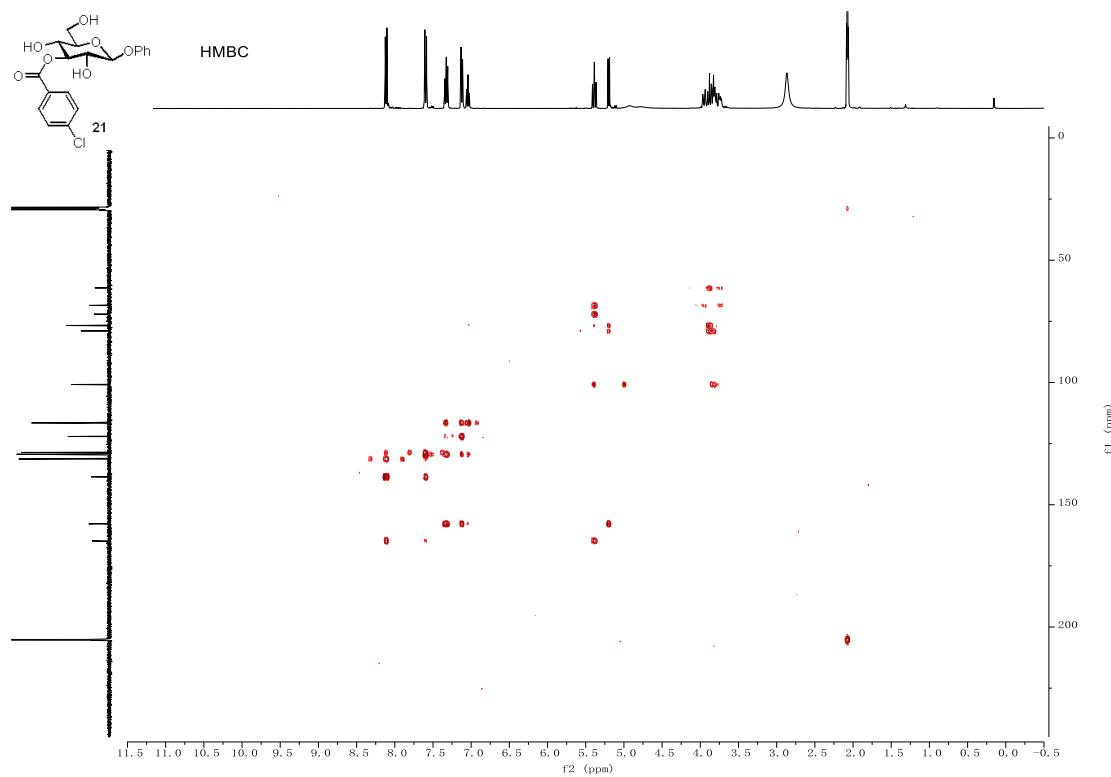


Figure S84. HMBC NMR Spectra of **21**

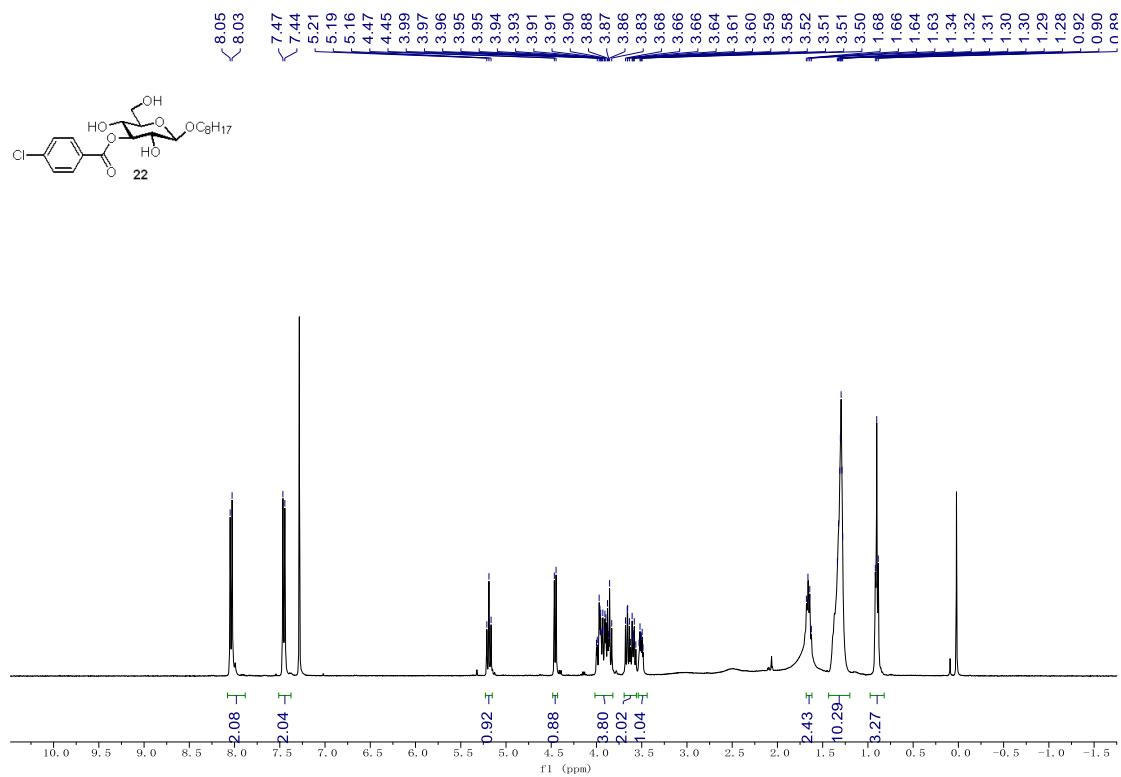


Figure S85. ^1H NMR Spectra of 22

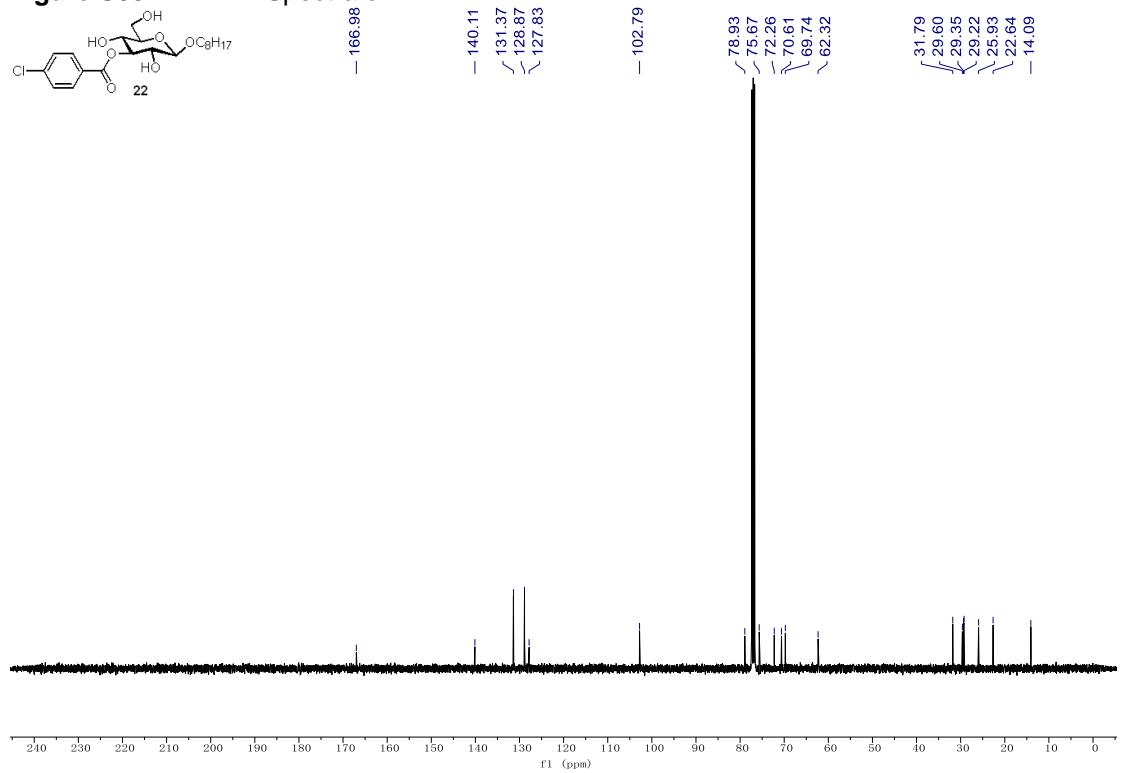


Figure S86. ^{13}C NMR Spectra of 22

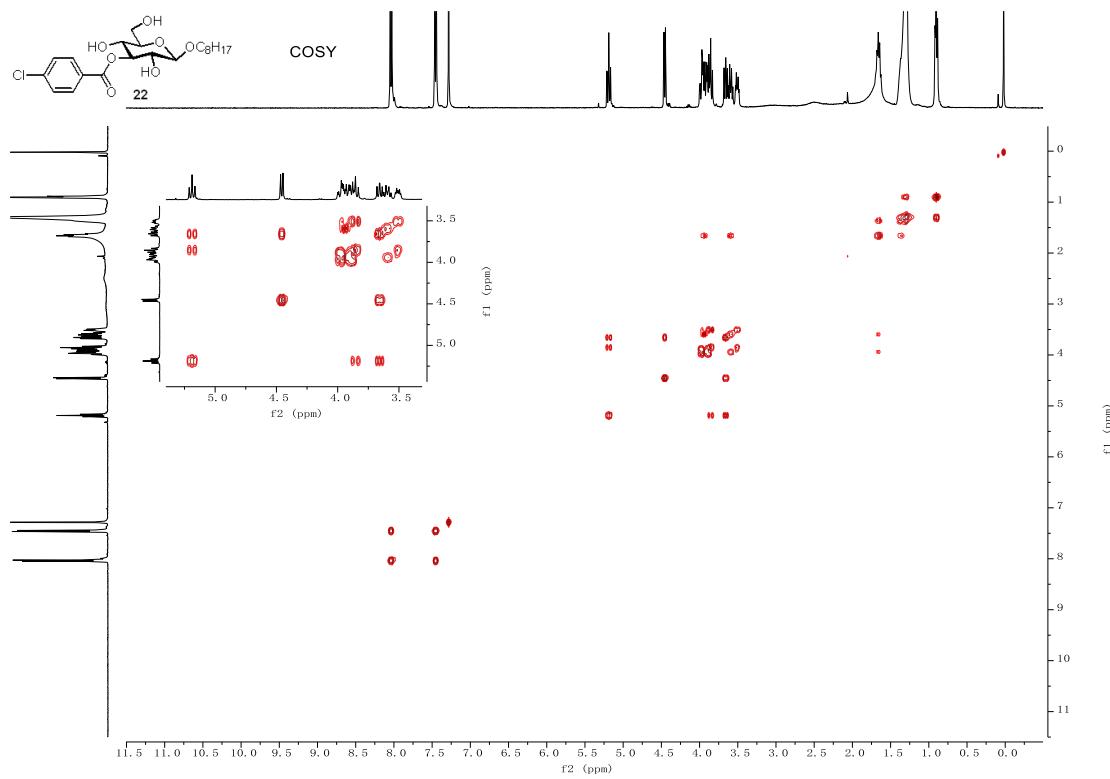


Figure S87. COSY NMR Spectra of 22

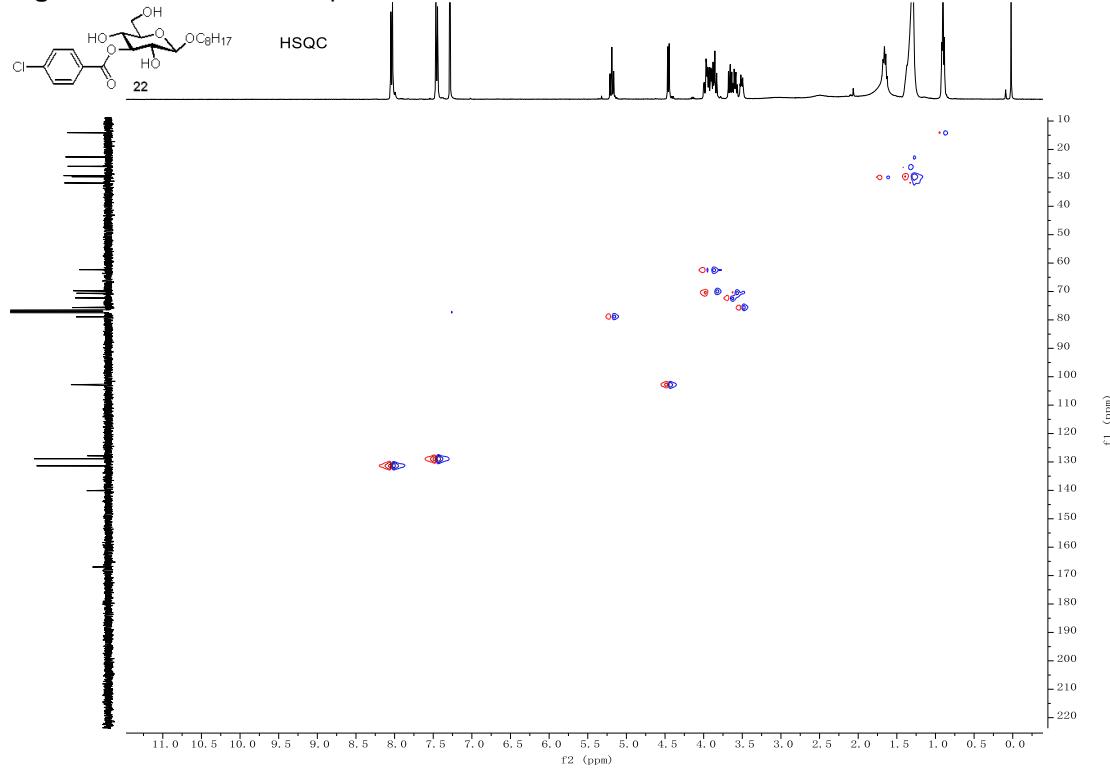


Figure S88. HSQC NMR Spectra of 22

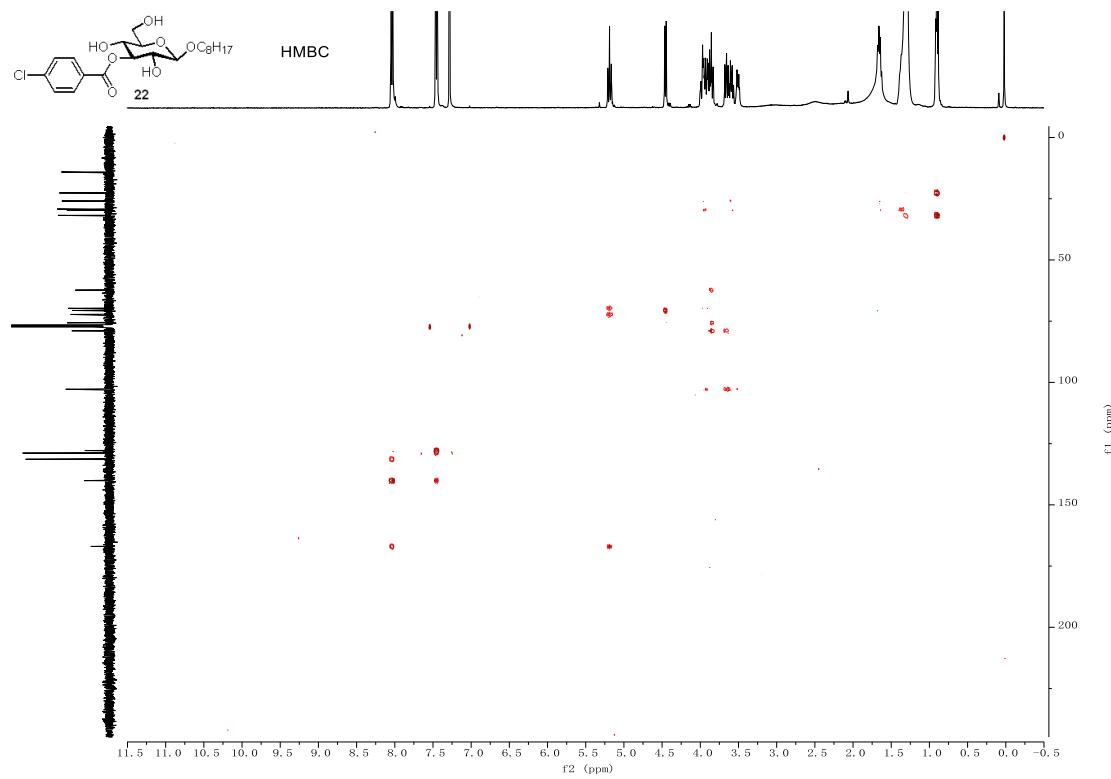


Figure S89. HMBC NMR Spectra of 22

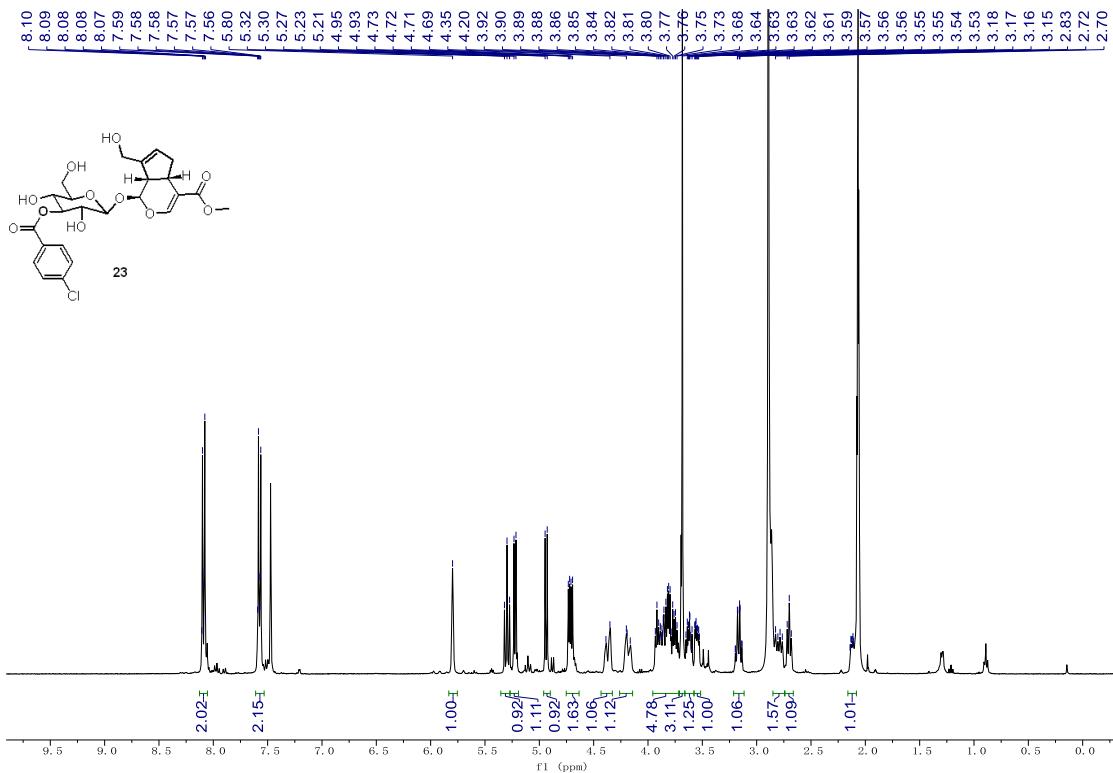


Figure S90. ^1H NMR Spectra of 23

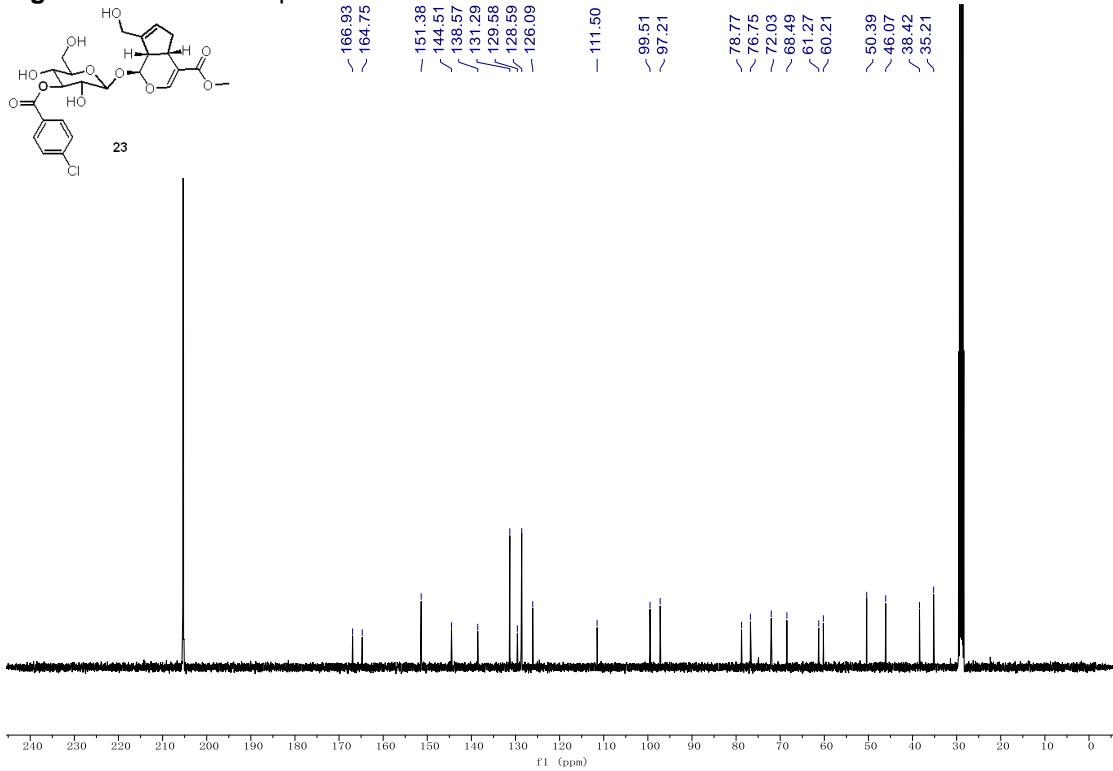


Figure S91. ^{13}C NMR Spectra of 23

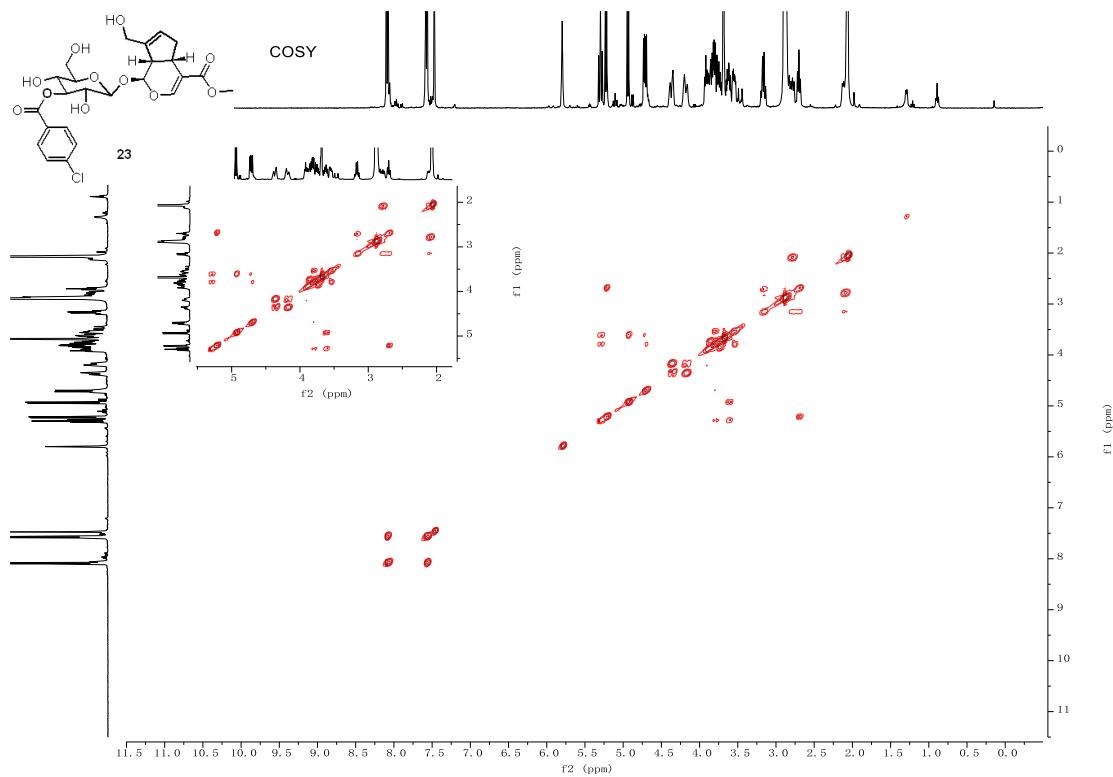


Figure S92. COSY NMR Spectra of 23

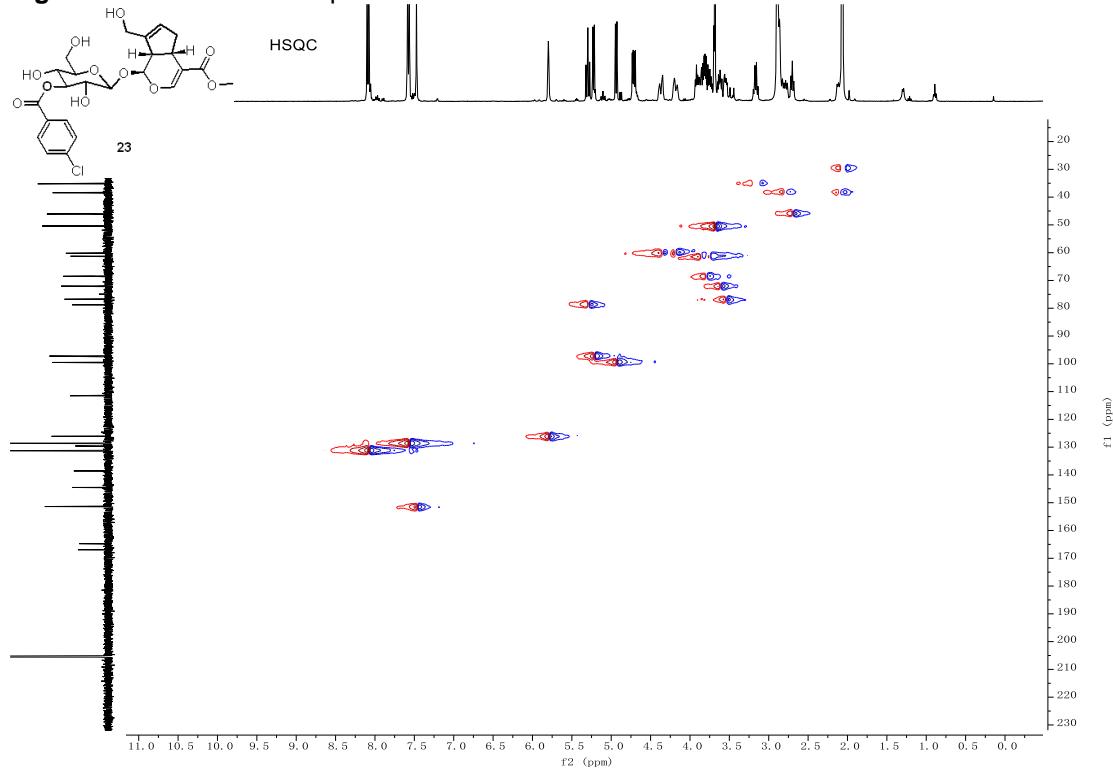


Figure S93. HSQC NMR Spectra of 23

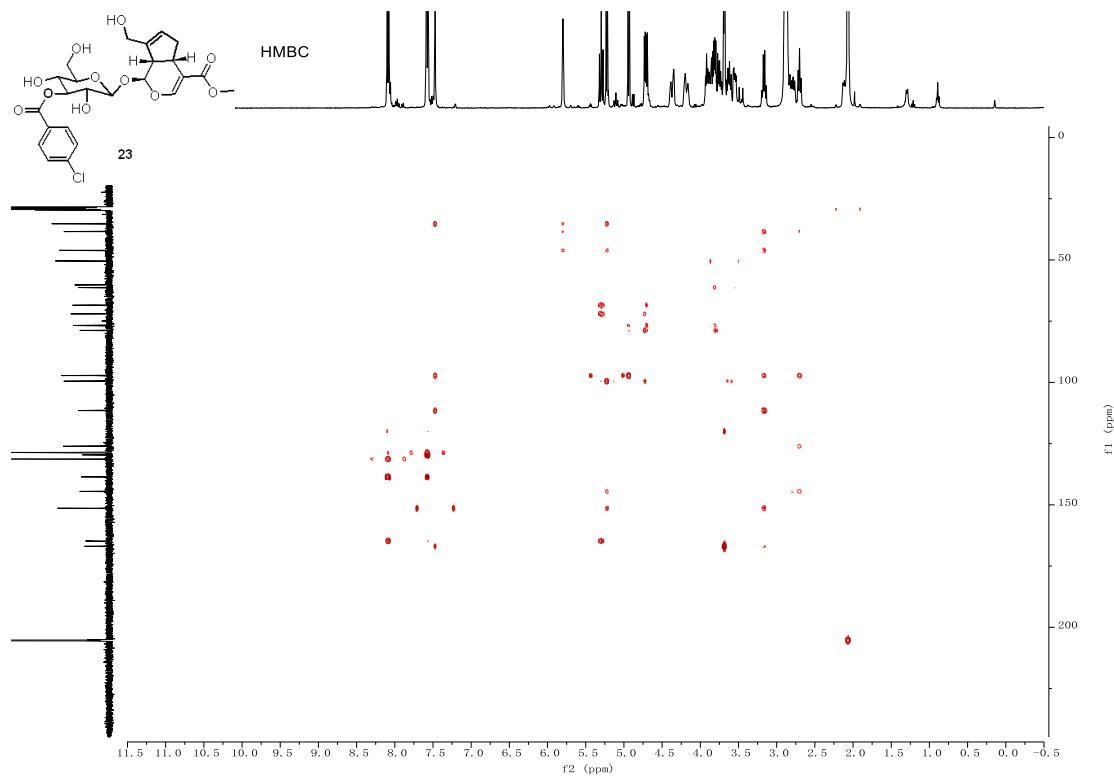
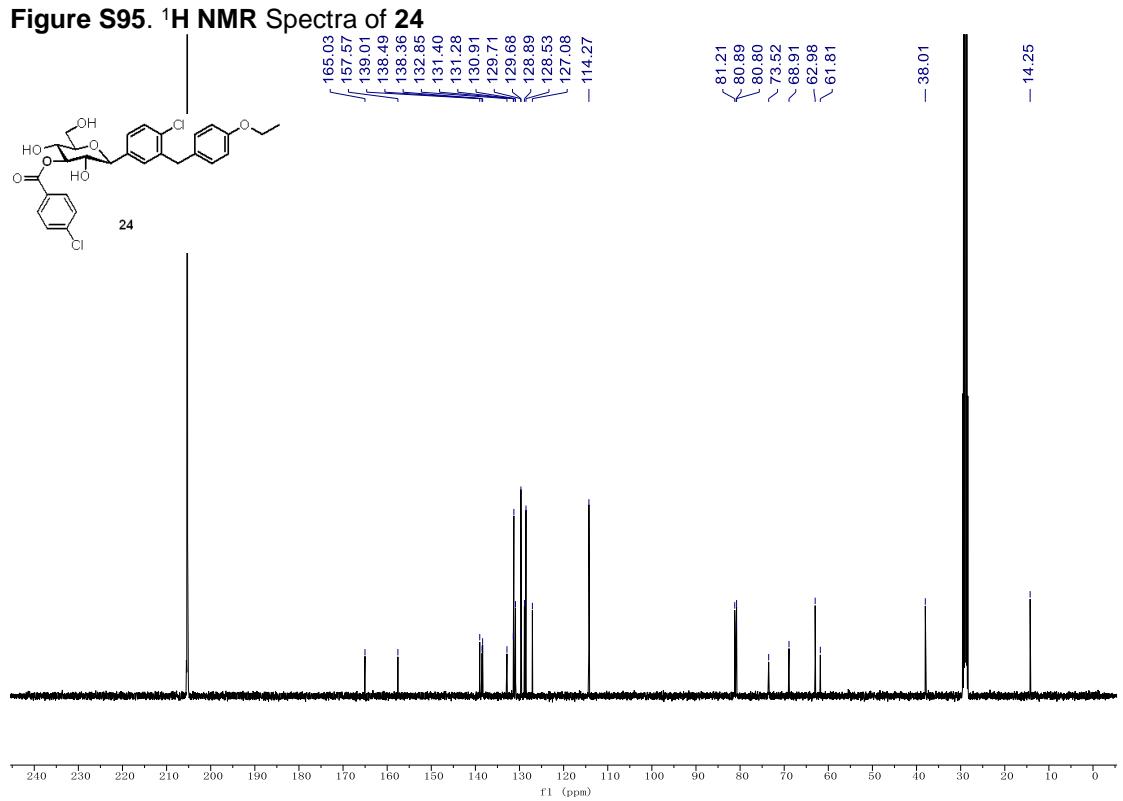
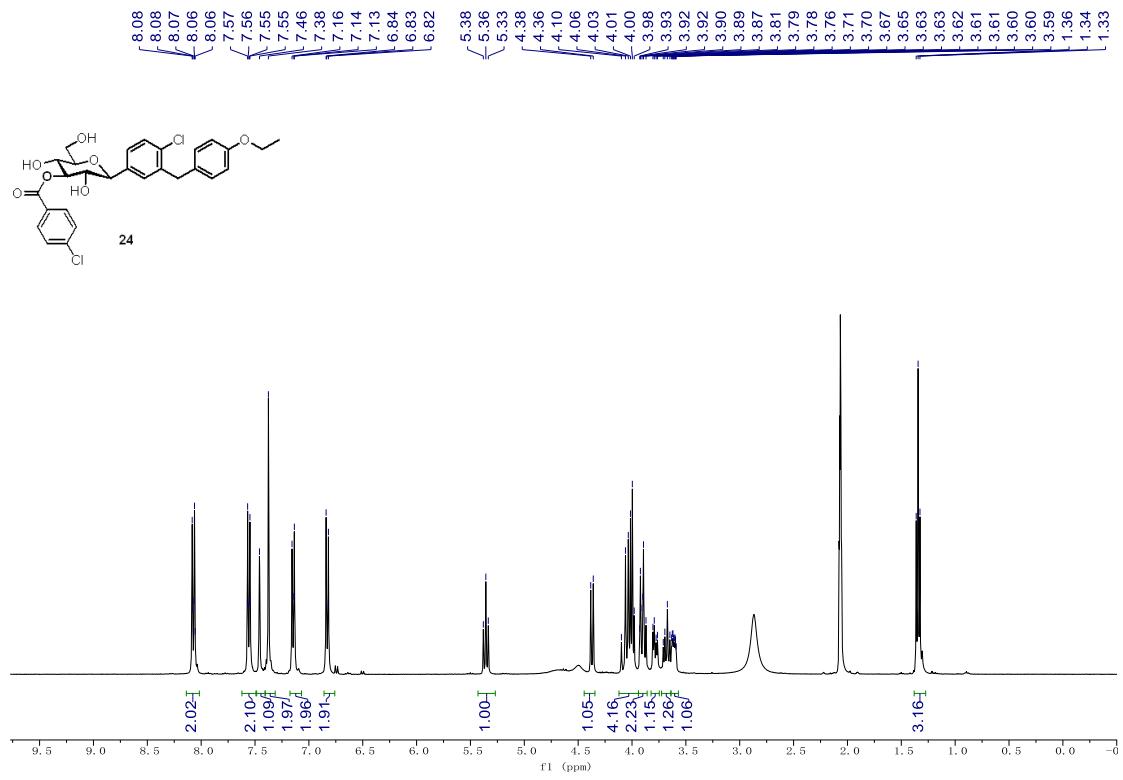


