Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Photoredox-catalyzed Protecting-group-free *C*-Glycosylation with Glycosyl sulfinate via Giese Reaction

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1. General Remarks

Experiments and Reagents; Reactions were carried out under an argon atmosphere unless noted otherwise. If the reactions were set using a glove box, those reactions were carried out under N_2 atmosphere. The water used for the reactions was distilled grade and was degassed by argon bubbling for 1 minute prior to use. The water used for purifications was distilled grade. Anhydrous MeOH, EtOH, DMSO, and DMF were purchased from Kanto Chemical Co. Ltd. and used for reactions without purification. Reactions were monitored by thin-layer chromatography using Merck Silica Gel 60 F254 plates. Flash chromatography was performed using flash silica gel 60N (spherical neutral, particle size 40–50 μm) purchased from Kanto Chemical Co. Ltd. or CHROMATOREX PSQ 60B (spherical neutral, particle size 60 μm) purchased from Fuji Silysia Chemical Co. Ltd. Photoredox reactions were performed with blue Kessil LED lamps 40 W (A160WE Tuna Blue), PhotoRedOx Box (Hepato Chem, HCK1006-01-016), and corresponding vial holder (Hepato Chem, HCK1006-01-019).

Instrumentation: NMR spectra were recorded 500 MHz Bruker Avance III, operating at 500 MHz for ^{1}H NMR, and 126 MHz for ^{13}C NMR. Chemical shifts were reported in the scale relative to $CHCl_3$ (δ 7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR) or D_2O (δ 4.79 ppm for ^{1}H NMR) or CD_3OD (δ 3.31 ppm for ^{1}H NMR, 49.00 ppm for ^{13}C NMR) as an internal reference. Splitting patterns are designated as s: singlet, d: doublet, t: triplet, q: quartet, br: broadening and m: multiplet. High-resolution mass spectrometry (HRMS) was obtained with Bruker MicrOTOF II. HPLC analysis was performed on JASCO HPLC system consisting of the followings: pump, PU-4180; detector, Biotage® ELSD-A120; column, TSKgel Amide-80 5μm or GL Sciences InertSustain Amide 5 μm; mobile phase, acetonitrile/10 mM $HCOONH_4$ aqueous solution, MeCN/H_2O or 0.1% TFA in MeCN/H_2O. Cyclic voltammetry and differential pulse voltammetry were measured by BAS ALS model 660C.

2. Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV)

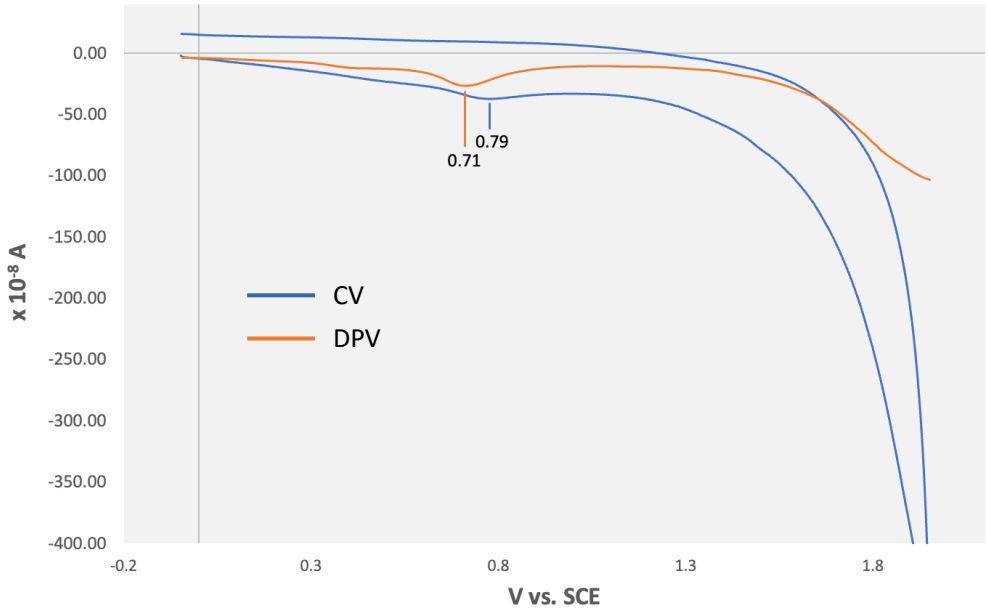


Figure S1. Cyclic voltammetry and differential pulse voltammetry of **4** vs. SCE in MeCN at 0.100 Vs^{-1}.
Conditions: **4** (1 mM) and tetrabuthylammonium hexafluorophosphate (0.1 M). A platinum working electrode, saturated $Ag/AgNO_3$ in MeCN reference electrode, and platinum mesh counter electrode were used. The X-axis was corrected from V vs. Ag/Ag^+ to V vs. SCE by subtracting 0.048 V. The peak top of DPV spectrum can be approximated to half-peak potential ($E_{p/2}$) of the corresponding peak current of the CV spectrum.

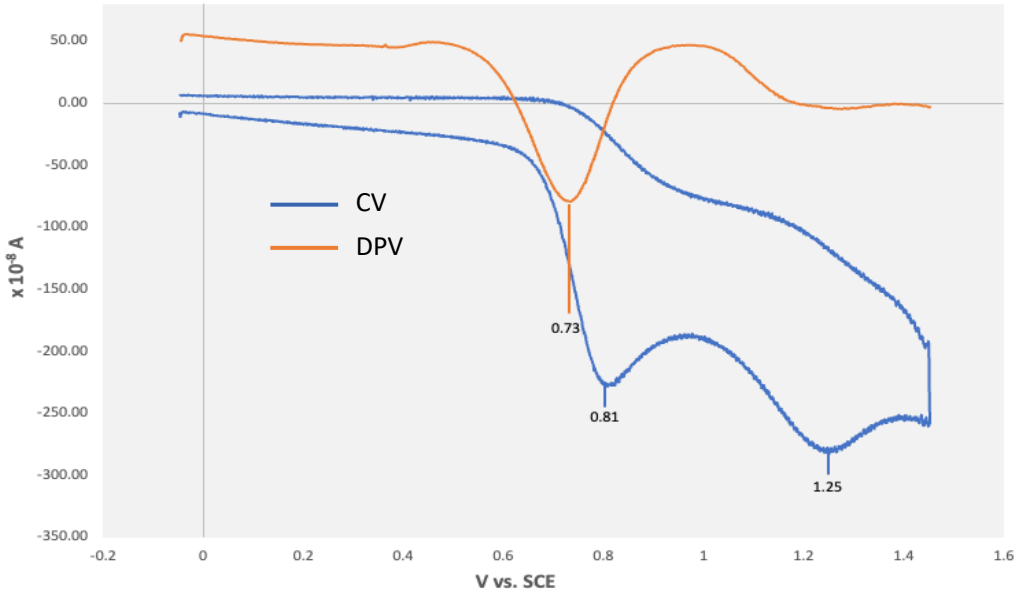
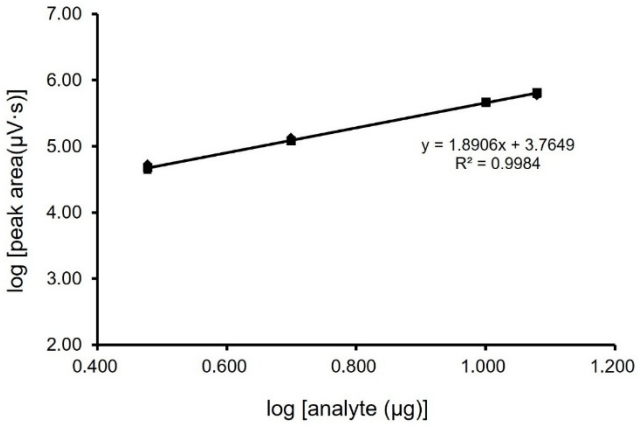


Figure S2. Cyclic voltammetry and differential pulse voltammetry of **4** vs. SCE in $MeOH/H_2O$ 4:1 at 0.100 Vs^{-1}.
Conditions: **4** (1 mM) and tetraethylammonium hexafluorophosphate (0.1 M). A glassy carbon working electrode, Ag/AgCl in aqueous saturated KCl reference electrode, and platinum mesh counter electrode were used. The X-axis was corrected from V vs. Ag/Ag^+ to V vs. SCE by subtracting 0.048 V. The peak top of DPV spectrum can be approximated to half-peak potential ($E_{p/2}$) of the corresponding peak current of the CV spectrum.

3. HPLC Analytical Data



$$I = km^b$$

$$\log I = b \log m + \log k$$

$$where\ I: peak\ area(\mu V \cdot s), m: weight\ of\ analyte, b\ and\ k: constant$$

Figure S3. Calibration curve of 5a for HPLC analysis[1]

Condition: TSKgel Amide-80 5 μm (φ 4.6 mm × 250 mm), Flow rate: 1.0 mL/min (MeCN/10 mM $HCOONH_4$ aq = 90:10 to 80:20, gradient: 3–10 min.), **5a** was detected by ELSD.

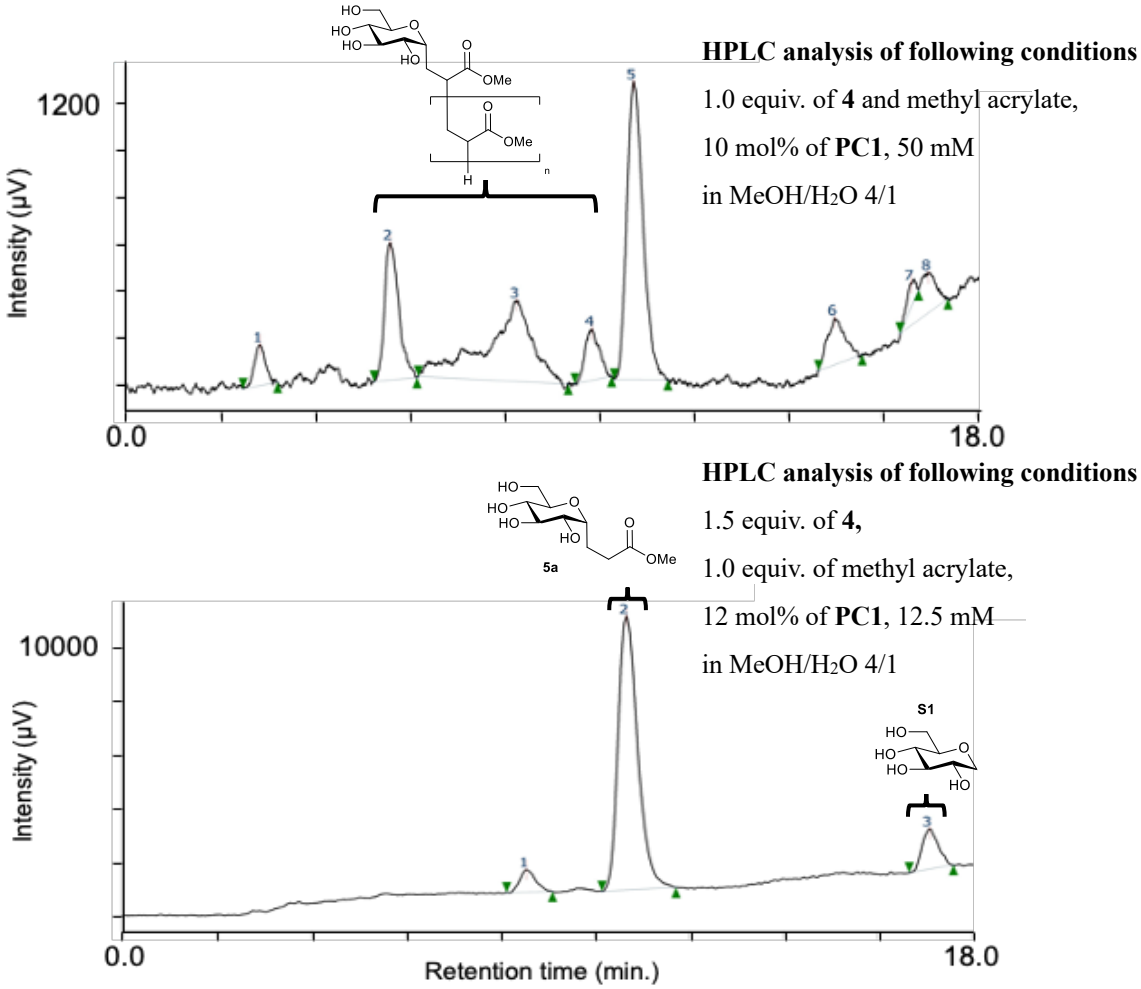
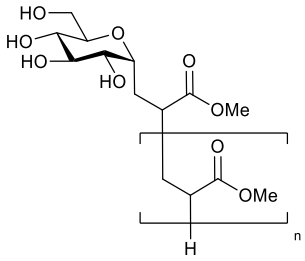


Figure S4. Representative HPLC charts (samples: crude mixture of the coupling reaction)

Condition: TSKgel Amide-80 5 μm (φ 4.6 mm × 250 mm), Flow rate: 1.0 mL/min (MeCN/10 mM $HCOONH_4$ aq = 90:10 to 80:20, gradient: 3–10 min.), detection: ELSD. **5a**: t_R = 10.7 min, **S1** (reduced byproduct): t_R = 17.1 min, oligo-acrylate byproduct: around 5–9 min



Oligo acrylate adduct

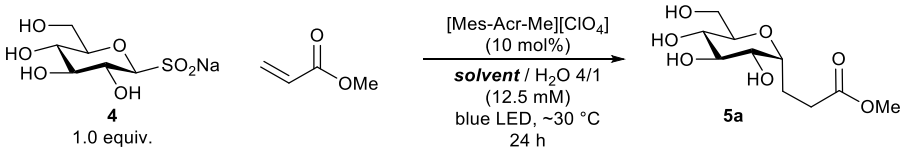
n = 1–5 was detected by ESI-MS. **HRMS-ESI (m/z)**:

n = 1: calcd for $C_{14}H_{24}NaO_9$ 359.1318, found 359.1308; n = 2: calcd for $C_{18}H_{30}NaO_{11}$ 445.1686, found 445.1665;

n = 3: calcd for $C_{22}H_{36}NaO_{13}$531.2054, found 531.2045; n = 4: calcd for $C_{26}H_{42}NaO_{15}$ 617.2421, found 617.2410;

n = 5: calcd for $C_{32}H_{48}NaO_{17}$ 703.2789, found 703.2769.

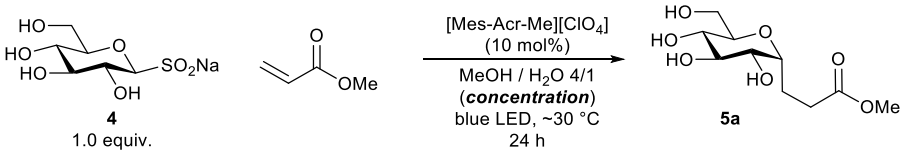
4. Investigations of Giese Addition Reaction



entry	solvent	**5a** [a]
1	MeOH	44%
2	DMSO	44%
3	DMF	41%
4	MeCN	27%
5	EtOH	19%

[a] Yields were determined by HPLC.

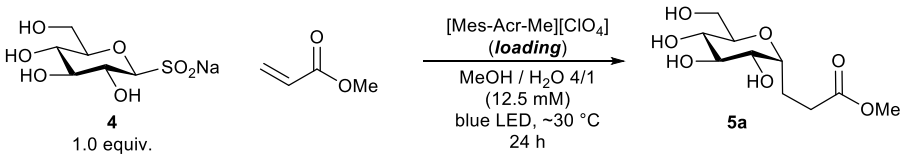
Table S1. Optimization of solvent



entry	concentration	**5a** [a]
1	50 mM	24%
2	25 mM	26%
3	12.5 mM	44%

[a] Yields were determined by HPLC.

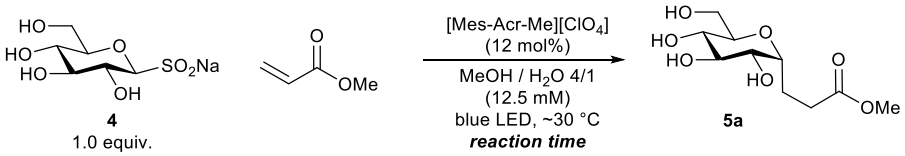
Table S2. Optimization of concentration



entry	loading	**5a** [a]
1	5 mol%	44%
2	8 mol%	43%
3	10 mol%	44%
4	12 mol%	56%
5	15 mol%	51%

[a] Yields were determined by HPLC.

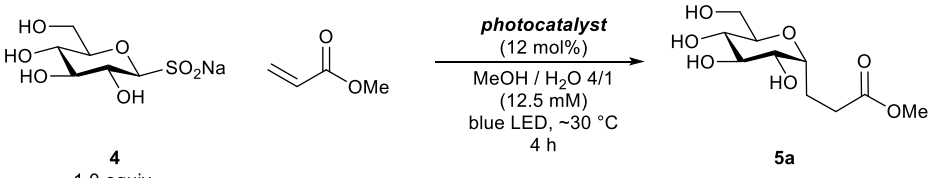
Table S3. Optimization of photocatalyst loading



entry	reaction time	5a [a]
1	4 h	52%
2	6 h	52%
3	8 h	54%
4	24 h	56%

[a] Yields were determined by HPLC.

Table S4. Screening of reaction time



entry	photcatalyst	E_{red}(*A/A$^-$) [c]	5a
1	**PC1**	+2.08 V	52%[a]
2	**PC4**	+1.21 V	58%[a]
3	**PC2**	+0.97 V	57%[a]
4	**PC6**	+1.18 V	44%[a]
5	**PC3**	+0.77 V	0%[a]
6[d]	**PC5**	+1.35 V	41%[b]

[a] Yields were determined by HPLC. [b] Yield was determined by 1H-NMR with sodium mesitylenesulfonate as an internal standard. [c] vs. SCE (in MeCN) [d] 10 mol%, MeOH (12.5 mM), 24 h. [e] Reported oxidation potentials of excieted state photocatalysts (PC*→PC$^-$) in MeCN.

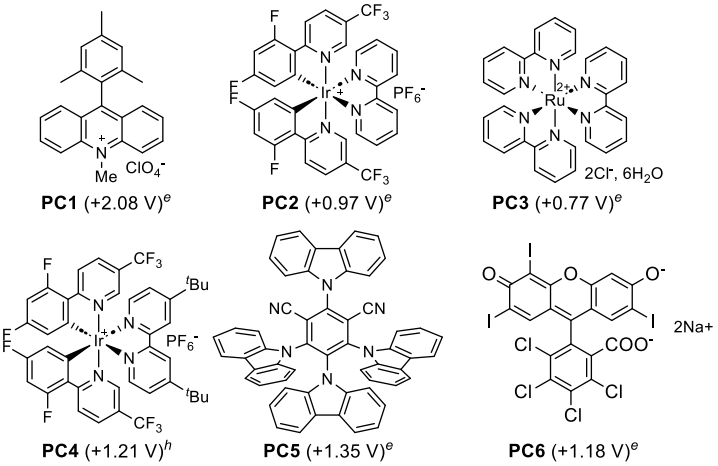
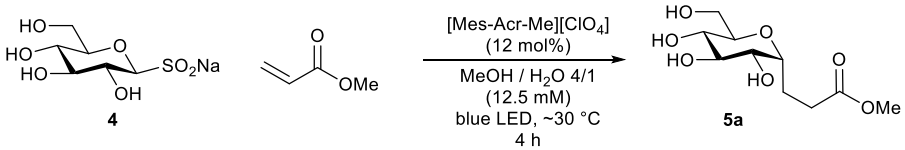


Table S5. Investigation of photocatalyst



entry	4	methl acrylate	5a[a]
1	1.0 equiv.	1.0 equiv.	52%
2	1.0 equiv.	1.2 equiv.	52%
3	1.0 equiv.	1.5 equiv.	61%
4	1.2 equiv.	1.0 equiv.	61%
5	1.5 equiv.	1.0 equiv.	79%

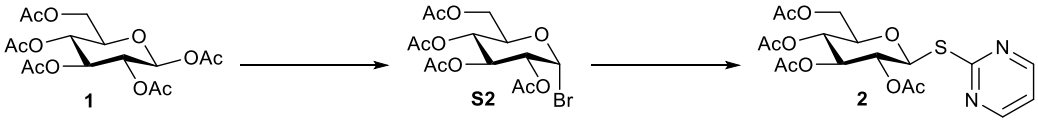
[a] Yields were determined by HPLC.

Table S6. Optimization of equivalents of 4 and methyl acrylate

5. Experimental Procedures

Synthesis of sulfinate donors

Compound 2



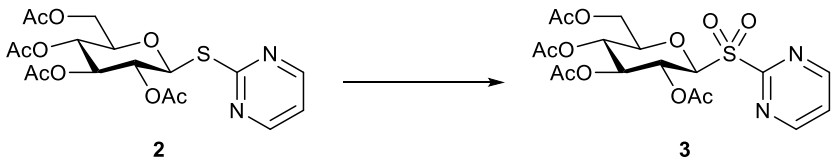
To a round bottom flask with **1** (1.17 g, 3.00 mmol, 1.0 equiv.) was added ca. 5.1 M HBr in AcOH (2.9 mL, 15 mmol, 5.0 equiv.) at room temperature. After stirring for 8 h at room temperature, the solution was poured into a mixture of EtOAc (20 mL), saturated aqueous $NaHCO_3$ (50 mL) and solid $NaHCO_3$ (ca 1 g). After separating layers, the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was dried by azeotrope with CH_2Cl_2 (2 x 10 mL) to give a crude mixture of **S2** (1.22 g, 2.99 mmol, >99 %) which was used directly for the next reaction.

To a crude mixture of **S2** (1.22 g, 2.99 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) was added a mixture of 2-mercaptopyrimidine (1.01 g, 8.97 mmol, 1.5 equiv.), Na_2CO_3 (1.11 g, 10.5 mmol, 3.5 equiv.) and tetrabutylammonium hydrogen sulfate (1.02 g, 2.99 mmol, 1.0 equiv.) in H_2O (10 mL) by pipet. After stirring for 3 h at rt, the reaction mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (Yamazen, ULTRAPACK Silica-40C, eluent: hexane/EtOAc = 55:45 to 40:60) to give **2** (1.17 g, 2.64 mmol, 88% from **1**) as a pale-yellow oil.

^{1}H NMR spectrum of the synthesized compound **2** was consistent to a previous report.[2]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.54 (d, *J* = 4.9 Hz, 2H), 7.04 (t, *J* = 4.9 Hz, 1H), 5.79 (d, *J* = 10.3 Hz, 1H), 5.34 (dd, *J* = 9.3, 9.3 Hz, 1H), 5.25 (dd, *J* = 10.3, 9.3 Hz, 1H), 5.17 (dd, *J* = 10.3, 9.3 Hz, 1H), 4.26 (dd, *J* = 12.7, 4.9 Hz, 1H), 4.11 (dt, *J* = 12.7, 2.4 Hz, 1H), 3.89 (ddd, *J* = 10.3, 4.9, 2.4 Hz, 1H), 2.034 (s, 3H), 2.030 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H).

Compound 3



*m*CPBA(21.5 g, 70 wt%, 87.2 mmol, 5.0 equiv.) in a round bottom flask was dried under vacuum. To the flask was added a solution of **2** (7.72 g, 17.4 mmol, 1.0 equiv.) and $NaHCO_3$ (1.47 g, 17.4 mmol, 1.0 equiv.) in CH_2Cl_2 (500 mL) at 0 °C. The temperature was warmed to 7 °C. After stirring for 48 h at 7 °C, the reaction mixture was treated with 1 M Na_2SO_3 (300 mL) and saturated aqueous $NaHCO_3$ (250 mL) at room temperature. After separating layers, the aqueous layer was extracted with CH_2Cl_2 (3 x 400 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (Yamazen ULATRAPACK Silica-

40D, eluent: hexane/EtOAc = 15:85 to 0:100) to give **3** (6.88 g, 14.5 mmol, 83%) as a white solid.

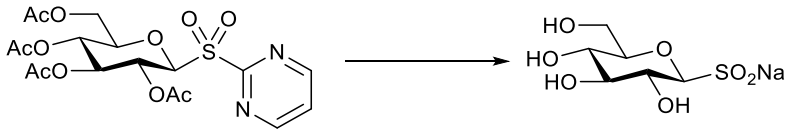
$[\alpha]_D^{24}$ –30.89 (c = 1.0, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.98 (d, *J* = 4.9 Hz, 2H), 7.60 (t, *J* = 4.9 Hz, 1H), 5.82 (dd, *J* = 10.1, 9.2 Hz, 1H), 5.33 (dd, *J* = 9.5, 9.2 Hz, 1H), 5.24 (d, *J* = 10.1 Hz, 1H), 5.08 (dd, *J* = 10.1, 9.5 Hz, 1H), 4.01 (dd, *J* = 12.5, 4.9 Hz, 1H), 3.93 (dd, *J* = 12.5, 2.1 Hz, 1H), 3.75 (ddd, *J* = 10.1, 4.9, 2.1 Hz, 1H), 2.05 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.91 (s, 3H)

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.30, 170.27, 169.27, 169.13, 164.30, 158.79 (2C), 124.13, 86.68, 76.63, 73.58, 67.52, 66.86, 61.43, 20.70, 20.69, 20.66, 20.62

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{18}H_{22}N_2NaO_{11}S$ 497.0842, found 497.0836.

Compound 4a



3 **4a**

A round bottom flask with **3** (2.00 g, 4.22 mmol, 1.0 equiv.) was brought into N_2 filled glove box. NaOMe (1.37 g, 25.3 mmol, 6.0 equiv.) was added to the flask. After taking out of glove box, reagent grade MeOH (70 mL) was added, and the reaction mixture was heated in 50 °C oil bath. After stirring for 8 h, the solution was treated with silica gel (5.0 g) and concentrated. The residue was filtered through a pad of silica gel (eluent: $CHCl_3$/MeOH 9:1 then $CHCl_3$/MeOH/H_2O 2:8:1). The filtration was concentrated. The resulting solid was dissolved in methanol (50 mL) at 60 °C and poured into ethanol (100 mL) through a glass filter, and hexane (30 mL) was added to the mixture to precipitate a white solid. The supernatant was removed by decantation, and the solid was dried under high vacuum to give **4a** (952 mg, 3.81 mmol, 90 %).

$[\alpha]_D^{25}$ -3.05 (c = 1.0, MeOH)

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.94 (dd, *J* = 12.2, 2.1 Hz, 1H), 3.77 (dd, *J* = 12.2, 5.8 Hz, 1H), 3.69 (dd, *J* = 8.9, 8.9 Hz, 1H), 3.61 (d, *J* = 8.9 Hz, 1H), 3.58 (dd, *J* = 8.9, 8.9 Hz, 1H), 3.48 (ddd, *J* = 9.8, 5.8, 2.1 Hz, 1H), 3.41 (dd, *J* = 9.8, 8.9 Hz, 1H)

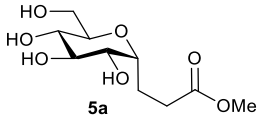
^{13}C NMR (126 MHz, $CDCl_3$): δ 92.70, 80.00, 77.12, 69.76, 69.16, 60.96

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_6H_{11}Na_2O_7S$ 273.0021, found 273.0022.

General procedure for the Giese type reaction with the glucosyl sulfinate.

To a 4 mL or 13 mL glass vial was added sulfinate donors (75 μmol, 1.5 equiv.), solution of photocatalyst and solution of acceptors (50 μmol, 1.0 equiv.) in MeOH/H_2O or MeOH/pH 7.0 phosphate buffer 4:1. The final concentration of acceptor was 12.5 or 50 mM. The mixture was stirred for 4 h or 16 h with irradiation of blue LED. The reaction temperature was maintained around 30 °C by cooling with a USB fan (φ11, 5W, the distance from reaction vial was ca. 15 cm). The reaction mixture was concentrated. The crude mixture was purified by silica gel column chromatography to give the product **5**.

Compound 5a



5a

General procedure was followed for sulfinate **4a** (18.8 mg, 75.0 μmol)**,** 9-mesityl-10-methylacridinium perchlorate (**PC1,** [Mes-Acr-Me][ClO_4], 2.5 mg, 6.0 μmol) and methyl acrylate (4.5 μL, 50 μmol) in MeOH/H_2O (4:1, final concentration: 12.5 mM) for 4 h. The crude mixture was purified by silica gel column chromatography (Biotage Sfär HC Duo 10 g, eluent: $CHCl_3$/MeOH 90:10 to 80:20) to give **5a** (9.3 mg, 37 μmol, 74%) as a colorless oil.

