Supplementary Information

NHC/B(OH)$_3$-Mediated C3-Selective Acylation of Unprotected Monosaccharides: Mechanistic Insights and Practical Applications

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1. Materials and Instrumentation

All reagents were obtained from Sigma-Aldrich, Alfa-Aesar, Acros Organics, TCI, J&K Scientific, Energy Chemical and were used without purification. Anhydrous solvents CH_3CN, EtOAc, DMF, DCM and DMSO were purchased from commercial suppliers and used directly without further treatments. THF was dried via standard protocols using Na and distillation. Other solvents were AR grade solvents. Proton (^1H), Carbon (^{13}C) NMR were recorded at 400 MHz, 101 MHz NMR spectrometer, respectively. ^1H NMR, ^{13}C NMR, ^{19}F NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer with BBFO probe. Chemical shifts (δ) for ^1H and ^{13}C NMR spectra are given in ppm relative to TMS. ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, brs = broad singlet), coupling constants (Hz), and integration. Highresolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with ESI mode unless otherwise stated. Reactions were examined by thin-layer chromatography (TLC) on Merck Silica Gel 60 F254 plates-visualized under UV light (254 nm), and/or staining with p-anisaldehyde which developed upon heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

2. Method for Determining Reaction Yields using HPLC Analysis

2.1 Preparation of standard solution (of purified product), and solution of the crude reaction mixture

The C2-, C3-, and C6-O-acylation product (isolated and purified) were accurately weighed and dissolved in methanol to form stock solutions of 0.12 mg/mL, 0.1 mg/mL and 0.0485 mg/mL, respectively. Appropriate quantities of C2-, C3-, and C6-O-acylation stock solutions were diluted with methanol into 10 mL volumetric flasks to form different concentrations of C2-O-acylation (0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 mg/mL), C3-O-acylation (0.015625, 0.03125, 0.0625, 0.125, 0.25, 0.5 and 1.0 mg/mL) and C6-O-acylation (0.0036375, 0.007275, 0.01455, 0.0291and 0.0485 mg/mL) standard solutions, which were then filtered through 0.45 μm membranes and were subsequently subjected to reverse phase HPLC analysis.

The yield of each of the acylation products of the catalytic reaction was measured by mixing the crude reaction mixture with methanol and diluted into a 50 mL volumetric flask, filtered through a 0.45 μm organic filtration membrane and set aside for HPLC analysis.

2.2 Chromatographic conditions

A Shimadzu LC-2030C 3D Plus High-Performance Liquid Chromatograph (Kyoto, Japan) was used to analyze the reaction products, equipped with a photo diode array (PDA) detector and a Waters XBridge C_{18} column (5 μm, 4.6×250 mm). The separation of C2-, C3-, and C6-O-acylation was achieved by applying gradient elution at a flow rate of 0.8 ml/min at 35 °C, the detection wavelength was 254 nm, and the injecting volume was 15 μL. The mobile phase was a three-phase system consisting of methanol (solvent A), acetonitrile (solvent B) and water (solvent C), and the proportion of solvent B at 20% was kept constant during the gradient elution, and 0–15 min, 0–8% A; 15–30 min, 8–20% A.

The retention times of C2-, C3-, and C6-O-acylation in HPLC analysis were 22.73 min, 12.45 min, and 26.62 min, respectively.

2.3 Establishment of calibration curve

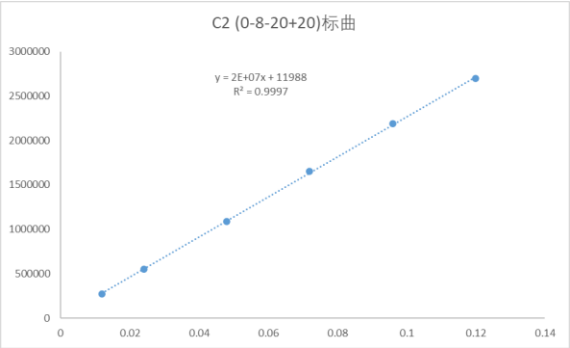
According to the chromatographic conditions described in "2.2", different concentrations of C2-, C3-, and C6-O-acylation standard solutions were injected into HPLC chromatograph for analysis sequentially, then calibration curves were established for C2-, C3-, and C6-O-acylation, respectively. The method was to establish the calibration curve using Microsoft

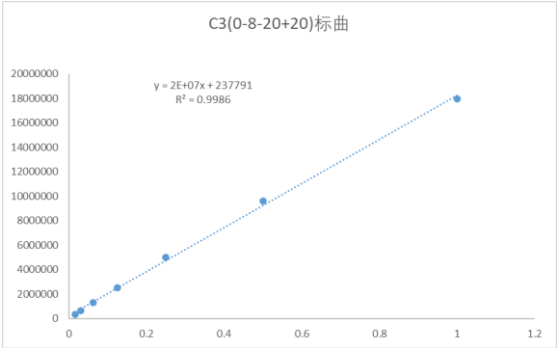
Excel 2016 software with the concentration of the standard solution as the horizontal coordinate and the peak area of the corresponding concentration as the vertical coordinate, and to calculate the retrospective equation and obtain the value of the regression coefficient "R^2".

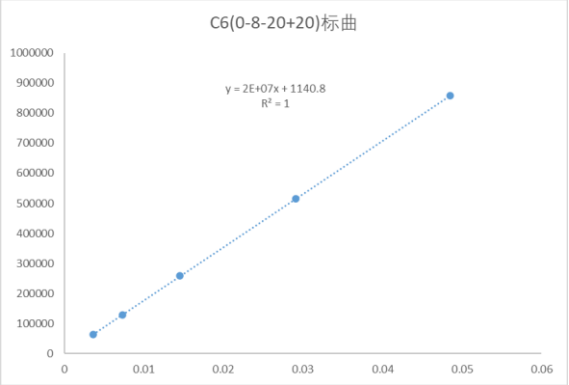
We established calibration curves for C2-, C3-, and C6-O-acylation and obtained their regression equations. The established calibration curves showed good linearity with R^2 values greater than 0.9981. Good linearity was observed for C2-O-acylation at 0.1-1.0 mg/mL, C3-O-acylation at 0.015625-1.0 mg/mL, and C6-O-acylation at 0.0036375-0.0485 mg/mL, respectively. The results are shown in Table S1.

Table S1 Calibration curve of C2-, C3-, and C6-O-acylation.

Analyte	Regression analysis	R^2	Liner range (mg/mL)
C2-O-acylation	y=2E+07x + 11988	0.9997	0.1-1.0
C3-O-acylation	y=2E+07x + 237791	0.9986	0.015625-1.0
C6-O-acylation	y=2E+07x + 1140.8	1	0.0036375-0.0485







2.4 Determination the yields of C2-, C3-, and C6-O-acylation *product of the catalytic reactions*

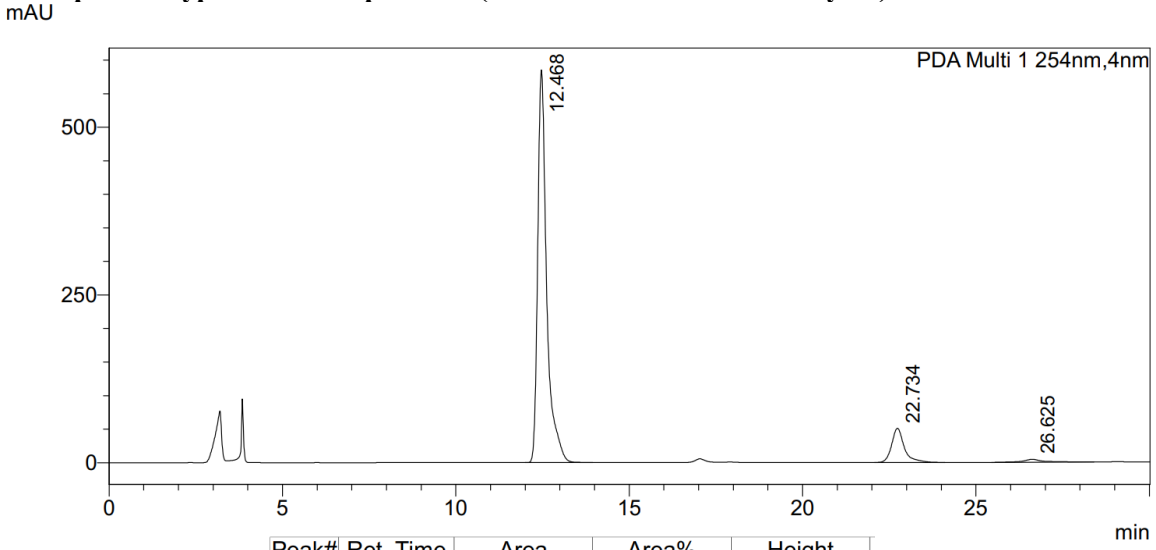
The crude reaction mixture was diluted to a 50 mL solution as described above and then was injected into the chromatograph according to the chromatographic conditions under "1.2" to obtain peak area. Substituting the peak area into the obtained regression equation, the concentration of the test solution was calculated, multiplied by the dilution times to obtain the mass of C2-, C3-, and C6-O-acylation in the reaction product, and then divided by the theoretical yields of C2-, C3- and, C6-O-acylation respectively to obtain the yields of C2-, C3-, and C6-O-acylatation.

3. General Procedures and Results.

3.1. General procedures and results of catalytic C3-selective acylation of saccharides

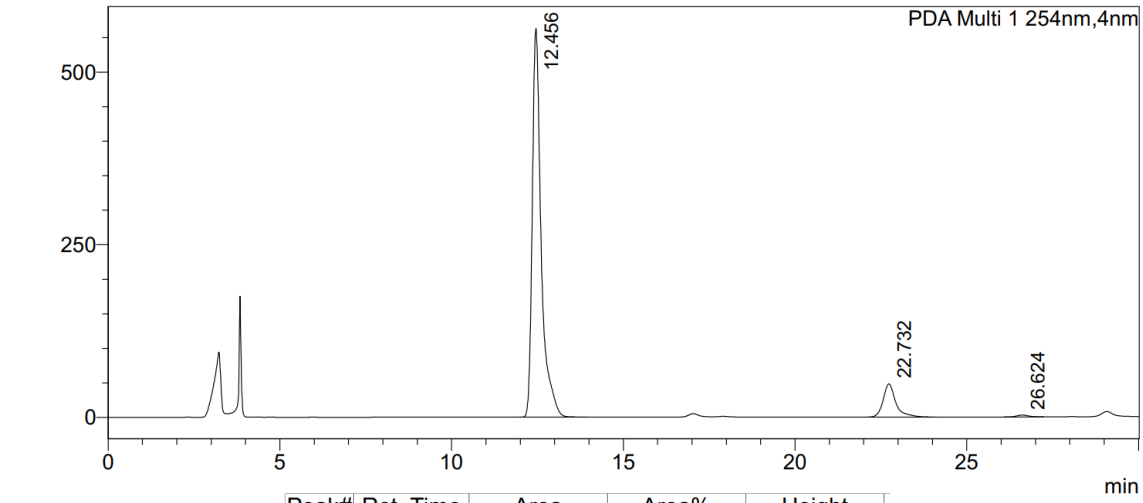
To a 4 mL vial, **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), NHC pre-catalyst (10 mol %), $B(OH)_3$ (1.5 equiv.), DQ (1.5 equiv.), and base (0.01 mmol, 0.1 equiv.) were added. Subsequently, 2 mL of solvent was introduced into the mixture. The reaction was allowed to stir vigorously at 50 ºC for 1-12 h. After cooling to the room temperature, the reaction mixture was directly diluted with methanol into 50 mL volumetric flasks to prepare the test solution. The above solution is injected into a 1.5 mL vial through a syringe and membrane filtration, and its content is determined by High-Performance Liquid Chromatography (HPLC).

Example of a typical HPLC spectrum (for results in Table S3 Entry 19)



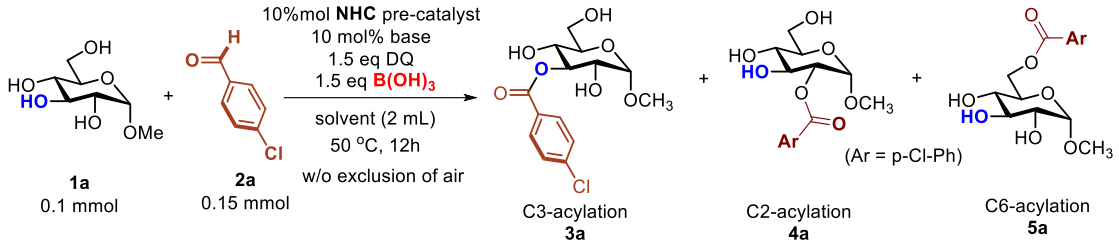
Peak#	Ret. Time	Area	Area%	Height
1	12.468	10528020	87.691	585023
2	22.734	1289367	10.739	50951
3	26.625	188458	1.570	4473
Total		12005845	100.000	640446

Example of a typical HPLC spectrum (for results in Table S3 Entry 23)



Peak#	Ret. Time	Area	Area%	Height
1	12.456	10177323	88.791	563331
2	22.732	1221961	10.661	48092
3	26.624	62793	0.548	2675
Total		11462078	100.000	614098

Table S2. Reaction conditions optimization for the synthesis of C3-O-acylation using different solvents and base (**Figure 2 of manuscript**).



Entry	Base / Solvent	K_2CO_3			KOAc			DMAP			Cs_2CO_3			DBU			pyridine			Na_3PO_4			Na_2CO_3			DABCO			^tBuONa		
		3a	Total	3a/4a	3a	Total	3a/4a	3a	Total	3a/4a	3a	Total	3a/4a	3a	Total	3a/4a	3a	Total	3a/4a	3a	Total	3a/4a	3a	Total	3a/4a	3a	Total	3a/4a	3a	Total	3a/4a
1	Toluene	0	0	0	0	0	19	0	0	21	0	0	9	0	1	15	0	0	19	0	1	5	0	0	1	0	0	0	0	0	0
2	Et_2O	0	0	7	1	1	7	1	2	8	0	0	9	3	3	7	2	2	9	2	2	3	0	1	1	2	2	7	0	0	3
3	$PhCF_3$	0	0	0	1	1	21	2	2	22	0	0	8	2	2	13	1	1	24	0	0	0	0	0	5	0	0	0	0	0	0
4	Hexane	1	1	3	4	5	3	1	1	1	1	1	1	2	2	1	2	2	1	1	1	0	1	1	0	0	0	0	0	0	0
5	o-Xylene	1	1	11	4	4	8	1	1	18	2	2	8	5	5	15	3	3	19	2	3	6	0	0	0	0	0	0	0	0	0
6	dichlorobenzene	4	5	24	5	7	12	2	3	18	1	1	14	1	2	13	3	5	22	1	1	4	3	4	10	0	1	0	3	4	0
7	MTBE	1	1	9	8	10	10	3	4	9	1	2	10	0	0	9	1	1	9	5	7	8	0	1	4	9	10	8	2	3	7
8	Chlorobenzene	8	9	26	24	27	14	3	3	18	16	17	22	3	4	16	4	4	27	8	10	9	5	7	0	14	16	0	9	10	0
9	$CHCl_3$	14	15	12	11	12	12	21	24	8	7	8	15	10	12	7	19	22	8	4	5	8	7	10	2	7	8	8	5	6	6
10	DCE	7	7	0	17	18	0	21	22	0	13	13	0	14	16	0	27	29	0	11	12	0	4	5	0	9	10	0	6	7	0
11	PrOAc	19	20	0	20	25	6	14	17	4	7	9	5	12	15	5	10	14	3	15	19	5	7	11	3	9	12	4	11	14	5
12	DCM	16	18	9	9	11	8	17	20	6	17	19	8	13	16	6	27	31	7	11	12	11	5	6	4	9	10	7	10	12	7
13	EtOAc	32	37	8	35	40	7	41	45	10	43	48	9	15	17	11	13	15	8	12	14	7	1	2	5	46	53	8	20	24	7
14	CH_3CN	33	1	4	7	10	4	53	64	5	45	55	6	58	69	6	3	4	4	3	5	3	0	1	0	48	59	5	10	14	4
15	Acetone	28	33	7	60	69	8	59	67	8	47	52	11	66	73	10	28	33	7	40	46	8	9	11	7	59	68	8	48	56	7
16	Dimethyl glycol	42	52	6	57	68	6	55	65	7	53	64	6	50	60	6	49	60	6	58	70	6	21	26	5	46	57	5	47	58	5
17	dioxane	56	70	5	39	50	5	45	57	5	35	47	4	42	55	5	26	34	4	46	59	4	16	22	4	43	57	4	40	54	4
18	THF	68	77	9	61	69	8	70	79	8	53	61	9	55	63	9	43	50	8	65	73	8	27	31	7	59	68	7	55	63	8
19	DMF	62	73	6	52	65	5	56	79	3	59	69	7	63	74	6	65	78	5	58	70	5	65	79	5	60	78	4	58	70	6
20	DMAc	69	78	7	61	72	6	62	80	4	69	78	9	70	79	8	57	68	6	68	79	7	69	80	7	68	82	5	65	75	7
21	NMP	73	84	7	66	78	6	68	87	4	65	75	8	70	79	8	71	83	6	71	82	7	75	87	7	72	86	5	75	87	6
22	DMSO	42	58	3	23	37	2	33	60	1	18	26	3	39	54	4	42	57	3	43	59	3	42	59	3	34	48	2	39	57	3

Table S3. Reaction conditions optimization for the synthesis of C3-O-acylation with THF as solvent.

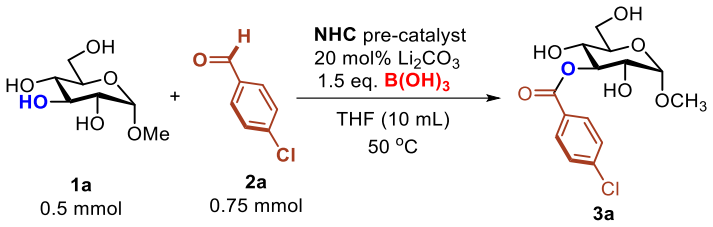
Entry	Base	3a（%）	4a (%)	5a (%)	Total（%）	C3: C2
1	No Base	33.98	4.62	0.82	39.42	7.36
2	K_2CO_3	68.33	7.75	0.82	76.91	8.81
3	KOAc	60.56	7.37	1.35	69.28	8.21
4	DMAP	69.58	8.24	0.81	78.63	8.45
5	Cs_2CO_3	53.08	6.03	1.94	61.04	8.81
6	DBU	55.08	6.06	1.67	62.80	9.09
7	Pyridine	43.45	5.59	1.44	50.48	7.77
8	Na_3PO_4	64.53	7.65	1.16	73.35	8.43
9	Na_2CO_3	26.77	3.62	0.97	31.35	7.40
10	DABCO	58.91	7.86	1.45	68.22	7.50
11	^{t}BuONa	52.08	7.64	1.74	61.46	6.81
12	^{t}BuOLi	73.27	9.57	0.93	83.77	7.66
13	^{t}BuOK	57.81	7.87	1.11	66.80	7.35
14	^{t}BuONa	54.55	7.14	1.33	63.03	7.64
15	NaOH	69.39	9.28	1.14	79.80	7.48
16	LiOH	63.31	10.24	2.42	75.97	6.18
17	KOH	71.02	9.12	0.65	80.78	7.79
18	NaOAc	71.41	9.95	0.70	82.06	7.18
19	K_3PO_4	74.85	9.11	0.46	84.42	8.21
20	$Na_2HPO_42H_2O$	64.64	8.53	1.73	74.91	7.58
21	$PhCO_2Na$	64.04	9.61	0.95	74.60	6.66
22	DABCO	55.79	7.58	1.50	64.86	7.36
23	Li_2CO_3	77.49	9.62	1.41	88.52	8.06
24	$KHCO_3$	55.22	7.38	0.94	63.53	7.49
25	$NaHCO_3$	53.24	7.23	1.74	62.22	7.36

Table S4. The progress and selectivity for reaction with Li_2CO_3 in THF at RT (**Figure 3A of manuscript**).

Entry	Reaction Time (h)	3a (%)	4a (%)	5a (%)	Total（%）	3a:4a
1	0.5	4	1	0	5	6
2	1	11	2	0	13	7
3	1.5	21	3	0	24	7
4	2	28	4	1	32	7
5	2.5	41	5	1	47	8
6	3	53	7	1	61	8
7	3.5	50	6	1	58	8
8	4	59	8	1	68	8
9	4.5	61	8	1	70	8
10	5	57	7	1	66	8
11	5.5	63	8	1	72	8
12	6	68	8	1	77	8
13	6.5	69	9	1	79	8

14	7	72	9	1	83	8
15	7.5	75	9	1	86	8
16	8	72	9	1	83	8
17	8.5	76	9	1	87	8
18	9	77	9	1	88	8
19	9.5	77	9	1	87	8
20	10	75	9	1	86	8
21	10.5	78	9	1	88	8
22	11	77	9	1	87	8
23	11.5	77	9	1	87	8
24	12	78	9	1	88	8

3.2 General Procedures for the recycle and reuse of $B(OH)_3$.

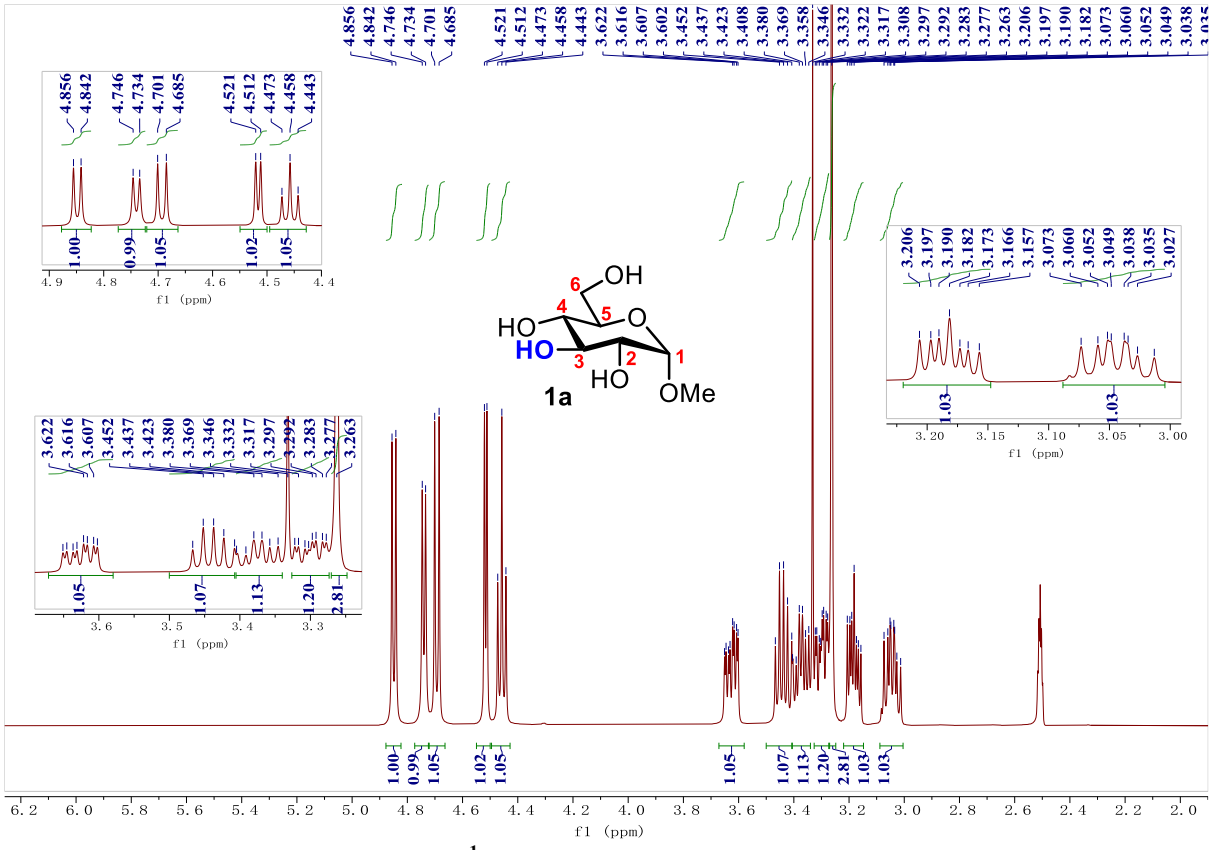


To a 20 mL vial, **1a** (0.5 mmol, 1.0 equiv.), **2a** (0.75 mmol, 1.5 equiv.), NHC pre-catalyst (10 mol %), B(OH)3 (1.5 equiv.), DQ (1.5 equiv.), and Li_2CO_3 (0.02 mmol, 0.2 equiv.) were added. Subsequently, 10 mL of THF was introduced into the mixture. The reaction was allowed to stir vigorously at 50 °C for 12 h. After cooling to the room temperature, the reaction mixture was extracted by EA/Water. Then the aqueous layer was dried by rotary evaporation to obtain the crude $B(OH)_3$. The crude $B(OH)_3$ without any purity was reused to afford the corresponding saccharide acylation products.

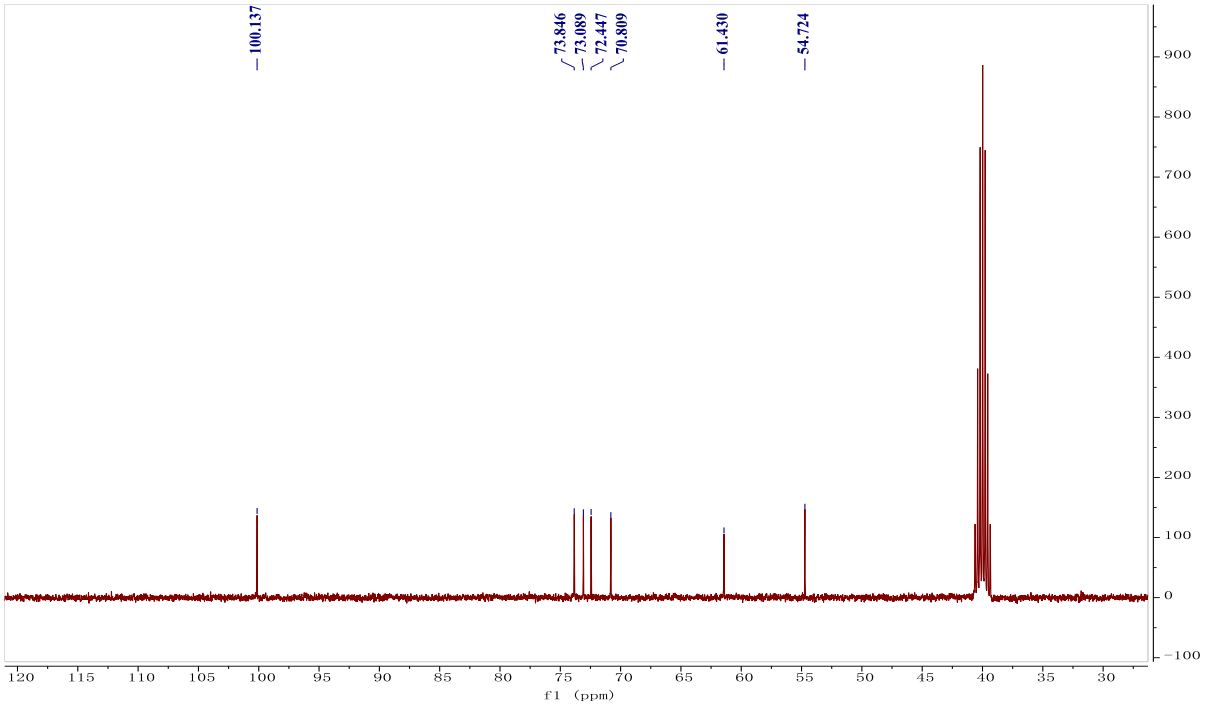
3.3 Experiments for the analysis of saccharide-boric acid adduct (reaction intermediate).

In order to achieve highly resolved NMR spectrums for clear analysis, the adduct between saccharide **1a** and boric acid (intermediate **I**) was pre-prepared (as a mixture with unreacted **1a**) using the following procedure. The NMR was taken using DMSO-d_6 as the solvent for well-resolved spectrum. As a technical note, this intermediate is also formed using other solvents in the catalytic reactions.