Figure S94. HMBC NMR Spectra of 23



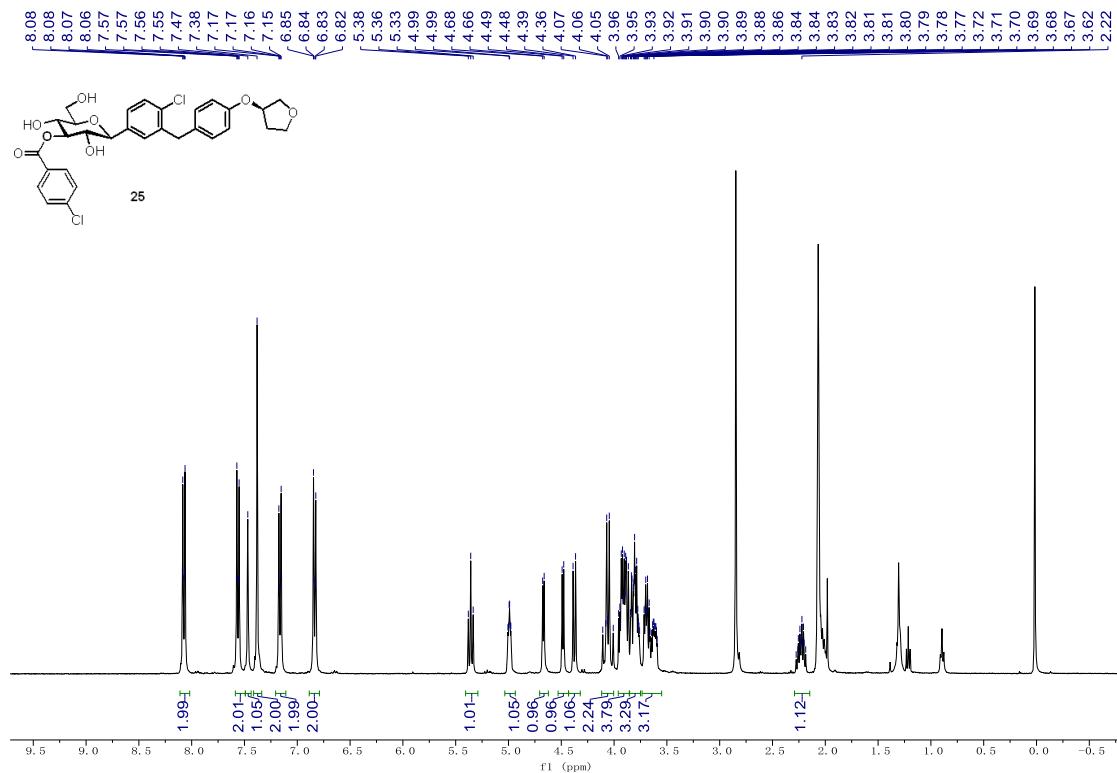


Figure S97. ^1H NMR Spectra of **25**

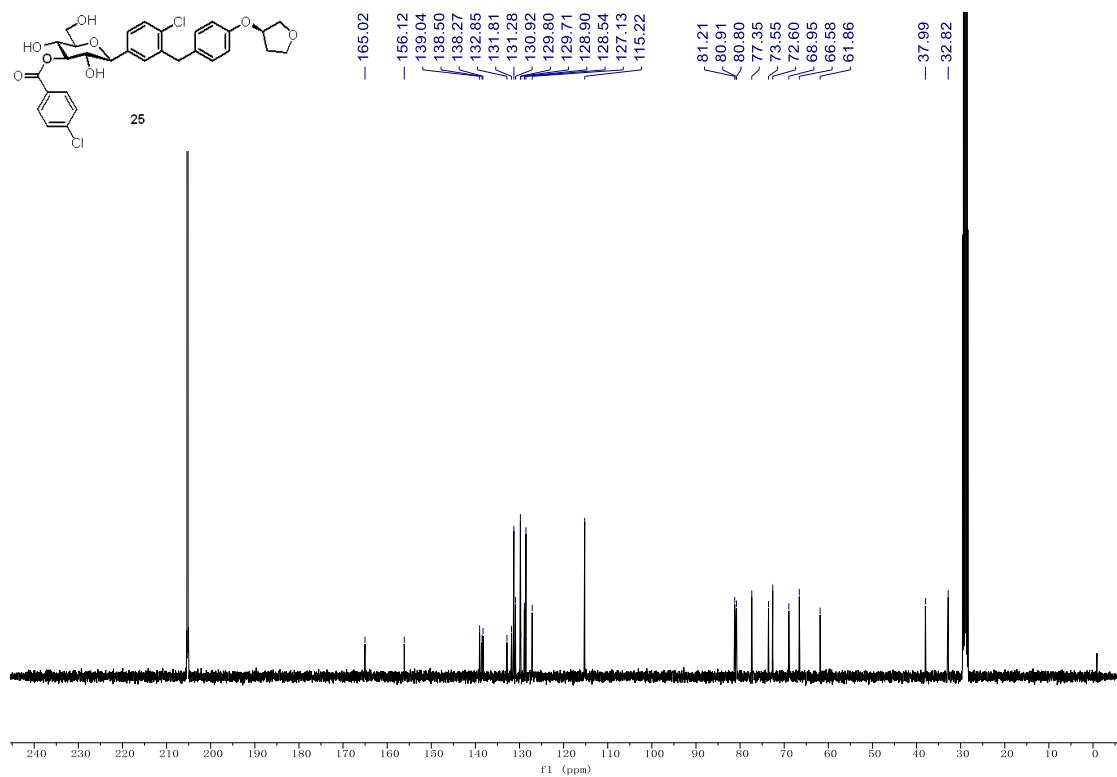


Figure S98. ^{13}C NMR Spectra of 25

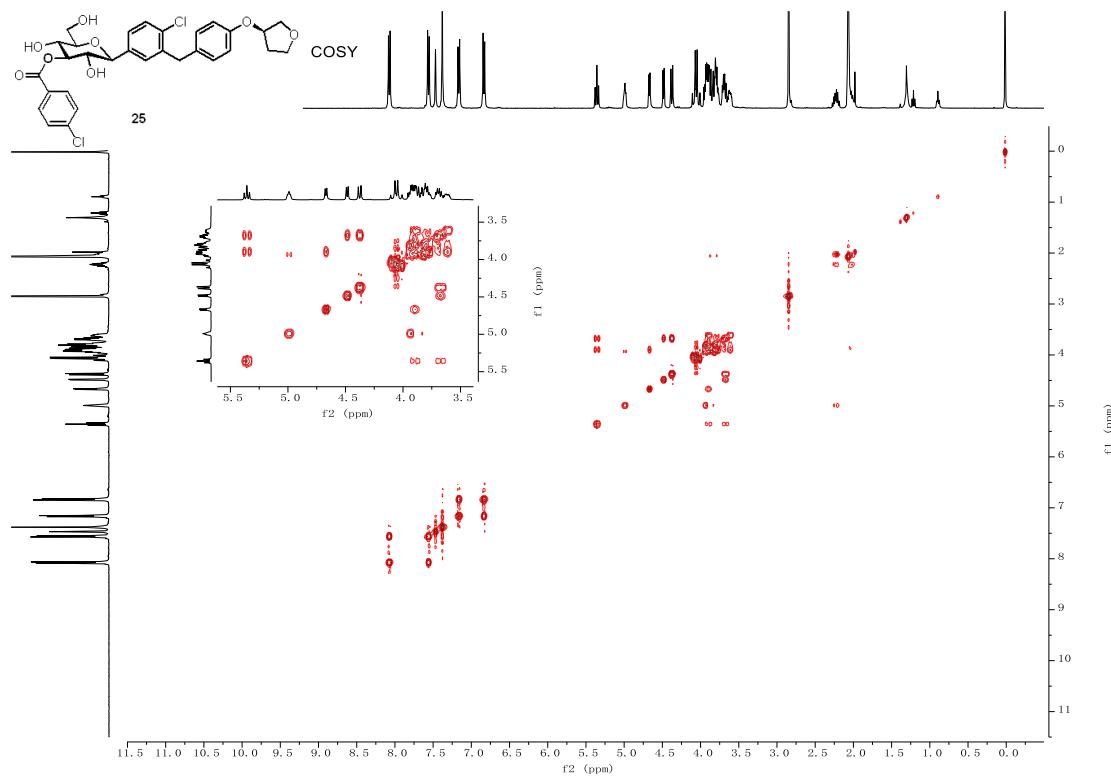


Figure S99. COSY NMR Spectra of 25

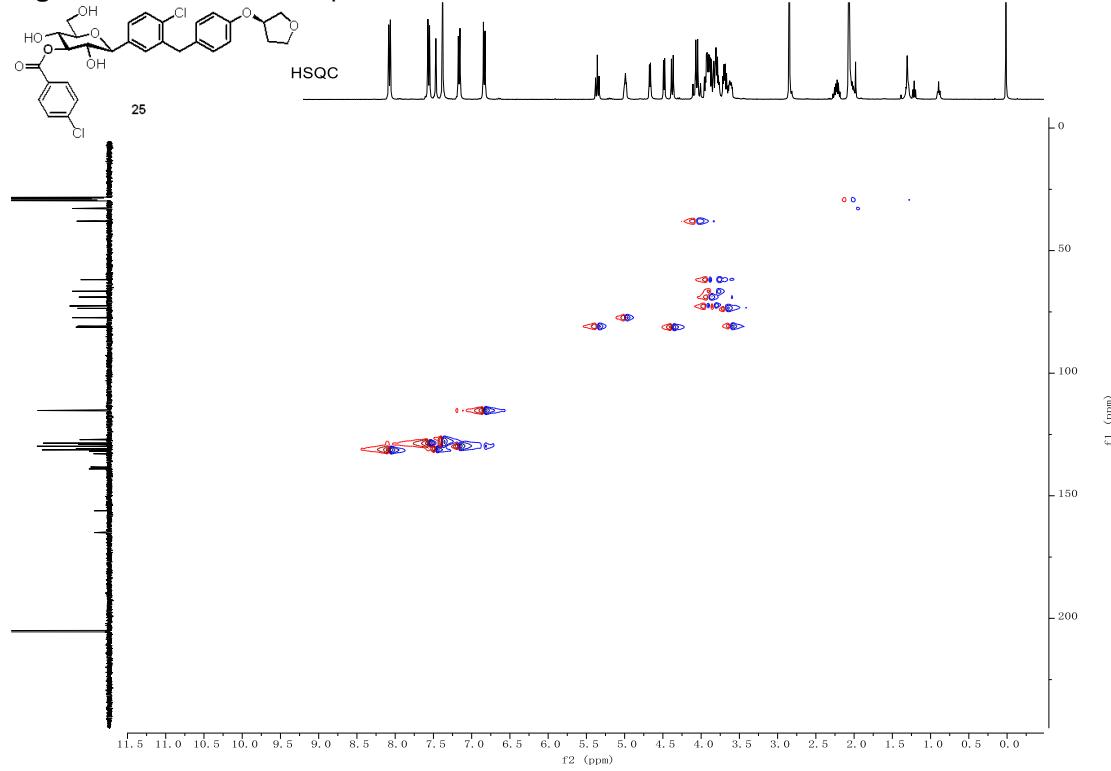


Figure S100. HSQC NMR Spectra of 25

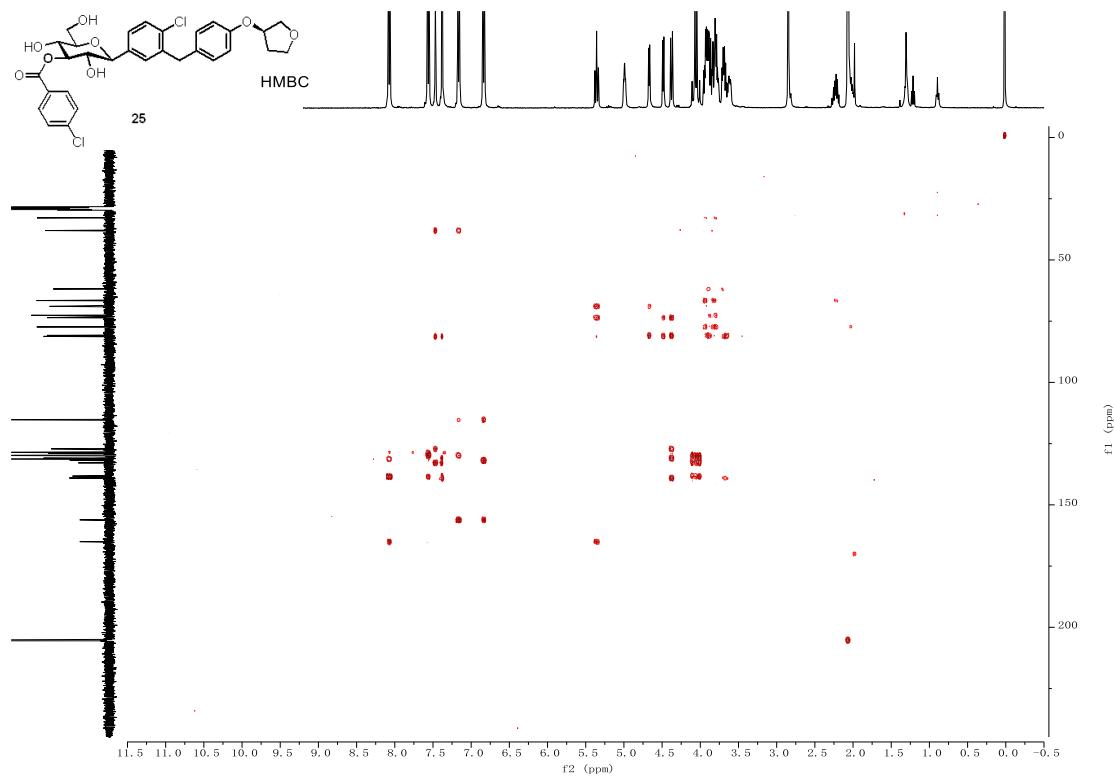


Figure S101. HMBC NMR Spectra of 25

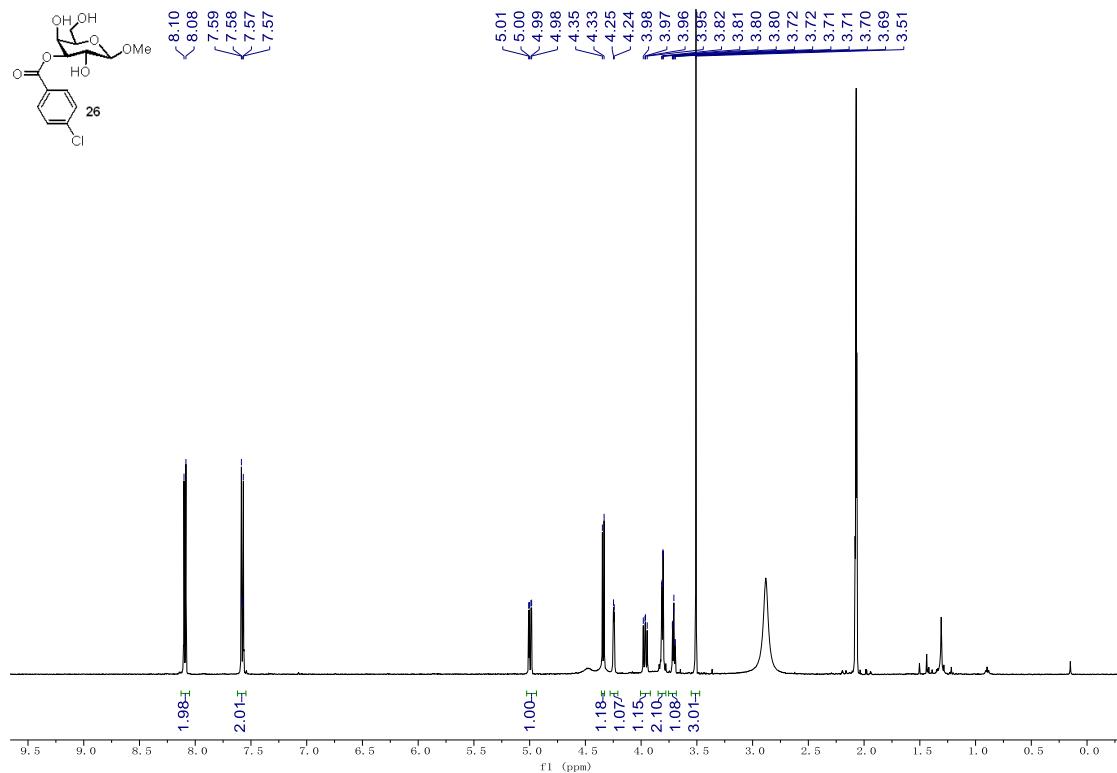


Figure S102. ^1H NMR Spectra of **26**

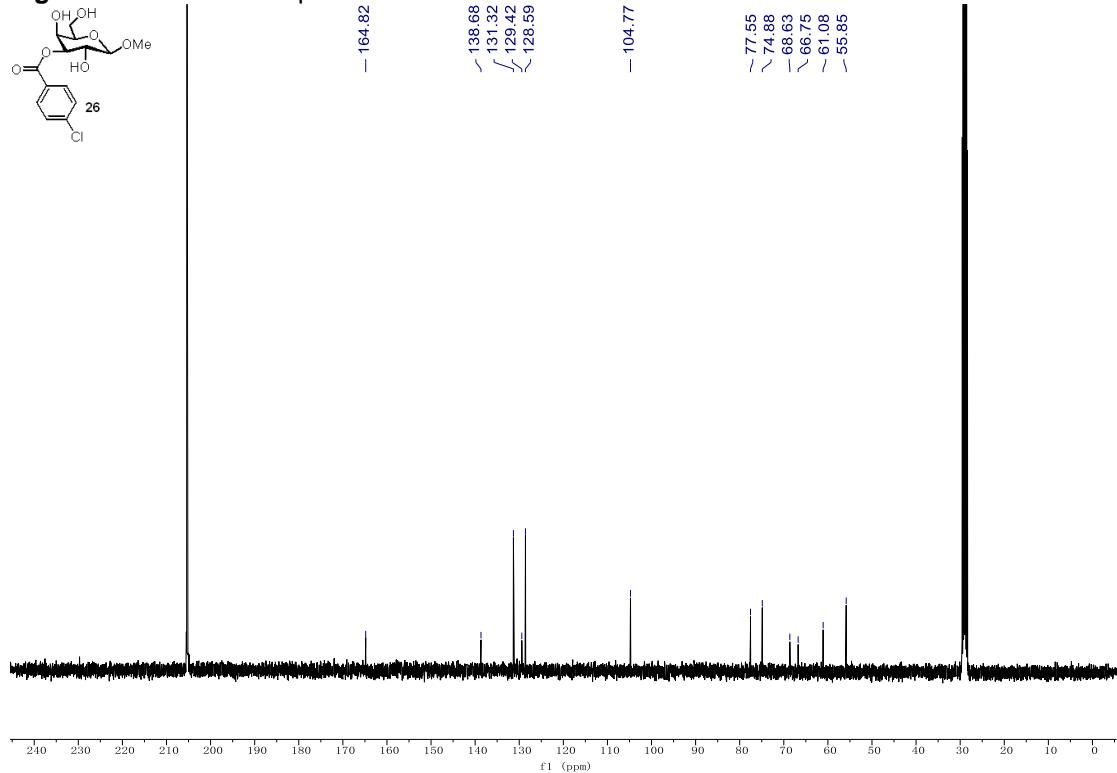


Figure S103. ^{13}C NMR Spectra of 26

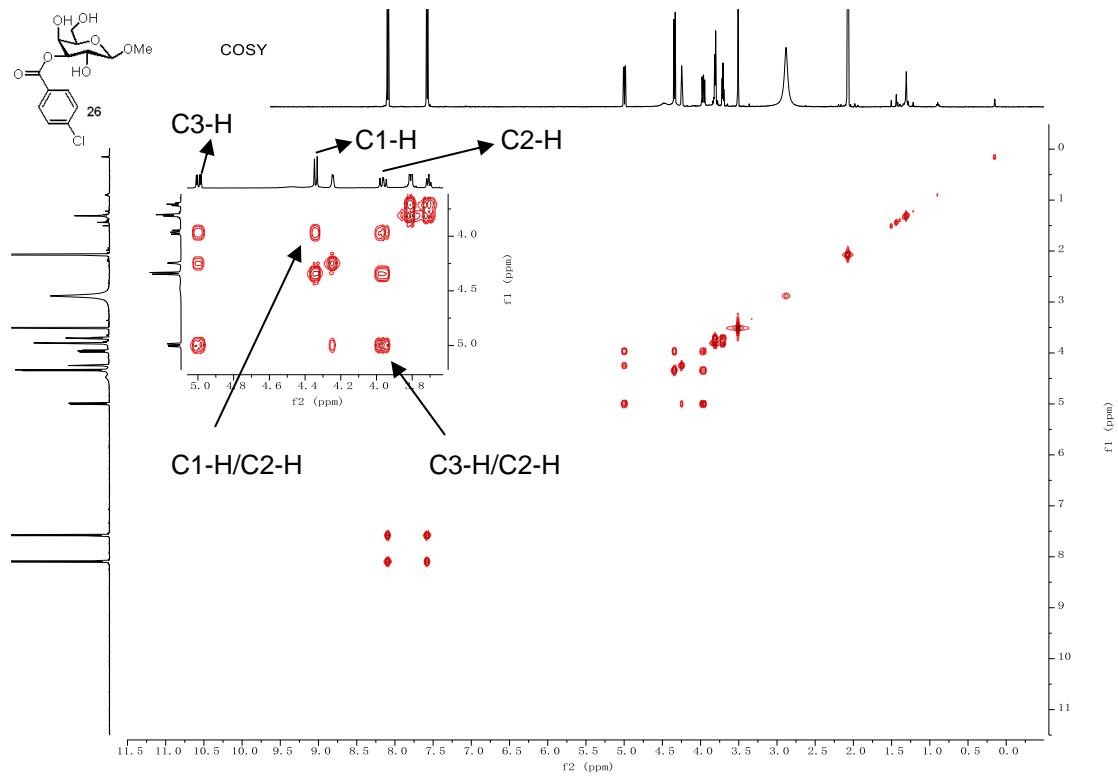


Figure S104. COSY NMR Spectra of **26**

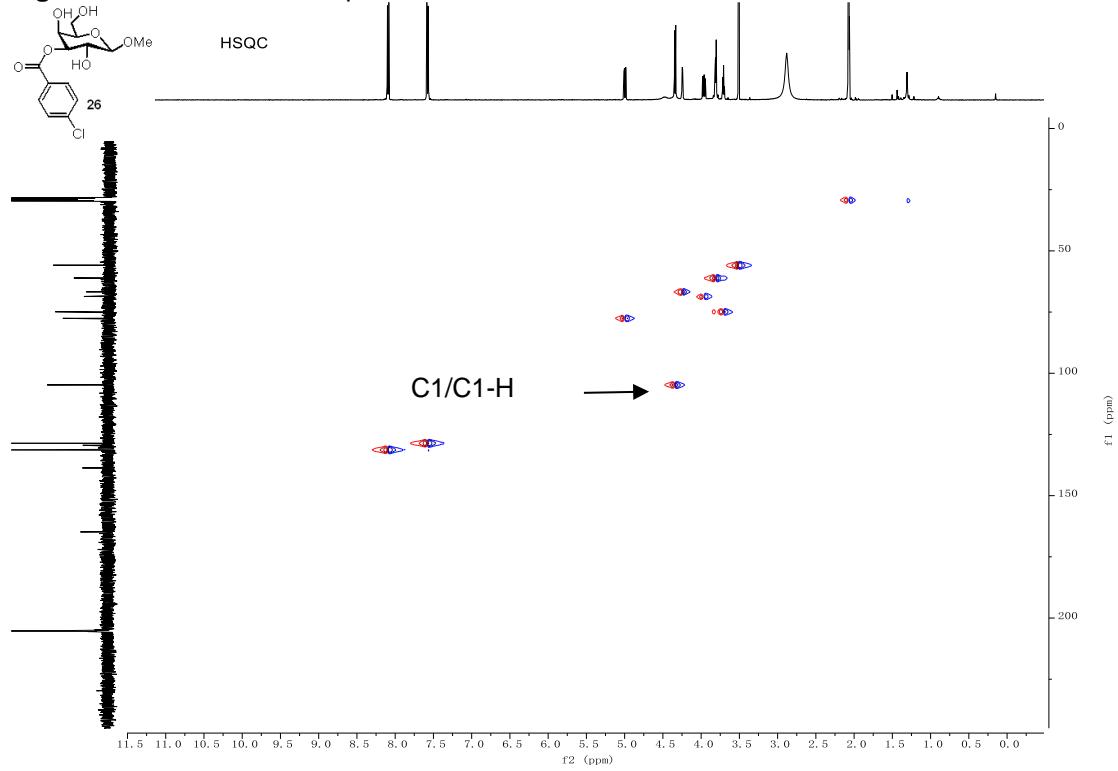


Figure S105. HSQC NMR Spectra of **26**

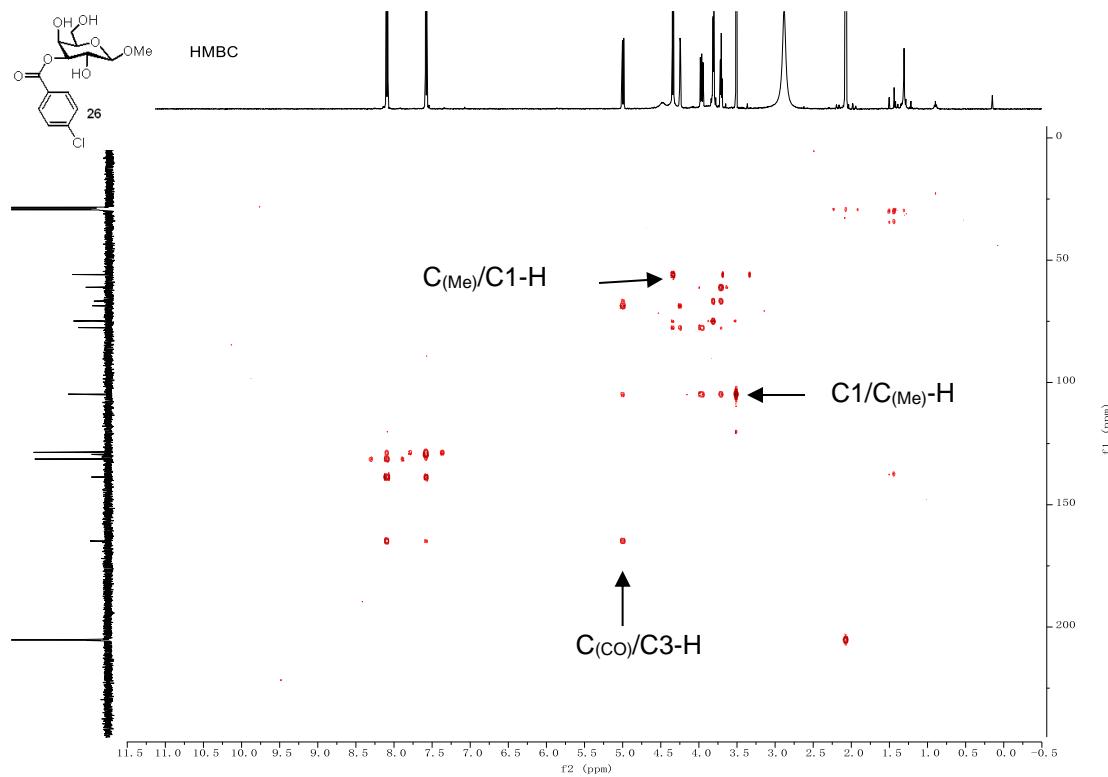


Figure S106. HMBC NMR Spectra of **26**

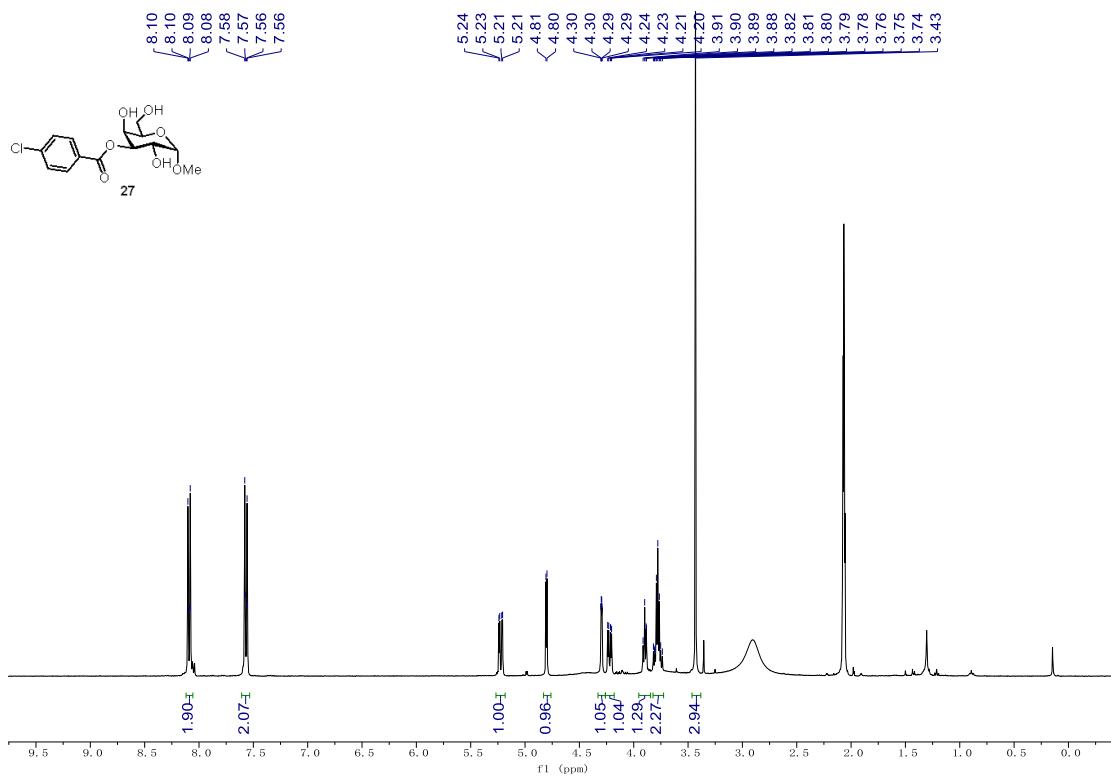


Figure S107. ¹H NMR Spectra of 27

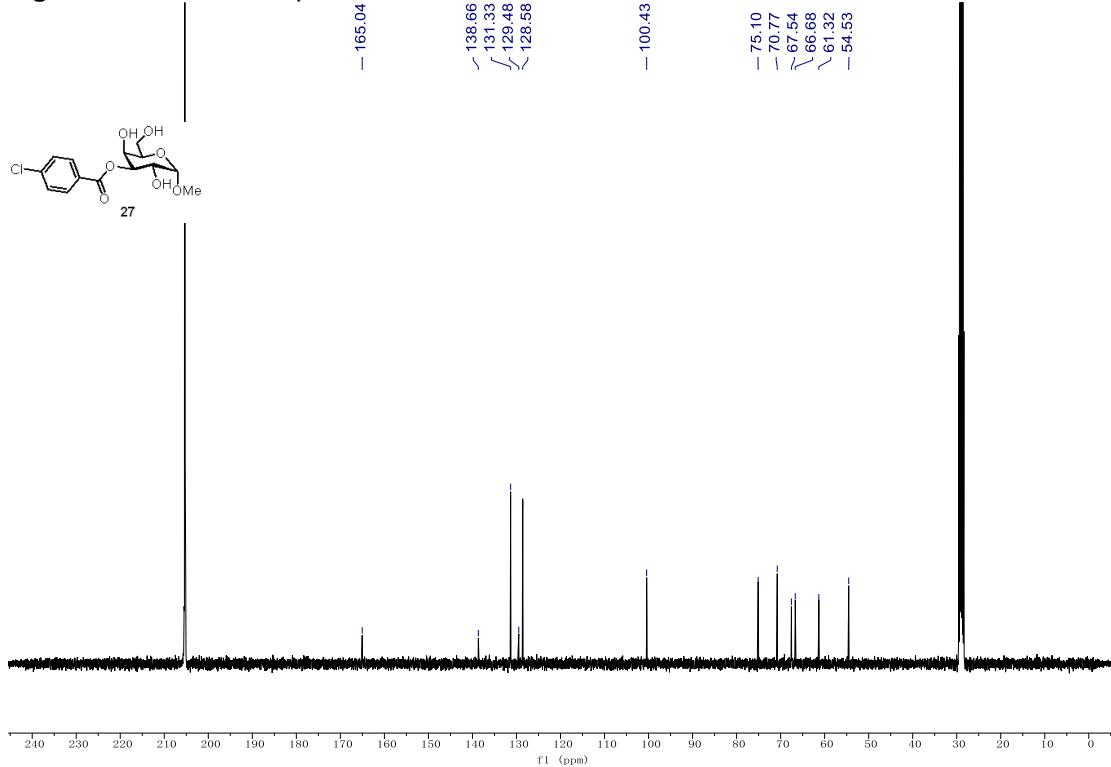


Figure S108. ¹³C NMR Spectra of 27

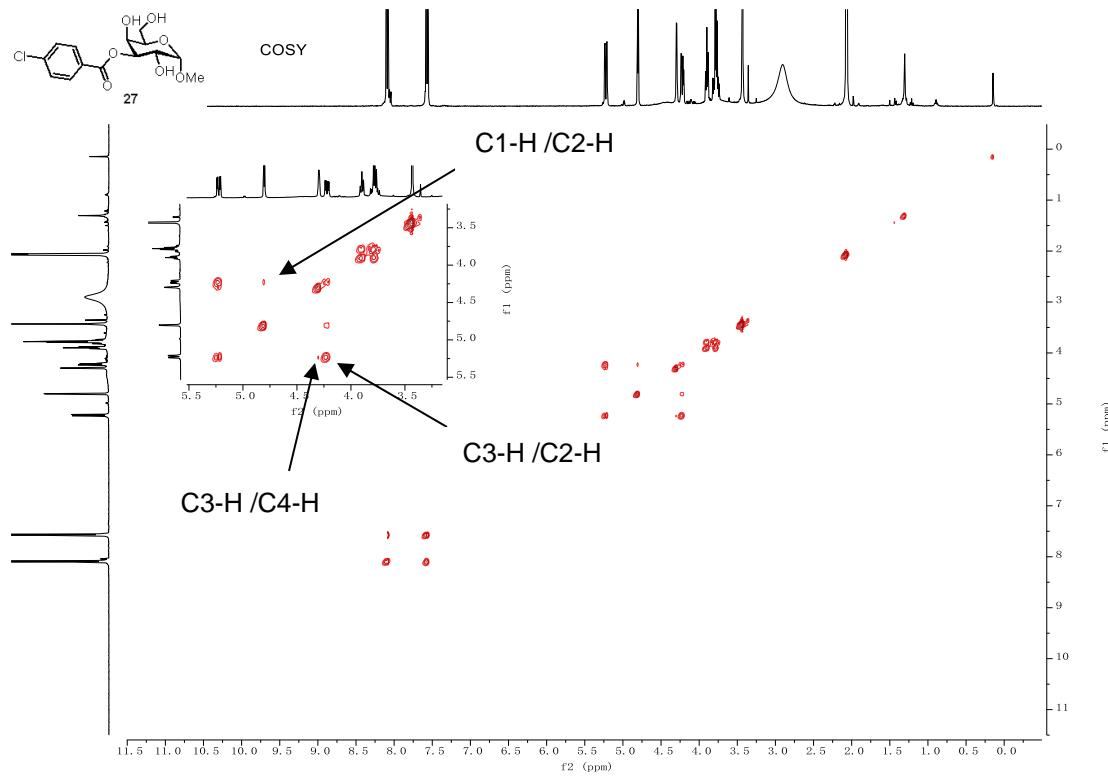


Figure S109. COSY NMR Spectra of **27**

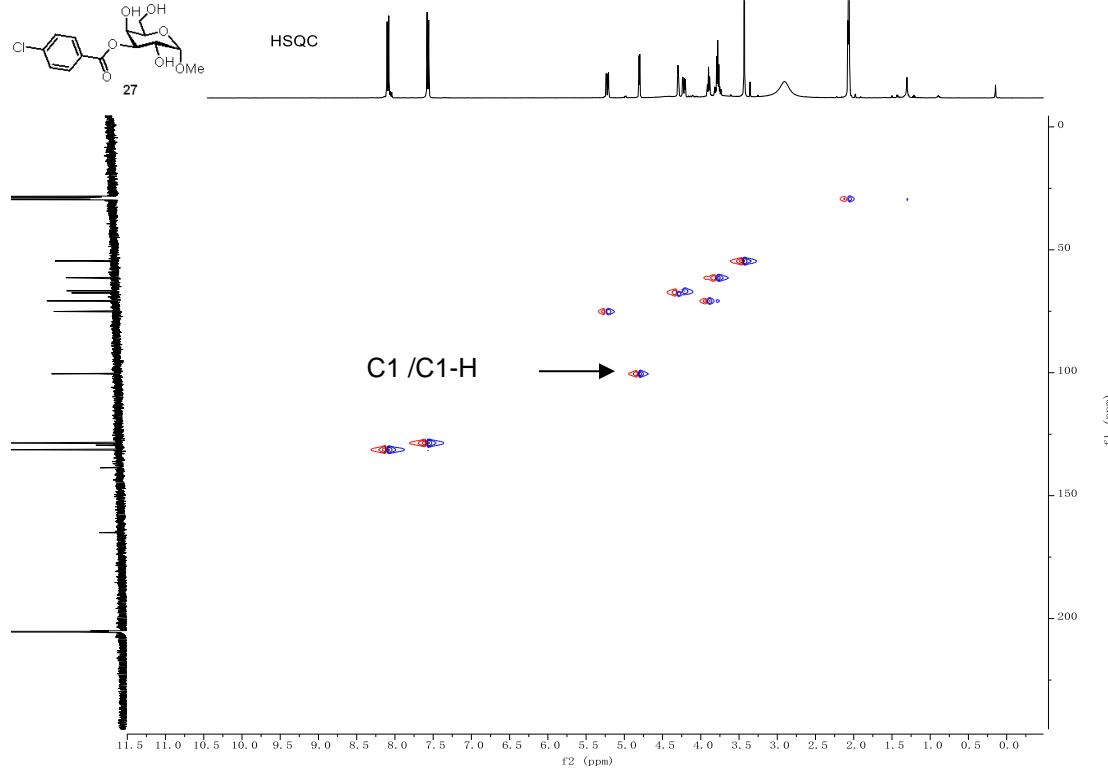


Figure S110. HSQC NMR Spectra of **27**

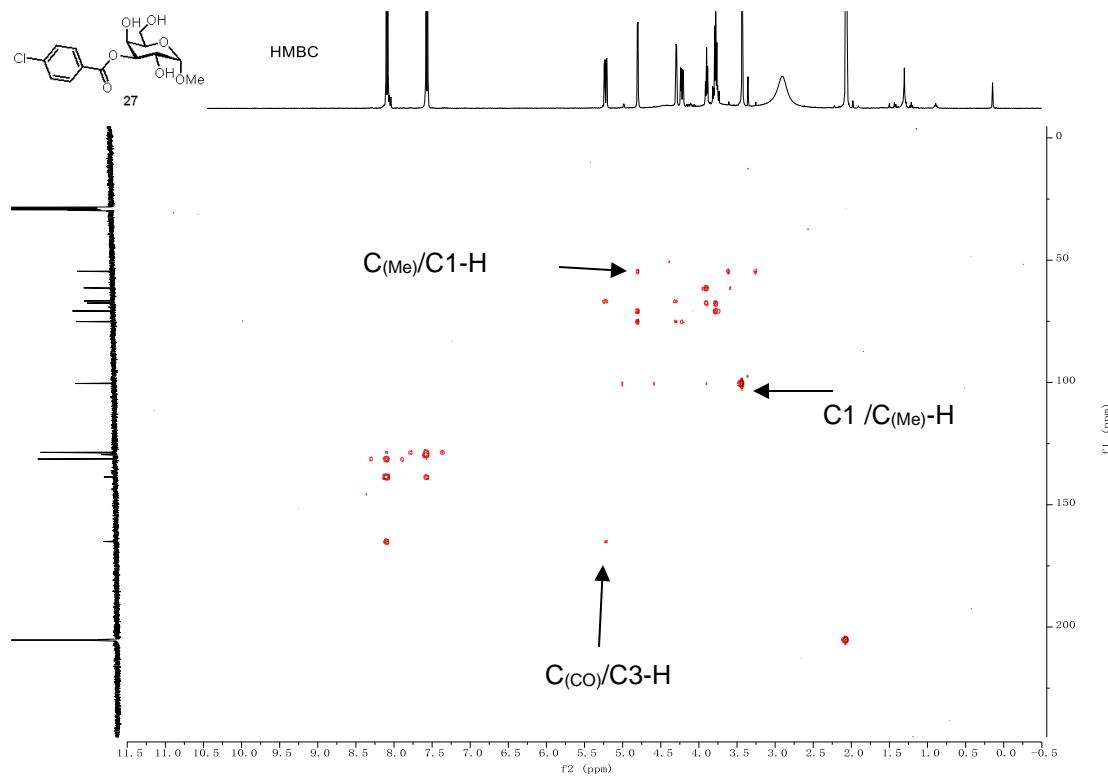


Figure S111. HMBC NMR Spectra of 27

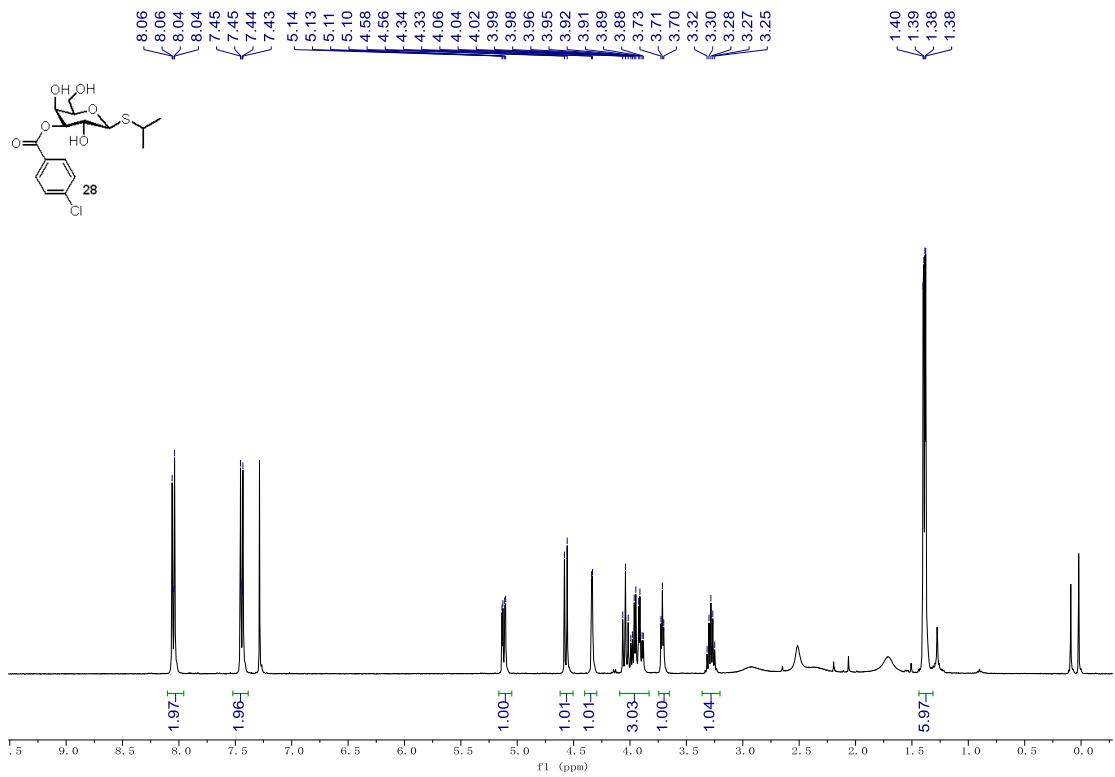


Figure S112. ¹H NMR Spectra of **28**

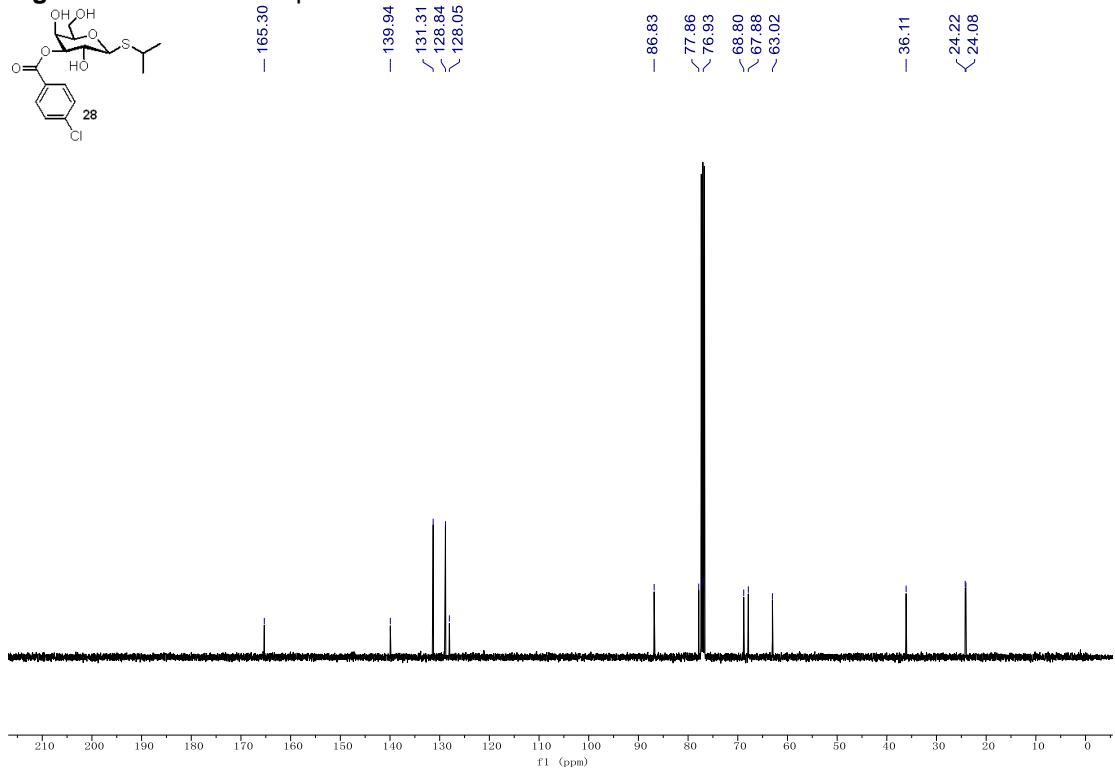


Figure S113. ¹³C NMR Spectra of **28**

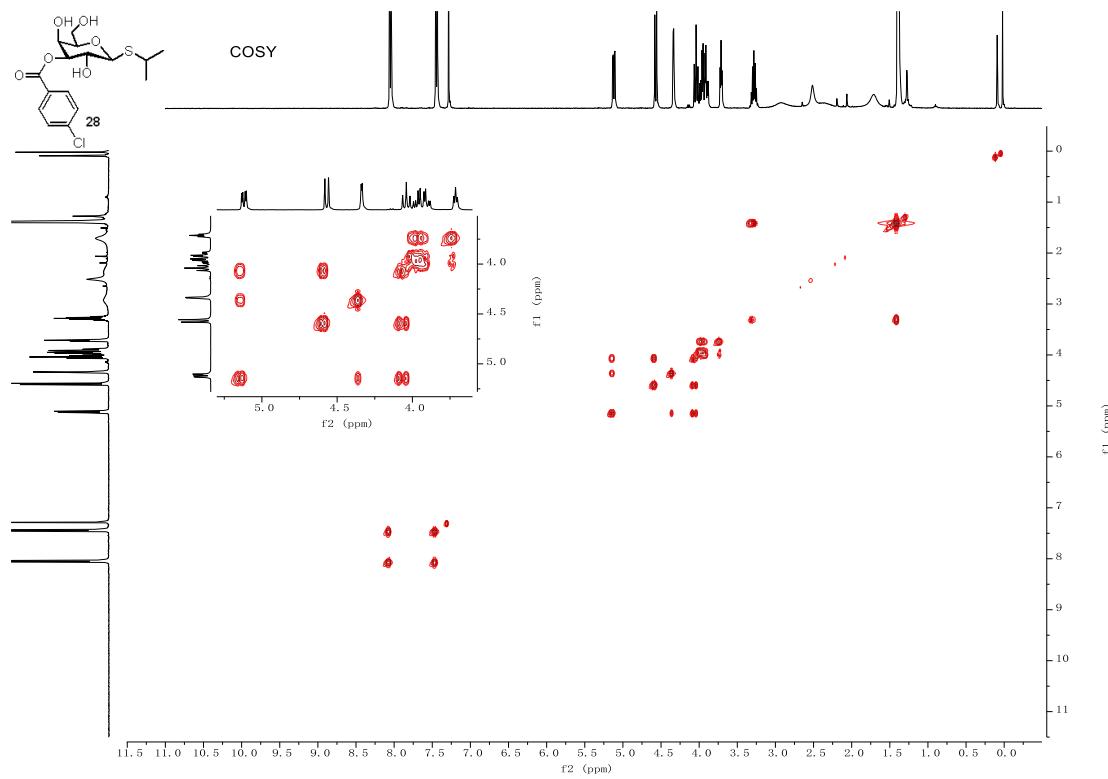


Figure S114. COSY NMR Spectra of **28**

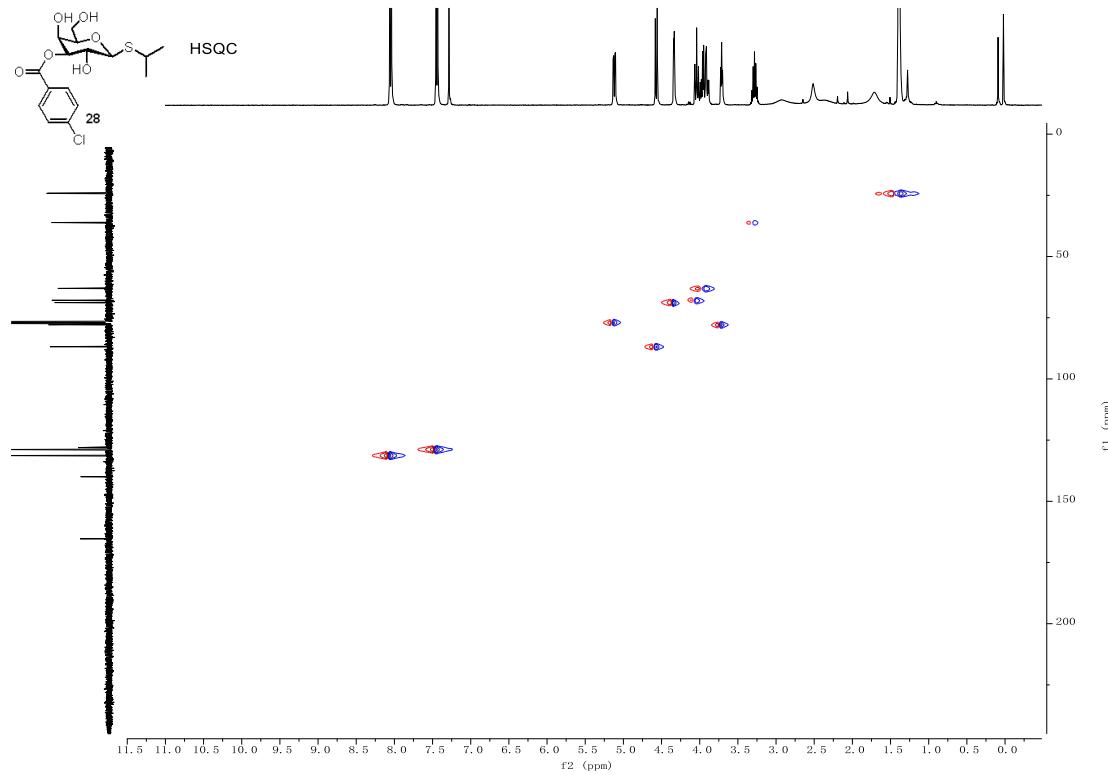


Figure S115. HSQC NMR Spectra of **28**

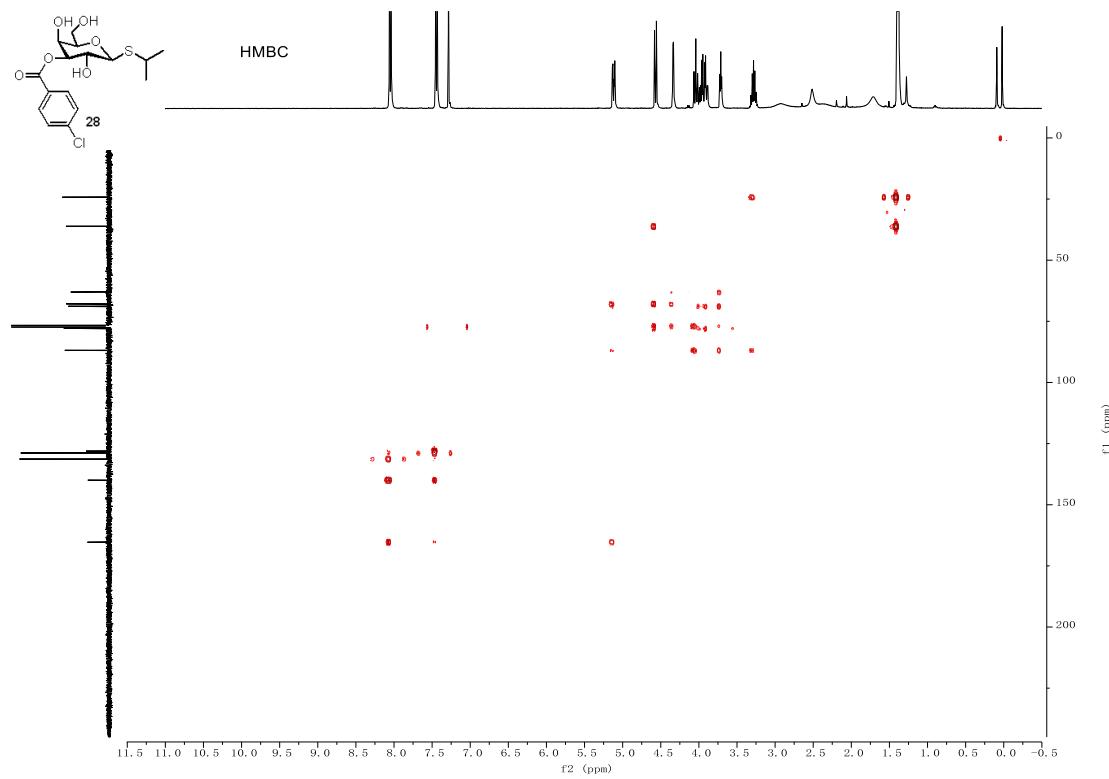


Figure S116. HMBC NMR Spectra of 28

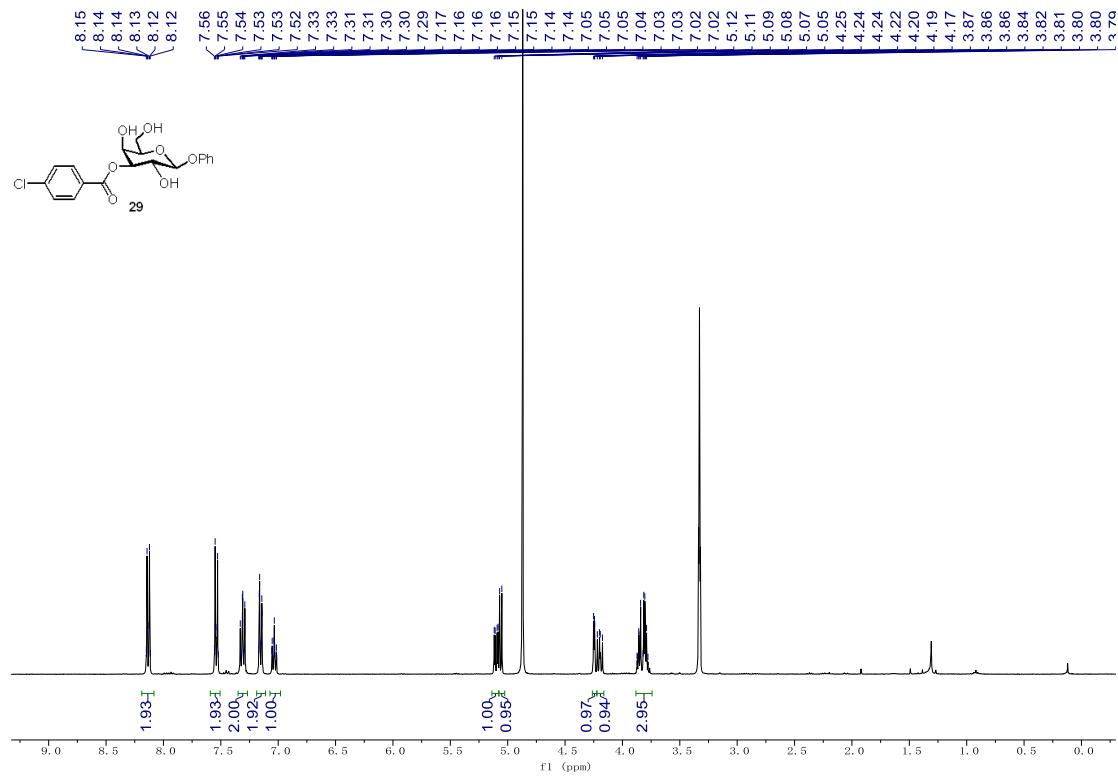


Figure S117. ^1H NMR Spectra of **29**

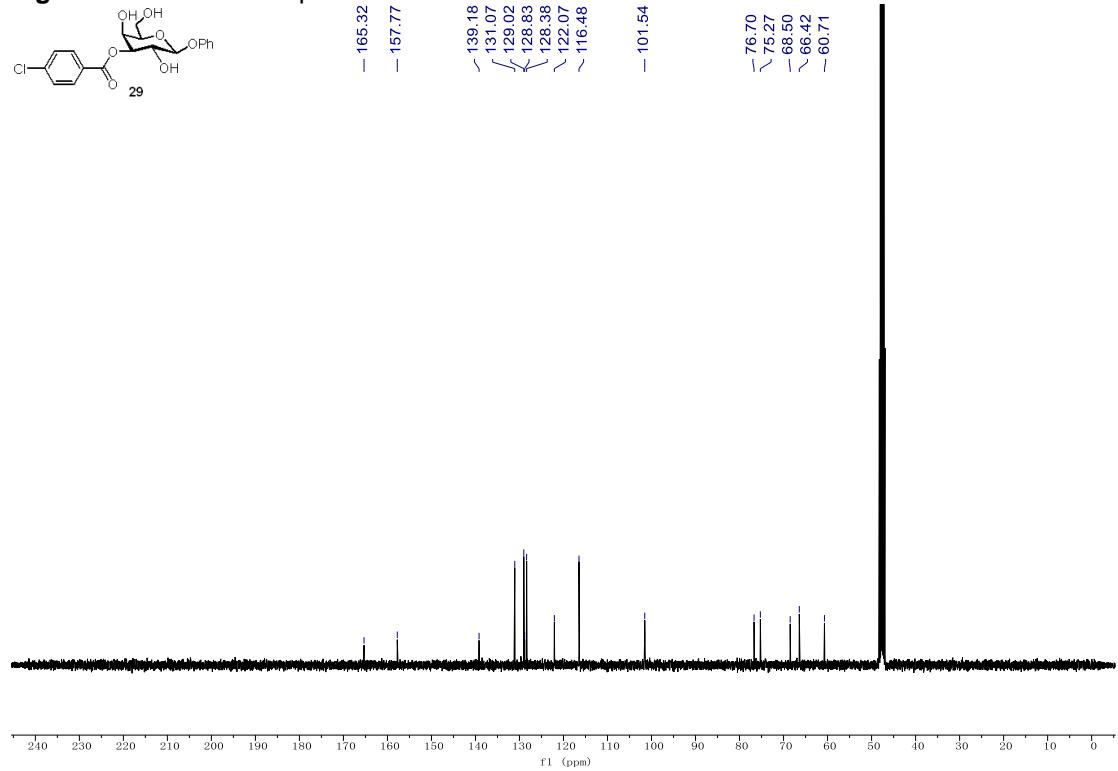


Figure S118. ^{13}C NMR Spectra of **29**

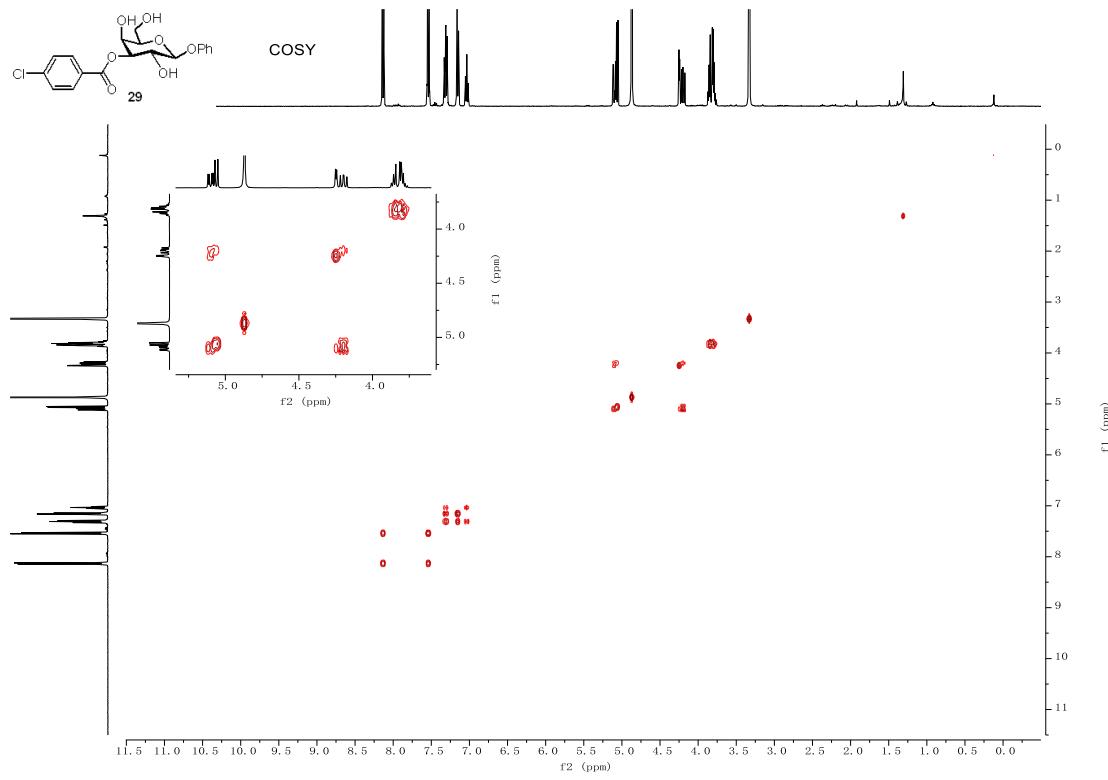


Figure S119. COSY NMR Spectra of **29**

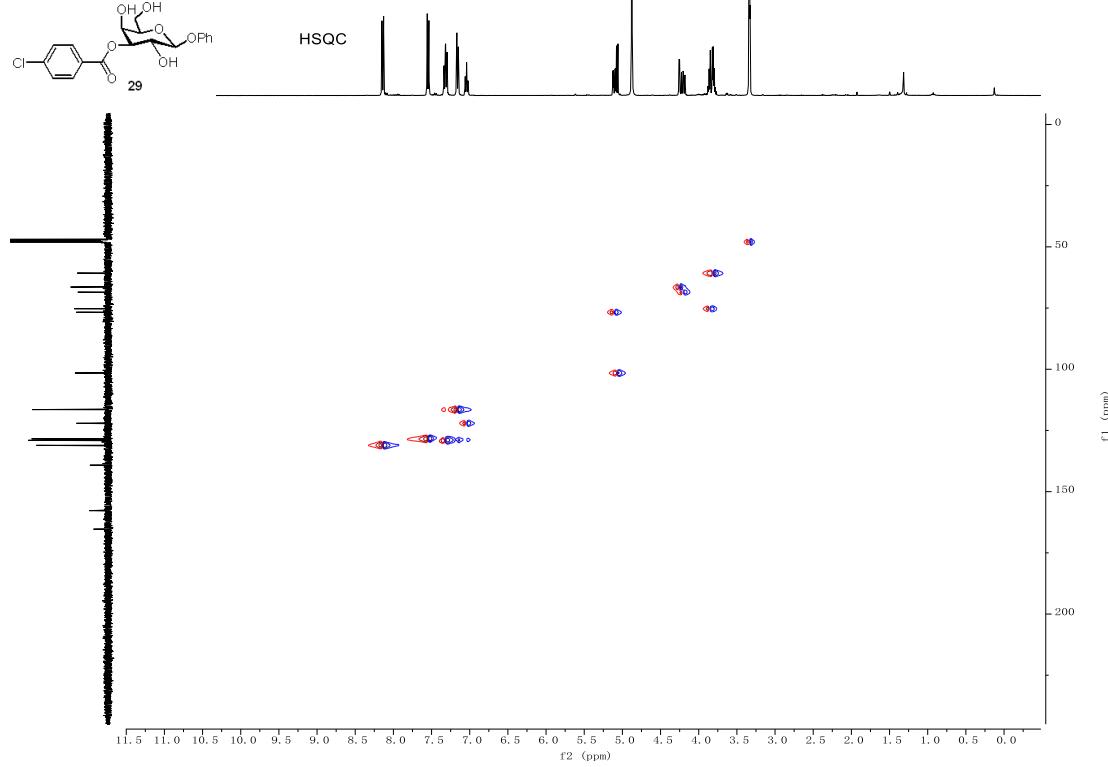


Figure S120. HSQC NMR Spectra of **29**

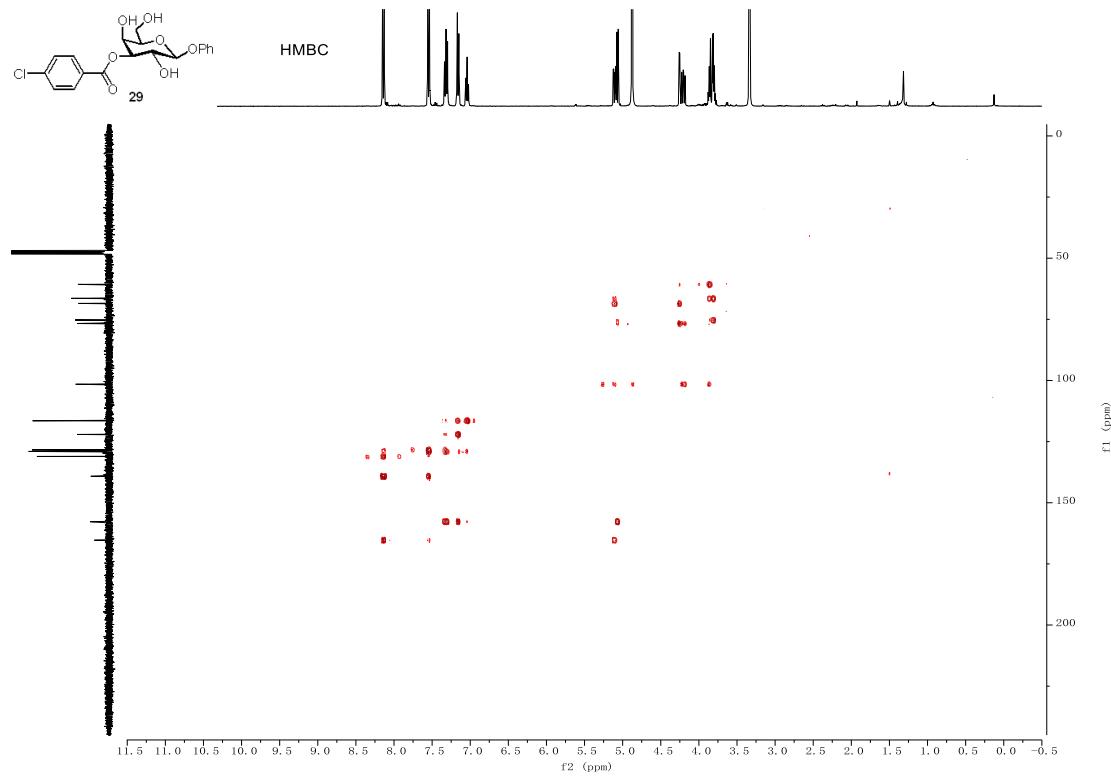


Figure S121. HMBC NMR Spectra of 29

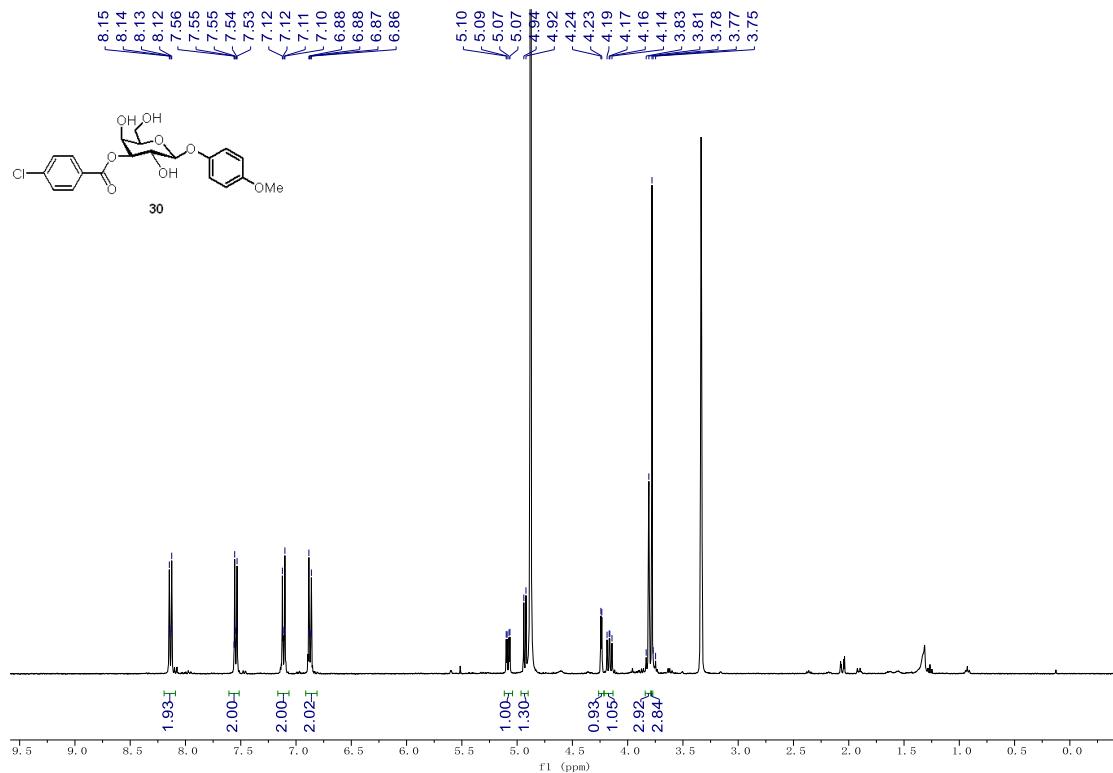


Figure S122. ^1H NMR Spectra of **30**

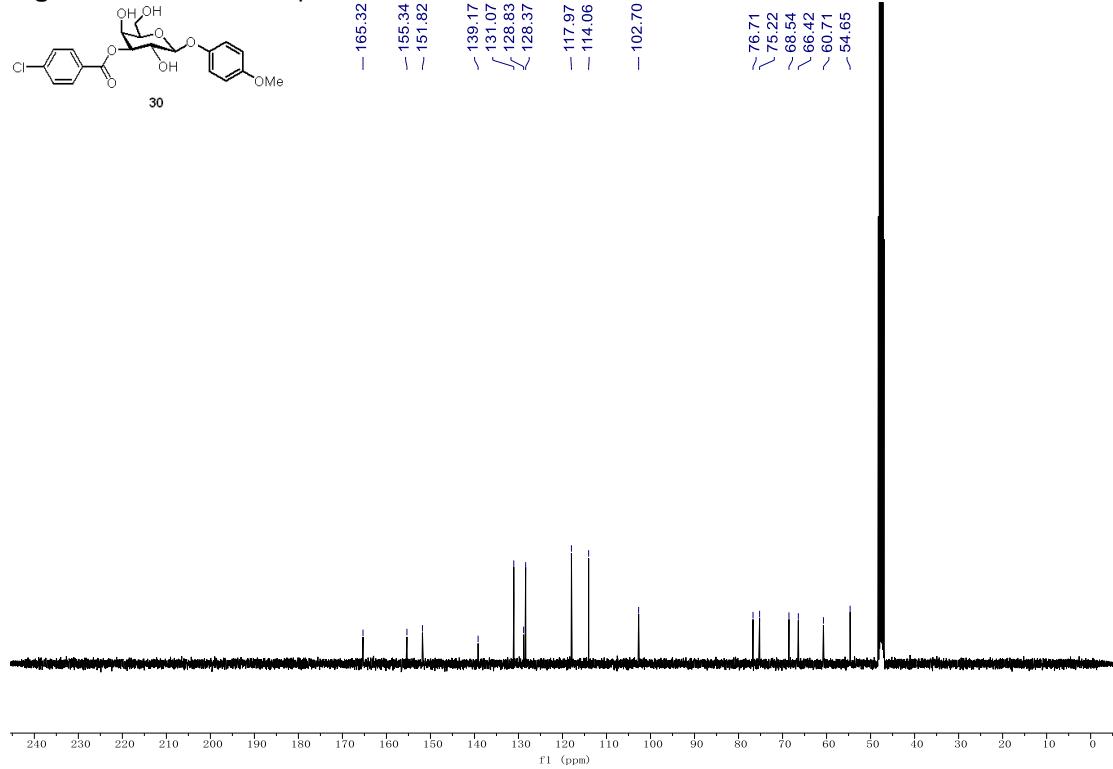


Figure S123. ^{13}C NMR Spectra of **30**

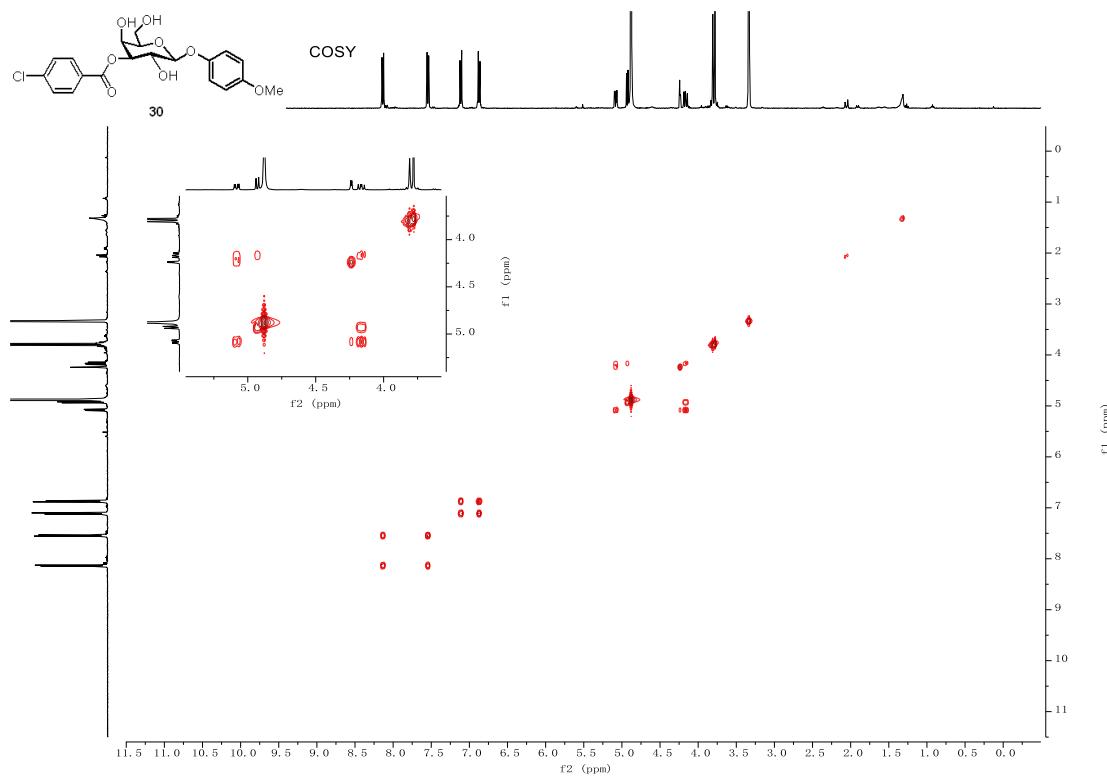


Figure S124. COSY NMR Spectra of **30**

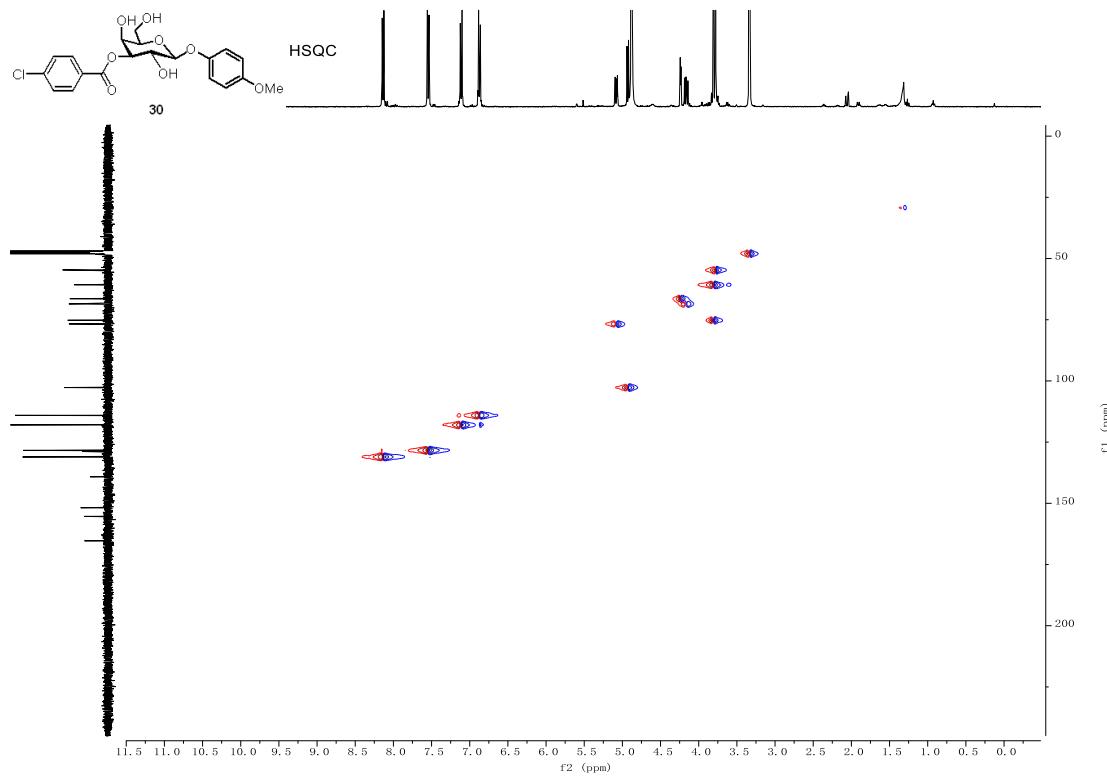


Figure S125. HSQC NMR Spectra of **30**

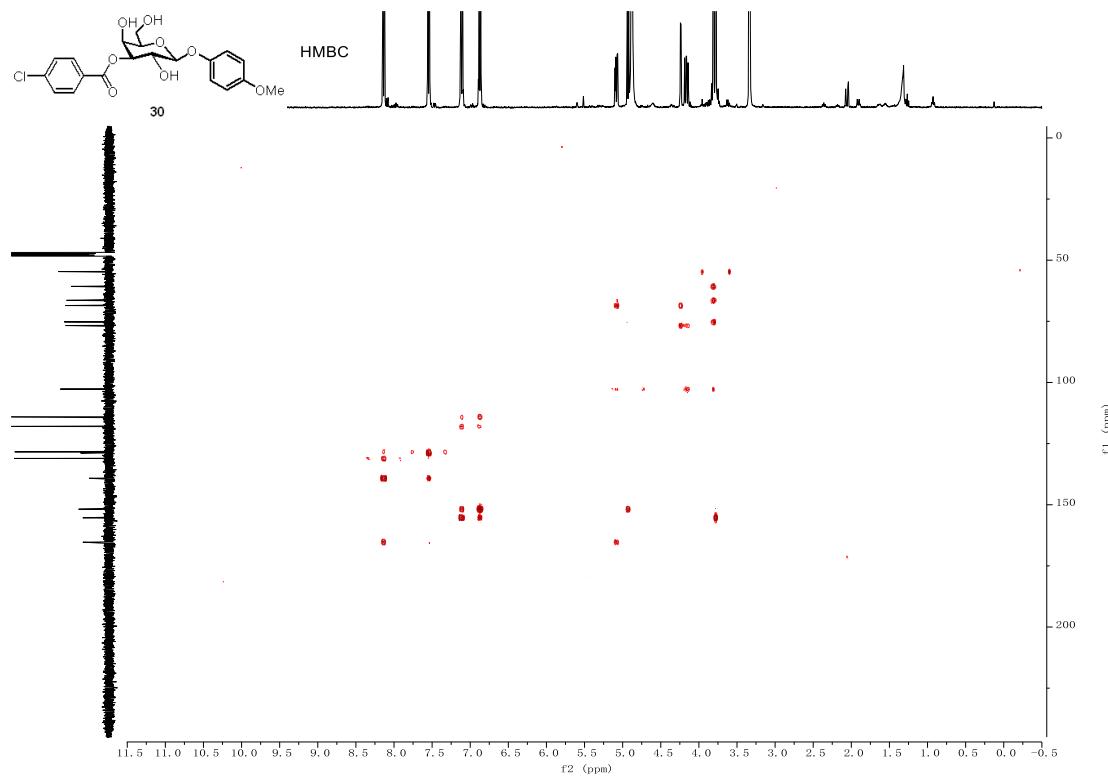


Figure S126. HMBC NMR Spectra of **30**

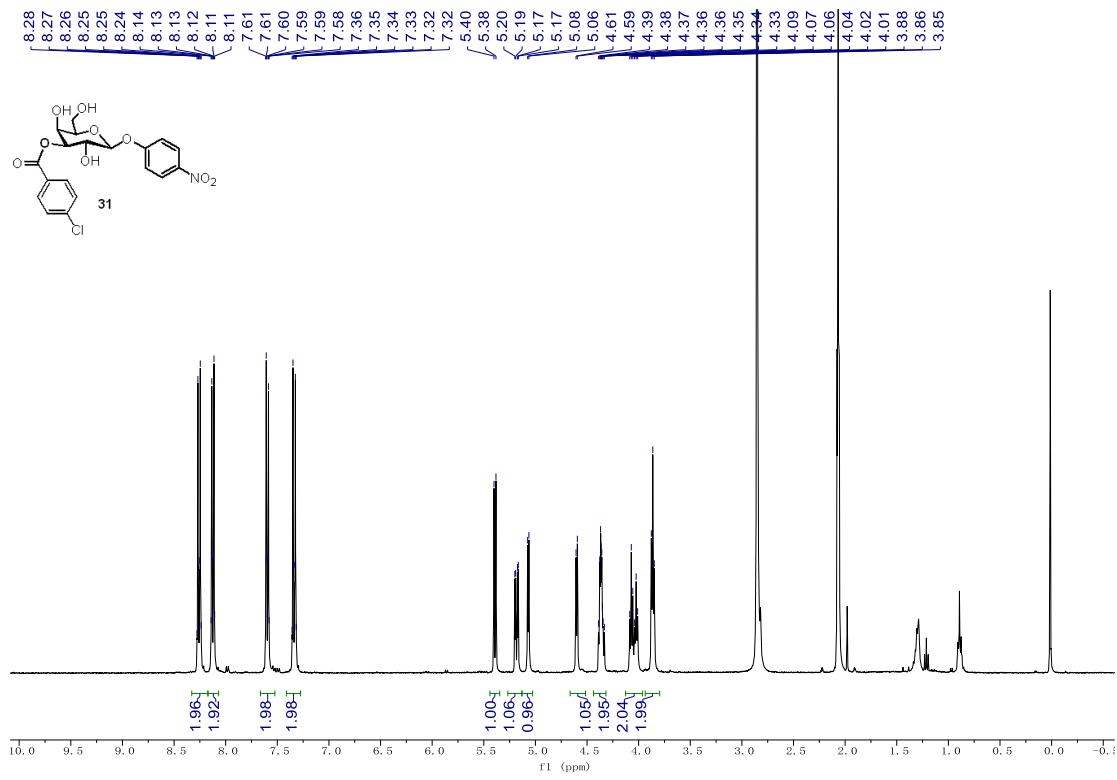


Figure S127. ^1H NMR Spectra of 31

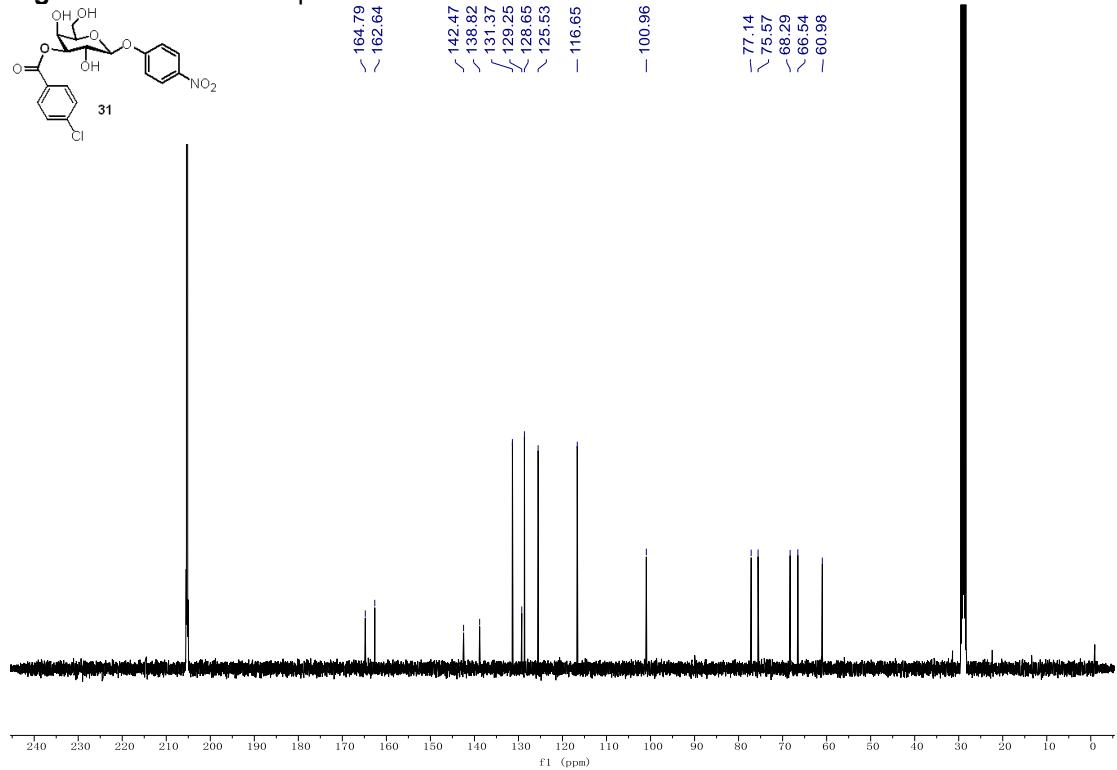


Figure S128. ^{13}C NMR Spectra of 31

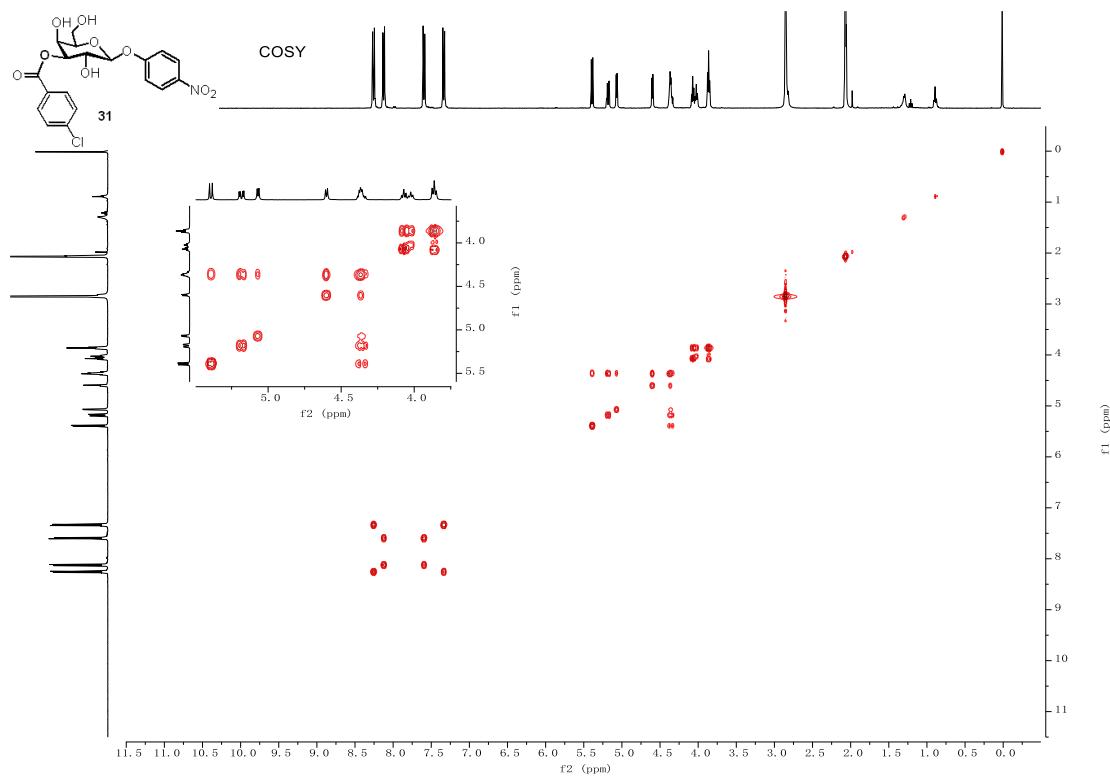


Figure S129. COSY NMR Spectra of **31**

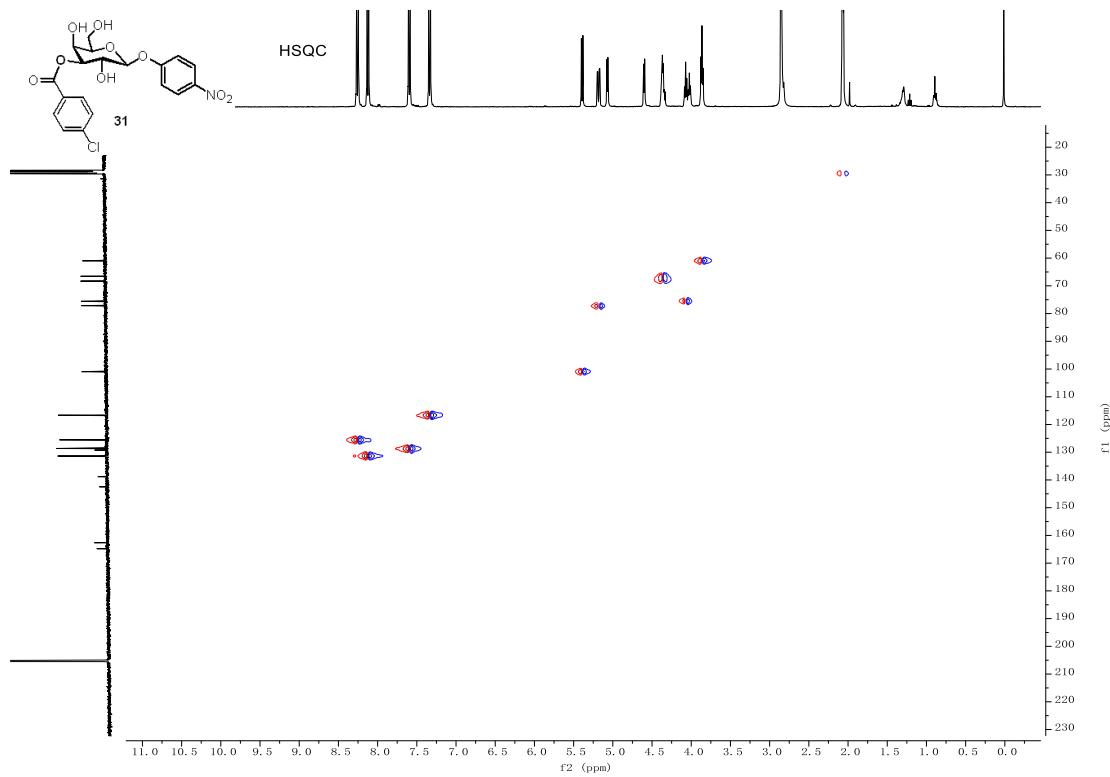


Figure S130. HSQC NMR Spectra of **31**

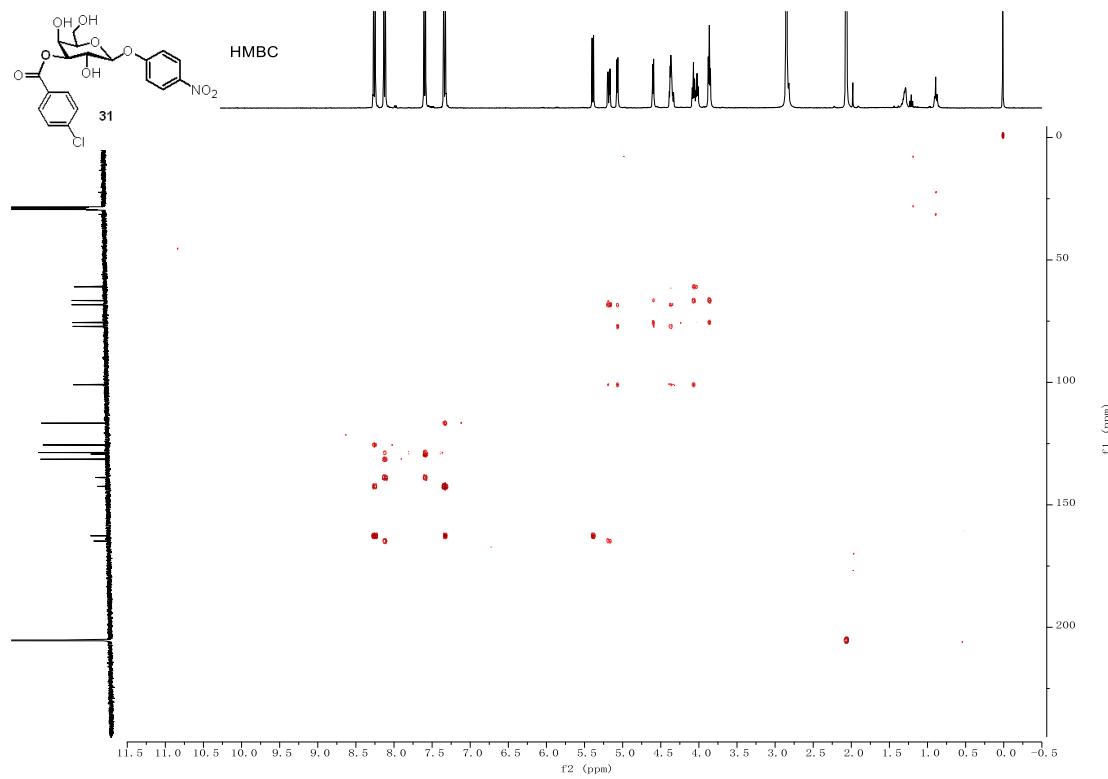


Figure S131. HMBC NMR Spectra of 31

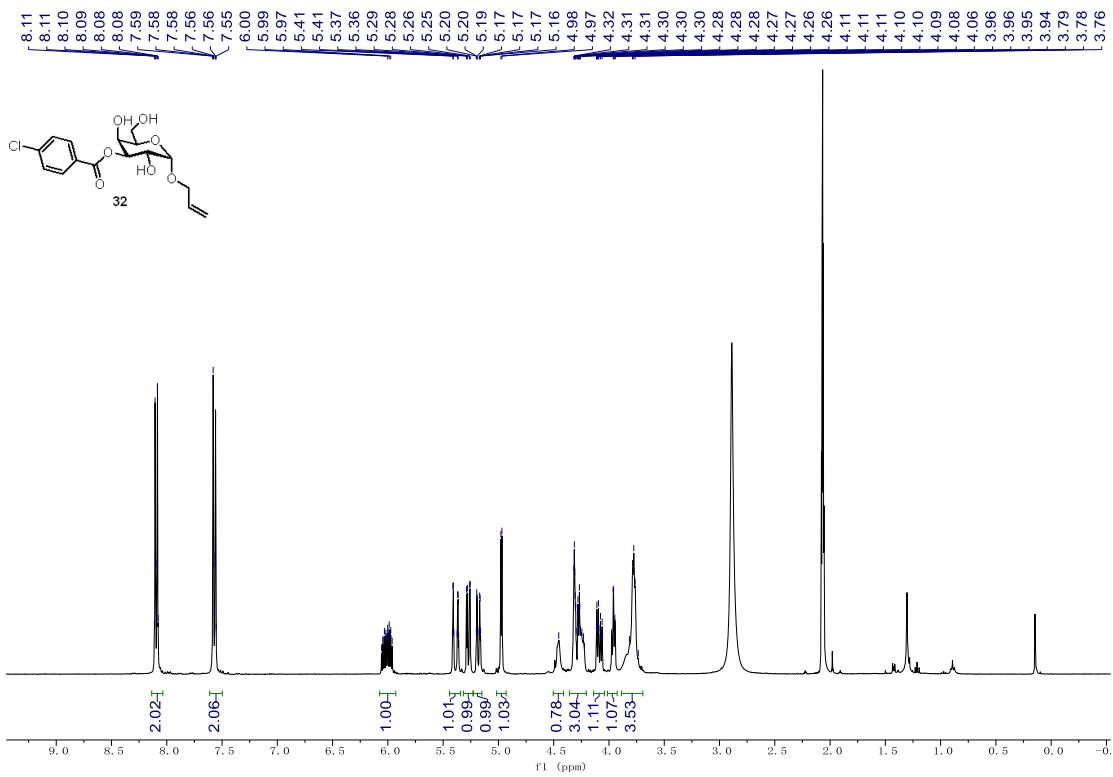


Figure S132. ^1H NMR Spectra of **32**

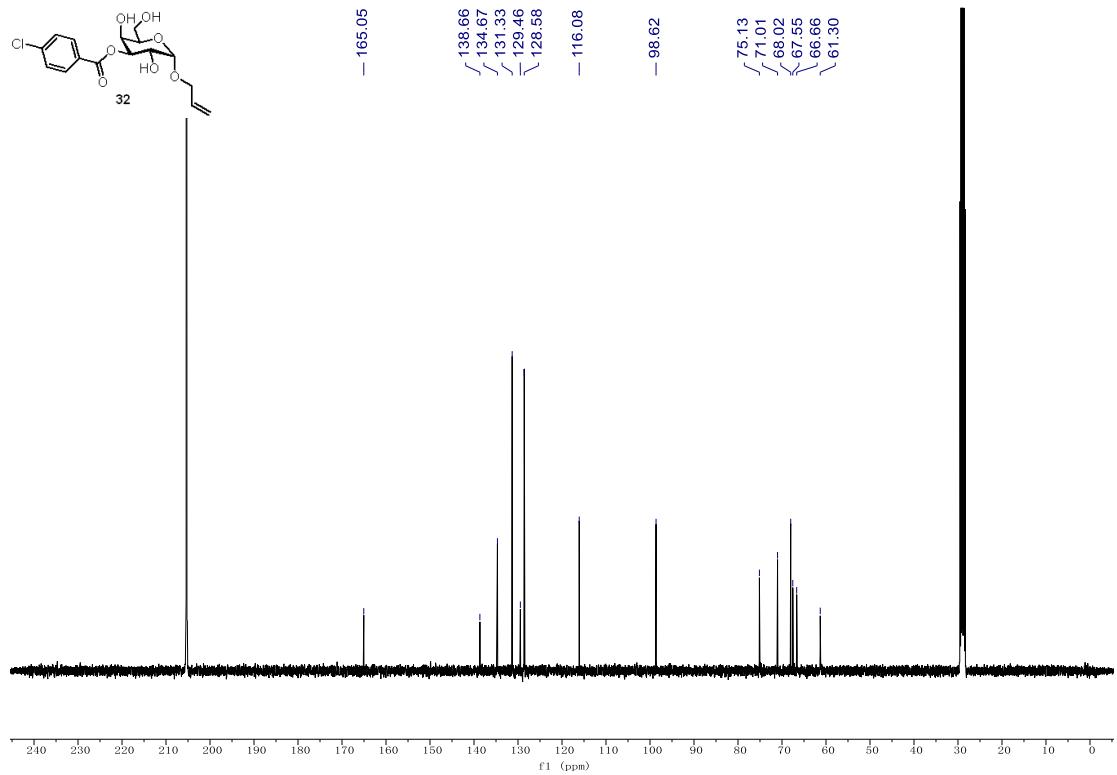


Figure S133. ^{13}C NMR Spectra of **32**

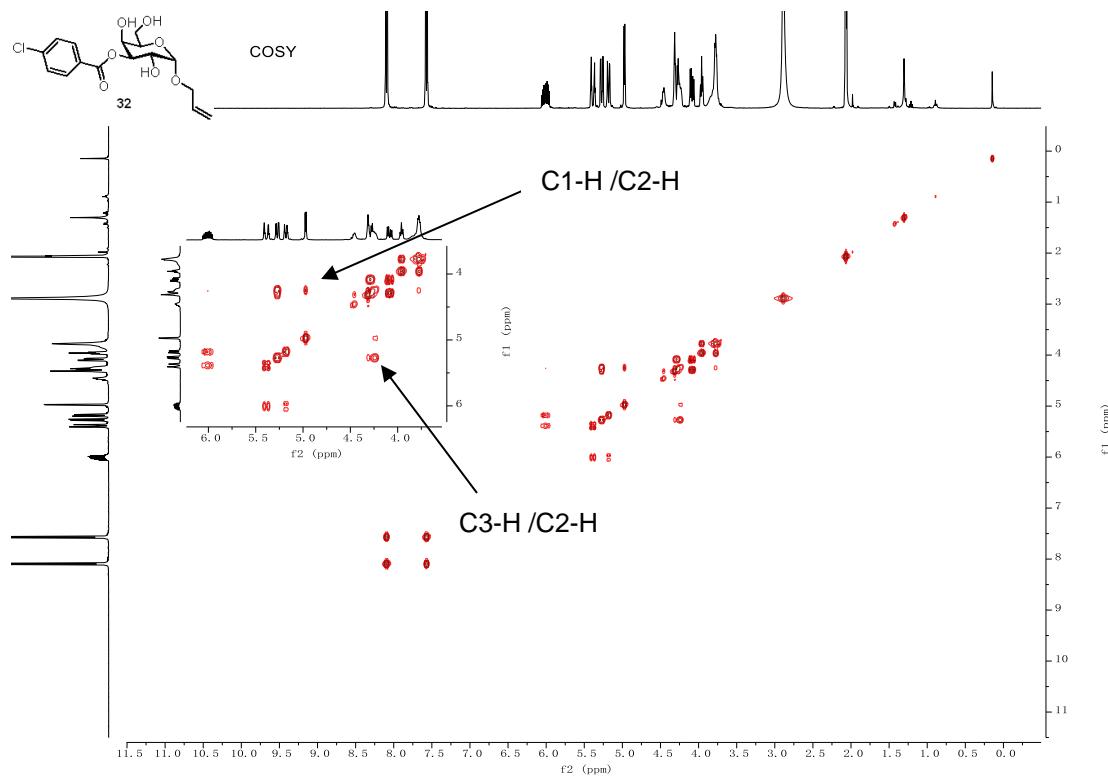


Figure S134. COSY NMR Spectra of **32**

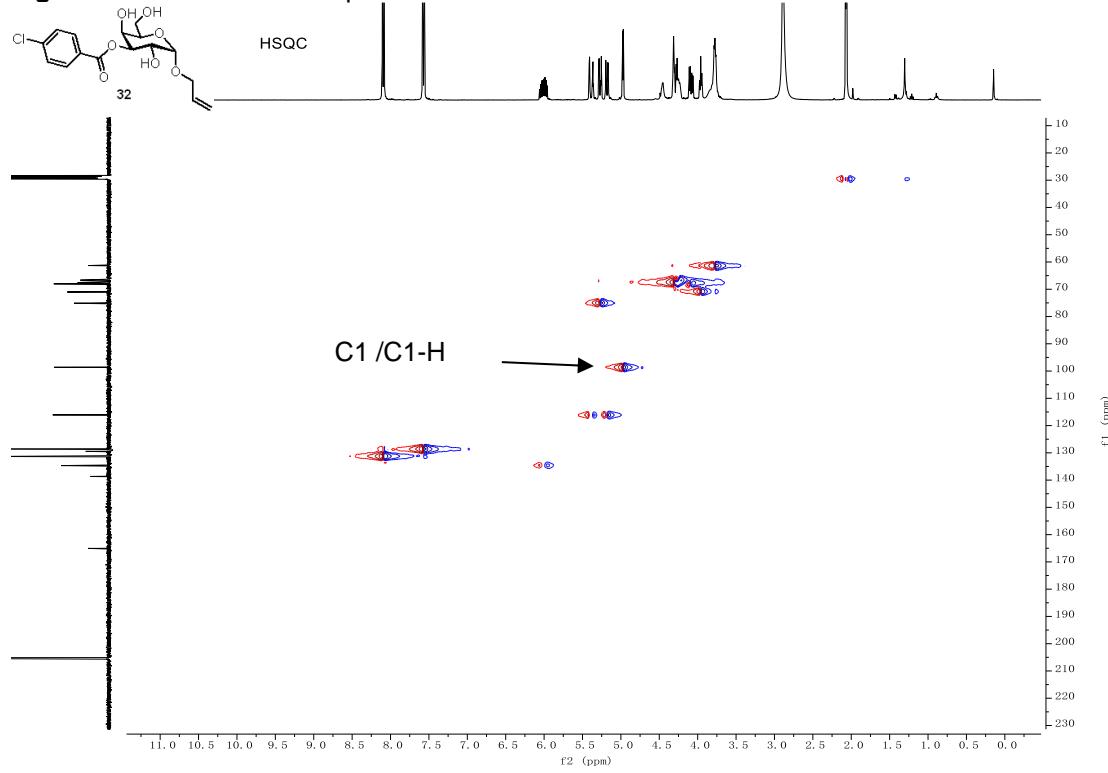


Figure S135. HSQC NMR Spectra of **32**

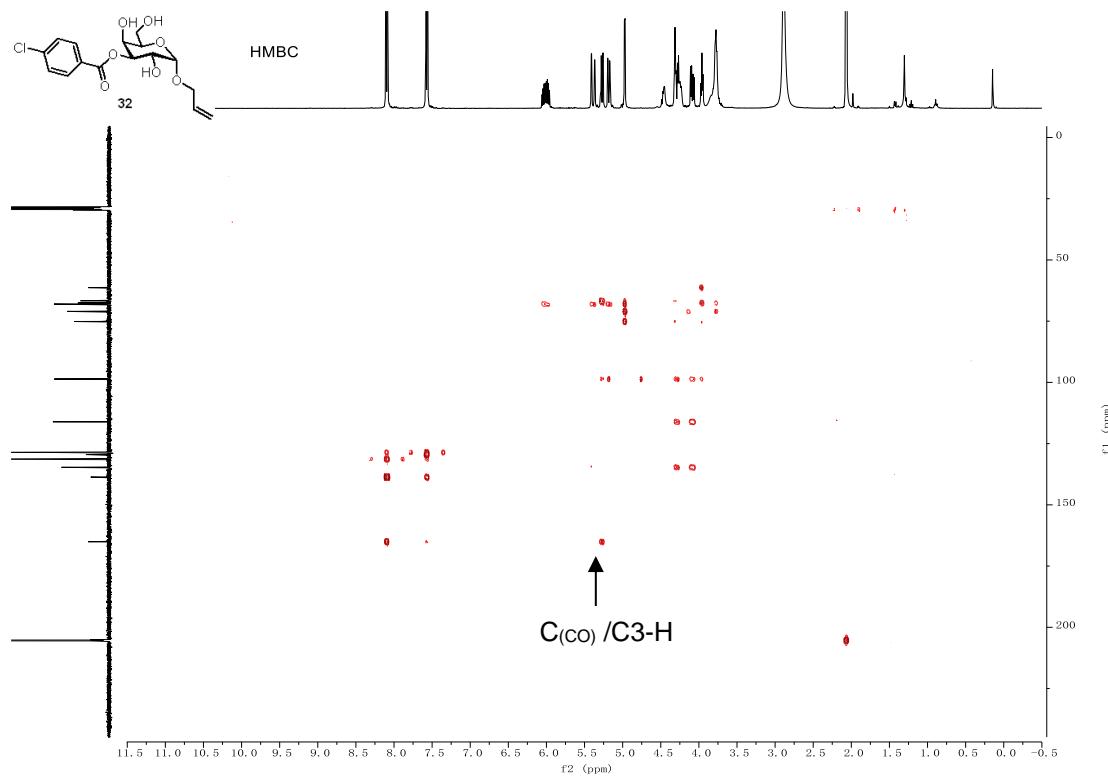


Figure S136. HMBC NMR Spectra of 32

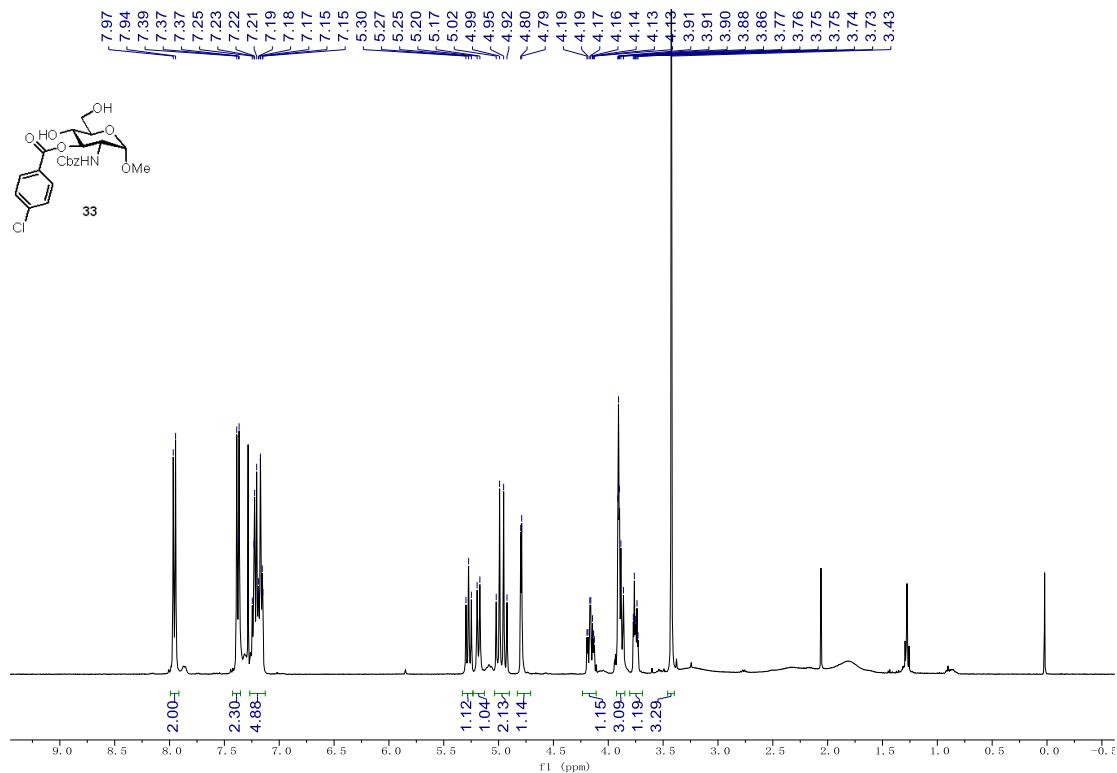


Figure S137. ^1H NMR Spectra of 33

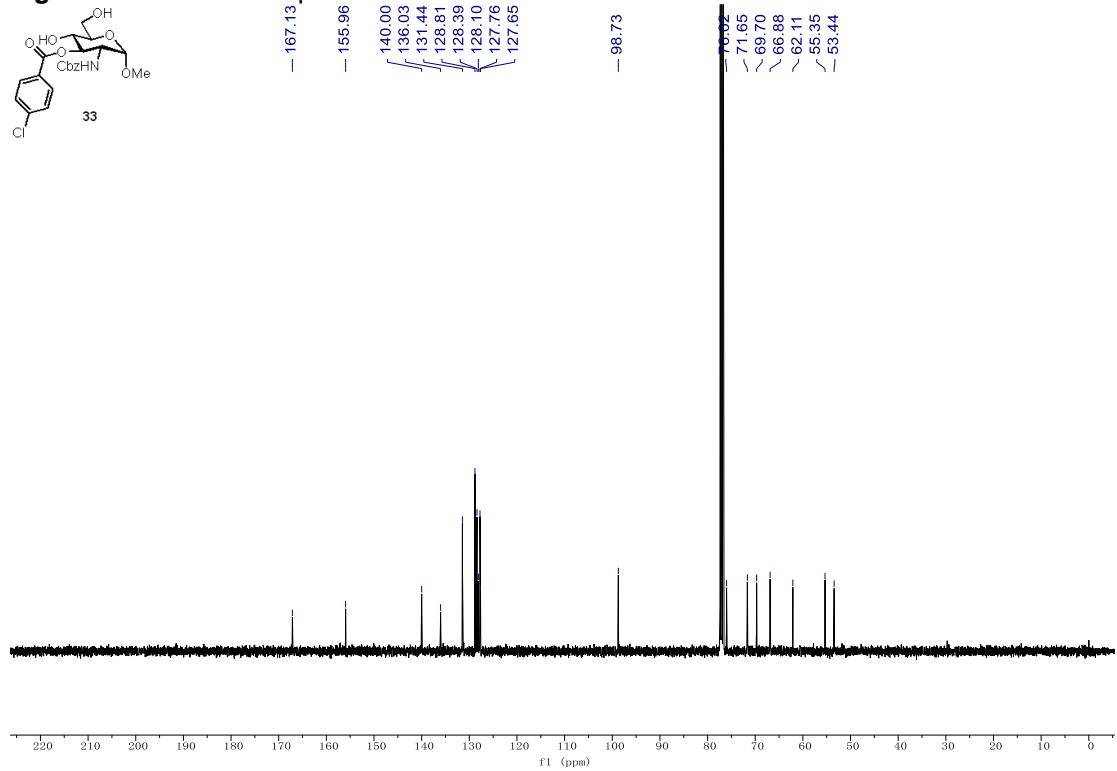
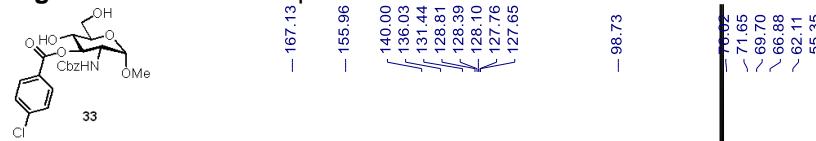