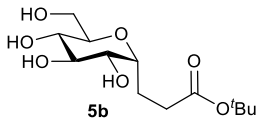
$[\alpha]_D^{25}$ 55.81 (c = 0.65, MeOH)

^{1}H-NMR (500 MHz,D_2O): δ 4.01 (ddd, *J* = 10.4, 6.1, 4.3 Hz, 1H), 3.81 (dd, *J* = 12.5, 2.4 Hz, 1H), 3.73 (dd, *J* = 9.8, 6.1 Hz, 1H), 3.71 (s, 3H), 3.70 (dd, *J* = 12.5, 5.5 Hz, 1H), 3.64 (dd, *J* = 9.8, 9.2 Hz, 1H), 3.50 (ddd, *J* = 9.8, 5.5, 2.4 Hz, 1H), 3.36 (dd, *J* = 9.8, 9.2 Hz, 1H), 2.53 (ddd, *J* = 16.5, 8.2, 6.4 Hz, 1H), 2.47 (ddd, *J* = 16.5, 8.9, 7.6 Hz, 1H), 2.07–1.92 (m, 2H)

^{13}C NMR (126 MHz, D_2O): δ 176.64, 75.19, 73.11, 72.50, 71.00, 70.13, 60.90, 52.21, 29.91, 19.41

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{10}H_{18}NaO_7$ 273.0950, found 273.0950.

Compound 5b



5b

General procedure was followed for sulfinate **4a** (18.8 mg, 75.0 μmol)**,** 9-mesityl-10-methylacridinium perchlorate (**PC1,** [Mes-Acr-Me][ClO_4], 2.5 mg, 6.0 μmol) and *t*-butyl acrylate (7.3 μL, 50 μmol) in MeOH/H_2O (4:1, final concentration: 12.5 mM) for 4 h. The crude mixture was purified by silica gel column chromatography (Biotage Sfär HC Duo 10 g, eluent: $CHCl_3$/MeOH 90:10 to 80:20) to give **5b** (8.8 mg, 30 μmol, 60%) as a colorless oil.

$[\alpha]_D^{25}$ 38.88 (c = 0.85, MeOH)

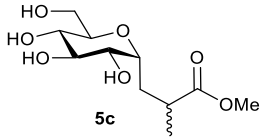
^{1}H-NMR (500 MHz, D_2O): δ 3.99 (ddd, *J* = 10.0, 5.9, 5.6 Hz, 1H), 3.83 (dd, *J* = 12.2, 2.2 Hz, 1H), 3.72 (dd, *J* = 9.8,

5.6 Hz, 1H), 3.70 (dd, *J* = 12.2, 5.4 Hz, 1H), 3.64 (dd, *J* = 9.8, 9.1 Hz, 1H), 3.51 (dd, *J* = 10.0, 5.4, 2.2 Hz, 1H), 3.36 (dd, *J* = 10.0, 9.1 Hz, 1H), 2.46 (ddd, *J* = 15.7, 7.6, 6.4 Hz, 1H), 2.35 (ddd, *J* = 15.7, 8.3, 7.8 Hz, 1H), 2.01–1.91 (m, 2H), 1.47 (s, 9H)

^{13}C NMR (126 MHz, D_2O): δ 175.46, 82.60, 75.04, 73.14, 72.51, 71.05, 70.18, 60.95, 31.26, 27.25 (3C), 19.54

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{13}H_{24}NaO_7$ 315.1420, found 315.1415.

Compound 5c



5c

General procedure was followed for sulfinate **4a** (18.8 mg, 75.0 µmol)**,** 9-mesityl-10-methylacridinium perchlorate (**PC1,** [Mes-Acr-Me][ClO_4], 2.5 mg, 6.0 µmol) and methyl methacrylate (5.3 µL, 50 µmol) in MeOH/H_2O (4:1, final concentration: 50 mM) for 4 h. The crude mixture was purified by silica gel column chromatography (Biotage Sfär HC Duo 10 g, eluent: $CHCl_3$/MeOH 90:10 to 80:20) to give **5c** (11.1 mg, 42 µmol, 84%, dr 3:1) as a colorless oil.

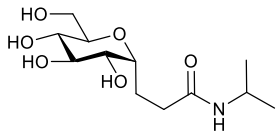
$[\alpha]_D^{25}$ 57.11 (c = 0.74, MeOH)

^{1}H-NMR (500 MHz,D_2O, a 3:1 mixture of diastereomers): δ 4.11 (ddd, *J* = 11.9, 5.5, 2.4 Hz, 0.25H), 4.02 (ddd, *J* = 10.7, 5.8, 5.2 Hz, 0.75H), 3.83 (dd, *J* = 12.5, 1.8 Hz, 0.75H), 3.76–3.68 (m, 5.25H), 3.66–3.60 (m, 1.0H), 3.55–3.48 (m, 1.0H), 3.43–3.34 (m, 1H), 2.77 (tdd, *J* = 7.3, 7.0, 6.1 Hz, 0.75H), 2.65 (tdd, *J* = 7.0, 7.0, 6.7 Hz, 0.25H), 2.14 (ddd, *J*. = 15.0, 11.9, 6.7 Hz, 0.25H), 2.00–1.88 (m, 1.5H), 1.72 (ddd, *J* = 15.0, 7.0, 2.4 Hz, 0.25H), 1.24 (d, *J* = 7.3 Hz, 2.25H), 1.21 (d, *J* = 7.0 Hz, 0.75H)

^{13}C NMR (126 MHz, D_2O, a 3:1 mixture of diastereomers): δ 180.19, 179.48, 74.29, 73.61, 73.07, 73.02, 72.73, 72.52, 70.91, 70.82, 70.15, 69.95, 60.92, 60.62, 52.34, 52.30, 36.54, 35.49, 27.88, 27.51, 16.94, 16.03

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{20}NaO_7$ 287.1107, found 287.1107.

Compound 5d



5d

General procedure was followed for sulfinate **4a** (18.8 mg, 75.0 µmol)**,** Ir[(dF(CF_3)ppy)$_2$bpy]PF_6 (**PC2**, 5.6 mg, 5.0 µmol) and *N*-^{i}Pr-acrylamide (5.7 mg, 50 µmol) in MeOH/H_2O (4:1, final concentration: 12.5 mM) for 16 h. The residue was purified by preparative HPLC (column: HILIC (amide); eluent: MeCN/H_2O 85:15; flow rate: 9 mL/min; detection: ELSD) to give **5d** (8.0 mg, 29 µmol, 57%) as a colorless oil.

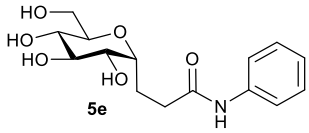
$[\alpha]_D^{26}$ 35.51 (c = 0.53, MeOH)

^{1}H NMR (500 MHz, D_2O): δ 3.96 (ddd, *J* = 11.6, 5.8, 3.7 Hz, 1H), 3,91 (septet, *J* = 6.4 Hz, 1 H), 3.84 (dd, *J* = 12.2, 2.4 Hz, 1H), 3.72 (dd, *J* = 10.1, 5.8 Hz, 1H), 3.70 (dd, *J* = 12.2, 5.8 Hz, 1H), 3.63 (dd, *J* = 10.1, 9.2 Hz, 1H), 3.52 (ddd, *J* = 9.8, 5.8, 2.4 Hz, 1H), 3.35 (dd, *J* = 9.8, 9.2 Hz, 1H), 2.33 (ddd, *J* = 14.7, 8.9, 6.1 Hz, 1H), 2.25 (ddd, *J* = 14.7, 7.9, 7.6 Hz, 1H), 2.04–1.88 (m, 2H), 1.14 (d, *J* = 6.4 Hz, 6H)

^{13}C NMR (126 MHz, D_2O): δ 174.66, 75.23, 73.12, 72.49, 71.01, 70.23, 61.03, 41.67, 31.96, 21.39, 21.28, 20.39

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{23}NNaO_6$ 300.1423, found 300.1412.

Compound **5e**



5e

General procedure was followed for sulfinate **4a** (18.8 mg, 75.0 µmol)**,** Ir[(dF(CF_3)ppy)$_2$bpy]PF_6 (**PC2**, 5.1 mg, 5.0 µmol) and *N*-phenylacrylamide (7.4 mg, 50 µmol) in MeOH/H_2O (4:1, final concentration: 12.5 mM) for 16 h. The crude mixture was purified by silica gel column chromatography (Biotage Sfär HC Duo 10g, eluent: $CHCl_3$/MeOH 90:10 to 80:20) to give **5e** (12.1 mg, 39 µmol, 78%) as a white solid.

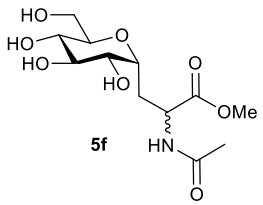
$[\alpha]_D^{25}$ 59.39 (c = 0.68, MeOH)

^{1}H NMR (500 MHz, CD_3OD): δ 7.56–7.53 (m, 2H), 7.32–7.27 (m, 2H), 7.10–7.05 (m, 1H), 3.94 (ddd, *J* = 10.4, 5.8, 5.2 Hz, 1H), 3.80 (dd, *J* = 11.6, 2.4 Hz, 1H), 3.63 (dd, *J* = 11.6, 5.8 Hz, 1H), 3.61. (dd, *J* = 9.2, 5.8 Hz, 1H), 3.55 (dd, *J* = 9.2, 8.2 Hz, 1H), 3.46 (ddd, *J* = 9.2, 5.8, 2.4 Hz, 1H), 3.25 (dd, *J* = 9.2, 8.2 Hz, 1H), 2.52 (ddd, *J* = 14.3, 7.9, 6.4 Hz, 1H), 2.42 (ddd, *J* = 14.3, 7.9, 7.6 Hz, 1H), 2.14–1.99 (m, 2H)

^{13}C NMR (126 MHz, CD_3OD): δ 174.38, 139.92, 129.75 (2C), 125.10, 121.24 (2C), 76.69, 75.21, 74.60, 73.00, 72.32, 63.16, 34.15, 22.15

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{15}H_{21}NNaO_6$ 334.1267, found 334.1266.

Compound **5f**



5f

General procedure was followed for sulfinate **4a** (18.8 mg, 75.0 µmol)**,** 9-mesityl-10-methylacridinium perchlorate (**PC1,** [Mes-Acr-Me][ClO_4], 2.5 mg, 6.0 µmol) and methyl 2-acetamidoacrylate (7.2 mg, 50 µmol) in MeOH/pH 7.0 phosphate buffer (4:1, final concentration: 12.5 mM) for 16 h. The crude mixture was filtrated through a pad of silica gel with $CHCl_3$/MeOH 4:1 and concentrated. The residue was purified by preparative HPLC (column: HILIC

(amide); eluent: MeCN/H_2O 85:15; flow rate: 9 mL/min; detection: ELSD) to give **5f** (7.3 mg, 24 μmol, 47%, dr 2.0:1) as a colorless oil.

Major isomer

$[\alpha]_D^{25}$ 44.23 (c = 0.45, MeOH)

^{1}H NMR (500 MHz, D_2O): δ 4.58 (dd, *J* = 6.7, 6.4 Hz, 1H), 4.15 (ddd, *J* = 10.1, 6.1, 4.0 Hz, 1H), 3.78 (s, 3H), 3.77–3.74 (m, 2H), 3.72 (dd, *J* = 9.8, 6.1 Hz, 1H), 3.59 (dd, *J* = 9.8, 9.2 Hz, 1H), 3.51 (ddd, *J* = 9.8, 4.3, 2.8 Hz, 1H), 3.40 (dd, *J* = 9.8, 9.2 Hz, 1H), 2.25–2.15 (m, 2H), 2.04 (s, 3H)

^{13}C NMR (126 MHz, D_2O): δ 173.99, 173.75, 73.02, 72.94 (2C), 70.59, 69.82, 60.62, 52.98, 50.52, 26.00, 21.62

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{21}NNaO_8$ 330.1165, found 330.1162.

Minor isomer

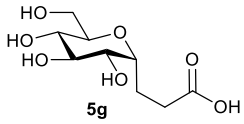
$[\alpha]_D^{27}$ 33.09 (c = 0.17, MeOH)

^{1}H NMR (500 MHz, D_2O): δ 4.54 (dd, *J* = 11.0, 4.0 Hz, 1H), 4.08 (ddd, *J* = 12.2, 6.1, 2.8 Hz, 1H), 3.84 (dd, *J* = 12.2, 2.1 Hz, 1H), 3.78 (s, 3H), 3.75 (dd, *J* = 9.8, 6.1 Hz, 1H), 3.72 (dd, *J* = 12.2, 5.5 Hz, 1H), 3.61 (dd, *J* = 9.8, 9.2 Hz, 1H), 3.57 (ddd, *J* = 10.1, 5.5, 2.1 Hz, 1H), 3.37 (dd, *J* = 10.1, 9.2 Hz, 1H), 2.34 (ddd, *J* = 15.6, 12.2, 4.0 Hz, 1H), 2.06 (s, 3H), 2.03 (ddd, *J* = 15.6, 11.0, 2.8 Hz, 1H)

^{13}C NMR (126 MHz, D_2O): δ 174.53, 174.28, 73.09, 72.91, 72.07, 70.47, 70.03, 60.90, 53.04, 49.32, 25.25, 21.61

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{21}NNaO8$ 330.1165, found 330.1156.

Compound 5g



5g

General procedure was followed for sulfinate **4a** (18.8 mg, 75.0 μmol)**,** Ir[(dF(CF_3)ppy)$_2$dtbpy]PF_6 (**PC4**, 5.6 mg, 5.0 μmol) and acrylic acid (3.4 μL, 50 μmol) in MeOH/pH 7.0 phosphate buffer (4:1, final concentration: 12.5 mM) for 16 h. The crude mixture was filtrated through a pad of silica gel with 1% AcOH in $CHCl_3$/MeOH/H_2O 10:10:1 and concentrated. The residue was purified by preparative HPLC (column: HILIC (amide); eluent: 0.1% TFA in MeCN/H_2O 85:15; flow rate: 9 mL/min; detection: ELSD) to give **5g** (4.8 mg, 20 μmol, 40%) as a colorless oil.

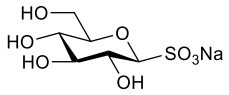
$[\alpha]_D^{26}$ 38.81 (c = 0.43, MeOH)

^{1}H NMR (500 MHz, D_2O): δ 4.01 (dd, *J* = 11.0, 5.8, 4.0 Hz, 1H), 3.80 (dd, *J* = 12.2, 2.4 Hz, 1H), 3.72 (dd, *J* = 9.8, 5.8 Hz, 1H), 3.69 (dd, *J* = 12.2, 5.5 Hz, 1H), 3.63 (dd, *J* = 9.8, 8.9 Hz, 1H), 3.50 (ddd, *J* = 10.1, 5.5, 2.4 Hz, 1H), 3.35 (dd, *J* = 10.1, 8.9 Hz, 1H), 2.55–2.41 (m, 2H), 2.05–1.91 (m, 2H)

^{13}C NMR (126 MHz, D_2O): δ 178.06, 75.18, 73.12, 72.50, 71.01, 70.13, 60.87, 29.95, 19.43

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_9H_{16}NaO_7$ 259.0794, found 259.0795.

Compound 4b



4b

General procedure was followed for sulfinate **4a** (12.5 mg, 50.0 µmol), $Ru(bpy)_3Cl_2·6H_2O$(**PC3**, 3.7 mg, 5.00 µmol) and methyl acrylate (4.5 µL, 50µmol) in MeOH/H_2O (4:1, without degassing, final concentration: 25 mM) for 6 h under air. The crude mixture was concentrated, triturated with $CHCl_3$ (1 mL) and EtOAc (1 mL) and filtrated. The residue was dissolved with H_2O and concentrated to give **4b** (7.5 mg, 28 µmol, 56%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.22 (d, *J* = 9.5 Hz, 1H), 3.92 (dd, *J* = 12.5, 2.1 Hz, 1H), 3.74 (dd, *J* = 12.5, 5.8 Hz, 1H), 3.68 (dd, *J* = 9.5, 9.2 Hz, 1H), 3.57 (dd, *J* = 9.5, 9.2 Hz, 1H), 3.53 (ddd, *J* = 9.8, 5.8, 2.1 Hz, 1H), 3.45 (dd, *J* = 9.8, 9.5Hz, 1H)

^{13}C NMR (126 MHz, $CDCl_3$): δ 87.90, 80.06, 76.67, 70.86, 68.99, 60.82

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_6H_{11}Na_2O_8S$ 288.9970, found 288.9963.

6. Computational Methods

6-1. Conformational Distribution Analysis

Conformational distribution analysis of unprotected glucosyl radical **7** was conducted using Spartan 20 (MMFF, solvent=CPCM:water) with the following torsion setting: "chair flip" for C1, C2, C3, C4, C5, and O, and "single bond rotation" (3 x 120°) for C2-O, C3-O, C4-O, C5-C6, and C6-O (see Figure S5, resulting in a total 15552 candidates). Resulting 208 conformers were further optimized by Gaussian 16 (um062x/6-311G(d,p)//uB3LYP/6-31G(d,p), solvent=SMD:water). Then, the optimized structures were classified into 10-type of conformations: $^{4}C_{1}$ (50), $^{1}C_{4}$ (67), $^{1}S_{3}$ (11), $^{1}S_{5}$ (37), $^{O}S_{2}$ (14), $B_{2,5}$ (3), $B_{O,3}$ (12), $B_{1,4}$ (4), $^{2}S_{O}$ (4), $^{5}S_{1}$ (6). The Gibbs energy of the most stable structure of each conformation were $^{4}C_{1}$ (0.0 kcal/mol), $^{1}C_{4}$ (+0.6 kcal/mol), $^{O}S_{2}$ (+1.7 kcal/mol), $^{1}S_{5}$ (+2.8 kcal/mol), $^{1}S_{3}$ (+2.9 kcal/mol), $B_{2,5}$ (+3.9 kcal/mol), $B_{O,3}$ (+3.9 kcal/mol), $B_{1,4}$ (+5.0 kcal/mol), $^{2}S_{O}$ (+5.6 kcal/mol), and $^{5}S_{1}$ (+6.0 kcal/mol) (Figure S6). It should be noted that the $B_{2,5}$ conformations tend to be converted into the $^{1}S_{5}$ or $^{O}S_{2}$ conformations during optimization. Therefore, the output files were carefully checked to confirm that the optimized conformations corresponded to the starting conformations. In this study, we classified the conformationally similar $B_{2,5}$, $^{1}S_{5}$, and $^{O}S_{2}$ by the dihedral angle between C5-C4-C1-O ($\theta_{C5\text{-}C4\text{-}C1\text{-}O}$, see Figure S7). Other boat and twist boat conformations are assigned by the similar way.

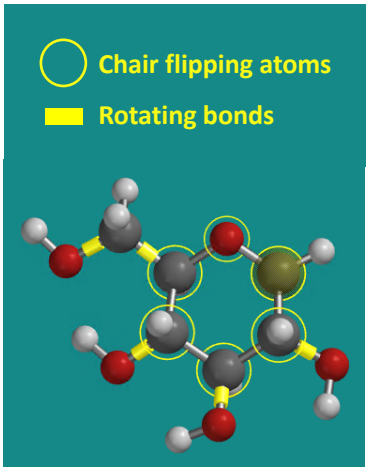


Figure S5. Torsion setting

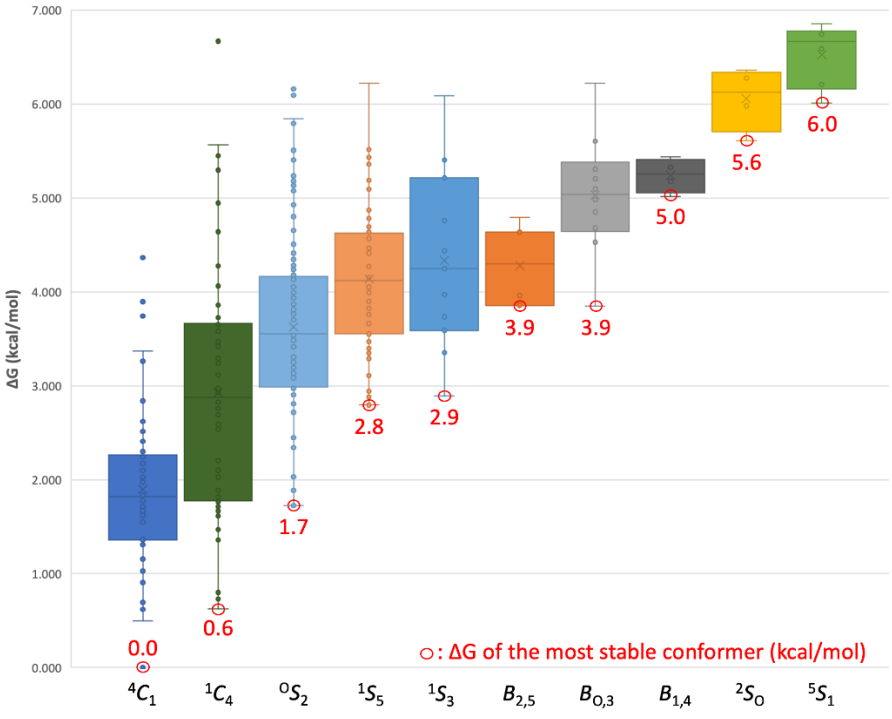


Figure S6. Boxplot of conformational distribution analysis

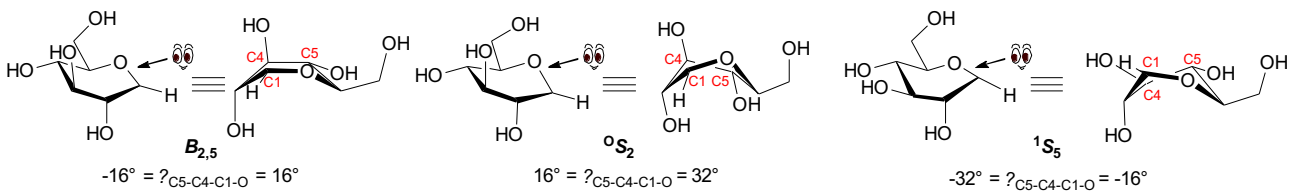


Figure S7. Definition of boat and twist boat conformations

6-2. Calculation of the Gibbs energy of *C*-glycosides 8α and 8β

Conformational distribution analysis and further optimization of the structures of **8α** and **8β** were performed on Spartan 20. Conformational distribution analysis (MMFF method) and subsequent optimization of their geometries (Hartree-Fock/3-21G) generated several structures with an energy threshold of ≤40 kJ/mol. Energy calculations were then performed (ωB97X-D/6-31G(d)), extracting conformers with an energy threshold of ≤15 kJ/mol. Finally, geometry optimization using ωB97X-D/6-31G(d) was performed to obtain the stable conformers with energy below 10 kJ/mol relative to the most stable conformer (Figure S6). The resulting conformers were further optimized with Gaussian 16 (um062x/6-311G(d,p)).

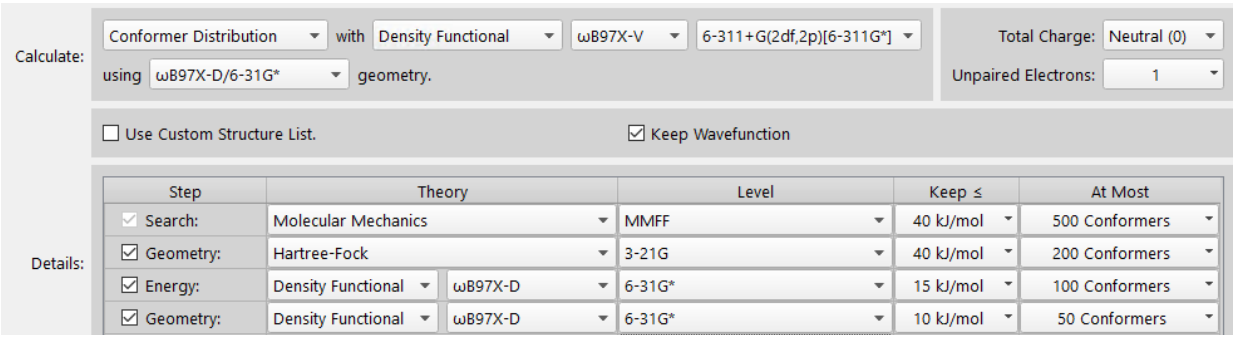


Figure S8. Exploration of the most stable conformer of 8a and 8b

6-3. Transition State Calculation

Transition state of the Giese reaction between glucosyl radical **7** and methyl acrylate to give **8α** and **8β** was explored using Reaction Plus (string method, B3LYP/6-31G(d,p)//B3LYP/3-21G*). The initial structure was generated using the most stable structure of $^{4}C_{1}$, $^{1}C_{4}$, $^{1}S_{3}$, $^{1}S_{5}$, $^{O}S_{2}$, and $B_{2,5}$ conformations. The Newman projection of the reaction point (between C1 of glucosyl radical and β-carbon of methyl acrylate) was set to be gauche. Therefore, three different initial structures for each conformer were investigated using B3LYP/3-21G* level theory. The resulting IRC plots were analyzed, and the most favored path was further optimized with string method using B3LYP/6-31G(d,p) level theory.

Then the resulting starting material (**SM**), transition state (**TS**), and product (**P**) were further optimized by Gaussian 16 (m062x/6-311G(d,p)). Direct optimization at m062x/6-311G(d,p) level theory sometimes fails to converge. For such cases, the geometry was optimized first with B3LYP/6-311G(d,p) or m062x/6-31G(d,p) and then with m062x/6-311G(d,p). In most cases, the transition state optimization required the addition of "opt=noeigen" option to converge properly. If the RMD values were not converged, the following keyword was added: opt=maxstep=N ($5 \leq N \leq 20$). The conformations of pyranose ring of output structures were carefully analyzed because the pyranose-ring frequently alter from that in the input structure.

Input for the first QST2 calculation of protecting-group-free Giese reaction:

#p opt=(calcall,qst2) ub3lyp/3-21g* scrf=(smd,solvent=water) string=nbeads=15

Input B for the second QST2 calculation of protecting-group-free Giese reaction:

#p opt=(calcall,qst2) ub3lyp/6-31g(d,p) scrf=(smd,solvent=water) string=nbeads=31

Input for the optimization/frequency of TS

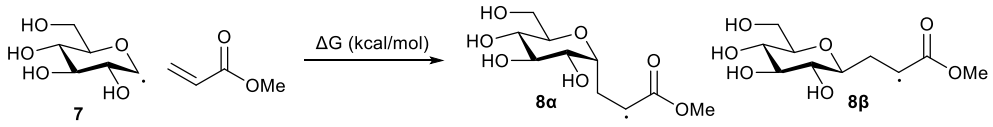
#p opt=(calcfc,ts,noeigen) freq um062x/6-311g(d,p) scrf=(smd,solvent=water)

Input for the optimization/frequency of SM and P

#p opt=calcfc freq um062x/6-311g(d,p) scrf=(smd,solvent=water)

6-4. Summary of the conformational distribution and TS calculation

Table S7 summarized the energy and sugar conformations at each transition states. The sum of the Gibbs energies of the separately calculated $^4C_1$ glucosyl radical and methyl acrylate was found to be more stable than the initial structure of IRC plot where $^4C_1$ glucosyl radical and methyl acrylate were interacting. Therefore, the relative energies were calculated based on sum of the Gibbs energies of $^4C_1$ glucosyl radical and methyl acrylate.



initial conformation of glucosyl radical	$^4C_1$	$^1C_4$	$^1S_3$	$^1S_5$	$^OS_2$	$B_{2,5}$
conformation at TS toward α-isomer **8α**	$^4C_1$	$^1C_4$	$^4C_1$	$^OS_2$ [b]	$^OS_2$	$^OS_2$ [b]
activation energy toward α-isomer **8α**[a]	+8.7	+15.1	(+8.7)	(+12.3)	+10.6	+12.3
conformation at TS toward β-isomer **8β**	$^4C_1$	$^1C_4$	E_3	$^1S_5$	$^1S_5$	$^1S_5$
activation energy toward α-isomer **8β**[a]	+14.4	+11.1	+12.8	+11.8	(+11.8)	(+11.8)

[a] ΔG (kcal/mol) based on sum of the Gibbs energies of the $^4C_1$ glucosyl radical **7** and methyl acrylate.