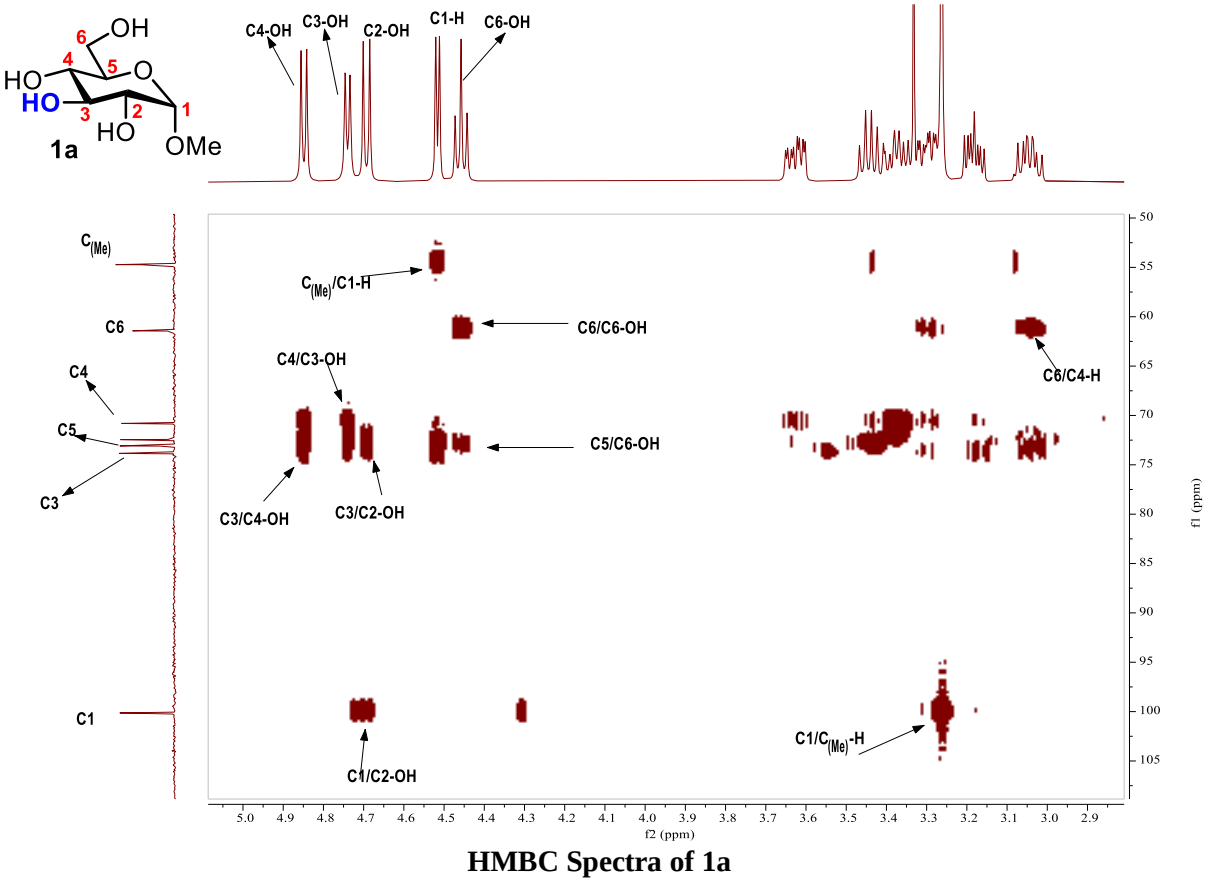
To a 50 mL vial, **1a** (5 mmol, 1.0 equiv.) and $B(OH)_3$ (1.0 equiv.) were added. Subsequently, 20 mL of toluene was introduced into the mixture. The reaction was refluxed at 120 °C for 48 h. After cooling to the room temperature, the solvent is removed via rotary evaporation to obtain a white solid (as a mixture of intermediate **I** and unreacted **1a** and boric acid). The ^{1}H NMR spectrum was obtained using DMSO-d_6 as the solvent.



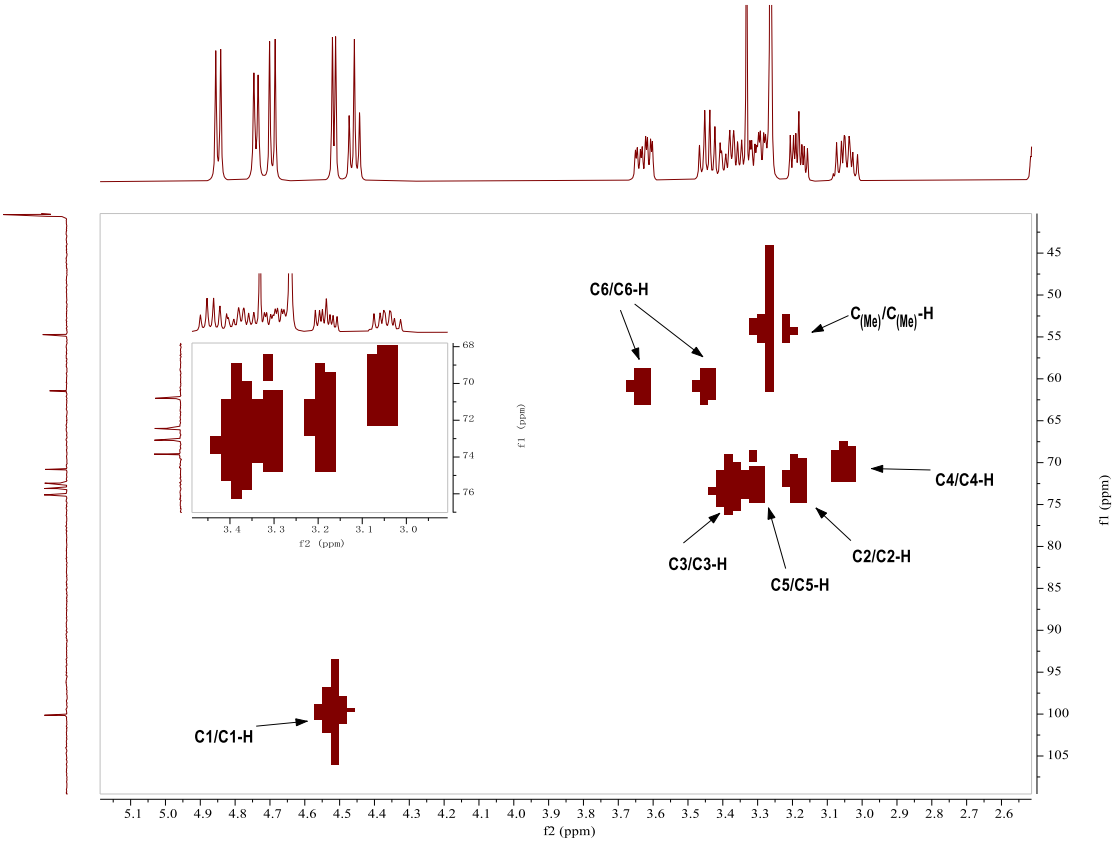
^{1}H NMR Spectra of **1a**



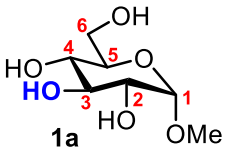
^{13}C NMR Spectra of 1a



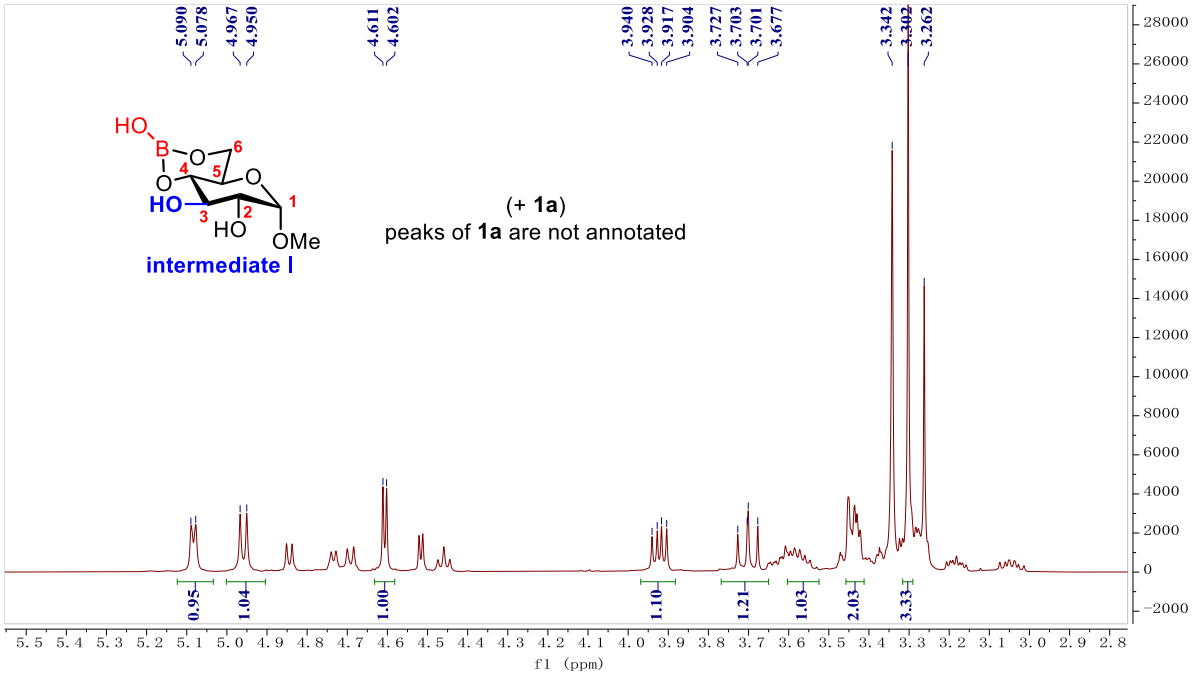
HMBC Spectra of 1a



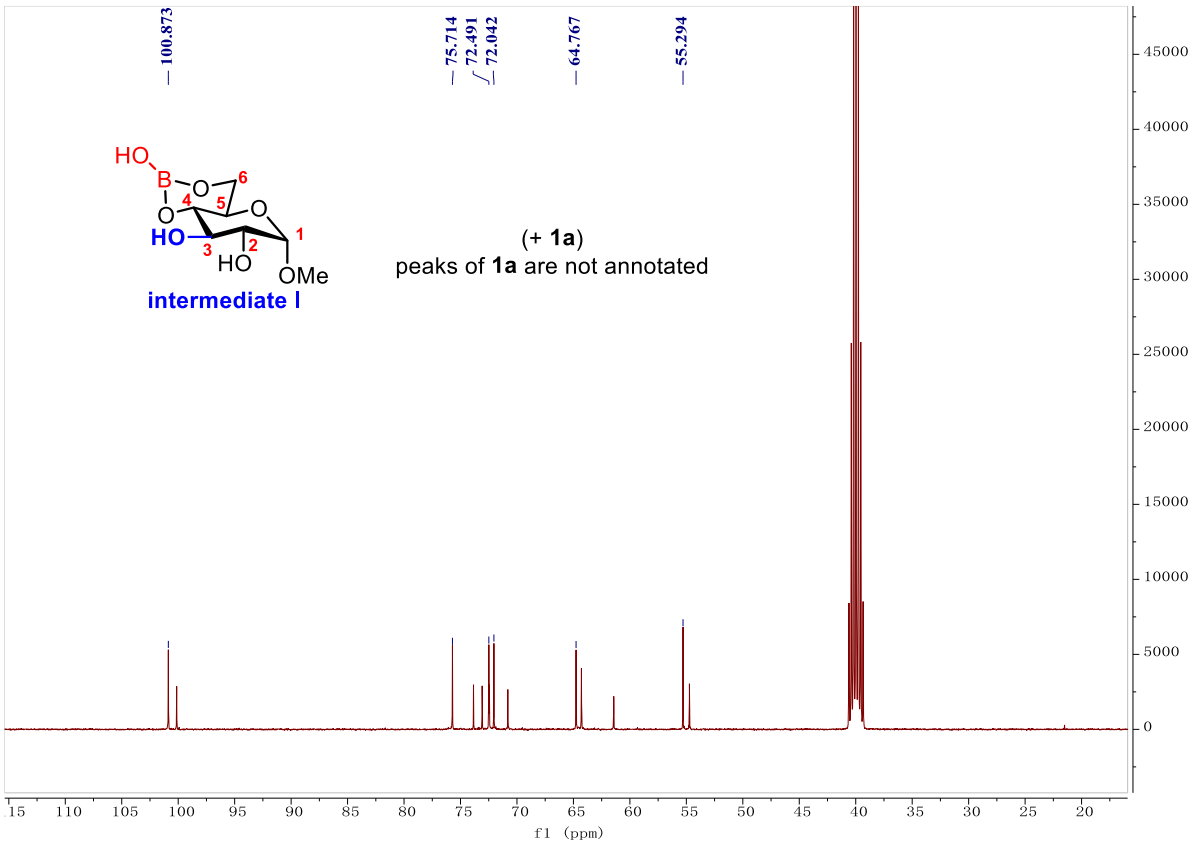
HMQC Spectra of 1a



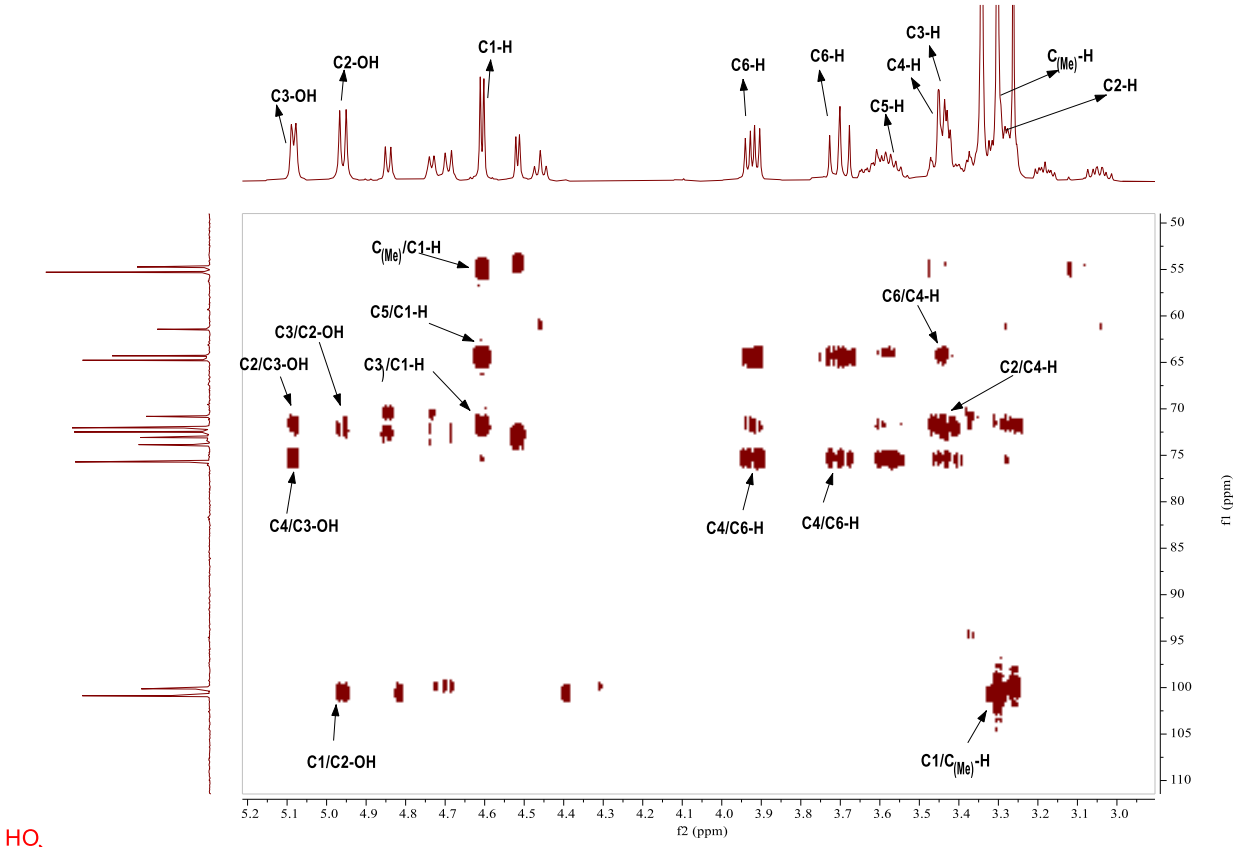
COSY Spectra of 1a



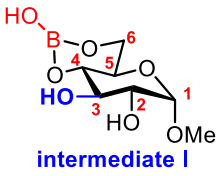
^{1}H NMR Spectra of mixture of 1a and intermediate I



^{13}C NMR Spectra of mixture of 1a and intermediate I

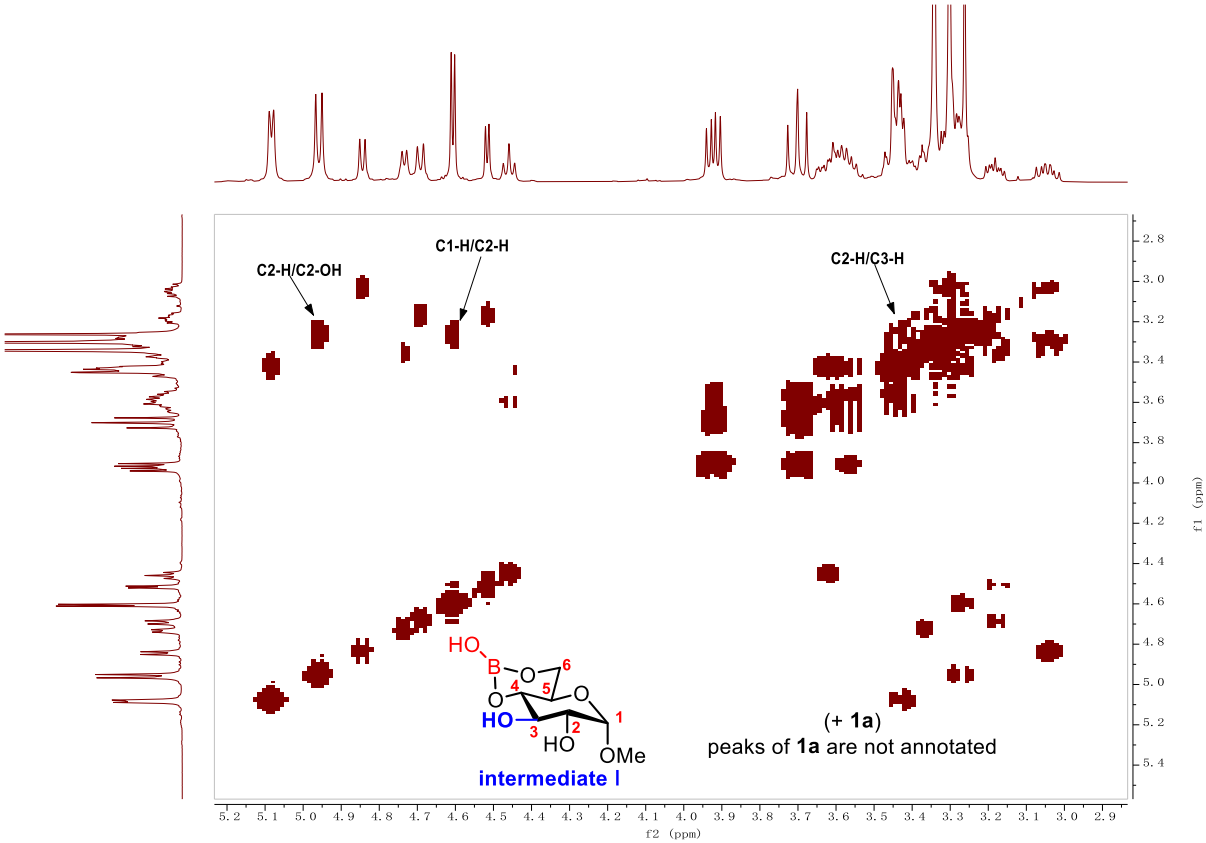


HMBC Spectra of mixture of 1a and intermediate Ⅰ



intermediate Ⅰ

HMQC Spectra of mixture of 1a and intermediate Ⅰ

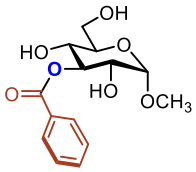


COSY Spectra of mixture of 1a and intermediate Ⅰ

4. Characterization of Products

Compound **3a**, **4a**, **5a** could be prepared and characterized according to literature procedures (ref. 61 of main text).

(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl benzoate (3b):



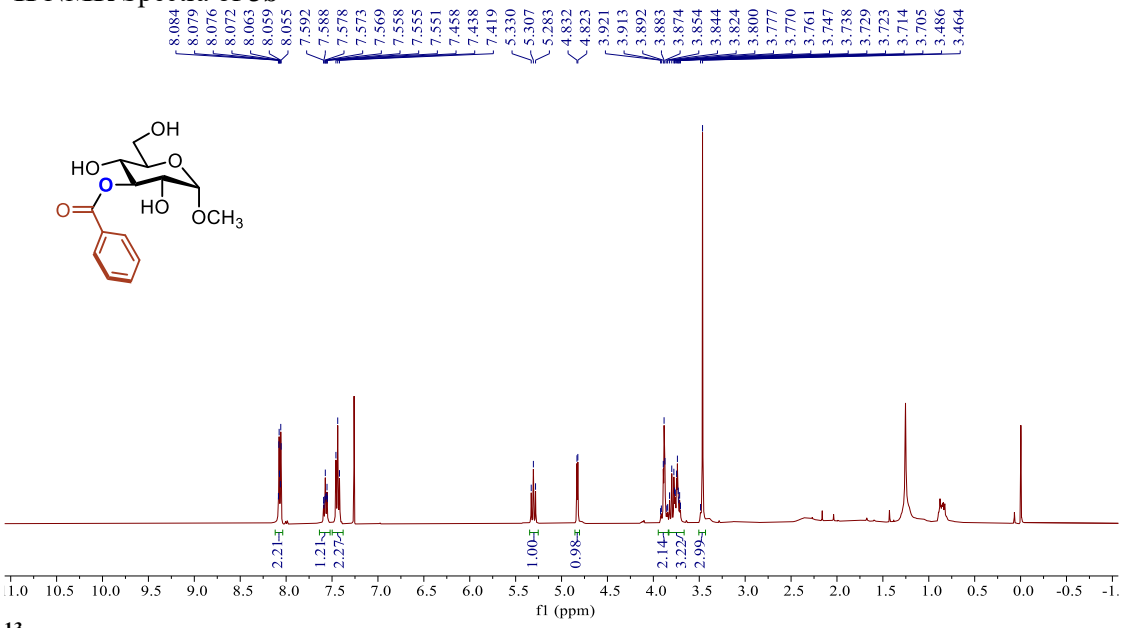
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 5 / 1), White solid, 72% yield, 21.4mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.05 (m, 2H), 7.59 – 7.55 (m, 1H), 7.43 (d, *J* = 7.7 Hz, 2H), 5.31 (t, *J* = 9.4 Hz, 1H), 4.83 (d, *J* = 3.8 Hz, 1H), 3.88 (t, *J* = 3.6 Hz, 2H), 3.82 – 3.70 (m, 3H), 3.46 (s, 3H).

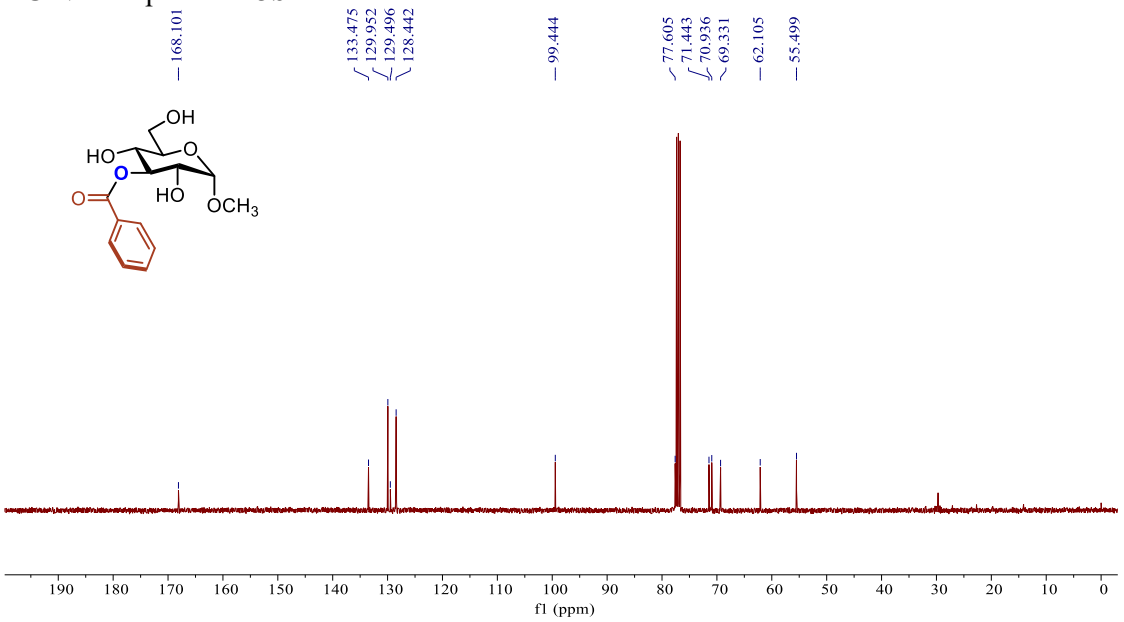
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.10, 133.47, 129.95, 129.50, 128.44, 99.44, 77.61, 71.44, 70.94, 69.33, 62.11, 55.50.

HRMS (ESI) Calcd for $C_{14}H_{18}O_7Na^+$ $[M+Na]^+$ 321.0945; Found: 321.0945.

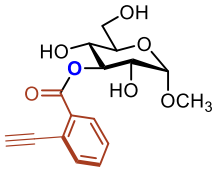
^{1}H NMR Spectra of **3b**



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



(2*R*,3*R*,4S,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 2-ethynylbenzoate (3c):



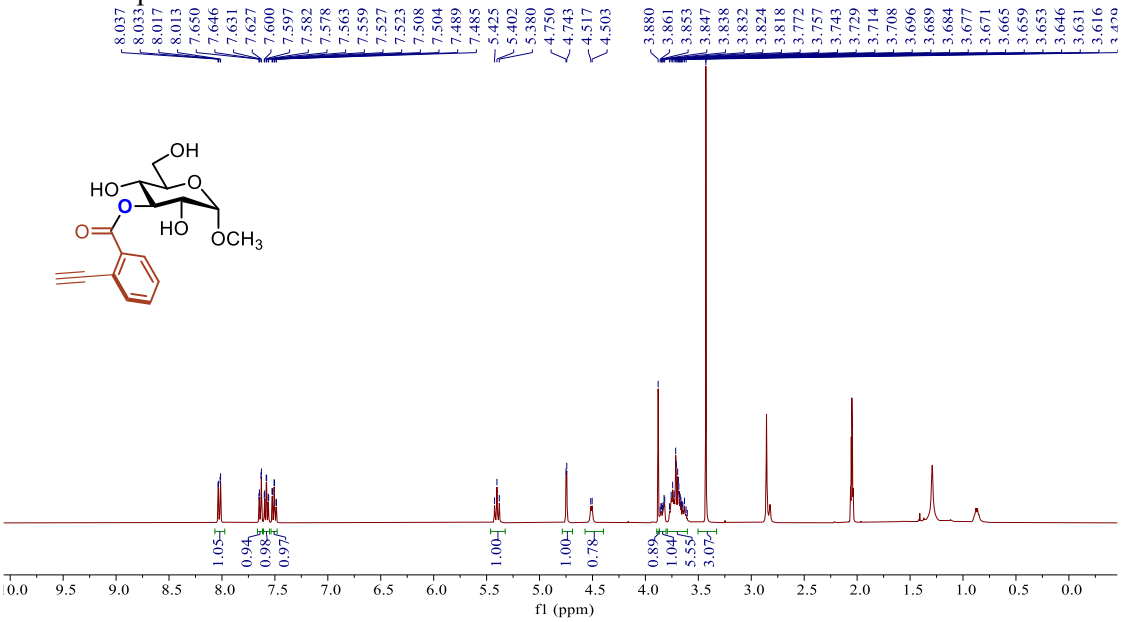
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 5 / 1), White solid, 82% yield, 26.4mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.01 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.62 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.56 (td, *J* = 7.5, 1.5 Hz, 1H), 7.49 (td, *J* = 7.6, 1.5 Hz, 1H), 5.39 (t, *J* = 9.0 Hz, 1H), 4.73 (d, *J* = 3.1 Hz, 1H), 3.68 (dtdd, *J* = 16.1, 13.5, 7.2, 3.4 Hz, 5H), 3.41 (s, 3H).

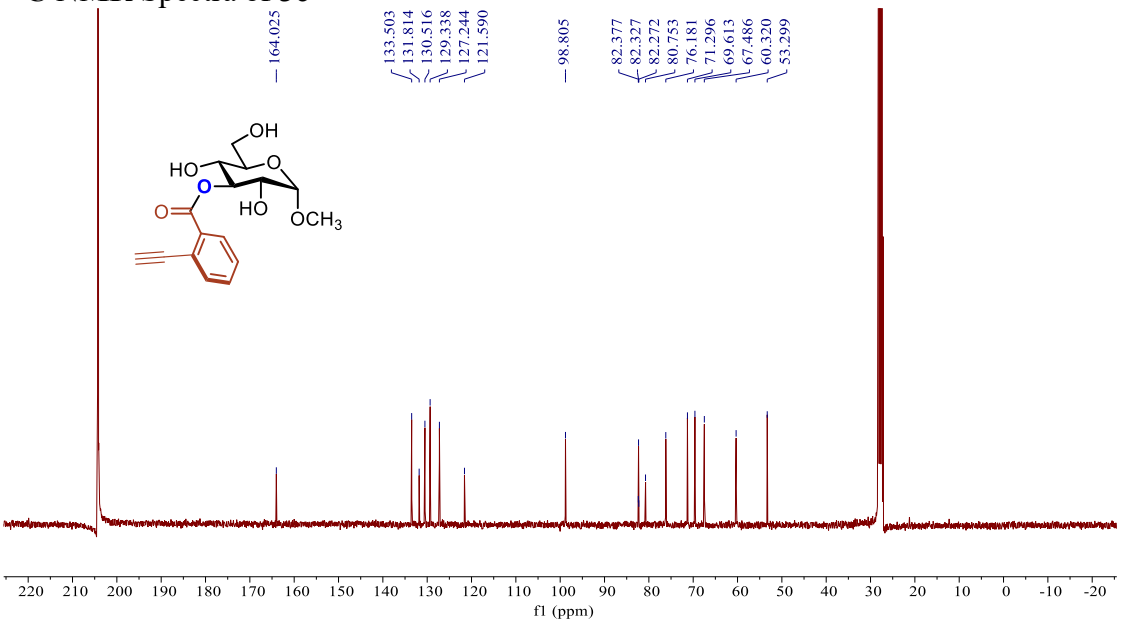
^{13}C NMR (100 MHz, Acetone-d_6) δ 164.03, 133.50, 131.81, 130.52, 129.34, 127.24, 121.59, 98.81, 82.38, 82.33, 82.27, 80.75, 76.18, 71.30, 69.61, 67.49, 60.32, 53.30.

HRMS (ESI) Calcd for $C_{16}H_{18}O_7Na^+$ [M+Na]$^+$ 345.0945; Found: 345.0944.

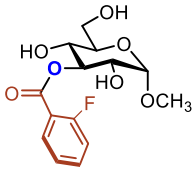
^{1}H NMR Spectra of **3c**



^{13}C NMR Spectra of **3c**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 2-fluorobenzoate (3d):



Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 84% yield, 26.5mg.