Figure S138. ^{13}C NMR Spectra of 33

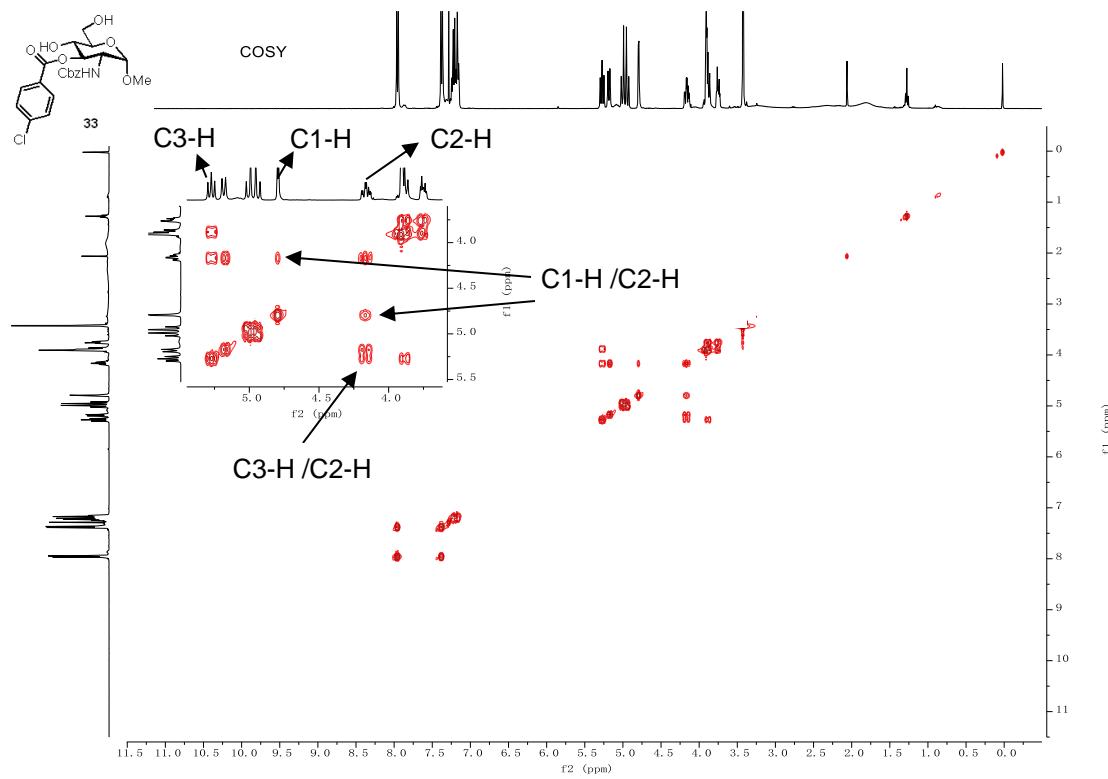


Figure S139. COSY NMR Spectra of 33

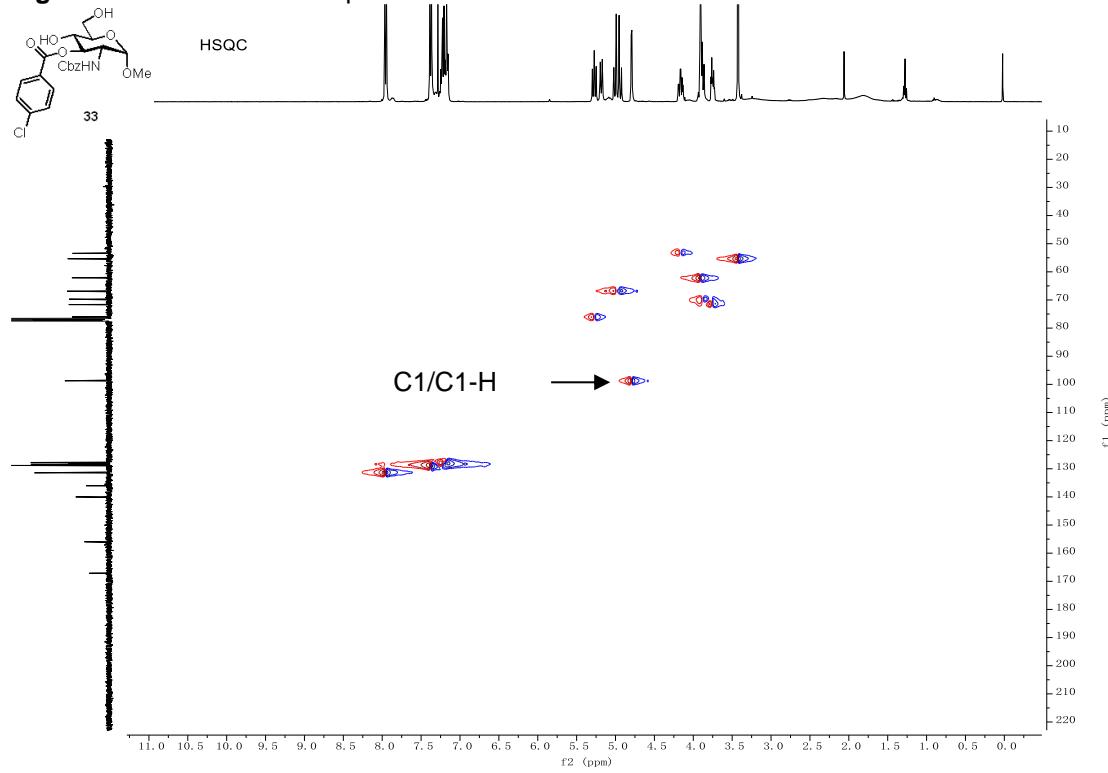


Figure S140. HSQC NMR Spectra of 33

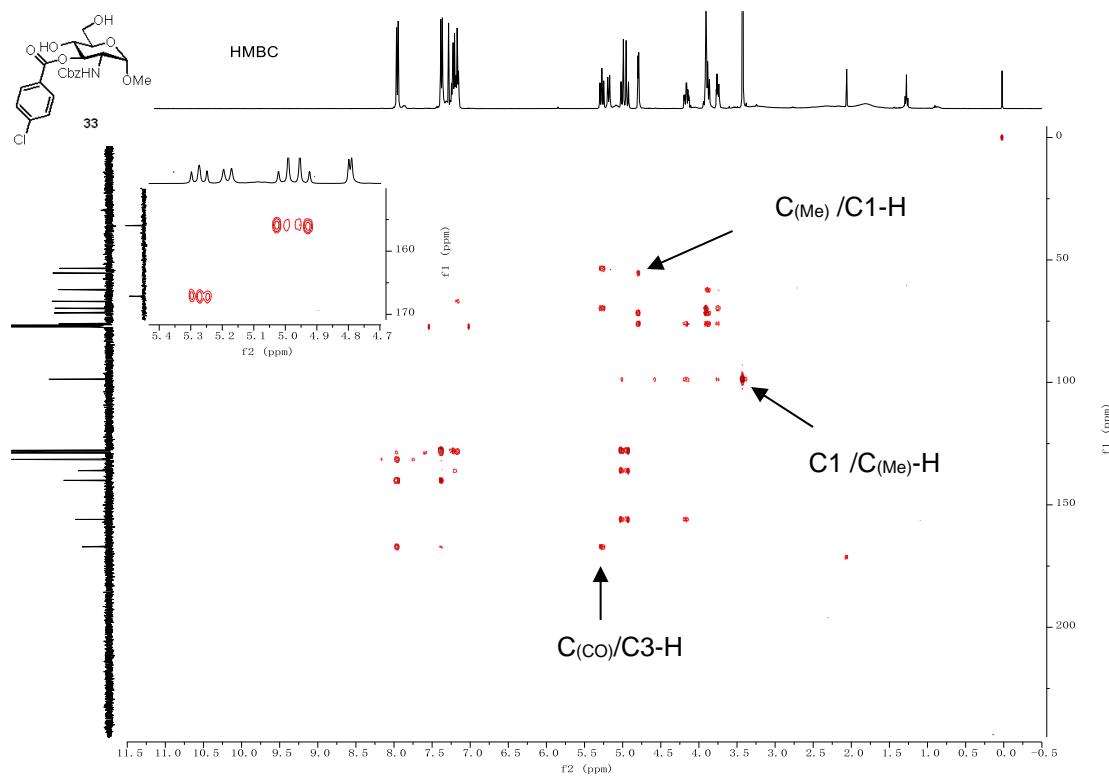


Figure S141. HMBC NMR Spectra of **33**

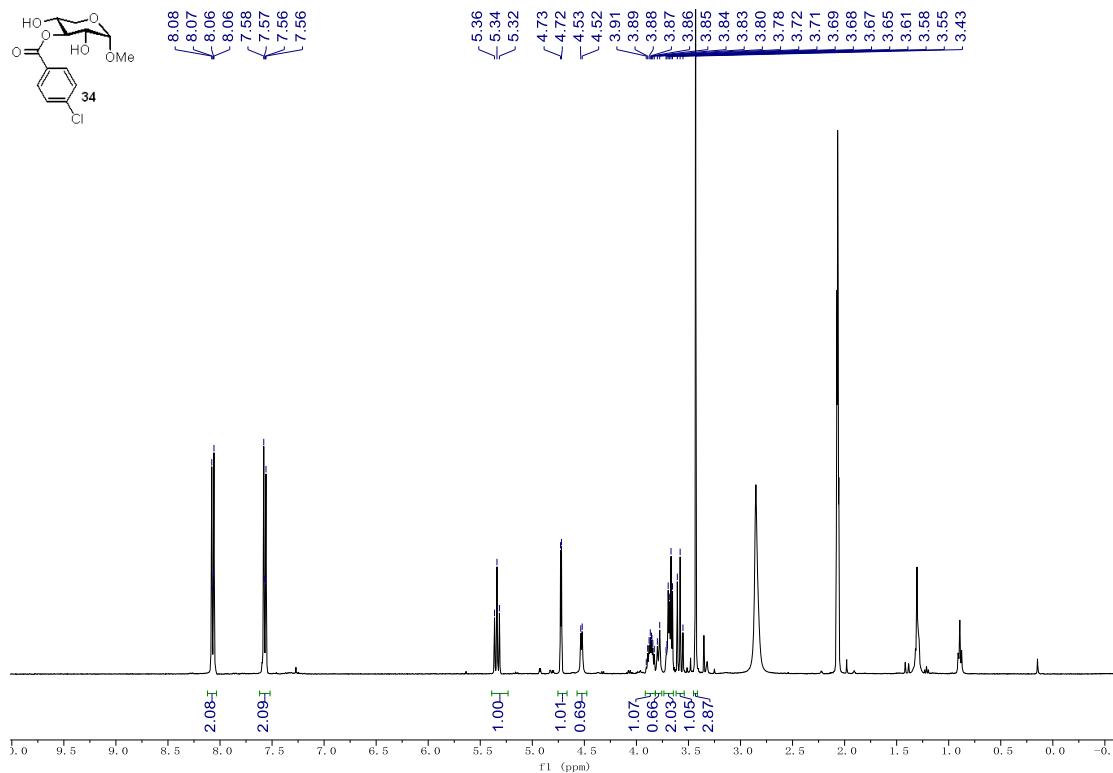


Figure S142. ^1H NMR Spectra of **34**

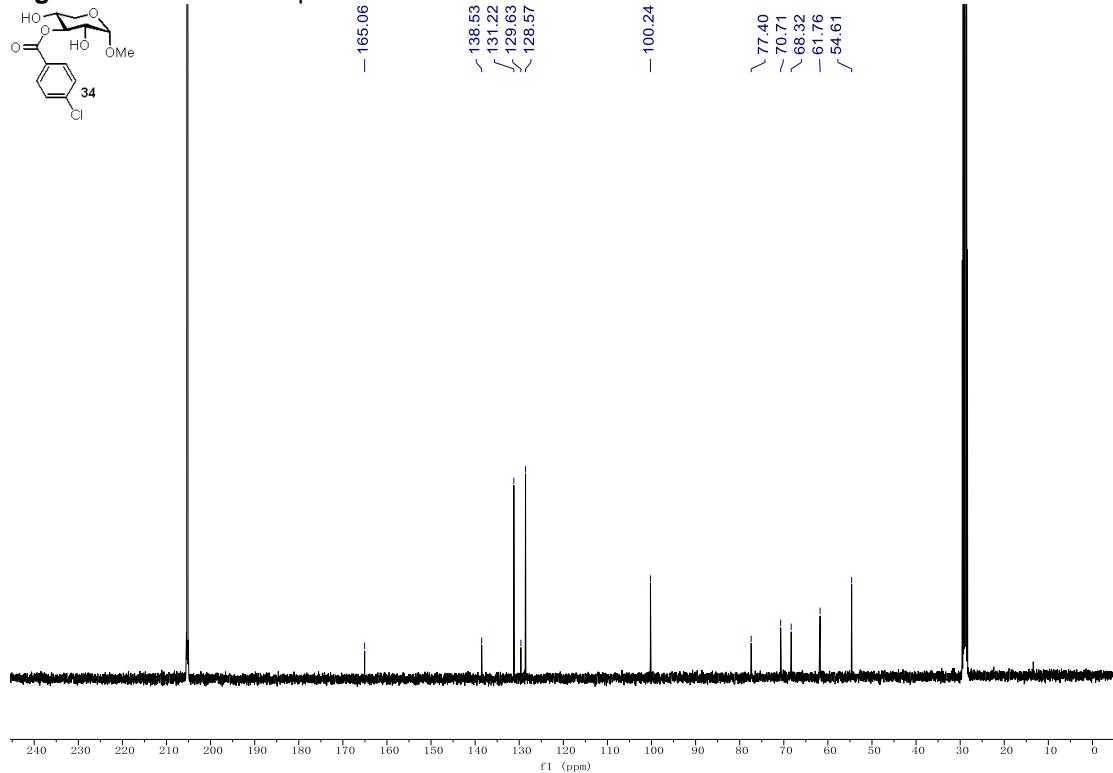


Figure S143. ^{13}C NMR Spectra of 34

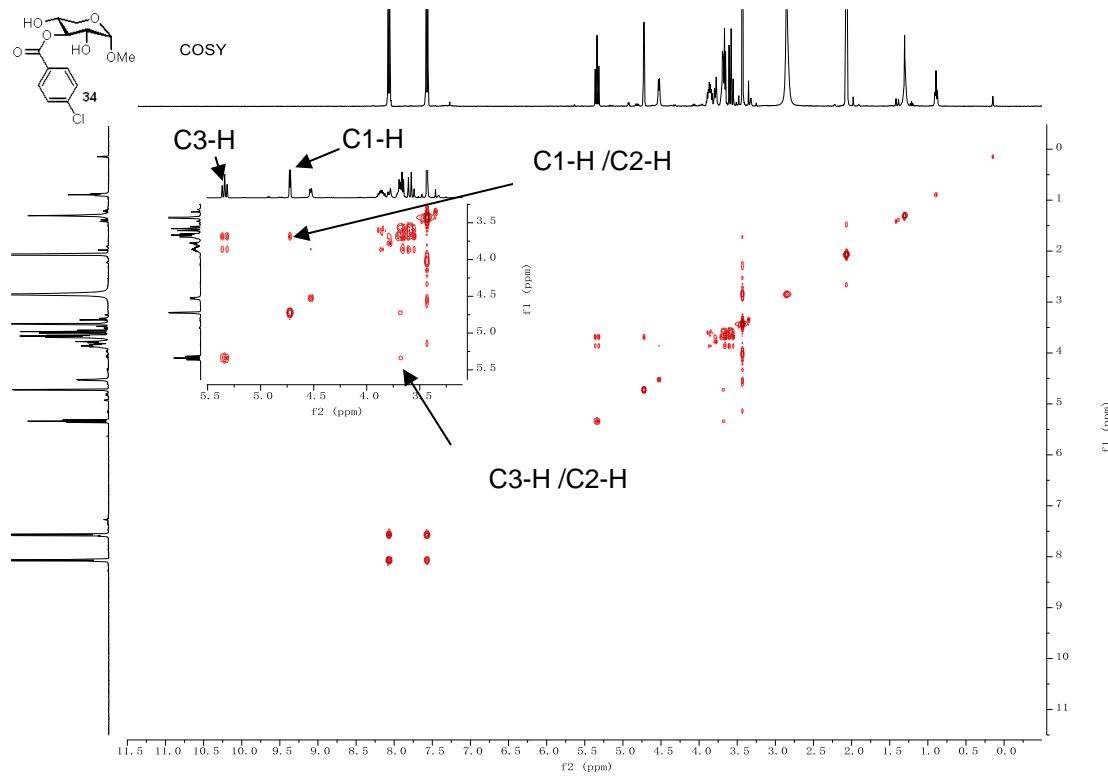


Figure S144. COSY NMR Spectra of 34

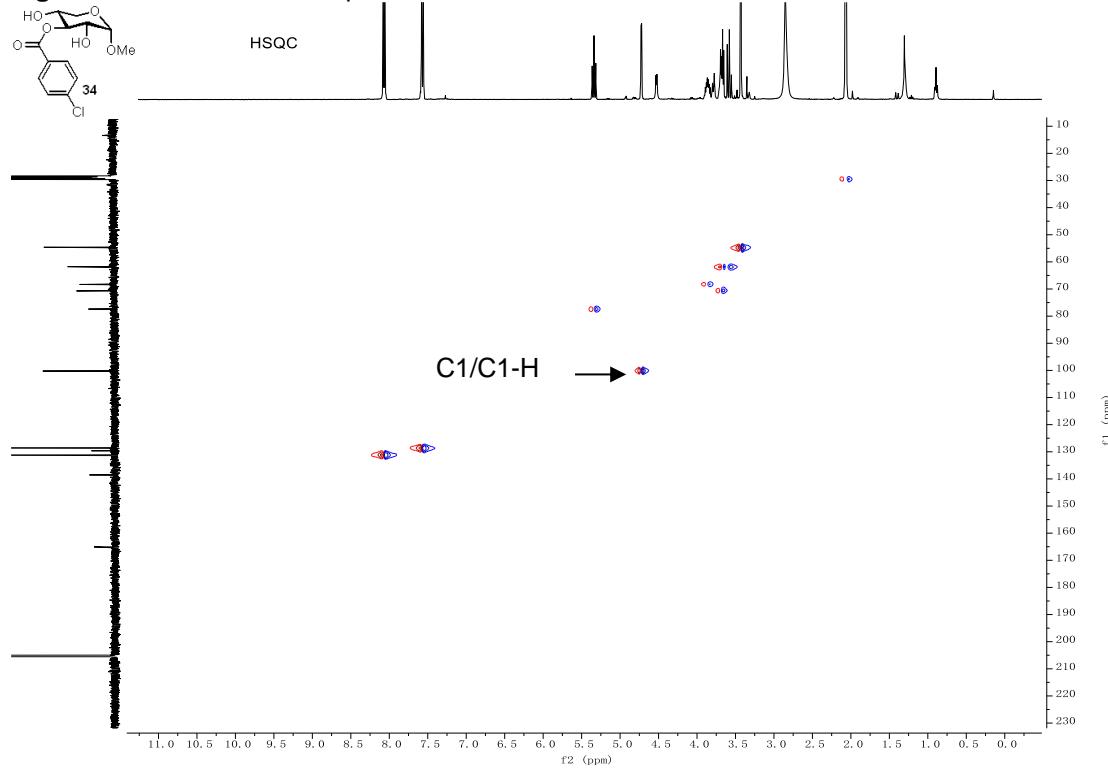


Figure S145. HSQC NMR Spectra of 34

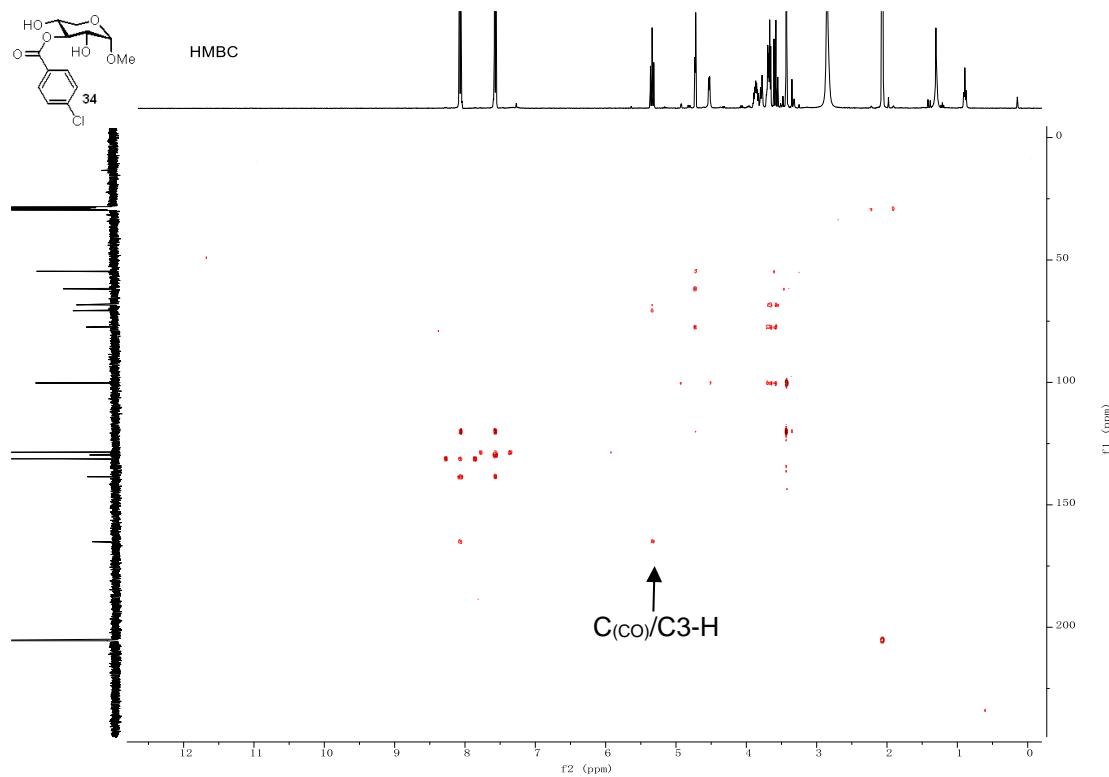


Figure S146. HMBC NMR Spectra of 34

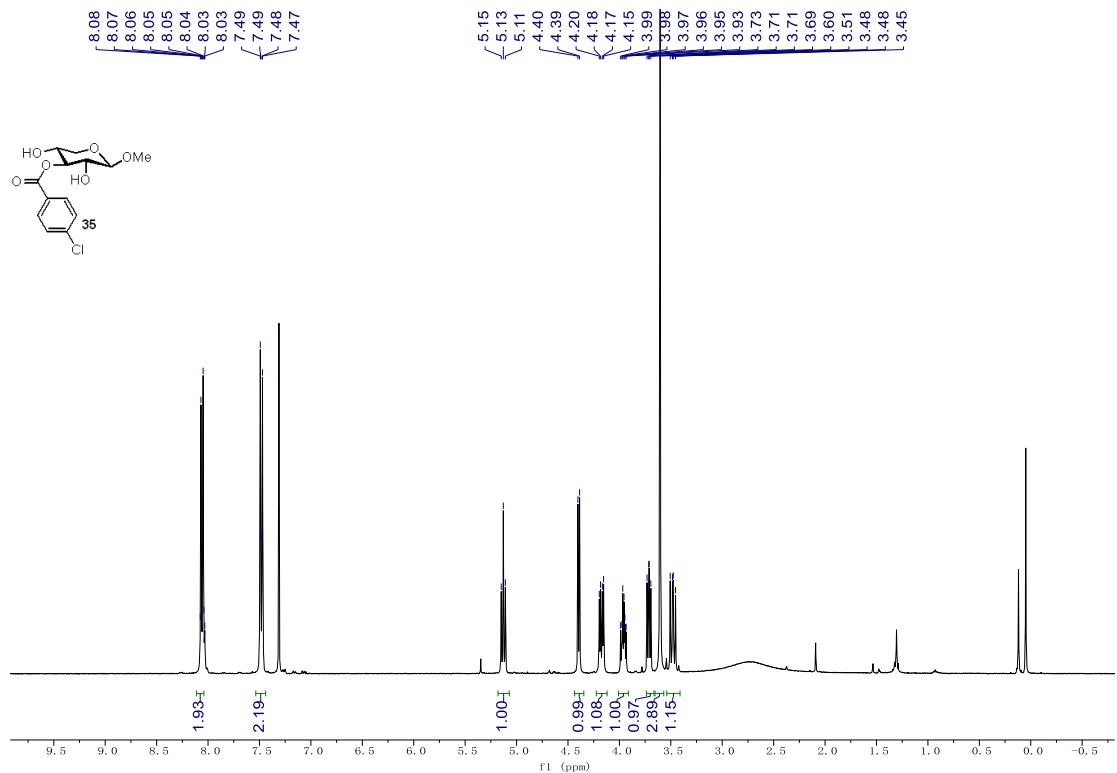


Figure S147. ^1H NMR Spectra of 35

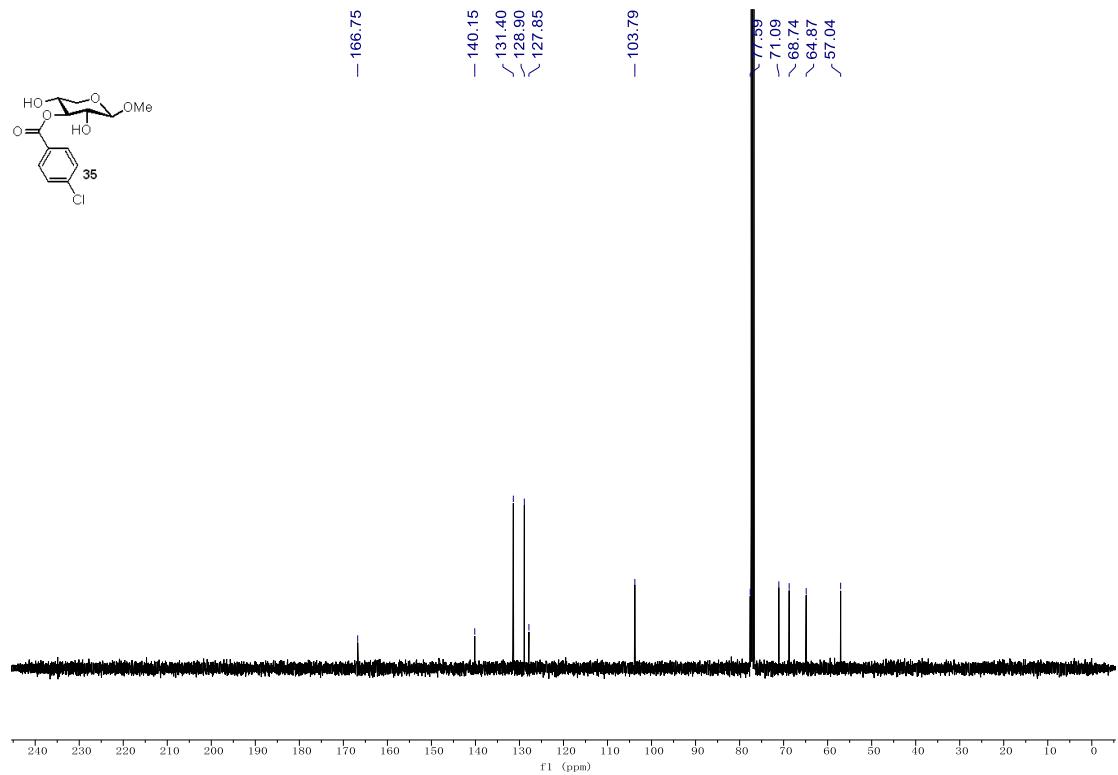


Figure S148. ^{13}C NMR Spectra of **35**

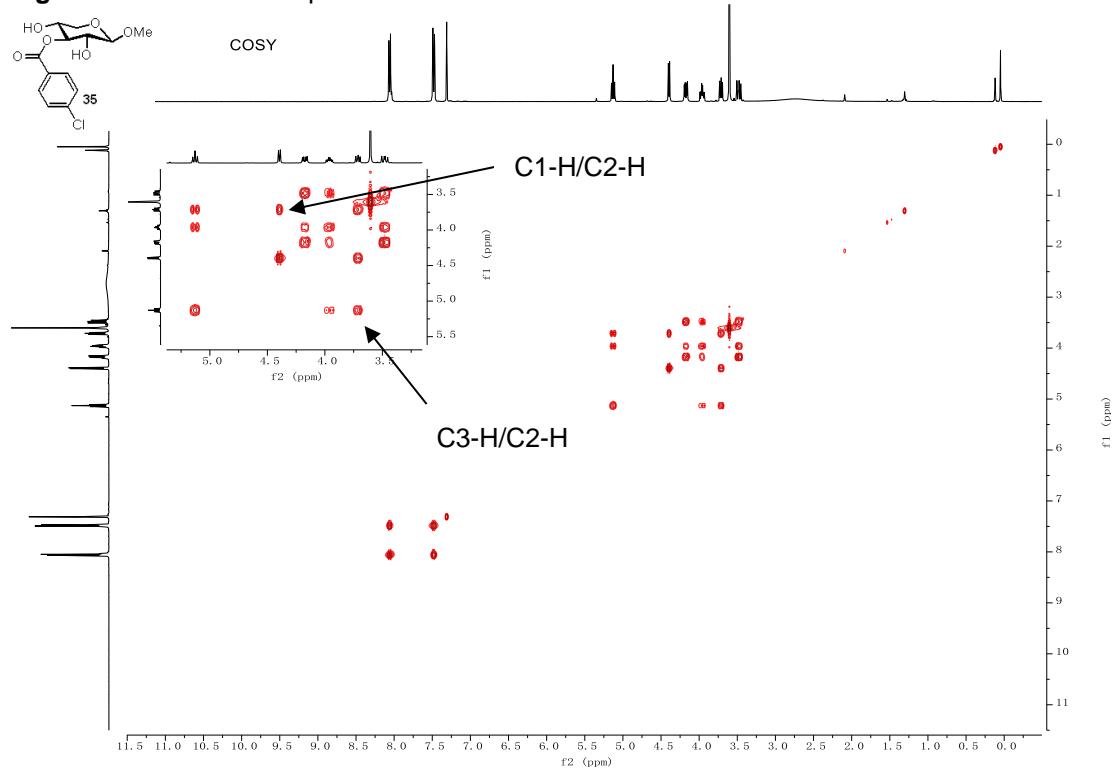


Figure S149. COSY NMR Spectra of **35**

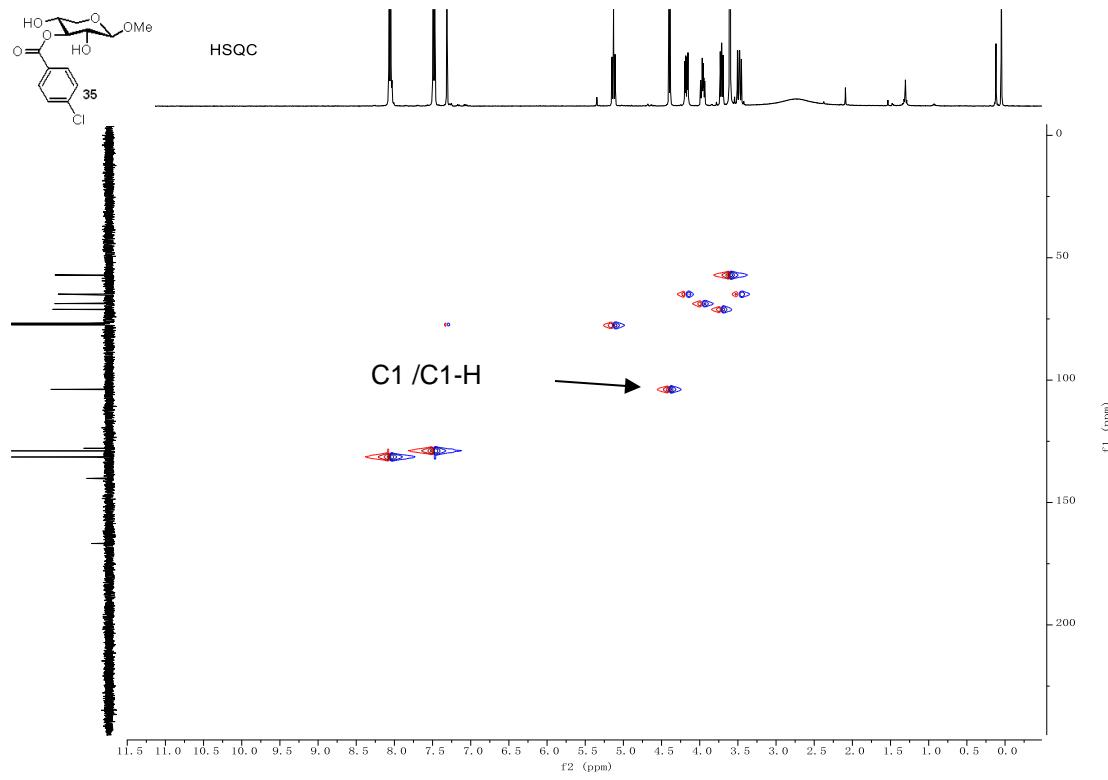


Figure S150. HSQC NMR Spectra of **35**

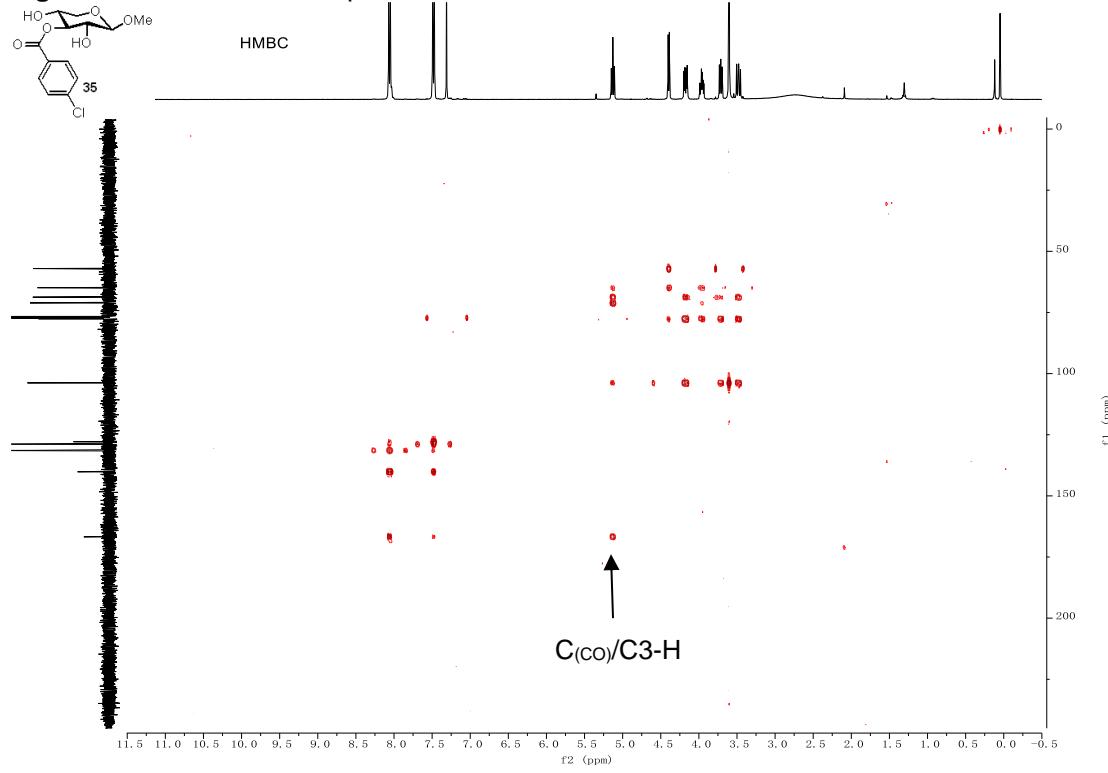


Figure S151. HMBC NMR Spectra of **35**

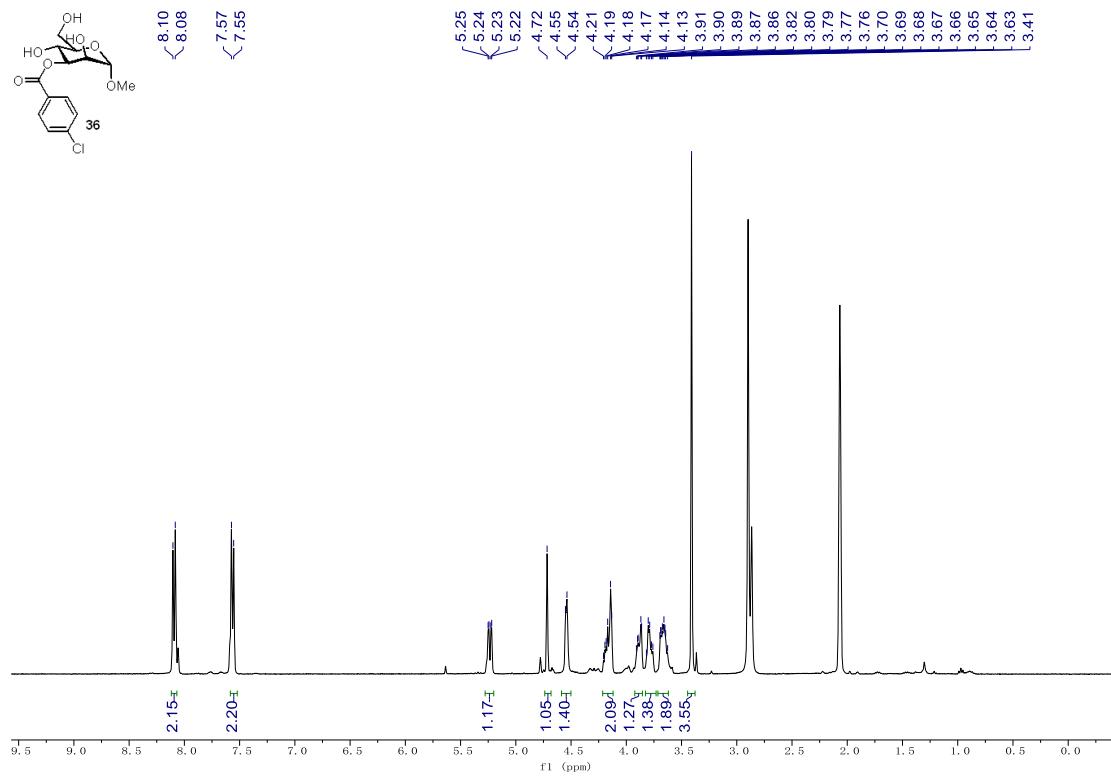


Figure S152. ^1H NMR Spectra of 36

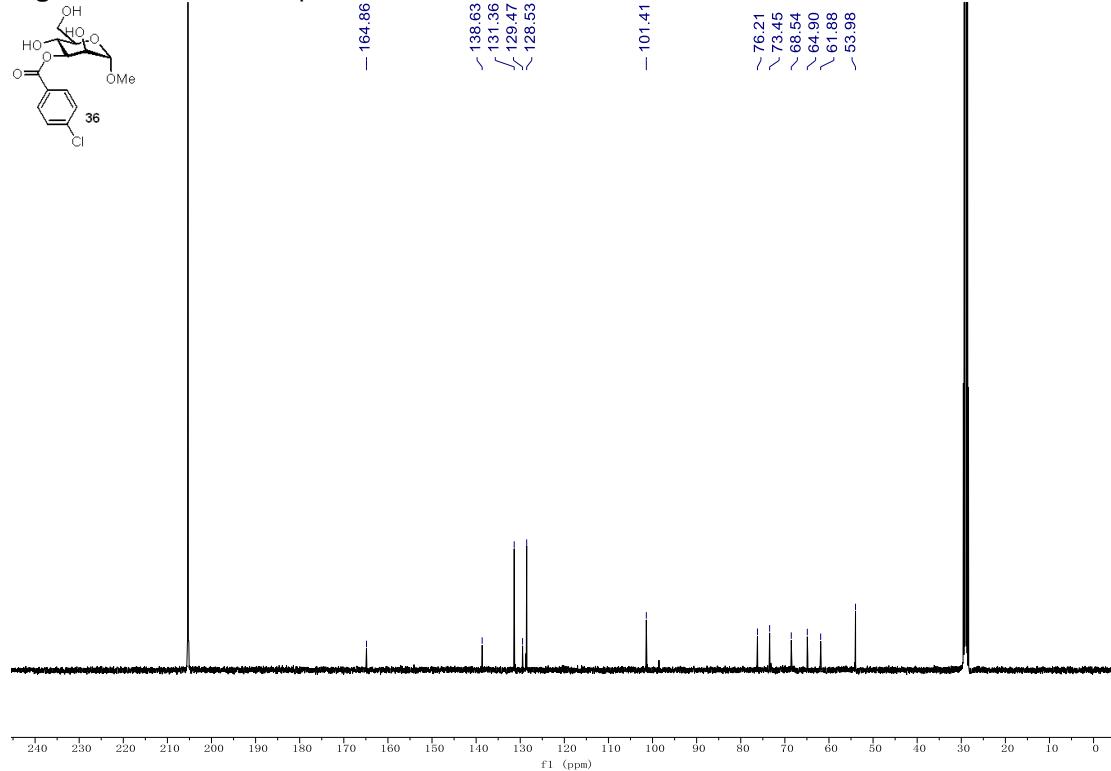


Figure S153. ^{13}C NMR Spectra of 36

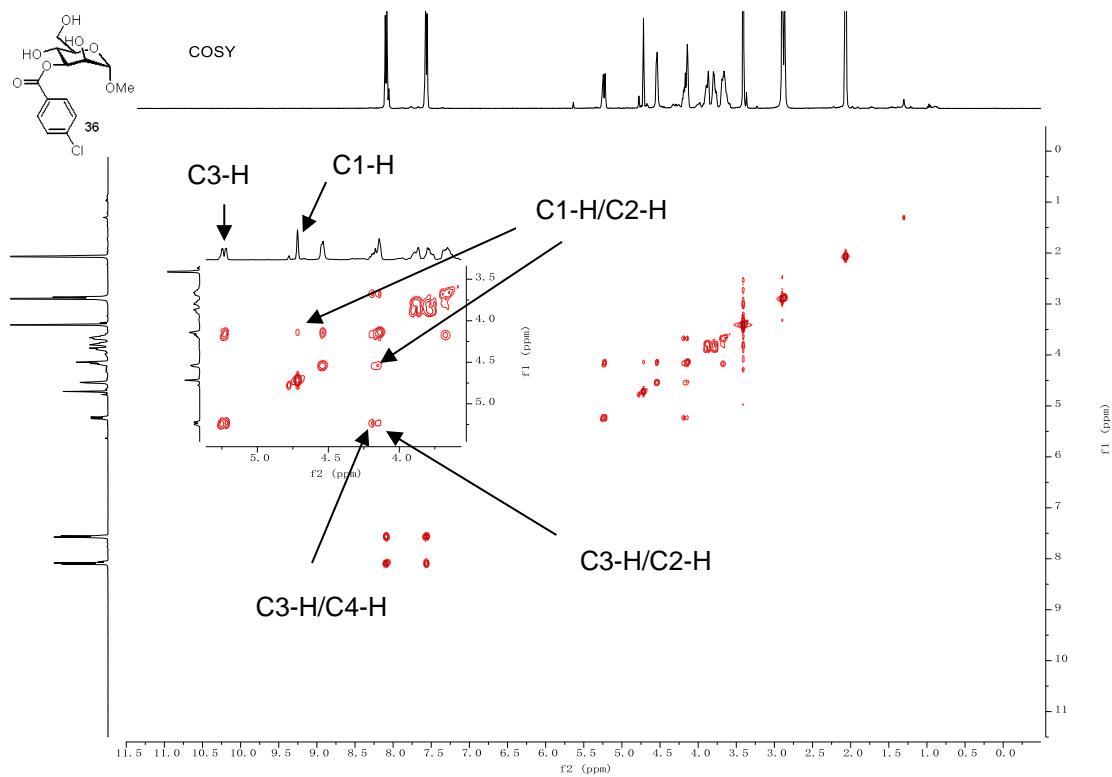


Figure S154. COSY NMR Spectra of **36**

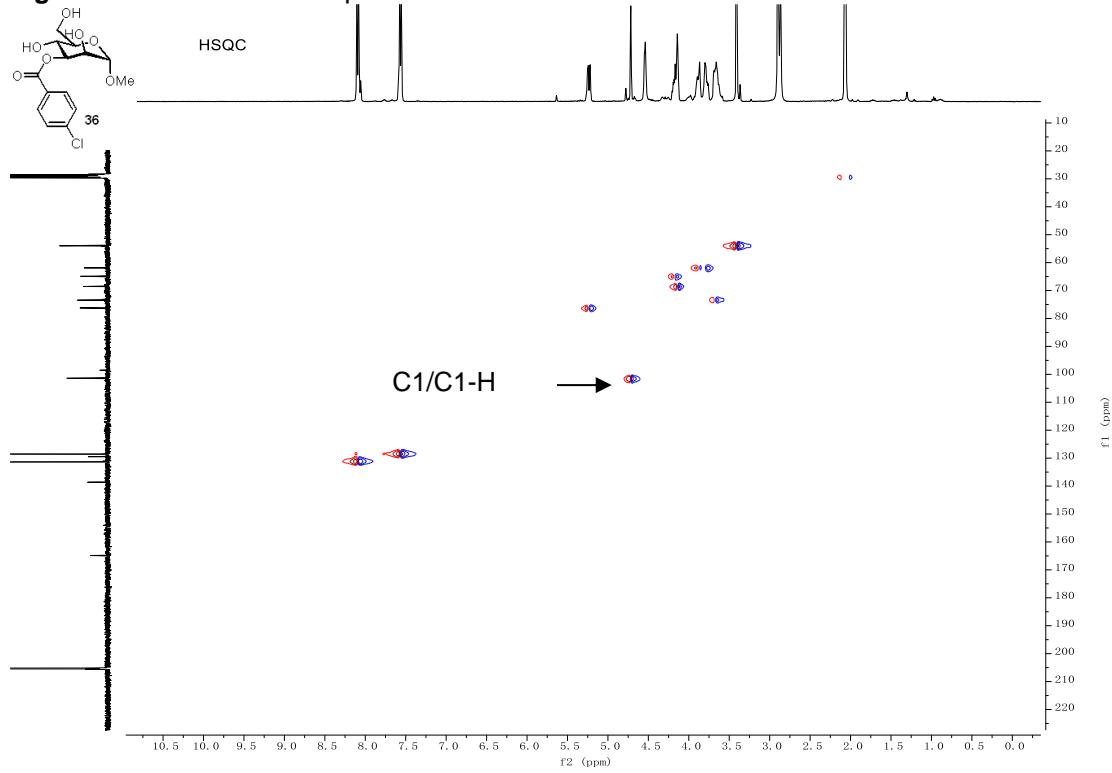


Figure S155. HSQC NMR Spectra of 36

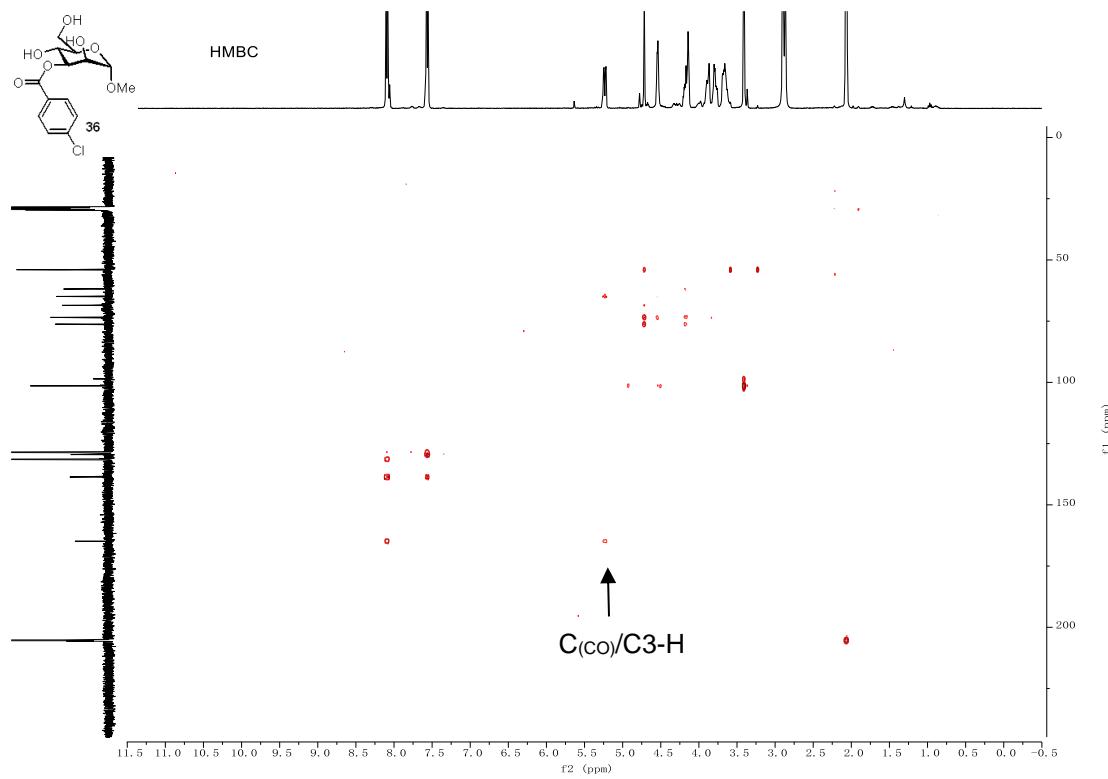


Figure S156. HMBC NMR Spectra of **36**

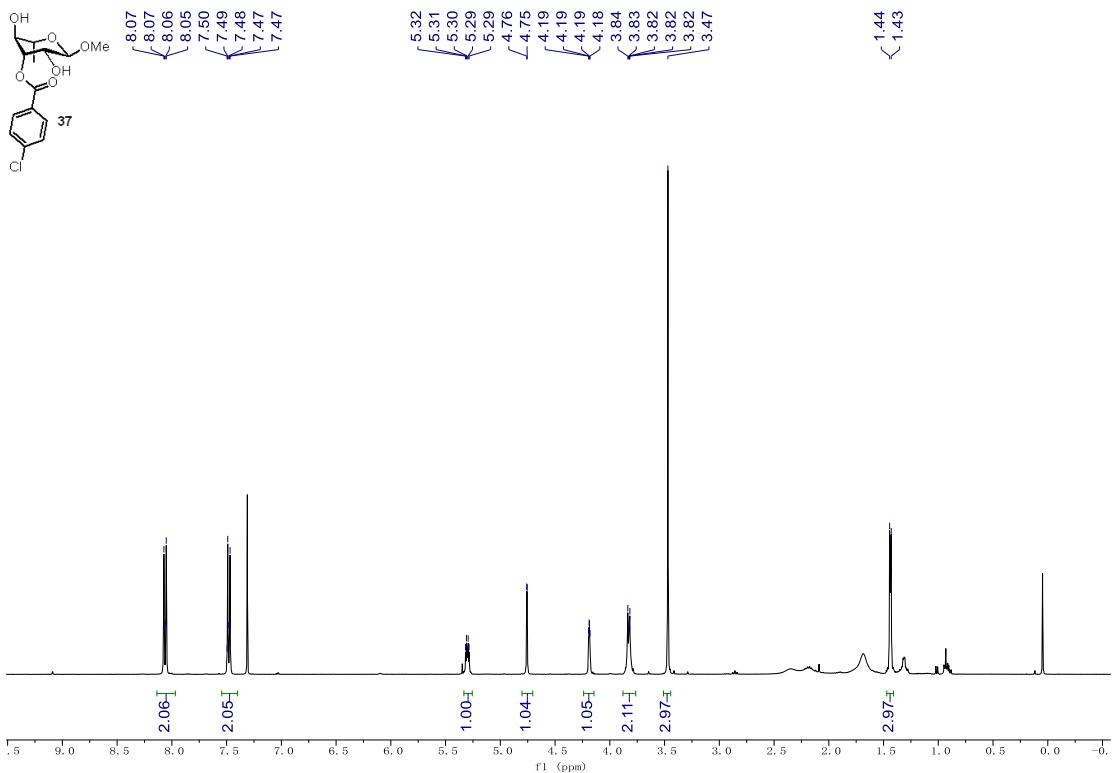


Figure S157. ^1H NMR Spectra of 37

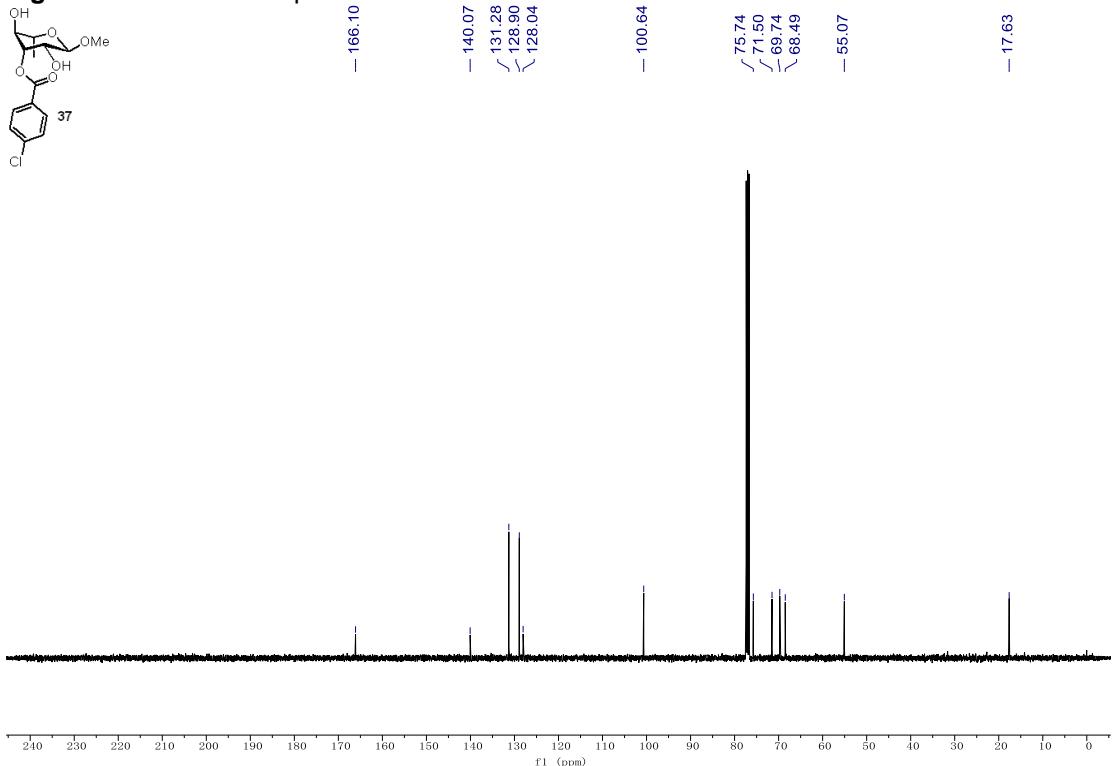


Figure S158. ^{13}C NMR Spectra of 37

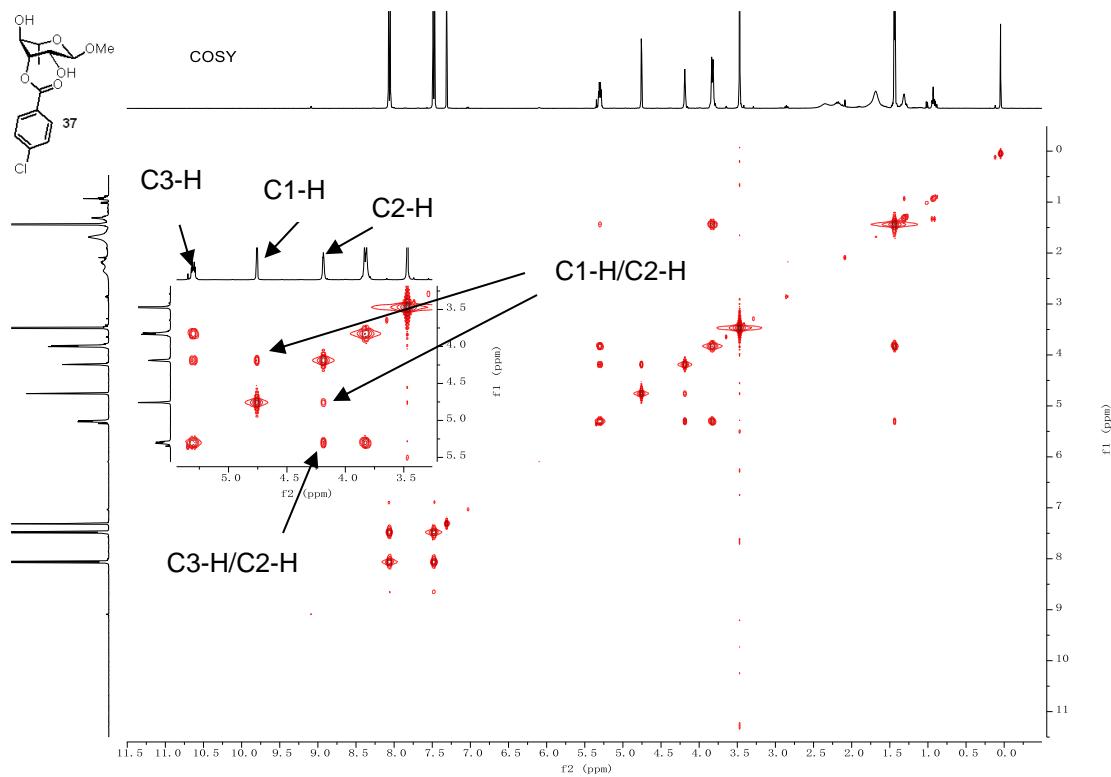


Figure S159. COSY NMR Spectra of 37

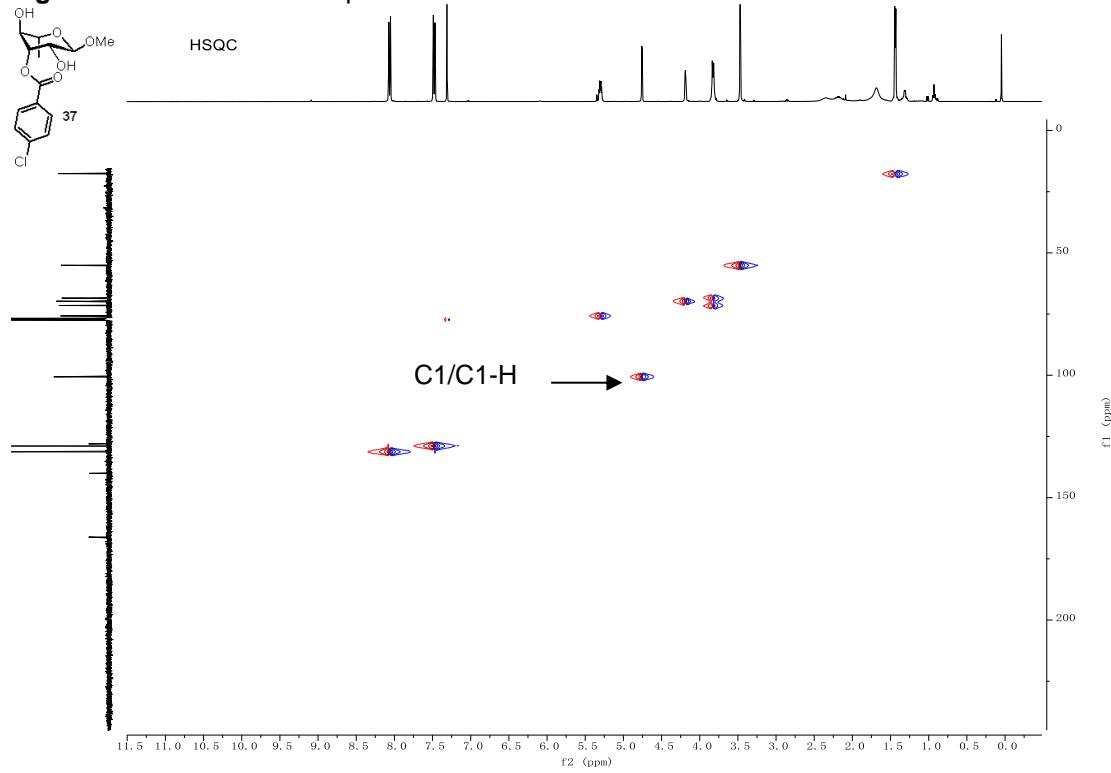


Figure S160. HSQC NMR Spectra of 37

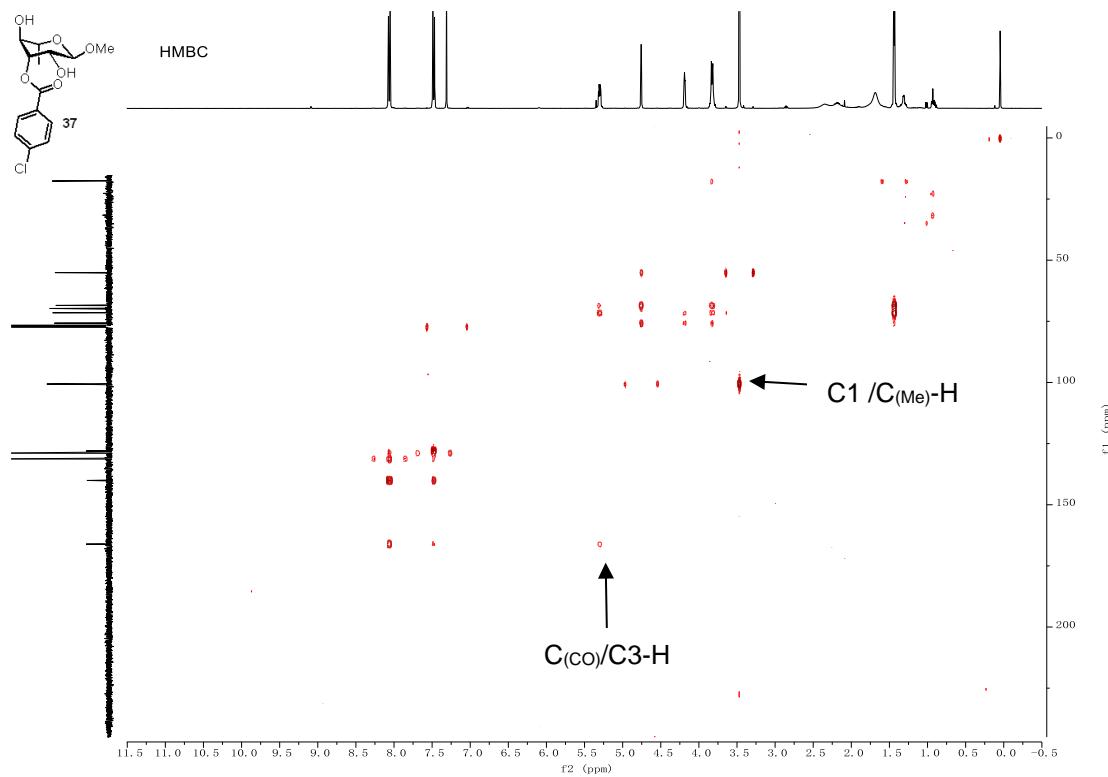


Figure S161. HMBC NMR Spectra of 37

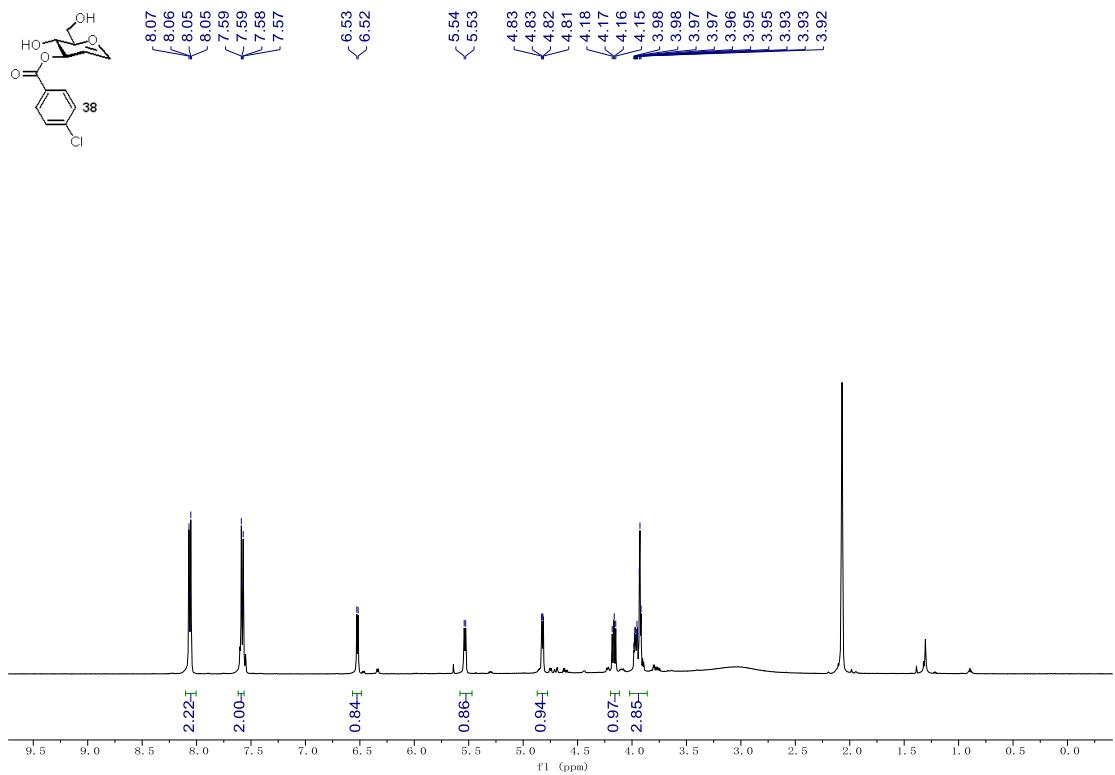


Figure S162. ^1H NMR Spectra of **38**

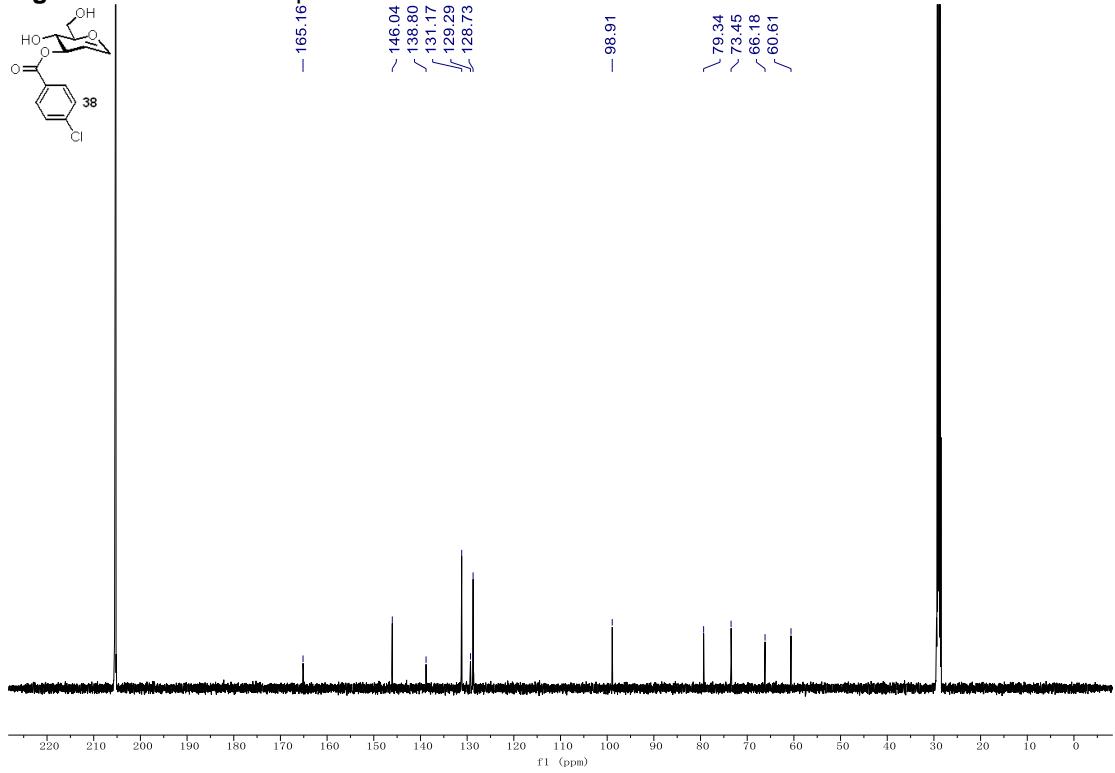


Figure S163. ^{13}C NMR Spectra of **38**

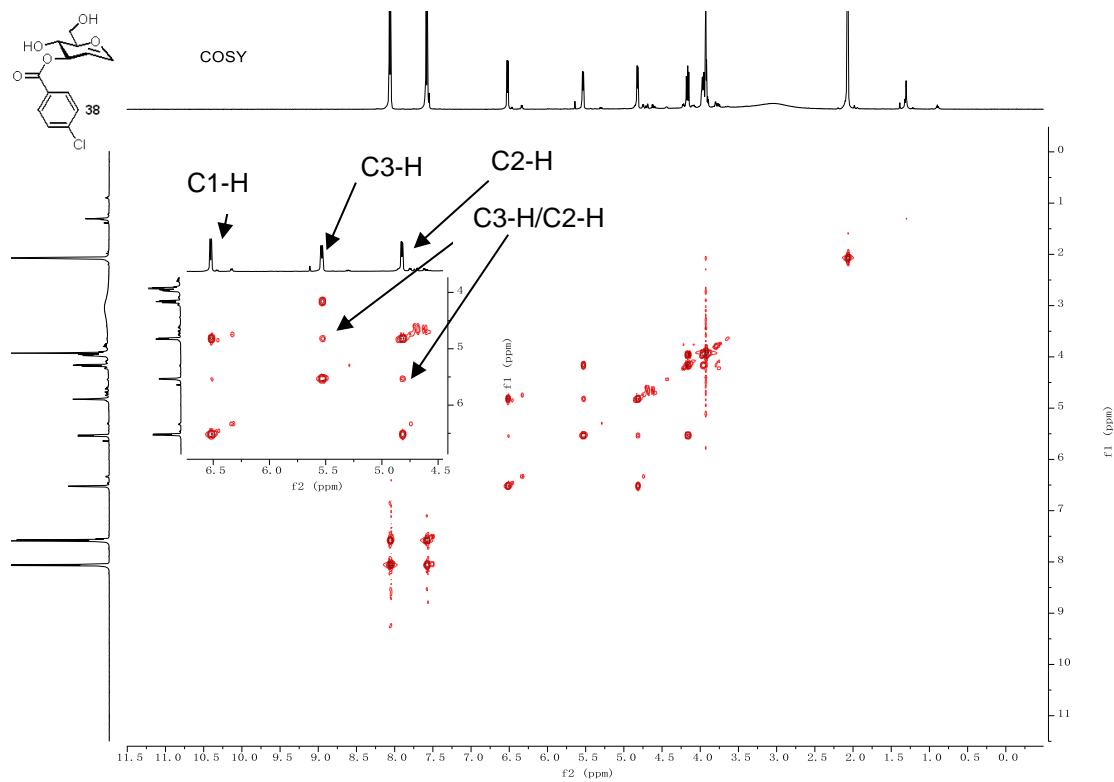


Figure S164. COSY NMR Spectra of 38

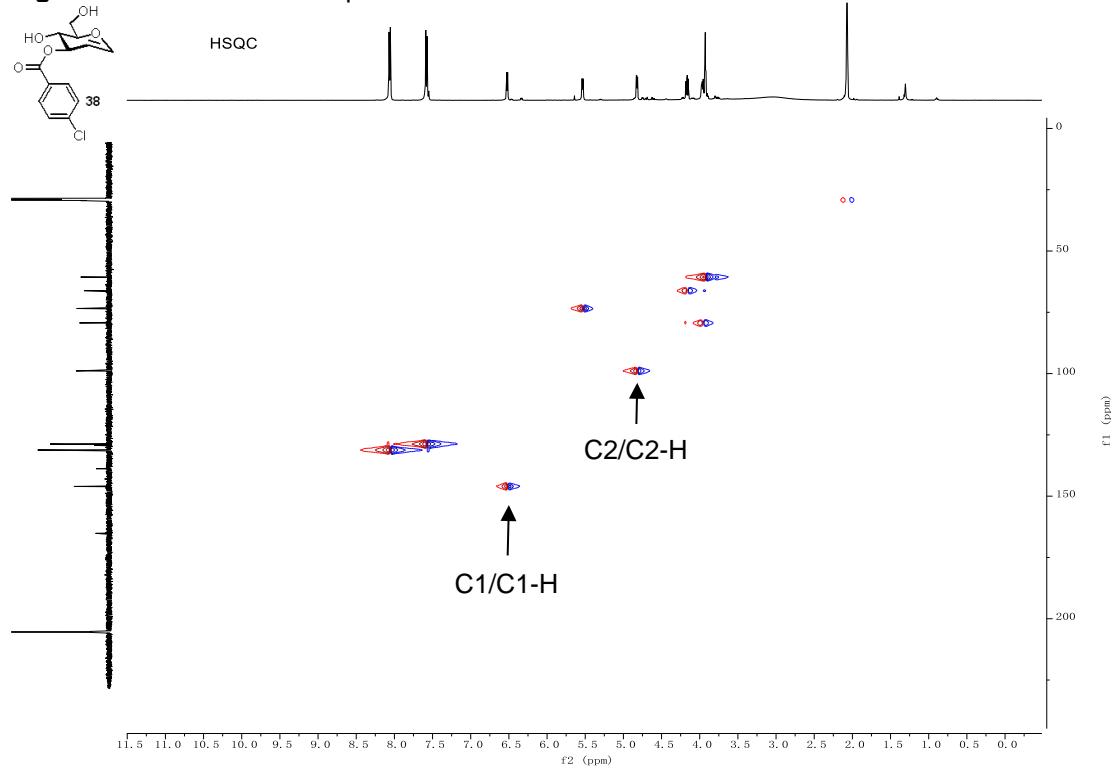


Figure S165. HSQC NMR Spectra of 38

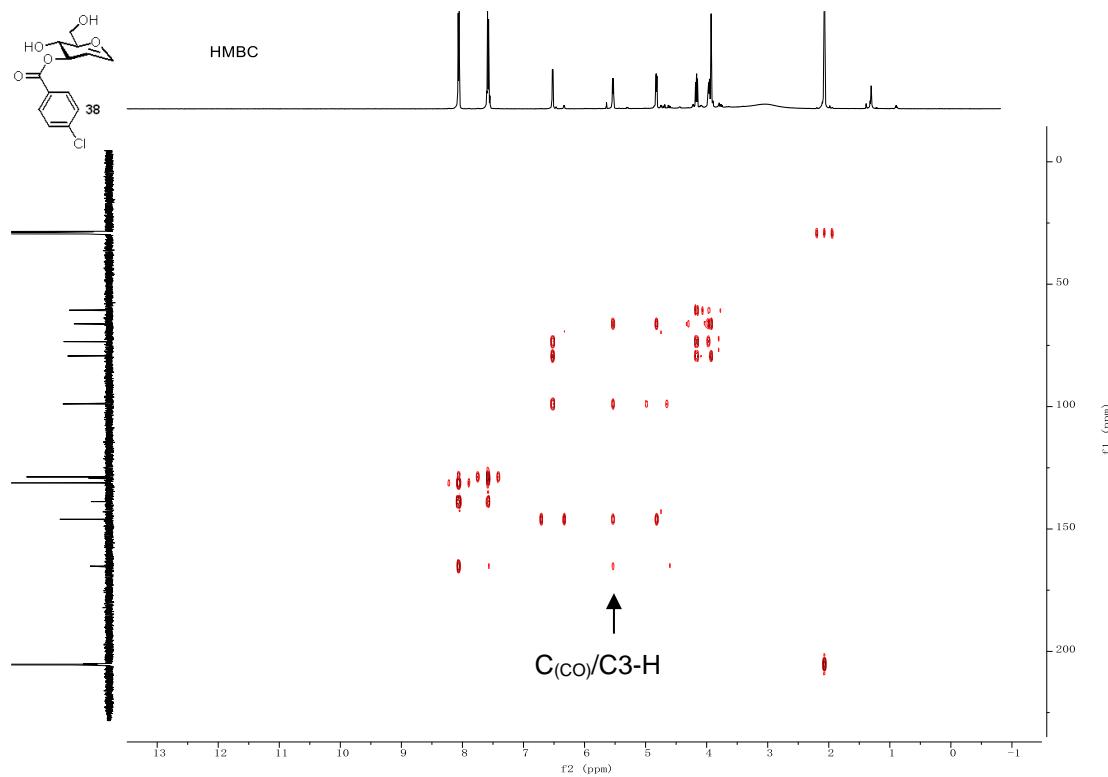


Figure S166. HMBC NMR Spectra of 38