[b] The pyranose ring was slightly distorted, forming intermediate structure between $^OS_2$ and $B_{2,5}$ conformations.

Table S7. Summary of transition state energies

6-5. Conformational distribution analysis and transition state calculation of tetraacetylglucosyl radical.

The $^4C_1$ and $B_{2,5}$ conformations of tetraacetylglucosyl radical **S3** were drawn from the corresponding conformations of unprotected glucosyl radical **7**. Following conformational distribution analysis (Spartan 20 (MMFF), freezing the pyranose ring) generated the conformers within 40 kJ/mol, which were optimized using Gaussian (um062x/6-311G(d,p), solvent=SMD:dichloromethane). In addition, the Gibbs energy of the reported $B_{2,5}$ and $^4C_1$ conformations are also calculated as well. The most favored conformations were used for generating the initial structure for the transition state calculation. The transition states to give α- and β-*C*-glycoside **S4α** and **S4β** were investigated using Reaction Plus (uB3LYP/6-31G//uB3LYP/3-21G*). The resulting **TS**, **SM**, **P** were further optimized using Gaussian 16 (um062x/6-311G(d,p), solvent=SMD:dichloromethane).

6-6. Transition state calculation of the Giese radical addition with tetraacetylglucosyl radical S3

Figure S9 summarized the transition state calculation of the radical addition of tetraacetylglucosyl radical **S3** to methyl acrylate to give **S4**. As a result of conformational distribution analysis, $^1S_5$ was found to be more stable than $B_{2,5}$ conformation. Nakamura *et al.* also reported the $^1S_5$ conformation was the most stable conformation, although they judged it as $B_{2,5}$ conformation.[3] Giese *et al.* suggested that glucosyl radical occupied the $B_{2,5}$ conformation judged by ESR spectrum, which could also be regarded as $^1S_5$ conformation.[4]

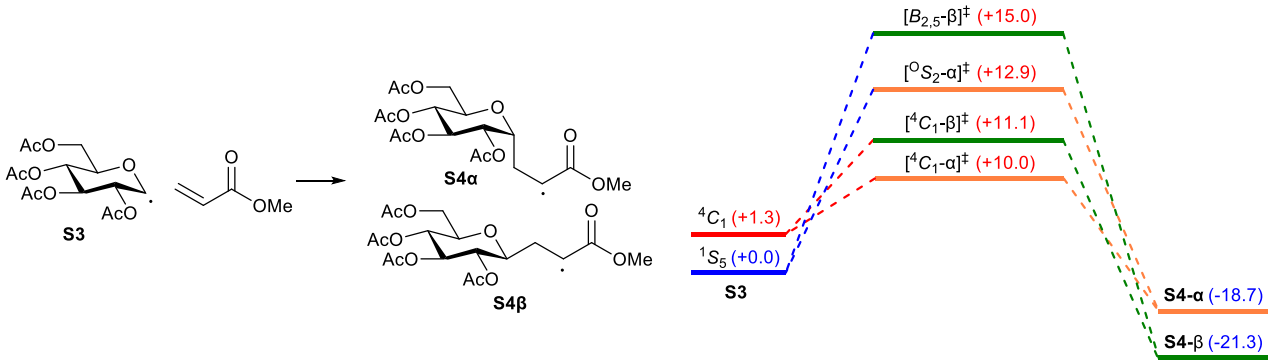
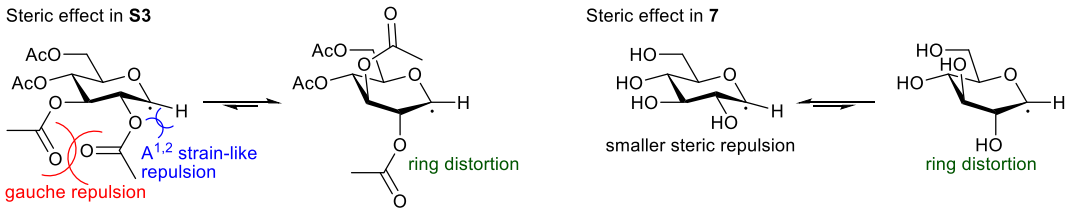


Figure S9. Summary of TS calculation of the Giese reaction with tetraacetylglucosyl radical S3

6-7. Discussion and summary of the computational study

The conformational analysis revealed that the most stable conformation for the protecting-group-free glucosyl radical **7** was " $^4C_1$ conformation ". In contrast, the " $B_{2,5}$ conformation (or $^1S_5$ conformation) ", is the most stable conformation of tetraacetylglucosylradical **S3**, which is attributable to both steric and stereo-electronic effects (Figure S8). The 2-OP and 3-OP groups of the protected glucosyl radical adopt a pseudo-axial position to reduce steric repulsion caused by gauche repulsion between 2-OP, 3-OP, and 4-OP, and steric repulsion between *H*1 and 2-OP, resulting in the formation of the $B_{2,5}$ conformation. These factors are negligible in the unprotected glucosyl radical, leading to the preferable existence of the $^4C_1$ conformation.

In terms of stereoelectronic effect, glucosyl radical is stabilized by the orbital interaction between n_O, $SOMO_{C1}$, and $\sigma_{C2\text{-}O}$*, known as the "quasi-homo-anomeric effect". While the spin density at C1 position of unprotected **7**-$B_{2,5}$ (+0.885) is lower than that of **7**-$^4C_1$ (+0.928) by 0.043, the spin density deference between acetyl-protected glucosyl radical **S3**-$B_{2,5}$ (+0.879) and **S3**-$^4C_1$ (+0.932) is 0.053, indicating greater stabilization by conformational conversion from $^4C_1$ to $B_{2,5}$ due to better delocalization of the spin density. These computational results suggests that the protection of the hydroxy groups of the glucosyl radical plays a crucial role in the stereoelectronic stabilization effect.



Summary of Mulliken spin density

	S3-$^4C_1$	**S3**-$B_{2,5}$	**7**-$^4C_1$	**7**-$B_{2,5}$
C-1	0.932	0.879	0.928	0.885
endo-O	0.077	0.115	0.078	0.107
O-2	0.002	0.043	0.001	0.047

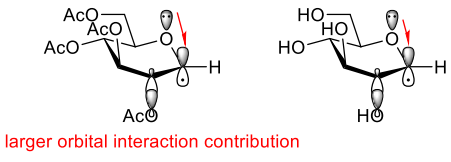
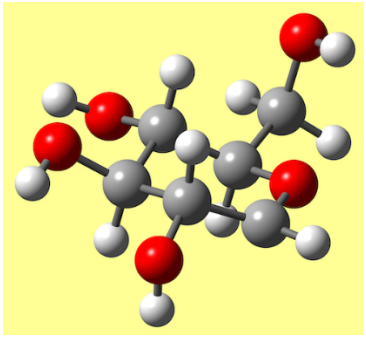


Figure S10. The nature of conformational stability of protected and unprotected glucosyl radicals

6-8. Structure of glucosyl radicals and transition states

Glucosyl radical: $^4C_1$ conformation



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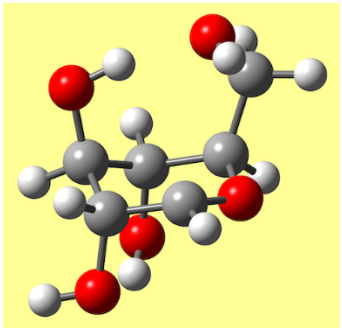
O	0.65129500	-1.54210600	-0.17534400
C	-1.60230400	-0.68394200	0.34171000
C	0.32551000	0.85502600	0.07105500
C	-1.15959000	0.67808800	-0.17301000
C	1.09519900	-0.25506500	-0.63424300
C	-0.69911800	-1.75833100	-0.17896200
H	-1.57301900	-0.65305800	1.43963800
H	0.51825700	0.80139800	1.14986500
H	-1.34888100	0.72514400	-1.25477100
H	0.91437900	-0.18189200	-1.71311600
H	-0.95314300	-2.79752100	-0.00707200
O	-2.95673500	-0.94869900	0.00834900
H	-3.00375200	-1.02743300	-0.95345500
O	-1.83189100	1.73411300	0.49164600
H	-2.77426600	1.63958800	0.30955400
O	0.78781200	2.08443200	-0.46047100
H	0.21593100	2.77623500	-0.10678600
C	2.58527400	-0.20816700	-0.36675200
H	2.98587900	0.73731000	-0.73112600
H	3.06554400	-1.02675400	-0.91218700
O	2.87519200	-0.28496300	1.02007500
H	2.47785400	-1.10089500	1.34663500

Glucosyl radical: $^{1}C_{4}$ conformation



G = -611.113687

Charge 0 Multiplicity 2

O	-0.28894200	0.54013000	1.50234900
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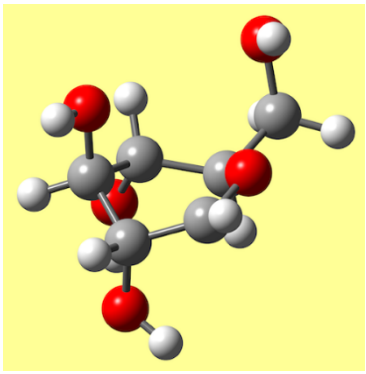
C	0.14453800	0.88776200	-0.90341900
C	0.69431300	-0.54129800	-1.02585800
C	-0.81798400	1.07947600	0.27591900
C	0.28180000	-0.70417000	1.43424000
H	1.43138100	-2.07582600	0.30099000
H	-0.39378000	1.13796100	-1.82023700
H	1.52506400	-0.51620400	-1.73340100
H	-0.88096000	2.15610000	0.44428800
H	0.41864400	-1.14055300	2.41625400
O	2.48253200	-0.28452700	0.51400200
H	2.77156800	-0.41974900	1.42451400
O	-0.25777700	-1.44991700	-1.53858800
H	-1.05853800	-1.39962000	-0.98435300
O	1.22336500	1.80921500	-0.78724600
H	1.85210500	1.42750900	-0.15631300
C	-2.24881600	0.58445600	0.09449900
H	-2.64383000	0.97294900	-0.84543800
H	-2.85314800	0.97353300	0.91686100
O	-2.37324000	-0.83478900	0.04283900
H	-2.20268400	-1.18774700	0.92531700

Glucosyl radical: $^{O}S_2$ conformation



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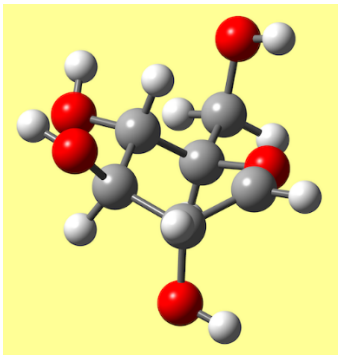
Charge 0 Multiplicity 2

O	0.49282000	-1.09171500	-0.89057700
C	-1.78147700	-0.54342100	-0.18172100
C	0.13689900	0.86940800	0.58330100
C	-1.03828400	-0.00412200	1.04489600
C	0.79998900	0.30092900	-0.69199400
C	-0.83837600	-1.39222700	-0.96128500
H	-2.64530400	-1.14049100	0.11931700
H	0.86445600	0.89251600	1.39619900
H	-1.70863600	0.61291100	1.64505200
H	0.42335900	0.85994000	-1.55464600
H	-1.01728700	-2.44053000	-1.15514600
O	-2.21636900	0.62586500	-0.90158300
H	-2.37715500	0.36449600	-1.81613900
O	-0.60348800	-1.06891500	1.87434500
H	0.09380400	-1.55120800	1.41174900
O	-0.25320600	2.21297500	0.35138000
H	-0.97337400	2.16867700	-0.29365200
C	2.30983100	0.38101600	-0.63641100
H	2.60204300	1.41967400	-0.47402400
H	2.73115000	0.03906300	-1.58667300
O	2.82352300	-0.37894400	0.44734300
H	2.52921000	-1.28867800	0.31998000

Glucosyl radical: $^{1}S_{5}$ conformation



G = -611.110227

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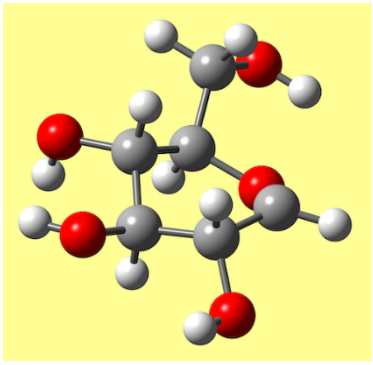
O	-0.46600800	-1.49714900	-0.41840500
C	1.79551400	-0.58933300	-0.16029900
C	-0.25345200	0.86475600	-0.01311000
C	1.26173300	0.83706900	0.08059600
C	-0.84202600	-0.45225500	0.49643200
C	0.81302400	-1.42234500	-0.89707400
H	2.71726900	-0.52371700	-0.74452400
H	-0.51760500	0.95770700	-1.07274900
H	1.55850500	1.13936200	1.09104500
H	-0.44730000	-0.68498900	1.49134700
H	1.08930600	-2.27577000	-1.50068700
O	2.08032800	-1.13528200	1.14566200
H	2.31174100	-2.06367400	1.02239500
O	1.74872800	1.75433300	-0.88450700
H	2.69434300	1.86722300	-0.73717500
O	-0.73646600	1.97147100	0.72615600
H	-1.61833000	2.18381400	0.39985200
C	-2.35401300	-0.44636200	0.54256400
H	-2.68924700	0.26075800	1.30144800
H	-2.70245600	-1.44563500	0.82228900
O	-2.91950300	-0.03530400	-0.69330000
H	-2.57754000	-0.62881300	-1.37272900

Glucosyl radical: $^{1}S_{3}$ conformation



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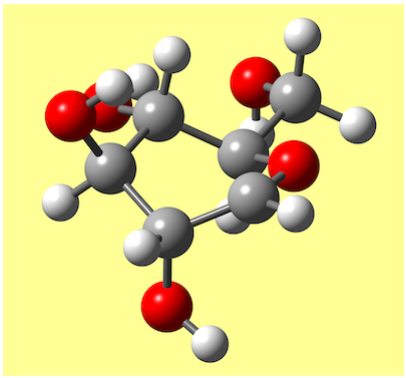
O	0.64933700	-1.26197500	-0.88290300
C	-1.44259900	-0.80267800	0.37509900
C	0.25593800	0.96426700	0.11410900
C	-1.19340100	0.59787400	-0.15561900
C	1.17572000	0.06975100	-0.71953800
C	-0.29633600	-1.68871100	0.01250400
H	-1.52807800	-0.73285000	1.46798800
H	0.46181600	0.83124300	1.17997400
H	-1.37068800	0.60154600	-1.24058000
H	1.24430100	0.49064300	-1.72703800
H	-0.43345200	-2.76207200	-0.00897100
O	-2.65213700	-1.35861500	-0.14687700
H	-3.38168900	-0.86058400	0.24115700
O	-2.08647400	1.48360200	0.49467900
H	-1.82864400	2.37885600	0.24289600
O	0.51634400	2.33057600	-0.16038900
H	0.37355700	2.48096000	-1.10406900
C	2.56635600	-0.04799100	-0.12190600
H	2.97899300	0.95381300	0.01173400
H	3.20981900	-0.60661700	-0.80803000
O	2.53271500	-0.66447400	1.15561400
H	2.20170900	-1.56292400	1.03604500

Glucosyl radical: $B_{2,5}$ conformation



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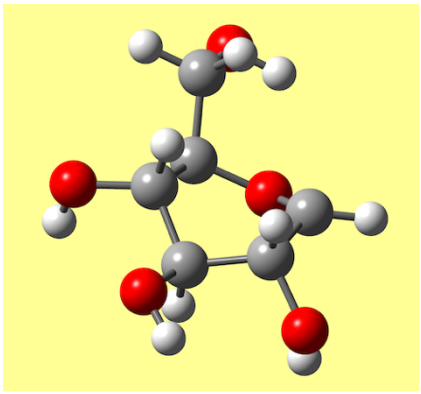
O	-0.10249900	-1.53295000	-0.72867900
C	1.88176400	-0.45251500	0.21733100
C	-0.26511500	0.83400800	-0.21243300
C	1.23619400	0.93471600	0.10078900
C	-0.83175900	-0.56635700	0.03903400
C	1.25595600	-1.39574400	-0.73697700
H	2.94642100	-0.36131000	-0.01094900
H	-0.38902700	1.03892800	-1.28628800
H	1.35854800	1.44778100	1.05587500
H	-0.75767700	-0.81096800	1.10355600
H	1.76698100	-2.22346900	-1.20702900
O	1.70331200	-0.85991100	1.58940200
H	1.95975600	-1.78777900	1.64928900
O	1.90622400	1.72680400	-0.86725200
H	1.85021400	1.26182500	-1.71215500
O	-0.94400700	1.80494700	0.56628400
H	-1.89256200	1.63056900	0.47823700
C	-2.27292000	-0.71023400	-0.43376100
H	-2.57628200	-1.75604300	-0.33679800
H	-2.33627500	-0.42240600	-1.48494500
O	-3.15581600	0.14742200	0.28002900
H	-3.21252100	-0.17087100	1.18902900

Glucosyl radical: $B_{O,3}$ conformation



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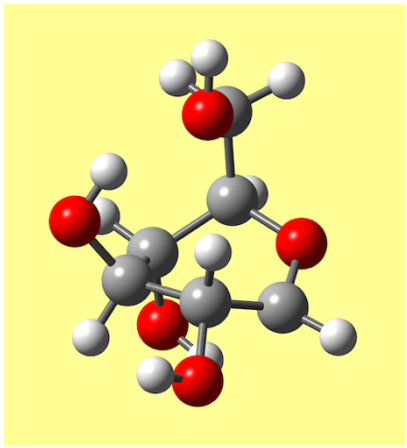
Charge 0 Multiplicity 2

O	0.74953500	-1.19170600	-0.59814800
C	-1.47565900	-0.86538600	0.42339900
C	0.04785200	1.05647100	0.21057200
C	-1.30115700	0.50819300	-0.21386600
C	1.16402600	0.16770700	-0.35691600
C	-0.23993200	-1.67964500	0.21271200
H	-1.66866100	-0.71672300	1.49118000
H	0.08588300	1.06070700	1.30558100
H	-1.31867000	0.39480800	-1.30830700
H	1.44916900	0.55168700	-1.33957500
H	-0.28252700	-2.76102300	0.23377100
O	-2.65800700	-1.50457800	-0.06476000
H	-2.51438900	-1.70332400	-0.99885600
O	-2.31745200	1.39826900	0.20535100
H	-3.15987300	0.96626200	0.01804200
O	0.25469000	2.40252900	-0.17698000
H	0.18742800	2.44993700	-1.13902100
C	2.37104200	0.13959400	0.55777000
H	2.07693900	-0.31992600	1.51028000
H	2.69805700	1.16343400	0.74801400
O	3.45877400	-0.55449500	-0.02846700
H	3.14929700	-1.44759800	-0.21910900

Glucosyl radical: $B_{1,4}$ conformation



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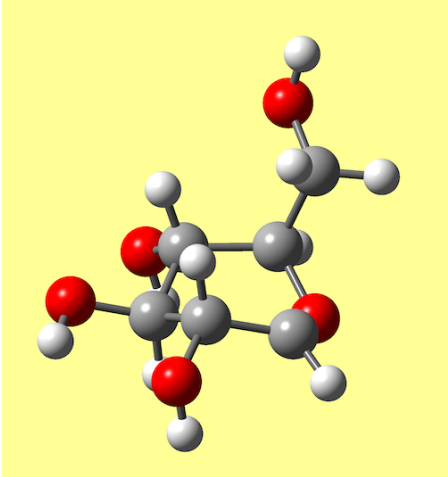
Charge 0 Multiplicity 2

O	0.55117500	1.05973900	-1.31518000
C	-1.23919100	-0.47387000	-0.57084400
C	0.27766300	0.71388600	1.09103200
C	-0.77071400	-0.39629800	0.90014200
C	1.25656300	0.85294900	-0.07345900
C	-0.76799800	0.70368300	-1.36051700
H	-0.82134200	-1.39649500	-0.99993500
H	0.84761200	0.49989200	1.99659300
H	-1.63348300	-0.10881800	1.50389300
H	1.82562400	1.76988400	0.09645000
H	-1.21718800	0.91161400	-2.32361900
O	-2.65585400	-0.49219200	-0.68877100
H	-2.96237900	-1.33864700	-0.34519200
O	-0.33465200	-1.65186700	1.38952900
H	0.41105400	-1.91141400	0.82325000
O	-0.37126000	1.96364900	1.30516500
H	-0.93734800	2.13745200	0.54018200
C	2.26592400	-0.26361900	-0.24028600
H	2.85526200	-0.33976100	0.67902500
H	2.93128000	-0.00200900	-1.06688300
O	1.59863100	-1.48931600	-0.52466100
H	2.26311400	-2.16218600	-0.70882600

Glucosyl radical: $^{2}S_{O}$ conformation



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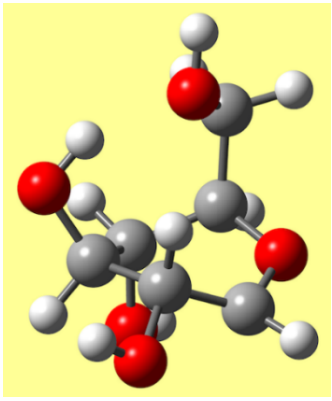
Charge 0 Multiplicity 2

O	-0.34268200	-1.26447900	1.18936700
C	1.39736400	-0.67843700	-0.44503800
C	-0.41508700	0.96069200	0.08768700
C	1.08349000	0.71021900	0.10857300
C	-1.19037500	-0.27875800	0.58553800
C	0.68831100	-1.69824900	0.39346200
H	1.08407200	-0.70630300	-1.49612700
H	-0.70637700	1.16504900	-0.94561200
H	1.43535700	0.74471200	1.15064600
H	-1.86967200	0.03948600	1.37721300
H	1.22625200	-2.53838400	0.81393300
O	2.80188000	-0.89875200	-0.47777100
H	3.11418800	-0.91843400	0.43640200
O	1.71619300	1.71693400	-0.65896900
H	2.64524100	1.46508900	-0.73208900
O	-0.75407200	2.13518000	0.80876500
H	-0.49903200	2.00129200	1.72981300
C	-2.00393700	-0.93225400	-0.52312500
H	-2.45517700	-1.85073200	-0.13480000
H	-1.35429000	-1.18762300	-1.36827500
O	-2.99219000	0.01056300	-0.90669300
H	-3.41219700	-0.30899100	-1.71127900

Glucosyl radical: $^{5}S_{1}$ conformation

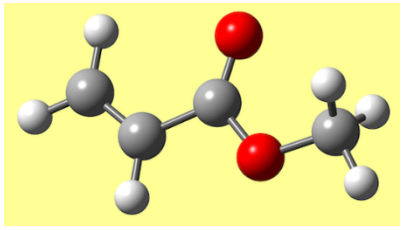


G = -611.105102

Charge 0 Multiplicity 2

O	-0.02179300	-1.70599500	-0.74108600
C	1.36446200	0.35066200	-0.62521500
C	-0.39046000	-0.20379400	1.12963100
C	0.57783500	0.86171700	0.59735100
C	-1.03288100	-0.98718600	-0.00985200
C	1.21825400	-1.12790700	-0.79416800
H	0.97259000	0.87973800	-1.50845100
H	-1.17412100	0.29059800	1.70537400
H	1.29643400	1.08534300	1.39040500
H	-1.67845600	-1.75410100	0.42017400
H	1.90104800	-1.66212300	-1.44186800
O	2.75894900	0.59818800	-0.51500200
H	2.89414700	1.54779000	-0.60978300
O	-0.12324000	2.04150400	0.21056100
H	-0.39620200	2.50058700	1.01427800
O	0.26650600	-1.09059100	2.02247100
H	0.97288400	-1.53572800	1.53466700
C	-1.82379600	-0.12795300	-1.00207000
H	-2.43210400	-0.78746500	-1.62187100
H	-1.13568700	0.40865900	-1.66132300
O	-2.69945500	0.77232800	-0.34514500
H	-2.14874700	1.50999500	-0.05005500

Methyl acrylate



Solvent=SMD:water

G = -306.359645

Charge 0 Multiplicity 1

C	-2.47725900	-0.00130400	0.00002700
H	-2.50691500	1.08323800	0.00017900
H	-3.42015800	-0.53443500	-0.00004100
C	-1.31843600	-0.64883700	-0.00007200
H	-1.24841900	-1.72953900	-0.00022500
C	-0.04275700	0.10435700	0.00002200
O	0.05962800	1.31149400	0.00020800
O	1.01094200	-0.71608500	-0.00012600
C	2.29866800	-0.08114500	-0.00005400
H	2.41276000	0.53410200	0.89226400
H	3.02416100	-0.88946800	-0.00021200
H	2.41271000	0.53440600	-0.89216900

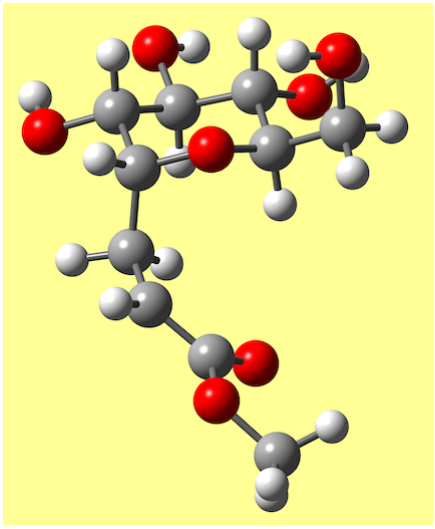
Solvent=SMD:dichloromethane

G = -306.362163

Charge 0 Multiplicity 1

C	-2.47690300	-0.00310200	0.00004100
H	-2.50187400	1.08177600	0.00020800
H	-3.42109400	-0.53466900	-0.00002400
C	-1.31752600	-0.64898000	-0.00007900
H	-1.24688100	-1.73009200	-0.00024600
C	-0.04037900	0.10981100	0.00001500
O	0.05938800	1.31128900	0.00019500
O	1.01039700	-0.71641400	-0.00012600
C	2.29514900	-0.08355300	-0.00004600
H	2.41337200	0.53480800	0.89046800
H	3.02280200	-0.89096900	-0.00018300
H	2.41334600	0.53508700	-0.89037000

α-Adduct 8α

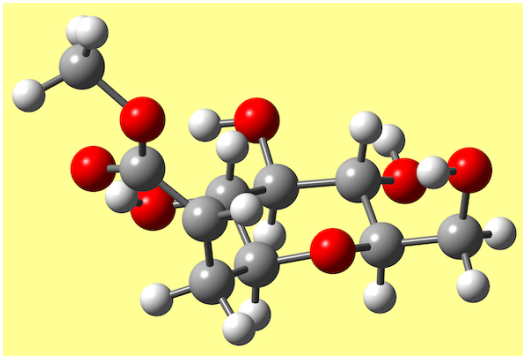


G = -917.505711

Charge 0 Multiplicity 2

C	0.49176200	1.08712900	0.06353000
C	1.99990700	0.96308700	0.27684800
C	2.35178500	-0.49126200	0.52194600
C	1.85577100	-1.34002200	-0.63400400
C	0.35961100	-1.13224400	-0.88193700
O	0.08695400	0.25819800	-1.03040300
C	-0.54508600	-1.78437000	0.18404500
C	-1.96617700	-1.62151700	-0.19899500
C	-2.78245600	-0.56838700	0.35820300
O	2.08841600	-2.71741900	-0.40135000
O	3.75614400	-0.68490200	0.60184000
O	2.41436900	1.69352700	1.42275000
C	0.04780100	2.48982600	-0.29592700
O	0.66662500	2.95294000	-1.48776300
O	-4.01833800	-0.54070700	-0.17470100
O	-2.42374600	0.22076200	1.21911200
C	-4.88975600	0.47736200	0.33309500
H	-0.01805800	0.78999600	0.98633500
H	2.52885500	1.31309200	-0.61606800
H	1.87625900	-0.81788600	1.45651500
H	2.38880700	-1.01427000	-1.53663600
H	0.11082300	-1.57388000	-1.84889900
H	-0.36117500	-1.35332500	1.16980300
H	-0.28961800	-2.84517300	0.21864600
H	-2.40172000	-2.24105800	-0.97252800
H	3.02475500	-2.81155900	-0.18908000
H	4.07754600	-0.14176900	1.33110200
H	2.55414900	2.61120200	1.16593400
H	-1.04326600	2.49757000	-0.39316700
H	0.32867900	3.17741900	0.50309300
H	0.46279000	2.30864700	-2.17588400
H	-5.83128500	0.34783500	-0.19329400
H	-5.03473200	0.35090600	1.40628100
H	-4.47516000	1.46545500	0.13115000