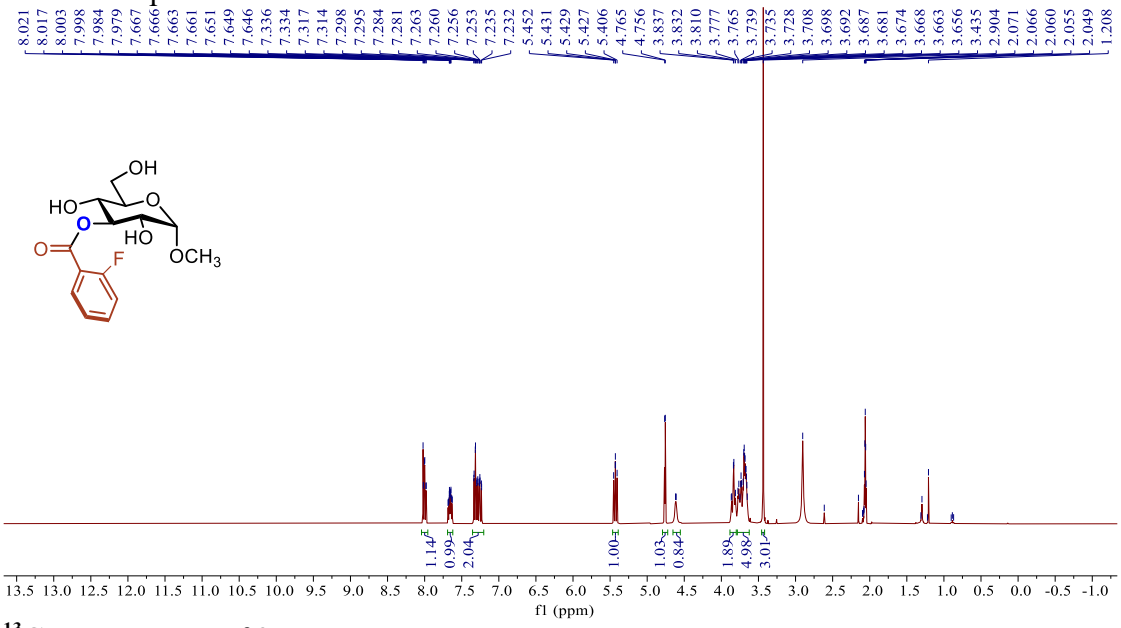
^{1}H NMR (400 MHz, Acetone-d_6) δ 8.04 – 7.96 (m, 1H), 7.72 – 7.60 (m, 1H), 7.36 – 7.21 (m, 2H), 5.47 – 5.38 (m, 1H), 4.76 (d, *J* = 3.6 Hz, 1H), 4.61 (d, *J* = 3.3 Hz, 0H), 3.88 – 3.79 (m, 2H), 3.79 – 3.62 (m, 5H), 3.44 (s, 3H).

^{13}C NMR (100 MHz, ACETONE-D_6) δ 162.25 (d, *J* = 3.71 Hz), 160.55 (d, *J* = 258.70 Hz), 133.35 (d, *J* = 8.74 Hz), 130.87, 122.84 (d, *J* = 3.85 Hz), 118.11 (d, *J* = 9.56 Hz), 115.56 (d, *J* = 22.10 Hz), 98.75, 75.98, 71.22, 69.60, 67.45, 60.25, 53.26.

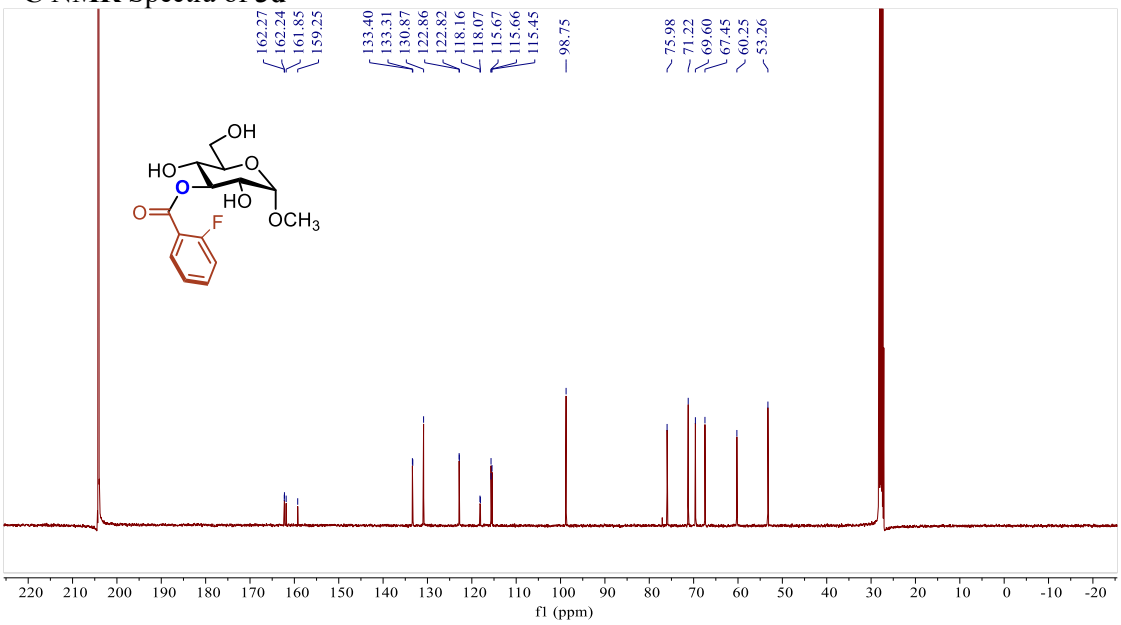
^{19}F NMR (376 MHz, Acetone) δ -110.74.

HRMS (ESI) Calcd for $C_{14}H_{17}FO_7Na^+$ $[M+Na]^+$ 339.0851; Found: 339.0851.

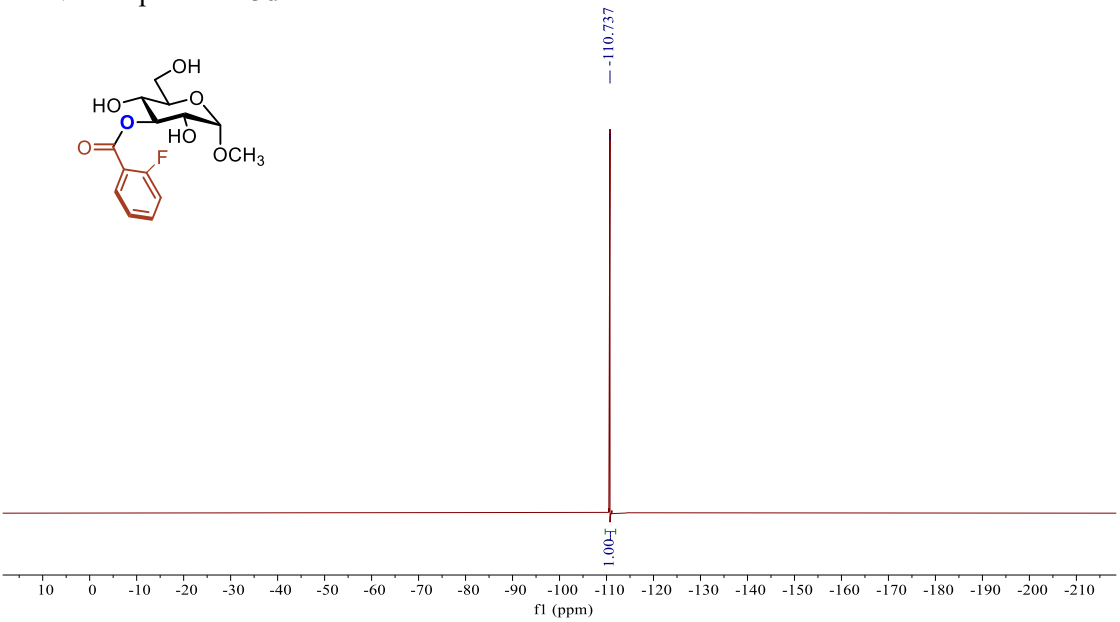
^{1}H NMR Spectra of **3d**



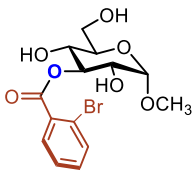
^{13}C NMR Spectra of **3d**



^{19}F NMR Spectra of **3d**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 2-bromobenzoate (3e):



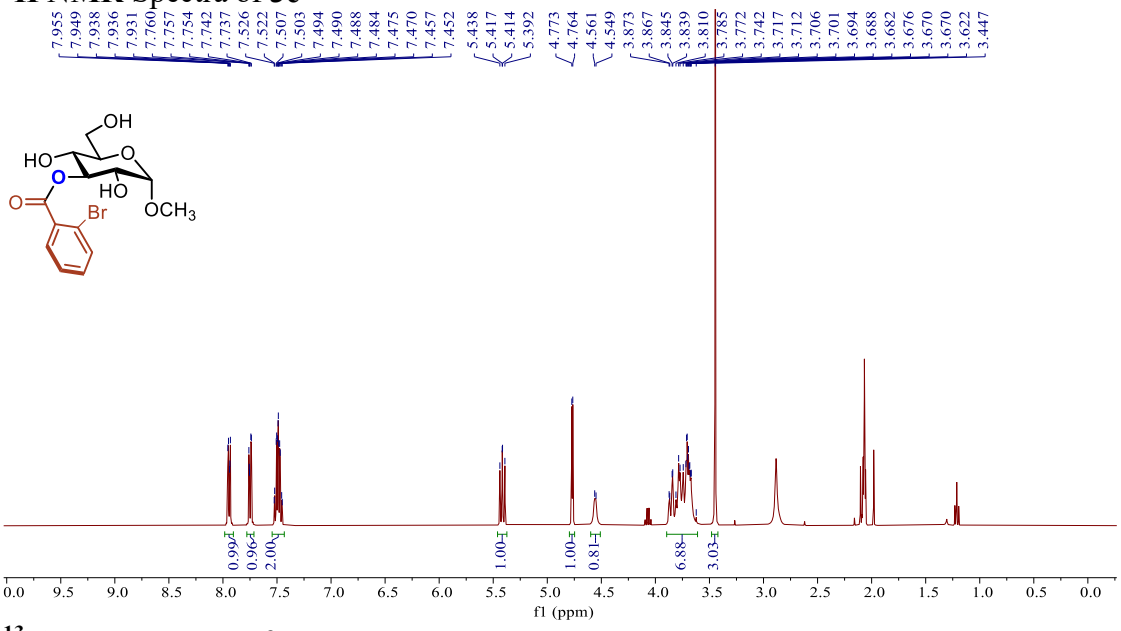
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 90% yield, 33.9mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.98 – 7.91 (m, 1H), 7.78 – 7.71 (m, 1H), 7.54 – 7.43 (m, 2H), 5.42 (dd, *J* = 9.8, 8.7 Hz, 1H), 4.77 (d, *J* = 3.6 Hz, 1H), 4.56 (d, *J* = 4.9 Hz, 1H), 3.90 – 3.62 (m, 6H), 3.45 (s, 3H).

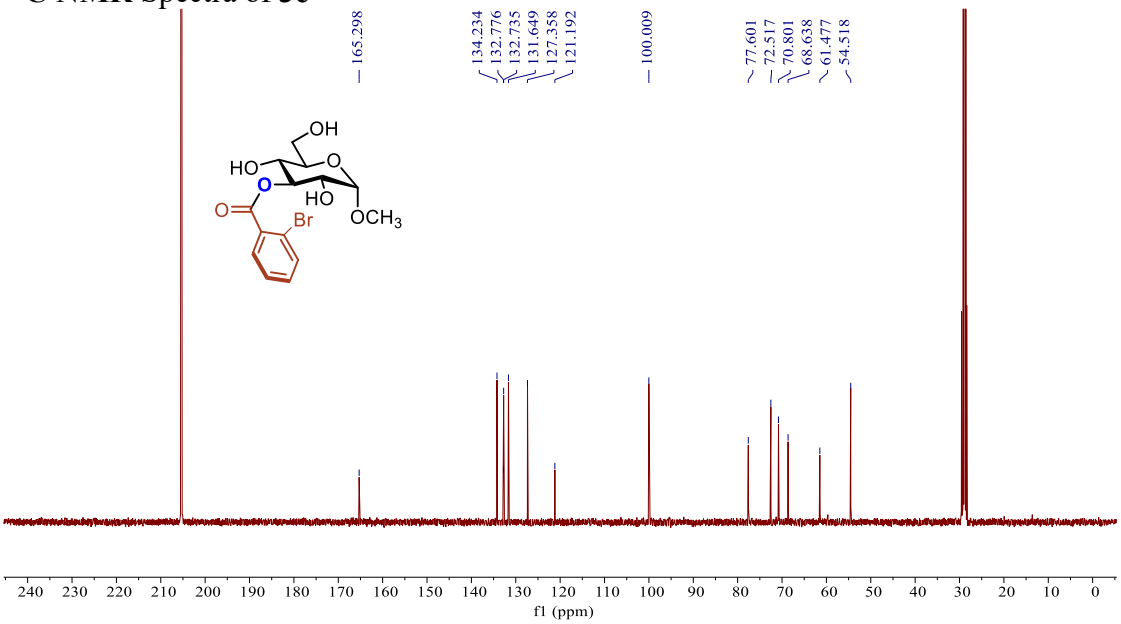
^{13}C NMR (101 MHz, Acetone-d_6) δ 165.30, 134.23, 132.78, 132.73, 131.65, 127.36, 121.19, 100.01, 77.60, 72.52, 70.80, 68.64, 61.48, 54.52.

HRMS (ESI) Calcd for $C_{14}H_{17}BrO_7Na^+$ $[M+Na]^+$ 399.0050; Found: 399.0049.

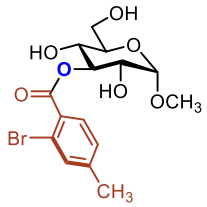
^{1}H NMR Spectra of **3e**



^{13}C NMR Spectra of **3e**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 2-bromo-4-methylbenzoate (3f):



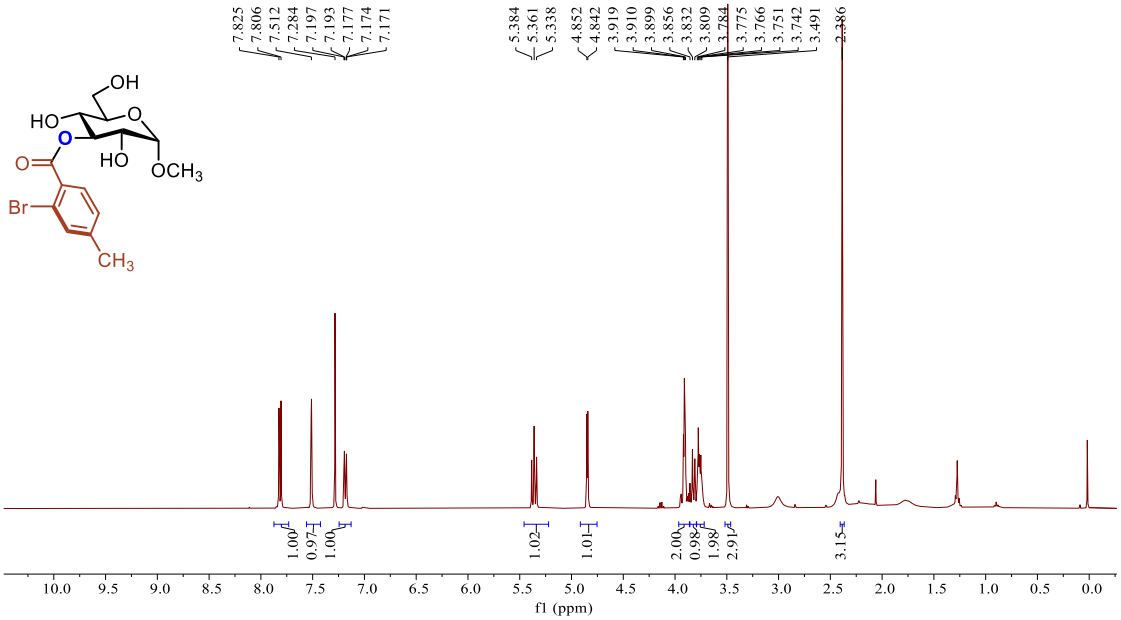
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 53% yield, 20.7mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.93 Hz, 1H), 7.51 (s, 0H), 7.19 (dd, *J* = 7.75, 1.48 Hz, 1H), 5.36 (t, *J* = 9.40 Hz, 1H), 4.85 (d, *J* = 3.79 Hz, 1H), 3.91 (t, *J* = 3.89 Hz, 2H), 3.83 (t, *J* = 9.40 Hz, 1H), 3.81 – 3.72 (m, 2H), 3.49 (s, 3H), 2.39 (s, 3H).

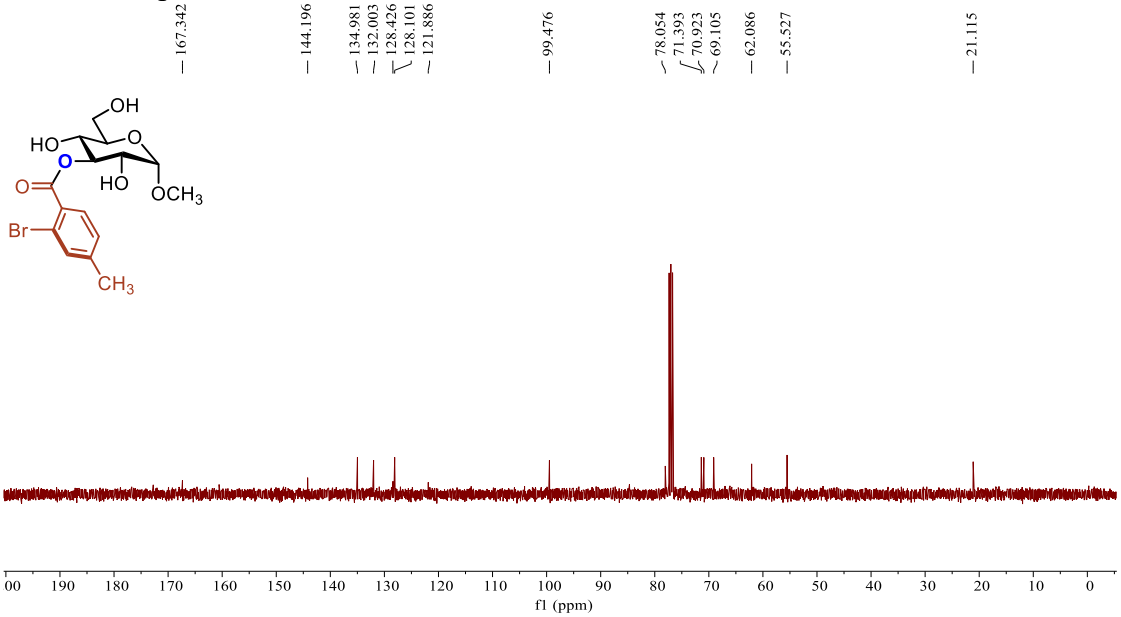
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.34, 144.20, 134.98, 132.00, 128.43, 128.10, 121.89, 99.48, 78.05, 71.39, 70.92, 69.10, 62.09, 55.53, 21.11.

HRMS (ESI) Calcd for $C_{15}H_{19}BrO_7Na^+$ $[M+Na]^+$ 415.0188; Found: 415.0186.

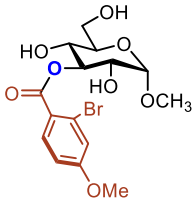
^{1}H NMR Spectra of **3f**



^{13}C NMR Spectra of **3f**



(2*R*,3*R*,4*R*,5*S*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 2-bromo-5-methoxybenzoate (3g):



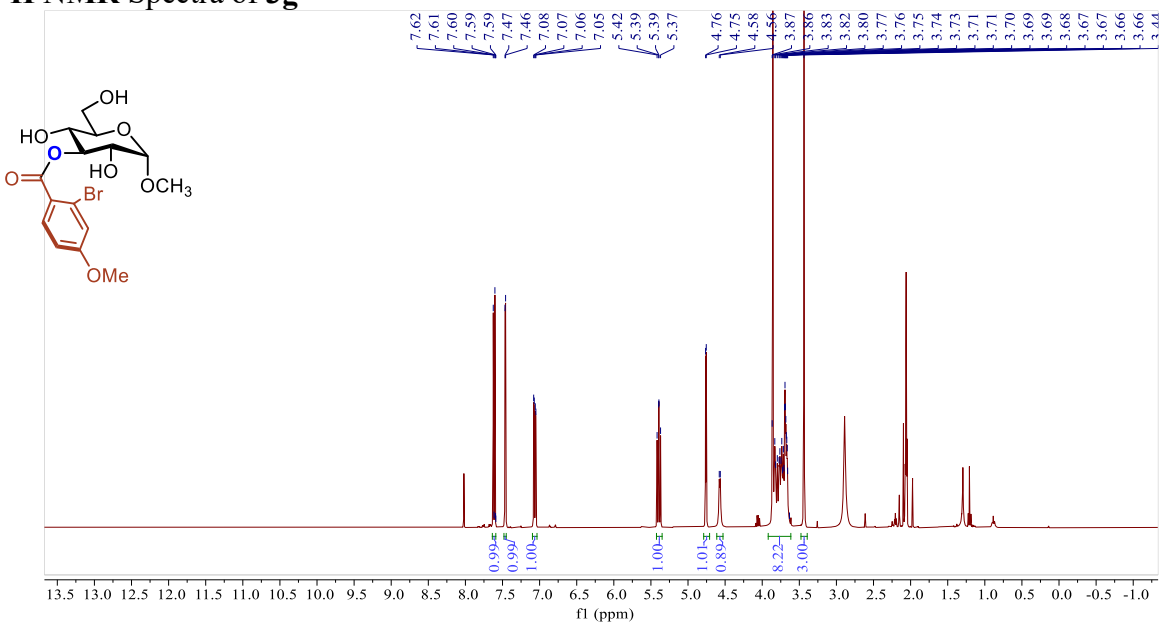
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 53% yield, 21.5mg.

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 7.61 (d, J = 8.8 Hz, 1H), 7.46 (d, J = 3.1 Hz, 1H), 7.07 (dd, J = 8.8, 3.1 Hz, 1H), 5.39 (t, J = 9.9, 8.9 Hz, 1H), 4.76 (d, J = 3.6 Hz, 1H), 4.57 (d, J = 5.7 Hz, 1H), 3.92 – 3.61 (m, 8H), 3.44 (s, 3H).

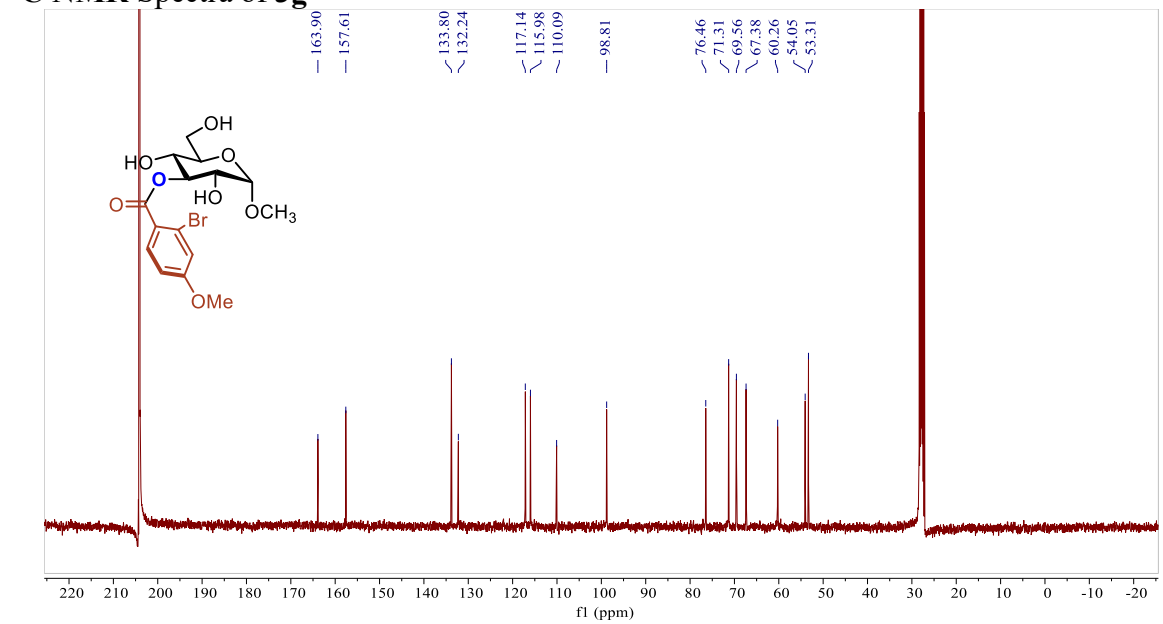
^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 163.90, 157.61, 133.80, 132.24, 117.14, 115.98, 110.09, 98.81, 76.46, 71.31, 69.56, 67.38, 60.26, 54.05, 53.31.

HRMS (ESI) Calcd for $C_{15}H_{19}BrO_8Na^+$ $[M+Na]^+$ 431.0137; Found: 431.0135.

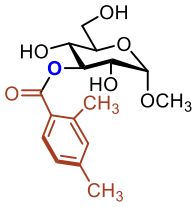
^{1}H NMR Spectra of **3g**



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



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 2,4-dimethylbenzoate (3h):



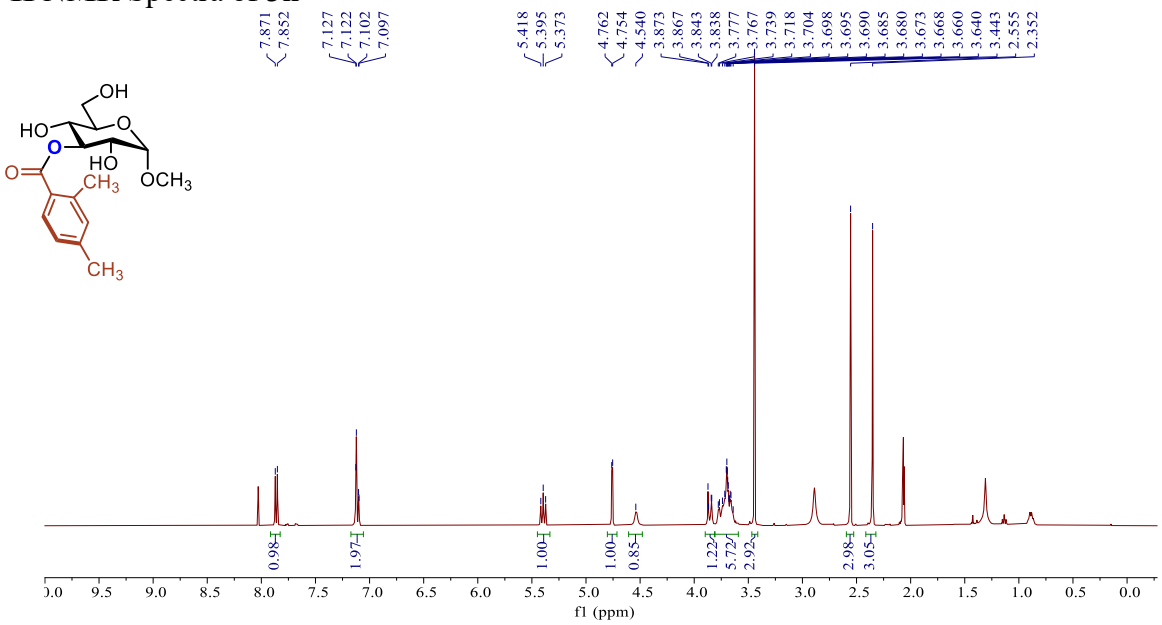
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 51% yield, 16.6mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.86 (d, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 5.40 (t, *J* = 8.9 Hz, 1H), 4.76 (d, *J* = 3.4 Hz, 1H), 4.54 (s, 1H), 3.87 – 3.84 (m, 1H), 3.78 – 3.64 (m, 3H), 3.44 (s, 3H), 2.55 (s, 3H), 2.35 (s, 3H).

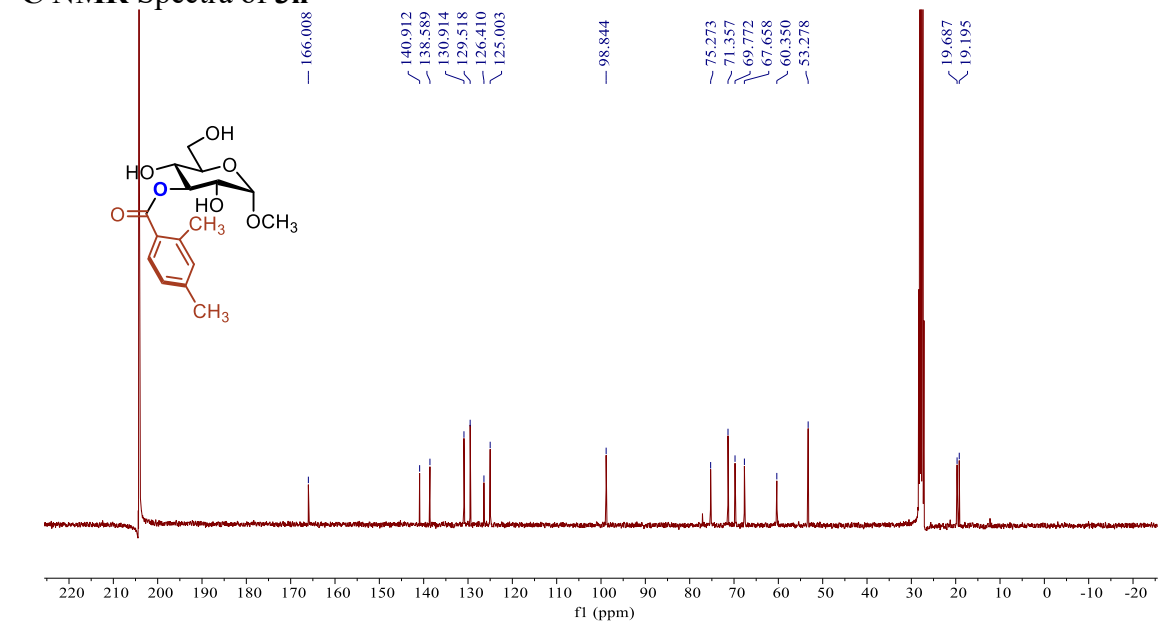
^{13}C NMR (100 MHz, ACETONE-d_6) δ 166.01, 140.91, 138.59, 130.91, 129.52, 126.41, 125.00, 98.84, 75.27, 71.36, 69.77, 67.66, 60.35, 53.28, 19.69, 19.20.