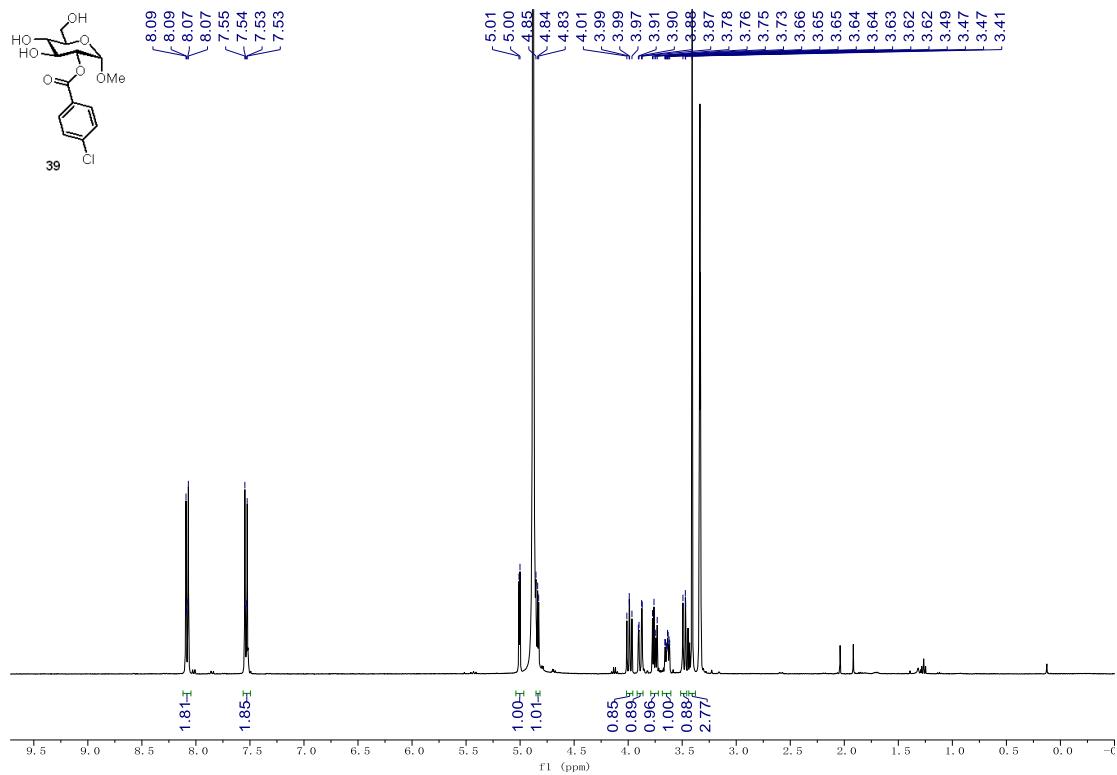


Figure S167. ^1H NMR Spectra of 39

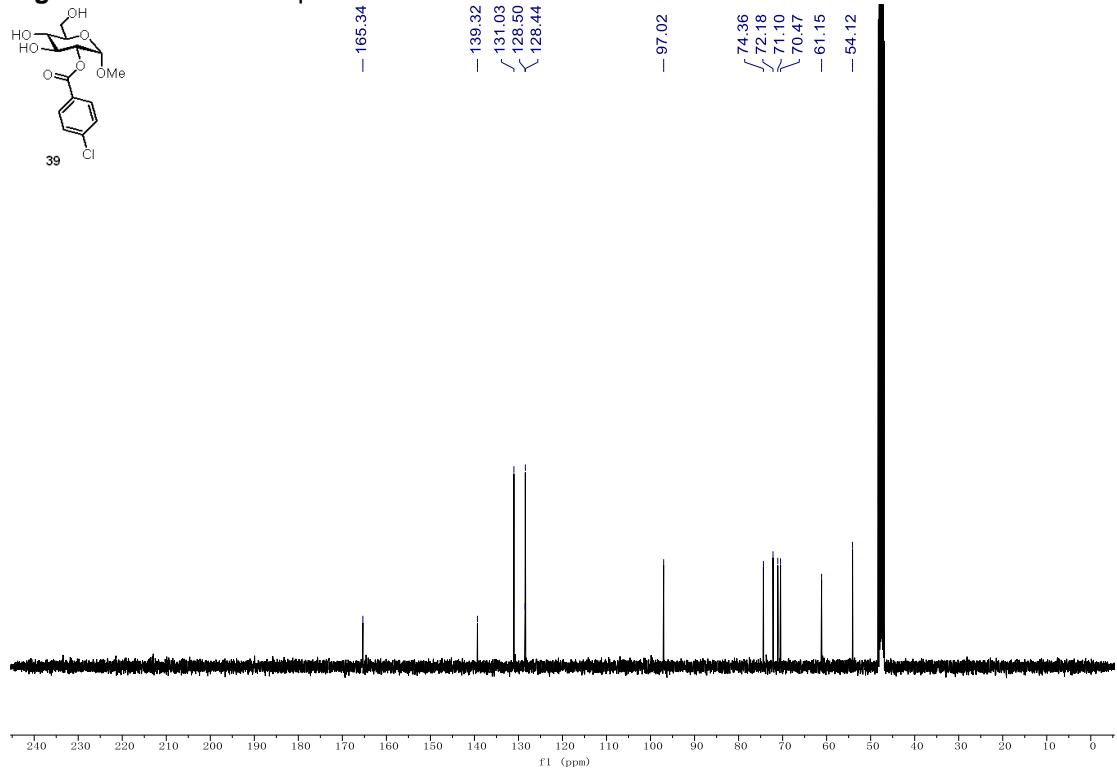


Figure S168. ^{13}C NMR Spectra of 39

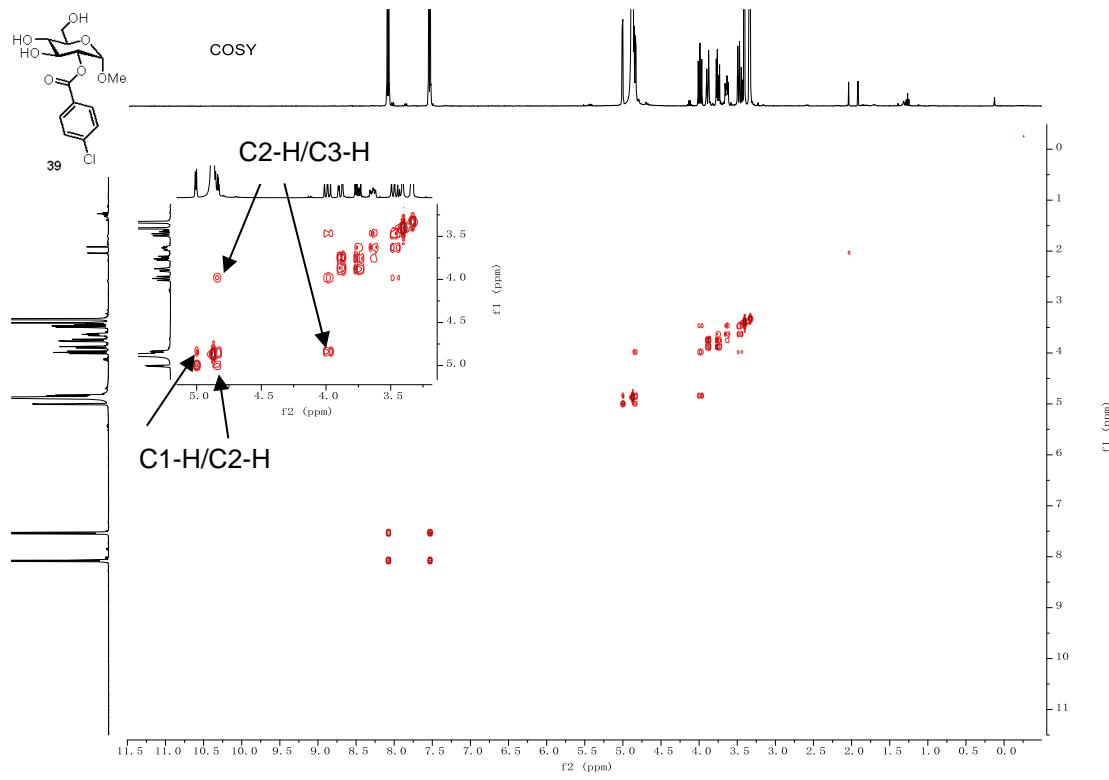


Figure S169. COSY NMR Spectra of 39

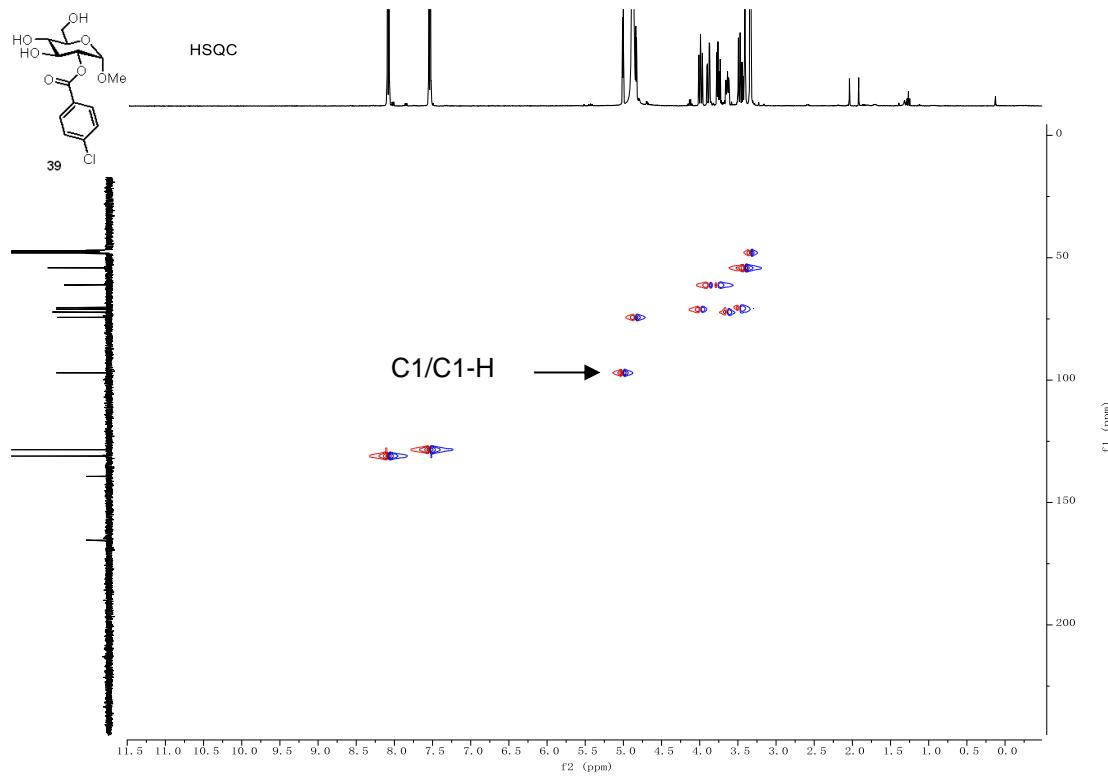


Figure S170. HSQC NMR Spectra of 39

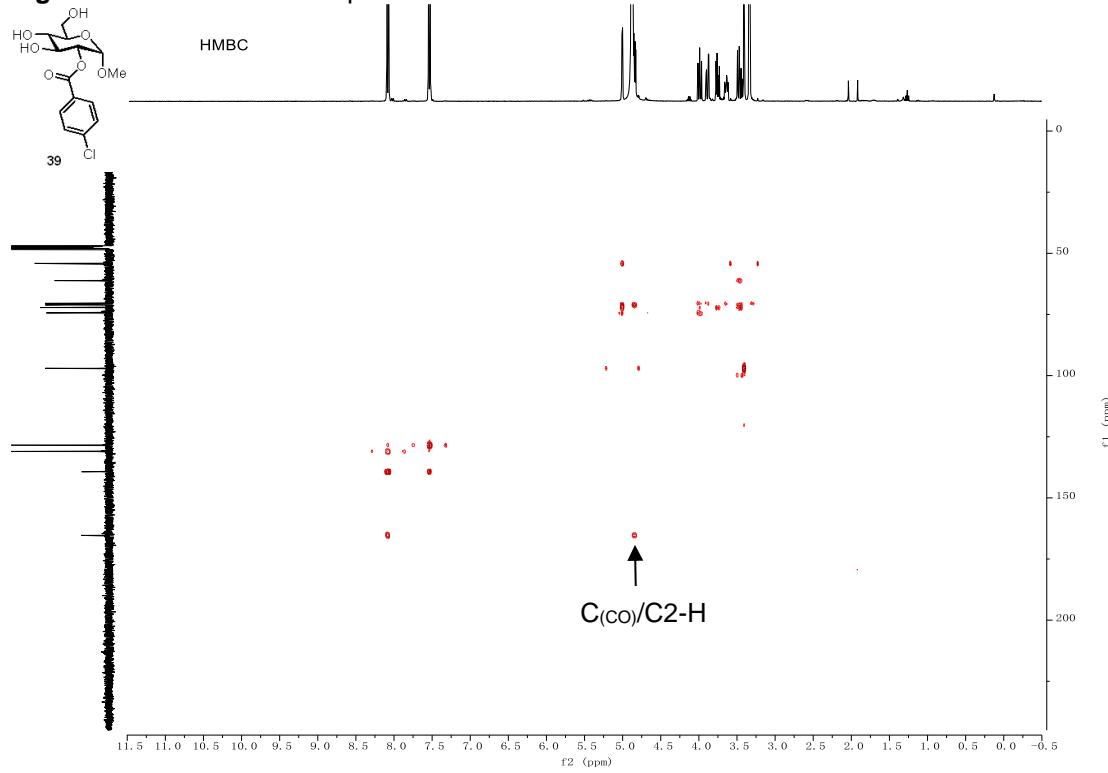


Figure S171. HMBC NMR Spectra of 39

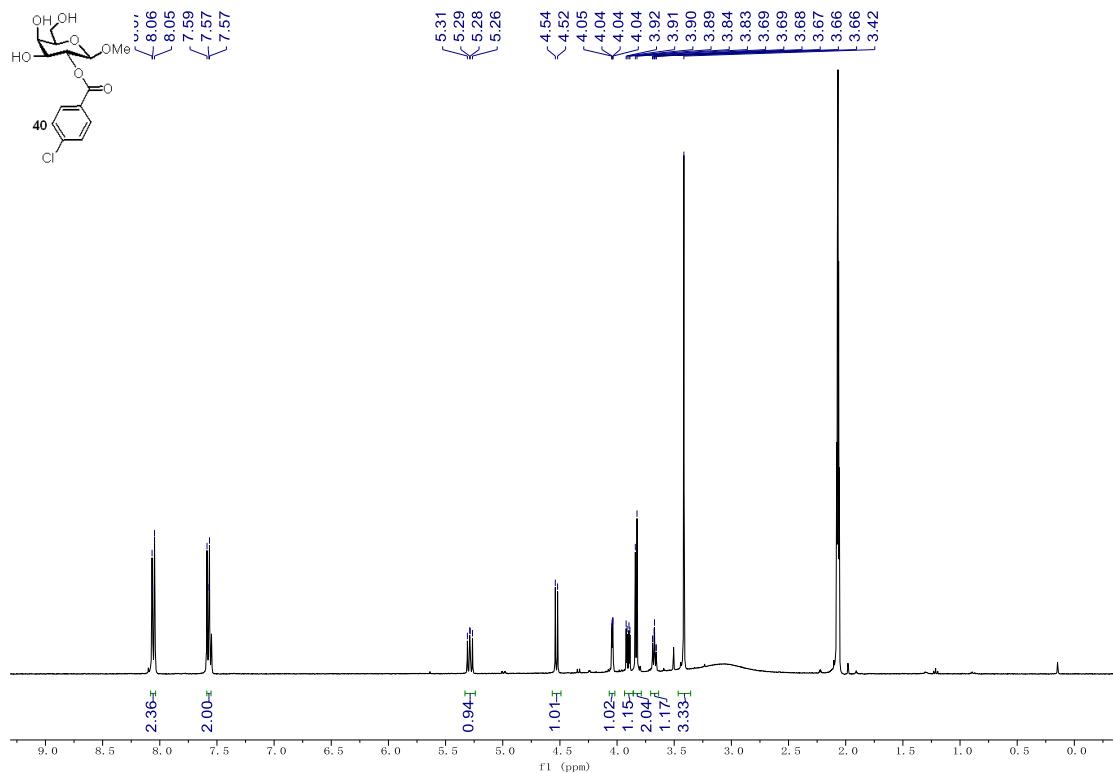


Figure S172. ^1H NMR Spectra of **40**

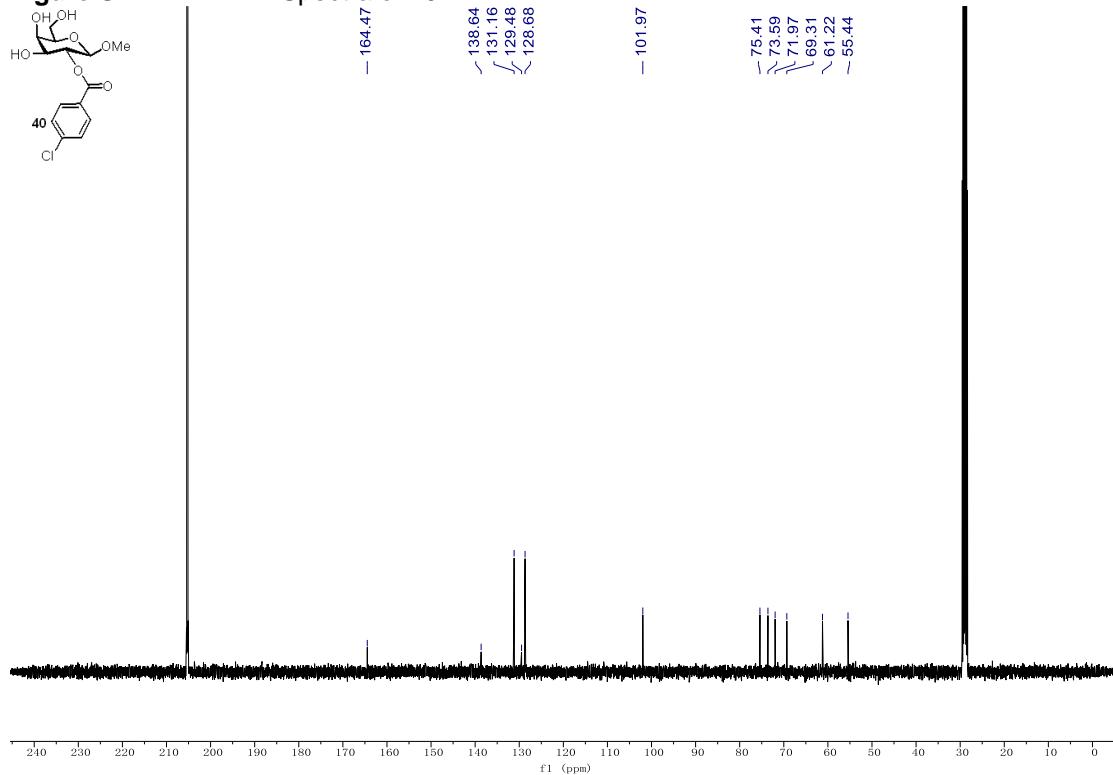


Figure S173. ^{13}C NMR Spectra of **40**

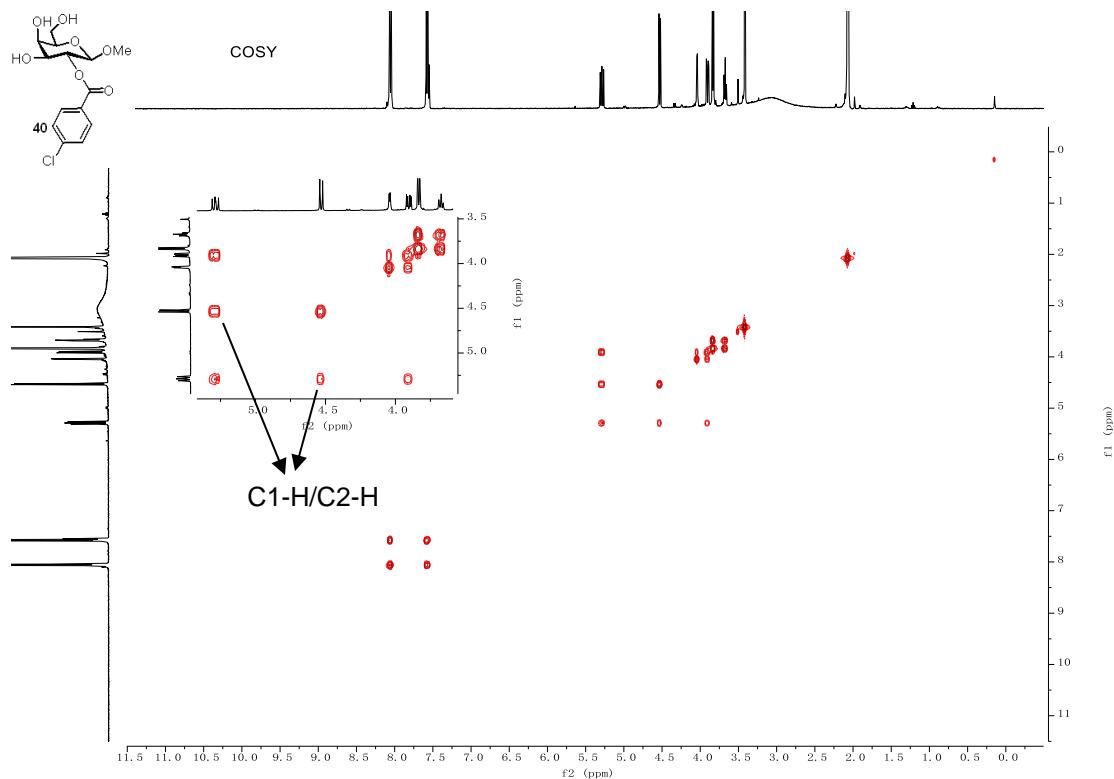


Figure S174. COSY NMR Spectra of **40**

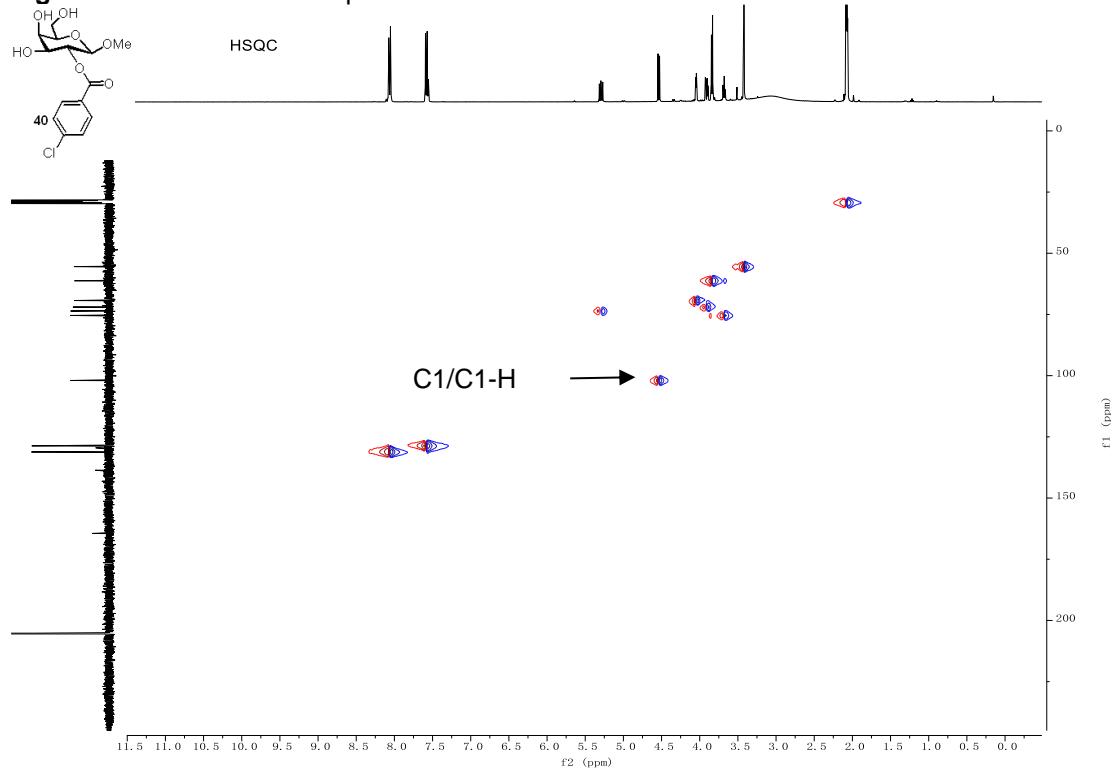


Figure S175. HSQC NMR Spectra of **40**

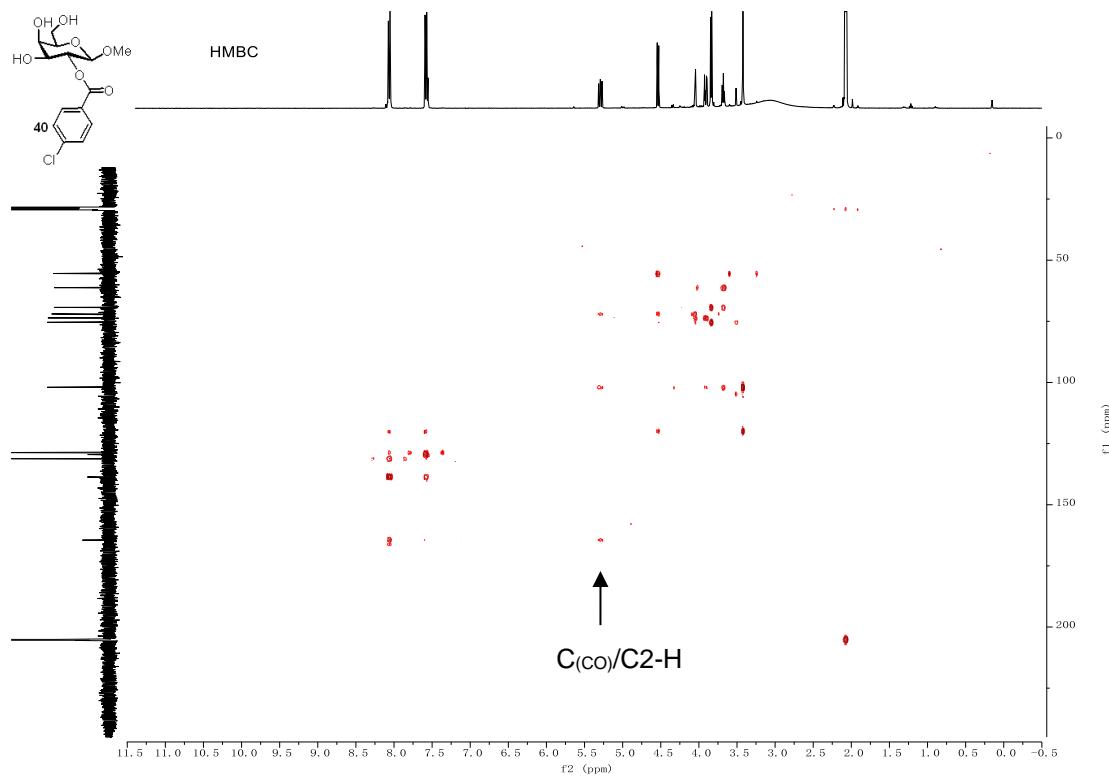


Figure S176. HMBC NMR Spectra of 40

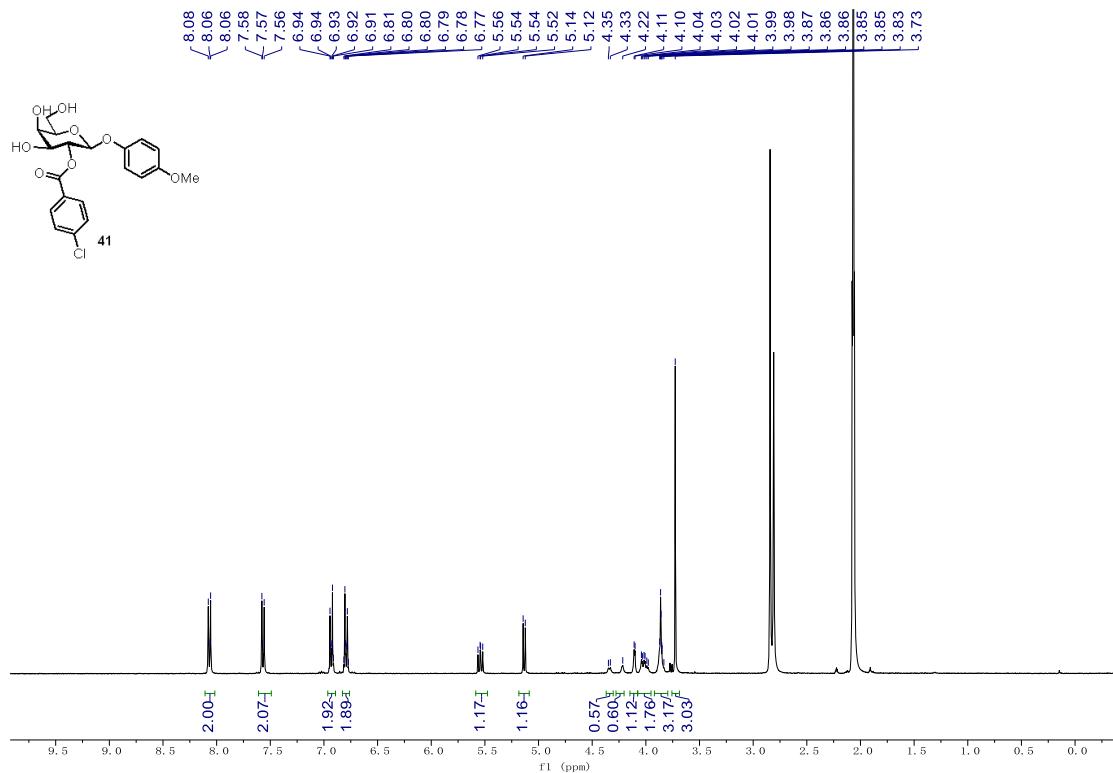


Figure S177. ^1H NMR Spectra of 41

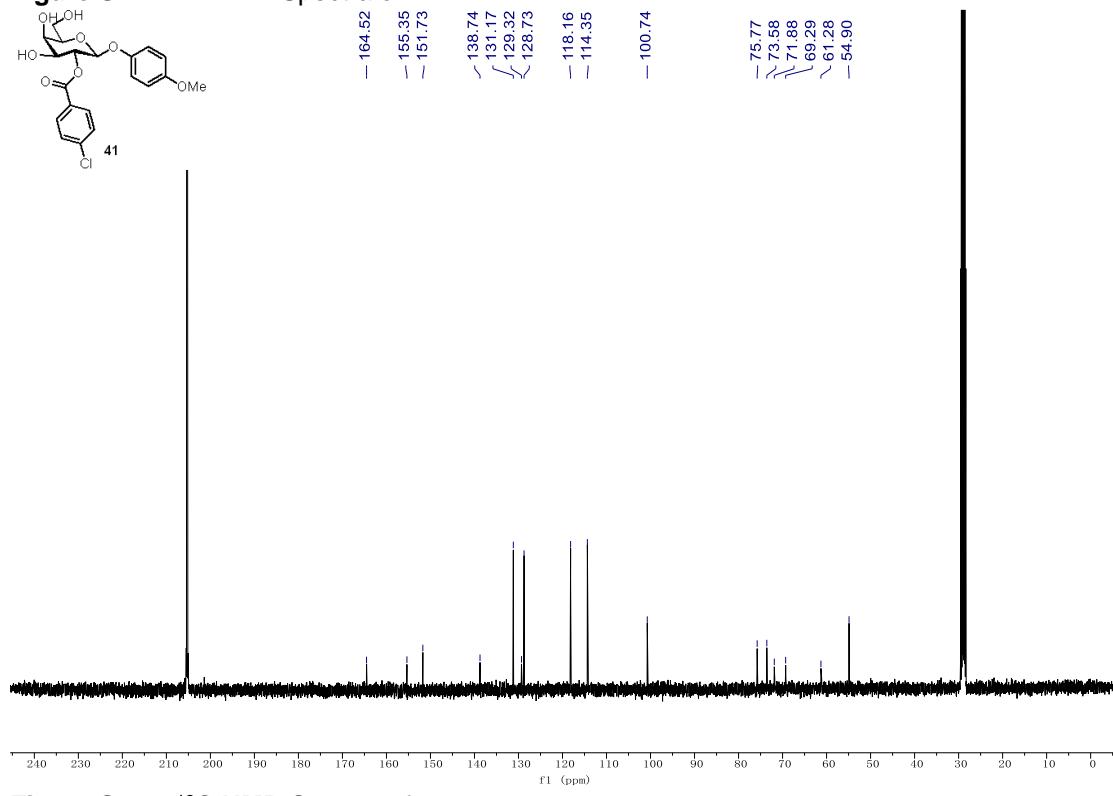


Figure S178. ^{13}C NMR Spectra of 41

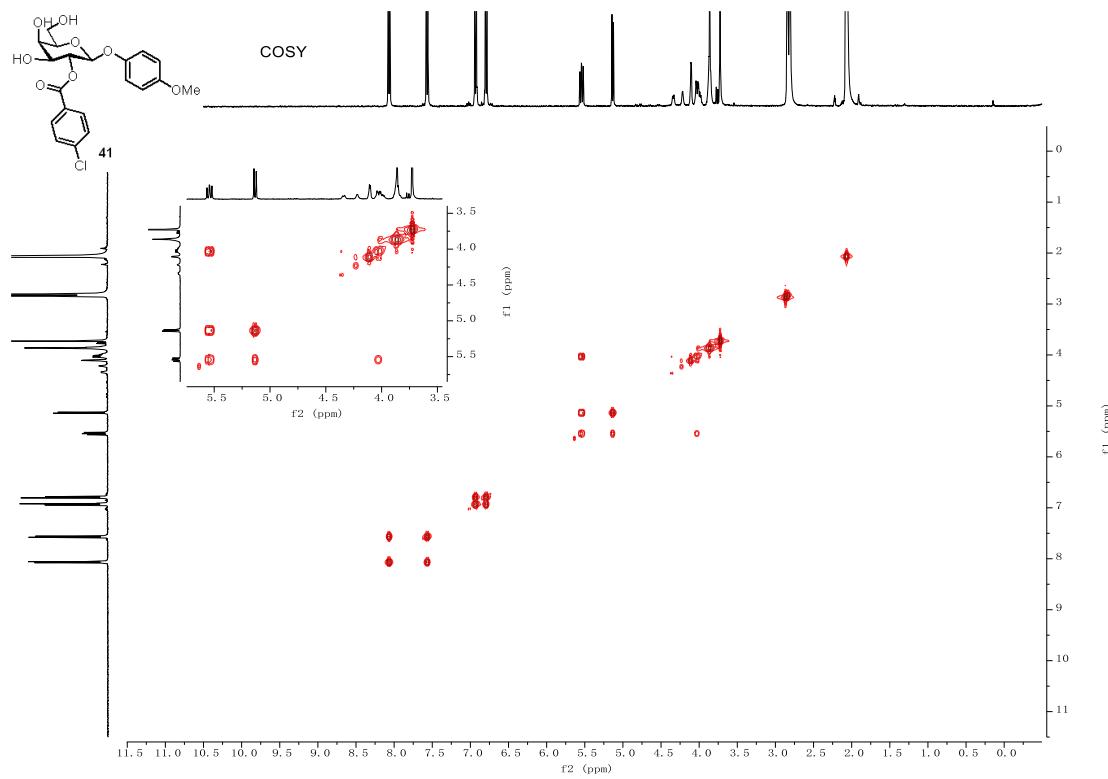


Figure S179. COSY NMR Spectra of **41**

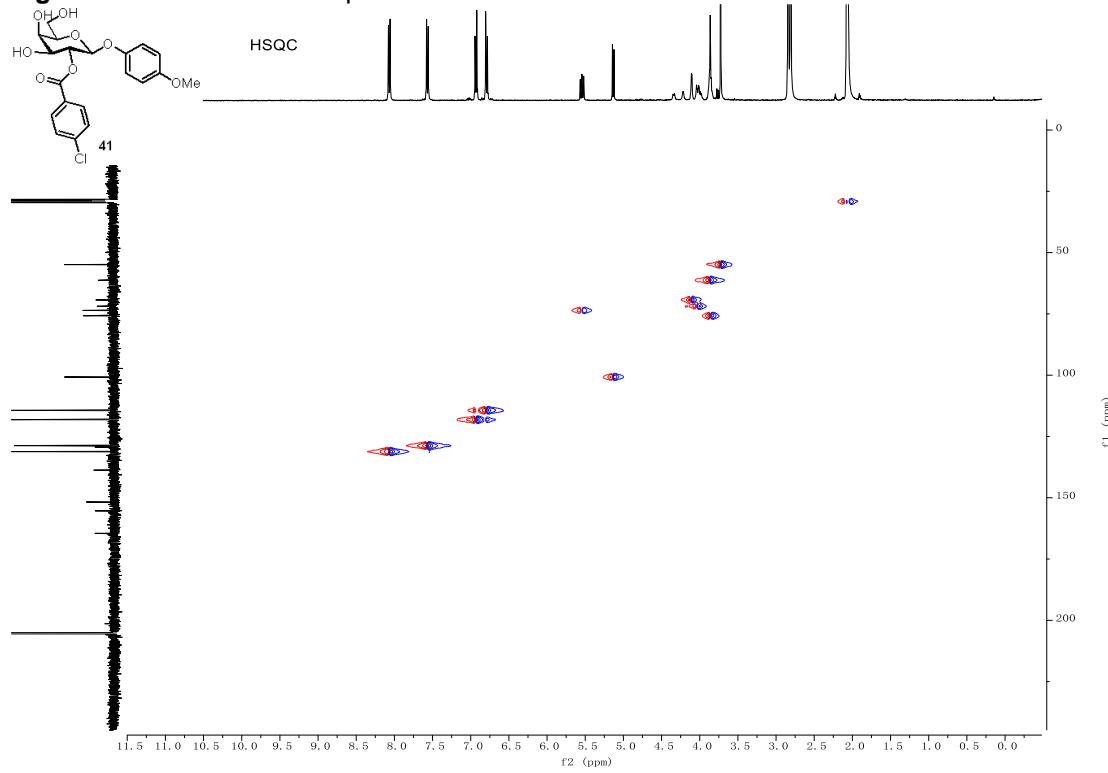


Figure S180. HSQC NMR Spectra of **41**

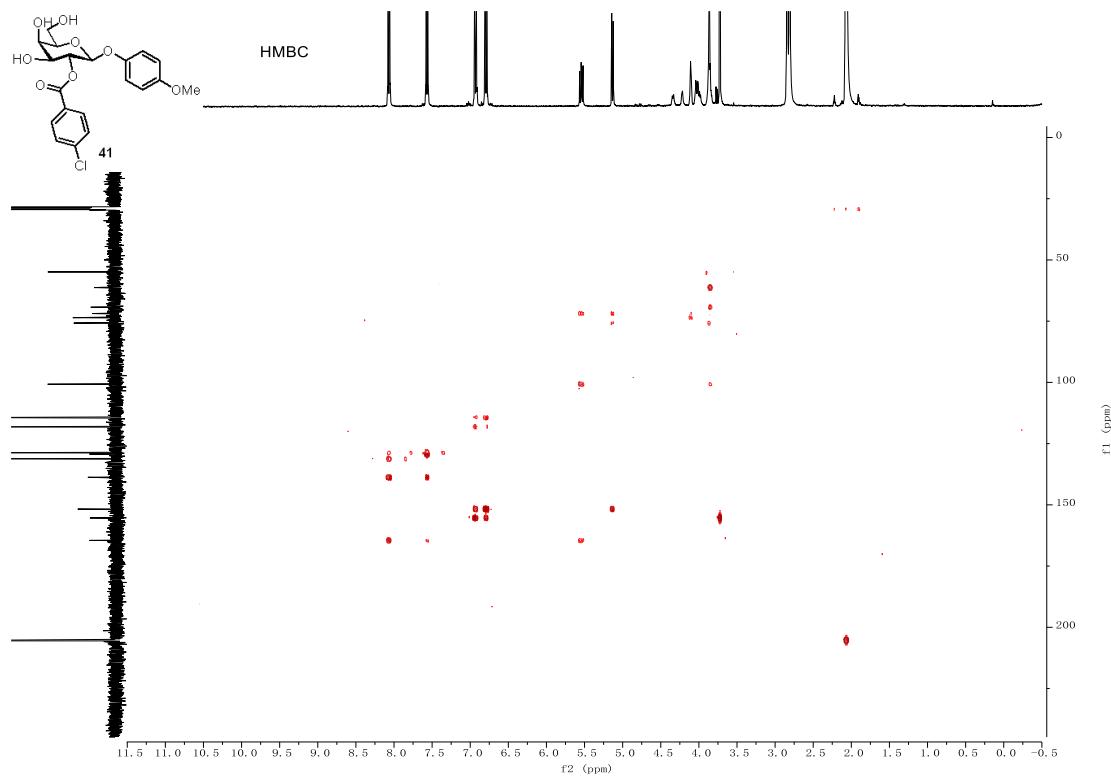


Figure S181. HMBC NMR Spectra of **41**

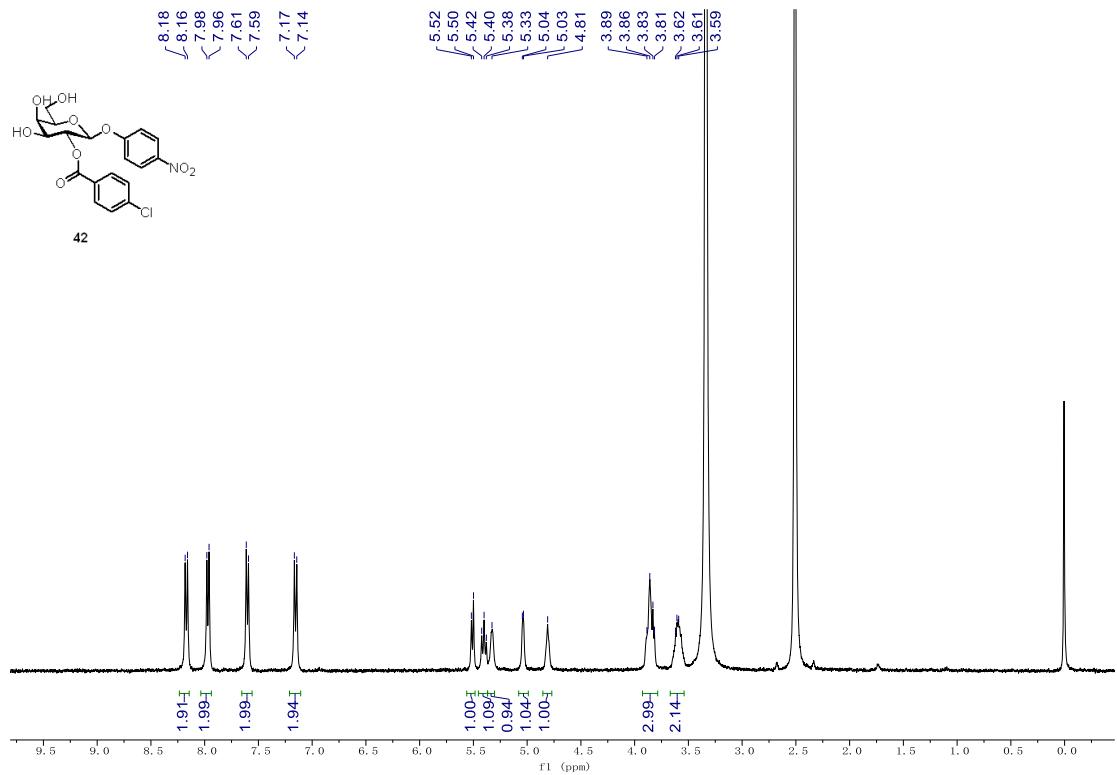


Figure S182. ^1H NMR Spectra of **42**

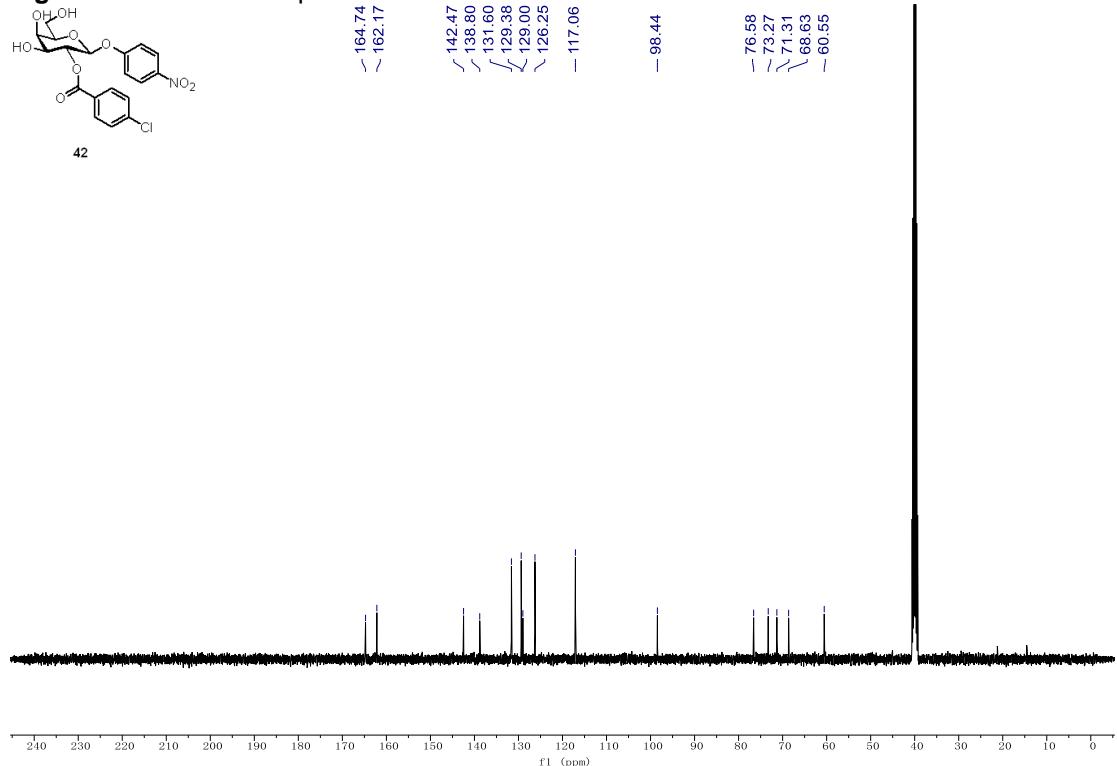


Figure S183. ^{13}C NMR Spectra of **42**

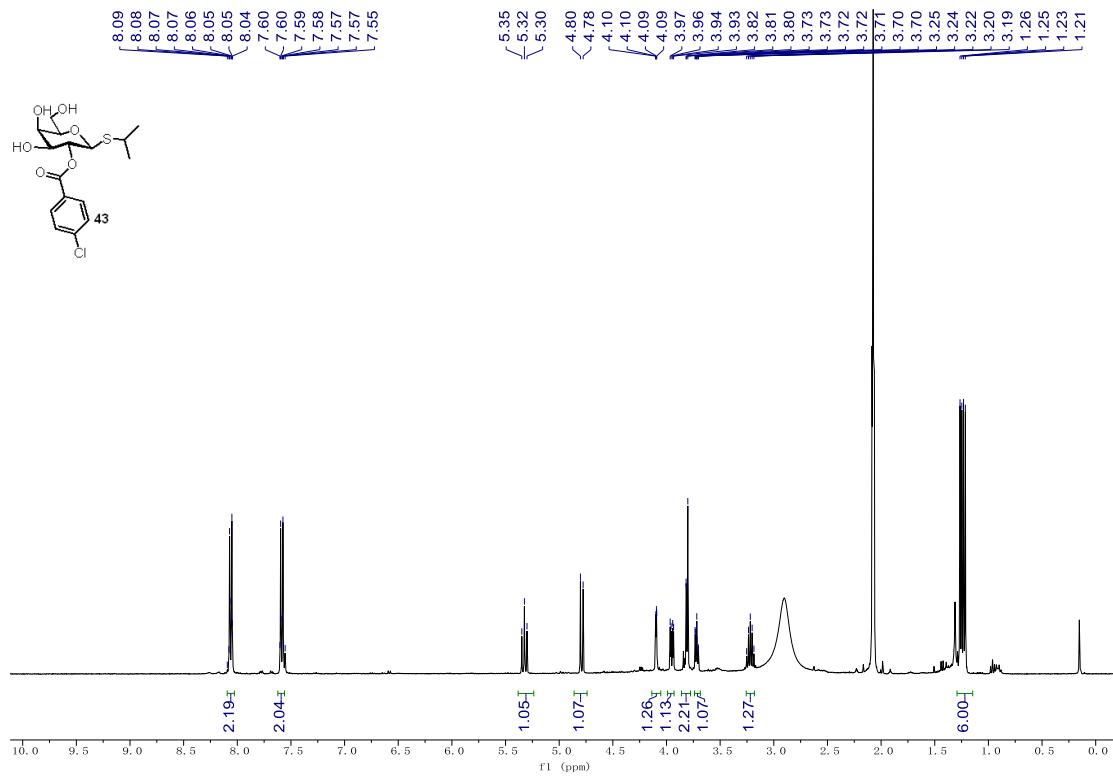


Figure S184. ^1H NMR Spectra of **43**

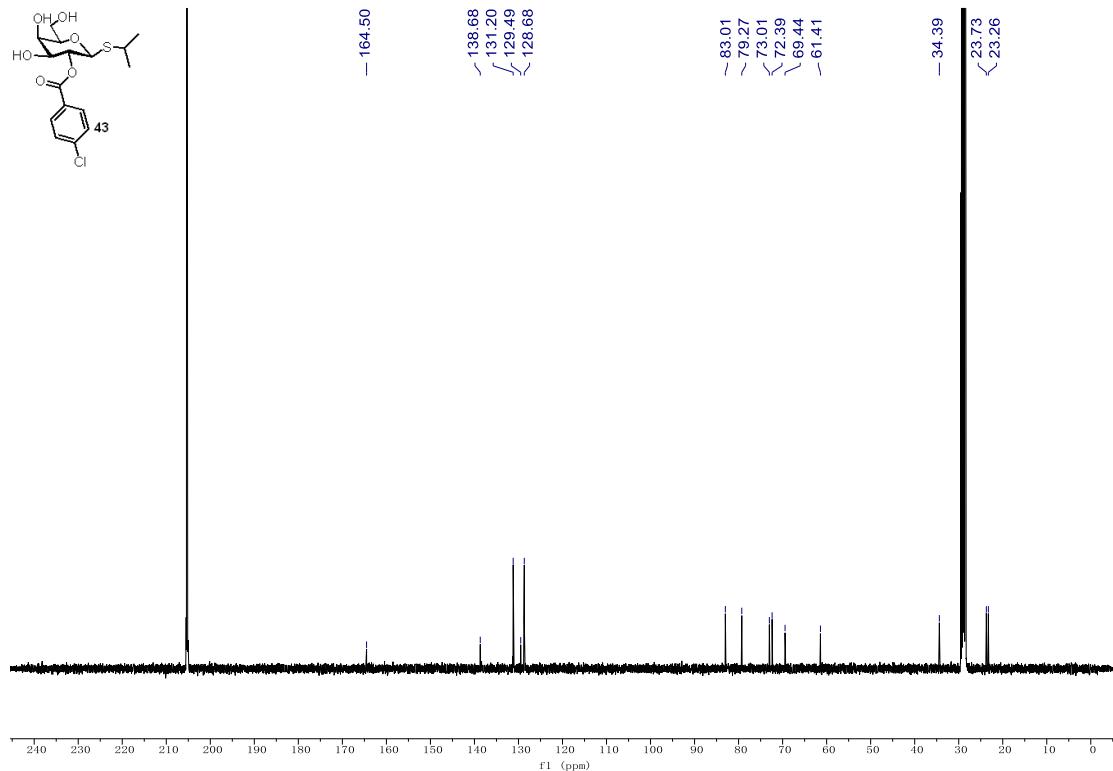


Figure S185. ^{13}C NMR Spectra of 43

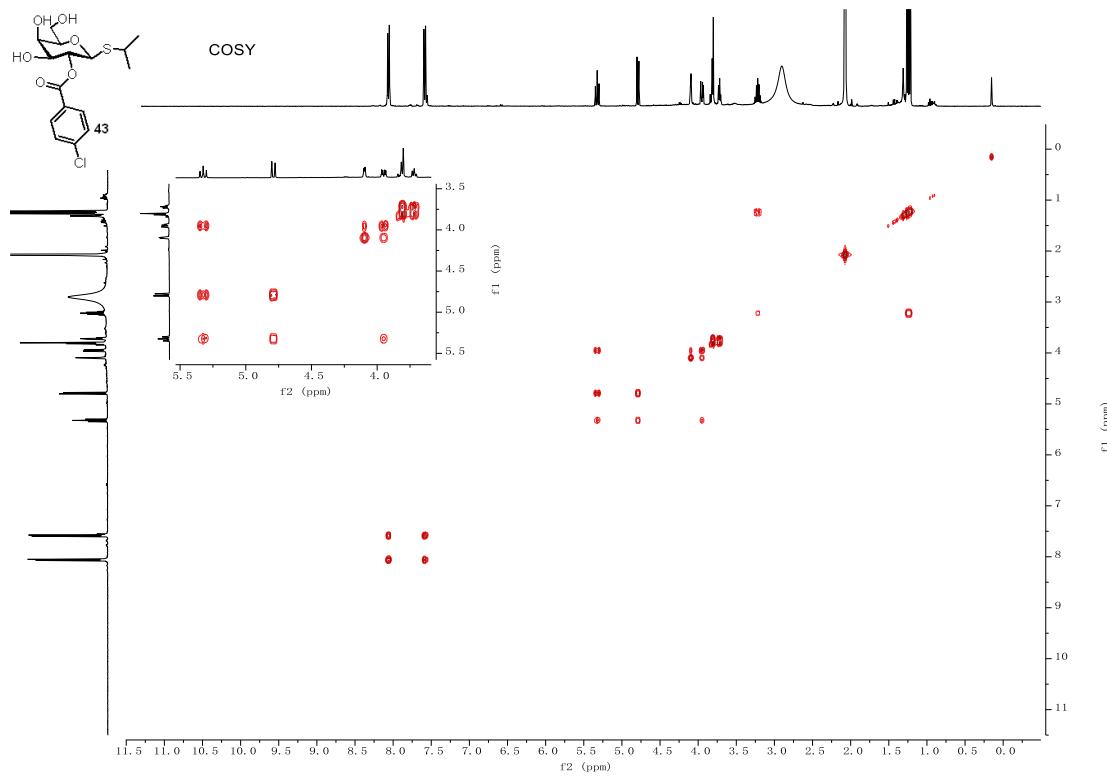


Figure S186. COSY NMR Spectra of **43**

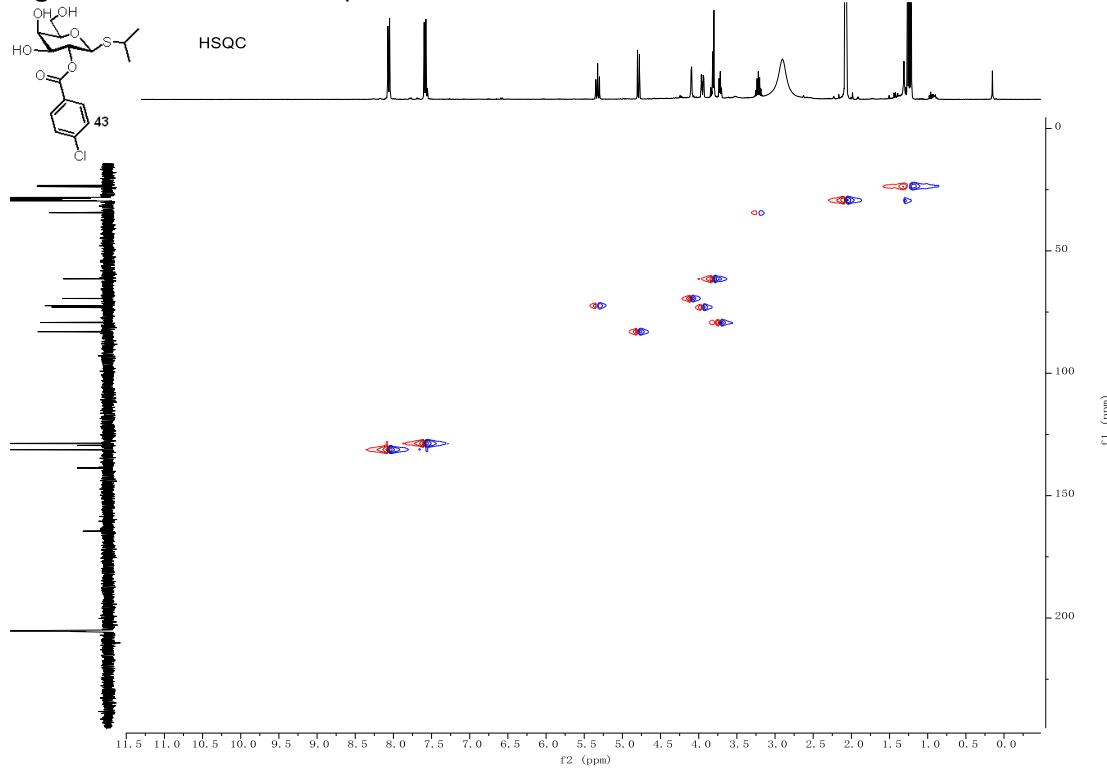


Figure S187. HSQC NMR Spectra of **43**

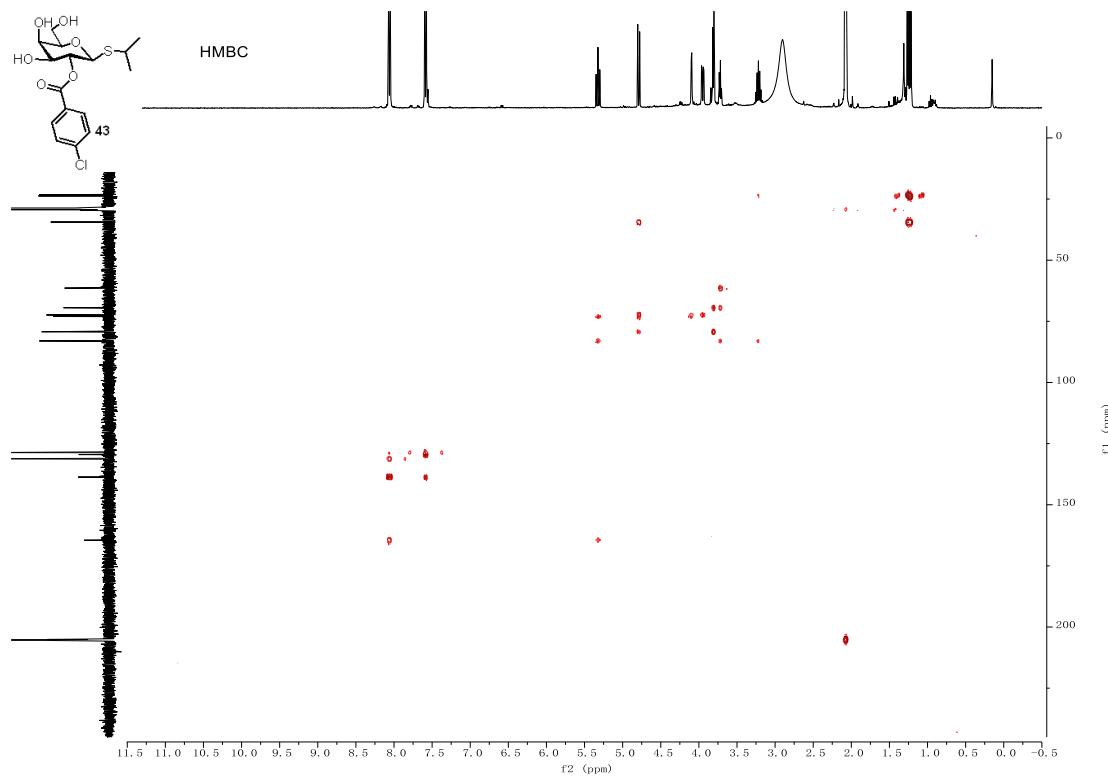


Figure S188. HMBC NMR Spectra of **43**

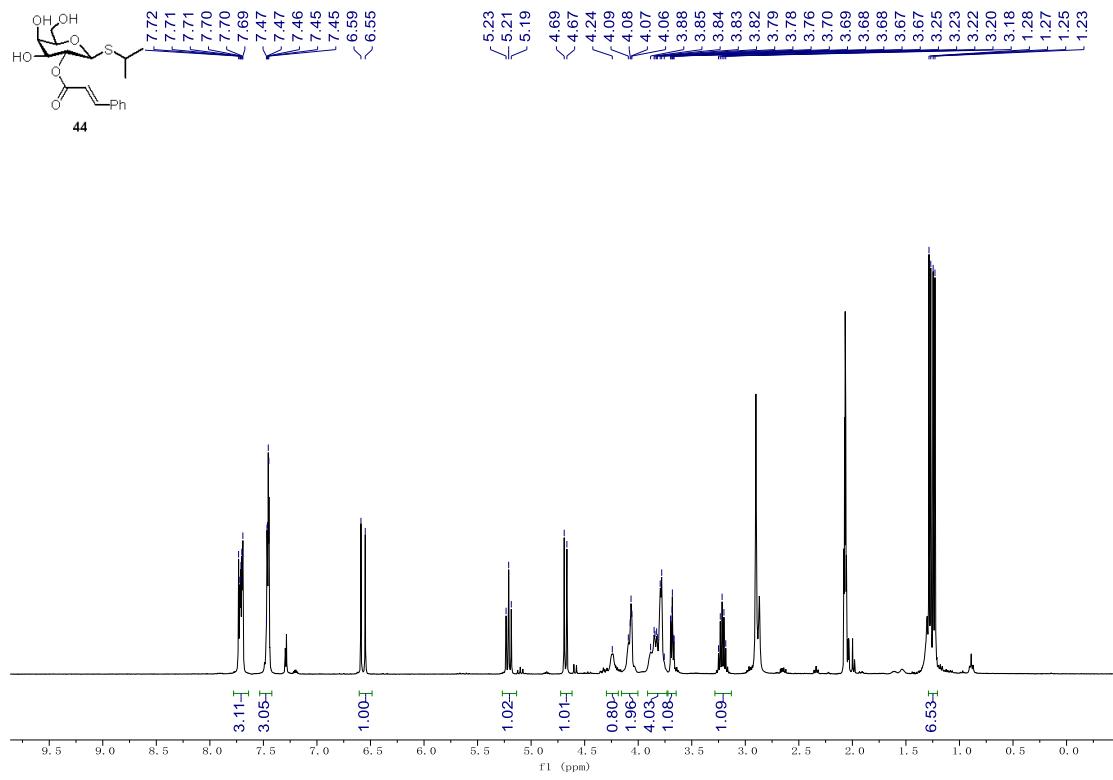


Figure S189. ^1H NMR Spectra of 44

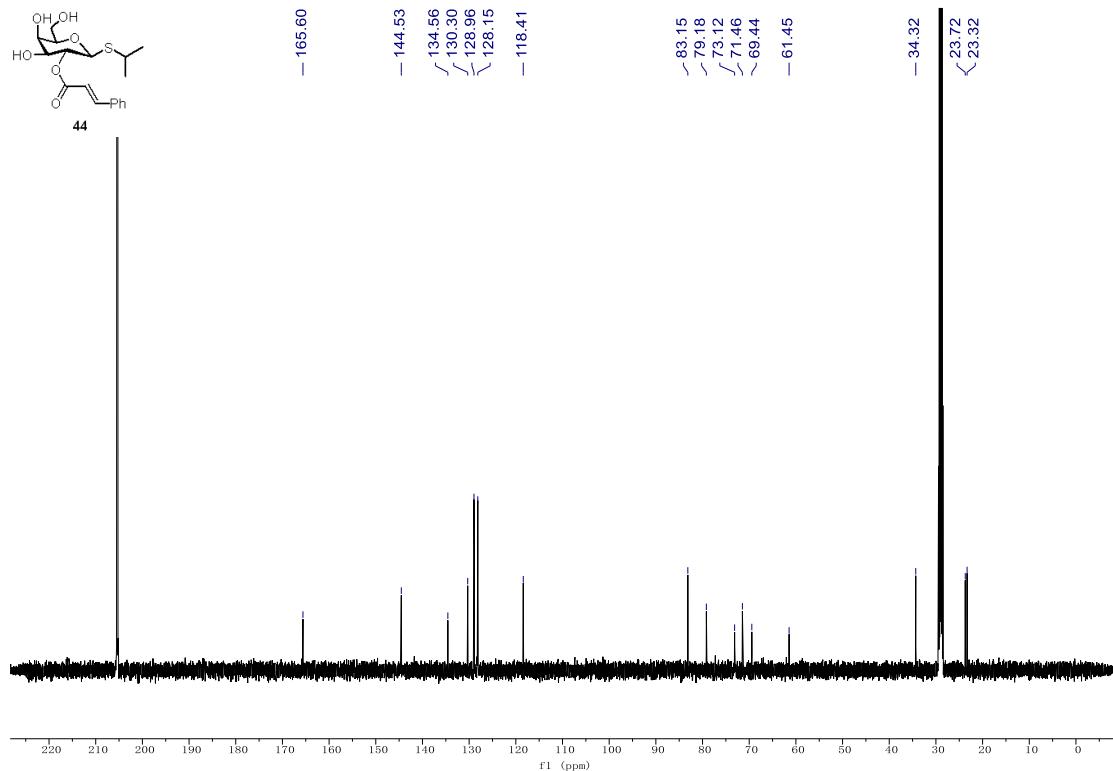
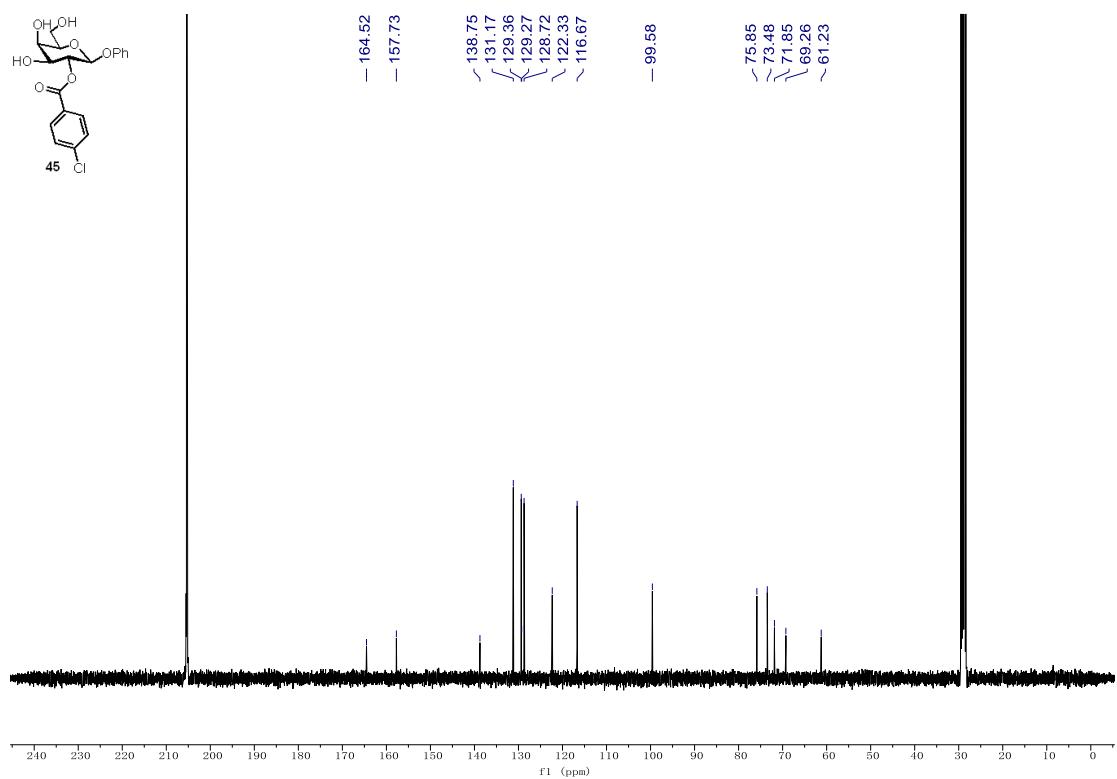
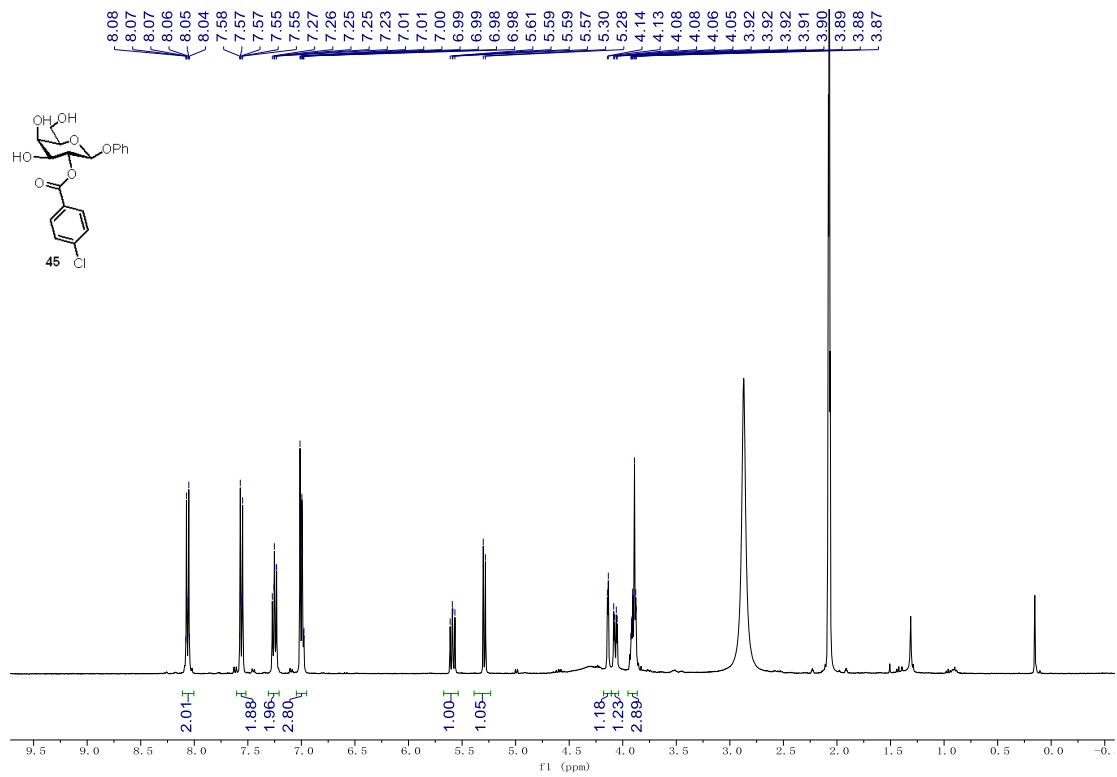


Figure S190. ^{13}C NMR Spectra of 44



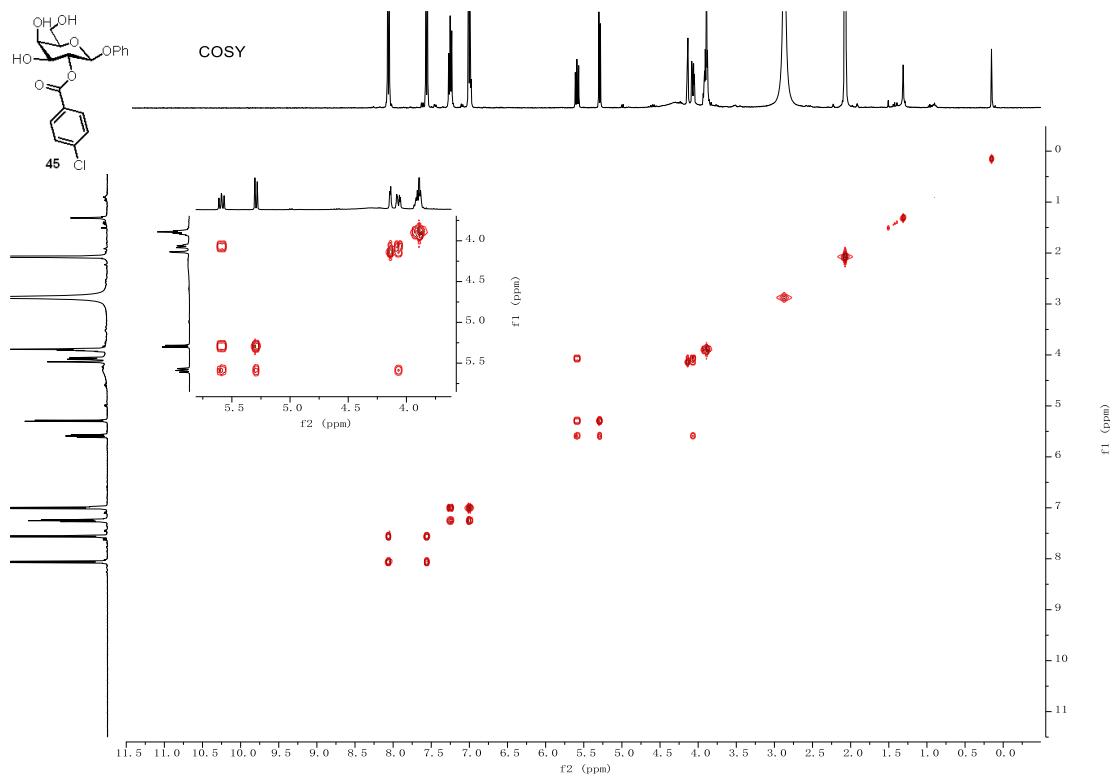


Figure S193. COSY NMR Spectra of **45**

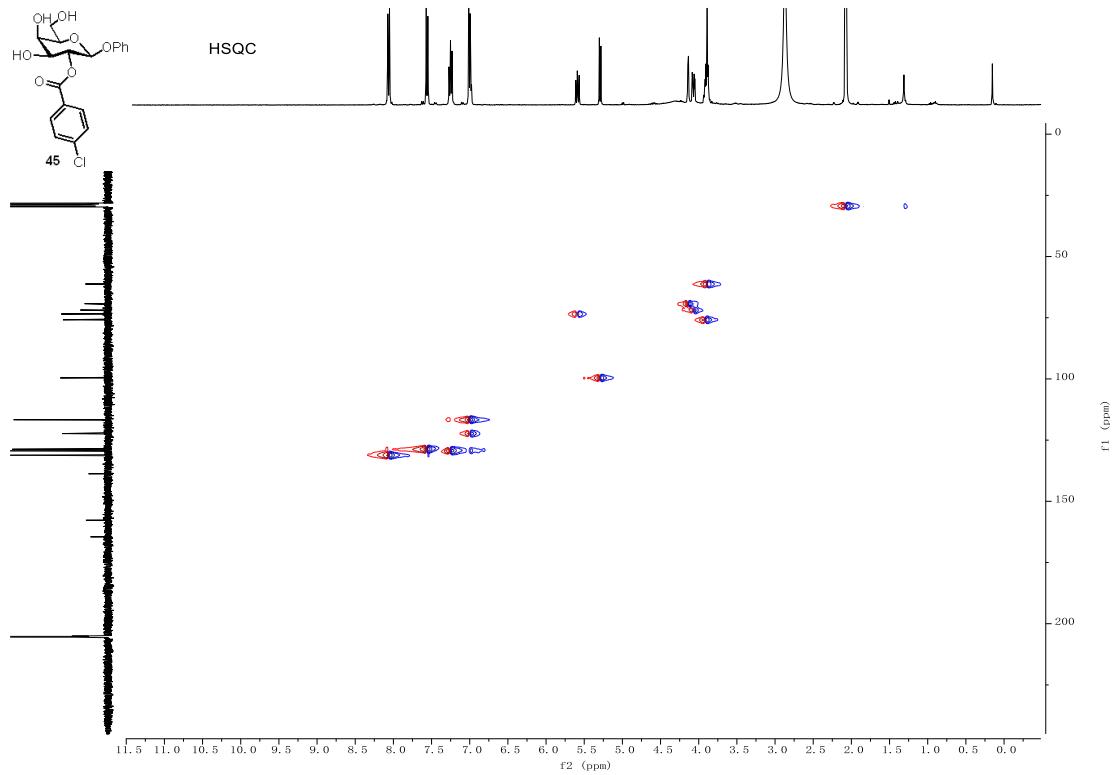


Figure S194. HSQC NMR Spectra of 45

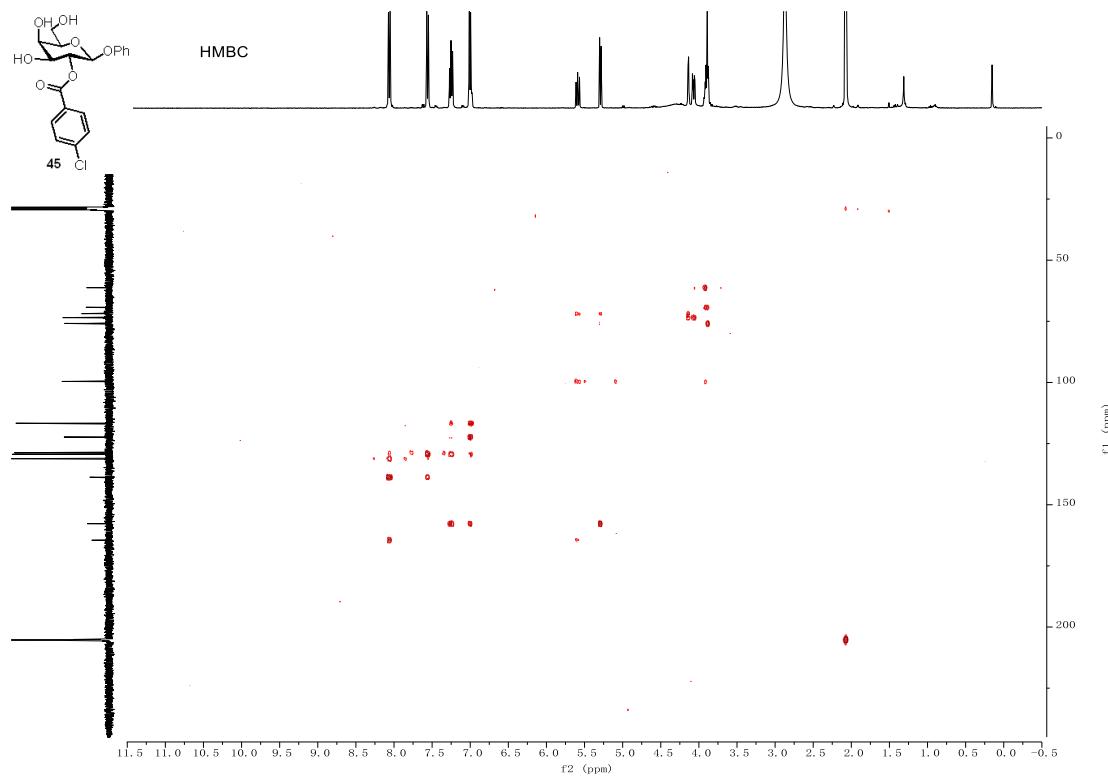
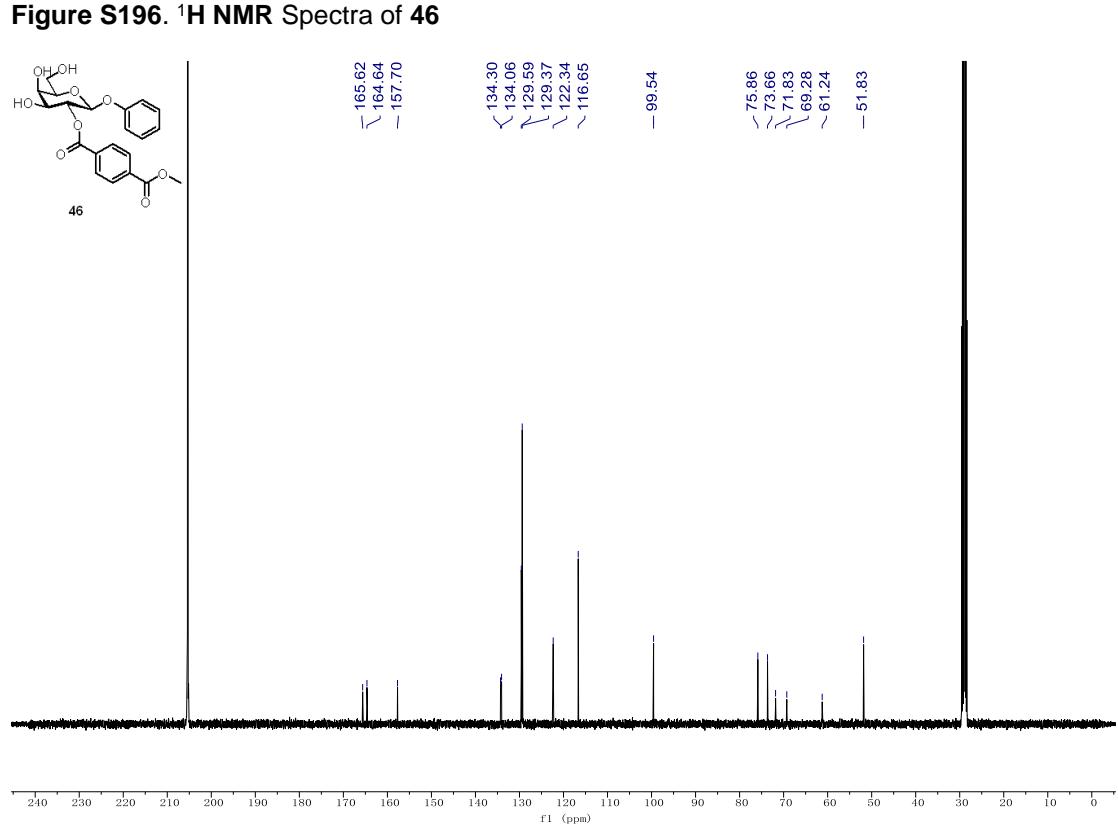
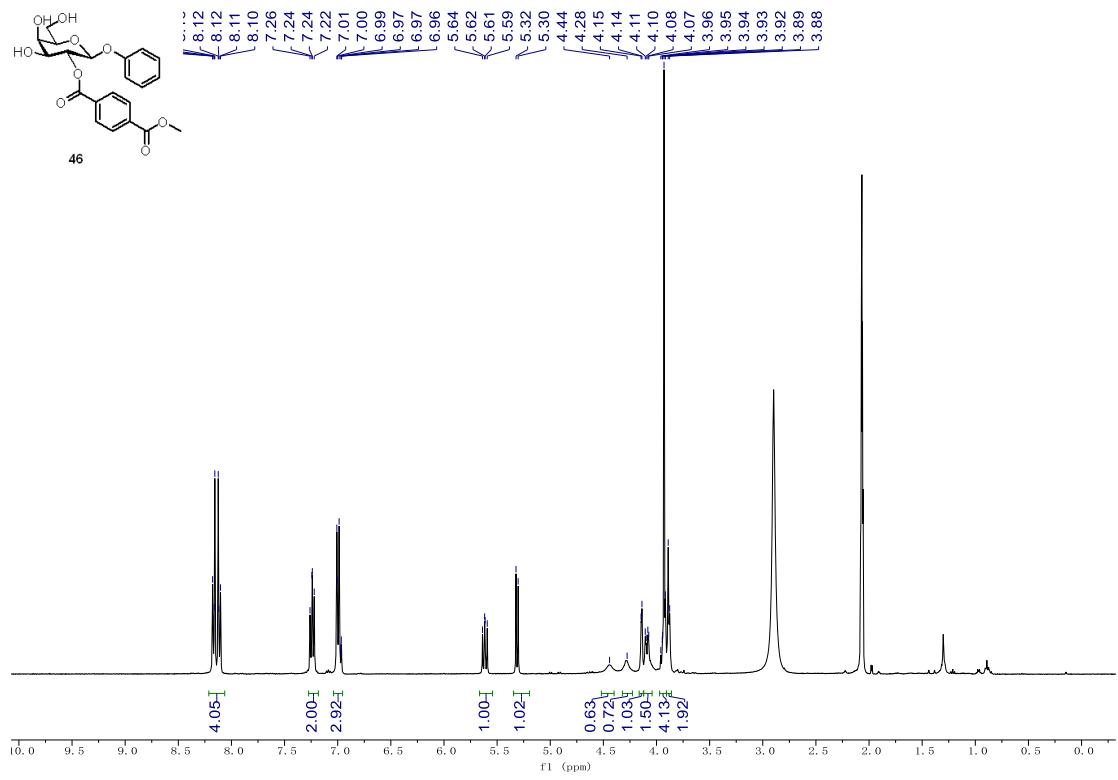