β-Adduct 8β

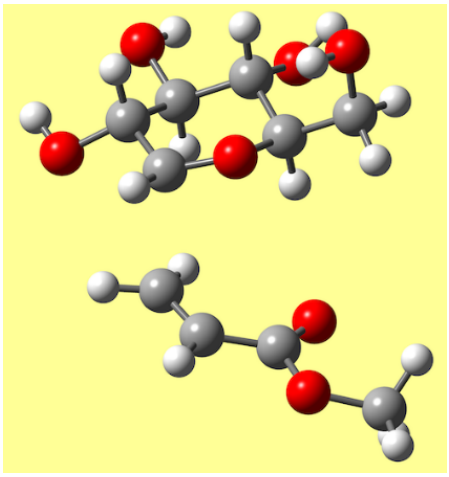


G = -917.509483

Charge 0 Multiplicity 2

C	-2.31558100	-0.70533800	0.46861500
C	-2.28436800	0.42898800	-0.55240900
C	-1.43967700	1.57788800	-0.03513400
C	-0.06154100	1.07608500	0.35188400
C	-0.21458200	-0.05564900	1.37059000
O	-0.98430100	-1.10305400	0.79015600
C	1.12189500	-0.64590700	1.83203500
C	1.93633300	-1.20284900	0.72235200
C	2.91166000	-0.37950000	0.04328800
O	0.66739700	2.16643000	0.88773700
O	-1.37174100	2.55181500	-1.06483400
O	-3.62329200	0.84105900	-0.77409000
C	-3.02194600	-1.94239000	-0.04942000
O	-2.40897000	-2.44623400	-1.22723200
O	3.62369900	-1.05448300	-0.86730700
O	3.08607100	0.81457000	0.25931900
C	4.60424500	-0.29168500	-1.58561100
H	-2.82710000	-0.35214600	1.37461800
H	-1.83641000	0.05829200	-1.48243600
H	-1.92413300	2.00247500	0.85535000
H	0.43051600	0.69014100	-0.55072100
H	-0.73958800	0.33554400	2.25254600
H	1.82146200	-2.22686000	0.39411800
H	1.60635500	1.93656300	0.81182500
H	-0.82064900	3.27278100	-0.73803500
H	-3.59213800	1.60476100	-1.36238600
H	-3.02596400	-2.69981900	0.74107300
H	-4.05275600	-1.69449100	-0.30181900
H	-1.48160800	-2.60487900	-1.01537300
H	5.07531400	-0.99169400	-2.26962600
H	4.12194400	0.51490100	-2.13775800
H	5.34007000	0.12002900	-0.89492100
H	1.67386200	0.14828800	2.34042100
H	0.90128400	-1.43256400	2.55599500

$^4C_1$ α-transition state



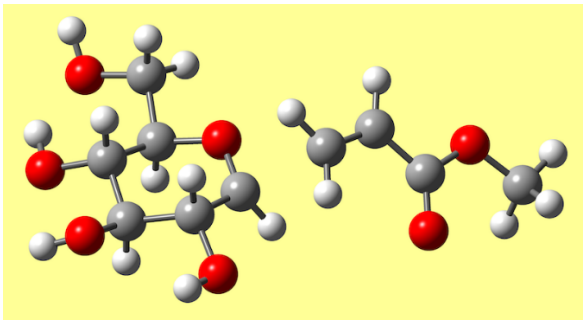
$G^{‡}$ = -917.826902

Glc-C1 – methyl acrylate-Cβ: 2.38051 Å

Charge 0 Multiplicity 2

C	0.32678700	0.99583800	-0.06238500
C	1.80932500	1.09432700	0.28603900
C	2.32935500	-0.30322700	0.56654000
C	2.11534700	-1.17954500	-0.65481400
C	0.72501100	-1.04806700	-1.20333700
O	0.15685100	0.18280900	-1.23945300
C	-0.73429100	-2.27992200	0.21786300
C	-1.96646500	-1.90162800	-0.19069700
C	-2.65478100	-0.77712400	0.43684200
O	2.34548000	-2.54972200	-0.37686300
O	3.71778300	-0.30514600	0.84952000
O	1.99399700	1.85587200	1.46809200
C	-0.32986200	2.32144300	-0.37216700
O	0.32813700	3.01220800	-1.42327900
O	-3.78917100	-0.45613500	-0.21198200
O	-2.28988300	-0.17488400	1.43218800
C	-4.53614800	0.63526800	0.34028400
H	-0.19992200	0.52281900	0.77248100
H	2.36408100	1.53169200	-0.55101200
H	1.76766000	-0.72177300	1.41238700
H	2.82251100	-0.83493300	-1.42765200
H	0.47656400	-1.63491000	-2.07972000
H	-0.29132400	-1.84205700	1.10727500
H	-0.26732400	-3.17222200	-0.17871200
H	-2.45942300	-2.36796100	-1.03447100
H	3.27368000	-2.63666300	-0.13023600
H	3.84977400	0.26156600	1.61883800
H	2.00493500	2.78977300	1.23141600
H	-1.38253400	2.14069600	-0.61774000
H	-0.28674600	2.95815000	0.51223000
H	0.30416800	2.43913000	-2.19858100
H	-5.41110400	0.74422600	-0.29461700
H	-4.83607100	0.41005600	1.36387900
H	-3.94014700	1.54820700	0.32343300

$^4C_1$ β-transition state



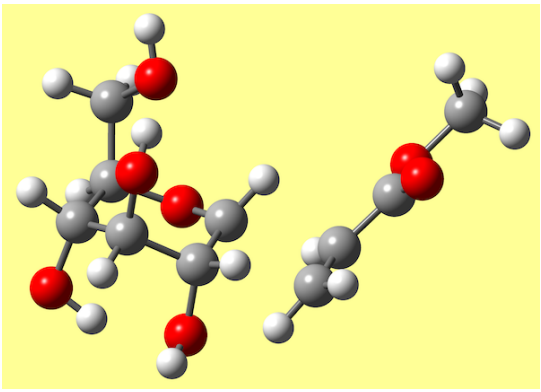
$G^{‡}$ = -917.451405

Glc-C1 – methyl acrylate-Cβ: 2.34180 Å

Charge 0 Multiplicity 2

O	-0.41650300	0.75567300	0.25056800
C	-2.75737000	0.09076700	0.08581000
C	-2.31044200	-1.28970800	-0.36695300
C	-0.93435200	-1.60835300	0.20669400
C	0.00202100	-0.49555100	-0.12828700
C	-1.70039900	1.13776100	-0.27682800
C	1.76940100	-0.86669400	1.36256300
C	2.67018000	0.11933200	1.17424000
C	3.67456200	-0.00625000	0.11623500
O	-0.40835500	-2.80563600	-0.33258800
O	-3.19800600	-2.30082100	0.08026400
O	-3.98868500	0.35608000	-0.56638100
C	-1.98045400	2.49857400	0.33332800
O	-3.22990800	2.95692600	-0.17301100
O	4.53290600	1.02530300	0.10916200
O	3.74624900	-0.91996200	-0.68426300
C	5.54889400	0.98607900	-0.90195100
H	-1.63744300	1.21477100	-1.36936000
H	-2.88797000	0.08251500	1.17701600
H	-2.24315100	-1.29527500	-1.46276900
H	-1.03985700	-1.68433400	1.29929600
H	0.60619900	-0.55962300	-1.03070600
H	2.65402200	1.04012600	1.74271700
H	-1.04590300	-3.50538200	-0.14762100
H	-4.05195300	-2.14753200	-0.34058700
H	-4.19432900	1.28843700	-0.40460500
H	-2.01269700	2.39383600	1.42234300
H	-1.17268400	3.18503600	0.06440800
H	-3.50921000	3.71492100	0.35120600
H	6.14100200	1.88564300	-0.75898700
H	6.17024500	0.09898500	-0.77863400
H	5.09519200	0.98384400	-1.89314900
H	1.05597700	-0.81389700	2.17714200
H	1.87873000	-1.81831800	0.85319000

$^1C_4$ α-transition state



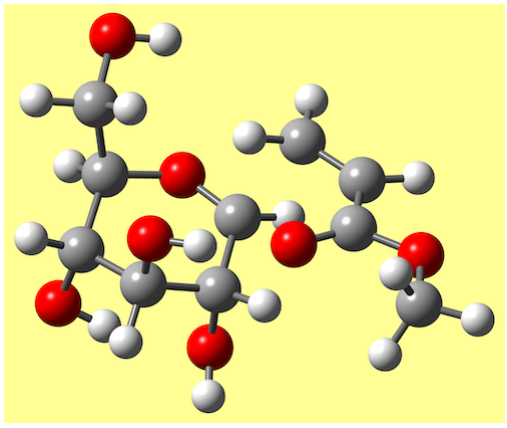
$G^{‡}$ = -917.450244

Glc-C1 – methyl acrylate-Cβ: 2.31764 Å

Charge 0 Multiplicity 2

O	-0.54008000	0.12103500	-1.00240900
C	-1.35156400	-1.16905200	0.89500300
C	-2.95273000	0.21728400	-0.47538700
C	-2.65914300	-0.34369500	0.92747500
C	-1.75031100	0.90516500	-1.14235600
C	-0.26981000	-0.36171500	0.25795800
H	-1.06182700	-1.42563300	1.91709100
H	-3.76029900	0.94860300	-0.39590400
H	-3.48085400	-1.01542200	1.18865200
H	-1.96031600	0.90416700	-2.21313800
H	0.37329600	0.25135100	0.87941000
O	-1.55537800	-2.34792000	0.10745400
H	-2.22443800	-2.88533300	0.55018300
O	-2.60891900	0.65489100	1.92429400
H	-2.03012800	1.37358700	1.60797300
O	-3.42508900	-0.82752200	-1.31847700
H	-2.78527500	-1.55059700	-1.24521500
C	-1.48838100	2.34916900	-0.76314200
H	-0.69306300	2.73354900	-1.40696800
H	-2.40100300	2.92597200	-0.94193900
O	-1.08573800	2.44161200	0.60171400
H	-1.03015500	3.37227200	0.84555400
C	1.45478300	-1.83867100	-0.20663300
H	2.51024200	-0.97926400	-1.85523200
C	3.36904000	-0.35591500	0.05419700
O	3.32490300	-0.27741300	1.26866900
O	4.31431400	0.26309600	-0.67145300
C	5.27567500	1.02362000	0.07215400
H	5.95173500	1.44588500	-0.66605200
H	4.77907300	1.81780000	0.62989700
H	5.82067200	0.37585400	0.75894600
C	2.42866400	-1.09935800	-0.78275800
H	0.78658400	-2.43881300	-0.81078800
H	1.47631600	-2.03721200	0.86013100

$^1C_4$ β-transition state



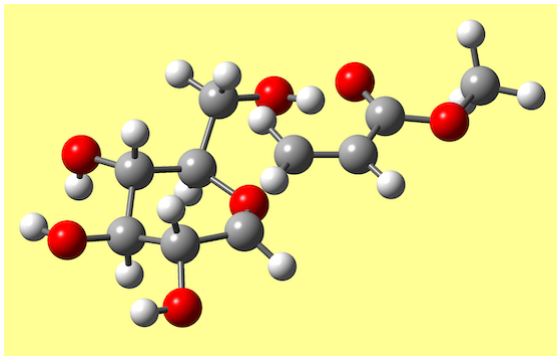
$G^{‡}$ = -917.456565

Glc-C1 – methyl acrylate-Cβ: 2.34900 Å

Charge 0 Multiplicity 2

O	1.91094900	0.50683400	1.20500400
C	0.23548000	-1.18803100	0.59115000
C	2.32984000	-0.93916900	-0.76673900
C	0.83556700	-1.27339900	-0.81789700
C	2.61324900	0.38292700	-0.05344000
C	0.63217500	0.06329700	1.30717500
H	-0.85614900	-1.23751500	0.54008900
H	2.70332900	-0.85119100	-1.78975700
H	0.73438800	-2.30936200	-1.16307500
H	3.66381000	0.37898500	0.24110100
H	0.26771100	0.18235400	2.32061600
O	0.72703700	-2.28425500	1.38463400
H	0.36423700	-3.10097900	1.01726400
O	0.21449300	-0.37835100	-1.71823800
H	-0.73929100	-0.33370300	-1.52915500
O	3.04743600	-2.00100600	-0.15353000
H	2.55920100	-2.24578900	0.64638500
C	2.36653500	1.63372000	-0.88425600
H	3.02596500	1.60324700	-1.75340900
H	1.33601700	1.68046200	-1.23589900
O	2.70153600	2.79722800	-0.14160200
H	2.14723100	2.79318000	0.64746200
C	-0.90013600	1.69225600	0.58861700
H	-0.36618000	2.38595300	1.22749400
H	-0.54063300	1.56933300	-0.42517600
C	-2.14459600	1.26584000	0.91409900
H	-2.60183700	1.47795300	1.87198700
C	-2.91235600	0.45883700	-0.02605000
O	-2.50788900	0.02357500	-1.09715100
O	-4.15893400	0.22419500	0.40143600
C	-4.98573700	-0.56693300	-0.46395300
H	-5.94195800	-0.65353600	0.04414800
H	-5.11000500	-0.06921800	-1.42549900
H	-4.54297900	-1.55199900	-0.61123800

E_3 β-transition state (from $^1S_3$ glucosyl radical)



$G^{‡}$ = -917.453977

Glc-C1 – methyl acrylate-Cβ: 2.37763 Å

Charge 0 Multiplicity 2

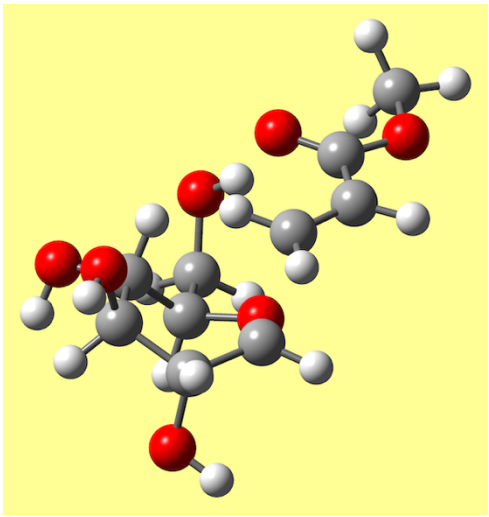
C	2.17497600	-1.71080600	0.56884400
H	2.57454500	-2.65976500	0.23499400
C	3.00087000	-0.53143100	0.35158700
O	2.68462500	0.62261900	0.60376400
O	4.19730000	-0.83714200	-0.17078300
C	5.07636300	0.26802400	-0.42039700
H	5.29153900	0.79746200	0.50769900
H	5.98499700	-0.16664900	-0.82742100
H	4.62782900	0.95207500	-1.14107100
C	0.93548800	-1.59878500	1.09560400
H	0.59466300	-0.65862800	1.51813700
H	0.35319600	-2.48502900	1.32072800
O	-0.28557000	0.18189600	-0.99189600
C	-1.93560600	-1.45343600	-0.07244300
C	-2.23924100	0.93731200	0.35606600
C	-2.90593400	-0.29756300	-0.21912000
C	-1.01253900	1.31467100	-0.47219000
C	-0.59778800	-1.09237100	-0.64959800
H	-1.84979500	-1.65727900	1.00575700
H	-1.94893400	0.72485200	1.39093100
H	-3.12975800	-0.13681200	-1.28316200
H	-1.35045200	1.86049700	-1.35923900
H	-0.13413700	-1.81090100	-1.31315600
O	-2.38377800	-2.62500200	-0.73705100
H	-3.15874500	-2.94430000	-0.25939900
O	-4.08221000	-0.62708200	0.49516600
H	-4.62183600	0.17230700	0.53393800
O	-3.13856200	2.03067800	0.43121300
H	-3.41859100	2.25125900	-0.46694800
C	-0.06502600	2.19000200	0.32589400
H	-0.62315100	3.06990400	0.65404800
H	0.27372000	1.64400000	1.21261500
O	1.03823900	2.62473200	-0.44736300
H	1.70518500	1.92771400	-0.37833000

$^1S_5$ β-transition state

$G^{‡}$ = -917.455529

Glc-C1 – methyl acrylate-Cβ: 2.36640 Å

Charge 0 Multiplicity 2



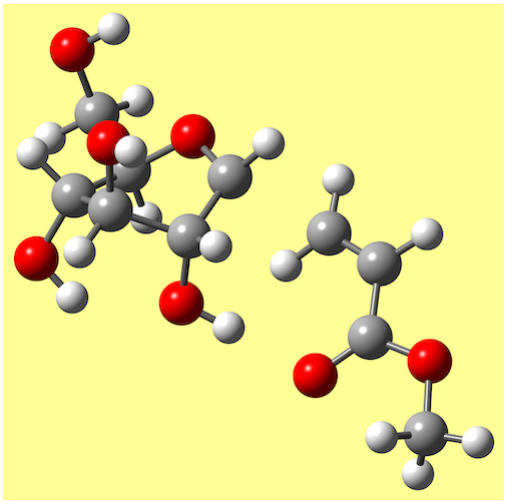
C	-1.81357700	-2.05710700	-0.08519100
H	-2.30168800	-2.75507300	0.58270100
C	-2.48314500	-0.79257800	-0.34357600
O	-2.05457600	0.10123100	-1.06256600
O	-3.64670600	-0.67537200	0.30986200
C	-4.33769700	0.56997900	0.13608400
H	-4.60773900	0.70943200	-0.91061900
H	-5.22983300	0.49894700	0.75184200
H	-3.71019300	1.39741900	0.46922900
C	1.43975000	0.90167200	-0.62847500
C	0.96293000	1.16430600	0.79805000
H	0.56487600	0.65813200	-1.23735300
O	2.01015900	2.06572100	-1.19898200
C	2.40085000	-0.28637900	-0.67381700
O	0.23369400	0.01221300	1.27355900
H	1.82396600	1.31556100	1.45861700
C	0.04986000	2.36844400	0.92136000
C	2.19232000	-1.25070400	0.50725900
H	3.42512100	0.09423000	-0.58758100
O	2.21341600	-0.92590400	-1.92488500
H	-0.42582000	2.32806600	1.90763500
O	-0.91293500	2.47781500	-0.11158900
H	0.66252700	3.26915400	0.87727400
H	2.40558900	-2.27121100	0.17493500
O	3.14009900	-0.85626600	1.51492100
H	3.00399300	-1.42406600	2.28309000
H	2.90743100	-1.58660700	-2.03166600
H	2.78673900	2.30367200	-0.67647200
H	-1.35887800	1.62574600	-0.23173000
C	0.80330000	-1.20037700	1.05158300
H	0.48774400	-1.94387400	1.77371100
C	-0.56455600	-2.25620500	-0.56521100
H	-0.05416000	-3.20019000	-0.41223400
H	-0.14508600	-1.58116000	-1.30233300

$^{O}S_2$ α-transition state

$G^{‡}$ = -917.457449

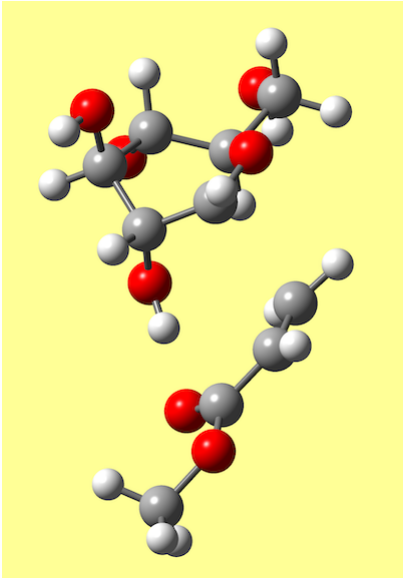
Glc-C1 – methyl acrylate-Cβ: 2.39790 Å

Charge 0 Multiplicity 2



H	1.01166800	1.26230700	-1.13302800
H	0.80024400	2.69073600	0.02024600
H	2.98887100	2.17121900	1.06696200
H	4.96929400	-1.64130600	0.29635800
H	5.57626600	-0.70905100	-1.09876300
H	6.36668200	-0.54473100	0.49553200
C	1.35521000	1.80316500	-0.25810500
O	2.96687300	-0.46991700	-0.91578600
C	3.35663900	0.41316800	-0.16114200
O	4.58883100	0.40291200	0.35634900
C	2.57177700	1.55963600	0.27738500
C	5.42351700	-0.70238900	-0.01973400
O	-1.50251800	1.16247800	0.50653800
C	-0.14600300	-0.87365200	0.59857800
C	-2.45271100	-0.94853200	-0.35020100
C	-1.51856800	-1.54948500	0.70703700
C	-2.14379600	0.54006000	-0.61847600
C	-0.34238200	0.58382100	0.91717900
H	0.55996000	-1.29706400	1.31906400
H	-3.47344800	-1.04797600	0.02179100
H	-1.41478000	-2.61991000	0.50521100
H	-1.47349000	0.60373000	-1.48128000
H	-0.02573500	0.96743300	1.87827400
O	0.27722800	-1.14120800	-0.73683900
H	1.21607200	-0.89874300	-0.82770700
O	-2.10685100	-1.31809500	1.97542300
H	-1.50929400	-1.65956700	2.65089700
O	-2.39419400	-1.65993200	-1.57536300
H	-1.46581500	-1.64899700	-1.84646100
C	-3.39526500	1.34834500	-0.88201700
H	-3.92711200	0.90657800	-1.72616200
H	-3.11777800	2.37576500	-1.13796400
O	-4.27423500	1.32454300	0.23214200
H	-3.77318200	1.63850700	0.99429400

$^{O}S_2$ α-transition state (from $B_{2,5}$ conformation)



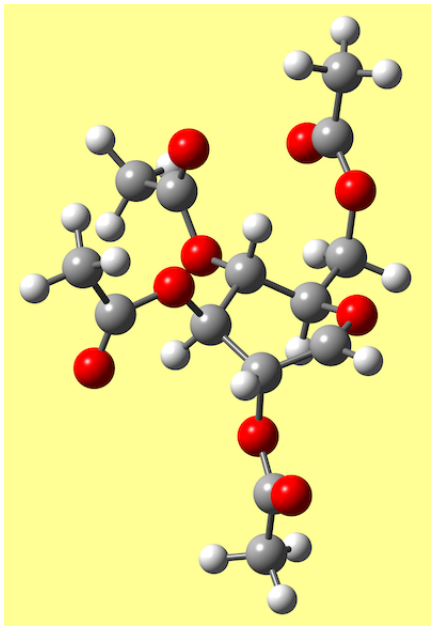
$G^{‡}$ = -917.454709

Glc-C1 – methyl acrylate-Cβ: 2.39667 Å

Charge 0 Multiplicity 2

H	-0.99930400	-1.62331800	-0.50194900
H	-0.92815800	-2.47482600	1.13680500
H	-3.16920800	-1.57403200	1.70407100
H	-4.95185500	1.61626700	-0.68626500
H	-5.47325200	0.20396400	-1.64374300
H	-6.39722700	0.68789700	-0.19255600
C	-1.42768700	-1.76997600	0.48340600
O	-2.90155200	0.05393000	-1.15682200
C	-3.37926000	-0.45205800	-0.14885000
O	-4.64701100	-0.23367400	0.21493400
C	-2.67155000	-1.32917600	0.77460800
C	-5.41012500	0.62839800	-0.64200900
O	1.39188400	-0.87644800	1.17204300
C	0.08943200	1.01713100	0.31628600
C	2.55990300	0.79683200	-0.16464000
C	1.44482700	1.73842500	0.30771300
C	2.16479900	-0.68227200	-0.01679000
H	-0.67907000	1.67455400	0.73578100
H	3.43498400	0.99524000	0.46582200
H	1.39381300	2.58445800	-0.38403600
H	1.56732400	-0.96629300	-0.88833800
O	-0.19649300	0.72212500	-1.04513500
H	-1.13110800	0.46071400	-1.11146300
O	1.78209000	2.16331200	1.61891800
H	1.07842800	2.74199000	1.93472200
O	2.85521900	1.08096300	-1.52330500
H	3.55940300	0.46899300	-1.77636000
C	3.37765600	-1.58643400	0.10663300
H	3.06126300	-2.62910400	0.19199100
H	3.94035300	-1.31350300	1.00150800
O	4.24670300	-1.39969300	-1.00526900
H	3.84324000	-1.82706300	-1.77003300
C	0.21762700	-0.18670800	1.21158500
H	-0.19007900	-0.15501300	2.21345800

Tetraacetylglucosyl radical: $B_{2,5}$ conformation ($^1S_5$-like)



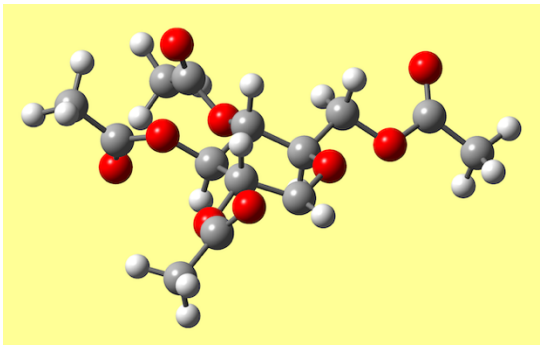
G = -1221.552778

Charge 0 Multiplicity 2

O	0.26918200	-2.05431300	-0.86971100
C	-0.36909400	-1.48826300	0.27868100
C	-0.46150600	0.02197500	0.06556100
C	0.92784400	0.62767000	0.12205100
C	1.95803600	-0.30743600	-0.53871200
C	1.31936800	-1.35346900	-1.36745800
H	0.23065700	-1.71412300	1.16938400
H	-0.90992900	0.21248400	-0.91081400
H	1.22246200	0.79339600	1.15959900
H	2.65869400	0.26336800	-1.14638800
H	1.82884400	-1.85421400	-2.17673900
O	2.69889000	-0.89160300	0.58040400
O	0.84705400	1.88126900	-0.55767700
O	-1.26692300	0.59332600	1.09229100
C	-1.72034300	-2.14543600	0.43365700
H	-1.60595300	-3.22772300	0.36495200
H	-2.15683400	-1.88044600	1.39462700
O	-2.58154700	-1.72932500	-0.63149600
C	3.89597800	-1.42568600	0.27810500
C	-2.31154200	1.37784600	0.72802000
C	1.86092200	2.74583600	-0.33492200
C	-3.74703400	-1.13052400	-0.31315600
O	4.34590400	-1.43642600	-0.83753700
O	-2.59964000	1.60116200	-0.41595700
O	2.79546000	2.47616900	0.37090500
O	-4.10867300	-0.94154700	0.81911900
C	-4.50222300	-0.74741000	-1.54729700
H	-3.87605000	-0.09865300	-2.16097200
H	-5.41798200	-0.23240700	-1.26765400
H	-4.73370200	-1.64495500	-2.12393000
C	1.64893500	4.02880500	-1.07595900
H	2.46950200	4.71050300	-0.86706000
H	0.69906300	4.47214100	-0.77259700
H	1.59397600	3.82066000	-2.14611400
C	-3.02741400	1.89297400	1.93562000

H	-3.86450100	2.51288900	1.62440500
H	-2.33570700	2.46960400	2.55228000
C	4.56584600	-1.98069400	1.49900000
H	3.92553600	-2.73984800	1.95149800
H	4.70658900	-1.18135900	2.22859000
H	5.52516800	-2.41229800	1.22420000
H	-3.38413300	1.04413000	2.52086700