HRMS (ESI) Calcd for $C_{16}H_{22}O_7Na^+$ $[M+Na]^+$ 349.1258; Found: 349.1259.

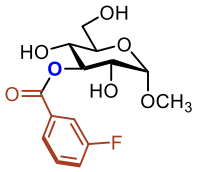
^{1}H NMR Spectra of **3h**



^{13}C NMR Spectra of **3h**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 3-fluorobenzoate (3i):



Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 51% yield, 16.1mg.

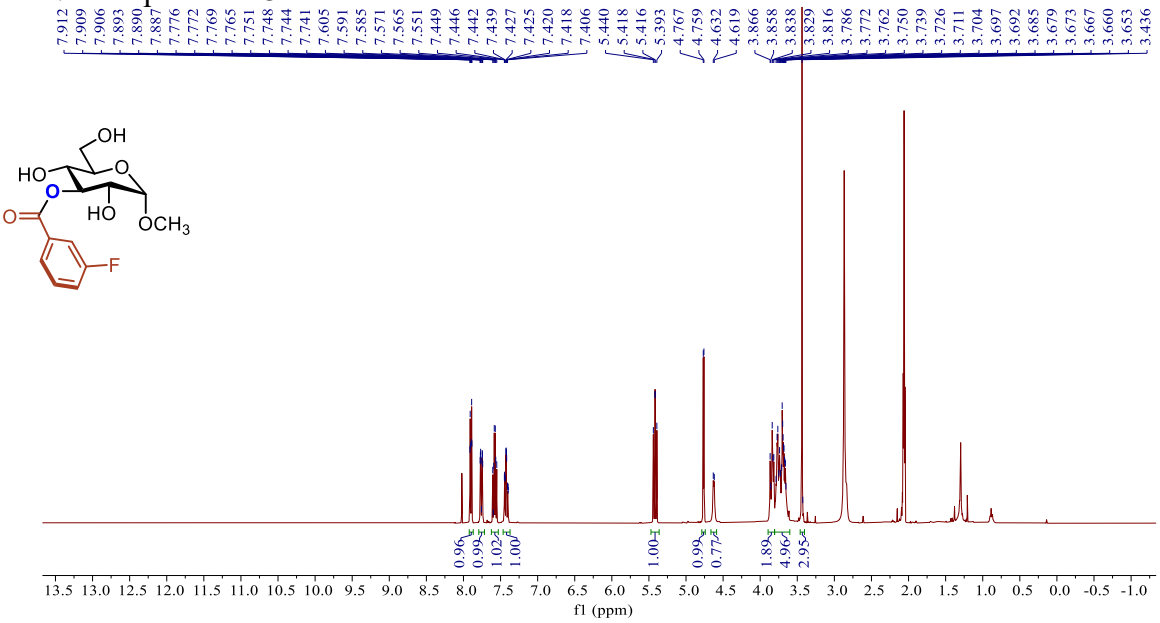
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.92 – 7.89 (m, 1H), 7.78 – 7.75 (m, 1H), 7.61 – 7.56 (m, 1H), 7.45 – 7.40 (m, 1H), 5.42 (dd, *J* = 9.9, 9.0 Hz, 1H), 4.77 (d, *J* = 3.6 Hz, 1H), 4.64 (d, *J* = 5.0 Hz, 1H), 3.87 – 3.83 (m, 2H), 3.78 – 3.67 (m, 2H), 3.44 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 163.64 (d, *J* = 2.81 Hz), 161.26 (d, *J* = 244.85 Hz), 132.05 (d, *J* = 7.51 Hz), 129.22 (d, *J* = 8.02 Hz), 124.33 (d, *J* = 2.29 Hz), 118.44 (d, *J* = 21.67 Hz), 114.81 (d, *J* = 23.36 Hz), 98.80, 76.36, 71.24, 69.55, 67.41, 60.29, 53.29.

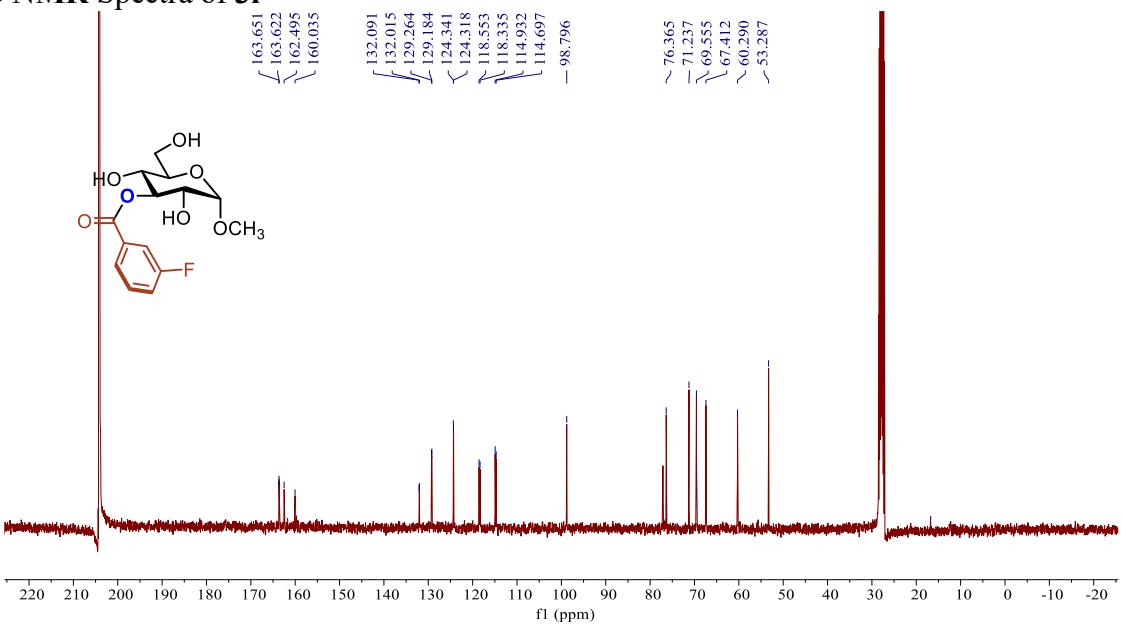
^{19}F NMR (376 MHz, Acetone) δ -114.32.

HRMS (ESI) Calcd for $C_{14}H_{17}FO_7Na^+$ [M+Na]$^+$ 339.0851; Found: 339.0851.

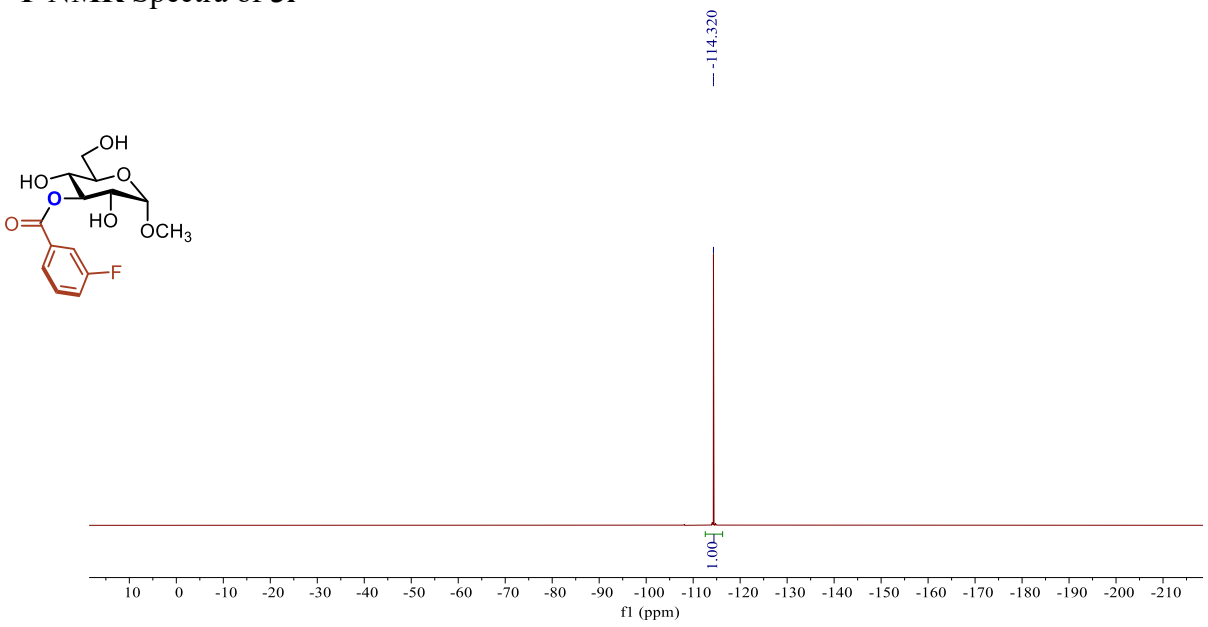
^{1}H NMR Spectra of **3i**



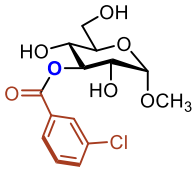
^{13}C NMR Spectra of **3i**



^{19}F NMR Spectra of **3i**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 3-chlorobenzoate (3j):



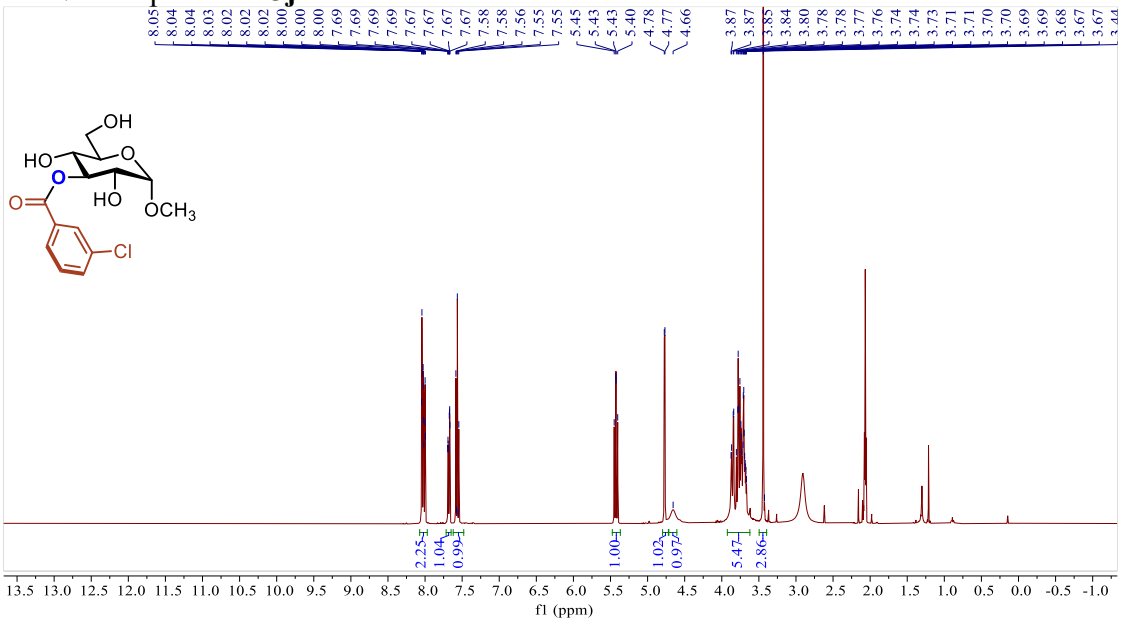
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 63% yield, 20.9mg

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.07 – 7.97 (m, 2H), 7.68 (ddd, *J* = 8.0, 2.2, 1.1 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 5.43 (dd, *J* = 9.8, 9.0 Hz, 1H), 4.77 (d, *J* = 3.6 Hz, 1H), 4.66 (s, 1H), 3.92 – 3.62 (m, 5H), 3.44 (s, 3H).

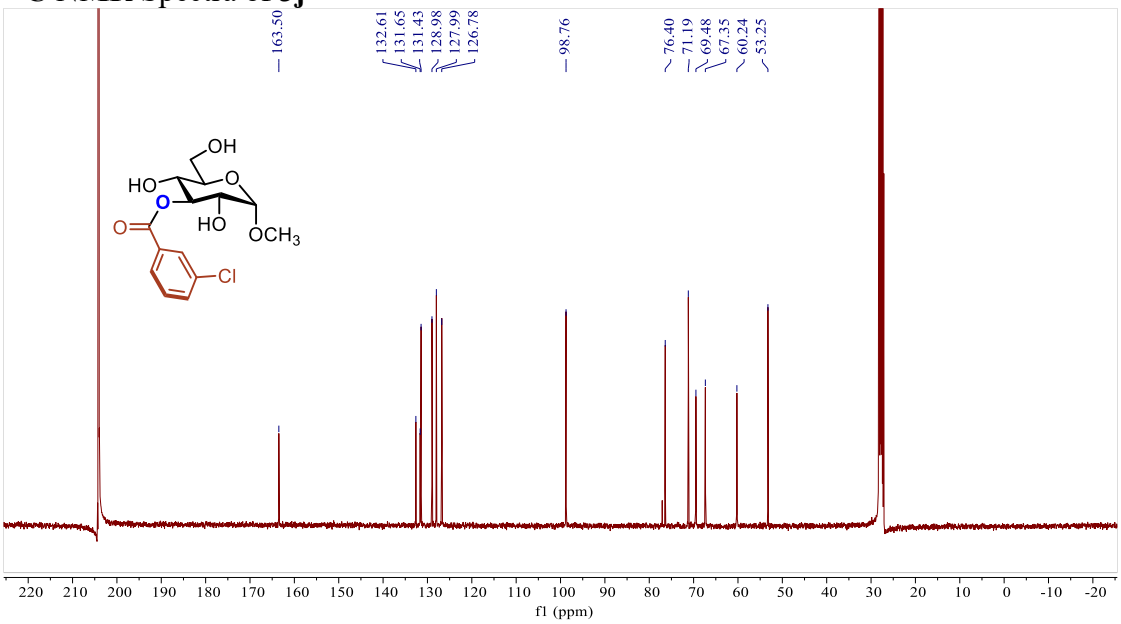
^{13}C NMR (101 MHz, Acetone-d_6) δ 163.50, 132.61, 131.65, 131.43, 128.98, 127.99, 126.78, 98.76, 76.40, 71.19, 69.48, 67.35, 60.24, 53.25.

HRMS (ESI) Calcd for $C_{14}H_{17}ClO_7Na^+$ $[M+Na]^+$ 355.0555; Found: 355.0558.

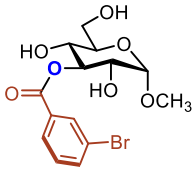
^{1}H NMR Spectra of **3j**



^{13}C NMR Spectra of **3j**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 3-bromobenzoate (3k):



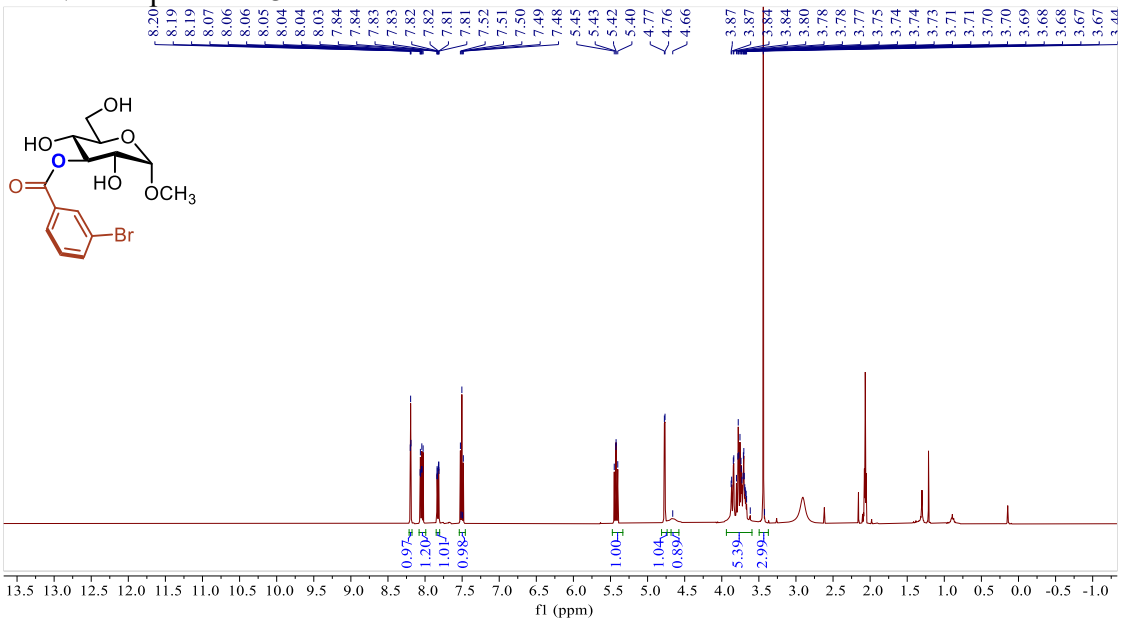
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 60% yield, 22.6mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.19 (t, *J* = 1.8 Hz, 1H), 8.08 – 7.99 (m, 1H), 7.83 (ddd, *J* = 7.9, 2.1, 1.0 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 5.43 (dd, *J* = 9.9, 9.0 Hz, 1H), 4.77 (d, *J* = 3.5 Hz, 1H), 4.66 (s, 1H), 3.94 – 3.59 (m, 5H), 3.44 (s, 3H).

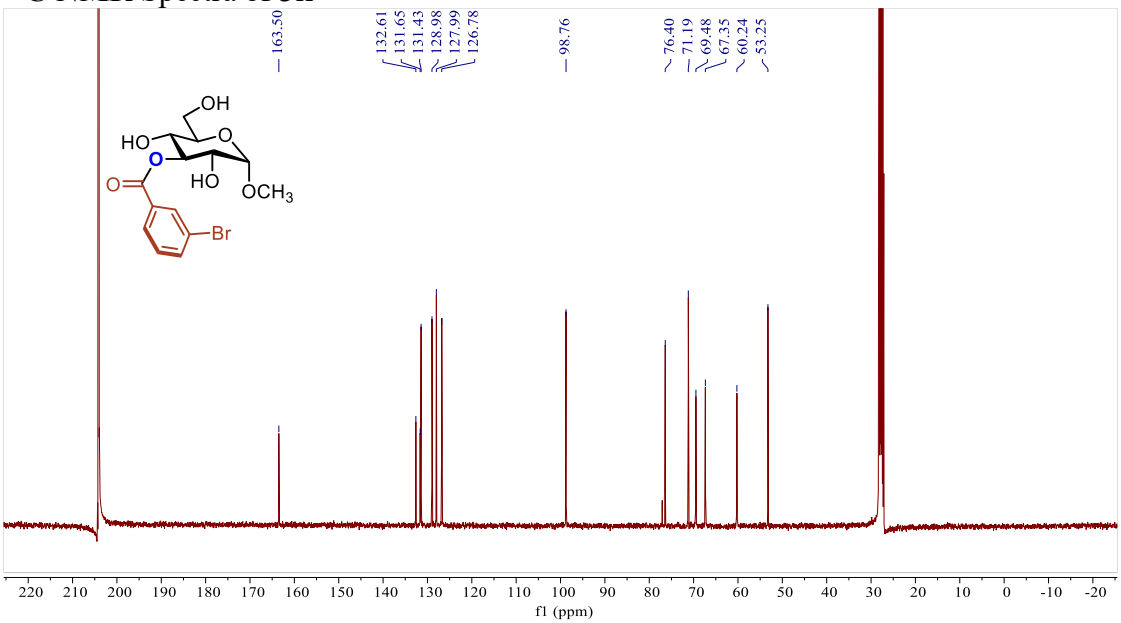
^{13}C NMR (101 MHz, Acetone-d_6) δ 163.50, 132.61, 131.65, 131.43, 128.98, 127.99, 126.78, 98.76, 76.40, 71.19, 69.48, 67.35, 60.24, 53.25.

HRMS (ESI) Calcd for $C_{14}H_{17}BrO_7Na^+$ $[M+Na]^+$ 399.0050; Found: 399.0049.

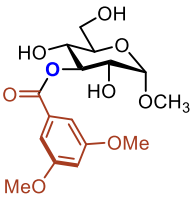
^{1}H NMR Spectra of **3k**



^{13}C NMR Spectra of **3k**



(2*R*,3*R*,4*R*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 3,5-dimethoxybenzoate (3l):



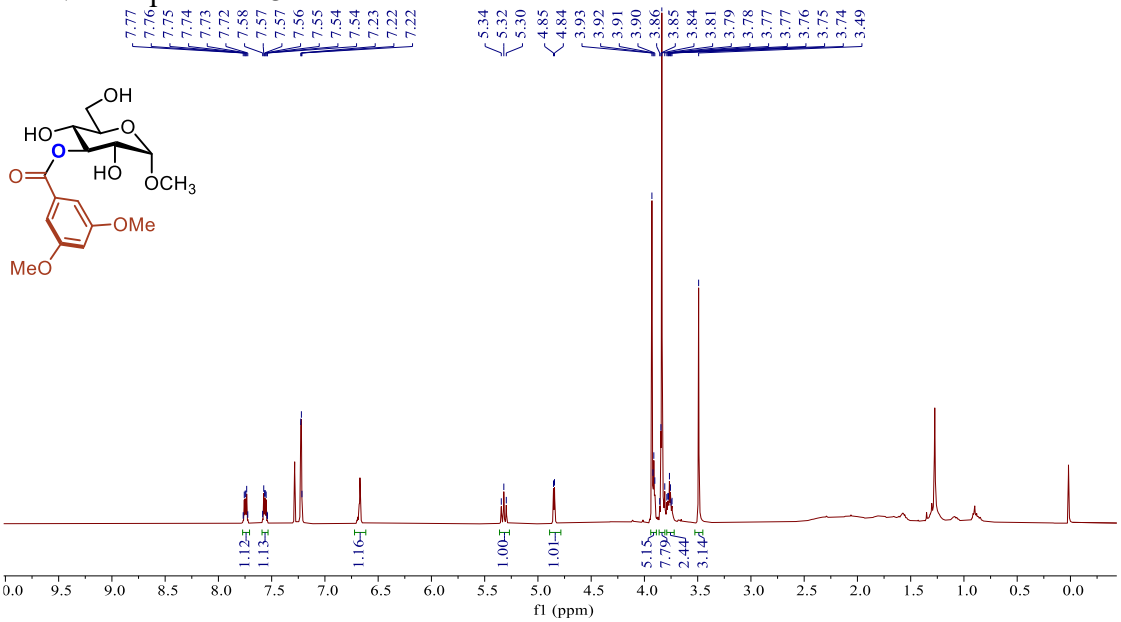
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid,72% yield, 25.8mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 5.7, 3.3 Hz, 1H), 7.56 (dd, *J* = 5.7, 3.3 Hz, 1H), 5.32 (t, *J* = 9.4 Hz, 1H), 4.85 (d, *J* = 3.8 Hz, 1H), 3.92 (d, *J* = 7.2 Hz, 5H), 3.84 (s, 8H), 3.76 (td, *J* = 6.0, 2.9 Hz, 2H), 3.49 (s, 3H).

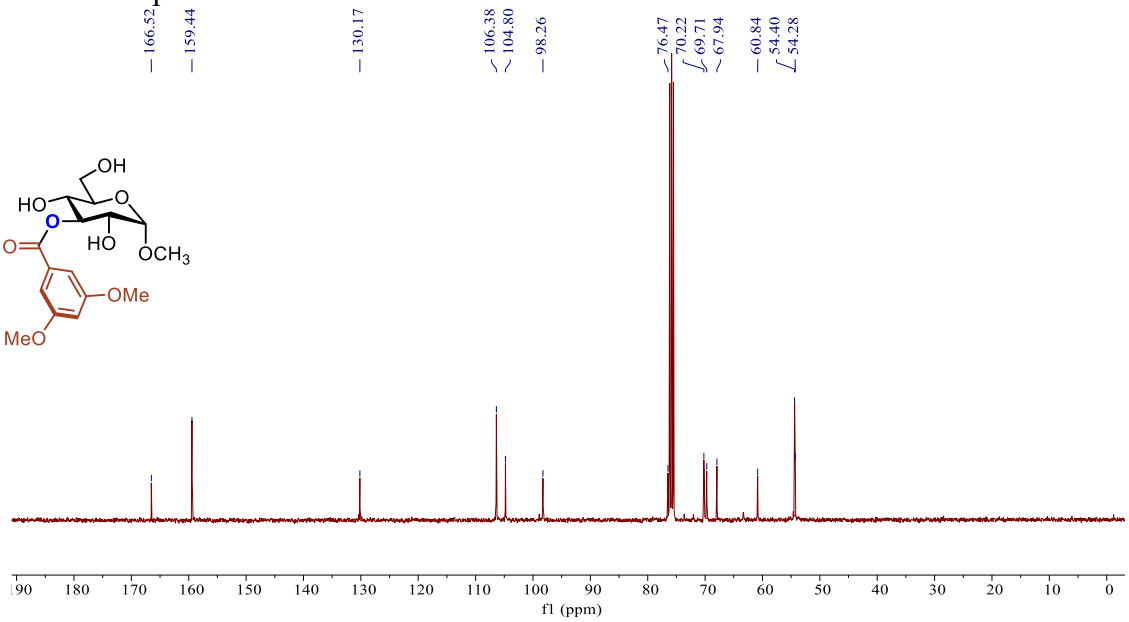
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.52, 159.44, 130.17, 106.38, 104.80, 98.26, 76.47, 70.22, 69.71, 67.94, 60.84, 54.40, 54.28.

HRMS (ESI) Calcd for $C_{15}H_{20}O_9Na^+$ $[M+Na]^+$ 381.1156; Found: 381.1155.

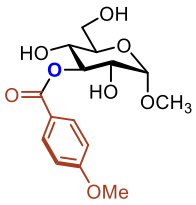
^{1}H NMR Spectra of **3l**



^{13}C NMR Spectra of **3l**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 4-methoxybenzoate (3m):



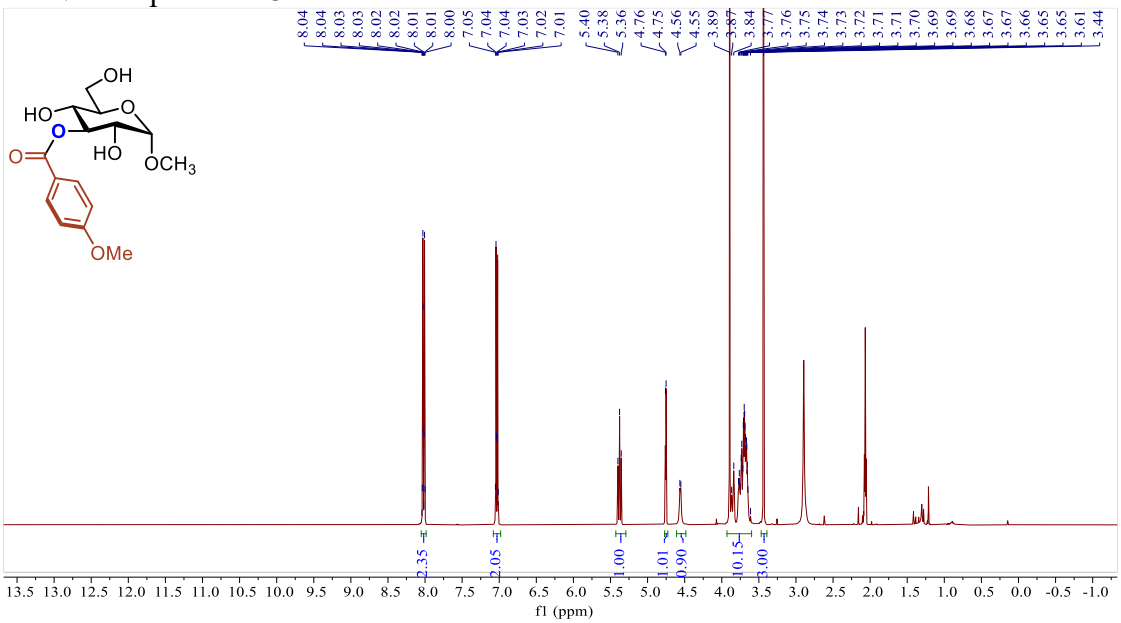
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 55% yield, 18mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.05 – 7.99 (m, 2H), 7.08 – 6.98 (m, 2H), 5.38 (t, *J* = 9.1 Hz, 1H), 4.75 (d, *J* = 3.3 Hz, 1H), 4.56 (d, *J* = 5.1 Hz, 1H), 3.93 – 3.60 (m, 10H), 3.44 (s, 3H).