Figure S195. HMBC NMR Spectra of **45**



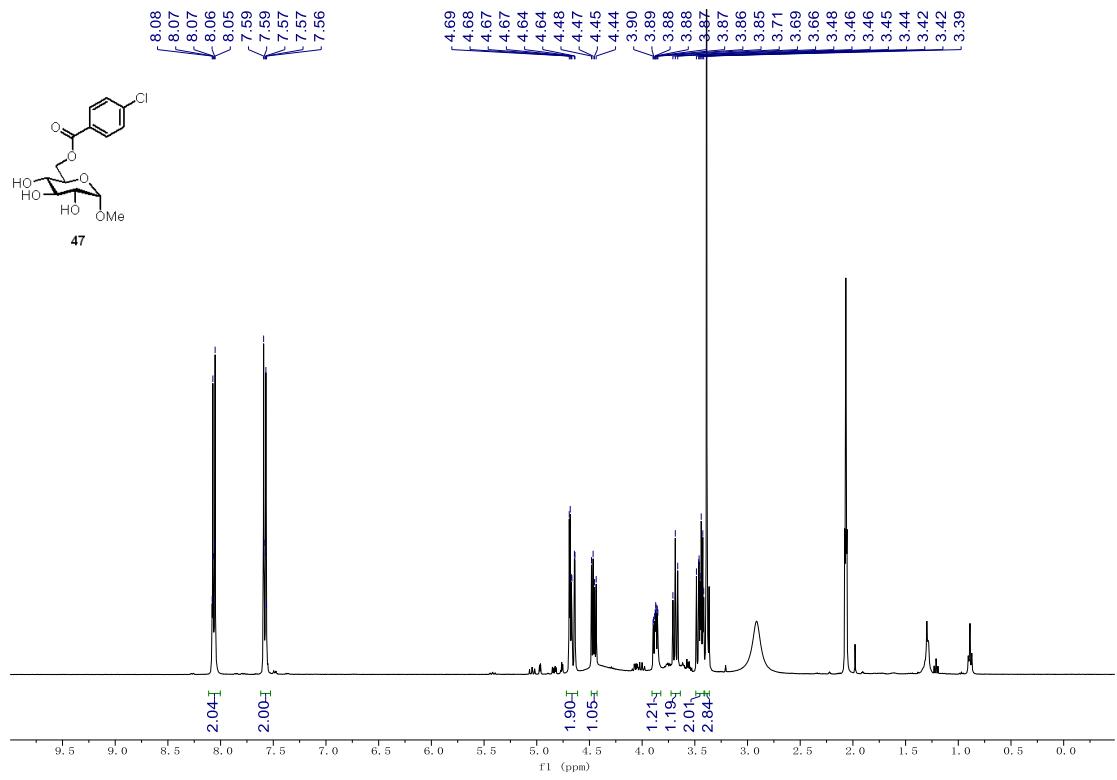


Figure S198. ^1H NMR Spectra of **47**

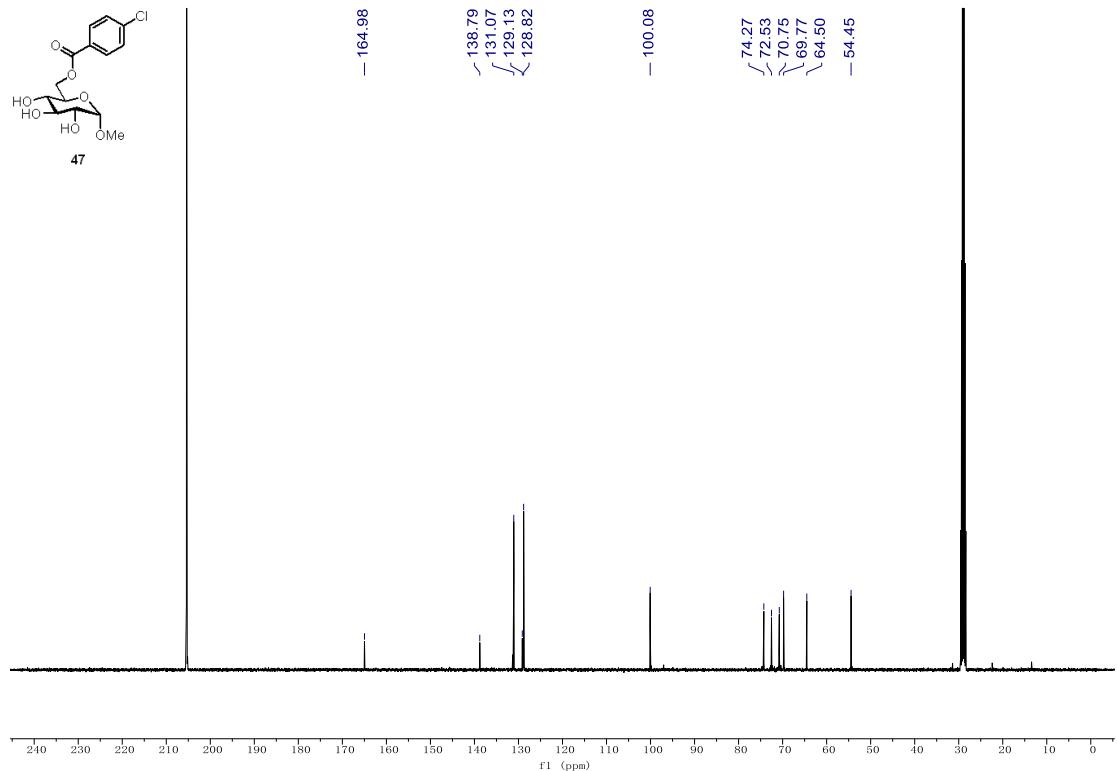


Figure S199. ^{13}C NMR Spectra of **47**

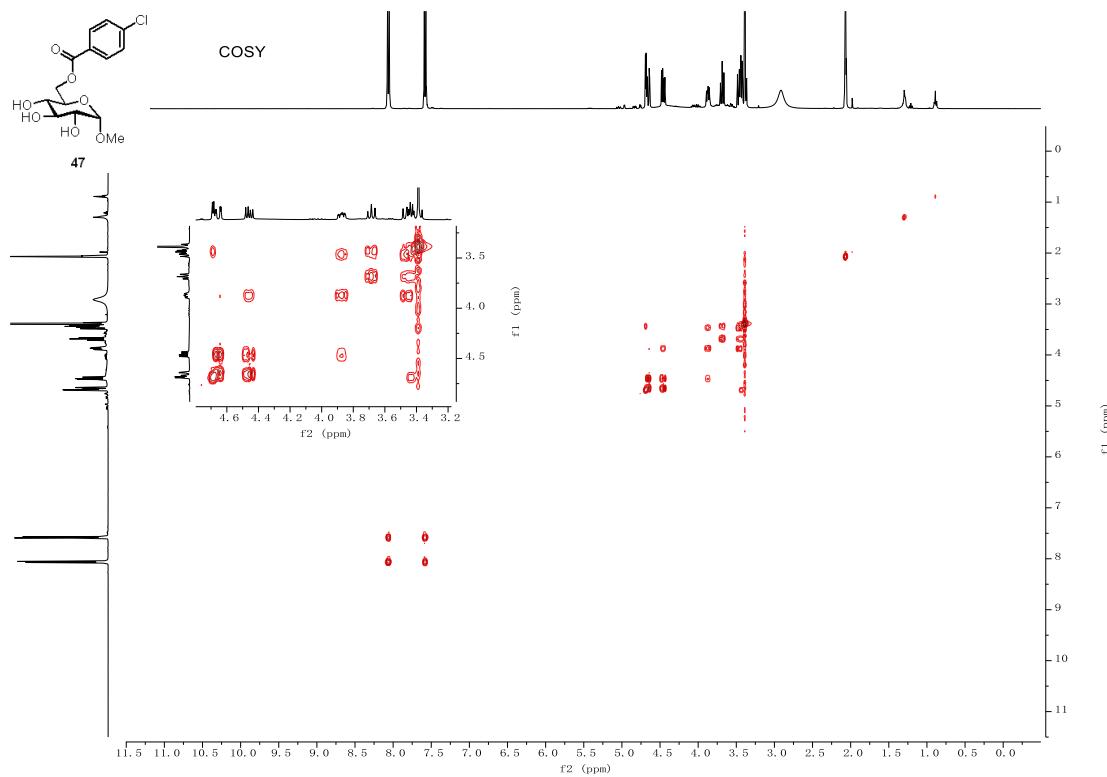


Figure S200. COSY NMR Spectra of **47**

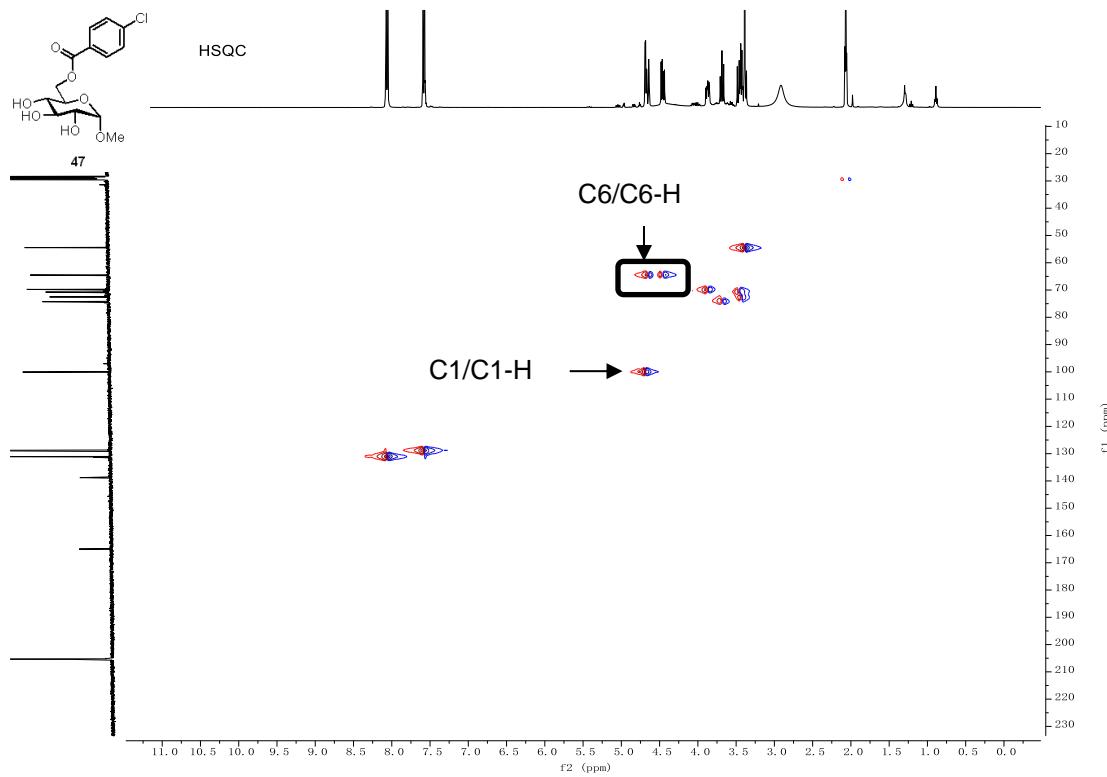


Figure S201. HSQC NMR Spectra of **47**

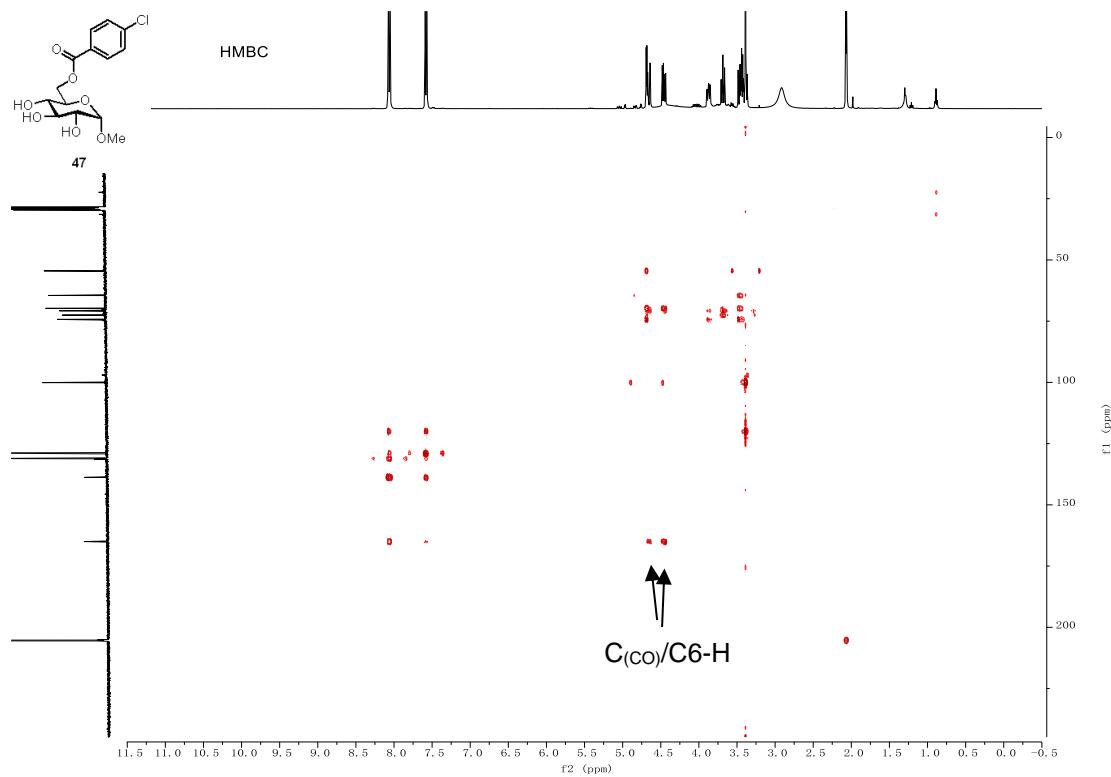


Figure S202. HMBC NMR Spectra of **47**

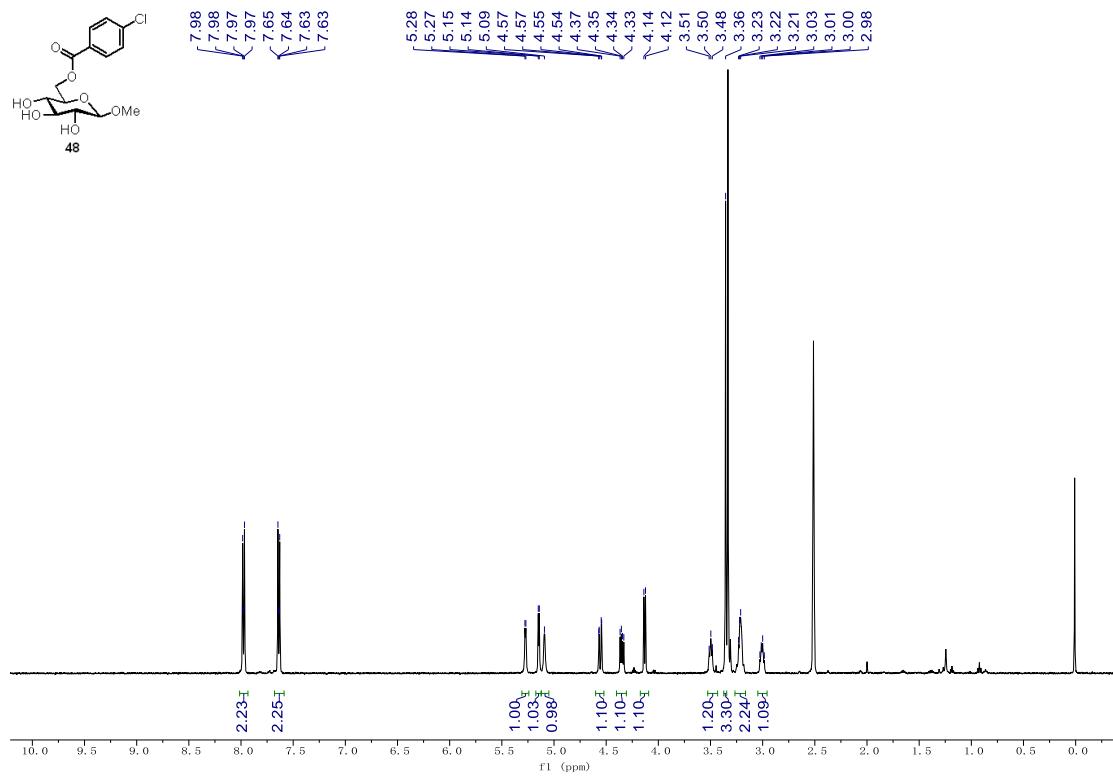


Figure S203. ^1H NMR Spectra of **48**

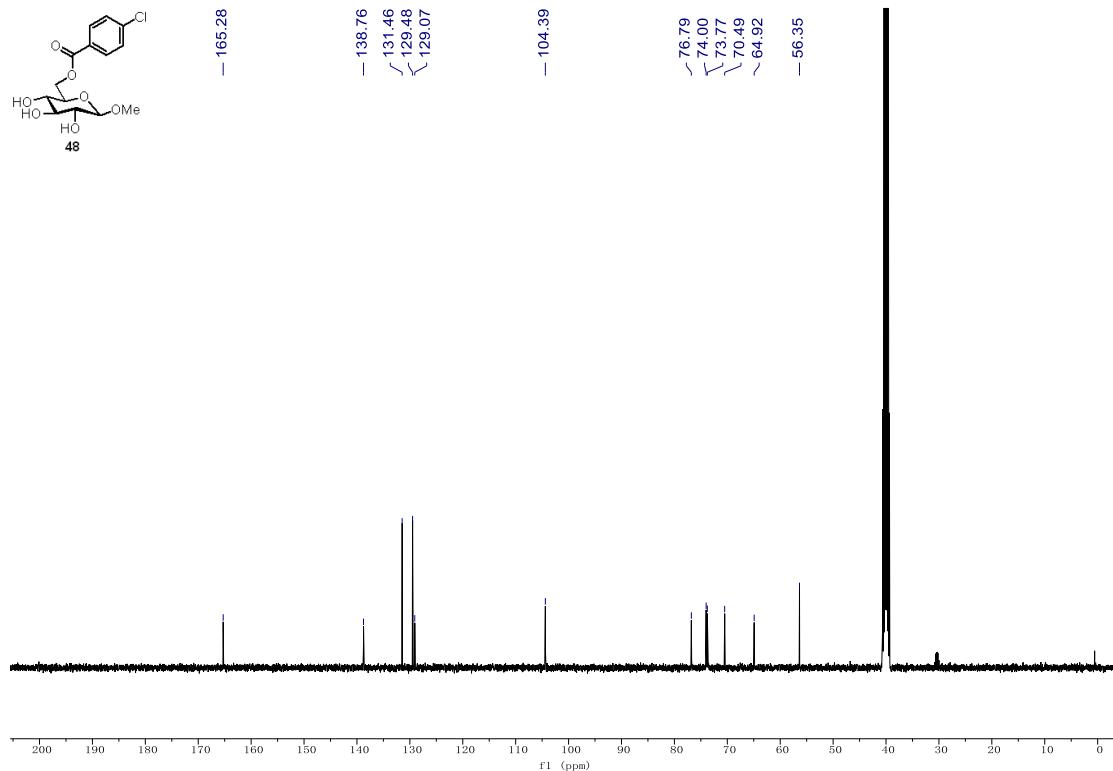


Figure S204. ^{13}C NMR Spectra of **48**

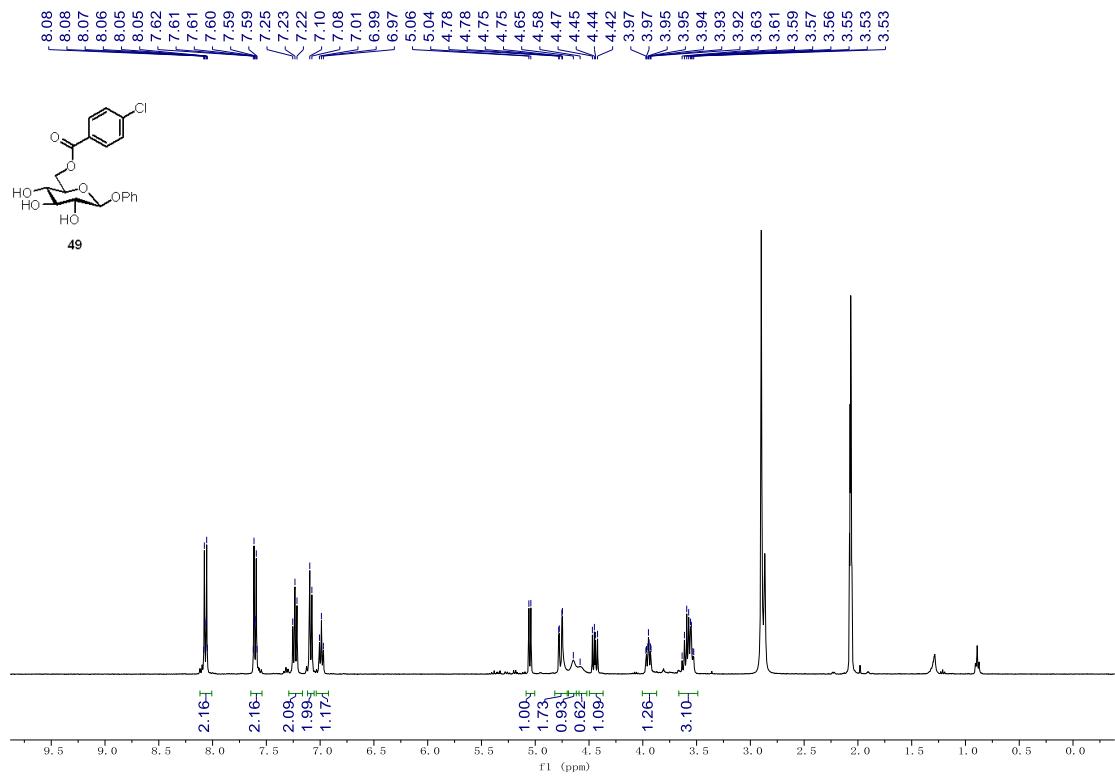


Figure S205. ^1H NMR Spectra of 49

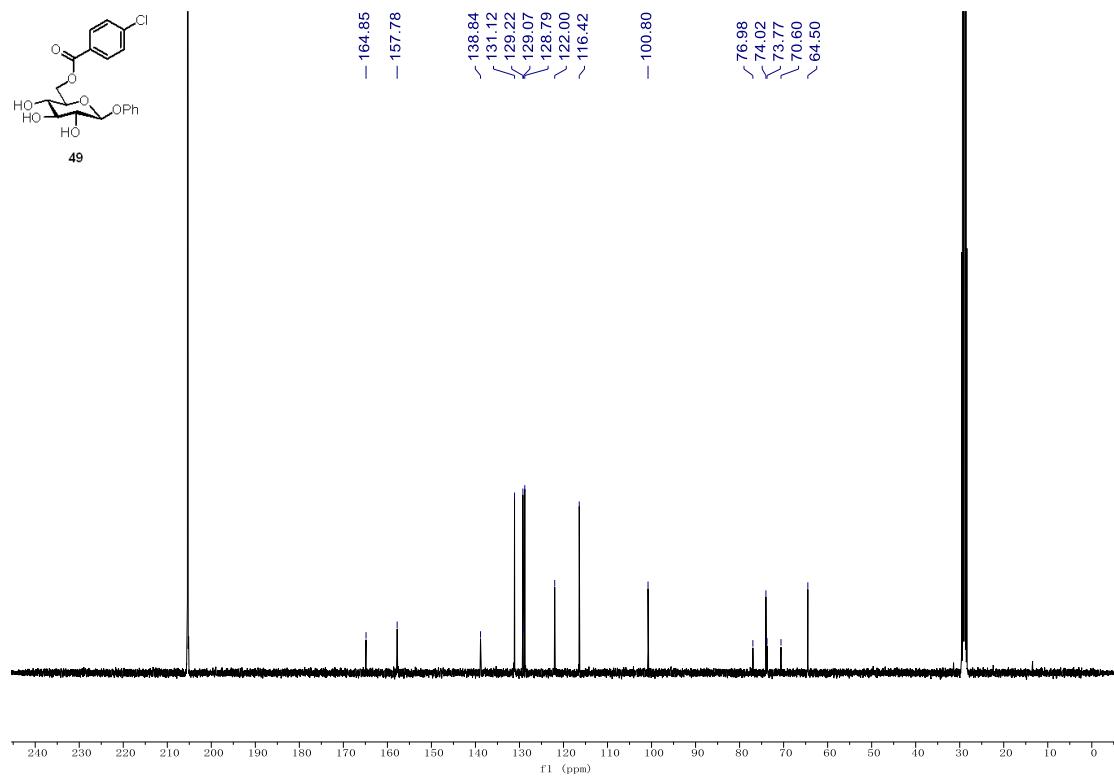


Figure S206. ^{13}C NMR Spectra of **49**

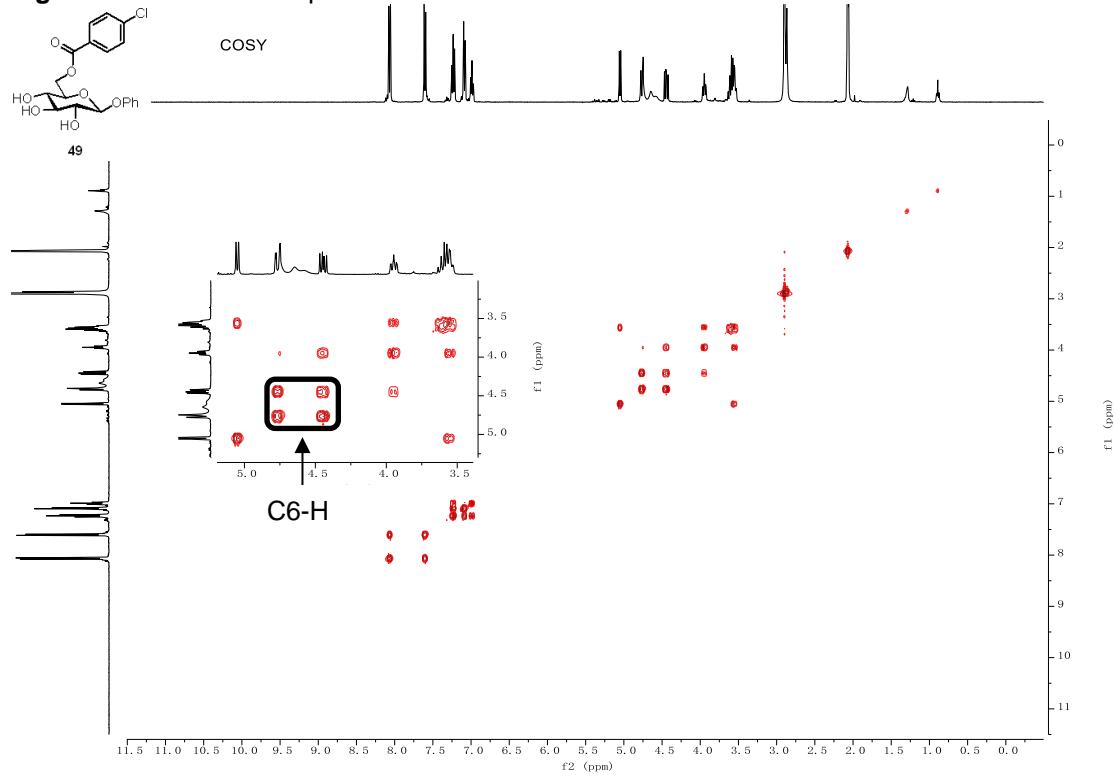


Figure S207. COSY NMR Spectra of **49**

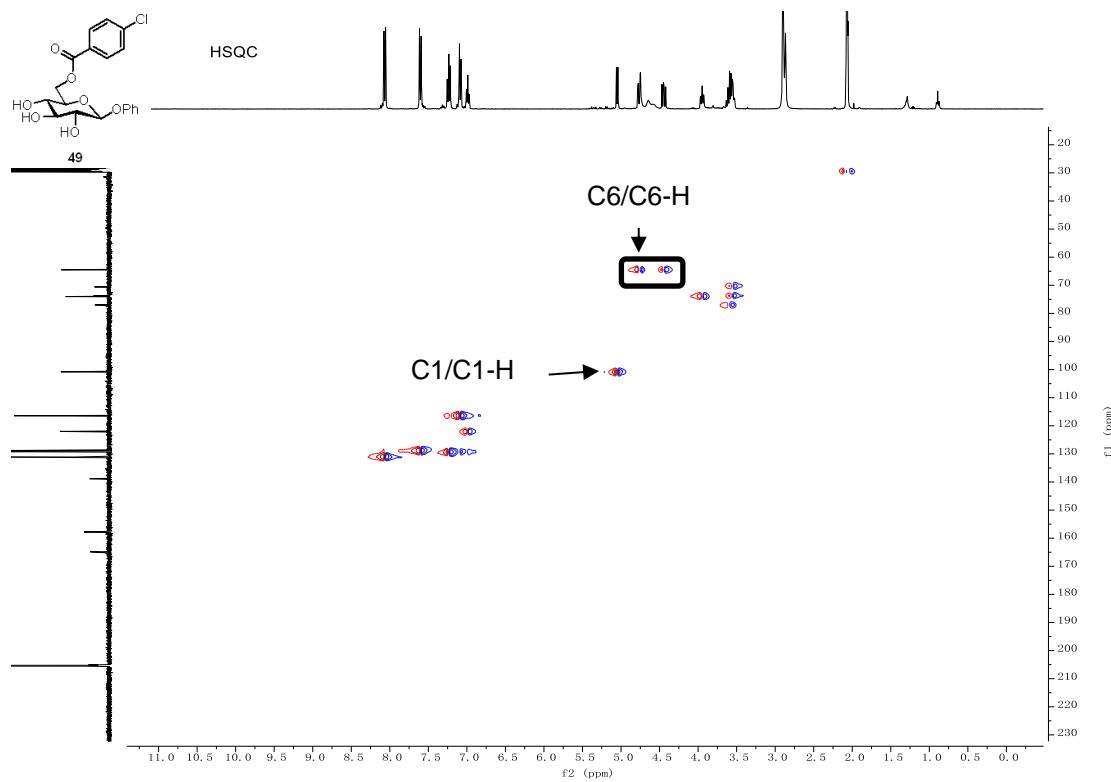


Figure S208. HSQC NMR Spectra of **49**

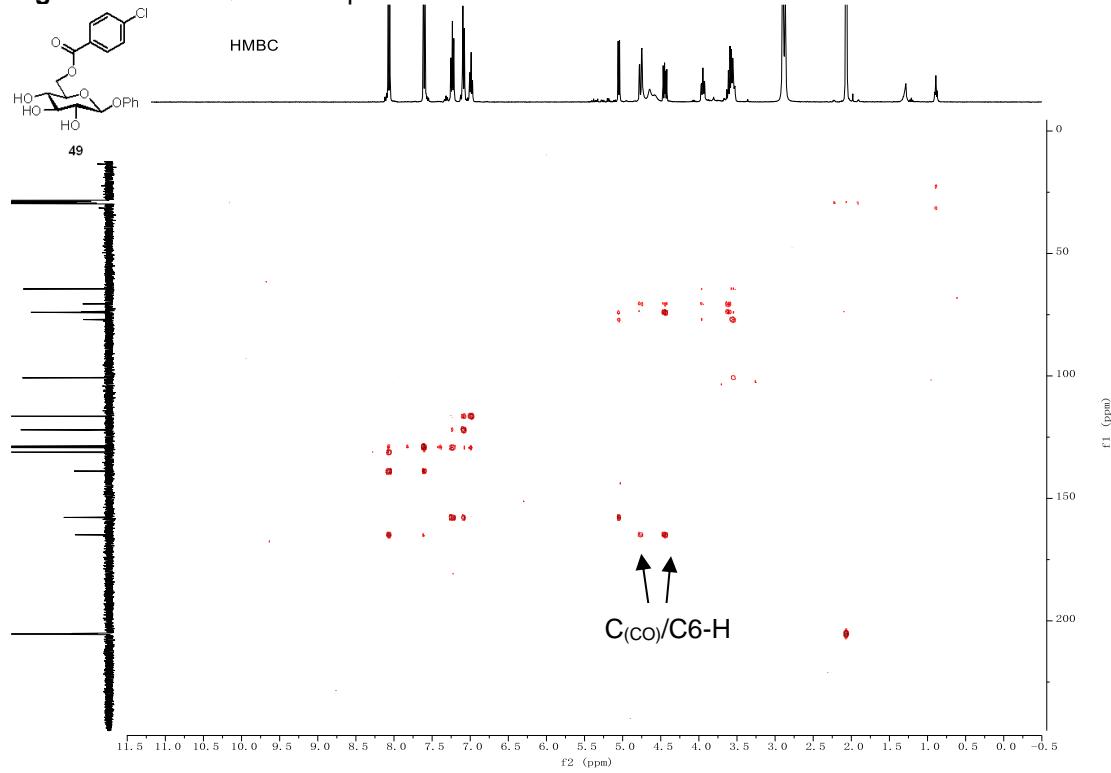


Figure S209. HMBC NMR Spectra of **49**

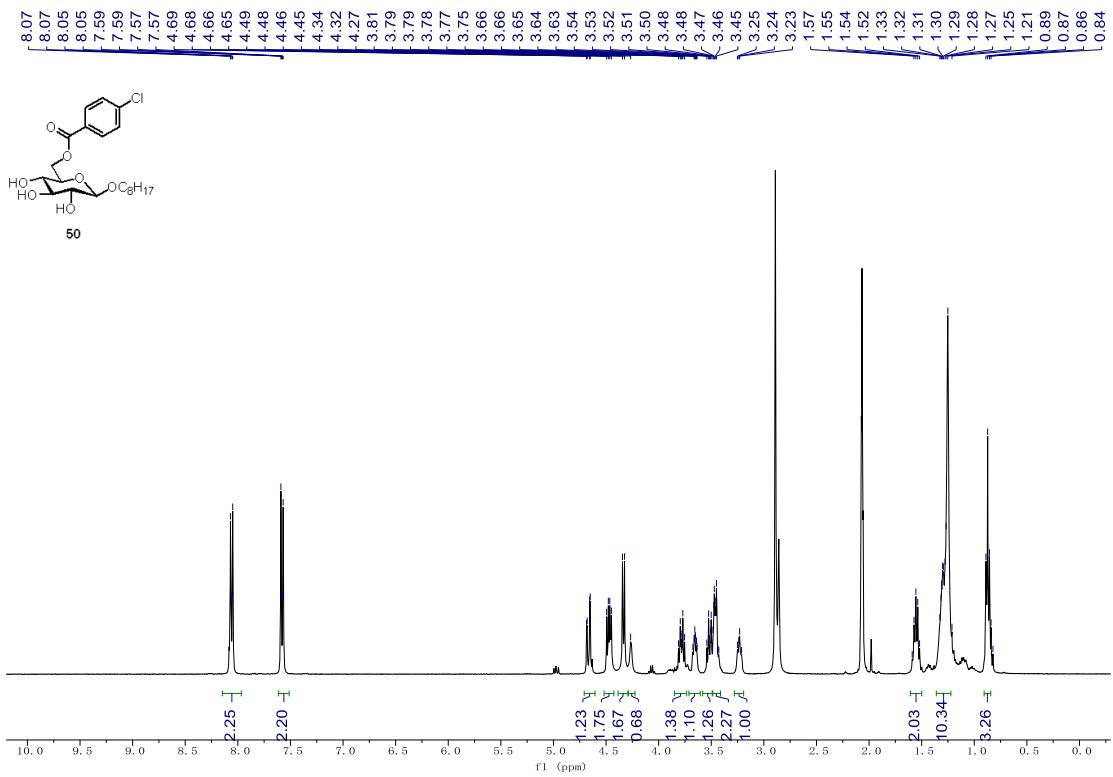


Figure S210. ^1H NMR Spectra of **50**

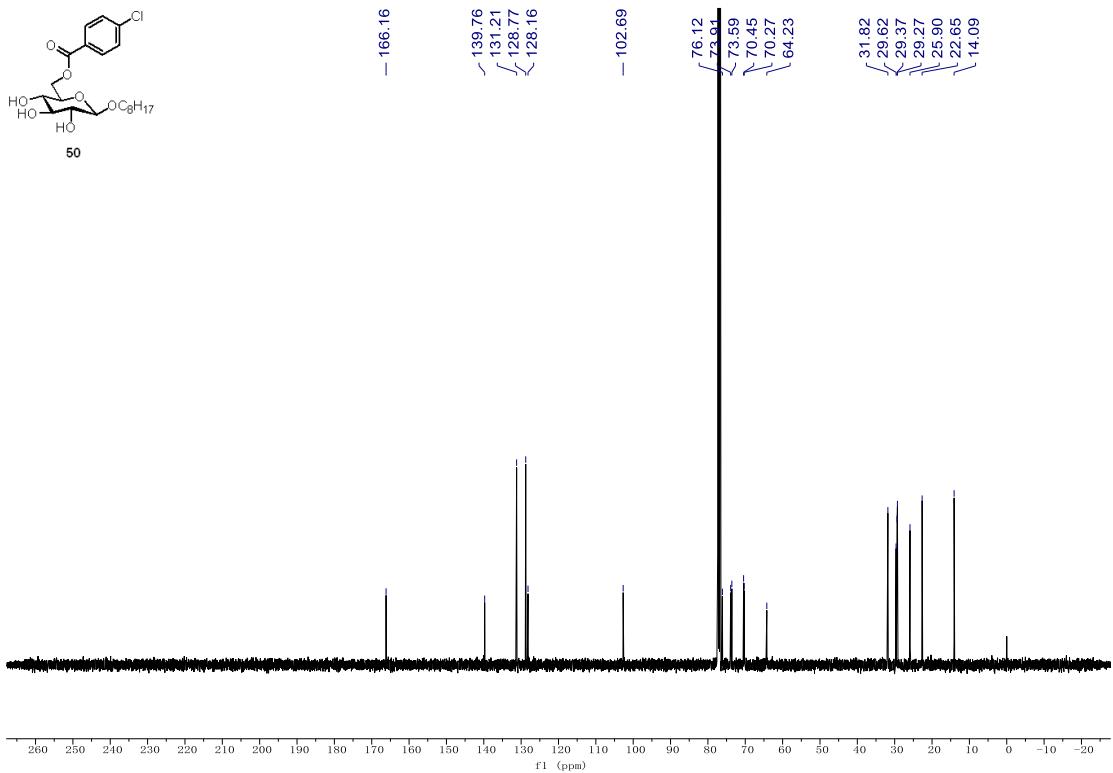


Figure S211. ^{13}C NMR Spectra of **50**

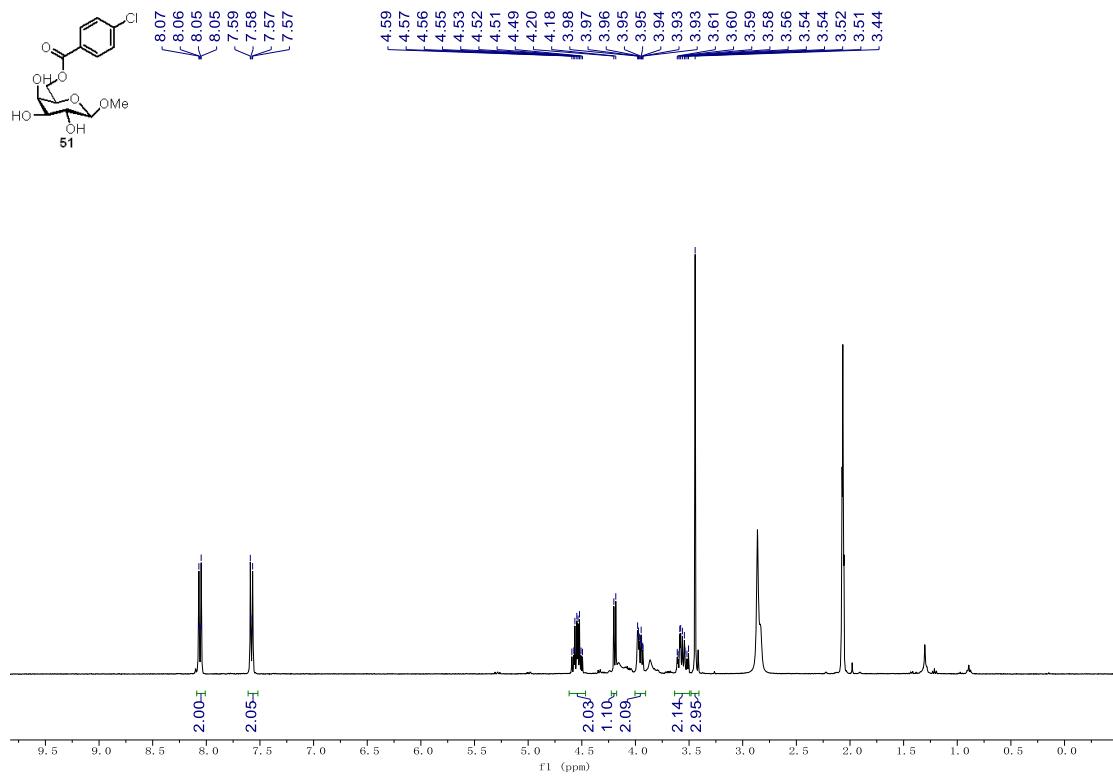


Figure S212. ^1H NMR Spectra of **51**

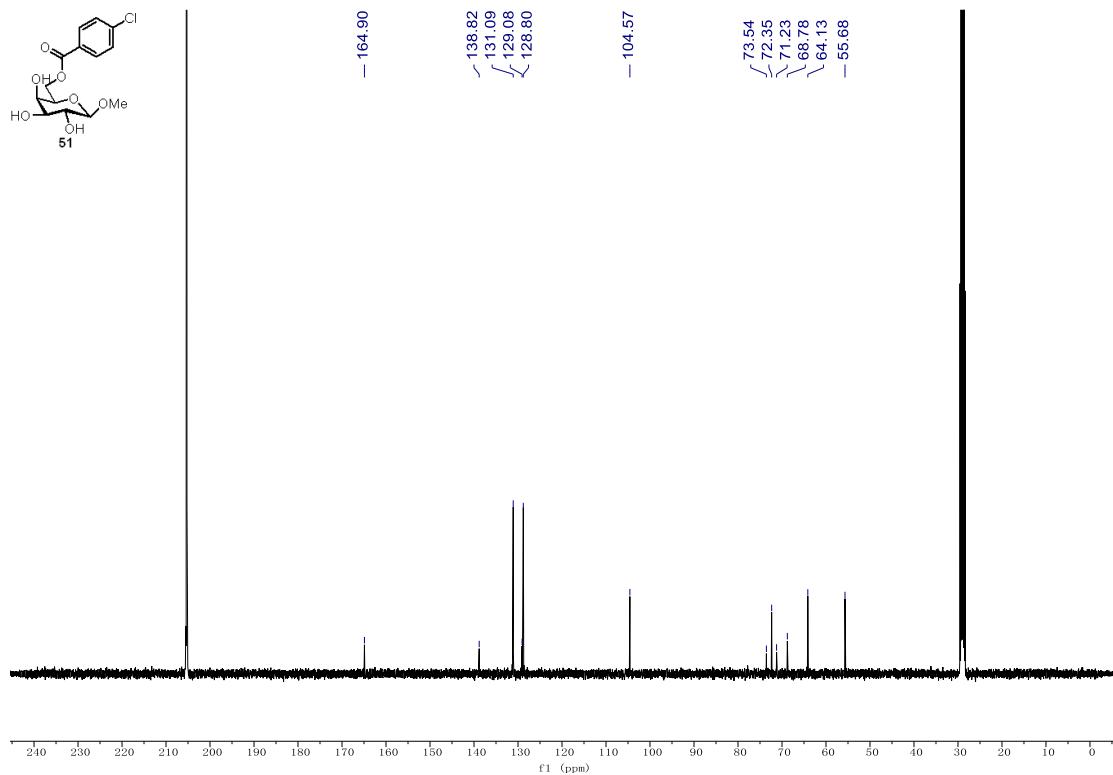


Figure S213. ^{13}C NMR Spectra of 51

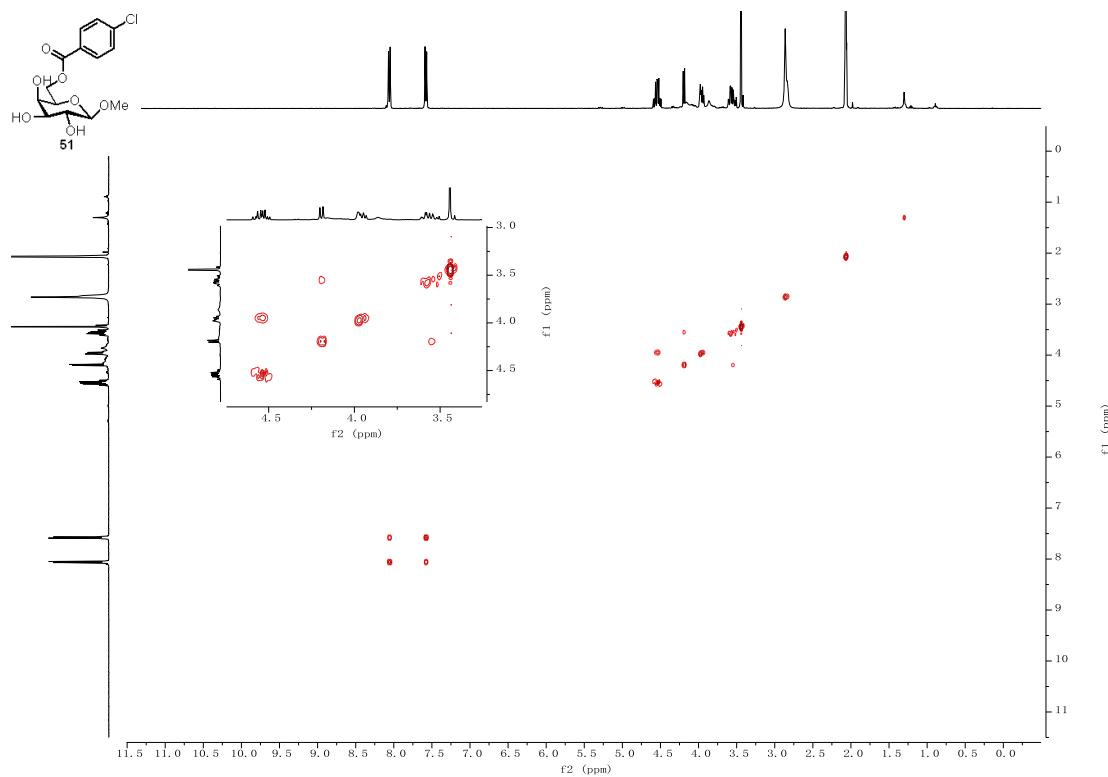


Figure S214. COSY NMR Spectra of **51**

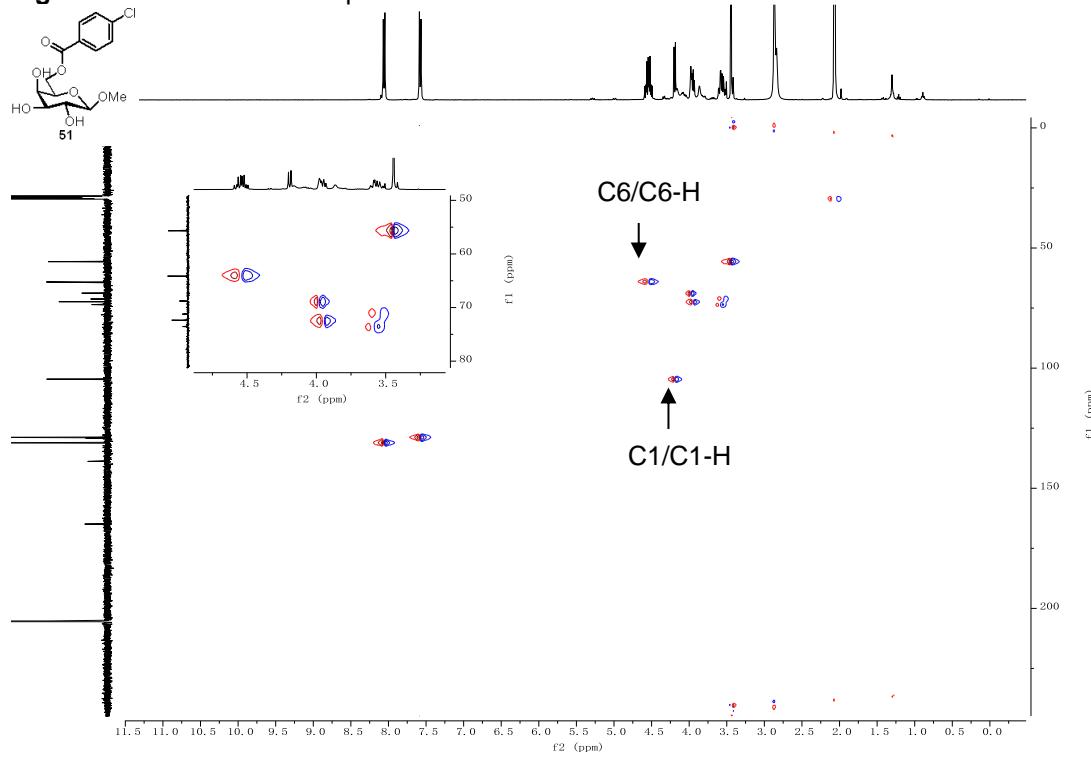


Figure S215. HSQC NMR Spectra of **51**

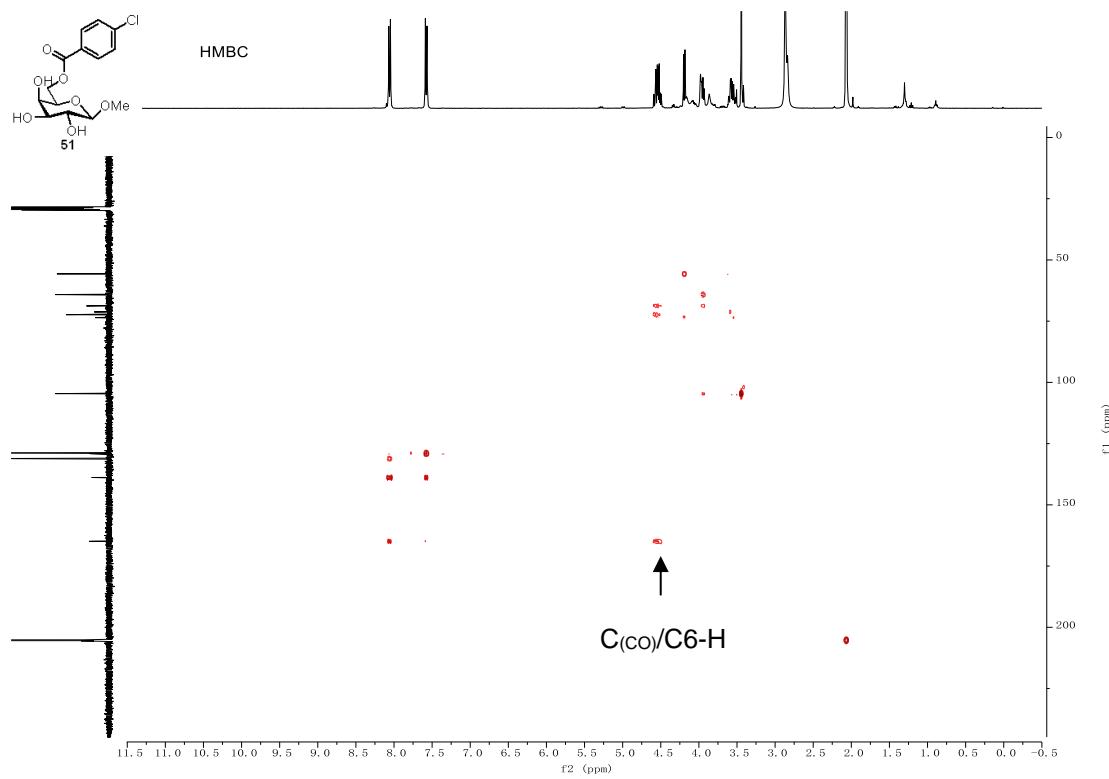


Figure S216. HMBC NMR Spectra of **51**

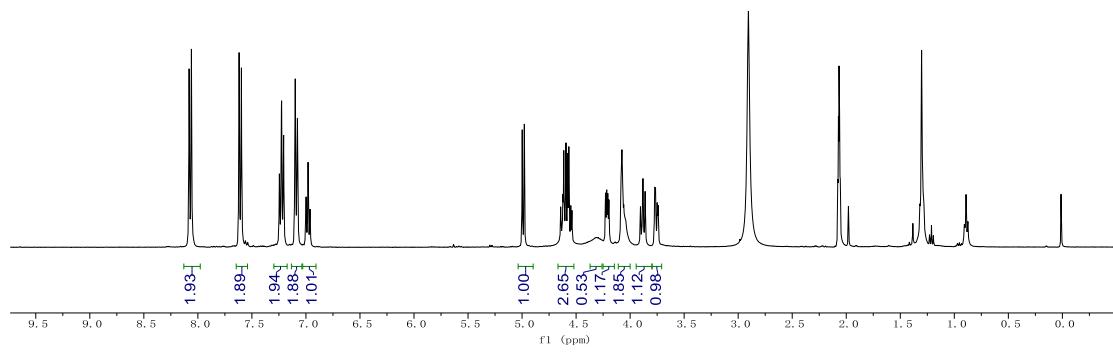
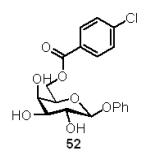