Tetraacetylglucosyl radical: $^4C_1$ conformation



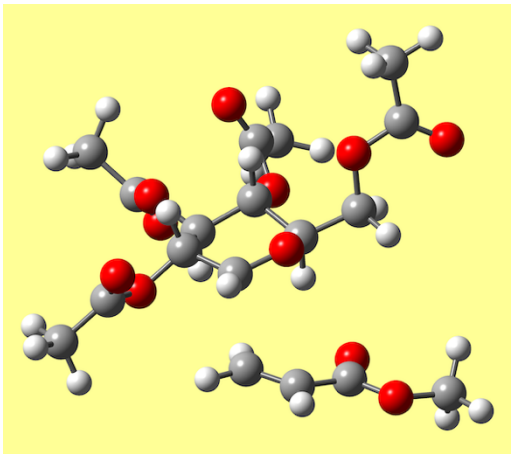
G = -1221.550765

Charge 0 Multiplicity 2

O	1.00059500	-1.80143200	0.24605100
C	-1.39327400	-1.33744700	0.24346500
C	0.27591800	0.52376600	0.24329200
C	-1.11581200	0.08707300	-0.20327600
C	1.32372600	-0.49231300	-0.21775000
C	-0.24396500	-2.24557400	-0.06861400
H	-1.60621200	-1.33661800	1.32064600
H	0.30138500	0.65185800	1.32914900
H	-1.18612900	0.16119200	-1.29107600
H	1.34893900	-0.50026300	-1.31386500
C	2.68812900	-0.15314100	0.32899200
O	0.63233900	1.74666700	-0.40564500
O	-2.12295400	0.89696500	0.40591000
O	-2.56972600	-1.75719000	-0.45540300
H	2.71645500	-0.33530300	1.40602500
H	2.93082600	0.89237900	0.13349300
O	3.62866700	-1.00188500	-0.33352700
H	-0.36049200	-3.31193500	0.07749100
C	-3.26070200	-2.78330100	0.08328600
C	-4.49537300	-3.07486000	-0.71221100
H	-5.14416900	-2.19700700	-0.70326800
H	-5.01254700	-3.92884900	-0.28218200
H	-4.22176100	-3.27861700	-1.74865900
O	-2.90231800	-3.36165200	1.07378800
C	-2.54885700	1.99746000	-0.24594600
C	-3.55006200	2.74564400	0.57669300
H	-4.31002000	2.06410100	0.95928100
H	-4.00259800	3.53182300	-0.02265200
H	-3.02525200	3.18329600	1.42926400
O	-2.14265300	2.32180100	-1.33048200
C	0.32312200	2.91543400	0.19922700
C	0.69701500	4.07362100	-0.67012700
H	0.04464400	4.06276900	-1.54619900
H	0.56563900	5.00165000	-0.11924700
H	1.72727800	3.97086100	-1.01230100

O	-0.19817300	2.97812300	1.27982000
C	4.91109200	-0.85265200	0.03858200
C	5.80861900	-1.78652900	-0.71515400
H	5.74581400	-1.56493500	-1.78219300
H	5.47404600	-2.81440900	-0.56660000
H	6.83213900	-1.66837400	-0.36833700
O	5.25729200	-0.05723500	0.87179800

Tetraacetyl $^4C_1$ α-transition state



$G^{‡}$ = -1527.899004

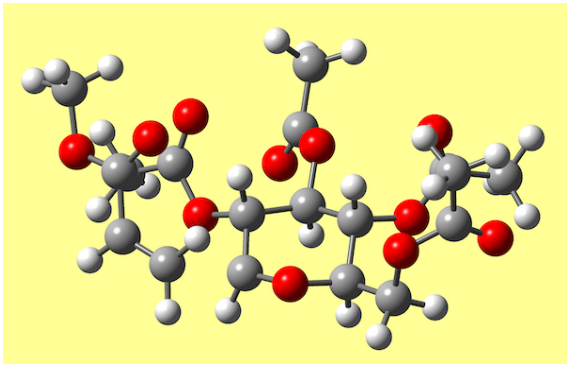
Glc-C1 – methyl acrylate-Cβ: 2.35345 Å

Charge 0 Multiplicity 2

C	-0.25988400	3.12139000	-0.61102400
C	-1.56545100	3.45681800	-0.49760300
C	-2.60414100	2.70037400	-1.20233800
O	-3.83000600	3.17433000	-0.93173800
O	-2.41917300	1.76391600	-1.95243800
C	-4.91148200	2.51182400	-1.59274700
H	0.50902200	3.75780200	-0.19038900
H	0.05598200	2.38129600	-1.34032900
H	-1.89607700	4.26273300	0.14595300
H	-4.79404400	2.57457200	-2.67531800
H	-4.95859800	1.46339500	-1.29491500
H	-5.81313600	3.03252300	-1.27972100
C	1.49371800	-0.07617200	-0.16679100
C	-0.97157200	-0.16173800	0.08895800
C	0.15382500	1.61568100	1.14977000
H	1.90008600	0.59144300	1.82279300
H	0.42635100	-1.55358100	0.99891800
H	1.42945500	0.35394600	-1.16932600
H	-1.06567500	0.38376300	-0.85562500
C	-2.22076700	-0.98457600	0.27361900
O	0.14723700	-1.90116800	-1.02707100
O	2.73132600	-0.77520000	-0.01686200
O	2.43489400	2.00920000	0.42577200
H	-2.42272200	-1.56908200	-0.62459400
H	-3.06921800	-0.32549100	0.46782200
O	-2.01372300	-1.85744800	1.38904100
H	0.08852600	2.36042800	1.93322600
C	2.94176700	2.84945300	1.35316000
C	3.92982600	3.79231600	0.73980900
H	3.43661000	4.38194500	-0.03539700
H	4.33450200	4.44643200	1.50791800
H	4.73019200	3.22125700	0.26648600
O	2.61542600	2.81394700	2.50904300
C	3.28027900	-1.35656800	-1.10245200

C	4.52297500	-2.10320800	-0.73112000
H	5.03981100	-2.42468000	-1.63202400
H	5.16968900	-1.47732800	-0.11594100
H	4.22999600	-2.97365100	-0.13925700
O	2.80155400	-1.28615000	-2.20324000
C	0.76441700	-3.10070300	-0.96364500
C	0.54265900	-3.87655700	-2.22336800
H	0.93689300	-4.88314200	-2.10755700
H	-0.52007400	-3.90462600	-2.46620100
H	1.06243200	-3.36197400	-3.03462700
O	1.41377900	-3.45631900	-0.01684600
C	-3.01146900	-2.71819900	1.65621500
C	-2.67145800	-3.59864600	2.82005400
H	-2.45308300	-2.98143000	3.69305400
H	-3.50347200	-4.26658000	3.02859700
H	-1.77477600	-4.17544000	2.58516300
O	-4.02953700	-2.74957700	1.01718800
C	0.30483100	-0.99843400	0.06730400
C	1.51246600	1.01752100	0.88835800
O	-0.90951500	0.78222100	1.16144400

Tetraacetyl $^4C_1$ β-transition state



$G^{‡}$ = -1527.897251

Glc-C1 – methyl acrylate-Cβ: 2.31548 Å

Charge 0 Multiplicity 2

C	-2.02959900	-3.02014800	-0.69637200
C	-3.24085000	-2.45676100	-0.50038300
C	-3.55264300	-1.81033700	0.78389400
O	-4.72930100	-1.16392000	0.73246300
O	-2.85886800	-1.83805100	1.77435000
C	-5.13144000	-0.51212400	1.94195500
H	-1.81792000	-3.59173000	-1.59219700
H	-1.33710900	-3.11754000	0.13398600
H	-3.99062800	-2.40489100	-1.28012500
H	-5.26450300	-1.24452700	2.73968100
H	-4.38542900	0.22460000	2.23811600
H	-6.07879300	-0.02824200	1.71528800
O	0.60432200	-1.96745600	-1.26092400
C	-0.92476400	-0.17544300	-0.67679500
C	1.54142100	0.10124800	-0.50452700
C	0.23279000	0.82963800	-0.77163800
C	1.70973800	-1.07358600	-1.46268300
C	-0.60686800	-1.38364000	-1.50824600
H	-1.07327600	-0.44400000	0.37521600
H	1.55172400	-0.26108600	0.52452700
H	0.24237200	1.29003900	-1.76287300
H	1.69679000	-0.71735000	-2.50063400
C	2.99685200	-1.83634900	-1.24066000
O	2.62605200	1.00108600	-0.71295000
O	0.13750200	1.84115500	0.23022700
O	-2.13246400	0.36150000	-1.21833300
H	3.83802200	-1.26154500	-1.62362400
H	2.93827300	-2.79533100	-1.75557600
O	3.18281700	-2.10558700	0.15225300
H	-0.95341300	-1.39689800	-2.54014800
C	-2.95648100	1.03943100	-0.39253700
C	-4.17752600	1.50658800	-1.11918500
H	-3.88119100	2.30546200	-1.80361000
H	-4.90264300	1.88680600	-0.40313300

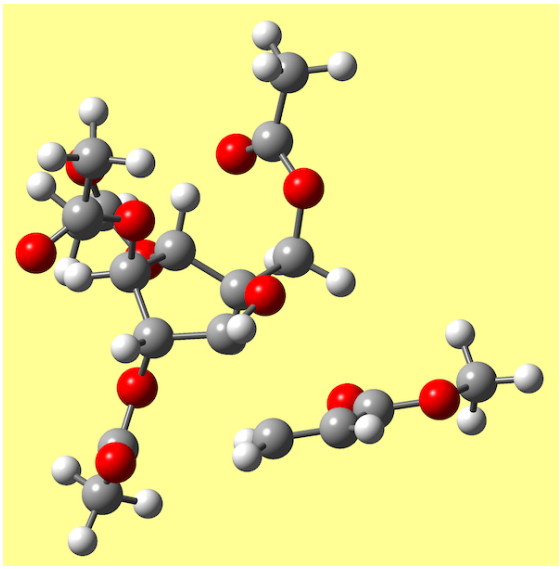
H	-4.60407100	0.69297000	-1.70562800
O	-2.70368700	1.24131700	0.76607000
C	-0.54139400	2.96837900	-0.06479300
C	-0.60505100	3.87434500	1.12373500
H	-0.94727100	4.85979200	0.81683300
H	0.36768100	3.93279200	1.61185500
H	-1.31544300	3.44069100	1.83198900
O	-1.03715400	3.17723800	-1.14047300
C	3.30636900	1.44011700	0.37539500
C	4.42062800	2.34965300	-0.03438600
H	4.03356100	3.15361400	-0.66188200
H	4.90423700	2.75420700	0.85124500
H	5.13828600	1.77209300	-0.62031000
O	3.03770600	1.11168700	1.49794200
C	4.24852200	-1.55113800	0.76811100
C	4.23828200	-1.86092700	2.23204500
H	4.08394600	-2.92866400	2.39008700
H	3.40527100	-1.32257000	2.68951200
H	5.17432200	-1.53553500	2.67928200
O	5.07423700	-0.88857400	0.19619200

Tetraacetyl $B_{2,5}$ α-transition state

$G^{‡}$ = -1527.894359

Glc-C1 – methyl acrylate-Cβ: 2.30397 Å

Charge 0 Multiplicity 2



O	-0.87173200	0.18550200	-1.03639900
C	-0.37214600	0.69087100	0.20399400
C	1.12281900	0.38224400	0.26483500
C	1.45021400	-1.03670500	-0.22339000
C	0.19268300	-1.90409800	-0.34391200
C	-0.85688800	-1.16645700	-1.13463800
C	-0.67809000	2.17147100	0.28721900
O	0.07323000	2.92808200	-0.67042900
O	1.50819800	0.58987900	1.61837600
O	2.02990500	-0.89647200	-1.52257000
O	-0.19236200	-2.16047200	1.02075700
C	-0.74583100	-3.36423900	1.29022200
C	-3.78595200	-0.86746700	-0.89728000
C	-3.98552800	0.42419500	-0.23893200
O	-4.83264000	1.20885500	-0.92403200
O	-3.46809500	0.77479800	0.80238100
C	-5.10171200	2.48831000	-0.34588700
H	-0.89313500	0.19779000	1.03009900
H	1.67691100	1.06355100	-0.38172900
H	2.15960300	-1.51691700	0.45079000
H	0.42237500	-2.84956300	-0.83167900
H	-1.05152000	-1.49487700	-2.14767000
H	-5.50492200	2.37731100	0.66138100
H	-4.19300400	3.09121700	-0.30766500
H	-5.83483500	2.95900200	-0.99649700
H	-2.58012000	-1.58873400	0.66253300
H	-2.83407100	-2.76819900	-0.74858900
H	-1.72734900	2.33125200	0.05034800
H	-0.46365900	2.52645600	1.29483200
C	-2.93691100	-1.76752200	-0.34690400
C	2.80242000	0.92773600	1.81369000
C	2.82656500	-1.90433000	-1.94336300
C	1.19802400	3.53475300	-0.24544200
O	-0.94709100	-4.19529000	0.44685200

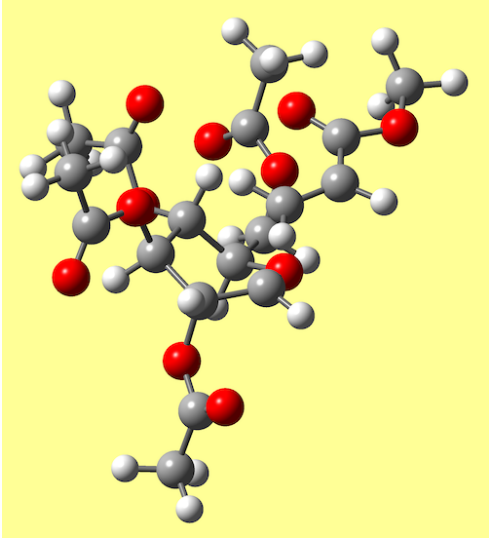
O	3.62045500	0.88424300	0.93485800
O	3.01943800	-2.89465200	-1.29141000
O	1.60458700	3.46190400	0.88547200
C	1.86251900	4.27646000	-1.36452400
H	2.70717700	4.84085800	-0.97758100
H	1.14496700	4.94006700	-1.84821500
H	2.20766700	3.55481600	-2.10856500
C	3.41202800	-1.60040200	-3.28673100
H	2.61165600	-1.37897700	-3.99424300
H	3.99783500	-2.44973400	-3.62897900
H	4.04516400	-0.71464400	-3.20704000
C	3.04189400	1.35422200	3.22679300
H	4.11088900	1.40743300	3.41832800
H	2.59267900	2.34124500	3.35974400
C	-1.07297900	-3.48664600	2.74605500
H	-1.42453500	-4.49364500	2.95621500
H	-1.84983200	-2.76107300	2.99793100
H	-0.19076600	-3.25480300	3.34382200
H	2.55902000	0.66403900	3.91874500
H	-4.27811700	-1.02927400	-1.84798800

Tetraacetyl $B_{2,5}$ β-transition state

$G^{‡}$ = -1527.892974

Glc-C1 – methyl acrylate-Cβ: 2.30802 Å

Charge 0 Multiplicity 2



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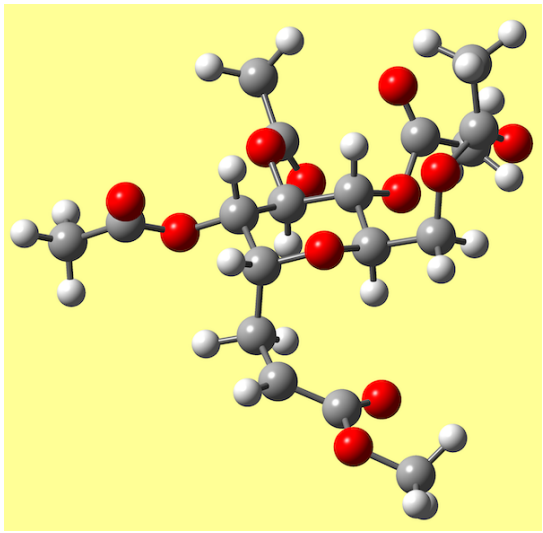
H	-0.37475500	-1.22983800	1.93707700
H	0.37886500	-4.12425700	1.16472100
H	3.95709000	-2.14827000	-0.35037900
H	4.45738600	-2.43334900	1.33748500
H	4.59766200	-3.74708800	0.13382400
C	-0.55667000	-2.25871600	1.64220500
O	2.12658200	-1.33376600	1.43903400
C	1.82580200	-2.48364000	1.20024300
O	2.70514400	-3.38688200	0.73628900
C	0.49487600	-3.06774500	1.37218600
C	4.01255900	-2.88660800	0.45018100
O	-0.21395700	-1.40395700	-1.23823300
C	0.05912300	-0.03833800	-1.57837300
C	-0.01104500	0.79697600	-0.30365800
C	-1.43947000	0.80152800	0.22346500
C	-2.19924600	-0.48991000	-0.12509200
C	-1.29449600	-1.62945900	-0.45222000
H	-0.69926500	0.29902200	-2.29554800
H	0.67977100	0.38209600	0.43587300
H	-1.98586000	1.63363600	-0.22317500
H	-2.86000300	-0.77597000	0.69302000
H	-1.72486900	-2.60977000	-0.60997400
O	-3.02218100	-0.14783200	-1.27442400
O	-1.35803000	0.99409600	1.63693800
O	0.35570600	2.13749800	-0.63262600
C	1.40476500	0.02701600	-2.26794100
H	1.47892800	-0.79243300	-2.98350300
H	1.50258900	0.97849900	-2.78677400
O	2.46636900	-0.12370700	-1.32267400
C	-4.09677500	-0.93431200	-1.49106300
C	1.26767700	2.77138400	0.14511700
C	-2.48693500	1.41454500	2.25157600
C	3.31183600	0.91391600	-1.14634800

O	-4.36178600	-1.88042900	-0.79836300
O	1.80352700	2.25532200	1.08608600
O	-3.51357600	1.60053000	1.65541900
O	3.25486100	1.92968000	-1.79132500
C	4.31373200	0.62383400	-0.07340500
H	3.82521500	0.10268100	0.74942900
H	4.76189700	1.55919100	0.25460800
H	5.09303400	-0.02182300	-0.48797800
C	-2.26644600	1.58891300	3.72106500
H	-3.15776500	2.01367600	4.17596000
H	-1.40319900	2.23377900	3.89020300
H	-2.04837600	0.61489600	4.16491400
C	1.49040400	4.16787200	-0.34357200
H	2.26106200	4.64403900	0.25765500
H	0.55655200	4.72903400	-0.27342800
C	-4.88031900	-0.46313900	-2.67740200
H	-4.23470100	-0.44702800	-3.55711000
H	-5.22931300	0.55529500	-2.49760600
H	-5.72576100	-1.12653200	-2.84183500
H	1.79352500	4.13266100	-1.39041100

Tetraacetyl α-*C*-glycoside ($^4C_1$ conformation)



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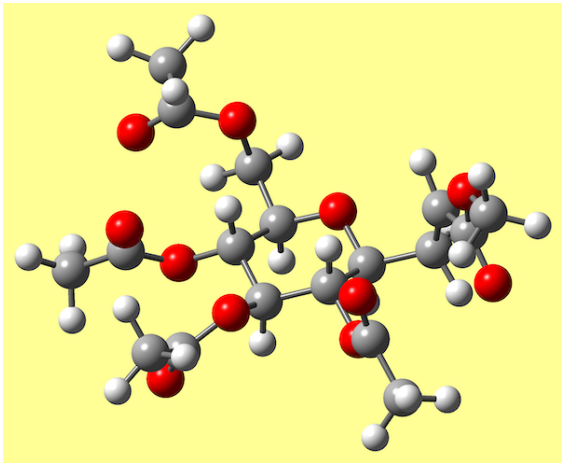
C	0.72321900	1.09871000	-0.32427600
C	-0.24764100	1.75866400	0.63996800
C	-1.57503300	0.99282500	0.75803400
O	-1.30219100	-0.36712400	1.05735000
C	-2.49379300	1.16003600	-0.47138500
C	-3.75531200	0.40921900	-0.26494900
C	-3.95763300	-0.89655900	-0.85849100
O	-0.45243600	3.08820800	0.15929400
O	1.97431800	1.76824200	-0.13503700
O	1.58631400	-1.06356000	-1.00392700
C	-0.42253000	-2.49999600	0.48769500
O	0.39968800	-2.65798900	1.65212000
O	-5.12922200	-1.44280900	-0.49382200
O	-3.17413400	-1.45317200	-1.60477900
C	-5.39830500	-2.73966200	-1.03315100
H	-0.98790400	-1.00494800	-0.89462600
H	1.38216300	-0.47429700	0.97368900
H	0.39639700	1.21477600	-1.36040900
H	0.21177200	1.80002300	1.63081000
H	-2.10352000	1.37265500	1.63340200
H	-1.99523800	0.82623400	-1.38413800
H	-2.70965600	2.22685400	-0.57483800
H	-4.51623800	0.78596500	0.40701400
H	-1.41797500	-2.85615800	0.75161800
H	-0.01934400	-3.09013200	-0.33286600
H	-6.37381600	-3.02412300	-0.64679300
H	-5.41795200	-2.70468400	-2.12325400
H	-4.64000200	-3.45347700	-0.70764800
C	1.61340900	-3.22219900	1.49851000
O	2.01097100	-3.68086500	0.45894300
C	2.39623600	-3.16990100	2.77475500
H	2.77762700	-2.15269700	2.89778800
H	1.75877700	-3.40036700	3.62761100

H	3.23394700	-3.86085600	2.71632900
C	2.91125400	-1.25203700	-0.83303500
O	3.51872500	-0.83259000	0.11718800
C	2.83013700	1.84122300	-1.17331700
O	2.57464400	1.42970400	-2.27391300
C	-0.87840700	4.00503000	1.05402000
O	-1.11462700	3.73574700	2.20105300
C	3.49132700	-2.00972900	-1.98394000
H	3.43912700	-1.37887500	-2.87436600
H	4.52599800	-2.26480600	-1.76819800
H	2.90253200	-2.90913400	-2.16408800
C	4.12106600	2.47105000	-0.75109800
H	3.93022600	3.38121000	-0.18236700
H	4.64195300	1.76558900	-0.09936700
H	4.72896000	2.68368400	-1.62713800
C	-1.00781200	5.35439400	0.41816600
H	-0.04123500	5.65752100	0.01227400
H	-1.71593300	5.29827100	-0.41077900
H	-1.34996700	6.07457500	1.15701300

Tetraacetyl β-*C*-glycoside ($^4C_1$ conformation)



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C	0.36929600	0.92587600	-0.73261000
C	-0.98514300	0.24220800	-0.66380000
C	-1.03487800	-0.93104900	-1.64239300
O	-0.02705800	-1.85397300	-1.25867200
C	-2.38564600	-1.64976400	-1.64683200
C	-2.88057800	-1.97164500	-0.28505800
C	-4.06706100	-1.31111000	0.22906500
O	-2.00394100	1.17710600	-1.00840600
O	0.37903300	1.89383400	0.32036200
O	2.74899100	0.42331100	-0.81826300
C	2.28972600	-2.41174500	-1.14876100
O	2.34121200	-2.70060500	0.25372400
O	-4.30092400	-1.60931300	1.51416200
O	-4.77282600	-0.56006300	-0.41741700
C	-5.39053700	-0.90358700	2.11431600
H	1.40685700	-1.00089300	-2.47490100
H	1.43142700	-0.42991000	0.53409900
H	0.50630000	1.42559700	-1.69517400
H	-1.15017600	-0.12044700	0.35311400
H	-0.82958600	-0.56776500	-2.65894000
H	-2.34271500	-2.65063200	0.36408400
H	1.97735300	-3.32724200	-1.65016300
H	3.27379200	-2.10876500	-1.50090300
H	-5.42528600	-1.23707100	3.14850400
H	-5.20839000	0.17095600	2.06644100
H	-6.32745100	-1.14015300	1.60817300
H	-3.11470000	-1.01870800	-2.15642000
H	-2.25122900	-2.56561000	-2.23185400
C	3.43048300	-2.30236200	0.94203500
C	3.48348400	0.93397400	0.19297700
C	1.15168800	2.98996400	0.18345800
C	-2.84425100	1.59585100	-0.03027600
O	4.39576700	-1.79895900	0.42925100

O	3.08821600	0.99276300	1.32751200
O	1.78998300	3.23093900	-0.80679000
O	-2.76213800	1.23569700	1.11238500
C	-3.86905900	2.53354700	-0.58562000
H	-4.48383900	2.92143100	0.22304900
H	-4.48994800	1.98236800	-1.29405700
H	-3.37817800	3.34901100	-1.11858300
C	1.11484000	3.82021300	1.42826000
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H	1.55884000	4.79361000	1.23398200
H	1.69214500	3.29638200	2.19418800
C	4.80660600	1.41833900	-0.30601400
H	5.30928300	0.61139500	-0.84007800
H	5.41134400	1.75593700	0.53204000
H	4.63679600	2.24101900	-1.00392700
C	3.25554700	-2.54346500	2.40961000
H	2.80153800	-3.51782700	2.58723600
H	2.58230600	-1.77664800	2.80212600
H	4.21825100	-2.46507700	2.90900000

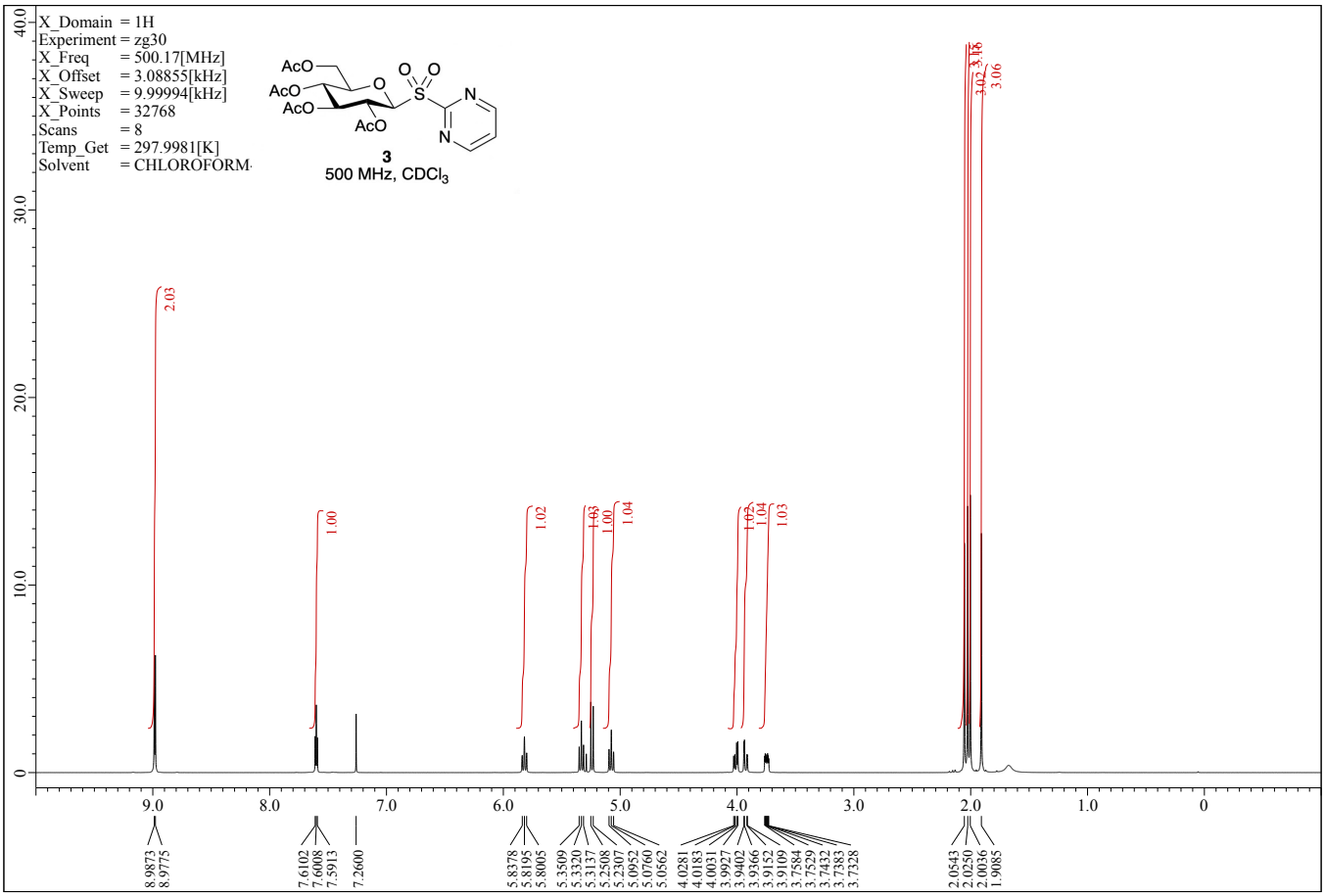
7. References

1 G. Guiochon, A. Moysan and C. Holley, *J. Liq. Chromatogr.*, 1988, **11**, 2457–2570.

2 Q. Chen and F. Kong, *Carbohydr. Res.*, 1995, **272**, 149–157.

3 L. Adak, S. Kawamura, G. Toma, T. Takenaka, K. Isozaki, H. Takaya, A. Orita, H. C. Li, T. K. M. Shing and M. Nakamura, *J. Am. Chem. Soc.*, 2017, **139**, 10693–10701.