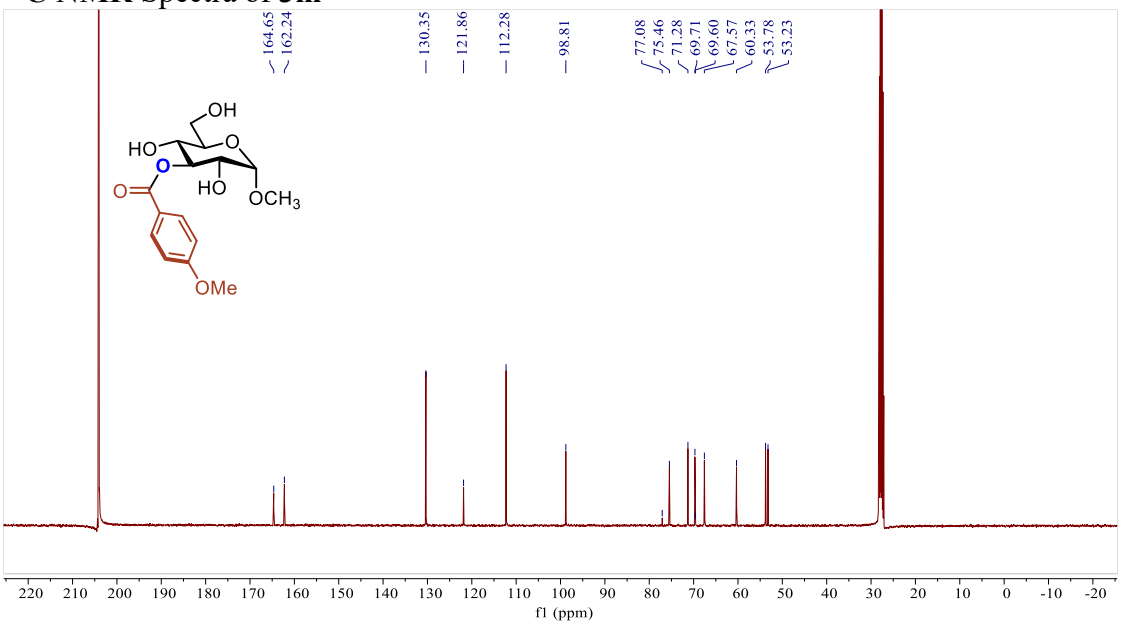
^{13}C NMR (101 MHz, Acetone-d_6) δ 164.65, 162.24, 130.35, 112.28, 98.81, 77.08, 75.46, 71.28, 69.71, 67.57, 60.33, 53.78, 53.23.

HRMS (ESI) Calcd for $C_{15}H_{20}O_8Na^+$ $[M+Na]^+$ 351.1050; Found: 351.1051.

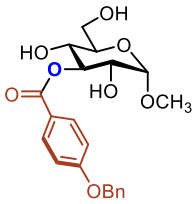
^{1}H NMR Spectra of **3m**



^{13}C NMR Spectra of **3m**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 4-(benzyloxy)benzoate (3n):



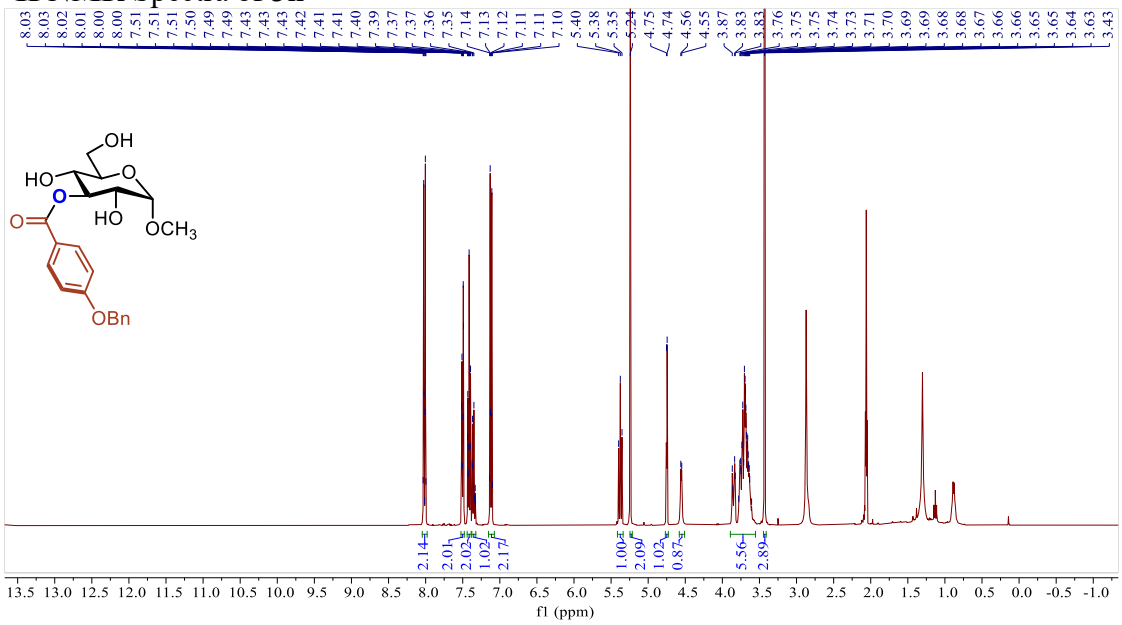
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 54% yield, 21.8mg

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.05 – 7.98 (m, 2H), 7.52 – 7.32 (m, 5H), 7.15 – 7.07 (m, 2H), 5.38 (t, *J* = 9.1 Hz, 1H), 5.24 (s, 2H), 4.75 (d, *J* = 3.4 Hz, 1H), 4.55 (d, *J* = 5.1 Hz, 1H), 3.89 – 3.55 (m, 6H), 3.43 (s, 3H).

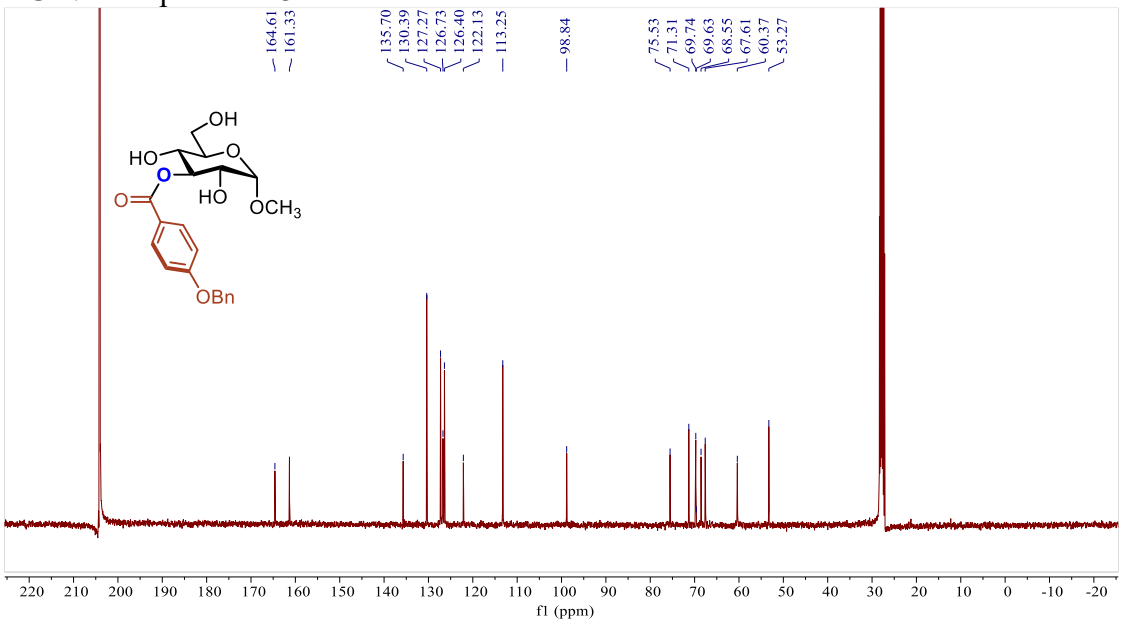
^{13}C NMR (101 MHz, Acetone-d_6) δ 164.61, 161.33, 135.70, 130.39, 127.27, 126.73, 126.40, 122.13, 113.25, 98.84, 75.53, 71.31, 69.74, 68.55, 67.61, 60.37, 53.27.

HRMS (ESI) Calcd for $C_{21}H_{24}O_8Na^+$ $[M+Na]^+$ 427.1363; Found: 427.1363.

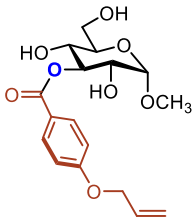
^{1}H NMR Spectra of **3n**



^{13}C NMR Spectra of **3n**



(2*R*,3*R*,4*R*,5*S*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 4-(allyloxy)benzoate (3o):



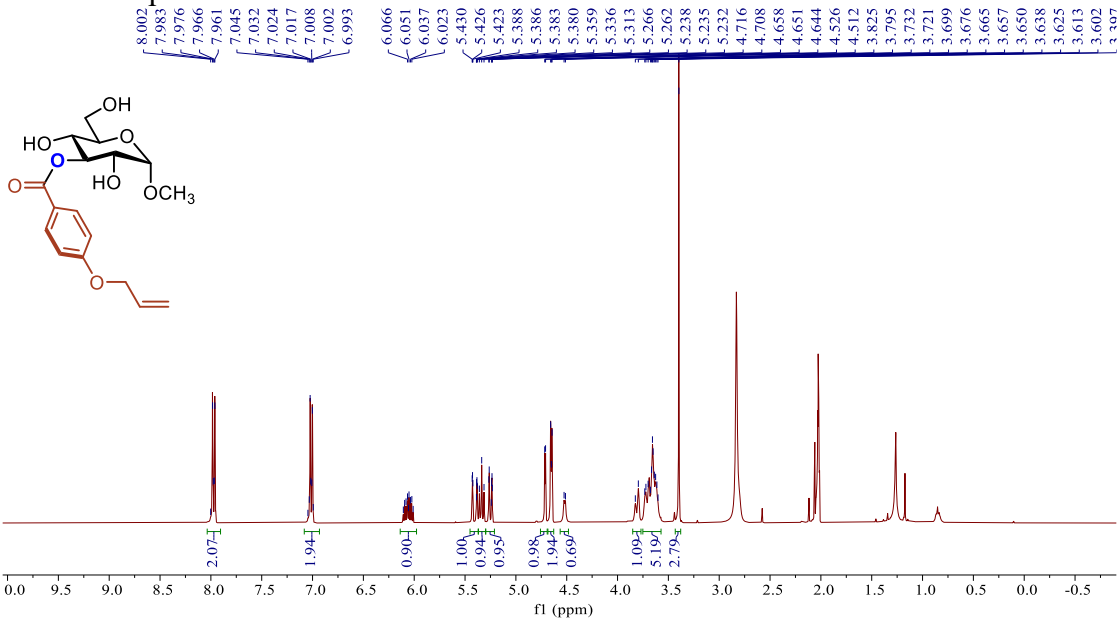
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 60% yield, 21.2mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.03 – 7.92 (m, 2H), 7.06 – 6.96 (m, 2H), 6.06 (ddt, *J* = 16.13, 10.44, 5.06 Hz, 1H), 5.40 (dt, *J* = 17.21, 1.37 Hz, 1H), 5.34 (t, *J* = 9.02 Hz, 1H), 5.27 – 5.23 (m, 1H), 4.71 (d, *J* = 3.30 Hz, 1H), 4.65 (d, *J* = 5.51 Hz, 2H), 4.52 (d, *J* = 5.44 Hz, 1H),f 3.81 (d, *J* = 11.72 Hz, 1H), 3.73 – 3.60 (m, 5H), 3.40 (s, 3H).

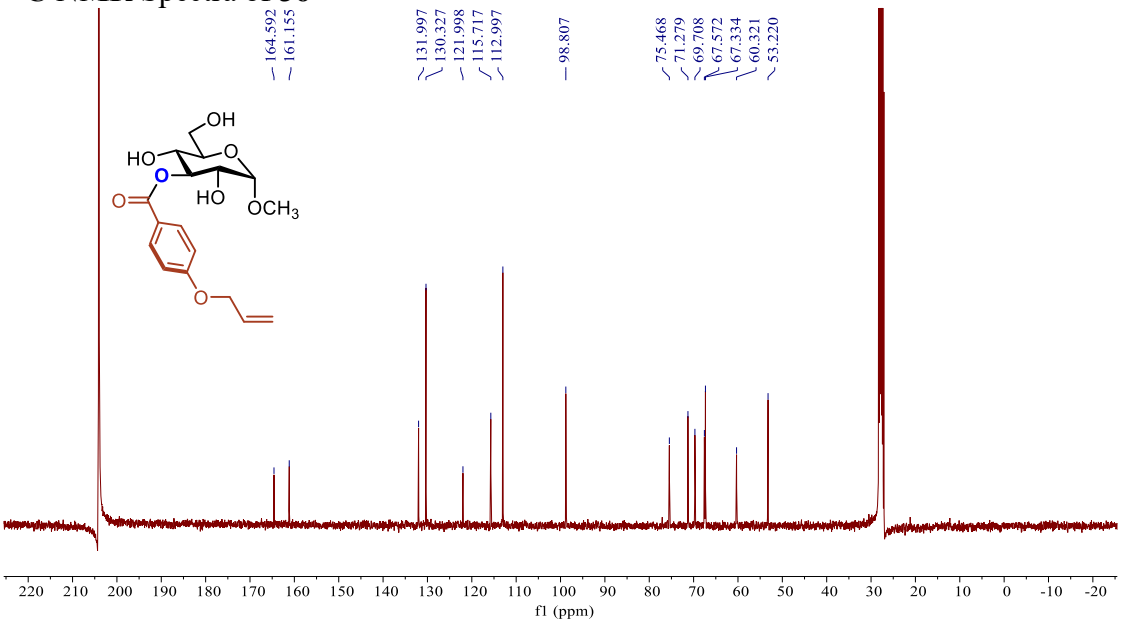
^{13}C NMR (101 MHz, Acetone-d_6) δ 164.59, 161.16, 132.00, 130.33, 122.00, 115.72, 113.00, 98.81, 75.47, 71.28, 69.71, 67.57, 67.47, 67.33, 60.32, 53.22.

HRMS (ESI) Calcd for $C_{17}H_{22}O_8Na^+$ [M+Na]$^+$ 377.1207; Found: 377.1207.

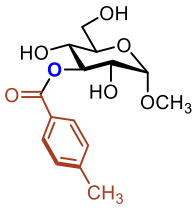
^{1}H NMR Spectra of **3o**



^{13}C NMR Spectra of **3o**



(2*R*,3*R*,4*R*,5*S*,6*R*)-3,5-dihydroxy-2-(hydroxymethyl)-6-(phenylthio)tetrahydro-2*H*-pyran-4-yl 4-methylbenzoate (3p):



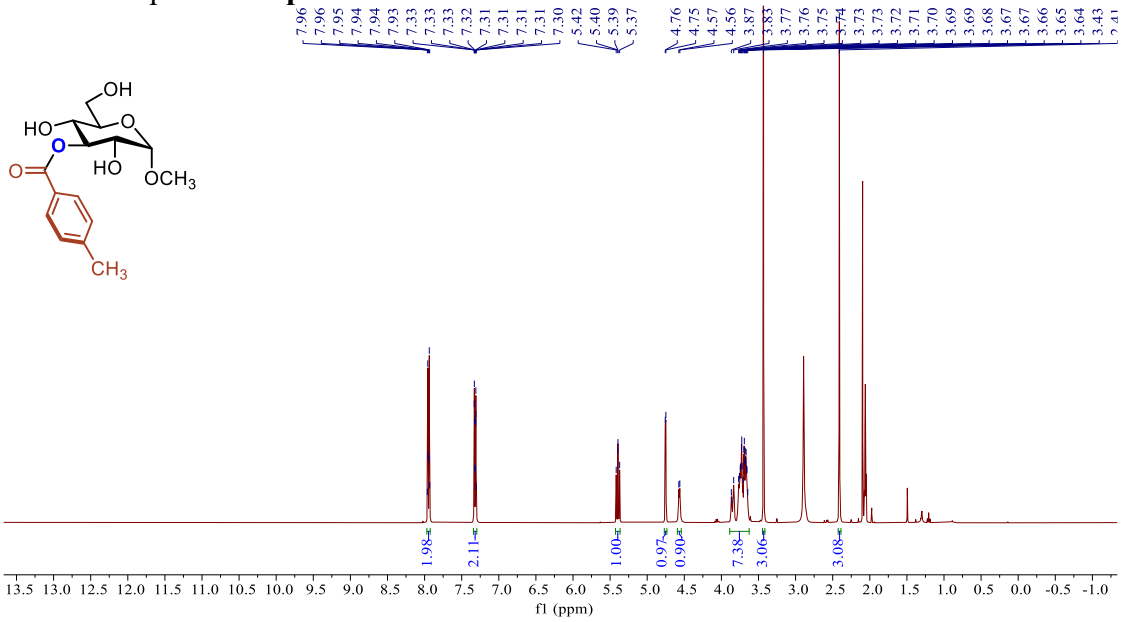
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 69% yield, 21.5mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.97 – 7.92 (m, 2H), 7.34 – 7.30 (m, 2H), 5.39 (t, J = 9.7, 8.8 Hz, 1H), 4.75 (d, J = 3.5 Hz, 1H), 4.57 (d, J = 5.3 Hz, 1H), 3.89 – 3.63 (m, 7H), 3.43 (s, 3H), 2.41 (s, 3H).

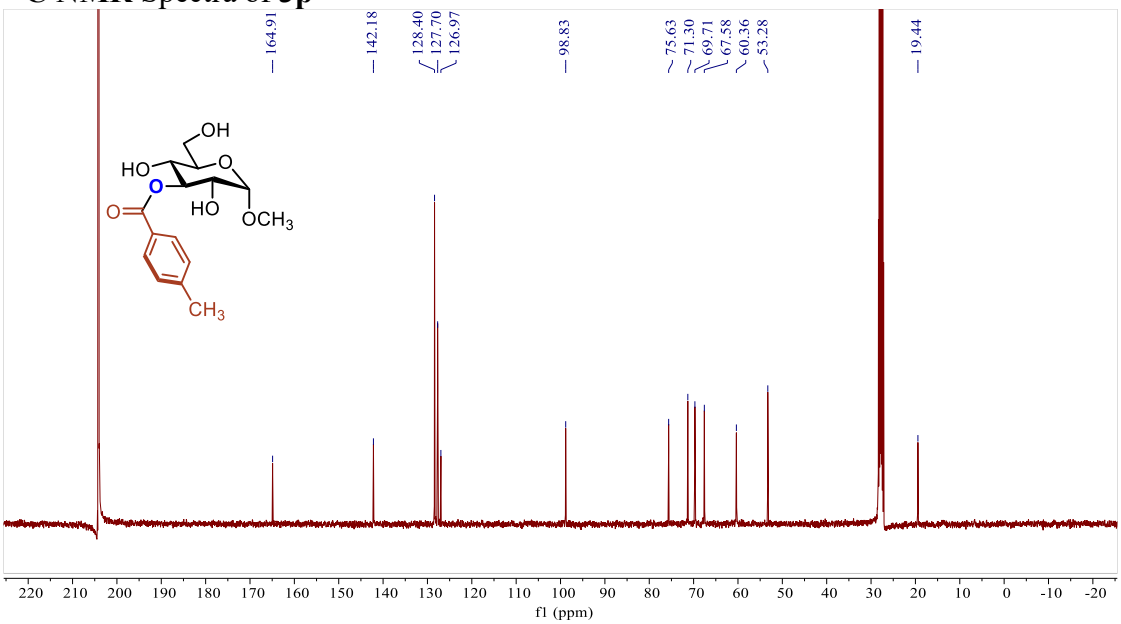
^{13}C NMR (101 MHz, Acetone-d_6) δ 164.91, 142.18, 128.40, 127.70, 126.97, 98.83, 75.63, 71.30, 69.71, 67.58, 60.36, 53.28, 19.44.

HRMS (ESI) Calcd for $C_{15}H_{20}O_7Na^+$ [M+Na]$^+$ 335.1101; Found: 335.1102.

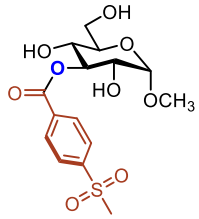
^{1}H NMR Spectra of **3p**



^{13}C NMR Spectra of **3p**



(2*R*,3*R*,4*R*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 4-(methylsulfonyl)benzoate (3q):



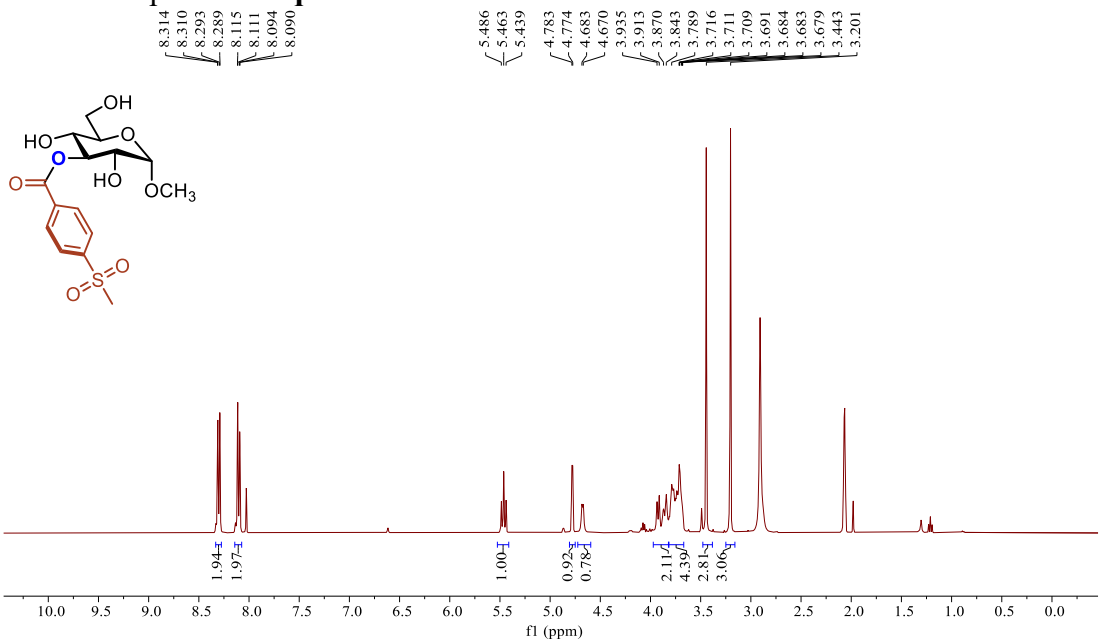
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 69% yield, 25.9mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.30 (dd, *J* = 8.37, 1.54 Hz, 2H), 8.10 (dd, *J* = 8.42, 1.57 Hz, 2H), 5.46 (t, *J* = 9.43 Hz, 1H), 4.78 (d, *J* = 3.63 Hz, 1H), 4.68 (d, *J* = 5.50 Hz, 1H), 3.89 (dd, *J* = 26.93, 9.92 Hz, 2H), 3.79 – 3.68 (m, 4H), 3.44 (s, 1H), 3.20 (s, 1H).

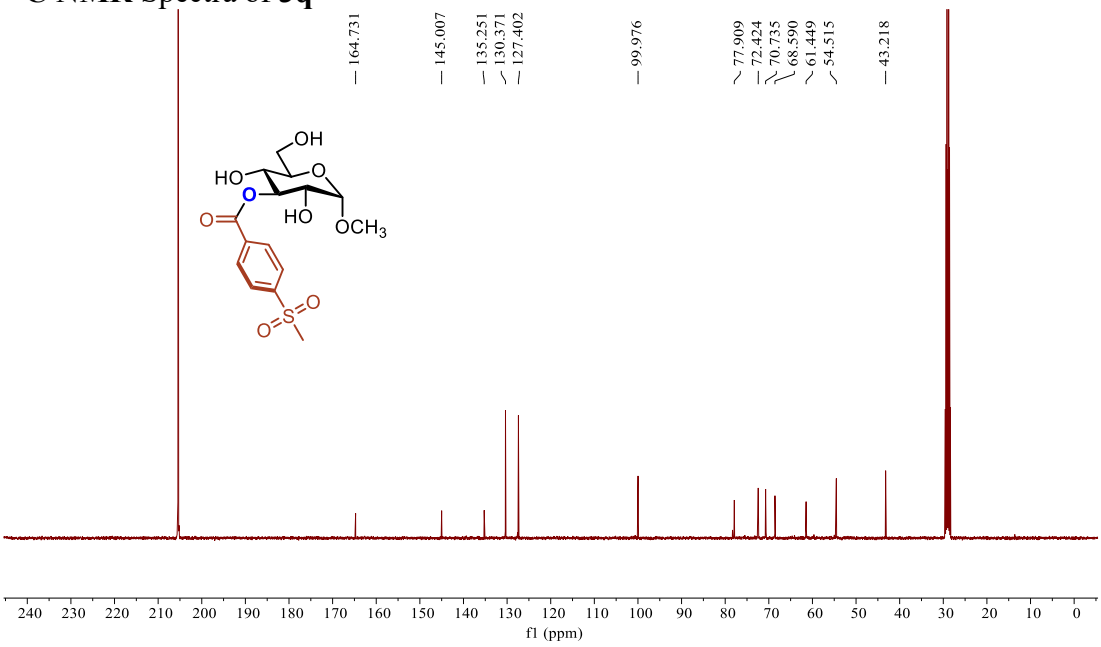
^{13}C NMR (101 MHz, Acetone-d_6) δ 164.73, 145.01, 135.25, 130.37, 127.40, 99.98, 77.91, 72.42, 70.73, 68.59, 61.45, 54.52, 43.22.

HRMS (ESI) Calcd for $C_{15}H_{20}O_9SNa^+$ [M+Na]$^+$ 399.0720; Found: 399.0721.

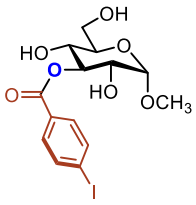
^{1}H NMR Spectra of **3q**



^{13}C NMR Spectra of **3q**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 4-iodobenzoate (3r):



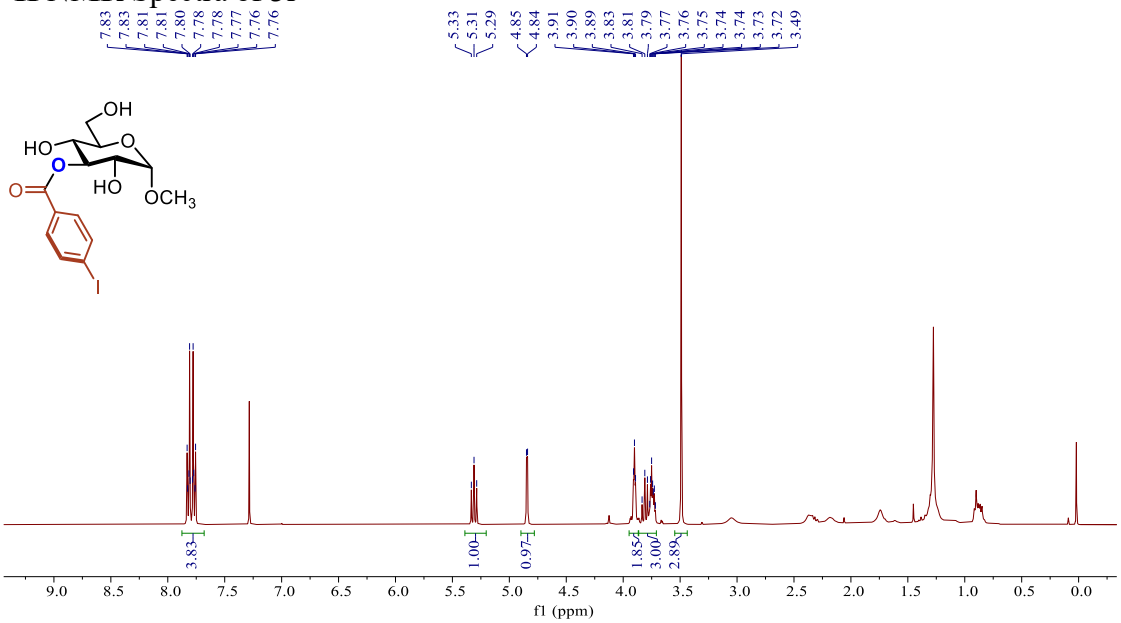
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 77% yield, 32.6mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 4H), 5.31 (t, *J* = 9.4 Hz, 1H), 4.84 (d, *J* = 3.8 Hz, 1H), 3.90 (t, *J* = 3.5 Hz, 2H), 3.83 – 3.72 (m, 3H), 3.49 (s, 3H).

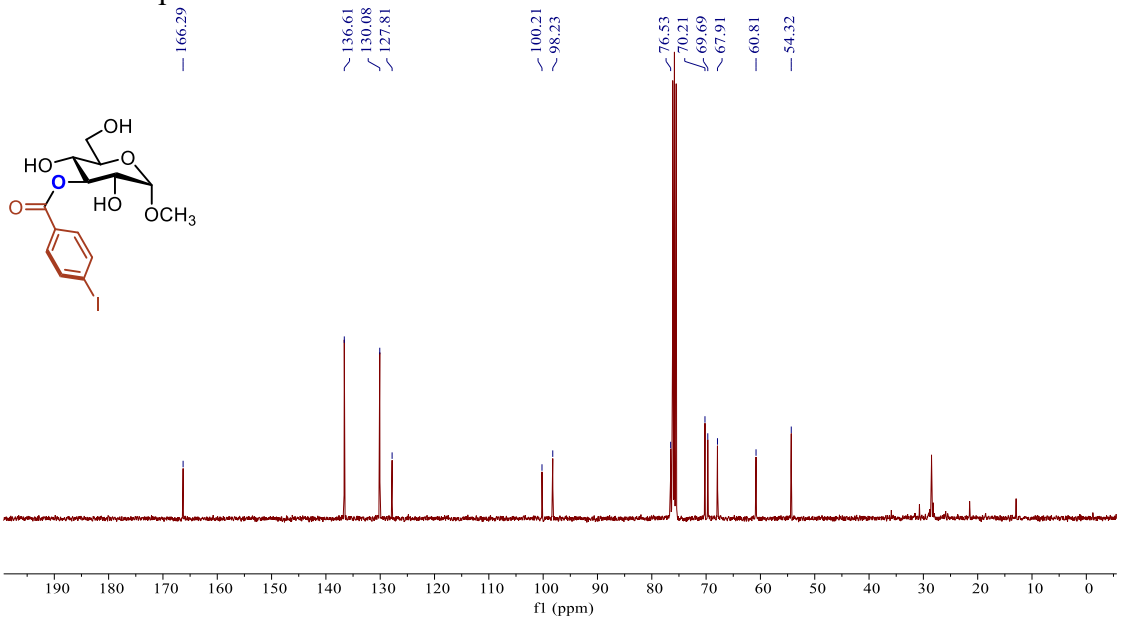
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.29, 136.61, 130.08, 127.81, 100.21, 98.23, 76.53, 70.21, 69.69, 67.91, 60.81, 54.32.