Figure S217. ¹H NMR Spectra of 52

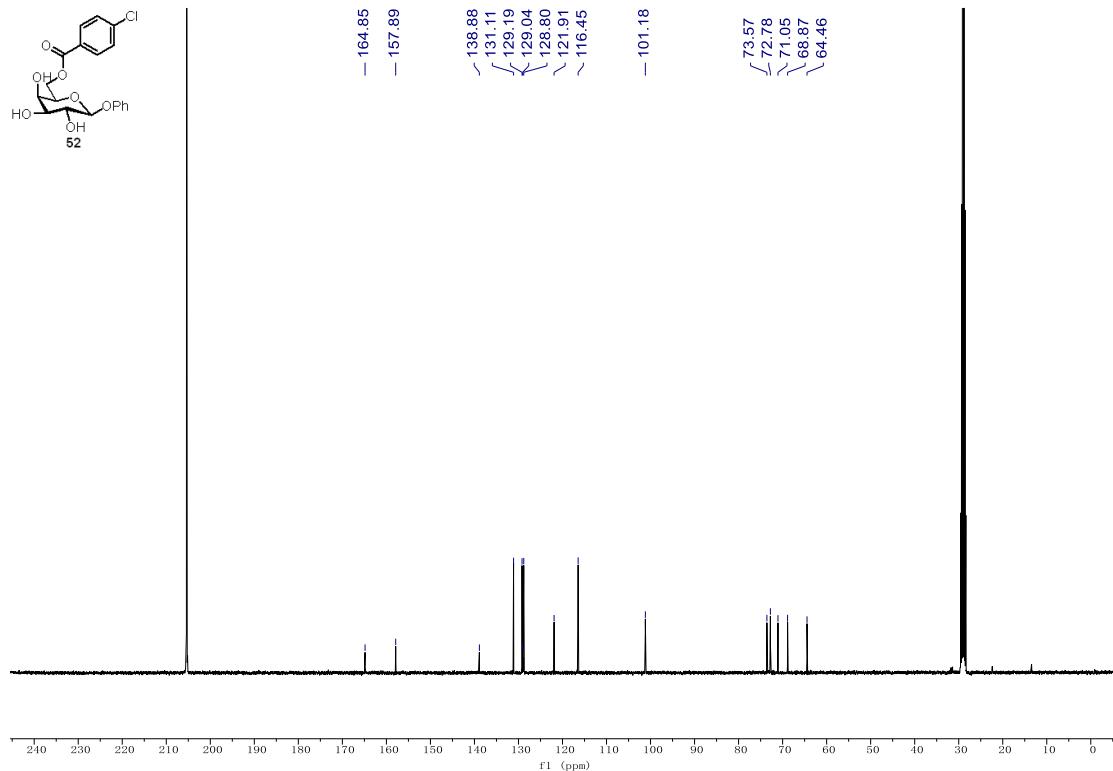


Figure S218. ¹³C NMR Spectra of 52

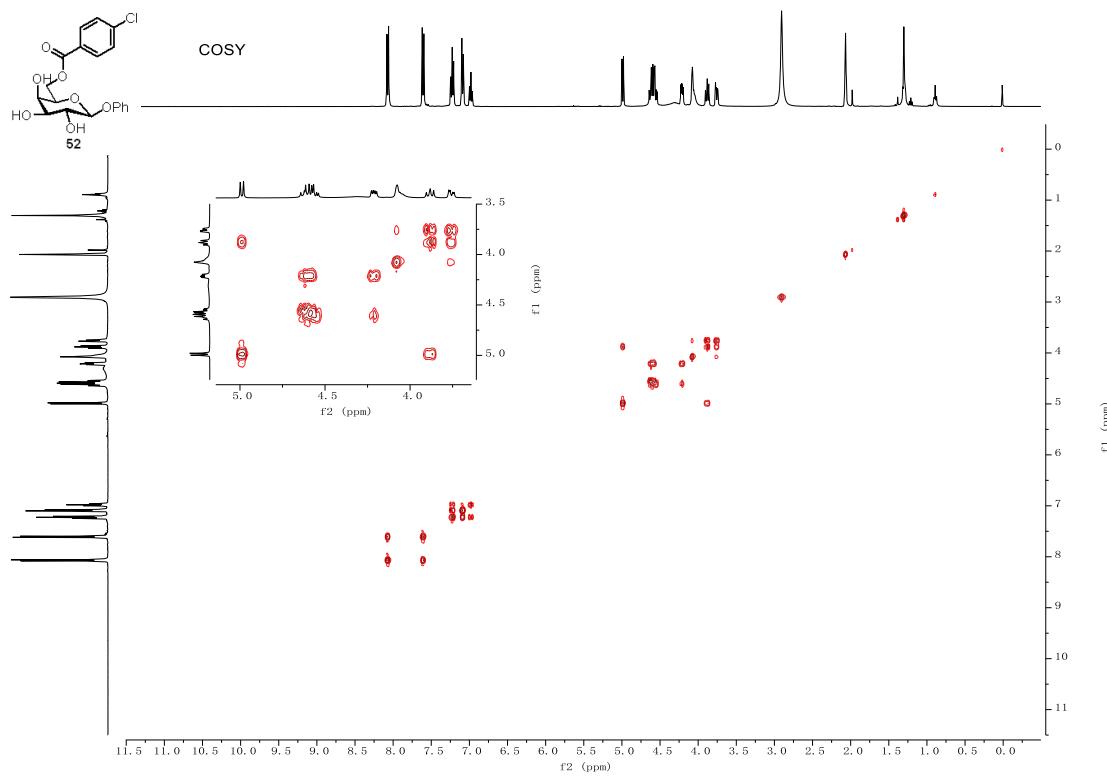


Figure S219. COSY NMR Spectra of **52**

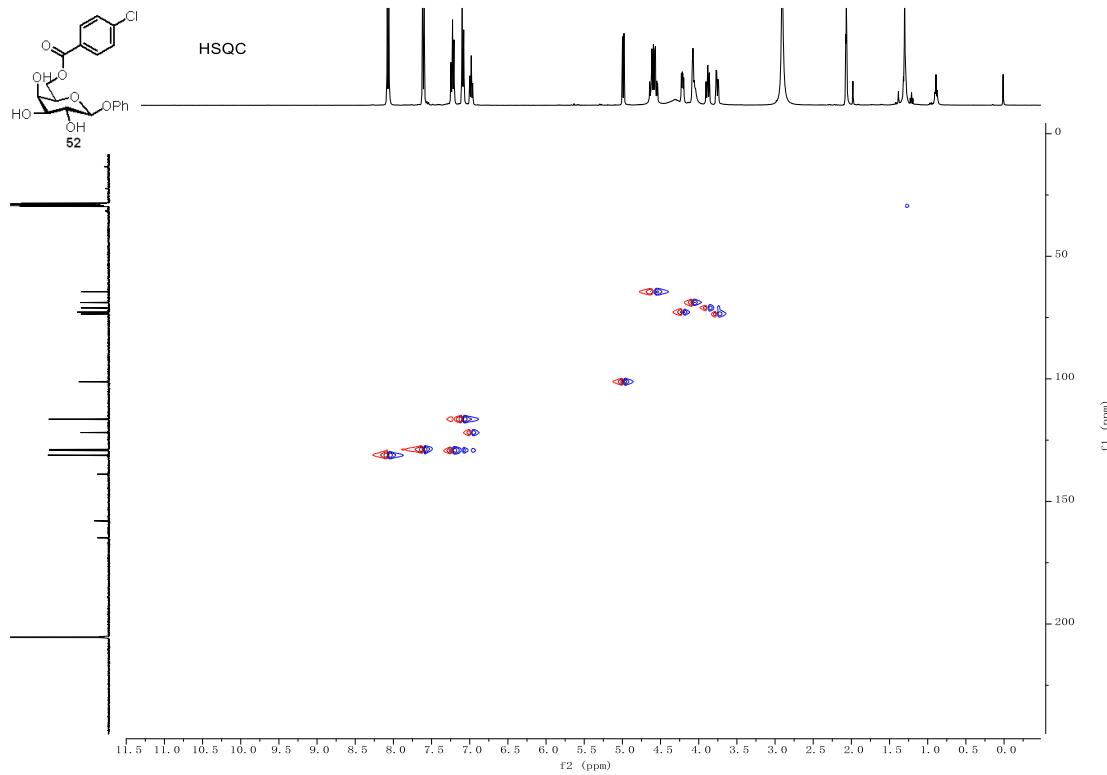


Figure S220. HSQC NMR Spectra of **52**

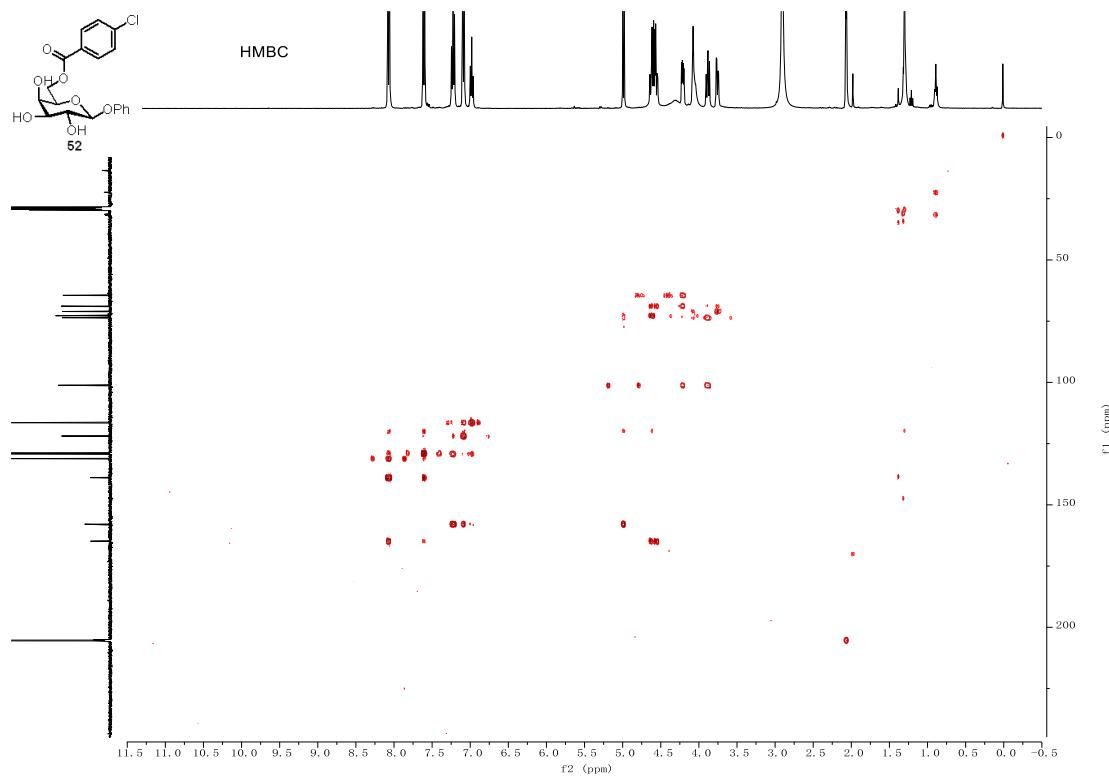


Figure S221. HMBC NMR Spectra of 52

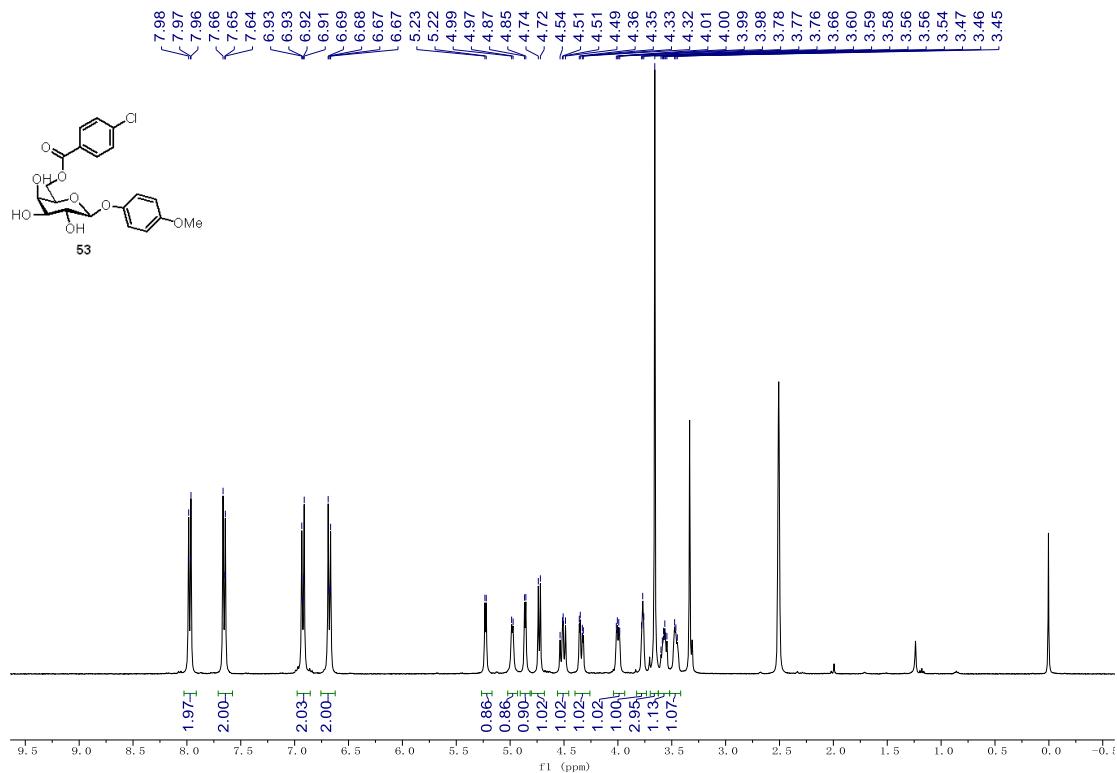


Figure S222. ^1H NMR Spectra of **53**

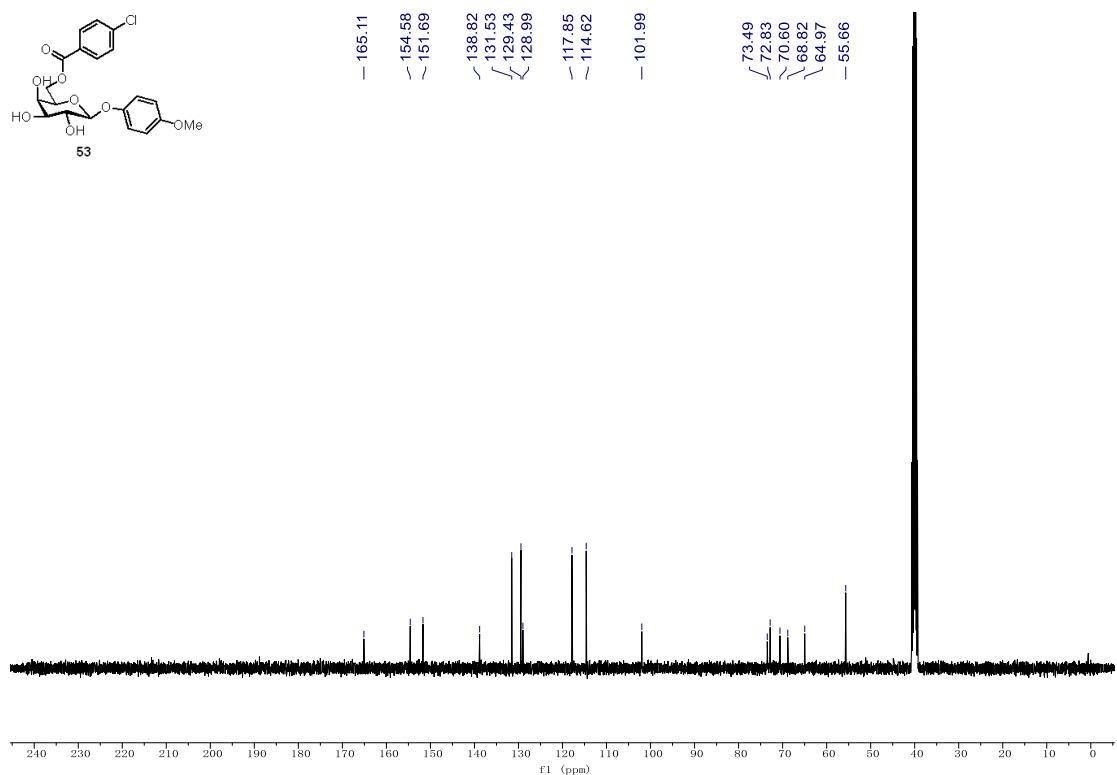


Figure S223. ^{13}C NMR Spectra of 53

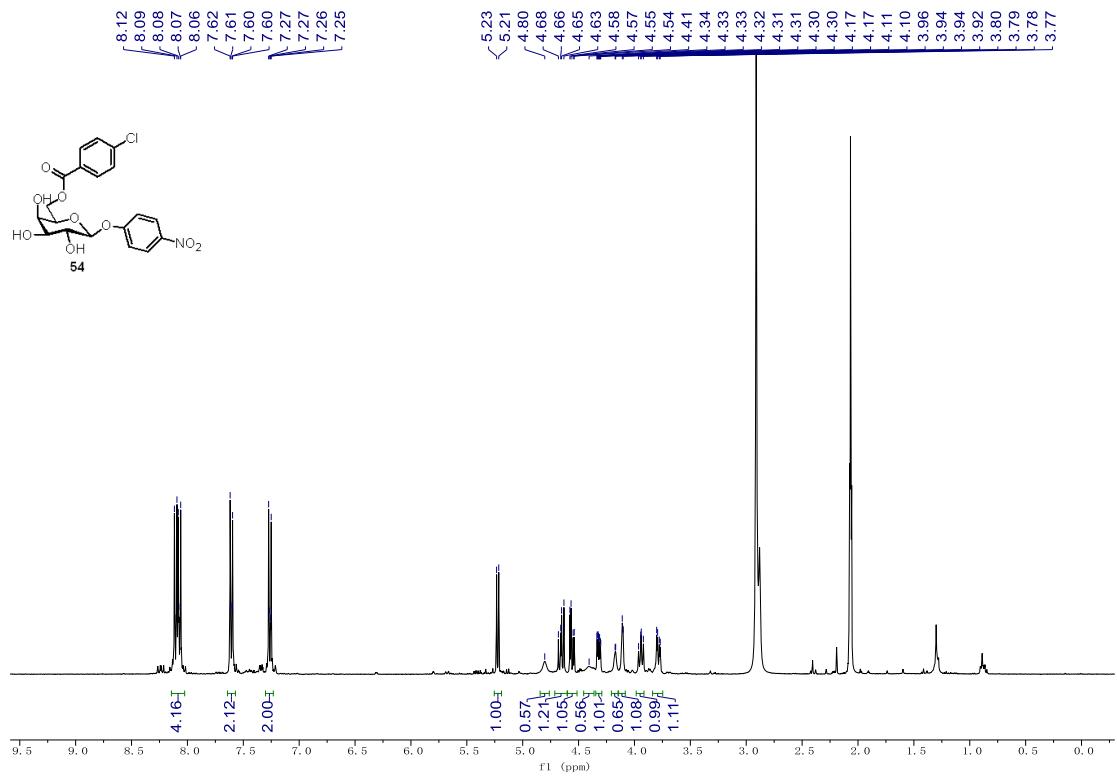


Figure S224. ^1H NMR Spectra of **54**

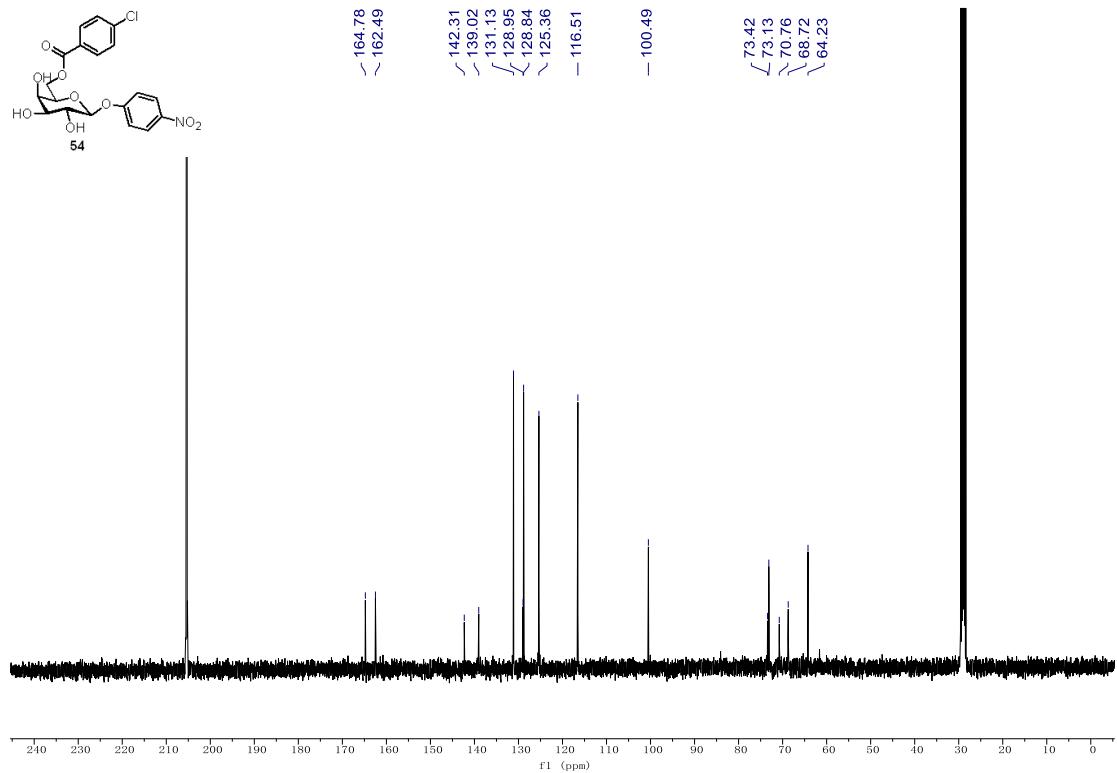


Figure S225. ^{13}C NMR Spectra of **54**

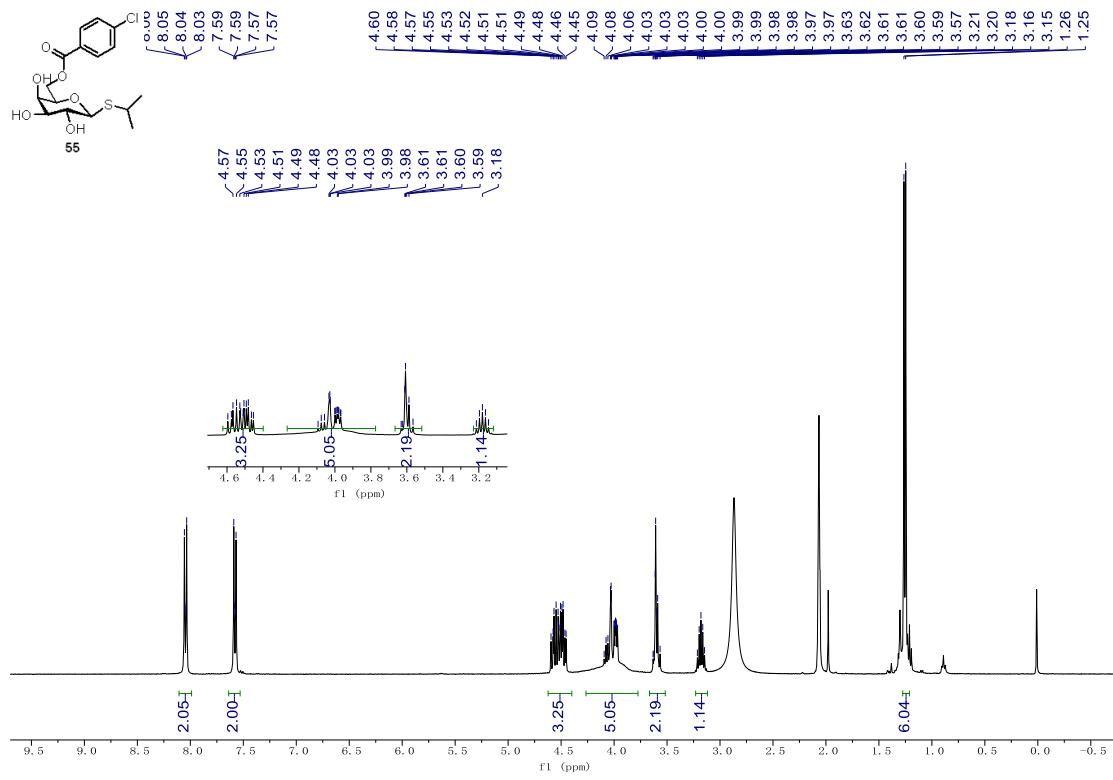


Figure S226. ^1H NMR Spectra of 55

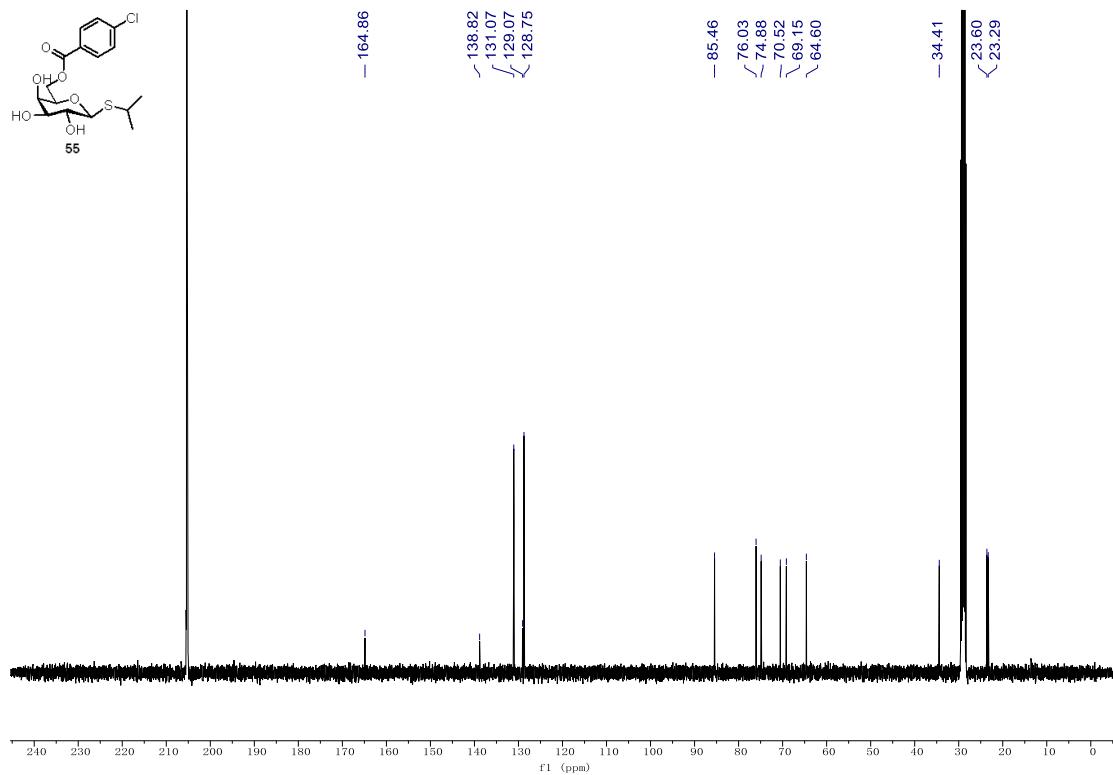


Figure S227. ^{13}C NMR Spectra of 55

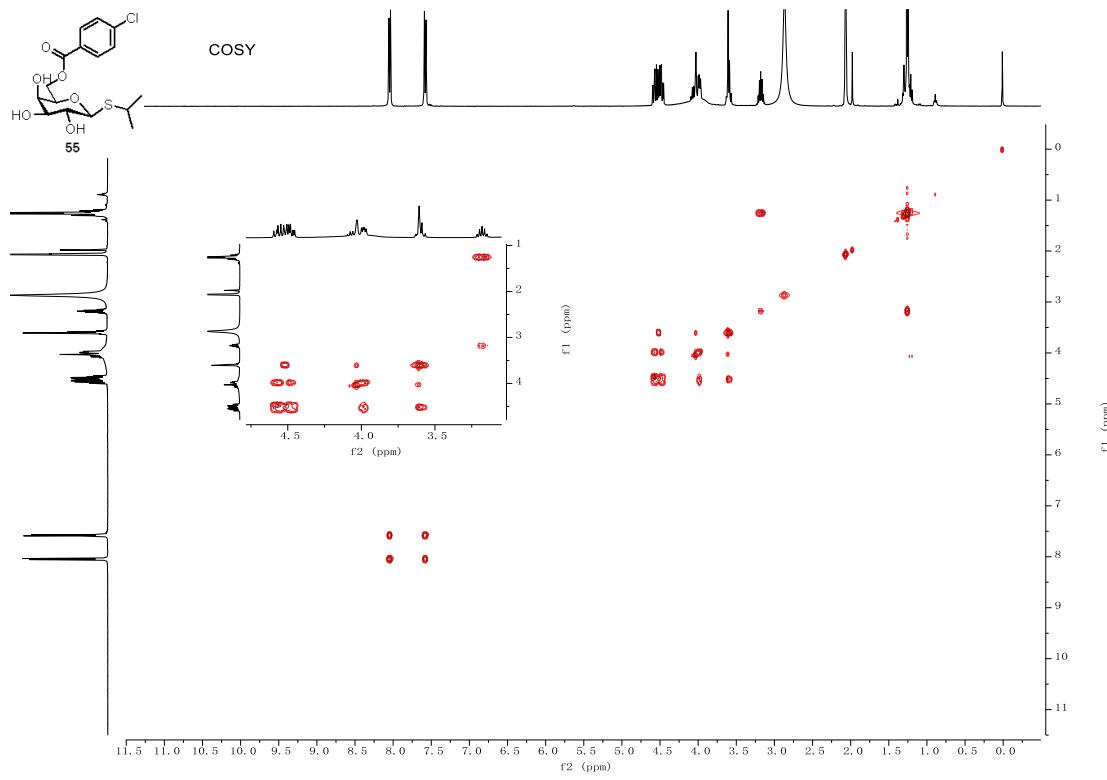


Figure S228. COSY NMR Spectra of **55**

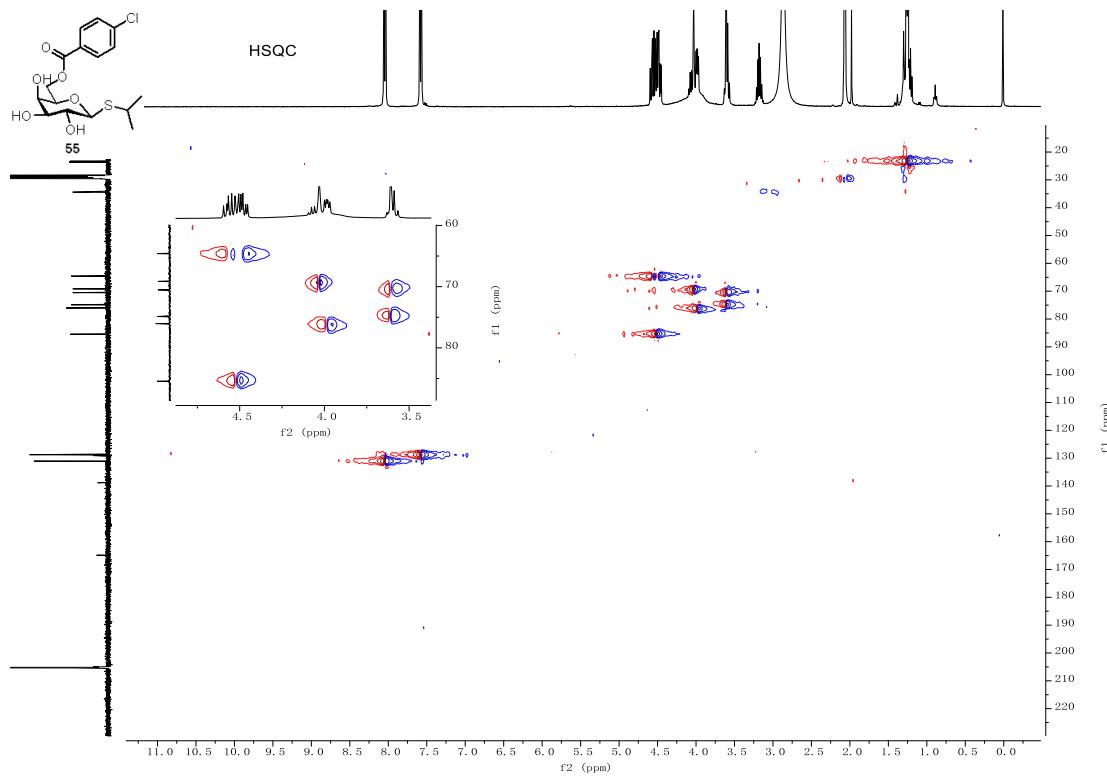


Figure S229. HSQC NMR Spectra of **55**

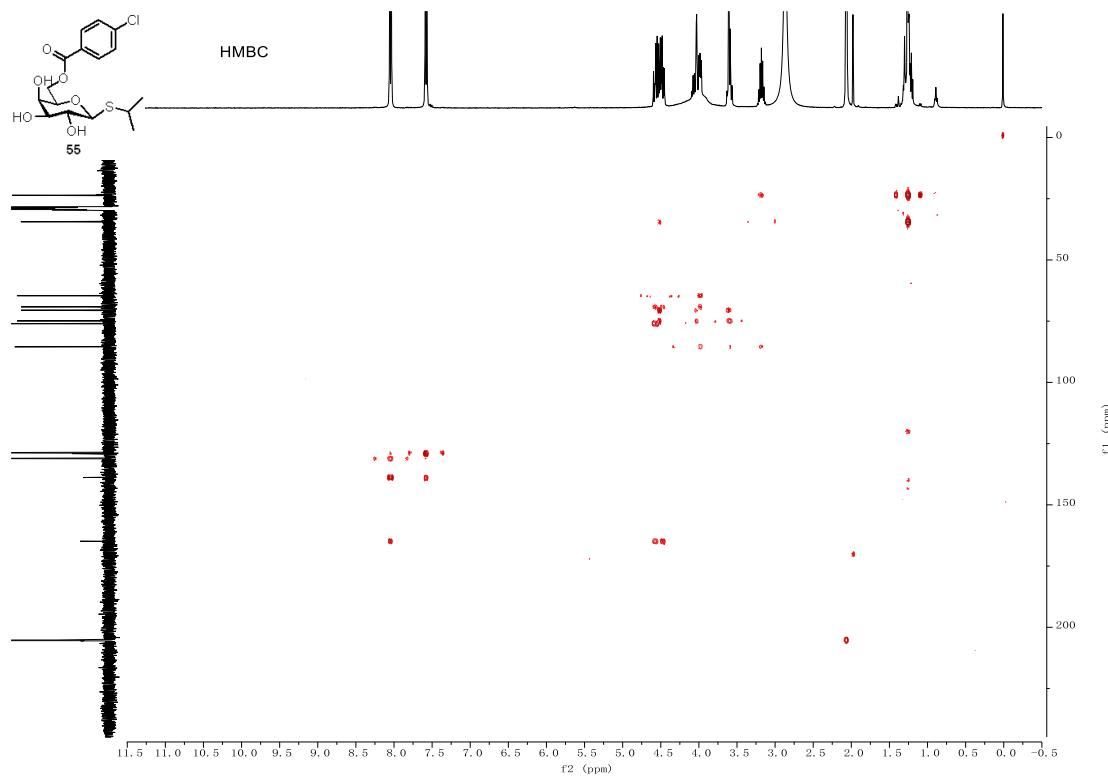


Figure S230. HMBC NMR Spectra of **55**

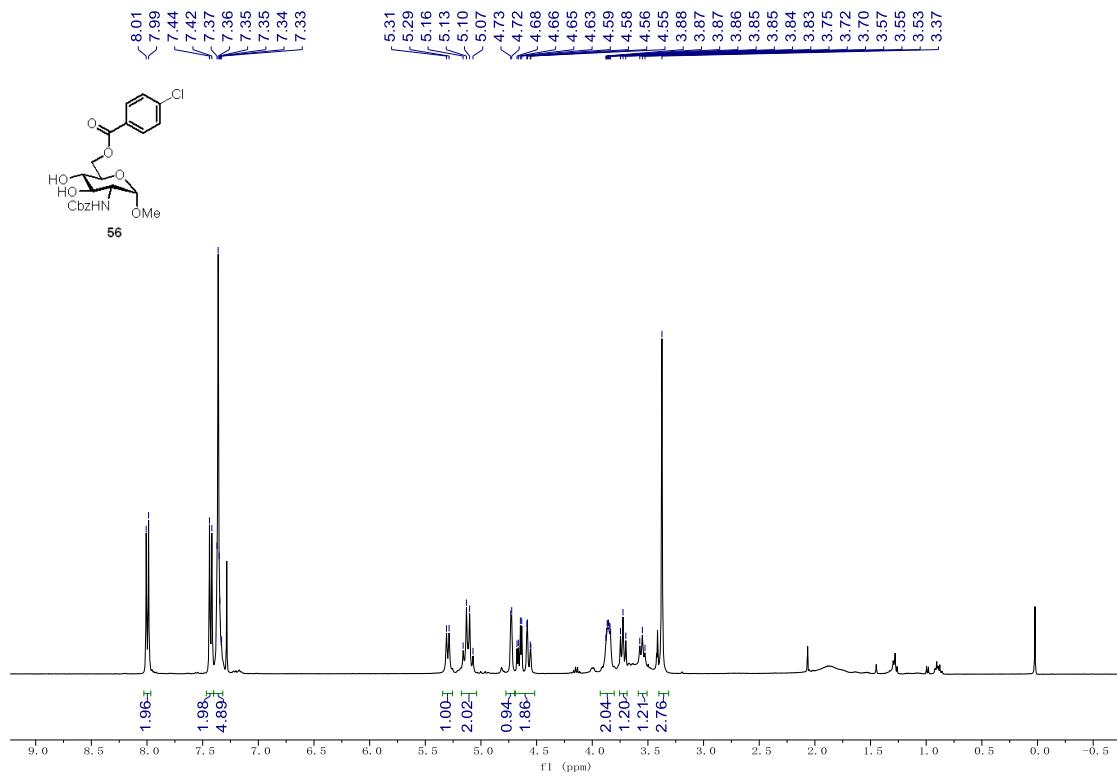


Figure S231. ^1H NMR Spectra of 56

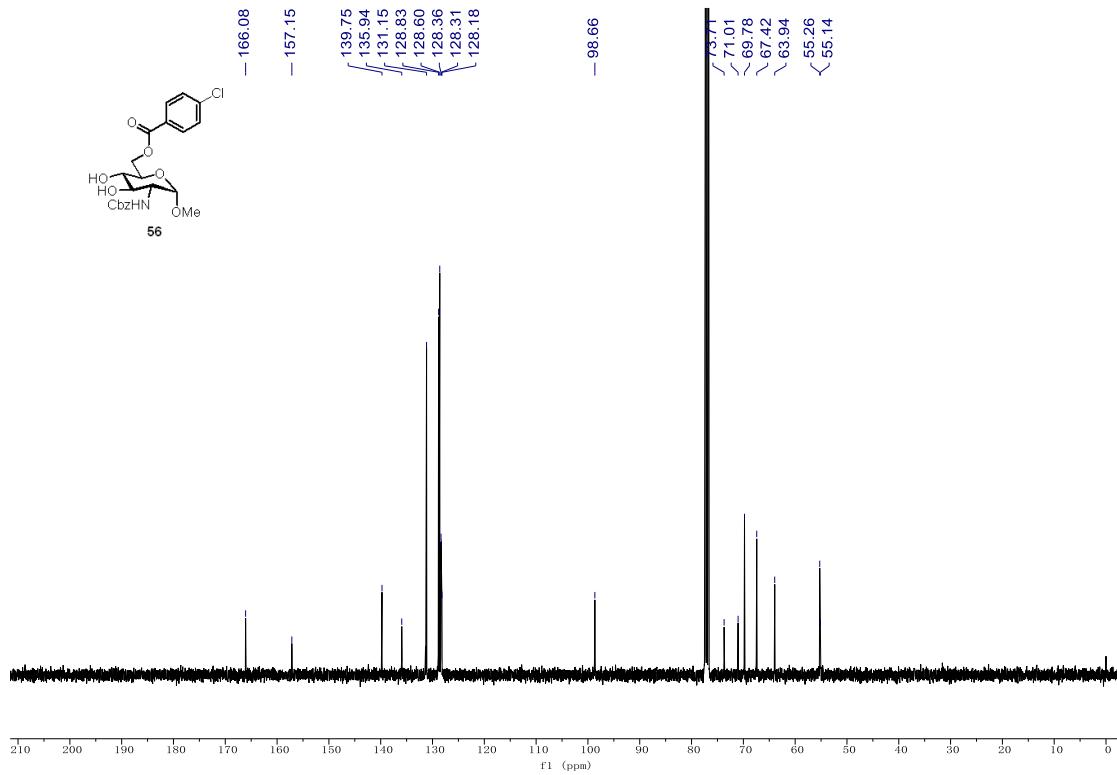


Figure S232. ^{13}C NMR Spectra of **56**

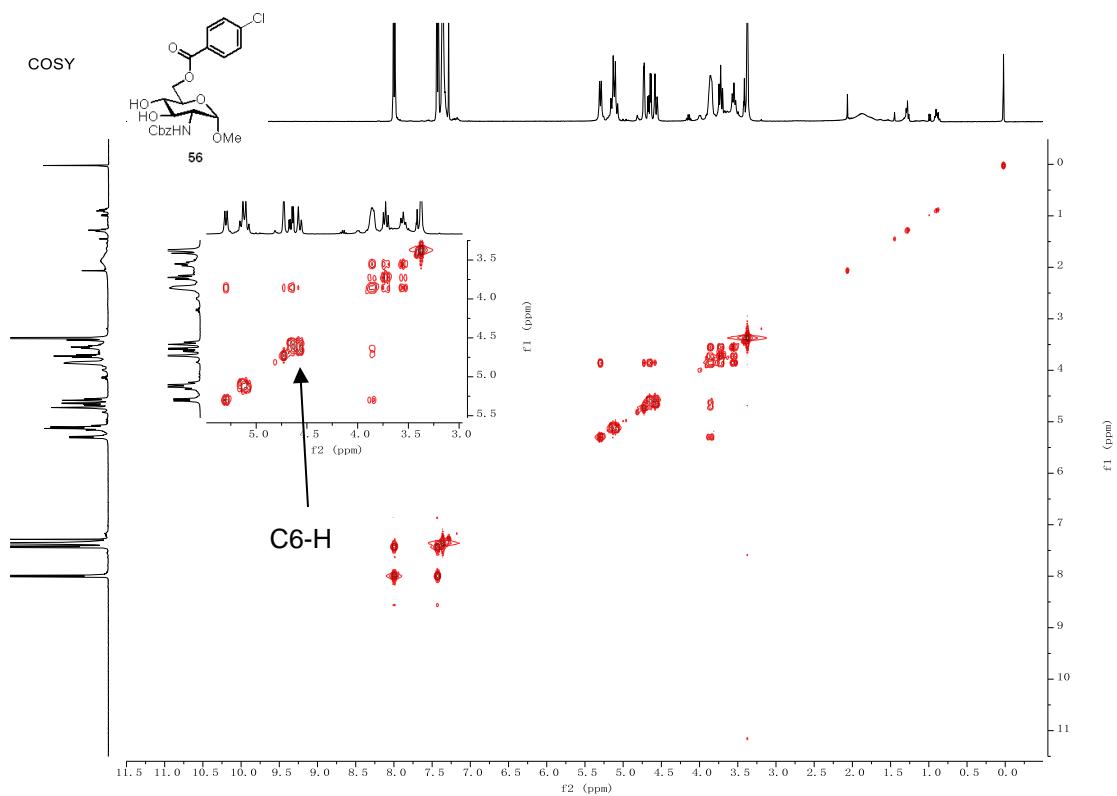


Figure S233. COSY NMR Spectra of **56**

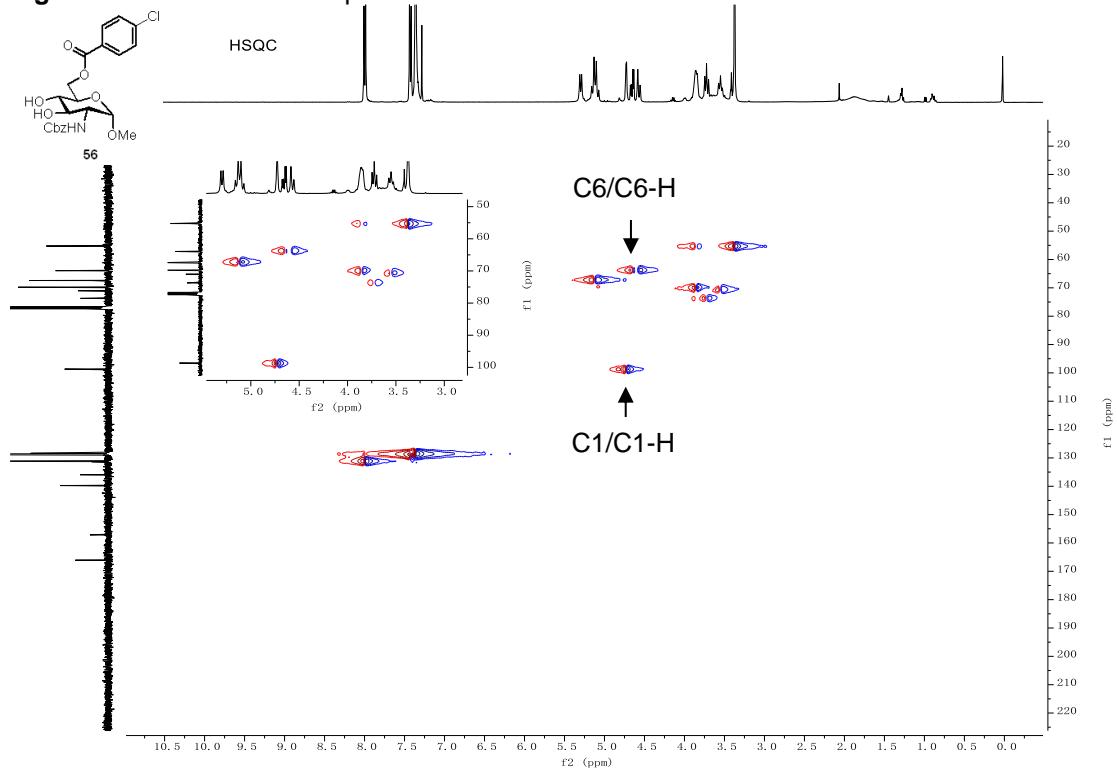


Figure S234. HSQC NMR Spectra of **56**

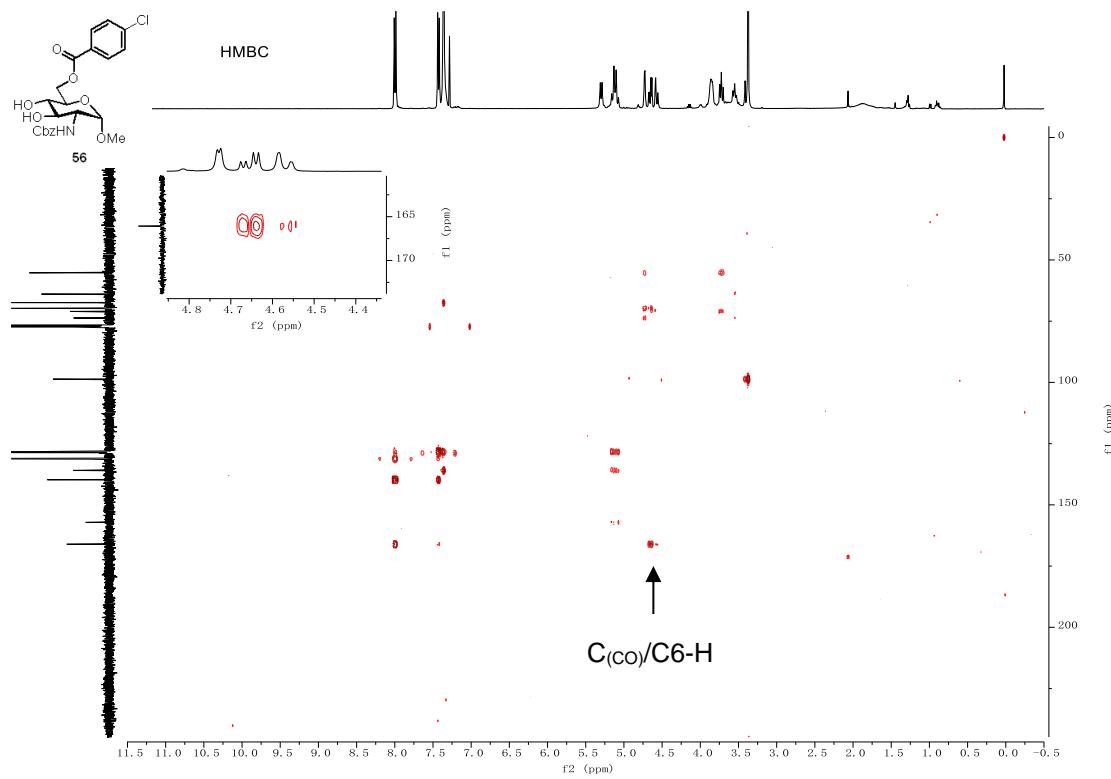


Figure S235. HMBC NMR Spectra of **56**

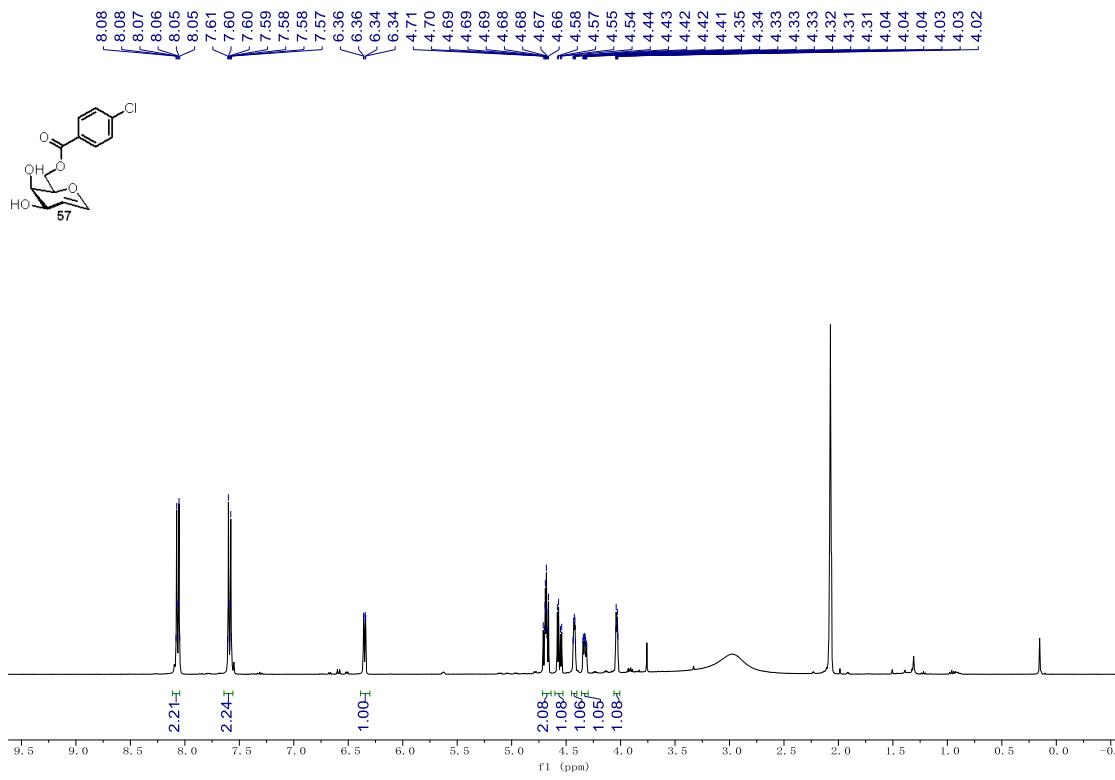


Figure S236. ^1H NMR Spectra of **57**

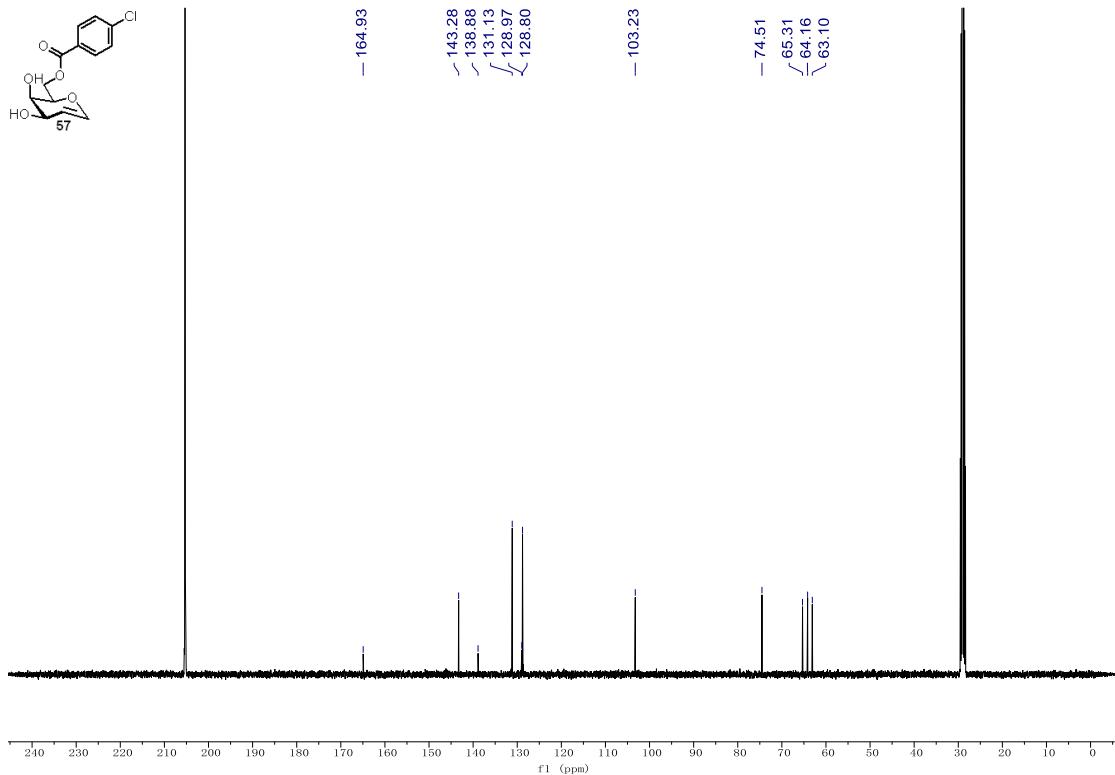


Figure S237. ^{13}C NMR Spectra of **57**

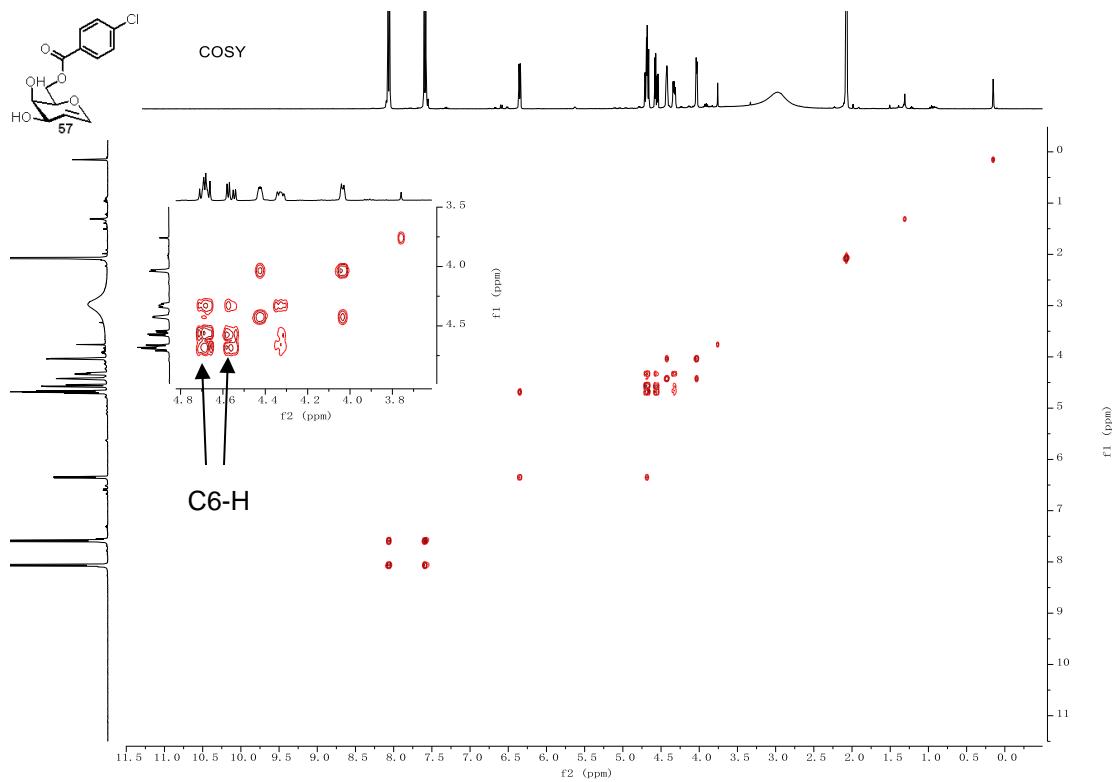


Figure S238. COSY NMR Spectra of **57**

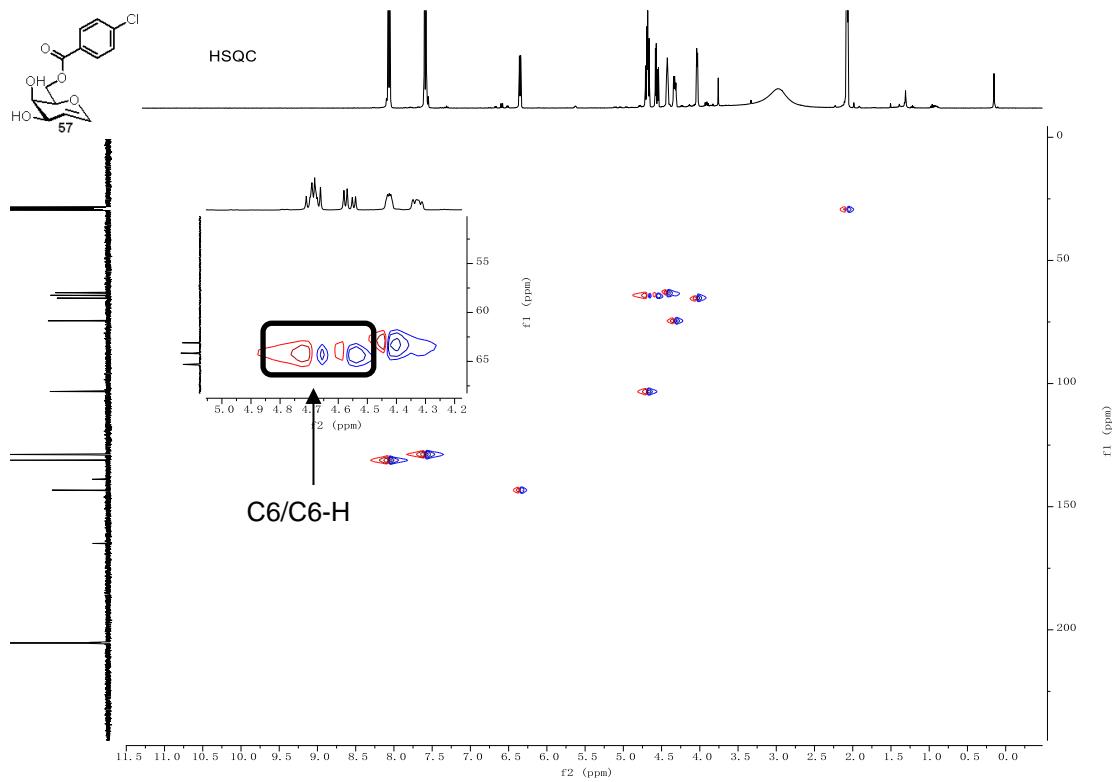


Figure S239. HSQC NMR Spectra of **57**

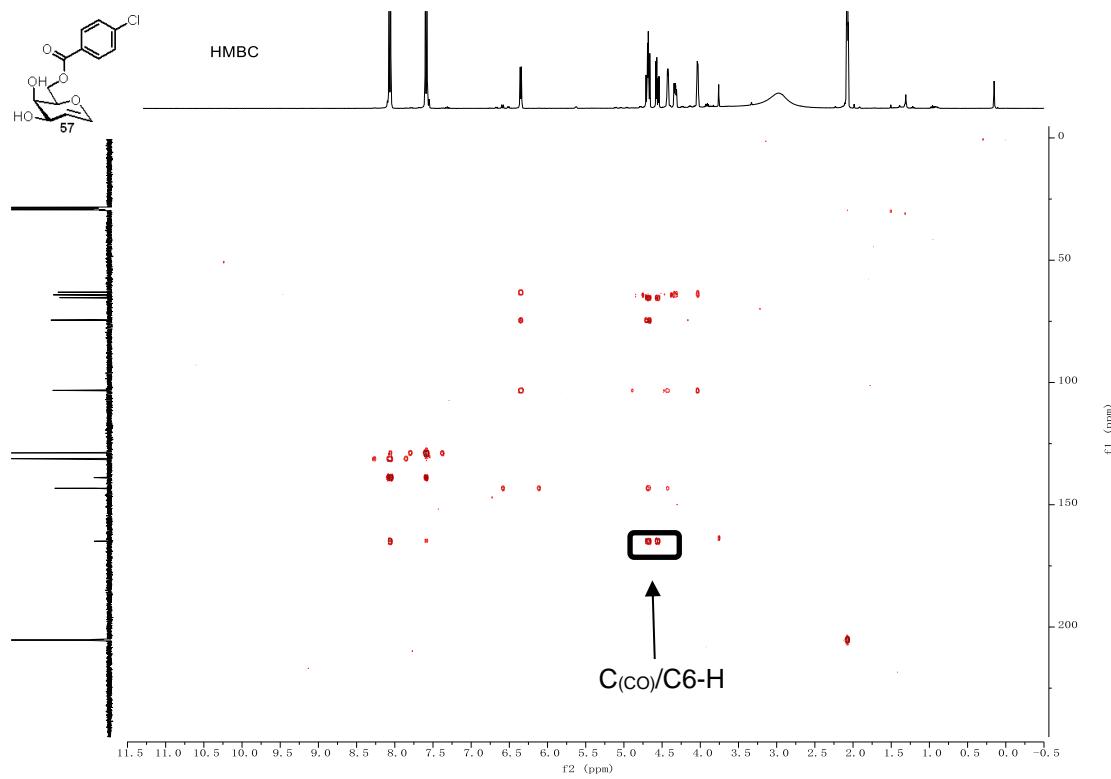


Figure S240. HMBC NMR Spectra of 57

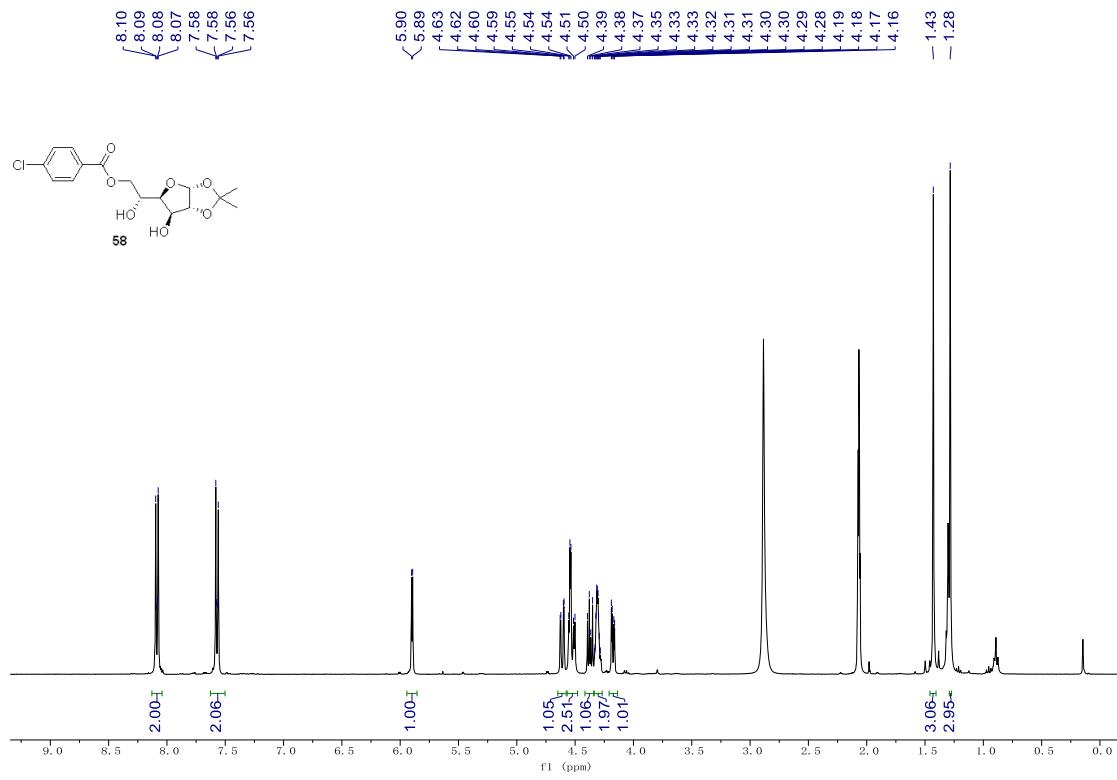


Figure S241. ^1H NMR Spectra of **58**

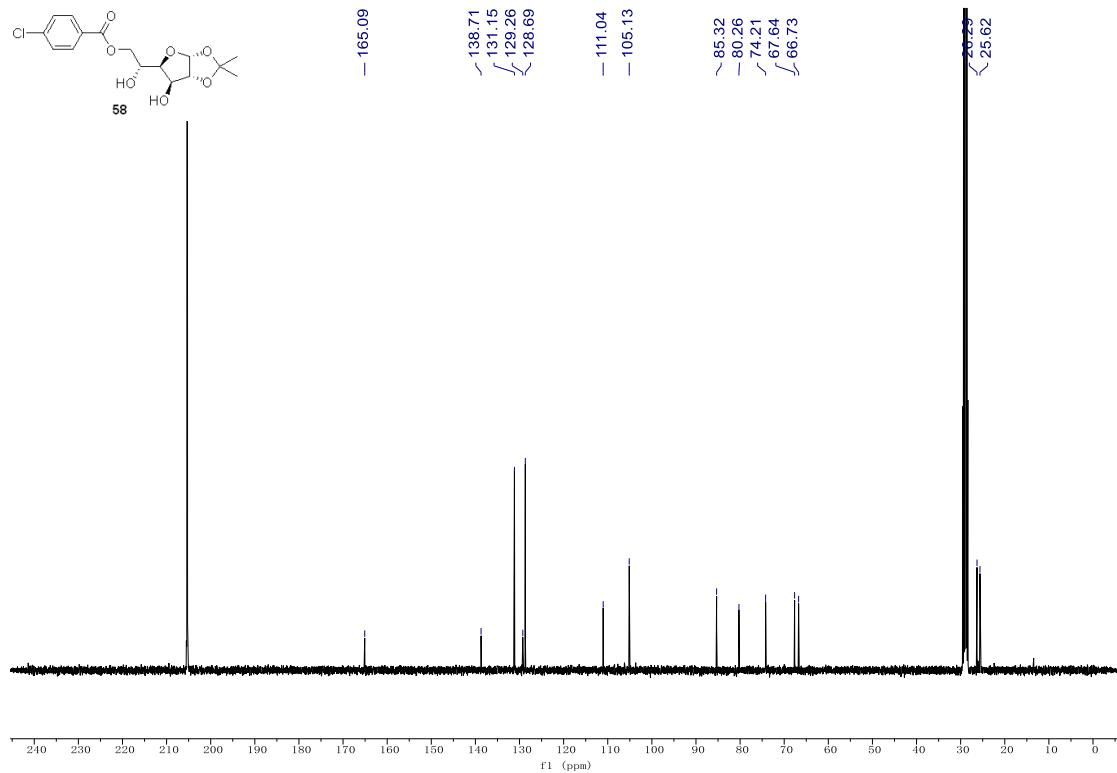


Figure S242. ^{13}C NMR Spectra of **58**

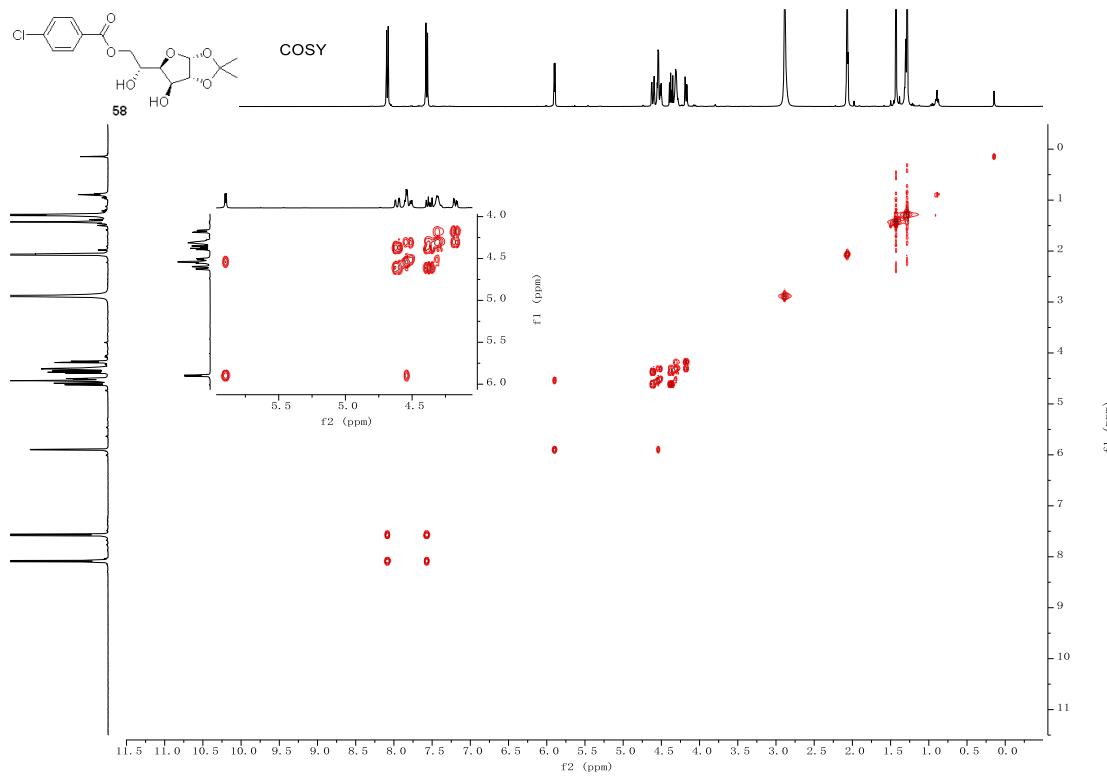


Figure S243. COSY NMR Spectra of **58**

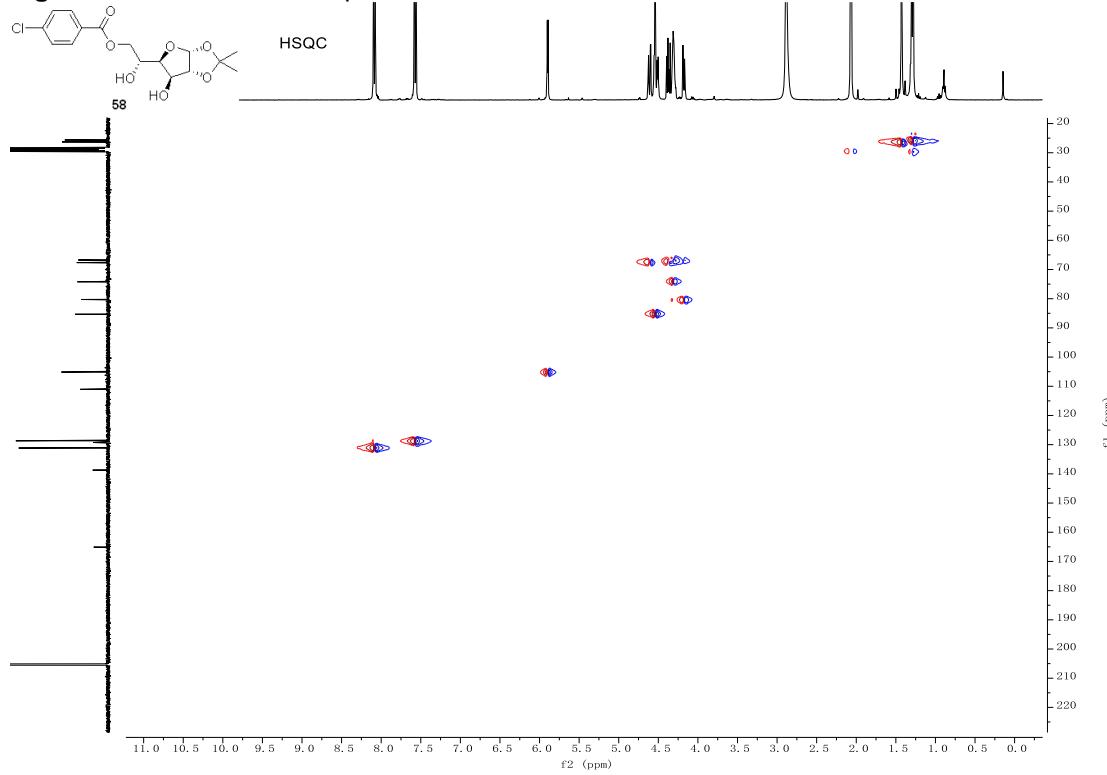


Figure S244. HSQC NMR Spectra of **58**

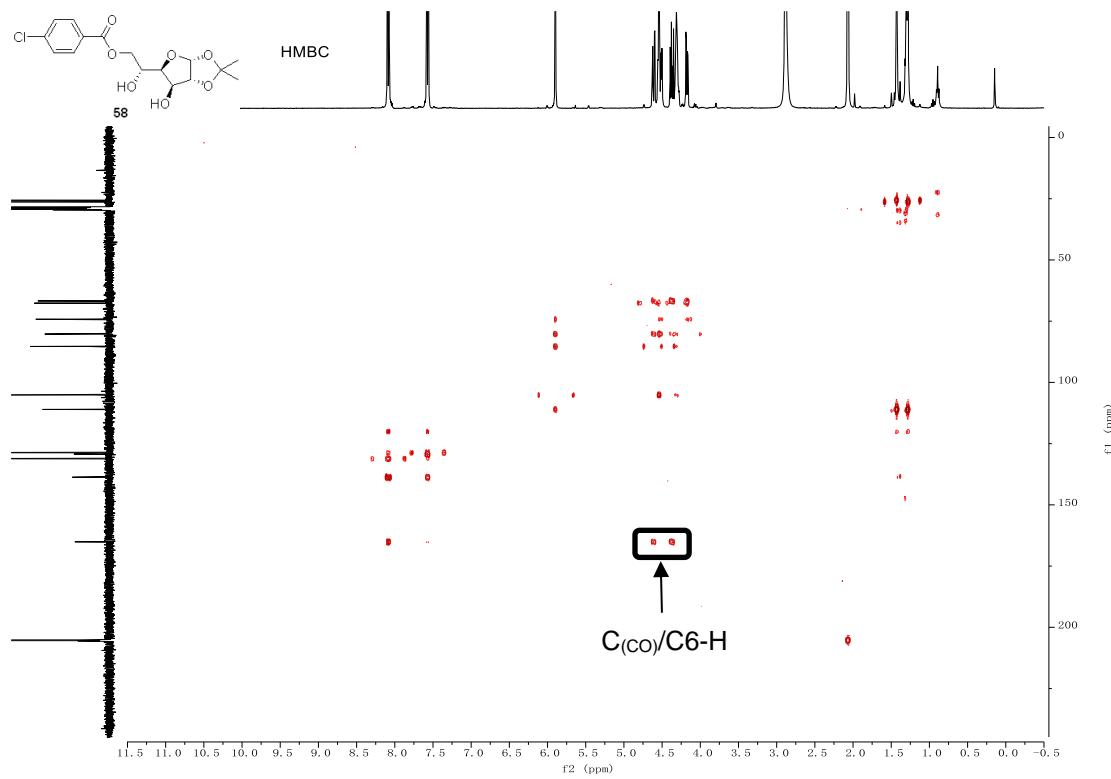


Figure S245. HMBC NMR Spectra of **58**

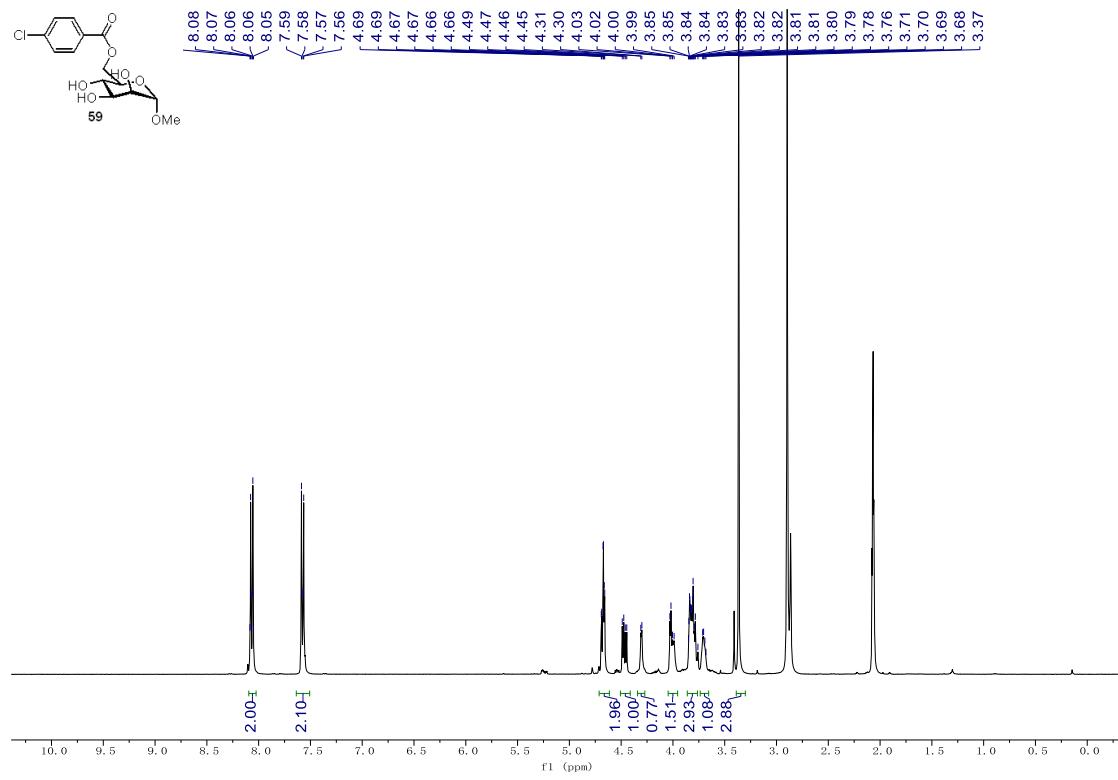


Figure S246. ^1H NMR Spectra of **59**

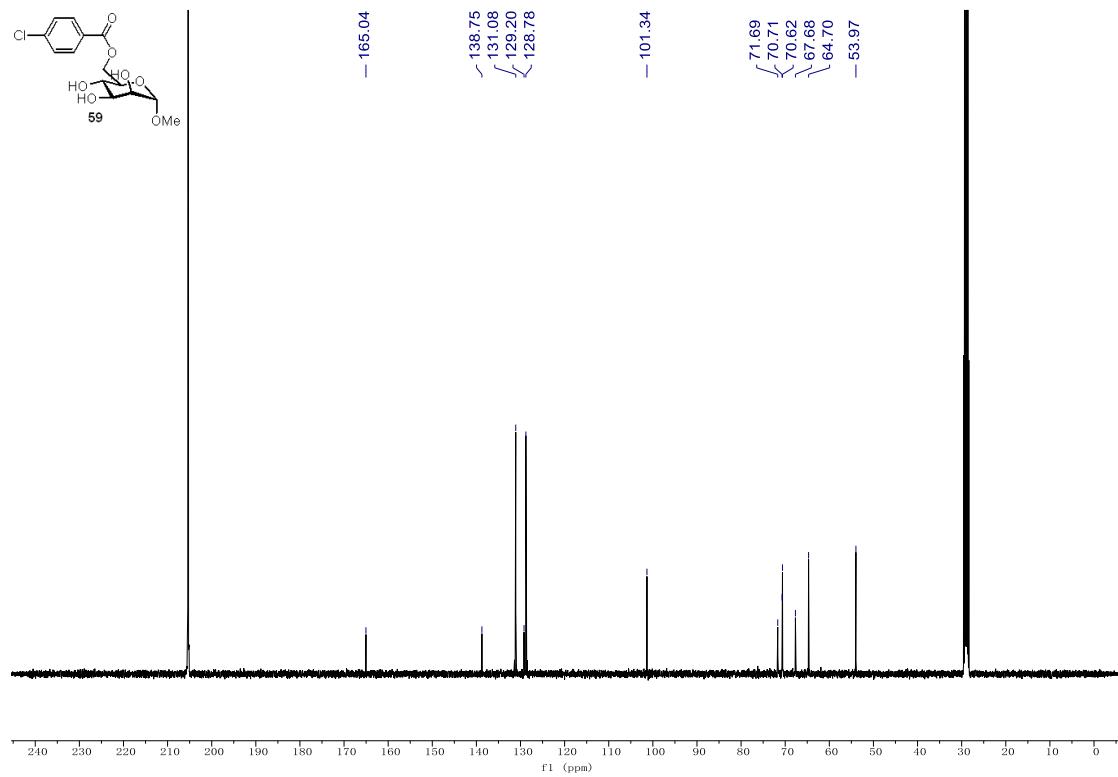


Figure S247. ^{13}C NMR Spectra of **59**

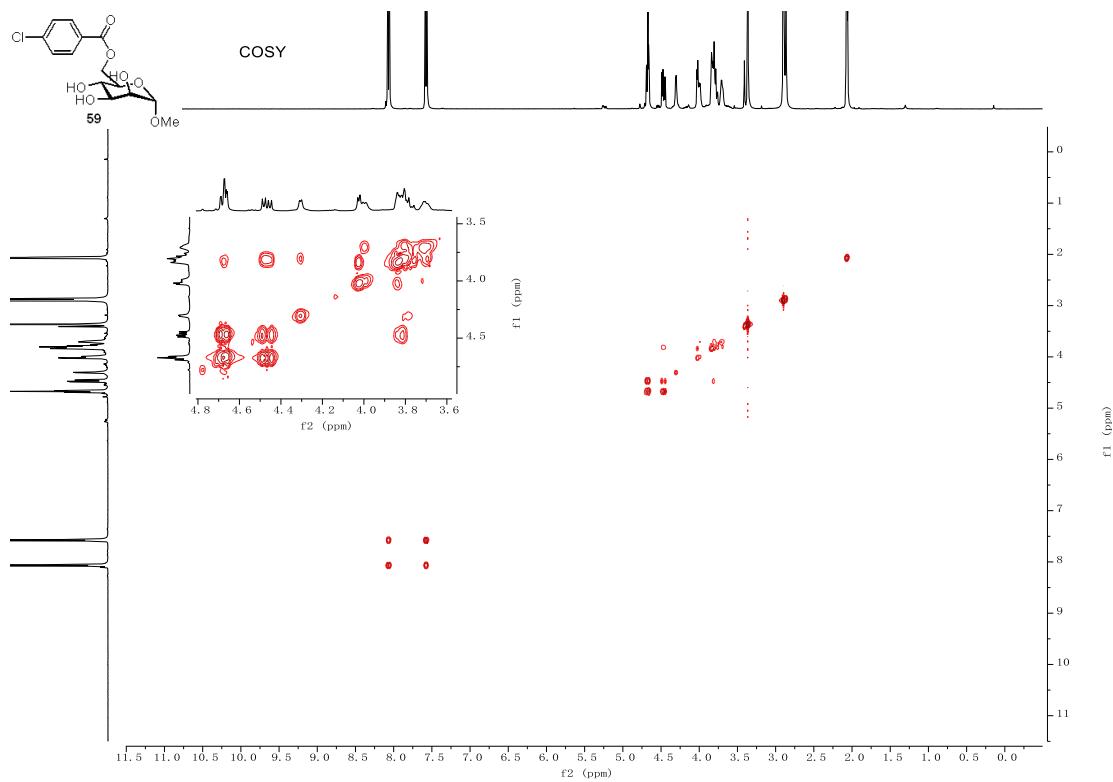


Figure S248. COSY NMR Spectra of **59**

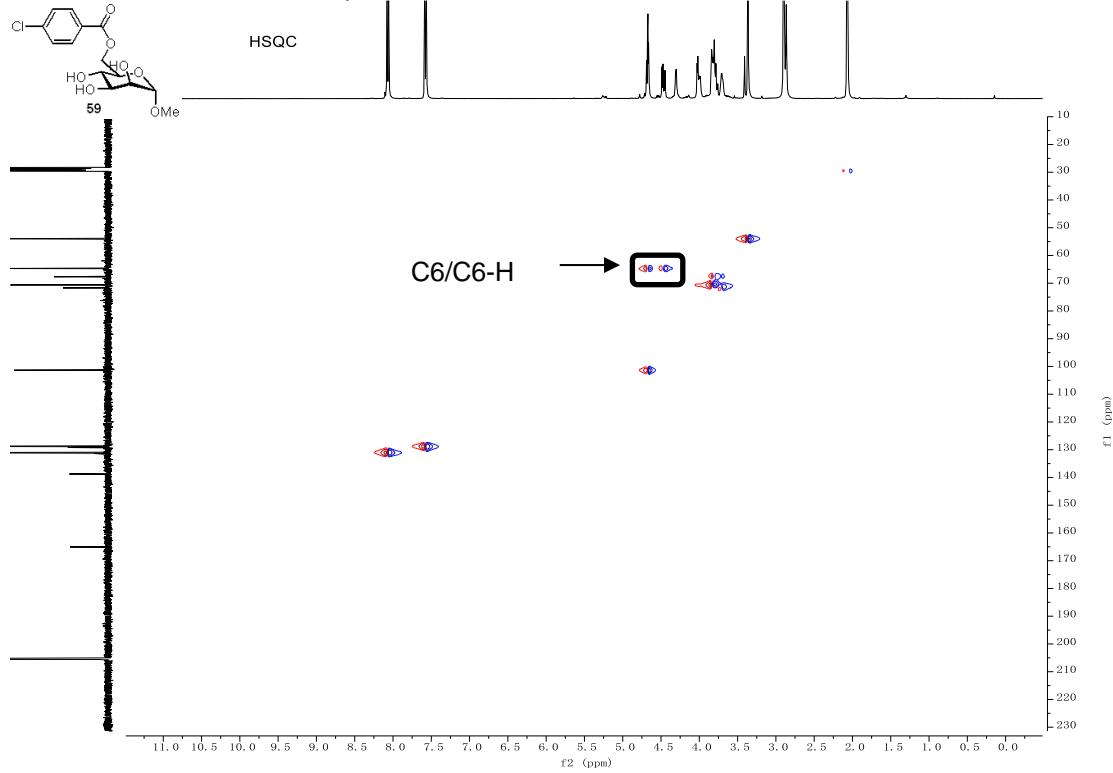


Figure S249. HSQC NMR Spectra of 59

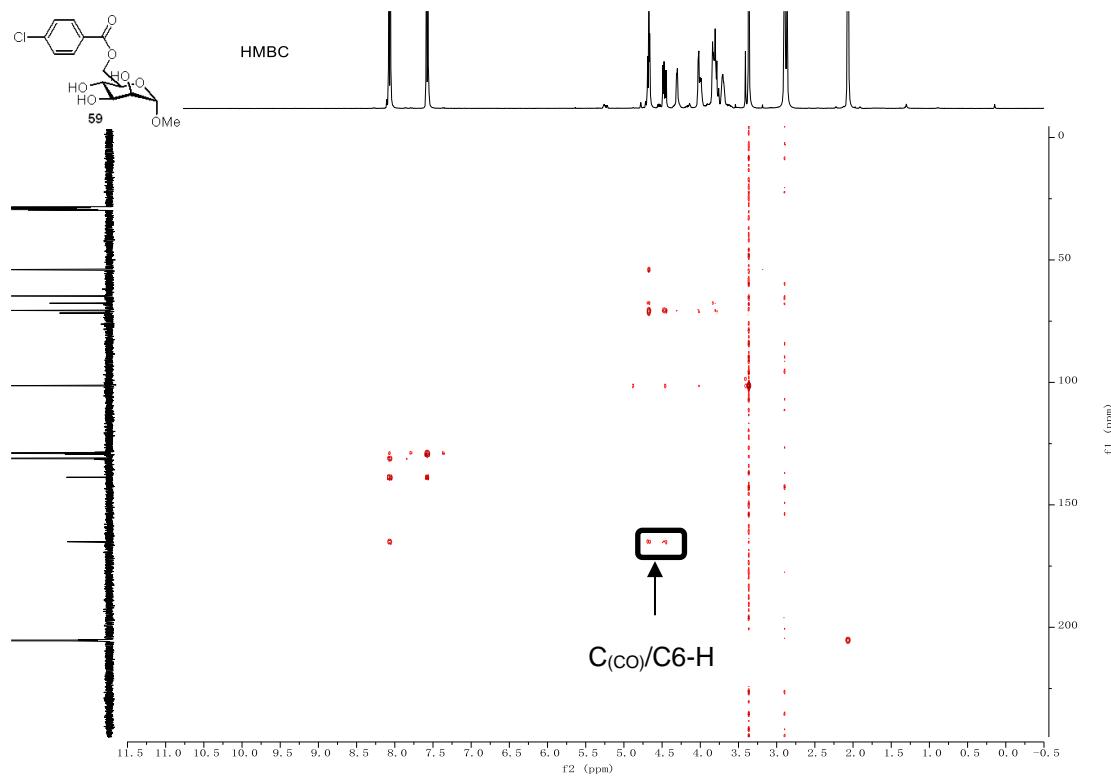


Figure S250. HMBC NMR Spectra of **59**

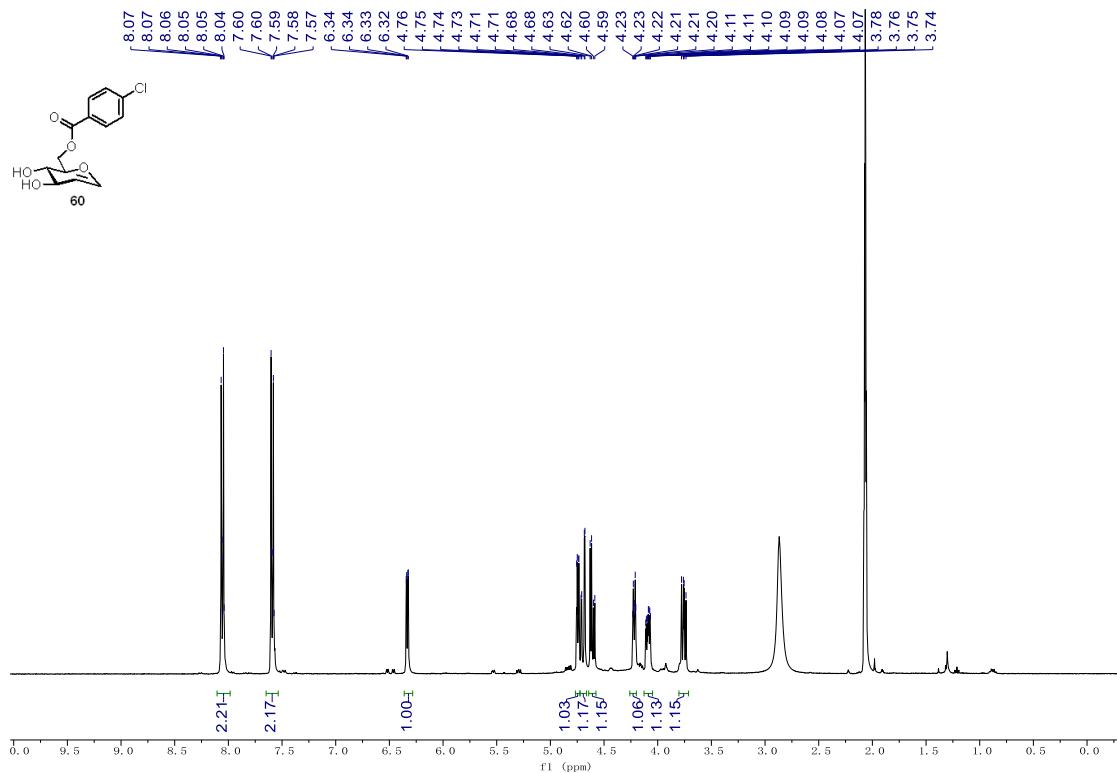


Figure S251. ^1H NMR Spectra of **60**

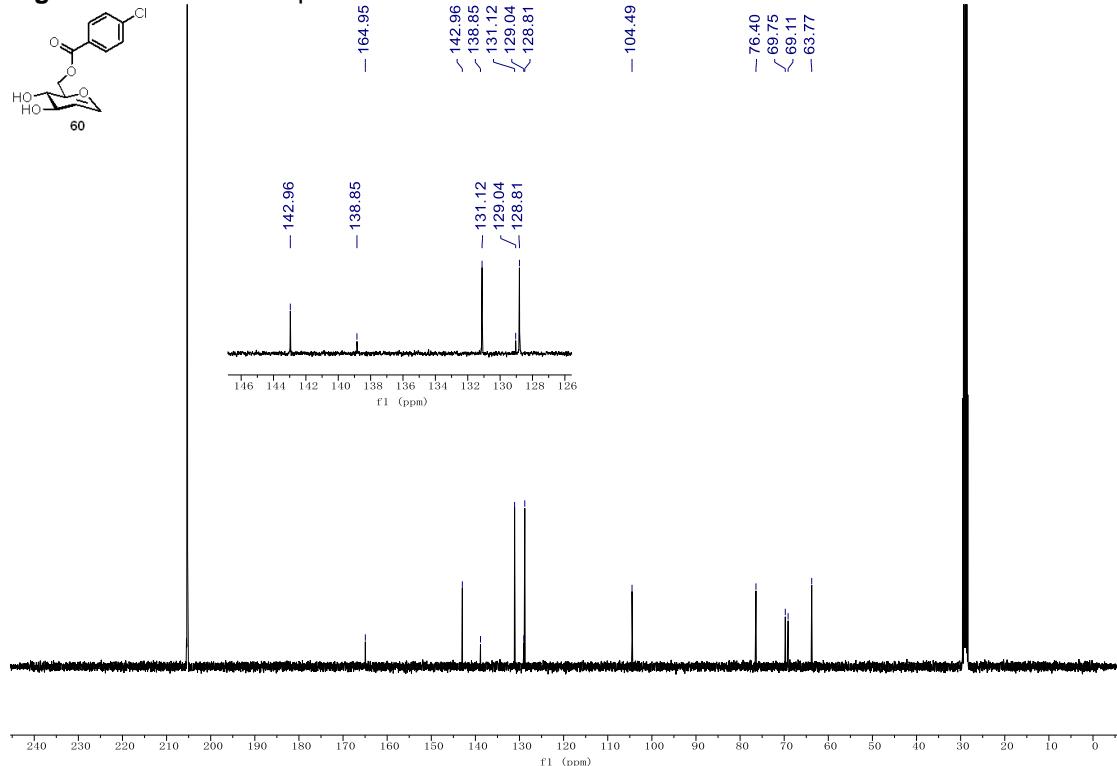


Figure S252. ^{13}C NMR Spectra of **60**

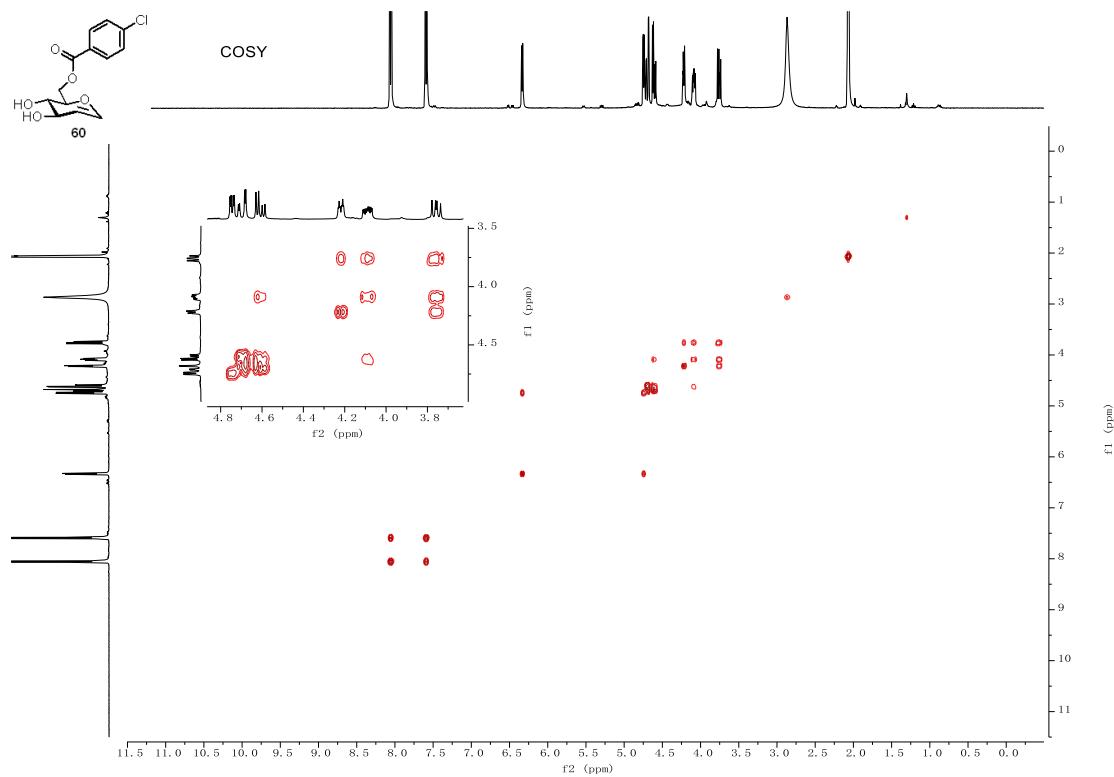


Figure S253. COSY NMR Spectra of **60**

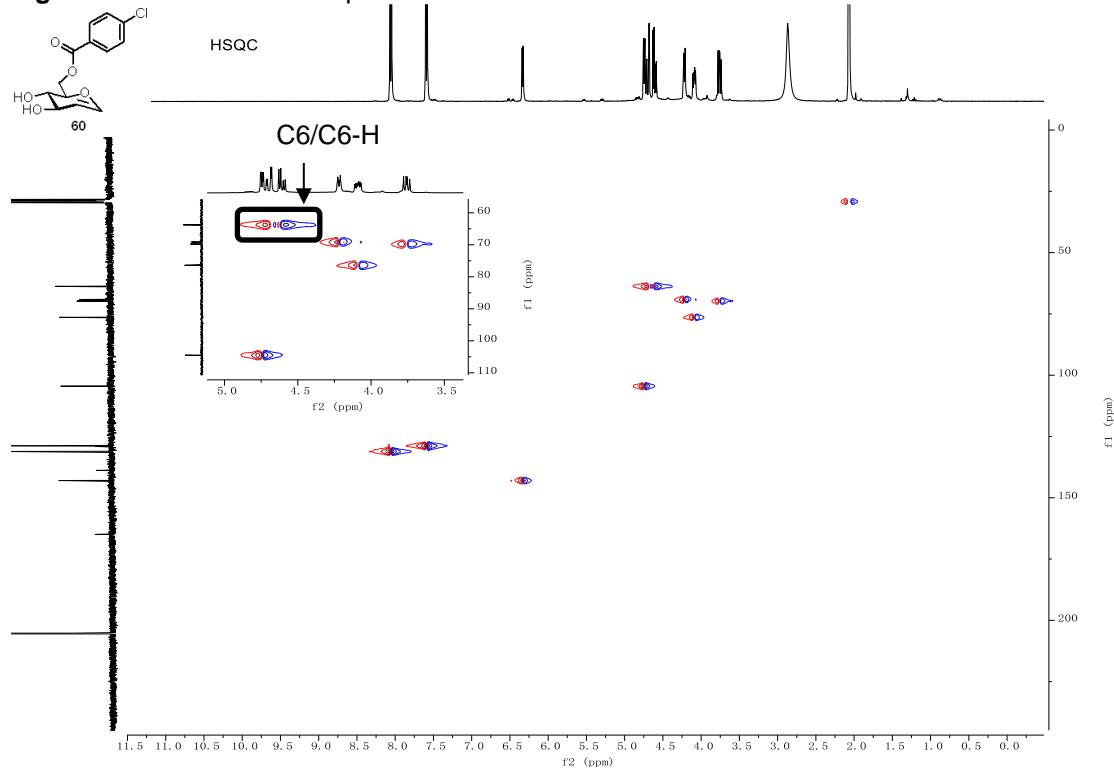


Figure S254. HSQC NMR Spectra of **60**

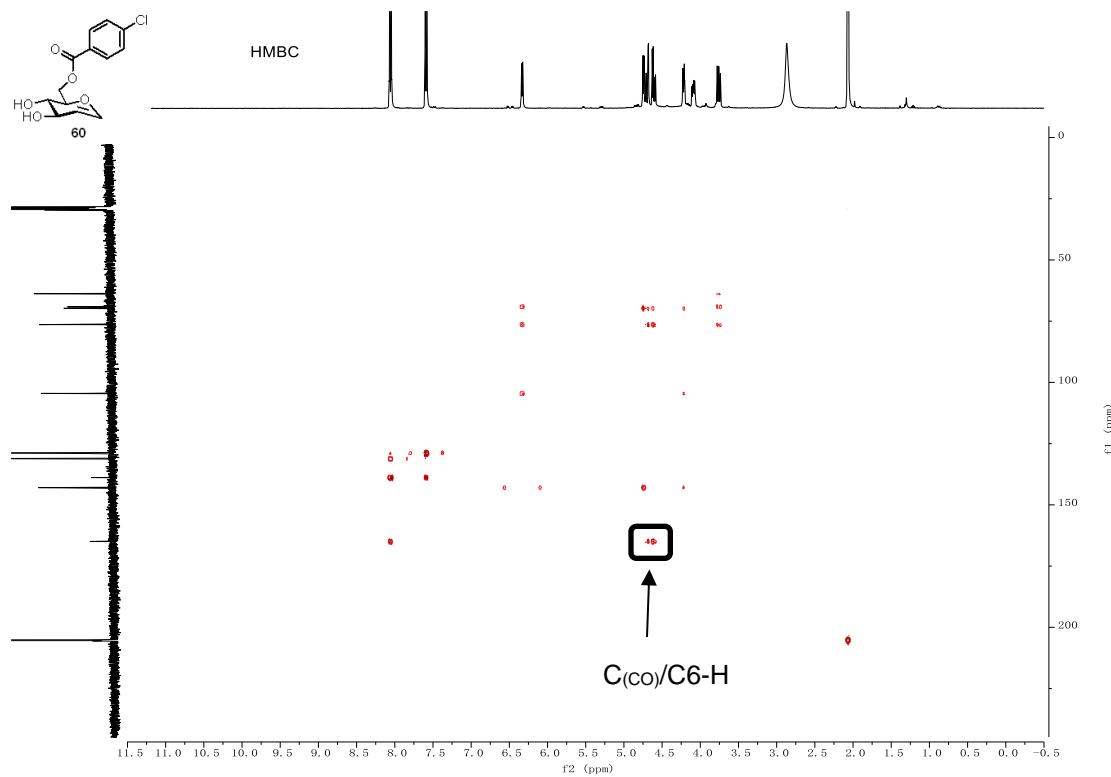


Figure S255. HMBC NMR Spectra of **60**

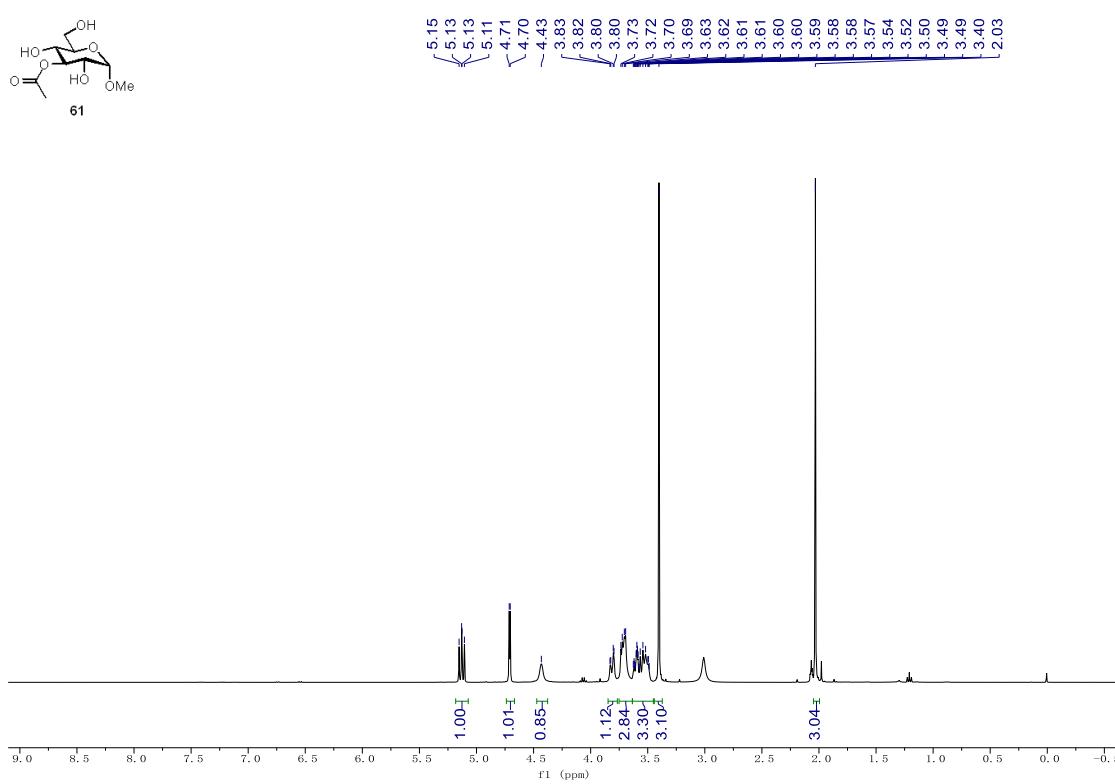


Figure S256. ^1H NMR Spectra of 61

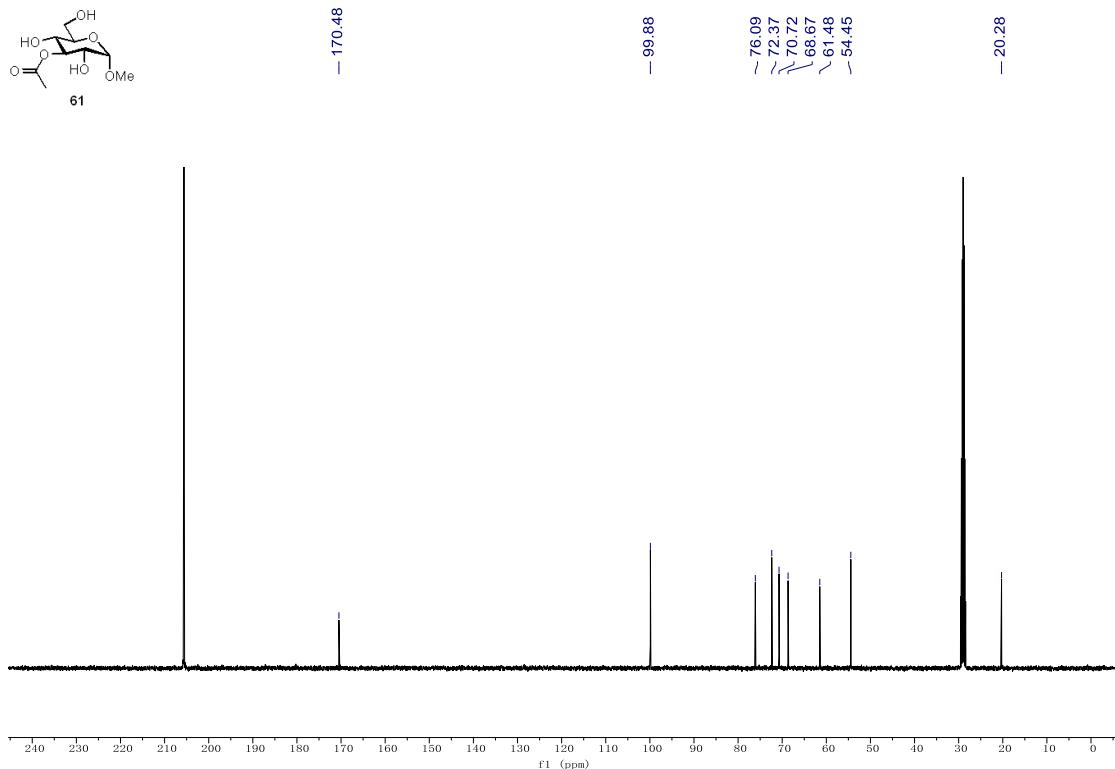


Figure S257. ^{13}C NMR Spectra of 61

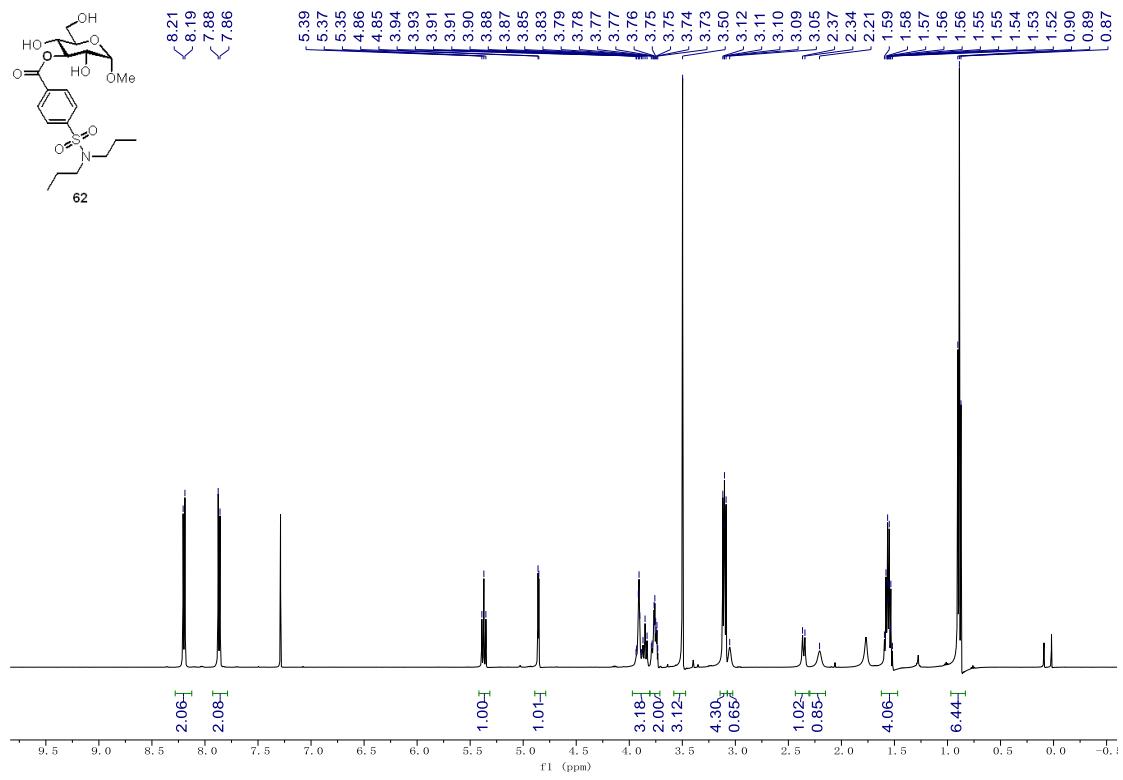


Figure S258. ^1H NMR Spectra of **62**

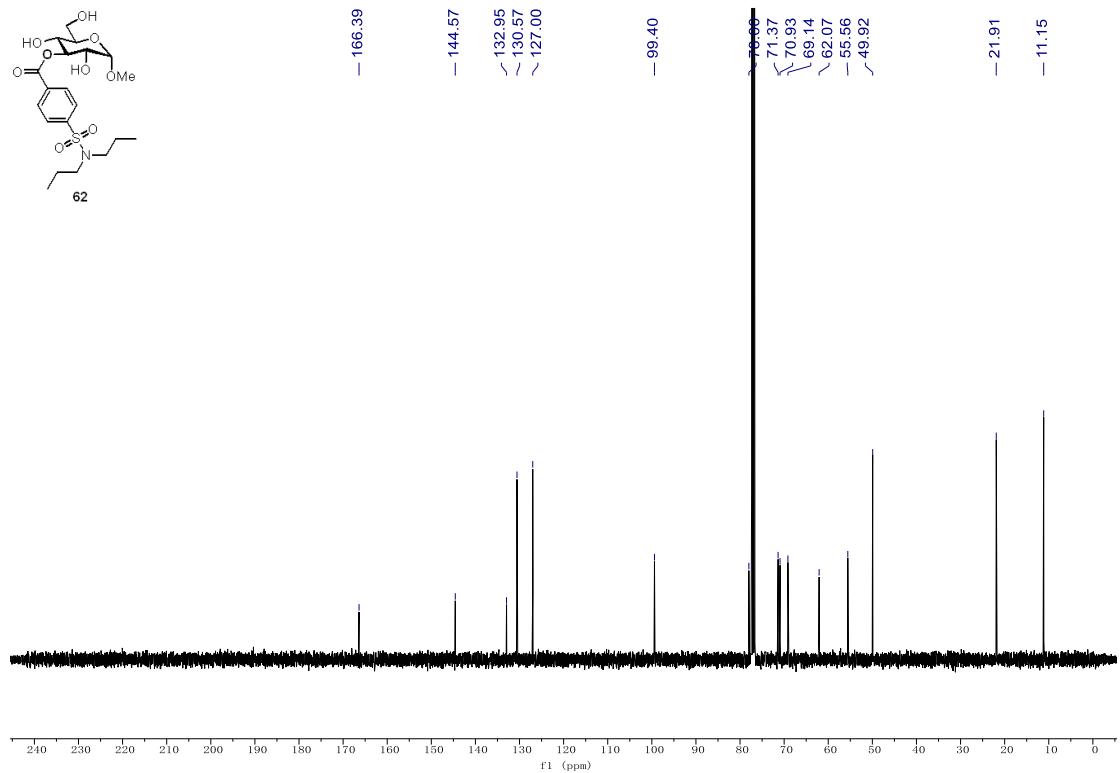


Figure S259. ^{13}C NMR Spectra of **62**

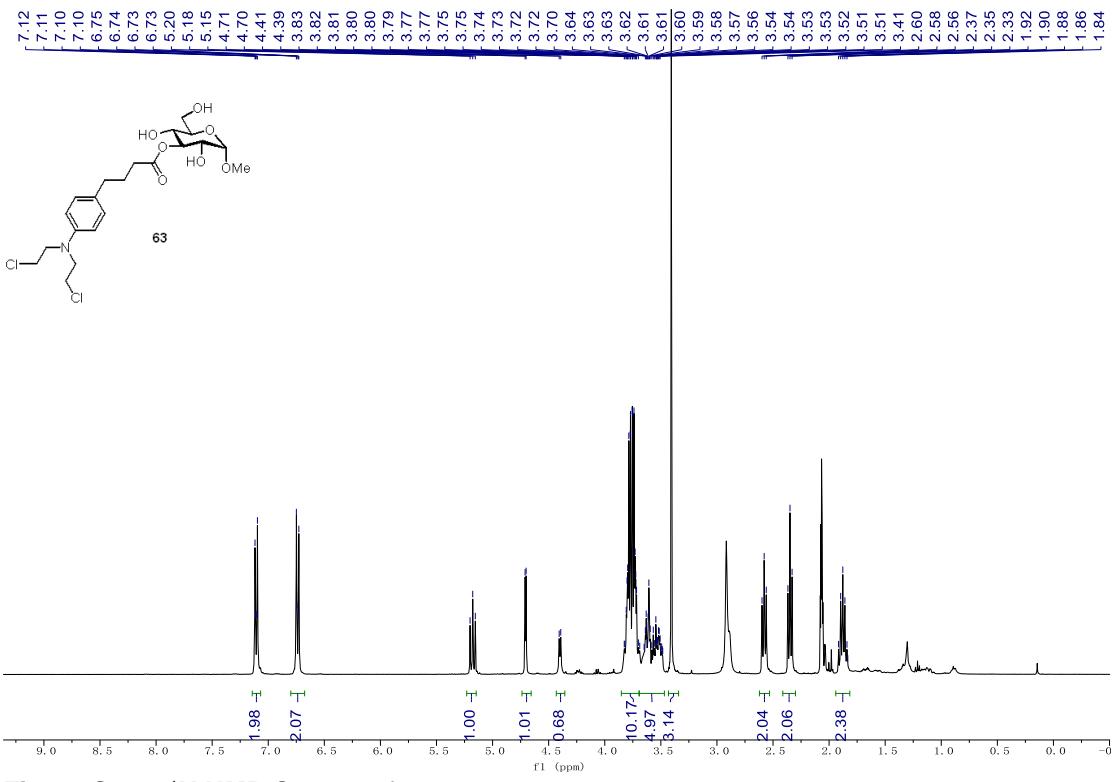


Figure S260. ¹H NMR Spectra of 63

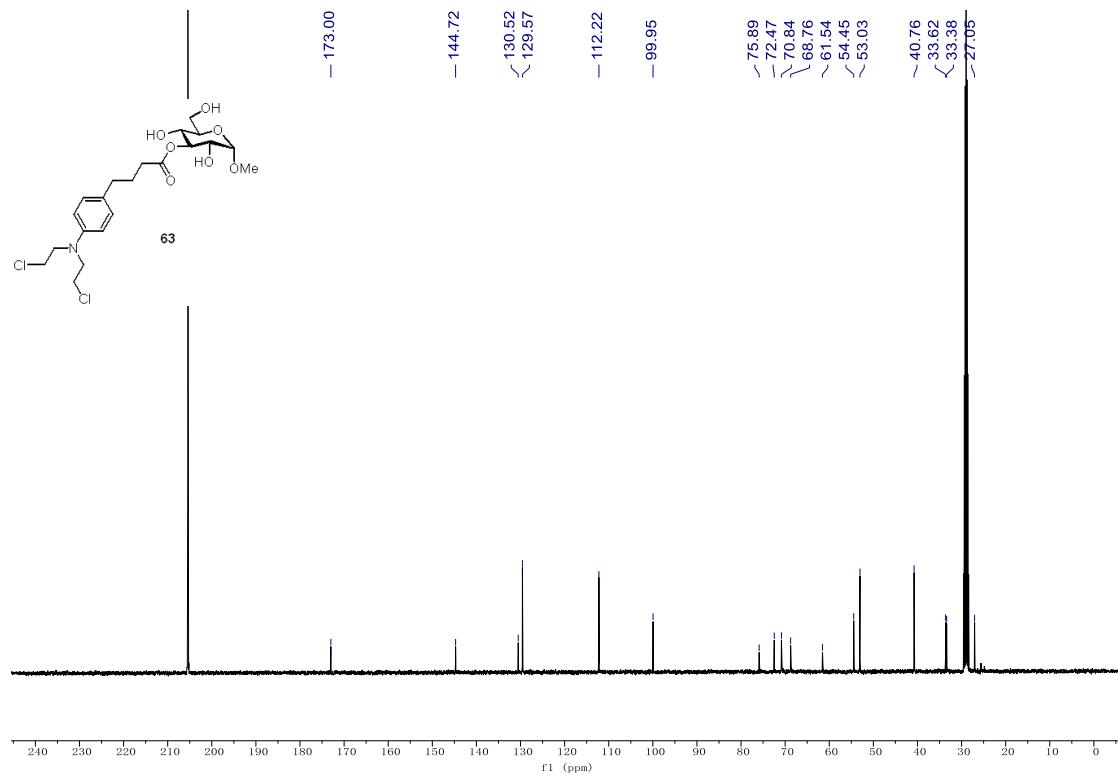
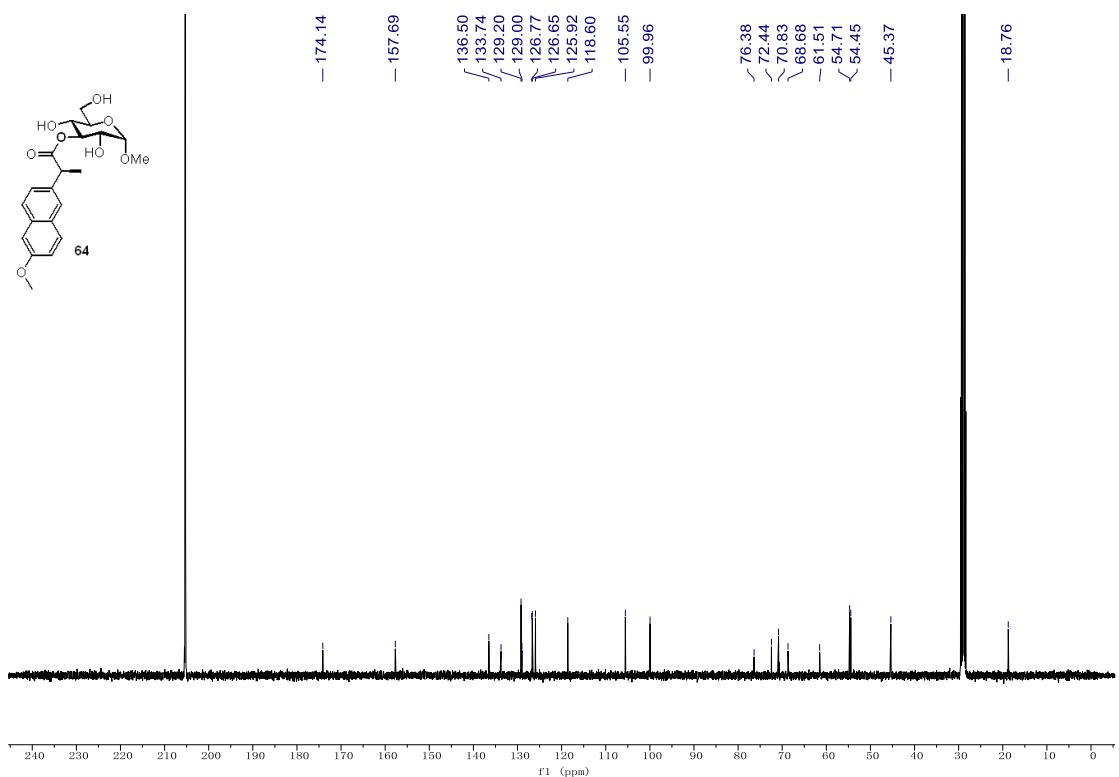
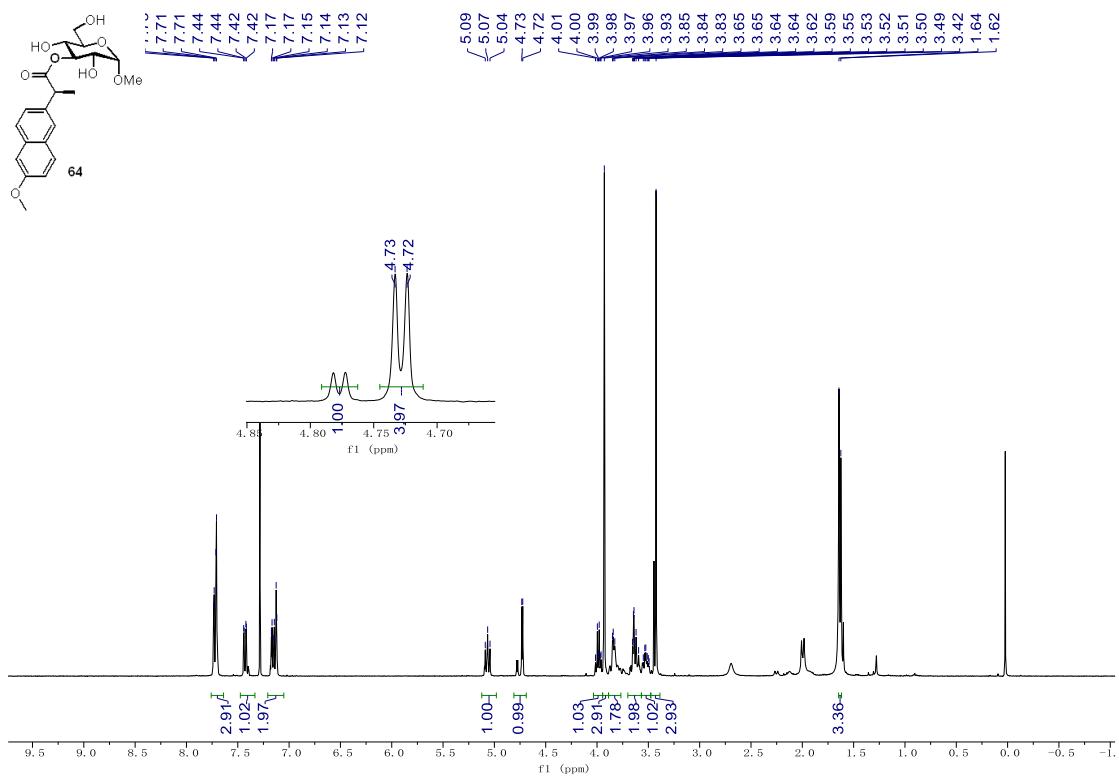