4 H.-G. Korth, R. Sustmann, J. Dupuis and B. Giese, *J. Chem. Soc. Perkin Trans. 2*, 1986, 1453–1459.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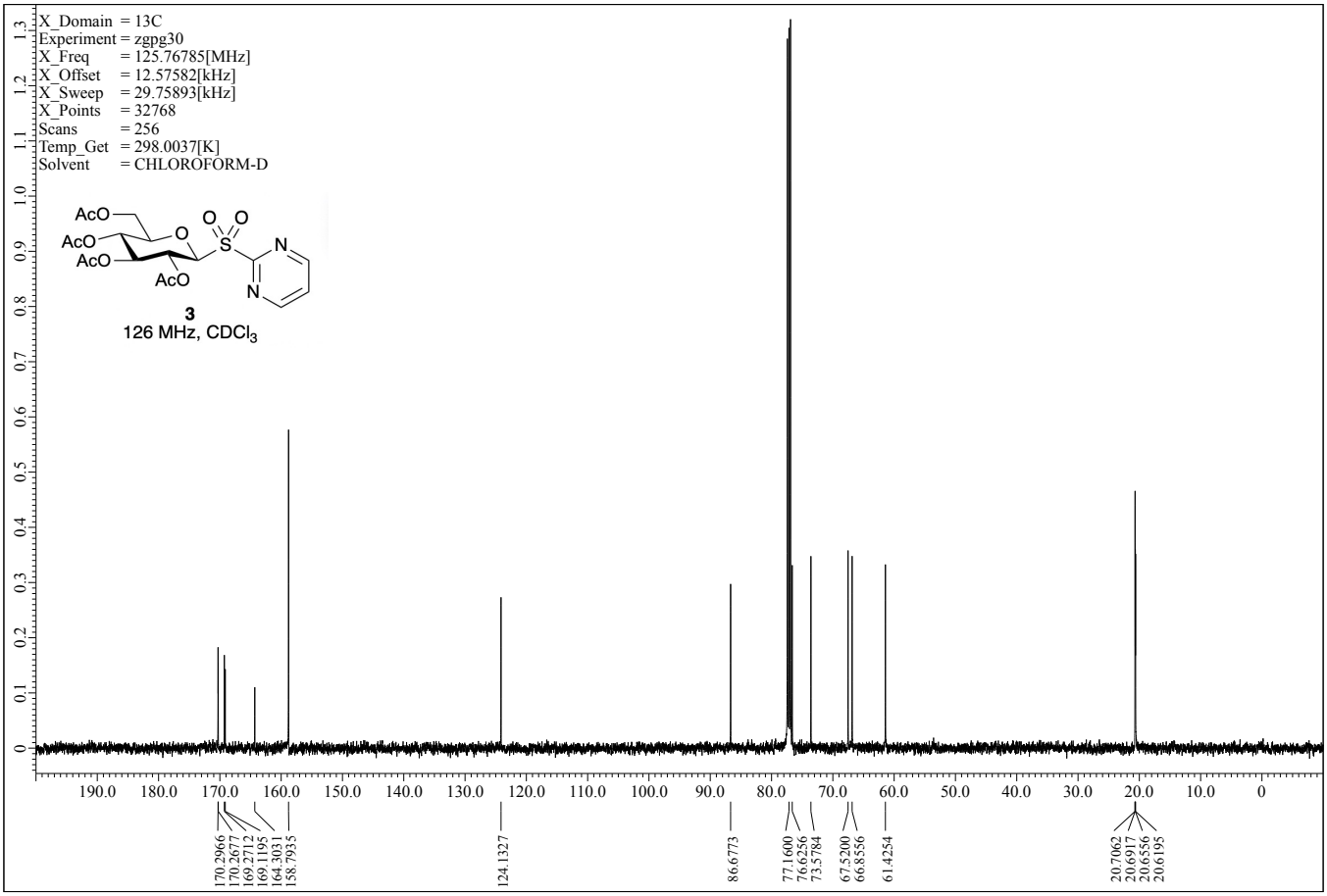
500 MHz, CDCl3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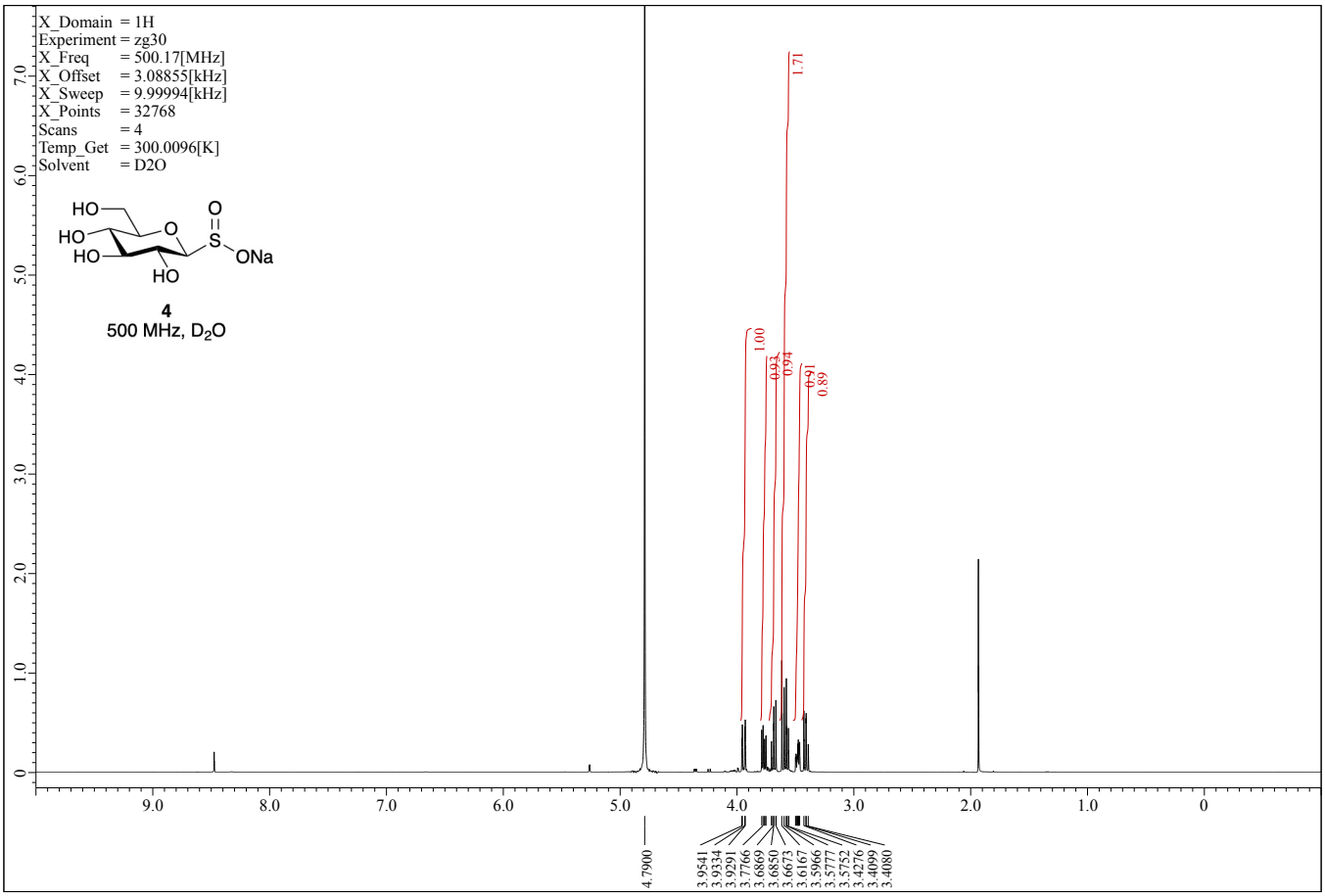
3
126 MHz, CDCl3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Scans = 4
Temp_Get = 300.0096[K]
Solvent = D2O
4
500 MHz, D2O
1.71
1.00
0.93
0.94
0.91
0.89
4.7900
3.9541
3.9334
3.9291
3.7766
3.6869
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3.6673
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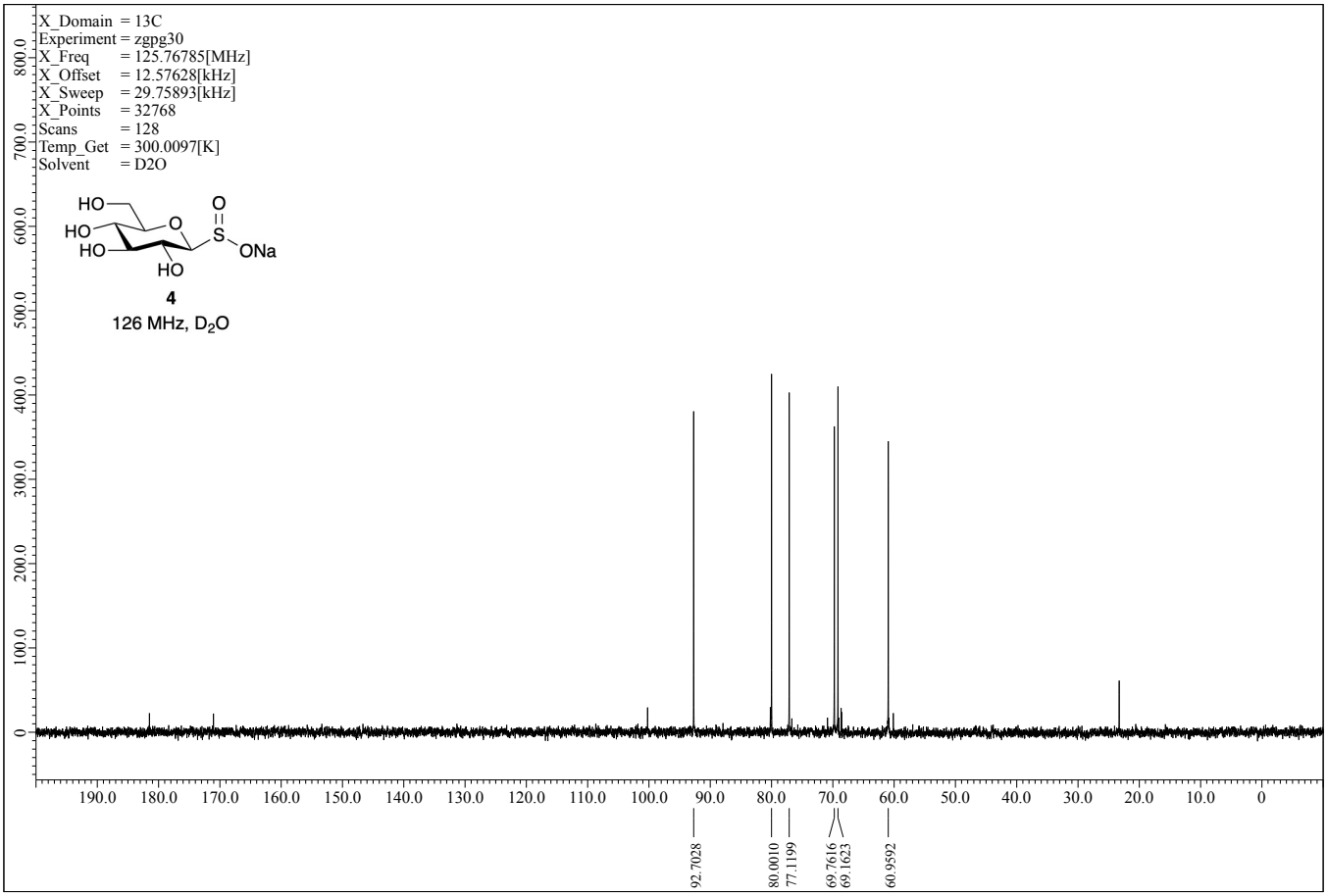
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Scans = 128
Temp_Get = 300.0097[K]
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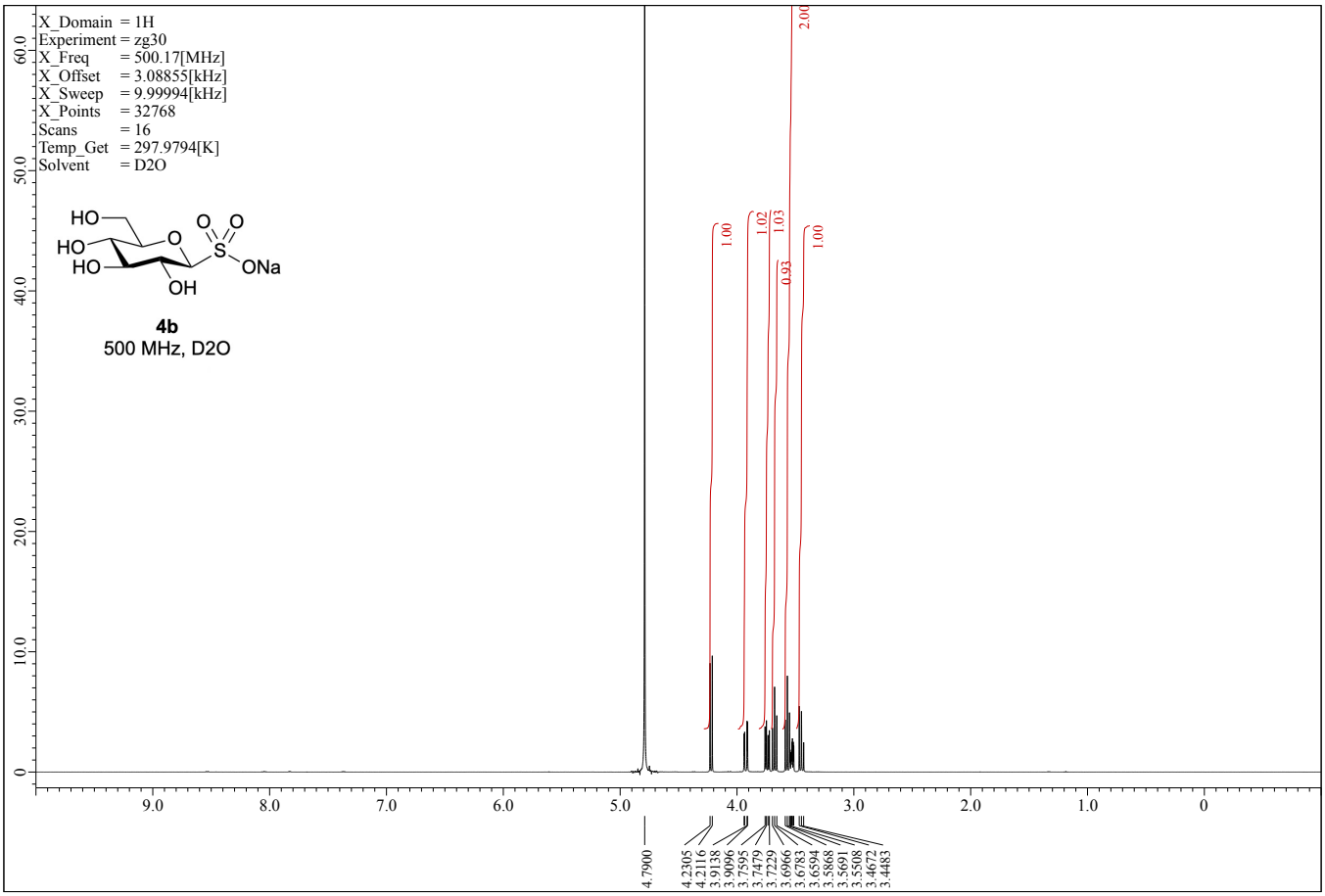
4
126 MHz, D2O
92.7028
80.0010
77.1199
69.7616
69.1623
60.9592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Scans = 16
Temp_Get = 297.9794[K]
Solvent = D2O
HO
HO
HO
O
O
O
S
ONa
OH
4b
500 MHz, D2O
1.00
1.02
1.03
0.93
1.00
4.7900
4.2305
4.2116
3.9138
3.9096
3.7595
3.7479
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3.5508
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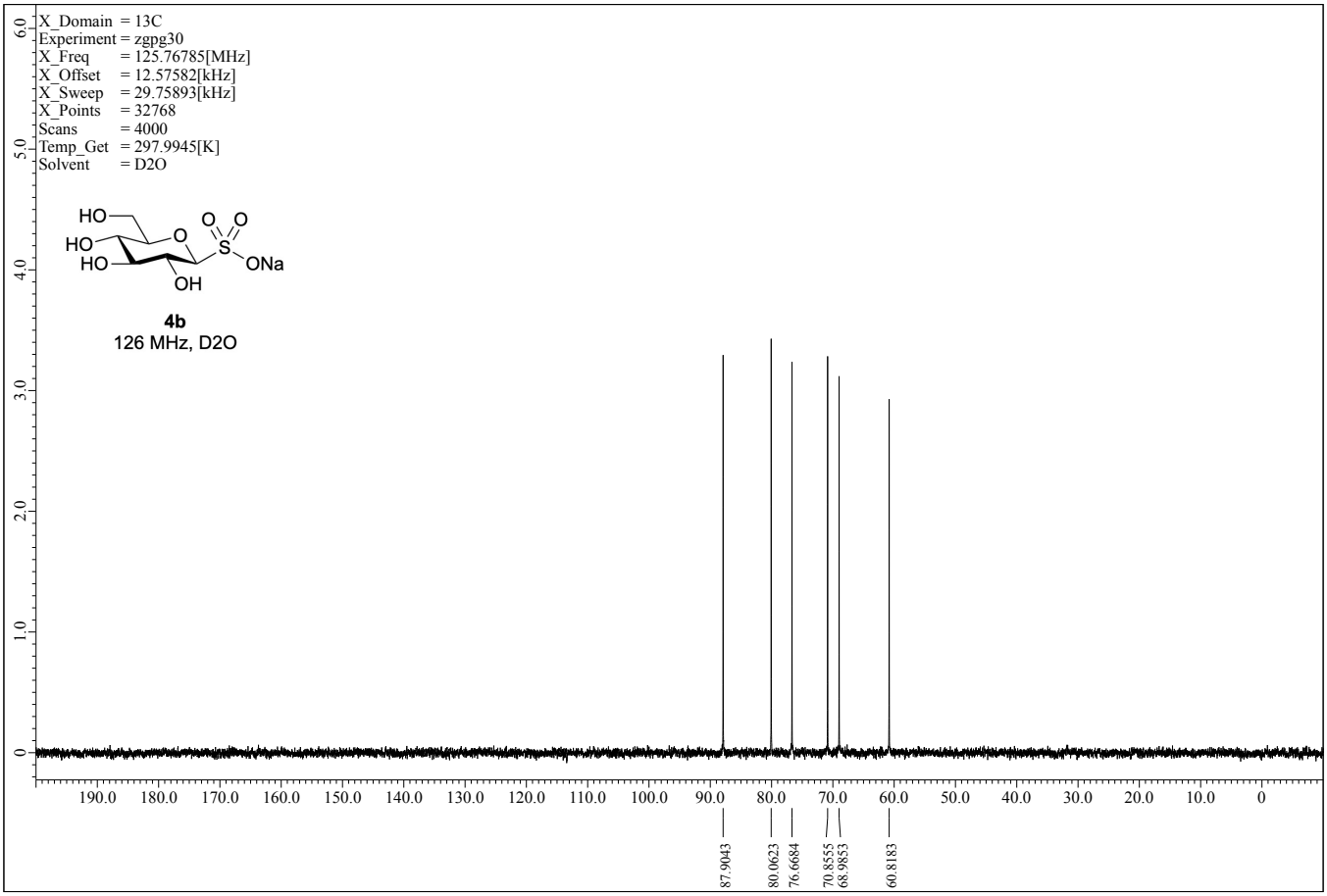
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HO
HO
HO
O
O
O
S
ONa
OH
4b
126 MHz, D2O
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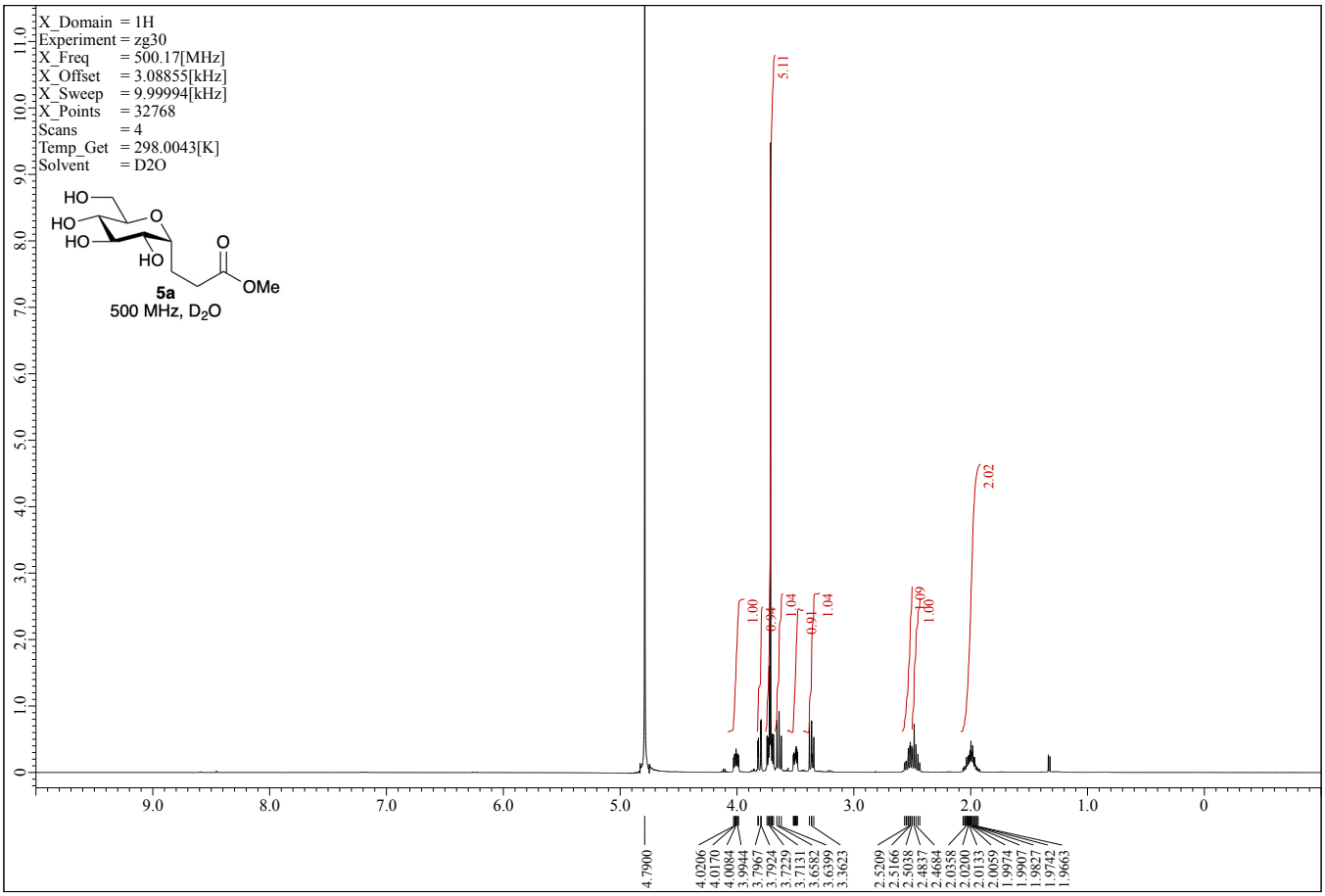
76.6684
70.8555
68.9853
60.8183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5a
500 MHz, D2O
5.11
2.02
1.00
0.94
1.04
0.91
1.04
1.09
1.00
4.7900
4.0206
4.0170
4.0084
3.9944
3.7967
3.7924
3.7229
3.7131
3.6582
3.6399
3.3623
2.5209
2.5166
2.5038
2.4837
2.4684
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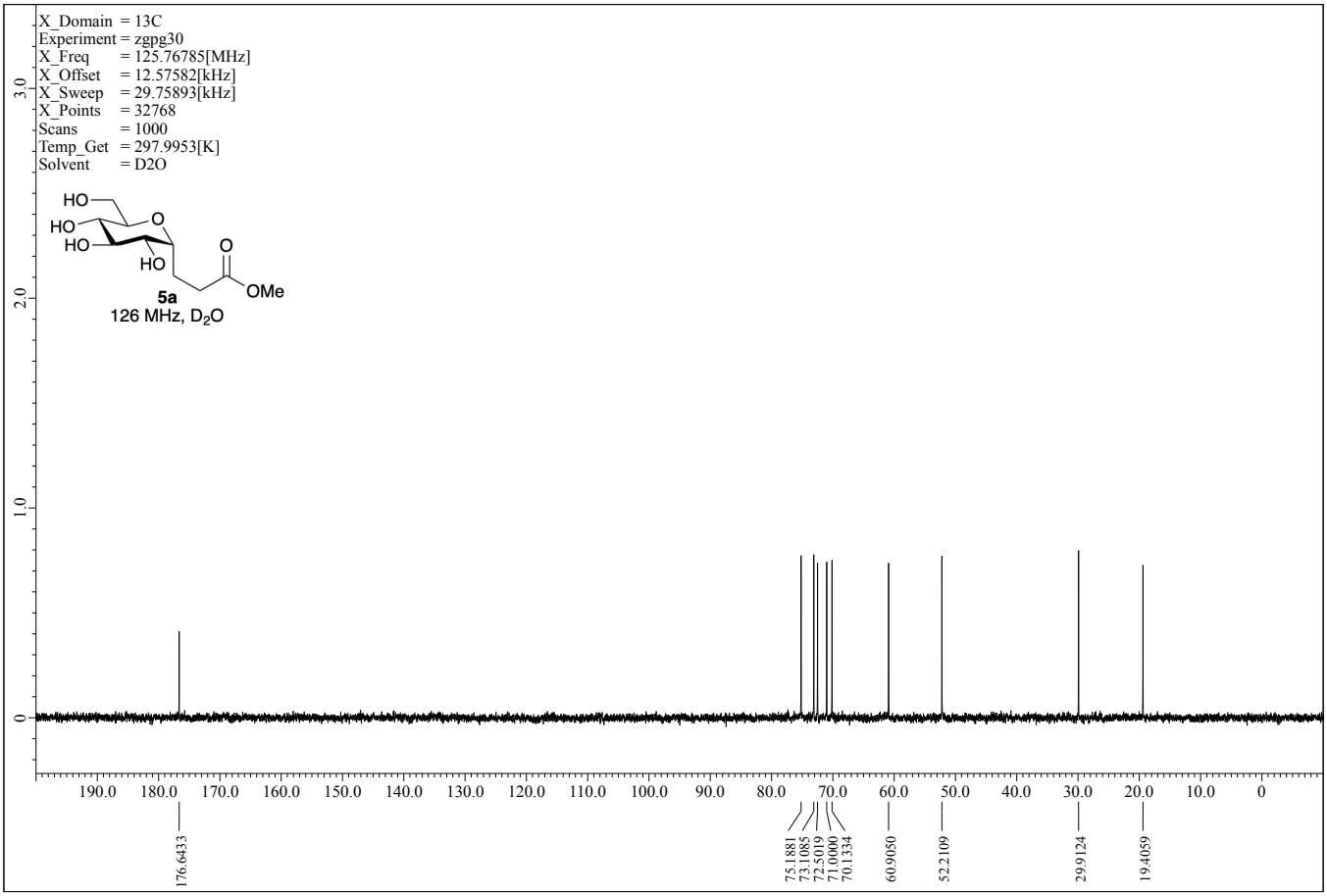
2.0059
1.9974
1.9907
1.9827
1.9742
1.9663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Scans = 1000
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5a
126 MHz, D2O
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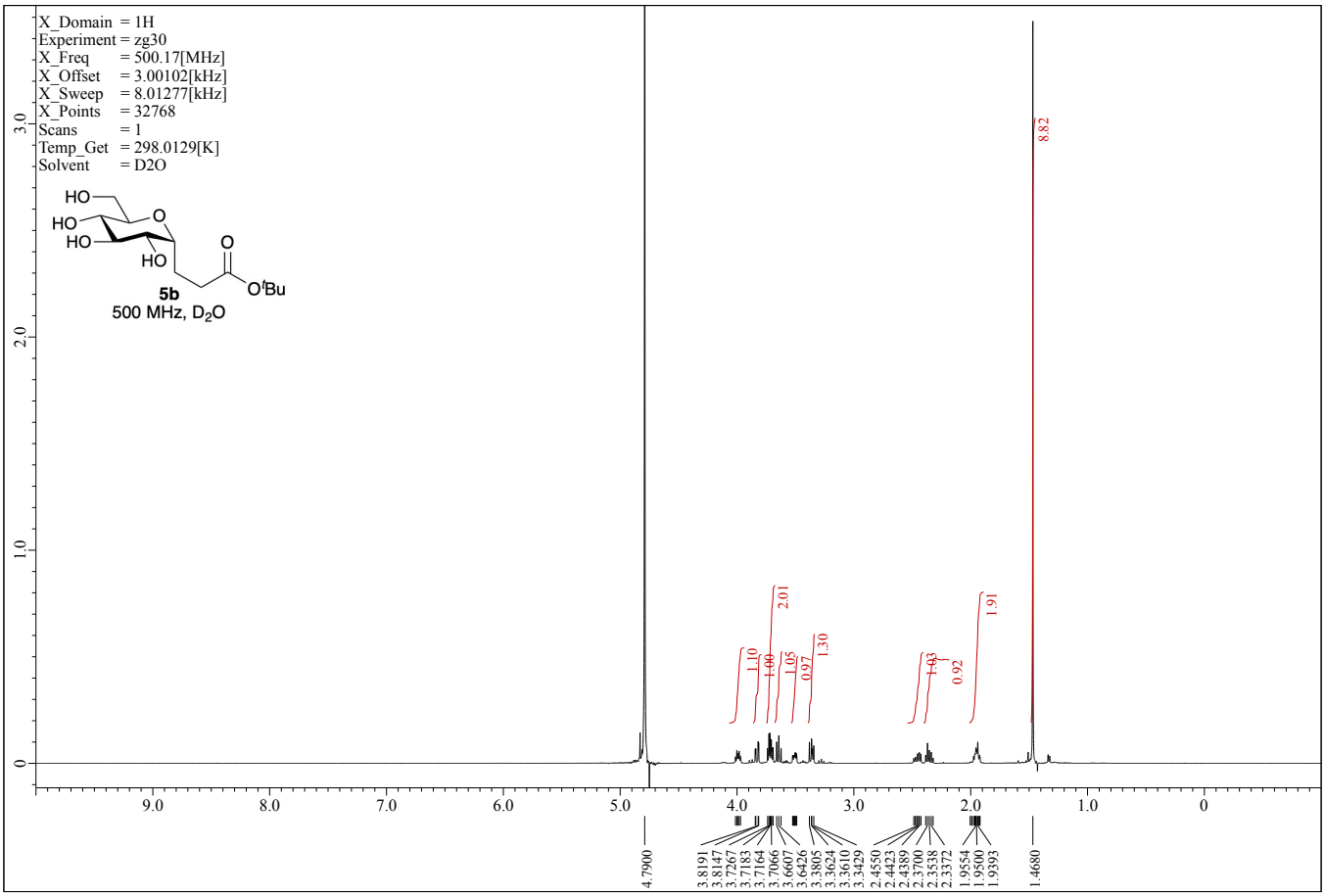
73.1085
72.5019
71.0000
70.1334
60.9050
52.2109
29.9124
19.4059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X_Points = 32768
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5b
500 MHz, D2O
8.82
2.01
1.91
1.30
1.10
1.00
1.05
0.97
1.03
0.92
4.7900
3.8191
3.8147
3.7267
3.7183
3.7164
3.7066
3.6607
3.6426
3.3805
3.3624
3.3610
3.3429
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2.3700
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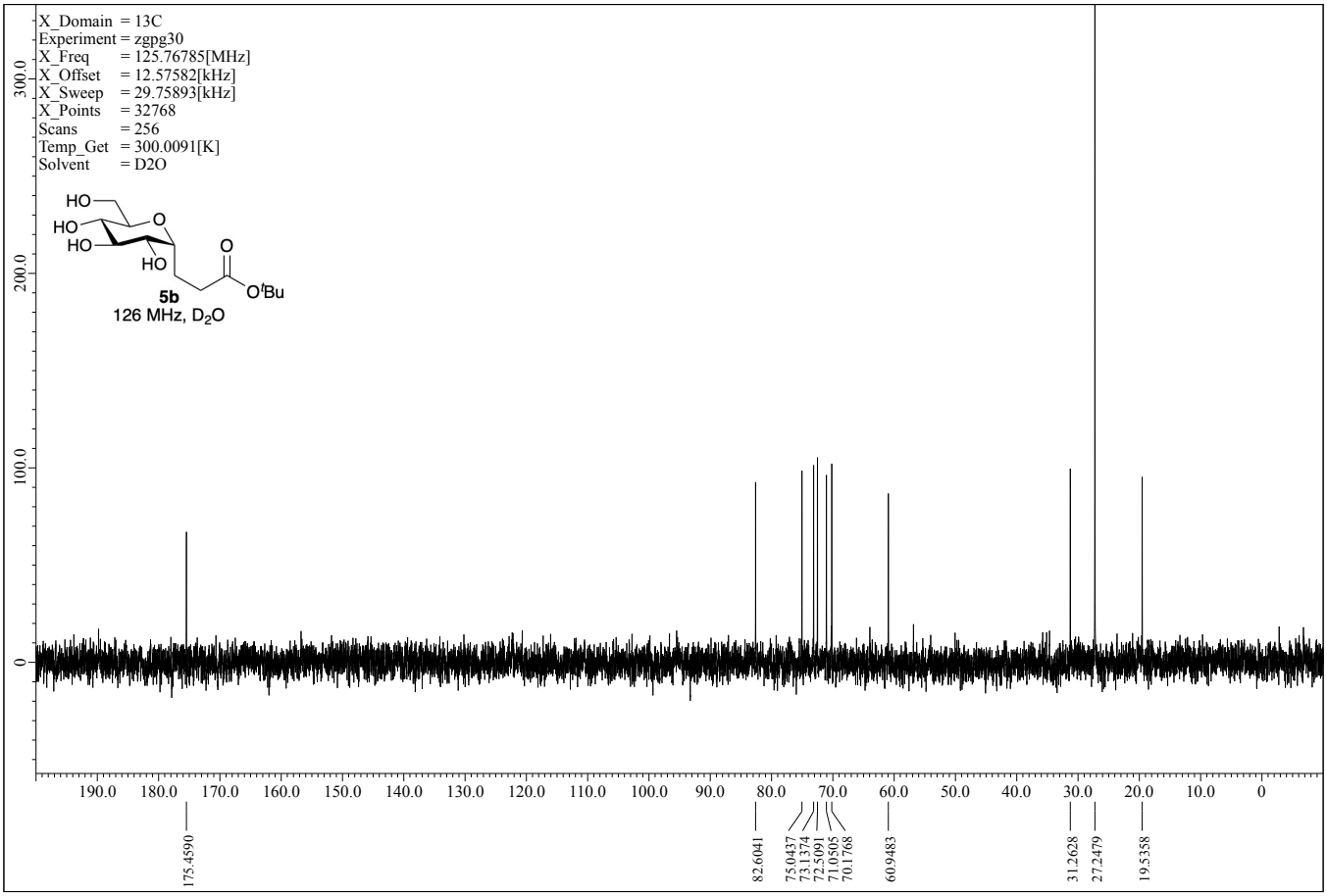
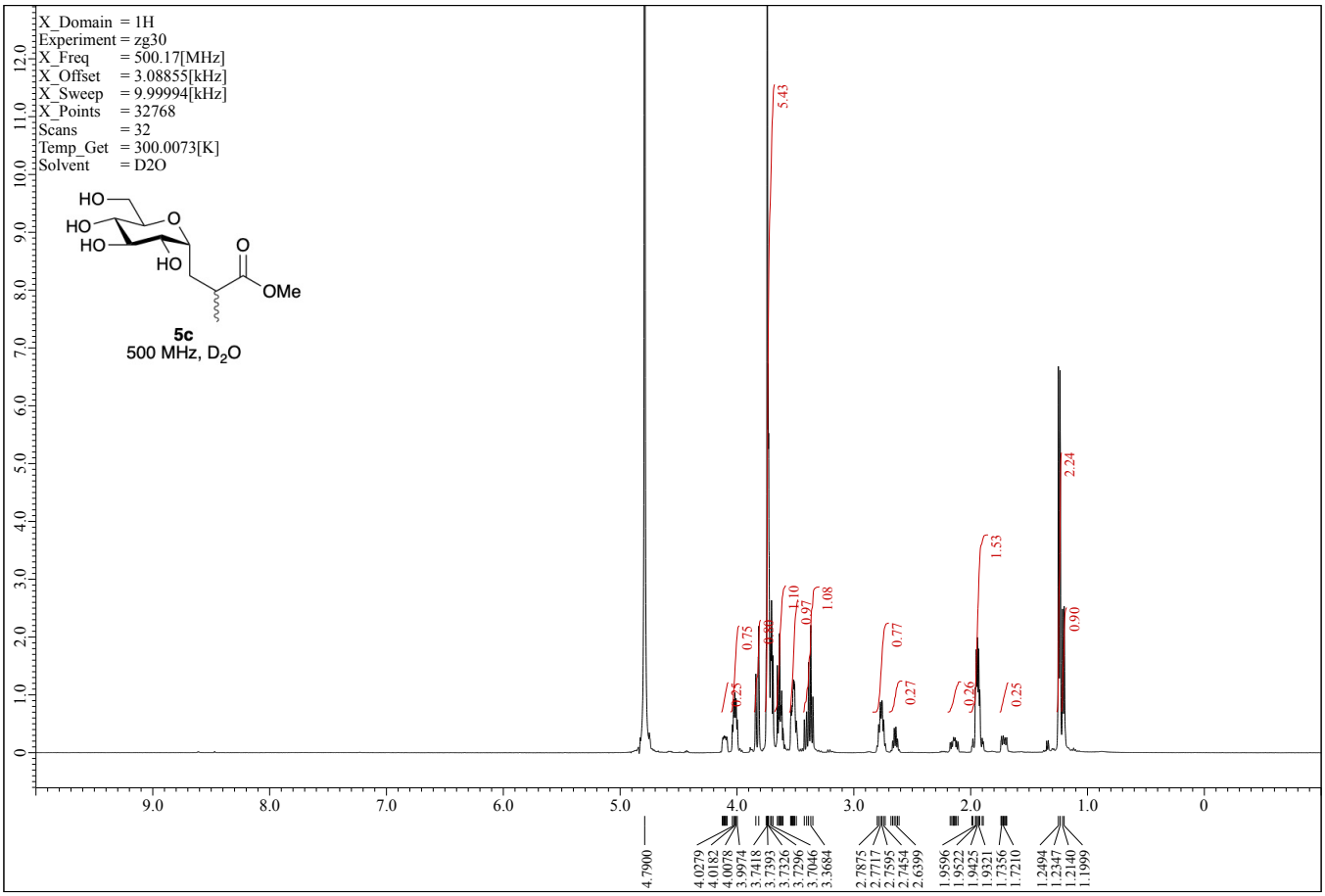
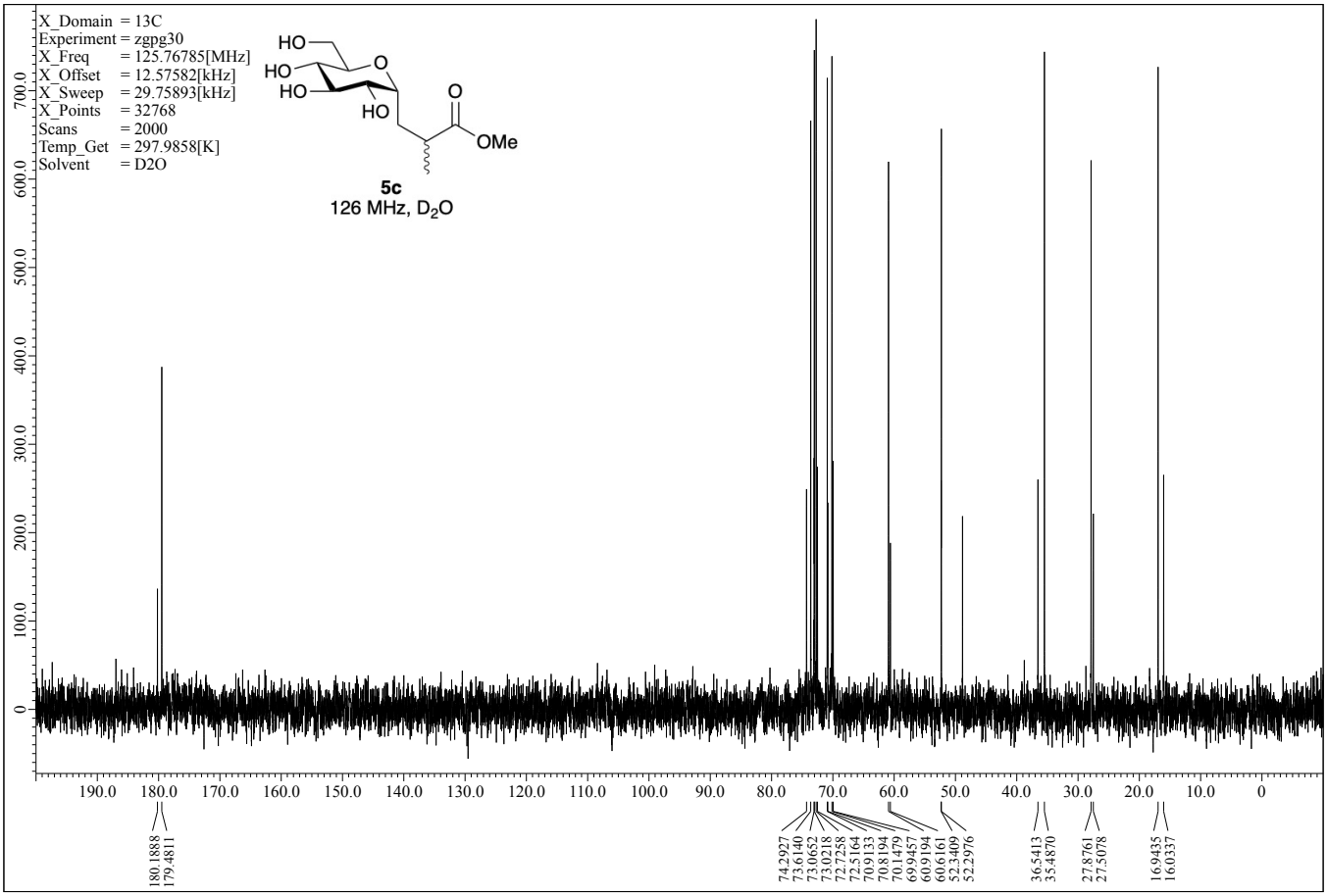
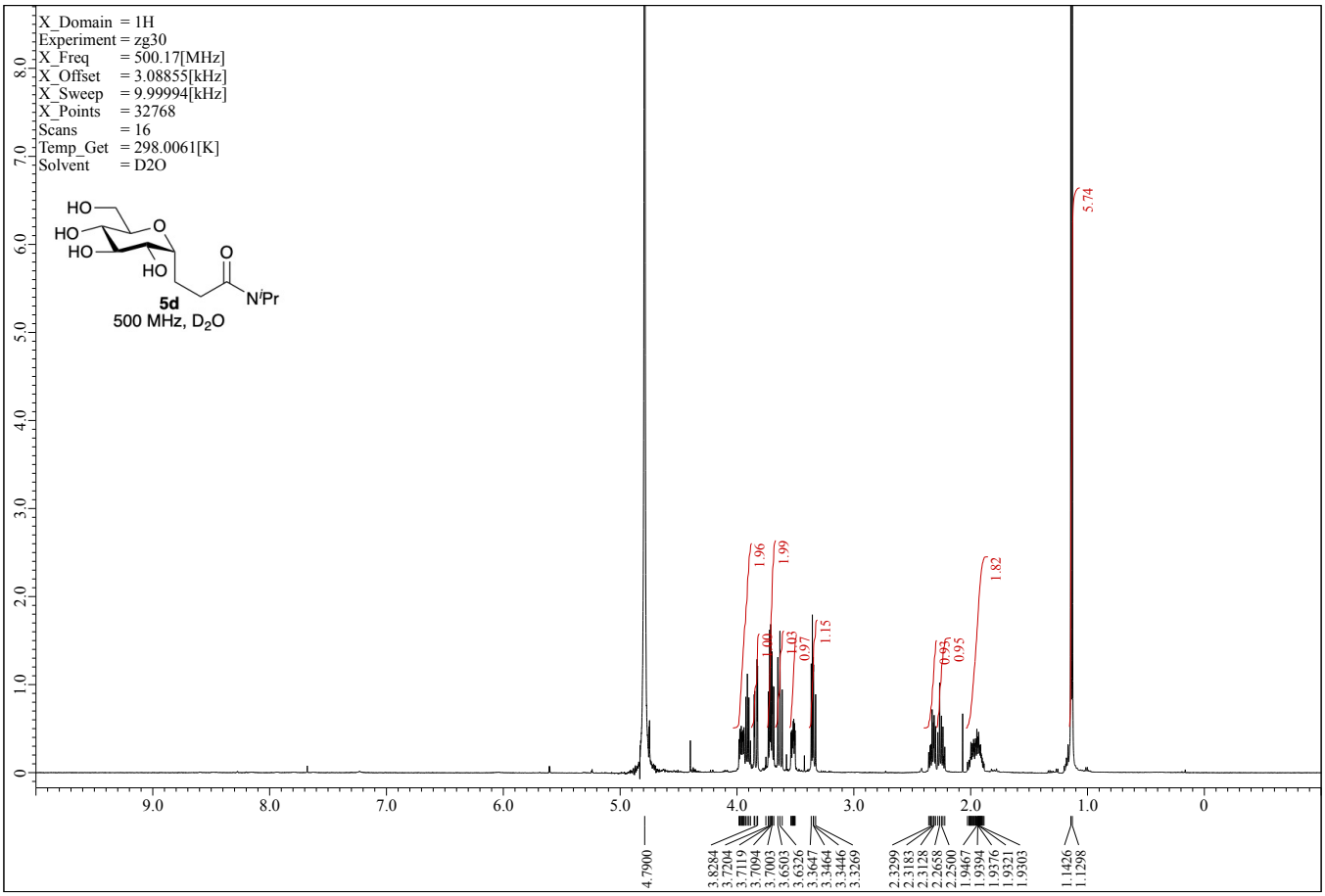
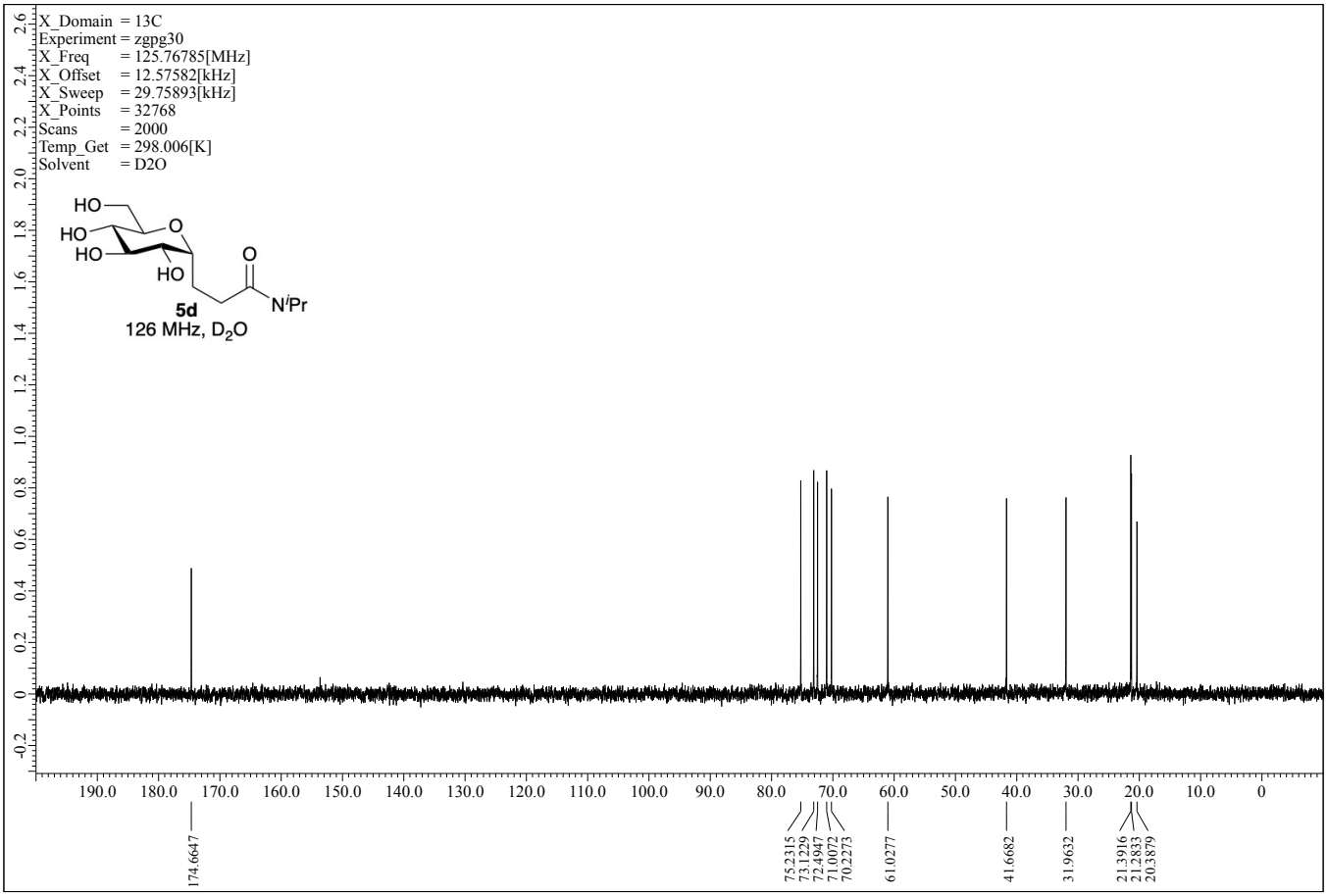
1.9500
1.9393
1.4680