HRMS (ESI) Calcd for $C_{14}H_{17}IO_7Na^+$ [M+Na]$^+$ 446.9911; Found: 446.9910.

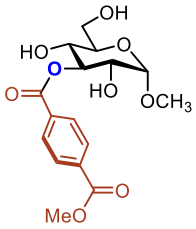
^{1}H NMR Spectra of **3r**



^{13}C NMR Spectra of **3r**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl methyl terephthalate (3s):



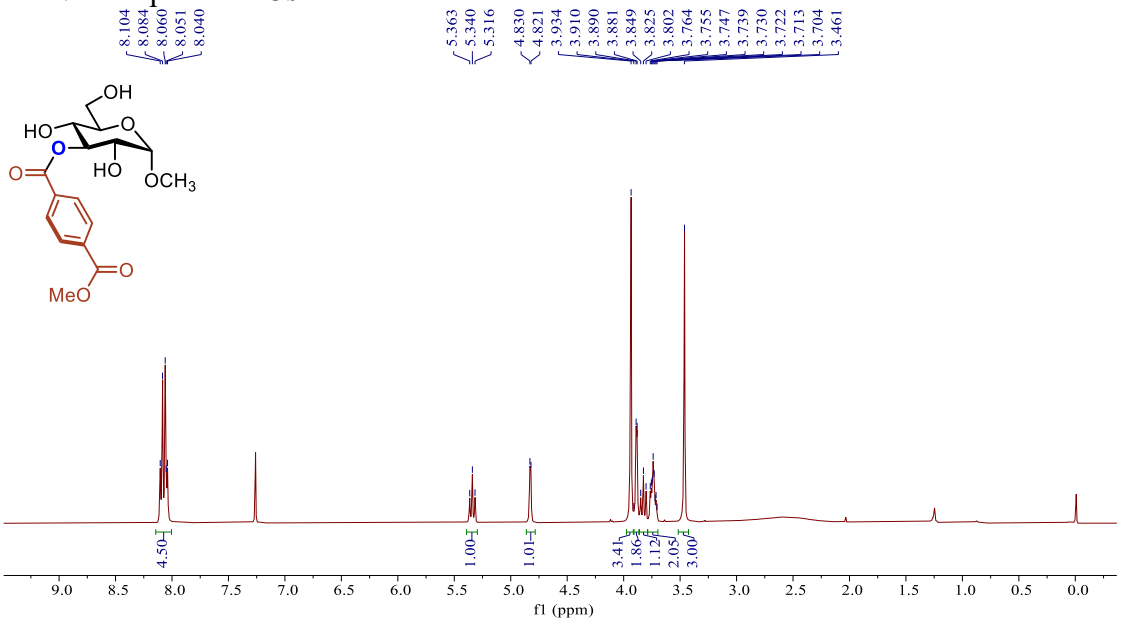
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 74% yield, 26.3mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (q, *J* = 8.2 Hz, 5H), 5.34 (t, *J* = 9.4 Hz, 1H), 4.83 (d, *J* = 3.7 Hz, 1H), 3.93 (s, 4H), 3.89 (d, *J* = 3.6 Hz, 2H), 3.83 (t, *J* = 9.4 Hz, 1H), 3.73 (td, *J* = 6.5, 3.3 Hz, 2H), 3.46 (s, 3H).

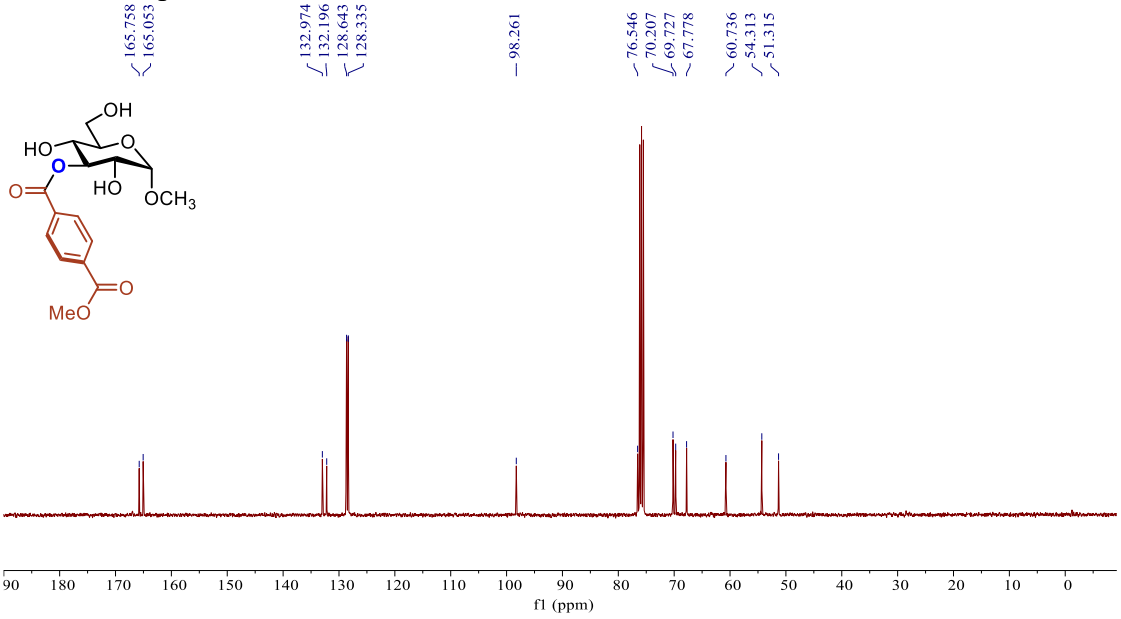
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.76, 165.05, 132.97, 132.20, 128.64, 128.33, 98.26, 76.55, 70.21, 69.73, 67.78, 60.74, 54.31, 51.32.

HRMS (ESI) Calcd for $C_{16}H_{20}O_9Na^+$ $[M+Na]^+$ 379.1000; Found: 379.0999.

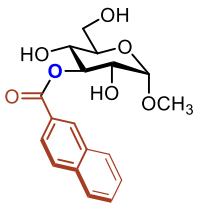
^{1}H NMR Spectra of **3s**



^{13}C NMR Spectra of **3s**



(2*R*,3*R*,4*R*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 2-naphthoate (3t):



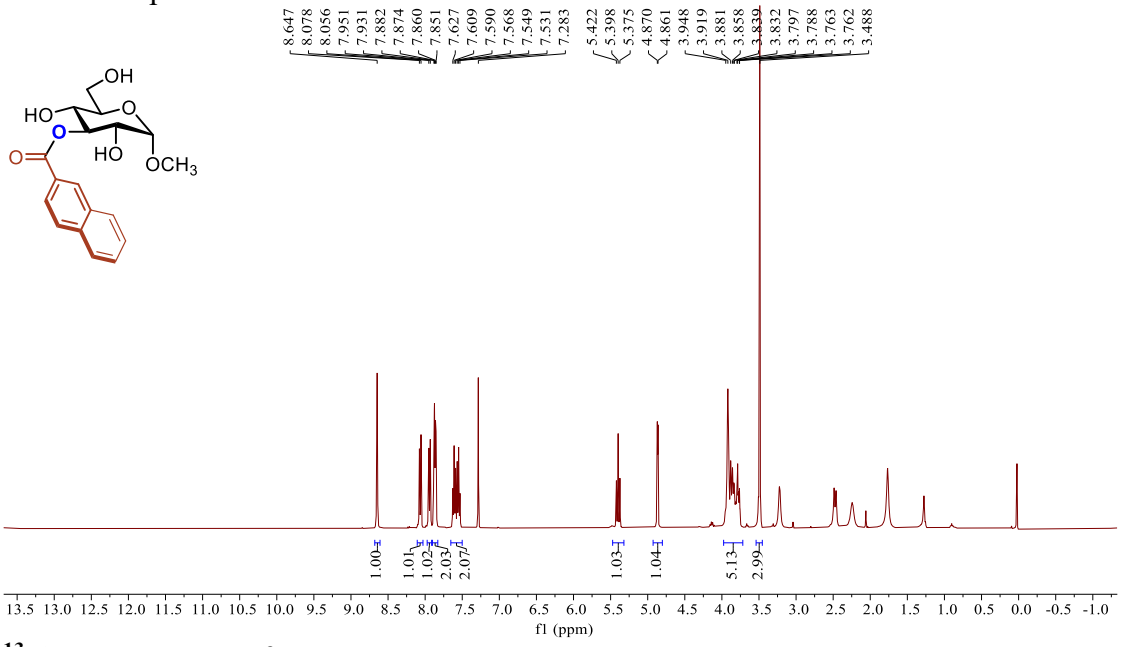
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 66% yield, 22.9mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.07 (d, *J* = 8.75 Hz, 1H), 7.94 (d, *J* = 8.10 Hz, 1H), 7.87 (dd, *J* = 8.87, 3.30 Hz, 2H), 7.58 (dt, *J* = 23.67, 7.22 Hz, 2H), 5.40 (t, *J* = 9.45 Hz, 1H), 4.87 (d, *J* = 3.74 Hz, 1H), 3.96 – 3.75 (m, 5H), 3.49 (s, 3H).

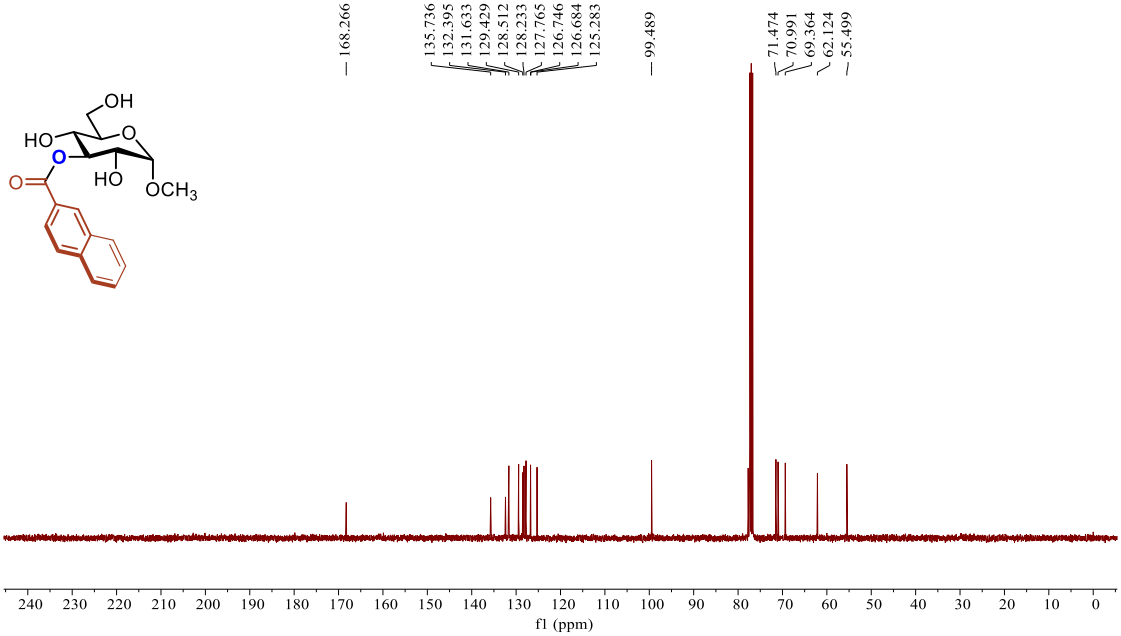
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.27, 135.74, 132.40, 131.63, 129.43, 128.51, 128.23, 127.76, 126.75, 126.68, 125.28, 99.49, 71.47, 70.99, 69.36, 62.12, 55.50.

HRMS (ESI) Calcd for $C_{18}H_{20}O_7Na^+$ $[M+Na]^+$ 371.1101; Found: 371.1101.

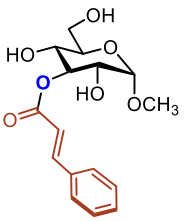
^{1}H NMR Spectra of **3t**



^{13}C NMR Spectra of **3t**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 3-phenylacrylate (3u):



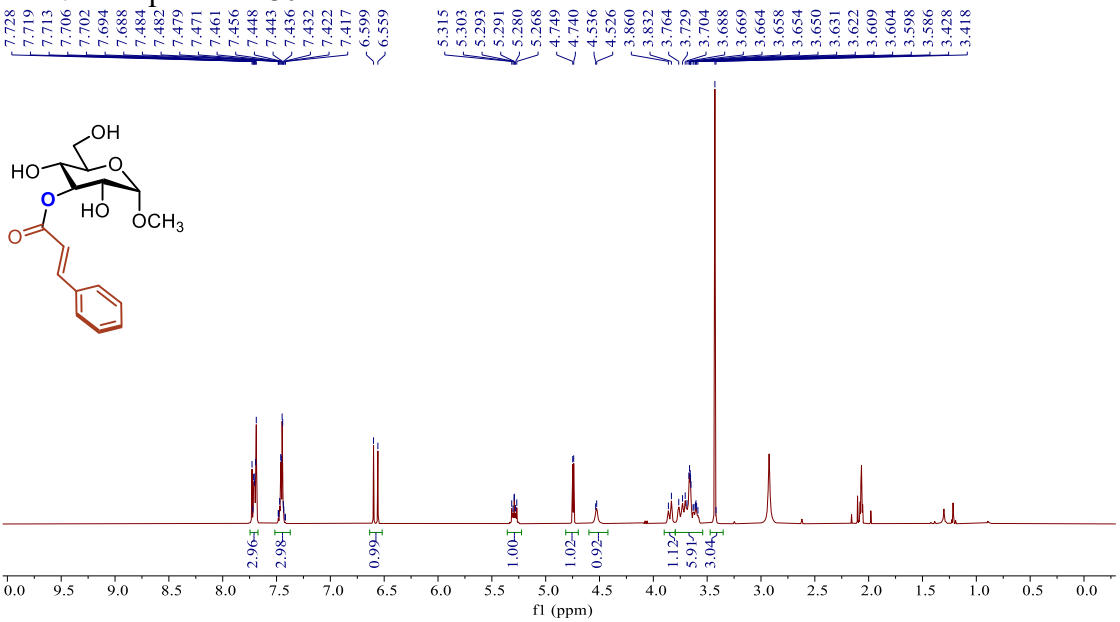
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 72% yield, 23.3mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.74 – 7.67 (m, 2H), 7.48 – 7.42 (m, 3H), 6.58 (d, *J* = 16.1 Hz, 1H), 5.36 – 5.23 (m, 1H), 4.74 (d, *J* = 3.6 Hz, 1H), 3.85 (d, *J* = 11.3 Hz, 1H), 3.76 – 3.59 (m, 6H), 3.43 (s, 3H).

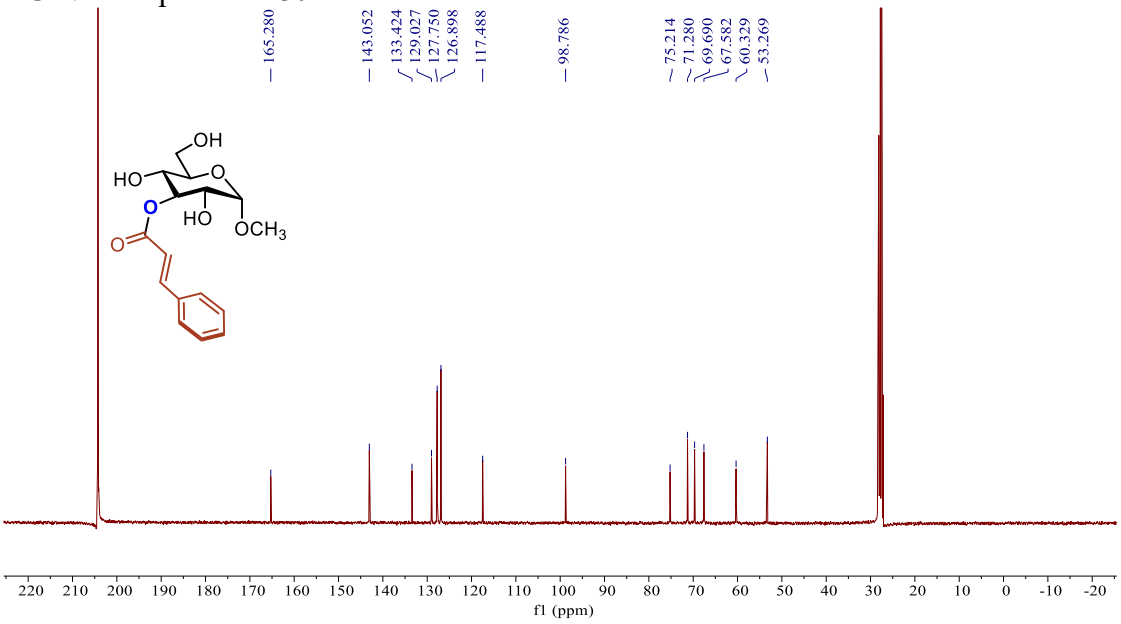
^{13}C NMR (100 MHz, Acetone-d_6) δ 165.28, 143.05, 133.42, 129.03, 127.75, 126.90, 117.49, 98.79, 75.21, 71.28, 69.69, 67.58, 60.33, 53.27.

HRMS (ESI) Calcd for $C_{16}H_{20}O_7Na^+$ [M+Na]$^+$ 247.1101; Found: 347.1105.

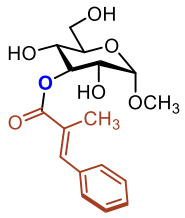
^{1}H NMR Spectra of **3u**



^{13}C NMR Spectra of **3u**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 2-methyl-3-phenylacrylate (3v):



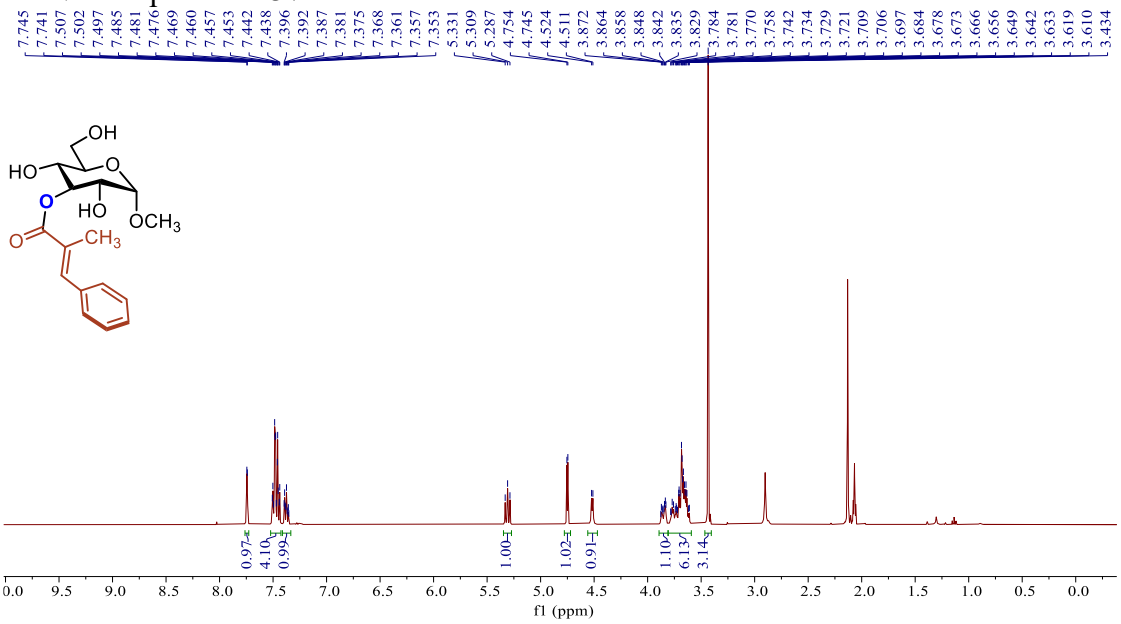
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 88% yield, 29.7mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.74 (d, *J* = 1.8 Hz, 1H), 7.51 – 7.44 (m, 4H), 7.40 – 7.35 (m, 1H), 5.31 (t, *J* = 8.9 Hz, 1H), 4.75 (d, *J* = 3.5 Hz, 1H), 4.52 (d, *J* = 5.0 Hz, 1H), 3.88 – 3.83 (m, 1H), 3.78 – 3.61 (m, 5H), 3.43 (s, 3H).

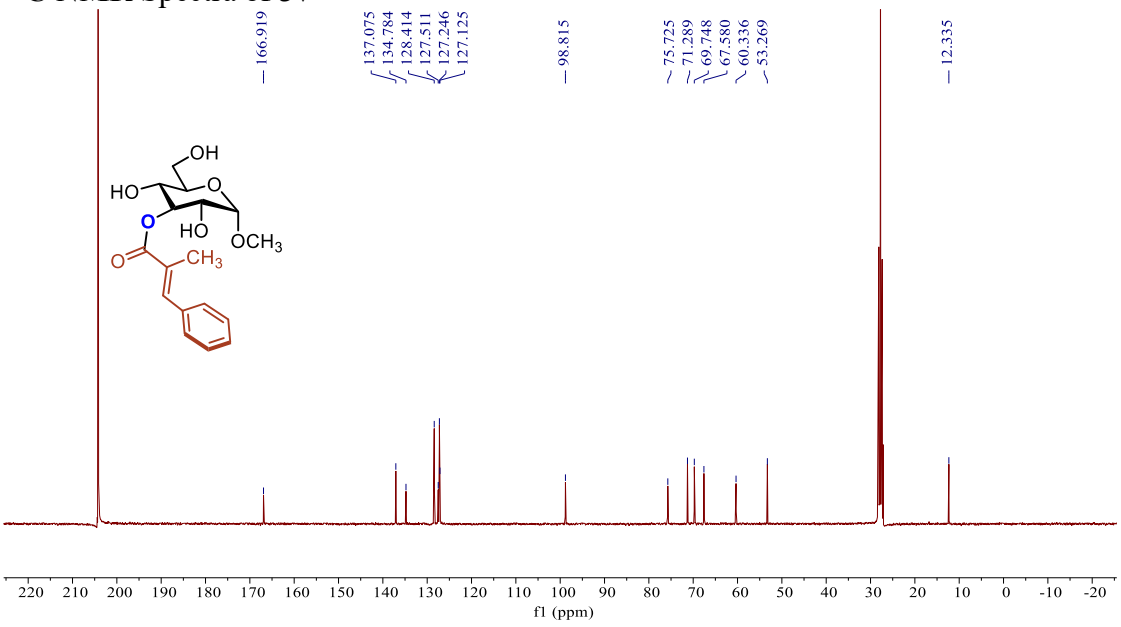
^{13}C NMR (100 MHz, Acetone-d_6) δ 166.92, 137.07, 134.78, 128.41, 127.51, 127.25, 127.12, 98.81, 75.73, 71.29, 69.75, 67.58, 60.34, 53.27, 12.33.

HRMS (ESI) Calcd for $C_{17}H_{22}O_7Na^+$ [M+Na]$^+$ 361.1258; Found: 361.1261.

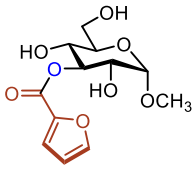
^{1}H NMR Spectra of **3v**



^{13}C NMR Spectra of **3v**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl furan-2-carboxylate (3w):



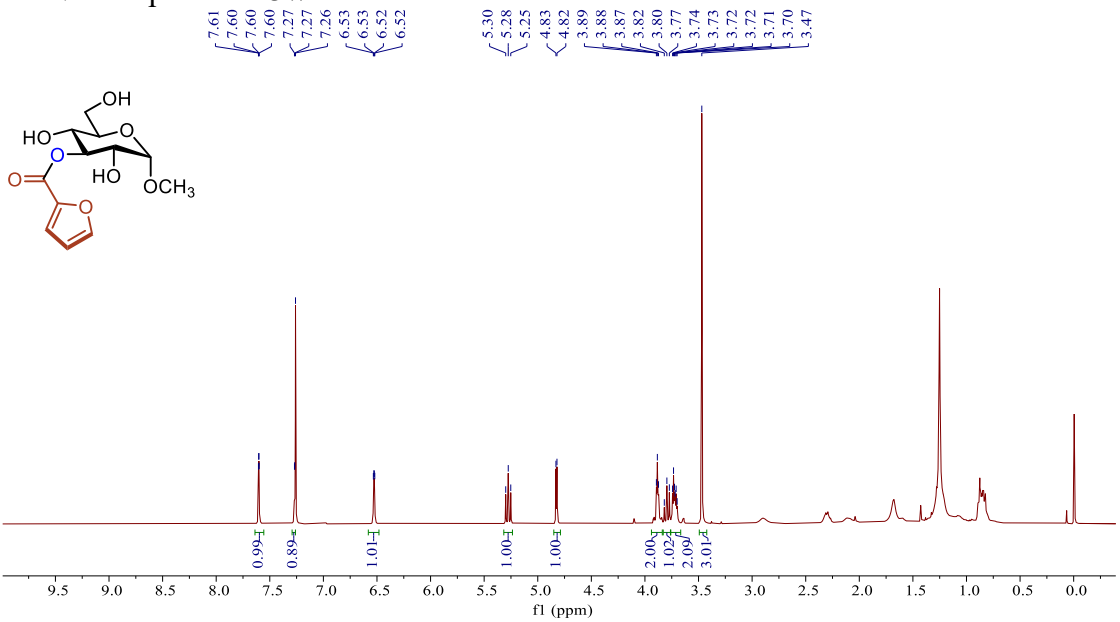
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 77% yield, 22.1mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 1.7, 0.9 Hz, 1H), 7.26 (d, *J* = 3.8 Hz, 2H), 6.53 (dd, *J* = 3.5, 1.7 Hz, 1H), 5.28 (t, *J* = 9.4 Hz, 1H), 4.83 (d, *J* = 3.8 Hz, 1H), 3.89 – 3.70 (m, 4H), 3.47 (s, 3H).

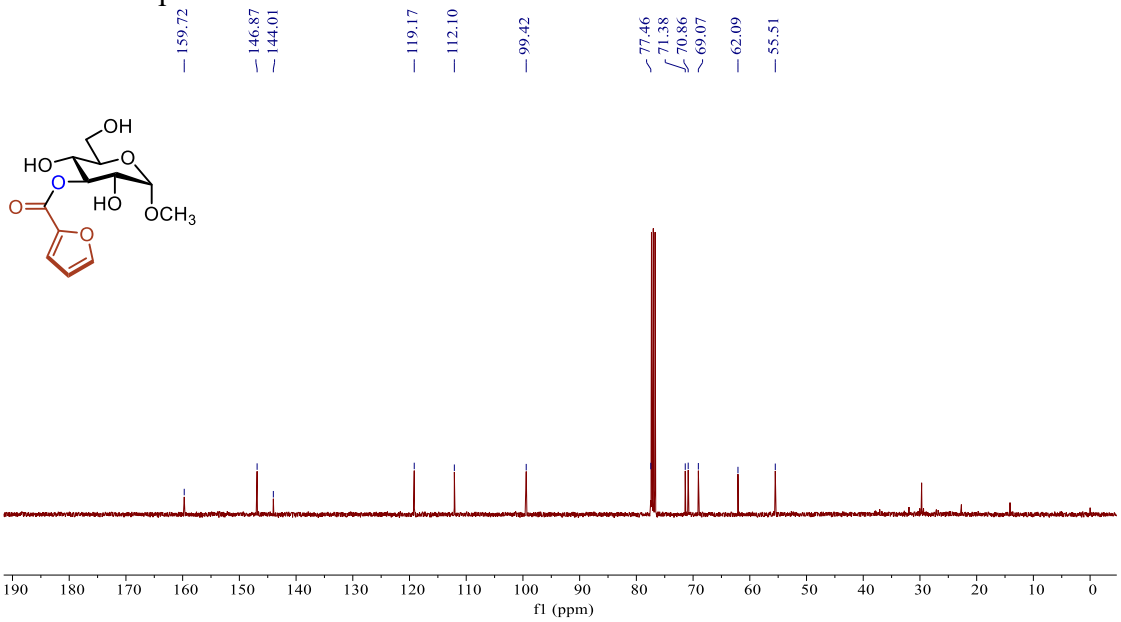
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.72, 146.87, 144.01, 119.17, 112.10, 99.42, 77.46, 71.38, 70.86, 69.07, 62.09, 55.51.

HRMS (ESI) Calcd for $C_{12}H_{16}O_8Na^+$ $[M+Na]^+$ 311.0737; Found: 311.0736.

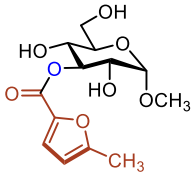
^{1}H NMR Spectra of **3w**



^{13}C NMR Spectra of **3w**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 5-methylfuran-2-carboxylate (3x):



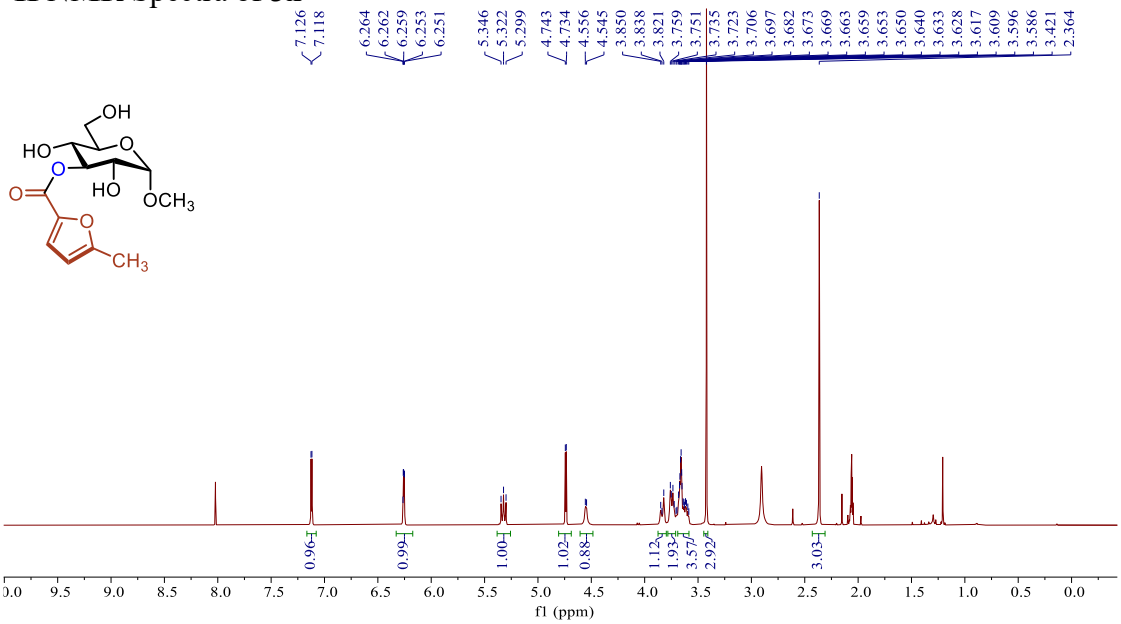
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 75% yield, 22.6 mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.12 (d, *J* = 3.38 Hz, 1H), 6.26 (dd, *J* = 3.34, 1.05 Hz, 1H), 5.32 (t, *J* = 9.41 Hz, 1H), 4.74 (d, *J* = 3.64 Hz, 1H), 4.55 (d, *J* = 4.51 Hz, 1H), 3.84 (d, *J* = 11.49 Hz, 1H), 3.76 – 3.71 (m, 1H), 3.70 – 3.58 (m, 3H), 3.42 (s, 3H), 2.36 (s, 2H).