Figure S261. ¹³C NMR Spectra of 63



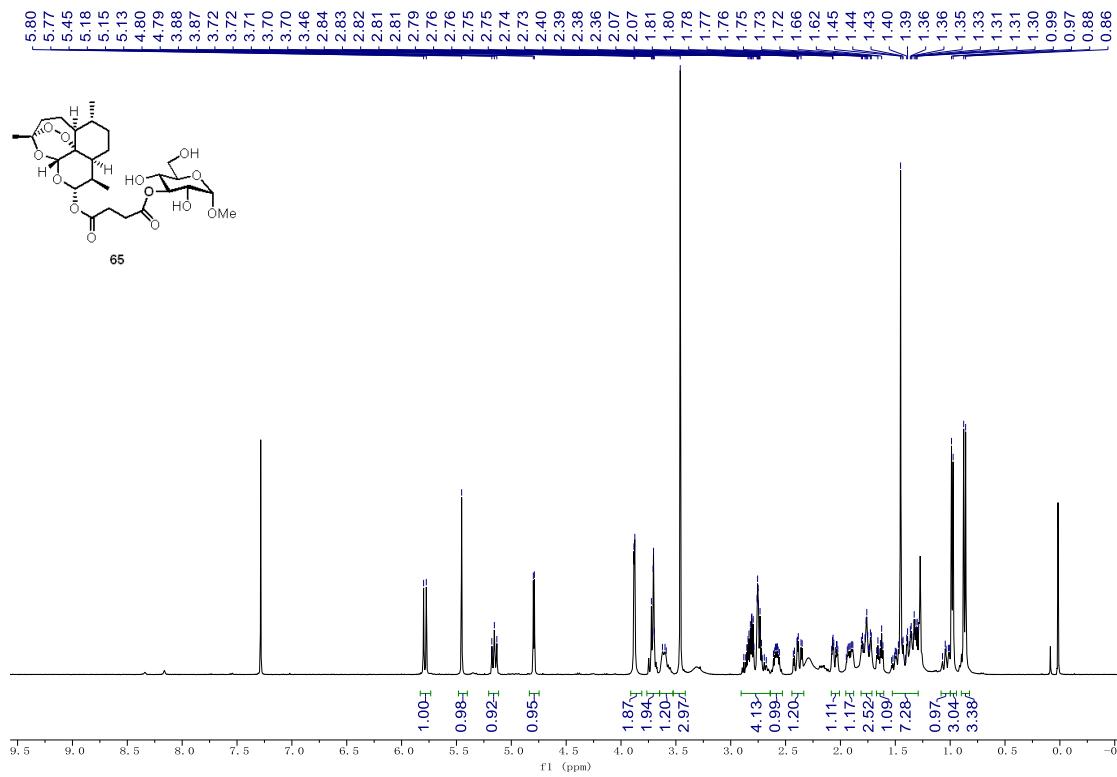


Figure S264. ^1H NMR Spectra of 65

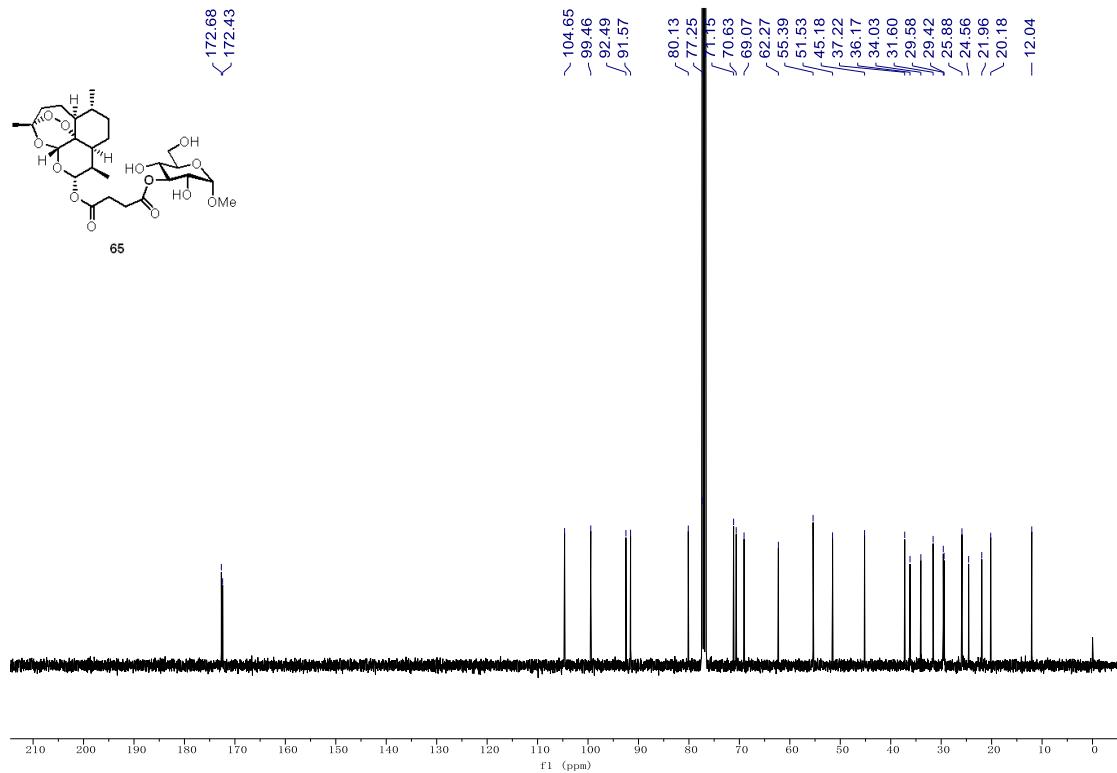


Figure S265. ^{13}C NMR Spectra of 65

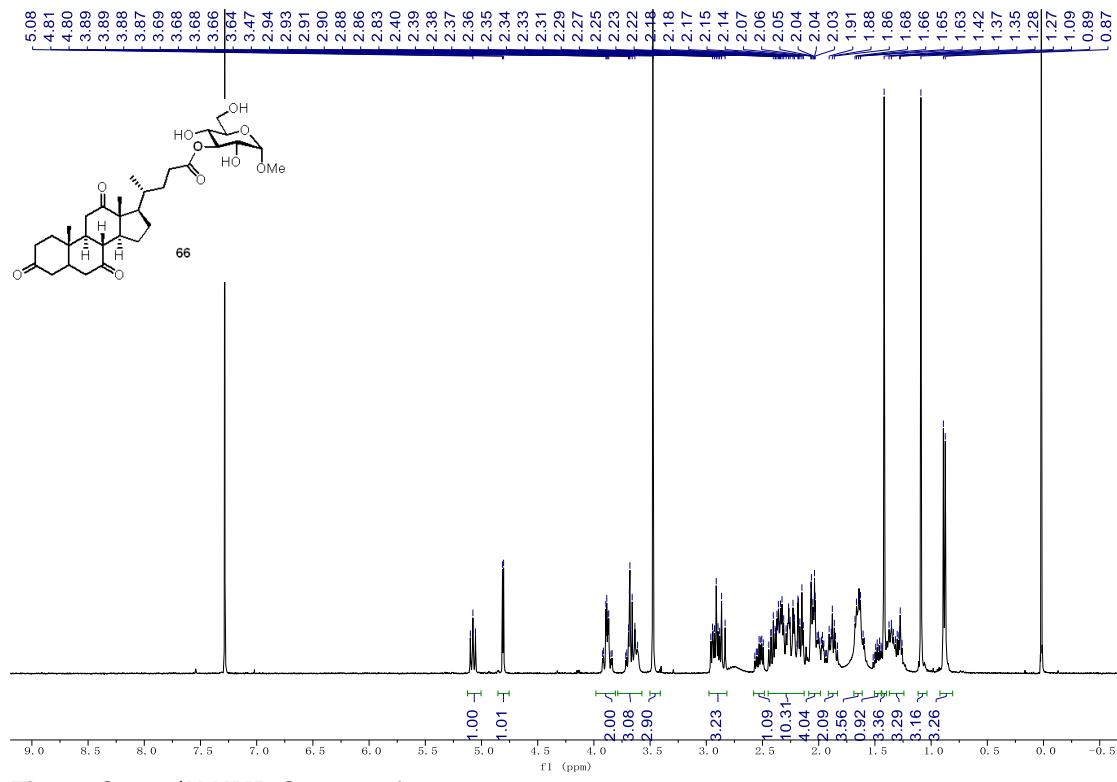


Figure S266. ^1H NMR Spectra of 66

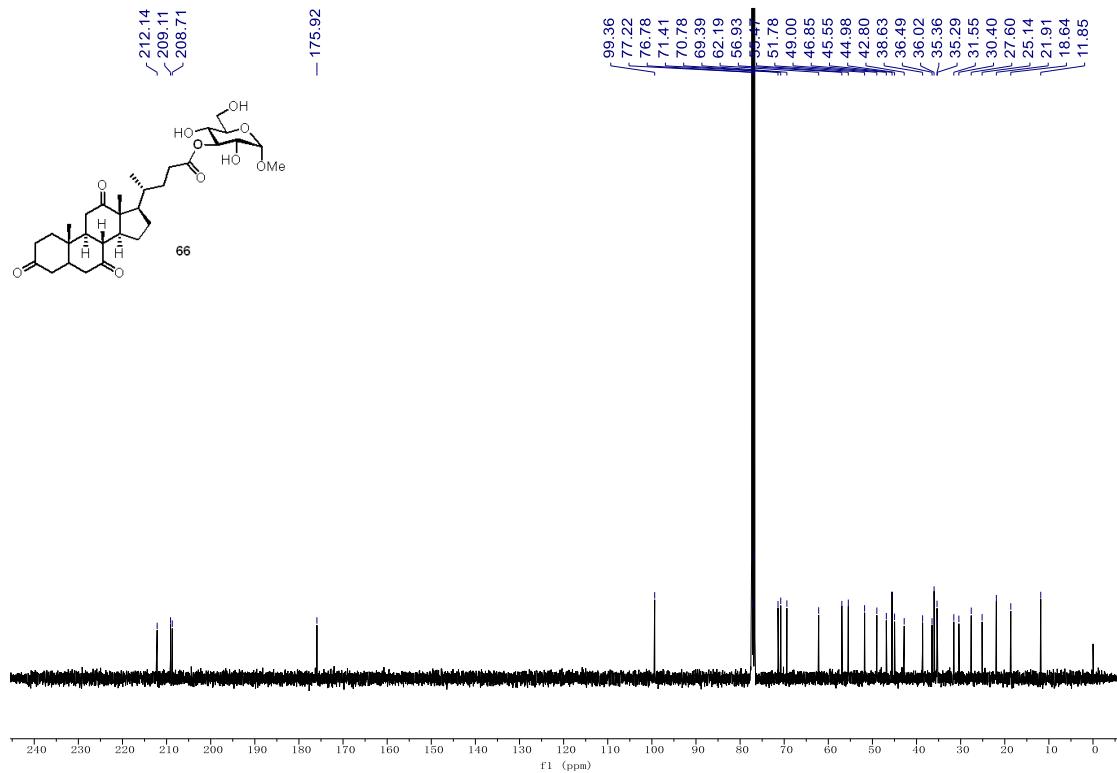


Figure S267. ^{13}C NMR Spectra of 66

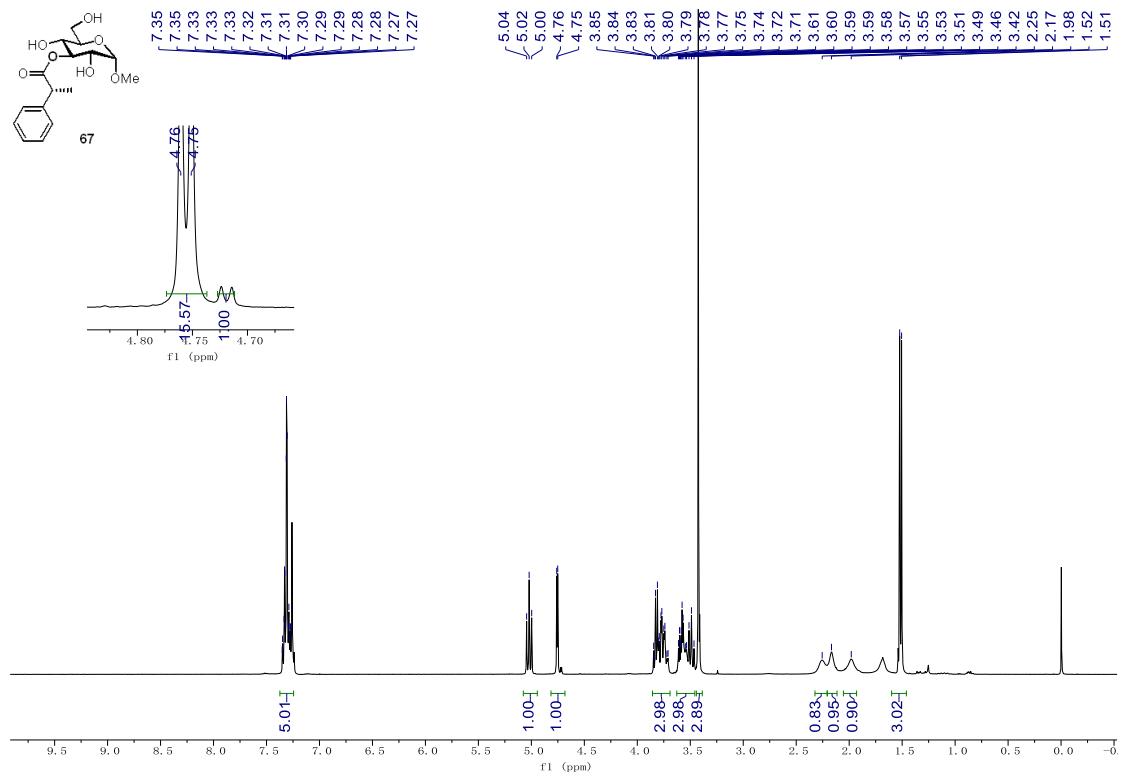


Figure S268. ^1H NMR Spectra of 67

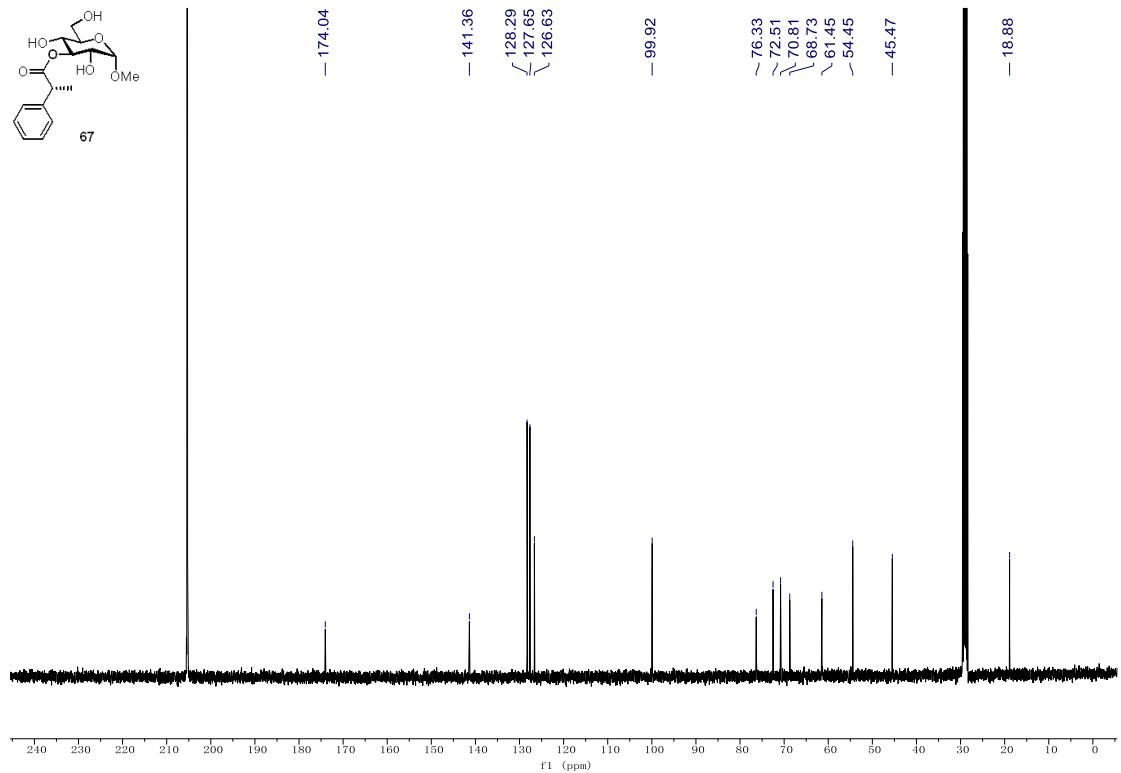


Figure S269. ^{13}C NMR Spectra of 67

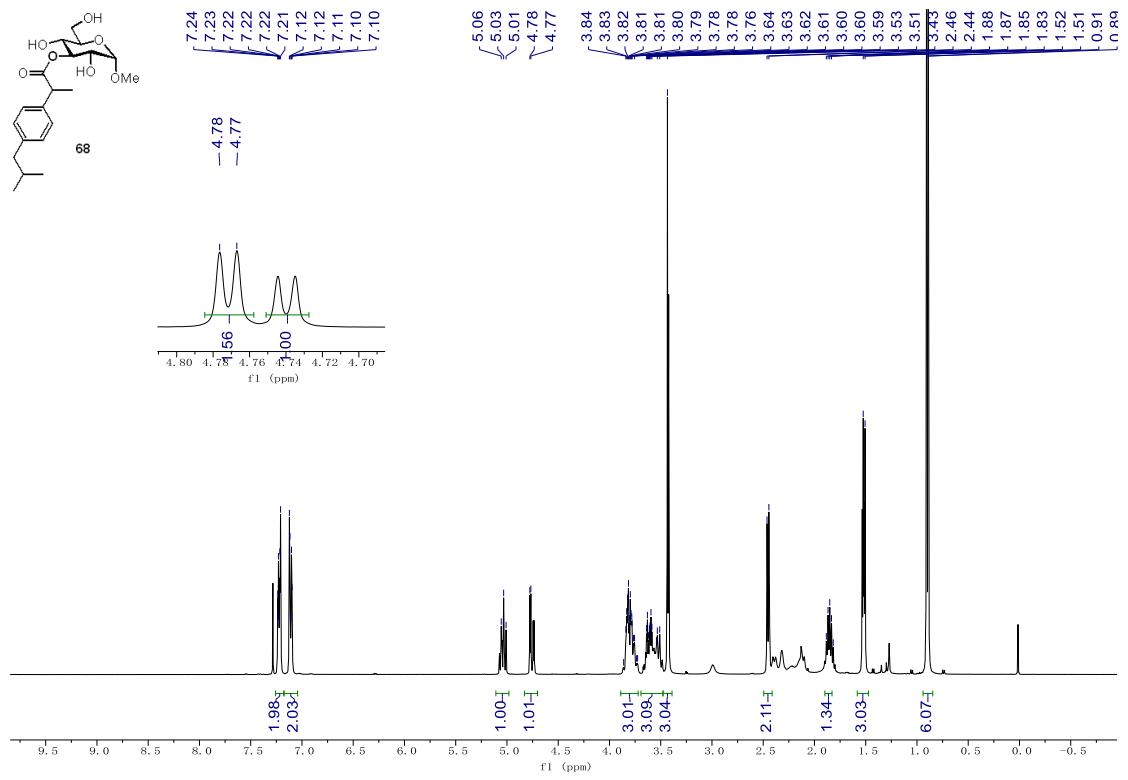


Figure S270. ^1H NMR Spectra of **68**

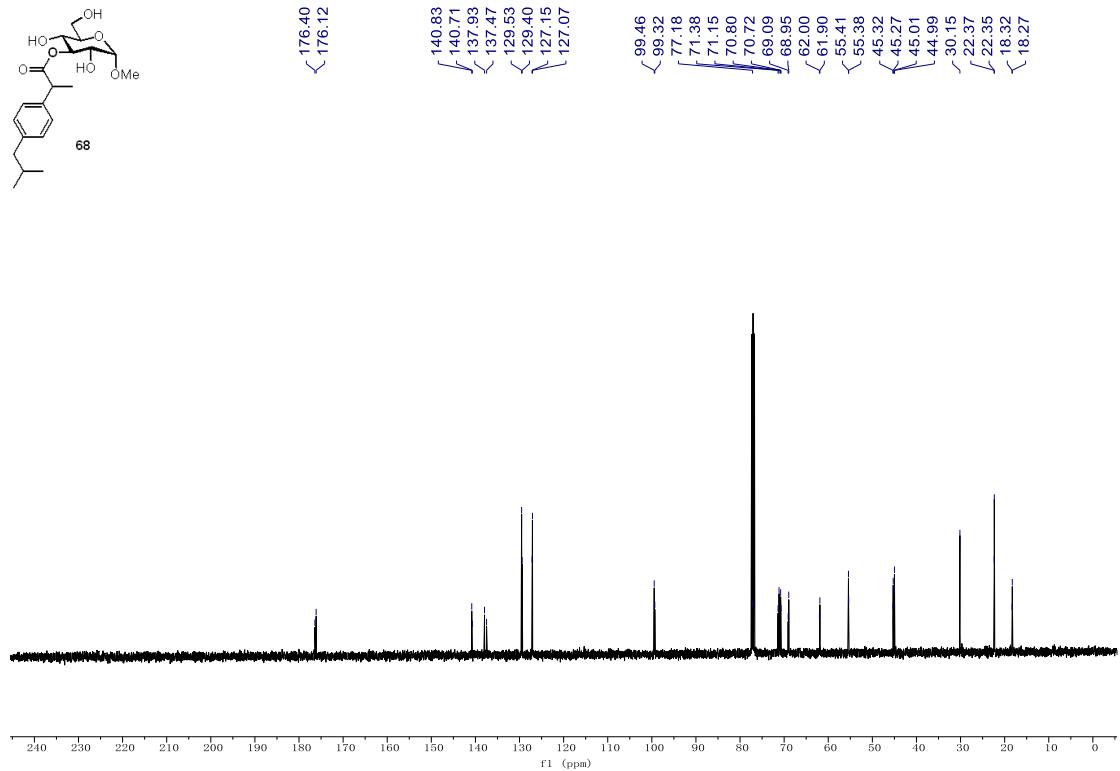


Figure S271. ^{13}C NMR Spectra of **68**

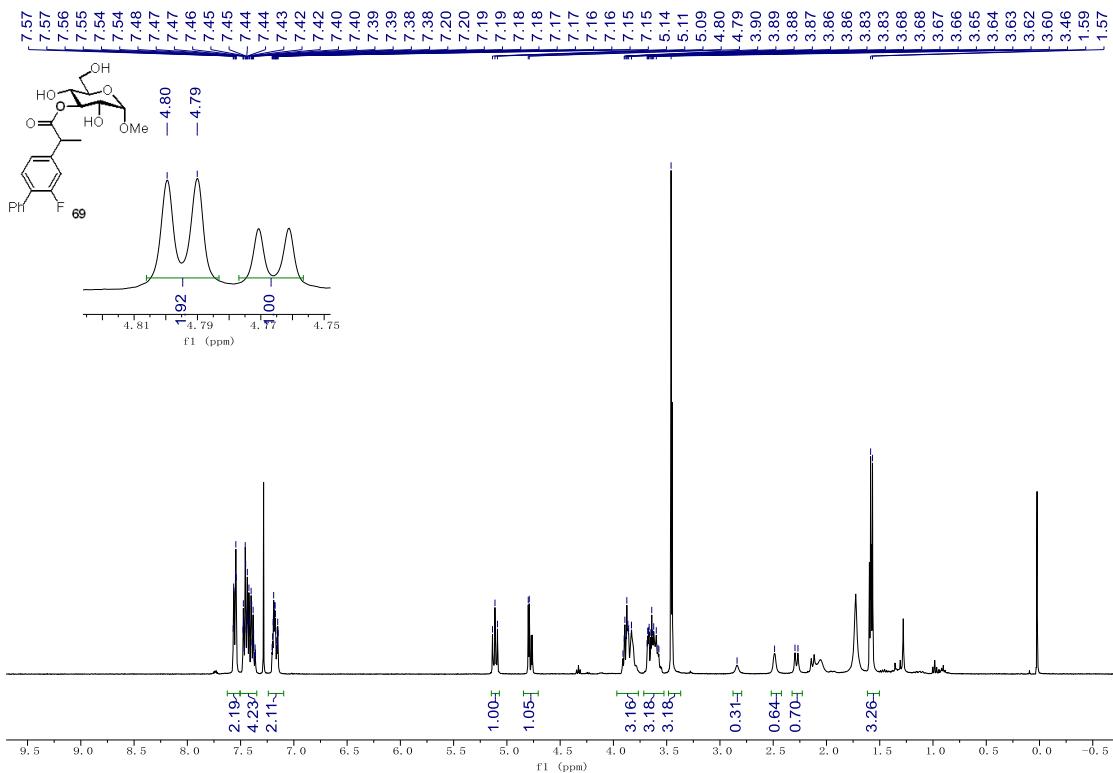


Figure S272. ^1H NMR Spectra of **69**

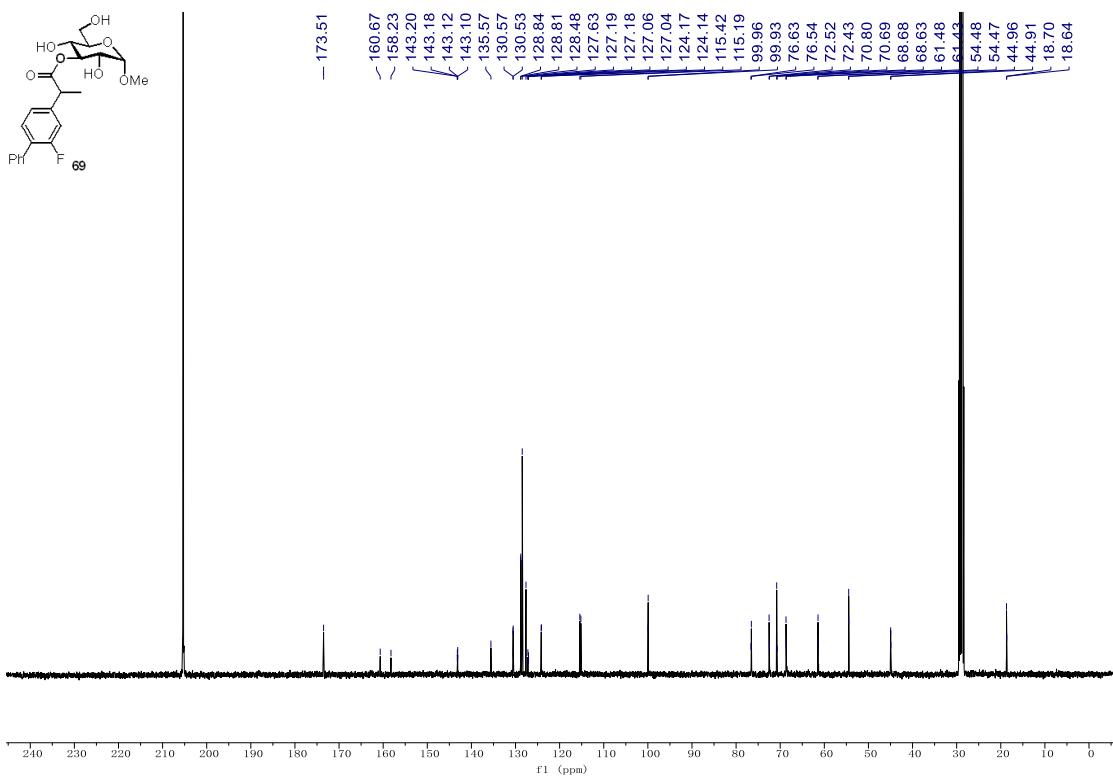


Figure S273. ^{13}C NMR Spectra of **69**

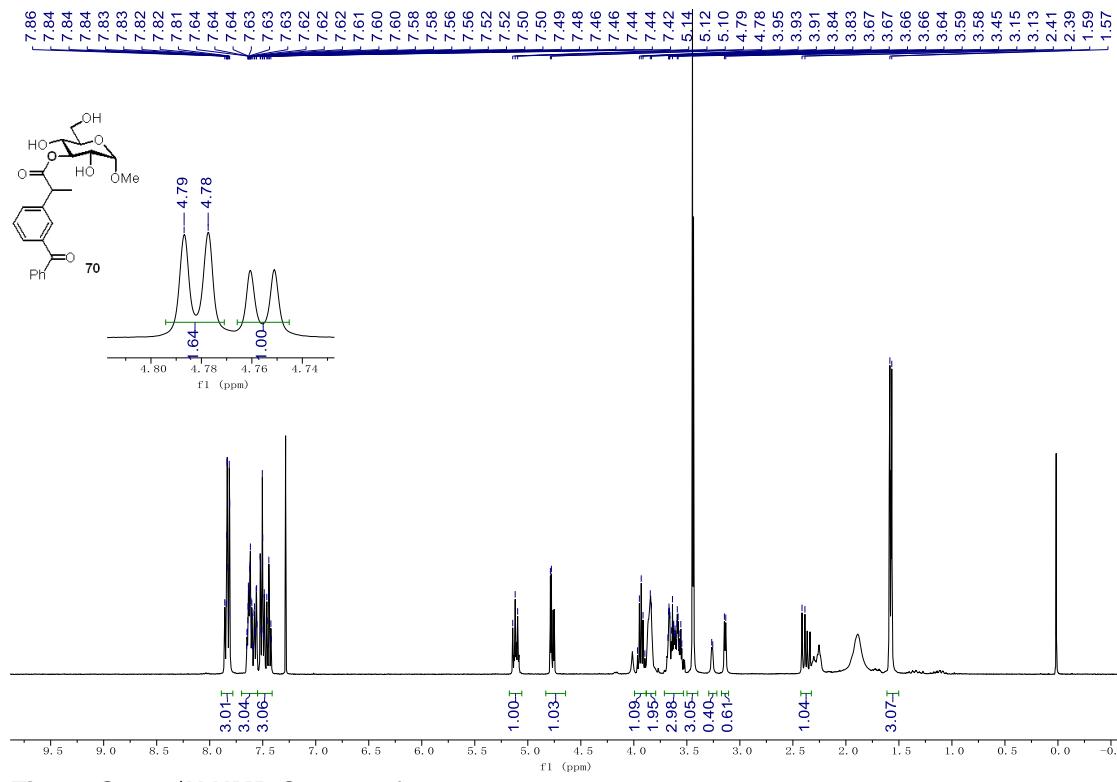


Figure S274. ^1H NMR Spectra of **70**

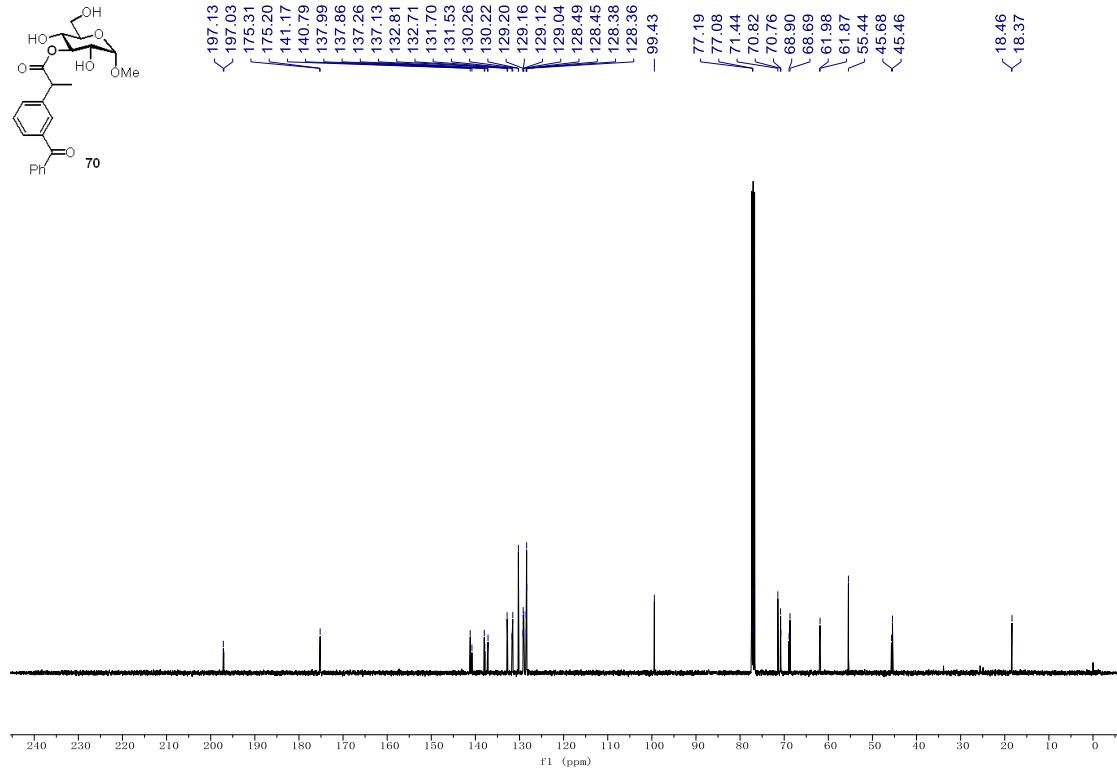


Figure S275. ^{13}C NMR Spectra of **70**

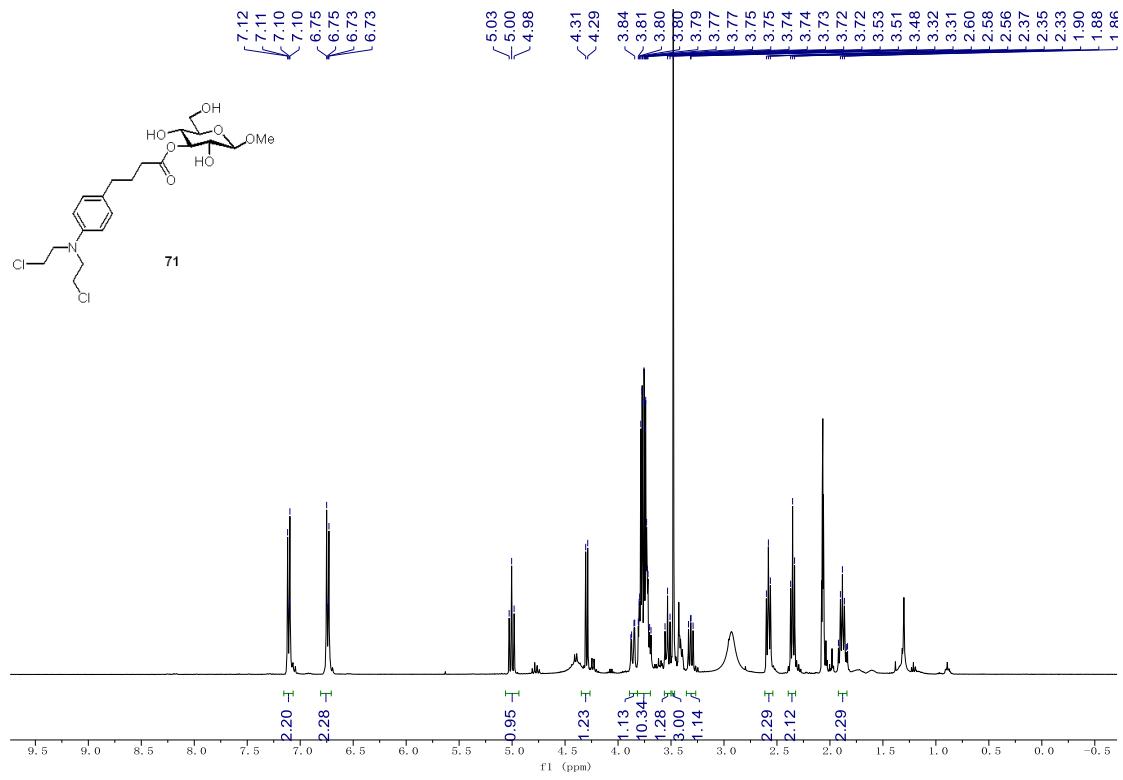


Figure S276. ^1H NMR Spectra of 71

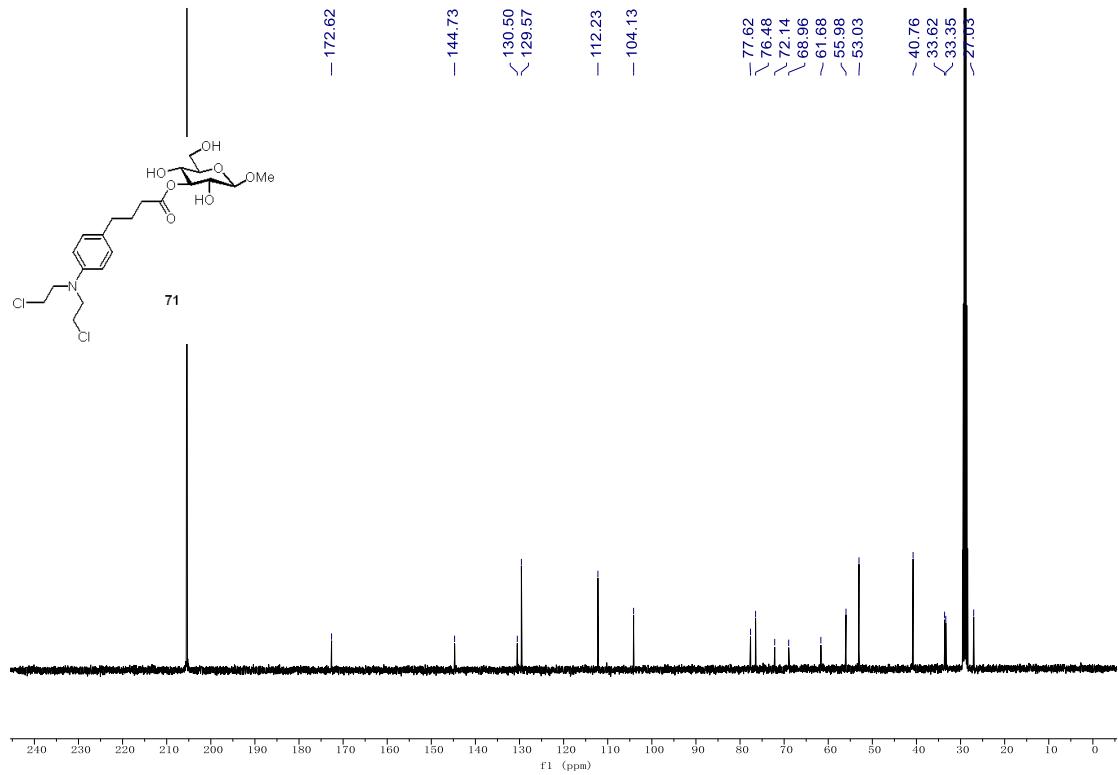


Figure S277. ^{13}C NMR Spectra of 71

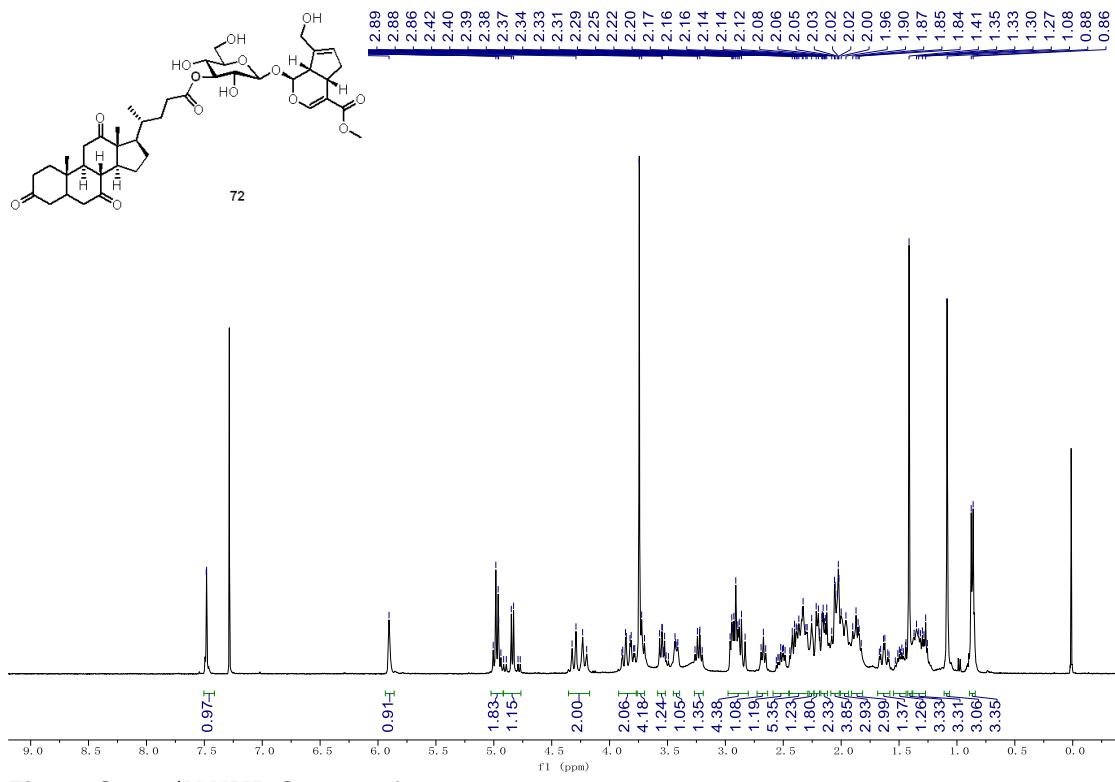


Figure S278. ^1H NMR Spectra of **72**

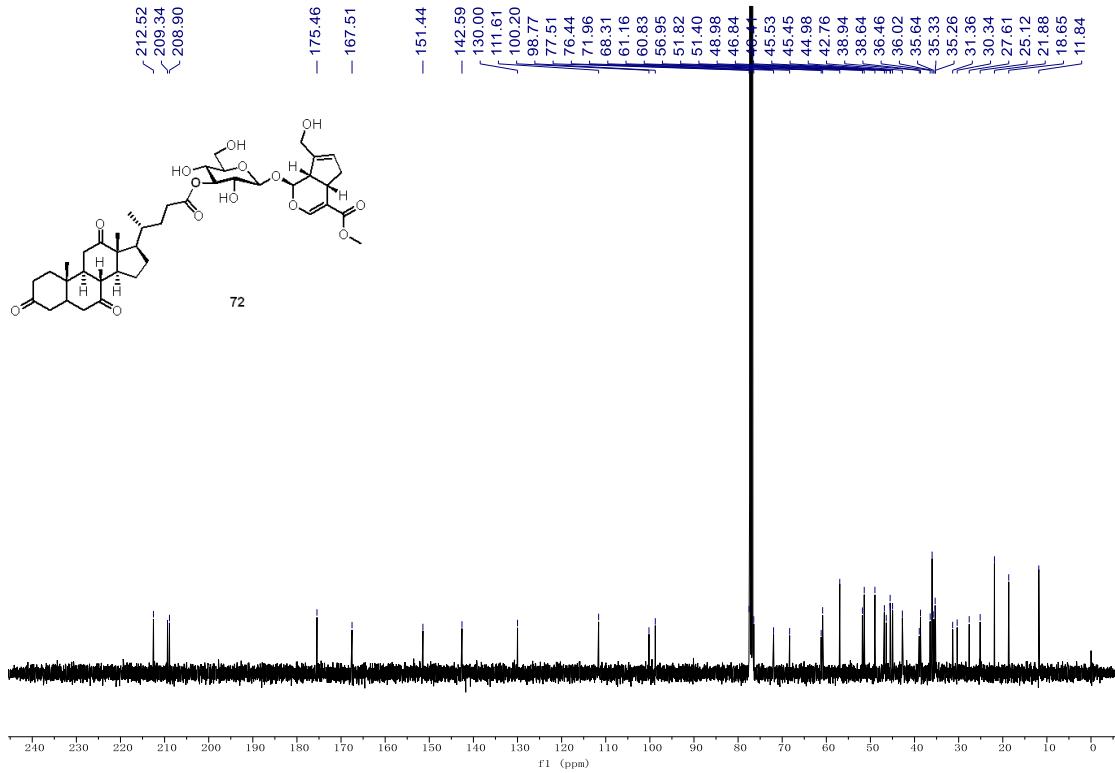


Figure S279. ^{13}C NMR Spectra of **72**

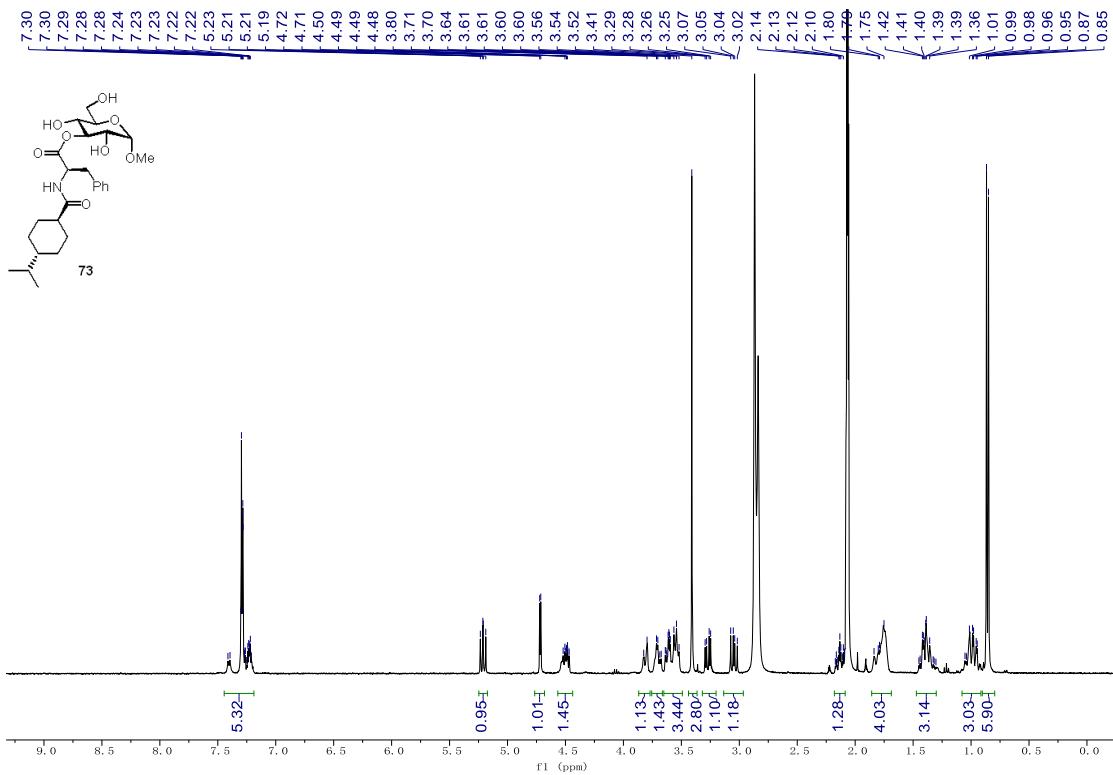


Figure S280. ^1H NMR Spectra of 73

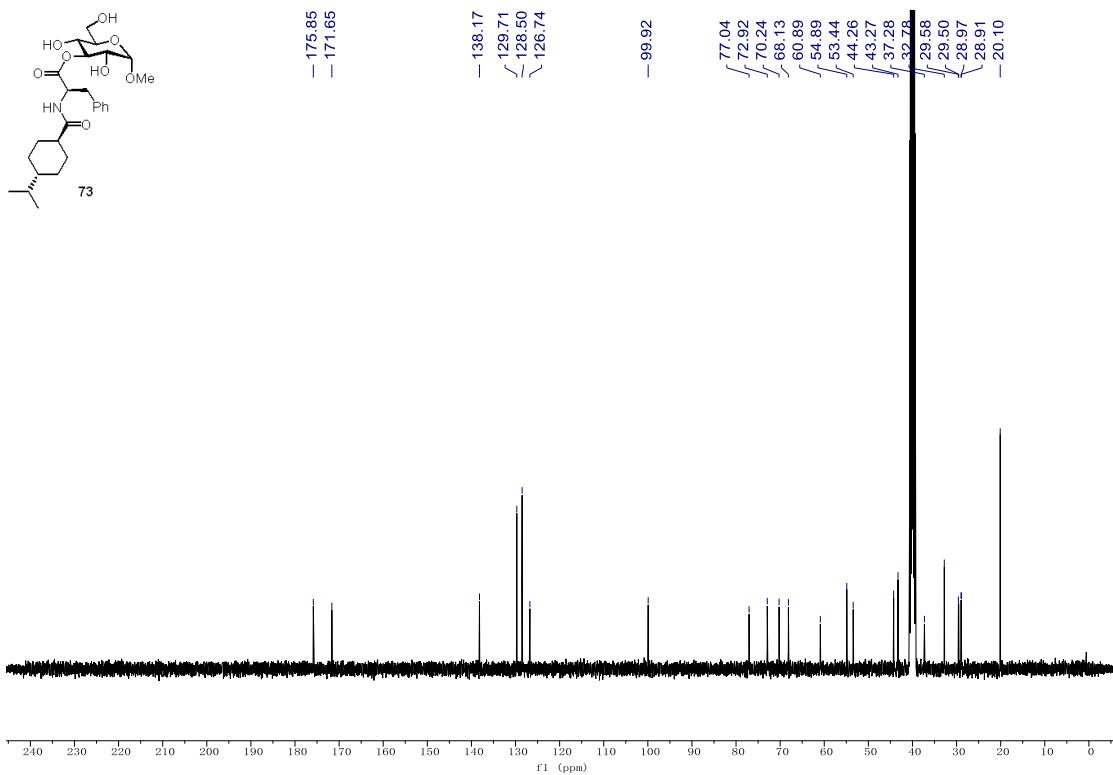


Figure S281. ^{13}C NMR Spectra of 73

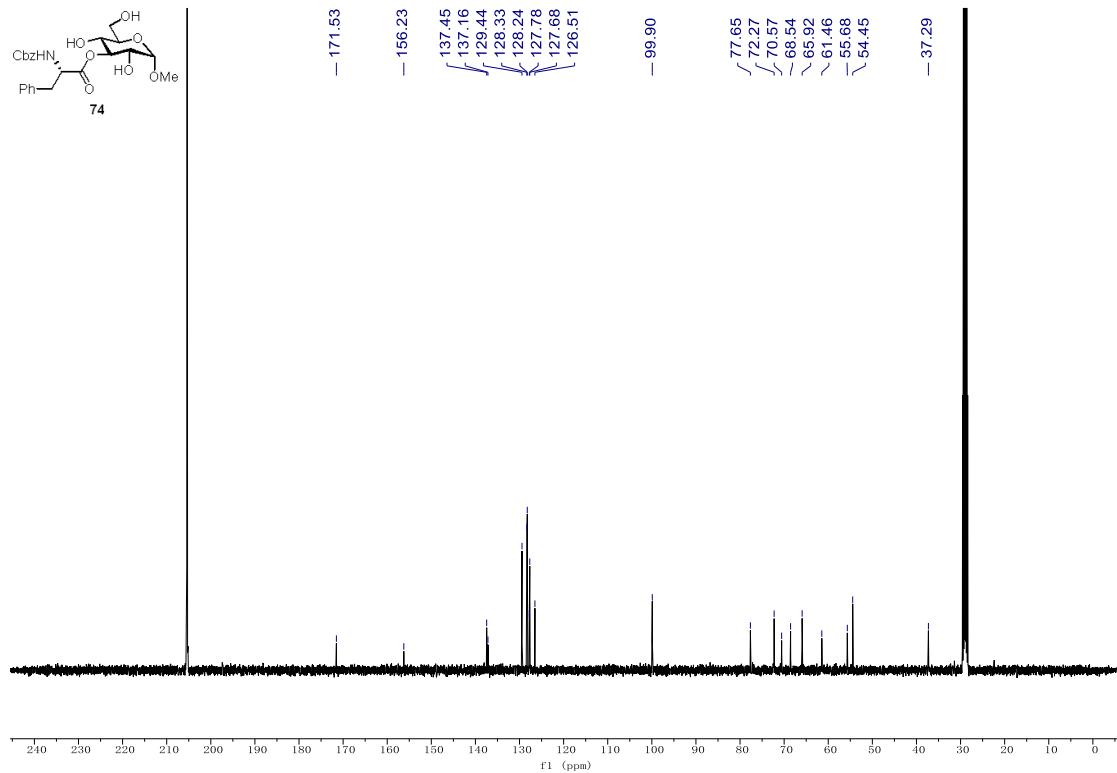
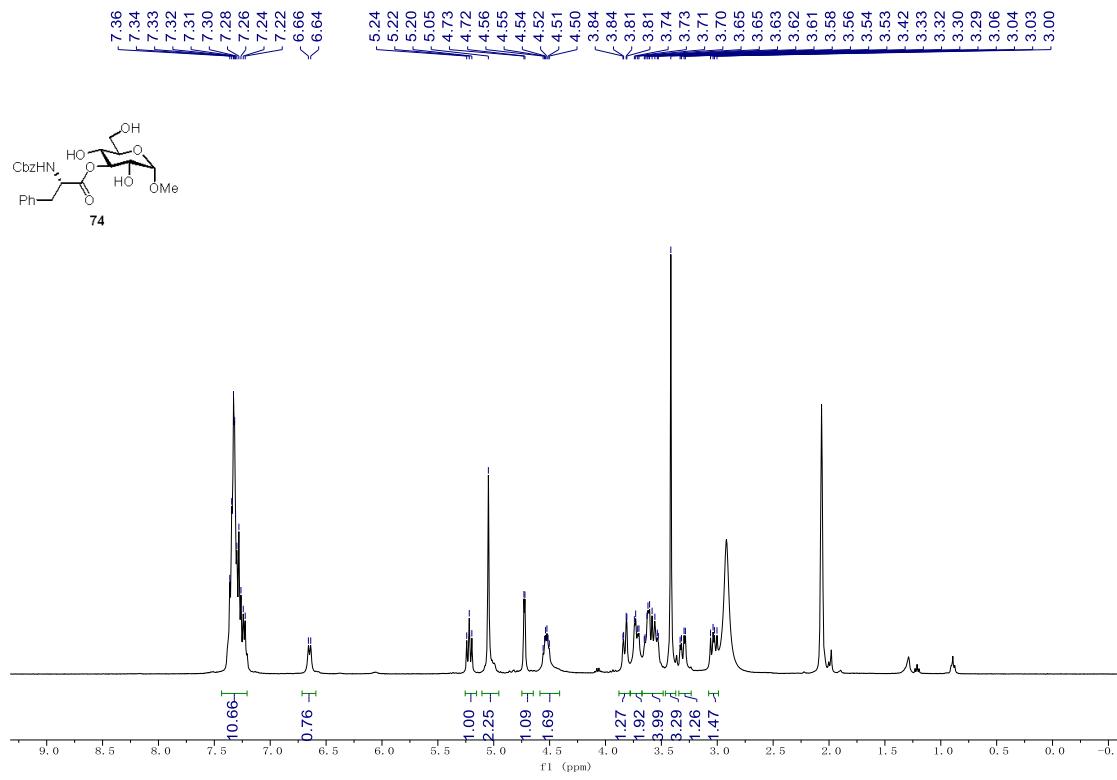


Figure S283. ¹³C NMR Spectra of 74

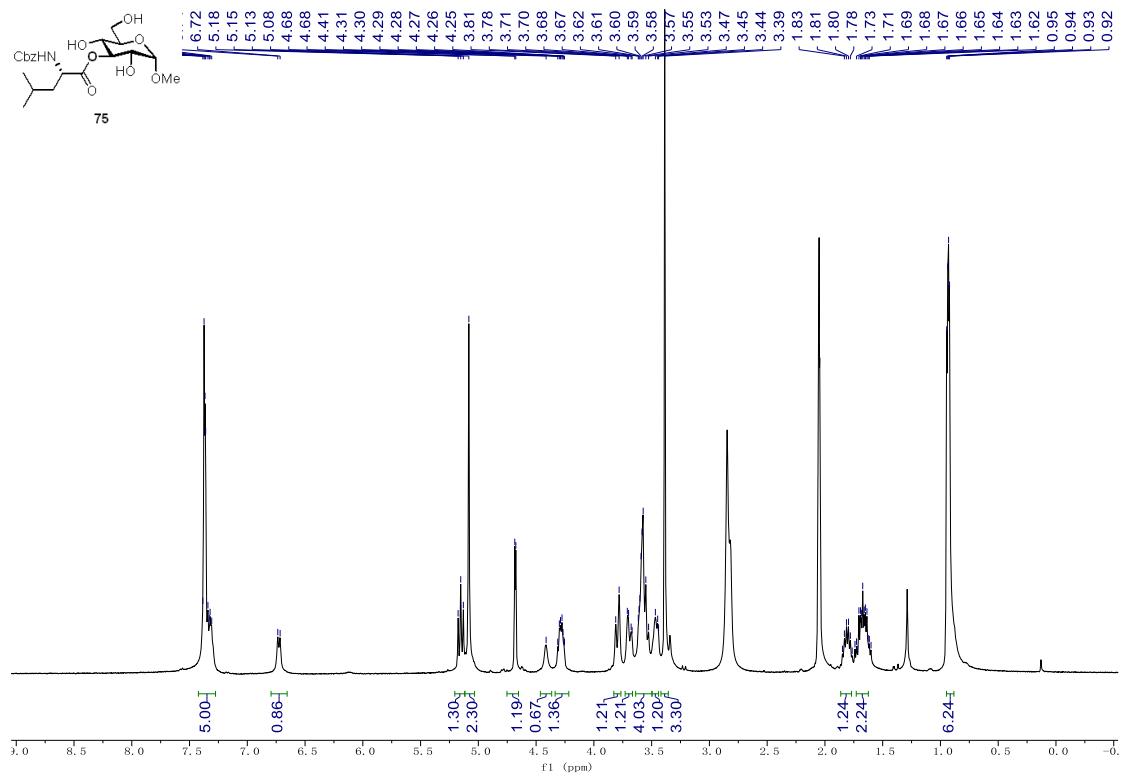


Figure S284. ^1H NMR Spectra of **75**

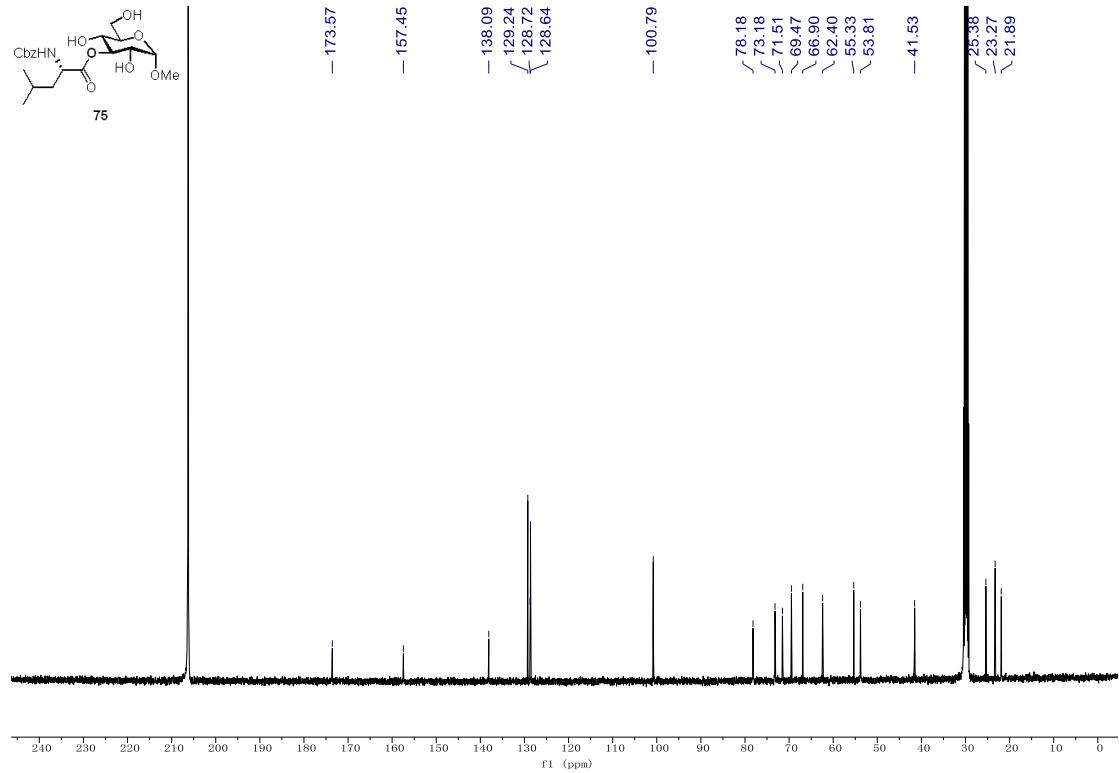


Figure S285. ^{13}C NMR Spectra of **75**

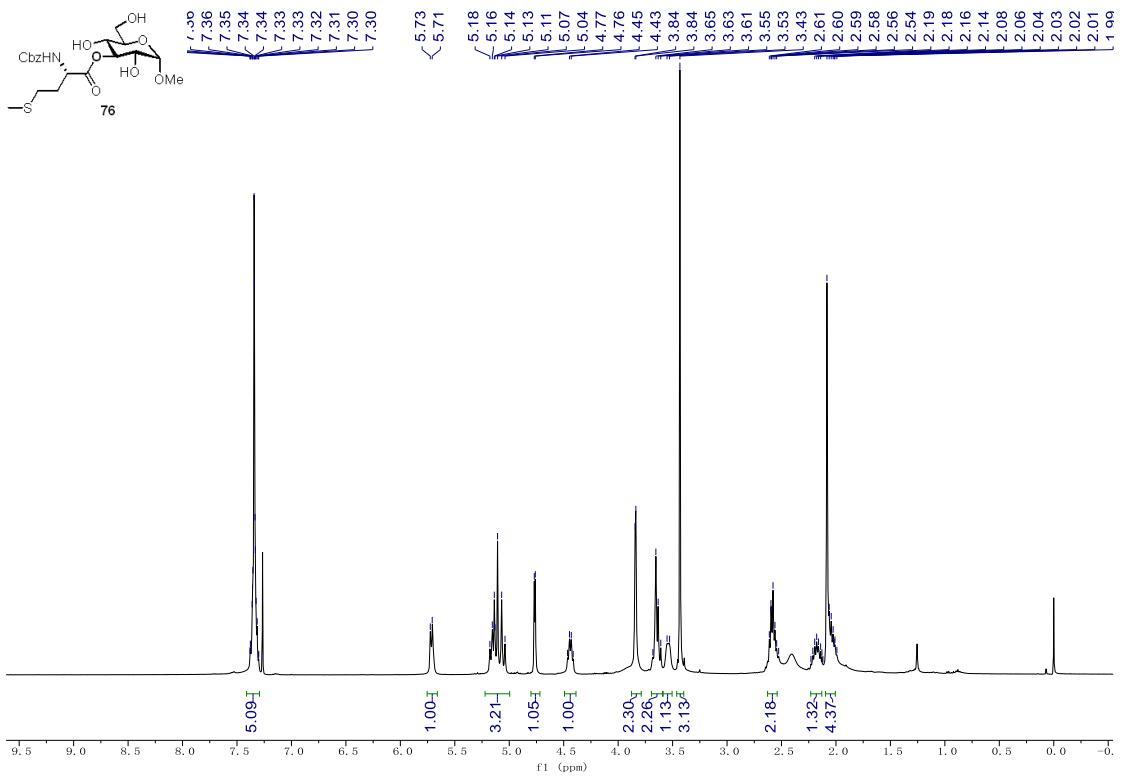


Figure S286. ^1H NMR Spectra of **76**

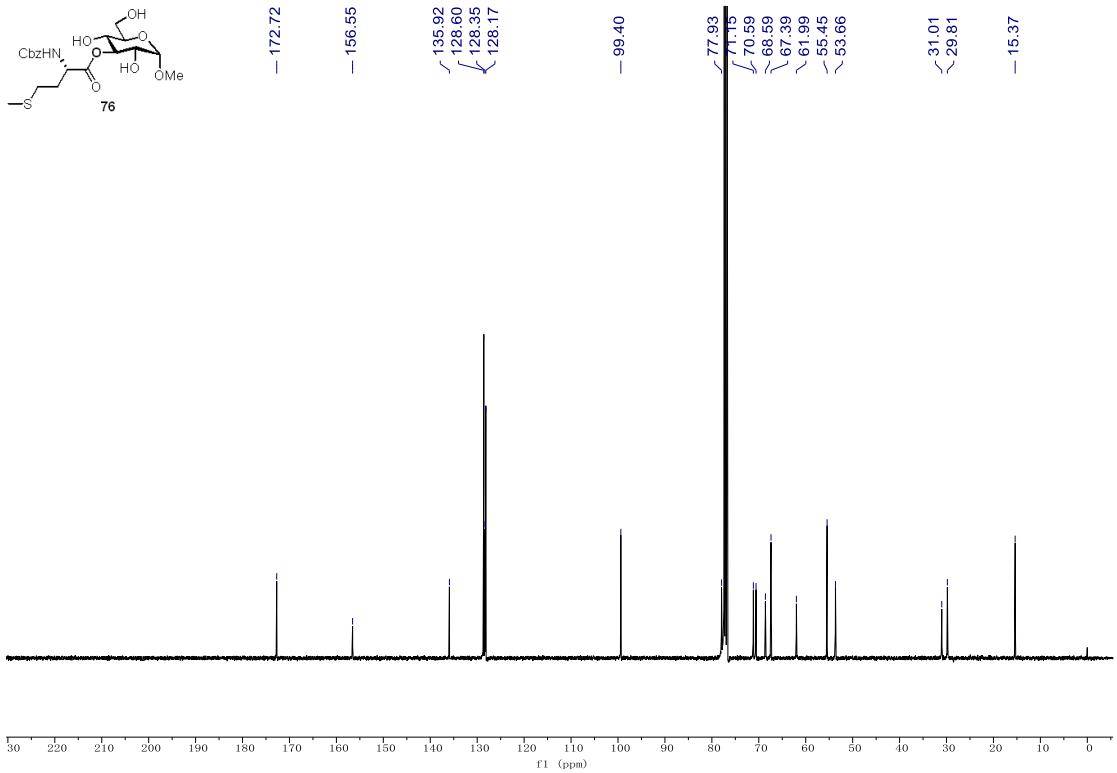


Figure S287. ^{13}C NMR Spectra of **76**

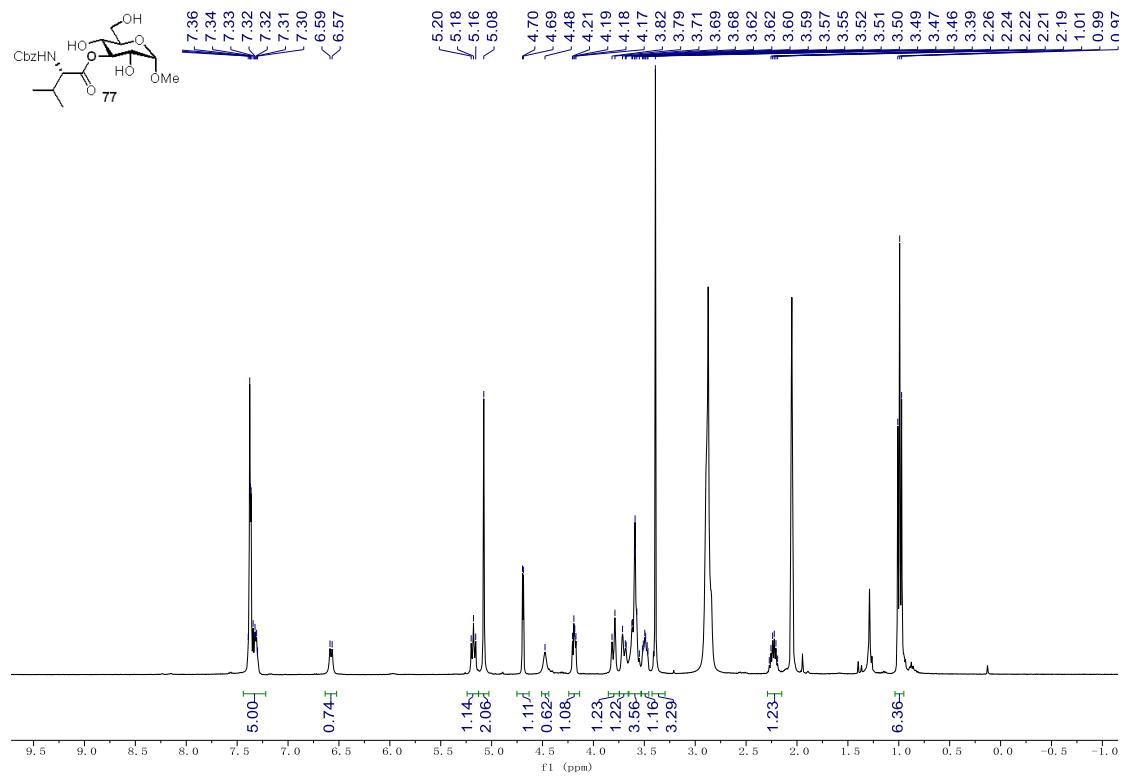


Figure S288. ^1H NMR Spectra of **77**

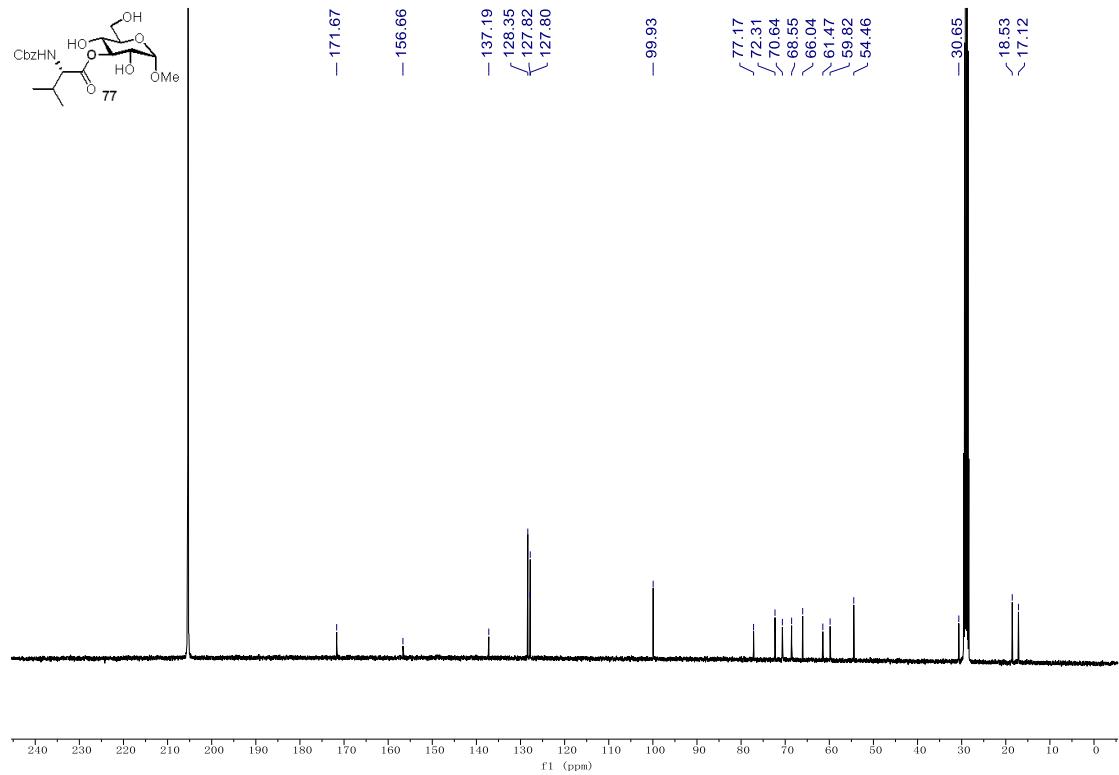


Figure S289. ^{13}C NMR Spectra of **77**

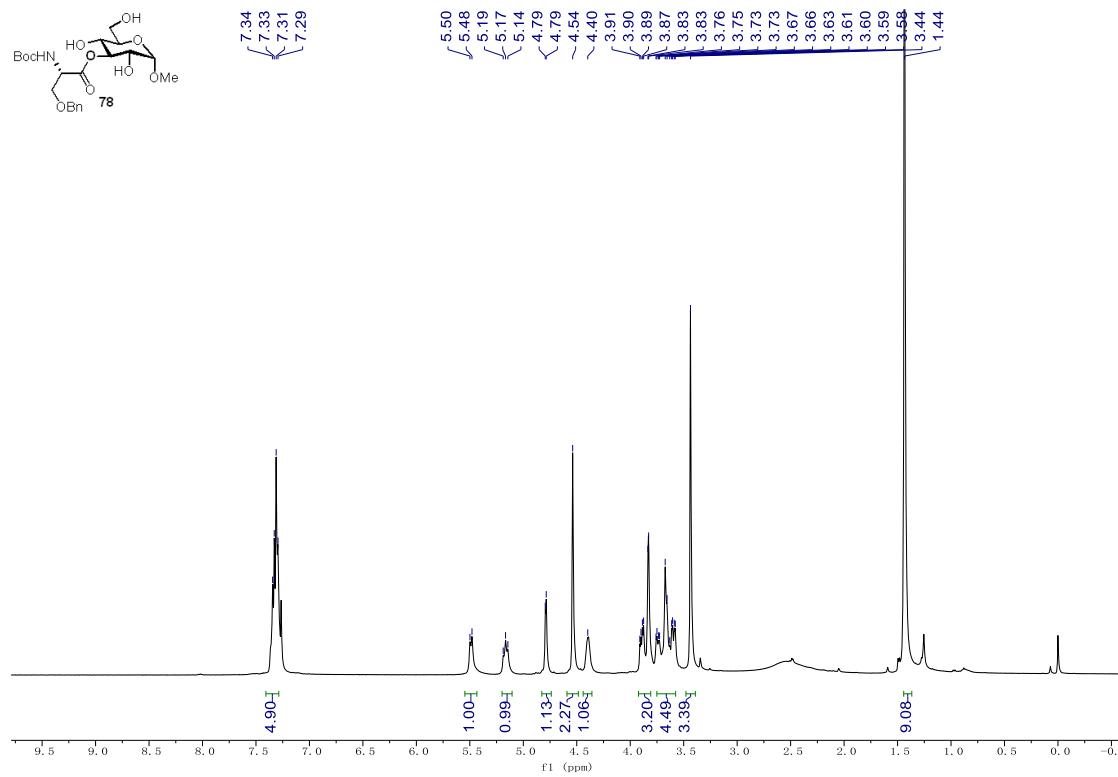


Figure S290. ^1H NMR Spectra of **78**

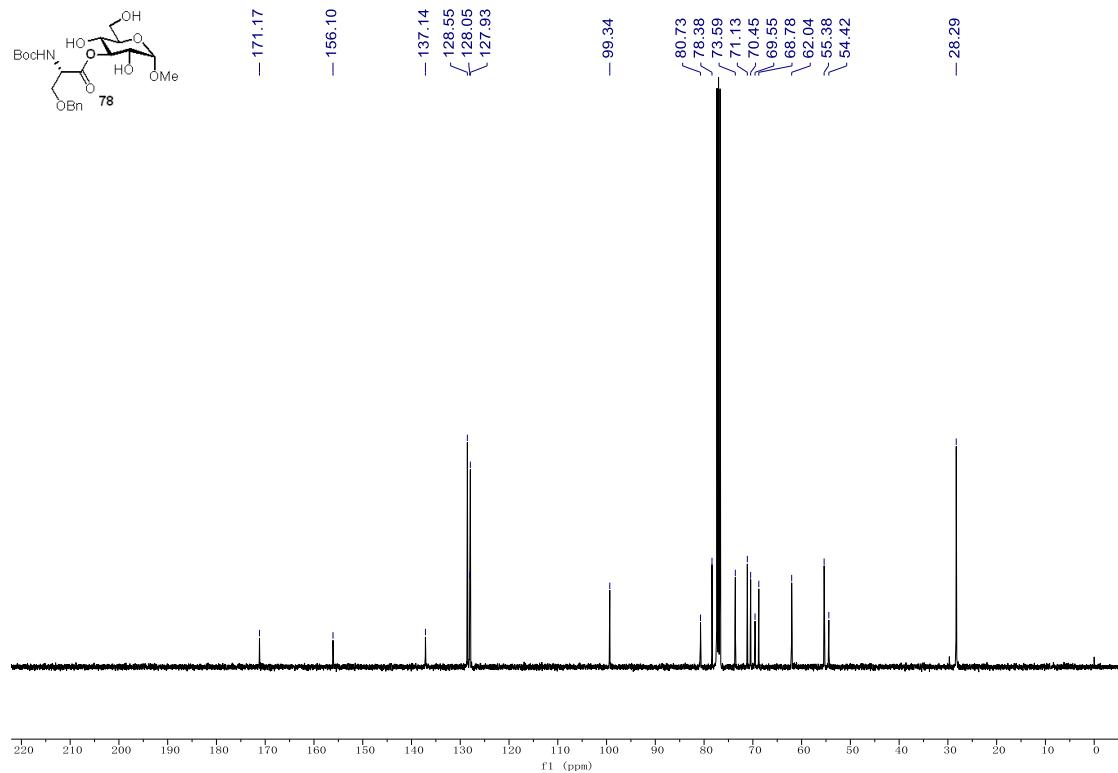


Figure S291. ^{13}C NMR Spectra of **78**

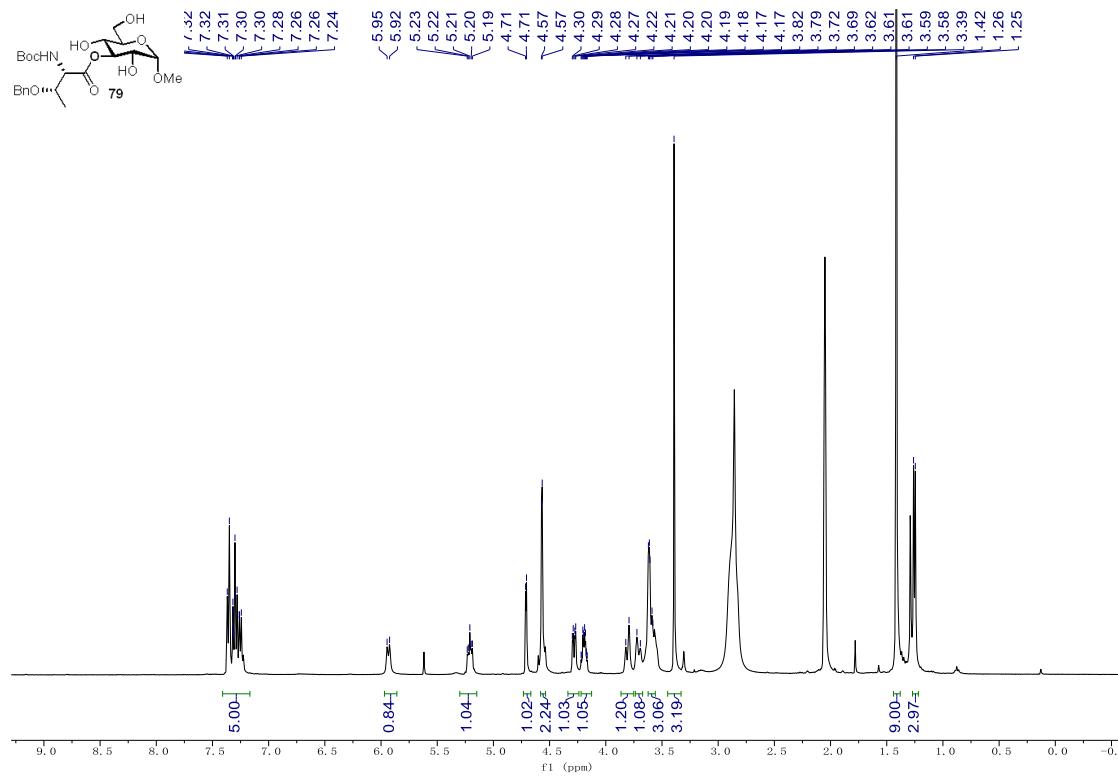


Figure S292. ^1H NMR Spectra of **79**

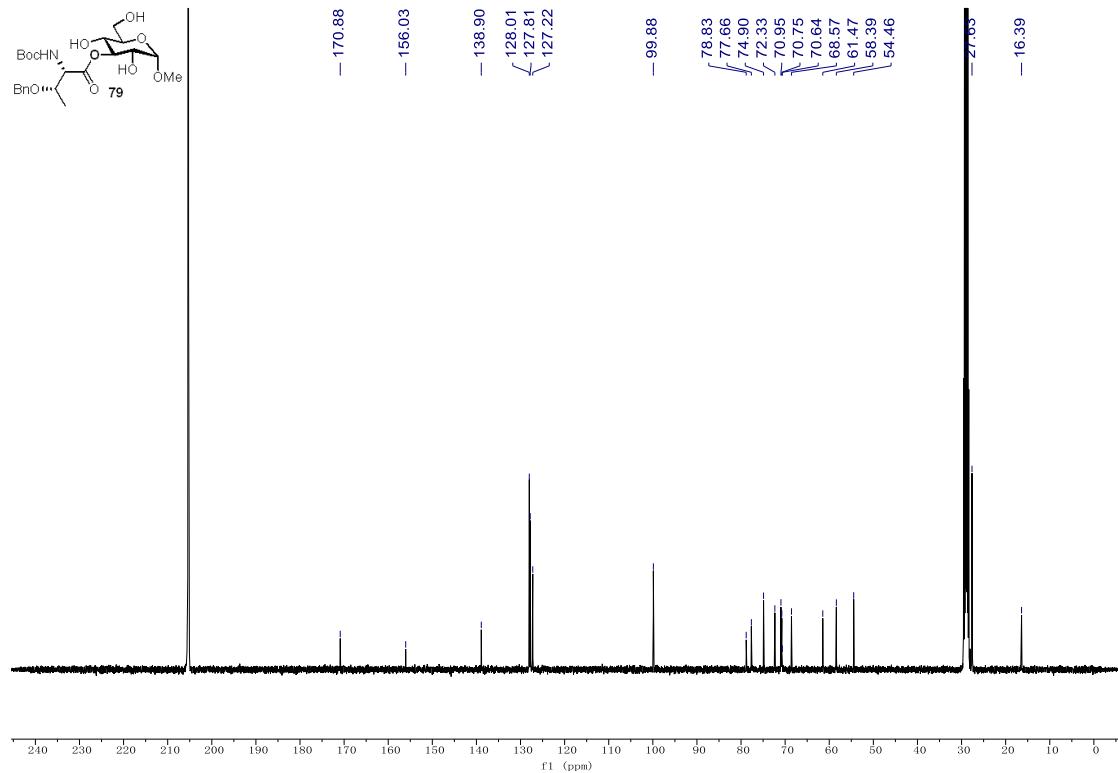


Figure S293. ^{13}C NMR Spectra of **79**

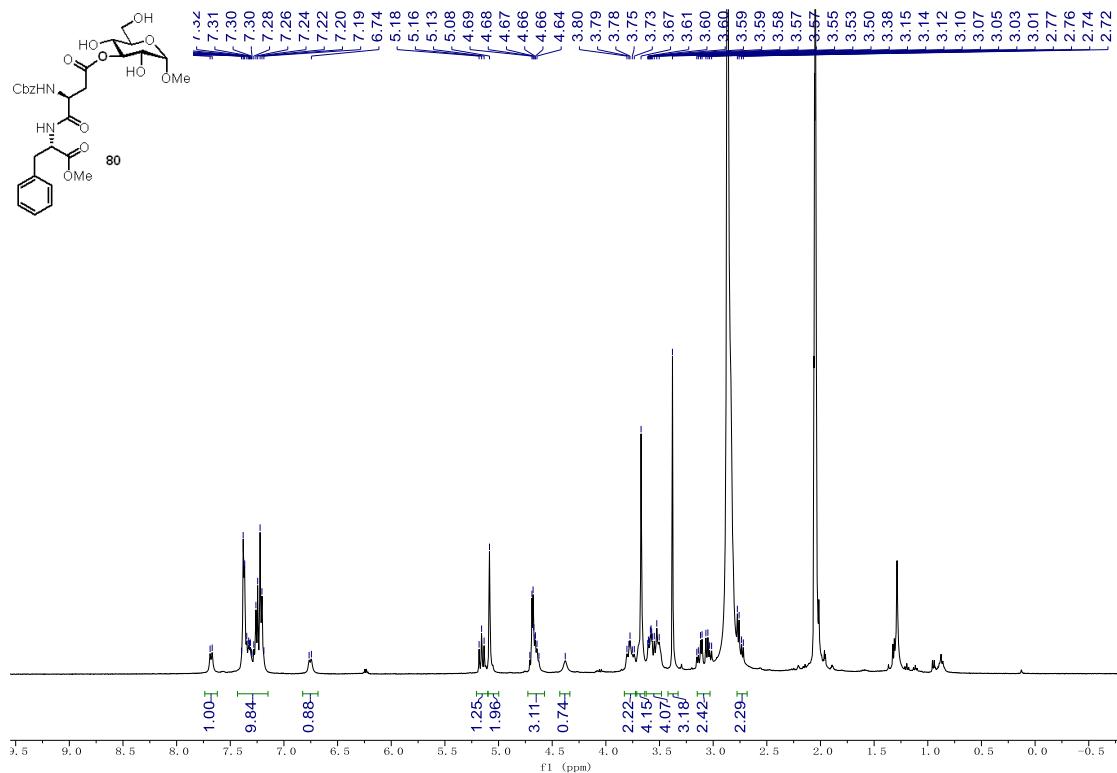


Figure S294. ^1H NMR Spectra of **80**

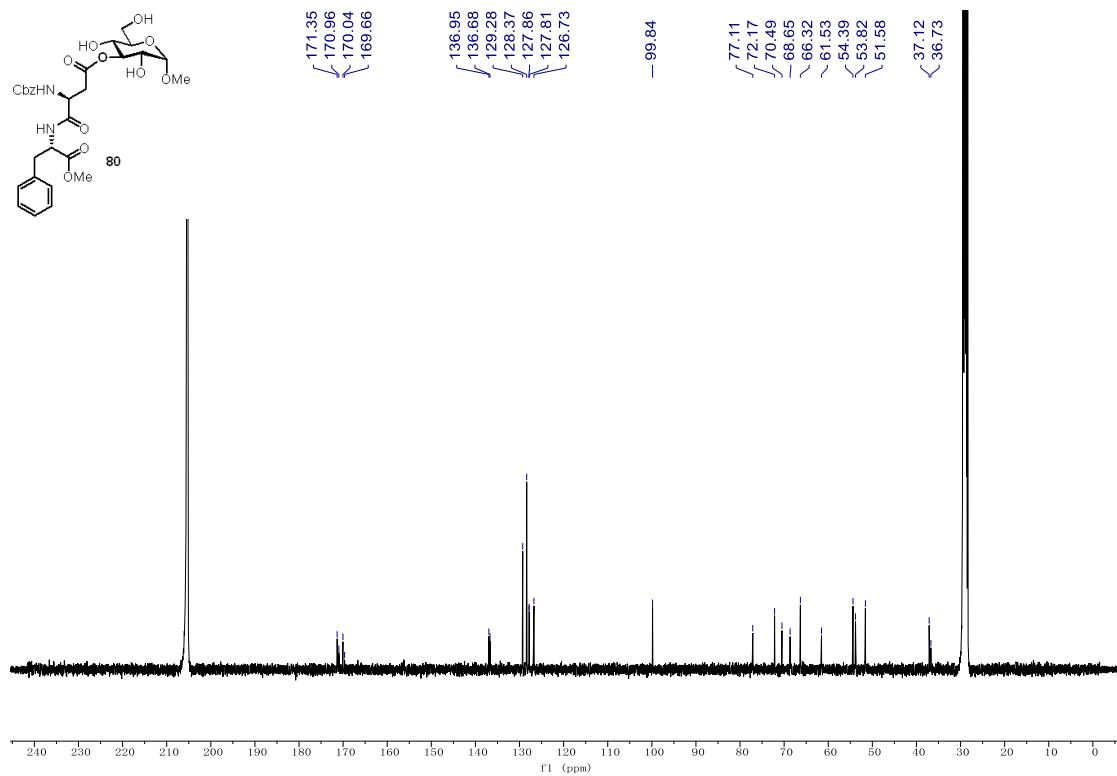


Figure S295. ^{13}C NMR Spectra of **80**

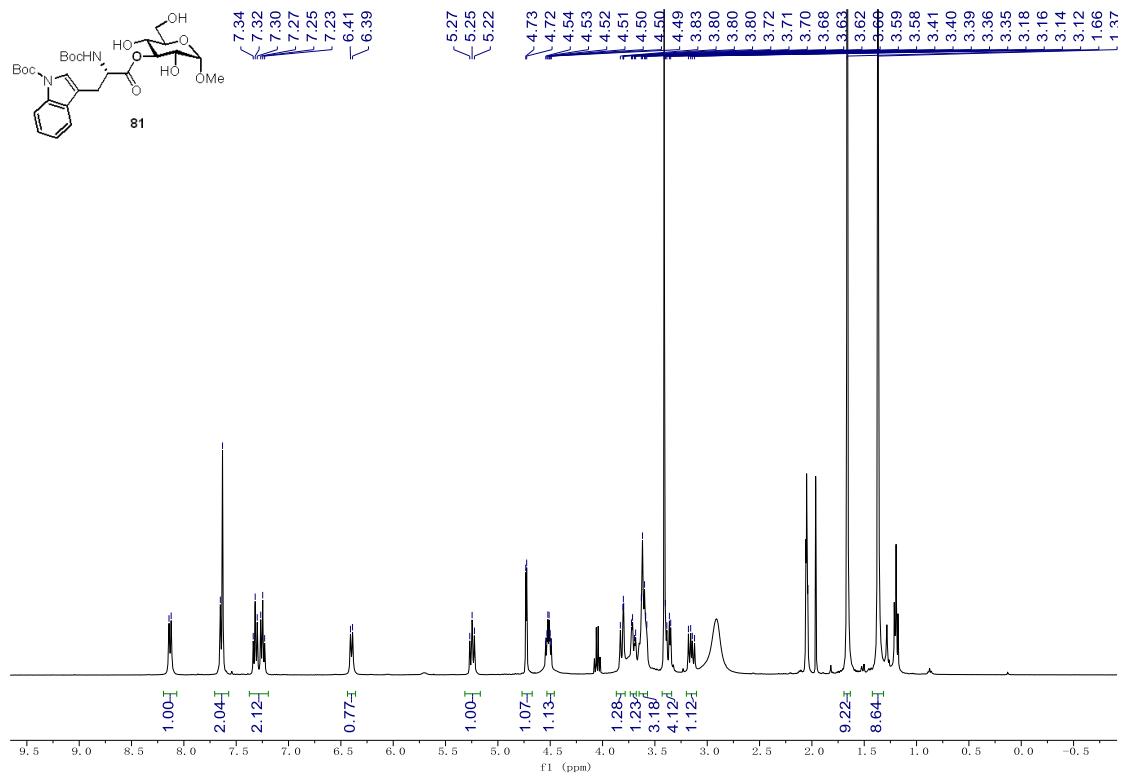


Figure S296. ^1H NMR Spectra of **81**

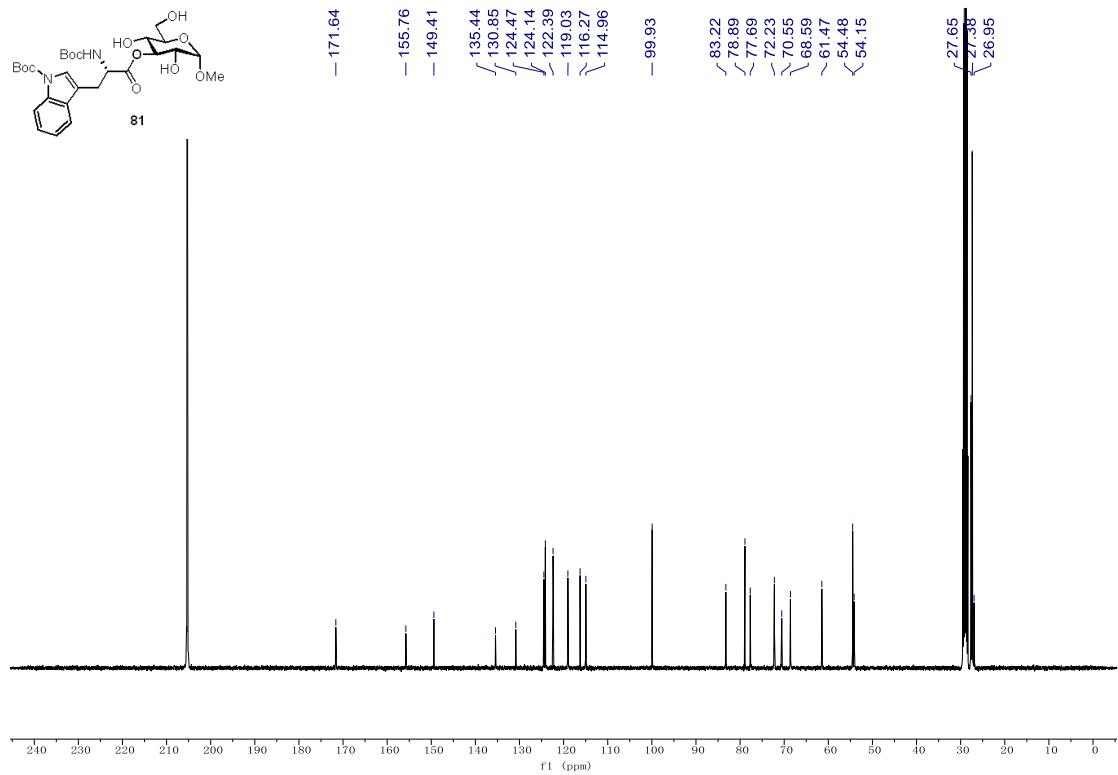


Figure S297. ^{13}C NMR Spectra of **81**

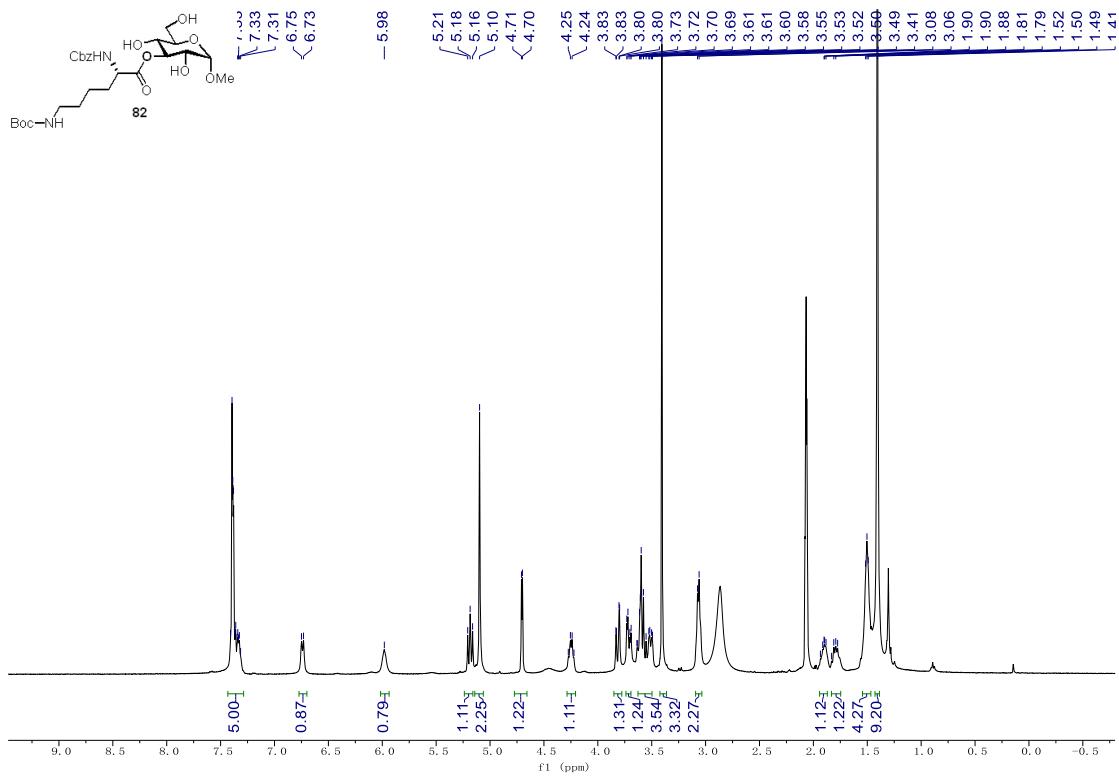


Figure S298. ^1H NMR Spectra of 82

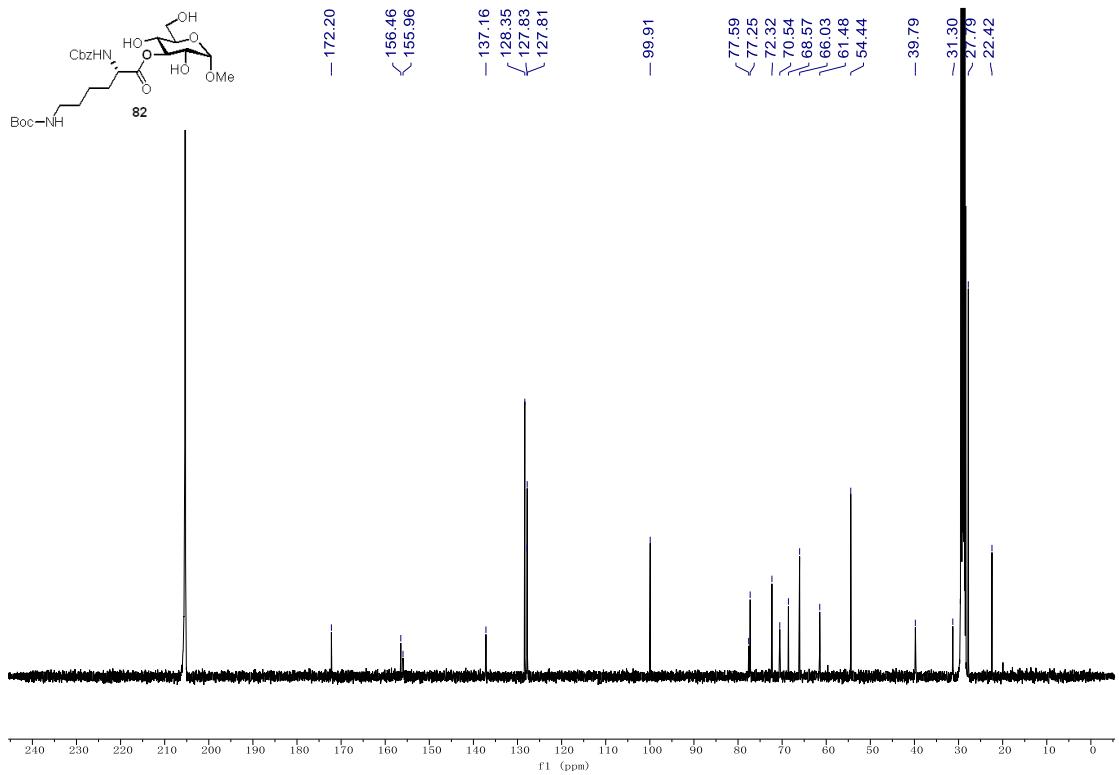


Figure S299. ^{13}C NMR Spectra of 82

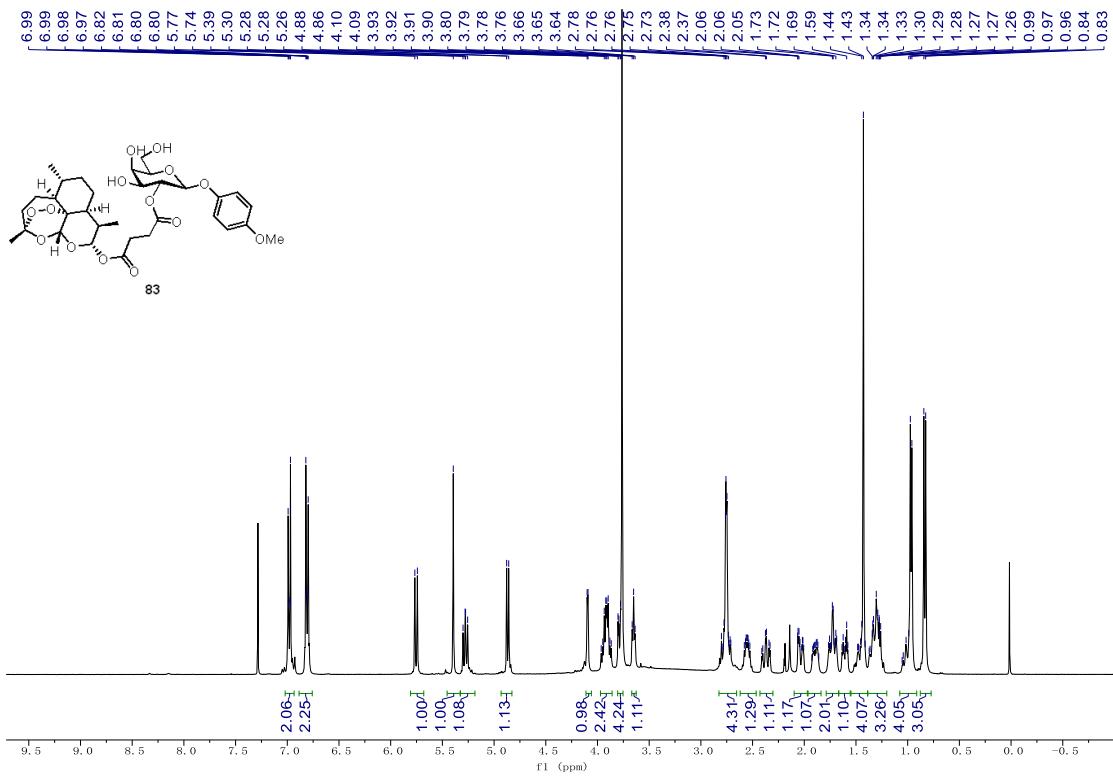


Figure S300. ^1H NMR Spectra of **83**

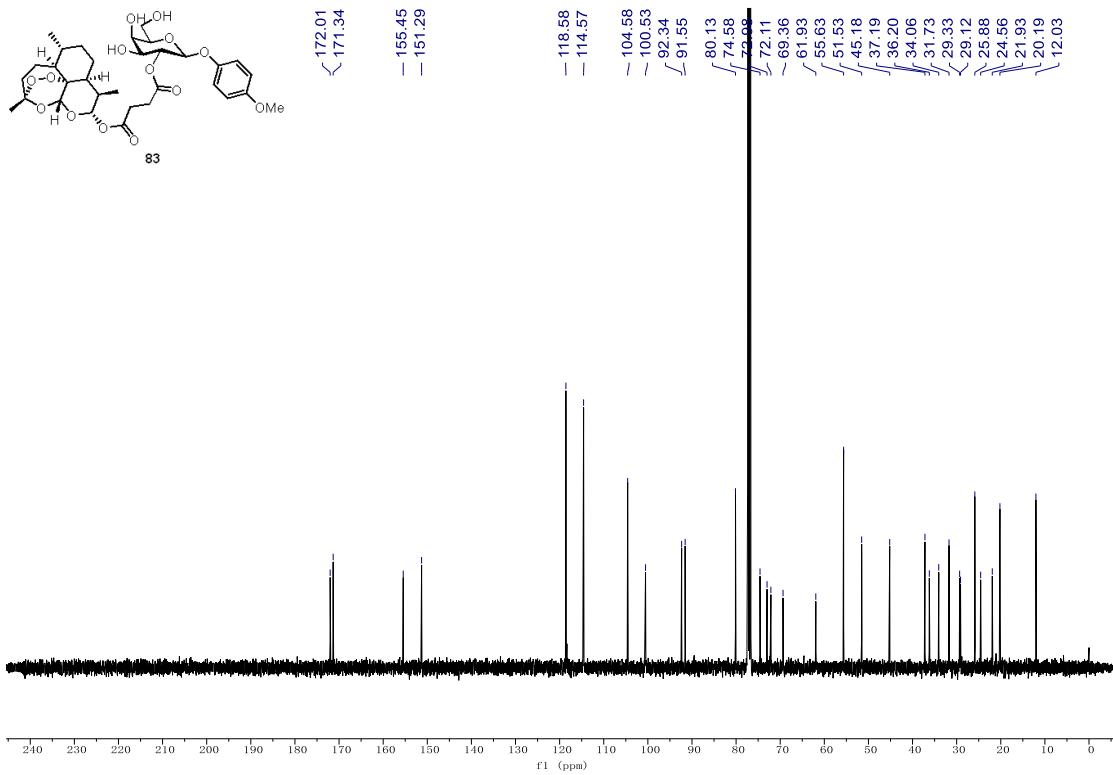


Figure S301. ^{13}C NMR Spectra of **83**

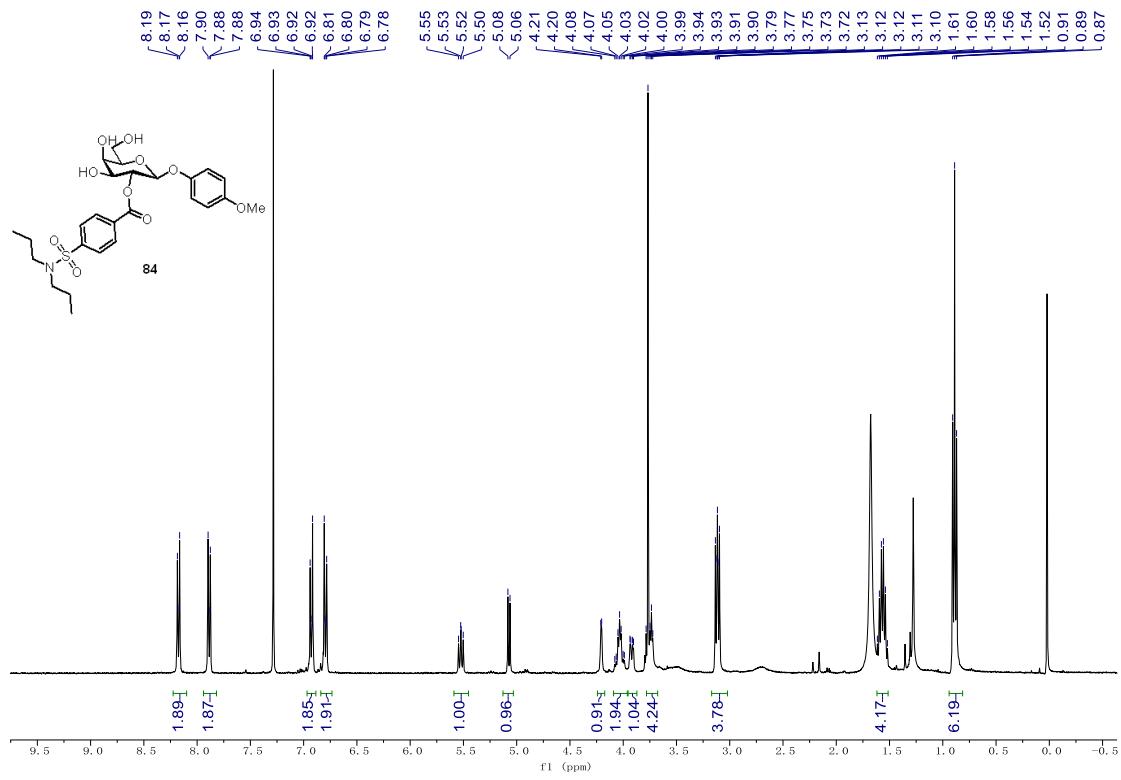


Figure S302. ^1H NMR Spectra of **84**

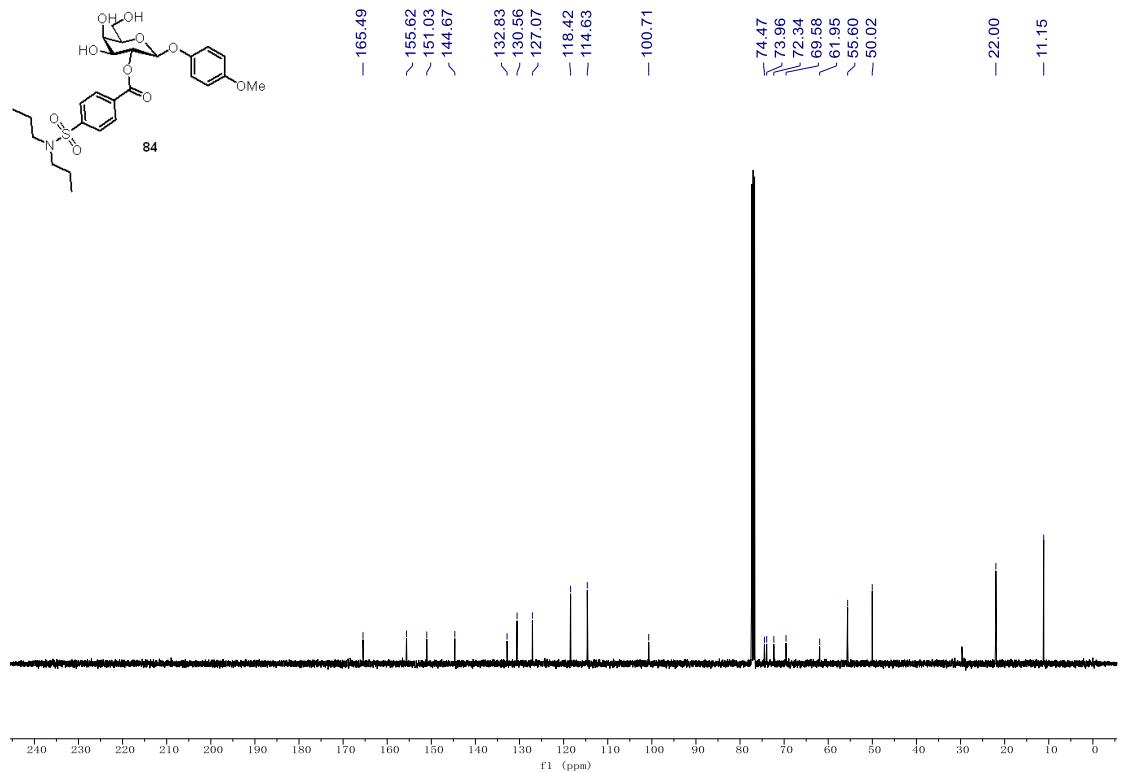


Figure S303. ^{13}C NMR Spectra of **84**

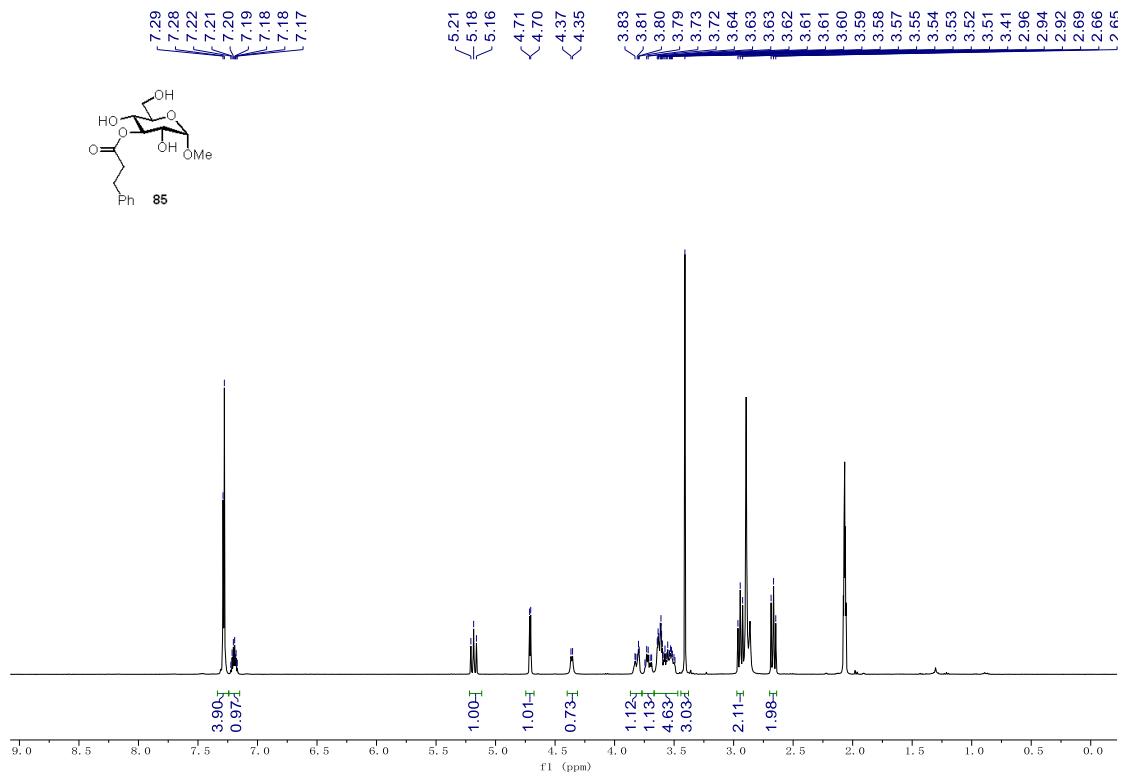


Figure S304. ^1H NMR Spectra of **85**

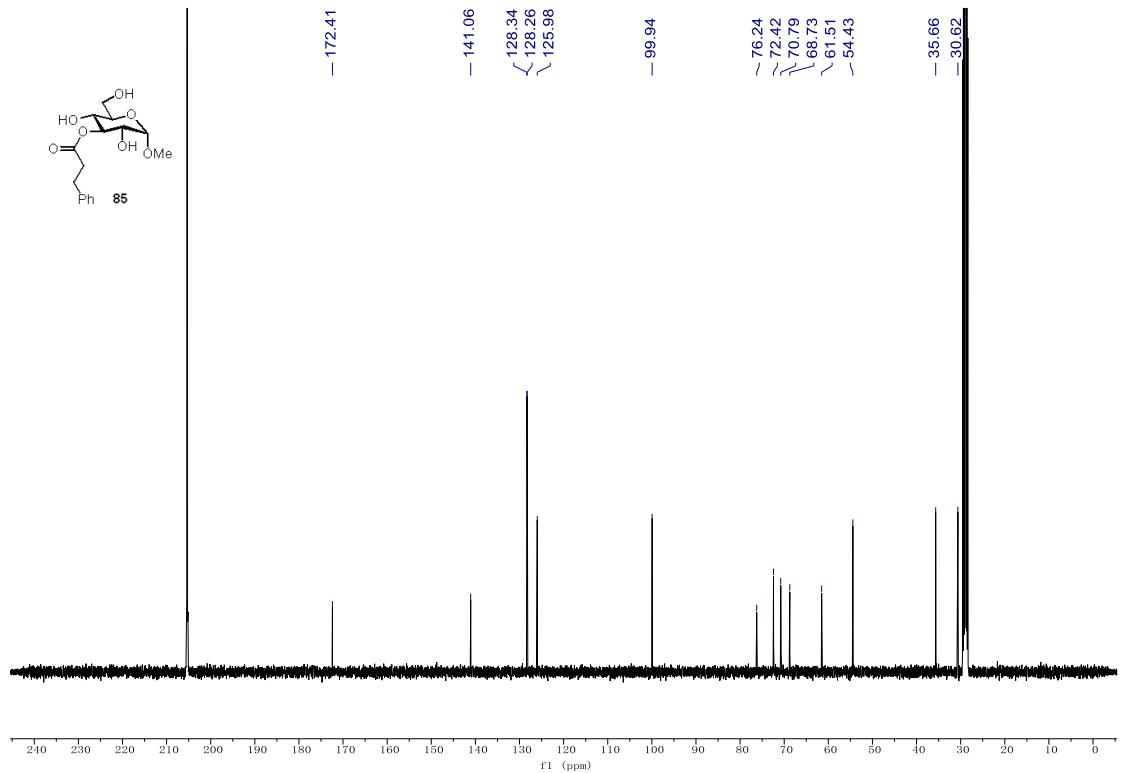
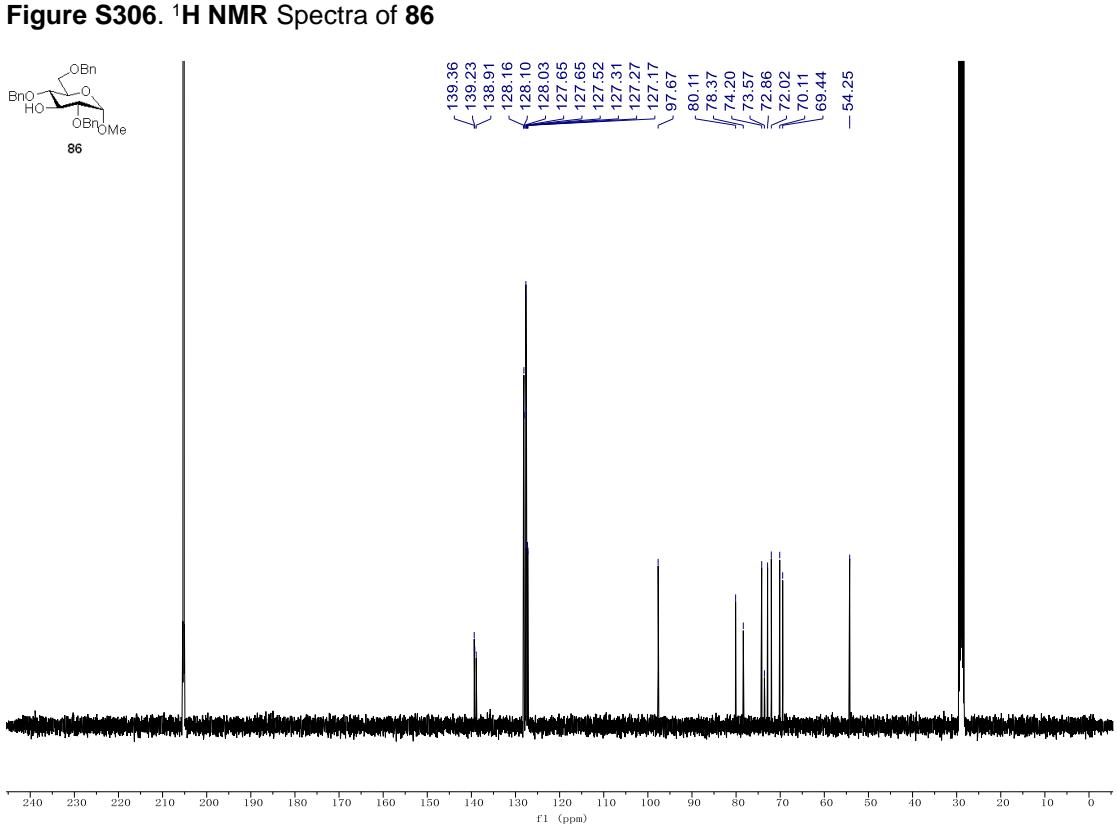
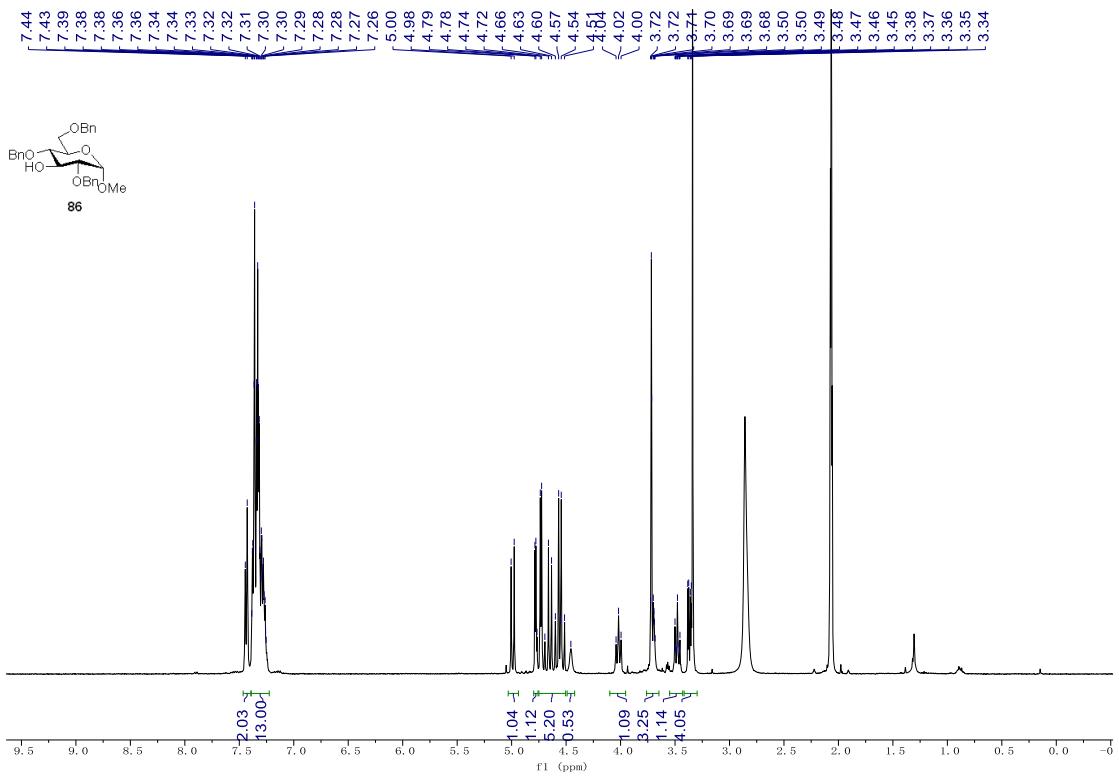