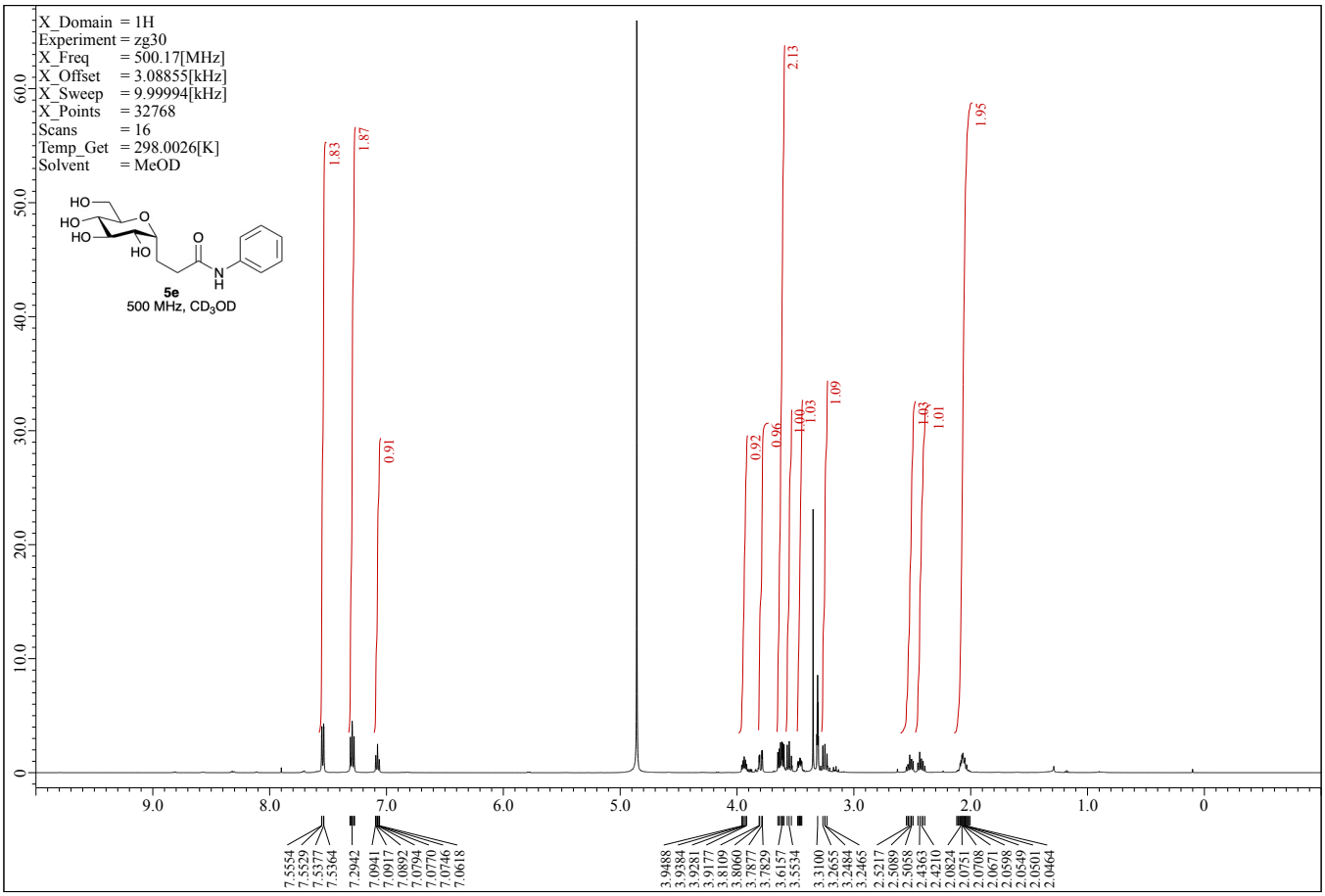

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.76785[MHz]
X_Offset = 12.57582[kHz]
X_Sweep = 29.75893[kHz]
X_Points = 32768
Scans = 256
Temp_Get = 300.0091[K]
Solvent = D2O
5b
126 MHz, D2O
175.4590
82.6041
75.0437
73.1374
72.5091
71.0505
70.1768
60.9483
31.2628
27.2479
19.5358