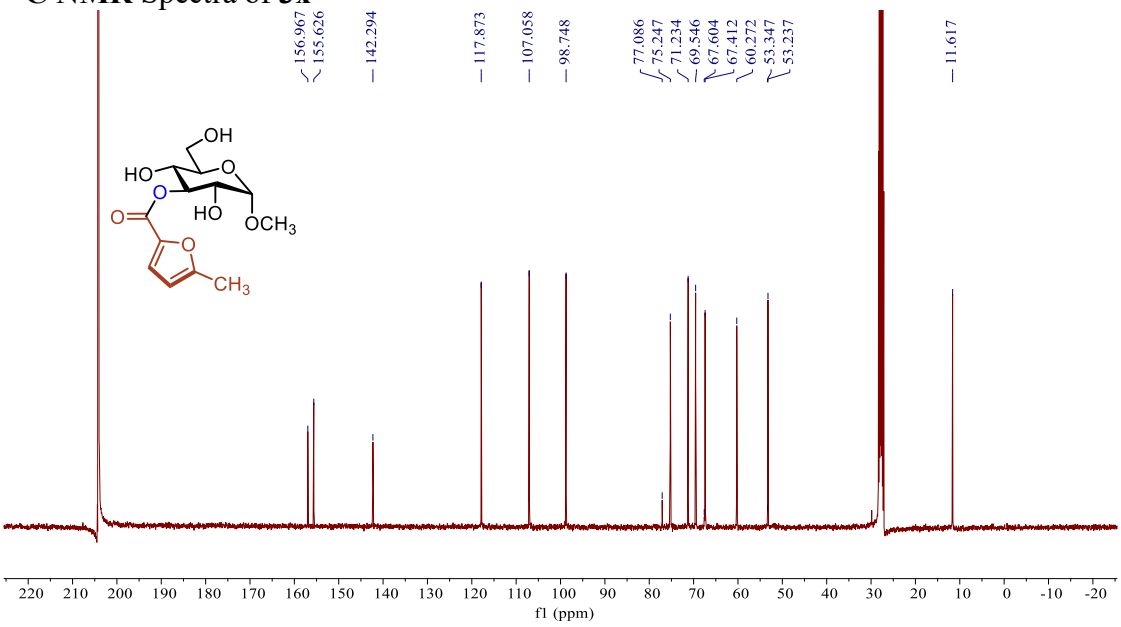
^{13}C NMR (100 MHz, Acetone-d_6) δ 156.97, 155.63, 142.29, 117.87, 107.06, 98.75, 75.25, 71.23, 69.55, 67.41, 60.27, 53.24, 11.62.

HRMS (ESI) Calcd for $C_{13}H_{18}O_8Na^+$ [M+Na]$^+$ 325.0894; Found: 325.0899.

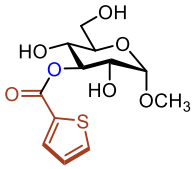
^{1}H NMR Spectra of **3x**



^{13}C NMR Spectra of **3x**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl thiophene-2-carboxylate (3y):



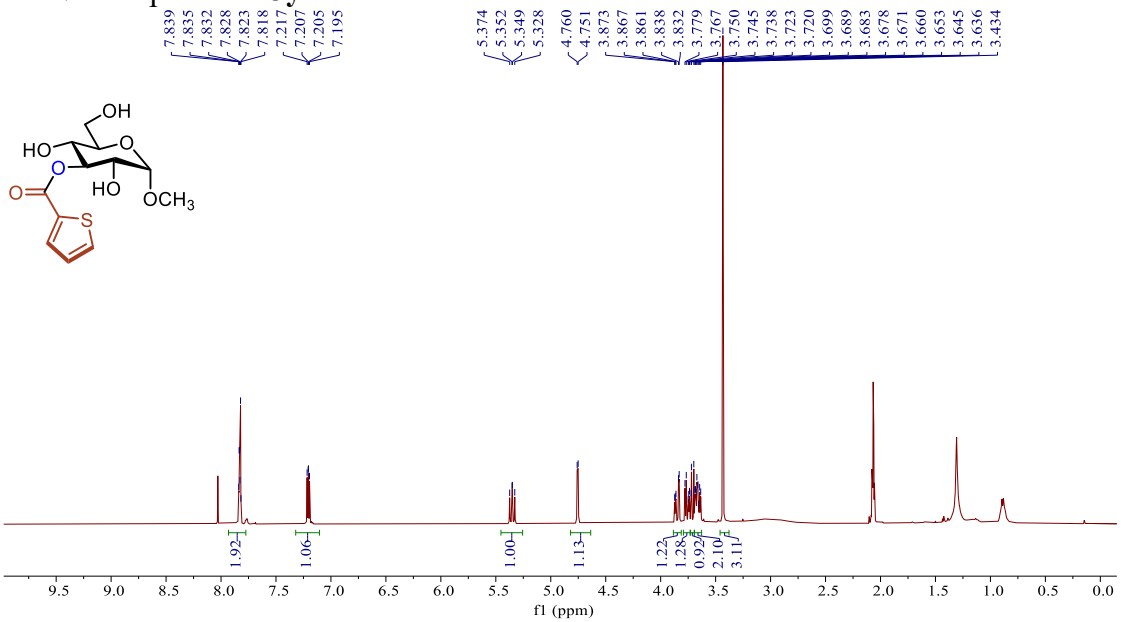
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 60% yield, 18.2mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.84 – 7.82 (m, 2H), 7.21 (dd, *J* = 4.9, 3.9 Hz, 1H), 5.35 (dd, *J* = 9.9, 8.6 Hz, 1H), 4.76 (d, *J* = 3.5 Hz, 1H), 3.87 – 3.83 (m, 1H), 3.78 – 3.74 (m, 1H), 3.71 (d, *J* = 8.6 Hz, 1H), 3.69 – 3.63 (m, 2H), 3.43 (s, 3H).

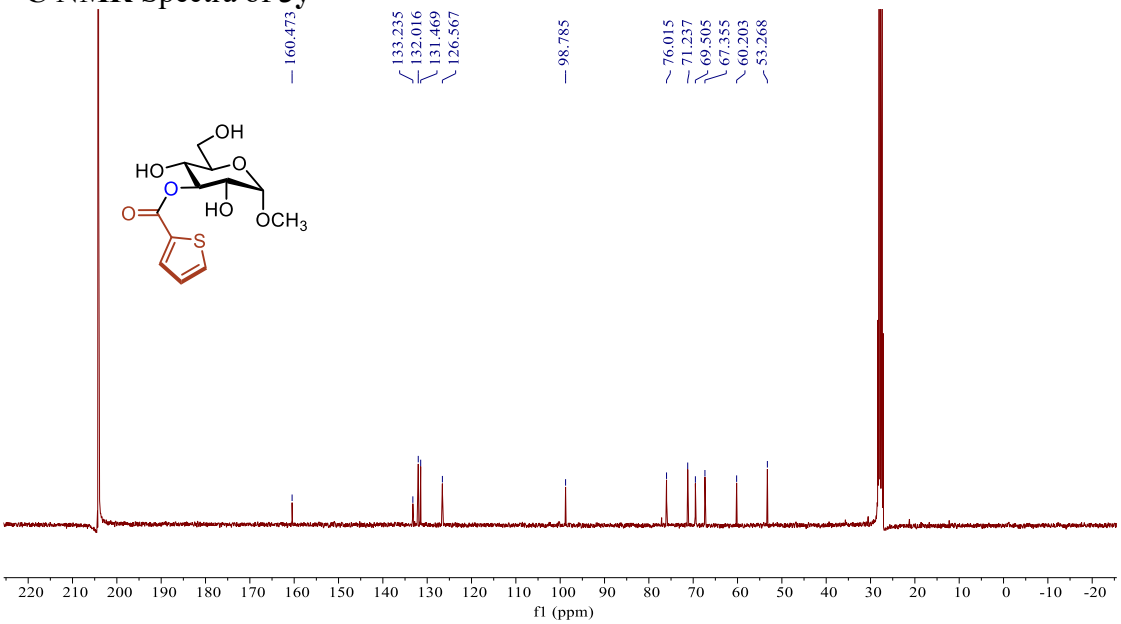
^{13}C NMR (100 MHz, Acetone-d_6) δ 160.47, 133.24, 132.02, 131.47, 126.57, 98.78, 76.01, 71.24, 69.50, 67.35, 60.20, 53.27.

HRMS (ESI) Calcd for $C_{12}H_{16}O_7SNa^+$ [M+Na]$^+$ 327.0509; Found: 327.0509.

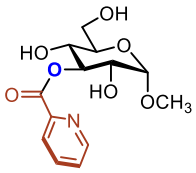
^{1}H NMR Spectra of **3y**



^{13}C NMR Spectra of **3y**



(2*R*,3*R*,4*S*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl picolinate (3z):



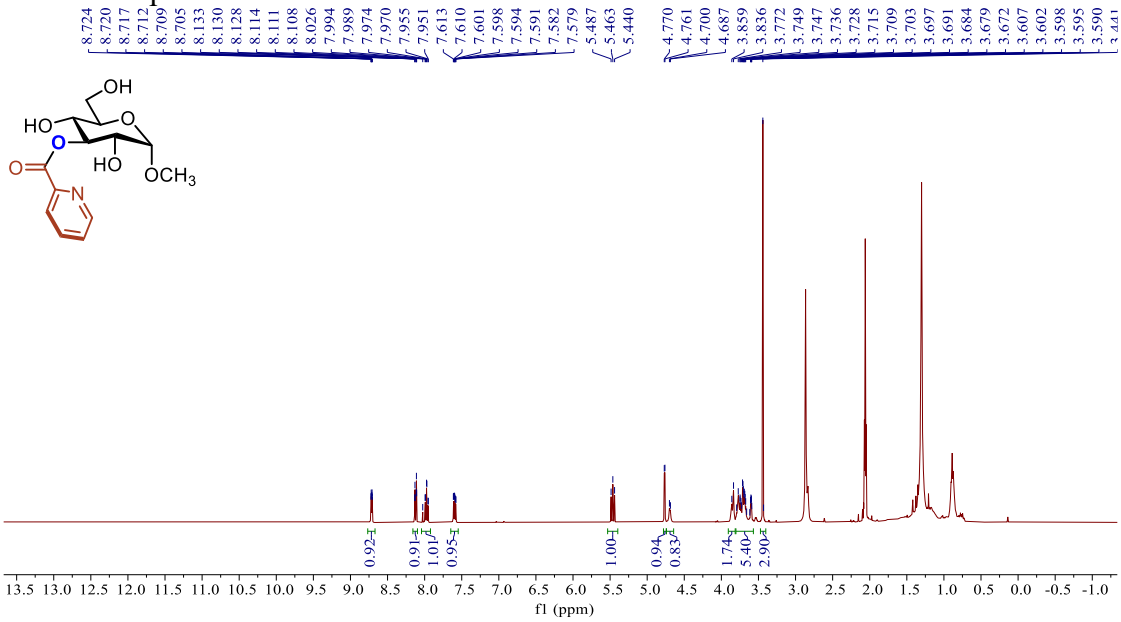
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 52% yield, 15.5mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.71 (dt, *J* = 4.6, 1.4 Hz, 1H), 8.12 (dt, *J* = 7.9, 1.1 Hz, 1H), 8.04 – 7.92 (m, 1H), 7.60 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 5.53 – 5.40 (m, 1H), 4.77 (d, *J* = 3.6 Hz, 1H), 4.69 (d, *J* = 5.3 Hz, 1H), 3.85 (d, *J* = 9.2 Hz, 2H), 3.80 – 3.57 (m, 5H), 3.44 (s, 3H).

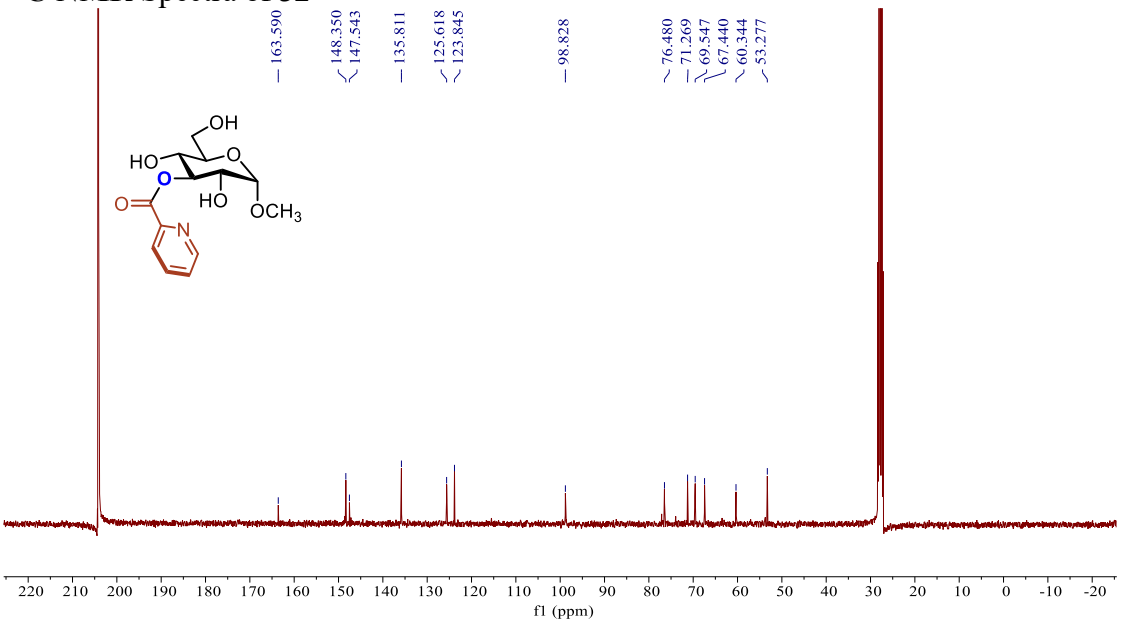
^{13}C NMR (100 MHz, Acetone-d_6) δ 163.59, 148.35, 147.54, 135.81, 125.62, 123.84, 98.83, 76.48, 71.27, 69.55, 67.44, 60.34, 53.28.

HRMS (ESI) Calcd for $C_{13}H_{17}NO_7Na^+$ $[M+Na]^+$ 322.0897; Found: 322.0892.

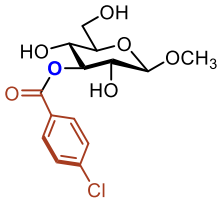
^{1}H NMR Spectra of **3z**



^{13}C NMR Spectra of **3z**



(2*R*,3*R*,4*R*,5*R*,6*R*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-4-yl 4-chlorobenzoate (3aa)



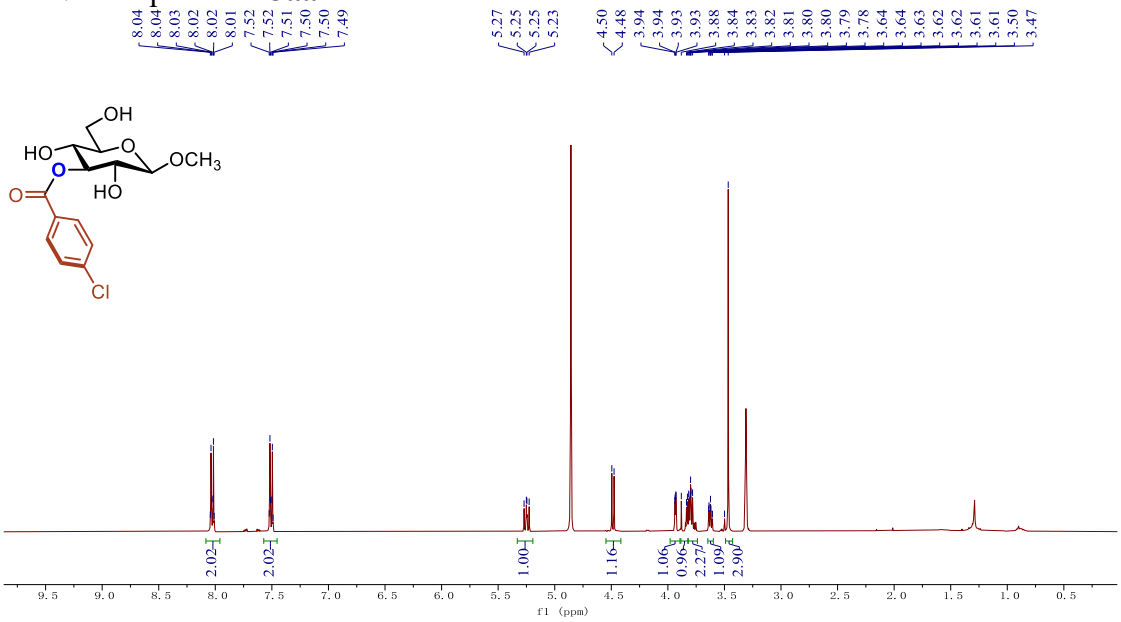
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 57% yield, 18.9mg.

^{1}H NMR (400 MHz, MeOD) δ 8.04 – 8.01 (m, 2H), 7.52 – 7.49 (m, 2H), 5.25 (dd, *J* = 10.0, 8.0 Hz, 1H), 4.49 (d, *J* = 8.0 Hz, 1H), 3.93 (dd, *J* = 3.4, 1.1 Hz, 1H), 3.83 (d, *J* = 3.4 Hz, 1H), 3.81 – 3.78 (m, 2H), 3.62 (ddd, *J* = 6.7, 5.4, 1.3 Hz, 1H), 3.47 (s, 3H).

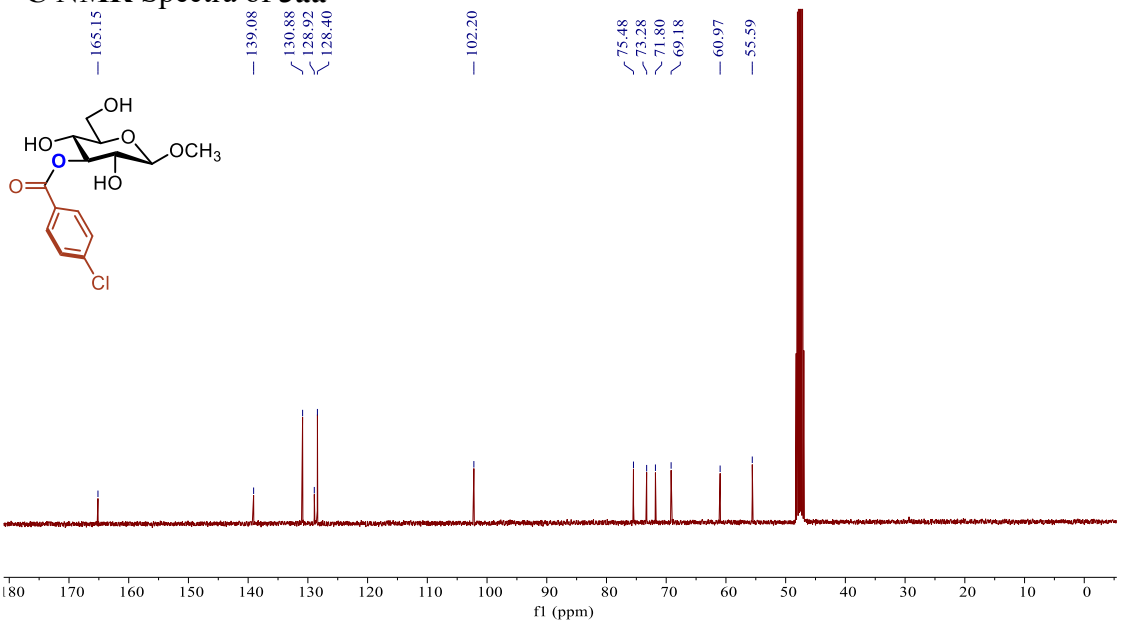
^{13}C NMR (101 MHz, MeOD) δ 165.15, 139.08, 130.88, 128.92, 128.40, 102.20, 75.48, 73.28, 71.80, 69.18, 60.97, 55.59.

HRMS (ESI) Calcd for $C_{14}H_{17}ClO_7Na^+$ $[M+Na]^+$ 355.0555; Found: 355.0556.

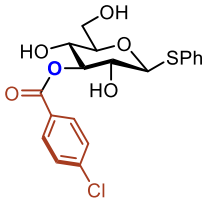
^{1}H NMR Spectra of **3aa**



^{13}C NMR Spectra of **3aa**



(2*R*,3*R*,4*R*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-(phenylthio)tetrahydro-2*H*-pyran-4-yl 4-chlorobenzoate (3ab):



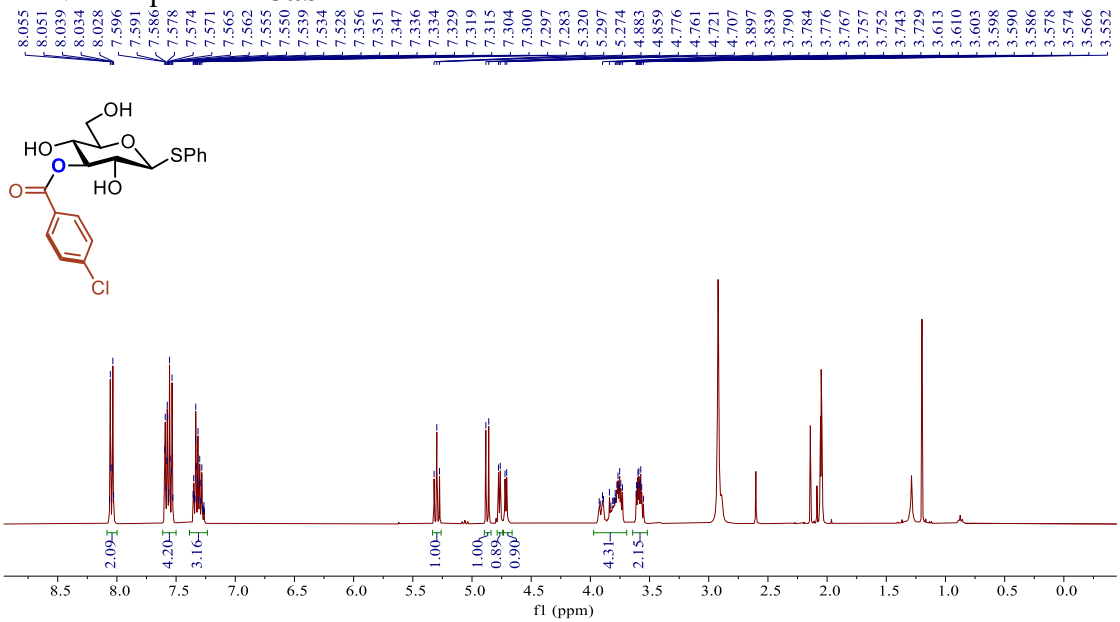
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 71% yield, 29.1mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.06 – 8.03 (m, 2H), 7.60 – 7.53 (m, 4H), 7.36 – 7.26 (m, 3H), 5.30 (t, *J* = 9.2 Hz, 1H), 4.87 (d, *J* = 9.8 Hz, 1H), 4.77 (d, *J* = 5.9 Hz, 1H), 4.71 (d, *J* = 5.7 Hz, 1H), 3.92 – 3.73 (m, 3H), 3.61 – 3.55 (m, 2H).

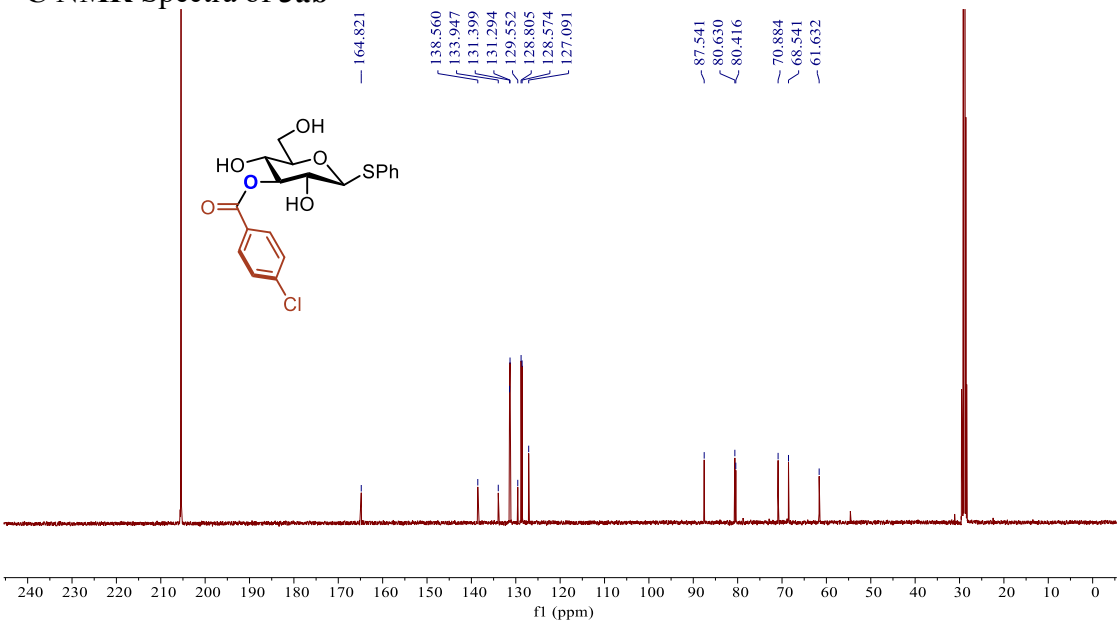
^{13}C NMR (101 MHz, Acetone-d_6) δ 164.82, 138.56, 133.95, 131.40, 131.29, 129.55, 128.81, 128.57, 127.09, 87.54, 80.63, 80.42, 70.88, 68.54, 61.63.

HRMS (ESI) Calcd for $C_{19}H_{19}ClO_6SNa^+$ $[M+Na]^+$ 433.0483; Found: 433.0484.

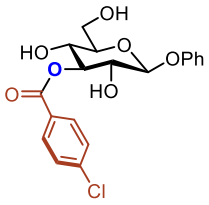
^{1}H NMR Spectra of **3ab**



^{13}C NMR Spectra of **3ab**



(2*R*,3*R*,4*R*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-phenoxytetrahydro-2*H*-pyran-4-yl 4-chlorobenzoate (3ac):



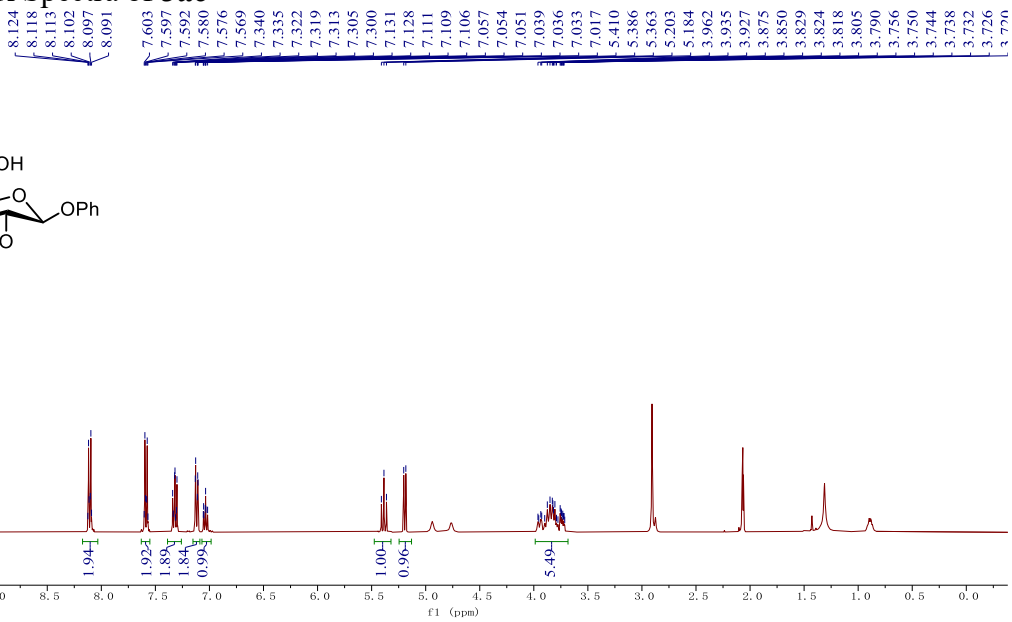
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 63% yield, 24.8mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.12 – 8.09 (m, 2H), 7.60 – 7.57 (m, 2H), 7.34 – 7.29 (m, 2H), 7.13 – 7.11 (m, 2H), 7.06 – 7.02 (m, 1H), 5.39 (t, J = 9.4 Hz, 1H), 5.19 (d, J = 7.8 Hz, 1H), 3.97 – 3.72 (m, 5H).