Figure S305. ^{13}C NMR Spectra of **85**



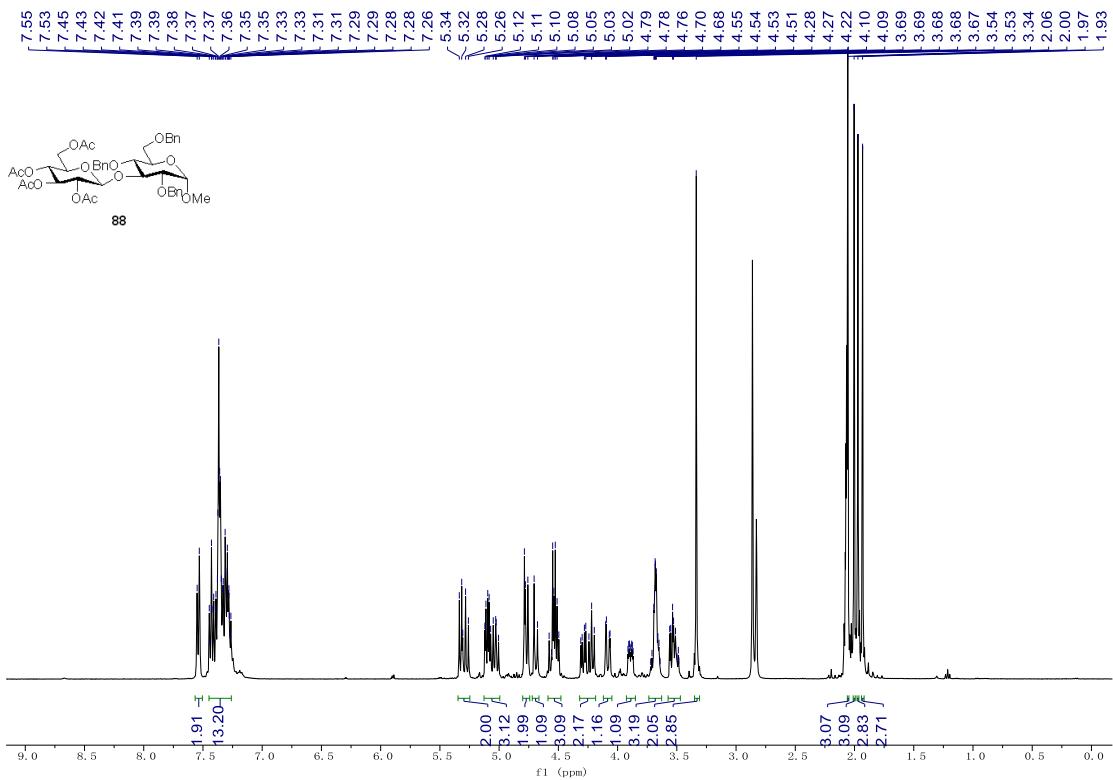


Figure S308. ^1H NMR Spectra of **88**

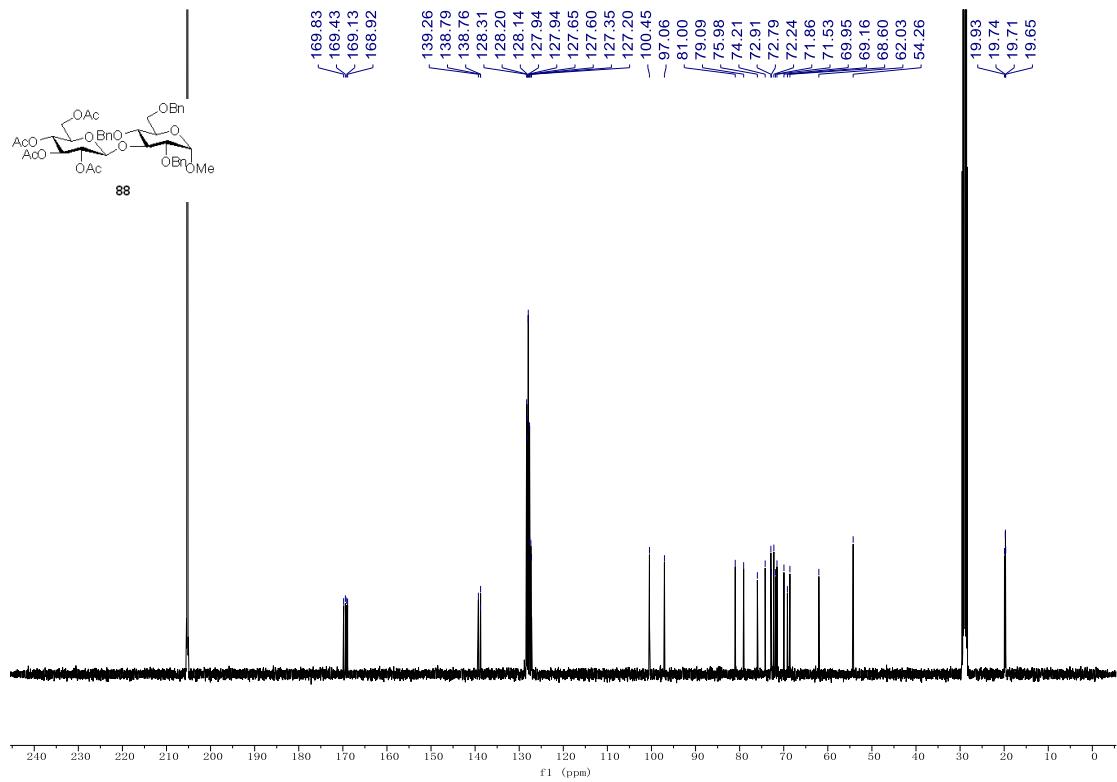


Figure S309. ^{13}C NMR Spectra of **88**

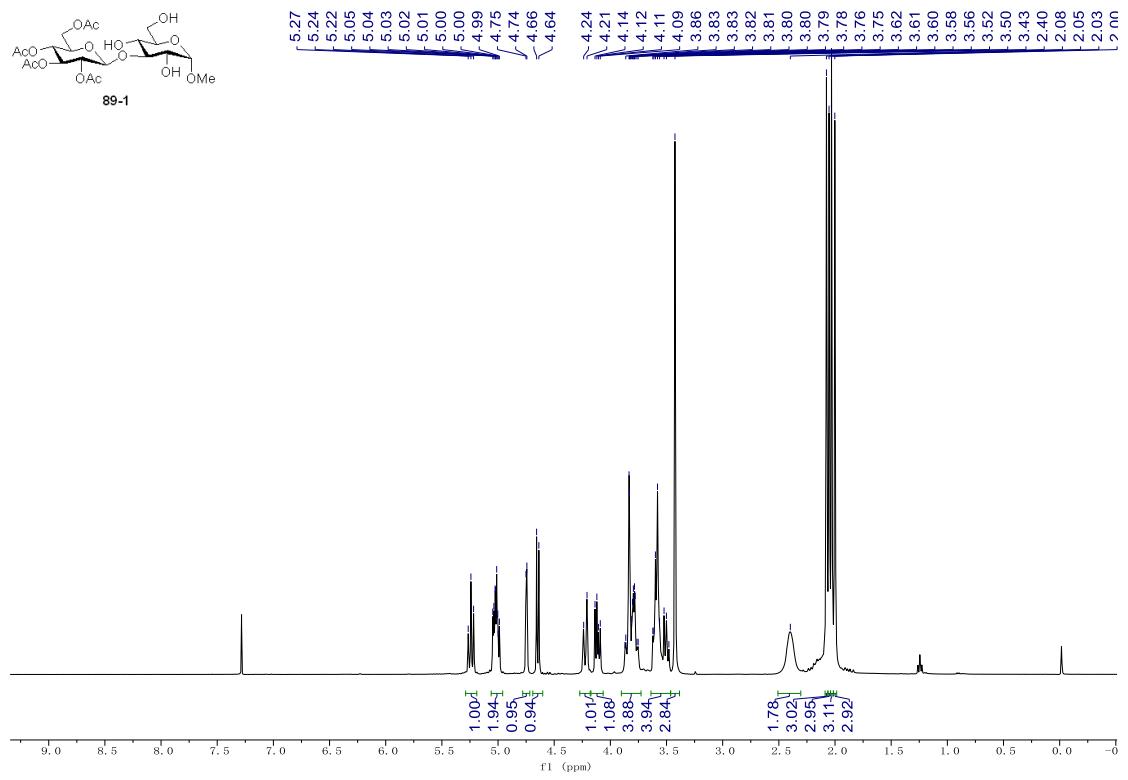


Figure S310. ^1H NMR Spectra of **89-1**

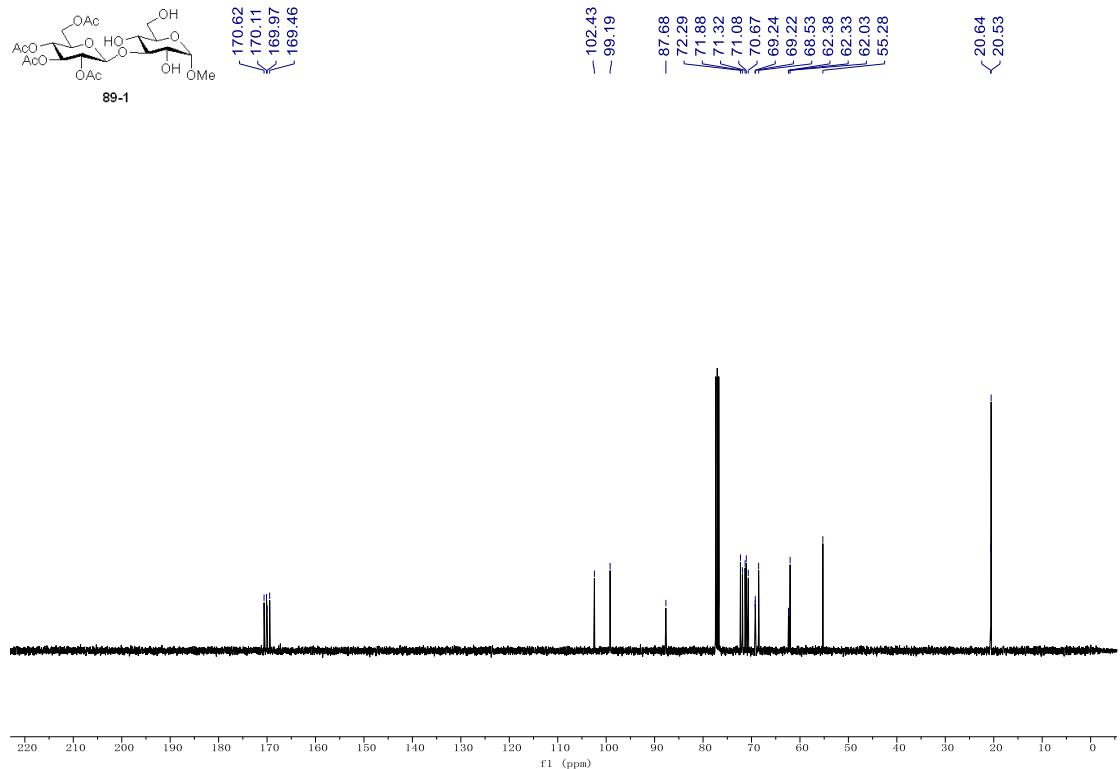


Figure S311. ^{13}C NMR Spectra of 89-1

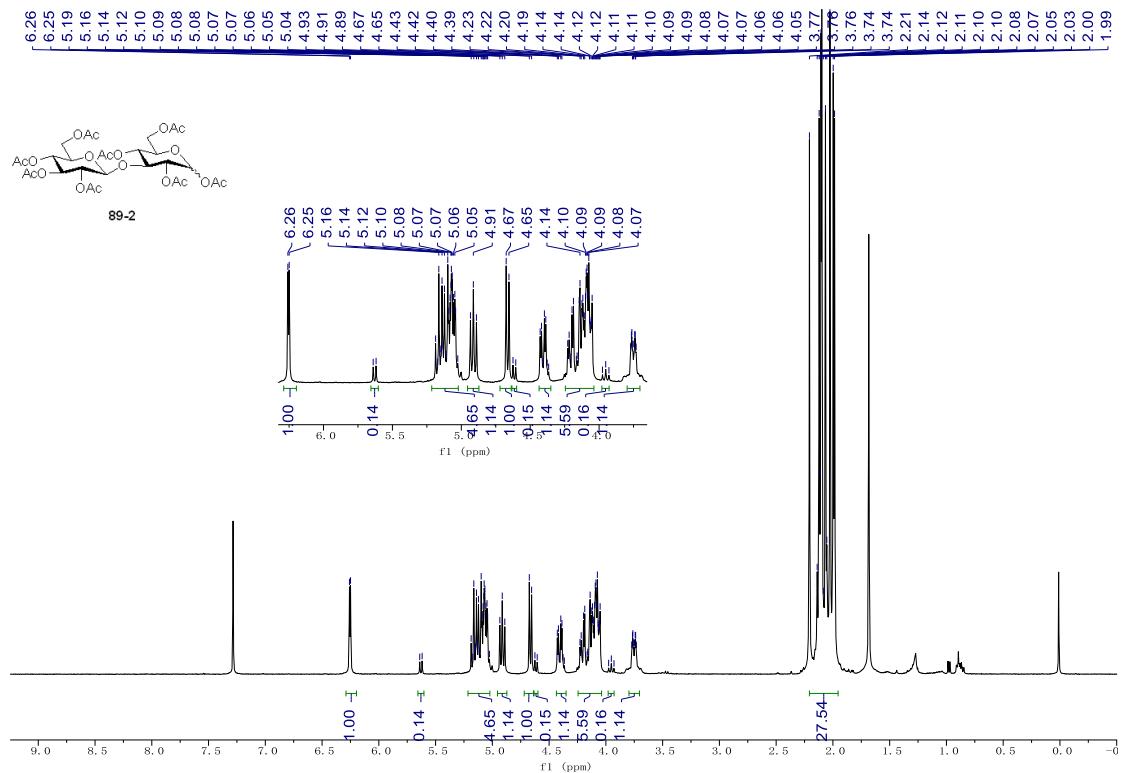


Figure S312. ^1H NMR Spectra of **89-2**

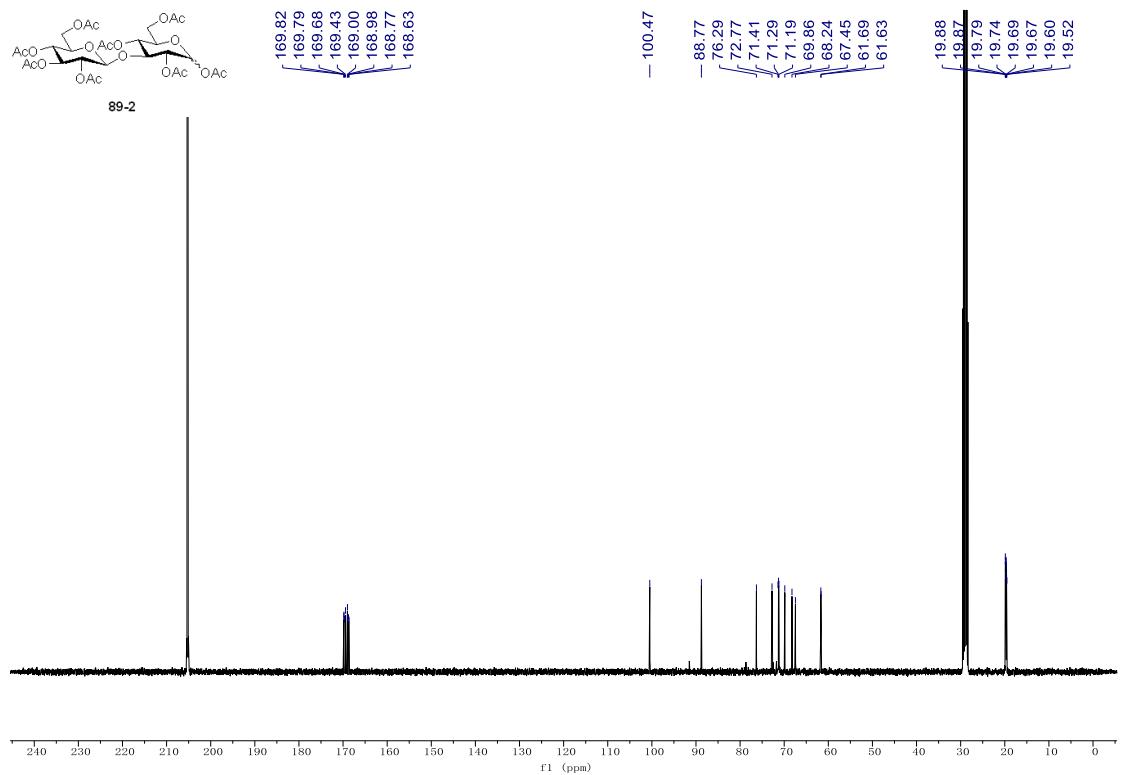


Figure S313. ^{13}C NMR Spectra of **89-2**

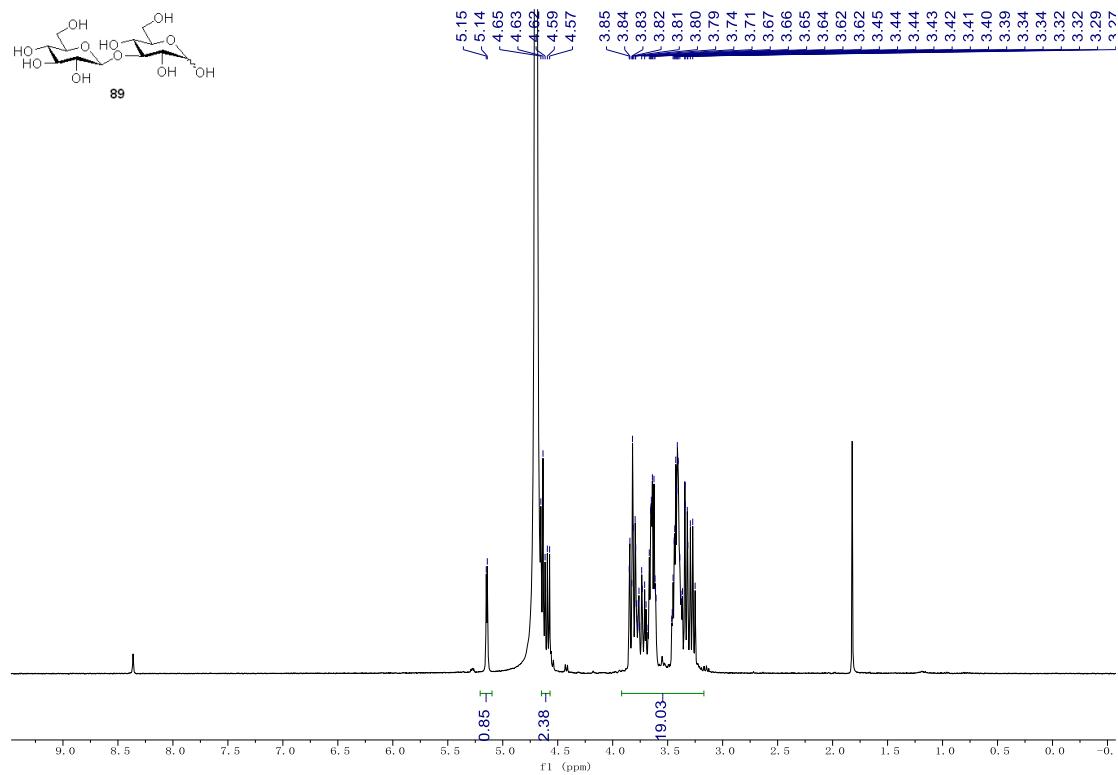


Figure S314. ^1H NMR Spectra of **89**

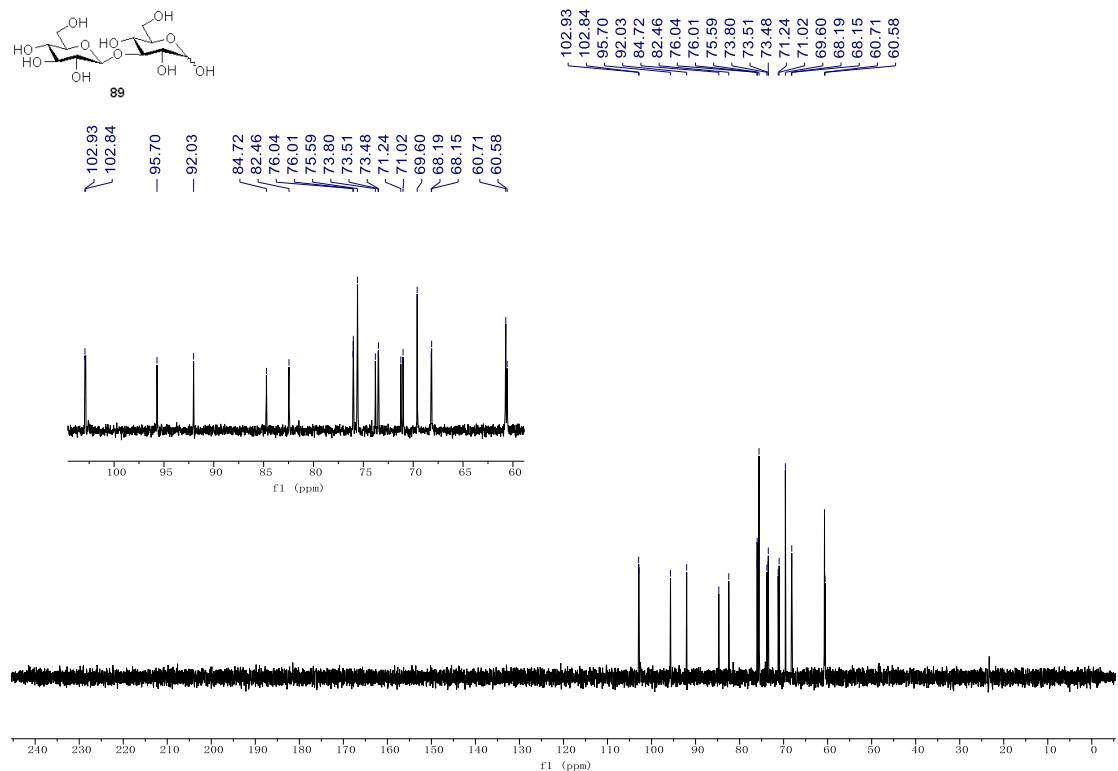
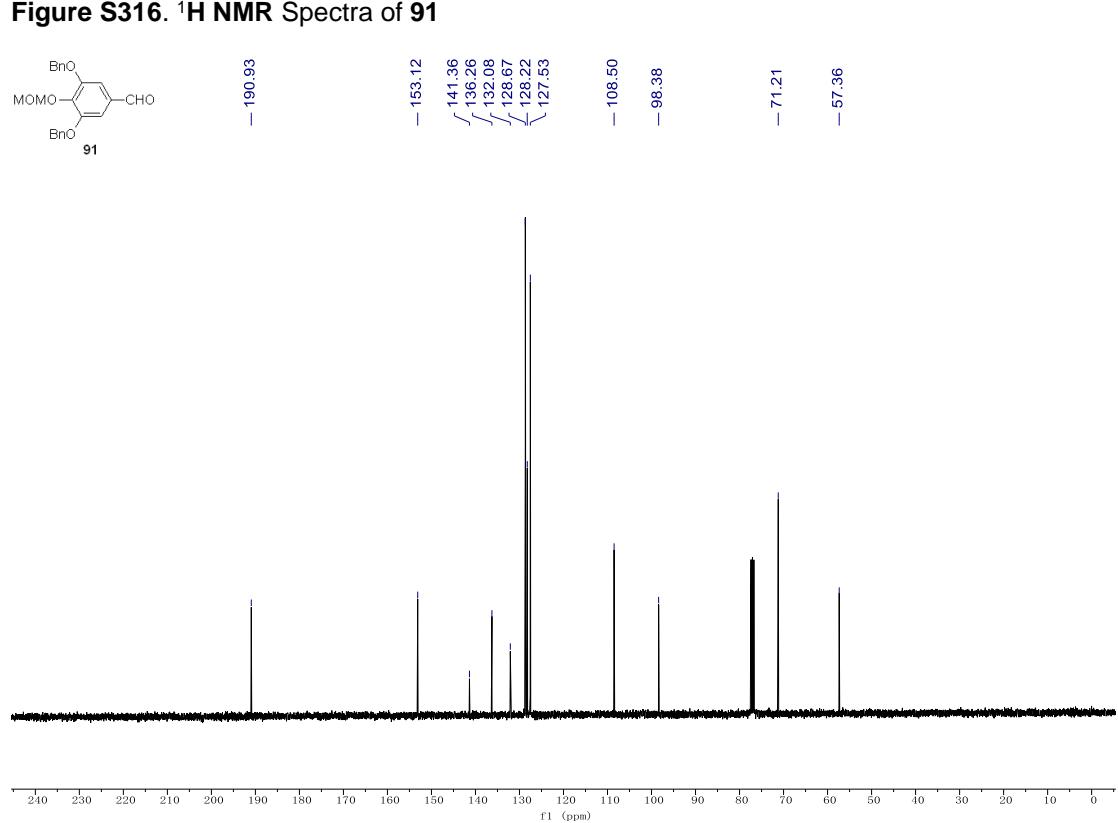
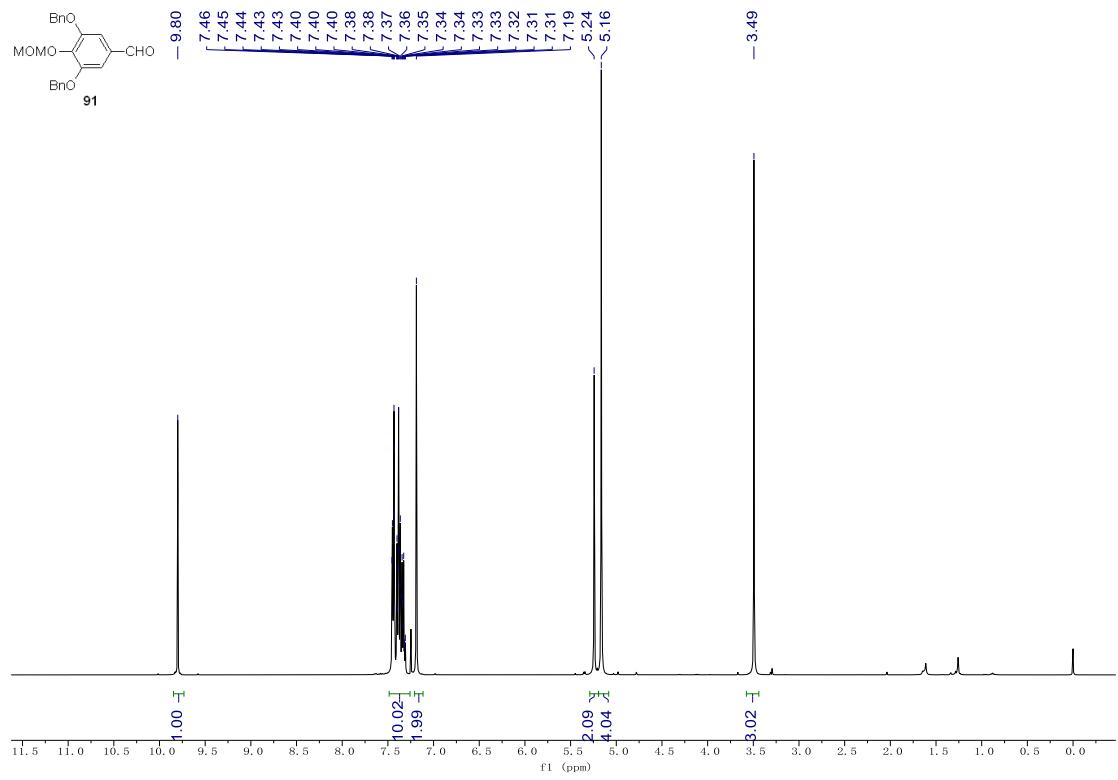
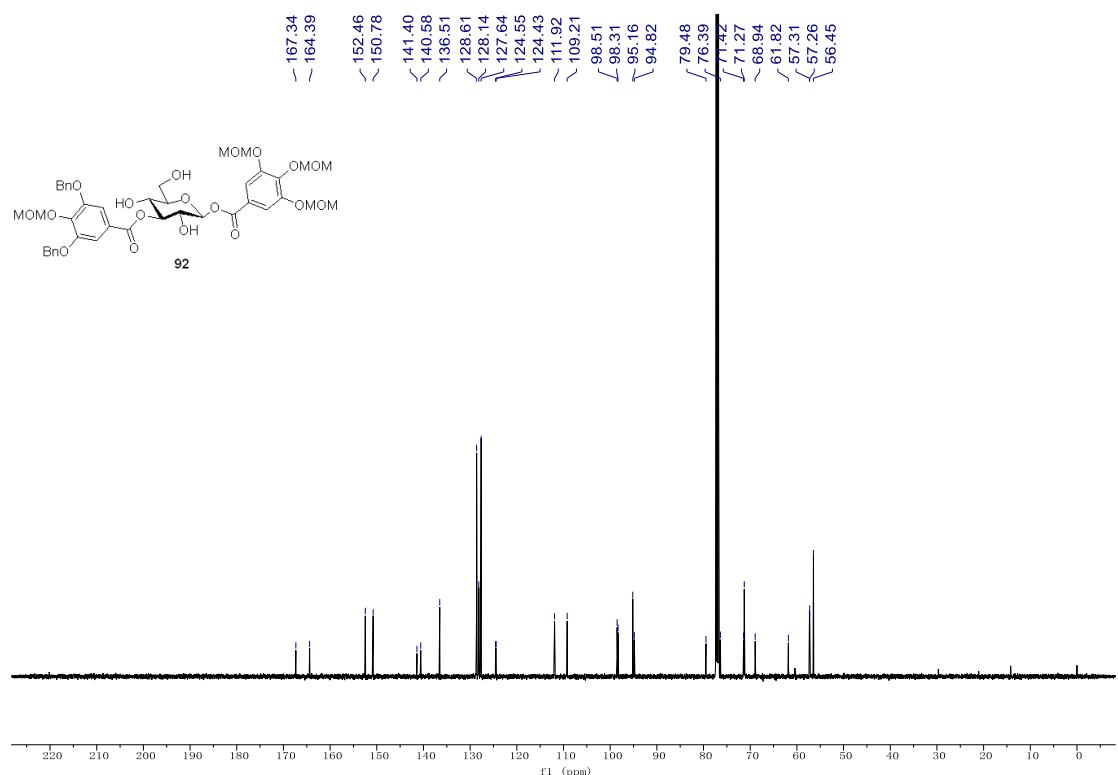
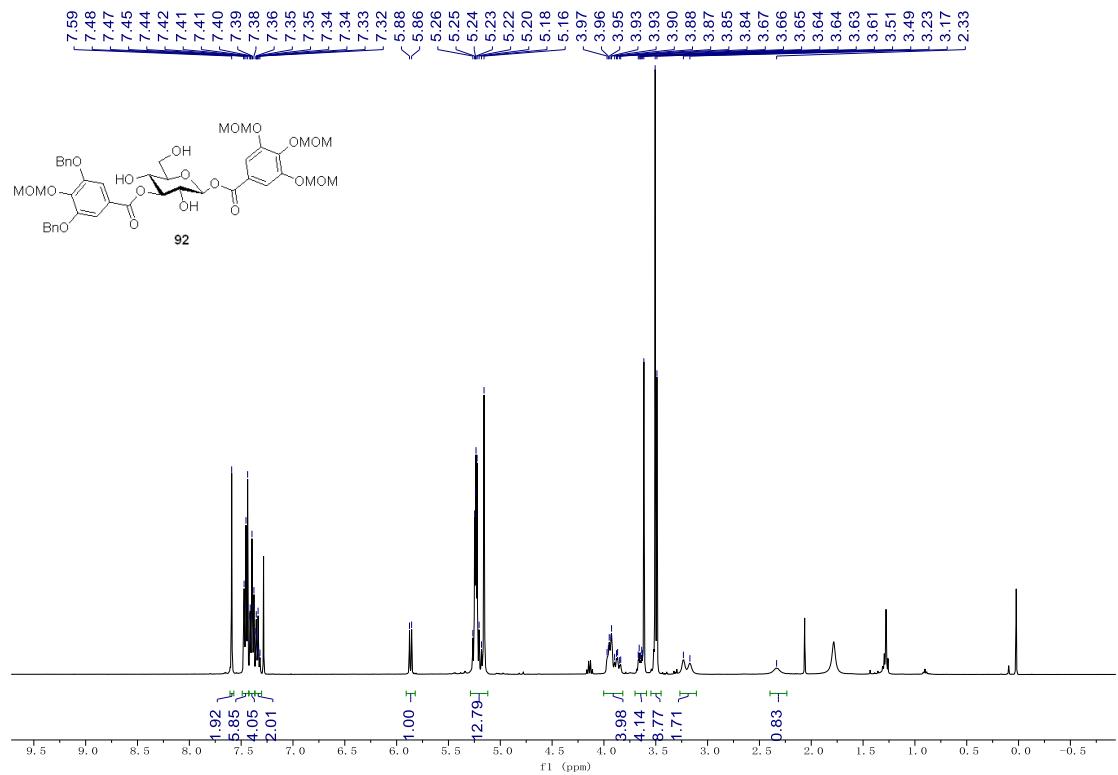


Figure S315. ^{13}C NMR Spectra of **89**





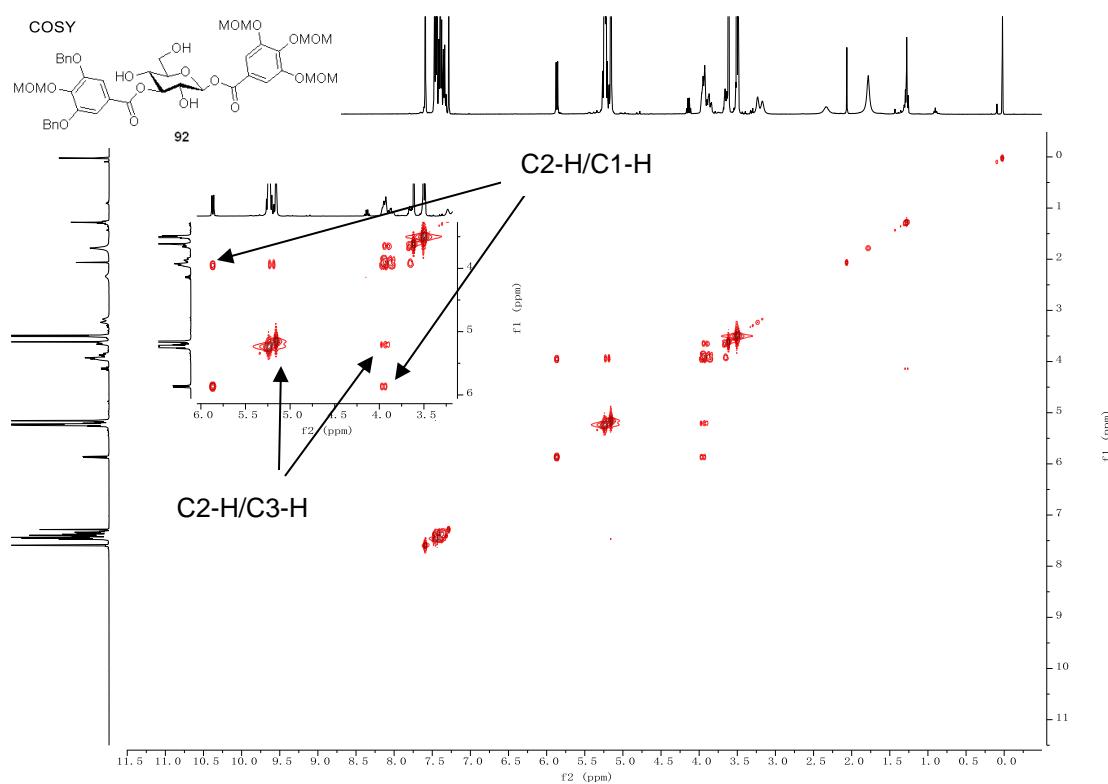


Figure S320. COSY NMR Spectra of **92**

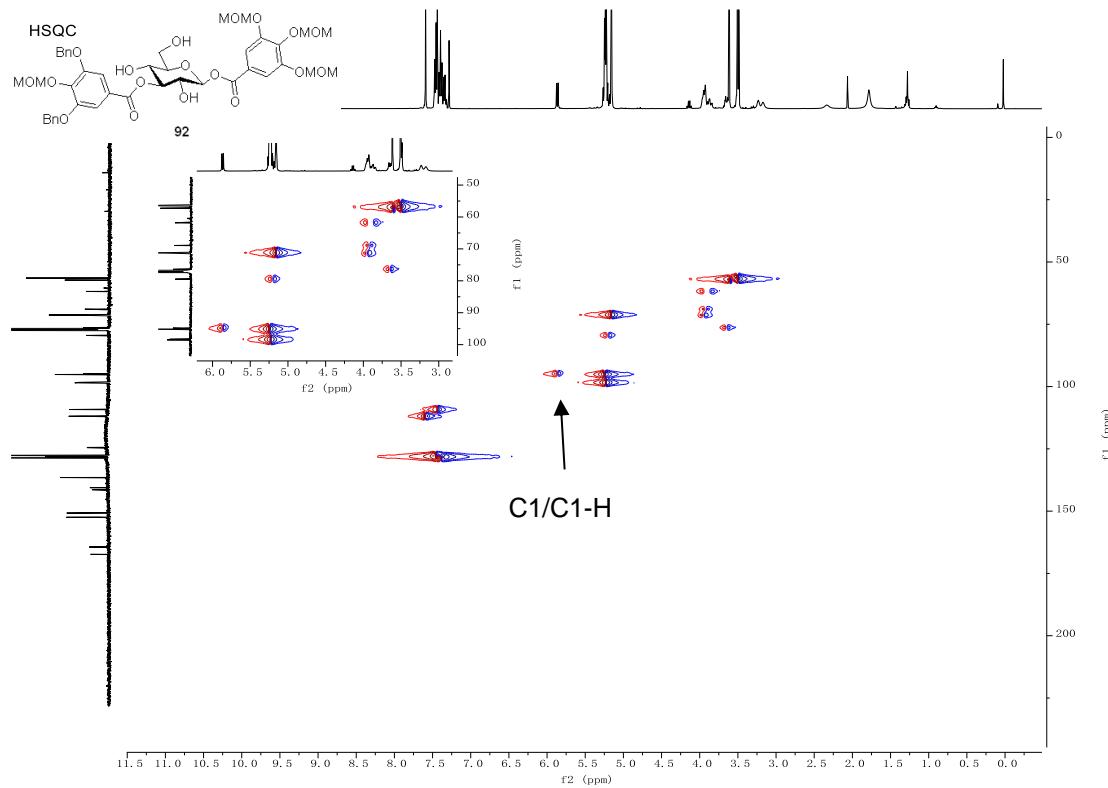


Figure S321. HSQC NMR Spectra of **92**

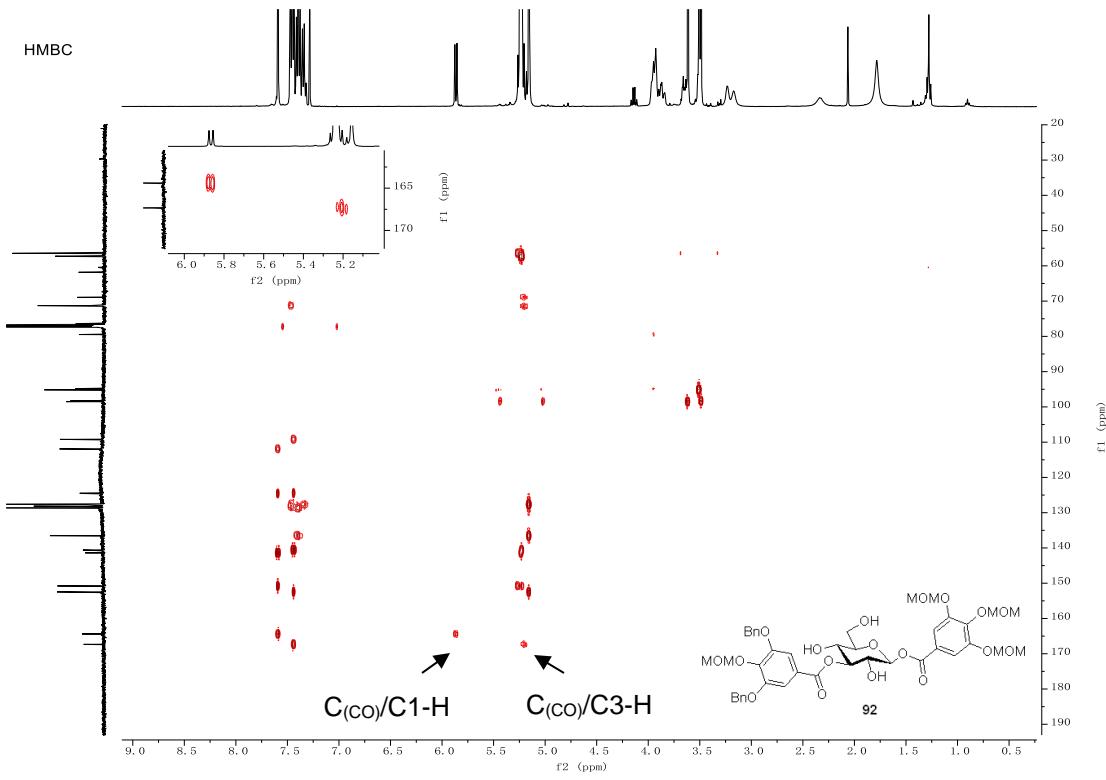


Figure S322. HMBC NMR Spectra of **92**

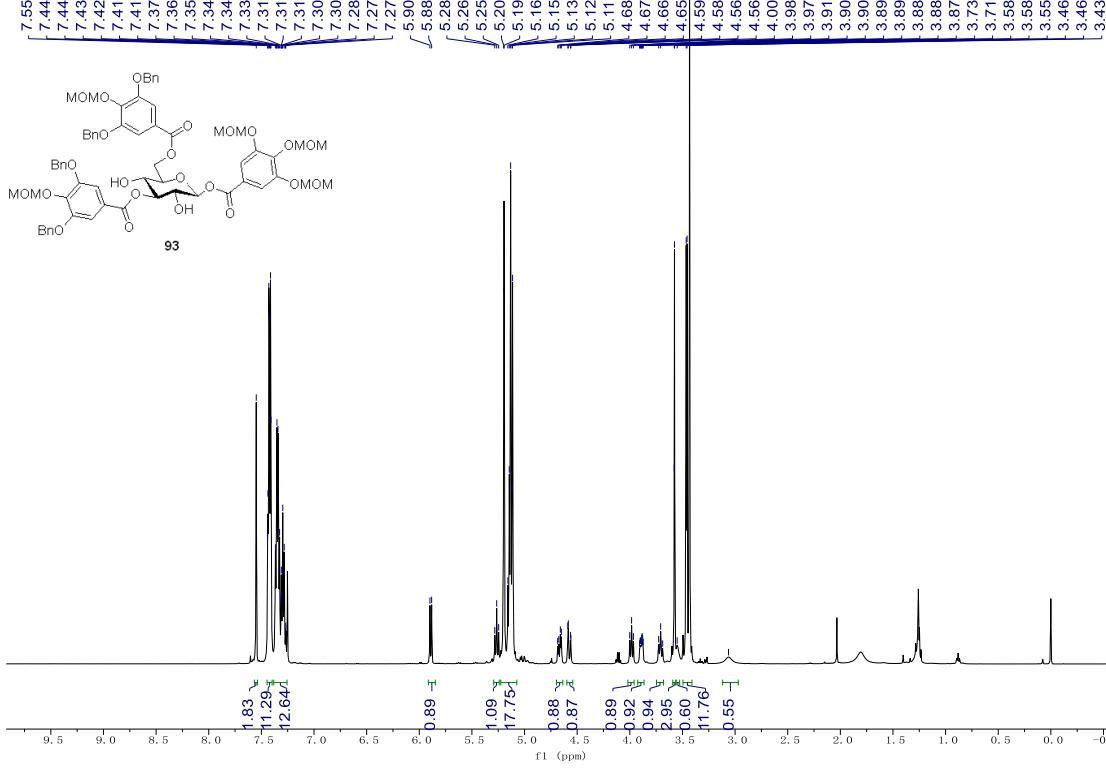


Figure S323. ^1H NMR Spectra of **93**

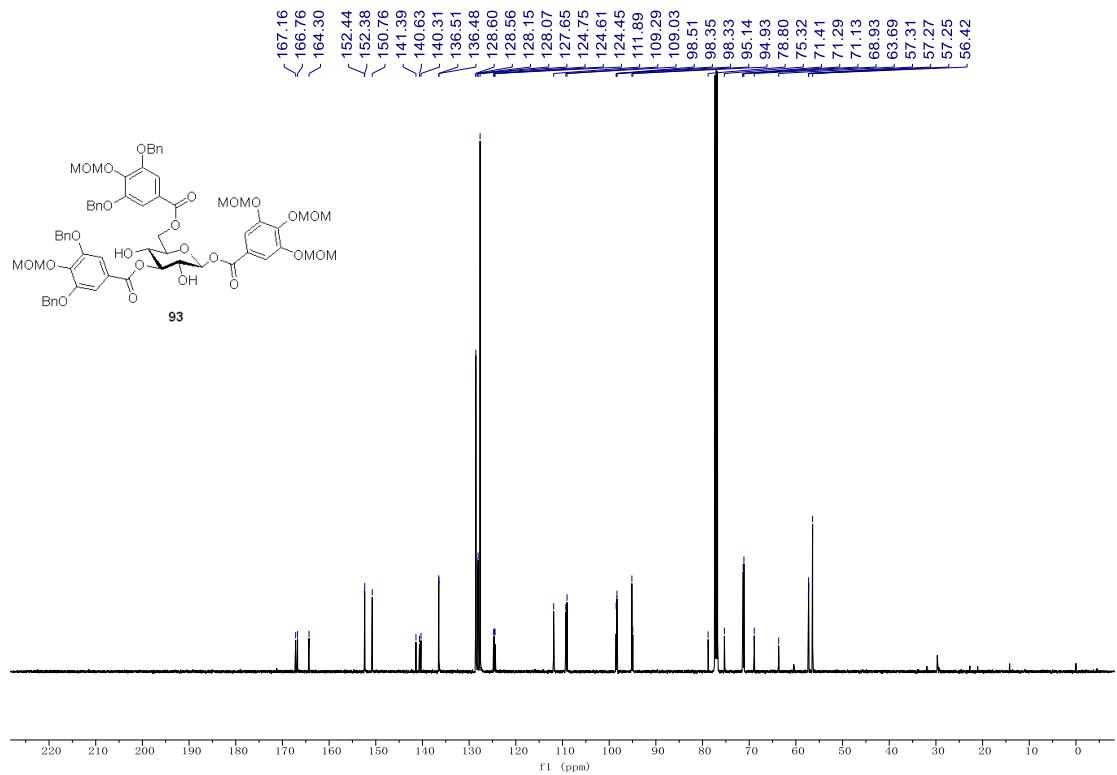


Figure S324. ^{13}C NMR Spectra of **93**

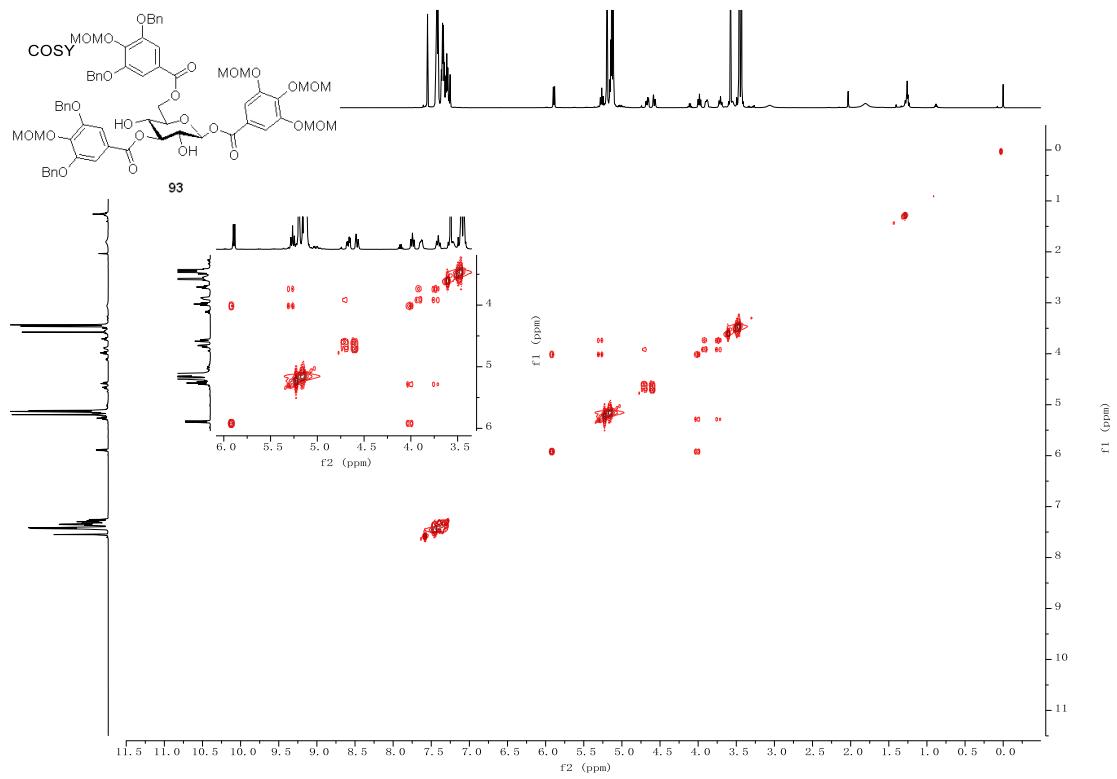


Figure S325. COSY NMR Spectra of **93**

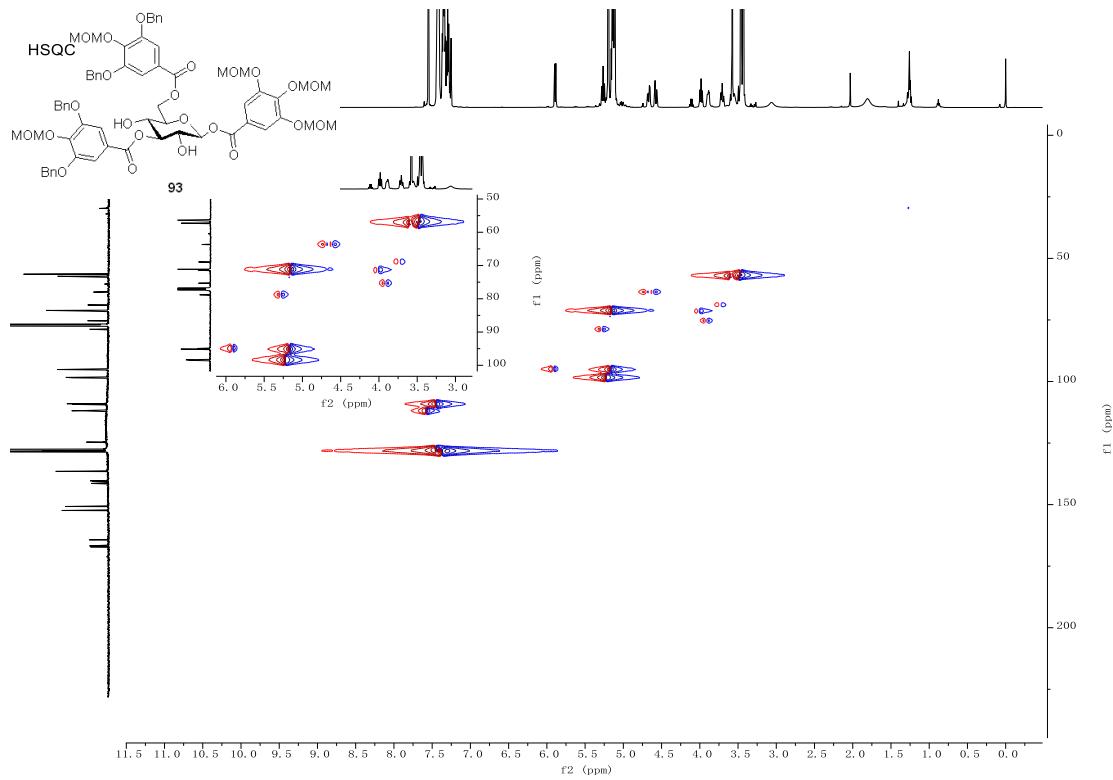


Figure S326. HSQC NMR Spectra of **93**

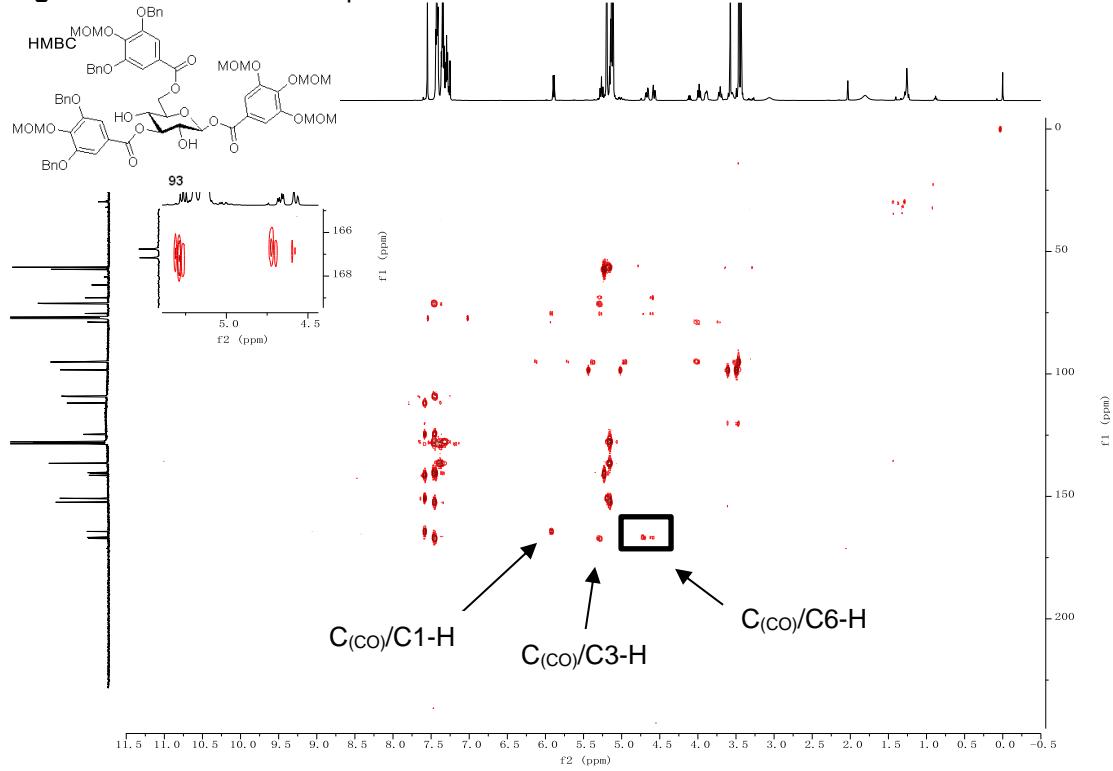


Figure S327. HMBC NMR Spectra of 93

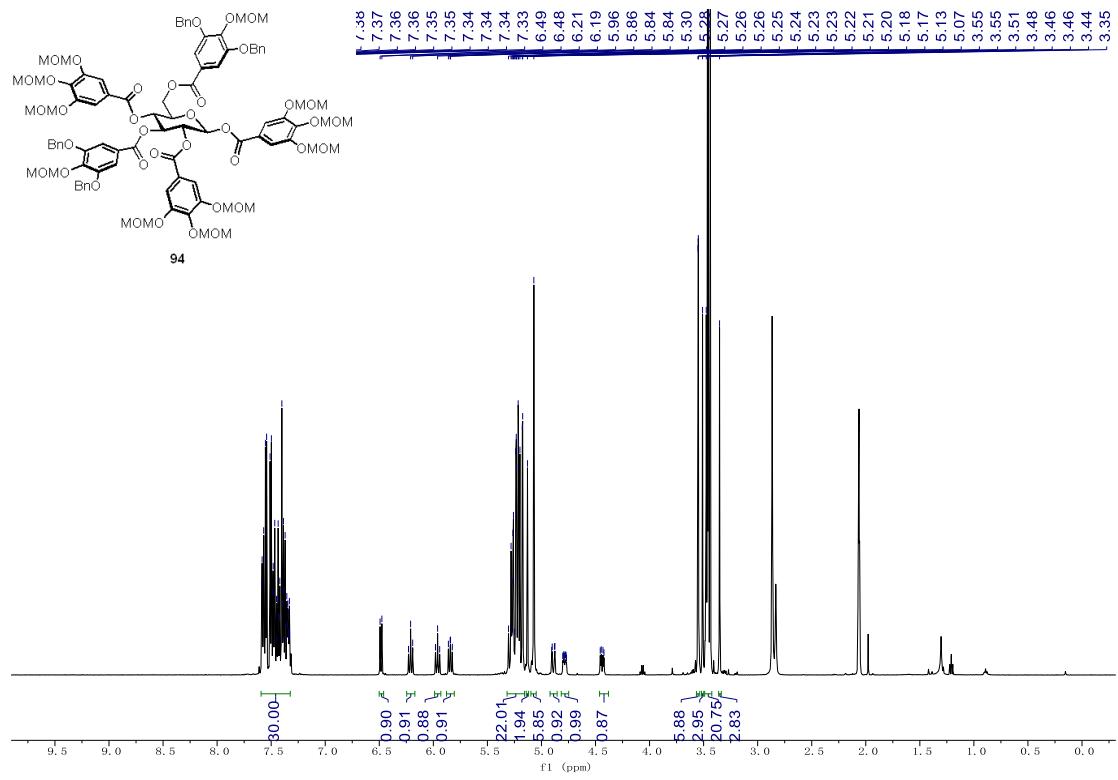


Figure S328. ^1H NMR Spectra of 94

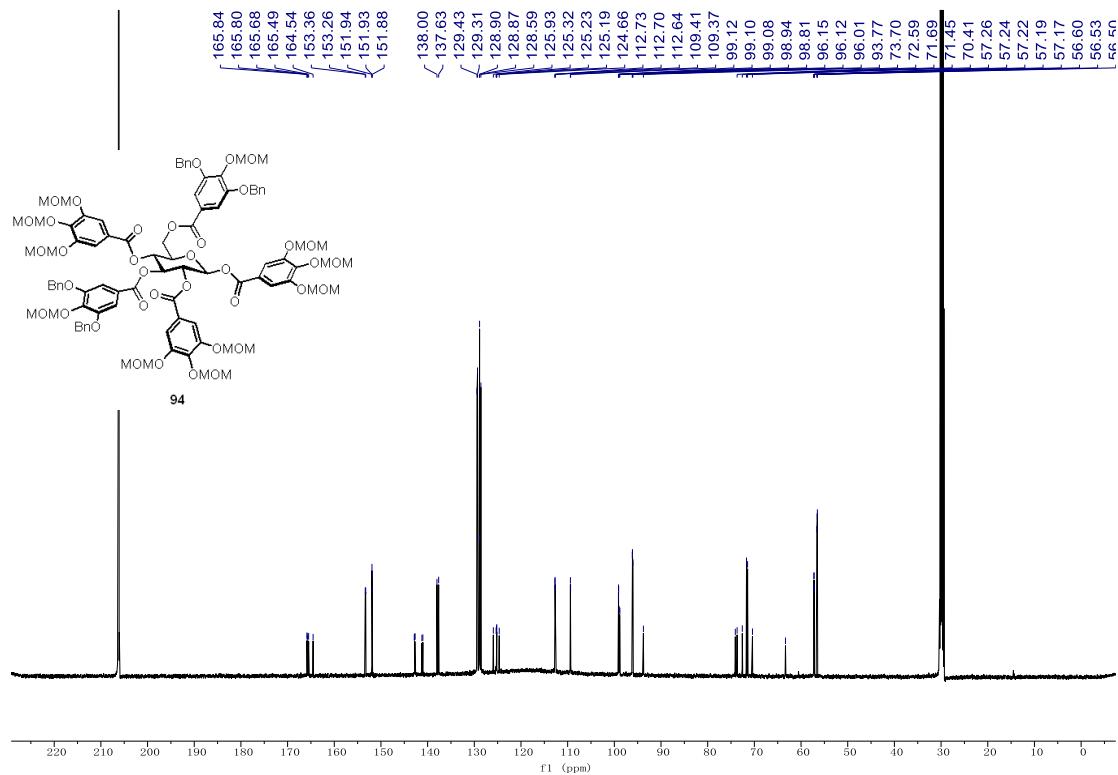


Figure S329. ^{13}C NMR Spectra of 94

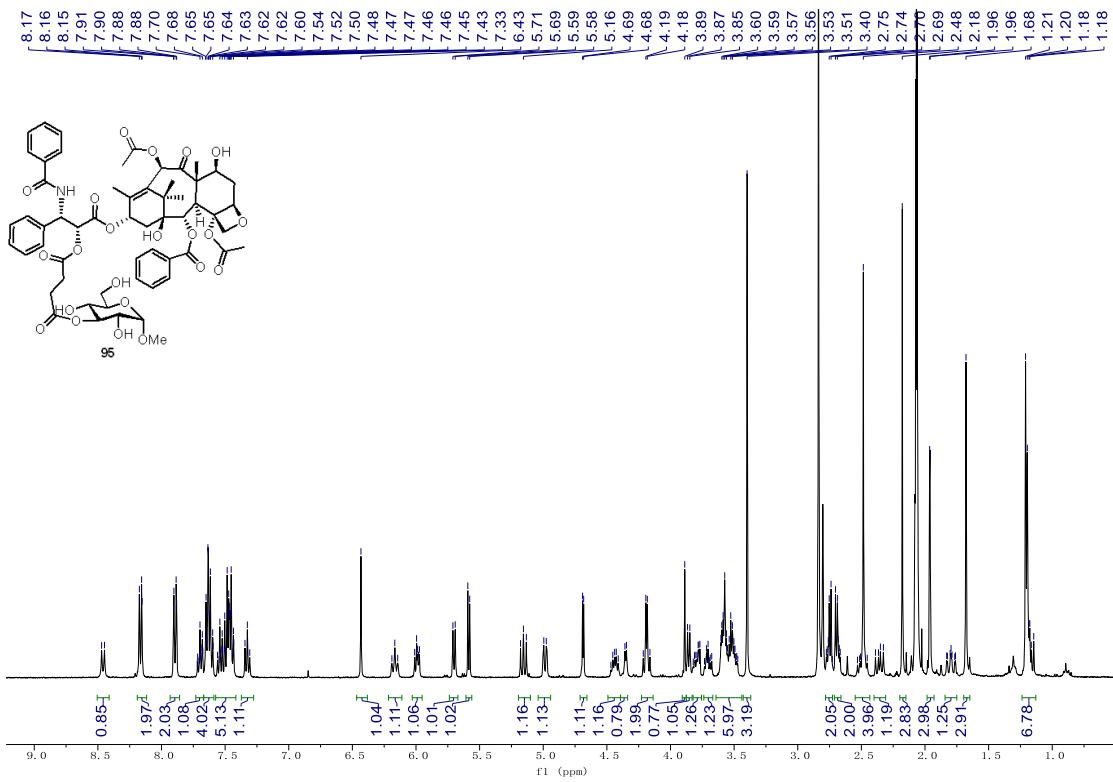


Figure S330. ^1H NMR Spectra of 95

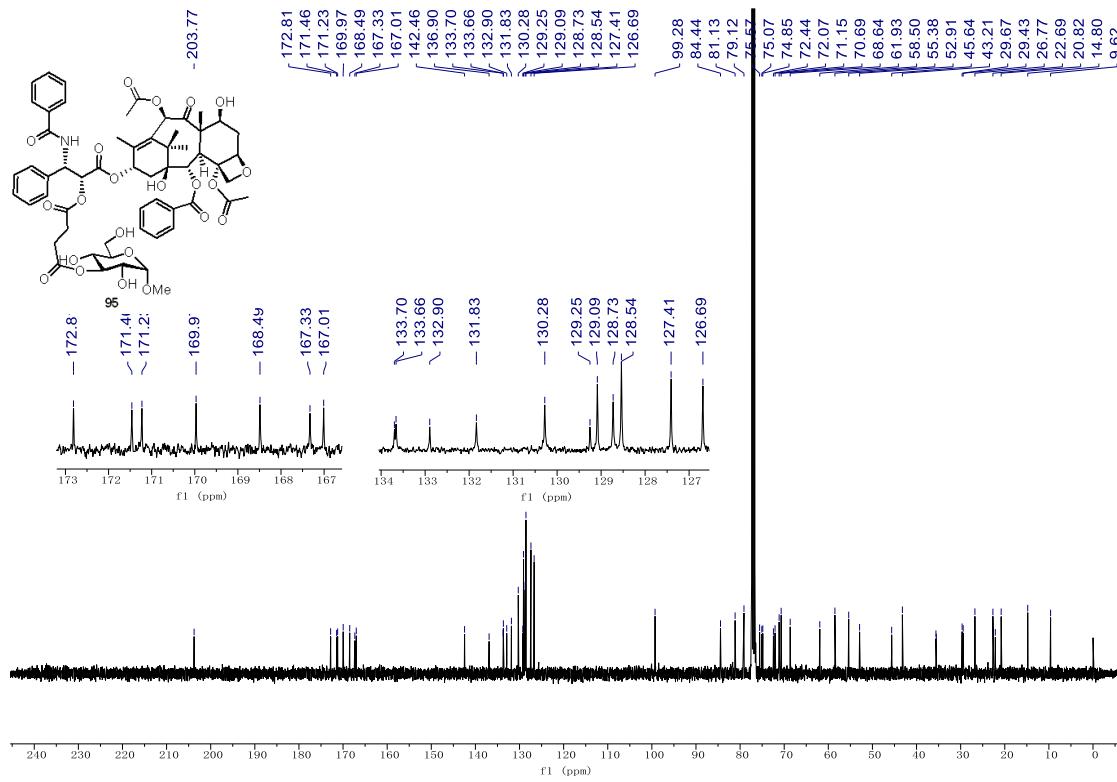


Figure S331. ^{13}C NMR Spectra of **95**

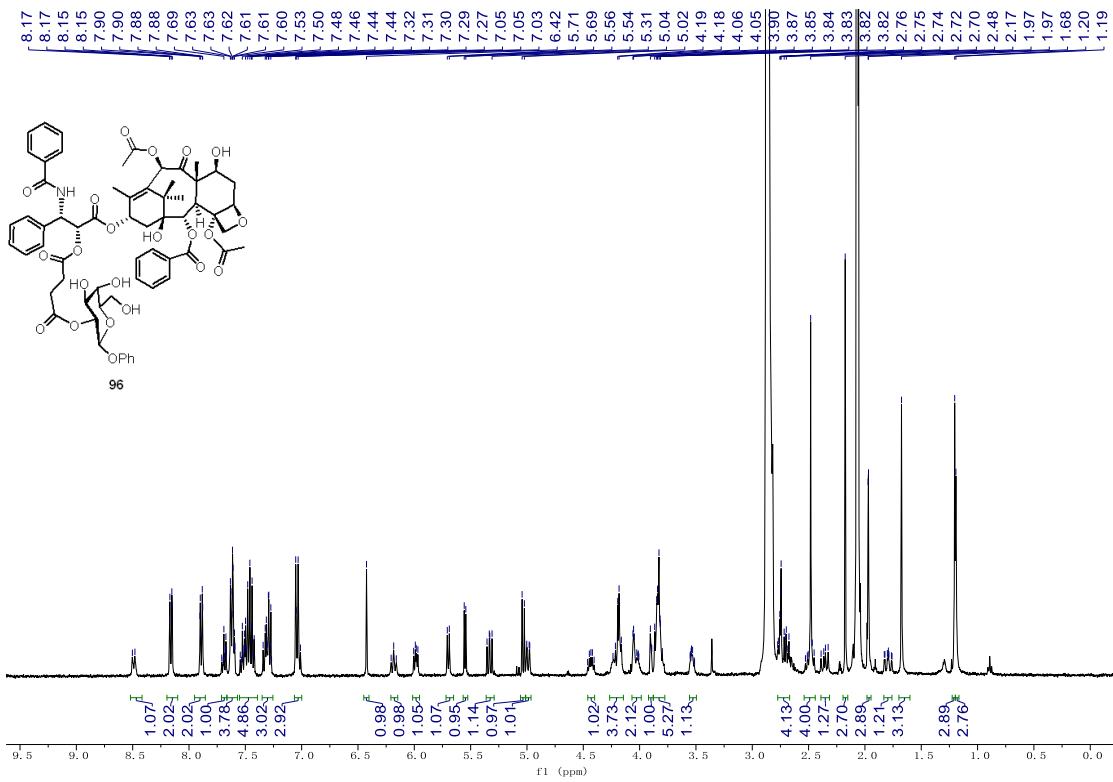


Figure S332. ¹H NMR Spectra of **96**

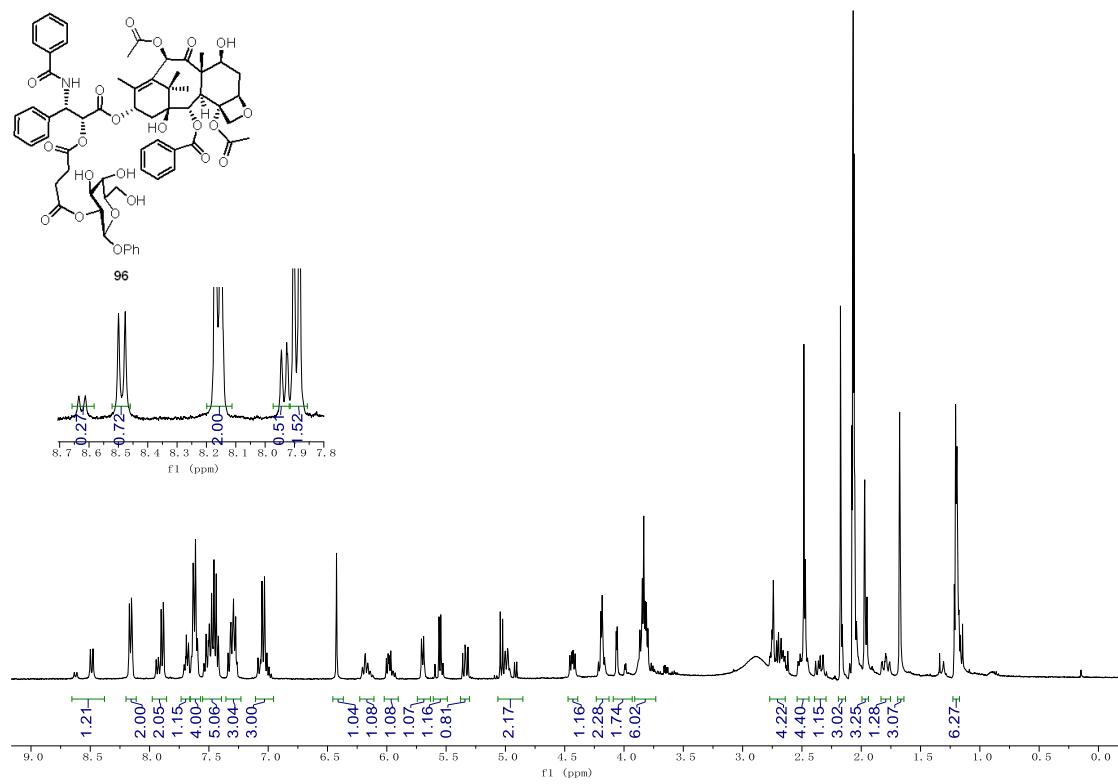


Figure S333. ¹H NMR Spectra of **96**

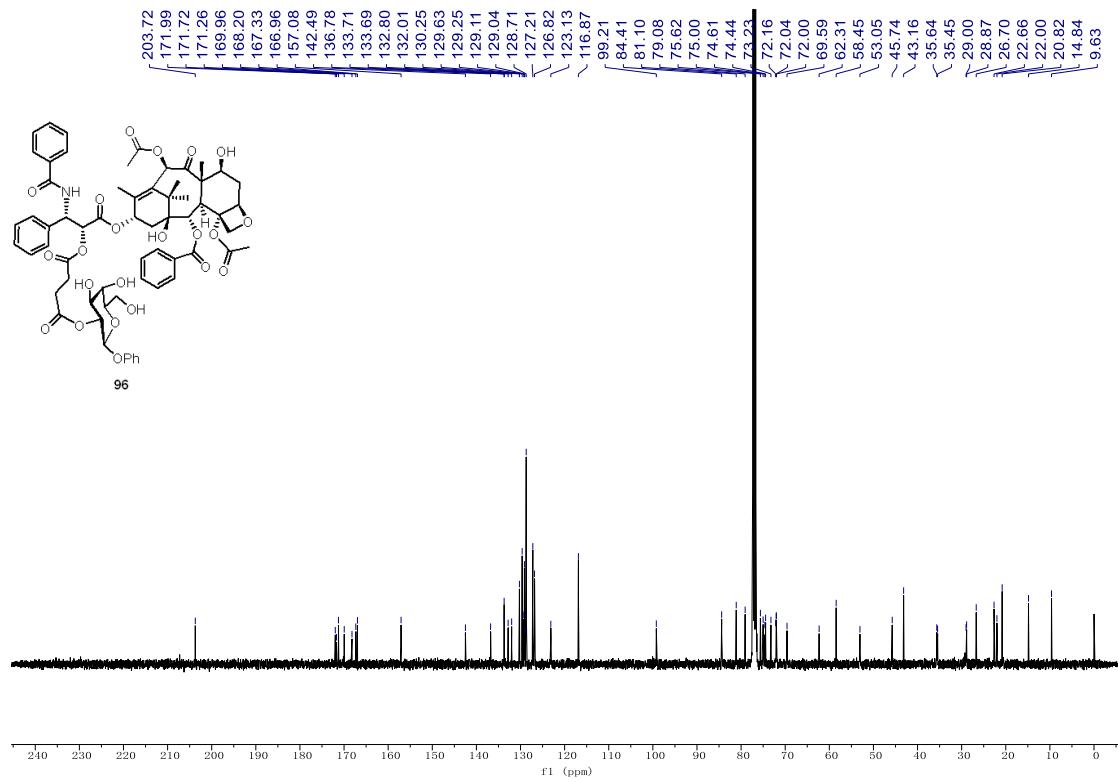


Figure S334. ^{13}C NMR Spectra of **96**