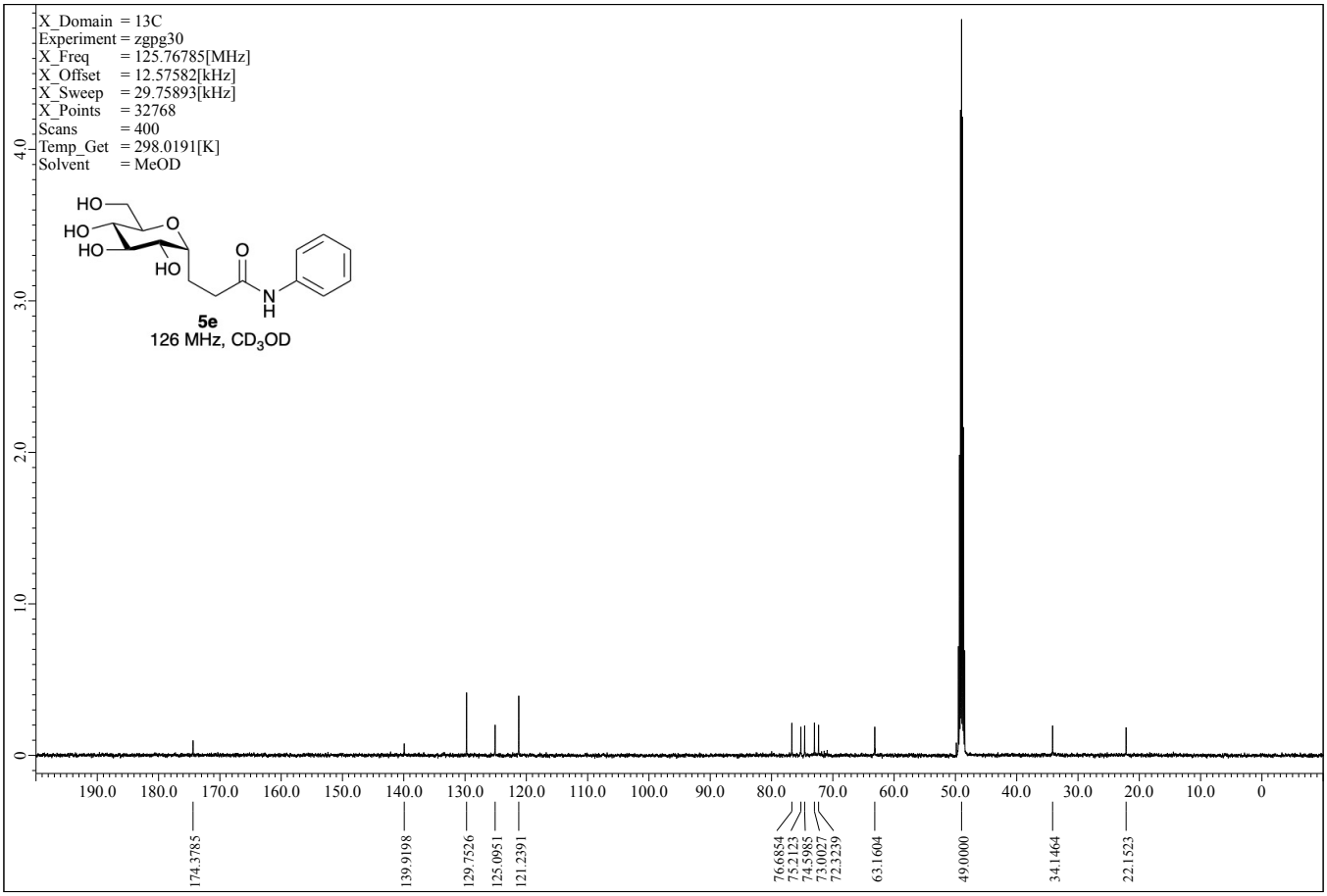

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17[MHz]
X_Offset = 3.08855[kHz]
X_Sweep = 9.99994[kHz]
X_Points = 32768
Scans = 32
Temp_Get = 300.0073[K]
Solvent = D2O
5c
500 MHz, D2O

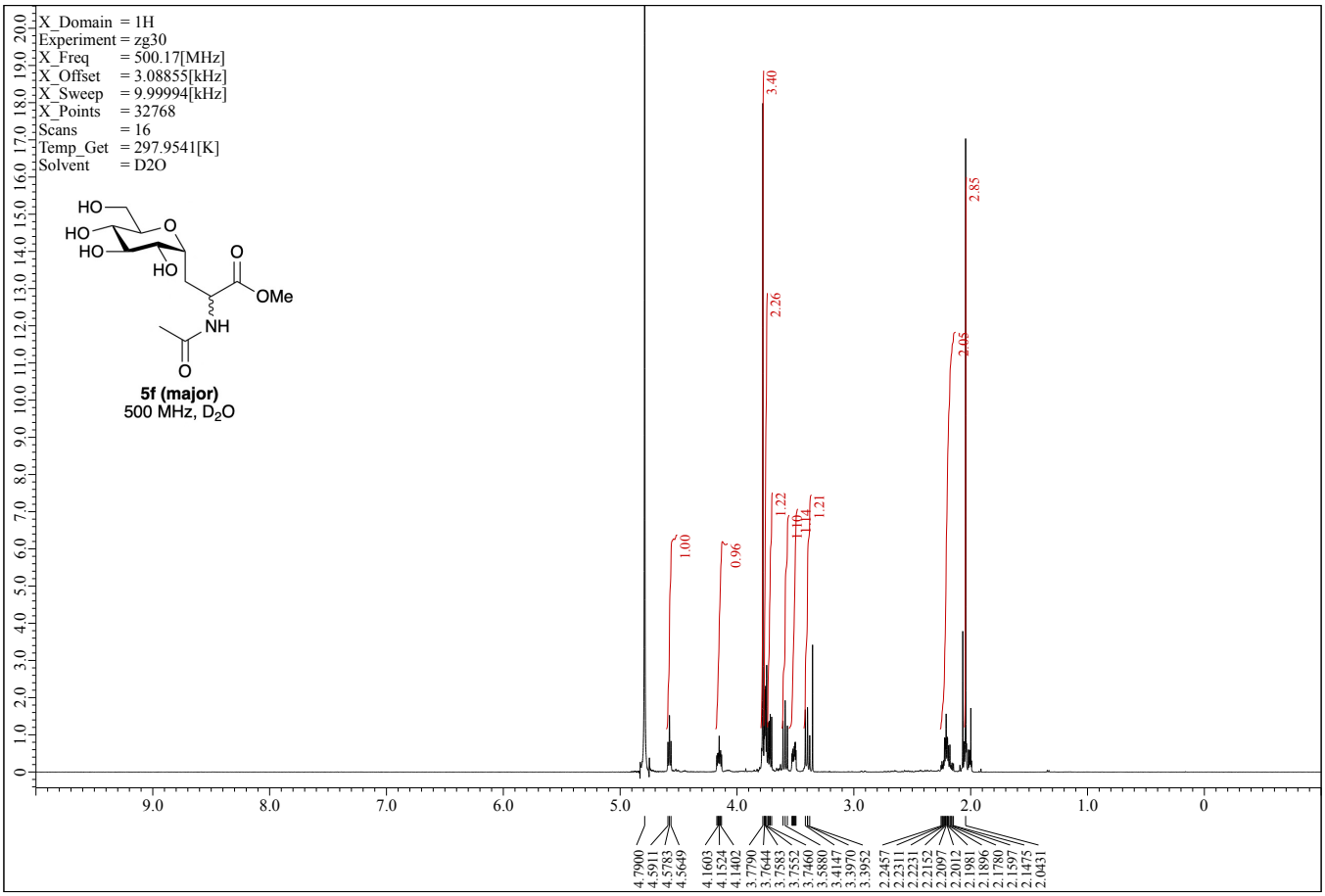

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.76785[MHz]
X_Offset = 12.57582[kHz]
X_Sweep = 29.75893[kHz]
X_Points = 32768
Scans = 2000
Temp_Get = 297.9858[K]
Solvent = D2O
5c
126 MHz, D2O

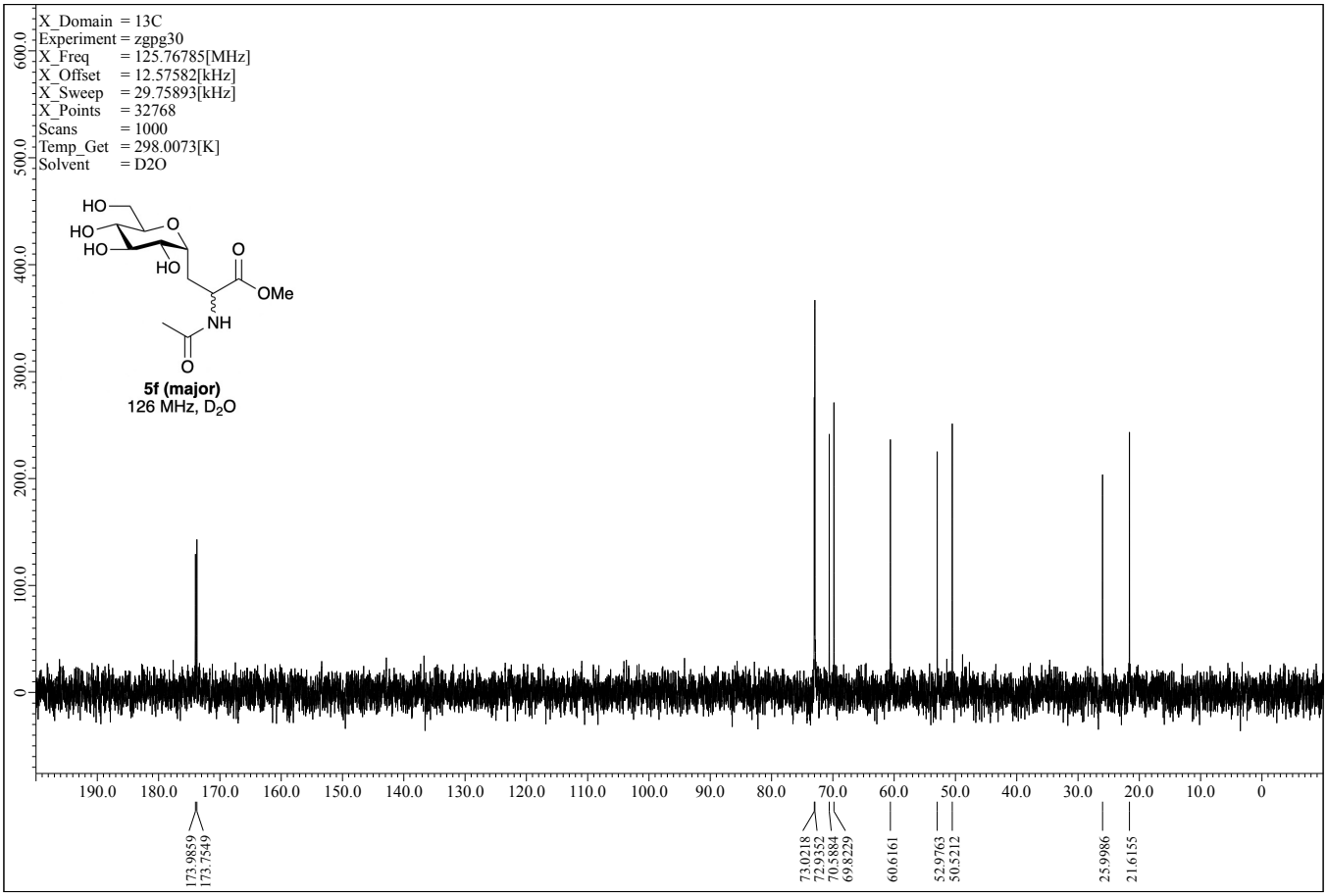

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17[MHz]
X_Offset = 3.08855[kHz]
X_Sweep = 9.99994[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 298.0061[K]
Solvent = D2O
5d
500 MHz, D2O
5.74
1.96
1.99
1.82
1.15
1.00
1.03
0.97
0.95
4.7900
3.8284
3.7204
3.7119
3.7094
3.7003
3.6503
3.6326
3.3647
3.3464
3.3446
3.3269
2.3299
2.3183
2.3128
2.2658
2.2500
1.9467
1.9394
1.9376
1.9321
1.9303
1.1426
1.1298

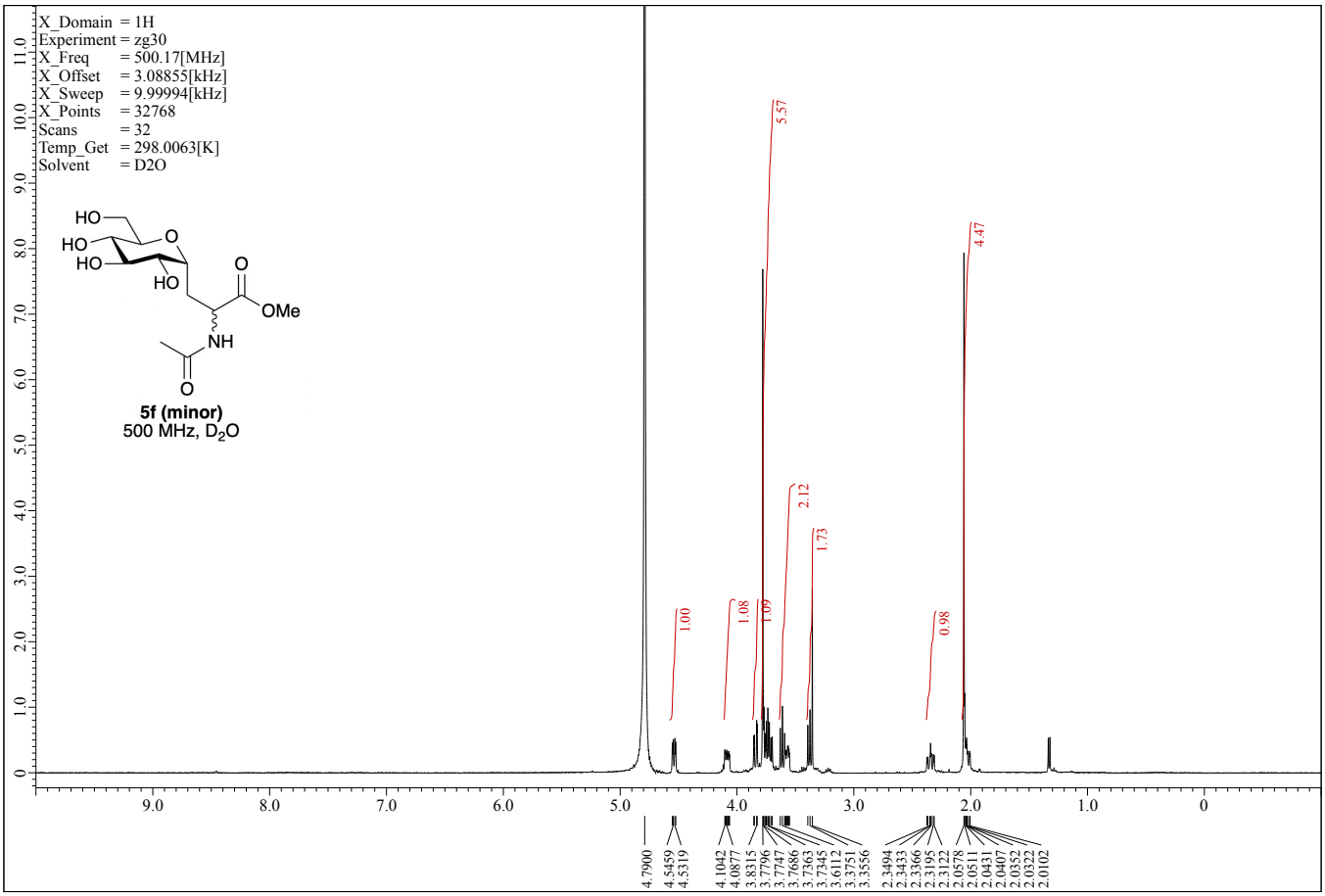

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.76785[MHz]
X_Offset = 12.57582[kHz]
X_Sweep = 29.75893[kHz]
X_Points = 32768
Scans = 2000
Temp_Get = 298.006[K]
Solvent = D2O
5d
126 MHz, D2O
174.6647
75.2315
73.1229
72.4947
71.0072
70.2273
61.0277
41.6682
31.9632
21.3916
21.2833
20.3879

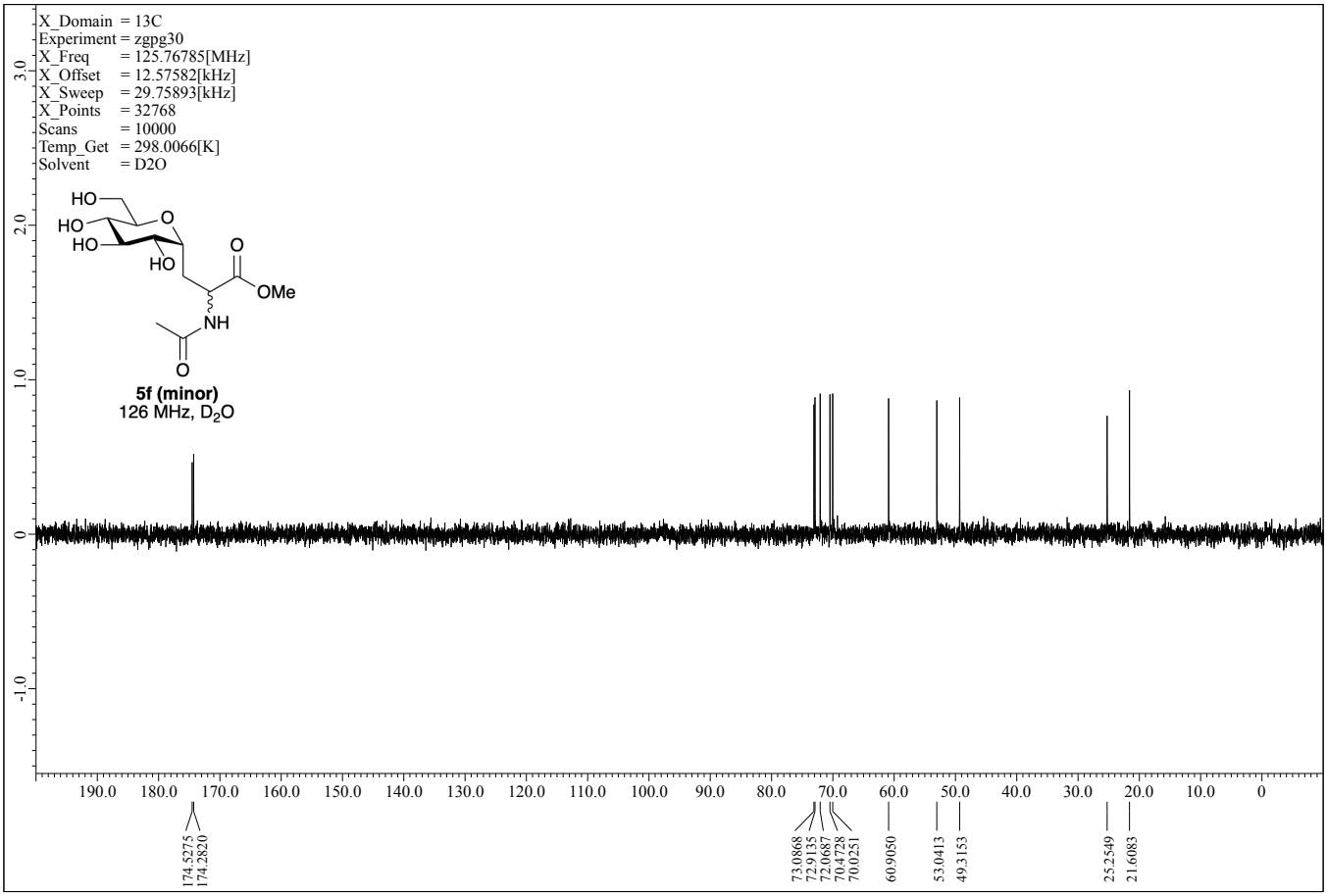

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17[MHz]
X_Offset = 3.08855[kHz]
X_Sweep = 9.99994[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 298.0026[K]
Solvent = MeOD
5e
500 MHz, CD3OD

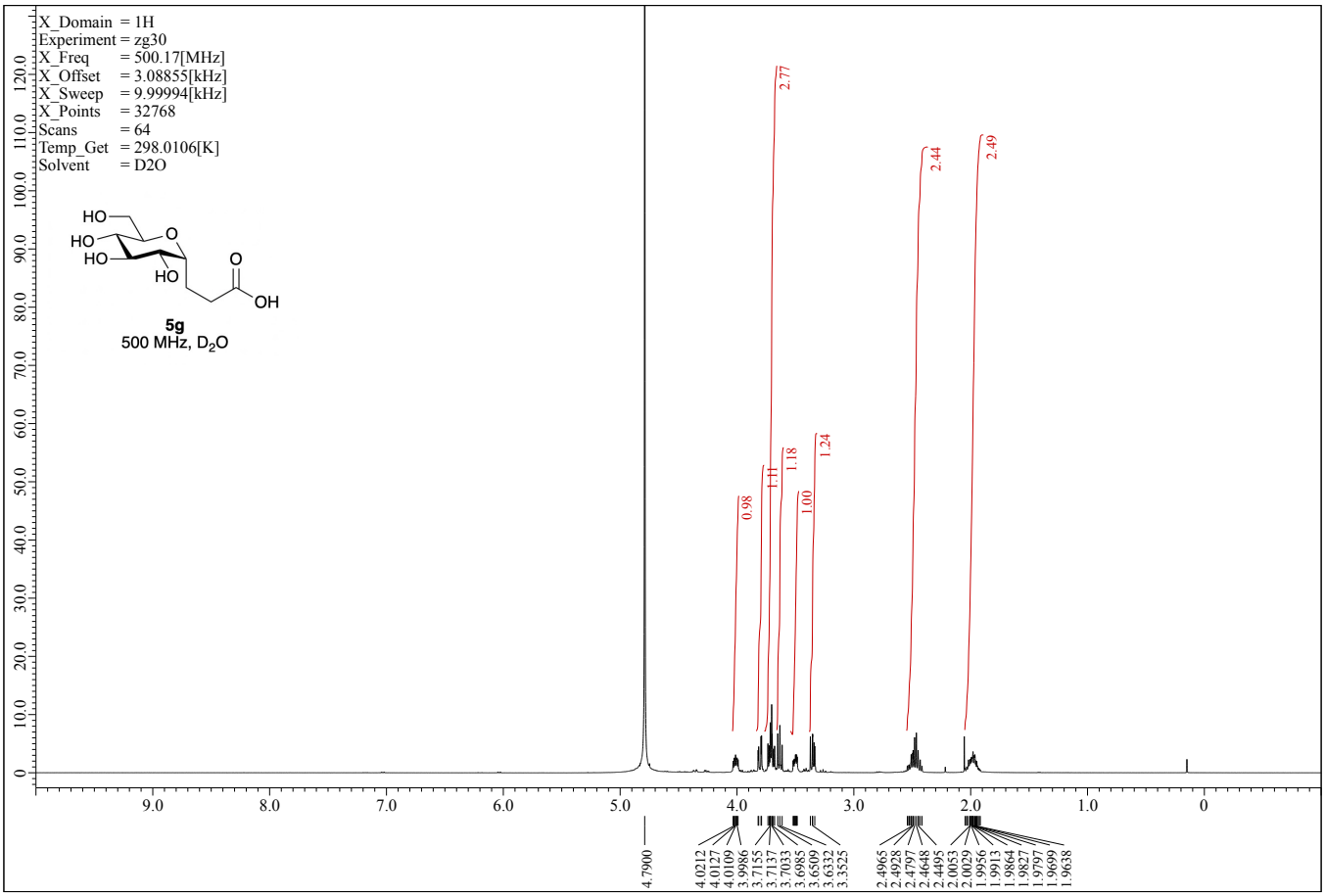

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.76785[MHz]
X_Offset = 12.57582[kHz]
X_Sweep = 29.75893[kHz]
X_Points = 32768
Scans = 400
Temp_Get = 298.0191[K]
Solvent = MeOD
5e
126 MHz, CD3OD

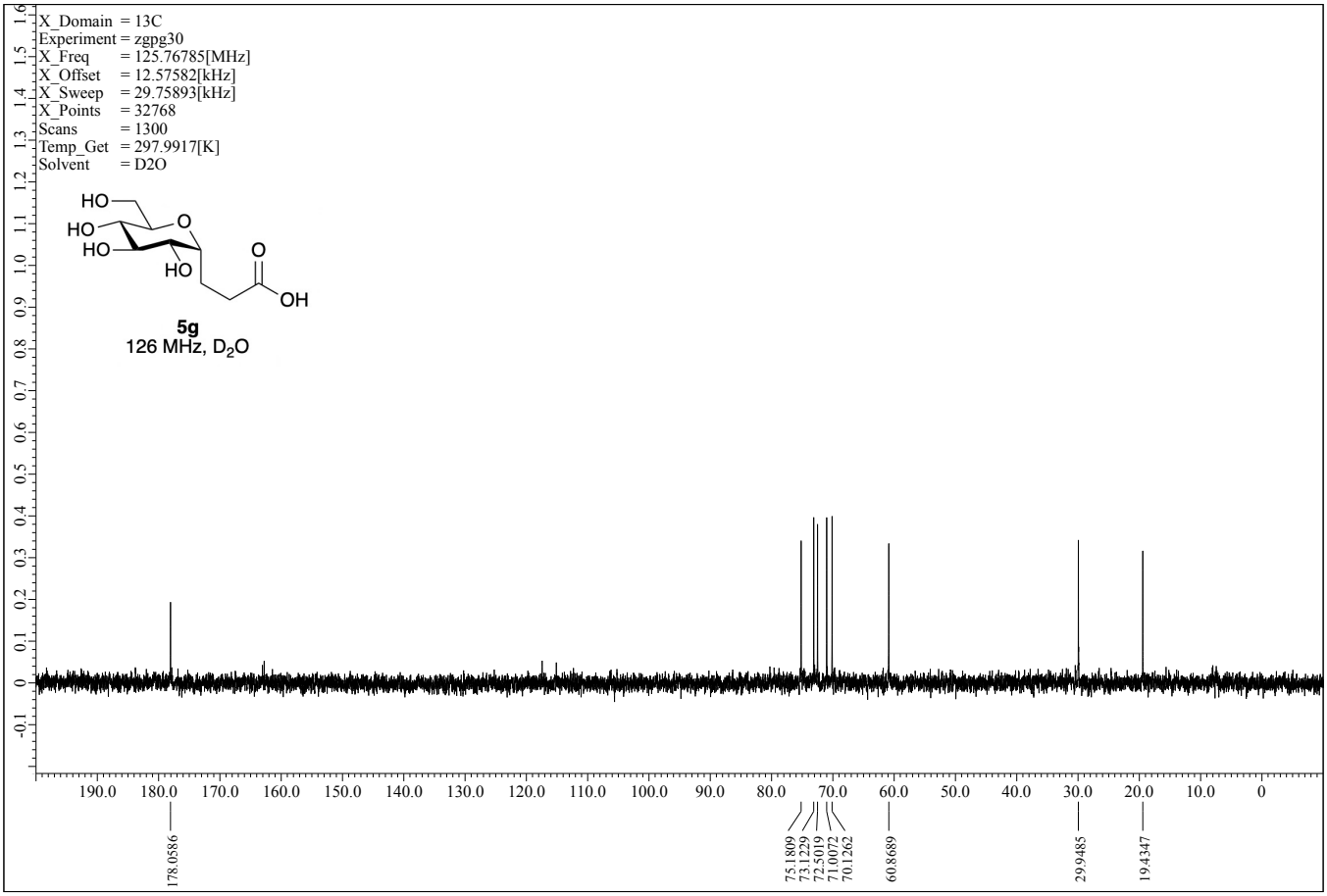

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17[MHz]
X_Offset = 3.08855[kHz]
X_Sweep = 9.99994[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 297.9541[K]
Solvent = D2O
HO
HO
HO
HO
O
O
OMe
NH
O
5f (major)
500 MHz, D2O
3.40
2.85
2.26
2.05
1.22
1.21
1.14
1.10
1.00
0.96
4.7900
4.5911
4.5783
4.5649
4.1603
4.1524
4.1402
3.7790
3.7644
3.7583
3.7552
3.7460
3.5880
3.4147
3.3970
3.3952
2.2457
2.2311
2.2231
2.2153
2.2097
2.2012
2.1981
2.1896
2.1780
2.1597
2.1475
2.0431


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.76785[MHz]
X_Offset = 12.57582[kHz]
X_Sweep = 29.75893[kHz]
X_Points = 32768
Scans = 1000
Temp_Get = 298.0073[K]
Solvent = D2O
HO
HO
HO
HO
O
O
OMe
NH
O
5f (major)
126 MHz, D2O
173.9859
173.7549
73.0218
72.9352
70.5884
69.8229
60.6161
52.9763
50.5212
25.9986
21.6155


X_Domain = 1H
Experiment = zg30
X_Freq = 500.17[MHz]
X_Offset = 3.08855[kHz]
X_Sweep = 9.99994[kHz]
X_Points = 32768
Scans = 32
Temp_Get = 298.0063[K]
Solvent = D2O
5f (minor)
500 MHz, D2O
5.57
4.47
2.12
1.73
1.00
1.08
1.09
0.98


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.76785[MHz]
X_Offset = 12.57582[kHz]
X_Sweep = 29.75893[kHz]
X_Points = 32768
Scans = 10000
Temp_Get = 298.0066[K]
Solvent = D2O
5f (minor)
126 MHz, D2O


X_Domain = 1H
Experiment = zg30
X_Freq = 500.17[MHz]
X_Offset = 3.08855[kHz]
X_Sweep = 9.99994[kHz]
X_Points = 32768
Scans = 64
Temp_Get = 298.0106[K]
Solvent = D2O
5g
500 MHz, D2O
2.77
2.44
2.49
0.98
1.11
1.18
1.24
1.00


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.76785[MHz]
X_Offset = 12.57582[kHz]
X_Sweep = 29.75893[kHz]
X_Points = 32768
Scans = 1300
Temp_Get = 297.9917[K]
Solvent = D2O
5g
126 MHz, D2O