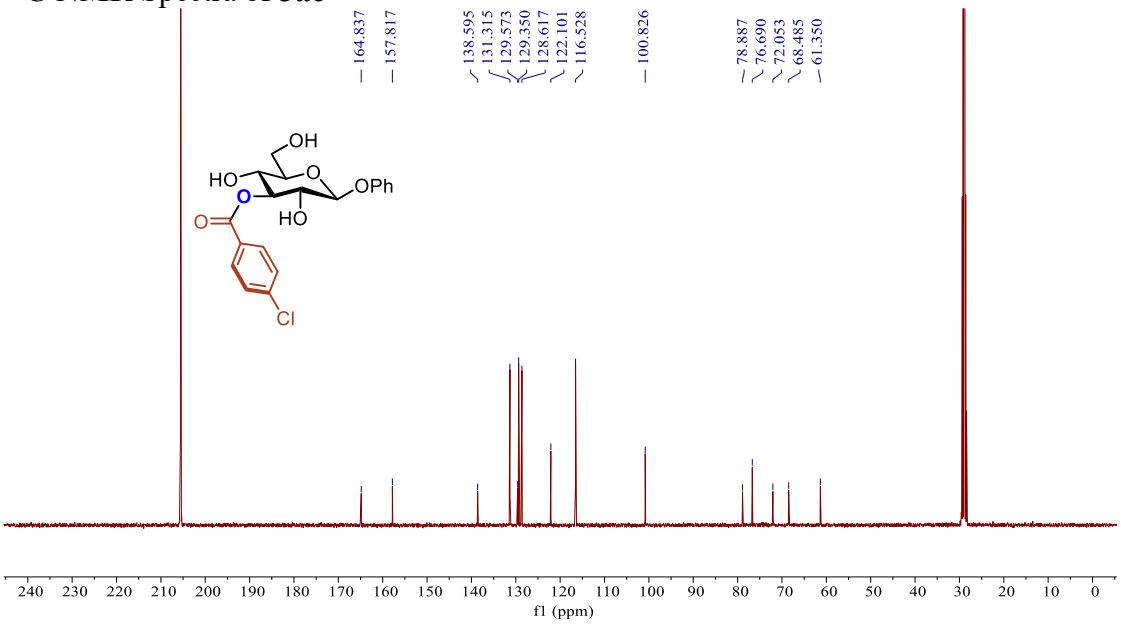
^{13}C NMR (101 MHz, Acetone-d_6) δ 164.84, 157.82, 138.60, 131.31, 129.57, 129.35, 128.62, 122.10, 116.53, 100.83, 78.89, 76.69, 72.05, 68.49, 61.35.

HRMS (ESI) Calcd for $C_{19}H_{19}ClO_7Na^+$ $[M+Na]^+$ 417.0712; Found: 417.0713.

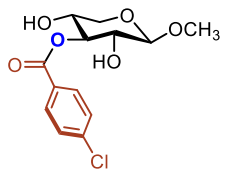
^{1}H NMR Spectra of **3ac**



^{13}C NMR Spectra of **3ac**



(2*R*,3*R*,4*R*,5*R*)-3,5-dihydroxy-2-methoxytetrahydro-2*H*-pyran-4-yl 4-chlorobenzoate (3ad):



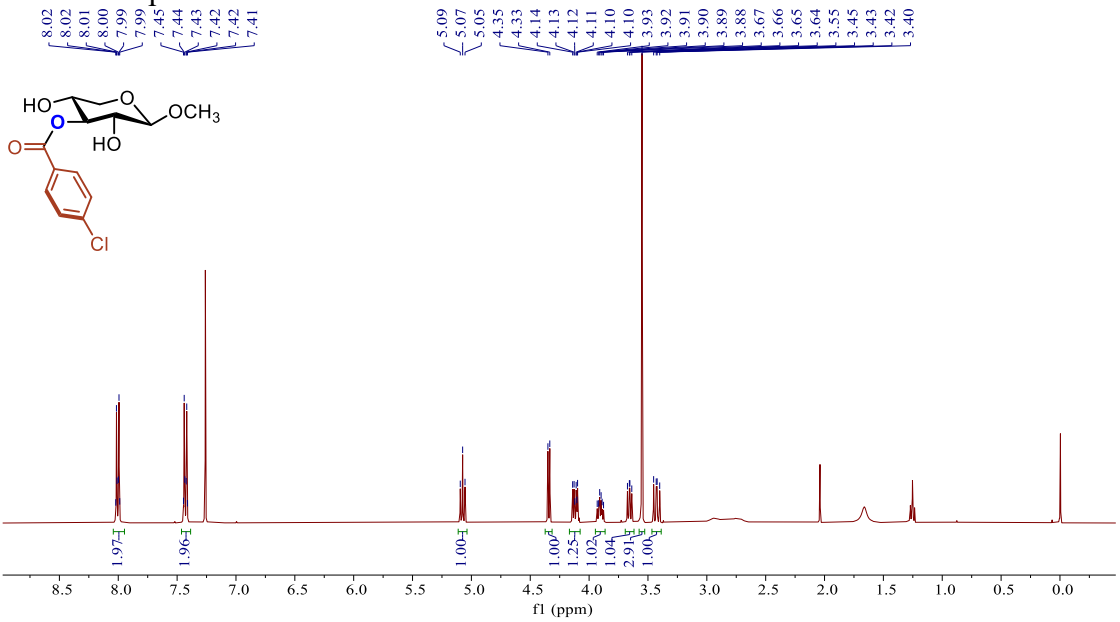
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 57% yield, 17.2mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 2H), 7.47 – 7.39 (m, 2H), 5.07 (t, *J* = 8.1 Hz, 1H), 4.34 (d, *J* = 6.4 Hz, 1H), 4.16 – 4.06 (m, 1H), 3.90 (td, *J* = 8.4, 4.9 Hz, 1H), 3.66 (dd, *J* = 8.2, 6.4 Hz, 1H), 3.55 (s, 3H), 3.43 (dd, *J* = 11.9, 8.7 Hz, 1H).

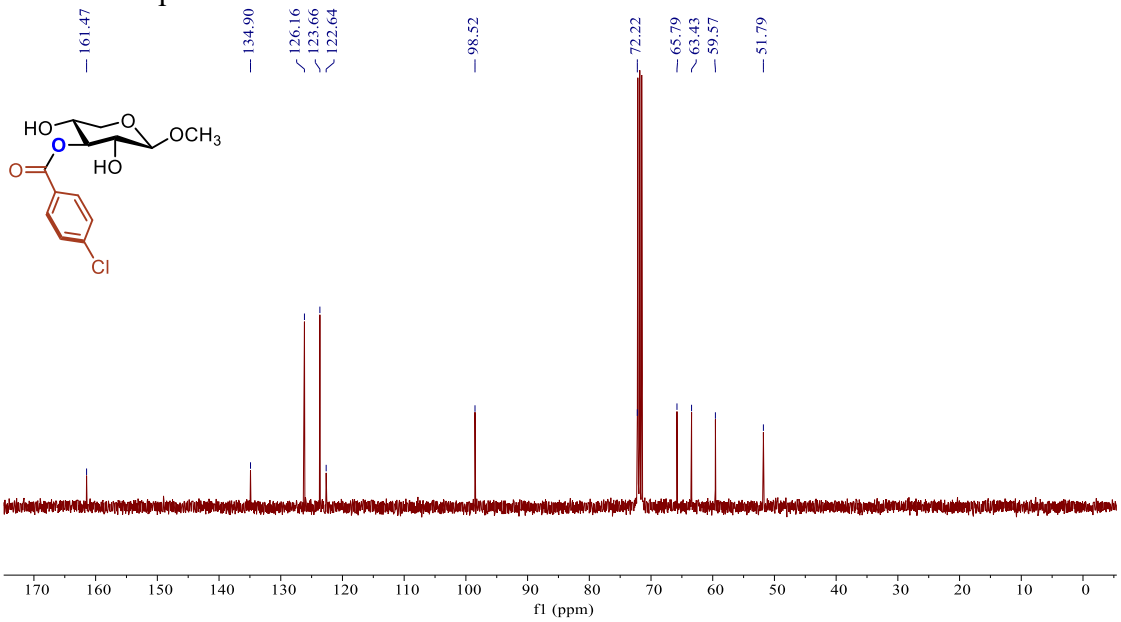
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.47, 134.90, 126.16, 123.66, 122.64, 98.52, 72.22, 65.79, 63.43, 59.57, 51.79.

HRMS (ESI) Calcd for $C_{13}H_{15}ClO_6Na^+$ $[M+Na]^+$ 325.0449; Found: 325.0448.

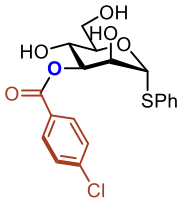
^{1}H NMR Spectra of **3ad**



^{13}C NMR Spectra of **3ad**



(2*R*,3*R*,4*R*,5*S*,6*R*)-3,5-dihydroxy-2-(hydroxymethyl)-6-(phenylthio)tetrahydro-2*H*-pyran-4-yl 4-chlorobenzoate (3ae):



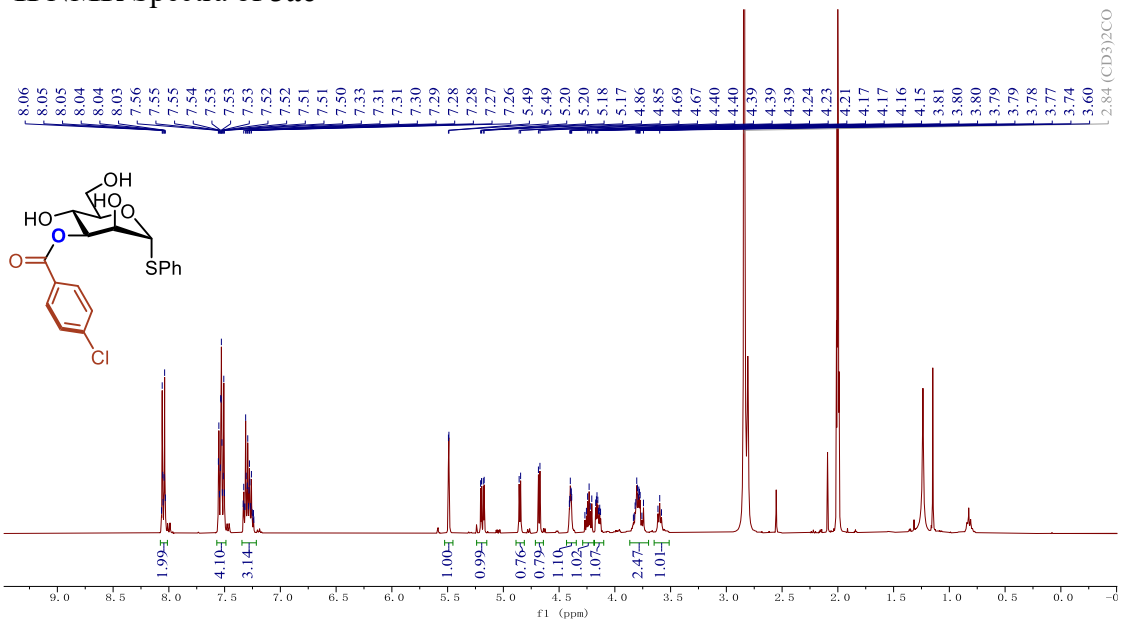
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 61% yield, 25mg.

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 8.07 – 8.03 (m, 2H), 7.56 – 7.50 (m, 4H), 7.33 – 7.24 (m, 3H), 5.49 (d, *J* = 1.7 Hz, 1H), 5.19 (dd, *J* = 9.5, 3.2 Hz, 1H), 4.85 (d, *J* = 5.3 Hz, 1H), 4.68 (d, *J* = 5.4 Hz, 1H), 4.40 (td, *J* = 3.3, 1.6 Hz, 1H), 4.27 – 4.21 (m, 1H), 4.15 (ddd, *J* = 9.7, 4.8, 2.8 Hz, 1H), 3.86 – 3.72 (m, 2H), 3.60 (t, *J* = 6.4 Hz, 1H).

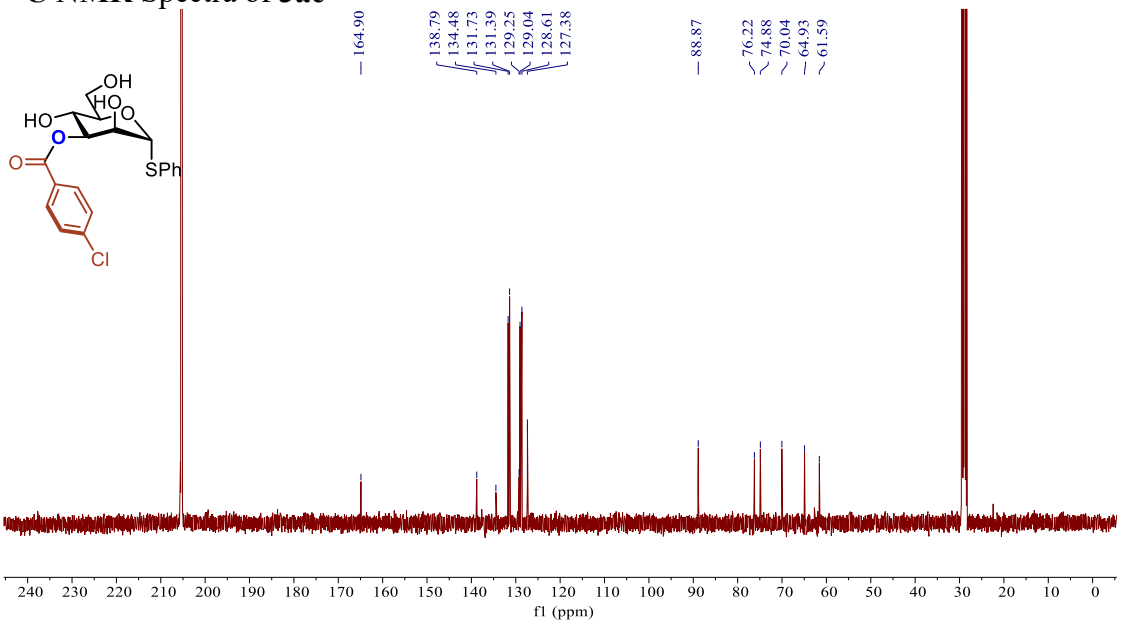
^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 164.90, 138.79, 134.48, 131.73, 131.39, 129.25, 129.04, 128.61, 127.38, 88.87, 76.22, 74.88, 70.04, 64.93, 61.59.

HRMS (ESI) Calcd for $C_{19}H_{19}ClO_6SNa^+$ [M+Na]$^+$ 433.0483; Found: 433.0483.

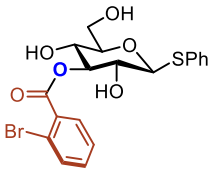
^{1}H NMR Spectra of **3ae**



^{13}C NMR Spectra of **3ae**



(2*R*,3*R*,4*R*,5*R*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-(phenylthio)tetrahydro-2*H*-pyran-4-yl 2-bromo-4-chlorobenzoate (3af)



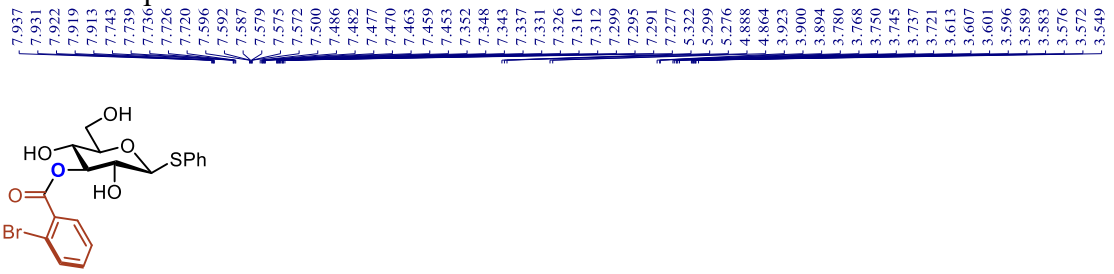
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid, 56% yield, 25.4mg.

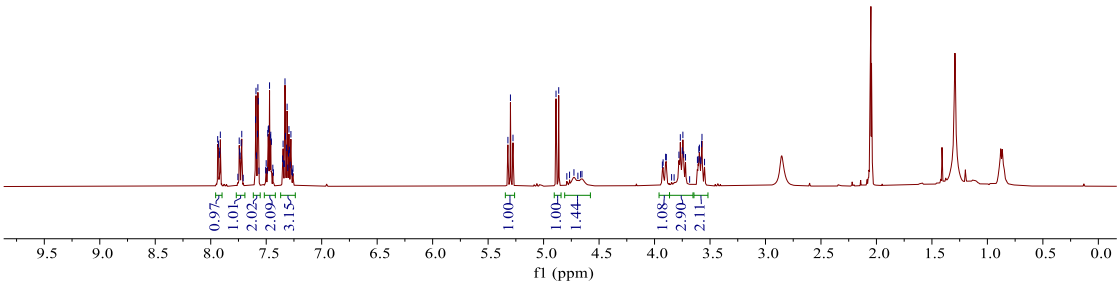
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.95 – 7.89 (m, 1H), 7.77 – 7.69 (m, 1H), 7.62 – 7.54 (m, 2H), 7.52 – 7.41 (m, 2H), 7.37 – 7.24 (m, 3H), 5.30 (t, J = 9.2 Hz, 1H), 4.88 (d, J = 9.8 Hz, 1H), 4.79 – 4.63 (m, 2H), 3.95 – 3.87 (m, 1H), 3.85 – 3.68 (m, 3H), 3.63 – 3.53 (m, 2H).

^{13}C NMR (101 MHz, Acetone-d_6) δ 164.92, 134.26, 133.97, 132.78, 132.62, 131.70, 131.39, 128.80, 127.35, 127.08, 121.27, 87.66, 80.69, 80.51, 70.88, 68.52, 61.59.

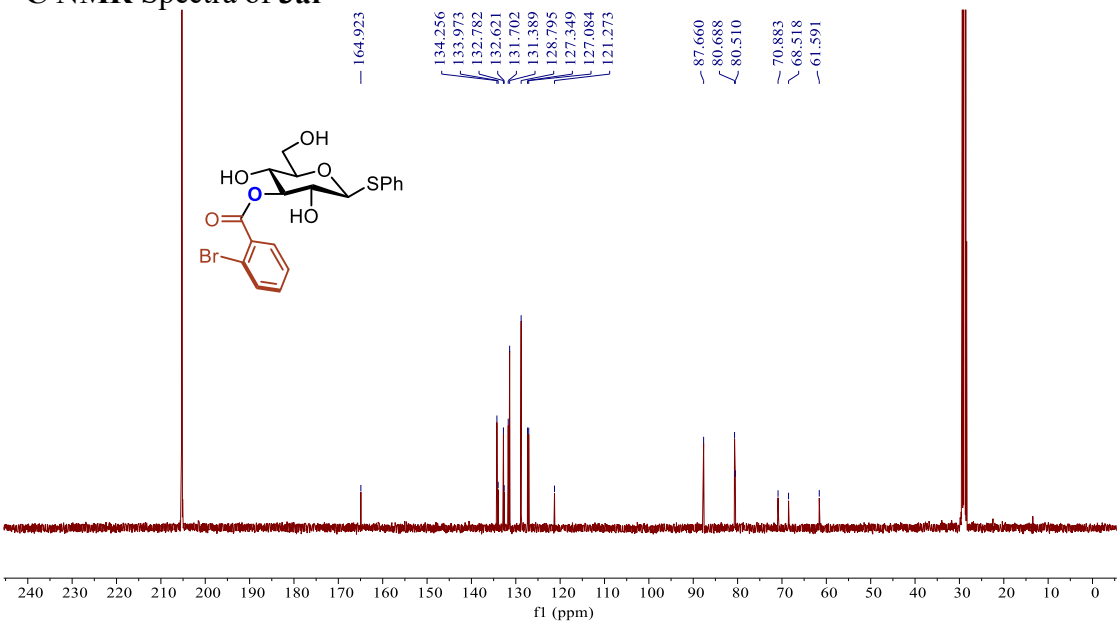
HRMS (ESI) Calcd for $C_{19}H_{19}BrO_6SNa^+$ $[M+Na]^+$ 478.9959; Found: 478.9957.

^{1}H NMR Spectra of **3af**

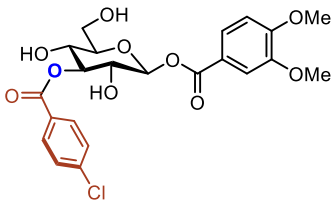




^{13}C NMR Spectra of **3af**



(2*S*,3*R*,4*R*,5*R*,6*R*)-4-((4-chlorobenzoyl)oxy)-3,5-dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl 3,4-dimethoxybenzoate (3ag):



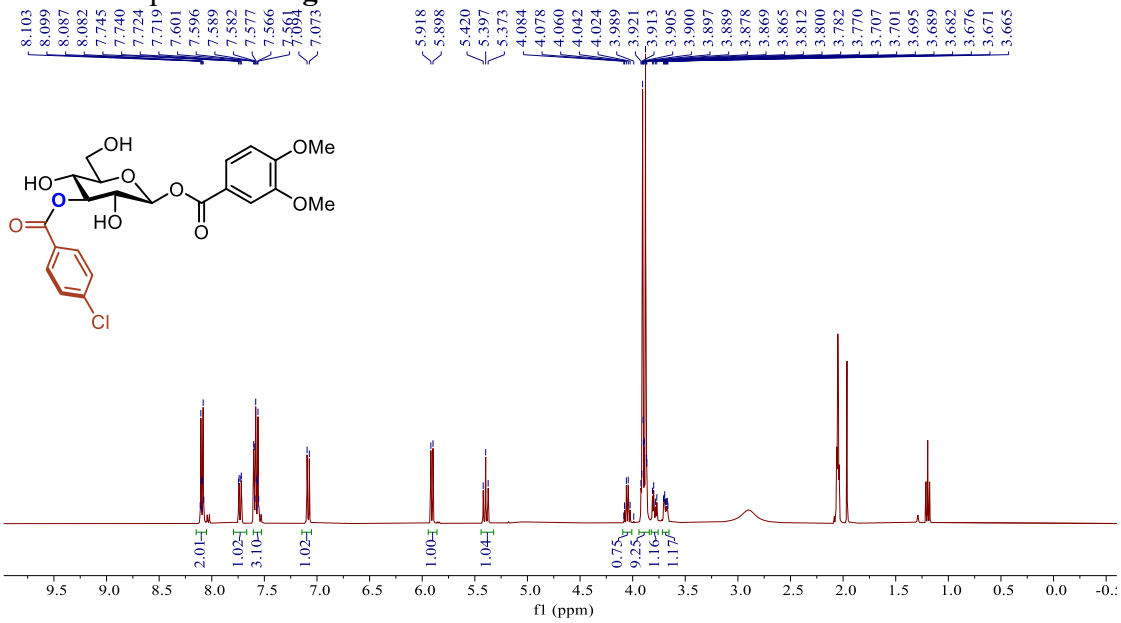
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid,53% yield, 25.5mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.11 – 8.08 (m, 2H), 7.73 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.60 – 7.55 (m, 3H), 7.08 (d, *J* = 8.5 Hz, 1H), 5.91 (d, *J* = 8.1 Hz, 1H), 5.40 (t, *J* = 9.4 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 1H), 3.92 – 3.86 (m, 9H), 3.81 – 3.77 (m, 1H), 3.71 – 3.66 (m, 1H).

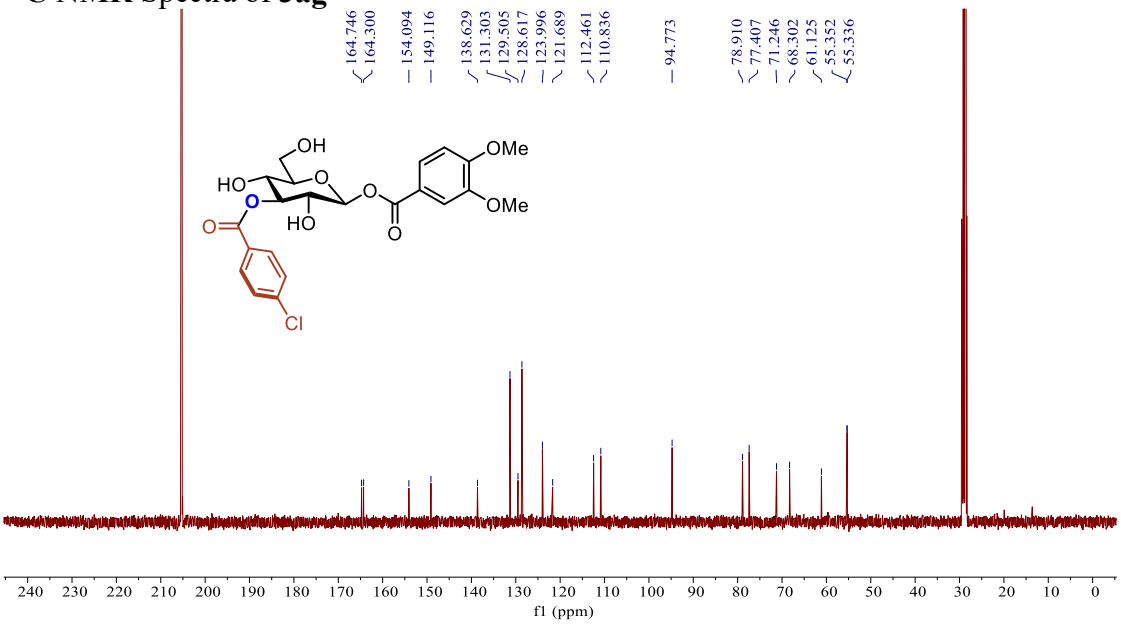
^{13}C NMR (100 MHz, Acetone-d_6) δ 164.75, 164.30, 154.09, 149.12, 138.63, 131.30, 129.50, 128.62, 124.00, 121.69, 112.46, 110.84, 94.77, 78.91, 77.41, 71.25, 68.30, 61.13, 55.35, 55.34.

HRMS (ESI) Calcd for $C_{22}H_{23}ClO_{10}Na^+$ [M+Na]$^+$ 505.0872; Found: 505.0872.

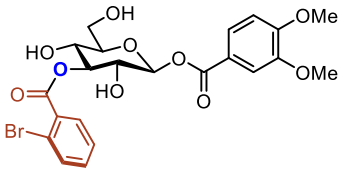
^{1}H NMR Spectra of **3ag**



^{13}C NMR Spectra of **3ag**



(2*S*,3*R*,4*R*,5*R*,6*R*)-4-((2-bromobenzoyl)oxy)-3,5-dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl 3,4-dimethoxybenzoate (3ah):



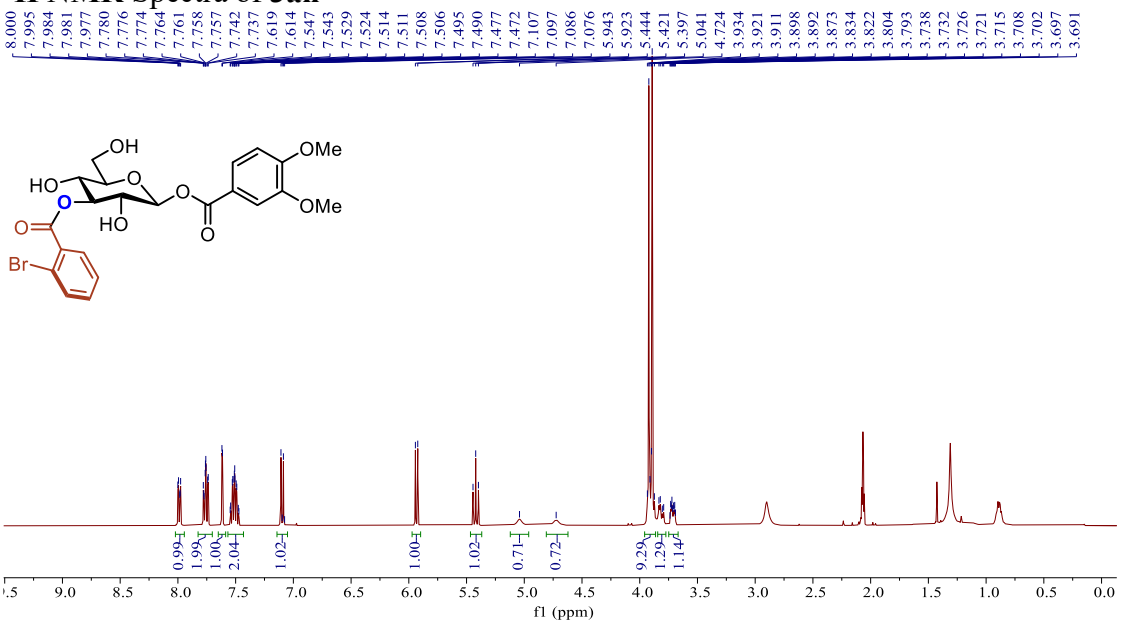
Purification by flash column chromatography on silica gel (ethyl acetate / hexane= 4 / 1), White solid,62% yield, 32.6mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.00 – 7.98 (m, 1H), 7.78 – 7.74 (m, 2H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.10 (d, *J* = 8.5 Hz, 1H), 5.93 (d, *J* = 8.1 Hz, 1H), 5.42 (t, *J* = 9.4 Hz, 1H), 5.04 (s, 1H), 4.72 (s, 1H), 3.91 (d, *J* = 11.6 Hz, 9H), 3.83 – 3.79 (m, 1H), 3.74 – 3.69 (m, 1H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 164.92, 164.32, 154.10, 149.11, 134.31, 132.86, 132.58, 131.72, 127.40, 124.02, 121.68, 121.28, 112.49, 110.83, 94.81, 79.04, 77.46, 71.24, 68.30, 61.12, 55.36.

HRMS (ESI) Calcd for $C_{22}H_{23}BrO_{10}Na^+$ [M+Na]$^+$ 551.0350; Found: 551.0351.

^{1}H NMR Spectra of **3ah**



^{13}C NMR Spectra of **3ah**